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Novel Synthesis of 1,2,3,4-Tetrahydropyrazino[1,2-*a*]indoles

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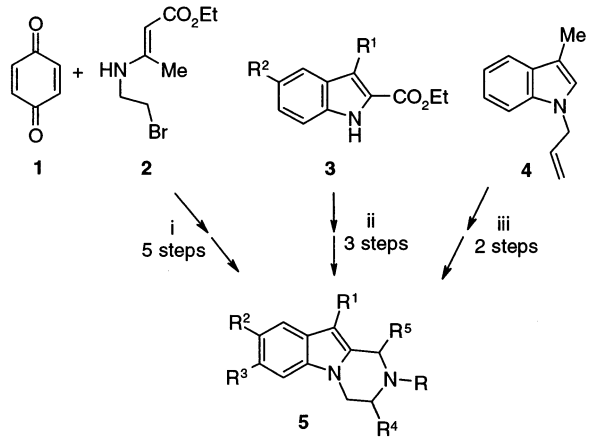
Abstract: Condensation of 2-(3-methyl-1*H*-indol-1-yl)ethylamine (**7**) with benzotriazole and formaldehyde gave 2-(1*H*-1,2,3-benzotriazol-1-ylmethyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (**8**) in 96% yield. Nucleophilic substitutions of the benzotriazolyl group in **8** with $NaBH_4$, NaCN, triethyl phosphite, allylsilanes, silyl enol ether and Grignard reagents afforded novel 10-methyl-1,2,3,4-tetrahydropyrazino-[1,2-*a*]indoles **9a**−**i** in 78−95% yields.

1,2,3,4-Tetrahydropyrazino[1,2-*a*]indoles are biologically active as antidepressants, anxiolitics,[1] central nervous system depressants, anticonvulsants,[2,3] antiserotonins and antihistamines,[4] protein kinase C inhibitors,[5,6] and 5-HT_{2A},5-HT_{2C} agonists.[7]

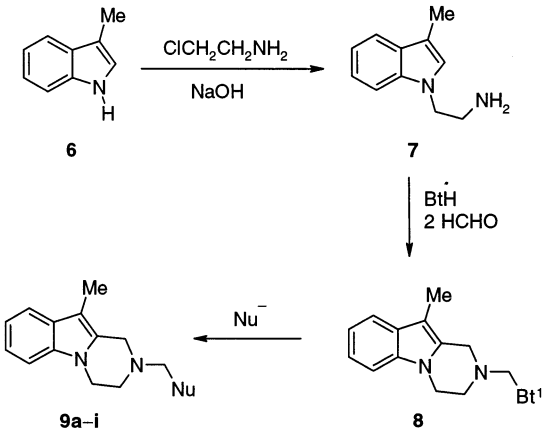
1,2,3,4-Tetrahydropyrazino[1,2-*a*]indoles **5** were previously prepared (Scheme 1) by three strategies: (i) from *p*-benzoquinone (**1**) and ethyl (*E*)-3-[(2-bromoethyl)amino]-2-butenoate (**2**) in five steps (cyclization, methylation and bromination, bromination, and a final condensation with arylamines);[8] (ii) from ethyl indole-2-carboxylates (**3**) in three steps by reaction with chloroacetonitrile followed by reduction and cyclization;[2,4] and (iii) from 1-allyl-3-methyl-1*H*-indole (**4**) and nitriles in the presence of the strongly electrophilic complex $Pd(CH_3CN)_4(BF_4)_2$, followed by reduction with $NaBH_4$.[9] These known methods

SCHEME 1[a]



[a] Reaction conditions. (i) To **5**: R = Ar; $R^1 = CO_2Et$; R^2 = OMe; R^3 = Br; R^4 = R = H. (ii) To **5**: R = R^3 = R^4 = R^5 = H; R^1 = H, Me, Ph; R^2 = H, Me, OMe, OEt, Br, Cl. (iii) To **5**: R = R^2 = R^3 = H; R^1 = R^4 = Me; R^5 = Me, Et, Ph.

SCHEME 2[a]



[a] BtH = benzotriazole.

gave 1,2,3,4-tetrahydropyrazino[1,2-*a*]indoles **5** in moderate overall yields.

We now report a simple and efficient access to 1,2,3,4-tetrahydropyrazino[1,2-*a*]indoles by cyclocondensation of 2-(3-methyl-1*H*-indol-1-yl)ethylamine (**7**) with benzotriazole and formaldehyde to construct the key benzotriazolyl intermediate **8**, followed by nucleophilic substitutions of the benzotriazolyl group to perform N-functionalization (Scheme 2). The reactive C−N bond of N-substituted benzotriazoles allows easy replacement of the benzotriazolyl group with other functionalities via nucleophilic substitutions, elimination, reduction, and cyclization.[10] The nearest precedent for the present approach is the work of Gatta and Chiavarelli,[11] who reacted 1-(2-aminoethyl)indole with γ-ketoacids and with *o*-acylbenzoic acids to give tetracyclic and pentacyclic pyrazino[1,2-

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TABLE 1. Isolated Yields of 10-Methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indoles 9a−i

compd	nucleophile (Lewis acid)	Nu	yield, %
9a	$NaBH_4$	−H	92
9b	NaCN	−CN	91
9c	$P(OEt)_3$ ($ZnBr_2$)	$-PO(OEt)_2$	92
9d	CH_2=C(Me)CH_2TMS (BF_3·Et_2O)	$-CH_2-C(Me)=CH_2$	78
9e	CH_2=$CHCH_2$TMS (BF_3·Et_2O)	$-CH_2CH=CH_2$	87
9f	CH_2=C(Ph)OTMS (BF_3·Et_2O)	$-CH_2COPh$	85
9g	PhMgBr	Ph	93
9h	4-MeC_6H_4MgBr	4-MeC_6H_4−	95
9i	Me—≡—MgBr	Me—≡	93

a]indole derivatives: no tricyclic compounds were prepared by this approach.

Results and Discussion

Preparation of 2-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (8). (cf. Scheme 2) 1-(2-Aminoethyl)indole was previously prepared in two steps from indole via reduction of 1-(cyanoethyl)indole with $LiAlH_4$.[12] Heating pyrrole or imidazole with 2-chloroethylamine in CH_3CN in the presence of NaOH and Bu_4NHSO_4 gave the β-aminoethyl derivatives.[13] We followed the second procedure[13] starting from 3-methylindole (**6**) and 2-chloroethylamine to obtain 2-(3-methyl-1*H*-indol-1-yl)ethylamine (**7**) in 85% yield.

Condensation of **7** with 1 equiv of benzotriazole and 2 equiv of formaldehyde (37% aqueous solution) in MeOH/H_2O at 25 °C gave 2-(1*H*-1,2,3-benzotriazol-1-ylmethyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (**8**) in 96% yield as a sole Bt[1] isomer. The subsequent nucleophilic substitutions of **8** are summarized in Table 1.

Nucleophilic Substitutions of 8 with $NaBH_4$, NaCN, Triethyl Phosphite, Allylsilanes, Silylenol Ethers, and Grignard Reagents. (cf. Table 1) We previously reported that a benzotriazolyl group attached at an α-carbon to a nitrogen atom is easily replaced by nucleophiles.[14] Treatment of **8** with 2 equiv of sodium borohydride in refluxing THF replaced the benzotriazole group with hydrogen to give 2,10-dimethyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (**9a**) in 92% yield. The *N*-methyl protons in **9a** appear at 2.53 ppm as a singlet. The benzotriazolyl group in **8** can be substituted by a cyano anion to afford 2-[10-methyl-3,4-dihydropyrazino-[1,2-*a*]indol-2(1*H*)-yl]acetonitrile (**9b**) in 91% yield.

The benzotriazolyl group of **8** was replaced by triethyl phosphite in the presence of $ZnBr_2$ to produce diethyl [10-methyl-3,4-dihydropyrazino[1,2-*a*]indol-2(1*H*)-yl]methylphosphonate (**9c**) in 92% yield. The nucleophilic substitutions of **8** with (2-methylpropenyl)trimethylsilane, allyltrimethylsilane, and 1-phenylvinyl trimethylsilyl ether in the presence of BF_3·Et_2O furnished **9d**, **9e,** and **9f** in 78, 87, and 85% yields, respectively. The Lewis acid $ZnBr_2$ or BF_3·Et_2O facilitates the loss of benzotriazolyl anion to form an iminium cation, which is then attacked by a nucleophile.[10]

Nucleophilic substitution of **8** with phenyl-, *p*-tolyl-, and 1-propynylmagnesium bromides in dry THF furnished the novel 2-substituted-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indoles **9g**−**i** in 93−95% yields. The structures of **9g**−**i** are supported by their ^1H and ^{13}C NMR spectra and microanalysis or HRMS results.

Thus, various useful functionalities were readily introduced to the 1,2,3,4-tetrahydropyrazino[1,2-*a*]indole ring system at the 2-position via nucleophilic substitutions of the benzotriazolyl group in **8**. However, the 3-position methyl group in **6** appears to be required because, without it, we failed and cyclization of the benzotriazolyl intermediate did not occur.

In summary, we have developed a short and efficient route to 10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indoles **9a**−**i** via Mannich reaction of 2-(3-methyl-1*H*-indol-1-yl)ethylamine (**7**) with benzotriazole and formaldehyde, followed by the nucleophilic substitutions of the benzotriazolyl group in **8** with other functionalities. Compared to the previous methods (multiple steps) for the preparation of 10-substituted 1,2,3,4-tetrahydropyrazino[1,2-*a*]-indoles, only two steps from 2-(3-methyl-1*H*-indol-1-yl)ethylamine, utilizing easily available reagents, now afford the desired products in good to excellent yields.

Experimental Section

THF was distilled from sodium/benzophenone prior to use. Melting points are uncorrected. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ (with TMS for ^1H and chloroform-*d* for ^{13}C as internal references). Elemental analyses were performed on a Carlo Erba EA-1108 instrument. Column chromatography was performed on silica gel (200−425 mesh). All of the reactions were carried out under N_2.

Procedure for the *N*-Alkylation of 3-Methylindole. To a solution of 3-methylindole (**6**, 2.62 g, 20 mmol) in dry CH_3CN (30 mL) were added powdered NaOH (1.76 g, 44 mmol) and tetrabutylammonium hydrogensulfate (0.23 g, 0.8 mmol). The mixture was stirred at 25 °C for 30 min, and then 2-chloroethylamine hydrochloride (2.67 g, 23 mmol) was added; the mixture was refluxed for 24 h. The inorganic solid was filtered off and washed with CH_2Cl_2. The combined filtrates were dried over anhydrous K_2CO_3 and concentrated. The residue was subjected to column chromatography (silica gel) with hexanes/EtOAc (1:1) as an eluent to give **7**.

Data for 2-(3-Methyl-1*H*-indol-1-yl)ethylamine (7):[13] colorless oil; yield, 85%; ^1H NMR δ 1.13 (s, 2H), 2.32 (s, 3H), 3.06 (t, J = 5.9 Hz, 2H), 4.11 (t, J = 5.9 Hz, 2H), 6.88 (s, 1H), 7.10 (t, J = 7.2 Hz, 1H), 7.17−7.22 (m, 1H), 7.30 (d, J = 8.1 Hz, 1H), 7.56 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 9.5, 42.2, 49.2, 109.1, 110.4, 118.6, 119.0, 121.4, 125.6, 128.8, 136.3.

Procedure for the Preparation of 2-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (8). To a solution of amine **7** (0.35 g, 2 mmol) and benzotriazole (0.24 g, 2 mmol) in CH_3OH/H_2O (10/1 mL) was added formaldehyde (37% aqueous solution; 0.32 g, 4 mmol). The mixture was stirred at room temperature for 8 h. The precipitate formed was filtered and washed with cold Et_2O to give the pure product, which was used directly for the subsequent reactions. For microanalysis purposes, the precipitate was recrystallized from $CHCl_3$/hexanes (1:1).

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Data for 2-(1*H*-1,2,3-Benzotriazol-1-ylmethyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (8): white microcrystals; yield, 96%; mp 152−153 °C; ^{1}H NMR δ 2.17 (s, 3H), 3.14 (t, J = 5.5 Hz, 2H), 3.97 (s, 2H), 4.02 (t, J = 5.5 Hz, 2H), 5.63 (s, 2H), 7.06−7.20 (m, 3H), 7.40 (t, J = 7.6 Hz,1H), 7.48 (d, J = 7.2 Hz, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 8.0, 41.8, 47.2, 48.3, 68.8, 104.8, 108.4, 109.7, 118.2, 119.3, 120.1, 120.8, 124.1, 126.7, 127.8, 128.6, 133.7, 135.8, 146.0. Anal. Calcd for $C_{19}H_{19}N_5$: C, 71.90; H, 6.03; N, 22.06. Found: C, 72.00; H, 6.17; N, 22.36.

Procedure for the Reduction of 8 with $NaBH_4$. A mixture of **8** (0.31 g, 1.0 mmol) and $NaBH_4$ (0.076 g, 2.0 mmol) was refluxed in dry THF (10 mL) overnight. After removal of the solvent in vacuo, the residue was diluted with EtOAc. The mixture was washed with 1 M NaOH and brine and dried over anhydrous $MgSO_4$. Evaporation of the solvent in vacuo afforded **9a**.

Data for 2,10-Dimethyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (9a): yellow needles (hexanes/EtOAc, 2:1); yield, 92%; mp 65−66 °C; ^{1}H NMR δ 2.20 (s, 3H), 2.53 (s, 3H), 2.89 (t, J = 5.5 Hz, 2H), 3.71 (s, 2H), 4.06 (t, J = 5.5 Hz, 2H), 7.07−7.17 (m, 2H), 7.23 (d, J = 7.4 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H); ^{13}C NMR δ 7.9, 41.8, 46.0, 52.2, 52.6, 104.1, 108.3, 118.0, 119.0, 120.5, 128.8, 130.1, 135.8. Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.92; H, 8.22; N, 13.97.

Procedure for the Nucleophilic Substitution of 8 with Sodium Cyanide: A mixture of **8** (0.31 g, 1.0 mmol) and NaCN (0.05 g, 1.0 mmol) in DMSO (5 mL) was stirred at room temperature for 36 h. The mixture was poured into 20 mL of water and extracted with CH_2Cl_2. The organic extracts were washed with 1 M NaOH, water, and brine and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography with hexanes/EtOAc (5:1) as an eluent to give **9b**.

Data for 2-[10-Methyl-3,4-dihydropyrazino[1,2-*a*]indol-2(1*H*)-yl]acetonitrile (9b): colorless needles (hexanes/EtOAc, 3:1); yield, 91%; mp 107−108 °C; ^{1}H NMR δ 2.20 (s, 3H), 3.06 (t, J = 5.5 Hz, 2H), 3.74 (s, 2H), 3.90 (s, 2H), 4.07 (t, J = 5.5 Hz, 2H), 7.08−7.24 (m, 3H), 7.51 (d, J = 7.5 Hz, 1H); ^{13}C NMR δ 7.9, 41.6, 45.8, 48.9, 49.5, 105.0, 108.4, 114.3, 118.2, 119.3, 120.9, 128.3, 128.7, 135.8. Anal. Calcd for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65. Found: C, 74.36; H, 6.95; N, 18.60.

Procedure for the Nucleophilic Substitution of 8 with Triethyl Phosphite. To a solution of **8** (0.31 g, 1.0 mmol) in dry CH_2Cl_2 (20 mL) at 0 °C were successively added $ZnBr_2$ (0.22 g, 1.2 mmol) and triethyl phosphite (0.16 mL, 1.2 mmol). The reaction mixture was stirred at 0 °C for 2 h and then at 25 °C for 16 h, and the reaction was quenched with H_2O. After extraction with CH_2Cl_2, the combined organic layers were washed with 1 M NaOH and brine and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography with hexanes/EtOAc (4:1) as an eluent to afford **9c**.

Data for Diethyl [10-Methyl-3,4-dihydropyrazino[1,2-*a*]-indol-2(1*H*)-yl]methylphosphonate (9c): yellow oil; yield, 92%; ^{1}H NMR δ 1.33 (t, J = 7.2 Hz, 6H), 2.19 (s, 3H), 3.00 (d, J = 11.8 Hz, 2H), 3.20 (t, J = 5.5 Hz, 2H), 3.96 (s, 2H), 4.04 (t, J = 5.5 Hz, 2H), 4.11−4.23 (m, 4H), 7.07−7.18 (m, 2H), 7.23 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H); ^{13}C NMR δ 7.9, 16.5 (d, J = 5.7 Hz), 41.5, 51.8, 52.0 (d, J = 7.4 Hz), 53.0 (d, J = 176.3 Hz), 62.3 (d, J = 6.3 Hz), 104.5, 108.3, 118.1, 119.1, 120.6, 128.6, 129.6, 135.8; HRMS m/z calcd for $C_{17}H_{26}N_2O_3P$ 337.1676 (M + 1), found 337.1699.

General Procedure for the Nucleophilic Substitution of 8 with Allylsilanes and Silyl Enol Ether. To a solution of **8** (0.31 g, 1.0 mmol), (2-methylpropenyl)trimethylsilane, and allyl trimethylsilane or 1-phenylvinyl trimethylsilyl ether (1.0 mmol) in dry CH_2Cl_2 (10 mL) under N_2 was added $BF_3{\cdot}Et_2O$ (1.0 mmol) at 0 °C. The mixture was stirred for 3 h and then warmed to room temperature and stirred for another 3 h. The mixture was washed with 5% $NaHCO_3$ and H_2O; the combined aqueous phase was extracted with EtOAc, and the combined organic layers were dried over anhydrous Na_2SO_4. After removal of the solvent in vacuo, the residue was purified by column chromatography (silica gel) with hexanes/EtOAc (5:1) as an eluent to afford **9d**−**f**.

Data for 2-(3-Methyl-3-butenyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (9d): yellow oil; yield, 78%; ^{1}H NMR δ 1.78 (s, 3H), 2.19 (s, 3H), 2.31−2.36 (m, 2H), 2.68−2.74 (m, 2H), 2.95 (t, J = 5.5 Hz, 2H), 3.77 (s, 2H), 4.02 (t, J = 5.5 Hz, 2H), 4.76 (br s, 1H), 4.79 (br s, 1H), 7.06−7.16 (m, 2H), 7.21 (d, J = 7.4 Hz, 1H), 7.48−7.51 (m, 1H); ^{13}C NMR δ 8.0, 22.7, 35.5, 41.7, 50.1, 50.5, 56.4, 104.2, 108.3, 111.2, 118.0, 119.0, 120.4, 128.8, 130.1, 135.8, 143.7; HRMS m/z calcd for $C_{17}H_{22}N_2$ 254.1782 (M), found 254.1780.

Data for 2-(3-Butenyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (9e): yellow oil; yield, 87%; ^{1}H NMR δ 2.20 (s, 3H), 2.34−2.42 (m, 2H), 2.64−2.70 (m, 2H), 2.96 (t, J = 5.6 Hz, 2H), 3.76 (s, 2H), 4.04 (t, J = 5.6 Hz, 2H), 5.04 (d, J = 10.2 Hz, 1H), 5.12 (dd, J = 17.2, 1.5 Hz, 1H), 5.79−5.93 (m, 1H), 7.06−7.17 (m, 2H), 7.22 (d, J = 7.4 Hz, 1H), 7.49 (d, J = 7.2 Hz, 1H); ^{13}C NMR δ 8.0, 31.7, 41.8, 50.1, 50.5, 57.3, 104.2, 108.3, 116.0, 118.0, 119.0, 120.5, 128.8, 130.1, 135.8, 136.2; HRMS m/z calcd for $C_{16}H_{20}N_2$ 240.1626 (M), found 240.1600.

Data for 3-[10-Methyl-3,4-dihydropyrazino[1,2-*a*]indol-2(1*H*)-yl]-1-phenyl-1-propanone (9f): yellow needles (hexanes/EtOAc, 2:1); yield, 85%; mp 93.5−94.5 °C; ^{1}H NMR δ 2.20 (s, 3H), 3.02 (t, J = 5.6 Hz, 2H), 3.09 (t, J = 7.3 Hz, 2H), 3.31 (t, J = 7.3 Hz, 2H), 3.83 (s, 2H), 4.05 (t, J = 5.6 Hz, 2H), 7.06−7.17 (m, 2H), 7.22 (d, J = 7.2 Hz, 1H), 7.46−7.51 (m, 3H), 7.56−7.61 (m, 1H), 7.98−8.02 (m, 2H); ^{13}C NMR δ 8.0, 36.7, 41.9, 50.2, 50.9, 52.8, 104.3, 108.3, 118.1, 119.1, 120.6, 128.0, 128.7, 128.8, 129.9, 133.2, 135.8, 136.9, 198.8. Anal. Calcd for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.33; H, 7.19; N, 8.84.

General Procedure for the Nucleophilic Substitution of 8 with Grignard Reagents. To a solution of **8** (1.0 mmol) in dry THF (10 mL) at 0 °C was added dropwise a solution of an appropriate Grignard reagent (1.2 mmol). The reaction mixture was allowed to warm to 25 °C and stirred for 0.5 h. Then, the mixture was refluxed for 2 h. After the mixture was cooled, the reaction was quenched with water and the mixture extracted with ether. The combined extracts were washed with 1 M NaOH and brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography with hexanes/EtOAc (6:1 to 3:1) as an eluent to give **9g**−**i** in 93−95% yields.

Data for 2-Benzyl-10-methyl-1,2,3,4-tetrahydropyrazino-[1,2-*a*]indole (9 g): colorless oil; yield, 93%; ^{1}H NMR δ 2.15 (s, 3H), 2.92 (t, J = 5.6 Hz, 2H), 3.73 (s, 2H), 3.77 (s, 2H), 4.01 (t, J = 5.6 Hz, 2H), 7.06−7.21 (m, 3H), 7.27−7.40 (m, 5H), 7.49 (d, J = 7.2 Hz, 1H); ^{13}C NMR δ 8.0, 41.8, 50.1, 50.3, 62.4, 104.2, 108.3, 118.0, 119.0, 120.5, 127.4, 128.4, 128.8, 129.0, 130.2, 135.8, 137.8; HRMS m/z calcd for $C_{19}H_{20}N_2$ 276.1626 (M), found 276.1617.

Data for 2-(4-Methylbenzyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (9h): yellow needles (hexanes/EtOAc, 2:1); yield, 95%; mp 98−99 °C; ^{1}H NMR δ 2.16 (s, 3H), 2.36 (s, 3H), 2.92 (t, J = 5.5 Hz, 2H), 3.70 (s, 2H), 3.77 (s, 2H), 4.02 (t, J = 5.6 Hz, 2H), 7.06−7.29 (m, 7H), 7.48−7.50 (m, 1H); ^{13}C NMR δ 8.0, 21.1, 41.8, 50.0, 50.2, 62.1, 104.2, 108.3, 118.0, 119.0, 120.4, 128.8, 129.0, 129.1, 130.3, 134.7, 135.8, 137.0. Anal. Calcd for $C_{20}H_{22}N_2$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.29; H, 7.62; N, 9.52.

Data for 2-(2-Butynyl)-10-methyl-1,2,3,4-tetrahydropyrazino[1,2-*a*]indole (9i): yellow needles (hexanes/ether, 1:1); yield, 93%; mp 112−113 °C; ^{1}H NMR δ 1.86 (t, J = 2.3 Hz, 3H), 2.20 (s, 3H), 3.02 (t, J = 5.6 Hz, 2H), 3.47−3.50 (m, 2H), 3.85 (s, 2H), 4.06 (t, J = 5.6 Hz, 2H), 7.06−7.17 (m, 2H), 7.22 (d, J = 8.4 Hz, 1H), 7.50 (d, J = 7.1 Hz, 1H); ^{13}C NMR δ 3.5, 8.0, 41.9, 47.2, 48.9, 49.6, 73.4, 81.7, 104.3, 108.3, 118.0, 119.0, 120.4, 128.8, 130.1, 135.8. Anal. Calcd for $C_{16}H_{18}N_2$: C 80.63; H 7.61; N, 11.75. Found: C, 80.54; H, 7.91; N, 11.70.

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