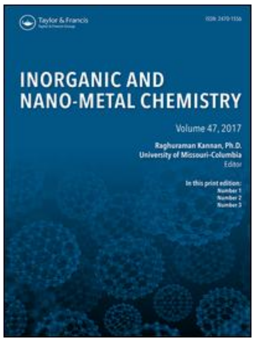

Inorganic and Nano-Metal Chemistry

ISSN: 2470-1556 (Print) 2470-1564 (Online) Journal homepage: https://www.tandfonline.com/loi/lsrt21

An efficient synthesis of highly substituted functionalized pyrroles via a four-component coupling reaction catalyzed by Fe(III)-Schiff base/SBA-15

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To cite this article: Ghasem Rezanejade Bardajee, Aseyeh Ghaedi, Hamideh Hazrati & Farnaz Jafarpour (2020): An efficient synthesis of highly substituted functionalized pyrroles via a four-component coupling reaction catalyzed by Fe(III)-Schiff base/SBA-15, Inorganic and Nano-Metal Chemistry, DOI: 10.1080/24701556.2020.1744650

To link to this article: https://doi.org/10.1080/24701556.2020.1744650

INORGANIC AND NANO-METAL CHEMISTRY
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An efficient synthesis of highly substituted functionalized pyrroles via a four-component coupling reaction catalyzed by Fe(III)-Schiff base/SBA-15

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ABSTRACT
An environmentally friendly, straightforward, and cheap synthesis of highly substituted functionalized pyrrole derivatives via one pot four-component reactions of 1,3-dicarbonyl compounds, amines, aromatic aldehydes, and nitroalkanes have been developed. This methodology provides desired pyrroles in good-to-excellent yields in the presence of Fe (III)-Schiff base/SBA-15 as a heterogeneous catalyst.

ARTICLE HISTORY
Received 17 October 2019
Accepted 24 February 2020

KEYWORDS
SBA-15; Fe (III)-Schiff base; pyrrole derivatives; heterogeneous catalysis

Introduction

The pyrrole heterocycle core is an important structural motif in wide varieties of biologically and medicinally vital compounds.[1] They has key roles such as anti-inflammatory drug (Ketorolac **1**)[2] (Figure 1), antitumor agents,[3] immunosuppressants[4] but also it has proven to be useful building block in organic synthesis.[5] The classical methods of preparing pyrrole compounds include Hantzsch and Paal–Knorr reactions.[6,7] Furthermore a variety of transition metal catalyzed reactions[8,9] and multicomponent coupling strategies[10,11] have been developed during the last decade. Despite the numerous approaches for the synthesis of pyrroles, a novel, simple process, straightforward and cheap synthetic method is still an attractive goal.

Mesoporous silicate-aluminosilicates are Santa Barbara Amorphous (SBA) materials characterized by uniform pore size (4.6–30 nm), well-defined pore structure and size-distribution, high surface area, high thermal stability and the capability to support a large panel of active species including Lewis acid metal ions. One of the most promising components of this family is SBA-15.[12]

SBA-15 materials have been well recognized as a promising support template for the synthesis of catalytic materials due to its uniform, hexagonally-arrayed channels with a narrow pore size distribution. These features, together with high surface area and hydrothermal stability, make it as an ideal support for the incorporation of various active molecules on its surface. Transition metals such as Fe, Pd, Cu, etc with acid Lewis character are suitable for supporting on SBA-15 for obtaining an active heterogeneous catalyst. In recent past decades, SBA-15 has witnessed remarkable advances in the field of heterogeneous catalysis due to its high surface area, tunable pore size distribution, high hydrothermal and mechanical stability.[12,13] Beside, Fe (III) complexes of Schiff base ligands was found to be very effective catalysts and have wide applications in organic synthesis. In fact, both Fe (III)-Schiff base and SBA-15 are important in catalytical activity.

Generally, Schiff base ligands are compounds with functional groups that contain carbon-nitrogen double bonds, coordinate metals through imine nitrogen and are prepared by the condensation of primary amines and aldehydes or ketones (Scheme 1).[13–20] The covalent anchoring of Fe (III)-Schiff base onto the SBA-15 is an effective way for extending benefits of the silica solid support to the Schiff base ligand. The benefits may include ease of work-up procedures, the potential for reuse of the supported catalysts, high activity and selectivity and metals leaching reduction.[19,21]

Multicomponent reactions are very popular due to their improved efficiency, a single-step procedure, avoiding complicated purification processes and saving both solvents and reagents.[14,15,20,21] There are several synthetic procedures for preparation of Pyrroles derivatives under different conditions for instance, One-pot four-component synthesis of highly substituted pyrroles in gluconic acid aqueous solution,[22] synthesis of new 3-cyanoacetamide pyrrole and 3-acetonitrile pyrrole derivatives,[23] Iron-Catalyzed Radical Cycloaddition of 2H-Azirines and Enamides for the Synthesis of Pyrroles,[24] Synthesis of Polyfunctionalized Pyrroles via a Tandem Reaction of Michael Addition and Intramolecular Cyanide-Mediated Nitrile-to-Nitrile Condensation.[25] However these compounds have been produced using different methodologies but low yields, hazardous chemicals and harsh reaction conditions are some of their drawbacks. For example acid aqueous solution,

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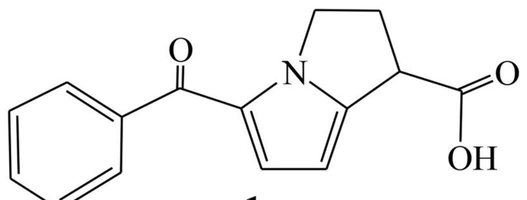

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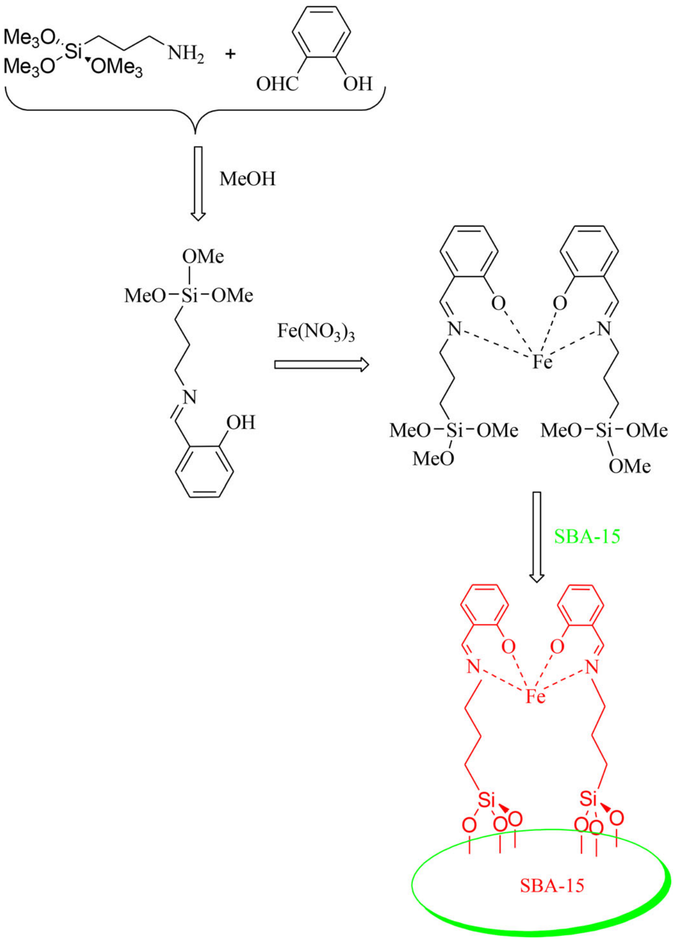
Figure 1. Ketorolac, a drug product containing pyrrole core.



Scheme 1. Preparation of Fe (III)-Schiff base/SBA-15

hazardous solvent, unrecyclable catalysts, low product yields for aromatic amines, use of expensive reagents and inaccessible starting materials, were used in these reactions.

Despite the mentioned disadvantages some reported procedures have opened new prospects for the synthesis pyrroles, in this paper, accessible initial materials, possible catalyst recycling, high activity and selectivity, high yield products and easy catalyst separation are considerable Therefore, we decided to develop a catalytic synthesis of pyrroles by means of a novel four-component domino reactions of 1,3-dicarbonyl compounds, aldehydes, amines, and nitroalkanes. The proposed mechanism for the synthesis of substituted pyrroles in the presence of Fe (III)-Schiff base/SBA-15 can be presented as follow (Scheme 2).

In this study, the use of a nontoxic and heterogeneous catalyst along with a simple and clean catalyst separation from reaction mixture, the reusable catalyst and no need for high boiling point chemical solvent, can confirm the environmentally friendly condition in this process. The use of mesostructure to link the iron (III) catalytic center to the solid support can provide good convenience without steric effects.[26] The role Fe (III)-Schiff base/SBA-15 is as Lewis acid and catalyst in pyrrole synthesis.

According to the proposed mechanism, the carbonyl groups were activated by Fe (III)-Schiff base/SBA-15 and then these were attacked by amine and nitro groups to give the intermediates 1 and 2. Next, the interaction between intermediate 1 and 2 and cyclization reaction and elimination of H_2O led to the formation of final product.

Results and discussion

Here, at first we report characterization of Fe (III)-Schiff base anchored on SBA-15, then its application as an efficient heterogeneous catalyst in four-component synthesis of highly substituted pyrroles.

Techniques for physicochemical characterization of nanomaterials such as FT-IR, N_2 adsorption/desorption (BET), X-ray diffraction (XRD), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA) were used to characterized the successful grafting of the Fe(III)-Schiff base onto SBA-15.

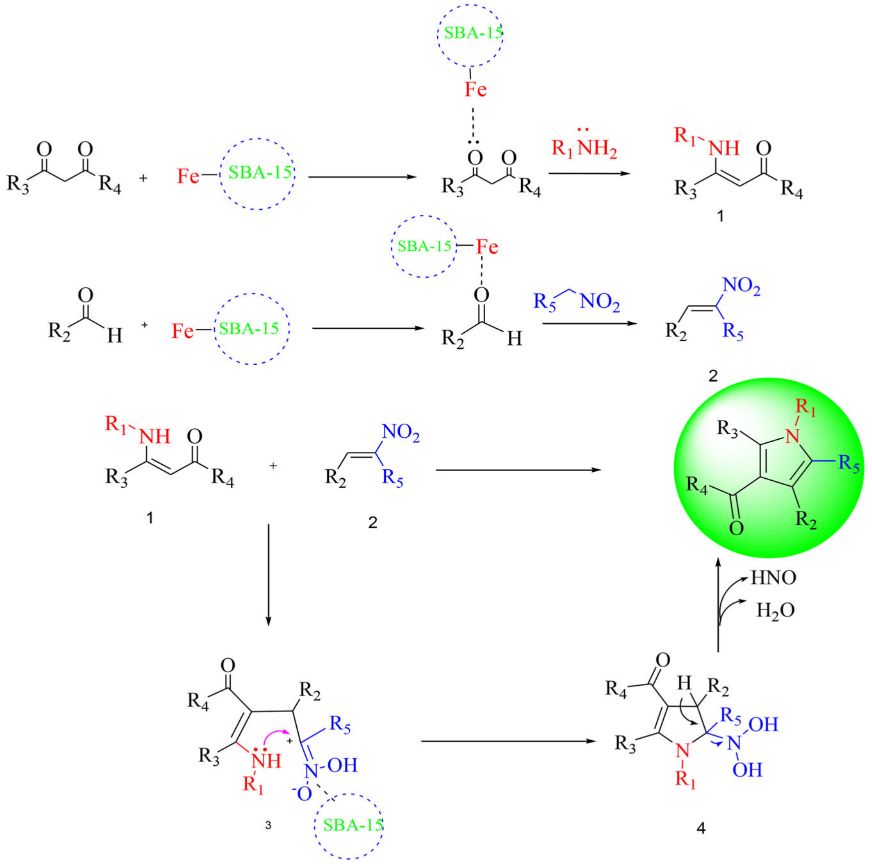
The FT-IR spectra of SBA-15 and Fe (III)-Schiff base/SBA-15 is shown in (Figure 2). According to the FTIR spectra of SBA-15, the bands are attributed to at 3413 cm^{-1} OH, 1631 cm^{-1} C=N, 1091 cm^{-1} Si-O-Si, 806 cm^{-1} Si-OH and 462 cm^{-1} Si-O separately. The FTIR spectra of Fe (III)–Schiff base/SBA-15 shows characteristic vibration peaks at 3417, 2900, 1606, 1103 cm^{-1} which are assigned to the vibrations of OH, -CH2, C=N, Si-O-Si, respectively.

Nitrogen adsorption/desorption isotherms and also size distributions of SBA-15 and Fe (III)-Schiff base/SBA-15 are shown in (Figure 3A). These isotherms are of type IV with H1-type hysteresis loops, according to the IUPAC classification,[22,27] typically for mesoporous materials. Furthermore, as can be seen in Table 1, the surface area and pore volume of Fe (III)-Schiff base/SBA-15 decreases in comparison with SBA-15, due to the anchoring of Fe (III)-Schiff base on SBA-15 surface.

In XRD pattern of both SBA-15 and Fe (III)-Schiff base/SBA-15 (Figure 3B), the peaks at about (100), (110), and (200) arise from ordered hexagonal unit cell of mesoporous materials. The lower angle in XRD pattern of Fe(III)-Schiff base/SBA-15 (Figure 3B), is due to the development of unit cell arises from the connection of the complex within SBA-15 and the lower intensities is due to a decrease in the mesoscopic order.[23,24,28,29]

The TEM image of the supported complex confirms the retaining of hexagonal structure of uniform linear channels of Fe (III)-Schiff base/SBA-15 (Figure 3C).

Thermo gravimetric (TG) analysis of the samples is presented in Figure 3D. TG analysis determines the amount of decomposition of species. The TG curve of both SBA-15 and Fe (III)-Schiff base/SBA-15 show a weight loses at around 100 °C which is attributed to the loss of physically adsorbed water. Besides, the thermogram of Fe (III)-Schiff-



Scheme 2. Proposed mechanism for the synthesis of substituted pyrroles in the presence of Fe (III)-Schiff base/SBA-15

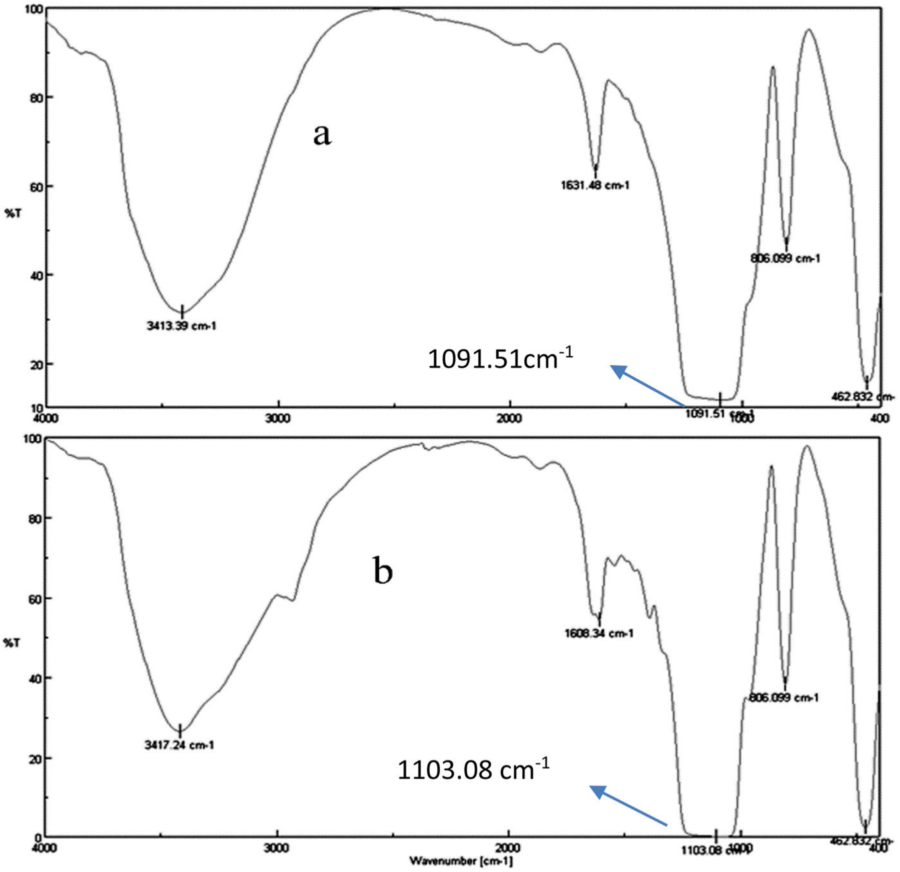


Figure 2. FT-IR spectra of (a) SBA-15 and (b) Fe (III)-Schiff base/SBA-15 Catalytic synthesis of heterocycles.

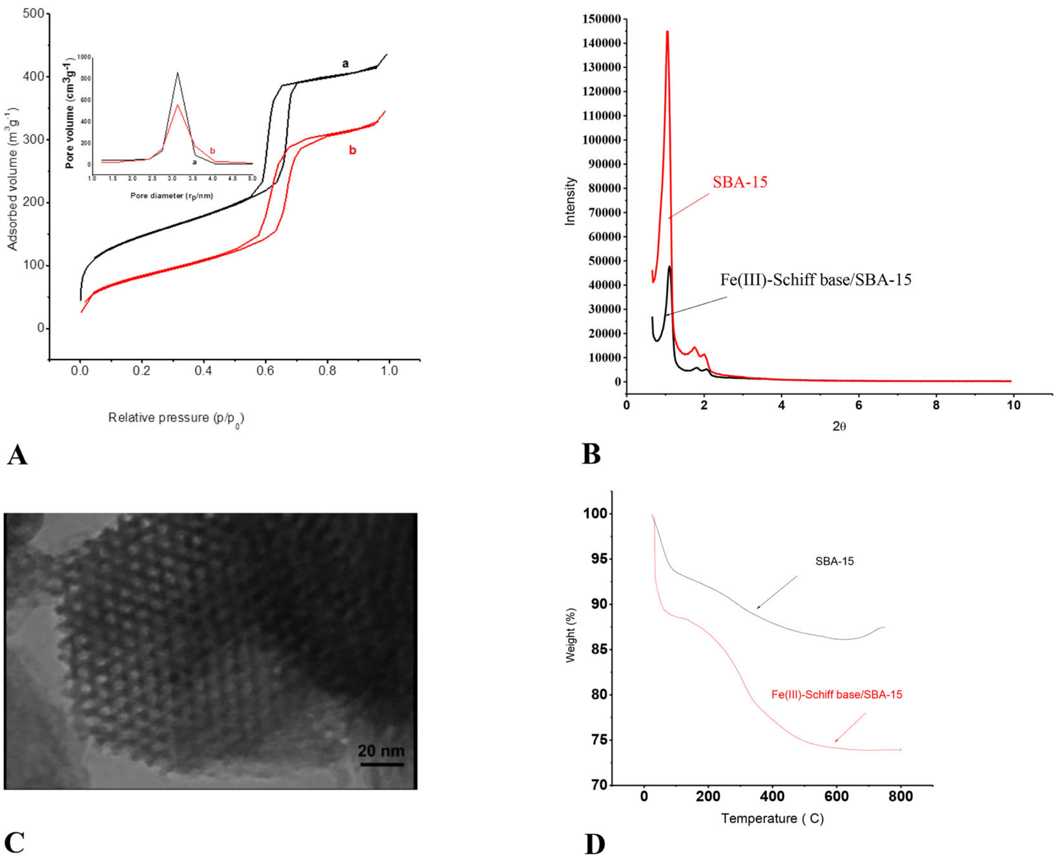


Figure 3. (A) Nitrogen adsorption/desorption isotherms and corresponding pore size distribution profile (inset) of (a) SBA-15 and (b) Fe (III)-Schiff base/SBA-15. (B) XRD patterns of SBA-15 and Fe (III)-Schiff base/SBA-15. (C) TEM images of Fe (III)-Schiff base/SBA-15. (D) Thermogravimetric analysis results of SBA-15 and Fe (III)-Schiff base/SBA-15.

Table 1. Textural properties of the SBA-15 and Fe (III)-Schiff base/SBA-15.

Materials	C(M)[a]	S^{b}_{BET}	V^{c}_{BJH}
SBA-15	–	539	1.01
Fe(III)-Schiff base/SBA-15	0.14	472	0.85

[a] Initial concentration of iron species (mmol g^{-1}).
[b] specific surface area (m^2 g^{-1}).
[c] pore volume (cm^3 g^{-1}).

base anchored SBA-15 represents another weight loss between 200 and 700 °C (Figure 3D) through the decomposition of the covalently bonded Schiff ligand.

After the survey of the structure and morphology of the prepared Fe (III)-Schiff base functionalized SBA-15, we intended to test its efficiency as heterogeneous catalysts for the preparation of pyrrole derivatives. At first, aromatic amine **2**, aldehyde **3**, acetylacetone **4**, and nitro methane **5** were selected as the model substrates to investigate the best reaction conditions (Table 2). Some parameters such as temperature, the type and amount of catalyst were examined to determine the efficiency of the model reaction. At first, we tried to accomplish this reaction at reflux temperature in the absence of catalyst, but it gave less than 5% yield after 12 hours. Then, we tried using anhydrous $FeCl_3$ and Fe (III)-Schiff base/SBA-15 as catalysts and we found that Fe (III)-Schiff base/SBA-15 was the most effective catalyst for this transformation. The best yield was obtained in the presence of 0.001 g (0.00014 mmol based on Fe ions) of Fe (III)-Schiff base/SBA-15, under reflux conditions (Table 2, entry 6).

With the optimal reaction conditions established in hand, the generality of the procedure was evaluated by reactions of various aromatic amines and aldehydes with nitroalkanes, and 1,3-dicarbonyl compounds (Table 3, entries 1–16). As can be seen, most of the examined substrates provided good to excellent yields. The first step of our investigation on the generality of the reaction, we next examined the scope of this reaction with various aromatic amines. The desired substituted pyrroles were afforded in almost good yields regardless of the aromatic substituent but the weakly electron-deficient halogen-containing aromatic amines and the aliphatic amine, afforded the target product in lower yield (Table 3, entries 13,14, and 11). We also tried to do the reaction with very strong electron-withdrawing group such as $-NO_2$, but the result was not satisfactory and the reaction was not followed anymore. Having successfully achieved the catalytic multicomponent synthesis of substituted pyrroles, the scope of the reaction was expanded by performing the reaction with various aromatic aldehydes. It seems that the reactivity is influenced by neither electron withdrawing nor electron donating functionalities. At last, when this methodology was applied to unsymmetrical 1,3-diketones, pyrroles **5k** and **5p** were chemo selectively formed, this could be attributed to the participation of the more activated acetyl group.

In continue, to test the lifetime and the reusability of the catalyst, a series of experiments were examined for the model reaction compound **5h**. For this, after completion of

Table 2. Screening of the reaction conditions for four-component coupling reactions of aromatic amine **1**, aldehyde **2**, acetylacetone **3**, and nitro methane **4**.[a]

Entry	Catalyst	Catalyst amount (g)	Temperature (°C)	Time (h)	Yield (%)[b]
1	–	–	reflux	12	<5
2	$FeCl_3$	0.008	reflux	12	36
3	Fe(III)-Schiff base/SBA-15	0.001	rt	12	50
4	Fe(III)-Schiff base/SBA-15	0.001	60	12	60
5	Fe(III)-Schiff base/SBA-15	0.001	reflux	6	70
6	Fe(III)-Schiff base/SBA-15	0.001	reflux	12	88 (87)[c,d]
7	Fe(III)-Schiff base/SBA-15	0.01	reflux	12	88
8	Fe(III)-Schiff base/SBA-15	0.0005	reflux	12	34
9	Fe(III)-Schiff base/SBA-15	0.001	reflux	24	79

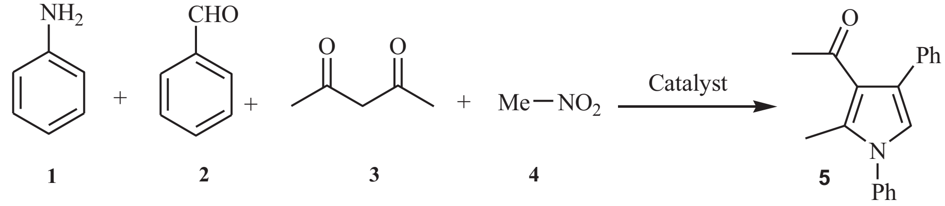
[a] All reactions were runing under the following conditions: Aromatic amine **1** (1.5 mmol), aldehyde **2** (1 mol) and acetylacetone **3** (1 mmol) in nitromethane **4** (1 mL) and catalyst (0.001 g) were heated for appropriate time.

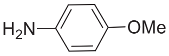
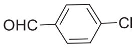
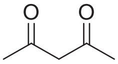
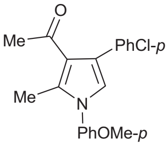
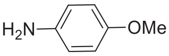
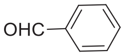
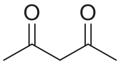
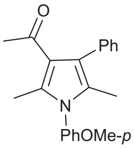
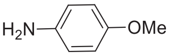
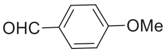
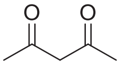
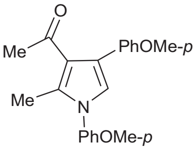
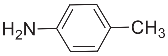
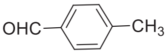
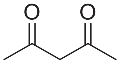
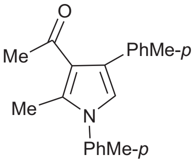
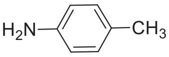
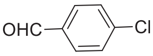
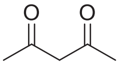
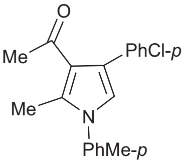
[b] % (based on GC yields).

[c] Optimum conditions.

[d] Isolated yield in parentheses.

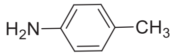
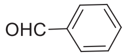
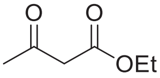
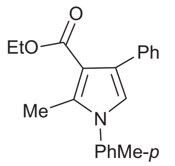
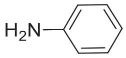
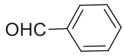
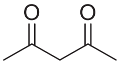
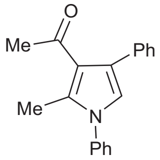
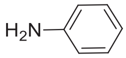
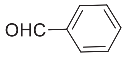
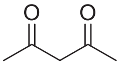
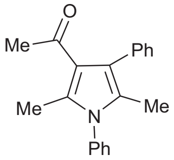
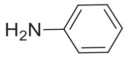
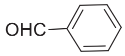
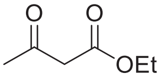
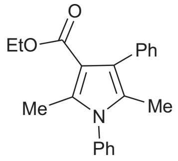
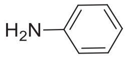
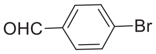
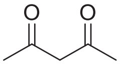
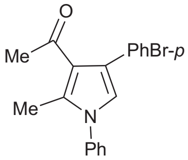
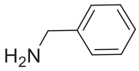
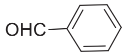
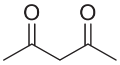
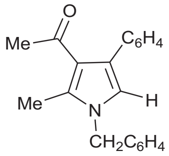
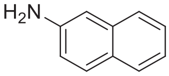
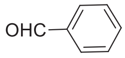
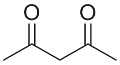
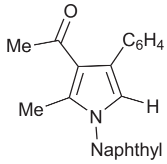
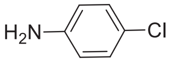
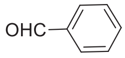
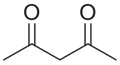
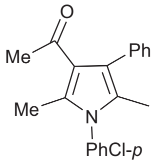
Table 3. Synthesis of desired heterocyclic derivatives catalyzed by Fe (III)-Schiff base/SBA-15[a].



Entry	Amine **1**	Aldehyde **2**	Nitroalkane **3**	1,3-dicarbonyl **4**	Product	Yield (%)	m.p.
1			CH_3NO_2		 **5a**	88	118–120
2			$CH_3CH_2NO_2$		 **5b**	78	126–128
3			CH_3NO_2		 **5c**	43	135–137
4			CH_3NO_2		 **5d**	63	92–93
5			CH_3NO_2		 **5e**	65	109–110

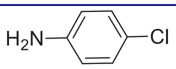
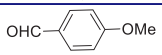
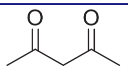
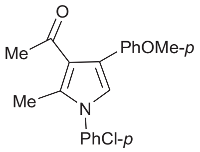
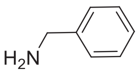
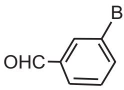
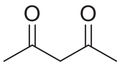
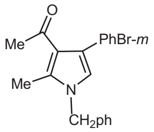
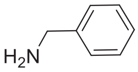
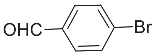
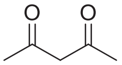
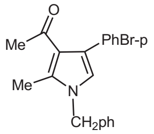
(*continued*)

Table 3. Continued.

Entry	Amine **1**	Aldehyde **2**	Nitroalkane **3**	1,3-dicarbonyl **4**	Product	Yield (%)	m.p.
6			CH_3NO_2		 **5f**	58	62–64
7			CH_3NO_2		 **5g**	78	104–106
8			$CH_3CH_2NO_2$		 **5h**	73	114–116
9			$CH_3CH_2NO_2$		 **5i**	70	82–83
10			CH_3NO_2		 **5j**	76	86–88
11			CH_3NO_2		 **5k**	43	53–55
12			CH_3NO_2			76	145–147
13			$CH_3CH_2NO_2$		 **5m**	60	142–144

(*continued*)

Table 3. Continued.

Entry	Amine **1**	Aldehyde **2**	Nitroalkane **3**	1,3-dicarbonyl **4**	Product	Yield (%)	m.p.
14			CH_3NO_2		 **5n**	51	115–118
15			CH_3NO_2		 **5o**	50	105–107
16			CH_3NO_2		 **5p**	52	115–117

[a] All reactions were carried out using aldehyde (0.1 mmol), amine (0.15 mmol), and 1,3-dicarbonyl compounds (0.1 mmol) with nitromethane (0.1 mL), catalyst (0.001 gr) under reflux,12–16 h. The structures of all products **5a-5p** were established by melting point, IR, ^{1}H NMR, and ^{13}C NMR spectra.[30–38]

Table 4. Reuse of the catalyst for the synthesis of 1-[4-(4-Chloro-phenyl)-1-(4-methoxy-phenyl)-2-methyl-1H-pyrrol-3-yl]-ethanone **6**.

Run	1	2	3	4	5	6
Yield[a] (%)	88	88	88	87	87	87

[a] Isolated yield.

the first reaction with 88% yield, the catalyst was separated and reused after washing with hot ethanol and drying at 80 °C for 60 min. The recovered catalyst was used again under the same reaction conditions and it showed excellent reusability over six runs (Table 4).

Conclusion

In conclusion, we have reported a one-pot, four-component protocol for the synthesis of highly substituted pyrroles in the presence of Fe (III)-Schiff base/SBA-12 as a catalyst. Using readily available and inexpensive starting materials, operational simplicity, good to excellent products yields and reusability of catalyst are prominent among the advantages of this new method.

Notes

1. Anchoring of Fe (III)-Schiff base complex on SBA-15: Synthesis of SBA-15 was carried out as previously reported by Huisgen et al.[34] Fe (III)-Schiff base complex was prepared by applying the procedure reported by Li et al.[35] Activated SBA-15 (1.5 g) was suspended in 20 mL methanol solution containing (0.38 g) Schiff base complex, and the mixture was stirred for 24 h. The solvent was removed using a rotary evaporator, and the resulting solid was dried at 80 °C overnight. The product was washed with MeOH and deionized until the washings were colourless to ensure that the non-covalently grafted complex and physisorbed metal species were removed. At last, the product was dried in an oven at 80 °C for 8 h (Scheme 1).
2. General procedure for the synthesis of pyrazine based heterocycles: A round-bottomed flask equipped with a magnet and condenser was charged with desired aldehyde (0.1 mmol), amine (0.15 mmol), and 1,3-dicarbonyl compounds (0.1 mmol) with nitromethane (0.1 mL), catalyst (Fe(III)-Schiff base/SBA-15, 0.001gr). The resulting mixture was heated at reflux temperature for the appropriate times, and the course of the reaction was monitored using TLC on silica gel (*n*-hexane/ethylacetate: 4/1). Finally, the reaction mixture was cooled and the crude mixture was purified by column chromatography after removal of excess amount of nitroalkan.

   Data for selected products:

   1-[4-(4-Chlorophenyl)-1-(4-methoxyphenyl)-2-methyl-1H-pyrrol-3-yl]-ethanone, compound 6:

   White powder; m.p. 118–120 °C; IR (KBr, *ν*, cm^{-1}): 3010, 2880, 1620, 1560, 1251.^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03(s, 3H), 2.10 (s, 3H), 3.70 (s, 3H), 6.71 (s, 1H), 6.99 (d, J = 8.9 Hz, 2H), 7.21 (d, J = 8.6 Hz, 2H), 7.24-7.33 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 12.7, 31.2, 55.4, 114.6, 121.1, 122.5, 124.3, 127.4, 128.6, 130.2, 131.1, 132.7, 134.5, 135.5, 159.6, 197.2.

   1-[1,4-Bis(4-methoxyphenyl)-2-methyl-1H-pyrrol-3-yl]-ethanone, compound 8:

   White powder; m.p. 135–137 °C; IR (KBr, v, cm^{-1}): 3010, 2884, 1625, 1502, 1263. ^{1}H NMR (300 MHz, $CDCl_3$): 2.05 (s, 3H), 2.32 (s, 3H), 3.85(s, 3H), 3.80 (s, 3H), 6.61 (s, 1H), 6.90-6.97 (m, 4H), 7.12–7.21 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): 12.0, 30.5, 55.0, 55.3, 113.7, 114.1, 120.5, 122.1, 125.4, 127.1, 128.3, 130.2, 131.6, 135.4, 158.4, 159.1, 197.7.

Acknowledgments

University of Tehran, School of Chemistry is thanked for financial support of this work.

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