Available online at www.sciencedirect.com
SCIENCE DIRECT
Tetrahedron
Tetrahedron 62 (2006) 1015–1024

A one-pot access to cycloalkano[1,2-*a*]indoles through an intramolecular alkyl migration reaction in indolylborates

Minoru Ishikura,[a,*] Wataru Ida[a] and Kazuo Yanada[b]

[a]*Faculty of Pharmaceutical Sciences, Health Sciences University of Hokkaido, Ishikari-Tobetsu, Hokkaido 061-0293, Japan*
[b]*Faculty of Pharmaceutical Sciences, Setsunan University, 45-1, Nagatoge-Cho, Hirakata, Osaka 573-0101, Japan*

Received 5 September 2005; accepted 11 October 2005

Available online 7 November 2005

Abstract—A novel one-pot protocol for the preparation of cycloalkano[1,2-*a*]indoles by way of an intramolecular alkyl migration reaction in cyclic indolylborates is described. NaOMe was found to act as a successful trialkylboryl-protecting group against to the lithiation at the C2 of the indole ring. Treatment of cyclic indolylborates with electrophiles produced cycloalkano-[1,2-*a*]indoles.

1. Introduction

The rich chemistry of organoboron compounds has provided fertile ground for the development of pivotal synthetic methodologies.[1] While an inter- or intramolecular alkyl migration from boron to carbon in organoboron compounds has been well recognized as a valuable synthetic tool for regioselective and stereospecific bond formation,[2] its use for intramolecular cyclization has been scarcely known.[3] In our continuing program to develop trialkyl(1*H*-indol-2-yl)borate as a versatile synthetic intermediate for the construction of indole derivatives,[4] an intramolecular alkyl migration from boron to the C2 of the indole ring in indolylborates has also been proven to be successful, leading to 2,3-disubstituted indoles in a one-pot treatment. Hence, we have become interested in the unprecedented use of the alkyl migration process in indolylborates, and previously reported a novel one-pot protocol for the preparation of carbazole derivatives based on the intramolecular 1,2-alkyl migration reaction in indolylborates, in which π-allyl palladium complexes were adopted as successful intramolecular electrophiles.[5]

As the core structure of [*a*]-annelated indole is present in a number of biologically active indole derivatives such as mitomycin and vincamine, the development of methods for the construction of [*a*]-annelated indole nuclei has been the subject of a number of reports.[6] We have set about the development of a novel one-pot access to [*a*]-annelated indoles by the use of the 1,2-alkyl migration process in indolylborate (**6**).[7]

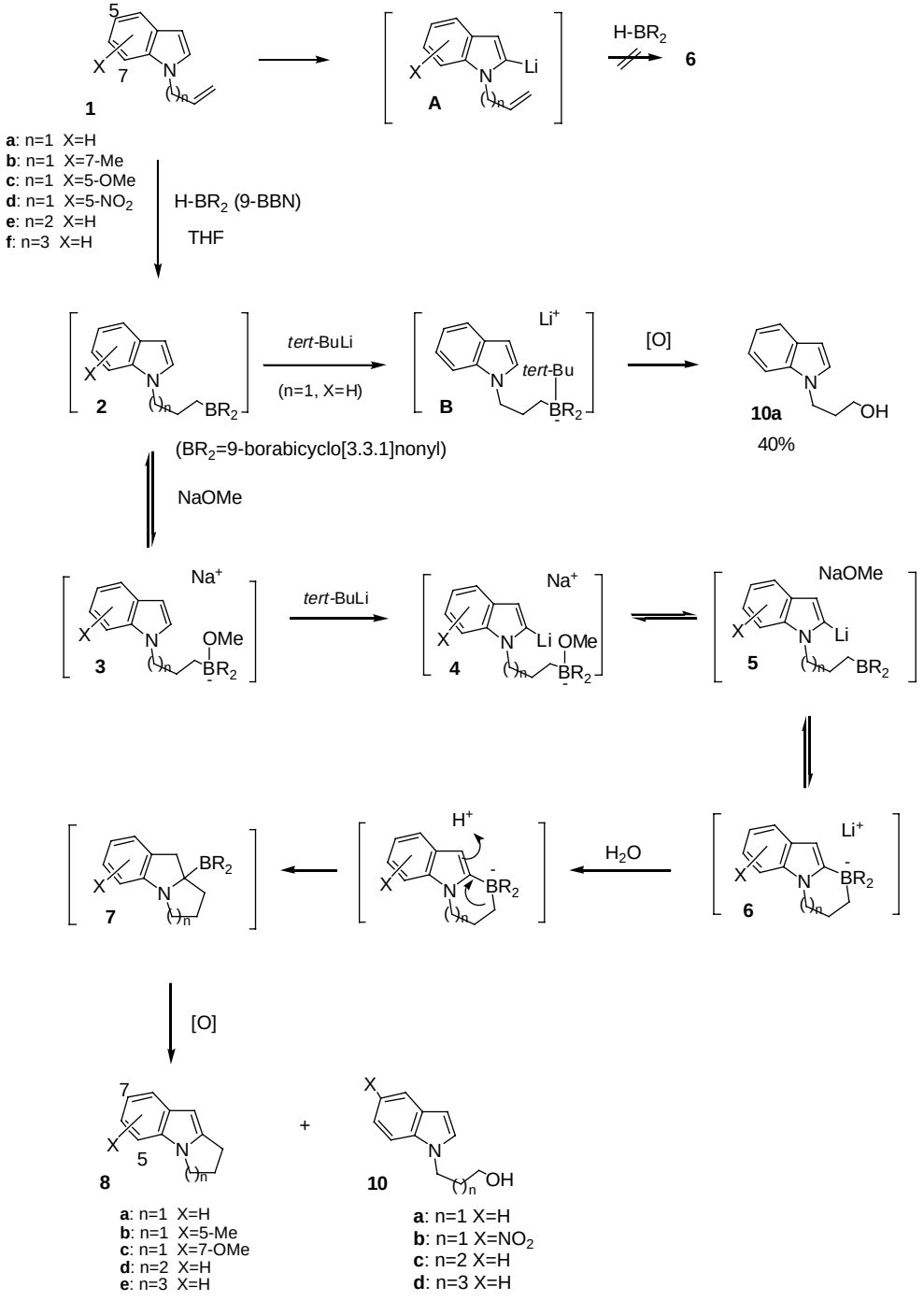
2. Results and discussion

As shown in Scheme 1, we initially envisioned that alkyl migration triggered by intermolecular attack of electrophile (H_2O) on the C-3 of the indole ring in cyclic indolylborate (**6**) might provide the cyclization product (**8**) after oxidation of **7**, in which implementation of the synthetic plan first required an adequate protocol for the in situ generation of **6**. Our initial expectation to form **6** via 2-lithioindole (**A**) involved straightforward lithiation of the starting indole (**1**), followed by treatment with dialkylboranes, but all attempted experiments have met with failure. Alternatively, we anticipated that if 2-lithioindole (**5**) is available by the lithiation at the C-2 of the indole ring of alkylborane (**2**), the following spontaneous cyclization might possibly provide cyclic indolylborate (**6**).

Initially, we attempted the lithiation with *tert*-BuLi at the C-2 of the indole ring in alkylboranes (**2**), readily generated by treatment of indole (**1a**) with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF at room temperature. However, an oxidative work-up of the reaction mixture allowed only the isolation of alcohol (**10a**) in 40% yield, which possibly involved the formation of tetraalkylborate (**B**) from the predominant interaction between the trialkylboryl group of **2** and *tert*-BuLi. With this in mind, we needed a feasible trialkylboryl-protecting group that would persist until the lithiation at the C2 of **2** was complete, and after that, would

Keywords: Cyclic indolylborate; Hydroboration; Intramolecular alkyl migration; [*a*]-Annelated indoles.
* Corresponding author. Tel./fax: +81 133 23 1245;
e-mail: ishikura@hoku-iryo-u.ac.jp

0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.10.045



Scheme 1.

be removed to restore the trialkylboryl group. We were pleased to find that the presence of NaOMe provided marked protection against the lithiation of **2** by the formation of methoxyborate (**3**), and the following work-up of the reaction mixture with H_2O_2 in NaOH solution afforded **8**, accompanied by a small amount of **10**. The reaction outcome can be interpreted as follows: (1) hydroboration of **1** with 9-BBN produces alkylborane (**2**). (2) Treatment of **2** with NaOMe forms methoxyborate (**3**). (3) Subsequent lithiation of **3** with *tert*-BuLi generates 2-lithioindole (**4**), which is accompanied by spontaneous formation of indolylborate (**6**) via elimination of the methoxide anion (**4** to **5**). (4) Intramolecular 1,2-alkyl migration in **6** provides [*a*]-annelated indole (**8**) after oxidation of **7**. Alcohols (**10**) were possibly produced by way of oxidation of **5** or **B**.

As summarized in Table 1, the use of NaOMe (1.1 equiv), *tert*-BuLi (2.2 equiv) and TMEDA (2.2 equiv) in THF was adequate to effect the one-pot transformation of **1a** to **8a**, and the conditions were applied to further investigations. Hydroboration of **5d** brought about **6** ($n=1$, $X=5$-NO_2) in situ, which was subsequently subjected to the reaction. However, the desired cyclization product was not obtained in this transformation and only alcohol (**10b**) was isolated from the complex reaction mixtures.

Table 1. One-pot preparation of **8** from **1**[a]

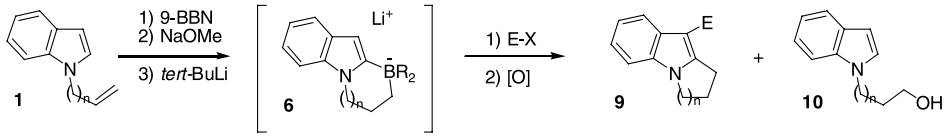
1	NaOMe (equiv)	*tert*-BuLi (equiv)	TMEDA (equiv)	Yield (%) of **8**	Yield (%) of **10**
$n=1$ X=H	—	2.2	2.2	**8a** (16)	**10a** (20)
$n=1$ X=H	1.1	2.2	2.2	**8a** (62)	—
$n=1$ X=H	2.2	2.2	2.2	**8a** (22)	**10a** (10)
$n=1$ X=H	1.1	1.1	2.2	**8a** (14)	**10a** (22)
$n=1$ X=H	1.1	3.0	2.2	**8a** (47)	**10a** (7)
$n=1$ X=H	1.1	2.2	—	**8a** (40)	**10a** (10)
$n=1$ X=H	1.1	2.2	1.1	**8a** (50)	**10a** (5)
$n=1$ X=7-Me	1.1	2.2	2.2	**8b** (53)	—
$n=1$ X=5-OMe	1.1	2.2	2.2	**8c** (60)	—
$n=1$ X=5-NO_2	1.1	2.2	2.2	—	**10b** (40)
$n=1$ X=H	1.1	2.2	2.2	**8d** (60)	**10c** (5)
$n=1$ X=H	1.1	2.2	2.2	**8e** (42)	**10d** (8)

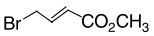
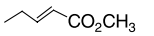
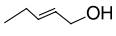
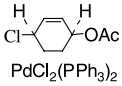
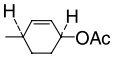
[a] Yield (%) of **8** and **10** based on **1**.

Treatment of **6** (X=H) with various electrophiles such as alkyl halides and π-allyl palladium complexes similarly produced [*a*]-annelated indoles (**9**), which allowed the introduction of various functional groups at the C3 of the indole ring (Table 2). On the reaction of indolylborate (**6**; $n=2$, X=H) with 3-bromocyclohexene, borinate (**9k**) was isolated as stable crystals in 35% yield after oxidation of the reaction mixture, which was in contrast to the formation of **9j** and **9l** from the reaction of **6** ($n=1,3$, X=H). Longer oxidation time and use of increased amount of H_2O_2 did not effect the production of **9k**. As there are examples of the successful use of diphenyliodonium ion as an electrophile toward the enolate anion,[8] the diphenyliodonium ion was also expected to be suitable for the promotion of the alkyl migration in **6**. The reaction of **6** (X=H, $n=1$) with diphenyliodonium chloride in THF under the same conditions afforded furanylindole (**9t**) in 30% yield as the only isolable product. This is probably due to the alkyl migration in **6** ($n=1$, X=H) caused by the electrophilic attack of the furanium ion (**C**) arising from the rapid oxidation of THF by diphenyliodonium ion[9] (Scheme 2).

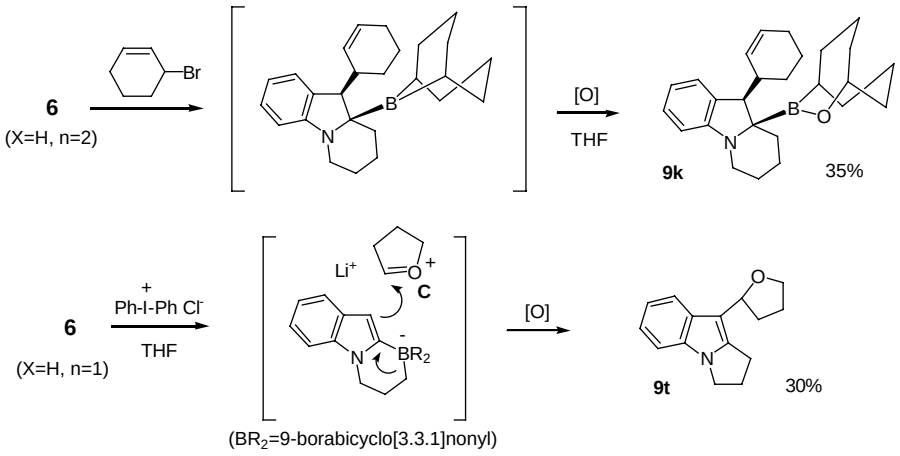
The alkyl migration reaction in indolylborates (**12**), derived from indoles (**11**) having a substituent at the olefinic carbon, was next examined. Indole (**11a**) was successfully

Table 2. One-pot preparation of **9** from **1** (X=H)[a]



E–X	E	*n*	Yield (%) of **9**	Yield (%) of **10**
CH_3–I	–CH_3	1	**9a** (55)	**10a** (10)
		2	**9b** (40)	**10c** (12)
		3	**9c** (30)	**10d** (22)
I–CH_2CN	–CH_2CN	1	**9d** (59)	**10a** (10)
		2	**9e** (40)	**10c** (10)
		3	**9f** (30)	**10d** (15)
Br–CH_2CH=CH_2	–CH_2CH=CH_2	1	**9g** (30)	**10a** (10)
		2	**9h** (30)	**10c** (15)
		3	**9i** (20)	**10d** (20)
		1	**9j** (42)	**10a** (10)
		2	—[b]	—
		3	**9l** (20)	**10d** (20)
		1	**9m** (55)	**10a** (10)
		2	**9n** (50)	**10c** (10)
		3	**9o** (39)	**10d** (10)
	–CH_2CH=CH_2	1	**9a** (60)	**10a** (10)
		2	**9b** (55)	**10c** (10)
		3	**9c** (26)	**10d** (15)
		1	**9p** (58)	**10a** (10)
		2	**9q** (50)	**10c** (15)
		3	**9i** (40)	**10d** (20)
		1	**9s** (42)	**10a** (10)

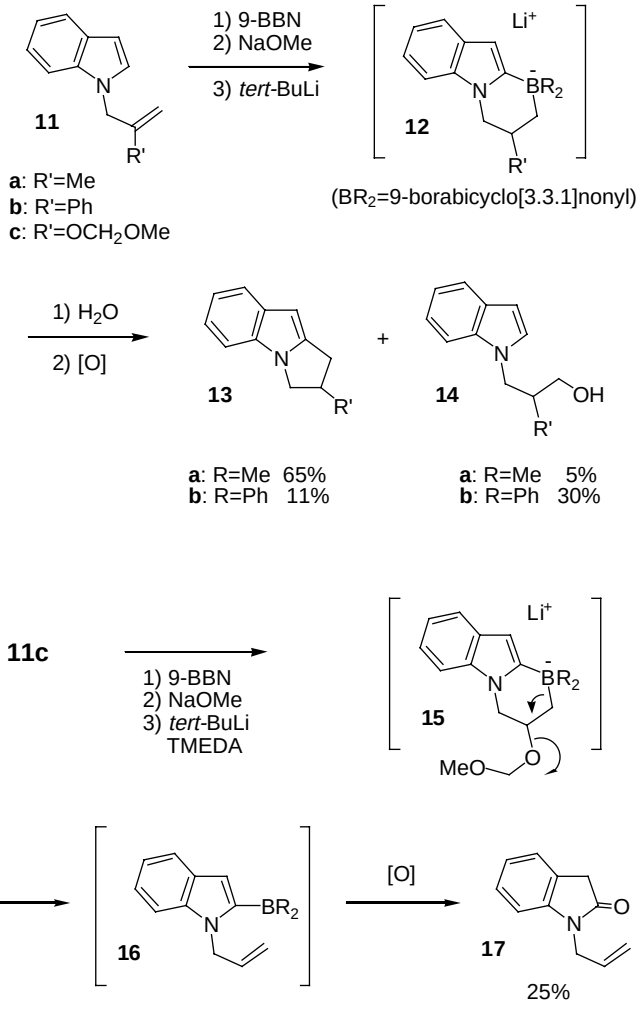
[a] Yield (%) of **9** and **10** based on **1**.
[b] Compound **9k** was isolated.



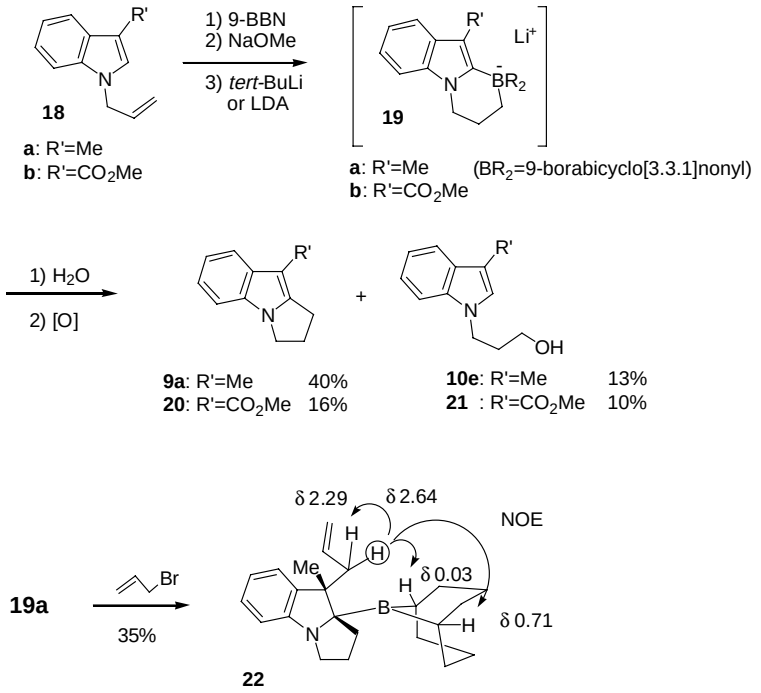
Scheme 2.

transformed to **13a** via **12** (R=Me). Otherwise, hydroboration of **11b** became much more sluggish, requiring forced reaction conditions (reflux for 2 h), and the following steps were less effective in giving **13b** in low yield, accompanied by a substantial amount of alcohol (**14b**). When indole (**11c**) bearing an alkoxy group was subjected to the alkyl migration reaction, 1-allyl-2-oxyindole (**17**) was isolated without the expected cyclization product. The rapid elimination of the alkoxy group from borate (**15**) predominantly took place to generate **16**, and the subsequent oxidation gave rise to **17**, as shown in Scheme 3.

Aqueous treatment of **19**, derived from indoles (**18**) bearing a substituent at the C-3 of the indole ring, affordrd [*a*]-annelated indoles (**9a**, **20**) and alcohols (**10e**, **21**), respectively (Scheme 4). In the case of **18b**, LDA was employed for the



Scheme 3.



Scheme 4.

lithiation at the C-2 of the indole ring in order to generate indolylborate (**19b**). Otherwise, simply treating **19a** with allyl bromide and the following work-up of the reaction mixture without a conventional oxidation allowed the isolation of alkylborane (**22**) in 35% yield as stable crystals. The reaction proceeded through the electrophilic attack of allyl bromide at the C-3 of the indole ring in **19a** with simultaneous alkyl migration in an *anti* manner[5] to produce **22**, whose structure was confirmed based on NOE experiments.

In summary, we have demonstrated a new one-pot access to cycloalkano[1,2-*a*]indoles (**9**) by way of the unprecedented use of an intramolecular alkyl migration process in indolylborate (**6**). Further extension of the protocol for the preparation of indole alkaloid is under way.

3. Experimental

3.1. General

Melting points were recorded on a Yamato MP21 and are uncorrected. MS and high-resolution MS spectra 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-ECA500 spectrometer, and chemical shifts are expressed in ppm (δ) with TMS as an internal reference. Medium pressure liquid chromatography (MPLC) was performed on silica gel (Silica Gel 60N, Kanto Chemical Co., Ltd).

3.2. General procedure for the preparation of 8

To a solution of **1** (2 mmol) in THF (10 mL), 9-BBN (0.5 M solution in THF, 2.2 mmol) was added at room temperature under an argon atmosphere, and the mixture was stirred for 1.5 h. Sodium methoxide (2.2 mmol) was added to the mixture, and after stirring for 30 min, TMEDA (4.4 mmol) and *tert*-BuLi (1.5 M solution in pentane, 4.4 mmol) were added to the mixture at −20 °C. After stirring for 2 h, the mixture was gradually raised to room temperature, and stirred for 4 h. To the reaction mixture, 20% NaOH (10 mL) and 30% H_2O_2 (2 mL) were added under ice-cooling and the whole was stirred for 30 min. The mixture was diluted with ethyl acetate (100 mL), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC to give **8** (with hexane/AcOEt=100:1) and **10** (with hexane/AcOEt=1:1).

3.2.1. 2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indole (8a). Mp 77–78 °C (lit.[10] 78–79 °C). ^{1}H NMR ($CDCl_3$) δ: 2.59 (tt, 2H, J=6.8, 7.3 Hz), 3.00 (t, 2H, J=7.3 Hz), 4.04 (t, 2H, J=6.8 Hz), 6.15 (s, 1H), 7.03 (dt, 1H, J=1.4, 7.1 Hz), 7.10 (dt, 1H, J=1.4, 7.1 Hz), 7.22 (d, 1H, J=7.1 Hz), 7.53 (d, 1H, J=7.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 24.1, 27.7, 43.4, 92.1, 109.3, 119.9, 120.1, 132.5, 133.2, 144.5. MS *m/z*: 157 (M^+).

3.2.2. 5-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (8b). Mp 90–91 °C (hexane). ^{1}H NMR ($CDCl_3$) δ: 2.64 (s, 3H), 2.55–2.65 (m, 2H), 2.94 (t, 2H, J=7.4 Hz), 4.36 (t, 2H, J=6.8 Hz), 6.11 (s, 1H), 6.81 (d, 1H, J=7.9 Hz), 6.91 (t, 1H, J=7.9 Hz), 7.34 (d, 1H, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 17.9, 23.7, 27.9, 46.5, 92.6, 118.1, 119.3, 120.2, 121.7, 132.3, 133.4, 144.7. MS *m/z*: 171 (M^+). Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.38; H, 7.55; N, 8.24.

3.2.3. 7-Methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (8c). Mp 85–87 °C (lit.[11] 84–85 °C). ^{1}H NMR ($CDCl_3$) δ: 2.50–2.60 (m, 2H), 2.97 (t, 2H, J=7.8 Hz), 3.83 (s, 3H),

3.98 (t, 2H, J=7.0 Hz), 6.08 (s, 1H), 6.77 (d, 1H, J=7.8 Hz), 7.02 (br s, 1H), 7.09 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 24.4, 27.7, 43.7, 55.9, 92.0, 102.6, 109.9, 128.1, 133.6, 145.3, 153.9. MS *m*/*z*: 187 (M^+).

3.2.4. 6,7,8,9-Tetrahydropyrido[1,2-*a*]indole (8d). Mp 58–59 °C (lit.[12] 57–58 °C). ^{1}H NMR ($CDCl_3$) δ: 1.80–1.95 (m, 2H), 2.00–2.15 (m, 2H), 2.97 (t, 2H, J=6.3 Hz), 3.00 (t, 2H, J=7.3 Hz), 4.04 (t, 2H, J=6.4 Hz), 6.14 (s, 1H), 7.06 (dt, 1H, J=1.5, 7.8 Hz), 7.13 (dt, 1H, J=1.5, 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, 23.3, 24.1, 42.1, 97.3, 108.4, 119.4, 119.9, 128.1, 136.1, 137.0. MS *m*/*z*: 171 (M^+).

3.2.5. 7,8,9,10-Tetrahydro-6*H*-azepino[1,2-*a*]indole (8e). Mp 86–85 °C (lit.[12] 83–85 °C). ^{1}H NMR ($CDCl_3$) δ: 2.59 (tt, 2H, J=6.8, 7.3 Hz), 3.00 (t, 2H, J=7.3 Hz), 4.04 (t, 2H, J=6.8 Hz), 6.15 (s, 1H), 7.03 (dt, 1H, J=1.4, 7.1 Hz), 7.10 (dt, 1H, J=1.4, 7.1 Hz), 7.22 (d, 1H, J=7.1 Hz), 7.53 (d, 1H, J=7.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 8.1, 28.6, 29.4, 31.0, 44.5, 98.9, 108.5, 118.8, 119.7, 120.2, 127.7, 136.8, 143.2. MS *m*/*z*: 185 (M^+).

3.3. General procedure for the preparation of 9

To a solution of **1** (2 mmol) in THF (10 mL), 9-BBN (0.5 M solution in THF, 2.2 mmol) was added at room temperature under an argon atmosphere, and the mixture was stirred for 1.5 h. Sodium methoxide (2.2 mmol) was added to the mixture, and after stirring for 30 min, TMEDA (4.4 mmol) and *tert*-BuLi (1.5 M solution in pentane, 4.4 mmol) were added to the mixture at −20 °C. After stirring for 2 h, the mixture was gradually raised to room temperature, and stirred for 4 h. Then, electrophile (5 mmol) was added, and the whole was stirred overnight (in the cases of alkyl halides) or heated under reflux for 3 h (in the cases of π-allyl palladium complexes). To the reaction mixture, 20% NaOH (10 mL) and 30% H_2O_2 (2 mL) were added under ice-cooling and the whole was stirred for 30 min. The mixture was diluted with ethyl acetate (100 mL), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC to give **9** (with hexane/AcOEt=100:1–10:1) and **10** (with hexane/AcOEt=1:1).

3.3.1. 9-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (9a). Mp 50–51 °C (lit.[13] 48–49 °C). ^{1}H NMR ($CDCl_3$) δ: 2.24 (s, 3H), 2.52 (m, 2H), 2.88 (t, 2H, J=7.3 Hz), 3.95 (t, 2H, J=6.9 Hz), 7.00–7.12 (m, 2H), 7.15 (d, 1H, J=7.8 Hz), 7.45 (d, 1H, J=7.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 8.8, 22.7, 27.5, 43.3, 100.4, 108.7, 118.1, 119.8, 133.0, 132.4, 141.1. MS *m*/*z*: 171 (M^+).

3.3.2. 5-Methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (9b). ^{1}H NMR ($CDCl_3$) δ: 1.88–1.94 (m, 2H), 2.04–2.10 (m, 2H), 2.24 (s, 3H), 2.90 (t, 2H, J=6.3 Hz), 4.03 (t, 2H, J=6.3 Hz), 7.11 (t, 1H, J=7.8 Hz), 7.17 (t, 1H, J=8.0 Hz), 7.25 (d, 1H, J=8.0 Hz), 7.52 (d, 1H, J=8.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 8.2, 21.4, 22.5, 23.7, 42.4, 104.8, 108.4, 117.8, 119.0, 120.2, 128.6, 133.0, 136.0. HR-MS *m*/*z*: Calcd for $C_{13}H_{15}N$: 185.1204. Found: 185.1192.

3.3.3. 11-Methyl-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]indole (9c). Mp 88–89 °C (hexane). ^{1}H NMR ($CDCl_3$) δ: 1.67–1.78 (m, 4H), 1.81–1.88 (m, 2H), 2.25 (s, 3H), 2.86 (t, 2H, J=5.8 Hz), 4.13 (t, 2H, J=5.2 Hz), 7.04 (t, 1H, J=7.8 Hz), 7.13 (t, 1H, J=7.8 Hz), 7.23 (d, 1H, J=8.0 Hz), 7.48 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 8.8, 25.5, 28.0, 29.8, 31.3, 44.6, 105.5, 108.2, 118.3, 120.4, 128.3, 135.8, 139.1. MS *m*/*z*: 199 (M^+). Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.42; H, 8.77; N, 7.01.

3.3.4. 9-Allyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (9d). IR (neat): 1660, 1640, 1610 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.55 (tt, 2H, J=7.2, 7.3 Hz), 2.92 (t, 2H, J=7.3 Hz), 3.45 (d, 2H, J=5.6 Hz), 3.99 (t, 2H, J=7.2 Hz), 5.00 (dd, 1H, J=1.5, 10.0 Hz), 5.10 (dd, 1H, J=1.7, 17.0 Hz), 6.02 (ddt, 1H, J=17.0, 10.0, 5.6 Hz), 7.03 (dd, 1H, J=7.8, 7.9 Hz), 7.09 (dd, 1H, J=7.8, 7.9 Hz), 7.18 (d, 1H, J=7.8 Hz), 7.49 (d, 1H, J=7.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.1, 27.6, 29.3, 43.3, 102.9, 109.1, 114.3, 118.4, 118.5, 119.9, 132.3, 132.4, 137.4, 141.5. HR-MS *m*/*z*: Calcd for $C_{14}H_{15}N$: 197.1203. Found: 197.1220.

3.3.5. 10-Allyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (9e). ^{1}H NMR ($CDCl_3$) δ: 1.88–1.94 (m, 2H), 2.05–2.11 (m, 2H), 2.89 (t, 2H, J=6.3 Hz), 3.47 (d, 2H, J=6.3 Hz), 4.04 (t, 2H, J=6.3 Hz), 5.01 (dd, 1H, J=1.0, 10.1 Hz), 5.09 (dd, 1H, J=1.0, 17.1 Hz), 5.99 (tdd, 1H, J=6.3, 10.1, 17.1 Hz), 7.09 (t, 1H, J=7.8 Hz), 7.15 (t, 1H, J=7.8 Hz), 7.26 (d, 1H, J=7.8 Hz), 7.54 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.2, 22.5, 23.5, 28.5, 42.4, 107.0, 108.5, 114.2, 118.0, 119.1, 120.2, 127.9, 133.5, 136.0, 137.5. HR-MS *m*/*z*: Calcd for $C_{15}H_{17}N$: 211.1361. Found: 211.1353.

3.3.6. 11-Allyl-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]indole (9f). ^{1}H NMR ($CDCl_3$) δ: 1.67–1.73 (m, 2H), 1.73–1.79 (m, 2H), 1.81–1.87 (m, 2H), 2.85 (t, 2H, J=5.2 Hz), 3.48 (td, 2H, J=1.7, 6.3 Hz), 4.15 (t, 2H, J=5.8 Hz), 4.96 (qd, 1H, J=1.5, 11.4 Hz), 5.03 (qd, 1H, J=1.5, 17.2 Hz), 5.96 (tdd, 1H, J=6.3, 11.4, 17.2 Hz), 7.03 (t, 1H, J=7.8 Hz), 7.13 (dt, 1H, J=1.5, 7.8 Hz), 7.25 (d, 1H, J=8.0 Hz), 7.50 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 25.5, 27.9, 28.8, 29.6, 31.2, 44.6, 107.7, 108.4, 114.1, 118.4, 118.5, 120.5, 127.6, 135.8, 138.1, 139.6. HR-MS *m*/*z*: Calcd for $C_{16}H_{19}N$: 225.1517. Found: 225.1526.

3.3.7. 2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indol-9-ylacetonitrile (9g). Mp 99–100 °C (hexane). IR ($CHCl_3$): 2430 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 2.55–2.65 (m, 2H), 3.03 (t, 2H, J=7.3 Hz), 3.73 (s, 2H), 4.00 (t, 2H, J=6.8 Hz), 7.11 (dt, 1H, J=1.0, 7.8 Hz), 7.15 (dt, 1H, J=1.0, 7.8 Hz), 7.21 (d, 1H, J=7.8 Hz), 7.46 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.5, 23.1, 27.5, 43.7, 93.4, 109.6, 117.5, 118.1, 119.3, 120.9, 130.9, 132.3, 142.5. MS *m*/*z*: 196 (M^+). Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.58; H, 6.25; N, 14.26.

3.3.8. 6,7,8,9-Tetrahydropyrido[1,2-*a*]indol-10-ylacetonitrile (9h). Mp 102–103 °C (hexane). IR ($CHCl_3$): 2428 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ: 1.91–1.97 (m, 2H), 2.06–2.12 (m, 2H), 2.94 (t, 2H, J=6.3 Hz), 3.74 (s, 3H), 4.04 (t, 2H, J=6.3 Hz), 7.16 (t, 1H, J=7.8 Hz), 7.19 (t, 1H, J=7.8 Hz), 7.28 (d, 1H, J=8.0 Hz), 7.55 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 12.7, 20.7, 22.3, 23.1, 42.3, 97.5, 108.9, 117.1, 118.2, 120.1, 121.1, 126.6, 134.6, 135.9.

MS *m/z*: 210 (M^+). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 79.74; H, 6.74; N, 13.20.

3.3.9. 7,8,9,10-Tetrahydro-6*H*-azepino[1,2-*a*]indol-11-ylacetonitrile (9i). Mp 102–103 °C (hexane). IR ($CHCl_3$): 2430 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.73–1.80 (m, 4H), 1.85–1.90 (m, 2H), 2.90 (t, 2H, J=5.1 Hz), 3.78 (s, 3H), 4.17 (t, 2H, J=5.1 Hz), 7.13 (t, 1H, J=7.8 Hz), 7.20 (dt, 1H, J=1.5, 7.8 Hz), 7.28 (d, 1H, J=8.0 Hz), 7.55 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 13.1, 25.6, 27.4, 29.3, 31.0, 44.8, 98.6, 108.9, 117.6, 118.5, 119.5, 121.4, 126.4, 135.8, 140.6. MS *m/z*: 224 (M^+). Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.22; H, 7.33; N, 12.35.

3.3.10. 9-Cyclohex-2-en-1-yl-2,3-dihydro-1*H*-pyrrolo-[1,2-*a*]indole (9j). Mp 53–54 °C (hexane). ^1H NMR ($CDCl_3$) δ: 1.62–1.71 (m, 1H), 1.72–1.83 (m, 2H9), 1.96–2.04 (m, 1H), 2.08–2.14 (m, 2H), 2.52–2.60 (m, 2H), 2.91–3.03 (m, 2H), 3.66–3.71 (m, 1H), 4.01 (t, 2H, J=7.0 Hz), 5.83 (s, 1H), 7.01 (t, 1H, J=7.8 Hz), 7.09 (t, 1H, J=7.8 Hz), 7.20 (d, 1H, J=8.0 Hz), 7.55 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.5, 24.1, 25.2, 27.7, 30.6, 32.7, 43.1, 109.1, 109.5, 118.2, 118.7, 119.9, 127.0, 131.0, 131.6, 132.3, 140.9. MS *m/z*: 237 (M^+). Anal. Calcd for $C_{17}H_{19}N+1/10H_2O$: C, 85.38; H, 8.09; N, 5.85. Found: C, 85.30; H, 8.22; N, 5.90.

3.3.11. *rel*-(9a*R*,10*S*)-10-Cyclohex-2-en-1-yl-9a-(9-oxa-10-borabicyclo[3.3.2]dec-10-yl)-6,7,8,9,9a,10-hexahydropyrido[1,2-*a*]indole (9k). Mp 209–210 °C (hexane/AcOEt). ^1H NMR ($CDCl_3$) δ: 0.74–0.83 (m, 1H), 1.30–2.10 (m, 24H), 2.40 (dd, 1H, J=2.8, 5.1 Hz), 2.91 (d, 1H, J=2.8 Hz), 3.51 (dt, 1H, J=2.8, 13.4 Hz), 3.60 (d, 1H, J=13.4 Hz), 4.80–4.86 (m, 1H), 5.63 (d, 1H, J=10.3 Hz), 5.72 (td, 1H, J=1.8, 10.3 Hz), 6.48 (d, 1H, J=7.5 Hz), 6.54 (t, 1H, J=7.5 Hz), 6.99 (d, 1H, J=6.9 Hz), 7.05 (t, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.1, 21.6, 22.1, 22.6, 23.6, 24.7, 24.8, 26.9, 27.1, 31.4, 33.9, 40.2, 43.9, 56.9, 67.6, 74.3, 108.2, 116.2, 126.2, 127.3, 128.7, 130.8, 131.8, 152.8. MS *m/z*: 388, 389 (M^+). Anal. Calcd for $C_{26}H_{36}BNO+1/4H_2O$: C, 79.28; H, 9.34; N, 3.55. Found: C, 79.03; H, 9.35; N, 3.53.

3.3.12. 11-Cyclohex-2-en-1-yl-7,8,9,10-tetrahydro-6*H*-azepino[1,2-*a*]indole (9l). Mp 94–95 °C (hexane). ^1H NMR ($CDCl_3$) δ: 1.62–1.94 (m, 10H), 2.09–2.25 (m, 2H), 2.83–2.93 (m, 2H), 3.63–3.70 (m, 1H), 4.09–4.19 (m, 2H), 5.79 (d, 1H, J=10.3 Hz), 5.85 (td, 1H, J=2.3, 9.7 Hz), 6.99 (t, 1H, J=8.0 Hz), 7.10 (t, 1H, J=8.0 Hz), 7.24 (d, 1H, J=8.4 Hz), 7.63 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.0, 25.2, 25.4, 28.2, 29.5, 31.2, 31.7, 33.7, 44.4, 108.4, 114.0, 118.1, 119.4, 120.2, 126.9, 127.0, 132.5, 135.8, 139.0. MS *m/z*: 265 (M^+). Anal. Calcd for $C_{19}H_{23}N+1/10H_2O$: C, 85.40; H, 8.75; N, 5.24. Found: 85.24; H, 8.72; N, 5.16.

3.3.13. Methyl (2*E*)-4-(2,3-dihydro-1*H*-pyrrolo[1,2-*a*]-indol-9-yl)but-2-enoate (9m). IR ($CHCl_3$): 1710, 1648 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.50–2.65 (m, 2H), 2.92 (t, 2H, J=7.5 Hz), 3.60 (d, 2H, J=6.3 Hz), 3.69 (s, 3H), 4.04 (t, 2H, J=6.8 Hz), 5.84 (td, 1H, J=1.8, 15.4 Hz), 7.05 (t, 1H, J=7.8 Hz), 7.10–7.19 (m, 2H), 7.21 (d, 1H, J=8.0 Hz), 7.43 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.3, 27.8, 27.9, 43.7, 51.4, 100.9, 109.5, 118.3, 118.9, 120.4, 120.9, 132.1, 132.6, 142.2, 148.1, 167.3. MS *m/z*: Calcd for $C_{16}H_{17}NO_2$: 255.1259. Found: 255.1258.

3.3.14. Methyl (2*E*)-4-(6,7,8,9-tetrahydropyrido[1,2-*a*]-indol-10-yl)-but-2-enoate (9n). Mp 84–85 °C (hexane). IR ($CHCl_3$): 1710, 1654 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.87–1.93 (m, 2H), 2.03–2.11 (m, 2H), 2.83 (t, 2H, J=6.3 Hz), 3.57 (dd, 2H, J=1.7, 6.3 Hz), 3.67 (s, 3H), 4.03 (t, 2H, J=6.3 Hz), 5.78 (td, 1H, J=1.7, 15.5 Hz), 7.08 (t, 1H, J=7.8 Hz), 7.14 (t, 1H, J=7.8 Hz), 7.25 (d, 1H, J=8.0 Hz), 7.43 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.1, 22.4, 23.4, 26.9, 42.3, 51.4, 104.8, 108.6, 117.7, 119.4, 120.5, 120.6, 127.6, 134.0, 136.0, 148.0, 167.3. MS *m/z*: 269 (M^+). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.80; H, 7.11; N, 5.20. Found: C, 75.71; H, 6.93; N, 5.11.

3.3.15. Methyl (2*E*)-4-(7,8,9,10-tetrahydro-6*H*-azepino-[1,2-*a*]indol-11-yl)but-2-enoate (9o). IR ($CHCl_3$): 1708 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.66–1.72 (m, 2H), 1.74–1.80 (m, 2H), 1.83–1.90 (m, 2H), 2.82 (t, 2H, J=5.2 Hz), 3.61 (dd, 2H, J=1.7, 6.3 Hz), 3.67 (s, 3H), 4.16 (t, 2H, J=4.6 Hz), 5.75 (dt, 1H, J=1.7, 15.5 Hz), 7.05 (t, 1H, J=8.0 Hz), 7.11 (dt, 1H, J=6.3, 15.5 Hz), 7.17 (t, 1H, J=8.0 Hz), 7.25 (d, 1H, J=8.0 Hz), 7.42 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 25.6, 27.3, 27.9, 29.5, 31.2, 42.0, 51.4, 105.6, 108.6, 118.1, 118.8, 120.7, 120.8, 127.4, 136.0, 140.2, 148.7, 167.4. MS *m/z*: Calcd for $C_{18}H_{21}NO_2$: 283.1572. Found: 283.1570.

3.3.16. (2*E*)-4-(2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]indol-9-yl)but-2-en-1-ol (9p). IR ($CHCl_3$): 3612 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.55–2.65 (m, 2H), 2.93 (t, 2H, J=7.5 Hz), 3.46 (d, 2H, J=6.9 Hz), 4.03 (t, 2H, J=6.8 Hz), 4.09 (br s, 2H), 5.71–5.78 (m, 1H), 5.90 (ttd, 1H, J=1.2, 6.3, 15.5 Hz), 7.03 (dt, 1H, J=1.0, 7.8 Hz), 7.10 (dt, 1H, J=1.0, 7.8 Hz), 7.20 (d, 1H, J=8.0 Hz), 7.48 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.3, 27.7, 43.4, 63.4, 103.1, 109.2, 118.5, 120.3, 129.0, 131.6, 132.2, 132.5, 141.5. HR-MS *m/z*: Calcd for $C_{15}H_{17}NO$: 227.1310. Found: 227.1305.

3.3.17. (2*E*)-4-(6,7,8,9-Tetrahydro-1*H*-pyrido[1,2-*a*]-indol-10-yl)but-2-en-1-ol (9q). IR ($CHCl_3$): 3612 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.86–1.93 (m, 2H), 2.03–2.10 (m, 2H), 2.87 (t, 2H, J=6.9 Hz), 3.44 (d, 2H, J=6.3 Hz), 4.03 (t, 2H, J=6.3 Hz), 4.07 (br s, 2H), 5.65–5.74 (m, 1H), 5.80–5.88 (m, 1H), 7.07 (t, 1H, J=8.0 Hz), 7.13 (t, 1H, J=8.0 Hz), 7.24 (d, 1H, J=8.0 Hz), 7.44 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.2, 22.5, 23.5, 26.9, 63.8, 107.1, 108.6, 117.9, 119.2, 120.3, 127.8, 128.8, 131.9, 133.4, 136.0. HR-MS *m/z*: Calcd for $C_{16}H_{19}NO$: 241.1466. Found: 241.1466.

3.3.18. (2*E*)-4-(7,8,9,10-Tetrahydro-6*H*-azepino[1,2-*a*]-indol-11-yl)but-2-en-1-ol (9r). IR ($CHCl_3$): 3612 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.65–1.91 (m, 6H), 2.85 (t, 2H, J=5.7 Hz), 3.48 (d, 2H, J=5.7 Hz), 4.06 (d, 2H, J=6.3 Hz), 4.15 (t, 2H, J=4.6 Hz), 5.64–5.71 (m, 1H), 5.84 (td, 1H, J=5.7, 15.1 Hz), 7.04 (t, 1H, J=7.8 Hz), 7.14 (t, 1H, J=7.8 Hz), 7.25 (d, 1H, J=8.0 Hz), 7.49 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 25.6, 27.2, 28.0, 29.6, 31.2, 44.6, 63.6, 107.9, 108.5, 118.4, 118.6, 120.6, 127.5, 128.7, 132.5, 135.9, 139.6. HR-MS *m/z*: Calcd for $C_{17}H_{12}NO$: 255.1623. Found: 255.1612.

3.3.19. *rel*-(1*R*,4*S*)-4-(2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]-indol-9-yl)cyclohex-2-en-1-yl acetate (9s). Mp 101–02 °C (hexane/AcOEt). IR ($CHCl_3$): 1720 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.86–1.94 (m, 1H), 1.94–2.00 (m, 1H), 2.09 (s, 3H), 2.55–2.65 (m, 2H), 2.99 (t, 2H, J=7.3 Hz), 3.60–3.66 (m, 2H), 4.02 (t, 2H, J=7.3 Hz), 5.30–5.36 (m, 1H), 5.88 (ddd, 1H, J=2.4, 4.0, 10.0 Hz), 6.10 (dd, 1H, J=2.4, 10.0 Hz), 7.04 (t, 1H, J=7.8 Hz), 7.11 (t, 1H, J=7.8 Hz), 7.21 (d, 1H, J=8.0 Hz), 7.54 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 21.4, 24.2, 26.2, 27.4, 27.8, 32.9, 43.2, 67.5, 107.9, 109.3, 118.5, 118.6, 120.2, 125.1, 131.5, 132.5, 136.8, 141.1, 170.8. MS *m*/*z*: 295 (M^+). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.02; H, 7.12; N, 4.49.

3.3.20. 9-(Tetrahydrofuran-2-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (9t). Mp 72–73 °C (hexane/AcOEt). ^1H NMR ($CDCl_3$) δ: 2.00–2.20 (m, 3H), 2.22–2.30 (m, 1H), 2.56–2.62 (m, 2H), 2.99–3.11 (m, 2H), 3.88–3.94 (m, 1H), 4.02 (t, 2H, J=6.9 Hz), 4.06–4.12 (m, 1H), 5.16 (t, 1H, J=7.4 Hz), 7.05 (t, 1H, J=8.0 Hz), 7.11 (t, 1H, J=8.0 Hz), 7.20 (d, 1H, J=8.0 Hz), 7.59 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 24.2, 26.6, 27.4, 43.5, 68.0, 75.4, 106.7, 109.5, 119.0, 119.4, 120.4, 131.1, 132.9, 141.8. MS *m*/*z*: 227 (M^+). Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.05; H, 7.68; N, 5.99.

3.3.21. 3-(1*H*-Indol-1-yl)propan-1-ol (10a). IR ($CHCl_3$): 3616 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.56 (br s, 1H), 2.03–2.10 (m, 2H), 3.58 (t, 2H, J=5.7 Hz), 4.28 (t, 2H, J=6.8 Hz), 6.51 (d, 1H, J=2.9 Hz), 7.09–7.15 (m, 2H), 7.22 (t, 1H, J=7.8 Hz), 7.39 (d, 1H, J=8.0 Hz), 7.64 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 32.7, 42.7, 59.6, 101.2, 109.4, 119.4, 121.1, 121.5, 128.0, 128.7, 136.1. HR-MS *m*/*z*: Calcd for $C_{11}H_{13}NO$: 175.0997. Found: 175.0982.

3.3.22. 3-(5-Nitro-1*H*-indol-1-yl)propan-1-ol (10b). Mp 85 °C (hexane/AcOEt). IR ($CHCl_3$): 3628 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.57 (br s, 1H), 2.03–2.12 (m, 2H), 3.61 (t, 2H, J=6.3 Hz), 4.34 (t, 2H, J=6.9 Hz), 6.68 (d, 1H, J=2.3 Hz), 7.28 (d, 1H, J=2.3 Hz), 7.41 (d, 1H, J=9.0 Hz), 8.10 (dd, 1H, J=1.7, 8.6 Hz), 8.58 (d, 1H, J=1.7 Hz). ^{13}C NMR ($CDCl_3$) δ: 32.6, 43.1, 59.0, 104.1, 109.3, 117.3, 118.3, 127.7, 131.2, 139.0, 141.6. MS *m*/*z*: 220 (M^+). Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.76; H, 5.51; N, 12.89.

3.3.23. 4-(1*H*-Indol-1-yl)butan-1-ol (10c). IR ($CHCl_3$): 3624 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.50–1.55 (m, 2H), 1.68 (br s, 1H), 1.87–1.94 (m, 2H), 3.59 (t, 2H, J=6.3 Hz), 4.15 (t, 2H, J=6.8 Hz), 6.55 (d, 2H, J=2.9 Hz), 7.09–7.14 (m, 2H), 7.22 (t, 1H, J=8.0 Hz), 7.36 (d, 1H, J=8.0 Hz), 7.64 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 26.8, 30.1, 46.2, 62.3, 101.1, 109.5, 119.4, 121.1, 121.5, 127.9, 128.7, 136.0. HR-MS *m*/*z*: Calcd for $C_{12}H_{15}NO$: 189.1154. Found: 189.1166.

3.3.24. 5-(1*H*-Indol-1-yl)pentan-1-ol (10d). IR ($CHCl_3$): 3620 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.35–1.40 (m, 2H), 1.53–1.60 (m, 2H), 1.83–1.90 (m, 2H), 3.60 (t, 2H, J=6.3 Hz), 4.13 (t, 2H, J=6.8 Hz), 6.49 (d, 1H, J=2.9 Hz), 7.08–7.12 (m, 2H), 7.21 (t, 1H, J=8.0 Hz), 7.34 (d, 1H, J=8.0 Hz), 7.63 (d, 1H, J=7.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 23.4, 30.2, 32.4, 46.4, 62.7, 101.0, 109.4, 119.3, 121.1, 121.4, 127.9, 128.7, 136.0. HR-MS *m*/*z*: Calcd for $C_{13}H_{17}NO$: 203.1310. Found: 203.1295.

3.4. General procedure for the preparation of 13, 14 and 17

The reaction using **11** was carried out according to the procedure for the prepatation of **8**. Hydroboration of **11b** with 9-BBN was effected under reflux for 2 h.

3.4.1. 2-Methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (13a). Mp 58–59 °C (hexane/AcOEt). ^1H NMR ($CDCl_3$) δ: 1.29 (d, 3H, J=6.9 Hz), 2.63 (dd, 1H, J=6.9, 15.9 Hz), 3.04–3.14 (m, 1H), 3.19 (dd, 1H, J=8.0, 15.9 Hz), 3.62 (dd, 1H, J=6.3, 9.7 Hz), 4.22 (dd, 1H, J=7.4, 9.7 Hz), 6.15 (s, 1H), 7.05 (dt, 1H, J=1.0, 7.8 Hz), 7.11 (td, 1H, J=1.0, 7.8 Hz), 7.21 (d, 1H, 8.0 Hz), 7.54 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 19.7, 33.0, 37.3, 50.9, 92.6, 109.3, 119.1, 120.2, 120.3, 132.8, 132.9, 144.2. MS *m*/*z*: 171 (M^+). Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.15; H, 7.64; N, 8.16.

3.4.2. 2-Phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (13b). ^1H NMR ($CDCl_3$) δ: 3.17 (dd, 1H, J=7.5, 15.9 Hz), 3.50 (dd, 1H, J=8.0, 15.9 Hz), 4.09 (dd, 1H, J=6.8, 9.9 Hz), 4.15–4.22 (m, 1H), 4.51 (dd, 1H, J=8.1, 9.9 Hz), 6.27 (s, 1H), 7.13 (t, 1H, J=7.8 Hz), 7.18 (t, 1H, J=7.8 Hz), 7.26–7.33 (m, 4H), 7.35–7.40 (m, 2H), 7.63 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 33.3, 47.9, 51.1, 93.0, 109.5, 119.4, 120.5, 120.6, 127.1, 127.2, 129.0, 132.9, 133.2, 142.9, 143.6. HR-MS *m*/*z*: Calcd for $C_{17}H_{15}N$: 233.1204. Found: 233.1210.

3.4.3. 3-(1*H*-Indol-1-yl)-2-methylpropan-1-ol (14a). IR ($CHCl_3$): 3624 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 0.97 (d, 3H, J=6.9 Hz), 1.37 (br s, 1H), 2.20–2.29 (m, 1H), 3.49 (d, 2H, J=4.0 Hz), 3.99 (dd, 1H, J=6.9, 14.3 Hz), 4.24 (dd, 1H, J=6.9, 14.3 Hz), 7.17–7.12 (m, 2H), 7.20 (t, 1H, J=8.0 Hz), 7.38 (d, 1H, J=8.0 Hz), 7.63 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 15.0, 36.9, 49.0, 65.1, 101.2, 109.6, 119.3, 121.0, 121.5, 128.6, 136.4. HR-MS *m*/*z*: Calcd for $C_{12}H_{15}NO$: 189.1154. Found: 189.1153.

3.4.4. 3-(1*H*-Indol-1-yl)-2-phenylindole (14b). IR ($CHCl_3$): 3624 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.42 (br s, 1H), 3.31–3.38 (m, 1H), 3.78 (br s, 2H), 4.33 (dd, 1H, J=6.9, 14.4 Hz), 4.59 (dd, 1H, J=8.0, 14.4 Hz), 6.42 (d, 1H, J=3.5 Hz), 6.92 (d, 1H, J=3.5 Hz), 7.10 (t, 1H, J=7.8 Hz), 7.18–7.23 (m, 3H), 7.25–7.31 (m, 1H), 7.31–7.39 (m, 3H), 7.62 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 48.3, 48.7, 64.1, 101.3, 109.5, 119.5, 121.1, 121.6, 127.5, 128.1, 128.5, 128.7, 129.0, 136.2, 139.9. HR-MS *m*/*z*: Calcd for $C_{17}H_{17}NO$: 251.1301. Found: 231.1304.

3.4.5. 1-Allyl-1,3-dihydro-2*H*-indol-2-one (17). IR (neat): 1708 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 3.55 (s, 2H), 4.34 (dt, 2H, J=5.1, 1.5 Hz), 5.21 (dd, 1H, J=1.0, 10.3 Hz), 5.23 (dd, 1H, J=1.0, 17.1 Hz), 5.84 (tdd, 1H, J=5.1, 10.3, 17.1 Hz), 6.81 (d, 1H, J=7.8 Hz), 7.02 (dt, 1H, J=1.0, 7.8 Hz), 7.23 (t, 1H, J=7.8 Hz), 7.24 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 35.7, 42.2, 108.9, 117.5, 122.3, 124.3, 124.4,

127.7, 131.4, 144.3, 174.7. HR-MS *m*/*z*: Calcd for $C_{11}H_{11}NO$: 173.0840. Found: 173.0822.

3.5. Procedure for the preparation of 9a, 20, 10e and 21 from 18

Conversion of **18a** to **9a** (40%) and **10a** (13%) was carried out according to the procedure for the preparation of **8**.

Reaction using **18b** was effected as follows: to a solution of **18b** (430 mg, 2 mmol) in THF (10 mL), 9-BBN (0.5 M solution in THF, 2.2 mmol) was added at room temperature under an argon atmosphere, and the mixture was stirred for 1.5 h. Sodium methoxide (118 mg, 2.2 mmol) was added to the mixture, and after stirring for 30 min, LDA (4.4 mmol) was added to the mixture at −78 °C. After stirring for 1 h, the mixture was gradually raised to room temperature, and stirred for 4 h. To the reaction mixture, 20% NaOH (10 mL) and 30% H_2O_2 (2 mL) were added under ice-cooling and the whole was stirred for 30 min. The mixture was diluted with ethyl acetate (100 mL), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC to give **20** (69 mg, 16%) (with hexane/AcOEt=50:1) and **21** (47 mg, 10%) (with hexane/AcOEt=1:1).

3.5.1. 3-(1*H*-3-Methylindol-1-yl)propan-1-ol (10e). IR ($CHCl_3$): 3624 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.01–2.07 (m, 2H), 2.32 (s, 3H), 3.58–3.63 (m, 2H), 4.21 (t, 2H, J=6.3 Hz), 6.88 (s, 1H), 7.09 (t, 1H, J=7.8 Hz), 7.19 (t, 1H, J=7.8 Hz), 7.33 (d, 1H, J=8.0 Hz), 7.56 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 9.6, 32.8, 42.3, 59.7, 109.1, 110.4, 118.6, 119.1, 121.4, 125.6, 128.8, 136.4. HR-MS *m*/*z*: Calcd for $C_{12}H_{15}NO$: 189.1154. Found: 189.1142.

3.5.2. Methyl 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole-9-carboxylate (20). Mp 92–93 °C (hexane). IR (neat): 1686 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 2.61–2.70 (m, 2H), 3.29 (t, 2H, J=7.5 Hz), 3.89 (s, 3H), 4.11 (t, 2H, J=5.8 Hz), 7.18–7.28 (m, 3H), 8.09 (d, 1H, J=8.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 26.2, 26.7, 44.5, 50.8, 99.5, 109.9, 121.5, 121.7, 121.8, 130.9, 132.7, 152.9, 166.0. HR-MS *m*/*z*: 215 (M^+). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: 72.53; H, 6.11; N, 6.46.

3.5.3. Methyl 1-(3-hydroxypropyl)-1*H*-indole-3-carboxylate (21). IR (neat): 1690 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 1.65 (br s, 1H), 2.03–2.11 (m, 2H), 3.60 (t, 2H, J=5.8 Hz), 3.90 (s, 3H), 4.32 (t, 2H, J=6.3 Hz), 7.25–7.29 (m, 2H), 7.39–7.42 (m, 1H), 8.15–8.19 (m, 1H). ^{13}C NMR ($CDCl_3$) δ: 32.1, 43.2, 51.1, 59.0, 107.1, 110.0, 121.8, 121.9, 122.8, 126.7, 134.6, 136.6, 165.7. HR-MS *m*/*z*: $C_{13}H_{15}NO_3$: 233.1051. Found: 233.1042.

3.5.4. *rel*-(9*R*,9a*S*)-9-Allyl-9a-(9-borabicyclo[3.3.1]non-9-yl)-9-methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]-indole (22). To a solution of **18a** (342 mg, 2 mmol) in THF (10 mL), 9-BBN (0.5 M solution in THF, 2.2 mmol) was added at room temperature under an argon atmosphere, and the mixture was stirred for 1.5 h. Sodium methoxide (118 mg, 2.2 mmol) was added to the mixture, and after stirring for 30 min, TMEDA (0.6 mL, 4.4 mmol) and *tert*-BuLi (1.5 M solution in pentane, 4.4 mmol) were added to the mixture at −20 °C. After stirring for 2 h, the mixture was gradually raised to room temperature, and stirred for 4 h. To the reaction mixture, allyl bromide (605 mg, 5 mmol) was added and the mixture was stirred at room temperature overnight. The mixture was diluted with ethyl acetate (100 mL), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC (hexane/AcOEt=100:1) to give **22** (232 mg, 35%).

Mp 127–128 °C (hexane/AcOEt). ^1H NMR ($CDCl_3$) δ: 0.03 (br s, 1H), 0.71 (br s, 1H), 1.22 (s, 3H), 1.15–1.35 (m, 1H), 1.38–1.88 (m, 13H), 2.03 (dd, 1H, J=7.4, 12.6 Hz), 2.10–2.20 (m, 1H), 2.29 (dd, 1H, J=9.7, 13.2 Hz), 2.64 (td, 1H, J=2.3, 13.2 Hz), 3.06 (dt, 1H, J=6.8, 11.4 Hz), 3.35 (t, 1H, J=9.7 Hz), 5.12 (d, 1H, J=10.1 Hz), 5.16 (d, 1H, J=17.2 Hz), 5.96 (dtd, 1H, J=4.6, 10.1, 17.2 Hz), 6.98 (dd, 1H, J=1.7, 8.3 Hz), 7.05 (dd, 1H, J=1.7, 7.8 Hz), 7.10–7.17 (m, 2H). ^{13}C NMR ($CDCl_3$) δ: 21.0, 23.4, 24.1, 26.6, 26.8, 31.6, 31.9, 32.7, 33.7, 43.1, 48.7, 52.1, 117.2, 117.9, 123.1, 125.7, 126.8, 136.7, 146.6, 148.2. MS *m*/*z*: 332, 333 (M^+). Anal. Calcd for $C_{23}H_{32}BN$: C, 82.87; H, 9.67; N, 4.20. Found: C, 82.74; H, 9.77; N, 4.16.

Acknowledgements

This was supported in part by 'Academic Frontier' Project for Private University: matching fund subsidy from Ministry of Education, Culture, Sports, Science and Technology, 2002–2006.

References and notes

1. (a) Brown, H. C. *Organic Synthesis via Boranes*; Wiley: New York, 1975. (b) Vaultier, M.; Carboni, B. Boron. In Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Comprehensive Organometallic Chemistry II; Pergamon Press: London, 1995; Vol. 11, pp 191–276. (c) Suzuki, A.; Brown, H. C.; Organic Synthesis via Boranes, Suzuki Coupling; Aldrich Chemical: Milwaukee, 2003; Vol. 3.
2. (a) Brown, H. C. The rich chemistry of vinylic organoboranes. In *Organic Synthesis Today and Tomorrow*; Trost, B. M., Hutchinson, C. R., Eds.; Pergamon, 1980; pp 121–137. (b) Negishi, E.; Idacavage, M. J. *Org. React.* **1985**, *33*, 1–246.
3. (a) Hawthrone, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 1886–1888. (b) Binger, P.; Koster, R. *Tetrahedron Lett.* **1961**, 156–160. (c) Brown, H. C.; Rhodes, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 4306–4308. (d) Merrill, R. E.; Allen, J. L.; Abramovitch, A.; Negishi, E. *Tetrahedron Lett.* **1977**, 1019–1022.
4. Ishikura, M. *Curr. Org. Chem.* **2002**, *6*, 507–521.
5. Ishikura, M.; Kato, H. *Tetrahedron* **2002**, *58*, 9827–9838.
6. (a) Verboom, W.; Reinhoudt, D. N. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 199–213. (b) Kozikowski, A. P.; Ma, D. *Tetrahedron Lett.* **1991**, *28*, 3317–3320. (c) Ziegler, F. E.; Jeroncic, L. O. *J. Org. Chem.* **1991**, *56*, 3479–3486. (d) Markgraf, J. H.; Snyder, S. A.; Vosburg, D. A. *Tetrahedron Lett.* **1998**, *39*, 1111–1112. (e) Esmaeili, A. A.; Kheybari, H. *J. Chem. Res., Synop.* **2002**, 456–466. (f) Colandrea, V. J.; Rajaraman, S.; Jimenez, L. S. *Org. Lett.* **2003**, *5*, 785–787. (g) Katritzky, A. R.; Verma, A. K.; He, H. Y.; Chandra, R.

J. Org. Chem. **2003**, *68*, 4938–4940. (h) Vigushin, D. M.; Brooke, G.; Willows, D.; Coobes, R. C.; Moody, C. J. *Bioorg. Med. Chem. Lett.* **2003**, *13*, 3661–3663. (i) Coleman, R. S.; Felpin, F. X.; Chen, W. *J. Org. Chem.* **2004**, *69*, 7309–7316. (j) Sechi, M.; Mura, A.; Sannia, L.; Orecchioni, M.; Paglietti, G. *ARKIVOC* **2004**, 97–106.

7. Ishikura, M.; Terashima, M. *Tetrahedron Lett.* **1992**, *33*, 6849–6852.
8. (a) Chen, K.; Koser, G. F. *J. Org. Chem.* **1991**, *56*, 5764. (b) Gao, P.; Portoghese, P. S. *J. Org. Chem.* **1995**, *60*, 2276.
9. Moriaty, R. M.; Prakash, O. *Org. React.* **2001**, *57*, 327–415.
10. Schweizer, E. E.; Light, K. N. *J. Org. Chem.* **1966**, *31*, 870–872.
11. Yamada, Y.; Yanagi, H.; Okada, H. *Agric. Biol. Chem.* **1974**, *38*, 381–386.
12. Bit, R. A.; Davis, P. D.; Hill, C. H.; Keech, E.; Vesey, D. R. *Tetrahedron* **1991**, *47*, 4645–4664.
13. Bailey, A. S.; Scott, P. W.; Vandrevala, M. H. *J. Chem. Soc., Perkin Trans. 1* **1980**, 97–101.