HETEROCYCLES, Vol. 63, No. 3, 2004, pp. 631 - 639
Received, 19th November, 2003, Accepted, 9th January, 2004, Published online, 19th January, 2004

SYNTHESIS OF AROMATIC RING FUSED PYRROLE DERIVATIVES BY PALLADIUM-CATALYZED ANNULATION OF *o*-IODOARYL-AMINES WITH ALLYL ACETATE

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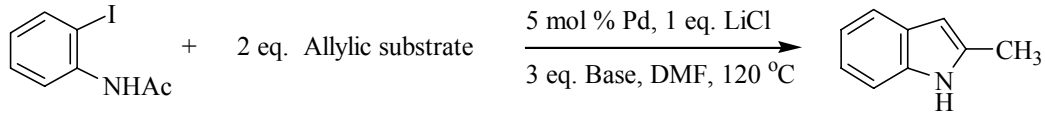
Abstract – Indoles, azaindoles, and pyrroloquinolines were obtained by palladium-catalyzed annulation of *o*-iodoarylamines with allyl acetate under 5 mol % $Pd(OAc)_2$, 1 equiv. LiCl, 3 equiv. K_2CO_3 , and 2 equiv. allyl acetate in DMF at 120°C.

π-Allylpalladium complexes are some of the most widely used synthetic intermediates in organic synthesis.[1] π-Allylpalladium complexes can be formed in several different ways from various organic substrates, such as allylic alcohols, halides, carboxylates, phosphates, vinylepoxides, *etc*.[1b] Catalytic transformation *via* π–allylpalladium intermediates has found widespread use in a number of important chemical processes, including allylic substitution with soft or hard nucleophiles, bis-oxidation of conjugated dienes, hydrogenolysis, transmetallation, and carbonylation.[1a] Specifically, the cyclization of a π–allylpalladium intermediate with soft or hard nucleophiles has been used to synthesize various carbocycles and heterocycles.[2] Larock and coworkers also reported intermolecular ring formation with 1,2-dienes,[3] 1,3-dienes,[4] 1,4-dienes,[5] and vinylic cyclopropane[6] using aromatic halides bearing functional groups in the *ortho* position to synthesize heterocycles. However, one-pot formation of heterocycles by intermolecular ring formation with allyl acetate is extremely rare. Recently, many intermolecular reactions with allyl acetate have been reported for the formation of carbon-carbon bonds,[7] carbon-nitrogen bonds,[8] and cycloaddition.[9] As part of our continuing interest in developing new synthetic methods for heterocycles,[10,11] we examined palladium-catalyzed annulation of various *ortho* iodoarylamines with

allylic substrates to synthesize various indole analogues. Indole analogues have attracted considerable attention in recent years, since indole is the core structure of many biologically active compounds.[12-14] Initially, we chose the palladium-catalyzed reaction of *N*-acetyl-2-iodoaniline with various allylic substrates to optimize the reaction conditions. The results are summarized in Table 1.

Table 1. Optimization of indole synthesis by palladium-catalyzed annulation with allylic substrates.

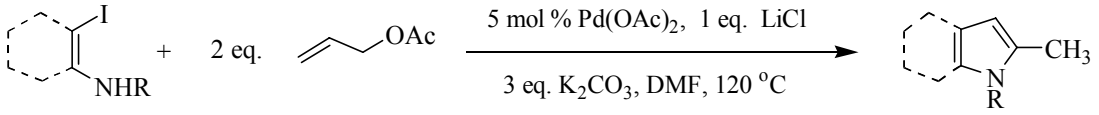


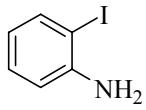
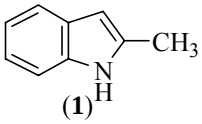
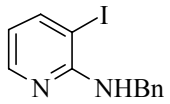
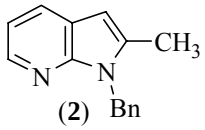
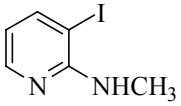
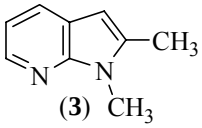
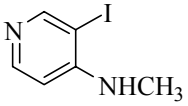
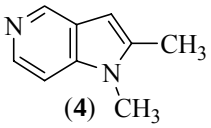
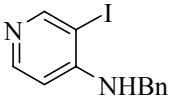
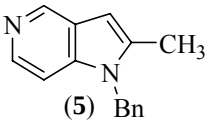
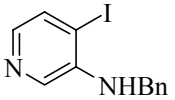
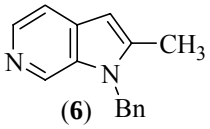
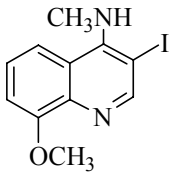
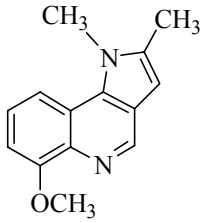
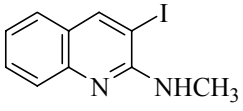
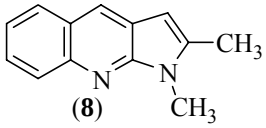
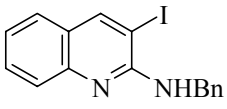
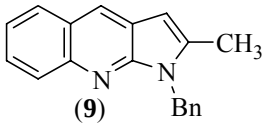
Entry[a]	Pd Source	Allylic Substrate	Base	Reaction Time (h)	Yields (%)
1	$Pd(OAc)_2$	CH_2=CH-CH_2OAc	K_2CO_3	13	67
2	〃	〃	KOAc	〃	63
3	$PdCl_2$	〃	K_2CO_3	15	60
4	〃	〃	KOAc	〃	65
5	$Pd(dba)_2$	〃	K_2CO_3	12	40
6	$Pd(Ph_3P)_2Cl_2$	〃	〃	48	<10
7	$Pd(Ph_3P)_4$	〃	〃	〃	<10
8	$Pd(OAc)_2$	CH_2=CH-$CH_2CO_2CH_3$	〃	〃	45
9	〃	CH_2=CH-$CH_2OC_6H_4$-4-NO_2	〃	〃	40
10	〃	CH_2=CH-$CH_2OC_6H_4$-4-Cl	〃	〃	25

[a] All reactions were run on a 0.5 mmol scale in 10 mL DMF.

First, we examined the effect of palladium species using 1 equiv. of LiCl and potassium bases (Entries 1-7). The reactions using $Pd(OAc)_2$ or $PdCl_2$ provided higher yields of deacetylated 2-methylindole than the other palladium species (Entries 1-4). We also examined the effects of several allylic substrates under K_2CO_3. The reaction using allyl acetate gave a higher yield of the desired product than the reactions using other allylic substrates (Entries 8-10). From these results, we decided that the optimum reaction conditions consisted of 5 mol % $Pd(OAc)_2$, 1 equiv. LiCl, 3 equiv. potassium base, and 2 equiv. allylic substrate in DMF at 120°C. Next, we examined the synthesis of various aromatic ring fused pyrrole derivatives with several *o*-iodoarylamines with allyl acetate under the optimized reaction conditions. The results are summarized in Table 2. The reaction using unprotected 2-iodoaniline provided a slightly lower yield of 2-methylindole than the reaction with *N*-acetyl 2-iodoaniline. We also examined the synthesis of 5-, 6-, and

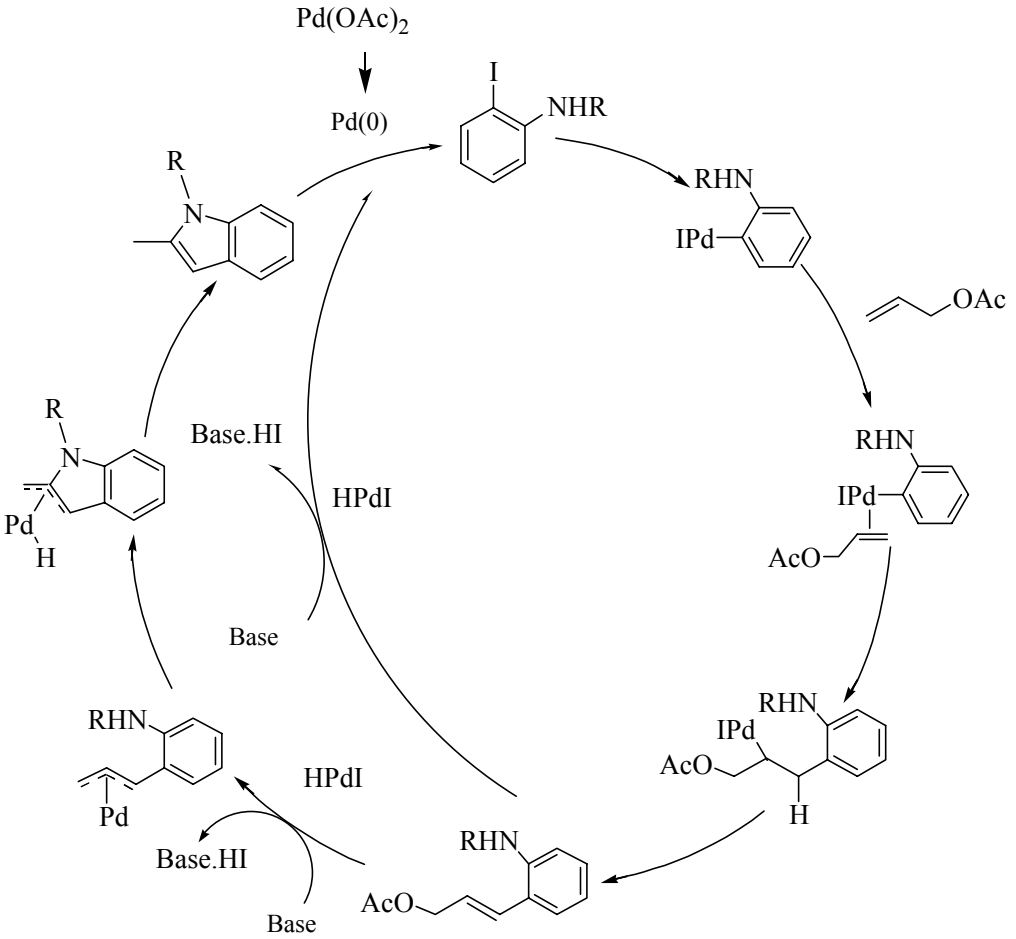
Table 2. Synthesis of aromatic ring fused pyrrole analogues by palladium-catalyzed annulation with *o*-iodoarylamines with allyl acetate.



Entry	Aryl iodide	Reaction time (h)	Product	Isolated yields (%)
1		24	 (**1**)	47
2		12	 (**2**)	65
3		48	 (**3**)	47
4		20	 (**4**)	56
5		20	 (**5**)	53
6		20	 (**6**)	45
7		36	 (**7**)	45
8		16	 (**8**)	67
9		40	 (**9**)	52

7-azaindoles from different *o*-iodoaminopyridines (Entries 2-6). The annulation reactions gave moderate yields of the desired azaindole. Finally, the reactions of *o*-iodoaminoquinolines afforded pyrrolo[3,2-*c*]quinoline and pyrrolo[2,3-*b*]quinolines in reasonable yields (Entries 7-9).

Considering our identification of the Heck product intermediate, the annulation might proceed *via* the route illustrated in Scheme 1. The formation of Pd(0) from $Pd(OAc)_2$ could proceed in the reaction medium. The palladium(0) complex reacts with aryl halide *via* oxidative addition. The arylpalladium complex next coordinates and adds the double bond of allyl acetate. The resulting palladium intermediate sequentially undergoes hydride elimination to generate the Heck product and palladium species. Subsequent π-allylpalladium formation, followed by intramolecular nucleophilic attack on the π-allylpalladium species generates the indole and regenerates Pd(0), which can be recycled.



Scheme 1

In summary, the palladium-catalyzed annulation of *o*-iodoarylamines with allyl acetate gave indole, azaindoles, and pyrroloquinolines in moderate yields. The annulation methodology might be applied to the synthesis of a variety of heterocycles by varying the *o*-functionalized aryl halide.

EXPERIMENTAL

Infrared spectra were obtained using a JASCO FT-IR 410 spectrometer. All the ^{1}H- and ^{13}C-NMR spectra were recorded on a Varian 400-MHz spectrometer. The chemical shifts are given as values relative to tetramethylsilane (TMS) as an internal standard. The GC/MS spectra were obtained on a Shimadzu QP 1000. The melting points were determined on a Mut-TEM apparatus and are uncorrected. Microanalyses were performed at Chungnam National University with a CE Instrument EA 1110. The products were purified by flash chromatography on 230- to 400-mesh ASTM 60 silica gel. All the bases and palladium species were purchased from Aldrich Chemical Co. The other chemicals were used as obtained from commercial sources, unless otherwise noted.

General procedure for preparing *o*-amino aryl halide [15]

2-Methylamino-3-iodoquinoline. *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. The mixture was stirred for 4 h at the same temperature. 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 rt 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, 4 H, 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-iodoquinoline (1.4 g, 4.84 mmol), methylamine (40% aqueous solution, 10 mL), and ethanol (10 mL) were added to a sealed tube. The reaction mixture was heated at 140°C for 10 h. The resulting mixture was poured into water and the product was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered, and concentrated. 2-Methylamino-3-iodoquinoline (1.0 g, 73%) was obtained by column chromatography using hexane/ethyl acetate (10:1): mp 84-85ºC; 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 (br s, 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. Calcd for $C_{10}H_9N_2I$: 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% yield by the substitution of 2-chloro-3-iodoquinoline with benzylamine: mp 179-180ºC (ethyl ether) ; 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. Calcd for $C_{16}H_{13}N_2I$: C, 53.35; H, 3.64; N, 7.78. Found: C, 53.40; H, 3.60; N, 7.75.

The starting *o*-aminoaryl halides were prepared using the above general procedures.

General synthetic procedure of aromatic ring fused pyrrole derivatives by palladium-catalyzed heteroannulation with allyl acetate

2-Methyl-1*H*-indole (1)[16]

Palladium acetate (6 mg, 0.025 mmol), LiCl (21 mg, 0.5 mmol), K_2CO_3 (207 mg, 1.5 mmol), allyl acetate (100 mg, 1.0 mmol), *N*-(2-iodophenyl)acetamide (130 mg, 0.5 mmol), and DMF (10 mL) were added to a pressure tube equipped with a stirring bar. After heating the reaction mixture for 13 h at 120ºC, 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 (20:1). 2-Methyl-1*H*-indole (**1**) (44 mg, 67%) was obtained as a white solid. mp 58-60ºC (hexane); ^{1}H-NMR ($CDCl_3$) δ 7.73 (br s, 1H, N-H), 7.42 (d, *J* = 8.4 Hz, 1H, Ar-H), 7.18 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.96-7.04 (m, 2H, Ar-H), 6.13 (s, 1H, Ar-H), 2.26 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ 135.92, 134.94, 128.94, 120.80, 119.50, 110.12, 100.28, 13.74; MS m/z (relative intensity): 131 (M^+, 100), 103 (20), 77 (20), 63 (10); Anal. Calcd for C_9H_9N: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.40; H, 6.91; N, 10.68.

1-Benzyl-2-methyl- 1*H*-pyrrolo[2,3-*b*]pyridine (**2**)

The compound (**2**) was obtained as a white solid in 65% yield from benzyl(3-iodopyridin-2-yl)amine and allyl acetate with a 12 h reaction. mp 103-104ºC (hexane); ^{1}H-NMR ($CDCl_3$) δ 8.23 (d, *J* = 4.4Hz, 1H, Ar-H), 7.80 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.02-7.37 (m, 6H, Ar-H), 6.24 (s, 1H, Ar-H), 5.52 (s, 2H, N-CH_2), 2.33 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ141.55, 137.93, 134.58, 128.50, 127.58, 127.09, 126.98, 126.34,

117.24, 115.78, 98.26, 44.76, 13.18; MS m/z (relative intensity): 222 (M^+, 10), 206 (21), 144 (16), 130 (21), 91 (100), 65 (24); Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.07; H, 6.34; N, 12.58.

1,2-Dimethyl-1*H*-pyrrolo[2,3-*b*]pyridine (3)[17]

The compound (**3**) was obtained as a yellow oil in 47% yield from methyl(3-iodopyridin-2-yl)amine and allyl acetate with a 48 h reaction. ^{1}H-NMR ($CDCl_3$) δ 8.22 (d, *J* = 4.0 Hz, 1H, Ar-H), 7.75 (d, *J* = 8.0 Hz, 1H, Ar-H), 6.98 (dd, *J* = 8.0 Hz, 4.0 Hz, Ar-H), 6.18 (s, 1H, Ar-H), 3.77 (s, 3H, N-CH_3), 2.44 (s, 3H, Ar-CH_3); MS m/z (relative intensity): 146 (M^+, 100), 131 (10), 118 (10), 104 (8), 73 (8), 63 (8); Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.91; H, 6.91; N, 19.19.

1,2-Dimethyl-1*H*-pyrrolo[3,2-*c*]pyridine (4)

The compound (**4**) was obtained as a white solid in 56% yield from (3-iodopyridin-4-yl)methylamine and allyl acetate with a 20 h reaction. mp 123-124ºC (hexane); ^{1}H-NMR ($CDCl_3$) δ 8.75 (s, 1H, Ar-H), 8.20 (d, *J* = 5.8 Hz, 1H, Ar-H), 7.10 (d, *J* = 5.8 Hz, 1H, Ar-H), 6.30 (s, 1H, Ar-H) 3.62 (s, 3H, N-CH_3), 2.40 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ142.18, 139.77, 138.00, 128.72, 104.13, 98.97, 29.45, 14.13, 13.69; MS m/z (relative intensity): 146 (M^+, 100), 131 (50), 97 (25), 71 (48), 57 (85); Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.95; H, 6.90; N, 19.14.

1-Benzyl-2-methyl- 1*H*-pyrrolo[2,3-*b*]pyridine (5)

The compound (**5**) was obtained as a white solid in 53% yield from (3-iodopyridin-4-yl)benzylamine and allyl acetate with a 20 h reaction. mp 102-104ºC; ^{1}H-NMR ($CDCl_3$) δ 8.82 (s, 1H, Ar-H), 8.21 (d, *J* = 5.6 Hz, 1H, Ar-H), 7.44 (d, *J* = 5.6 Hz, 1H, Ar-H), 7.16-7.32 (m, 5H, Ar-H), 6.40 (s, 1H, Ar-H), 5.29 (s, 3H, N-CH_3), 2.37 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ142.03, 140.93, 139.75, 138.21, 136.61, 128.82, 128.79, 127.57, 126.25, 125.82, 104.62, 99.93, 40.60, 12.76; MS m/z (relative intensity): 222 (M^+, 10), 91 (14), 84 (90), 48(100); Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.03; H, 6.35; N, 12.62.

1-Benzyl-2-methyl- 1*H*-pyrrolo[2,3-*c*]pyridine (6)

The compound (**6**) was obtained as a yellow oil in 45% yield from benzyl(4-iodopyridin-3-yl)amine and allyl acetate with a 20 h reaction. ; ^{1}H-NMR ($CDCl_3$) δ 8.60 (s, 1H, Ar-H), 8.18 (d, *J* = 5.6 Hz, 1H, Ar-H), 7.44 (d, *J* = 5.6 Hz, 1H, Ar-H), 7.25-7.35 (m, 5H, Ar-H), 6.35 (s, 1H, Ar-H), 5.37 (s, 2H, N-CH_2), 2.41 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ144.30, 141.49, 138.10, 136.60, 133.19, 131.46, 128.86, 127.62, 125.87, 114.23, 100.42, 46.86, 12.87; MS m/z (relative intensity): 222 (M^+, 35), 149 (10), 91 (100), 65(15); Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.04; H, 6.36; N, 12.61.

6-Methoxy-1,2-dimethyl-1*H*-pyrrolo[3,2-*c*]quinoline (**7**)

The compound (**7**) was obtained as a yellow oil in 45% yield from (3-iodo-8-methoxyquinolin-4-yl) methylamine and allyl acetate in a 36 h reaction. ^{1}H-NMR ($CDCl_3$) δ 9.07 (s, 1H, Ar-H), 7.97(d, *J* = 8.8 Hz, 1H, Ar-H), 7.46 (t, *J* = 8.2 Hz, 1H, Ar-H), 6.99 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.49 (s, 1H, Ar-H), 4.10 (s, 3H, O-CH_3), 4.09 (s, 3H, N-CH_3), 2.28 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ 155.97, 147.59, 143.92, 136.91, 125.93, 125.30, 121.25, 112.34, 104.81, 100.94, 56.21, 55.89, 33.78, 13.29; MS m/z (relative intensity): 225 (M^+, 100), 197 (45), 181 (10) ; Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38. Found: C, 74.29; H, 6.22; N, 12.40.

1,2-Dimethy-1*H*-pyrrolo[2,3-*b*]quinoline (**8**)

The compound (**8**) was obtained as a yellow solid in 67% yield from methyl(3-iodoquinolin-2-yl)amine and allyl acetate in a 16 h reaction. mp 111-112ºC; ^{1}H-NMR ($CDCl_3$) δ 8.19 (s, 1H, Ar-H), 8.06(d, *J* = 8.0 Hz, 1H, Ar-H), 7.87 (d, *J* = 8.0 Hz , 1H, Ar-H), 7.59 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.36 (t, *J* = 7.6 Hz, 1H, Ar-H), 6.30 (s, 1H, Ar-H), 3.86 (s, 3H, N-CH_3), 2.51 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ 150.37, 144.19, 142.22, 127.94, 127.57, 127.01, 125.31, 124.77, 122.44, 122.30, 96.88, 20.09, 13.64; MS m/z (relative intensity) 196 (M^+, 100), 181 (59), 167 (17), 98 (30); Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.55; H, 6.19; N, 14.26.

1-Benzyl-2-methyl-1*H*-pyrrolo[2,3-*b*]quinoline (**9**)

The compound (**9**) was obtained as a yellow solid in 52% yield from benzyl(3-iodoquinolin-2-yl)amine and allyl acetate in a 40 h reaction. mp 111-112ºC; ^{1}H-NMR ($CDCl_3$) δ 8.24 (s, 1H, Ar-H), 8.04 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.88 (d, *J* = 8.0 Hz , 1H, Ar-H), 7.57 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.36 (t, *J* = 7.6 Hz, 1H, Ar-H), 7.08-7.24 (m, 5H, Ar-H), 6.32 (s, 1H, Ar-H), 5.60 (s, 2H, N-CH_2), 2.36 (s, 3H, Ar-CH_3); ^{13}C-NMR ($CDCl_3$) δ 144.35, 142.12, 138.19, 128.53, 128.49, 127.89, 127.81, 127.07, 126.97, 126.61, 125.33, 125.01, 122.55, 122.10, 97.73, 44.86, 13.78; MS m/z (relative intensity): 272 (M^+, 55), 257 (25), 195 (17), 181 (25), 91 (100), 65 (34); Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.79; H, 5.92; N, 10.29. Found: C, 83.76; H, 5.93; N, 10.30.

ACKNOWLEDGMENTS

This work was supported by a grant (No. R11-2002-100-03002-2) from the ERC program of the Korea Science & Engineering Foundation.

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