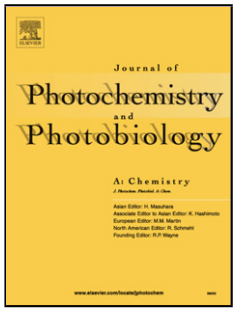

Title: Efficient synthesis, fluorescence and DFT studies of different substituted 2-chloroquinoline-4-amines and benzo[*g*][1,8]Naphthyridine Derivatives

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PII: S1010-6030(16)30440-3
DOI: http://dx.doi.org/doi:10.1016/j.jphotochem.2016.08.014
Reference: JPC 10327

To appear in: *Journal of Photochemistry and Photobiology A: Chemistry*

Received date: 1-6-2016
Revised date: 8-8-2016
Accepted date: 8-8-2016

Please cite this article as: A.M.Magesh Selva Kumar, B.Vijaya Pandiyan, S.Mohana Roopan, S.P.Rajendran, Efficient synthesis, fluorescence and DFT studies of different substituted 2-chloroquinoline-4-amines and benzo[g][1,8]Naphthyridine Derivatives, Journal of Photochemistry and Photobiology A: Chemistry http://dx.doi.org/10.1016/j.jphotochem.2016.08.014

<AT>Efficient synthesis, fluorescence and DFT studies of different substituted
2-chloroquinoline-4-amines and benzo[*g*][1,8] Naphthyridine Derivatives

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<ABS-Head><ABS-HEAD>Graphical abstract ► **RESEARCH HIGHLIGHTS**► A unique and efficient synthesis of novel 2-chloroquinoline-4-amines► and benzo[*g*][1,8]naphthyridines.► The major advantage of the protocol is that it does not any catalyst.► Arrival of products at lesser reaction time.► Influence of electron donor-acceptor substituent's on photophysical of► A synthesized compound has been studied.► Photophysical and theoretical (DFT) studies are in close co-relation.

<ABS-HEAD>ABSTRACT

<ABS-P>An efficient and single step strategy for synthesizing new functionalized benzo[*b*][1,8]naphthyridine derivatives is presented. Benzo[*g*][1,8]naphthyridines have been synthesized by the condensation of substituted 2-chloroquinoline-3-carbaldehydes with various 2-chloroquinoline-4-amines, 1*H*-Indazole-6-amine in basic medium. The electro luminescence and photophysical properties of a series of benzo[*g*][1,8]naphthyridines **5(a-d**), **6(a-d**) and 2-chloroquinoline-4-amines **3(a-f**) are reported and investigated with the aim of arriving at good fluorescent materials. Moreover, the effect of electron donor-acceptor substituent on fluorescence properties of all molecules has been investigated along with their fluorescent quantum yields. Furthermore we analyzed for band gap energy associated with HOMO-LUMO, through density functional (DFT M06-HF) studies. The experimental observations are in close agreement with the theoretical calculation. All the synthesized compounds were identified on the basis of their NMR, Mass spectral data analyses.

<KWD>Keywords:

2-Chloroquinoline-3-carbaldehydes

2-Chloroquinoline-4-amines

Benzo[*g*]-1*H*-Indazolo[5,6-*b*][1,8]naphthyridines

Benzo[*g*][3,4-*b*]-2,6-dichloroquino[1,8]naphthyridines

Fluorescence of benzo[*g*][1,8]naphthyridines

HOMO-LUMO Energy level diagrams of benzo[*g*][1,8]naphthyridines.

<H1>1. Introduction

In organic synthesis, functional group transformations have significant importance. The different substituted heterocyclic compounds have received much interest and attention especially due to their pharmacological activities [1]. Particularly amino quinolines have attracted considerable interest because their derivatives display a wide range of pharmacological activities [2-8]. A recent investigation indicated that new diarylamides and diarylureas 8-amino (acetamido)quinoline, novel pyrano[3,2-*f*] quinoline, phenanthroline derivatives display enhanced activity towards different cancer cell lines,[9,10] and azole-quinoline exhibit excellent photophysical properties [11]. Keeping all these pharmacological and photo physical/ luminescent profiles in mind we have identified new substituted amino quinolines. The present work involves the chemical modification of 2-chloro-4-azido quinolines at **C_4** position to 2-chloroquinolines-4-amines.

Various naphthyridine derivatives have received considerable attention over the past years because of their wide range of biological activities [12-16]. In recent literature survey indicates that various fused angular, linear naphthyridine systems exhibit fluorescence behavior [17-21] because of the presence of π-π*, σ-π* and n-π* conjugation systems, different electronic states. Such naphthyridines system exhibit fluorescence activities like benzo[*b*][1,8] naphthyridines-3-carbonitrile [22], 5-(3,4Dichlorophenyl)-5,6-dihyrobenzo[*b*]naphtha[2,1-*g*][1,8] naphthyridine [23], 2,5-Diphenylbenzo[*h*][1,6]naphthyridines [24], **Figs 1,2,3.** Moreover, we synthesized different substituted 2-chloroquinoline-4-amine derivatives [25-29] and studied for photo physical activity in selective organic solvent. A number of angular, linear naphthyridines that have been prepared in our laboratory were subjected to absorption and emission studies. In

present phase of research, we report a new way synthesis of benzo[*g*][1,8] naphthyridines **5(a-d**) and **6(a-d**) starting from 2-chloroquinoline-3-carbaldehydes [30-32]. The photophysical properties were compared by absorption and emission maxima with reference to donor and acceptor substitution in it. The substituent effect on the performance of these were studied by calculating highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies gaps values by **Gaussian09** software [33]. The fluorescence properties of 2-chloroquinoline-4-amines **3(a-f**), benzo[*g*]-1*H*-Indazolo[5,6-*b*][1,8]naphthyridines **5(a-d**), benzo [*g*][3,4-*b*]2,6-dichloroquino[1,8]naphthyridines **6(a-d**) was systematically investigated by fluorescence spectroscopy.
Some examples of fluorescent active molecules

<H1>2. Experimental sections
<H2>2.1. General

Melting points (mp) were determined on a Mettler FP 51 apparatus (Mettler Instruments, Switzerland) and are uncorrected. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on Bruker AV-400 spectrometer. Chemical shifts were reported in ppm from internal tetramethylsilane (TMS) internal reference and are given δ-unit. The solvents for NMR spectra were deuterio-chloroform ($CDCl_3$) and Deuterio-Dimethylsulphoxide (DMSO-d_6). Infrared spectra were taken on Shimadzu FTIR-8201PC (Schimadzu, Japan) instrument in potassium bromide KBr pellets unless otherwise stated. Absorption spectral measurements were carried out using JASCO V-630 UV–visible spectrophotometer. Quartz cuvettes of path length 1 cm were used to record the absorption spectra. The emission spectral studies were performed with JASCO FP-6600 spectrofluorometer equipped with a 1 cm quartz cuvette and exciting the samples at their absorption maximum wavelength ($\lambda_{abs.max}$). The concentration of the solute was maintained at 10^{-3} M solution in absolute methanol for all experiments. The photophysical properties of these compounds were determined with respect to the absorption ($\lambda_{abs.\ max.}$), fluorescence maxima ($\lambda_{flu.\ max.}$) of these compounds and their quantum yields (ϕ_f) were calculated by previous literature methods by using Rhodamine-6G as reference standard (ϕ_{ref}=0.95 in 0.1 M CH_3OH) [44-46]. UV-visible absorption spectra were recorded in the range of 200 to 600 nm and

fluorescence monitored in the range of 400-700nm. The ESI-MS were recorded on a Thermo Scientific mass spectrometer (mass spectrometer ESI-MS). Microanalyses were performed on a Vario EL III model CHNS analyzer (Vario, Germany) at the Department of Chemistry, Bharathiar University, Coimbatore–46, Tamil Nadu, India. Column chromatography was carried out on silica gel (SD Fine Chemicals, 60–120 mesh). Solutions were concentrated in a rotary evaporator under reduced pressure. All reactions were monitored by thin layer chromatography (TLC), carried out on 0.2 mm silica gel 60 F254 (Merck) plates using UV light (254 nm and 366 nm) and Fluorescence light (400 nm and 600 nm) for detection. Common reagents-grade chemicals were commercially available and were used without further purification or prepared by standard literature procedures.

Computational details:

All the computations in the present study were performed by DFT theory in the frame work of M06HF/6-31G (d, p) level of theory which is carried out on all 12 molecules Gaussian09W programme. Since, *Shang et al.* [50] clearly reported the M06HF functional gave more satisfactory results for photochemistry calculations. All these molecules are first optimized with that level of theories. Then, all the optimized model structures correspond to the minima in the potential energy surface, because no imaginary frequencies were observed. Molecular orbital (MO) compositional analyses were carried out by chemissian software.

<H2>2.2. Synthetic procedures

<H3>2.2.1. General procedure for synthesis of 2-chloro-4-azido quinolines **2(a-f**)

To a vigorously stirred solution of 2,4-dichloroquinoline **1(a-f)** its derivatives (9 mmol) in DMF (20 mL) at 55^0C, sodium azide (9 mmol) was added slowly for 15 min, the whole reaction was stirred for 3-4 hrs. After the completion of reaction as it indicated by TLC spot change, the reaction mixture was poured into crushed ice, filtered, dried and chromatographed over silica gel using petroleum ether: ethyl acetate (92:8) (v/v) as eluent which yielded yellow/white colored compound **2(a-f)**, it was recrystallised from ethyl acetate.

<H4>2.2.1.1. 2-Chloro-4-azidoquinoline (**2a)**

Yield: 72%; white solid; mp 104-106°C. IR (KBr, cm^{-1}): 1302, 1565, 2126, 2911. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (s, 1H, Ar-H), 7.56 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.78 (t, *J*=7.6 Hz, 1H, Ar-H),

8.02 (t, *J*=8.4 Hz, 1H, Ar-H), 7.96 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 109.38, 120.46, 122.41, 124.22, 126.89, 128.44, 131.66, 148.44, 148.52, 150.48; ESI-MS (m/z): calcd for $[M+H]^+$ 204.62, found 204.83; Anal. Calcd for $C_9H_5ClN_4$: C, 52.83; H, 2.46; N, 27.38 Found: C, 52.79; H, 2.44; N, 27.44.

<H4>2.2.1.2. 6-Methyl-2-chloro-4-azidoquinoline (**2b)**
Yield: 82%; yellow solid; mp 98-99°C. IR (KBr, cm^{-1}): 1306, 1567, 2130, 3052. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.52 (s, 3H, CH_3), 7.08 (s, 1H, Ar-H), 7.57 (d, *J* = 6.4 Hz, 1H, Ar-H), 7.76 (s, 1H, Ar-H), 7.86 (d, *J*=6.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.71, 109.31, 120.38, 121.31, 124.14, 128.13, 133.80, 137.10, 146.99, 147.77, 149.51. ESI-MS (m/z): calcd for $[M+H]^+$ 218.04, found 218.01; Anal. Calcd for $C_{10}H_7ClN_4$: C, 54.93; H, 3.23; N, 25.62 Found: C, 54.88; H, 3.26; N, 25.64.

<H4>2.2.1.3. 6-Dichloro-4-azidoquinoline (**2c)**
Yield: 82%; white solid; mp 103–105°C. IR (KBr, cm^{-1}): 1320, 1562, 2126, 3047. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (s, 1H, Ar-H), 7.67 (dd, *J* = 8.8, 1.6 Hz, 1H, Ar-H), 7.91 (d, *J*=9.2 Hz, 1H, Ar-H), 7.99 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.12, 121.10, 121.62, 130.00, 132.54, 133.00, 146.80, 147.71, 150.79. ESI-MS (m/z): calcd for $[M+H]^+$ 239.06, found 239.21; for Anal. Calcd for $C_{10}H_4Cl_2N_4$: C, 45.22; H, 1.69; N, 23.44 Found: C, 45.18; H, 1.74; N, 23.43.

<H4>1.1.1.1. 6-Methoxy-2-chloro-4-azidoquinoline (***2d)***
Yield: 77%; yellow solid; mp108-109°C. IR (KBr, cm^{-1}): 1312, 1560, 2127, 2918. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 3H, OCH_3), 7.14 (s, 1H, ArH), 7.70 (d, *J* = 8.8 Hz, 1H, Ar-H), 8.00 (s, 1H, Ar-H), 7.99 (d, *J*=9.2 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 41.71, 110.13, 121.10, 121.63, 130.00, 130.55, 133.00, 146.81, 147.72, 150.79, 149.51. ESI-MS (m/z): calcd for $[M+H]^+$ 234.64, found 234.89; Anal. Calcd for $C_{10}H_7ClN_4O$: C, 51.19; H, 3.01; N, 23.88 Found: C, 51.23; H, 2.97; N, 23.86.

<H4>2.2.1.5. 8-Methyl-2-chloro-4-azidoquinoline (**2e)**

Yield: 83%; white solid; mp 98–102°C. IR (KBr, cm^{-1}): 1315, 1567, 2125, 2963. ^1H NMR (400 MHz, $CDCl_3$): δ 2.74 (s, 3H, CH_3), 7.12 (s, 1H, Ar-H), 7.42 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.61 (d, *J*=7.2 Hz, 1H, Ar-H), 7.87 (d, *J*=8.4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.10, 109.18, 120.15, 120.49, 126.52, 131.78, 136.68, 147.69, 148.51, 149.35. ESI-MS (m/z): calcd for $[M + H]^+$ 218.64, found 218.93; Anal. Calcd for $C_{10}H_7ClN_4$: C, 54.93; H, 3.23; N, 25.62 Found: C, 54.89; H, 3.25; N, 25.64.

<H4>2.2.1.6. Benzo[b]-2-chloro-4-azidoquinoline (**2f)**
Yield: 87%; white solid; mp 104-106°C. IR (KBr, cm^{-1}): 1317, 1617, 2126, 2923. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 1H, Ar-H), 7.58-8.04(m, 5H, Ar-H), 9.16 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.15, 118.79, 120.41, 122.36, 125.22, 127.80, 127.91, 129.11, 129.35, 130.06, 134.22, 147.38, 149.76. ESI-MS (m/z): calcd for $[M + H]^+$ 254.67, found 254.71; Anal. Calcd for $C_{13}H_7ClN_4$: C, 61.31; H, 2.77; N, 22.00 Found: C, 61.35; H, 2.71; N, 22.02.

<H2>2.3. General procedure Synthesis of 2-chloro quinoline-4-amines **3(a-f**)
The 2-chloro-4-azido quinolines (4 mmol) compound ***2(a-f)*** was taken in 20 mL methanol and (4 mmol) of sodium dithionite was added and refluxed for 3-6 hour on water bath. After the completion of reaction as it indicated by TLC spot change, the reaction mixture was poured into crushed ice, filtered, dried and chromatographed over silica gel using petroleum ether: ethyl acetate (80:20) (v/v) as eluent which pure light yellow/white colored needles compound ***3(a-f)***. It was recrystallised from absolute methanol.
<H3>2.3.1. 2-Chloroquinoline-4-amine (**3a)**
Yield: 91%; white needles; mp 180-183°C. IR (KBr, cm^{-1}): 1643, 2970, 3182, 3312, 3459. ^1H NMR (400 MHz, DMSO-d_6): δ 6.51 (s, 1H, Ar-H), 7.17(s, 2H, NH_2), 7.46-7.42 (m, 1H, Ar-H), 7.70-7.63(m, 2H, Ar-H), 8.17 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 100.50, 117.63, 122.44, 124.29, 127.89, 130.24, 147.99, 150.55, 154.13. ESI-MS (m/z): calcd for $[M + H]^+$ 178.62, found 179.00; Anal. Calcd for $C_9H_7ClN_2$: C, 60.52; H, 3.95; N, 15.68 Found: C, 60.56; H, 3.89; N, 15.70.

<H3>2.3.2. 6-Methyl-2-chloroquinoline-4-amine (**3b)**
Yield: 79%; white solid; mp 160-162°C. IR (KBr, cm^{-1}): 1647, 2961, 3181, 3319, 3452. ^1H NMR (400 MHz, DMSO-d_6): δ 2.45 (s, 3H, CH_3), 6.48 (s, 1H, Ar-H), 7.05(s, 2H, NH_2), 7.50

(dd, *J*=6.8, 2.0 Hz, 1H, Ar-H), 7.59(d, *J*= 8.8 Hz, 1H, Ar-H), 7.95 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.14, 100.48, 117.50, 121.41, 127.68, 132.06, 133.65, 146.37, 149.72, 153.60. ESI-MS (m/z): calcd for $[M + H]^+$ 192.64, found 193.01; Anal. Calcd for $C_{10}H_9ClN_2$: C, 62.35; H, 4.71; N, 14.54 Found: C, 62.31; H, 4.76; N, 14.53.

<H3>2.3.3. 2,6-Dichloroquinoline-4-amine (**3c)**
Yield: 89%; white needles; mp 240-241°C. IR (KBr, cm^{-1}): 1643, 2970, 3233, 3329, 3465. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.60 (s, 1H, Ar-H), 7.33 (s, 2H, NH_2), 7.72 (dd, *J*=9.2, 2.4 Hz, 1H, Ar-H), 7.76(dd, *J*= 9.2, 2.00 Hz, 1H, Ar-H), 8.37 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 101.23, 118.47, 121.76, 128.80, 130.02, 130.63, 146.55, 151.02, 153.50. ESI-MS (m/z): calcd for $[M + H]^+$ 213.06, found 212.94; Anal. Calcd for $C_9H_6Cl_2N_2$: C, 50.73; H, 2.84; N, 13.15 Found: C, 50.68; H, 2.91; N, 13.13.

<H3>2.3.4. 6-Methoxy-2-chloroquinoline-4-amine (**3d)**
Yield: 61%; white needles; mp 139-141°C. IR (KBr, cm^{-1}): 1646, 2970, 3169, 3315, 3453. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.91 (s, 3H, OCH_3), 4.71 (s, 2H, NH_2), 6.59 (s, 1H, Ar-H), 6.92 (s, 1H, Ar-H), 7.33 (d, *J*=9.2 Hz, 1H, Ar-H), 7.84 (d, *J*= 9.2 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 41.32, 100.48, 117.50, 121.41, 127.68, 132.06, 133.65, 146.37, 149.72, 153.60. ESI-MS (m/z): calcd for $[M + H]^+$ 208.64, found 209.01; Anal. Calcd for $C_{10}H_9ClN_2O$: C, 57.57; H, 4.35; N, 13.43 Found: C, 57.50; H, 4.37; N, 13.48.

<H3>2.3.5. 8-Methyl-2-chloroquinoline-4-amine (**3e)**
Yield: 96%; white solid; mp 160-162°C. IR (KBr, cm^{-1}): 1628, 2958, 3235, 3392, 3491. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.72 (s, 3H, CH_3), 4.77 (s, 2H, NH_2), 6.59 (s, 1H, Ar-H), 7.32 (d, *J*=7.2 Hz, 1H, Ar-H), 7.53(d, *J*= 8.4 Hz, 1H, Ar-H), 7.55 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.49, 103.17, 117.62, 117.84, 124.87, 130.68, 137.25, 147.55, 150.41, 151.62. ESI-MS (m/z): calcd for $[M + H]^+$ 192.64, found 193.00; Anal. Calcd for $C_{10}H_9ClN_2$: C, 62.35; H, 4.71; N, 14.54 Found: C, 62.32; H, 4.77; N, 14.51.

<H3>2.3.6. Benzo[h]-2-chloroquinoline-4-amine (**3f)**
Yield: 89%; white solid; mp 133-136°C. IR (KBr, cm^{-1}): 1624, 2925, 3198, 3982, 3401. ^{1}H NMR (400 MHz, DMSO-d_6): δ 6.76 (s, 1H, Ar-H), 7.23 (s, 2H, NH_2), 7.78-7.71 (m, 2H, Ar-H), 7.88 (d, *J*=9.2 Hz, 1H, Ar-H), 8.04 (d, *J*= 6.4 Hz, 1H, Ar-H), 8.14 (d, *J*= 9.2 Hz, 1H, Ar-H), 9.00 (d, *J*= 6.4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 102.84, 113.80, 119.62, 124.27, 124.59, 126.69, 127.65, 128.19, 130.13, 133.58, 145.94, 149.75, 154.39. ESI-MS (m/z): calcd for $[M-H]^+$ 228.68, found 227.11; Anal. Calcd for $C_{13}H_9ClN_2$: C, 68.28; H, 3.97; N, 12.25 Found: C, 62.33; H, 3.91; N, 12.19.

*2.4. General procedure Synthesis of benzo[g]-1H-Indazolo[5,6-b][1,8]naphthyridines **5(a-d).***

The 2-chloroquinolines-3-carbaldehyes (2 mmol) compound **4(a-d)** was taken in 10 mL (DMF) and 1*H*-Indazole-6-amine (2 mmol) was added and refluxed for 2-3 hours 160-180^{0}C on a mantle. After the completion of reaction as it indicated by TLC spot change, the reaction mixture was slowly poured in ice water, filtered, dried and chromatographed over silica gel using Ethyl acetate: Methanol (90:10) (v/v) as eluent which pure orange / green colored solid compound **5(a-d)**. It was recrystallised from absolute methanol.
<H3>**2.4.1.** *Benzo[g]-1H-Indazolo[5,6-b][1,8]naphthyridine (**5a)***
Yield: 60%; light orange solid; mp 282-285°C. IR (KBr, cm^{-1}): 1563, 2926, 3390. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.02 (s, 1H, Ar-H), 7.43 (d, *J* = 7.6 Hz, 1H, Ar-H), 7.39 (s, 1H, Ar-H), 7.59-7.65 (m, 5H, Ar-H), 7.70 (d, *J*=8.8 Hz, 1H, Ar-H), 12.47 (s, 1H, for NH).^{13}C NMR (100 MHz, DMSO-d_6): δ 116.98, 117.73, 118.92, 119.94, 125.66, 126.38, 128.47, 128.57, 128.98, 131.29, 132.07, 133.71, 133.94, 137.15, 146.08, 150.51, 158.71, 165.97. ESI-MS (m/z): calcd for $[M+H]^+$ 270.29, found 270.21; Anal. Calcd for $C_{17}H_{10}N_4$: C, 75.54; H, 3.73; N, 20.73 Found: C, 75.58; H, 3.69; N, 20.70.

<H3>2.4.2. 8-Methylbenzo[g]-1H-Indazolo[5,6-b][1,8]naphthyridine (**5b)**
Yield: 54%; orange solid; mp >290°C. IR (KBr, cm^{-1}): 1589, 1626, 2922, 3357. ^{1}H NMR(400 MHz, DMSO-d_6): δ 2.71 (s, 3H, CH_3), 7.41-7.39(m, 3H, Ar-H), 7.60-7.56(m, 3H, Ar-H), 7.83 (dd, *J*=8.8,2.4Hz, 1H, Ar-H), 8.08 (d, *J*=8.8Hz, 1H, Ar-H), 13.53(s, 1H for NH).^{13}C NMR (100 MHz, DMSO-d_6): δ 23.31, 124.40, 125.51, 128.50, 128.84, 129.24, 129.38, 130.88, 131.22, 134.35, 143.33, 145.25, 154.38, 168.74. ESI-MS (m/z): calcd for $[M+H]^+$ 284.31, found 284.49; Anal. Calcd for $C_{18}H_{12}N_4$: C, 76.04; H, 4.25; N, 19.71 Found: C, 75.97; H, 4.23; N, **19.76.**
<H3>2.4.3. 8-Methoxybenzo[g]-1H-Indazolo[5,6-b][1,8]naphthyridine (**5c)**

Yield: 47%; orange solid; mp 287-290°C. IR (KBr, cm^{-1}): 1576, 1630, 2922, 3234. ^{1}H NMR(400 MHz, DMSO-d_6): δ 3.61 (s, 3H, OCH_3), 7.13 (s, 1H, Ar-H), 7.19 (s, 1H, Ar-H), 7.28(s, 1H, Ar-H), 7.57 (d, *J*=7.6 Hz, 1H, Ar-H), 7.64 (s, 1H, Ar-H), 7.74 (d, *J*=7.6 Hz, 1H, Ar-H), 8.03 (s, 1H, Ar-H), 8.90 (s, 1H, Ar-H), 9.01(bs, s, for NH). ESI-MS (m/z): calcd for $[M - H]^+$ 300.31, found 299.04; Anal. Calcd for $C_{18}H_{12}N_4O$: C, 71.99; H, 4.03; N, 18.66 Found: C, 71.97; H, 43.97; N, 18.69.

<H3>2.4.4. Naphtho[g]-1H-Indazolo[5,6-b][1,8]naphthyridine (**5d)**
Yield: 56%; yellow solid; mp 278-281°C. IR (KBr, cm^{-1}): 1576, 1615, 2925, 3405. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.35 (d, *J*=7.6 Hz, 1H, Ar-H), 7.37 (s, 1H, Ar-H), 7.43 (d, *J*=8.00 Hz, 1H, Ar-H), 7.63 (t, *J*=7.2Hz, 1H, Ar-H), 7.80 (d, *J*=6.8Hz, 1H, Ar-H), 8.22 (d, *J*=8.8 Hz, 1H, Ar-H), 8.29(s, 1H, Ar-H), 8.80 (d, *J*=8.00 Hz,1H, Ar-H), 9.85 (s, 1H, Ar-H), 11.86 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 109.78, 101.46, 115.59, 121.34, 121.81, 124.61, 125.35, 125.51, 125.61, 127.81, 127.98, 128.29, 128.76, 129.04, 133.62, 134.19, 137.47, 140.55, 141.77, 155.82. ESI-MS (m/z): calcd for $[M -H]^+$ 320.11, found 319.19; Anal. Calcd for $C_{21}H_{12}N_4$: C, 78.73; H, 3.78; N, 17.49 Found: C, 78.76; H, 3.75; N, 17.45.

<H2>2.5. General procedure Synthesis of benzo[g][3,4-b]-2,6-dichloroquinoline [1,8] naphthyridines **6(a-d**)
The 2-chloroquinolines-3-carbaldehyes (2 mmol) compound **4(a-d**) was taken in 10 mL (DMF) and 2-chloroquinoline-4-amine (2 mmol) derivatives (**3c, 3e**) were added and refluxed for 2 hours 160-180^{0}C on a mantle. After the completion of reaction as it indicated by TLC spot change, the reaction mixture was slowly poured in ice water, filtered, dried and chromatographed over silica gel using Ethyl acetate: Methanol (95:05) (v/v) as eluent which pure green/yellow colored solid compound **6(a-d)**. It was recrystallised from absolute methanol.
<H3>2.5.1. 10-Methylbenzo[g][3,4-b]-2,6-dichloroquinoline[1,8]naphthyridine (**6a)**
Yield: 43%; green solid; mp 243-245^{0}C. IR (KBr, cm^{-1}): 1439, 1516, 1590, 1641. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.51 (s, 3H, CH_3), 7.21(d, *J*=8.4 Hz, 1H, Ar-H), 7.45 (s, 1H, Ar-H), 7.59 (d, *J*=8.00 Hz, 1H, Ar-H), 7.85 (d, *J*=8.8 Hz, 1H, Ar-H), 8.11 (s, 1H, Ar-H), 8.16 (d, *J*=8.00 Hz, 1H, Ar-H), 9.00 (s, 1H, Ar-H), 9.14 (s, 1H, Ar-H).^{13}C NMR (100 MHz, DMSO-d_6): δ 21.69, 101.33, 115.61, 121.30, 124.91, 126.34, 126.63, 126.75, 129.07, 130.12, 130.39, 133.59, 137.62, 143.17,

148.08, 149.47, 155.92. ESI-MS (m/z): calcd for $[M + H]^+$ 363.23, found 363.34; Anal. Calcd for $C_{20}H_{11}Cl_2N_3$: C, 65.95; H, 3.04; N, 11.54 Found: C, 65.89; H, 2.99; N, 11.54.

<H3>**2.5.2.** *10-Methoxybenzo[g][3,4-b]-2,6-dichloroquinoline[1,8]naphthyridine (**6b**)*
Yield: 40%; orange solid; mp 260-262°C. IR (KBr, cm^{-1}): 1464, 1491, 1583, 1516. ^1H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H, OCH_3), 7.02 (s, 1H, Ar-H), 7.19-7.15 (m, 1H,Ar-H), 7.36-7.30 (m, 3H, Ar-H), 7.40 (s, 1H, Ar-H), 7.80 (d, *J*=9.2 Hz, 1H, Ar-H), 7.86 (d, *J*=8.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.75, 99.33, 100.98, 108.51, 120.38, 121.02, 123.11, 125.33, 128.87, 129.47, 141.07, 143.07, 145.92, 146.03, 146.74, 157.14, 157.95. ESI-MS (m/z): calcd for $[M + H]^+$ 379.23, found 379.92; Anal. Calcd for $C_{20}H_{11}Cl_2N_3O$: C, 63.18; H, 2.92; N, 11.05 Found: C, 63.22; H, 2.90; N, 11.09.

<H3>**2.5.3.** *12-Methoxybenzo[g][3,4-b]-2,6-dichloroquinoline[1,8]naphthyridine (**6c**)*
Yield: 49%; yellow solid; mp 276 °C. IR (KBr, cm^{-1}): 1464, 1583, 1650. ^1H NMR (400 MHz, $CDCl_3$): δ 3.89 (s, 3H, OCH_3), 7.00(s, 1H, Ar-H), 7.19 (s, 1H, Ar-H), 7.32-7.28 (m, 3H, Ar-H), 7.38 (s, 1H, Ar-H), 7.79 (d, *J*=9.2 Hz, 1H, Ar-H), 7.84 (d, *J*=9.2 Hz, 1H, Ar-H).^{13}C NMR (100 MHz, $CDCl_3$): δ 54.74, 99.30, 100.96, 108.48, 120.35, 121.00, 123.09, 125.30, 128.84, 129.45, 141.63, 143.04, 143.88, 146.01, 146.71, 157.12, 157.93. ESI-MS (m/z): calcd for $[M + H]^+$ 379.03, found 378.65; Anal. Calcd for $C_{20}H_{11}Cl_2N_3O$: C, 63.18; H, 2.92; N, 11.05 Found: C, 63.15; H, 2.88; N, 11.09.

<H3>**2.5.4.** *Naphtho[g][3,4-b]-1-Methyl-6-chloroquinoline[1,8]naphthyridine (**6d**)*
Yield: 54%; green solid; mp 267-269^{0}C. IR (KBr, cm^{-1}): 1439, 1515, 1575, 1640. ^1H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3H, CH_3), 6.97 (s, 1H, Ar-H), 7.00 (s, 1H, Ar-H) 7.20-7.18 (m, 2H, Ar-H), 7.29 (dd, *J*=8.4, 1.6 Hz, 1H, Ar-H), 7.49 (t, *J*=8.4 Hz, 1H, Ar-H), 7.51 (s, 1H, Ar-H), 7.66 (s, 1H, Ar-H), 7.74 (d, *J*=8.4 Hz 1H, Ar-H), 7.81 (d, *J*=8.4 Hz, 1H, Ar-H), 7.99 (d, *J*=8.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.39, 108.57, 110.26, 118.41, 119.83, 121.07, 122.03, 123.84, 127.23, 127.55, 128.04, 129.02, 130.01, 130.07, 130.81, 135.35, 142.38, 148.72, 148.78,

149.32, 149.81, 150.38, 150.43. ESI-MS (m/z): calcd for $[M + H]^+$ 379.09, found 379.09; Anal. Calcd for $C_{24}H_{14}ClN_3$: C, 75.89; H, 3.72; N, 11.06 Found: C, 75.85; H, 3.70; N, 11.09.

<H1>3. RESULT AND DISCUSSION

<H2>3.1. Synthesis of 2-chloroquinoline-4-amines (Ortho chloroquinoline Para amines) **3(a-f**)

The starting material 2-chloroquinoline-4-amines **3(a-f)** required for the synthesis of 1,8-naphthyridines were synthesized by developing a novel route. Recently we have reported **3c** by azidation-reduction procedure by Rajendran *et al*. [34]. The 2,4,-dichloroquinolines **1(a-f)** were synthesized by literature methods [35,36], which were then reacted with sodium azide in DMF at 55^0C stirring for 2-3hrs, furnished 2-Chloro-4-azidoquinolines **2(a-f)** in good yields. We reported here in successfully reduced 2-Chloro-4-azido quinolines **2(a-f)** in one step using sodium dithionite ($Na_2S_2O_4$) in methanol for refluxing temperature to afford 2-Chloroquinoline-4-amines **3(a-f)** in excellent yields Table 1. The structures of compounds **3(a-f**) were assigned using spectroscopy methods. For instance, IR spectrum of compound **3b** showed stretching for C=N, C-H at 1647, 2961cm^{-1}, and NH_2 at 3319, 3452 cm^{-1}. The ^{1}H NMR spectrum of in (DMSO-d_6) showed the resonance at δ 2.45 for methyl protons, two singlet's at δ 6.48, 8.14 corresponding to C_3-H,C_5-H protons and two doublets were observed at 7.50 (dd, J=8.4, 2.0 Hz, 1H), 7.59 (d, J= 8.8 Hz, 1H), corresponding to C_7-H,C_8-H proton respectively, 7.05 were assignable for NH_2 proton respectively. ^{13}C NMR spectra confirmed the presence of 10 carbons. The ESI-MS spectrum showed the molecular ion peak at *m/z* 193.01. From these details, the structure of the compound was confirmed as 6-Methyl-2-chloroquinoline-4-amine **3b**. The reaction sequence was extended to other derivatives of 2-chloroquinoine-4-amines **3(a-f**) **Scheme 1**. The synthetic procedure is very simple when compared with other previously reported synthetic methods [25-29]. However, we have modified the workup procedure and synthesized **3c** with better overall yield of **3(a-f**), which make this method a simple and convenient one.

<H2>3.2. Synthesis of benzo[g]-1H-Indazolo[5,6-b][1,8]naphthyridines **5(a-d**)

Distinguished from classical sequential two-component synthetic procedure, multicomponent reactions (MCRs) involve the use of three or more synthons for the product formation [37-41]. To the best of our knowledge, only a few references exist concerning the synthesis of [1,8] napthyridines [42,43]. K.J.R.Prasad and Co-workers [43] have reported the synthesis of Indazolo[2,3-*b*] dibenzo [*b,g*][1,8]naphthyridines analogues in two steps in conventional method and single step using micro wave method by varying different metal catalyst and organic solvents. Now, here in we have reported benzo[*g*]-1*H*-Indazolo[5,6-*b*] [1,8] naphthyridines **5(a-d**) 55-75% yields, a simple efficient method to these heterocycles would be attractive by under basic solvent conditions no catalyst and short duration of reaction time in Table 2

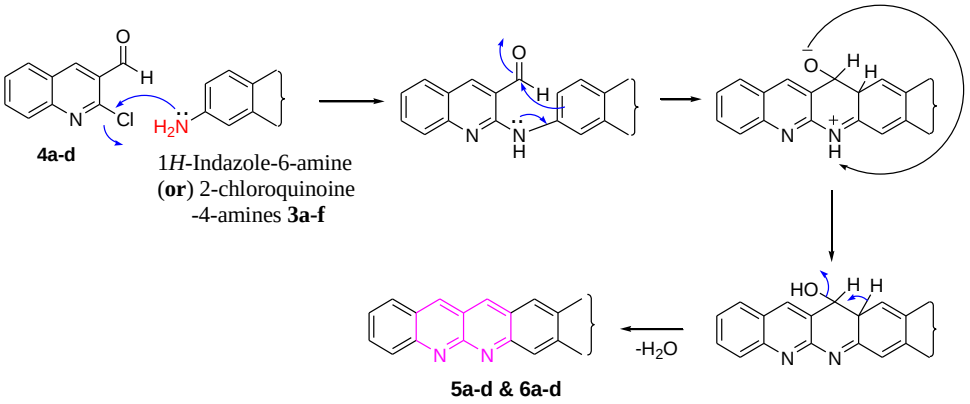
Hence equal mole ratio of 2-chloroquinoline-3-carbaldehydes and respective and 1*H*-Indazole-6-amine in 10mL of DMF heated with 160^0C for 2-3 hrs. The reaction progress was monitored by various percentages in TLC. After completion of reaction it was noted that the yielded a single product and no side product, (minor isomer) was obtained. The structure of compounds **5(a-d)** was assigned using spectroscopy and analytical methods. For instance, IR spectrum of compound **5b** showed stretching for C=N at 1589cm^{-1}, and 3357 cm^{-1} for NH stretching. The ^{1}H NMR spectrum **5b** of in (DMSO-d_6) showed that singlet at δ 2.70 corresponds to C_8–CH_3 protons respectively, all the aromatic protons multiplet at δ 7.41-7.39 (C_3,C_4 and C_{13}-H), δ 7.60-7.56 (C_5,C_6 and C_7-H) except for two protons doublets, which were very much deshielded δ 7.83 (*J* =8.8Hz, C_9-H) and δ 8.05 (*J*=8.8Hz, C_{10}-H) one broad singlet was observed at 13.53 corresponds to Indazolo NH protons and ^{13}C NMR spectra confirmed the presence of 18 carbons. The ESI-MS mass spectrum of reveals a molecular ion peak at *m/z* 284.49. From these details, the structure of the compound was confirmed as 8-Methyl benzo[*g*]-1*H*-Indazolo[5,6-

b][1,8]naphthyridine **5b**. The reaction sequence was extended to other derivatives of **5(a-d)** **Scheme 2**.

<H2>1.2. Synthesis of benzo[*g*][3,4-*b*]-2,6-dichloro quinoline[1,8]naphthyridines ***6(a-d)***

Moreover, we have developed a convenient route for new synthetic derivatives of linear fused 1,8-naphthyridines for using some of 2-chloroquinoline-4-amine derivatives Table 3. Hence equal mole ratio of 2-chloroquinoline-3-carbaldehydes **4(a-d)** and respective 2-chloroquinloine-4-amines **3c, 3e** in 10mL of DMF heating 180^0C for 2hr, after completion of reaction, yielded a single product indicated thin layer chromatography (TLC). The structures of compounds **6(a-d**) were assigned using spectroscopy methods. For instance, IR spectrum of compound **6c** showed stretching for C=N at 1583cm^{-1}, and 1464 cm^{-1} for C-N stretching and disappearance of **4c** –CHO stretching at 1745cm^{-1}. The ^{1}H NMR spectrum of in (DMSO-d_6) showed the resonance at δ 3.89 ppm for methoxy protons C_{12}–OCH_3, and the remaining aromatic protons resonance at δ 7.00-7.86 ppm expected chemical shifts and splitting pattern. Both the sharp singlet at 10.50 ppm corresponding to **4c** -CHO and another singlet at δ 6.60 pertaining to C_3-H protons disappeared corresponding to 2,6-dichloroquinoline-4-amine **3c** C_3-H protons, and ^{13}C NMR spectra confirmed the presence of 20 carbons. The ESI-MS mass spectrum showed the molecular ion peak at *m/z* 379.09. From these details, the structure of the compound was confirmed as 12-Methoxybenzo[*g*][3,4-*b*]-2,6-dichloroquinoline[1,8] naphthyridine **6c**. The reaction sequence was extended to other derivatives of benzo[*g*][3,4-*b*]-6-chloroquinoline[1,8] naphthyridines **6(a-d), Scheme 3**.

Proposed mechanism for scheme 2 and 3



Furthermore, we observed blue light-emission of all synthesized compounds **3(a-f), 5(a-d)** and **6(a-d)** with naked eyes under fluorescence wave length (400-600 nm) in methanol; hence we think these compounds are good conditions for studying their photo physicalproperties. In the beginning we performed the band gap energy HOMO-LUMO with the DFT calculations.

<H1>4. PHOTOPHYSICAL PROPERTIES

<H2>*4.1. Fluorescence properties of 2-chloroquinoline-4-amines **3(a-f)**, benzo[g]-1H-Indazolo[5,6-b] [1,8]naphthyridines **5(a-d)** and benzo[g][3,4-b]-2,6-dichloroquino[1,8]naphthyridines **6(a-d**)*

The UV-Visible absorption and emission spectra of compounds **3(a-f**) in polar solvent (methanol) were studied. Further, the fluorescence quantum yield of each compounds **3(a-f**) were also determined by the standard literature method using Rodamine-6G as a reference standard (ϕ_{ref}=0.95 in 0.1 M CH_3OH) [44-46]. The concentration of the compounds **3(a-f)** were prepared at 10^{-3} M in absolute methanol. The UV-Visible absorption and emission spectra of compounds **3(a-f**) were studied in the range of 200-400 nm ($\lambda_{abs.\ max}$) and 400-700 nm ($\lambda_{f.\ max.}$), respectively, and the results are summarized in Table 4. It can be seen from Table 4 that the **3d**, **3f** shows fluorescence maxima at 516 and 487 nm, respectively. Moreover, **3a**, **3b**, **3e** shows emission maxima at 449, 485, 486 nm. As a whole that fluorescence maxima of compounds **3d**, **3f** occur at longer wavelength when compared to that of **3a**, **3b**, **3c**, **3e**. This is due to the presence of strong σ-π*, π-π* electron donor, -OCH_3, -CH-CH=CH-CH- groups on ring (A) of **3d**, **3f**. The

lower emission maxima of compounds **3a**, **3b**, **3e** owing to presence of electron withdrawing groups for CH_3 on ring (A) at ortho, para position **Fig**. **4** due to the +I effect. Another interesting feature is that chloro substituent molecules **3c** have high fluorescence maxima, but less fluorescence quantum yield compared to compounds **3d**, **3f** (ϕ= 0.235). This difference may be attributed the quenching of fluorescence with chlorine atoms as present in ring (A). Comparative emission spectra of **3(a-f**) are represented in **Fig. 5**.

In the recent past, several literatures have reported that naphthyridines exhibit high fluorescence properties. The synthesis of novel L-shaped π-extended compounds for

pyrrolo[1,2-*a*][1,8]naphthyridines systems and their interaction with dichloromethane has been reported by Tateno *et al*. [47]. Further, the same authors have well studied the photophysical studies of pyrrolo[1,2-*a*] [1,8]naphthyridines as well as frontier MOs and energy levels of pyrrolo[1,2-*a*] [1,8] naphthyridines compounds [48]. In our present studies, we have carried out the absorption and emission properties of newly synthesized benzo[*g*]-1*H*-Indazolo[5,6-*b*][1,8] naphthyridines **5(a-d)** and benzo[*g*][3,4-*b*]-2,6-dichloro quinoline [1,8]naphthyridines **6(a-d)**. The compounds **5c**, **5d**, **6b**, **6c** and **6d** show florescence maxima at 542, 532, 552, 554 and 532 nm. However some of 1,8-naphthyridines **5a**,**5b**,**6a** show less emission maxima at 492,498,514 nm, respectively. The substituted 1,8-naphthyridines has showed high fluorescence maxima, mainly, the compounds **5c**, **5d**, **6b**, **6c** and **6d** exhibit longer wavelength than that of **5a**, **5b**, **6a**.

This attribute due to the presence of strong π-π*, n-π* electron donor, more conjugation groups on ring (A) of compounds **5c**, **5d**, **6b**, **6c** and **6d** (**Figs. 6** and **8).** The methoxy -OCH_3 and more conjugated compounds showed high quantum yields (ϕ_f=0.48-0.37) and fluorescent quantum yield of all the compounds are summarized in Table 4. The emission spectra of compounds **5(a-d)** and **6(a-d)** are shown in **Figs. 7** and **9**.

*5. DFT study of 2-chloroquinoline-4-amines **3(a-f)**, benzo[g]-1H-Indazolo[5,6-b][1,8] naphthyridines **5(a-d)** and benzo[g][3,4-b]-2,6-dichloroquino [1,8] naphthyridines **6(a-d)***

The HOMO-LUMO band gap is an important phenomena in explaining applications corresponding to the fluorescence properties and DFT calculation [49]. D.P.Sheler *et al*. [22] have earlier approached the synthesis of naphthyridines with HOMO-LUMO energy band gap up to 7eV which florescence between 400-700 nm that found with applications in OLEDs. To the best of our knowledge, there is no results in computational literature survey for 2-chloroquinoline-4-amines **3(a-f)** substituted 1,8-naphthyridines **5a, 5b, 5d** and **6(b-d)**, our research group first explored and analyzed experimentally and theoretically. Hence we calculated the HOMO-LUMO band gap energy values corresponding to all new molecules through M06HF/6-31G (d, p) level of theory which is given in **Tables 5**. The computational calculations of Table 5 compounds **3d** (9.48 eV)**, 6b** (7.49 eV) and **6c** (7.58 eV) shows low gap values compared to other compounds, because methoxy $–OCH_3$, group present in ring (A) as compared to ring B, C, D and E the 3D images are given in **Figs**. **4**&**8** the donor chromaphore $–OCH_3$ on ring (A) play an important role in increasing electron density and lowering the electron hole gap. Furthermore compounds **3d**, **6b, 6c** bearing methoxy $–OCH_3$ group on ring (A) shows low gap values indicating higher overlapping of HOMO-LUMO orbital's which shows red shifted (Bathochromic) in it, fluorescence maxima and high fluorescence quantum yields as compared to other molecules are briefly discussed in Table 5**. When compared parent molecule with substituent of R = -CH=CH=CH=CH- molecule, There has a contradiction results in HOMO – LUMO gap. These are deeply discussed in supporting information** [51,52]**.** The HOMO-LUMO energies for all these compounds are close to each other, the energy level diagrams of compounds **3(a-f)**, **5a,5b,5d** and **6(b-d)** using the **Gaussian 09** program package on **Figs. 10-12** are given below.

<H1>6. Conclusion

In conclusion, we have developed a direct and efficient approach to the synthesis of benzo[*g*][1,8]naphthyridines from simple synthons 2-chloroquinoline-3-carbaldehydes, 1*H*-Indazole-6-amine and 2-chloroquinolne-4-amines. The reaction proceed by simple condensation under basic medium conditions without any catalyst furnishing benzo[*g*]-1*H*-Indazolo[5,6-*b*][1,8]naphthyridines **5(a-d**), benzo[*g*][3,4-*b*]-2,6-dichloroquinoline[1,8]naphthyridines **6(a-d**) in good yields. This method is much more efficient due to short reactions times and easy separation process. Desired products were obtained in excellent yields. The products synthesized were subjected to photophysical studies and DFT theoretical evaluation. The emission properties of methoxy substituted compounds **3d**, **6b**, **6c** established high fluorescence quantum yields (ϕ_f=0.25-0.48) compared to all other molecules discussed with Table 5 because of presence of donor chromophore in ring (A) compared to other (B), (C), (D), (E) rings. The synthesized compounds were subjected to DFT computational study. It is evident from the computational studies that HOMO-LUMO energy gap is comparatively low for methoxy substituted compounds and hence experimentally the methoxy substituted compounds showed relatively higher emission properties. Finally, all of new compounds were subjected to UV-Vis absorption and fluorescence emission studies in absolute methanol at ambient temperature and the results have been interpreted. Further scope of methodology is been exploited and various biological application studies are currently progressing in our laboratory.

<ACK>Acknowledgements

The authors gratefully acknowledge the Department of Science and Technology (DST), New Delhi for DST-PURSE fellowships for financial support to this research work. We thank Prof. Dr. P. Kolandaivel, Professor and Head, Director of Physical Sciences, Department of Physics, Bharathiar University, Coimbatore – 641 046, Tamil Nadu, India, for voluble suggestions and computational facilities in the DFT theoretical studies.

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</BIBL>
<Figure>Fig. 1 Benzo [b] [1, 8] naphthyridines-3-carbonitrile [22]

<Figure>Fig. 2 5-(3, 4-Dichlorophenyl)-5, 6-dihyrobenzo[b] naphtha [2, 1-g][1,8] naphthyridine

[23]

<Figure>Fig. 3 2, 5-Diphenylbenzo[h][1,6] naphthyridines [24]

<Figure>Fig. **4** 3D picture of 2-choloroquinoline-4-amine **3a**
Fig. 5 Fluorescence spectra of **3(a-f)** in methanol
<Figure>Fig. **6** 3D picture of 8-Methyl benzo [*g*]-1*H* Indazolo[5,6-*g*][1,8]naphthyridine **5b**

Fig. 7 Fluorescence spectra of **5(a-d)** in methanol
<Figure>Fig. **8** 3D picture of 12-Methoxybenzo [*g*]
[3,4-*g*]-2,6-dichloro quinoline [1,8] naphthyridine **6c**
Fig. 9 Fluorescence spectra of **6(a-d)** in methanol
<Figure>Fig. **10** Frontier Molecular Orbital's (FMO) energy level of **3(a-f)**

<Figure>Fig. **11** Frontier Molecular Orbital's (FMO) energy level of **5a, 5b**& **5d**

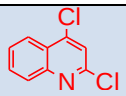
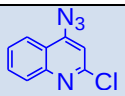
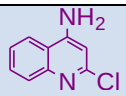
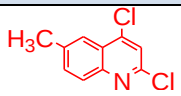
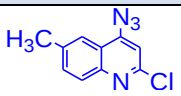
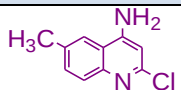
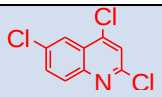
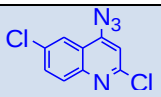
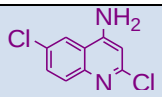
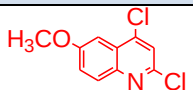
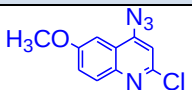
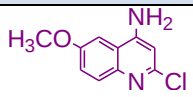
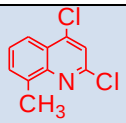
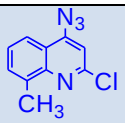
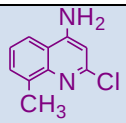
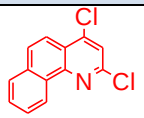
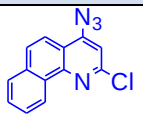
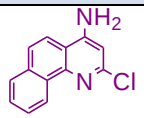
<Figure>Fig. **12** Frontier Molecular Orbital's (FMO) energy level **6b, 6c, 6d**

<Figure>**Scheme 1** Synthesis of 2-chloroquinoline-4-amines **3(a-f)**.

<Figure>**Scheme 2** Synthesis of benzo[*g*]-1*H*-Indazolo[5,6-*b*][1,8]naphthyridine **5a-d**.

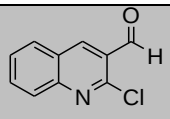
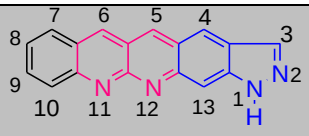
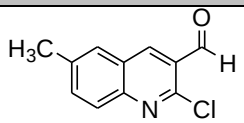
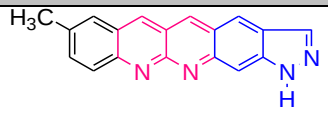
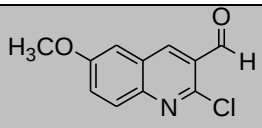
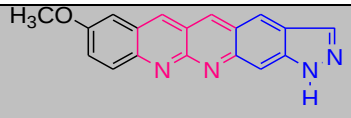
<Figure>**Scheme 3** Synthesis of benzo[*g*][3,4-*b*]-6-chloroquinoline[1,8]naphthyridines **6a-d**

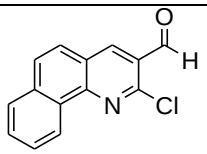
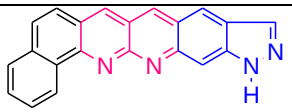
<Table>Table 1 Optimization of reaction conditions [a,b]

Entry	**Substrate 1a-f**	Substrate **2a-f**	Product **3a-f**	Reaction time (h)	Yield[c] (%)
1				3	91
2				3	79
3				3.5	89
4				4.5	61
5				4.5	96
6				3	89

[a]NaN_3, DMF, 55 ^{0}C, 3h, [b]$Na_2S_2O_4$, methanol, [c]Isolated yields.

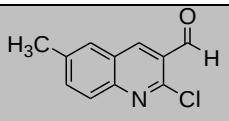
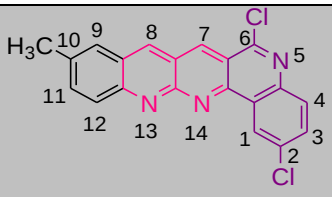
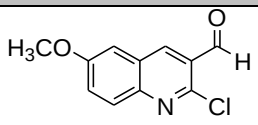
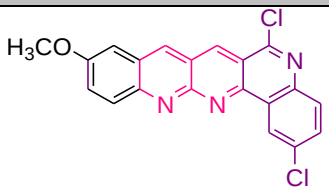
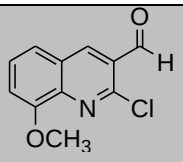
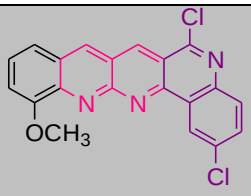
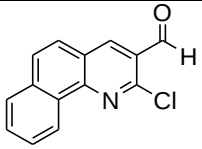
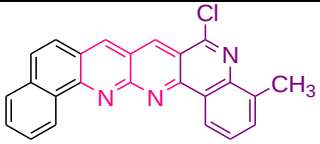
<Table>Table 2 Optimization of reaction conditions [d]

Entry	**Substrate 4(a-d)**	Product **5(a-d)**	Time(h)	Yield (%)[e]
1			2.5	60
2			2	54
3			3	47

4			2.5	56

[d]DMF, 160[0]C, 2-3h, [e]Isolated yields.

<Table>Table 3 Optimization of reaction conditions [f]

Entry	**Substrate 4(a-d)**	Product **6(a-d)**	Time(h)	Yield (%)[g]
1			1.5	43
2			2	40
3			2	49
4			2	54

[f]DMF,180[0]C, 2hr, [g] Isolated yields.

<Table>Table 4 The photophysical data for electronic absorption (UV $\lambda_{abs.max.}$), fluorescence (Em. $\lambda_{flu.max.}$) and quantum yield (ϕ_f) of compounds **3(a-f)**, **5(a-d)** and **6(a-d)** in absolute methanol at ambient temperature.

Entry	Comps.	R_1	R_2	R_3	$\lambda_{abs.}CH_3OH$	$\lambda_{flu.}CH_3OH$	ϕ_f
1	**3a**	H	H	H	299	449	0.136
2	**3b**	CH_3	H	H	306	485	0.135
3	**3c**	Cl	H	H	315	487	0.165

4	**3d**	OCH_3	H	H	334	516	0.235
5	**3e**	H	H	CH_3	309	486	0.059
6	**3f**	-CH CH=CH-CH-			260	487	0.226
7	**5a**	H	H	H	334	492	0.288
8	**5b**	CH_3	H	H	342	498	0.318
9	**5c**	OCH_3	H	H	352	542	0.446
10	**5d**	-CH CH=CH-CH-			418	532	0.370
11	**6a**	CH_3	H	H	331	514	0.254
12	**6b**	OCH_3	H	H	363	552	0.482
13	**6c**	H	H	OCH_3	406	554	0.426
14	**6d**	-CH CH=CH-CH-			426	532	0.278

<Table>Table 5: The molecular electronic properties (HOMO-LUMO band energy GAP) of the **3a-f**, **5a**, **5b**, **5d** and **6b,6c,d)** compounds calculated with M06HF/6-31G(d, p) level of theory.

Entry	Comps.	R_1	R_2	R_3	HOMO (eV)	LUMO (eV)	GAP(eV)
1	**3a**	H	H	H	-9.00	0.84	9.84
2	**3b**	CH_3	H	H	-8.89	0.93	9.83
3	**3c**	Cl	H	H	-9.16	0.54	9.70
4	**3d**	OCH_3	H	H	-8.62	0.85	9.48
5	**3e**	H	H	CH_3	-8.87	0.88	9.76
6	**3f**	-CH=CH-CH=CH	H	H	-8.73	0.81	9.54

7	**5a**	H	H	H	-7.88	-1.01	6.86
8	**5b**	CH_3	H	H	-7.83	-0.94	6.88
9	**5d**	-CH=CH-CH=CH-	H	H	-7.94	-0.90	7.03
10	**6b**	OCH_3	H	H	-8.67	-1.18	7.49
11	**6c**	H	H	OCH_3	-8.68	-1.10	7.58
12	**6d**	-CH=CH-CH=CH-	H	H	-8.82	-0.93	7.89

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