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Original Research Article

Synthesis of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles using $ZnFe_2O_4$ magnetic nanoparticles

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KEYWORDS

Biaryl

Multi-component reaction

Nano $ZnFe_2O_4$

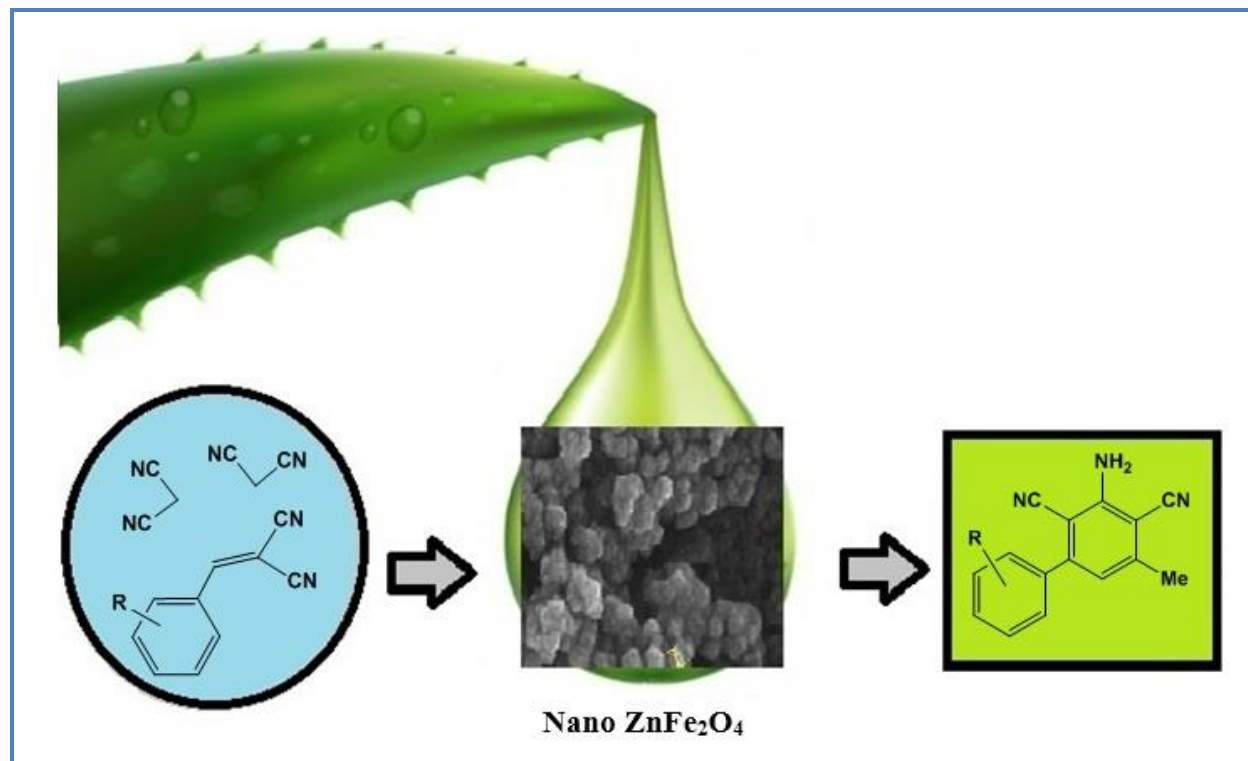
Malononitrile

Aloe vera

ABSTRACT

This work studies an efficient, one-pot pseudo multi-component synthesis of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles. This reaction performed under solvent free conditions in the presence of $ZnFe_2O_4$ magnetic nanoparticles. The $ZnFe_2O_4$ nanoparticles were prepared by an eco-friendly hydrothermal method using aloe vera plant extract solution. Herein 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles were synthesized via a simple reaction between the arylidene malononitrile, malononitrile and sodium carbonate in ethanol at room temperature in the presence of $ZnFe_2O_4$ magnetic nanoparticles. Eco friendly, excellent yields of the product, short reaction time, inexpensive, and readily available starting material are the main advantages of this method.

Graphical Abstract



Introduction

Dicyanoanilines, possessing electron-donor and acceptor substituents are significantly interesting and important. They are extremely fluorescent materials, so they are very useful to utilize as an important substrates for nonlinear optical materials and molecular electronic devices [1–5]. In addition, some dicyanoanilines show biological property, such as antileishmanial activity [6]. The cyano and amino groups can be converted into various functional groups. Therefore these dicyanoanilines can be used as starting materials for synthesizing a great number of aromatic compounds. Over the last decade, there have been reported many methods for the synthesis of dicyanoanilines [1, 7–10]. They are typically prepared from (i) a reaction between malononitrile and α,β -unsaturated ketones [11], (ii) reaction of ynones and malononitrile [12], (iii) one-pot tandem reaction of (alkylidene)malononitriles with nitroolefins in the presence of a base [13], (iv) ringtransformation of functionalized 2*H*-pyran-2-ones with malononitrile [14], (v) the three-component reaction of aldehydes, ketones and malononitrile under solvent-free conditions [7] (vi) and reaction between arylidenemalononitriles, dialkyl acetylenedicarboxylates and malononitrile catalyzed by 1-methylimidazole [15], or (vii) reactions between nitrostyrenes and excess malononitrile [10].

Magnetic nanoparticles (MNPs) for example zinc ferrite magnetic nanoparticles could catalyze organic reactions in a mild and environment friendly manner. Furthermore these catalysts have many advantages such as use of minimum amount of reagent and energy, high yield of products easy reaction, simple work-up procedure and minimize byproduct, efficiency and recyclability are the main advantages of these catalysts [16, 17]. In recent decades there have been reported many papers regarding use of Magnetic nanoparticles in organic synthesis due to its low cost and efficacy [18–20]. Also recently, many synthetic methods have been developed for the preparation of ZnFe_2O_4 nanoparticles: sol-gel process [21], coprecipitation [22], microemulsion-based synthesis [23], radio frequency-sputtering [24], microwave-hydrothermal assisted ionic liquid [25], hydrothermal synthesis [26] and mechanical activation [27]. In this work, ZnFe_2O_4 magnetic nanoparticles were prepared *via* the auto-combustion assisted sol-gel method [28].

As a part of our efforts on the development of simple methods to prepare organic compounds from readily available building blocks and simple catalyst [29–32] herein we report a simple and efficient method for the synthesis of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles using ZnFe_2O_4 magnetic nano particles as catalyst (Scheme 1).

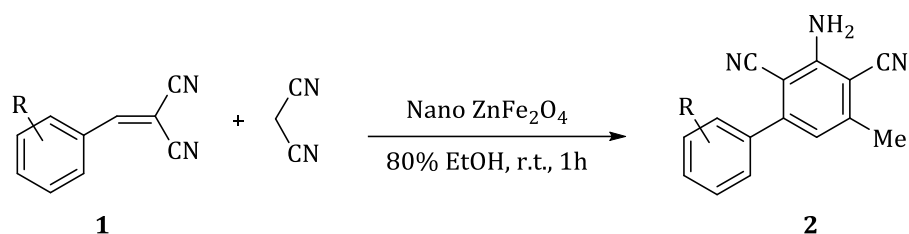
Experimental

Materials and methods

All starting materials and solvents were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification ZnFe_2O_4 magnetic nanoparticles were synthesized *via* the auto combustion assisted sol-gel method by *aleo vera* extract solution [33]. The progress of the reaction was monitored by TLC. Melting points were measured on an Electro-thermal 9100 apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra (CDCl_3) were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.1 and 75.4 MHz respectively. The experiments were performed using a microwave oven (ETHOS 1600, Milestone) with a maximum power of 900 W specially designed for organic synthesis. Elemental analyses for C, H and N were performed using a CHN-O-Rapid analyzer and the instrument model was Eager 300 for EA11112. To confirm nano- ZnFe_2O_4 the SEM image of ZnFe_2O_4 magnetic nanoparticles was carried out in Figures 1.

General procedure for the synthesis of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles 2a-f

The reaction was carried out by first mixing benzilidenmalononitrile (1 mmol, 0.154 g), malononitrile (3 mmol, 0.196 g), and NaOH (1 mmol, 0.040 g) in the presence of ZnFe_2O_4 magnetic nanoparticles **2** in the presence of nano- ZnFe_2O_4 (0.010 mmol, 0.002 g) in ethanol % 80 (5 mL). After



Scheme 1. Pseudo multi-component synthesis of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles

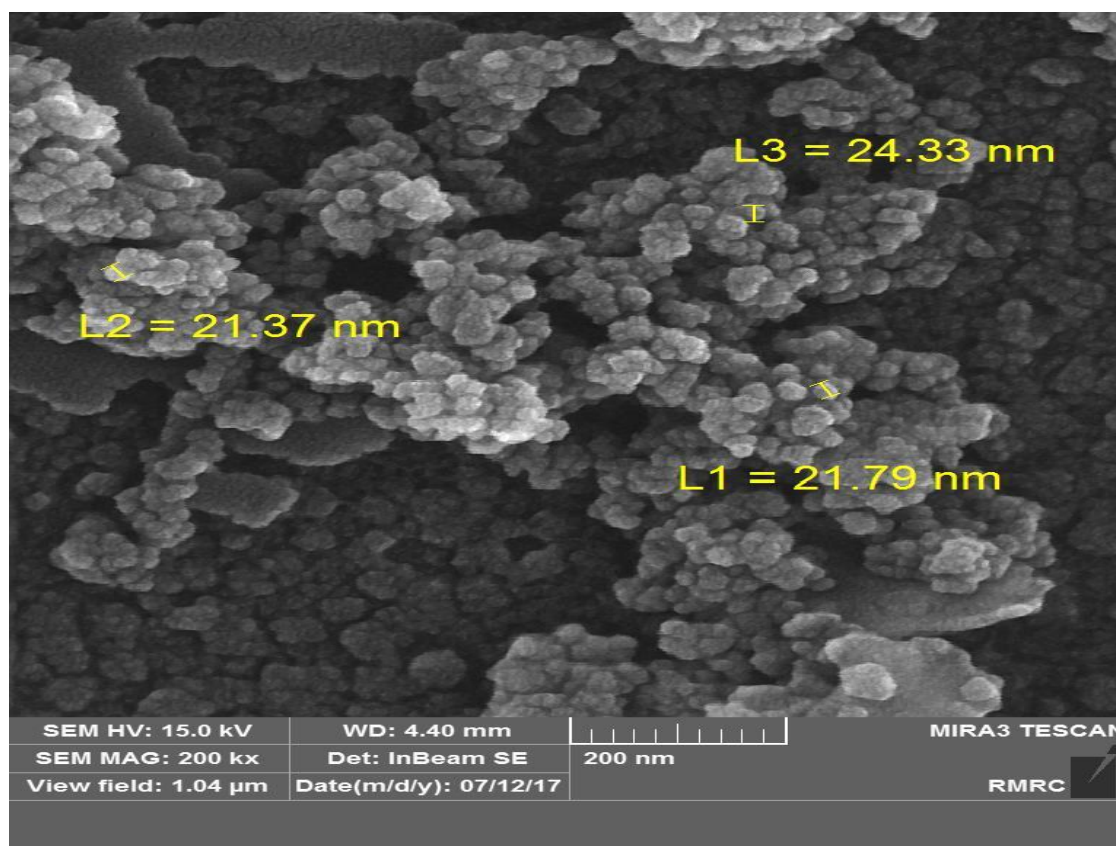


Figure 1. SEM image of ZnFe_2O_4 magnetic nanoparticles (The average nano particle size is 23 nm)

60 minutes stirring at room temperature the TLC clearly indicated formation of the corresponding product **2a**. Then ZnFe_2O_4 magnetic nanoparticles were separated by a magnet. After that, the solvent was removed and the product was separated and purified by a silica gel column chromatography with ethyl acetate as eluent. The **2a** product was recrystallized as a light yellow crystals from ethanol. The isolated yield was 0.221 g 95%, ^1H NMR, and ^{13}C NMR analysis of the pure product confirmed the structure of the product **2a**. It was as a colorless crystals. Mp 190-191 °C. IR (KBr) ($\nu_{\text{max}}/\text{cm}^{-1}$): 3475, 3352 and 3241 (NH), 2228 (CN), 1646, 1585, 1472, 1286, 1220, 858, 771, and 696. ^1H NMR (500.1 MHz, DMSO): δ 2.43 (3H, s, CH_3), 6.66 (2H, br. s, NH_2), 6.72 (1H, s, CH), 7.49-7.51 (5H, m, 5 CH). ^{13}C

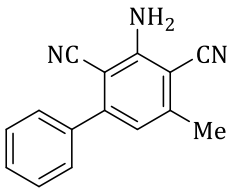
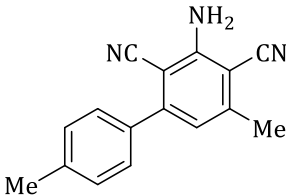
NMR (125.8 MHz, DMSO): δ 20.8 (CH₃), 92.7 and 95.7 (2 CN), 115.4 and 116.0 (2 C), 119.0, 128.3, 128.6 and 129.2 (4 CH), 137.6, 148.1, 149.5 and 153.3 (4 C). Anal. Calcd. for C₁₉H₁₁BrN₆O₃: C, 50.57; H, 2.46; N, 18.62. Found: C, 50.18; H, 2.32; N 18.51. MS (20 eV): m/z (%) = 233 (100) [M⁺], 205 (40), 191 (15), 168 (16), 151 (20), 117 (12), 76 (8).

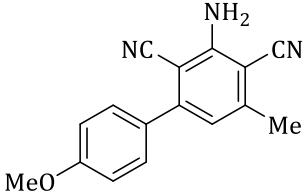
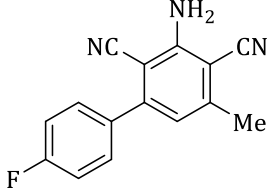
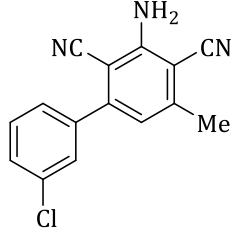
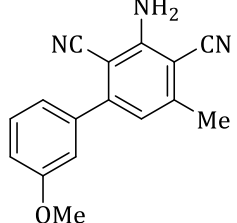
Results and discussion

Arylidenmalononitrile and malononitrile in the presence of ZnFe₂O₄ magnetic nano particles in ethanol, produced 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles **2a-f** in good to excellent yields (Table 1). This reaction was carried out as a one-pot and pseudo multi-component reaction.

The ¹H NMR spectrum of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles **2a** exhibited two single sharp singlets due to the methyl group (δ = 2.43) and an aromatic hydrogen (δ = 6.72). A fairly broad signal at δ = 6.66 was observed for the amine group, along with characteristic multiple signals for five aromatic H atoms at δ = 7.49 - 7.51. The ¹H-decoupled ¹³C NMR spectrum of **2a**, showed 13 distinct resonances. The methyl group resonated at δ = 20.8 and two quaternary carbons bonded to nitrile groups resonated at δ = 92.7 and 95.7 and the signals for the two nitrile carbons were evident at 115.4 and 116.0. In addition, four methines and four quaternary carbons, all in the aromatic region

Table 1. One-pot and pseudo multi-component synthesis of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles **2a-f** in the presence of nano-ZnFe₂O₄

Entry	Product	Yield (%) ^a	Melting point (°C)
1		5	190-191
2		93	220-222

3		90	193-194
4		95	264-266
5		93	238-240
6		88	200-202

^a Yield of isolated products

were in agreement with the structure of the product. Three doublet of doublet signals at $\delta = 3.17$, 3.89 and 5.48 ppm with $J_{\text{HH}} = 17.3$, 12.5 and 7.6 Hz due to the three CH groups.

To optimize this reaction, the **2a** preparation was selected as a model, and then the effects of nano-ZnFe₂O₄ amounts to the reaction yields were tested. The results of these experiments were displayed in [Table 2](#). All of these tests were done in room temperature. As can be seen from [Table 2](#), the highest yield was obtained in the presence of 17 mol% of nano-ZnFe₂O₄.

Table 2. Synthesis of **2a** in the presence of various amount of nano-ZnFe₂O₄

Entry	Nano-ZnFe ₂ O ₄ (mol%)	Time (min)	Yield (%) ^a
1	0	60	22
2	2	60	38

3	5	60	45
4	8	60	60
5	11	60	75
6	14	60	82
7	17	60	95
8	20	60	95

^aYield of isolated products

Conclusion

In conclusion, we have developed a simple and efficient method for the synthesis of 3-amino-5-methyl-[1,1'-biaryl]-2,4-dicarbonitriles in the presence of ZnFe₂O₄ magnetic nanoparticles. Excellent yields of products, Short reaction times, and mild reaction conditions, inexpensive and readily available starting chemicals and catalyst, use of simple chemicals, eco friendly, and high atomic economy are the main advantages of this method.

Acknowledgments

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Disclosure statement

No potential conflict of interest was reported by the authors.

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