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SYNTHESES OF 2-FORMYL-, 2,3-DIFORMYL- AND 8-FORMYL-1-AZAAZULENES †

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Abstract – 2-Styryl-1-azaazulenes were synthesized by two ways: a) Suzuki coupling of 2-bromo-1-azaazulenes with *trans*-2-phenylvinylboronic acid b) Condensation of 2-methyl-1-azaazulene, being synthesized by Negishi coupling of 2-bromo-1-azaazulene with dimethylzinc, with benzaldehyde. Oxidative cleavage of 2-styryl-1-azaazulenes with OsO_4-KIO_4 gave 2-formyl-1-azaazulenes. 8-Formyl-1-azaazulenes were synthesized by the reaction of 1-azaazulenes with 2-lithio-1,3-dithiane followed by the hydrolysis.

INTRODUCTION

Formylazulenes are known as useful key products for synthesizing various azulene derivatives and fused non-alternant aromatics. Formyl-1-azaazulenes are also considered that they have potential versatile utilities for synthesizing numerous 1-azaazulenes and azaazulene-fused heterocycles, but only 3-formyl-1-azaazulene derivatives were known. Although researches for introduction of formyl group on azulene ring were devoted in azulene chemistry,[1-5] Vilsmeier-Haack reaction was only method for introducing of formyl group at C-3 position of 1-azaazulene ring[6] in azaazulene chemistry. In the line of

† Dedicated to late Professor Dr. Ivar Ugi.

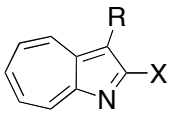
our investigation of azaazulene chemistry,[7-9] it is important to exploit the synthetic method of formyl-1-azaazulenes. It is known that formation of formylazulenes were achieved by oxidation of methylazulene[10-12] and by oxidative cleavage of styrylazulene.[1] In spite of the synthetic utility, synthetic studies of methyl-1-azaazulenes[6,13,14] and styryl-1-azaazulenes[15] were few. We recently reported that Suzuki coupling for introducing aryl groups onto 1-azaazulene ring[16] and Sonogashira-Hagihara coupling for ethynyl groups onto 1-azaazulene ring[17,18] were achieved successfully. Therefore, it is expected that Negishi coupling for introducing methyl groups onto 1-azaazulene ring and Suzuki coupling for introducing styryl group onto 1-azaazulene ring would be available methods. In this paper, we wish to report the synthesis of 2-methyl-1-azaazulene by Negishi coupling and successive formation of 2-styryl-1-azaazulene, and the synthesis of 2-styryl-1-azaazulene by Suzuki coupling. Furthermore, the formation of 2-formylazulenes by oxidative cleavage of 2-styrylazulenes is also mentioned.

On the aldehyde synthesis, it is known that the deprotection of 2-substituted 1,3-dithiane is an excellent method.[19-29] We reported that 8-aryl-1-azaazulenes were easily prepared by the reaction of aryl lithium with 1-azaazulenes.[16,30,31] Therefore, it is expected that the reaction of 2-lithio-1,3-dithine[32] with 1-azaazulenes and successive hydrolysis would give 8-formyl-1-azaazulenes. So we examined the reaction.

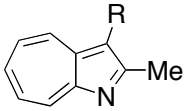
RESULTS AND DISCUSSION

Synthesis of 2-methyl- and 2-styryl-1-azaazulenes

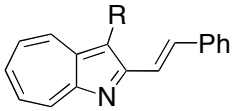
Two synthetic reports of 2-methyl-1-azaazulene (**2a**) were found; where **2a** was obtained as blue or purple syrup but its character was obscure.[14,15] Therefore, we examined the synthesis of 2-methyl-1-azaazulene by Negishi coupling at first. 2-Methyl-1-azaazulene (**2a**) was obtained as yellow solution by the treatment of 2-bromo-1-azaazulene (**1a**) with $ZnMe_2$ in the presence of $PdCl_2$(dppf), but when the solvent was evaporated, **2a** was turned to blue substance. Therefore, **2a** was obtained in 88% yield as picrate, which can be stored at rt. 2-Methyl-1-azaazulene (**2a**) can be liberated from the picrate of **2a** by passing through alumina column. Similar treatment of **1b** and **1c** with $ZnMe_2$ in the presence of $PdCl_2$(dppf) gave picrates of **2b** and **2c** in 63% and 67% yields, respectively.



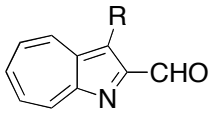
1a : X = Br, R = H
1b : X = Br, R = Br
1c : X = Br, R = Me
1d : X = Br, R = CHO



2a : R = H
2b : R = Br
2c : R = Me



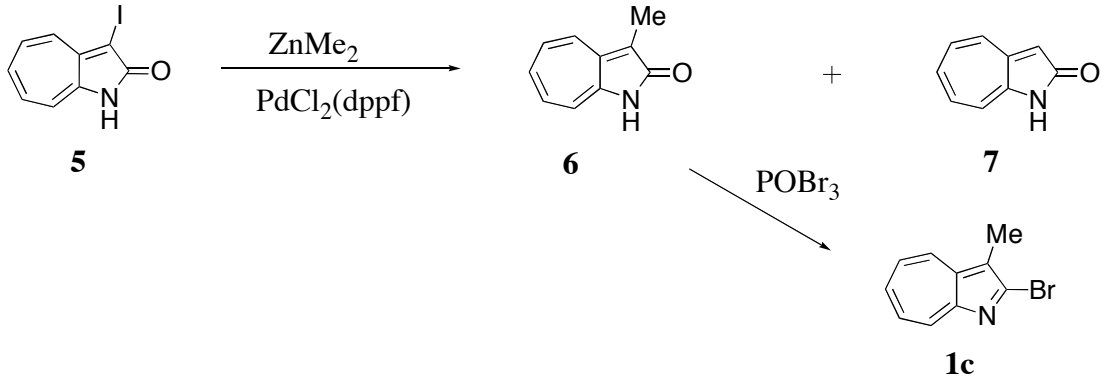
3a : R = H
3b : R = Br
3c : R = Me
3d : R = CHO



4a : R = H
4b : R = Br
4c : R = Me
4d : R = CHO

Bromination of **1a** with NBS in the presence of benzoyl peroxide gave **1c**, which was consistent with the Negishi coupling product of **1b**, and methyl group was not brominated. The results show that C-2 position of 1-azaazulene ring is more reactive than C-3 on the Negishi coupling, and the result is same that C-2 position is reactive than C-3 on the Suzuki coupling[16] and the Sonogashira coupling[18].

Compound **1c** could be easily prepared from **6** with $POBr_3$, but the reported synthesis of **6** was rather troublesome.[6] Therefore we examined the synthesis of **6** by another route. We previously showed that 3-iodo-1-azaazulene is reactive on the Suzuki coupling.[16] So, it is considered that 3-iodo-1-azaazulen-2(1*H*)-one (**5**) would be reactive to Negishi coupling. Indeed, **5** underwent the reaction with $ZnMe_2$ in the presence of $PdCl_2$(dppf) and **6** was obtained in 75% yield together with **7** (9%). Treatment of **6** with $POBr_3$ at 110 ℃ for 1 h gave **1c** in 97% yield.



5 **6** **7** **1c**

Next, we examined the synthesis of 2-styryl-1-azaazulenes by the condensation reaction of 2-methyl-1-azaazulene with benzaldehyde. Treatment 2-methyl-1-azaazulene (**2a**), liberated from its picrate, with benzaldehyde in the presence of *t*-BuOK and 18-crown-6 gave 2-styryl-1-azaazulene (**3a**) in 64% yield. Although **3a** was obtained, this method is unsatisfied because of instability of 2-methyl-1-azaazulenes.

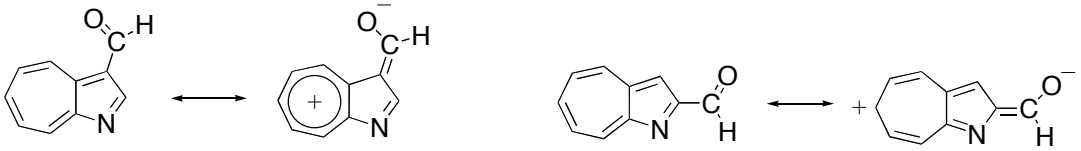
We next examined the synthesis of 2-styryl-1-azaazulenes by the Suzuki coupling of 2-bromo-1-azaazulenes. Thus, treatment of **1a** with *trans*-2-phenylvinylboronic acid in the presence of $PdCl_2(PPh_3)_2$ and K_2CO_3 in toluene at 110 ℃ for 5 h gave **3a** in 71% yield. Similar treatment of **1b**, **1c**, and **1d** with *trans*-2-phenylvinylboronic acid gave **3b** (88%), **3c** (64% along with 31% of **1c**), and **3d** (95%), respectively.

Synthesis of 2-formyl-1-azaazulenes

The Lemieux-Johnson oxidation[33] would be effective for oxidative cleavage of the ethylenic linkage of 2-styryl-1-azaazulenes as well as 2-styrylazulenes.[1] Thus, the reaction of 2-styryl-1-azaazulenes (**3a**-**d**) with KIO_4 in aq. dioxane in the presence of OsO_4 underwent oxidative cleavage and gave the corresponding 2-formyl-1-azaazulenes (**4a**-**c**) in 28-46% yields along with some recovered **3a**-**c**.

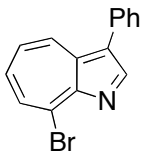
The 2-formyl-1-azaazulenes (**4a**-**c**) were slightly unstable and changed into brown substance on heating or stand for long time at rt. These structures were deduced by there spectroscopic data. Synthesis of 2,3-diformyl-1-azaazulene (**4c**) by the Vilsmeier-Haack reaction of **4a** is undesirable for the instability of **4a**. Therefore it is thought that the Lemieux-Johnson oxidation of **3d** would be preferred. Indeed, treatment of 3-formyl-2-styryl-1-azaazulene (**3d**) with KIO_4 in aq. dioxane in the presence of OsO_4 gave 2,3-diformyl-1-azaazulene (**4d**) as stable crystals in 84% yield.

The IR spectra of 2-formyl-1-azaazulenes (**4a**-**c**) show absorption owing to carbonyl groups around 1690 cm^{-1}. In the IR spectrum of **4d**, two carbonyl signals at 1690 and 1653 cm^{-1} were appeared. They are assigned as the former is formyl group at C-2 and the latter is that at C-3. In the ^1H NMR spectra of **4a**-**c**, singlet signals due to the formyl group are appeared at δ 10.54-10.66, together with signals due to the seven-membered ring protons. In the ^1H NMR spectra of **4d**, two formyl proton singlets are observed at δ 10.65 and 10.97; the former is assigned to the formyl proton at C-2 and the latter is that at C-3. These results would be thought that the conjugation of the formyl group at C-3 with 1-azaazulene ring is favored and the polarization of the formyl group is larger than 2-formyl group, because the resonance form of the formyl group at C-2 with 1-azaazulene is a quinoido form.



Synthesis of 8-formyl-1-azaazulenes

As similar for 2-formyl-1-azaazulenes, synthesis of 8-formyl-1-azaazulenes was examined. The Suzuki coupling of 8-bromo-3-phenyl-1-azaazulene (**8**) with *trans*-2-phenylvinylboronic acid in the presence of $PdCl_2(PPh_3)_2$ and K_2CO_3 in toluene at 40 ℃ for 8 h gave **9** in 66% yield. The Lemieux-Johnson oxidation of **9** gave only trace amounts of **10**. In the ^1H NMR spectrum of **10**, a singlet due to the formyl group is appeared at δ 11.90.



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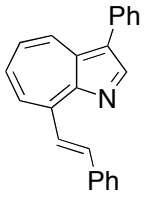

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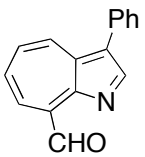

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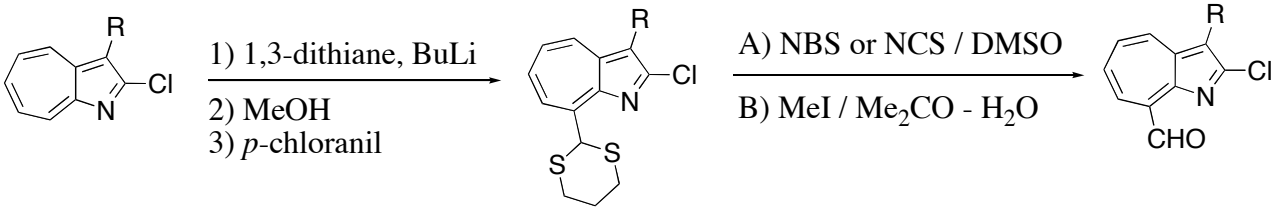
Because the Lemieux-Johnson oxidation of 8-formyl-1-azaazulene did not give satisfactory result, we

explored for another method. It is thought that introduction of 1,3-dithian-2-yl group, being a synthetic equivalent of formyl group, would be an excellent method.[19-28] Therefore, the reaction of 2-lithio-1,3-dithine with 1-azaazulenes and successive hydrolysis was examined.

Reaction of **11a** with 2-lithio-1,3-dithiane and successive treatment of MeOH followed by dehydrogenation with *p*-chloranil gave **12a** in 86% yield. In the similar manner, reactions of **11b** and **11c** gave **12b** and **12c** in 98 and 68% yields, respectively. In the ^{1}H NMR spectra of **12a**-**c**, H-7 protons resonated at low field (δ 8.41-8.42). The phenomena would be attributed to the anisotropy of the sulfur atom in 1,3-dithianyl group at C-8.

As it is anticipated the instability of **13**, mild hydrolytic conditions were desired. Therefore, the hydrolysis of dithioacetal using chloramine-T[27-29] was examined at first. Treatment of **12a** with chloramine-T in aq. MeOH-EtOH for 1 h at rt gave 2-chloro-8-formyl-1-azaazulene (**13a**) in 12% yield. Compound **13a** was unstable under heating and changed to brown powders upon storage at rt. The IR spectrum **13a** shows absorption owing to carbonyl group at 1695 cm^{-1}. In its ^{1}H NMR spectrum, 1H-singlet due to the formyl group is appeared at δ 11.65, together with signals due to the seven-membered ring proton signals. In the reaction **13a** was obtained but yield was low. Therefore, we examined the another methods.

It is known that the hydrolysis of 1,3-dithiane using NBS in the presence of moist DMSO is useful method for preparation of aldehyde.[22,23] Thus treatment of **12a** with an equivalent of NBS in the presence of DMSO in chloroform at rt for 16 h gave **13b** in 36% yield. Same product (**13b**) was obtained by the reaction of **12b** with 0.2 equivalent of NBS in the presence of DMSO in chloroform at rt for 26 h in 58% yield. When **12a** was treated with 0.2 equivalent of NBS, compound (**12b**) was obtained in 19% yield together with **12a** (72%), and **13a** was not obtained at all. Therefore, the bromination at C-3 of **12a** underwent preferentially. We next examined the reaction of **12a** with NCS in the presence of DMSO in chloroform at rt for 15 h, and obtained **13a** in 25% yield. Treatment of **12c** with NBS gave **13c** in 50% yield.



11a : R = H
11b : R = Br
11c : R = CO_2Et

12a : R = H
12b : R = Br
12c : R = CO_2Et

13a : R = H
13b : R = Br
13c : R = CO_2Et

Recently, as the mild conditions, hydrolysis of 2-substituted 1,3-dithianes using CH_3I was reported.[24-26]

We next examined the reaction of **12a** with CH_3I at 30 ℃ for 21 h and obtained **13a** in 8% yield along with **12a** (10%). Similar reaction of **12b** and **12c** with CH_3I at 30 ℃ for 48 h gave **13b** (50% yield along with 47% of **12b**) and **13c** (68% yield along with 25% of **12c**), respectively.

CONCLUSION

Syntheses of 2-formyl-1-azaazulenes and 8-formyl-1-azaazulenes were achieved. 2-Formyl-1-azaazulenes were synthesized by the oxidative cleavage of 2-styryl-1-azaazulenes with OsO_4-KIO_4. 2-Styryl-1-azaazulenes were synthesized by two ways: a) Suzuki coupling of 2-bromo-1-azaazulenes with *trans*-2-phenylvinylboronic acid b) Condensation of 2-methyl-1-azaazulene, being synthesized by Negishi coupling of 2-bromo-1-azaazulene with dimethylzinc, with benzaldehyde. 8-Formyl-1-azaazulenes were synthesized by the reaction of 1-azaazulenes with 2-lithio-1,3-dithiane followed by the hydrolysis using chloramine-T, NBS (or NCS), or MeI.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ^{1}H NMR spectra (including HH-COSY and CH-COSY NMR) were recorded on a Bruker AVANCE 400S (400 MHz) and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400S (100.6 MHz) using deuteriochloroform as a solvent with tetramethylsilane as an internal standard unless otherwise stated; *J* values are recorded in Hz. IR spectra were recorded for KBr pellets on a Nicolet FT-IR AVTAR 370DTGS unless otherwise stated. Electronic spectra were recorded with JASCO V-570 spectrophotometer using chloroform as a solvent. MS spectra were taken with on an LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kieselgel 60 and activated alumina C300 were used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Synthesis of 2-methyl-1-azaazulenes

Under argon atmosphere, a mixture of 2-bromo-1-azaazulene (**1a**) (0.047 g, 0.23 mmol), $PdCl_2$(dppf) (0.006 g, 0.01 mmol), and 1 M $ZnMe_2$ in heptane (0.40 mL, 0.40 mmol) in THF (10 mL) was heated for 1 h at 80 ℃ in a sealed tube. To the mixture water was added, and the mixture was extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed with EtOAc-EtOH (10 : 1) to give a yellow solution of 2-methyl-1-azaazulene (**2a**). The solution was

concentrated in vacuo at rt. Addition of saturated EtOH solution of picric acid (1.0 mL) to the concentrated solution.of **2a** gave a picrate of **2a** (0.085 g, 88%). 2-Methyl-1-azaazulene (**2a**) was liberated from the picrate of **2a** by passing over alumina column. Compound (**2a**) was rather unstable and changed to unidentified blue substance on heating.

Picrate of **2a**: Yellow needles (from EtOH), mp 198-199 ℃ (lit.,[14] green crystals, mp 196-198 ℃); δ_H(DMSO-d_6) 2.82 (3H, s, CH_3), 7.60 (1H, s, H-3), 8.40 (1H, dd, *J* 10.0 and 9.6, H-5), 8.44 (1H, dd, *J* 10.0 and 9.6, H-7), 8.56 (2H, s, H-phenyl), 8.59 (1H, t, *J* 10.0, H-6), 8.94 (1H, d, *J* 9.6, H-8), and 9.15 (1H, d, *J* 9.6, H-4). *Anal.* Calcd for $C_{16}H_{12}N_4O_7$: C, 51.62; H, 3.25; N, 15.05. Found: C, 51.74; H, 3.28; N, 15.11.

In a similar manner, picrate of **2b** and picrate of **2c** were obtained in 63% and 67% yield, respectively.

Picrate of **2b**: Yellow needles (from EtOH), mp 189-190 ℃ (decomp); δ_H(DMSO-d_6) 2.81 (3H, s, CH_3), 8.52 (2H, dd, *J* 10.0 and 9.6, H-5,7), 8.56 (2H, s, H-phenyl), 8.69 (1H, dd, *J* 10.0 and 9.6, H-6), 8.99 (1H, d, *J* 9.6, H-8), and 9.00 (1H, d, *J* 10.0, H-4). *Anal.* Calcd for $C_{16}H_{11}N_4O_7Br$: C, 42.52; H, 2.46; N, 12.42. Found: C, 42.41; H, 2.55; N, 12.23.

Picrate of **2c**: Yellow needles (from EtOH), mp 210-212 ℃ (decomp); δ_H(DMSO-d_6) 2.51 (3H, s, CH_3), 2.77 (3H, s, CH_3), 8.36 (1H, dd, *J* 10.0 and 9.6, H-5), 8.38 (1H, dd, *J* 10.0 and 9.6, H-7), 8.55 (2H, s, H-phenyl), 8.56 (1H, dd, *J* 10.0 and 9.6, H-6), 8.94 (1H, d, *J* 9.6, H-8), and 9.15 (1H, d, *J* 10.0, H-4). *Anal.* Calcd for $C_{17}H_{14}N_4O_7$: C, 52.85; H, 3.65; N, 14.50. Found: C, 52.67; H, 3.80; N, 14.42.

Synthesis of 3-methyl-1-azaazulen-2(1*H*)-one

Under argon atmosphere, a mixture of 2-iodo-1-azaazulen-2(1*H*)-one (**5**) (1.380 g, 5.09 mmol), $PdCl_2$(dppf) (0.030 g, 0.05 mmol), and 1 M $ZnMe_2$ in heptane (7.50 mL, 7.50 mmol) in 1,4-dioxane (30 mL) was heated for 2 h at 110 ℃ in a sealed tube. To the mixture water was added, and the mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporation of the extract gave yellow crystals (0.713 g) which is a (10 : 1) mixture of 3-methyl-1-azaazulen-2(1*H*)-one (**6**) and 3-1-azaazulen-2(1*H*)-one (**7**) by ^{1}H NMR spectra. Chromatography of the mixture with EtOAc-$CHCl_3$ (1 : 1) gave **6** (0.620 g, 77%) and **7** (0.070 g, 9%).

6: Yellow needles (from AcOEt-CH_2Cl_2), mp 218-220 ℃ (lit.,[6] mp 220 ℃); δ_H 2.17 (3H, s, CH_3), 6.83 (1H, dd, *J* 10.7 and 8.9, H-7), 7.54 (1H, dd, *J* 10.7 and 9.2, H-6), 7.54 (1H, dd, *J* 11.0 and 9.2, H-5), 7.09, (1H, d, *J* 8.9, H-8), 7.40 (1H, d, *J* 11.0, H-4), and 11,93 (1H, s, NH); δ_C 7.8, 112.7, 113.4, 126.9, 128.5, 130.1, 130.9, 140.9, 144.2, and 172.1; ν_{max} / cm^{-1} 1681 (C=O). *Anal.* Calcd for $C_{10}H_9NO$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.41; H, 5.75; N, 8.76.

Synthesis of 2-bromo-3-methyl-1-azaazulene

A mixture of **5** (0.438 g, 2.75 mmol) and $POBr_3$ (1.20 g, 4.18 mmol) was heated at 110 ℃ for 1 h. To the mixture water was added, and the mixture mixture was neutralized with $NaHCO_3$, then extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and the extract was evaporated. Chromatography of the residue with EtOAc-hexane (1 : 5) gave **1c** (0.593 g, 97%).

1c: Yellow needles (from hexane-CH_2Cl_2), mp 104-106 ℃; δ_H 2.53, 7.65 (1H, dd, *J* 10.0 and 9.8, H-5), 7.72 (1H, dd, *J* 10.0 and 9.6, H-7), 7.88 (1H, dd, *J* 10.0 and 9.8, H-6), 8.34 (1H, d, *J* 10.0, H-4), and 8.58 (1H, d, *J* 9.6, H-8); δ_C 10.4, 121.9, 128.6, 129.6, 132.9, 135.0, 137.9, 142.9, 149.5, and 156.0; ν_{max} / cm^{-1} 2844 (CH_3), 731 (C-Br); λ_{max} nm (log ε) 281 (4.67), 295 (4.37, sh), 319 (3.59), 331 (3.67), 346 (3.62), 361 (3.26), 398 (2.59), 420 (2.68), 493 (3.10), 515 (3.05, sh), and 555 (2.68, sh). *Anal*. Calcd for $C_{10}H_8NBr$: C, 54.08; H, 3.63; N, 6.31. Found: C, 54.34; H, 3.55; N, 6.28.

Synthesis of 2-bromo-3-formyl-1-azaazulene

A mixture of 2-formyl-1-azaazulen-2(1*H*)-one (0.104 g, 0.60 mmol) and $POBr_3$ (0.57 g, 1.98 mmol) was heated at 110 ℃ for 1 h. To the mixture water was added, and the mixture was neutralized with $NaHCO_3$, then extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and the extract was evaporated. Chromatography of the residue with $CHCl_3$ gave **1d** (0.123 g, 87%).

1d: Yellow powders (from hexane-CH_2Cl_2), mp 166-167 ℃; δ_H 8.09 (1H, ddd, *J* 10.0, 9.6 and 0.8, H-5), 8.10 (1H, ddt, *J* 10.0, 9.8, and 0.8, H-7), 8.20 (1H, ddt, *J* 10.0, 9.6 and 1.0, H-6), 8.81 (1H, dd, *J* 9.8 and 1.0,, H-8), 9.79 (1H, dd, *J* 10.0 and 1.0, H-4), and 10.33 (1H, s, CHO); δ_C 120.1, 133.4, 135.5, 137.1, 138.5, 141.1, 145.3, 153.1, 159.3, and 187.3; ν_{max} / cm^{-1} 1651 (C=O); λ_{max} nm (log ε) 280 (4.21, sh), 299 (4.58), 330 (3.95), 358 (3.68), 437 (2.96, sh), 448 (2.97), and 481 (2.71, sh). *Anal*. Calcd for $C_{10}H_8NBr$: C, 54.08; H, 3.63; N, 6.31. Found: C, 54.23; H, 3.61; N, 6.28.

Reaction of 2-methyl-1-azaazulene with NBS

A mixture of 2-methyl-1-azaazulene (**2a**), prepared from the picrate of **2a** (0.051 g, 0.14 mmol) by passing through alumina column, NBS (0.037 g, 0.21 mmol) and benzoyl peroxide (0.002 g) in CCl_4 (10.0 mL) was stirred for 10 min at 0 ℃, then stirred for 2 h at rt. The mixture was evaporated and the residue was chromatographed with EtOAc to give a yellow solution of **2b**. The solution was concentrated in vacuo at rt. Addition of saturated picric acid solution in EtOH (1.0 mL) to the concentrated solution of **2b** gave a picrate of **2b** (0.0322 g, 52%).

Synthesis of 2-styryl-1-azaazulene from 2-methyl-1-azaazulene

A mixture of 2-methyl-1-azaazulene (**2a**), prepared from the picrate of **2a** (0.0584 g, 0.15 mmol) by passing through alumina column, *t*-BuOK (0.0462 g, 0.41 mmol), 18-crown-6 (0.0967 g, 0.36 mmol), and benzaldehyde (0.15 mL, 0,15 mmol) in Et_2O (5.0 mL) was stirred for 5 min at rt. To the mixture water was added, and the mixture was extracted with Et_2O. The extract was dried over Na_2SO_4, and evaporated. Chromatography of the residue with EtOAc gave 2-stylyl-1-azaazulene (0.0219 g, 64%).

3a: Red needles (from hexane-CH_2Cl_2), mp 139-140 ℃ (lit.,[13] mp 139-140 ℃); δ_H 7.33 (1H, t, *J* 7.6, H-*p*-phenyl), 7.41 (2H, dd, *J* 7.6 and 7.2, H-*m*-phenyl), 7.49 (1H, s, H-3), 7.54 (1H, d, *J* 16.2 Hz, *trans*-CH=CH), 7.54-7.58 (1H, m, H-5), 7.67 (2H, d, *J* 7.2, H-*o*-phenyl), 7.70-7.74 (2H, m, H-6 and 7), 7.90 (1H, d, *J* 16.2, *trans*-CH=CH), 8.42 (1H, d, *J* 9.6, H-4), and 8.56 (1H, d, *J* 10.4, H-8); δ_C 112.8, 123.5, 127.4, 128.7, 128.8, 128.9, 130.0, 134.1, 134.5, 136.2, 136.4, 136.8, 147.7, 159.0, and 166.1; ν_{max} / cm^{-1} 971 (*trans*-CH=CH). *Anal*. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.67; N, 6.06. Found: C, 88.30; H, 5.72; N, 5.98.

Synthesis of 2-styryl-1-azaazulenes from 2-bromo-1-azaazulenes with *trans*-2-phenylvinylboronic acid

Under argon atmosphere, a mixture of 2-bromo-1-azaazulene (**1b**) (0.108 g, 0.52 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.02 mmol), *trans*-2-phenylvinylboronic acid (0.112 g, 0.75 mmol), K_2CO_3 (0.139 g, 1.10 mmol) in toluene (10 mL) was heated for 5 h at 110 ℃ in a sealed tube. To the mixture water was added, and the mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. Chromatography of the residue with $CHCl_3$ gave 2-strlyl-1-azaazulene (**3a**) (0.085 g, 71%).

In a similar manner, we obtained **3b** (88%), **3c** (64% along with 31% of **1c**), and **3d** (95%).

3b: Red needles (from hexane-CH_2Cl_2), mp 140-141 ℃; δ_H 7.36 (1H, t, *J* 7.2, H-*p*-phenyl), 7.43 (2H, dd, *J* 7.4 and 7.2, H-*m*-phenyl), 7.60 (1H, d, *J* 16.0, *trans*-CH=CH), 7.69 (1H, t, *J* 10.0, H-5), 7.73 (2H, d, *J* 7.4, H-*o*-phenyl), 7.70-7.80 (2H, m, H-6 and 7), 8.20 (1H, d, *J* 16.0, *trans*-CH=CH); 8.40 (1H, d, *J* 10.0, H-4), and 8.55 (1H, d, *J* 9.2, H-8); δ_C 102.9, 120.0, 127.8, 128.9, 129.2, 129.4, 130.5, 133.4, 135.3, 136.6, 137.3, 137.8, 143.9, 157.6, and 161.6; ν_{max} / cm^{-1} 961 (*trans*-CH=CH); λ_{max} nm (log ε) 258 (4.13), 273 (4.15), 301 (4.40), 308 (4.43, sh), 338 (4.33, sh), 347 (4.50), 382 (4.23, sh), 396 (4.33), 418 (4.28), 515 (3.53, sh), 531 (3.56), and 570 (3.29, sh). *Anal*. Calcd for $C_{17}H_{12}NBr$: C, 65.83; H, 3.90; N, 4.52. Found: C, 65.75; H, 3.82; N, 4.73.

3c: Red micro needles, mp 128-129 ℃; δ_H 2.56 (3H, s, CH_3), 7.30 (1H, t, *J* 7.4, H-*p*-phenyl), 7.36 (2H, dd, *J* 7.4 and 7.2, H-*m*-phenyl), 7.44 (1H, dd, *J* 10.4 and 9.6, H-5), 7.51 (1H, d, *J* 16.0, *trans*-CH=CH), 7.68 (2H, d, *J* 7.4, H-*o*-phenyl), 7.65-7.75 (2H, m, H-6 and 7), 8.10 (1H, d, *J* 16.0, *trans*-CH=CH); 8.25

(1H, d, *J* 9.6, H-4), and 8.55 (1H, d, *J* 10.0, H-8); δ_C 9.3, 120.7, 121.3, 127.4, 127.5, 128.6, 128.8, 129.3, 131.9, 134.0, 135.8, 136.0, 137.2, 144.9, 158.2, and 163.1; ν_{max} / cm^{-1} (neat) 975 (*trans*-CH=CH); λ_{max} nm (log ε) 274 (3.91, sh), 300 (4.01), 355 (4.33), 388 (3.92, sh), 475 (3.83, sh), 497 (3.93), and 525 (3.73, sh). *Anal*. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.25; H, 6.22; N, 5.60.

3d: Brownish orange plates (from hexane-AcOEt), mp 134-135 ℃; δ_H 7.39 (1H, dd, *J* 7.8 and 1.4, H-*p*-phenyl), 7.45 (2H, dd, *J* 7.8 and 7.1, H-*m*-phenyl), 7.75 (2H, dd, *J* 7.1 and 1.4 H-*o*-phenyl), 7.90-8.01, (3H, m, H-5, 6, and 7), 7.97 (1H, d, *J* 15.8, *trans*-CH=CH), 8.27 (1H, d, *J* 15.8, *trans*-CH=CH), 8.71 (1H, dm, *J* 10.4, H-8), 9.51 (1H, dd, *J* 10.0 and 2.0, H-4), and 10.71 (1H, s, CHO); δ_C 118.9, 119.7, 127.9, 128.9, 129.5, 133.9, 134.1, 135.8, 136.1, 137.0, 138.8, 139.9, 147.3, 160.9, 168.0, and 185.5; ν_{max} / cm^{-1} 1655 (C=O) and 1638 (*trans*-PhCH=HCAz) and 983 (*trans*-CH=CH); λ_{max} nm (log ε) 283 (4.31, sh), 293 (4.33, sh), 329 (4.49), 391 (4.31, sh), 405 (4.33), 455 (3.85, sh), 472 (3.90), and 522 (2.70, sh). *Anal*. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.32; H, 4.98; N, 5.57.

Synthesis of 2-formyl-1-azaazulenes

General Procedure: To a mixture of 2-styryl-1-azaazulenes and OsO_4 (1-2% by weight) in aq dioxane (dioxane : H_2O = 7 : 3), an aliquot of KIO_4 (2-4 molar equivalents) was added for 30 min at rt under stirring. After stirring for 4 h, the mixture was filtered through a pad of celite. The celite was washed with water and $CHCl_3$. Combined filtrate was extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. Chromatography of the residue with EtOAc gave 2-formyl-1-azaazulenes.

2-Formyl-1-azaazulene (4a). 2-Styryl-1-azaazulene (**3a**) (0.1035 g, 0.447 mmol)) was treated according to the general procedure to give **4a** (0.020g, 28%) as red purple powders (from hexane-CH_2Cl_2), mp 96-101 ℃; δ_H 7.78 (1H, dd, *J* 10.0 and 9.6, H-5), 7.92 (1H, t, *J* 10.0, H-7), 7.92 (1H, s, H-3), 8.10 (1H, t, *J* 10.0, H-6), 8.83 (1H, d, *J* 9.6, H-4), 8.95 (1H, d, *J* 10.0, H-8), and 10.54 (1H, s, CHO); δ_C 114.3, 129.6, 130.4, 141.2, 141.3, 141.5, 147.2, 157.9, 160.6, and 191.0; ν_{max} / cm^{-1} 1690 (C=O); *m/z* 157 (M^+). 2,4-DNP of **4a**: brown powders (from hexane-CH_2Cl_2), mp 244-246 ℃. *Anal*. Calcd for $C_{16}H_{11}N_5O_4$: C, 56.98; H, 3.29; N, 20.76. Found: C, 56.84; H, 2.46; N, 20.99.

3-Bromo-2-formyl-1-azaazulene (4b). 3-Bromo-2-styryl-1-azaazulene (**3b**) (0.0544 g, 0.16 mmol) was treated according to the general procedure for 9 h to give **3b** (0.010 g, 37%) and **4b** (0.0189 g, 46%) as red needles (from hexane-CH_2Cl_2), mp 111-112 ℃; δ_H 7.89 (1H, t, *J* 10.0, H-5), 7.95 (1H, t, *J* 10.0, H-7), 8.16 (1H, t, *J* 10.0, H-6), 8.85 (1H, dd *J* 10.0, H-4), 8.92 (1H, d, *J* 10.0, H-8), and 10.60 (1H, s, CHO); δ_C 103.7, 130.0, 131.0, 140.3, 142.6, 142.9, 144.7, 154.1, 156.7, and 189.0; ν_{max} / cm^{-1} 1693 (C=O); λ_{max} nm (log ε) 290 (4.55), 296 (4.54, sh), 330 (3.84), 346 (3.84), 369 (3.21, sh), 458 (2.74, sh), 518 (2.93, sh), 553, (2.95), and 600 (2.72, sh). *Anal*. Calcd for $C_{10}H_6NOBr$: C, 50.88; H, 2.56; N, 5.93. Found: C,

50.74; H, 2.66; N, 5.83.

2-Formyl-3-methyl-1-azaazulene (4c). 3-Methyl-2-styryl-1-azaazulene (**3c**) (0.0519 g, 0.21 mmol) was treated according to the general procedure to give **3c** (0.176 g, 34%) and **4c** (0.0105 g, 29%) as purple needles (from hexane-CH_2Cl_2), mp 101-106 ℃; δ_H 2.84 (3H, s, CH_3), 7.72 (1H, dd, *J* 10.0 and 9.6, H-5), 7.80 (1H, dd, *J* 10.0 and 9.6, H-7), 8.03 (1H, t, *J* 10.0, H-6), 8.68 (1H, d, *J* 9.6, H-4), 8.83 (1H, d, *J* 9.6, H-8), and 10.66 (1H, s, CHO); δ_C 9.7, 125.4, 128.1, 129.6, 138.7, 140.8, 141.5, 145.8, 156.3, 157.0 and 192.5; ν_{max} / cm^{-1} 1688 (C=O); λ_{max} nm (log ε) 265 (4.12, sh), 280 (4.23), 304 (3.97, sh), 347 (3.96), 363 (3.98), 379 (3.85, sh), 468 (2.95), 526 (2.88, sh), and 586 (2.63, sh).

2,3-Diformyl-1-azaazulene (4d). 3-Formyl-2-styryl-1-azaazulene (**3d**) (0.1549 g, 0.60 mmol) was treated according to the general procedure for 6 h to give **4d** (93.2mg, 84%) as red needles (from hexane-AcOEt), mp 144-145 ℃; δ_H 8.13 (1H, t, *J* 10.0, H-5), 8.15 (1H, t, *J* 10.0, H-7), 8.31 (1H, t, *J* 10 and, H-6), 9.08 (1H, d, *J* 9.6, H-8), 10.0 (1H, d, *J* 10.0, H-4), 10,65 (1H, s, CHO), and 10.97 (1H, s, CHO); δ_C 122.6, 133.6, 134.9, 143.1, 143.7, 143.8, 146.0, 159.2, 161.1, 188.6, and 192.0; ν_{max} / cm^{-1} 1690 and 1653 (C=O); λ_{max} nm (log ε) 278 (4.36, sh), 294 (4.52), 335 (3.98), 351 (3.74, sh), 466 (3.00, sh), 494 (3.90), and 525 (2.90, sh). *Anal*. Calcd for $C_{11}H_7NO_2$: C, 71.35; H, 3.81; N, 7.56. Found: C, 71.42; H, 3.88; N, 7.43.

Synthesis of 3-phenyl-8-styryl-1-azaazulene from 8-bromo-3-phenyl-1-azaazulene with *trans*-2-phenylvinylboronic acid

Under argon atmosphere, a mixture of 8-bromo-3-phenyl-1-azaazulene (**8**) (0.284 g, 1.00 mmol), $PdCl_2(PPh_3)_2$ (0.007 g, 0.02 mmol), *trans*-2-phenylvinylboronic acid (0.222 g, 1.50 mmol), K_2CO_3 (0.189 g, 1.50 mmol) in toluene (10 mL) was heated for 8 h at 40 ℃ in a sealed tube. To the mixture water was added, and the mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. Chromatography of the residue with $CHCl_3$ gave 3-phenyl-8-stylyl-1-azaazulene (**9**) (0.204 g, 66%).

9: Purple oil; δ_H 7.34-7.45 (3H, m, H-*m*,*p*-phenyl)), 7.46 (1H, t, *J* 10.0, H-5), 7.49-7.54 (3H, m, H-*m*,*p*-phenyl), 7.59-7.62 (2H, m, H-*o*-phenyl), 7.60 (1H, d, *J* 16.4, *trans*-CH=CH), 7.77 (2H, d, *J* 7.2,H-*o*-phenyl)), 7.84 (1H, t, *J* 10.0, H-6), 8.18 (1H, d, *J* 10.0, H-7), 8.63 (1H, d, *J* 10.0, H-4), 8.82 (1H, s, H-2), and 8.98 (1H, d, *J* 16.4, *trans*-CH=CH); δ_C 125.9, 127.0, 127.2, 127.8, 127.9, 128.8, 129.0, 129.1, 129.5, 129.7, 134.6, 134.9, 136.2, 136.9, 137.1, 141.4, 144.5, 154.3, and 155.0; ν_{max} / cm^{-1} (neat) 969 (*trans*-CH=CH). *Anal*. Calcd for $C_{23}H_{17}N$: C, 89.87; H, 5.57; N, 4.56. Found: C, 89.77; H, 5.59; N, 4.46.

Reaction of 2-chloro-1-azaazulene with 2-lithio-1,3-dithiane

Under argon atmosphere, 1.5 M butyl lithium (3.40 mL, 5.50 mmol) was added to the solution of 1,3-

dithiane (0.656 g, 5.50 mmol) in dry THF (30 mL) at –80 ℃, then the mixture was stirred for 1 h. To the mixture 2-chloro-1-azaazulene (**11a**) (0.600 g, 3.65 mmol) in dry THF (30 mL) was added at –80 ℃, and temperature was raised to –20 ℃ under stirring for 1.5 h, then MeOH (2 mL) was added. After the mixture was warm to rt, tetrachloro-*p*-benzoquinone (1.300 g, 5.50 mmol) was added to the mixture and the mixture was stirred for 24 h. To the mixture was added water, and the mixture was extracted with $CHCl_3$, then the extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel column with $CHCl_3$ to give 2-chloro-8-(1,3-dithian-2-yl)-1-azaazulene (**12a**) (0.892 g, 86%).

In a similar manner, **12b** and **12c** were obtained in 98% and 68% yield, respectively.

12a: Orange needles (from hexane-CH_2Cl_2), mp 169-170 ℃; δ_H 2,07 (1H, dtt, *J* 14.2, 12.6, and 3.6, *ax*-C<u>H</u>CH$_2$S), 2.30 (1H, dtt, *J* 14.2, 2.4, and 2.4, *eq*-C<u>H</u>CH$_2$S), 2.99 (2H, ddd, *J* 14.4, 3.6, and 2.0, SC<u>H</u>$_2$), 3.36 (2H, ddd, *J* 14.8, 12.6, and 2.4, SC<u>H</u>$_2$), 7.01 (1H, s, SC<u>H</u>S), 7.31 (1H, s, H-3), 7.63, (1H, t, *J* 9.6, H-5), 7.91, (1H, dd, *J* 10.8 and 9.6, H-6), 8.25 (1H, d, *J* 10.8, H-4), and 8.42 (1H, d, *J* 9.6, H-7); δ_C 25.2, 31.9, 48.5, 113.7, 129.8, 131.3, 137.7, 145.6, 147.1, 152.3, and 156.6; *m/z* (rel intensity) 283 (M^+, 12), 281 (M^+, 76), 209 (45), 207 (100), 177 (26), 163 (26), 128 (25), and 106 (33); λ_{max} nm (log ε) 275 (4.52), 294 (4.27, sh), 327 (3.73), 340 (3.67), 448, (3.03, sh), 471 (3.16), and 520 (2.83, sh). *Anal*. Calcd for $C_{13}H_{12}NClS_2$: C, 55.40; H, 4.29; N, 4.97. Found: C, 55.63; H, 4.35; N, 4.84.

12b: Red powders (from hexane-CH_2Cl_2), mp 190 ℃ (decomp); δ_H 2,06 (1H, dtt, *J* 14.8, 3.6, and 2.0, *eq*- C<u>H</u>CH$_2$S), 2.29 (1H, dtt, *J* 14.4, 12.4, and 2.0, *ax*-C<u>H</u>CH$_2$S), 2.97 (2H, ddd, *J* 14.4, 3.6, and 2.4, SC<u>H</u>$_2$), 3.32 (2H, ddd, *J* 14.8, 12.4, and 2.4, SC<u>H</u>$_2$), 7.03 (1H, s, SC<u>H</u>S), 7.72, (1H, dd, *J* 10.4 and 9.6, H-5), 7.96, (1H, t, *J* 9.6, H-6), 8.27 (1H, d, *J* 10.4, H-4), and 8.41 (1H, d, *J* 9.6, H-7); δ_C 25.2, 31.9, 47.9, 101.4, 130.2, 131.9, 134.8, 138.9, 143.1, 146.8, 151.1, and 155.5; λ_{max} nm (log ε) 288 (4.55), 298 (4.50, sh), 335 (3.72), 350 (3.61, sh), 365 (3.42, sh), 495, (3.12), 507 (3.11, sh), and 552 (2.79, sh). *Anal*. Calcd for $C_{13}H_{11}NBrClS_2$: C, 43.29; H, 3.07; N, 3.88. Found: C, 43.33; H, 3.01; N, 3.92.

12c: Yellow powders (from hexane-CH_2Cl_2), mp 171-172 ℃; δ_H 1.48 (3H, t, *J* 7.2, CH_3), 2,04 (1H, dtt, *J* 13.4, 3.6, and 2.0, *eq*-C<u>H</u>CH$_2$S), 2.28 (1H, dtt, *J* 14.4, 12.4, and 2.0, *ax*- C<u>H</u>CH$_2$S), 2.97 (2H, ddd, *J* 14.4, 3.6, and 2.0, SC<u>H</u>$_2$), 3.31 (2H, ddd, *J* 13.4, 12.4, and 2.0, SC<u>H</u>$_2$), 7.05 (1H, s, SC<u>H</u>S), 7.89, (1H, t, *J* 10.0, H-5), 8.05, (1H, dd, *J* 10.8 and 10.0, H-6), 8.41 (1H, d, *J* 10.8, H-7), and 9.58 (1H, d, *J* 10.0, H-4); δ_C 14.4, 25.1, 32.0, 48.5, 60.7, 113.0, 133.1, 134.1, 137.1, 139.5, 147.0, 147.9, 153.4, 158.1, and 163.3; λ_{max} nm (log ε) 288 (4.48, sh), 295 (4.55), 316 (4.16), 335 (3.94, sh), 353 (3.79, sh), 488, (3.14, sh), 497 (3.03), and 520 (3.03, sh). *Anal*. Calcd for $C_{16}H_{16}NO_2ClS_2$: C, 54.34; H, 4.56; N, 3.96. Found: C, 54.44; H, 4.51; N, 4.06.

Synthesis of 2-chloro-8-formyl-1-azaazulenes (13) by hydrolysis of 12

a) Hydrolysis using chloramine-T. To the mixed solution (90 mL) of EtOH : 85% aq CH_3OH (1 : 2) of 2-chloro-8-(1,3-dithian-2-yl)-1-azaazulene (**12a**) was added chloramine-T (0.704 g, 2.50 mmol) in 85% aq CH_3OH (20 mL), and the mixture was stirred for 1 h at rt. To the mixture, 2M NaOH solution (20 mL), and the mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed with $CHCl_3$ gave **13a** (0.034 g, 12%).

b) General method of hydrolysis using NBS. A mixture of **12b** (0.120 g, 0.30 mmol), NBS (0.012 g, 0.07 mmol), and DMSO (0.12 mL, 1.65 mmol) in $CHCl_3$ (15 mL) was stirred for 26 h at rt, then poured into water (30 mL). The mixture was extracted with $CHCl_3$, and the extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed with $CHCl_3$ gave **13b** (0.052 g, 58%).

c) Hydrolysis using NCS. A mixture of **12a** (0.142 g, 0.50 mmol), NCS (0.013 g, 0.10 mmol), and DMSO (0.18 mL, 2.50 mmol) in $CHCl_3$ (15 mL) was stirred for 26 h at rt, then poured into water (30 mL). The mixture was extracted with $CHCl_3$, and the extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed with $CHCl_3$ gave **13a** (0.028 g, 25%).

d) General method using CH_3I. To the solution of **12b** was added MeI (4.8 mL, 76 mmol) in Me_2CO-H_2O (100 : 0.05, 12.6 mL), and the mixture was stirred for 48 h at 30 ℃, then poured into water (30 mL). The mixture was extracted with $CHCl_3$, and the extract was dried over Na_2SO_4, and evaporated. The residue was chlromatographed with $CHCl_3$ gave **13b** (0.135 g, 50%) and **12b** (0.168 g, 47%).

13a: Orange needles (from hexane-CH_2Cl_2), mp 100-105 ℃ (decomp); δ_H 7.35 (1H, s, H-3), 7.82 (1H, dd, *J* 9.8 and 9.7, H-5), 8.04 (1H, dd, *J* 10.0 and 9.7, H-6), 8.34 (1H, d, *J* 9.8, H-4), 8.55 (1H, d, *J* 10.0, H-7), and 11.65 (1H, s, CHO); ν_{max} / cm^{-1} 1695 (C=O).

13b: Orange needles (from hexane-CH_2Cl_2), mp 190-193 ℃ (decomp); δ_H 7.91 (1H, dd, *J* 10.0 and 9.6, H-5), 8.10 (1H, t, *J* 10.0, H-6), 8.36 (1H, d, *J* 9.6, H-4), 8.52 (1H, d, *J* 10.0, H-7), and 11.63 (1H, s, CHO); δ_C 110.0, 127.5, 128.8, 132.3, 134.9, 136.9, 138.7, 145.8, 159.2, and 193.0; ν_{max} / cm^{-1} 1690 (C=O); λ_{max} nm (log ε) 255 (4.12, sh), 290 (4.44, sh), 296 (4.49), 318 (4.17), 343 (3.89, sh), 374 (3.25, sh), 539 (3.18), 546, (3.17, sh), and 605 (2.87, sh). *Anal.* Calcd for $C_{10}H_5NOBrCl$: C, 44.40; H, 1.86; N, 5.18. Found: C, 44.51; H, 2.12; N, 5.06.

13c: Orange needles (from hexane-CH_2Cl_2), mp 105-109 ℃ (decomp); δ_H 1.51, (3H, t, *J* 7.2, CH_3), 4.53 (2H, q, *J* 7.2, OCH_2), 8.11 (1H, dd, *J* 10.4 and 9.6, H-5), 8.21 (1H, dd, *J* 10.0 and 9.6, H-6), 8.51 (1H, d, *J* 10.0, H-7), 9.69 (1H, d, *J* 10.4, H-4), and 11.63 (1H, s, CHO); δ_C 14.4, 61.0, 112.1, 130.3, 135.0, 135.5, 137.6, 139.3, 156.6, 161.0, 163.0, and 193.2; ν_{max} / cm^{-1} 1697 (C=O); λ_{max} nm (log ε) 288 (4.48, sh), 295 (4.55), 316 (4.16), 335 (3.94, sh), 353 (3.79, sh), 488, (3.14, sh), 497 (3.15), and 520 (3.03, sh). *Anal.* Calcd for $C_{13}H_{10}NO_3Cl$: C, 59.22; H, 3.82; N, 5.31. Found: C, 59.28; H, 3.98; N, 5.22.

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