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ORIGINAL PAPER

Arylbenzo[*h*][1, 6]naphthyridine Derivatives: Synthesis and Photophysical Properties

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Abstract *Suzuki-Miyaura* cross coupling was successfully used for C5-arylation in 4-amino-2-chloroquinoline-3-carbaldehyde using arylbornic acid and tetrakistriphenylphosphine palladium catalyst in water. *Friedländer condensation* reaction on 4-amino-2-chloro/2-arylquinoline-*3*-carbaldehyde and aromatic ketones gave novel aryl and diarylbenzo[*h*][1, 6]naphthyridines in good yields. Fluorescence quantum yields were increased by introducing C2 and C5 π donor aryl benzo[*h*][1, 6]naphthyridines derivatives.

Keywords Benzo[*h*][1, 6]naphthyridines · Fluorescence quantum yields · *Suzuki-Miyaura* cross coupling reaction · *Friedländer condensation* reaction · Tetrakistriphenylphosphine

Introduction

Photoinduced intramolecular electron transfer processes are playing important role in importing photo physical and photo chemical properties to organic molecules constituting π-donor-acceptor conjugated system connected finally by single bond. The charge transfer excited states are the cause of induced photo physical properties of the molecule. The widely accepted proposals explaining photo physical properties are TICT (twisted intermolecular charge transfer) state model [1–3] and push pull mechanism [4, 5] of donor-aceptor auxochromes and chromophores. The perpendicular geometry was the question recently arise as an inherent precondition to obtained intramolecular charge transfer in such systems [6–8] The nonlinear molecules possessing optical properties showing transitions from electronics to photonics are the required materials [9] for potential applications in optical data storage, telecommunications and optical signal processing and optical switching [10–17]. The fused heterocyclics are rigid and stable systems possess high heat and photochemical stability, are suitable material for optoelectronic devises. The hetero atoms in the molecule act as an auxiliary donor-acceptor to increase fluorescence quantum yields through push pull mechanism [18, 19]. We have reported [20–23] the synthesis and fluorescent properties of dipyrazolo[3,4-*b*:3,4-*d*]pyridines (DPP), pyrazolo[3,4-*b*]pyrrolo[2,3-*d*]pyridines (PPP) and pyridine-3-carbonitriles. It was observed that the fluorescent properties of these candidates are depending upon the nature of donor-acceptor substituents on the C4-aryl, also causes for the perpendicular geometry for TICT state. This paper report the *Suzuki–Miyaura* cross coupling on 4-amino-2-chloroquinoline-*3*-carbaldehyde to form 4-amino-2-arylquinoline-3-carbaldehyde i.e. C2-arylation without protection of other groups, which were used to prepare 5-chloro-2-arylbenzo[*h*][1, 6]naphthyridines **8(a-d)** and 2,5-diarylbenzo[*h*][1, 6]naphthyridines **9(a-h)** and further study of their fluorescence properties.

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Results and Discussion

Sylvain Rault and co-workers [24] have been reported the synthesis of benzo[*h*][1, 6]naphthy- ridines analogues *via* rearrangement of hexahydro-*5 H*-pyrrolo[*2,1-c*][1, 4] benzodiazepines in 12% yield. We have obtained 5-chloro-2-arylbenzo[*h*][1, 6] naphthyridines **8(a-d)** and 2,5-diarylbenzo[*h*][1, 6]naphthyridines **9(a-h)** 60–85% yields.

4-Amino-2-oxo-1,2-dihydroxyquinoline-3-carboxylate [25] **2** was obtained by cyclocondensation of diethylmalonate and 2-cyanoaniline **1** in basic medium. The chlorination of this compound with phosphorousoxychloride at reflux temperature yielded ethyl 4-amino-2-chloroquinoline-3-carboxylate **3** in 76% yield, which on LAH reduction furnish *4*-amino-*2*-chloroquinolin-*3*-yl) methanol **4** in 87% yield.

Compound **4** on MnO_2 oxidation afforded required synthon 4-amino-2-chloroquinoline-3-carbaldehyde **5** in 73% yields (Scheme 1). The structures of compounds **3, 4** and **5** were confirmed by spectroscopic characterization data. For instance, IR spectrum of **5** showed stretching for NH_2 at 3293, 3261 cm^{-1} and CHO at 1719, 2705 $cm.^{-1}$ The ^1H NMR in DMSO-d_6 showed NH_2 protons splited in two broad singlets at δ 8.97 and δ 9.87 (D_2O exchangeable) due to the intramolecular hydrogen bonding between CHO and NH_2 group. The highly deshielded aldehydic proton was observed at δ 10.30 and the rest of aromatic protons appeared at δ 7.60–8.46. The mass spectrum and elemental analysis also match with the proposed structure of **5**. *Friedländer condensation* on 4-amino-2-chloroquinoline-3-carbaldehyde **5** with substituted aromatic ketones (**7a-d**) in ammonium acetate as green solvent and reagent at 120°C furnished 5-chloro-2-aryllbenzo[*h*][1, 6]naphthyridine (**8a-d**) in 65–80% yields (Scheme 1).

The photophysical study of benzo[*h*][1, 6]naphthyridines **8** showed C2-aryl dependent fluorescence quantum yields. The presence of auxochrome (donor) on C2-aryl increases while chromophore (acceptor) on C2-aryl decreases the absorption and emission λ_{max}. This observation inspired us to study the substituent effect at C5-aryl of this molecule. For C5-arylation after trying by several methods, the *Suzuki-Miyaura* cross-coupling reaction [26–29] gave satisfactory results because its mild reaction conditions required here due to presence of active functional groups. The tetrakistriphenylphosphine palladium as a heterogeneous catalyst in water and 1,2-dimethoxyethane co-solvent in 3.5: 3 mL gave 4-amino-2-arylquinoline-3-carboaldehyde **6** in 82–87% yield. Interestingly, this one pot reaction did not need the protection of CHO and NH_2 group. Further, the *Friedlander* reaction on compound **6** with aromatic ketones in ammonium acetate, furnished diarylbenzo[*h*][1, 6]naphthyridines (**9a-h**) in 65–82% yields (Scheme 2, Table 1).

Photo Physical Properties

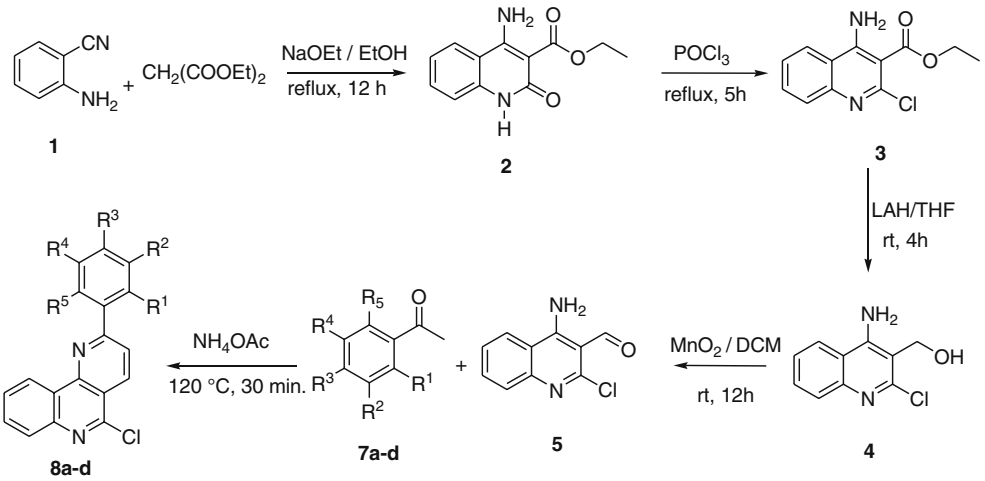
The benzo[*h*][1, 6]naphthyridines **8(a-d), 9(a-h)** are colorless solids. The photo physical properties of these compounds were determined with respect to quinine sulphate as reference standard, using 0.1 mg/ml solution in chloroform shows UV absorption and fluorescence emission in the range of 343–390 nm and 415–498 nm respectively (Table 1). In series of arylbenzo[*h*][1, 6] naphthyridines **8(a-d)** the strong π-donor aryl on C2-position shows large bathochromic shift of absorption and emission with low stoke's shift, and high quantum yields (Table 1, entry 8b, 8c).

For instance, compound **8c**, having C2-(2,4,6-tri-OCH_3) Ph shows λ_{Max}=381 nm, λ_{Flu}=480nm, stock shift at 5,564 cm^{-1} and Φ_F=0.24 (Table 1, Entry 3), while strong acceptor C2 (4-NO_2Ph) in compound **8d** shows λ_{Max}=343, λ_{Flu}=446nm, stock shift=7,840 cm^{-1} and Φ_F=0.18 (Table 1, entry 4). i.e. In arylbenzo[*h*][1, 6]naphthyridines **8** the C2-donar shows increase while C2-acceptor on shows decrease in the fluorescence quantum yields. Interestingly, introduction of C5-phenyl shows decreasing of photo physical properties, but C5-(4-OCH_3Ph) and C5-(4-NO_2Ph) shows large to moderate increase in fluorescence properties. e.g. Compounds **9(a-c)** having C5-Ph show lower absorption in the range of 345–3,364 nm, emission 415–446 nm and quantum yield Φ_F=0.15–0.19 as compared with compounds **8(a-c)**, which showed absorption in the range of 360–381 nm, emission 460–480 nm and quantum yield Φ_F=0.019–0.24. The push pull mechanism of donor OCH_3, and SP^2 'N' and twisting of C2 and C5-aryl auxochromes in **9(d-f)** or chromphores in **9(g-h)** of benzo [*h*][1, 6]naptharidines showed increase in fluorescence properties. Auxochromes and chromophores both groups help to increase absorption and emission as compared with H on C5-Ph (Fig. 1)

Semi-Empirical Study of Benzo[h][1, 6]napthyridine Derivatives 8, 9

The TICT and push pull mechanism of donor-acceptor chromophores, affect the electronic transitions in the molecule, these electronic transition import the fluorescence properties to the molecule. The physical parameters HOMO-LUMO, energy, ionization potential, heat of formation are useful parameters to predict photophysical properties and are calculated theoretically by using PM6 model [30, 31]. It was observed that compounds having low HOMO-LUMO gap showed higher absorption and emission wave length and hence showed high fluorescence or quantum yields. e.g. compound **8c**, having absorption 381 nm, emission 480 nm and quantum yields φ_F=0.24

Scheme 1 Synthesis of Arylbenzo[*h*][1, 6]naphthyridine derivatives



have lowest HOMO-LUMO gap=7.284. Similarly, in case of 2, 5-diarylbenzo[*h*][1, 6]naphthyridines **9f**, having higher absorption 390 nm and emission 498 nm maxima and quantum yield φ_F=0.26 showed lowest HOMO-LUMO gap=7.068. The high heat of formation and ionization potential showed high thermal stability, which indicate that these compounds are suitable candidates for photo electronic devices.

Conclusion

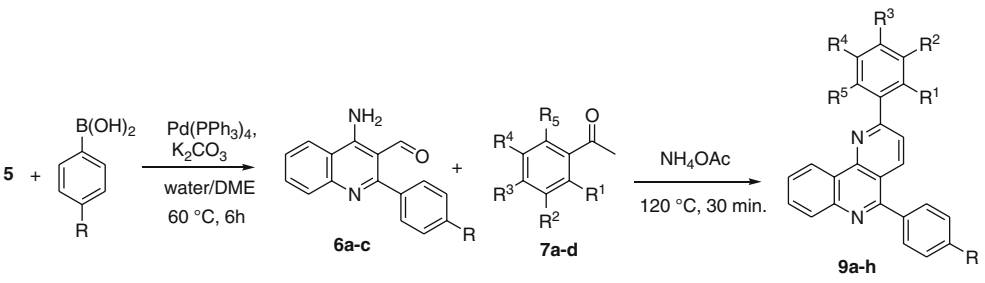
The C2-arylation was carried out by *Suzuki–Miyaura* cross coupling under mild reaction conditions without protection to active functional groups in presence of tetrakistriphenylphosphine palladium as a heterogeneous catalyst in aqueous medium. *Friedländer condensation* in ammonium acetate yield novel aryl and diarylbenzo[*h*] [1, 6]naphthyridines in good yields. Arylbenzo[*h*][1, 6]naphthyridines with C2-π-donor and C5-π-donor-acceptor fluorophores to aryl showed large bathochromic shift of absorption and emission with low Stoke's shift, and high quantum yields, while π-acceptor on C2-aryl chromophores shows hypsocromic shift of absorption and emission properties.

Experimental

General

Melting points were determined on a *Barnstead Electro Thermal* melting point apparatus, Mod. No. IA-9200 in open capillary tubes and are uncorrected. The ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Varian *XL*-300 spectrometer. Chemical shifts were reported in ppm from internal tetramethylsilane standard and are given δ-unit. The solvent for NMR spectra was deuterio-chloroform unless otherwise stated. Infrared spectra were taken on Shimadzu IR-408, instrument in potassium bromide pellets unless otherwise stated. UV spectra were recorded on a Shimadzu UV-1601 UV–VIS Spectrophotometer. Fluorescence spectra were recorded using RF-5301 PC Spectrofluorophotometer, compounds for UV and fluorescence measurements were dissolved in chloroform. UV and fluorescence scan were recorded from 200 to 600 nm. Elemental analyses were determined using Thermo Quest Model No. flash EA 1112-Elemental Analyzer within ± 0.3 of the theoretical percentage. High-resolution mass spectra were obtained with a Mat 112 Varian Mat Bremen (70*eV*) mass spectrometer. Column

Scheme 2 Synthesis of Di-arylbenzo[*h*][1, 6]naphthyridine derivatives



6a R= H
6b R = *P*-OMe
6c R = *p*-NO_2

Table 1 The photophysical data for electronic absorption (UVλ_{Max}), fluorescence (Emλ_{Max}) and quantum yield (φ_F) of compounds **8** and **9** in $CHCl_3$ at room temperature

Entry	Comp[d]	R	7a-d					$\lambda_{Abs.}$ $CHCl_3$	$\lambda_{Flu.}$ $CHCl_3$	Epsilon ε cm^{-1}	Φ_F
			R^1	R^2	R^3	R^4	R^5				
1	8a	–	H	H	H	H	H	345	460	7,288	0.19
2	8b	–	H	H	OCH_3	OCH_3	H	377	475	6,640	0.22
3	8c	–	OCH_3	H	OCH_3	H	OCH_3	381	480	5,564	0.24
4	8d	–	H	H	NO_2	H	H	343	446	7,840	0.18
5	9a	H	H	H	H	H	H	345	415	6,279	0.15
5	9b	H	H	H	OCH_3	OCH_3	H	358	425	5,479	0.18
7	9c	H	OCH_3	H	OCH_3	H	OCH_3	364	446	8,695	0.19
8	9d	OCH_3	H	H	H	H	H	366	460	7,544	0.19
9	9e	OCH_3	H	H	OCH_3	OCH_3	H	388	481	4,607	0.22
10	9f	OCH_3	OCH_3	H	OCH_3	H	OCH_3	390	498	4,725	0.26
11	9g	NO_2	H	H	OCH_3	OCH_3	H	366	460	7,544	0.18
12	9h	NO_2	OCH_3	H	OCH_3	H	OCH_3	376	471	5,884	0.21

chromatography was carried out on silica gel (*SD* Fine Chemicals, 100–200 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 F_{254} (Merck) plates using *UV* light (254 and 366 nm) for detection. Common reagents-grade chemicals are either commercially available and were used without further purification or prepared by standard literature procedures.

Ethyl 4-amino-2-oxo-1,2-dihydroxyquinoline-3-carboxylate (2) Yield: 41%. M.p.: 269–270 °C [*Lit. Mp 269* °C] [22]

Ethyl 4-amino-2-chloroquinoline-3-carboxylate (3) A mixture of compound **2** (21.55 mmol, 5.0 g) in $POCl_3$ (50 mL) was refluxed for 5 h. (TLC monitoring, CH_2Cl_2/MeOH 10:1). After cooling the reaction mixture was slowly poured in ice water (250 mL) and neutralized with NH_4OH. This aqueous solution was extracted with CH_2Cl_2 (100 mL×2), dried over sodium sulphate and concentrated to yield crude solid, which was further purified by FC (using 20% CH_2Cl_2/petroleum ether as an eluent) to give compound **3.** Yield: 4.1 g (76.1%), yellowish white solid, mp. 197–199 °C; IR (KBr): 3376, 3263, 1673, 1614, 767 $cm.^{-1}$; ^1H NMR (DMSO-d_6) δ: 1.47 (t, 3 H, J=7.2 Hz, OCH_2CH_3), 4.48 (q, 2 H, J=7.15 Hz, OCH_2CH_3), 6.83 (bs, 2 H, NH_2), 7.51–7.88 (m, 4 H, ArH). ^{13}C NMR (DMSO-d_6) δ: 13.8, 61.3, 103.8, 117.2, 123.1, 125.5, 127.6, 131.7, 146.3, 147.2, 152.6, 165.7. MS m/z (%): 251.1 (M+1) (100), 253.1 (M+2) (20). Anal. Calcd for $C_{12}H_{11}ClN_2O_2$ (250.68): C, 57.50; H, 4.42; N, 11.17%. Found:C, 57.32; H, 4.53; N, 11.18%.

4-Amino-2-chloroquinolin-3-yl-methanol (4) Add dropwise solution of compound **3** (16.00 mmol, 4.0 g) dissolved in dry THF (10 mL), in the flask flushed with nitrogen

Table II The molecular electronic properties, HOMO-LUMO energy gap of benzo [*h*] [1, 6]naphthyridines **8** and **9**

Comp[d]	Heat of formation (K cal.)	Ionization potential	HOMO	LUMO	GAP
8a	92.03	9.316	-9.317	-1.301	8.016
8b	-32.30	9.066	-9.066	-0.842	8.224
8c	15.55	8.569	-8.570	-1.286	7.284
8d	-230.93	9.616	-9.617	-1.789	7.828
9a	123.69	9.111	-9.111	-1.048	8.063
9b	47.49	8.479	-8.479	-0.992	7.487
9c	-0.111	8.863	-8.864	-0.601	8.263
9d	-148.09	8.979	-8.980	-0.919	8.061
9e	7.911	8.407	-8.407	-0.948	7.459
9f	42.41	8.621	-8.621	-1.553	7.068
9 g	-5.603	9.181	-9.181	-1.381	7.800
9 h	8.411	8.914	-8.914	-1.038	7.876

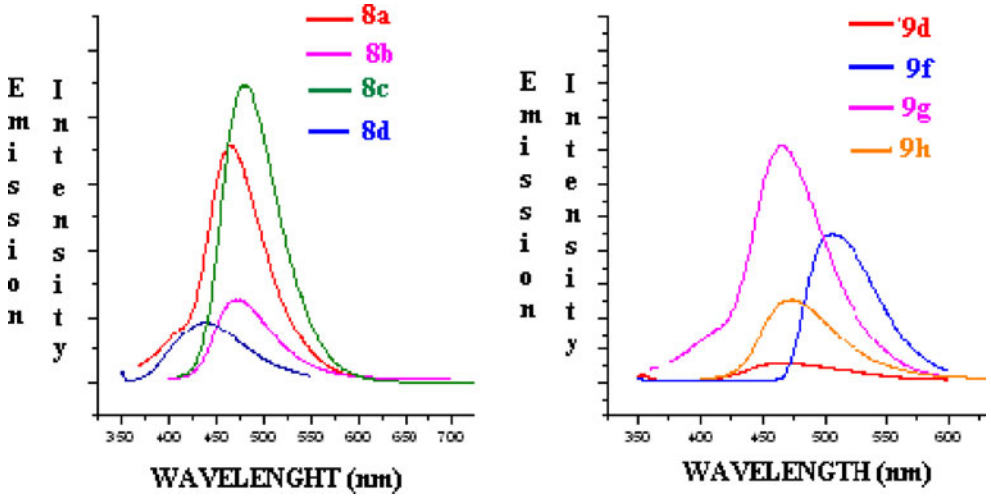


Fig. 1 Fluorescence spectra of compounds **8** and **9** respectively

containing LAH (48.00 mmol, 1.8 g) in a dry THF (15 mL) at 10–15 °C. The reaction mixture was stirrer at room temperature for 4 h (TLC monitoring, CH_2Cl_2/MeOH 10:2). It was quenched by dropwise addition of saturated sodium sulphate solution (20 mL) at room temperature (COUTION-EXOTHERMIC). This aqueous mixture was extracted with EtOAc (100 ml×2), dried over sodium sulphate, and concentrated to yield pure compound **4.** Yield: 2.6 g (87.1%), white solid, mp. 185–187 °C; IR (KBr): 3490, 3424, 3343, 1617,cm.$^{-1}$; ^{1}H NMR ($CDCl_3$) δ: 4.74 (d, 2 H, *J*=6.0 Hz, CH_2), 5.0 (t, 1 H, *J*=5.4 Hz, OH), 7.00 (bs, 2 H, NH_2), 7.41–7.65 (m, 4 H, ArH). ^{13}C NMR (DMSO-d_6) δ: 57.4, 109.6, 118.1, 122.4, 124.4, 127.7, 129.9, 146.5, 151.0, 152.3. MS m/z (%): 209.0 (M+1) (100), 211.0 (M+2) (25). Anal. Calcd. for $C_{10}H_9ClN_2O$ (208.64): C, 57.57; H, 4.35; N, 13.43%. Found: C, 57.41; H, 4.43; N, 13.45%.

4-Amino-2-chloroquinoline-3-carbaldehyde (5) In the solution of compound **4** (12.5 mmol, 2.6 g) in dry DCM (20 mL) was added MnO_2 (3.5 g) and the reaction mixture was stirred at room temperature for 12 h. (TLC monitoring CH_2Cl_2/MeOH, 9:1). The MnO_2 was filtered, washed with DCM and then evaporating under reduced pressure. The obtained solid was recrystallized from EtOAc to yield title compound **5**. Yield: 2.1 g (73.3%), off white solid, mp. 278–280 °C; IR (KBr): 3293, 3261, 2705, 1719 cm.$^{-1}$; ^{1}H NMR ($CDCl_3$) δ: 7.60–7.84 (m, 4 H, ArH), 8.97 (bs, 1 H, NH_2), 9.87 (bs, 1 H, NH_2), 10.3 (s, 1 H, CHO). ^{13}C NMR (DMSO-d_6) δ: 104.5, 118.3, 123.8, 126.0, 128.2, 133.2, 146.9, 152.6, 156.2, 191.6. MS m/z (%): 207.1 (M+1) (100), 209.0 (M+2) (20). Anal. Calcd. for $C_{10}H_7ClN_2O$ (206.63): C, 58.13; H, 3.41; N, 13.56%. Found: C, 58.28; H, 3.27; N, 13.75%.

4-Amino-2-phenylquinoline-3-carbaldehyde (6a-c) In a flask flushed with nitrogen, compound **5** (2.90 g, 14.0 mmol), tetrakistriphenylphosphine palladium (0.70 mmol), K_2CO_3 (28.0 mmol) and appropriate arylboronic acid (18.2 mmol) in water: DME (3.5:3 mL) were added sequentially. The reaction mixture was heated to 60–65 °C temperature for 5-6 h (TLC monitoring, CH_2Cl_2/MeOH 9:1). After completion of reaction, the solid catalyst was filtered out, washed with diethyl ether. The aqueous solution was then extracted with diethyl ether (50 mL×3). The ether layer was dried over anhydrous sodium sulphate and then evaporated under reduced pressure; the residue was chromatographed over silica gel column and eluted with chloroform-methanol (9.5: 0.5) to isolate the pure product.

4-Amino-2-phenylquinoline-3-carbaldehyde (6a) Yield: 2.8 g (82%), off white solid, mp. 201–203 °C. IR (KBr): 3444, 3307, 2769, 1710 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 7.49–7.58 (m, 5 H, Ar-H), 7.76-7.85 (m, 4 H, ArH), 8.68 (bs, 1 H, NH_2), 9.70 (bs, 1 H, NH_2), 9.79 (s, 1 H, CHO). ^{13}C NMR (DMSO-d_6) δ: 106.8, 117.5, 123.3, 125.2, 128.0, 128.0, 128.6, 129.2, 129.8, 129.8, 132.4, 138.9, 139.8, 147.8, 154.7, 163.2. MS m/z (%): 249.1 (M+1) (100). Anal. Calcd. For $C_{16}H_{12}N_2O$ (248.28): C, 77.40; H, 4.87; N, 11.28%. Found: C, 77.21; H, 4.95; N, 11.03%.

4-Amino-2-(4-methoxyphenyl)quinoline-3-carbaldehyde (6b) Yield: 3.4 g (87%), brownish solid, mp. 176–178 °C; IR (KBr): 3452, 3310, 2780, 1715, 1603 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.83 (s, 3 H, OCH_3), 7.05 (d, 2 H, *J*=9.0 Hz, ArH), 7.51 (d, 2 H, *J*=9.0 Hz, ArH), 7.62–8.46 (m, 4 H, ArH), 8.62 (bs, 1 H, NH_2), 9.54 (bs, 1 H, NH_2), 9.83 (s, 1 H, CHO). ^{13}C NMR (DMSO-d_6) δ: 55.2, 106.8, 113.4, 113.4, 117.4, 123.3, 124.9, 129.1, 131.1, 131.4, 131.4, 132.3, 148.0, 154.7, 159.6, 162.7, 192.5. MS m/z (%): 279.1 (M+1) (100), Anal. Calcd for $C_{17}H_{14}N_2O_2$ (278.31): C, 73.37; H, 5.07, N, 10.07%. Found: C, 73.54; H, 4.96, N, 10.21%.

4-Amino-2-(4-nitrophenyl)quinoline-3-carbaldehyde (6c) Yield: 3.5 g (85%), pale yellowish prism, mp. 181-182 °C; IR (KBr): 3481, 3284, 2701, 1649, 1530, 1332 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 7.54 (d, 2 H, *J*=8.2 Hz, ArH), 7.97 (d, 2 H, *J*= 8.2 Hz, ArH), 8.34–8.48 (m, 4 H, Ar-H), 8.52 (bs, 1 H, NH_2), 9.54 (bs, 1 H, NH_2), 9.80 (s, 1 H, CHO). ^{13}C NMR (DMSO-d_6) δ: 101.2, 117.2, 122.9, 122.9, 123.0, 125.6, 128.9, 129.2, 129.2, 131.6, 146.7, 149.4, 153.4, 157.4, 167.8, 192.5. MS m/z (%): 294.08 (M+1) (100). Anal. Calcd for $C_{16}H_{11}N_3O_3$ (293.28): C, 65.53; H, 3.78; N, 14.33%. Found: C, 65.59; H, 3.82; N, 14.29%.

5-chloro-2-benzo[h][1, 6]naphthyridines (8a-d) Mixture of 4-amino-2-chloroquinoline-3-carbaldehyde ***5*** (0.050 g, 0.24 mmol), appropriate acetophenones **7a-d** (0.24 mmol) and ammonium acetate (1.20 mmol) was heated at 120 °C for 20 min. (TLC monitoring, CH_2Cl_2/MeOH 10:0.5). The mixture was then cooled to room temperature and stirred in water (1.5 mL). The obtained solid was collected by suction filtration. The crude compound was recrystallized from absolute ethanol.

5-Chloro-2-phenylbenzo[h][1, 6]naphthyridine (8a) Yield: 0.058 g (80%), off white crystals, mp. 179–181 °C; IR (KBr): 3028, 3012, 1644, 1593 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 7.62–7.71 (m, 5 H, ArH), 8.20 (d, 1 H, *J*=8.2 Hz, ArH), 8.35 (d, 1 H, *J*=8.2 Hz, ArH), 8.42–8.51 (m, 4 H, ArH). ^{13}C NMR (DMSO-d_6) δ: 118.1, 119.8, 120.1, 122.4, 123.5, 123.5, 125.1, 125.1, 128.2, 129.7, 129.7, 132.1, 133.4, 137.2, 141.5, 145.1, 150.4, 155.8. MS m/z (%): 291.1 (M+ 1) (100), 293.1 (M+2) (22). Anal. Calcd. for $C_{18}H_{11}ClN_2$ (290.75): C, 74.36; H, 3.81, N, 9.63%. Found: C, 74.40; H, 3.75; N, 9.67%.

5-Chloro-2-(3,4-dimethoxyphenyl)benzo[h][1, 6]naphthyridines (8b) Yield: 0.052 g (62%), colorless crystals, mp. 198–200 °C; IR (KBr): 3020, 3015, 1630, 1590 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.85 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 7.12 (dd, 1 H, *J*=8.5 & 3.2 Hz, ArH), 7.85 (d, 1 H, *J*=8.5 Hz, ArH), 7.87 (d, 1 H, *J*=7.6 Hz, ArH), 7.97 (d, 1 H, *J*=3.2 Hz, ArH), 8.25–8.30 (m, 4 H, ArH), 9.20 (d, 1 H, *J*=7.6 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 55.4, 55.4, 111.5, 112.3, 117.6, 120.1, 123.9, 125.0, 127.0, 128.3, 129.7, 129.7, 130.5, 136.8, 138.5, 144.9, 148.1, 151.2, 158.5, 160.1. MS m/z (%): 351.1 (M+1) (100), 353.08 (M+2) (23). Anal. Calcd. for $C_{20}H_{15}ClN_2O_2$ (350.8): C, 68.48; H, 4.31; N, 7.99%. Found: C, 68.50; H, 4.51; N, 8.01%.

5-Chloro-2-(2, 4, 6-trimethoxyphenyl)benzo[h][1, 6]naphthyridine (8c) Yield: 0.060 g (65%), colorless prism, mp. 215–218 °C; IR (KBr): 3032, 3010, 1632, 1601 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.81 (s, 3 H, OCH_3), 3.99 (s, 6 H, OCH_3), 7.14 (s, 2 H, ArH), 7.60–7.91 (m, 4 H, ArH), 8.13 (d, 1 H, *J*=8.1 Hz, ArH), 9.28 (d, 1 H, *J*=8.1 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 56.2, 56.2, 62.2, 65.1, 104.9, 104.9, 118.1, 120.2, 123.6, 129.7, 129.7, 131.1, 135.0, 137.0, 137.0, 146.1, 148.9, 154.9, 154.9, 157.1, 166.7. MS m/z (%): 381.1 (M+1) (100), 383.1 (M+2) (20). Anal. Calcd. For $C_{21}H_{17}ClN_2O_3$ (380.82): C, 66.23; H, 4.50; N, 7.36%. Found: C, 66.27; H, 4.61; N, 7.40%.

5-Chloro-2-(4-nitrophenyl)benzo[h][1, 6]naphthyridine (8d) Yellowish prism Yield: 0.055 g (68%),, mp. 207–209 °C; IR (KBr): 3033, 3015, 1552, 1330 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 7.65–7.74 (m, 4 H, ArH), 8.22 (d, 2 H, *J*=8.2 Hz, ArH), 8.38 (d, 1 H, *J*=8.7 Hz, ArH), 9.12 (d, 1 H, *J*=8.7 Hz, ArH), 9.28 (d, 2 H, *J*=8.2 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 117.1, 119.9, 120.5, 121.4, 124.1, 124.1, 126.7, 126.7, 128.2, 129.7, 129.7, 133.0, 133.4, 137.2, 142.1, 145.1, 151.4, 191.2. MS m/z (%): 336.15 (M+1) (100), 337.15 (M+2) (21). Anal. Calcd. for $C_{18}H_{10}ClN_3O_2$ (335.74): C, 64.39; H, 3.00; N, 12.52%. Found: C, 64.42; H, 2.98; N, 12.62%.

2,5-Diphenylbenzo[h][1, 6]naphthyridine (9a-h) A mixture of 4-amino-2-aryl quinoline-3-carboxaldehyde **6a-c** (0.20 mmol) and appropriate acetophenones **7a-h** (0.20 mmol) in ammonium acetate (0.077 g, 1.0 mmol) was heated at 120 °C for 20 min. (TLC monitoring, CH_2Cl_2/MeOH 10:1). The reaction mixture was then cooled to room temperature and poured in cold water (2.0 mL). The precipitated solid was collected by suction filtration. dried and recrystallized from ethanol to obtain solid.

2, 5-Diphenylbenzo[h][1, 6]naphthyridine (9a) Yield: 0.055 g (82%), colorless crystals, mp. 129-132 °C; IR (KBr): 3024, 3010, 1615 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 7.58–7.61 (m, 3 H, ArH), 7.62–7.67 (m, 3 H, ArH), 7.76–7.79 (m, 2 H, ArH), 7.89–7.94 (m 2 H, ArH), 8.15 (d, 1 H, *J*=8.1 Hz, ArH), 8.41–8.46 (m, 4 H, ArH), 9.25 (d, 1 H, *J*=8.1 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 118.0, 119.8, 123.4, 124.2, 127.3, 127.5, 127.5, 128.4, 128.4, 129.0, 129.0, 129.0, 129.3, 129.7, 129.7, 130.4, 130.6, 137.1, 137.7, 138.2, 145.5, 148.1, 158.4, 159.8. MS m/z (%): 332.8 (M^+) (100), 333.8 (M+1) (20). Anal. Calcd. for $C_{24}H_{16}N_2$ (332.4): C, 86.72; H, 4.85; N, 8.43%.Found: C,86.54; H, 4.70; N, 8.53%.

2-(3,4-Dimehoxyphenyl)-5-phenylbenzo[h][1, 6]naphthyridine (9b) Yield: 0.052 g (66%), colorless crystals, mp. 193–195 °C; IR (KBr): 3035, 3012, 1610 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.87 (s, 3 H, OCH_3), 3.96 (s, 3 H, OCH_3), 7.14 (dd, 1 H, *J*=8.4 & 2.9 Hz, ArH), 7.61–7.62 (m, 3 H, ArH), 7.76–7.78 (m, 2 H, ArH), 7.81 (d, 1 H, *J*=8.4 Hz, ArH), 7.88 (d, 1 H, *J*=2.9 Hz, ArH), 7.96 (d, 1 H, *J*= 8.4 Hz, ArH), 8.15 (d, 1 H, *J*=8.4 Hz, ArH), 8.27–8.37 (m, 4 H, ArH). ^{13}C NMR (DMSO-d_6) δ: 55.62, 55.62, 110.5,

111.7, 117.6, 119.3, 123.4, 124.2, 127.2, 128.3, 128.3, 129.0, 129.1, 129.7, 129.7, 130.3, 130.5, 136.6, 138.3, 145.6, 145.6, 149.1, 149.1, 151.1, 158.2, 159.7. MS m/z (%): 393.2 (M+1) (100), Anal. Calcd. for $C_{26}H_{20}N_2O_2$ (392.45): C, 79.57; H, 5.14; N, 7.14%. Found: C, 79.39; H, 5.26; N, 7.29%.

5-Phenyl-2-(2,4,6-trimethoxyphenyl) benzo[h][1, 6]naphthyridine (9c) Yield: 0.057 g (67%). coloerless crystals, mp. 228–230 °C; IR (KBr): 3033, 3018, 1620, 1210, cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.78 (s, 3 H, OCH_3), 3.97 (s, 6 H, OCH_3), 7.62–7.63 (m, 3 H, ArH), 7.73 (s, 2 H, ArH), 7.77–7.85 (m, 4 H, ArH), 7.89 (s, 2 H, ArH), 8.15 (d, 1 H, *J*= 8.1 Hz, ArH), 9.25 (d, 1 H, *J*=8.1 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 56.0, 56.0, 60.2, 64.9, 105.1, 105.1, 117.9, 119.9, 123.6, 124.2, 128.4, 129.1, 129.1, 129.2, 129.7, 129.7, 130.6, 133.2, 136.9, 136.9, 145.7, 148.1, 153.3, 153.3, 153.3, 158.4, 165.6. MS m/z (%): 423.2 (M+1) (99), 424.2 (M+2) (22). Anal. Calcd. for $C_{27}H_{22}N_2O_3$ (422.48): C, 76.76; H, 5.25; N, 6.63%. Found: C, 76.51; H, 5.30; N, 6.44%.

5-(4-Methoxyphenyl)-2-phenylbenzo[h][1, 6]naphthyridine (9d) Yield: 0.046 g (68%), colorless crystals, mp. 197–199 °C; IR (KBr): 3041, 3021, 1607, 1251 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 4.00 (s, 3 H, OCH_3), 7.12–7.24 (m, 5 H, ArH), 7.26 (d, 2 H, *J*=8.2 Hz, ArH), 7.71–7.94 (m, 4 H, ArH), 8.01 (d, 2 H, *J*=8.2 Hz, ArH), 8.44 (d, 1 H, *J*= 9.0 Hz, ArH), 8.75 (d, 1 H, *J*=9. 0 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 55.2, 118.0, 119.8, 123.4, 124.2, 127.3, 127.5, 127.5, 128.4, 128.4, 129.0, 129.0, 129.0, 129.2, 129.7, 129.7, 130.4, 130.6, 137.1, 137.7, 138.2, 145.5, 148.1, 158.4, 159.8. MS m/z (%): 363.15 (M+1) (100). Anal. Calcd. for $C_{25}H_{18}N_2O$ (362.4): C, 82.85; H, 5.01; N, 7.73%. Found; C, 83.01; H, 5.09; N, 7.81%.

2-(3,4-Dimethoxyphenyl)-5-(4-methoxyphenyl)benzo[h][1, 6]naphthyridine (9e) Yield: 0.051 g (67%), colorless crystals, mp. 193–195 °C; IR (KBr): 3034, 3012, 1605 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.87-3.88 (s, 6 H, OCH_3), 3.96 (s, 3 H, OCH_3),7.29(d, 2 H, *J*=8.2 Hz, ArH), 7.34 (dd, 1 H, *J*=8.6 & 2.8 Hz, ArH), 7.64 (d, 1 H, *J*= 8.6 Hz, ArH), 7.79–7.98 (m, 4 H, ArH), 8.11 (d, 1 H, *J*= 2.8 Hz, ArH), 8.14 (d, 2 H, *J*=8.2 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 55.3, 55.6, 55.6, 110.5, 111.7, 117.6, 119.3, 123.4, 124.2, 127.2, 128.3, 128.3, 129.0, 129.1, 129.7, 130.3, 130.5, 136.6, 136.6, 138.3, 145.6, 145.6, 149.1, 149.1, 151.1, 158.2, 159.7. MS m/z (%): 423.1 (M+1) (99), Anal. Calcd. for $C_{27}H_{22}N_2O_3$ (422.48): C, 76.76; H, 5.25; N, 6.63%. Found: C, 76.89; H, 5.41; N, 6.82%.

5-(4-Methoxyphenyl-2-(2,4,6-trimethoxyphenyl)benzo[h][1, 6]naphthyridine (9f) Yield: 0.056 g (69%), off white crystals, m.p. 199–201 °C; IR (KBr): 3032, 3016, 1600, 1240 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.78 (s, 3 H, OCH_3), 3.89 (s, 3 H, OCH_3), 3.97 (s, 6 H, OCH_3), 7.16 (d, 2 H, *J*= 8.4 Hz, ArH), 7.73 (s, 2 H, ArH), 7.89 (d, 2 H, *J*=8.4 Hz, ArH), 8.12 (d, 1 H, *J*=8.1 Hz, ArH), 8.36–8.47 (m, 4 H, ArH), 9.21(d, 1 H, *J*=8.1 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 55.3, 56.1, 60.1, 105.1, 105.1, 113.8, 113.8, 117.9 119.8, 123.4, 124.0, 127.0, 129.0, 130.5, 130.6, 131.3, 131.3, 133.0, 136.9, 139.8, 145.7, 148.0, 153.3, 153.3, 158.0, 159.3, 160.0, 162.1. MS m/z (%): 453.2 (M+1) (100). Anal. Calcd. for $C_{28}H_{24}N_2O_4$ (452.5): C, 74.32; H, 5.35; N, 6.19%. Found; C, 74.14; H, 5.26; N, 6.34%.

2-(3,4-Dimethoxyphenyl)-5-(4-nitrophenyl)benzo[h][1, 6] naphthyridine (9 g) Yield: 0.055 g (74%), reddish crystals, mp. 222–225 °C; IR (KBr): 3132, 3040, 1610, 1540, 1310 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.85 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 7.19 (dd, *J*=9.1 & 2.8 Hz, ArH), 7.42 (d, 1 H, *J*=9.1 Hz, ArH), 7.62 (d, 1 H, *J*=2.8 Hz, ArH), 7.72 (d, 2 H, *J*=8.2 Hz, ArH), 7.80–8.10 (m, 4 H, ArH), 8.16 (d, 1 H, *J*=8.5 Hz, ArH), 8.32 (d, 2 H, *J*=8.2 Hz, ArH), 9.25 (d, 1 H, *J*=8.5 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 56.1, 56.1, 111.0, 111.5, 118.1, 119.7, 124.0, 124.5, 127.9, 128.5, 128.9, 129.1, 129.6, 129.9, 130.7, 131.2, 136.5, 136.5, 139.2, 146.0, 146.0, 149.2, 149.2, 151.2, 159.1, 190.2. MS m/z (%): 438.5 (M+1) (99). Anal. Calcd. For $C_{26}H_{19}N_3O_4$ (437.45): C, 71.39; H, 4.38; N, 9.61%. Found: C, 71.35; H, 4.40; N, 9.55%.

2-(2,4,6-Trimethoxyphenyl)-5-(4-nitrophenyl)benzo[h][1, 6] naphthyridine (9 h) Yield: 0.058 g (73%), off white crystals, mp. 186–189 °C; IR (KBr): 3033, 3014, 1615 cm.$^{-1}$; ^{1}H NMR (DMSO-d_6) δ: 3.80 (s, 3 H, OCH_3), 3.92 (s, 6 H, OCH_3), 7.16 (d, 2 H, *J*=9.0 Hz, ArH), 7.72–7.80 (m, 4 H, ArH), 7.85 (d, 1 H, *J*=8.0 Hz, ArH), 8.15 (d, 2 H, *J*= 9.0 Hz, ArH), 8.32 (s, 2 H, ArH), 9.22 (d, 1 H, *J*=8.0 Hz, ArH). ^{13}C NMR (DMSO-d_6) δ: 56.10, 56.10, 60.2, 106.1, 106.1, 114.0, 114.0, 118.0, 119.1, 123.5, 124.0, 127.1, 129.2, 131.1, 131.5, 131.7, 131.7, 133.5, 137.1, 140.1, 145.9, 149.0, 154.1, 158.5, 159.5, 191.0. MS m/z (%): 468.15 (M+1) (100). Anal. Calcd. For $C_{27}H_{21}N_3O_5$ (467.47): C, 69.37; H, 4.53; N, 8.99%. Found: C, 69.40; H, 4.56; N, 9.05%.

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