SYNTHESIS AND REACTIONS OF 3- AND 8-ETHYNYL-1-AZAAZULENES

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Abstract — 3-Iodo-1-azaazulenes were easily ethynylated by Sonogashira-Hagihara reaction to give 3-ethynyl-1-azaazulenes. Cyclization of 2-amino-3-ethynyl-1-azaazulene was achieved by heating in the presence of copper(II) acetate or copper(II) trifluoromethanesulfonate, and 1,9-diaza-1*H*-cyclopent[*a*]azulene derivatives were obtained. Reaction of 2-chloro-1-azaazulene with lithium phenylacetylide gave 3-chloro-1-(2-chloro-1-azaazulen-8-yl)-2-phenyl-2a-aza-2*H*-cyclopent[*cd*]azulene together with 2-chloro-8-phenylethynyl-1-azaazulene.

INTRODUCTION

The chemistry of azaazulenes is of interest for their physical and chemical properties as well as physiological properties.[1] It is known that 2-ethynylaniline easily cyclized to give substituted indoles.[2—5] Therefore, it is considered that an introduction of acetylenic substituent to azaazulene ring would bring a new type of hetero-fused azaazulenes. Although synthesis of some ethynylazulenes are appeared[6—8] and known as useful species for the construction of fused azulene systems in the chemistry of azulenes,[7,8] no report is appeared for the synthesis of ethynylazaazulenes so far. As a continuation of our studies on the preparation of new azaazulene-fused heterocycles,[1] we examined the synthesis of ethynyl-1-azaazulenes. Sonogashira-Hagihara reaction[9] is a well-known superior method for the synthesis of disubstituted acetylenes from aryl halide with terminal acetylene. Therefore we performed the reaction for introducing ethynyl group to C-3 on 1-azaazulene nuclei by Sonogashira-Hagihara reaction at first. It is known that reaction of alkyllithium reagent mainly added to 8-position on 1-azaazulene nuclei.[10—14] Therefore, we next investigated the reaction of lithium acetylide with 2-chloro-1-azaazulene.

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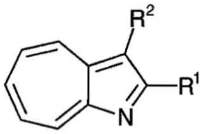
† Dedicated to Professor A. I. Meyers on occasion of his 70th birthday.

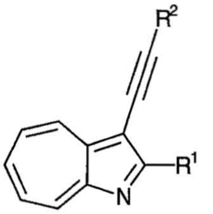
RESULTS AND DISCUSSION

Treatment of 2-chloro-3-iodo-1-azaazulene (**1b**), prepared from 2-chloro-1-azaazulene (**1a**) and *N*-iodosuccinimide (NIS) in a good yield, with trimethylsilylacetylene in the presence of dichlorobis(triphenylphosphine)palladium(II)—copper(I) iodide for 3 h gave 2-chloro-3-trimethylsilylethynyl-1-azaazulene (**2a**) in 85% yield. Similarly, the reactions of 2-amino-3-iodo-1-azaazulene (**1d**), prepared from 2-amino-1-azaazulene (**1c**) and NIS, with phenylacetylene or trimethylsilylacetylene were performed, and the corresponding 2-amino-3-ethynyl-1-azaazulenes (**2b** and **2c**) were obtained in 90 and 98% yields, respectively.

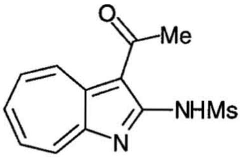
Compounds (**2b** and **2c**) were easily mesylated by the treatment with methanesulfonyl chloride to give **2d** and **2e** in 34 and 88% yields, respectively. When 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (**2e**) was heated in DMF, a hydrolysis of ethynyl moiety occurred and 3-acetyl-2-mesylamino-1-azaazulene (**3**) was obtained in 60% yield.



1a : R^1 = Cl, R^2 = H
1b : R^1 = Cl, R^2 = I
1c : R^1 = NH_2, R^2 = H
1d : R^1 = NH_2, R^2 = I



2a : R^1 = Cl, R^2 = TMS
2b : R^1 = NH_2, R^2 = Ph
2c : R^1 = NH_2, R^2 = TMS
2d : R^1 = NHMs, R^2 = Ph
2e : R^1 = NHMs, R^2 = TMS
2f : R^1 = NHMs, R^2 = H



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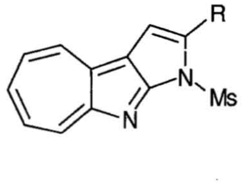


4a : R = Ph
4b : R = TMS
4c : R = H

We next investigated the cyclization of 2-amino-3-ethynyl-1-azaazulenes (**2b**—**2e**). It is known that 2-ethynylaniline derivatives cyclized to substituted indole derivatives.[2—5] According to the method by Jose,[4] 2-amino-3-trimethylsilylethynyl-1-azaazulene (**2c**) was treated with copper(I) iodide in DMF, but the reaction showed a complex feature and no distinct product was obtained. It is also known that 2-trimethylsilylethynyl-*N*-mesylaniline derivatives afforded substituted indole derivatives,[5] but a similar treatment of 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (**2e**) with potassium in refluxing acetonitrile did not react. Treatment of **2e** with tetrabutylammonium fluoride (TBAF) did not cyclize and produced 3-ethynyl-2-mesylamino-1-azaazulene (**2f**) in 51% yield.

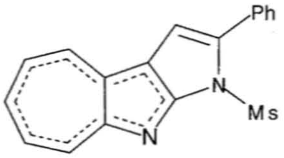
Cyclizations of the 3-ethynyl-1-azaazulene derivatives (**2d**—**2f**) were achieved in the presence of the Lewis acid catalyst, such as copper(II) acetate and copper(II) trifluoromethanesulfonate. Thus the treatment of **2d** in the presence of the Lewis acid gave 1-mesyl-2-phenyl-1,9-diaza-1*H*-cyclopenta[*a*]azulene (**4a**). Similar reaction of **2e** or **2f** gave 1-mesyl-1,9-diaza-1*H*-cyclopenta[*a*]azulene (**4c**), where **4b** was not obtained; in the reaction of **2e**, trimethylsilyl group was eliminated. Results were listed in Table 1.

Table 1. Cyclization reactions of 3-ethynyl-2-mesylamino-1-azaazulenes (**2d**—**2f**).

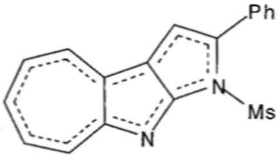
Run	Compound	Catalyst (equiv.)	Time / h	Product	Yield / %
1	**2d**	$Cu(OAc)_2$ (0.1)	84	**4a**	trace
2	**2d**	$Cu(OAc)_2$ (0.2)	84	**4a**	2
3	**2d**	$Cu(OAc)_2$ (1.0)	84	**4a**	19
4	**2d**	$Cu(OTf)_2$ (0.1)	74	**4a**	31
5	**2d**	$Cu(OTf)_2$ (0.2)	72	**4a**	49
6	**2d**	$Cu(OTf)_2$ (1.0)	4	**4a**	49
7	**2e**	$Cu(OTf)_2$ (1.0)	4	**4c**	31
8	**2f**	$Cu(OTf)_2$ (1.0)	2	**4c**	12

The compound (**4a**) was analyzed as $C_{18}H_{14}N_2O_2S$ from its MS (*m/z* 322, M^+) and elemental analysis. In the ^1H NMR spectrum of **4a**, a 1H signal attributed to H-3 was observed at δ 6.87 as a singlet together with a methyl singlet (δ 3.25), five seven-membered ring protons, and phenyl signals. A signal attributed to trimethylsilyl group was not observed. From the results, the compound (**4a**) was deduced as 1-mesyl-2-phenyl-1,9-diaza-1*H*-cyclopent[*a*]azulene, and confirmed by X-Ray structure analysis. The ORTEP drawing[15] of **4a** is shown in Figure 1. The structure of **4c** was deduced by the comparison of its spectral data with those of **4a**.

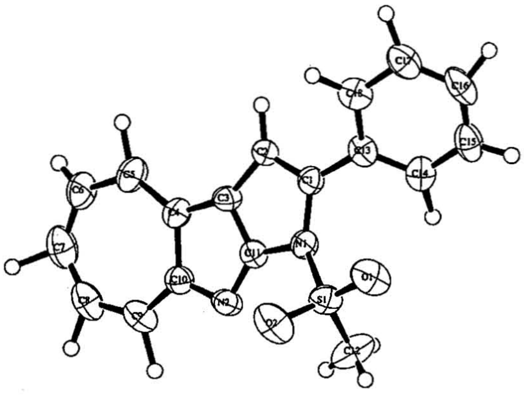
In the bond lengths of **4a**, as shown in Figure 2, a bond-alternation of the seven-membered ring is not observed (1.38—1.39 Å). The bondlengths of N(1)—C(2) (1.44 Å) and C(3)—C(3a) (1.43 Å) are adequate to sp^2—sp^2 single bond. From the results, it is considered that the compound (**4a**) has a styrylazulene structure (**A**) rather than a peripheral 14π structure (**B**).



A



B



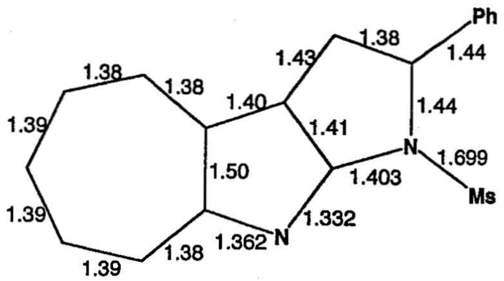


Figure 1. An ORTEP drawing of **4a** with thermal ellipsoids (50% probability).

Figure 2. Bond lengths of **4a** (Å).

We next tried to synthesize 8-ethynyl-1-azaazulenes by Sonogashira-Hagihara reaction of 8-bromo-3-phenyl-1-azaazulene, but the reaction did not proceed. Therefore we examined the synthesis of 8-ethynyl-1-azaazulenes by addition-elimination reaction of 1-azaazulene with an acetylide.

Treatment of **1a** with lithium phenylacetylide, prepared from butyl lithium and phenylacetylene, and a subsequent treatment of water and tetrachloro-1,4-benzoquinone (chloranil) gave 2-chloro-8-phenylethynyl-1-azaazulene (**5**) (13%) and 3-chloro-1-(2-chloro-1-azaazulen-8-yl)-2-phenyl-2a-aza-2*H*-cyclopent[*cd*]azulene (**6**) (86%). Compound (**6**) was analyzed as 2 : 1 adduct from its MS (*m/z* 426, M^+) and elemental analysis, and the structure of **6** was determined by X-Ray structure analysis. The ORTEP drawing[15] of **6** is shown in Figure 3.

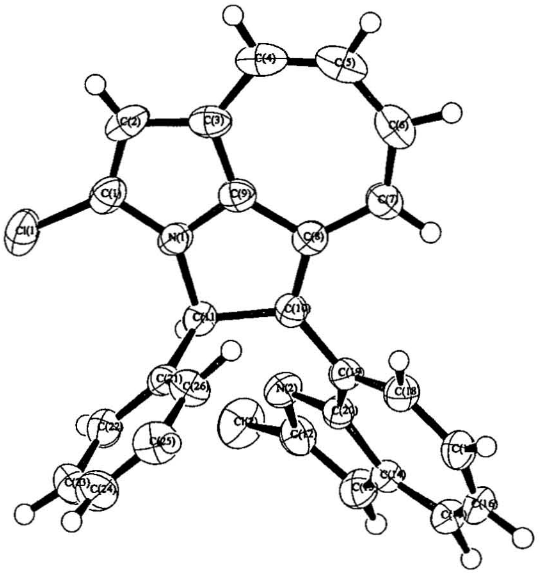
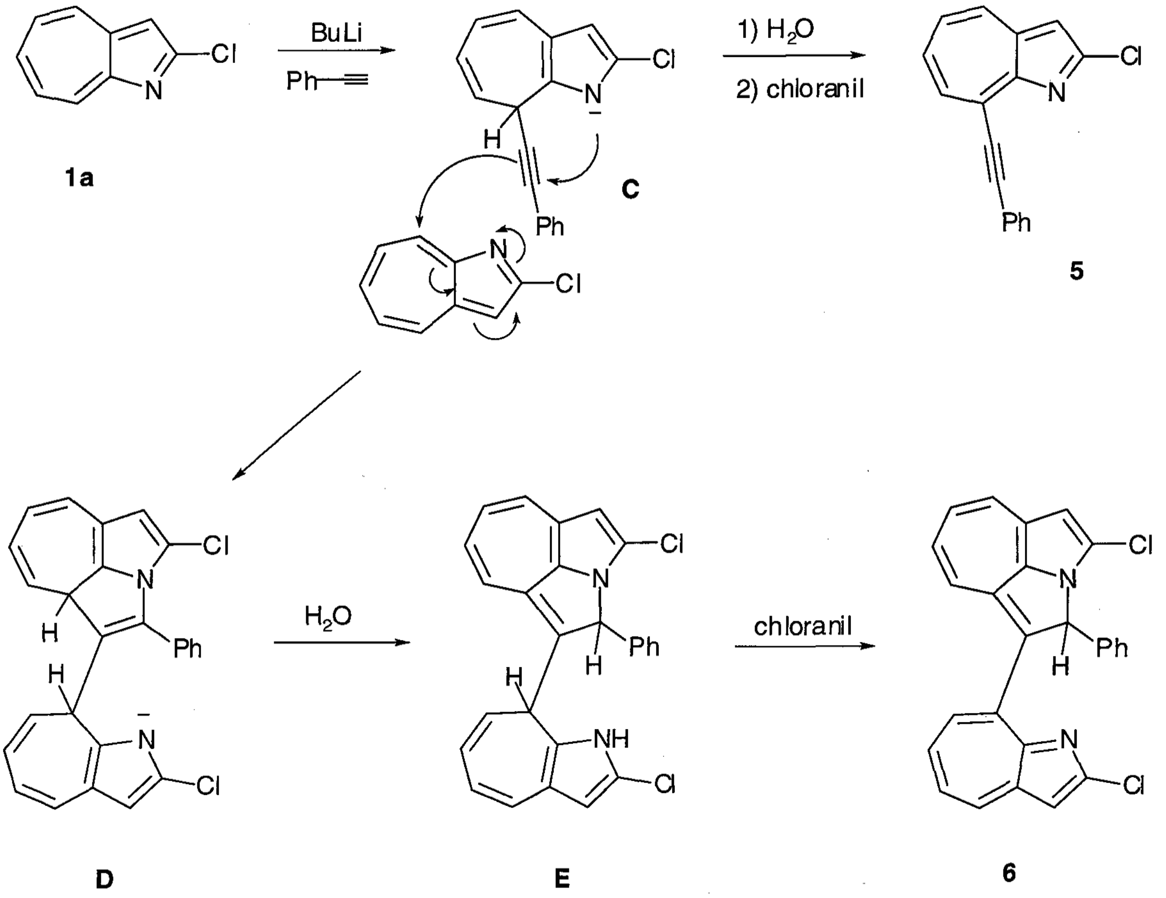


Figure 3. An ORTEP drawing of **6** with thermal ellipsoids (50% probability).

A plausible mechanism is shown in the Scheme 1. An attack of phenylacetylide to C-8 on **1a** produces the intermediate (**C**). Quenching of **C** with water and successive dehydrogenation affords **5**. Reaction of **C** with another molar of **1a**, attending by cyclization, gives **D**. Quenching of **D** with water and a successive dehydrogenation furnishes **6**.



Scheme 1

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 Impact 410. 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 (**1b**) (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 tetrahydrofuran (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, 40.00 mmol). After stirring for 48 h, water was added and the mixture was extracted with dichloromethane. The solvent was dried over sodium sulfate and evaporated. The residue was chromatographed on silica gel column with ethyl acetate—hexane (1 : 1) to give 2-chloro-3-trimethylsilylethynyl-1-azaazulene (**2a**) (0.448 g, 85%).

In a similar manner, 2-amino-3-phenylethynyl-1-azaazulene (**2b**) and 2-amino-3-trimethylsilylethynyl-1-azaazulene (**2c**) were obtained from 2-amino-1-azaazulene (**1b**) in 90 and 98% yields, respectively.

2a: Yellow powder (from hexane-dichloromethane), mp 81—82 ℃; δ_H 0.30 (9H, s), 7.75 (1H, dd, *J* 10.3 and 9.9), 7.81 (1H, dd, *J* 9.9 and 9.8), 7.92 (1H, dd, *J* 10.3 and 9.6), 8.55 (1H, d, *J* 9.6) and 8.56 (1H, d, *J* 9.8); 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; ν_{max} / cm^{-1} 2141 (C≡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.

2b: Red needles (from hexane-chloroform), mp 164—165 ℃; δ_H 5.85 (2H, br s), 7.31—7.59 (8H, m), 7.94 (1H, d, *J* 9.6) and 8.13 (1H, d, *J* 9.7); δ_C 81.2, 94.0, 98.4, 123.6, 127.3, 128.0, 128.3, 128.4, 130.1, 131.3, 131.6, 131.7, 148.1, 158.9, and 168.4; ν_{max} / cm^{-1} 3463, 3292 (NH), and 2186 (C≡C); *m/z* (rel intensity) 244 (M$^+$, 100), 219 (9), 189 (6), and 122 (7). *Anal.* Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.55; H, 5.01; N, 11.44.

2c: Red prisms (from hexane-dichloromethane), mp 197—199 ℃; δ_H 0.31 (9H, s), 5.71 (2H, br s), 7.38 (1H, dd, *J* 10.0 and 9.7), 7.44 (1H, dd, *J* 9.7 and 9.6), 7.51 (1H, t, *J* 9.7), 7.92 (1H, d, *J* 9.6) and 8.03 (1H, d, *J* 10.0); δ_C 0.30, 94.0, 96.9, 103.6, 127.4, 128.2, 130.2, 131.6, 131.7, 148.7, 158.7, and 168.7; ν_{max} / cm^{-1} 3464, 3295 (NH), and 2141 (C≡C); *m/z* (rel intensity) 240 (M$^+$, 100), 225 (95), 209 (19), 195 (19), 181 (15), 113 (12), and 105 (37). *Anal.* Calcd for $C_{14}H_{16}N_2Si$: C, 69.95; H, 6.71; N, 11.65. Found: C, 69.91; H, 6.67; N, 11.69.

Synthesis of 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (2e)

Under argon atmosphere, to the solution of 2-amino-3-trimethylsilylethynyl-1-azaazulene (**2c**) (0.030 g, 0.13 mmol) in tetrahydrofuran (2.0 mL) on ice bath methanesulfonyl chloride (0.02 mL, 0.14 mmol) and triethylamine (0.02 mL, 0.27 mmol) were added, successively, and the mixture was stirred for 2 h under cooling, then stirred for 6 h at rt. The mixture was quenched with water and extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated. Chromatography of the residue with ethyl acetate gave 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (**2e**) (0.035 g, 88%).

In a similar manner, 2-mesylamino-3-phenylethynyl-1-azaazulene (**2d**) was obtained in 34% yield together with recovered (**2c**) in 32% yield.

2d: Red needles (from hexane-chloroform), mp 228—230 ℃; δ_H 3.18 (3H, s), 7.23 (1H, dd, *J* 9.1 and

2.7), 7.31—7.39 (6H, m), 7.59—7.62 (2H, m), 8.01 (1H, d, *J* 10.8), and 11.0 (1H, br); δ_C (DMSO-d$_6$) 42.0, 55.3, 81.5, 98.1, 99.1, 121.1, 123.0, 129.0, 129.1, 130.9, 131.6, 134.2, 135.0, 135.1, 144.9, and 158.1; ν_{max} / cm^{-1} 3251 (NH), and 2202 (C≡C); *m/z* (rel intensity) 322 (M$^+$, 100), 287 (10), 243 (81), 216 (35), and 189 (13). *Anal.* Calcd for $C_{18}H_{14}N_2O_2S$: C, 67.06; H, 4.38; N, 8.69. Found: C, 67.12; H, 4.34; N, 8.62.

2e: Red plates (from hexane-dichloromethane), mp 184—187 ℃; δ_H 0.29 (9H, s), 3.16 (3H, s), 7.24 (1H, dd, *J* 9.9 and 9.2), 7.36 (1H, dd, *J* 9.9 and 9.8), 7.37 (1H, dd, *J* 10.8 and 9.8), 7.51 (1H, d, *J* 9.2), 7.91 (1H, d, *J* 10.8) and 11.11 (1H, br s); δ_C 0.10, 42.5, 94.7, 101.2, 105.1, 119.4, 131.4, 133.3, 133.7, 133.8, 144.8, 145.8, and 158.9; ν_{max} / cm^{-1} 3443 (NH), and 2142 (C≡C); *m/z* (rel intensity) 318 (M$^+$, 100), 303 (43), 240 (44), 225 (65), 209 (76), and 181 (45). *Anal.* Calcd for $C_{15}H_{18}N_2SSi$: C, 56.57; H, 5.70; N, 8.80. Found: C, 56.73; H, 5.91; N, 8.63.

Hydrolysis of 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (2e)

Under argon atmosphere, a solution of 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (**2e**) (0.050 g, 0.21 mmol) in DMF (2.0 mL) in a sealed tube was heated at 120 ℃ for 28 h. To the solution water was added, and the mixture was extracted with ethyl acetate. The extract was dried over sodium sulfate and evaporated. Chromatography of the residue with ethyl acetate—hexane (1 : 1) gave 3-acetyl-2-mesylamino-1-azaazulene (**3**) (0.033 g, 60%).

3: Yellow needles (from chloroform), mp 251—255 ℃; δ_H 2.73 (3H, s), 3.18 (3H, s), 7.61 (1H, dd, *J* 9.8 and 9.7), 7.70 (1H, dd, *J* 9.6 and 9.0), 7.79 (1H, dd, *J* 9.7 and 9.6), 7.80 (1H, d, *J* 9.8), 9.53 (1H, d, *J* 9.0), and 11.30 (1H, br s); δ_C 31.8, 42.4, 110.4, 124.6, 133.2, 136.8, 137.6, 139.1, 145.3, 147.8, 157.2, and 195.0; ν_{max} / cm^{-1} 1665 (C=O); *m/z* (rel intensity) 264 (M$^+$, 15), 249 (12), 185 (100), 171 (15), 157 (18), 115 (17), and 89 (7). *Anal.* Calcd for $C_{15}H_{18}N_2SSi$: C, 54.53; H, 4.58; N, 10.60. Found: C, 54.64; H, 4.60; N, 10.44.

Reaction of 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (2e) with TBAF

Under argon atmosphere, a solution of 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (**2e**) (0.036 g, 0.15 mmol) and TBAF (0.08 mL, 0.30 mmol) in THF (2.0 mL) was stirred for 2 h at room temperature. To the mixture water was added, and the mixture was extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated. Chromatography of the residue with ethyl acetate—hexane (1 : 1) gave 2-mesylamino-3-ethynyl-1-azaazulene (**2f**) (0.019 g, 51%).

2f: Red powder (from hexane-chloroform), mp 160 ℃ (decomp); δ_H 3.17 (3H, s), 3.64 (1H, s), 7.27—7.31 (1H, m), 7.35—7.43 (3H, m), 7.98 (1H, d, *J* 10.9), and 10.99 (1H, br s); δ_C 43.0, 74.4, 87.5, 98.9, 119.5, 131.6, 133.8, 134.1, 134.5, 144.8, 146.5, and 159.7. *Anal.* Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09; N, 11.37. Found: C, 58.49; H, 4.22; N, 11.32.

Cyclizations of 2-mesylamino-3-phenylethynyl-1-azaazulene (2d) and 2-mesylamino-3-trimethylsilylethynyl-1-azaazulene (2e)

Typical procedure — A mixture of 2-mesylamino-3-phenylethynyl-1-azaazulene (**2d**) (0.081 g, 0.25 mmol) and copper(II) trifluoromethanesulfonate (0.072 g, 0.25 mmol) in dichloroethane (5.0 mL) was refluxed for 4 h. Water was added to the mixture, and the mixture was extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated. Chromatography of the residue with chloroform gave 1-mesyl-2-phenyl-1,9-diaza-1*H*-cyclopent[*a*]azulene (**4a**) (0.040 g, 49%).

In a similar manner, the reaction of **2d**, **2e** and **2f** were performed in the presence of copper(II) trifluoromethanesulfonate or copper(II) acetate. The results were listed in Table 1.

4a: Yellow needles (from chloroform), mp 173—176 ℃; δ_H 3.25 (3H, s), 6.87 (1H, s), 7.43—7.64 (3H, m), 7.61—7.64 (2H, m), 7.73 (1H, dd, *J* 9.8 and 9.6), 7.83 (1H, t, *J* 9.8), 7.93 (1H, t, *J* 9.8), 8.68 (1H, d, *J* 9.6), and 8.89 (1H, d, *J* 9.8); δ_C 42.2, 106.9, 118.1, 128.2, 128.7, 129.1, 129.7, 130.5, 132.7, 133.2, 135.6, 136.7, 137.0, 143.1, 161.1, and 163.7; *m/z* (rel intensity) 322 (M^+, 26), 243 (100), 216 (13), 189 (7), and 113 (9). *Anal.* Calcd for $C_{18}H_{14}N_2O_2S$: C, 67.06; H, 4.38; N, 8.69. Found: C, 67.09; H, 4.44; N, 8.58.

4c: Red powder (from hexane-chloroform) , mp 136—138 ℃; δ_H 3.50 (3H, s), 6.92 (1H, d, *J* 3.8), 7.50 (1H, d, *J* 3.8), 7.80 (1H, dd, *J* 10.3 and 9.8), 7.88 (1H, t, *J* 9.8), 7.98 (1H, dd, *J* 10.3 and 10.0), 8.73 (1H, d, *J* 9.8), and 8.90 (1H, d, *J* 10.0); δ_C 40.8, 102.8, 117.6, 125.4, 127.5, 128.3, 131.6, 134.9, 135.1, 135.4, 158.9, and 160.3; *m/z* (rel intensity) 246 (M^+, 95), 167 (100), 140 (69), 113 (24), and 89 (12). *Anal.* Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.52; H, 4.09; N, 11.37. Found: C, 58.56; H, 4.13; N, 11.22.

Reaction of 2-chloro-1-azaazulene (1a) with lithium phenylacetylide

To the solution of phenylacetylene (0.12 mL, 1.10 mmol) in dry THF (5.0 mL) at –90 ℃ (liquid N_2 / Et_2O) under argon was introduced slowly a solution of butyllithium (0.72 mL, 1.10 mmol), and the temperature was elevated to –30 ℃ with stirring for 3 h, then the solution was cooled to –90 ℃. Then 2-chloro-1-azaazulene (**1a**) (0.326 g, 2.00 mmol) was added to the mixture and stirring was continued for 10 h with raising the temperature to rt. The mixture was cooled to –90 ℃, water (1.0 mL) was added to the mixture, then stirring was continued for 2 h with raising the temperature to –30 ℃. The mixture was again cooled to –90 ℃, and tetrachloro-1,4-benzoquinone (chloranil) (0.246 g, 1.00 mmol) was added to the mixture. After stirring for 12 h with raising the temperature to rt, the mixture was poured to water and extracted with dichloromethane. The extract was dried over sodium sulfate and evaporated. Chromatography of the residue with benzene gave 3-chloro-1-(2-chloro-1-azaazulen-8-yl)-2-phenyl-2a-aza-2*H*-cyclopent[*cd*]azulene (**6**) (0.367 g, 86%) and 2-chloro-8-phenylethynyl-1-azaazulene (**5**) (0.071 g, 13%).

5: Red micro-needles (from hexane-dichloromethane) , mp 96—99 ℃; δ_H 7.22 (1H, s), 7.38—7.41 (3H, m), 7.57 (1H, dd, *J* 9.9 and 9.6), 7.73—7.75 (2H, m), 7.74 (1H, dd, *J* 10.8 and 9.6), 8.00 (1H, d, *J* 10.8), and 8.33 (1H, d, *J* 9.9); δ_C 89.8, 101.3, 113.1, 122.3, 128.3, 129.4, 129.5, 130.3, 132.4, 134.2, 134.3, 135.7, 146.0, 155.2, and 157.67; ν_{max} / cm^{-1} 2204 ($C\equiv C$); *m/z* (rel intensity) 263 (M^+, 95), 229 (100), 212 (5), 200 (86), 188 (11), 175 (27), 150 (24), 126 (15), 114 (83), 100 (62), 87(37), and 75 (32). *Anal.* Calcd for $C_{17}H_{10}NCl$: C, 77.42; H, 3.82; N, 5.31. Found: C, 77.34; H, 3.86; N, 5.30.

6: Blue-violet plates (from hexane-dichloromethane), mp >300 ℃; δ_H 5.79 (1H, dd, *J* 11.1 and 8.6), 6.00 (1H, s), 6.17 (1H, dd, *J* 11.7 and 8.6), 6.48 (1H, d, *J* 11.1), 6.59 (1H, d, *J* 11.7), 6.93—7.00 (6H, m), 7.18 (1H, dd, *J* 9.6), 7.40 dd, *J* 10.8 and 9.4), 7.67 (1H, d, *J* 11.1), 7.86 (1H, s), and 8.03 (1H, d, *J* 9.7); δ_C 50.3, 71.3, 108.9, 111.9, 117.7, 118.8, 118.9, 122.1, 123.5, 127.1, 127.2, 127.6, 127.7, 127.9, 128.8, 130.9, 131.0, 133.6, 133.8, 135.5, 136.3, 138.1, 141.6, 144.3, 145.2, and 150.7; *m/z* (rel intensity) 426 (M^+, 51), 391 (83), 355 (10), 264 (21), 248 (100), 228 (14), 163, (11), 147 (24), 87 (227), and 77 (10). *Anal.* Calcd for $C_{26}H_{16}N_2 Cl_2$: C, 73.08; H, 3.77; N, 6.56. Found: C, 73.05; H, 3.72; N, 6.64.

X-Ray structure determination

Crystal data of 4a: Black prism, $C_{29}H_{19}N_2O_2S$, M=322.38, orthorhombic, space group $Pca2_1$, a=17.322(3), b=6.047(3), c=14.665(3) Å, V=1536.1(7) Å^3, Z=4, D_{calcd}=1.394 g/cm^3, crystal dimensions 0.12 x 0.44 x 0.64 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. Total 2070 reflections were collected using ω–2θ scan technique with in a 2θ range of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using 207 variables refined with 968 reflections [$I > 2\sigma(I)$]. The weighting scheme $\omega = 4Fo^2/\sigma^2(Fo^2)$ gave satisfactory agreement analyses. The final refinement converged to R = 0.053 and Rw = 0.040.

Crystal data of 6: Black prism, $C_{29}H_{19}N_2Cl_2$, M=466.39, triclinic, space group P-1, a=11.228(4), b=11.946(6), c=9.938(3) Å, α=107.76(3)°, β=100.78(3)°, γ=62.15(3)°, V=1120.9(9) Å^3, Z=2, D_{calcd}=1.382 g/cm^3, crystal dimensions 0.66 x 0.64 x 1.00 mm. Data were measured on a Rigaku AFC 5S radiation diffractometer with graphite-monochromated Mo-Kα radiation. A total 5387 reflections (5140 unique) were collected using ω–2θ scan technique with in a 2θ range of 55.0°. The structure was solved by direct methods and refined by a full-matrix least-squares method using 470 variables refined with 2995 reflections [$I > 2\sigma(I)$]. The weighting scheme $\omega = 4Fo^2/\sigma^2(Fo^2)$ gave satisfactory agreement analyses. The final refinement converged to R = 0.047 and Rw = 0.035.

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