

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

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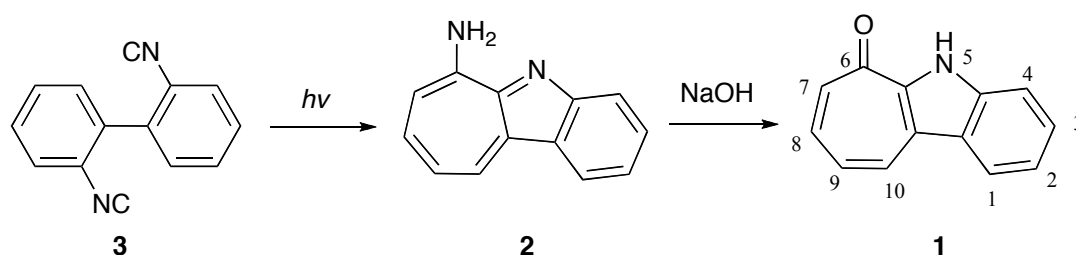
Abstract – The title compound, 5,6-dihydrocyclohepta[*b*]indol-6-one (**1**), was synthesized from 2-chlorotropone (**7**) by a two-step sequence involving Pd-catalyzed amination with 2-bromoaniline (**15**) and subsequent Pd-catalyzed intramolecular Heck reaction. Besides its synthetic detail, some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

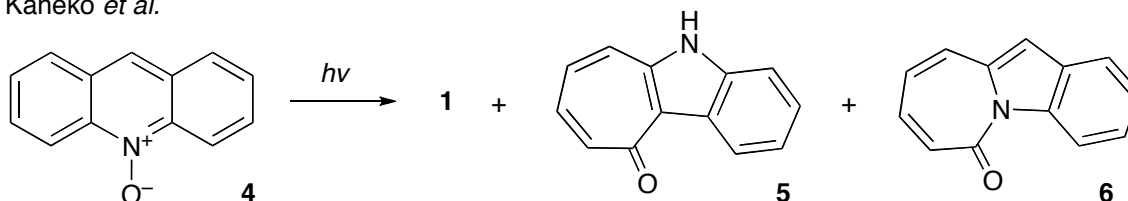
INTRODUCTION

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-azabenz[*b*]azulene (**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,

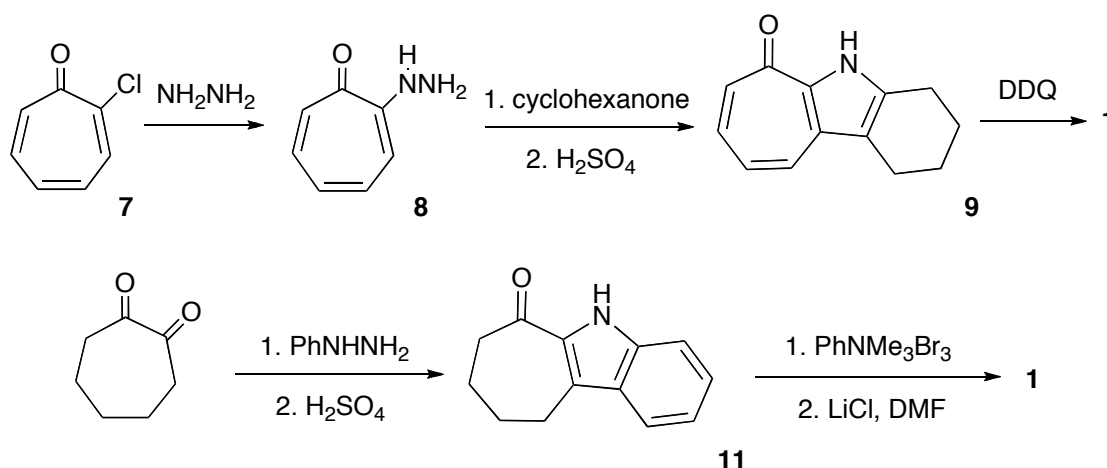
Boyer *et al.*



Kaneko *et al.*

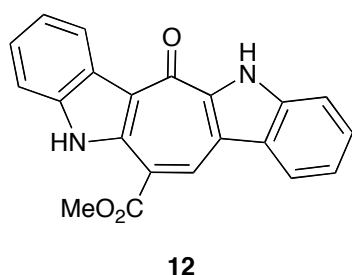


Nozoe and Yamane *et al.*



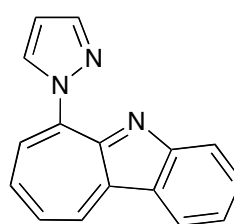
Scheme 1. Previously reported synthetic methods for **1**

caulersin (**12**), whose synthetic benzo analogs show potent antitumor activity.⁷ Meanwhile, 1-azaazulenyl compounds have recently been paid attention to as a ligand,⁸ 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.⁹ 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



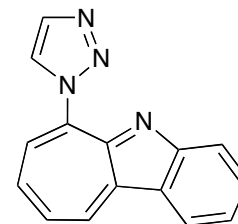
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Chart 1. Structure of caulersin (**12**).



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Chart 2. Structures of **13** and **14**.



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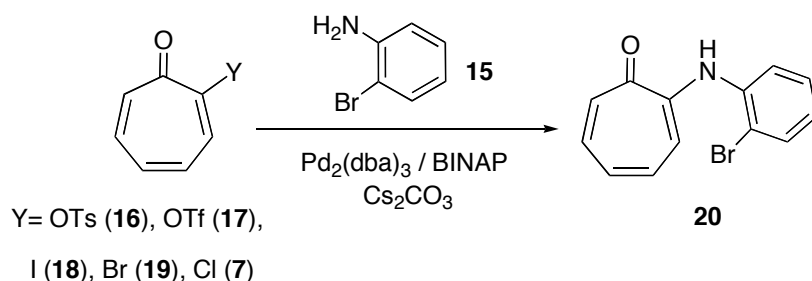
interaction with metal ions. Also, transformation of **1** into azole-substituted 5-azabenz[*b*]azulenes, **13** and **14**, as a potential ligand is described.

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-anilino tropones could be obtained by nucleophilic substitution reaction of various troponone derivatives having a leaving group at the 2-position with some unhindered anilines,¹⁰ Brookhart *et al.* reported that reaction of sterically hindered aniline with 2-tosyloxypiprone (**16**) gave the ring-contraction compound as a major product.¹¹ They devised Pd-catalyzed amination using 2-triflatropone (**17**) as an alternative method for synthesizing 2-anilino tropones. 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)troponone (**20**) in our study. The results are listed in Table 1. 2-Iodotroponone (**18**) and 2-bromotroponone (**19**) were used in addition to **7**, **16**, and **17**.

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



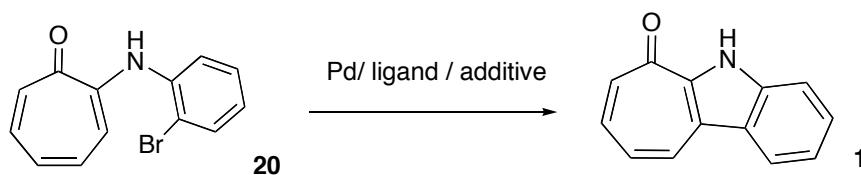
entry	Y	Pd / BINAP ^a	solvent / temp / time	yield of 20 (%) ^b
1	OTs	3 mol% Pd ₂ (dba) ₃ / 6 mol% BINAP	toluene / 80°C / 6 h	15 ^c
2	OTs	3 mol% Pd ₂ (dba) ₃ / 6 mol% BINAP	toluene / reflux / 12 h	25
3	OTf	3 mol% Pd ₂ (dba) ₃ / 6 mol% BINAP	toluene / 80°C / 6 h	52
4	I	3 mol% Pd ₂ (dba) ₃ / 6 mol% BINAP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

^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.¹² 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**

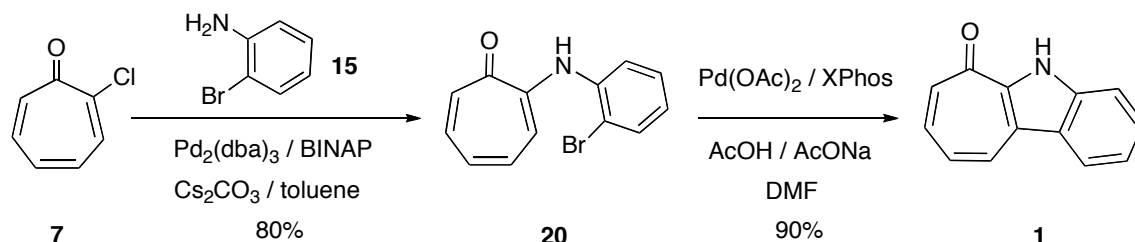


entry	Pd / ligand / additive	solvent / temp / time	yield of 1 (%) ^a
1	3 mol% Pd ₂ (dba) ₃ / 6 mol% P(<i>t</i> -Bu) ₃ / 1.0 eq DABCO	CH ₃ CN / reflux / 18 h	trace
2	5 mol% Pd(OAc) ₂ / 20 mol% P(<i>o</i> -tol) ₃ / 1.3 eq Et ₃ N	dioxane / reflux / 27 h	0
3	10 mol% Pd(OAc) ₂ / 40 mol% P(<i>o</i> -tol) ₃ / 1.3 eq Et ₃ N	DMF / reflux / 18 h	6
4	2 mol% Pd(PPh ₃) ₄ / 2.0 eq NaHCO ₃	HMPA / 80°C / 23 h	29 ^b
5	5 mol% Pd(OAc) ₂ / 1.0 eq (Bu) ₄ N ⁺ Br ⁻	DMF / reflux / 9 h	22
6	10 mol% Pd(OAc) ₂ / 10 mol% P(<i>o</i> -tol) ₃ / 1.3 eq K ₂ CO ₃	DMF / reflux / 23 h	57
7	10 mol% Pd(OAc) ₂ / 40 mol% P(<i>o</i> -tol) ₃ / 1.3 eq K ₂ CO ₃	DMF / reflux / 23 h	54
8	10 mol% Pd(OAc) ₂ / 20 mol% P(<i>o</i> -tol) ₃ / 1.0 eq AcOH / 2.0 eq AcONa	DMF / reflux / 8 h	79
9	10 mol% Pd(OAc) ₂ / 20 mol% P(<i>o</i> -tol) ₃ / 3.0 eq AcOH / 0.5 eq AcONa	DMF / reflux / 8 h	40 ^c
10	10 mol% Pd(OAc) ₂ / 20 mol% XPhos / 1.0 eq AcOH / 2.0 eq AcONa	DMF / reflux / 27 h	90
11	10 mol% Pd(OAc) ₂ / 20 mol% XPhos / 2.0 eq AcOH / 2.0 eq AcONa	DMF / reflux / 27 h	73 ^c

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

Next, with a substantial amount of **20** in a 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, XPhos¹³ (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 ¹H and ¹³C NMR signals are assigned with the aid of HMQC and HMBC spectra (Figure 1). Behavior of **1** in both acidic (CF₃CO₂D) and basic (NaOD/D₂O/DMSO-*d*₆) media was also investigated by ¹H NMR analysis. The average chemical shift (8.29 ppm) of hydrogens on the sp² carbon atoms in CF₃CO₂D shows a down-field shift compared with

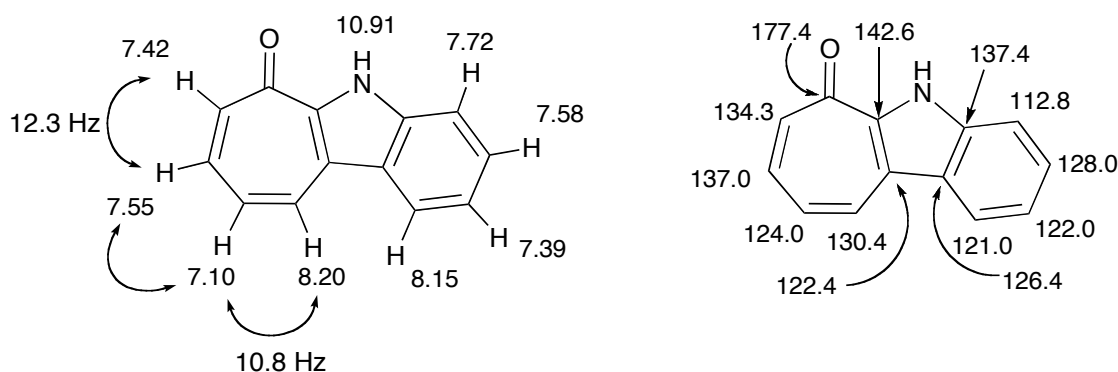
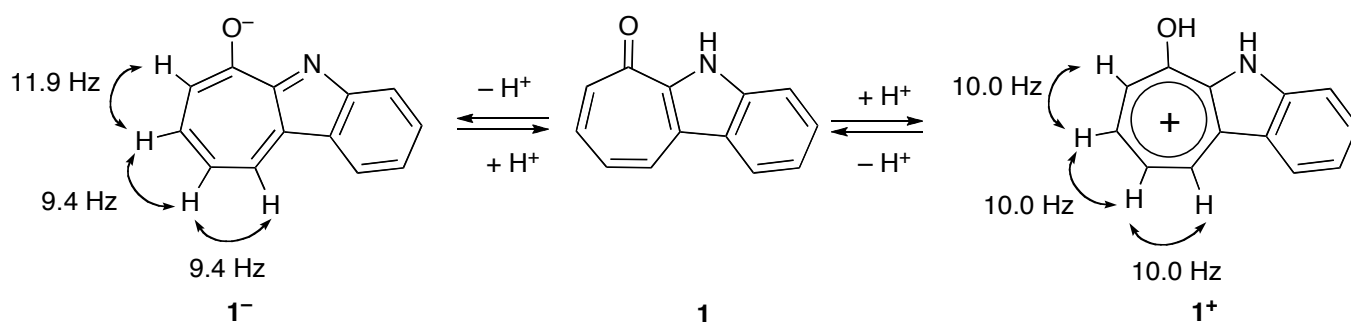


Figure 1. Assigned ¹H (left) and ¹³C (right) NMR signals (δppm) and selected coupling constants of **1**.



Scheme 3. Selected coupling constants of protonated and deprotonated species of **1**.

that (7.61 ppm) in CDCl_3 , supporting generation of the protonated species $\mathbf{1}^+$. It is worth noting that $^3J_{\text{H-H}}$ coupling constants between hydrogens on the seven-membered ring are same, evidencing formation of the delocalized tropylium ion structure in $\mathbf{1}^+$ (Scheme 3). On the other hand, the average chemical shift in $\text{NaOD/D}_2\text{O/DMSO-}d_6$ (7.64 ppm) shows a very small up-field shift. However, more convergent $^3J_{\text{H-H}}$ coupling constants compared with those observed in CDCl_3 suggest generation of deprotonated species $\mathbf{1}^-$. Although electron density of the azaazulene ring increases in $\mathbf{1}^-$, a deshielding effect of the ring perimeter may compensate the shielding effect of negative charge in $\mathbf{1}^-$, resulting in the slight up-field shift.

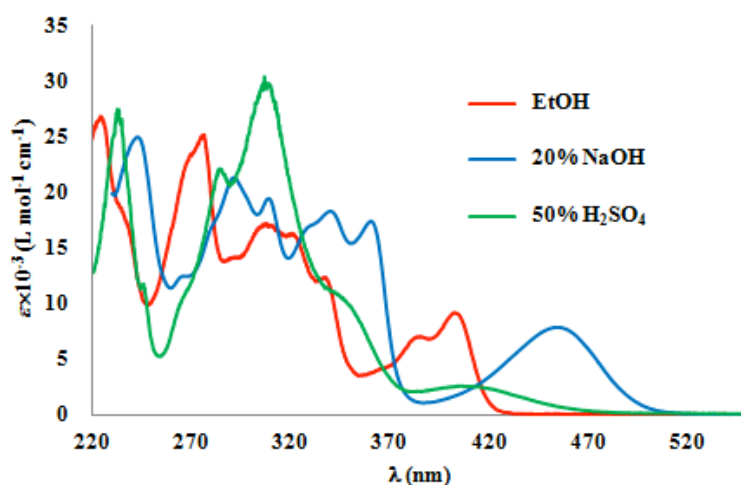


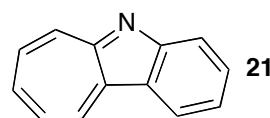
Figure 2. Absorption spectra of **1** in neutral, acidic, and basic media.

Changes of UV-vis spectra in acidic and basic media (Figure 2) also evidence the formation of ionic species, $\mathbf{1}^+$ and $\mathbf{1}^-$. 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 $\text{p}K_a$ and $\text{p}K_b$ 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 3. Acidity and basicity of **1** and related compounds

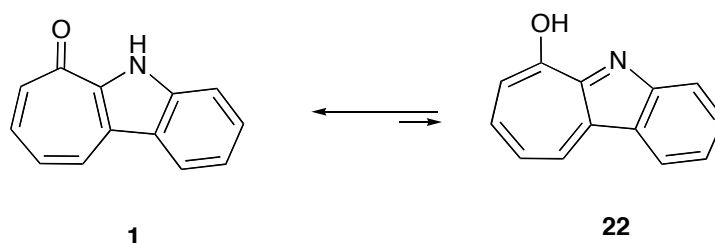
compound	$\text{p}K_a$	$\text{p}K_b$
1	13.6	12.9
indole ^{a)}	20.95	—
pyrrole ^{a)}	23.05	—
2-aminotropone ^{b)}	—	11.79
tropone ^{c)}	—	15.02
21 ^{d)}	—	7.3

^{a)} Measured in DMSO. Taken from ref 14. ^{b)} Measured in hydrochloric acid solutions. Taken from ref 15. ^{c)} Measured in sulfuric acid solutions. Taken from ref 16. ^{d)} Measured in 50% aqueous MeOH. Taken from ref 2. See below for the structure of **21**.



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6-azabenz[*b*]azulene (**21**).² 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-aminotropone and far lower than that of **21**. These results are consistent to the previously suggested conclusion⁴ that **1** exist as a tropone-containing structure, depicted as **1**, not as its tautomeric azaazulene structure of **22** (Scheme 4).



Scheme 4. Tautomerism of **1**.

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 Ca^{2+} and Mg^{2+} . In the presence of divalent Zn^{2+} , 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 Zn^{2+} was observed at 497 nm. It is worth noting that an emission quantum yield ($\Phi = 1.2 \times 10^{-2}$) in the presence of Zn^{2+} is 23 times greater than that ($\Phi = 5.3 \times 10^{-4}$) without metal ion.¹⁷

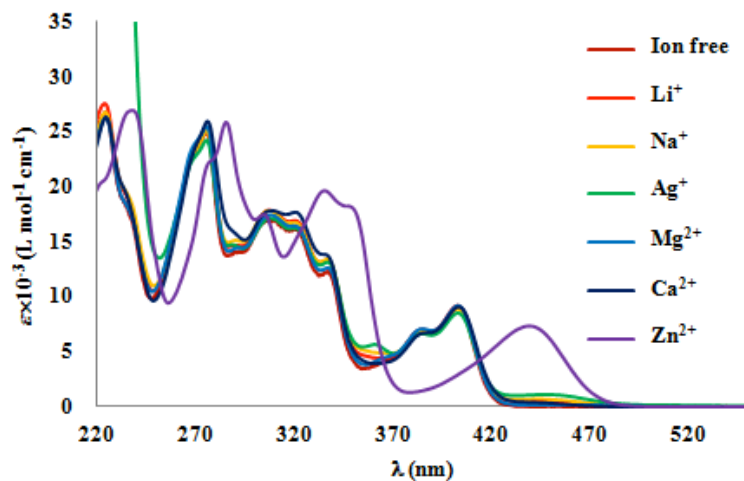
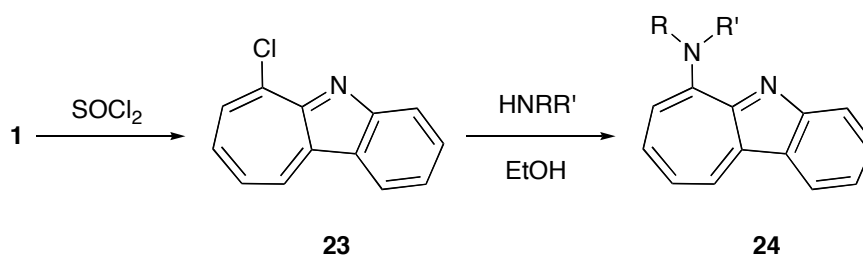


Figure 3. Absorption spectra of **1** in the presence of various metal ions.

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

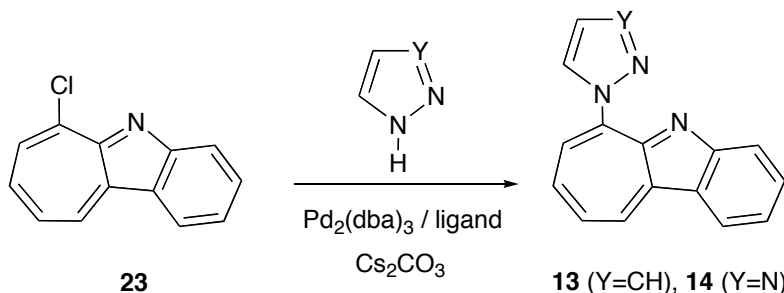
Yamane *et al.* reported the transformation of **1** into various amine-substituted 5-azabenz[*b*]azulenes (**24**) via 6-chloro-5-azabenz[*b*]azulene (**23**).⁴ Nucleophilic substitution



Scheme 5. Synthesis of 6-amino-5-azabenz[*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

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

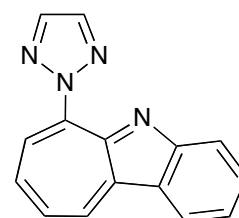


entry	azole ^a	Pd ₂ (dba) ₃ / ligand ^b	solvent / temp / time	yield [%] ^c (product)
1	pyrazole	2.5 mol% Pd ₂ (dba) ₃ / 5 mol% XPhos	dioxane / reflux / 6 h	9 (13)
2	pyrazole	3 mol% Pd ₂ (dba) ₃ / 6 mol% BINAP	toluene / reflux / 9 h	77 (13)
3	triazole	6 mol% Pd ₂ (dba) ₃ / 12 mol% BINAP	toluene / 80°C / 14 h	69 (14)
4	triazole	10 mol% Pd ₂ (dba) ₃ / 20 mol% BINAP	toluene / 90°C / 20 h	72 (14)

^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.

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 Pd₂(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



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because of its facile hydrolysis to **1** during chromatographic purification, as **Chart 3**. Structure of **24**. 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**.¹⁸ This emission behavior is resemble to that seen in azulenes. A p*K*_b 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 p*K*_b unit than the parent 6-azabenz[*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

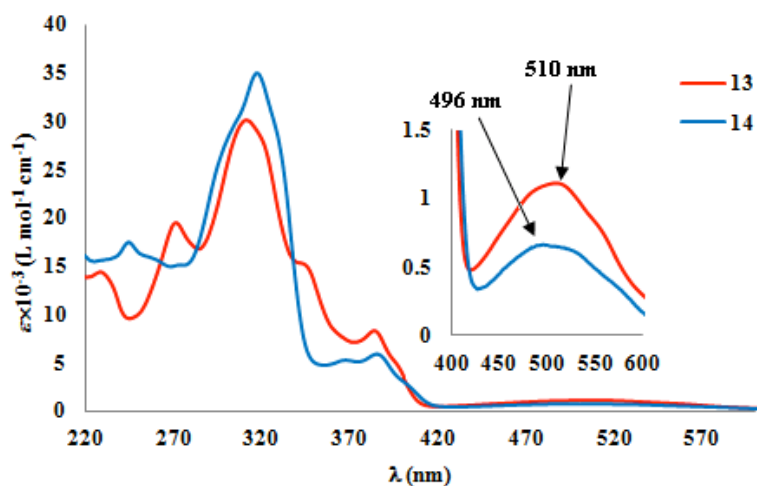


Figure 4. Absorption spectra of **13** and **14** in EtOH.

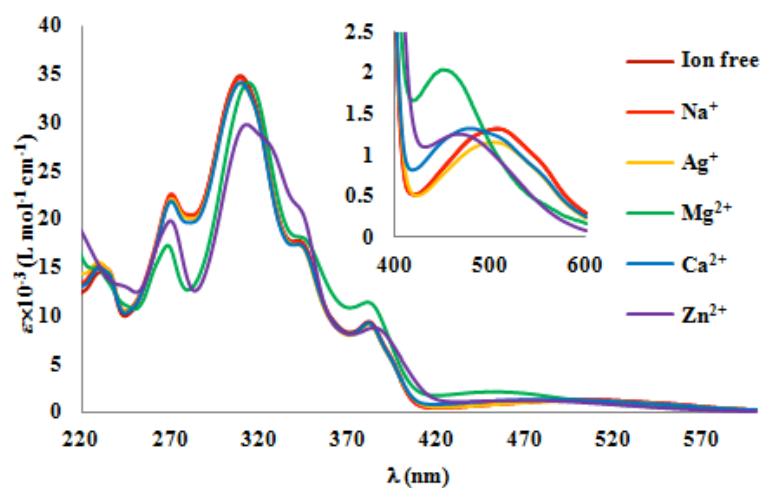


Figure 5. Absorption spectra of **13** in the presence of various metal ions.

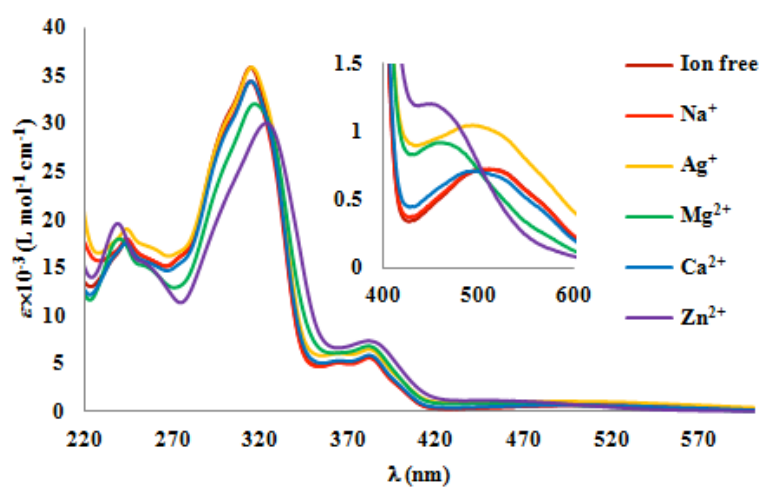


Figure 6. Absorption spectra of **14** in the presence of various metal ions.

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-chlorotropone (**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. ^1H and ^{13}C -NMR spectra were recorded with tetramethylsilane as internal standard on a JEOL λ 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, $\text{Pd}_2(\text{dba})_3$, $\text{Pd}(\text{PPh}_3)_4$, and Cs_2CO_3 were purchased from Sigma-Aldrich Japan, Inc. BINAP, tri-*o*-tolylphosphine and 2-bromoaniline were purchased from Tokyo Kasei Industrial Co. $\text{Pd}(\text{OAc})_2$ was purchased from Wako Chem. 2-Holotropone were prepared according to the literature method of Doering.¹⁹ 6-Chloro-5-azabenz[*b*]azulene (**23**) was prepared from **1** according to the literature method of Nozoe.⁴ Emission quantum yields were determined by comparison of a total emission area with that of anthracene ($\Phi = 0.27$, 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), $\text{Pd}_2(\text{dba})_3$ (55 mg, 0.060 mM), BINAP (75 mg, 0.12 mM), and Cs_2CO_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. ^1H 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_{\max} = 3427brm, 3236m, 1547vs cm⁻¹; UV-vis (EtOH) λ_{\max} = 236 (log ϵ = 4.25), 341 (3.99), 400 (4.10) 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 μ L, 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^{3a}]. 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-9), 8.25 (d, J = 10.0 Hz, H-7), 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; ¹H NMR (NaOD/D₂O/DMSO-*d*₆) δ = 6.95 (t, J = 9.4 Hz, H-9), 7.18 (d, J = 11.9 Hz, H-7), 7.27 (t, J = 8.2 Hz, H-2), 7.46 (t, J = 8.2 Hz, H-3), 7.52 (dd, J = 11.9, 9.4 Hz, H-8), 7.83 (d, J = 8.2 Hz, H-4), 8.21 (d, J = 8.2 Hz, H-1), 8.43 (d, J = 9.4 Hz, H-10) ppm; ¹³C NMR (NaOD/D₂O/DMSO-*d*₆) δ = 119.4, 120.7, 121.3, 121.9, 127.4, 128.5, 129.6, 130.6, 132.4, 137.8, 152.3, 155.8, 182.2 ppm;

6-(1*H*-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 μ M), BINAP (6 mg, 14 μ M), 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 (ddd, 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) ν_{\max} = 1454s, 1382s, 1334s, 1203s, 1041s, 654s, 755s, 730s cm^{-1} ; UV-vis (EtOH) λ_{\max} = 271 ($\log \epsilon = 4.29$), 311 (4.48), 350 (4.12), 383 (3.92), 510 (3.04) nm; MS (70 eV) m/z (rel int) = 246 ($M^+ + 1$, 21), 245 (M^+ , 100), 244 (27), 218 (83), 217 (30), 192 (22), 190 (15), 177 (14), 151 (12). HRMS m/z Calcd for $C_{16}H_{11}N_3$ (M^+) 245.0953, found: 245.0915. *Anal.* Calcd for $C_{16}H_{11}N_3$: C, 78.35; H, 4.52; N, 17.13%. Found: C, 78.26; H, 4.79; N, 16.97%.

6-(1*H*-1,2,3-Triazol-1-yl)-5-azabenz[*b*]azulene (**14**)

A mixture of **23** (45 mg, 0.21 mM), 1,2,3-triazole (29 mg, 0.42 mM), $\text{Pd}_2(\text{dba})_3$ (19 mg, 0.021 mM), BINAP (26 mg, 0.042 mM), and Cs_2CO_3 (137 mg, 0.420 mM) in 5 mL of toluene was heated at 90 °C on an oil bath for 20 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/ CH_2Cl_2 (40/60) to give 37 mg (72% yield) of **14** as violet needles. Mp 189–191 °C. ^1H NMR (CDCl_3) δ = 7.60 (td, $J = 8.0, 0.8$ Hz, H-2), 7.86 (m, H-3,9), 7.98 (d, $J = 1.2$ Hz, triazolyl-H), 7.99 (td, $J = 10.2, 1.0$ Hz, H-8), 8.13 (dt, $J = 8.0, 0.8$ Hz, H-4), 8.43 (dt, $J = 8.0, 0.9$ Hz, H-1), 8.79 (d, $J = 10.2$ Hz, H-7), 8.94 (dd, $J = 8.6, 1.0$ Hz, H-10), 9.51 (d, $J = 1.2$ Hz, triazolyl-H), ppm; ^{13}C NMR (CDCl_3) δ = 120.8(C-4), 121.2 (C-1), 123.1 (C-2), 127.4 (C-7), 128.1 (C-9), 129.0 (C-10b), 130.0 (C-3), 130.8 (C-10), 132.2 (C-8), 134.4 (triazole C-4), 134.9 (triazole C-5), 139.3 (C-6), 145.1 (C-10a), 151.7 (C-5a), 156.9 (C-4a) ppm; IR (KBr) ν_{\max} = 3348m, 3168m, 3109s, 3047m, 1616w, 1604m, 1517w, 1475w, 1458s, 1437w, 1394s, 1357m, 1330m, 1321w, 1236s, 1070s, 1016s, 789m, 758s, 727s cm^{-1} ; UV-vis (EtOH) λ_{\max} = 245 ($\log \epsilon = 4.18$), 258sh (4.17), 274 (4.12), 300sh (4.38), 317 (4.48), 368 (3.55), 385 (3.70), 401sh (3.39), 514 (2.78) nm; MS (70 eV) m/z (rel int) = 246 (M^+ , 3), 218 (100), 217 (27), 190 (18), 177 (12), 167 (9), 151 (9), 150 (6), 108 (8), 106 (7), 77 (7), 57 (8). HRMS m/z Calcd for $C_{16}H_{11}N_4$ (M^+) 246.0911, found: 246.0904.

Determination 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 $\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$ 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 Hammett acidity function (H_0)-dependent absorption spectra. The absorption peak at 402 nm was used and solutions used are as follows; H_3PO_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**.

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