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SYNTESIS AND REACTIONS OF 3-ETYNYL-2-(TRIPHENYLPHOSPHOIMINO)-1-AZAAZULENES †

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Abstract – 3-(Trimethylsilylethynyl)- and 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulenes were synthesized by the Appel reaction of the corresponding 2-amino-3-ethynyl-1-azaazulenes. Reaction of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene (**8b**) with $Cu(OTf)_2$ gave 3-(2-oxophenethyl)-2-(triphenylphosphoimino)-1-azaazulene (**11**), 3-(1,2-dioxophenethyl)-2-(triphenylphosphoimino)-1-azaazulene (**12**), and 2-amino-3-(1,2-dioxophenethyl)-1-azaazulene (**13**). The structure of **13** was decided by X-ray structure analysis, and the structure of **12** was discussed by molecular orbital calculation. Reaction of **8b** with aryl isocyanate in the presence of benzoyl peroxide gave 1,10-diazabenz[*a*]azulene derivative.

INTRODUCTION

It is known that the iminophosphoranes, chemical species having the nitrogen-phosphorus double bond, reveal synthetic versatility for the construction of fused heterocycles.[1-4] We reported the synthesis and some reactions of phosphoimino-1-azaazulene derivatives (**1** and **2**), where some types of tandem aza-Wittig reaction / cyclization and tandem aza-Wittig reaction / heterocumulene-mediated cyclization underwent and gave a lot of azaazulene-fused heterocycles.[5-8] Aryl conjugated acetylene is also an attractive subject to synthesize a new type of heterocycles. Recently, we reported the synthesis of aryl conjugated ethynylazaazulenes (**3**), which afforded thiophene-fused 1-azaazulenes (**4**) (Scheme 1).[9] We also reported that 3-ethynyl-2-(mesylamino)-1-azaazulenes (**5**) underwent cyclization and gave 1,9-diaza-1*H*-cyclopent[*a*]azulene derivatives (**6**) in the presence of $Cu(OAc)_2$ or $Cu(OTf)_2$ (Scheme 2).[10] In the recent studies about heteroaromatics such as carbolines and ellipticine analogues, benzannulated enyne-carbodiimides and *o*-ethynylaryliminophosphoranes were used as key intermediates.[11-17] In the line of our studies about 1-azaazulenes,[18-20] we investigated the synthesis and reaction of 3-ethynyl-2-(triphenylphosphoimino)-1-azaazulenes.

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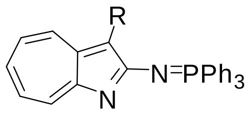
† Dedicated to Professor Ekkehard Winterfeldt on the occasion of his 75th birthday.



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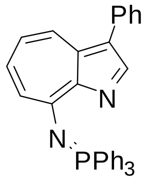

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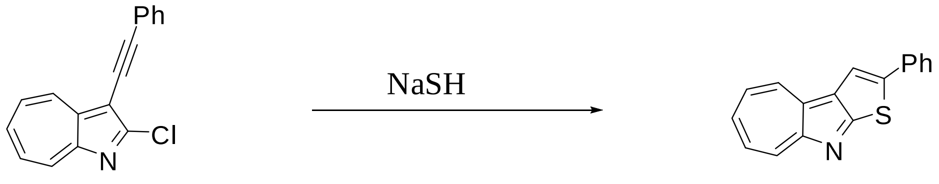
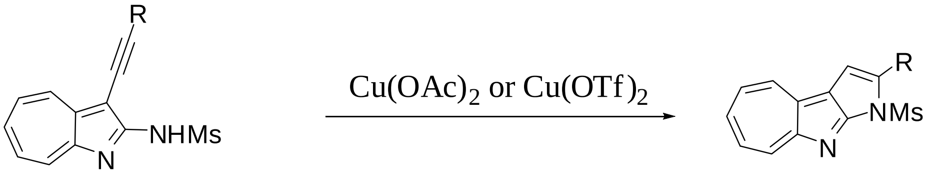


3 **4**

Scheme 1



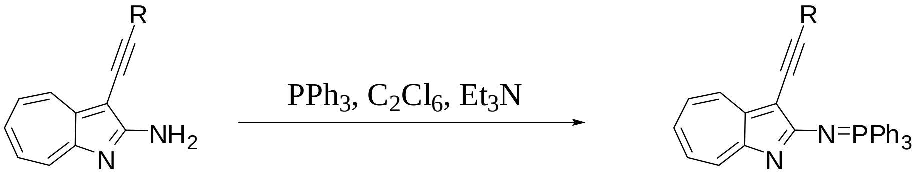
5 : R = H, TMS, Ph

6 : R = H, TMS, Ph

Scheme 2

RESULTS AND DISCUSSION

3-(Trimethylsilylethynyl)- and 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulenes (**8**) were synthesized by the Appel reaction of the corresponding 2-amino-3-ethynyl-1-azaazulenes. Thus treatment of **7a**[10] with PPh_3 and hexachloroethane in the presence of Et_3N in benzene under reflux for 1 h gave **8a** in 95% yield. Similar treatment of **7b**[10] gave **8b** in 98% yield.



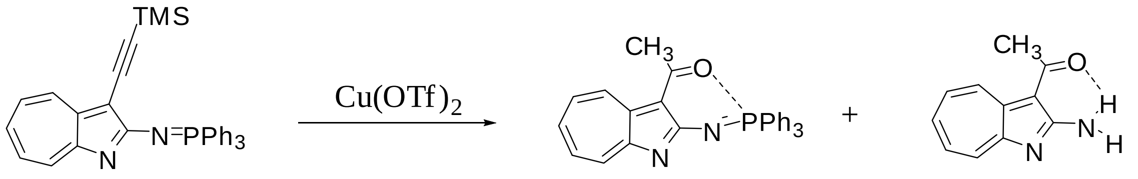
7a : R = TMS
7b : R = Ph

8a : R = TMS
8b : R = Ph

As 3-ethynyl-2-(mesylamino)-1-azaazulene underwent cyclization in the presence of copper-catalyst,[10] we examined the reaction of **8** with copper-catalyst at first.

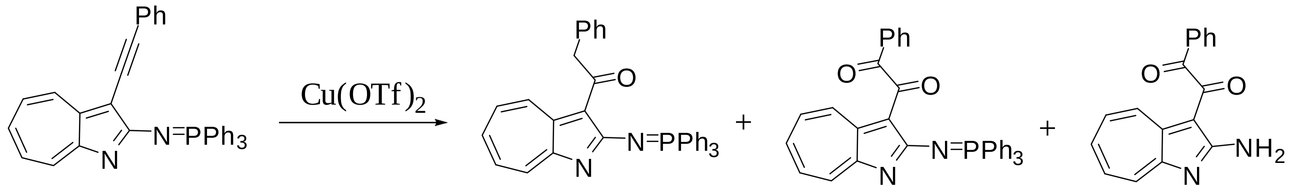
Reaction of **8a** under heating at 90 ℃ for 24 h in the presence of CuI in dry 1,2-dichloroethane in a sealed tube did not proceed at all. On the other hand, the reaction of **8a** with $Cu(OTf)_2$ under same condition proceeded and gave 3-acetyl-2-(triphenylphosphoimino)-1-azaazulene (**9**) and 3-acetyl-2-amino-1-azaazulene (**10**) in 8% and 10% yields, respectively. The reaction in dry benzene gave **9** and **10** in 18% and 17% yields, respectively. These structures were deduced by spectroscopic data as well as elemental analysis. In the IR spectrum of **9**, a carbonyl signal was seen at extremely low wave number (1603 cm^{-1}). This suggests that appreciable coordinative interaction between O-atom and P-atom would be existed.

Although it took things simple that hydrolysis of **8a** occurred in the reaction, the result of no reaction of **8a** with CuI could not be explained. Therefore, we next examined the reaction of **8b** with Lewis acids.



8a **9** **10**

Reaction of **8b** in the presence of CuI, $ZnCl_2$, or $Yb(OTf)_3$ under heating in a sealed tube did not proceed at all. Heating of **8b** in the presence of $Pd(OAc)_2$ in a sealed tube gave a complex mixture. Only the reaction of **8b** in the presence of $Cu(OTf)_2$ gave distinct results. Thus treatment of **8b** with an equivalent molar of $Cu(OTf)_2$ in dry 1,2-dichloroethane under heating at 90 ℃ for 24 h in a sealed tube gave **11** (trace), **12** (3%), and **13** (18%).

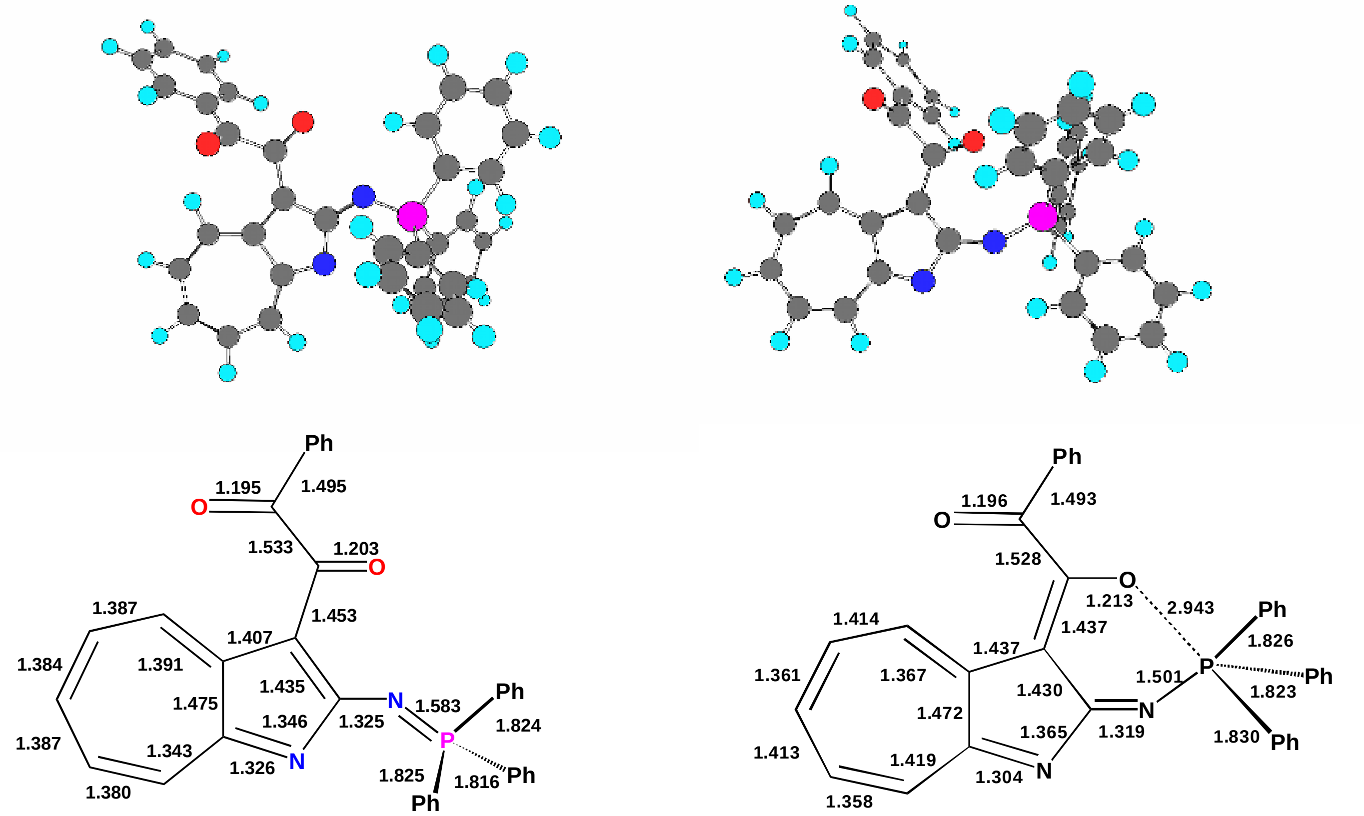


8b **11** **12** **13**

The structures of obtained compounds were deduced by the spectroscopic data as well as elemental analysis. In the ^{1}H NMR spectrum of **11**, methylene protons were observed at δ 4.95 together with phenyl protons and seven-membered ring protons. In its ^{13}C NMR spectrum, a signal at δ 48.68 owing to a methylene carbon and a signal at δ 196.90 owing to a carbonyl carbon were observed. In its IR spectrum, carbonyl peak was seen at 1626 cm^{-1}.

In the ^{1}H NMR spectrum of **12**, methylene protons were not observed. In its ^{13}C NMR spectrum, two signals at δ 192.29 and 195.25 owing to carbonyl carbons were observed. In its IR spectrum, two carbonyl peaks were seen at 1677 and 1600 cm^{-1}. In addition, a sharp signal owing to P-O-C was appeared at 1111 and 883 cm^{-1}. These suggest that one carbonyl oxygen is free and the other carbonyl oxygen could have appreciable coordinative interaction with P-atom. Unfortunately, the compound (**12**) was unstable on the X-ray analysis conditions and we had not ascertained which carbonyl oxygen links P-atom. Therefore, to clarify the consideration, we performed the molecular orbital calculation by Gaussian '03 using RHF/6-31G*[21] (Figure 1). Two optimized stable structures (**12A** and **12B**) existed, and **12B** was more stable than **12A** (about 6.3 kcal/mol). In the calculation of the structure of **12B**, the bond distance between O and P was 2.943 Å, and this lies midway between O-P covalent bond (1.79 Å) and van der Waals radius of O and P (3.30 Å). It is reported that phospa-oxa-azulene (**14**) showed the bond lengths 2.00-2.36 Å.[22-24] Although the bond distance of **12B** is longer than those of

14, above results suggest that **12** exists as resonance hybrid of **12B**. The bond alternation of the seven-membered ring exists. In addition, one of the bond angles of O-P-C(phenyl) was 178.5 °, and the bond length of the P-C(phenyl) bond (1.380 Å) was slightly longer than those of the other P-C(phenyl) bonds (1.823 and 1.826 Å). The results supported the consideration.



12A **12B**

Figure 1. Calculated bond lengths (Å) and the optimized structures of **12A** and **12B**.

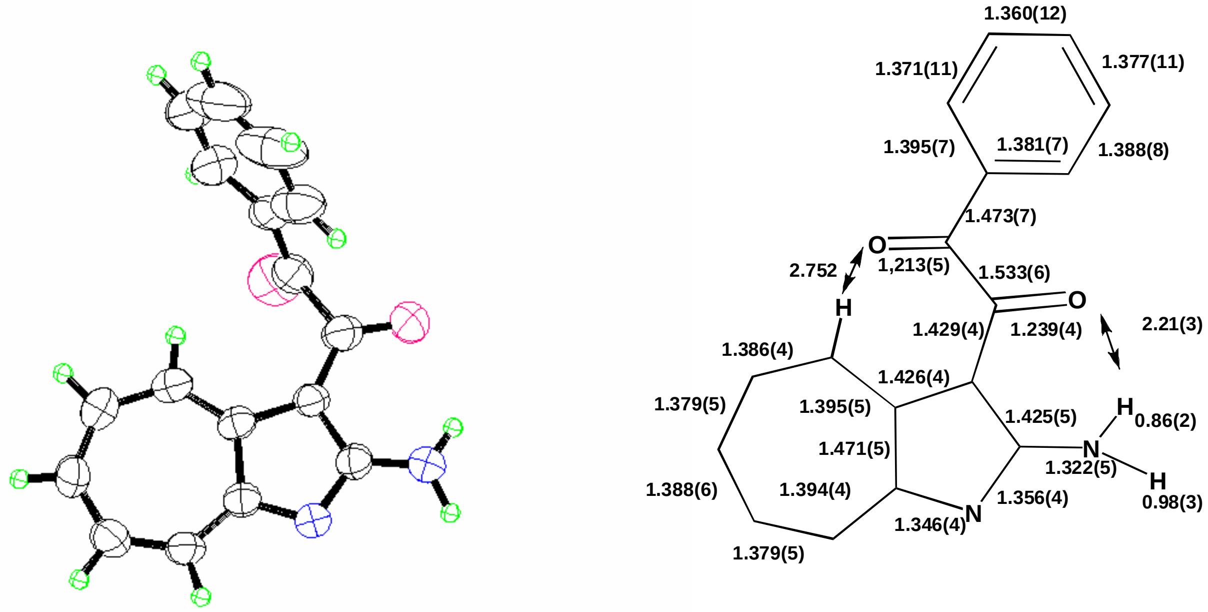
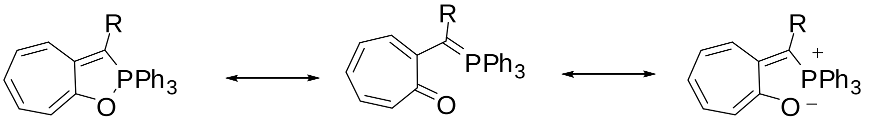
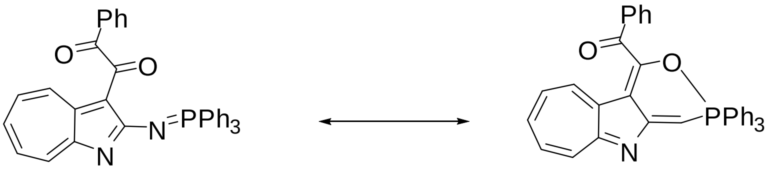


Figure 2. ORTEP drawing with thermal ellipsoids (50% probability) and bond lengths of **13**.

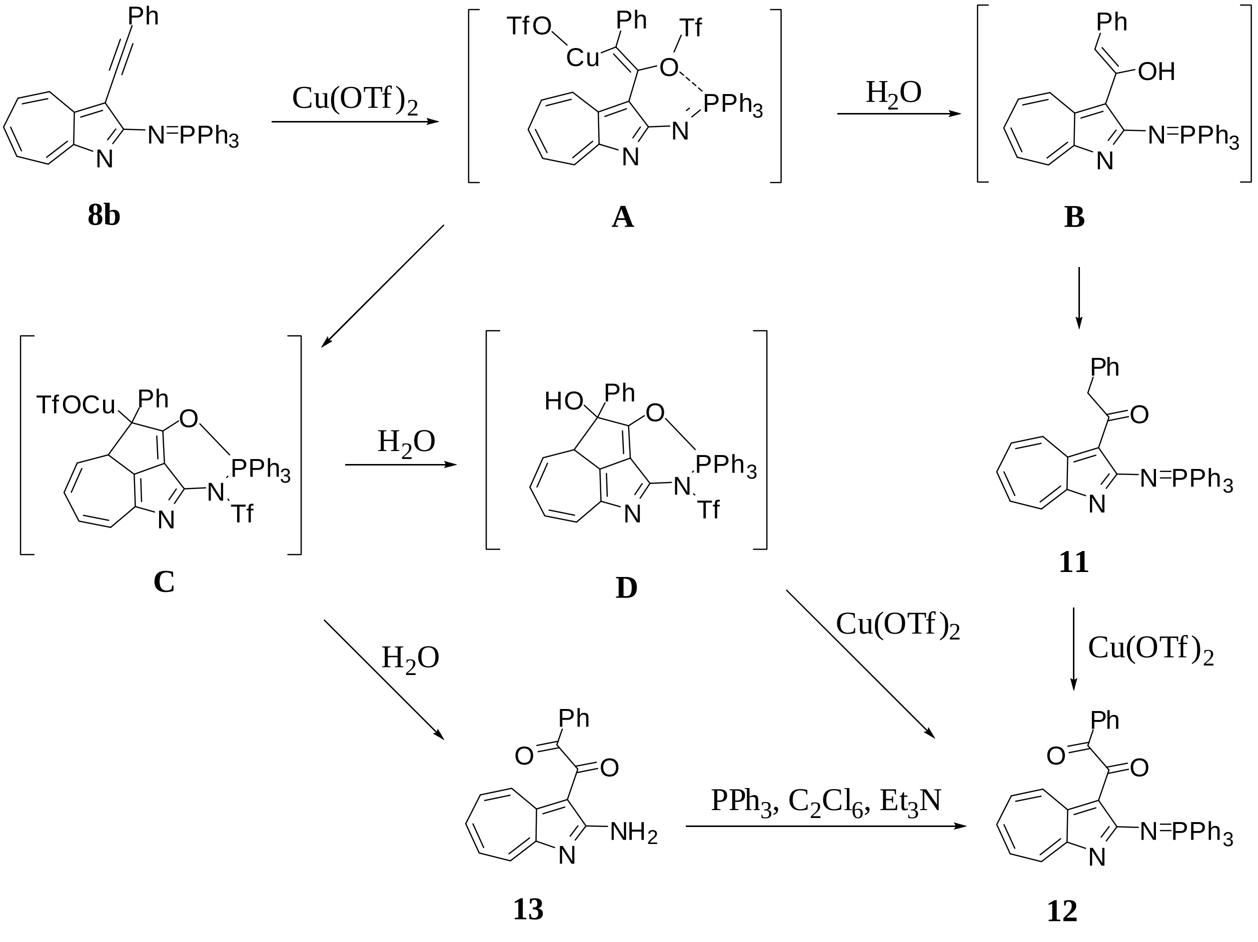


14 : R = H, CH_3, CO_2Et, CN



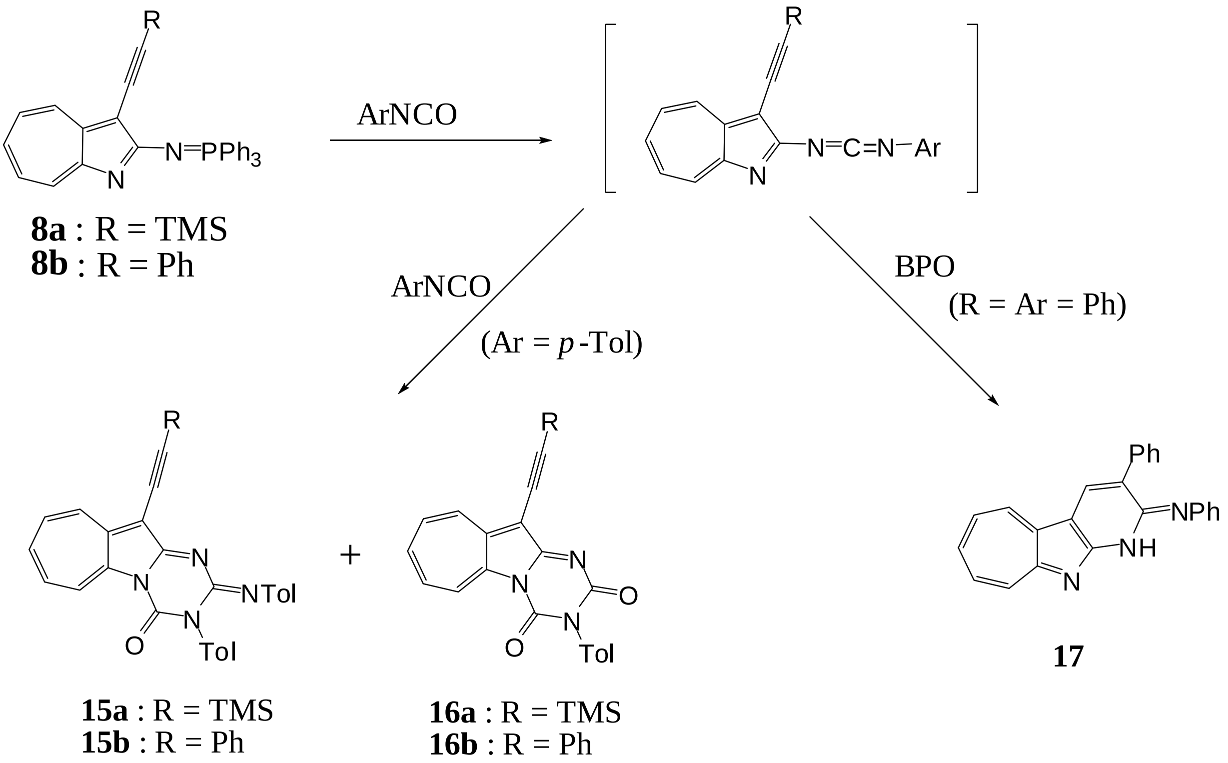
12 **12B**

The structure of **13** was decided by X-ray structure analysis. ORTEP drawing and bond lengths are shown in Figure 2. Hydrogen bonding between one carbonyl group and NH was observed (2.21 Å). Another carbonyl group existed at out of 1-azaazulene plane. In the IR spectrum of **13**, two carbonyl signals were seen at 1673 and 1633 cm^{-1}. The latter would be owing to a hydrogen bonding carbonyl group. Treatment of **13** with PPh_3 and hexachloroethane in the presence of Et_3N in benzene under reflux for 5 h gave **12** in 96% yield. This supports the structure of **12**.



Scheme 3

In these reactions, oxidation of the ethynyl group with $Cu(OTf)_2$ proceeded. To clarify the reaction mechanism, we carried out some additional examinations. When 0.1 equivalent molar of $Cu(OTf)_2$ was used on the reaction with **8b**, only trace of **12** was obtained along with recovery of **8b** (85%). Therefore, it is considered that stoichiometric reaction was occurred. When the reaction of **8b** with an equivalent molar of $Cu(OTf)_2$ was carried out under heating for 12 h, **11** (25%) and **12** (2%) were obtained along with **8b** (32%). Prolonged reaction resulted in increase of **12** and **13**: the reaction for 48 h gave **12** (18%) and **13** (33%), and the reaction for 96 h gave **12** (8%) and **13** (44%). When the reaction was carried out in benzene for 8 h at 90 ℃ in a sealed tube, **11** (13), **12** (5%), and **13** (41%) were obtained. Treatment of **11** with $Cu(OTf)_2$ for 20 h gave **12** in 41% yield and formation of **13** was not observed. Work-up by chromatography of **12** did not give **13** at all. This suggested that **13** would be formed from the intermediate complex of **8b** and $Cu(OTf)_2$. Reaction of **7b** with $Cu(OTf)_2$ did not undergo in the conditions, and **13** was not obtained. From these results, we tentatively suggest the reaction mechanisms as shown in Scheme 3.[25]



We previously reported that reaction of 2-(triphenylphosphoimino)-1-azaazulene with aryl isocyanate proceeded via 2-aryl 1-azaazulen-2-yl carbodiimide intermediate. It is known that enyne-carbodiimides proceeded cyclization to give heteroaromatics such as carbolines and ellipticine analogues,[11-17] and underwent Pouson-Khand type reaction in the presence of $Mo(CO)_6$.[26] Therefore, we next examined the reaction of **8** with aryl isocyanate. Reaction of **8a** with *p*-tolyl isocyanate in benzene at rt did no reaction. When the reaction was carried out in xylene under reflux for 48 h, **15a** was obtained in 34% yield. Treatment of **8b** with *p*-tolyl isocyanate in xylene for 9 h at 90 ℃ in a sealed tube gave **15b** (30%) and **16b** (12%). In the reaction, ethynyl group was not reacted, and the reaction was similar to the reported one.[8] Next we carried out the reaction in the presence of Lewis acid. When **8b** was treated with *p*-tolyl isocyanate in the presence of $ZnCl_2$ in xylene under reflux for

0.5 h, **15b** was obtained in 82% yield. In this time, reaction rate was accelerated, but the reaction was same. Reaction of **8b** with phenyl isocyanate in the presence of $Mo(CO)_6$ in xylene under reflux for 24 h gave **7b** (24%) and **8b** (13%), and no distinct cyclization product was isolated. Reaction of **8b** in the presence of $Cu(OTf)_2$ in benzene under reflux for 24 h gave **11** (49%) and **12** (6%). In this reaction, oxidation of the ethynyl group occurred preferentially, and isocyanate did not take part in.

It is reported that the cyclization of *N*,*N'*-(*o*-ethynylphenyl)carbodiimides proceeded in radical reaction.[16] Therefore we treated **8a** with phenyl isocyanate in the presence of benzoyl peroxide, and obtained **17** in 5% yield together with unidentified red substance. In the ^{1}H NMR spectrum of **17**, a vinylic proton was observed at δ 6.32 and broad NH signal was observed at δ 8.5-9.4, together with phenyl protons and seven-membered ring protons. In its IR spectrum, a peak at 3445 cm^{-1} attributed to NH and a peak at 1591 cm^{-1} attributed to C=N. From these results, we assigned the structure.

CONCLUSION

3-(Phenylethynyl)- and 3-(trimethylsilylethynyl)-2-(triphenyl-phosphoimino)-1-azaazulenes were synthesized in excellent yields by the Appel reaction of the corresponding 2-amino-3-ethynyl-1-azaazulenes with PPh_3 and hexachloroethane in the presence of Et_3N. Oxidation of ethynyl group underwent by the treatment of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene (**8b**) with $Cu(OTf)_2$ to give 3-(2-oxophenethyl)-2-(triphenylphosphoimino)-1-azaazulene (**11**), 3-(1,2-dioxophenethyl)-2-(triphenylphosphoimino)-1-azaazulene (**12**), and 2-amino-3-(1,2-dioxophenethyl)-1-azaazulene (**13**). The structure of **13** was decided by X-ray structure analysis, and the structure of **12** was discussed by molecular orbital calculation. Reaction of **8b** with aryl isocyanate in the presence of benzoyl peroxide gave 1,10-diazabenz[*a*]azulene derivative via *N*-(1-azaazulen-2-yl)-*N'*-phenylcarbodiimide intermediacy.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Mps are measured using 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; *J* value 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-570 spectrophotometer using chloroform as a solvent. Elemental analyses were taken with a Perkin Elmer 2400II. Kiselgel 60 was used for column chromatography and Kiselgel 60G was used for thin-layer chromatography.

Synthesis of 3-(trimethylsilylethynyl)-2-(triphenylphosphoimino)-1-azaazulene

Under argon atmosphere, a mixture of 2-amino-3-(trimethylsilylethynyl)-1-azaazulene (**7a**)[10] (0.1205 g, 0.50 mmol) in dry benzene (30.0 mL) were added consecutively Et_3N (4.0 mL, 33.6 mmol), PPh_3 (0.170 g, 0.65 mmol) and hexachloroethane (0.1537 g, 0.65 mmol). After refluxed for 1 h, the precipitate was filtered off. The filtrate was evaporated, and the residue was chromatographed with hexane-AcOEt (4 :

1) to give **8a** (0.2384 g, 95%).

8a: Red powders (from hexane-benzene), mp 109-111 ℃; δ_H 0.34 (9H, s), 7.14 (1H, dd, *J* 10.0, 9.2), 7.27 (1H, dd, *J* 10.0, 9.6), 7.29 (1H, dd, *J* 10.0, 9.2), 7.42-7.46 (6H, m), 7.51-7.55 (3H, m), 7.63 (1H, d, *J* 9.2), 7.92-7.98 (6H, m), 7.96 (1H, d, *J* 10.0); δ_C 0.99, 85.83, 85.56, 101.07 (*J* 16.0), 125.59, 126.98, 128.70, 128.83, 129.07, 129.23, 129.68, 130.23, 130.91, 132.32, 133.34, 133.73, 133.83, and 149.21; ν_{max} / cm^{-1} 2129 (C≡C), 1577 (C=N), and 1472 (P-Ph); λ_{max} nm^{-1} 307 (4.50, sh), 316 (4.58), 333 (4.34, sh), 350 (4.27, sh), 387 (3.90), 405 (3.90), 433 (3.80), 466 (3.64), 475 (3.64, sh), 510 (3.51, sh), and 552 (3.03, sh). *Anal.* Calcd for $C_{32}H_{29}N_2PSi \cdot 0.5C_6H_6$: C, 77.89; H, 5.98; N, 5.19. Found: C, 77.64; H, 5.88; N, 5.21.

Synthesis of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene

Under argon atmosphere, a mixture of 2-amino-3-(phenylethynyl)-1-azaazulene (**7b**)[10] (0.2106 g, 0.86 mmol) in dry benzene (30.0 mL) were added consecutively Et_3N (4.0 mL, 33.6 mmol), PPh_3 (0.268 g, 1.03 mmol) and hexachloroethane (0.2415 g, 1.03 mmol). After refluxed for 1 h, the precipitate was filtered off. The filtrate was evaporated, and the residue was chromatographed with hexane-AcOEt (4 : 1) to give **8b** (0.4166 g, 98%).

8b: Red prisms (from hexane-CH_2Cl_2), mp 164-165 ℃; δ_H 7.15 (1H, dd, *J* 9.9, 9.6), 7.28 (1H, dd, *J* 10.1, 9.4), 7.29 (1H, dd, *J* 9.9, 9.6), 7.30 (1H, t, *J* 7.8), 7.35 (2H, dd, *J* 7.8, 7.1), 7.42-7.47 (6H, m), 7.49-7.55 (3H, m), 7.59 (2H, d, *J* 7.1), 7.63 (1H, d, *J* 9.6), 7.93-7.99 (6H, m), 8.05 (1H, d, *J* 10.1); δ_C 85.77, 97.45, 102.00 (d, *J* 21.7), 125.54, 125.63, 126.95, 127.43, 128.53, 128.84 (d, *J* 16.6), 128.88, 129.35, 129.71, 130.35, 130.85, 131.69, 132.34 (d, *J* 2.9), 133.79 (d, *J* 10.0), 148.73, 159.52, 175.09, and 175.14; ν_{max} / cm^{-1} 2190 (C≡C), 1582 (C=N), and 1451 (P-Ph); λ_{max} nm^{-1} 276 (4.49), 297 (4.49), 322 (4.51), 379 (3.81, sh), 388 (3.80), 448 (3.94), and 506 (3.66, sh). *Anal.* Calcd for $C_{35}H_{25}N_2P$: C, 83.32; H, 4.99; N, 5.55. Found: C, 83.05; H, 4.94; N, 5.27.

Reaction of 3-(trimethylsilylethynyl)-2-(triphenylphosphoimino)-1-azaazulene in the presence of Lewis acid

Typical procedure - Under argon atmosphere, a mixture of 3-(trimethylsilylethynyl)-2-(triphenylphosphoimino)-1-azaazulene (0.1502 g, 0.30 mmol) and $Cu(OTf)_2$ (0.1085 g, 0.30 mmol) in dry 1,2-dichloroethane (5 mL) was heated at 90 ℃ for 24 h in a sealed tube. The precipitate was filtered off, and the filtrate was evaporated. Chromatography of the residue with hexane-AcOEt (1 : 1) gave **9** (0.0113 g, 8%) and **10** (0.0054 g, 10%).

9: Yellow prisms (from hexane-CH_2Cl_2), mp 260-262 ℃; δ_H 3.02 (3H, s), 7.30 (1H, dd, *J* 10.4, 9.7), 7.48 (1H, dd, *J* 10.4, 9.8), 7.47-7.49 (6H, m), 7.55 (1H, dd, *J* 10.2, 9.7), 7.53-7.58 (3H, m), 7.74 (1H, d, *J* 9.8), 7.89-7.94 (6H, m), 9.30 (1H, d, *J* 10.2); δ_C 48.68, 125.87, 127.59, 127.80, 128.13, 128.47, 128.52, 128.59, 128.78, 129.63, 129.77, 129.88, 131.36, 132.04 (d, *J* 8.0), 132.70, 133.33, 133.43, 133.53, 196.90; ν_{max} / cm^{-1} 1608 (C=O) and 1491 (P-Ph). *Anal.* Calcd for $C_{29}H_{25}N_2OP$: C, 78.01; H, 5.19; N, 6.27. Found: C, 78.24; H, 5.20; N, 6.55.

10: Yellow prisms (from hexane-CH_2Cl_2), mp 198-200 ℃; δ_H 3.02 (3H, s), 7.30 (1H, dd, *J* 10.4, 9.7), 7.48 (1H, dd, *J* 10.4, 9.8), 7.55 (1H, dd, *J* 10.2, 9.7), 7.74 (1H, d, *J* 9.8), 9.30 (1H, d, *J* 10.2); δ_C 110.93, 127.87, 128.19, 128.29, 128.42, 128.87, 128.96, 129.62, 129.75, 132.01 (d, *J* 12.0), 132.87, 133.23, 133.33, 134.25, 134.74 (d, *J* 12.0), 192.29, 195.25; ν_{max} / cm^{-1} 3383 (NH) and 1635 (C=O). *Anal.* Calcd for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04. Found: C, 70.98; H, 5.54; N, 14.75.

Reaction of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene in the presence of Lewis acid

Typical procedure - Under argon atmosphere, a mixture of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene (**8b**) (0.1212 g, 0.24 mmol) and $Cu(OTf)_2$ (0.082 g, 0.24 mmol) in dry benzene (5 mL) was heated at 90 ℃ for 8 h in a sealed tube. The precipitate was filtered off, and the filtrate was evaporated. Chromatography of the residue with hexane-AcOEt (1 : 1) gave **8b** (0.0021 g, 2%), **11** (0.0167 g, 13%), **12** (0.0064 g, 5%), and **13** (0.0244 g, 41%).

11: Yellow prisms (from hexane-CH_2Cl_2), mp 192.5-194 ℃; δ_H 4.95 (2H, s), 7.17 (1H, t, *J* 7.2), 7.23 (2H, dd, *J* 7.4, 7.2), 7.29 (1H, dd, *J* 10.4, 9.6), 7.38 (2H, d, *J* 7.4), 7.39 (1H, dd, *J* 10.2, 9.6), 7.43-7.47 (6H, m), 7.48 (1H, dd, *J* 10.4, 10.1), 7.53-7.57 (3H, m), 7.71 (1H, d, *J* 10.1), 7.85-7.90 (6H, m), 9.26 (1H, d, *J* 10.2); δ_C 48.68, 125.87, 127.59, 127.80, 128.13, 128.47, 128.52, 128.59, 129.63, 129.77, 129.88, 131.36, 132.03, 132.05, 132.70, 133.33, 133.43, 133.53, 196.90; ν_{max} / cm^{-1} 1626 (C=O) and 1467 (P-Ph); λ_{max} nm^{-1} 276 (4.33), 319 (4.47), 392 (4.04), and 438 (3.89). *Anal.* Calcd for $C_{35}H_{27}N_2OP$: C, 80.44; H, 5.21; N, 5.36. Found: C, 79.91; H, 4.97; N, 5.12.

12: Yellow prisms (from MeCN), mp 206.5-208 ℃; δ_H 7.31 (2H, dd, *J* 8.4, 7.4), 7.33-7.39 (6H, m), 7.35-7.40 (1H, m), 7.45 (1H, dt, *J* 7.4, 1.4), 7.46-7.51 (3H, m), 7.54-7.59 (7H, m), 7.62 (1H, dd, *J* 10.2, 9.8), 7.77 (1H, d, *J* 10.1), 7.96 (2H, dd, *J* 8.4, 1.4), 9.28 (1H, d, *J* 9.8); δ_C 110.93, 127.87, 128.19, 128.29, 128.42, 128.87, 128.96, 129.62, 129.75, 132.01 (d, *J* 12.0), 132.87, 133.23, 133.33, 134.25, 134.74 (d, *J* 12.0), 192.29, 195.25; ν_{max} / cm^{-1} 1677 and 1600 (C=O), and 1492 (P-Ph); λ_{max} nm^{-1} 275 (4.44), 325 (4.58), 396 (4.13), 450 (3.80, sh), and 467 (3.90). *Anal.* Calcd for $C_{35}H_{27}N_2O_2P$: C, 78.35; H, 4.70; N, 5.22. Found: C, 78.24; H, 4.55; N, 5.07.

13: Yellow prisms (from MeCN), mp 209-210.5 ℃; δ_H 6.8-8.0 (br, 2H, NH_2), 7.49-7.52 (2H, dd, *J* 8.5, 7.4, Ph-*m*), 7.52-7.55 (2H, m, H-5, H-6), 7.66 (1H, dt, *J* 7.4, 2.8, Ph-*p*), 7.46-7.51 (1H, m, H-7), 8.02 (1H, m, H-4), 8.07 (2H, dd, *J* 8.5, 1.2, Ph-*o*), 8.05 (1H, d, *J* 10.2, H-8); δ_C 103.78, 122.39, 128.09, 129.12, 130.23, 131.36, 133.18, 133.44, 134.47, 134.85, 135.88, 163.83, 189.48, 194.89; ν_{max} / cm^{-1} 3408 (NH), 1673 and 1634 (C=O); λ_{max} nm^{-1} 263 (4.40), 300 (4.56), 359 (3.95, sh), 374 (3.89, sh), and 442 (3.88). *Anal.* Calcd for $C_{17}H_{12}N_2O_2$: C, 73.90; H, 4.38; N, 10.14. Found: C, 73.44; H, 4.55; N, 10.33.

Reaction of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene in the presence of Lewis acid

Under argon atmosphere, a mixture of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene (**11**) (0.0242 g, 0.046 mmol) and $Cu(OTf)_2$ (0.0166 g, 0.046 mmol) in dry benzene (5 mL) was heated at 90 ℃ for 20 h in a sealed tube. The precipitate was filtered off, and the filtrate was evaporated. Chromatography of the residue with hexane-AcOEt (1 : 1) gave **12** (0.0102 g, 41%).

Appel reaction of 13

Under argon atmosphere, a mixture of 2-amino-3-(1,2-dioxo-phenethyl-1-azaazulene (**13**) (0.0055 g, 0.02 mmol) in dry benzene (20.0 mL) were added consecutively Et_3N (4.0 mL, 33.6 mmol), PPh_3 (0.0053 g, 0.02 mmol) and hexachloroethane (0.0047 g, 0.02 mmol). After refluxed for 5 h, the precipitate was filtered off. The filtrate was evaporated, and the residue was chromatographed with hexane-AcOEt (5 : 1) to give **12** (0.0103 g, 96%).

Reaction of 3-(trimethylsilylethynyl)-2-(triphenylphosphoimino)-1-azaazulene with aryl isocyanate

Under argon atmosphere, a mixture of 3-(trimethylsilylethynyl)-2-(triphenylphosphoimino)-1-azaazulene (**a**) (0.2504 g, 0.50 mmol) and *p*-tolyl isocyanate (0.073 g, 0.50 mmol) in dry xylene (20 mL) was heated under reflux for 48 h, and the solvent was evaporated. Chromatography of the residue with hexane-AcOEt (1 : 1) gave **15a** (0.0817 g, 34%).

15a: Dark green micro needles (from MeCN), mp 179.5-181 ℃; δ_H 0.23 (9H, s), 2.27 (3H, s), 2.41 (3H, s), 6.92 (1H, dd, *J* 11.2, 9.2), 7.00 (2H, d, *J* 8.3), 7.06 (1H, dd, *J* 11.1, 9.2), 7.07 (1H, dd, *J* 11.2, 9.4), 7.12 (2H, d, *J* 8.3), 7.23 (2H, d, *J* 8.3), 7.31 (2H, d, *J* 8.3), 7.64 (1H, d, *J* 11.1), 8.59 (1H, d, *J* 9.4); δ_C 21.06, 21.46, 93.81, 101.02, 106.95, 121.98, 124.07, 126.70, 124.06, 128.51, 128.65, 130.34, 132.26, 132.73, 133.58, 134.40, 135.02, 135.52, 142.89, 148.41, 148.87, and 155.84; ν_{max} / cm^{-1} 2145 (C≡C) and 1716 (C=O); λ_{max} nm^{-1} 298 (4.46), 481 (4.33), 560 (3.82, sh), and 630 (3.03, sh). *Anal.* Calcd for $C_{30}H_{28}N_4OSi$: C, 73.74; H, 5.78; N, 11.47. Found: C, 73.54; H, 5.60; N, 11.03.

Reaction of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene with aryl isocyanate

Under argon atmosphere, a mixture of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene (**8b**) (0.2018 g, 0.40 mmol) and *p*-tolyl isocyanate (0.158 g, 1.20 mmol) in dry xylene (20 mL) was heated at 90 ℃ for 9 h, and the solvent was evaporated. Chromatography of the residue with hexane-AcOEt (4 : 1) gave **15b** (0.0594 g, 30%) and **16b** (0.0194 g, 12%).

15b: Dark green micro needles (from MeCN), mp >300 ℃; δ_H 2.32 (3H, s), 2.43 (3H, s), 6.92 (1H, dd, *J* 11.2, 9.8), 7.04 (1H, dd, *J* 11.2, 9.3), 7.09 (2H, d, *J* 8.3), 7.10 (1H, ddd, *J* 11.2, 9.8, 1.0), 7.14 (2H, d, *J* 8.3), 7.27 (2H, d, *J* 8.3), 7.33 (2H, d, *J* 8.3), 7.35-7.36 (3H, m), 7.48-7.50 (2H, m), 7.71 (1H, d, *J* 11.2), 8.58 (1H, d, *J* 9.3); δ_C 21.03, 21.37, 85.03, 100.44, 101.04, 118.56, 120.27, 122.81, 123.93, 128.37, 128.49, 128.67, 128.71, 128.91, 130.26, 130.55, 131.66, 132.83, 135.16, 137.58, 142.91, 147.88, and 155.75; ν_{max} / cm^{-1} 2194 (C≡C), 1714 (C=O); λ_{max} nm^{-1} 283 (4.50), 310 (4.40), 485 (4.29), 600 (3.42, sh), and 655 2.76 (sh). *Anal.* Calcd for $C_{33}H_{24}N_4O$: C, 80.47; H, 4.91; N, 11.37. Found: C, 80.32; H, 4.76; N, 11.70.

16b: Yellow needles (from MeCN), mp >300 ℃; δ_H 2.42 (3H, s), 7.23 (2H, d, *J* 8.5), 7.27-7.36 (2H, m), 7.34 (2H, d, *J* 8.3), 7.37-7.40 (3H, m), 7.41 (1H, ddd, *J* 11.0, 8.8, 1.4), 7.63-7.65 (2H, m), 8.08 (1H, d, *J* 11.0), 9.04 (1H, dd, *J* 8.9, 1.4); δ_C 21.29, 88.23, 100.48, 102.60, 122.59, 123.72, 127.90, 128.40, 128.91, 130.29, 131.90, 131.99, 133.23, 134.64, 135.67, 136.21, 139.04, 142.03, 148.49, 148.73, and 159.18; ν_{max} / cm^{-1} 2112 (C≡C), 1740, 1685 (C=O); λ_{max} nm^{-1} 302 (4.52), 454 (4.23, sh), 466 (4.26), and 522 (3.56, sh). *Anal.* Calcd for $C_{26}H_{17}N_3O_2$: C, 77.41; H, 4.25; N, 10.42. Found: C, 77.95; H, 3.95; N, 10.36.

Reaction of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene with aryl isocyanate in the presence of Lewis acid

Under argon atmosphere, a mixture of **8b** (0.011 g, 0.020 mmol), *p*-tolyl isocyanate (0.008 g, 0.060 mmol), and $ZnCl_2$ (0.0027 g, 0.020 mmol) in dry xylene (20 mL) was heated under reflux for 0.5 h, and the solvent was evaporated. Chromatography of the residue with hexane-AcOEt (1 : 1) gave **15b** (0.0081 g, 82%).

Reaction of 3-(phenylethynyl)-2-(triphenylphosphoimino)-1-azaazulene with aryl isocyanate in the

presence of benzoyl peroxide

Under argon atmosphere, a mixture of **8b** (0.101 g, 0.20 mmol), *p*-tolyl isocyanate (0.050 mL, 0.22 mmol), and benzoyl peroxide (0.003 g) in dry xylene (20 mL) was stirred at rt for 1 h, and after the heating the mixture at 90 ℃ for 9 h, the temperature was elevated to 150 ℃ and reaction was continued 48 h. The precipitate was filtered off, and the filtrate was evaporated. Then the solvent was evaporated, and chromatography of the residue with hexane-$CHCl_3$ (1 : 1) gave **17** (0.0032 g, 5%), unidentified red needles (0.0146 g), and recovered (**8b**) (0.030 g, 30%).

17: Green powders (from hexane), mp 179-183 ℃; δ_H 6.32 (1H, s), 7.31 (1H, t, *J* 7.6), 7.47 (2H, t, *J* 7.6), 7.54 (2H, dd, *J* 7.6, 7.2), 7.63 (1H, t, *J* 7.2), 7.76 (1H, dd, *J* 10.8, 10.0, H-5), 7.78-7.82 (1H, m, H-6), 7.80 (2H, d, *J* 7.6), 7.83-7.85 (1H, m, H-7), 8.43 (2H, d, *J* 7.6), 8.59 (1H, d, *J* 10.0, H-4), 8.76 (1H, m, H-8); δ_C 107.57, 122.63, 127.56, 128.03, 128.81, 128.87, 129.09, 130.19, 130.54, 133.00, 134.54, 135.16, 135.77, 136.27, 136.56, 137.58, 142.17, 144.92, 150.52, and, 152.81; ν_{max} / cm^{-1} 3445 (N-H), 1591 (C=N ; λ_{max} nm^{-1} 286 (4.27, sh), 296 (4.31), 354 (4.40, sh), 363 (4.43), 420 (3.52), 450 (3.61), 472 (3.57, sh), 563 (3.18, sh), 592 (3.21), and 664 (2.97, sh). *Anal.* Calcd for $C_{24}H_{17}N_3$: C, 82.97; H, 4.93; N, 12.10. Found: C, 82.88; H, 4.75; N, 12.37.

X-Ray structure determination

Crystal data of 13: Yellow needle, $C_{17}H_{12}N_2O_2$, M = 276.29, monoclinic, space group $P2_1/c$, a = 14.484(8) Å, b = 6.996(15) Å, c = 15.310(10) Å, β = 117.72(4)°, V = 1373.3(32) $Å^3$, Z = 4, D_{calc} = 1.336 g/cm^3, crystal dimension 0.88 x 0.32 x 0.12 mm. Data were measured on a Rigaku AFC 5S radiation diffractmeter with graphite-monochromated Mo-Kα radiation. Total 3254 reflections (3133 unique) were collected using ω-2θ scan technique with in a 2θ range of 55.0°. The structure was solved by direct methods (SIR92),[27] and expanded using Fourier techniques (DIRDIF99),[28] and refined by a full-matrix least-squares method using 208 variables refined with 1265 reflections [$I > 2\sigma(I)$]. The non-hydrogen atoms were anisotropically. The final refinement converged to R = 0.0491 and Rw = 0.0307. All calculations were performed using the CrystalStructure[29,30] crystallographic software package.

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