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A Novel Entry to Pyrido[4,3-*b*]carbazoles: An Efficient Synthesis of Ellipticine

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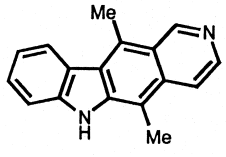
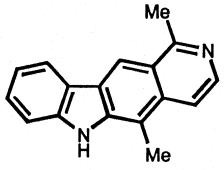
Abstract—The palladium catalyzed tandem cyclization–cross-coupling reaction of indolylborate (**2**) with vinyl bromide (**9**) was developed for the preparation of pyrido[4,3-*b*]carbazole as a key reaction. The cross-coupling reaction of **2a** provided hexatriene (**10**), and then cyclization of **10** to pyrido[4,3-*b*]carbazole (**12**) was effected with irradiation or Lewis acid. Using indolylborate (**2c**) for the cross-coupling reaction, a novel construction of ellipticine was attained through similar reaction sequences.

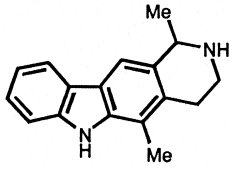
Ellipticine is a member of pyrido[4,3-*b*]carbazole alkaloids (such as olivacine, janetine, strellidimine) with a planar structure, and was isolated from the stems of *Ochrosia elliptica* Labill (Apocynaceae).[1] *Strychnos dinklagei* Gilg. proved to be a good source of pyridocarbazole alkaloids of the ellipticine series.[2] In 1967, ellipticine and its derivatives were found to possess promising antitumor activities,[3] which, since then, has prompted a vast range of investigation of the structure–activity relationships of this structurally simple alkaloid.[4] To date, numerous efforts have also been invested in developing efficient synthetic avenues to ellipticine and its structurally modified derivatives, which are well documented.[5]



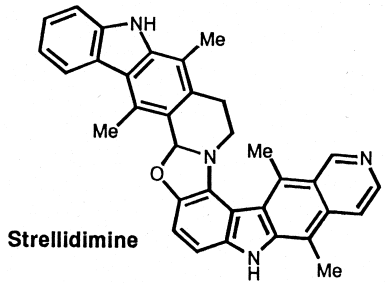
Ellipticine



Olivacine



Janetine



Strellidimine

Prompted by our previous work dealing with the palladium catalyzed tandem cyclization–cross-coupling reaction of indolylborate (**2**),[6] we have become interested in the construction of pyrido[4,3-*b*]carbazole based on this protocol, a part of which has been reported previously.[7] Our synthetic approach is outlined in Scheme 1, wherein pyrido[4,3-*b*]carbazole (**5**) was viewed as arising from the cyclization of hexatriene (**4**). The hitherto known cyclization of a similar hexatriene system has been conducted on the thermal electrocyclic process involving pyridine 3,4-quinodimethane and indole 2,3-quinodimethane intermediates at high temperature.[8] In our case, hexatriene (**4**) is an isolable product of the palladium catalyzed tandem cyclization–cross-coupling reaction of indolylborate (**2**) with vinyl bromide (**3**). We now report the full details of a novel construction of pyrido[4,3-*b*]carbazoles and the total synthesis of ellipticine by the use of the palladium catalyzed tandem cyclization–cross-coupling reaction of indolylborates (**2**) with vinyl bromides (**9**) as a key reaction.

Vinyl bromides (**9**), requisite for the cross-coupling reaction with **2**, were prepared according to the sequences outlined in

Keywords: indolylborate; pyrido[4,3-*b*]carbazole; cross-coupling reaction; ellipticine.

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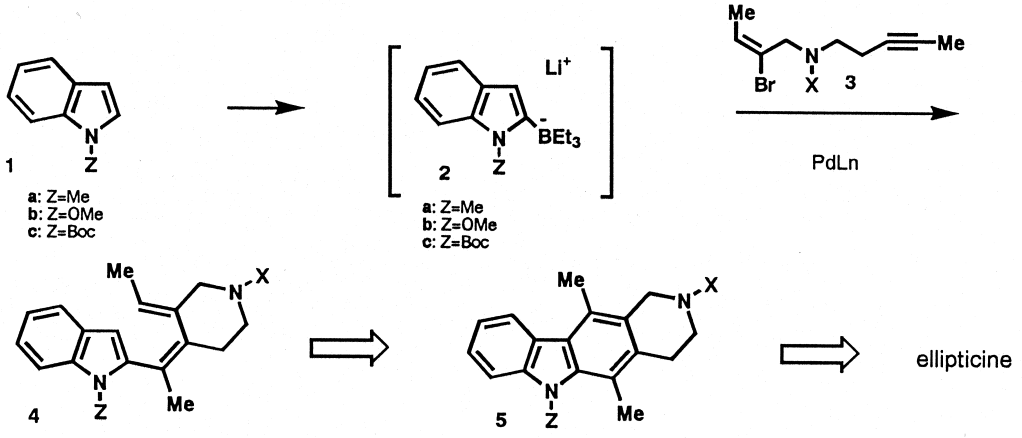
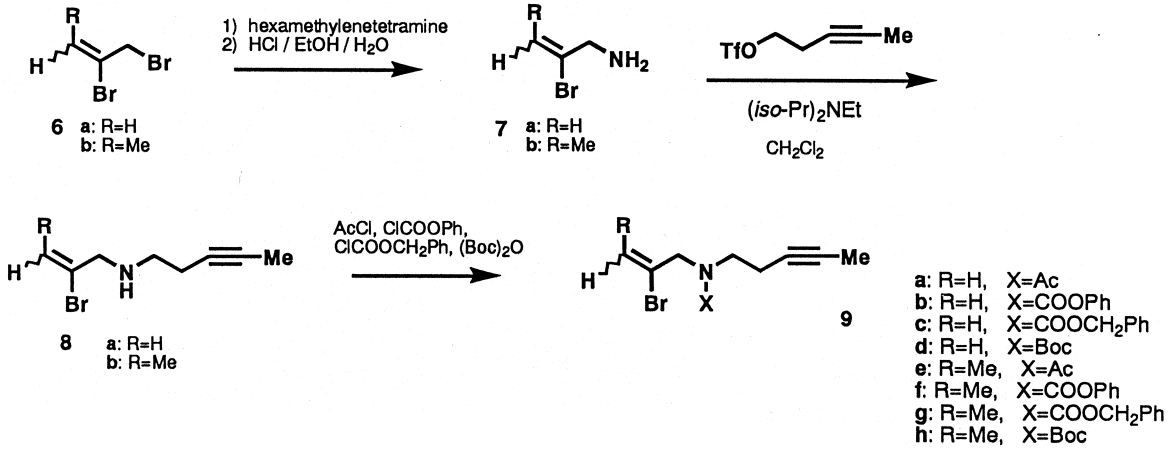
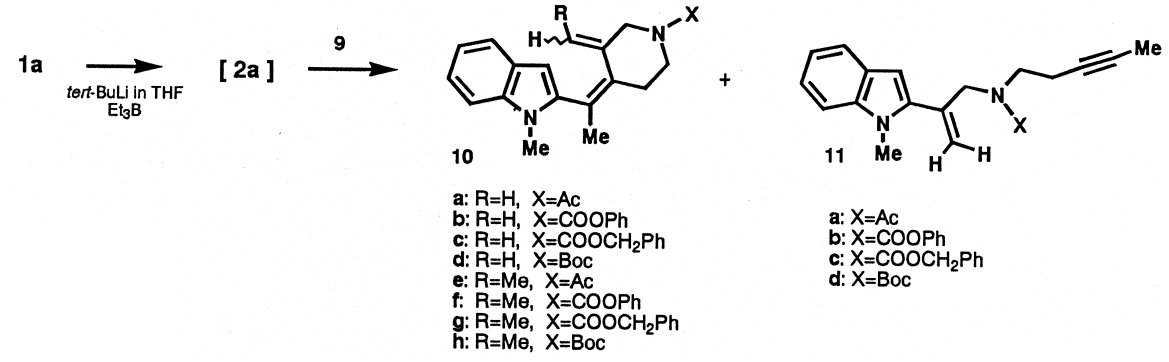


Scheme 1.



Scheme 2.



Scheme 3.

Scheme 2. Allylamine (**7a**) was readily obtained by the treatment of hexamethylenetetramine and commercially available 2,3-dibromopropene (**6a**) according to the literature.[9] Similar treatment of hexamethylenetetramine with a mixture of (*E*)- and (*Z*)-1,2-dibromo-2-butene (**6b**), derived from a *cis–trans* mixture of crotyl alcohol in several steps,[10] provided an isomeric mixture of (*E*)- and (*Z*)-**7b**. Alkylation of allylamines (**7**) with pent-3-ynyl trifluoromethanesulfonate gave **8**, and subsequent protection of a *sec*-amino group in **8** provided vinyl bromides (**9**).

The palladium catalyzed tandem cyclization–cross-coupling reaction was carried out by heating **2a** [generated in situ from 1-methylindole (**1a**) (2 equiv.) and *tert*-butyllithium, followed by treatment with triethylborane] with **9** in the presence of a catalytic amount of palladium complex in THF under argon atmosphere at 60°C (Scheme 3), and these results are summarized in Table 1, which discloses the crucial role of Ph_3P on the reaction outcome. The reaction of **2a** with **9a–d** led to the formation of hexatrienes (**10a–d**) and vinylindoles (**11**). Use of Pd complex without Ph_3P

Table 1. Reaction of indolyborate (**2a**) with vinyl bromides (**9**)

R	X	PdLn	Yield (%)[a]	
			10	**11**
H	Ac	$Pd(Oac)_2$	43 (**10a**)	29 (**11a**)
H	Ac	$PdCl_2(CH_3CN)_2$	43 (**10a**)	30 (**11a**)
H	Ac	$Pd_2(dba)_3{\cdot}CHCl_3$	44 (**10a**)	30 (**11a**)
H	Ac	$Pd_2(dba)_3{\cdot}CHCl_3+4PPh_3$	10 (**10a**)	60 (**11a**)
H	Ac	$PdCl_2(PPh_3)_2$	5 (**10a**)	62 (**11a**)
H	Ac	$Pd(PPh_3)_4$	8 (**10a**)	61 (**11a**)
H	COOPh	$Ph(OAc)_2$	44 (**10b**)	29 (**11b**)
H	COOPh	$PdCl_2(CH_3CN)_2$	48 (**10b**)	29 (**11b**)
H	COOPh	$Pd_2(dba){\cdot}CHCl_3$	45 (**10b**)	30 (**11b**)
H	COOPh	$Pd_2(dba)_3{\cdot}CHCl_3+4PPh_3$	19 (**10b**)	53 (**11b**)
H	COOPh	$PdCl_2(PPh_3)_2$	16 (**10b**)	56 (**11b**)
H	COOPh	$Pd(PPh_3)_4$	10 (**10b**)	59 (**11b**)
H	$COOCH_2Ph$	$Pd(OAc)_2$	39 (**10c**)	18 (**11c**)
H	$COOCH_2Ph$	$Pd_2(dba)_3{\cdot}CHCl_3$	45 (**10c**)	30 (**11c**)
H	Boc	$Pd(OAc)_2$	20 (**10d**)	11 (**11d**)
H	Boc	$Pd_2(dba)_3{\cdot}CHCl_3$	43 (**10d**)	22 (**11d**)
Me	Ac	$Pd(OAc)_2$	23 (**10e**)	–
Me	Ac	$PdCl_2(CH_3CN)_2$	35 (**10e**)	–
Me	Ac	$Pd_2(dba)_3{\cdot}CHCl_3$	26 (**10e**)	–
Me	Ac	$Pd_2(dba)_3{\cdot}CHCl_3+4PPh_3$	60 (**10e**)	–
Me	Ac	$PdCl_2(PPh_3)_2$	67 (**10e**)	–
Me	Ac	$Pd(PPh_3)_4$	46 (**10e**)	–
Me	COOPh	$Pd(OAc)_2$	14 (**10f**)	–
Me	COOPh	$PdCl_2(CH_3CN)_2$	30 (**10f**)	–
Me	COOPh	$Pd_2(dba)_3{\cdot}CHCl_3$	25 (**10f**)	–
Me	COOPh	$Pd_2(dba)_3{\cdot}CHCl_3+4PPh_3$	71 (**10f**)	–
Me	COOPh	$PdCl_2(PPh_3)_2$	70(**10f**)	–
Me	COOPh	$Pd(PPh_3)_4$	34 (**10f**)	–
Me	$COOCH_2Ph$	$Pd_2(dba)_3{\cdot}CHCl_3+4PPh_3$	66 (**10g**)	–
Me	$COOCH_2Ph$	$PdCl_2(PPh_3)_2$	68 (**10g**)	–
Me	Boc	$Pd_2(dba)_3{\cdot}CHCl_3+4PPh_3$	67 (**10h**)	–
Me	Boc	$PdCl_2(PPh_3)_2$	69 (**10h**)	–

[a] Isolated yields (%) based on indole (**1**).

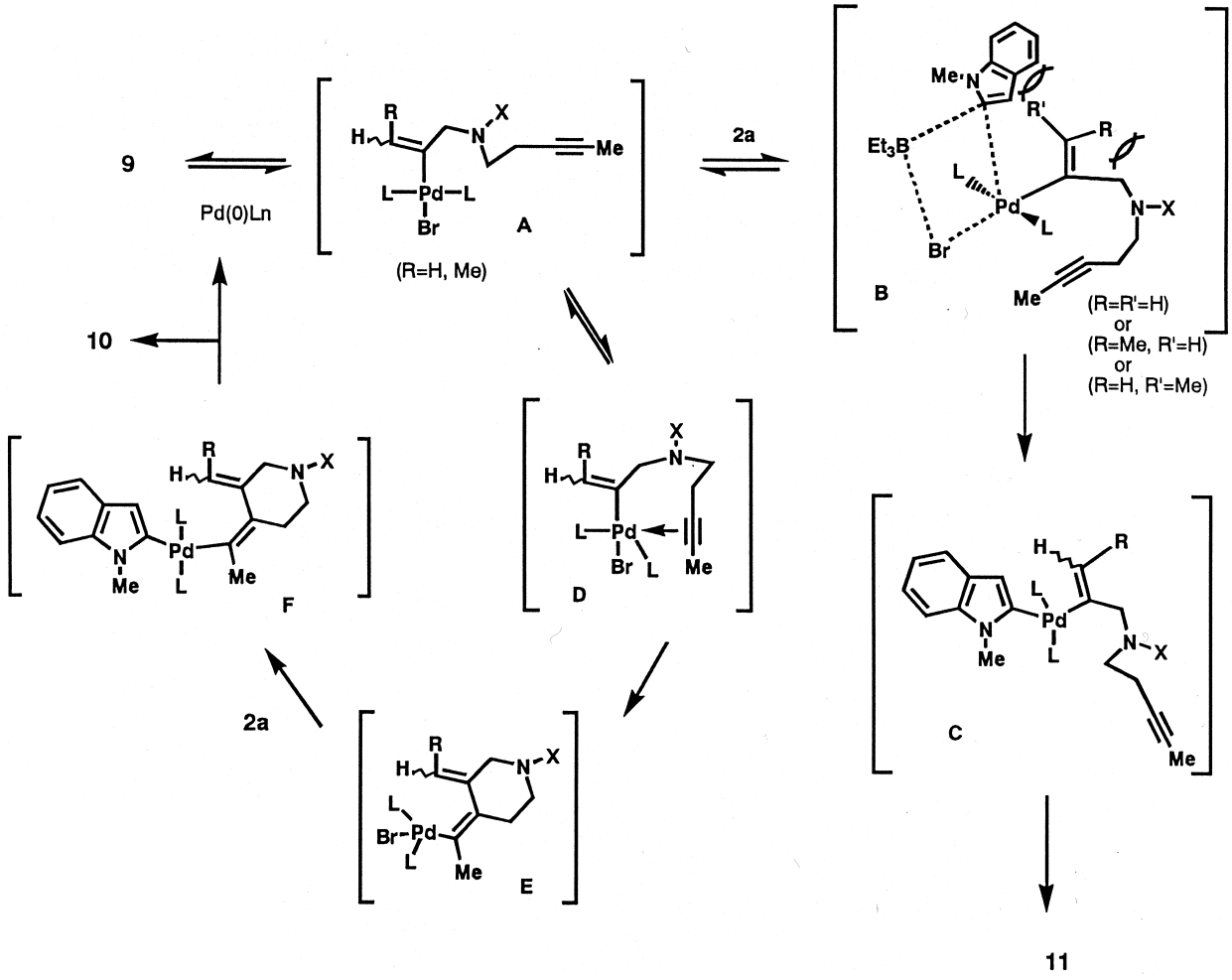
effectively drives the reaction in the direction of preferential formation of desired **10a**–**d**, while the reaction in the presence of Pd complex with Ph_3P meets with the predominant formation of **11a**,**b**. In contrast to these trends, the observation that hexatrienes (**10e**–**h**) are invaluably sole products, and using Pd complex with Ph_3P appreciably increases the yields of **10e**–**h** on the reaction of **2a** with **9e**–**h**, is notable.

The outcome of the present reaction of **2a** with **9** would be understandable (Scheme 4). Catalytically active Pd(0) species [Pd(0)Ln], generated in the reaction medium, undergoes an oxidative addition to **9** to produce vinylpalladium complex (**A**). Through a faster transmetallation with **2a**, complex (**A**) produces **11** via complex (**C**). For the putative transmetallation step, the well known four-centered σ-bond metathesis process [transition state (**B**)] seems to be acceptable.[11] If the acetylene bond is complexed intramolecularly to Pd, complex (**E**) results from complex (**D**) via carbopalladation, and subsequent transmetallation between complex (**E**) and **2a** brings about complex (**F**). Reductive elimination from complex (**F**) forms **10** and Pd(0) species. Stabilization of complex (**A**) by ligation of Ph_3P through d–π backbonding is likely to change significantly the reactivity, which implies that the transmetallation beteween complex (**A**) (L=PPh_3) with anionic **2a** seems to precede weaker side-on complexation of the acetylene bond to Pd [complex (**D**)]. Thus, on reaction of **2a** with **9a**–**d** using Pd complex ligated by PPh_3, the pronounced tendency to form **11** rather than **10a**–**d** is perceivable. Otherwise, on reaction of **2a** with **9e**–**h**, the transition state (**B**) involves spatial repulsive interaction arising from the methyl group on the vinyl carbon (R=H, R′=Me or R=Me, R′=H in **B**), which diminishes the transmetallation step and enhances the formation of **10e**–**h**.

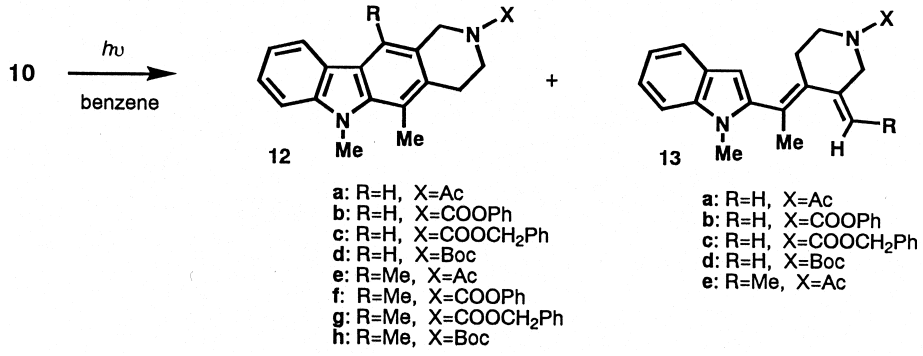
With an effective preparation of hexatrienes (**10**) in hand, we then turned our attention to the conversion of **10** to pyridocarbazoles (**12**). As a photocyclization protocol represents a great potential for the conversion of styrylindoles to carbazoles,[12] a study was firstly undertaken to explore if this photo-cyclization protocol would be effective for the conversion of **10** to pyridocarbazoles (**12**). Irradiation of **10** was undertaken with a high-pressure mercury lamp in benzene to afford the desired **12** as an oxidized form and/or isomeric hexatrienes (**13**)[13] (Scheme 5). Irradiation of **10f**–**h** produced **12f**–**h**, solely, except for the case of **10e** giving **12e** accompanied by substantial photochemical isomerization to **13e**, while the reaction of **10a**–**d** led to the concomitant formation of **12a**–**d** and **13a**–**d** (Table 2).

As complexation of an unsaturated system with a Lewis acid is known to lower the activation energy to accelerate some pericyclic reactions,[14] a study was also undertaken to explore whether a Lewis acid would also be effective for cyclization of **10**. The reaction of **10** with 2 equiv. of Lewis acid in CH_2Cl_2 was carried out to give the desired **12** and spiroindolines (**14**), where the ratio of **12**:**14** was apparently affected by the nature of the Lewis acid used (Scheme 6 and Table 3). Thus, $TiCl_4$ was found to effect the desired conversion of **10** to **12** with pronounced selectivity. Otherwise, BF_3OEt_2, and ZnI_2 mediated reactions of **10** led to spiroindolines (**14**), in which a 1:1 mixture of diastereomeric isomers **14f** and **14f′** was obtained from **10f**. Structural elucidation of **14** was based on X-ray crystal analysis of **14a**[7] and their spectral data (see Experimental section). Exposure of **10a** to trifluoroacetic acid again promoted the spiroannelation leading to **14a**, and thus, a postulated path is shown in Scheme 7 which involves initial attack of acid at the 3-position of the indole ring of **10a**, followed by spiroannulation. The NOE experiments confirmed the twisted conformation of **10a**, which was also supported by the optimized structure in $CHCl_3$ obtained by the MM3-AM1 method[15] (Fig. 1). Thus, a great tendency of acid mediated spiroannulation to **14** as well as photochemical isomerization to **13** is ascribable to the distortion of this hexatriene system of **10**.

Since the desired pyrido[4,3-*b*]carbazole (**12**) was obtained, efforts were focused on developing further conversion protocols to 6-methylellipticine derivatives. Removal of the carbobenzyloxy group in **12c** and **12g** was attained smoothly under normal catalytic hydrogenation conditions using 20% $Pd(OH)_2$ on **C**, giving **15a** and **15b**, respectively. Completion of this sequence was undertaken to oxidize **15** with MnO_2 to **17**, which could be conducted under much milder conditions rather than the heretofore adapted protocol using Pd–C at high temperature (200°C).[5] Heating **15a** and **15b** with MnO_2 in AcOEt under reflux gave 11-demethyl-6-methylellipticine (**17a**) in 62% yield and 6-methylellipticine (**17b**)[16] in 60% yield. Mild oxidation of **15b** in CH_2Cl_2 at room temperature allowed the isolation



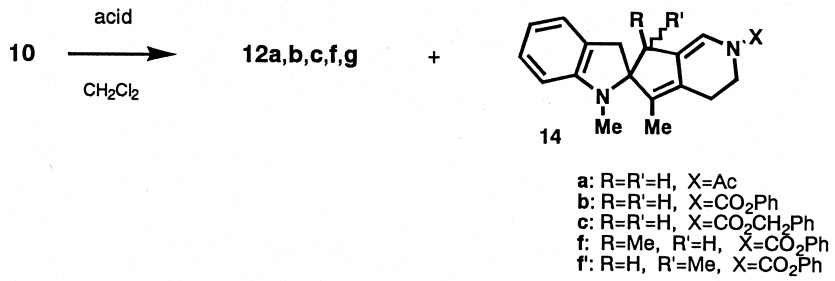
Scheme 4.



Scheme 5.

Table 2. Photocyclization of hexatriene (**10**)

R	X	Yield (%)		R	X	Yield (%)	
		12	**13**			**12**	**13**
H	Ac	15 (**12a**)	50 (**13a**)	Me	Ac	21 (**12e**)	50 (**13e**)
H	COOPh	35 (**12b**)	30 (**13b**)	Me	COOPh	48 (**12f**)	–
H	$COOCH_2Ph$	38 (**12c**)	30 (**13c**)	Me	$COOCH_2Ph$	50 (**12g**)	–
H	Boc	41 (**12d**)	28 (**13d**)	Me	Boc	56 (**12h**)	–



Scheme 6.

of **16** in 56% yield, which was converted to **17b** in 60% yield on heating with MnO_2 in AcOEt under reflux (see Scheme 8).

Hereupon, we have aimed for the total synthesis of ellipticine, which implies that the present protocol requires indolylborate (**2**) bearing a removable protecting group at the 1-position since ellipticine does not position a substituent at this position.

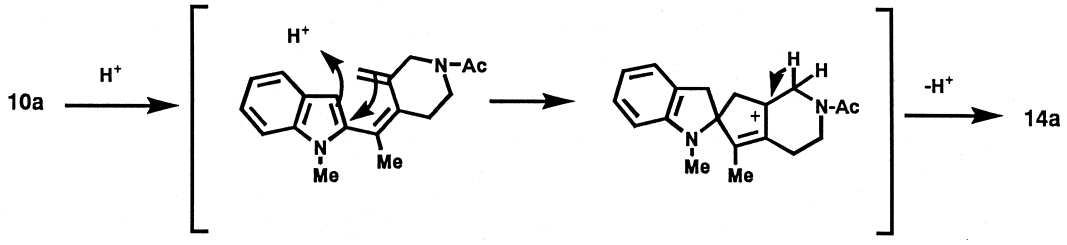
The cross-coupling reaction of 1-methoxyindolylborate (**2b**), derived from indole (**1b**) in situ, with **9c** in the presence of $Pd_2(dba)_3{\cdot}CHCl_3$ in THF at 60°C under argon atmosphere provided hexatriene (**18**) in 51% yield and vinylindole (**19**) in 18% yield (Scheme 9). Attempted cyclization of **18** to pyrido[4,3-*b*]carbazole, using photocyclization or an acid promoted cyclization protocol, resulted in a complex mixture, which is consistent with the known labilities of 1-methoxyindole derivatives under acidic and photochemical conditions.[17] This sequence was not pursued in further detail.

Table 3. Acid promoted cyclization of hexatriene (**10**)

R	X	Acid	Condition[a]	Yield (%)[b]	
				12	**14**
H	Ac	$BF_3{\cdot}OEt_2$	A	–	67 (**14a**)
H	Ac	TFA	A	–	68 (**14a**)
H	COOPh	$BF_3{\cdot}OEt_2$	A	–	41 (**14b**)
H	$COOCH_2Ph$	$BF_3{\cdot}OEt_2$	A	–	35 (**14c**)
H	Boc	$BF_3{\cdot}OEt_2$	A	–	–
H	Ac	ZnI_2	B	–	53 (**14a**)
H	COOPh	ZnI_2	B	–	45 (**14b**)
H	$COOCH_2Ph$	ZnI_2	B	–	65 (**14c**)
H	Boc	ZnI_2	B	–	–
H	Ac	$TiCl_4$	C	50 (**12a**)	17 (**14a**)
H	COOPh	$TiCl_4$	C	73 (**12b**)	–
H	$COOCH_2Ph$	$TiCl_4$	C	48 (**12c**)	–
H	Boc	$TiCl_4$	C	–	–
Me	COOPh	$BF_3{\cdot}OEt_2$	B	–	40 (**14f**+**14f′**)[c]
Me	COOPh	$TiCl_4$	C	70 (**12d**)	–
Me	$COOCH_2Ph$	$TiCl_4$	C	40 (**12e**)	–

[a] A: at rt for 3 h; B: at rt for 20 h; C: at −78°C for 4 h.
[b] Isolated yield (%).
[c] **14f**:**14f′**=1:1 mixture.

In summary, a novel route to ellipticine and its derivatives has been realized through the palladium catalyzed tandem cyclization–cross-coupling reaction of indolylborate (**2**) as a key reaction. The one-pot tandem cyclization–cross-coupling reaction of **2a** with **9** provides hexatriene (**10**) and the conversion of **10** to pyrido[4,3-*b*]carbazole (**12**) could be effected by irradiation and with $TiCl_4$. In addition, it was found that cyclization of **10** mediated by $BF_3{\cdot}OEt_2$ undergoes spiroannelation to produce spiroindoline (**13**). Subsequently, **12** could be converted to 6-methylellipticine via oxidation. Furthermore, a novel access to ellipticine was realized by using indolylborate **2c** through the present sequences.



Scheme 7.

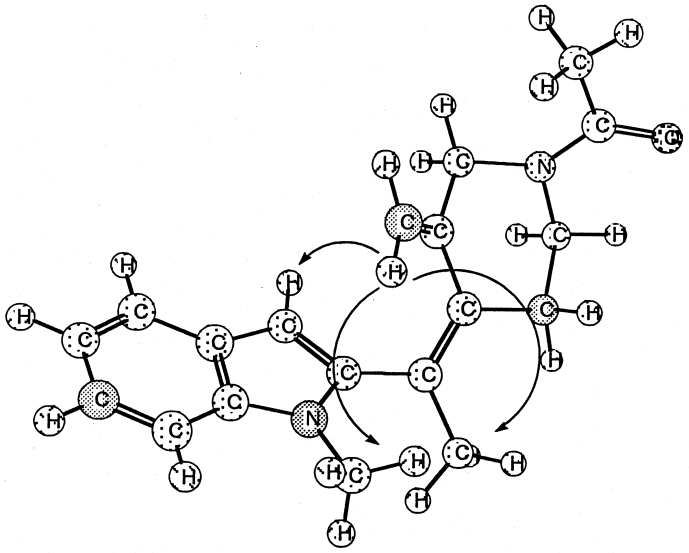
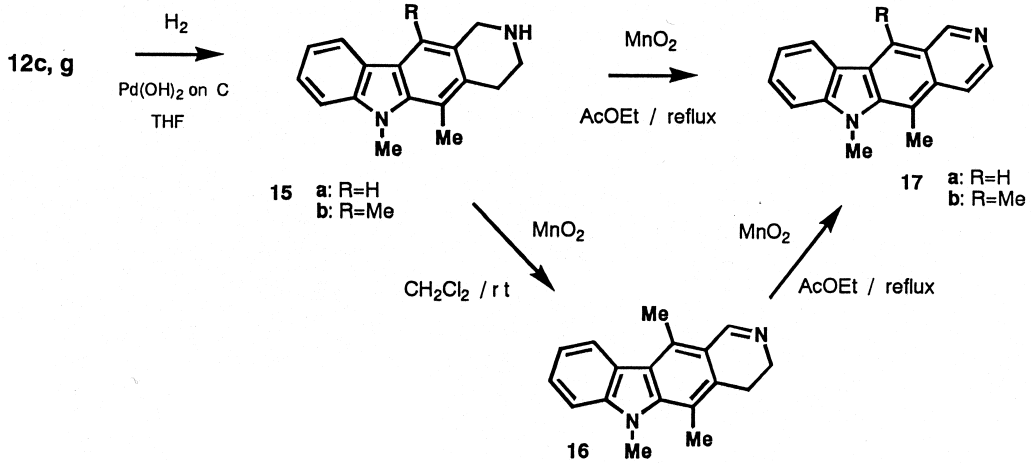
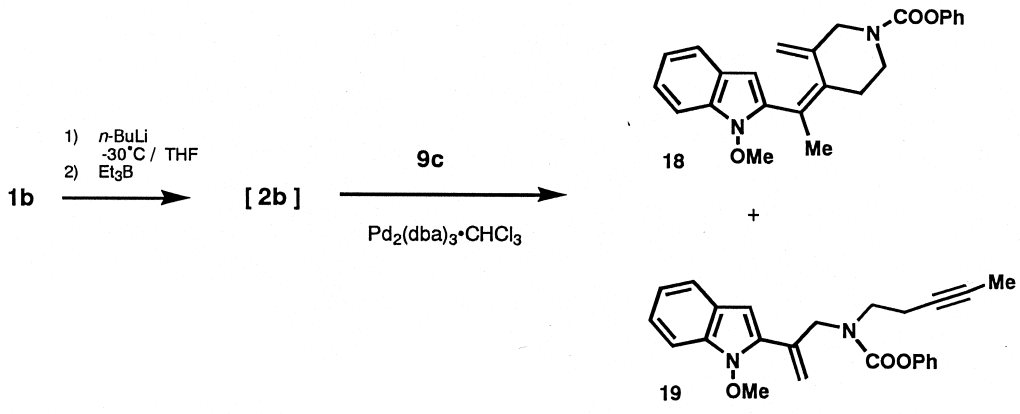


Figure 1. Optimized structure of hexatriene (**10a**) and NOE correlations.



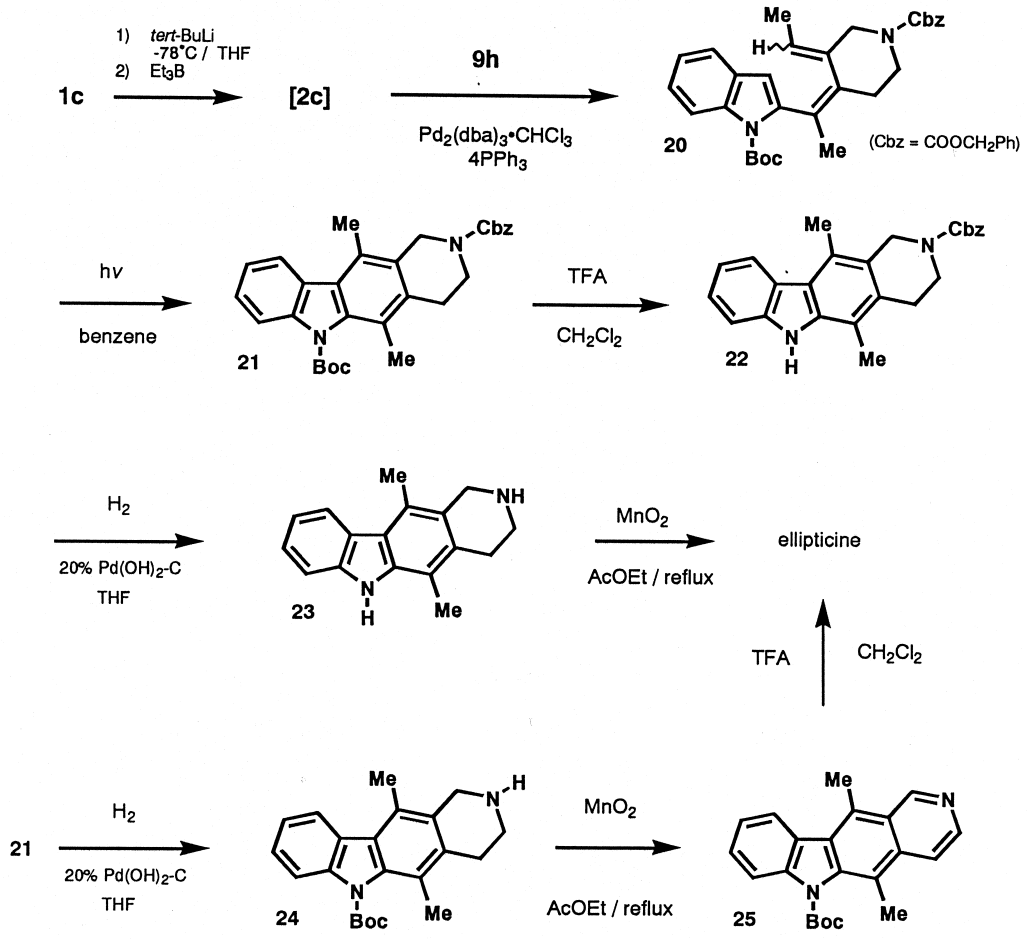
Scheme 8.



Scheme 9.

Experimental

Melting points were recorded on a Yamato MP21. All melting points and boiling points are uncorrected. MS and high-resolution MS were recorded on a Micromass AutoSpec 3100 mass spectrometer. IR spectra were measured on a Hitachi Model 270-30 spectrometer. The NMR experiments were performed with a JEOL JNM-LA300 or JNM-EX400



Scheme 10.

spectrometer, and chemical shifts are expressed in ppm (δ) with tetramethylsilane (TMS) as an internal reference. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, br=broad. Medium pressure liquid chromatography (MPLC) and flash chromatography were performed on silica gel (silica gel 60N, Kanto Chemical Co., Inc.). Dehydrated tetrahydrofuran (THF) and diethyl ether (Et_2O) were purchased from Kanto Chemical Co., Inc.

(2-Bromoprop-2-enyl)pent-3-ynylamine (8a). Trifluoromethanesulfonic anhydride (10 ml, 59 mmol) was added dropwise to a solution of diisopropylethylamine (7.7 g, 59 mmol) and 3-pentyn-1-ol (4.6 g, 54 mmol) in CH_2Cl_2 (100 ml) under ice-cooling, and stirring was continued for 20 min. Then, this solution was added dropwise to a solution of 2-bromoprop-2-enylamine (**7a**)[9] (14.7 g, 108 mmol) and diisopropylethylamine (7.7 g, 59 mmol) in CH_2Cl_2 (100 ml) under ice-cooling, and the whole mixture was stirred at room temperature overnight. After the mixture was concentrated in vacuo, the residue was extracted with ether, and the organic layer was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was distilled under reduced pressure to give 8.4 g (77%) of **8a**. Bp 76–78°C/1 mmHg. IR (neat): 3312, 1626 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.78 (t, 3H, J=2.5 Hz), 2.30–2.35 (m, 2H), 2.60–2.70 (m, 2H), 3.48 (s, 2H), 5.55 (s, 1H), 5.81 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 3.5, 19.9, 46.6, 57.1, 76.8, 76.9, 117.3, 133.4. Anal. Calcd for $C_8H_{12}BrN$: C, 47.55; H, 5.98; N, 6.93. Found: C, 47.48; H, 5.91; N, 7.00.

(2-Bromobut-2-enyl)pent-3-ynylamine (8b). According to the above procedure, 9.9 g (75%) of **8b** was obtained from 3-pentyn-1-ol (5.2 g, 62 mmol) and 2-bromobut-2-enylamine (**7b**) (18.5 g, 123 mmol). Bp 80–81°C/0.5 mmHg. IR (neat): 3312, 1656 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.73 (d, 1.5H, J=7 Hz), 1.77 (d, 1.5H, J=7 Hz), 1.79 (t, 3H, J=2.5 Hz), 2.20 (br s, 1H), 2.25–2.38 (m, 2H), 2.57–2.68 (m, 2H), 3.48 (s, 1H), 3.53 (s, 1H), 5.95 (q, 0.5H, J=7 Hz), 6.09 (q, 0.5H, J=7 Hz). ^{13}C NMR ($CDCl_3$) δ: 3.3, 14.9, 16.4, 19.7, 46.2, 46.3, 50.6, 57.4, 76.6, 76.7, 76.8, 124.9, 125.0, 128.0, 129.1. Anal. Calcd for $C_9H_{14}BrN$: C, 50.07; H, 6.52; N, 6.48. Found: C, 49.96; H, 6.51; N, 6.47.

***N*-(2-Bromoprop-2-enyl)-*N*-pent-3-ynylacetamide (9a).** Acetyl chloride (1.7 ml, 24 mmol) was added dropwise to a solution of **8a** (4 g, 20 mmol) and triethylamine (2.4 g, 24 mmol) in CH_2Cl_2 (100 ml) under ice-cooling, and the mixture was stirred for 2 h at room temperature. The mixture was concentrated in vacuo, the residue was extracted with ether and the extract was washed with water and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was distilled under reduced pressure to give 3.9 g (79%) of **9a**. Bp 66–67°C/1 mmHg. IR

(neat): 1658 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.78 (m, 3H), 2.12 and 2.22 (two s, 3H), 3.43–3.48 (m, 2H), 4.23–5.59 (m, 2H), 4.23 and 4.30 (two s, 2H), 5.59 and 5.65 (two s, 2H), 5.75 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 3.37, 3.44, 17.9, 18.8, 21.5, 45.3, 46.9, 52.2, 57.2, 75.2, 76.5, 77.1, 78.4, 117.6, 118.0, 128.5, 128.6, 170.6, 170.8. Anal. Calcd for $C_{10}H_{14}BrNO$: C, 49.20; H, 5.78; N, 5.74. Found: C, 49.13; H, 5.78; N, 5.51.

***N*-(2-Bromoprop-2-enyl)-*N*-pent-3-ynylphenoxycarboxamide (9b).** According to the above procedure, 2.1 g (74%) of **9b** was obtained from **8a** (1.8 g, 9 mmol) and phenyl chloroformate (1.4 ml, 11 mmol). Mp 74–75°C (recryst. from hexane). IR ($CHCl_3$): 1718, 1640, 1630 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.78 (t, 3H, J=2.5 Hz), 2.40–2.60 (m, 2H), 3.48 (t, 1H, J=7.3 Hz), 3.57 (t, 1H, J=7.3 Hz), 4.29 (s, 1H), 4.38 (s, 1H), 5.65 (dd, 1H, J=1, 6 Hz), 5.84 (d, 1H, J=1 Hz), 7.05–7.16 (m, 2H), 7.19 (t, 1H, J=7.3 Hz), 7.30–7.40 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 3.4, 18.2, 18.8, 46.2, 46.8, 55.3, 55.5, 75.7, 76.1, 77.3, 77.6, 117.7, 118.6, 121.5, 125.4, 129.1, 151.1, 128.6, 129.0, 154.0, 154.4. Anal. Calcd for $C_{15}H_{16}BrNO_2$: C, 55.92; H, 5.00; N, 4.35. Found: C, 55.88; H, 5.07; N, 4.26.

***N*-(2-Bromoprop-2-enyl)-*N*-pent-3-ynyl(phenylmethoxy)carboxamide (9c).** According to the above procedure, 3 g (75%) of **9c** was obtained from **8a** (2.5 g, 12 mmol) and benzyl chloroformate (2.1 ml, 15 mmol). Bp 160°C/1 mmHg. IR (neat): 1708 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.74 (t, 3H, J=2.5 Hz), 2.30–2.50 (m, 2H), 3.30–3.50 (m, 2H), 4.21 and 4.24 (two s, 2H), 5.14 and 5.17 (two s, 2H), 5.55 and 5.58 (two s, 2H), 5.67 and 5.75 (two s, 1H), 7.20–7.50 (m, 5H). ^{13}C NMR ($CDCl_3$) δ: 3.7, 18.5, 19.1, 46.2, 46.9, 55.5, 67.3, 67.4, 75.9, 76.2, 77.4, 77.5, 117.5, 118.2, 127.8, 128.0, 128.4, 128.5, 129.0, 136.8, 155.8, 156.2. Anal. Calcd for $C_{16}H_{18}BrNO_2$: C, 57.16; H, 5.40; N, 4.17. Found: C, 57.30; H, 5.48; N, 4.12.

(*tert*-Butoxy)-*N*-(2-bromoprop-2-enyl)-*N*-pent-3-ynylcarboxamide (9d). According to the above procedure, 1.3 g (89%) of **9d** was obtained from **8a** (1 g, 5 mmol) and di-*tert*-butyl dicarbonate (1.4 ml, 6 mmol). Bp 115°C/0.5 mmHg. IR (neat): 1704 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.45 and 1.47 (two s, 9H), 1.76 (t, 3H, J=2.5 Hz), 2.36 (br s, 2H), 3.30–3.50 (m, 2H), 4.11 and 4.15 (two s, 2H), 5.55 (s, 1H), 5.69 and 5.71 (two s, 1H). ^{13}C NMR δ: 3.3, 18.4, 18.6, 28.2, 46.2, 54.7, 55.4, 76.1, 76.4, 80.2, 116.5, 117.1, 129.6, 129.8, 154.7, 155.0. Anal. Calcd for $C_{13}H_{20}BrNO_2$: C, 51.67; H, 6.67; N, 4.63. Found: C, 51.63; H, 6.61; N, 4.60.

***N*-(2-Bromobut-2-enyl)-*N*-pent-3-ynylacetamide (9e).** According to the above procedure, 2 g (78%) of **9e** was obtained from **8b** (2.2 g, 10 mmol) and acetyl chloride (0.9 ml, 12 mmol). Bp 125°C/1 mmHg. IR (neat): 1648 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.70–1.85 (m, 6H), 2.15–2.23 (m, 3H), 2.30–2.45 (m, 2H), 3.35–3.54 (m, 2H), 4.23, 4.32, 4.33 and 4.39 (four s, 2H), 5.93 (q, 0.5H, J=7 Hz), 6.10–6.24 (m, 0.5H). ^{13}C NMR ($CDCl_3$) δ: 3.1, 3.2, 14.8, 14.9, 16.3, 16.4, 17.5, 17.6, 18.4, 18.5, 21.3, 21.4, 21.7, 43.7, 44.4, 45.6, 46.2, 50.6, 51.8, 57.1, 75.0, 75.1, 76.4, 76.5, 76.7, 76.9, 78.0, 120.5, 120.9, 123.3, 125.5, 125.9, 131.1, 131.2, 170.3, 170.4, 170.5. Anal. Calcd for $C_{11}H_{16}BrNO$: C, 51.18; H, 6.25; N, 5.43. Found: C, 51.01; H, 6.11; N, 5.38.

***N*-(2-Bromobut-2-enyl)-*N*-pent-3-ynylphenoxycarboxamide (9f).** According to the above procedure, 1.9 g (80%) of **9f** was obtained from **8b** (1.5 g, 7 mmol) and phenyl chloroformate (1 ml, 8 mmol). Bp 170°C/0.5 mmHg. IR (neat): 1722 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.77–1.85 (m, 6H), 2.40–2.60 (m, 2H), 3.40–3.65 (m, 2H), 4.31, 4.39 and 4.49 (three s, 2H), 5.95–6.25 (m, 1H), 7.13 (d, 2H, J=7.8 Hz), 7.19 (dt, 1H, J=1, 7.8 Hz), 7.35 (t, 2H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 3.5, 16.6, 18.1, 45.9, 46.2, 55.7, 55.9, 75.8, 76.3, 77.1, 77.2, 121.6, 123.5, 123.9, 125.3, 126.2, 127.1, 129.2, 151.3, 154.2, 154.6. Anal. Calcd for $C_{16}H_{18}BrNO_2$: C, 57.17; H, 5.28; N, 4.12. Found: C, 57.15; H, 5.39; N, 4.16.

***N*-(2-Bromobut-2-enyl)-*N*-pent-3-ynyl(phenylmethoxy)carboxamide (9g).** According to the above procedure, 12.6 g (78%) of **9g** was obtained from **8b** (9.9 g, 46 mmol) and benzyl chloroformate (7.8 ml, 55 mmol). Bp 180°C/0.5 mmHg. IR (neat): 1712 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.69–1.85 (m, 6H), 2.27–2.48 (m, 2H), 3.34–3.46 (m, 2H), 4.23, 4.26, 4.30 and 4.35 (four s, 2H), 5.14 and 5.17 (two s, 2H), 5.79–6.20 (m, 1H), 7.25–7.42 (m, 5H). ^{13}C-NMR ($CDCl_3$) δ: 3.4, 14.9, 15.1, 16.5, 16.6, 18.2, 18.7, 18.8, 45.4, 46.3, 49.0, 49.2, 55.4, 55.5, 67.2, 67.3, 67.4, 76.1, 76.3, 76.4, 77.2, 77.3, 121.1, 121.5, 124.0, 125.5, 126.2, 127.8, 127.9, 128.0, 128.4, 128.5, 130.7, 131.3, 136.5, 136.6, 155.7, 156.0. Anal. Calcd for $C_{17}H_{20}BrNO_2$: C, 58.30; H, 5.76; N, 4.00. Found: C, 58.37; H, 5.79; N, 3.94.

***N*-(2-Bromobut-2-enyl)(*tert*-butoxy)-*N*-pent-3-ynylcarboxamide (9h).** According to the above procedure, 2.6 g (81%) of **9h** was obtained from **8b** (2.2 g, 10 mmol) and di-*tert*-butyl dicarbonate (2.8 ml, 12 mmol). Bp 131°C/0.5 mmHg. IR (neat): 1702 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.47 (s, 9H), 1.72–1.81 (m, 6H), 2.36 (br s, 2H), 3.22–3.40 (m, 2H), 4.14, 4.18, 4.25 and 4.28 (four s, 2H), 5.82–5.95 (m, 0.5H), 6.05–6.18 (m, 0.5H). ^{13}C NMR ($CDCl_3$) δ: 3.5, 15.0, 16.6, 18.3, 18.7, 28.4, 45.5, 45.7, 48.4, 48.9, 54.9, 55.6, 80.1, 124.9, 125.4, 129.9, 130.7, 155.0. Anal. Calcd for $C_{14}H_{20}BrNO_2$: C, 53.15; H, 6.96; N, 4.41. Found: C, 53.17; H, 7.01; N, 4.43.

General procedure for the palladium catalyzed cross-coupling reaction of indolylborate (2a) with vinyl bromides (9)

To a solution of indolylborate (**2a**) in THF (15 ml), generated in situ from the treatment of 1-methylindole (**1a**) (2 mmol) with *tert*-butyllithium (2.4 mmol), and the subsequent addition of triethylborane (2.4 mmol) under argon atmosphere, were added vinyl bromide (**9**) (1 mmol) and palladium salt (0.05 mmol), and the mixture was heated at 60°C for 1–3 h. The reaction mixture was treated with 10% NaOH (10 ml) and 30% H_2O_2 (2 ml) under ice-cooling for 15 min. The mixture was diluted with AcOEt (50 ml), washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was separated by medium pressure liquid chromatography with hexane–AcOEt as an eluent to give **10** and/or **11**.

1-Acetyl-3-methylene-4-[(1-methylindol-2-yl)ethylidene]-piperidine (10a). IR (neat): 1642 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.05 and 2.06 (two s, 3H), 2.09 and 2.14 (two s, 3H), 2.59 (t, 1H, J=6 Hz), 2.67 (t, 1H, J=6 Hz), 3.53 and 3.56 (two s, 3H), 3.59 (t, 1H, J=6 Hz), 3.75 (t, 1H, J=6 Hz), 4.02 (s, 1H), 4.16 (s, 1H), 4.39 and 4.40 (two s, 1H), 4.79 and 4.87 (two s, 1H), 6.23 and 6.27 (two s, 1H), 7.05–7.10 (m, 1H), 7.13–7.20 (m, 1H), 7.25–7.30 (m, 1H), 7.54 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.1, 21.3, 21.5, 29.9, 30.2, 30.6, 40.5, 44.3, 49.7, 53.6, 99.5, 99.7, 109.2, 109.3, 115.9, 116.9, 119.5, 120.1, 120.2, 121.0, 123.9, 124.1, 127.8, 127.9, 135.5, 136.2, 136.9, 140.1, 140.5, 142.2, 142.4, 169.0, 169.3. High-resolution MS m/z: Calcd for $C_{19}H_{22}N_2O$: 294.1731. Found: 294.1747.

Phenyl 3-methylene-4-[(1-methylindol-2-yl)ethylidene]-piperidine-1-carboxylate (10b). Mp 117–118°C (recryst. from hexane–AcOEt). IR ($CHCl_3$): 1712 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.08 (s, 3H), 2.69 (d, 2H, J=2.2 Hz), 3.56 and 3.57 (two s, 3H), 3.65–3.85 (m, 2H), 4.14 and 4.23 (two s, 2H), 4.43 (s, 1H), 4.87 (s, 1H), 6.27 (s, 1H), 7.05–7.25 (m, 5H), 7.26 (d, 1H, J=8.3 Hz), 7.30–7.40 (m, 2H), 7.54 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.1, 21.2, 30.2, 42.7, 43.0, 51.3, 51.8, 99.6, 109.2, 116.2, 116.7, 119.4, 120.1, 121.7, 123.9, 125.2, 127.9, 129.2, 135.8, 136.1, 136.9, 140.0, 140.3, 142.3, 151.3, 153.6. MS m/z: 372 (M^+), 357, 263. Anal. Calcd for $C_{24}H_{24}N_2O_2+1/10H_2O$: C, 77.02; H, 6.51; N, 7.48. Found: C, 77.00; H, 6.48; N, 7.43.

Phenylmethyl 3-methylene-4-[(1-methylindol-2-yl)ethylidene]piperidine-1-carboxylate (10c). IR (neat): 1706 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.04 (s, 3H), 2.61(br s, 2H), 3.52 (s, 3H), 3.61–3.71 (m, 2H), 4.08 (s, 2H), 4.38 (s, 1H), 4.74–4.90 (m, 1H), 5.15 (s, 2H), 6.24 (s, 1H), 7.07 (dt, 1H, J=1, 7.3 Hz), 7.16 (dt, 1H, J=1, 7.3 Hz), 7.20–7.45 (m, 6H), 7.53 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.1, 30.2, 30.2, 42.5, 51.2, 67.1, 99.6, 109.2, 116.0, 116.3, 119.4, 120.1, 120.9, 123.6, 127.9, 128.0, 128.4, 136.3, 136.7, 136.8, 140.5, 142.4, 155.2. High-resolution MS m/z: Calcd for $C_{25}H_{26}N_2O_2$: 386.1993. Found: 386.1994.

***tert*-Butyl 3-methylene-4-[(1-methylindol-2-yl)ethylidene]-piperidine-1-carboxylate (10d).** IR (neat): 1690 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.47 (s, 9H), 2.05 (s, 3H), 2.59 (t, 2H, J=6 Hz), 3.55 (s, 3H), 3.50–3.60 (m, 2H), 3.99 (s, 2H), 4.36 (s, 1H), 4.79 (br s, 1H), 6.25 (s, 1H), 7.07 (t, 1H, J=7.8 Hz), 7.16 (t, 1H, J=7.8 Hz), 7.26 (d, 1H, J=7.8 Hz), 7.52 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.1, 28.4, 30.1, 30.3, 42.0, 51.4, 79.7, 99.5, 109.1, 115.6, 119.3, 120.0, 120.8, 123.2, 127.8, 136.7, 136.8, 140.9, 142.5, 154.7. High-resolution MS m/z: Calcd for $C_{22}H_{28}N_2O_2$: 352.2149. Found: 352.2154.

1-Acetyl-3-ethylidene-4-[1-methylindol-2-yl)ethylidene]-piperidine (10e). IR (neat): 1634 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.39 and 1.41 (two d, 3H, J=7 Hz), 2.06 (br s, 3H), 2.64–2.73 (m, 2H), 3.54 and 3.57 (two s, 3H), 3.70–3.85 (m, 2H), 4.24 and 4.33 (two s, 2H), 5.11 (q, 1H, J=7 Hz), 6.24 and 6.26 (two s, 1H), 7.07 (t, 1H, J=6.8 Hz), 7.10–7.25 (m, 5H), 7.37 (t, 2H, J=7.8 Hz), 7.54 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.4, 13.5, 21.0, 21.3, 21.5, 21.6, 30.0, 30.2, 30.3. 30.9, 40.5, 43.3, 44.4, 46.8, 99.6, 99.8, 109.0, 109.1, 119.2, 119.9, 120.0, 120.7, 120.8, 122.5, 122.6, 125.4, 126.7, 127.8, 127.9, 128.4, 131.8, 131.9, 132.2, 136.7, 136.9, 137.7, 142.7, 142.8, 169.1, 169.2. High-resolution MS m/z: Calcd for $C_{20}H_{24}N_2O$: 308.1889. Found: 308.1886.

Phenyl 3-ethylidene-4-[(1-methylindol-2-yl)ethylidene]-piperidine-1-carboxylate (10f). IR (neat): 1712 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.39 (m, 3H), 2.06 (s, 3H), 2.67 (m, 2H), 3.53 and 3.56 (two s, 3H), 3.60–3.85 (m, 2H), 4.24 (s, 1H), 4.33 (s, 1H), 5.09 (q, 1H, J=7 Hz), 6.24 and 6.25 (two s, 1H), 7.00–7.30 (m, 6H), 7.30–7.45 (m, 2H), 7.53 (d, 1H, J=7.5 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.5, 21.1, 21.3, 30.3, 30.3, 30.7, 42.9, 43.2, 45.1, 45.4, 99.8, 99.9, 109.1, 119.3, 119.9, 120.7, 121.7, 122.5, 125.2, 125.9, 126.5, 128.0, 129.2, 132.2, 132.5, 136.9, 137.1, 137.6, 142.9, 151.4, 153.8. High-resolution MS m/z: Calcd for $C_{25}H_{26}N_2O_2$: 386.1993. Found: 386.2003.

Phenylmethyl 3-ethylidene-4-[(1-methylindol-2-yl)ethylidene]piperidine-1-carboxylate (10g). IR (neat): 1702 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.34 (d, 3H, J=6.6 Hz), 2.02 (s, 3H), 2.59 (br s, 2H), 3.48 (s, 3H), 3.60–3.75 (m, 2H), 4.10–4.25 (m, 2H), 4.95–5.10 (m, 1H), 5.17 (s, 2H), 6.17–6.27 (m, 1H), 7.06 (t, 1H, J=7.8 Hz), 7.15 (t, 1H, J=7.8 Hz), 7.22 (d, 1H, J=8.3 Hz), 7.28–7.45 (m, 5H), 7.52 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.4, 21.3, 30.3, 30.5, 42.7, 44.9, 67.1, 99.8, 109.1, 119.2, 119.9, 120.7, 122.3, 125.6, 126.1, 127.9, 128.0, 128.1, 128.5, 132.6, 136.8, 136.9, 143.0, 155.4. High-resolution MS m/z: Calcd for $C_{26}H_{28}N_2O_2$: 400.2149. Found: 400.2161.

***tert*-Butyl 3-ethylidene-4-[(1-methylindol-2-yl)ethylidene]-piperidine-1-carboxylate (10h).** IR (neat): 1648 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.36 (d, 3H, J=7 Hz), 1.48 (s, 9H), 2.03 (s, 3H), 2.57 (t, 2H, J=6 Hz), 3.51 (s, 3H), 3.50–3.60 (m, 2H), 4.03–4.20 (m, 2H), 4.98–5.08 (m, 1H), 7.06 (t, 1H, J=7.8 Hz), 7.15 (t, 1H, J=7.8 Hz), 7.23 (d, 1H, J=8.3 Hz), 7.52 (d, 1H, J=7.8 Hz). ^{13}C NMR δ: 13.4, 21.2, 28.5, 30.3, 30.5, 42.5, 45.2, 79.6, 99.8, 109.1, 119.2, 119.9, 120.6, 121.8, 124.8, 128.0, 133.4, 136.9, 143.1, 154.9. High-resolution MS m/z: Calcd for $C_{23}H_{30}N_2O_2$: 366.2307. Found: 366.2297.

***N*-[2-(1-Methylindol-2-yl)prop-2-enyl-*N*-pent-3-ynyl-acetamide (11a).** IR (neat): 1648 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.76 and 1.77 (two t, 3H, J=2.5 Hz), 2.10 and 2.16 (two s, 3H), 2.35–2.50 (m, 2H), 3.41 (t, 1H, J=7 Hz), 3.53 (t, 1H, J=7 Hz), 3.76 and 3.78 (two s, 3H), 4.35 (s, 1H), 4.43 (s, 1H), 5.31 and 5.37 (two s, 1H), 5.39 and 5.41 (two s, 1H), 6.45 and 6.49 (two s, 1H), 7.05–7.15 (m, 1H), 7.20–7.35 (m, 2H), 7.53–7.63 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 3.3, 3.4, 18.0, 18.7, 21.3, 21.4, 31.1, 31.2, 45.8, 46.9, 49.2, 54.1, 75.3, 78.2, 101.1, 101.5, 109.5, 109.6, 115.8, 116.7, 119.7, 120.0, 120.6, 121.9, 122.3, 127.3, 127.4, 135.3, 135.7, 137.8, 138.3, 138.7, 170.5, 171.0. High-resolution MS m/z: Calcd for $C_{19}H_{22}N_2O$: 294.1731. Found: 294.1763.

***N*-[2-(1-Methylindol-2-yl)prop-2-enyl]-*N*-pent-3-ynyl-phenoxycarboxamide (11b).** IR (neat): 1722 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.77 and 1.79 (two t, 3H, J=2.4 Hz), 2.45–2.54 (m, 2H), 3.45–3.60 (m, 2H), 3.74 and 3.78 (two s, 3H), 4.44 (s, 1H), 4.50 (s, 1H), 5.37 (s, 1H), 5.54 (d, 1H, J=7.4 Hz), 6.51 and 6.54 (two s, 1H), 6.96 (d, 1H,

J=7.8 Hz), 7.01 (d, 1H, *J*=7.8 Hz), 7.10–7.40 (m, 6H), 7.55–7.65 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 3.4, 18.2, 18.8, 30.9, 31.1, 46.1, 46.9, 52.5, 52.9, 75.9, 76.3, 77.2, 77.5, 101.5, 101.6, 109.5, 117.0, 117.4, 119.7, 119.8, 120.5, 120.6, 121.5, 121.6, 122.0, 122.1, 125.2, 127.4, 127.5, 129.2, 135.9, 136.3, 138.2, 138.3, 138.4, 138.5, 151.1, 151.2, 154.3, 154.6. High-resolution MS *m/z*: Calcd for $C_{24}H_{24}N_2O_2$: 372.1836. Found: 372.1813.

***N*-[2-(1-Methylindol-2-yl)prop-2-enyl]-*N*-pent-3-ynyl-(phenylmethoxy)carboxamide (11c).** IR (neat): 1702 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.74 and 1.75 (two s, 2H), 2.34 and 2.43 (two br s, 2H), 3.38 and 3.45 (two t, 2H, *J*=7 Hz), 3.50 and 3.76 (two s, 3H), 4.31 and 4.39 (two s, 2H), 5.08 and 5.13 (two s, 2H), 5.25 and 5.31 (two s, 1H), 5.38 and 5.44 (two s, 1H), 6.38 and 6.50 (two s, 1H), 7.10 (t, 1H, *J*=7.3 Hz), 7.20–7.40 (m, 7H), 7.50–7.65 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 3.3, 18.2, 18.6, 30.7, 31.0, 45.7, 46.8, 52.2, 67.1, 67.2, 76.4, 76.8, 77.1, 77.2, 101.2, 101.5, 109.5, 116.4, 116.9, 119.7, 120.6, 121.9, 127.4, 127.5, 127.8, 127.9, 128.3, 136.0, 136.1, 136.4, 136.6, 138.1, 138.4, 155.8, 156.0. High-resolution MS *m/z*: Calcd for $C_{25}H_{26}N_2O_2$: 386.1993. Found: 386.1965.

(*tert*-Butoxy)-*N*-[2-(1-methylindol-2-yl)prop-2-enyl]-*N*-pent-3-ynylcarboxamide (11d). IR (neat): 1692 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.41 and 1.43 (two s, 9H), 1.76 (t, 3H, *J*=2.6 Hz), 2.28–2.43 (m, 2H), 3.28 and 3.39 (two t, 2H, *J*=7 Hz), 3.74 and 3.76 (two s, 3H), 4.23 and 4.30 (two s, 2H), 5.28 (d, 1H, *J*=7.8 Hz), 5.40 (s, 1H), 6.43 and 6.49 (two s, 1H), 7.10 (t, 1H, *J*=7 Hz), 7.22 (t, 1H, *J*=7.8 Hz), 7.31 (d, 1H, *J*=7.8 Hz), 7.57 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 3.4, 18.4, 18.7, 28.3, 30.9, 31.1, 46.3, 51.8, 52.6, 76.4, 76.7, 76.9, 79.8, 101.1, 101.4, 109.4, 116.1, 116.4, 119.6, 119.8, 120.5, 121.8, 127.5, 136.5, 138.3, 138.8, 155.3. High-resolution MS *m/z*: Calcd for $C_{23}H_{30}N_2O_2$: 366.2307. Found: 366.2297.

General procedure for the photocyclization of 10

A solution of **10** (100 mg) in benzene (10 ml) was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter under ice-cooling for 3 h. The solvent was removed, and the residue was separated by medium pressure liquid chromatography with hexane–AcOEt as an eluent to give **12** and/or **13**.

General procedure for the acid promoted cyclization of 10

Acid (2 mmol) was added to a solution of **10** (1 mmol) in CH_2Cl_2 (20 ml), and stirring was continued (reaction temperature and time are shown in Table 3). The mixture was diluted with AcOEt (50 ml), washed with 10% NaOH and water, and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was separated by medium pressure liquid chromatography with hexane–AcOEt as an eluent to give **12** and/or **14**.

2-Acetyl-5,6-dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]-carbazole (12a). Mp 194°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1632 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.18 and 2.21 (two s, 3H), 2.71 and 2.72 (two s, 3H), 2.95 (t, 1H, *J*=6 Hz), 3.01 (t, 1H, *J*=6 Hz), 3.72 (t, 1H, *J*=6 Hz), 3.87 (t, 1H, *J*=6 Hz), 4.06 and 4.08 (two s, 3H), 4.77 (s, 1H), 4.87 (s, 1H), 7.20 (dt, 1H, *J*=3, 7 Hz), 7.34 (t, 1H, *J*=7.8 Hz), 7.40–7.50 (m, 1H), 7.68 and 7.72 (two s, 1H), 7.98 (dd, 1H, *J*=3, 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.6, 14.7, 21.6, 21.8, 26.6, 27.4, 33.3, 40.2, 44.5, 44.6, 48.9, 108.6, 108.8, 115.1, 115.8, 119.0, 119.6, 119.8, 117.9, 118.6 (s), 122.2, 122.5, 122.6, 124.3, 125.2, 131.3, 132.1, 139.5, 139.7, 142.6, 142.7, 169.3. MS *m/z*: 292 (M^+), 233, 221. Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.05; H, 6.90; N, 9.58. Found: C, 77.79; H, 6.99; N, 9.47.

Phenyl 5,6-dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole-2-carboxylate (12b). Mp 172–173°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1710 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.71 (s, 3H), 3.00–3.10 (m, 2H), 3.80–3.95 (m, 2H), 4.04 (s, 3H), 4.85 (s, 1H), 4.98 (s, 1H), 7.10–7.25 (m, 4H), 7.30–7.40 (m, 3H), 7.44 (t, 1H, *J*=7.3 Hz), 7.71 (s, 1H), 7.98 (d, 1H, *J*=7.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 4.6, 26.6, 26.9, 33.3, 42.2, 42.7, 46.6, 46.9, 108.7, 115.5, 115.2, 118.1, 118.5, 118.9, 119.7, 121.7, 122.3, 122.6, 124.9, 124.5, 125.2, 125.7, 129.2, 131.5, 139.6, 14206, 151.5, 153.8. MS *m/z*: 370 (M^+), 293, 277. Anal. Calcd for $C_{24}H_{22}N_2O_2$: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.73; H, 6.12; N, 7.51.

Phenylmethyl 5,6-dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole-2-carboxylate (12c). Mp 150–151°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.72 (s, 3H), 2.97 (br, 2H), 3.79 (br, 2H), 4.08 (s, 3H), 4.81 (s, 2H), 5.19 (s, 2H), 7.19 (t, 1H, *J*=7.3 Hz), 7.25–7.50 (m, 7H), 7.60–7.70 (m, 1H), 7.98 (br 1H). ^{13}C-NMR ($CDCl_3$) δ: 14.5, 26.8, 33.2, 42.0, 46.4, 67.1, 108.6, 115.2, 115.4 (s), 118.1, 118.3, 118.8, 119.7, 122.2, 122.6, 124.7, 125.1, 125.6, 127.9, 128.5, 131.6, 136.9, 139.4, 142.6, 155.4. MS *m/z*: 384 (M^+), 293, 249. Anal. Calcd for $C_{25}H_{24}N_2O_2$: C, 78.12; H, 6.29; N, 7.28. Found: C, 77.92; H, 6.43; N, 7.35.

***tert*-Butyl 5,6-dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]-carbazole-2-carboxylate (12d).** Mp 158°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1680 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.50 (s, 9H), 2.72 (s, 3H), 2.94 (t, 3H, *J*=6 Hz), 3.71 (br s, 2H), 4.07 (s, 3H), 4.73 (s, 2H), 7.18 (dt, 1H, *J*=1, 7.8 Hz), 7.33 (d, 1H, *J*=8.3 Hz), 7.43 (dt, 1H, *J*=1, 7.8 Hz), 8.00 (d, 1H, *J*=8.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.6, 27.0, 28.5, 33.4, 108.6, 115.3, 118.9, 119.7, 122.2, 122.7, 125.6, 132.0, 139.5, 142.7, 154.9. MS *m/z*: 350 (M^+), 293, 249. Anal. Calcd for $C_{22}H_{26}N_2O_2$: C, 75.13; H, 7.54; N, 7.87. Found: C, 75.39; H, 7.47; N, 7.99.

2-Acetyl-5,6,11-trimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]-carbazole (12e). Mp 181–182°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1632 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.21 and 2.24 (two s, 3H), 2.72 and 2.73 (two s, 3H), 2.77 and 2.79 (two s, 3H), 2.96 (t, 1H, *J*=6 Hz), 3.02 (t, 1H, *J*=6 Hz), 3.73 (t, 1H, *J*=6 Hz), 3.87 (t, 1H, *J*=6 Hz), 4.08 and 4.09 (two s, 3H), 4.77 (s, 1H), 4.89 (s,1H), 7.22 (dt, 1H, *J*=4, 7.8 Hz), 7.39 (t, 1H, *J*=7 Hz), 7.43–7.50 (m, 1H), 8.22 (dd, 1H, *J*=3.5, 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.8, 14.9, 15.4, 15.5, 21.6, 21.9, 27.1, 27.9, 33.7, 39.5, 42.5, 44.0, 46.8, 108.5, 108.6, 115.3, 116.1, 118.9, 121.1, 121.3, 122.4, 122.6, 122.7, 123.3, 123.4, 123.5, 125.0, 125.1, 126.6, 127.6, 131.1, 132.1, 139.4, 139.7, 142.8, 142.9,

169.2. MS *m*/*z*: 306 (M^+), 291, 263, 249, 235. Anal. Calcd for $C_{20}H_{22}N_2O+1/10H_2O$: C, 77.88; H, 7.28; N, 9.06. Found: C, 77.94 H, 7.25; N, 9.09.

Phenyl 5,6,11-trimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]-carbazole-2-carboxylate (12f). Mp 171–172°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1706 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.71 (s, 3H), 2.76 (s, 3H), 3.00–3.10 (m, 2H), 3.80–4.00 (m, 2H), 4.05 (s, 3H), 4.86 (s, 1H), 4.97 (s, 1H), 7.13–7.25 (m, 4H), 7.33–7.40 (m, 3H), 7.45 (t, 1H, *J*=7.8 Hz), 8.21 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.9, 15.4, 27.2, 27.5, 33.6, 41.6, 42.2, 44.5, 45.0, 108.5, 115.6, 115.9, 118.9, 121.2, 121.8, 122.6, 123.0, 123.4, 125.0, 125.2, 125.3, 127.0, 127.3, 129.2, 131.4, 131.5, 139.6, 142.9, 151.5, 153.8, 153.9. MS *m*/*z*: 384 (M^+), 291. Anal. Calcd for $C_{25}H_{24}N_2O_2$: C, 78.10; H, 6.29; N, 7.29. Found: C, 77.97; H, 6.47; N, 7.28.

Phenylmethyl 5,6,11-trimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole-2-carboxylate (12g). Mp 130–132°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1688 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.70 (s, 3H), 2.60–2.75 (m, 3H), 2.90–3.00 (m, 2H), 4.07 (s, 3H), 4.81 (s, 2H), 5.21 (s, 2H), 7.21 (t, 1H, *J*=7.8 Hz), 7.30–7.50 (m, 7H), 8.21 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.8, 15.3, 27.3, 27.5, 33.6, 41.5, 44.4, 67.1, 108.5, 118.8, 121.1, 122.6, 123.5, 124.9, 127.8, 128.5, 136.9, 139.5, 142.9, 155.5. MS *m*/*z*: 398 (M^+), 307, 263. Anal. Calcd for $C_{26}H_{26}N_2O_2$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.12; H, 6.69; N, 7.01.

***tert*-Butyl 5,6,11-trimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole-2-carboxylate (12h).** Mp 148–149°C (recryst. from ethyl acetate). IR ($CHCl_3$): 1680 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.51 (s, 9H), 2.68 (s, 3H), 2.74 (s, 3H), 2.89–2.98 (m, 2H), 3.65–3.74 (m, 2H), 4.05 (s, 3H), 4.73 (s, 2H), 7.20 (t, 1H, *J*=7.8 Hz), 7.36 (d, 1H, *J*=7.8 Hz), 7.44 (t, 1H, *J*=7.3 Hz), 8.20 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.7, 14.9, 27.5, 28.2, 28.5, 33.0, 33.4, 79.6, 108.4, 108.5, 115.6, 118.7, 121.0, 122.6, 123.5, 124.7, 124.8, 124.9, 131.8, 139.4, 142.9, 154.9. MS *m*/*z*: 364 (M^+), 307, 263. Anal. Calcd for $C_{23}H_{28}N_2O_2$: C, 75.79; H, 7.74; N, 7.69. Found: C, 75.81; H, 7.68; N, 7.52.

1-Acetyl-3-methylene-4-[(1-methylindol-2-yl)ethylidene]-piperidine (13a). IR (neat): 1638 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.03 and 2.08 (two s, 3H), 2.14 (s, 3H), 2.00–2.30 (m, 2H), 3.38 (t, 1H, *J*=6 Hz), 3.50–3.60 (m, 1H), 3.59 and 3.60 (s, 3H), 4.05 (s, 1H), 4.23 (s, 1H), 5.13 (d, 1H, *J*=1 Hz), 5.34 and 5.41 (two s, 1H), 6.28 and 6.29 (two s, 1H), 7.11 (dt, 1H, *J*=1.3, 7 Hz), 7.21 (dt, 1H, *J*=1.3, 7.8 Hz), 7.31 (d, 1H, *J*=8.3 Hz), 7.58 (dd, 1H, *J*=1.3, 7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.0, 22.1, 29.9, 32.1, 32.6, 42.0, 46.1, 49.4, 54.1, 99.6, 99.7, 109.3, 114.9, 115.7, 119.6, 120.2, 121.2, 124.7, 127.9, 137.0, 137.4, 137.5, 140.7, 141.3, 141.4, 168.8, 168.9. High-resolution MS *m*/*z*: Calcd for $C_{19}H_{22}N_2O$: 294.1731. Found: 294.1709.

Phenyl 3-methylene-4-[(1-methylindol-2-yl)ethylidene]-piperidine-1-carboxylate (13b). IR (neat): 1714 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.17 (s, 3H), 2.22–2.33 (m, 2H), 3.45–3.65 (m, 2H), 3.62 (s, 3H), 4.15–4.35 (m, 2H), 5.16 (s, 1H), 5.42 (s, 1H), 6.30 (s, 1H), 7.11 (t, 1H, *J*=7.8 Hz), 7.21 (t, 1H, *J*=7.8 Hz), 7.28–7.40 (m, 6H), 7.59 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.1, 29.9, 32.1, 32.5, 44.5, 44.7, 51.6, 52.2, 99.7, 109.3, 115.2, 115.6, 119.6, 120.2, 121.2, 121.7, 124.6, 125.2, 127.9, 129.2, 137.0, 137.6, 140.7, 141.1, 141.4, 151.3, 153.5. High-resolution MS *m*/*z*: Calcd for $C_{24}H_{24}N_2O_2$: 372.1836. Found: 372.1818.

Phenylmethyl 3-methylene-4-[(1-methylindol-2-yl)ethylidene]piperidine-1-carboxylate (13c). IR (neat): 1706 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.13 (s, 3H), 2.15–2.25 (m, 2H), 3.40–3.50 (m, 2H), 3.58 (s, 3H), 4.12 (s, 2H), 5.05–5.20 (m, 3H), 5.25–5.50 (m, 1H), 6.27 (s, 1H), 7.10 (t, 1H, *J*=7.8 Hz), 7.20 (t, 1H, *J*=7.8 Hz), 7.27–7.45 (m, 6H), 7.57 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 22.0, 29.9, 32.3, 44.2, 51.6, 67.1, 99.6, 109.3, 115.1, 119.6, 120.2, 121.1, 124.2, 127.8, 127.9, 128.4, 136.7, 137.0, 137.9, 141.2, 141.5, 155.1. High-resolution MS *m*/*z*: Calcd for $C_{25}H_{26}N_2O_2$: 386.1993. Found: 386.2024.

***tert*-Butyl 3-methylene-4-[(1-methylindol-2-yl)ethylidene]-piperidine-1-carboxylate (13d).** IR (neat): 1680 cm^{-1}. ^1H-NMR ($CDCl_3$) δ: 1.45 (s, 9H), 2.05–2.20 (m, 2H), 2.13 (s, 3H), 3.20–3.33 (m, 2H), 3.59 (s, 3H), 3.95–4.10 (m, 2H), 5.08 (s, 1H), 5.25–5.40 (m, 1H), 7.10 (dt, 1H, *J*=1, 6.8 Hz), 7.20 (dt, 1H, *J*=1, 6.8 Hz), 7.31 (d, 1H, *J*=7.8 Hz), 7.58 (d, 1H, *J*=7.8 Hz). ^{13}C NMR δ: 22.0, 28.5, 29.9, 32.6, 44.1, 51.2, 79.7, 99.7, 109.3, 114.8, 119.6, 120.2, 121.1, 123.9, 128.1, 137.1, 138.4, 141.7, 154.7. High-resolution MS *m*/*z*: Calcd for $C_{22}H_{28}N_2O_2$: 352.2194. Found: 352.2154.

1-Acetyl-3-ethylidene-4-[(1-methylindol-2-yl)ethylidene]-piperidine (13e). IR (neat): 1626 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.87 (d, 3H, *J*=6.8 Hz), 2.04 (s, 3H), 2.09 (s, 3H), 2.10–2.23 (m, 2H), 3.38 (q, 1H, *J*=6 Hz), 3.50–3.60 (m, 1H), 3.57 and 3.58 (two s, 3H), 4.12 and 4.30 (two s, 2H), 5.65 (q, 1H, *J*=6.8 Hz), 6.26 and 6.27 (two s, 1H), 7.10 (t, 1H, *J*=6.8 Hz), 7.19 (t, 1H, *J*=6.8 Hz), 7.30 (d, 1H, *J*=7.8 Hz), 7.57 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.4, 21.4, 21.6, 22.0, 22.1, 29.8, 32.0, 32.6, 42.3, 43.0, 46.3, 47.1, 99.4, 99.5, 109.2, 119.5, 120.1, 121.0, 123.4, 124.0, 125.3, 127.9, 128.0, 132.9, 133.3, 137.0, 139.0, 139.3, 141.9, 168.8, 168.9. High-resolution MS *m*/*z*: Calcd for $C_{20}H_{24}N_2O$: 308.1878. Found: 304.1894.

2-Acetyl-5,10-dimethylspiro[2,3,4,6,7-pentahydrocyclopenta[1,2-*c*]pyridine-6,2′-indoline] (14a). Mp 124–125°C (recryst. from hexane–ethyl acetate). IR ($CHCl_3$): 1630 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.60 (s, 3H), 2.17 and 2.19 (two s, 3H), 2.53 (s, 3H), 2.45–2.60 (m, 3H), 2.78 and 2.80 (two dd, 1H, *J*=1.5, 16 Hz), 2.86 and 2.87 (two d, 1H, *J*=16 Hz), 3.15 and 3.17 (two d, 1H, *J*=16 Hz), 3.60–3.90 (m, 2H), 6.20–6.30 (m, 1H), 6.61 and 6.59 (two t, 1H, *J*=1.5, 7.8 Hz), 6.93–7.13 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.3, 21.7, 22.0, 22.9, 23.5, 28.3, 36.2, 39.4, 40.7, 43.9, 80.9, 105.1, 114.4, 115.3, 116.8, 123.8, 127.4, 127.5, 127.6, 127.9, 132.6, 133.3, 137.2, 137.7, 151.8, 167.2, 167.9. MS *m*/*z*: 308 (M^+), 293, 251, 188. Anal. Calcd for $C_{19}H_{22}N_2O+1/5H_2O$: C, 76.57; H, 7.57; N, 9.40. Found: C, 76.74; H, 7.63; N, 9.47.

Phenyl 5,10-dimethylspiro[2,3,4,6,7-pentahydrocyclopenta[1,2-*c*]pyridine-6,2′-indoline]-2-carboxylate (14b). IR (neat): 1710 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.61 (s, 3H),

2.55 (s, 3H), 2.50–2.60 (m, 3H), 2.81 (d, 1H, *J*=16 Hz), 2.89 (d, 1H, *J*=16 Hz), 3.19 (d, 1H, *J*=16 Hz), 3.70–4.00 (m, 2H), 6.31 (d, 1H, *J*=7.8 Hz), 6.61 (t, 1H, *J*=7.8 Hz), 6.66 and 6.71 (two s, 1H), 7.00–7.30 (m, 5H), 7.33–7.45 (m, 2H). ^{13}C NMR δ: 10.3, 23.0, 23.2, 28.4, 36.2, 40.8, 41.9, 42.4, 80.9, 105.1, 114.5, 115.3, 116.8, 121.6, 123.8, 125.5, 126.7, 127.3, 127.5, 127.6, 129.3, 132.5, 132.8, 137.1, 137.4, 151.2, 151.8, 151.9. High-resolution MS *m*/*z*: Calcd for $C_{24}H_{24}N_2O_2$: 372.1836. Found: 372.1860.

Phenylmethyl 5,10-dimethylspiro[2,3,4,6,7-pentahydrocyclopenta[1,2-*c*]pyridine-6,2′-indoline]-2-carboxylate (14c). IR (neat): 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.57 (s, 3H), 2.51 (s, 3H), 2.45–2.55 (m, 3H), 2.74 (d, 1H, *J*=16 Hz), 2.85 (d, 1H, *J*=16 Hz), 3.15 (d, 1H, *J*=16 Hz), 3.55–3.68 (m, 2H), 5.19 (s, 2H), 6.29 (d, 1H, *J*=7.8 Hz), 6.60 (t, 1H, *J*=7.8 Hz), 6.53 and 6.65 (two s, 1H), 7.01 (d, 1H, *J*=7.8 Hz), 7.06 (t, 1H, *J*=7.8 Hz), 7.30–7.40 (m, 5H). ^{13}C NMR ($CDCl_3$) δ: 10.2, 23.1, 28.3, 36.3, 40.8, 41.7, 67.5, 80.9, 105.0, 114.7, 115.4, 116.7, 123.7, 125.8, 126.3, 127.5, 128.1, 128.2, 128.5, 133.0, 136.4, 136.6, 151.9, 153.2. High-resolution MS *m*/*z*: Calcd for $C_{25}H_{26}N_2O_2$: 386.1993. Found: 386.2031.

Phenyl *rel*-(11*S*, 7*R*)-5,7,10-trimethylspiro[2,3,4,6,7-pentahydrocyclopenta[1,2-*c*]pyridine-6,2′-indoline] (14f). IR (neat): 1720 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.14 and 1.15 (two d, 3H, *J*=7 Hz), 1.50 (s, 3H), 2.47 and 2.49 (two s, 3H), 2.47–2.57 (m, 1H), 2.57–2.68 (m, 1H), 2.77 (q, 1H, *J*=7 Hz), 2.99 (d, 1H, *J*=6 Hz), 3.21 and 3.22 (two d, 1H, *J*=6 Hz), 3.60–3.80 (m, 1H), 3.95–4.10 (m, 1H), 6.25 (d, 1H, *J*=7.8 Hz), 6.57 (t, 1H, *J*=7.3 Hz), 6.64 and 6.65 (two s, 1H), 6.99 (d, 1H, *J*=7 Hz), 7.05 (t, 1H, *J*=7.3 Hz), 7.16 (d, 2H, *J*=7.8 Hz), 7.22 (t, 1H, *J*=7.8 Hz), 7.35–7.42 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 10.6, 11.6, 11.8, 22.6, 22.8, 30.4, 30.5, 39.3, 39.4, 42.4, 42.8, 44.9, 81.8, 104.1, 113.9, 114.6, 116.2, 116.3, 121.6, 121.8, 123.3, 125.6, 127.4, 127.7, 128.4, 129.3, 129.4, 131.5, 131.7, 132.7, 133.2, 135.7, 136.1, 151.2, 151.3, 152.0, 152.2, 152.8. High-resolution MS *m*/*z*: Calcd for $C_{25}H_{26}N_2O_2$: 386.1995. Found: 386.2021.

Phenyl *rel*-(7*S*,11*S*)-5,7,10-trimethylspiro[2,3,4,6,7-pentahydrocyclopenta[1,2-*c*]pyridine-6,2′-indoline] (14f′). IR (neat): 1720 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.11 and 1.13 (two d, 3H, *J*=6 Hz), 1.57 (s, 3H), 2.55 (t, 2H, *J*=6.5 Hz), 2.58 and 2.60 (two s, 3H), 2.82 and 2.83 (two d, 1H, *J*=6 Hz), 2.98 (q, 1H, *J*=6 Hz), 3.14 (d, 1H, *J*=6 Hz), 3.65 and 3.71 (two dt, 1H, *J*=6.5, 7 Hz), 3.92 and 4.01 (two dt, 1H, *J*=6.5, 7 Hz), 6.30 (d, 1H, *J*=7.8 Hz), 6.55–6.63 (m, 2H), 6.99 (d, 1H, *J*=6.8 Hz), 7.05 (t, 1H, *J*=7.8 Hz), 7.10–7.19 (m, 2H), 7.22 (t, 1H, *J*=7.8 Hz), 7.33–7.42 (m, 2H). ^{13}C NMR δ: 10.6, 15.4, 15.5, 22.7, 22.9, 28.5, 34.0, 34.1, 38.9, 39.0, 42.0, 42.4, 83.8, 104.5, 114.2, 114.9, 115.3, 116.2, 120.4, 121.6, 121.7, 123.3, 125.5, 127.4, 127.9, 129.3, 129.5, 130.9, 131.2, 132.6, 133.1, 137.0, 137.4, 151.1, 151.2, 151.9, 152.0, 152.1. High-resolution MS *m*/*z*: Calcd for $C_{25}H_{26}N_2O_2$: 386.1995. Found: 386.1992.

5,6-Dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole (15a). A solution of **12c** (100 mg) in THF (15 ml) in the presence of 20% $Pd(OH)_2$ on carbon (10 mg) was stirred under atmospheric pressure of hydrogen at room temperature for 3 h. The catalyst and solvent were removed, and the residue was crystallized from ether to give 58 mg (90%) of **15a**, which was used for the next reaction without further purification. Mp 152–154°C. IR ($CHCl_3$): 3100 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.84 (br s, 1H), 2.66 (s, 3H), 2.84 (t, 2H, *J*=6 Hz), 3.24 (t, 2H *J*=6 Hz), 4.05 (s, 3H), 4.19 (s, 2H), 7.16 (t, 1H, *J*=7.8 Hz), 7.31 (d, 1H, *J*=8.3 Hz), 7.42 (t, 1H, *J*=7.8 Hz), 7.59 (s, 1H), 7.96 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.3, 27.9, 39.3, 44.7, 49.5, 108.5, 115.1, 118.6, 118.7, 119.6, 121.8, 122.8, 125.3, 127.4, 131.6, 139.4, 142.6. High-resolution MS *m*/*z*: Calcd for $C_{17}H_{18}N_2$: 250.1502. Found: 250.1469.

5,6,11-Trimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole (15b). According to the above procedure, **12g** (100 mg) was converted to 59 mg (90%) of **15b**. Mp 163–165°C. IR ($CHCl_3$): 3000 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.65 (s, 3H), 2.67 (s, 3H), 2.85 (t, 2H, *J*=6 Hz), 3.19 (t, 2H, *J*=6 Hz), 4.04 (s, 3H), 4.18 (s, 2H), 7.19 (dt, 1H, *J*=1, 7.8 Hz), 7.35 (d, 1H, *J*=7.8 Hz), 7.43 (t, 1H, *J*=7.8 Hz), 8.20 (d, 1H, *J*=8.3 Hz). ^{13}C NMR δ: 15.1, 15.7, 29.2, 34.3, 44.6, 47.9, 109.0, 116.7, 119.3, 121.4, 123.2, 124.3, 125.3, 126.1, 127.5, 132.5, 143.5, 140.1. High-resolution MS *m*/*z*: Calcd for $C_{18}H_{20}N_2$: 264.1714. Found: 264.1724.

5,6,11-Trimethyl-3,4-dihydropyrido[4,3-*b*]carbazole (16). A mixture of **15b** (180 mg) and active MnO_2 (1 g) in CH_2Cl_2 was stirred at room temperature overnight. After insoluble material and solvent were removed, the residue was separated by flash chromatography (SiO_2) with CH_2Cl_2:MeOH (50:1) as an eluent to give 100 mg (56%) of **16**. Mp 215–216°C (recryst. from AcOEt). IR ($CHCl_3$): 1620, 1572 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.71 (s, 3H), 2.88 (t, 2H, *J*=7 Hz), 2.97 (s, 3H), 3.74 (t, 2H, *J*=7 Hz), 4.12 (s, 3H), 7.28 (dt, 1H, *J*=1, 7.3 Hz), 7.42 (d, 1H, *J*=7.8 Hz), 7.49 (dt, 1H, *J*=1, 7.3 Hz), 8.21 (d, 1H, *J*=8.3 Hz), 8.89 (s, 1H). ^{13}C NMR δ: 14.6, 15.1, 23.9, 33.3, 46.2, 108.8, 114.8, 119.1, 120.8, 122.6, 123.6, 125.3, 131.3, 134.4, 142.1, 142.4, 158.9. High-resolution MS *m*/*z*: Calcd for $C_{18}H_{18}N_2$: 262.1469. Found: 262.1458. Anal. Calcd for $C_{18}H_{18}N_2+1/10H_2O$: C, 81.84; H, 6.94; N, 10.60. Found: C, 81.67; H, 7.08; N, 10.33.

5,6-Dimethylpyrido[4,3-*b*]carbazole (17a). A mixture of **15a** (90 mg) and active MnO_2 (1 g) in AcOEt (50 ml) was heated under reflux for 20 h. After insoluble material and solvent were removed, the residue was separated by flash chromatography with CH_2Cl_2:MeOH (50:1) as eluent to give 60 mg (62%) of **17a**. Mp 158–159°C (recryst. from AcOEt). IR ($CHCl_3$): 1606 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 3.13 (s, 3H), 4.21 (s, 3H), 7.34 (t, 1H, *J*=7.3 Hz), 7.43 (d, 1H, *J*=8.3 Hz), 7.62 (t, 1H, *J*=7.3 Hz), 7.99 (d, 1H, *J*=7.3 Hz), 8.23 (d, 1H, *J*=7.8 Hz), 8.46 (d, 1H, *J*=6.3 Hz), 8.60 (s, 1H), 9.39 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 13.7, 29.7, 33.7, 108.8, 111.2, 116.3, 117.5, 120.0, 120.8, 122.4, 123.5, 127.1, 128.1, 134.3, 139.6, 144.8, 152.4. Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.73; H, 5.86; N, 11.12. High-resolution MS *m*/*z*: Calcd for $C_{17}H_{14}N_2$: 246.1158. Found: 246.1147.

Preparation of 5,6,11-trimethylpyrido[4,3-*b*]carbazole (17b). (i) A mixture of **15b** (60 mg) and active MnO_2 (500 mg) in AcOEt (20 ml) was heated under reflux for

20 h. After insoluble material and solvent were removed, the residue was separated by flash chromatography with CH_2Cl_2:MeOH (50:1) as eluent to give 30 mg (60%) of **17b**. (ii) A mixture of **16** (50 mg) and active MnO_2 (500 mg) in AcOEt (20 ml) was heated under reflux overnight. After insoluble material and solvent were removed, the residue was separated by flash chromatography with CH_2Cl_2:MeOH (40:1) as eluent to give 30 mg (60%) of **17b**. Mp 210–211°C (recryst. from EtOH) (lit.[15] mp 211–212°C). ^{1}H NMR ($CDCl_3$) δ: 3.06 (s, 3H), 3.26 (s, 3H), 4.13 (s, 3H), 7.32 and 7.58 (two t, 2H, *J*=7 Hz), 7.40 (d, 1H, *J*=8 Hz), 7.90 (d, 1H, *J*=6 Hz), 8.36 (d, 1H, *J*=8 Hz), 8.50 (d, 1H, *J*=7 Hz), 9.70 (s, 1H). ^{13}C NMR δ: 13.9, 14.6, 33.9, 108.4, 108.5, 115.9, 119.6, 122.7, 123.5, 123.9, 124.7, 127.1, 128.7, 134.4, 141.0, 141.9, 145.1, 149.7. Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.94; H, 6.39; N, 10.76.

The cross-coupling reaction of indolylborate (2b) with vinyl bromide (9c)

To a solution of indolylborate (**2b**) in THF (15 ml), generated in situ from the treatment of indole (**1b**) (294 mg, 2 mmol) with *n*-butyllithium (2.4 mmol), and the subsequent addition of triethylborane (2.4 mmol) under argon atmosphere, were added bromide (**9c**) (321 mg, 1 mmol) and $Pd_2(dba)_3{\cdot}CHCl_3$ (51 mg, 0.05 mmol), and the mixture was heated at 60°C for 1 h. The reaction mixture was treated with 10% NaOH (10 ml) and 30% H_2O_2 (2 ml) under ice-cooling for 15 min. The mixture was diluted with AcOEt (50 ml), washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was separated by medium pressure liquid chromatography with hexane:AcOEt (10:1) as eluent to give 197 mg (51%) of **18** and 69 mg (18%) of **19**.

Phenyl 4-[(1-methoxyindol-2-yl)ethylidene]-3-methylenepiperidine-1-carboxylate (18). IR (neat): 1718 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.16 (s, 3H), 2.65–2.73 (m, 2H), 3.70–3.85 (m, 2H), 3.88 (s, 3H), 4.21 and 4.32 (two s, 2H), 4.54 (s, 1H), 4.88 (s,1H), 6.21 (s, 1H), 7.07 (t, 1H, *J*=6.8 Hz), 7.10–7.15 (m, 2H), 7.15–7.23 (m, 2H), 7.33–7.40 (m, 3H), 7.51 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 20.1, 30.6, 31.1, 42.9, 43.3, 51.7, 52.0, 64.8, 97.5, 108.1, 114.9, 115.2, 120.2, 120.4, 120.5, 121.7, 121.9, 123.6, 125.2, 129.2, 131.9, 136.5, 136.6, 137.6, 141.4, 141.7, 151.3, 153.5, 153.7. High-resolution MS *m*/*z*: Calcd for $C_{24}H_{24}N_2O_3$: 388.1785. Found: 388.1805.

***N*-[2-(1-Methoxyindol-2-yl)prop-2-enyl-*N*-pent-3-ynylphenoxy-1-carboxamide (19).** IR (neat): 1712 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.78 (t, 3H, *J*=2.5 Hz), 2.45–2.60 (m, 2H), 3.50–3.60 (m, 2H), 3.86 and 3.89 (two s, 3H), 4.55 and 4.62 (two s, 2H), 5.45 (s, 1H), 6.01 and 6.07 (two s, 1H), 6.46 and 6.56 (two s, 1H), 7.05–7.15 (m, 3H), 7.15–7.25 (m, 2H), 7.30–7.45 (m, 3H), 7.50–7.60 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 3.5, 18.1, 18.7, 45.4, 46.8, 51.2, 63.9, 75.8, 76.3, 77.3, 77.6, 98.8, 99.4, 108.5, 114.7, 116.0, 120.3, 120.6, 120.7, 121.0, 121.2, 121.6, 122.1, 123.2, 123.5, 125.3, 129.2, 132.9, 133.0, 133.4, 133.7, 133.9, 151.3, 154.5, 154.7. High-resolution MS *m*/*z*: Calcd for $C_{24}H_{24}N_2O_3$: 388.1785. Found: 388.1794.

The cross-coupling reaction of indolylborate (2c) with vinyl bromide (9h)

To a solution of indolylborate (**2c**) in THF (180 ml) [generated in situ from the treatment of indole (**1c**) (2.4 g, 11 mmol) with *tert*-butyllithium (13 mmol), and the subsequent addition of triethylborane (13 mmol) under argon atmosphere], were added bromide (**9h**) (1.9 g, 5.4 mmol) and $Pd_2Cl_2(PPh_3)_2$ (100 mg, 0.14 mmol), and the mixture was heated at 60°C for 4 h. The reaction mixture was treated with 10% NaOH (50 ml) and 30% H_2O_2 (10 ml) under ice-cooling for 15 min. The mixture was diluted with AcOEt (500 ml), washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was separated by medium pressure liquid chromatography with hexane:AcOEt (10:1) as eluent to give 1.7 g (64%) of **20**.

Phenylmethyl 4-({1-[(*tert*-butyl)oxycarbonyl]indol-2-yl}-ethylidene)-3-ethylidenepiperidine-1-carboxylate (20). IR (neat): 1724, 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.30–1.50 (m, 3H), 1.61 (s, 9H), 1.90 (s, 3H), 2.32 (br s, 1H), 2.64 (br s, 1H), 3.50–3.80 (m, 3H), 4.40–4.55 (m, 1H), 5.17 (s, 2H), 5.10–5.25 (m, 1H), 7.17 (t, 1H, *J*=7.3 Hz), 7.23 (t, 1H, *J*=7.3 Hz), 7.30–7.45 (m, 6H), 8.14 (d, 1H, *J*=8.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.4. 20.3, 28.0, 30.3, 42.8, 45.6, 67.1, 83.3, 106.4, 115.3, 120.1, 122.6, 123.3, 123.9, 125.1, 127.8, 127.9, 128.4, 129.6, 133.7, 135.1, 136.4, 136.8, 142.7, 149.9, 155.4. High-resolution MS *m*/*z*: Calcd for $C_{30}H_{34}N_2O_4$: 486.25185. Found: 486.25213.

Phenylmethyl 6-[(*tert*-butyl)oxycarbonyl]-5,11-dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole-2-carboxylate (21). A solution of **20** (100 mg) in benzene (10 ml) was irradiated with a 100 W high-pressure mercury lamp through a Pyrex filter under ice-cooling for 4 h. The solvent was removed, and the residue was separated by medium pressure liquid chromatography with hexane:AcOEt (10:1) as eluent to give 40 mg (41%) of **21**. Mp 145°C (recryst. from EtOH). IR ($CHCl_3$): 1720, 1694 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.67 (s, 9H), 2.31 (s, 3H), 2.70 (br s, 3H), 2.92 (br s, 2H), 3.75–3.83 (m, 2H), 4.78 (s, 2H), 5.21 (s, 2H), 7.30–7.45 (m, 7H), 8.08 (d, 1H, *J*=8.3 Hz), 8.12 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.1, 17.2, 27.3, 28.1, 41.2, 44.5, 67.1, 83.7, 114.9, 117.0, 122.4, 122.9, 123.5, 124.2, 126.0, 127.3, 127.9, 128.0, 128.5, 132.7, 136.9, 138.0, 140.8, 151.3, 155.4. High-resolution MS *m*/*z*: Calcd for $C_{30}H_{32}N_2O_4$: 484.2362. Found: 484.2355. Anal. Calcd for $C_{30}H_{32}N_2O_4+1/5H_2O$: C, 73.80; H, 6.69; N, 5.73. Found: C, 73.63; H, 6.77; N, 5.62.

Phenylmethyl 5,11-dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole-2-carboxylate (22). A mixture of **21** (45 mg) and TFA (1 ml) in CH_2Cl_2 (10 ml) was stirred for 3 h at room temperature. The mixture was diluted with AcOEt (50 ml), washed with 10% NaOH (20 ml) and water, and dried over anhydrous $MgSO_4$. The solvent was removed, and the residue was separated by medium pressure liquid chromatography with hexane:AcOEt (5:1) to give 30 mg (88%) of **22**. Mp 208°C (recryst. from EtOH). IR ($CHCl_3$): 3484, 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.41 (s, 3H), 2.74 (s, 3H), 2.95 (br s, 2H), 3.78 (br s, 2H), 4.81 (s, 2H), 5.21 (s, 2H), 7.22 (t, 1H, *J*=7.3 Hz), 7.27–7.50

(m, 6H), 7.93 (br s, 1H), 8.20 (d, 1H, *J*=7.8 Hz). ^{13}C NMR δ: 12.8, 15.2, 26.7, 26.9, 41.5, 44.4, 67.1, 110.4, 114.2, 119.3, 120.2, 122.7, 122.9, 123.2, 124.4, 124.9, 127.9, 128.0, 128.5, 130.4, 136.9, 137.8, 139.8, 155.5. High-resolution MS *m*/*z*: Calcd for $C_{25}H_{24}N_2O_2$: 384.1837. Found: 384.1835. Anal. Calcd for $C_{25}H_{24}N_2O_2+1/5H_2O$: C, 77.37; H, 6.33; N, 7.21. Found: C, 77.22; H, 6.44; N, 6.95.

5,11-Dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]carbazole (23). A solution of **22** (100 mg) in THF (15 ml) in the presence of 20% $Pd(OH)_2$ on active carbon (10 mg) was stirred under atmospheric pressure of hydrogen at room temperature for 2 h. The catalyst and solvent were removed, and the residue was crystallized from ether to give 58 mg (90%) of **23**, which was used for the next reaction without further purification due to its instability. IR ($CHCl_3$): 3308, 3132, 3080 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.63 (br s, 1H), 2.39 (s, 3H), 2.70 (s, 3H), 2.88 (t, 2H, *J*=6 Hz), 3.20 (t, 2H, *J*=6 Hz), 4.19 (s, 2H), 7.20 (t, 1H, *J*=7.8 Hz), 7.37 (t, 1H, *J*=7.8 Hz), 7.41 (d, 1H, *J*=7.8 Hz), 7.89 (br s, 1H), 8.20 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 12.5, 15.0, 28.0, 43.8, 47.1, 110.3, 114.7, 119.1, 119.8, 122.6, 124.6, 124.7, 125.5, 126.7, 130.8, 137.7, 139.8. High-resolution MS *m*/*z*: Calcd for $C_{17}H_{18}N_2$: 250.1469. Found: 250.1455.

***tert*-Butyl 5,11-dimethyl-1,2,3,4-tetrahydropyrido[4,3-*b*]-carbazole-6-carboxylate (24).** A solution of **21** (270 mg) in THF (30 ml) in the presence of 20% $Pd(OH)_2$ on carbon (20 mg) was stirred under atmospheric pressure of hydrogen at room temperature for 2 h. Removal of catalyst and solvent gave 175 mg (90%) of **24**, which was used for the next reaction without further purification due to its instability. IR (neat): 3312, 1726 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.66 (s, 9H), 1.89 (br s, 1H), 2.28 (s, 3H), 2.62 (s, 3H), 2.83 (t, 2H, *J*=6 Hz), 3.18 (t, 2H, *J*=6 Hz), 4.15 (s, 2H), 7.31 (t, 1H, *J*=7.8 Hz), 7.40 (t, 1H, *J*=7.8 Hz), 8.08 (d, 1H, *J*=8.3 Hz), 8.10 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 14.7, 16.8, 28.0, 28.1, 43.5, 47.0, 83.4, 114.8, 121.9, 122.3, 122.8, 123.6, 125.7, 126., 127.5, 129.7, 133.1, 137.6, 140.8, 151.4. High-resolution MS *m*/*z*: Calcd for $C_{22}H_{26}N_2O_2$: 350.1994. Found: 350.1997.

***tert*-Butyl 5,11-dimethylpyrido[4,3-*b*]carbazole-6-carboxylate (25).** A mixture of **24** (170 mg) and active MnO_2 (2 g) in AcOEt (50 ml) was heated under reflux for 40 h. The insoluble material and solvent were removed, and the residue was separated by flash column chromatography with CH_2Cl_2:MeOH (50:1) to give 110 mg (65%) of **25**. Mp 131–132°C (recryst. from AcOEt–hexane). IR ($CHCl_3$): 1730, 1602 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.69 (s, 9H), 2.67 (s, 3H), 3.18 (s, 3H), 7.40 (t, 1H, *J*=7.3 Hz), 7.51 (t, 1H, *J*=7.3 Hz), 7.91 (d, 1H, *J*=6 Hz), 8.13 (d, 1H, *J*=8.3 Hz), 8.24 (d, 1H, *J*=7.8 Hz), 8.55 (d, 1H, *J*=6 Hz), 9.67 (s, 1H). ^{13}C NMR ($CDCl_3$) δ: 14.4, 16.7, 28.1, 84.2, 115.1, 116.7, 117.1, 123.4, 123.6, 125.1, 126.4, 126.8, 127.6, 127.7, 135.2, 139.6, 141.8, 142.2, 149.4, 151.0. High-resolution MS *m*/*z*: Calcd for $C_{22}H_{22}N_2O_2$: 346.1681. Found: 346.1686. Anal. Calcd for $C_{22}H_{22}N_2O_2$: C, 76.27; H, 6.40 N, 8.09. Found: C, 76.18; H, 6.55; N, 7.95.

Ellipticine. A mixture of **25** (100 mg) and TFA (1 ml) in CH_2Cl_2 (30 ml) was stirred at room temperature overnight. Then, 10% NaOH (2 ml) and AcOEt (50 ml) were added, the organic layer was washed with water, and dried over $MgSO_4$. After the solvent was removed, the residue was separated by flash chromatography with CH_2Cl_2:MeOH (30:1) to give 60 mg (84%) of ellipticine as orange crystals. Mp 315–317°C (recryst. from ethyl acetate) (lit.[5b] mp 312–314°C). ^{1}H NMR (CD_3OD) δ: 2.79 (s, 3H), 3.25 (s, 3H), 7.26 (ddd, 1H, *J*=1.5, 6.9, 8.3 Hz), 7.45–7.56 (m, 2H), 7.96 (dd, 1H, *J*=1, 6 Hz), 8.32 (d, 1H, *J*=6 Hz), 8.35 (d, 1H, *J*=7.8 Hz), 9.57 (s, 1H). High-resolution MS *m*/*z*: Calcd for $C_{17}H_{14}N_2$: 246.1157. Found: 246.1131.

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