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Kröhnke reaction in aqueous media: one-pot clean synthesis of 4′-aryl-2,2′:6′,2″-terpyridines

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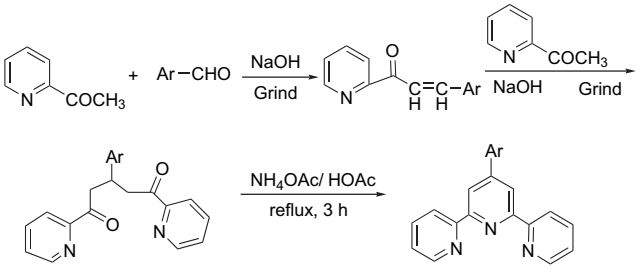
Abstract—A clean aqueous Kröhnke reaction process has been accomplished via a one-pot procedure of 2-acetylpyridine with aromatic aldehyde and ammonium acetate under microwave irradiation or conventional heating conditions. This method is convenient, economic and environmental friendly.

1. Introduction

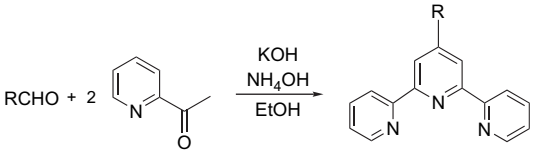
In the most recent decades, the use of an aqueous media[1] has been under extensive investigation for organic synthesis and also to exploit hydrophobic effect.[2] Water has a high dielectric constant with a permanent dipole moment, which allows the coupling between the oscillating electric field and the molecular tumbling to occur with high efficient heating. Hence, at elevated temperature it acts as a pseudo-organic solvent. Isolation of products is also facilitated due to the decreased solubility of organic material upon post reaction cooling.[3] On the other hand, organic reaction in water without using harmful organic solvents is also one of the current focuses because water is abundant, nontoxic and environment-friendly compared with organic solvents used accordingly.[4] Many reactions have been accomplished in aqueous media. Such as Michael reactions,[5] Claisen rearrangements,[6] Mannich reactions,[7] Reformatsky reactions,[8] Tsuji–Trost reaction,[9] Barbier-type reactions,[10] Aldol-type reactions[11] and Fries rearrangement reactions[12]. However, to the best of our knowledge, the Kröhnke reaction in aqueous media has rarely been reported.

Kröhnke type pyridines[13] and other substituted pyridines including the related terpyridines[14] are prominent building blocks in supramolecular chemistry because of their π-stacking ability, and directed H-bond formation. Substitute-2,2′:6′,2″-terpyridines (tpys) ligands have attracted widespread attention due to their ability to form complexes with transition metals, so tpys are applied extensively in coordination chemistry.[15] The applications of tpys have been found in various fields such as supramolecular chemistry,[16] asymmetric catalysis,[17] photosensitization[18] and antitumor chemo-therapeutics.[19]

The methods to synthesize tpys were general through Kröhnke reaction or improved Kröhnke reaction (Schemes 1–3).[20–22]



Scheme 1.



Scheme 2.

Conventional synthesis of tpys suffered from many disadvantages such as multi-step procedure, long reaction time, low yield, use of organic solvents and toxic reagents.

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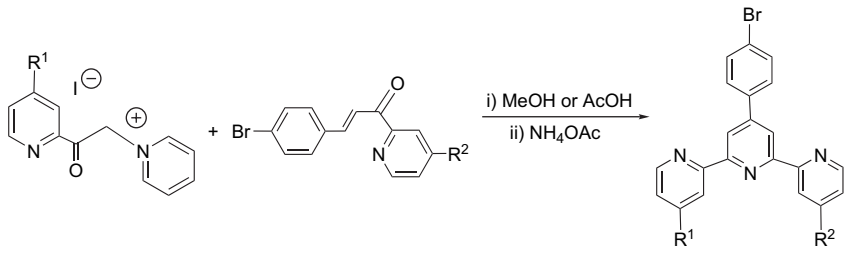
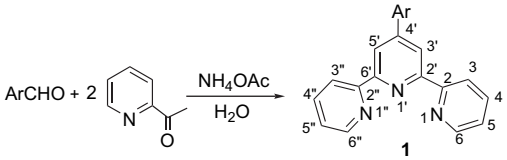


Scheme 3.

Recently, we have reported a facile one-pot reaction for the synthesis of tpys using 2-acetylpyridine, aromatic aldehydes and ammonium acetate in glycol under MWI.[23,24] However, this method using organic solvents, which was harmful compared with water, was still not a green synthesis. Therefore, the development of simple and clean methods for the preparation of tpys is strongly desirable. On the other hand, for the stringent and growing environmental regulations, organic chemists are requested to develop environmentally benign synthetic methods. One of the most promising approaches is to perform organic reactions in aqueous media, including microwave irradiation and conventional heating techniques.

Herein, we have developed a first facile and clean Kröhnke reaction for the synthesis of 4′-aryl-2,2′:6′,2″-terpyridines **1** in aqueous media under either microwave irradiation or conventional heating conditions (Scheme 4).



Scheme 4.

2. Results and discussion

Treatment of aromatic aldehyde (2 mmol) with 2-acetylpyridine (4 mmol) and ammonium acetate (4 mmol) in aqueous medium afforded the target products **1** in excellent yields. The procedure was simple and easy to operate.

To optimize the reaction temperature, the reaction of 2-acetylpyridine, 4-chlorobenzaldehyde and ammonium acetate was carried out using water as solvent at temperatures ranging from 90 to 150 °C in an increment of 10 °C each time. The results are shown in Table 1 (entries 1–7).

We found that the yield of product **1a** was improved and the reaction time was shortened as the temperature was increased from 90 to 130 °C (Table 1, entries 1–5). The yield plateaued when temperature was further increased to 140 and 150 °C (Table 1, entries 6 and 7). Therefore, 130 °C was chosen for all further reactions.

The power of MWI was optimized by carrying out the same reaction at 50, 100, 150, 200, 250 and 300 W at 130 °C. The results are summarized in Table 2. It was shown that MWI at 200 W (entry 4) gave the highest yield. Therefore, a microwave power of 200 W was chosen as the optimum power.

Table 1. Temperature optimization for synthesis of **1a**

Entry	Temp (°C)	Microwave irradiation[a]		Conventional heating	
		Time (min)	Yield (%)	Time (min)	Yield (%)
1	90	30	75	400	62
2	100	24	81	340	70
3	110	21	83	300	73
4	120	18	87	270	75
5	130	16	91	240	78
6	140	17	90	260	76
7	150	16	88	240	75

[a] The power of MWI was the maximum power of 300 W.

Table 2. Power optimization for synthesis of **1a** under MWI at 130 °C

Entry	Power (W)	Time (min)	Yield (%)
1	50	16	46
2	100	16	61
3	150	16	88
4	200	16	92
5	250	16	92
6	300	16	91

Furthermore, the volume of water was found to be important as well in this reaction. When 2.0 mL water (Table 3, entry 3) was used as solvent, the yield was the highest. The results are summarized in Table 3.

Under these optimized reaction conditions, we synthesized a series of products **1** under both microwave irradiation and conventional heating conditions. The results (Table 4, entries 1–11) indicated that MWI exhibited several advantages over the conventional heating by significantly reducing the reaction time and improving the reaction yields.

The scope of the reaction regarding the aldehydes was examined and found that the substituted groups of aromatic aldehydes, such as electron-withdrawing groups and electron-donating groups, can tolerate the reaction conditions with excellent yields.

Table 3. Volume of water optimization for synthesis of **1a** at 130 °C

Entry	Vol (mL)[a]	Microwave irradiation[b]		Conventional heating	
		Time (min)	Yield (%)	Time (min)	Yield (%)
1	1.0	16	86	240	68
2	1.5	16	90	240	75
3	2.0	16	91	240	78
4	2.5	16	88	240	74
5	3.0	16	85	240	70

[a] The product **1a** was synthesized by the reaction of aromatic aldehyde (2 mmol), 2-acetylpyridine (4 mmol) and ammonium acetate (4 mmol) in different volumes of water.
[b] The power of MWI was 200 W.

Table 4. Synthesis of **1** under microwave irradiation and conventional heating in a thermostated oil bath at 130 °C

Entry	Compound	Ar	Mp (lit.)/°C	Microwave irradiation[a]		Conventional heating	
				Time (min)	Yield (lit.)/%	Time (min)	Yield (%)
1	**1a**	4-ClC_6H_4	154–156 (173–175)[23]	16	92 (91)[23]	240	78
2	**1b**	4-BrC_6H_4	143–145 (154–156)[23]	16	91 (89)[23]	180	81
3	**1c**	2-ClC_6H_4	139–140 (156–157)[23]	16	90 (88)[23]	180	70
4	**1d**	4-FC_6H_4	184–185 (161–162)[23]	18	90 (89)[23]	240	72
5	**1e**	2,4-$Cl_2C_6H_3$	176–178 (158.4–159.3)[23]	28	88 (84)[23]	300	80
6	**1f**	3,4-$OCH_2OC_6H_3$	188–190	16	89	180	72
7	**1g**	3,4,5-$(CH_3O)_3C_6H_2$	187–188	18	93	240	80
8	**1h**	4-$NO_2C_6H_4$	158–159 (195–197)[23]	22	92 (89)[23]	300	80
9	**1i**	3-$NO_2C_6H_4$	178–181 (199–200)[23]	22	87 (83)[23]	300	75
10	**1j**	4-OH-3-$NO_2C_6H_3$	274–276	24	88	300	73
11	**1k**	C_6H_5	207–210 (210–211)[23]	24	82 (80)[23]	300	71

[a] The power of MWI was 200 W.

In the experiments, the phase separation of the desired product in solid form from the aqueous media can facilitate product purification by filtration instead of tedious column chromatography and reduce the usage of volatile organic solvent. A distinct phase separation is exhibited in Figure 1 as the reaction proceeded to completion.

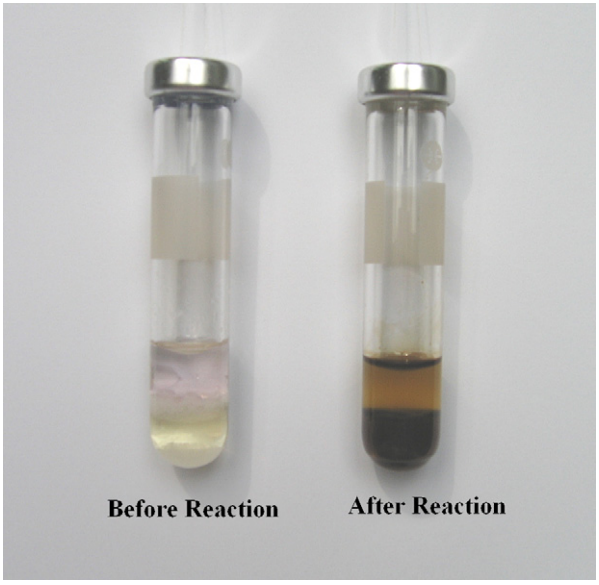
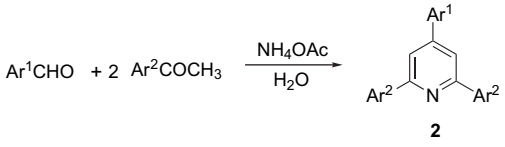


Figure 1. The photo of the reaction.

In order to examine the efficiency and applicability of this reaction, aromatic ketone instead of 2-acetylpyridine was employed to react with aromatic aldehyde and ammonium acetate in aqueous media under both microwave irradiation and conventional heating conditions. To our delight, the reaction proceeded smoothly. A series of 2,4,6-triarylpyridines **2** were obtained in excellent yields (Scheme 5 and entries 1–18 of Table 5). This method avoided multi-step procedure effectively by using organic solvents.[23–25]

Furthermore, this versatile method was also suitable for the indan-1-one. The products 11-aryldiindeno[1,2-*b*:2′,1′-*e*]-pyridines **3** were obtained in good yields under both



Scheme 5.

Table 5. Synthesis of **2** under microwave irradiation and conventional heating in a thermostated oil bath at 130 °C

Entry	Compound	Ar^1	Ar^2	Mp (lit.)/°C	Microwave irradiation[a]		Conventional heating	
					Time (min)	Yields (lit.)/%	Time (min)	Yields (%)
1	**2a**	4-ClC_6H_4	3-$NO_2C_6H_4$	280–281 (285.6–286.6)[23]	8	94 (92)[23]	150	80
2	**2b**	4-ClC_6H_4	4-$CH_3C_6H_4$	202–203 (200.6–202)[23]	9	91 (90)[23]	180	76
3	**2c**	4-ClC_6H_4	2-ClC_6H_4	160–162 (155.8–156)[23]	9	92 (91)[23]	180	78
4	**2d**	4-ClC_6H_4	4-FC_6H_4	200–201 (209.4–210.1)[23]	6	94 (92)[23]	150	82
5	**2e**	4-ClC_6H_4	2,4-$Cl_2C_6H_3$	183–185 (176.4–177.0)[23]	6	96 (95)[23]	150	85
6	**2f**	4-BrC_6H_4	4-$NO_2C_6H_4$	>300	6	95	150	81
7	**2g**	4-$NO_2C_6H_4$	4-$NO_2C_6H_4$	>300	6	93	150	84
8	**2h**	4-$NO_2C_6H_4$	4-$CH_3OC_6H_4$	145–147 (143.1–144.7)[23]	10	91 (90)[23]	240	82
9	**2i**	3-$NO_2C_6H_4$	3-$NO_2C_6H_4$	>300 (>300)[23]	6	93 (91)[23]	180	80
10	**2j**	4-$CH_3OC_6H_4$	2,4-$Cl_2C_6H_3$	168–169 (161.0–161.8)[23]	8	90 (89)[23]	180	78
11	**2k**	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	138–139 (136–137)[23]	10	93 (92)[23]	220	81
12	**2l**	4-BrC_6H_4	3-$NO_2C_6H_4$	>300	6	94	150	80
13	**2m**	2-ClC_6H_4	2,4-$Cl_2C_6H_3$	208–210 (201.2–201.6)[23]	9	92 (89)[23]	180	79
14	**2n**	4-FC_6H_4	3-$NO_2C_6H_4$	>300	6	90	150	82
15	**2o**	C_6H_5	2,4-$Cl_2C_6H_3$	163–164 (160.1–161)[23]	10	90 (88)[23]	240	78
16	**2p**	2,4-$Cl_2C_6H_3$	2,4-$Cl_2C_6H_3$	201–202 (203.9–204.8)[23]	6	94 (91)[23]	180	83
17	**2q**	3,4-$Cl_2C_6H_3$	2,4-$Cl_2C_6H_3$	159–160 (152.9–154.8)[23]	6	91 (90)[23]	190	82
18	**2r**	3-Indole	4-$CH_3OC_6H_4$	229–230 (232.0–233.0)[23]	10	92 (89)[23]	240	82

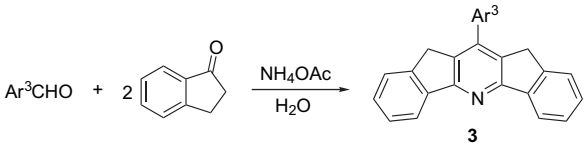
[a] The power of MWI was 200 W.

Table 6. Synthesis of **3** under microwave irradiation and conventional heating in a thermostated oil bath at 130 °C

Entry	Compound	Ar^3	Mp (lit.)/°C	Microwave irradiation[a]		Conventional heating	
				Time (min)	Yields (lit.)/%	Time (min)	Yields (%)
1	**3a**	4-ClC_6H_4	>300 (>300)[24]	8	96 (95)[24]	150	80
2	**3b**	4-FC_6H_4	>300	9	90	180	78
3	**3c**	4-$CH_3OC_6H_4$	256–257 (251.8–252.2)[23]	8	95 (93)[23]	150	83
4	**3d**	4-$CH_3C_6H_4$	>300	8	89	160	75
5	**3e**	2,4-$Cl_2C_6H_3$	>300	10	90	200	77
6	**3f**	4-BrC_6H_4	>300 (>300)[24]	8	97 (96)[24]	150	82
7	**3g**	3,4-$OCH_2OC_6H_3$	>300 (>300)[24]	8	95 (93)[24]	150	80
8	**3h**	3-Indole	>300 (>300)[23]	9	92 (90)[23]	180	81

[a] The power of MWI was 200 W.

microwave irradiation and conventional heating conditions (Scheme 6 and entries 1–8 of Table 6).



Scheme 6.

All the products were characterized by IR, ^1H NMR spectra and elemental analyses. Furthermore, the structure of **1k** was established by an X-ray crystallographic analysis.[26] The molecular structure of **1k** is shown in Figure 2.

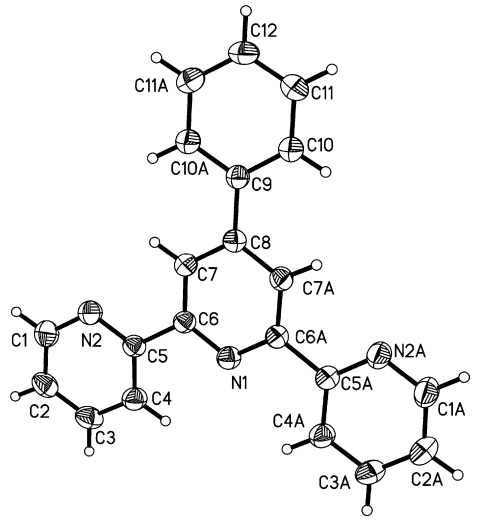


Figure 2. ORTEP diagram of **1k**.

3. Conclusion

We have successfully developed an aqueous Kröhnke reaction procedure under either MWI or conventional heating condition.

4. Experimental

4.1. General information and the microwave reactor

Microwave syntheses were carried out on microwave oven Emrys™ Creator from Personal Chemistry, Uppsala, Sweden. Melting points were determined in open capillaries and are uncorrected. IR spectra were recorded on a TENSOR 27 spectrometer in KBr. ^1H NMR spectra were measured on a DPX 400 spectrometer operating at 400 MHz, using DMSO-d_6 as solvent and TMS as an internal standard. Elemental analyses were determined by using a Perkin–Elmer 240c elemental analysis instrument.

4.2. General procedure for one-pot synthesis of terpyridines 1, triarylpyridines 2 and diindeno pyridines 3 in aqueous medium under microwave irradiation and conventional heating conditions

All microwave-assisted reactions were performed in a monomodal Emrys™ Creator from Personal Chemistry, Uppsala, Sweden. Typically, in a 10 mL Emrys™ reaction vial, appropriate aldehyde (2 mmol), NH_4OAc (4 mmol), 2-acetylpyridine (4 mmol), or aromatic ketone (4 mmol) or indan-1-one (4 mmol) and water (2 mL) were mixed and then capped. The mixture was irradiated by microwave at 200 W at 130 °C or heated in an oil bath at 130 °C for a given time. The automatic mode stirring helped the mixing and uniform heating of the reactants. Upon completion, monitored by TLC, the reaction mixture was cooled to room temperature, filtered to give the crude products, which were further purified by recrystallization from 95% EtOH.

4.2.1. 4′-(4-Chlorophenyl)-2,2′:6′,2″-terpyridine (1a). A white solid; IR (KBr) 1585, 1567, 1546, 1469, 1441, 1411, 1383, 1091, 1012, 826, 789 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.83 (d, J=5.2 Hz, 2H, 6,6″-H), 8.72 (s, 2H, 3′,5′-H), 8.64 (d, J=8.0 Hz, 2H, 3,3″-H), 8.07 (dd, J_1=8.0, J_2=6.8 Hz, 2H, 4,4″-H), 7.99 (d, J=8.8 Hz, 2H, ArH), 7.66 (d, J=8.8 Hz, 2H, ArH), 7.55 (dd, J_1=6.8 Hz, J_2=5.2 Hz, 2H, 5,5″-H). Anal. Calcd for $C_{21}H_{14}ClN_3$: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.31; H, 4.12; N, 12.19.

4.2.2. 4′-(4-Bromophenyl)-2,2′:6′,2″-terpyridine (1b). A white solid; IR (KBr) 1584, 1567, 1550, 1490, 1408, 889, 823, 789 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.82 (d, J=5.2 Hz, 2H, 6,6″-H), 8.71 (s, 2H, 3′,5′-H), 8.67 (d, J=8.0 Hz, 2H, 3,3″-H), 8.04 (dd, J_1=8.0 Hz, J_2=6.8 Hz, 2H, 4,4″-H), 7.91 (d, J=8.0 Hz, 2H, ArH), 7.78 (d, J=8.0 Hz, 2H, ArH), 7.53 (dd, J_1=6.8 Hz, J_2=5.2 Hz, 2H, 5,5″-H). Anal. Calcd for $C_{21}H_{14}BrN_3$: C, 64.96; H, 3.63; N, 10.82. Found: C, 65.01; H, 3.68; N, 10.78.

4.2.3. 4′-(2-Chlorophenyl)-2,2′:6′,2″-terpyridine (1c). A white solid; IR (KBr) 1585, 1567, 1551, 1467, 1442, 1392,

1088, 1040, 991, 790, 779, 749 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.81 (d, J=5.2 Hz, 2H, 6,6″-H), 8.51 (s, 2H, 3′,5′-H), 8.47 (d, J=8.0 Hz, 2H, 3,3″-H), 8.27 (dd, J_1=8.4 Hz, J_2=8.0 Hz, 2H, 4,4″-H), 8.05 (dd, J_1=8.4 Hz, J_2=5.2 Hz, 2H, 5,5″-H), 7.70–7.50 (m, 4H, ArH). Anal. Calcd for $C_{21}H_{14}ClN_3$: C, 73.36; H, 4.10; N, 12.22. Found: C, 73.29; H, 4.11; N, 12.24.

4.2.4. 4′-(4-Fluorophenyl)-2,2′:6′,2″-terpyridine (1d). A white solid; IR (KBr) 1585, 1567, 1552, 1512, 1466, 1416, 1386, 1225, 1161, 1039, 991, 832, 788, 733 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.77 (d, J=5.2 Hz, 2H, 6,6″-H), 8.70 (s, 2H, 3′,5′-H), 8.67 (d, J=8.4 Hz, 2H, 3,3″-H), 8.05 (dd, J_1=8.8 Hz, J_2=8.4 Hz, 2H, 4,4″-H), 7.99 (dd, J_1=8.8 Hz, J_2=5.2 Hz, 2H, 5,5″-H), 7.53 (d, J=8.8 Hz, 2H, ArH), 7.40 (d, J=8.8 Hz, 2H, ArH). Anal. Calcd for $C_{21}H_{14}FN_3$: C, 77.05; H, 4.31; N, 12.84. Found: C, 69.97; H, 4.34; N, 12.87.

4.2.5. 4′-(2,4-Dichlorophenyl)-2,2′:6′,2″-terpyridine (1e). A white solid; IR (KBr) 1583, 1568, 1544, 1468, 1402, 993, 816, 793 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.81 (d, J=6.0 Hz, 2H, 6,6″-H), 8.77 (d, J=8.0 Hz, 2H, 3,3″-H), 8.48 (s, 2H, 3′,5′-H), 8.05 (dd, J_1=8.4 Hz, J_2=8.0 Hz, 2H, 4,4″-H), 7.70 (dd, J_1=8.4 Hz, J_2=6.0 Hz, 2H, 5,5″-H), 7.51–7.54 (m, 3H, ArH). Anal. Calcd for $C_{21}H_{13}Cl_2N_3$: C, 66.68; H, 3.46; N, 11.11. Found: C, 66.73; H, 3.51; N, 11.20.

4.2.6. 4′-(3,4-Methylenedioxylphenyl)-2,2′:6′,2″-terpyridine (1f). A white solid; IR (KBr) 1585, 1567, 1545, 1453, 1400, 1359, 1110, 991, 856, 786, 731, 640 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.76 (d, J=4.8 Hz, 2H, 6,6″-H), 8.67 (d, J=8.0 Hz, 2H, 3,3″-H), 8.64 (s, 2H, 3′,5′-H), 8.06–8.02 (m, 2H, 4,4″-H), 7.53 (dd, J_1=7.0 Hz, J_2=4.8 Hz, 2H, 5,5″-H), 7.51 (d, J=1.6 Hz, 2H, ArH), 7.13 (d, J=8.4 Hz, 1H, ArH), 6.15 (s, 2H, CH_2). Anal. Calcd for $C_{22}H_{15}N_3O_2$: C, 74.78; H, 4.28; N, 11.89. Found: C, 74.69; H, 4.36; N, 11.95.

4.2.7. 4′-(3,4,5-Trimethoxyphenyl)-2,2′:6′,2″-terpyridine (1g). A white solid; IR (KBr) 1586, 1568, 1546, 1469, 1441, 1416, 1389, 1086, 1008, 827, 788, 659 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.79 (d, J=3.6 Hz, 2H, 6,6″-H), 8.69 (s, 2H, 3′,5′-H), 8.67 (d, J=8.0 Hz, 2H, 3,3″-H), 8.07–8.03 (m, 2H, 4,4″-H), 7.56–7.52 (m, 2H, 5,5″-H), 7.14 (s, 2H, ArH), 3.98 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3). Anal. Calcd for $C_{24}H_{21}N_3O_3$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.23; H, 5.21; N, 10.43.

4.2.8. 4′-(4-Nitrophenyl)-2,2′:6′,2″-terpyridine (1h). A white solid; IR (KBr) 1584, 1567, 1550, 1415, 1386, 1350, 1107, 991, 854, 789, 754, 694 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.85 (d, J=6.4 Hz, 2H, 6,6″-H), 8.74 (s, 2H, 3′,5′-H), 8.66 (d, J=8.4 Hz, 2H, 3,3″-H), 8.63 (d, J=9.2 Hz, 2H, ArH), 8.20 (d, J=9.2 Hz, 2H, ArH), 8.04 (dd, J_1=8.4 Hz, J_2=7.25 Hz, 2H, 4,4″-H), 7.53 (dd, J_1=7.2 Hz, J_2=6.4 Hz, 2H, 5,5″-H). Anal. Calcd for $C_{21}H_{14}N_4O_2$: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.08; H, 4.08; N, 15.80.

4.2.9. 4′-(3-Nitrophenyl)-2,2′:6′,2″-terpyridine (1i). A white solid; IR (KBr) 1585, 1567, 1527, 1470, 1390, 1348, 1075, 993, 885, 781, 733 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.83 (d, J=5.6 Hz, 2H, 6,6″-H), 8.77 (s, 2H, 3′,5′-H), 8.68 (d, J=8.0 Hz, 2H, 3,3″-H), 8.64 (s, 1H, ArH), 8.63 (d, J=8.0 Hz, 1H, ArH), 8.42 (d, J=8.4 Hz, 1H, ArH), 8.04 (dd, J_1=8.0 Hz, J_2=7.2 Hz, 2H, 4,4″-H), 7.88 (dd, J_1=8.4 Hz, J_2=8.0 Hz, 1H, ArH), 7.55 (dd, J_1=7.2 Hz, J_2=5.6 Hz, 2H, 5,5″-H). Anal. Calcd for $C_{21}H_{14}N_4O_2$: C, 71.18; H, 3.98; N, 15.81. Found: C, 71.26; H, 4.02; N, 15.70.

4.2.10. 4′-(4-Hydroxy-3-nitrophenyl)-2,2′:6′,2″-terpyridine (1j). A white solid; IR (KBr) 1576, 1558, 1539, 1473, 1420, 1340, 1060, 941, 898, 737 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H, OH), 8.80 (s, 1H, ArH), 8.30 (d, J=7.2 Hz, 2H, 6,6″-H), 8.08 (s, 2H, 3′,5′-H), 7.83 (d, J=8.4 Hz, 2H, 3,3″-H), 7.30 (dd, J_1=8.8 Hz, J_2=4.0 Hz, 2H, 4,4″-H), 7.21 (d, J=8.8 Hz, 2H, 5,5″-H), 6.90 (m, 1H, ArH), 6.69 (m, 1H, ArH). Anal. Calcd for $C_{21}H_{14}N_4O_3$: C, 68.10; H, 3.81; N, 15.13. Found: C, 68.21; H, 3.92; N, 15.21.

4.2.11. 4′-Phenyl-2,2′:6′,2″-terpyridine (1k). A white solid; IR (KBr) 1583, 1567, 1550, 1468, 1392, 993, 892, 796 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.82 (d, J=4.8 Hz, 2H, 6,6″-H), 8.72 (s, 2H, 3′,5′-H), 8.68 (d, J=8.0 Hz, 2H, 3,3″-H), 8.04 (dd, J_1=8.0 Hz, J_2=6.4 Hz, 2H, 4,4″-H), 7.93 (dd, J_1=6.4 Hz, J_2=4.8 Hz, 2H, 5,5″-H), 7.63–7.52 (m, 5H, ArH). Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.50; H, 4.87; N, 13.63.

4.2.12. 4-(4-Chlorophenyl)-2,6-bis(3-nitrophenyl)pyridine (2a). A yellow solid; IR (KBr) 1602, 1493, 1437, 1386, 881, 819, 755, 729, 715 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.14 (s, 2H, ArH), 8.82 (d, J=8.0 Hz, 2H, ArH), 8.51 (s, 2H, Pyridine-H), 8.36 (d, J=8.0 Hz, 2H, ArH), 8.21 (d, J=8.0 Hz, 2H, ArH), 7.85–7.90 (m, 2H, ArH), 7.66 (d, J=8.0 Hz, 2H, ArH). Anal. Calcd for $C_{23}H_{14}ClN_3O_4$: C, 63.97; H, 3.27; N, 9.73. Found: C, 64.04; H, 3.17; N, 9.88.

4.2.13. 4-(4-Chlorophenyl)-2,6-di *p*-tolylpyridine (2b). A yellow solid; IR (KBr) 1602, 1578, 1542, 1492, 1421, 1384, 875, 786 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.22 (d, J=8.0 Hz, 4H, ArH), 8.13 (s, 2H, Pyridine-H), 8.08 (d, J=8.4 Hz, 2H, ArH), 7.79–7.77 (m, 2H, ArH), 7.61 (d, J=8.0 Hz, 2H, ArH), 7.35 (d, J=8.0 Hz, 2H, ArH), 2.39 (s, 6H, 2×CH_3). Anal. Calcd for $C_{25}H_{20}ClN$: C, 81.18; H, 5.45; N, 3.79. Found: C, 81.26; H, 5.50; N, 3.87.

4.2.14. 2,6-Bis(2-chlorophenyl)-4-(4-chlorophenyl)pyridine (2c). A yellow solid; IR (KBr) 1605, 1577, 1545, 1494, 1476, 1441, 1386, 890, 824, 768 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.98–7.95 (m, 2H, ArH), 7.80 (s, 2H, Pyridine-H), 7.75–7.73 (m, 2H, ArH), 7.63–7.59 (m, 4H, ArH), 7.52–7.48 (m, 4H, ArH). Anal. Calcd for $C_{23}H_{14}Cl_3N$: C, 67.26; H, 3.44; N, 3.41. Found: C, 67.42; H, 3.54; N, 3.47.

4.2.15. 4-(4-Chlorophenyl)-2,6-bis(4-fluorophenyl)pyridine (2d). A yellow solid; IR (KBr) 1607, 1546, 1493, 1423, 1384, 828, 780, 750 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.41–8.37 (m, 2H, ArH), 8.21 (s, 2H,

Pyridine-H), 8.13–8.09 (m, 2H, ArH), 7.76–7.74 (m, 2H, ArH), 7.64–7.59 (m, 2H, ArH), 7.39–7.35 (m, 4H, ArH). Anal. Calcd for $C_{23}H_{14}ClF_2N$: C, 73.12; H, 3.73; N, 3.71. Found: C, 73.20; H, 3.83; N, 3.79.

4.2.16. 2,6-Bis(2,4-dichlorophenyl)-4-(4-chlorophenyl)-pyridine (2e). A yellow solid; IR (KBr) 1602, 1551, 1493, 1473, 1423, 1365, 888, 858, 786 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.04 (s, 2H, Pyridine-H), 7.98–7.96 (m, 2H, ArH), 7.81–7.79 (m, 4H, ArH), 7.64–7.59 (m, 4H, ArH). Anal. Calcd for $C_{23}H_{12}Cl_5N$: C, 57.60; H, 2.52; N, 2.92. Found: C, 57.58; H, 2.63; N, 2.87.

4.2.17. 4-(4-Bromophenyl)-2,6-bis(4-nitrophenyl)pyridine (2f). A yellow solid; IR (KBr) 1595, 1516, 1487, 1429, 1383, 1346, 1107, 1071, 1009, 857, 822, 734 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.78 (d, J=8.8 Hz, 1H, ArH), 8.67 (d, J=8.4 Hz, 2H, ArH), 8.60 (dd, J_1=8.8 Hz, J_2=1.6 Hz, 1H, ArH), 8.53 (s, 2H, Pyridine-H), 8.50–8.39 (m, 4H, ArH), 8.14–8.12 (m, 1H, ArH), 7.90–7.80 (m, 3H, ArH). Anal. Calcd for $C_{23}H_{14}BrN_3O_4$: C, 58.00; H, 2.96; N, 8.82. Found: C, 58.09; H, 2.85; N, 8.90.

4.2.18. 2,4,6-Tris(4-nitrophenyl)pyridine (2g). A yellow solid; IR (KBr) 1599, 1570, 1516, 1410, 1347, 1211, 1107, 891, 849, 828, 744 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.45 (s, 1H, ArH), 8.42 (s, 1H, ArH), 8.33–8.19 (m, 6H, ArH), 8.17 (s, 2H, Pyridine-H), 7.93 (d, J=7.6 Hz, 2H, ArH), 7.90–7.85 (m, 1H, ArH), 7.78 (d, J=8.8 Hz, 1H, ArH). Anal. Calcd for $C_{23}H_{14}N_4O_6$: C, 62.45; H, 3.19; N, 12.66. Found: C, 62.57; H, 3.26; N, 12.51.

4.2.19. 2,6-Bis(4-methoxyphenyl)-4-(4-nitrophenyl)pyridine (2h). A yellow solid; IR (KBr) 1606, 1546, 1516, 1428, 1346, 832, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.39–8.29 (m, 8H, ArH), 8.15 (s, 2H, Pyridine-H), 7.12–7.09 (m, 4H, ArH), 3.88 (s, 6H, 2×OCH_3). Anal. Calcd for $C_{25}H_{20}N_2O_4$: C, 72.80; H, 4.89; N, 6.79. Found: C, 72.93; H, 4.77; N, 6.63.

4.2.20. 2,4,6-Tris(3-nitrophenyl)pyridine (2i). A yellow solid; IR (KBr) 1602, 1525, 1350, 874, 818, 802, 727 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 9.17 (s, 2H, ArH), 8.95–8.94 (m, 1H, ArH), 8.87–8.85 (m, 2H, ArH), 8.63 (s, 2H, Pyridine-H), 8.61–8.60 (m, 1H, ArH), 8.41–8.37 (m, 3H, ArH), 7.95–7.88 (m, 3H, ArH). Anal. Calcd for $C_{23}H_{14}N_4O_6$: C, 62.45; H, 3.19; N, 12.66. Found: C, 62.53; H, 3.08; N, 12.57.

4.2.21. 2,6-Bis(2,4-dichlorophenyl)-4-(4-methoxyphenyl)pyridine (2j). A yellow solid; IR (KBr) 1602, 1554, 1514, 1472, 1429, 1365, 885, 857, 843, 798 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.97 (s, 2H, Pyridine-H), 7.89–7.87 (m, 2H, ArH), 7.79–7.77 (m, 4H, ArH), 7.59–7.57 (m, 2H, ArH), 7.11–7.09 (m, 2H, ArH), 3.84 (s, 3H, OCH_3). Anal. Calcd for $C_{24}H_{15}Cl_4NO$: C, 60.66; H, 3.18; N, 2.95. Found: C, 60.62; H, 3.21; N, 2.87.

4.2.22. 2,4,6-Tris(4-methoxyphenyl)pyridine (2k). A yellow solid; IR (KBr) 1608, 1543, 1510, 1461, 1427, 1392, 823 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.21 (m, 4H, ArH), 8.02 (s, 2H, Pyridine-H), 8.01–7.99 (m, 2H, ArH), 7.12–7.08 (m, 6H, ArH), 3.85 (s, 9H, 3×OCH_3). Anal. Calcd for $C_{26}H_{23}NO_3$: C, 78.57; H, 5.83; N, 3.52. Found: C, 78.49; H, 5.76; N, 3.56.

4.2.23. 4-(4-Bromophenyl)-2,6-bis(3-nitrophenyl)pyridine (2l). A yellow solid; IR (KBr) 1601, 1585, 1526, 1486, 1402, 1347, 1298, 1071, 1008, 935, 806, 710 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 2H, Pyridine-H), 8.62 (d, J=7.6 Hz, 1H, ArH), 8.51 (dd, J_1=7.6 Hz, J_2=2.0 Hz, 2H, ArH), 8.11–7.87 (m, 5H, ArH), 7.84 (s, 1H, ArH), 7.80 (s, 1H, ArH), 7.70 (d, J=8.4 Hz, 2H, ArH). Anal. Calcd for $C_{23}H_{14}BrN_3O_4$: C, 58.00; H, 2.96; N, 8.82. Found: C, 58.08; H, 2.88; N, 8.94.

4.2.24. 2,6-Bis(2,4-dichlorophenyl)-4-(4-chlorophenyl)-pyridine (2m). A yellow solid; IR (KBr) 1609, 1541, 1474, 1433, 1398, 1085, 1052, 1034, 987, 890 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 2H, Pyridine-H), 7.82–7.79 (m, 4H, ArH), 7.67–7.61 (m, 2H, ArH), 7.60–7.57 (m, 2H, ArH), 7.54–7.51 (m, 2H, ArH). Anal. Calcd for $C_{23}H_{12}Cl_5N$: C, 57.60; H, 2.52; N, 2.92. Found: C, 57.62; H, 2.49; N, 2.89.

4.2.25. 4-(4-Fluorophenyl)-2,6-bis(3-nitrophenyl)pyridine (2n). A yellow solid; IR (KBr) 1572, 1557, 1504, 1492, 1440, 1396, 1364, 1284, 1085, 1016, 852, 831, 742, 704 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.84 (s, 2H, Pyridine-H), 8.61 (d, J=7.6 Hz, 1H, ArH), 8.50 (d, J=8.8 Hz, 1H, ArH), 8.36 (dd, J_1=8.0 Hz, J_2=2.0 Hz, 1H, ArH), 8.06–8.02 (m, 3H, ArH), 7.99 (s, 1H, ArH), 7.89 (t, J=7.6 Hz, 2H, ArH), 7.83 (s, 1H, ArH), 7.34 (t, J=8.8 Hz, 2H, ArH). Anal. Calcd for $C_{23}H_{14}FN_3O_4$: C, 66.51; H, 3.40; N, 10.12. Found: C, 66.63; H, 3.51; N, 10.03.

4.2.26. 2,6-Bis(2,4-dichlorophenyl)-4-phenylpyridine (2o). A yellow solid; IR (KBr) 1597, 1556, 1541, 1474, 1411, 1368, 816 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.06 (s, 2H, Pyridine-H), 7.93–7.91 (m, 2H, ArH), 7.82–7.79 (m, 4H, ArH), 7.61–7.50 (m, 5H, ArH). Anal. Calcd for $C_{23}H_{13}Cl_4N$: C, 62.05; H, 2.94; N, 3.15. Found: C, 62.10; H, 2.87; N, 3.24.

4.2.27. 2,4,6-Tris(2,4-dichlorophenyl)pyridine (2p). A yellow solid; IR (KBr) 1598, 1557, 1538, 1471, 1414, 1363, 1050, 872, 813 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.87 (s, 2H, Pyridine-H), 7.82–7.79 (m, 4H, ArH), 7.75–7.53 (m, 1H, ArH), 7.70–7.68 (m, 1H, ArH), 7.61–7.58 (m, 3H, ArH). Anal. Calcd for $C_{23}H_{11}Cl_6N$: C, 53.74; H, 2.16; N, 2.72. Found: C, 53.62; H, 2.10; N, 2.81.

4.2.28. 2,6-Bis(2,4-dichlorophenyl)-4-(3,4-dichlorophenyl)pyridine (2q). A yellow solid; IR (KBr) 1603, 1551, 1473, 1420, 1389, 1363, 1322, 993, 857, 813 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 7.82–7.79 (m, 3H, ArH), 7.78 (s, 2H, Pyridine-H), 7.71–7.57 (m, 3H, ArH), 7.48–7.37 (m, 3H, ArH). Anal. Calcd for $C_{23}H_{11}Cl_6N$: C, 53.74; H, 2.16; N, 2.72. Found: C, 53.70; H, 2.21; N, 2.63.

4.2.29. 3-(2,6-Bis(4-methoxyphenyl)pyridin-4-yl)-1*H*-indole (2r). A yellow solid; IR (KBr) 3135, 3105, 2829, 1599, 1512, 1458, 1421, 1342, 880, 801 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.75 (s, 1H, indole-NH), 8.27–8.24 (m, 4H, ArH), 8.11–8.08 (m, 1H, ArH), 8.08 (s, 2H, Pyridine-H), 7.58–7.51 (m, 2H, ArH), 7.24–7.22 (m, 2H,

ArH), 7.12–7.10 (m, 4H, ArH), 3.86 (s, 6H, OCH_3). Anal. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.78; H, 5.46; N, 6.89. Found: C, 79.85; H, 5.66; N, 6.78.

4.2.30. 11-(4-Chlorophenyl)diindeno[1,2-*b*:2′,1′-*e*]pyridine (3a). A yellow solid; IR (KBr) 1601, 1572, 1557, 1491, 1466, 1364, 1284, 1182, 1085, 1017, 852, 832, 704 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.13 (d, J=7.6 Hz, 2H, 5,6-H), 7.86 (d, J=8.0 Hz, 2H, ArH), 7.66 (d, J=7.2 Hz, 2H, 2,9-H), 7.64 (t, J=7.2 Hz, 2H, 3,8-H), 7.52 (t, J=7.2 Hz, 2H, 4,7-H), 7.46 (d, J=8.0 Hz, 2H, ArH), 3.97 (s, 4H, 1,10-H). Anal. Calcd for $C_{25}H_{16}ClN$: C, 82.07; H, 4.41; N, 3.83. Found: C, 82.13; H, 4.35; N, 3.69.

4.2.31. 11-(4-Fluorophenyl)diindeno[1,2-*b*:2′,1′-*e*]pyridine (3b). A yellow solid; IR (KBr) 1588, 1526, 1509, 1434, 1348, 1209, 1161, 1084, 1004, 830, 755 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.13 (d, J=8.0 Hz, 2H, 5,6-H), 7.85 (d, J=8.0 Hz, 2H, ArH), 7.66 (d, J=7.2 Hz, 2H, 2,9-H), 7.64 (t, J=7.2 Hz, 2H, 3,8-H), 7.53 (t, J=7.2 Hz, 2H, 4,7-H), 7.48 (d, J=8.0 Hz, 2H, ArH), 3.97 (s, 4H, 1,10-H). Anal. Calcd for $C_{25}H_{16}FN$: C, 85.94; H, 4.62; N, 4.01. Found: C, 85.87; H, 4.59; N, 4.13.

4.2.32. 11-(4-Methoxyphenyl)diindeno[1,2-*b*:2′,1′-*e*]pyridine (3c). A yellow solid; IR (KBr) 1612, 1561, 1517, 1464, 1440, 1288, 1025, 859, 831, 776 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.11 (d, J=7.2 Hz, 2H, 5,6-H), 7.76 (d, J=8.0 Hz, 2H, ArH), 7.63 (d, J=7.2 Hz, 2H, 2,9-H), 7.51 (t, J=7.2 Hz, 2H, 3,8-H), 7.45 (t, J=7.2 Hz, 2H, 4,7-H), 7.14 (d, J=8.0 Hz, 2H, ArH), 3.95 (s, 4H, 1,10-H), 3.87 (s, 3H, OCH_3). Anal. Calcd for $C_{26}H_{19}NO$: C, 86.40; H, 5.30; N, 3.88. Found: C, 86.55; H, 5.26; N, 3.92.

4.2.33. 11-(*p*-Tolyl)diindeno[1,2-*b*:2′,1′-*e*]pyridine (3d). A yellow solid; IR (KBr) 1600, 1562, 1519, 1463, 1290, 850, 770 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.17 (d, J=8.0 Hz, 2H, 5,6-H), 8.12 (d, J=8.0 Hz, 2H, ArH), 7.85 (d, J=7.2 Hz, 2H, 2,9-H), 7.66 (t, J=7.2 Hz, 2H, 3,8-H), 7.64 (t, J=7.2 Hz, 2H, 4,7-H), 7.50 (d, J=8.0 Hz, 2H, ArH), 3.97 (s, 4H, 1,10-H), 2.35 (s, 3H, CH_3). Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.49; H, 5.46; N, 4.12.

4.2.34. 11-(2,4-Dichlorophenyl)diindeno[1,2-*b*:2′,1′-*e*]-pyridine (3e). A yellow solid; IR (KBr) 1602, 1559, 1517, 1459, 1288, 854, 767 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.13 (d, J=8.0 Hz, 2H, 5,6-H), 7.97 (d, J=8.0 Hz, 2H, ArH), 7.82 (d, J=7.2 Hz, 2H, 2,9-H), 7.73 (d, J=7.2 Hz, 2H, 3,8-H), 7.67 (d, J=8.0 Hz, 2H, 4,7-H), 7.60 (d, J=8.0 Hz, 1H, ArH), 4.12 (s, 4H, 1,10-H). Anal. Calcd for $C_{25}H_{15}Cl_2N$: C, 75.01; H, 3.78; N, 3.50. Found: C, 75.12; H, 3.90; N, 3.62.

4.2.35. 11-(4-Bromophenyl)diindeno[1,2-*b*:2′,1′-*e*]pyridine (3f). A yellow solid; IR (KBr) 1595, 1570, 1556, 1488, 1364, 1284, 1181, 1067, 1011, 850, 742 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, J=7.2 Hz, 2H, 5,6-H), 7.82 (d, J=8.0 Hz, 2H, ArH), 7.78 (d, J=7.2 Hz, 2H, 2,9-H), 7.73 (t, J=7.2 Hz, 2H, 3,8-H), 7.64 (t, J=7.2 Hz, 2H, 4,7-H), 7.50 (d, J=8.0 Hz, 2H, ArH), 3.96 (s, 4H, 1,10-H). Anal. Calcd for $C_{25}H_{16}BrN$: C, 73.18; H, 3.93; N, 3.41. Found: C, 73.24; H, 3.86; N, 3.34.

4.2.36. 11-(3,4-Methylenedioxylphenyl)diindeno[1,2-*b*:2′,1′-*e*]pyridine (3g). A yellow solid; IR (KBr) 1601, 1563, 1488, 1443, 1367, 1285, 1237, 1180, 1113, 1036, 920, 823, 745 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.11 (d, J=7.6 Hz, 2H, 5,6-H), 7.78 (d, J=7.6 Hz, 2H, ArH), 7.71 (d, J=8.0 Hz, 2H, 2,9-H), 7.65 (d, J=7.2 Hz, 2H, 3,8-H), 7.50 (t, J=7.2 Hz, 2H, 4,7-H), 7.12 (s, 1H, ArH), 6.15 (d, J=6.4 Hz, 2H, CH_2), 3.98 (s, 4H, 1,10-H). Anal. Calcd for $C_{26}H_{17}NO_2$: C, 83.18; H, 4.56; N, 3.73. Found: C, 83.23; H, 4.39; N, 3.68.

4.2.37. 11-(1*H*-Indol-3-yl)diindeno[1,2-*b*:2′,1′-*e*]pyridine (3h). A yellow solid; IR (KBr) 3292, 1573, 1559, 1491, 767, 794, 738 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 11.68 (s, 1H, indole-NH), 8.13 (d, J=7.6 Hz, 2H, 5,6-H), 7.96 (s, 1H, ArH), 7.62 (d, J=7.6 Hz, 2H, 2,9-H), 7.57 (s, 1H, ArH), 7.55 (s, 1H, ArH), 7.51 (t, J=7.2 Hz, 2H, 5,6-H), 7.44 (t, J=7.2 Hz, 2H, 3,8-H), 7.23 (t, J=7.2 Hz, 1H, ArH), 7.10 (t, J=7.2 Hz, 1H, ArH), 3.94 (s, 4H, 1,10-H). Anal. Calcd for $C_{27}H_{18}N_2$: C, 87.54; H, 4.90; N, 7.56. Found: C, 87.61; H, 4.86; N, 7.59.

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26. The single-crystal growth was carried out in ethanol at room temperature. X-ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer. Crystal data for **1k**: $C_{21}H_{15}N_3$, colourless, crystal dimension 0.36×0.33×0.23 mm, Triclinic, space group *P*-1, a=12.27 (4), b=11.97 (4), c=11.10 (3) Å, $\alpha=\beta=\gamma=90.00^\circ$, V=1630 (9) Å^3, M_r=317.36, Z=4, D_c=1.293 g/cm^3, λ=0.71073 Å, μ (Mo Kα)=0.080 mm^{-1}, F (000)=664, S=1.003, R_1=0.0398, wR_2=0.0928. Crystallographic data for the structure of **1k** reported in this letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-618883.