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SYNTHESIS OF [POLY(2-PYRIDYL)-SUBSTITUTED]-1-AZAAZULENES

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Abstract – 2-(2-Pyridyl)-1-azaazulenes were derived from 2-bromo- or 2-iodo-1-azaazulenes and 3-(2-pyridyl)-1-azaazulenes were derived from 3-iodo-1-azaazulenes by Suzuki coupling. Reaction of 3-iodo-1-azaazulenes with B(NPDEA) gave corresponding 3-(2-pyridyl)-1-azaazulenes together with 3-borylated-2-chloor-1-azaazulene (**9a**) or 3,3'-bi(2-methoxy-1-azaazulene) (**10b**). Reactions of 8-(2-pyridyl)-1-azaazulene with 2-pyridyllithium gave 4,8-di(2-pyridyl)- and 6,8-di(2-pyridyl)-1-azaazulenes. Reactions of 4,8-di(2-pyridyl)-1-azaazulene with 2-pyridyllithium gave 4,6,8-tri(2-pyridyl)-1-azaazulene. The reactivity of the seven-menbered ring is C8 > C6 > C4. Reaction of 3-(2-pyridyl)-1-azaazulenes with 2-pyridyllithium gave 3,4-di(2-pyridyl)- and 3,8-di(2-pyridyl)-1-azaazulenes.

INTRODUCTION

In the chemistry of 1-azaazulenes,[1] pyridyl-1-azaazulenes are especially of interest for their physical and chemical properties for comparison with pyridyl-azulenes,[2] but synthetic reports were few. Recently, we reported the synthesis and some properties of 2-(2-pyridyl)-1-azaazulene (**1a**)[3] and 8-(2-pyridyl)-1-azaazulene (**2a,b**),[4,5] which behaved as bidentate ligands. We previously reported that Suzuki coupling of halo-1-azaazulene is suitable for introducing aryl group on five-membered ring of 1-azaazulene,[4] and the addition-dehydrogenation reaction of aryllithium is good method for introducing aryl groups to 8-position of 1-azaazulenes.[4] Therefore, for synthesis of poly(2-pyridyl)-1-azaazulenes, we exploited the combination of Suzuki coupling and the addition-dehydration reaction of 2-pyridyllithium with (2-pyridyl)-1-azaazulenes.

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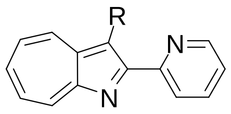
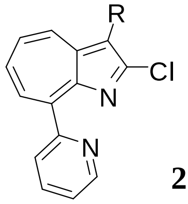
† Dedicated to Professor Emeritus Keiichiro Fukumoto on occasion of his 75th birthday.



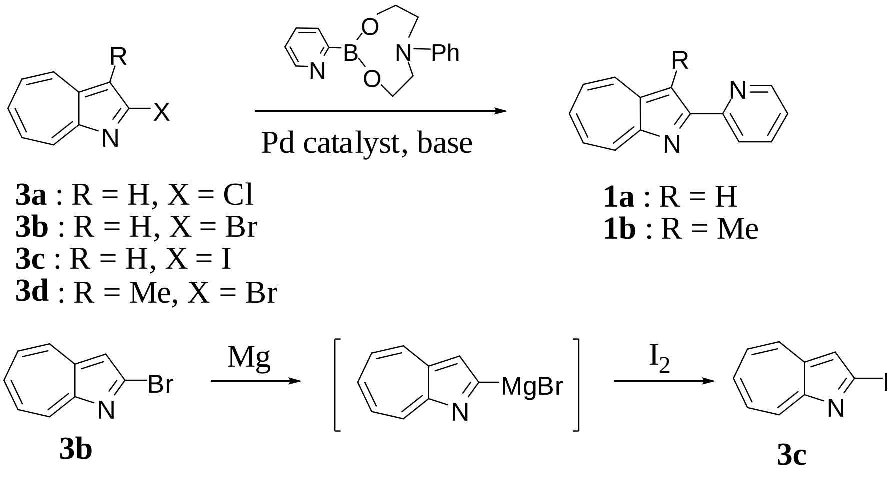
1a : R = H
1b : R = Me



2a : R = H
2b : R = CO_2Et

RESULTS AND DISCUSSION

Reaction of 2-chloro-1-azaazulene (**3a**) did not undergo Suzuki coupling. Reaction of 2-bromo-1-azaazulene (**3b**) with pyridineboronic acid *N*-phenyl-diethylamine ester (B(NPDEA)) in the presence of $PdCl_2(PPh_3)_2$, CuI, and K_2CO_3 in dry THF under heating for 24 h at 80 ℃ in a sealed tube gave a 2-(2-pyridyl)-1-azaazulene-Cu complex. Using Cs_2CO_3 as base in the reaction gave similar result. Treatment of the complex with aq. Solution of EDTA gave free 2-(2-pyridyl)-1-azaazulene (**1a**) (23%) together with recovered **3b** (14%). When the reaction was carried out using 2-iodo-1-azaazulene (**3c**), which was produced in 66% yield by the treatment of **3b** with Mg-metal and I_2, the yield was slightly raised to 25%. Similar reaction of 2-bromo-3-methyl-1-azaazulene (**3d**) with B(NPDEA) gave 3-methyl-2-(2-pyridyl)-1-azaazulene (**1b**) (12%).



3a : R = H, X = Cl
3b : R = H, X = Br
3c : R = H, X = I
3d : R = Me, X = Br

1a : R = H
1b : R = Me

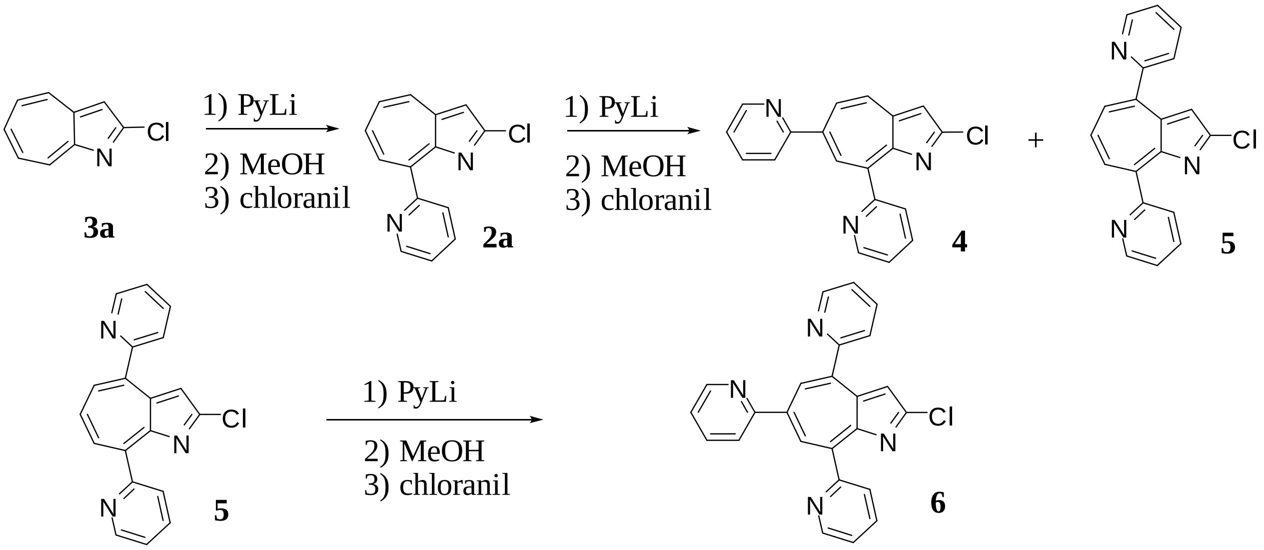
3b

3c

Treatment of 2-chloro-8-(2-pyridyl)-1-azaazulene (**2a**) with an equivalent molar of 2-pyridyllithium (PyLi) followed by MeOH gave only recovered (**2a**) in over 80% yield. Treatment of **2a** with excess molar of PyLi (2.4 eq. mole) at -80 ℃ for 0.5 h followed by MeOH gave addition products, and a successive dehydrogenation of the intermediates with tetrachloro-*o*-benzoquinone (*o*-chloranil) at 50 ℃ for 17 h afforded 2-chloro-6,8-di(2-pyridyl)-1-azaazulene (**4**) and 2-chloro-4,8-di(2-pyridyl)-1-azaazulene (**5**) in 58% and 4% yields, respectively. Reaction of **5** with PyLi under similar conditions to that descrived above gave 2-chloro-4,6,8-tri(2-pyridyl)-1-azaazulene (**6**) in 68% yield. Further treatment of **6** with an excess equivalent of PyLi proceeded but only unstable yellow tar was obtained in spite of the treatment with *o*-chloranil at 50 ℃ for 6 d, along with recovered (**6**) (4%). In the reaction, the addition reaction would undergo but successive dehydrogenation would be prevented, being ascribable to the steric hindrance. The results showed that the reactivity of the seven-menbered ring is C8 > C6 > C4.

In the similar manner, we examined of **1a** with PyLi, but the reaction did not undergo and **1a** (97%) was recovered. Chelation of Li^+ with **1a** would keep apart the pyridyl moiety from seven-membered ring and this would cause to prevent the reaction.

The structures of obtained products were deduced by spectroscopic data as well as elemental analysis. Electronic spectra of **3a**, **2a**, **4**, and **6** were shown in Fig. 1. It is shown that introduction of pyridine on 1-azaazulene nuclei caused bathochromic shift.



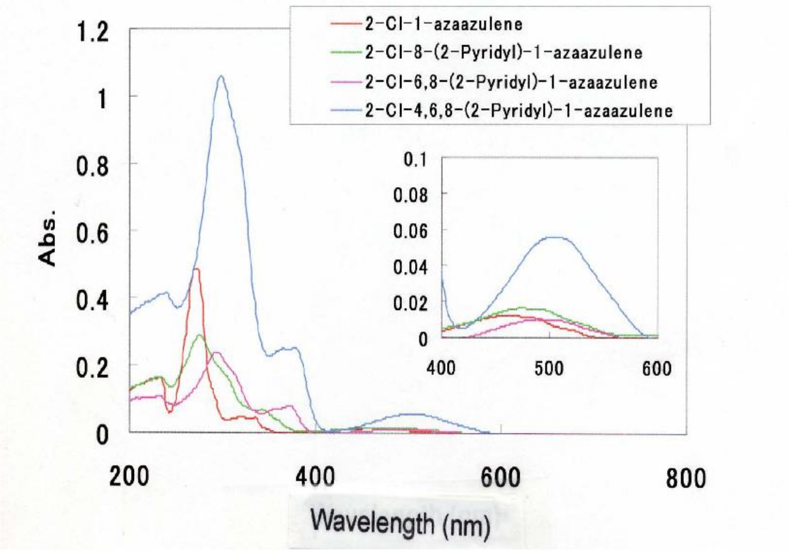
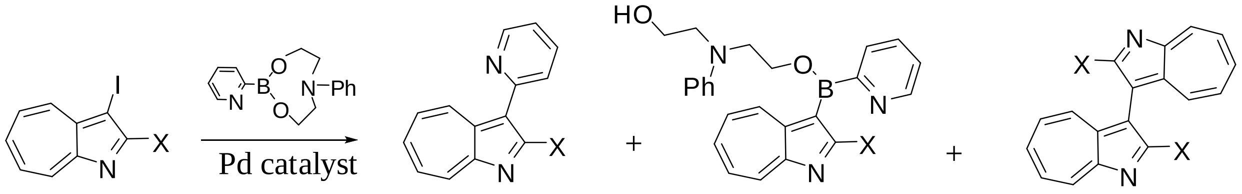


Figure 1. Electronic spectra of pyridyl-1-azaazulenes

Reaction of 2-chloro-3-iodo-1-azaazulene (**7a**) with B(NPDEA) in the presence of PPh_3, $Pd(OAc)_2$, K_2CO_3, and CuI in dry THF under heating for 24 h at 80 ℃ in a sealed tube gave 2-chloro-3-(2-pyridyl)-1-azaazulene (**8a**) (50%) together with (2-chloro-1-azaazulen-3-yl)-(2-pyridyl)-[*N*-(2-hydroxylethyl)]-(*N*-phenyl)aminoethylborate (**9a**) (3%). Similar treatment of 3-iodo-2-methoxy-1-azaazulene (**7b**) with B(NPDEA) in the presence of $PdCl_2(PPh_3)_2$, K_2CO_3 , and CuI in dry THF under heating for 3 h at 80 ℃ in a sealed tube gave 2-methoxy-3-(2-pyridyl)-1-azaazulene (**8b**) (84%) together with 3,3'-bi(2-methoxy-1-azaazulene) (**10b**)

(6%).

We previously reported that reaction of **7a** with bis(pinacolato)diborane gave **11** and **10a**. Therefore, it is thought that **9** would be produced by the reaction of **7** and B(NPDEA). Successive reaction of **9b** and **7b** would produce **10b** under the conditions. Lower reactivity of **9a** than **9b** and **11** would cause to give none of **10a**.

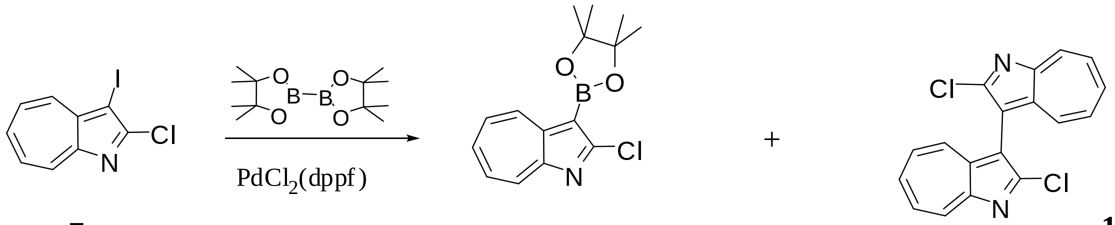


7a : X = Cl
7b : X = OMe

8a : X = Cl
8b : X = OMe

9a : X = Cl
9b : X = OMe

10a : X = Cl
10b : X = OMe

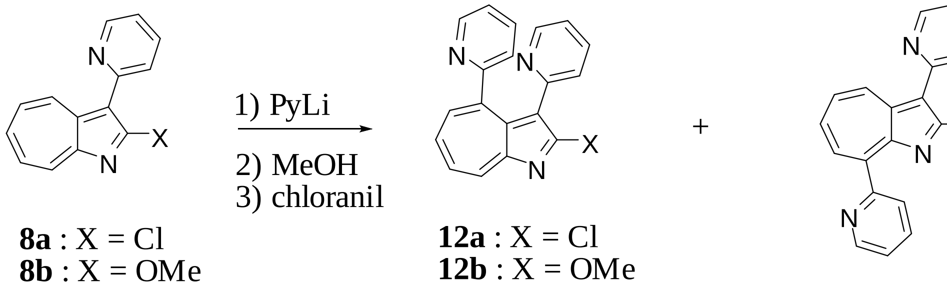


7a

11

10a

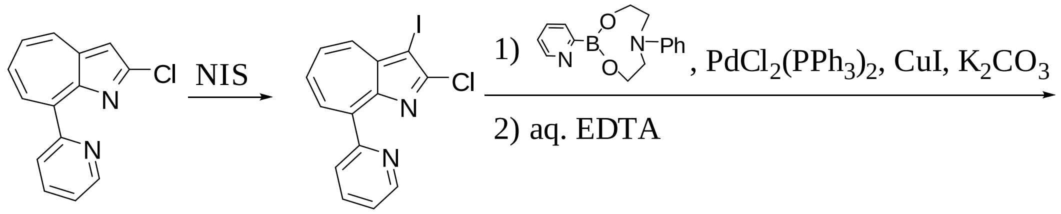
We examined the following reaction of **8** with PyLi similarly. Treatment of **8a** with PyLi followed by quenching with MeOH and successive dehydrogenation gave a mixture of **12a** (30%), **13a** (30%), **12b** (7%), and **13b** (9%). Compounds **12b** and **13b** would form via a substitution of **12a** and **13a** by methoxide. Existence of aryl group at C-3 would enhance the reactivity of C-2.[4] Similar reaction of **8b** with PyLi gave **12b** (26%) and **13b** (30%). In these reactions, attacks of PyLi at C-4 and C-8 of 1-azaazulene nuclei were practically equal, and 3,6-di(2-pyridyl)-1-azaazulenes were not obtained. Coordination of electropositive lithium atom of the reagent on nitrogen atoms of 1-azaazulene and pyridine is thought to controll the reaction position.



8a : X = Cl
8b : X = OMe

12a : X = Cl
12b : X = OMe

13a : X = Cl
13b : X = OMe



14-Cu complex

2a

14

To expect the formation of **13a**, we performed Suzuki coupling of **14**. In the reaction, only insoluble dark material, which was considered to be **14**-Cu complex, was precipitated. Previously, we reported about the formation of Cu-complex with **2a**.[4]

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Mps were 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 $CDCl_3$ 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 Avatar 370DTGS. Electronic spectra were recorded with JASCO V-670 spectrophotometer using $CHCl_3$ as a solvent. MS spectra were taken with an LC-MS Waters Integrity System. Elemental analyses were taken with a Perkin Elmer 2400II. Kieselgel 60 was used for column chromatography and Kieselgel 60G was used for thin-layer chromatography.

Synthesis of 2-iodo-1-azaazulene (3c)

Under argon atmosphere, Mg (0.032 g, 1.3 mmol) was activated by stirring overnight with small amounts of iodine. A mixture of the Mg, iodine (0.300 g, 1.2 mmol), and 2-bromo-1-azaazulene (**3b**) (0.207 g, 1.0 mmol) in dry THF (20 mL) was heated at 80 ℃ for 5 h. To the mixture was added water (30 mL), then the mixture was extracted with $CHCl_3$. The extract was dried over sodium sulfate and evaporated. Chromatography of the residue with hexane-$CHCl_3$ (1 : 1) gave 2-iodo-1-azaazulene (**3c**) (0.177 g, 66%). **3c**: Red needles (from hexane-CH_2Cl_2), mp 71-74 ℃: δ_H 7.56 (1H, s, H-3), 7.68 (1H, dd, J 9.9 and 9.7, H-7), 7.77 (1H, t, J 9.9, H-5), 7.93 (1H, t, J 9.9, H-6), 8.51 (1H, d, J 9.9, H-4), and 8.66 (1H, d, J 9.7, H-8); *m/z* (rel intensity) 255 (M^+, 100), 207 (8), 128 (39), 127 (21), 101 (44), and 77 (25). *Anal.* Calcd for C_9H_6NI: C, 42.38; H, 2.37; N, 5.49. Found: C, 42.53; H, 2.29; N, 5.33.

Synthesis of 2-(2-pyridyl)-1-azaazulene

A) Under argon atmosphere, a mixture of **3b** (0.104 g, 0.50 mmol), pyridineboronic acid *N*-phenyldiethylamine ester (B(NPDEA)) (0.402 g, 1.5 mmol), $PdCl_2(PPh_3)_2$ (0.0175 g, 0.025 mmol, 5 mol%), CuI (0.280 g, 1.5 mmol), K_2CO_3 (0.138 g, 1,0 mmol) in THF (20 mL) was stirred for 4 h at 80℃. The precipitate was collected by filtration and washed with water and $CHCl_3$. The precipitate was suspended in EDTA (1.0 g, 2.5 mmol) and water (10 mL), then the suspension was stirred for 24 h at 80℃. The suspension was combined with the filtrate and washed solution, and the mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel column with hexane-$CHCl_3$ (1 : 1) to give 2-(2-pyridyl)-1-azaazulene[3] (**1a**)

(0.024 g, 23%) and recovered **3b** (0.015 g, 14%).

B) Under argon atmosphere, a mixture of **3c** (0.1335 g, 0.50 mmol), B(NPDEA) (0.400 g, 1.5 mmol), $PdCl_2(PPh_3)_2$ (0.0175 g, 0.025 mmol, 5 mol%)、CuI (0.285 g, 1.5 mmol), Cs_2CO_3 (0.243 g, 0.75 mmol) in THF (10 mL) was stirred for 4 h at 80 ℃. The precipitate was collected by filtration and washed with water and $CHCl_3$. The precipitate was suspended in EDTA (1.0 g, 2.5 mmol) and water (10 mL), then the suspension was stirred for 24 h at 80 ℃. The suspension was combined with the filtrate and washed solution, and the mixture was extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel column with hexane-$CHCl_3$ (1 : 1) to give **1a** (0.025 g, 25%).

In the similar manner, 3-methyl-2-(2-pyridyl)-1-azaazulene (**1b**) was obtained in 12%.

1b: Red violet powders (from hexane-CH_2Cl_2), mp 86-89 ℃: ^{1}H NMR δ 2.96 (3H, s, Me), 7.31 (1H, ddd, *J* 7.7, 4.7, and 1.0, H-5'), 7.60 (1H, dd, *J* 9.9 and 9.8 H-5), 7.69 (1H, dd, *J* 9.8 and 9.6, H-7), 7.81 (1H, t, *J* 9.8, H-6), 7.85 (1H, ddd, *J* 7.9, 7.5, and 0.9, H-4'), 8.47 (1H, dd, *J* 7.9 and 1.0, H-3'), 8.48 (1H, d, *J* 9.9, H-4), 8.67 (1H, d, *J* 9.6, H-8), and 8.81 (1H, dd, *J* 4.7 and 0.7, H-6'): ^{13}C NMR δ 11.12, 122.13, 123.00, 124.76, 127.26, 128.76, 134.15, 136.17, 136.41, 137.58, 145.83, 149.46, 155.78, 157.22, and 162.81. *Anal.* Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.55; H, 5.45; N, 12.59.

Reaction of 2-chloro-3-iodo-1-azaazulene (7a) with B(NPDEA)

Under argon atmosphere, a mixture of **7a** (0.288 g, 1.00 mmol), B(NPDEA) (0.800 g, 3.00 mmol), PPh_3 (0.053 g, 0.20 mmol), $Pd(OAc)_2$ (0.011 g, 0.02 mmol, 5mol%), CuI (0.570 g, 3.00 mmol), and K_2CO_3 (0.276 g, 2.00 mmol) in dry THF (20 mL) was heated for 24 h at 80 ℃ in a sealed tube. The mixture was poured into water and extracted with $CHCl_3$. The extract was dried over Na_2SO_4 and evaporated. The residue was chromatographed on silica gel column with hexane-EtOAc (5 : 3) to give 2-chloro-3-(2-pyridyl)-1-azaazulene (**8a**) (0.122 g, 50%) and (2-chloro-1-azaazulen-3-yl)-(2-pyridyl)-[*N*-(2-hydroxylethyl)]-(*N*-phenyl)aminoethylborate (**9a**) (0.012 g, 3%).

8a: Orange needles (from hexane-CH_2Cl_2), mp 127-129 ℃: ^{1}H NMR δ_H 7.30 (1H, ddd, *J* 7.9, 4.9, and 1.5, H-5'), 7.77 (1H, dd, *J* 10.1 and 9.8, H-5), 7.83 (1H, dd, *J* 10.8 and 9.7, H-7), 7.86 (1H, ddd, *J* 7.3, 1.5, and 0.9, H-3'), 7.92 (1H, ddd, *J* 7.9, 7.3, and 1.7, H-4'), 7.97 (1H, ddd, *J* 10.8, 9.8, and 0.9, H-6), 8.66 (1H, dd, *J* 9.7 and 0.9, H-8), 8.81 (1H, ddd, *J* 4.9, 1.7 and 0.9, H-6'), and 9.21 (1H, d, *J* 10.1, H-4): ^{13}C NMR δ 121.76, 121.81, 125.03, 130.92, 131.16, 136.31, 136.50, 136.60, 139.11, 144.15, 149.69, 152.27, 155.49, and 155.92; λ_{max} nm (log ε) 280 (4.56), 299 (4.60), 330 (3.91), 363 (3.81), and 483 (3.09). *Anal.* Calcd for $C_{14}H_9N_2Cl$: C, 69.86; H, 3.77; N, 11.64. Found: C, 69.63; H, 4.05; N, 11.59.

9a: Orange powders (from hexane-CH_2Cl_2), mp 137-138 ℃: ^{1}H NMR δ 3.62 (2H, d, *J* 5.1, NCH_2), 3.83 (2H, t, *J* 5.1, NCH_2), 3.92, (2H, t, *J* 5.7, OCH_2), 4.60 (1H, br s, OH), 5.03 (2H, t, *J* 5.7, OCH_2), 6.64 (1H, t, *J* 7.2, H-*p*-phenyl), 6.82 (2H, d, *J* 8.8, H-*o*-phenyl), 7.11 (2H, dd, *J* 8.8 and 7.2, H-*m*-phenyl), 7.18 (1H, ddd, *J* 7.5, 4.9, and 1.1, H-Py-4), 7.55-7.65 (3H, m, H-5, 6, and 7), 7.76 (1H, ddd, *J* 8.0, 7.5, and 1.8, H-Py-5), 7.93 (1H, ddd, *J* 8.0, 1.1, and 0.9, H-Py-3), 8.25-8.30 (1H, m, H-8), 8.74 (1H, ddd, *J* 4.9, 1.8, and 0.9, H-Py-6), and 9.35 (1H, dm, J 10.9, H-4): ^{13}C NMR δ 52.07, 55.17, 60.09, 109.57, 112.81, 116.99, 119.66, 123.83, 129.13, 130.74, 131.02, 131.21, 133.07, 134.81, 136.21, 144.37, 148.24, 149.22, 153.23, 155.00, and 172.10; λ_{max} nm (log ε) 284 (4.57), 306 (4.58), 314 (4.58), 375 (3.85, sh), 387 (3.86), and 461 (3.37). *Anal.* Calcd for $C_{24}H_{23}N_3O_2BCl$: C, 66.77; H, 5.37; N, 9.73. Found: C, 66.29; H, 5.28; N, 9.55.

Reaction of 3-iodo-2-methoxy-1-azaazulene (7b) with B(NPDEA)

Under argon atmosphere, a mixture of **7b** (0.143 g, 0.50 mmol), B(NPDEA) (0.400 g, 1.00 mmol), CuI (0.286 g, 1.00 mmol), $PdCl_2(PPh_3)_2$ (0.018 g, 0.026 mmol, 5mol%), and K_2CO_3 (0.140 g, 1.0 mmol) in dry THF (15 mL) was heated for 3 h at 80 ℃ in a sealed tube. Then the solvent was evaporated. The residue was chromatographed on silica gel column with hexane-$CHCl_3$ (1 : 1) to give **8b** (0.099 g, 84%) and 3,3'-bis(2-methoxy-1-azaazulene) (**10b**) (0.0045 g, 6%).

8b: Red prisms (from hexane-CH_2Cl_2), mp 88-89 ℃: ^{1}H NMR δ 4.36 (3H, s, OCH_3), 7.13 (1H, dd, *J* 7.2, and 4.6, H-5'), 7.50-7.61 (3H, m, H-5,6,7), 7.73 (1H, td, *J* 8.1 and 7.2 , H-4'), 7.99 (1H, d, *J* 8.1, H-3'), 8.27-8.33 (1H, m, H-8), 8.74 (1H, d, *J* 4.6, H-6'), and 9.43-9.52 (1H, m, H-4): ^{13}C NMR δ 56.58, 109.54, 120.46, 123.67, 130.42, 130.80, 131.21, 133.08, 134.52, 136.10, 144.47, 149.15, 153.53, 155.61, and 173.18; λ_{max} nm (log ε) 285 (4.53), 308 (4.57, sh), 315 (4.60), and 461 (3.41). *Anal.* Calcd for $C_{15}H_{12}N_2O$: C, 76.25; H, 5.12; N, 11.86. Found: C, 76.15; H, 5.28; N, 11.80.

10b: Red prisms (from hexane-CH_2Cl_2), mp 223-225 ℃: ^{1}H NMR δ 4.30 (6H, s, OCH_3), 7.39 (2H, dddd, *J* 10.4, 9.8,1.2 and 0.9, H-5,5'), 7.54 (2H, ddd, *J* 9.8, 9.2 and 0.6, H-7,7'), 7.60 (2H, dd, *J* 9.9 and 9.8, H-6,6'), 7.86 (2H, dd, *J* 9.2 and 0.6, H-4,4'), and 8.29 (1H, dd, *J* 10.4 and 1.2, H-8,8'). *Anal.* Calcd for $C_{20}H_{16}N_2O_2$: C, 75.93; H, 5.10; N, 8.86. Found: C, 75.88; H, 5.22; N, 8.60.

Reaction of 2-chloro-8-(2-pyridyl)-1-azaazulene (2a) with 2-pyridyllithium

Under argon atmosphere, 1.5 M butyllithium (1.7 mL, 2.60 mmol) was added to the solution of 2-bromopyridine (0.23 mL, 2.40 mmol) in dry THF (15 mL) at –90 ℃. To the mixture **2a** (0.240 g, 1.00 mmol) in dry THF (15 mL) was added, and the mixture was stirred for 15 min at –80 ℃, then MeOH (10 mL) was added. After the mixture was warm to rt, *o*-chloranil (0.260 g, 2.4 mmol) was added to the mixture and the mixture was stirred for 17 h at 50 ℃. The mixture was poured into water and extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel column with ACOEt-hexane (2 : 5) to give 2-chloro-6,8-bis(2-pyridyl)-1-azaazulene (**4**) (0.185 g, 58%) and 2-chloro-4,8-bis(2-pyridyl)-1-azaazulene (**5**) (0.013 g, 4%).

4: Orange needles (from hexane-CH_2Cl_2), mp 168-170 ℃: ^{1}H NMR δ 7.31 (1H, s, H-3), 7.36 (1H, ddd, *J* 7.5, 4.7, and 1.1, H-5''), 7.39 (1H, ddd, *J* 7.3, 4.8, and 1.3, H-5'), 7.82 (1H, dd, *J* 8.0 and 7.5, H-4''), 7.87 (1H, dd, *J* 7.9 and 7.3, H-4'), 7.93 (1H, dd, *J* 8.0 and 1.1, H-3''), 8.30 (1H, dd, *J* 7.9 and 1.3, H-3'), 8.36 (1H, dd, *J* 10.4 and 1.9, H-5), 8.57 (1H, d, *J* 10.4, H-4), 8.78 (1H, d, *J* 4.7, H-6''), 8.81 (1H, d, *J* 4.8 , H-6'), and 8.91 (1H, s, H-7): ^{13}C NMR δ 113.49, 123.54, 123.86, 129.05, 129.72, 134.08, 134.30, 136.19, 137.58, 145.09, 148.15, 148.22, 150.08, 150.32, 152.71, 158.86, 158.52, and 159.94; λ_{max} nm (log ε) 294 (4.38), 358 (3.84), 372 (3.89), and 492 (3.00). *Anal.* Calcd for $C_{19}H_{12}N_3Cl$: C, 71.81; H, 3.81; N, 12.98. Found: C, 71.80; H, 4.12; N, 12.93.

5: Orange brown needles (from hexane-CH_2Cl_2), mp 168-170 ℃: ^{1}H NMR δ 7.18 (1H, s, H-3), 7.40 (1H, ddd, *J* 7.5, 4.8, and 0.8, H-5’), 7.46 (1H, ddd, *J* 7.6, 4.8, and 0.8, H-5’’), 7.75 (1H, dd, *J* 7.8 and 0.8, H-3’’), 7.87 (1H, d, *J* 9.7 H-5), 7.88 (1H, ddd *J* 7.9, 7.5 and 1.9, H-4’), 7.91 (1H, ddd, *J* 7.8, 7.6 and 1.7, H-4’’), 8.04 (1H, dd, *J* 10.8 and 9.7, H-6), 8.27 (1H, dd, *J* 7.9 and 0.8, H-3’), 8.33 (1H, d, *J* 10.8, H-7), 8.82 (1H, dd, *J* 4.8 and 1.9, H-6’), and 8.85 (1H, dd, *J* 4.8 and 1.7, H-6’’): ^{13}C NMR δ 112.71, 123.47, 123.54, 124.72, 129.05, 128.76, 131.68, 133.20, 135.75, 136.12, 136.72, 146.06, 146.26, 146.43, 149.63, 150.07, 153.58, 157.35, 157.89, and 159.47; λ_{max} nm (log ε) 286 (4.63), 348 (3.80, sh), and 494 (3.30). *Anal.* Calcd for $C_{19}H_{12}N_3Cl$: C, 71.81; H, 3.81; N, 12.98. Found: C, 71.88; H, 4.02; N, 12.89.

Reaction of 2-chloro-4,8-di(2-pyridyl)-1-azaazulene (5) with 2-pyridyllithium

Under argon atmosphere, 1.5 M butyllithium (1.25 mL, 1.95 mmol) was added to the solution of 2-bromopyridine (0.172 mL, 1.80 mmol) in dry THF (15 mL) at –90 ℃, and the mixture was stirred for 30 min. To the mixture **5** (0.160 g, 0.50 mmol) in dry THF (15 mL) was added, and the mixture was stirred for 30 min at –80 ℃, then MeOH (10 mL) was added. After the mixture was warm to rt, *o*-chloranil (0.260 g, 2.4 mmol) was added to the mixture and the mixture was stirred for 17 h at 50 ℃. The mixture was poured into water and extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel column with EtOAc-hexane (1 : 1) to give 2-chloro-4,6,8-tris(2-pyridyl)-1-azaazulene (**6**) (0.134 g, 68%).

6: Orange needles (from hexane-CH_2Cl_2), mp 211-214 ℃: ^{1}H NMR δ 7.18 (1H, s, H-3), 7.33 (1H, ddd, *J* 7.8, 4.8, and 1.0, H-5’’’), 7.40 (1H, ddd, *J* 7.9, 5.0, and 1.1, H-5’’), 7.45 (1H, ddd, *J* 7.8, 4.9, and 1.1, H-5’), 7.80 (1H, dt, *J* 7.8 and 1.0, H-3’’’), 7.82 (1H, td, *J* 7.8, and 1.0, H-4’’’), 7.88 (1H, td, *J* 7.9 and 1.8, H-4’’), 7.91 (1H, td, *J* 7.8 and 1.8, H-4’), 7.96 (1H, dt, *J* 7.9, and 0.9, H-3’’), 8.27 (1H, dt, *J* 7.8 and 1.0, H-3’), 8.60 (1H, d, *J* 1.6, H-5), 8.75 (1H, ddd, *J* 4.8, 1.7 and 0.9, H-6’’’), 8.83 (1H, ddd, *J* 5.0, 1.8, and 0.9, H-6’’), 8.84 (1H, ddd, *J* 5.0, 0.8, and 0.9, H-6’), and 8.91 (1H, d, *J* 1.6, H-7): ^{13}C NMR δ 113.01, 123.14, 123.31, 123.45, 123.52, 124.84, 128.78, 131.98, 133.34, 135.73, 136.73, 137.16, 145.23, 145.65, 235.73, 146.87, 149.64, 149.84, 150.00, 153.21, 157.71, 158.26, 159.66, and 159.82; λ_{max} nm (log ε) 298 (5.02), 314 (4.95, sh), 365 (4.40), 378 (4.40), and 506 (3.74). *Anal.* Calcd for $C_{24}H_{15}N_4Cl$: C, 73.00; H, 3.83; N, 14.19. Found: C, 73.03; H, 4.09; N, 13.92.

Reaction of 2-chloro-3-(2-pyridyl)-1-azaazulene (8a) with 2-pyridyllithium

Under argon atmosphere, 1.5 M butyllithium (0.89 mL, 1,40 mmol) was added to the solution of 2-bromopyridine (0.12 mL, 1.20 mmol) in dry THF (15 mL) at –90 ℃. To the mixture **8a** (0.150 g, 0.62 mmol) in dry THF (20 mL) was added, and the mixture was stirred for 15 min at –80 ℃, then MeOH (10 mL) was added. After the mixture was warm to rt, *o*-chloranil (0.260 g, 2.4 mmol) was added to the mixture and the mixture was stirred for 17 h at 50 ℃. The mixture was poured into water and extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel column with EtOAc-hexane (1 : 1) to give 2-chloro-3,8-bis(2-pyridyl)-1-azaazulene (**13a**) (0.058 g, 30%), 2-chloro-3,4-bis(2-pyridyl)-1-azaazulene (**12a**) (0.038 g, 30%), 2-methoxy-3,8-bis(2-pyridyl)-1-azaazulene (**13b**) (0.017 g, 9%) and

2-methoxy-3,4-bis(2-pyridyl)-1-azaazulene (**12b**) (0.014 g, 7%).

12a: Red brown prisms (from hexane-CH_2Cl_2), mp 179-182 ℃: ^{1}H NMR δ 6.92 (1H, ddd, *J* 7.4, 4.9, and 0.9, H-5''), 6.98 (1H, ddd, *J* 7.6, 4.1, and 0.9, H-5'), 7.13 (1H, dt, *J* 7.7 and 0.9, H-3'), 7.15 (1H, dt, *J* 7.7 and 0.9, H-3''), 7.26 (1H, ddd, *J* 7.7, 7.4, and 1.7, H-4'), 7.41 (1H, ddd, *J* 7.7, 7.4 and 1.9, H-4''), 7.88 (1H, dd, *J* 9.8 and 9.5, H-7), 7.95 (1H, dd, *J* 10.1 and 1.3, H-5), 8.01 (1H, ddd, *J* 10.1, 9.5, and 1.0, H-6), 8.24 (1H, dd, *J* 4.9 and 1.9, H-6'), 8.34 (1H, dd, *J* 4.9 and 1.7, H-6''), and 8.78 (1H, dd, *J* 9.8 and 1.0, H-8): ^{13}C NMR δ 119.64, 121.33, 122.55, 124.42, 125.02, 129.48, 133.72, 134.04, 136.11, 136.34, 139.28, 146.45, 147.80, 147.83, 151.94, 156.21, 157.05, and 157.49; λ_{max} nm (log ε) 290 (4.60), 338 (3.83, sh), and 490 (3.20). *Anal.* Calcd for $C_{19}H_{12}N_3Cl$: C, 71.81; H, 3.81; N, 13.22. Found: C, 71.70; H, 3.87; N, 13.31.

13a: Orange powders (from hexane-CH_2Cl_2), mp 197-198 ℃: ^{1}H NMR δ 7.33 (1H, ddd, *J* 6.8, 4.1, and 0.9, H-5''), 7.42 (1H, ddd, *J* 7.6, 4.1, and 0.9, H-5'), 7.77 (1H, dd, *J* 10.1 and 9.4, H-5), 7.89 (3H, m, H-3'', 4', and H-4''), 8.04 (1H, dd, *J* 10.8, 9.7, and 0.8, H-6), 8.31 (1H, td, *J* 8.9 and 0.9, H-3'), 8.37 (1H, d, *J* 10.8, H-7), 8.83 (1H, dd, *J* 4.1 and 0.9, H-6'), 8.85 (1H, dd, *J* 4.3 and 1.0, H-6''), and 9.19 (1H, dd, *J* 10.1 and 0.8, H-4): ^{13}C NMR δ 120.80, 121.38, 122.52, 124.44, 127.63, 129.48, 133.01, 134.80, 135.09, 135.48, 137.14, 144.46, 145.35, 148.66, 148.71, 151.37, 154.50, and 156.15; λ_{max} nm (log ε) 276 (4.42), 314 (4.56), 348 (4.14, sh), and 496 (3.21). *Anal.* Calcd for $C_{19}H_{12}N_3Cl$: C, 71.81; H, 3.81; N, 13.22. Found: C, 71.67; H, 3.98; N, 13.11.

12b: Orange powders (from hexane-CH_2Cl_2), mp 137-139 ℃: ^{1}H NMR δ 4.31 (3H, s, OCH_3), 6.84 (1H, ddd, *J* 7.5, 4.9, and 1.3, H-5''), 6.93 (1H, ddd, *J* 7.4, 4.9, and 1.3, H-5'), 7.10 (1H, dt, *J* 7.7 and 0.9, H-3'), 7.13 (1H, dt, *J* 7.9 and 1.0, H-3''), 7.21 (1H, td, *J* 7.8, and 1.7, H-4'), 7.33 (1H, ddd, *J* 7.7, 7.5 and 1.8, H-4''), 7.66 (2H, m , H-5 and 7), 7.76 (1H, m, H-6), 8.19 (1H, ddd, *J* 4.9, 1.7, and 0.9, H-6'), 8.33 (1H, ddd, J 4.9, 1.7, and 0.9, H-6''), and 8.41 (1H, m, H-8): ^{13}C NMR δ 56.64, 112.87, 119.89, 121.74, 125.05, 125.46, 130.21, 131.34, 132.54, 134.29, 134.77, 134.88, 140.77, 143.31, 148.56, 148.61, 153.09, 157.16, 159.72, and 173.93; λ_{max} nm (log ε) 290 (4.56), 295 (4.56), 374 (3.75), 391 (3.77), and 466 (3.33). *Anal.* Calcd for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.82; N, 13.41. Found: C, 69.63; H, 4.05; N, 11.59.

13b: Orange powders (from hexane-CH_2Cl_2), mp 142-143 ℃: ^{1}H NMR δ 4.26 (3H, s, OCH_3), 7.17 (1H, ddd, *J* 7.8, 4.9, and 1.0, H-5''), 7.35 (1H, ddd, *J* 7.4, 4.2, and 1.0, H-5'), 7.61 (1H, dd, *J* 10.4, 9.2 and 0.6, H-5), 7.71 1H, ddd, *J* 10.8, 9.2 and 1.0, H-6), 7.76 (1H, ddd, *J* 8.0, 7.8, and 1.9, H-4''), 7.82 (1H, td, *J* 7.4 and 1.8, H-4'), 7.98 (1H, ddd, *J* 8.0, 1.0, and 0.9, H-3''), 8.15 (1H, d, *J* 10.8, H-7), 8.31 (1H, ddd, *J* 7.4, 1.0, and 0.9 and 1.0, H-3'), 8.77 (1H, ddd, *J* 4.8, 1.8, and 0.9, H-6''), 8.82 (1H, ddd, *J* 4.2, 1.8, and 0.9, H-6'), and 9.49 (1H, dd, *J* 10.4 and 1.0, H-4): ^{13}C NMR δ 56.95, 110.11, 120.94, 123.00, 124.42, 128.78, 130.57, 133.26, 133.73, 134.01, 135.38, 136.56, 141.66, 146.32, 149.64, 152.40, 153.99, 158.98, and 173.40; λ_{max} nm (log ε) 279 (4.32), 325 (4.49), 354 (4.08, sh), 394 (3.79), and 476 (3.39). *Anal.* Calcd for $C_{20}H_{15}N_3O$: C, 76.66; H, 4.82; N, 13.41. Found: C, 69.63; H, 4.05; N, 11.59.

Reaction of 2-methoxy-3-(2-pyridyl)-1-azaazulene (8b) with 2-pyridyllithium

Under argon atmosphere, 1.5 M butyllithium (0.48 mL, 0.75 mmol) was added to the solution of 2-bromopyridine (0.064 mL, 0.68 mmol) in dry THF (10 mL) at –90 ℃. To the mixture **8b** (0.080 g, 0.34 mmol) in dry THF (15 mL) was added, and the mixture was stirred for 15 min at –80 ℃, then MeOH (10 mL) was added. After the mixture was warm to rt, *o*-chloranil (0.070 g, 0.68 mmol) was added to the mixture and the mixture was stirred for 17 h at 50 °C. The mixture was poured into water and extracted with $CHCl_3$. The extract was dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel column with EtOAc-hexane (1 : 1) to give **13b** (0.032 g, 30%) and **12b** (0.028 g, 26%).

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