Regioselective Synthesis of Benzo[g]- and Benzo[f]quinolines by Reaction of Chalcones with Naphthalen-2-amine

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Abstract—Reactions of 4- and 4'-substituted chalcones with naphthalen-2-amine afforded isomeric benzo[g]and benzo[f]quinoline derivatives. Depending on the substituent in the initial chalcone, the cyclization follows two pathways through different intermediates. The product structure was confirmed by IR, ¹H and ¹³C NMR, and mass spectra and X-ray analysis.

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Benzoquinolines can be synthesized by the classical Skraup, Doebner–Miller, Doebner, Knorr, and Friedländer reactions which were originally proposed for the synthesis of quinolines. Some alternative ways of constructing benzo[f]- [1–15] and benzo[g]quinoline heterocyclic systems [16–19] have also been reported, and these methods in any case utilize the aromatic ring of naphthalen-2-amine.

Heterocyclization could lead to the formation of linearly or angularly fused isomers. For example, β -aminotetralin reacted with glycerol in the presence of concentrated sulfuric acid and nitrobenzene or β -nitrotetralin as oxidant (analog of Skraup reaction) to produce 65% of a mixture of 5,6- and 6,7-tetramethylenequinolines which were then converted to the corresponding benzo[*f*]- and benzo[*g*]quinolines [20]. The isomers were successfully separated by treatment with picric acid and subsequent extraction of the picrates with ethanol. The extract contained 60% of benzo[*g*]quinolinium picrate and 27% of benzo[*f*]- quinolinium picrate. Analogous reaction of glycerol with naphthalen-2-amine in the presence of sulfuric acid also afforded isomeric benzo[*f*]- and benzo[*g*]- quinolines, the angularly fused isomer being the major product [21]. Benzo[f]quinoline was formed as the only product in the condensation catalyzed by zinc chloride. The reaction of naphthalen-2-amine with dibenzoylmethane gave a mixture of benzo[f]- and benzo[g]quinoline derivatives [22].

We previously showed [23] that the condensation of substituted chalcones with primary aromatic amines of the aniline series in anhydrous ethanol in the presence of the corresponding amine hydrochloride as catalysts gives unsaturated Schiff bases or β -arylamino ketones, depending on the electronic properties of substituents in the initial chalcone. The present work was aimed at elucidating whether the regularities observed in [23] are valid for the reaction of chalcones with naphthalen-2-amine. The reaction was regioselective at both initial addition and cyclization steps.

Benzylideneacetophenones **1a–1h** reacted with naphthalen-2-amine (**2**) in anhydrous methanol in the presence of naphthalen-2-amine hydrochloride as catalyst to give 3-(naphthalen-2-ylamino)prop-2-en-1-ones **3** or unsaturated Schiff bases **4** (Scheme 1). Presumably, as with substituted anilines, the reaction direction





 $R^{1} = H, R^{2} = O_{2}N(\mathbf{a}), Cl(\mathbf{b}), Br(\mathbf{c}); R^{1} = Me_{2}N, R^{2} = H(\mathbf{d}); R^{1} = H, R^{2} = MeO(\mathbf{e}); R^{1} = Br, R^{2} = H(\mathbf{f});$ $R^{1} = Cl, R^{2} = H(\mathbf{g}); R^{1} = R^{2} = H(\mathbf{h}).$

is determined by electronic properties of substituents in chalcone 1. The presence of an electron-withdrawing nitro group in the aromatic ring of the ketone fragment favors formation of intermediate 3, whereas chalcones with weakly acceptor or donor substituents in both benzene rings give rise to Schiff base intermediate 4. The nitro group in 1a reduces the polarity of the carbonyl group and increases polarization of the $C^{\alpha}=C^{\beta}$ bond.

Intermediates **3** and **4** possess two nucleophilic centers in the α - and γ -positions of the naphthalene fragment. Heterocyclization involving the α -carbon

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atom afforded angularly fused tricyclic structures **5** and **7**, whereas alternative cyclization through the γ -carbon atom led to the formation of linearly fused isomers **6** and **8** (Scheme 1). The structure of compounds **5–8** was determined on the basis of their IR, ¹H and ¹³C NMR, and mass spectra and elemental analyses, and the structures of **5** and **7d** were proved by X-ray analysis.

Regioselective formation of benzo[*f*]quinolines was observed previously in the three-component condensation of acetophenones with benzaldehydes and naphthalen-2-amines catalyzed by HCl [24]. In the first



Fig. 1. Structure of the molecule of 1-(4-nitrophenyl)-3-phenylbenzo[*f*]quinoline (**5**) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

stage, two intermediates were formed, the corresponding chalcone and *N*-(benzylidene)naphthalen-2-amine. The latter reacted with acetophenone to give β -arylamino ketone which underwent hydramine fission in acid medium to produce chalcone **1h** and naphthalen-2-amine (**2**). The latter reacted wth each other to form intermediate **4h** where the vinylic β -carbon atom is likely to coordinate to C^a of the naphthalene fragment, and the cyclization furnished benzo[*f*]quinoline **7h**.

In this work, the reaction was carried out under milder conditions. The use of anhydrous solvent and



Fig. 2. Structure of the molecule of 1-(4-dimethylamino-phenyl)-3-phenylbenzo[<math>f]quinoline (7d) according to the X-ray diffraction data. Non-hydrogen atoms are shown as thermal vibration ellipsoids with a probability of 50%.

ammonium salt as catalyst allows formation of both unsaturated Schiff base and β -arylamino ketone and their subsequent heterocyclization. The isomer ratio was determined by GC/MS. It was found that in all cases the corresponding benzo[*f*]quinoline (angular isomer) was the major product; it was characterized by a shorter retention time than the linearly fused isomer (benzo[*g*]quinoline). Linear isomers **6**, **8b**, **8c**, **8f**, and **8g** were detected by GC/MS, but only compound **8d** was isolated as individual compound in the reaction with chalcone **1d** derived from 4-(dimethylamino)benzaldehyde and acetophenone.

The formation of compounds 7 and 8 from intermediate 4, as well as the formation of 5 and 6 from intermediate 3, is accompanied by loss of two hydrogen atoms, most probably, as a result of oxidation with atmospheric oxygen. Simple calculations showed that the available air is sufficient to oxidize intermediate 4 or 3. However, chromatographic study of the reaction $1d \rightarrow 7d + 8d$ revealed that the process is more complicated. In the reaction mixture we detected the product of reduction of the C=C bond in the initial chalcone, and its amount increased as the reaction progressed. These findings suggest that the initial chalcone acts as hydrogen acceptor.

Figure 1 shows the molecular structure of compound 5 in crystal. All bond lengths and bond angles in molecule 5 approach the corresponding reference values. The benzoquinoline fragment is not planar, and it can be represented as a part of a helix, in contrast to 1-unsubstituted benzo[f]quinolines with almost planar tricyclic system [25, 26]. The dihedral angles between the mean-square planes of the pyridine ring and $C^4C^5C^6C^7C^8C^9$ and $C^8C^9C^{10}C^{11}C^{12}C^{13}$ fragments are 4.6 and 10.0°, respectively. The phenyl substituent is almost coplanar to the pyridine ring, whereas the *p*-nitrophenyl substituent is turned through a dihedral angle of 66.5° with respect to the pyridine ring. Molecules 5 in crystal are packed in parallel layers, where the neighboring aromatic fragments of molecules in the adjacent layers approach each other to a distance of ~3.4–3.7 Å due to weak π – π -stacking interactions stabilizing the layered structure.

The X-ray diffraction data for compound **5** were obtained from a $0.67 \times 0.41 \times 0.22$ -mm yellow single crystal on an Xcalibur R diffractometer with a CCD detector according to standard procedure [Mo K_{α} radiation, 295(2) K, ω -scanning through a step of 1 deg] [27]. A correction for absorption was applied empirically by the SCALE3 ABSPACK algorithm [27].

Monoclinic crystal system, space group *P*-1; unit cell parameters: a = 8.7263(14), b = 9.7151(13), c =12.4512(18) Å; $\alpha = 69.683(13)$, $\beta = 70.802(14)$, $\gamma =$ $88.946(12)^\circ$; V = 929.4(2) Å³; $C_{25}H_{16}N_2O_2$; Z = 2. The structure was solved by the direct method (SHELXS-97) and was refined against F^2 by the fullmatrix least-squares method in anisotropic approximation for all non-hydrogen atoms (SHELXL-97) [28]. The positions of hydrogen atoms were refined according to the riding model in isotropic approximation with dependent thermal parameters. Final divergence factors: $R_1 = 0.0512$, $wR_2 = 0.1403$ [for 3286 reflections with $I > 2\sigma(I)$]; $R_1 = 0.0655$, $wR_2 = 0.1502$ (for 4256 independent reflections); goodness of fit S = 1.105.

Figure 2 shows the molecular structure of compound **7d** according to the X-ray diffraction data. The geometric parameters (bond lengths and bond angles) of molecule **7d** are typical of structurally related compounds. The phenyl substituent lies in the heterocycle plane. The C⁴ atom is characterized by the largest deviation (0.225 Å) from the mean-square plane formed by the system consisting of 20 atoms. This may be due to perturbation effect of the dimethylaminophenyl group which is turned through a dihedral angle of ~66° with respect to the heterocycle plane.

The X-ray diffraction data for compound 7d were acquired on an Xcalibur E four-circle diffractometer with a CCD detector from a $0.25 \times 0.2 \times 0.15$ -mm fragment of a colorless single crystal. The data were collected at 295(2) K and processed according to standard procedure [Mo K_{α} radiation, $\lambda 0.71073$ Å; $\omega/2\theta$ -scanning with a step of 1 deg]. A correction for absorption was applied empirically [29] using Olex2 [30], and the structure was solved using Superflip [31]. The structure was refined against \tilde{F}^2 by the full-matrix leastsquares method in anisotropic approximation for all non-hydrogen atoms (SHELXL [28]). Hydrogen atoms were placed in geometrically calculated positions which were refined in isotropic approximation with dependent thermal parameters according to the riding model. Triclinic crystal system, space group P-1; unit cell parameters: a = 9.4559(8), b = 10.1272(6), c =10.8339(6) Å; $\alpha = 91.089(5)$, $\beta = 95.785(6)$, $\gamma =$ $105.521(6)^{\circ}$; $V = 993.40(11) \text{ Å}^3$; $C_{27}H_{22}N_2$; Z = 2. Final divergence factors: $R_1 = 0.0597$, $wR_2 = 0.1591$ [for 3306 reflections with $I > 2\sigma(I)$; $R_1 = 0.1023$, $wR_2 =$ 0.1921 (for all 5394 independent reflections); goodness of fit S = 1.009.

The X-ray diffraction data for compounds **5** and **7d** were deposited to the Cambridge Crystallographic

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Data Centre (CCDC entry nos. 1490079 and 1490087, respectively) and are available free of charge at *www.ccdc.cam.ac.uk/data_request/cif*.

Signals in the NMR spectra were assigned with account taken of published data for 1,3-diphenylbenzo-[f]quinoline as model [32], whose ¹H NMR spectrum spectrum is fairly simple. In addition, the data of [24] were used. Compounds 5, 7d, and 8d were analyzed using DEPT135, DEPTq, HSQC (direct ¹³C-¹H couplings) and HMBC (long-range ¹³C-¹H correlations) NMR techniques. The ¹H NMR spectra of angularly fused benzoquinolines 5 and 7b-7g characteristically showed a singlet of the 2-H proton at δ 7.65–7.97 ppm, a doublet of 7-H at δ 7.88–8.17 ppm (${}^{3}J \approx$ 7.6, ${}^{4}J \approx$ 1.5 Hz), and doublets of 5-H and 6-H at δ 7.76–8.06 and 7.80–8.01 ppm, respectively (${}^{3}J \approx 7.6$ Hz). Signals in the ¹H NMR spectra of linearly fused benzo[g]quinolines were observed in a stronger field relative to the corresponding signals of their angular isomers $(\Delta \delta = 0.1 - 0.3 \text{ ppm}).$

EXPERIMENTAL

The IR spectra were recorded on a Bruker IFS 66ps spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra of 5, 7d. and 8d were measured on a Bruker instrument at 400 MHz for ¹H (relative to tetramethylsilane as internal standard) and 100 MHz for ¹³C (relative to the solvent signal). The NMR spectra of the other compounds were recorded on a Varian Mercury Plus 300 spectrometer at 300 MHz for ¹H (relative to hexamethyldisiloxane as internal standard) and 75 MHz for 13 C (relative to the CDCl₃ signal). The products were isolated by column chromatography on Silicagel 60 (0.063–0.2 mm, Alfa Aesar). Their purity was checked by GC/MS on an Agilent Technologies 6890N/5975B GC/MS system (HP-5ms capillary column, 30000× 0.25 mm; injector temperature 260°C, oven temperature programming at a rate of 20-40 deg/min; carrier gas He, flow rate 1 mL/min; electron impact, 70 eV). The elemental analyses were obtained on a Leco CHNS 9321P analyzer (USA). The melting points were determined with a PTP melting point apparatus.

 α,β -Unsaturated ketones **1a–1h** were synthesized by aldol condensation of the corresponding acetophenones with benzaldehydes according to standard procedure [33]. Their physical constants were consistent with reference data [34].

1,3-Diarylbenzo[f]quinolines 5a and 7b-7h and 2,4-diarylbenzo[g]quinolines 6 and 8b-8g (general

procedure). A mixture of 6 mmol of chalcone 1a-1h, 6 mmol of naphthalen-2-amine (2), and 0.6 mmol of naphthalen-2-amine hydrochloride in 3 mL of anhydrous methanol was heated for 6 h (12 h in the synthesis of 7d and 8d) at 100°C in a sealed ampule. The mixture was cooled, and the crystalline product was filtered off and purified by column chromatography on silica gel using petroleum ether (40–70°C)–ethyl acetate (0 to 10 vol % of the latter) as eluent.

1-(4-Nitrophenyl)-3-phenylbenzo[f]quinoline (5). Greenish prisms, mp 210-212°C (from EtOAc). IR spectrum, v, cm⁻¹: 1595, 1580, 1544, 1512 (NO₂, asym.), 1342 (NO₂, sym.), 1305, 1205, 1285, 1260, 1105, 833, 774, 688, 661. ¹H NMR spectrum (CDCl₃), δ, ppm: 7.23 (1H, p'-H, ${}^{3}J = 8.1$, 8.1, ${}^{4}J = 1.5$ Hz), 7.50-7.59 m (5H, 8-H, 9-H, 10-H, m'-H), 7.67 d (2H, o-H, ${}^{3}J$ = 12.0 Hz), 7.76 s (1H, 2-H), 7.93 d (1H, 7-H, ${}^{3}J = 8.0$ Hz), 8.03 d (1H, 6-H, ${}^{3}J = 8.0$ Hz), 8.16 d (1H, 5-H, ${}^{3}J = 8.0$ Hz), 8.26 d (2H, o'-H, ${}^{3}J = 8.0$ Hz), 8.42 d (2H, *m*-H, ${}^{3}J = 8.0$ Hz). ${}^{13}C$ NMR spectrum (CDCl₃), δ_C, ppm: 120.57, 121.47, 123.97, 125.32, 126.34, 126.83, 127.19, 128.40, 128.45, 128.55, 129.07, 129.11, 131.33, 132.53, 138.02, 145.92, 147.19, 149.16, 149.38, 155.06. Mass spectrum, m/z $(I_{\text{rel}}, \%)$: 376 (100) $[M]^+$, 329 (44), 251 (14), 164 (23). Found, %: C 78.11; H 4.18; N 7.31. C₂₅H₁₆N₂O₂. Calculated, %: C 79.77; H 4.28; N 7.44.

4-(4-Nitrophenyl)-2-phenylbenzo[g]quinoline (6) was not isolated in the pure state. Mass spectrum, m/z (I_{rel} , %): 377 (27) $[M + 1]^+$, 376 (100) $[M]^+$, 377 (34) $[M - 1]^+$, 346 (13), 329 (41), 164 (16).

3-(4-Chlorophenyl)-1-phenylbenzo[f]quinoline (**7b**). Colorless plates, mp 156–157°C (from EtOH). IR spectrum, v, cm⁻¹: 1577, 1544, 1525, 1491, 1451, 1360, 1331, 1283, 1255, 1106, 1255, 1106, 1093, 1014, 883, 869, 754, 699. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.17 d.d (1H, *p*-H, ³*J* = 7.8, 7.8 Hz), 7.36 d (2H, m'-H, ³*J* = 8.4 Hz), 7.41–7.51 m (6H, H_{arom}), 7.64 d (1H, H_{arom}, ³*J* = 8.4 Hz), 7.70 s (1H, 2-H), 7.82 d (1H, H_{arom}, ³*J* = 7.8 Hz), 7.93 d (1H, 5-H, ³*J* = 9.0 Hz), 8.08 d (1H, 6-H, ³*J* = 8.7 Hz), 8.17 d (2H, *o'*-H, *J* = 7.2 Hz). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 121.57, 121.62, 122.46, 125.61, 126.53, 127.32, 127.80, 128.69, 128.81, 129.02, 129.42, 129.79, 131.54, 132.87, 132.88, 134.21, 138.76, 141.36, 147.68, 149.77, 155.39. Found, %: C 80.68; H 4.39; N 3.88. C₂₅H₁₆ClN. Calculated, %: C 82.07; H 4.41; N 3.83.

3-(4-Bromophenyl)-1-phenylbenzo[f]quinoline (7c). Colorless plates, mp 179–180°C (from EtOH). IR spectrum, v, cm⁻¹: 1576, 1543, 1067, 1011, 751, 694. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.16 d.d (1H, *p*-H, ³*J* = 7.5, 7.5 Hz), 7.28 d (2H, *m*-H, ³*J* = 8.1 Hz), 7.38–7.49 m (4H, H_{arom}), 7.62 m (3H, H_{arom}), 7.68 s (1H, 2-H), 7.80 d (1H, 7-H, ³*J* = 8.1 Hz), 7.91 d (1H, 5-H, ³*J* = 9.3 Hz), 8.06 d (1H, 6-H, ³*J* = 9.3 Hz), 8.16 d (2H, *o'*-H, ³*J* = 8.1 Hz). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 121.49, 122.32, 122.34, 125.57, 126.52, 127.29, 127.78, 128.66, 128.79, 129.01, 129.34, 130.07, 131.52, 132.34, 132.84, 138.73, 141.81, 1247.60, 149.75, 155.36. Mass spectrum, *m/z* (*I*_{rel}, %): 411/409 (100) [*M*]⁺, 330 (76), 250 (40), 226 (14), 165 (79), 150 (19). Found, %: C 72.77; H 3.75; N 3.12. C₂₅H₁₆BrN. Calculated, %: C 73.18; H 3.93; N 3.41.

1-(4-Dimethylaminophenyl)-3-phenylbenzo[f]quinoline (7d). Yellow-brown prisms, mp 171–174°C (from EtOH). IR spectrum (film), v, cm⁻¹: 1677, 1607, 1579 1545, 1514, 1480, 1451, 1361, 1115, 836, 755, 696. ¹H NMR spectrum (CDCl₃), δ , ppm: 2.99 s (6H, NMe₂), 6.88 d (2H, *m*-H, J = 8.4 Hz), 7.24 d.d (1H, p'-H, J = 7.5, 7.5 Hz), 7.32 d (2H, H_{arom}, J = 8.4 Hz), 7.51–7.59 m (4H, H_{arom}), 7.90 d (1H, H_{arom} , J =7.8 Hz), 7.91 s (1H, 2-H), 8.00 d (1H, 7-H, ${}^{3}J$ = 7.2 Hz), 8.02 d (1H, 5-H, ${}^{3}J = 9.0$ Hz), 8.12 d (1H, 6-H, ${}^{3}J = 9.0$ Hz), 8.32 d (2H, o'-H, ${}^{3}J = 7.5$ Hz). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 40.06, 111.73, 112.25, 121.55, 124.77, 125.68, 126.84, 127.59, 127.91, 128.21, 128.55, 128.74, 129.58, 130.14, 130.64, 132.25, 138.80, 149.12, 149.35, 149.82, 154.81. Mass spectrum, m/z (I_{rel} , %): 377 (29) $[M + 1]^+$, 376 (100) $[M]^+$, 377 (24) $[M-1]^+$, 346 (15), 329 (46), 251 (12), 164 (16). Found, %: C 85.96; H 5.97; N 7.17. C₂₇H₂₂N₂. Calculated, %: C 86.60; H 5.92; N 7.48.

3-(4-Methoxyphenyl)-1-phenylbenzo[f]quinoline (7e). Colorless plates, mp 173–174°C (from EtOH). IR spectrum, v, cm⁻¹: 1605, 1579, 1546, 1509, 1363, 1285, 1244, 1177, 1022, 893, 872, 839, 774, 694. ¹H NMR spectrum (CDCl₃), δ , ppm: 3.85 s (3H, OMe), 7.00 d (2H, *m*-H, ${}^{3}J = 8.1$ Hz), 7.14 d.d (1H, p'-H, ${}^{3}J$ = 8.1, 7.5 Hz), 7.32 d (2H, o-H, ${}^{3}J$ = 8.4 Hz), 7.38-7.50 m (4H, H_{arom}), 7.74 m (2H, 2-H, H_{arom}), 7.80 d (1H, 7-H, ${}^{3}J = 8.1$ Hz), 7.92 d (1H, 5-H, ${}^{3}J =$ 8.7 Hz), 8.08 d (1H, 6-H, ${}^{3}J = 8.7$ Hz), 8.18 d (2H, o-H, ${}^{3}J = 8.1$ Hz). ${}^{13}C$ NMR spectrum (CDCl₃), δ_{C} , ppm: 55.28, 114.57, 121.96, 122.95, 125.42, 126.33, 127.33, 127.93, 128.51, 128.75, 129.04, 129.19, 129.54, 129.81, 131.33, 132.82, 135.20, 139.02, 148.87, 149.76, 155.31, 159.53. Found, %: C 85.75; H 5.27; N 3.84. C₂₆H₁₉NO. Calculated, %: C 86.40; H 5.30; N 3.88.

1-(4-Bromophenyl)-3-phenylbenzo[*f***]quinoline** (**7f).** Colorless plates, mp 179–180°C (from EtOH). IR

spectrum, v, cm⁻¹: 1576, 1544, 1354, 951, 799, 675. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.06 d.d (1H, *p'*-H, ³*J* = 8.7, 7.2 Hz), 7.34–7.39 m (4H, 8-H, 9-H, *m'*-H), 7.40–7.46 m (4H, 10-H, *o*-H), 7.53 d (2H, *o*-H, ³*J* = 8.4 Hz), 7.57 d (1H, H_{arom}, ³*J* = 8.4 Hz), 7.65 s (1H, 2-H), 7.76 d (1H, 5-H, ³*J* = 8.1 Hz), 7.88 d (1H, 6-H, ³*J* = 8.1 Hz), 8.00 d (2H, *o'*-H, ³*J* = 8.4 Hz). ¹³C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 121.28, 122.90, 123.84, 125.57, 126.54, 128.01, 128.17, 128.30, 128.60, 128.86, 128.90, 129.22, 129.61, 131.65, 131.89, 132.90, 137.80, 142.81, 149.30, 149.71, 153.95. Mass spectrum, *m/z* (*I*_{rel}, %): 411/409 (100) [*M*]⁺, 328 (68), 327 (17), 326 (123), 252 (25), 251 (20), 228 (17), 226 (15), 164 (57), 163 (36), 150 (21). Found, %: C 72.87; H 3.93; N 3.11. C₂₅H₁₆BrN. Calculated, %: C 73.18; H 3.93; N 3.41.

1-(4-Chlorophenyl)-3-phenylbenzo[f]quinoline (7g). Colorless plates, mp 173–174°C (from EtOH). IR spectrum, v, cm⁻¹: 1576, 1545, 1491, 1355, 1280, 1256, 1167, 1089, 1010, 834, 772, 753, 700. ¹H NMR spectrum (CDCl₃), δ , ppm: 7.13 d.d.d (1H, p'-H, ${}^{3}J =$ 7.5, 7.5, ${}^{4}J = 0.9$ Hz), 7.41–7.52 m (8H, H_{arom}), 7.63 d $(1H, H_{arom}, {}^{3}J = 9.0 \text{ Hz}), 7.72 \text{ s} (2-H), 7.84 \text{ d} (1H, 7-H)$ ${}^{3}J = 8.1$ Hz), 7.95 d (1H, 5-H, ${}^{3}J = 9.0$ Hz), 8.07 d (1H, 6-H, ${}^{3}J = 9.3$ Hz), 8.15 d (2H, o'-H, ${}^{3}J = 8.4$ Hz). ¹³C NMR spectrum (CDCl₃), δ_{C} , ppm: 121.40, 122.89, 125.60, 126.56, 127.02, 128.18, 128.32, 128.61, 128.94, 129.25, 129.64, 131.67, 132.93, 135.47, 137.37, 137.77, 142.85, 149.32, 153.99. Mass spectrum, m/z ($I_{\rm rel}$, %): 365 (100) $[M]^+$, 328 (17), 330 (76), 252 (31), 251 (24), 228 (12), 226 (13), 164 (36), 163 (28), 150 (15). Found, %: C 81.26; H 4.40; N 3.86. C₂₅H₁₆ClN. Calculated, %: C 82.07; H 4.41; N 3.83.

1,3-Diphenylbenzo[*f*]**quinoline** (7h). mp 142–143°C; published data [32]: mp 144–145°C. ¹H NMR spectrum (DMSO-*d*₆), δ , ppm: 7.18 d.d.d (1H, *p'*-H, ³*J* = 8.1, 8.1, ⁴*J* = 1.5 Hz), 7.51–7.61 m (10H, 8-H, 9-H, 10-H, *o*-H, *m*-H, *p*-H, *m'*-H), 7.97 s (1H, 2-H), 8.01 d.d (1H, 7-H, ³*J* = 8.0, ⁴*J* = 1.6 Hz), 8.06 d (1H, 5-H, ³*J* = 8.0 Hz), 8.15 d (1H, 6-H, ³*J* = 8.0 Hz), 8.35 d (2H, *o'*-H, ³*J* = 8.0 Hz). ¹³C NMR spectrum (DMSO-*d*₆), δ_{C} , ppm: 121.65, 122.51, 126.17, 127.22, 127.63, 127.74, 128.70, 128.83, 129.31, 129.53, 129.80, 130.08, 132.13, 133.03, 138.44, 142.68, 149.45, 149.50, 154.84. Found, %: C 89.64; H 5.05; N 3.91. C₂₅H₁₇N. Calculated, %: C 90.60; H 5.17; N 4.23.

4-(Dimethylaminophenyl)-2-phenylbenzo[g]quinoline (8d). Yellow powder, mp 220–222°C. IR spectrum (film), v, cm⁻¹: 1609, 1579, 1530, 1364, 1196, 836, 802, 754. ¹H NMR spectrum (CDCl₃), δ , ppm: 3.02 s (6H, NMe₂), 6.86 d (2H, *m*-H, ${}^{3}J$ = 8.7 Hz), 7.16 d.d (1H, 8-H, ${}^{3}J$ = 7.5, 7.5 Hz), 7.47–7.55 m (4H, 7-H, *m*'-H, *p*'-H), 7.59–7.60 m (3H, 6-H, *o*-H), 8.00 d (2H, *o*'-H, ${}^{3}J$ = 7.5 Hz), 8.09 d (1H, 9-H, ${}^{3}J$ = 8.7 Hz). 13 C NMR spectrum (CDCl₃), $\delta_{\rm C}$, ppm: 39.77, 111.69, 120.40, 121.23, 124.89, 125.47, 127.22, 127.48, 127.78, 127.87, 127.94, 128.05, 128.62, 129.32, 130.84, 132.09, 142.71, 148.49, 148.78, 150.89, 154.77. Found, %: C 85.30; H 5.84; N 7.02. C₂₇H₂₂N₂. Calculated, %: C 86.60; H 5.92; N 7.48.

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