Synthesis of 9,9-Disubstituted 9*H*-Pyrrolo[1,2-*a*]indoles by Hydriodic Acid-Catalyzed Cyclization of 1-[2-(1-Aryl(or methyl)ethenyl)phenyl]-1*H*-pyrroles

by **Kazuhiro Kobayashi***, **Kenichi Hashimoto**, **Hiroo Hashimoto**, **Hideaki Kondo**, and **Hisatoshi Konishi**

Division of Applied Chemistry, Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Koyama-minami, Tottori 680-8552, Japan (phone/fax: +81-857-315263; e-mail: kkoba@chem.tottori-u.ac.jp)

A novel method is reported for the synthesis of 9,9-disubstituted 9*H*-pyrrolo[1,2-*a*]indoles. Cyclization of 1-[2-(1-aryl(or methyl)ethenyl)phenyl]-1*H*-pyrroles, which can be easily prepared from 2-(1-aryl(or methyl)ethenyl)anilines, proceeds smoothly, in general, at 0° in the presence of a catalytic (or an equimolar) amount of HI in MeCN to provide the desired products.

Introduction. – 9*H*-Pyrrolo[1,2-*a*]indoles have attracted much attention due to their structural resemblance to cytostatic mytomycine derivatives [1]. Although a number of methods for the preparation of 9*H*-pyrrolo[1,2-*a*]indoles have recently been published [2], there have been only few reports on the synthesis of 9,9-disubstituted derivatives [1a][3]. For example, *Cartoon* and *Cheeseman* have reported a synthesis 9,9-diphenyl-9*H*-pyrrolo[1,2-*a*]indole by the reaction of 1-(2-lithiophenyl)-1*H*-pyrrole with benzophenone, followed by acid-catalyzed cyclization of the resulting adducts [3]. Therefore, we embarked upon development of a convenient method for their preparation. In this article, we report that the hydriodic acid-catalyzed (or mediated) cyclization of 1-[2-(1-aryl(or methyl)ethenyl)phenyl]-1*H*-pyrroles **2** offers an efficient method for the preparation of 9,9-disubstituted 9*H*-pyrrolo[1,2-*a*]indoles **3**.

Results and Discussion. – Our preparation of 9,9-disubstituted 9*H*-pyrrolo[1,2-*a*]-indoles **3** is conducted as illustrated in *Scheme 1*. Thus, exposure of 1-[2-(1-arylethenyl)phenyl]-1*H*-pyrroles **2a**–**2i**, which were readily available from the corresponding 2-(1-arylethenyl)benzenamines **1a**–**1i** and 2,5-dimethoxytetrahydrofuran in AcOH under the reported conditions [4], to a catalytic or an equimolar amount of concentrated HI in MeCN at 0° led to 9-aryl-9-methyl-9*H*-pyrrolo[1,2-*a*]indoles **3a**–**3i** in generally good yields, as compiled in the *Table*. While most of the cyclization reactions of **2** proceeded smoothly in the presence of 0.1 mol-equiv. of HI to give the corresponding desired products **3** in good yields, those of **2** with a Cl substituent at either of the benzene rings, *i.e.*, **2d** and **2h**, required an equimolar amount of HI and extended reaction times to afford the corresponding desired products **3d** and **3h**, respectively, in somewhat lower yields (*Entries 4* and *8*). This is attributable to the lower reactivity of the vinyl moiety of these precursors to protonation due to an electron-deficient benzene ring.

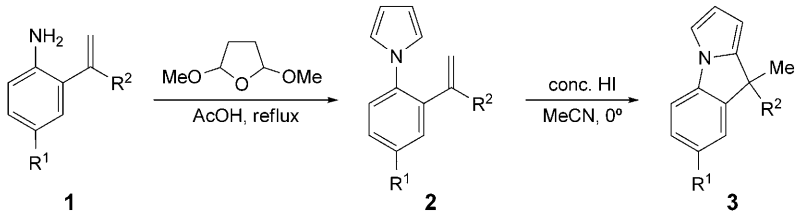
The probable pathway to **3** from **2** is depicted in *Scheme 2*. Protonation of the vinyl moiety of **2** generates a carbocation in α-position to the benzene ring ($\rightarrow$**4**), which is

Table. *Preparation of 9*H*-Pyrrolo[1,2-*a*]indoles* **3**

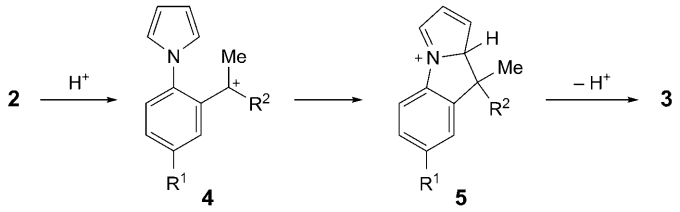
Entry	**1**	**2**	Yield[a]) [%]	HI [equiv.]	Time	**3**	Yield[a]) [%]
1	**1a** R^1 = H, R^2 = Ph	**2a**	74	0.1	1 h	**3a**	93
2	**1b** R^1 = H, R^2 = *m*-Tol	**2b**	70	0.1	1 h	**3b**	82
3	**1c** R^1 = H, R^2 = *p*-Tol	**2c**	78	0.1	1 h	**3c**	91
4	**1d** R^1 = H, R^2 = 4-Cl–C_6H_4	**2d**	81	1	12 h	**3d**	78
5	**1e** R^1 = H, R^2 = 3-MeO–C_6H_4	**2e**	67	0.1	1 h	**3e**	80
6	**1f** R^1 = H, R^2 = 4-MeO–C_6H_4	**2f**	73	0.1	10 min	**3f**	88
7	**1g** R^1 = H, R^2 = 3,4-$(MeO)_2$–C_6H_3	**2g**	72	0.1	5 min	**3g**	92
8	**1h** R^1 = Cl, R^2 = Ph	**2h**	74	1	12 h	**3h**	67
9	**1i** R^1 = MeO, R^2 = Ph	**2i**	75	0.1	3.5 h	**3i**	83
10	**1j** R^1 = H, R^2 = Me	**2j**	79	1	12 h	**3j**	34[b])

[a]) Yields of isolated products. [b]) Carried out at room temperature.

Scheme 1



Scheme 2



attacked by C(2) of the pyrrole ring to give the intermediate **5**. Subsequent deprotonation of **5** gives rise to **3**.

The reaction of 1-[2-(1-methylethenyl)phenyl]-1*H*-pyrrole (**2j**) occurred scarcely at 0°, but it proceeded slowly at room temperature to give the corresponding desired product, 9,9-dimethyl-9*H*-pyrrolo[1,2-*a*]indole (**3j**), in rather low yield (*Entry 10*). This result indicates that the benzyl cation intermediate (**4**, R^2 = Me) from **2j** is less stable than those (**4**, R^2 = Ar) from the other precursors **2a**–**2i**, which give particularly well-stabilized benzylic carbocations.

It should be noted that all attempts to prepare 9-ethyl-9-phenyl-9*H*-pyrrolo[1,2-*a*]-indole from 1-[2-(1-phenylprop-1-enyl)phenyl]-1*H*-pyrrole were unsuccessful; the reaction with an equimolar amount of HI at 0° was extremely reluctant, and the

reaction at elevated reaction temperature resulted in the formation of an intractable mixture of products, from which only a trace amount of the desired product was isolated as a mixture with structurally undefined products. Presumably, the Me substituent in the β-position of the vinyl moiety of the starting material renders the cyclization difficult.

In summary, we have demonstrated that the HI-catalyzed (or -mediated) cyclization reaction of 1-[2-(1-aryl(or methyl)ethenyl)phenyl]-1*H*-pyrroles allows convenient access to 9,9-disubstituted 9*H*-pyrrolo[1,2-*a*]indoles. The mild conditions, simplicity, and efficiency makes this method attractive.

Experimental Part

General. All of the org. solvents used in this study were dried over appropriate drying agents and distilled prior to use. TLC: *Merck* silica gel *60 PF_{254}*. Column chromatography (CC): *Wako Gel* C-200E. M.p.: *Laboratory Devices MEL-TEMP II* melting-point apparatus; uncorrected. IR Spectra: *Shimadzu FT-IR-8300* spectrophotometer. NMR Spectra: *JEOL ECP500* FT-NMR spectrometer (^{1}H: 500 and ^{13}C: 125 MHz); in $CDCl_3$ with TMS as an internal reference. LR-MS (EI, 70 eV): *JEOL JMS AX505 HA* spectrometer.

2-(Prop-1-en-2-yl)benzenamine (**1j**) was commercially available. *2-(1-Arylethenyl)benzenamines* **1a** [5], **1c** [6], **1d** [7], **1f** [5], **1g** [5], **1h** [8], and **1i** [9] were prepared by the reported procedures. All other chemicals used in this study were commercially available.

2-(1-Arylethenyl)benzenamines **1b** and **1e**. These compounds were prepared from 1-(2-aminophenyl)ethanone by a sequence practically same as that described for the preparation of the above 2-(1-arylethenyl)benzenamines [5–9].

2-[1-(3-Methylphenyl)ethenyl]benzenamine (**1b**). 1-(2-Aminophenyl)ethanone was treated with 3.5 mol of 3-methylphenylmagnesium bromide in THF at 0° to give 1-(2-aminophenyl)-1-(3-methylphenyl)ethanol. Yield: 99%. Yellow oil. R_f (CH_2Cl_2) 0.40. IR (neat): 3383, 1607. ^{1}H-NMR: 1.86 (*s*, 3 H); 2.32 (*s*, 3 H); 3.67 (br. *s*, 2 H); 3.92 (br. *s*, 1 H); 6.65 (*dd*, *J* = 8.2, 1.4, 1 H); 6.87 (*ddd*, *J* = 7.8, 7.3, 1.4, 1 H); 7.05 (*dd*, *J* = 7.3, 0.9, 1 H); 7.14 (*ddd*, *J* = 7.8, 7.3, 1.4, 1 H); 7.17–7.20 (*m*, 2 H); 7.24 (*s*, 1 H); 7.41 (*dd*, *J* = 7.8, 1.4, 1 H). Anal. calc. for $C_{15}H_{17}NO$ (227.30): C 79.26, H 7.54, N 6.16; found: C 79.16, H 7.63, N 5.94.

The above alcohol was dehydrated by heating at 160° (neat) for 40 min to give **1b**. Yield: 62%. Pale-yellow oil. R_f (THF/hexane 1:10) 0.40. IR (neat): 3472, 3379, 1614. ^{1}H-NMR: 2.32 (*s*, 3 H); 3.55 (br. *s*, 2 H); 5.33 (*d*, *J* = 1.8, 1 H); 5.76 (*d*, *J* = 1.8, 1 H); 6.69 (*dd*, *J* = 7.8, 0.9, 1 H); 6.79 (*ddd*, *J* = 7.8, 7.3, 0.9, 1 H); 7.11 (*dd*, *J* = 7.8, 1.4, 2 H); 7.14–7.22 (*m*, 4 H). Anal. calc. for $C_{15}H_{15}N$ (209.29): C 86.08, H 7.22, N 6.69; found: C 86.09, H 7.20, N 6.68.

2-[1-(3-Methoxyphenyl)ethenyl]benzenamine (**1e**). 1-(2-Aminophenyl)ethanone was treated with 3.5 mol of 3-methoxyphenylmagnesium bromide in THF at 0° to give 1-(2-aminophenyl)-1-(3-methoxyphenyl)ethanol. Yield: 90%. Yellow oil. R_f (THF/hexane 1:5) 0.22. IR (neat): 3460, 3383, 1614. ^{1}H-NMR: 1.86 (*s*, 3 H); 3.65 (br. *s*, 2 H); 3.78 (*s*, 3 H); 4.08 (br. *s*, 1 H); 6.65 (*d*, *J* = 7.8, 1 H); 6.78 (*dd*, *J* = 8.2, 2.3, 1 H); 6.88 (*ddd*, *J* = 7.8, 7.3, 1.4, 1 H); 6.90 (*dd*, *J* = 7.8, 1.8, 1 H); 7.04 (*dd*, *J* = 2.3, 1.8, 1 H); 7.14 (*ddd*, *J* = 7.8, 7.3, 1.4, 1 H); 7.21 (*dd*, *J* = 8.2, 7.8, 1 H); 7.41 (*dd*, *J* = 7.8, 1.4, 1 H). Anal. calc. for $C_{15}H_{17}NO_2$ (243.30): C 74.05, H 7.04, N 5.76; found: C 74.15, H 7.12, N 5.64.

The above alcohol was dehydrated by heating at 220° (neat) for 20 min to give **1e**. Yield: 63%. Yellow solid. M.p. 60–62° (hexane/Et_2O). IR (KBr): 3466, 3376, 1609. ^{1}H-NMR: 3.55 (br. *s*, 2 H); 3.78 (*s*, 3 H); 5.36 (*d*, *J* = 1.4, 1 H); 5.79 (*d*, *J* = 1.4, 1 H); 6.68 (*d*, *J* = 8.2, 1 H); 6.79 (*ddd*, *J* = 7.8, 7.3, 0.9, 1 H); 6.84 (*dd*, *J* = 8.2, 2.3, 1 H); 6.93 (*dd*, *J* = 2.3, 1.4, 1 H); 6.95 (*dd*, *J* = 7.8, 0.9, 1 H); 7.11 (*dd*, *J* = 7.8, 0.9, 1 H); 7.15 (*ddd*, *J* = 7.8, 7.3, 1.4, 1 H); 7.23 (*dd*, *J* = 8.2, 7.8, 1 H). Anal. calc. for $C_{15}H_{15}NO$ (225.29): C 79.97, H 6.71, N 6.22; found: C 79.72, H 6.72, N 6.13.

*1-(2-Ethenylaryl)-1*H*-pyrroles* **2**. These compounds were prepared by reacting **1** with 2,5-dimethoxytetrahydrofuran in AcOH at reflux temp. [4].

*1-[2-(1-Phenylethenyl)phenyl]-1*H-*pyrrole* (**2a**). Colorless oil. R_f (Et_2O/hexane 1:20) 0.63. IR (neat): 1603. ^{1}H-NMR: 5.06 (*s*, 1 H); 5.59 (*d*, *J* = 0.9, 1 H); 6.28 (*t*, *J* = 2.3, 2 H); 6.86 (*t*, *J* = 2.3, 2 H); 7.28–7.36 (*m*, 9 H). Anal. calc. for $C_{18}H_{15}N$ (245.32): C 88.13, H 6.16, N 5.71; found: C 88.10, H 6.20, N 5.63.

*1-[2-[1-(3-Methylphenyl)ethenyl]phenyl]-1*H-*pyrrole* (**2b**). Colorless oil. R_f ($CHCl_3$/hexane 1:10) 0.36. IR (neat): 1614, 1601. ^{1}H-NMR: 2.24 (*s*, 3 H); 5.17 (*s*, 1 H); 5.58 (*s*, 1 H); 6.02 (*dd*, *J* = 2.3, 1.8, 2 H); 6.66 (*dd*, *J* = 2.3, 1.8, 2 H); 6.94 (*s*, 1 H); 6.95 (*d*, *J* = 7.8, 1 H); 6.99 (*d*, *J* = 7.3, 1 H); 7.06 (*dd*, *J* = 7.8, 7.3, 1 H); 7.33 (*dd*, *J* = 7.8, 7.3, 1 H); 7.36–7.47 (*m*, 3 H). Anal. calc. for $C_{19}H_{17}N$ (259.35): C 87.99, H 6.61, N 5.40; found: C 87.98, H 6.78, N 5.14.

*1-[2-[1-(4-Methylphenyl)ethenyl]phenyl}-1*H-*pyrrole* (**2c**). Colorless needles. M.p. 44–46° (hexane/Et_2O). IR (neat): 1609. ^{1}H-NMR: 2.28 (*s*, 3 H); 5.14 (*d*, *J* = 0.9, 1 H); 5.57 (*d*, *J* = 0.9, 1 H); 6.03 (*t*, *J* = 2.3, 2 H); 6.68 (*t*, *J* = 2.3, 2 H); 6.98 (*d*, *J* = 8.2, 2 H); 7.05 (*d*, *J* = 8.2, 2 H); 7.31–7.42 (*m*, 4 H). Anal. calc. for $C_{19}H_{17}N$ (259.35): C 87.99, H 6.61, N 5.40; found: C 87.87, H 6.65, N 5.24.

*1-[2-[1-(4-Chlorophenyl)ethenyl]phenyl]-1*H-*pyrrole* (**2d**). Yellow oil. R_f (THF/hexane 1:15) 0.60. IR (neat): 1614. ^{1}H-NMR: 5.29 (*s*, 1 H); 5,57 (*s*, 1 H); 6.00 (*dd*, *J* = 2.3, 1.8, 2 H); 6.61 (*dd*, *J* = 2.3, 1.8, 2 H); 7.02 (*d*, *J* = 8.7, 2 H); 7.10 (*d*, *J* = 8.7, 2 H); 7.31 (*dd*, *J* = 7.8, 0.9, 1 H); 7.35–7.45 (*m*, 3 H). Anal. calc. for $C_{18}H_{14}ClN$ (279.76): C 77.28, H 5.04, N 5.01; found: C 77.26, H 5.09, N 4.92.

*1-[2-[1-(3-Methoxyphenyl)ethenyl]phenyl}-1*H-*pyrrole* (**2e**). Colorless oil. R_f (Et_2O/hexane 1:5) 0.60. IR (neat): 1599. ^{1}H-NMR: 3.73 (*s*, 3 H); 5.22 (*s*, 1 H); 5.61 (*s*, 1 H); 6.03 (*t*, *J* = 2.3, 2 H); 6.65–6.68 (*m*, 3 H); 6.72–6.75 (*m*, 2 H); 7.09 (*dd*, *J* = 8.2, 7.8, 1 H); 7.31–7.43 (*m*, 4 H). Anal. calc. for $C_{19}H_{17}NO$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.65, H 6.34, N 5.03.

*1-[2-[1-(4-Methoxyphenyl)ethenyl]phenyl}-1*H-*pyrrole* (**2f**). Colorless oil. R_f (THF/hexane 1:10) 0.60. IR (neat): 1607. ^{1}H-NMR: 3.75 (*s*, 3 H); 5.11 (*d*, *J* = 0.9, 1 H); 5.33 (*d*, *J* = 0.9, 1 H); 6.03 (*t*, *J* = 2.3, 2 H); 6.67 (*t*, *J* = 2.3, 2 H); 6.69 (*d*, *J* = 8.7, 2 H); 7.08 (*d*, *J* = 8.7, 2 H); 7.31–7.43 (*m*, 4 H). Anal. calc. for $C_{19}H_{17}NO$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.63, H 6.21, N 5.04.

*1-[2-[1-(3,4-Dimethoxyphenyl)ethenyl]phenyl}-1*H-*pyrrole* (**2g**). White solid. M.p. 74–76° (hexane/Et_2O). IR (KBr): 1607. ^{1}H-NMR: 3.78 (*s*, 3 H); 3.83 (*s*, 3 H); 5.14 (*s*, 1 H); 5.52 (*s*, 1 H); 6.04 (*dd*, *J* = 2.3, 1.8, 2 H); 6.63–6.67 (*m*, 4 H); 6.71 (*d*, *J* = 1.8, 1 H); 7.32 (*dd*, *J* = 7.8, 0.9, 1 H); 7.34–7.43 (*m*, 3 H). Anal. calc. for $C_{20}H_{19}NO_2$ (305.37): C 78.66, H 6.27, N 4.59; found: C 78.59, H 6.41, N 4.51.

*1-[4-Chloro-2-(1-phenylethenyl)phenyl]-1*H-*pyrrole* (**2h**). White solid. M.p. 62–63° (hexane/Et_2O). IR (KBr): 1611. ^{1}H-NMR: 5.25 (*s*, 1 H); 5.62 (*s*, 1 H); 6.00 (*t*, *J* = 2.3, 2 H); 6.60 (*t*, *J* = 2.3, 2 H); 7.10–7.12 (*m*, 2 H); 7.15–7.19 (*m*, 3 H); 7.25 (*d*, *J* = 9.2, 1 H); 7.38–7.40 (*m*, 2 H). Anal. calc. for $C_{18}H_{14}ClN$ (279.76): C 77.28, H 5.04, N 5.01; found: C 77.27, H 5.01, N 4.91.

*1-[4-Methoxy-2-(1-phenylethenyl)phenyl]-1*H-*pyrrole* (**2i**). White solid. M.p. 51–52° (hexane). IR (KBr): 1611. ^{1}H-NMR: 3.85 (*s*, 3 H); 5.21 (*s*, 1 H); 5.57 (*s*, 1 H); 5.98 (*t*, *J* = 1.8, 2 H); 6.56 (*t*, *J* = 1.8, 2 H), 6.91–6.95 (*m*, 2 H); 7.14–7.18 (*m*, 5 H); 7.23 (*d*, *J* = 8.2, 1 H). Anal. calc. for $C_{19}H_{17}NO$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.61, H 6.24, N 5.02.

*1-[2-(Prop-1-en-2-yl)phenyl]-1*H-*pyrrole* (**2j**). Colorless liquid. R_f (Et_2O/hexane 1:20) 0.71. IR (neat): 1600. ^{1}H-NMR: 1.54 (*s*, 3 H); 5.06 (*s*, 1 H); 5.09 (*s*, 1 H); 6.28 (*dd*, *J* = 2.3, 1.8, 2 H); 6.86 (*dd*, *J* = 2.3, 1.8, 2 H); 7.26–7.35 (*m*, 4 H). Anal. calc. for $C_{13}H_{13}N$ (183.25): C 85.21, H 7.15, N 7.64; found: C 84.93, H 7.21, N 7.53.

*9*H-*Pyrrolo[1,2-a]indoles* **3**. *General Procedure.* To a stirred soln. of **2** (1.0 mmol) in MeCN (12 ml) at 0° was added conc. HI (the quantity as indicated in the *Table*). After stirring for the time indicated in *Table 1*, sat. aq. $NaHCO_3$ (10 ml) and 10% aq. $Na_2S_2O_3$ (5 ml) were added, and MeCN was evaporated. The org. materials were extracted with Et_2O (3 × 10 ml), and the combined extracts were washed with brine (10 ml) and dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by CC (SiO_2) to give **3**.

*9-Methyl-9-phenyl-9*H-*pyrrolo[1,2-a]indole* (**3a**). Pale-yellow oil. R_f (Et_2O/hexane 1:20) 0.53. IR (neat): 1615. ^{1}H-NMR: 1.91 (*s*, 3 H); 6.01 (*dd*, *J* = 2.7, 0.9, 1 H); 6.39 (*dd*, *J* = 2.7, 2.3, 1 H); 7.04–7.09 (*m*, 2 H); 7.18 (*tt*, *J* = 7.3, 1.4, 1 H); 7.24–7.28 (*m*, 5 H); 7.32 (*dd*, *J* = 7.8, 1.4, 2 H). ^{13}C-NMR: 26.81; 48.96; 101.19; 109.52; 109.84; 113.47; 123.59; 124.80; 126.21; 126.55; 127.66; 128.39; 139.44; 144.91; 145.13; 145.39. MS: 245 (45, M^+), 230 (100). Anal. calc. for $C_{18}H_{15}N$ (245.32): C 88.13, H 6.16, N 5.71; found: C 87.85, H 6.31, N 5.58.

*9-Methyl-9-(3-methylphenyl)-9*H-*pyrrolo[1,2-*a*]indole* (**3b**). Yellow oil. R_f (hexane) 0.27. IR (neat): 1614. ^{1}H-NMR: 1.89 (*s*, 3 H); 2.28 (*s*, 3 H); 6.01 (*dd*, *J* = 3.2, 1.4, 1 H); 6.39 (*dd*, *J* = 3.2, 2.7, 1 H); 7.00 (*d*, *J* = 7.8, 1 H); 7.04 – 7.08 (*m*, 2 H); 7.11 – 7.17 (*m*, 3 H); 7.24 – 7.29 (*m*, 3 H). ^{13}C-NMR: 21.59; 26.90; 48.87; 101.14; 109.43; 109.79; 113.42; 123.28; 123.55; 124.78; 126.88; 127.34; 127.57; 128.26; 137.90; 139.41; 144.98; 145.00; 145.45. MS: 259 (51, M^+), 244 (100). Anal. calc. for $C_{19}H_{17}N$ (259.35): C 87.99, H 6.61, N 5.40; found: C 87.95, H 6.65, N 5.11.

*9-Methyl-9-(4-methylphenyl)-9*H-*pyrrolo[1,2-*a*]indole* (**3c**).Yellow oil. R_f (Et_2O/hexane 1:20) 0.50. IR (neat): 1614. ^{1}H-NMR: 1.88 (*s*, 3 H); 2.28 (*s*, 3 H); 6.00 (*dd*, *J* = 3.2, 0.9, 1 H); 6.38 (*t*, *J* = 3.2, 1 H); 7.03 – 7.07 (*m*, 3 H); 7.20 (*d*, *J* = 8.2, 2 H); 7.23 – 7.29 (*m*, 4 H). ^{13}C-NMR: 20.88; 26.81; 48.64; 101.05; 109.42; 109.79; 113.42; 123.56; 124.70; 126.08; 127.55; 129.07; 136.12; 139.39; 142.16; 145.08; 145.54. MS: 259 (45, M^+), 244 (100). Anal. calc. for $C_{19}H_{17}N$ (259.35): C 87.99, H 6.61, N 5.40; found: C 87.93, H 6.72, N 5.31.

*9-(4-Chlorophenyl)-9-methyl-9*H-*pyrrolo[1,2-*a*]indole* (**3d**). Pale-yellow solid. M.p. 76 – 78° (hexane/Et_2O). IR (KBr): 1616. ^{1}H-NMR: 1.88 (*s*, 3 H); 5.99 (*d*, *J* = 3.2, 1 H); 6.38 (*dd*, *J* = 3.2, 2.7, 1 H); 7.06 – 7.08 (*m*, 2 H); 7.20 – 7.31 (*m*, 7 H). ^{13}C-NMR: 26.63; 48.46; 101.25; 109.70; 109.94; 113.57; 123.69; 124.62; 127.68; 127.87; 128.45; 132.41; 139.37; 143.75; 144.46; 144.88. MS: 279 (45, M^+), 264 (100). Anal. calc. for $C_{18}H_{14}ClN$ (279.76): C 77.28, H 5.04, N 5.01; found: C 77.08; H 5.06; N 4.95.

*9-(3-Methoxyphenyl)-9-methyl-9*H-*pyrrolo[1,2-*a*]indole* (**3e**).Yellow oil. R_f (CH_2Cl_2/hexane 1:5) 0.25. IR (neat): 1607. ^{1}H-NMR: 1.88 (*s*, 3 H); 3.74 (*s*, 3 H); 6.02 (*dd*, *J* = 2.3, 1.4, 1 H); 6.38 (*dd*, *J* = 3.2, 2.8, 1 H); 6.72 (*dt*, *J* = 8.2, 0.9, 1 H); 6.89 – 6.91 (*m*, 2 H); 7.05 – 7.08 (*m*, 2 H); 7.18 (*dd*, *J* = 8.3, 7.8, 1 H); 7.20 – 7.28 (*m*, 3 H). ^{13}C-NMR: 26.82; 48.92; 55.12; 101.24; 109.51; 109.82; 111.06; 112.90; 113.45; 118.77; 123.55; 124.75; 127.66; 129.34; 141.75; 144.65; 145.12; 146.81; 159.51. MS: 275 (43, M^+), 260 (100). Anal. calc. for $C_{19}H_{17}NO$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.84, H 6.34, N 5.09.

*9-(4-Methoxyphenyl)-9-methyl-9*H-*pyrrolo[1,2-*a*]indole* (**3f**). Pale-yellow solid. M.p. 108 – 110° (hexane/Et_2O). IR (KBr): 1616. ^{1}H-NMR: 1.87 (*s*, 3 H); 3.75 (*s*, 3 H); 5.99 (*dd*, *J* = 3.2, 0.9, 1 H); 6.38 (*t*, *J* = 3.2, 1 H); 6.79 (*d*, *J* = 9.2, 2 H); 7.04 – 7.07 (*m*, 2 H); 7.22 – 7.27 (*m*, 5 H). ^{13}C-NMR: 26.94; 48.33; 55.20; 100.98; 109.41; 109.79; 113.42; 113.69; 123.35; 123.63; 127.26; 127.54; 137.23; 139.33; 145.18; 145.60; 158.20. MS: 275 (38, M^+), 260 (100). Anal. calc. for $C_{19}H_{17}NO$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.66, H 6.26, N 4.92.

*9-(3,4-Dimethoxyphenyl)-9-methyl-9*H-*pyrrolo[1,2-*a*]indole* (**3g**). White solid. M.p. 135 – 137° (hexane). IR (KBr): 1609. ^{1}H-NMR: 1.88 (*s*, 3 H); 3.76 (*s*, 3 H); 3.83 (*s*, 3 H); 6.02 (*dd*, *J* = 3.2, 0.9, 1 H); 6.39 (*t*, *J* = 3.2, 1 H); 6.77 (*d*, *J* = 8.7, 1 H); 6.78 (*d*, *J* = 2.3, 1 H); 6.93 (*dd*, *J* = 8.7, 2.3, 1 H); 7.05 – 7.09 (*m*, 2 H); 7.27 – 7.28 (*m*, 3 H). ^{13}C-NMR: 27.17; 48.65; 55.84; 55.93; 101.11; 109.48; 109.84; 110.13; 110.96; 113.44; 118.29; 123.54; 124.62; 127.61; 137.72; 139.31; 144.93; 145.32; 147.79; 148.69. MS: 305 (37, M^+), 290 (100). Anal. calc. for $C_{20}H_{19}NO_2$ (305.37): C 78.66, H 6.27, N 4.59; found: C 78.77, H 6.11, N 4.61.

*7-Chloro-9-methyl-9-phenyl-9*H-*pyrrolo[1,2-*a*]indole* (**3h**). Yellow oil. R_f (CH_2Cl_2/hexane 1:10) 0.44. IR (neat): 1614. ^{1}H-NMR: 1.89 (*s*, 3 H); 6.00 (*dd*, *J* = 3.2, 0.9, 1 H); 6.39 (*dd*, *J* = 3.2, 2.7, 1 H); 7.02 (*d*, *J* = 2.7, 1 H); 7.17 – 7.30 (*m*, 8 H). ^{13}C-NMR: 26.62; 49.13; 101.65; 109.67; 110.64; 113.95; 125.26; 126.13; 126.84; 127.70; 128.54; 128.80; 138.01; 144.33; 145.26; 146.77. MS: 279 (36, M^+), 284 (100). Anal. calc. for $C_{18}H_{14}ClN$ (279.76): C 77.28, H 5.04, N 5.01; found: C 77.23, H 5.11, N 4.88.

*7-Methoxy-9-methyl-9-phenyl-9*H-*pyrrolo[1,2-*a*]indole* (**3i**). Pale-yellow solid. M.p. 71 – 73° (hexane). IR (KBr): 1597. ^{1}H-NMR: 1.89 (*s*, 3 H); 3.77 (*s*, 3 H); 5.98 (*d*, *J* = 3.2, 1 H); 6.35 (*dd*, *J* = 3.2, 2.3, 1 H); 6.79 (*dd*, *J* = 8.7, 2.3, 1 H); 6.82 (*d*, *J* = 2.3, 1 H); 7.00 (*d*, *J* = 2.3, 1 H); 7.18 (*d*, *J* = 8.2, 1 H), 7.19 (*d*, *J* = 7.3, 1 H); 7.26 (*dd*, *J* = 7.8, 7.3, 2 H); 7.31 (*d*, *J* = 7.8, 2 H). ^{13}C-NMR: 26.81; 49.18; 55.76; 101.01; 109.22; 110.03; 111.77; 111.98; 122.80; 126.19; 126.56; 128.40; 133.48; 145.09; 145.27; 146.45; 156.60. MS: 275 (34, M^+), 260 (100). Anal. calc. for $C_{19}H_{17}NO$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.85, H 6.47, N 4.95.

*9,9-Dimethyl-9*H-*pyrrolo[1,2-*a*]indole* (**3j**). Pale-yellow solid. M.p. 56 – 58° (hexane). IR (KBr): 1618. ^{1}H-NMR: 1.51 (*s*, 6 H); 6.02 (*d*, *J* = 3.2, 1 H); 6.36 (*dd*, *J* = 3.2, 2.7, 1 H); 7.00 (*dd*, *J* = 2.7, 0.9, 1 H); 7.10 (*td*, *J* = 7.3, 1.4, 1 H); 7.22 (*d*, *J* = 7.3, 1 H); 7.27 (*td*, *J* = 7.3, 1.4, 1 H); 7.32 (*d*, *J* = 7.3, 1 H). ^{13}C-NMR: 28.00; 41.24; 99.27; 109.23; 109.66; 113.02; 123.19; 123.31; 127.35; 139.41; 145.47; 146.35. MS: 183 (22, M^+), 178 (100). Anal. calc. for $C_{13}H_{13}N$ (183.25): C 85.21, H 7.15, N 7.64; found: C 85.06, H 7.24, N 7.53.

We thank Mrs. *Miyuki Tanmatsu* for recording the mass spectra and performing combustion analyses.

REFERENCES

[1] a) W. Verboom, B. H. M. Lammerink, R. J. M. Egberink, D. N. Reinhoudt, S. Harkema, *J. Org. Chem*. **1985**, *50*, 3797; b) K. Foggasy, K. Kovács, G. N. Keserű, L. Tőke, F. Faigl, *J. Chem. Soc., Perkin Trans. 1* **2001**, 1039.

[2] K. Kobayashi, A. Takanohashi, K. Hashimoto, O. Morikawa, H. Konishi, *Tetrahedron* **2006**, *62*, 3158; H. Ren, P. Knochel, *Angew. Chem., Int. Ed*. **2006**, *45*, 3462; G. Abbiati, A. Cosoni, V. Canevari, D. Nava, E. Rossi, *Org. Lett*. **2006**, *8*, 4839; K. Kobayashi, Y. Himei, S. Fukamachi, M. Tanmatsu, O. Morikawa, H. Konishi, *Tetrahedron* **2007**, *63*, 4356; S. J. Hwang, S. H. Cho, S. Chang, *J. Am. Chem. Soc*. **2008**, *130*, 16158; K. Wood, D. S. Black, N. Kumar, *Tetrahedron Lett.* **2009**, *50*, 574; F. Aiello, A. Garofalo, F. Grande, *Tetrahedron* **2010**, *66*, 274; A. P. Gaywood, H. McNab, *Synthesis* **2010**, 1361; X.-T. Liu, L. Hao, M. Lin, L. Chen, Z.-P. Zhan, *Org. Biomol. Chem*. **2010**, *8*, 3064; M. Tobisu, S. Imoto, S. Ito, N. Chatani, *J. Org. Chem*. **2010**, *75*, 4835.

[3] M. E. K. Cartoon, G. W. H. Cheeseman, *J. Organomet. Chem*. **1981**, *212*, 1.

[4] A. D. Josey, E. L. Jenner, *J. Org. Chem*. **1962**, *27*, 2466.

[5] K. Kobayashi, K. Takagoshi, S. Kondo, O. Morikawa, H. Konishi, *Bull. Chem. Soc. Jpn*. **2004**, *77*, 553.

[6] R. Stoermer, H. Fincke, *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 3115.

[7] T. Yaegashi, S. Sawada, N. Nagata, T. Furuta, T. Yokokura, T. Miyasaka, *Chem. Pharm. Bull*. **1994**, *42*, 2518.

[8] K. Kobayashi, K. Miyamoto, O. Morikawa, H. Konishi, *Bull. Chem. Soc. Jpn*. **2005**, *78*, 886.

[9] A. Arienti, F. Bigi, R. Maggi, E. Marzi, P. Moggi, M. Rastelli, G. Sartori, F. Tarantola, *Tetrahedron* **1997**, *53*, 3795.

Received February 28, 2011