



ZEOLITE BETA: AN EFFICIENT CATALYST FOR THE PREPARATION OF 2,4,6-TRIARYLPYRIDINES UNDER SOLVENT-FREE CONDITION

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ABSTRACT

An efficient procedure for the synthesis of 2,4,6-triarylpyridines by one-pot multi-component condensation of aldehydes, acetophenones and ammoniumacetate in the presence of zeolite beta, has been described. This method has several advantages such as; excellent yields, short reaction times, easy work-up procedure, solvent-free condition and the use of a reusable nano catalyst.

KEYWORDS: Heterocycles, Multi-component reactions, 2,4,6-Triarylpyridine, One-pot synthesis.

INTRODUCTION

Multi-component reactions have been recently gained special attention because of their benefits than the multi-step reactions that use a large amount of solvent, reactants and energyⁱ. Multi-component reactions are referred to one-pot processes, during which three or more substances are combined to generate a complex structureⁱⁱ. These reactions are highly efficient, quick, simple, clean, low cost, environmentally benign and usually without side productsⁱⁱⁱ. Pyridines are an important class of heterocyclic compounds and widely used in different fields of science such as biology, pharmacology, biochemistry and chemistry^{iv}. Pyridine derivatives are used in the synthesis of sensors^v, asymmetric catalysts^{vi} and photochemical reaction inhibitors^{vii}. Furthermore, they are shown various pharmaceutical activities. For example; anti-inflammatory, anti-microbial and anti-HIV^{viii} properties have been detected for pyridine derivatives. In recent years, the synthesis of pyridine moiety *via* multi-component reactions have been performed using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ^{ix}, $\text{SiO}_2\text{-VO}(\text{OH})_2$ ^x, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ ^{xi}, ZrOCl_2 ^{xii}, $\text{Bi}(\text{OTf})_3$ ^{xiii}, MgAl_2O_4 ^{xiv} and so on as catalyst. Although some of these methods are valuable, most of them suffer from disadvantages such as long reaction times, low yields of products, harsh reaction conditions, the use of toxic solvents and/or non-reusable catalyst. So, the development of new and mild catalytic protocol for the synthesis of substituted pyridine is still in demand. In this study, we used zeolite beta as catalyst for the synthesis of 2,4,6-triarylpyridines.

Zeolites are a group of crystalline and porous aluminosilicate compounds and have a three-dimensional tetrahedral lattice, constructed from SiO_4 and AlO_4 that create holes and canals in the structure of zeolite^{xv}. In the holes of zeolites, alkaline and earth metal cations are commonly enclosed. In most cases, Ca^{2+} , K^+ and Na^+ and in some cases Li^+ , Mg^{2+} , Sr^{2+} and Ba^{2+} are found^{xvi}. Since 1960, zeolites have been extensively used as catalyst in a wide variety of industrial transformations^{xvii} due to their biocompatibility, non-toxicity, thermal and mechanical stability, crystallinity, cheapness, high surface area, easy construction and high absorption properties^{xviii}. Zeolite beta is a synthetic zeolite with high acidity and high content of silicon that is a good choice for industrial applications specially in petrochemical industry. Herein, we describe a clean and efficient method for the synthesis of 2,4,6-triarylpyridines from aldehydes, acetophenones and ammonium acetate in the presence of zeolite beta as a reusable catalyst (Scheme1).

EXPERIMENTAL SECTION

Chemicals and apparatus

All required materials were obtained from Merck and Aldrich companies. IR spectra were recorded using KBr pellet on a Shimadzu 435-U-04 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained using Bruker DRX-300 AVANCE spectrometer in DMSO-d_6 . Melting points were determined with an Electrothermal 9100 apparatus. The X-ray diffraction (XRD) pattern of the catalyst was taken using Philips PW 1730 apparatus. Field-emission scanning electron microscopy (FESEM) was performed with a Hitachi S-1460 instrument at an AC voltage of 15 kV.

General procedure for the synthesis of zeolite beta

Zeolite beta has been synthesized by hydrothermal reaction. Initially, a solution of NaOH (0.188 g) and sodium aluminate (0.762 g) in deionized H_2O (40 ml) was prepared and stirred at room temperature for 40 min and then stirred at 70–90 °C for 50 min. The solution was then cooled to room temperature and tetraethyl ammonium hydroxide (13.56 g) was added. A silica containing solution was prepared from colloidal silico Ludox HS-40 and deionized water and this solution was added to the first solution. The formed gel was then shaken for 30 seconds and transferred into a Teflon autoclave and heated at 150 °C for 6 days. In the next step, autoclave was removed from oven and quenched with cold water, filtered and washed with distilled water until obtaining $\text{pH} \leq 8$. The precipitate was dried at 75 °C during 1 day.

General procedure for the synthesis of 2,4,6-triarylpyridines

Zeolite beta was added to a mixture of benzaldehyde (1 mmol, 0.106 g), acetophenone (2 mmol, 0.240 g) and ammonium acetate (3 mmol, 0.231 g) and the resulting mixture was stirred at 80 °C. Progress of the reaction was monitored by TLC (4:1; *n*-hexane/ ethylacetate). After completion of the reaction, hot ethanol (5 ml) and then, crushed ice was added. The precipitate was filtered and purified by recrystallization in ethanol to afford corresponding 2,4,6-triarylpyridine derivatives in excellent yields (Table 2). All products were characterized by melting point, IR and ^1H and ^{13}C NMR spectra (**4a-o**).

2,4,6-triphenylpyridine (4a), IR (KBr): 3069, 1597, 1552, 1494, 1440, 1398, 1178, 1074, 1027, 867, 759, 692 cm^{-1} ; ^1H NMR (400 MHz, DMSO-d_6): δ 8.37 (d, 2H, $J = 7.2$ Hz, ArH), 8.33 (d, 2H, $J = 7.5$ Hz, ArH), 8.20 (s, 2H, ArH), 8.06 (d, 2H, $J = 7.4$ Hz, ArH), 7.60–7.50 (m, 9H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 157.0, 150.1, 139.3, 139.2, 129.7, 129.7, 128.7, 128.4, 127.8, 127.4, 117.0.

4-(4-hydroxyphenyl)-2,6-diphenylpyridine (4b), IR (KBr): 3197, 1603, 1546, 1519, 1398, 839, 776, 696 cm^{-1} ; ^1H -NMR (400 MHz, DMSO-d_6): δ 9.90 (s, 1H), 8.32 (d, 4H, $J = 7.5$ Hz),

8.13 (s, 2H), 7.93 (d, 2H, $J = 8.1$ Hz), 7.57–7.47 (m, 6H), 6.95 (d, 2H, $J = 8.1$ Hz); ^{13}C -NMR (100 MHz, DMSO- d_6): δ 159.2, 156.7, 149.8, 139.4, 129.5, 129.1, 128.5, 127.3, 116.3, 116.1.

4-(3-hydroxyphenyl)-2,6-diphenylpyridine(**4c**), IR (KBr): 3034, 1606, 1596, 1543, 1493, 1198, 764 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 9.73 (s, 1H, OH), 8.37 (d, 4H, $J = 8$ Hz, ArH), 8.17 (s, 2H, ArH), 7.61 (t, 4H, $J = 8$ Hz, ArH), 7.56–7.48 (m, 3H, ArH), 7.44–7.42 (m, 2H, ArH), 6.98 (d, 1H, $J = 8$ Hz, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ 158.0, 156.4, 149.8, 139.2, 138.8, 130.1, 129.2, 128.7, 126.9, 118.0, 116.5, 116.2, 114.0.

4-(4-chlorophenyl)-2,6-diphenylpyridine (**4d**), IR (KBr): 3061, 1599, 1543, 1489, 1449, 1414, 1384, 1237, 1090, 1013, 825, 773, 692 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.39 (d, 2H, $J = 7.1$ Hz, ArH), 8.34 (d, 2H, $J = 7.8$ Hz, ArH), 8.14 (s, 2H, ArH), 7.81 (d, 2H, $J = 7.9$ Hz), 7.62 (d, 2H, $J = 7.9$ Hz, ArH), 7.56–7.53 (m, 6H, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ 157.1, 148.6, 139.2, 136.9, 134.7, 129.6, 129.5, 129.4, 129.2, 116.9.

2,6-diphenyl-4-(4-tolyl)pyridine(**4e**), IR (KBr): 3034, 2936, 1598, 1548, 1442, 1398, 1286, 1254, 1203, 1170, 1036, 871, 775, 691 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.35 (d, 2H, $J = 7.3$ Hz, ArH), 8.29 (d, 2H, $J = 7.5$ Hz, ArH), 8.14 (s, 2H, ArH), 7.93 (d, 2H, $J = 7.8$ Hz, ArH), 7.58 (t, 2H, $J = 7.6$ Hz, ArH), 7.50 (t, 2H, $J = 7.6$ Hz, ArH), 7.47 (t, 2H, $J = 7.7$ Hz, ArH), 7.35 (d, 2H, $J = 7.8$ Hz, ArH), 2.48 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 157.0, 149.0, 139.4, 135.2, 130.1, 129.6, 129.2, 127.5, 127.4, 116.7, 21.3.

4-(3-nitrophenyl)-2,6-diphenylpyridine(**4f**), IR (KBr): 1603, 1526, 1438, 1397, 1350, 775, 740, 690 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.84 (s, 1H), 8.51 (d, 1H, $J = 7.5$ Hz), 8.38–8.28 (m, 7H), 7.86 (t, 1H, $J = 7.9$ Hz), 7.64–7.49 (m, 6H); ^{13}C NMR (100 MHz, DMSO- d_6): δ 157.1, 149.0, 147.8, 139.9, 138.9, 134.6, 131.0, 129.8, 129.1, 127.5, 124.3, 122.6, 117.3.

4-(4-methoxyphenyl)-2,6-diphenylpyridine (**4g**), IR (KBr): 3035, 2936, 1596, 1547, 1486, 1444, 1398, 1285, 1255, 1204, 1171, 1037, 750, 691 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.38 (d, 2H, $J = 7.6$ Hz, ArH), 8.30 (d, 2H, $J = 7.3$ Hz, ArH), 8.14 (s, 2H, ArH), 8.03 (d, 2H, $J = 7.1$ Hz, ArH), 7.61 (t, 4H, $J = 6.8$ Hz, ArH), 7.50 (t, 4H, $J = 6.8$ Hz, ArH), 7.48 (d, 2H, $J = 7.3$ Hz, ArH), 7.1 (d, 2H, $J = 7.1$ Hz, ArH), 3.82 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 160.8, 156.9, 149.5, 139.4, 130.4, 130.3, 129.6, 129.1, 127.4, 116.4, 115.0, 55.8.

4-(3-methoxyphenyl)-2,6-diphenylpyridine (**4h**), IR (KBr): 3034, 2936, 1596, 1547, 1486, 1444, 1398, 1285, 1255, 1204, 1171, 1037, 872, 775, 692 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.36 (d, 2H, $J = 7.5$ Hz, ArH), 8.30 (d, 2H, $J = 7.6$ Hz, ArH), 8.14 (s, 2H, ArH), 7.59–7.50 (m, 8H, ArH), 7.46 (d, 1H, $J = 7.4$ Hz, ArH), 6.89 (t, 1H, $J = 7.4$ Hz, ArH), 3.70 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 160.4, 157.0, 150.0, 139.8, 139.3, 130.6, 129.7, 129.2, 127.5, 120.1, 117.2, 115.4, 113.2, 55.8.

4-(2-furyl)-2,6-diphenylpyridine(**4i**), IR (KBr): 3058, 1606, 1541, 1487, 1454, 1414, 1244, 1158, 1073, 1010, 868, 772, 690 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.30 (d, 2H, $J = 7.6$ Hz, ArH), 8.20 (d, 2H, $J = 7.5$ Hz, ArH), 8.14 (s, 2H, ArH), 7.96 (s, 1H, ArH), 7.57–7.47 (m, 7H, ArH), 6.75–6.74 (d, 1H, $J = 8.1$ Hz, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ 110.9, 113.0, 113.1, 127.2, 129.2, 129.8, 130.0, 139.6, 145.2, 151.4, 157.0.

4-phenyl-2,6-bis(4-tolyl)pyridine(**4j**), IR(KBr): 3063, 1587, 1554, 1490, 1438, 1395, 1181, 1079, 1024, 867, 759, 692 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.36 (d, 4H, $J = 7.5$ Hz, ArH), 8.18 (d, 2H, $J = 7.8$ Hz, ArH), 7.58 (t, 3H, $J = 7.5$ Hz, ArH), 7.21 (s, 2H, ArH), 7.10 (d, 4H, $J = 7.7$ Hz, ArH), 2.35 (s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 157.6, 150.3, 139.1, 136.9, 136.6, 131.0, 128.9, 127.6, 127.1, 117.3, 20.9.

2,6-bis(4-chlorophenyl)-4-phenylpyridine(**4k**), IR (KBr): 3052, 1598, 1544, 1490, 1449, 1413, 1384, 1239, 1174, 1091, 1012, 829, 761, 694 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.42 (d, 2H, $J = 7.6$ Hz, ArH), 8.33 (d, 2H, $J = 7.5$ Hz, ArH), 8.23 (s, 2H, ArH), 8.04 (d, 2H, $J = 7.7$ Hz, ArH), 7.61–7.50 (m, 7H, ArH); ^{13}C NMR (100 MHz, DMSO- d_6): δ 155.8, 150.3, 137.9, 134.7, 129.9, 129.6, 127.9, 117.3.

4-(4-chlorophenyl)-2,6-bis-(4-tolyl)pyridine(**4l**), IR (KBr): 3028, 1655, 1599,1491, 1407, 1224, 774 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.14 (d, 2H, $J = 8$ Hz, ArH), 8.05–7.99 (m, 4H,ArH), 7.78 (d, 2H, $J = 16$ Hz, ArH), 7.69 (d, 3H, $J = 8$ Hz, ArH), 7.45 (d, 3H, $J = 8$ Hz, ArH), 2.47(s, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 188.5,143.7, 142.1, 135.0, 134.9, 133.7, 130.5, 129.4, 128.9, 128.7, 123.2, 21.2.

2,4,6-tris(4-tolyl)pyridine (**4m**), IR (KBr): 3068, 1576, 1558, 1493, 1442, 1386, 1173, 1065, 1027, 864, 750, 688 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.39–8.33 (m, 6H, ArH), 7.72 (s, 2H, ArH), 7.14–7.12 (m, 6H, ArH), 2.32 (s, 6H,2 CH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 157.8, 150.4, 141.1, 136.9, 136.6, 131.0, 129.3, 127.7, 117.5, 21.1, 20.9 .

2,6-bis(4-chlorophenyl)-4-(4-tolyl)-pyridine(**4n**), IR (KBr): 3030, 2361, 1602, 1543, 1491, 831, 811 cm^{-1} ; ^1H -NMR (400MHz, DMSO- d_6): δ 8.37 (d, 4H, $J = 8.3\text{Hz}$),8.24 (s, 2H), 7.98 (d, 2H, $J = 7.8$ Hz), 7.61 (d, 4H, $J = 8.3\text{Hz}$),7.38 (d, 2H, $J = 7.9$ Hz), 2.41 (s, 3H); ^{13}C -NMR (100 MHz,DMSO- d_6): δ 155.1, 149.5, 139.1, 137.3, 134.3, 134.0, 129.5,129.1, 128.6, 127.1, 116.4, 20.7.

4-(4-methoxy)-2,6-bis(4-tolyl)pyridine(**4o**), IR(KBr): 3040, 2943, 1588, 1543, 1475, 1440, 1398, 1285, 1252, 1210, 1175, 1031, 753, 695 cm^{-1} ; ^1H NMR (400 MHz, DMSO- d_6): δ 8.35 (d, 4H, $J = 7.6$ Hz, ArH), 8.42 (s, 2H, ArH), 8.14 (d, 2H, $J = 7.1$ Hz, ArH),7.32 (d, 4H, $J = 7.3$ Hz, ArH), 6.95 (d, 2H, $J = 7.1$ Hz, ArH), 3.82 (s, 3H, OCH_3), 2.28 (s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 159.1, 157.7, 150.5, 142.6, 136.9, 130.9, 129.6, 127.7, 117.1, 114.4, 55.3, 20.8.

RESULTS AND DISCUSSION

Characterization of zeolite beta

The X-ray diffraction (XRD) diagram of zeolite beta has been shown in figure 1. Two characterized peaks at $2\theta=8$ and $20-25$ exhibit high crystallinity in the zeolite beta.

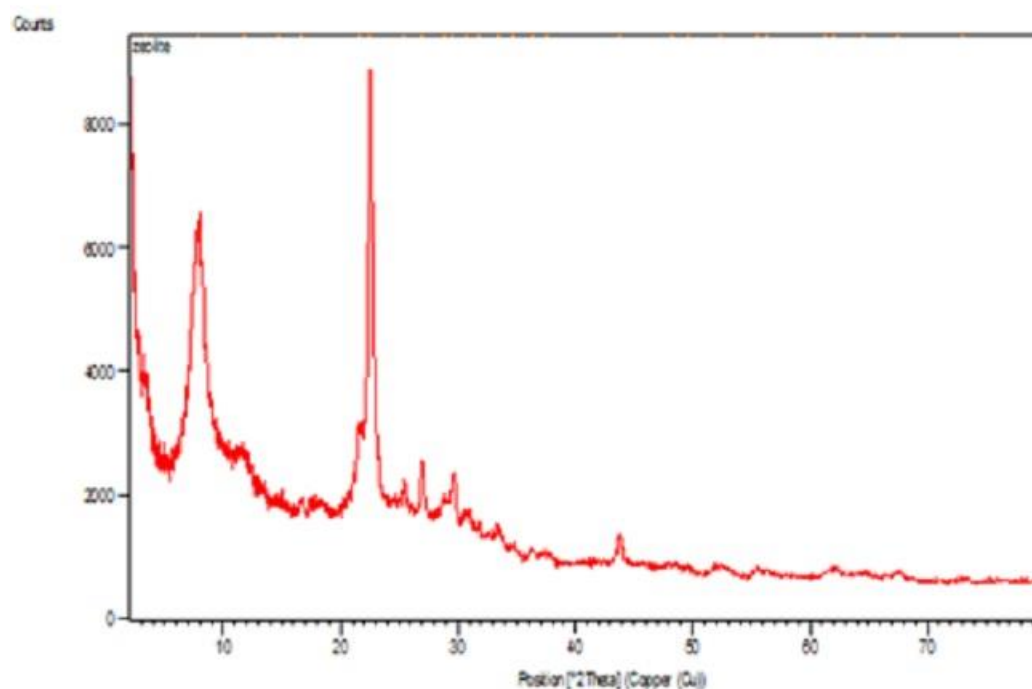


Figure 1. The XRD diagram of zeolite beta.

The EDX analyses of zeolite beta shows the elemental content of the zeolite (Figure 2).

The Scanning Electronic Microscopy (SEM) image of zeolite beta has been presented in figure 3. The spherical shape of zeolite beta crystals is clearly observable and the average size of nanoparticles has been estimated about 9.92 nm.

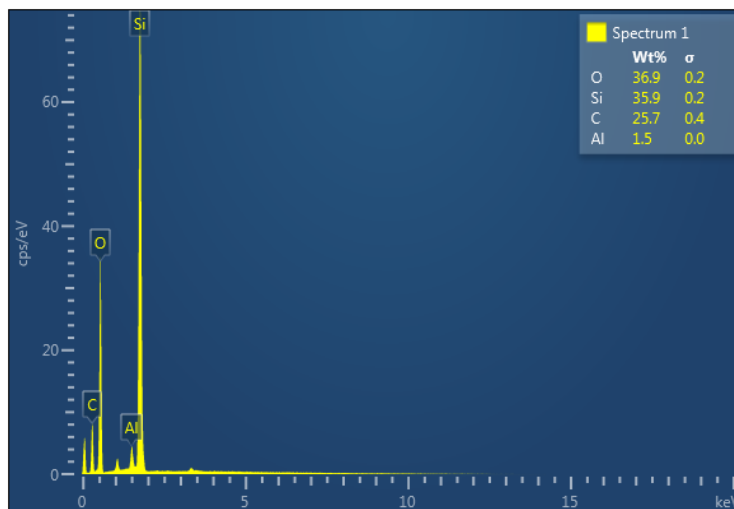


Figure 2. The EDX diagram of zeolite beta.

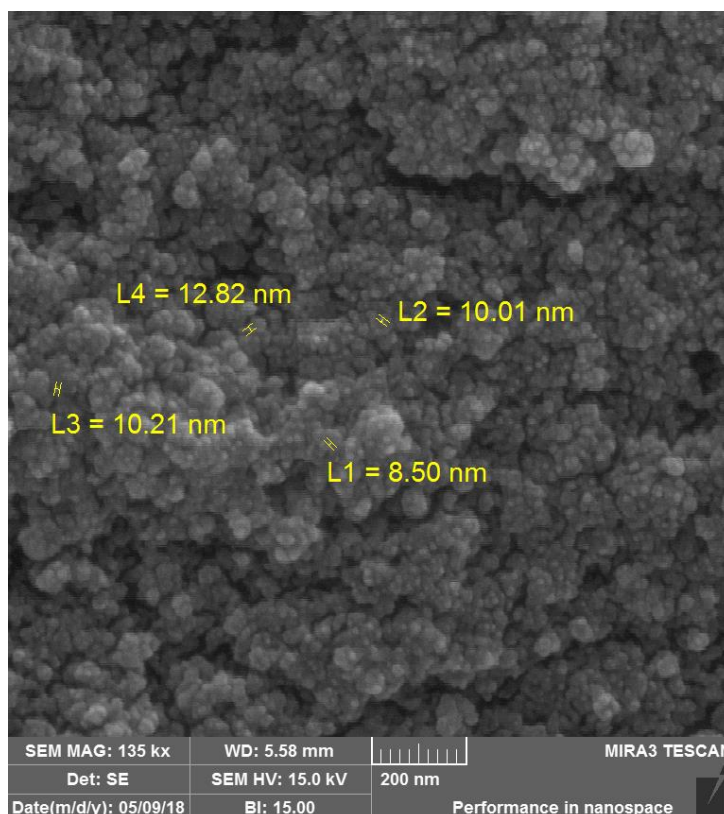


Figure 3. The FESEM image of zeolite beta.

Synthesis of 2,4,6-triarylpyridines catalyzed by zeolite beta

After characterization of zeolite beta, it was used in the synthesis of 2,4,6-triarylpyridines *via* multi-component reaction. At first, the reaction of benzaldehyde, acetophenone and

ammoniumacetate was chosen as model reaction. Then the reaction parameters such as molar ratios of starting materials and catalyst, solvent and temperature were optimized in model reaction (Table1, entries1-10). The best result was obtained in the reaction of benzaldehyde (1mmol), acetophenone (2mmol) and ammonium acetate (3mmol) in the presence of zeolite beta(0.004gr) at 80 °C and in the absence of solvent. Under this condition, desired 2,4,6-triphenyl pyridine was generated in 92% yield after 45 min (Table1, entry1). In order to show the importance of catalyst, the model reaction was also performed in the absence of catalyst which no product was detected after 45 min (Table1, entry10).

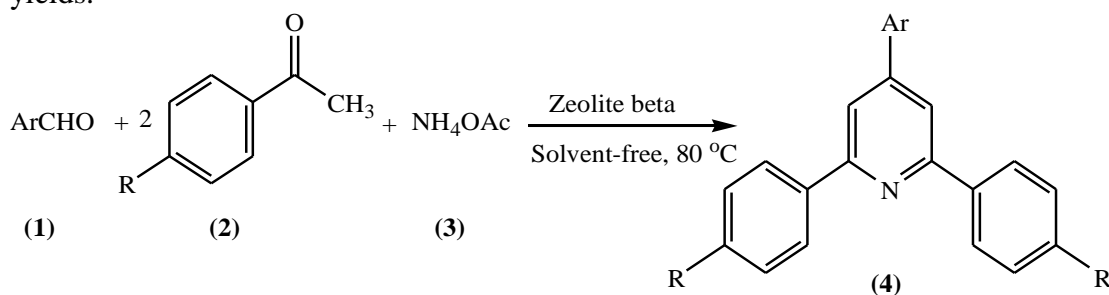
Table 1
Optimization of the reaction conditions.

| Entry | Amount of catalyst (gr) | Solvent | Temperature(°C) | Time(min) | Yield ^{1,2} (%) |
|-------|-------------------------|-----------------------------|-----------------|-----------|--------------------------|
| 1 | 0.004 | ----- | 80 | 45 | 92 |
| 2 | 0.002 | ----- | 80 | 60 | 83 |
| 3 | 0.012 | ----- | 80 | 60 | 80 |
| 4 | 0.032 | ----- | 80 | 60 | 75 |
| 5 | 0.004 | H ₂ O | 100 | 45 | 0 |
| 6 | 0.004 | EtOH | 80 | 45 | 0 |
| 7 | 0.004 | H ₂ O: EtOH(1:1) | 85 | 45 | 0 |
| 8 | 0.004 | ----- | 60 | 45 | 80 |
| 9 | 0.004 | ----- | 100 | 45 | 88 |
| 10 | 0.000 | ----- | 80 | 45 | 0 |

¹Molar ratios of benzaldehyde: acetophenone: ammonium acetate was 1:2:3 in all experiments.

²Isolated yield

In the next step, the generality of the current method was investigated by the reaction of different aromatic aldehydes, acetophenone and ammonium acetate under optimized conditions (Scheme1, Table2). Corresponding pyridines were generated in good to excellent yields.



Scheme 1. Zeolite beta catalyzed synthesis of 2,4,6-triarylpyridine derivatives

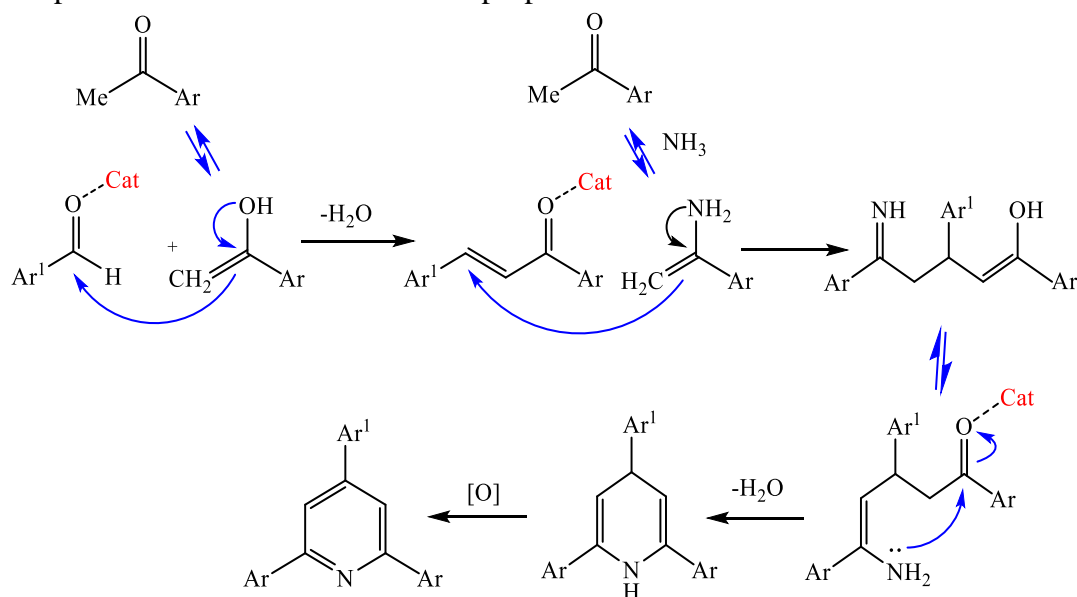
Table 2

Synthesis of 2,4,6-triarylpyridines using zeolite beta as catalyst.

| Entry | Ar | R | Product | Time (min) | Yield ¹ (%) | Mp (°C) | Lit. (°C) | Mp |
|-------|---|-----------------|-----------|------------|------------------------|---------|-------------------------|----|
| 1 | C ₆ H ₅ | H | 4a | 45 | 92 | 134-136 | 135-137 ^{xiv} | |
| 2 | 4-HO-C ₆ H ₄ | H | 4b | 15 | 96 | 194-196 | 196-198 ^{xix} | |
| 3 | 3-HO-C ₆ H ₄ | H | 4c | 30 | 92 | 183-184 | 183-185 ^{xx} | |
| 4 | 4-Cl-C ₆ H ₄ | H | 4d | 90 | 85 | 126-127 | 127-128 ^{xiv} | |
| 5 | 4-CH ₃ -C ₆ H ₄ | H | 4e | 60 | 92 | 115-117 | 119-120 ^{xiv} | |
| 6 | 3-NO ₂ -C ₆ H ₄ | H | 4f | 140 | 80 | 126-128 | 127-129 ^{xix} | |
| 7 | 4-CH ₃ O-C ₆ H ₄ | H | 4g | 180 | 75 | 99-101 | 98-100 ^{xiv} | |
| 8 | 3-CH ₃ O-C ₆ H ₄ | H | 4h | 220 | 75 | 123-125 | 124-127 ^{xiv} | |
| 9 | Furyl | H | 4i | 150 | 82 | 161-163 | 160-162 ^{xiv} | |
| 10 | C ₆ H ₅ | CH ₃ | 4j | 90 | 92 | 156-158 | 154-156 ^{xiv} | |
| 11 | C ₆ H ₅ | Cl | 4k | 60 | 83 | 187-189 | 188-190 ^{xxi} | |
| 12 | 4-Cl-C ₆ H ₄ | CH ₃ | 4l | 110 | 88 | 197-199 | 199-201 ^{xxii} | |
| 13 | 4-CH ₃ -C ₆ H ₄ | CH ₃ | 4m | 100 | 85 | 175-178 | 174-176 ^{xiv} | |
| 14 | 4-CH ₃ -C ₆ H ₄ | Cl | 4n | 180 | 80 | 201-201 | 202-204 ^{xix} | |
| 15 | 4-CH ₃ O-C ₆ H ₄ | CH ₃ | 4o | 230 | 81 | 154-156 | 156-158 ^{xiv} | |

¹Isolated yield.

Although the actual mechanism of this reaction is unclear, a reasonable mechanism for the synthesis of 2,4,6-triarylpyridines from aldehydes, acetophenones and ammonium acetate in the presence of zeolite beta has been proposed in scheme 2.

**Scheme 2.** The mechanism of 2,4,6-triarylpyridine synthesis.

Recovery and reuse of the catalyst is highly desirable for a catalytic process. In this regard, the recyclability of zeolite beta was investigated in the reaction of benzaldehyde, acetophenone and ammonium acetate under the optimized reaction conditions. After completion of the reaction, acetonitrile (5 ml) was added and the zeolite beta was separated from the product by filtration. The recovered catalyst was washed, dried at room temperature,

and reused in the next cycle. Recovery and reusing were performed 5 times and no significant loss of its catalytic activity was observed in comparison with the fresh catalyst (Figure 4). Furthermore, the FESEM image of recovered catalyst has been presented in figure 5.

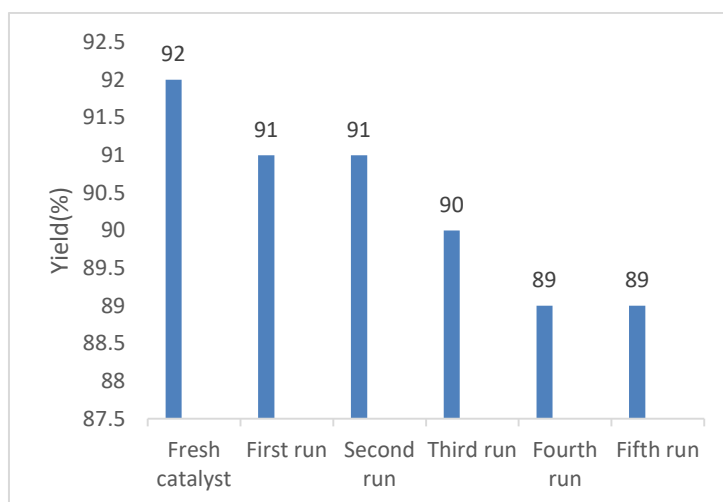


Figure 4. Reusability of zeolite beta in the model reaction.

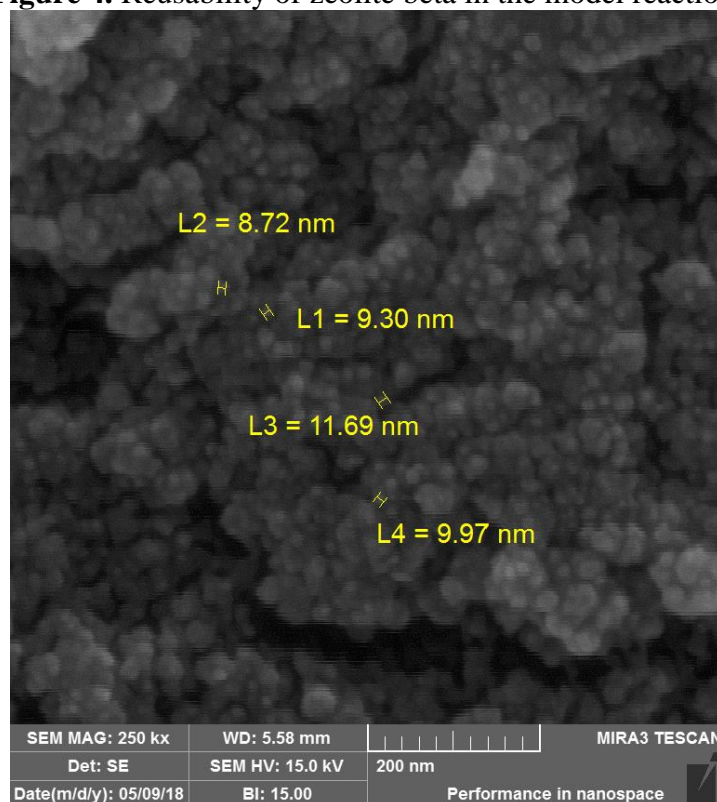


Figure 5. The FESEM image of recovered zeolite beta.

Finally, the efficiency of the present method has been compared with reported methods for the synthesis of 2,4,6-triarylpyridine. The results clearly demonstrate that zeolite beta is more efficient than the other reagents for this reaction.

Table 3

Comparison of the efficiency of different methods for the synthesis of 2,4,6-triarylpyridines.

| Entry | Catalyst | Condition | Time(min) | Yield ^{ref.} (%) |
|-------|---|----------------------|-----------|---------------------------|
| 1 | I ₂ | Solvent-free, 120°C | 360 | 56 ^{xxiii} |
| 2 | Cyanuric chloride | Solvent-free, 130°C | 240 | 70 ^{xxiv} |
| 3 | Bi(OTf) ₃ | Solvent-free, 120°C | 120 | 89 ^{xiii} |
| 4 | [HO ₃ S(CH ₂) ₄ MIM][HSO ₄] | Solvent-free, 120°C | 180 | 88 ^{xxv} |
| 5 | MgAl ₂ O ₄ | Solvent-free, 120°C | 180 | 85 ^{xiv} |
| 6 | TCT | Solvent-free, 130°C | 240 | 70 ^{xxiv} |
| 7 | PFPAT ¹ | Solvent-free, 120°C | 120 | 89 ^{xxii} |
| 8 | HClO ₄ -SiO ₂ | Solvent-free, 120°C | 240 | 80 ^{xxvi} |
| 9 | TCCA ² | Solvent-free, 130°C | 240 | 82 ^{xxvii} |
| 10 | DBH ³ | Solvent-free, 120 °C | 180 | 90 ^{xxviii} |
| 11 | Zeolite beta | Solvent-free, 80°C | 45 | 92 ^{This work} |

¹Pentafluorophenylammonium triflate²Trichloroisocyanuric acid³ 1,3-Dibromo-5,5- dimethylhydantoin

CONCLUSION

In summary, we have described a convenient method for the synthesis of 2,4,6-triarylpyridines *via* multi-component reaction from benzaldehydes, acetophenones and ammonium acetate using zeolite beta as catalyst. Absence of solvent, high yields of products, short reaction times, mild reaction condition, easy work-up procedure in combination with non-toxicity, efficiency, high surface area, stability, cheapness, reusability and nano character of the catalyst are noteworthy advantages of the present method.

ACKNOWLEDGEMENT

The authors thank Hakim Sabzevari University for the financial support of this work.

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Received on July 21, 2019.