

RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Iron/acetic acid mediated synthesis of 6,7-dihydrodibenzo [b,j] [1,7] phenanthroline derivatives *via* intramolecular reductive cyclization

R. R. Rajawinslin, Sachin S. Ichake, Veerababurao Kavala, Sachin D. Gawande, Yi-Hsiang Huang, Chun-Wei Kuo, and Ching-Fa Yao*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

An efficient iron/acetic acid mediated intramolecular reductive cyclization protocol for the synthesis of novel 6,7-dihydrodibenzo[b,j][1,7] phenanthroline derivatives is described. In this two-step procedure, aldol addition and reductive cyclization methods are effectively utilized for the construction of C-C and C-N bonds. This highly efficient process proceeds under mild conditions, tolerates different functional groups, and provides various substituted 6,7-dihydrodibenzo [b,j] [1,7]phenanthroline derivatives in good to excellent yields. In addition, various synthetic utilities of these derivatives are also described.

Dibenzophenanthroline is an important class of nitrogen containing polycyclic motif, that is found in numerous natural and synthetic products. They have been known to exhibit a wide variety of biological activities such as anticancer, antibacterial and anti-parasitic properties.¹⁻⁵ In particular, the antitumor activity of these heterocycles has been well discussed in many papers. For instance compounds **I**,¹ **II**² and **III**³ are potential anticancer agents targeting human telomeric DNA. Compound **IV** (Ascidiemin) exhibits significant *invitro* and *invivo* cytotoxic activities against several tumor cell lines.⁴ Compound **V** (Luotonin A) is a well known alkaloid, cytotoxic towards the murine leukemia P-388 cell line.⁵ In addition, certain types of dibenzophenanthroline derivatives are used for the synthesis of chelating ligands⁶ and in the manufacture of organic semiconductor materials.⁷

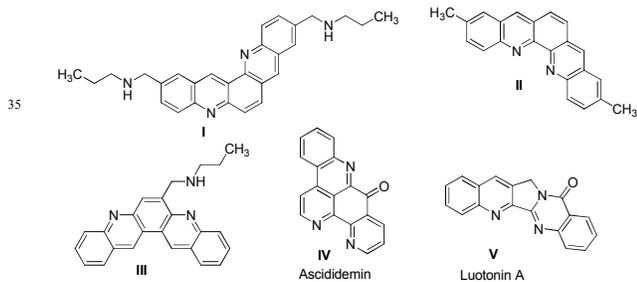


Figure 1: Biologically active polycyclic heteroaromatic compounds

Up to now, only two kinds of 6,7-dihydrodibenzophenanthroline derivatives are documented in the literature,⁸ which are 6,7-dihydrodibenzo[b,j][4,7]phenanthroline (**A**) and 6,7-dihydrodibenzo[b,j][1,10]phenanthroline (**B**) (Figure 2). However, according to the structural arrangements, we hypothesized a third possible derivative of 6,7-dihydrodibenzophenanthroline, which is 6,7-dihydrodibenzo[b,j][1,7]phenanthroline (**C**). This third classification is interesting, because its skeleton is unknown in the literature and previously reported methodologies⁸ are not suitable for its preparation. Furthermore, the aromatized product of these skeletons are possessing interesting biological activities.¹ Therefore, we attempted to explore this new class of compounds by developing an efficient synthetic method.

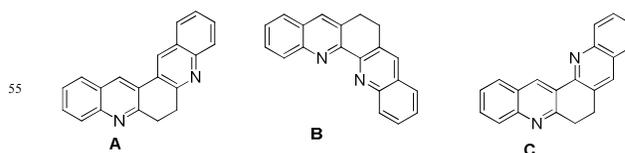
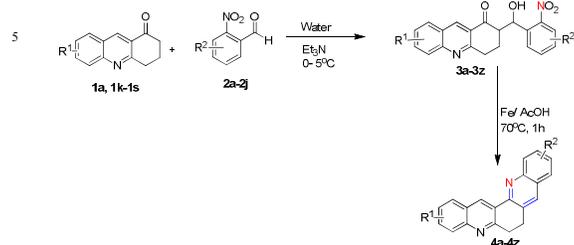


Figure 2: Different types of 6,7 dihydrodibenzo phenanthrolines

C-C and C-N bond forming reactions are of fundamental importance in synthetic organic chemistry. Aldol reaction is one of the most powerful tools for the construction of C-C bonds,⁹ and reductive cyclization is an useful reaction for C-N bond formation.¹⁰ Hence, these two methods were effectively utilized for the synthesis of 6,7-dihydrodibenzo[b,j][1,7]phenanthroline derivatives. In a recent publication, we reported an one pot synthesis of acridinone and quinoline derivatives from 2-nitrobenzaldehyde and various 1,3- diketones by using iron/acetic acid system.¹¹ These acridinone and quinoline derivatives are well known structural scaffolds in medicinal chemistry and possess useful pharmacological and biological activities.¹² As a continuation of our research on the development of new protocols for the synthesis of N-heterocycles¹³ and to explore the utilities of acridinone derivatives, we wish to report an efficient protocol for the synthesis of 6,7-dihydrodibenzo [b,j][1,7] phenanthroline derivatives.

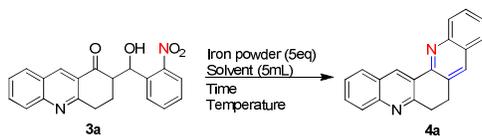
Our two steps synthetic strategy involves the aldol addition of 2-nitrobenzaldehyde on acridinone derivatives, which upon treatment with iron/acetic acid produces the corresponding 6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline derivatives (Scheme 1).



Scheme 1: Outline of the synthetic route to 6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline derivatives

Initially, we focused our attention to synthesize the starting materials. At first, acridinone derivatives (**1a**, **1k-1s**) were prepared by the recently reported protocol developed by our group¹¹ and the substrates (**3a-3z**) were prepared *via* base mediated aldol addition in water. When acridinone derivatives were treated with 2-nitrobenzaldehyde in water in the presence of triethylamine at 0-5°C, the expected product (**3a**) was formed in good yield. When this compound was treated with iron/acetic acid at room temperature, the desired product 6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (**4a**) was formed after 6h in 38% yield. The structure of the product was confirmed by ¹H, ¹³C NMR spectroscopy, MS, HRMS, and single-crystal X-ray analysis (Figure 3). Aiming to increase the yield of the product and also to decrease the reaction time, we tested the reaction at different temperature. At 50 °C, the yield of the product was increased to 73% in 1.5h. Interestingly, at 70 °C, the expected product (**4a**) was obtained as the sole product in 86% yield after 1h. However, there was no increment in product yield as well as no decrement in the reaction time was observed, when the reaction was conducted at 90 °C and under reflux conditions (Table 1). In order to study the relationship between the reagent

Table 1. Optimization of reaction conditions



Entry ^a	Solvent	Temp (°C)	Time (h)	Yield (%) ^b
1	Acetic acid	r.t.	6	38
2	Acetic acid	50	1.5	73
3	Acetic acid	70	1	86
4	Acetic acid	90	1	85
5	Acetic acid	Reflux	1	78

^aAll the reactions were performed on 1mmol scale. ^bIsolated yields.

amount and the product yields we conducted the reactions with 1, 2, 3,4 and 5 equivalents of iron powder in acetic acid (5 mL), at 70°C. When 5 equivalents of iron powder were used, the starting material (**3a**) was completely converted into desired product (**4a**) in 1 h. However, for the other cases, the starting material was not completely consumed, even after 12 h. From this experimental result, it is confirmed that 5 equivalents of iron powder is the optimum amount for this reaction.

Table 2. Synthesis of various substituted 6,7-dihydro dibenzo[*b,j*][1,7]phenanthroline by Fe/AcOH mediated intramolecular reductive cyclization

Entry ^a	R ¹	R ² , R ³ , R ⁴ , R ⁵	Product	Yield (%) ^b
1	R ¹ =H	R ² , R ³ , R ⁴ , R ⁵ =H	4a	86
2	R ¹ =H	R ² , R ³ , R ⁵ =H R ⁴ =F	4b	84
3	R ¹ =H	R ² , R ³ , R ⁴ , R ⁵ =H R ⁴ =Cl	4c	80
4	R ¹ =H	R ² , R ³ , R ⁵ =H R ⁴ =Br	4d	85
5	R ¹ =H	R ² , R ³ , R ⁴ , R ⁵ =H R ⁴ =CH ₃	4e	76
6	R ¹ =H	R ² , R ⁴ , R ⁵ =H R ³ =Br	4f	81
7	R ¹ =H	R ² , R ⁵ =H R ³ , R ⁴ =OCH ₃	4g	78
8	R ¹ =H	R ² , R ⁵ =H R ³ , R ⁴ =OBn	4h	73
9	R ¹ =H	R ² , R ⁵ =H R ³ , R ⁴ =-OCH ₂ -	4i	82
10	R ¹ =H	R ³ , R ⁴ =H R ² , R ⁵ =OCH ₃	4j	76

^aAll the reactions were performed on a 1 mmol scale. ^bYields were refers to isolated and purified compounds.

Encouraged by this interesting result, we applied the same reaction conditions to the different substituted 2-(hydroxy(2-nitrophenyl)methyl)-3,4-dihydroacridin-1(2H)-ones (**3a-3j**), which are obtained from different substituted 2-nitrobenzaldehydes. The results are summarized in Table 2. It is

interesting to note that, the reactions of substrates bearing both electron withdrawing groups (F, Cl, Br) as well as electron donating groups (CH₃, OCH₃, OBn) proceeded with equal ease and produced the desired products in good to excellent yields (Table 2, entries 1-10).

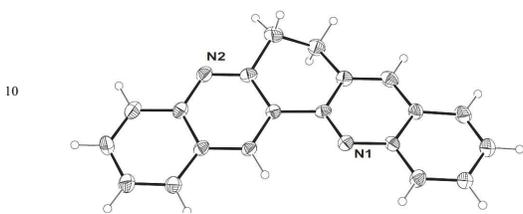


Figure 3: Crystal structure of compound **4a**²⁴

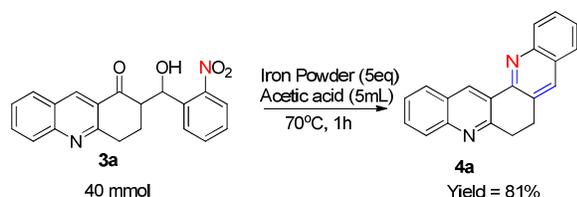
Table 3. Substrate scope of Fe/AcOH-mediated intramolecular reductive cyclization

Entry ^a	R ¹ , R ² , R ³ , R ⁴	R ⁵ , R ⁶ , R ⁷ , R ⁸	Product	Yield (%) ^b
1	R ² = F R ¹ , R ³ , R ⁴ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		82
2	R ² = Cl R ¹ , R ³ , R ⁴ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		81
3	R ² = Br R ¹ , R ³ , R ⁴ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		87
4	R ² = CH ₃ R ¹ , R ³ , R ⁴ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		72
5	R ⁴ = Cl R ¹ , R ² , R ³ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		91
6	R ⁴ = Br R ¹ , R ² , R ³ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		90
7	R ⁴ = CH ₃ R ¹ , R ² , R ³ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		87
8	R ² , R ³ = OCH ₃ R ¹ , R ⁴ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		74

Entry ^a	R ¹ , R ² , R ³ , R ⁴	R ⁵ , R ⁶ , R ⁷ , R ⁸	Product	Yield (%) ^b
9	R ² , R ³ = -OCH ₂ - R ¹ , R ⁴ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		80
10	R ² = F R ¹ , R ³ , R ⁴ = H	R ⁷ = F R ⁵ , R ⁶ , R ⁸ = H		79
11	R ² = Cl R ¹ , R ² , R ⁴ , R ³ = H	R ⁷ = Cl R ⁵ , R ⁶ , R ⁸ = H		80
12	R ² = Br R ¹ , R ² , R ⁴ , R ³ = H	R ⁷ = Br R ⁵ , R ⁶ , R ⁸ = H		83
13	R ² = CH ₃ R ¹ , R ² , R ⁴ , R ³ = H	R ⁷ = CH ₃ R ⁵ , R ⁶ , R ⁸ = H		73
14	R ² , R ³ = -OCH ₂ - R ¹ , R ⁴ = H	R ⁶ , R ⁷ = -OCH ₂ - R ⁵ , R ⁸ = H		77
15	R ² = Cl R ¹ , R ² , R ⁴ , R ³ = H	R ⁷ = Br R ⁵ , R ⁶ , R ⁸ = H		79
16	R ¹ , R ² , R ³ , R ⁴ = H	R ⁵ , R ⁶ , R ⁷ , R ⁸ = H		85

^aAll the reactions were performed on a 1 mmol scale. ^bYields were refers to isolated and purified compounds.

Next, we turned our attention to examine the substrate scope of this method. In this regard, various 2-(hydroxy(2-nitrophenyl)methyl)-3,4-dihydroacridin-1(2H)-ones (**3k-3s**) having substitution on acridinone ring was tested. At first, compounds bearing substituents on R² position of acridinone ring were examined. The substrates bearing both electron withdrawing substituents (F, Cl and Br) and electron donating substituent (CH₃) gave good to excellent yields of products (Table 3, entries 1-4). Then, to our delight, we obtained excellent yields of product for the R⁴ substituted substrates (entries 5-7). In the case of disubstituted substrates also, the reaction produced good yields of products (entries 8 and 9). To extend the scope of our protocol, we selected substrates bearing substituents on both acridinone and phenyl rings (**3t-3y**), the reaction proceeded smoothly and produced good yields of products (entries 10-15). Finally, we applied this method to a dimethyl substituted derivative, 2-(hydroxy(2-nitrophenyl)methyl)-3,3-dimethyl-3,4-dihydroacridin-1(2H)-one (**3z**) which was prepared from 3,3-dimethyl-3,4-dihydroacridin-1(2H)-one and 2-nitrobenzaldehyde. Under the optimized conditions, the compound **3z** undergone reductive cyclization and produced the desired product (**4z**) in excellent yield.



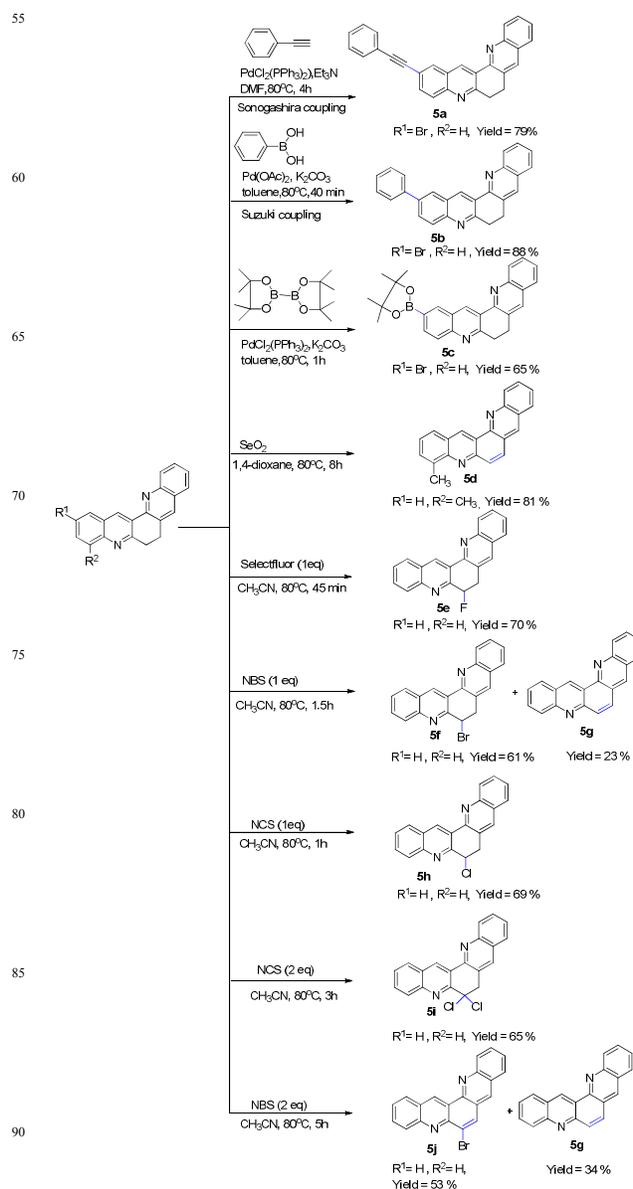
Scheme 2. Large-scale synthesis of 6,7-dihydrodibenzo $[b,j][1,7]$ phenanthroline (**4a**)

To illustrate the scalability of our protocol, we performed the reductive cyclization reaction in gram scale. 13.9g (40 mmol) of 2-(hydroxy(2-nitrophenyl)methyl)-3,4-dihydroacridin-1(2H)-one (**3a**) was treated with 11.2g of iron powder and 80 ml acetic acid at 70 °C. The desired product 6,7-dihydrodibenzo $[b,j][1,7]$ phenanthroline (**4a**) was obtained in 81% yield. Hence, this protocol is applicable for gram scale preparations (Scheme 2).

Moreover, based on the previously reported protocols, we tested the reaction in one-pot condition without the isolation of aldol addition/condensation products. Firstly, we performed the reaction via *in-situ* formation of 2-aminobenzaldehydes. The reaction failed to produce the desired product in the $\text{SnCl}_2/\text{ZnCl}_2$ system^{10g} and only a trace amount of product was formed in $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ system.^{10h} In the former case, the starting acridinone (**1a**) derivative was decomposed, however, in later case the starting acridinone (**1a**) was intact and 2-aminobenzaldehyde was decomposed due to high temperature of the reaction. Since aldol reaction can be performed in acidic conditions,¹⁴ we conducted the reaction in the presence weak and strong acids. The expected aldol addition/condensation product was not formed in both cases. The experimental results reveal that these methods are not applicable to the synthesis of 6,7-dihydrodibenzo $[b,j][1,7]$ phenanthroline derivatives.

Next, we sought to demonstrate the synthetic utility of the obtained polycyclic compounds (Scheme 3). The presence of bromo group at the C-2 position of 6,7-dihydrodibenzo $[b,j][1,7]$ phenanthroline allows us to make further structural elaboration through conventional C-C bond formation reactions. Sonogashira¹⁵ and Suzuki¹⁶ reactions are well known cross-coupling reactions for the formation of carbon-carbon bonds. In this regard, for Sonogashira coupling, we treated 2-bromo-6,7-dihydrodibenzo $[b,j][1,7]$ phenanthroline (**4m**) with phenyl acetylene in the presence of bis(triphenylphosphine)palladium(II) dichloride catalyst in DMF solvent. The expected product (**5a**) was formed in 79% yield. For Suzuki coupling, compound (**4m**) was treated with phenyl boronic acid in the presence of palladium acetate in toluene at 80 °C, the C-C coupled product (**5b**) was formed in excellent yield. Next, borylation¹⁷ was carried out using bis(pinacolato)diboron to synthesize compound (**5c**) in the presence of bis(triphenylphosphine)palladium(II) dichloride catalyst in toluene at 80 °C. Compounds with boronic acid group are extensively used in drug industry for producing various

chemotherapeutic agents. We assume that compound (**5c**) can be easily converted to various boronic acid derivatives.¹⁸



Scheme 3. Synthetic utility of 6,7-dihydrodibenzo $[b,j][1,7]$ phenanthroline derivatives^{a,b}

^aAll the reactions were performed on a 1 mmol scale. ^bYields were refers to isolated and purified compounds.

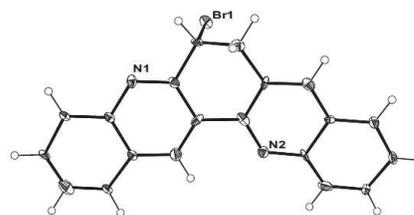


Figure 4: Crystal structure of compound **5f**²⁴

Our succeeding target was oxidation because polycyclic heteroaromatic compounds have been proved to be attractive intermediates for the synthesis of various best selling drugs.¹⁻⁵ To our surprise, 4-methyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (**4q**) was oxidized and produced an aromatized compound (**5d**) when treated with SeO₂ as oxidizing agent.¹⁹ Based on this interesting result, we presume that all our newly synthesized compounds can be easily converted to aromatic molecules.

Further, insertion of functional groups such as fluoro, bromo and chloro groups to 6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (**4a**) would be beneficial for the production of pharmaceutically important and valuable compounds, and also this strategy could widen the scope of all the newly synthesized molecules. Selectfluor is a stable, nonvolatile, user-friendly reagent, widely used to introduce fluorine atoms into organic compounds electrophilically.²⁰ Recently, we reported the selective fluorination of isoxazoline *N*-oxides *via* C–C bond cleavage by using Selectfluor.²¹ When 6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (**4a**) was treated with 1 equivalent of Selectfluor in acetonitrile at 80 °C, the reaction proceeded smoothly and compound **5e** was formed in good yield. Similarly, NBS and NCS are the most extensively used electrophilic reagents for bromination²² and chlorination,²³ respectively. When compound **4a** was treated with 1 equivalent of NBS in acetonitrile at 80 °C, the expected product **5f** was formed in 61% yield along with small amount of an aromatic compound (**5g**). The formation of **5g** is due to the oxidizing property of NBS. The structure of the product (**5f**) was confirmed by single-crystal X-ray analysis (Figure 4).

On the otherhand, the reaction of **4a** with 1 equivalent of NCS in acetonitrile at 80°C, produced compound **5h** as the sole product in 69% yield after 1h. Next, we examined the effect of 2 equivalents of NCS and NBS in the same reaction conditions. When compound **4a** was treated with 2 equivalents of NCS, the reaction produced a geminal dichloride (**5i**) in good yield. However, when 2 equivalents of NBS was treated with compound **4a**, the reaction proceeded with simultaneous bromination and aromatization which produced an interesting compound **5h** in moderate yield along with compound **5g** in 34% yield. Conclusively, C-C coupling, borylation, aromatization and the possible addition of different functional groups (fluoro, bromo and chloro) means that our products could be structurally modified into valuable compounds (**5a–5j**), and so they might be useful for the development of new therapeutic agents in the future.

Conclusions

In conclusion, we have developed an efficient iron/acetic acid mediated intramolecular reductive cyclization protocol for the synthesis of novel group of 6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline derivatives, from easily available starting materials. The broad substrate scope and good to excellent yields of the products made this methodology interesting and also this protocol is applicable for gram scale preparations. Further, we

revealed that our compounds can be structurally modified to obtain various useful compounds for the development of new therapeutic agents.

Experimental section

General Remarks: Reagents and solvents were purchased from commercial suppliers and were used directly without any further purification unless otherwise stated. Column chromatography was performed on 63–200 mesh silica gel. ¹H and ¹³C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts are reported in parts per million (ppm) on the δ scale by using CDCl₃ as an internal standard, and coupling constants are expressed in Hertz (Hz). IR spectra were recorded with an FTIR spectrometer, and data are reported in cm⁻¹. Melting points were recorded by using an Electro Thermal capillary melting point apparatus.

General procedure for the synthesis of starting materials (**3a** – **3z**)

To a stirred solution of acridinone derivative (1 mmol) and 2-nitrobenzaldehyde (1.1 mmol) in water (2 mL) at ice cold condition, triethylamine (0.6 ml) was added in drop wise manner. The reaction was monitored by TLC. After the completion of the reaction (6-13h), ice water (10 mL) was added to the reaction mixture, the solid product formed was filtered and dried. This crude product was washed with 15% EtOAc/Hexane (5 mL) to obtain pure product. Characterization data for a representative compound **3a** are given below.

2-(hydroxy(2-nitrophenyl)methyl)-3,4-dihydroacridin-1(2H)-one (**3a**)

Brown solid; Yield: 78%. m.p. 205-207 °C, IR [KBr, cm⁻¹] 1644, 1521, 1340, 1171, 787, 749; ¹H NMR (400 MHz, CDCl₃): δ 8.88 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 5.73 (dd, *J* = 2.7, 7.7 Hz, 1H), 4.72 (d, *J* = 2.9 Hz, 1H), 3.36-3.30 (m, 1H), 3.23-3.14 (m, 1H), 3.09-3.03 (m, 1H), 2.24-2.13 (m, 1H), 1.89-1.83 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 201.1, 161.4, 150.2, 149.1, 138.0, 136.3, 133.5, 133.0, 130.0, 129.4, 129.0, 128.8, 127.1, 126.8, 126.0, 124.3, 70.2, 55.2, 33.1, 25.3 MS *m/z* (relative intensity): 349 (100); HRMS (ESI⁺) calcd for C₂₀H₁₇N₂O₄ ([M⁺H]⁺): 349.1188, found 349.1179.

General procedure for the synthesis of 6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline derivatives (**4a–4z**)

Iron powder (5 mmol) was added to a stirred solution of substrate (1mmol) in acetic acid (5 mL). This mixture was heated to 70°C for 1h. After the completion of reaction (TLC), the reaction mixture was cooled to room temperature and acetic acid was removed under reduced pressure. The resulting mixture was dissolved in EtOAc and then filtered to remove the iron impurities. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

(Note: Because of solubility problem, for the compounds **4f**, **4g**, **4h**, **4j** and **4r** the mixture were diluted with CH₂Cl₂ instead of EtOAc, then filtered.)

Spectral data**6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4a)**

White solid; Yield: 86%. m.p. 156-158 °C, IR [KBr, cm^{-1}] 3054, 2953, 1605, 1498, 1421, 1145, 915, 746; ^1H NMR (400 MHz, CDCl_3): δ 9.30 (s, 1H), 8.17 (d, $J = 8.5$ Hz, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.3$ Hz, 2H), 7.79 (d, $J = 8.1$ Hz, 1H), 7.75-7.68 (m, 2H), 7.53 (dd, $J = 7.8, 15.0$ Hz, 2H), 3.41 (dd, $J = 5.4, 8.4$ Hz, 2H), 3.31 (t, $J = 6.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.8, 152.3, 148.3, 148.0, 134.5, 133.6, 130.5, 130.4, 129.5, 129.3, 129.1, 128.7, 128.6, 128.3, 128.2, 127.3, 126.8, 126.5, 32.5, 28.4; MS m/z (relative intensity): 283 (100); HRMS (ESI $^+$) calcd for $\text{C}_{20}\text{H}_{15}\text{N}_2$ ($[\text{M}^+ \text{H}]^+$): 283.1235, found 283.1236.

10-fluoro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4b)

White solid; Yield: 84%. m.p. 185-187 °C, IR [KBr, cm^{-1}] 1628, 1498, 1316, 1243, 1217, 825, 749; ^1H NMR (400 MHz, CDCl_3): δ 9.25 (s, 1H), 8.16 (dd, $J = 5.2, 9.2$ Hz, 1H), 8.06 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 7.6$ Hz, 2H), 7.95 (s, 1H), 7.75-7.71 (m, 1H), 7.56 (t, $J = 7.2$ Hz, 1H), 7.49-7.43 (m, 1H), 7.39 (dd, $J = 2.8, 8.8$ Hz, 1H), 3.40 (dd, $J = 5.2, 8.0$ Hz, 2H), 3.31 (dd, $J = 4.4, 11.6$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 162.1, 159.6, 151.7, 148.4, 145.1, 133.7 (d, $J = 5.0$ Hz), 133.4, 132.0, 131.9, 131.3, 130.5, 129.0, 128.7, 128.3, 128.2 (d, $J = 15.0$ Hz), 126.5, 119.5 (d, $J = 26.0$ Hz), 110.3 (d, $J = 21.0$ Hz), 32.4, 28.4; MS m/z (relative intensity): 301 (100); HRMS (ESI $^+$) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{F}$ ($[\text{M}^+ \text{H}]^+$): 301.1141, found 301.1133.

10-chloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4c)

Greenish white solid; Yield: 80%. m.p. 224-226 °C, IR [KBr, cm^{-1}] 1594, 1493, 1479, 1434, 1200, 1073, 921, 825; ^1H NMR (400 MHz, CDCl_3): δ 9.22 (s, 1H), 8.05 (t, $J = 9.0$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.86 (s, 1H), 7.74-7.70 (m, 2H), 7.60 (dd, $J = 2.4, 8.8$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 3.38 (dd, $J = 5.6, 8.4$ Hz, 2H), 3.28 (dd, $J = 5.4, 13.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.6, 152.5, 148.4, 146.3, 133.6, 133.4, 132.4, 131.4, 131.0, 130.6, 130.2, 129.0, 128.8, 128.7, 128.2, 128.1, 126.5, 125.9, 32.3, 28.3; MS m/z (relative intensity): 317 (100); HRMS (ESI $^+$) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2^{35}\text{Cl}$ ($[\text{M}^+ \text{H}]^+$): 317.0846, found 317.0851.

10-bromo-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4d)

White solid; Yield: 85%. m.p. 240-242 °C, IR [KBr, cm^{-1}] 1644, 1493, 1431, 1201, 1059, 914, 824, 751; ^1H NMR (400 MHz, CDCl_3): δ 9.24 (s, 1H), 8.06-7.96 (m, 3H), 7.90 (d, $J = 2.0$ Hz, 1H), 7.87 (s, 1H), 7.75-7.70 (m, 2H), 7.55-7.51 (m, 1H), 3.41-3.36 (m, 2H), 3.31-3.27 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.6, 152.7, 148.4, 146.5, 133.7, 133.3, 132.7, 131.4, 131.2, 130.6, 129.3, 129.0, 128.7, 128.2, 128.1, 126.5, 120.6, 32.2, 28.3; MS m/z (relative intensity): 361 (100); HRMS (ESI $^+$) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2^{79}\text{Br}$ ($[\text{M}^+ \text{H}]^+$): 361.0340, found 361.0338.

10-methyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4e)

White solid; Yield: 76%. m.p. 131 - 133 °C, IR [KBr, cm^{-1}] 2920, 2846, 1595, 1498, 1155, 765, 733; ^1H NMR (400 MHz, CDCl_3): δ 9.29 (s, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 8.00 (d, $J = 8.0$ Hz, 1H), 7.95 (s, 1H), 7.74 - 7.70 (m, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.55 - 7.52 (m, 2H), 7.39 (t, $J = 7.4$ Hz, 1H), 3.42 - 3.37 (m, 2H), 3.30 (dd, $J = 6.0, 13.2$ Hz, 2H), 2.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.9, 150.8, 148.3, 146.9, 137.5, 134.6, 133.4, 130.3, 129.9, 129.3, 129.1, 129.0, 128.7, 128.3, 128.2, 126.6, 126.3, 125.2, 32.5, 28.1, 18.1; MS m/z (relative intensity): 297 (100);

HRMS (ESI $^+$) calcd for $\text{C}_{21}\text{H}_{17}\text{N}_2$ ($[\text{M}^+ \text{H}]^+$): 297.1392, found 297.1391.

11-bromo-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4f)

White solid; Yield: 81%. m.p. 234-236 °C, IR [KBr, cm^{-1}] 1493, 1478, 1434, 1201, 1056, 911, 823; ^1H NMR (400 MHz, CDCl_3): δ 9.27 (s, 1H), 8.05 (t, $J = 8.0$ Hz, 1H), 7.99 (dd, $J = 2.6, 10.2$ Hz, 2H), 7.93 (d, $J = 2.4$ Hz, 1H), 7.90 (s, 1H), 7.76-7.72 (m, 2H), 7.56-7.52 (m, 1H), 3.42-3.38 (m, 2H), 3.33-3.29 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.6, 152.7, 148.3, 146.5, 133.8, 133.4, 132.8, 131.4, 131.2, 130.7, 129.3, 129.1, 128.6, 128.3, 128.2, 126.6, 120.6, 32.2, 28.3; MS m/z (relative intensity): 361 (100); HRMS (ESI $^+$) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{Br}$ ($[\text{M}^+ \text{H}]^+$): 361.0340, found 361.0352.

10,11-dimethoxy-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4g)

White solid; Yield: 78%. m.p. 266-268 °C, IR [KBr, cm^{-1}] 2936, 2830, 1623, 1502, 1248, 1013, 844, 755; ^1H NMR (400 MHz, CDCl_3): δ 9.17 (s, 1H), 8.04 (d, $J = 8.8$ Hz, 1H), 7.95 (d, $J = 7.6$ Hz, 1H), 7.82 (s, 1H), 7.71-7.67 (m, 1H), 7.52-7.47 (m, 2H), 6.99 (s, 1H), 4.06 (s, 3H), 4.00 (s, 3H), 3.37 (dd, $J = 5.6, 8.4$ Hz, 2H), 3.24 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.8, 152.4, 150.2, 149.9, 148.0, 144.9, 132.9, 132.5, 130.0, 128.8, 128.7, 128.6, 128.2, 126.3, 123.9, 108.1, 104.7, 56.3, 56.2, 32.6, 28.1; MS m/z (relative intensity): 343 (100); HRMS (ESI $^+$) calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_2$ ($[\text{M}^+ \text{H}]^+$): 343.1447, found 343.1440.

10,11-bis(benzyloxy)-6,7-dihydrodibenzo[*b,j*][1,7]**phenanthroline (4h)**

Yellow solid; Yield: 73%. m.p. 196-198 °C, IR [KBr, cm^{-1}] 1622, 1496, 1450, 1390, 1314, 1249, 1002, 908, 734; ^1H NMR (400 MHz, CDCl_3): δ 9.18 (s, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 7.6$ Hz, 1H), 7.79 (s, 1H), 7.72-7.68 (m, 1H), 7.57-7.50 (m, 6H), 7.43-7.38 (m, 4H), 7.36-7.31 (m, 2H), 7.09 (s, 1H), 5.36 (s, 2H), 5.30 (s, 2H), 3.36 (dd, $J = 5.5, 8.4$ Hz, 2H), 3.22 (t, $J = 6.9$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.8, 152.0, 150.0, 149.6, 147.9, 144.9, 136.9, 136.8, 132.9, 132.6, 130.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 128.1, 127.3, 127.2, 126.3, 124.0, 110.1, 107.5, 71.0, 70.7, 32.5, 28.0; MS m/z (relative intensity): 495 (100); HRMS (ESI $^+$) calcd for $\text{C}_{34}\text{H}_{27}\text{N}_2\text{O}_2$ ($[\text{M}^+ \text{H}]^+$): 495.2073, found 495.2089.

6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*b*]benzo[*j*][1,7]**phenanthroline (4i)**

Greenish white solid; Yield: 82%. m.p. 232 - 234 °C, IR [KBr, cm^{-1}] 2351, 1497, 1463, 1389, 1229, 1178, 1034, 857, 779; ^1H NMR (400 MHz, CDCl_3): δ 9.17 (s, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.79 (s, 1H), 7.72 - 7.68 (m, 1H), 7.53 - 7.49 (m, 1H), 7.44 (s, 1H), 7.00 (s, 1H), 6.09 (s, 2H), 3.36 (dd, $J = 5.6, 8.4$ Hz, 2H), 3.22 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.7, 150.7, 149.9, 148.2, 148.1, 146.1, 133.6, 132.6, 130.1, 128.9, 128.7, 128.6, 128.6, 128.3, 126.3, 125.3, 105.9, 102.4, 101.8, 32.5, 28.0; MS m/z (relative intensity): 327 (100); HRMS (ESI $^+$) calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_2$ ($[\text{M}^+ \text{H}]^+$): 327.1134, found 327.1134.

9,12-dimethoxy-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4j)

Yellow solid; Yield: 76%. m.p. 204-206 °C, IR [KBr, cm^{-1}] 1648, 1602, 1479, 1383, 1262, 1162, 1088, 725; ^1H NMR (400 MHz, CDCl_3): δ 9.34 (s, 1H), 8.40 (s, 1H), 8.02 (dd, $J = 8.2, 18.4$ Hz,

2H), 7.72–7.68 (m, 1H), 7.53–7.49 (m, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 6.73 (d, $J = 8.4$ Hz, 1H), 4.09 (s, 3H), 3.96 (s, 3H), 3.41–3.37 (m, 2H), 3.31 (dd, $J = 5.7, 8.1$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 159.8, 151.4, 149.7, 148.7, 148.2, 140.2, 133.8, 130.3, 130.1, 129.6, 129.1, 128.6, 128.5, 128.2, 126.3, 121.6, 107.0, 104.0, 56.5, 56.0, 32.4, 28.3; MS m/z (relative intensity): 343 (100); HRMS (ESI^+) calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_2$ ($[\text{M}^+ \text{H}]^+$): 343.1447, found 343.1451.

2-fluoro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4k)

Brown solid; Yield: 82%. m.p. 180–182 °C, IR [KBr, cm^{-1}] 1597, 1566, 1498, 1367, 1215, 990, 825, 755; ^1H NMR (400 MHz, CDCl_3); δ 9.23 (s, 1H), 8.16 (d, $J = 8.4$ Hz, 1H), 8.07–8.02 (m, 2H), 7.79 (d, $J = 8.0$ Hz, 1H), 7.73–7.68 (m, 1H), 7.59 (dd, $J = 2.8, 8.8$ Hz, 1H), 7.55–7.46 (m, 2H), 3.41–3.37 (m, 2H), 3.31 (dd, $J = 5.8, 7.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 161.7, 159.2, 159.1 (d, $J = 2.0$ Hz), 151.8, 147.9, 145.4, 134.5, 132.8 (d, $J = 5.0$ Hz), 131.1 (d, $J = 9.0$ Hz), 130.4, 129.6, 129.3 (d, $J = 16.0$ Hz), 128.8 (d, $J = 10.0$ Hz), 128.4, 127.3, 126.9, 120.4 (d, $J = 26.0$ Hz), 111.9 (d, $J = 21.0$ Hz), 32.3, 28.2; MS m/z (relative intensity): 301 (100); HRMS (ESI^+) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2\text{F}$ ($[\text{M}^+ \text{H}]^+$): 301.1141, found 301.1133.

2-chloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4l)

White solid; Yield: 81%. m.p. 195–197 °C, IR [KBr, cm^{-1}] 2962, 2848, 1594, 1491, 1244, 1071, 995, 917, 824; ^1H NMR (400 MHz, CDCl_3); δ 9.12 (s, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.94 (t, $J = 6.8$ Hz, 2H), 7.90 (d, $J = 2.0$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.70–7.66 (m, 1H), 7.61 (dd, $J = 2.2, 9.0$ Hz, 1H), 7.52–7.48 (m, 1H), 3.37–3.33 (m, 2H), 3.26 (dd, $J = 4.2, 11.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 160.1, 151.6, 147.9, 146.6, 134.4, 132.4, 132.0, 131.1, 130.3, 130.2, 129.5, 129.4, 129.3, 128.7, 128.3, 127.4, 127.3, 126.9, 32.3, 28.1; MS m/z (relative intensity): 317 (100); HRMS (ESI^+) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2$ ^{35}Cl ($[\text{M}^+ \text{H}]^+$): 317.0846, found 317.0843.

2-bromo-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4m)

White solid; Yield: 87%. m.p. 210–212 °C, IR [KBr, cm^{-1}] 1592, 1493, 1397, 1259, 1059, 992, 910, 824; ^1H NMR (400 MHz, CDCl_3); δ 9.16 (s, 1H), 8.15 (d, $J = 8.5$ Hz, 1H), 8.11 (d, $J = 2.2$ Hz, 1H), 7.97 (s, 1H), 7.90 (d, $J = 8.9$ Hz, 1H), 7.78–7.74 (m, 2H), 7.72–7.68 (m, 1H), 7.54–7.50 (m, 1H), 3.38–3.35 (m, 2H), 3.28 (t, $J = 6.9$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 160.3, 151.6, 147.9, 146.8, 134.5, 133.7, 132.3, 130.8, 130.4, 130.3, 129.6, 129.5, 129.4, 129.3, 128.3, 127.3, 127.0, 120.1, 32.4, 28.1; MS m/z (relative intensity): 361 (100); HRMS (ESI^+) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2$ ^{79}Br ($[\text{M}^+ \text{H}]^+$): 361.0340, found 361.0334.

2-methyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4n)

White solid; Yield: 78%. m.p. 115–117 °C, IR [KBr, cm^{-1}] 1641, 1597, 1496, 1247, 1135, 995, 827, 758; ^1H NMR (400 MHz, CDCl_3); δ 9.21 (s, 1H), 8.16 (d, $J = 8.5$ Hz, 1H), 8.00 (s, 1H), 7.95 (d, $J = 8.6$ Hz, 1H), 7.77 (t, $J = 8.5$ Hz, 2H), 7.71–7.61 (m, 1H), 7.57–7.49 (m, 2H), 3.40–3.37 (m, 2H), 3.30 (t, $J = 6.7$ Hz, 2H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3); δ 158.9, 152.4, 148.0, 146.9, 136.2, 134.4, 133.0, 132.8, 130.4, 129.5, 129.2, 128.5, 128.3, 128.2, 127.8, 127.3, 126.7, 32.4, 28.4, 21.7; MS m/z (relative intensity): 297 (100); HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{17}\text{N}_2$ ($[\text{M}^+ \text{H}]^+$): 297.1392 found 297.1387.

4-chloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4o)

White solid; Yield: 91%. m.p. 226–228 °C, IR [KBr, cm^{-1}] 1648, 1633, 1496, 1428, 1321, 1006, 928, 789, 747; ^1H NMR (400

MHz, CDCl_3); δ 9.18 (s, 1H), 8.11 (d, $J = 8.4$ Hz, 1H), 7.89 (s, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.77 (d, $J = 6.8$ Hz, 1H), 7.72–7.65 (m, 2H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.38 (t, $J = 7.6$ Hz, 1H), 3.45 (dd, $J = 6.0, 8.0$ Hz, 2H), 3.24 (t, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 160.8, 151.5, 147.8, 144.3, 134.4, 133.6, 132.8, 130.3, 130.2, 129.5, 129.4, 129.3, 128.3, 128.0, 127.2, 126.8, 126.1, 32.5, 28.0; MS m/z (relative intensity): 317 (100); HRMS (ESI^+) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2$ ^{35}Cl ($[\text{M}^+ \text{H}]^+$): 317.0846, found 317.0843.

4-bromo-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4p)

Yellow solid; Yield: 90%. m.p. 225–227 °C, IR [KBr, cm^{-1}] 1652, 1644, 1536, 1134, 998, 929, 785, 743; ^1H NMR (400 MHz, CDCl_3); δ 9.25 (s, 1H), 8.15 (d, $J = 8.4$ Hz, 1H), 8.03 (dd, $J = 1.2, 7.2$ Hz, 1H), 8.00 (s, 1H), 7.95 (dd, $J = 1.0, 8.0$ Hz, 1H), 7.78 (d, $J = 8.0$ Hz, 1H), 7.72–7.68 (m, 1H), 7.54–7.50 (m, 1H), 7.37 (t, $J = 7.8$ Hz, 1H), 3.49 (dd, $J = 5.8, 8.2$ Hz, 2H), 3.31 (t, $J = 7.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 161.1, 151.7, 147.9, 145.2, 134.5, 133.9, 133.8, 130.5, 129.6, 129.5, 129.4, 128.9, 128.4, 127.3, 127.0, 126.8, 124.2, 32.6, 28.2; MS m/z (relative intensity): 361 (100); HRMS (ESI^+) calcd for $\text{C}_{20}\text{H}_{14}\text{N}_2$ ^{79}Br ($[\text{M}^+ \text{H}]^+$): 361.0340, found 361.0341.

4-methyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4q)

White solid; Yield: 87%. m.p. 164–166 °C, IR [KBr, cm^{-1}] 1639, 1597, 1497, 1432, 1262, 1153, 906, 789, 754; ^1H NMR (400 MHz, CDCl_3); δ 9.23 (s, 1H), 8.17 (d, $J = 8.4$ Hz, 1H), 7.97 (s, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.71–7.67 (m, 1H), 7.56 (d, $J = 6.9$ Hz, 1H), 7.52–7.48 (m, 1H), 7.41 (t, $J = 7.6$ Hz, 1H), 3.41 (dd, $J = 5.4, 8.4$ Hz, 2H), 3.29 (t, $J = 6.9$ Hz, 2H), 2.85 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3); δ 158.7, 152.5, 147.9, 147.4, 136.6, 134.3, 133.6, 130.6, 130.5, 129.5, 129.2, 128.2, 128.1, 127.2, 127.0, 126.6, 126.0, 32.6, 28.5, 18.1; MS m/z (relative intensity): 297 (100); HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{17}\text{N}_2$ ($[\text{M}^+ \text{H}]^+$): 297.1392, found 297.1387.

2,3-dimethoxy-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4r)

Yellow solid; Yield: 74%. m.p. 201–203 °C, IR [KBr, cm^{-1}] 2932, 2835, 1624, 1594, 1504, 1428, 1260, 1016, 748; ^1H NMR (400 MHz, CDCl_3); δ 9.15 (s, 1H), 8.13 (d, $J = 8.4$ Hz, 1H), 7.95 (s, 1H), 7.75 (d, $J = 8.0$ Hz, 1H), 7.70–7.65 (m, 1H), 7.52–7.47 (m, 2H), 7.21 (s, 1H), 4.05 (s, 3H), 4.03 (s, 3H), 3.37–3.33 (m, 2H), 3.26 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 157.5, 153.4, 152.6, 149.7, 147.8, 145.5, 134.1, 131.7, 130.2, 129.3, 129.1, 128.0, 127.2, 126.8, 126.4, 123.5, 107.4, 106.2, 56.3, 56.1, 32.0, 28.4; MS m/z (relative intensity): 343 (100); HRMS (ESI^+) calcd for $\text{C}_{22}\text{H}_{19}\text{N}_2\text{O}_2$ ($[\text{M}^+ \text{H}]^+$): 343.1447, found 343.1447.

6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*j*]benzo[*b*][1,7]

phenanthroline (4s)

White solid; Yield: 80%. m.p. 198–200 °C, IR [KBr, cm^{-1}] 1592, 1498, 1466, 1240, 1205, 1038, 943, 844 759; ^1H NMR (400 MHz, CDCl_3); δ 9.09 (s, 1H), 8.14 (d, $J = 8.4$ Hz, 1H), 7.98 (s, 1H), 7.77 (d, $J = 7.6$ Hz, 1H), 7.70–7.66 (m, 1H), 7.52–7.48 (m, 1H), 7.35 (s, 1H), 7.22 (s, 1H), 6.12 (s, 2H), 3.34–3.31 (m, 2H), 3.29–3.25 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3); δ 157.7, 152.5, 151.7, 147.9, 147.8, 146.9, 134.3, 132.4, 130.3, 129.4, 129.2, 128.2, 127.3, 126.9, 126.6, 125.0, 105.4, 103.9, 101.9, 32.0, 28.5; MS m/z (relative intensity): 327 (100); HRMS (ESI^+) calcd for $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}_2$ ($[\text{M}^+ \text{H}]^+$): 327.1134, found 327.1136.

2,10-difluoro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4t)

Brown solid; Yield: 79%. m.p. 200-202 °C, IR [KBr, cm⁻¹] 1557, 1502, 1436, 1219, 997, 822; ¹H NMR (400 MHz, CDCl₃): δ 9.17 (s, 1H), 8.15 (dd, *J* = 5.2, 9.2 Hz, 1H), 8.04 (dd, *J* = 5.4, 9.0 Hz, 1H), 7.94 (s, 1H), 7.57 (dd, *J* = 2.8, 8.8 Hz, 1H), 7.50-7.44 (m, 2H), 7.38 (dd, *J* = 2.6, 9.0 Hz, 1H), 3.39- 3.35 (m, 2H), 3.29 (dd, *J* = 5.8, 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 162.2, 161.7, 159.7, 159.3, 158.9 (d, *J* = 2.0 Hz), 151.3 (d, *J* = 3.0 Hz), 145.4, 145.1, 133.8 (d, *J* = 5.0 Hz), 132.6 (d, *J* = 5.0 Hz), 132.0 (d, *J* = 9.0 Hz), 131.2 (t, *J* = 9.0 Hz), 129.0, 128.8 (t, *J* = 11.0 Hz), 120.6 (d, *J* = 25.0 Hz), 119.6 (d, *J* = 26.0 Hz), 111.7 (d, *J* = 21.0 Hz), 110.3 (d, *J* = 21.0 Hz), 32.2, 28.3; MS *m/z* (relative intensity): 319 (100); HRMS (ESI⁺) calcd for C₂₀H₁₃N₂F₂ ([M⁺ H]⁺): 319.1047, found 319.1041.

2,10-dichloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4u)

Brown solid; Yield: 80%. m.p. 260-262 °C, IR [KBr, cm⁻¹] 2307, 1469, 1180, 1059, 908, 818, 706; ¹H NMR (400 MHz, CDCl₃): δ 9.14 (s, 1H), 8.07 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.93 (d, *J* = 2.4 Hz, 1H), 7.90 (s, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.66-7.61 (m, 2H), 7.25 (s, 1H), 7.39-7.36 (m, 2H), 3.29 (dd, *J* = 5.7, 8.1 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 159.9, 152.0, 146.7, 146.3, 133.5, 132.7, 132.6, 132.2, 131.4, 131.3, 131.1, 130.4, 130.3, 129.0, 128.9, 128.7, 127.5, 126.0, 32.2, 28.2; MS *m/z* (relative intensity): 351 (100); HRMS (ESI⁺) calcd for C₂₀H₁₃N₂³⁵Cl₂ ([M⁺ H]⁺): 351.0456, found 351.0452.

2,10-dibromo-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4v)

Yellow solid; Yield: 83%. m.p. 268-270 °C, IR [KBr, cm⁻¹] 1588, 1483, 123, 1193, 1054, 910, 820; ¹H NMR (400 MHz, CDCl₃): δ 9.14 (s, 1H), 8.11 (d, *J* = 2.1 Hz, 1H), 8.00 (d, *J* = 8.9 Hz, 1H), 7.92 (d, *J* = 2.3 Hz, 2H), 7.89 (s, 1H), 7.79-7.74 (m, 2H), 3.39-3.35 (m, 2H), 3.29 (dd, *J* = 5.6, 8.0 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 160.1, 152.1, 146.9, 146.5, 133.9, 133.4, 132.9, 132.5, 131.3, 131.2, 130.9, 130.5, 129.4, 129.3, 129.0, 120.9, 120.3, 32.2, 28.1; MS *m/z* (relative intensity): 438 (50); HRMS (ESI⁺) calcd for C₂₀H₁₃N₂⁷⁹Br₂ ([M⁺ H]⁺): 438.9445, found 438.9449.

2,10-dimethyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4w)

White solid; Yield: 73%. m.p. 149-151 °C, IR [KBr, cm⁻¹] 1642, 1599, 1490, 1428, 1153, 992, 825, 763; ¹H NMR (400 MHz, CDCl₃): δ 9.23 (s, 1H), 7.96 (d, *J* = 9.9 Hz, 2H), 7.78 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.57-7.53 (m, 2H), 7.40 (dd, *J* = 7.3, 7.8 Hz, 1H), 3.40-3.37 (m, 2H), 3.30 (dd, *J* = 5.7, 8.3 Hz, 2H), 2.95 (s, 3H), 2.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 159.0, 151.0, 146.9, 137.5, 136.1, 134.6, 132.8, 132.6, 130.0, 129.3, 129.0, 128.4, 128.3, 128.2, 127.9, 126.5, 125.3, 32.4, 28.2, 21.7, 18.2; MS *m/z* (relative intensity): 311 (100); HRMS (ESI⁺) calcd for C₂₂H₁₉N₂ ([M⁺ H]⁺): 311.1548, found 311.1556.

6,7-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*b*][1,3]dioxolo[4',5':4,5]benzo[1,2-*j*][1,7]phenanthroline (4x)

Yellow solid; Yield: 77%. m.p. 275-277 °C, IR [KBr, cm⁻¹] 1642, 1495, 1461, 1373, 1232, 1035, 947, 839, 782; ¹H NMR (400 MHz, CDCl₃): δ 8.95 (s, 1H), 7.75 (s, 1H), 7.40 (s, 1H), 7.32 (s, 1H), 7.17 (s, 1H), 6.98 (s, 1H), 6.09 (d, *J* = 2.2 Hz, 4H), 3.27 (dd, *J* = 5.2, 8.0 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 157.5, 151.4, 150.5, 150.2, 148.0, 147.7, 146.5, 146.0, 133.4, 131.5, 128.4, 127.0, 125.1, 125.0, 105.8, 105.4, 103.8, 102.4, 101.9, 101.8, 32.0, 28.1; MS *m/z* (relative

intensity): 371 (100); HRMS (ESI⁺) calcd for C₂₂H₁₅N₂O₄ ([M⁺ H]⁺): 371.1032, found 371.1035.

10-bromo-2-chloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4y)

White solid; Yield: 79%. m.p. 238-240 °C, IR [KBr, cm⁻¹] 2352, 1646, 1593, 1485, 1316, 1240, 1164, 1071, 912, 823; ¹H NMR (400 MHz, CDCl₃): δ 9.17 (s, 1H), 8.00 (dd, *J* = 9.0, 11.0 Hz, 2H), 7.95 (dd, *J* = 2.2, 5.0 Hz, 2H), 7.92 (s, 1H), 7.76 (dd, *J* = 2.2, 9.0 Hz, 1H), 7.65 (dd, *J* = 2.2, 9.0 Hz, 1H), 3.41- 3.37 (m, 2H), 3.31 (dd, *J* = 5.8, 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 160.0, 152.2, 146.7, 146.5, 133.5, 132.9, 132.7, 132.2, 131.4, 131.3, 131.2, 130.3, 129.4, 129.3, 129.1, 128.8, 127.5, 120.9, 32.2, 28.2; MS *m/z* (relative intensity): 394 (80); HRMS (ESI⁺) calcd for C₂₀H₁₃N₂BrCl ([M⁺ H]⁺): 394.9951 found 394.9953.

7,7-dimethyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (4z)

White solid; Yield: 85%. m.p. 170-172 °C, IR [KBr, cm⁻¹] 3060, 2960, 1593, 1498, 1466, 1411, 1125, 911, 862; ¹H NMR (400 MHz, CDCl₃): δ 9.32 (s, 1H), 8.18 (d, *J* = 7.2 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.84 (dd, *J* = 1.0, 8.1 Hz, 1H), 7.75-7.69 (m, 2H), 7.57-7.52 (m, 2H), 3.31 (s, 2H), 1.47 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 158.8, 151.3, 148.6, 147.5, 139.2, 133.5, 131.4, 130.3, 129.5, 129.4; 129.1, 128.7, 128.5, 128.3, 127.7, 126.8, 126.4, 47.0, 35.4, 28.9; MS *m/z* (relative intensity): 311 (100); HRMS (ESI⁺) calcd for C₂₂H₁₉N₂ ([M⁺ H]⁺): 311.1548 found 311.1548.

Procedure for the synthesis of 2-(phenylethynyl)-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5a)

To a solution of **4m** (1 mmol) and phenyl acetylene (1.2 mmol) in DMF (4 mL) was added PdCl₂(PPh₃)₂ (10 mol%) under nitrogen atmosphere. The reaction was then stirred at room temperature for 5 minutes followed by the addition of Et₃N (2 mmol). The reaction mixture was stirred at 80 °C in an oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction (4h), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate (3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was evaporated under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

2-(phenylethynyl)-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5a)

Yellow solid; Yield: 79%. m.p. 197-199 °C, IR [KBr, cm⁻¹] 1642, 1597, 1492, 992, 834, 752; ¹H NMR (400 MHz, CDCl₃): δ 9.25 (s, 1H), 8.18 (d, *J* = 8.6 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.83-7.78 (m, 2H), 7.73-7.69 (m, 1H), 7.62-7.58 (m, 2H), 7.55-7.51 (m, 1H), 7.41-7.36 (m, 3H), 3.42-3.40 (m, 2H), 3.39-3.29 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 160.5, 151.9, 148.0, 147.7, 134.5, 133.1, 132.2, 131.9, 130.3, 129.6, 129.4, 129.2, 128.8, 128.7, 128.6, 128.3, 128.0, 127.3, 126.9, 123.2, 121.4, 90.7, 89.3, 32.5, 28.2; MS *m/z* (relative intensity): 383 (100); HRMS (ESI⁺) calcd for C₂₈H₁₉N₂ ([M⁺ H]⁺): 383.1548, found 383.1537.

Procedure for the synthesis of 2-phenyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5b)

To a solution of **4m** (1 mmol) and phenylboronic acid (1.2 mmol) in toluene (6 mL) was added Pd(OAc)₂ (10 mol%) under nitrogen

atmosphere. The reaction was then stirred at room temperature for 5 minutes followed by the addition of K_2CO_3 (2 mmol). The reaction mixture was stirred at $80^\circ C$ in an oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction (40 min), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate (3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

2-phenyl-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5b)

White solid; Yield: 88%. m.p. $223-225^\circ C$, IR [KBr, cm^{-1}] 2355, 1594, 1491, 1435, 1167, 995, 935, 832, 755; 1H NMR (400 MHz, $CDCl_3$): δ 9.34 (s, 1H), 8.18 (t, $J = 3.6$ Hz, 1H), 8.12 (d, $J = 8.7$ Hz, 1H), 8.01-7.96 (m, 2H), 7.80-7.68 (m, 4H), 7.54-7.50 (m, 3H) 7.43-7.39 (m, 1H), 3.44-3.40 (m, 2H), 3.33 (dd, $J = 4.6$, 11.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 152.1, 147.9, 147.7, 140.5, 139.1, 134.4, 133.7, 130.3, 130.1, 129.5, 129.3, 129.1, 128.9, 128.4, 128.3, 127.8, 127.6, 127.5, 127.3, 126.8, 126.6, 32.4, 28.3; MS m/z (relative intensity): 359(100); HRMS (ESI⁺) calcd for $C_{26}H_{19}N_2$ ($[M^+ H]^+$): 359.1548, found 359.1543.

Procedure for the synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5c)

To a solution of **4m** (1mmol) and bis(pinacolato)diboron (1.2 mmol) in toluene (5 mL) was added $PdCl_2(PPh_3)_2$ (10 mol%) under nitrogen atmosphere. The reaction was then stirred at room temperature for 5 minutes followed by the addition of K_2CO_3 (1.5 mmol). The reaction mixture was stirred at $80^\circ C$ in an oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction (1h), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate (3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5c)

White solid; Yield: 65%. m.p. $103-105^\circ C$, IR [KBr, cm^{-1}] 1622, 1496, 1448, 1378, 1341, 1142, 1082, 964, 856, 754; 1H NMR (400 MHz, $CDCl_3$): δ 9.34 (s, 1H), 8.53 (s, 1H), 8.15 (d, $J = 8.0$ Hz, 1H), 8.02 (t, $J = 8.0$ Hz, 2H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.71-7.67 (m, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 3.42-3.38 (m, 2H), 3.31 (dd, $J = 4.6$, 12.2 Hz, 2H), 1.40 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 152.2, 149.8, 148.0, 137.4, 135.3, 134.3, 134.2, 130.3, 129.6, 129.2, 128.7, 128.2, 127.7, 127.6, 127.2, 126.8, 84.3, 75.2, 32.6, 28.3, 25.0; MS m/z (relative intensity): 409 (100); HRMS (ESI⁺) calcd for $C_{26}H_{26}BN_2O_2$ ($[M^+ H]^+$): 409.2087, found 409.2083.

Procedure for the synthesis of 4-methyldibenzo[*b,j*][1,7]phenanthroline (5d)

Compound **4q** (1 mmol) was dissolved in 1,4-dioxane (3 mL) in a round-bottomed flask (25 mL). Selenium dioxide (2 mmol) dissolved in 1,4-dioxane (2 mL) and water (0.2 mL) was added to

this mixture at room temperature and was heated at $80^\circ C$ in an oil bath. The progress of the reaction was monitored by TLC. After completion of the reaction (8h), the reaction mixture was cooled to room temperature and 1,4-dioxane was removed under reduced pressure. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product (**5d**).

4-methyldibenzo[*b,j*][1,7]phenanthroline (5d): Yellow solid; Yield: 81%. m.p. $216-218^\circ C$, IR [KBr, cm^{-1}] 1598, 1487, 1368, 1167, 895, 726; 1H NMR (400 MHz, $CDCl_3$): δ 10.12 (s, 1H), 8.58 (s, 1H), 8.38 (d, $J = 8.9$ Hz, 1H), 8.07 (d, $J = 8.1$ Hz, 1H), 8.01 (t, $J = 7.5$ Hz, 1H), 7.97 (s, 1H), 7.91 (d, $J = 9.4$ Hz, 1H), 7.87-7.83 (m, 1H), 7.70 (dd, $J = 1.0, 7.8$ Hz, 1H), 7.64-7.60 (m, 1H), 7.55-7.52 (m, 1H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 148.6, 148.2, 147.8, 137.3, 135.2, 133.9, 13.6, 130.5, 130.3, 130.2, 129.7, 128.1, 127.5, 127.3, 127.1, 126.6, 126.3, 125.4, 124.8, 18.5; MS m/z (relative intensity): 294(100); HRMS (EI⁺) calcd for $C_{21}H_{14}N_2$ ($[M^+]$): 294.1157, found 294.1164.

Procedure for the synthesis of 6-fluoro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5e)

Selectfluor (1 mmol) was added to a stirred solution of compound **4a** (1 mmol) in acetonitrile (3 mL) at room temperature. This mixture was heated at $80^\circ C$ in an oil bath and the progress of reaction was monitored by TLC. After completion of the reaction (45 min), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate (3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product. The compound was obtained with little inseparable impurities.

6-fluoro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5e)

White solid; Yield: 70%. m.p. $201-203^\circ C$, IR [KBr, cm^{-1}] 3056, 2361, 1597, 1498, 1419, 1001, 836, 755; 1H NMR (400 MHz, $CDCl_3$): δ 9.48 (s, 1H), 8.21 (dd, $J = 2.6$, 8.5 Hz, 2H), 8.12 (s, 1H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.83-7.78 (m, 2H), 7.75-7.71 (m, 1H), 7.64 (t, $J = 7.5$ Hz, 1H), 7.57-7.53 (m, 1H), 6.03 (dt, $J = 3.8$, 49.3 Hz, 1H), 3.83-3.75 (m, 1H), 3.67-3.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7 (d, $J = 17.0$ Hz), 150.5, 148.3 (d, $J = 38.0$ Hz), 136.3, 134.5, 130.9, 129.7 (d, $J = 2.0$ Hz), 129.6, 129.3, 129.1, 128.4, 127.9, 127.8, 127.4, 127.1, 125.3 (d, $J = 4.0$ Hz), 90.0, 88.3, 35.0 (d, $J = 24.0$ Hz); MS m/z (relative intensity): 301(100); HRMS (ESI⁺) calcd for $C_{20}H_{14}N_2 F$ ($[M^+ H]^+$): 301.1141, found 301.1142.

Procedure for the synthesis of 6-bromo-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5f)

NBS (1 mmol) was added to a stirred solution of compound **4a** (1 mmol) in acetonitrile (5 mL) at room temperature. This mixture was heated at $80^\circ C$ in an oil bath and the progress of reaction was monitored by TLC. After completion of the reaction (1.5 h), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate

(3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

6-bromo-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5f) Yellow solid; Yield: 61%. m.p. 296-298 °C, IR [KBr, cm⁻¹] 2357, 1594, 1497, 1421, 1264, 996, 798, 756; ¹H NMR (400 MHz, CDCl₃): δ 9.45 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 8.8 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.79-7.73 (m, 2H), 7.62-7.54 (m, 2H), 5.87 (t, *J* = 3.0 Hz, 1H), 3.95-3.89 (m, 1H), 3.75 (dd, *J* = 2.4, 16.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 158.8, 150.5, 148.2, 148.0, 136.0, 135.0, 131.0, 129.8, 129.6, 129.4, 129.1, 128.9, 128.3, 127.7, 127.4, 127.2, 126.9, 126.3, 48.8, 38.1; MS *m/z* (relative intensity): 361(100); HRMS (ESI⁺) calcd for C₂₀H₁₄N₂ Br ([M⁺ H]⁺): 361.0340, found 361.0341.

dibenzo[*b,j*][1,7]phenanthroline (5g): Yellow solid; m.p. 219-221 °C, IR [KBr, cm⁻¹] 1635, 1494, 1262, 1133, 910, 854, 819, 736; ¹H NMR (400 MHz, CDCl₃): δ 10.19 (s, 1H), 8.61 (s, 1H), 8.39 (d, *J* = 8.8 Hz, 1H), 8.30 (d, *J* = 8.8 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.95 (s, 2H), 7.89-7.84 (m, 2H), 7.68-7.62 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 151.3, 149.3, 148.1, 147.8, 135.3, 133.9, 131.3, 130.9, 130.4, 129.8, 129.6, 129.3, 128.2, 127.6, 127.2, 126.7, 126.6, 125.8, 124.7; MS *m/z* (relative intensity): 281(100); HRMS (ESI⁺) calcd for C₂₀H₁₃N₂ ([M⁺ H]⁺): 281.1079, found 281.1079.

Procedure for the synthesis of 6-chloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5h):

NCS (1 mmol) was added to a stirred solution of compound **4a** (1 mmol) in acetonitrile (5 mL) at room temperature. This mixture was heated at 80°C in an oil bath and the progress of reaction was monitored by TLC. After completion of the reaction (1h), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate (3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

6-chloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5h) Yellow solid; Yield: 69%. m.p. 291-293 °C, IR [KBr, cm⁻¹] 1637, 1595, 1496, 1423, 1267, 1164, 957, 754; ¹H NMR (400 MHz, CDCl₃): δ 9.42 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 8.09 (s, 1H), 8.02 (d, *J* = 8.2 Hz, 1H), 7.81-7.69 (m, 3H), 7.60-7.51 (m, 2H), 5.67 (t, *J* = 3.3 Hz, 1H), 3.83-3.78 (m, 1H), 3.65 (dd, *J* = 2.8, 16.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 156.2, 150.5, 148.3, 148.1, 136.2, 134.9, 130.9, 129.8, 129.7, 129.5, 129.1, 129.0, 128.4, 127.7, 127.4, 127.1, 127.0, 125.7, 57.7, 37.6; MS *m/z* (relative intensity): 317(100); HRMS (ESI⁺) calcd for C₂₀H₁₄N₂ Cl ([M⁺ H]⁺): 317.0846, found 317.0845.

Procedure for the synthesis of 6,6-dichloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5i) NCS (2 mmol) was added to a stirred solution of compound **4a** (1 mmol) in acetonitrile (5 mL) at room temperature. This mixture was heated at 80°C in an oil bath and the progress of reaction was

monitored by TLC. After completion of the reaction (3h), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate (3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

6,6-dichloro-6,7-dihydrodibenzo[*b,j*][1,7]phenanthroline (5i) Yellow solid; Yield: 65%. m.p. 254-256 °C, IR [KBr, cm⁻¹] 1642, 1492, 1260, 1117, 970, 932, 805, 738; ¹H NMR (400 MHz, CDCl₃): δ 9.53 (s, 1H), 8.27 (t, *J* = 10.0 Hz, 2H), 8.12 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.86-7.75 (m, 3H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 4.26 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 154.7, 150.0, 148.0, 147.9, 135.7, 134.9, 131.3, 130.3, 130.1, 129.5, 128.9, 128.4, 128.1, 127.6, 127.5, 127.2, 126.0, 125.2, 86.0, 49.9; MS *m/z* (relative intensity): 351 (100); HRMS (ESI⁺) calcd for C₂₀H₁₃N₂ Cl₂ ([M⁺ H]⁺): 351.0456, found 351.0455.

Procedure for the synthesis of 6-bromodibenzo[*b,j*][1,7]phenanthroline (5j)

NBS (2 mmol) was added to a stirred solution of compound **4a** (1 mmol) in acetonitrile (5 mL) at room temperature. This mixture was heated at 80°C in an oil bath and the progress of reaction was monitored by TLC. After completion of the reaction (5h), the reaction mixture was cooled to room temperature and was added to brine (15 mL). The organic phase was extracted with ethyl acetate (3x15 mL). The combined organic extracts were dried with magnesium sulfate and filtered. The solvent was evaporated under reduced pressure. The solvent was removed under reduced pressure and the crude product thus obtained was purified by column chromatography to obtain the pure product.

6-bromodibenzo[*b,j*][1,7]phenanthroline (5j): Yellow solid; Yield: 53%. m.p. 211-213 °C, IR [KBr, cm⁻¹] 1644, 1492, 1113, 803, 743; ¹H NMR (400 MHz, CDCl₃): δ 10.21 (s, 1H), 8.53 (s, 1H), 8.45 – 8.36 (m, 3H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.93 – 7.85 (m, 2H), 7.72 – 7.62 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 149.2, 147.8, 147.4, 147.3, 134.5, 134.4, 133.8, 131.2, 130.7, 130.1, 129.8, 129.0, 128.2, 127.6, 127.4, 127.3, 127.1, 126.1, 125.2, 124.9; MS *m/z* (relative intensity): 359 (100); HRMS (ESI⁺) calcd for C₂₀H₁₂N₂ Br ([M⁺ H]⁺): 359.0184, found 359.0183.

Acknowledgments

Financial support for this work by the Ministry of Science and Technology of the Republic of China (MOST 103-2113-M-003-008-MY3), National Taiwan Normal University (103-07-C) and Instrumentation Centre at National Taiwan Normal University is gratefully acknowledged. The authors are grateful to Mr. Ting-Shen Kuo, Ms. Hsiu-Ni Huan and Ms. Chiu-Hui He for providing X-ray, mass and NMR spectral data presented in this paper

Notes and references

Department of Chemistry, National Taiwan Normal University, 88, Sec. 4, Tingchow Road, Taipei-116, Taiwan, R.O.C.
E-mail: cheyaocf@ntnu.edu.tw, cheyaocf@yahoo.com.tw

- Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/
- 5 1 (a) O. Baudoin, C. Marchand, M. P. Teulade-Fichou, J. P. Vigneron, J.-S. Sun, T. Garestier, C. Helene and J.-M. Lehn, *Chem. Eur. J.*, 1998, **4**, 1504; b) J. E. Bakali, F. Klupscha, A. Guédinb, B. Brassart, G. Fontaine, A. Farce, P. Roussel, R. Houssin, J.-L. Bernier, P. Chavatte, J.-L. Mergny, J.-F. Riou and J.-P. Hénicharta, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 3434; c) P. Alberti, L. Lacroix, L. Guittat, C. Helene and J.-L. Mergny, *Mini. Rev. Med.Chem.*, 2003, **3**, 23.
- 2 M. P. Teulade-Fichou, C. Carrasco, L. Guittat, C. Bailly, P. Alberti, J. L. Mergny, A. David, J. M. Lehn and W. D. Wilson, *J. Am. Chem. Soc.*, 2003, **125**, 4732.
- 15 3 (a) P. Alberti, P. Schmitt, C.-H. Nguyen, C. Rivalle, M. Hoarau, D.S. Grierson and J.-L. Mergny, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 1071; b) M. Keppler, O. Zegrocka, L. Strekowski and K. R. Foxa, *FEBS Lett.*, 1999, **447**, 223; c) M. P. Teulade-Fichou, D. Perrin, A. Boutorine, D. Polverari, J.-P. Vigneron, J.-M. Lehn, J.-S. Sun, T. Garestier, and C. Helene, *J. Am. Chem. Soc.*, 2001, **123**, 9283.
- 4 (a) A. Artese, G. Costa, S. Distinto, F. Moraca, F. Ortuso, L. Parrotta and S. Alcaro, *Eur. J. Med. Chem.*, 2013, **68**, 139; b) E. Delfourme, F. Darro, N. B. Subielos, C. Decaestecker, J. Bastide, A. Frydman and R. Kiss, *J. Med. Chem.*, 2001, **44**, 3275; c) I. N. Petersen, F. Crestey and J. L. Kristensen, *Chem. Commun.*, 2012, **48**, 9092.
- 5 (a) S. Dallavalle, L. Merlini, G. L. Beretta, S. Tinelli and F. Zunino, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 5757; b) T. Harayama, A. Hori, G. Serban, Y. Morikami, T. Matsumoto, H. Abe and Y. Takeuchi, *Tetrahedron*, 2004, **60**, 10645; c) S. P. Chavan and R. Sivappa, *Tetrahedron*, 2004, **60**, 9931; d) J. J. Mason and J. Bergman, *Org. Biomol. Chem.*, 2007, **5**, 2486; e) A. Cagir, S. H. Jones, R. Gao, B. M. Eisenhauer and S. M. Hecht, *J. Am. Chem. Soc.*, 2003, **125**, 13628.
- 6 (a) F. Wu and R. P. Thummel, *Inorg. Chim. Acta.*, 2002, **327**, 26; b) Y. Jahng, J. Hazelrigg, D. Kimball, E. Riesgo, F. Wu and R. P. Thummel, *Inorg. Chem.*, 1997, **36**, 5390; c) Y.-Z. Hu, G. Zhang and R. P. Thummel, *Org. Lett.*, 2003, **5**, 2251; d) M. E. Cucciolo and A. Vitagliano, *Organometallics*, 1992, **11**, 3954; e) J.-L. Mergny, L. Lacroix, M.-P. Teulade-Fichou, C. Hounsou, L. Guittat, M. Hoarau, P. B. Arimondo, J.-P. Vigneron, J.-M. Lehn, J.-F. Riou, T. Garestier and C. Helene, *Proc. Natl. Acad. Sci.*, 2001, **98**, 3062.
- 7 G. Albano, P. Belsler, L. D. Cola, M. T. Gandolfi, *Chem. Commun.*, 1999, 1171.
- 8 (a) V. Sridharan, P. Ribelles, T. Ramos and J. C. Menendez, *J. Org. Chem.*, 2009, **74**, 5715; b) O. Baudoin, M.-P. Teulade-Fichou, J.-P. Vigneron and J.-M. Lehn, *J. Org. Chem.*, 1997, **62**, 5458; c) C. Jacquelin, N. Saettel, C. Hounsou and M.-P. Teulade-Fichou, *Tetrahedron Lett.*, 2005, **46**, 2589; d) Y. Jahng, J. Hazelrigg, D. Kimball, E. Riesgo, F. Wu and R. P. Thummel, *Inorg. Chem.*, 1997, **36**, 5390; e) R. P. Thummel and F. Lefoulon, *J. Org. Chem.*, 1985, **50**, 666.
- 50 9 (a) A. H. Henseler, C. Ayats and M. A. Peric, *Adv. Synth. Catal.*, 2014, **356**, 1795; b) V. Maya, M. Raj and V. K. Singh, *Org. Lett.*, 2007, **9**, 2593; c) S. Luo, J. Li, H. Xu, L. Zhang and J.-P. Cheng, *Org. Lett.*, 2007, **9**, 3675; d) Z. Tang, Z.-H. Yang, X.-H. Chen, L.-F. Cun, A.-Q. Mi, Y.-Z. Jiang and L.-Z. Gong, *J. Am. Chem. Soc.*, 2005, **127**, 9285; e) Y. Hayashi, T. Sumiya, J. Takahashi, H. Gotoh, T. Urushima and M. Shoji, *Angew. Chem. Int. Ed.*, 2006, **45**, 958; f) Y. Zhou and Z. Shan, *J. Org. Chem.*, 2006, **71**, 9510.
- 10 (a) C. Ramesh, P. M. Lei, D. Janreddy, V. Kavala, C.-W. Kuo and C.-F. Yao, *J. Org. Chem.*, 2012, **77**, 8451; (b) D. Janreddy, V. Kavala, J. W. Bosco, C.-W. Kuo and C.-F. Yao, *Eur. J. Org. Chem.*, 2011, 2360; (c) C. Ramesh, V. Kavala, B. R. Raju, C.-W. Kuo and C.-F. Yao, *Tetrahedron Lett.*, 2010, **51**, 5234; (d) C. Ramesh, B. R. Raju, V. Kavala, C.-W. Kuo and C.-F. Yao, *Tetrahedron*, 2011, **67**, 1187; (e) C. Ramesh, V. Kavala, B. R. Raju, C.-W. Kuo and C.-F. Yao, *Tetrahedron Lett.*, 2009, **50**, 4037; f) C. Bolm, J. Legros, J. L. Paih and L. Zani, *Chem. Rev.*, 2004, **104**, 6217.
- 65 (g) B. R. McNaughton and B. L. Miller, *Org. Lett.*, 2003, **5**, 4257; (h) C. L. Diedrich, D. Haase, W. Saak, and J. Christoffers, *Eur. J. Org. Chem.*, 2008, 1811. (i) T. A. Bryson, J. M. Gibson, J. J. Stewart, H. Voegtle, A. Tiwari, J. H. Dawson, W. Marley and B. Harmon, *Green Chem.*, 2003, **5**, 177; j) A.-H. Li, D. J. Beard, H. Coate, A. Honda, M. Kadalbajoo, A. Kleinberg, R. Laufer, K. M. Mulvihill, A. Nigro, P. Rastogi, D. Sherman, K. W. Siu, A. G. Steinig, T. Wang, D. Werner, A. P. Crew, and M. J. Mulvihill, *Synthesis*, 2010, **10**, 1678.
- 11 R. R. Rajawinslin, S. D. Gawande, V. Kavala, Y.-H. Huang, C.-W. Kuo, T.-S. Kuo, M.-L. Chen, C.-H. He and C.-F. Yao, *RSC Adv.*, 2014, **4**, 37806.
- 12 (a) G. M. Shutske and J. D. Tomer IV, *J. Heterocycl. Chem.*, 1993, **30**, 23; (b) L. Paloque, P. Verhaeghe, M. Casanova, C. C. Ducros, A. Dumetre, L. Mbatchi, S. Hutter, M. K. Rabet, M. Laget, V. Remusat, S. Rault, P. Rathelot, N. Azas and P. Vanelle, *Euro. J. Med. Chem.*, 2012, **54**, 75; d) P. Ornaghi, D. Rotili, G. Sbardella, A. Mai and P. Filetici, *Biochem Pharmacol.*, 2005, **70**, 911; e) N. Mulakayala, D. Rambabu, M. R. Raja, M. Chaitanya, C. S. Kumar, A. M. Kalle, G. R. Krishna, C. M. Reddy, M. V. Basaveswararao and M. Pal, *Bioorg. Med. Chem.*, 2012, **20**, 759; f) A. D. Yapi, N. Desbois, J. M. Chezal, O. Chavignon, J. C. Teulade, A. Valentin and Y. Blache, *Eur. J. Med. Chem.*, 2010, **45**, 2854; g) A. A. Joshi, S. S. Narkhede and C. L. Viswanathan, *Bioorg. Med. Chem. Lett.*, 2005, **15**, 73;
- 13 (a) S. D. Gawande, M. R. Zanwar, V. Kavala, C.-W. Kuo, R. R. Rajawinslin and C.-F. Yao, *Adv. Synth. Catal.*, 2015, **357**, 168; b) S. D. Gawande, V. Kavala, M. R. Zanwar, C.-W. Kuo, W.-C. Huang, T.-S. Kuo, H.-N. Huang, C.-H. He and C.-F. Yao, *Adv. Synth. Catal.*, 2014, **356**, 2599; c) S. D. Gawande, V. Kavala, M. R. Zanwar, C.-W. Kuo, H.-N. Huang, C.-H. He, T.-S. Kuo and C.-F. Yao, *Adv. Synth. Catal.*, 2013, **355**, 3022; d) M. R. Zanwar, S. D. Gawande, V. Kavala, C.-W. Kuo and C.-F. Yao, *Adv. Synth. Catal.*, 2014, **356**, 3849.
- 14 (a) A. Sultan, A. R. Raza, M. Abbas, K. M. Khan, M. N. Tahir and N. Saari, *Molecules*, 2013, **18**, 10081; (b) D. Kumar, G. Kaur, A. Negi, S. Kumar, S. Singh, and R. Kumar, *Bioorg. Chem.* 2014, **57**, 57; (c) I. Braulio, T. Harlem, Q. Jairo, A. Rodrigo, N. Manuel, S. Adolfo, S. Maximiliano, Z. Susana, and L. John, *Heterocycl. Commun.*, 2003, **9**, 153; (d) G. Karthikeyan and P. T. Perumal, *J. Heterocyclic Chem.*, 2004, **41**, 1039.
- 15 (a) M. Karak, L. C. A. Barbosa and G. C. Hargaden, *RSC Adv.*, 2014, **4**, 53442; b) A. M. Thomas, A. Sujatha and G. Anilkumar, *RSC Adv.*, 2014, **4**, 21688; c) J. L. Bolliger and C. M. Frech, *Adv. Synth. Catal.*, 2009, **351**, 891; d) T. Vlaar, E. Ruijter and R. V. A. Orru, *Adv. Synth. Catal.*, 2011, **353**, 809; e) Y. Liang, Y.-X. Xie, J.-H. Li, *J. Org. Chem.*, 2006, **71**, 379.
- 110 16 (a) G. Herve, G. Sartori, G. Enderlin, G. Mackenzie and C. Len, *RSC Adv.*, 2014, **4**, 18558; b) K. L. Billingsley, K. W. Anderson and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2006, **45**, 3484; c) J. H. Kirchhoff, M. R. Netherton, I. D. Hills and G. C. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 13662; d) R. Rossi, F. Bellina and M. Lessi, *Adv. Synth. Catal.*, 2012, **354**, 1181; e) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.

- 17 (a) W. K. Chow, O. Y. Yuen, P. Y. Choy, C. M. So, C. P. Lau, W.T. Wong and F. Y. Kwong *RSC Adv.*, 2013,**3**, 12518; b) T. Ishiyama, M. Murata and N. Miyaura, *J. Org. Chem.*, 1995, **60**, 7508; c) A. L. S. Thompson, G. W. Kabalka, M. R. Akula and J. W. Huffman, *Synthesis*, 2005, 547; d) J. Takagi, A. Kamon, T. Ishiyama and N. Miyaura, *Synlett.*, 2002, **11**,1880; e) J. Takagi, K. Takahashi, T. Ishiyama and N. Miyaura, *J. Am. Chem. Soc.*, 2002, **124**, 8001.
- 18 (a) T. Leermann, F. R. Leroux and F. Colobert, *Org. Lett.*, 2011, **13**, 4479; b) J. M. Murphy, C. C. Tzschucke and J. F. Hartwig, *Org. Lett.*, 2007, **9**, 757.
- 19 M. Curini, F. Epifano, S. Genovese, M. C. Marcotullio and O. Rosati, *Org. Lett.*, 2005, **7**, 1331.
- 20 (a) P. T. Nyffeler, S. G. Duron, M. D. Burkart, S. P. Vincent and C. H. Wong, *Angew. Chem.*, 2005, **117**, 196; b) A. Khazaei, S. Rahmati, A. K. Nezhad and S. Saednia, *J. Fluorine Chem.*, 2012, **137**, 123; c) G. R. Krow, D. Gandla, W. Guo, R. A. Centafont, G. Lin, C. D. Brosse, P. E. Sonnet, C. W. Ross, H. G. Ramjit and K. C. Cannon, *J. Org. Chem.*, 2008, **73**, 2122.
- 21 R.R. Rajawinslin, M. J. Raihan, D. Janreddy, V. Kavala, C.-W. Kuo, T.-S. Kuo, M.-L. Chen, C.-H. He and C.-F. Yao, *Eur. J. Org. Chem.*, 2013, 5743; b) R. R. Rajawinslin, M. J. Raihan, D. Janreddy, V. Kavala, C.-W. Kuo, T.-S. Kuo, M.-L. Chen, C.-H. He and C.-F. Yao *Tetrahedron*, 2014, **70**, 7505.
- 22 (a) M. J. Raihan, V. Kavala, Q. Z. Guan, C.-W. Kuo, S. Kataria, S. Shishodia, D. Janreddy, P. M. Habib and C.-F. Yao, *Adv. Synth. Catal.*, 2012, **354**, 2251; b) M. J. Raihan, R. R. Rajawinslin, V. Kavala, C.-W. Kuo, T.-S. Kuo, C.-H. He, H. N. Huang and C.-F. Yao, *J. Org. Chem.*, 2013, **78**, 8872.
- 23 (a) G. K. S. Prakash, T. Mathew, D. Hoole, P. M. Esteves, Q. Wang, G. Rasul and G. A. Olah, *J. Am. Chem. Soc.*, 2004, **126**, 15770; b) H. Wu and J. Hynes, Jr., *Org. Lett.*, 2010, **12**, 1192.
- 24 CCDC numbers 1050602 (**4a**) and 1052475 (**5f**), contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Graphical abstract

An efficient iron/acetic acid mediated intramolecular reductive cyclization protocol was developed for the synthesis of novel 6,7-dihydrobenzo[*b*,*l*]1,7] phenanthroline derivatives.

