Synthesis of Pyrrolo[2,3-*b*]quinolines by Palladium-catalyzed Heteroannulation

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Received April 21, 2003

Palladium-catalyzed heteroannulation of 2-amino-3-iodoquinoline derivatives and 1-trimethylsilyl internal alkynes provided highly regioselective pyrrolo[2,3-*b*]quinolines with trimethylsilyl group next to the nitrogen atom in the pyrrole ring.

Key Words : Pyrrolo[2,3-*b*]quinolines, Palladium, Internal alkynes, Heteroannulation

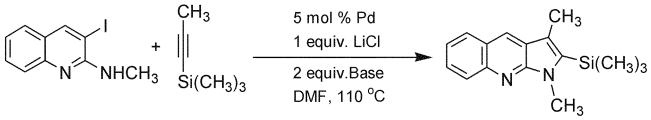
Introduction

Pyrrolo[2,3-*b*]quinolines are chemically interesting molecules due to their structural similarity to furo[2,3-*b*]quinolines, which occur widely in natural biologically active products.[1] Pyrrolo[2,3-*b*]quinolines have also a wide variety of biological activities, including anti-inflammatory, anticonvulsant, antihypertensive, antipyretic, analgesic, anti-MDR, and anticancer activity.[2] Many synthetic methods for pyrrolo[2,3-*b*]-quinolines[2a] have been reported, including pyrolysis of azepine derivatives,[3] photolysis of 3-(2-aminobenzylidene)-pyrrolidin-2(1H)-ones,[4] cyclization of 2-chloro-3-(2-chloroethyl)-quinoline,[5] cyclization of *N*-phenyl-3-aminopropiolamides,[6] reaction of 3-(lithiomethyl)quinoline with nitriles,[7] and the aza-Wittig/electrocyclic ring-closure/nitrene insertion process.[8] However, only a few synthetic methods have been described for totally aromatic 1*H*-pyrrolo[2,3-*b*]quinolines with limited substituents.[7-9] Larock and coworkers reported a palladium-catalyzed intermolecular reaction of *o*-haloarylamine and internal alkynes to give indoles in one operation.[10] The heteroannulation method could be an effective synthetic procedure for preparing a variety of heterocycles.[11] Therefore, we applied the synthetic method to the synthesis of heterocyclic azaindoles[12] and pyrrolo[3,2-*c*]quinolines.[13] Here, we report the convenient synthesis of 2,3-disubstituted pyrrolo[2,3-*b*]quinolines using palladium-catalyzed heteroannulation.

Results and Discussion

The 2-chloro-3-iodoquinoline was prepared by regioselective lithiation of 2-chloroquinoline with LDA followed by treatment with I_2 as an electrophile to prepare starting materials for palladium-catalyzed heteroannulation. The substitution reaction of 2-chloro-3-iodoquinoline with the corresponding amines afforded *N*-alkyl or aryl 2-amino-3-iodoquinolines in 70-80% yields.[14] Initially, we optimized the reaction of 2-methylamino-3-iodoquinoline and 1-trimethylsilyl propyne with various palladium species and bases. The results are summarized in Table 1. We first examined the effect of different palladium species on the product yield using KOAc as the base and DMF as the solvent. The reaction using $Pd(dba)_2$ or $Pd(OAc)_2$ as the palladium source provided the similar isolated yield, while $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$ gave lower yields of the desired products (entries 1-4). We also examined the effect of different bases with $Pd(OAc)_2$ as a palladium sources. The $Pd(OAc)_2$ was selected due to stability of palladium in reaction medium. The reaction using LiOAc gave the best isolated yields among the examined six bases (entries 4-9). The maximum yield of the desired product was obtained under 5 mol % $Pd(OAc)_2$, 1 equivalent of LiCl, 2 equivalents of LiOAc, and 2 equivalents of alkyne in DMF at 110 °C.

Table 1. Optimization of palladium-catalyzed heteroannulation for pyrrolo[2,3-*b*]quinolines

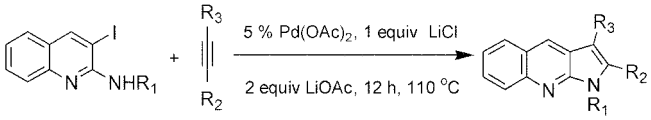


Entry[a]	Palladium Source	Base	Reaction time (h)	Isolated yields (%)
1	$Pd(dba)_2$	KOAc	14	65
2	$Pd(PPh_3)_2Cl_2$	KOAc	14	54
3	$Pd(PPh_3)_4$	KOAc	20	50
4	$Pd(OAc)_2$	KOAc	10	65
5	$Pd(OAc)_2$	LiOAc	10	75
6	$Pd(OAc)_2$	Na_2CO_3	10	50
7	$Pd(OAc)_2$	K_2CO_3	10	60
8	$Pd(OAc)_2$	Cs_2CO_3	10	67
9	$Pd(OAc)_2$	Et_3N	10	60

[a]Actual amounts of reagents used: 0.5 mmol aryl halide, 1.0 mmol alkyne, 0.5 mmol LiCl, 0.025 mmol Pd source, 1 mmol base, and 10 mL of DMF.

The reactions using various 2-amino-3-iodoquinolines and internal alkynes were examined under optimized reaction conditions to give diverse pyrrolo[2,3-*b*]quinolines. The results are summarized in Table 2. Previously, we found that the bulkiness of the substituents on the acetylene and the amine played a major role in determining the regioselectivity of alkyne insertion. The heteroaryl palladium intermediate usually added to the less hindered carbon of the internal alkyne. Heteroannulation using 1-trimethylsilyl alkynes provided highly regioselective products with the trimethylsilyl group next to the nitrogen atom in the pyrrole ring (entries 1-7). By contrast, the reactions using 1-phenyl-

Table 2. Synthesis of pyrrolo[2.3-*b*]quinolines by palladium-catalyzed heteroannulation



Entry[a]	R_1	R_2	R_3	Isolated yield (%)
1	Bn	$Si(CH_3)_3$	CH_3	65
2	Ph	$Si(CH_3)_3$	CH_3	67
3	CH_3	$Si(CH_3)_3$	$(CH_2)_3CH_3$	72
4	CH_3	$Si(CH_3)_3$	CH_2OH	63
5	CH_3	$Si(CH_3)_3$	CH_2CH_2OH	60
6	Bn	$Si(CH_3)_3$	Ph	65
7	Bn	$Si(CH_3)_3$	3-thiophene	57
8	Bn	$CH_3(CH_2)_2$	$CH_3(CH_2)_2$	74
9	Bn	Ph	Ph	80
10[b]	Ph	Ph	CH_3	84 (2 : 1)

[a]All reactions were run on a 0.5 mmol scale with 10 mL of DMF. [b]The isomeric ratio of R_2 and R_3 was determined by H^1 NMR spectroscopy.

propyne provided two regio-isomeric products (entry 10). The major isomer had a phenyl substituent next to the nitrogen atom in the pyrrole ring.

Conclusions

The palladium-catalyzed heteroannulation of 2-amino-3-iodoquinoline derivatives with 1-trimethylsilyl internal alkynes provided a convenient new route for the synthesis of various 1,2,3-trisubstituted pyrrolo[2,3-*b*]quinolines. Specially, the heteroannulation provided highly regioselective products with the trimethylsilyl group next to the nitrogen atom in the pyrrole ring. The 2-trimethylsilyl group of pyrrolo[2,3-*b*]quinolines could be transformed into another functional group to overcome selectivity problem of heteroannulation in unsymmetric alkynes.

Experimental Section

The infrared spectra were obtained on Jasco FT-IR 410 spectrometer. All ^{1}H- and ^{13}C NMR Spectra were recorded on a varian 400 MHz spectrometer. Chemical shift are given as value with reference to tetramethylsilane (TMS) as an internal standard. The GC-MS spectra were obtained on a Shimazu QP 1000 GC-MS. Melting points were determined on Mut-TEM apparatus and are uncorrected. Microanalyses were performed by Chungnam national university with CE Instrument EA 1110. Products were purified by flash chromatography on 230-400 mesh ASTM 60 silicagel. All of bases, LiCl and palladium species were purchased from Aldrich Chemical Co. The other chemicals were used directly as obtained from commercial sources unless otherwise noted.

Preparation of Starting Materials

2-Methylamino-3-iodoquinoline.[14] *n*-BuLi (2.5 M in hexane, 20 mL, 50 mmol) was slowly added to a magnetically stirred solution of diisopropylamine (5.05 g, 50 mmol) in dry THF (125 mL) under N_2 at −78 °C. The solution of LDA was stirred at −78 °C for 1 h. 2-chloroquinoline (8.2 g, 50 mmol) in THF (25 mL) was added slowly to the reaction mixture at −78 °C and stirred for 4 h at the same temperature at −78 °C. The iodine solution (15.2 g, 50 mL THF) was slowly added to a solution of lithiated 2-chloroquinoline. The resulting solution was stirred for 2 h at −78 °C and allowed to warm to room temperature over 5 h. After removing the solvent under reduced pressure, the residue was extracted using Et_2O and decolorized with saturated $NaHSO_3$ aqueous solution. The organic layer was dried over $MgSO_4$, filtered, and concentrated. 2-Chloro-3-iodoquinoline (10.8 g, 75%) was obtained by column chromatography with hexane/ethyl acetate (10 : 1): mp; 145-146 °C; IR (KBr) 3050, 3030, 1610, 1575, 1560, 1545, 1485 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.40 (s, 1H, ArH), 7.90-7.30 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$) δ 162.7, 148.7, 146.3, 132.1, 128.7, 128.2, 127.9, 126.8, 84.7; Ms m/z (relative intensity): 289 (M^+, 38), 254 (26), 128 (30), 106 (48), 91 (100), 65 (28).

2-Chloro-3-iodo-quinoline (1.4 g, 4.84 mmol), methylamine (40% aqueous solution, 10 mL), and ethanol (10 mL) were added to sealed tube and was reacted at 140 °C for 10 h. The resulting mixture was extracted using ethyl acetate and water. The organic layer was dried over $MgSO_4$, filtered, and concentrated. 2-Methylamino-3-iodoquinoline[14a] (1.0 g, 73%) was obtained by column chromatography using hexane/ethyl acetate (10 : 1): mp; 84-85 °C; IR (KBr) 3420, 3040, 2990, 2950, 2900, 1615, 1595, 1555, 1525 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.30 (s, 1H, ArH), 7.85-7.00 (m, 4H, ArH), 5.25 (brs, 1H, NH), 3.15 (d, 3H, J = 5.6 Hz, N-CH_3); ^{13}C NMR ($CDCl_3$) δ 154.2, 146.4, 139.8, 130.0, 127.1, 126.4, 126.3, 124.9, 122.4, 29.4; Ms m/z (relative intensity): 284 (M^+, 38), 155 (28), 125 (42), 106 (52), 91 (100), 65 (21); Anal. Calc. for $C_{10}H_9IN_2$: C, 42.28; H, 3.19; N, 9.86. Found: C, 42.35; H, 3.17; N, 9.84.

2-Benzylamino-3-iodoquinoline. This compound was prepared in 75% yields by the substitution of 2-chloro-3-iodo-quinoline with benzylamine: mp; 179-180 °C; IR (KBr) 3397, 3025, 1582, 1510, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.35 (s, 1H, ArH), 7.73-7.17 (m, 9H, ArH), 5.55 (br s, 1H, NH), 4.81 (d, 2H, J = 5.6 Hz, $ArCH_2$); ^{13}C NMR ($CDCl_3$) δ 153.2, 147.3, 146.5, 129.3, 130.1, 128.6, 127.9, 127.3, 126.4, 126.3, 125.0, 122.6, 83.2, 46.4; Ms m/z (relative intensity): 360 (M^+, 36), 231 (29), 128 (28), 116 (33), 106 (100), 91 (48), 65 (28); Anal. Calc. for $C_{16}H_{13}IN_2$: C, 53.35; H, 3.64; N, 7.78. Found: C, 53.40; H, 3.60; N, 7.75.

2-Phenylamino-3-iodoquinoline. This compound was prepared in 70% yield by the substitution of 2-chloro-3-iodoquinoline with aniline: mp; 150-151 °C; IR (KBr) 3305, 3110, 1594, 1480, 908, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.43 (s, 1H, ArH), 7.89-7.07 (m, 10H, ArH, NH); ^{13}C NMR ($CDCl_3$) δ 150.2, 147.1, 146.6, 140.0, 130.2, 128.8, 127.0, 126.2, 125.5, 123.6, 122.9, 119.5, 83.5; Ms m/z (relative intensity): 345 (M^+, 100), 218 (54), 109 (43); Anal. Calc. for $C_{15}H_{11}IN_2$: C, 52.04; H, 3.20; N, 8.09. Found: C, 52.11; H, 3.18; N, 8.07.

Trimethyl-thiophen-3-ylethynyl-silane. 3-Iodo-thiophene (2.1 g, 10.0 mmol), (trimethylsilyl)-acetylene (1.1 g, 12.0

mmol), and $PdCl_2(PPh_3)_2$ (140 mg, 2 mol %) were added in 40 mL of Et_3N. After stirring the mixture for 5 min, CuI (20 mg, 1 mol %) was added. The resulting solution was heated for 3 h at 50 °C under nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature, and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure, and residue was purified by column chromatography. Trimethyl-thiophen-3-ylethynyl-silane was obtained 90% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 7.23-7.18 (m, 2H, ArH), 7.04 (d, 1H, J = 8.0 Hz, ArH), 0.48 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 127.9, 127.3, 126.6, 126.1, 69.9, 62.9, –0.1; Ms m/z (relative intensity): 180 (M^+, 100), 97 (52), 24 (14).

4-Trimethylsilyl-3-butyn-1-ol. *n*-BuLi (2.5 M in hexane, 80 mL, 0.2 mol) was added in 500 mL of THF at −15 °C. 3-Butyn-1-ol (7.0 g, 0.1mol) was dissolved in 50 mL of THF and the solution was slowly added to *n*-butyllithium solution. Subsequently, chlorotrimethylsilane (24 g, 0.2 mol) was introduced over a period of 30 min with cooling at −15 °C. The resulting mixture was stirred for 3 h at room temperature, and poured into 100 mL of 10% acetic acid. The reaction mixture was stirred for 1h at room temperature, and neutralized with aqueous sodium bicarbonate. Diethyl ether was added to the reaction mixture, and organic layer was separated form aqueous layer. The organic layer was dried over magnesium sulfate and filtered. Diethyl ether was removed by evaporation in water bath and the residue was distilled through a 40 cm Vigreux column, giving the desired alcohol (11 g, 81%); b.p 90 °C/25 mmHg; ^{1}H NMR ($CDCl_3$) δ 3.64 (t, 2H, J = 7.0 Hz, $C\underline{H}_2O$), 2.46 (t, 2H, J = 7.0 Hz, $C\underline{H}_2$), 2.38 (br, 1H, OH), 0.12 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($C\underline{D}Cl_3$) δ 103.4, 69.8, 60.5, 23.8, –0.1; Ms m/z (relative intensity): 142 (M^+, 100), 140 (42), 125 (22).

General Procedure of the palladium-catalyzed heteroannulation of internal alkynes. Palladium acetate (6 mg, 0.025 mmol), LiCl (22 mg, 0.5 mmol), LiOAc (66 mg, 1.0 mmol), 2-methylamino-3-iodoquinoline (142 mg, 0.5 mmol), 1-trimethylsilylpropyne (112 mg, 1.0 mmol), and DMF (10 mL) were added to a pressure tube equipped with a stirring bar. After heating the reaction mixture for 10 h at 110 °C, the resulting solution was diluted with ethyl acetate and washed with saturated aqueous ammonium chloride. The organic layer was dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography using hexane-ethyl acetate. 1,3-Dimethyl-2-trimethylsilyl-pyrrolo[2,3-*b*]-quinoline (100 mg, 75%) was obtained as a yellow solid: mp; 86-87 °C; IR (KBr) 3059, 2950, 1606, 1568, 1441, 1245, 870, 843, 749 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.28 (s, 1H, ArH), 8.12 (d, 1H, J = 8.0 Hz, ArH), 7.95 (d, 1H, J = 8.0 Hz, ArH), 7.66-7.62 (m, 1H, ArH), 7.41-7.37 (m, 1H, ArH), 4.04 (s, 3H, NCH_3), 2.51 (s, 1H, $ArCH_3$), 0.52 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 151.8, 145.7, 140.8, 128.4, 127.7, 127.7, 125.3, 124.0, 123.3, 122.2, 118.0, 31.5, 10.9, 1.1; Ms m/z (relative intensity): 268 (M^+, 100), 253 (57), 209 (15), 195 (46), 126 (18); Anal. Calc. for $C_{16}H_{20}N_2Si$: C, 71.59; H, 7.51; N, 10.44. Found: C, 71.64; H, 7.49; N, 10.39. The following compounds were obtained using the above general procedure.

1-Benzyl-3-methyl-2-trimethylsilylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 65% yield from the reaction of 2-benzylamino-3-iodoquinoline with 1-trimetylsilyl-1-propyne: mp; 111-112 °C; IR (KBr) 2920, 1605, 1494, 1130, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.33 (s, 1H, ArH), 8.02-7.94 (m, 2H, ArH), 7.62-7.54 (m, 1H, ArH), 7.41-7.32 (m, 1H, ArH), 7.26-7.17 (m, 3H, ArH), 6.82-6.78 (m, 2H, ArH), 5.81 (s, 2H, $ArCH_2$), 2.55 (s, 3H, $ArCH_3$), 0.26 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 148.7, 145.2, 138.7, 128.3, 127.5, 127.4, 127.2, 126.8, 125.8, 124.9, 124.4, 121.5, 120.8, 116.7, 94.7, 46.0, 10.4, 0.3; Ms m/z (relative intensity): 344 (M^+, 100), 271 (22), 253 (50), 221 (40), 207 (35), 195 (24), 91 (86), 73 (31), 59 (35); Anal. Calc. for $C_{22}H_{24}N_2Si$: C, 76.70; H, 7.02; N, 8.13. Found: C, 76.75; H, 7.04; N, 8.10.

3-Methyl-1-phenyl-2-trimethylsilylpyrrolo[2,3-b]quinoline. This compound was obtained as a yellow solid in 67% yield from the reaction of 2-phenylamino-3-iodoquinoline with 1-trimetylsilyl-1-propyne: mp; 117-118 °C; IR (KBr) 2925, 1632, 1536, 1451, 1138, 836 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.32 (s, 1H, ArH), 7.98-7.93 (m, 2H, ArH), 7.57-7.44 (m, 6H, ArH), 7.38-7.36 (m, 1H, ArH), 2.52 (s, 3H, $ArCH_3$), 0.14 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 146.0, 142.0, 139.8, 129.6, 129.3, 129.0, 128.4, 128.2, 128.0, 127.6, 125.3, 124.4, 123.4, 122.7, 119.9, 11.3, 0.7; Ms m/z (relative intensity): 330 (M^+, 100), 315 (67), 285 (27), 257 (17), 239 (40), 150 (65), 91 (14), 73 (24), 43 (41); Anal. Calc. for $C_{21}H_{22}N_2Si$: C, 76.32; H, 6.71; N, 8.48. Found: C, 76.36; H, 6.74; N, 8.45.

3-Butyl-1-methyl-2-trimethylsilylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 72% yield from the reaction of 2-methylamino-3-iodoquinoline with 1-trimetylsilyl-1-hexyne: mp; 96-97 °C; IR (KBr) 3048, 2950, 1610, 1553, 1440, 1238, 870, 752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.25 (s, 1H, ArH), 8.11 (d, 1H, J = 8.0 Hz, ArH), 7.97 (d, 1H, J =8.0 Hz, ArH), 7.68-7.63 (m, 1H, ArH), 7.42-7.35 (m, 1H, ArH), 4.01 (s, 3H, NCH_3), 2.51 (t, 2H, J = 6.8 Hz, $ArC\underline{H}_2CH_2$-), 1.58-1.44 (m, 2H, $ArCH_2C\underline{H}_2$-), 1.05-0.96 (m, 2H, $-CH_2$), 0.84 (t, 3H, J = 7.2 Hz, $-CH_2C\underline{H}_3$), 0.07 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 150.3, 145.7, 140.8, 128.6, 127.6, 127.6, 125.3, 123.9, 123.3, 122.4, 117.8, 32.4, 18.7, 14.6, 10.1, 9.0, 1.0; Ms m/z (relative intensity): 310 (M^+, 100), 281 (46), 253 (25), 209 (43), 195 (21), 126 (16); Anal. Calc. for $C_{19}H_{26}N_2Si$: C, 73.49; H, 8.44; N, 9.02. Found: C, 73.46; H, 8.40; N, 9.08.

(1-Methyl-2-trimethylsilanyl-pyrrolo[2,3-*b*]quinolin-3-yl)-methanol. This compound was obtained as a yellow solid in 63% yield from the reaction of 2-methylamino-3-iodoquinoline with 3-trimetylsilyl-2-propyl-1ol: mp; 81-82 °C; IR (KBr) 3305, 3061, 2940, 1615, 1460, 1248, 870, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.26 (s, 1H, ArH), 8.14 (d, 1H, J = 8.0 Hz, ArH), 8.01 (d, 1H, J = 8.0 Hz, ArH), 7.69-7.64 (m, 1H, ArH), 7.43-7.39 (m, 1H, ArH), 4.75 (s, 2H, $ArC\underline{H}_2OH$), 4.01 (s, 3H, NCH_3), 0.55 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 152.1, 145.7, 140.8, 128.5, 127.9, 127.7, 125.4, 124.4, 123.3, 123.0, 118.2, 59.8, 33.3, 1.0; Ms m/z (relative intensity): 284 (M^+, 100), 253 (61), 209 (25), 195 (41), 126 (23); Anal. Calc. for $C_{16}H_{20}N_2OSi$: C, 67.56; H, 7.09; N,

9.85. Found: C, 67.60; H, 7.13; N, 9.81.

2-(1-Methyl-2-trimethylsilanyl-pyrrolo[2,3-*b*]quinolin-3-yl)-ethanol. This compound was obtained as a yellow solid in 60% yield from the reaction of 2-methylamino-3-iodoquinoline with 4-trimethylsilyl-3-butyn-1-ol: mp; 87-88 °C; IR (KBr) 3310, 3065, 2890, 1632, 1520, 1252, 867, 788, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.24 (s, 1H, ArH), 8.15 (d, 1H, J = 8.0 Hz, ArH), 7.98 (d, 1H, J = 8.0 Hz, ArH), 7.70-7.66 (m, 1H, ArH), 7.42-7.39 (m, 1H, ArH), 4.68-4.63 (m, 2H, $ArCH_2C\underline{H}_2OH$), 4.05 (s, 3H, NCH_3), 2.71 (t, 2H, J = 7.0 Hz, $ArC\underline{H}_2CH_2OH$), 0.51 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 152.2, 145.8, 140.8, 128.6, 128.0, 127.7, 125.4, 124.4, 123.3, 122.8, 118.3, 58.5, 33.2, 23.6, 1.1; Ms m/z (relative intensity): 298 (M^+, 57), 253 (100), 209 (31), 195 (51), 126 (18); Anal. Calc. for $C_{17}H_{22}N_2OSi$: C, 68.58; H, 7.43; N, 9.39. Found: C, 68.63; H, 7.41; N, 9.36.

1-Benzyl-3-phenyl-2-trimethylsilylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 65% yield from the reaction of 2-benzylamino-3-iodoquinoline with 1-trimethylphenyl acetylene: mp; 114-115 °C; IR (KBr) 3029, 2927, 1602, 1570, 1429, 1249, 845, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.19 (s, 1H, ArH), 8.08 (d, 1H, J = 8.0 Hz, ArH), 7.85 (d, 1H, J = 8.0 Hz, ArH), 7.62-7.14 (m, 10H, ArH), 6.95-6.93 (m, 2H, ArH), 5.94 (s, 2H, $ArCH_2$), 0.03 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 145.8, 142.0, 139.1, 136.0, 131.8, 131.1, 129.2, 128.5, 128.5, 128.4, 128.3, 128.1, 127.8, 127.3, 126.9, 126.8, 126.1, 124.8, 122.7, 47.2, 0.8; Ms m/z (relative intensity): 406 (M^+, 100), 333 (54), 315 (34), 216 (20), 91 (67), 73 (44), 65 (17); Anal. Calc. for $C_{27}H_{26}N_2Si$: C, 79.76; H, 6.45; N, 6.89. Found: C, 79.82; H, 6.44; N 6.92.

1-Benzyl-3-thiophen-3-yl-2-trimethylsilylpyrrolo[2,3-*b*]-quinoline. This compound was obtained as a yellow solid in 57% yield from the reaction of 2-benzylamino-3-iodoquinoline with trimethyl-thiophen-3-ylethynyl-silane: mp; 151-152 °C; IR (KBr) 3026, 2922, 1598, 1562, 1436, 1240, 747, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.21 (s, 1H, ArH), 8.05 (dd, 1H, J = 8.2, 0.6 Hz, ArH), 7.89 (d, 1H, J = 8.2 Hz, ArH), 7.66-7.15 (m, 8H, ArH), 6.96-6.92 (m, 2H, ArH), 5.91 (s, 2H, $ArCH_2$), 0.08 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 150.9, 145.3, 141.8, 138.5, 135.3, 129.8, 127.8, 127.7, 127.4, 127.3, 126.3, 125.8, 125.5, 124.4, 124.2, 123.6, 122.2, 122.0, 120.2, 46.4, 0.5; Ms m/z (relative intensity): 412 (M^+, 100), 328 (20), 253 (48), 221 (38), 207 (36), 195 (22), 91 (75), 59 (18); Anal. Calc. for $C_{25}H_{24}N_2SSi$: C, 72.77; H, 5.86; N, 6.79. Found: C, 72.82; H, 5.79; N 6.78.

1-Benzyl-2,3-dipropylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 74% yield from the reaction of 2-benzylamino-3-iodoquinoline with 4-octyne: mp; 129-130 °C; IR (KBr) 2959, 2870, 1486, 1242, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.17 (s, 1H, ArH), 8.09 (d, 1H, J = 8.2 Hz, ArH), 7.88 (d, 1H, J = 8.2 Hz, ArH), 7.65-7.58 (m, 1H, ArH), 7.41-7.35 (m, 1H, ArH), 7.25-7.15 (m, 5H, ArH), 5.70 (s, 1H, $ArCH_2$), 2.84-2.71 (m, 2H, $ArC\underline{H}_2CH_2$-), 1.76-1.61 (m, 2H, $ArCH_2C\underline{H}_2$-), 1.06-0.95 (m, 3H, $-CH_2C\underline{H}_3$); ^{13}C NMR ($CDCl_3$) δ 150.2, 144.8, 137.9, 128.4, 128.2, 128.0, 127.9, 127.4, 127.2, 124.5, 124.4, 123.4, 122.1, 114.9, 92.8, 53.5, 26.7, 26.6, 25.6, 24.7, 13.3, 13.0; Ms m/z (relative intensity): 342 (M^+, 75), 299 (16), 256 (39), 165 (20), 154 (15), 127 (13), 91 (100), 65 (34); Anal. Calc. for $C_{24}H_{26}N_2$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.12; H, 7.68; N 8.20.

1-Benzyl-2,3-diphenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 80% yield from the reaction of 2-benzylamino-3-iodoquinoline with diphenylacetylene: mp; 219-220 °C; IR (KBr) 3050, 1600, 1569, 1422, 1387, 788 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.52 (s, 1H, ArH), 8.14 (d, 1H, J = 8.4 Hz, ArH), 7.92 (d, 1H, J = 8.4 Hz, ArH), 7.64-7.61 (m, 2H, ArH), 7.41-6.98 (m, 15H, ArH), 5.60 (s, 2H, $ArCH_2$); ^{13}C NMR ($CDCl_3$) δ 150.2, 145.5, 141.4, 138.5, 134.1, 131.6, 131.2, 130.9, 129.6, 128.6, 128.4, 128.3, 128.3, 128.2, 128.1, 127.7, 127.3, 127.0, 126.3, 126.0, 125.4, 122.9, 122.0, 46.0; Ms m/z (relative intensity): 410 (M^+, 100), 333 (41), 317 (60), 214 (11), 166 (17), 91 (77), 65 (18); Anal. Calc. for $C_{30}H_{22}N_2$: C, 87.77; H, 5.40; N, 6.82. Found: C, 87.73; H, 5.42; N 6.85.

Acknowledgments. This work was supported by Korea Research Foundation Grant (KRF-2001-015-DP0330).

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