NOVEL EFFICIENT SYNTHESIS AND PROPERTIES OF 5,6-DIHYDROCYCLOHEPTA[b]INDOL-6-ONE, AND ITS TRANSFORMATION TO 6-AZOLYL-5-AZABENZ[b]AZULENES

Mitsunori Oda,* Kunihiro Ito, Hiroshi Takagi, and Yurie Fujiwara

Department of Chemistry, Faculty of Science, Shinshu University, Asahi 3-1-1, Matsumoto, Nagano, 390-8621 Japan, e-mail: mituoda@shinshu-u.ac.jp

Abstract – The title compound, 5,6-dihydrocyclohepta[b]indol-6-one (1), was synthesized from 2-chlorotropone (7) by a two-step sequence involving Pd-catalyzed amination with 2-bromoaniline (15) and subsequent Pd-catalyzed intramolecular Heck reaction. Besides its synthetic detail, some physical properties of 1, such as acidity, basicity and spectroscopic behavior, were also reported. Compound 1 was transformed into 6-(1H-pyrazol-1-yl)- and 6-(1H-1,2,3-triazol-1-yl)-5-azabenz[b]azulenes (13 and 14) as a potential ligand.

This paper is dedicated to Professor Dr. Ei-ichi Negishi on the occasion of his 77th birthday

INTRODUCTION

The title compound, 5,6-dihydrocyclohepta[b]indol-6-one (1),1 has been known since 1972. Boyer et al. reported the synthesis of 1 by basic hydrolysis of 6-amino-5-azabenzbazulene (2), which was obtained in the photochemical intramolecular insertion reaction of 2,2’-diisocyanobiphenyl (3) (Scheme 1).2 Almost at the same time, Kaneko et al. reported that 1 formed in the photochemical rearrangement of acridine 10-oxide (4), accompanied with 5 and 6.3 Later, Nozoe and Yamane et al. applied the Fischer indole synthesis to substrates containing a seven-membered ring and found two synthetic ways to 1 on a preparative scale.4,5 In one way, 9 was synthesized by the reaction of cyclohexanone and 2-hydrazinotropone (8), which can be obtained from 2-chlorotropone (7), and, then, dehydrogenation of 9 provided 1. In another way, 11 was synthesized by the Fischer indole synthesis with the phenylhydrazone of cycloheptane-1,2-dione (10), and 1 was obtained by dehydrogenation of 11 via a brominated intermediate. Interestingly, the carbon framework of 1 can be found in a marine bis(indole) alkaloid,
Boyer et al.

\[
\begin{array}{c}
\text{CN} \\
\text{NC}
\end{array}
\xrightarrow{hv} \begin{array}{c}
\text{NH}_2 \\
\text{N}
\end{array}
\xrightarrow{\text{NaOH}} \begin{array}{c}
\text{H} \\
\text{N}
\end{array}
\]

Kaneko et al.

\[
\begin{array}{c}
\text{hv} \\
\text{N}^+ \\
\text{O}^–
\end{array}
\xrightarrow{} \begin{array}{c}
\text{1} + \text{5} \\
\text{5} + \text{6}
\end{array}
\]

Nozoe and Yamane et al.

\[
\begin{array}{c}
\text{O} \\
\text{Cl}
\end{array}
\xrightarrow{\text{NH}_2\text{NH}_2} \begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\xrightarrow{1. \text{cyclohexanone}} \begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\xrightarrow{2. \text{H}_2\text{SO}_4} \begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{O}
\end{array}
\xrightarrow{1. \text{PhNHNNH}_2} \begin{array}{c}
\text{O}
\end{array}
\xrightarrow{2. \text{H}_2\text{SO}_4} \begin{array}{c}
\text{O}
\end{array}
\xrightarrow{1. \text{PhNMe}_3\text{Br}_3} \begin{array}{c}
\text{O}
\end{array}
\]

Scheme 1. Previously reported synthetic methods for 1

caulersin (12), whose synthetic benzo analogs show potent antitumor activity. Meanwhile, 1-azaazulenyl compounds have recently been paid attention to as a ligand, and, hence, we have been interested in 1 as a bidentate ligand structurally related to 1-azaazulenens and application of its metal complex for functionalized materials, particularly as an electroluminescent compound. Therefore, we have been curious to know basic properties of 1 for investigation of its metal complexation and also required a more convenient synthesis of 1. In this paper, we describe an alternative efficient synthesis of 1, and its properties such as acidity, basicity and...
interaction with metal ions. Also, transformation of 1 into azole-substituted 5-azaben[z]azulenes, 13 and 14, as a potential ligand is described.

RESULTS AND DISCUSSION
Development of a new synthetic method for 1
In this study, a short-step strategy for synthesizing 1 from 2-substituted tropones and 2-bromoaniline (15) by Pd-catalyzed amination and subsequent intramolecular Heck reaction was investigated. Although it has been known that 2-anilinotropones could be obtained by nucleophilic substitution reaction of various tropone derivatives having a leaving group at the 2-position with some unhindered anilines, Brookhart et al. reported that reaction of sterically hindered aniline with 2-tosyloxytropone (16) gave the ring-contraction compound as a major product. They devised Pd-catalyzed amination using 2-triflatotropone (17) as an alternative method for synthesizing 2-anilinotropones. Since 15 does not react with various 2-substituted tropones under conventional conditions, the Pd-catalyzed amination under reaction conditions reported by Brookhart et al. was applied to preparation of 2-(2-bromoanilino)tropone (20) in our study. The results are listed in Table 1. 2-Iodotropone (18) and 2-bromotropone (19) were used in addition to 7, 16, and 17.

Table 1. Palladium-catalyzed amination of 2-substituted tropones with 15

<table>
<thead>
<tr>
<th>entry</th>
<th>Y</th>
<th>Pd / BINAP a</th>
<th>solvent / temp / time</th>
<th>yield of 20 (%) b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>OTs</td>
<td>3 mol% Pd2(dba)3 / 6 mol% BINAP</td>
<td>toluene / 80°C / 6 h</td>
<td>15 c</td>
</tr>
<tr>
<td>2</td>
<td>OTs</td>
<td>3 mol% Pd2(dba)3 / 6 mol% BINAP</td>
<td>toluene / reflux / 12 h</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>OTf</td>
<td>3 mol% Pd2(dba)3 / 6 mol% BINAP</td>
<td>toluene / 80°C / 6 h</td>
<td>52</td>
</tr>
<tr>
<td>4</td>
<td>I</td>
<td>3 mol% Pd2(dba)3 / 6 mol% BINAP</td>
<td>toluene / reflux / 20 h</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>Br</td>
<td>3 mol% Pd2(dba)3 / 6 mol% BINAP</td>
<td>toluene / reflux / 15 h</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>Cl</td>
<td>3 mol% Pd2(dba)3 / 6 mol% BINAP</td>
<td>toluene / reflux / 12 h</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>Cl</td>
<td>1 mol% Pd2(dba)3 / 2 mol% BINAP</td>
<td>toluene / reflux / 16 h</td>
<td>52</td>
</tr>
<tr>
<td>8</td>
<td>Cl</td>
<td>5 mol% Pd2(dba)3 / 10 mol% BINAP</td>
<td>toluene / reflux / 4 h</td>
<td>71</td>
</tr>
<tr>
<td>9</td>
<td>Cl</td>
<td>3 mol% Pd2(dba)3 / 6 mol% BINAP</td>
<td>xylene / reflux / 5 h</td>
<td>60</td>
</tr>
</tbody>
</table>

a 1.2 eq. of 15 and 1.4 eq. of Cs2CO3 were used in all reactions, b Isolated yield after chromatography, c Recovery (36%) of 16 was observed.
Among the 2-substituted tropones used, 7 was surprisingly found to be the most reactive under the conditions and 20 was obtained in a satisfactory yield (Table 1, entry 6). The order of reactivity of arylhalides in Pd-catalyzed aminations is usually iodide > bromide > chloride. Therefore, polarizability of C–X bond has been thought to be important in an oxidative insertion of Pd(0). However, the order of reactivity of 2-halotropones in our amination is roughly chloride > bromide > iodide (Table 1, entries 4, 5, and 6), as seen in ionic nucleophilic substitution reactions of arylhalides. This reactivity suggests that charge density at the C-2 atom seems to play an important role in this amination reaction.

Table 2. Palladium-catalyzed intramolecular Heck reaction of 20

<table>
<thead>
<tr>
<th>entry</th>
<th>Pd / ligand / additive</th>
<th>solvent / temp / time</th>
<th>yield of 1 (%) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3 mol% Pd₂(dba)₃ / 6 mol% P(t-Bu)₃ / 1.0 eq DABCO</td>
<td>CH₃CN / reflux / 18 h</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>5 mol% Pd(OAc)₂ / 20 mol% P(o-tol)₃ / 1.3 eq Et₃N</td>
<td>dioxane / reflux / 27 h</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>10 mol% Pd(OAc)₂ / 40 mol% P(o-tol)₃ / 1.3 eq Et₃N</td>
<td>DMF / reflux / 18 h</td>
<td>6</td>
</tr>
<tr>
<td>4</td>
<td>2 mol% Pd(PPh₃)₄ / 2.0 eq NaHCO₃</td>
<td>HMPA / 80°C / 23 h</td>
<td>29 b</td>
</tr>
<tr>
<td>5</td>
<td>5 mol% Pd(OAc)₂ / 1.0 eq (Bu)₂N⁺Br⁻</td>
<td>DMF / reflux / 9 h</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>10 mol% Pd(OAc)₂ / 10 mol% P(o-tol)₃ / 1.3 eq K₂CO₃</td>
<td>DMF / reflux / 23 h</td>
<td>57</td>
</tr>
<tr>
<td>7</td>
<td>10 mol% Pd(OAc)₂ / 40 mol% P(o-tol)₃ / 1.3 eq K₂CO₃</td>
<td>DMF / reflux / 23 h</td>
<td>54</td>
</tr>
<tr>
<td>8</td>
<td>10 mol% Pd(OAc)₂ / 20 mol% P(o-tol)₃ / 1.0 eq AcOH / 2.0 eq AcONa</td>
<td>DMF / reflux / 8 h</td>
<td>79</td>
</tr>
<tr>
<td>9</td>
<td>10 mol% Pd(OAc)₂ / 20 mol% P(o-tol)₃ / 3.0 eq AcOH / 0.5 eq AcONa</td>
<td>DMF / reflux / 8 h</td>
<td>40 c</td>
</tr>
<tr>
<td>10</td>
<td>10 mol% Pd(OAc)₂ / 20 mol% XPhos / 1.0 eq AcOH / 2.0 eq AcONa</td>
<td>DMF / reflux / 27 h</td>
<td>90</td>
</tr>
<tr>
<td>11</td>
<td>10 mol% Pd(OAc)₂ / 20 mol% XPhos / 2.0 eq AcOH / 2.0 eq AcONa</td>
<td>DMF / reflux / 27 h</td>
<td>73 c</td>
</tr>
</tbody>
</table>

a Isolated yield after chromatography, b accompanied with 5% yield of cyclohepta[b][1,4]benzoxazine, c accompanied with a reduction product, 2-anilinotropone.

Next, with a substantial amount of 20 in hand, its intramolecular Heck reaction was examined to complete synthesis of the title compound 1. We applied Heck reaction conditions with various palladium catalysts and phosphine ligands. The results are summarized in Table 2. Under the conditions of entries 1–5, the yields of 1 were poor or none. Although 1 was obtained under the conditions with Pd(OAc)₂/P(o-tol)₃/K₂CO₃/DMF (Table 2, entries 6 and 7), the yields of 1 were still moderate. Addition of weak base and its conjugated acid was found effective to improve the yield (Table 2, entry 8). However, under acidic conditions with a larger amount of acetic acid the yield of 1 was reduced, accompanied with
formation of a reduction product (Table 2, entries 9 and 11). The satisfactory yield of 90% was achieved under the conditions with sterically hindered ligand, XPhos\(^1\) (Table 2, entry 10). The title compound 1 is now available in two steps from 7 and 15 in good yields (Scheme 2). Although palladium reagents are used in these two procedures, transformation to 1 from 7 in one pot was not achieved yet in spite of extensive attempts.

Scheme 2. Summary of the synthesis of 1

Some physical properties of 1

Compound 1 was isolated as yellow prisms. Although some spectral data were previously reported, those were renewed by data measured with high-resolution machines. All \(^1\)H and \(^1^3\)C NMR signals are assigned with the aid of HMQC and HMBC spectra (Figure 1). Behavior of 1 in both acidic (CF\(_3\)CO\(_2\)D) and basic (NaOD/D\(_2\)O/DMSO-\(d\)\(_6\)) media was also investigated by \(^1\)H NMR analysis. The average chemical shift (8.29 ppm) of hydrogens on the sp2 carbon atoms in CF\(_3\)CO\(_2\)D shows a down-fielded shift compared with

Figure 1. Assigned \(^1\)H (left) and \(^1^3\)C (right) NMR signals (\(\delta\)ppm) and selected coupling constants of 1.

Scheme 3. Selected coupling constants of protonated and deprotonated species of 1.
that (7.61 ppm) in CDCl₃, supporting generation of the protonated species 1⁺. It is worth noting that ³J_H-H coupling constants between hydrogens on the seven-membered ring are same, evidencing formation of the delocalized tropylium ion structure in 1⁺ (Scheme 3). On the other hand, the average chemical shift in NaOD/D₂O/DMSO-d₆ (7.64 ppm) shows a very small up-field shift. However, more convergent ³J_H-H coupling constants compared with those observed in CDCl₃ suggest generation of deprotonated species 1⁻.

Although electron density of the azaazulene ring increases in 1⁻, a deshielding effect of the ring perimeter may compensate the shielding effect of negative charge in 1⁻, resulting in the slight up-field shift.

![Figure 2](image_url)  
**Figure 2.** Absorption spectra of 1 in neutral, acidic, and basic media.

Changes of UV-vis spectra in acidic and basic media (Figure 2) also evidence the formation of ionic species, 1⁺ and 1⁻. While the spectrum of 1 in EtOH displays mainly four bands at 224, 276, 307 and 403 nm, the spectrum in a 50% sulfuric acid solution shows a slight red-shift of the long-wave maximum (407 nm) with a hypochromic effect and also distinct hyperchromic effect of the maximum around 310 nm. The spectrum in a 20% NaOH solution shows a clear red-shift of all bands. Particularly, the long-wave maximum shifts by 52 nm compared with that in EtOH. Based on these spectral changes, values of pKₐ and pKₐ for 1 were determined by a titration method. Table 3 shows the values of 1 and related compounds, indole,¹⁴ pyrrole,¹⁴ 2-aminotropone,¹⁵ tropone¹⁶ and

<table>
<thead>
<tr>
<th>Table 3. Acidity and basicity of 1 and related compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>compound</td>
</tr>
<tr>
<td>-----------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>indole</td>
</tr>
<tr>
<td>pyrrole</td>
</tr>
<tr>
<td>2-aminotropone</td>
</tr>
<tr>
<td>tropone</td>
</tr>
<tr>
<td>21</td>
</tr>
</tbody>
</table>

¹Measured in DMSO. Taken from ref 14. ¹²Measured in hydrochloric acid solutions. Taken from ref 15. ¹³Measured in sulfuric acid solutions. Taken from ref 16. ¹⁴Measured in 50% aqueous MeOH. Taken from ref 2. See below for the structure of 21.
6-azabenzo[b]azulene (21). The relatively stronger acidity of 1 compared with those of indole and pyrrole can be attributed to the annelation of an electron-withdrawing tropone to the indole skeleton. The basicity of 1 is between those of tropone and 2-amino-tropone and far lower than that of 21. These results are consistent to the previously suggested conclusion that 1 exist as a tropone-containing structure, depicted as 1, not as its tautomeric azaazulene structure of 22 (Scheme 4).

In order to investigate interaction between 1 and metal ions, absorption spectra of 1 in the presence of a large excess (500 eq.) of several metal ions as the perchlorate were measured. Clear spectral change was not observed in the presence of monovalent ions, such as Li⁺, Na⁺ and Ag⁺, and divalent Ca²⁺ and Mg²⁺. In the presence of divalent Zn²⁺, the long-wave maximum was observed at 439 nm, showing a clear red-shift (Figure 3). Emission upon excitation at 439 nm in the presence of Zn²⁺ was observed at 497 nm. It is worth noting that an emission quantum yield (Φ = 1.2 x 10⁻²) in the presence of Zn²⁺ is 23 times greater than that (Φ = 5.3 x 10⁻⁴) without metal ion.¹⁷

**Figure 3.** Absorption spectra of 1 in the presence of various metal ions.

**Synthesis and properties of 6-azolyl-5-azabenzo[b]azulenes**

Yamane et al. reported the transformation of 1 into various amine-substituted 5-azabenzo[b]azulenes (24) via 6-chloro-5-azabenzo[b]azulene (23).⁴ Nucleophilic substitution

**Scheme 5.** Synthesis of 6-amino-5-azabenzo[b]azulenes 24 by Yamane et al.
reactions of 23 with amines and hydrazines provide various 6-substituted derivatives in good yields by simply heating in EtOH (Scheme 5). However, less nucleophilic azoles react with 23 neither in refluxing EtOH nor under base-assisted conditions. Hence, Pd-catalyzed amination was examined. The results are shown in Table 4. The desired products 13 and 14 were obtained in good yields under the conditions Pd(dba)3/BINAP/Cs2CO3 in refluxing toluene (entries 2–4). In the reaction with 1,2,3-triazole, a small amount of the 2-triazolyl isomer 24 was observed as another product by 1H NMR analysis of the crude reaction mixture. However, 24 was not isolated because of its facile hydrolysis to 1 during chromatographic purification, as seen in hydrolysis of 2. Compound 14 is more sensitive to acid and base than 13. Compounds 13 and 14 were isolated as violet crystals, having weak visible absorptions at 510 and 496 nm in EtOH, respectively (Figure 4). While no emission was observed upon excitation at those long-wave maxima, emissions at 435 nm were observed upon excitation at 383 for 13 and 385 nm for 14. This emission behavior is resemble to that seen in azulenes. A pKb value of 13 was determined to be 8.4 by a UV-vis titration method, though basicity of 14 could not be determined because of its instability in acid and basic aqueous solutions. The value shows that 13 is less basic by 1.1 pKb unit than the parent 6-azabenzo[b]azulene (21), indicating that the pyrazole moiety shows electron-withdrawing functionality. Absorption spectra of 13 and 14 in the presence of a large excess (500 eq.) of metal ions are also examined. The results are shown in Figures. 5 and 6. A blue-shifts of the long-wave absorption maxima with a hyperchromic effect for

Table 4. Palladium-catalyzed amination of 23 with pyrazole and triazole

<table>
<thead>
<tr>
<th>entry</th>
<th>azolea</th>
<th>Pd(dba)3 / ligand b</th>
<th>solvent / temp / time</th>
<th>yield [%]c (product)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pyrazole</td>
<td>2.5 mol% Pd(dba)3 / 5 mol% XPhos</td>
<td>dioxane / reflux / 6 h</td>
<td>9 (13)</td>
</tr>
<tr>
<td>2</td>
<td>pyrazole</td>
<td>3 mol% Pd(dba)3 / 6 mol% BINAP</td>
<td>toluene / reflux / 9 h</td>
<td>77 (13)</td>
</tr>
<tr>
<td>3</td>
<td>triazole</td>
<td>6 mol% Pd(dba)3 / 12 mol% BINAP</td>
<td>toluene / 80°C / 14 h</td>
<td>69 (14)</td>
</tr>
<tr>
<td>4</td>
<td>triazole</td>
<td>10 mol% Pd(dba)3 / 20 mol% BINAP</td>
<td>toluene / 90°C / 20 h</td>
<td>72 (14)</td>
</tr>
</tbody>
</table>

a 2.0 eq. of azole was used in all reactions, b 2.0 eq. of Cs2CO3 were used in all reactions, c Isolated yield after chromatography.

Mg$^{2+}$ and Zn$^{2+}$ was observed for 13 and 14, suggesting that coordination of metal ions with their nitrogen on the 6 position occurs, though it is not clear whether azole nitrogens participate in the coordination or
not so far. Interestingly, 13 interacts much strongly with Mg$^{2+}$, while 14 dose with Zn$^{2+}$. However, clear change of their emission spectra in the presence of metal ions was not observed.

**CONCLUSION**

It has been demonstrated that the title compound 1 can be efficiently synthesized from 2-chlorotropone (7) by Pd-catalyzed amination with 2-bromoaniline (15) and subsequent by Pd-catalyzed intramolecular Heck reaction. Various 2-substituted tropones were subjected to the amination and it was revealed that, among the tropones used, 2-chlorotropones (7) reacts most effectively. In the intramolecular Heck reaction, it was found that addition of weak acid and its conjugated base and use of a sterically hindered ligand was valid to improve the yield. Basicity and acidity of 1 were disclosed and its interaction with metal ions in solution was studied. The Pd-catalyzed amination of 23, derived from 1, with azoles gave the azolyl products 13 and 14. Some spectroscopic properties of these compounds were also clarified.

**EXPERIMENTAL**

Melting points were measured on a Yanaco MP-3. IR spectra were recorded on a JEOL Diamond-20 spectrometer. UV-vis spectra were measured on a Shimadzu UV-2550 spectrometer. Emission spectra were recorded on a Shimadzu RF-5300PC spectrometer. $^1$H and $^{13}$C-NMR spectra were recorded with tetramethylsilane as internal standard on a JEOL $\lambda$400 NMR instruments. Mass spectra were measured on a JMS-700 mass spectrometer. Column chromatography was done with Silica gel 60N from Kanto Chem., Inc. X-Phos, Pd$_2$(dba)$_3$, Pd(PPh$_3$)$_4$, and Cs$_2$CO$_3$ were purchased from Sigma-Aldrich Japan, Inc. BINAP, tri-o-tolylphosphine and 2-bromoaniline were purchased from Tokyo Kasei Industrial Co. Pd(OAc)$_2$ was purchased from Wako Chem. 2-Holotropones were prepared according to the literature method of Doering. 6-Chloro-5-azabenz[b]azulene (23) was prepared from 1 according to the literature method of Nozoe. Emission quantum yields were determined by comparison of a total emission area with that of anthracene (Φ = 0.27, upon excitation at 356 nm in ethanol).

**2-(2-Bromoanilino)tropone (20)**

A mixture of 7 (281 mg, 2.00 mM), 2-bromoaniline (413 mg, 2.40 mM), Pd$_2$(dba)$_3$ (55 mg, 0.060 mM), BINAP (75 mg, 0.12 mM), and Cs$_2$CO$_3$ (912 mg, 2.80 mM) in 5 mL of toluene was refluxed on an oil bath for 12 h. The resulted reaction mixture was passed through a Celite pad and washed with toluene. After evaporation of the filtrate, the residue was purified by silica gel column chromatography with AcOEt/Hexane (30/70) to give 444 mg (80% yield) of 20 as slightly brown needles. Mp 84–85 °C. $^1$H NMR (CDCl$_3$) $\delta = 6.82$ (td, $J = 8.4$, 0.8 Hz, 1H), 6.98 (d, $J = 10.4$ Hz, 1H), 7.12 (m, 2H), 7.30–7.35 (m, 2H), 7.38 (t, $J = 8.4$ Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 10.8$ Hz, 1H), 8.75 (brs, 1H) ppm; $^{13}$C
NMR (CDCl₃) δ = 110.8, 120.0, 125.2, 125.4, 127.2, 128.3, 131.4, 133.9, 135.7, 137.0, 137.5, 152.7, 177.2 ppm; IR (KBr) ν<sub>max</sub> = 3427 brm, 3236 m, 1547 vs cm<sup>−1</sup>; UV-vis (EtOH) λ<sub>max</sub> = 236 (log ε = 4.25), 341 (3.99), 400 (4.1) nm; MS (70 eV) m/z (rel int) = 277 (M⁺, 12), 275 (M⁺, 11), 276 (19), 197 (38), 196 (100), 168 (17), 167 (53), 98 (15), 77 (15). Anal. Calcd for C₁₃H₁₀BrNO: C, 56.55; H, 3.65; N, 5.07%. Found: C, 56.76; H, 3.77; N, 5.15%.

5,6-Dihydrocyclohepta[b]indol-6-one (1)
A mixture of 20 (215 mg, 0.779 mM), XPhos (74 mg, 0.16 mM), Pd(OAc)₂ (18 mg, 0.080 mM), NaOAc (128 mg, 1.56 mM), and AcOH (47 µL, 0.78 mM) in 5 mL of DMF was refluxed on an oil bath for 27 h. The resulted reaction mixture was passed through a Celite pad and washed with CH₂Cl₂. After evaporation of the filtrate, the residue was purified by silica gel column chromatography with AcOEt/Hexane (40/60) to give 137 mg (90% yield) of 1 as yellow prisms. Mp 255–256 °C [lit. 249.5–250.5, 1 250–252, 2 245–246°C<sup>3a</sup>].

1H NMR (CDCl₃) δ = 7.10 (ddd, J = 10.8, 8.8, 1.0 Hz, H-9), 7.39 (tt, J = 8.0, 1.2 Hz, H-2), 7.42 (dt, J = 12.3, 1.0 Hz, H-7), 7.55 (ddd, J = 12.3, 8.8, 1.0 Hz, H-8), 7.58 (tt, J = 8.0, 1.2 Hz, H-3), 7.72 (dm, J = 8.0 Hz, H-4), 8.15 (dm, J = 8.0 Hz, H-1), 8.20 (dm, J = 10.8 Hz, H-10), 10.91 (brs, N-H) ppm; 1H NMR (CF₃CO₂D) δ = 7.69 (m, H-2), 7.90–7.95 (m, H-3,4), 8.19 (t, J = 10.0 Hz, H-7), 8.25 (d, J = 10.0 Hz, H-9), 8.42 (t, J = 8.4 Hz, H-8), 8.48 (d, J = 8.4 Hz, H-1), 9.35 (d, J = 10.0 Hz, H-10) ppm; 13C NMR (CF₃CO₂D) δ = 115.3, 123.4, 126.6, 127.1, 128.1, 134.1, 135.7, 138.2, 139.9, 141.8, 142.5, 144.8, 183.1 ppm; 6-(1H-Pyrazol-1-yl)-5-azabenz[b]azulene (13)
A mixture of 23 (45 mg, 0.21 mM), pyrazole (29 mg, 0.42 mM), Pd₂(dba)₃ (9 mg, 7 µM), BINAP (6 mg, 14 µM), and Cs₂CO₃ (137 mg, 0.420 mM) in 5 mL of toluene was refluxed on an oil bath for 9 h. The resulted reaction mixture was passed through a Celite pad and washed with toluene. After evaporation of the filtrate, the residue was purified by silica gel column chromatography with AcOEt/CHCl₃ (30/70) to give 40 mg (77% yield) of 13 as violet needles. Mp 135–136 °C. 1H NMR (CDCl₃) δ = 6.64 (dd, J = 2.7, 1.3 Hz, pyrazolyl-H), 7.54 (ddd, J = 8.1, 7.7, 1.0 Hz, H-2), 7.69 (ddd, J = 10.3, 8.9, 0.5 Hz, H-9), 7.80 (ddd, J = 8.1, 7.7, 1.0 Hz, H-3), 7.89 (dd, J = 1.3, 0.5 Hz, pyrazolyl-H), 7.94 (ddd, J = 10.6, 10.3, 1.0 Hz, H-8), 8.13 (dt, J = 8.1, 1.0 Hz, H-4), 8.38 (dt, J = 8.1, 1.0 Hz, H-1), 8.82 (dd, J = 10.6, 1.1 Hz, H-7), 8.88 (dd, J = 8.9, 1.1, 0.5 Hz, H-10), 9.65 (dd, J = 2.7, 0.5 Hz, pyrazolyl-H), ppm; 13C NMR (CDCl₃) δ = 107.8 (pyrazole C-4), 120.8 (C-4), 120.9 (C-1), 122.9 (C-2), 125.9 (C-7), 127.5 (C-9), 127.8 (C-10b),
131.0 (C-3), 131.2 (C-10), 135.0 (C-8), 135.5 (pyrazole C-5), 142.1 (pyrazole C-3), 142.6 (C-6), 143.8 (C-10a), 152.1 (C-5a), 156.3 (C-4a) ppm; IR (KBr) $\nu_{\text{max}} = 1454\text{~s}, 1382\text{~s}, 1334\text{~s}, 1203\text{~s}, 654\text{~s}, 755\text{~s},$

730s cm$^{-1}$; UV-vis (EtOH) $\lambda_{\text{max}} = 3348\text{~m}, 3168\text{~m}, 3109\text{~s}, 3047\text{~m}, 1616\text{~w}, 1604\text{~m}, 1517\text{~w}, 1475\text{~w}, 1458\text{~s}, 1437\text{~w}, 1394\text{~s}, 1357\text{~m}, 1321\text{~w}, 1236\text{~s}, 1070\text{~s}, 1016\text{~s}, 789\text{~m}, 758\text{~s}, 727\text{~s}$ cm$^{-1}$; UV-vis (EtOH) $\lambda_{\text{max}} = 245\text{~(M}^+\text{, 3), 218\text{~(100), 217\text{~(27), 190\text{~(18), 177\text{~(12), 167\text{~(9), 151\text{~(9), 150\text{~(6), 108\text{~(8), 106\text{~(7), 77\text{~(7), 57\text{~(8), HRMS $m/z$ Calcd for C}_{16}H_{11}N_{4}(M^+) 246.0911, found: 246.0904.}$

Determinant of acidity and basicity for 1 and 13

The acidity of 1 and basicity of 13 were determined from titration curves based on pH-dependent absorption spectra in 50% aqueous ethanol solutions by a curve fitting method using KaleidaGraph program. The absorption peak at 455 nm for acidity of 1 and the absorption peak at 383 nm for basicity of 13 were used. Buffer solutions used for measurements of basicity of 13 are as follows; AcOH/AcONa at a range of pH 4.35~7.40 and KH$_2$PO$_4$/Na$_2$HPO$_4$ at a range of pH 6.97~8.92. Instead buffer solutions, NaOH solutions were used a range of pH 10.50~14.00 for measurements of acidity of 1. The basicity of 1 was determined from titration curves based on Hammet acitity function ($H_0$)-dependent absorption spectra. The absorption peak at 402 nm was used and solutions used are as follows; H$_3$PO$_4$ solutions at a range of
$H_0$–0.37~1.45 and $H_2SO_4$ solutions at a range of $H_0$–2.06~0.02.

ACKNOWLEDGEMENTS

We deeply thank emeritus Prof. Kunihide Fujimori at Shinshu University for giving us an authentic sample of 1. We also thank Mr Hiroki Okamoto and Ms Yuko Yamaga for their technical assistance to prepare compound 14.

REFERENCES AND NOTES

1. The compound has also been called as indolo[2,3-b]tropone.
9. A part of this study, development of the novel synthetic procedure of 1, has been briefly reported; J. Jin, K. Ito, F. Takahashi, and M. Oda, Chem. Lett., 2010, 39, 861.


17. Upon excitation at 403 nm in EtOH, **1** emits light with a maximum at 439 nm. The quantum yield was obtained in a molar concentration of **1** less than 10⁻⁵ mol/L.

18. Emission quantum yields for **13** and **14** are 7.4 x 10⁻⁴ and 3.8 x 10⁻⁴, respectively. Quantum yields were obtained in molar concentrations of these substrates less than 10⁻⁴ mol/L.