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A general and green chemistry approach for the synthesis of 2,4,6-triarylpyridines

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ABSTRACT
A green and convenient approach for the synthesis of 2,4,6-triarylpyridine by the reaction of aromatic aldehydes, acetophenone derivatives, and ammonium acetate in lactic acid under solvent free condition is described. This method provides several advantages such as environmental friendliness, shorter reaction time, excellent yields, and simple workup procedure.
Keyword: *Green protocol, 2,4,6-triarylpyridine, multi-component reaction, lactic acid, solvent-free conditions.*

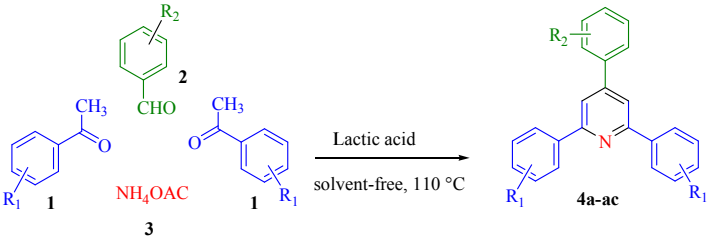
1. INTRODUCTION

In recent years, emergent awareness about ecological safety and global warming has caused worldwide concern about the use of renewable sources and reduction of waste. This has shifted the paradigm toward the use of ecofriendly and green protocols in all phases of chemical construction and can be appreciated by creative research that widely addresses the issues of atom economy, economy of steps, and avoidance of hazardous chemicals [1]. Development of efficient and environmentally friendly synthetic methodologies for the synthesis of compound libraries of medicinal scaffolds is as an attractive area of research in both academic and pharmaceutical industry [2].

Multicomponent reactions (MCR) in solvent less will be one of the most apt approaches, which will meet the requirements of green chemistry as well as for developing libraries of medicinal scaffolds [3].

Compounds containing pyridine rings are of considerable interest in the synthesis of pharmacological and biologically active materials. For examples these structures show different activities such as anesthetic, antimalarial, antioxidant, anticonvulsant, antibacterial and antiparasitic properties [4]. Therefore, preparation of pyridine derivatives has been attracted considerable attention from the past and in recent years. Despite their importance from pharmacological and synthetic point of view, comparatively methods for the preparation of 2,4,6-triaryl pyridines (commonly named as Krohnke pyridines) have been reported in the literature [5]. Newly of these methods is the cyclo-condensation reaction of acetophenones, benzaldehydes and NH_4OAc using conventional heating and refluxing approaches in the presence of Brønsted and Lewis acid catalysts [6].

However, most of these synthetic methods suffer from drawbacks such as employing toxic reagents, strongly acidic or basic conditions, expensive and complex catalysts or reagents, harsh reaction conditions, many tedious steps, and in most cases, low yields of the products and long reaction times that restrict their usage in practical applications. Considering the above points, and also in continuation of our interest on multicomponent organic reactions [7-10], we report here a novel method for preparation of 2,4,6-triarylpyridines from a solvent-less reaction of acetophenones, aryl aldehydes, and ammonium acetate in the presence of lactic acid under solvent-free conditions (Scheme 1).



Scheme 1. Lactic acid catalyzed synthesis of 2,4,6-triarylpyridines 4.

2. EXPERIMENTAL SECTION

Melting points of all compounds were measured on an Electrothermal 9100 apparatus. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker DRX- 300 Avance instruments with DMSO as a solvent. All reagents and solvents obtained from Fluka and Merck were used without further purification.

2.1. General procedure for the synthesis of 2,4,6-triarylpyridines (4a-r).

A mixture of aldehyde (1.0 mmol), 4-Chloroacetophenone (2.0 mmol), 1.3 mol % ammonia source (NH_4OAc) and lactic acid (0.06 g) was heated at 110 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, ethanol was added to the mixture and the soluble catalyst was filtered off. Then, the residue was recrystallized from EtOH.

***4-(4-bromophenyl)-2,6-bis(3-nitrophenyl)pyridine (4a)*:** Yield: 89%; m.p. 186-188 °C ; ^1H NMR (300 MHz, DMSO-d_6): 7.75 (d, 2H, *J*=8.4 Hz, $H_{aromatic}$), 7.83 (t, 2H, *J*=8.1 Hz, $H_{aromatic}$), 8.08 (d, 2H, *J*=8.7 Hz, $H_{aromatic}$), 8.32 (dd, 2H, *J*=1.2 Hz, *J*=6.9 Hz, $H_{aromatic}$), 8.75 (d, 2H, *J*=8.1 Hz, $H_{aromatic}$), 9.06 (s, 2H, $H_{aromatic}$).

4-(4-bromophenyl)-2,6-bis(4-chlorophenyl)pyridine (4b): Yield: (92%); m.p. 144-145 °C ; ^1H NMR (300 MHz, DMSO-d_6): δ = 7.62 (d, 4H, J=8.7 Hz, $H_{aromatic}$), 7.77 (d, 2H, J=8.7 Hz, $H_{aromatic}$),

8.06 (d, 2H, J=8.7 Hz, $H_{aromatic}$), 8.27 (s, 2H, $H_{aromatic}$), 8.37 (d, 4H, J=8.7 Hz, $H_{aromatic}$).

4-(2,6-dip-tolylpyridin-4-yl)phenol (4c): Yield: (80%); m.p. 163-165 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.40 (s, 6H, CH_3), 6.94 (d, 2H, J=8.4 Hz, $H_{aromatic}$), 7.35 (d, 4H, J=8.1Hz, $H_{aromatic}$), 7.90 (d, 2H, J=8.7 Hz, $H_{aromatic}$), 8.05 (s, 2H, $H_{aromatic}$), 8.21 (d, 4H, J=8.1 Hz, $H_{aromatic}$), 9.86 (s, 1H, OH).

2,6-bis(4-chlorophenyl)-4-phenylpyridine (4d): Yield: (87%); m.p. 120-122 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.53-7.63 (m, 7H, $H_{aromatic}$), 8.05-8.08 (m, 2H, $H_{aromatic}$), 8.26 (s, 2H, $H_{aromatic}$), 8.38 (d, 4H, $H_{aromatic}$).

4-(4-bromophenyl)-2,6-dip-tolylpyridine (4e): Yield: (89%); m.p. 234-236 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.40 (s, 6H, CH_3), 7.36 (d, 4H, J=7.8 Hz, $H_{aromatic}$), 7.76 (d, 2H, J=8.4Hz, $H_{aromatic}$), 8.02 (d, 2H, J=8.4 Hz, $H_{aromatic}$), 8.14 (s, 2H, $H_{aromatic}$), 8.23 (d, 4H, J=8.1 Hz, $H_{aromatic}$).

2,6-bis(4-chlorophenyl)-4-(2-methoxyphenyl)pyridine (4f): Yield: (93%); m.p. 166-168 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.84 (s, 3H, OCH_3), 7.13 (td, 1H, J=7.5 Hz, J=0.9 Hz, $H_{aromatic}$), 7.22 (d, 1H, J=7.8 Hz, $H_{aromatic}$), 7.46-7.66 (m, 6H, $H_{aromatic}$), 8.05 (s, 2H, $H_{aromatic}$), 8.28 (dd, 4H, J=6.9 Hz, J=1.8 Hz, $H_{aromatic}$).

2-(4-(4-chlorophenyl)-6-(2-hydroxyphenyl)pyridin-2-yl)phenol (4g): Yield: (79%); m.p. 287-289 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.74 (s, 1H, $H_{aromatic}$), 7.01-7.10 (m, 3H, $H_{aromatic}$), 7.39-7.60 (m, 10H, $H_{aromatic}$), 7.79-7.86 (m, 1H, $H_{aromatic}$), 8.04-8.10 (m, 1H, $H_{aromatic}$).

2-(4-(4-bromophenyl)-6-(2-hydroxyphenyl)pyridin-2-yl)phenol (4h): Yield: (75%); m.p. 252-254 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.71 (s, 1H, $H_{aromatic}$), 7.05-7.10 (m, 2H, $H_{aromatic}$), 7.34 (t, 3H, J=8.7 Hz, $H_{aromatic}$), 7.51-7.71 (m, 5H, $H_{aromatic}$), 7.79-7.86 (m, 2H, $H_{aromatic}$), 8.01 (s, 1H, $H_{aromatic}$), 10.00 (s, 2H, OH).

2,4,6-tris(4-chlorophenyl)pyridine (4i): Yield: (95%); m.p. 271-273 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.60-7.66 (m, 6H, $H_{aromatic}$), 8.13 (d, 2H, J=8.4 Hz, $H_{aromatic}$), 8.28 (s, 2H, $H_{aromatic}$), 8.38 (d, 4H, $H_{aromatic}$).

4-(4-nitrophenyl)-2,6-diphenylpyridine (4j): Yield: (87%); m.p. 192-194 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.58-7.63 (m, 3H, $H_{aromatic}$), 7.69-7.75 (m, 1H, $H_{aromatic}$), 7.84 (d, 1H, J=15.6 Hz, $H_{aromatic}$), 8.14 (s, 1H, $H_{aromatic}$), 8.18-8.21 (m, 7H, $H_{aromatic}$), 8.28-8.32 (m, 3H, $H_{aromatic}$).

2,6-bis(4-chlorophenyl)-4-(4-nitrophenyl)pyridine (4k): Yield: (94%); m.p. 188-190 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.58-7.65 (m, 3H, $H_{aromatic}$), 7.80-7.85 (m, 2H, $H_{aromatic}$), 7.97 (d, 1H, J=8.7 Hz, $H_{aromatic}$), 8.20-8.26 (m, 2H, $H_{aromatic}$), 8.33-8.39 (m, 6H, $H_{aromatic}$).

4-(4-chlorophenyl)-2,6-dip-tolylpyridine (4l): Yield: (95%); m.p. 201-203 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.39 (s, 6H, CH_3), 7.36 (d, 4H, J=6 Hz, $H_{aromatic}$), 7.61-7.63 (m, 2H, $H_{aromatic}$), 8.04-8.06 (d, 2H, $H_{aromatic}$), 8.10 (s, 2H, $H_{aromatic}$), 8.20 (d, 4H, J=6.3 Hz, $H_{aromatic}$).

4-(4-chlorophenyl)-2,6-dip-tolylpyridine (4m): Yield: (94%); m.p. 189–190 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.86 (s, 3H, OCH_3), 7.11 (d, 2H, J=8.7 Hz, $H_{aromatic}$), 7.59 (d, 4H, J=8.7 Hz, $H_{aromatic}$), 8.03 (d, 2H, J=8.7 Hz, $H_{aromatic}$), 8.19 (s, 2H, $H_{aromatic}$), 8.35 (d, 4H, J=8.4 Hz, $H_{aromatic}$).

4-(4-fluorophenyl)-2,6-dip-tolylpyridine(4n): Yield: 95%; m.p. 202-204 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): 2.40 (s, 6H, CH_3),7.36 (d, 4H, *J*=8.1 Hz, $H_{aromatic}$), 7.42 (d, 2H, *J*=9 Hz, $H_{aromatic}$), 8.10-8.15 (m, 4H, $H_{aromatic}$), 8.24 (d, 4H, *J*=8.1 Hz, $H_{aromatic}$), ^{13}C NMR (300 MHz, DMSO-d6): δ = 156.87, 148.7, 139.52, 136.5, 134.7, 130.1, 130.0, 129.7, 127.3, 116.5, 116.2, 21.3.

4-(4-methoxyphenyl)-2,6-bis(3-nitrophenyl)pyridine(4o): Yield: 89%; m.p. 221-223 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): 3.85 (s, 3H, OCH_3), 6.75-8.59 (m, 12H, $H_{aromatic}$), 8.80 (s, 1H, $H_{aromatic}$), 9.08 (s, 1H, $H_{aromatic}$), ^{13}C NMR (300 MHz, DMSO-d6): δ = 154.8, 149.0, 140.7, 133.8, 130.9, 130.8, 129.5, 124.4, 121.9, 118.0, 114.9, 55.8.

2,6-bis(4-chlorophenyl)-4-(4-fluorophenyl)pyridine (4p): Yield: 96%; m.p. 242-244 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): 7.41 (t, 2H, *J*=8.7 Hz, $H_{aromatic}$), 7.60 (d, 4H, *J*=8.4 Hz, $H_{aromatic}$), 8.11-8.16 (m, 4H, $H_{aromatic}$), 8.24 (s, 2H, $H_{aromatic}$), 8.37 (d, 4H, *J*=8.4 Hz, $H_{aromatic}$), ^{13}C NMR (300 MHz, DMSO-d6): δ = 165.16, 155.7, 149.1, 137.8, 134.6, 134.3, 130.1, 130.2, 129.7, 129.4, 129.2, 117.2, 116.5, 116.2.

2,6-bis(4-chlorophenyl)-4-(3-fluorophenyl)pyridine (4q): Yield: 95%; m.p. 250-252 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): 7.33-7.38 (m, 1H, $H_{aromatic}$), 7.57-7.61 (m, 5H, $H_{aromatic}$), 7.90-8.00 (m, 2H, $H_{aromatic}$), 8.25-8.28 (m, 2H, $H_{aromatic}$), 8.34-8.40 (m, 4H, $H_{aromatic}$), ^{13}C NMR (300 MHz, DMSO-d6): δ = 164.8, 161.6, 155.8, 148.8, 140.2, 140.1, 137.7, 134.7, 131.5, 131.3, 129.7, 129.4, 129.1, 123.9, 117.3, 116.7,116.4, 114.9, 114.6.

2,6-bis(4-chlorophenyl)-4-(thiophen-2-yl)pyridine (4r): Yield: 90%; m.p. 172-174 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): 7.29-7.31 (m, 1H, $H_{aromatic}$), 7.62 (d, 4H, *J*=8.7 Hz, $H_{aromatic}$), 7.81-7.83 (m, 1H, $H_{aromatic}$), 8.13 (dd, 1H, *J*=0.9 Hz, *J*=3 Hz, $H_{aromatic}$), 8.18 (s, 2H, $H_{aromatic}$), 8.35 (d, 4H, *J*=8.4 Hz, $H_{aromatic}$), ^{13}C NMR (300 MHz, DMSO-d6): δ = 155.9, 143.8, 140.9, 137.5, 134.7, 129.2, 129.1, 127.9, 115.4.

4-(2-bromophenyl)-2,6-bis(4-chlorophenyl)pyridine (4s): Yield: 95%; m.p. 165-167 °C ; ^{1}H NMR (300 MHz, DMSO-d_6): 7.41 (t, 2H, *J*=8.7 Hz, $H_{aromatic}$), 7.61 (d, 4H, *J*=8.7 Hz, $H_{aromatic}$), 8.13-8.17 (m, 4H, $H_{aromatic}$), 8.25 (d, 2H, *J*=2.7 Hz, $H_{aromatic}$), 8.38 (d, 4H, *J*=7.6 Hz, $H_{aromatic}$), ^{13}C NMR (300 MHz, DMSO-d6): δ = 150.3, 148.8, 144.5, 142.6, 136.0, 133.8, 131.3, 130.4, 130.0, 129.4, 128.1, 124.3, 122.9.

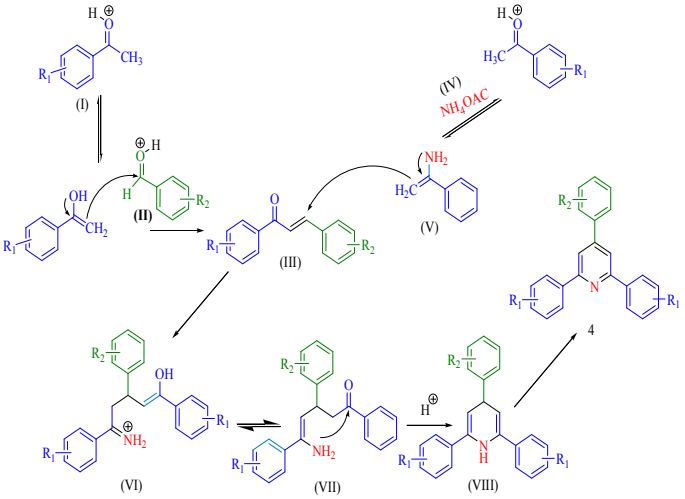
3. RESULTS SECTION

Solvent-free conditions are especially important for providing an eco-friendly system. The number of publications reporting solvent-free condition for the heterocyclic synthesis has increased rapidly in recent years [11]. One advantage of solvent-free reaction, in comparison to the reaction in molecular solvent, is that the compounds formed are often sufficiently pure to

circumvent extensive purification using chromatography. Therefore, due to the increasing demand in modern organic processes for avoiding expensive purification, we decided to investigate the efficiency of Lactic acid as catalyst in the synthesis of 2,4,6-triarylpyridines under solvent-free conditions. Initially, to optimize the reaction conditions such as temperature and amount of catalyst (Lactic acid), the reaction between 4-Chloroacetophenone (2 mmol), benzaldehyde (1 mmol), and NH_4OAc (1.3 mmol) was selected as a model. In the absence of the catalyst, 4a was obtained in a trace amount after 4 h. whereas good results were obtained in the presence of lactic acid. The optimum amount of catalyst was 0.06g, a higher amount of the catalyst did not increase the yield noticeably. The effect of temperature was investigated by carrying out the same model reaction at different temperatures under solvent-free conditions. The yield increased as the reaction temperature was raised and at 110 °C the product was obtained in high yield. Higher temperatures did not increase the yield noticeably. (Table 1)

To evaluate the generality of this model reaction we then prepared a range of 2,4,6-triarylpyridines under the optimized reaction conditions and the results obtained are summarized in Table 2. (Table 2) All the reaction with substituted benzaldehydes preceded very cleanly at optimized reaction conditions and no undesirable side reaction were observed, although the yields were dependent on the substituent. The results in Table 2 show that electron-withdrawing groups such as nitro, and chloro at the phenyl ring of benzaldehyde favored the formation of product. In contrast, electron-donating groups gave slightly lower yields (Table 2). As shown in Table 1, the shortest time and best yield were achieved at 110 °C.

The proposed mechanism for the formation of 2,4,6-triarylpyridines is depicted in Scheme 2. The reaction involves four major stages: Aldol condensation, Michael addition, cyclization, and oxidation. Initially, acetophenone (I) in the presence of lactic acid is converted into its enol form which gives nucleophilic addition to the arylaldehyde (II), which is activated by the catalyst, to afford aldol condensation product (III). Then, a molecule of acetophenone is condensed with an ammonia source (IV) and enamine (V) is formed. Carboxyl group of lactic acid enhances the electron deficiency on carbonyl group of (III) which easily could be attacked by (V) in a Michael addition reaction to afford intermediate (VI). The following cyclisation provides dihydropyridine (VIII). Finally, air oxidation gives the final product (IX). $H_{14}[NaP_5W_{30}O_{110}]$ [16], ZnO [17], n-TSA [18], $ZrOCl_2$ [19], PFPAT[20], in the synthesis of 2,4,6-triaryl pyridines (Table 3).



Scheme 2. Suggested mechanism for synthesis 2,4,6-triarylpyridines**.**

As shown in Table 3, lactic acid can act as an effective catalyst with respect to reaction times and the yield of the product.

Table 1 Effect of Lactic acid amount and temperature on the synthesis of 2,4,6-triphenylpyridine (model reaction).[a]

Entry	Temperature (°C)	Catalyst (g)	Yield [a] (%)
1	r.t	0.081	Trace
2	90	0.081	63
3	100	0.081	81
4	110	0.081	91
5	120	0.081	85
6	110	0.020	68
7	110	0.042	75
8	110	0.060	87

Table 2 Synthesis of 2,4,6-triarylpyridines derivatives.

Entry	R_1	R_2	Time (min)	Yield (%)[a]	Product	M.p. (lit. m.p.) (°C)
1	3-NO_2-C_6H_4	4-Br-C_6H_4	60	89	**4a**	186-188(187-188)[17]
2	4-Cl-C6H4	4-Br-C_6H_4	50	92	**4b**	144–145(143-145)[22]
3	4-Me-C_6H_4	4-OH-C_6H_4	90	80	**4c**	163-165(161-163)[23]
4	4-Cl-C_6H_4	Ph	100	87	**4d**	120-122(123-125)[22]
5	4-Me-C_6H_4	4-Br-C_6H_4	85	89	**4e**	234-236(236-240)[22]
6	4-Cl-C_6H_4	2-OMe-C_6H_4	75	92	**4f**	166-168(164-166)[22]
7	2-OH-C_6H_4	4-Cl-C_6H_4	100	79	**4g**	287-289(286-287)[17]
8	2-OH-C_6H_4	4-Br-C_6H_4	95	75	**4h**	252-254(253-254)[17]
9	4-Cl-C_6H_4	4-Cl-C_6H_4	45	95	**4i**	271-273(269-270)[23]
10	Ph	4-NO_2-C_6H_4	80	87	**4j**	192-194(195-197)[22]
11	4-Cl-C_6H_4	4-NO_2-C_6H_4	50	94	**4k**	188-190(189-192)[19]

Entry	R_1	R_2	Time (min)	Yield (%)[a]	Product	M.p. (lit. m.p.) (°C)
12	4-Me-C_6H_4	4-Cl-C_6H_4	90	95	**4l**	201–203(199-201)[20]
13	4-Cl-C_6H_4	4-OMe-C_6H_4	40	94	**4m**	189–190(190–191)[22]
14	4-Me-C_6H_4	4-F-C_6H_4	35	95	**4n**	202-204
15	3-NO_2-C_6H_4	4-OMe-C_6H_4	65	89	**4o**	210-212
16	4-Cl-C_6H_4	4-F-C_6H_4	30	96	**4p**	242–244
17	4-Cl-C_6H_5	3-F-C_6H_4	32	95	**4q**	250-252
18	4-Cl-C_6H_5	2-Thienyl	55	90	**4r**	172-174

[a] Isolated yield.

Table 3. Synthesis of 2,4,6-triarylpyridines using different catalysts [a]

Entry	Catalyst	Condition	Temperature/°C	Time/min	Yield (%)[b]
1	2,4,6-trichloro-1,3,5-triazine	solvent-free	120 °C	240-450	58-86
2	I_2	solvent-free	120 °C	360	48-61
3	SiO_2-$HClO_4$	solvent-free	120 °C	240-360	68-88
4	$[HO_3S(CH_2)_4MIM][HSO_4]$	solvent-free	120 °C	90-220	82-93
5	$H_{14}[NaP_5W_{30}O_{110}]$ [98]	solvent-free	120 °C	210-420	50-98
6	ZnO	solvent-free	120 °C	20-150	75-95
7	n-TSA	solvent-free	110 °C	80-150	82-95
8	$ZrOCl_2$	solvent-free	100 °C	170-240	85-92
9	PFPAT	solvent-free	120 °C	120	89
10	Cyanuric chloride	solvent-free	120 °C	240	70
11	Lactic acid	solvent-free	110 °C	30-120	75-94

[a] *Reaction conditions: 4-Chloroacetophenone, benzaldehyde and NH_4OAc in the presence of catalyst*
[b] *Isolated yield.*

4. CONCLUSIONS

In conclusion, we have demonstrated a very concise, efficient, environmentally benign, atom economical, and facile protocol for the synthesis of 2,4,6-triarylpyridine derivatives in the presence of lactic acid via a multicomponent reaction. This new chemistry would provide a simple, compatible, and potentially powerful method for the modular construction of 2,4,6-triarylpyridine derivatives. The prominent advantages of this method are mild reaction conditions, high atom economy, shorter reaction times, and higher yields. Meanwhile, the green nature of lactic acid makes this an environmentally friendly protocol amenable for scale-up.

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6. ACKNOWLEDGEMENTS

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