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ELECTROCHEMICAL SYNTHESIS OF SUBSTITUTED INDOLIZINES; UV AND FLUORESCENCE SPECTRA

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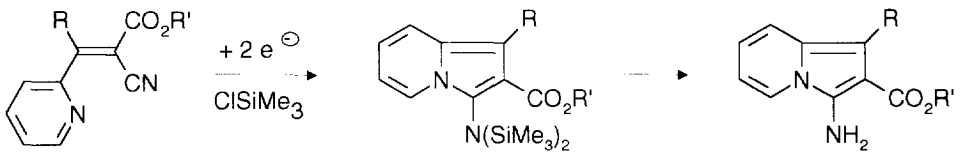
Abstract: 2-Cyano-3-(2-pyridyl)methylacrylates form substituted indolizines upon electrochemical reduction in the presence of chlorotrimethylsilane. All indolizines prepared by this procedure show intense fluorescence in solution and in the crystalline state.

Indolizine (pyrrolo-[1,2- a]pyridine) is isomeric to indole and isoindole and is found in many natural products, [1,2,3] mainly in its hydrogenated state. Indolizines were mostly prepared from substituted pyridines and the five membered ring is formed in several steps. [1,4-11]

We found a short and efficient access to substituted indolizines from 2-cyano-3-pyridylacrylates **1**, which can easily be prepared from 2-acylpyridines and cyanoacetate. [12,13,14] The electrochemical reduction of **1** in dry acetonitrile and in the presence of chlorotrimethylsilane leads in one step to the indolizine **2**. The overall reaction is shown in scheme 1.



1 **2a** **2b**

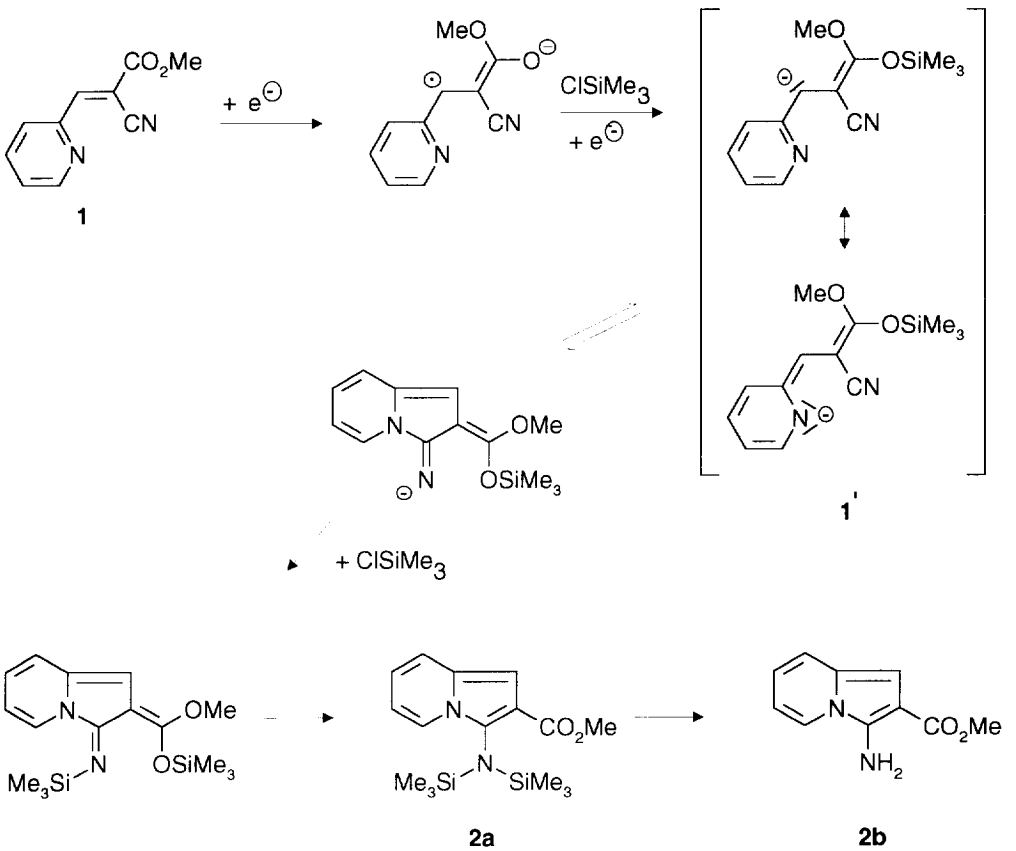
Scheme 1

Comparable with the electrochemical reaction is the reduction of **1** with diisobutyl-aluminumhydride, which leads to the amino derivative **2b** (R=H, R'=Et) in 45% yield. [15] The electrochemical procedure showed to be a more general and versatile method for the synthesis of indolizines allowing a variety of substituents in **1**.

Compounds **1** are electrochemically reduced at potentials between -1.2 V and -1.7 V (vs. SCE). The anion radicals are fairly stable in acetonitrile (peak current ratio i_a/i_c= < 0.5 - 1.0) and the second reduction peak (dianion) lies very close at - 1.3 V to - 1. 7 V. When R is an aryl group the reversibility of the reduction steps is much enhanced (i_a/i_c close to 1), indicating a dimerization at this position as a possible side reaction to the formation of the indolizines. A plausible mechanism for the formation of **2a** is given in scheme 2.

Transfer of an electron, silylation at the ester enolate centre and transfer of a second electron leads to the anion **1'**. The nitrogen atom of the pyridine ring now attacks the adjacent cyano group. This cyclization reaction is fixed by silylation at the exocyclic nitrogen atom. A final 1,5- sigmatropic migration of a silyl group leads to

2a. After aqueous workup **2a** and sometimes also the desilylated product **2b** are isolated. The structure of **2a** was proved by an X-ray analysis. [16]



1 1' 2a 2b

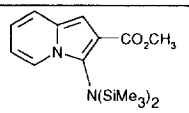
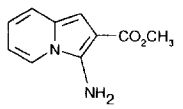
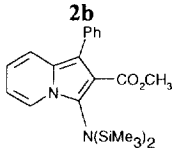
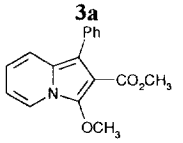
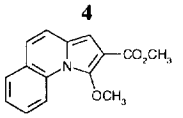
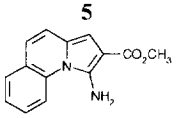
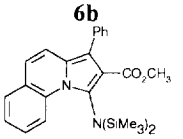
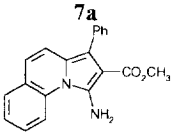
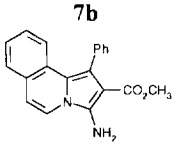
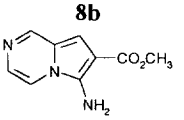
Scheme 2

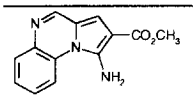
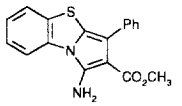
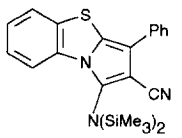
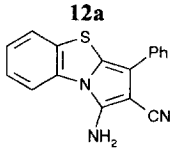
Some examples for the synthesis of indolizine derivatives are given in table 1. Substituents in 3-position decrease the rate of dimerization at the radical anion state and therefor increase the yield of indolizine. The cyclization to the indolizine fails with only a few exceptions (**4** and **5**) after replacing the cyano group by an ester function. Starting from quinoline and isoquinoline derivatives of **1** benzo anellated indolizines can also be prepared in good yields (**5-8**). The pyrazine and the quinoxaline derivative of **1** lead to the azaindolizines **9b** and **10b**. Cyclization could also be achieved with benzthiazole derivatives of **1** leading to the heterocycles **11** and **12**.

These indolizines are electron rich aromatic compounds which can be oxidized at potentials between 0.5 V and 1.0 V (vs. SCE, table 1)

The oxidation wave is only reversible, if there is a substituent at C-1, indicating a dimerization of the cation radical at this position. Oxidative dimerizations of indolizines at C-3 are known.[17, 18, 19]

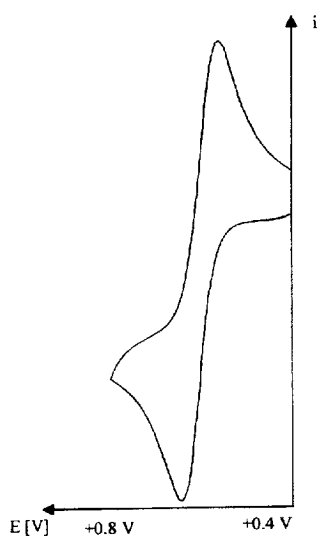
Table 1: Yields, absorption and fluorescence spectra and oxidation potentials of indolizines **2a - 12b**

compound	yield [%]	$\lambda_{max\,(Abs.)}$ [nm] [a] ε[dm^{3}mol^{-1}cm^{-1}]	$\lambda_{max\,(Em.)}$ [nm] [a]	$E_{1/2}$ [V] [b]
 **2a**	49	240 (28 800), 300 (2 400), 370 (2 400)	446, 464	+ 0.81 (irr.)
 **2b**	47	250 (28 200), 300 (4 600), 400 (2 700)	507	+ 0.37 [c] (irr.)
 **3a**	78	234 (17 200), 302 (4 700), 385 (2 100)	471	+ 0.71 (rev.)
 **4**	30	234 (29 800), 296 (6 900), 386 (3 900)	472	+ 0.74 [c] (irr.)
 **5**	39	250 (38 300), 335 (8 900)	426	+ 0.89 [c] (irr.)
 **6b**	44	240 (24 600), 260 (14 300), 384 (4 300)	474	+ 0.52 (irr.)
 **7a**	86	234 (17 200), 302 (4 700), 378 (2 100)	--- [d]	+ 0.84 (rev.)
 **7b**	40	240 (27 400), 396 (6 900)	--- [d]	--- [d]
 **8b**	69	272 (42 200), 354 (7 000)	501	+ 0.56 [c] (irr.) + 0.74 [c] (irr.)
 **9b**	29	224 (19 100), 254 (26 700), 412 (3 800)	471	--- [d]

compound	yield [%]	$\lambda_{max\,(Abs.)}$ [nm] ε[dm^{3}mol^{-1}cm^{-1}]	$\lambda_{max\,(Em.)}$ [nm]	$E_{1/2}$ [V]
 **10b**	49	242 (21 500), 276 (6 800), 390 (4 200)	480	+ 0.71 [c] (irr.)
 **11b**	16	256 (33 200), 280 (6 800), 311 (11 500)	--- [d]	+ 0.54 (rev.)
 **12a**	58	254 (43 900), 279 (9 800), 303 (16 600)	--- [d]	+ 1.04 (rev.)
 **12b**	65	251 (33 000), 313 (12 800)	--- [d]	+ 0.65 (irr.)

a) CH_3OH; b) CH_3CN, Pr_4NBF_4, vs SCE, 0.3 V/s; c) anodic peak potential; d) not yet measured

When the oxidation step is irreversible an additional cathodic peak appears between +0.3 V and -0.1 V on the backward sweep. This peak corresponds to the reduction of a product formed from the radical cation.



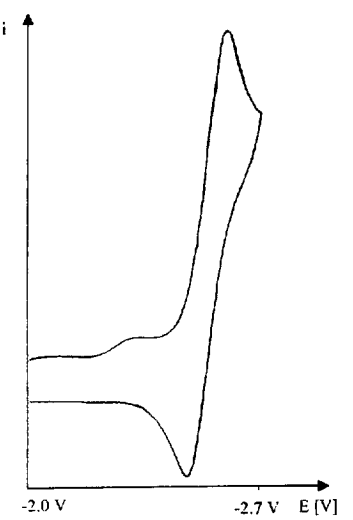


Figure 1:a) Oxidation of **3a**; CH_3CN, Pr_4NBF_4, Pt, 0.3 V/s.

b) Reduction of **3a**; CH_3CN, Pr_4NBF_4, vs SCE, Hg, 0.3 V/s.

Some indolizines like **3a**, **7a** and **12a** also form stable cation radicals. The oxidation potential is shifted to more positives values in N-silylated products, and when the ester is replaced by a nitrile group.

In spite of the high electron density of the aromatic ring some indolizines can also be reduced electrochemically. **3a** shows a reversible reduction wave at -2.54 V (vs. SCE). In the silylated products the lone pair of the exocyclic nitrogen atom is out of conjugation with the aromatic ring by steric reasons, rendering the reduction potential less negative. The free amino derivatives are only reduced beyond -2.6 V. The reduction wave is therefore obscured by the cathodic limit of the background electrolyte.

All indolizines listed in table 1 are coloured due to long wave absorption maxima between 350 and 400 nm. Again all indolizines show intense fluorescence at 450-500 nm upon irradiation at the long wave absorption maximum. The shift between absorption and fluorescence amounts to about 80 nm to 90 nm. Representative spectra of **10b** are shown in figure 2. For **2a** and **2b** the fluorescence has also been measured in the crystalline state.

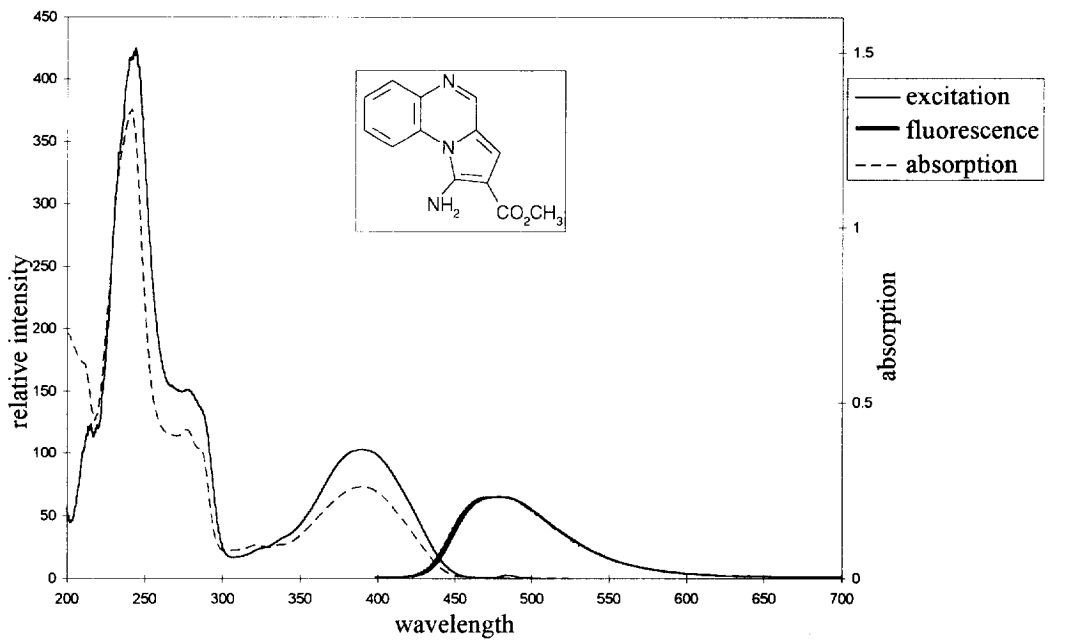


Figure 2: Absorption, fluorescence and excitation spectra of **10b.**

The indolizine derivatives described in this paper could be used as fluorescent dyes. Measurements of the electrochemoluminescence are under investigation.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded at 400 MHz on a Bruker ARX 400, at 250 MHz on a Bruker WM 250 or at 60 MHz on a Varian ASS. EM 360 spectrometer using TMS δ_H 0.0 as an internal reference. All J values are given in Hz. ^{13}C NMR spectra were recorded on Bruker ARX 400 and WM 250. Absorption spectra were measured using a Hitachi U 2000 spectrophotometer, and the emission spectra were recorded at a F-4500 fluorescence spectrophotometer. Mass spectra are obtained on a Finnigan MAT 112S/SS200 spectrometer. Melting points are not corrected. Elemental analyses: Heraeus CHN-Rapid instrument. For preparative electrochemistry a Bank Wenking ST 72 instrument is used as potentiostat and a Wenking SSI 70 as integrator.

General procedure for preparative electrochemistry

The preparative electrolysis were performed in a cylindrical divided cell with a mercury cathode and a platinum anode, using dry acetonitrile as solvent and tetraethylammonium chloride as supporting electrolyte. To the anolyte was added 6 ml cyclohexene. After the addition of 10 mmol of starting material and 40 mmol of chlorotrimethylsilane to the catholyte the electrolysis was run under controlled potential at 0°C.

At the end of the electrolysis the catholyte was poured into aqueous sodium bicarbonate and extracted with methylene chloride. The solution was dried over sodium sulfate. After evaporation of the solvent the crude product was purified by column chromatography (silca gel, methylene chloride/ethyl acetate).

General procedure for desilylation

To a solution of the silyl compound in dry tetrahydrofuran is added a 2 fold excess of tetrabutylammonium fluoride. After 10 min the solution was poured into aqueous sodium bicarbonate, extracted with methylene chloride and dried over sodium sulfate. The solvent was removed and residue was purified by column chromatography on silica gel and methylene chloride/ethyl acetate as eluent.

1-Bis-(trimethylsilyl)-amino-2-methoxycarbonyl -pyrrolo[1,2-a]pyridine **(2a)**. Yield: 49 %, mp. 88°C; UV (CH_3CN) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 240 (28 800), 300 (2 400), 370 (2 400); IR (cm^{-1}) 1720 (C=O), 1630 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 0.07 (s, 18H, Si-C$\underline{H}_3$), 3.84 (s, 3H, -OC$\underline{H}_3$), 6.43-6.59 (m, 2H, Ar-$\underline{H}$), 6.71 (s, 1H, Ar-$\underline{H}$), 7.20-7.25 (m, 1H, Ar-H), 7.76-7.79 (m, 1H, Ar-$\underline{H}$); ^{13}C NMR (62.89 MHz, $CDCl_3$) 1.81 (Si-$\underline{C}H_3$), 50.86 (-O$\underline{C}H_3$), 99.47 ($\underline{C}$H), 112.12 ($\underline{C}$H), 113.94 (quart. C), 117.9 ($\underline{C}$H), 120.83 ($\underline{C}$H), 122.48 ($\underline{C}$H), 128.41 (quart. C), 131.77 (quart. C), 165.83 (C=O) ; Found: C 56.95, H 7.91, N 8.34; $C_{16}H_{26}N_2O_2Si_2$ requires C 57.49, H 7.78, N 8.38%

1-Amino-2-methoxycarbonyl-pyrrolo[1,2-a]pyridine **(2b)**. Yield: 47 %, mp. 103-106°C; UV (CH_3CN) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 250 (28 200), 300 (4 600), 400 (2 700); IR (cm^{-1}) 3415 (NH_2), 3314 (NH_2), 1660 (C=O), 1640 (C=C), 1620 (C=C); ^{1}H NMR (250 MHz, Acetom-d_6) 3.80 (s, 3H, -OC$\underline{H}_3$), 5.75 (s, 2H, N$\underline{H}_2$), 6.39-6.47 (m, 3H, Ar-$\underline{H}$), 7.17-7.23 (m, 1H, Ar-$\underline{H}$), 7.70-7.74 (m, 1H, Ar-$\underline{H}$); ^{13}C NMR (62.89 MHz, Aceton-d_6) 50.93

1640 (C=C), 1620 (C=C); ^{1}H NMR (250 MHz, Acetom-d_6) 3.80 (s, 3H, -OC<u>H</u>$_3$), 5.75 (s, 2H, N<u>H</u>$_2$), 6.39-6.47 (m, 3H, Ar-<u>H</u>), 7.17-7.23 (m, 1H, Ar-<u>H</u>), 7.70-7.74 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (62.89 MHz, Aceton-d_6) 50.93 (-O<u>C</u>H$_3$), 97.13 (<u>C</u>H) 99.60 (quart.C), 111.47 (<u>C</u>H), 115.90 (<u>C</u>H), 121.18 (<u>C</u>H), 121.29 (<u>C</u>H), 126.49 (quart. C), 137.29 (quart. C), 167.31 (C=O); Found: C 62.99, H 5.46, N 14.49; $C_{10}H_{10}N_2O_2$ requires C 63.16, H 5.26, N 14.74%

1-Bis-(trimethylsilyl)-amino-2-methoxycarbonyl-3-phenyl-pyrrolo[1,2-a]pyridine **(3a)**. Yield: 78 %, mp. 121°C; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 234 (17 200), 302 (4 700), 385 (2 100); IR (cm^{-1}) 1700 (C=O), 1600 (C=C) ; ^{1}H NMR (250 MHz, $CDCl_3$) 0.11 (s, 18 H, Si-C<u>H</u>$_3$), 3.70 (s, 3H, -OC<u>H</u>$_3$), 6.48-6.59 (m, 2H, Ar-<u>H</u>), 7.25-7.40 (m, 6H, Ar-<u>H</u>), 7.79-7.84 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (62.89 MHz, $CDCl_3$) 1.65 (6C, Si-<u>C</u>H$_3$), 50.72 (-O<u>C</u>H$_3$), 111.62 (<u>C</u>H), 112.35 (quart. C), 113.55 (quart. C), 117.44 (<u>C</u>H), 118.85 (<u>C</u>H), 121.28 (<u>C</u>H), 125..94 (quart. C), 125.96 (<u>C</u>H), 127.83 (2C, <u>C</u>H), 130.31 (2C, <u>C</u>H), 130.93 (quart. C), 135.13 (quart.C), 166.05 (<u>C</u>=O);Found: C 64.19, H 7.52, N 7.10 ; $C_{22}H_{30}N_2O_2Si_2$ requires C 64.39, H 7.31, N 6.95%

1-Methoxy-2-methoxycarbonyl-3-phenyl-pyrrolo[1,2-a]pyridine **(4)**. Yield: 30 % ; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 234 (29 800), 296 (6 900), 386 (3 900); IR (cm^{-1}) 1660 (C=O), 1600 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.75 (s, 3H,-OC<u>H</u>$_3$), 4.12 (s, 3H, -OC<u>H</u>$_3$), 6.49-6.59 (m, 2H, Ar-<u>H</u>), 7.25-7.44 (m, 6H, Ar-<u>H</u>), 7.77-7.84 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (62.89 MHz, $CDCl_3$) 51.16 (-O<u>C</u>H$_3$), 62.54 (-O<u>C</u>H$_3$), 103.14 (quart. C), 112.22 (<u>C</u>H), 112.69 (quart. C), 117.6 (<u>C</u>H), 119.05 (<u>C</u>H), 119.96 (<u>C</u>H), 123.36 (quart. C), 126.32 (<u>C</u>H), 127.17 (2C, <u>C</u>H), 130.56 (2C, <u>C</u>H), 134.52 (quart. C), 141.14 (quart. C), 164.88 (C=O) ; Found: C 72.35, H 5.48, N 5.20 ; $C_{17}H_{15}NO_3$ requires C 72.60, H 5.34, N 4.98%

1-Methoxy-2-methoxycarbonyl-pyrrolo[1,2-a]quinoline **(5)**. Yield: 39 %, mp 134°C; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 250 (38 300), 335 (8 900); IR (cm^{-1}) 1700 (C=O), 1630 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.90 (s, 3H, -OC<u>H</u>$_3$), 4.17 (s, 3H, -OC<u>H</u>$_3$), 6.70 (s, 1H, Ar-<u>H</u>), 6.86 (d, 1H, Ar-<u>H</u>, J_{AB}=9.4), 7.10 (d, 1H, Ar-<u>H</u>, J_{AB}=9.4), 7.30-7.50 (m, 2H, Ar-<u>H</u>), 7.53-7.57 (m, 1H, Ar-<u>H</u>), 8.71-8.73 (m, 1 H, Ar-<u>H</u>) ; ^{13}C NMR (62.89 MHz, $CDCl_3$) 51.22 (-O<u>C</u>H$_3$), 62.55 (-O<u>C</u>H$_3$), 101.16 (<u>C</u>H), 104.03 (quart. C), 117.07 (<u>C</u>H), 119.27 (<u>C</u>H), 119.64 (<u>C</u>H), 124.35 (quart. C), 124.68 (<u>C</u>H), 125.49 (quart. C), 127.66 (<u>C</u>H), 128.22 (<u>C</u>H), 133.78 (quart. C), 147.54 (quart. C), 164.37 (C=O); Found: C 70.34, H 5.56, N 5.45; $C_{15}H_{13}NO_3$ requires C 70.59, H 5.10, N 5.49%

1-Amino-2-methoxycarbonyl-pyrrolo[1,2-a]quinoline **(6b)**. Yield: 44 %, mp. 110°C; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 240 (24 600), 260 (14 300), 384 (4 300); IR (cm^{-1}) 3340 (NH_2), 3260 (NH_2), 1670 (C=O), 1600 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.86 (s, 3H, -OC<u>H</u>$_3$), 5.46 (s, 2H, N<u>H</u>$_2$), 6.58 (s, 1H, Ar-<u>H</u>), 6.68 (d,1H, Ar-<u>H</u>, J_{AB}=9.4), 7.00 (d, 1H, Ar-<u>H</u>, J_{AB}=9.4), 7.02-7.39 (m, 2H, Ar-<u>H</u>), 7.45-7.49 (dd, 1H, Ar-<u>H</u>,

J_{AB}=7.5, J_{AC}=1.7), 8.47 (d, 1H, Ar-H, J_{AB}=8.4); ^{13}C NMR (62.89 MHz, $CDCl_3$) 50.92 (-OCH3), 100.03 (quart.C), 100.70 (CH), 115.85 (CH), 118.07 (CH), 119.89 (CH), 124.32 (CH), 125.54 (quart. C), 126.38 (quart. C), 126.60 (CH), 128.13 (CH), 134.68 (quart. C), 142.65 (quart. C), 167.13 (C=O); Found: C 68.73, H 5.18, N 11.43; $C_{14}H_{12}N_2O_2$ requires C 69.99, H 5.03, N 11.88%

1-Bis-(trimethylsilyl)-amino-2-methoxycarbonyl-3-phenyl-pyrrolo[1,2-a]quinoline (**7a**). Yield: 86 %, mp. 112°C; UV (CH_3OH) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 234 (25 700), 254 (26 900), 358 (8 100), (2 100); IR (cm^{-1}) 1700 (C=O), 1590 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 0.19 (s, 18H, Si-CH_3), 3.65 (s, 3H,-OCH_3), 6.85 (d, 1H, Ar-H, J_{AB}=9.4), 7.22 (d, 1H, Ar-H, J_{AB}=9.4), 7.26-7.46 (m, 7H, Ar-H), 7.54-7.58 (d, 1H, Ar-H, J_{AB}=7.5), 9.37-9.41 (m, 1H, Ar-H); ^{13}C NMR (62.89 MHz, $CDCl_3$) 1.49 (6C, Si-CH_3), 50.75 (-OCH_3), 114.02 (quart. C), 116.64 (quart. C), 118.28 (CH), 118.46 (CH), 119.47 (CH), 124.21 (CH), 124.87 (quart. C), 125.79 (CH), 126.29 (CH), 126.35 (quart. C), 127.86 (2C, CH), 128.18 (CH), 136.27 (2C, CH), 135.01 (quart. C), 135.06 (quart. C), 137.12 (quart. C), 166.18 (C=O); Found: C 67.65, H 7.24, N 6.19; $C_{26}H_{32}N_2O_2Si_2$ requires C 67.83, H 6.96, N 6.09%

1-Amino-2-methoxycarbonyl-3-phenyl-pyrrolo[1,2-a]quinoline (**7b**). Yield: 40 %, mp. 184°C; UV (CH_3OH) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 240 (27 400), 396 (6 900); IR (cm^{-1}) 3400 (NH_2), 3320 (NH_2), 1670 (C=O), 1600 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.65 (s, 3H, -OCH_3), 5.70 (2H, NH_2), 6.64 (d, 1H, Ar-H, J_{AB}=9.5), 6.98 (d, 1H, Ar-H, J_{AB}=9.5), 7.23-7.43 (m, 7H, Ar-H), 7.44-7.48 (d, 1H, Ar-H, J_{AB}=7.6), 8.52-8.54 (m, 1H, Ar-H); ^{13}C NMR (62.89 MHz, $CDCl_3$) 50.57 (-OCH_3), 98.89 (quart. C), 116.13 (CH), 116.16 (quart. C), 118.34 (CH), 118.78 (CH), 123.89 (quart. C), 124.47 (CH), 126.48 (CH), 126.65 (CH), 127.51 (2C, CH), 128.05 (CH), 130.84 (2C, CH), 134.50 (quart. C), 134.75 (quart. C), 143.48 (quart. C), 167.61 (C=O); Found: C 75.95, H 5.24, N 8.72; $C_{20}H_{16}N_2O_2$ requires C 75.93, H 5.10, N 8.86%

1-Amino-2-methoxycarbonyl-3-phenyl-pyrrolo[1,2-a]isoquinoline (**8b**). Yield: 69 %, mp. 136°C; UV (CH_3OH) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 272 (42 200), 354 (7 000); IR (cm^{-1}) 3440 (NH_2), 3300 (NH_2), 1690 (C=O), 1600 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.49 (s, 3H, -OCH_3), 6.13 (s, 2H, NH_2), 6.73 (d, 1H, Ar-H, J_{AB}=7.6), 6.95-7.17 (m, 3H, Ar-H), 7.34-7.69 (m, 6H, Ar-H), 7.75 (d, 1H, Ar-H, J_{AB}=7.6); ^{13}C NMR (62.89 MHz, $CDCl_3$) 50.34 (-OCH_3), 98.00 (quart. C), 112.47 (CH), 117.21 (quart. C), 119.15 (quart. C), 120.50 (CH), 122.81 (CH), 125.75 (CH), 127.60 (CH), 127..91 (CH), 127.95 (CH),128.46(quart.C),128.87 (2C, CH), 131.18 (quart. C), 131.57 (2C, CH), 138.45 (quart. C), 140.26 (quart. C), 167.23 (C=O) ; Found: C 75.95, H 5.27, N 8.80; $C_{20}H_{16}N_2O_2$ requires C 75.93, H 5.10, N 8.86%

6-Amino-7-methoxycarbonyl-pyrrolo[1,2-a]pyrazine (**9b**). Yield: 29 %, mp. 150°C; UV (CH_3OH) λ_{max} (ε $dm^3mol^{-1}cm^{-1}$) 224 (19 100), 254 (26 700), 412 (3 800); IR (cm^{-1}) 3420 (NH_2), 3340 (NH_2), 1690 (C=O), 1640

(C=C), 1630 (C=C), 1600 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.89 (s, 3H, -OC<u>H</u>$_3$), 5.17 (s, 2H, N<u>H</u>$_2$), 6.95 (s, 1H, Ar-<u>H</u>), 7.27 (d, 1H, Ar-<u>H</u>, J_{AB}=5.1), 7,34 (d, 1H, Ar-<u>H</u>, J_{AB}=5.1), 8.59 (d, 1H, Ar-<u>H</u>, J_{AC}=1.3); ^{13}C NMR (62.89 MHz, $CDCl_3$) 51.34 (-O<u>C</u>H$_3$), 102.47 (quart. C), 102.98 (<u>C</u>H), 112.29 (<u>C</u>H), 121.91 (quart. C), 127.21 (<u>C</u>H), 135.62 (quart. C), 147.57 (<u>C</u>H), 166.30 (C=O); Found: C 56.72, H 4.68, N 21.85; $C_9H_9N_3O_2$ requires C 56.54, H 4.75, N 21.98%

1-Amino-2-methoxycarbonyl-pyrrolo[1,2-a]quinoxaline **(10b)**. Yield: 49 %, mp. 138°C; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 242 (21 500), 276 (6 800), 390 (4 200); IR (cm^{-1}) 3370 (NH_2), 3250 (NH_2), 1740 (C=O), 1630, 1600 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.89 (s, 3H, -OC<u>H</u>$_3$), 5.66 (s, 2H, NH_2), 6.98 (s, 1H, Ar-<u>H</u>), 7.33-7.50 (m, 2H, Ar-<u>H</u>), 7.76-7.82 (m, 1H, Ar-<u>H</u>), 8.18-8.24 (m, 1H, Ar-<u>H</u>), 8.45 (s, 1H, Ar-<u>H</u>); ^{13}C NMR (62.89 MHz, $CDCl_3$) 51.21 (-O<u>C</u>H$_3$), 101.65 (quart. C), 106.73 (<u>C</u>H), 115.11 (<u>C</u>H), 120.67 (quart. C), 125.70 (<u>C</u>H), 126.62 (<u>C</u>H), 128.86 (quart. C), 129.73 (<u>C</u>H), 137.67 (quart. C), 142.96 (quart. C), 147.07 (<u>C</u>H), 166.48 (C=O); Found: C 64.57, H 5.13, N 17.90; $C_{13}H_{11}N_3O_2$ requires C 64.72, H 4.60, N 17.42%

4-Amino-3-methoxycarbonyl-1-phenyl-pyrrolo[1,2-b]benzothiazole **(11b)**. Yield: 16 %, mp. 164°C; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 256 (33 200), 280 (6 800), 311 (11 500); IR (cm^{-1}) 3380 (NH_2), 3300-3360 (NH_2), 1650 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 3.67 (s, 3H, -OC<u>H</u>$_3$), 6.19 (s, 2H, NH_2), 7.19-7.47 (m, 7H, Ar-<u>H</u>), 7.66-7.69 (m, 1H, Ar-<u>H</u>), 8.01-8.05 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (62.89 MHz, $CDCl_3$) 50.39 (-O<u>C</u>H$_3$), 98.40 (quart. C), 113.12 (quart.C), 114.68 (<u>C</u>H) 119.36 (quart. C), 124.58 (<u>C</u>H), 125.56 (<u>C</u>H), 126.48 (<u>C</u>H), 126.64 (<u>C</u>H), 128.56 (2C, <u>C</u>H), 129.50 (2C, <u>C</u>H), 131.80 (quart.C), 135.08 (quart. C), 136.20 (quart. C), 143.91 (quart. C), 166.82 (C=O); Found: C 66.88, H 4.57, N 8.70; $C_{18}H_{14}N_2O_2S$ requires C 67.08, H 4.35, N 8.70%

4-*Bis-(trimethylsilyl)-amino-3-cyano-1-phenyl-pyrrolo[1,2-b]benzothiazole* **(12a)**. Yield: 58 %, mp. 155°C; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 254 (43 900), 279 (9 800), 303 (16 600); IR (cm^{-1}) 2220 (CN), 1600 (C=C); ^{1}H NMR (250 MHz, $CDCl_3$) 0.27 (s, 18H, Si-C<u>H</u>$_3$), 7.26-7.51 (m, 5H, Ar-<u>H</u>), 7.62-7.66 (m, 1H, Ar-<u>H</u>),7.74-7.77 (m, 2H, Ar-<u>H</u>), 8.14-8.18 (m, 1H, Ar-<u>H</u>); ^{13}C NMR (62.89 MHz, $CDCl_3$) 1.89 (6C, Si-<u>C</u>H$_3$), 93.73 (quart. C), 113.07 (quart. C), 114.83 (<u>C</u>H), 117.34 (quart. C), 120.62 (quart. C), 123.88 (<u>C</u>H), 125.08 (<u>C</u>H), 125.31 (<u>C</u>H), 125.85 (2C, <u>C</u>H), 126.48 (<u>C</u>H), 129.01 (2C, <u>C</u>H), 131.67 (quart.C), 132.63 (quart. C), 134.15 (quart. C), 140.99 (quart. C); Found: C 63.88, H 6.15, N 9.65; $C_{23}H_{27}N_3Si_2S$ requires C 63.74, H 6.24, N 9.70%

4-Amino-3-cyano-1-phenyl-pyrrolo[1,2-b]benzothiazole **(12b)**. Yield: 65 %, mp. 135°C; UV (CH_3OH) λ_{max} (ε dm^{3}mol^{-1}cm^{-1}) 251 (33 000), 313 (12 800); IR (cm^{-1}) 3380 (NH_2), 3320 (NH_2), 2210 (CN), 1630,1600

(C=C); ^{1}H NMR (250 MHz, DMSO-d_6) 6.40 (s, 2H, NH_2), 7.25-7.56 (m, 7H, Ar-H), 7.85-7.89 (dd, 1H, Ar-H, J_{AB}=7.9 Hz, J_{AC}=1.4 Hz), 7.94-8.18 (dd, 1H, Ar-H, J_{AB}=9.3 Hz, J_{AC}=1.2 Hz); Found: C 70.48, H 3.88, N 14.41; $C_{17}H_{11}N_3S$ requires C 70.59, H 3.81, N 14.53%

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