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A facile synthesis of 9-dialkylamino-9*H*-pyrrolo[1,2-*a*]indoles via iminium salts generated from 2-(pyrrol-1-yl)-benzaldehydes and secondary amine hydrochlorides in the presence of NaI/TMSCl/Et_3N

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Abstract—The NaI/TMSCl/Et_3N-mediated condensation between 2-(pyrrol-1-yl)benzaldehydes and secondary amine hydrochlorides followed by intramolecular trapping of the resulting iminium carbon by the 2-position of the pyrrole ring afforded corresponding 9-dialkylamino-9*H*-pyrrolo[1,2-*a*]indoles generally in good yields.

1. Introduction

Recently, Rish et al. reported that reactions of secondary amines with aldehydes were mediated by NaI/TMSCl/Et_3N to generate the corresponding iminium salts, which were used for the in situ α-aminoalkylation of enamines to provide β-amino ketones.[1] We envisaged that 2-(pyrrol-1-yl)benzaldehydes **1**, which are easily prepared from the respective anthranilates as reported previously,[2,3] and secondary amine hydrochlorides would generate the respective iminium salts **2** under the Risch's conditions and that these iminium salts should undergo intramolecular cyclization to give 9-dialkylamino-9*H*-pyrrolo[1,2-*a*]indoles **3**. We wish to describe here the results of our investigation, which offer a simple and versatile method for preparing this class of molecules.[4] The 9*H*-pyrrolo[1,2-*a*]indole skeleton has held considerable interest, because it is the basic framework of cytostatic mytomycine derivatives.[5] The previous synthetic route to 9-amino-9*H*-pyrrolo[1,2-*a*]indole derivatives involved cyclization of *N*-alkyl-2-(pyrrol-1-yl)benzamide derivatives with phosphoryl chloride leading to the corresponding 9-alkylimino-9*H*-pyrrolo[1,2-*a*]indole derivatives, which was converted into 9-alkylamino-9*H*-pyrrolo[1,2-*a*]indole by $NaBH_4$ reduction.[6] Our new method enabled us to prepare a range of 9-dialkylamino derivatives from 2-(pyrrol-1-yl)benzaldehydes **1** in one-pot.

2. Results and discussion

We began our study examining a reaction of 2-(pyrrol-1-yl)benzaldehyde (**1a**) with dimethylamine hydrochloride in the presence of chlorotrimethylsilane, sodium iodide, and triethylamine in acetonitrile (Method A). It was found that the reaction mixture was stirred for a day at room temperature to give, after usual workup, 9-dimethylaminopyrrolo[1,2-*a*]indole (**3a**) in high yield, as shown in Scheme 1 and Table 1 (entry 1). Under the same reaction conditions 9-diethylaminopyrrolo[1,2-*a*]indole (**3b**) and 7-chloro-9-dimethylaminopyrrolo[1,2-*a*]indole (**3i**) were obtained in high yields (entries 2 and 9). When **1a** was allowed to react with free secondary amines, such as diisopropylamine, pyrrolidine, and morpholine, triethylamine hydrochloride was used (Method B); the corresponding desired amino-pyrrolo[1,2-*a*]indoles **3c–e** were obtained similarly (entries 3–5). While good yields of **3d** and **3e** were produced, the yield of **3c** was rather lower. This is thought to be attributable to the bulkiness of diisopropylamine. The use of this quaternary salt was found to be essential for the production of these products; in the absence of this salt the reactions gave intractable mixtures of products containing **1a**, and not a trace of the desired product was obtained in each case. It indicates that somewhat acidic media are essential for the generation of the iminium salts **2**.

Keywords: Iminium salt; Iodotrimethylsilane; Pyrrole; Pyrroloindole; Secondary amine.
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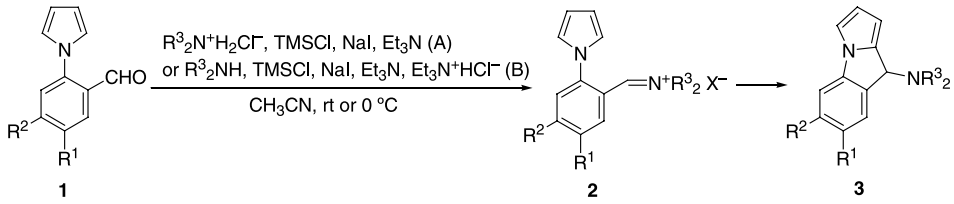

Scheme 1.

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

Entry	**1**	$R^3{}_2NH$	Method	Temperature	**3** (Yield %)[a]
1	**1a** ($R^1=R^2=H$)	Me_2NH	A	rt	**3a** (84)
2	**1a**	Et_2NH	A	rt	**3b** (84)
3	**1a**	*i*-Pr_2NH	B	rt	**3c** (40)
4	**1a**	Pyrrolidine	B	rt	**3d** (80)
5	**1a**	Morpholine	B	rt	**3e** (77)
6	**1b** ($R^1=R^2=OMe$)	Me_2NH	A	0 °C	**3f** (82)
7	**1b**	Et_2NH	A	0 °C	**3g** (73)
8	**1b**	Piperidine	B	0 °C	**3h** (68)
9	**1c** ($R^1=Cl$, $R^2=H$)	Me_2NH	A	rt	**3i** (83)

[a] Isolated yields after chromatography on silica gel.

The reactions using 4,5-dimethoxy-2-(pyrrol-1-yl)benzaldehyde (**1b**) were conducted at 0 °C, in due consideration of the lability of methoxy moieties to iodotrimethylsilane generated in situ, to give the desired products **3f–h** in good yields (entries 6–8). Indeed, treatment of **1b** with dimethylamine hydrochloride at room temperature under the same conditions resulted in the formation of a rather complex mixture, from which only 21% yield of the desired product **3f** was isolated.

In summary, the reaction sequence outlined in Scheme 1 provides a facile route to a range of 9-dialkylamino-9*H*-pyrro[1,2-*a*]indole derivatives from 2-(pyrrol-1-yl)benzaldehydes via intramolecular cyclization of the corresponding iminium salts. This method may be of value in organic synthesis because of the ease of operation as well as the ready availability of the starting materials.

3. Experimental

3.1. General

The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 1600 Series FT IR spectrometer. The ^1H NMR spectra were determined using $SiMe_4$ as an internal reference with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz in $CDCl_3$. The ^{13}C NMR spectra were determined using $SiMe_4$ as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz in $CDCl_3$. Low resolution mass spectra were recorded on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 PF_{254}. All of the solvents used were dried over appropriate drying agents and distilled under argon prior to use.

3.2. Starting materials

Methyl 2-(pyrrol-1-yl)benzoate was prepared according to the procedure reported by Josey et al.[7] 2-(Pyrrol-1-yl)benzyl alcohol was prepared by LAH reduction of methyl 2-(pyrrol-1-yl)benzoate under conditions reported by Garofalo et al.[3] All other chemicals used in this study were commercially available.

3.2.1. 2-(Pyrrol-1-yl)benzaldehyde (1a).[3] To a stirred solution of 2-(pyrrol-1-yl)benzyl alcohol (1.7 g, 10 mmol) in CH_2Cl_2 (60 mL) containing Celite (20 g) was added PCC (6.2 g, 29 mmol) portionwise. After 30 min, the mixture was filtered by suction. The filtrate was washed with 5% hydrochloric acid twice and then brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was distilled by Kugelrohr to give **6** (0.98 g, 60%) as a yellow liquid; bp 130 °C (bath temp)/0.45 Torr (lit.[3] bp 72 °C/0.05 Torr).

3.2.2. Methyl 4,5-dimethoxy-2-(pyrrol-1-yl)benzoate. This compound was prepared from methyl 2-amino-4,5-dimethoxybenzoate under conditions reported by Josey et al.[7] for the preparation of methyl 2-(pyrrol-1-yl)benzoate in 68% yield; a pale yellow solid; mp 93–94 °C (hexane–CH_2Cl_2); IR (KBr disk) 1725 cm^{-1}; ^1H NMR δ 3.68 (3H, s), 3.91 (3H, s), 3.96 (3H, s), 6.29 (2H, dd, $J=2.3$, 2.0 Hz), 6.77 (2H, dd, $J=2.3$, 2.0 Hz), 6.84 (1H, s), 7.38 (1H, s); MS *m/z* 261 (M^+, 100). Calcd for $C_{14}H_{15}NO_4$: C, 64.36; H, 5.79; N, 5.36. Found: C, 64.25; H, 6.05; N, 5.46.

3.2.3. 4,5-Dimethoxy-2-(pyrrol-1-yl)benzyl alcohol. This compound was prepared by LAH reduction of methyl 4,5-dimethoxy-2-(pyrrol-1-yl)benzoate under conditions reported by Garofalo et al.[3] for the preparation of 2-(1-pyrrolyl)benzyl alcohol in 93% yield; a pale-yellow solid; mp 100 °C (hexane–Et_2O); IR (KBr disk) 3518, 1612 cm^{-1}; ^1H NMR δ 1.57 (1H, t, $J=5.6$ Hz), 3.87 (3H, s), 3.95 (3H, s), 4.46 (2H, d, $J=5.6$ Hz), 6.31 (2H, dd, $J=2.3$, 2.0 Hz), 6.8195 (1H, dd, $J=2.3$, 2.0 Hz), 6.8201 (1H, s), 7.04

(1H, s). Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 67.01; H, 6.22; N, 5.91.

3.2.4. 4,5-Dimethoxy-2-(pyrrol-1-yl)benzaldehyde (1b). This compound was prepared from 4,5-dimethoxy-2-(pyrrol-1-yl)benzyl alcohol according to the procedure for the preparation of **1a** in 67% yield; a pale-yellow solid; mp 135–136 °C (hexane–CH_2Cl_2); IR (KBr disk) 2866, 2790, 1674 cm^{-1}; ^1H NMR δ 3.96 (3H, s), 3.97 (3H, s), 6.37 (2H, dd, $J=2.3$, 2.0 Hz), 6.86 (1H, s), 6.91 (2H, dd, $J=2.3$, 2.0 Hz), 7.45 (1H, s), 9.62 (1H, s). Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.51; H, 5.71; N, 6.05.

3.2.5. Ethyl 2-amino-5-chlorobenzoate.[8] To a solution of 2-amino-5-chlorobenzoic acid (1.7 g, 9.8 mmol) in EtOH (27 mL) was added concd H_2SO_4 (2 mL). The mixture was heated at reflux temperature for 18 h. The mixture was neutralized by adding saturated aqueous $NaHCO_3$, and the precipitate was collected by filtration. The crude product was recrystallization from hexane–Et_2O to give the title compound in a pure form (1.6 g, 80%) as a pale-yellow solid; mp 78–79 °C (hexane–Et_2O); IR (KBr disk) 3456, 3357, 1687, 1616 cm^{-1}; ^1H NMR δ 1.39 (3H, t, $J=7.3$ Hz), 4.33 (2H, q, $J=7.3$ Hz), 5.73 (2H, br s), 6.60 (1H, d, $J=8.9$ Hz), 7.20 (1H, dd, $J=8.9$, 2.6 Hz), 7.83 (1H, d, $J=2.6$ Hz).

3.2.6. Ethyl 5-chloro-2-(pyrrol-1-yl)benzoate. This compound was prepared from ethyl 2-amino-5-chlorobenzoate under conditions reported by Josey et al.[7] for the preparation of methyl 2-(pyrrol-1-yl)benzoate in 68% yield; a pale-yellow liquid; 156 °C/0.7 mmHg; IR (neat) 1720 cm^{-1}; ^1H NMR δ 1.14 (3H, t, $J=7.3$ Hz), 4.17 (2H, q, $J=7.3$ Hz), 6.30 (2H, dd, $J=2.3$, 2.0 Hz), 6.77 (2H, dd, $J=2.3$, 2.0 Hz), 7.31 (1H, d, $J=8.6$ Hz), 7.50 (1H, dd, $J=8.6$, 2.6 Hz), 7.77 (1H, d, $J=2.6$ Hz). Calcd for $C_{13}H_{12}ClNO$: C, 62.53; H, 4.84; N, 5.61. Found: C, 62.53; H, 4.94; N, 5.52.

3.2.7. 5-Chloro-2-(pyrrol-1-yl)benzyl alcohol. This compound was prepared by LAH reduction of ethyl 5-chloro-2-(pyrrol-1-yl)benzoate under conditions reported by Garofalo et al.[3] for the preparation of 2-(1-pyrrolyl)benzyl alcohol in 86% yield; colorless needles; mp 99–100 °C (hexane–Et_2O); IR (KBr disk) 3318 cm^{-1}; ^1H NMR δ 1.67 (1H, t, $J=5.9$ Hz), 4.54 (2H, d, $J=5.9$ Hz), 6.33 (2H, dd, $J=2.3$, 2.0 Hz), 6.80 (2H, dd, $J=2.3$, 2.0 Hz), 7.23 (1H, d, $J=8.6$ Hz), 7.33 (1H, dd, $J=8.6$, 2.3 Hz), 7.59 (1H, d, $J=2.3$ Hz). Calcd for $C_{11}H_{10}ClNO$: C, 63.62; H, 4.85; N, 6.75. Found: C, 63.32; H, 5.01; N, 6.52.

3.2.8. 5-Chloro-2-(pyrrol-1-yl)benzaldehyde (1c). This compound was prepared from 5-chloro-2-(pyrrol-1-yl)-benzyl alcohol according to the procedure for the preparation of **1a** in 68% yield; a yellow liquid; bp 170 °C (bath temp)/0.5 mmHg; IR (neat) 2863, 2745, 1694 cm^{-1}; ^1H NMR δ 6.40 (2H, t, $J=2.3$, 2.0 Hz), 6.90 (2H, t, $J=2.3$, 2.0 Hz), 7.39 (1H, d, $J=8.6$ Hz), 7.62 (1H, dd, $J=8.6$, 2.6 Hz), 7.95 (1H, d, $J=2.6$ Hz), 9.75 (1H, s); MS *m/z* 205 (M^+, 19), 177 (48), 115 (100). Calcd for $C_{11}H_8ClNO$: C, 64.25; H, 3.92; N, 6.81. Found: C, 64.23; H, 4.13; N, 6.76.

3.3. Typical procedure for the preparation of 3 (Method A at room temperature)

3.3.1. 9-Dimethylamino-9*H*-pyrrolo[1,2-*a*]indole (3a). To a stirred mixture of NaI (0.34 g, 2.3 mmol), dimethylamine hydrochloride (92 mg, 1.1 mmol), Et_3N (0.23 g, 2.3 mmol), and Me_3SiCl (0.25 g, 2.3 mmol) in acetonitrile (2.3 mL) (Risch's conditions)[1] at room temperature was added 2-(pyrrol-1-yl)benzaldehyde (**1a**) (0.15 g, 0.90 mmol). The mixture was stirred for a day at the same temperature and diluted with CH_2Cl_2 (20 mL). The resulting mixture was washed with saturated aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was subjected to chromatography on SiO_2 (1:3 EtOAc/hexane) to give **3a** (0.15 g, 84%) as a pale-yellow solid; mp 64–65 °C (hexane); IR (KBr disk) 1617 cm^{-1}; ^1H NMR δ 2.23 (6H, s), 4.91 (1H, s), 6.22 (1H, ddd, $J=3.3$, 1.3, 1.0 Hz), 6.35 (1H, dd, $J=3.3$, 3.0 Hz), 7.05 (1H, dt, $J=3.0$, 1.0 Hz), 7.10 (1H, td, $J=7.6$, 1.0 Hz), 7.19 (1H, d, $J=7.6$ Hz), 7.31 (1H, t, $J=7.6$ Hz), 7.50 (1H, d, $J=7.6$ Hz); MS *m/z* 198 (M^+, 41), 154 (100). Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.74; H, 7.24; N, 13.94.

3.3.2. 9-Diethylamino-9*H*-pyrrolo[1,2-*a*]indole (3b). A pale-yellow oil; R_f 0.33 (1:5 EtOAc/hexane); IR (neat) 1618 cm^{-1}; ^1H NMR δ 1.06 (6H, t, $J=7.3$ Hz), 2.35–2.55 (4H, m), 5.09 (1H, s), 6.17 (1H, dt, $J=3.3$, 1.0 Hz), 6.34 (1H, dd, $J=3.3$, 2.6 Hz), 7.04 (1H, d, $J=3.0$ Hz), 7.09 (1H, ddd, $J=7.6$, 7.3, 1.0 Hz), 7.18 (1H, d, $J=7.6$ Hz), 7.29 (1H, t, $J=7.6$ Hz), 7.50 (1H, d, $J=7.3$ Hz); MS *m/z* 226 (M^+, 56), 154 (100). Calcd for $C_{15}H_{18}N_2$: C, 79.61; H, 8.02; N, 12.38. Found: C, 79.58; H, 8.08; N, 12.37.

3.3.3. 7-Chloro-9-dimethylamino-9*H*-pyrrolo[1,2-*a*]indole (3i). A pale-yellow oil; R_f 0.39 (1:3 EtOAc/hexane); IR (neat) 1615 cm^{-1}; ^1H NMR δ 2.22 (6H, s), 4.89 (1H, s), 6.23 (1H, ddd, $J=3.3$, 1.3, 1.0 Hz), 6.36 (1H, dd, $J=3.3$, 3.0 Hz), 7.02 (1H, d, $J=3.0$ Hz), 7.10 (1H, $J=8.2$ Hz), 7.28 (1H, dd, $J=8.2$, 1.6 Hz), 7.48 (1H, d, $J=1.6$ Hz); MS *m/z* 232 (M^+, 43), 188 (100). Calcd for $C_{13}H_{13}ClN_2$: C, 67.10; H, 5.63; N, 12.04. Found: C, 66.95; H, 5.61; N, 12.11.

3.4. Typical procedure for the preparation of 3 (Method B at room temperature)

3.4.1. 9-Pyrrolidino-9*H*-pyrrolo[1,2-*a*]indole (3d). To a stirred mixture of NaI (0.34 g, 2.2 mmol), pyrrolidine (72 mg, 1.0 mmol), Et_3N (0.10 g, 1.0 mmol), triethylamine hydrochloride (0.15 g, 1.1 mmol), and Me_3SiCl (0.24 g, 2.2 mmol) in acetonitrile (2.2 mL) at room temperature was added 2-(pyrrol-1-yl)benzaldehyde (**1a**) (0.16 g, 0.96 mmol). The mixture was stirred at the same temperature for a day. Work-up and purification were carried out in a manner similar to those described for the preparation of **3a** to afford **3d** (0.17 g, 80%) as a pale-yellow solid; mp 64–65 °C (hexane–Et_2O); IR (KBr disk) 1616 cm^{-1}; the ^1H NMR data for this product were identical to those described in the literature.[6a]

3.4.2. 9-Diisopropylamino-9*H*-pyrrolo[1,2-*a*]indole (3c). A pale-yellow solid; mp 37–39 °C (hexane–Et_2O); IR (KBr disk) 1616 cm^{-1}; ^1H NMR δ 1.04 (6H, d, $J=6.6$ Hz), 1.12

(6H, d, J=6.6 Hz), 2.85–3.0 (2H, m), 5.02 (1H, s), 6.13 (1H, dt, J=3.3, 1.3 Hz), 6.34 (1H, dd, J=3.3, 2.7 Hz), 7.0–7.15 (2H, m), 7.17 (1H, d, J=7.3 Hz), 7.27 (1H, t, J=7.3 Hz), 7.41 (1H, d, J=7.3 Hz); MS m/z 254 (M^+, 7.8), 154 (100). Calcd for $C_{17}H_{22}N_2$: C, 80.27; H, 8.72; N, 11.01. Found: C, 80.15; H, 9.00; N, 11.01.

3.4.3. 9-Morpholino-9*H*-pyrrolo[1,2-*a*]indole (3e). A pale-yellow solid; mp 138–140 °C (hexane–Et_2O); IR (KBr disk) 1616 cm^{-1}; ^1H NMR δ 2.51 (4H, t, J=5.6 Hz), 3.68 (4H, t, J=5.6 Hz), 4.89 (1H, s), 6.23 (1H, ddd, J=3.3, 1.3, 1.0 Hz), 6.35 (1H, dd, J=3.3, 3.0 Hz), 7.05 (1H, dt, J=3.0, 1.0 Hz), 7.10 (1H, td, J=7.6, 1.0 Hz), 7.18 (1H, d J=7.6 Hz), 7.31 (1H, td, J=7.6, 1.0 Hz), 7.51 (1H, d, J=7.6 Hz); MS m/z 240 (M^+, 13), 154 (100). Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 75.23; H, 6.63; N, 11.53.

3.5. Typical procedure for the preparation of 3 (Method A at 0 °C)

3.5.1. 9-Dimethylamino-6,7-dimethoxy-9*H*-pyrrolo[1,2-*a*]indole (3f). To a stirred mixture of NaI (0.33 g, 2.2 mmol), dimethylamine hydrochloride (81 mg, 0.99 mmol), Et_3N (0.20 g, 2.0 mmol), and Me_3SiCl (0.24 g, 2.2 mmol) in acetonitrile (2.2 mL) at 0 °C was added a solution of 4,5-dimethoxy-2-(pyrrol-1-yl)benzaldehyde (**1b**) (0.22 g, 0.95 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at the same temperature for 2 days. Work-up and purification were carried out in a manner similar to those described for the preparation of **3a** to afford **3f** (0.20 g, 82%) as a pale-yellow solid; mp 157–158 °C (hexane–Et_2O); IR (KBr disk) 1622 cm^{-1}; ^1H NMR δ 2.22 (6H, s), 3.90 (3H, s), 3.95 (3H, s), 4.84 (1H, s), 6.21 (1H, ddd, J=3.3, 1.3, 1.0 Hz), 6.32 (1H, dd, J=3.3, 2.6 Hz), 6.80 (1H, s), 7.00 (1H, d, J=2.6 Hz), 7.09 (1H, s); ^{13}C NMR δ 40.70, 56.29, 56.53, 64.33, 94.79, 105.52, 109.88, 110.19, 112.09, 127.00, 134.39, 134.58, 145.81, 149.58; MS m/z 258 (M^+, 28), 214 (100). Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.84. Found: C, 69.52; H, 7.01; N, 11.01.

3.5.2. 9-Diethylamino-6,7-dimethoxy-9*H*-pyrrolo[1,2-*a*]indole (3g). A pale-yellow solid; mp 106–107 °C (hexane–Et_2O); IR (KBr disk) 1620 cm^{-1}; ^1H NMR δ 1.08 (6H, t, J=7.3 Hz), 2.35–2.6 (4H, m), 3.91 (3H, s), 3.95 (3H, s), 5.02 (1H, s), 6.15 (1H, ddd, J=3.3, 1.3, 1.0 Hz), 6.30 (1H, t, J=3.0 Hz), 6.80 (1H, s), 6.99 (1H, d, J=2.6 Hz), 7.08 (1H, s); ^{13}C NMR δ 13.88, 44.92, 56.28, 56.59, 60.12, 94.73, 104.75, 109.79, 109.95, 112.07, 128.25, 134.56, 136.03, 145.76, 149.39; MS m/z 286 (M^+, 17), 214 (100). Calcd for $C_{17}H_{22}N_2O_2$: C, 71.30; H, 7.74; N, 9.78. Found: C, 71.11; H, 7.76; N, 9.73.

3.5.3. 6,7-Dimethoxy-9-piperidino-9*H*-pyrrolo[1,2-*a*]indole (3h) (Method B at 0 °C). To a stirred mixture of NaI (0.35 g, 2.3 mmol), piperidine (90 mg, 1.1 mmol), Et_3N (0.11 g, 1.1 mmol), triethylamine hydrochloride (0.15 g, 1.1 mmol), and Me_3SiCl (0.26 g, 2.4 mmol) in acetonitrile (2.3 mL) at 0 °C was added a solution of 4,5-dimethoxy-2-(pyrrol-1-yl)benzaldehyde (**1b**) (0.23 g, 1.0 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred at the same temperature for 36 h. Work-up and purification were carried out in a manner similar to those described for the preparation of **3a** to afford **3h** (0.20 g, 68%) as a pale-yellow solid; mp 160–161 °C (hexane–Et_2O); IR (KBr disk) 1620 cm^{-1}; ^1H NMR δ 1.35–1.45 (2H, m), 1.5–1.65 (4H, m), 2.4–2.5 (4H, m), 3.91 (3H, s), 3.94 (3H, s), 4.81 (1H, s), 6.18 (1H, dt, J=3.3, 1.0 Hz), 6.31 (1H, dd, J=3.3, 2.6 Hz), 6.78 (1H, s), 6.98 (1H, d, J=2.6 Hz), 7.12 (1H, s); ^{13}C NMR δ 24.45, 26.16, 49.70, 56.30, 56.67, 64.85, 94.70, 105.39, 109.91, 110.28, 111.96, 127.08, 134.70, 135.43, 145.71, 149.46; MS m/z 298 (M^+, 25), 214 (100). Calcd for $C_{18}H_{22}N_2O_2$: C, 72.46; H, 7.43; N, 9.39. Found: C, 72.38; H, 7.58; N, 9.35.

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