

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

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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 mytomycin 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 benzo-phenone, 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**.

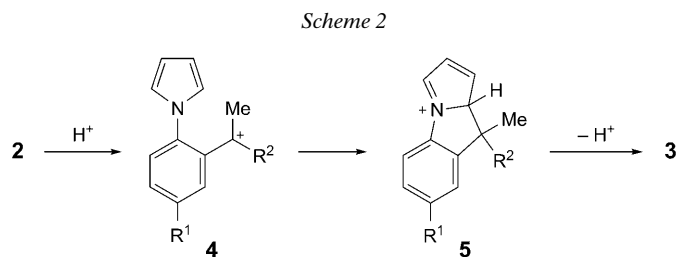
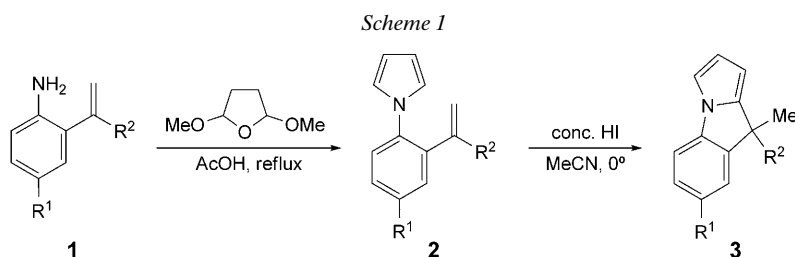
Results and Discussion. – Our preparation of 9,9-disubstituted 9*H*-pyrrolo[1,2-*a*]indoles **3** is conducted as illustrated in *Scheme 1*. Thus, exposure of 1-[2-(1-arylethenyl)phenyl]-1*H*-pyrroles **2a–2i**, which were readily available from the corresponding 2-(1-arylethenyl)benzenamines **1a–1i** 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 9H-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 = <i>m</i> -Tol	2b	70	0.1	1 h	3b	82
3	1c R ¹ = H, R ² = <i>p</i> -Tol	2c	78	0.1	1 h	3c	91
4	1d R ¹ = H, R ² = 4-Cl-C ₆ H ₄	2d	81	1	12 h	3d	78
5	1e R ¹ = H, R ² = 3-MeO-C ₆ H ₄	2e	67	0.1	1 h	3e	80
6	1f R ¹ = H, R ² = 4-MeO-C ₆ H ₄	2f	73	0.1	10 min	3f	88
7	1g R ¹ = H, R ² = 3,4-(MeO) ₂ -C ₆ H 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.



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**, R² = Me) from **2j** is less stable than those (**4**, R² = 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 (¹H: 500 and ¹³C: 125 MHz); in CDCl₃ 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 (CH₂Cl₂) 0.40. IR (neat): 3383, 1607. ¹H-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 C₁₅H₁₇NO (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. ¹H-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 C₁₅H₁₅N (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. ¹H-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 C₁₅H₁₇NO₂ (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/Et₂O). IR (KBr): 3466, 3376, 1609. ¹H-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 C₁₅H₁₅NO (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]-1H-pyrrole (2a). Colorless oil. R_f (Et₂O/hexane 1:20) 0.63. IR (neat): 1603. ¹H-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 C₁₈H₁₅N (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]-1H-pyrrole (2b). Colorless oil. R_f (CHCl₃/hexane 1:10) 0.36. IR (neat): 1614, 1601. ¹H-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 C₁₉H₁₇N (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]-1H-pyrrole (2c). Colorless needles. M.p. 44–46° (hexane/Et₂O). IR (neat): 1609. ¹H-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 C₁₉H₁₇N (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]-1H-pyrrole (2d). Yellow oil. R_f (THF/hexane 1:15) 0.60. IR (neat): 1614. ¹H-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 C₁₈H₁₄ClN (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]-1H-pyrrole (2e). Colorless oil. R_f (Et₂O/hexane 1:5) 0.60. IR (neat): 1599. ¹H-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 C₁₉H₁₇NO (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]-1H-pyrrole (2f). Colorless oil. R_f (THF/hexane 1:10) 0.60. IR (neat): 1607. ¹H-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 C₁₉H₁₇NO (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]-1H-pyrrole (2g). White solid. M.p. 74–76° (hexane/Et₂O). IR (KBr): 1607. ¹H-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 C₂₀H₁₉NO₂ (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]-1H-pyrrole (2h). White solid. M.p. 62–63° (hexane/Et₂O). IR (KBr): 1611. ¹H-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 C₁₈H₁₄ClN (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]-1H-pyrrole (2i). White solid. M.p. 51–52° (hexane). IR (KBr): 1611. ¹H-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 C₁₉H₁₇NO (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]-1H-pyrrole (2j). Colorless liquid. R_f (Et₂O/hexane 1:20) 0.71. IR (neat): 1600. ¹H-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 C₁₃H₁₃N (183.25): C 85.21, H 7.15, N 7.64; found: C 84.93, H 7.21, N 7.53.

9H-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. NaHCO₃ (10 ml) and 10% aq. Na₂S₂O₃ (5 ml) were added, and MeCN was evaporated. The org. materials were extracted with Et₂O (3 × 10 ml), and the combined extracts were washed with brine (10 ml) and dried (Na₂SO₄). After evaporation of the solvent, the residue was purified by CC (SiO₂) to give **3**.

9-Methyl-9-phenyl-9H-pyrrolo[1,2-a]indole (3a). Pale-yellow oil. R_f (Et₂O/hexane 1:20) 0.53. IR (neat): 1615. ¹H-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). ¹³C-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 C₁₈H₁₅N (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)-9H-pyrrolo[1,2-a]indole (3b). Yellow oil. R_f (hexane) 0.27. IR (neat): 1614. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{19}\text{H}_{17}\text{N}$ (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)-9H-pyrrolo[1,2-a]indole (3c). Yellow oil. R_f (Et_2O /hexane 1:20) 0.50. IR (neat): 1614. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{19}\text{H}_{17}\text{N}$ (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-9H-pyrrolo[1,2-a]indole (3d). Pale-yellow solid. M.p. 76–78° (hexane/ Et_2O). IR (KBr): 1616. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{18}\text{H}_{14}\text{ClN}$ (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-9H-pyrrolo[1,2-a]indole (3e). Yellow oil. R_f (CH_2Cl_2 /hexane 1:5) 0.25. IR (neat): 1607. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{19}\text{H}_{17}\text{NO}$ (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-9H-pyrrolo[1,2-a]indole (3f). Pale-yellow solid. M.p. 108–110° (hexane/ Et_2O). IR (KBr): 1616. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{19}\text{H}_{17}\text{NO}$ (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-9H-pyrrolo[1,2-a]indole (3g). White solid. M.p. 135–137° (hexane). IR (KBr): 1609. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{20}\text{H}_{19}\text{NO}_2$ (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-9H-pyrrolo[1,2-a]indole (3h). Yellow oil. R_f (CH_2Cl_2 /hexane 1:10) 0.44. IR (neat): 1614. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{18}\text{H}_{14}\text{ClN}$ (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-9H-pyrrolo[1,2-a]indole (3i). Pale-yellow solid. M.p. 71–73° (hexane). IR (KBr): 1597. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{19}\text{H}_{17}\text{NO}$ (275.34): C 82.88, H 6.22, N 5.09; found: C 82.85, H 6.47, N 4.95.

9,9-Dimethyl-9H-pyrrolo[1,2-a]indole (3j). Pale-yellow solid. M.p. 56–58° (hexane). IR (KBr): 1618. $^1\text{H-NMR}$: 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). $^{13}\text{C-NMR}$: 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 $\text{C}_{13}\text{H}_{13}\text{N}$ (183.25): C 85.21, H 7.15, N 7.64; found: C 85.06, H 7.24, N 7.53.

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