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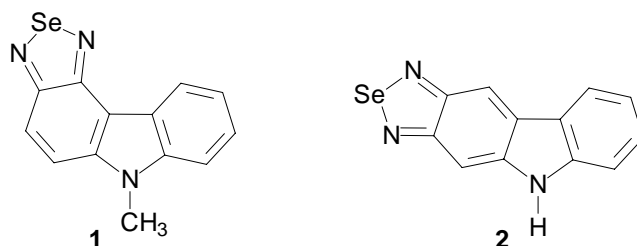
5*H*-[1,2,5]SELENADIAZOLO[3,4-*f*]INDOLE AS A MASKED FORM OF 5,6-DIAMINOINDOLE

Jealux Okwakol and Spiros Grivas*

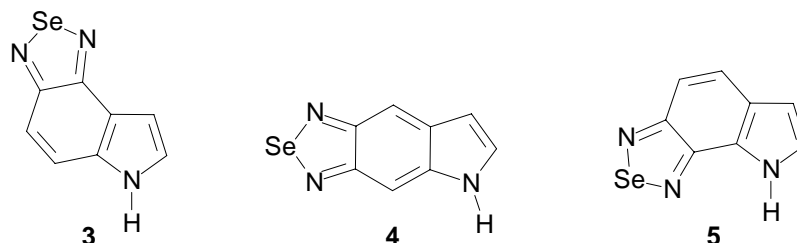
Unit for Organic Chemistry, Department of Biosciences, Karolinska Institute; Södertörn University College, Novum Research Park, SE-141 57 Huddinge, Sweden, E-mail: spiros.grivas@biosci.ki.se

Abstract – 6-Nitroindoline (**9**) was converted into 1-acetyl-5,6-aminoindoline (**12**) which was then transformed *via* selenadiazoles (**13–15**) to the title selenadiazoloindole (**4**) by two alternative 3-step synthetic sequences in 38–42% overall yield from **12**. The unstable 5,6-diaminoindole (**16**) was then obtained by reductive deselenation of **4**. Fully assigned ^1H , ^{13}C and ^{77}Se NMR spectral data for the title indole (**4**) and ^{77}Se NMR spectral data for the intermediate selenadiazoles (**13–15**) are presented.

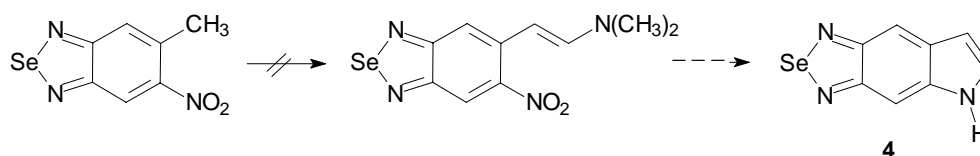
Derivatives of 2,1,3-benzoselenadiazole and related thiadiazoles and oxadiazoles have shown to be useful synthetic intermediates and potential pharmaceutical and agricultural products, polymers and other industrially interesting materials.¹ Recent syntheses, properties and a compilation of fully assigned ^1H , ^{13}C , and ^{77}Se NMR spectral data of 2,1,3-benzoselenadiazoles have been reviewed.¹ The angular benzoselenadiazoloindole (**1**) and its linear analogue (**2**) were suspected to be carcinogenic some fifty years ago.² They can be synthesized from the condensation of SeO_2 with the corresponding 3,4-diaminocarbazole^{2,3} and 2,3-diaminocarbazole.^{2,4}



We have recently reported the synthesis of the parent heterocyclic ring system of **1**, i.e. selenadiazoloindole (**3**) and its isomeric indole (**5**) by applying the Batcho–Leimgruber methodology^{5,6} on 4-methyl-5-nitro- and 5-methyl-4-nitro-2,1,3-benzoselenadiazole.^{7,8}

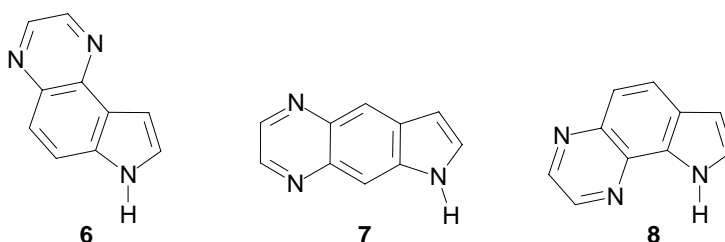


However, the parent heterocyclic ring system of **2**, i.e. the linear title selenadiazoloindole (**4**) has not to date appeared in the literature and could not be obtained by the method we employed for the preparation of **3** and **5**, Scheme 1.⁸



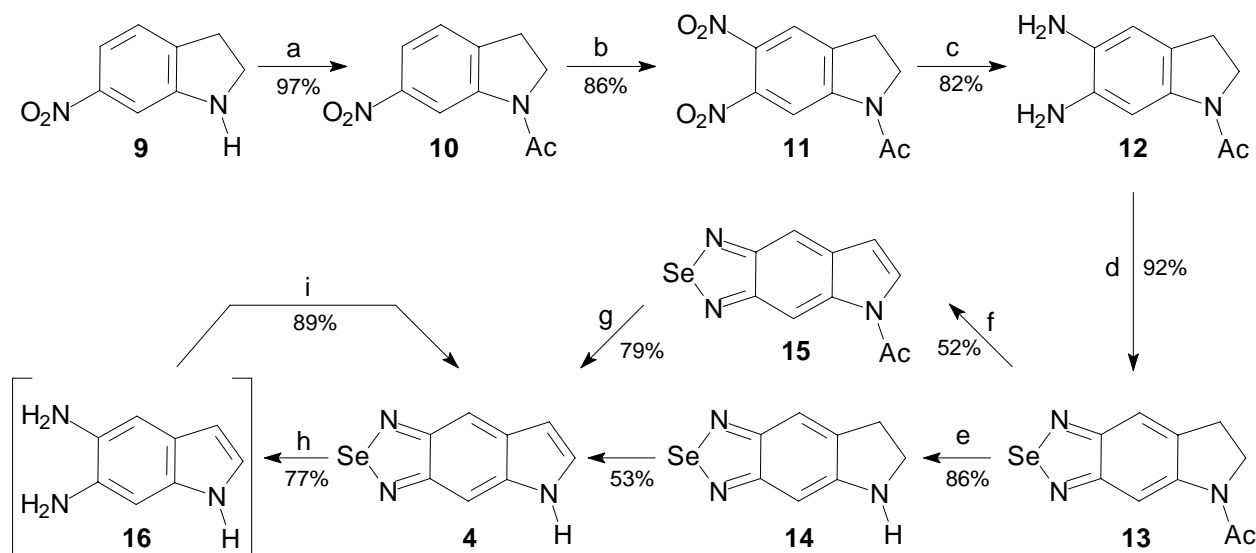
Scheme 1. Previously attempted⁸ Batcho–Leimgruber synthesis of the title selenadiazoloindole (**4**) from 5-methyl-6-nitro-2,1,3-benzoselenadiazole.

As a part of a synthetic project towards the preparation of pyrroloquinoxalines, such as compounds (**6–8**) and derivatives thereof that are bioisosterically related to bioactive imidazoquinoxalines,⁹ imidazonaphthyridines^{10,11} and imidazoquinolines,¹¹ we needed all three isomers (**3–5**).



Reductive deselenation of 2,1,3-benzoselenadiazoles has previously given us highly substituted *ortho*-diaminonitrophenols,¹² nitrobenzenediamines^{9,12–16} and nitrobenzenetriamines⁹ that are laborious to obtain otherwise. Moreover, 4-nitrobenzimidazoles¹⁵ and 5-nitroquinoxalines,^{12,14,16} which are difficult to prepare by direct nitration, could then be synthesized in a regiospecific and regioselective way from the so obtained *ortho*-diaminobenzenes. In connection to this, compounds (**3–5**) were also considered as masked forms of the more or less unstable 4,5-, 5,6- and 6,7-diaminoindole⁷ that can easily be obtained after the deselenation of the stable selenadiazoloindoles (**3–5**). We now report a different approach that

indeed allowed the preparation of the unprecedented **4** and the new 5,6-diaminoindole (**16**) thereof (Scheme 2).



Scheme 2. (a) Ac_2O , reflux; (b) conc. $\text{H}_2\text{SO}_4/\text{H}_2\text{NCONH}_3^+\text{NO}_3^-$, $-15\text{ }^\circ\text{C}$ or $\text{Ac}_2\text{O}/\text{fum. HNO}_3$, $15\text{--}50\text{ }^\circ\text{C}$; (c) H_2 , 10% Pd/C, EtOH/Et₃N, 100 psi, rt, or Raney Ni, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, rt; (d) SeO_2 , 1 M HCl, $70\text{ }^\circ\text{C}$; (e) conc. HCl, reflux; (f) DDQ, THF/1,4-dioxane, $85\text{ }^\circ\text{C}$; (g) Na_2CO_3 , EtOH, $65\text{ }^\circ\text{C}$; (h) Raney Ni, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$, MeOH; (i) aq. SeO_2 , MeOH, $70\text{ }^\circ\text{C}$.

The desired selenadiazoloindole (**4**) was successfully obtained from the known 1-acetyl-5,6-diaminoindole (**12**)¹⁷ via the new 2,1,3-benzoselenadiazoles (**13–15**). Commercially available 2,3-dihydroindole (indoline) was converted into **12** in 55% overall yield via compounds (**9–11**) according to the literature.¹⁷ For the sake of convenience and its reported ability to regioselective nitrations, apart from Ac_2O and fuming HNO_3 as in reference 17 we also tried urea nitrate in sulfuric acid^{18,19} for the nitration of indoline to the 6-nitro derivative (**9**)¹⁷ that is commercially available but relatively expensive. Classical acetylation of **9** to **10**¹⁷ followed by nitration with $\text{H}_2\text{NCONH}_3^+\text{NO}_3^-$ in conc. H_2SO_4 ¹⁸ furnished the acetylated 5,6-dinitroindoline derivative (**11**)¹⁷ in 86% yield. In addition to the Raney Ni/hydrazine hydrate reduction¹⁷ of **11** to **12** we also treated **11** with H_2 in the presence of 10% Pd/C in EtOH/Et₃N²⁰ at 100 psi and the resulting diaminoindoline (**12**)¹⁷ was immediately treated with SeO_2 to give the new selenadiazole derivative (**13**) in 92% yield. Our overall yield to diamine (**12**) by using the alternative reagents and conditions was comparable to that obtained when we followed the published procedure.¹⁷

Two alternative approaches were explored to obtain **4** from **13**. In the first, derivative (**13**) was deacetylated by heating in conc. HCl to **14**, which on dehydrogenation gave **4** while in the other, **13** was first dehydrogenated to **15** and subsequently hydrolyzed to **4** by heating with Na_2CO_3 in ethanol. Neither of the approaches had an overall superior advantage over the other. While the deacetylations were easily carried out, the dehydrogenation of both **13** and **14** gave moderate yields of **15** and **4** respectively (50–

55%). Oxidative dehydrogenations were successful with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)²¹ when a mixture of 1,4-dioxane and THF was used; DDQ in 1,4-dioxane alone did not accomplish the desired dehydrogenation. Attempts with K₂CO₃ or Na₂CO₃ in nitromethane or nitrobenzene,²² with active MnO₂²³ and also with chloranil²⁴ were not satisfactory. An alternative method involving trichloroisocyanuric acid in combination with DBU²⁵ was not successful either. In analogy with our previous work,⁷ reductive deselenation of **4** by hydrazine hydrate and Raney nickel afforded the air-sensitive 5,6-diaminoindole (**16**) in good yields (75–85%). Condensation of diamine (**16**) with SeO₂ yielded the title indole (**4**) which was identical to that obtained from **14** and **15**.

Table. ⁷⁷Se-NMR chemical shifts

Compound:	13	14	15	4
δ _{Se} (ppm):	1528.5	1496.4	1538.6	1511.7

The ⁷⁷Se-NMR chemical shifts of indolines (**13**) and (**14**) and indoles (**4**) and (**15**) are shown in the Table. Interestingly, the shift of the angular isomers (**3**) and (**5**) was δ 1497.6 and 1498.1,^{7,8} while that of the linear **4** was δ 1511.7 under identical conditions. The effects of the acetyl group and that of the pyrrole and pyrrolidine rings on the 2,1,3-benzoselenadiazole are reflected on the ⁷⁷Se-NMR chemical shifts.

In conclusion, we have now completed the syntheses of all three isomeric indoles in the series (**3–5**)^{7,8} that can be used as masked forms of the relatively unstable 4,5-, 5,6- and 6,7-diaminoindoles. The efficient reductive deselenation of **3–5** affords the *ortho*-diaminoindoles which can be useful for the preparation of indole heterocycles thereof. Because indoline and indole derivatives possess physiological and pharmacological activities, and also are suitable building blocks for the synthesis of e.g., marine alkaloids and important pharmacophores, new syntheses and biological evaluation of such derivatives are continually investigated.^{26,27}

EXPERIMENTAL

Analytical TLC was performed using aluminium plates precoated with silica gel 60 F254 (Merck) and visualized by UV light and the Van Urk's reagent. Flash chromatography was carried out on silica gel 60 (35–70 μ, Grace). Melting points (uncorrected) were determined on a Büchi Melting Point B-545. All NMR spectra were recorded on a Bruker DPX 300 spectrometer at 25 °C. ¹H- and ¹³C-NMR signals were referenced to the solvent (DMSO-*d*₆ δ_H 2.50 and δ_C 39.5). Gradient HMBC and PENDANT experiments were used for the assignments. Coupling constants are given in Hz and without sign. In ⁷⁷Se-NMR spectral experiments, saturated aqueous selenous acid was used as an external reference (11.5 M, H₂SeO₃ δ_{Se} 1300.47) and the samples were dissolved in and locked on DMSO-*d*₆. The IR spectra were recorded on an Avatar 330 FT-IR (neat) or a Perkin Elmer 1600 FT-IR (KBr) instrument. The EI (70 eV, direct

insertion) MS spectrum of **4** was recorded on a Micromass Platform instrument. Ions containing isotopes other than ^{80}Se are not listed. Elemental composition was determined by fast atom bombardment (FAB) HRMS on a Jeol JMS-SX102 instrument. Unless otherwise stated all organic solvents were of analytical grade and were used as purchased. Solvent mixtures are defined by volume ratios (v/v). Petrol refers to petroleum ether 70–80 °C.

6-Nitroindoline (9). This compound was prepared by nitration of indoline as described¹⁷ (conc. $\text{H}_2\text{SO}_4/\text{fum. HNO}_3$) and also as follows: To chilled conc. sulfuric acid (100 mL) at -10 °C was added commercial indoline (10.0 g, 84 mmol) carefully in small portions. After all the indoline was added, urea nitrate (15.0 g, 122 mmol) was also added carefully and in small portions while maintaining the temperature below -5 °C. The reaction was continued at temperature between -5 and 0 °C and monitored on TLC (EtOAc/heptane, 1:4, R_f 0.25). After all the starting material had been consumed, the reaction mixture was poured onto crushed ice (100 g) and under cooling was treated with 28% ammonia solution to a pH ~ 8 . The resulted red precipitate was filtered off, washed with cold water (50 mL) and recrystallized (aq. MeOH) to give **9** (9.8 g, 71%). The nitroindoline so obtained was identical with a commercial sample.

1-Acetyl-6-nitroindoline (10). This compound was prepared in 97% yield as described,¹⁷ mp $155\text{--}156$ °C (aq. MeOH) (lit.,¹⁷ $153\text{--}154$ °C); $^1\text{H-NMR}$: δ 8.76 (1H, d, J 2.1), 7.89 (1H, dd, J 2.3, 8.2), 7.47 (1H, d, J 8.2), 4.19 (2H, t, J 8.7), 3.26 (2H, t, J 8.4) and 2.19 (s, 3H); $^{13}\text{C-NMR}$ δ 169.61 (CO), 146.87 (C), 143.80 (C), 140.50 (C), 125.39 (CH), 118.71 (CH), 109.69 (CH), 48.79 (CH_2), 27.50 (CH_2) and 23.91 (CH_3).

1-Acetyl-5,6-dinitroindoline (11). This compound was prepared by nitration of **10** as described¹⁷ ($\text{Ac}_2\text{O}/\text{fum. HNO}_3$) and also as follows: Urea nitrate (5.6 g, 45.5 mmol) was added to a cooled solution of **10** (4.7 g, 22.8 mmol) in conc. sulfuric acid (60 mL) in small portions, while maintaining the temperature just under 0 °C. After all addition the temperature was allowed to rise gradually to ambient and the mixture was left stirring overnight. TLC (EtOAc/ CH_2Cl_2 , 1:1, R_f 0.43) revealed that all the starting material had been consumed. The mixture was poured onto ice water. The resulted yellow precipitate was washed with cold water to neutral pH and recrystallized (toluene) to give fine yellow needles of the product (**11**) (4.9 g, 86%); mp $190\text{--}192$ °C (lit.,¹⁷ $192\text{--}192.5$ °C); $^1\text{H-NMR}$: δ 8.44 (1H, s, 7-H), 8.12 (1H, s, 4-H, J 1.1), 4.26 (2H, t, 2- CH_2 , J 8.7), 3.29 (2H, t, 3- CH_2 , J 8.7) and 2.24 (3H, s, CH_3); $^{13}\text{C-NMR}$: δ 170.54 (CO), 147.35 (7a-C), 143.22 (6-C), 138.05 (3a-C), 136.08 (5-C), 122.23 (4-C), 110.23 (7-C), 49.33 (2-C), 27.16 (3-C) and 23.92 (CH_3).

1-Acetyl-5,6-diaminoindoline (12). This compound was prepared by reduction of **11** as described¹⁷ (hydrazine-Raney Ni) and also as follows: Compound (**11**) (3.35 g, 13.3 mmol) and 10% Pd-C (0.6 g) were added to a mixture of dry ethanol (60 mL) and Et_3N (16 mL) and hydrogenated at 100 psi for a period of 40 min after which the mixture was filtered through celite which was then washed with hot CH_2Cl_2 (2 x 10 mL) with the help of a water aspirator. The filtrate was concentrated *in vacuo* leaving a

fine grey powder of **12** (2.1 g, 82% yield) after drying at 130 °C in order to remove crystalline water; mp 198–199 °C (aq. EtOH) (lit.,¹⁷ 212–213 °C); ¹H-NMR: δ 7.41 (1H, s), 6.38 (1H, s), 4.30 (4H, br s, 2 x NH₂), 3.93 (2H, t, *J* 8.3), 2.90 (2H, t, *J* 8.3) and 2.06 (3H, s, CH₃); ¹³C-NMR: δ 166.38, 134.33, 133.49, 130.92, 119.43, 110.86, 103.79, 48.41, 27.07 and 23.81; IR (KBr) ν 3384, 3347, 3325, 3302, 3195, 1632, 1601, 1497 and 1425 cm⁻¹.

5-Acetyl-6,7-dihydro-5H-[1,2,5]selenadiazolo[3,4-*f*]indole (13). To a heated solution of **12** (1.8 g, 9.4 mmol) in 1 M HCl (50 mL) at 90 °C was added selenium dioxide (2.2 g, 19.8 mmol) in small portions. There was immediate precipitation. After total addition, the mixture was stirred for an extra 5 min before it was cooled to rt and filtered. The precipitate was washed with cold water and recrystallized (aq. EtOH) to give after air-drying brownish **13** (2.3 g, 92%); mp 218–219 °C. *Anal.* Calcd for C₁₀H₉N₃OSe: C, 45.13; H, 3.41; N, 15.79; O, 6.01; Se, 29.67. Found: C, 44.96; H, 3.56; N, 15.58; HRMS: found [M + H]⁺, 267.9990; C₁₀H₁₀N₃OSe requires *m/z*, 267.9989; ¹H-NMR δ 8.21 (1H, s), 7.59 (1H, s), 4.20 (2H, t, *J* 7.9), 3.23 (2H, t, *J* 7.6) and 2.26 (3H, s); ¹³C-NMR: δ 170.22, 160.46, 157.92, 144.95, 141.23, 117.11, 104.23, 49.19, 26.26 and 24.36; IR (neat) ν 2886, 1673, 1625, 1543, 1443, 1378, 1317 and 1183 cm⁻¹.

6,7-Dihydro-5H-[1,2,5]selenadiazolo[3,4-*f*]indole (14). Compound (**13**) (0.5 g, 1.9 mmol) was refluxed in conc. HCl (10 mL) for 45 min, TLC (EtOAc/*n*-hexane, 1:3, R_f 0.42). The mixture was allowed to cool to rt and poured onto crushed ice (15 g). The resulted precipitate was filtered off, washed with cold water and recrystallized (aq. EtOH) to give after air-drying dark-brown **14** (0.36 g, 86%); mp 205–207 °C. *Anal.* Calcd for C₈H₇N₃Se: C, 42.87; H, 3.15; N, 18.75; Se, 35.23. Found: C, 42.51; H, 3.34; N, 18.53; HRMS: found [M + H]⁺, 225.9883; C₈H₈N₃Se requires *m/z*, 225.9884; ¹H-NMR: δ 7.35 (1H, s), 6.9 (1H, br s, NH), 6.30 (1H, s), 3.60 (2H, dt, *J* 0.9, 7.4) and 3.07 (2H, dt, *J* 1.8, 7.3); ¹³C-NMR: δ 161.95 (C), 157.59 (C), 154.32 (C), 142.96 (C), 116.57 (CH), 89.70 (CH), 46.05 (CH₂) and 27.60 (CH₂); IR (neat) ν 3425, 3356, 3055, 2947, 2255, 1637, 1580, 1496, 1459, 1414, 1298 and 757 cm⁻¹.

5-Acetyl-5H-[1,2,5]selenadiazolo[3,4-*f*]indole (15). To a solution of **13** (0.5 g, 1.9 mmol) in a mixture of 1,4-dioxane (30 mL) and THF (5 mL) was added DDQ (1.14 g, 5 mmol) in one portion and the solution heated at 85 °C overnight. TLC (EtOAc/petrol, 1:1, R_f 0.44) showed no further change after extended heating for another 1.5 h. After cooling to rt the reaction mixture was concentrated *in vacuo* and the resulting residue was dissolved in 0.1 M NaOH (20 mL) and then extracted with dichloromethane (3 x 10 mL). Flash chromatography (EtOAc/petrol, 1:1) gave brown **15** (0.28 g, 52%); mp 205–206 °C (aq. EtOH); *Anal.* Calcd for C₁₀H₇N₃OSe: C, 45.47; H, 2.67; N, 15.91; O, 6.06; Se, 29.89. Found: C, 45.19; H, 2.79; N, 15.76; HRMS: found [M + H]⁺, 265.9849; C₁₀H₈N₃OSe requires *m/z*, 265.9851; ¹H-NMR: δ 8.66 (1H, s), 8.04 (1H, d, *J* 4.1), 7.95 (1H, s), 6.80 (1H, d, *J* 4.0) and 2.63 (3H, s); ¹³C-NMR: δ 168.85 (CO), 158.70 (C), 157.59 (C), 138.90 (C), 136.64 (C), 134.38 (CH), 111.31 (CH), 108.02 (CH), 106.27 (CH) and 23.70 (CH₂); IR (neat) ν 3215, 2908, 1627, 1527, 1441, 1408, 1313, 1260, 1098, 809 and 743 cm⁻¹.

5H-[1,2,5]selenadiazolo[3,4-f]indole (4). *Alternative 1 via 15:* To a dilute solution of **15** (0.15 g, 0.57 mmol) in dry ethanol (60 mL) was added sodium carbonate (1.2 g, 11.3 mmol) in one portion and heated at 65 °C. There was a colour change of the mixture from yellow to brown. Stirring was continued at this temperature and TLC monitoring (EtOAc, R_f 0.53) showed that the reaction was complete after about 15 min. The mixture was filtered with the help of a water aspirator and the filtrate was concentrated *in vacuo*. Chromatography of the residue on silica (EtOAc/n-hexane, 1:3) afforded **4** (0.1 g, 79%) as a reddish solid; mp 149–151 °C (MeOH). *Anal.* Calcd for $C_8H_5N_3Se$: C, 43.26; H, 2.27; N, 18.92; Se, 35.55. Found: C, 43.08; H, 2.39; N, 18.79; HRMS: found $[M + H]^+$, 223.9728; $C_8H_6N_3Se$ requires m/z , 223.9729; EIMS m/z (rel. int): 223 (70, M), 196 (18), 143 (100), 116 (39), 89 (16) and 77 (23); 1H -NMR: δ 10.8 (1H, br s, NH), 7.89 (1H, s, 8-H), 7.63 (1H, d, 6-H, J 3.3), 7.60 (1H, s, 4-H) and 6.42 (1H, d, 7-H, J 3.3); ^{13}C -NMR: δ 157.95 (3a-C), 156.99 (8a-C), 142.65 (7a-C), 136.98 (4a-C), 135.71 (8-C), 108.87 (4-C), 100.31 (7-C) and 97.99 (6-C); IR (neat) ν 3209, 2859, 1725, 1646, 1586, 1522, 1410, 1314, 1287, 1098, 1040, 875, 808, 736, 706 and 555 cm^{-1} .

Alternative 2 via 14: Compound (**14**) (0.3 g, 1.3 mmol) was suspended in a mixture of THF and 1,4-dioxane (40 mL, 1:7) and DDQ (0.4 g, 1.8 mmol) was added to the stirred suspension at rt. Colour change was observed as the DDQ was added. After stirring at 85 °C for 3 h there was no significant change in the reaction mixture. The reaction was monitored by TLC (EtOAc, R_f 0.53) sprayed by the Van Urk's reagent. The mixture was filtered and the filtrate treated with 30% NaOH to a pH 7–8, extracted with dichloromethane (2 x 30 mL), brine and dried with Na_2SO_4 . The filtrate was concentrated *in vacuo* depositing **4** as a red powder (0.16 g, 53%) identical to that obtained from **15**.

Alternative 3 via 5,6-diaminoindole (16): Compound (**4**) (0.13 g, 0.59 mmol) was deselenated with hydrazine hydrate and Raney Ni as previously⁷ described for the synthesis of 6,7-diaminoindole to afford after filtration *via* celite and evaporation of the solvents 5,6-diaminoindole (**16**) (0.065 g, 75%) as a dark red solid gradually decomposing [1H -NMR: δ 10.1 (1H, br s, NH), 6.83 (1H, t, J 2.6), 6.64 (1H, d, J 1.4), 6.57 (1H, s), 5.99 (1H, t, J 2.5), 4.2 (2H, br s, NH_2) and 3.9 (2H, br s, NH_2); ^{13}C -NMR: δ 133.26 (C), 131.00 (C), 130.30 (C), 120.87 (CH), 120.05 (C), 104.57 (CH), 99.60 (CH) and 96.42 (CH)]. The evaporation residue was immediately refluxed with SeO_2 (0.09 g, 0.81 mmol) in methanol/ H_2O (80 mL, 1:1) for 1 h under nitrogen to afford after chromatography on silica (EtOAc/n-hexane, 1:3) pure **4** (0.11 g, 85%) identical to that obtained from **14** or **15**.

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