Benzo[1,2-*c*:3,4-*c*']bis[1,2,5]selenadiazole, [1,2,5]Selenadiazolo-[3,4-*e*]-2,1,3-benzothiadiazole, Furazanobenzo-2,1,3-thiadiazole, Furazanobenzo-2,1,3-selenadiazole and Related Heterocyclic Systems

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The first synthesis of benzo[1,2-*c*:3,4- *c*']bis[1,2,5]selenadiazole has been developed starting from commercially available 4-nitrobenzo-2,1,3-selenadiazole. Improved syntheses of the related heterocycles [1,2,5]selenadiazolo[3,4-*e*]-2,1,3-benzothiadiazole, furazanobenzo-2,1,3-thiadiazole and furazanobenzo-2,1,3-selenadiazole are also reported.

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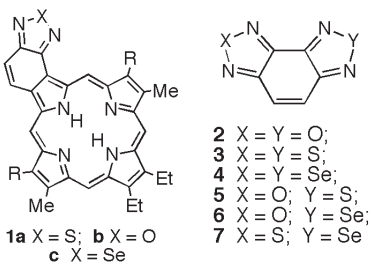
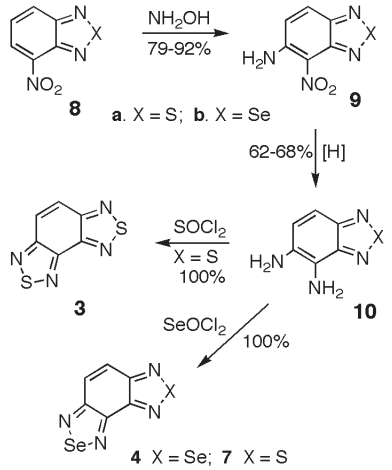
There is presently a great deal of interest in the synthesis of porphyrins that show strong absorption bands above 650 nm [1]. These types of derivatives have been mooted for applications that range from the design of novel materials [2] to photosensitizers for medicinal applications [3]. Fusion of aromatic rings to porphyrin systems often induces relatively small effects on the porphyrin chromophore [1,4], although porphyrins with fused acenaphthylene rings have been shown to have highly modified UV-vis spectra [5-7]. Porphyrins with fused heterocyclic rings have been little explored up to this time, although these have the potential to have many valuable properties. Recently, we have shown that porphyrins with fused benzothiadiazole, benzoxadiazole and benzoselenadiazole units **1a-c** have very unusual UV-vis spectra, and the related zinc complexes exhibit strong absorption bands between 600 and 650 nm [7-9]. These results encouraged us to consider the synthesis of porphyrins fused to the related tricyclic systems **2**-**7**. In principle, the *c*-annelated pyrroles required for porphyrin synthesis can be prepared by reaction of the related nitro-derivatives with isocyanoacetate esters in the presence of a non-nucleophilic base such as DBU [5-13]. Although five of these heterocycles are known compounds, the diselena-tricycle **4** has not been described previously. In this paper, we report the first synthesis of benzo[1,2-*c*:3,4- *c*']bis[1,2,5]selenadiazole (**4**) by a three step route starting from commercially available 4-nitrobenzo-2,1,3-selenadiazole (**8b**). In addition, improved routes to heterocycles **5**-**7** are described and a comparison of the spectroscopic properties for this matched set of tricycles is presented [14].



Although 4,5-furazanobenzofurazan (**2**) [15,16] and benzo[1,2-*c*:3,4-*c*']bis[1,2,5]thiadiazole (**3**) [17] are reasonably well studied systems, little or no work has been carried out on the remaining heterocycles **4**-**7**. Tricycle **3** can be prepared in good yields from 4-nitrobenzo-2,1,3-thiadiazole (**8a**) (Scheme 1). Amination under basic conditions with hydroxylamine gave the nitroamine **9a** in 92% yield, and this is readily reduced to the corresponding diamine **10a** with sodium hydrosulfite ($Na_2S_2O_4$) in boiling water [17]. This brilliant red colored diamine can then be cyclized with thionyl chloride in refluxing pyridine to give **3** in quantitative yield. The related tricycle [1,2,5]selenadiazolo[3,4-*e*]-2,1,3-benzothiadiazole (**7**) has previously been prepared in 62% yield under optimized conditions by reacting diamine **10a** with selenium dioxide [18]. We find that quantitative yields of **7** are obtained by cyclizing **10a** with selenium oxychloride in refluxing chloroform-pyridine (Scheme 1), conditions that represent a significantly improved procedure for preparing this little studied heterocycle.

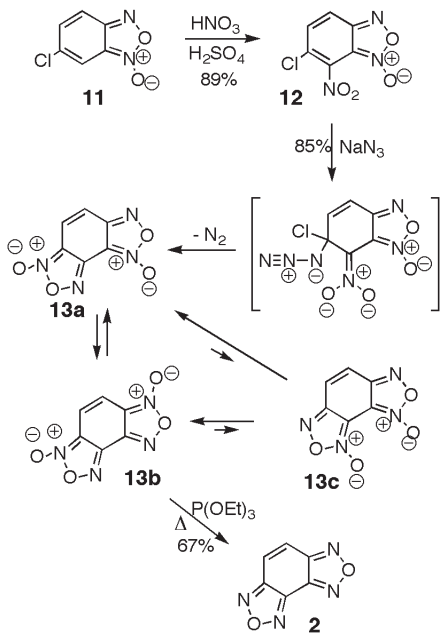
Scheme 1



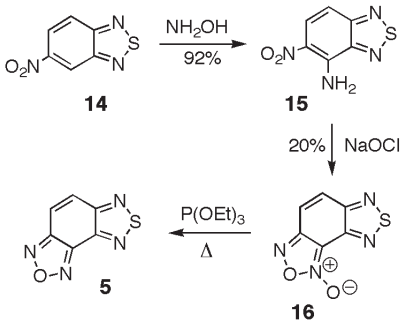
Given the success of these syntheses, this approach was adapted for the preparation of the new heterocyclic system benzo[1,2-*c*:3,4- *c*']bis[1,2,5]selenadiazole (**4**). Amination of 4-nitrobenzo-2,1,3-selenadiazole (**8b**) with hydroxylamine and potassium hydroxide gave the nitroamine **9b** in 79% yield (Scheme 1). Unfortunately, unlike the previous work on **9a**, reduction of the nitro group for **9b** with sodium hydrosulfite gave poor results. However, the required diamine **10b** could be obtained in 62% yield by adapting the conditions reported by Pesin and coworkers using ferrous sulfate in aqueous ammonia as the reducing agent [19]. Cyclization of **10b** with selenium oxychloride in refluxing chloroform-pyridine gave **4** in quantitative yield.

Furazanobenzofurazan (**2**) was prepared by adapting literature procedures [15,16]. Commercially available 5-chlorobenzofuroxan (**11**) was nitrated with nitric acid and sulfuric acid to give the bright orange colored compound 5-chloro-4-nitrobenzofuroxan **12** in 90% yield (Scheme 2). This was cyclized with sodium azide in a methanol-acetone-water mixture to give furoxanobenzofuroxan **13** in 85% yield. Deoxygenation of the bis-*N*-oxide was achieved by treatment with triethyl phosphite. In the original work, the excess triethyl phosphite was removed by distillation and, following chromatography, **2** was isolated in 51% yield [16]. In our hands, the best results were obtained when the excess triethyl phosphite was hydrolysed with 2 *N* hydrochloric acid and the product was purified by flash chromatography on silica eluting with petroleum ether. These conditions gave **2** in 67% yield.

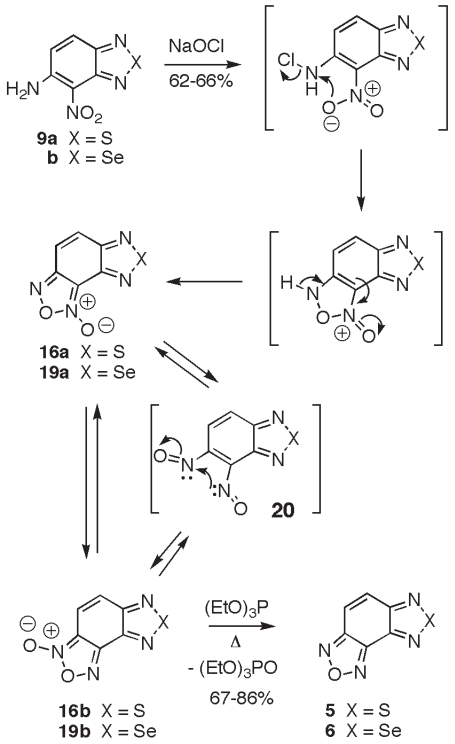
Scheme 2



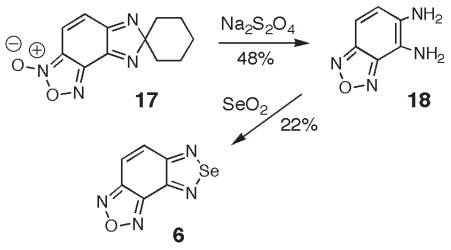
Scheme 3



Scheme 4



Scheme 5



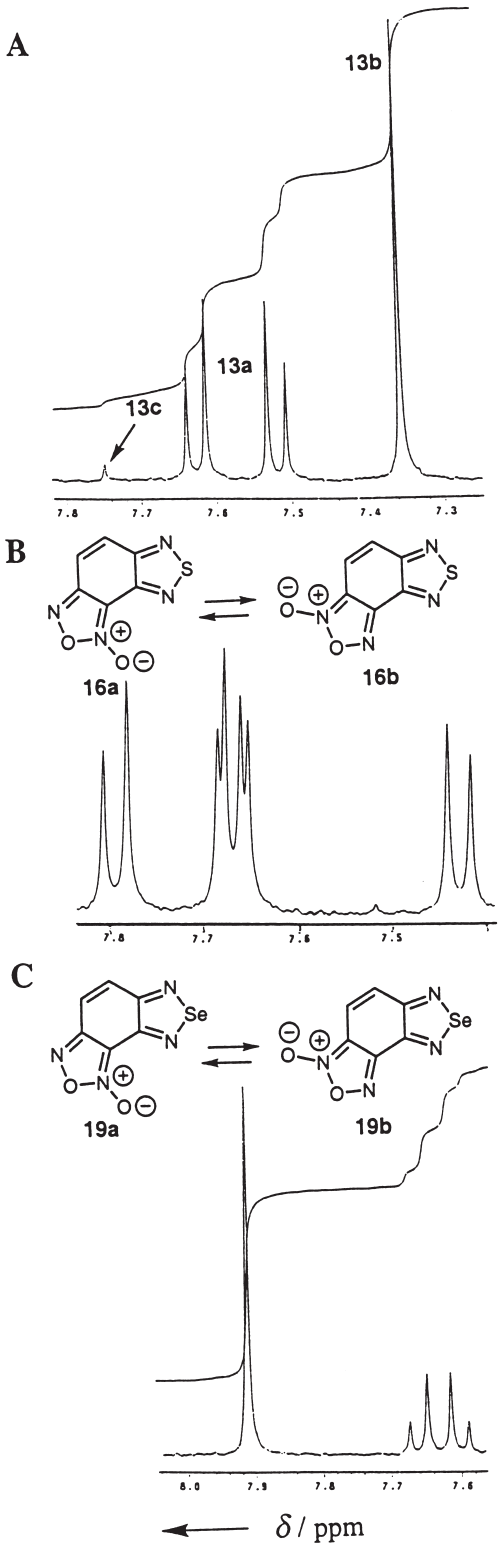


Figure 1. 400 MHz proton NMR spectra of heterocyclic *N*-oxides, showing the presence of isomers due to a ring opening-ring closing equilibrium process.

A. Proton NMR spectrum of 4,5-furoxanofuroxan **13** in perdeuteriated dimethylsulfoxide showing the presence of three isomers **13a**, **13b** and **13c**.

B. Proton NMR spectrum of furoxanobenzothiadiazole **16** in deuteriochloroform showing the presence of two isomers **16a** and **16b**.

C. Proton NMR spectrum of furoxanobenzoselenadiazole **19** in perdeuteriated dimethylsulfoxide showing the presence of two isomers **19a** and **19b**.

Furazanobenzothiadiazole **5** was previously prepared (Scheme 3) from 5-nitrobenzothiadiazole **14** in modest overall yield [20]. In this study, reaction of **14** with hydroxylamine afforded the 4-amino-derivative **15** in 92% yield. Ghosh and Everitt cyclized nitroamine **15** with sodium hypochlorite to give furoxanobenzothiadiazole **16** in 20% yield [20]. This can then be deoxygenated with triethyl phosphite to give **5**. We obtained superior results by synthesizing **5** from 5-amino-4-nitrobenzothiadiazole **9a** (Scheme 4). Cyclization of **9a** with sodium hypochlorite gave **16** in 62% yield, and subsequent deoxygenation with triethyl phosphite afforded tricycle **5** as a light brown powder in 67% yield. This represents a 37% overall yield in three steps from commercially available 4-nitrobenzothiadiazole **8a**, whereas Ghosh and Everitt only obtained **5** in an overall 11.4% yield in their 3 step synthesis from 5-nitrobenzothiadiazole **14** [20].

Furazanobenzo-2,1,3-selenadiazole **6** was previously prepared by Cada *et al*. from the spirocycle **17** (Scheme 5) [21]. Reduction of **17** with sodium hydrosulfite gave the diamine **18**, and this was cyclized with selenium dioxide to give **6** in 22% yield [21]. Apart from the low yield in the final step, the synthesis of the key precursor **17** requires multiple steps and this cannot be considered to be a practical route to this heterocyclic system. We adapted the chemistry we had used to prepare heterocycle **5** in the synthesis of the selenium analogue **6** (Scheme 4). Treatment of nitroamine **9b** with sodium hypochlorite and potassium hydroxide in ethanol gave the *N*-oxide **19** in 66% yield. This could then be deoxygenated with triethyl phosphite to give **6** in 86% yield. The overall yield in this case from commercially available 4-nitrobenzoselenadiazole **8b** was 44%, again representing a considerable improvement over the previous methodology for **6**.

N-Oxide derivatives were generated as intermediates in the synthesis of heterocycles **2**, **5** and **6**. Previous investigations of furoxanobenzofuroxan **13** by Boulton *et al*. had demonstrated that the *N*-oxides existed in equilibrium between three isomeric forms **13a**, **13b** and **13c** [15]. Isomer **13c** is less favored due to steric interactions and is present as a minor form. The original study was performed using a 60 MHz NMR spectrometer [15]. Figure 1A displays the 400 MHz proton NMR spectrum for **13**, and this confirms the presence of all three forms. This type of equilibration is also observed for furoxanobenzothiadiazole **16** and furoxanobenzoselenadiazole **19**, although only two forms are possible for these *N*-oxides. The 400 MHz proton NMR spectrum of **16** in deuteriochloroform (Figure 1B) shows the presence of two sets of doublets for **16a** and **16b**, where the former represents approximately 55% of the equilibrium mixture. However, it is worth noting that these equilibria are solvent and concentration dependent. In perdeuteriated dimethylsulfoxide, **16** gave a poorer quality proton NMR spectrum where the two isomers were present in a ratio of 3:1. The 400 MHz proton NMR spectrum of selenium *N*-oxide **19** in perdeuteriated dimethylsulfoxide shows the presence of two similar isomers **19a** and **19b** in a ratio of 6:4. The major isomer produces a singlet at 7.9 ppm, presumably due to the two protons having identical chemical shift values, while the other species gives rise to an AB quartet near 7.6 ppm (Figure 1C). Again, this equilibrium was solvent dependent and in a mixture of perdeuteriated dimethylsulfoxide and deuteriochloroform the proton NMR spectrum showed the two isomers in the ratio of 3:1. The interconversion must involve a ring opening-ring closing mechanism most likely involving a dinitroso-intermediate **20** (Scheme 4). The presence of these equilibrium mixtures could also be observed in the carbon-13 NMR spectra for **13**, **16** and **19**.

As **2-7** are a matched set of heterocycles with all possible combinations of oxygen, sulfur and selenium, the spectroscopic properties were compared and contrasted. Full NMR data is provided in the experimental section, although the proton NMR spectra are limited due to the presence of only two hydrogen atoms in these structures. For the symmetrical heterocycles **2**, **3** and **4** in perdeuteriated dimethylsulfoxide, the proton NMR spectrum consisted of a singlet at 7.84, 8.17 and 7.81 ppm, respectively. These data suggest a higher diatropic character in the sulfur heterocycles. The asymmetrical heterocycles **5-7** gave AB quartets in the same chemical shift region.

The UV-vis spectra for the heterocycles in methanol showed considerable variation. The symmetrical systems, as expected, gave the simplest spectra and showed a major band that underwent strong bathochromic shifts going from O to S to Se. The oxygen system **2** showed fine structure with a strong band near 230 nm. The sulfur version **3** gave this band at 281 nm, while the new selenium heterocycle gave the main band at 312 nm (Figure 2). A second band was present for all three systems at 203-205 nm. The mixed SSe heterocycle **7** gave a spectrum that showed features intermediary between **5** and **6**, as might be expected, and two main bands were observed at 204 and 294 nm. However, **5** gave three bands at 202, 251 and 308 nm, while **6** afforded three bands at 203, 261 and 331 nm, with additional fine structure evident for the longer wavelength absorption.

The EI MS fragmentation patterns were also of interest. All of these systems were robust to this technique and gave the molecular ion as the base peak. Furazanobenzofurazan **2** gave a fragment ion at m/z 132 corresponding to loss of NO·, while benzo[1,2-*c*:3,4-*c*']bis[1,2,5]thiadiazole (**3**) gave a peak at m/z 167 corresponding to loss of HCN (Figure 3). These fragmentations are consistent with previous observations for benzoxadiazoles and benzothiadiazoles [22]. Although the bis-selenium system **4** gave a very small cluster near m/z 262 corresponding to loss of

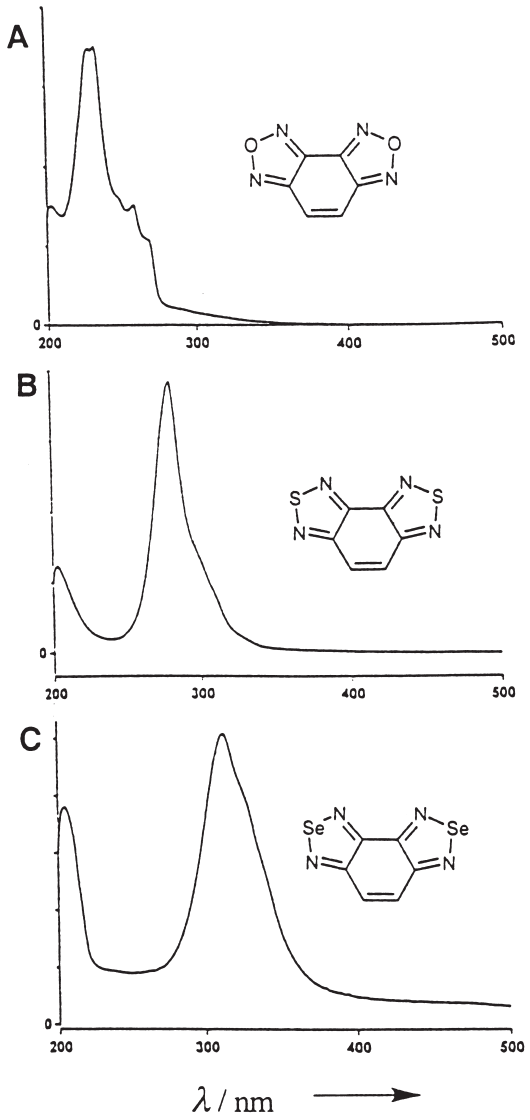


Figure 2. UV spectra of symmetrical heterocycles **2** (A), **3** (B) and **4** (C) in methanol.

HCN, the main fragment ion was a cluster centered on m/z 160 that corresponds to Se_2^+. The mixed systems gave similar data to **2** and **3**. The OS and OSe systems **5** and **6**, respectively, both gave fragment ions corresponding to loss of NO·, while the SSe system **7** showed loss of HCN. Hence, the data demonstrates that loss of NO· occurs where this is possible and loss of HCN is only observed when oxygen is not present. However, loss of HCN does not seem to be very favored for the SeSe system **4**. It is also worth noting that the selenium containing heterocycles all show characteristic clusters for the molecular ions and fragment ions due to the presence of five naturally occurring isotopes for this element.

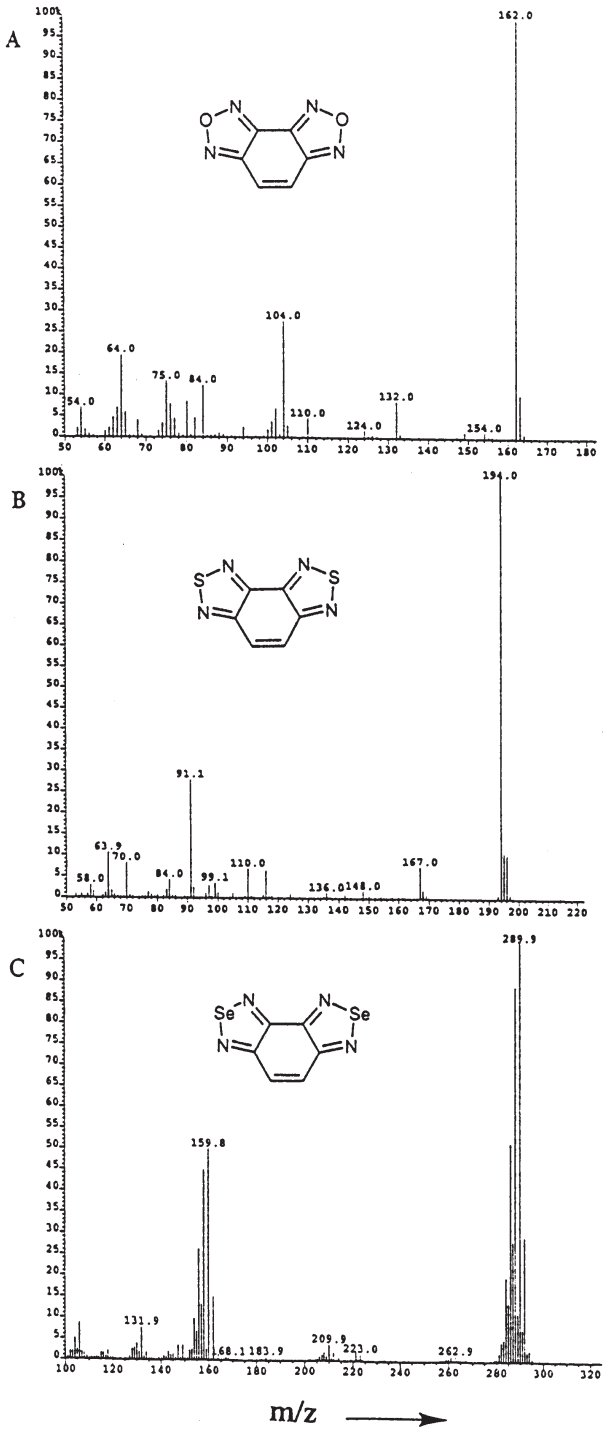


Figure 3. 70 eV electron impact mass spectra of **2** (A), **3** (B) and **4** (C).

In conclusion, benzo[1,2-*c*:3,4- *c*']bis[1,2,5]selenadiazole **4** has been synthesized for the first time and superior routes to the related heterocycles **5**-**7** have been developed. These systems are potentially useful in the synthesis of novel highly conjugated porphyrin systems. In addition,

interesting *N*-oxides were prepared as intermediates in the synthesis of heterocycles **2**, **5** and **6**.

EXPERIMENTAL

Nuclear magnetic resonance spectra were obtained on a Varian NMR spectrometer operating at 400 MHz (proton) and 100 MHz (C-13), respectively, in deuteriochloroform or hexadeuteriodimethylsulfoxide solvents. Chemical shifts are reported to the residual chloroform ^{1}H NMR signal at 7.26 ppm and the C-13 signal at 77.23 ppm, or the analogous dimethylsulfoxide signals at 2.49 and 39.7 ppm, respectively. UV spectra were recorded on a Varian Cary 1 Bio UV-visible spectrophotometer. Electron impact mass spectral determinations were made at the Mass Spectral Laboratory, School of Chemical Sciences, University of Illinois at Urbana-Champaign, supported in part by a grant from the National Institute of General Medical Sciences (GM 27029). Elemental analyses were obtained from the School of Chemical Sciences Microanalysis Laboratory at the University of Illinois. Melting points were taken on a Mel-Temp apparatus and are uncorrected. 4-Nitro-2,1,3-benzothiadiazole, 4-nitro-2,1,3-benzoselenadiazole, 5-chloro-4-nitrobenzofuroxan, triethyl phosphite and selenium oxychloride were purchased from Aldrich or Acros. Sodium hypochlorite solution, available chlorine content 10-13%, was purchased from Aldrich. Concentrated aqueous ammonia (29.05% w/v) was obtained from Fisher; 12% w/v aqueous ammonia was prepared by diluting 41.3 mL of the concentrated ammonia solution to a volume of 100 mL with deionized water. Solvents were all of reagent grade and were obtained from Fisher.

5-Amino-4-nitro-2,1,3-benzothiadiazole (**9a**).

4-Nitro-2,1,3-benzothiadiazole (4.00 g) was dissolved in hot methanol (175 mL) in a 500 mL three-necked flask equipped with an addition funnel, a drying tube, a stir bar and a thermometer. Hydroxylamine hydrochloride was added to the hot solution, after which the flask was immediately cooled to -15 °C in a dry ice/acetone bath while maintaining vigorous stirring of the mixture. A solution of potassium hydroxide (15.0 g) in methanol (100 mL) was then added dropwise, maintaining the temperature at ≤ -10 °C . Once the addition was complete, the dark solution was allowed to warm to room temperature. The solution was then stirred into 1.25 L of water, and the resulting green precipitate collected by suction filtration and dried *in vacuo* to give the title compound (4.03 g, 92%) as a green powder, mp 278-279 °C (lit. mp [17] 278-279 °C); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.42 (1H, d, *J* = 9.6 Hz), 7.99 (1H, d, *J* = 9.2 Hz), 9.02 (2H, br s); ^{13}C nmr (dimethylsulfoxide-d_6): δ 119.3, 127.8, 128.7, 150.2, 150.6, 151.4.

5-Amino-4-nitro-2,1,3-benzoselenadiazole (**9b**).

The nitro-amine **9b** was prepared from 4-nitro-2,1,3-benzoselenadiazole (5.00 g) and hydroxylamine hydrochloride (7.36 g) under the foregoing conditions. The reaction solution was poured into 1.25 L of water and gave an olive green precipitate. This was collected by suction filtration and dried *in vacuo* to give **9b** (4.20 g, 79%) as a pale green powder, mp 294-295 °C (lit. mp [23] 295 °C); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.37 (1H, d, *J* = 9.6 Hz), 7.80 (1H, d, *J* = 9.6 Hz), 9.08 (2H, br s); ^{13}C nmr (dimethylsulfoxide-d_6): δ 121.1, 127.9, 130.7, 151.9, 154.1, 156.3.

4,5-Diamino-2,1,3-benzothiadiazole (**10a**).

5-Amino-4-nitro-2,1,3-benzothiadiazole (**9a**) (4.0 g) was suspended in an 800 mL beaker with 188 mL of hot water. The solution was vigorously stirred and heated on a hot plate until boiling, and sodium hydrosulfite (16.88 g) was added over a 30 second period causing the solution to turn a deep red color and foam. Heating was continued for an additional 2 minutes, after which the solution was filtered through a preheated funnel and filtration flask. The filtrate was cooled to room temperature and the red precipitate collected by suction filtration and recrystallized from water. Following vacuum drying, the diamine (2.3 g, 68%) was obtained as a bright red powder, mp 167-168 °C (lit. mp [17] 168-169 °C); ^{1}H nmr (dimethylsulfoxide-d_6): δ 4.94 (2H, br s), 5.10 (2H, br s), 7.16 (1H, d, *J* = 8.8 Hz), 7.24 (1H, d, *J* = 9.2 Hz); ^{13}C nmr (dimethylsulfoxide-d_6): δ 109.2, 120.9, 127.1, 131.2, 149.1, 150.9.

4,5-Diamino-2,1,3-benzoselenadiazole (**10b**).

Ferrous sulfate heptahydrate (12.3 g) was added in three portions to a suspension of 5-amino-4-nitro-2,1,3-benzoselenadiazole (**9b**) (1.54 g) in 12% aqueous ammonia (68 mL), while stirring with moderate heating (45-50 °C). The mixture was then brought to a boil and stirred for 30 minutes, after which the solution was filtered through a preheated funnel and filtration flask. The black residue on the filter paper was set aside. The fitrate was cooled in an ice bath for 45 minutes, and the resulting precipitate collected by suction filtration and saved as product A. The set aside black residue was redissolved in the remaining filtrate and the mixture vigorously stirred while heating to boiling temperatures for an additional 15 minutes. The mixture was again filtered hot through an oven heated filtration funnel, and the black residue on the filter paper discarded. The filtrate was allowed to cool to room temperature and refrigerated overnight. The resulting precipitate was collected by filtration and saved as product B. The remaining filtrate was extracted with 3 x 200 mL of ethyl acetate, dried over sodium sulfate and evaporated on a rotary evaporator to give product C. The product fractions A, B and C were combined to give the diamine (0.84 g, 62%) as black crystals, mp 51-52 °C (lit. mp [19] 51 °C); ^{1}H nmr (dimethylsulfoxide-d_6): δ 4.72 (2H, br s), 5.04 (2H, br s), 6.97 (1H, d, *J* = 9 Hz), 7.17 (1H, d, *J* = 9 Hz); ^{13}C nmr (dimethylsulfoxide-d_6): δ 111.6, 120.8, 128.4, 129.9, 140.3, 149.6.

Benzo[1,2-*c*:3,4-*c*']bis[2,1,3]thiadiazole (**3**).

A solution of thionyl chloride (3 mL) in chloroform (1.8 mL) was added dropwise over a 10 minute period to a stirred suspension of 4,5-diamino-2,1,3-benzothiadiazole (**10a**; 0.600 g) in chloroform (10.2 mL) and pyridine (3 mL). The resulting solution was stirred under reflux for 15 minutes. The solvents were removed under reduced pressure to give a brown solid. This was scraped into ice water and allowed to stir for 1 hour. The resulting suspension was collected by suction filtration and dried *in vacuo* overnight to afford **3** (0.593 g, 100%) as a reddish-brown solid, mp 179-180 °C (lit. mp [17] 179.5-180.5 °C); uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 203 (4.07), 281 nm (4.55); ^{1}H nmr (dimethylsulfoxide-d_6): δ 8.17 (1H, s); ^{13}C nmr (dimethylsulfoxide-d_6): δ 124.6, 148.6, 156.8; ms: (electron impact) m/z (relative intensity) 196 (10), 195 (11), 194 (100) (M^+), 167 (7.5).

Benzo[1,2-*c*:3,4-*c*']bis[2,1,3]selenadiazole (**4**).

A solution of selenium oxychloride (4 mL) in chloroform (2.6 mL) was added dropwise over a 15 minute period to a stirred sus-

pension of 4,5-diamino-2,1,3-benzoselenadiazole (**10b**; 0.800 g) in chloroform (13.4 mL) and pyridine (4 mL). The resulting solution was stirred under reflux for 15 minutes. The solvents were removed under reduced pressure to give a brown tar. This was scraped into ice-water and allowed to stir for 1 hour. The resulting suspension was suction filtered to collect the solid which was dried *in vacuo* overnight to afford **4** (1.08 g, 100%) as a reddish-brown solid, mp 318 °C, dec.; uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 205 (4.00), 312 (4.13), 393 nm (sh, 3.15); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.81 (2H, s); ^{13}C nmr (dimethylsulfoxide-d_6): δ 126.9, 155.5, 161.2; ms: (electron impact) m/z (relative intensity) 293.9 (2.7), 292.9 (2.3), 291.9 (29), 290.9 (7.6), 289.9 (100) (M^+), 288.9 (11), 287.9 (89), 286.9 (28), 285.9 (52), 284.9 (14), 283.9 (20), 282.9 (5.2), 282.9 (4.6), 281.9 (4.6), 161.8 (15), 159.8 (50) (Se_2^+), 157.9 (45), 156.9 (13), 155.9 (26), 154.9 (7), 153.9 (10). HRMS (EI): Calcd for $C_6H_2N_4{}^{78}Se_2$ (285.8625); Found 285.8631, Δ = -0.5 mDa, error -1.9 ppm.

Anal. Calcd. for $C_6H_2N_4Se_2$: C, 25.02; H, 0.70. Found: C, 25.23; H, 0.78.

[1,2,5]Selenadiazolo[3,4-*e*]-2,1,3-benzothiadiazole (**7**).

A solution of selenium oxychloride (4 mL) in chloroform (2.6 mL) was added dropwise over a 15 minute period to a stirred suspension of 4,5-diamino-2,1,3-benzothiadiazole (**10a**; 0.800 g) in chloroform (13.4 mL) and pyridine (4 mL). The resulting solution was stirred under reflux for 15 minutes. The solvents were removed under reduced pressure to give a brown tar. This was scraped into ice water and allowed to stir for 1 hour. The resulting suspension was suction filtered to collect the solid which was dried *in vacuo* overnight to afford **4** (0.97 g, 100%) as a reddish-brown solid, mp 235-236 °C (lit mp [18] 234-235 °C); uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 204 (4.17), 294 (4.41), 326 nm (sh, 3.19); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.93-8.02 (2H, AB quartet, *J* = 10 Hz); ^{13}C nmr (dimethylsulfoxide-d_6): δ 123.8, 127.5, 151.0, 153.2, 157.0, 161.1; ms: (electron impact) m/z (relative intensity) 245 (2.1), 244 (24), 243 (10), 242 (100) (M^+), 241 (6.1), 240 (51), 239 (19), 238 (21), 217 (4.9), 216 (2.3), 215 (21), 213 (11).

5-Chloro-4-nitrobenzofurazan (**12**).

5-Chlorobenzofuroxan (10.0 g) was dissolved in sulfuric acid (60 mL) and cooled to 0 °C in an ice-salt bath. Nitric acid (4.03 g) in concentrated sulfuric acid (10 mL) was added over 15 minutes, while maintaining the temperature of the mixture at ≤ 5 °C. The solution was poured with stirring into ice-water, and the resulting orange precipitate collected by filtration and dried *in vacuo* overnight. The nitro compound (11.3 g, 90%) was obtained as bright orange crystals, mp 79-80 °C (lit. mp [15] 78-81 °C); ^{1}H nmr (deuteriochloroform): δ 7.27 (1H, d, *J* = 10 Hz), 7.60 (1H, d, *J* = 9.6 Hz); ^{13}C nmr (dimethylsulfoxide-d_6): δ 95.8, 110.3, 116.5, 141.1, 149.1, 166.9.

4,5-Furoxanobenzofuroxan (**13**).

A solution of sodium azide (1.24 g) in an acetone-methanol-water mixture (10 mL, 1:2:2) was added to a stirred solution of 5-chloro-4-nitrobenzofurazan (4.00 g) in an acetone-methanol mixture (8 mL, 1:1). Once spontaneous effervescence had ceased (approximately 1 hour), the product was precipitated by the dropwise addition of water. In some cases an oil formed. However, upon overnight refrigeration, a deep orange solid formed and this was collected by suction filtration. Recrystallization from ethanol gave furoxanobenzofuroxan (3.06 g, 85%) as an orange powder, mp 93-94 °C (lit mp [15] 94-95 °C); uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 202 (4.02), 236 (3.84), 284 (4.02), 309 (4.12), 322 (4.16), 340 nm (3.97); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.39 (2H, s, isomer **13b**), 7.57 (1H, d, *J* = 9.6 Hz, isomer **13a**), 7.67 (1H, d, *J* = 10 Hz, isomer **13a**), 7.80 (2H, s, isomer **13c**); ^{13}C nmr (dimethylsulfoxide-d_6): δ 104.4, 112.0, 113.6, 116.5, 120.1, 120.9, 142.2, 144.9, 153.2.

4,5-Furazanobenzofurazan (**2**).

A solution of 4,5-furoxanobenzofuroxan (0.50 g) in triethyl phosphite (10 mL) was refluxed under nitrogen for 1 hour. The mixture was poured into 2 *N* hydrochloric acid and stirred as it boiled in an exothermic reaction for 5 minutes. The resulting solution was extracted with dichloromethane (3 x 200 mL), dried over sodium sulfate, and the solvent removed under reduced pressure. The residue was dissolved in a small volume of dichloromethane and place on a silica gel flash chromatography column. This was eluted initially with petroleum ether (60-90°) and then the polarity was gradually increased to 50/50 dichloromethane-petroleum ether. Evaporation of the solvent on a rotary evaporator gave a yellow oil, but this solidified on cooling in an ice bath to give **2** (0.28 g, 67%) as bright yellow crystals, mp 59-60 °C (lit. mp [16] 60-61 °C); uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 203 (4.05), 229 (4.42), 234 (4.42), 259 nm (4.05); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.84 (2H, s); ^{13}C nmr (dimethylsulfoxide-d_6): δ 122.5, 141.4, 151.2; ms: (electron impact) m/z (relative intensity) 163 (10), 162 (100) (M^+), 132 (8.7).

Furoxanobenzothiadiazole (**16**).

5-Amino-4-nitro-2,1,3-benzothiadiazole (0.50 g) was dissolved in a 10% w/v solution of potassium hydroxide in ethanol (375 mL) with vigorous stirring and moderate heating. The suspension was then cooled to ≤ -10 °C and treated with aqueous sodium hypochlorite solution (available chlorine 10-13%, 67 mL). The coolant bath was removed and the solution allowed to warm to room temperature and stir for 1 hour. Reduction of the volume under reduced pressure to about 100 mL, followed by dilution with 100 mL of water, gave a precipitate and this was collected by suction filtration and dried *in vacuo* overnight. The title *N*-oxide (0.31 g, 62%) was obtained as a buff solid, mp 144-145 °C (lit. mp [20] 144-145 °C); uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 208 (4.02), 268 (4.18), 326 nm (3.88); ^{1}H nmr (deuteriochloroform): δ 7.43 (1H, d, *J* = 9.6 Hz, isomer **16a**), 7.65-7.69 (2H, 2 overlapping doublets, isomers **16a/b**), 7.79 (1H, d, *J* = 9.6 Hz, isomer **16b**); ^{13}C nmr (dimethylsulfoxide-d_6): δ 116.4, 121.2, 125.1, 128.3, 153.3, 156.4, 158.0.

Furoxanobenzoselenadiazole (**19**).

5-Amino-4-nitro-2,1,3-benzoselenadiazole (0.60 g) was dissolved in a 10% w/v solution of potassium hydroxide in ethanol (375 mL) with vigorous stirring and moderate heating. The suspension was then cooled to ≤ -10 °C and treated with aqueous sodium hypochlorite solution (available chlorine 10-13%, 67 mL). The coolant bath was removed and the solution allowed to warm to room temperature and stir for 1 hour. Reduction of the volume under reduced pressure to about 100 mL, followed by dilution with 100 mL of water, gave a precipitate and this was collected by suction filtration and dried *in vacuo* overnight. Recrystallization from chloroform-hexanes gave the *N*-oxide (0.39 g, 66%) was obtained as a peach colored powder, mp [20]

245-246 °C; uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 214 (3.81), 287 (4.05), 339 (3.87), 363 nm (3.74); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.44 (1H, d, J = 10 Hz, isomer **19b**), 7.64 (1H, d, *J* = 10 Hz, isomer **19b**), 7.74 (2H, s, isomer **19a**); ^{13}C nmr (dimethylsulfoxide-d_6): δ 115.2, 120.0, 128.2, 131.2, 153.3, 160.1, 161.7.

Anal. Calcd. for $C_6H_2N_4O_2Se$: C, 29.89; H, 0.84. Found: C, 29.98; H, 0.83.

Furazanobenzo-2,1,3-thiadiazole (**5**).

Furoxanobenzothiadiazole (0.80 g) was dissolved in triethyl phosphite (15 mL) and heated under reflux for 1 hour under nitrogen. The resulting reddish solution was poured into 2 *N* hydrochloric acid (15 mL) and stirred as it boiled in an exothermic reaction for 5 minutes. The flask was allowed to cool in the freezer for 15 minutes. The resulting precipitate was collected by suction filtration and dried *in vacuo* to afford the tricycle (0.48 g, 67%) as a pale brown powder, mp 131 °C (lit. mp [20] 130-131 °C); uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 202 (3.67), 251 (3.86), 308 nm (3.67); ^{1}H nmr (dimethylsulfoxide-d_6): δ 8.08-8.15 (2H, AB quartet, *J* = 10 Hz); ^{13}C nmr (dimethylsulfoxide-d_6): δ 118.9, 128.5, 144.2, 144.8, 150.9, 157.4; ms: (electron impact) m/z (relative intensity) 180 (5.6), 179 (10), 178 (100) (M^+), 149 (2.4), 148 (22).

Furazanobenzo-2,1,3-selenadiazole (**6**).

Furoxanobenzoselenadiazole (0.45 g) was dissolved in triethyl phosphite (10 mL) and heated under reflux for 1 hour under nitrogen. The resulting reddish solution was poured into 2 *N* hydrochloric acid (10 mL) and stirred as it boiled in an exothermic reaction for 5 minutes. The flask was allowed to cool in the freezer for 15 minutes. The resulting precipitate was collected by suction filtration and dried *in vacuo* to afford the tricycle (0.36 g, 86%) as a brown powder, mp 196-197 °C (lit. mp [21] 196 °C); uv (methanol): λ_{max} ($\log_{10}\varepsilon$) 203 (4.06), 261 (4.08), 331 nm (3.93); ^{1}H nmr (dimethylsulfoxide-d_6): δ 7.90 (1H, d, *J* = 9.6 Hz), 7.98 (1H, d, *J* = 10 Hz); ^{13}C nmr (dimethylsulfoxide-d_6): δ 117.7, 131.6, 147.0, 148.2, 151.3, 160.9; ms: (electron impact) m/z (relative intensity) 228 (19), 227 (8.9), 226 (100) (M^+), 225 (4.8), 224 (51), 223 (18), 222 (20), 198 (2.8), 196 (13), 194 (7).

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