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THE INVESTIGATIONS IN 2,3'-BIQUINOLINE SERIES. 25*. SYNTHESIS OF 4-(2-QUINOLINYL)-PYRROLO[1,2-*a*]QUINOLINES AND 4-(2-QUINOLYL)-IMIDAZO[1,2-*a*]QUINOLINES

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A method has been developed for the synthesis of 4-(2-quinolinyl)-1,2,3,3a-tetrahydropyrrolo-[1,2-a]quinolines based on the 1,3-dipolar cycloaddition reaction of α,β-unsaturated carbonyl compounds to 2,3'-biquinolinium salts. Oxidation in benzene using MnO_2 gave 4-(2-quinolinyl)-pyrrolo[1,2-a]quinolines. It was found that a side product of the 1,3-dipolar cycloaddition is 7,14-dibenzoyl-6,13-di(2-quinolyl)-6a,7,13a,14-tetrahydro-7a,14a-diazadibenzo[a,h]anthracene. Reaction of 1'-phenacyl-2,3'-biquinolinium salts with hydroxylamine in acetic acid gave 4-(2-quinolyl)imidazo-[1,2-a]quinolines.

Keywords: 2,3'-biquinoline, 1'-R-3-(2-quinolyl)quinolinium bromides, 7,14-dibenzoyl-6,13-di(2-quinolyl)-6a,7,13a,14-tetrahydro-7a,14a-diazadibenzo[*a,h*]anthracene, α,β-unsaturated carbonyl compounds, 4-(2-quinolyl)imidazo[1,2-*a*]quinolines, 4-(2-quinolinyl)pyrrolo[1,2-*a*]quinolines, 4-(2-quinolinyl)-1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinolines, cyclization.

We have previously developed a method for the synthesis of 1'-R-2,3'-biquinolinium salts **1** [2]. These compounds have been used as starting materials in the preparation of various 2,3'-biquinoline derivatives, *viz.* dihydro derivatives [2-6], biquinolones [7], and thiones [8, 9]. This report concerns the synthesis of previously unknown 4-(2-quinolinyl)pyrrolo[1,2-*a*]quinolines and 4-(2-quinolyl)imidazo[1,2-*a*]quinolines based on them.

We have shown that the reactions of the conjugated bases of salts **1a,b** (prepared by treating the corresponding salts with Et_3N in CH_2Cl_2 or with AcONa in AcOH) with the α,β-enones and nitriles of α,β-unsaturated carboxylic acids give 4-(2-quinolinyl)-1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinolines **3** in 44-82% yield.

The reaction occurs diastereospecifically. The ^1H NMR spectra show signals for only one diastereomer whose configuration we were unable to determine. The side product formed was that of the reaction of the starting salt with its conjugate base. In the case of the phenacyl salt **1a** it could be isolated and characterized.

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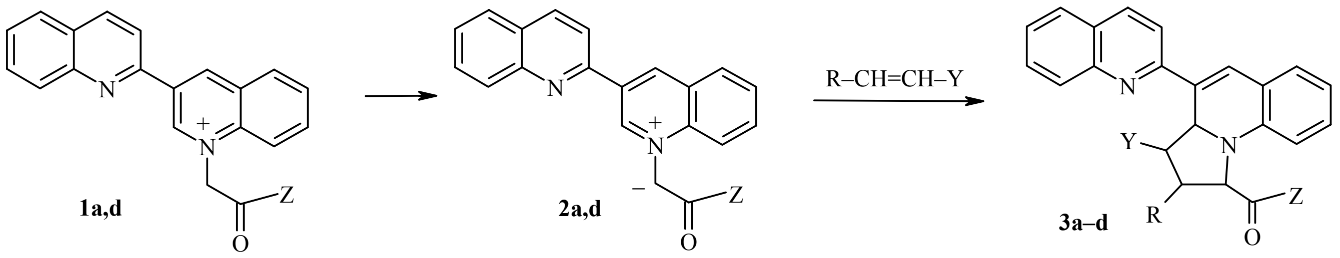
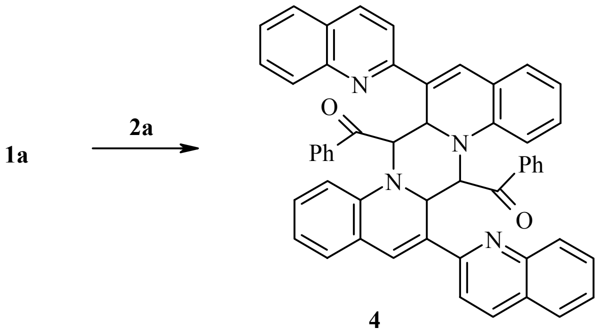
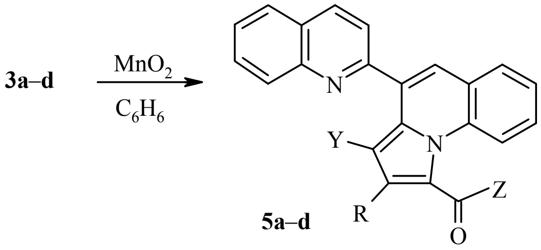


1, **2 a** Z = Ph, **d** Z = OEt; **3 a** R = Z = Ph, Y = COPh, **b** R = H, Z = Ph, Y = CN,
c R = H, Z = OEt, Y = COMe, **d** R = H, Z = OEt, Y = CN

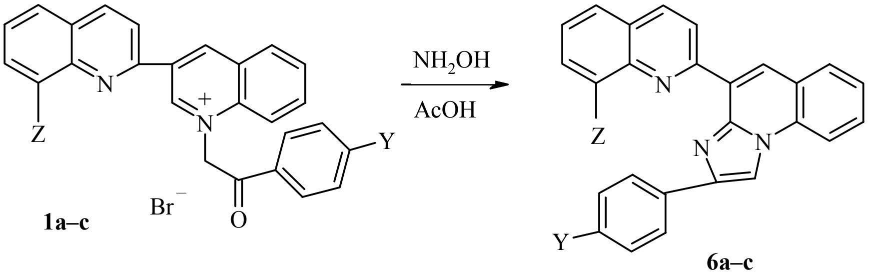


Oxidation of compounds **3a-d** gave a quantitative yield of the previously unknown 4-(2-quinolinyl)-pyrrolo[1,2-*a*]quinolines **5a-d**.



3, **5 a** R = Z = Ph, Y = COPh, **b** R = H, Z = Ph, Y = CN, **c** R = H, Z = OEt,
Y = COMe, **d** R = H, Z = OEt, Y = CN

The next part of our work was related to the synthesis of the previously unknown 4-(2-quinolyl)-imidazo[1,2-*a*]quinolines **6a-c** from the biquinolinium salts **1a-c**. We have shown that these compounds can be prepared in quantitative yield by reaction of salts **1a-c** with hydroxylamine in AcOH.



1, 6 a Z = Y = H, **b** Z = NO_2, Y = H, **c** Z = NO_2, Y = Cl

Reduction of the nitro derivatives **6b,c** with hydrazine on Raney nickel in alcohol gave a quantitative yield of the amines **7a,b** (see Experimental).

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker DRX-500 instrument (500 MHz) and ^{13}C NMR spectra on a Bruker AM-300 (75 MHz) using TMS as internal standard. Monitoring of the reaction course and the purity of the compounds synthesized was performed on Silufol UV-254 plates using the solvent system ethyl acetate–petroleum ether (1:1).

Synthesis of 4-(2-Quinolinyl)-1,2,3,3a-tetrahdropyrrolo[1,2-*a*]quinolines by a 1,3-Dipolar Cycloaddition Reaction (General Methods). A. A mixture of the corresponding 1'-R-3'-(2-quinolyl)quinolinium halide (2 mmol), the dipolarophile (2.4 mmol), and triethylamine (0.5 ml) in methylene chloride (10 ml) was stirred for 2 h at ~ 20ºC, chloroform was added (30 ml), washed with water (3×20 ml), and the solvent was evaporated. The red-yellow crystals or oil obtained were crystallized from benzene or benzene and hexane. The residue insoluble in benzene during crystallization was compound **4**. It could be purified by washing the residue with benzene (2×20 ml).

B. A mixture of the corresponding 1'-R-3'-(2-quinolyl)quinolinium halide (2 mmol), the dipolarophile (2.4 mmol), and sodium acetate (0.9 g, 5 mmol) in glacial acetic acid (10 ml) was stirred at ~ 20ºC for 1 h, poured into water (50 ml), neutralized with 25% ammonia solution, extracted with chloroform (3×20 ml), and the solvent was evaporated. The red-yellow crystals or oil were crystallized from benzene or benzene and hexane.

1,3-Dibenzoyl-2-phenyl-4-(2-quinolyl)-1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinoline (3a) was prepared from 1'-phenacyl-3'-(2-quinolyl)quinolinium bromide and the chalcone. By method A the yield was 0.95 g (82%) and by method B 1.02 g (88%); mp 187-188ºC (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 4.24 (1H, dd, $J_{1,2}$ = 9.75, $J_{2,3}$ = 2.2, H-2); 5.35 (1H, dd, $J_{2,3}$ = 2.2, $J_{3,3a}$ = 5.55, H-3); 6.11 (1H, d, $J_{1,2}$ = 9.75, H-1); 6.19 (1H, d, $J_{8,9}$ = 8.0, H-9); 6.59 (1H, dd, $J_{6,7}$ = 7.4, $J_{7,8}$ = 7.3, H-7); 6.72 (2H, m, H-8,4 (2-C_6H_5)); 6.88 (1H, d, $J_{3,3a}$ = 5.5, H-3a); 6.95 (1H, d, $J_{6,7}$ = 7.4, H-6); 7.06 (1H, s, H-5); 7.15 (4H, m, H-2,3,5,6 (2-C_6H_5)); 7.2-7.4 (8H, m, H-3,4,5 (1-COC_6H_5), H-2,3,4,5,6 (3-COC_6H_5)); 7.42 (1H, dd, $J_{5',6'}$ = 8.1, $J_{6',7'}$ = 7.1, H-6'); 7.45 (1H, d, $J_{3',4'}$ = 9.0, H-3'); 7.59 (1H, dd, $J_{6',7'}$ = 7.1, $J_{7',8'}$ = 8.2, H-7'); 7.66 (1H, d, $J_{5',6'}$ = 8.1, H-5'); 7.75 (1H, d, $J_{7',8'}$ = 8.2, H-8'); 7.78 (2H d, *J* = 7.8, H-2,6 (1-COC_6H_5)); 7.82 (1H, d, $J_{3',4'}$ = 9.0, H-4'). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 48.90 (1C); 56.90 (1C); 64.03 (1C); 68.04 (1C); 109.04 (1C); 116.40 (1C); 116.93 (1C); 117.53 (1C); 119.66 (1C); 126.26 (1C); 126.52 (1C); 126.74 (1C); 126.93 (1C); 127.05 (1C); 127.29 (2C); 127.63 (2C); 127.72 (2C); 127.90 (1C); 128.06 (2C); 128.12 (1C); 128.26 (1C); 128.39 (1C); 128.74 (2C); 129.08 (1C); 130.35 (1C); 131.75 (1C); 132.74 (1C); 135.24 (1C); 135.94 (1C); 136.74 (1C); 143.16 (1C); 146.24 (1C); 154.41 (1C); 198.79 (1C); 200.64 (1C). Found, %: C 84.65; H 5.11; N 4.73. $C_{41}H_{30}N_2O_2$. Calculated, %: C 84.51; H 5.19; N 4.81.

1-Benzoyl-3-cyano-4-(2-quinolyl)-1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinoline (3b) was prepared from 1'-phenacyl-3'-(2-quinolyl)quinolinium bromide and acrylonitrile. By method A the yield was 0.62 g (72%) and by method B 0.78 g (91%); mp 252-253ºC (benzene and hexane). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 2.34 (1H, ddd, J_{het} = 13.3, J_{2Ha3} = 7.45, J_{2Ha1} = 9.0, 2-C$\underline{\text{H}}$*a*H*b*); 2.87 (2H, ddd, J_{het} = 13.3, J_{2Hb3} = 6.8, J_{2Hb1} = 7.75, 2-CH*a*$\underline{\text{H}}$*b*); 4.58 (1H, ddd, J_{2Ha3} = 7.45, J_{2Hb3} = 6.8, $J_{3,3a}$ = 4.3, H-3); 5.56 (1H, d, $J_{3,3a}$ = 4.3, H-3*a*); 5.74 (1H, dd, J_{2Ha1} = 9.0, $J_{2Hb\text{-}1}$ = 7.75, H-1); 6.18 (1H, d, $J_{8,9}$ = 7.8, H-9); 6.65 (1H, dd, $J_{7,8}$ = 7.4, $J_{6,7}$ = 7.5, H-7); 7.05 (1H, dd, $J_{7,8}$ = 7.4, $J_{8,9}$ = 7.8, H-8); 7.21 (1H, d, $J_{6,7}$ = 7.5, H-6); 7.59 (1H, dd, $J_{5',6'}$ = 7.8, $J_{6',7'}$ = 7.7, H-6'); 7.63 (2H, t, *J* = 7.8, H-3,5 (C_6H_5)); 7.74 (2H, m, H-7',4 (C_6H_5)); 7.76 (1H, s, H-5); 7.96 (1H, d, $J_{5',6'}$ = 7.8, H-5'); 7.99 (3H, d, $J_{7',8'}$ = 8.1, H-8'); 8.13 (1H, d, $J_{3',4'}$ = 8.7, H-3'); 8.19 (2H, d, *J* = 7.8, H-2,6 (C_6H_5)); 8.37 (1H, d, $J_{3',4'}$ = 8.7, H-4'). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 31.64 (1C); 35.71 (1C); 60.92 (1C); 62.93 (1C); 109.71 (1C); 117.14 (1C); 117.53 (1C); 119.51 (1C); 120.44 (1C); 126.39 (1C); 126.73 (1C); 127.57 (1C); 128. 61 (2C); 128.73 (1C); 128.79 (1C);

128.96 (2C); 129.33 (1C); 129.59 (1C); 129.75 (1C); 130.87 (1C); 133.85 (1C); 134.16 (1C); 136.04 (1C); 142.50 (1C); 146.81 (1C); 154.39 (1C); 197.72 (1C). Found, %: C 81.61; H 4.89; N 9.77. $C_{29}H_{21}N_3O$. Calculated, %: C 81.48; H 4.95; N 9.83.

3-Acetyl-1-ethoxycarbonyl-4-(2-quinolyl)-1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinoline (3c) was prepared from 1'-(2-ethoxy-2-oxoethyl)-3'-(2-quinolyl)quinolinium iodide and methyl vinyl ketone. Using method A the yield was 0.47 g (57%) and method B 0.71 g (86%); mp 143-144ºC (benzene and hexane). ^{1}H NMR spectrum, ($CDCl_3$), δ, ppm (*J*, Hz): 1.27 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 1.59 (3H, s, CH_3); 2.09 (2H, ddd, J_{het} = 13.35, J_{2Ha3} = 6.8, J_{2Ha1} = 7.7, 2-C$\underline{H}$*a*H*b*); 2.39 (2H, ddd, J_{het} = 13.35, J_{2Hb3} = 7.5, J_{2Hb1} = 9.0, 2-CH*a*$\underline{H}$*b*); 4.22 (2H, t, *J* = 7.2, $C\underline{H}_2CH_3$); 4.28 (1H, ddd, J_{2Ha3} = 6.8, J_{2Hb3} = 7.5, $J_{3,3a}$ = 4.3, H-3); 4.48 (1H, dd, J_{2Ha1} = 7.7, J_{2Hb1} = 9.0, H-1); 5.68 (1H, d, $J_{3,3a}$ = 4.3, H-3a); 6.27 (1H, d, $J_{8,9}$ = 7.8, H-9); 6.58 (1H, dd, $J_{7,8}$ = 7.4, $J_{6,7}$ = 7.5, H-7); 7.07 (1H, dd, $J_{7,8}$ = 7.4, $J_{8,9}$ = 7.8, H-8); 7.09 (1H, d, $J_{6,7}$ = 7.5, H-6); 7.58 (1H, s, H-5); 7.59 (1H, dd, $J_{5',6'}$ = 7.8, $J_{6',7'}$ = 7.7, H-6'); 7.79 (1H, dd, $J_{6',7'}$ = 7.7, $J_{7',8'}$ = 8.2, H-7'); 7.98 (1H, d, $J_{5',6'}$ = 7.8, H-5'); 8.02 (1H, d, $J_{7',8'}$ = 8.2, H-8'); 8.10 (1H, d, $J_{3',4'}$ = 8.7, H-3'); 8.38 (1H, d, $J_{3',4'}$ = 8.7, H-4'). Found, %: C 75.82; H 5.81; N 6.77. $C_{26}H_{24}N_2O_3$. Calculated, %: C 75.71; H 5.86; N 6.79.

3-Cyano-1-ethoxycarbonyl-4-(2-quinolyl)-1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinoline (3d) was prepared from 1'-(2-ethoxy-2-oxoethyl)-3'-(2-quinolyl)quinolinium iodide and acrylonitrile. Yield by method A 0.54 g (68%) and by method B 0.7 g (89%); mp 178-179ºC (benzene and hexane). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.35 (3H, t, *J* = 7.2, $CH_2C\underline{H}_3$); 2.49 (1H, ddd, J_{het} = 13.3, J_{2Ha3} = 7.45, J_{2Ha1} = 9.0, 2-C$\underline{H}$*a*H*b*); 2.71 (1H, ddd, J_{het} = 13.3, J_{2Hb3} = 6.8, J_{2Hb1} = 7.75, 2-CH*a*$\underline{H}$*b*); 4.29 (2H, q, *J* = 7.2, $C\underline{H}_2CH_3$); 4.58 (1H, ddd, J_{2Ha3} = 7.45, J_{2Hb3} = 6.8, $J_{3,3a}$ = 4.3, H-3); 4.59 (1H, dd, J_{2Ha1} = 9.0, J_{2Hb1} = 7.75, H-1); 5.78 (1H, d, $J_{3,3a}$ = 4.3, H-3a); 6.39 (1H, d, $J_{8,9}$ = 7.8, H-9); 6.71 (1H, dd, $J_{7,8}$ = 7.4, $J_{6,7}$ = 7.5, H-7); 7.11 (1H, dd, $J_{6,8}$ = 1.6, $J_{6,7}$ = 7.5, H-6); 7.15 (1H, dd, $J_{7,8}$ = 7.4, $J_{8,9}$ = 7.8, H-8); 7.40 (1H, s, H-5); 7.52 (1H, dd, $J_{5',6'}$ = 7.8, $J_{6',7'}$ = 7.7, H-6'); 7.72 (1H, dd, $J_{6',7'}$ = 7.7, $J_{7',8'}$ = 8.1, H-7'); 7.75 (1H, d, $J_{5',6'}$ = 7.8, H-5'); 7.88 (1H, d, $J_{3',4'}$ = 8.7, H-3'); 7.97 (3H, d, $J_{7',8'}$ = 8.1, H-8'); 8.14 (1H, d, $J_{3',4'}$ = 8.7, H-4'). Found, %: C 76.06; H 5.30; N 10.57. $C_{25}H_{21}N_3O_2$. Calculated, %: C 75.93; H 5.35; N 10.63.

7,14-Dibenzoyl-6,13-di(2-quinolyl)-6a,7,13a,14-tetrahydro-7a,14a-diazadibenzo[*a,h*]anthracene (4) was synthesized as the side product in the reaction of 1'-phenacyl-3'-(2-quinolyl)quinolinium bromide and acrylonitrile, using method A the yield was 0.31 g (21%); mp 294-296ºC (alcohol). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 6.39 (2H, d, *J* = 3.65, H-6a,13a); 6.60 (2H, d, *J* = 3.65, H-7,14); 6.81 (2H, dd, $J_{3(10),4(11)}$ = 7.8, $J_{2(9),3(10)}$ = 7.3, H-3,10); 7.05 (6H, m, H-3,5 (C_6H_5), H-2,10); 7.26 (2H, s, H-5,12); 7.29 (2H, d, $J_{3(10),4(11)}$ = 7.8, H-4,11); 7.36 (2H, dd, $J_{2(9),3(10)}$ = 7.3, $J_{1(8),2(9)}$ = 8.0, H-1,9); 7.47 (2H, t, *J* = 6.7, H-4 (C_6H_5)); 7.62 (6H, m, H-2,6 (C_6H_5), H-6'); 7.84 (2H, d, $J_{5',6'}$ = 7.8, H-5'); 7.93 (2H, dd, $J_{6',7'}$ = 7.2, $J_{7',8'}$ = 8.1, H-7'); 7.98 (2H, d, $J_{7',8'}$ = 8.1, H-8'); 8.23 (2H, d, $J_{3',4'}$ = 8.45, H-3'); 8.29 (2H, d, $J_{3',4'}$ = 8.45, H-4'). Found, %: C 83.55; H 4.81; N 7.39. $C_{52}H_{36}N_4O_2$. Calculated, %: C 83.40; H 4.85; N 7.48.

Synthesis of 4-(2-Quinolinyl)pyrrolo[1,2-*a*]quinolines 5a-d (General Method). A mixture of the corresponding 4-(2-quinolinyl)-1,2,3,3a-tetrahydropyrrolo[1,2-*a*]quinoline (1 mmol) and activated MnO_2 (0.44 g, 5 mmol) in benzene (15 ml) was refluxed and the reaction was monitored by TLC (~ 3 h). The solution was filtered hot and the precipitate was washed with hot benzene (2×10 ml). The obtained solutions were combined and evaporated.

1,3-Dibenzoyl-2-phenyl-4-(2-quinolyl)pyrrolo[1,2-*a*]quinoline (5a). Yield 0.56 g (quantitative); mp 196-197ºC (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 6.9 (5H, m, 2-C_6H_5); 7.15 (5H, m, H-3,5 (1-COC_6H_5), H-3,4,5 (3-COC_6H_5)); 7.23 (2H, d, *J* = 7.65, H-2,6 (3-COC_6H_5)); 7.36 (3H, m, H-7,8,6'); 7.46 (4H, m, H-7',2,4,6 (1-COC_6H_5)); 7.53 (1H, s, H-5); 7.66 (1H, d, $J_{6,7}$ = 7.5, H-6); 7.69 (1H, d, $J_{8,9}$ = 7.8, H-9); 7.76 (1H, d, $J_{5',6'}$ = 7.8, H-5'); 8.78 (3H, d, $J_{7',8'}$ = 8.1, H-8'); 7.82 (1H, d, $J_{3',4'}$ = 8.45, H-3'); 8.97 (1H, d, $J_{3',4'}$ = 8.45, H-4'). Found, %: C 85.22; H 4.48; N 4.77. $C_{41}H_{26}N_2O_2$. Calculated, %: C 85.10; H 4.53; N 4.84.

1-Benzoyl-3-cyano-4-(2-quinolyl)pyrrolo[1,2-*a*]quinoline (5b). Yield 0.4 g (quantitative); mp 236-238ºC (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.15 (3H, m, H-3,4,5 (C_6H_5)); 7.46 (2H, d, J = 6.8, H-2,6 (C_6H_5)); 7.54 (1H, dd, $J_{7,8}$ = 7.4, $J_{6,7}$ = 7.5, H-7); 7.63 (1H, dd, $J_{5',6'}$= 7.8, $J_{6',7'}$ = 7.7, H-6'); 7.68 (1H, dd, $J_{7,8}$ = 7.4, $J_{8,9}$ = 7.8, H-8); 7.74 (1H, d, $J_{6,7}$ = 7.5, H-6); 7.81 (1H, s, H-2); 7.83 (1H, dd, $J_{6',7'}$ = 7.7, $J_{7',8'}$= 8.0, H-7'); 7.85 (1H, s, H-5); 7.88 (1H, d, $J_{8,9}$ = 7.8, H-9); 7.93 (1H, d, $J_{5',6'}$ = 7.8, H-5'); 8.22 (1H, d, $J_{7',8'}$= 8.0, H-8'); 8.32 (1H, d, $J_{3',4'}$= 8.8, H-3'); 8.39 (1H, d, $J_{3',4'}$= 8.8, H-4'). Found, %: C 82.36; H 3.99; N 9.87. $C_{29}H_{17}N_3O$. Calculated, %: C 82.25; H 4.05; N 9.92.

3-Acetyl-1-ethoxycarbonyl-4-(2-quinolyl)pyrrolo[1,2-*a*]quinoline (5c). Yield 0.4 g (quantitative); mp 185-186ºC (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.34 (3H, t, J = 7.1, $CH_2C\underline{H}_3$); 4.42 (2H, q, J = 7.1, $C\underline{H}_2CH_3$); 1.63 (3H, s, $COCH_3$); 7.55 (1H, dd, $J_{7,8}$ = 7.4, $J_{6,7}$ = 7.48, H-7); 7.63 (1H, dd, $J_{5',6'}$ = 7.8, $J_{6',7'}$ = 7.7, H-6'); 7.68 (1H, dd, $J_{7,8}$ = 7.4, $J_{8,9}$ = 7.8, H-8); 7.76 (1H, d, $J_{6,7}$ = 7.5, H-6); 7.79 (1H, s, H-2); 7.81 (1H, dd, $J_{6',7'}$ = 7.7, $J_{7',8'}$ = 8.0, H-7'); 7.82 (1H, s, H-5); 7.88 (1H, d, $J_{8,9}$ = 7.8, H-9); 7.92 (1H, d, $J_{5',6'}$ = 7.8, H-5'); 8.22 (3H, d, $J_{7',8'}$ = 8.0, H-8'); 8.37 (1H, d, $J_{3',4'}$ = 8.7, H-3'); 8.32 (1H, d, $J_{3',4'}$ = 8.7, H-4'). Found, %: C 76.57; H 4.89; N 6.85. $C_{26}H_{20}N_2O_3$. Calculated, %: C 76.46; H 4.94; N 6.86.

3-Cyano-1-ethoxycarbonyl-4-(2'-quinolyl)pyrrolo[1,2-*a*]quinoline (5d). Yield 0.57 g (quantitative); mp 219-220ºC (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 1.43 (3H, t, J = 7.2, $CH_2C\underline{H}_3$); 4.48 (2H, q, J = 7.2, $C\underline{H}_2CH_3$); 7.55 (1H, dd, $J_{7,8}$ = 7.4, $J_{6,7}$ = 7.5, H-7); 7.63 (1H, dd, $J_{5',6'}$ = 7.8, $J_{6',7'}$ = 7.7, H-6'); 7.68 (1H, dd, $J_{7,8}$ = 7.4, $J_{8,9}$ = 7.8, H-8); 7.76 (1H, d, $J_{6,7}$ = 7.5, H-6); 7.79 (1H, s, H-2); 7.81 (1H, dd, $J_{6',7'}$ = 7.7, $J_{7,'8'}$= 8.0, H-7'); 7.82 (1H, s, H-5); 7.88 (1H, d, $J_{8,9}$ = 7.8, H-9); 7.92 (1H, d, $J_{5',6'}$ = 7.8, H-5'); 8.22 (1H, d, $J_{7',8'}$= 8.0, H-8'); 8.37 (1H, d, $J_{3',4'}$ = 8.7, H-3'); 8.38 (1H, d, $J_{3',4'}$ = 8.7, H-4'). Found, %: C 76.83; H 4.33; N 10.69. $C_{25}H_{17}N_3O_2$. Calculated, %: C 76.71; H 4.38; N 10.73.

Synthesis of 4-(2-Quinolyl)imidazo[1,2-*a*]quinolines 6a-c (General Method). A mixture of the corresponding salt **1a-c** (1 mmol), hydroxylamine hydrochloride (0.139 g, 2 mmol), and sodium acetate (0.25 g, 3 mmol) in acetic acid (10 ml) was stirred at 55-60ºC for 3 h, cooled, water (50 ml) was added, and neutralized with ammonia solution. The precipitate was filtered.

2-Phenyl-4-(2'-quinolyl)imidazo[1,2-*a*]quinoline (6a). Yield 0.36 g (quantitative); mp 137-138ºC (benzene). ^{1}H NMR spectrum (DMF-d_7), δ, ppm (*J*, Hz): 7.39 (1H, t, J = 7.6, H-4 (C_6H_5)); 7.55 (2H, dd, J = 7.6, J = 7.4, H-3,5 (C_6H_5)); 7.65 (1H, dd, $J_{6,7}$ = 10.9, $J_{7,8}$ = 7.0, H-7); 7.70 (1H, dd, $J_{6',7'}$ = 6.6, $J_{7',8'}$ = 8.1, H-7'); 7.86 (1H, dd, $J_{8,9}$ = 8.5, $J_{7,8}$ = 7.0, H-8); 7.88 (1H, dd, $J_{6',7'}$ = 6.6, $J_{5',6'}$ = 8.2, H-6); 8.13 (1H, d, $J_{7',8'}$ = 8.1, H-8'); 8.23 (1H, d, $J_{5',6'}$ = 8.2, H-5'); 8.25 (2H, d, J = 7.4, H-2,6 (C_6H_5)); 8.28 (1H, d, $J_{6,7}$ = 10.9, H-6); 8.55 (1H, d, $J_{8,9}$ = 8.5, H-9); 8.65 (1H, d, $J_{3',4'}$ = 8.55, H-4'); 8.87 (1H, s, H-5); 9.43 (1H, s, H-1); 9.53 (1H, d, $J_{3',4'}$ = 8.55, H-3'). Found, %: C 84.18; H 4.58; N 11.24. $C_{26}H_{17}N_3$. Calculated, %: C 84.07; H 4.62; N 11.31.

4-(8-Nitro-2-quinolyl)-2-phenylimidazo[1,2-*a*]quinoline (6b). Yield 0.41 g (quantitative); mp 235-237ºC (benzene). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 7.37 (1H, t, J = 7.6, H-4 (C_6H_5)); 7.51 (2H, dd, J = 7.6, J = 7.4, H-3,5 (C_6H_5)); 7.61 (1H, dd, $J_{6,7}$ = 10.7, $J_{7,8}$ = 7.0, H-7); 7.80 (1H, dd, $J_{6',7'}$ = 7.4, $J_{5',6'}$ = 8.2, H-6'); 7.86 (1H, dd, $J_{8,9}$ = 8.5, $J_{7,8}$ = 7.0, H-8); 8.14 (2H, d, J = 7.4, H-2,6 (C_6H_5)); 8.18 (1H, d, $J_{6,7}$ = 10.7, H-6); 8.35 (1H, d, $J_{5',6'}$ = 8.2, H-5'); 8.37 (1H, d, $J_{6',7'}$ = 7.4, H-7'); 8.45 (1H, d, $J_{8,9}$ = 8.5, H-9); 8.57 (1H, s, H-5); 8.80 (1H, d, $J_{3',4'}$ = 8.55, H-4'); 9.34 (1H, s, H-1); 9.54 (1H, d, $J_{3',4'}$ = 8.55, H-3'). Found, %: C 75.18; H 3.79; N 13.41. $C_{26}H_{16}N_4O_2$. Calculated, %: C 74.99; H 3.87; N 13.45.

2-(4-Chlorophenyl)-4-(8-nitro-2-quinolyl)imidazo[1,2-*a*]quinoline (6c). Yield 0.44 g (quantitative); mp 152-153ºC (benzene). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 7.56 (2H, d, J = 7.9, H-3,5 (Ar)); 7.62 (1H, dd, $J_{6,7}$ = 10.7, $J_{7,8}$ = 7.0, H-7); 7.81 (1H, dd, $J_{6',7'}$ = 7.4, $J_{5',6'}$ = 8.2, H-6'); 7.86 (1H, dd, $J_{8,9}$ = 8.5, $J_{7,8}$ = 7.0, H-8); 8.18 (1H, d, $J_{6,7}$ = 10.7, H-6); 8.24 (2H, d, J = 7.9, H-2,6 (Ar)); 8.35 (1H, d, $J_{5',6'}$ = 8.2, H-5'); 8.38 (1H, d, $J_{6',7'}$ = 7.4, H-7'); 8.46 (1H, d, $J_{8,9}$ = 8.5, H-9); 8.57 (1H, s, H-5); 8.82 (1H, d, $J_{3',4'}$ = 8.55, H-4'); 9.34 (1H, s, H-1); 9.53 (1H, d, $J_{3',4'}$ = 8.55, H-3'). Found, %: C 69.41; H 3.31; N 12.36. $C_{26}H_{15}ClN_4O_2$. Calculated, %: C 69.26; H 3.35; N 12.43.

Reduction of Compounds 6b,c (General Method). Hydrazine hydrate (85%, 0.5 g, 10 mmol) was added to a mixture of the corresponding compound **6** (1 mmol) and Raney nickel (0.5 g) in alcohol (50 ml). The product was stirred at 50ºC for 3h with TLC monitoring, filtered, the alcohol evaporated, and the residue was treated with water (50 ml) and then extracted with benzene (3×30 ml). The solvent was evaporated to give yellow-green crystals.

4-(8-Amino-2-quinolyl)-2-phenylimidazo[1,2-*a*]quinoline (7a) Yield 0.38 g (quantitative); mp 215-217ºC (benzene). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 6.30 (2H, br. s, NH$_2$); 6.91 (1H, dd, $J_{6',7'}$ = 7.6, $J_{5',7'}$ = 1.0, H-7'); 7.11 (1H, dd, $J_{5',6'}$ = 7.9, $J_{5',7'}$ = 1.0, H-5'); 7.34 (1H, dd, $J_{6',7'}$ = 7.6, $J_{5',6'}$ = 7.9, H-6'); 7.37 (1H, t, *J* = 7.6, H-4 (C$_6$H$_5$)); 7.53 (2H, dd, *J* = 7.6, *J* = 7.3, H-3,5 (C$_6$H$_5$)); 7.63 (1H, dd, $J_{6,7}$ = 10.9, $J_{7,8}$ = 7.0, H-7); 7.82 (1H, dd, $J_{8,9}$ = 8.6, $J_{7,8}$ = 7.0, H-8); 8.17 (2H, d, *J* = 7.4, H-2,6 (C$_6$H$_5$)); 8.26 (1H, d, $J_{6,7}$ = 10.9, H-6); 8.39 (1H, d, $J_{3',4'}$ = 8.55, H-4'); 8.44 (1H, d, $J_{8,9}$ = 8.6, H-9); 9.13 (1H, s, H-5); 9.35 (1H, s, H-1); 9.50 (1H, d, $J_{3',4'}$ = 8.55, H-3'). Found, %: C 80.92; H 4.63; N 14.45. $C_{26}H_{18}N_4$. Calculated, %: C 80.81; H 4.69; N 14.50.

4-(8-Amino-2-quinolyl)-2-(4-chlorophenyl)imidazo[1,2-*a*]quinoline (7b). Yield 0.42 g (quantitative); mp 133-135ºC (benzene). ^{1}H NMR spectrum (DMSO-d$_6$), δ, ppm (*J*, Hz): 5.12 (2H, br. s, NH$_2$); 6.99 (1H, dd, $J_{6',7'}$ = 7.6, $J_{5',7'}$ = 1.0, H-7'); 7.18 (1H, dd, $J_{5',6'}$ = 7.9, $J_{5',7'}$ = 1.0, H-5'); 7.37 (1H, dd, $J_{6',7'}$ = 7.6, $J_{5',6'}$ = 7.9, H-6'); 7.54 (2H, d, *J* = 7.9, H-3,5 (Ar)); 7.65 (1H, dd, $J_{6,7}$ = 10.9, $J_{7,8}$ = 7.0, H-7); 7.88 (1H, dd, $J_{8,9}$ = 8.6, $J_{7,8}$ = 7.0, H-8); 8.26 (1H, d, $J_{6,7}$ = 10.9, H-6); 8.29 (2H, d, *J* = 8.0, H-2,6 (Ar)); 8.45 (1H, d, $J_{8,9}$ = 8.6, H-9); 8.59 (1H, d, $J_{3',4'}$ = 8.55, H-4'); 8.88 (1H, s, H-5); 9.41 (1H, s, H-1); 9.52 (1H, d, $J_{3',4'}$ = 8.55, H-3'). Found, %: C 74.34; H 4.01; N 13.27. $C_{26}H_{17}ClN_4$. Calculated, %: C 74.19; H 4.07; N 13.31.

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