for

One Pot Synthesis of *N*-Substituted Diaza[12]annulenes

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I. General

Solvents were dried, distilled, and stored under N₂. *N*-(2,4-dinitrophenyl)pyridinium chloride was prepared according to the literature.¹ Other reagents were purchased and used without further purification. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer and a JEOL AL-400 spectrometer, respectively. Elemental and FAB-MS analyses were carried out on a Yanagimoto MT-5 CHN corder and a JEOL JMS-700, respectively. *m*-Nitrobenzylalcohol was used as a matrix. UV-vis spectra were obtained by a JASCO V-560 spectrometer. Cyclic voltammetry was performed in a DMSO solution containing 0.10 M [Et₄N]BF₄ with a BAS 100B. Melting point was determined by a Nikon LABOPHOTO-POL microscope with a hot stage.

II. Synthesis

Synthesis of 3a.

N-(2,4-dinitrophenyl)pyridinium chloride (**1**) (1.41 g, 5.0 mmol) and 2,5-dimethylaniline (**2a**) (1.21 g, 10.0 mmol) were dissolved in 5 mL of dry ethanol under N₂. After the solution was refluxed for 12 h under nitrogen, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum, and the resulting solid was extracted with water (50 mL). Evaporation of water gave a brown solid, which was chromatographed on silica gel with chloroform to

afford compound **3a** as a hygroscopic brown solid (0.44 g, 40%).

M.p. 179-181 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.26 (d, $J = 5.9$ Hz, 4H), 8.85 (t, $J = 7.6$ Hz, 2H), 8.33 (t, $J = 6.6$ Hz, 4H), 7.51 (s, 2H), 7.42 (d, $J = 8.8$ Hz, 4H), 2.34 (s, 6H), 2.06 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO}-d_6$): δ 147.2, 146.1, 142.0, 137.4, 131.9, 131.7, 129.2,

128.5, 126.5, 20.4, 16.4. FAB-MS: $[\text{M}+\text{H}^+] = 441, 439$. Anal. Calcd for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 68.27; H, 6.61; N, 6.12. Found: C, 68.15; H, 6.44; N, 5.98.

Synthesis of **3b**.

1 (1.40 g, 5.0 mmol) and *p*-anisidine (**2b**) (1.23 g, 10.0 mmol) were dissolved in 8 mL of dry ethanol under N_2 . After the solution was refluxed for 12 h, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum, and the resulting solid was washed with acetone (200 mL). Compound **3b** was collected by filtration, dried under vacuum, and obtained as a light brown powder (0.92 g, 83%).

M.p. 125-126 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.20 (d, $J = 5.6$ Hz, 4H), 8.73 (t, $J = 6.8$ Hz, 2H), 8.27 (t, $J = 6.8$ Hz, 4H), 7.83 (d, $J = 8.8$ Hz, 4H), 7.26 (d, $J = 8.8$ Hz, 4H), 3.87 (s, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $\text{DMSO}-d_6$): δ 161.2, 146.1,

145.0, 136.0, 128.2, 126.2, 115.3, 56.1. FAB-MS: $[\text{M}+\text{H}^+] = 443, 447$. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{Cl}_2\text{N}_2\text{O}_2 \cdot 0.5\text{H}_2\text{O}$: C, 63.72; H, 5.57; N, 6.19. Found: C, 63.55; H, 5.40; N, 6.02.

Synthesis of **3c**.

1 (1.40 g, 5.0 mmol) and 4-fluoroaniline (**2c**) (1.17 g, 10.5 mmol) were dissolved in 8 mL of dry ethanol under N_2 . After the solution was refluxed for 12 h, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum, and the resulting solid was washed with acetone (200 mL). **3c** was collected by filtration, dried under vacuum, and obtained as a light brown powder (0.65 g, 62%).

M.p. 77-78 °C. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 9.35 (d, $J = 5.6$ Hz, 4H), 8.79 (t, $J = 8.0$ Hz, 2H), 8.31 (t, $J = 6.8$ Hz, 4H), 7.98 (q, J

= 8.8 Hz, 4H), 7.62 (t, J = 8.8 Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 149.9, 146.6, 143.9, 128.1, 127.5, 117.1, 116.9. FAB-MS: $[\text{M}+\text{H}^+] = 413, 417$. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{Cl}_2\text{F}_2 \cdot 0.5\text{H}_2\text{O}$: C, 61.69; H, 4.47; N, 6.54. Found: C, 61.49; H, 4.23; N, 6.61.

Synthesis of 3d and 4d.

1 (1.49 g, 5.3 mmol) and 4-chloroaniline (**2d**) (1.33 g, 10.4 mmol) were dissolved in 8 mL of dry ethanol under N_2 . After the solution was refluxed for 12 h, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum, and the resulting solid was washed with acetone (200 mL). A mixture of **3d** and **4d** was collected by filtration. **3d** was obtained by repeating wash the mixture with acetone and drying under vacuum as a light brown powder (0.94 g, 73%). Evaporation of the solvent of the filtrate gave the mixture of **3d** and **4d** as a brown solid. The yield of **4d** was estimated from peak integral of the ^1H NMR spectrum of the mixture.

Data of 3d. M.p. 119-122 °C. ^1H NMR (400 MHz, DMSO- d_6): δ 9.38 (d, J = 5.6 Hz, 4H), 8.79 (t, J = 7.6 Hz, 2H), 8.32 (t, J = 6.8 Hz, 4H), 7.95 (d, J = 9.2 Hz, 4H), 7.84 (d, J = 9.2 Hz, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 147.0, 145.2, 141.6, 136.1, 130.2, 128.3, 127.0. FAB-MS: $[\text{M}+\text{H}^+] = 451, 460$. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{Cl}_4 \cdot 0.8\text{H}_2\text{O}$: C, 56.70; H, 4.11; N, 6.01. Found: C, 56.58; H, 4.22; N, 5.88.

Data of 4d. ^1H NMR (400 MHz, DMSO- d_6): δ 13.05 (d, J = 13.2 Hz, 2H), 8.93 (t, J = 12.0 Hz, 2H), 7.54 (d, J = 8.8 Hz, 4H), 7.47 (d, J = 8.8 Hz, 4H), 6.56 (t, J = 11.2 Hz, 1H). FAB-MS: $[\text{M}+\text{H}^+] = 353, 359$.

Synthesis of 3e and 4e.

1 (7.04 g, 25.0 mmol) and 4-bromoaniline (**2e**) (8.60 g, 50.0 mmol) were dissolved in 16 mL of dry ethanol under N_2 . After the solution was refluxed for 12 h, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum, and the resulting solid was washed with chloroform (200 mL). A mixture of **3e** and **4e** was collected by

filtration. **3e** was obtained by repeating wash the mixture with acetone and drying under vacuum as a light brown powder (5.13 g, 76%). Evaporation of the solvent of the filtrate gave the mixture of **3e** and **4e** as a brown solid. The yield of **4e** was estimated from peak integral of the ^1H NMR spectrum of the mixture.

Data of 3e. M.p. 122-125 °C. ^1H NMR (400 MHz, DMSO- d_6): δ 9.33 (d, J = 4.8 Hz, 4H), 8.79 (t, J = 8.0 Hz, 2H), 8.31 (t, J = 7.2 Hz, 4H), 7.98 (d, J = 8.6 Hz, 4H), 7.85 (d, J = 8.6 Hz, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 146.8, 145.0, 141.9, 133.0, 128.1, 127.0, 124.7. FAB-MS: $[\text{M}+\text{H}^+] = 539, 543, 547$. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{Br}_2\text{Cl}_2 \cdot 0.5\text{H}_2\text{O}$: C, 48.03; H, 3.48; N, 5.09. Found: C, 47.92; H, 3.64; N, 4.51.

Data of 4e. ^1H NMR (400 MHz, DMSO- d_6): δ 13.05 (d, J = 13.2 Hz, 2H), 8.93 (t, J = 12.0 Hz, 2H), 7.54 (d, J = 8.8 Hz, 4H), 7.47 (d, J = 8.8 Hz, 4H), 6.56 (t, J = 11.2 Hz, 1H). FAB-MS: $[\text{M}+\text{H}^+] = 441, 443, 445$.

Synthesis of **3f** and **4f**.

1 (1.44 g, 5.1 mmol) and 4-iodoaniline (**2f**) (2.19 g, 10.0 mmol) were dissolved in 8 mL of dry ethanol under N_2 . After the solution was refluxed for 12 h, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. The solvent was evaporated under vacuum, and the resulting solid was washed with chloroform (200 mL). A mixture of **3f** and **4f** was collected by filtration. **3f** was obtained by repeating wash the mixture with acetone and drying under vacuum as a light brown powder (0.74 g, 46%). Evaporation of the solvent of the filtrate gave the mixture of **3f** and **4f** as a brown solid. The yield of **4f** was estimated from peak integral of the ^1H NMR spectrum of the mixture.

Data of 3f. M.p. 122-124 °C. ^1H NMR (400 MHz, DMSO- d_6): δ 9.34 (d, J = 5.6 Hz, 4H), 8.79 (t, J = 8.0 Hz, 2H), 8.30 (t, J = 6.8 Hz, 4H), 8.12 (d, J = 8.4 Hz, 4H), 7.69 (d, J = 8.0 Hz, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, DMSO- d_6): δ 146.9, 145.0, 142.5, 139.0, 128.3, 127.0, 98.9. FAB-MS: $[\text{M}+\text{H}^+] = 508, 512$. Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{N}_2\text{Cl}_2\text{I}_2 \cdot 0.5\text{H}_2\text{O}$: C, 41.02; H, 2.97; N, 4.35. Found: C, 40.91; H, 3.06; N, 4.22.

Data of 4f. ^1H NMR (400 MHz, DMSO- d_6): ^1H NMR (400 MHz, DMSO- d_6): δ 12.95 (d, $J = 12.8$ Hz, 2H), 8.92 (t, $J = 11.6$

Hz, 2H), 7.81 (d, $J = 8.0$ Hz, 4H), 7.46 (d, $J = 8.0$ Hz, 4H), 6.55 (t, $J = 11.2$ Hz, 1H).

Synthesis of 3g.

1 (1.41 g, 5.0 mmol) and *n*-hexylamine (**2g**) (1.01 g, 10.0 mmol) were dissolved in 8 mL of dry ethanol under N_2 . After the solution was refluxed for 12 h, 2,4-dinitroaniline precipitated from the reaction solution was removed by filtration. Evaporation of the solvent under vacuum gave dark brown solid, which was dissolved in DMSO (1 mL) and poured into hexane (200 mL). The obtained brown solid was extracted with water (200 mL), evaporation of the solvent and dried under vacuum provided **3g** as a light brown powder (0.40 g, 60%).

M.p. 97-100 °C. ^1H NMR (400 MHz, CDCl_3):

δ 9.49 (d, $J = 5.6$ Hz, 4H), 8.56 (t, $J = 7.6$ Hz, 2H), 8.22 (t, $J = 7.2$ Hz, 4H), 4.95 (t, $J = 7.6$ Hz, 4H), 2.04 (t, $J = 7.6$ Hz, 4H), 1.27 (m, 12H), 0.83 (t, J

= 6.8 Hz, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 145.3, 144.9, 128.5, 61.8, 31.6, 31.0, 25.5, 22.2, 13.8. Anal. Calcd for $\text{C}_{22}\text{H}_{36}\text{N}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$: C, 71.69; H, 8.14; N, 4.92. Found: C, 71.50; H, 8.29; N, 4.77.

III. Reference

1. Zincke, Th.; Heuser, G.; Möller, W. *Ann.* **1904**, 333, 296.

VI. ^1H and ^{13}C NMR spectra