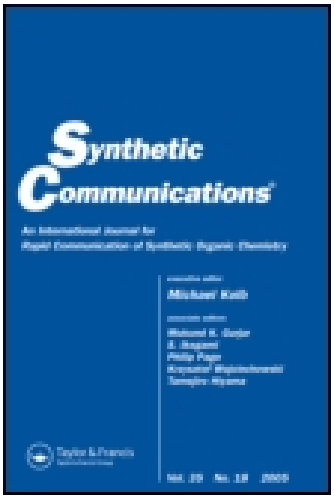

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Facile Synthesis of Alkyl and Aryl Substituted Dibenzo[b,g][1,8]naphthyridin-5-ones

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FACILE SYNTHESIS OF ALKYL AND ARYL SUBSTITUTED DIBENZO[*b,g*][1,8]-NAPHTHYRIDIN-5-ONES

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The reaction of 2,4-dichloroquinolines with* o*-aminoacetophenone and* o*-aminobenzophenone under neat conditions yielded 2′-acetyl and 2′-benzoyl substituted-4-chloro-2-(N-phenylamino)quinolines, respectively, which on treatment with sodium methoxide afforded the 2′-substituted-4-methoxy-2-(N-phenylamino)quinolines. These potential intermediates, on polyphosphoric acid–catalyzed cyclization at two different temperatures, gave the respective 6-methyl and 6-phenyl substituted dibenzo[b,g][1,8]naphthyridin-5-ones. These temperature differences for the formation of the final products were due to the in situ formation of the respective 2′-substituted-2-(N-phenylamino)quinolin-4-ones from the chloro and methoxy intermediates. The naphthyridin-5-ones were subjected to N-methylation, where the methyl group in the 1-position was found to hinder the reaction sterically, consequently increasing the reaction time to more than that of the other derivatives.

Keywords: 2,4-Dichloroquinolines; 2′-substituted-4-chloro-2-(*N*-phenylamino)quinolines; 2′-substituted-4-methoxy-2-(*N*-phenylamino)quinolines; 6-methyl and 6-phenyldibenzo[*b,g*][1,8]naphthyridin-5-ones; *N*-methylation

INTRODUCTION

The process of drug discovery has always influenced synthetic organic chemists to construct compounds possessing reactive functional groups. In this view, the amino-substituted quinolines (e.g., chloroquine, primaquine) derived from the amine functional group serve as low-cost antimalarial drugs, curing billions of infections in poverty-stricken malaria-endemic regions of the world for the past few decades.[1] Some of the anilinoquinolines also serve as synthetic antimalarials[2] and have been exploited in deriving various heterocycles such as dibenzonaphthyridines and indoloquinolines. The reaction of chloroquinolines has been extensively studied in an aim to derive biologically active substituted quinolines[3,4] and also to synthesize some naphthyridine analogs.[5] Research on the chemistry of naphthyridines has expanded considerably in recent years, and one recent report states that replacing the quinoline moiety by a naphthyridine moiety in primaquine analog enhanced its antimalarial

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activity.[6] Numerous reports have pertained to these heterocycles acting as CB_2 selective agonists,[7] antitumor,[8] anti-HIV,[9] and anticancer agents[10] and also as effective bridging ligands in the field of inorganic chemistry.[11] Particularly some of the dibenzonaphthyridines, that is, quinoline dimers, act as potent and selective 3-phosphoinostide-dependent kinase-I inhibitors.[12] Many reports represent the synthesis of simple naphthyridines,[13] benzonaphthyridines,[14] and dibenzonaphthridines,[15,16] and very few accomplish their construction through anilinoquinolines.[17,18]

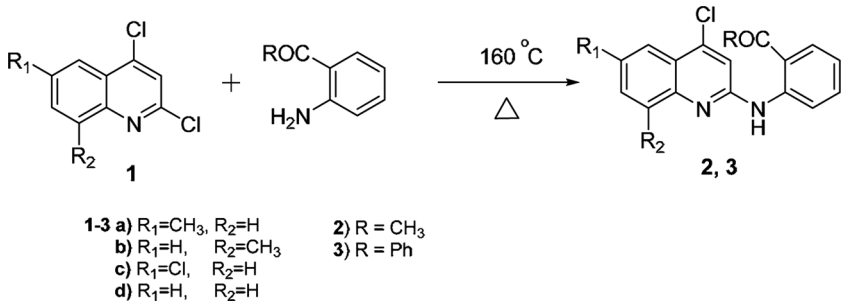
In this article, we report the synthesis of alkyl and aryl substituted dibenzonaphthyridines utilizing 2,4-dichloroquinolines involving the anilinoquinolines (ie., 2′-acetyl and 2′-benzoyl-substituted 4-chloro-2-(*N*-phenylamino)quinolines and 2′-acetyl and 2′-benzoyl-substituted 4-methoxy-2-(*N*-phenylamino)quinoline) as potential intermediates.

RESULTS AND DISCUSSION

The object of the present investigation was to study the reaction of 2,4-dichloroquinolines **1** with *o*-aminoacetophenone and *o*-aminobenzophenone to get the respective 2′-acetyl and 2′-benzoyl(phenylamino)substitution at 2,4- and 2,4-positions of the quinoline moiety, which in turn can be utilized as potential intermediates in deriving the linear and angular alkyl as well as aryl substituted dibenzonaphthyridines.

In view of these considerations, 2,4-dichloroquinolines (**1a–d**) were reacted with *o*-aminoacetophenone under neat conditions at 160 °C for half an hour. The only product obtained, irrespective of the molar ratio of *o*-aminoacetophenone, was assigned as the 2-substituted product, namely, 2′-acetyl-4-chloro-2-(*N*-phenylamino)quinolines (**2a–d**), on the basis of the reactivity of the 2- and 4-chloro group of the 2,4-dichloroquinoline.[19,20] Similarly, **1a–d** under the same condition was reacted with *o*-aminobenzophenone to afford 2′-benzoyl-4-chloro-2-(*N*-phenylamino)-quinolines (**3a–d**) (Scheme 1).

In the ^{1}H NMR spectrum of the anilinoquinolines **2** and **3**, the C_2-NH appeared as a broad singlet around δ 11.00 ppm. All the aromatic protons appeared between the region around δ 7.00–8.00 ppm except for one proton doublet, which was shifted abnormally to the downfield region around δ 9.50 ppm. With the help of advanced NMR studies such as distortionless enhancement by polarization



Scheme 1. Preparation of 2′-acetyl and 2′-benzoyl-substituted 4-chloroanilinoquinolines.

Table 1. Assignment of the coupling protons for all the aromatic protons of **2b**

No.	Aromatic proton	Coupling protons
1	7.02 (t, 1H, C'_4-H, $J = 7.20$ Hz)	7.65 (t, 1H, C'_5-H, 7.23 Hz), 7.95 (d, 1H, C'_3-H, $J = 8.10$ Hz)
2	7.32 (t, 1H, C_6-H, $J = 7.28$ Hz)	7.95 (d, 1H, C_5-H, $J = 8.10$ Hz), 7.55 (d, 1H, C_7-H, $J = 7.20$ Hz)
3	7.55 (d, 1H, C_7-H, $J = 7.20$ Hz)	7.32 (t, 1H, C_6-H, 7.28 Hz)
4	7.65 (t, 1H, C'_5-H, $J = 7.23$ Hz)	9.47 (d, 1H, C'_6-H, $J = 8.70$ Hz), 7.00 (t, 1H, C'_4-H, $J = 7.20$ Hz)
5	7.95 (d, 1H, C_5-H, $J = 8.10$ Hz)	7.32 (t, 1H, C_6-H, $J = 7.28$ Hz)
6	7.95 (d, 1H, C'_3-H, $J = 8.10$ Hz)	7.02 (t, 1H, C'_4-H, $J = 7.20$ Hz)
7	9.47 (d, 1H, C'_6-H, $J = 8.70$ Hz)	7.65 (t, 1H, C'_5-H, $J = 7.23$ Hz)

transfer (DEPT-135), correlation spectroscopy (H,H-COSY), and heteronuclear multiple bond correlation (HMBC), the deshielded proton of the 2′-acetyl-4-chloro-8-methyl-2-(*N*-phenylamino)quinoline (**2b**) was assigned for C'_6-H. A one-proton doublet at δ 9.47 ($J = 8.70$ Hz) and a one-proton triplet at δ 7.65 ($J = 7.23$ Hz) have an H,H-COSY connection, which is characteristic of C'_6- and C'_5-protons. The assignment of coupling protons for all the other aromatic protons using H,H-COSY is mentioned in Table 1. The DEPT-135 spectrum displayed 8 −CH signals besides the methyl and the carbonyl carbons, the remaining being the quaternary carbons. The peculiar C'_6-proton has HMBC connectivity with C'_1- and C'_5-carbons. The connectivity of all other protons with the carbons is shown in Fig. 1, and the values are presented in Table 2.

The reason for the C'_6-H to be deshielded abnormally could be that the hydrogen bonding between the C_2-NH and 2′-carbonyl group fixes the molecule in a particular plane where the C'_6-H gets oriented in the quinoline ring, experiencing a reinforced anisotropic effect, and thereby shifting the proton around δ 9.50 ppm. The orientation of the molecule **2** could be assigned as represented in Fig. 2. The same reasoning can be extended to 2′-benzoyl-4-chloro-2-(*N*-phenylamino)quinoline (**3**), where the C'_6-H behaves similarly.

To derive the naphthyridine by acid catalyst cyclization, **2a–d** were heated in the presence of polyphosphoric acid (PPA). The reaction started to proceed only at the temperature of 205–210 °C and completed in 5 h. Analyzing the product through spectral means revealed a broad singlet for the NH group, and the formed product was assigned as 6-methyldibenzo[*b,g*][1,8]naphthyridin-5-ones (**4a–d**) and

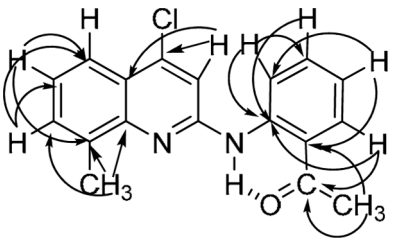


Figure 1. HMBC connectivity of **2b**.

Table 2. HMBC connectivity of the protons with the carbons of **2b**

No.	^{1}H NMR	HMBC ^2J, ^3J
1	2.71 (s, 3H, C_2'-CO-CH_3)	C_2'-CO, C_2'
2	2.83 (s, 3H, C_8-CH_3)	C_{8a}, C_7, C_8
3	7.11 (s, 1H, C_3-H)	C_4, C_{4a}
4	7.02 (t, 1H, C_6-H, $J=7.20$ Hz)	C_6', C_2'
5	7.32 (t, 1H, C_6-H, $J=7.28$ Hz)	C_5, C_8
6	7.55 (d, 1H, C_7-H, $J=7.20$ Hz)	C_5, C_6
7	7.65 (t, 1H, C_5'-H, $J=7.23$ Hz)	C_1'
8	7.95 (d, 1H, C_3'-H, $J=8.10$ Hz)	C_2'-CO, C_1'
9	7.95 (d, 1H, C_5-H, $J=8.10$ Hz)	—
10	9.47 (d, 1H, C_6'-H, $J=8.70$ Hz)	C_5', C_1'

not the expected product (**6**). Under similar conditions, **3a–d** afforded 6-phenyldibenzo[*b,g*][1,8]naphthyridin-5-ones (**5a–d**) (Scheme 2).

Here, the mechanism for the conversion of **2** and **3** to **4** and **5** under PPA conditions (Scheme 3) might be the protonation of the ring nitrogen of **2** and **3** to give the intermediate **I** followed by the *ipso* attack of the $-OP_2O_6H(R_3)_2$ ion to

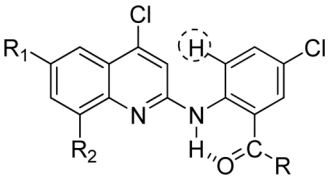
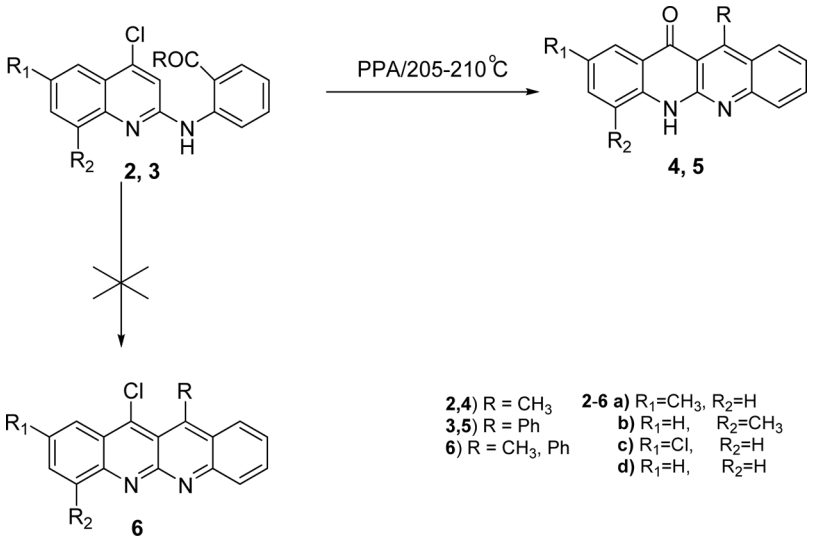
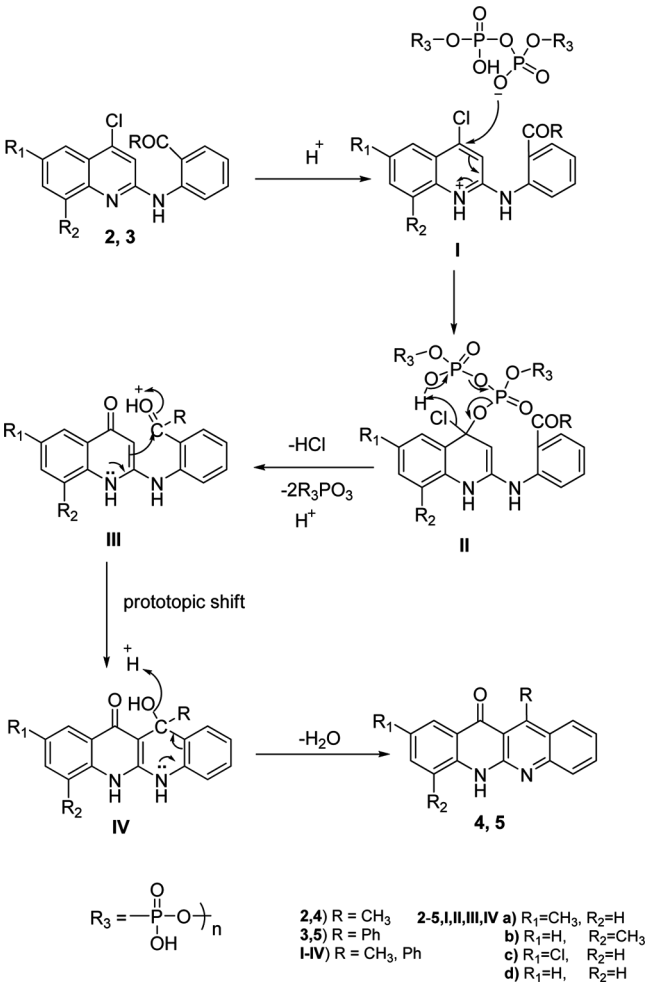


Figure 2. Representation of the orientation of the molecule **2, 3**.



Scheme 2. Preparation of dibenzo[*b,g*][1,8]naphthyridin-5-ones.

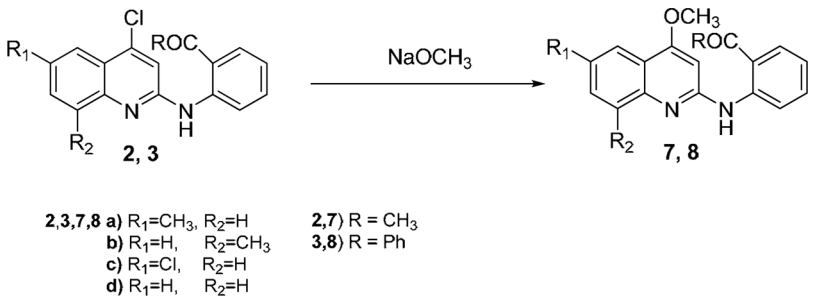


Scheme 3. Mechanism for the formation of dibenzo[*b,g*][1,8]naphthyridin-5-ones.

the C_4-carbon, yielding the intermediate **II**, which subsequently on intramolecular elimination of HCl molecule afforded the intermediate **III** (2′-substituted-4′-chloro-2-(*N*-phenylamino)quinolin-4-one). The intermediate **III**, on internal electrophilic attack on the positively induced 2′-carbonyl carbon, afforded the intermediate **IV**, which on subsequent loss of the water molecule yielded the final products **4** and **5**.

It was assumed that the nonfeasibility of the reaction of **2** and **3** at lower temperature might be due to the deactivating nature of the chloro group, which inhibits the internal electrophilic substitution at the C_3-position of the quinoline moiety. To confirm the statement, we thought to convert the 4-chloro groups of **2** and **3** to 4-methoxy groups in order to proceed with the reaction at lower temperature.

With this motivation, **2a–d** were treated with sodium methoxide for 10 h to afford the respective 2′-acetyl-4-methoxy-2-(*N*-phenylamino)quinolines (**7a–d**).



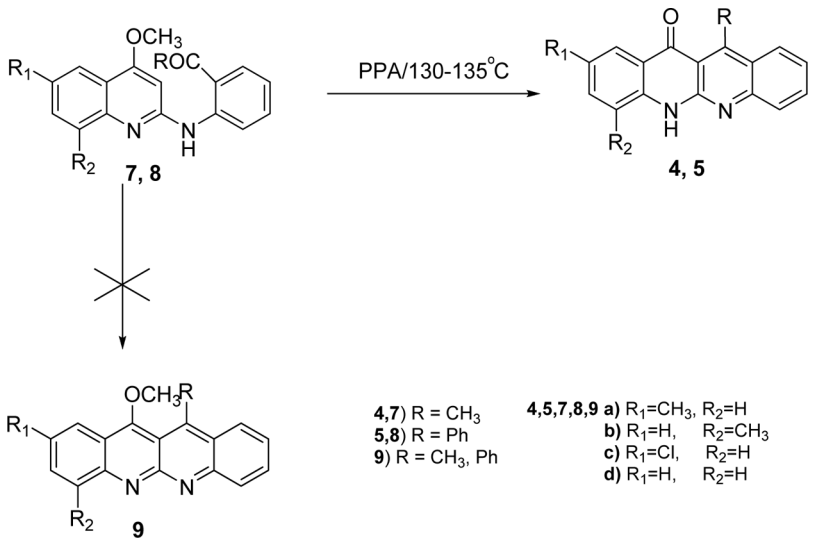
Scheme 4. Preparation of 2′-acetyl and 2′-benzoyl-substituted 4-methoxyanilinoquinolines.

The same reaction was extended to **3a–d** to yield the corresponding 2′-benzoyl-4-methoxy-2-(*N*-phenylamino)quinolines (**8a–d**). (Scheme 4). In this case, the same C'_6-H behaves abnormally, deshielding around δ 9.50 ppm in the ^{1}H NMR.

Compounds **7a–d** were then subjected to PPA and monitored for the initiation of the reaction by gradually increasing the temperature. At 130–135 °C, the reaction proceeded and completed in 4 h. Surprisingly, the products matched well with the earlier formed products **4a–d** and not the expected product **9**. Similarly, **8a–d** afforded **3a–d** (Scheme 5).

The reason for the formation of the products **4** and **5** could be predicted as the acid-catalyzed ether cleavage of the OCH_3 group[21] of **7** and **8** to the intermediate **III** (2′-substituted-2-(*N*-phenylamino)quinolin-4-one), which further gets cyclized to the final products **4** and **5** by the same mechanism mentioned earlier.

The formation of the final products **4** and **5** from **2** and **3** and **7** and **8** on PPA varied in their yields, and they are compared in Table 3.



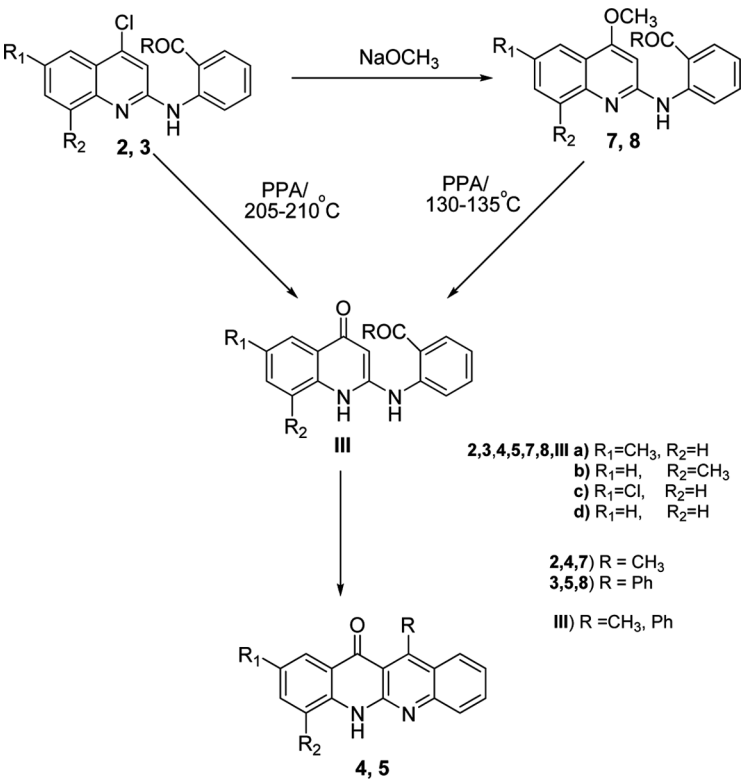
Scheme 5. Preparation of dibenzo[*b,g*][1,8]naphthyridin-5-ones.

Table 3. Comparision of the yields of the final products **4** and **5** obtained from **2, 3** and **7, 8**

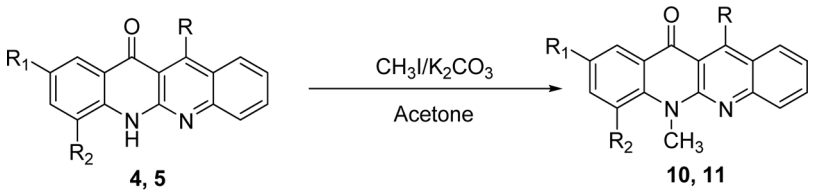
	Yields (%)			
	Synthesis of **4**		Synthesis of **5**	
Compounds **4**, **5**	From **2**	From **7**	From **3**	From **8**
a	20	31	22	33
b	18	30	21	32
c	17	27	18	28
d	20	30	21	31

The formation of the final products **4** and **5** from **2** and **3** and **7** and **8** on PPA at two different temperatures might be caused by the formation of the intermediate **III**, which further on internal electrophilic cyclization leads to the final products (Scheme 6).

To test the *N*-methylation reaction of **4**, it was refluxed with methyl iodide in the presence of ignited potassium carbonate and acetone. The product was formed in 1 h, and was identified as *N*-methylated product, namely, 6,N_{12}-dimethyldibenzo[*b,g*][1,8]naphthyridin-5-ones (**10**). The reaction was generalized



Scheme 6. Overall scheme for the preparation of dibenzo[*b,g*][1,8]naphthyridin-5-ones.



4,5,10,11 a) R_1=CH_3, R_2=H **4,10**) R = CH_3
b) R_1=H, R_2=CH_3 **5,11**) R = Ph
c) R_1=Cl, R_2=H
d) R_1=H, R_2=H

Scheme 7. *N*-Methylation reaction of the dibenzo[*b,g*][1,8]naphthyridin-5-ones **11**.

for the naphthyridine derivatives **4a, c, d** to obtain **10a, c, d**, except 1,6-dimethyldibenzo[*b,g*][1,8]naphthyridin-5-one (**4b**) took 5 h for the formation of 1,6,N_{12},-trimethyldibenzo[*b,g*][1,8]naphthyridin-5-one (**10b**) and could be predicted because the approach of methyl iodide toward the ring N_{12}-H of the naphthyridine was sterically hindered by the C_1-methyl group. The similar sequence of methylation reaction was also found with **5a–d** to afford the respective N_{12}-methyl-6-phenyldibenzo[*b,g*][1,8]naphthyridin-5-one (**11a–d**) (Scheme 7).

CONCLUSION

From the experimental work, it may be concluded that the reaction of 2,4-dichloroquinolines (**1**) with equal or excess moles of *o*-aminoacetophenone and *o*-aminobenzophenone resulted only in the formation of monosubstituted anilinoquinolines **2** and **3**.

The acid-catalyzed internal electrophilic cyclization reaction of **2** and **3** under PPA at 205–210 °C yielded the respective 6-substituted dibenzo[*b,g*][1,8]naphthyridin-5-one **4** and **5** through the intermediate 2′-substituted-2-(*N*-phenylamino)quinolin-4-one (**III**).

The treatment of **2** and **3** with sodium methoxide yielded 2′-substituted methoxyanilnoquinolines **7** and **8**, which on PPA conditions at 130–135 °C resulted in **4** and **5** via the same intermediate **III**.

The temperature difference for the formation of **4** and **5** from **2** and **3** and **7** and **8** is the reflection of the conversion of Cl and OCH_3 to the OH group (intermediate **III**) under the same acidic conditions. The difference in the yield of the final products **4** and **5** from **2** and **3** and **7** and **8** may also echo this statement.

EXPERIMENTAL

Melting points (mp) were determined on a Mettler FP 51apparatus (Mettler Instruments, Switzerland) and are uncorrected. They are expressed in degree centigrade (°C). Infrared (IR) spectra were recorded on a Schimadzu Fourier transform (FT)–IR-8201PC spectrophotometer (Schimadzu, Japan) using KBr discs. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX 400 [400 MHz (^{1}H) and

100 MHz (^{13}C)] spectrometer, and 2D-NMR were recorded on a Bruker AV 300-MHz instrument using tetramethylsilane (TMS) as an internal reference. The chemical shifts are expressed in parts per million (ppm). Mass spectra (MS) were recorded on an AutoSpec EI+Shimadzu QP 2010 Plus gas chromatography (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 thin-layer chromatography (TLC) with plates coated with silica gel G, with petroleum ether and ethyl acetate as developing solvents.

Preparation of 2′-Acetyl and 2′-Benzoyl Substituted 4-Chloro-2-(N-phenylamino)quinolines (2, 3) from 2,4-Dichloroquinolines (1): General Procedure

An appropriate mixture of 2,4-dichloroquinolines (**1**, 0.004 mol) was reacted with *o*-aminoacetophenone and *o*-aminobenzophenone (0.004 mol or excess) under neat conditions at 160 °C for half an hour. The product was washed with water, adsorbed, and purified using silica-gel column chromatography and eluted with petroleum ether–ethyl acetate (98:2 and 99:1) to get **2** and **3**, respectively. Both were recrystallized from ethanol.

Selected Data

Compound 2a. Colorless prisms. Mp 145–147 °C. Yield: 0.868 g, 70%. IR ν_{max} (cm^{-1}): 3421 (NH), 1631 (C=O), 1579, 1518, 1149. ^{1}H NMR ($CDCl_3$)δ: 2.61 (s, 3H, C_6-CH_3), 2.68 (s, 3H, $COCH_3$), 7.14–7.94 (m, 6H, C_3-, C_7-, C_8-, C_3'-, C_4'-, C_5'-H), 7.98 (s, 1H, C_5-H), 9.48 (d, 1H, C_6'-H, $J = 8.61$ Hz), 11.57 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 18.6 ($COCH_3$), 22.7 (C_6-CH_3), 114.3 (C_3), 119.4 (C_4'), 119.8 (C_4), 120.5 (C_2'), 121.7 (C_6'), 122.6 (C_5), 124.0 (C_3'), 130.6 (C_8), 131.8 (C_7), 133.0 (C_6), 138.9 (C_5'), 143.9 (C_1'), 147.5 (C_{4a}), 148.3 (C_{8a}), 150.9 (C_2), 202.6 (C=O). MS: m/z (%) 312/310 (M^+, 15/49), 295 (10), 293 (10), 267 (48), 260 (10), 120 (33), 77 (10), 44 (100). Anal. calcd. for $C_{18}H_{15}N_2ClO$: C, 69.68; H, 4.84; N, 9.03. Found: C, 69.31; H, 4.99; N, 8.96%.

Compound 2b. Colorless needles. Mp 146–148 °C. Yield: 0.893 g, 72%. IR ν_{max} (cm^{-1}): 3426 (NH), 1628 (C=O), 1577, 1518, 1145. ^{1}H NMR ($CDCl_3$) δ: 2.71 (s, 3H, $COCH_3$), 2.83 (s, 3H, C_8-CH_3), 6.91–8.23 (m, 7H, C_3-, C_5-, C_6-, C_7-, C_3'-, C_4'-, C_5'-H), 9.47 (d, 1H, C_6'-H, $J = 8.70$ Hz), 11.09 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 18.8 ($COCH_3$), 28.5 (C_8-CH_3), 114.3 (C_3), 119.4 (C_4'), 119.5 (C_4), 120.5 (C_2'), 121.7 (C_6'), 122.5 (C_5), 124.0 (C_3'), 130.8 (C_6), 132.0 (C_7), 135.4 (C_8), 138.9 (C_5'), 143.9 (C_1'), 146.9 (C_{4a}), 149.6 (C_{8a}), 150.9 (C_2), 202.6 (C=O). MS: m/z (%) 312/310 (M^+, 17/51), 295 (15), 293 (10), 267 (32), 254 (15), 120 (44), 77 (38), 44 (100). Anal. calcd. for $C_{18}H_{15}N_2ClO$: C, 69.68; H, 4.84; N, 9.03. Found: C, 69.79; H, 4.91; N, 8.92%.

Compound 2c. White solid Mp 149–151 °C. Yield: 0.924 g, 70%. IR ν_{max} (cm^{-1}): 3425 (NH), 1630 (C=O), 1571, 1527, 1134. ^{1}H NMR ($CDCl_3$) δ: 2.72 (s, 3H, $COCH_3$), 7.03–7.95 (m, 6H, C_3-, C_7-, C_8-, C_3'-, C_4'-, C_5'-H), 8.03 (d, 1H, C_5-H,

$J = 2.50$ Hz), 9.39 (d, 1H, C'_6-H, $J = 8.64$ Hz), 11.86 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 18.7 ($COCH_3$), 114.3 (C_3), 119.4 (C'_4), 119.3 (C_4), 120.5 (C'_2), 121.7 (C'_6), 122.0 (C_5), 124.0 (C'_3), 130.5 (C_8), 131.2 (C_7), 132.3 (C_6), 138.9 (C'_5), 143.9 (C'_1), 147.3 (C_{4a}), 148.2 (C_{8a}), 150.9 (C_2), 202.6 (C=O). MS: *m*/*z* (%) 334/332/330 (M^+, 11/28/50), 315 (30), 314 (28), 295 (36), 160 (10), 120 (49), 77 (35), 44 (100). Anal. calcd. for $C_{17}H_{12}N_2Cl_2O$: C, 61.82; H, 3.64; N, 8.49. Found: C, 61.74; H, 3.81; N, 8.34%.

Compound 2d. Colorless prisms. Mp 141–143 °C. Yield: 0.864 g, 73%. IR ν_{max} (cm^{-1}): 3422 (NH), 1629 (C=O), 1581, 1517, 1136. ^{1}H NMR ($CDCl_3$) δ: 2.69 (s, 3H, $COCH_3$), 7.08–8.02 (m, 8H, C_3-, C_5-, C_6-, C_7-, C_8-, C'_3-, C'_4-, C'_5-H), 9.43 (d, 1H, C'_6-H, $J = 8.66$ Hz), 11.58 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 18.6 ($COCH_3$), 114.3 (C_3), 119.8 (C'_4), 119.4 (C_4), 120.5 (C'_2), 121.7 (C'_6), 122.5 (C_5), 124.0 (C'_3), 130.8 (C_6), 132.0 (C_8), 132.8 (C_7), 138.9 (C'_5), 143.9 (C'_1), 146.9 (C_{4a}), 149.6 (C_{8a}), 150.9 (C_2), 202.6 (C=O). MS: *m*/*z* (%) 298/296 (M^+, 18/56), 295 (30), 281 (10), 268 (48), 160 (12), 120 (46), 77 (18), 44 (100). Anal. calcd. for $C_{17}H_{13}N_2ClO$: C, 68.92; H, 4.39; N, 9.46. Found: C, 69.03; H, 4.48; N, 9.34%.

Compound 3a. Pale yellow prisms. Mp 168–170 °C. Yield: 1.057 g, 71%. IR ν_{max} (cm^{-1}): 3430 (NH), 1634 (C=O), 1579, 1525, 1156. ^{1}H NMR ($CDCl_3$) δ: 2.55 (s, 3H, C_6-CH_3), 6.98–7.82 (m, 11H, C_3-, C_7-, C_8-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5-, C''_6-H), 7.87 (s, 1H, C_5-H), 9.19 (d, 1H, C'_6-H, $J = 8.26$ Hz), 11.02 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 21.5 (C_6-CH_3), 114.3 (C_3), 119.8 (C'_4), 122.5 (C_4), 123.8 (C'_2), 126.9 (C'_6), 128.3 (C_5), 129.4 (C''_2, C''_6), 129.7 (C''_3, C''_5), 130.1 (C''_4), 130.0 (C'_3), 131.3 (C_8), 133.2 (C_7), 133.9 (C_6), 136.4 (C'_5), 138.6 (C''_1), 142.3 (C'_1), 146.0 (C_{4a}), 150.3 (C_{8a}), 151.9 (C_2), 168.8 (C=O). MS: *m*/*z* (%) 374/372 (M^+, 15/55), 371 (25), 357 (12), 344 (40), 295 (45), 105 (37), 77 (79), 44 (100). Anal. calcd. for $C_{23}H_{17}N_2ClO$: C, 74.19; H, 4.56; N, 7.53. Found: C, 74.11; H, 4.70; N, 7.41%.

Compound 3b. Pale yellow needles. Mp 166–168 °C. Yield: 1.010 g, 74%. IR ν_{max} (cm^{-1}): 3431 (NH), 1631 (C=O), 1589, 1524, 1148. ^{1}H NMR ($CDCl_3$) δ: 2.73 (s, 3H, C_8-CH_3), 7.00–7.95 (m, 11H, C_3-, C_6-, C_7-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5-, C''_6-H), 7.99 (d, 1H, C_5-H, $J = 8.32$ Hz), 9.35 (d, 1H, C'_6-H, $J = 8.37$ Hz), 11.01 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 19.8 (C_8-CH_3), 114.3 (C_3), 119.8 (C'_4), 122.5 (C_4), 123.8 (C'_2), 126.9 (C'_6), 128.1 (C_5), 129.4 (C''_2, C''_6), 129.7 (C''_3, C''_5), 130.1 (C''_4), 130.0 (C'_3), 131.5 (C_6), 132.8 (C_7), 136.1 (C_8), 136.4 (C'_5), 138.6 (C''_1), 142.3 (C'_1), 146.1 (C_{4a}), 150.1 (C_{8a}), 151.8 (C_2), 168.8 (C=O). MS: *m*/*z* (%) 374/372 (M^+, 19/64), 371 (15), 357 (22), 344 (33), 295 (41), 105 (47), 77 (75), 44 (100). Anal. calcd. for $C_{23}H_{17}N_2ClO$: C, 74.19; H, 4.56; N, 7.53. Found: C, 74.31; H, 4.63; N, 7.44%.

Compound 3c. Pale yellow solid. Mp 170–172 °C. Yield: 1.098 g, 70%. IR ν_{max} (cm^{-1}): 3430 (NH), 1631 (C=O), 1585, 1519, 1146. ^{1}H NMR ($CDCl_3$) δ: 7.02–7.92 (m, 11H, C_3-, C_7-, C_8-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5-, C''_6-H), 8.04 (s, 1H, C_5-H), 9.31 (d, 1H, C'_6-H, $J = 8.39$ Hz), 10.94 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 114.3 (C_3), 119.8 (C'_4), 122.3 (C_4), 123.8 (C'_2), 126.9 (C'_6), 127.8 (C_5), 129.4 (C''_2, C''_6), 129.7 (C''_3, C''_5), 130.1 (C''_4), 130.0 (C'_3), 130.9 (C_8), 131.8 (C_7), 133.0 (C_6), 136.4 (C'_5), 138.6 (C''_1), 142.3 (C'_1), 145.8 (C_{4a}), 150.0 (C_{8a}), 151.7 (C_2), 168.8 (C=O). MS: *m*/*z* (%) 396/394/392 (M^+, 20/42/78), 391 (30), 364 (36), 357 (25),

166 (20), 0105 (51), 77 (63), 44 (100). Anal. calcd. for $C_{22}H_{14}N_2Cl_2O$: C, 67.35; H, 3.57; N, 7.14. Found: C, 67.22; H, 3.69; N, 7.25%.

Compound 3d. Pale yellow prisms. Mp 163–165 °C. Yield: 1.031 g 72%. IR ν_{max} (cm^{-1}): 3427 (NH), 1633 (C=O), 1584, 1526, 1150. ^1H NMR ($CDCl_3$) δ: 6.98–7.90 (m, 12H, C_3-, C_6-, C_7-, C_8-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5-, C''_6-H), 8.07 (dd, 1H, C_5-H, $J_1 = 1.15$ Hz, $J_2 = 8.31$ Hz), 9.28 (d, 1H, C'_6-H, $J = 8.42$ Hz), 10.98 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 114.3 (C_3), 119.8 (C'_4), 123.1 (C_4), 123.8 (C'_2), 126.9 (C'_6), 128.5 (C_5), 129.4 (C''_2, C''_6), 129.7 (C''_3, C''_5), 130.1 (C''_4), 130.0 (C'_3), 131.1 (C_6), 131.4 (C_8), 132.9 (C_7), 136.4 (C'_5), 138.6 (C''_1), 142.3 (C'_1), 145.6 (C_{4a}), 149.9 (C_{8a}), 151.8 (C_2), 168.8 (C=O). MS: m/z (%) 360/358 (M^+, 20/65), 357 (48), 330 (26), 281 (29), 166 (22), 105 (51), 77 (82), 44 (100). Anal. calcd. for $C_{22}H_{15}N_2ClO$: C, 73.74; H, 4.19; N, 7.82. Found: C, 73.61; H, 4.17; N, 7.89%.

Preparation of 6-Methyl and 6-Phenyl Substituted Dibenzo[b,g]-[1,8]naphthyridin-5-ones (4, 5) from 2′-Acetyl and 2′-Benzoyl Substituted 4-Chloro-2-(N-phenylamino)quinolines (2, 3): General Procedure

2′-Acetyl and 2′-benzoyl substituted 4-chloro-2-(*N*-phenylamino)quinolines (**2** and **3**, 0.002 mol) were added to polyphosphoric acid (6 g of P_2O_5 in 3 mL of H_3PO_4) and heated at 205–210 °C for 5 h. The reaction was monitored using TLC. After the completion of the reaction, the reaction mixture was poured into ice water, extracted with ethyl acetate, and purified by column chromatography using silica gel, and the product was eluted with a petroleum ether–ethyl acetate (95:5 and 96:4) mixture to get **4** and **5**, respectively. Both were recrystallized from methanol.

Selected Data

Compound 4a. Colorless needles. Mp 189–191 °C. Yield: 0.110 g, 20%. IR ν_{max} (cm^{-1}): 3418 (NH), 1649 (C=O), 1611, 1566, and 1463. ^1H NMR ($CDCl_3$) δ: 2.39 (s, 3H, C_3-CH_3), 3.41 (s, 3H, C_6-CH_3), 7.16–7.97 (m, 6H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-H), 8.11 (s, 1H, C_4-H), 9.22 (b s, 1H, N_{12}-H. ^{13}C NMR ($CDCl_3$) δ: 18.9 (C_3-CH_3), 28.6 (C_6-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.5 (C_1), 128.0 (C_4), 128.2 (C_2), 129.7 (C_3), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6 (C_{10a}), 150.8 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: m/z (%) 274 (M^+, 77), 273 (100), 259 (18), 254 (11), 235 (22), 234 (12), 184 (14), 77 (51). Anal. calcd. for $C_{18}H_{14}N_2O$: C, 78.83; H, 5.11; N, 10.22. Found: C, 78.89; H, 5.16; N, 10.30%.

Compound 4b. Colorless prisms. Mp 191–193 °C. Yield: 0.098 g, 18%. IR ν_{max} (cm^{-1}): 3421 (NH), 1648 (C=O), 1606, 1564, and 1472. ^1H NMR ($CDCl_3$) δ: 2.54 (s, 3H, C_1-CH_3), 3.38 (s, 3H, C_6-CH_3), 7.12–8.01 (m, 6H, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-H), 8.20 (d, 1H, C_4-H, $J = 8.23$ Hz), 9.52 (b s, 1H, N_{12}-H). ^{13}C NMR ($CDCl_3$) δ: 16.8 (C_1-CH_3), 28.6 (C_6-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.6 (C_3), 127.8 (C_4), 128.0 (C_2), 130.6 (C_1), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6 (C_{10a}), 150.8 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: m/z (%) 274 (M^+, 82), 273 (100), 259 (18), 254 (11), 235 (22), 234 (12),

184 (14), 77 (51). Anal. calcd. for $C_{18}H_{14}N_2O$: C, 78.83; H, 5.11; N, 10.22. Found: C, 78.77; H, 5.05; N, 10.32%.

Compound 4c. White solid. Mp 198–200 °C. Yield: 0.099 g, 17%. IR ν_{max} (cm^{-1}): 3420 (NH), 1646 (C=O), 1607, 1551, and 1471. ^1H NMR ($CDCl_3$) δ: 3.35 (s, 3H, C_6-CH_3), 7.14–7.95 (m, 6H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-H), 8.13 (d, 1H, C_4-H, $J = 2.16$ Hz), 9.41 (b s, 1H, N_{12}-H). ^{13}C NMR ($CDCl_3$) δ: 28.6 (C_6-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.4 (C_1), 127.8 (C_4), 128.0 (C_2), 129.3 (C_3), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6 (C_{10a}), 150.8 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: m/z 296/294 (M^+, 34/100), 293 (91), 279 (17), 274 (26), 235 (52), 234 (12), 184 (15), 77 (45). Anal. calcd. for $C_{17}H_{11}N_2ClO$: C, 69.39; H, 3.74; N, 9.52. Found: C, 69.26; H, 3.75; N, 9.46%.

Compound 4d. Colorless prisms. Mp 187–189 °C. Yield: 0.094 g, 20%. IR ν_{max} (cm^{-1}): 3419 (NH), 1648 (C=O), 1610, 1558, and 1474. ^1H NMR ($CDCl_3$) δ: 3.36 (s, 3H, C_6-CH_3), 7.21–8.03 (m, 7H, C_1-, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-H), 8.11 (dd, 1H, C_4-H, $J_1 = 1.42$ Hz, $J_2 = 8.12$ Hz), 9.29 (b s, 1H, N_{12}-H). ^{13}C NMR ($CDCl_3$) δ: 28.6 (C_6-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.5 (C_3), 127.6 (C_4), 127.8 (C_1), 128.6 (C_2), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6 (C_{10a}), 150.8 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: m/z (%) 260 (M^+, 83), 259 (100), 245 (20), 244 (23), 233 (18), 232 (10), 184 (12), 77 (30). Anal. calcd. for $C_{17}H_{12}N_2O$: C, 78.46; H, 4.62; N, 10.77. Found: C, 78.51; H, 4.59; N, 10.83%.

Compound 5a. Colorless needles. Mp 203–205 °C. Yield: 0.148 g, 22%. IR ν_{max} (cm^{-1}): 3426 (NH), 1649 (C=O), 1610, 1564, and 1476. ^1H NMR ($CDCl_3$) δ: 2.38 (s, 3H, C_3-CH_3), 7.11–7.87 (m, 11H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5-, C'_6-H), 8.02 (s, 1H, C_4-H), 8.69 (b s, 1H, N_{12}-H). ^{13}C NMR ($CDCl_3$) δ: 18.6 (C_3-CH_3), 121.0 (C_8), 122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 128.0 (C_1), 128.1 (C_4), 128.3 (C_2), 130.0 (C_3), 133.4 (C'_1), 137.3 (C_6), 138.8 (C_{6a}), 147.8 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 150.9 (C_{12a}), 153.4 (C_{11a}), 179.6 (C=O). MS: m/z (%) 336 (M^+, 75), 335 (100), 321 (11), 260 (23), 259 (32), 202 (33), 184 (36), 77 (61). Anal. calcd. for $C_{23}H_{16}N_2O$: C, 82.14; H, 4.76; N, 8.33. Found: C, 82.09; H, 4.68; N, 8.26%.

Compound 5b. Colorless prisms. Mp 201–203 °C. Yield: 0.141 g, 21%. IR ν_{max} (cm^{-1}): 3427 (NH), 1646 (C=O), 1605, 1566, and 1483. ^1H NMR ($CDCl_3$) δ: 2.58 (s, 3H, C_1-CH_3), 7.08–7.86 (m, 11H, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5-, C'_6-H), 8.11 (d, 1H, C_4-H, $J = 8.15$ Hz), 8.55 (b s, 1H, N_{12}-H). ^{13}C NMR ($CDCl_3$) δ: 16.8 (C_1-CH_3), 121.0 (C_8), 122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 127.8 (C_3), 128.0 (C_4), 128.2 (C_2), 130.8 (C_1), 133.4 (C'_1), 137.3 (C_6), 138.8 (C_{6a}), 147.6 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 151.3 (C_{12a}), 153.5 (C_{11a}), 179.6 (C=O). MS: m/z (%) 336 (M^+, 75), 335 (100), 321 (21), 260 (27), 259 (12), 202 (19), 184 (30), 77 (59). Anal. calcd. for $C_{23}H_{16}N_2O$: C, 82.14; H, 4.76; N, 8.33. Found: C, 82.05; H, 4.65; N, 8.36%.

Compound 5c. White solid. Mp 209–211 °C. Yield: 0.135 g, 18%. IR ν_{max} (cm^{-1}): 3430 (NH), 1642 (C=O), 1601, 1559, and 1471. ^1H NMR ($CDCl_3$) δ: 7.08–7.88 (m, 11H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5-, C'_6-H), 8.18 (d, 1H, C_4-H, $J = 2.38$ Hz), 8.94 (b s, 1H, N_{12}-H). ^{13}C NMR ($CDCl_3$) δ: 121.0 (C_8),

122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 127.9 (C_1), 128.0 (C_4), 128.1 (C_2), 129.4 (C_3), 133.4 (C'_1), 137.3 (C_6), 138.8 (C_{6a}), 147.6 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 150.8 (C_{12a}), 153.4 (C_{11a}), 179.6 (C=O). MS: m/z 358/356 (M^+, 32/100), 355 (75), 341 (26), 321 (11), 280 (14), 279 (21), 184 (23), 75 (42). Anal. calcd. for $C_{22}H_{13}N_2ClO$: C, 74.16; H, 3.65; N, 7.87. Found: C, 74.08; H, 23.57; N, 7.96%.

Compound 5d. Colorless prisms. Mp 200–202 °C. Yield: 0.135 g, 21%. IR ν_{max} (cm^{-1}): 3429 (NH), 1647 (C=O), 1607, 1560, and 1478. ^1H NMR ($CDCl_3$) δ: 7.27–7.81 (m, 12H, C_1-, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5-, C'_6-H), 8.21 (dd, 1H, C_4-H, $J_1 = 1.30$ Hz, $J_2 = 8.08$ Hz), 8.83 (b s, 1H, N_{12}-H). ^{13}C NMR ($CDCl_3$) δ: 121.0 (C_8), 122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 127.9 (C_1), 128.2 (C_4), 128.9 (C_3), 129.4 (C_2), 133.4 (C'_1), 137.1 (C_6), 138.8 (C_{6a}), 147.6 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 151.0 (C_{12a}), 153.4 (C_{11a}), 179.6 (C=O). MS: m/z (%) 322 (M^+, 100), 321 (82), 296 (22), 246 (18), 245 (34), 183 (12), 77 (35), 75 (46). Anal. calcd. for $C_{22}H_{14}N_2O$: C, 81.99; H, 4.35; N, 8.70. Found: C, 82.03; H, 4.31; N, 8.79%.

Preparation of 2′-Acetyl and 2′-Benzoyl Substituted 4-Methoxy-2-(N-phenylamino)quinolines (7, 8) from 2′-Acetyl and 2′-Benzoyl Substituted 4-Chloro-2-(N-phenylamino)quinolines (2, 3): General Procedure

2′-Acetyl and 2′-benzoyl substituted 4-chloro-2-(*N*-phenylamino)quinolines (**2** and **3**, 0.002 mol) were added to sodium methoxide solution (2 g of sodium in 15 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 diluted HCl. The resulting precipitate was filtered, dried, and subjected to purification by column chromatography over silica gel using a petroleum ether–ethyl acetate (94:6 and 95:5) mixture to get **7** and **8**, respectively. Both were recrystallized from methanol.

Selected Data

Compound 7a. Colorless prisms. Mp 166–168 °C. Yield: 0.275 g, 45%. IR ν_{max} (cm^{-1}): 3432 (NH), 1629 (C=O), and 1598, 1528, and 1236 (OCH_3). ^1H NMR ($CDCl_3$) δ: 2.55 (s, 3H, C_6-CH_3), 2.61 (s, 3H, $COCH_3$), 4.07 (s, 3H, OCH_3), 6.42 (s, 1H, C_3-H), 7.11–7.82 (m, 5H, C_7-, C_8-, C'_3-, C'_4-, C'_5-H), 7.93 (s, 1H, C_5-H), 9.44 (d, 1H, C'_6-H, $J = 8.42$ Hz), 10.97 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 18.9 ($COCH_3$), 22.1 (C_6-CH_3), 53.6 (O-CH_3), 91.8 (C_3), 118.0 (C'_4), 119.1 (C_4), 120.8 (C'_2) 121.7 (C'_6) 122.3 (C_5), 130.5 (C'_3), 132.0 (C_8), 132.9 (C_7), 134.1 (C_6), 134.3 (C'_5), 142.6 (C'_1), 146.8 (C_{4a}), 152.7 (C_{8a}), 163.2 (C_2), 199.1 (C=O). MS: m/z (%) 306 (M^+, 61), 305 (22), 291 (21), 278 (35), 276 (14), 275 (26), 105 (48), 77 (100). Anal. calcd. for $C_{19}H_{18}N_2O_2$: C, 74.51; H, 5.88; N, 9.15. Found: C, 74.38; H, 5.99; N, 9.04%.

Compound 7b. Colorless needles. Mp 164–166 °C. Yield: 0.263 g, 43%. IR ν_{max} (cm^{-1}): 3436 (NH), 1630 (C=O), 1586, 1520, 1234 (OCH_3). ^1H NMR ($CDCl_3$) δ: 2.59 (s, 3H, $COCH_3$), 2.71 (s, 3H, C_8-CH_3), 4.11 (s, 3H, OCH_3), 6.39 (s, 1H, C_3-H), 7.09–7.80 (m, 5H, C_6-, C_7-, C'_3-, C'_4-, C'_5-H), 7.85 (d, 1H, C_5-H, $J = 8.40$ Hz), 9.43 (d, 1H, C'_6-H, $J = 8.47$ Hz), 11.05 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 18.9 ($COCH_3$), 27.3 (C_8-CH_3), 53.7 (O-CH_3), 91.8 (C_3), 118.0 (C'_4), 119.0 (C_4), 120.8 (C'_2), 121.7 (C'_6), 122.6 (C_5), 130.5 (C'_3), 131.6 (C_6), 133.6 (C_7), 134.3 (C'_5), 136.4 (C_8), 142.6 (C'_1), 146.9 (C_{4a}), 155.1 (C_{8a}), 163.5 (C_2), 199.1 (C=O). MS: *m*/*z* (%) 306 (M^+, 57), 305 (22), 291 (42), 278 (25), 276 (42), 105 (50), 77 (100), 44 (75). Anal. calcd. for $C_{19}H_{18}N_2O_2$: C, 74.51; H, 5.88; N, 9.15. Found: C, 74.46; H, 5.87; N, 9.09%.

Compound 7c. White solid. Mp 169–171 °C. Yield: 0.261 g, 40%. IR ν_{max} (cm^{-1}): 3432 (NH), 1631 (C=O), 1585, 1524, 1238 (OCH_3). ^1H NMR ($CDCl_3$) δ: 2.61 (s, 3H, $COCH_3$), 4.09 (s, 3H, OCH_3), 6.38 (s, 1H, C_3-H), 7.14–7.84 (m, 5H, C_7-, C_8-, C'_3-, C'_4-, C'_5-H), 8.08 (s, 1H, C_5-H), 9.39 (d, 1H, C'_6-H, $J = 8.48$ Hz), 11.03 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) 18.9 ($COCH_3$), 53.6 (O-CH_3), 91.8 (C_3), 118.0 (C'_4), 119.1 (C_4), 120.8 (C'_2) 121.7 (C'_6) 122.0 (C_5), 130.5 (C'_3), 132.0 (C_8), 132.9 (C_7), 133.8 (C_6), 134.3 (C'_5), 142.6 (C'_1), 146.5 (C_{4a}), 152.7 (C_{8a}), 163.2 (C_2), 199.1 (C=O). MS: *m*/*z* (%) 328/326 (M^+, 20/73), 325 (15), 311 (19), 298 (24), 296 (12), 105 (33), 77 (100), 44 (41). Anal. calcd. for $C_{18}H_{15}N_2ClO_2$: C, 66.26; H, 4.60; N, 8.59. Found: C, 66.12; H, 4.65; N, 8.60%.

Compound 7d. Colorless prisms. Mp 160–162 °C. Yield: 0.239 g, 41%. IR ν_{max} (cm^{-1}): 3429 (NH), 1633 (C=O), 1580, 1520, 1234 (OCH_3). ^1H NMR ($CDCl_3$) δ: 2.58 (s, 3H, $COCH_3$), 4.10 (s, 3H, OCH_3), 6.41 (s, 1H, C_3-H), 7.15–7.96 (m, 7H, C_5-, C_6-, C_7-, C_8-, C'_3-, C'_4-, C'_5-H), 9.37 (d, 1H, C'_6-H, $J = 8.62$ Hz), 11.02 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) 18.9 ($COCH_3$), 53.7 (O-CH_3), 91.8 (C_3), 118.0 (C'_4), 119.0 (C_4), 120.8 (C'_2) 121.7 (C'_6) 122.4 (C_5), 130.5 (C'_3), 131.5 (C_6), 133.6 (C_8), 133.9 (C_7), 134.3 (C'_5), 142.6 (C'_1), 146.9 (C_{4a}), 155.1 (C_{8a}), 164.0 (C_2), 199.1 (C=O). MS: *m*/*z* (%) 292 (M^+, 68), 291 (27), 277 (31), 264 (32), 261 (17), 105 (40), 77 (100), 44 (46). Anal. calcd. for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59. Found: C, 74.08; H, 5.50; N, 9.65%.

Compound 8a. Colorless prisms. Mp 174–176 °C. Yield: 0.346 g, 47%. IR ν_{max} (cm^{-1}): 3432 (NH), 1627 (C=O), 1595, 1522, and 1238 (OCH_3). ^1H NMR ($CDCl_3$) δ: 2.52 (s, 3H, C_6-CH_3), 4.07 (s, 3H, OCH_3), 6.30 (s, 1H, C_3-H), 7.25–7.81 (m, 10H, C_7-, C_8-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5, -C''_6-H), 7.92 (s, 1H, C_5-H), 9.48 (d, 1H, C'_6-H, $J = 8.64$ Hz), 10.97 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 21.1 (C_6-CH_3), 55.8 (O-CH_3), 92.3 (C_3), 118.0 (C'_4), 119.4 (C_4), 121.3 (C'_2), 121.8 (C'_6), 122.8 (C_5), 128.4 (C''_2, C''_6), 129.6 (C''_3, C''_5), 130.4 (C''_4), 131.1 (C'_3), 132.3 (C_8), 133.2 (C_7), 133.8 (C_6), 134.2 (C'_5), 138.9 (C''_1), 143.0 (C'_1), 146.9 (C_{4a}), 152.9 (C_{8a}), 163.4 (C_2), 199.2 (C=O). MS: *m*/*z* (%) 368 (M^+, 55), 367 (22), 353 (36), 337 (12), 291 (15), 105 (51), 77 (100), 44 (64). Anal. calcd. for $C_{24}H_{20}N_2O_2$: C, 78.26; H, 5.43; N, 7.61. Found: C, 78.37; H, 5.46; N, 7.55%.

Compound 8b. Colorless needles. Mp 177–179 °C. Yield: 0.353 g, 48%. IR ν_{max} (cm^{-1}): 3433 (NH), 1631 (C=O), 1585, 1519, 1233 (OCH_3). ^1H NMR ($CDCl_3$) δ: 2.76 (s, 3H, C_8-CH_3), 4.04 (s, 3H, OCH_3), 6.29 (s, 1H, C_3-H), 7.21–7.75 (m, 10H,

C_6-, C_7-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5-, - C''_6-H), 7.93 (d, 1H, C_5-H, $J = 8.33$ Hz), 9.50 (d, 1H, C'_6-H, $J = 8.62$ Hz), 11.04 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 18.7 (C_8-CH_3), 55.7 (O-CH_3), 92.2 (C_3), 118.0 (C'_4), 119.4 (C_4), 121.3 (C'_2), 121.8 (C'_6), 123.0 (C_5), 128.4 (C''_2, C''_6), 129.6 (C''_3, C''_5), 130.4 (C''_4), 131.1 (C'_3), 131.8 (C_6), 133.6 (C_7), 134.0 (C_8), 134.2 (C'_5), 138.9 (C''_1), 143.0 (C'_1), 146.7 (C_{4a}), 153.1 (C_{8a}), 163.4 (C_2), 199.2 (C=O). MS: *m/z* (%) 368 (M^+, 61), 367 (15), 353 (46), 337 (22), 291 (10), 105 (56), 77 (100), 44 (74). Anal. calcd. for $C_{24}H_{20}N_2O_2$: C, 78.26; H, 5.43; N, 7.61. Found: C, 78.32; H, 5.36; N, 7.65%.

Compound 8c. White solid. Mp 180–182 °C. Yield: 0.326 g, 42%. IR ν_{max} (cm^{-1}): 3434 (NH), 1632 (C=O), 1588, 1526, 1239 (OCH_3). ^{1}H NMR ($CDCl_3$) δ: 4.10 (s, 3H, OCH_3), 6.33 (s, 1H, C_3-H), 7.48–7.88 (m, 10H, C_7-, C_8-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5-, C''_6-H), 8.09 (s, 1H, C_5-H), 9.49 (d, 1H, C'_6-H, $J = 8.68$ Hz), 10.94 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 55.8 (O-CH_3), 92.3 (C_3), 118.0 (C'_4), 119.1 (C_4), 121.3 (C'_2) 121.8 (C'_6) 122.1 (C_5) 128.4 (C''_2, C''_6), 129.6 (C''_3, C''_5), 130.4 (C''_4), 131.1 (C'_3), 131.9 (C_8), 132.6 (C_7), 133.1 (C_6), 134.2 (C'_5), 138.9 (C''_1), 143.0 (C'_1), 146.1 (C_{4a}), 152.5 (C_{8a}), 163.3 (C_2), 199.2 (C=O). MS: *m/z* (%) 390/388 (M^+, 20/73), 387 (15), 373 (12), 357 (26), 353 (12), 105 (16), 77 (100), 44 (36). Anal. calcd. for $C_{23}H_{17}N_2ClO_2$: C, 71.13; H, 4.38; N, 7.22. Found: C, 71.05; H, 4.45; N, 7.36%.

Compound 8d. Colorless prisms. Mp 171–173 °C. Yield: 0.304 g, 43%. IR ν_{max} (cm^{-1}): 3429 (NH), 1634 (C=O), 1589, 1521, 1233 (OCH_3). ^{1}H NMR ($CDCl_3$) δ: 4.09 (s, 3H, OCH_3), 6.30 (s, 1H, C_3-H), 7.44–7.94 (m, 11H, C_6-, C_7-, C_8-, C'_3-, C'_4-, C'_5-, C''_2-, C''_3-, C''_4-, C''_5-, C''_6-H), 8.01 (dd, 1H, C_5-H, $J_1 = 1.81$ Hz, $J_2 = 8.36$ Hz), 9.52 (d, 1H, C'_6-H, $J = 8.61$ Hz), 10.99 (b s, 1H, C_2-NH). ^{13}C NMR ($CDCl_3$) δ: 55.8 (O-CH_3), 92.3 (C_3), 118.0 (C'_4), 119.3 (C_4), 121.3 (C'_2), 121.8 (C'_6), 122.5 (C_5), 128.4 (C''_2, C''_6), 129.6 (C''_3, C''_5), 130.4 (C''_4), 131.1 (C'_3), 131.6 (C_6), 133.4 (C_8), 133.7 (C_7), 134.2 (C'_5), 138.9 (C''_1), 143.0 (C'_1), 145.9 (C_{4a}), 152.3 (C_{8a}), 163.3 (C_2), 199.2 (C=O). MS: *m/z* (%) 354 (M^+, 68), 353 (16), 339 (33), 323 (16), 277 (20), 105 (44), 77 (100), 44 (51). Anal. calcd. for $C_{23}H_{18}N_2O_2$: C, 77.97; H, 5.09; N, 7.91. Found: C, 78.03; H, 5.12; N, 8.01%.

Preparation of 6-Methyl and 6-Phenyl Substituted Dibenzo[b,g]-[1,8]naphthyridin-5-ones (4, 5) from 2′-Acetyl and 2′-Benzoyl Substituted 4-Methoxy-2-(N-phenylamino)quinolines (7, 8): General Procedure

2′-Acetyl and 2′-benzoyl substituted 4-methoxy-2-(*N*-phenylamino)quinoline (**7** and **8**, 0.002 mol) were added to polyphosphoric acid (6 g of P_2O_5 in 3 mL of H_3PO_4) and heated at 130–135 °C for 4 h. The reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was poured into ice water, extracted with ethyl acetate, and purified by column chromatography using silica gel, and the product eluted with a petroleum ether–ethyl acetate (95:5 and 96:4) mixture to get **4** and **5**, respectively. The product was recrystallized from methanol. From the TLC, mixed melting point, and super-impossible IR spectra, the products were identified as **4** and **5**, which were obtained earlier from the reaction of **2** and **3**. The yields

of the products **4** and **5** obtained from this reaction are compared with the yields obtained from **2** and **3** in Table 3.

Preparation of 6,N_{12}-Dimethyldibenzo[b,g][1,8]naphthyridin-5-ones (10) and N_{12}-Methyl-6-phenyldibenzo[b,g][1,8]naphthyridin-5-ones (11) from 6-Methyl and 6-Phenyl Substituted dibenzo[b,g][1,8]-naphthyridin-5-ones (4, 5): General Procedure

6-Methyl and 6-phenyl substituted dibenzo[*b,g*][1,8]naphthyridin-5-ones (**4a, c**, and **d**, 0.001 mol) were refluxed with methyl iodide (1 mL) in the presence of ignited potassium carbonate (2 g) and acetone (10 mL) for 1 h except **4b** and **5b** took 5 h for the formation of **10b** and **11b** respectively. 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, neutralized with diluted HCl, and extracted with ethyl acetate. Purification by column chromatography over silica gel using petroleum ether–ethyl acetate (98:2 and 99:1) mixture as eluant yielded **10** and **11**, respectively. Both were recrystallized from ethanol.

Selected Data

Compound 10a. Pale yellow needles. Mp 174–176 °C. Yield: 0.115 g, 40%. IR ν_{max} (cm^{-1}): 1645 (C=O), 1598, 1561, 1483, and 1165. ^{1}H NMR ($CDCl_3$) δ: 2.38 (s, 3H, C_3-CH_3), 3.39 (s, 3H, C_6-CH_3), 4.01 (s, 3H, N_{12}-CH_3), 7.17–7.80 (m, 6H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-H), 8.10 (s, 1H, C_4-H). ^{13}C NMR ($CDCl_3$) δ: 18.8 (C_3-CH_3), 28.6 (C_6-CH_3), 43.0 (N_{12}-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.5 (C_1), 127.9 (C_4), 128.0 (C_2), 129.7 (C_3), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6 (C_{10a}), 151.4 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: *m/z* (%) 288 (M^+, 100), 287 (45), 273 (17), 258 (16), 257 (18), 166 (18), 77 (32), 44 (72). Anal. calcd. for $C_{19}H_{16}N_2O$: C, 79.17; H, 5.56; N, 9.72. Found: C, 79.25; H, 5.61; N, 9.70%.

Compound 10b. Pale yellow needles. Mp 172–174 °C. Yield: 0.124 g, 43%. IR ν_{max} (cm^{-1}): 1642 (C=O), 1594, 1558, 1487, and 1161. ^{1}H NMR ($CDCl_3$) δ: 2.55 (s, 3H, C_1-CH_3), 3.36 (s, 3H, C_6-CH_3), 4.09 (s, 3H, N_{12}-CH_3), 7.17–7.92 (m, 6H, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-H), 8.20 (d, 1H, C_4-H, $J = 8.21$ Hz). ^{13}C NMR ($CDCl_3$) δ: 16.8 (C_1-CH_3), 28.6 (C_6-CH_3), 43.0 (N_{12}-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.5 (C_3), 127.7 (C_4), 127.9 (C_2), 130.4 (C_1), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6 (C_{10a}), 150.4 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: *m/z* (%) 288 (M^+, 100), 287 (33), 273 (24), 258 (11), 257 (12), 166 (14), 77 (22), 44 (70). Anal. calcd. for $C_{19}H_{16}N_2O$: C, 79.17; H, 5.56; N, 9.72. Found: C, 79.22; H, 5.64; N, 9.66%.

Compound 10c. Pale yellow solid. Mp 178–180 °C. Yield: 0.117 g, 38%. IR ν_{max} (cm^{-1}): 1640 (C=O), 1610, 1558, 1484, and 1170. ^{1}H NMR ($CDCl_3$) δ: 3.35 (s, 3H, C_6-CH_3), 4.23 (s, 3H, N_{12}-CH_3), 7.25–7.98 (m, 6H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-H), 8.27 (d, 1H, C_4-H, $J = 2.56$ Hz). ^{13}C NMR ($CDCl_3$) δ: 28.6 (C_6-CH_3), 43.0 (N_{12}-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.1 (C_1), 127.7 (C_4), 127.9 (C_2), 129.2 (C_3), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6

(C_{10a}), 150.4 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: m/z (%) 310/308 (M^+, 19/82), 307 (100), 293 (20), 273 (16), 272 (25), 166 (16), 77 (44), 41 (68). Anal. calcd. for $C_{18}H_{13}N_2ClO$: C, 70.13; H, 4.22; N, 9.09. Found: C, 70.01; H, 4.29; N, 9.13%.

Compound 10d. Pale yellow prisms. Mp 171–173 °C. Yield: 0.112 g, 41%. IR ν_{max} (cm^{-1}): 1648 (C=O), 1600, 1557, 1475, and 1171. ^1H NMR ($CDCl_3$) δ: 3.34 (s, 3H, C_6-CH_3), 4.18 (s, 3H, N_{12}-CH_3), 7.54–7.90 (m, 7H, C_1-, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-H), 8.25 (d, 1H, C_4-H, $J = 8.39$ Hz). ^{13}C NMR ($CDCl_3$) δ: 28.6 (C_6-CH_3), 43.0 (N_{12}-CH_3), 121.3 (C_8), 122.1 (C_7), 126.5 (C_{10}), 127.4 (C_9), 127.2 (C_1), 127.7 (C_4), 127.9 (C_2), 129.2 (C_3), 137.9 (C_6), 138.6 (C_{6a}), 147.6 (C_{4a}), 148.2 (C_{5a}), 149.6 (C_{10a}), 150.4 (C_{12a}), 153.2 (C_{11a}), 180.4 (C=O). MS: m/z (%) 274 (M^+, 100), 273 (33), 261 (18), 248 (19), 247 (10), 166 (23), 77 (55), 41 (44). Anal. calcd. for $C_{18}H_{14}N_2O$: C, 78.83; H, 5.11; N, 10.22. Found: C, 78.78; H, 5.00; N, 10.26%.

Compound 11a. Pale yellow needles. Mp 182–184 °C. Yield: 0.154 g, 44%. IR ν_{max} (cm^{-1}): 1648 (C=O), 1602, 1565, 1480, and 1175. ^1H NMR ($CDCl_3$) δ: 2.37 (s, 3H, C_3-CH_3), 4.09 (s, 3H, N_{12}-CH_3), 7.23–7.90 (m, 11H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5-, C'_6-H), 7.96 (s, 1H, C_4-H). ^{13}C NMR ($CDCl_3$) δ: 18.6 (C_3-CH_3), 43.2 (N_{12}-CH_3), 121.0 (C_8), 122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 127.8 (C_1), 128.0 (C_4), 128.2 (C_2), 129.8 (C_3), 133.4 (C'_1), 137.3 (C_6), 138.8 (C_{6a}), 147.8 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 151.5 (C_{12a}), 153.7 (C_{11a}), 179.6 (C=O). MS: m/z (%) 350 (M^+, 100), 349 (35), 335 (14), 320 (12), 319 (18), 272 (10), 166 (19), 77 (38). Anal. calcd. for $C_{24}H_{18}N_2O$: C, 82.29; H, 5.14; N, 8.00. Found: C, 82.36; H, 5.11; N, 8.06%.

Compound 11b. Pale yellow needles. Mp 180–182 °C. Yield: 0.181 g, 47%. IR ν_{max} (cm^{-1}): 1645 (C=O), 1607, 1568, 1484, and 1169. ^1H NMR ($CDCl_3$) δ: 2.55 (s, 3H, C_1-CH_3), 4.11 (s, 3H, N_{12}-CH_3), 7.17–7.92 (m, 11H, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5-, and C'_6-H), 8.21 (d, 1H, C_4-H, $J = 8.30$ Hz. ^{13}C NMR ($CDCl_3$) δ: 16.8 (C_1-CH_3), 43.2 (N_{12}-CH_3), 121.0 (C_8), 122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 127.6 (C_3), 127.8 (C_4), 128.0 (C_2), 130.4 (C_1), 133.4 (C'_1), 137.3 (C_6), 138.8 (C_{6a}), 147.6 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 151.5 (C_{12a}), 153.7 (C_{11a}), 179.6 (C=O). MS: m/z (%) 350 (M^+, 100), 349 (35), 335 (14), 320 (12), 319 (18), 272 (10), 166 (19), 77 (38). Anal. calcd. for $C_{24}H_{18}N_2O$: C, 82.29; H, 5.14; N, 8.00. Found: C, 82.36; H, 5.11; N, 8.06%.

Compound 11c. Pale yellow solid. Mp 186–188 °C. Yield: 0.152 g, 41%. IR ν_{max} (cm^{-1}): 1642 (C=O), 1605, 1560, 1481, and 1175. ^1H NMR ($CDCl_3$) δ: 4.21 (s, 3H, N_{12}-CH_3), 7.26–7.97 (m, 11H, C_1-, C_2-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5-, C'_6-H), 8.27 (d, 1H, C_4-H, $J = 2.46$ Hz). ^{13}C NMR ($CDCl_3$) δ: 43.2 (N_{12}-CH_3), 121.0 (C_8), 122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 127.8 (C_1), 128.0 (C_4), 128.1 (C_2), 129.3 (C_3), 133.4 (C'_1), 137.3 (C_6), 138.8 (C_{6a}), 147.6 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 151.5 (C_{12a}), 153.7 (C_{11a}), 179.6 (C=O). MS: m/z (%) 372/370 (M^+, 22/80), 369 (100), 355 (20), 335 (32), 334 (15), 166 (18), 77 (74), 41 (55). Anal. calcd. for $C_{23}H_{15}N_2ClO$: C, 74.60; H, 4.05; N, 7.57. Found: C, 74.65; H, 3.98; N, 7.63%.

Compound 11d. Pale yellow prisms. Mp 179–181 °C. Yield: 0.141 g, 42%. IR ν_{max} (cm^{-1}): 1645 (C=O), 1606, 1560, 1477, and 1170. ^1H NMR ($CDCl_3$) δ:

4.16 (s, 3H, N_{12}-CH_3), 7.54–7.90 (m, 12H, C_1-, C_2-, C_3-, C_7-, C_8-, C_9-, C_{10}-, C'_2-, C'_3-, C'_4-, C'_5- and C'_6-H), 8.19 (d, 1H, C_4-H, $J = 8.44$ Hz). ^{13}C NMR ($CDCl_3$) δ: 43.2 (N_{12}-CH_3), 121.0 (C_8), 122.7 (C_7), 125.8 (C'_2, C'_6), 126.2 (C'_3, C'_4, C'_5), 126.7 (C_{10}), 127.6 (C_9), 127.7 (C_1), 128.1 (C_4), 128.8 (C_3), 129.2 (C_2), 133.4 (C'_1), 137.1 (C_6), 138.8 (C_{6a}), 147.6 (C_{4a}), 148.3 (C_{5a}), 149.7 (C_{10a}), 151.5 (C_{12a}), 153.7 (C_{11a}), 179.6 (C=O). MS: *m*/*z* (%) 336 (M^+, 100), 335 (27), 322 (17), 321 (20), 252 (13), 166 (24), 77 (58), 41 (49). Anal. calcd. for $C_{23}H_{15}N_2ClO$: C, 82.14; H, 4.76; N, 8.33. Found: C, 82.05; H, 4.81; N, 8.37%.

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