SYNTHESIS OF 2-ARYLAMINO-1-AZAAZULENES

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Abstract – A series of 2-arylamino-1-azaazulenes were synthesized by the Buchwald-Hartwig cross coupling reaction. The resulting compounds were characterized by $^1$H NMR, $^{13}$C NMR, HRMS analyses, and elemental analysis. X-Ray crystallographic analysis revealed that 2-(1-naphthylamino)-1-azaazulene exists in dimeric form with two intermolecular N–H⋯N hydrogen bonds in its crystal structure.

Nitrogen-containing heteroaromatic compounds are one of the most popular and important class of organic compounds studied in different fields of modern day research. Azaazulenes are the structural isomers of quinoline and the heteroatomic analogues of azulene. In particular, 1-azaazulenes exhibit remarkable physical and chemical properties such as a large dipole moment ($\mu = 3.05$ D),\(^1\) unique reactivity, and potential biological activities.\(^2\) In recent years, 2-amino-1-azaazulene derivatives have been studied as a ligand for metal ions,\(^6\)\(^7\) and as anticancer agents.\(^7\)\(^8\) Especially, 2-arylamino-1-azaazulenes are potentially bioactive and hence deserve more attention from the scientific community. However, there are limited reports on the synthesis, and chemical and physical properties. 2-Arylamino-1-azaazulenes were synthesized by only amination of 2-halo-1-azaazulenes.\(^6\)^{8-12} The arylation of 2-amino-1-azaazulenes have not been investigated. Here we report the synthesis of a novel series of 2-arylamino-1-azaazulenes via Buchwald-Hartwig cross coupling, along with the study of their UV-Vis absorption properties. The arylation of 2-amino-1-azaazulenes were not succeeded under the same condition of amination of 2-haloazaazulenes. We found that 2-arylamino-1-azaazulenes were successfully synthesized by Buchwald-Hartwig cross coupling using phosphine ligand such as Xantphos and BINAP.

All 2-arylamino-1-azaazulenes were successfully synthesized by the Buchwald-Hartwig cross coupling reaction of aryl halide and arylamine. $^{1a}$ was synthesized by using a slightly modified version of the

Dedicated to Prof. Dr. Masakatsu Shibasaki on the occasion of his 70th birthday
The reaction of 2-bromo-1-azaazulene 2a and 2-aminoazulene 3 in the presence of Pd$_2$(dba)$_3$, Xantphos (9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene), Cs$_2$CO$_3$, and 18-crown-6 (Scheme 1) gave 1a in 24% yield. In this reaction, 1-(1-azaazulen-2-yl)-2-aminoazulene 4 was also obtained in 18% yield. Under a non-catalytic condition, both 1a and 4 could not be obtained. This result indicated that 4 was generated as by-product of Pd catalyzed cross coupling reaction. However, only 32% of product yield was obtained when the same reagent system was applied for the synthesis of 1b. In an attempt to enhance the product yield, the palladium catalyst and phosphine ligand were changed to Pd(dppf)Cl$_2$ and BINAP (2,2’-bis(diphenylphosphino)-1,1’-binaphthyl). Under these reaction conditions, 1b was obtained in 70% yield. 1c was also obtained in 30% yield by using the same catalyst and ligand (Scheme 2). 2-Arylamino-1-azaazulenes 6, 8, 10, and 12 were synthesized under the conditions similar to those used for 1a, in 26%, 13%, 28%, and 51% yields, respectively (Scheme 3–5). 1b, 1c, and 8 could be also synthesized under a non-catalytic reaction in 9%, 3%, and 75% yields, respectively. On the other hands, 6, 10, and 12 were not obtained by a non-catalytic reaction. Therefore, the Buchwald-Hartwig cross coupling reaction of 2-aminoazaazulene was useful for synthesis of 2-arylamino-1-azaazulenes. We note that 8 was already synthesized by another method.

**Scheme 1**

**Scheme 2**

**Scheme 3**
The molecular structure of 10 was successfully determined by single-crystal X-ray diffraction analysis (Figure 1 and Table 1). To the best of our knowledge, this is the first report of the crystal structure of 2-arylamino-1-azaazulenes. Single crystals of 10 were obtained by recrystallization from ethyl acetate at...
room temperature. The azaazulene core and amino group including the hydrogen on the N atom are highly planar. The dihedral angle between the plane of the azaazulene core and the naphthalene ring is 51.62°. The C1–N1 (1.3629(13) Å) and C1–N2 (1.3530(14) Å) bonds are slightly longer than the C2–N2 bond (1.4179(13) Å) and comparable to the aromatic C–N bond such as that in pyridine. The aminoazaazulene unit forms two intermolecular N2–H⋯N1 hydrogen bonds (1.989 Å) between the two monomers (Figure 1b). In other words, 10 exists as a dimer in crystal state. The CH⋯π interactions between H on C8 of the azaazulene and naphthalene ring seems to be exist in a dimer form.

UV-Vis absorption spectra of 2-arylamino-1-azaazulenes and 2d are shown in Figure 2. In comparison to 2d, all 2-arylamino-1-azaazulenes showed a large molar extinction coefficient ε and redshift. For example, the longest absorption wavelength of 1a red-shifted by about 50 nm compared with that of 2d. This indicates the delocalization of the π electrons on azaazulene and the amine through two tautomeric forms 1a and 1a' (Scheme 6). This type of tautomerism is known for bis(1-azaazulen-2-yl)amines. We observed that red shift of absorption spectrum of 1a by addition of hydrochloric acid to methanol solution of 1a. This result also indicated that the existence of the two tautomeric forms. The details of tautomerism and pKa values are currently under investigation. The ε value for ethyl ester-substituted 1b at 440 nm, which is the absorption maximum in the visible region, is about 1.5 times larger than that for 1a and 1c (Figure 2a), and about 2 times larger than that for other 2-arylamino-1-azaazulenes (Figure 2b).

Figure 2. UV-Vis spectra of (a) 1a–1c and 2d and (b) 1a, 2d, 6, 8, 10, and 12 in THF

Scheme 6
In summary, a series of 2-arylamino-1-azaazulenes were successfully synthesized in moderate to yields. X-Ray crystallographic analysis of 10 reveals a highly planar structure that straddles the azaazulene core and amino group including the hydrogen on the N atom. Moreover, the plane of the azaazulene core and the naphthalene ring is twisted. As per the crystal structure, 10 forms a dimer with two intermolecular N–H····N hydrogen bonds. The UV-Vis absorption spectra of the 2-arylamino-1-azaazulenes show a large $\varepsilon$ and redshift compared with the case of amino azulene 2d, in the visible region. Additionally, $\varepsilon$ of the ethyl ester-substituted 1b is larger than that for 1a, 1c, and other 2-arylamino-1-azaazulenes.

**EXPERIMENTAL**

Unless otherwise indicated, all reactions were carried out under argon atmosphere. All solvents were distilled, dried over 3Å or 4Å molecular sieves, and degassed using nitrogen before use. Column chromatography was performed using Wako gel C-200 (spherical, neutral). Aniline, Cs$_2$CO$_3$, 18-crown-6, and BINAP were purchased from Wako Pure Chemical Industries. 1-Naphthylamine, 2-bromonaphthalene, and Xantphos were purchased from Tokyo Chemical Industry Co. Ltd. Pd$_2$(dba)$_3$ was purchased from Strem Chemicals Inc. Pd(dpff)Cl$_2$ was purchased from Sigma-Aldrich. 1,4-Dioxane and THF were purchased from KANTO Chemicals.

All NMR spectra were recorded on a JEOL ECP-300 (300 MHz) or ECP-500 (500 MHz) spectrometer. $^1$H NMR (300 or 500 MHz) and $^{13}$C-{$^1$H} NMR (75 or 126 MHz) spectra were recorded using tetramethylsilane as an internal standard. IR spectra were recorded with a JASCO FT-IR 6100 spectrometer, and UV-Vis-near infrared (NIR) spectra were recorded with a JASCO V670 spectrometer. Melting points were recorded using a Bibby Stuart Scientific SMP3 instrument; all melting points reported are uncorrected. HR-ESI mass spectra were recorded on a JEOL JMS-T100CS AccuTOF CS spectrometer. Elemental analyses were carried out using a PerkinElmer 2400II CHNS analyzer. Crystal data were collected using a Bruker AXS SMART APEX CCD X-ray diffractometer equipped with monochromatic Mo Kα radiation (0.7107 Å). Empirical absorption corrections using equivalent reflections and Lorentzian polarization corrections were performed using the SADABS program.$^{19}$ All data were collected with SMART and Bruker SAINTPLUS (Version 6.45) software packages. The structures were solved using the SHELXA-97 program$^{20}$ and refined against $R^2$ by using SHELXL-97.$^{21}$ Deposition number CCDC-1500558 for compound No. 10. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). 2d$^{22}$ and 5$^{23}$ were prepared according to literature methods.
Synthesis of 2a

Compound 2a was synthesized as per the literature method for the synthesis of 2-bromo-3-methyl-1-azaazulene.24

A mixture of 1-azaazulenone25 (0.22 g, 1.5 mmol) and phosphorus(V) oxybromide (1.5g, 5.2 mmol) was stirred for 30 min at 120 °C. Ice water was added to the reaction mixture, followed by neutralization with aqueous NaHCO₃ solution. The mixture was extracted with CHCl₃, and the organic layer was washed with water and dried with MgSO₄. After filtration and evaporation, the crude product was purified by silica gel column chromatography using CHCl₃ as the eluent. The first red fraction to elute from the column was collected. Recrystallization from hexane gave 2,3-dibromo-1-azaazulene 13 as red crystals (27%). And the second orange fraction to elute from the column was collected. Recrystallization from hexane gave 2a as orange crystals (20%).

2a: mp 57.0-57.9 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.33 (s, 1H), 7.67 (t, J = 9.5 Hz, 1H), 7.77 (t, J = 9.5 Hz, 1H), 8.61 (d, J = 9.5 Hz, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 115.8, 130.1, 130.5, 134.4, 135.6, 138.3, 147.1, 147.4, 156.8. HR-MS (HR-ESI-TOF) m/z calc. for C₉H₇⁷BrN: 207.9762 [M+H]⁺; found: 207.9761.

13: mp 143.9-144.7 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.75 (t, J = 9.5 Hz, 1H), 7.78 (t, J = 9.5 Hz, 1H), 7.95 (t, J = 9.5 Hz, 1H), 8.41 (d, J = 9.5 Hz, 1H), 8.56 (d, J = 9.5 Hz, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 103.7, 130.5, 130.9, 134.8, 136.6, 139.4, 143.2, 148.4, 155.7. HR-MS (HR-ESI-TOF) m/z calc. for C₉H₇⁷Br₈¹BrN: 287.8847 [M+H]⁺; found: 287.8847.

Synthesis of 2b

A mixture of ethyl 1,2'-dihydro-2-oxo-1-azaazulene-3-carboxylate25 (0.33 g, 1.4 mmol) and phosphorus(V) oxychloride (1.8 g, 11.8 mmol) was stirred for 2 h at 110 °C. Ice water was added to the reaction mixture, followed by neutralization with aqueous NaHCO₃ solution. The mixture was extracted with CHCl₃, and the organic layer was dried over Na₂SO₄. After filtration and evaporation, the crude product was purified by silica gel column chromatography using CHCl₃ as the eluent. The first yellow fraction to elute from the column was collected. Recrystallization from hexane gave 2b as yellow crystals (73%).

2b: mp 84.5-85.5 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.46 (t, J = 7.5 Hz, 3H), 4.46 (q, J = 7.5 Hz, 2H), 7.93 (t, J = 9.5 Hz, 1H), 7.96 (t, J = 9.5 Hz, 1H), 8.03 (t, J = 9.5 Hz, 1H), 8.66 (d, J = 9.5 Hz, 1H), 9.52 (d, J = 9.5 Hz, 1H). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 14.3, 60.5, 111.7, 133.0, 133.2, 137.1, 137.5, 139.8, 147.0, 156.7, 158.9, 163.2. HR-MS (HR-ESI-TOF) m/z calc. for C₁₂H₁₀NO₂Cl: 258.0298 [M+Na]⁺; found: 258.0298. Anal. Calcd for C₁₂H₁₀NO₂Cl: C, 61.16; H, 4.28; N, 5.94. Found: C, 61.00; H, 4.10; N, 5.93.


Synthesis of 2c

Compound 2c was prepared by a slight modification of the literature method.\(^{25}\)

A mixture of 3-cyano-1-azaazulenone\(^{25}\) (1.20 g, 7.05 mmol) and phosphorus(V) oxychloride (8.20 g, 53.5 mmol) was stirred for 1 h at 115 °C. Ice water was added to the reaction mixture, followed by neutralization using aqueous NaHCO\(_3\) solution. The mixture was extracted with CHCl\(_3\), and the organic layer was dried over Na\(_2\)SO\(_4\). After filtration and evaporation, the crude product was purified by silica gel column chromatography using CHCl\(_3\) as the eluent. The second yellow fraction to elute from the column was collected. Recrystallization from AcOEt gave 2c as gold needle-like crystals (57%).

2c: mp 231.8-233.0 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 8.03 (t, J = 9.5 \text{ Hz}, 1\text{H}), 8.08 (t, J = 9.5 \text{ Hz}, 1\text{H}), 8.16 (t, J = 9.5 \text{ Hz}, 1\text{H}), 8.70 (d, J = 9.5 \text{ Hz}, 1\text{H}), 8.75 (d, J = 9.5 \text{ Hz}, 1\text{H})\). \(^{13}\)C\{\(^1\)H\} NMR (126 MHz, CDCl\(_3\)): \(\delta 96.0, 113.3, 133.6, 134.2, 135.2, 138.7, 140.9, 149.3, 156.8, 159.5\). HR-MS (HR-ESI-TOF) \(m/z\) calc. for C\(_{10}\)H\(_5\)N\(_2\)Cl: 211.0039 [M+Na]^+; found: 211.0039. Anal. Calcd for C\(_{10}\)H\(_5\)N\(_2\)Cl: C, 63.68; H, 2.67; N, 14.85. Found: C, 63.45; H, 2.46; N, 14.77.

Synthesis of 2e

Compound 2e was prepared by a slight modification of the literature method.\(^{26}\)

A mixture of 1-azaazulenone\(^{25}\) (0.20 g, 1.4 mmol) and phosphorus(V) oxychloride (1.8 g, 11.8 mmol) was stirred for 2 h at 110 °C. Ice water was added to the reaction mixture, followed by neutralization with aqueous NaHCO\(_3\) solution. The mixture was extracted with CHCl\(_3\), and the organic layer was dried over Na\(_2\)SO\(_4\). After filtration and evaporation, the crude product was purified by silica gel column chromatography using CHCl\(_3\) as the eluent. The first yellow fraction to elute from the column gave 2e as orange crystals (68%).

2e: mp 72.2-73.5 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta 7.20 (s, 1\text{H}), 7.65 (t, J = 9.5 \text{ Hz}, 1\text{H}), 7.75 (t, J = 9.5 \text{ Hz}, 1\text{H}), 7.84 (t, J = 9.5 \text{ Hz}, 1\text{H}), 8.40 (d, J = 9.5 \text{ Hz}, 1\text{H}), 8.55 (d, J = 9.5 \text{ Hz}, 1\text{H})\). \(^{13}\)C\{\(^1\)H\} NMR (126 MHz, CDCl\(_3\)): \(\delta 112.1, 130.1, 130.5, 134.6, 135.7, 138.0, 147.2, 156.2, 157.7\). HR-MS (HR-ESI-TOF) \(m/z\) calc. for C\(_9\)H\(_7\)ClN\(_2\): 164.0267 [M+H]^+; found: 164.0262. Anal. Calcd for C\(_9\)H\(_8\)NCl: C, 66.07; H, 3.70; N, 8.56. Found: C, 65.93; H, 3.53; N, 8.51.

Synthesis of 3

Compound 3 was prepared by a slight modification of the reported method.\(^{27}\)

To a solution of KOH (4.0 g), EtOH (5.0 mL), and water (1.0 mL), diethyl 2-aminoazulene-1,3-dicarboxylate\(^{28,29}\) (0.75 g, 2.65 mmol) was added. The reaction mixture was refluxed for 30 min with continuous stirring. After cooling to room temperature, the reaction mixture was neutralized using hydrochloric acid to obtain a yellow precipitate. The yellow solid was filtered out,
added to pyridine (5 mL), and refluxed for 30 min. After removal of pyridine under reduced pressure, the crude product was purified by silica gel column chromatography using CHCl₃ as the eluent. The second red fraction to elute from the column was collected and recrystallized from hexane to give 3 as red needle-like crystals (82%). Compound 3 can also be synthesized by another method.³⁰

3: mp 92.2-93.4 °C. ¹H NMR (500 MHz, CDCl₃): δ 4.56 (s, 2H), 6.66 (s, 2H), 7.15 (t, J = 9.5 Hz, 2H), 7.28 (t, J = 9.5 Hz, 1H), 7.91 (d, J = 9.5 Hz, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 102.8, 124.3, 128.5, 129.8, 141.8, 156.5. HR-MS (HR-ESI-TOF) m/z calc. for C₁₀H₁₀N: 144.0813 [M+H]+; found: 144.0808. Anal. Calcd for C₁₀H₉N: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.69; H, 6.35; N, 9.88.

General procedure for the synthesis of 2-arylamino-1-azaazulenes

A mixture of the aryl halide (0.20 mmol), arylamine (0.28 mmol), Pd catalyst (6 mol%), phosphine ligand (4 equiv to Pd), Cs₂CO₃ (0.24 mmol), and 18-crown-6 (10 mol%) was refluxed in dry THF or 1,4-dioxane (6 mL) for 24 h in a sealed tube. Then, 20 mL of brine was added and the resulting mixture was extracted with CHCl₃. The combined organic layers were dried over anhydrous Na₂SO₄. After filtration and evaporation, the crude product was purified by silica gel column chromatography using CHCl₃ as the eluent. The product was recrystallized from AcOEt.

Synthesis of 1a

The first red purple fraction to elute from the column gave 4 as a red purple powder (18%). The sixth dark red fraction to elute gave 1a as a dark red powder (24%).

1a: mp > 212.8 °C (decomp.). ¹H NMR (500 MHz, DMSO-d₆): δ 7.11 (s, 1H), 7.21 (t, J = 9.5 Hz, 2H), 7.40 (t, J = 9.5 Hz, 1H), 7.47-7.52 (m, 2H), 7.58-7.63 (m, 1H), 7.65 (s, 2H), 8.13 (d, J = 9.5 Hz, 1H), 8.15 (d, J = 9.5 Hz, 2H), 8.19-8.23 (m, 1H), 11.07 (s, 1H). ¹³C{¹H} NMR (126 MHz, DMSO-d₆): δ 101.5, 106.1, 124.2, 127.7, 129.2, 129.4, 130.3, 131.1, 131.5, 131.9, 140.2, 146.9, 149.2, 157.5, 163.6. HRMS (HR-ESI-TOF) m/z calc. for C₁₉H₁₅N₂: 271.1235 [M+H]+; found: 271.1241. Anal. Calcd for C₁₉H₁₄N₂: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.17; H, 5.20; N, 10.20.

4: mp 172.9-174.6 °C. ¹H NMR (500 MHz, CDCl₃): δ 6.69 (s, 1H), 7.16 (t, J = 9.0 Hz, 1H), 7.23 (t, J = 9.0 Hz, 1H), 7.29 (t, J = 9.0 Hz, 1H), 7.51 (t, J = 9.5 Hz, 1H), 7.57 (t, J = 9.5 Hz, 1H), 7.63 (t, J = 9.5 Hz, 1H), 7.82 (d, J = 9.5 Hz, 1H), 7.87 (s, 1H), 8.35 (d, J = 9.0 Hz, 1H), 8.41 (d, J = 9.5 Hz, 1H), 8.57 (d, J = 9.0 Hz, 1H) (NH proton was not appeared). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 105.6, 107.9, 112.4, 126.9, 127.6, 127.8, 129.4, 130.4, 130.7, 131.5, 131.7, 132.4, 134.1, 141.6, 146.0, 147.5, 158.5, 160.4, 165.3. HR-MS (HR-ESI-TOF) m/z calc. for C₁₀H₁₅N₂: 271.1235 [M+H]+; found: 271.1235.
Synthesis of 1b
A reaction mixture was refluxed in THF. The first red fraction to elute from the column gave 1b as a red powder (70%).

1b: mp 151.5-153.5 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.55 (t, \(J = 6.5\) Hz, 3H), 4.55 (q, \(J = 6.5\) Hz, 2H), 7.21 (t, \(J = 9.5\) Hz, 2H), 7.44 (t, \(J = 9.5\) Hz, 1H), 7.64 (t, \(J = 9.5\) Hz, 1H), 7.75 (t, \(J = 9.5\) Hz, 1H), 7.80-7.84 (m, 3H), 8.22 (d, \(J = 9.5\) Hz, 2H), 8.64 (d, \(J = 9.5\) Hz, 1H), 10.54 (s, 1H).

\(^13\)C{\(^1\)H} NMR (126 MHz, CDCl\(_3\)): \(\delta\) 14.7, 60.7, 99.3, 107.4, 124.4, 131.4, 132.3, 132.9, 133.2, 133.7, 133.9, 134.1, 140.6, 146.8, 147.2, 160.6, 164.2, 166.6. HR-MS (HR-ESI-TOF) \(m/z\) calc. for C\(_{22}\)H\(_{19}\)N\(_2\)O\(_2\): 343.1447 [M+H]+; found: 343.1448.

IR (KBr, \(\nu/cm^{-1}\)): 3469 (N-H), 3272 (Aryl), 2979 (C-H), 1650 (C=O).

Anal. Calcd for C\(_{22}\)H\(_{18}\)N\(_2\)O\(_2\): C, 77.17; H, 5.30; N, 8.18. Found: C, 77.01; H, 5.17; N, 8.12.

Synthesis of 1c
A reaction mixture was refluxed in 1,4-dioxane. The third yellow brown fraction to elute from the column gave 1c as a yellow brown powder (30%).

1c: mp > 278.3 °C (decomp.). \(^1\)H NMR (500 MHz, DMSO-d\(_6\)): \(\delta\) 7.24 (t, \(J = 9.5\) Hz, 2H), 7.47 (t, \(J = 9.5\) Hz, 1H), 7.84 (t, \(J = 9.5\) Hz, 2H), 7.92 (t, \(J = 9.5\) Hz, 1H), 7.98 (t, \(J = 9.5\) Hz, 1H), 8.23 (d, \(J = 9.5\) Hz, 2H), 8.30 (d, \(J = 9.5\) Hz, 1H), 8.44 (d, \(J = 9.5\) Hz, 1H), 11.35 (s, 1H).

\(^13\)C{\(^1\)H} NMR (126 MHz, DMSO-d\(_6\)): \(\delta\) 81.4, 107.5, 114.9, 124.1, 128.6, 131.6, 132.4, 133.0, 133.7, 134.7, 134.8, 139.6, 148.1, 150.2, 159.0, 162.7. HR-MS (HR-ESI-TOF) \(m/z\) calc. for C\(_{20}\)H\(_{13}\)N\(_3\)Na: 318.1007 [M+Na]+; found: 318.1005. IR (KBr, \(\nu/cm^{-1}\)): 3469 (N-H), 3272, 3138 (Aryl), 3023 (C-H), 2214 (C=\(\equiv\)N).

Anal. Calcd for C\(_{20}\)H\(_{13}\)N\(_3\): C, 81.34; H, 4.44; N, 14.23. Found: C, 81.09; H, 4.40; N, 14.16.

Synthesis of 6
The fifth dark red fraction to elute from the column gave 6 as a dark red powder (26%).

6: mp > 193.4 °C (decomp.). \(^1\)H NMR (500 MHz, DMSO-d\(_6\)): \(\delta\) 7.10 (s, 1H), 7.20 (d, \(J = 4.0\) Hz, 2H), 7.50 (t, \(J = 4.0\) Hz, 1H), 7.52 (t, \(J = 9.0\) Hz, 1H), 7.56 (t, \(J = 9.0\) Hz, 1H), 7.64 (t, \(J = 9.0\) Hz, 1H), 7.99 (d, \(J = 9.0\) Hz, 2H), 8.18 (d, \(J = 9.0\) Hz, 1H), 8.26 (d, \(J = 9.0\) Hz, 1H), 10.74 (s, 1H).

\(^13\)C{\(^1\)H} NMR (126 MHz, DMSO-d\(_6\)): \(\delta\) 103.0, 112.9, 118.2, 128.7, 129.6, 130.1, 130.4, 131.6, 132.5, 135.4, 136.4, 146.1, 150.4, 158.8, 163.5. HR-MS (HR-APCI-TOF) \(m/z\) calc. for C\(_{19}\)H\(_{15}\)N\(_2\): 271.1235 [M+H]+; found: 271.1238. Anal. Calcd for C\(_{19}\)H\(_{14}\)N\(_2\): C, 84.42; H, 5.22; N, 10.36. Found: C, 84.37; H, 5.09; N, 10.31.

Synthesis of 8
The fourth yellow fraction to elute from the column gave \(8^\text{12}\) as a yellow powder (13%).
8: mp 148.8-151.1 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.94 (s, 1H), 7.12 (t, $J$ = 7.2 Hz, 1H), 7.34-7.40 (m, 4H), 7.47-7.52 (m, 3H), 7.99 (t, $J$ = 9.5 Hz, 2H) (NH proton was not appeared). $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 98.5, 119.8, 123.3, 126.7, 128.4, 129.3, 129.7, 130.6, 130.7, 140.3, 148.4, 157.6, 165.2. HR-MS (HR-ESI-TOF) m/z calc. for C$_{15}$H$_{13}$N$_2$: 221.1079 [M+H]$^+$; found: 221.1076. Anal. Calcd for C$_{15}$H$_{12}$N$_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.47; H, 5.43; N, 12.57.

Synthesis of 10
The fourth yellow fraction to elute from the column gave 10 as a yellow powder (28%).

10: mp 195.9-196.9 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.70 (s, 1H), 7.36-7.39 (m, 2H), 7.45-7.50 (m, 1H), 7.51-7.56 (m, 3H), 7.76 (d, $J$ = 8.0 Hz, 1H), 7.82 (d, $J$ = 8.0 Hz, 1H), 7.90-7.94 (m, 3H), 8.18 (d, $J$ = 8.0 Hz, 1H) (NH proton was not appeared). $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 98.5, 119.0, 122.0, 125.5, 125.7, 126.3, 126.4, 126.5, 128.2, 128.4, 128.5, 129.8, 130.7, 130.8, 134.5, 135.8, 148.3, 157.3, 166.5. HR-MS (HR-ESI-TOF) m/z calc. for C$_{19}$H$_{15}$N$_2$: 271.1235 [M+H]$^+$; found: 271.1221. Anal. Calcd for C$_{19}$H$_{14}$N$_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.14; H, 5.19; N, 10.29.

Synthesis of 12
The fourth yellow fraction to elute from the column gave 12 as a yellow powder (51%).

12: mp 200.7-202.1 °C. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.02 (s, 1H), 7.39-7.46 (m, 3H), 7.47-7.50 (m, 1H), 7.53-7.56 (m, 2H), 7.81 (t, $J$ = 7.0 Hz, 2H), 7.86 (d, $J$ = 8.5 Hz, 1H), 7.95 (d, $J$ = 2.0 Hz, 1H), 8.03 (dd, $J$ = 2.0, 8.5 Hz, 1H), 8.06 (d, $J$ = 8.5 Hz, 1H) (NH proton was not appeared). $^{13}$C{$^1$H} NMR (126 MHz, CDCl$_3$): $\delta$ 98.6, 115.4, 120.5, 124.7, 126.7, 126.7, 127.1, 127.7, 129.1, 129.3, 130.2, 130.3, 131.0, 131.4, 134.2, 137.6, 148.4, 156.6, 164.2. HR-MS (HR-ESI-TOF) m/z calc. for C$_{19}$H$_{14}$N$_2$: 271.1235 [M+H]$^+$; found: 271.1234.

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