DIRECTED LITHIATION OF 1-(*tert*-BUTOXYCARBONYL)INDOLINES. A CONVENIENT ROUTE TO 7-SUBSTITUTED INDOLINES

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Abstract- 1-(*tert*-Butoxycarbonyl)indolines were regioselectively lithiated at 7-position with *s*-BuLi-TMEDA in ether or THF at -78 °C. The lithiated species were reacted with a range of electrophiles to give 7-substituted indoline derivatives.

Regioselective functionalization of the indole nucleus is important for the synthesis of biologically active indole natural products.[1] The selective functionalization at 3- and 2-positions is easily accomplished *via* electrophilic substitution[2] and lithiation[3] strategies, respectively. However, due to profound reactivity of the pyrrole moiety, the direct functionalization of the benzenoid ring is difficult. Therefore, in order to functionalize benzenoid ring, the indole-indoline synthetic interconversion[4] is often employed. In this approach, indoles are tentatively reduced to indolines (2,3-dihydroindoles) and, after functionalization of the aromatic ring, indoles are regenerated by oxidation. By using this methodology, Somei *et al.*[5] developed a procedure for 7-selective functionalization[6] of indole. They employed the chelation-controlled C-7 thallation of 1-acetylindoline as a key reaction. Since the thallated intermediate is convertible to a variety of 7-substituted indolines, this method seems to be highly useful. However, utilization of the toxic thallium reagent is not favorable. Recently, Beak and Lee[7] reported on the α-lithiation of *N*-*tert*-butoxycarbonyl secondary amines. They mentioned, however, in the case of 1-(*tert*-butoxycarbonyl)-1,2,3,4-tetrahydroquinoline, lithiation occurred at 8-position of the aromatic ring. We applied this directed lithiation to the 1-(*tert*-butoxycarbonyl)indoline system in order to establish a new general route to 7-functionalized indolines.

RESULTS AND DISCUSSIONS

The C-7 selective lithiation of 1-(*tert*-butoxycarbonyl)indoline (**1a**) was accomplished with *s*-BuLi-TMEDA in ether at -78°C for 1 h. Quenching the lithio species with Me_3SiCl afforded 1-(*tert*-butoxycarbonyl)-7-trimethylsilylindoline (**2a**) in 83% yield (Table 1; Entry 1). These lithiation conditions are essential for the regiospecific and efficient generation of the C-7 lithio species. When **1a** was lithiated with *s*-BuLi-TMEDA in THF at -78°C for 1 h followed by treatment with Me_3SiCl, the yield of **2a** decreased to 50% and 1-(*tert*-butoxycarbonyl)-2-trimethylsilylindoline (**3**), derived from the C-2 lithio species, was isolated in 9% yield as an undesirable regioisomer. The lithiation of **1a** with *s*-BuLi in ether without using TMEDA was slow at -78°C, and the compound (**2a**) was obtained in only 22% yield after 1 h lithiation followed by Me_3SiCl quenching. When *n*-BuLi-TMEDA was used as a base, lithiation did not occur at all at -78°C within 1 h in both ether and THF.

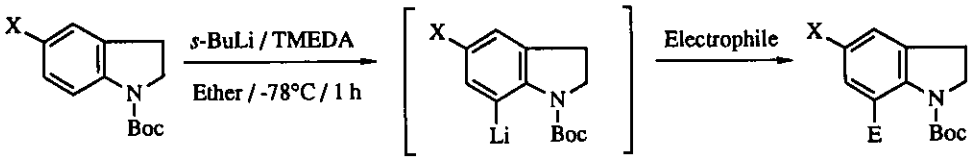
Using the lithiation conditions thus established, reaction with other common electrophiles was examined. The results are summarized in Table 1. Reactions with Bu_3SnCl, PhSSPh, I_2, 1,2-dibromoethane, hexachloroethane, MeI, and CO_2 furnished the expected 7-substituted 1-(*tert*-butoxycarbonyl)indolines (**2b-h**) in good yields (Entries 2-8).

On the other hand, the reaction with DMF afforded 7-indolinecarbaldehyde (**2i**) in which *tert*-butoxycarbonyl group was removed (Entry 9). In the case of the reactions with *p*-anisaldehyde and propionaldehyde, the cyclic carbamates (**2j,k**) were obtained (Entries 10 and 11).[8] These unexpected products may be formed by the intramolecular attack of the intermediate lithium alkoxides to the *tert*-butoxycarbonyl group. The formation of **2j** and **2k** is a good chemical evidence of the C-7 selective lithiation.

Entries 12 and 13 show that the lithiation occurs selectively at the C-7 position even in the presence of moderately *ortho*-directing methoxy[9] or chlorine[10] group on the aromatic ring. The regioselectivity was apparent from the *meta* coupling constants of the aromatic absorptions in ^1H nmr spectra of the compounds (**2l**) and (**2m**). Although THF was used as a solvent for the lithiation of **1c** due to its poor solubility in ether, none of C-2 silylated product was isolated. In compound (**1c**), the acidity of the C-7 proton may be much higher than the C-2 proton due to inductive electron-withdrawing effect of chlorine.[10]

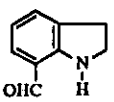
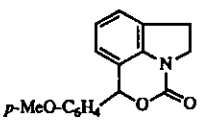
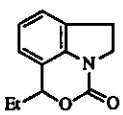
In conclusion, we have established a 7-selective lithiation of 1-(*tert*-butoxycarbonyl)indolines. This reaction should be a convenient and useful method for the synthesis of 7-substituted indoles in view of easy introduction and removal of *tert*-butoxycarbonyl group[11] and the well-established indole-indoline synthetic interconversion.[4]

Table 1. Synthesis of 7-Substituted Indolines *via* Directed Lithiation of 1-(*tert*-Butoxycarbonyl)indolines



1a: X=H
1b: X=OMe
1c: X=Cl

Boc=CO_2t-Bu **2a-m**

Entry	1-(Boc)indoline	Electrophile	Product	X	E	Yield(%)
1	**1a**	Me_3SiCl	**2a**	H	Me_3Si	83
2	**1a**	Bu_3SnCl	**2b**	H	Bu_3Sn	65
3	**1a**	PhSSPh	**2c**	H	PhS	72
4	**1a**	I_2	**2d**	H	I	59
5	**1a**	$BrCH_2CH_2Br$	**2e**	H	Br	57
6	**1a**	Cl_3CCCl_3	**2f**	H	Cl	61
7	**1a**	MeI	**2g**	H	Me	91
8	**1a**	CO_2	**2h**	H	CO_2H	56
9	**1a**	DMF	**2i**			42
10	**1a**	*p*-MeO-C_6H_4-CHO	**2j**			51
11	**1a**	Et-CHO	**2k**			40
12	**1b**	Me_3SiCl	**2l**	MeO	Me_3Si	73
13	**1c**[a]	Me_3SiCl	**2m**	Cl	Me_3Si	75

[a] Compound (**1c**) was lithiated in THF.

EXPERIMENTAL

General. Melting points were determined with a Yamagimoto micromelting points apparatus and were uncorrected. Ir spectra were recorded with JASCO IR-810 spectrophotometer. ^{1}H Nmr spectra were obtained with JEOL JNM-GX400 (400 MHz) machine using TMS as an internal standard. Mass spectra were recorded with JEOL JMS-DX303 spectrometer. Elemental analyses were performed at the microanalytical laboratory in Nagasaki University. Kügelrohr distillations were performed with Büchi GKR-50 or Shibata GTO-350RG apparatus. For column chromatography, Merck silica gel 60 (230-400 mesh) was employed, except otherwise mentioned. Ether and THF used for lithiations were distilled from Na-benzophenone ketyl under N_2 prior to use.

1-(*tert*-Butoxycarbonyl)indoline (1a). To a stirred solution of freshly distilled indoline (15.2 g, 128 mmol) in THF (160 ml) was added di-*tert*-butyl dicarbonate (33.4 g, 153 mmol). The mixture was stirred overnight at ambient temperature and evaporated. The residual liquid was purified twice by Kügelrohr distillation to give **1a** (22.8 g, 81%): bp 150°C(oven temp.)/0.2 mmHg; ir(neat) 1700 cm^{-1} (C=O); ^{1}H nmr (DMSO-d_6, 100°C[12]) δ 1.51 (9H, s, *t*-Bu), 3.04 (2H, t, *J*=8.5 Hz, H-3), 3.89 (2H, t, *J*=8.5 Hz, H-2), 6.88 (1H, t, *J*=7.3 Hz, H-5), 7.09 (1H, dd, *J*=8.1 and 7.3 Hz, H-6), 7.14 (1H, d, *J*=7.3 Hz, H-4), 7.58 (1H, d, *J*=8.1 Hz, H-7); ms *m/z* 219 (M$^+$, 27), 163 (100), 146 (13), 119 (63), 91 (18), 57 (80), 41 (25). *Anal.* Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 71.10; H, 7.79; N, 6.57.

1-(*tert*-Butoxycarbonyl)-5-methoxyindoline (1b). According to a literature procedure,[13] 5-methoxyindole (4.42 g, 30 mmol) was reduced by $NaBH_3CN$ (5.66 g, 90 mmol) in acetic acid (60 ml) to give 5-methoxyindoline (3.65 g, 82%); bp 100°C(Kügelrohr, oven temp.)/0.2 mmHg. This compound (3.65 g, 24.5 mmol) was treated with di-*tert*-butyl dicarbonate (6.98 g, 32 mmol) in a similar manner as described above to give **1b** (5.26 g, 86%) as a colorless plates after recrystallization from ether-pentane: mp 87-88°C; ir(KBr) 1690 cm^{-1} (C=O); ^{1}H nmr (DMSO-d_6, 100°C[12]) δ 1.50 (9H, s, *t*-Bu), 3.01 (2H, t, *J*=8.4 Hz, H-3), 3.70 (3H, s, OMe), 3.88 (2H, t, *J*=8.4 Hz, H-2), 6.67 (1H, dd, *J*=8.8 and 2.6 Hz, H-6), 6.77 (1H, s, H-4), 7.47 (1H, d, *J*=8.8 Hz, H-7); ms *m/z* 249 (M$^+$, 50), 193 (100), 149 (17), 134 (31), 57 (32), 41 (10). *Anal.* Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.61. Found: C, 67.24; H, 7.63; N, 5.64.

1-(*tert*-Butoxycarbonyl)-5-chloroindoline (1c). 5-Chloroindole (6.85 g, 45.2 mmol) was reduced by $NaBH_3CN$ (8.52 g, 136 mmol) in acetic acid (100ml) to give 5-chloroindoline (6.41 g, 92%); bp 130°C (Kügelrohr, oven temp.)/0.3 mmHg. A mixture of the indoline (1.57 g, 10.2 mmol), di-*tert*-butyl dicarbonate (2.68 g, 12.3 mmol), and ether (40 ml) was allowed to react overnight at room temperature. The precipitated colorless crystals were collected by filtration to give **1c** (2.26 g, 87%): mp 130-130.5°C (ether); ir(KBr) 1705

cm^{-1} (C=O); ^{1}H nmr (DMSO-d_6, 100°C[12]) δ 1.51 (9H, s, *t*-Bu), 3.05 (2H, t, *J*=8.5 Hz, H-3), 3.91 (2H, t, *J*=8.5 Hz, H-2), 7.12 (1H, d, *J*=8.4 Hz, H-6), 7.18 (1H, s, H-4), 7.55 (1H, d, *J*=8.4 Hz, H-7); ms *m/z* 253 (M^+, 16), 197 (84), 180 (9), 153 (41), 117 (14), 89 (8), 57(100), 41 (22). *Anal.* Calcd for $C_{13}H_{16}NO_2Cl$: C, 61.54; H, 6.36; N, 5.52; Cl, 13.97. Found: C, 61.34; H, 6.34; N, 5.53; Cl, 14.21.

Directed Lithiation of 1-(*tert*-Butoxycarbonyl)indolines (1a-c). Synthesis of 7-Substituted 1-(*tert*-Butoxycarbonyl)indolines (2a-m). General Procedure. Under an argon atmosphere, a 1.3 M solution of *s*-BuLi in cyclohexane (1.85 ml, 2.4 mmol) was added dropwise to a stirred solution of **1a** or **1b** (2.0 mmol) and TMEDA (0.4 ml, 2.65 mmol) in ether (10 ml) at -78°C. [For lithiation of **1c** (2.0 mmol), THF (20 ml) was used as a solvent due to poor solubility.] After stirring for 1 h, an appropriate electrophile (3-8 mmol) was added as a neat liquid or an ether solution. After 30 min, the dry ice-acetone bath was removed and the mixture was stirred for 1 h. The reaction mixture was quenched with water or 10% aqueous NH_4Cl and the products were extracted with ether. The extract was washed with water and brine solution, dried (Na_2SO_4), and evaporated. The residue was purified by silica gel column chromatography using the following eluents: benzene for **2a**, **2c**, **2g**, **2i**, **2l**; 1:1 benzene-hexane for **2m**; 5:1 hexane-AcOEt for **2d**, **2e**, **2f**; 2:1 hexane-AcOEt for **2k**.

1-(*tert*-Butoxycarbonyl)-7-trimethylsilylindoline (2a): mp 114-114.5°C (pentane); ir (KBr) 1705 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$) δ 0.28 (s, 9H, $SiMe_3$), 1.53 (9H, s, *t*-Bu), 2.97 (2H, t, *J*=8.1 Hz, H-3), 4.02 (2H, t, *J*=8.1 Hz, H-2), 7.01 (1H, t, *J*=7.3 Hz, H-5), 7.16 (1H, dq, *J*=7.3 and 1.1 Hz, H-4), 7.38 (1H, dd, *J*=7.3 and 1.1 Hz, H-6); ms *m/z* 291 (M^+, 9), 220 (100), 191 (10), 175 (10), 133 (8), 57 (59), 41 (10). *Anal.* Calcd for $C_{16}H_{25}NO_2Si$: C, 65.93; H, 8.65; N, 4.81. Found: C, 65.94; H, 8.61; N, 4.78.

1-(*tert*-Butoxycarbonyl)-7-tributylstannylindoline (2b). This compound was purified by alumina column chromatography (hexane). Purification with silica gel caused loss of tributylstannyl group: oil; ir (neat) 1690 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$) δ 0.86 (9H, t, *J*=7.3 Hz, CH_3 of Bu), 0.98 (6H, m, CH_2 of Bu), 1.31 (6H, sextet, *J*=7.3 Hz, CH_2 of Bu), 1.5 (6H, m, CH_2 of Bu), 1.52 (9H, s, *t*-Bu), 3.00 (2H, t, *J*=8.4 Hz, H-3), 3.95 (2H, t, *J*=8.4 Hz, H-2), 6.93 (1H, t, *J*=7.3 Hz, H-5), 7.10 (1H, dd, *J*=7.3 and 1.1 Hz, H-4), 7.32 (1H, d, *J*=7.3 Hz, H-6); ms *m/z* 451 (27), 395 (68), 281 (17), 219 (24), 163 (78), 119 (46), 57 (52), 44 (100), 40 (75). *Anal.* Calcd for $C_{25}H_{43}NO_2Sn$: C, 59.07; H, 8.53; N, 2.76. Found: C, 59.04; H, 8.52; N, 2.75.

1-(*tert*-Butoxycarbonyl)-7-phenylthioindoline (2c): mp 114-115°C (ether-pentane); ir (KBr) 1695 cm^{-1} (C=O); ^{1}H nmr ($CDCl_3$) δ 1.57 (9H, s, *t*-Bu), 3.04 (2H, t, *J*=8.1 Hz, H-3), 4.14 (2H, t, *J*=8.1 Hz, H-2), 6.87 (1H, dd, *J*=8.1 and 7.0 Hz, H-5), 6.93 (1H, dd, *J*=8.1 and 1.1 Hz, H-6), 7.02 (1H, dd, *J*=7.0 and 1.1

Hz, H-4), 7.20-7.28 (3H, m, SPh), 7.33 (2H, m, SPh); ms *m/z* 327 (M^+, 27), 271 (16), 227 (100), 117 (15), 57 (49), 41 (14). HRms Calcd for $C_{19}H_{21}NO_2S$: *m/z* 327.1293. Found: *m/z* 327.1297.

1-(*tert*-Butoxycarbonyl)-7-iodoindoline (2d): oil; ir (neat) 1710 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 1.56 (9H, s, *t*-Bu), 3.02 (2H, t, *J*=7.7 Hz, H-3), 4.10 (2H, t, *J*=7.7 Hz, H-2), 6.74 (1H, dd, *J*=8.1 and 7.3 Hz, H-5), 7.16 (1H, dq, *J*=7.3 and 1.1 Hz, H-4), 7.62 (1H, dd, *J*=8.1 and 1.1 Hz, H-6); ms *m/z* 345 (M^+, 29), 289 (20), 272 (6), 245 (76), 117 (26), 90 (13), 57 (100), 41 (19). *Anal.* Calcd for $C_{13}H_{16}NO_2I$: C, 45.24; H, 4.67; N, 4.06. Found: C, 45.50; H, 4.55; N, 4.11.

7-Bromo-1-(*tert*-butoxycarbonyl)indoline (2e): mp 81.5-82°C (pentane); ir (KBr) 1690 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 1.54 (9H, s, *t*-Bu), 3.03 (2H, t, *J*=7.7 Hz, H-3), 4.11 (2H, t, *J*=7.7 Hz, H-2), 6.89 (1H, dd, *J*=8.1 and 7.3 Hz, H-5), 7.13 (1H, dd, *J*=7.3 and 1.1 Hz, H-4), 7.35 (1H, dd, *J*=8.1 and 0.7 Hz, H-6); ms *m/z* 299 (M^+, 11), 297 (M^+, 11), 243 (8), 241 (9), 226 (6), 224(6), 199 (47), 197 (50), 117 (32), 90 (12), 57 (100), 41 (22). *Anal.* Calcd for $C_{13}H_{16}NO_2Br$: C, 52.37; H, 5.41; N, 4.70; Br, 26.80. Found: C, 52.37; H, 5.36; N, 4.59; Br, 26.88.

1-(*tert*-Butoxycarbonyl)-7-chloroindoline (2f): mp 84.5-85°C (pentane); ir (KBr) 1690 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 1.54 (9H, s, *t*-Bu), 3.02 (2H, t, *J*=7.7 Hz, H-3), 4.10 (2H, t, *J*=7.7 Hz, H-2), 6.96 (1H, dd, *J*=8.1 and 7.3 Hz, H-5), 7.09 (1H, dd, *J*=7.3 and 1.1 Hz, H-4), 7.17 (1H, dd, *J*=8.1 and 0.7 Hz, H-6); ms *m/z* 253 (M^+, 24), 197 (17), 180 (18), 153 (100), 117 (22), 89 (10), 57 (73), 41 (14). *Anal.* Calcd for $C_{13}H_{16}NO_2Cl$: C, 61.54; H, 6.36; N, 5.52; Cl, 13.97. Found: C, 61.52; H, 6.39; N, 5.51; Cl, 13.96.

1-(*tert*-Butoxycarbonyl)-7-methylindoline (2g): bp 110°C (oven temp.)/0.2 mmHg; ir (neat) 1710 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 1.52 (9H, s, *t*-Bu), 2.29 (3H, s, Me), 2.96 (2H, t, *J*=7.7 Hz, H-3), 4.06 (2H, t, *J*=7.7 Hz, H-2), 6.93-7.04 (3H, m, H-4, H-5, and H-6); ms *m/z* 233 (M^+, 24), 177 (60), 160 (14), 133 (52), 103 (36), 91 (22), 57 (100), 41 (34). *Anal.* Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.17; H, 8.27; N, 6.07.

1-(*tert*-Butoxycarbonyl)indoline-7-carboxylic acid (2h): mp 208°C (decomp.) (CH_2Cl_2/ether); ir (KBr) 3400-2200 (OH),1695 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 1.50 (9H, s, *t*-Bu), 3.07 (2H, t, *J*=8.1 Hz, H-3), 4.15 (2H, t, *J*=8.1 Hz, H-2), 7.04 (1H, t, *J*=7.7 Hz, H-5), 7.32 (1H, dd, *J*=7.7 and 1.1 Hz, H-4), 7.59 (1H, d, *J*=7.7 Hz, H-6); ms *m/z* 263 (M^+, 13), 190 (18), 163 (85), 145 (95), 117 (27), 89 (15), 57 (100), 41 (40). *Anal.* Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.67; H, 6.38; N, 5.30.

7-Indolinecarbaldehyde (2i): yellow needles, mp 44-45°C (pentane); ir (KBr) 3410 (NH), 1650 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 3.06 (2H, t, *J*=8.4 Hz, H-3), 3.79 (2H, t, *J*=8.4 Hz, H-2), 6.61 (1H, dd, *J*=8.1 and 7.0 Hz, H-5), 6.73 (1H, br s, NH), 7.18 (1H, ddt, *J*=7.0, 0.7, and 1.1 Hz, H-4), 7.29 (1H, dd, *J*=8.1 and

0.7 Hz, H-6), 9.83 (1H, s, CHO); ms *m/z* 147 (M^+, 100), 118 (82), 103 (33), 91 (52). *Anal.* Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.37; H, 6.23; N, 9.46.

5,6-Dihydro-1-(*p*-methoxyphenyl)-1*H*,3*H*-pyrrolo[3,2,1-*ij*]-3,1-benzoxazin-3-one (2j): mp 160-161°C (decomp.) (CH_2Cl_2-ether); ir (KBr) 1690 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 3.29 (2H, t, *J*=8.5 Hz, H-6), 3.81 (3H, s, OMe), 4.15 (2H, t, *J*=8.5 Hz, H-5), 6.42 (1H, s, H-1), 6.70 (1H, d, *J*=7.7 Hz, H-9), 6.90 (2H, m, H-3'and H-5'), 6.94 (1H, t, *J*=7.7 Hz, H-8), 7.16 (1H, d, *J*=7.7 Hz, H-7), 7.28 (2H, m, H-2'and H-6'); ms *m/z* 281 (M^+, 11), 236 (100), 222 (43), 193 (22), 103 (16), 69 (23), 41 (21). *Anal.* Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.68; H, 5.45; N, 4.99.

1-Ethyl-5,6-dihydro-1*H*,3*H*-pyrrolo[3,2,1-*ij*]-3,1-benzoxazin-3-one (2k): viscous oil which on standing solidified, mp 64-69 °C; ir (neat) 1720 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 1.06 (3H, t, *J*=7.3 Hz, CH_3 of Et), 1.92-2.09 (2H, m, CH_2 of Et), 3.24 (2H, t, *J*=8.4 Hz, H-6), 4.09 (2H, m, H-5), 5.45 (1H, t, *J*=5.5 Hz, H-1), 6.90 (1H, d, *J*=7.7 Hz, H-9), 6.98 (1H, dd, *J*=7.7 and 7.3 Hz, H-8), 7.13 (1H, d, *J*=7.3 Hz, H-7); ms *m/z* 203 (M^+, 39), 174 (32), 159 (41), 144 (25), 117 (11), 57 (14), 32 (24), 28 (100). HRms Calcd for $C_{12}H_{13}NO_2$ *m/z* 203.0946. Found *m/z* 203.0948.

1-(*tert*-Butoxycarbonyl)-5-methoxy-7-trimethylsilylindoline (2l): mp 78°C (pentane); ir (KBr) 1705 cm^{-1} (C=O); ^1H nmr($CDCl_3$) δ 0.28 (9H, s, $SiMe_3$), 1.52 (9H, s, *t*-Bu), 2.94 (2H, t, *J*=7.7 Hz, H-3), 3.77 (3H, s, OMe), 4.01 (2H, t, *J*=7.7 Hz, H-2), 6.75 (1H, dt, *J*=2.9 and 1.5 Hz, H-4), 6.91 (1H, d, *J*=2.9 Hz, H-6); ms *m/z* 321 (M^+, 13), 265 (16), 250 (100), 220 (9), 190 (11), 57 (30), 41 (8). *Anal.* Calcd for $C_{17}H_{27}NO_3Si$: C, 63.51; H, 8.46; N, 4.36. Found: C, 63.38; H, 8.37; N, 4.35.

1-(*tert*-Butoxycarbonyl)-5-chloro-7-trimethylsilylindoline (2m): mp 103-104°C (pentane); ir (KBr) 1695 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ 0.28 (9H, s, $SiMe_3$), 1.52 (9H, s, *t*-Bu), 2.95 (2H, t, *J*=8.1 Hz, H-3), 4.02 (2H, t, *J*=8.1 Hz, H-2), 7.11 (1H, dt, *J*=2.2 and 1.1 Hz, H-4), 7.30 (1H, d, *J*=2.2 Hz, H-6); ms *m/z* 325 (M^+, 11), 269 (8), 254 (100), 225 (10), 209 (7), 167 (6), 57 (80), 41 (11). *Anal.* Calcd for $C_{16}H_{24}NO_2ClSi$: C, 58.97; H, 7.42; N, 4.30. Found: C, 58.80; H, 7.30; N, 4.33.

1-(*tert*-Butoxycarbonyl)-2-trimethylsilylindoline (3): oil; ir (neat) 1690 cm^{-1} (C=O); ^1H nmr ($CDCl_3$) δ -0.02 (9H, s, $SiMe_3$), 1.56 (9H, s, *t*-Bu), 2.87 (1H, dd, *J*=15.8 and 3.3 Hz, H-3), 3.43 (1H, dd, *J*=15.8 and 11.7 Hz, H-3), 4.02 (1H, dd, *J*=11.7 and 3.3 Hz, H-2), 6.90 (1H, td, *J*=7.3 and 1.1 Hz, H-5), 7.08-7.14 (2H, m, H-4 and H-6), 7.59 (1H, br s, H-7); ms *m/z* 291 (M^+, 31), 235 (67), 220 (27), 191 (82), 176 (30), 143 (20), 118 (81), 73 (91), 57 (100), 41 (23). HRms Calcd for $C_{16}H_{25}NO_2Si$ *m/z* 291.1655. Found *m/z* 291.1658.

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