

A General and Facile Synthesis of Heterocyclo[*b*]-Fused Carbazoles

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1-Methyl-2-bromo-3-[(benzotriazol-1-yl)methyl]indole (**2**), available from the regioselective bromination of 1-methyl-3-[(benzotriazol-1-yl)methyl]indole (**1**), undergoes halogen–lithium exchange with *t*-BuLi. The resulting carbanion **4** reacts with thiophene-3-carboxaldehyde, furan-3-carboxaldehyde, thiophene-2-carboxaldehyde, furan-2-carboxaldehyde, and indole-3-carboxaldehyde. Subsequent quenching with methyl iodide affords the corresponding methyl ether intermediates **6a–e** in excellent yields. Refluxing intermediates **6a–e** in 1,2,4-trichlorobenzene or 1,2-dichlorobenzene causes intramolecular cyclization followed by aromatization. 5-Methylthieno[3,2-*b*]carbazole (**8a**), 5-methylfuro[3,2-*b*]carbazole (**8b**), 5-methylthieno[2,3-*b*]carbazole (**8c**), 5-methylfuro[2,3-*b*]carbazole (**8d**), and 5,11-dimethylindolo[3,2-*b*]carbazole (**8e**) are thus obtained in 31–67% yields.

Introduction

Heterocyclo[*b*]-fused carbazole systems are of considerable contemporary interest and importance. Numerous pyrido[3,4- and 4,3-*b*]carbazoles and indolo[2,1-*b*]carbazoles of this class are present in natural products and/or possess interesting biological activities.^{1–3}

Several synthetic routes to indolo[*b*]carbazoles have been reported: (i) indolo[3,2-*b*]carbazole and indolo[2,3-*b*]carbazole were first prepared in *ca.* 10% yield by vapor phase cyclodehydrogenation of *N,N'*-diphenylphenylenediamines;⁴ (ii) Robinson successfully Fischer-indolized cyclohexane-1,4-dione to synthesize indolo[3,2-*b*]carbazole in moderate yield (35%);⁵ (iii) condensation of indole and formaldehyde in the presence of a strong acid provided easy access to symmetrical indolo[3,2-*b*]carbazoles in 22–26% yields;⁶ (iv) 4,9-dihydropyrano[3,4-*b*]indol-1(3*H*)-ones were transformed to indolo[3,2-*b*]carbazoles in 25–31% yields by heating with mineral acids;⁷ (v) reductive ring closure of dinitrodiphenylbenzenes with triethyl phosphite as the reducing agent furnished indolocarbazoles,⁸ however, the starting materials were not readily available. Many elegant approaches have also been reported for the preparation of pyrido[*b*]carbazoles.^{9–11} However, none of these previous methods are general for the construction of heterocyclo[*b*]-fused carbazoles; they are specific for either indolocarbazole or pyridocarbazole systems. In fact, thieno[*b*]carbazole and furo[*b*]carbazole systems were, to our knowledge, previously unknown.

Herein we delineate a general and facile approach for the construction of heterocyclo[*b*]-fused carbazoles which is exemplified by the preparation of examples of the indolo[3,2-*b*]carbazole, thieno[2,3-*b*]carbazole, thieno[3,2-*b*]carbazole, furo[2,3-*b*]carbazole, and furo[3,2-*b*]carbazole ring systems all using the readily available precursor 1-methyl-3-[(benzotriazol-1-yl)methyl]indole (**1**). Our recent work has demonstrated the versatility of benzotriazolylalkyl-substituted heterocycles for the synthesis of 1,1-bis(heteroaryl)alkanes¹² and the utility of 1-methyl-3-[(benzotriazol-1-yl)methyl]indole (**1**) for the synthesis of a wide range of 3-substituted indoles.¹³ Compound **1** has now been further developed to provide an efficient route to various heterocyclo[*b*]-fused carbazoles.

Results and Discussion

The requisite 1-methyl-3-[(benzotriazol-1-yl)methyl]indole (**1**) was prepared in 50% yield from 1-methylindole as described in our earlier work.¹³ As shown in Scheme 1, a key step in the preparation of heterocyclo[*b*]-fused carbazoles **8** is the generation of the 2-lithio derivative **4**. Although the direct 2-lithiation of many indoles is well documented,^{14–16} the lithiation of 1-methyl-3-[(benzotriazol-1-yl)methyl]indole (**1**) occurs regioselectively at the side-chain CH₂ group, due to the electron-withdrawing nature of the benzotriazolyl group, as previously reported.¹³

Thus, 2-bromoindole **2** was chosen as our target molecule for the regioselective generation of 2-lithioindole **4** since halogen–metal exchange methodology has been efficiently employed for the formation of reactive carbanions.^{9,17} Regioselective bromination of **1** was readily accomplished using bromine in CH₂Cl₂ to give the 2-bromoindole **2** in 80% yield. Selective bromination at the 2-position was indicated by the disappearance of the 1H singlet (2-proton of indole) at *ca.* 7.0 ppm in the ¹H NMR spectrum of **2**.

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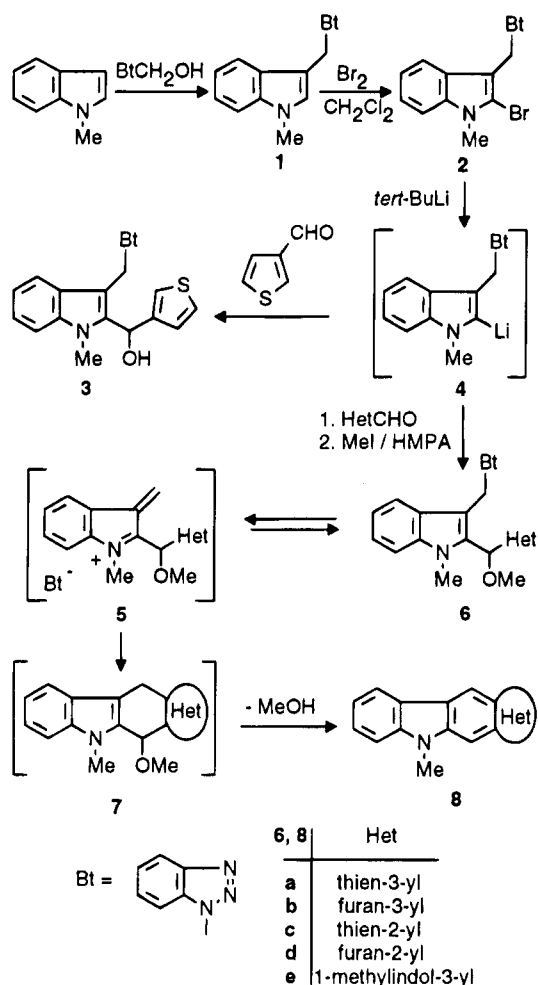
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Scheme 1



In accordance with expectations, the lithiation of **2** occurred exclusively at the 2-position to form 1-methyl-2-lithio-3-[(benzotriazol-1-yl)methyl]indole (**4**), without any detectable side-chain lithiation. Thus, treatment of **2** with 1.2 equiv of *tert*-butyllithium ($-78\text{ }^{\circ}\text{C}$, THF) resulted in the immediate formation of a deep brown color due to anion **4**. After 5 min, this solution was treated with thiophene-3-carboxaldehyde, followed by methyl iodide and HMPA to protect the oxygen anion formed. Intermediate product **6a** was thus furnished. Similar reactions with furan-3-carboxaldehyde, thiophene-2-carboxaldehyde, furan-2-carboxaldehyde, and indole-3-carboxaldehyde afforded analogs **6b–e** in excellent yields (Table 1). The structures of **6a–e** were confirmed by elemental analyses (Table 1) and NMR spectral data (Experimental Section). The chiral center in these compounds induces magnetic nonequivalence of the two methylene group protons between the benzotriazole and indole rings, as indicated by the presence of an AB quartet at *ca.* 6.0 ppm in their ^1H NMR spectra. Detailed assignments of the NMR spectra are given in the supplementary material.

Previous papers from this laboratory have demonstrated that various types of benzotriazole derivatives reversibly ionize to yield small quantities of the benzotriazole anion and the corresponding carbocations.¹⁸ We have also demonstrated that Lewis acids can efficiently

facilitate the ionization of benzotriazole derivatives.¹² Due to such ionization, the benzotriazole auxiliary group can be displaced by various nucleophiles.^{19–22} By analogy with other benzotriazole derivatives, compounds **6** presumably exist in equilibrium with small amounts of ion pairs **5** under certain reaction conditions. Accordingly, we treated compounds **6** with Lewis acids in an attempt to induce cyclization: however, derivatives **6** were unstable in the presence of Lewis acids such as zinc bromide, and even at low temperatures ($-10\text{ }^{\circ}\text{C}$), oligomers were formed immediately.

By contrast, high temperatures successfully effected the desired ionization and ring closure. Thus, refluxing a solution of compounds **6a–d** respectively in 1,2,4-trichlorobenzene (*ca.* $216\text{ }^{\circ}\text{C}$) for 2 days furnished the corresponding desired products 5-methylthieno[3,2-*b*]-carbazole (**8a**), 5-methylfuro[3,2-*b*]-carbazole (**8b**), 5-methylthieno[2,3-*b*]-carbazole (**8c**), and 5-methylfuro[2,3-*b*]-carbazole (**8d**) in yields of 43–67% (Table 2). Compound **6e** is less stable and more reactive than **6a–d**, and its cyclization was accomplished by refluxing in 1,2-dichlorobenzene (*ca.* $180\text{ }^{\circ}\text{C}$) to give 5,11-dimethylindolo[3,2-*b*]-carbazole (**8e**) in 31% yield. These transformations are envisioned to proceed *via* intramolecular cyclization to form intermediates **7**, which undergo aromatization *in situ* by loss of a molecule of methanol to afford the desired products **8**. Thieno[3,2-*b*]-carbazole **8a**, furo[3,2-*b*]-carbazole **8b**, thieno[2,3-*b*]-carbazole **8c**, and furo[2,3-*b*]-carbazole **8d** are new compounds and are the first examples of the previously unknown tetracyclic condensed systems. The structures of **8a–d** (see Scheme 2) are fully supported by elemental analyses and NMR spectral data (see Experimental Section for peak positions and the supplementary material for tentative assignments). The two ^1H singlets (4,10-protons) in the region 7.4–8.5 ppm in the ^1H NMR spectra of **8a–c** are characteristic of these fused carbazole ring systems. 5,11-Dimethylindolo[3,2-*b*]-carbazole (**8e**) is a known compound,²³ and its structure was also confirmed by C,H,N analysis and NMR spectral data (see Experimental Section). A 2H singlet at 7.93 ppm (6,12-protons) in the ^1H NMR spectrum is indicative of a symmetrical structure.

Attempted cyclization of compound **3** (which was prepared in 91% yield in a similar way to **6a** but without subsequent protection of the oxygen anion as shown in Scheme 1) was unsuccessful, although a trace of product **8a** was detected by ^1H NMR spectroscopy. The presence of a labile hydroxy group might be responsible for the results obtained.

In conclusion, a general, facile route to heterocyclo[*b*]-fused carbazoles has been developed starting from 1-methylindole. An attractive feature of this synthetic approach is that a wide variety of heterocyclo[*b*]-fused carbazoles can be readily accessible by appropriate choice of the heteroaryl aldehydes. In this work, five heterocyclo[*b*]-fused carbazoles (**8a–e**) have been synthesized, among which **8a–d** are the first examples of the thieno[3,2-*b*]-carbazole, furo[3,2-*b*]-carbazole, thieno[2,3-*b*]-carbazole, and furo[2,3-*b*]-carbazole ring systems, respectively, to be prepared.

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Table 1. Preparation of Intermediate Products 6a–e

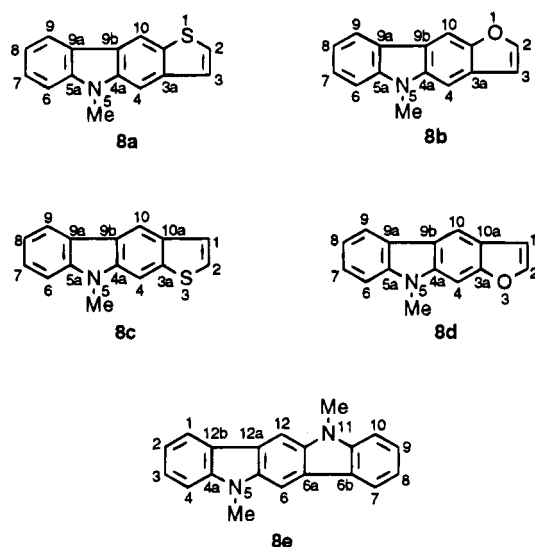
compd	yield (%)	het	mp (°C)	molecular formula	analysis					
					found			required		
					C	H	N	C	H	N
6a	81	thien-3-yl	117–118	C ₂₂ H ₂₀ N ₄ OS	67.69	5.14	14.48	68.02	5.19	14.42
6b	86	furan-3-yl	79–80	C ₂₂ H ₂₀ N ₄ O ₂	70.59	5.08	15.15	70.94	5.42	15.05
6c	88	thien-2-yl	54–55	C ₂₂ H ₂₀ N ₄ OS	68.39	5.29	14.21	68.02	5.19	14.42
6d	84	furan-2-yl	oil	C ₂₂ H ₂₀ N ₄ O ₂	70.61	5.11	15.29	70.94	5.42	15.05
6e	88	1-methylindol-3-yl	98–99	C ₂₇ H ₂₅ N ₅ O	74.35	5.78	15.70	74.46	5.79	16.08

Table 2. Preparation of Heterocyclo[b]-Fused Carbazoles 8a–e

compd	yield (%)	mp (°C)	molecular formula	analysis					
				found			required		
				C	H	N	C	H	N
8a	55	168–169	C ₁₅ H ₁₁ NS	75.79	4.70	5.84	75.92	4.67	5.90
8b	67	121–122	C ₁₅ H ₁₁ NO	81.36	5.00	6.25	81.42	5.01	6.33
8c	56	177–178	C ₁₅ H ₁₁ NS	76.06	4.66	5.83	75.92	4.67	5.90
8d	43	116–117	C ₁₅ H ₁₁ NO	81.74	5.10	6.30	81.42	5.01	6.33
8e	31	287–288 ^a	C ₂₀ H ₁₆ N ₂	84.84	5.86	9.66	84.48	5.67	9.85

^a Lit. mp 295–296 °C.²³

Scheme 2



Experimental Section

General. Melting points were determined with a hot-stage apparatus and are uncorrected. NMR spectra were taken in CDCl₃ with tetramethylsilane as the internal standard for ¹H (300 MHz) or solvent as the internal standard for ¹³C (75 MHz). Assignments for ¹³C NMR spectra were confirmed by APT experiments where necessary. Tetrahydrofuran was distilled under nitrogen immediately prior to use from sodium/benzophenone. All reactions with air-sensitive compounds were carried out under an argon atmosphere. Column chromatography was conducted with silica gel 230–400 mesh. 1-(Hydroxymethyl)benzotriazole and 1-methyl-3-[(benzotriazol-1-yl)methyl]indole (1) were prepared according to our previously reported procedure.¹³

1-Methyl-2-bromo-3-[(benzotriazol-1-yl)methyl]indole (2). To a solution of 1-methyl-3-[(benzotriazol-1-yl)methyl]indole (1) (2.1 g, 8.2 mmol) in methylene chloride (100 mL) at 0 °C was added dropwise a solution of bromine (1.3 g, 8.2 mmol) in methylene chloride (30 mL). After the addition was complete, the reaction mixture was further stirred at 0 °C for 45 min. Cold sodium bicarbonate solution (5%, 70 mL) was added. The organic layer was further washed with sodium bicarbonate solution (5%, 70 mL) followed by water. After the solution was dried over MgSO₄, the solvent was evaporated. The crude product was washed with hot ethyl acetate (20 mL) to give the pure compound in 80% yield: mp 145–146 °C; ¹H NMR δ 3.71 (s, 3H), 5.96 (s, 2H), 7.04–7.07 (m, 1H), 7.15–

7.27 (m, 3H), 7.30–7.35 (m, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H); ¹³C NMR δ 31.5, 44.3, 107.9, 109.4, 110.0, 115.0, 118.5, 119.7, 120.6, 122.5, 123.6, 126.2, 127.0, 132.4, 136.8, 146.1. Anal. Calcd for C₁₆H₁₃N₄Br: C, 56.32; H, 3.84; N, 16.42. Found: C, 56.46; H, 3.86; N, 16.48.

1-Methyl-2-[(1-hydroxy-1-thien-3-yl)methyl]-3-[(benzotriazol-1-yl)methyl]indole (3). To a solution of 1-methyl-2-bromo-3-[(benzotriazol-1-yl)methyl]indole (2) (1.2 g, 3.5 mmol) in THF (40 mL) at –78 °C under argon was added *t*-BuLi (2.5 mL, 1.7 M in pentane, 4.2 mmol). After 5 min, thiophene-3-carboxaldehyde (0.47 g, 4.2 mmol) in THF (8 mL) was added dropwise. The reaction mixture was stirred at –78 °C for 2 h, and the reaction was quenched with water. The organic layer was washed with water and dried (MgSO₄). The solvent was evaporated, and the residue was subjected to column chromatography (hexanes:ethyl acetate = 3:1) to afford pure product (91%): mp 78–79 °C; ¹H NMR δ 3.34 (s, 3H), 5.32 (d, *J* = 4.2 Hz, 1H), 5.63 (d, *J* = 15.4 Hz, 1H), 5.70 (d, *J* = 15.4 Hz, 1H), 6.38 (d, *J* = 4.2 Hz, 1H), 6.60 (d, *J* = 5.1 Hz, 1H), 6.87–7.08 (m, 7H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H); ¹³C NMR δ 30.5, 42.3, 64.8, 105.9, 109.3, 109.9, 118.2, 119.2, 119.9, 121.2, 122.2, 123.7, 126.0 (2C), 126.4, 127.0, 132.4, 137.0, 139.2, 142.8, 145.4. Anal. Calcd for C₂₁H₁₆N₄OS: C, 67.36; H, 4.85; N, 14.96. Found: C, 67.68; H, 4.94; N, 14.93.

General Procedure for the Preparation of Intermediate Products 6a–e. To a solution of 1-methyl-2-bromo-3-[(benzotriazol-1-yl)methyl]indole (2) (1.2 g, 3.5 mmol) in THF (40 mL) at –78 °C under argon was added *t*-BuLi (2.5 mL, 1.7 M in pentane, 4.2 mmol). The color immediately changed to deep brown. After 5 min, the appropriate aldehyde (4.2 mmol) in THF (8 mL) was added dropwise. The reaction mixture was stirred at –78 °C for 2 h. Methyl iodide (1.7 mL) and HMPA (30 mL) were then added. The mixture was allowed to warm to room temperature and was stirred overnight. After an aqueous workup, the crude product was subjected to column chromatography (hexanes:ethyl acetate = 3:1) to give the pure compound.

1-Methyl-2-[(1-methoxy-1-thien-3-yl)methyl]-3-[(benzotriazol-1-yl)methyl]indole (6a): ¹H NMR δ 3.18 (s, 3H), 3.54 (s, 3H), 5.98 (s, 1H), 6.05 (d, *J* = 15.5 Hz, 1H), 6.14 (d, *J* = 15.5 Hz, 1H), 6.69 (d, *J* = 5.0 Hz, 1H), 6.86–6.92 (m, 1H), 7.14–7.36 (m, 7H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.94–7.98 (m, 1H); ¹³C NMR δ 30.7, 42.6, 56.5, 73.9, 107.9, 109.4, 109.9, 118.3, 119.7, 120.3, 121.5, 122.5, 123.6, 125.9, 126.0, 126.5, 127.0, 132.4, 136.2, 137.3, 140.7, 146.1.

1-Methyl-2-[(1-methoxy-1-furan-3-yl)methyl]-3-[(benzotriazol-1-yl)methyl]indole (6b): ¹H NMR δ 3.61 (s, 3H), 3.62 (s, 3H), 5.91 (d, *J* = 1.4 Hz, 1H), 6.03 (s, 1H), 6.04 (d, *J* = 15.4 Hz, 1H), 6.11 (d, *J* = 15.4 Hz, 1H), 7.06 (d, *J* = 1.4 Hz, 1H), 7.18–7.29 (m, 6H), 7.36–7.39 (m, 1H), 7.76 (d, *J* = 7.0

Hz, 1H), 7.94–7.98 (m, 1H); ^{13}C NMR δ 30.7, 42.5, 56.3, 70.8, 107.7, 108.9, 109.4, 109.9, 118.2, 119.6, 120.2, 122.5, 123.5, 124.9, 126.5, 126.9, 132.4, 135.7, 137.3, 139.5, 143.2, 146.0.

1-Methyl-2-[(1-methoxy-1-thien-2-yl)methyl]-3-[(benzotriazol-1-yl)methyl]indole (6c): ^1H NMR δ 3.18 (s, 3H), 3.58 (s, 3H), 6.04 (d, J = 14.2 Hz, 1H), 6.12 (d, J = 14.2 Hz, 1H), 6.14 (s, 1H), 6.40 (dd, J_1 = 2.5 Hz, J_2 = 1.4 Hz, 1H), 6.76 (dd, J_1 = 5.0 Hz, J_2 = 3.7 Hz, 1H), 7.15–7.37 (m, 7H), 7.74 (d, J = 7.6 Hz, 1H), 7.93–7.96 (m, 1H); ^{13}C NMR δ 30.9, 42.5, 56.6, 73.7, 108.2, 109.4, 109.9, 118.4, 119.6, 120.3, 122.6, 123.5, 124.4, 125.5, 126.4, 126.5, 126.8, 132.4, 135.5, 137.3, 143.1, 146.0.

1-Methyl-2-[(1-methoxy-1-furan-2-yl)methyl]-3-[(benzotriazol-1-yl)methyl]indole (6d): ^1H NMR δ 3.26 (s, 3H), 3.75 (s, 3H), 5.96 (s, 1H), 6.01–6.06 (m, 2H), 6.14 (d, J = 15.5 Hz, 1H), 6.22 (dd, J_1 = 3.3 Hz, J_2 = 1.9 Hz, 1H), 7.14–7.31 (m, 7H), 7.67 (d, J = 7.9 Hz, 1H), 7.95 (dd, J = 6.9 and 2.9 Hz, 1H); ^{13}C NMR δ 30.9, 42.8, 56.7, 71.6, 107.6, 108.4, 109.4, 110.0, 110.1, 118.4, 119.4, 120.2, 122.5, 123.4, 126.5, 126.7, 132.4, 134.0, 137.2, 142.6, 146.0, 151.2.

1-Methyl-2-[[methoxy(1-methylindol-3-yl)]methyl]-3-[(benzotriazol-1-yl)methyl]indole (6e): ^1H NMR δ 3.23 (s, 3H), 3.41 (s, 3H), 3.59 (s, 3H), 5.99 (d, J = 15.2 Hz, 1H), 6.14 (d, J = 15.2 Hz, 1H), 6.15 (s, 1H), 6.26 (s, 1H), 6.98–7.02 (m, 2H), 7.07–7.23 (m, 7H), 7.43 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.83 (d, J = 8.1 Hz, 1H); ^{13}C NMR δ 31.0, 32.5, 42.9, 56.5, 72.6, 107.4, 109.3, 109.4, 110.3, 113.4, 118.8, 119.5, 119.6, 119.7, 120.3, 122.0, 122.3, 123.4, 126.5 (2C), 127.0, 127.5, 132.6, 136.7, 137.3 (2C), 146.0.

General Procedure for the Preparation of Heterocyclo[b]-Fused Carbazoles 8a–e. A solution of the corresponding intermediate product **6** (1.6 mmol) in 1,2,4-trichlorobenzene (40 mL) (for **6a–d**) or 1,2-dichlorobenzene (40 mL) (for **6e**) was refluxed under argon for 48 h. The solvent was evaporated, and the residue was subjected to column chromatography (hexanes:methylene chloride = 4:1) to give the pure product.

5-Methylthieno[3,2-*b*]carbazole (8a): ^1H NMR δ 3.80 (s, 3H), 7.20 (t, J = 7.7 Hz, 1H), 7.38–7.51 (m, 4H), 7.72 (s, 1H), 8.08 (d, J = 7.7 Hz, 1H), 8.48 (s, 1H); ^{13}C NMR δ 28.2, 100.8, 107.3, 112.4, 117.8, 119.3, 120.8, 121.5, 122.7, 125.4, 125.8, 130.4, 137.4, 139.1, 141.3.

5-Methylfuro[3,2-*b*]carbazole (8b): ^1H NMR δ 3.79 (s, 3H), 6.86 (d, J = 2.2 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.33 (d, J = 7.7 Hz, 1H), 7.42 (s, 1H), 7.47 (t, J = 7.7 Hz, 1H), 7.69 (d, J = 2.2 Hz, 1H), 8.10 (d, J = 7.7 Hz, 1H), 8.15 (s, 1H); ^{13}C NMR δ 29.2, 98.4, 101.8, 106.7, 108.1, 118.3, 120.1, 121.4, 122.8, 125.8, 126.7, 138.8, 142.1, 145.7, 150.2.

5-Methylthieno[2,3-*b*]carbazole (8c): ^1H NMR δ 3.79 (s, 3H), 7.21–7.37 (m, 3H), 7.43 (d, J = 5.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.76 (s, 1H), 8.13 (d, J = 7.5 Hz, 1H), 8.45 (s, 1H); ^{13}C NMR δ 29.2, 100.7, 108.2, 114.4, 118.7, 120.3, 122.5, 122.8, 122.9, 123.8, 126.1, 133.0, 138.6, 140.3, 142.2.

5-Methylfuro[2,3-*b*]carbazole (8d): ^1H NMR δ 3.82 (s, 3H), 6.88 (d, J = 2.3 Hz, 1H), 7.22–7.25 (m, 1H), 7.35–7.46 (m, 3H), 7.62 (d, J = 2.3 Hz, 1H), 8.11 (d, J = 8.0 Hz, 1H), 8.21 (s, 1H); ^{13}C NMR δ 29.3, 90.6, 106.7, 108.1, 111.5, 118.7, 119.9, 120.5, 120.9, 122.9, 125.3, 141.9, 143.9, 148.4, 154.8.

5,11-Dimethylindolo[3,2-*b*]carbazole (8e): ^1H NMR δ 3.87 (s, 6H), 7.14–7.19 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.40–7.43 (m, 2H), 7.93 (s, 2H), 8.12 (d, J = 7.8 Hz, 2H); ^{13}C NMR δ 29.4, 98.6, 108.1, 118.1, 120.1, 122.8, 122.9, 125.7, 136.8, 142.2.

Supplementary Material Available: Detailed assignments of ^1H and ^{13}C NMR spectra for compounds **2**, **3**, **6a–e**, and **8a–e** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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