AN EFFICIENT SYNTHESIS OF 2, 4, 6 TRI ARYL PYRIDINES USING AMMONIUM CARBONATE IN WATER UNDER SEALED CONDITIONS

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ABSTRACT
Krohnke 2, 4, 6-Triarylpyridines (TAPs) are efficiently synthesized by using various reactants with ammonium carbonate in water under sealed conditions. Using this protocol, Krohnke pyridines (4a-4q) are prepared in higher yields and purities than with other methodologies without the use of a catalyst or an organic solvent.

KEYWORDS
Sealed conditions, Ammonium carbonate, Water and 2, 4, 6-Triarylpyridines.

INTRODUCTION
Organic transformations in water without using hazardous reagents or solvents are of considerable interest, because of its environmental acceptability, abundance and low cost1. Pyridines derivatives represent an important class of six-membered heterocycles widespread in a number of biologically active natural products2 and pharmaceutical drugs3. They have noticeable applications in many fields of chemistry4. In particular 2, 4, 6-triarylpyridine is of immense interest because of its unique position in medicinal chemistry5, such as topoisomerase I and II inhibitory activity, cytotoxicity6 against several human cancer cell lines7 antitumor activity8. Recent studies providing impetus for further studies in
utilizing this scaffold in new therapeutic drug classes\textsuperscript{9}.

In addition, the excellent thermal stabilities of these pyridines have instigated a growing interest for their use as monomeric building blocks useful in the development of thin film vortex fluidic device\textsuperscript{10}, building blocks for the preparation of chiral ligands\textsuperscript{11}. TAPs show promising potential as scintillators that will allow liquid scintillation counting to be carried out at high efficiency in strongly acidic solution and new materials with important photo-or electrochemical properties\textsuperscript{12}. Some examples are used as pharmaceuticals, dyes, additives, agrochemicals, and also in qualitative and quantitative analyses\textsuperscript{13}. Moreover, they are prominent synthons in supramolecular chemistry, with their \(\pi\)-stacking ability along with directional H-bonding capacity\textsuperscript{14}. In addition, the excellent thermal stabilities of these pyridines have gained considerable interest for their use as monomeric building blocks in thin films and organometallic polymers\textsuperscript{15}.

Traditionally TAPs have been synthesized using the reaction of N-phenacylpyridinium salts with \(\alpha, \beta\) - unsaturated ketones in the presence of NH\textsubscript{4}OAc\textsuperscript{16}. Recently, several new and improved methods and procedures have been developed for the synthesis of TAP’s all of these methods use NH\textsubscript{4}OAc as a source of ammonia which include arylation of methylthiopyridines via Ni-induced Grignard reactions reactions of phenacylidene dimethylsulfurane with chalcones and NH\textsubscript{4}OAc\textsuperscript{17}, pyrolysis of 1-vinyl-1, 2-dihydropyridines\textsuperscript{18}, reactions of a-ketoketene dithioacetals with methyl ketones in the presence of NH\textsubscript{4}OAc\textsuperscript{19}, additions of lithiated b-enaminophosphonates to chalcones\textsuperscript{20}, reactions of a-benzotriazolyl ketones with a, b-unsaturated ketones and NH\textsubscript{4}OAc\textsuperscript{21}, and solvent-free reactions\textsuperscript{22a,b} between acetophenones, aryl aldehydes, and NH\textsubscript{4}OAc for the synthesis of tri-aryl pyridines using NaOH in PEG-400\textsuperscript{23}. There have been plethora of catalysts used for this reactions such as PEG-300 along with NaOH\textsuperscript{26}, catalytic amount of acetic acid\textsuperscript{27}, HClO\textsubscript{4} - SiO\textsubscript{2}\textsuperscript{28}, preyssler type heteropoly acid H\textsubscript{14}[NaP\textsubscript{5}W\textsubscript{3}O\textsubscript{11}O\textsubscript{4}]\textsuperscript{29}, wet 2, 4, 6-trichloro-1, 3, 5-triazine (TCT)\textsuperscript{30}, 3-methyl-1-(4-sulfonylbutyl) imidazolium hydrogen sulfate [HO\textsubscript{3}S(CH\textsubscript{2})\textsubscript{3}MIM] [HSO\textsubscript{4}] and a Bronsted acidic ionic liquid\textsuperscript{31}, Bismuth triflate\textsuperscript{32}. But, most of these protocols are having one or more drawbacks, thus leaving room for further improvements.

EXPERIMENTAL

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

A mixture of the acetophenone (2.1mmol), aromatic aldehyde (1.2mmol) and anhydrous ammonium carbonate (2mmol) in water was heated in a sealed tube at 150°C for 4 h. The reaction was monitored by TLC (Thin layer chromatography) n-hexane-EtOAc (6:4). After completion of the reaction, reaction mixture was cooled to room temperature and the residue was eluted by using n-hexane-EtOAc (5:1) through column chromatography. The residue was recrystallized from absolute EtOH.

RESULTS AND DISCUSSION

We were interested in studying synthesis of 2, 4, 6 tri aryl pyridines using ammonium carbonate in aqueous media using ammonium carbonate with the aim to develop an operationally simple method for the synthesis of a large range of TAPs. Ammonium carbonate is a low melting (58°C) and less toxic (LD\textsubscript{50} = 1497mg/kg) solid. In aqueous media it decomposes to produce two moles of ammonia. Under solvent-free conditions the reaction proceeded in a considerably lower yield due to sublimation of ammonium carbonate. There was no significant change on the results observed using high equiv (0.5-1) of ammonium carbonate, suggests that hydrogen bonding, mild buffered pH of the reaction media and the assistance of water to break down (NH\textsubscript{4})\textsubscript{2}CO\textsubscript{3} may all be responsible for acceleration of the reaction rate.

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Although the preparation of 2, 4, 6 tri aryl pyridines has been known there is no report on the effect of the ammonia source on this reaction (Scheme No.1). Thus, we studied a model four-component condensation of acetophenone, benzaldehyde and an ammonium salt (mole ratio = 2:1:1) in water under different conditions (Table No.1). We were pleased to find that among the conditions screened, the corresponding TAPs was obtained quantitatively with (NH₄)₂CO₃ at 80-150°C in water (entry 10) in the absence of any catalyst. This process is economically viable than the previously reported procedures.

*Isolated yields*

The optimized conditions required heating with 35 mol % of ammonium carbonate in water for four hours at 140-150°C under the sealed conditions. In order to study the scope and generality of the ammonium carbonate-catalyzed 2, 4, 6 tri aryl pyridines synthesis in water, a series of TAPs were synthesized from the substituted aromatic aldehydes, and aromatic ketones (Scheme No.2). In all cases, the desired products were isolated in excellent yields (Table No.2).

The optimized reaction conditions further extended to the condensation of other aldehydes with aromatic ketone (Scheme No.2, 4a-4q), chalcone with aromatic ketone (Scheme No.3), chalcone and ammonium carbonate (Scheme No.4), at 80-150°C. Aromatic aldehydes bearing both electron-deficient and electron-rich substituent have afforded the desired TAPs in excellent yields.

**SPECTRAL DATA**

**2, 4, 6-Triphenylpyridine (4a)**

White solid, M.P. 135-137°C, IR (KBr, cm⁻¹): 3069, 1597, 1552, 1494, 1440, 1398, 1178, 1074, 1027, 867, 759, 692. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 8.21(2H, d, J = 7.2 Hz, H Ar); 7.93(2H, s, H Ar); 7.79(2H, d, J = 7.2 Hz, H Ar); 7.53(2H, d, J = 7.4 Hz, H Ar); 7.40-7.34 (9H, m, H Ar). ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 157.2; 150.0; 139.8; 139.2; 129.8; 129.3; 128.9; 127.7; 127.2; 117.8. HRMS [M+H]^+: 308.1214; Found, %: C 89.78; H 5.51; N 4.50. C₂₃H₁₇N. Calculated, %: C 89.87; H 5.57; N 4.56.

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4-(4-Chlorophenyl)-2, 6-diphenylpyridine (4b)

White solid, M.P. 127-128°C, IR (KBr, cm⁻¹): 3061, 1599, 1543, 1489, 1449, 1414, 1384, 1237, 1090, 1013, 825, 773, 692. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm) 8.59 (2H, d, J = 7.2 Hz, H Ar); 8.53 (2H, d, J = 7.8 Hz, H Ar); 8.14 (2H, s, H Ar); 7.84 (2H, d, J = 7.8 Hz, H Ar); 7.66 (2H, d, J = 7.8 Hz, H Ar); 7.56-7.52 (6H, m, H Ar). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 157.8; 149.0; 139.0; 136.1; 134.6; 129.8; 129.6; 129.5; 129.0; 117.0. HRMS [M+H]^+: 342.4899, Found, %: C 80.32; H 4.55; N 4.01. C₂₃H₁₉ClN. Calculated, %: C 80.81; H 4.72; N 4.10.

4-(2-Fluorophenyl)-2, 6-diphenylpyridine (4c)

White solid, M.P. 122-123°C, IR (KBr, cm⁻¹): 157.4; 158.3; 152.3; 138.8; 135.2; 132.2; 130.0; 129.8; 128.0; 117.0. HRMS [M+H]^+: 338.3823, Found, %: C 84.53; H 4.96; N 4.30.

4-(3-Methoxyphenyl)-2, 6-diphenylpyridine (4d)

White solid, M.P. 122-123°C, IR (KBr, cm⁻¹): 3069, 2936, 1598, 1547, 1486, 1444, 1398, 1285, 1255, 1209, 1171, 1037, 782, 775, 692. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 8.13 (4H, d, J = 7.5 Hz, H Ar); 7.94 (4H, d, J = 7.5 Hz, H Ar); 7.34-7.33 (4H, s, H Ar); 7.09-7.04 (4H, d, J = 7.9 Hz, H Ar). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 160.0; 157.4; 149.2; 139.3; 130.9; 129.2; 127.9; 126.9; 125.2; 124.0; 118.1; 116.4; HRMS [M+H]^+: 338.3823, Found, %: C 84.53; H 4.75; N 4.23. C₂₃H₁₆FN. Calculated, %: C 84.90; H 4.96; N 4.30.
= 6.3 Hz, H Ar); 2.35 (3H, s, CH₃). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 157.0; 149.9; 139.8; 135.4; 130.3; 129.8; 129.3; 127.5; 127.1; 116.4; 21.5. HRMS [M+H]+: 322.1726, Found, %: C 89.52; H 5.78; N 4.28. C₂₃H₁₉N. Calculated, %: C 89.68; H 5.96; N 4.36.

4-(4-Methoxyphenyl)-2, 6-diphenylpyridine (4f)
White solid, M.P. 98-100°C, IR (KBr, cm⁻¹): 3035, 2936, 1596, 1547, 1486, 1444, 1398, 1285, 1255, 1204, 1171, 1037, 750, 691. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 8.01 (4H, d, J = 6.9 Hz, H Ar); 7.87 (2H, d, J = 7.2 Hz, H Ar); 7.35 (4H, d, J = 6.9 Hz, H Ar); 7.319-7.286 (2H, s, H Ar); 6.88 (4H, d, J = 7.2 Hz, H Ar); 3.76 (3H, s, OCH₃). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 160.4; 157.1; 150.7; 139.9; 139.4; 130.3; 129.8; 129.3; 127.1; 120.9; 116.9; 115.4; 113.4; 53.5. HRMS [M+H]+: 338.1501, Found, %: C 85.12; H 5.24; N 4.02. C₂₃H₁₀NO. Calculated, %: C 85.43; H 5.68; N 4.15.

N, N-Dimethyl-4-(2, 6-diphenylpyridin-4-yl)benzenamine (4g)
Yellow solid, M.P. 137-139°C, IR (KBr, cm⁻¹): 3037, 2936, 1598, 1525, 1489, 1442, 1398, 1352, 1233, 1199, 1168, 1066, 1023, 818, 773, 695. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 8.02 (2H, s, H Ar); 7.77 (4H, d, J = 7.2 Hz, H Ar); 7.52 (2H, d, J = 7.2 Hz, H Ar); 7.22-7.11 (6H, m, H Ar); 6.8 (2H, d, J = 7.2 Hz, H Ar); 3.76 (3H, s, OCH₃). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 155.4; 152.2; 150.5; 136.2; 129.9; 129.0; 128.7; 127.0; 118.8; 114.4; 42.2. HRMS [M+H]+: 338.1501, Found, %: C 85.24; H 6.21; N 7.87. C₂₃H₂₂N₂. Calculated, %: C 85.68; H 6.33; N 7.99.

2, 6-Bis (4-chlorophenyl)-4-phenylpyridine (4h)
White solid, M.P. 177-178°C, IR (KBr, cm⁻¹): 3052, 2928, 1602, 1543, 1512, 1489, 1426, 1381, 1291, 1247, 1177, 1088, 1011, 824. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 7.97 (4H, d, J = 6.3 Hz, H Ar); 7.86 (2H, s, H Ar); 7.22-7.42 (5H, m, H Ar); 7.14 (4H, d, J = 6.3 Hz, H Ar); 2.23 (6H, s, CH₃). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 158.1; 150.7; 138.2; 137.2; 132.3; 129.8; 129.3; 128.5; 126.9; 117.6; 19.15. HRMS [M+H]+: 336.1666, Found, %: C 89.28; H 6.17; N 4.02. C₂₃H₁₂Cl₂N. Calculated, %: C 89.51; H 6.31; N 4.18.

4-(4-Pyridinyl)-2, 6-diphenylpyridine (4i)
Colorless crystals, M.P. 187-188°C, IR (KBr, cm⁻¹): 3050, 1562, 1544, 1450, 1413, 1384, 1239, 1174, 1078, 1015, 829, 678. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.76 (2H, d, J = 4.7 Hz, 2CH); 8.18 (4H, d, J = 7.5 Hz, 4CH); 7.84 (2H, s, 2CH); 7.61 (2H, d, J = 7.4 Hz, 2CH); 7.51 (4H, d, J = 7.4 Hz, 4CH), 7.45 (2H, d, J = 7.4 Hz, 2CH). ¹³C NMR (75 MHz, CDCl₃): 157.91; 150.52; 147.31; 146.49; 139.00; 129.37; 127.88; 127.09; 121.65; 116.58. HRMS [M+H]+: 309.5263, Found, %: C 85.23; H 5.09; N 8.98. C₂₂H₁₆N₂. Calculated, %: C 85.69; H 5.23; N 9.08.

4-(Furan-2-yl)-2, 6-diphenylpyridine (4j)
Light-brown solid, M.P. 167-169°C, IR (KBr, cm⁻¹): 3058, 1606, 1541, 1487, 1454, 1414, 1244, 1158, 1073, 1010, 868, 772, 690. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 8.30 (2H, d, J = 7.6 Hz, H Ar); 8.20 (2H, d, J = 7.5 Hz, H Ar); 8.14 (2H, s, H Ar); 7.96 (1H, s, H Ar); 7.57-7.47 (7H, m, H Ar); 6.75 (1H, d, J = 8.1 Hz, H Ar). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 157.0; 151.4; 145.2; 139.6; 130.0; 129.8; 129.2; 127.2; 113.1; 113.0; 110.9. HRMS [M+H]+: 298.4825, Found, %: C 84.65; H 4.98; N 4.36. C₂₁H₁₆NO. Calculated, %: C 84.82; H 5.08; N 4.71.

2, 6-Bis (4-Methylphenyl)-4-phenylpyridine (4k)
White solid, M.P. 158-159°C, IR (KBr, cm⁻¹): 3052, 2928, 1602, 1543, 1512, 1489, 1426, 1381, 1291, 1247, 1177, 1088, 1011, 824. ¹H NMR (300 MHz, DMSO-d₆): δ (ppm): 7.97 (4H, d, J = 6.3 Hz, H Ar); 7.86 (2H, s, H Ar); 7.22-7.42 (5H, m, H Ar); 7.14 (4H, d, J = 6.3 Hz, H Ar); 2.23 (6H, s, CH₃). ¹³C NMR (75 MHz, DMSO-d₆): δ (ppm): 158.1; 150.7; 138.2; 137.2; 132.3; 129.8; 129.3; 128.5; 126.9; 117.6; 19.15. HRMS [M+H]+: 336.1666, Found, %: C 89.28; H 6.17; N 4.02. C₂₃H₁₂Cl₂N. Calculated, %: C 89.51; H 6.31; N 4.18.
(125.8 MHz, CDCl$_3$): $d = 116.9, 124.3, 127.1, 128.1, 128.8, 129.4$ (6CH), 139.0, 145.4, 147.8, 148.2. HRMS $[M+H]^+$: 353.3627, Found, %: C 78.05; H 7.83. C$_{23}$H$_{16}$N$_2$O$_2$. Calculated, %: C 78.39; H 4.58; N 7.95.

2, 6-Bis (4-methylphenyl)-4-(4-chlorophenyl) pyridine (4m)
White solid, M.P. 198-200°C, IR (KBr, cm$^{-1}$): 3062, 2932, 1595, 1490, 1460, 1411, 1383, 1265, 1211, 1176, 1089, 1012, 833, 787. $^1$H NMR (300 MHz, DMSO-$d_6$), $\delta$ (ppm): 8.40 (2H, d, $J = 7.5$ Hz, H Ar); 8.31 (2H, d, $J = 7.4$ Hz, H Ar); 8.20 (2H, s, H Ar); 7.62 (2H, d, $J = 7.6$ Hz, H Ar); 7.55-7.52 (4H, m, H Ar); 7.42 (1H, d, $J = 7.3$ Hz, H Ar); 7.05 (1H, d, $J = 7.4$, H Ar); 2.88 (6H, s, CH$_3$). $^{13}$C NMR (75 MHz, DMSO-$d_6$), $\delta$, (ppm): 161.2; 155.2; 152.0; 138.9; 134.3; 132.9; 130.3; 129.3; 129.0; 119.7; 118.0; 114.8; 111.1; 15.8. $[M+H]^+$: 390.2140, Found, %: C 81.02; H 5.39; N 3.69. C$_{25}$H$_{20}$ClN. Calculated, %: C 81.18; H 5.45; N 3.79.

4-(4-Nitrophenyl)-2, 6-bis (4-methylphenyl) pyridine (4n)
Colorless crystals, M.P. 143-144°C, IR (KBr, cm$^{-1}$): 3062, 2932, 1595, 1490, 1460, 1411, 1383, 1265, 1210, 1175, 1085, 1011, 830, 785; $^1$H NMR (300 MHz, DMSO-$d_6$), $\delta$ (ppm): 8.31 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 7.2$ Hz, 4H), 7.76 (2H, s, H Ar), 7.61 (d, $J = 8.4$ Hz, 2H), 6.92 (2H, s, H Ar), 2.86 (6H, s, CH$_3$). $^{13}$C NMR (125.8 MHz, DMSO-$d_6$): $\delta$ (ppm): 150.2, 146.3, 139.2, 129.2, 129.0, 119.7; 118.0; 114.8; 111.1; 15.8. $[M+H]^+$: 381.2140, Found, %: C 81.02; H 5.39; N 3.69. C$_{23}$H$_{16}$N$_2$O$_2$. Calculated, %: C 81.18; H 5.45; N 3.79.

4, 4', 4''-(pyridine-2, 4, 6-triyl) triphenol (4p)
Yellow solid, M.P. 283-284°C, IR (KBr, cm$^{-1}$): 3294, 1708, 1513, 1393, 1234, 1175, 831; $^1$H NMR (300MHz, DMSO-$d_6$): $\delta$ (ppm) 9.82 (s, 1H, OH), 9.73 (s, 2H, OH), 8.12 (d, $J = 8.7$ Hz, 4H), 7.87 (s, 2H, H Ar), 7.44 (d, $J = 8.4$ Hz, 2H), 6.90-6.84 (m, 6H); $^{13}$C NMR (75MHz, DMSO-$d_6$): $\delta$ (ppm) 158.2, 158.1, 156.4, 148.9, 130.1, 128.9, 128.6, 128.0, 115.9, 115.4, 113.5; $[M+H]^+$: 356.1196, Found, %: C 77.35; H 4.55; N 3.68. C$_{23}$H$_{17}$NO$_3$. Calculated, %: C 77.73; H 4.82; N 3.94.

4-(2, 6-diphenylpyridin-4-yl) phenol (4q)
Yellow solid, M.P. 206-208°C, IR (KBr, cm$^{-1}$): 3426, 2358, 1560, 1512, 1393, 835, 685. $^1$H NMR (300MHz, DMSO-$d_6$): $\delta$ (ppm): 9.87 (s, 1H, OH), 8.31 (d, $J = 6.9$ Hz, 4H), 8.12 (s, 2H, H Ar), 7.86 (d, $J = 7.2$ Hz, 2H), 7.57-7.42 (m, 6H), 6.92 (d, $J = 6.9$ Hz, 2H); $^{13}$C NMR (75MHz, DMSO-$d_6$): $\delta$ (ppm) 158.2, 157.3, 150.2, 139.8, 130.4, 129.4, 128.0, 128.4, 127.9, 117.3, 116.2; $[M+H]^+$: 324.0928, Found, %: C 85.23; H 5.15; N 4.19. C$_{23}$H$_{17}$NO. Calculated, %: C 85.42; H 5.30; N 4.33.

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Table No.1: Catalyst-free synthesis of 2, 4, 6 Tri aryl pyridines with various ammonium salts in water under sealed conditions

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Table No.2: Synthesis of 2, 4, 6 Tri aryl pyridines under sealed conditions with ammonium carbonate as source of ammonia

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<td>N</td>
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<tr>
<td>11</td>
<td>H₅C</td>
<td></td>
<td>4k</td>
<td>91</td>
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</tbody>
</table>
Scheme No.1: Catalyst-free synthesis 2, 4, 6 Triaryl pyridines with various ammonium salts in water under

\[
2 \text{ArCOCH}_3 + \text{Ammonium salt} + \text{PhCHO} \xrightarrow{\text{Solvent}} \\text{2, 4, 6 Triaryl pyridines (4a-4q)}
\]

Scheme No.2: Synthesis of 2, 4, 6 Tri aryl pyridines under sealed conditions with ammonium carbonate as source of ammonia

\[
2 \text{ArCOMe} + \text{Ar}^1\text{CHO} + \text{NH}_4(\text{CO}_3)_2 \xrightarrow{\text{Tap water, 150 °C Seal tube}} \text{4a-4q}
\]

Scheme No.3: Two component 2, 4, 6 Tri aryl pyridines from chalcone and ammonium carbonate under sealed conditions

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Scheme No.4: Three component 2, 4, 6 Tri aryl pyridines from chalcone acetophenone and with ammonium carbonate under sealed conditions

Figure No.1: $^1$H NMR Spectra of 2, 4, 6-Triphenylpyridine (4a)

Figure No.2: $^{13}$C NMR Spectra of 2, 4, 6-Triphenylpyridine (4a)

Figure No.3: HRMS Spectra of 2, 4, 6-Triphenylpyridine (4a)
Figure No.4: $^1$H NMR Spectra of 4-(4-Chlorophenyl)-2, 6-diphenylpyridine (4b)

Figure No.5: $^{13}$C NMR Spectra of 4-(4-Chlorophenyl)-2, 6-diphenylpyridine (4b)

Figure No.6: HRMS Spectra of 4-(4-Chlorophenyl)-2, 6-diphenylpyridine (4b)

Figure No.7: $^1$H NMR Spectra of 4-(4-Methylphenyl)-2, 6-diphenylpyridine (4e)
Figure No.8: $^{13}$C NMR Spectra of 4-(4-Methylphenyl)-2, 6-diphenylpyridine (4e)

Figure No.9: HRMS Spectra of 4-(4-Methylphenyl)-2, 6-diphenylpyridine (4e)

Figure No.10: $^1$H NMR Spectra of $N$, $N$-Dimethyl-4-(2, 6-diphenylpyridin-4-yl) benzenamine (4g)

Figure No.11: $^{13}$C NMR Spectra of $N$, $N$-Dimethyl-4-(2, 6-diphenylpyridin-4-yl) benzenamine (4g)
Figure No.12: HRMS Spectra of N, N-Dimethyl-4-(2, 6-diphenylpyridin-4-yl)benzenamine (4g)

Figure No.13: $^1$H NMR Spectra of 2, 6-Bis (4-Methylphenyl)-4-phenylpyridine (4k)

Figure No.14: $^{13}$C NMR Spectra of 2, 6-Bis (4-Methylphenyl)-4-phenylpyridine (4k)

Figure No.15: HRMS Spectra of 2, 6-Bis (4-Methylphenyl)-4-phenylpyridine (4k)
CONCLUSION
We have developed an efficient and facile method for the synthesis of 2,4,6 tri arylpyridines. Ammonium carbonate as a source of ammonia, water media, use of simple and readily available starting materials, excellent yields short reactions times are the main advantages of this reaction.

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CONFLICT OF INTEREST
We declare that we have no conflict of interest.

Figure No.16: $^1$H NMR Spectra of 4-(2, 6-diphenylpyridin-4-yl) phenol (4q)

Figure No.17: $^{13}$C NMR Spectra of 4-(2, 6-diphenylpyridin-4-yl) phenol (4q)

Figure No.18: HRMS Spectra of 4-(2, 6-diphenylpyridin-4-yl) phenol (4q)
BIBLIOGRAPHY


(c) Sweetman B A,


22. (a) Shabnam Mahernia, Mehdi Adib Mohammad Mahdavi, Meisam Nosrati. A solvent-free reaction between acetophenone oximes and epoxy styrenes: an efficient Available online: www.uptodateresearchpublication.com


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