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RAPID COMMUNICATION

Synthesis and Fluorescence Investigation of Differently Substituted Benzo[*b*][1,8]Naphthyridines: Interaction with Different Solvents and Bovine Serum Albumin (BSA)

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Abstract A series of benzo[*b*][1, 8]naphthyridines has been synthesized by *Friedländer* condensation of 2-aminoquinoline-3-carbaldehyde **1** (o-aminoaldehyde) with active methylenes in basic medium. The fluorescence spectroscopic properties of some representative compounds has been studied in different organic solvents; moreover interaction with bovine serum albumin (BSA) in phosphate buffer was examined by UV–vis and fluorescence spectroscopy. The effect of electron donor-acceptor substituents on fluorescence properties of benzo[*b*][1, 8]naphthyridines **13(a-n)** has been investigated along with their fluorescent quantum yields.

Keywords Fluorophore · Solvatochromic effect · Bovine serum albumin (BSA) · Phosphate buffer · HOMO- LUMO

Introduction

In recent years, carbon rich organic compounds with a high degree of π-conjugation has received much attention because of their unique property as an ideal materials for advanced electronic and photonic applications, such as organic light-emitting diodes (OLEDs), liquid-crystal displays, thin-film transistors, solar cell and optical storage devices [1–19]. Large π-electron donor-acceptor compounds like ADMS, 9-(4-N,N-dimethylaminophenyl)-anthracene, has been the subject of intensive investigations during past decade. Recently, several donor and/or acceptor substituted compounds related to carbazoles, acridines etc. were synthesized and photoinduced charged separation has been intensively studied [20–22]. The 4-N,N-dimethylaminophenyl derivatives of bis-pyrazolo[3,4-*b*;4'3'-*e*]pyridine and pyrazolo[3,4-*b*]quinoline are further representatives of bulky π-electron donor-acceptor compounds and were recently investigated in some detail both experimentally [23–28] as well as semiempirically [26, 29–31]. These are highly emissive in non-polar solvents and shows charge separation and dual fluorescence in polar protic solvents. The donor-acceptor diphenylpolyenes capable of fluorescing from their charge-transfer excited states and were studied for microenvironment of micelles and proteins [32–35]. From literature, it was observed that the photophysical properties of heterocyclic compounds in different organic solvents were little explored. Prompted with these literature reports, we undertook the synthesis and study photophysical properties of benzonaphthyridines obtained from 2-aminoquinoline-3-carbaldehyde (o-aminoaldehyde) **1**. The construction of ring structures from orthoaminoaldehyde as a starting material has wide applicability for the annulation of various heterocyclic systems [36–56].

In our earlier communications [57–61], we have reported the synthetic utility of heterocyclic o-aminoaldehyde in which annulation of heterocyclic system on pyrazole and pyrazolopyridine nucleus were performed and recently [62] synthesis of fluorescent benzo[*b*][1, 8]naphthyridine-3-carbonitrile using **1** has been reported. In this communication, we extend the work towards the synthesis of several linear polycyclic heterocycles from **1** and studied their photophysical properties. We also studied the effect of specific solvent-fluorophore interaction on absorption and emission of flurophore **13k**, **15b** as well as fluorescence properties of **13d**, **13k**, **15a** and **15b** in aqueous buffer and

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in bovine serum albumin (BSA) (a well known protein responsible for transport of a variety of ligands [63]) are studied. Photophysical properties of **13(a-n)** are also studied and compared absorption and emission maxima with reference to donor and acceptor substituents on D ring (Fig. 1). The substituent effect on the performance of **13(a-n)** and **15(a-d)** are studied by calculating HOMO, LUMO energies and electron hole gap by using MOPAC-2009 to investigate the fluorescence properties of **13** and **15**.

Result and Discussion

In continuation of our efforts to explore the synthetic applicability of o-aminoaldehyde **1** [62], we report herein condensation of **1** with different reactive methylenes to obtained polycyclic heterocycles. Thus, *Friedländer* condensation of **1a** or **1b** with active methylene nitriles such as malononitrile/cyanoacetamide in ethanol using piperidine as a base under reflux yielded 2-aminobenzo[*b*][1, 8] naphthyridine-3-carbonitrile **3(a-b)** and 2-aminobenzo[*b*] [1, 8]naphthyridine-3-carboxymide **5(a-b)** respectively in 83-87% yield. In this cyclization, the reactive methylene undergoes Aldol condensation with carbonyl of **1** then intramolecular attack of amino on nitrile to yield **3** or **5**. However, the course of reaction of **1** with cyanoacetic ester **6a** or diethyl malonate **6b** is different under similar reaction conditions in which Aldol type condensation of aldehyde carbonyl of **1** with active methylene, then SN^2 attack of $-NH_2$ functionality on to ester, displacing ethoxy group. This cyclocondensation furnished tricyclic benzo[*b*][1, 8]naphthyridine derivatives **7(a-d)** in good yield. It was interesting to observe that when condensation partner of **1** is acetoacetic ester **8** then *Friedländer* condensation occur via usual combined Schiff base formation and then Aldol condensation to furnished **9(a-b)** in 83-84% yield. Surprisingly, ester functionality in **7(c-d)** and **9(a-b)** remains intact in the product, under basic reaction condition. Cyclocondensation of **1a** or **1b** with aliphatic ketones **10(a-b)** and substituted acetophenones **12(a-g)** under similar reaction condition smoothly yielded benzo[*b*][1, 8]naphthyridine **11(a-d)** and **13(a-n)** respectively in excellent yield.

Reactions of o-aminoaldehyde **1** (2-aminoquinoline-3-carbaldehyde) with cyclic ketones are especially valuable for the construction of polycondensed heterocyclic rings. The synthesis of pentacyclic linear heterocycles can be achieved by condensation of **1a** or **1b** with indanone **14(a-b)**. However, this condensation was unsuccessful under mild base such as piperidine, hence; this cyclocondensation was achieved by using strong base such as ethanolic KOH. Thus, condensation of **1a** or **1b** with indanone **14(a-b)** yielded 9,10-dimethoxy-7H-benzo[*b*]indeno[1,2-*g*][1, 8] naphthyridine **15(a-d)** in 80–89% yield (Scheme 1). Substituents of **13(a-n)** and **15(a-d)** are summarized in Tables 1 and 4. Synthesised compounds were characterized by spectroscopic and analytical methods. The spectroscopic data of **15b** is discussed here. The ^{1}H NMR of **15b** shows three singlet at 3.88, 3.96 and 4.05 ppm corresponds to protons of three methoxy groups, singlet at 3.75 ppm corresponds to methylene protons. All aromatic protons shows expected chemical shifts and splitting patterns which resembles with the structure of **15b**. The mass spectrum of **15b** reveals a molecular ion peak m/z at 358. The ^{13}C NMR spectrum of this compound in agreement with the structure proposed. (Scheme 1)

Semi-empirical study of Benzo[*b*][1, 8]naphthyridine 13(a-n) and 2,9,10-trimethoxy-7H-benzo[*b*]indeno[1,2-*g*][1, 8]naphthyridine 15(a-d)

The heterocycles which are useful as Organic Light Emitting Diodes (OLED) should fluoresces between 400–700 nm and HOMO/LUMO or 'electron-hole' gap in the

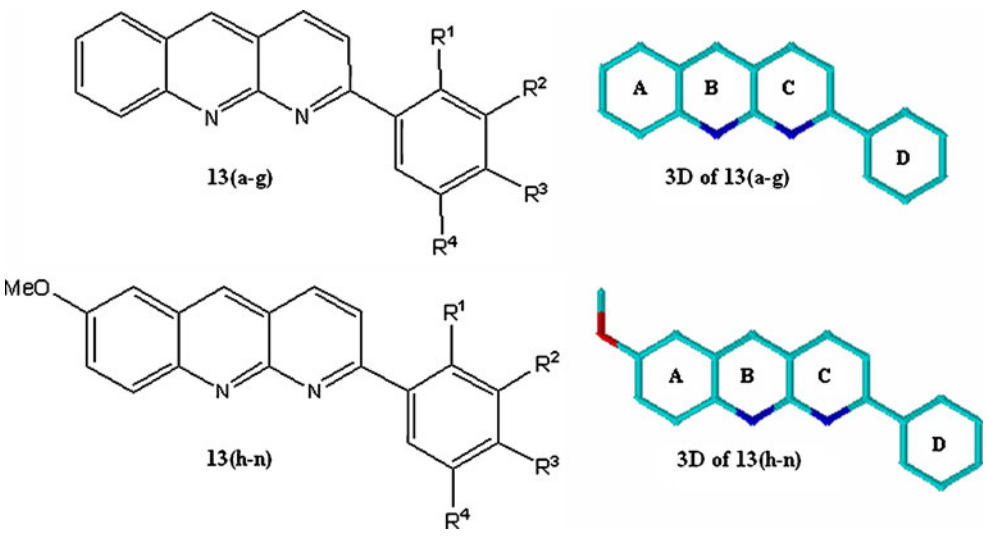
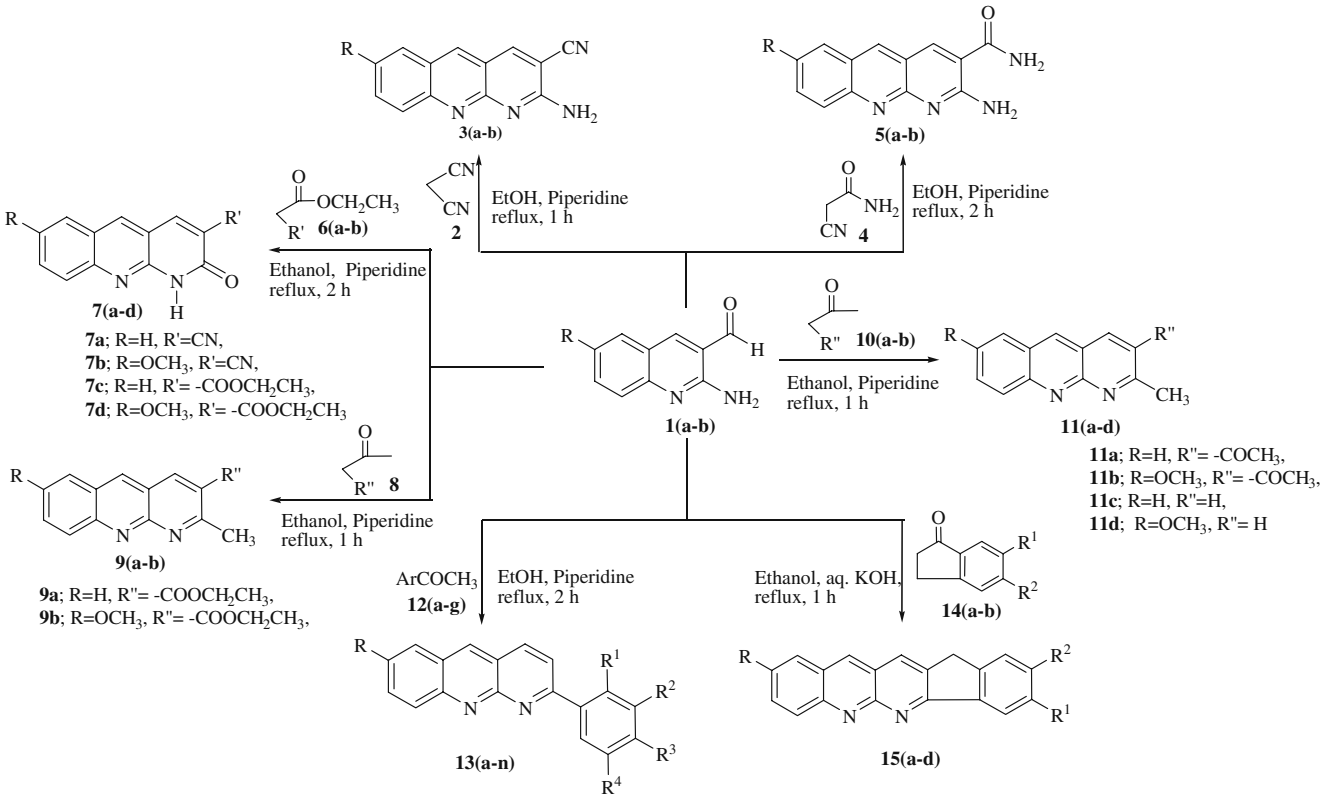


Fig. 1 3D picture of benzo[*b*][1, 8]naphthyridine **13(a-g)** and **13(h-n)**



Scheme 1 Synthesis of Benzo[*b*][1,8]naphthyridines

Table 1 The molecular electronic properties (HOMO-LUMO energy, GAP) of the 2-(4-Bromophenyl)benzo[*b*][1, 8]naphthyridine **13(a-n)** and 9,10-dimethoxy-7H-benzo[*b*]indeno[1,2-*g*][1, 8]naphthyridine **15(a-d)**

Comp.	R	R^1	R^2	R^3	R^4	HOMO (eV)	LUMO (eV)	GAP (eV)
13a	H	H	H	Br	H	-9.116	-1.601	7.515
13b	H	H	H	Cl	H	-9.156	-1.556	7.600
13c	H	H	CF_3	H	CF_3	-9.616	-2.987	6.629
13d	H	H	H	OCH_3	H	-8.672	-1.369	7.303
13e	H	H	OCH_3	OCH_3	H	-8.401	-1.408	6.993
13f	H	H	H	CH_3	H	-8.848	-1.387	7.461
13g	H	H	H	NO_2	H	-10.288	-2.587	7.701
13h	OCH_3	H	H	Br	H	-9.187	-1.572	7.615
13i	OCH_3	H	H	Cl	H	-9.079	-1.580	7.499
13j	OCH_3	H	CF_3	H	CF_3	-8.987	-1.750	7.237
13k	OCH_3	H	H	OCH_3	H	-8.513	-1.330	7.183
13l	OCH_3	H	OCH_3	OCH_3	H	-8.247	-1.368	6.879
13m	OCH_3	H	H	CH_3	H	-8.527	-1.342	7.185
13n	OCH_3	H	H	NO_2	H	-8.994	-1.311	7.683
15a	H	OCH_3	OCH_3	–	–	-8.329	-1.315	7.014
15b	OCH_3	OCH_3	OCH_3	–	–	-8.234	-1.289	6.945
15c	H	H	H	–	–	-8.849	-1.366	7.483
15d	OCH_3	H	H	–	–	-8.787	-1.327	7.460

GAP = E_{LUMO}-E_{HOMO}

range 2.7–3.0 eV i.e. low gap [64]. Prompted with these quotations, we have calculated HOMO-LUMO energies, electron hole gap of compounds **13** and **15** by using MOPAC-2009 (Version 8.331) [65, 66] and are summarized in Table 1. The charge is more concentrated on ring **D** as compared to ring **A**, **B** and **C** (Fig. 1). The donor chromophores (-CF_3,-OCH_3 groups) on ring **D** plays an important role in increasing the electron density and lowering electron hole gap. Compounds **13c**, **13d**, **13e**, **13j**, **13k**, **13l** and **13m** shows low GAP values indicating higher overlapping of HOMO or LUMO orbitals which shows red shift and high quantum yields. On the other hand, HOMO-LUMO energies of compound **13g** and **13n** shows increase in GAP values due to presence of inductively and mesomerically electron withdrawing chromophore (-NO_2) i.e. lower overlapping of atomic orbitals, this shows blue shift and low quantum yields. Among **15**, methoxy substituted derivatives **15a** and **15b** shows low GAP values, it fluoresces at longer wavelength and high quantum yields as compared to **15c** and **15d**. (Table 1)

Photophysical Properties

Effect of Solvent

The effects of solvents on fluorescence spectra are the result of specific interactions between the solvent and the fluorophore. Specific interactions are produced by one or a few neighboring molecules and are determined by specific chemical properties of both the fluorophore and the solvent [67, 68]. Specific effects can be due to hydrogen bonding, acid–base chemistry or charge-transfer interactions, to name a few of the possible origins. The emission spectra of fluorophore are depends both on orientation polarizability of the solvent and chemical structure of fluorophore and solvent. Therefore solvent effect can cause large change in emission of fluorophore and hence more easily observed spectral shifts. The solvent-fluorophore interactions can be studied by examining the UV/vis and fluorescence spectra of fluorophore in variety of solvents. Thus, absorption and emission spectra of **13k** and **15b** were undertaken in variety of solvents such as non-polar aprotic (n-Hexane), polar aprotic (THF, DMF, acetonitrile, acetone) and polar protic (Methanol, Ethanol) at room temperature at same concentration i.e. 1.0×10^{-3} M. The absorption and fluorescence spectral data of **13k** and **15b** in different organic solvents are summarized in Table 2 and graphically represented in Fig. 2. The fluorescence maxima of these compounds are greatly affected by the solvent polarity. Such a behavior indicates that the fluorescent state is not the same as the initially populated locally excited state (LE state), but it is a polar state with a charge transfer character. We observed that as the solvent polarity is increased further, the emission spectra continue to shift to longer wavelength and each monomer shows a certain solvatochromism in both the absorption and the emission spectrum. The $\lambda_{abs.\ max.}$ and $\lambda_{em.\ max.}$ of fluorophore **13k** and **15b** are significantly red-shifted as the solvent polarity is increased from n-Hexane to acetonitrile. In non-polar aprotic solvents (such as n-Hexane), the fluorescence intensities are weak as well as a shift of the emission spectrum to shorter wavelength. It has been reported that in nitrogen heterocycles (e.g. quinoline, isoquinoline and acridine) there is a $^1n\pi^*$ state very close to the π-π^* state [69, 70]. In fact, in hydrocarbon solvents, the lowest excited singlet state in these molecules is of ^1n, π^* type. Most of these nitrogen heterocycles are weakly or non-fluorescent in non-polar and aprotic solvents. However, in polar-aprotic and

Table 2 Absorption maximum ($\lambda_{abs.\ max.}$), fluorescence emission maximum ($\lambda_{em.\ max.}$) and fluorescence quantum yield (ϕ_F) of 7-Methoxy-2-(4-methoxyphenyl)benzo[*b*][1, 8]- naphthyridine **13k** and 2,9,10-trimethoxy-7H-benzo[*b*]indeno[1,2-*g*][1, 8]naphthyridine **15b** in various solvents (ca 10^{-3}) at room temp[a]

Solvent	**13k**			**15b**		
	$\lambda_{abs.\ max.}$ [nm][a]	$\lambda_{em.\ max.}$ [nm][b]	ϕ_F[c]	$\lambda_{abs.\ max.}$ [nm][a]	$\lambda_{em.\ max.}$ [nm][b]	ϕ_F[c]
Hexane	388	464	0.25	373	469	0.29
THF	391	472	0.27	376	475	0.31
Methanol	402	480	0.29	379	479	0.33
Ethanol	399	478	0.28	380	481	0.34
Acetonitrile	396	484	0.32	387	489	0.36
DMF	398	486	0.33	381	489	0.37
Acetone	444	550	0.44	398	525	0.42

All measurements were performed under degassed conditions

[a] $\lambda_{abs.}$ is the absorption band at about 10^{-3} M in the different solvents

[b] $\lambda_{em.}$ is the fluorescence band at about 10^{-3} M in the different solvents

[c] Fluorescence quantum yields; the values (± 0.01-0.03) are relative to that of quinine sulphate (0.57 in 10^{-3} M H_2SO_4)

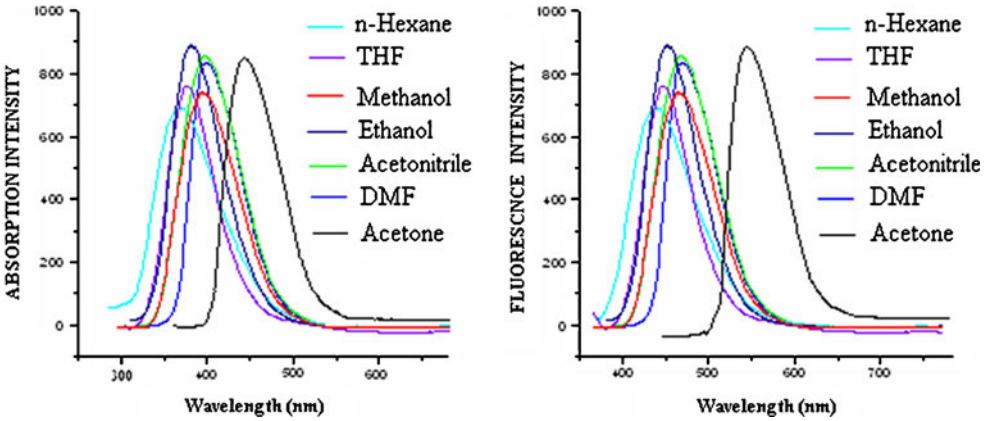


Fig. 2 UV–vis absorption ($\lambda_{abs.\ max.}$) and fluorescence ($\lambda_{em.\ max.}$) spectra of **13k** in solvents of different polarity

protic solvents, they become strongly fluorescent due to a reversal of n, π* and π, π* states [69, 70]. Thus, π- π* is the lowest energy transition in these molecules in protic solvents. In protic solvents, the energy gap between ^{1}n, π* and ^{1}π, π* (lowest excited singlet state) is probably very small. In general, in the emission spectra, the emission bands are found to be similar in acetonitrile and DMF. On the other hand, in ethanol and methanol, the emission band shifts to the blue it may be due to intramolecular hydrogen bond interaction between solvent and fluorophore. As the absorption band shifts to the blue, the emission band also shifts to the local emission from the hydrogen bonded clusters. Thus, intramolecular hydrogen bonding between solvent-fluorophore interaction can often be identified by examining the emission spectra in different concentration of methanol. We thought that, fluorescence may increases as solvent polarity increases by increasing % of water, but surprisingly, we observed that intensity of this emission band to gradually increases and we noted that emission corresponding to only the monomer at 476 nm of **13k** (Fig. 3). We observed that, emission is maximum in acetone because of acetone have keto-enol tautomerism due to this, conjugation increases as a result fluorophore may be fluoresces to longer wavelength in acetone. Thus UV/vis and fluorescence spectra of compounds **3(a-b)**, **5 (a-b)**, **7(a-d)**, **9(a-b)**, **11(a-d)**, **13(a-n)** and **15(a-d)** are taken in acetone. Fluorescence quantum yield of each were determined by standard literature procedure using quinine sulphate as a reference standard [71, 72] and are given in Tables 2, 3 and 4.

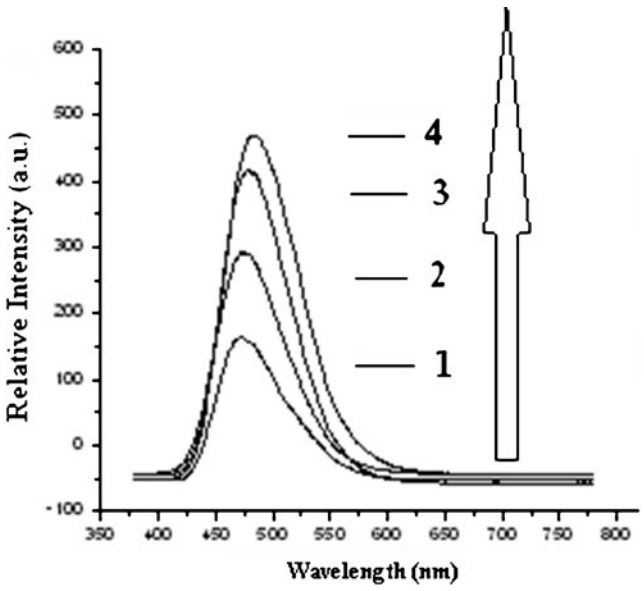


Fig. 3 Fluorescence emission spectra of **13k** in methanol to which water was added. The % of water in the solvent were 1) 10% 2) 20% 3) 30% 4) 40%

Table 3 Absorption maximum ($\lambda_{abs.\ max.}$), fluorescence emission maximum ($\lambda_{em.\ max.}$) and fluorescence quantum yield (ϕ_F) of 2-aminobenzo[*b*][1, 8]naphthyridine-3-carbonitrile **3 (a-b),** 2-aminobenzo[*b*][1, 8]naphthyridine-3-carboxymide **5(a-b)**, 1,2-dihydro-2-oxobenzo[*b*][1, 8]naphthyridine-3-carbonitrile **7(a-d)**, Ethyl-2-methylbenzo[*b*][1, 8]- naphthyridine-3-carboxylate **9(a-b)** and 1-(2-methylbenzo[*b*][1, 8]naphthyridin-3-yl)- ethanone **11(a-d)** in acetone as the solvent (ca.10^{-3}) at room temperature

Comp.	$\lambda_{abs.\ max.}$ [nm][a]	$\lambda_{em.\ max.}$ [nm][b]	ϕ_F[c]
3a	387	483	0.34
3b	401	499	0.38
5a	392	491	0.36
5b	415	510	0.40
7a	392	476	0.30
7b	398	485	0.32
7c	377	465	0.26
7d	382	483	0.32
9a	362	468	0.26
9b	370	476	0.29
11a	372	470	0.28
11b	375	482	0.35
11c	368	480	0.33
11d	371	487	0.36

All measurements were performed under degassed conditions

[a] $\lambda_{abs.}$ is the absorption band at about 10^{-3} M in acetone

[b] $\lambda_{em.}$ is the fluorescence band at about 10^{-3} M in acetone

[c] Fluorescence quantum yields; the values (± 0.01-0.03) are relative to that of quinine sulphate (0.57 in 10^{-3} M H_2SO_4)

Table 4 Absorption maximum ($\lambda_{abs.\ max.}$), fluorescence emission maximum ($\lambda_{em.\ max.}$) and fluorescence quantum yield (ϕ_F) of 2-(4-Bromophenyl)benzo[*b*][1, 8]naphthyridine **13(a-n)** and 9,10-dimethoxy-7H-benzo[*b*]indeno[1,2-*g*][1, 8]naphthyridine **15(a-d)** in acetone as the solvent (ca. 10^{-3}) at room temperature [a]

Comp.	R	R^1	R^2	R^3	R^4	$\lambda_{abs.\ max.}$ [nm][b]	$\lambda_{em.\ max.}$ [nm][c]	ϕ_F[d]
13a	H	H	H	Br	H	398	469	0.29
13b	H	H	H	Cl	H	392	474	0.31
13c	H	H	CF_3	H	CF_3	378	484	0.35
13d	H	H	H	OCH_3	H	426	566	0.47
13e	H	H	OCH_3	OCH_3	H	382	483	0.35
13f	H	H	H	CH_3	H	388	480	0.34
13g	H	H	H	NO_2	H	383	441	0.18
13h	OCH_3	H	H	Br	H	414	480	0.33
13i	OCH_3	H	H	Cl	H	403	481	0.34
13j	OCH_3	H	CF_3	H	CF_3	384	504	0.40
13k	OCH_3	H	H	OCH_3	H	444	550	0.44
13l	OCH_3	H	OCH_3	OCH_3	H	401	498	0.39
13m	OCH_3	H	H	CH_3	H	397	491	0.38
13n	OCH_3	H	H	NO_2	H	394	449	0.19
15a	H	OCH_3	OCH_3	–	–	370	484	0.35
15b	OCH_3	OCH_3	OCH_3	–	–	398	525	0.42
15c	H	H	H	–	–	371	476	0.31
15d	OCH_3	H	H	–	–	373	483	0.34

[a] All measurements were performed under degassed conditions. [b] $\lambda_{abs.}$ is the absorption band at about 10^{-3} M in acetone. [c] $\lambda_{em.}$ is the fluorescence band at about 10^{-3} M in acetone. [d] Fluorescence quantum yields; the values (± 0.01-0.03) are relative to that of quinine sulphate (0.57 in 10^{-3} M H_2SO_4)

Effect of Concentration

We also examined the effect of concentration on the fluorescence emission of **13k** in acetone. By increasing the concentration from 1.0×10^{-7} M (Fig. 4, line 1) to 1.0×10^{-3} M (Fig. 4, line 4), we observed that intensity of this emission band to gradually increases, and we noted that the emission corresponding to only the monomer at 550 nm (Fig. 4).

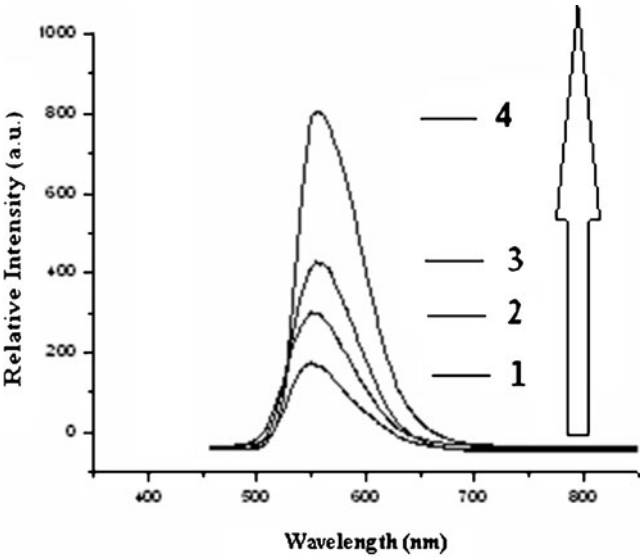


Fig. 4 Effect of concentration on the fluorescence emission spectra of **13k** recorded in acetone at room temperature (1) 1.0×10^{-7} M, (2) 1.0×10^{-6} M, (3) 1.0×10^{-5} M, (4) 1.0×10^{-3}

Effect of Electron Donor-Acceptor Substituents

From the Table 4, it was observed that fluorescence maxima of the compound **13(h-n)** are larger than **13(a-g)** may be due to presence of strong π-electron donor group i.e. -OCH_3 on the **A** ring except **13d** (Fig. 1). The 3D picture of the benzonaphthyridines **13(a-n)** is depicted in Fig. 1. From the Table 4, it was noted that compound **13c**, **13d**, **13e**, **13j, 13k** and **13l** shows fluorescence band appearing at longer wavelength was substantially bathochromically shifted, we ascribe to the increased π-electron density on the **D** ring, arising from the electron donating nature of -CF_3 group (σ-π electron donor) at C_3 & C_5 position (**13c**, **13j**) and -OCH_3 group (π-electron donor) at para position (**13d**, **13k**), at C_3 & C_4 position (**13e**, **13l**) respectively. Among **13**, the **13d** and **13k** displayed the largest bathochromic shift of absorption and fluorescence bands, which could be attributed to the methoxy group at para position on ring **D** having strongest electron donating ability having different substituents. On the other hand, blue shift was observed in **13g** and **13n** due to presence of electron acceptor group i.e. -NO_2 group at para position on ring **D**. Another interesting feature was that

halo substituted molecules (compounds **13a**, **13b**, **13h** and **13i**) shows less fluorescence, quantum yield than methoxy substituted compounds (φ_F**=0.39-0.44**). This may be due to the quenching of fluorescence with halogen atoms as the substitution. The comparative absorption and emission spectra of compounds **13j**, **13k** and **13n** are graphically presented in Fig. 5. We also noted that among **15**, the methoxy substituted compounds i.e. **15(a-b)** shows more fluorescence and quantum yields as compare to **15(c-d)** may be due to presence of -OCH_3 group in **15(a-b)** [R^1=R^2=OCH_3] (Table 4).

The Effect of BSA on the Fluorescence Emission of Compounds 13d, 13k, 15a and 15b in Phosphate Buffer

In order to examine the interaction of **13d**, **13k, 15a** and **15b** with bovine serum albumin (BSA), the fluorescence titrations with BSA, was carried out in phosphate buffer of pH 7.4. The absorption and fluorescent spectral data of **13d**, **13k**, **15a** and **15b** are collected in Table 5 and $\lambda_{em.\ max.}$ is graphically presented in Fig. 6. We observed the blue shift of $\lambda_{em.\ max.}$ for **13d**, **13k**, **15a** and **15b**. We also examined the effect of increasing BSA concentration on fluorescence emission and noted that gradually increase in the concentration of BSA in the solutions of **13k** in phosphate buffer results in an enhancement of the fluorescence emission and quantum yield (ϕ_F) (Fig. 7). The blue shift in the $\lambda_{em.\ max.}$ suggests that the polarities of the protein environments in which the benzo[*b*][1, 8]naphthyridines are located are less that the polarity of the bulk aqueous phase since similar blue shifts are observed in less polar organic solvents. This shows the binding of the probes to a hydrophobic site of the protein.

Table 5 Absorption maximum ($\lambda_{abs.\ max.}$), fluorescence emission maximum ($\lambda_{em.\ max.}$) and fluorescence quantum yield (ϕ_F) of benzo[*b*][1, 8]naphthyridine (**13d**, **13k**) and 9,10-dimethoxy-7H-benzo[*b*]indeno[1,2-*g*][1, 8]naphthyridine (**15a**, **15b**) in phosphate buffer (pH, 7.4) and BSA (5.0×10^{-6} mol L^{-1})

Compound	$\lambda_{abs.\ max.}$ (nm)		$\lambda_{em.\ max.}$ (nm)		ϕ_F (± 0.002)	
	Buffer	BSA	Buffer	BSA	Buffer	BSA
13d	390	391	572	504	0.42	0.46
13k	397	398	560	496	0.40	0.45
15a	386	388	488	440	0.33	0.38
15b	393	392	533	472	0.39	0.42

Conclusion

In summary, the tetracyclic and pentacyclic linear heterocycles are synthesized by *Friedländer* condensation of activemethylene nitrile, active methylene and cyclic ketone such as indanone with **1**. Our methods have several additional advantages such as milder reaction condition, shorter reaction time, scalable and lack of side product. UV–vis absorption and emission spectroscopic studies of **13k** and **15b** have been done in three types of solvents i.e. non-polar aprotic, polar aprotic, polar protic and it exhibit solvatochromic fluorescence emission in organic solvents. The interaction of **13d**, **13k**, **15a** and **15b** with BSA have been investigated by UV–vis absorption and fluorescence spectroscopy and observed that the $\lambda_{em.\ max.}$ gets blue-shifted upon binding with BSA. However the fluorescence intensity enhancement is linear with the increasing in BSA concentration (**13k**). The fluorescence properties of benzo[*b*][1, 8]naphthyridines **13(a-n)** depend upon the nature of substituents present on ring **D**. Thus, benzo[*b*][1, 8]naphthyridines **13(a-n)** bearing electron-releasing group i.e. substituents like di-CF_3 and -OMe (Compound **13c**, **13j, 13d, 13e**, **13k** and **13l**) on ring **D** (Fig. 1) fluoresces at longer wavelength as compared with the electron-withdrawing group like -NO_2 (Compound **13g**, **13n**) on ring **D** (Fig. 1) at the para position. From empirical calculations, we revels that benzo[*b*][1, 8]

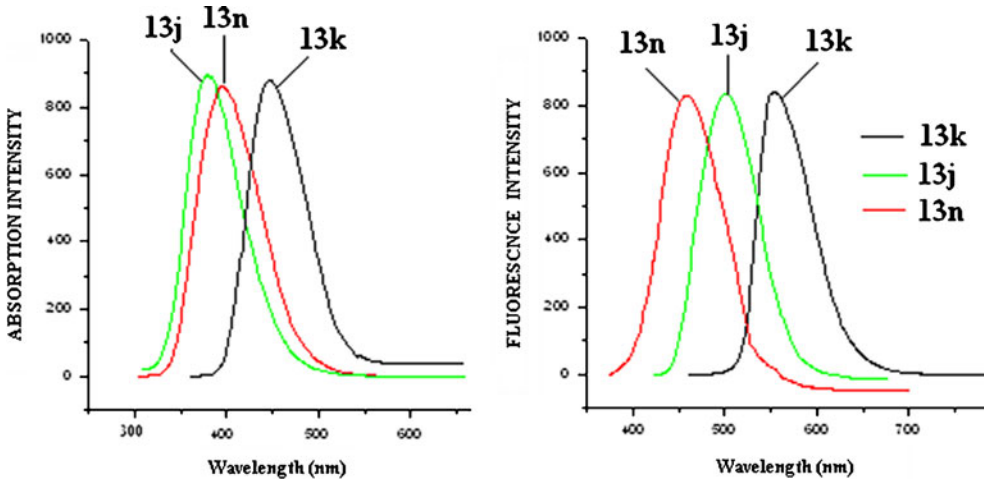


Fig. 5 The comparative absorption (UV $\lambda_{Max.}$) and fluorescence (Em $\lambda_{Max.}$) spectra of compounds **13j**, **13k** and **13n** respectively

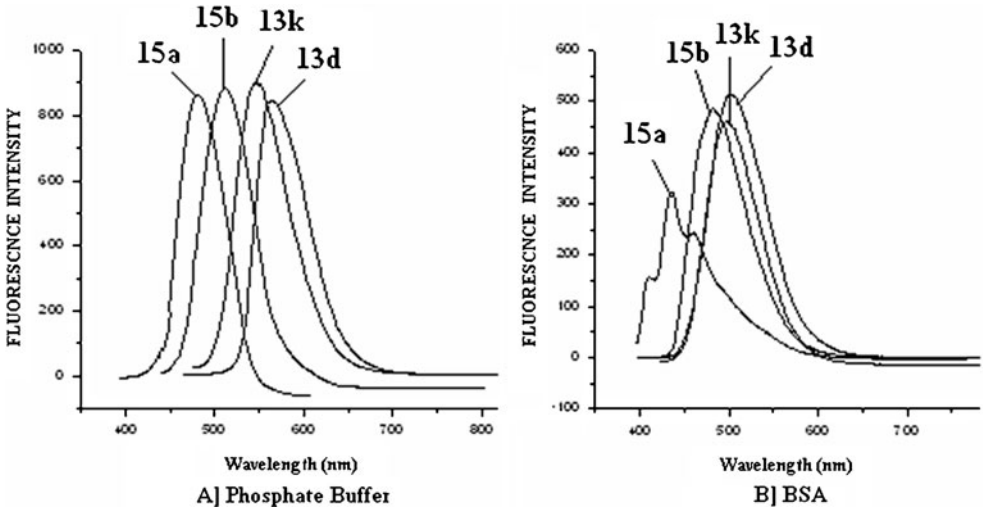


Fig. 6 Comparative fluorescence (Em $\lambda_{Max.}$) spectra of **13d**, **13k**, **15a** and **15b**: A] In Phosphate Buffer, B] In BSA

naphthyridines (**13a-n** and **15a-d**) which shows low electron hole gap values (e.g. **13c**, **13d**, **13e**, **13j**, **13k**, **13l**, **13m**, **15a** and **15b**) are fluoresces at longer wavelength and have high quantum yields, while compounds with higher electron hole gap (e.g. **13b**, **13g**, **13h** and **13n**) are fluoresces at shorter wavelength with low quantum yields and are in agreement with theoretical observations. This study has brought out interesting substituent and solvent-dependent fluorescence properties of benzonaphthyridines. The efficient blue light emission and physical and chemical stability makes these benzonaphthyridine derivatives as a promising family of materials which may be useful in photophysical applications. All these synthesized compounds are addition to the library of new heterocyclic compounds.

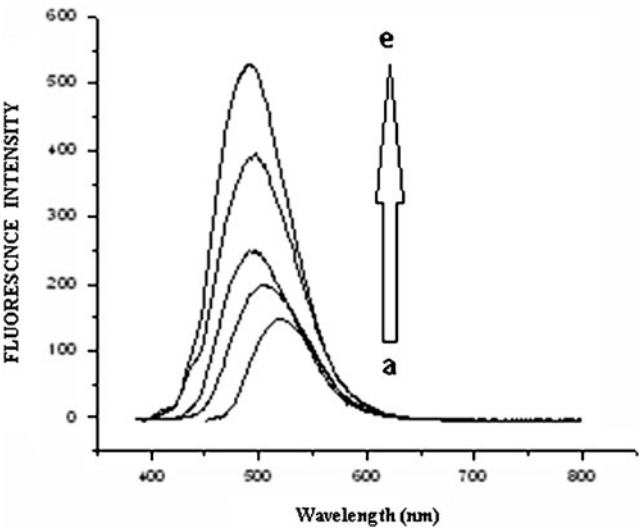


Fig. 7 Fluorescence emission spectra of **13k** with increasing BSA concentration; curves a-e correspond to [BSA] 1.0, 2.0, 3.0, 4.0 and 5.0 (x 10^{-6} mol L^{-1}), respectively

Experimental

General

Bovine serum albumin (BSA) and Quinine sulphate was purchased from HiMedia Laboratories Pvt. Ltd. Mumbai (India) and Research-Lab Fine Chem Industries, Mumbai (India) respectively. All other chemicals, reagents and solvents were obtained from LOBA Chemie. Pvt. Ltd., Mumbai (India), Spectrochem, Mumbai (India) and E. Merck (India). All AR-grade organic solvents were dried and freshly distilled prior to use. The UV-grade solvents were used for spectral studies. Melting points were determined on a Gallenkamp melting point apparatus, Mod. MFB595 in open capillary tubes and are uncorrected. Fourier transform infrared (FTIR) spectra in KBr disk were measured on a Shimadzu FTIR-408 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 MHz spectrometer using tetramethylsilane (TMS) as internal standard and solvents are deuterio-chloroform ($CDCl_3$) and deuterio-dimethylsulphoxide (DMSO-d_6). Chemical shifts are reported in ppm from internal tetramethylsilane standard and are given in δ-units. High-resolution mass spectra are obtained with a Mat 112 Varian Mat Bremen (70 eV) mass spectrometer. Elemental analyses are performed on a Hosli CH-Analyzer and are within ± 0.3 of the theoretical percentage. The absorption spectra were measured using a Shimadzu UV-1601 UV–VIS spectrophotometer. The fluorescence spectra were recorded on a RF-5301 PC spectrofluorophotometer by exciting the samples at their absorption maximum ($\lambda_{abs.\ max.}$). Compounds for UV and fluorescence measurements are dissolved in acetone, UV and fluorescence scan are recorded from 200 to 600 nm. The Φ_f relative to quinine sulphate in 1.0×10^{-3} mol L^{-1} H_2SO_4 (Φ_f=0.57) was measured at room temperature by standard literature procedure [73–75]. Both

samples and standard were excited at the same excitation wavelength and the optical density (OD) of the standard and the sample was adjusted to be nearly equal. For all electronic spectroscopic studies (absorption, fluorescence excitation and emission) 1.0×10^{-3} mol L^{-1} solutions of the compounds were used. All reactions are monitored by thin layer chromatography, carried out on 0.2 mm silica gel 60 F_{254} (Merck) plates using UV light (250 and 400 nm) and Fluorescence light (400 and 600 nm) for detection. For fluorescence quenching studies, the required amount of BSA solution (in phosphate buffer) and the required amount of benzo[*b*][1, 8]naphthyridines solution in dimethylsulphoxide (DMSO) (1.0×10^{-4} mol L^{-1}) were taken in a 5 ml volumetric flask. Since the benzo[*b*][1, 8]naphthyridines are sparingly soluble in water, their stock solutions were prepared in DMSO, which is used as a solvent for interaction studies of serum albumins [76].

Synthesis

Synthesis of 2-Aminobenzo[b][1, 8]Naphthyridine-3-Carbonitrile (3a, b) A mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.01 mol) & malononitrile **2** (0.01 mol) in ethanol (10 mL) containing catalytic amount of piperidine was refluxed for 1 h. After completion of reaction (TLC checked), reaction mixture was cooled to room temperature. The separated solid product was collected by suction filtration, washed with cold methanol (10 mL), dried under vacuum and recrystallized from Ethanol: DMF (90:10) (v: v).

2-Aminobenzo[b][1, 8]Naphthyridine-3-Carbonitrile (3a) Yield: 0.184 g (83%), recrystallized from Ethanol: DMF (90:10) to afford yellow solid; M.p. 283–286 °C, IR (KBr): 3,413 m, 3,375 m, 2,911 s, 2,219 s, 1,633 scm^{-1}. ^{1}H NMR (300 MHz DMSO-d_6) δ: 7.39 (dd, 1 H, *J*=8.2 & 8.5 Hz, Ar-H), 7.53 (bs, 2 H, NH), 7.77 (dd, 1 H, *J*=8.5 & 8.1 Hz, Ar-H), 7.92 (d, 1 H, *J*=8.2 Hz, Ar-H), 8.08 (d, 1 H, *J*= 8.1 Hz, Ar-H), 8.66 (s, 1 H, Ar-H), 8.78 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 220 [M^+] (20), 193 (30), 150 (20), 136 (60), 105 (40), 77 (40). Anal. Calcd. for $C_{13}H_8N_4$ (220.23): C, 70.90; H, 3.63; N, 25.45% Found: C, 70.93; H, 3.60; N, 25.46%

7-Methoxy-2-Amino[b][1, 8]Naphthyridine-3-Carbonitrile (3b) Yield: 0.218 g (87%), recrystalized from Ethanol: DMF (80: 20) to afford yellow needles; M.p. 278–281 °C. IR (KBr): 3,442 m, 3,378 m, 2,914 s, 2,230 s, 1,621 s, 1,019 mcm^{-1}.^{1}H NMR (300 MHz DMSO-d_6) δ: 3.93 (s, 3 H, OCH_3), 6.99 (bs, 2 H, NH), 7.43 (d, 1 H, *J*=9.0 Hz, Ar-H), 7.51 (s, 1 H, Ar-H), 8.24 (d, 1 H, *J*=9.0 Hz, Ar-H), 9.21 (s, 1 H, Ar-H), 9.44 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz DMSO-d_6) δ: 58.32, 98.26, 108.11, 112.44, 122.78, 123.36, 128.21, 132.66, 133.43, 146.53, 148.27, 156.34, 158.74, 159.63. MS (70 eV) m/z (%): 250 [M^+] (79), 223 (44), 207 (49), 130 (51), 69 (28), 44 (61), 32 (74). Anal. Calcd. for $C_{14}H_{10}N_4O$ (250.26): C, 67.20; H, 4.00; N, 22.40% Found: C, 67.18; H, 3.98; N, 22.38%

Synthesis of 2-Aminobenzo[b][1, 8]Naphthyridine-3-Carboxymide (5a, b) A mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.01 mol) & cyanoacetamide **4** (0.01 mol) in ethanol (10 mL) containing catalytic amount of piperidine was refluxed for 2 h. After completion of reaction (TLC checked), reaction mixture was cooled to room temperature. The separated solid product was collected by suction filtration, washed with cold methanol (10 mL), dried under vacuum and recrystallized from Ethanol: DMF (70: 30) (v: v).

2-Aminobenzo[b][1, 8]Naphthyridine-3-Carboxymide (5a) Yield 0.204 g (85%), recrystallised from Ethanol: DMF (70: 30) to afford yellow solid; M.p. 289–292 °C, IR (KBr): 3,440 m, 3,410 m, 3,245 m, 3,197 m, 2,929 m, 1,671 s, 1,613 scm^{-1}, ^{1}H NMR (300 MHz DMSO-d_6) δ: 7.15 (dd, 1 H, *J*=7.9 & 8.2 Hz, Ar-H), 7.46 (bs, 2 H, NH), 7.89 (dd, 1 H, *J*=8.2 & 8.6 Hz, Ar-H), 8.04 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.17 (d, 1 H, *J*=8.6 Hz, Ar-H), 8.40 (bs, 2 H, NH), 8.82 (s, 1 H, Ar-H), 8.96 (s,1 H, Ar-H). MS (70 eV) m/z (%): 238 [M^+] (78), 221 (31), 194 (76), 166 (62), 139 (59), 110 (45), 77 (67). Anal. Calcd. for $C_{13}H_{10}N_4O$ (238.24): C, 65.54; H, 4.20; N, 23.52% Found: C, 65.55; H, 4.21; N, 23.55%

2-Amino-7-Methoxybenzo[b][1, 8]Naphthyridine-3-Carboxymide (5b) Yield 0.232 g (86%), recrystallised from Ethanol: DMF (80:20) to afford yellow prism, M.p. 283–285 °C. IR (KBr): 3,448 m, 3,419 m, 3,266 m, 3,207 m, 2,955 s, 1,675 s, 1,612 s, 1,022 mcm^{-1}. ^{1}H NMR (300 MHz DMSO-d_6) δ: 4.01 (s, 3 H, OCH_3), 7.10 (d, 1 H, *J*=8.7 Hz, Ar- H), 7.21 (s, 1 H, Ar-H), 7.72 (bs, 2 H, NH), 7.98 (d, 1 H, *J*=8.7 Hz, Ar-H), 8.34 (bs, 2 H, NH), 8.61 (s, 1 H, Ar-H), 8.65 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz DMSO-d_6) δ: 55.47, 105.04, 114.51, 115.62, 118.23, 120.37, 130.19, 138.19, 139.98, 152.95, 155.91, 159.36, 161.94, 169.00. MS (70 eV) m/z (%): 268 [M^+] (77), 251 (41), 225 (73), 196 (29), 181 (33), 44 (49), 32 (71). Anal. Calcd. for $C_{14}H_{12}N_4O_2$ (268.27): C, 62.68; H, 4.47; N, 20.89%. Found: C, 62.66; H, 4.48; N, 20.88%.

Synthesis of 1,2-Dihydro-2-Oxobenzo[b][1, 8]Naphthyridine-3-Carbonitrile (7 a-d) A mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.01 mol) & ethylcyanoacetate (**6a**) (0.01 mol) in ethanol (10 mL) containing catalytic amount of piperidine was refluxed for 2 h. After completion of reaction (TLC checked), reaction mixture was cooled to room temperature. The separated solid product was collected by suction filtration, washed with cold methanol or pet-ether,

dried under suction and recrystallized from Ethanol: DMF (80: 20) (v: v) or Ethanol.

1,2-Dihydro-2-Oxobenzo[b][1, 8]Naphthyridine-3-Carbonitrile (7a) Yield: 0.179 g (80%), recrystalized from Ethanol: DMF (80: 20) to afford pale yellow crystal; M.p. 261–264 °C. IR (KBr): 3,240 m, 2,912 m, 2,244 s, 1,674 s, 1,601 scm^{-1}. ^1H NMR (300 MHz DMSO-d_6) δ: 7.22 (bs, 1 H, NH), 7.84 (dd, 1 H, *J*=8.2 & 8.6 Hz, Ar-H), 7.97 (dd, 1 H, *J*=8.6 & 8.0 Hz, Ar-H), 8.09 (d, 1 H, *J*=8.2 Hz, Ar-H), 8.39 (d, 1 H, *J*=8.0 Hz, Ar-H), 9.02 (s, 1 H, Ar-H), 9.13 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 221 [M^+] (85), 193 (96), 178 (87), 150 (61), 127 (67), 96 (54), 77 (42), 44 (64). Anal. Calcd. for $C_{13}H_7N_3O$ (221.21): C, 70.58; H, 3.16; N, 19.00%. Found: C, 70.56; H, 3.18; N, 18.98%.

1,2-Dihydro-7-Methoxy-2-Oxobenzo[b][1, 8]Naphthyridine-3-Carbonitrile (7b) Yield: 0.218 g (86%), recrystalized from Ethanol: DMF (70: 30) to afford yellow needles; M.p. 256–258 °C. IR (KBr): 3,256 m, 2,902 m, 2,239 s, 1,669 s, 1,598 s, 1,027 mcm^{-1}.^1H NMR (300 MHz DMSO-d_6) δ: 4.03 (s, 3 H, OCH_3), 6.92 (bs, 1 H, NH), 7.25 (d, 1 H, *J*= 8.6 Hz, Ar-H), 7.47 (s, 1 H, Ar-H), 8.12 (d, 1 H, *J*=8.6 Hz, Ar-H), 9.31 (s, 1 H, Ar-H), 9.49 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz DMSO-d_6) δ: 58.13, 98.47, 107.46, 109.11, 114.45, 123.65, 124.73, 126.88, 129.40, 135.29, 145.73, 154.32, 158.23, 166.30. MS (70 eV) m/z (%): 251 [M^+] (72), 223 (67), 208 (51), 193 (38), 180 (89), 153 (62), 126 (60), 44 (81). Anal. Calcd. for $C_{14}H_9N_3O_2$ (251.24): C, 66.93; H, 3.58; N, 16.73% Found: C, 66.96; H, 3.60; N, 16.71%

Ethyl-1,2-Dihydro-2-Oxobenzo[b][1, 8]Naphthyridine-3-Carboxylate (7c) Yield: 0.232 g (86%), recrystalized from ethanol to afford pale yellow solid; M.p. 195–198 °C. IR (KBr): 3,221 m, 2,901 s, 1,738 s, 1,669 s, 1,618 s, 1,022 m cm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ: 1.77 (t, 3 H, *J*= 5.3 Hz, CH_3), 4.34 (q, 2 H, *J*=5.3 Hz, CH_2), 7.18 (bs, 1 H, NH), 7.29 (dd, 1 H, *J*=7.7 & 8.1 Hz, Ar-H), 7.57 (dd, 1 H, *J*=8.1 & 8.4 Hz, Ar-H), 7.92 (d, 1 H, *J*=7.7 Hz, Ar-H), 8.32 (d, 1 H, *J*=8.4 Hz, Ar-H), 9.12 (s, 1 H, Ar-H), 9.23 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 268 [M^+] (79), 223 (66), 195 (76), 166 (59), 122 (64), 77 (48), 45 (34). Anal. Calcd. for $C_{15}H_{12}N_2O_3$ (268.27): C, 67.16; H, 4.47; N, 10.44% Found: C, 67.18; H, 4.45; N, 10.42%

Ethyl-1,2-Dihydro-7-Methoxy-2-Oxobenzo[b][1, 8]Naphthyridine-3-Carboxylate (7d) Yield: 0.260 g (87%), recrystalized from ethanol to afford yellow needles; M.p. 185–188 °C. IR (KBr): 3,249 m, 2,912 s, 1,737 s, 1,674 m, 1,601 s, 1,027 scm^{-1}.^1H NMR (300 MHz $CDCl_3$) δ: 1.88 (t, 3 H, *J*=5.2 Hz, CH_3), 3.98 (s, 3 H, OCH_3), 4.28 (q, 2 H, *J*=5.2 Hz, CH_2), 6.28 (bs, 1 H, NH), 7.31 (d, 1 H, *J*= 8.6 Hz, Ar-H), 7.61 (s, 1 H, Ar-H), 8.29 (d, 1 H, *J*=8.6 Hz, Ar-H), 9.20 (s, 1 H, Ar-H), 9.40 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz DMSO-d_6) δ: 19.22, 55.89, 66.72, 104.22, 120.51, 121.20, 121.88, 122.26, 126.47, 132.77, 135.24, 141.02, 152.13, 161.23, 162.88, 167.34. MS (70 eV) m/z (%): 298 [M^+] (76), 253 (68), 226 (91), 198 (79), 183 (51), 127 (52), 44 (31). Anal. Calcd. for $C_{16}H_{14}N_2O_4$ (298.29): C, 64.42; H, 4.69; N, 9.39% Found: C, 64.43; H, 4.71; N, 9.37%

Synthesis of Ethyl-2-Methylbenzo[b][1, 8]Naphthyridine-3-Carboxylate (9 a-b) A mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.01 mol) & ethylacetoacetate (**8**) (0.01 mol) in ethanol (10 mL) containing 2-3 drops of piperidine was refluxed for 1 h. After completion of reaction (TLC checked), reaction mass dumped over ice-crushed water (20 mL) and stirred for the 30 mins., separated solid was filtered by suction, washed with cold n-hexane (20 mL), dried under vacuum and recrystallized from Ethanol or Toluene.

Ethyl-2-Methylbenzo[b][1, 8]Naphthyridine-3-Carboxylate (9a) Yield: 0.222 g (83%), recrystalized from ethanol to afford yellow crystal; M.p. 264-267 °C. IR (KBr): 2,945 m, 1,738 s, 1,612 s, 1,018 mcm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ: 1.69 (t, 3 H, *J*=5.9 Hz, CH_3), 2.79 (s, 3 H, CH_3), 4.33 (q, 2 H, *J*=5.9 Hz, CH_2), 7.34 (dd, 1 H, *J*=8.2 & 8.7 Hz, Ar-H), 7.79 (dd, 1 H, *J*=8.7 & 8.1 Hz, Ar-H), 8.09 (d, 1 H, *J*= 8.2 Hz, Ar-H), 8.36 (d, 1 H, *J*=8.1 Hz, Ar-H), 8.78 (s, 1 H, Ar-H), 9.19 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 266 [M^+] (95), 251 (89), 213 (85), 197 (64), 158 (80), 77 (71), 69 (47), 53 (38). Anal. Calcd. for $C_{16}H_{14}N_2O_2$ (266.29): C, 72.18; H, 5.26; N, 10.52% Found: C, 72.15; H, 5.24; N, 10.50%

Ethyl-7-Methoxy-2-Methylbenzo[b][1, 8]Naphthyridine-3-Carboxylate (9b) Yield: 0.249 g (84%), recrystalized from ethanol to afford yellow needles; M.p. 257-260 °C. IR (KBr): 2,940 m, 1,740, 1,619 s, 1,024 mcm^{-1}.^1H NMR (300 MHz $CDCl_3$) δ: 1.72 (t, 3 H, *J*=4.8 Hz, CH_3), 2.66 (s, 3 H, CH_3), 3.96 (s, 3 H, OCH_3), 4.43 (q, 2 H, *J*=4.8 Hz, CH_2), 7.43 (d, 1 H, *J*=8.8 Hz, Ar-H), 7.56 (s, 1 H, Ar-H), 8.24 (d, 1 H, *J*=8.8 Hz, Ar-H), 9.21 (s, 1 H, Ar-H), 9.44 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz $CDCl_3$) δ: 19.24, 26.72, 59.33, 68.45, 110.21, 121.47, 123.57, 126.94, 129.78, 132.43, 137.44, 138.73, 147.87, 154.27, 158.94, 159.64, 169.09. MS (70 eV) m/z (%): 296 [M^+] (69), 277 (94), 253 (74), 224 (41), 182 (57), 152 (59), 127 (49), 77 (64), 44 (88). Anal. Calcd. for $C_{17}H_{16}N_2O_3$ (296.32): C, 68.91; H, 5.40; N, 9.45%. Found: C, 68.90; H, 5.42; N, 9.47%.

Synthesis of 1-(2-Methylbenzo[b][1, 8]Naphthyridin-3-yl) Ethanone (11 a-d) A mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.01 mol) & acetyl acetone (**10a**) (0.01 mol) in ethanol (10 mL) containing 2-3 drops of

piperidine was refluxed for 1 h. After completion of reaction (TLC checked), reaction mass dumped over ice-crushed water (20 mL) and stirred for the 30 mins., separated solid was filtered by suction, washed with cold n-hexane (20 mL), dried under vacuum and recrystallized from Ethanol or Toluene.

1-(2-Methylbenzo[b][1, 8]Naphthyridin-3-yl)Ethanone (11a) Yield: 0.201 g (85%), recrystalized from ethanol to afford faint yellow solid; M.p. 204-206 °C. IR (KBr): 2,945 s, 1,705 s, 1,632 scm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ: 2.55 (s, 3 H, CH_3), 2.89 (s, 3 H, CH_3), 7.46 (dd, 1 H, *J*=7.8 & 8.4 Hz, Ar-H), 7.83 (dd, 1 H, *J*=8.4 & 8.3 Hz, Ar-H), 8.17 (d, 1 H, *J*=7.8 Hz, Ar-H), 8.29 (d, 1 H, *J*=8.3 Hz, Ar-H), 8.78 (s, 1 H, Ar-H), 9.19 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 236 [M^+] (79), 221 (74), 205 (67), 193 (47), 190 (69), 152 (39), 121 (49), 77 (64), 44 (81), 31 (64). Anal. Calcd. for $C_{15}H_{12}N_2O$ (236.27): C, 76.27; H, 5.08; N, 11.86% Found: C, 76.28; H, 5.10; N, 11.88%

1-(7-Methoxy-2-Methylbenzo[b][1, 8]Naphthyridin-3-yl) Ethanone (11b) Yield: 0.230 g (86%), recrystalized from ethanol to afford pale yellow needles; M.p. 214-217 °C. IR (KBr): 2,959 m, 1,712 s, 1,620 s, 1,024 scm^{-1}.^1H NMR (300 MHz $CDCl_3$) δ: 2.44 (s, 3 H, CH_3), 2.72 (s, 3 H, CH_3), 4.09 (s, 3 H, OCH_3), 7.31 (d, 1 H, *J*=8.8 Hz, Ar-H), 7.46 (s, 1 H, Ar-H), 8.18 (d, 1 H, *J*=8.8 Hz, Ar-H), 9.11 (s, 1 H, Ar-H), 9.39 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz $CDCl_3$) δ: 18.24, 28.76, 59.84, 109.44, 124.31, 125.74, 129.16, 133.43, 135.24, 136.37, 138.47, 147.89, 156.74, 159.21, 161.47, 187.20. MS (70 eV) m/z (%): 266 [M^+] (100), 251 (94), 223 (32), 182 (95), 139 (46), 44 (51). Anal. Calcd. for $C_{16}H_{14}N_2O_2$ (266.29): C, 72.18; H, 5.26; N, 10.52%. Found: C, 72.19; H, 5.29; N, 10.50%.

2-Methylbenzo[b][1, 8]Naphthyridine (11c) Yield: 0.155 g (79%), recrystalized from toluene to afford faint yellow solid; M.p. 90-93 °C. IR (KBr): 2,978 s, 1,626 scm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ: 2.92 (s, 3 H, CH_3), 7.22 (dd, 1 H, *J*= 7.9 & 8.7 Hz, Ar-H), 7.37 (d, 1 H, *J*=8.5 Hz, Ar-H), 7.67 (dd, 1 H, *J*=8.7 & 8.3 Hz, Ar-H), 8.14 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.25 (d, 1 H, *J*=8.3 Hz, Ar-H), 8.48 (d, 1 H, *J*= 8.5 Hz, Ar-H), 9.25 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz $CDCl_3$) δ: 24.11, 121.55, 123.47, 126.74, 127.41, 127.94, 128.56, 129.47, 135.67, 138.66, 148.72, 153.48, 157.49. Anal. Calcd. for $C_{13}H_{10}N_2$ (194.23): C, 80.41; H, 5.15; N, 14.43% Found: C, 80.43; H, 5.17; N, 14.49%

7-Methoxy-2-Methylbenzo[b][1, 8]Naphthyridine (11d) Yield: 0.187 g (83%), recrystalized from toulene to afford green needles; M.p. 84-86 °C. IR (KBr): 2,968 s, 1,618 s, 1,025 mcm^{-1}.^1H NMR (300 MHz $CDCl_3$) δ: 3.12 (s, 3 H, CH_3), 4.02 (s, 3 H, OCH_3), 7.29 (d, 1 H, J=8.2 Hz, Ar-H), 7.48 (d, 1 H, *J*=9.0 Hz, Ar-H), 7.56 (s, 1 H, Ar-H), 8.31 (d, 1 H, *J*=9.0 Hz, Ar-H), 8.57 (d, 1 H, *J*=8.2 Hz, Ar-H), 9.37 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 224 [M^+] (82), 201 (77), 181 (64), 152 (47), 77 (87), 51 (78). Anal. Calcd. for $C_{14}H_{12}N_2O$ (224.26): C, 75.00; H, 5.35; N, 12.50% Found: C, 75.02; H, 5.37; N, 12.48%

Syntesis of 2-(4-Bromophenyl)Benzo[b][1, 8]Naphthyridine (13 a-n) A solution of **1a-b** (0.001 mol) and p-bromoacetophenone (**12a**) (0.001 mol) in ethanol (10 mL) containing catalytic amount of piperidine was refluxed for 2 h. Completion of the reaction was monitored by thin layer chromatography (TLC). The mixture was then cooled to room temperature; the separated solid product was collected by suction filtration, washed with pet-ether, dried and recrystallized from ethanol.

2-(4-Bromophenyl)Benzo[b][1, 8]Naphthyridine (13a) Yield: 0.301 g (90%), recrystalized from ethanol to afford faint yellow solid; M.p. 95-98 °C. IR (KBr): 3,018 m, 1,640 scm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ: 7.46 (dd, 1 H, *J*=8.2 & 8.6 Hz, Ar-H), 7.52 (d, 2 H, *J*=8.3 Hz, Ar-H), 7.77 (dd, 1 H, *J*=8.6 & 8.1 Hz, Ar-H), 7.92 (d, 1 H, *J*= 8.2 Hz, Ar-H), 8.02 (d, 1 H, *J*=8.1 Hz, Ar H), 8.12 (d, 1 H, *J*=7.8 Hz, Ar-H), 8.22 (d, 2 H, *J*=8.3 Hz, Ar-H), 8.42 (d, 1 H, *J*=7.8 Hz, Ar-H), 9.23 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 334 [M^+] (84), 336 [M+2] (80), 255 (89), 212 (68), 207 (59), 179 (63), 77 (78). Anal. Calcd. for $C_{18}H_{11}N_2Br$ (335.20): C, 64.67; H, 3.29; N, 8.38% Found: C, 64.65; H, 3.30; N, 8.39%

2-(4-Chlorophenyl)Benzo[b][1, 8]Naphthyridine (13b) Yield: 0.233 g (80%), recrystalized from ethanol to afford faint brown solid; M.p. 120-123 °C. IR (KBr): 3,030 m, 1,646 scm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ: 7.29 (dd, 1 H, *J*=8.1 & 8.4 Hz, Ar-H), 7.42 (d, 2 H, *J*=8.3 Hz, Ar-H), 7.57 (dd, 1 H, *J*=8.4 & 8.5 Hz, Ar-H), 7.79 (d, 1 H, *J*= 8.1 Hz, Ar-H), 8.10 (d, 1 H, *J*=8.5 Hz, Ar H), 8.22 (d, 1 H, *J*=7.8 Hz, Ar-H), 8.36 (d, 2 H, *J*=8.3 Hz, Ar-H), 8.51 (d, 1 H, *J*=7.8 Hz, Ar-H), 9.03 (s, 1 H, Ar-H). Anal. Calcd. for $C_{18}H_{11}N_2Cl$ (290.75): C, 74.48; H, 3.79; N, 9.65% Found: C, 74.52; H, 3.77; N, 9.68%

2-(3,5-Bis(trifluoromethyl)Phenyl)Benzo[b][1, 8] Naphthyridine (13c) Yield: 0.344 g (87%), recrystalized from ethanol to afford yellow solid; M.p. 102-105 °C. IR (KBr): 3,028 m, 1,649 scm^{-1}. ^1H NMR (300 MHz $CDCl_3$) δ: 7.38 (dd, 1 H, *J*=8.3 & 8.7 Hz, Ar-H), 7.60 (dd, 1 H, *J*= 8.7 & 8.5 Hz, Ar-H), 7.84 (d, 1 H, *J*=8.3 Hz, Ar-H), 7.93 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.18 (d, 1 H, *J*=8.5 Hz, Ar-H), 8.34 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.42 (s, 1 H, Ar-H), 9.24 (s, 2 H, Ar-H), 9.47 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 392 [M^+] (59), 351 (78), 323 (80), 254 (66), 254 (56), 213 (47), 179

(79). Anal. Calcd. for $C_{20}H_{10}N_2F_6$ (392.30): C, 61.22; H, 2.55; N, 7.14% Found: C, 61.23; H, 2.56; N, 7.12%

2-(4-Methoxyphenyl)Benzo[b][1, 8]Naphthyridine (13d) Yield: 0.252 g (88%), recrystalized from ethanol to afford pale yellow needles; M.p. 114-117 °C. IR (KBr): 3,031 m, 1,649 s, 1,027 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 3.98 (s, 3 H, OCH_3), 7.10 (d, 2 H, *J*=9.2 Hz, Ar-H), 7.46 (dd, 1 H, *J*=8.0 & 8.4 Hz, Ar-H), 7.67 (dd, 1 H, *J*=8.4 & 8.3 Hz, Ar-H), 7.88 (d, 1 H, *J*=8.0 Hz, Ar-H), 7.94 (d, 2 H, *J*=9.2 Hz, Ar-H), 8.02 (d, 1 H, *J*=7.7 Hz, Ar-H), 8.19 (d, 1 H, *J*=8.3 Hz, Ar-H), 8.28 (d, 1 H, *J*=7.7 Hz, Ar-H), 9.25 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 286 [M$^+$] (100), 271 (68), 255 (35), 242 (42), 121 (29), 63 (32), 39 (22). Anal. Calcd. for $C_{19}H_{14}N_2O$ (286.33): C, 79.72; H, 4.89; N, 9.79% Found: C, 79.73; H, 4.90; N, 9.77%

2-(2,3-Dimethoxyphenyl)Benzo[b][1, 8]Naphthyridine (13e) Yield: 0.275 g (87%), recrystalized from ethanol to afford yellow crystal; M.p. 119-122 °C. IR (KBr): 3,029 m, 1,646 s, 1,022 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 3.60 (s, 6 H, 2×OCH_3), 7.08 (d, 1 H, *J*=8.7 Hz, Ar-H), 7.26 (dd, 1 H, *J*=2.5 & 8.7 Hz, Ar-H), 7.38 (d, 1 H, *J*=2.5 Hz, Ar-H), 7.49 (dd, 1 H, *J*=8.1 & 8.8 Hz, Ar-H), 7.83 (dd, 1 H, *J*=8.8 & 7.9 Hz, Ar-H), 7.96 (d, 1 H, *J*=8.1 Hz, Ar-H), 8.16 (d, 1 H, *J*=7.8 Hz, Ar-H), 8.20 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.29 (d, 1 H, *J*=7.8 Hz, Ar-H), 9.12 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz $CDCl_3$) δ: 57.43, 56.79, 115.20, 117.47, 120.12, 121.47, 125.33, 127.12, 127.49, 128.32, 128.78, 129.28, 129.82, 135.43, 137.77, 145.64, 149.74, 152.64, 156.57, 159.71. Anal. Calcd. for $C_{20}H_{16}N_2O_2$ (316.35): C, 75.94; H, 5.06; N, 8.86% Found: C, 75.92; H, 5.08; N, 8.88%

2-p-Tolylbenzo[b][1, 8]Naphthyridine (13f) Yield: 0.237 g (87%), recrystalized from ethanol to afford yellow solid; M.p. 92-95 °C. IR (KBr): 3,004 m, 1,640 scm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 2.48 (s, 3 H, CH_3), 7.44 (d, 2 H, *J*=8.7 Hz, Ar-H), 7.60 (dd, 1 H, *J*=8.2 & 8.5 Hz, Ar-H), 7.98 (dd, 1 H, *J*=8.5 & 8.1 Hz, Ar-H), 8.07 (d, 1 H, *J* =8.2 Hz, Ar-H), 8.29 (d, 2 H, *J*=8.7 Hz, Ar-H), 8.42 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.59 (d, 1 H, *J*=8.1 Hz, Ar-H), 8.68 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.97 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 270 [M$^+$] (81), 255 (62), 241 (32), 152 (29), 134 (61), 89 (32). Anal. Calcd. for $C_{19}H_{14}N_2$ (270.33): C, 84.44; H, 5.18; N, 10.37% Found: C, 84.45; H, 5.17; N, 10.35%

2-(4-Nitrophenyl)Benzo[b][1, 8]Naphthyridine (13 g) Yield: 0.239 g (79%), recrystalized from ethanol to afford brown solid; M.p. 115-118 °C. IR (KBr): 3,033 m, 1,540 m, 1,372 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 7.45 (dd, 1 H, *J*=7.9 & 7.8 Hz, Ar-H), 7.54 (d, 2 H, *J*=8.8 Hz, Ar-H), 7.68 (dd, 1 H, *J*=7.8 & 8.0 Hz, Ar-H), 8.02 (d, 1 H, *J*= 7.9 Hz, Ar-H), 8.22 (d, 1 H, *J*=8.0 Hz, Ar-H), 8.36 (d, 1 H, *J*=8.9 Hz, Ar-H), 8.43 (d, 1 H, *J*=8.9 Hz, Ar-H), 8.56 (d, 2 H, *J*=8.8 Hz, Ar-H), 9.18 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 301 [M+] (88), 255 (82), 179 (55), 77 (68). Anal. Calcd. for $C_{18}H_{11}N_3O_2$ (301.30): C, 71.76; H, 3.65; N, 13.95% Found: C, 71.77; H, 3.66; N, 13.97%

2-(4-Bromophenyl)-7-Methoxybenzo[b][1, 8]Naphthyridine (13 h) Yield: 0.312 g (85%), recrystalized from ethanol to afford yellow solid; M.p. 248-249 °C. IR (KBr): 3,010 m, 1,642 s, 1,040 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 4.07 (s, 3 H, OCH_3), 7.34 (d, 1 H, *J*=9.3 Hz, Ar-H), 7.46 (s, 1 H, Ar-H), 7.89 (d, 2 H, *J*=8.1 Hz, Ar- H), 8.04 (d, 1 H, *J*= 7.8 Hz, Ar-H), 8.19 (d, 2 H, *J*=8.1 Hz, Ar-H), 8.35 (d, 1 H, *J*=9.3 Hz, Ar-H), 9.05 (d, 1 H, *J*=7.8 Hz, Ar-H), 9.46 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz $CDCl_3$) δ: 57.21, 109.42, 122.74, 123.24, 123.66, 126.47, 127.89, 129.30 (2 C's), 131.51, 133.46 (2 C's), 135.66, 136.94, 138.40, 145.55, 153.26, 156.19, 158.74. MS (70 eV) m/z (%): 364 [M$^+$] (89), 366 [M+2] (88), 285 (45), 242 (57), 142 (32), 121 (51). Anal. Calcd. for $C_{19}H_{13}N_2BrO$ (365.23): C, 62.63; H, 3.57; N, 7.69% Found: C, 62.64; H, 3.56; N, 7.70%

2-(4-Chlorophenyl)-7-Methoxybenzo[b][1, 8]Naphthyridine (13i) Yield: 0.267 g (83%), recrystalized from ethanol to afford yellow crystals; M.p. 254-257 °C. IR (KBr): 3,026 m, 1,635 s, 1,038 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 4.02 (s, 3 H, OCH_3), 7.18 (d, 1 H, *J*=9.1 Hz, Ar-H), 7.33 (s, 1 H, Ar-H), 7.74 (d, 2 H, *J*=8.3 Hz, Ar- H), 7.93 (d, 1 H, *J*= 7.5 Hz, Ar-H), 8.12 (d, 2 H, *J*=8.3 Hz, Ar-H), 8.43 (d, 1 H, *J*=9.1 Hz, Ar-H), 9.17 (d, 1 H, *J*=7.5 Hz, Ar-H), 9.33 (s, 1 H, Ar-H). Anal. Calcd. for $C_{19}H_{13}N_2ClO$ (320.77): C, 71.25; H, 4.06; N, 8.75% Found: C, 71.22; H, 4.09; N, 8.77%

2-(3,5-Bis(Trifluoromethyl)Phenyl)-7-Methoxybenzo[b][1, 8]Naphthyridine (13j) Yield: 0.359 g (85%), recrystalized from ethanol to afford faint green solid; M.p. 199-202 °C. IR (KBr): 3,024 m, 1,642 s, 1,032 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 4.05 (s, 3 H, OCH_3), 7.39 (d, 1 H, *J*= 9.1 Hz, Ar-H), 7.57 (s, 1 H, Ar-H), 8.08 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.27 (d, 1 H, *J*=9.1 Hz, Ar-H), 8.43 (s, 1 H, Ar-H), 8.78 (s, 2 H, Ar-H), 8.91 (d, 1 H, *J*=7.9 Hz, Ar-H), 9.52 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 423 [M+1] (100), 380 (69), 354 (74), 310 (18), 285 (64). Anal. Calcd. for $C_{21}H_{12}N_2F_6O$ (422.32): C, 59.71; H, 2.84; N, 6.63% Found: C, 59.70; H, 2.85; N, 6.64%

7-Methoxy-2-(4-Methoxyphenyl)Benzo[b][1, 8]Naphthyridine (13k) Yield: 0.272 g (86%), recrystalized from ethanol to afford yellow solid; M.p. 229-232 °C. IR (KBr): 3,021 m, 1,639 s, 1,036 mcm^{-1}. ^{1}H NMR (300 MHz DMSO-d_6) δ: 3.89 (s, 3 H, OCH_3), 4.02 (s, 3 H, OCH_3), 7.21 (d, 2 H, *J*= 8.5 Hz, Ar-H), 7.39 (d, 1 H, *J*=8.2 Hz, Ar-H), 7.50 (s, 1 H,

Ar-H), 7.64 (d, 2 H, *J*=8.5 Hz, Ar-H), 8.12 (d, 1 H, *J*= 8.1 Hz, Ar-H), 8.22 (d, 1 H, *J*=8.2 Hz, Ar-H), 8.84 (d, 1 H, *J*=8.1 Hz, Ar-H), 9.38 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz $CDCl_3$) δ: 55.39, 55.62, 105.80, 114.13 (2 C's), 117.76, 118.57, 121.45, 122.95, 129.05, 129.68 (2 C's), 131.20, 136.62, 137.75, 153.01, 155.26, 161.18, 161.70, 162.10. MS (70 eV) m/z (%): 316 [M^+] (100), 301 (32), 230 (19), 158 (15), 115 (12). Anal. Calcd. for $C_{20}H_{16}N_2O_2$ (316.35): C, 75.94; H, 5.06; N, 8.86% Found: C, 75.95; H, 5.08; N, 8.87%

7-Methoxy-2-(2,3-Dimethoxyphenyl)Benzo[b][1, 8]Naphthyridine (13 l) Yield: 0.307 g (88%), recrystalized from ethanol to afford yellow crystals; M.p. 238-241 °C. IR (KBr): 3,026 m, 1,635 s, 1,038 mcm^{-1}. ^{1}H NMR (300 MHz DMSO-d_6) δ: 3.80 (s, 6 H, 2×OCH_3), 4.04 (s, 3 H, OCH_3), 7.10 (d, 1 H, *J*=9.2 Hz, Ar-H), 7.18 (dd, 1 H, *J*=2.4 & 9.2 Hz, Ar-H), 7.29 (d, 1 H, *J*=2.4 Hz, Ar-H), 7.41 (d, 1 H, *J*=8.6 Hz, Ar-H), 7.52 (s, 1 H, Ar-H), 7.97 (d, 1 H, *J*=8.2 Hz, Ar-H), 8.25 (d, 1 H, *J*=8.6 Hz, Ar-H), 8.95 (d, 1 H, *J*=8.2 Hz, Ar-H), 9.32 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 345 [M-1] (100), 331 (49), 315 (42), 300 (41), 286 (19), 151 (19), 108 (12). Anal. Calcd. for $C_{21}H_{18}N_2O_3$ (346.38): C, 72.83; H, 5.20; N, 8.09% Found: C, 72.85; H, 5.21; N, 8.10%

7-Methoxy-2-p-Tolylbenzo[b][1, 8]Naphthyridine (13 m) Yield: 0.261 g (87%), recrystalized from ethanol to afford yellow prism; M.p. 208-211 °C. IR (KBr): 3,035 m, 1,625 s, 1,026 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 2.47 (s, 3 H, CH_3), 3.98 (s, 3 H, OCH_3), 7.35 (d, 1 H, *J*=8.7 Hz, Ar-H), 7.49 (d, 2 H, *J*=8.5 Hz, Ar-H), 7.59 (s, 1 H, Ar- H), 7.95 (d, 2 H, *J*=8.5 Hz, Ar-H), 8.12 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.25 (d, 1 H, *J*=8.7 Hz, Ar-H), 8.49 (d, 1 H, *J*=7.9 Hz, Ar-H), 8.83 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 300 [M^+] (97), 285 (92), 209 (77), 77 (89). Anal. Calcd. for $C_{20}H_{16}N_2O$ (300.35): C, 80.00; H, 5.33; N, 9.33% Found: C, 79.98; H, 5.32; N, 9.35%

7-Methoxy-2-(4-Nitrophenyl)Benzo[b][1, 8]Naphthyridine (13n) Yield: 0.265 g (80%), recrystalized from ethanol to afford yellow solid; M.p. 191-194 °C, IR (KBr): 3,020 m, 1,642 s, 1,559 m, 1,367 m, 1,045 mcm^{-1}. ^{1}H NMR (300 MHz DMSO-d_6) δ: 4.03 (s, 3 H, OCH_3), 7.32 (d, 2 H, *J*=8.3 Hz, Ar-H), 7.48 (d, 1 H, *J*=8.5 Hz, Ar-H), 7.52 (s, 1 H, Ar-H), 8.01 (d, 1 H, *J*=7.7 Hz, Ar-H), 8.19 (d, 1 H, *J*=8.5 Hz, Ar-H), 8.30 (d, 2 H, *J*=8.3 Hz, Ar-H), 8.98 (d, 1 H, *J*=7.7 Hz, Ar-H), 9.37 (s, 1 H, Ar-H). Anal. Calcd. for $C_{19}H_{13}N_3O_3$ (331.33): C, 68.88; H, 3.92; N, 12.68% Found: C, 68.89; H, 3.94; N, 12.70%

Synthesis of 9,10-Dimethoxy-7H-Benzo[b]Indeno[1,2-g][1, 8] Naphthyridine (15 a-d) The mixture of 2-aminoquinoline-3-carbaldehyde (**1a-b**) (0.01 mol) & indanone (**14a-b**) (0.01 mol) in ethanolic potassium hydroxide solution (10 mL, 2%) was refluxed for 1 h. Completion of the reaction was monitored by Thin Layer Chromatography (TLC). The mixture was then dumped over ice-crushed water (20 mL) and stirred for the 30 mins. The separated solid product was collected by suction filtration, washed with pet-ether, dried and recrystallized from Methanol.

9,10-Dimethoxy-7H-Benzo[b]Indeno[1,2-g][1, 8]Naphthyridine (15a) Yield: 0.281 g (85%), recrystalized from Methanol to afford yellow solid; M.p. 269-272 °C. IR (KBr): 2,997 m, 2,968 m, 1,618 s, 1,024 mcm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 3.89 (s, 2 H, CH_2), 3.95 (s, 3 H, OCH_3), 4.01 (s, 3 H, OCH_3), 6.78 (s, 1 H, Ar-H), 7.34 (dd, 1 H, *J*=7.8 & 8.7 Hz, Ar-H), 7.55 (s, 1 H, Ar-H), 7.79 (dd, 1 H, *J*=8.7 & 8.1 Hz, Ar-H), 8.09 (d, 1 H, *J*=7.8 Hz, Ar-H), 8.36 (d, 1 H, *J*=8.1 Hz, Ar-H), 8.78 (s, 1 H, Ar-H), 9.19 (s, 1 H, Ar-H). Anal. Calcd. for $C_{21}H_{16}N_2O_2$ (328.36): C, 76.82; H, 4.87; N, 8.53% Found: C, 76.84; H, 4.88; N, 8.55%

2,9,10-Trimethoxy-7H-Benzo[b]Indeno[1,2-g][1, 8]Naphthyridine (15b) Yield: 0.319 g (89%), recrystalized from Methanol to afford yellow needles; M.p. 231-233 °C. IR (KBr): 3,012 s, 2,977 m, 1,607 s, 1,011 mcm^{-1}.^{1}H NMR (300 MHz $CDCl_3$) δ: 3.75 (s, 2 H, CH_2), 3.88 (s, 3 H, OCH_3), 3.96 (s, 3 H, OCH_3), 4.05 (s, 3 H, OCH_3), 6.87 (s, 1 H, Ar-H), 7.43 (d, 1 H, *J*=8.8 Hz, Ar-H), 7.51 (s, 1 H, Ar-H), 7.67 (s, 1 H, Ar-H), 8.94 (d, 1 H, *J*=8.8 Hz, Ar-H), 9.21 (s, 1 H, Ar-H), 9.44 (s, 1 H, Ar-H). ^{13}C NMR (75 MHz $CDCl_3$) δ: 33.47, 55.55, 56.16, 56.38, 104.87, 105.77, 107.41, 113.81, 118.60, 120.77, 122.48, 128.86, 130.57, 132.14, 134.45, 136.43, 149.77, 151.94, 152.73, 155.69, 161.68, 166.94. MS (70 eV) m/z (%): 358 [M^+] (58), 327 (51), 288 (56), 207 (57), 189 (50), 175 (62), 164 (82), 150 (87), 131 (74), 118 (70), 91 (68), 63 (42). Anal. Calcd. for $C_{22}H_{18}N_2O_3$ (358.39): C, 73.74; H, 5.02; N, 7.82%. Found: C, 73.75; H, 5.04; N, 7.84%.

7H-Benzo[b]Indeno[1,2-g][1, 8]Naphthyridine (15c) Yield: 0.217 g (80%), recrystalized from Methanol to afford yellow solid; M.p. 277-280 °C. IR (KBr): 3,014 m, 2,968 m, 1,618 scm^{-1}. ^{1}H NMR (300 MHz $CDCl_3$) δ: 3.94 (s, 2 H, CH_2), 7.24-7.32 (m, 4 H, Ar-H), 7.42 (dd, 1 H, *J*= 8.2 & 8.4 Hz, Ar-H), 7.79 (dd, 1 H, *J*=8.4 & 8.1 Hz, Ar-H), 8.09 (d, 1 H, *J*=8.2 Hz, Ar-H), 8.36 (d, 1 H, *J*=8.1 Hz, Ar-H), 8.78 (s, 1 H, Ar-H), 9.19 (s, 1 H, Ar-H). Anal. Calcd. for $C_{19}H_{12}N_2$ (268.31): C, 85.07; H, 4.47; N, 10.44%. Found: C, 85.10; H, 4.48; N, 10.45%.

2-Methoxy-7H-Benzo[b]indeno[1,2-g][1, 8]Naphthyridine (15d) Yield: 0.259 g (86%), recrystalized from Methanol to afford yellow needles; M.p. 252-255 °C. IR (KBr): 3,012 m, 2,968 m, 1,611 s, 1,011 mcm^{-1}.^{1}H NMR

(300 MHz $CDCl_3$) δ: 3.82 (s, 2 H, CH_2), 4.05 (s, 3 H, OCH_3), 7.09-7.38 (m, 4 H, Ar-H), 7.43 (d, 1 H, J=8.6 Hz, Ar-H), 7.51 (s, 1 H, Ar-H), 8.24 (d, 1 H, J=8.6 Hz, Ar-H), 9.21 (s, 1 H, Ar-H), 9.44 (s, 1 H, Ar-H). MS (70 eV) m/z (%): 298 [M^+] (100), 277 (32), 255 (64), 227 (32), 149 (38), 128 (45), 114 (18), 77 (13). Anal. Calcd. for $C_{20}H_{14}N_2O$ (298.34): C, 80.53; H, 4.69; N, 9.39%. Found: C, 80.55; H, 4.70; N, 9.40%.

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