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A CONVENIENT DIVERSIFICATION OF PYRROLO[2,3-*b*]-QUINOLINES BY IODONATION AND PALLADIUM-CATALYZED COUPLING REACTIONS

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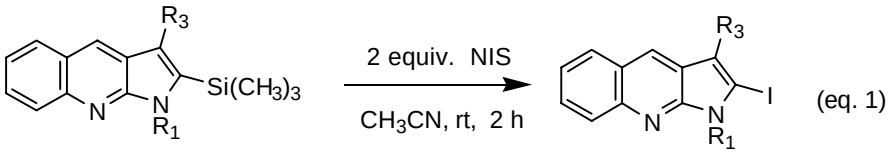
Abstract – The 2-trimethylsilylpyrrolo[2,3-*b*]quinolines were easily transformed into 2-iodopyrrolo[2,3-*b*]quinolines under NIS/CH_3CN. The palladium-catalyzed Heck, Stille, and Suzuki coupling reactions of 2-iodo[2,3-*b*]quinolines provided diverse 1,2,3-trisubstituted pyrrolo[2,3-*b*]quinolines in moderate to high yields.

Contemporary organic chemistry is paying more attention to development of methods for the synthesis of condensed heterocyclic compounds. The interest in such compounds is due to the prospect of seeking new biologically active substances.[1] Recently, Larock and coworkers reported a palladium-catalyzed intermolecular reaction of *o*-haloarylamine with internal alkynes to give indoles in one operation.[2] The heteroannulation method could be an effective synthetic procedure for preparing a variety of heterocycles.[3] We applied the heteroannulation to synthesize condensed heterocyclic compounds such as azaindoles,[4] pyrrolo[3,2-*c*]quinolines,[5] and pyrrolo[2,3-*b*]quinolines.[6] Specially, pyrrolo[2,3-*b*]quinolines have shown a wide variety of biological activities, including anti-inflammatory, anticonvulsant, antihypertensive, antipyretic, analgesic, anti-MDR, and anticancer activity.[7] Although many synthetic methods for pyrrolo[2,3-*b*]quinolines have been reported in the literature,[8-15] but few papers showed manipulation of pyrrolo[2,3-*b*]quinolines. Here, we report a convenient diversification of pyrrolo[2,3-*b*]quinolines by iodination and palladium-catalyzed coupling reactions.

The heteroannulation reactions using various 2-amino-3-iodoquinolines with 1-trimethylsilyl internal alkynes provided pyrrolo[2,3-*b*]quinolines with the trimethylsilyl group next to the nitrogen atom in the pyrrole ring. By contrast, the reactions using asymmetric aromatic alkynes provided two regioisomeric products. To overcome the regioisomeric problem of asymmetric aromatic alkynes, we examined the preparation of 2-iodopyrrolo[2,3-*b*]quinolines and their applications to palladium-catalyzed coupling

reactions. The 2-iodo-3-substituted pyrrolo[2,3-*b*]quinolines were prepared by reacting 2-trimethylsilyl-3-substituted pyrrolo[2,3-*b*]quinolines[6] with 2 equivalents of NIS in acetonitrile as the solvent (eq. 1).[16]

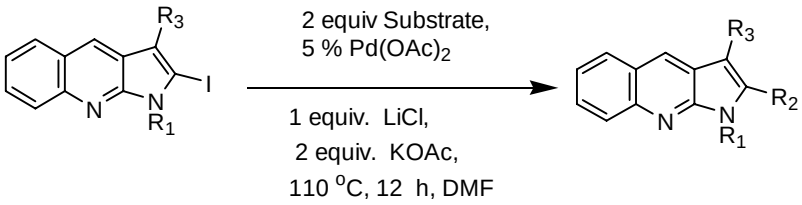


(eq. 1)

R_1	R_3	Yield (%)
CH_3	CH_3	85
CH_3	Ph	73
Bn	CH_3	77
Bn	Ph	71
Ph	CH_3	75

The reaction using ICl instead of NIS resulted in the concurrent formation of 2-chloropyrrolo[2,3-*b*]quinolines, which did not react in the coupling reactions. The palladium-catalyzed coupling reactions were performed with 2-iodo-3-substituted pyrrolo[2,3-*b*]quinolines and various boric acids, alkenes, and stannyl compounds. The results are summarized in Table 1.

Table1. Palladium-catalyzed functionalization at the 2-position of pyrrolo[2,3-*b*]quinolines.



Entry[a]	Substrate	R_1	R_2	R_3	Yield (%)[b]
1	$PhB(OH)_2$	CH_3	Ph	CH_3	70
2	4-$CH_3OPhB(OH)_2$	CH_3	4-CH_3OPh	CH_3	65
3	4-$FPh(OH)_2$	CH_3	4-FPh	CH_3	67
4	4-$CH_3OPhB(OH)_2$	Bn	4-CH_3OPh	Ph	64
5	$PhB(OH)_2$	Bn	Ph	CH_3	72
6	4-$FPhB(OH)_2$	Bn	4-FPh	CH_3	64
7	4-$CH_3OPhB(OH)_2$	Ph	4-CH_3OPh	CH_3	68
8	CH_2=$CHCH_2OH$	Bn	CH_2CH_2CHO	Ph	57
9	CH_2=$CHCH(OH)CH_3$	Bn	$CH_2CH_2COCH_3$	Ph	56
10	CH_2=$CHCO_2CH_3$	Bn	CH=$CHCO_2CH_3$	CH_3	70
11	CH_2=$CHCOCH_3$	CH_3	CH=$CHCOCH_3$	CH_3	68
12	CH_2=$CHSn(C_4H_9)_3$	Bn	CH=CH	Ph	64

13	CH_2=CHSn(C_4H_9)$_3$	Ph	CH_2=CH	CH_3	68
14	CH_2=CHSn(C_4H_9)$_3$	CH_3	CH_2=CH	Ph	70

[a] All the reactions were run on a 0.5-mmol scale with 10 mL of DMF.

[b] Isolated yields.

The reactions using 2-iodo-3-substituted pyrrolo[2,3-*b*]quinoline with several phenylboric acids provided 2-phenylpyrrolo[2,3-*b*]quinolines with high yields of the desired products (Entries 1-7). The Suzuki coupling proceeded very well with various phenyl boric acids without any electronic effect of the phenyl substituents. We further examined 2-alkyl substitution of pyrrolo[2,3-*b*]quinolines using the Heck reaction, since this could not be introduced easily using previous synthetic methods. The reaction using 1-benzyl-2-iodopyrrolo[2,3-*b*]quinolines and alkenes provided 2-alkylpyrrolo[2,3-*b*]quinolines in moderate yields (Entries 8-11). Especially, the reactions using allylic alcohol gave further migrated carbonyl products (Entries 8 and 9). Finally, the reactions using tributyl(vinyl)tin were examined. The vinyl-substituted products were obtained with reasonable yields.

In summary, the facile iodination of 2-trimethylsilylpyrrolo[2,3-*b*]quinolines provided various 2-iodopyrrolo[2,3-*b*]quinolines, which is useful for coupling reactions. Specially, the palladium-catalyzed coupling of 2-iodo-3-substituted pyrrolo[2,3-*b*]quinolines tremendously broadens the synthetic scope of pyrrolo[2,3-*b*]quinolines.

EXPERIMENTAL

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.

General synthetic procedure of 2-trimethylsilylpyrrolo[2,3-*b*]quinolines by palladium-catalyzed heteroannulation of internal alkynes.[6]

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 (10ml) 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-trimethylsilylpyrrolo[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}; ^1H 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. Calcd 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.

General procedure for the preparation of 2-iodopyrrolo[2,3-*b*]quinolines

1,3-Dimethyl-2-trimethylsilylpyrroloquinoline (134 mg, 0.5 mmol) was dissolved in 10 mL of acetonitrile, and *N*-iodosuccinimide (225 mg, 1mmol) was slowly added to the reaction solution. The reaction mixture was stirred for 2 h at rt. The resulting solution was concentrated, and the residue was purified by silica gel column chromatography using hexane-ethyl acetate (10:1). 1,3-Dimethyl-2-iodopyrrolo[2,3-*b*]quinoline (137 mg, 85 %) was obtained as a yellow solid: mp 106-107 °C; IR (KBr) 3850, 2910, 1612, 1444, 1325, 755 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.12 (s, 1H, ArH), 8.06 (d, 1H, *J* = 8.8 Hz, ArH), 7.87 (d, 1H, *J* = 8.4 Hz, ArH), 7.64-7.60 (m, 1H, ArH), 7.39-7.35 (m, 1H, ArH), 3.87 (s, 3H, NCH_3), 2.33(s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 150.1, 144.7, 128.2, 128.0, 127.7, 124.4, 124.1, 122.9, 122.1, 115.0, 93.9, 32.7, 12.6; MS m/z (relative intensity): 322 (M^+, 88), 321 (12), 195 (100), 154 (37), 127 (35), 97 (12), 75 (11); Anal. Calcd for $C_{13}H_{11}N_2I$: C, 48.47; H, 3.44; N, 8.70. Found: C, 48.42; H, 3.45; N, 8.72. The following compounds were obtained using the above general procedure.

2-Iodo-1-methyl-3-phenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 73 % yield from the iodination of 3-methyl-1-phenyl-2-trimethylsilylpyrrolo[2,3-*b*]quinoline: mp 115-116 °C; IR (KBr) 2523, 2360, 1599, 1441, 1385, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.35 (s, 1H, ArH), 8.20 (d, 1H, *J* = 8.4 Hz, ArH), 7.89-7.87 (m, 1H, ArH), 7.70-7.62 (m, 3H, ArH), 7.55-7.52 (m, 2H, ArH), 7.45-7.40 (m, 2H, ArH), 4.08 (s, 3H, NCH_3); ^{13}C NMR ($CDCl_3$) δ 149.3, 144.1, 134.1, 129.7, 128.8, 128.7, 128.4, 127.4, 127.1, 126.4, 124.5, 123.5, 121.8, 121.1, 93.5, 33.6; MS m/z (%): 384 (M^+, 12), 257 (6), 191 (15), 128 (18), 107 (47), 84 (71), 77 (34), 43 (100); Anal. Calcd for $C_{18}H_{13}N_2I$: C, 56.27; H, 3.41; N, 7.29. Found: C, 56.33; H, 3.40; N, 7.33.

1-Benzyl-2-iodo-3-methylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 77 % yield from the iodination of 1-benzyl-3-methyl-2-trimethylsilylpyrrolo[2,3-*b*]quinoline: mp 124-125 °C; IR (KBr) 3018, 2909, 1613, 1566, 1438, 1417, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.14 (s, 1H, ArH), 8.05 (d, 1H, *J* = 8.4 Hz, ArH), 7.88-7.86 (m, 1H, ArH), 7.62-7.58 (m, 1H, ArH), 7.38-7.34 (m, 1H, ArH), 7.23-7.16 (m, 5H, ArH), 5.61 (s, 2H, $ArCH_2$), 2.32 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 150.3, 144.9, 137.9, 128.4, 128.2, 128.0, 127.9, 127.3, 127.1, 124.5, 124.4, 123.0, 122.1, 115.8, 92.8, 48.5, 12.7; MS m/z (relative intensity): 398 (M^+, 67), 321 (13), 271 (49), 256 (14), 154 (14), 127 (18), 91 (100), 65 (20); Anal. Calcd for $C_{19}H_{15}N_2I$: C, 57.30; H, 3.80; N, 7.03. Found: C, 57.35; H, 3.82; N, 6.99.

1-Benzyl-2-iodo-3-phenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 71 % yield from the iodination of 1-benzyl-3-phenyl-2-trimethylsilylpyrrolo[2,3-*b*]quinoline: mp 139-140 °C; IR (KBr) 3023, 2915, 1631, 1582, 1435, 1395, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.39 (s, 1H, ArH), 8.13 (d, 1H, *J* = 8.2 Hz, ArH), 7.93 (dd, 1H, *J* = 8.2, 1.2 Hz, ArH), 7.71-7.66 (m, 3H, ArH), 7.58-7.53 (m, 2H, ArH), 7.47-7.43 (m, 2H, ArH), 7.39-7.26 (m, 5H, ArH), 5.83 (s, 2H, $ArCH_2$); ^{13}C NMR ($CDCl_3$) δ 150.3, 145.2, 137.7, 134.3, 129.8, 128.7, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.6, 127.3, 125.6, 125.0, 123.4, 121.5, 92.2, 49.0; MS m/z (relative intensity): 460 (M^+, 100), 333 (13), 271 (35), 256 (16), 154 (21), 127 (29), 91 (52), 65 (15); Anal. Calcd for $C_{24}H_{17}N_2I$: C, 62.62; H, 3.72; N, 6.09. Found: C, 62.58; H, 3.70; N, 6.07.

2-Iodo-3-methyl-1-phenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 75 % yield from the iodination of 3-methyl-1-phenyl-2-trimethylsilylpyrrolo[2,3-*b*]quinoline: mp 125-126 °C; IR (KBr) 2941, 1652, 1556, 1385, 869 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.27 (s, 1H, ArH), 7.98-7.93 (m, 2H, ArH), 7.60-7.56 (m, 3H, ArH), 7.53-7.49 (m, 3H, ArH), 7.48-7.38 (m, 1H, ArH), 2.47 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 151.1, 145.2, 138.1, 129.6, 129.0, 128.4, 128.1, 128.0, 124.7, 124.6, 123.4, 122.5, 117.2, 94.1, 29.7, 13.0; MS m/z (relative intensity): 384 (M^+, 100), 257 (37), 242 (20), 216 (17), 128 (53), 107 (27), 94 (31); Anal. Calcd for $C_{18}H_{13}N_2I$: C, 56.27; H, 3.41; N, 7.29. Found: C, 56.34; H, 3.39; N, 7.30.

General procedure for the palladium-catalyzed coupling reactions

Palladium acetate (6 mg, 0.025 mmol), LiCl (22 mg, 0.5 mmol), KOAc (98 mg, 1.0 mmol), 2-iodopyrrolo[2,3-*b*]quinoline (0.5 mmol), appropriate substrate (1.0 mmol) , and DMF (10 mL) were added to pressure tube equipped with stirring bar. After heating the reaction mixture for 12 h at 110 ^oC, the resulting solution was diluted with ethyl acetate and washed with saturated aqueous

ammonium chloride. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane-ethyl acetate. The following compounds were obtained using the above general procedure.

1,3-Dimethyl-2-phenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow oil in 70 % yield from 1,3-dimethyl-2-iodo-pyrrolo[2,3-*b*]quinoline with phenylboronic acid: IR (neat) 2930, 1630, 1252, 940, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.26 (s, 1H, ArH), 8.13 (d, 1H, *J* = 8.0 Hz, ArH), 7.93 (dd, 1H, *J* = 8.0, 0.8 Hz, ArH), 7.64-7.60 (m, 1H, ArH), 7.54-7.45 (m, 5H, ArH), 7.41-7.38 (m, 1H, ArH), 3.79 (s, 3H, NCH_3), 2.35 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 150.4, 145.2, 141.5, 131.2, 130.3, 128.5, 128.4, 128.2, 127.7, 127.4, 125.2, 124.6, 123.3, 122.5, 106.2, 29.8, 9.3; MS m/z (relative intensity): 272 (M^+, 100), 255 (16), 195 (33), 135 (29), 128 (50), 122 (20), 100 (10); Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.83; H, 5.90; N, 10.27.

2-(4-Methoxyphenyl)-1,3-dimethylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 65 % yield from the reaction of 1,3-dimethyl-2-iodopyrrolo[2,3-*b*]quinoline with 4-methoxyphenylboronic acid: mp 115-116 °C; IR (KBr) 2925, 1609, 1509, 1254, 1041, 744 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.27 (s, 1H, ArH), 8.13 (d, 1H, *J* = 8.0 Hz, ArH), 7.95 (d, 1H, *J* = 8.0 Hz, ArH), 7.64-7.60 (m, 1H, ArH), 7.42-7.38 (m, 2H, ArH), 7.08-7.04 (m, 2H, ArH), 6.81-6.74 (m, 1H, ArH), 3.90 (s, 3H, OCH_3), 3.78 (s, 3H, NCH_3), 2.35 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 159.7, 150.4, 145.1, 141.5, 131.6, 128.2, 127.6, 125.1, 124.6, 123.5, 122.5, 116.1, 114.8, 114.0, 105.8, 55.4, 29.8, 9.3; MS m/z (relative intensity): 302 (M^+, 30), 196 (10), 166 (27), 143 (35), 99 (100), 70 (27), 56 (23), 41 (28); Anal. Calcd for $C_{20}H_{18}N_2O$: C, 79.44; H, 6.00; N, 9.26. Found: C, 79.40; H, 6.02; N, 9.23.

2-(4-Fluorophenyl)-1,3-dimethylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 67 % yield from the reaction of 1,3-dimethyl-2-iodopyrrolo[2,3-*b*]quinoline with 4-fluoro-phenylboronic acid: mp 110-111 °C; IR (KBr) 2938, 1650, 1390, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.28 (s, 1H, ArH), 8.12 (d, 1H, *J* = 8.4 Hz, ArH), 7.95 (dd, 1H, *J* = 8.4, 0.8 Hz, ArH), 7.65-7.61 (m, 1H, ArH), 7.46-7.38 (m, 3H, ArH), 7.25-7.21 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 162.8 ($^1J_{C-F}$ = 246 Hz), 150.3, 145.3, 140.4, 132.1 ($^3J_{C-F}$ = 8 Hz), 128.2, 127.8, 127.6, 127.3, 125.3, 124.6, 123.1, 122.6, 115.7 ($^2J_{C-F}$ = 21 Hz), 106.4, 29.8, 9.2; MS m/z (relative intensity): 290 (M^+, 34), 196 (20), 166 (31), 143 (29), 99 (100), 70 (28), 56 (24), 41 (32); Anal. Calcd for $C_{19}H_{15}N_2F$: C, 78.60; H, 5.21; N, 9.65. Found: C, 78.64; H, 5.18; N, 9.64.

1-Benzyl-2-(4-methoxyphenyl)-phenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 64 % yield from the reaction of 1-benzyl-2-iodo-3-phenylpyrrolo[2,3-*b*]quinoline with 4-methoxy-phenylboronic acid: mp 135-136 °C; IR (KBr) 2923, 1603, 1423, 1249, 1130, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.51 (s, 1H, ArH), 8.12 (d, 1H, *J* = 8.4 Hz, ArH), 7.93 (d, 1H, *J* = 8.4 Hz, ArH), 7.67-7.61 (m, 1H, ArH), 7.42-7.30 (m, 5H, ArH), 7.23-7.13 (m, 6H, ArH), 7.03-7.00 (m, 2H, ArH), 6.85-6.83 (m, 2H, ArH), 5.59 (s, 2H, $ArCH_2$), 3.82 (s, 3H, OCH_3); ^{13}C NMR ($CDCl_3$) δ 159.8, 150.2, 145.4, 141.4, 138.7, 134.3, 132.2, 129.6, 128.4, 128.3, 128.1, 127.6, 127.2, 127.0, 126.2, 126.0, 125.9, 125.4, 123.3, 122.9, 121.9, 113.9, 112.7, 55.2, 45.9; MS m/z (relative intensity): 440 (M^+, 25), 305 (10), 224 (35), 143 (40), 99 (49), 70 (27), 56 (100), 41 (28); Anal. Calcd for $C_{31}H_{24}N_2O$: C, 84.52; H, 5.49; N, 6.36. Found: C, 84.50; H, 5.46; N, 6.38.

1-Benzyl-3-methyl-2-phenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 72 % yield from the reaction of 1-benzyl-2-iodo-3-methylpyrrolo [2,3-*b*]quinoline with phenylboronic acid: mp 128-129 °C; IR (KBr) 2936, 1620, 1246, 938, 742 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.30 (s, 1H, ArH), 8.11 (d, 1H, *J* = 8.4 Hz, ArH), 7.96 (dd, 1H, *J* = 8.4, 1.2 Hz, ArH), 7.64-7.60 (m, 1H, ArH), 7.42-7.38 (m, 4H, ArH), 7.29-7.27 (m, 2H, ArH), 7.11-7.08 (m, 3H, ArH), 6.90-6.88 (m, 2H, ArH), 5.53 (s, 2H, $ArCH_2$), 2.32 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 150.5, 145.4, 141.4, 138.8, 131.4, 130.4, 128.4, 128.3, 128.1, 128.1, 128.0, 127.4, 127.1, 126.8, 125.2, 124.9, 123.3, 122.6, 107.1, 45.9, 9.2; MS m/z (relative intensity): 348 (M^+, 100), 333 (19), 271 (54), 154 (25), 127 (19), 91 (63), 65 (10); Anal. Calcd for $C_{25}H_{20}N_2$: C, 86.17; H, 5.79; N, 8.04. Found: C, 86.12; H, 5.77; N, 8.02.

1-Benzyl-2-(4-fluorophenyl)-3-methylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 64 % yield from the reaction of 1-benzyl-2-iodo-3-methylpyrrolo[2,3-*b*]quinoline with 4-fluorophenylboronic acid: mp 122-123 °C; IR (KBr) 2912, 1610, 1260, 731 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.30 (s, 1H, ArH), 8.10 (d, 1H, *J* = 8.2 Hz, ArH), 7.96 (dd, 1H, *J* = 8.2, 1.0 Hz, ArH), 7.64-7.60 (m, 1H, ArH), 7.43-7.39 (m, 1H, ArH), 7.24-7.21 (m, 2H, ArH), 7.11-7.07 (m, 5H, ArH), 6.89-6.86 (m, 2H, ArH), 5.50 (s, 2H, $ArCH_2$), 2.29 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 162.8 ($^{1}J_{C\text{-}F}$ = 247.6 Hz), 150.3, 145.4, 140.3, 138.7, 132.1 ($^{3}J_{C\text{-}F}$ = 8.5 Hz), 128.2, 128.1, 128.0, 127.5, 127.4, 127.0, 126.9, 125.3, 124.9, 123.1, 122.7, 115.5 ($^{2}J_{C\text{-}F}$ = 21.9 Hz), 107.4, 45.9, 9.2; MS m/z (relative intensity): 367 (M^+, 26), 348 (10), 290 (100), 195 (11), 145 (48), 137 (52), 95 (75), 81 (50), 43 (30); Anal. Calcd for $C_{25}H_{19}N_2F$: C, 81.94; H, 5.23; N, 7.64. Found: C, 81.88; H, 5.22; N, 7.61.

2-(4-Methoxyphenyl)-3-methyl-1-phenylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 68 % isolated yield from the reaction of 1-phenyl-2-iodo-3-methyl pyrrolo[2,3-*b*]quinoline with 4-methoxy phenyl boronic acid: mp 130-131 °C; IR (KBr) 2920, 1615, 1400, 1252, 1115, 1031, 726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.27 (s, 1H, ArH), 8.04 (d, 1H, *J* = 8.2 Hz, ArH), 7.94 (d, 1H, *J* = 8.2 Hz, ArH), 7.76-7.71 (m, 1H, ArH), 7.61-7.26 (m, 6H, ArH), 7.07-6.78 (m, 2H, ArH), 6.69-6.65 (m, 2H, ArH), 3.71 (s, 3H, OCH_3), 2.26 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 158.2, 149.9, 142.4, 138.7, 133.6, 132.3, 129.3, 128.7, 128.3, 127.9, 127.2, 126.3, 126.2, 126.0, 125.8, 125.4, 122.3, 121.8, 111.4, 46.1, 32.2; MS m/z (relative intensity): 364 (M^+, 25), 229 (10), 204 (100), 143 (40), 99 (50), 70 (17), 56 (23); Anal. Calcd for $C_{25}H_{20}N_2O$: C, 82.39; H, 5.53; N, 7.69. Found: C, 82.42; H, 5.52; N, 7.72.

3-(1-Benzyl-3-phenylpyrrolo[2,3-*b*]quinolin-2-yl)propionaldehyde. This compound was obtained as a yellow oil in 57 % yield from the reaction of 1-benzyl-2-iodo-3-phenyl pyrrolo[2,3-*b*]quinoline with allyl alcohol . IR (neat) 2931, 1772, 1560, 1342, 1053, 812 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 9.82 (s, 1H, COH), 8.31 (s, 1H, ArH), 8.15 (d, 1H, *J* = 8.2 Hz, ArH), 7.95 (d, 1H, *J* = 8.2 Hz, ArH), 7.73-7.64 (m, 1H, ArH), 7.57-7.21 (m, 11H, ArH), 5.78 (s, 2H, $ArCH_2$), 3.18 (t, 2H, *J* = 8.0 Hz, $ArC\underline{H}_2CH_2$), 2.71 (t, 2H, *J* = 8.0 Hz, $C\underline{H}_2COH$); ^{13}C NMR ($CDCl_3$) δ 200.0, 150.3, 145.2, 137.8, 134.3, 129.8, 128.7, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 127.6, 127.4, 125.6, 125.1, 123.4, 121.6, 92.2, 52.3, 48.6, 10.6; MS m/z (relative intensity): 390 (M^+, 100), 333 (57), 305 (24), 143 (38), 99 (51), 70 (29), 56 (11), 41 (30); Anal. Calcd for $C_{27}H_{22}N_2O$: C, 83.05; H, 5.68; N, 7.17. Found: C, 83.10; H, 5.71; N, 7.15.

4-(1-Benzyl-3-phenylpyrrolo[2,3-*b*]quinolin-2-yl)butan-2-one. This compound was obtained as a yellow oil in 56 % yield from the reaction of 1-benzyl-2-iodo-3-phenylpyrrolo[2,3-*b*]quinoline with 3-buten-2-ol. IR (neat) 2903, 1752, 1423, 1350, 1210, 842, 723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.33 (s, 1H, ArH), 8.11 (d, 1H, *J* = 8.0 Hz, ArH), 7.90 (d, 1H, *J* = 8.0 Hz, ArH), 7.66-7.59 (m, 1H, ArH), 7.52-7.16 (m, 11H, ArH), 5.74 (s, 2H, $ArCH_2$), 3.14 (t, 2H, *J* = 8.0 Hz, $ArC\underline{H}_2CH_2$), 2.41 (t, 2H, *J* = 8.0 Hz, CH_2CO), 1.90 (s, 3H, $COCH_3$); ^{13}C NMR ($CDCl_3$) δ207.1, 150.3, 145.3, 137.8, 134.4, 129.8, 128.7, 128.6, 128.5, 128.6, 128.3, 128.3, 128.2, 127.6, 127.4, 125.7, 125.2, 123.4, 121.6, 92.8, 50.1, 46.6, 25.1, 11.1; MS m/z (relative intensity): 404 (M^+, 74), 340 (56), 322 (26), 143 (40), 99 (100), 70 (25), 56 (16), 41 (24); Anal. Calcd for $C_{28}H_{24}N_2O$: C, 83.14; H, 5.98; N, 6.93. Found: C, 83.18; H, 5.95; N, 6.97.

3-(1-Benzyl-3-methylpyrrolo[2,3-*b*]quinolin-2-yl)acrylic acid methyl ester. This compound was obtained as a yellow solid in 70 % yield from the reaction of 1-benzyl-2-iodo-

3-methylpyrrolo[2,3-*b*]quinoline with methyl acylate: mp 157-158 ℃; IR (KBr) 1710, 1595, 1434, 1216, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.38 (s, 1H, ArH), 8.05 (d, 1H, *J* = 8.0 Hz, ArH), 7.95 (d, 1H, *J* = 8.0 Hz, ArH), 7.82 (d, 1H, *J* = 16.6 Hz, =CH-), 7.66-7.64 (m, 1H, ArH), 7.44-7.39 (m, 1H, ArH), 7.29-7.20 (m, 3H, ArH), 7.16-7.14 (m, 2H, ArH), 6.33 (d, 1H, *J* = 16.6 Hz, -CH=), 5.76 (s, 2H, $ArCH_2$), 3.79 (s, 3H, $COOCH_3$), 2.57 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 197.4, 150.2, 146.6, 138.0, 132.4, 130.8, 129.4, 128.7, 128.5, 128.4, 128.1, 127.4, 126.9, 126.7, 125.0, 123.0, 120.8, 51.8, 45.5, 29.7, 10.7; MS m/z (relative intensity): 356 (M^+, 40), 297 (35), 265 (23), 205 (56), 91 (100), 65 (23); Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.86. Found: C, 77.45; H, 5.68; N, 7.84.

4-(1,3-Dimethylpyrrolo[2,3-*b*]quinolin-2-yl)but-3-en-2-one. This compound was obtained as a yellow oil in 68 % yield from the reaction of 1,3-dimethyl-2-iodopyrrolo[2,3-*b*]quinoline with methyl vinylketone: mp 173-174 ℃; IR (KBr) 2937, 2366, 1705, 1602, 1250, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.32 (s, 1H, ArH), 8.06 (d, 1H, *J* = 8.0 Hz, ArH), 7.91 (dd, 1H, *J* = 8.0, 0.8 Hz, ArH), 7.73 (d, 1H, *J* = 16.4 Hz, =CH-), 7.67-7.63 (m, 1H, ArH), 7.41-7.37 (m, 1H, ArH), 6.76 (d, 1H, *J* = 16.4 Hz, -CH=), 4.02 (s, 3H, NCH_3), 2.55 (s, 3H, $COCH_3$), 2.43 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ 197.4, 146.7, 134.8, 130.4, 128.7, 128.5, 127.8, 127.0, 124.8, 124.6, 123.0, 122.5, 118.9, 114.5, 29.6, 28.3, 10.5; MS m/z (relative intensity) : 264 (M^+, 67), 249 (100), 221 (58), 205 (31), 110 (37), 43 (21); Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.27; H, 6.12; N, 10.56.

1-Benzyl-3-phenyl-2-vinylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 64 % yield from the reaction of 1-benzyl-2-iodo-3-phenylpyrrolo[2,3-*b*]quinoline with tributyl(vinyl)tin: mp 168-169 ℃; IR (KBr) 2905, 1640, 1325, 1264, 1100, 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.37 (s, 1H, ArH), 8.07 (d, 1H, *J* = 8.2 Hz, ArH), 7.89 (d, 1H, *J* = 8.2 Hz, ArH), 7.63-7.19 (m, 12H, ArH), 6.81-6.74 (m, 1H, -CH=), 5.82 (s, 2H, $ArCH_2$), 5.56 (dd, 1H, *J* = 18, 0.8 Hz, $=CH_2$), 5.41 (dd, 1H, *J* = 12.2, 0.8 Hz, $=CH_2$); ^{13}C NMR ($CDCl_3$) δ 145.9, 138.7, 134.3, 132.5, 130.1, 128.7, 128.7, 128.2, 128.1, 127.8, 127.1, 126.8, 126.6, 126.2, 125.7, 125.5, 123.0, 121.2, 94.4, 45.8, 29.1, 13.7; MS m/z (relative intensity): 360 (M^+, 27), 333 (56), 224 (35), 143 (34), 99 (46), 70 (22), 56 (100), 41 (26); Anal. Calcd for $C_{26}H_{20}N_2$: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.61; H, 5.60; N, 7.79.

3-Methyl-1-phenyl-2-vinylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 68 % yield from the reaction of 1-phenyl-2-iodo-3-methylpyrrolo[2,3-*b*]quinoline with tributyl(vinyl)tin: mp 149-150 ℃; IR (KBr) 2931, 1628, 1402, 1246, 1203, 832 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.25 (s, 1H, ArH), 8.0-7.94 (m, 2H, ArH), 7.62-7.56 (m, 3H, ArH), 7.50-7.41 (m, 1H, ArH), 6.72-6.55 (m, 1H, -CH=),

5.52 (d, 1H, *J* = 18.2, 0.8 Hz =CH_2), 5.44 (d, 1H, *J* = 12.0, 0.8 Hz, =CH_2), 2.55 (s, 3H, $ArCH_3$); ^{13}C NMR ($CDCl_3$) δ146.0, 142.0, 139.8, 135.2, 129.6, 129.3, 129.0, 128.4, 128.2, 128.0, 127.6, 125.3, 124.4, 123.4, 122.7, 119.9, 118.5, 11.0; MS m/z (relative intensity): 284 (M^+, 100), 257 (38), 242 (19), 216 (21), 128 (55), 107 (29), 94 (34); Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.44; H, 5.68; N, 9.88.

1-Methyl-3-phenyl-2-vinylpyrrolo[2,3-*b*]quinoline. This compound was obtained as a yellow solid in 70 % yield from the reaction of 1-methyl-2-iodo-3-phenylpyrrolo[2,3-*b*]quinoline with tributyl(vinyl)tin: mp 141-142 ℃; IR (KBr) 2892, 1645, 1341, 1256, 1223, 982, 762, 562 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.38 (s, 1H, ArH), 8.22 (d, 1H, *J* = 8.4 Hz, ArH), 7.90-7.86 (m, 1H, ArH), 7.71-7.62 (m, 3H, ArH), 7.57-7.52 (m, 2H, ArH), 7.46-7.41 (m, 2H, ArH), 6.94-6.79 (m, 1H, -CH=), 5.78 (dd, 1H, *J* = 18.0, 0.8 Hz, =CH_2), 5.64 (dd, 1H, *J* = 12.0, 0.8 Hz, =CH_2), 3.91 (s, 3H, NCH_3); ^{13}C NMR ($CDCl_3$) δ146.1, 143.6, 136.6, 135.8, 135.7, 129.7, 129.2, 129.0, 128.5, 128.1, 127.7, 127.0, 126.4, 125.0, 118.4, 117.0, 91.7, 31.2; MS m/z (relative intensity): 284 (M^+, 34), 257 (13), 191 (18), 128 (26), 107 (31), 84 (41), 77 (100), 43 (54); Anal. Calcd for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.50; H, 5.64; N, 9.86.

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