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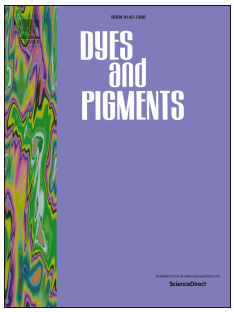

Synthesis, Photophysical and Acidochromic Properties of a Series of Tetrahydrodibenzo[a,i]phenanthridine Chromophores

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Synthesis, Photophysical and Acidochromic Properties of a Series of Tetrahydrodibenzo[a,i]phenanthridine Chromophores

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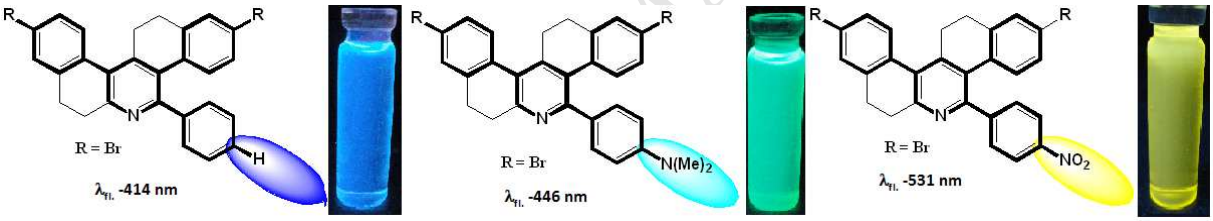
Graphical abstract



Abstract

A series of luminescent 5-aryl-tetrahydrodibenzo[a,i]phenanthridines was developed through modified synthetic protocol using $SnCl_2$- acetic acid as a catalyst. The synthesis was consistent with various functionalities and significantly improves the yields. These derivatives exhibit large molar absorption coefficients and higher Stokes shift values in the range 9739-2628 cm^{-1}. The donor and acceptor groups significantly induced the charge transfer character leading to widespread emission properties in the range of 390-531 nm with moderate quantum yields. The protonation and quaternization studies of these derivatives revealed the formation of a new red

shifted absorption band followed by hyperchromic effect in emission, which could be used as an acidochromic sensor.

1. Introduction

Phenanthridine structure is one of the most important core structures found in a variety of natural products and biologically important molecules with a wide range of biological activities including antibacterial, antiprotozoal, antitumor and antiviral activities [1-3]. In addition, the high charge mobility of this heterocyclic system provides pronounced photoconducting, optoelectrical switching, and photovoltaic properties [4-6], which are key features in the field of laser dyes, sensors and electroluminescence [7-9]. The kind of functional groups those can be tolerated is limited in the Bischler-Napieralski cyclization [10-12] since this method uses P_4O_{10}, $POCl_3$, or PCl_5 at elevated temperature, most of the reported methods require multi-step synthesis, metal catalysts, strict anhydrous conditions and offered poor yields and low diversity [13-17]. Thus, there is a pressing need for more efficient, versatile and simpler synthetic methods for the construction of phenanthridine based scaffolds.

Organic light emitting compounds have attracted immense research interest on account of their potential applications in organic light-emitting diodes (OLEDs), solar cells, laser dyes, photosensitizers, biomolecular labels, and molecular probes [18-20]. The development of such luminescent materials, based on highly conjugated species such as polycyclic aromatic hydrocarbons, has contributed to applications in optoelectronic devices and thin film transistors. The most prominently known species, including rhodamine, squaraine, cyanine, pyrazoline, quinoline, imidazopyridine and bodipy derivatives, have been extensively studied [21-27]. Besides, fluorophores incorporating donors and acceptors bound to an extended π-conjugated chelate have been profoundly studied for various applications ranging from biological sensing

and imaging to the search for new electroluminescent devices [28-31]. These molecules with ring-fused structures have attracted notable attention because their flat and rigid-π-conjugated skeletons bring about a set of desired properties such as intense luminescence, good thermal stability and high carrier mobility that are important in terms of their applications in high performance optoelectronics [32-36]. Rigid structures can effectively restrict molecular rotations, which usually cause serious fluorescence quenching and flat π-conjugated skeletons. This may facilitate charge transport due to intermolecular π-electron delocalization. Introducing suitable donor and acceptor groups in this type of π-plane have proved to be an efficient way to tune their photophysical properties.

In the construction of these light emitting materials, tunable emission color and high solid-state quantum efficiency are two important issues in terms of optoelectronic applications of materials. As far as the fluorescence efficiency is concerned, several fluorophores give out a strong emission when dissolved in solvents and they become weak fluorophores in the solid state due to either attractive dipole–dipole interactions or intermolecular π-stacking [37-38]. Consequently, these can be used as solid forms in most of the applications. However, the modality of the quenching process is much more important.

Recent literature demonstrates the continuous investigation for fashionable molecules with exceptional fluorescence properties, and significant promise has been seen in donor-π-acceptor conjugated molecules. Herein, we implemented this strategy to obtain a family of fluorophores based on tetrahydrodibenzo[a,i]phenanthridine moieties [39-41]. Synthesized derivatives resembled with 2,3,5-triphenylpyridine (**2,3,5TPP**) and the phenyl groups at 3rd and 5th position of pyridine cyclizes *via* ethane bridge to 4th and 6thposition and forms 5-aryl-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridines (**THDPs**) (Chart 1). Owing to the ethane bridge,

the phenyl ring rigidity in structures increased. This can effectively restrict molecular rotations and flat-π-conjugated skeletons may facilitate π-electron delocalization. The photophysical properties of phenanthridine moieties have recently attracted significant attention [42-43] but the optical studies of **THDPs**have not been reported so far. In this report, we describe the synthesis and optical properties of light emitting **THDPs** in one-pot reaction of substituted benzaldehydes, ammonium acetate and 2-tetralone using catalytic amount of $SnCl_2$ in good yields.

2. Results and discussion

2.1 Synthesis and optimization

Initially, the reaction of 6-bromo-2-tetralone (**6Br2T**) (2 mmol), benzaldehyde (1 mmol) and ammonium acetate (1 mmol) in ethanol was examined in the presence of catalytic amount of various Lewis acids $ZnCl_2$, $FeCl_3$,CuCl, $CuCl_2$, $Cu(Ac)_2$, CAN, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$, $MnCl_2.4H_2O$, $LaCl_3$, $SnCl_4$, and $SnCl_2.2H_2O$ (Table 1). The formation of the mixture of two products was observed in most of the cases. Interestingly, we ended up with **THDP** (**5a)** up to 40 % yield in 24 h, in the presence of $SnCl_2.2H_2O$. For the optimization and identification of the suitable solvent and effective reaction conditions, **6Br2T**, benzaldehyde, ammonium acetate and 10 mol% of catalyst were selected as prototype. Among the chosen solvents, EtOH was considered the best for the synthesis of phenanthridines. Although acetonitrile, methanol and isopropanol allowed the reaction to take place at a faster rate, the yield was lesser than the yield obtained using EtOH as solvent. THF, DCM, dioxane and DMF gave low yields along with side products, and no desired product was obtained with water and toluene. In order to examine the role of additives, we performed the same reaction with different additives in ethanol. For this, we employed 15 mol% catalyst and 1equivalent of additive as a model reaction in ethanol at room temperature. Interestingly, there was significant change in the reaction time and yield when we

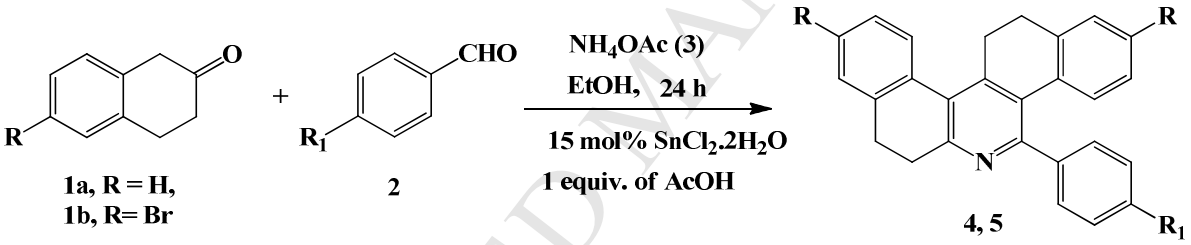
used acetic acid as an additive in the presence of $SnCl_2$. Then, we thought it would be of interest to know the catalytic activity of $SnCl_2$ to synthesize substituted phenanthridines by this MCR in the presence of acetic acid. For this, one equivalent of benzaldehyde was treated with ammonium acetate in ethanol and warmed in water bath for 5 min to form aldimine *in situ*. Similarly; two equivalents of **6Br2T** and one equivalent of acetic acid in ethanol were mixed separately and warmed to form binapthalenone. The aldimine and binapthalenone, thus obtained, were mixed together in the presence of catalyst and warmed for 5 min. This was kept aside for 24 h after which it gave a yield up to 74%.

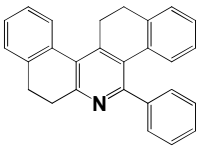
To our knowledge, we identified one report in literature for the synthesis of **THDPs** with moderate yields [39]. But in the present protocol, we obtained excellent yields up to 64% with 15mol% of $SnCl_2$ and 1equivalent of acetic acid under the optimized reaction conditions. After finding the optimal conditions for the three components (**1–3**) one-pot reaction, we carried out these reactions with a diverse range of aromatic aldehydes and tetralones to explore the generality of the reaction, which tuned the photophysical properties as shown in Scheme 1. The reaction between 2-tetralone (**2T**) and substituted benzaldehydes gave moderate to good yields in catalyst-free conditions. When the reaction was carried out with **6Br2T**, low yields were obtained under catalyst-free conditions (**5a**, **5c** and **5h**) however moderate to good yields were obtained under catalytic conditions, and excellent yields were achieved with **2T** (**4a**, **4d** and **4h**). In case of **2T**, electron donating groups bearing aldehydes gave lower yields compared to electron withdrawing groups as well as parent in contrast to **6Br2T**. Overall, good yields were obtained in **2T** compared to **6Br2T**, synthesized derivatives and their yields were given in Scheme 1. Furthermore, with this effective catalytic system, we synthesized phenanthridine derivatives irrespective of position of the substituents in aldehyde system. The **THDPs** structures

were confirmed by the FTIR, ^{1}H NMR, ^{13}C NMR, HRMS analysis and X-ray crystallography. The single crystal of **4g** was grown in 1:1ethanol and THF solvent mixture, and X-ray crystallographic structure is given in Fig. 1. Details of the experimental procedures and data for structural characterization are disclosed in the Supporting Information (SI). In addition, these compounds were strongly fluorescent in the solution state due to an intramolecular charge transfer (ICT) process.

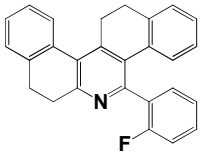
Scheme 1. Synthesis of substituted **THDPs** using $SnCl_2$ as catalyst.

(*) Yields were obtained without $SnCl_2$ was given in brackets for compounds **4a**, **4d**, **4h**, **5a**, **5c** and **5f.**

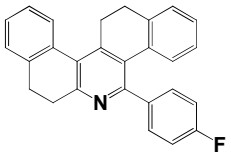




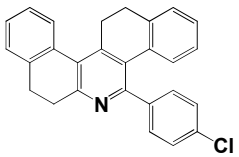
4a, 89% (85%)*



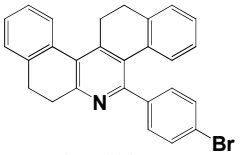
4b, 79%



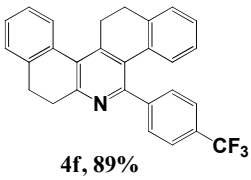
4c, 88%



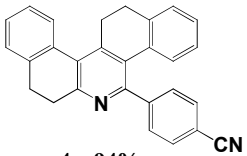
4d, 89% (74%)*



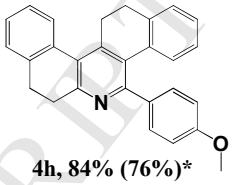
4e, 79%



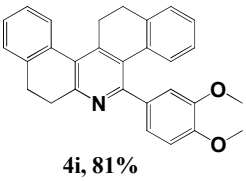
4f, 89%



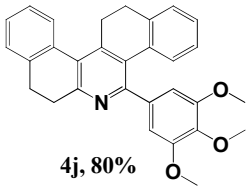
4g, 94%



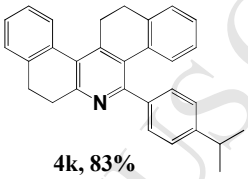
4h, 84% (76%)*



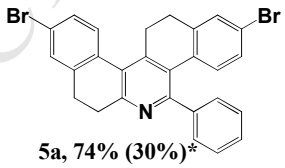
4i, 81%



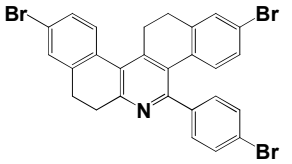
4j, 80%



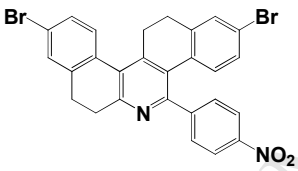
4k, 83%



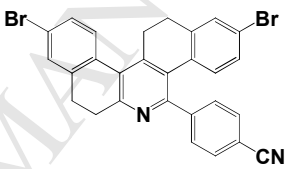
5a, 74% (30%)*



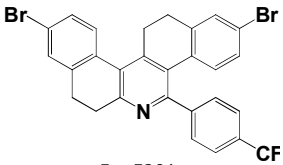
5b, 49%



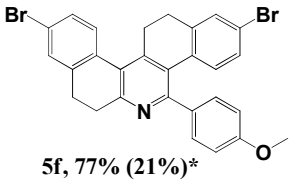
5c, 59% (15%)*



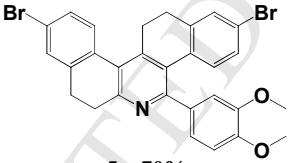
5d, 58%



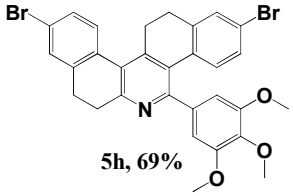
5e, 59%



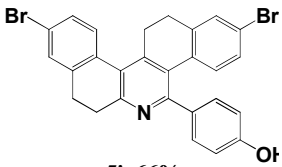
5f, 77% (21%)*



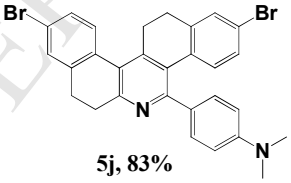
5g, 70%



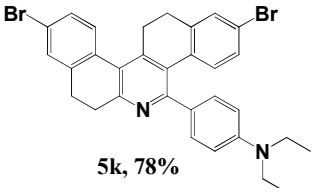
5h, 69%



5i, 66%



5j, 83%



5k, 78%

2.2 Photophysical studies

Since the optical properties of compounds possessing the THDPs have not been extensively explored, we decided to study the absorption and emission characteristics of dyes (Table 2). The photophysical properties of the prepared compounds were thoroughly investigated by UV/Vis and fluorescence spectroscopy in $CHCl_3$ at room temperature, as shown in Fig. 2. The UV/Vis spectra showed strong absorption bands at λ_{max} = 262-300 nm, and these were accompanied in all cases by two to three distinct, broad, structure less maxima at lower energy with molar absorption coefficients (ε) ranging from 3200 to 100000 L/mol.cm (Table 2). In general, the lower energy absorption band of **2T** derivatives (**4a-4k**) were blue shifted compared to **6Br2T** derivatives (**5a-5k**), which could be attributed to the presence of bromine on fused phenanthridine moiety, slightly inducing the structural perturbations in ground state through donor-acceptor nature.

The addition of appropriate substituents known to enhance intramolecular charge transfer (ICT) character, aided **THDPs** derivatives to emitted strong fluorescence in the blue-green-yellow region (390−531 nm). Predominantly large Stokes shift values of 9739-2628 cm^{-1} except **5j** and **5k** (854 and 151 cm^{-1}) were obtained for the compounds under investigation. As observed in related structures, this phenomenon indicates large differences (vibrational, electronic, geometric) between the Franck−Condon state and the excited state. Notably, the solid state emission maxima of **4a-4k** were red shifted when compared to solution with the exception of **4g**, which was blue shifted by 10 nm. On the contrary, the solid state emission maxima of **5a-5k** were blue shifted when compared to that of the solution with the exception of **5a**, **5j** and **5k**, which were red shifted. The solid state fluorescence spectra of selected compounds are given in Fig. 3. Fluorescence quantum yields (Φ_F) were determined in solution using quinine sulfate as

reference Φ_F = 0.55 in H_2SO_4 1 N, λ_{ex} = 366 nm for dyes and it is clear that all the derivatives exhibit low to moderate quantum yields.

Further, the nature of the functional groups present on the phenanthridine moiety significantly tuned the optical properties of these derivatives. For example, the emission maxima of **4h** (415 nm) and **4k** (421 nm) were slightly red shifted by 8 and 14 nm when compared to that of **4a** (407 nm) shown in Fig. 1a & 2a. In fact, phenanthridines **5j** and **5k** possessing dialkyl amino groups displayed bathochromically shifted absorptioncompared to dye **5a**. A similar trend was observed for fluorescence, although the emission maximum of compound **5f** and **5i** possessing methoxy and hydroxyl groups were in the same region as **5j** and **5k** having amine groups (i.e., 446 nm and 447 nm), dyes **5j** and **5k** lead to the lowest Stokes shift in this library (**5j**: 854 and **5k**: 151 cm^{-1}). The corresponding trend was not observed for electron withdrawing groups of compounds **5d** (434 nm) and **5e** (419 nm) which possessed cyano and trifluoromethyl groups and they were in the different emission region to that of nitro **5c** (i.e., 531 nm), which exhibited highest Stokes shift in this library (9739 cm^{-1}) as shown in Fig. 1b & 2b. However, the effect of halogen groups on the photophysical properties of these derivatives was not significant. Obviously, increasing the number of methoxy groups in phenanthridines **4h-j** had no considerable impact on their optical properties, indeed the presence of an additional methoxy groups in **5f-h** dyes triggered color change from blue to green region which could be detected by hand held UV-lamp (λ=365 nm) even though there is no much changes in emission maxima (Fig. 6). This observation helped us to conclude that the incorporation of donor and acceptor groups lead to increase in ICT character. Based on the above results we have developed 5-substituted-tetrahydrodibenzo[a,i]phenanthridines based D-π-A chromophore that exhibit sensor applications and the detailed studies are under progress.

2.3 Protonation studies

It has been previously demonstrated that 4,6-bis(arylvinyl)pyrimidines, 4-arylvinyl-2,6-di-(pyridine-2-yl)pyrimidines, quinazolines and diazine derivatives could function as a colorimetric and luminescent pH sensor due to the basic character of their nitrogen atom/s of the heterocycles [44-46]. Similarly, the nitrogen atom located on the pyridine ring of phenanthridine had basic character, and therefore we demonstrated the ability of related phenanthridines to function as a colorimetric and luminescent pH sensor. The phenanthridines described in this paper showed significant absorbance and luminescence changes in $CHCl_3$ solutions upon the addition of trifluoroacetic acid (TFA), and these changes were reversible on neutralization with base triethylamine (TEA).

The changes observed in the UV−vis spectra of **4a** upon addition of TFA are illustrated in Fig 4. The UV-Vis spectra of compound **4a** (60 μM) exhibited an intense absorption band at 267 nm with a shoulder at 317 nm, ascribed to the phenanthridine moiety. An increase in the concentration of TFA led to the progressive attenuation of the absorption band for the neutral compound and the appearance of a new, red shifted band corresponded to the protonated species (see the Supporting Information for spectra of compounds **4g** and **4h**). In addition, we observed a decrease and a slight red shifting of the absorption band from 267 nm to 279 nm, and the appearance of a new band at 335 nm along with the formation of isobestic points at 310 and 322 nm. This bathochromic shift of the absorption band and the formation of the new band could be attributed to generation of protonated species of compound **4a**, which facilitates intramolecular charge transfer (ICT) from the donor to the phenanthridine moiety.

In Fig. 5, compound **4a** (60 μM) exhibits an emission band at 407 nm with a Stokes shift of 90 nm, when excited at 317 nm. This fluorescence emission was probably due to the lone pair

of electrons on the nitrogen atom in conjugation with the phenyl group. Upon addition of TFA (0–100 equiv.), unlike quenching in diazines, a four fold increase with 5 nm red shift of the fluorescence emission band at 412 nm was observed along with the change in fluorescence intensity from light to dark blue (inset, Fig. 5). Similar results were obtained when an electron donor on phenyl ring such as –MeO (**4h**) was specifically employed (ESI, Fig. S6). Further, the UV-vis and emission intensity of compound **4g** was not significantly affected as a function of the TFA concentration (ESI, Fig. S6). Thus, from these results we conclude that the acid induced protonation of compound **4a** amplified the phenomenon responsible for the observed fluorescence hyperchromic effect. The absorbance and emission changes of selected neutral and protonated species are disclosed in Table 3 (Fig. 6). From Table 3, it is clear that compounds **5j** and **5k** show fluorescence quenching upon addition of acid which was assigned to disorganization of protonated species by second protonation at dialkylamino functionality consequently disrupting the ICT nature.

2.4 Quaternization studies

Owing to the lone pair of electrons located on nitrogen atom/s of the pyridine ring in phenanthridine, it exhibits fluorescence in both solid and dissolved solutions. Hence, it was employed as cell permeant and fluorescing DNA Probes [47]. Quaternization of nitrogen atom or the use of lone pair of electrons significantly alters the optical properties of these derivatives. Hence, we demonstrated the utility of lone pair of electrons as a function of quaternization of nitrogen atom using boron trifluoride. The changes observed in the absorption and emission spectra of **4a** (60 μM) upon addition of boron trifluoride are illustrated in Fig. 7. The increase in concentration of BF_3 showed progressive changes in the absorption band for the neutral compound followed by the appearance of a new red shifted band attributed to the quaternized

species. In addition, a decrease and slight red shifting of the absorption band from 267 nm to 283 nm and the formation of a new band at 345 nm was observed along with the formation of isobestic points at 324 nm. As far as fluorescence response is concerned, upon addition of BF_3 (0–10 equiv.), a fivefold increase in the fluorescence emission i.e. hyperchromic band at 416 nm was observed along with a fluorescence color change from light to dark blue. Further, the applications of these quaternized species in the field of fluorescence based sensors are studying in detail in our laboratory.

3. Conclusions

In summary, we have developed $SnCl_2$ catalyzed modified synthetic protocol for the synthesis of 5-aryl-tetrahydrodibenzo[a,i]phenanthridines in moderate to good yields. These derivatives were highly fluorescent in both solid and solution with large molar absorption coefficients and exhibited higher Stokes shift values. Further, the donor and acceptor groups present on these derivatives significantly altered their optical properties and were also necessary to induce the charge transfer character. An unsubstituted dye **5a** emitted deep blue emission at 414 nm. Considerably, the bathochromically shifted emission of 33 nm for **5j** was observed with respect to dye **5a**, where **5j** consisted of an electron donating group such as dimethyl amine. This was more pronounced in the case of **5c**, possessing strong electron withdrawing nitro group in which 116 nm red shifted yellow emission was observed. Increasing the methoxy groups in phenanthridines **4h-j** and **5f-h** did not have considerable impact on their emission maxima; however **5f-h** showed significant color change from blue to green region which could be attributed to increasing ICT character. Further, the protonation and quaternization species of these derivatives showedhyperchromic effect in emission, which can virtually be used in fluorescence-based sensor applications.

4. Experimental section

4.1 General information

All organic chemicals and solvents were purchased from Sigma Aldrich, SDFine and they were used without further purification. ^{1}H and ^{13}C NMR spectra were taken on Bruker 300 MHz using $CDCl_3$ as the solvent with TMS as an internal standard. Melting points were measured on Microprocessor based melting point apparatus and were not corrected. HRMS values were obtained on Joel GC Mate II GC- Mass Spectrometer. FTIR spectra of the synthesized organic compounds were recorded using a Jasco-4100 spectrometer instrument. UV-Visible spectra were taken using Hitachi U-2910 spectrophotometer. Fluorescence spectra in solution and solid were measured using Hitachi F-7000 fluorescence spectrometer. The fluorescence quantum yields (Φ_F) were measured with quinine sulfate (Φ_F) 0.55 in 1N H_2SO_4 solution as a standard, λ_{ex} = 366nm. Analytical Thin-layer chromatography (TLC) was performed on pre-coated plates (Merck, silica gel 60 F254). Silica gel (60-120 mesh) was used for column chromatography. Single crystal X–ray diffraction data were taken on Bruker kappa APEXII. The structures were solved by direct methods.

4.2 General procedure for the preparation of compound 4a-k.

A mixture of substituted benzaldehydes **(2)** (10 mmol) and ammonium acetate **(3)** (11 mmol) was taken in a 100ml conical flask containing 10ml absolute ethanol at room temperature, sealed and warmed using water bath for 5min until the dissolution of the solid contents. After bringing the reaction mixture to room temperature, 15 mol% $SnCl_2$, 1equivalent acetic acid and 2-tetralone **(1)** (20 mmol) were added, sealed, and the mixture was warmed for 5 min. The reaction mixture was then kept aside for 24 h in open air. After the completion of the reaction as monitored by TLC, the resulting product was purified by column chromatography over silica gel

(60-120 mesh) using n-hexane and ethyl acetate mixture (9:1) as eluent to give the compounds (**4a-k**). The solid thus obtained was further purified by recrystallizing in 1:1 ethanol and tetrahydrofuran mixture.

5-phenyl-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine (4a):

White solid; Melting point: 223-225 ^{o}C: IR (KBr): 3066, 3034, 2960, 2929, 2831, 2326, 1737, 1544, 1487, 1425, 1396, 1290, 1089, 945, 835, 759, 744, 617 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.79-2.75 (t, *J* =8.0 Hz, 2H), 2.97-2.93 (t, *J* =8.0 Hz, 2H), 3.16-3.08 (m, 4H), 6.88-6.87 (d, *J* =4.0 Hz, 2H), 7.13-7.09 (m, 1H), 7.36-7.24 (m,7H), 7.46-7.43 (dd, *J* = 16.0, 4.0 Hz, 2H), 7.52-7.50 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.2, 29.5, 29.6, 33.2, 125.6, 126.0, 126.9, 126.9, 127.5, 127.7, 127.8, 127.9, 128.4, 128.7, 128.8, 129.7, 129.8, 133.0, 133.1, 138.7, 139.7, 142.1, 145.7, 154.0, 158.1; HRMS for $C_{27}H_{21}N$ Calculated [M^{+}] m/z 359.1674, Found 359.1660.

5-(2-fluorophenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4b):

Yellow solid; Melting point: 249-251 ^{o}C: IR (KBr): 3076, 3020, 2952, 2904, 2881, 2837, 2326, 1739, 1544, 1490, 1454, 1433, 1423, 1394, 1301, 1215, 1155,1080, 945, 806, 744 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.77-2.73 (t, *J* =8.0 Hz, 2H), 3.28-2.95 (m, 6H), 6.90-6.88 (m, 2H), 6.99-6.95 (t, *J* =8.0 Hz, 1H), 7.16-7.12 (m, 1H), 7.37-7.22 (m, 6H), 7.55-7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.1, 29.4, 29.5, 33.1, 115.9, 116.1, 124.6, 124.7, 125.9, 126.1, 127.0, 127.2, 127.3, 127.8, 127.9, 128.2, 128.8, 129.8, 129.9, 130.1, 130.2, 130.5, 131.7, 131.8, 132.9, 133.2, 138.7, 139.7, 145.2, 148.3, 158.2, 158.4, 160.9; HRMS for $C_{27}H_{20}FN$ Calculated [M^{+}] m/z 377.1580, Found 377.1580.

5-(4-fluorophenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4c):

Pale yellow solid; Melting point: 216-218 ^{o}C: IR (KBr): 3055, 3019, 2945, 2833, 2326, 1745, 1600, 1504, 1454, 1392, 1217, 1091, 999, 950, 839, 744, 617, 484 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.70-2.67 (t, *J* =6.0 Hz, 2H), 2.89-2.86 (t, *J* =6.0 Hz, 2H), 3.01-2.98 (t, *J* =6.0 Hz, 2H), 3.07-3.04 (t, *J* =6.0 Hz, 2H), 6.83-6.78 (m, 2H), 6.96-6.92 (t, *J* =8.0 Hz, 2H), 7.07-7.03 (t, *J* =8.0 Hz, 1H), 7.27-7.16 (m, 4H), 7.37-7.33 (t, *J* = 8.0, 1H), 7.43-7.41(d, *J* =8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm:29.2, 29.4, 29.5, 33.2, 115.2, 115.4, 125.7, 126.1, 127.0, 127.1, 127.6, 127.7, 127.9, 128.7, 128.8, 129.5, 131.6, 131.7, 132.8, 132.9, 138.0, 138.1, 138.7, 139.6, 145.8, 152.7, 158.2, 161.4, 163.9; HRMS for $C_{27}H_{20}FN$ Calculated [M^+] m/z 377.1580, Found 377.1588.

5-(4-chlorophenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4d):

Yellow solid; Melting point: 239-241 ^{o}C: IR (KBr): 3066, 3037, 2960, 2929, 2879, 2831, 2326, 1942, 1911, 1743, 1658, 1537, 1487, 1425, 1394, 1344, 1290, 1089, 1001, 835, 773, 617 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.78-2.75 (t, *J* =6.0 Hz, 2H), 2.97-2.94 (t, *J* =6.0 Hz, 2H), 3.09-3.06 (t, *J* =6.0 Hz, 2H), 3.15-3.12 (t, *J* =6.0 Hz, 2H), 6.90-6.88 (d, *J* =8.0 Hz, 1H), 6.95-6.91 (t, *J* =8.0 Hz, 1H), 7.16-7.12 (t, *J* =8.0 Hz, 1H), 7.41-7.25 (m, 8H), 7.51-7.49 (d, *J* = 8.0, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.2, 29.4, 29.5, 33.2, 125.8, 126.1, 127.0, 127.2, 127.8, 127.8, 127.9, 128.6, 128.7, 128.9, 129.6, 131.31, 132.7, 132.9, 133.8, 138.7, 139.7, 140.5, 145.8, 152.5, 158.3; HRMS for $C_{27}H_{20}ClN$ Calculated [M^+] m/z 393.1284, Found 393.1286.

5-(4-bromophenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4e):

Yellow solid; Melting point: 223-225 ^{o}C: IR (KBr): 3063, 3027, 2966, 2927, 2879, 2822, 2329, 1922, 1910, 1741, 1638, 1534, 1481, 1415, 1374, 1340, 1291, 1099, 964, 831, 753, 611cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.78-2.75 (t, *J* =6.0 Hz, 2H), 2.96-2.93 (t, *J* =6.0 Hz, 2H), 3.07-3.05 (t, *J* =4.0 Hz, 2H), 3.13-3.09 (t, *J* =8.0 Hz, 2H), 6.90-6.88 (d, *J* =8.0 Hz, 1H), 6.95-6.91 (t,

J =8.0 Hz, 1H), 7.16-7.12 (t, *J* =8.0 Hz, 1H), 7.35-7.24 (m, 6H), 7.46-7.44 (d, *J* = 8.0, 2H), 7.51-7.49 (d, *J* = 8.0, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.2, 29.4, 29.5, 33.1, 122.1, 125.8, 126.1, 127.0, 127.2, 127.8, 127.8, 127.9, 128.7, 128.9, 129.5, 131.5, 131.6, 132.7, 132.9, 138.7, 139.6, 141.0, 145.9, 152.5, 158.3; HRMS for $C_{27}H_{20}BrN$ Calculated [M^+] m/z 437.0779, Found 437.0758.

5-(4-(trifluoromethyl)phenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4f):

Yellow solid; Melting point: 200-202 ^oC: IR (KBr): 3064, 3033, 2953, 2841, 2326, 1735, 1689, 1614, 1541, 1429, 1396, 1321, 1309, 1168, 1153, 1097, 1018, 950, 835, 765, 671 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.81-2.78 (t, *J* =6.0 Hz, 2H), 2.98-2.95 (t, *J* =6.0 Hz, 2H), 3.10-3.07 (t, *J* =6.0 Hz, 2H), 3.18-3.15 (t, *J* =6.0 Hz, 2H), 6.84-6.82 (d, *J* =8.0 Hz, 1H), 6.94-6.90 (t, *J* =8.0 Hz, 1H), 7.18-7.14 (t, *J* =8.0 Hz, 1H), 7.38-7.25 (m, 4H), 7.53-7.51 (d, *J* = 8.0, 1H), 7.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.1, 29.4, 29.5, 33.1, 125.3, 125.4, 125.6, 125.9, 126.2, 127.1, 127.4, 127.9, 127.9, 128.1, 128.8, 129.2, 129.6, 129.9, 130.3, 132.4, 132.8, 138.8, 139.7, 145.7, 145.9, 152.2, 158.4; HRMS for $C_{28}H_{20}F_3N$ Calculated [M^+] m/z 427.1548, Found 384.1555.

4-(7,8,13,14-tetrahydrodibenzo[a,i]phenanthridin-5-yl)benzonitrile(4g):

White yellow solid; Melting point: 272-274 ^oC: IR (KBr): 3053, 3037, 2947, 2897, 2839, 2326, 2222, 1735, 1604, 1541, 1425, 1394, 1290, 1157, 1107, 947, 842, 742, 617, 559 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.80-2.77 (t, *J* =6.0 Hz, 2H), 2.97-2.94 (t, *J* =6.0 Hz, 2H), 3.09-3.06 (t, *J* =6.0 Hz, 2H), 3.17-3.13 (t, *J* =6.0 Hz, 2H), 6.79-6.77 (d, *J* =8.0 Hz, 1H), 6.94-6.90 (t, *J* =8.0 Hz, 1H), 7.19-7.15 (t, *J* =8.0 Hz, 1H), 7.38-7.25 (m, 4H), 7.53-7.50 (d, *J* = 12.0, 1H), 7.57-7.53 (d, *J* = 16.0 Hz, 2H), 7.63-7.59 (d, *J* = 16.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.1, 29.4, 29.5, 33.1, 111.4, 119.0, 125.9, 126.2, 127.3, 127.6, 128.0, 128.1, 128.4, 128.8, 129.3,

129.6, 130.7, 132.2, 132.6, 138.8, 139.7, 146.1, 146.7, 151.2, 158.6; HRMS for $C_{28}H_{20}N_2$ Calculated [M^+] m/z 384.1626, Found 384.1637.

5-(4-methoxyphenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4h):

Pale yellow solid; Melting point: 246-248 ^oC: IR (KBr): 3049, 3032, 2993, 2900, 2833, 2326, 1745, 1604, 1543, 1508, 1396, 1290, 1230, 1105, 1029, 879, 833, 746, 817, 586 cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) ppm: 2.77-2.74 (t, *J* =6.0 Hz, 2H), 2.95-2.92 (t, *J* =6.0 Hz, 2H), 3.08-3.06 (t, *J* =4.0 Hz, 2H), 3.13-3.09 (t, *J* =8.0 Hz, 2H), 3.82 (s, 3H), 6.87-6.85 (d, *J* =8.0 Hz, 2H), 6.93-6.89 (t, *J* =8.0 Hz, 1H), 6.97-6.95 (d, *J* =8.0 Hz, 1H), 7.13-7.09 (t, *J* =8.0 Hz, 1H), 7.35-7.23 (m, 4H), 7.40-7.38 (d, *J* = 8.0, 2H), 7.50-7.48 (d, *J* = 8.0, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.3, 29.5, 29.6, 33.2, 55.3, 113.8, 125.7, 126.0, 126.8, 127.1, 127.5, 127.8, 128.6, 128.7, 129.5, 131.1, 133.2, 133.3, 134.5, 138.7, 139.6, 145.7, 153.6, 158.1, 159.4; HRMS for $C_{28}H_{23}NO$ Calculated [M^+] m/z 389.1780, Found 389.1789.

5-(3,4-dimethoxyphenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4i):

White solid; Melting point: 188-190 ^oC: IR (KBr): 3067, 3019, 2962, 2891, 2835, 2326, 1743, 1694, 1510, 1452, 1413, 1394, 1271, 1249, 1222, 1138, 1126, 1026, 860, 804, 748 cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) ppm: 2.71-2.68 (t, *J* =6.0 Hz, 2H), 2.89-2.86 (t, *J* =6.0 Hz, 2H), 3.06-2.99 (m, 4H), 3.66 (s, 3H), 3.82 (s, 3H), 6.76-6.74 (d, *J* =8.0 Hz, 1H), 6.90-6.82 (m, 3H), 6.96-6.94 (d, *J* =8.0 Hz, 1H), 7.06-7.02 (t, *J* =8.0 Hz, 1H), 7.28-7.16 (m, 4H), 7.44-7.42 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.2, 29.5, 29.5, 33.2, 55.7, 55.9, 111.1, 113.2, 122.5, 125.6, 126.0, 126.8, 126.9, 127.27, 127.6, 127.8, 128.6, 129.5, 133.1, 133.2, 134.6, 138.6, 139.6, 148.6, 148.9, 153.5, 158.0; HRMS for $C_{28}H_{23}NO$ Calculated [M^+] m/z 419.1885, Found 419.1893.

5-(3,4,5-trimethoxyphenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4j):

White solid; Melting point: 218-220 ^{o}C: IR (KBr): 3047, 3008, 2939, 2899, 2873, 2829, 2326, 2301, 1737, 1579, 1502, 1454, 1392, 1367, 1344, 1263, 1126, 993, 761 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.72-2.68 (t, *J* =8.0 Hz, 2H), 2.90-2.87 (t, *J* =6.0 Hz, 2H), 3.09-2.01 (m, 4H), 3.46 (s, 6H), 3.78 (s, 3H), 6.59 (s, 2H), 6.91-6.87 (t, *J* =8.0 Hz, 2H), 7.07-7.03 (t, *J* =6.0 Hz. 1H), 7.30-7.16 (m, 4H), 7.44-7.42 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.2, 29.4, 29.5, 33.1, 56.0, 60.9, 107.2, 125.7, 126.1, 126.8, 127.0, 127.5, 127.7, 127.9, 128.7, 128.7, 129.5, 132.8, 133.0, 137.2, 138.0, 138.5, 139.6, 145.8, 153.1, 153.5, 158.0; HRMS for $C_{28}H_{23}NO$ Calculated [M^{+}] m/z 449.1991, Found 449.1997.

5-(4-isopropylphenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(4k):

White solid; Melting point: 176-178 ^{o}C: IR (KBr): 3046, 3032, 2958, 2873, 2837, 2326, 1745, 1541, 1427, 1396, 1288, 1228, 1051, 840, 759, 742, 623 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 1.26-1.24 (d, *J* =8.0 Hz, 6H), 2.78-2.75 (t, *J* =6.0 Hz, 2H), 2.96-2.88 (m, 3H), 3.10-3.07 (t, *J* =6.0 Hz, 2H), 3.15-3.12 (t, *J* =6.0 Hz, 2H), 3.82 (s, 3H), 6.90-6.86 (t, *J* =8.0 Hz, 1H), 6.95-6.92 (d, *J* =8.0 Hz, 1H), 7.13-7.09 (t, *J* =8.0 Hz, 1H), 7.19-7.17 (d, *J* = 8.0, 2H), 7.37-7.23 (m, 6H), 7.51-7.49 (d, *J* = 8.0, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 24.0, 29.2, 29.5, 29.5, 33.2, 33.9, 125.6, 126.0, 126.4, 126.8, 126.8, 127.2, 127.5, 127.8, 128.7, 129.6, 129.6, 133.1, 133.2, 138.6, 139.5, 139.70, 145.6, 148.5, 154.1, 158.0; HRMS for $C_{30}H_{27}N$ Calculated [M^{+}] m/z 401.2143, Found 401.2144.

4.3 General procedure for the preparation of compound 5a-k.

These compounds were prepared usingsubstituted benzaldehydes **(2)** (10mmol), ammonium acetate **(3)** (11mmol), 15 mol% $SnCl_2$, 1equivalent of acetic acid and 6-bromo-2-tetralone **(1)** (20 mmol) according to the similar procedure mentioned in **4a-k**.

2,10-dibromo-5-phenyl-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(5a):

Pale yellow solid; Melting point: 242-244 ^{o}C: IR (KBr): 3116, 3032, 2954, 2871, 2799, 2326, 1737, 1527, 1475, 1435, 1382, 1217, 1074, 821, 761, 696, 655, 617 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.77-2.74 (t, *J* =6.0 Hz, 2H), 2.94-2.90 (t, *J* =8.0 Hz, 2H), 3.09-3.05 (t, *J* =6.0 Hz, 4H), 6.72-6.70 (d, *J* =8.0 Hz, 1H), 7.01-6.99 (d, *J* =8.0 Hz, 1H) 7.35-7.33 (m, 4H), 7.45-7.40 (m, 4H), 7.50 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 28.9, 29.2, 29.2, 32.9, 120.9, 121.6, 126.8, 128.1, 128.3, 128.4, 128.6, 128.8, 129.2, 129.6, 129.8, 130.0, 130.9, 131.0, 131.6, 131.6, 131.8, 131.9, 140.7, 141.5, 141.8, 145.2, 154.2, 158.0;HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 514.9884, Found 514.9880.

2,10-dibromo-5-(4-bromophenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(5b):

Brown solid; Melting point: 295-297 ^{o}C: IR (KBr): 3089, 3006, 2956, 2899, 2841, 2326, 1734, 1726, 1678, 1587, 1475, 1381, 1274, 1186, 1093, 919, 792, 611 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.80-2.77 (t, *J* =6.0 Hz, 2H), 2.98-2.91 (m, 2H), 3.12-3.07 (m,4H), 6.78-6.76 (d, *J* =8.0 Hz, 1H), 7.11-7.09 (d, *J* =8.0 Hz, 1H), 7.38-7.34 (t, *J* =8.0 Hz, 3H), 7.53-7.43 (m , 5H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 28.9, 29.1, 29.1, 32.7, 121.3, 121.8, 122.6, 127.1, 128.2, 129.0, 129.3, 130.0, 130.0, 130.9, 130.9, 131.4, 131.6, 131.7, 140.7, 141.7, 145.6, 152.6, 158.1; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 596.1505, Found 596.1505.

2,10-dibromo-5-(4-nitrophenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(5c):

Yellow solid; Melting point: 262-264 ^{o}C: IR (KBr): 3117, 3030, 2954, 2839, 2345, 1726, 1589, 1512, 1475, 1377, 1342, 1282, 1083, 817, 674, 630, 616 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.80-2.77 (t, *J* =6.0 Hz, 2H), 2.95-2.90 (m, 2H), 3.12-3.02 (m,4H), 6.14-6.12 (d, *J* =8.0 Hz, 1H), 6.65-6.63 (d, *J* = 8.0 Hz, 1H), 6.91-6.89 (d, *J* =8.0 Hz, 1H), 7.52-7.31 (m,5H), 7.63-7.61 (d, *J* = 8.0 Hz, 1H), 8.22-8.20 (d, *J* = 8.0 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm:28.7, 28.9, 29.0, 29.1, 32.6, 32.8, 121.4, 121.8, 122.1, 123.8, 124.5, 126.2, 127.8, 128.8, 129.2, 129.3, 130.1,

130.7, 130.8, 130.8, 131.8, 140.6, 140.8, 141.6 ,141.8, 145.6, 146.2, 147.4, 147.5, 148.0, 151.4, 158.5, 158.8; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 559.9735, Found 559.9744.

4-(2,10-dibromo-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridin-5-yl)benzonitrile(5d):

White solid; Melting point: >300 ^oC: IR (KBr): 3111, 3018, 2954, 2841, 2326, 2171, 1741, 1531, 1475, 1381, 1274, 1228, 1186, 1093, 999, 825, 794, 613, 569 cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) ppm: 2.79-2.76 (t, *J* =6.0 Hz, 2H), 2.95-2.92 (t, *J* =6.0 Hz, 2H), 3.11-3.04 (m,4H), 6.65-6.63 (d, *J* =8.0 Hz, 1H), 7.07-7.04 (dd, *J* =16.8, 4.0 Hz, 1H), 7.36-7.34 (d, *J* =8.0 Hz, 1H), 7.47-7.45 (d, *J* =8.0 Hz, 2H), 7.52 (s, 1H), 7.57-7.55 (d, *J* =8.0 Hz, 2H), 7.66-7.64 (d, *J* =8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 28.7, 29.0, 29.1, 32.8, 111.7, 118.8, 121.7, 122.0, 127.6, 128.5, 129.1, 129.3, 130.0, 130.3, 130.6, 130.9, 131.0, 131.0, 131.4, 132.3, 140.8, 141.8, 145.5, 146.1, 151.7, 158.4; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 539.9837, Found 539.9833.

2,10-dibromo-5-(4-(trifluoromethyl)phenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(5e):

Yellow solid; Melting point: 296-298 ^oC: IR (KBr): 3102, 3015, 2954, 2895, 2835, 1763, 1529, 1477, 1381, 1315, 1290, 1170, 1118, 1107, 1093, 1060, 877, 817, 798, 626 cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) ppm: 2.79-2.76 (t, *J* =6.0 Hz, 2H), 2.95-2.91 (t, *J* =8.0 Hz, 2H), 3.11-3.04 (m,4H), 6.68-6.66 (d, *J* =8.0 Hz, 1H), 7.06-7.04 (d, *J* =8.0 Hz, 1H), 7.36-7.34 (d, *J* =8.0 Hz, 3H), 7.36-7.34 (d, *J* =8.0 Hz, 1H), 7.47-7.44 (d, *J* =8.0 Hz, 2H), 7.52 (s, 1H), 7.57-7.55 (d, *J* =8.0 Hz, 2H), 7.63-7.61 (d, *J* =8.0 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 28.8, 29.1, 29.2, 30.9, 32.8, 121.4, 121.9, 122.8, 125.5, 125.5, 127.4, 128.4, 129.0, 129.3, 129.9, 130.0, 130.1, 130.2, 130.9, 130.9, 131.2, 131.5, 140.7, 141.8, 145.1, 145.4, 152.4, 158.3; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 582.9758, Found 582.9760.

2,10-dibromo-5-(4-methoxyphenyl)-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridine(5f):

White solid; Melting point: 264-266 ^{o}C: IR (KBr): 3110, 3024, 2959, 2866, 1815, 1661, 1606, 1504, 1449, 1375, 1320, 1245, 1187, 1071, 978, 926, 748, 643 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.76-2.73 (t, *J* =6.0 Hz, 2H), 2.93-2.90 (t, *J* =6.0 Hz, 2H), 3.07-3.04 (t, *J* =6.0 Hz,4H), 6.81-6.79 (d, *J* =8.0 Hz, 1H), 6.89-6.87 (d, *J* = 8.0 Hz, 2H), 7.05-7.03 (d, *J* =8.0 Hz, 1H), 7.44-7.32 (m,4H), 7.49 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 28.9, 29.2, 29.2, 32.9, 55.3, 114.0, 120.8, 121.4, 126.4, 127.8, 128.9, 129.1, 129.8, 129.9, 130.8, 130.9, 131.0, 131.9, 132.1, 133.9, 140.6, 141.7, 145.2, 153.9, 158.0, 159.6; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 544.9990, Found 544.9990.

2,10-dibromo-5-(3,4-dimethoxyphenyl)-7,8,13,14-tetrahydrodibenzo[a,i] phenanthridine(5g):

White solid; Melting point: 232-234 ^{o}C: IR (KBr): 3104, 3057, 3010, 2971, 2831, 1799, 1589, 1512, 1462, 1417, 1382, 1332, 1251, 1172, 1028, 796 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.79-2.76 (t, *J* =6.0 Hz, 2H), 2.96-2.93 (t, *J* =6.0 Hz, 2H), 3.11-3.07 (m,4H), 3.81 (s, 3H), 3.93 (s, 3H), 6.86-6.81 (m, 2H), 6.99-6.97 (d, *J* =8.0 Hz, 1H), 7.01 (s, 1H) 7.08-7.06 (d, *J* =8.0 Hz, 1H), 7.37-7.35 (d , *J* =8.0 Hz, 1H), 7.42 (s, 1H), 7.47-7.45 (d , *J* =8.0 Hz, 1H), 7.53 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 25.6, 28.9, 29.2, 32.7, 55.8, 55.9, 67.9, 111.1, 112.9, 120.8, 121.6, 122.5, 126.6, 128.0, 128.9, 129.2, 129.8, 129.9, 130.8, 130.9, 131.8, 132.0, 133.7, 140.5, 141.7, 145.4, 148.9, 149.2, 153.7, 157.9; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 575.0096, Found 575.0090.

2,10-dibromo-5-(3,4,5-trimethoxyphenyl)-7,8,13,14-tetrahydrodibenzo[a,i] phenanthridine(5h):

White solid; Melting point: 271-273 ^{o}C: IR (KBr): 3101, 3019, 2941, 2897, 2831, 2335, 1737, 1583, 1506, 1463, 1423, 1390, 1236, 1124, 1103, 1001, 813, 696, 575 cm^{-1}: ^{1}H NMR (400 MHz,

$CDCl_3$) ppm: 2.77-2.74 (t, *J* =6.0 Hz, 2H), 2.94-2.91 (t, *J* =6.0 Hz, 2H), 3.09-3.06 (t, *J* =6.0 Hz, 4H), 3.74 (s, 6H), 3.89 (s, 3H), 6.63 (s, 2H), 6.82-6.80 (d, *J* =8.0 Hz, 1H), 7.09-7.07 (d, *J* =8.0 Hz, 1H) 7.35-7.33 (d, *J* =8.0 Hz, 1H), 7.40 (s, 1H), 7.46-7.44 (d , *J* =8.0 Hz, 1H), 7.51 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 28.8, 29.2, 32.8, 56.1, 60.9, 107.1, 120.9, 121.6, 126.9, 128.0, 128.9, 129.2, 129.8, 130.0, 130.9, 130.9, 131.7, 131.7, 136.7, 138.3, 140.5, 141.7, 145.2, 153.3, 153.8, 157.9; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 605.0201, Found 605.0206.

4-(2,10-dibromo-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridin-5-yl)phenol(5i):

White solid; Melting point: >300 ^{o}C: IR (KBr): 3333, 3097, 3002, 2949, 2337, 1737, 1724, 1608, 1587, 1514, 1479, 1392, 1274, 1215, 1002, 889, 867, 821, 798, 742, 615 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.76-2.73 (t, *J* =6.0 Hz, 2H), 2.91 (m, 4H), 3.05-3.02 (t, *J* =6.0 Hz, 2H), 6.75-6.72 (d, *J* =8.0 Hz, 2H), 6.79-6.77 (d, *J* = 8.0 Hz, 1H), 7.15-7.13 (d, *J* =8.0 Hz, 1H), 7.19-7.17 (d, *J* =8.0 Hz,2H), 7.56-7.50 (m,3H), 7.65 (s,1H), 9.63 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 28.2, 28.2, 32.2, 115.0, 119.9, 120.7, 125.4, 127.0, 128.2, 128.9, 129.7, 130.4, 130.4, 130.5, 130.9, 131.6, 131.9, 132.2, 141.3, 141.7, 145.4, 153.5, 157.3, 157.4; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 530.9833, Found 530.9830.

4-(2,10-dibromo-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridin-5-yl)-N,N-dimethylaniline(5j):

Pale green solid; Melting point: 243-245 ^{o}C: IR (KBr): 3114, 3022, 2970, 2831, 2326, 1737, 1606, 1514, 1475, 1427, 1384, 1371, 1338, 1313, 1255, 1186, 1089, 1068, 889, 817, 617 cm^{-1}: ^{1}H NMR (400 MHz, $CDCl_3$) ppm: 2.75-2.72 (t, *J* =6.0 Hz, 2H), 2.91-2.88 (t, *J* =6.0 Hz, 2H), 2.98 (s, 6H), 3.05-3.02 (m,4H), 6.68-6.66 (d, *J* =8.0 Hz, 2H), 6.93-6.91 (d, *J* = 8.0 Hz, 1H), 7.06-7.04 (d, *J* =8.0 Hz, 1H), 7.33-7.29 (t, *J* =8.0 Hz, 3H), 7.43-7.39 (t, *J* =8.0 Hz, 2H), 7.48 (s, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 29.0, 29.3, 32.9, 40.4, 112.2, 120.5, 121.2, 125.8,

127.5, 128.8, 129.1, 129.1, 129.7, 129.9, 130.7, 130.7, 130.9, 132.1, 132.6, 140.5, 141.7, 145.1, 150.4, 154.50, 157.96; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 586.0619, Found 586.0615.

4-(2,10-dibromo-7,8,13,14-tetrahydrodibenzo[a,i]phenanthridin-5-yl)-N,N-diethylaniline(5k):

Pale green solid; Melting point: >300 ^oC: IR (KBr): 3100, 3010, 2970, 2950, 2818, 2330, 1880, 1726, 1606, 1519, 1473, 1421, 1386, 1359, 1224, 1197, 1159, 1097, 997, 871, 813, 615, 578 cm^{-1}: ^1H NMR (400 MHz, $CDCl_3$) ppm: 1.18-1.15 (t, *J* =6.0 Hz, 3H), 2.75-2.72 (t, *J* =6.0 Hz, 2H), 2.91-2.88 (t, *J* =6.0 Hz, 2H), 3.06-3.01 (m,4H), 3.40-3.34 (q, *J* =6.0 Hz, 2H), 6.62-6.60 (d, *J* =8.0 Hz, 2H), 7.01-6.99 (d, *J* = 8.0 Hz, 1H), 7.07-7.05 (d, *J* =8.0 Hz, 1H), 7.43-7.25 (m, 5H), 7.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) ppm: 12.6, 29.0, 29.3, 29.3, 33.0, 44.4, 111.6, 120.4, 121.1, 125.5, 127.3, 128.1, 128.8, 129.0, 129.6, 129.9, 130.7, 130.9, 130.9, 132.2, 132.8, 140.5, 141.7, 145.0, 147.7, 154.6, 157.9; HRMS for $C_{27}H_{19}Br_2N$ Calculated [M^+] m/z 558.0306, Found 558.0309.

Supporting Information

^1H and ^{13}C NMR spectra for all compounds and Optical data were included. This material is available free of charge *via* the Internet at

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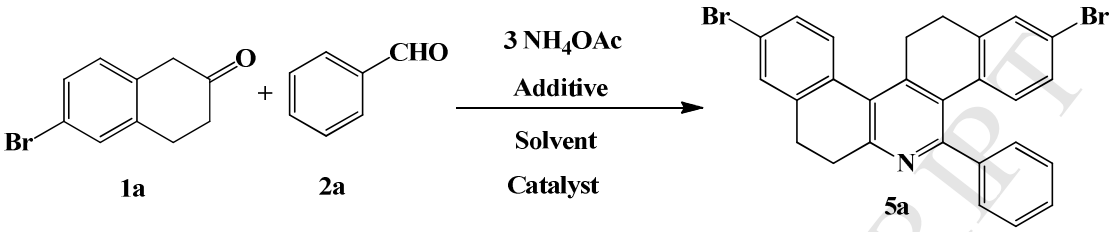
Tables

Table 1. Screening of reaction conditions for the one-pot synthesis of 5-aryl-tetrahydrodibenzo[a,i]phenanthridines.



1a 2a 5a

Entry	Catalyst	Additive	Mol%	Solvent	Time(h)	Yield(%)
1	$ZnCl_2$		10	EtOH	24	30
2	$FeCl_3$		10	EtOH	24	38
3	CuCl		10	EtOH	24	NDP
4	$CuCl_2$		10	EtOH	24	NDP
5	$Cu(Ac)_2$		10	EtOH	24	29
6	CAN		10	EtOH	24	28
7	$NiCl_2.6H_2O$		10	EtOH	24	30
8	$CoCl_2.6H_2O$		10	EtOH	24	26
9	$MnCl_2.4H_2O$		10	EtOH	24	22
10	$LaCl_3.6H_2O$		10	EtOH	24	31
11	$SnCl_4$		10	EtOH	24	40
12	$SnCl_2.2H_2O$	AcOH	1	EtOH	24	40
13	$SnCl_2.2H_2O$	AcOH	2	EtOH	24	44
14	$SnCl_2.2H_2O$	AcOH	5	EtOH	24	45
15	$SnCl_2.2H_2O$	AcOH	10	EtOH	24	50
16	$SnCl_2.2H_2O$	AcOH	12	EtOH	24	54
17	$SnCl_2.2H_2O$	AcOH	15	EtOH	24	74

18	$SnCl_2.2H_2O$	AcOH	20	EtOH	24	74
19	$SnCl_2.2H_2O$	AcOH	15	DMF	24	20
20	$SnCl_2.2H_2O$	AcOH	15	Dioxane	24	32
21	$SnCl_2.2H_2O$	AcOH	15	IPA	24	24
22	$SnCl_2.2H_2O$	AcOH	15	MeOH	24	51
23	$SnCl_2.2H_2O$	AcOH	15	CH_3CN	24	31
24	$SnCl_2.2H_2O$	AcOH	15	DCM	24	20
25	$SnCl_2.2H_2O$	AcOH	15	THF	24	17
26	$SnCl_2.2H_2O$	AcOH	15	Toluene	24	NDP
27	$SnCl_2.2H_2O$	Piperidine	15	EtOH	24	NDP
28	$SnCl_2.2H_2O$	NaOEt	15	EtOH	24	39
30	$SnCl_2.2H_2O$	Ag_2O	15	EtOH	24	31
31	$SnCl_2.2H_2O$	1N HCl	15	EtOH	24	41
32	$SnCl_2.2H_2O$	L-Proline	15	EtOH	24	NDP
33	$SnCl_2.2H_2O$	-	15	EtOH	24	40
34	No catalyst	-	-	EtOH	24	30
35	$SnCl_2.2H_2O$		15	Water	24	NDP

NDP = No Desired product.

Table 2. Optical properties of 5-aryl-tetrahydrodibenzo[a,i]phenanthridines in chloroform.

Compound	$\lambda_{abs.}$ nm (ε 10^3 $M^{-1}cm^{-1}$)	$\lambda_{fl.}$ nm $CHCl_3$	$\lambda_{fl.}$ nm solid	Stoke's shift cm^{-1}	$^a\Phi_{fl}$
4a	269 (99.9), 317 (39.7)	407	416	6,975	0.031
4b	269 (43.3), 292 (30.6), 323 (14.3)	398	413	5,834	0.057
4c	266 (30.9), 293 (19.4), 322 (12.1)	390	413	5,414	0.037
4d	269 (35.7), 293 (29.1), 329 (16.0)	420	433	6,585	0.061
4e	270 (37.8), 293 (29.0), 325 (18.4)	419	378, 456	6,902	0.062
4f	271 (87.5), 296 (64.8), 327 (36.7)	417	419, 504	6,600	0.140
4g	272 (96.7), 284 (86.1), 326 (51.4),	432	422	7,526	0.519
4h	269 (99.9), 325 (55.7), 373 (18.9)	415	441	2,713	0.071
4i	262 (60.2), 324 (35.6)	414	415	6,709	0.137
4j	271 (59.2), 321 (27.8)	417	358	7,171	0.139
4k	269 (99.9), 293 (76.8), 359 (17.4)	421	436	4,102	0.044
5a	293 (99.7), 343 (37.9)	414	425	5000	0.046
5b	269 (48.0), 323 (24.0)	417	410	6,978	0.076
5c	288 (65.1), 350 (22.9)	531	465,507	9,739	0.015
5d	293 (99.1), 348 (28.7), 399 (3.2)	434	418	2,021	0.250
5e	290 (61.5), 346 (15.0)	419	405,478	5,035	0.047
5f	300 (99.9), 361 (52.4)	436	411	4,765	0.084
5g	284 (99.6), 342 (35.1), 375 (23.3)	416	405	2,628	0.174
5h	280 (99.9), 374 (25.0)	420	422	2,928	0.147
5i	286 (100.0), 367 (29.9)	434	-	4,206	0.050
5j	281 (100.0), 430 (29.5)	446	495	834	0.179

5k	285 (100.0), 444 (16.7)	447	483	151	0.239

[a] The fluorescence quantum yields (Φ_f) were estimated with quinine sulfate (Φ_f) 0.55 in 1N H_2SO_4 solution as a standard, λ_{ex} = 366 nm.

Table 3. Absorbance and emission changes of selected compounds with addition of TFA.

Compound	**Ab_{max} (nm)**		**Fl_{max} (nm)**		**Fl_{max} changed fold**
	Without TFA	**With TFA**	**Without TFA**	**With TFA**	
4a	267,317	279,355	407	412	4
4g	269,323	271,353	437	441	4
4h	272,324	272,324	421	420	0.1
5f	244,278,322	242,300, 360	429	443	14
5g	244,276,324	242, 280,296,364	421	473	6.5
5h	246,288,348	242, 300, 352	425,471	498	4.5, 5.7
5j	276,360,420	242,286,430	453	412,544	-3.8, -5.1
5k	274,372,436	242,296,440	458	412,542	-3, -26

- Indicates the decreasing fold in fluorescence.

Charts

Figures

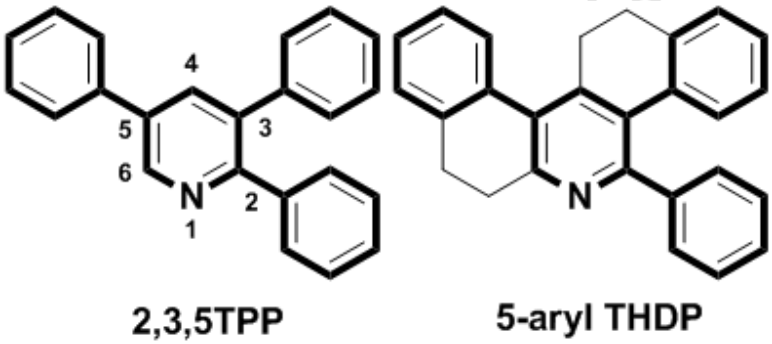


Chart 1. Structures of 2,3,5 TPP and THDP**.**

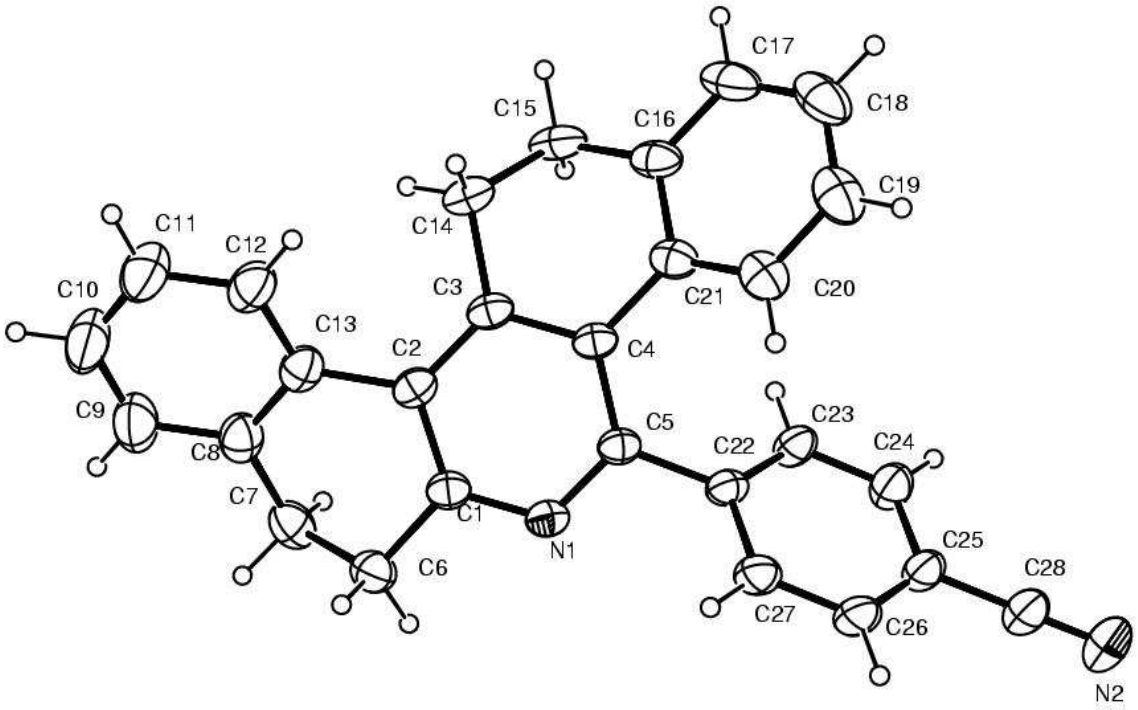


Figure 1. Ortep diagram of 5-aryl-tetrahydrodibenzo[a,i]phenanthridine **4g (**CCDC 744695).

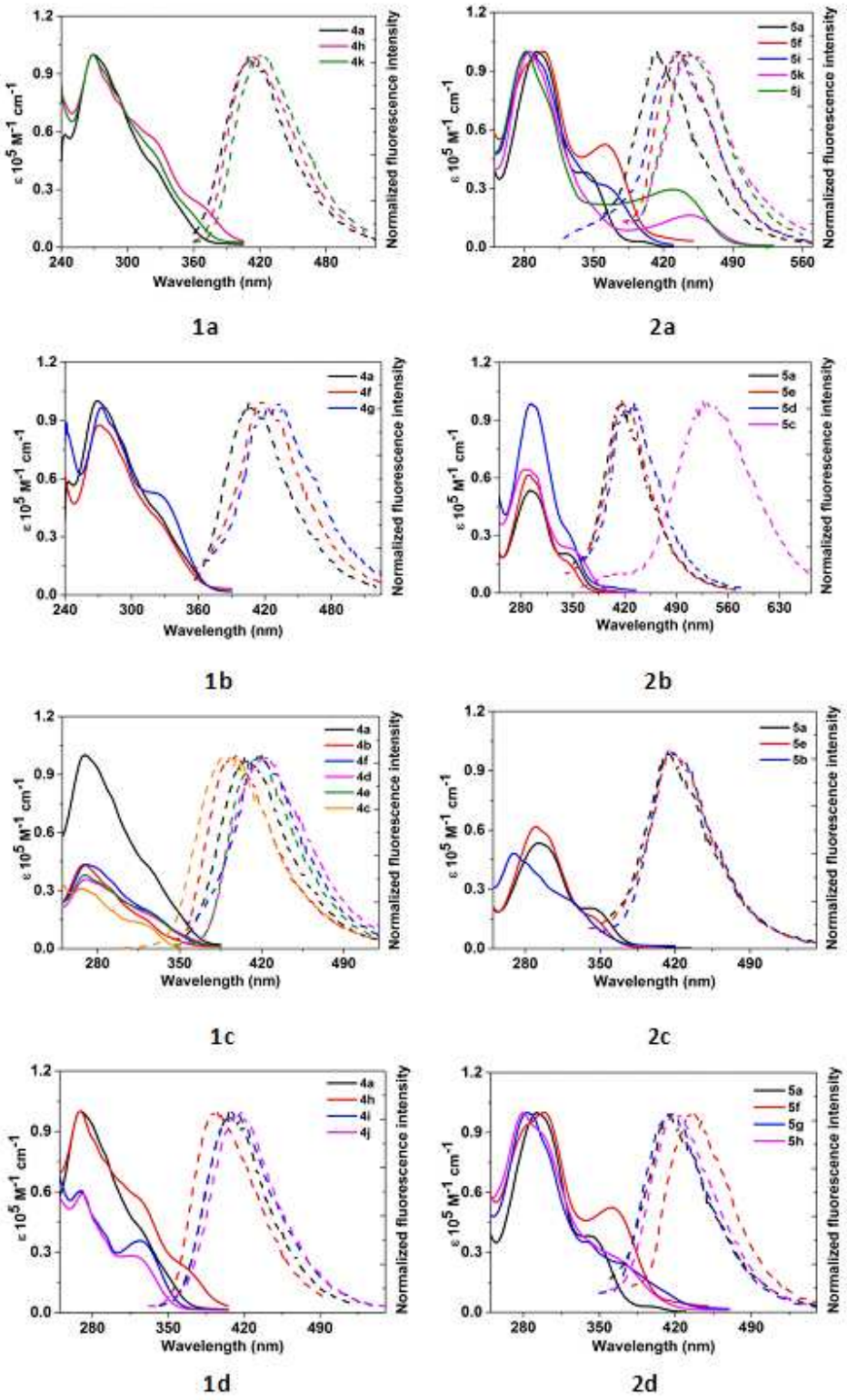


Figure 2. UV-visible and fluorescence spectra of substituted phenanthridines measured in chloroform solution.

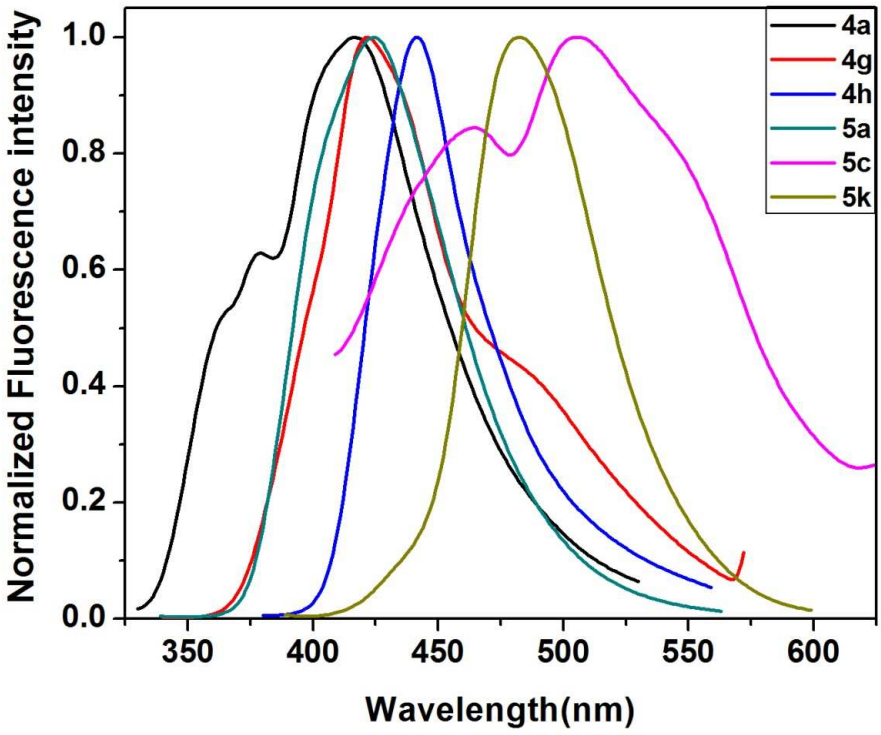


Figure 3. Solid state fluorescence spectra of selected compounds.

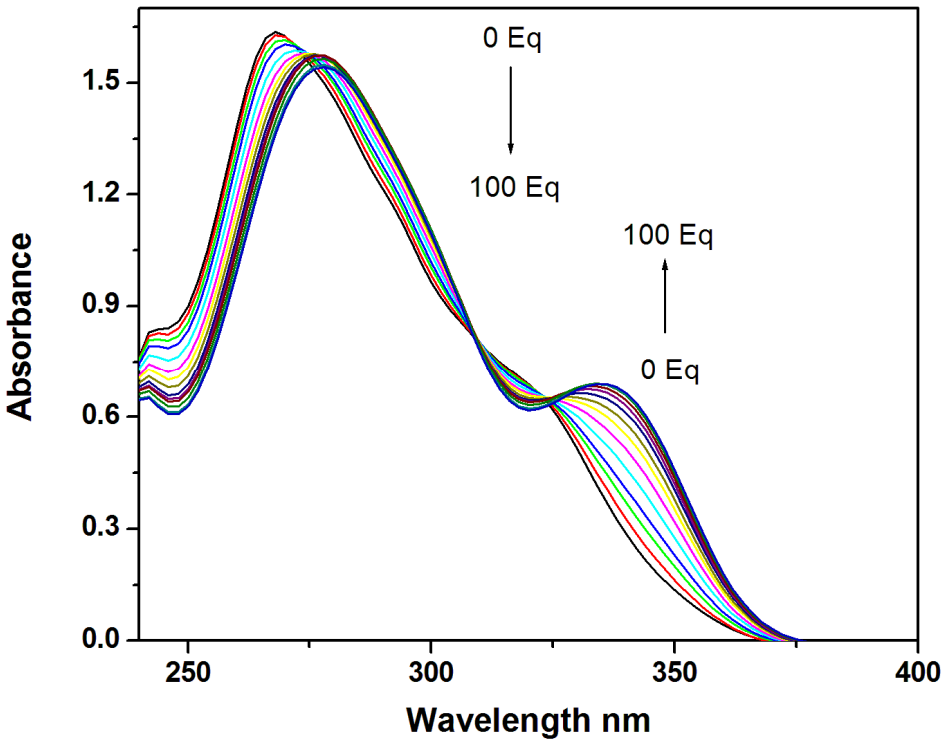


Figure 4. UV−vis spectral changes of **4a** upon addition of TFA.

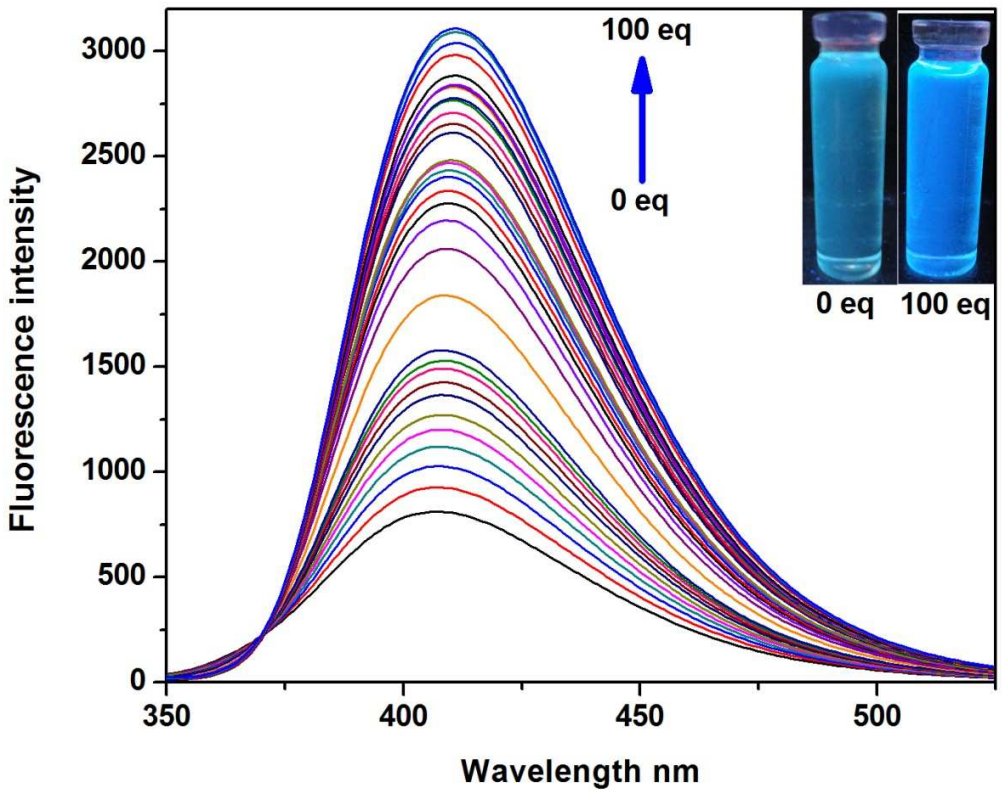


Figure 5. Fluorescence spectra of **4a** upon addition of TFA.

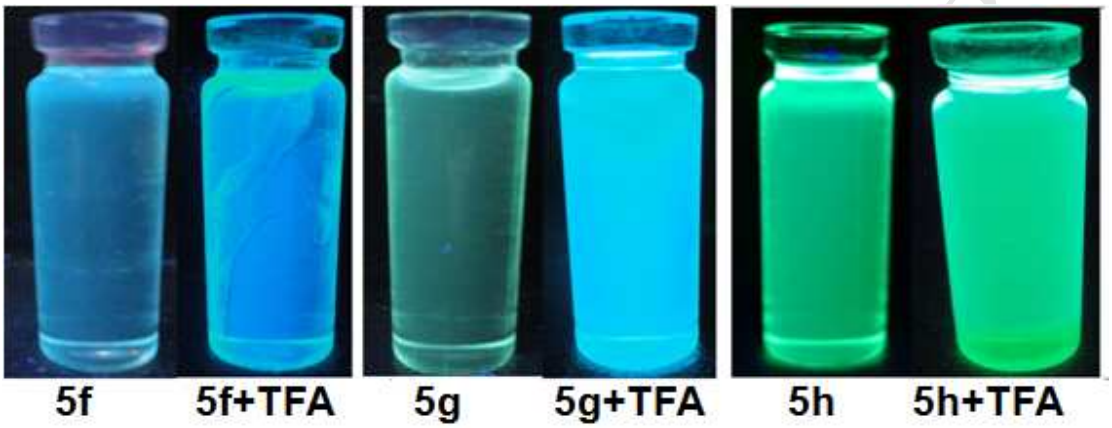


Figure 6. Changes observed in **5f, 5g** and **5h** taken under UV light before and after addition of TFA.

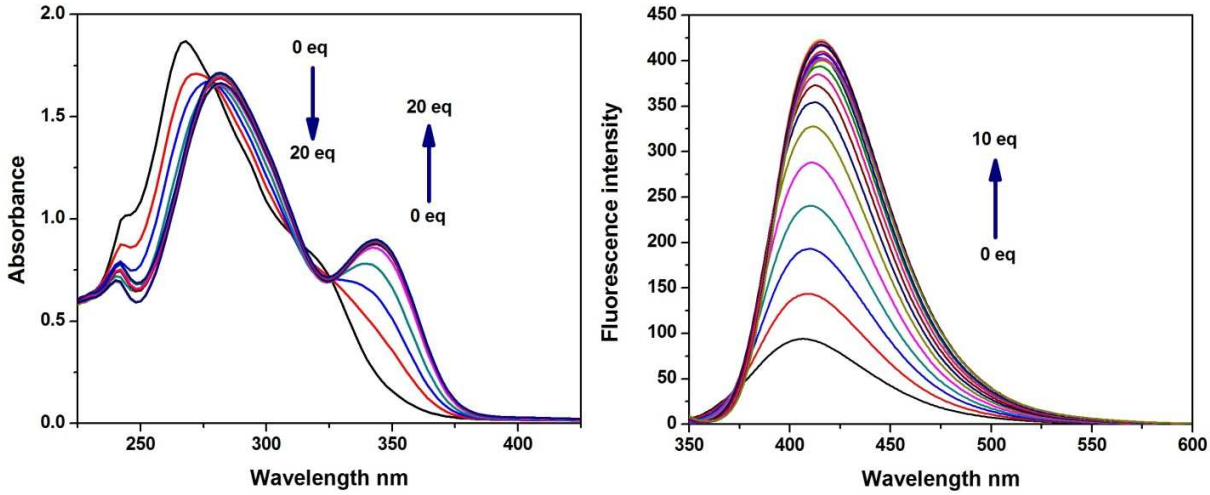


Figure 7. Changes observed in the UV-Vis and fluorescence spectra of **4a** upon addition of BF_3.

Highlights

- Luminescent 5-aryl-tetrahydrodibenzo[a,i]phenanthridines were developed by modified synthetic protocol using $SnCl_2$.
- The donor and acceptor groups significantly induced the charge transfer character leading to widespread emission properties
- The protonation and quaternization of these derivatives showed hyperchromic effect in emission, which can be used in fluorescence-based sensor applications.
- 5-substituted-tetrahydrodibenzo[a,i]phenanthridines based D-π-A chromophore that exhibits sensor applications and the detailed studies are under progress.