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# A synthetic use of the intramolecular alkyl migration process in indolylborates for intramolecular cyclization: a novel construction of carbazole derivatives

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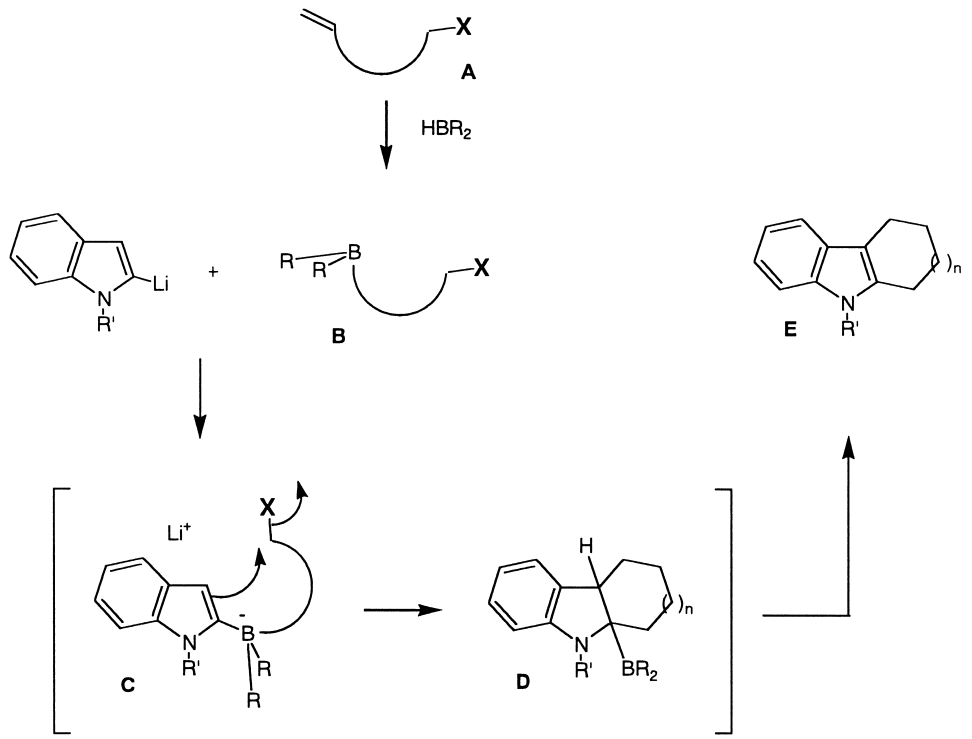
**Abstract**—The intramolecular alkyl migration reaction in indolylborates was developed for the one-pot construction of carbazoles via intramolecular cyclization in which π-allylpalladium complexes were successfully adopted as an acceptor for the indole nucleophile. 

The indole framework has been widely accepted as a pivotal structure with representatives in numerous natural isolates and medicinal agents, and, therefore, indole derivatives have been for a long time the target of synthetic chemists.[1] In connection with our project directed toward the synthetic applications of heteroarylboron compounds,[2] we have recently been developing a new access to indole derivatives based on indolylborates **2**, an example of which showed that a cross-coupling protocol using indolylborate was of apparent value in indole alkaloid synthesis.[3]

An intramolecular 1,2-alkyl migration from boron to carbon




**Scheme 1.**

*Keywords*: indolylborate; intramolecular alkyl migration; palladium catalyst; carbazoles.

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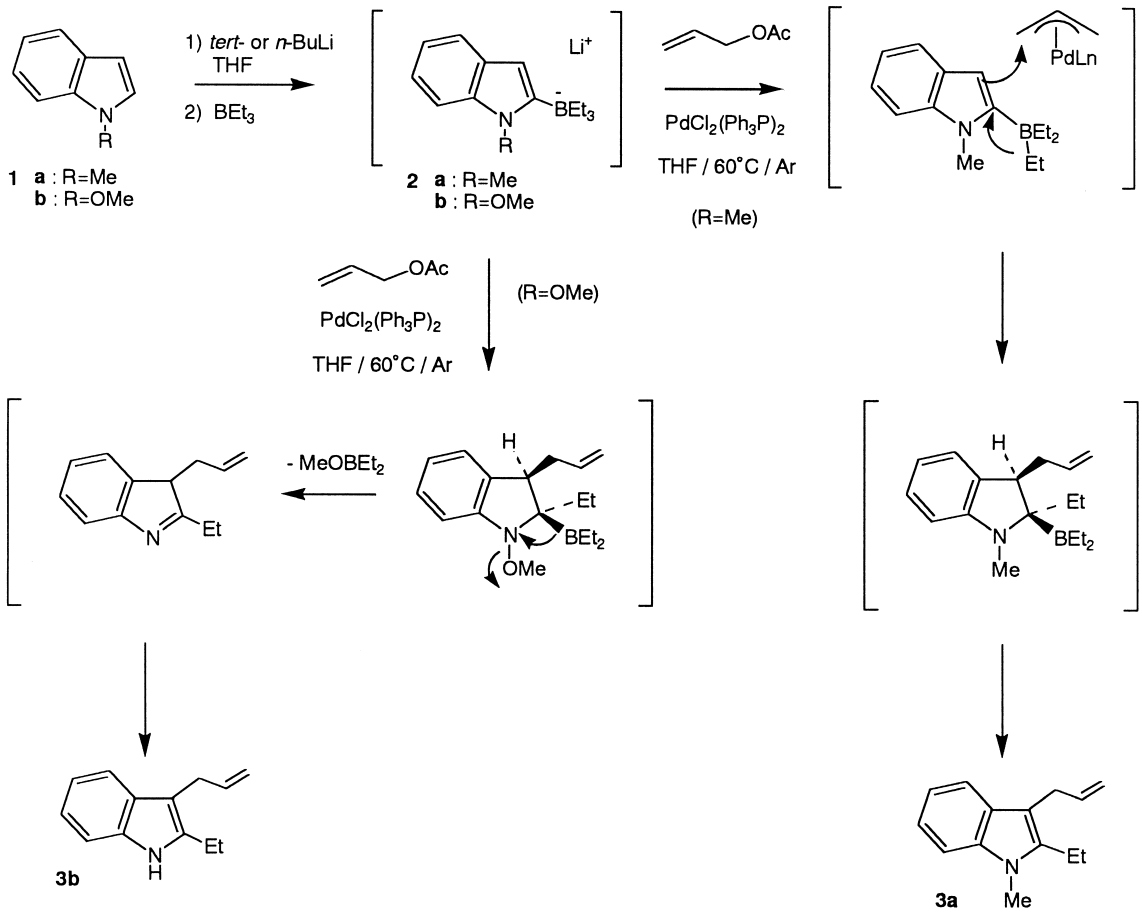
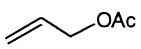
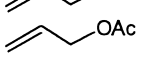
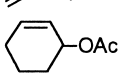
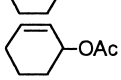
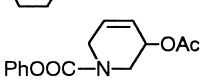
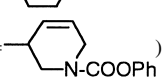
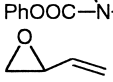
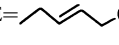
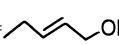


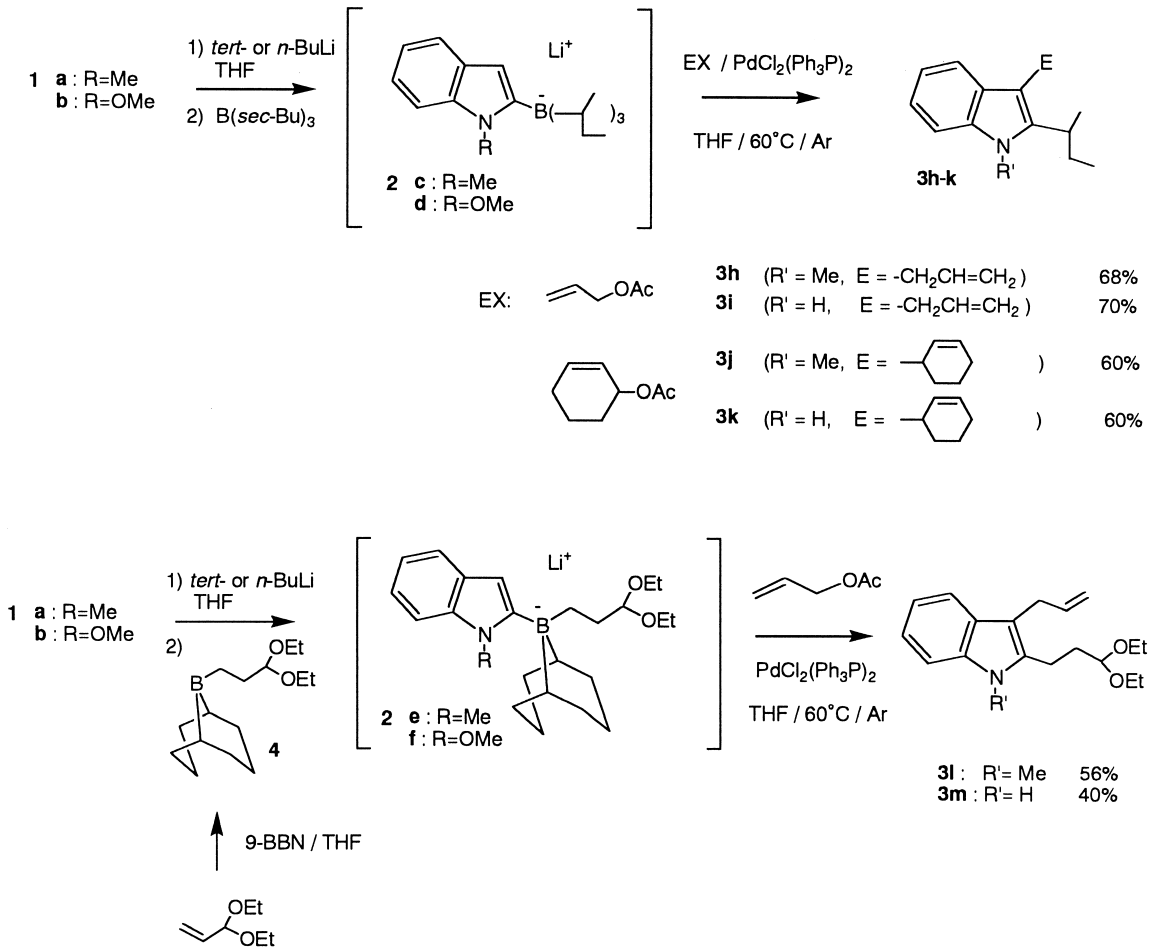

**Scheme 2.**

in trialkylalkenylborate has been well identified as a useful protocol for carbon–carbon bond formation,[4] and the alkyl migration process has been also shown to be successful in furan-, pyrrole-, indole-, and pyridine-substituted borane compounds.[5] Recently, we have embarked upon extending the scope of this migration process in indolylborate **2** to an intramolecular cyclization enabling the one-pot construction of poly-cyclic indole derivatives, and these results are reported in this paper.[6]

As depicted in Scheme 1, we envisioned that an alkyl migration triggered by an intramolecular nucleophilic attack of the C-3 of the indole ring on the electrophilic site (X) in indolylborate **C** might provide the cyclization product **E** via

**Table 1**. Reaction of indolylborates (**2**) with π-allylpalladium complexes

| **2** | Allyl esters vinyl epoxide | **3** | Yield (%) | **3a–g** |
|---|---|---|---|---|
| **2a** |  | **3a** | 75 | (R′=Me, E=$-CH_2CH{=}CH_2$) |
| **2b** |  | **3b** | 70 | (R′=H, E=$-CH_2CH{=}CH_2$) |
| **2a** |  | **3c** | 75 | (R′=Me, E=  ) |
| **2b** |  | **3d** | 73 | (R′=H, E=  ) |
| **2a** |  | **3e** | 60 | (R′=Me, E=  ) |
| **2a** |  | **3f** | 60 | (R′=Me, E=  ) |
| **2b** |  | **3g** | 58 | (R′=H, E=  ) |



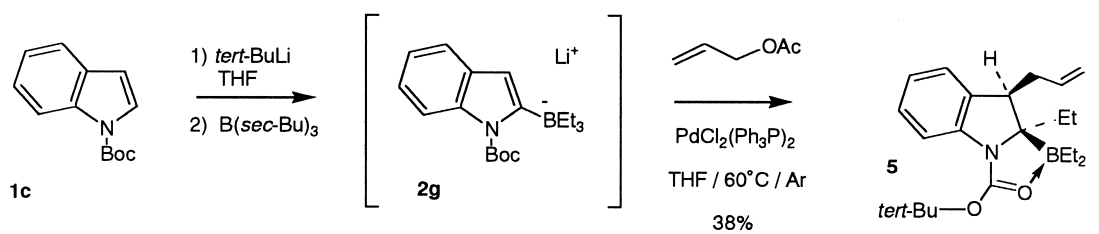

**Scheme 3.**

**D** in a one-pot manner. However, there are restrictions in that the precursor of electrophilic site (X) must be left intact in both the hydroboration of **A** with dialkylborane (borane formation) and the reaction of 2-lithioindole with **B** (borate formation). Also, the precursor (X) must be feasibly labile toward the indole nucleophile in the alkyl migration-cyclization steps (from **C** to **D**). Thus, we speculated that allyl ester could favorably withstand both the borane and borate formations, and that a π-allylpalladium complex carried by the oxidative addition of an allyl ester to the palladium (0) compound is an activated form capable of accepting the indole nucleophile in the cyclization step.

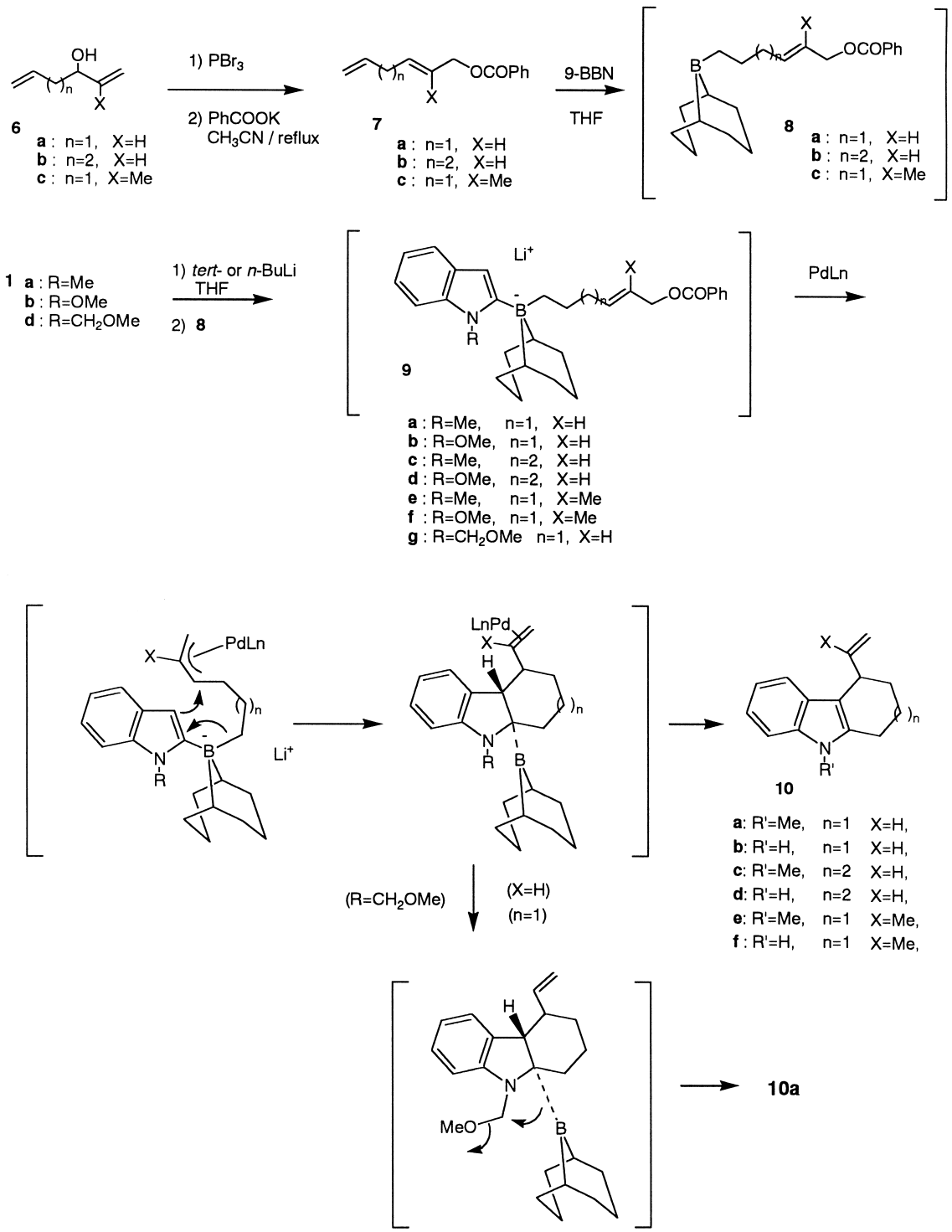
Thus, our study commenced with an intermolecular reaction of allyl acetate with indolylborates **2** in the presence of a catalytic amount of palladium complex in order to show the availability of π-allyl-palladium complexes as electrophiles in the alkyl migration step.

Simply, to a THF solution of indolylborate **2a** generated from indole **1a**,[7] allyl acetate (1.5 equiv.) and $PdCl_2(Ph_3P)_2$ (5 mol%) were added, and the mixture was heated at 60°C under an argon atmosphere. The reaction proceeded successfully to give 3-allyl-2-ethyl-1-methylindole **3a**, in which the ethyl group migrated from boron to carbon (C2 of the indole) at the opposite side from the nucleophilic approach (C3 of the indole) to π-allylpalladium complexes.[8] Otherwise, **3b** was the product from the reaction of **2b**, generated from **1b**,[7] with allyl acetate in the presence of $PdCl_2(Ph_3P)_2$, accompanied by the elimination of the OMe group (Scheme 2). As summarized in Table 1, various π-allylpalladium complexes, carried from allyl acetates and vinyl epoxide with a catalytic amount of $PdCl_2(Ph_3P)_2$, exerted sufficient electrophilicity toward the indole nucleophile, giving rise to **3** in good yields.

Subjection of indolylborates **2c**–**f** with sterically encumbered




**Scheme 4.**




**Scheme 5.**

trialkylboryl groups [(*sec*-butyl)$_3$B, and **4**] to the alkyl migration reaction with allyl acetate in the presence of $PdCl_2(Ph_3P)_2$ was also effective in producing indoles **3h**–**m** in modest to good yields (Scheme 3).

Otherwise, treating indolylborate **2g** (derived from indole **1c**),[7] which contained a weak electron-withdrawing Boc group at the 1-position of the indole ring, with allyl acetate in the presence of $PdCl_2(PPh_3P)_2$ allowed the isolation of alkylborane **5** (38% yield), which is stable possibly owing to the intramolecular coordination of the oxygen of Boc group to boron (Scheme 4). Borane **5** was resistant to conventional oxidation with $H_2O_2$ under basic conditions at 0°C even after the elongation of the reaction time.

Having established the availability of π-allylpalladium complexes as electrophiles capable of promoting the intramolecular alkyl migration, we next sought to extend this protocol to the intramolecular cyclization process in a one-pot manner from indoles **1**. Thus, indolylborates **9** were

**Table 2**. Formation of **10** through intramolecular cyclization

| 9 | PdLn | Yield of **10**[a] (%) |
|---|---|---|
| **9a** | $Pd(Ph_3P)_4$ | **10a** (56) |
| **9b** | $Pd(Ph_3P)_4$ | **10b** (27) |
| **9b** | $Pd_2(dba)_3{\cdot}CHCl_3+4Ph_3P$ | **10b** (56) |
| **9c** | $Pd(Ph_3P)_4$ | **10c** (40) |
| **9d** | $Pd(Ph_3P)_4$ | **10d** (26) |
| **9d** | $Pd_2(dba)_3{\cdot}CHCl_3+4Ph_3P$ | **10d** (23) |
| **9e** | $Pd(Ph_3P)_4$ | **10e** (40) |
| **9f** | $Pd(Ph_3P)_4$ | **10f** (25) |
| **9f** | $Pd_2(dba)_3{\cdot}CHCl_3+4Ph_3P$ | **10f** (34) |
| **9g** | $Pd(Ph_3P)_4$ | **10a** (6) |
| **9g** | $Pd_2(dba)_3{\cdot}CHCl_3+4Ph_3P$ | **10a** (13) |

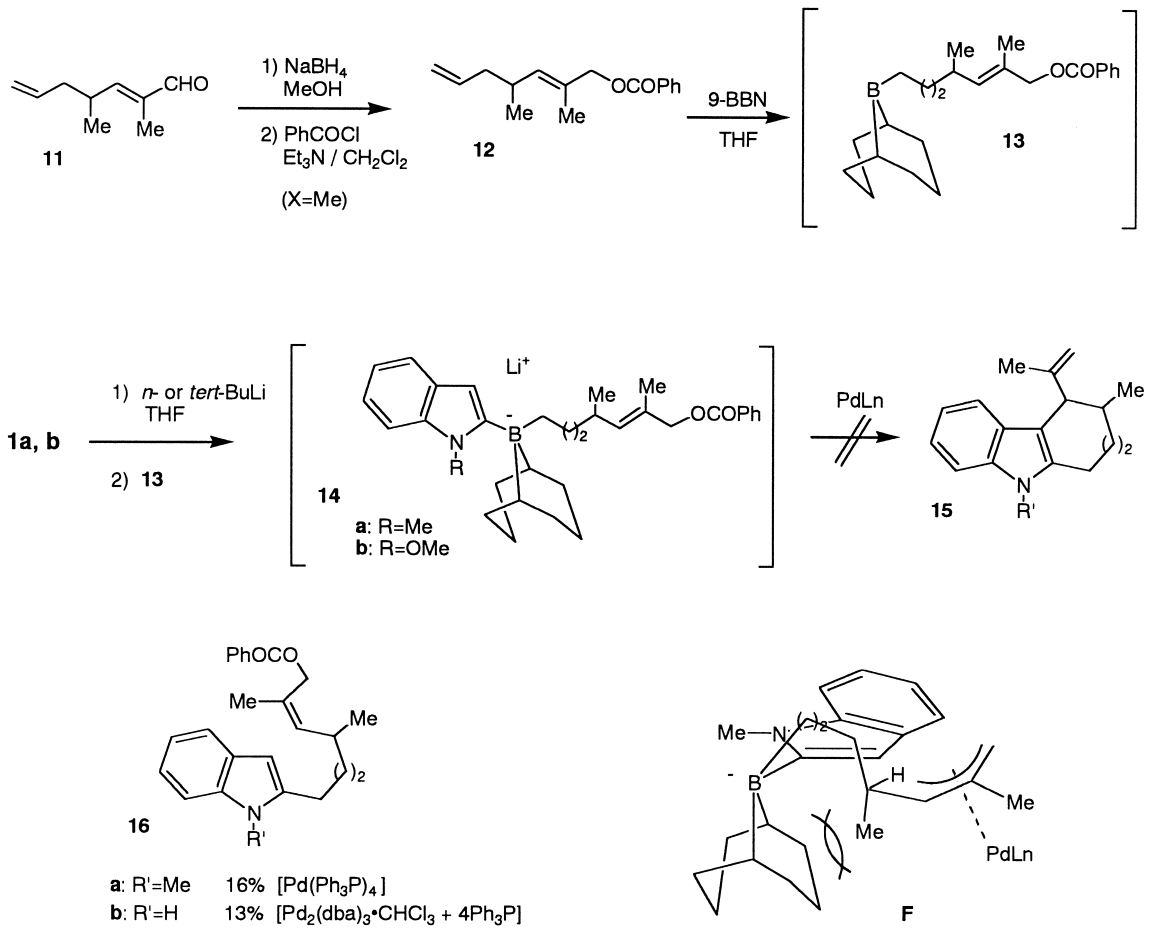
[a] Yields (%) based on indoles (**1**).

initially exposed to the intramolecular cyclization reaction. Allylalcohols **6**, obtained by the reaction of allylmagnesium and butenylmagnesium bromides with acrolein and matacrolein,[9] were converted to benzoates **7** through treatment with $PBr_3$, followed by heating with potassium benzoate in acetnitrile.[9] The requisite alkylboranes **8** were generated in situ in THF by hydroboration of dienes **7** with 9-BBN, and the subsequent addition of **8** to a THF solution of 2-lithioindoles derived from **1** generated indolylborates **9a–f** in situ. Heating a mixture of **9a–f** with a palladium complex (10 mol%) at 60°C in THF afforded the expected carbazoles **10** through intramolecular alkyl migration triggered by an intramolecular nucleophilic attack of the C-3 of the indole ring on the π-allylpalladium complex.

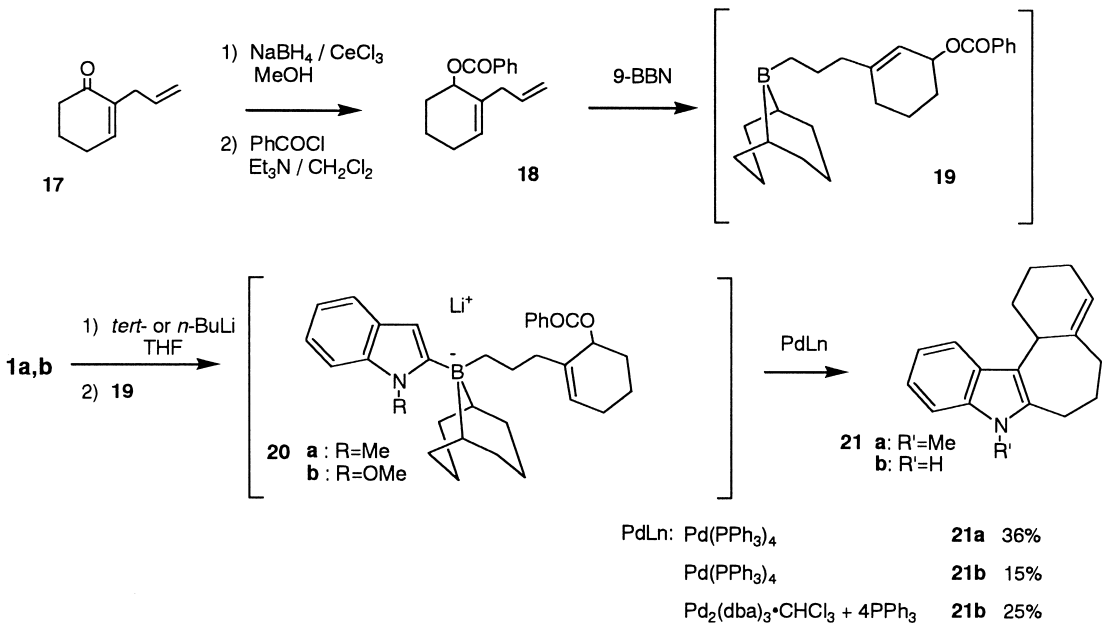
Formation of **10a** was also observed from the cyclization reaction of **9g**, which can be interpreted by adopting the cascade of alkyl-boryl migration that was reported in our previous paper[10] (Scheme 5, Table 2).

Hydroboration of ester **12** in THF (derived from commercially available aldehyde **11** via conventional chemical transformations) brought about alkylborane **13** in situ, and the subsequent treatment of 2-lithioindoles, carried from **1a**,**b**, with **13** generated indolylborates **14** that were subjected to the cyclization reaction. However, the desired products 15 were not isolated in these reactions and only small amounts of 2-alkylindoles **16** were obtained through a simple 1,2-alkyl migration reaction on quenching the reaction. Inspection of the molecular model revealed that the inefficiency of the cyclization using **14** could be due to significant spatial repulsion between the Me group and the 9-BBN ring that is present in intermediate **F** (Scheme 6).

Next, extension of the cyclization protocol to the construction of a tetracyclic framework in a one-pot manner was examined. Ester **18** was obtained from the known ketone **17**[11] by reduction ($NaBH_4/CeCl_3{\cdot}7H_2O$) and subsequent benzoylation ($PhCOCl/Et_3N$). Hydroboration of **18** with 9-BBN led to alkylborane **19** in situ, and the subsequent treatment of **19** with 2-lithio derivatives of **1a**,**b** generated indolylborates **20a**,**b** in situ. Heating **20** with a catalytic amount of Pd complex at 60°C readily produced tetracyclic indoles **21** (Scheme 7).



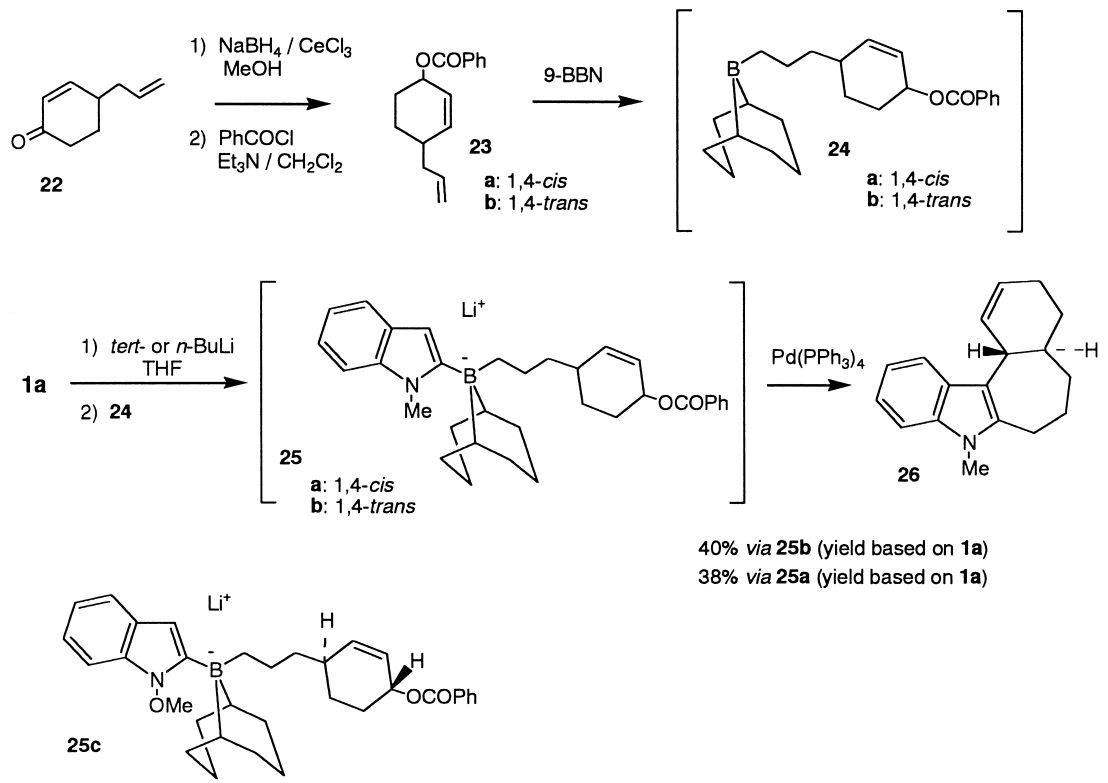

**Scheme 6.**



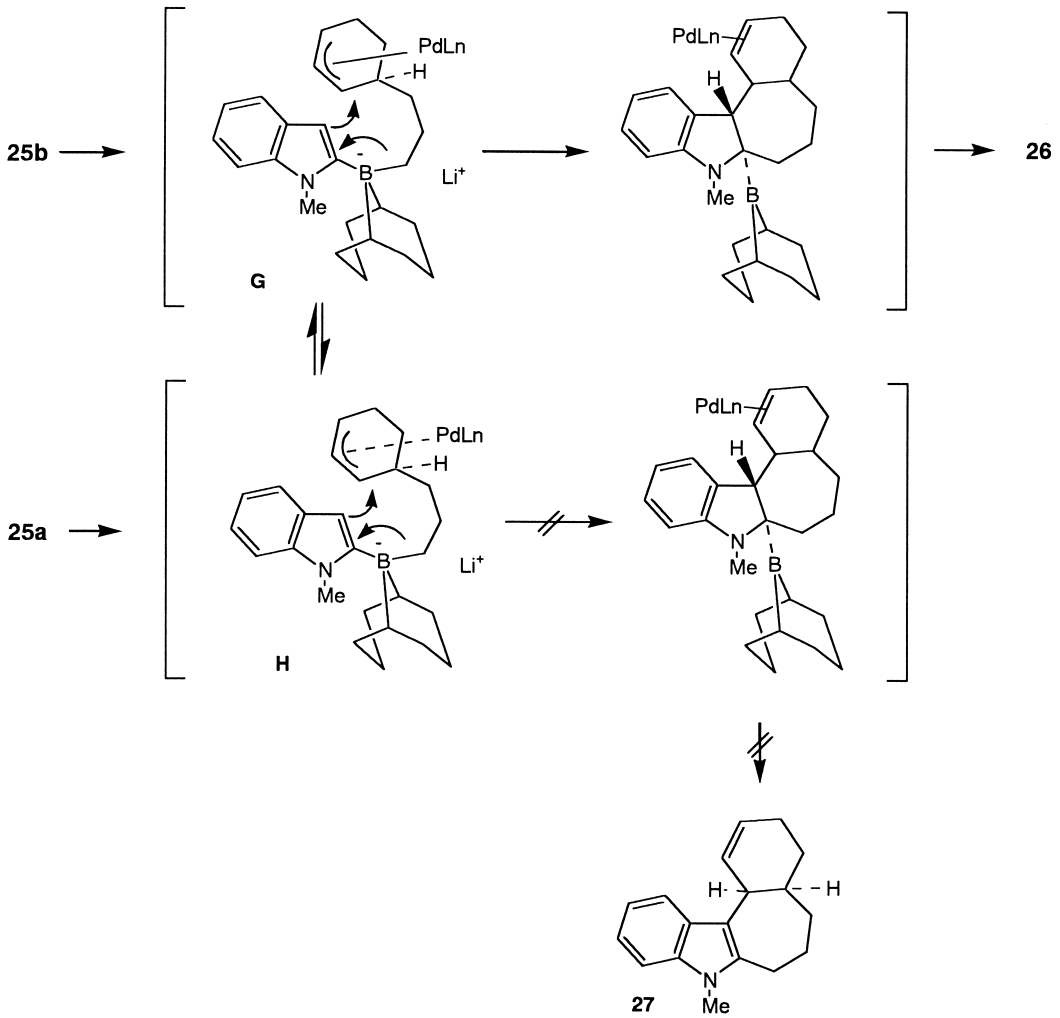

**Scheme 7.**

The known ketone **22**[12] was converted to a mixture of 1,4-*cis* and *trans* isomers **23a**,**b** by conventional methods and the isomeric mixture was separated by MPLC. An initial study, which was undertaken using a mixture of indolylborates **25** derived from 2-lithio-1-methylindole and an isomeric mixture of **24**, in the presence of $Pd(Ph_3P)_4$ (10 mol%), afforded tetracyclic indole **26** as a single isomer, whose structure has previously been determined by single crystal X-ray analysis.[6] Again, **26** was the sole product even when the separate reactions by using **25a** and **25b** were performed (Scheme 8). An attempted reaction with indolylborate **25c** derived from 2-lithio-1-methoxyindole and **24b** gave no isolable products, probably due to the decomposition of the products during work-up and/or $SiO_2$ column.

The cyclization reaction proceeds through the nucleophilic attack of indole on the π-allylpalladium complex from the




**Scheme 8.**




**Scheme 9.**

opposite side of the palladium with a simultaneous alkyl migration in an *anti* manner, the stereochemical requirement of which made the formation of **27** via complex **H** unfavorable, possibly, due to steric repulsion.[8] The sole formation of **26** from the separate reactions of **25a** and **25b** is explicable given an isomerization between the π-allylpalladium complexes **G** and **H**[13] (Scheme 9).

In summary, we were able to open a new, one-pot intramolecular cyclization protocol for carbazole derivatives based on the intramolecular alkyl migration reaction in indolylborates **9**, **14**, **20**, **25**. Extension of the present protocol to the preparation of natural indole isolates is in progress.

## 1. 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 Auto-Spec 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 spectrometer, and chemical shifts are expressed in ppm ($\delta$) 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) was performed on silica gel (Silica gel 60 N, Kanto Chemical Co., Inc.). Dehydrated tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were purchased from Kanto Chemical Co., Inc.

### 1.1. General procedure for the intermolecular reaction of indolylborates (2) with allyl acetates and vinyl epoxide in the presence of $PdCl_2(PPh_3)_2$

To a solution of indolylborates (**2**) generated from indoles (**1**) (2 mmol) and trialkylboranes (2.4 mmol) in THF (10 ml) in situ under an argon atmosphere,[7] allyl esters (3 mmol) or vinyl epoxide (3 mmol) and palladium complex (0.1 mmol) were added, and the mixture was heated at 60°C for 1 h. After cooling, 10% NaOH (10 ml) and 30% $H_2O_2$ (5 ml) were added under ice-cooling, and the whole was stirred for 10 min. The mixture was diluted with AcOEt (100 ml), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane/AcOEt as an eluent to give **3**.

**1.1.1. 2-Ethyl-1-methyl-3-(prop-2-enyl)indole (3a).** IR (neat): 1614 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.19 (t, 3H, $J$=7.3 Hz), 2.75 (q, 2H, $J$=7.3 Hz), 3.48 (ddd, 2H, $J$=1.5, 3.5,

6.5 Hz), 3.67 (s, 3H), 4.97 (ddd, 1H, *J*=1.5, 3.5, 10.3 Hz), 5.06 (ddd, 1H, *J*=2, 3.5, 17.1 Hz), 5.98 (tdd, 1H, *J*=6.5, 10.3, 17.1 Hz), 7.06 (dt, 1H, *J*=1, 7.3 Hz), 7.13 (dt, 1H, *J*=2, 8.3 Hz), 7.22 (d, 1H, *J*=8.3 Hz), 7.50 (d, 1H, *J*=7.8 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 14.5, 17.6, 28.9, 29.1, 107.9, 108.6, 114.1, 118.3, 118.8, 120.6, 127.7, 136.8, 138.0, 138.8. HR-MS *m/z*: Calcd for $C_{14}H_{17}N$: 199.1361. Found: 199.1362.

**1.1.2. 3-Allyl-2-ethylindole (3b).** IR (neat): 3412 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 1.22 (t, 3H, *J*=7.8 Hz), 2.70 (q, 2H, *J*=7.8 Hz), 3.44 (dd, 2H, *J*=1.7, 6.4 Hz), 4.97 (d, 1H, *J*=10.3 Hz), 5.05 (d, 1H, *J*=17.1 Hz), 5.91–6.03 (m, 1H), 7.03–7.12 (m, 2H), 7.22 (d, 1H, *J*=8.3 Hz), 7.49 (d, 1H, *J*=7.3 Hz), 7.70 (br s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 14.2, 19.3, 28.5, 108.3, 110.3, 114.3, 118.3, 119.1, 120.9, 128.7, 135.2, 137.1, 137.6. HR-MS *m/z*: Calcd for $C_{13}H_{15}N$: 185.1205. Found: 185.1211.

**1.1.3. 3-(Cyclohex-2-enyl)-2-ethyl-1-methylindole (3c).** Mp 65–66°C (from AcOEt/hexane). IR ($CHCl_3$): 2932 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 1.20 (t, 3H, *J*=7.3 Hz), 1.68–1.80 (m, 1H), 1.84–1.97 (m, 3H), 2.08–2.28 (m, 2H), 2.80 (q, 2H, *J*=7.3 Hz), 3.60–3.66 (m, 1H), 3.67 (s, 3H), 5.75–5.81 (m, 1H), 5.83–5.90 (m, 1H), 7.01 (dt, 1H, *J*=1.5, 7.6 Hz), 7.13 (dt, 1H, *J*=1.5, 7.6 Hz), 7.25 (d, 1H, *J*=8.3 Hz), 7.64 (d, 1H, *J*=8.3 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 15.0, 17.6, 23.0, 25.0, 29.1, 31.4, 33.8, 108.6, 114.1, 118.3, 119.4, 120.3, 126.8, 126.9, 132.3, 136.7, 138.1. MS *m/z*: 239 ($M^+$). Anal. Calcd for $C_{17}H_{21}N$: C, 85.31; H, 8.84; N, 5.85. Found: C, 85.36; H, 9.00; N, 5.79.

**1.1.4. 3-(Cyclohex-2-enyl)-2-ethylindole (3d).** Mp 109–110°C (from AcOEt/hexane). IR ($CHCl_3$): 3488 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 1.23 (t, 3H, *J*=7.5 Hz), 1.64–1.78 (m, 1H), 1.78–1.96 (m, 3H), 2.06–2.26 (m, 2H), 2.73 (q, 2H, *J*=7.7 Hz), 3.57–3.68 (m, 1H), 5.78 (d, 1H, *J*=11.3 Hz), 5.82–5.89 (m, 1H), 7.02 (dt, 1H, *J*=1.5, 6.8 Hz), 7.08 (dt, 1H, *J*=1.5, 6.8 Hz), 7.21 (d, 1H, *J*=7.8 Hz), 7.57–7.65 (m, 2H). $^{13}$C NMR ($CDCl_3$) $\delta$: 14.7, 19.5, 22.8, 25.1, 31.0, 33.4, 110.3, 114.6, 118.7, 119.4, 120.7, 127.1, 127.9, 131.9, 135.3, 136.4. MS *m/z*: 225 ($M^+$). Anal. Calcd for $C_{16}H_{19}N$: C, 85.29; H, 8.50; N, 6.22. Found: C, 85.33; H, 8.44; N, 6.27.

**1.1.5. Phenyl 5-(2-ethyl-1-methylindol-3-yl)-1,2,5,6-tetrahydropyridine-1-carboxylate (3e).** IR (neat): 1720 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 1.17 (t, 3H, *J*=7.5 Hz), 2.75 (q, 2H, *J*=7.5 Hz), 3.26 and 3.47 (two d, 1H, *J*=11.3 Hz), 3.55 (s, 3H), 3.85–4.10 (m, 2H), 4.20–4.30 (m, 1H), 4.41 and 4.52 (two d, 1H, *J*=17.8 Hz), 5.80–5.90 (m, 1H), 6.00–6.10 (m, 1H), 6.95–7.18 (m, 5H), 7.21 (d, 1H, *J*=7.8 Hz), 7.25–7.35 (m, 2H), 7.59 (d, 1H, *J*=7.8 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 15.0, 17.7, 29.3, 33.3, 33.8, 43.7, 46.7, 47.6, 108.9, 109.2, 118.5, 118.7, 120.4, 121.4, 121.5, 122.9, 123.4, 124.9, 126.4, 129.1, 131.2, 131.5, 136.8, 139.2, 139.3, 151.4, 153.6, 153.9. HR-MS *m/z*: Calcd for $C_{23}H_{24}N_2O_2$: 360.1837. Found: 360.1808.

**1.1.6. (2*E*)-4-(2-Ethyl-1-methylindol-3-yl)but-2-en-1-ol (3f).** IR (neat): 3368 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 1.12 (t, 3H, *J*=7.5 Hz), 2.28 (br s, 1H), 2.65 (q, 2H, *J*=7.5 Hz), 3.39 (d, 2H, *J*=6.4 Hz), 3.50 (s, 3H), 3.88 (d, 2H, *J*=5.9 Hz), 5.55 (td, 1H, *J*=5.9, 15.3 Hz), 5.73 (td, 1H, *J*=5.9, 15.3 Hz), 7.01 (ddd, 1H, *J*=1.5, 6.9, 7.8 Hz), 7.08 (ddd, 1H, *J*=1.5, 6.9, 7.3 Hz), 7.13 (d, 1H, *J*=7.3 Hz), 7.45 (d, 1H, *J*=7.8 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 14.4, 17.4, 27.0, 29.0, 62.9, 107.7, 108.4, 117.9, 118.5, 120.4, 127.4, 128.6, 131.5, 136.4, 138.5. HR-MS *m/z*: Calcd for $C_{15}H_{19}NO$: 229.1466. Found: 229.1466

**1.1.7. (2*E*)-4-(2-Ethylindol-3-yl)but-2-en-1-ol (3g).** IR (neat): 3412 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 1.20 (t, 3H, *J*=7.3 Hz), 1.87 (br s, 1H), 2.66 (q, 2H, *J*=7.3 Hz), 3.41 (d, 2H, *J*=5.9 Hz), 3.97 (d, 2H, *J*=5.4 Hz), 5.54–5.66 (m, 1H), 5.74–5.84 (m, 1H), 7.02–7.12 (m, 2H), 7.19 (d, 1H, *J*=7.5 Hz), 7.46 (d, 1H, *J*=7.5 Hz), 7.91 (br s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 14.3, 19.3, 26.9, 63.4, 108.2, 110.4, 118.2, 119.0, 120.9, 128.5, 128.7, 131.8, 135.2, 137.2. HR-MS *m/z*: Calcd for $C_{14}H_{17}NO$: 215.1310. Found: 215.1308.

**1.1.8. 3-Allyl-2-(*sec*-butyl)-1-methylindole (3h).** IR (neat): 1638, 1610 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 0.87 (t, 3H, *J*=7.3 Hz), 1.37 (d, 3H, *J*=7.3 Hz), 1.69–1.89 (m, 2H), 3.01–3.12 (m, 1H), 3.53 (td, 2H, *J*=1.5, 5.9 Hz), 3.72 (s, 3H), 4.97 (dd, 1H, *J*=2.1, 10 Hz), 5.04 (dd, 1H, *J*=2.1, 10 Hz), 5.96 (tdd, 1H, *J*=5.9, 10.2, 17.1 Hz), 7.06 (t, 1H, *J*=7.8 Hz), 7.15 (t, 1H, *J*=8.3 Hz), 7.25 (d, 1H, *J*=8.3 Hz), 7.50 (d, 1H, *J*=7.8 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 12.9, 20.0, 29.1, 30.6, 33.0, 108.6, 114.2, 118.3, 118.7, 120.6, 128.2, 136.9, 138.0, 140.6. HR-MS *m/z*: Calcd for $C_{16}H_{21}N$: 227.1674. Found: 227.1677.

**1.1.9. 3-Allyl-2-(*sec*-butyl)indole (3i).** IR (neat): 3240 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 0.86 (t, 3H, *J*=7.3 Hz), 1.29 (d, 3H, *J*=6.8 Hz), 1.56–1.74 (m, 2H), 2.92–3.03 (m, 1H), 3.46 (td, 2H, *J*=1.5, 6.3 Hz), 4.98 (ddd, 1H, *J*=1.5, 3.5, 10.1 Hz), 5.06 (ddd, 1H, *J*=1.5, 3.5, 17.1 Hz), 5.97 (tdd, 1H, *J*=6.3, 10.1, 17.1 Hz), 7.06 (dd, 1H, *J*=1.5, 7.3 Hz), 7.11 (ddd, 1H, *J*=1.5, 7.4, 7.8 Hz), 7.29 (d, 1H, *J*=7.8 Hz), 7.51 (d, 1H, *J*=7.3 Hz), 7.74 (br s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 12.5, 20.7, 28.6, 30.0, 32.6, 108.6, 110.3, 114.3, 118.4, 119.0, 120.9, 128.7, 135.3, 137.8, 140.0. HR-MS *m/z*: Calcd for $C_{15}H_{19}N$: 213.1517. Found: 213.1506.

**1.1.10. 2-(*sec*-Butyl)-3-(cyclohex-2-enyl)-1-methylindole (3j).** IR (neat): 1736, 1470 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 0.88 (t, 3H, *J*=7.3 Hz), 1.38 (d, 3H, *J*=7.3 Hz), 1.65–1.85 (m, 3H), 1.85–2.00 (m, 3H), 2.08–2.30 (m, 2H), 3.06–3.20 (m, 1H), 3.67–3.78 (m, 1H), 3.72 (s, 3H), 5.72–5.80 (m, 1H), 5.81–5.88 (m, 1H), 7.00 (dt, 1H, *J*=1.5, 7.3 Hz), 7.13 (dt, 1H, *J*=1.5, 7.3 Hz), 7.23 (d, 1H, *J*=7.8 Hz), 7.65 (d, 1H, *J*=7.8 Hz). $^{13}$C NMR ($CDCl_3$) $\delta$: 12.9, 13.0, 20.2, 20.3, 23.2, 23.3, 25.1, 29.2, 30.7, 30.9, 31.0, 32.7, 32.8, 34.0, 108.6, 108.7, 114.9, 115.0, 118.2, 119.8, 120.4, 126.6, 126.7, 126.9, 127.0, 132.5, 132.6, 137.1, 137.2, 139.8, 139.9. HR-MS *m/z*: Calcd for $C_{18}H_{22}N$: 267.1987. Found: 269.1987.

**1.1.11. 2-(*sec*-Butyl)-3-(cyclohex-2-enyl)indole (3k).** IR (neat): 3484, 1460 cm$^{-1}$. $^1$H NMR ($CDCl_3$) $\delta$: 0.86 and 0.87 (two t, 3H, *J*=7.5 Hz), 1.28 and 1.29 (two d, 3H, *J*=7.5 Hz), 1.55–1.80 (m, 4H), 1.82–1.95 (m, 3H), 2.10–2.25 (m, 1H), 3.00–3.10 (m, 1H), 3.60–3.70 (m, 1H), 5.65–6.00 (m, 2H), 7.01 (t, 1H, *J*=7.8 Hz), 7.08 (t, 1H, *J*=8.3 Hz), 7.27 (d, 1H, *J*=8.3 Hz), 7.63 (d, 1H, *J*=7.8 Hz), 7.69 (br s, 1H). $^{13}$C NMR ($CDCl_3$) $\delta$: 12.3, 12.4, 18.8, 21.1, 21.4, 23.0, 24.8, 25.1, 28.3, 30.1, 30.2, 31.0, 31.1, 32.4, 33.4, 33.5, 68.2,

110.4, 114.9, 118.5, 119.6, 119.7, 120.6, 125.6, 126.9, 127.0, 127.7, 132.2, 132.3, 132.7, 135.4, 138.9, 139.0. HR-MS *m/z*: Calcd for $C_{18}H_{23}N$: 253.1831. Found: 253.1815.

**1.1.12. 3-Allyl-2-(3,3-diethoxypropyl)-1-methylindole (3l).** IR (neat): 3484, 1460 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.21 (dt, 6H, $J$=1.5, 7.1 Hz), 1.80–1.90 (m, 2H), 2.82 (t, 2H, $J$=7.8 Hz), 3.43–3.53 (m, 4H), 3.64 (s, 3H), 3.60–3.70 (m, 2H), 4.48 (t, 1H, $J$=5.4 Hz), 4.97 (dd, 1H, $J$=1.5, 10.3 Hz), 5.05 (td, 1H, $J$=1.5, 17.1 Hz), 5.97 (dtdd, 1H, $J$=1.5, 5.8, 10.3, 17.1 Hz), 7.05 (t, 1H, $J$=7.8 Hz), 7.14 (t, 1H, $J$=8.3 Hz), 7.22 (d, 1H, $J$=8.3 Hz), 7.50 (d, 1H, $J$=7.8 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 15.4, 19.5, 28.9, 29.5, 33.8, 61.3, 102.1, 108.7, 114.3, 118.4, 118.8, 120.7, 127.7, 136.6, 136.8, 137.8. HR-MS *m/z*: Calcd for $C_{19}H_{27}NO_2$: 301.2042. Found: 301.2039.

**1.1.13. 3-Allyl-2-(3,3-diethoxypropyl)indole (3m).** IR (neat): 3404 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.23 (t, 6H, $J$=7.3 Hz), 1.95 (q, 2H, $J$=7.3 Hz), 2.79 (t, 2H, $J$=7.3 Hz), 3.42–3.53 (m, 4H), 3.62–3.71 (m, 2H), 4.51 (t, 1H, $J$=5.5 Hz), 4.98 (dd, 1H, $J$=1.9, 10.1 Hz), 5.05 (dd, 1H, $J$=1.9, 17.3 Hz), 5.97 (tdd, 1H, $J$=6.3, 10.1, 17.3 Hz), 7.05 (dt, 1H, $J$=1.5, 7.8 Hz), 7.10 (dt, 1H, $J$=1.5, 8.3 Hz), 7.24 (d, 1H, $J$=8.3 Hz), 7.49 (d, 1H, $J$=7.8 Hz), 8.30 (br s, 1H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 15.3, 21.0, 28.5, 33.2, 61.4, 102.2, 108.9, 110.4, 114.4, 118.4, 119.0, 121.0, 128.6, 135.1, 135.3, 137.6. HR-MS *m/z*: Calcd for $C_{18}H_{25}NO_2$: 287.1885. Found: 287.1884.

**1.1.14. *tert*-Butyl *rel*-(2*S*,3*R*)-3-allyl-2-diethylboranyl-2-ethyl-2,3-dihydroindole-1-carboxylate (5).** Mp 75–77°C (from hexane). IR ($CHCl_3$): 1570 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 0.29–0.41 (m, 1H), 0.56–0.67 (m, 3H), 0.70 (t, 3H, $J$=7.3 Hz), 0.76 (t, 3H, $J$=7.3 Hz), 0.85 (t, 3H, $J$=7.3 Hz), 1.45–1.58 (m, 1H), 1.62 (s, 9H), 1.72–1.83 (m, 1H), 2.27 (td, 1H, $J$=9.3, 14.2 Hz), 2.50–2.59 (m, 1H), 2.99 (dd, 1H, $J$=5.4, 10.3 Hz), 5.00 (d, 1H, $J$=16.6 Hz), 5.05 (d, 1H, $J$=10.3 Hz), 5.87–5.99 (m, 1H), 6.98 (dt, 1H, $J$=1.5, 7 Hz), 7.17 (t, 1H, $J$=7.8 Hz), 7.20 (dd, 1H, $J$=1, 7.3 Hz), 7.27 (d, 1H, $J$=7.8 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 8.5, 9.7, 9.9, 10.2, 13.4, 28.4, 32.2, 39.7, 48.4, 68.5, 87.0, 113.4, 116.0, 123.6, 126.4, 127.1, 138.1, 138.7, 140.7, 158.2. MS *m/z*: 355 ($M^+$). Anal. Calcd for $C_{22}H_{34}NO_2B$: C, 74.37; H, 9.65; N, 3.94. Found: C, 74.47; H, 9.69; N, 4.03.

### 1.2. General procedure for the intramolecular cyclization reaction using indolylborates (9, 14, 20, 25)

To a solution of dienes (**7**, **12**, **18**, **23**) (3 mmol) in THF (5 ml) at room temperature under an argon atmosphere, 9-BBN (0.5 M solution in THF, 6 ml, 3 mmol) was added, and the whole was stirred for 1 h. The resulted solution of alkylboranes (**8**, **13**, **19**, **24**) was added to a solution of 2-lithioindoles [generated from indoles (**1**) (2 mmol) and *tert*- or *n*-BuLi (2.4 mmol) in THF (10 ml) under an argon atmosphere],[7] generating indolylborates (**9**, **14**, **20**, **25**) in situ. The mixture was heated with palladium complex (0.1 mmol) at 60°C for 2 h. After cooling, 10% NaOH (10 ml) and 30% $H_2O_2$ (5 ml) were added under ice-cooling, and the mixture was stirred for 10 min. The mixture was diluted with AcOEt (100 ml), washed with brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane/AcOEt=50:1 as an eluent to give **10**, **15**, **21**, and **26**.

**1.2.1. 2*E*-Hexa-2,5-dienyl benzoate (7a).** Bp 115°C/1 mmHg. IR (neat): 1720 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 2.75–2.90 (m, 2H), 4.78 (dd, 2H, $J$=1.5, 6.5 Hz), 5.03 (d, 1H, $J$=10.5 Hz), 5.08 (d, 1H, $J$=16.3 Hz), 5.73 (ddd, 1H, $J$=1.5, 6.5, 16.3 Hz), 5.76–5.90 (m, 2H), 7.25 (d, 1H, $J$=8.3 Hz), 7.42 (dd, 2H, $J$=7.8, 8.3 Hz), 8.05 (dd, 2H, $J$=1.5, 7.8 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 36.0, 65.1, 115.6, 124.9, 128.0, 129.3, 130.1, 133.2, 135.5, 165.9. HR-MS *m/z*: Calcd for $C_{13}H_{14}O_2$: 202.0994. Found: 202.1002.

**1.2.2. 2*E*-Hepta-2,6-dienyl benzoate (7b).** Bp 120°C/1 mmHg. IR (neat): 1720 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 2.13–2.24 (m, 4H), 4.77 (d, 2H, $J$=6.3 Hz), 4.98 (dd, 1H, $J$=2.0, 10.1 Hz), 5.03 (dd, 1H, $J$=2.0, 17.3 Hz), 5.66–5.76 (m, 1H), 5.76–5.95 (m, 2H), 7.44 (dd, 2H, $J$=7.8, 8.3 Hz), 7.55 (dd, 1H, $J$=1.5, 7.8 Hz), 8.05 (dd, 2H, $J$=1.5, 8.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 31.6, 33.0, 65.5, 115.0, 124.5, 128.3, 129.6, 130.5, 132.8, 135.4, 137.7, 166.2. MS *m/z*: 218 ($M^+$). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.57; H, 7.53.

**1.2.3. (2*E*)-2,4-Dimethylhexa-2,5-dienyl benzoate (7c).** Bp 115°C/1 mmHg. IR (neat): 1720 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.75, 1.82 and 1.87 (three s, 3H), 2.48–2.63 (m, 0.5H), 2.81–2.94 (m, 1.5H), 4.74 and 4.84 (two s, 2H), 4.90–5.15 (m, 2H), 5.48 and 5.60 (two t, 1H, $J$=7.3 Hz), 5.74–5.88 (m, 1H), 7.44 (t, 1H, $J$=7.8 Hz), 7.48 (t, 1H, $J$=7.8 Hz), 7.56 and 7.62 (two td, 1H, $J$=1.5, 7.8 Hz), 8.06 and 8.11 (two dd, 1H, $J$=1.5, 8.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.0, 18.5, 21.5, 32.0, 32.1, 37.4, 63.5, 64.3, 113.0, 115.0, 117.7, 126.4, 126.7, 128.3, 128.5, 129.6, 130.2, 130.3, 130.5, 131.2, 131.4, 132.9, 133.4, 133.7, 136.2, 136.6, 142.7, 165.7, 166.4. HR-MS *m/z*: Calcd for $C_{14}H_{16}O_2$: 216.1150. Found: 216.1152.

**1.2.4. 9-Methyl-4-vinyl-2,3,4,9-tetrahydro-1*H*-carbazole (10a).** Mp 61–63°C (from AcOEt/hexane). IR ($CHCl_3$): 1632, 1612 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.65–1.80 (m, 1H), 1.80–1.90 (m, 1H), 1.90–2.10 (m, 2H), 2.60–2.80 (m, 2H), 3.60–3.70 (m, 1H), 3.62 (s, 3H), 5.07 (dd, 1H, $J$=1.5, 9.5 Hz), 5.13 (dd, 1H, $J$=1.5, 17.1 Hz), 5.96 (ddd, 1H, $J$=7.5, 9.5, 17.1 Hz), 7.02 (dt, 1H, $J$=1.5, 7.8 Hz), 7.13 (dt, 1H, $J$=1.5, 7.8 Hz), 7.24 (d, 1H, $J$=8.3 Hz), 7.53 (d, 1H, $J$=8.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 20.3, 22.1, 28.8, 30.0, 37.5, 108.5, 110.1, 114.1, 118.5, 118.8, 120.4, 127.1, 135.9, 136.8, 142.3. MS *m/z*: 211 ($M^+$). Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.35; H, 7.90; N, 6.72.

**1.2.5. 4-Vinyl-2,3,4,9-tetrahydro-1*H*-carbazole (10b).** IR (neat): 3412 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.65–1.85 (m, 2H), 1.88–1.99 (m, 2H), 2.55–2.70 (m, 2H), 3.55–3.65 (m, 1H), 5.05 (dd, 1H, $J$=1.5, 10.3 Hz), 5.11 (d, 1H, $J$=17.1 Hz), 5.94 (ddd, 1H, $J$=7.3, 10.3, 17.1 Hz), 7.03 (t, 1H, $J$=7.3 Hz), 7.10 (t, 1H, $J$=7.3 Hz), 7.18 (d, 1H, $J$=7.8 Hz), 7.51 (d, 1H, $J$=7.8 Hz), 7.57 (br s, 1H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 20.4, 23.2, 30.4, 37.6, 110.3, 110.9, 114.2, 118.9, 119.0, 120.8, 127.6, 135.7, 142.4. HR-MS *m/z*: Calcd for $C_{14}H_{15}N$: 197.1205. Found: 197.1208.

**1.2.6. 5-Methyl-10-vinyl-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indole (10c).** Mp 58–59°C (from EtOH). IR ($CHCl_3$): 1632, 1610 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.53–1.65 (m, 1H), 1.82–1.93 (m, 3H), 1.96–2.05 (m, 1H), 2.07–2.15 (m, 1H), 2.75 (ddd, 1H, *J*=2.7, 11.5, 15.7 Hz), 2.94 (ddd, 1H, *J*=2.7, 6.6, 15.7 Hz), 3.67 (s, 3H), 3.96–4.01 (m, 1H), 4.78 (td, 1H, *J*=1.7, 16.6 Hz), 4.98 (td, 1H, *J*=1.7, 10.2 Hz), 6.03 (ddd, 1H, *J*=5.9, 10.2, 16.6 Hz), 7.05 (dt, 1H, *J*=1, 5, 7.8 Hz), 7.13 (dt, 1H, *J*=1.5, 8.3 Hz), 7.23 (d, 1H, *J*=8.3 Hz), 7.45 (d, 1H, *J*=7.8 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 25.6, 25.8, 27.2, 29.5, 33.2, 38.8, 108.7, 113.6, 114.1, 117.6, 118.7, 120.4, 127.9, 136.1, 138.0, 140.9. MS *m*/*z*: 225 ($M^+$). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.00; H, 8.50; N, 6.23.

**1.2.7. 10-Vinyl-5,6,7,8,9,10-hexahydrocyclohepta[*b*]indole (10d).** IR (neat): 3408 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.45–1.63 (m, 1H), 1.78–2.02 (m, 4H), 2.06–2.19 (m, 1H), 2.70–2.80 (m, 1H), 2.80–2.92 (m, 1H), 3.90–4.00 (m, 1H), 4.76 (td, 1H, *J*=1.9, 16.6 Hz), 4.99 (td, 1H, *J*=1.5, 9.7 Hz), 6.01 (ddd, 1H, *J*=5.8, 10.3, 16.8 Hz), 7.03–7.12 (m, 2H), 7.26 (dd, 1H, *J*=1.5, 7.3 Hz), 7.44 (d, 1H, *J*=7.3 Hz), 7.70 (br s, 1H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 25.7, 27.5, 29.1, 33.6, 38.7, 110.2, 113.8, 114.3, 117.7, 119.1, 120.8, 129.4, 134.4, 137.3, 140.8. HR-MS *m*/*z*: Calcd for $C_{15}H_{17}N$: 211.1361. Found: 211.1343.

**1.2.8. 4-Isopropenyl-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (10e).** Mp 88–90°C (from hexane). IR ($CHCl_3$): 1642 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.71 (s, 3H), 1.74–1.95 (m, 3H), 1.98–2.07 (m, 1H), 2.70 (t, 2H, *J*=5.9 Hz), 3.61 (s, 3H), 3.62–3.68 (m, 1H), 4.77–4.80 (m, 1H), 4.86–4.90 (m, 1H), 7.01 (dt, 1H, *J*=1.5, 7.3 Hz), 7.12 (dt, 1H, *J*=1.5, 7.8 Hz), 7.24 (d, 1H, *J*=7.8 Hz), 7.48 (d, 1H, *J*=7.8 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 20.0, 21.1, 22.2, 29.0, 29.1, 41.7, 108.3, 110.4, 112.0, 118.6, 118.8, 120.3, 127.1, 136.5, 136.8, 148.5. MS *m*/*z*: 225 ($M^+$). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.27; H, 8.63; N, 6.24.

**1.2.9. 4-Isopropenyl-2,3,4,9-tetrahydro-1*H*-carbazole (10f).** Mp 113–114°C (from EtOH). IR ($CHCl_3$): 3476 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.71 (s, 3H), 1.74–1.86 (m, 2H), 1.89–2.05 (m, 2H), 2.64–2.80 (m, 2H), 3.59–3.68 (m, 1H), 4.75–4.81 (m, 1H), 4.85–4.91 (m, 1H), 7.02 (dt, 1H, *J*=1.5, 7.5 Hz), 7.09 (dt, 1H, *J*=1.5, 7.5 Hz), 7.26 (d, 1H, *J*=7.8 Hz), 7.47 (d, 1H, *J*=7.8 Hz), 7.70 (br s, 1H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 19.9, 21.2, 23.3, 29.3, 41.5, 110.2, 111.3, 112.0, 118.9, 119.0, 120.8, 127.7, 134.9, 135.7, 148.4. MS *m*/*z*: 211 ($M^+$). Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.24; H, 8.20; N, 6.62.

**1.2.10. (2*E*)-2-Methylhexa-2,5-dienyl benzoate (12).** Bp 110°C/1 mmHg. IR (neat): 1718 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 0.98 (d, 3H, *J*=6.8 Hz), 1.74 (s, 3H), 2.05 (t, 2H, *J*=6.8 Hz), 2.49 and 2.52 (two q, 1H, *J*=6.8 Hz), 4.70 (s, 2H), 4.98 (d, 1H, *J*=10.2 Hz), 5.00 (d, 1H, *J*=17.1 Hz), 5.34 and 5.79 (two s, 1H), 5.74 and 5.76 (two ddd, 1H, *J*=6.8, 10.2, 17.1 Hz), 7.43 (t, 2H, *J*=7.8 Hz), 7.54 (t, 1H, *J*=7.8 Hz), 8.05 (d, 2H, *J*=8.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.2, 20.2, 32.2, 41.5, 70.5, 115.8, 128.3, 128.9, 129.5, 130.5, 132.8, 135.3, 136.8, 166.2. HR-MS *m*/*z*: Calcd for $C_{16}H_{20}O_2$: 244.1463. Found: 244.1456.

**1.2.11. (2*Z*)-2,4-Dimethyl-6-(1-methylindol-2-yl)hex-2-enyl benzoate (16a).** IR (neat): 1718 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 0.98 (d, 3H, *J*=6.8 Hz), 1.31–1.43 (m, 1H), 1.43–1.55 (m, 1H), 1.58–1.74 (m, 2H), 1.75 (s, 3H), 2.42–2.54 (m, 1H), 2.70 (t, 2H, *J*=7.5 Hz), 3.60 (s, 3H), 4.70 (s, 2H), 5.33 (d, 1H, *J*=10.3 Hz), 6.22 (s, 1H), 7.05 (dt, 1H, *J*=1, 7.8 Hz), 7.14 (dt, 1H, *J*=1, 8.3 Hz), 7.22 (d, 1H, *J*=8.3 Hz), 7.40 (t, 2H, *J*=7.8 Hz), 7.48–7.56 (m, 2H), 8.04 (d, 2H, *J*=7.8 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.3, 20.9, 26.6, 26.9, 29.3, 32.2, 37.1, 70.7, 98.7, 108.7, 119.2, 119.7, 120.4, 127.9, 128.3, 129.0, 129.6, 130.4, 132.8, 135.9, 137.3, 141.4, 166.4. HR-MS *m*/*z*: Calcd for $C_{25}H_{29}NO_2$: 375.2198. Found: 375.2196.

**1.2.12. (2*Z*)-2,4-Dimethyl-6-(indol-2-yl)hex-2-enyl benzoate (16b).** IR (neat): 3404, 1706 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 0.95 (d, 3H, *J*=6.8 Hz), 1.22–1.35 (m, 1H), 1.40–1.50 (m, 1H), 1.60–1.75 (m, 2H), 1.73 (s, 3H), 2.40–2.50 (m, 1H), 2.71 (dt, 2H, *J*=2.9, 7.3 Hz), 4.68 (d, 1H, *J*=12.2 Hz), 4.74 (d, 1H, *J*=12.2 Hz), 5.30 (d, 1H, *J*=9.7 Hz), 6.21 (s, 1H), 7.03–7.13 (m, 2H), 7.28 (d, 1H, *J*=7.3 Hz), 7.41 (t, 2H, *J*=7.8 Hz), 7.48–7.57 (m, 2H), 8.06 (d, 2H, *J*=8.3 Hz), 8.08 (br s, 1H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 14.2, 20.9, 27.0, 28.2, 32.1, 36.8, 70.8, 99.5, 110.4, 119.5, 119.7, 120.8, 128.4, 128.8, 128.9, 129.6, 130.4, 132.9, 135.8, 139.8, 166.6. HR-MS *m*/*z*: Calcd for $C_{24}H_{27}NO_2$: 361.2042. Found: 361.2041.

**1.2.13. Preparation of 2-allylcyclohex-2-enyl benzoate (18).** To a mixture of **17**[11] (2 g, 15 mmol) and $CeCl_3{\cdot}7H_2O$ (6.7 g, 18 mmol) in MeOH (100 ml), $NaBH_4$ (570 mg, 15 mmol) was added portionwise under ice-cooling. After stirring for 30 min at rt, the mixture was concentrated on rotary evaporator. The residue was diluted with AcOEt (100 ml), washed brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane/AcOEt (10:1) as an eluent to give 1.8 g (87%) of *2-allylcyclohex-2-enol*.

Colorless oil. IR (neat): 3324 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.53 (br s, 1H), 1.55–1.62 (m, 1H), 1.62–1.69 (m, 1H), 1.69–1.73 (m, 1H), 1.73–1.82 (m, 1H), 1.91–2.02 (m, 1H), 2.80–2.94 (m, 2H), 4.03–4.12 (m, 1H), 5.03–5.13 (m, 2H), 5.58 (t, 1H, *J*=3.7 Hz), 5.86 (tdd, 1H, *J*=6.8, 10.8, 17.1 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 17.9, 25.4, 32.0, 38.8, 66.7, 115.9, 126.1, 136.9, 137.6. HR-MS *m*/*z*: Calcd for $C_9H_{14}O$: 138.1045. Found: 138.1042.

Benzoyl chloride (1.68 g, 10 mmol) was added to a solution of 2-allylcyclohex-2-enol (1.38 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in $CH_2Cl_2$ (200 ml) under ice-cooling, and the whole was stirred for 1 h. The mixture was concentrated on rotary evaporator. The residue was diluted with ether (100 ml), washed with water, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane/AcOEt (40:1) as an eluent to 1.8 g (74%) of **18**.

Bp 142°C/1 mmHg. IR (neat): 1716 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.60–1.80 (m, 2H), 1.83–1.99 (m, 2H), 1.99–2.10 (m, 1H), 2.11–2.22 (m, 1H), 2.79 (d, 2H, *J*=5.9 Hz), 4.97–5.00 (m, 1H), 5.02 (d, 1H, *J*=4.4 Hz), 5.50–5.56 (m, 1H), 5.74–5.86 (m, 2H), 7.42 (t, 2H, *J*=7.8 Hz), 7.58 (t, 1H, *J*=7.3 Hz), 8.06 (dd, 2H, *J*=1.5, 8.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 18.3,

25.2, 29.0, 38.7, 69.7, 116.3, 128.2, 128.7, 129.6, 130.7, 132.7, 134.3, 135.9, 166.2. MS *m/z*: 242 ($M^+$). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.12; H, 7.33.

**1.2.14. 8-Methyl-1,2,3,5,6,7,8,12c-octahydrobenzo[3,4]-cyclohepta[1,2-*b*]indole (21a).** Mp 84–85°C (from EtOH). IR ($CHCl_3$): 1610 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.65 (ddd, 1H, *J*=2.5, 10.2, 12.3 Hz), 1.70–1.95 (m, 4H), 2.05–2.25 (m, 4H), 2.24 (dd, 1H, *J*=7.5, 13.3 Hz), 2.63 (ddd, 1H, *J*=1.5, 5.4, 14.7 Hz), 3.06 (ddd, 1H, *J*=6.4, 12.7, 14.7 Hz), 3.64 (s, 3H), 3.70–3.79 (m, 1H), 5.59 (d, 1H, *J*=2.9 Hz), 7.06 (t, 1H, *J*=7.8 Hz), 7.13 (t, 1H, *J*=7.8 Hz), 7.25 (d, 1H, *J*=7.8 Hz), 7.56 (d, 1H, *J*=7.8 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 20.1, 22.8, 25.6, 27.8, 28.9, 31.3, 31.8, 38.2, 109.2, 113.0, 117.6, 118.6, 120.1, 123.5, 127.3, 135.4, 136.4, 139.3. MS *m/z*: 251 ($M^+$). Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.09; H, 8.42; N, 5.43.

**1.2.15. 1,2,3,5,6,7,8,12c-Octahydrobenzo[3,4]cyclohepta-[1,2-*b*]indole (21b).** Mp 122–123°C (from AcOEt/hexane). IR ($CHCl_3$): 3476 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.63–1.82 (m, 3H), 1.86–1.95 (m, 2H), 2.08–2.16 (m, 3H), 2.18–2.26 (m, 1H), 2.31 (td, 1H, *J*=4.9, 12.7 Hz), 2.41 (td, 1H, *J*=4.2, 14.1 Hz), 3.18 (td, 1H, *J*=9.7, 15.1 Hz), 3.64–3.75 (m, 1H), 5.59–5.66 (m, 1H), 7.05–7.13 (m, 2H), 7.28 (dd, 1H, *J*=2.5, 5.9 Hz), 7.52 (dd, 1H, *J*=2.5, 5.9 Hz), 7.62 (br s, 1H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 22.4, 23.5, 25.7, 27.6, 31.0, 32.2, 38.2, 110.5, 113.2, 117.9, 119.0, 120.4, 124.0, 128.6, 134.0, 134.7, 138.9. MS *m/z*: 237 ($M^+$). Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.14; H, 8.25; N, 5.70.

**1.2.16. Preparation of 4-allylcyclohex-2-enyl benzoate (23).** To a mixture of **22**[12] (2 g, 15 mmol) and $CeCl_3 \cdot 7H_2O$ (6.7 g, 18 mmol) in MeOH (100 ml), $NaBH_4$ (570 mg, 15 mmol) was added portionwise under ice-cooling. After stirring for 30 min at rt, the mixture was concentrated on rotary evaporator. The residue was diluted with AcOEt (100 ml), washed brine, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane/AcOEt (7:1) as an eluent to give a 1,4-*trans* and *cis* isomeric mixture of *4-allylcyclohex-2-enol* (1.55 g, 75%).

Colorless oil. IR (neat): 3612 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.20–1.32 (m, 1H), 1.40–1.52 (m, 1H), 1.64 (br s, 1H), 1.70–1.80 (m, 1H), 1.80–1.89 (m, 1H), 1.97–2.13 (m, 2H), 2.13–2.22 (m, 1H), 4.17–4.25 (m, 1H), 4.99–5.08 (m, 2H), 5.66–5.73 (m, 2H), 5.73–5.83 (m, 1H). $^{13}C$ NMR ($CDCl_3$) $\delta$: 26.6, 31.7, 35.0, 40.1, 66.7, 116.1, 130.7, 133.4, 136.4. HR-MS *m/z*: $C_9H_{14}O$: 138.1045. Found: 138.1030.

Benzoyl chloride (1.68 g, 12 mmol) was added to a solution of 4-allylcyclohex-2-enol (1.38 g, 10 mmol) and triethylamine (2.02 g, 20 mmol) in $CH_2Cl_2$ (200 ml) under ice-cooling, and the whole was stirred for 1 h. The mixture was concentrated on rotary evaporator. The residue was diluted with ether (100 ml), washed with water, and dried over $MgSO_4$. The solvent was removed, and the residue was separated by MPLC with hexane/AcOEt (40:1) as an eluent to 360 mg (15%) of **23a** and 1.1 g (45%) of **23b**.

**1.2.17. *rel*-(1*S*,4*S*)-4-Allylcyclohex-2-enyl benzoate (23a).** Bp 147°C/1 mmHg. IR (neat): 1712 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.48–1.59 (m, 1H), 1.73–1.90 (m, 2H), 2.10–2.22 (m, 1H), 2.17 (d, 2H, *J*=5.4 Hz), 5.06 (d, 1H, *J*=10.2 Hz), 5.08 (d, 1H, *J*=17.1 Hz), 5.45 (dd, 1H, *J*=4.3, 7.5 Hz), 5.82 (tdd, 1H, *J*=7.5, 10.2, 17.1 Hz), 5.88 (dd, 1H, *J*=4.3, 10.2 Hz), 5.94 (d, 2H, *J*=10.2 Hz), 7.43 (t, 2H, *J*=7.3 Hz), 7.54 (t, 1H, *J*=7.3 Hz), 8.05 (d, 2H, *J*=7.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 24.4, 27.5, 35.3, 39.7, 67.7, 116.4, 125.0, 128.3, 129.6, 130.8, 132.7, 136.4, 137.4, 166.1. HR-MS *m/z*: Calcd for $C_{16}H_{18}O_2$: 242.1307. Found: 242.1323.

**1.2.18. *rel*-(1*S*,4*R*)-4-Allylcyclohex-2-enyl benzoate (23b).** Bp 147°C/1 mmHg. IR (neat): 1714 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.36–1.46 (m, 1H), 1.68–1.78 (m, 1H), 1.90–1.99 (m, 1H), 2.00–2.23 (m, 3H), 2.23–2.34 (m, 1H), 5.05 (d, 1H, *J*=10.2 Hz), 5.06 (d, 1H, *J*=17.3 Hz), 5.51–5.57 (m, 1H), 5.77–5.88 (m, 3H), 7.42 (t, 2H, *J*=7.3 Hz), 7.54 (t, 1H, *J*=7.3 Hz), 8.05 (dd, 2H, *J*=1.5, 7.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 26.2, 27.6, 34.9, 39.8, 70.0, 116.4, 126.5, 128.2, 129.6, 130.7, 132.7, 135.7, 136.3, 166.3. HR-MS *m/z*: Calcd for $C_{16}H_{18}O_2$: 242.1307. Found: 242.1325.

**1.2.19. 8-Methyl-3,4,4a,5,6,7,8,12c-octahydrobenzo[3,4]-cyclohepta[1,2-*b*]indole (26).** Mp 129–130°C (from AcOEt/hexane). IR ($CHCl_3$): 1650, 1605 $cm^{-1}$. $^1H$ NMR ($CDCl_3$) $\delta$: 1.35–1.50 (m, 2H), 1.50–1.75 (m, 3H), 1.90–2.05 (m, 2H), 2.05–2.25 (m, 2H), 2.78 (ddd, 1H, *J*=1.9, 11.8, 15.1 Hz), 2.98 (ddd, 1H, *J*=2.5, 6.0, 15.1 Hz), 3.54 (br s, 1H), 3.64 (s, 3H), 5.96–6.03 (m, 1H), 6.37 (d, 1H, *J*=10.3 Hz), 6.98 (dq, 1H, *J*=1.5, 7.9 Hz), 7.09 (dq, 1H, *J*=1.5, 7.9 Hz), 7.23 (d, 1H, *J*=8.3 Hz), 7.90 (d, 1H, *J*=8.3 Hz). $^{13}C$ NMR ($CDCl_3$) $\delta$: 24.5, 25.1, 27.2, 29.2, 31.8, 38.9, 40.6, 42.2, 108.9, 115.1, 118.4, 119.8, 119.9, 126.3, 126.7, 130.9, 136.1, 140.1. MS *m/z*: 251 ($M^+$). Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.57. Found: C, 86.02; H, 8.57; N, 5.47.

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