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TETRAHEDRON

A Simple Synthesis of Aminoazapolycyclic Compounds via a Photochemically Induced Cyclization Reaction of 3-Amino-2-alkene Imines in an Acid Medium

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Abstract: We describe the synthesis of benzo-, dibenzo- and naphthoquinolines substituted by alkyl-, arylamino or a NH_2 group from irradiation of 3-naphthyl- and 3-phenanthryl-2-alkene imines under mild reaction conditions. This reaction is suitable for the preparation of four-ring aminoazapolycyclic compounds containing a non-aromatic ring. The compounds obtained can potentially be used in medicinal chemistry.

Keywords: Imines, Quinolines, Polycyclic heterocyclic compounds

INTRODUCTION

The quinoline and, in particular, the benzoquinoline skeletons are found in many substances with biological activity or industrial applications.[1,2] Moreover, aminoquinolines and aminobenzoquinolines are widely used in medicinal chemistry due to their pharmacological properties. For example, they are used against protozoal diseases (malaria, amebiasis, giardiasis) and display anthelmintic activity;[2] they have been used for the treatment of gastric disorders,[3] and applied as antihypertensive and antiinflammatory agents,[4] and aminoacridine derivatives have produced some improvements in Alzheimer's disease.[2a] Furthermore, aminoquinolines are adequate substrates for the synthesis of azasteroids,[5] compounds which also exhibit interesting pharmacological properties.[6]

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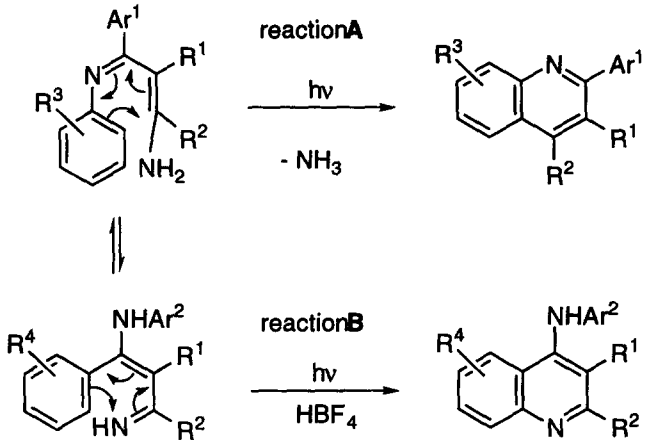
We have previously reported the preparation of substituted quinolines by the irradiation of 3-amino-2-alkene imines.[7-9] These alkene imines show an equilibrium between two tautomers that can both participate in photocyclization processes depending on the reaction conditions (Scheme 1). Thus, irradiation in a neutral medium allows the preparation of substituted quinolines (Scheme 1, reaction **A**)[7] while irradiation in the presence of tetrafluoroboric acid leads to the formation of 4-(arylamino)quinolines (Scheme 1, reaction **B**).[8] By the inclusion of benzo units in the ring that participates in the electrocyclization described in reaction **A**, our methodology permits the synthesis of benzoquinolines.[9]



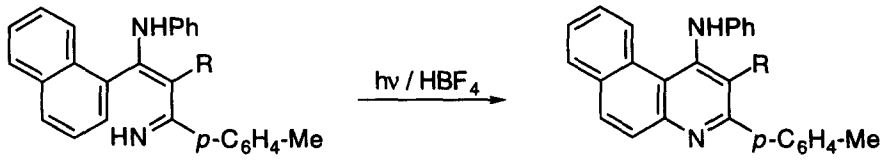
Scheme 1

Taking into account the growing significance of the aminobenzoquinoline derivatives, we felt that it would be of interest to synthesize these polycyclic systems using our methodology. Herein, we wish to report a simple preparation of aminobenzoquinolines from irradiation of 3-amino-2-alkene imines in acid medium.

RESULTS AND DISCUSSION

First, we prepared the 3-(1-naphthyl)-3-(phenylamino)-1-*p*-tolyl-2-alkene imine **1**,[10] in which, according to Scheme 1 (reaction **B**), the naphthyl group should be the active ring in the cyclization. The ultraviolet spectrum of compound **1** in the presence of an excess of tetrafluoroboric acid shows the displacement of the band at 362 nm to the visible region (366 nm). A 2×10^{-2} M methanolic solution of this compound, also containing the equivalent

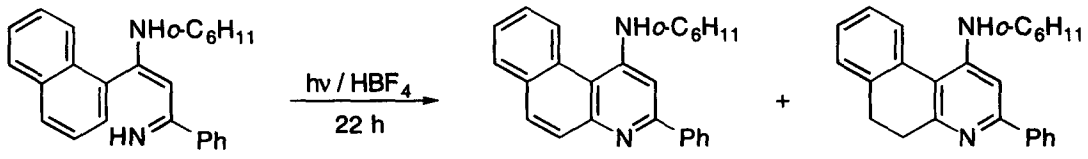
quantity of HBF_4, was irradiated with a 125 W medium-pressure mercury lamp through quartz; reaction was monitored by ^1H NMR spectroscopy. The complete consumption of the starting material occurred after 23 h. The resulting product was purified by column chromatography (silica gel, hexane/Et_2O, 2:1), recrystallized (hexane/Et_2O) and identified as 4-(phenylamino)-2-*p*-tolylbenzo[*f*]quinoline **2** by its spectroscopic data (^1H and ^{13}C NMR) and mass spectrometry (Scheme 2). Taking advantage of the simplicity of the functionalization of 3-amino-2-alkene imines at the 2-position,[11] we carried out the preparation of 2-benzyl-3-(1-naphthyl)-3-(phenylamino)-1-*p*-tolyl-2-alkene imine **3** from compound **1**. Irradiation of **3** leads to the formation of the corresponding 3-benzyl-4-(phenylamino)benzo[*f*]quinoline **4** (Scheme 2).



1 R = H — 23 h — **2** (40%)
3 R = CH_2Ph — 24 h — **4** (45%)

Scheme 2

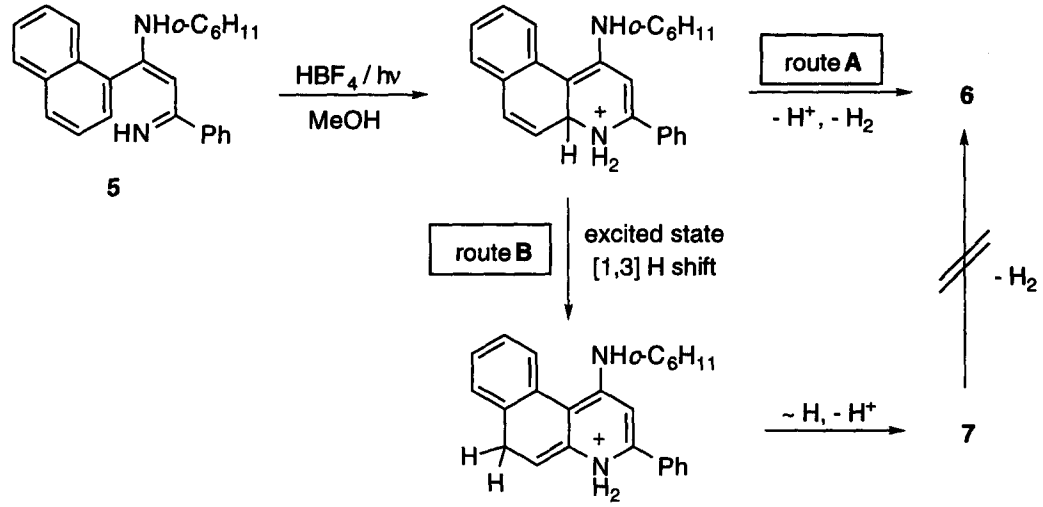
We had previously investigated the photochemical behavior of the 3-(arylamino)-2-alkene imine[7-9] but not that of the 3-(alkylamino) analogues. We therefore performed the irradiation of 3-(cyclohexylamino)-3-(1-naphthyl)-1-phenyl-2-alkene imine **5** (prepared according to ref 10) for 22 h. In this case, the presence of two photoproducts in the crude reaction was observed. After separation and purification by column chromatography (silica gel, hexane/Et_2O, 2:1), their spectroscopic data revealed the formation of the expected aminobenzo[*f*]quinoline **6** and the dihydro derivate **7** (Scheme 3).



5 — **6** (21%) + **7** (10%)

Scheme 3

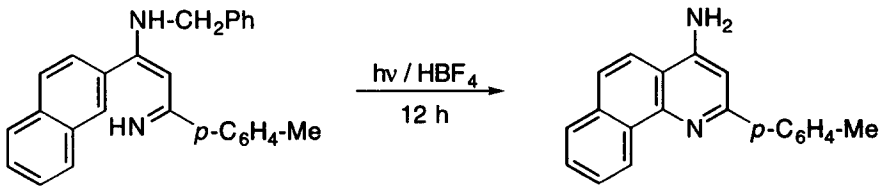
The dihydro compound **7** could be the precursor of quinoline **6**. In order to check this possibility, we irradiated **7** in the absence and in the presence of an oxidising agent (O_2 and/or I_2). In both cases, we did not observe any change, which implies that compound **7** cannot be an intermediate in the reaction path to obtain **6**. We propose an initial six π-electron photoanelation process with formation of a secondary amine[8] which loses molecular hydrogen under irradiation[12] thus yielding the aminoquinoline **6** (Scheme 4, route **A**). An alternative route supposes that, after photocyclization, excited state [1,3]-hydrogen shift and enamine-imine tautomerism (assisted by the presence of acid) occur to give the dihydro derivative **7** (Scheme 4, route **B**). The formation of these dihydro compounds was not observed for 3-(arylamino)-2-alkene imine, which is in agreement with the larger lifetime measured for the excited state of alkylamines compared to that of arylamines.[13]



Scheme 4

The feasibility of the 3-(arylamino)-2-alkene imine's participation in the formation of (alkylamino)benzoquinolines is very interesting because, if the alkyl group can easily be removed, this allows the preparation of benzoquinolines substituted by a NH_2 group, compounds that have been recently used as an entry to Tröger's base analogs.[14] Thus, the irradiation of 3-(benzylamino)-3-(2-naphthyl)-1-*p*-tolyl-2-alkene imine **8** (prepared according to ref 10) for 12 h directly gave the 4-amino-2-*p*-tolylbenzo[*h*]quinoline **9** (Scheme 5). Only the regioisomer represented in Scheme 5 was detectable in the crude

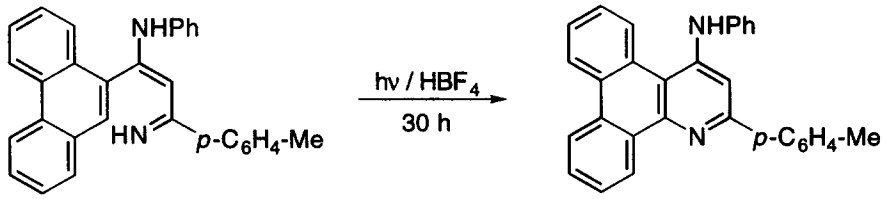
mixture (^{1}H NMR, 300 MHz). This regiochemistry is related to the photocyclizations of 3-amino-2-alkene imines in a neutral medium[9] and that of conjugated arylalkenes described in the literature.[15]



8 **9** (45%)

Scheme 5

Next, we were interested in using our methodology for the synthesis of dibenzo- or naphtho-quinolines. First, we selected the alkene imine **10**[10] as the starting material because it should yield only one regioisomer. This was indeed the case; the irradiation of **10** for 30 h gave the 4-(phenylamino)-2-*p*-tolyldibenzo[*f,h*]quinoline **11** (Scheme 6).



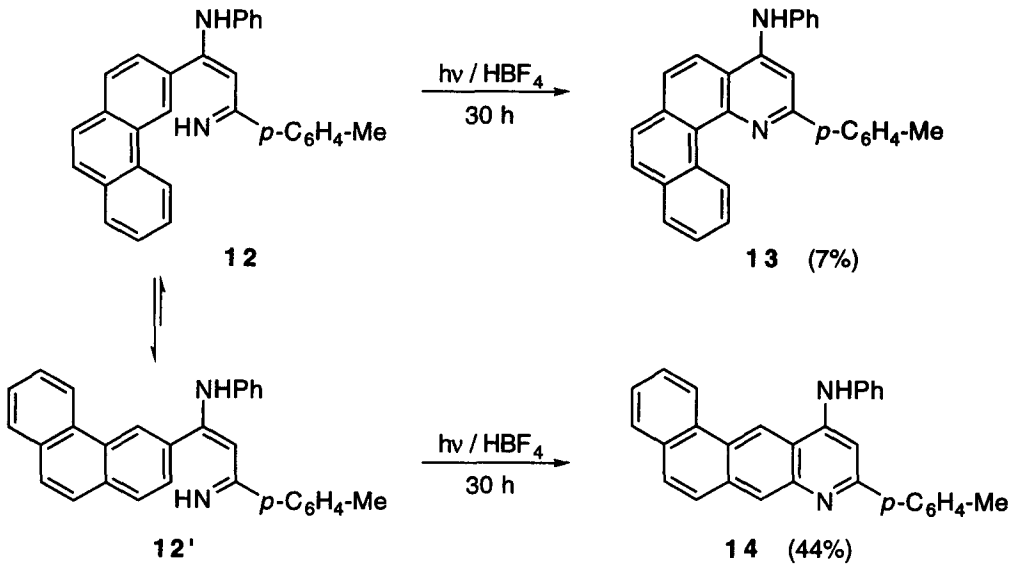
10 **11** (36%)

Scheme 6

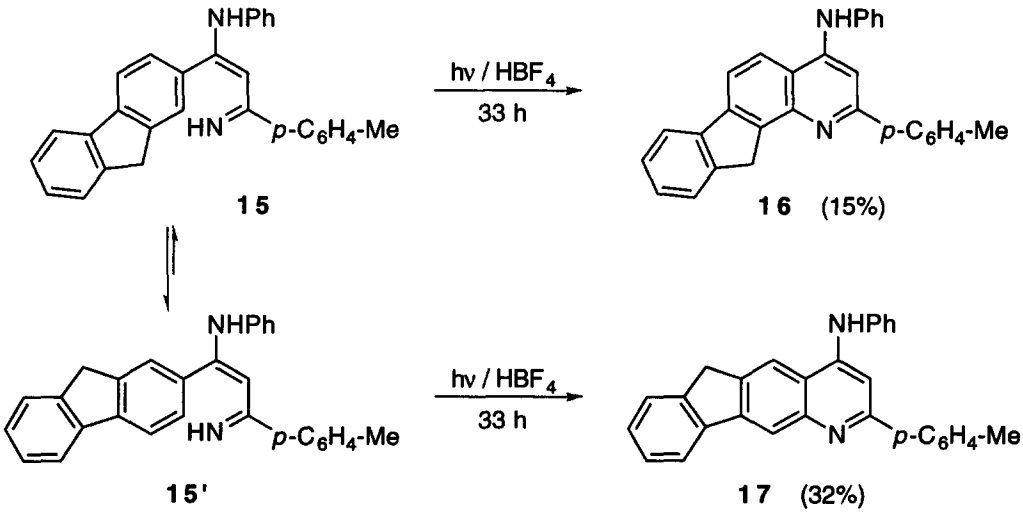
Interestingly, despite the fact that the 4-position should be preferentially involved in the cyclization due to electronic effects,[15] the irradiation of the 3-(3-phenanthryl)alkene imine **12** for 30 h gave only 7% of the expected naphtho[2,1-*h*]quinoline **13** while the 4-(phenylamino)-2-*p*-tolylnaphtho[1,2-*g*]quinoline **14** was the major product (Scheme 7). This regiochemistry may be explained considering that steric factors play an important role in the course of the reaction.

In the same way, we prepared[10] and irradiated the 2-fluorenyl-3-(phenylamino)-1-*p*-tolyl-2-alkene imine **15** for 33 h. After the usual work-up procedure, we isolated the

indeno[3,2-*h*]quinoline **16** and the indeno[2,3-*g*]quinoline **17** (Scheme 8). Again, the steric factors apparently determine the regioisomer ratio as **17** is the major product.



Scheme 7



Scheme 8

In conclusion, the irradiation of 3-naphthyl- and 3-phenanthryl-2-alkene imines allows the synthesis of benzo-, dibenzo- and naphtho-quinolines substituted by alkyl-, arylamino or a NH_2 group under mild reaction conditions. Furthermore, this reaction is suitable for the

preparation of four-ring aminoazapolycyclic compounds with a non-aromatic ring. The importance of 4-aminobenzoquinolines in medicinal chemistry and their potential use as an entry to Tröger's base analogs enhances the significance of the compounds described herein.

EXPERIMENTAL

^1H and ^{13}C spectra were recorded on a Bruker ARX-300 spectrometer in $CDCl_3$ with TMS as internal standard. Electrospray mass spectra were obtained on an HP 5989 B apparatus with an HP 59987 A interface, in positive-ion mode with methanol-water-acetic acid (60:35:5) as the mobile phase. Elemental analyses were made using a CE Instrument Model 1110. All solvents were purified by standard procedures and freshly destilled prior to use. Reagents were of commercial grades (Aldrich). 3-Amino-2-alkene imines (**1**, **5**, **8**, **10**, **12**, and **15**) were prepared in accordance with the methods described in ref 10. Alkene imine **3** was synthesized from **1** according to ref 11.

Irradiation of 3-amino-2-alkene imines in acid medium; General procedure: A solution of the corresponding 3-amino-2-alkene imine (1 mmol) and HBF_4 (1 mmol, 0.14 mL of a 54% ethereal solution) in anhydrous MeOH (50 mL) was irradiated, at room temperature under an Ar atmosphere, using a medium-pressure mercury lamp (125 W) until the complete consumption of the starting material had occurred (monitored by ^1H NMR spectroscopy, see Schemes 2-3 and 5-8). The solvent was evaporated under reduced pressure and the residue was treated with $NaHCO_3$ (25 mL, 10% aq solution) and extracted with Et_2O (3 x 25 mL). The organic layer was dried (Na_2SO_4), filtered and the solvent removed under reduced pressure. The resulting products were separated and/or purified by column chromatography (silica gel, hexane/Et_2O, 2:1) and recrystallized (hexane/Et_2O). The yields described refer to isolated products, relative to the starting alkene imine.

4-(Phenylamino)-2-*p*-tolylbenzo[*f*]quinoline 2. mp 203-205 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3H), 6.8 (s, 1H), 7.2 (t, *J* = 7.5 Hz, 1H), 7.3-7.6 (m, 8H), 7.7 (s, 1H), 7.90-8.0 (m, 5H), 9.1 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 104.8, 115.2, 121.3, 123.7, 124.8, 126.0, 126.6, 127.2, 129.2, 129.3, 129.4, 129.6, 129.8, 130.9, 132.3, 136.8, 139.1, 140.7, 150.1, 150.7, 156.8; ESMS *m/z* 361 (MH^+). Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.64, H, 5.59, N, 7.77. Found: C, 86.38, H, 5.65, N, 7.63%.

3-Benzyl-4-(phenylamino)-2-*p*-tolylbenzo[*f*]quinoline 4. mp 173-174 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3H), 4.21 (s, 2H), 6.0 (s, 1H), 6.4 (d, *J* = 9 Hz, 2H), 6.8 (t, *J* = 7.5 Hz, 1H), 7.0 (t, *J* = 7.5 Hz, 2H), 7.2-7.5 (m, 10H), 7.8 (m, 1H), 8.0 (d, *J* = 9 Hz, 1H), 8.1 (d, *J* = 9 Hz, 1H), 9.2 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 35.2, 115.0, 120.3, 120.6, 126.5, 126.6, 126.7, 127.1, 127.2, 127.7. 128.2, 128.8, 128.8, 128.9, 129.0, 129.1, 129.1, 131.4, 132.1, 137.8, 138.1, 139.1, 142.9, 146.2, 149.0, 160.5; ESMS

m/z 451 (MH^+). Anal. Calcd for $C_{33}H_{26}N_2$: C, 87.97, H, 5.82, N, 6.22. Found: C, 87.63, H, 5.90, N, 6.11%.

4-(Cyclohexylamino)-2-phenylbenzo[*f*]quinoline 6. mp 124-126 °C; ^1H NMR ($CDCl_3$) δ 1.4-1.9 (m, 8H), 2.2 (m, 2H), 3.6 (m, 1H), 5.6 (d, *J* = 6.6 Hz, 1H), 7.1 (s, 1H), 7.4-7.6 (m, 5H), 7.8 (d, *J* = 9 Hz, 1H), 7.9 (m, 2H), 8.1 (m, 2H), 8.9 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.7, 25.8, 32.8, 51.8, 100.2, 113.3, 123.7, 125.4, 126.4, 127.5, 128.6, 128.7, 129.3, 129.5, 129.6, 130.2, 132.1, 140.6, 149.9, 151.8, 156.9; ESMS *m/z* 353 (MH^+). Anal. Calcd for $C_{25}H_{24}N_2$: C, 85.19, H, 6.86, N, 7.95. Found: C, 84.96, H, 6.87, N, 7.90%.

4-(Cyclohexylamino)-2-phenyl-7,8-dihydrobenzo[*f*]quinoline 7. mp 62-64 °C; ^1H NMR ($CDCl_3$) δ 1.3-1.8 (m, 8H), 2.1 (m, 2H), 2.8-3.0 (m, 4H), 3.5 (m, 1H), 5.2 (d, *J* = 7.5 Hz, 1H), 6.9 (s, 1H), 7.2-7.5 (m, 6H), 7.9 (d, *J* = 7.8 Hz, 1H), 8.0 (m, 2H).; ^{13}C NMR ($CDCl_3$) δ 24.7, 25.7, 29.3, 32.9, 33.1, 50.0, 102.1, 113.4, 124.2, 126.4, 126.6, 127.0, 128.4, 128.5, 128.5, 132.7, 139.3, 140.5, 149.5, 156.0, 159.5; ESMS *m/z* 355 (MH^+). Anal. Calcd for $C_{25}H_{26}N_2$: C, 84.71, H, 7.39, N, 7.90. Found: C, 84.33, H, 7.47, N, 8.19%.

4-Amino-2-*p*-tolylbenzo[*h*]quinoline 9. mp 135-137 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3H), 4.6 (s, 2H), 7.2 (s, 1H), 7.3 (d, *J* = 8.4 Hz, 2H), 7.6 (d, *J* = 9.3 Hz, 1H), 7.6-7.7 (m, 3H), 7.8 (d, *J* = 9 Hz, 1H), 8.1 (d, *J* = 8.4 Hz, 2H), 9.5 (d, *J* = 6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 156.6, 149.3, 144.3, 140.9, 138.3, 133.0, 130.9, 129.7, 129.1, 128.4, 128.3, 128.2, 128.1, 127.6, 127.4, 127.2, 126.6, 125.3, 124.8, 123.2, 118.9; ESMS *m/z* 285 (MH^+). Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48, H, 5.67, N, 9.85. Found: C, 84.23, H, 5.58, N, 9.88%.

4-(Phenylamino)-2-*p*-tolyldibenzo[*f,h*]quinoline 11. mp 205-207 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3H), 6.8 (s, 1H), 7.7 (t, *J* = 7.5 Hz, 1H), 7.3-7.4 (m, 6H), 7.5 (t, *J* = 8.4 Hz, 1H), 7.6 (t, *J* = 6.9 Hz, 1H), 7.7 (m, 2H), 7.8 (s, 1H), 8.1 (d, *J* = 8.1 Hz, 2H), 8.6 (m, 1H), 8.7 (d, *J* = 7.5 Hz, 1H), 9.1 (d, *J* = 8.1 Hz, 1H), 9.5 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.4, 105.1, 113.6, 121.2, 122.2, 123.6, 124.1, 125.3, 126.2, 126.6, 126.7, 127.1, 127.4, 128.7, 129.1, 129.4, 129.8, 130.3, 131.4, 131.6, 136.8, 139.1, 140.7, 148.4, 149.5, 155.4; ESMS *m/z* 411 (MH^+). Anal. Calcd for $C_{30}H_{22}N_2$: C, 87.77, H, 5.40, N, 6.82. Found: C, 87.30, H, 5.24, N, 6.59%.

4-(Phenylamino)-2-*p*-tolylnaphtho[2,1-*h*]quinoline 13. oil; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3H), 7.0(s, 1H), 7.2 (m, 1H), 7.3 (d, *J* = 8.1 Hz, 2H), 7.4-7.5 (m, 4H), 7.6 (s, 1H), 7.6-7.9 (m, 5H), 8.0 (d, *J* = 8.1 Hz, 2H), 8.6 (s, 1H), 8.8 (d, *J* = 8.1 Hz, 1H), 9.2 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 99.6, 113.4,

118.6, 122.4, 122.7, 124.4, 124.6, 127.0, 127.1, 127.2, 127.4, 127.8, 128.2, 128.4, 128.9, 129.4, 129.8, 129.8, 130.4, 132.0,133.6, 139.3, 140.3, 148.0, 158.7; ESMS *m/z* 411 (MH^+). Anal. Calcd for $C_{30}H_{22}N_2$: C, 87.77, H, 5.40, N, 6.82. Found: C, 87.34, H, 5.42, N, 7.12%.

4-(Phenylamino)-2-*p*-tolylnaphtho[3,2-*h*]quinoline 14. mp 124-126 °C; ^1H NMR ($CDCl_3$) δ 2.5 (s, 3H), 6.6 (s, 1H), 7.2 (t, *J* = 7.2 Hz, 1H), 7.3-7.5 (m, 6H), 7.7 (t, *J* = 6.6 Hz, 1H), 7.7 (s, 1H), 7.8-8.0 (m, 7H), 8.1 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.3, 101.3, 117.6, 118.1, 121.6, 123.9, 126.1, 126.8, 126.9, 126.9, 127.1, 127.7, 128.3, 129.5, 129.6, 129.8, 131.5, 132.0, 133.8, 134.1, 138.0, 139.0, 140.8, 148.0, 149.2, 156.2; ESMS *m/z* 411 (MH^+). Anal. Calcd for $C_{30}H_{22}N_2$: C, 87.77, H, 5.40, N, 6.82. Found: C, 87.53, H, 5.37, N, 6.87%.

4-(Phenylamino)-2-*p*-tolylindeno[3,2-*h*]quinoline 16. mp 156-157 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3H), 4.5 (s, 2H), 6.7 (s, 1H), 7.2 (td, *J* = 1.2 Hz, *J* = 7.5 Hz, 1H), 7.3 (d, *J* = 7.8 Hz, 2H), 7.4-7.5 (m, 6H), 7.5 (s, 1H), 7.7 (d, *J* = 6.9 Hz, 1H), 7.9 (m, 3H), 8.0 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.3, 36.2, 99.8, 117.6, 117.8, 119.1, 120.0, 122.1, 124.1, 125.2, 126.6, 126.9, 127.3, 129.3, 129.7, 137.5, 139.1, 140.3, 142.0, 142.4, 142.5, 144.6, 146.7, 148.1, 157.6; ESMS *m/z* 399 (MH^+). Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.41, H, 5.56, N, 7.03. Found: C, 87.38, H, 5.53, N, 7.08%.

4-(Phenylamino)-2-*p*-tolylindeno[2,3-*g*]quinoline 17. mp 211-212 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3H), 4.1 (s, 2H), 6.6 (s, 1H), 7.2 (td, *J* = 1.2 Hz, *J* = 7.2 Hz, 1H), 7.3 (d, *J* = 8.4 Hz, 2H), 7.3-7.5 (m, 6H), 7.5 (s, 1H), 7.6 (d, *J* = 7.5 Hz, 1H), 7.9 (d, *J* = 8.1 Hz, 2H), 8.0 (d, *J* = 7.2 Hz, 1H).8.0 (s, 1H), 8.5 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3, 36.6, 100.3, 115.0, 118.2, 120.2, 121.2, 121.9, 124.0, 125.2, 127.2, 127.3, 128.1, 129.3, 129.7, 137.6, 138.9, 140.4, 140.5, 140.8, 144.0, 144.1, 147.5, 149.1, 157.6; ESMS *m/z* 399 (MH^+). Anal. Calcd for $C_{29}H_{22}N_2$: C, 87.41, H, 5.56, N, 7.03. Found: C, 87.25, H, 5.45, N, 6.97%.

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