Effect of Substituents in the Syntheses of Phenyl-Substituted Dibenzonaphthyridines

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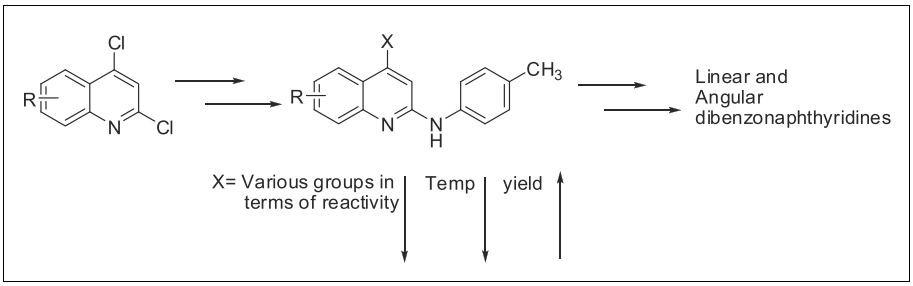

A facile and elegant syntheses of linear and angular phenyl-substituted dibenzonaphthyridines from 2,4-dichloroquinolines through anilinoquinolines have been developed. The substituents in the 4th position of the anilinoquinoline and the temperature were found to play a vital role in the regulation of the yield towards the synthesis of the final compounds. The methyl group in the 7th position of the naphthyridin-11-ones was found to hinder the N-methylation reaction sterically, consequently increasing the reaction time than other derivatives.

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INTRODUCTION

The discovery of cinchona alkaloids as antimalarial agents has turned the quinoline (π-electron deficient heterocycle) core to become one of the privileged structures for the design and the development of potential new drugs. A literature survey revealed that the reactions of chloroquinolines have been studied extensively, the objective being to obtain substitution products possessing biological activity [1–3]. Some of the amino substituted quinolines, for example, chloroquine and pamaquine, act as potent antimalarial drugs against *Plasmodium falciparum* [4]. Several anilinoquinolines were established as synthetic antimalarials [5] and have been utilized as synthons in deriving various fused heterocycles such as dibenzonaphthyridines [6] and indoloquinoline alkaloids [7]. Research on naphthyridine chemistry has been expanded considerably in recent years in connection with the fact that these heterocycles exceptionally own a broad spectrum of their biological activities such as anti-arrhythmic [8], anti-analgesic [9], therapy of disease of human including AIDS [10, 11], and cancer [12]. Particularly, some dibenzonaphthyridines, that is, quinoline dimers, act as selective 3-phosphoinositide-dependent kinase-I inhibitors [13]. Many reports represent the synthesis of functionalized naphthyridine derivatives [14–16], linear dibenzonaphthridines [17, 18], and angular dibenzonaphthridines [19–21], and only very few accomplish their construction through anilinoquinolines [6, 22].

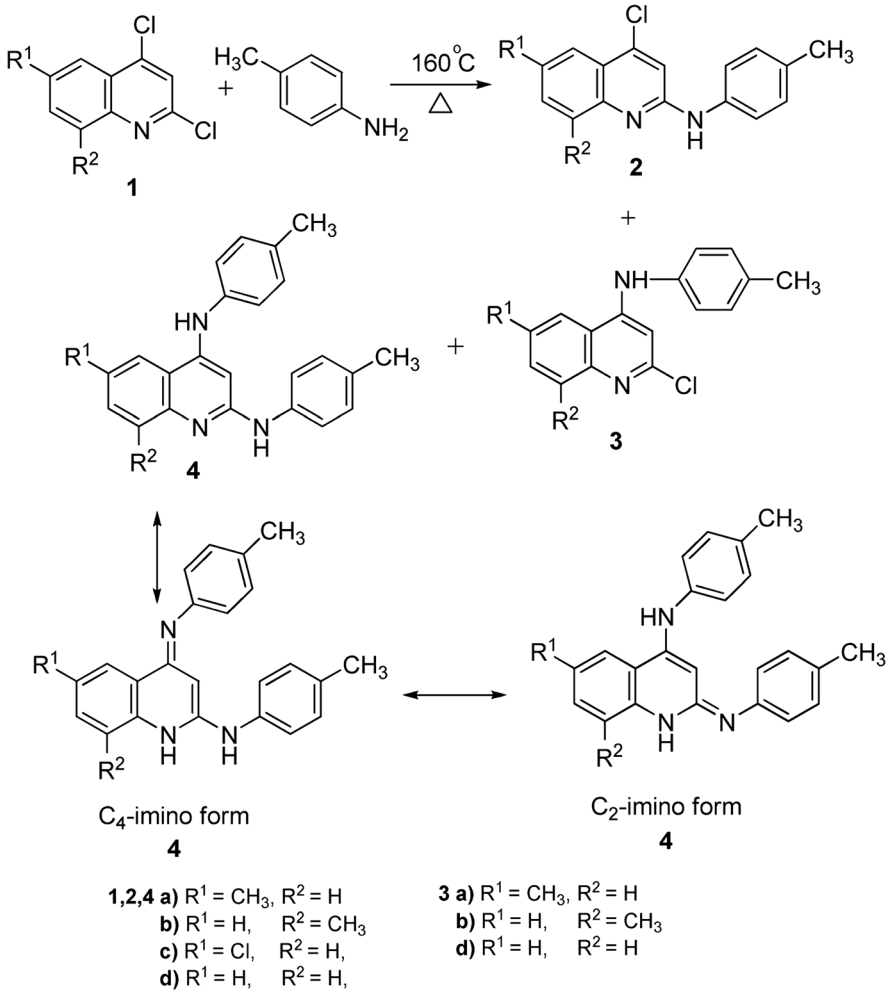
A study of literature divulged no facile method for the construction of phenyl-substituted dibenzonaphthyridines from anilinoquinolines utilizing Bernthsen reaction condition involving benzoic acid and polyphosporic acid [23]. Herein, we report the synthesis of linear and angular, phenyl-substituted dibenzonaphthyridines by the reaction of 2,4-dichloroquinolines *via* various 4-substituted anilinoquinolines utilizing Bernthsen reaction condition. These anilinoquinolines were prepared by a simple and convenient methodology from 2,4-dichloroquinolines. Surprisingly, it was observed that the formation of the linear and angular dibenzonaphthyridines were substituent and temperature dependent with the regulation of yields of the final product.

RESULTS AND DISCUSSION

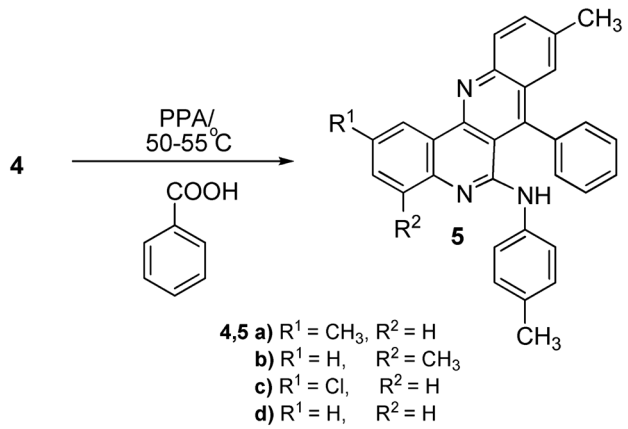
With the motive to prepare various substituted anilinoquinolines, the precursor 2,4-dichloroquinoline (**1**) was reacted with *p*-toluidine under neat condition at 160°C to afford three products (anilinoquinolines) (Scheme 1). The first and the second eluted product were assigned as 4-chloro-4′-methyl-2-(*N*-phenylamino)quinoline (**2**) and 2-chloro-4′-methyl-4-(*N*-phenylamino)quinoline (**3**), respectively, on the basis of the reactivity of the chloro group at the second and fourth positions of the 2,4-dichloroquinoline [24, 25]. The last eluted product was assigned as 4′,4″-dimethyl-2,4-bis-(*N*-phenylamino)quinoline (**4**), which was found to be in tautomeric equilibrium with the two imino forms on the basis of its IR and NMR spectra.

To get the naphthyridine, **4** was reacted with benzoic acid in presence of PPA as catalyst (Scheme 2). The reaction was initiated at 50–55°C to obtain a single product. Here, the chance of getting the linear naphthyridine has not been

Scheme 1. Preparation of anilinoquinolines **2**, **3**, and **4**.



Scheme 2. Preparation of angular dibenzonaphthyridine **5**.



observed and the only formed product was assigned as the thermodynamically more stable angular isomer namely, 9,4′-dimethyl-7-phenyl-6-(*N*-phenylamino)dibenzo[*b,h*][1,6]naphthyridine (**5**) on the basis of its higher melting point [26] and finally confirmed by crystallographic studies (Fig. 1).

The mechanism (Scheme 3) involves initially benzoylation at the C3-position of the quinoline moiety, which further cyclizes *via* the ortho position of the C4 NH rather than the C2 NH in turn getting the more stable angular isomer.

The other possibilities of C2′ and/or C2″-benzoylation of *N*-phenyl ring are ruled out on the basis of the following observation:

1. If C2′ and C2″-benzoylation take place, it would have resulted in the formation of **6** (Fig. 2) (Slight excess benzoic is used in the reaction).
2. The two activating N-aryl groups at C2- and C4-position highly favor the electrophilic substitution at C3-position.

Compound **2** under the same reaction condition did not proceed for long hours and even in the steam bath temperature, which may be due to the deactivating nature of the chloro group inhibiting electrophilic substitution at the

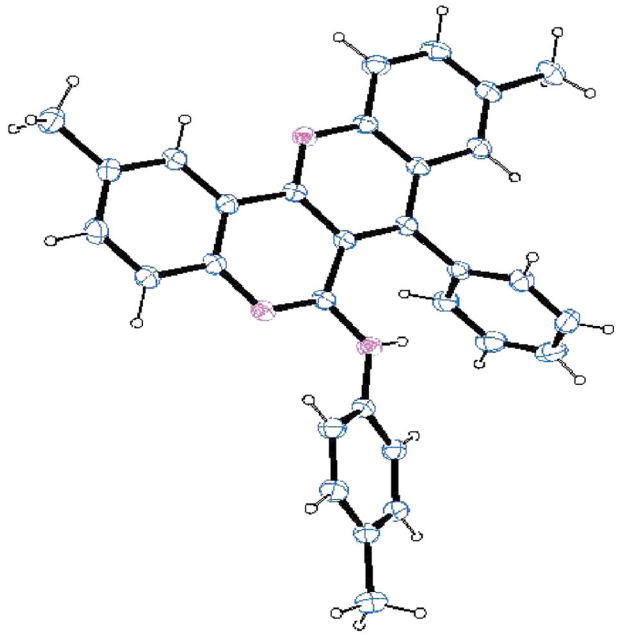
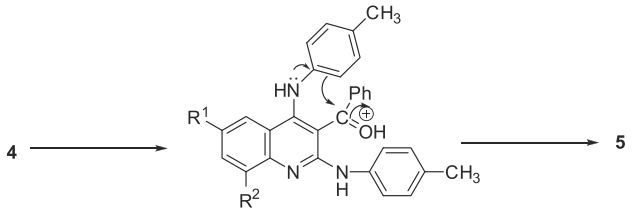


Figure 1. ORTEP diagram of 2,9,4′-trimethyl-7-phenyl-6-*N*-(phenylamino) dibenzo[*b,h*][1,6]naphthyridine (**5a**).

Scheme 3. Mechanism for the formation of angular isomer **5**.



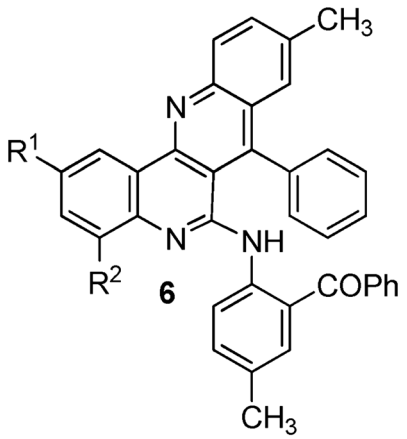


Figure 2. 2′-Benzoyl-9,4′-dimethyl-7-phenyl-6-(N-phenylamino)dibenzo [*b,h*][1,6]naphthyridine.

C3-position. The conversion of the Cl → OCH_3 was effected by the treatment of sodium methoxide on **2** and the obtained product 4-methoxy-4′-methyl-2-(*N*-phenylamino)quinoline (**7**) was reacted with benzoic acid only at 140–145°C. Analyzing the product through spectral means revealed the absence of OCH_3 protons. The appearance of carbonyl group in its IR spectrum and ^{13}C-NMR spectrum provided us the confidence that the OCH_3 group might be cleaved under acidic condition [24, 27] to give the cyclized product. Finally, the mass spectrum confirmed the compound to be the linear dibenzonaphthyridine, namely 2-methyl-12-phenyldibenzo [*b,g*][1,8]naphthyridin-11(6*H*)-one (**8**).

We felt quite uncertain whether the ether cleavage would have taken place before or after the cyclization. Hence, to examine, compound **7** was treated with PPA and at 140–145°C to afforded 4′-methyl-2-(*N*-phenylamino) quinolin-4-(1*H*)-one (**9**). Thus, the obtained 4-oxo compound was then subjected to the benzoic acid and PPA condition and surprisingly found that the reaction was initiated at 90–95°C to afford **8**. It has been proved that the reaction of **7** with benzoic acid and PPA yielding **8** proceeded *via* **9** (Scheme 4).

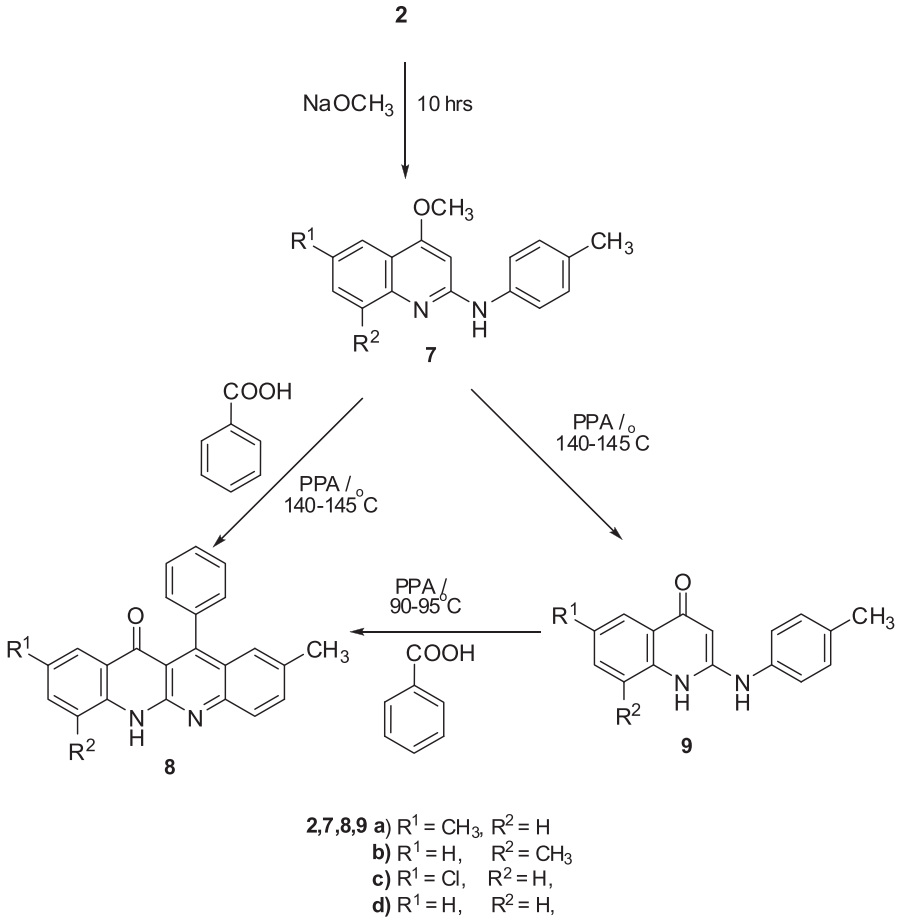
The above observations paved way to examine **2** under the similar condition in getting the respective naphthyridine by gradually increasing the temperature to higher degrees. Only at 230–235°C, compound **2** reacted with benzoic acid and the product obtained matched **8**, which concluded that the **2** was converted to **9** at the specified temperature and then reacted with benzoic acid similar to the earlier case. This was further confirmed from the reaction of **2** with PPA at 230–235°C to get the corresponding 4-oxo compound **9** (Scheme 5).

Here, the mechanism for the conversion of **2** to **9** under PPA condition (Scheme 6) might be the protonation of the ring nitrogen of **2** to give the intermediate **I** followed by the ipso attack of the $OP_2O_6HR_2$ ion to the C4-carbon yielded the intermediate **II**, which subsequently on intramolecular elimination of HCl molecule afforded **9**. The reaction mechanism was cross-checked with 2,4-dichloroquinoline (**1**), which on reaction with PPA yielded the respective 2,4-dihydroxyquinolines [28].

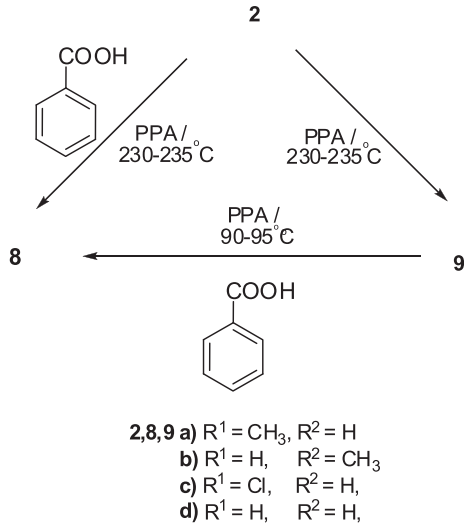
The linear naphthyridine **8** obtained as a result of **7**, **9**, and **2** (all proceeding *via* **9**), varied in their yields. Compound **9** was comparatively found to give major yield followed by **7** and then **2**, which were contradictory with respective of their reaction temperature ensuring unnoticeable effect with the reaction time. This could be visualized as the reflection of the yields in the conversion of **7**–**9**, **2**–**9**, and **9**–**8**. The comparision of the yields for their conversion is presented in the Table 1.

To test the N-methylation reaction of dibenzonaphthyridin-11-one, compound **8** was refluxed with methyl iodide in presence of ignited potassium carbonate and acetone. The product was formed in the duration of 1 h, which was

Scheme 4. Preparation of linear dibenzonaphthyridine **9** from **7**.



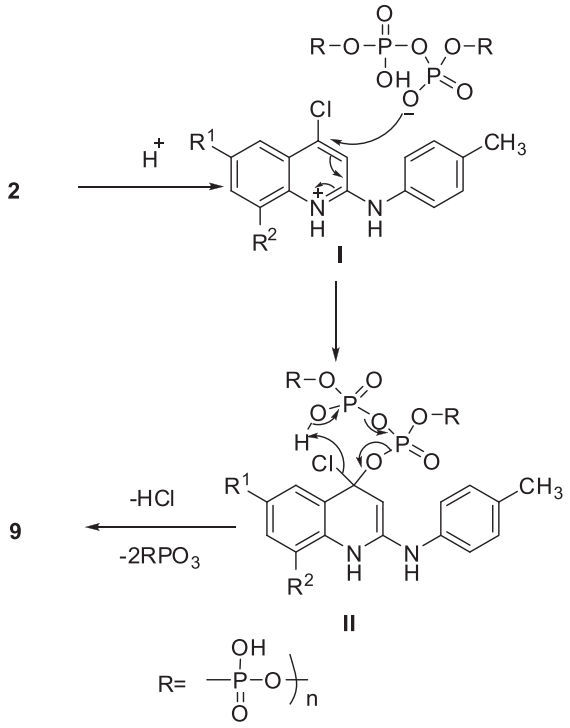
Scheme 5. Preparation of linear dibenzonaphthyridine **8** from **2**.



identified as N-methylated product namely 2,6-dimethyl-12-phenyldibenzo[*b,g*][1,8]naphthyridin-11(6H)-one (**10**). The reaction was generalized for other naphthyridine derivatives with an exception that the 2,7-dimethyl-12-phenyldibenzo [*b,g*][1,8]naphthyridin-11(6*H*)-one (**8b**) took longer hours (5 h) for the formation of 2,6,7-trimethyl-12-phenyldibenzo [*b,g*][1,8]naphthyridin-11(6*H*)-one (**10b**), which might be due to the steric hinderance of C7 methyl group (Scheme 7).

In search for the reactivity of the anilinoquinoline holding H at the fourth position (neither activating nor deactivating group), compound **2** was dechlorinated with zinc powder and acetic acid to afford 4′-methyl-2-(*N*-phenylamino)quinoline (**11**), which had peculiar coupling constant values for C3 and C4 protons (J = 9.00 Hz) in its ^{1}H-NMR spectrum. In an alternate method, structure of the product was cross-checked by the reaction of 2-chloroquinoline and *p*-toluidine under neat condition. Thus, the anilinoquinoline **11** where H at fourth position was subjected to Bernthsen condition and observed that the reaction was initiated at 190–195°C to afford 2-methyl-12-phenyldibenzo[*b,g*][1,8]naphthyridine (**12**) (Scheme 8). Here, a perceptible concept was the yield, which was very less than the other cases even in the case of **2** yielding **8** at 230–235°C. The above sequence of annulation reaction was also extended to substituted benzoic acid, that

Scheme 6. Mechanism for the conversion of **2**–**9**.

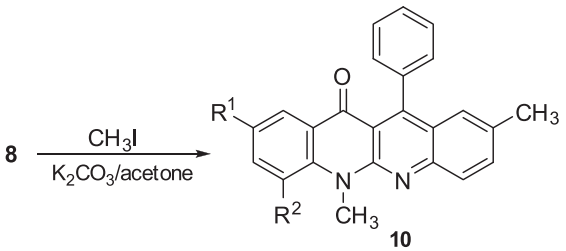


is, *p*-toluic acid, *o*-chlorobenzoic acid, and also with naphthoic acid, which ended up in the similar type of result (Scheme 9).

CONCLUSIONS

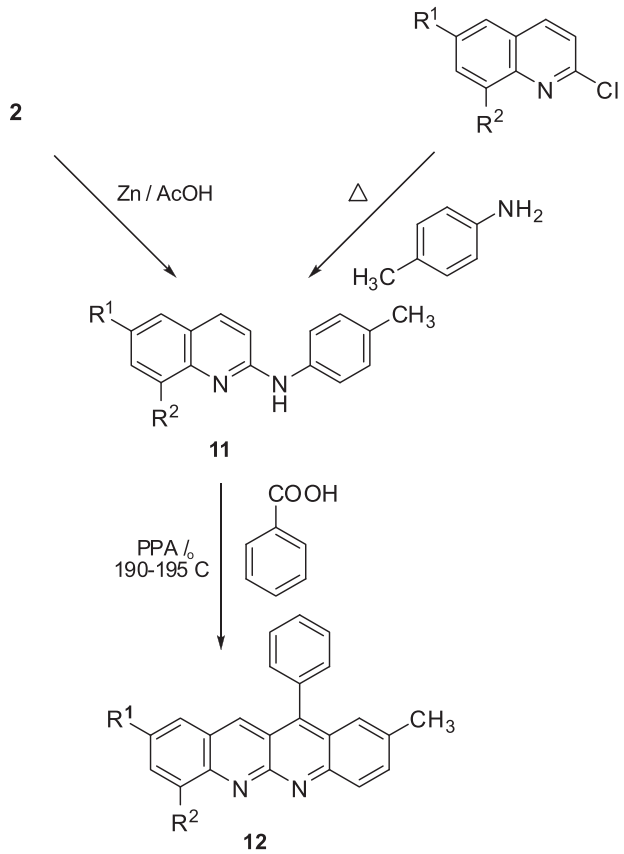
Using Bernthsen reaction condition involving benzoic acid and PPA, a facile and elegant method in synthesizing the linear and angular phenyl-substituted dibenzonaphthyridines from 2,4-dichloroquinolines through 4-substituted-2-(*N*-phenylamino)quinolines (anilinoquinolines) have been developed. The bis-2-(*N*-phenylamino)quinoline (**4**) underwent the reaction at 50–55°C, whereas the 4-methoxy-2-(*N*-phenylamino)quinoline (**7**) and 4-chloro-2-(*N*-phenylamino) quinoline (**2**) proceeded the same at 140–145°C and 230–235°C, respectively, *via* the 4-oxo-2-(*N*-phenylamino)quinoline (**9**), which took only 90–95°C to proceed. The 2-(*N*-phenylamino)quinoline (**11**) proceeded at the temperature range190–195°C to give **12**.

Scheme 7. N-methylation of the dibenzonaphthyridin-11-one **8**.



8,10 a) $R^1 = CH_3$, $R^2 = H$
b) $R^1 = H$, $R^2 = CH_3$
c) $R^1 = Cl$, $R^2 = H$,
d) $R^1 = H$, $R^2 = H$,

Scheme 8. Preparation of linear dibenzonaphthyridine **12** from **11**.



2,11 a) $R^1 = CH_3$, $R^2 = H$
b) $R^1 = H$, $R^2 = CH_3$
c) $R^1 = Cl$, $R^2 = H$,
d) $R^1 = H$, $R^2 = H$,

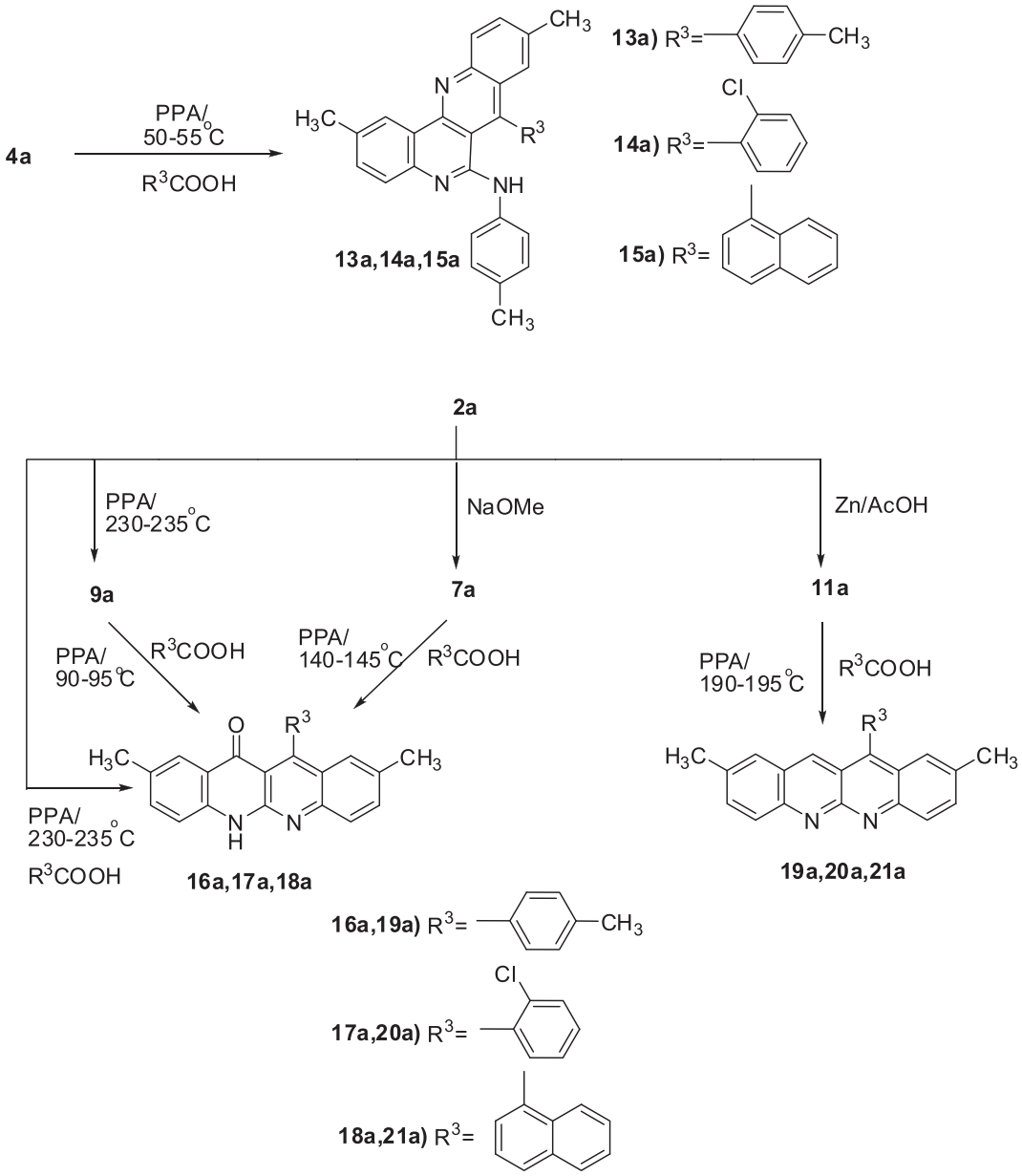
12 a) $R^1 = CH_3$, $R^2 = H$
b) $R^1 = H$, $R^2 = CH_3$
d) $R^1 = H$, $R^2 = H$,

Table 1

Comparision of the yields for the formation of **8** from **2**, **7**, and **9**.

Conversion of **7**–**9**	Conversion of **7**–**8**	Conversion of **2**–**9**	Conversion of **2**–**8**	Conversion of **9**–**8**
7a–**9a** (42%)	**7a**–**8a** (20%)	**2a**–**9a** (30%)	**2a**–**8a** (14%)	**9a**–**8a** (49%)
7b–**9b** (40%)	**7b**–**8b** (22%)	**2b**–**9b** (32%)	**2b**–**8b** (16%)	**9b**–**8b** (51%)
7c–**9c** (38%)	**7c**–**8c** (19%)	**2c**–**9c** (29%)	**2c**–**8c** (15%)	**9c**–**8c** (50%)
7d–**9d** (40%)	**7d**–**8d** (23%)	**2d**–**9d** (32%)	**2d**–**8d** (17%)	**9d**–**8d** (52%)

Scheme 9. Preparation of other substituted dibenzonaphthyridines.



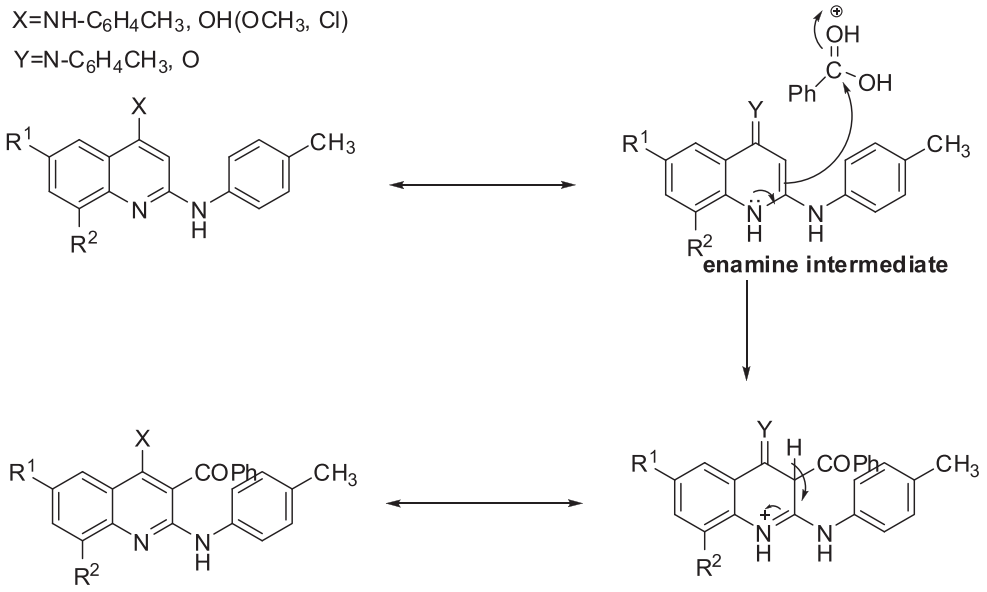
In the 4-substituted-2-(*N*-phenylamino)quinoline, while coming down the substitution from NH $C_6H_4CH_3$, OH, OCH_3 and Cl, the yields were poor accompanying higher temperature as there is a diminishing slope from activating groups to deactivating group, provided the OCH_3 and Cl groups were converted to OH. The exception noted for the reaction of compound **11** where X = H (neither activating nor deactivating group) proceeded at the expected temperature but with unexpected lower yield. This could be reasoned mechanistically as below;

For the groups where [X = NH $C_6H_4CH_3$ and OH (OCH_3 and Cl)], the mechanism for the formation of naphthyridine moiety would have taken place initially by the electrophilic substitution (benzoylation) at the C3-position of the quinoline *via* the enamine form (Scheme 10).

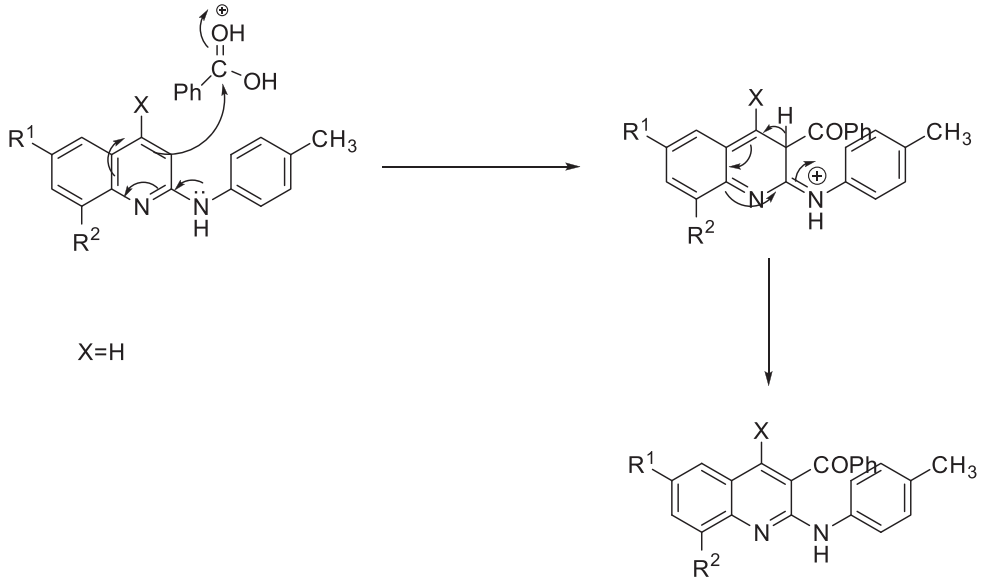
But in the last case where (X = H) the mechanism might be proposed such that the electrophilic substitution at C3-position takes place only by the disruption of the aromatic sextet in the carbocyclic ring thereby reducing the yield comparatively (Scheme 11).

The effect of the various substituents in the fourth position of the anilinoquinoline toward the synthesis of the linear and angular phenyl-substituted dibenzonaphthyridines has been correlated with the temperature and the yield graphically

Scheme 10. Mechanism involving enamine intermediate.



Scheme 11. Mechanism involving disruption of aromaticity in carbocyclic ring.

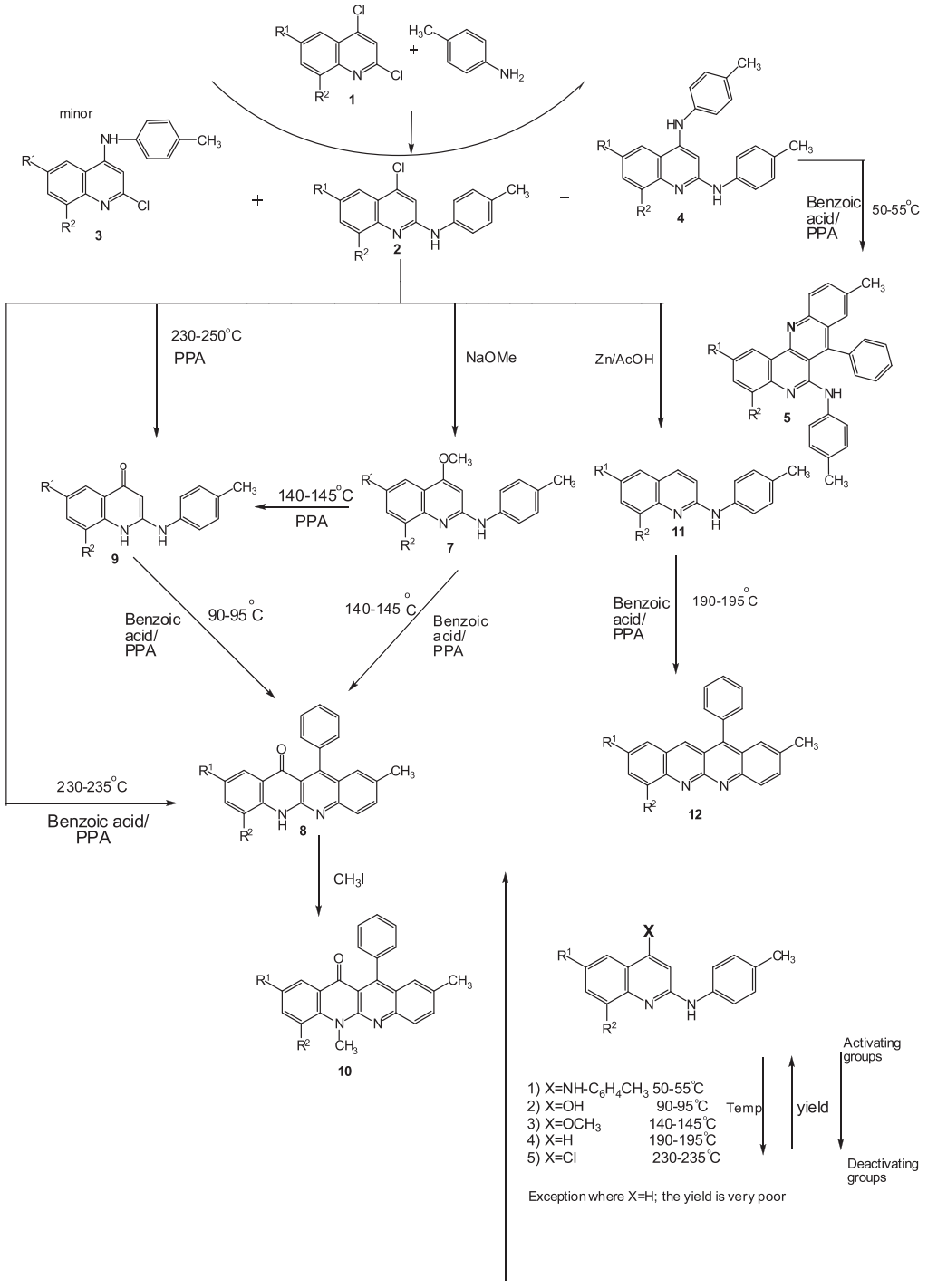


(Fig. 3). Besides benzoic acid, this annulation reaction was also found to work well with *p*-toluic acid, *o*-chlorobenzoic acid, and naphthoic acid.

EXPERIMENTAL

General experiment methods. Melting points (mp) were determined on Mettler FP 51apparatus (Mettler Instruments, Switzerland) and are uncorrected. IR spectra were recorded on Schimadzu FTIR-8201PC spectrophotometer (Schimadzu, Japan) using KBr disc. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker AMX 400 [400 MHz (^{1}H) and 100 MHz (^{13}C)), AV 300 (300 MHz (^{1}H) and 75 MHz (^{13}C)] and Bruker AV III 500 [500 MHz (^{1}H) and 125 MHz (^{13}C)] NMR spectrometer using tetramethylsilane as an internal reference. The chemical shifts are expressed in parts per million (ppm). Mass spectra (MS) were recorded on AutoSpec EI+ shimadzu QP 2010 PLUS GC-MS mass spectrometer. Microanalyses were performed on a Vario EL III model CHNS analyzer (Vario, Germany) at the Department of Chemistry, Bharathiar University. The purity of the products was tested by TLC with plates coated with silica gel-G with petroleum ether, ethyl acetate, and methanol as developing solvents.

Scheme 12. Overall scheme for the synthesis of linear and angular dibenzonaphthyridines.



Reaction of 1 with *p*-toluidine; preparation of 4-chloro-4′-methyl-2-(*N*-phenylamino)quinoline (2), 2-chloro-4′-methyl-4-(*N*-phenylamino)quinoline (3), and 4′,4″-dimethyl-2,4-bis-(*N*-phenylamino)quinoline (4). A mixture of appropriate 2,4-dichloroquinoline (**1**, 10 mmol) and *p*-toluidine (10 mmol) was heated under neat condition at 160°C for half an hour. The product obtained was washed with water, dried, which showed a mixture of three products on TLC, separated by column chromatography over silica gel, and eluted with petroleum ether:ethyl acetate (99:1) and (98:2) mixture to get 4-chloro-4′-methyl-2-(*N*-phenylamino)quinoline (**2**) (recrystallized using ethanol) and 2-chloro-4′-methyl-4-(*N*-phenylamino) quinoline (**3**) (recrystallized using ethanol), respectively, and ethyl acetate:methanol (95:5) mixture to get 4′,4″-dimethyl-2,4-bis-(*N*-phenyl amino)quinoline (**4**). It was recrystallized using methanol.

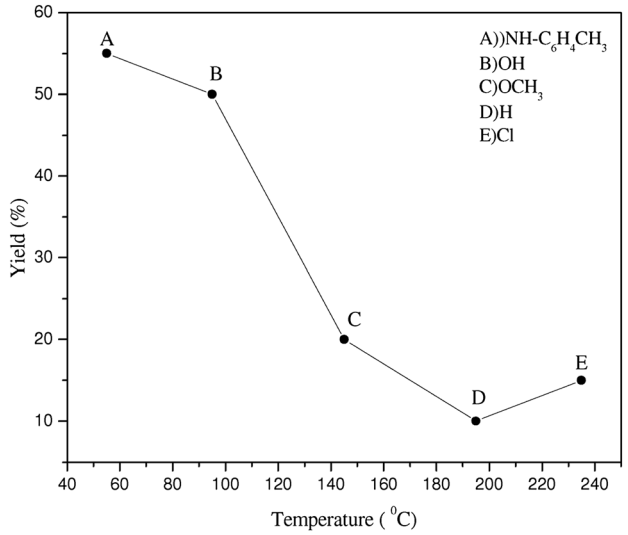


Figure 3. Graphical representation correlating temperature, yield and the nature of substituent in the synthesis of dibenzonaphthyridines.

Reaction of 2,4-dichloro-6-methylquinoline (1a) with *p*-toluidine

4-Chloro-6,4′-dimethyl-2-(N-phenylamino)quinoline (2a). Pale yellow prisms; mp: 118–120°C; Yield: 0.705 g (25%); IR (KBr): υ 3245 (NH), 1596 (C N), 1517, 1112 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, C4′ CH_3), 2.50 (s, 3H, C6 CH_3), 6.67 (br s, 1H, C2 NH), 7.05 (s, 1H, 3-H), 7.18 (d, *J* = 8.12 Hz, 2H, 3′-, 5′-H), 7.35 (d, *J* = 8.24 Hz, 2H, 2′-6′-H), 7.45 (d, *J* = 8.48 Hz, 1H, 7-H), 7.64 (d, *J* = 8.48 Hz, 1H, 8-H), 7.80 (s, 1H, 5-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.0, 21.7, 110.5, 120.6, 122.0, 122.5, 130.2, 131.0, 131.2, 132.5, 135.2, 137.4, 143.9, 148.2, 154.0 ppm; MS (EI) *m/z* 282(M^+, 100), 284(M+2, 34), 281(80), 265(35), 247(60), 246(30), 220(25), 90(48), 77(48); Anal. Calcd for $C_{17}H_{15}N_2Cl$ (282): C, 72.34; H, 5.32; N, 9.92. Found: C, 72.10; H, 5.28; N, 9.73.

2-Chloro-6,4′-dimethyl-4-(N-phenylamino)quinoline (3a). Colorless prisms; mp: 125–127°C; Yield: 0.085 g (3%); IR (KBr): υ 3260 (NH), 1592 (C N), 1510, 1090 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, C4′ CH_3), 2.54 (s, 3H, C6 CH_3), 6.62 (br s, 1H, C4 NH), 6.76 (s, 1H, 3-H), 7.18–7.20 (m, 2H, 3′-, 5′-H), 7.24–7.26 (m, 2H, 2′-, 6′-H), 7.51 (d, *J* = 8.58, 1H, 7-H), 7.62 (d, *J* = 8.52 Hz, 1H, 8-H), 7.83 (s, 1H, 5-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.0, 21.7, 108.2, 120.0, 122.3, 122.8, 130.2, 131.0, 131.4, 133.0, 135.9, 137.8, 144.2, 149.0, 154.3 ppm; MS (EI) *m/z* 284(M+2, 38), 282(M^+, 100), 280(75), 279(70), 268(55), 245(58), 243(20), 85(12), 76(49); Anal. Calcd for $C_{17}H_{15}N_2Cl$ (282):C, 72.34; H, 5.32; N, 9.92. Found: C, 72.20; H, 5.21; N, 9.80.

6,4′,4″-Trimethyl-2,4-bis-(N-phenylamino)quinoline (4a). White solid; mp >300°C: Yield: 1.062 g (30%): IR (KBr): υ 3425 (NH), 1642(C N), 1597 (C N), 1532, 1274 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H, C4" CH_3), 2.35 (s, 3H, C4′ CH_3), 2.47 (s, 3H, C6 CH_3), 6.17 (s, 1H, 3-H), 7.19–7.30 (m, 8H, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 5″-, 6″-H), 7.62 (d, *J* = 8.36 Hz, 1H, 7-H), 7.70 (d, *J* = 8.48 Hz, 1H, 8-H), 8.34 (s, 1H, 5-H), 9.89 (s, 1H, C4 NH), 10.09 (s, 1H, C2 NH), 12.52 (s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ 18.5, 20.1, 85.6, 113.8, 121.5, 123.6, 123.7, 124.9, 126.5, 130.1, 130.3, 132.2, 132.6, 136.5, 154.3, 155.6 ppm; MS (EI) *m/z* 353(M^+, 100), 352(89), 338(15), 245(25), 244(35), 105(18), 92(65), 77(35); Anal.Calcd. for $C_{24}H_{23}N_3$ (353): C, 81.59; H, 6.51; N, 11.90: Found: C, 81.39; H, 6.40; N, 12.21.

Reaction of 2,4-Dichloro-8-methylquinoline (1b) with *p*-toluidine

4-Chloro-8,4′-dimethyl-2-(N-phenylamino)quinoline (2b). Pale yellow prisms; mp: 125–127°C; Yield: 0.846 g (30%); IR (KBr) υ 3340 (NH), 1600 (C N), 1529, 1079 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, C4′ CH_3), 2.70 (s, 3H, C8 CH_3), 6.64 (br s, 1H, C2 NH), 7.03 (s, 1H, 3-H), 7.19 (d, *J* = 8.19 Hz, 2H, 3′-, 5′-H), 7.23–7.51 (m, 3H, 6-, 2′-, 6′-H), 7.52 (d, *J* = 8.34 Hz, 1H, 7-H), 7.90 (d, *J* = 8.20 Hz, 1H, 5-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.4, 20.8, 111.0, 120.5, 121.8, 122.1, 129.7, 130.5, 130.9, 132.8, 134.9, 137.3, 143.3, 147.4, 153.0 ppm; MS (EI) *m/z* 282(M^+, 100), 284(M+2, 33), 281(92), 265(10), 247(50), 246(15), 140(30), 84(30), 77(20); Anal. Calcd for $C_{17}H_{15}N_2Cl$ (282): C, 72.34; H, 5.32; N, 9.92. Found: C, 72.13; H, 5.54; N, 9.32.

2-Chloro-8,4′-dimethyl-4-(N-phenylamino)quinoline (3b). Colorless prisms; mp: 132–134°C; Yield: 0.113 g (4%); IR (KBr): υ 3275 (NH), 1596 (C N), 1525, 1085 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H, C4′ CH_3), 2.68 (s, 3H, C8 CH_3), 6.25 (s, 1H, 3-H), 6.67 (br s, 1H, C4 NH), 7.12–7.19 (m, 4H, 2′-, 3′-, 5′-, 6′-H), 7.43–7.54 (m, 2H, 6-, 7-H), 7.86 (d, *J* = 7.88 Hz, 1H, 5-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.4, 20.8, 111.2, 120.3, 121.3, 121.9, 130.6, 131.5, 132.4, 133.2, 136.2, 138.0, 143.4, 150.1, 154.9 ppm; MS (EI) *m/z* 282(M^+, 100), 284(M+2, 34), 281(24), 267(18), 265(15), 252(15), 247(22), 140(16), 49(56); Anal. Calcd for $C_{17}H_{15}N_2Cl$ (282): C, 72.34; H, 5.32; N, 9.92. Found: C, 72.19; H, 5.40; N, 9.70.

8, 4′,4″-Trimethyl-2,4-bis-(N-phenylamino)quinoline (4b). White solid; mp >300°C: Yield: 1.239 g (35%): IR (KBr): υ 3408 (NH), 1639 (C N), 1602 (C N), 1515, 1275 cm^{-1}; H-NMR (400 MHz, DMSO-d_6): δ 2.30 (s, 3H, C4" CH_3), 2.32 (s, 3H, C4′ CH_3), 2.63 (s, 3H, C8 CH_3), 6.14 (s, 1H, 3-H), 7.07–7.30 (m, 8H, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 5″-, 6″-H), 7.31 (t, *J* = 7.58 Hz, 1H, 6-H), 7.69 (d, *J* = 6.92 Hz, 1H, 7-H), 8.34 (d, *J* = 8.08 Hz, 1H, 5-H), 10.00 (s, 1H, C4 NH), 10.85 (s, 1H, C2 NH), 12.03 (s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ 18.2, 20.5, 83.5, 114.5, 121.3, 123.1, 123.7, 124.7, 126.2, 130.1, 133.7, 133.9, 135.6, 135.9, 152.3, 153.6 ppm; MS (EI) *m/z* 353(M^+, 100), 352(78), 336 (8), 247(16), 245(15), 232(10), 154(10), 106(15), 91(55), 89(15), 79 (18), 77(38), 65(40); Anal.Calcd. for $C_{24}H_{23}N_3$ (353): C, 81.59; H, 6.51; N, 11.90: Found: C, 81.39; H, 6.40; N, 12.21.

Reaction of 2,4,6-trichloroquinoline (1c) with *p*-toluidine

4,6-Dichloro-4′-methyl-2-(N-phenylamino)quinoline (2c). Pale yellow needles; mp: 130–132°C: Yield: 0.604 g (20%): IR (KBr): υ 3241 (NH), 1617 (C N), 1517, 1084 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, C4′ CH_3), 6.80 (br s, 1H, C2 NH), 7.05 (s, 1H, 3-H), 7.19 (m, 2H, 3′-, 5′-H), 7.35 (m, 2H, 2′-, 6′-H), 7.53 (dd, J_1 = 8.94, J_2 = 2.28 Hz, 1H, 7-H), 7.65 (d, *J* = 8.88 Hz, 1H, 8-H), 7.99 (d, *J* = 2.24, Hz,1H, 5-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.3, 109.8, 121.7, 121.9, 122.3, 129.8, 132.5, 132.8, 133.6, 134.2, 136.5, 145.0, 149.1, 155.2 ppm; MS (EI) *m/z* 306(M+4, 32), 304(M+2, 62), 302(M^+, 100), 301(85), 287(70), 286(30), 285(15), 267(61), 165(45), 77(42); Anal. Calcd for $C_{16}H_{12}N_2Cl_2$ (302): C, 63.58; H, 3.97; N, 9.27. Found: C, 63.13; H, 4.03; N, 9.87.

6-Chloro-4′,4″-dimethyl-2,4-bis-(N-phenyl amino) quinoline (4c). Dirty white powder; m.p >300°C; Yield :1.047 g (28%): IR(KBr): υ 3255 (NH), 1640 (C N), 1585 (C N), 1530, 1080 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.28 (s, 3H, C4″ CH_3), 2.33 (s, 3H, C4′ CH_3), 6.30 (s, 1H, 3-H), 7.16–7.41 (m, 8H, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 5″-, 6″-H), 7.70–7.81 (m, 2H, 7-, 8-H), 8.48 (s, 1H, 5-H), 9.45 (s, 1H, C4 NH), 9.76 (s, 1H, C2 NH), 12.50 (s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): 17.9, 86.9, 115.6, 122.6, 123.4, 123.8, 125.5, 127.8, 131.3, 133.4, 133.5, 137.0, 138.3, 153.4, 153.8 ppm; MS (EI) *m/z* 375(M+2, 35), 373(M^+, 100), 372(78),

371(12), 358(21), 337(25), 247(54), 161(15), 149(23), 107(33), 91 (44), 90(, 21), 78(29); Anal. Calcd. for $C_{23}H_{20}N_3Cl$ (373): C, 73.99; H, 5.36; N, 11.26. Found: C, 73.85; H, 5.40; N, 11.17.

Reaction of 2,4-Dichloroquinoline (1d) with *p*-toluidine

4-Chloro-4′-methyl-2-(N-phenylamino)quinoline (2d). Pale yellow needles; mp: 115–117°C; Yield: 0.670 g (25%); IR (KBr): υ 3246 (NH), 1595 (C N), 1517, 1144 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.37 (s, 3H, C4′ CH_3), 6.74 (br s, 1H, C2 NH), 7.07 (s, 1H, 3-H), 7.09 (d, *J* = 8.12 Hz, 2H, 3′- and 5′-H), 7.32–7.37 (m, 3H, 7-, 2′-, 6′-H), 7.62 (t, *J* = 7.64 Hz, 1H, 6-H), 7.74 (d, *J* = 8.24 Hz, 1H, 8-H), 8.03 (d, *J* = 8.24 Hz, 1H, 5-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.8, 111.7, 122.8, 123.0, 123.5, 128.7, 131.3, 132.9, 133.1, 135.7, 139.8, 146.2, 150.3, 155.8 ppm; MS (EI) *m/z* 268 (M^+, 100), 270(M+2, 32), 253(70), 251(25), 232(40), 218(32), 185(30), 164(25), 77(28); Anal. calcd for $C_{16}H_{13}N_2Cl$ (268): C, 71.64; H, 4.85; N, 10.45. Found: C, 71.40; H, 5.12; N, 10.33.

2-Chloro-4′-methyl-4-(N-phenylamino)quinoline (3d). Colorless prisms; mp: 123–125°C; Yield: 0.107 g (4%); IR (KBr): υ 3246 (NH), 1595 (C N), 1517, 1144 cm^{-1}; ^{1}H-NMR (400MHz, $CDCl_3$): δ 2.40 (s, 3H, C4′ CH_3), 6.68 (br s, 1H C4 NH), 6.79 (s, 1H, 3-H), 7.20–7.22 (m, 2H, 3′- and 5′-H), 7.26–7.28 (m, 2H, 2′-, 6′-H), 7.50–7.72 (m, 2H, 6-, 7-H), 7.86 (d, *J* = 8.10 Hz 1H, 8-H), 7.95 (d, *J* = 8.10 Hz, 1H, 5-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.8, 109.8, 122.4, 122.8, 123.1, 128.6, 130.4, 132.0, 132.9, 135.5, 139.4, 145.6, 149.3, 156.0 ppm; MS (EI) *m/z* 270(M+2, 25), 268 (M^+, 96), 267(100), 253(65), 254(28), 233(47), 232(21), 77(42), 73(30); Anal. Calcd. for $C_{16}H_{13}N_2Cl$ (268): C, 71.64; H, 4.85; N, 10.45. Found: C, 71.45; H, 5.05; N, 10.30.

4′,4″-Dimethyl-2,4-bis-(N-phenylamino)quinoline (4d). White solid; mp >300 °C; Yield: 1.017 g (30%): IR (KBr): υ 3464 (NH), 1650 (C N), 1598 (C N), 1521, 1380 cm^{-1}: H-NMR (400 MHz, DMSO-d_6): δ 2.32 (s, 3H, C4″ CH_3), 2.35 (s, 3H, C4′ CH_3), 6.17 (s, 1H, 3-H), 7.21–7.31 (m, 8H, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 5″-, 6″-H), 7.51–7.79 (m, 3H, 6-, 7-, 8-H), 8.51 (d, *J* = 8.08 Hz, 1H, 5-H), 9.99 (s, 1H, C4 NH), 10.17 (s, 1H, C2 NH), 12.59 (s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ 18.1, 87.1, 116.0, 121.9, 123.1, 123.9, 125.6, 126.9, 132.3, 133.0, 133.8, 140.0, 142.3, 154.1, 155.9 ppm; MS (EI) *m/z* 339(M^+,97), 338(100), 324(23), 323(15), 309(28), 307(12), 160(16), 75(59); Anal. Calcd for $C_{23}H_{21}N_3$(339): C, 81.42; H, 6.19; N, 12.39. Found: C, 81.77; H, 5.98; N, 12.25.

Preparation of 9,4″-dimethyl-7-phenyl-6-(*N*-phenylamino) dibenzo[*b,h*][1,6]naphthyridine (5). An appropriate mixture of 4′,4″-dimethyl-2,4-bis-(*N*-phenylamino)quinoline (**4**, 1 mmol) and benzoic acid (1.1 mmol) was added to polyphosphoric acid (3 g of P_2O_5 in 1.5 mL of H_3PO_4) and kept at 50–55°C for 5 h. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was poured into ice water and neutralized with saturated $NaHCO_3$ solution to remove the excess of benzoic acid. The precipitate was filtered, dried, and purified by column chromatography over silica gel using petroleum ether:ethyl acetate (99:1) mixture to get **5**. It was recrystallized using ethyl acetate.

2,9,4′-Trimethyl-7-phenyl-6-(N-phenylamino)dibenzo[b,h][1,6] naphthyridine (5a). Orange prisms; mp: 253–255°C; Yield: 0.1670 g (38%); IR (KBr): υ 3425 (NH), 1598 (C N), 1518, 1348 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H, C9 CH_3), 2.45 (s, 3H, C4′ CH_3), 2.61 (s, 3H, C2 CH_3), 6.95–7.76 (m, 14H, 3-, 4-, 8-, 10-, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 4″-, 5″-, 6″-H and C6 NH), 8.26 (d, *J* = 8.68 Hz, 1H, 11-H), 8.96 (s, 1H, 1-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.5, 19.9, 22.2, 112.6, 119.8, 123.1, 123.3, 124.2, 124.6, 125.2, 125.8, 126.6, 127.3, 128.8, 129.2, 129.5, 129.9, 130.1, 132.1, 133.9, 137.0, 137.3, 144.5, 147.8, 148.7. 150.4 ppm; MS (EI) *m/z* 439(M^+, 88), 438(100), 423(28), 394(16), 345(150), 210(12), 76(36), 44(70); Anal. Calcd. for $C_{31}H_{25}N_3$ (439): C, 84.74; H, 5.69; N, 9.57. Found: C, 84.66; H, 5.57; N, 9.77.

4,9,4′-Trimethyl-7-phenyl-6-(N-phenylamino)dibenzo[b,h][1,6] naphthyridine (5b). Pale orange prisms; mp: 255–257°C; Yield: 0.1760 g (40%); IR (KBr) υ 3422 (NH), 1594 (C N), 1519, 1344 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H, C9 CH_3), 2.42 (s, 3H, C4″ CH_3), 2.74 (s, 3H, C4 CH_3), 7.03–7.77 (m, 14H, 2-, 3-, 8-, 10-, 2′-, 3′-, 5′-, 6″-, 2″-, 3″-, 4″-, 5″-, 6″-H and C6 NH), 8.23 (d, *J* = 8.70 Hz, 1H, 11-H) 9.05 (d, *J* = 7.80 Hz, 1H, 1-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 18.7, 20.7, 22.0, 111.7, 119.1, 122.4, 122.5, 122.9, 123.3, 123.8, 124.0, 125.1, 126.6, 129.0, 129.3, 129.7, 129.9, 131.5, 133.6, 133.9, 136.2, 137.4, 144.0, 147.4, 148.9, 149.5 ppm; MS (EI) *m/z* 439(M^+, 65), 438 (100), 346(10), 220(26), 211(12), 148(10), 65(10), 44(65); Anal. Calcd. for $C_{31}H_{25}N_3$ (439); C, 84.74; H, 5.69; N, 9.57. Found: C, 84.64; H, 5.62; N, 9.60.

2-Chloro-9,4′-dimethyl-7-phenyl-6-(N-phenylamino)dibenzo [b,h][1,6] naphthyridine (5c). Pale yellow solid; mp: 265–267°C; Yield: 0.1610 g (35%); IR (KBr): υ 3412 (NH), 1570 (C N), 1511, 1323 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H, C9 CH_3), 2.43 (s, 3H, C4′ CH_3), 7.01–7.69 (m, 14H, 3-, 4-, 8-, 10-, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 4″-, 5″-, 6″-H and C6 NH), 8.23 (d, *J* = 8.70 Hz, 1H, 11-H), 9.11 (d, *J* = 2.4 Hz, 1H, 1-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.8, 20.7, 113.8, 118.6, 122.9, 123.6, 123.9, 124.4, 125.2, 125.8, 126.7, 127.1, 128.8, 130.0, 130.2, 130.7, 133.1, 133.5, 134.2, 137.8, 138.0, 143.6, 148.0, 149.1, 151.5 ppm; MS (EI) *m/z* 461(M+2, 38), 459(M^+, 100), 458(95), 429(21), 394(31), 366(12), 344(18), 220(21), 45(44); Anal. Calcd. for $C_{30}H_{22}N_3Cl$ (459): C, 78.43; H, 4.79; N, 9.15. Found: C, 78.32; H, 4.81; N, 9.09.

9,4′-Dimethyl-7-phenyl-6-(N-phenylamino)dibenzo[b,h][1,6] naphthyridine (5d). Pale yellow prisms; mp: 252–254°C; Yield: 0.1570 g (37%); IR (KBr): υ 3414 (NH), 1575 (C N), 1512, 1335 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H, C9 CH_3), 2.42 (s, 3H, C4′ CH_3), 7.01–7.78 (m, 15H, 2-, 3-, 4-, 8-, 10-, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 4″-, 5″-, 6″-H and C6 NH), 8.23 (d, *J* = 8.70 Hz, 1H, 11-H), 9.15 (d, *J* = 7.80 Hz, 1H, 1-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.3, 20.4, 115.6, 119.8, 123.1, 123.7, 124.0, 124.3, 124.9, 125.6, 126.4, 128.1, 129.4, 131.0, 131.4, 131.8, 134.2, 134.6, 135.0, 138.1, 138.5, 144.6, 148.9, 150.1, 153.6 ppm; MS (EI) *m/z* 425(M^+, 92), 428(100), 413(36), 397(28), 393(18), 217(14), 164(15), 44(51); Anal. Calcd. for $C_{30}H_{23}N_3$ (425): C, 84.71; H, 5.41; N, 9.88. Found C, 84.84; H, 5.35; N, 9.81.

Preparation of 4-methoxy-4′-methyl-2-(*N*-phenylamino) quinoline (7). 4-Chloro-4′-methyl-2-(*N*-phenylamino)quinoline (**2**, 4 mmol) was added to sodium methoxide solution (5 g of sodium in 30 mL of methanol) and heated over the water bath for 10 h. The reaction was monitored by TLC. After the completion of the reaction, excess methanol was evaporated, and the reaction mixture was poured into ice water and neutralized with dil. HCl. The resulting precipitate was filtered, dried, and subjected to purification by column chromatography over silica gel using petroleum ether:ethyl acetate (95:5) mixture to get **7**. It was recrystallized using methanol.

4-Methoxy-6,4′-dimethyl-2-(N-phenylamino)quinoline (7a). Colorless needles; mp: 138–140°C; Yield: 0.411 g (37%); IR (KBr): υ 3390 (NH), 1601, 1527, 1449, 1242 (O CH_3) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.34 (s, 3H, C4′ CH_3), 2.45 (s, 3H,

C6 CH_3), 3.90 (s, 3H, O CH_3), 6.30 (s, 1H, 3-H), 6.96 (br s, 1H, C2 NH), 7.14–7.34 (m, 4H, 2′-, 3′-, 5′-, 6′-H), 7.38 (d, *J* = 8.40 Hz, 1H, 7-H), 7.58 (d, *J* = 8.40 Hz, 1H, 8-H), 7.77 (s, 1H, 5-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.3, 21.1, 55.2, 90.0, 117.3, 120.6, 121.9, 122.4, 130.2, 132.6, 134.2, 135.0, 138.6, 149.9, 155.4, 164.6 ppm; MS (EI) *m/z* 278(M^+, 100), 277(86), 263(35), 262(22), 248 (25), 247(10), 78(45), 77(53); Anal. Calcd. for $C_{18}H_{18}N_2O$ (278): C, 77.70; H, 6.48; N, 10.07 Found: C, 77.65; H, 6.52; N, 10.00.

4-Methoxy-8,4′-dimethyl-2-(N-phenylamino)quinoline (7b). Colorless prisms; mp: 145–147°C Yield: 0.423 g (38%); IR (KBr): υ 3410 (NH), 1600, 1518, 1490, 1245 (O CH_3) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.35 (s, 3H, C4′ CH_3), 2.68 (s, 3H, C8 CH_3), 3.93 (s, 3H, O CH_3), 6.24 (s, 1H, 3-H), 6.76 (br s, 1H, C2 NH), 7.12–7.18 (m, 4H, 2′-, 3′-, 5′-, 6′-H), 7.44 (d, *J* = 6.80 Hz, 1H, 7-H), 7.52 (t, *J* = 8.12 Hz, 1H, 6-H), 7.86 (d, *J* = 8.80 Hz, 1H, 5-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.5, 20.8, 55.5, 89.3, 117.8, 119.4, 120.4, 121.8, 129.6, 130.5, 132.1, 133.9, 138.0, 147.2, 154.6, 163.4 ppm; MS (EI) *m/z* 278(M^+, 100), 277 (67), 263(30), 262(18), 248(16), 247(15), 85(30), 43(30), 41(22); Anal. Calcd. for $C_{18}H_{18}N_2O$ (278) C, 77.70; H, 6.48; N, 10.07. Found: C, 77.73; H, 6.41; N, 9,98.

6-Chloro-4-methoxy-4′-methyl-2-(N-phenylamino)quinoline (7c). Dirty white solid; mp: 150–152°C; Yield: 0.417 g (35%); IR (KBr) υ 3405 (NH), 1610, 1530, 1454, 1240 (O CH_3) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H, C4′ CH_3), 3.97 (s, 3H, O CH_3), 6.20 (s, 1H, 3-H), 7.26–7.64 (m, 7H, 2′-, 3′-, 5′-, 6′, 7-, 8-H and C2 NH), 7.98 (s, 1H, 5-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.8, 56.7, 91.1, 114.3, 117.5, 120.7, 122.3, 130.6, 132.7, 134.3, 134.8, 137.8, 150.1, 156.2, 165.2 ppm; MS (EI) *m/z* 300(M+2, 36), 298(M^+, 100), 297(75), 296(42), 283(47), 268(12), 156(28), 144(10), 45(25); Anal. Calcd. for $C_{17}H_{15}N_2ClO$ (298): C, 68.46; H, 5.03; N, 9.34. Found: C, 68.34; H, 5.00; N, 9.20.

4-Methoxy-4′-methyl-2-(N-phenylamino)quinoline (7d). White solid; mp: 135–137°C; Yield: 0.422 g (40%) IR (KBr) υ 3395 (NH), 1595, 1525, 1500, 1248 (O CH_3) cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H, C4′ CH_3), 3.93 (s, 3H, O CH_3), 6.31 (s, 1H, 3-H), 6.63 (br s, 1H, C2 NH), 7.18–7.34 (m, 5H, 2′-, 3′-, 5′-, 6′-, 7-H), 7.56–7.61 (m, 1H, 6-H), 7.72 (d, *J* = 8.10 Hz, 1H, 8-H), 7.99 (d, *J* = 8.10 Hz, 1H, 5-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.9, 54.3, 89.1, 113.4, 117.8, 119.8, 122.5, 131.7, 132.1, 134.0, 134.5, 136.9, 149.1, 154.3, 163.1 ppm; MS (EI) *m/z* 264(M^+, 98), 263(100), 249(66), 234(22), 160(12), 88(11), 44(43), 43(27); Anal. Calcd. for $C_{17}H_{16}N_2O$ (264): C, 77.27; H, 6.06; N, 10.61. Found: C, 77.20; H, 5.98; N, 10.55.

Preparation of 2-methyl-12-phenyldibenzo[*b,g*][1,8] naphthyridin-11(6*H*)-one (8). 4-Methoxy-4′-methyl-2-(*N*-phenylamino)quinoline (**7**, 2 mmol) was reacted with benzoic acid (2.1 mmol) in presence of polyphosphoric acid (6 g of P_2O_5 in 3 mL of H_3PO_4) at 140–145°C for 6 h. The reaction was monitored by using TLC. After the completion of the reaction, the reaction mixture was poured into ice, and the excess benzoic acid was neutralized with $NaHCO_3$, extracted with ethyl acetate, purified by column chromatography using silica gel, and product eluted with petroleum ether:ethyl acetate (96:4) mixture to get **8**, which was recrystallized using methanol.

2,9-Dimethyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (8a). Pale yellow needles; mp: 190–192°C; Yield: 0.1400 g (20%); IR (KBr) υ 3447 (NH), 1620 (C O) 1550 1481 1446 cm^{-1}; ^{1}H-NMR δ (400 MHz, $CDCl_3$): δ 2.52 (s, 3H, C2 CH_3), 2.59 (s, 3H, C9 CH_3), 7.67–7.95 (m, 9H, 1-, 3-, 4-, 8-, 2′-, 3′-, 4′-, 5′-, 6′-H), 8.09 (d, *J* = 8.70 Hz, 1H, 7-H), 8.36 (s, 1H, 10-H), 9.20 (br s, 1H, N-6-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 17.0, 21.4, 119.4, 119.6, 121.6, 121.8, 123.0, 123.4, 126.4, 126.9, 127.0, 127.6, 127.8, 128.1, 134.7, 135.5, 138.6, 139.3, 148.2, 154.6, 182.3 (C O) ppm; MS (EI) *m/z* 350(M^+, 100), 349(87), 335(25), 334(18), 178(22), 176(10), 165(12), 74(35); Anal. Calcd. for $C_{24}H_{18}N_2O$ (350): C, 82.29; H, 5.14; N, 8.00. Found: C, 82.25; H, 5.08; N, 7.94.

2,7-Dimethyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (8b). Pale yellow prisms; mp: 195–197°C; Yield: 0.1540 g (22%); IR (KBr) υ 3425 (NH), 1628 (C O), 1550, 1484, 1460 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, C2 CH_3), 2.58 (s, 3H, C7 CH_3), 7.06–7.64 (m, 9H, 1-, 3-, 4-, 9-, 2′-, 3′-, 4′-, 5′-, 6′-H), 7.85 (d, *J* = 8.60 Hz, 1H, 8-H), 8.11 (d, *J* = 7.80 Hz, 1H, 10-H), 8.58 (br s, 1H, N-6-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 16.9, 21.7, 120.2, 121.1, 121.5, 122.9, 125.6, 125.8, 126.2, 126.8, 127.5, 127.8, 128.1, 134.2, 135.2, 138.2, 139.0, 148.0, 149.2, 153.4, 181.0 (C O) ppm; MS (EI) *m/z* 350(M^+, 90), 349(100), 335(20), 333(10), 175(15), 174(15), 167(15), 77(48); Anal. Calcd. for $C_{24}H_{18}N_2O$ (350): C, 82.29; H, 5.14; N, 8.00. Found: C, 82.34; H, 5.16; N, 8.06.

9-Chloro-2-methyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (8c). Pale yellow solid; mp: 200–202°C; Yield 0.141 g (19%); IR (KBr) υ 3430 (NH), 1625 (C O), 1555 1482, 1452 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, C2 CH_3), 7.20–7.64 (m, 9H, 1-, 3-, 4-, 8-, 2′-, 3′-, 4′-, 5′-, 6′-H), 7.84 (d, *J* = 8.45 Hz, 1H, 7-H), 8.20 (d, *J* = 2.40 Hz, 1H, 10-H), 9.12 (br s, 1H, N-6-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 17.5, 120.5, 121.6, 121.9, 122.4, 122.8, 125.9, 126.1, 126.8, 126.9, 130.0, 130.7, 131.6, 133.8, 135.6, 139.2, 139.5, 148.9, 155.3, 182.6 (C O) ppm; MS (EI) *m/z* 372(M+2, 31), 370(M^+, 100), 355(22), 354(39), 335(15), 334(12), 177(18), 175(10), 77(29); Anal. Calcd. for $C_{23}H_{15}N_2ClO$ (370): C, 74.59; H, 4.05; N, 7.57. Found: C, 74.47; H, 4.00; N, 7.63.

2-Methyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (8d). Pale yellow needles; mp: 186–188°C; Yield: 1.5460 g (23%); IR (KBr): υ 3440 (NH), 1623 (C O), 1555, 1482, 1439 cm^{-1}; ^{1}H-NMR δ (400 MHz, $CDCl_3$): δ 2.41 (s, 3H, C2 CH_3), 7.16–7.72 (m, 10H, 1-, 3-, 4-, 8-, 9-, 2′-, 3′-, 4′-, 5′-, 6′-H), 7.87 (d, *J* = 8.70 Hz, 1H, 7-H), 8.30 (d, *J* = 7.80 Hz, 1H, 10-H), 9.10 (br s, 1H, N-6-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 16.9, 119.9, 121.0, 121.5, 122.1, 122.7, 125.3, 125.9, 126.5, 127.0, 130.1, 130.8, 131.7, 132.3, 135.3, 138.6, 139.2, 149.3, 154.6, 181.6 (C O) ppm; MS (EI) *m/z* 336(M^+, 94), 335(100), 334(29), 321(44), 320(15), 319 (12), 179(22), 76(45); Anal. Calcd. for $C_{23}H_{16}N_2O$ (336): C, 82.14; H, 4.76; N, 8.33. Found: C, 82.10; H, 4.80; N, 8.40

Preparation of 4′-methyl-2-(*N*-phenylamino)quinolin-4 (1H)-one (9). 4-Methoxy-4′-methyl-2-(*N*-phenylamino)quinoline (**7**, 1 mmol) was added to PPA (3 g of P_2O_5 in 1.5 mL of H_3PO_4) and heated to 140–145°C for 4 h. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was poured into crushed ice. The precipitate obtained was filtered, dried, subjected to column chromatography and the product eluted with petroleum ether:ethyl acetate (70:30) mixture to get **7**. It was recrystallized using methanol.

6,4′-Dimethyl-2-(N-phenylamino)quinolin-4(1H)-one (9a). White solid; mp: 280–282°C; Yield: 0.111 g (42%); IR (KBr) 3468 (NH), 1624 (C O), 1598, 1510, 1130 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.29 (s, 3H, C4′ CH_3), 2.39 (s, 3H, C6 CH_3), 6.20 (s, 1H, 3-H), 7.11–7.76 (m, 7H, 7-, 8-, 2′-, 3′-, 5′-, 6′-H and C2 NH), 7.78 (s, 1H, 5-H), 9.40 (br s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ 20.6, 20.8, 91.5, 118.2, 119.0, 122.5, 123.2, 130.1, 132.9, 133.5, 134.5, 135.2, 138.0,

152.9, 185.6 (C O) ppm; MS (EI) *m/z* 264(M^+, 38), 263(45), 247 (12), 246(10), 131(10), 85(20), 71(32), 57(70), 43(100); Anal. Calcd. for $C_{17}H_{16}N_2O$ (264): C, 77.27; H, 6.06; N, 10.61. Found: C, 77.20; H, 6.10; N, 10.55.

8,4′-Dimethyl-2-(N-phenylamino)quinolin-4(1H)-one (9b). Colorless prisms; mp: 285–287°C; Yield: 0.106 g (40%); IR (KBr): 3462 (NH), 1626 (C O), 1590, 1505, 1265, 1111 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.24 (s, 3H, C4′ CH_3), 2.54 (s, 3H, C8 CH_3), 6.17 (s, 1H, 3-H), 6.99–7.74 (m, 7H, 6-, 7-, 2′-, 3′-, 5′-, 6′-H and C2 NH), 7.79 (d, *J* = 7.48 Hz, 1H, 5-H), 9.06 (br s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ 19.9, 21.3, 92.1, 118.5, 119.2, 122.7, 123.0, 130.6, 133.0, 133.4, 134.6, 135.5, 138.3, 153.1, 186.0 (C O) ppm; MS (EI) *m/z* 264 (M^+, 74), 263(53), 246(16), 130(12), 84(46), 56(75), 44(100), 43 (83); Anal. Calcd. for $C_{17}H_{16}N_2O$ (264) C, 77.27; H, 6.06; N, 10.61: Found: C, 76.20; H, 6.00; N, 10.68.

6-Chloro-4′-methyl-2-(N-phenylamino)quinolin-4(1H)-one (9c). White solid; mp: 288–300°C; Yield: 0.108 g (38%); IR (KBr): 3470 (NH), 1621 (C O), 1607, 1511, 1139 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.26 (s, 3H, C4′ CH_3), 6.50 (s, 1H, 3-H), 7.10–7.82 (m, 7H, 7-, 8-, 2′-, 3′-, 5′-, 6′-H and C2 NH) 7.84 (d, *J* = 2.00 Hz, 1H, 5-H), 9.05 (br s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): δ 20.7, 93.4, 119.0, 119.6, 123.7, 123.8, 130.3, 130.6, 133.5, 133.9, 135.2, 139.3, 154.9, 186.5 (C O) ppm; MS (EI) *m/z* 286(M+2, 23) 284(M^+, 75), 266(17), 251(28), 156(15), 135(18), 44 (92), 43(100); Anal. Calcd. for $C_{16}H_{13}N_2ClO$ (284): C, 67.61; H, 4.58; N, 9.86. Found: C, 67.65; H, 4.61; N, 9.81.

4′-Methyl-2-(N-phenylamino)quinolin-4(1H)-one (9d). Colorless needles; mp: 278–280°C; Yield: 0.010 g (40%); IR (KBr): 3465 (NH), 1628 (C O), 1600, 1515, 1120 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6): δ 2.27 (s, 3H, C4′ CH_3), 6.01 (s, 1H, C3 H), 7.20–8.20 (m, 8H, 6-, 7-, 8-, 2′-, 3′-, 5′-, 6′-H and C2 NH), 8.14 (d, *J* = 8.00 Hz, 1H, 5-H), 9.45 (br s, 1H, N-1-H) ppm; ^{13}C-NMR (100 MHz, DMSO-d_6): 19.8, 91.0, 118.6, 119.3, 122.0, 123.2, 130.1, 130.7, 133.0, 133.4, 134.9, 138.4, 153.3, 184.2 (C O) ppm; MS (EI) *m/z* 250(M^+, 89), 232(28), 217(37), 216(14), 159(18), 157(10), 46(31), 44(100); Anal. Calcd. for $C_{16}H_{14}N_2O$ (250): C, 76.80; H, 5.60; N, 11.20. Found: C, 76.76; H, 5.56; N, 11.24.

Preparation of 2,6-dimethyl-12-phenyldibenzo[*b,g*][1,8] naphthyridin-11(6H)-one (10). 2-Methyl-12-phenyldibenzo[*b, g*][1,8]naphthyridin-11(6H)-one (**8**, 1 mmol) was refluxed with methyl iodide (1 mL) in presence of ignited potassium carbonate (2 g) and acetone (10mL) for 1 h with an exception that 2,7-dimethyl-12-phenyldibenzo[*b,g*][1,8]naphthyridin-11 (6H)-one (**8b**) took 5 h. The reaction was monitored by TLC. After the completion of the reaction, the excess acetone was evaporated, and the reaction mixture was poured into ice water and neutralized with dil. HCl, extracted with ethyl acetate, and purified by column chromatography over silica gel using petroleum ether:ethyl acetate (99:1) mixture as eluant to get **10**. It was recrystallized using ethanol.

2,6,9-Trimethyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (10a). Pale yellow prisms; mp: 182–184°C; Yield: 0.101 g (28%); IR (KBr): 1640 (C O), 1600, 1550, 1473, 1360 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.39 (two overlapping singlets 6H, C2 CH_3 and C9 CH_3), 4.24 (s, 3H, N-6-CH_3), 7.12–7.87 (m, 10H, 1-, 3-, 4-, 8-, 7-, 2′-, 3′-, 4′-, 5′-H and C6′-H), 8.07 (s, 1H, C10 H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 20.6, 21.8, 31.5, 114.6, 115.0, 122.9, 125.1, 126.8, 127.7, 127.9, 128.1, 128.3, 130.9, 133.8, 134.2, 134.9, 135.9, 140.2, 148.2, 149.9, 154.3, 180.2 (C O) ppm; MS (EI) *m/z* 364(M^+, 100), 363(95), 349(27), 348(15), 280(35), 279(16), 75(13), 44(56); Anal. Calcd. for $C_{25}H_{20}N_2O$ (364): C, 82.42; H, 5.50; N, 7.69. Found: C, 82.35; H, 5.42; N, 7.60.

2,6,7-Trimethyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (10b). Pale yellow needles; mp: 184–186°C; Yield: 0.095 g (26%); IR (KBr): 1638 (C O), 1595, 1548, 1470, 1358 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 3H, C2 CH_3), 2.73 (s, 3H, C7 CH_3), 4.13 (s, 3H, N-6-CH_3) 7.10–7.96 (m, 10H, 1-, 3-, 4-, 8-, 9-, 2′-, 3′-, 4′-, 5′-, 6′-H), 8.08 (dd, J_1 = 7.84 Hz, J_2 = 1.26 Hz, 1H, C10-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 20.4, 21.6, 31.2, 114.3, 114.6, 122.2, 124.7, 126.4, 127.2, 127.5, 127.7, 128.0, 130.5, 133.8, 134.6, 135.7, 139.0, 140.8, 147.6, 149.6, 153.0, 179.6 (C O) ppm; MS (EI) *m/z* 364(M^+, 90), 363(100), 349 (18), 348(15), 347(10), 282(12), 83(30), 56(30); Anal. Calcd. for $C_{25}H_{20}N_2O$ (364): C, 82.42; H, 5.50; N, 7.69. Found: C, 82.50; H, 5.55; N, 7.75.

9-Chloro-2, 6-dimethyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (10c). Pale yellow solid; mp 190–192°C; Yield: 0.096 g (25%); IR (KBr): 1639 (C O), 1599, 1551, 1470, 1354 cm^{-1}; ^{1}H-NMR δ (400 MHz, $CDCl_3$): 2.39 (s, 3H, C2 CH_3), 4.24 (s, 3H, N-6-CH_3), 7.20–7.94 (m, 10H, 1-, 3-, 4-, 7-, 8-, 2′-, 3′-, 4′-, 5′,- and 6′-H), 8.28 (d, *J* = 2.56 Hz, 1H, 10-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 21.0, 33.5, 115.9, 116.3, 123.5, 126.2, 127.8, 127.9, 128.1, 128.9, 131.0, 134.0, 134.3, 134.5, 135.0, 136.6, 141.3, 148.8, 149.6, 155.0, 181.1 (C O) ppm; MS (EI) *m/z* 386(M+2, 39), 384(M^+, 100), 383(86), 369(55), 349(23), 264(15), 263(12), 87(45), 43(49); Anal. Calcd. for $C_{24}H_{17}N_2ClO$ (384): C, 75.00; H, 4.43; N, 7.29. Found: C, 75.09; H, 4.38; N, 7.35.

2,6-Dimethyl-12-phenyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (10d). Pale yellow solid; mp: 178–180°C; Yield: 0.105 g (30%); IR (KBr): 1641 (C O), 1601, 1552, 1484, 1369 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.58 (s, 3H, C2 CH_3), 4.45 (s, 3H, N-6-CH_3), 7.36–8.13 (m, 11 H, 1-, 3-, 4-, 7-, 8-, 9-, 2′-, 3′-, 4′-, 5′-, 6′-H), 8.52 (d, *J* = 6.90 Hz, 1H, 10-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 20.6, 32.3, 114.4, 114.9, 121.4, 125.3, 127.7, 127.9, 128.3, 128.5, 130.3, 130.6, 134.4, 134.6, 134.9, 135.1, 136.8, 143.4, 149.6, 154.9, 180.3 (C O) ppm; MS (EI) *m/z* 350(M^+, 95), 349(100), 335(32), 334(16), 279(23), 278(19), 75(17), 44(78); Anal. Calcd. for $C_{24}H_{18}N_2O$ (350): C, 82.29; H, 5.14; N, 8.00. Found: C, 82.35; H, 5.09; N, 7.95.

Preparation of 4′-methyl-2-(*N*-phenylamino)quinoline (11). 4-Chloro-4′-methyl-2-(*N*-phenylamino)quinoline (**2**, 2 mmol) was refluxed with activated zinc powder (5 g) and acetic acid (20 mL) for 1 h. The reaction was monitored by TLC, and after the completion of the reaction, the reaction mixture was filtered and poured into ice water, extracted using ethyl acetate, purified by column chromatography over silica gel, and the product eluted with petroleum ether:ethyl acetate (97:3) mixture to get **11**, which was recrystallized using ethyl acetate.

6,4′-Dimethyl-2-(N-phenylamino)quinoline (11a). Colorless needles; mp: 130–132°C; Yield: 0.238 g (48%); IR (KBr): 3399 (NH), 1605, 1535, 1400, 1260 cm^{-1}; ^{1}H-NMR δ (300 MHz, $CDCl_3$): δ 2.37 (s, 3H, C4′ CH_3), 2.48 (s, 3H, C6 CH_3), 6.93 (d, *J* = 9.00 Hz, 1H, 3-H), 7.11 (br s, 1H, C2 NH), 7.16–7.72 (m, 7H, 5-, 7-, 8-, 2′-, 3′-, 5′-, 6′-H), 7.80 (d, *J* = 9.00 Hz, 1H, 4-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.0, 21.2, 112.0, 119.1, 123.0, 123.5, 125.7, 130.1, 130.3, 132.6, 134.9, 137.9, 138.1, 145.9, 154.0 ppm; MS (EI) *m/z* 248(M^+, 97), 247(100), 232(25), 231(15), 230(10), 115(15), 77(40), 76(32); Anal. Calcd. for $C_{17}H_{16}N_2$ (248): C, 82.26; H, 6.45; N, 11.29. Found: C, 82.20; H, 6.42; N, 11.38.

8,4′-Dimethyl-2-(N-phenylamino)quinoline (11b). Colorless needles; mp: 133–135°C; Yield: 0.248 g (50%); IR (KBr): 3408 (NH), 1598, 1525, 1390, 1251 cm^{-1}; ^{1}H-NMR (300 MHz $CDCl_3$): δ 2.35 (s, 3H, C4′ CH_3), 2.61 (s, 3H, C8 CH_3), 6.85 (br s, 1H, C2 NH), 7.00 (d, *J* = 9.12 Hz, 1H, 3-H), 7.10–7.63 (m, 7H, 5-, 6-, 7-, 2′-, 3′-, 5′-, 6′-H), 8.10 (d, *J* = 9.08 Hz, 1H, 4-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 18.2, 20.8, 111.6, 119.9, 122.6, 123.7, 125.3, 129.5, 129.9, 132.0, 134.5, 137.7, 137.9, 146.5, 153.3 ppm; MS (EI) *m/z* 248(M^+, 98), 247(100), 232(12), 230(10), 115(24), 103(10), 77(12), 65(12); Anal. Calcd. for $C_{17}H_{16}N_2$ (248): C, 82.26; H, 6.45; N, 11.29. Found: C, 82.30; H, 6.39; N, 11.31.

6-Chloro-4′-methyl-2-(N-phenylamino)quinoline (11c). White amorphous solid; mp: 137–139°C; Yield: 0.225 g (42%); IR (KBr): 3412 (NH), 1609, 1496, 1348, 1260 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H, C4′ CH_3), 6.92–6.95 (d, *J* = 9.00 Hz, 2H, 3-H and C2- NH overlapped), 7.16–7.68 (m, 7H, 5-, 7-, 8-, 2′-, 3′-, 5′-, 6′-H), 7.78 (d, *J* = 9.00 Hz, 1H, 4-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): 18.8, 113.0, 120.1, 123.5, 123.9, 126.1, 131.6, 131.9, 135.4, 135.9, 138.2, 138.5, 146.2, 155.2 ppm; MS (EI) *m/z* 270(M+2, 35), 268(M^+, 97), 267(100), 252(39), 233(23), 231(18), 211(12), 76(34), 75(16); Anal. Calcd. for; $C_{16}H_{13}N_2Cl$ (268): C, 71.64; H, 4.85; N, 10.45. Found: C, 71.60; H, 4.90; N, 10.53.

4′-Methyl-2-(N-phenylamino)quinoline (11d). Colorless needles; mp: 126–128°C; Yield: 0.211 g (45%): IR (KBr): 3403 (NH), 1601, 1531, 1398, 1253 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.55 (s, 3H, C4′ CH_3), 7.15–7.18 (d, *J* = 9.00 Hz, 2H, 3-H and C2 NH overlapped), 7.35–7.98 (m, 8H, 5-, 6-, 7-, 8-, 2′-, 3′-, 5′-, 6′-H), 8.17 (d, *J* = 9.00 Hz, 1H, 4-H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$): δ 17.9, 112.2, 119.4, 122.3, 123.5, 127.2, 130.6, 132.5, 135.6, 135.7, 137.4, 138.1, 145.3, 154.0 ppm; MS (EI) *m/z* 234 (M^+, 88), 233(100), 219(26), 209(15), 175(21), 152(15), 77(18), 76(23); Anal. Calcd. for $C_{16}H_{14}N_2$ (234): C, 82.05; H, 5.98; N, 11.97. Found: C, 81.98; H, 6.02; N, 12.00.

Preparation of 2-methyl-12-phenyldibenzo[*b,g*][1,8] naphthyridine (12). 4′-Methyl-2-(*N*-phenylamino)quinoline (**11**, 1 mmol) was reacted with benzoic acid (1.1 mmol) in presence of polyphosphoric acid (3 g of P_2O_5 in 1.5 mL of H_3PO_4) at 190–195° C for 15 h. After the completion of the reaction, the excess benzoic acid was neutralized with $NaHCO_3$, and the reaction mixture was poured into ice water, extracted using ethyl acetate, purified by column chromatography using silica gel as adsorbent, and the product eluted with petroleum ether:ethyl acetate (92:8) mixture to get **12**. It was recrystallized using methanol.

2,9-Dimethyl-12-phenyldibenzo[b,g][1,8]naphthyridine (12a). Dark brown prisms; mp: 210–212°C; Yield: 0.033 g (10%); IR (KBr): 1612, 1585, 1455, 1350, 1190 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.47 (s, 3H, C2 CH_3), 2.53 (s, 3H, C9 CH_3), 7.31–8.30 (m, 11H, 1-, 3-, 4-, 7-, 8-, 10-, 2′-, 3′-, 4′-, 5′-, 6′-H), 8.59 (s, 1H, C11 H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 20.9, 21.4, 117.8, 121.0, 123.9, 126.3, 126.6, 127.5, 127.6, 129.7, 130.2, 131.5, 131.7, 132.4, 132.6, 134.4, 136.5, 137.1, 146.0, 154.4, 156.3 ppm; MS (EI) *m/z* 334(M^+, 30), 333(100), 332(32), 331(12), 257 (10), 166(15), 71(12), 43(33); Anal. Calcd. for $C_{24}H_{18}N_2$ (334): C, 86.23; H, 5.39; N, 8.38. Found: C, 86.30; H, 5.31; N, 8.39.

2,7-Dimethyl-12-phenyldibenzo[b,g][1,8]naphthyridine (12b). Brown prisms; mp: 205–207°C; Yield: 0.040 g (12%); IR (KBr): 1608, 1580, 1451, 1351, 1188 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H, C2 CH_3), 3.06 (s, 3H, C7 CH_3), 7.46–8.38 (m, 11H, 1-, 3-, 4-, 8-, 9-, 10-,2′-, 3′-, 4′-, 5′-, 6′-H), 8.70 (s, 1H, C11 H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 20.5, 21.9, 118.0, 121.3, 124.2, 126.8, 127.6, 127.9, 130.3, 130.5, 131.8, 132.0, 132.8, 132.9, 133.2, 133.6, 134.8, 137.2, 145.4, 155.3, 156.8 ppm; MS (EI) *m/z* 334(M^+, 45), 333(100), 332(27), 330(16), 255(12), 254 (10), 164(18), 75(42); Anal. Calcd. for $C_{24}H_{18}N_2$ (334): C, 86.23; H, 5.39; N, 8.38. Found: C, 86.25; H, 5.45; N, 8.30

2-Methyl-12-phenyldibenzo[b,g][1,8]naphthyridine (12d). Brown solid; mp: 203–205°C; Yield: 0.038 g (12%); IR (KBr): 1605, 1589, 1459, 1348, 1198 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 3H, C2 CH_3), 7.39–8.36 (m, 12H, 1-, 3-, 4-, 7-, 8-, 9-, 10-, 2′-, 3′-, 4′-, 5′-, 6′-H), 8.74 (s, 1H, 11-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 20.7, 118.5, 121.0, 124.1, 126.3, 127.4, 127.6, 130.4, 130.9, 132.0, 132.4, 132.9, 133.1, 133.4, 133.5, 134.5, 136.8, 145.9, 155.0, 156.1 ppm; MS (EI) *m/z* 320(M^+, 56), 319 (100), 318(25), 305(34), 254(19), 252(12), 76(40), 43(72); Anal. Calcd. for $C_{23}H_{16}N_2$ (320): C, 86.25; H, 5.00; N, 8.75. Found: C, 86.28; H, 4.93; N, 8.79.

Preparation of 2,9,4′-trimethyl-7-(*p*-tolyl)-6-(*N*-phenylamino) dibenzo[*b,h*][1,6]naphthyridine (13a), 7-(2-chlorophenyl)-2,9,4′-trimethyl-6-(*N*-phenylamino)dibenzo[*b,h*][1,6]naphthyridine (14a), and 2,9,4′-trimethyl-7-(naphthalen-1-yl)-6-(*N*-phenylamino) dibenzo[*b,h*][1,6]naphthyridine (15a). An appropriate mixture of 6,4′,4″-trimethyl-2,4-bis-(*N*-phenylamino)quinoline (**4a**, 1 mmol) and the respective carboxylic acid [*p*-toluic acid/ *o*-chlorobenzoic acid/1-naphthoic acid (each1.1 mmol)] was added to polyphosphoric acid (3 g of P_2O_5 in 1.5 mL of H_3PO_4) and kept at 50–55°C for 5 h. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was poured into ice water and neutralized with saturated $NaHCO_3$ solution to remove the excess carboxylic acid. The precipitate was filtered, dried, and purified by column chromatography over silica gel using petroleum ether:ethyl acetate (99:1) mixture to get **13a**, **14a**, and **15a**. The products were recrystallized using ethyl acetate.

2,9,4′-Trimethyl-7-(p-tolyl)-6-(N-phenylamino)dibenzo[b,h] [1,6]naphthyridine (13a). Orange prisms; mp: 254–256°C; Yield: 0.1767 g (39%); IR (KBr): υ 3435 (NH), 1588 (C N), 1528, 1340 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.27 (s, 3H, C9 CH_3), 2.45 (s, 3H, C4′ CH_3), 2.60 (s, 3H, C4″ CH_3), 2.62 (s, 3H, C2 CH_3), 7.03–7.65 (m, 13H, 3-, 4-, 8-, 10-, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 5″-, 6″-H and C6 NH), 8.25 (d, *J* = 8.00 Hz, 1H, 11-H), 8.95 (s, 1H, 1-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.9, 19.1, 21.8, 22.9, 111.3, 120.1, 123.5, 123.8, 124.0, 124.9, 125.4, 125.8, 126.9, 127.6, 128.8, 129.1, 129.7, 129.9, 130.5, 131.8, 132.4, 134.0, 137.4, 137.9, 144.1, 148.0, 149.1. 151.3 ppm; MS (EI) *m/z* 453(M^+, 70), 452(100), 438(45), 423(20), 345(15), 210 (20), 76(35), 44(80); Anal. Calcd. for $C_{32}H_{27}N_3$ (453): C, 84.77; H, 5.96; N, 9.27. Found: C, 84.65; H, 5.58; N, 9.77.

7-(2-Chlorophenyl)-2,9,4′-trimethyl-6-(N-phenylamino)dibenzo [b,h][1,6]naphthyridine (14a). Orange prisms; mp: 258–260°C; Yield: 0.1656 g (35%); IR (KBr): υ 3422 (NH), 1590 (C N), 1512, 1338 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.28 (s, 3H, C9 CH_3), 2.46 (s, 3H, C4′ CH_3), 2.61 (s, 3H, C2 CH_3), 7.03–7.77 (m, 13H, 3-, 4-, 8-, 10-, 2′-, 3′-, 5′-, 6′-, 3″-, 4″-,5″-, 6″-H, and C6 NH), 8.28 (d, *J* = 8.80 Hz, 1H, 11-H), 8.97 (s, 1H, 1-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 17.9, 20.1, 22.4, 113.2, 120.4, 123.9, 123.7, 124.6, 125.0, 125.3, 126.1, 126.7, 127.1, 127.4, 128.8, 129.2, 129.3, 129.5, 129.9, 130.4, 130.6, 132.6, 134.2, 137.2, 137.4, 144.5, 147.8, 148.7. 151.5 ppm; MS (EI) *m/z* 475 (M+2, 32), 473(M^+, 100), 458(65), 438(35), 396 (35), 394(10), 344(25), 210(15), 76(30), 44(62); Anal. Calcd. for $C_{31}H_{24}ClN_3$ (473): C, 78.65; H, 5.07; N, 8.88. Found: C, 78.24; H, 5.17; N, 8.51.

2,9,4′-Trimethyl-7-(naphthalen-1-yl)-6-(N-phenylamino) dibenzo[b,h][1,6]naphthyridine (15a). Orange prisms; mp: 260–262° C; Yield: 0.1858 g (38%); IR (KBr): υ 3425 (NH), 1598 (C N), 1520, 1345 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 2.11 (s, 3H, C9 CH_3), 2.24 (s, 3H, C4′ CH_3), 2.55 (s, 3H, C2 CH_3), 7.02–8.18 (m, 16H, 3-, 4-, 8-, 10-, 2′-, 3′-, 5′-, 6′-, 2″-, 3″-, 4″-, 5″-, 6″- 7″-, 8″-H, and C6 NH), 8.23 (d, *J* = 8.40 Hz, 1H, 11-H), 8.94 (s, 1H, 1-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 18.5, 19.9, 22.2, 112.6, 119.8, 123.1, 123.3, 124.2, 124.6, 125.2, 125.4, 125.8, 126.3, 126.6, 127.3, 128.3, 128.8, 129.2, 129.5, 129.9, 130.1, 132.1, 133.3, 133.9, 134.2, 137.0, 137.3, 144.5, 147.8, 148.7. 150.4 ppm; MS (EI) *m/z* 489(M^+, 88), 488(100), 474(20), 458(12), 420(10), 348 (25), 210 (12), 76(36); Anal. Calcd. for $C_{35}H_{27}N_3$ (489): C, 85.88; H, 5.56; N, 8.58. Found: C, 85.66; H, 5.39; N, 8.95.

Preparation of 2,9-dimethyl-12-(4′-methylphenyl)dibenzo [b,g][1,8]naphthyridin-11(6H)-one (16a), 12(2-chlorophenyl)-2,9-dimethyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (17a), and 2,9-dimethyl-12-(naphthalene-1-yl)dibenzo[b,g][1,8]naphthyridin-11 (6H)-one (18a). 4-Methoxy-6,4′-dimethyl-2-(*N*-phenylamino) quinoline (**7a**, 2 mmol) was reacted with the respective carboxylic acids [*p*-toluic acid/ *o*-chlorobenzoic acid/1-naphthoic acid (each 2.1 mmol)] in presence of polyphosphoric acid (6 g of P_2O_5 in 3 mL of H_3PO_4) at 140–145°C for 6 h. The reaction was monitored by using TLC. After the completion of the reaction, the reaction mixture was poured into ice, and the excess carboxylic acid was neutralized with $NaHCO_3$, extracted with ethyl acetate, purified by column chromatography using silica gel, and product eluted with petroleum ether:ethyl acetate (96:4) mixture to get **16a**, **17a**, and **18a**, which were recrystallized using methanol.

2,9-Dimethyl-12-(p-tolyl)dibenzo[b,g][1,8]naphthyridin-11(6H)-one (16a). Pale yellow needles; mp: 195–197°C; Yield: 0.1674 g (23%); IR (KBr) υ 3439 (NH), 1624 (C O) 1547, 1481, 1451 cm^{-1}; ^{1}H-NMR δ (400 MHz, $CDCl_3$): δ 2.40 (s, 3H, C2 CH_3), 2.53 (s, 3H, C9 CH_3), 2.69 (s, 3H, C4′ CH_3), 7.07–8.03 (m, 8H, 1-, 3-, 4-, 8-, 2′-, 3′-, 5′-, 6′-H), 8.12 (d, *J* = 7.20 Hz, 1H, 7-H), 8.26 (s, 1H, 10-H), 9.16 (br s, 1H, N6 H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 17.0, 21.4, 21.9, 119.4, 119.6, 121.6, 121.8, 123.0, 123.4, 126.4, 126.9, 127.0, 127.6, 127.8, 128.1, 131.5, 134.7, 135.5, 138.6, 139.3, 148.2, 154.6, 182.3 (C O) ppm; MS (EI) *m/z* 364(M^+, 100), 363(80), 349(15), 334(18), 320(10), 176(15), 164(10), 74(40); Anal. Calcd. for $C_{25}H_{20}N_2O$ (364): C, 82.42; H, 5.49; N, 7.69. Found: C, 82.21; H, 5.56; N, 7.84.

12(2-Chlorophenyl)-2,9-dimethyldibenzo[b,g][1,8]naphthyridin-11(6H)-one (17a). Pale yellow needles; mp: 201–203°C; Yield: 0.1459 g (19%); IR (KBr) υ 3440 (NH), 1625 (C O) 1542, 1472, 1040 cm^{-1}; ^{1}H-NMR δ (400 MHz, $CDCl_3$): δ 2.39 (s, 3H, C2 CH_3), 2.55 (s, 3H, C9 CH_3), 7.03–8.08 (m, 8H, 1-, 3-, 4-, 8-, 3′-, 4′-, 5′-, 6′-H), 8.10 (d, *J* = 8.00 Hz, 1H, 7-H), 8.33 (s, 1H, 10-H), 9.08 (br s, 1H, N-6-H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 17.0, 21.4, 119.4, 119.6, 121.6, 121.8, 123.0, 123.4, 126.4, 126.9, 127.0, 127.3, 127.6, 127.8, 128.1, 129.3, 132.1 134.7, 135.5, 138.6, 139.3, 148.2, 154.6, 182.3 (C O) ppm; MS (EI) *m/z* 386 (M+2, 35), 384(M^+, 100), 369(45), 349(20), 335(15), 178(10), 176(15), 164(15), 74(50); Anal. Calcd. for $C_{24}H_{17}ClN_2O$ (384): C, 75.00; H, 4.43; N, 7.29. Found: C, 74.89; H, 4.58; N, 7.46.

2,9-Dimethyl-12-(naphthalen-1-yl)dibenzo[b,g][1,8] naphthyridin-11(6H)-one (18a). Pale yellow needles; mp: 205–207° C; Yield: 0.1760 g (22%); IR (KBr) υ 3410 (NH), 1618(C O) 1561, 1480, 1342 cm^{-1}; ^{1}H-NMR δ (400 MHz, $CDCl_3$): δ 2.51 (s, 3H, C2 CH_3), 2.60 (s, 3H, C9 CH_3), 7.52–8.31 (m, 11H, 1-, 3-, 4-, 8-, 2′-, 3′-, 4′-, 5′-, 6′-, 7′-, 8′-H), 8.41 (d, *J* = 8.40 Hz, 1H, 7-H), 8.29 (s, 1H, 10-H), 9.19 (br s, 1H, N6 H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 17.0, 21.4, 119.4, 119.6, 121.6, 121.8, 123.0, 123.4, 125.4, 126.2, 126.4, 126.9, 127.0, 128.4, 127.6, 127.8, 128.1, 132.6, 134.2, 134.7, 135.5, 138.6, 139.3, 148.2, 154.6, 182.3 (C O) ppm; MS (EI) *m/z* 400(M^+, 100), 399(82), 384(18), 383(15), 234(25), 176(12), 165(20), 74(30); Anal. Calcd. for $C_{28}H_{20}N_2O$ (400): C, 84.00; H, 5.00; N, 7.00. Found: C, 83.89; H, 5.05; N, 7.08.

Preparation of 2,9-dimethyl-12-(*p*-tolyl)dibenzo[*b,g*][1,8] naphthyridine (19a), 12-(2′-chlorophenyl-2,9-dimethyl)-dibenzo[*b,g*][1,8]naphthyridine (20a), and 2,9-dimethyl-12-(naphthalen-1-yl)dibenzo[*b,g*][1,8]naphthyridine (21a). 6,4′-Dimethyl-2-(*N*-phenylamino)quinoline (**11a**, 1 mmol) was reacted with the respective carboxylic acids [*p*-toluic acid/ *o*-chlorobenzoic acid/1-naphthoic acid (each 1.1 mmol)] in presence of polyphosphoric acid (3 g of P_2O_5 in 1.5 mL of H_3PO_4) at 190–195°C for 15 h. After the completion of the reaction, the excess carboxylic acid was neutralized with $NaHCO_3$, and the reaction mixture was poured into ice water, extracted using ethyl acetate, purified by column chromatography using silica gel as adsorbent, and the product eluted with petroleum ether:ethyl acetate (92:8) mixture to get **19a**, **20a**, and **21a**. The compounds were recrystallized using methanol.

2,9-Dimethyl-12-(p-tolyl)dibenzo[b,g][1,8]naphthyridine (19a). Dark brown prisms; mp: 214–216°C; Yield: 0.045 g (13%); IR (KBr): 1610, 1578, 1450, 1341, 1175 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.29 (s, 3H, C2 CH_3), 2.34 (s, 3H, C9 CH_3), 2.40 (s, 3H, C4′ CH_3) 7.08–7.90 (m, 10H, 1-, 3-, 4-, 7-, 8-, 10-, 2′-, 3′-, 5′-, 6′-H), 8.45 (s, 1H, C11 H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 20.9, 21.4, 22.0, 117.8, 121.0, 123.9, 126.3, 126.6, 127.5, 127.6, 129.7, 130.2, 131.5, 131.7, 132.0, 132.4, 132.6, 134.4, 136.5, 137.1, 146.0, 154.4, 156.3 ppm; MS (EI) *m/z* 348 (M^+, 85), 347(100), 332(42), 331(18), 256(12), 166(12), 75(25), 43(48); Anal. Calcd. for $C_{25}H_{20}N_2$ (348): C, 86.21; H, 5.75; N, 8.04. Found: C, 86.36; H, 5.52; N, 8.12.

12-(2-Chlorophenyl)-2,9-dimethyldibenzo[b,g][1,8] naphthyridine (20a). Dark brown prisms; mp: 219–221°C; Yield: 0.080 g (11%); IR (KBr): 1606, 1591, 1436, 1369, 1179 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.30 (s, 3H, C2 CH_3), 2.34 (s, 3H, C9 CH_3), 7.05–8.00 (m, 10H, 1-, 3-, 4-, 7-, 8-, 10-, 3′-, 4′-, 5′-, 6′-H), 8.66 (s, 1H, C11-H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 20.9, 21.4, 117.8, 121.0, 123.9, 126.3, 126.6, 127.2, 127.5, 127.6, 129.5, 129.7, 130.2, 131.5, 131.7, 132.3, 132.4, 132.6, 134.4, 136.5, 137.1, 146.0, 154.4, 156.3 ppm; MS (EI) *m/z* 370 (M+2, 32) 368(M^+, 100), 367 (75), 352(20), 334 (10), 332(30), 256(10), 166(12), 74(12), 43 (55); Anal. Calcd. for $C_{24}H_{17}ClN_2$ (368): C, 78.26; H, 4.61; N, 7.60. Found: C, 78.33; H, 4.56; N, 7.69.

2,9-Dimethyl-12-(naphthalen-1-yl)dibenzo[b,g][1,8] naphthyridine (21a). Dark brown prisms; mp: 210–212°C; Yield: 0.099 g (13%); IR (KBr): 1610, 1581, 1449, 1342, 1200 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ 2.33 (s, 3H, C2 CH_3), 2.39 (s, 3H, C9 CH_3), 6.99–8.27 (m, 13H, 1-, 3-, 4-, 7-, 8-, 10-, 2′-, 3′-, 4′-, 5′-, 6′-, 7′-, 8′-H), 8.74 (s, 1H, C11 H) ppm; ^{13}C-NMR (125 MHz, $CDCl_3$): δ 20.9, 21.4, 117.8, 121.0, 123.9, 125.3, 126.2, 126.3, 126.6, 127.5, 127.6, 128.4, 129.7, 130.2, 131.5, 131.7, 132.4, 132.5, 132.6, 134.2, 134.4, 136.5, 137.1, 146.0, 154.4, 156.3 ppm; MS (EI) *m/z* 384(M^+, 65), 383(100), 382(20), 369(15), 354 (25), 257(10), 234(15), 76(35), 44(70); Anal. Calcd. for $C_{28}H_{20}N_2$ (384): C, 87.50; H, 5.20; N, 7.30. Found: C, 87.54; H, 5.24; N, 7.21.

X-ray crystallographic data. Crystallographic data of the structure **5a** in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. CCDC No. 720669. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK or e-mail: deposit@ccdc.cam.ac.uk.

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[28] 2,4-Dichloroquinolines (1, 1 mmol) on reaction with PPA (3 g of P2O5 in 1.5 mL H_3PO_4) at 200°C yielded the corresponding 2,4-dihydroxyquinolines. The yield of the product was 70%.