Solvent-Free Synthesis of New 2,4,6-Triarylpyridines Catalyzed by a Brønsted Acidic Ionic Liquid as a Green and Reusable Catalyst

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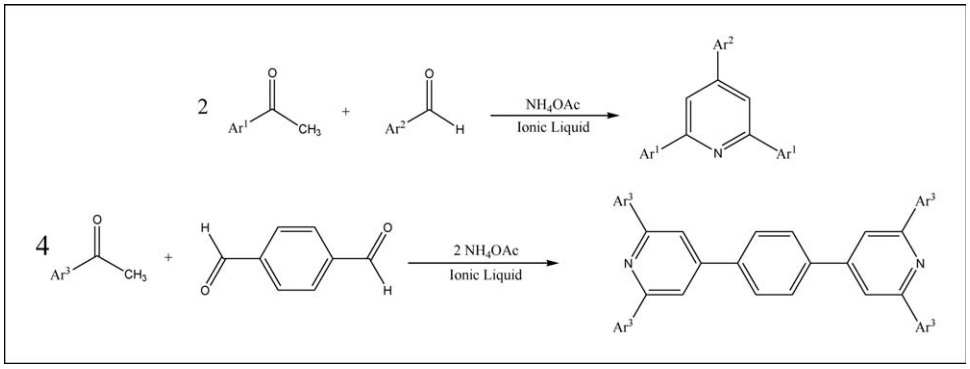

Some new 4-(aryl)-2,6-di-2-naphthylpyridines and 4-(aryl)-2,6-di-2-thienylpyridines have been prepared through three-component condensation of 2-acetylnaphthalene or 2-acetylthiophene, aromatic aldehydes, and ammonium acetate in presence of 1-(4-sulfonylbutyl) pyridinium hydrogensulfate $[(CH_2)_4SO_3HPy][HSO_4]$, a Brønsted acidic ionic liquid as a green and reusable catalyst in solvent-free conditions. Also some new 4,4'-(1,4-phenylene)-bis-(2,6-di-aryl pyridine) was prepared.

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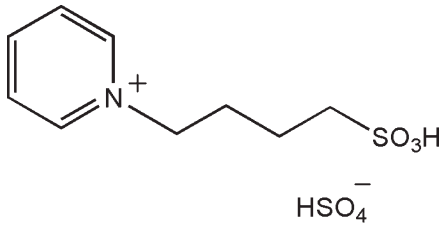
INTRODUCTION

The pyridine ring systems are of interest because of the occurrence of their saturated and partially saturated derivatives in biologically active compounds and natural products such as NAD nucleotides, pyridoxol (vitamin B6), and pyridine alkaloids [1]. Because of their π-stacking ability, some pyridines are used in supramolecular chemistry [2]. Some examples are used as pharmaceuticals (as antimalarial, vasodilator, anesthetic, anticonvulsant, and antiepileptic), dyes, additives (as antioxidant), agrochemicals (as fungicidal, pesticidal, and herbicidal), veterinary (as anthelmintic, antibacterial, and antiparasitic), and also in qualitative and quantitative analysis [1,3–6].

Owing to their wide range of pharmacological activity and industrial and synthesis applications, a number of methods have been reported for the synthesis of Kröhnke-type pyridines [7]. Previously, 2,4,6-triarylpyridines have been prepared by the condensation of 1,5-diketones with formamide-formic acid [8] and by other synthetic procedures including the Chichibabin method [9–12]. Following this procedure, the yields of single products are low because of the formation of mixtures of pyridines and various by-products [12]. These compounds have also been synthesized through the reaction of *N*-phenacylpyridinium salts with α,β-unsaturated ketones in the presence of ammonium acetate [7,13]. However, the pyridinium salts and the unsaturated ketones have to be synthesized first, so this method is relatively expensive. More recently, many improved methods for preparation of 2,4,6-triarylpyridines have been reported such as reaction of a-ketoketene dithioacetals with methyl ketones in the presence of ammonium acetate [14], reaction of *N*-phosphinylethanimines with aldehydes [15], addition of lithiated β-enaminophosphonates to chalcones [16], condensation of acetophenones, benzaldehydes, and NH_4OAc in the presence of NaOH under solvent-free condition [17] and one-pot reaction of acetophenones, benzaldehydes and NH_4OAc both with and without catalyst [18].

Ionic liquids (ILs) have received great attention in diverse areas ranging from synthetic and catalytic chemistry to biotechnology, electrochemistry, and material science [19–22]. The fixation of known homogeneous

Scheme 1. Structure of the catalyst.



$[(CH_2)_4SO_3HPy][HSO_4]$

catalysts on room temperature ionic liquids (RTILs) is an ideal combination to achieve the advantages of both homogeneous and heterogeneous catalysis [23–25].

The introduction of Brønsted-acidic functional groups into cations or anions of the ILs, especially the $-SO_3H$ functional groups, obviously enhanced their acidities and water solubilities [26–28]. Therefore Brønsted acidic ILs can be used as highly efficient acidic catalysts. 1-(4-sulfonylbutyl) pyridinium hydrogensulfate $[(CH_2)_4SO_3HPy][HSO_4]$ is one of Brønsted acidic ILs that can be easily prepared from the inexpensive available reagents [29].

Promoted by these findings and because of our interest in the synthesis of new heterocyclic compounds with potential biological activities, in this article, we wish to report an efficient approach to the synthesis of new 2,4,6-triarylpyridines (3a-j), (4a-g), and (7a-e) using 1-(4-sulfonylbutyl) pyridinium hydrogensulfate $[(CH_2)_4SO_3HPy][HSO_4]$ (Scheme 1), a Brønsted acidic IL, as a green and reusable catalyst (Schemes 2 and 3).

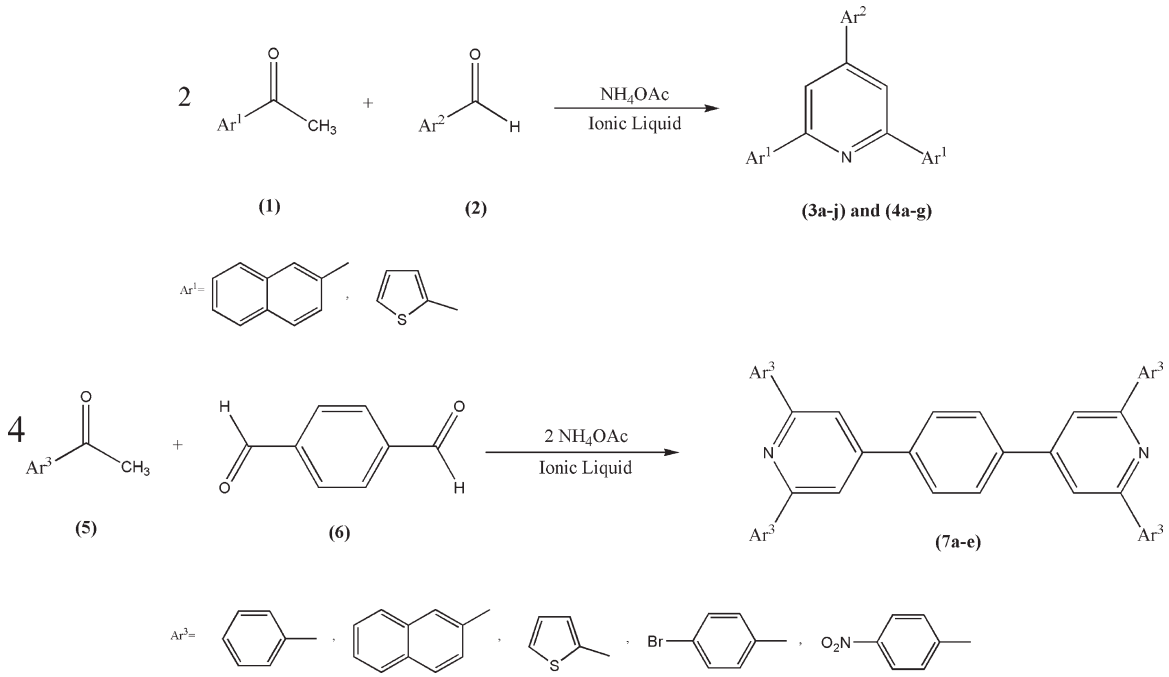
RESULTS AND DISCUSSION

Knowing the chemical and pharmacological importance of the Kröhnke pyridines, we have recently focused on introducing a facile and efficient synthesis of these pyridines. Thus, a range of 4-(aryl)-2,6-di-2-naphthylpyridines were synthesized by heating a mixture of 2-acetylnaphthalene or 2-acetylthiophene, aromatic aldehydes and NH_4OAc in the presence of 1-(4-sulfonylbutyl) pyridinium hydrogensulfate $[(CH_2)_4SO_3HPy][HSO_4]$, in solvent-free conditions. Also, we synthesized a series of bis pyridines by heating a mixture of terephthalaldehyde, an acetophenone and NH_4OAc in the presence of this IL. The products recrystallized and showed a single spot on TLC and were pure enough for all practical purposes. The results are summarized in Tables 1–3.

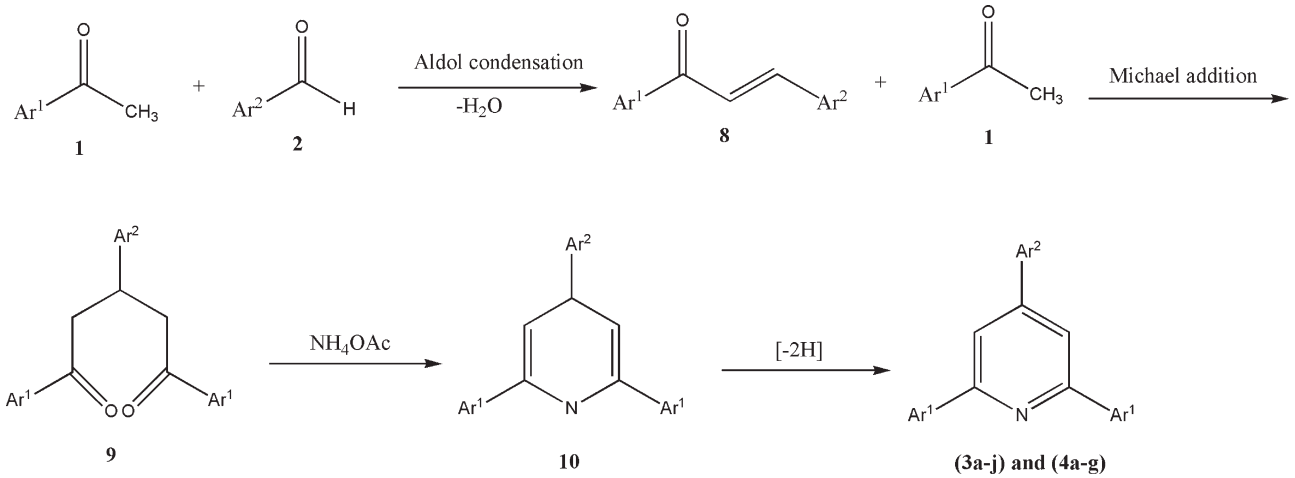
Mechanistically, it is reasonable that the first step involves an Aldol condensation of an 2-acetylnaphthalene or 2-acetylthiophene with aromatic aldehyde and after losing of water and Michael addition to the second mole of 2-acetylnaphthalene or 2-acetylthiophene, leading to 1,3,5-diaryl-1,5-diketone **9**. Then through the interaction of ammonium acetate and **9**, and oxidation of 2,4,6-triaryl-1,4-dihydropyridine **10**, by air, the product **3, 4** can be obtained (Scheme 3).

With IL $[(CH_2)_4SO_3HPy][HSO_4]$, the effect of the catalyst to substrate molar ratio on the reaction was investigated in model reaction **3e** (4-chloro benzaldehyde and 2-acetylnaphthalene) to optimize the reaction conditions. The reaction was carried out at around the melting point

Scheme 2. Synthesis of triarylpyridine.



Scheme 3. Mechanism of the reaction.



of ammonium acetate (120°C). It was found that the use of 5% mol ratio of catalyst gave low yield even after longer reaction duration. In comparison, 10% mol ratio of the catalyst, led to a 70% yield of product. Increasing in the amount of catalyst could not bring much better results (Table 4). Therefore, all compounds were synthesized with 10% mol ratio of the catalyst at 120°C.

In conclusion, we have reported a highly efficient and easy access method for the synthesis of biological significance 2,4,6-triarylpyridines. Our method has several advantages including mild conditions, good yields, utilize cheap available ammonium source, simple operation, and work-up. The reaction times are shorter and the yields are high. It's also noteworthy to mention that the catalyst can be recovered and reused without loss of its structure and activity.

EXPERIMENTAL

All chemicals were commercially available and used without further purification. Melting points were recorded on an electrothermal type 9100 melting point apparatus. The FTIR spectrometer used was Bruker Tensor 27. The FTIR spectra were taken using KBr pellets. The ^{1}HNMR (500 MHz) spectra were recorded on a Bruker DRX 500 spectrometer. The mass spectra were determined on a Shimadzu GCMS 17A instrument. Elemental analysis was performed on a Thermo Finnigan Flash EA microanalyzer. The purity of the substances and the progress of the reactions were monitored by TLC on silica gel.

Typical procedure for the synthesis of 4-(Aryl)-2,6-di-2-naphthylpyridines. A mixture of an aromatic aldehyde (1.0 mmol), 2-acetylnaphthalene or 2-acetylthiophene (2.0 mmol), NH_4OAc (1.3 mol %) and $[(CH_2)_4SO_3HPy][HSO_4]$ (10 mol %) was heated on the oil bath at 120°C. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. The precipitate was filtered off and recrystallized from THF to give the pure product (Scheme 2).

Typical procedure for the synthesis of 4,4′-(1,4-phenylene)-bis-(2,6-di-aryl pyridine). A mixture of an terephthalaldehyde (1.0 mmol), an acetophenone (4.0 mmol), NH_4OAc (1.3 mol %) and $[(CH_2)_4SO_3HPy][HSO_4]$ (10 mol %) was heated on the oil bath at 120°C. The progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature. The precipitate was filtered off and recrystallized from DMSO to give the pure product (Scheme 2).

Table 1

Synthesis of new 4-(aryl)-2,6-di-2-naphthylpyridines (**3a-j**).

Entry	Ar^1	Ar^2	Time (min)	Yield (%)[a]	M.p. (°C)
3a	2-naphthyl	4-$OMeC_6H_4$	60	88	185-187
3b	2-naphthyl	3-MeC_6H_4	80	78	99-101
3c	2-naphthyl	4-MeC_6H_4	70	75	163-165
3d	2-naphthyl	3-ClC_6H_4	70	80	123-125
3e	2-naphthyl	4-ClC_6H_4	55	85	180-182
3f	2-naphthyl	3-BrC_6H_4	75	73	139-141
3g	2-naphthyl	2-OHC_6H_4	80	70	196-198
3h	2-naphthyl	2-$NO_2C_6H_4$	60	83	147-149
3i	2-naphthyl	3-$NO_2C_6H_4$	60	70	198-200
3j	2-naphthyl	4-$NO_2C_6H_4$	50	85	231-233

[a] Yields refer to isolated products.

Table 2

Synthesis of new 4-(aryl)-2,6-di-2-thienylpyridines (**4a-g**).

Entry	Ar^1	Ar^2	Time (min)	Yield (%)[a]	M.p. (°C)
4a	2-thienyl	4-MeC_6H_4	35	71	117-119
4b	2-thienyl	3-ClC_6H_4	25	76	82-85
4c	2-thienyl	4-ClC_6H_4	35	85	133-131
4d	2-thienyl	3-BrC_6H_4	25	81	84-86
4e	2-thienyl	2-$NO_2C_6H_4$	25	70	143-145
4f	2-thienyl	3-$NO_2C_6H_4$	25	79	150-152
4g	2-thienyl	4-$NO_2C_6H_4$	15	75	224-226

[a] Yields refer to isolated products.

Table 3

Synthesis of new 4,4′-(1,4-phenylene)-bis-(2,6-di-aryl pyridine) **(7a-e)**.

Entry	Ar^3	Time (min.)	Yield (%)[a]	M.p. (°C)
7a	2-naphthyl	85	92	243-245
7b	2-thienyl	80	91	190-192
7c	C_6H_5	80	90	187-189
7d	4-BrC_6H_4	75	95	288-290
7e	4-$NO_2C_6H_4$	70	95	266-268

[a] Yields refer to isolated products.

Recycling of the catalyst. In our studies, the recycle of catalyst $[(CH_2)_4SO_3HPy][HSO_4]$ was also investigated by using the preparation of **3e** as a model. The product was isolated from aqueous solution by extraction and the aqueous phase was washed with Et_2O, and then reused in the same reactions. In second run, the yield of product **3e** was obtained 81% (with a minor decrease in yield).

Spectral data. ***4-(4-Methoxyphenyl)-2,6-di-2-naphthylpyridine 3a.*** FTIR (KBr disc): ν = 1600, 1542, 1514, 1246, 1179, 1026, 826, 753 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 3.86 (s, 3H, CH_3O), 7.10-7.25 (d, 2H), 7.52-7.68 (m, 4H), 8-8.16 (m, 8H), 8.39 (s, 2H), 8.52-8.68 (d, 2H), 8.95 (s, 2H); *m/z*: 437. *Anal*. Calcd. for $C_{32}H_{23}NO$: C, 87.84; H, 5.30; N, 3.20. Found: C, 87.65; H, 5.37; N, 3.30.

4-(3-Methylphenyl)-2,6-di-2-naphthylpyridine 3b. FTIR (KBr disc): ν = 1664, 1604, 1315, 1182, 1052, 985, 821, 785 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 2.38 (s, 3H, CH_3), 7.30 (d, 1H, *J* = 7.5 Hz), 7.38 (t, 1H, *J* = 7.5 Hz), 7.66 (t, 3H, *J* = 7 Hz), 7.71 (t, 3H, *J* = 7 Hz), 8.02-8.04 (d, 1H), 8.06-8.18 (m, 9H), 8.93 (s, 2H); MS, *m/z*: 421. *Anal*. Calcd. for $C_{32}H_{23}N$: C, 91.18; H, 5.50; N, 3.32. Found: C, 91.40; H, 5.60; N, 3.20.

4-(4-Methylphenyl)-2,6-di-2-naphthylpyridine 3c. FTIR (KBr disc): ν = 1594, 1542, 1393, 1194, 856, 814, 756 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 2.43 (s, 3H, CH_3), 7.43 (d, 2H, *J* = 8 Hz), 7.57-7.62 (m, 4H), 8.00 (m, 2H, *J* = 9 Hz), 8.05 (d, 2H, *J* = 8 Hz), 8.11 (d, 2H, *J* = 8.5 Hz), 8.14 (d, 2H, *J* = 9 Hz), 8.40 (s, 2H), 8.58 (d, 2H, *J* = 8.5 Hz), 8.95 (s, 2H); MS, *m/z*: 421. *Anal*. Calcd. for $C_{32}H_{23}N$: C, 91.18; H, 5.50; N, 3.32. Found: C, 91.42; H, 5.59; N, 3.20.

4-(3-Chlorophenyl)-2,6-di-2-naphthylpyridine 3d. FTIR (KBr disc): ν = 1663, 1605, 1179, 1050, 984, 820, 789 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.49-7.54 (m, 2H), 7.67 (t, 2H, *J* = 6.5 Hz), 7.71 (t, 2H, *J* = 6.5 Hz), 7.80 (d, 1H, *J* = 15.5 Hz), 7.88 (d, 2H, *J* = 6.5 Hz), 8.03 (d, 1H, *J* = 8 Hz), 8.07 (d, 1H, *J* = 8 Hz), 8.12-8.16 (m, 5H), 8.22 (d, 2H, *J* = 15.5 Hz), 8.98 (s, 2H) ; MS, *m/z*: 441. *Anal*. Calcd. for $C_{31}H_{20}ClN$: C, 84.25; H, 4.56; N, 3.17. Found: C, 84.20; H, 4.60; N, 3.25.

4-(4-Chlorophenyl)-2,6-di-2-naphthylpyridine 3e. FTIR (KBr disc): ν = 1676, 1597, 1541, 1508, 1091, 819, 759 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.49-7.64 (m, 4H), 7.66 (d, 2H, *J* = 8 Hz), 8.02 (d, 2H, *J* = 8.5 Hz), 8.10-8.14 (m, 4H), 8.19 (d, 2H, *J* = 8 Hz), 8.43 (s, 2H), 8.58 (d, 2H, *J* = 8.5 Hz), 8.96 (s, 2H) ;MS, *m/z*: 441. *Anal*. Calcd. for $C_{31}H_{20}ClN$: C, 84.25; H, 4.56; N, 3.17. Found: C, 84.18; H, 4.60; N, 3.27.

4-(3-Bromophenyl)-2,6-di-2-naphthylpyridine 3f. FTIR (KBr disc): ν = 1662, 1606, 1179, 975, 820, 794 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.44 (t, 1H, *J* = 8 Hz), 7.64-7.70 (m, 5H), 7.78 (d, 1H, *J* = 15.5 Hz), 7.90 (d, 2H, *J* = 8 Hz), 8.02-8.07 (m, 2H), 8.14-8.22 (m, 5H), 8.24 (d, 2H, *J* = 15.5 Hz), 8.97 (s, 2H) ; MS, *m/z*: 485. *Anal*. Calcd. for $C_{31}H_{20}BrN$: C, 76.55; H, 4.14; N, 2.88. Found: C, 76.70; H, 4.25; N, 2.75.

4-(2-Hydroxyphenyl)-2,6-di-2-naphthylpyridine 3g. FTIR (KBr disc): ν =3423 (OH), 1636, 1529, 1122, 1005, 827, 758 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.50-7.52 (t, 1H, *J* = 8.5 Hz), 7.62-7.67 (m, 4H), 7.68-7.75 (m, 1H), 8.01-8.04 (m, 2H), 8.05 (d, 2H, *J* = 8.5 Hz), 8.14-8.28 (m, 5H), 8.55 (d, 1H, *J* = 8.5 Hz), 8.63 (s, 2H), 8.91 (s, 2H), 9.08 (broad, 1H, OH); MS, *m/z*: 423. *Anal*. Calcd. for $C_{31}H_{21}NO$: C, 87.92; H, 5.00; N, 3.31. Found: C, 88.05; H, 5.10; N, 3.22.

4-(2-Nitrophenyl)-2,6-di-2-naphthylpyridine 3h. FTIR (KBr disc): ν = 1655, 1593, 1529, 1354, 850, 742 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.57-7.62 (m, 5H), 7.79-7.87 (m, 2H), 7.94 (t, 1H, *J* = 7.6 Hz), 8-8.03 (m, 2H), 8.09-8.12 (m, 5H), 8.18 (s, 2H), 8.52-8.55 (d, 1H, *J* = 7.6 Hz), 8.89 (s, 2H); MS, *m/z*: 452. *Anal*. Calcd. for $C_{31}H_{20}N_2O_2$: C, 82.28; H, 4.45; N, 6.19. Found: C, 82.30; H, 4.52; N, 6.15.

4-(3-Nitrophenyl)-2,6-di-2-naphthylpyridine 3i. FTIR (KBr disc): ν = 1602, 1529, 1344, 830, 758cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.58-7.63 (m, 4H), 7.90 (t, 1H, *J* = 8 Hz), 8-8.02 (m, 2H), 8.10-8.15 (m, 4H), 8.39 (d, 1H, *J* = 8 Hz), 8.51 (s, 2H), 8.57-8.61 (m, 3H), 8.90 (s, 1H), 8.97 (s, 2H); MS, *m/z*: 452. *Anal*. Calcd. for $C_{31}H_{20}N_2O_2$: C, 82.28; H, 4.45; N, 6.19. Found: C, 82.30; H, 4.55; N, 6.17.

4-(4-Nitrophenyl)-2,6-di-2-naphthylpyridine 3j. FTIR (KBr disc): ν = 1660, 1592, 1548, 1343, 953, 825, 758 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.58-7.63 (m, 4H), 8-8.02 (m, 2H), 8.13 (d, 4H, *J* = 8.8 Hz), 8.43 (s, 4H), 8.50 (s, 2H), 8.59 (d, 2H, *J* = 8.8 Hz), 8.98 (s, 2H); MS, *m/z*: 452 *Anal*. Calcd. for $C_{31}H_{20}N_2O_2$: C, 82.28; H, 4.45; N, 6.19. Found: C, 82.32; H, 4.50; N, 6.16.

4-(4-Methylphenyl)-2,6-di-2-thienylpyridine 4a. FTIR (KBr disc): ν = 1647, 1592, 1589, 1414, 987, 815, 723 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 2.49 (s, 3H), 7.27-7.32 (m, 4H), 7.68-7.72 (d, 1H), 7.77-7.85 (m, 3H), 8.05 (d, 2H, *J* = 4.8 Hz), 8.32 (d, 2H, *J* = 4.8 Hz); MS, *m/z*: 333. *Anal*. Calcd. for $C_{20}H_{15}NS_2$: C, 72.03; H, 4.53; N, 4.20. Found: C, 72.20; H, 4.60; N, 4.14.

4-(3-Chlorophenyl)-2,6-di-2-thienylpyridine 4b. FTIR (KBr disc): ν =1647, 1601, 1411, 977, 784, 711 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.35 (t, 2H, *J* = 4 Hz), 7.74-7.78 (t, 1H), 7.85 (d, 1H), 8.09-8.13 (m, 3H), 8.27-8.29 (d, 1H, *J* = 7.2 Hz), 8.34 (d, 1H, *J* = 7.2 Hz), 8.45 (d, 2H, *J* = 4 Hz), 8.79 (s, 1H); MS, *m/z*: 353. *Anal*. Calcd. for $C_{19}H_{12}ClNS_2$: C, 64.48; H, 3.42; N, 3.96. Found: C, 64.61; H, 3.50; N, 3.85.

4-(4-Chlorophenyl)-2,6-di-2-thienylpyridine 4c. FTIR (KBr disc): ν = 1646, 1596, 1415, 982, 816, 727 cm^{-1}; ^{1}HNMR ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.33 (t, 2H, *J* = 3.6 Hz),

Table 4

The effects of catalyst amount on the synthesis of **3e**.

Entry	Catalyst amount (% mole)	Time (min.)	Yield (%)
1	5	110	45
2	10	60	70
3	15	50	78
4	20	45	86

7.53-7.55 (d, 2H), 7.70-7.74 (d, 1H), 7.89-7.95 (m, 3H), 8.07-8.09 (d, 2H), 8.35-8.37 (d, 2H, J = 3.6 Hz); MS, *m*/*z*: 353. *Anal*. Calcd. for $C_{19}H_{12}ClNS_2$: C, 64.48; H, 3.42; N, 3.96. Found: C, 64.61; H, 3.55; N, 3.88.

4-(3-Bromophenyl)-2,6-di-2-thienylpyridine 4d. FTIR (KBr disc): ν = 1646, 1600, 1411, 977, 784, 711 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d6) δ: 7.35 (t, 2H, J = 4 Hz), 7.74-7.78 (t, 1H), 7.85 (d, 1H), 8.09-8.13 (m, 3H), 8.27-8.29 (d, 1H, J = 7.2 Hz), 8.34 (d, 1H, J = 7.2 Hz), 8.45 (d, 2H, J = 4 Hz), 8.79 (s, 1H); MS, *m*/*z*: 396. *Anal*. Calcd. for $C_{19}H_{12}BrNS_2$: C, 57.29; H, 3.04; N, 3.52. Found: C, 57.15; H, 3.15; N, 3.58.

4-(2-Nitrophenyl)-2,6-di-2-thienylpyridine 4e. FTIR (KBr disc): ν = 1654, 1605, 1510, 1414, 1342, cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.34 (t, 2H, J = 4 Hz), 7.71 (t, 1H, J = 8.4 Hz), 7.85 (t, 1H, J = 8.4 Hz), 7.89 (s, 1H), 7.96-8 (m, 1H), 8.11 (t, 3H, J = 8.8 Hz), 8.18 (d, 1H, J = 8.8 Hz), 8.36 (d, 2H, J = 4 Hz); MS, *m*/*z*: 364. *Anal*. Calcd. for $C_{19}H_{12}N_2O_2S_2$: C, 62.62; H, 3.32; N, 7.69. Found: C, 62.75; H, 3.25; N, 7.73.

4-(3-Nitrophenyl)-2,6-di-2-thienylpyridine 4f. FTIR (KBr disc): ν = 1649, 1599, 1531, 1409, 1350, cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.35 (t, 2H, J = 4 Hz), 7.74-7.78 (t, 1H), 7.85 (d, 1H), 8.09-8.13 (m, 3H), 8.27-8.29 (d, 1H, J = 7.2 Hz), 8.34 (d, 1H, J = 7.2 Hz), 8.45 (d, 2H, J = 4 Hz), 8.79 (s, 1H); MS, *m*/*z*: 364. *Anal*. Calcd. for $C_{19}H_{12}N_2O_2S_2$: C, 62.62; H, 3.32; N, 7.69. Found: C, 62.75; H, 3.23; N, 7.75.

4-(4-Nitrophenyl)-2,6-di-2-thienylpyridine 4g. FTIR (KBr disc): ν = 1650, 1602, 1509, 1417, 1339, 759 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.35 (t, 2H, J = 4 Hz), 7.79-7.83 (d, 1H), 8.06 (s, 1H), 8.10-8.13 (m, 2H), 8.17 (d, 2H, J = 8.8 Hz), 8.29 (d, 2H, J = 8.8 Hz), 8.41(d, 2H, J = 4 Hz); MS, *m*/*z*: 364. *Anal*. Calcd. for $C_{19}H_{12}N_2O_2S_2$: C, 62.62; H, 3.32; N, 7.69. Found: C, 62.78; H, 3.25; N, 7.80.

4,4'-(1,4-Phenylene)-bis-(2,6-di-2-naphtyl pyridine) 7a. FTIR (KBr disc): ν = 1656, 1626, 1183, 977, 819 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.66-7.73 (m, 7H), 7.87 (d, 3H, J = 15.6 Hz), 8.04 (d, 4H, J = 7.6 Hz), 8.08-8.10 (d, 9H), 8.18 (t, 7H, J = 7.6 Hz), 8.25 (d, 3H, J = 15.6 Hz), 8.99 (s, 3H); MS, *m*/*z*: 736. *Anal*. Calcd. for $C_{56}H_{36}N_2$: C, 91.27; H, 4.92; N, 3.80. Found: C, 91.45; H, 4.85; N, 3.93.

4,4'-(1,4-Phenylene)-bis-(2,6-di-2-thienyl pyridine) 7b. FTIR (KBr disc): ν = 1648, 1588, 1419, 973, 819, 720 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.34 (t, 2H, J = 4 Hz), 7.48 (d, 1H, J = 16.4 Hz), 7.75-7.79 (m, 3H), 7.83-7.87 (d, 1H, J = 16.4 Hz), 7.90-7.93 (m, 1H), 7.97-8.00 (m, 8H), 8.08-8.10 (d, 2H), 8.39 (d, 2H, J = 4 Hz); MS, *m*/*z*: 560. *Anal*. Calcd. for $C_{32}H_{20}N_2S_4$: C, 68.54; H, 3.59; N, 5.00. Found: C, 68.67; H, 3.70; N, 4.94.

4,4'-(1,4-Phenylene)-bis-(2,6-di-phenyl pyridine) 7c. FTIR (KBr disc): ν = 1655, 1605, 1509, 1417, 1336, 1224, 979, 832, 770 cm-1; ^{1}HNMR (500 MHz, DMSO-d6) δ: 7.59 (t, 7H, J = 7.5 Hz), 7.69 (t, 3H, J = 7.5 Hz), 7.79 (d, 3H, J = 15.5 Hz), 7.99 (s, 6H), 8.04 (d, 3H, J = 15.5 Hz), 8.18 (d, 6H, J = 7.5 Hz); MS, *m*/*z*: 536. *Anal*. Calcd. for $C_{40}H_{28}N_2$: C, 89.52; H, 5.26; N, 5.22. Found: C, 89.65; H, 5.15; N, 5.33.

4,4'-(1,4-Phenylene)-bis-(2,6-di-4-bromo phenyl pyridine) 7d. FTIR (KBr disc): ν = 1655, 1607, 1418, 1336, 1221, 978, 817 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.80 (t, 9H, J = 9 Hz), 8.00 (s, 6H), 8.01-8.04 (d, 3H), 8.13 (d, 6H, J = 9 Hz); MS, *m*/*z*: 848. *Anal*. Calcd. for $C_{40}H_{24}Br_4N_2$: C, 56.37; H, 2.84; N, 3.29. Found: C, 56.50; H, 2.91; N, 3.24.

4,4'-(1,4-Phenylene)-bis-(2,6-di-4-nitro phenyl pyridine) 7e. FTIR (KBr disc): ν = 1666, 1585, 1523, 1335, 1213, 811 cm^{-1}; ^{1}HNMR (500 MHz, DMSO-d_6) δ: 7.84 (d, 4H, J = 15.5 Hz), 8.03 (s, 5H), 8.07 (d, 3H, J = 15.5 Hz), 8.39-8.41 (s, 12H); MS, *m*/*z*: 716. *Anal*. Calcd. for $C_{40}H_{24}N_6O_8$: C, 67.04; H, 3.38; N, 11.73. Found: C, 67.20; H, 3.29; N, 11.85.

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