

Pr³⁺ doped CoFe₂O₄: A highly efficient, magnetically recoverable and reusable catalyst for one-pot four-component synthesis of multisubstituted pyrroles

Firoz A. Kalam Khan^a, Amol M. Pachpinde^b, Mallinath M. Langade^b, Kishan S. Lohar^c, Sunil M. Patange^c, Omprakash G. Bhusnure^d, Jaiprakash N. Sangshetti^{a,*}

^aDr. Rafiq Zakaria Campus, Y.B. Chavan College of Pharmacy, Aurangabad 431001, (M.S.), India.

^bDepartment of Chemistry, Jawahar Art Science and Commerce College, Andur, Osmanabad 413603, (M. S.), India.

^cMaterials Research Laboratory, Srikrishna Mahavidyalaya Gunjoti, Omerga, Osmanabad 413 613, (M. S.), India.

^dDepartment of Quality Assurance, Channabasweshwar Pharmacy College, Latur 413512, (M. S.), India.

Received 14 October 2015; received in revised form 13 December 2015; accepted 18 December

ABSTRACT

A facile and highly efficient one-pot synthesis of multisubstituted pyrrole derivatives is reported via a four-component reaction of amines, aldehydes, acetylacetone and nitromethane using Pr³⁺ doped CoFe₂O₄ as a catalyst in solvent free conditions at 90°C. The catalyst is easily recoverable using magnet and could be reused without a significant loss of catalytic activity. Even after five runs for the reaction, the catalytic activity of Pr³⁺ doped CoFe₂O₄ was almost the same as that of the freshly used catalyst. The proposed method is advantageous due to its little catalyst loading, short reaction time, catalyst reusability, and excellent yields.

Keywords: Pr³⁺ doped CoFe₂O₄; Multisubstituted pyrroles; Recoverable using magnet; Catalyst reusability.

1. Introduction

Multicomponent reactions (MCRs) [1-3] have become important tools for the efficient and rapid generation of structurally complex target compounds with predefined functionality in chemical biology and drug discovery [4-6]. These reactions are often discovered by serendipity, but rational design strategies are now playing an increasing role because of their convergent nature, superior atom economy, and straightforward experimental procedures in the construction of target compounds by the introduction of several diversity elements in a single operation, resulting in substantial minimizations of waste, labor, time, and cost. MCRs, a powerful and virtually reliable target-guided synthetic approach, has extensively been used and applied for the rapid construction of molecular-level complex architectures, and interest from different branches of science is expanding exponentially [7]. Pyrrole is one of the important heterocycle owing to its

antitumor, anti-inflammatory, antibacterial, antioxidant and antifungal properties [8-10]. In addition, pyrrole derivatives are also important in materials science [11]. These utilities continue to attract interest in the development of new synthetic methods for pyrrole derivatives. The traditional routes to their synthesis are multistep reactions, as illustrated by the Paal-Knorr cyclization of 1,4-dicarbonyls with ammonia or primary amines [12,13]. This method suffers from several drawbacks, such as stepwise reactions, narrow substrate scope, and lack of the variation of substituents on the pyrrole ring due to the unity of starting materials. For all these reasons, the search for new atom-economical and green synthetic methods, which avoid the use of special reagents, cost, time, and steps from readily available and inexpensive materials for the synthesis of multi-substituted pyrrole derivatives, has attracted much attention [14,15]. Combining the advantages of multicomponent reaction and the magnetic nano-catalysts, the development of a new atom-efficient and environmentally friendly synthetic procedure for the efficient preparation of structurally diverse pyrroles is therefore an interesting challenge.

*Corresponding author email: jnsangshetti@rediffmail.com
Tel./Fax: +91 240 238 1129

With the increasing demand for “green chemistry”, the use of efficient and recoverable supported heterogeneous catalysts has become one of the most important topics of research in synthetic organic chemistry, material science, and engineering. One of the most attractive alternatives to catalysts is the use of magnetic ferrites, which have witnessed increasing popularity due to their high surface areas and improved dispersability in the reaction medium [16, 17]. Specifically, magnetic ferrite catalysts can be recovered using an external magnet due to the paramagnetic character. This makes the removal and recycling of the catalyst much easier than filtration and centrifugation. Inspired by the utilization of Pr³⁺ doped CoFe₂O₄ as a magnetically recoverable and reusable catalyst and as a part of our continuous interest in the field of multicomponent reactions [18-28], herein we wish to report an efficient one-pot four-component synthesis of multisubstituted pyrrole derivatives via reaction of amines, aldehydes, acetylacetone and nitromethane in high yields and short reaction times by using Pr³⁺ doped CoFe₂O₄ with as a green, robust and easily recoverable catalyst (Scheme 1).

2. Experimental

2.1. Chemicals and apparatus

All solvents, chemicals, and reagents were purchased from Merck, Avra Synthesis and Sigma-Aldrich chemical companies. The purity of the synthesized compounds was checked by TLC. Melting points were determined in capillary tubes and were uncorrected. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded on a Varian-Gemini spectrometer and are reported as parts per million (ppm) downfield from a tetramethylsilane internal standard. The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). Mass spectra were taken with Micromass- QUATTRO-II of WATER mass spectrometer.

2.2. General procedure for the synthesis of multisubstituted pyrrole derivatives 5(a-k)

The mixture of amine **1** (1.0 mmol), aldehyde **2** (1.0 mmol), acetylacetone **3** (1.0 mmol), nitromethane **4** (1.0 mL) and Pr_xCoFe_{2-x}O₄ (x= 0.05) (5 mol %) was stirred at 90 °C (Scheme 1). The completion of the reaction was checked by TLC (n-hexane: ethyl acetate

4:1). Upon completion of the reaction, the reaction mixture was cooled to room temperature and 10 ml of ethyl acetate was added. The pyrrole derivatives were dissolved in ethyl acetate and the catalyst was separated magnetically, washed with ethyl acetate and used for subsequent cycles. Pure products were obtained by evaporation of the solvent, followed by recrystallization from ethanol. The melting points were recorded and compared with the corresponding literature melting point and found to be matching with those.

Selected spectral data

1-(4-hydroxyphenyl)-2-methyl-4-phenyl-3-acetyl-1H-pyrrole (**5f**):

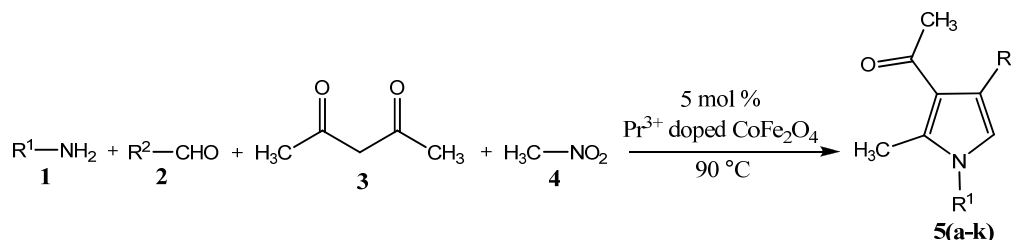
Orange solid. m.p.= 150-152°C. ¹HNMR (400 MHz, CDCl₃): δ = 2.07 (s, 3H, -CH₃), 2.44 (s, 3H, CH₃-C=O), 4.70 (br, 1H, Ar-OH), 6.24 (s, 1H, -CH- of pyrrole), 6.90-7.40 (m, 4H, ArH), 7.45-7.53 (m, 5H, ArH) ppm. ¹³CNMR (100 MHz, CDCl₃): δ= 13.35, 38.62, 117.41, 120.24, 122.53, 126.24, 127.05, 127.55, 128.57, 129.21, 132.54, 135.14, 138.45, 160.25, 189.67 ppm. MS (EI, 70 eV): *m/z* = 292.24 [M+H]⁺.

4-(4-hydroxyphenyl)-2-methyl-1-phenyl-3-acetyl-1H-pyrrole (**5k**):

Orange solid. m.p.= 174-176°C; ¹HNMR (400 MHz, CDCl₃): δ = 1.98 (s, 3H, -CH₃), 2.34 (s, 3H, CH₃-C=O), 5.19 (br, 1H, Ar-OH), 6.39 (s, 1H, -CH- of pyrrole), 7.10 (d, *J* = 8.4 Hz, 2H, ArH), 7.25 (d, *J* = 6.9 Hz, 2H, ArH), 7.45-7.60 (m, 5H, ArH) ppm. ¹³CNMR (100 MHz, CDCl₃): δ= 14.15, 32.05, 116.45, 119.68, 123.61, 125.23, 126.94, 128.32, 129.14, 130.54, 131.73, 134.11, 139.23, 154.15, 190.58 ppm. MS (EI, 70 eV): *m/z* = 292.34 [M+H]⁺.

3. Results and Discussion

Pr³⁺ doped CoFe₂O₄ ferrites were prepared by our research group [29] through sol-gel auto-combustion route to achieve homogeneous mixing of the chemical constituents on the atomic scale and better sinterability. Analytical grade cobalt nitrate (Co(NO₃)₂·3H₂O), praseodymium nitrate Pr(NO₃)₃·6H₂O, ferric nitrate (Fe(NO₃)₃·9H₂O) and citric acid (C₆H₈O₇·H₂O), were used to prepare the Pr_xCoFe_{2-x}O₄ (x= 0.0, 0.025, 0.05, and 0.1). Reaction procedure was carried out in air atmosphere without protection of inert gases.



Scheme 1. Synthesis of multisubstituted pyrroles **5(a-k)**.

The prepared powder was then annealed at 600°C for 4 h. The particle size was studied by scanning electron microscope (SEM). The SEM micrographs are shown in Figure 1(a-d), which shows good spherical shaped particles in the material. The SEM pictures also indicate nearly uniform distribution of particles.

Initially, to study the catalytic efficiency of Pr^{3+} doped CoFe_2O_4 , all the four $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.0, 0.025, 0.05$ and 0.1) ferrites were screened to find out the best ferrite composition using synthesis of 2-methyl-1,4-diphenyl-3-acetyl-1H-pyrrole (**5a**) as the model reaction. The reaction was carried out with aniline **1** (1.0 mmol), benzaldehyde **2** (1.0 mmol), acetylacetone **3** (1.0 mmol), nitromethane **4** (1.0 mL) using $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.0, 0.025, 0.05$ and 0.1) ferrites (20 mol %) as catalyst (Table 1). The title compound **5a** was isolated with 95 % yield in the presence of $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) in a shorter reaction time (1.5 h) than with other ferrites i.e. $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.0, 0.025$ and 0.1). Thus, $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) was found to be the best catalyst among screened Pr^{3+} doped CoFe_2O_4 ferrites in terms of yield and reaction kinetic.

After deciding the catalyst, the amount of $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$), that is, the catalyst load was optimized

for model reaction (**5a**). The catalyst was added in amounts of 30, 20, 15, 10, 5, and 0 mol %. The results indicate that an increase in amount of catalyst from 20 mol % to 30 mol % did not show any change in yield and time of reaction (Table 1, Entry 5). Also, when the catalyst load was decreased sequentially from 20 mol % to 5 mol %, the results indicate, there were no change in yield and time of the reaction (Table 1, Entries 6, 7 and 8). When no catalyst was added (Table 1, Entry 9) for model reaction (**5a**), there was only a small amount (yield 15 %) of product obtained after 6 h. Therefore, 5 mol % of the $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x = 0.05$) the catalyst was assumed to ensure the best yield (95 %) in a short reaction time (1.5 h). Thus, our results make the process under study more attractive and interesting from the viewpoint of economy and simplicity.

Following the optimized reaction conditions, a variety of multisubstituted pyrrole derivatives **5(a-k)** were synthesized (Scheme 1) in good yields (Table 2). As shown in Table 2, anilines bearing either electron-withdrawing or electron-releasing groups gave the corresponding pyrroles (**5a-5f**) in high yields (85-97 %).

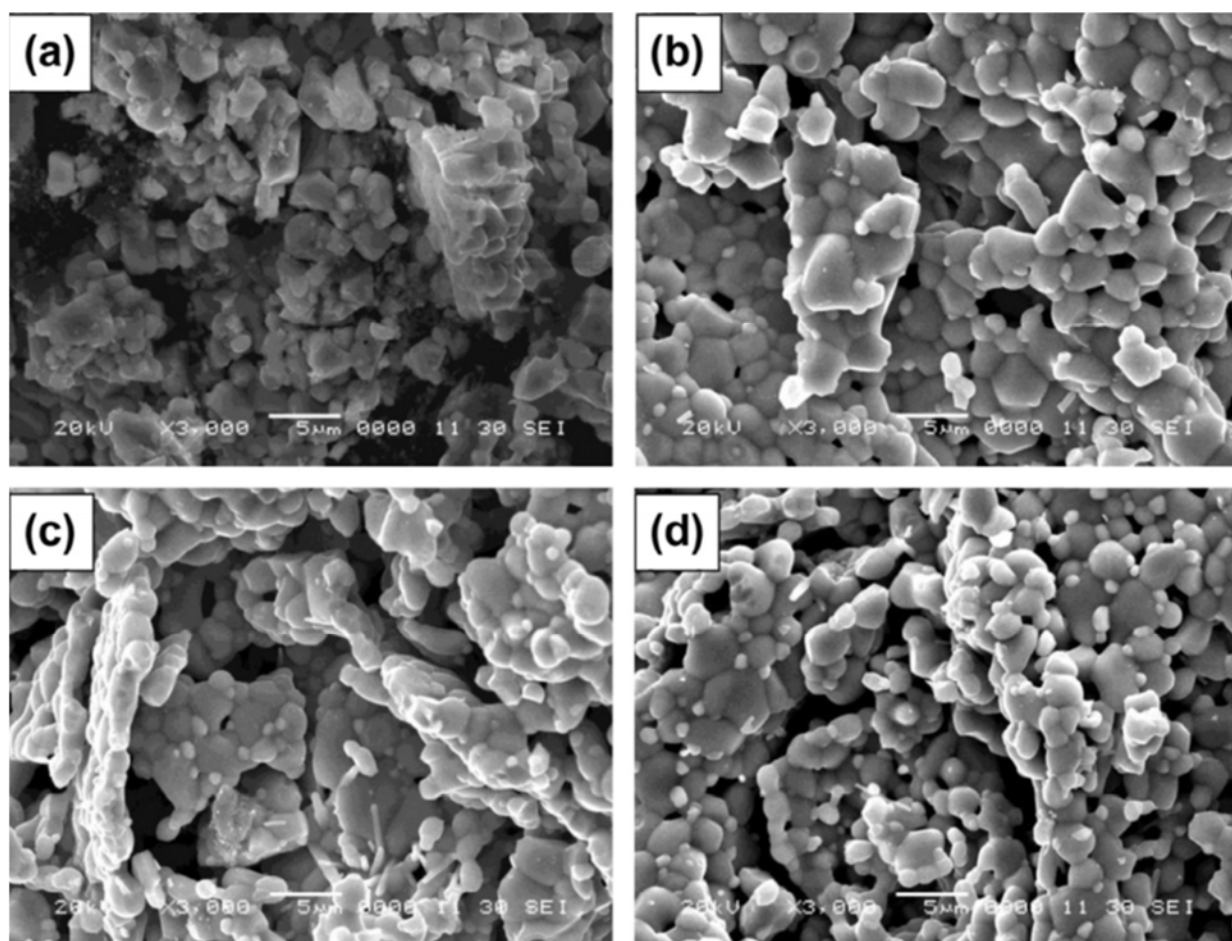


Fig. 1. SEM images of $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$, where (a) $x = 0.0$, (b) $x = 0.025$, (c) $x = 0.05$, and (d) $x = 0.1$.

Table 1. Optimization of reaction conditions and catalyst load (mol %) of Pr³⁺ doped CoFe₂O₄ for the synthesis of **5a**.

Entry	Catalyst	Catalyst (mol %)	Time (h)	Yield of 5a (%) ^a
1	Pr _x CoFe _{2-x} O ₄ (x = 0.0)	20	4	70
2	Pr _x CoFe _{2-x} O ₄ (x = 0.025)	20	5	72
3	Pr _x CoFe _{2-x} O ₄ (x = 0.05)	20	1.5	95
4	Pr _x CoFe _{2-x} O ₄ (x = 0.1)	20	4.5	78
5	Pr _x CoFe _{2-x} O ₄ (x = 0.05)	30	1.5	95
6	Pr _x CoFe _{2-x} O ₄ (x = 0.05)	15	1.5	95
7	Pr _x CoFe _{2-x} O ₄ (x = 0.05)	10	1.5	95
8	Pr _x CoFe _{2-x} O ₄ (x = 0.05)	5	1.5	95
9	No catalyst	-	6	15

^aHereinafter, isolated yield of pure product.

In addition, it was specifically considerable that anilines bearing electron-releasing groups such as -CH₃ (**5e**, yield 97 %) and -OH (**5f**, yield 96 %) reacted very smoothly and gave higher yields (Table 2, Entries 5 and 6) while electron-withdrawing substitutions such as -F (**5b**, yield 90 %), -Cl (**5c**, yield 88 %) and -NO₂ (**5d**, yield 85%) showed less reactivity in this cyclization reaction (Table 2, Entries 2, 3 and 4). Similarly, benzaldehydes bearing electron-withdrawing substituents such as -F (**5g**, yield 85 %), -Cl (**5h**, yield 87 %) and NO₂ (**5i**, yield 83) gave less yields when compared with electron-donating substituents such as -CH₃ (**5j**, yield 93 %) and -OH (**5k**, yield 95 %) (Table 2, Entries 7-11). Thus, these successful results greatly proved that this procedure was extendable to various substrates in four-component reactions, generating moderate to high yields of the multisubstituted pyrrole derivatives **5(a-k)**.

Catalyst reusability is of major concern in heterogeneous catalysis. The recovery and reusability of the catalyst was investigated in this reaction for model reaction **5a**. The reaction mixture of aniline **1** (1.0 mmol), benzaldehyde **2** (1.0 mmol), acetylacetone **3** (1.0 mmol), nitromethane **4** (1.0 mL) and 5 mol % of Pr_xCoFe_{2-x}O₄ (x = 0.05) as the catalyst was refluxed at 90 °C. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The compound was dissolved in 10 mL ethyl acetate and catalyst recycling was achieved by fixing the catalyst magnetically at the bottom of the flask with a strong magnet, after which the solution was taken off with a pipette. The solid (i.e., catalyst) was washed twice with ethyl acetate and dried to remove residual solvents, and then reused directly in the model reaction for next round without further purification.

Table 2. One-pot four-component synthesis of multisubstituted pyrroles **5(a-k)**.

Entry	R ¹	R ²	Product	Time (h)	Yield (%) ^a	m.p. (°C)		Ref.
						Found	Reported	
1	C ₆ H ₅	C ₆ H ₅	5a	1.5	95	104-106	106-107	[30]
2	4-F-C ₆ H ₄	C ₆ H ₅	5b	2	90	132-124	130-131	[30]
3	4-Cl-C ₆ H ₄	C ₆ H ₅	5c	2.5	88	126-128	127-128	[30]
4	4-NO ₂ -C ₆ H ₄	C ₆ H ₅	5d	2.5	85	170-172	171-172	[30]
5	4-CH ₃ -C ₆ H ₄	C ₆ H ₅	5e	1	97	106-108	109-111	[30]
6	4-OH-C ₆ H ₄	C ₆ H ₅	5f	1.5	96	150-152	155-158]	[31]
7	C ₆ H ₅	4-F-C ₆ H ₄	5g	2	85	128-130	127-128	[32]
8	C ₆ H ₅	4-Cl-C ₆ H ₄	5h	2	87	148-150	146-147	[32]
9	C ₆ H ₅	4-NO ₂ -C ₆ H ₄	5i	2.5	83	Oil	Oil	[30]
10	C ₆ H ₅	4-CH ₃ -C ₆ H ₄	5j	1	93	Oil	Oil	[32]
11	C ₆ H ₅	4-OH-C ₆ H ₄	5k	1.5	95	174-176	170-171	[31]

^aHereinafter, isolated yield of pure product.

The catalyst was consecutively reused five times without any noticeable loss of its catalytic activity (Cycle number and yield of **5a**: 1, 95 %; 2, 95 %; 3, 94 %; 4, 94 %; 5, 93 %). $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x=0.05$) is highly magnetic and their saturation magnetization values are found to be 59.25 emu/g [29], which are much higher than other reported magnetic catalysts. Therefore, they could be easily and almost completely separated by an external magnet which is of a great advantage for a heterogeneous catalyst.

The work-up of these reactions was very clean as there were no tedious steps were involved for obtaining the desired compounds in pure form and in good yields. After recrystallization, compounds have been obtained in high purity, thus no chromatographic techniques were used for purification of the compounds. The catalysts were also easily separated from reaction mixture with the help of magnet. To the best of our knowledge, the synthesis of multi-substituted pyrrole derivatives **5(a-k)** using Pr^{3+} doped CoFe_2O_4 as the catalyst has not been reported previously. The catalyst is not only efficient but also mild and easy to handle.

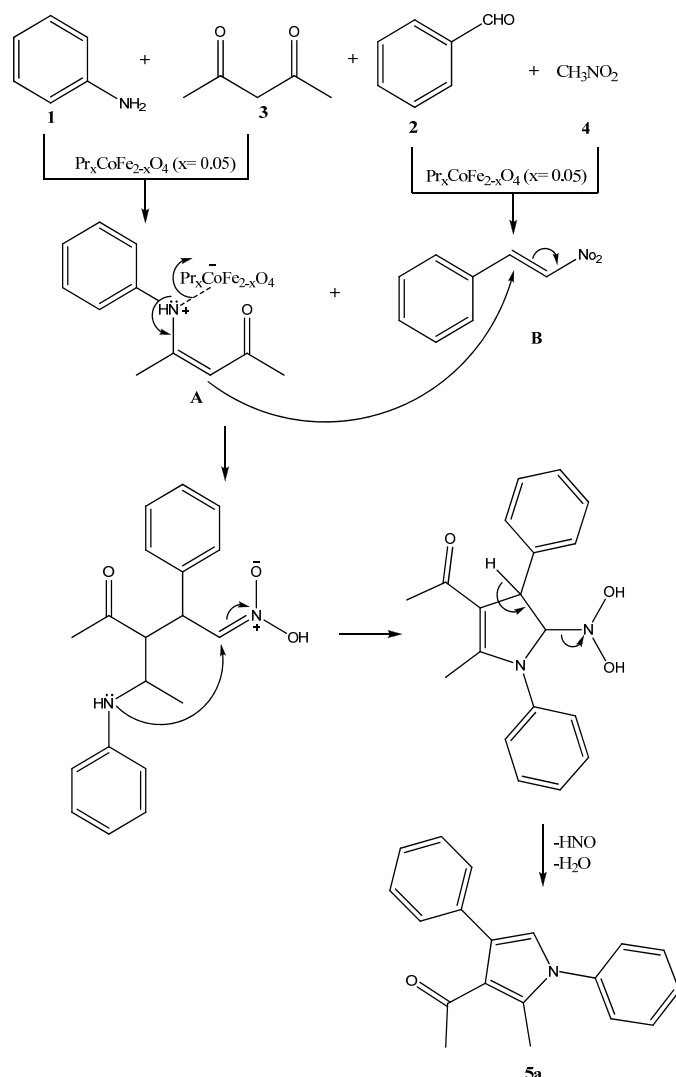
A plausible mechanism for the formation of pyrrole derivatives is proposed in Scheme 2. The intermediates (Z)-4-(phenylamino) pent-3-en-2-one (**A**) from aniline **1** and acetylacetone **3** and (E)-(2-nitrovinyl) benzene (**B**) from benzaldehyde **2** and nitromethane **4** could be generated in the presence of a $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x=0.05$). These two intermediates reacted via Michael addition, followed by intramolecular cyclization with the elimination of nitroxyl (HNO) and water to lead to the final product **5** [30].

4. Conclusions

In conclusion, we have developed a highly efficient one-pot four-component method for the synthesis of multisubstituted pyrrole derivatives from amines, aldehydes, acetylacetone and nitromethane using $\text{Pr}_x\text{CoFe}_{2-x}\text{O}_4$ ($x=0.05$) as a heterogenous catalyst. A wide range of amines and aldehydes can be tolerated, giving the structural diversity of pyrrole derivatives in good to excellent yields. Also, the method overcomes the earlier disadvantages and, therefore, will be of general use and interest to synthetic chemists. Finally, the catalysts could be easily recovered and reused five times without a significant loss of activity, showing good potential for industrial application.

Acknowledgment

The authors thank Mrs. Fatima Rafiq Zakaria, Chairman Maulana Azad Educational Trust, and Dr. Zahid Zaheer, Principal, Y.B. Chavan College of Pharmacy, Dr. Rafiq Zakaria Campus, Aurangabad, 431001 (M.S.) India, for providing laboratory facilities.



Scheme 2. Plausible mechanism for synthesis of pyrrole derivatives **5a**.

References

- [1] L. Banfi, A. Basso, L. Giardini, R. Riva, V. Rocca, G. Guanti, *Eur. J. Org. Chem.* 1 (2011) 100-109.
- [2] N. Ma, B. Jiang, G. Zhang, S.J. Tu, W. Wever, G. Li, *Green Chem.* 12 (2010) 1357-1361.
- [3] C.L. Floch, E.L. Gall, E. Leonel, J. Koubaet, T. Martens, P. Retailleau, *Eur. J. Org. Chem.* 2010 (2010) 5279-5286.
- [4] C. Haurena, E.L. Gall, S. Sengmany, T. Martens, M. Troupel, *J. Org. Chem.* 75 (2010) 2645-2650.
- [5] M. Adib, E. Sheikhi, A. Kavooosi, H.R. Bijanzadeh, *Tetrahedron* 47 (2010) 9263-9269.
- [6] W.B. Chen, Z.J. Wu, Q.L. Pei, L.F. Cun, X.M. Zhang, W.C. Yuan, *Org. Lett.* 12 (2010) 3132-3135.
- [7] M.S. Singh, S. Chowdhury, *RSC Adv.* 2 (2012) 4547-4592.
- [8] J.R. Rosien, W. Seichter, M. Mazik, *Org. Biomol. Chem.* 11 (2013) 6569-6579.

- [9] J.T. Manka, A.L. Rodriguez, R.D. Morrison, D.F. Venable, H.P. Cho, A.L. Blobaum, J.S. Daniels, C.M. Niswender, P.J. Conn, C.W. Lindsley, K.A. Emmitte, *Bioorg. Med. Chem. Lett.* 23 (2013) 5091-5096.
- [10] M.Z. Wang, H. Xu, T.W. Liu, Q. Feng, S.J. Yu, S.H. Wang, Z.M. Li, *Eur. J. Med. Chem.* 46 (2011) 1463-1472.
- [11] Y.Q. Yang, Q. Zhang, J.F. Zheng, S.B. Zhang, *Polymer* 54 (2013) 3254-3260.
- [12] D. Bandyopadhyay, S. Mukherjee, J.C. Granados, J.D. Short, B.K. Banik, *Eur. J. Med. Chem.* 50 (2012) 209-221.
- [13] F.P. Ma, P.H. Li, B.L. Li, L.P. Mo, N. Liu, H.J. Kang, Y.N. Liu, Z.H. Zhang, *Appl. Catal. A* 457 (2013) 34-41.
- [14] J.B. Bharate, R. Sharma, S. Aravinda, V.K. Gupta, B. Singh, S.B. Bharate, R.A. Vishwakarma, *RSC Adv.* 3 (2013) 21736-21742.
- [15] S. Madabhushi, V.S. Vangipuram, K.K.R. Mallu, N. Chinthala, C.R. Beeram, *Adv. Synth. Catal.* 354 (2012) 1413-1416.
- [16] G. Pacchioni, *Surf. Rev. Lett.* 7 (2000) 277-306.
- [17] L.D. Pachon, J.H. van Maarseveen, G. Rothenberg, *Adv. Synth. Catal.* 347 (2005) 811-815.
- [18] J.N. Sangshetti, F.A.K. Khan, C.S. Kute, Z. Zaheer, R.Z. Ahmed, *Russ. J. Org. Chem.* 51 (2015) 69-73.
- [19] J.N. Sangshetti, F.A.K. Khan, R.S. Chouthe, Z. Zaheer, R.Z. Ahmed, *J. Taibah Univ. Sci.* 9 (2015) 548-554.
- [20] A.P.G. Nikalje, M.S. Ghodke, F.A.K. Khan, J.N. Sangshetti, *Chinese Chem. Lett.* 26 (2015) 108-112.
- [21] Z. Zaheer, F.A.K. Khan, J.N. Sangshetti, R.H. Patil, *EXCLI J.* 14 (2015), 935-947.
- [22] J.N. Sangshetti, N.D. Kokare, S.A. Kotharkar, D.B. Shinde, *Chinese Chem. Lett.* 19 (2008) 762-766.
- [23] J.N. Sangshetti, N.D. Kokare, D.B. Shinde, *Chinese Chem. Lett.* 18 (2007) 1305-1308.
- [24] J.N. Sangshetti, N.D. Kokare, D.B. Shinde, *Russ. J. Org. Chem.* 45 (2009) 1116-1118.
- [25] J.N. Sangshetti, D.B. Shinde, *Bioorg. Med. Chem. Lett.* 20 (2010) 742-745.
- [26] J.N. Sangshetti, S.A.M.K. Ansari, D.B. Shinde, *Chinese Chem. Lett.* 22 (2011) 163-166.
- [27] J.N. Sangshetti, F.A.K. Khan, R.S. Chouthe, M.G. Damale, D.B. Shinde, *Chinese Chem. Lett.* 25 (2014) 1033-1038.
- [28] J.N. Sangshetti, P.P. Dharmadhikari, R.S. Chouthe, B. Fatema, V. Lad, V. Karande, S.N. Darandale, D.B. Shinde, *Bioorg. Med. Chem. Lett.* 23 (2013) 2250-2253.
- [29] A.M. Pachpinde, M.M. Langade, K.S. Lohar, S.M. Patange, S.E. Shirsath, *Chem. Phys.* 429 (2014) 20-26.
- [30] B.L. Li, M. Zhang, H.C. Hu, X. Dub, Z.H. Zhang, *New J. Chem.* 38 (2014) 2435-2442.
- [31] N. Gupta, K.N. Singh, J. Singh, *J. Mol. Liq.* 199 (2014) 470-473.
- [32] B.L. Li, H.C. Hu, L.P. Mo, Z.H. Zhang, *RSC Adv.* 4 (2014) 12929-12943.