# General and Efficient Approaches to Fused [1,2-*a*]Pyrroles and [1,2-*a*]Indoles

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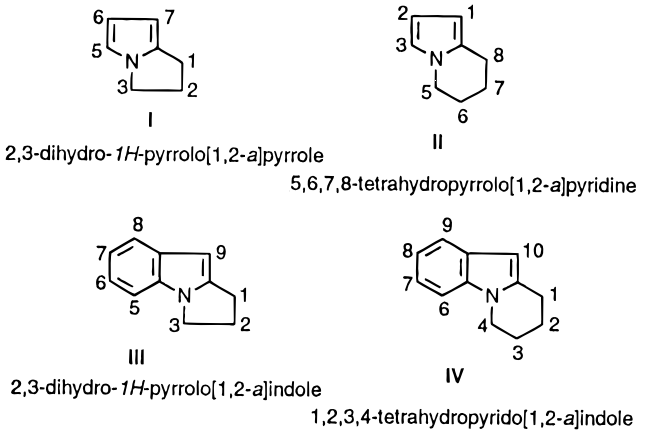
2-[(Benzotriazol-1-yl)methyl]pyrroles **4a**−**c**, and **15a**,**b** and -indoles **23**, prepared as previously reported,[1,2] were converted into the corresponding fused [1,2-*a*]pyrroles **8a**−**c**, and **18a**,**b** and fused [1,2-*a*]indoles **25**, **27** by intramolecular cyclizations; the formations of **25** and **27** involve [3 + 2] and [3 + 3] annulations. The benzotriazolyl-CH-ring moieties of intermediates **8a**,**b**, **18a**,**b**, **25,** and **27** were further elaborated: (i) acylation of **8a** and subsequent reduction and elimination promoted by $LiAlH_4$ to give product **6**; (ii) nucleophilic displacements of the benzotriazolyl moiety with NaCN, NaSPh, and Grignard reagents to afford compounds **9**, **11**, **12**, **20**, **29**, and **32**, respectively; (iii) base-assisted eliminations of benzotriazole from **8b** and **18a** to form the unsaturated fused [1,2-*a*]pyrroles **10** and **17**; (iv) reactions of **18b** and **25** with α,β-unsaturated ketone and aldehyde followed by acid-assisted elimination of the benzotriazolyl group to yield tricyclic compound **21** and product **31**; and (v) Lewis acid promoted dimerization of **27** to form the fused indolo[3,2-*b*]carbazole **33**.

## Introduction

Fused [1,2-*a*]pyrrole alkaloids, including both 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (**I**) and 5,6,7,8-tetrahydropyrrolo[1,2-*a*]pyridine (**II**) derivatives (Chart 1), are biologically active and widely distributed in nature.[3−5] Consequently, there has been an ongoing interest in the synthesis of ring systems **I** and **II**.[6−12] Although numerous synthetic approaches to the fused [1,2-*a*]pyrroles **I** and **II** have been described, no general route has utilized precursors of type pyrrolyl-2-$CH_2X$ (in which X is both an electron-withdrawing and a leaving group) to build the fused ring and, subsequently, to enable further modification by replacement of the functionality X.

Due to the pharmacological importance of mitomycins,[13−15] the syntheses of mitomycin skeletons and mitomycin-like compounds 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-indole (**III**) and 1,2,3,4-tetrahydropyrido[1,2-*a*]indole (**IV**) (Chart 1) in the search for new drugs has attracted much attention. Recent examples for the preparation of such fused [1,2-*a*]indoles **III** include (i) facile intramolecular radical cyclizations;[16−20] (ii) intramolecular cyclization by photolysis;[21,22] (iii) classical intramolecular nucleophilic substitution;[23,24] (iv) intramolecular cycloaddition reaction by thermolysis of the corresponding tosylhydrazones;[25] (v) Dieckmann/ring expansion;[26] (iii) a one-pot procedure *via* cyclic trialkyl(indol-2-yl)borate;[27] (iv) samarium(II) iodide-promoted intramolecular hydroxyalkylations of 3-formylindoles;[28] and (v) C-2 side-chain modification of

**Chart 1**

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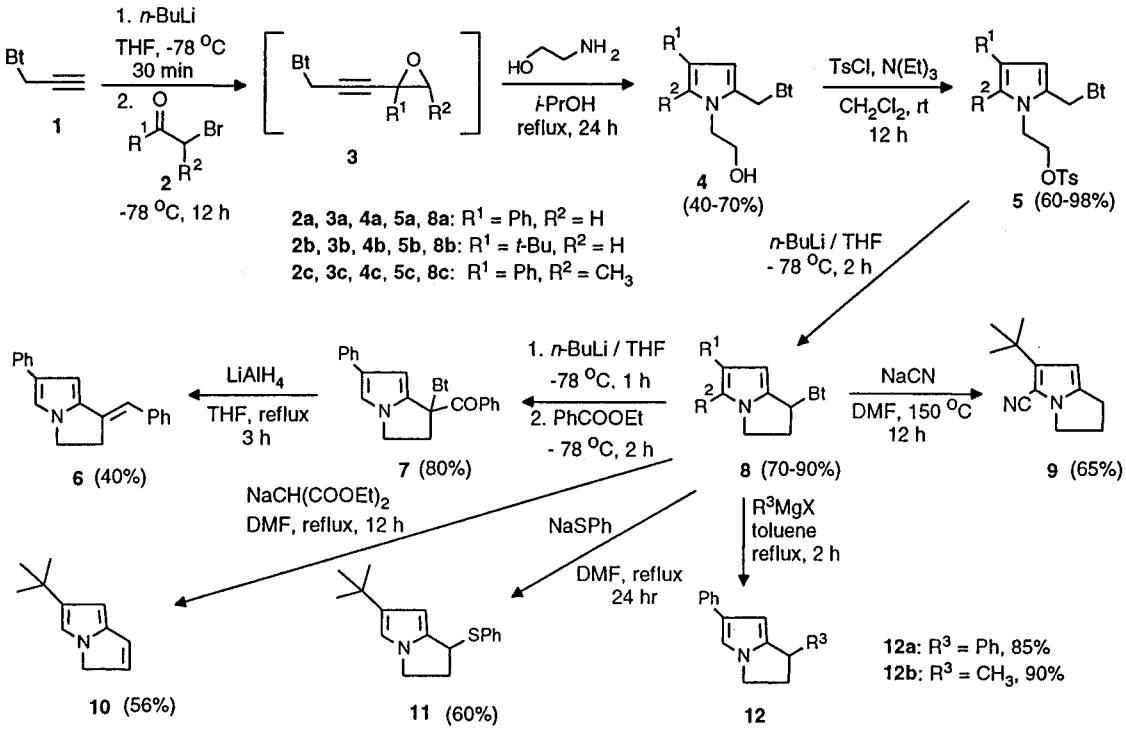
**Scheme 1**




2-methyl-3-alkylindoles *via* 3-methylthioindoles.[29] In contrast, syntheses of 1,2,3,4-tetrahydropyrido[1,2-*a*]-indole (**IV**) derivatives are less explored. Recent synthetic methods for the construction of ring system **IV** mainly involve intramolecular radical cyclization,[17−20] classical intramolecular nucleophilic substitution,[24] and the Dieckmann/ring expansion approach.[26]

Our previous studies demonstrated 2-[(benzotriazol-1-yl)methyl]pyrroles and -indole to be versatile intermediates in the synthesis of pyrrole and indole derivatives.[1,2,30] The important feature of 2-(benzotriazol-1-yl)-methyl side chains attached to electron-rich pyrrole and indole nuclei is that the benzotriazolyl moiety behaves as both an anion-stabilizing and a good leaving group, which allows a wide range of electrophiles and nucleophiles to be introduced onto a carbon atom attached to the 2-position by successive deprotonation, reaction with an electrophile, and replacement of the benzotriazolyl group with a nucleophile. Herein, we report our further investigations on the use of 2-[(benzotriazol-1-yl)methyl]-pyrroles and -indole for the synthesis of the fused [1,2-*a*]pyrroles **I** and **II** and -indoles **III** and **IV**.

## Results and Discussion

**Synthesis of 1-(Benzotriazol-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrroles 8a−c, 8-(Benzotriazol-1-yl)-5,6,7,8-tetrahydropyrrolo[1,2-*a*]pyridines 18a,b, 1-(Benzotriazol-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-indole (25), and 1-(Benzotriazol-1-yl)-1,2,3,4-tetrahydropyrido[1,2-*a*]indole (27).** In our previous paper, we reported that 2-[(benzotriazol-1-yl)methyl]pyrroles can be easily obtained by the reaction of alkynyloxiranes, derived from 1-propargylbenzotriazole (**1**) and α-bromo ketones **2** or **13**, with primary amines.[1] To construct the fused [1,2-*a*]pyrroles, we examined the intramolecular cyclization of the *N*-functionalized-alkyl-2-[(benzotriazol-1-yl)methyl]pyrroles **4a**−**c** and **15a**,**b** (Schemes 1 and 2), a strategy similar to that reported for the synthesis of 1,2-dihydro-3*H*-pyrrolo[1,2-*a*]pyrrole-1-carboxylic acids.[6]

This strategy called for the reaction of 2-hydroxyethylamine and 3-hydroxypropylamine with alkynyloxiranes **3** and **14** which are available in up to 90% yields (based on GCMS) by treatment of 1-propargylbenzotriazole (**1**) with 1 equiv of *n*-BuLi followed by reaction with an α-bromo ketone (**2** or **13**) at −78 °C for 12 h. The preparation of compounds of type **3** and **14** by this method seems quite general, and the scope depends on the availability of α-bromo carbonyl compounds. The compounds **3a**−**c** and **14a**,**b** were stable at room temperature but decomposed upon heating above 60 °C. We found it effective to use alkynyloxiranes **3a**−**c** and **14a**,**b**, after aqueous workup, without further purification. They were refluxed with 2-hydroxyethylamine or 3-hydroxypropylamine in *i*-PrOH for 24−48 h to give the corresponding pyrroles **4a**−**c** and **15a**,**b** in good yields.

An initial attempt to transform **4a** into fused [1,2-*a*]-pyrrole **8a** was carried out in onepot: **4a** was treated with 1 equiv of LDA, followed by reaction with tosyl chloride to generate tosylate **5a**, which underwent intramolecular cyclization upon treatment with LDA or *n*-BuLi to give **8a** in fairly low yield. However, the overall yield was dramatically improved by the isolation of tosylate **5a** using a two-step procedure. Thus, compounds **4a**−**c** or **15a**,**b** were reacted with tosyl chloride in methylene chloride in the presence of triethylamine to afford tosylates **5a**−**c** or **16a**,**b** in high yields. The intramolecular cyclizations of **5a**−**c** and **16a**,**b** *via* lithiation at the benzotriazol-1-ylmethyl group and subsequent nucleophilic substitution of tosylate gave 1-(benzotriazol-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrroles **8a**−**c** and 8-(benzotriazol-1-yl)-5,6,7,8-tetrahydropyrrolo[1,2-*a*]pyridines **18a**,**b** in good yields. Compounds **18a**,**b** were obtained

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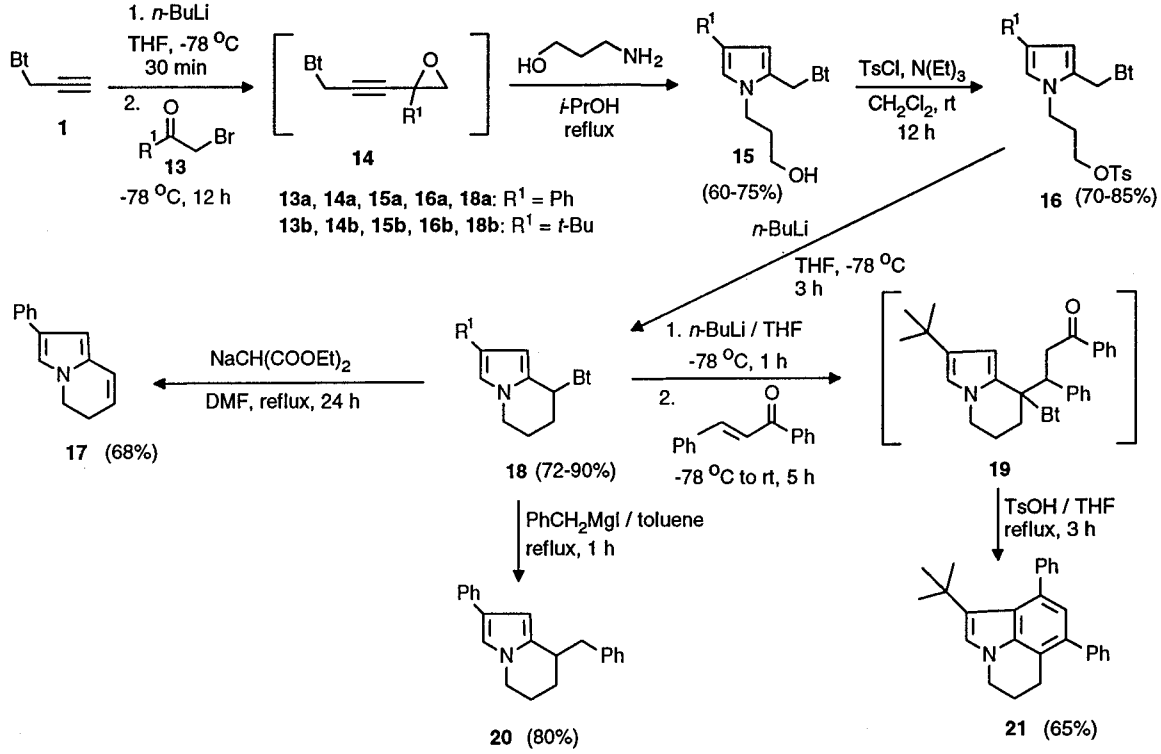
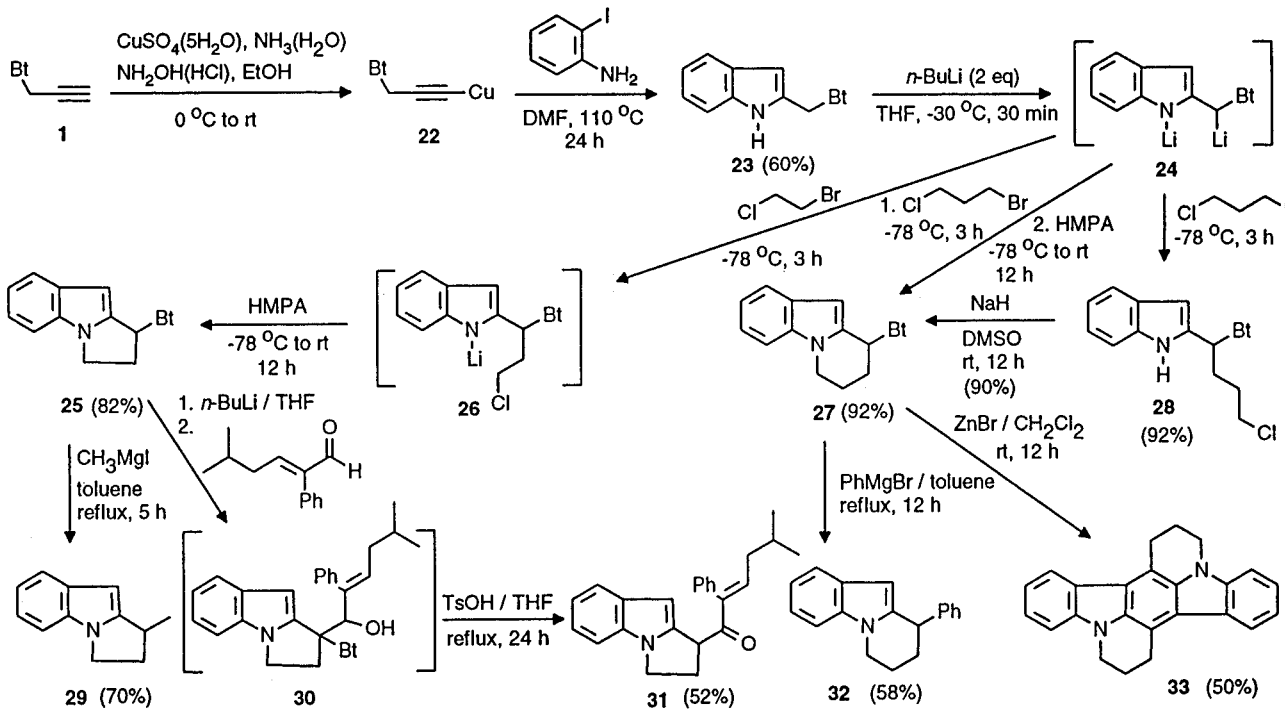
**Scheme 2**




in good purity after aqueous workup, based on $^1$H NMR and GCMS; therefore they were used directly for synthetic manipulation without further purification.

2-[(Benzotriazol-1-yl)methyl]indole (**23**) was readily prepared from 1-propargylbenzotriazole (**1**) *via* a coupling reaction of the copper salt **22** with *o*-iodoaniline (Scheme 3). Lithiation of **23** with 2 equiv of *n*-BuLi in THF at −30 °C for 30 min generated dianion **24**, previously shown to exhibit interesting reactivity on alkylation.[2] An attempt to synthesize **23** by direct palladium-catalyzed reaction[31] of 1-propargylbenzotriazole (**1**) with *o*-iodoaniline failed. Dianion **24** should couple with a dielectrophile to form a fused five- or six-membered ring *via* [3 + 2] or [3 + 3] annulation given proper choice of the dielectrophile. Indeed, when dianion **24** was treated with 1 equiv of 1-bromo-2-chloroethane at −78 °C for 3 h, followed by addition of HMPA as a cosolvent at room temperature for 12 h, 1-(benzotriazol-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (**25**) was obtained in high yield. 1-(Benzotriazol-1-yl)-1,2,3,4-tetrahydropyrido[1,2-*a*]indole (**27**) was similarly obtained using 1-bromo-3-chloropropane as the dielectrophile. A reaction pathway through intermediate **26** and the *N*-lithium salt of **28** is supported by the isolation of compound **28** after treat-

**Scheme 3**



ment of **24** with 1-bromo-3-chloropropane at −78 °C for 3 h. The monoalkylated compound **28** can be transformed into **27** in excellent yield by intramolecular cyclization in DMSO in the presence of sodium hydride. Importantly, the cyclizations of **26** and **28** occurred regiospecifically at the indole nitrogen and no trace of reaction at indole 3-position was found by $^1$H NMR or GCMS. Other functionalized dielectrophiles should enable construction of other functionalized fused ring systems.

**Synthetic Manipulations of the Benzotriazol-1-yl Group Attached to Fused [1,2-*a*]Pyrroles 8a,b and 18a,b and [1,2-*a*]Indoles 25 and 27.** The synthetic versatility of 2-(benzotriazol-1-yl)methyl substituents attached to pyrroles and indoles, in terms of anion stabilization and the good leaving ability of the benzotriazolyl group, have already been exploited in our previous work.[1,2] Since the reactions at five- and six-membered-ring carbon atoms are similar to those of open chains, the reactivity of benzotriazol-1-yl attached methine groups of the compounds **8a**,**b, 18a**,**b**, **25,** and **27** should be similar to their open chain analogs. In the present study, we examined the reactivity of **8a**,**b**; the reactivity of **8c** was presumed to be similar to that of **8a**,**b**.

In the pyrrole systems **8a**,**b** and **18a**,**b,** the nucleophilic substitutions of the benzotriazolyl group with sodium thiophenolate and Grignard reagents occurred smoothly to give the products **11**, **12a**,**b**, and **20** in good yields. As in the open chain analog,[1] the reaction of **8b** with sodium cyanide in DMF at 150 °C afforded the "abnormal" product **9** in 65% yield, in which the cyano group added to the 5-position of the pyrrole ring. Surprisingly, unlike the open chain case,[1] treatment of **8b** and **18a** with sodium malonate in refluxing DMF gave the corresponding elimination products **10** and **17** instead of expected substitution products. Moreover, use of sodium hydride and potassium *tert*-butoxide as bases did not give any reaction and the starting materials **8b** and **18a** were recovered. The partially unsaturated products **10** and **17** were not stable, and they decomposed after several days at room temperature, upon exposure to air.

Due to the anion-stabilizing ability of the benzotriazolyl group, the intermediates **8a**,**b** and **18a**,**b** can be transformed into various functionalized fused [1,2-*a*]pyrroles by sequential lithiation, alkylation, and substitution of benzotriazolyl groups, as exemplified in the synthesis of compounds **6** and **21**. Compound **8a** was acylated by treatment with *n*-BuLi, followed by reaction with ethyl benzoate to form intermediate **7** in 80% yield which was reacted with $LiAlH_4$ in THF to form the phenylmethylenated fused [1,2-*a*]pyrrole **6**. The reaction pathway probably involved reductive elimination (by hydride addition to an immonium cation formed by heterolysis of the Bt group) of the benzotriazolyl (Bt) group, reduction of the carbonyl group, and subsequent elimination of hydroxy group. The structure of the isolated *trans*-isomer **6** was confirmed by an NOE spectrum. As with the open chain analog,[30] the lithium derivative of compound **18b** reacted with *trans*-chalcone to give adduct **19** which was refluxed with *p*-toluenesulfonic acid in THF to give the tricyclic fused indole **21**.

Apparently as compared to the pyrrole analogs **8** and **18**, the benzene ring in fused [1,2-*a*]indole systems **25** and **27** induces less effective cation formation at benzotriazolyl-attached carbons in compounds **25** and **27** which are thus less susceptible to nucleophilic substitution than **8** and **18**. Hence, no reactions of **25** and **27** occurred with sodium thiophenolate and sodium cyanide. However, Grignard reagents converted **25** and **27** into products **29** and **32**, respectively, in good yields. Interestingly, the reaction of the lithium derivative of compound **25** with 5-methyl-2-phenyl-2-hexenal gave 1,2-addition intermediate **30** which upon treatment with *p*-toluenesulfonic acid in THF formed the insertion product **31** *via* a pinacol type of rearrangement.[32] Compound **27** also underwent zinc bromide-promoted dimerization, followed by dehydrogenation on exposure to air, to give the fused indolo-[3,2-*b*]carbazole **33** in 50% yield. The novel structure **33** is related to products of interesting biological activity.[33]

In conclusion, general and efficient syntheses of fused [1,2-*a*]pyrroles and -indoles have been described. These approaches start from readily available starting materials and involve ring synthesis of benzotriazolyl-attached fused [1,2-*a*]pyrroles **8a**−**c** and **18a**,**b** *via* intramolecular cyclizations and fused [1,2-*a*]indoles **25** and **27** *via* [3 + 2] and [3 + 3] annulations. The intermediates **8a**−**c**, **18a**,**b**, **25,** and **27** were further transformed by alkylation and replacement of the benzotriazolyl group to provide a variety of functionalized fused [1,2-*a*]pyrrole and -indole derivatives. Moreover, the 3-unsubstituted positions of pyrrole and indole rings allow further synthetic manipulations.

## Experimental Section

**General Comments.** Melting points were determined on a hot-stage microscope and are uncorrected. $^1$H and NOE NMR spectra were recorded on a 300 MHz spectrometer using TMS as the internal standard and $CDCl_3$ as the solvent. $^{13}$C NMR spectra were recorded at 75 MHz on the same instrument with the solvent peak ($CDCl_3$) as the reference. HRMS and elemental analyses (C, H, N) were carried out within the department.

1-Propargylbenzotriazole (**1**)[34] and 2-(benzotriazol-1-yl)-methylindole (**23**)[2] were prepared according to previously reported procedures.

**General Procedure for the Preparation of 2-[(Benzotriazol-1-yl)methyl]-pyrroles 4a−c and 15a,b.** To a solution of 1-propargylbenzotriazole (**1**) (3.2 g, 20 mmol) in THF (100 mL) was added a solution of *n*-BuLi (20 mmol, 12.5 mL, 1.6 M in hexane) at −78 °C; the solution was stirred at this temperature for 30 min. A solution of the appropriate α-bromo ketone **2** or **13** (20 mmol) in THF (10 mL) was added, and the reaction mixture was stirred at −78 °C for 20 h. A saturated $NH_4Cl$ solution (100 mL) was added, and the solution was extracted with $Et_2O$ (200 mL). The organic phase was separated, washed with a saturated $NH_4Cl$ solution (3 × 100 mL), and dried ($MgSO_4$).

After removal of the solvent the residue was dissolved in *i*-PrOH, 2-hydroxyethylamine or 3-hydroxypropylamine (40 mmol) was added, and the solution was refluxed for 24 h. *i*-PrOH was removed and the residue subjected to column chromatography or recrystallization to afford the corresponding products **4a**−**c** and **15a**,**b.**

***N*-(2-Hydroxyethyl)-2-[(benzotriazol-1-yl)methyl]-4-phenylpyrrole (4a):** purified by recrystallization from EtOAc/hexane (1:3), white microcrystals, yield 65%; mp 142−143 °C; $^1$H NMR $\delta$ 7.98 (d, $J$ = 8.3 Hz, 1 H), 7.73 (d, $J$ = 8.3 Hz, 1 H), 7.43−7.48 (m, 3 H), 7.32−7.37 (m, 1 H), 7.24−7.29 (m, 2 H), 7.13 (d, $J$ = 2.0 Hz, 1 H), 7.06−7.14 (m, 1 H), 6.60 (d, $J$ = 2.0 Hz, 1 H), 6.00 (s, 2 H), 4.94 (t, $J$ = 5.2 Hz, 1 H), 4.07 (t, $J$ = 5.4 Hz, 2 H), 3.60 (q, $J$ = 5.2 Hz, 2 H); $^{13}$C NMR $\delta$ 145.4, 134.9, 132.2, 128.2, 126.9, 126.4, 124.8, 124.0, 123.5, 122.6, 119.6, 118.9, 110.3, 107.6, 61.3, 48.9, 43.8. Anal. Calcd for $C_{19}H_{18}N_4O$: C, 71.68; H, 5.70; N, 17.60. Found: C, 72.10; H, 5.68; N, 17.80.

***N*-(2-Hydroxyethyl)-2-[(benzotriazol-1-yl)methyl]-4-*tert*-butylpyrrole (4b):** purified by column chromatography

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using EtOAc/hexane (1:1) as the eluent, white powder, yield 70%; mp 102−104 °C; $^1$H NMR $\delta$ 8.00 (d, $J$ = 8.2 Hz, 1 H), 7.30−7.45 (m, 3 H), 6.51 (d, $J$ = 2.0 Hz, 1 H), 6.31 (d, $J$ = 2.0 Hz, 1 H), 5.85 (s, 2 H), 4.00 (t, $J$ = 5.4 Hz, 2 H), 3.61 (q, $J$ = 5.4, 2 H), 2.28 (t, $J$ = 5.4 Hz, 1 H), 1.23 (s, 9 H); $^{13}$C NMR $\delta$ 146.2, 135.1, 132.8, 127.4, 124.1, 124.0, 119.8, 118.4, 110.2, 109.3, 62.6, 48.9, 45.0, 31.7, 30.5. Anal. Calcd for $C_{17}H_{22}N_4O$: C, 68.43; H, 7.43; N, 18.78. Found: C, 68.49; H, 7.55; N, 18.93.

***N*-(2-Hydroxyethyl)-2-[(benzotriazol-1-yl)methyl]-4-phenyl-5-methylpyrrole (4c):** purified by column chromatography using EtOAc/hexane (3:7) as the eluent, white powder, yield 40%; mp 171−173 °C; $^1$H NMR $\delta$ 8.05 (d, $J$ = 8.3 Hz, 1 H), 7.59 (d, $J$ = 8.3 Hz, 1 H), 7.33−7.46 (m, 6 H), 7.21−7.27 (m, 1 H), 6.51 (s, 1 H), 5.97 (s, 2 H), 4.14 (t, $J$ = 5.8 Hz, 2 H), 3.64 (q, $J$ = 5.6 Hz, 2 H), 2.32 (s, 3 H), 1.95 (t, $J$ = 5.7 Hz, 1 H); $^{13}$C NMR $\delta$ 145.6, 136.3, 132.3, 127.8, 127.4, 126.7, 126.5, 124.7, 123.9, 123.4, 120.9, 119.1, 109.9, 109.7, 61.1, 10.6. Anal. Calcd for $C_{20}H_{20}N_4O$: C, 72.27; H, 6.06; N, 16.85. Found: C, 72.23; H, 6.14; N, 16.87.

***N*-(3-Hydroxypropyl)-2-[(benzotriazol-1-yl)methyl]-4-phenylpyrrole (15a):** purified by column chromatography using EtOAc/hexane (3:7) as the eluent, yellow oil, yield 60%; $^1$H NMR $\delta$ 8.02 (d, $J$ = 8.1 Hz, 1 H), 7.47−7.53 (m, 3 H), 7.30−7.40 (m, 4 H), 7.19 (t, $J$ = 8.7 Hz, 1 H), 7.01 (s, 1 H), 6.64 (d, $J$ = 1.7 Hz, 1 H), 5.87 (s, 2 H), 4.09 (t, $J$ = 6.8 Hz, 2 H), 3.56 (t, $J$ = 5.5 Hz, 2 H), 3.10 (s, 1 H), 1.70−1.75 (m, 2 H); $^{13}$C NMR $\delta$ 145.0, 135.0, 132.6, 128.5, 127.4, 125.5, 125.4, 124.7, 124.0, 123.9, 119.6, 110.1, 108.6, 58.6, 44.6, 43.3, 33.7. Anal. Calcd for $C_{20}H_{20}N_4O$: C, 72.27; H, 6.06; N, 16.85. Found: C, 72.00; H, 6.12; N, 16.92.

***N*-(3-Hydroxypropyl)-2-[(benzotriazol-1-yl)methyl]-4-*tert*-butylpyrrole (15b):** purified by column chromatography using EtOAc/hexane (3:7) as the eluent, white powder, yield 75%; mp 83−85 °C; $^1$H NMR $\delta$ 8.01 (d, $J$ = 8.2 Hz, 1 H), 7.31−7.46 (m, 3 H), 6.48 (s, 1 H), 6.29 (d, $J$ = 1.7 Hz, 1 H), 5.83 (s, 2 H), 3.98 (t, $J$ = 7.2 Hz, 2 H), 3.55 (t, $J$ = 5.9 Hz, 2 H), 2.43 (brs, 1 H), 1.64−1.69 (m, 2 H), 1.23 (s, 9 H); $^{13}$C NMR $\delta$ 146.2, 135.0, 132.8, 127.3, 124.0, 123.7, 119.7, 117.9, 110.3, 108.9, 59.2, 45.0, 43.2, 33.9, 31.7, 30.5. Anal. Calcd for $C_{18}H_{24}N_4O$: C, 69.20; H, 7.74; N, 17.93. Found: C, 69.57; H, 7.76; N, 17.90.

**General Procedure for the Preparation of Tosylates 5a−c and 16a,b.** To a solution of compound **4** or **15** (10 mmol) in $CH_2Cl_2$ (60 mL) was added triethylamine (15 mL). Toluenesulfonic acid chloride (5.87 g, 30 mmol) was added in portions over a period of 1 h, and the reaction mixture was stirred at room temperature overnight. The reaction solution was washed with a 2 N HCl solution (50 mL), followed by a 10% $NaHCO_3$ solution (50 mL) and water (3 × 50 mL). The organic layer was separated and dried ($MgSO_4$) and the solvent removed to give the product **5a**−**c** or **16a**,**b**.

***N*-(2-Tosylethyl)-2-[(benzotriazol-1-yl)methyl]-4-phenylpyrrole (5a):** purified by recrystallization from EtOAc/hexane (1:1), white powder, yield 98%; mp 121−122 °C; $^1$H NMR $\delta$ 8.03 (d, $J$ = 8.1 Hz, 1 H), 7.51 (d, $J$ = 8.3 Hz, 3 H), 7.46−7.33 (m, 6 H), 7.21 (t, $J$ = 7.2 Hz, 1 H), 7.09 (d, $J$ = 8.5 Hz, 2 H), 6.81 (d, $J$ = 1.9 Hz, 1 H), 6.59 (d, $J$ = 1.9 Hz, 1 H), 5.78 (s, 2 H), 4.20 (t, $J$ = 4.7 Hz, 2 H), 4.01 (t, $J$ = 4.7 Hz, 2 H), 2.25 (s, 3 H); $^{13}$C NMR $\delta$ 146.2, 144.9, 134.6, 132.4, 131.8, 129.7, 128.6, 127.5, 125.8, 125.7, 124.7, 124.5, 124.0, 119.8, 119.7, 109.9, 109.2, 69.0, 45.4, 44.2, 21.4. Anal. Calcd for $C_{26}H_{24}N_4O_3S$: C, 66.08; H, 5.12; N, 11.86. Found: C, 66.08; H, 5.08; N, 11.86.

***N*-(2-Tosylethyl)-2-[(benzotriazol-1-yl)methyl]-4-*tert*-butylpyrrole (5b):** purified by recrystallization from EtOAc/hexane (1:1), white needles, yield 98%; mp 96−98 °C; $^1$H NMR $\delta$ 8.03 (d, $J$ = 8.2 Hz, 1 H), 7.61 (d, $J$ = 8.3 Hz, 2 H), 7.33−7.44 (m, 3 H), 7.26 (d, $J$ = 8.1 Hz, 2 H), 6.41 (d, $J$ = 2.0 Hz, 1 H), 6.28 (d, $J$ = 2.0 Hz, 1 H), 5.74 (s, 2 H), 4.16 (t, $J$ = 5.3 Hz, 2 H), 3.96 (t, $J$ = 5.3 Hz, 2 H), 2.43 (s, 3 H), 1.22 (s, 9 H); $^{13}$C NMR $\delta$ 146.3, 144.6, 135.4, 132.6, 132.4, 129.8, 127.7, 127.4, 124.0, 123.9, 119.9, 118.6, 110.0, 109.6, 69.1, 45.3, 44.6, 31.6, 30.4, 21.6. Anal. Calcd for $C_{24}H_{28}N_4O_3S$: C, 63.69; H, 6.24; N, 12.38. Found: C, 63.69; H, 6.24; N, 12.38.

***N*-(2-Tosylethyl)-2-[(benzotriazol-1-yl)methyl]-4-phenyl-5-methylpyrrole (5c):** purified by recrystallization from EtOAc/hexane (1:1), white powder, yield 60%; mp 128−130 °C; $^1$H NMR $\delta$ 8.02 (d, $J$ = 8.1 Hz, 1 H), 7.44−7.59 (m, 2 H), 7.20−7.42 (m, 10 H), 6.44 (s, 1 H), 5.82 (s, 2 H), 4.25 (t, $J$ = 5.1 Hz, 2 H), 4.03 (t, $J$ = 5.3 Hz, 2 H), 2.34 (s, 3 H), 2.15 (s, 3 H); $^{13}$C NMR $\delta$ 146.2, 144.9, 136.2, 132.5, 131.9, 129.8, 128.3, 127.8, 127.6, 127.4, 127.1, 125.5, 123.9, 123.8, 122.0, 119.8, 111.2, 110.0, 68.3, 44.6, 42.4, 21.4, 11.0. Anal. Calcd for $C_{27}H_{26}N_4O_3S$: N, 11.51. Found: N, 11.09.

***N*-(3-Tosylpropyl)-2-[(benzotriazol-1-yl)methyl]-4-phenylpyrrole (16a):** purified by column chromatography using EtOAc/hexane (1:1) as the eluent, white powder, yield 85%; mp 101−102 °C; $^1$H NMR $\delta$ 8.02 (d, $J$ = 8.2 Hz, 1 H), 7.76 (d, $J$ = 8.3 Hz, 2 H), 7.25−7.49 (m, 9 H), 7.18 (t, $J$ = 7.3 Hz, 1 H), 6.87 (d, $J$ = 2.0 Hz, 1 H), 6.66 (d, $J$ = 2.0 Hz, 1 H), 5.81 (s, 2 H), 3.98 (t, $J$ = 6.9 Hz, 2 H), 3.90 (t, $J$ = 5.7 Hz, 2 H), 2.41 (s, 3 H), 1.70−1.74 (m, 2 H); $^{13}$C NMR $\delta$ 146.0, 145.0, 134.8, 132.6, 129.9, 128.7, 127.8, 127.7, 125.8, 125.1, 124.9, 124.4, 124.3, 119.8, 110.1, 109.5, 66.7, 44.7, 42.9, 30.4, 21.6. Anal. Calcd for $C_{27}H_{26}N_4O_3S$: C, 66.65; H, 5.39; N, 11.51. Found: C, 66.66; H, 5.56; N, 11.63.

***N*-(3-Tosylpropyl)-2-[(benzotriazol-1-yl)methyl]-4-*tert*-butylpyrrole (16b):** purified by column chromatography using EtOAc/hexane (3:7) as the eluent, white powder, yield 70%; mp 83−85 °C; $^1$H NMR $\delta$ 8.02 (d, $J$ = 8.2 Hz, 1 H), 7.78 (d, $J$ = 8.1 Hz, 2 H), 7.33−7.42 (m, 5 H), 6.37 (d, $J$ = 1.7 Hz, 1 H), 6.23 (d, $J$ = 1.7 Hz, 1 H), 5.74 (s, 2 H), 3.87−3.91 (m, 4 H), 2.45 (s, 3 H), 1.65−1.69 (m, 2 H), 1.21 (s, 9 H); $^{13}$C NMR $\delta$ 146.3, 144.9, 135.2, 132.7, 129.9, 128.9, 127.9, 127.4, 123.9, 123.6, 119.9, 118.2, 110.1, 109.5, 67.0, 44.8, 42.6, 31.6, 30.5, 30.4, 21.6. Anal. Calcd for $C_{25}H_{30}N_4O_3S$: C, 64.35; H, 6.48; N, 12.01. Found: C, 64.36; H, 6.42; N, 12.68.

**General Procedure for the Preparation of Fused [1,2-*a*]Pyrroles 8a−c and 18a,b.** To a solution of tosylate **5** or **16** (10 mmol) in THF (80 mL) was added a solution of *n*-BuLi (10 mmol, 6.25 mL, 1.6 M in hexane) at −78 °C. The reaction mixture was stirred and allowed to warm to room temperature overnight. The reaction was quenched with saturated $NH_4Cl$ solution (50 mL), extracted with EtOAc, washed with brine (3 × 50 mL), and dried ($MgSO_4$). The solvent was removed to give the crude product which was purified by column chromatography to give the corresponding compounds **5a**−**c**. The crude products **18a**−**c** were used directly for the synthesis of compounds **17**, **20** and **21** without further purification, and the yields were determined by GCMS (Scheme 2).

**1-(Benzotriazol-1-yl)-6-phenyl-2,3-dihydro-1*H*-pyrrolizine (8a):** purified by column chromatography using EtOAc/hexane (1:2) as the eluent, yellow oil, yield 75%; $^1$H NMR $\delta$ 8.02−8.08 (m, 1 H), 7.48 (d, $J$ =7.2 Hz, 2 H), 7.30−7.34 (m, 4 H), 7.15−7.19 (m, 2 H), 6.65−6.69 (m, 1 H), 6.55 (dd, $J$ = 8.0 and 2.7 Hz, 1 H), 6.33 (s, 1 H), 4.26−4.35 (m, 1 H), 4.15−4.22 (m, 1 H), 3.20−3.32 (m, 1 H), 2.78−2.87 (m, 1 H); $^{13}$C NMR $\delta$ 146.4, 135.7, 132.8, 131.7, 130.7, 128.6, 127.4, 125.7, 124.9, 123.8, 119.9, 112.3, 109.7, 100.8, 56.5, 45.4, 36.3. Anal. Calcd for $C_{19}H_{17}N_4O$: C, 75.72; H, 5.69; N, 18.59. Found: C, 75.38; H, 5.31; N, 18.41.

**1-(Benzotriazol-1-yl)-6-*tert*-butyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (8b):** purified by column chromatography using EtOAc/hexane (1:2) as the eluent, yellow oil, yield 90%; $^1$H NMR $\delta$ 8.02−8.06 (m, 1 H), 7.27−7.35 (m, 2 H), 6.68 (d, $J$ = 1.4 Hz, 1 H), 6.50−6.53 (m, 1 H), 6.34−6.39 (m, 1 H), 5.98 (d, $J$ = 1.4 Hz, 1 H), 4.09−4.23 (m, 2 H), 3.18−3.31 (m, 1 H), 2.71−2.80 (m, 1 H),1.25 (s, 9 H); $^{13}$C NMR $\delta$ 146.3, 142.4, 131.8, 131.3, 127.2, 123.7, 119.9, 110.8, 110.0, 100.9, 56.9, 45.2, 36.7, 31.9, 31.1. Anal. Calcd for $C_{17}H_{20}N_4$: C, 72.83; H, 7.19; N, 19.98. Found: C, 72.55; H, 7.44; N, 20.31.

**1-(Benzotriazol-1-yl)-5-methyl-6-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (8c):** purified by column chromatography using EtOAc/hexane (1:2) as the eluent, yellow oil, yield 70%; $^1$H NMR $\delta$ 8.03−8.06 (m, 1 H), 7.28−7.41 (m, 6 H), 7.16−7.22 (m, 1 H), 6.81−6.85 (m, 1 H), 6.50 (dd, $J$ = 8.0 Hz and 2.7 Hz, 1 H), 6.17 (s, 1 H), 4.06−4.25 (m, 2 H), 3.18−3.38 (m, 1 H), 2.85−2.95 (m, 1 H), 2.46 (s, 3 H); $^{13}$C NMR $\delta$ 146.3, 136.9, 131.7, 129.5, 128.2, 127.3, 127.2, 126.4, 125.2, 123.7, 121.4, 119.8, 109.8, 102.2, 56.6, 43.4, 35.9, 11.2. Anal. Calcd for $C_{17}H_{20}N_4$: C, 76.41; H, 5.77; N, 17.82. Found: C, 76.18; H, 6.00; N, 17.59.

**Preparation of 1-(Benzotriazol-1-yl)-1-(phenylcarbonyl)-6-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (7).**

To a solution of compound **8a** (0.97 g, 3.2 mmol) in THF (80 mL) was added a solution of *n*-BuLi (2 mL, 3.2 mmol, 1.6 M in hexane) at −78 °C. After 30 min, ethyl benzoate (0.48 g, 3.2 mmol) was added and the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched with saturated $NH_4Cl$ solution (100 mL), extracted with EtOAc (100 mL), and dried ($MgSO_4$). The solvent was removed and the product isolated as yellow needles (1.03 g, 80% yield) by column chromatography using EtOAc/hexane (1:2) as the eluent: mp 175−178 °C; $^1$H NMR $\delta$ 8.05−8.08 (m, 1 H), 7.67 (d, $J$ = 8.6 Hz, 2 H), 7.44−7.47 (m, 3 H), 7.29−7.38 (m, 6 H), 7.15−7.21 (m, 2 H), 6.62−6.67 (m, 1 H), 6.48 (s, 1 H), 4.24−4.32 (m, 1 H), 4.10−4.20 (m, 1 H), 2.91−2.99 (m, 1 H); $^{13}$C NMR $\delta$ 190.0, 146.4, 135.3, 133.8, 133.4, 131.9, 130.6, 130.4, 129.6, 128.7, 128.5, 128.1, 126.1, 125.2, 124.3, 120.4, 113.9, 110.6, 105.1, 74.2, 45.1, 41.0. Anal. Calcd for $C_{26}H_{20}N_4O$: C, 77.21; H, 4.98; N, 13.85. Found: C, 77.27; H, 5.00; N, 13.65.

**Preparation of 1-(Phenylmethylene)-6-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (6).** To a solution of $LiAlH_4$ (0.087 g, 2.3 mmol) in THF (30 mL) was added a solution of compound **7** (0.45 g, 1.1 mmol) at room temperature, and the reaction mixture was refluxed for 4 h. After cooling, EtOAc (50 mL) and water (50 mL) were added. The organic layer was separated, washed with water (3 × 50 mL), and dried ($MgSO_4$). The solvent was evaporated off, and the solid residue was washed with diethyl ether to give the product **6** (0.12 g, 40% yield) as white powder: mp 188−189 °C; $^1$H NMR $\delta$ 7.53 (d, $J$ = 7.7 Hz, 2 H), 7.31−7.37 (m, 6 H), 7.17−7.23 (m, 2 H), 7.03 (s, 1 H), 6.74 (d, $J$ = 1.9 Hz, 1 H), 6.56 (s, 1 H), 4.16 (t, $J$ = 6.3 Hz, 2 H), 3.45 (t, $J$ = 6.3 Hz, 2 H); $^{13}$C NMR $\delta$ 140.1, 138.1, 136.1, 131.6, 128.6, 128.5, 128.0, 126.0, 125.6, 125.1, 117.3, 113.0, 111.2, 96.1, 45.5, 33.2. Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.32; N, 5.16. Found: C, 88.74; H, 6.42; N, 5.25.

**Preparation of 5-Cyano-6-*tert*-butyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (9).** A solution of **8b** (0.60 g, 2.14 mmol) and NaCN (0.51 g, 10 mmol) in DMF (30 mL) was refluxed for 12 h. After cooling, $Et_2O$ (50 mL) and water (50 mL) were added and the organic phase was separated, washed with NaOH solution (2 N, 2 × 50 mL), and dried ($MgSO_4$). After removal of the solvent under reduce pressure, the residue was purified by column chromatography using $CH_2Cl_2$/hexane (1:4) as the eluent to give product **9** as a yellow oil (0.62 g, 65%): $^1$H NMR $\delta$ 5.79 (s, 1 H), 3.88−3.96 (m, 2 H), 2.73−2.91 (m, 2 H), 2.50 (t, $J$ = 7.4 Hz, 2 H), 1.34 (s, 9 H); $^{13}$C NMR $\delta$ 151.0, 141.6, 115.7, 99.5, 46.4, 32.0, 31.0, 31.8, 26.6; HRMS calcd for $C_{12}H_{16}N_2$ 118.1313 ($M^+$), found 118.1321.

**General Procedure for the Preparation of 6-*tert*-Butyl-3*H*-pyrrolo[1,2-*a*]pyrrole (10) and 2-Phenyl-5,6-dihydropyrrolo[1,2-*a*]pyridine (17).** To a solution of diethyl malonate (0.34 g, 2 mmol) in DMF was added sodium hydride (0.08 g, 2 mmol) at room temperature. After the solution was stirred for 30 min, compound **8b** or **18a** (1 mmol) in DMF (5 mL) was added and the reaction mixture was refluxed for 12−24 h. After cooling, $Et_2O$ (50 mL) and water (50 mL) were added and the organic phase was separated, washed with water (3 × 30 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was separated by column chromatography using $CH_2Cl_2$/hexane (1:4) to afford the corresponding **10** or **17**.

**6-*tert*-Butyl-3*H*-pyrrolo[1,2-*a*]pyrrole (10):** yellow oil, 56% yield; $^1$H NMR $\delta$ 6.87 (s, 1 H), 6.22 (d, $J$ = 8.9 Hz, 2 H), 5.79 (s, 1 H), 4.43 (s, 2 H), 1.21 (s, 9 H); $^{13}$C NMR $\delta$ 153.3, 141.7, 116.1, 114.9, 111.2, 95.9, 50.9, 32.9, 30.1; HRMS calcd for $C_{11}H_{15}N$ 161.1205 ($M^+$), found 161.1205.

**2-Phenyl-5,6-dihydropyrrolo[1,2-*a*]pyridine (17):** yellow oil, 68% yield; $^1$H NMR $\delta$ 7.49 (d, $J$ = 7.1 Hz, 2 H), 7.31 (t, $J$ = 7.6 Hz, 2 H), 7.15 (t, $J$ = 7.3 Hz, 1 H), 6.86 (d, $J$ = 1.6 Hz, 1 H), 6.45 (d, $J$ = 9.8 Hz, 1 H), 6.31 (d, $J$ = 1.6 Hz, 1 H), 5.71−5.77 (m, 1 H), 3.97 (t, $J$ = 7.2 Hz, 2 H), 2.48−2.55 (m, 2 H); $^{13}$C NMR $\delta$ 135.8, 130.2, 128.6, 125.3, 124.9, 122.4, 120.1, 119.5, 117.8, 103.7, 43.8, 24.4; HRMS calcd for $C_{14}H_{13}N$ 195.1048 ($M^+$), found 195.1075.

**Preparation of 1-(phenylthio)-6-*tert*-butyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (11).** A solution of **8b** (0.50 g, 2 mmol) and sodium thiophenolate (0.66g, 5 mmol) in DMF (50 mL) was refluxed for 24 h. After cooling, water (50 mL) and $Et_2O$ (100 mL) were added and the organic phase was separated, washed with water (3 x 50 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was separated by column chromatography using $CH_2Cl_2$/hexane (1:4) as the eluent to give the product **11** as a yellow oil (0.33 g, 60% yield): $^1$H NMR $\delta$ 7.50 (d, $J$ = 8.2 Hz, 1 H), 7.34−7.40 (m, 2 H), 7.22−7.33 (m, 2 H), 6.39 (d, $J$ = 1.5 Hz, 1 H), 5.83 (d, $J$ = 1.5 Hz, 1 H), 4.69 (dd, $J$ = 7.5 and 2.9 Hz, 1 H), 3.82−3.94 (m, 2 H), 2.85−2.97 (m, 1 H), 2.47−2.56 (m, 1 H), 1.23 (s, 9 H); $^{13}$C NMR $\delta$ 141.1, 135.4, 135.3, 131.9, 128.8, 127.0, 109.7, 98.9, 44.9, 44.4, 36.5, 31.9, 31.1. Anal. Calcd for $C_{17}H_{21}NS$: N, 5.16. Found: N, 5.47.

**General Procedure for the Nucleophilic Substitution of 8a and 18a with Grignard Reagents.** To a solution of **8a** or **18a** (2 mmol) in toluene (30 mL) under argon was added a solution of an appropriate Grignard reagent (Schemes 1 and 2) (4 mmol) in $Et_2O$, and the reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressure, and the residue was extracted with $Et_2O$ (2 × 50 mL). The combined $Et_2O$ solution was washed with water (2 × 50 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography using $CH_2Cl_2$/hexane (1:4) as the eluent to give the corresponding product **12a**,**b** or **20**.

**1,6-Diphenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (12a):** yellow oil, 85% yield; $^1$H NMR $\delta$ 7.50 (d, $J$ = 7.1 Hz, 2 H), 7.20−7.38 (m, 7 H), 7.14 (t, $J$ = 7.4 Hz, 1 H), 6.99 (s, 1 H), 6.14 (d, $J$ = 1.0 Hz, 1 H), 4.40 (t, $J$ = 7.7 Hz, 1 H), 4.11−4.16 (m, 1 H), 3.95−4.10 (m, 1 H), 2.91−2.97 (m, 1 H), 2.39−2.45 (m, 1 H); $^{13}$C NMR $\delta$ 143.4, 140.4, 136.5, 129.4, 128.6, 128.5, 127.4, 126.7, 125.2, 124.9, 110.7, 98.4, 45.9, 43.6, 38.6; HRMS calcd for $C_{19}H_{17}N$ 259.1361 ($M^+$), found 259.1358.

**1-Methyl-6-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]pyrrole (12b):** yellow oil, 90% yield; $^1$H NMR $\delta$ 7.51 (d, $J$ = 7.1 Hz, 2 H), 7.32 (t, $J$ = 7.7 Hz, 2 H), 7.14 (t, $J$ = 7.4 Hz, 1 H), 6.88 (d, $J$ = 1.5 Hz, 1 H), 6.14 (d, $J$ = 1.2 Hz, 1 H), 4.00−4.06 (m, 1 H), 3.86−3.98 (m, 1 H), 3.21−3.34 (m, 1 H), 2.57−2.71 (m, 1 H), 2.00−2.12 (m, 1 H), 1.34 (d, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR $\delta$ 143.3, 136.4, 128.9, 128.4, 125.0, 124.9, 110.2, 96.2, 45.9, 36.7, 32.2, 19.7; HRMS calcd for $C_{14}H_{15}N$ 197.1205 ($M^+$), found 197.1267.

**2-Phenyl-8-benzyl-5,6,7,8-tetrahydropyrrolo[1,2-*a*]pyridine (20):** yellow oil, 80% yield; $^1$H NMR $\delta$ 7.48 (d, $J$ = 7.1 Hz, 2 H), 7.09−7.36 (m, 8 H), 6.80 (d, $J$ = 1.7 Hz, 1 H), 6.26 (d, $J$ = 1.7 Hz, 1 H), 3.81−3.97 (m, 2 H), 3.30 (dd, $J$ = 13.5 and 5.0 Hz, 1 H), 3.04−3.07 (m, 1 H), 2.68 (dd, $J$ = 13.5 and 9.8 Hz, 1 H), 1.94−2.00 (m, 1 H), 1.74−1.85 (m, 2 H), 1.34−1.39 (m, 1 H); $^{13}$C NMR $\delta$ 140.0, 136.1, 134.5, 129.2, 128.4, 128.3, 126.1, 125.1, 124.9, 124.2, 115.6, 102.0, 45.4, 41.8, 36.1, 26.7, 22.5; HRMS calcd for $C_{21}H_{21}N$ 288.1752 ($M^+$), found 288.1745.

**Preparation of Fused Indole 21.** To a solution of compound **18b** (0.80 g, 2.7 mmol) in THF (100 mL) was added a solution of *n*-BuLi (1.69 mL, 1.6 M in hexane) at −78 °C and the reaction mixture was stirred at this temperature for 30 min. A solution of *trans*-chalcone ((0.60 g, 2.7 mmol) in THF (10 mL) was added, and the reaction mixture was stirred and allowed to warm to room temperature overnight. The reaction was quenched with saturated $NH_4Cl$ solution (100 mL) and EtOAc (100 mL) added. The organic phase was separated, washed with water (3 × 100 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure to give the crude oily product **19** which was dissolved in THF (100 mL). To the solution of **19** was added *p*-toluenesulfonic acid monohydrate (0.19 g, 1 mmol), and the reaction mixture was refluxed for 3 h. After cooling, EtOAc (100 mL) and water (100 mL) were added, and the organic layer was separated, washed with water (3 × 300 mL), and dried ($MgSO_4$). After removal of the solvent, the residue was subjected to column chromatography using $CH_2Cl_2$/hexane (1:4) as the eluent to give compound **21** as white powder (0.49 g, 65%); mp 150−151 °C; $^1$H NMR $\delta$ 7.26−7.49 (m, 10 H), 6.97 (s, 1 H), 6.84 (s, 1 H), 4.12 (t, $J$ = 5.6 Hz, 2 H), 3.03 (t, $J$ = 6.0 Hz, 2H), 2.14−2.17 (m, 2 H), 1.08 (s, 9 H); $^{13}$C NMR $\delta$ 145.4, 141.0, 135.5, 133.9, 131.4, 130.7, 129.6, 127.9, 127.2, 126.8, 126.3, 126.1,

124.6, 1222.1, 117.9, 44.1, 32.1, 31.2, 24.2, 22.4. Anal. Calcd for $C_{27}H_{27}N$: N, 3.83. Found: N 3.63.

**General Procedure for the Preparation of 1-(Benzotriazol-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (25) and 1-[(Benzotriazol-1-yl)methyl]-1,2,3,4-tetrahydropyrido-[1,2-*a*]indole (27). One-Pot Method**. To a solution of 2-[(benzotriazol-1-yl)methyl]indole (**23**) (5 mmol) in THF (50 mL) was added a solution of *n*-BuLi (6.25 mL, 10 mmol, 1.6 M in hexane) at −78 °C. The temperature was allowed to warm to −30 °C, and the reaction mixture was stirred at this temperature for 30 min. After being cooled to −78 °C, a solution of 1-chloro-2-bromoethane or 1-chloro-3-bromopropane (5 mmol) in THF (5 mL) was added and the reaction mixture stirred at −78 °C for a further 3 h. HMPA (2 mL) was added, and the reaction solution was allowed to warm to room temperature and stirred overnight. Water (100 mL) and EtOAc (100 mL) were poured into the reaction mixture, and the organic phase was separated, washed with water (3 × 100 mL), and dried ($MgSO_4$). After removal of the solvent, the crystalline residue was recrystallized from EtOAc/hexane (1:3) to afford the corresponding **25** or **27**.

**1-(Benzotriazol-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (25):** white plates, 82% yield; mp 164−165 °C; $^1$H NMR $\delta$ 8.02 (d, $J$ = 6.9 Hz, 1 H), 7.56 (d, $J$ = 8.0 Hz, 1 H), 7.37 (d, $J$ = 8.2 Hz, 1 H), 7.21−7.31 (m, 4 H), 7.12 (t, $J$ = 7.6 Hz, 1 H), 6.82 (d, $J$ = 6.7 Hz, 1 H), 6.62 (dd, $J$ = 8.3 Hz, 1 H), 6.28 (s, 1 H), 4.38−4.46 (m, 1 H), 4.18−4.26 (m, 1 H), 3.21−3.34 (m, 1 H), 2.94−3.04 (m, 1 H); $^{13}$C NMR $\delta$ 146.4, 138.6, 132.6, 132.5, 131.5, 127.3, 123.9, 121.9, 121.6, 120.0, 110.0, 109.7, 95.6, 56.0, 42.7, 35.8. Anal. Calcd for $C_{17}H_{14}N_4$: C, 74.42; H, 5.15; N, 20.43. Found: C, 74.50; H, 5.20; N, 20.51.

**1-[(Benzotriazol-1-yl)methyl]-1,2,3,4-tetrahydropyrido-[1,2-*a*]indole (27):** white needles, 92% yield; mp 161−163 °C; $^1$H NMR $\delta$ 8.08 (d, $J$ = 8.5 Hz, 1 H), 7.50 (d, $J$ = 7.8 Hz, 1 H), 7.42 (d, $J$ = 8.1 Hz, 1 H), 7.25−7.34 (m, 3 H), 7.13 (t, $J$ = 7.9 Hz, 1 H), 6.89 (d, $J$ = 8.4 Hz, 1 H), 6.53 (t, $J$ = 7.2 Hz, 1 H), 6.09 (s, 1 H), 4.35−4.17 (m, 2 H), 2.48−2.60 (m, 2 H), 2.21−2.41 (m, 2 H); $^{13}$C NMR $\delta$ 146.4, 136.4, 132.2, 132.1, 127.7, 127.2, 123.8, 122.0, 120.9, 120.4, 120.2, 110.7, 109.4, 100.8, 55.1, 42.1, 28.8, 21.3. Anal. Calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.92; H, 5.57; N, 19.45.

**Two Step Method.** To a solution of compound **23** (2.5 g, 10.1 mmol) in THF (150 mL) was added a solution of *n*-BuLi (12.63 mL, 20.2 mmol, 1.6 M in hexane) at −78 °C, and the temperature was raised to −30 °C. The reaction mixture was stirred at this temperature for 30 min and cooled to −78 °C. A solution of 1-chloro-3-bromopropane (1.60 g, 10.1 mmol) in THF (10 mL) was added, and the mixture was stirred for 3 h at −78 °C. The reaction was quenched with saturated $NH_4Cl$ solution and extracted with EtOAc (100 mL), and the organic phase was separated, washed with water (3 × 100 mL), and dried ($MgSO_4$). After removal of the solvent, the crystalline residue was recrystallized from EtOAc/hexane (1:4) to give the product **28** as white needles (3.02 g, 92% yield): mp 136−138 °C; $^1$H NMR $\delta$ 9.36 (s, 1 H), 7.84 (d, $J$ = 8.4 Hz, 1 H), 7.66 (d, $J$ = 7.7 Hz, 1 H), 7.31−7.40 (m, 3 H), 7.11−7.28 (m, 3 H), 6.76 (s, 1 H), 6.23 (t, $J$ = 7.8 Hz, 1 H), 3.53−3.63 (m, 2 H), 2.76−2.85 (m, 2 H), 1.84−1.94 (m, 1 H), 1.69−1.76 (m, 1 H); $^{13}$C NMR $\delta$ 146.0,136.9, 134.3, 132.1, 127.7, 127.5, 124.3, 122.8, 120.8, 120.2, 119.7, 111.4, 109.9, 101.8, 57.6, 44.0, 31.1, 29.1. Anal. Calcd for $C_{18}H_{17}ClN_4$: C, 66.56; H, 5.28; N, 17.25. Found: C, 66.22; H, 5.36; N, 17.20.

To a solution of compound **28** (1.62 g, 5 mmol) in DMSO (20 mL) was added sodium hydride (0.15 g, 5 mmol, 80% in dispersion in mineral oil) at room temperature, and the reaction mixture was stirred at this temperature for 12 h. EtOAc (50 mL) and water (50 mL) were added, and the organic phase was separated, washed with water (3 × 50 mL), and dried ($MgSO_4$). The solvent was removed under reduced pressure to give the crystalline residue which was recrystallized from EtOAc/hexane (1:3) to afford product **27** (1.30 g, 90% yield).

**General Procedure for the Reaction of 1-(Benzotriazol-1-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (25) and 1-[(Benzotriazol-1-yl)methyl]-1,2,3,4-tetrahydropyrido-[1,2-*a*]indole (27) with Grignard Reagents.** To a solution of **25** or **27** (2.5 mmol) in toluene (30 mL) under argon was added a solution of Grignard reagent (Scheme 1) (5 mmol) in $Et_2O$ (10 mL), and the reaction was refluxed for the time indicated in Scheme 3. The solvent was removed under reduced pressure, and the residue was extracted with $Et_2O$ (2 × 50 mL). The combined organic solution was washed with water (3 × 50 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was separated by column chromatography using $Et_2O$/hexane (1:1) as the eluent to give the corresponding product **29** or **32**.

**1-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (29):** white needles, 70% yield; mp 49−50 °C; $^1$H NMR $\delta$ 7.57 (d, $J$ = 7.1 Hz, 1 H), 7.24 (d, $J$ = 7.7 Hz, 1 H), 7.04−7.20 (m, 2 H), 6.16 (s, 1 H), 4.07−4.15 (m, 1 H), 3.92−4.01 (m, 2 H), 3.35−3.42 (m, 1 H), 2.71−2.81 (m, 1 H), 2.12−2.22 (m, 1 H), 1.39 (d, $J$ = 6.9 Hz, 3 H); $^{13}$C NMR $\delta$ 149.6, 133.0, 132.5, 120.4, 120.2, 119.0, 109.3, 91.4, 43.1, 36.9, 32.1, 19.5. Anal. Calcd for $C_{12}H_{13}N$: N, 8.18. Found: N, 7.94.

**1-Phenyl-1,2,3,4-tetrahydropyrido[1,2-*a*]indole (32):** yellow oil, 58% yield; $^1$H NMR $\delta$ 7.46 (d, $J$ = 7.8 Hz, 1 H), 7.21−7.33 (m, 6 H), 7.16 (t, $J$ = 7.7 Hz, 1 H), 7.06 (t, $J$ = 8.0 Hz, 1 H), 5.92 (s, 1 H), 4.17−4.25 (m, 2 H), 3.94−4.03 (m, 1 H), 2.18−2.23 (m, 2 H), 1.91−2.16 (m, 2 H); $^{13}$C NMR $\delta$ 144.4, 140.4, 136.3, 128.3, 128.1, 126.6, 120.5, 119.9, 119.7, 108.8, 99.5, 42.4, 42.3, 30.8, 22.2. Anal. Calcd for $C_{18}H_{17}N$: C, 87.40; H, 6.93; N, 5.67. Found: C, 87.14; H, 7.35; N, 5.32.

**Preparation of 1-(*trans*-5-Methyl-2-phenyl-1-oxo-2-hexenyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (31).** To a stirred solution of compound **25** (0.82 g, 3 mmol) in THF (100 mL) was added a solution of *n*-BuLi (1.88 mL, 3 mmol) at −78 °C. After 30 min, a solution of 5-methyl-2-phenyl-2-hexenal (0.56 g, 3 mmol) in THF (10 mL) was added and the reaction mixture was allowed to warm to room temperature overnight. The reaction was quenched with saturated $NH_4Cl$ solution (100 mL) and extracted with EtOAc (100 mL). The organic phase was separated, washed with water (3 × 100 mL), and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was dissolved in THF (50 mL). To this THF solution was added *p*-toluenesulfonic acid monohydrate (0.57 g, 3 mmol), and the resulting reaction mixture was refluxed for 24 h. After cooling, EtOAc (50 mL) and water (50 mL) were added, and the organic layer was separated, washed with water (3 × 50 mL), and dried ($MgSO_4$). The solvent was removed to give an oily residue which was subjected to column chromatography using EtOAc/hexane (1:4) as the eluent to afford the product **31** as a white solid (0.54 g, 52% yield): mp 146−148 °C; $^1$H NMR $\delta$ 7.54 (d, $J$ = 7.8 Hz, 1 H), 7.29−7.40 (m, 3 H), 7.23 (d, $J$ = 8.1 Hz, 1 H), 7.03−7.16 (m, 5 H), 6.18 (s, 1 H), 4.83 (dd, $J$ = 8.2 and 4.4 Hz, 1 H), 4.17−4.26 (m, 1 H), 4.04−4.11 (m, 1 H), 3.07−3.15 (m, 1 H), 2.63−2.69 (m,1 H), 2.12 (t, $J$ =7.1 Hz, 2 H), 1.81−1.90 (m, 1 H), 0.96 (d, $J$ = 6.6 Hz, 6 H); $^{13}$C NMR $\delta$ 196.8, 144.5, 143.0, 141.7, 135.8, 132.9, 132.6, 129.7, 128.2, 127.5, 121.0, 120.7, 119.4, 109.6, 94.3, 44.9, 43.4, 38.9, 30.8, 28.6, 22.6, 22.5. Anal. Calcd for $C_{24}H_{25}NO$: N, 4.08. Found: N, 3.97.

**Preparation of Fused Indolo[3,2-*b*]carbazole 33.** To a solution of compound **27** (1.16 g, 4.03 mmol) in $CH_2Cl_2$ (30 mL) was added $ZnBr_2$ (1.00 g, 4.4 mmol), and the reaction mixture stirred at room temperature for 12 h. The reaction solution was filtered. The filtrate was washed with water (3 × 50 mL) and dried ($MgSO_4$). After evaporation of the solvent, the product was separated by column chromatography using $CH_2Cl_2$/hexane (1:4) as the eluent to afford product **32** as yellow powder (0.67 g, 50% yield): $^1$H NMR $\delta$ 8.24 (d, $J$ = 7.7 Hz, 2 H), 7.40−7.49 (m, 4 H), 7.20−7.28 (m, 2 H), 4.33 (t, $J$ = 5.2 Hz, 4 H), 3.64 (t, $J$ = 5.4 Hz, 4 H), 2.50−2.54 (m, 4 H); $^{13}$C NMR $\delta$ 124.8, 122.4, 117.6, 113.8, 40.9, 23.3, 22.6 (other quaternary carbon signals were not observed due to the poor solubility of the sample in organic solvents); HRMS calcd for $C_{24}H_{20}N_2$ 336.1627 ($M^+$), found 336.1627.

**Supporting Information Available:** HRMS and NMR spectra of compounds **9**, **10**, **12a**, **12b**, **17**, **20**, and **33** (14 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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