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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

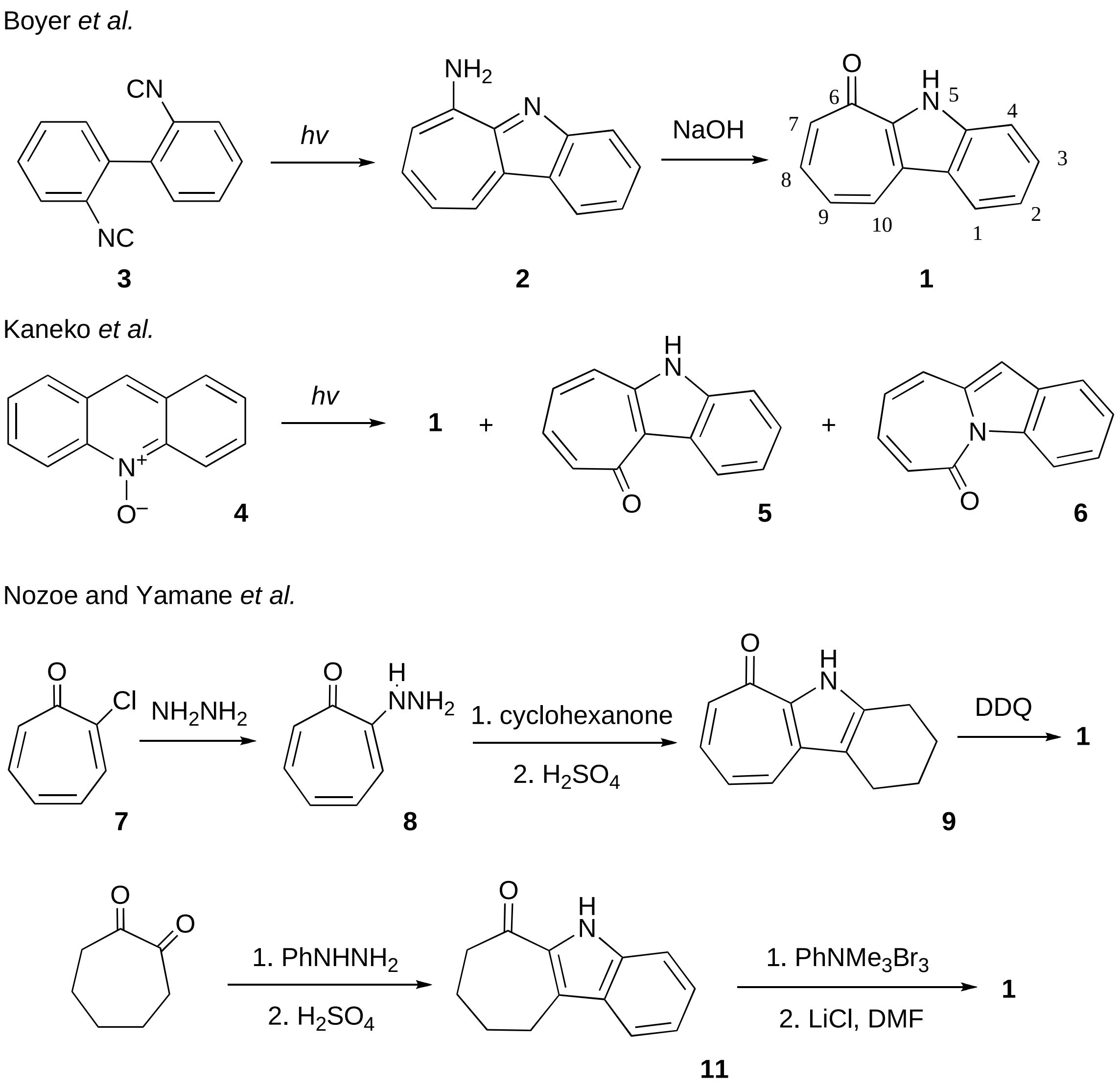
Department of Chemistry, Faculty of Science, Shinshu University, Asahi 3-1-1, Matsumoto, Nagano, 390-8621 Japan, e-mail: mituoda@shinshu-u.ac.jp

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-(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,



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 acidity, basicity and

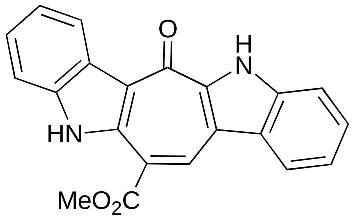


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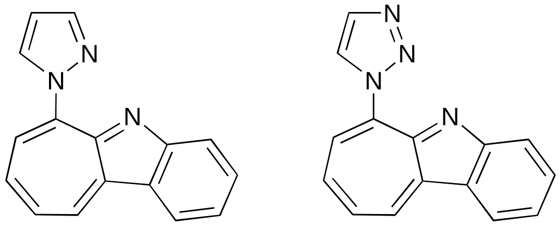
Chart 1. Structure of caulersin (**12**).



13 14

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

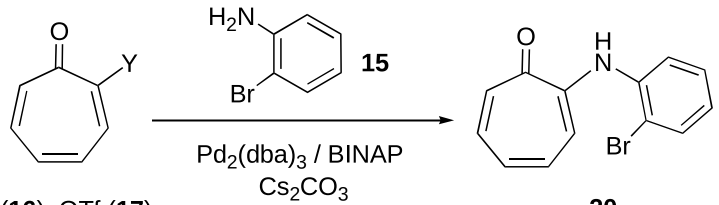
interaction with metal ions. Also, transformation of **1** into azole-substituted 5-azabenz[*b*]azulenes, **13** and **14**, as a potential ligand is described.

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-anilinotropones could be obtained by nucleophilic substitution reaction of various tropone 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-tosyloxytropone (**16**) gave the ring-contraction compound as a major product.[11] They deviced 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**



Y= OTs (**16**), OTf (**17**),
I (**18**), Br (**19**), Cl (**7**)

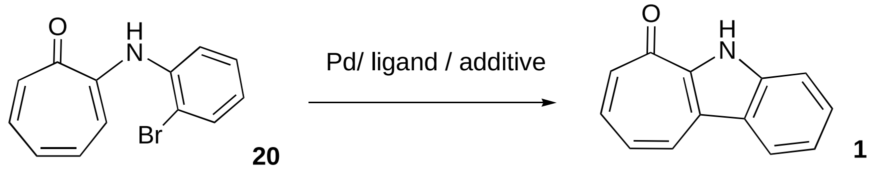
20

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 Cs_2CO_3 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 obatained 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-halorotropones 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.

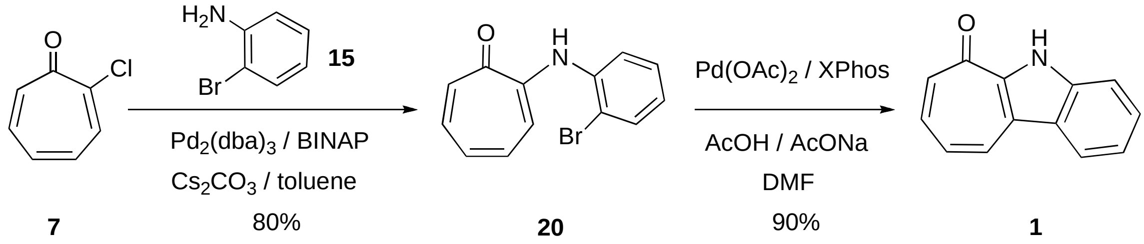
Table 2. Palladium-catalyzed intramolecular Heck reaction of **20**



entry	Pd / ligand / additive	solvent / temp / time	yield of **1** (%) [a]
1	3 mol% $Pd_2(dba)_3$ / 6 mol% $P(t\text{-}Bu)_3$ / 1.0 eq DABCO	CH_3CN / reflux / 18 h	trace
2	5 mol% $Pd(OAc)_2$ / 20 mol% $P(o\text{-}tol)_3$ / 1.3 eq Et_3N	dioxane / reflux / 27 h	0
3	10 mol% $Pd(OAc)_2$ / 40 mol% $P(o\text{-}tol)_3$ / 1.3 eq Et_3N	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 $(Bu)_4N^+Br^-$	DMF / reflux / 9 h	22
6	10 mol% $Pd(OAc)_2$ / 10 mol% $P(o\text{-}tol)_3$ / 1.3 eq K_2CO_3	DMF / reflux / 23 h	57
7	10 mol% $Pd(OAc)_2$ / 40 mol% $P(o\text{-}tol)_3$ / 1.3 eq K_2CO_3	DMF / reflux / 23 h	54
8	10 mol% $Pd(OAc)_2$ / 20 mol% $P(o\text{-}tol)_3$ / 1.0 eq AcOH / 2.0 eq AcONa	DMF / reflux / 8 h	79
9	10 mol% $Pd(OAc)_2$ / 20 mol% $P(o\text{-}tol)_3$ / 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-anilinotropone.

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 $Pd(OAc)_2/P(o\text{-}tol)_3/K_2CO_3$/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[13] (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 procedurers, 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 ^{13}C NMR signals are assigned with the aid of HMQC and HMBC spectra (Figure 1). Behavior of **1** in both acidic (CF_3CO_2D) and basic ($NaOD/D_2O/DMSO$-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_3CO_2D shows a down-filed shift compared with

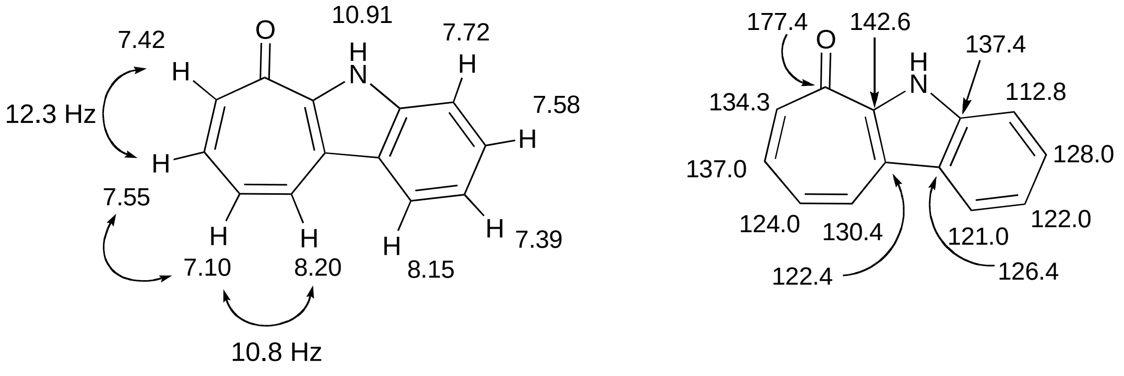
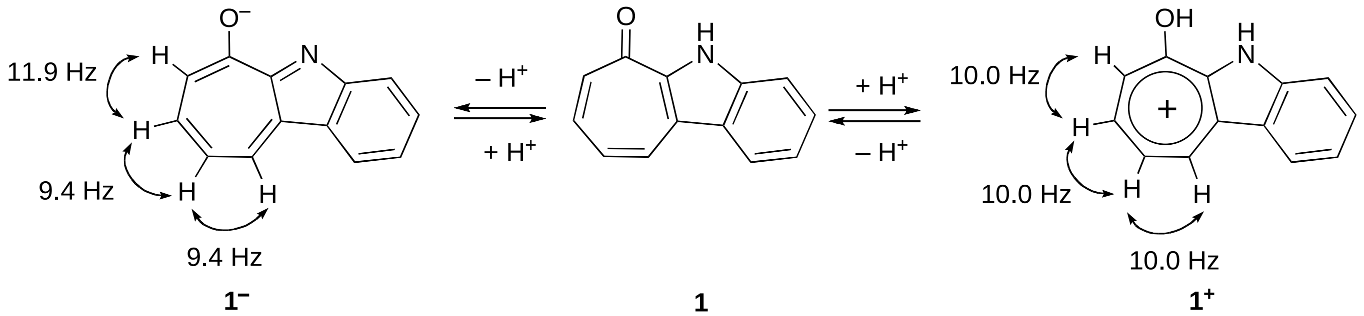


Figure 1. Assigned ^{1}H (left) and ^{13}C (right) NMR signals (™ppm) and selected coupling constants of **1**.



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

that (7.61 ppm) in $CDCl_3$, supporting generation of the protonated species **1**$^+$. It is worth noting that $^3J_{H\text{–}H}$ 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/D_2O/DMSO-d_6 (7.64 ppm) shows a very small up-field shift. However, more convergent $^3J_{H\text{–}H}$ coupling constants compared with those observed in $CDCl_3$ 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.

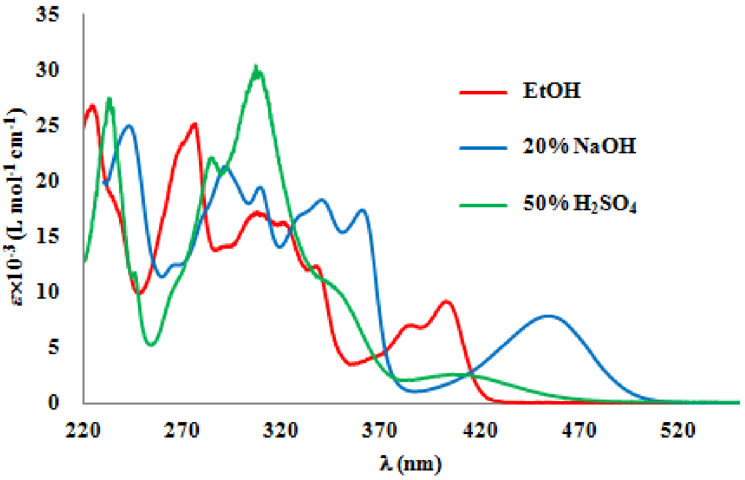


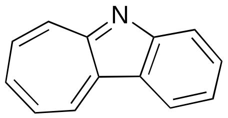
Figure 2. Absorption spectra of **1** in neutral, acidic, and basic media.

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 pK_a and pK_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] tropone[16] and

Table 3. Acidity and basicity of **1** and related compounds

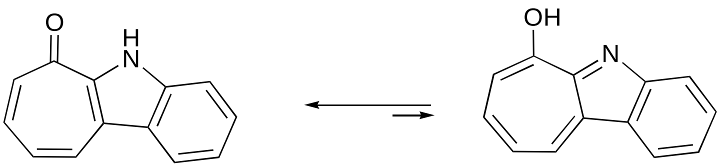
compound	pK_a	pK_b
1	13.6	12.9
indole[a)]	20.95	—
pyrrole[a)]	23.05	—
2-aminotropone[b)]	—	11.79
tropone[c)]	—	15.02
21 [d)]	—	7.3

[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**.



21

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



1

22

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 monovalant 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]

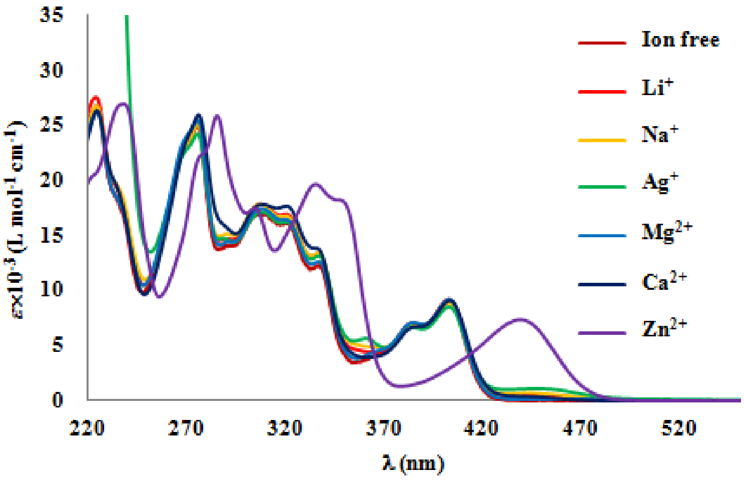
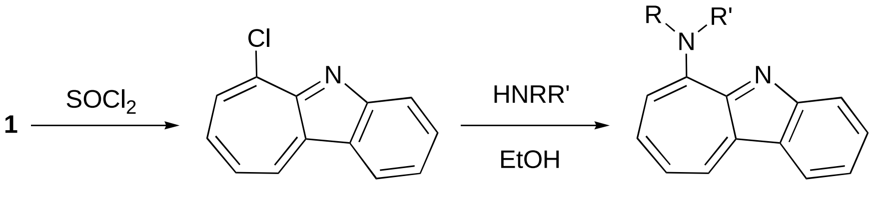


Figure 3. Absorption spectra of **1** in the presence of various metal ions.

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



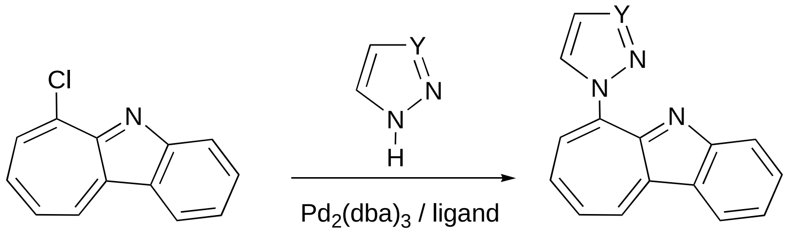
23

24

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 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 $Pd_2(dba)_3$/BINAP/Cs_2CO_3 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**.[18] This emission behavior is resemble to that seen in azulenes. A pK_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 pK_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

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



23

13 (Y=CH), **14** (Y=N)

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 Cs_2CO_3 were used in all reactions,
[c] Isolated yield after chromatography.

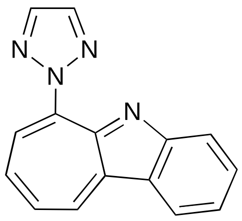


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Chart 3. Structure of **24**.

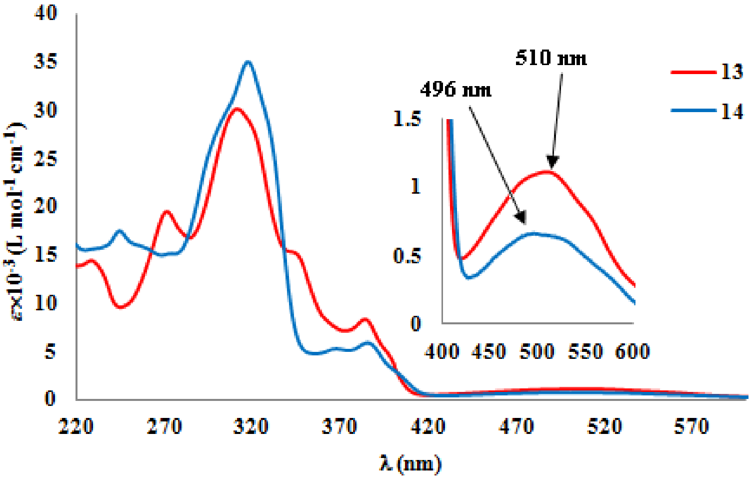

Figure 4. Absorption spectra of **13** and **14** in EtOH.

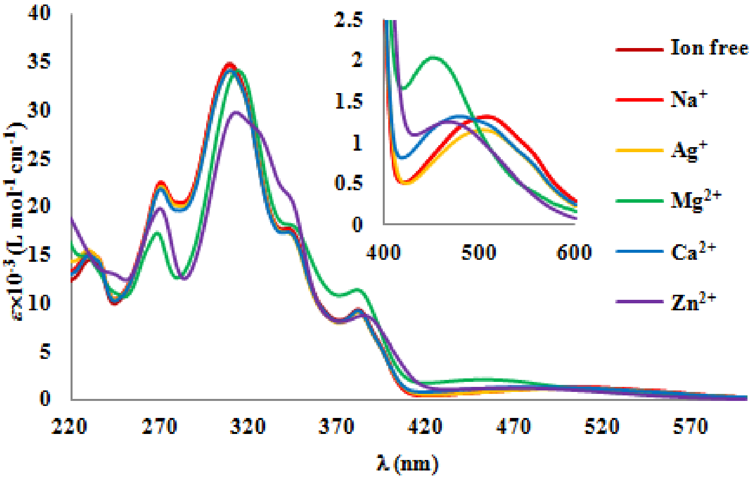

Figure 5. Absorption spectra of **13** in the presence of various metal ions.

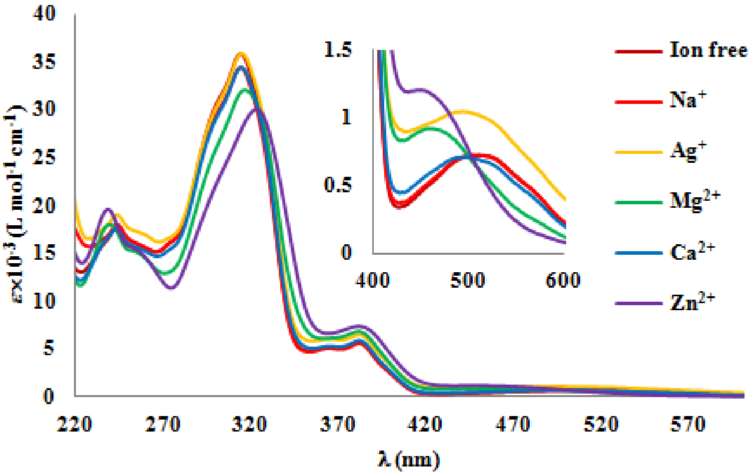

Figure 6. Absorption spectra of **14** in the presence of various metal ions.

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-chrorotropone (**7**) by Pd-catalyzed amination with 2-bromoamniline (**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 λ400 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_2CO_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.[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), $Pd_2(dba)_3$ (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. ^{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 ($CDCl_3$) 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 $C_{13}H_{10}BrNO$: 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 CH_2Cl_2. 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 ($CDCl_3$) 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 (CF_3CO_2D) 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; ^{13}C NMR (CF_3CO_2D) 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/D_2O/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; ^{13}C NMR (NaOD/D_2O/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), $Pd_2(dba)_3$ (9 mg, 7 μM), BINAP (6 mg, 14 μM), and Cs_2CO_3 (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/$CHCl_3$ (30/70) to give 40 mg (77% yield) of **13** as violet needles. Mp 135–136 ˚C. ^1H NMR ($CDCl_3$) 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; ^{13}C NMR ($CDCl_3$) 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 (logε = 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), $Pd_2(dba)_3$ (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. ^{1}H 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 (logε = 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 KH_2PO_4/Na_2HPO_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_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.

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18. Emission quauntum 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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