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Supplementary Experimental Section

Melting points were determined using a Gallenkamp hot-stage apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer (^{13}C at 62.9 MHz). IR spectra were recorded as KBr discs on a Pye Unicam SP 1050 spectrometer. Low resolution mass spectra were measured on a VG-12-253J spectrometer, EI at 70eV and CI by NH_3 and are given in terms of m/e (relative intensity). Where indicated mass spectra were recorded by alternate chemical ionisation/electron impact (ACE). C-13 coupling patterns are supported by DEPT experiments.

Materials were generally obtained from Aldrich or BDH and were purified by standard literature procedures.^{14,25} 3-Chloro-4-nitropyridine 1-oxide was prepared by the method of Talik and Talik.²⁶ Column chromatography was carried out using BDH Kieselgel 60 (230-400 mesh).

Bis(2-amino-3-pyridyl) disulfide (6)

A mixture of 2-t-butylthiazolo[4,5-b]pyridine (2) (2.63g, 13.7 mmol)¹² and 10% aqueous sodium hydroxide (44 mL, 0.11 mol) was heated under reflux for 6h. After this time the starting material was still visible as an oil on the surface and so further sodium hydroxide pellets (4.44g, 0.11 mol) were added and the reflux was continued for another 6h. The cooled solution was washed with dichloromethane (50 mL) and then neutralised with conc. HCl. Continuous extraction of the aqueous solution with ethyl acetate yielded the product (0.93 g, 54%) after 2 days. Further product was collected after filtering the aqueous suspension to remove insoluble white solid, evaporation of the filtrate to dryness and extraction with boiling ethyl acetate. Removal of the solvent after several extractions gave further disulfide (0.70 g), bringing the total yield of 6 to 95%, mp 158°C; ^1H NMR ($\text{DMSO}-d_6$) δ 6.35 (br s, NH_2 , 4H), 6.47 (dd, $J = 4.8, 7.5$ Hz, H-5, 2H), 7.27 (dd, $J = 1.8, 7.5$ Hz, H-4, 2H), 7.99 (dd, $J = 1.8, 4.8$ Hz, H-6, 2H); ^{13}C NMR δ ($\text{DMSO}-d_6$) 111.5 (s, C-3), 112.6 (d,

C-5), 143.1 (d, C-4), 149.9 (d, C-6), 159.4 (s, C-2); IR 3470, 3300, 3160, 1630, 1580, 1560, 1470, 1445, 1330, 1290, 1245, 1075, 665; MS m/z (relative intensity) 250 (M^+ , 23), 217 (2), 125 (100), 98 (42), 81 (28), 71 (16), 54 (20), 39 (49); HRMS calcd for $C_{10}H_{10}N_4S_2$ 250.0347, found 250.0336. Anal. Calcd for $C_{10}H_{10}N_4S_2$ (250.03): C, 47.98; H, 4.03; N, 22.38. Found: C, 47.69; H, 3.96; N, 22.09.

Bis(2-oxo-3(1H)-pyridyl) disulfide (7)

A solution of **6** (1.28 g, 5.1 mmol) in distilled water (15 mL) and 98% H_2SO_4 (2.8 mL) was carefully treated at 0°C with a solution of sodium nitrite (1.8 g) in water (3 mL). After stirring at 0°C for 1h, room temperature for 1h and then 70°C for 2h to decompose the diazonium compound, the resulting suspension was cooled and filtered to give **7** (0.92 g, 71%), mp 225°C; 1H NMR (DMSO- d_6) δ 6.26 (apparent t, J = 6.8 Hz, H-5, 2H), 7.33 (dd, J = ca. 1.7, 6.4 Hz, H-4, 2H), 7.44 (dd, J = 1.7, 7.1 Hz, H-6, 2H), 12.03 (br, NH, 2H); ^{13}C NMR δ (DMSO- d_6) 105.7 (d, C-5), 126.1 (s, C-3), 132.8 (d, C-4 or C-6), 134.9 (d, C-6 or C-4), 160.0 (s, C-2); IR 3440, 3100, 3000, 1640, 1610, 1530, 1460, 1430, 1135, 1260, 1210, 1135, 1040, 970, 935, 875, 770, 760; MS m/z (relative intensity) 252 (M^+ , 21), 220 (7), 127 (100), 99 (42), 82 (10), 71 (32), 54 (32), 45 (25), 39 (28); HRMS calcd for $C_{10}H_8N_2O_2S_2$ 252.0027, found 252.0025.

3-Mercapto-2(1H)-pyridinone (1)

A mixture of the disulfide **7** (0.435g, 1.7 mmol) and hydrazine (1 mL) in ethanol (3 mL) was refluxed for 1h under an argon atmosphere. The cooled mixture was filtered to collect the product which was washed with ethanol and dried to give **(1)** (0.37 g, 84%); mp 175-176°C; 1H NMR* (DMSO- d_6) δ 6.27 (br, H-5, SH, NH, 3H), 6.87 (br, H-4, 1H), 7.35 (br, H-6, 1H); IR 2260-3400 (br, SH, NH), 1640, 1610, 1520, 1445, 1425, 1305, 1270, 1250, 1195, 1120, 1090, 1065, 1045, 965, 950, 895,

* All peaks were very broad and could not really be assigned properly due to solubility problems. The ^{13}C NMR spectrum could not be measured.

865, 765; MS m/z (relative intensity) 127 (M^+ , 100), 99 (18), 72 (7), 54 (4), 45 (9); HRMS calcd. for C_5H_5NOS 127.0092, found 127.0089.

4-Azaphenoxathiine (10)

A mixture of (1) (0.370 g, 2.9 mmol) and sodium methoxide (0.370 g, 6.85 mmol) in dry methanol (30 mL) was heated under reflux for 48h. The solvent was removed by rotary evaporation and the resulting pale brown solid ($mp > 300^\circ C$) was dissolved in dry DMF (35 mL) to which was added the 1-chloro-2-nitrobenzene (0.460 g, 2.9 mmol). The mixture darkened and was heated under reflux for 6h under an argon atmosphere. On cooling, distilled water (10 mL) was added, the solution was extracted with chloroform (4 x 80 mL) and dried ($MgSO_4$). The extracts were evaporated under high vacuum to ensure complete removal of DMF. Purification by bulb to bulb distillation at $125^\circ C/0.2$ mm Hg gave **10** (0.239, 41%). 1H NMR ($CDCl_3$) δ 6.97 (dd, $J = 4.9, 7.6$ Hz, H-2, 1H), 7.00-7.18 (m, H-6, 7, 8 and 9, 4H), 7.39 (dd, $J = 1.8, 7.6$ Hz, H-1, 1H), 8.02 (dd, $J = 1.8, 4.9$ Hz, H-3, 1H); ^{13}C NMR ($CDCl_3$) δ 115.83 (s, C-10a), 118.15 (s, C-9a), 118.51 (d, C-6), 120.98 (d, C-2), 125.09 (d, C-8), 126.27 (d, C-7), 128.09 (d, C-9), 135.65 (d, C-1), 145.68 (d, C-3), 151.48 (s, C-5a), 157.45 (s, C-4a); IR 3070, 1590, 1575, 1480, 1450, 1410, 1295, 1270, 1250, 1230, 1210, 1130, 1080, 1045, 1030, 935, 890, 815, 785, 750; MS ACE EI m/z (relative intensity) 201 (M^+ , 100), 187 (8), 172 (73), 169 (68), 157 (81), 146 (39), 140 (30), 129 (20), 114 (11), 102 (30), 69 (33); CI m/z (relative intensity) 202 ($(M+H)^+$, 100), 169 (11), 157 (9), 146 (5), 129 (3), 102 (7), 82 (3), 69 (8), 63 (10); HRMS calcd for $C_{11}H_7NOS$ 201.0248, found 201.0284.

1,6-Diazaphenoxathiine (12)

The procedure described above for the synthesis of **10** was used, except that 2-chloro-3-nitropyridine (0.460g, 2.9 mmol) was used instead of 1-chloro-2-nitrobenzene. The crude product was purified by column chromatography (silica, 25% ether in hexane). After recrystallisation from ether, the product (**12**) (0.258g, 44%)

was obtained as off-white needles, mp 112-114°C. ^1H NMR (CDCl_3) δ 7.02 (dd, J = 4.9, 7.6 Hz, H-8, 1H), 7.08 (dd, J = ca. 4.7, 8.2 Hz, H-3, 1H), 7.28 (dd, J = 1.5, 8.2 Hz, H-4, 1H), 7.45 (dd, J = 1.8, 7.6 Hz, H-9, 1H), 8.04 (dd, J = ca. 1.8, 4.9 Hz, H-7, 1H), 8.15 (dd, J = ca. 1.5, 4.7 Hz, H-2, 1H); ^{13}C NMR (CDCl_3) δ 115.42 (s, C-9a), 121.33 (d, C-8), 122.80 (d, C-3), 124.71 (d, C-4), 136.22 (d, C-9), 142.03 (s, C-10a), 145.48 (d, C-2), 145.89 (d, C-7), 147.83 (s, C-4a), 155.71 (s, C-5a); IR 3060, 1580, 1570, 1445, 1410, 1280, 1230, 1205, 1130, 1090, 1080, 1050, 980, 905, 825, 800, 790, 750, 740, 720; MS ACE EI m/z (relative intensity) 202 (M^+ , 100), 174 (12), 158 (38), 147 (9), 120 (1), 103 (2), 82 (4), 69 (7), 64 (2); CI m/z (relative intensity) 203 ($(\text{M}+\text{H})^+$, 100), 174 (1); HRMS (CI) calcd for $\text{C}_{10}\text{H}_6\text{N}_2\text{OS}$ 202.0201, found 202.0201. Anal. Calcd for $\text{C}_{10}\text{H}_6\text{N}_2\text{OS}$ (202.02): C, 59.39; H, 2.99; N, 13.86. Found C, 59.55; H, 3.07; N, 13.70.

2,6-Diazaphenoxathiine 2-oxide (14)

The procedure described above for the synthesis of **10** was used, except that 3-chloro-4-nitropyridine 1-oxide (0.506g, 2.9 mmol) was used instead of 1-chloro-2-nitrobenzene. The product (0.328g, 52%) was isolated by continuous extraction of the neutralised aqueous reaction mixture with ethyl acetate. Recrystallisation from ethyl acetate gave buff coloured needles, mp 223°C; ^1H NMR ($\text{DMSO}-d_6$) δ 7.18 (d, J = 7.1 Hz, H-4, 1H), 7.21 (dd, J = 4.8, 7.6 Hz, H-8, 1H), 7.82 (dd, J = 1.8, 7.6 Hz, H-9, 1H), 8.01 (dd, J = 2.1, 7.1 Hz, H-3, 1H), 8.08 (dd, J = 1.8, 4.8 Hz, H-7, 1H), 8.34 (d, J = 2.1 Hz, H-1, 1H); ^{13}C NMR ($\text{DMSO}-d_6$) δ 112.27 (s, C-9a), 114.99 (d, C-4), 118.42 (s, C-10a), 122.40 (d, C-8), 135.57 (d, C-3), 137.21 (d, C-9), 138.46 (d, C-1), 146.30 (d, C-7), 147.36 (s, C-4a), 154.98 (s, C-5a); IR 1585, 1475, 1450, 1430, 1410, 1270, 1235, 1220, 1205, 1140, 1120, 1085, 1045, 880, 840, 810, 795, 785, 730; MS ACE EI m/z (relative intensity) 218 (M^+ , 100), 202 (89), 175 (31), 162 (2), 135 (2), 109 (1), 82 (18), 69 (28), 50 (12); CI m/z (relative intensity) 219 ($(\text{M}+\text{H})^+$, 100), 203 (80); HRMS calcd for $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_2\text{S}$ 218.0150, found 218.0163. Anal. Calcd. for

$\text{C}_{10}\text{H}_6\text{N}_2\text{O}_2\text{S}$ (218.02): C, 55.03; H, 2.77; N, 12.84. Found C, 55.13; H, 2.89; N, 12.74.

2,6-Diazaphenoxathiine (15)

A solution of **14** (0.280 g, 1.3 mmol) and phosphorus trichloride (0.2 mL, excess) in chloroform (20 mL) was heated under reflux for 2h. The mixture was cooled, distilled water (40 mL) was cautiously added and the mixture was neutralised with cold sodium hydroxide solution. The organic layer was removed and the aqueous solution was further extracted with chloroform (3 x 80 mL). The combined extracts were dried (MgSO_4) and concentrated to yield **15** (0.20g, 77%) which was sublimed at $105^\circ\text{C}/0.1$ mm Hg to an off-white solid which softens and then melts at $92.5\text{--}93.5^\circ\text{C}$; ^1H NMR (CDCl_3) δ 6.95 (d, $J = 5$ Hz, H-4, 1H), 7.04 (dd, $J = \text{ca. } 4.8, 7.5$ Hz, H-8, 1H), 7.43 (d, $J = 7.5$ Hz, H-9, 1H), 8.04 (d, $J = 5$ Hz, H-3, 1H), 8.23 (s, H-1, 1H), 8.32 (d, $J = 4.8$ Hz, H-7, 1H); ^{13}C NMR (CDCl_3) δ 113.10 (d, C-4), 114.42 (s, C-9a), 115.68 (s, C-10a), 121.92 (d, C-8), 136.30 (d, C-9), 146.03 (d, C-7), 146.83 (d, C-3), 149.83 (d, C-1), 155.67 (s, C-5a), 157.72 (s, C-4a); IR 3060, 1590, 1580, 1560, 1555, 1485, 1420, 1400, 1295, 1270, 1250, 1225, 1170, 1110, 1070, 1050, 1030, 905, 810, 800, 735; MS ACE EI m/z (relative intensity) 202 (M^+ , 100), 175 (36), 158 (7), 82 (8), 69 (9), 50 (4); CI m/z (relative intensity) 203 ($(\text{M}+\text{H}^+)$, 100), 175 (5); HRMS calcd for $\text{C}_{10}\text{H}_6\text{N}_2\text{OS}$ 202.0201, found 202.0226. Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{N}_2\text{OS}$ (202.02): C, 59.39; H, 2.99; N, 13.86. Found C, 59.42; H, 3.06; N, 13.66.