An Efficient Microwave-assisted Synthesis Furo[3,4-*b*]-[4,7]phenanthroline and Indeno[2,1-*b*][4,7]phenanthroline Derivatives in Water

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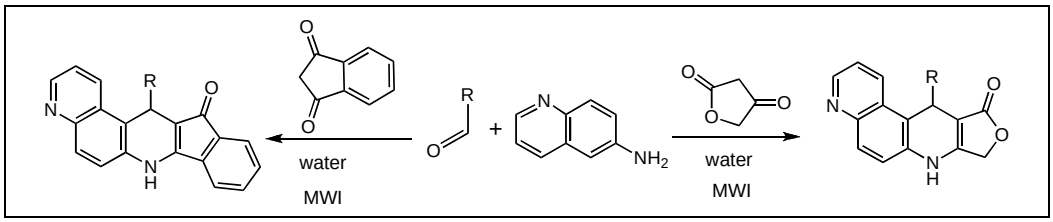

A series of furo[3,4-*b*][4,7]phenanthroline and indeno[2,1-*b*][4,7]phenanthroline derivatives were synthesized *via* a three-component reaction of aromatic aldehydes, 6-aminoquinoline and either tetronic acid or 1,3-indanedione in water, under microwave irradiation without use of any catalyst. This green procedure offers several advantages including operational simplicity, clean reaction, and increased safety for small-scale high-speed synthesis.

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INTRODUCTION

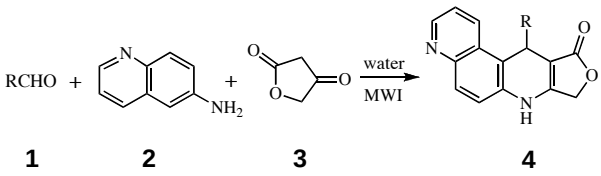
The similar polarity of classic organic solvents and high-temperature water has aroused much interest in the investigation of organic transformations in aqueous media [1]. In addition to being a safe, readily available and environmentally friendly solvent [2], water has also been recognized as an effective reaction medium with unique properties and possibilities for many organic reactions [3]. Simultaneously, high density microwave irradiation (MWI) has matured into a reliable and useful methodology for accelerating small-scale reactions [4]. Thus, it has become clear that the combined approach of microwave superheating and an aqueous medium offers a nearly synergistic strategy in the sense that the combination in itself offers greater potential than the two parts in isolation [5]. Overall, the development of new methods with reduced environmental impact is of increasing importance. The use of water as a nontoxic reaction medium, together with the employment of energy-efficient microwave heating [6], must be considered to be both promising and enabling green alternatives.

Furopyridine is one of the most important "privileged medicinal scaffolds," which are molecular frameworks used for the development of pharmaceutical agents for diverse applications. Compounds incorporating this motif show a wide range of pharmacological activities such as antipsychotic [7], antianaphylactic [8], antiproliferative [9], anticonvulsant [10], and anthelmintic activities [11], and can also be used as calcium influx promoters [12], HIV-1 nonnucleosidereverse transcriptase inhibitors [13], and acetylcholinesterase inhibitors [14].

Compounds with the 4,7-phenanthroline motif, analogs of ergot alkaloids, possess high and versatile pharmacological effects, such as serotonin antagonism, vasoconstriction, oxytocic and psychotropic activities [15]. And they are also used as inhibitors of the pituitary hormone prolactin [16] and fungicides [17].

Furopyridines [18] and 4,7-phenanthroline [19] have been reported widely in the literature, but the synthesis of the compounds incorporating both 4,7-phenanthroline and furopyridine motifs have been neglected. Here we wish to report a facile, rapid and green methodology for the synthesis of furo[3,4-*b*][4,7]phenanthroline by three-component condensations in water under microwave irradiation (Scheme 1).

Scheme 1



1 **2** **3** **4**

RESULTS AND DISCUSSION

To explore the scope and versatility of this method, various reaction conditions were investigated, including solvent and temperature variations. Highlighted in Table 1 for compound **4a**, for example, is the influence of solvent and temperature on the reaction yield. The MW-assisted reaction of 4-fluorobenzaldehyde (**1a**, 1.0 mmol), 6-aminoquinoline (**2**, 1.0 mmol) and tetronic acid (**3**, 1.0 mmol) was examined using glycol, glacial acetic acid,

ethanol water and *N,N*-dimethylformamide as solvent (2.0 mL) at 100 °C, respectively. All the reactions were carried out at the maximum power of 250 W. The results are summarized in Table 1.

It was shown in Table 1 that the reaction using glycol or water as the solvent resulted in higher yields and shorter reaction time than those using AcOH, DMF or EtOH as solvents (Table 1**,** entries 1–5). Considering environmental friendliness and the avoidance of using toxic organic reagents, water was chosen as the solvent for all further microwave-assisted reactions.

To further optimize reaction conditions, the same reaction was carried out in water at temperatures ranging from 90 to 140 °C, with an increment of 10 °C each time. The yield of product **4a** was increased and the reaction time was shortened as the temperature was increased from 90 °C to 120 °C (Table 1, entries 6-8). However, further increase of the temperature to 130-140 °C failed to improve the yield of product **4a** (Table 1, entries 9-10). Therefore, 120 °C was chosen as the reaction temperature for all further microwave-assisted reactions.

Table 1

Optimization of reaction conditions of compound **4a**

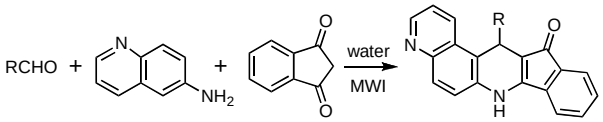
Entry	Solvent	T / °C	Time / min	Yield / %
1	Glycol	100	10	88
2	HOAc	100	12	82
3	EtOH	100	14	79
4	water	100	10	87
5	DMF	100	13	75
6	water	90	12	84
7	water	110	9	89
8	water	120	6	94
9	water	130	7	92
10	water	140	7	90

The maximum power of microwave irradiation was optimized by carrying out the same reaction at powers of 100, 150, 200, 250 and 300 W respectively, using water as solvent at 120 °C. When the power was at 100–200 W, the time taken for the temperature to reach 120 °C was too long. Microwave irradiation at 250 W gave the highest yield and the maximum temperature reached during the reaction was 122 °C. Therefore, microwave power of 250 W was chosen as the optimum power.

The use of these optimal microwave experimental conditions [water, 120 °C] for the reactions of different aromatic aldehydes afforded good yields of furo[3,4-*b*]-[4,7]phenanthroline derivatives. The results (Table 3, entries 1-11) show that aromatic aldehydes bearing either electron-donating (such as alkoxyl groups) or electron-withdrawing (such as nitro or halide groups) functional groups were all suitable for the synthesis of compounds **4**. Moreover, a heterocyclic aldehyde, thiophene-2-carbaldehyde (Table 3, entry 12), still showed high reactivity and clean reaction under these standard conditions.

In order to expand the scope of the method, the replacement of tetronic acid **3** with 1,3-indanedione **5** was also examined. This is particularly attractive because compounds containing the indenopyridine motif show a wide range of biological activities, such as calcium antagonistic [20], antioxidant [21], antihistamine, and antidepressant [22] properties, and also act as phosphodiesterase (PDE) inhibitors [23] and as NK-1 and dopamine receptor ligands [24]. To our delight, the reactions proceeded smoothly under the above optimized conditions and a series of indeno[2,1-b][4,7]phenan-throline derivatives (Scheme 2) was obtained in excellent yields. The results are summarized in Table 2.

Scheme 2



1 **2** **5** **6**

Table 2

The synthesis of some of compounds **4** and **6** under both MW and CH conditions (120 °C)

Entry	**4** or **6**	MW		CH	
		Time / min	Yield / %	Time / h	Yield / %
1	**4a**	6	94	4	75
2	**4e**	7	92	3	54
3	**4f**	8	90	3	49
4	**4l**	8	94	4	51
5	**6b**	7	93	4	70
6	**6f**	9	91	4	41
7	**6h**	8	92	3	61
8	**6l**	8	92	4	47

Additionally, to demonstrate the purely nonthermal microwave effects, the same temperature was applied to synthesize some of products **4** and **6** under classical heating (CH) conditions. The results listed in Table 2 showed the specific activation of this reaction under microwave heating. Simultaneously, the reaction times was strikingly shortened to minutes from hours required in traditional heating condition, and the yields were increased obviously too. The reason may be attributed to the consequence of both thermal effects and specific effects induced by the microwave field [25]. The reactants in these MCRs contain dipoles and proceed *via* relatively polar intermediates, which enhance their interactions with MW and consequently benefit significantly from MW irradiation in regard to more efficient reaction time, yield and product purity.

Although the detailed mechanism of the above reaction remains to be fully clarified, the formation of furo[3,4-*b*]-[4,7]phenanthroline **4** could be explained by a possible

reaction sequence presented in Scheme 3. The product **4** may be synthesized *via* sequential condensation, addition, cyclization and elimination. The condensation between aldehyde **1** and tetronic acid **3** leads to intermediate **7**, Michael addition between **7** and **2** would give **8**, which upon intermolecular cyclization and dehydration to generate the product **4**.

Scheme 3

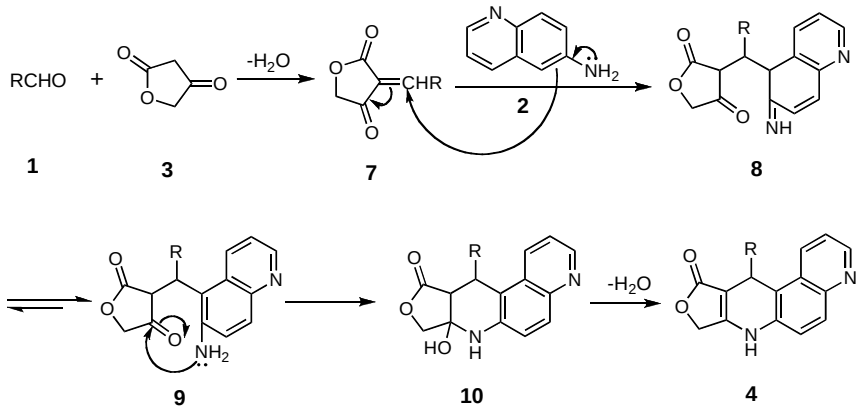


Table 3
Synthesis of **4** and **6** under microwave irradiation at 120 °C

Entry	Product	R	Time / min	Yield / %
1	**4a**	4-FC_6H_4	6	94
2	**4b**	4-ClC_6H_4	7	93
3	**4c**	4-BrC_6H_4	6	95
4	**4d**	4-$CH_3OC_6H_4$	8	92
5	**4e**	2,4-$Cl_2C_6H_3$	7	92
6	**4f**	3,4-$(CH_3O)_2C_6H_3$	8	90
7	**4g**	3-$NO_2C_6H_4$	6	94
8	**4h**	3,4-$OCH_2OC_6H_3$	7	93
9	**4i**	4-$CH_3C_6H_4$	5	96
10	**4j**	C_6H_5	6	93
11	**4k**	4-OH-3-$NO_2C_6H_3$	7	96
12	**4l**	thiophen-2-yl	8	94
13	**6a**	4-FC_6H_4	8	92
14	**6b**	4-ClC_6H_4	7	93
15	**6c**	4-BrC_6H_4	8	93(61)[19(b)]
16	**6d**	4-$CH_3OC_6H_4$	9	92
17	**6e**	2,4-$Cl_2C_6H_3$	7	94
18	**6f**	3,4-$(CH_3O)_2C_6H_3$	9	91
19	**6g**	3-$NO_2C_6H_4$	6	94(72)[19(b)]
20	**6h**	3,4-$OCH_2OC_6H_3$	8	92
21	**6i**	4-$CH_3C_6H_4$	7	94
22	**6j**	C_6H_5	7	94
23	**6k**	4-OH-3-$NO_2C_6H_3$	8	91
24	**6l**	thiophen-2-yl	8	92

In summary, we have developed a three-component reaction of an aldehyde, 6-aminoquinoline and either tetronic acid or 1,3-indanedione in high-temperature water, and have shown its application to the synthesis of a number of furo[3,4-*b*][4,7]phenanthroline and indeno-[2,1-*b*][4,7]phenanthroline derivatives. This green procedure offers several advantages including operational simplicity, clean reactions, increased safety for small-scale high-speed synthesis, and minimal environmental impact that make it a useful and attractive process for the synthesis of these compounds.

EXPERIMENTAL

Microwave irradiation was carried out with a microwave oven Emrys™ Creator from Personal Chemistry, Uppsala, Sweden. Melting points were determined in the open capillaries and were

uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^1H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer using TMS as an internal standard and DMSO-d_6 as solvent. Elemental analysis was determined by using a Perkin-Elmer 240c elemental analysis instrument.

General procedure for the one-pot synthesis of furo[3,4-*b*][4,7]phenanthroline derivatives 4 in water under microwave irradiation conditions. Typically, in a 10-mL Emrys™ reaction vial, aldehyde **1** (1 mmol), 6-aminoquinoline **2** (1 mmol), tetronic acid **3** (1 mmol) and water (2 mL) were mixed and then capped. The mixture was irradiated for a given time at 120 °C under microwave irradiation (initial power 200 W and maximum power 250 W). Upon completion, monitored by TLC, the reaction mixture was filtered to give the crude product, which was further purified by recrystallization from EtOH (95%) to give pure furo[3,4-*b*][4,7]phenanthroline derivatives **4**.

General procedure for the one-pot synthesis of indeno[2,1-*b*][4,7]phenanthroline derivatives 6 in water under microwave irradiation conditions. Typically, in a 10-mL Emrys™ reaction vial, aldehyde **1** (1 mmol), 6-aminoquinoline **2** (1 mmol), 1,3-indanedione **5** (1 mmol) and water (2 mL) were mixed and then capped. The mixture was irradiated for a given time at 120 °C under microwave irradiation (initial power 200 W and maximum power 250 W). Upon completion, monitored by TLC, the reaction mixture was filtered to give the crude product, which was further purified by recrystallization from EtOH (95%) to give pure indeno[2,1-*b*][4,7]phenanthroline derivatives **6**.

11-(4-Fluorophenyl)-8,11-dihydrofuro[3,4-*b*][4,7]phenanthrolin-10(7*H*)-one (4a). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3238, 3065, 3046, 1725, 1650, 1577, 1416, 1285, 1177, 1099, 961 cm^{-1}; ^1H nmr: δ 9.63 (s, 1H, NH), 8.16–8.15 (m, 1H, ArH), 7.51 (d, 1H, J = 8.8 Hz, ArH), 7.42 (d, 1H, J = 8.8 Hz, ArH), 6.77–6.74 (m, 2H, ArH), 6.70–6.66 (m, 2H, ArH), 6.39–6.34 (m, 2H, ArH), 5.20 (s, 1H, CH), 4.35–4.26 (m, 2H, CH_2). *Anal*. Calcd for $C_{20}H_{13}FN_2O_2$: C, 72.28; H, 3.94; N, 8.43. Found C, 72.36; H, 3.85; N, 8.35.

11-(4-Chlorophenyl)-8,11-dihydrofuro[3,4-*b*][4,7]phenanthrolin-10(7*H*)-one (4b). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3235, 3135, 3054, 2978, 1932, 1722, 1650, 1530, 1487, 1415, 1283, 1160, 1106, 962, 739, 696 cm^{-1}; ^1H nmr: δ 9.61 (s, 1H, NH), 8.10–8.06 (m, 1H, ArH), 7.42 (d, 1H, J = 8.4 Hz, ArH), 7.34 (d, 1H, J = 8.8 Hz, ArH), 6.85 (d, 1H, J = 8.8 Hz, ArH), 6.73–6.66 (m, 1H, ArH), 6.60–6.55 (m, 4H, ArH), 5.10 (s, 1H, CH), 4.27–4.19 (m, 2H, CH_2). *Anal*. Calcd for $C_{20}H_{13}ClN_2O_2$: C, 68.87; H, 3.76; N, 8.03. Found C, 68.95; H, 3.65; N, 7.96.

11-(4-Bromophenyl)-8,11-dihydrofuro[3,4-*b*][4,7]phenanthrolin-10(7*H*)-one (4c). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3233, 3135, 3051, 1721, 1650, 1592, 1577, 1531, 1439, 1282, 1180, 1070, 962, 688 cm^{-1}; ^1H nmr: δ 9.60 (s, 1H, NH), 8.10–8.00 (m, 1H, ArH), 7.36 (d, 1H, J = 8.4 Hz, ArH), 7.26 (d, 1H, J = 8.8 Hz, ArH), 6.80 (d, 1H, J = 8.8 Hz, ArH), 6.65–6.60 (m, 3H, ArH), 6.47 (d, 2H, J = 8.0 Hz, ArH), 5.02 (s, 1H, CH), 4.21–4.11 (m, 2H, CH_2). *Anal*. Calcd for $C_{20}H_{13}BrN_2O_2$: C, 61.09; H, 3.33; N, 7.12. Found C, 61.15; H, 3.26; N, 7.05.

11-(4-Methoxyphenyl)-8,11-dihydrofuro[3,4-*b*][4,7]phenanthrolin-10(7*H*)-one (4d). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3249, 3114, 2996, 2868, 2833, 1722, 1650, 1580, 1468, 1398, 1302, 1210, 1110, 962, 846, 673 cm^{-1}; ^1H nmr: δ 10.41 (s, 1H, NH), 8.68–8.67 (m, 1H, ArH), 8.23 (d, 1H, J = 8.4 Hz, ArH), 7.94 (d, 1H, J = 9.2 Hz, ArH), 7.52 (d, 1H, J = 9.2 Hz, ArH), 7.38–7.35 (m, 1H, ArH), 7.12 (d, 2H, J = 8.8 Hz, ArH), 6.76 (d, 2H, J = 8.8 Hz, ArH), 5.67 (s, 1H, CH), 5.00–4.89 (m, 2H, CH_2), 3.65 (s, 3H, OCH_3). *Anal*. Calcd for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13. Found C, 73.35; H, 4.61; N, 8.10.

11-(2,4-Dichlorophenyl)-8,11-dihydrofuro[3,4-*b*][4,7]-phenanthrolin-10(7*H*)-one (4e). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3238, 3127, 3063, 2932, 1723, 1653, 1580, 1467, 1396, 1353, 1255, 1097, 862, 762, 620 cm^{-1}; ^1H nmr: δ 10.58 (s, 1H, NH), 8.69–8.68 (m, 1H, ArH), 8.00–7.94 (m, 2H, ArH), 7.55–7.49 (m, 2H, ArH), 7.43–7.40 (m, 1H, ArH),7.26 (d, 1H, J = 8.0 Hz, ArH), 7.12 (s, 1H, ArH), 6.01 (s, 1H, CH), 5.02–4.93 (m, 2H, CH_2). *Anal*. Calcd for $C_{20}H_{12}Cl_2N_2O_2$: C, 62.68; H, 3.16; N, 7.31. Found C, 62.60; H, 3.11; N, 7.24.

11-(3,4-Dimethoxyphenyl)-8,11-dihydrofuro[3,4-*b*][4,7]-phenanthrolin-10(7*H*)-one (4f). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3246, 3177, 2996, 2932, 2835, 1726, 1656, 1594, 1466, 1350, 1293, 1164, 1013, 961, 830, 684 cm^{-1}; ^1H nmr: δ 10.40 (s, 1H, NH), 8.68–8.67 (m, 1H, ArH), 8.25 (d, 1H, J = 8.4 Hz, ArH), 7.94 (d, 1H, J = 9.2 Hz, ArH), 7.52 (d, 1H, J =8.8 Hz, ArH), 7.38–7.35 (m, 1H, ArH), 7.02 (s, 1H, ArH), 6.72 (d, 1H, J = 8.0 Hz, ArH), 6.46 (d, 1H, J = 8.4 Hz, ArH), 5.67 (s, 1H, CH), 5.00–4.89 (m, 2H, CH_2), 3.68 (s, 3H, OCH_3), 3.62 (s, 3H, OCH_3). *Anal*. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48; Found C, 70.68; H, 4.80; N, 7.50.

11-(3-Nitrophenyl)-8,11-dihydrofuro[3,4-*b*][4,7]phenanthrolin-10(7*H*)-one (4g). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3230, 3111, 3073, 1723, 1649, 1607, 1469, 1431, 1301, 1247, 1158, 1072, 964, 733 cm^{-1}; ^1H nmr: δ 10.60 (s, 1H, NH), 8.70–8.69 (m, 1H, ArH), 8.23 (d, 1H, J = 8.8 Hz, ArH), 6.10 (s, 1H, ArH), 8.02–7.98 (m, 2H, ArH), 7.66 (d, 1H, J = 7.6 Hz, ArH), 7.59–7.51 (m, 2H, ArH), 7.39–7.36 (m, 1H, ArH), 6.03 (s, 1H, CH), 5.05–4.94 (m, 2H, CH_2). *Anal*. Calcd for $C_{20}H_{13}N_3O_4$: C, 66.85; H, 3.65; N, 11.69. Found C, 66.93; H, 3.58; N, 11.56.

11-(Benzo[*d*][1,3]dioxo-5-yl)-8,11-dihydrofuro[3,4-*b*][4,7]-phenanthrolin-10(7*H*)-one (4h). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3184, 3111, 3066, 1721, 1649, 1610, 1469, 1438, 1353, 1258, 1165, 1039, 965, 753 cm^{-1}; ^1H nmr: δ 10.44 (s, 1H, NH), 8.69–8.68 (m, 1H, ArH), 8.26 (d, 1H, J = 8.4 Hz, ArH), 7.94 (d, 1H, J = 8.8 Hz, ArH), 7.51 (d, 1H, J = 8.8 Hz, ArH), 7.40–7.37 (m, 1H, ArH), 6.79 (s, 1H, ArH), 6.72 (d, 1H, J = 8.0 Hz, ArH), 6.61 (d, 1H, J = 8.0 Hz, ArH), 5.92-5.89(m, 2H, CH_2), 5.66 (s, 1H, CH), 5.01–4.89 (m, 2H, CH_2). *Anal*. Calcd for $C_{21}H_{14}N_2O_4$: C, 70.39; H, 3.94; N, 7.82. Found C, 70.32; H, 3.95; N, 7.80.

11-*p*-Tolylfuro[3,4-*b*][4,7]phenanthrolin-10(7*H*,8*H*,11*H*)-one (4i). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3218, 3135, 3046, 2931, 2858, 1723, 1649, 1593, 1468, 1352, 1286, 1175, 1011, 961, 829, 673 cm^{-1}; ^1H nmr: δ 10.43 (s, 1H, NH), 8.68–8.67 (m, 1H, ArH), 8.21 (d, 1H, J = 8.8 Hz, ArH), 7.94 (d,

1H, J = 8.8 Hz, ArH), 7.52 (d, 1H, J =8.8 Hz, ArH), 7.37–7.34 (m, 1H, ArH), 7.09 (d, 2H, J = 7.6 Hz, ArH), 7.00 (d, 2H, J = 7.6Hz, ArH), 5.67 (s, 1H, CH), 5.00–4.89 (m, 2H, CH_2), 2.17(s, 3H, CH_3). *Anal.* Calcd for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found C, 76.80; H, 4.88; N, 8.55.

11-Phenyl-8,11-dihydrofuro[3,4-*b*][4,7]phenanthrolin-10(7*H*)-one (4j). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3273, 3143, 3063, 2935, 2870, 1727, 1652, 1579, 1508, 1397, 1292, 1181, 1127, 962, 759, 701 cm^{-1}; ^1H nmr: δ 10.46 (s, 1H, NH), 8.68–8.67 (m, 1H, ArH), 8.22 (d, 1H, J = 8.4 Hz, ArH), 7.95 (d, 1H, J = 8.8 Hz, ArH), 7.53 (d, 1H, J = 8.8 Hz, ArH), 7.38–7.35 (m, 1H, ArH), 7.22–7.19 (m, 4H, ArH), 7.10–7.06 (m, 1H, ArH), 5.73 (s, 1H, CH), 5.01–4.91 (m, 2H, CH_2). *Anal.* Calcd for $C_{20}H_{14}N_2O_2$: C, 76.42; H, 4.49; N, 8.91. Found C, 76.56; H, 4.42; N, 8.82.

11-(4-Hydroxy-3-nitrophenyl)-8,11-dihydrofuro[3,4-*b*]-[4,7]phenanthrolin-10(7*H*)-one (4k). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3218, 3064, 1722, 1649, 1607, 1468, 1431, 1330, 1235, 1135, 1078, 828, 753 cm^{-1}; ^1H nmr: δ 10.83 (s, 1H, OH), 10.52 (s, 1H, NH), 8.70–8.69 (m, 1H, ArH), 8.24 (d, 1H, J = 8.4 Hz, ArH), 7.97 (d, 1H, J = 9.2 Hz, ArH), 7.73 (s, 1H, ArH), 7.54 (d, 1H, J = 8.8 Hz, ArH), 7.41–7.35 (m, 2H, ArH), 6.99 (d, 1H, J = 8.8 Hz, ArH), 5.82 (s, 1H, CH), 5.03–4.92 (m, 2H, CH_2). *Anal.* Calcd for $C_{20}H_{13}N_3O_5$: C, 64.00; H, 3.49; N, 11.20. Found C, 64.03; H, 3.52; N, 11.25.

11-(Thiophen-2-yl)-8,11-dihydrofuro[3,4-*b*][4,7]phenanthrolin-10(7*H*)-one (4l). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3261, 3146, 3064, 1724, 1665, 1614, 1467, 1430, 1356, 1257, 1165, 1074, 960, 752 cm^{-1}; ^1H nmr: δ 10.54 (s, 1H, NH), 8.73–8.72 (m, 1H, ArH), 8.41 (d, 1H, J = 8.4 Hz, ArH), 7.96 (d, 1H, J = 8.8 Hz, ArH), 7.51 (d, 1H, J = 9.2 Hz, ArH), 7.45-7.42 (m, 1H, ArH), 7.23–7.22 (m, 1H, ArH), 6.92 (s, 1H, ArH), 6.85–6.84 (m, 1H, ArH), 6.09 (s, 1H, CH), 5.05–4.93 (m, 2H, CH_2). *Anal.* Calcd for $C_{18}H_{12}N_2O_2S$: C, 67.48; H, 3.78; N, 8.74; S, 10.01. Found C, 67.45; H, 3.80; N, 8.72; S, 10.00.

13-(4-Fluorophenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6a). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3230, 3043, 1714, 1608, 1577, 1504, 1433, 1373, 1259, 1144, 1076, 929, 878 cm^{-1}; ^1H nmr: δ 10.53 (s, 1H, NH), 8.86–8.85 (m, 1H, ArH), 8.32–8.25 (m, 2H, ArH), 8.06 (d, 1H, J = 7.6 Hz, ArH), 7.80–7.78 (m, 1H, ArH), 7.67–7.60 (m, 3H, ArH), 7.54–7.45 (m, 4H, ArH), 7.31–7.27 (m, 1H, ArH), 5.82 (s, 1H, CH). *Anal.* Calcd for $C_{25}H_{15}FN_2O$: C, 79.35; H, 4.00; N, 7.40. Found C, 79.46; H, 3.95; N, 7.35.

13-(4-Chlorophenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6b). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3238, 3043, 1714, 1608, 1577, 1504, 1433, 1373, 1259, 1144, 1076, 923, 856 cm^{-1}; ^1H nmr: δ 10.35 (s, 1H, NH), 8.88–8.87 (m, 1H, ArH), 8.36–8.30 (m, 2H, ArH), 8.09 (d, 1H, J = 7.6 Hz, ArH), 7.83–7.80 (m, 1H, ArH), 7.75–7.68 (m, 3H, ArH), 7.66–7.61 (m, 2H, ArH), 7.52 (d, 2H, J = 8.4 Hz, ArH), 7.35–7.31 (m, 1H, ArH), 6.00 (s, 1H, CH). *Anal.* Calcd for $C_{25}H_{15}ClN_2O$: C, 76.05; H, 3.83; N, 7.09. Found C, 76.13; H, 3.75; N, 7.00.

13-(4-Bromophenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6c). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3242, 3060, 1715, 1682, 1665, 1605, 1466, 1282, 1155, 1071, 1006, 930, 709 cm^{-1}; ^1H nmr: δ 10.45 (s, 1H, NH), 8.88–8.87 (m, 1H, ArH), 8.35–8.28 (m, 2H, ArH), 8.09–8.07 (m, 1H, ArH), 7.85–7.79 (m, 3H, ArH), 7.65–7.62 (m, 2H, ArH), 7.45 (d, 2H, J = 8.4 Hz, ArH), 7.38 (d, 1H, J = 8.4 Hz, ArH), 7.34–7.31 (m, 1H, ArH), 5.92 (s, 1H, CH). *Anal.* Calcd for $C_{25}H_{15}BrN_2O$: C, 68.35; H, 3.44; N, 6.38. Found C, 68.46; H, 3.32; N, 6.29.

13-(4-Methoxyphenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6d). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3248, 3040, 1713, 1678, 1664, 1573, 1439, 1256, 1155, 1057, 1006, 937, 847 cm^{-1}; ^1H nmr: δ 10.40 (s, 1H, NH), 8.86–8.85 (m, 1H, ArH), 8.33–8.24 (m, 2H, ArH), 8.08–8.06 (m, 2H, ArH), 7.87–7.81 (m, 2H, ArH), 7.77–7.70 (m, 3H, ArH), 7.58 (d, 2H, J = 8.4 Hz, ArH), 7.36–7.30 (m, 1H, ArH), 5.94 (s, 1H, CH), 3.63(s, 3H, OCH_3). *Anal.* Calcd for $C_{26}H_{18}N_2O_2$: C, 79.98; H, 4.65; N, 7.17. Found C, 79.95; H, 4.60; N, 7.20.

13-(2,4-Dichlorophenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6e). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3240, 3050, 1715, 1610, 1568, 1508, 1426, 1375, 1262, 1140, 1066, 933, 846 cm^{-1}; ^1H nmr: δ 10.36 (s, 1H, NH), 8.87–8.86 (m, 1H, ArH), 8.35–8.32 (m, 2H, ArH), 8.05 (d, 1H, J = 7.6 Hz, ArH), 7.80 (s, 1H, ArH), 7.74–7.68 (m, 2H, ArH), 7.65–7.62 (m, 2H, ArH), 7.50 (d, 2H, J = 8.4 Hz, ArH), 7.35–7.30 (m, 1H, ArH), 5.99 (s, 1H, CH). *Anal.* Calcd for $C_{25}H_{14}Cl_2N_2O$: C, 69.94; H, 3.29; N, 6.53. Found C, 69.90; H, 3.30; N, 6.55.

13-(3,4-Dimethoxyphenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6f). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3236, 3088, 1713, 1685, 1611, 1571, 1458, 1203, 1150, 1055, 1004, 743, 654 cm^{-1}; ^1H nmr: δ 10.43 (s, 1H, NH), 8.71 (s, 1H, ArH), 8.20 (d, 1H, J = 7.6 Hz, ArH), 8.09–8.03 (m, 3H, ArH), 7.70–7.59 (m, 3H, ArH), 7.52 (d, 2H, J = 8.4 Hz, ArH), 7.33–7.30 (m, 2H, ArH), 5.90 (s, 1H, CH), 3.76 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3). *Anal.* Calcd for $C_{27}H_{20}N_2O_3$: C, 77.13; H, 4.78; N, 6.66. Found C, 77.15; H, 4.80; N, 6.70.

13-(3-Nitrophenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6g). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3233, 3087, 1716, 1684, 1664, 1604, 1457, 1260, 1157, 1078, 1006, 936, 700 cm^{-1}; ^1H nmr: δ 10.50 (s, 1H, NH), 8.89–8.88 (m, 1H, ArH), 8.54–8.52 (m, 2H, ArH), 8.40–8.33 (m, 2H, ArH), 8.13–8.11 (m, 1H, ArH), 7.92–7.82 (m, 3H, ArH), 7.71–7.62 (m, 3H, ArH), 7.30–7.27 (m, 1H, ArH), 6.03 (s, 1H, CH). *Anal.* Calcd for $C_{25}H_{15}N_3O_3$: C, 74.07; H, 3.73; N, 10.36. Found C, 74.10; H, 3.75; N, 10.35.

13-(Benzo[*d*][1,3]dioxo-6-yl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6h). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 323O, 3089, 1712, 1688, 1660, 1601, 1450, 1268, 1159, 1088, 1006, 960, 746 cm^{-1}; ^1H nmr: δ 10.39 (s, 1H, NH), 8.86–8.85 (m, 1H, ArH), 8.32–8.28 (m, 1H, ArH), 8.07 (d, 1H, J = 8.0 Hz, ArH), 7.83–7.80 (m, 3H, ArH), 7.66 (s, 1H, ArH) , 7.54–7.45 (m, 4H, ArH), 7.33–7.30 (m, 1H, ArH), 5.90 (s, 1H, CH), 5.01-4.89(m, 2H,CH_2). *Anal.* Calcd for $C_{26}H_{16}N_2O_3$: C, 77.22; H, 3.99; N, 6.93. Found C, 77.20; H, 3.95; N, 6.96.

13-*p*-Tolyl-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6i). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3234,

3026, 1714, 1606, 1575, 1507, 1457, 1371, 1260, 1153, 1077, 929, 846 cm^{-1}; ^1H nmr: δ 10.41 (s, 1H, NH), 8.88–8.87 (m, 1H, ArH), 8.35–8.30 (m, 2H, ArH), 8.06 (d, 1H, J = 8.0 Hz, ArH), 7.85-7.78 (m, 2H, ArH), 7.66–7.61 (m, 2H, ArH), 7.46 (d, 2H, J = 8.4 Hz, ArH), 7.36–7.30 (m, 3H, ArH), 6.00 (s, 1H, CH). *Anal*. Calcd for $C_{26}H_{13}N_2O$: C, 83.40; H, 4.85; N, 7.48. Found C, 83.42; H, 4.86; N, 7.52.

13-Phenyl-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6j). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3238, 3043, 1714, 1608, 1577, 1504, 1433, 1373, 1259, 1144, 1076, 923, 856 cm^{-1}; ^1H nmr: δ 10.41 (s, 1H, NH), 8.85–8.84 (m, 1H, ArH), 8.36–8.29 (m, 2H, ArH), 8.11 (d, 1H, J = 7.2 Hz, ArH), 7.83–7.80 (m, 1H, ArH), 7.69–7.60 (m, 5H, ArH), 7.47–7.45 (m, 1H, ArH), 7.41–7.34 (m, 1H, ArH), 7.28–7.25 (m, 1H, ArH), 7.22–7.16 (m, 1H, ArH), 5.83 (s, 1H, CH). *Anal*. Calcd for $C_{25}H_{16}N_2O$: C, 83.31; H, 4.47; N, 7.77. Found C, 83.45; H, 4.38; N, 7.65.

13-(4-Hydroxy-3-nitrophenyl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6k). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3236, 3080, 1715, 1668, 1580, 1518, 1444, 1393, 1260, 1122, 1060, 940, 860 cm^{-1}; ^1H nmr: δ 10.80 (s, 1H, OH), 10.48 (s, 1H, NH), 8.87–8.86 (m, 1H, ArH), 8.51–8.47 (m, 2H, ArH), 8.32 (d, 2H, J = 8.4 Hz, ArH), 8.12 (s, 1H, ArH), 7.88–7.70 (m, 2H, ArH), 7.66–7.60 (m, 2H, ArH), 7.50–7.22 (m, 2H, ArH), 6.02 (s, 1H, CH). *Anal*. Calcd for $C_{25}H_{15}N_3O_4$: C, 71.25; H, 3.59; N, 9.97. Found C, 71.30; H, 3.60; N, 9.95.

13-(Thiophen-2-yl)-7*H*-indeno[2,1-*b*][4,7]phenanthrolin-12(13*H*)-one (6l). This compound was obtained according to above general procedure, mp>300 °C; ir (potassium bromide): 3235, 3050, 1712, 1653, 1578, 1472, 1396, 1255, 1157, 1077, 945, 847 cm^{-1}; ^1H nmr: δ 10.40 (s, 1H, NH), 8.90–8.89 (m, 1H, ArH), 8.34–8.28 (m, 2H, ArH), 8.09 (d, 1H, J = 7.6 Hz, ArH), 7.99–7.98 (m, 1H, ArH), 7.81 (t, 1H, J = 7.2 Hz, ArH), 7.76–7.69 (m, 2H, ArH), 7.63 (t, 1H, J = 7.2 Hz, ArH), 7.40–7.33 (m, 3H, ArH), 5.99 (s, 1H, CH). *Anal*. Calcd for $C_{23}H_{14}N_2OS$: C, 75.39; H, 3.85; N, 7.64; S, 8.75. Found C, 75.35; H, 3.88; N, 7.65; S, 8.78.

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