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SYNTHESIS OF ARYL CONJUGATED (1-AZAAZULENYL)ACETYLENES AND FACILE SYNTHESIS OF THIOPHENE FUSED 1-AZAAZULENES

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Abstract — 3-Ethynyl-1-azaazulene derivatives were obtained by Sonogashira-Hagihara reaction of 3-iodo-2-chloro-1-azaazulenes, and 2-(phenylethynyl)-1-azaazulenes were obtained by the reaction of 2-bromo-1-azaazulenes. Glaser reaction of 2-chloro-3-ethynyl-1-azaazulenes gave 1,4-bis(2-chloro-1-azaazulen-3-yl)-1,3-butadiyne. Treatment of 2-chloro-3-ethynyl-1-azaazulene derivatives with sodium hydrosulfide gave corresponding 1-thia-9-azacyclopent[*a*]azulene derivatives in good yield.

INTRODUCTION

Recently, studies about aryl conjugated ethynylazulenes have been attractively subjected because of their potential functionality such as numerous optical, electrochemical, and electrical properties, and as precursors for the construction of fused azulene systems.[1-14] The chemistry of azaazulenes is of interest for their physical and chemical properties as well as physiological properties.[15] Chemistry of ethynylazaazulenes are also would have a versatile potentiality for construction of novel fused heterocycles and numerous optical, electrochemical, and electrical properties. Although their reports were few, recently we reported about synthesis of 3-ethynyl-1-azaazulene and 8-ethynyl-1-azaazulene.[16] In a continuation of our studies, we developed the preparation of new azaazulene-fused heterocycles[15] from azaazulenes using ethynylation and cyclization as follows.

Sonogashira-Hagihara reaction[17] is well-known as a superior method for the synthesis of disubstituted

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† Dedicated to Professor Yoshito Kishi on the occasion of his 70th birthday.

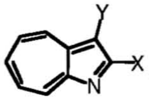
acetylenes from aryl halide and terminal acetylene. Therefore we examined to introduce ethynyl group to C-3 on 1-azaazulene nuclei by Sonogashira-Hagihara reaction first of all. And then we studied Glaser condensation[18] of 2-chloro-3-ethynyl-1-azaazulenes due to synthesize 1,4-bis(2-chloro-1-azaazulen-3-yl)-1,3-butadiyne. Thereafter we developed the cyclization of these heteroaryl alkynes using sodium hydroxide.

RESULTS AND DISCUSSION

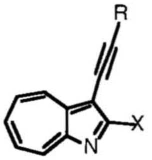
Synthesis of aryl conjugated ethynyl-1-azaazulenes

We previously reported the synthesis of 2-chloro-3-(trimethylsilylethynyl)-1-azaazulene (**2a**) by Sonogashira-Hagihara reaction of 2-chloro-3-iodo-1-azaazulene (**1a**) with trimethylsilylacetylene.[16] Compound (**2a**) was easily desilylated by the treatment with KF to give **2b** in 84% yield. Reaction of **1a** with 1.5 equivalent of phenylacetylene in the presence of dichlorobis(triphenylphosphine)palladium(II) and copper(I) iodide in dry THF for 30 min at rt gave **2c** in 76% yield together with and 2,3-di(phenylethynyl)-1-azaazulene (**3**) in 12% yield. 2-Chloro-1-azaazulene (**1b**) did not undergo Sonogashira-Hagihara reaction with phenylacetylene but 2-bromo-1-azaazulene (**1c**) underwent Sonogashira-Hagihara reaction to give 2-(phenylethynyl)-1-azaazulene (**4a**) in 51% yield. Sonogashira-Hagihara reaction of 2-bromo-3-chloro-1-azaazulene (**1d**) with phenylacetylene gave 3-chloro-2-(phenylethynyl)-1-azaazulene (**4b**) in 64% yield. Sonogashira-Hagihara reaction of 2,3-dibromo-1-azaazulene (**1e**) with phenylacetylene gave **4c** in 62% yield and 2-bromo-3-(phenylethynyl)-1-azaazulene (**2d**) was not obtained. The structures of **4b** and **4c** were unequivocally confirmed by the comparison with the products (**4b** and **4c**), prepared by the reaction of **4a** with NCS and NBS. Above results were similar to the Suzuki coupling of halogen substituted 1-azaazulenes: we previously reported that the Suzuki coupling of **1a** with phenylboronic acid gave 2-chloro-3-phenyl-1-azaazulene and 2,3-diphenyl-1-azaazulene, and the Suzuki coupling of 2-bromo-1-azaazulene (**1b**) with phenylboronic acid gave 2-phenyl-1-azaazulene in good yield.[19]

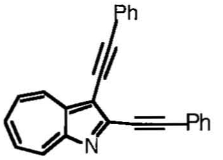
It is considered that adoption of Sonogashira-Hagihara reaction to **1a** with **2b** could give 1,2-bis(2-chloro-1-azaazulen-3-yl)acetylene (**5**). Thus treatment of 2-chloro-3-iodo-1-azaazulene (**1a**) with 2-chloro-3-ethynyl-1-azaazulene in the presence of tetrakis (triphenylphosphine)palladium and copper(I) iodide in dry THF for 18 h at rt gave (**5**) (59%).



1a : X = Cl, Y = I
1b : X = Cl, Y = H
1c : X = Br, Y = H
1d : X = Br, Y = Cl
1e : X = Br, Y = Br



2a : R = TMS, X = Cl
2b : R = H, X = Cl
2c : R = Ph, X = Cl
2d : R = Ph, X = Br



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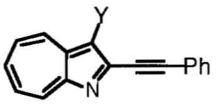
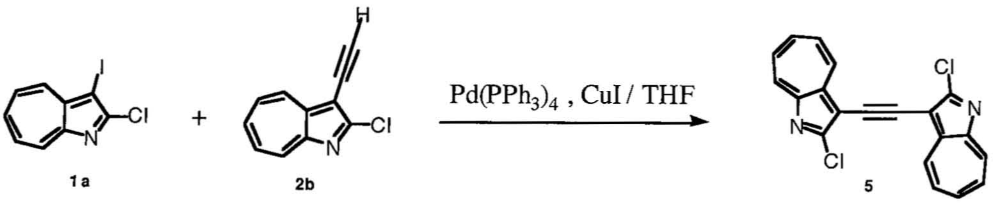
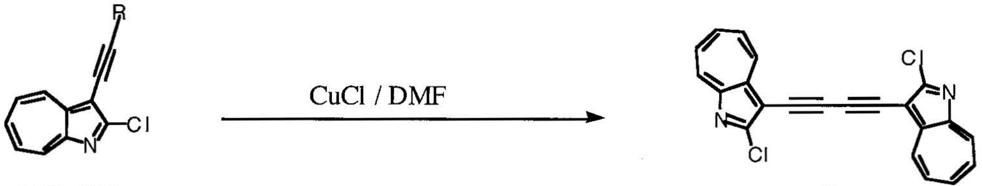


4a : Y = H
4b : Y = Cl
4c : Y = Br



Next, for synthesis of 1,4-bis(1-azaazulen-3-yl)-1,3-butadiyne, we carried out Glaser type reaction of **2**. Treatment of **2a** with copper(I) chloride in DMF under stirring for 6 h at 60 ℃ gave 1,4-bis(2-chloro-1-azaazulen-3-yl)-1,3-butadiyne (**6**) in 71% yield. Similar compound (**6**) was obtained from **2b** at rt in 56% yield.

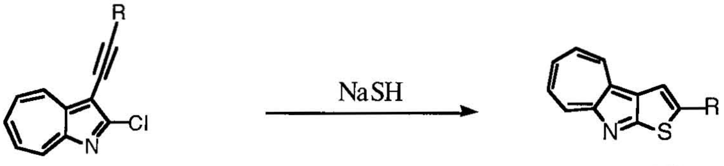


2a : R = TMS
2b : R = H

6

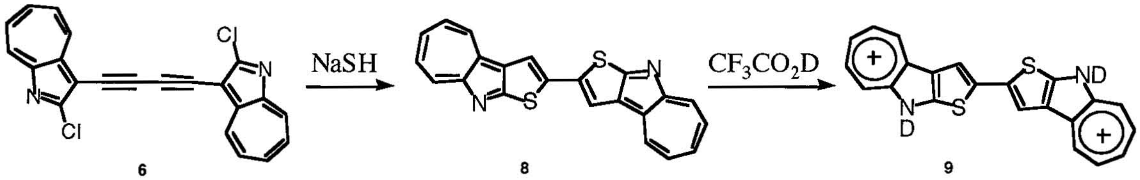
Synthesis of thiophene fused 1-azaazulenes

It is known that (*o*-chloro-heteroaryl)acetylene with sodium hydrosulfide to give thiophene fused hetroaromatics.[20,21] Therefore we applied it to 2-chloro-3-ethynyl-1-azaazulenes (**2a**, **2c**). Treatment of 2-chloro-3-trimethylsilylethynyl-1-azaazulene (**2a**) and sodium hydrosulfide in ethanol under reflux for 4 h gave reddish purple needles in 75% yield. This compound was analyzed as $C_{11}H_7NS$ from its MS (M^+, *m/z* 185) and elemental analyses. In its ^1H NMR spectrum, a couples of doublets are seen at δ 7.31 (d, *J* 5.6, H-2) and 7.52 (d, *J* 5.6, H-3) together with five seven-membered ring protons at δ 7.65 (ddd, *J* 10.3, 9.8, and 0.7, H-5), 7.76 (ddd, *J* 10.3, 9.9 and 0.7, H-7), 7.85 (dddd, *J* 9.9, 9.8, 0.8, and 0.7, H-6), 8.62 (dd, *J* 10.3 and 0.7, H-4), and 8.69 (ddd, *J* 10.3, and 0.8, H-8). From the results, we assigned the product as 1-thia-9-azacyclopent[*a*]azulene[22] (**7b**). In the reaction, **7a** was not obtained. Similarly, the reaction of **2c** with sodium hydrosulfide gave **7c** in 73%. In the ^1H NMR spectrum of **7c**, five seven-membered ring protons at δ 7.67 (t, *J* 9.8, H-5), 7.72 (s, H-3), 7.76 (dd, *J* 9.9 and 9.8, H-7), 7.87 (t, *J* 9.8, H-6), 8.64 (d, *J* 9.8, H-4), and 8.67 (d, *J* 9.9, H-8). The results of the ^1H NMR spectra of **7b** and **7c** show that these compound had not bond- alternation of seven-menbered ring. The structure of **7c** was confirmed by X-Ray structure analysis at a temperature −180 ± 1 ℃ (Figure 1).



2a : R = TMS
2c : R = Ph

7a : R = TMS
7b : R = H
7c : R = Ph



6 **8** **9**

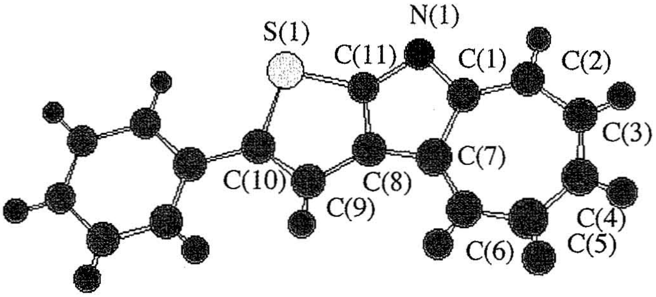


Figure. 1. X-Ray structure of **7c**.
Selective bond lengths (Å): S(1)-C(10) 1.774(2), S(1)-C(11) 1.722(2), N(1)-C(1) 1.362(2), N(1)-C(11) 1.356(2), C(1)-C(2) 1.388(3), C(1)-C(7) 1.495(3), C(2)-C(3) 1.388(3), C(3)-C(4) 1.388(3), C(4)-C(5) 1.396(3), C(5)-C(6) 1.384(3), C(6)-C(7) 1.392(3), C(7)-C(8) 1.405(3), C(8)-C(9) 1.428(3), C(8)-C(11) 1.407(3), C(9)-C(10) 1.371(3)

The result showed that the bond-alternation of seven-membered ring did not exist and consisted with the consideration from ^{1}H NMR spectral analysis.

When **6** was treated with sodium hydrosulfide, 2,2'-bis(1-thia-9-azacyclopent[*a*]azulene (**8**) was obtained in 59% yield. Compound (**8**) was fairly soluble in organic solvent such as chloroform or acetonitrile, therefore NMR spectra were measured in CF_3CO_2D. In its ^{1}H NMR spectrum, low-field resonated seven-membered ring protons were observed at δ 8.67 (2H, dd, J 10.0 and 9.9, H-5, 5'), 8.69 (2H, dd, J 10.0 and 9.9, H-7, 7'), 8.62 (2H, t, J 9.9, H-6, 6'), 9.14 (2H, d, J 10.0, H-4, 4'), and 9.35 (2H, d, J 10.0, H-8, 8') and a singlet peak was at δ 8.13 (2H, s, H-3, 3'). The ^{1}H NMR spectrum suggested that nitrogens of **8** in CF_3CO_2D were protonated to give the dication (**9**).

CONCLUSION

We obtained 3-ethynyl and 2-ethynyl –1-azaazulene derivatives by Sonogashira-Hagihara reaction of 3-iodo-2-chloro-1-azaazulene and 2-bromo-1-azaazulenes, respectively. Glaser reaction of 2-chloro-3-ethynyl-1-azaazulenes gave 1,4-bis(2-chloro-1-azaazulen-3-yl)-1,3-butadiyne. Construction of 1-thia-9-azacyclopent[*a*]azulenes were achieved by the treatment of 2-chloro-3-ethynyl-1-azaazulene derivatives with sodium hydrosulfide in good yield.

EXPERIMENTAL

Mps are measured using a Yanagimoto micro-melting apparatus and uncorrected. ^{1}H NMR spectra 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. Electronic spectra were recorded with JASCO V-570 spectrophotometer. MS spectra were taken with on 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-chloro-3-(trimethylsilylethynyl)-1-azaazulene (2a)

Under argon atmosphere, a mixture of 2-chloro-3-iodo-1-azaazulene (**1a**) (0.586 g, 2.02 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.042 g, 0.06 mmol), and copper(I) iodide (0.038 g, 0.20 mmol) in dry THF (7.0 mL) was stirred for 30 min at rt. To the mixture trimethylsilylacetylene (0.36 mL, 2.60 mmol) was added dropwise, followed by diisopropylamine (3.0 mL). After stirring for 48 h, water was added and the mixture was extracted with CH_2Cl_2. The solvent was dried over sodium sulfate and evaporated. The residue was chromatographed on silica gel column with EtOAc-hexane (1 : 1) to give 2-chloro-3-(trimethylsilylethynyl)-1-azaazulene (**2a**) (0.448 g, 85%).

2a: Yellow powder (from hexane-CH_2Cl_2), mp 81-82 ℃; δ_H 0.30 (9H, s, $(C\underline{H}_3)_3Si$), 7.75 (1H, dd, *J* 10.3 and 9.6, H-5), 7.81 (1H, dd, *J* 9.9 and 9.8, H-7), 7.92 (1H, dd, *J* 10.3 and 9.9, H-6), 8.55 (1H, d, *J* 9.6, H-4) and 8.56 (1H, d, *J* 9.8, H-8); δ_C 0.40, 95.0, 103.8, 104.2, 130.3, 131.2, 135.0, 136.3, 138.9, 152.2, 155.3, and 159.1; λ_{max} ($CHCl_3$) nm (log ε) 293 (4.58, sh), 300 (4.65), 327 (3.63), 347 (3.61), 363 (3.72), 382 (3.81), 500 (3.07), 566 (2.70, sh), and 585 (2.53, sh); ν_{max} / cm^{-1} 2141 ($C\equiv C$); *m/z* (rel intensity) 259 (M^+, 75), 244 (100), 208 (11), 166 (12), and 139 (8). *Anal.* Calcd for $C_{14}H_{14}NClSi$: C, 64.72; H, 5.43; N, 5.39. Found: C, 64.68; H, 5.48; N, 5.42.

Synthesis of 2-chloro-3-ethynyl-1-azaazulene (2b)

Under argon atmosphere, the solution of 2-chloro-3-trimethylsilylethynyl-1-azaazulene (**2b**) (0.104 g, 0.40 mmol) and KF (0.044 g, 0.75 mmol) in water (2.0 mL) - DMF (10.0 mL) was stirred for 40 min at rt. The mixture was quenched with water and extracted with EtOAc. The extract was dried over Na_2SO_4 and evaporated. Chromatography of the residue with hexane-EtOAc (1 : 1) gave 2-chloro-3-ethynyl-1-azaazulene (**2c**) (0.063 g, 84%).

2b: Red powder (from hexane-$CHCl_3$), mp 136-139 ℃ (decomp); δ_H 3.69 (1H, s, $C\equiv CH$), 7.79 (1H, ddd, *J* 9.8 and 9.7, H-5), 7.85 (1H, dd, *J* 10.0 and 9.8, H-7), 7.96 (1H, dd, *J* 10.0 and 9.8, H-6), 8.59 (1H, d, *J* 9.7, H-4), and 8.61 (1H, d, *J* 9.8, H-8); δ_C 74.59, 85.93, 106.23, 130.77, 131.64, 134.89, 136.59, 139.17, 147.78, 155.34, and 159.10; λ_{max} ($CHCl_3$) nm (log ε) 287 (4.58), 295 (4.61), 326 (3.60), 337 (3.59), 354 (3.56), 374 (3.66), 482 (3.02), and 570 (2.45, sh); ν_{max} / cm^{-1} 3204 ($C\equiv CH$) and 2099 ($C\equiv C$). *Anal.* Calcd for $C_{11}H_6NCl$: C, 70.42; H, 3.22; N, 7.47. Found: C, 70.33; H, 3.17; N, 7.41.

Reaction of 2-chloro-3-iodo-1-azaazulene with phenylacetylene

Under argon atmosphere, a mixture of 2-chloro-3-iodo-1-azaazulene (**1a**) (0.591 g, 2.04 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.060 g, 0.085 mmol), and copper(I) iodide (0.062 g, 0.326 mmol) in dry THF (10.0 mL) was stirred for 30 min at rt. To the mixture phenylacetylene (0.40 mL, 3.64 mmol) was added dropwise, followed by triethylamine (4.0 mL). After stirring for 48 h, water was added and the mixture was extracted with $CHCl_3$. The solvent was dried over Na_2SO_4 and evaporated. Chromatography of the residue with $CHCl_3$ to give 2-chloro-3-(phenylethynyl)-1-azaazulene (**2c**) (0.410g, 76%) and 2,3-di(phenylethynyl)-1-azaazulene (**3**) (0.078 g, 12%).

2c: Reddish purple needles (from hexane- CH_2Cl_2), mp 106-107 ℃; δ_H 7.31-7.39 (3H, m, H-*mp*-phenyl), 7.61 (2H, dm, *J* 6,9, H-*o*-phenyl), 7.65 (1H, dd, *J* 10.1 and 9.7, H-5), 7.71 (1H, t, *J* 9.9, H-7), 7.83 (1H, dddd, *J* 10.1, 9.9, 0.7, and 0.4, H-6), 8.46 (1H, dd, *J* 9.7 and 0.7, H-4), and 8.50 (1H, dd, *J* 9.9 and 0.4, H-8); δ_C 80.04, 98.07, 107.30, 123.05, 128.39, 128.42, 130.36, 131.25, 131.46, 134.80, 136.24, 139.06, 146.48, 155.25, and 158.53; λ_{max} ($CHCl_3$) nm (log ε) 290 (4.43, sh), 305 (4.56), 317 (4.52), 380 (3.97), 395 (3.90, sh), and 511 (3.07); ν_{max} / cm^{-1} 2202 ($C\equiv C$). *Anal.* Calcd for $C_{17}H_{10}NCl$: C, 77.42; H, 3.82; N, 5.31. Found: C, 77.51; H, 3.90; N, 5.28.

3: Reddish purple needles (from hexane- CH_2Cl_2), mp 151-152 ℃; δ_H 7.33-7.43 (6H, m, H-*mp*-phenyl), 7.66 (2H, dm, *J* 8.2, H-*o*-phenyl), 7.71 (1H, dd, *J* 9.9 and 9.5, H-5), 7.72 (2H, dm, *J* 7.8, H-*o*-phenyl), 7.77 (1H, dd, *J* 9.8 and 9.7, H-7), 7.83 (1H, dd, *J* 9.9 and 9.8, H-6), 8.62 (1H, d, *J* 9.5, H-4), and 8.68 (1H, d, *J* 9.7, H-8); δ_C 81.61, 86.03, 97.94, 99.50, 112.98, 122.46, 123.61, 128.30, 128.49, 128.51, 129.44, 129.74, 131.04, 131.53, 132.41, 135.60, 137.00, 139.13, 146.72, 151.83, and 157.82; λ_{max} ($CHCl_3$) nm (log ε) 295 (4.43, sh), 345 (4.66), 390 (4.17), 410 (3.77, sh), and 558 (3.31); ν_{max} / cm^{-1} 2201 ($C\equiv C$). *Anal.* Calcd for $C_{25}H_{15}N$: C, 91.16; H, 4.59; N, 4.25. Found: C, 91.24; H, 4.52; N, 4.40.

Reaction of 2-bromo-3-chloro-1-azaazulene with phenylacetylene

Under argon atmosphere, a mixture of 2-bromo-3-chloro-1-azaazulene (**1d**) (0.201 g, 0.83 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.020 g, 0.028 mmol), and copper(I) iodide (0.010 g, 0.053 mmol) in dry THF (10.0 mL) was stirred for 30 min at rt. To the mixture phenylacetylene (0.23 mL, 2.09 mmol) was added dropwise, followed by triethylamine (1.0 mL). After stirring for 13 h, water was added and the mixture was extracted with CH_2Cl_2. The solvent was dried over Na_2SO_4 and evaporated. Chromatography of the residue with $CHCl_3$ to give 3-chloro-2-(phenylethynyl)-1-azaazulene (**4b**) (0.140 g, 64%)

4b: Reddish purple needles (from hexane- CH_2Cl_2), mp 89-90 ℃; δ_H 7.36-7.44 (3H, m, H-*mp*-phenyl), 7.69 (1H, like t, *J* 10.2, H-5), 7.67-7.74 (2H, m, H-*o*-phenyl), 7.76 (1H, like t, *J* 9.9, H-7), 7.87 (1H, like t, *J* 9.9, H-6), 8.44 (1H, d, *J* 9.8, H-4), and 8.57 (1H, d, *J* 9.7, H-8); δ_C 84.39, 100.35, 117.98, 122.13, 128.50, 129.24, 129.58, 130.28, 132.39, 133.81, 137.41, 139.18, 140.94, 147.12, and 156.05; λ_{max} ($CHCl_3$) nm (log ε) 261 (4.14, sh), 295 (4.44), 317 (4.39), 331 (4.53), 366 (4.15, sh), 375 (4.15), 394 (4.19), 532 (3.39), 538 (3.39), and 580 (3.14, sh); ν_{max} / cm^{-1} 2206 ($C\equiv C$). *Anal.* Calcd for $C_{17}H_{10}NCl$: C, 77.42; H, 3.82; N, 5.31. Found: C, 77.39; H, 3.78; N, 5.35.

Reaction of 2,3-dibromo-1-azaazulene with phenylacetylene

Under argon atmosphere, a mixture of 2,3-dibromo-1-azaazulene (**1e**) (0.203 g, 0.71 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.050 g, 0.07 mmol), and copper(I) iodide (0.020 g, 0.11 mmol) in dry THF (10.0 mL) was stirred for 30 min at rt. To the mixture phenylacetylene (0.20 mL, 1.8 mmol) was added dropwise, followed by triethylamine (1.0 mL). After stirring for 8 h, water was added and the mixture was extracted with CH_2Cl_2. The solvent was dried over Na_2SO_4 and evaporated.

Chromatography of the residue with $CHCl_3$ to give 3-bromo-2-(phenylethynyl)-1-azaazulene (**4c**) (0.135 g, 62%).

4c: Reddish purple needles (from hexane- CH_2Cl_2), mp 91-92 ℃; δ_H 7.36-7.44 (3H, m, H-*m,p*-phenyl), 7.71-7.74 (2H, m, H-*o*-phenyl), 7.73 (1H, t, *J* 9.9, H-5), 7.80 (1H, t, *J* 9.7, H-7), 7.88 (1H, dd, *J* 9.9 and 9.7, H-6), 8.44 (1H, d, *J* 9.9, H-4), and 8.59 (1H, d, *J* 9.7, H-8); δ_C 85.24, 99.89, 105.91, 122.17, 128.50, 129.57, 130.44, 132.41, 135.08, 137.07, 139.01, 142.98, 149.23, and 157.04; λ_{max} ($CHCl_3$) nm (log ε) 262 (4.16, sh), 296 (4.51), 316 (4.46), 331 (4.61), 369 (4.19, sh), 375 (4.21), 394 (4.29), 526 (3.46), 536 (3.47), and 578 (3.20, sh); ν_{max} / cm^{-1} 2206 (C≡C). *Anal.* Calcd for $C_{17}H_{10}NBr$: C, 66.26; H, 3.27; N, 4.55. Found: C, 66.45; H, 3.22; N, 4.37.

Reacrion of 2-bromo-1-azaazulene (1c)

Under argon atmosphere, a mixture of 2-bromo-1-azaazulene (**1c**) (0.100 g, 0.48 mmol), dichlorobis(triphenylphosphine)palladium(II) (0.01 g, 0.014 mmol), and copper(I) iodide (0.020 g, 0.11 mmol) in dry THF (4.0 mL) was stirred for 30 min at rt. To the mixture phenylacetylene (0.12 mL, 1.09 mmol) was added dropwise, followed by triethylamine (2.0 mL). After stirring for 14 h, water was added and the mixture was extracted with CH_2Cl_2. The solvent was dried over Na_2SO_4 and evaporated. Chromatography of the residue with $CHCl_3$ to give 2-(phenylethynyl)-1-azaazulene (**4a**) (0.050 g, 51%).

4a: Reddish purple needles (from hexane- CH_2Cl_2), mp 94-95 ℃; δ_H 7.30-7.40 (3H, m, H-*m,p*-phenyl), 7.53 (1H, s, H-3), 7.60 (1H, t, *J* 9.8, H-5), 7.63-7.68 (2H, m, H-*o*-phenyl), 7.74 (1H, dd, *J* 9.9 and 9.7, H-7), 7.83 (1H, dd, *J* 9.9 and 9.8, H-6), 8.45 (1H, d, *J* 9.8, H-4), and 8.65 (1H, d, *J* 9.7, H-8); δ_C 86.99, 96.01, 117.90, 122.50, 128.43, 129.14, 129.18, 129.98, 132.14, 135.41, 136.16, 137.92, 146.90, 149.97, and 157.89; λ_{max} ($CHCl_3$) nm (log ε) 283 (4.53), 321 (4.47), 368 84.25), 387 (4.30), 495 (3.41, sh), 507 (3.43), and 541 (3.16, sh); ν_{max} / cm^{-1} 2202 (C≡C). *Anal.* Calcd for $C_{17}H_{11}N$: C, 89.06; H, 4.84; N, 6.11. Found: C, 89.34; H, 4.63; N, 6.08.

Halogenation of 2-(phenylethynyl)-1-azaazulene

A mixture of 2-(phenylethynyl)-1-azaazulene (**4a**) (0.111 g, 0.48 mmol) , NCS (0.091 g, 0.680 mmol), and dibenzoylperoxide (0.005 g) in $CHCl_3$ was stirred for 48 h. To the mixture water was added, and the mixture was extracted with $CHCl_3$. The extract was washed with aq. $NaHSO_3$ solution, then the solvent was dried over Na_2SO_4 and evaporated. Chromatography of the residue with $CHCl_3$ gave 3-chloro-2-(phenylethynyl)-1-azaazulene (**4b**) (0.072 mg, 62%).

In a similar manner, reaction of **4a** with NBS gave 3-bromo-2-(phenylethynyl)-1-azaazulene (**4c**) in 65% yield.

Synthesis of 1,2-bis(2-chloro-1-azaazulen-3-yl)acetylene (5)

Under argon atmosphere, a mixture of 2-chloro-3-iodo-1-azaazulene (**1a**) (0.064 g, 0.221 mmol), 2-chloro-3-ethynyl-1-azaazulene (0.039 g, 0.208 mmol), tetrakis(triphenylphosphine)palladium (0.010 g, 0.014 mmol), and copper(I) iodide (0.015 g, 0.079 mmol) in dry THF (20.0 mL) was stirred for 18 h at rt. To the mixture 10% NH_4Cl solution was added and the mixture was extracted with CH_2Cl_2. The extract was dried over

Na_2SO_4 and evaporated. Chromatography of the residue with $CHCl_3$ gave 1,2-bis(2-chloro-1-azaazulen-3-yl)acetylene (**5**) (0.043 g, 59%).

5: Reddish brown needles (from $CHCl_3$-EtOAc), mp 181-189 ℃ (decomp); δ_H 7.86 (2H, dd, *J* 9.7 and 9.5, H-5, 5'), 7.88 (2H, t, *J* 9.7, H-7, 7'), 7.98 (2H, t, *J* 9.7, H-6, 6'), 8.62 (2H, d, *J* 9.5, H-4, 4'), and 8.78 (2H, d, *J* 9.7, H-8, 8'); δ_C 88.79, 107.63, 130.71, 131.52, 135.27, 136.58, 139.28, 146.56, and 158.80; λ_{max} ($CHCl_3$) nm (log ε) 268 (4.48), 290 (4.47, sh), 307 (4.58, sh), 315 (4.63), 405 (4.26), 430 (4.29), and 511 (3.42). *Anal.* Calcd for $C_{20}H_{10}N_2Cl_2$: C, 68.79; H, 2.89; N, 8.02. Found: C, 68.74; H, 3.06; N, 7.90.

Synthesis of 1,4-bis(2-chloro-1-azaazulen-3-yl)-1,3-butadiyne (6)

a) A mixture of 2-chloro-3-(trimethylsilylethynyl)-1-azaazulene (**2a**) (0.051 g, 0.196 mmol) and copper(I) chloride (0.028 g, 0.283mmol) in DMF (0.5 mL) was stirred for 6 h at 60 ℃. The solution was acidified with 1M HCl and the mixture was extracted with CH_2Cl_2. The extract was washed with aq.$NaHCO_3$ and was dried over Na_2SO_4 and evaporated. Chromatography of the residue with $CHCl_3$ gave 1,4-bis(2-chloro-1-azaazulen-3-yl)-1,3-butadiyne (**6**) (0.026 g, 71%).

b) A mixture of 2-chloro-3-ethynyl-1-azaazulene (**2b**) (0.047 g, 0.250 mmol) and copper(I) chloride (0.019 g, 0.192mmol) in DMF (0.5 mL) was stirred for 6 h at rt. The solution was acidified with 1M HCl and the mixture was extracted with CH_2Cl_2. The extract was washed with aq.$NaHCO_3$ and was dried over Na_2SO_4 and evaporated. Chromatography of the residue with $CHCl_3$ gave **6** (0.026 g, 56%).

6: Reddish brown needles (from EtOH-EtOAc), mp 161-162 ℃; δ_H (CF_3CO_2D) 8.67 (2H, dd, *J* 10.0 and 9.9, H-5, 5'), 8.69 (2H, dd, *J* 10.0 and 9.9, H-7, 7'), 8.82 (2H, t, *J* 9.9, H-6, 6'), 9,14 (H, d, *J* 10.0, H-4, 4'), and 9.35 (2H, d, *J* 10.0, H-8, 8'); δ_C (CF_3CO_2D) 109.02, 136.94, 141.43, 141.72, 144.37, 147.22, 147.29, 148.45, 149.69; λ_{max} ($CHCl_3$) nm (log ε) 261 (4.52), 283 (4.60), 299 84.64), 313 (4.69), 326 (4.45, sh), 384 (4.27, sh), 402 (4.37), 430 (4.23), 486 (3.50), and 574 (3.11, sh); ν_{max} / cm^{-1} 2186 and 2136 ($C\equiv C$). *Anal.* Calcd for $C_{22}H_{10}N_2Cl_2 \cdot 0.8C_2H_5OH$: C, 69.32; H, 3.62; N, 6.74. Found: C, 69.52; H, 3.44; N, 6.70.

Synthesis of 1-thia-9-azacyclopent[*a*]azulene (7b)

A solution of 2-chloro-3-(trimethylsilylethynyl)-1-azaazulene (0.124 g, 0.477 mmol) and sodium hydrosulfide (0.102 g, 1.82 mmol) in EtOH (8 mL) was heated under reflux for 4 h, then evaporated. To the residue water was added, then the solution was neutralized with 2M HCl, and the mixture was extracted with CH_2Cl_2. The solvent was dried over Na_2SO_4 and evaporated. Chromatography of the residue with hexane-EtOAc (3 : 1) gave 1-thia-9-azacyclopent[*a*]azulene (**7b**) (0.066 g, 75%).

7b: Reddish purple needles (from hexane-$CHCl_3$), mp 94-95 ℃ (lit.[22] mp 94-95 ℃); δ_H 7.31 (1H, d, *J* 5.6, H-2), 7.52 (1H, d, *J* 5.6, H-3), 7.65 (1H, ddd, *J* 10.3, 9.8, and 0.7, H-5), 7.76 (1H, ddd, *J* 10.3, 9.9 and 0.7, H-7), 7.85 (1H, dddd, *J* 9.9, 9.8, 0.8, and 0.7, H-6), 8.62 (1H, dd, *J* 10.3 and 0.7, H-4), and 8.69 (1H, ddd, *J* 10.3, and 0.8, H-8); δ_C 116.72, 125.49, 128.28, 129.08, 131.33, 131.95, 135.29, 136.61, 137.11, 161.61, and 171.80; λ_{max} ($CHCl_3$) nm (log ε) 274 (4.31), 307 (4.68), 326 (4.25), 357 (3.829, 387 (3.47), 528 (2.62), 570 (2.49, sh), 622 (2.12, sh); *m/z* (rel intensity) 185 (M^+, 100). *Anal.* Calcd for $C_{11}H_7NS$: C, 71.32; H, 3.81 N, 7.56. Found: C, 71.41; H, 4.00; N, 7.28.

Synthesis of 2-phenyl-1-thia-9-azacyclopent[*a*]azulene (7c)

A solution of 2-chloro-3-(phenylethynyl)-1-azaazulene (0.082 g, 0.31 mmol) and sodium hydrosulfide (0.10 g, 1.78 mmol) in EtOH (8 mL) was heated under reflux for 4 h, then evaporated. To the mixture water was added, then the mixture was neutralized with 2M HCl, and extracted with CH_2Cl_2. The solvent was dried over Na_2SO_4 and evaporated. Chromatography of the residue with hexane-EtOAc(3 : 1) gave 2-phenyl-1-thia-9-azacyclopent[*a*]azulene (**7c**) (0.059 g, 73%).

7c: Purple needles (from MeCN-EtOH), mp 145-146 ℃; δ_H 7.31 (1H, dd, *J* 7.4 and 0.9, H-*p*-phenyl), 7.42 (2H, dd, *J* 7.8 and 7.4, H-*m*-phenyl), 7.67 (1H, t, *J* 9.8, H-5), 7.72 (1H, s, H-3), 7.73 (2H, *J* 7.8 and 0.9, H-*o*-phenyl), 7.76 (1H, dd, *J* 9.9 and 9.8, H-7), 7.87 (1H, t, *J* 9.8, H-6), 8.64 (1H, d, *J* 9.8, H-4), and 8.67 (1H, d, *J* 9.9, H-8); δ_C 111.90, 126.06, 127.91, 128.21, 129.01, 129.23, 132.21, 132.45, 135.11, 136.87, 137.02, 144.01, 161.35, and 171.45; λ_{max} ($CHCl_3$) nm (log ε) 324 (4.77), 334 (4.76), 357(4.01, sh), 399 (4.04), 411 (4.00, sh), 537 (2.84), 557 (2.85), 602 (2.68, sh), and 660 (2.16, sh). *Anal.* Calcd for $C_{17}H_{11}NS$: C, 78.13; H, 4.24; N, 5.36. Found: C, 77.94; H, 4.18; N, 5.15.

Synthesis of 2,2'-bis(1-thia-9-azacyclopent[*a*]azulene) (8)

A solution of 1,4-di(2-chloro-1-azaazulen-3-yl)-1,3-butadiyne (**6**) (0.029 g, 0.083 mmol) and sodium hydrosulfide (0.030 g, 0.54 mmol) in EtOH (8 mL) was heated under reflux for 5 h, then evaporated. To the residue water was added, then the solution was neutralized with 2M HCl, and the mixture was extracted with dichloromethane. The solvent was dried over Na_2SO_4 and evaporated. Chromatography of the residue with hexane-ethyl acetate (3 : 1) gave 2,2'-bis(1-thia-9-azacyclopent[*a*]azulene) (**8**) (0.018 g, 59%).

8: Green needles (from $CHCl_3$-EtOAc), mp >300 ℃; δ_H (CF_3CO_2D) 8.13 (2H, s, H-3, 3'), 8.67 (2H, dd, *J* 10.0 and 9.9, H-5, 5'), 8.69 (2H, dd, *J* 10.0 and 9.9, H-7, 7'), 8.62 (2H, t, *J* 9.9, H-6, 6'), 9.14 (2H, d, *J* 10.0, H-4, 4'), and 9.35 (2H, d, *J* 10.0, H-8, 8'); δ_C (CF_3CO_2D) 116.66, 133.93, 135.47, 138.19, 139.80, 139.96, 140.27, 142.35, 147.10, 153.74, and 156.78; λ_{max} ($CHCl_3$) nm (log ε) 282 (4.20), 303 (4.23), 353 (4.70), 401 (4.23, sh), 441 (4.49), 555 (3.54), 577 (3.54), and 632 (3.38, sh). *Anal.* Calcd for $C_{22}H_{12}N_2S_2$: C, 71.71; H, 3.28 N, 7.60. Found: C, 71.63; H, 3.34; N, 7.48

X-Ray structure determination

Crystal data of 7c: Red platelet, $C_{17}H_{11}NS$, M = 261.34, orthorhombic, space group $Pca2_1$, a = 21.2179(5), b = 5.92811(10), c = 7.61454(10) Å, V = 1228.61(3) Å^3, Z = 4, D_{calcd} = 1.413 g/cm^3, crystal dimensions 0.20 x 0.20 x 0.03 mm. Data were measured on a Rigaku PAXIS-RAPID radiation diffractometer with graphite-monochromated Cu-Kα radiation (λ = 154187 Å). The data were collected at a temperature −180 ± 1 ℃ to a maximum 2θ of 136.5°. A sweep of data was done using ω scan from 80.0 to 260.0° in 30.0° step. Of the 9625 reflections that was collected, 2132 were unique. The structure was solved by direct methods and expanded using Fourier techniques, and refined by a full-matrix least-squares method using 173 variables refined with 2132 reflections [$I > 2\sigma(I)$]. The non-hydrogen atoms were anisotropically. The final refinement converged to R = 0.0349 and Rw = 0.0903.

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