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FACILE SYNTHESIS OF 4*H*-1,3-BENZOSELENAZINES BY THE ARYNE REACTION

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Abstract - Attempts to prepare benzoselenazoles by trapping benzynes with selenoureas failed. These reactions gave instead symmetrically substituted diaryl diselenides. However, when the selenoureas were converted to selenoazadienes, 4*H*-1,3-benzoselenazines were obtained in excellent yields. Furthermore, addition of the selenium atom of the selenoazadienes occurred regioselectively at the position 1 of 3-methoxybenzyne and 3,4-dimethoxybenzyne.

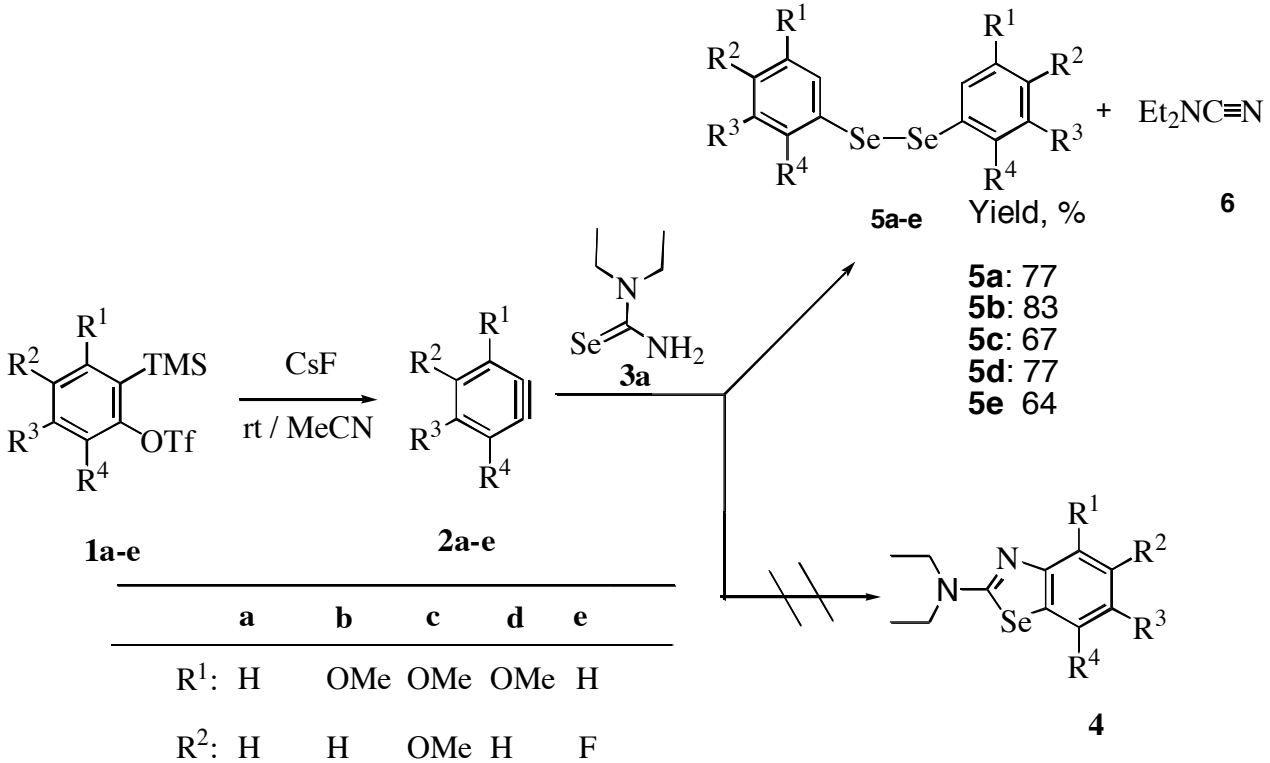
INTRODUCTION

We recently prepared benzo[4,5]thieno[2,3-*b*]pyridines[1] and benzo[4,5]seleno[2,3-*b*]pyridines[2] by the reaction of various benzynes with the respective sulfur and selenium containing Barton esters. We next turned our attention to preparing benzoselenazoles by trapping benzynes (**2a-e**) generated from the reaction of 2-trimethylsilylphenyl triflates (**1a-e**)[3] with selenourea derivatives (**3a-c**). The derivatives (**3a-c**) were prepared by the reaction of cyanamides with LiAlSeH in the presence of HCl.[4] This improved method, which is superior to most previous ones which invariable used highly toxic materials such as poisonous hydrogen selenides, has led to the facile preparation of selenium-nitrogen and sulfur-nitrogen heterocycles.

RESULTS AND DISCUSSION

We chose **1a-e** as benzyne precursors since benzyne generation occurs at room temperature under non-basic conditions. We initially studied the reaction of **1a-e** with N^1, N^1-diethylselenourea (**3a**). However, as shown in Scheme 1, these reactions gave no aryne addition products (**4a-e**), but rather produced diaryl

diselenides (**5a-e**) plus *N,N*-diethylcyanamide (**6**). Interestingly **6** was the starting material for the synthesis of **3a**. So the net result of this reaction is the transfer of a selenium atom to benzyne (**2a-e**). A



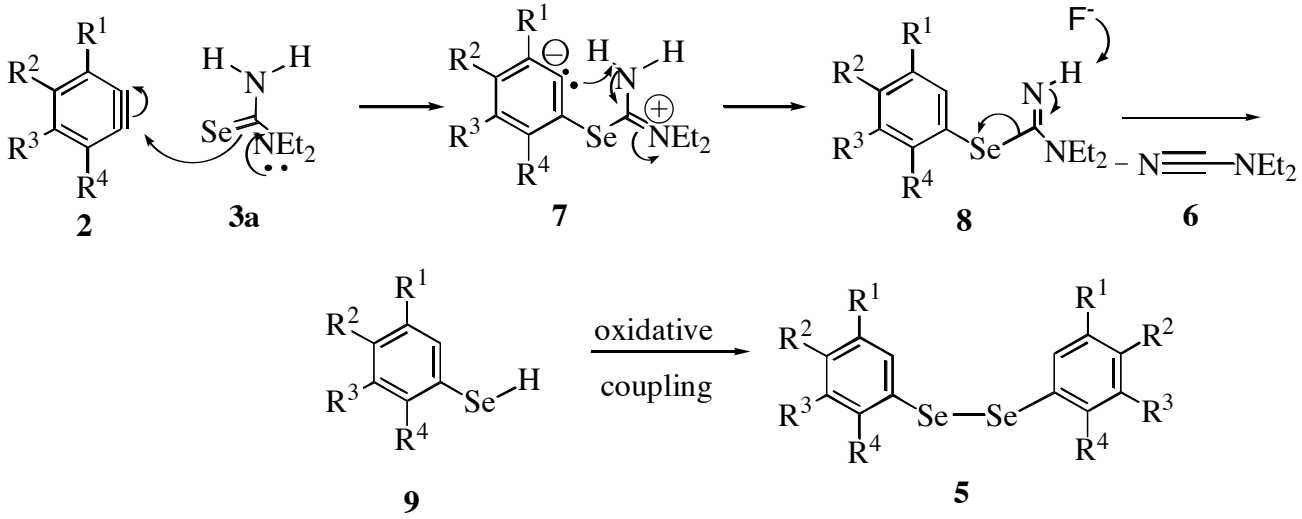
	a	b	c	d	e
R^1:	H	OMe	OMe	OMe	H
R^2:	H	H	OMe	H	F
R^3:	H	H	H	H	F
R^4:	H	OMe	H	H	H

Scheme 1

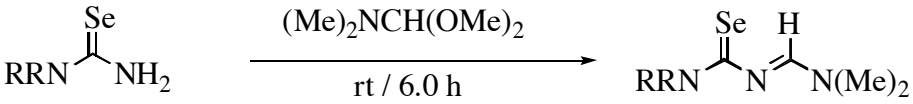
possible mechanism for the synthesis of **5a-e** is shown in Scheme 2. Thus, addition of the Se atom of **3** to benzyne (**2**) gives an adduct (**7**) from which a hydrogen atom from the amino group is transferred to the negatively charged carbon yielding intermediate (**8**). Fluoride ion induced elimination of cyanamide (**6**) from **8** gives ArSeH (**9**) that oxidatively dimerizes to **5.**

We thus changed our strategy by converting the selenoureas (**3a-c**) to the corresponding selenoazadienes (**10a-c**) by the method of Koketsu (see Scheme 3).[5] In this way, the interfering reaction of fluoride ion and the N-H postulated in Scheme 2 would be obviated. The initial reactions were quenched with NH_4Cl and water to yield at least two polar compounds which LC/MS indicated them to be N-oxide derivatives. These compounds could not be separated. However, when the reaction mixture was treated with $NaBH_4$ and methanol the titled compounds (**11a-o**) were formed in excellent yields. The results are listed in the Table 1. The compounds were identified by ^{1}H NMR and ^{13}C NMR spectrum and in the case of compounds (**11d**) by X-Ray crystallographic analysis. The X-Ray structure of **11d** clearly shows that

addition of the Se atom occurs regioselectively to position 1 of 3- methoxybenzyne (**2d**). A possible mechanism for this reaction is shown in Scheme 4 using the reaction of **10a** with **1d** as typical example.



Scheme 2

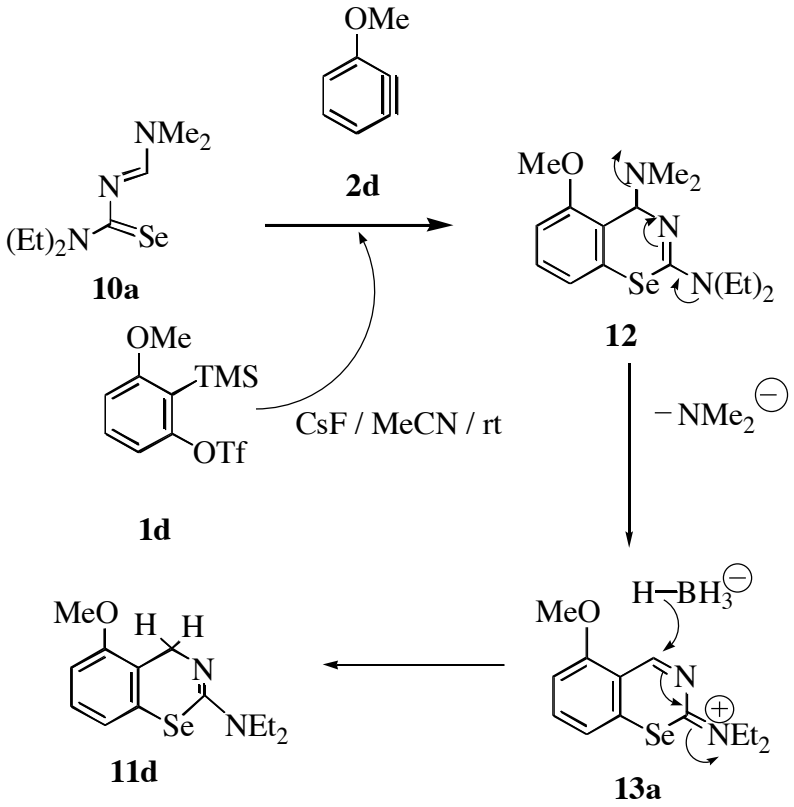


	R	R		Yield (%)
3a	Et	Et	**10a**	72
3b	-$(CH)_4$-		**10b**	84
3c	-$(CH_2)_5$-		**10c**	94

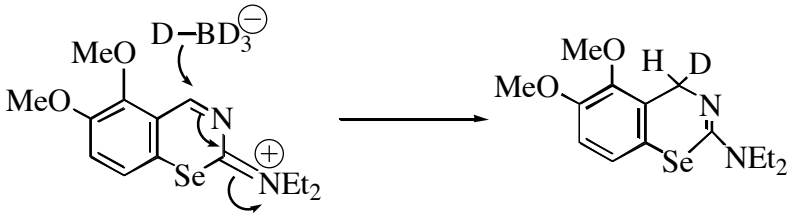
Scheme 3

Thus, the azadiene (**10a**) cycloadds to 3-methoxybenzyne (**2d**) *via* a [4n+2] process to give adduct (**12**). This intermediate then undergoes loss of the diethylamide group to give cationic species (**13a**) which then is reduced by hydride addition at the C-4 position to give observed products. Support for the last step was obtained by using by carrying out the reaction of 3,4-dimethoxybenzyne (**2c**) and dimethylamino derivative (**10a**) with $NaBD_4$ and observing the formation of 4-deuterio-2-diethylamino-5,6-dimethoxy-4*H*-1,3-benzoselenazine (**11p**). This intermediate then undergoes loss of the diethylamide group to give cationic species (**13a**) which then is reduced by hydride addition at the C-4 position to give observed products. The observation that 4-deuterio-2-diethylamino-5,6-dimethoxy-4*H*-1,3-benzoselenazine (**11p**) was the product of the reaction of either 3,4-dimethoxybenzyne (**2c**) or the dimethylamino derivative (**10a**) with $NaBD_4$ lends support for the hydride addition step. This is shown in Scheme 5. To our

knowledge, there has been no report of the elimination amide group by hydride ion. The mechanism shown in Scheme 4 does represents a reasonable sequence of events; however, further work is necessary to establish the mechanism of the reaction.



Scheme 4



Scheme 5

In conclusion, we have shown that a variety of 4*H*-1,3-benzoselenazines can be prepared in excellent yields by the reaction of selenoazadienes with arynes.

EXPERIMENTAL

General Data: Melting points were taken on a Mel-Temp capillary apparatus and are uncorrected with respect to stem correction. IR spectra were recorded on a Nicolet Magna-IRTM 550 FTIR spectrophoto-

meter and the ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AVANCE DRX-400 Multi-nuclear NMR spectrometer. Chemical shifts are reported in reference to TMS as internal standard. The glassware was heated overnight in an oven at 125 ºC prior to use. All the benzyne reactions were done under an atmosphere of dry O_2-free Ar via balloon.

General procedure for the synthesis of diaryl diselenides (5a-e)

To a solution containing 179 mg (1 mmol) of N^1,N^1-diethylselenourea (**3a**) and 1 mmol of the appropriate 2-trimethylsilylphenyl triflate (**1a-e**) in 50 mL of acetonitrile under Ar at rt was added 304 mg (2 mmol) of CsF. After stirring for 6 h, 5 mL of water was added and the resulting solution concentrated. The residue was dissolved in 15 mL of methylene chloride and the resulting solution washed with water (2 X 10 mL), dried (Na_2SO_4), filtered and evaporated. The residue was purified by column chromatography (silica gel; hexane/ethyl acetate/triethylamine 30:20:1) to isolate diaryl diselenides (**5a-e**). Their physical and spectral properties are given below.

Diphenyl diselenide (5a)

Yellow needles (hexane), mp: 64 – 65 ºC (lit.,[6] 63 – 65 ºC). ^{1}H NMR (400 MHz, Acetone-d_6): δ 7.29-7.35 (m, 6 H), 7.64-7.67 (m, 4 H).

Di-(2,5-dimethoxyphenyl) diselenide (5b)

Viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 6 H), 3.82 (s, 6 H), 6.78 (s, 2 H), 7.20 (s, 2 H). HRMS Calcd for $C_{16}H_{18}O_4Se_2$: 433.95355. Found: 433.95352. Anal. Calcd for $C_{16}H_{18}O_4Se_2$: C, 44.46; H, 4.20. Found: C, 44.58; H, 4.26.

Di-(3,4-dimethoxyphenyl) diselenide (5c)

Yellow crystals (EtOH), mp: 109-111 ºC (lit.,[7] 108-110 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 6 H), 3.89 (s, 6 H), 6.78 (d, J = 8.2 Hz, 2 H), 7.11 (s, 2 H), 7.18 (d, J = 8.2 Hz, 2 H).

Di-(3-methoxyphenyl) diselenide (5d)

Red brown oil, bp: 192 - 194 ºC (lit.,[8] 194 ºC). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.79 (s, 6 H), 6.78-6.70 (m, 1 H), 7.19-7.23 (m, 4 H), 7.28 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 113.1, 116.5, 123.4, 129.8,131.8, 159.8.

Di-(3,4-difluorophenyl) diselenide (5e)

Viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05-7.13 (m, 2 H), 7.28-7.36 (m, 2 H), 7.44-7.47 (m, 2 H). HRMS Calcd for $C_{12}H_6F_4Se_2$: 385.87360. Found: 385.87359. Anal. Calcd for $C_{12}H_6F_4Se_2$: C, 37.5; H, 1.57. Found: C, 37.62; H, 1.51.

General procedure for the synthesis of 4*H*-1,3-benzoselenazines 11a-o.

To a solution of 1.1 mmol of 2-trimethylsilylphenyl triflate (**1a-e**) and 1 mmol of *N*-(dimethylaminomethylidene)selenourea (**10a-c**) in 50 mL of acetonitrile under Ar at rt was added 304 mg

(2 mmol) of CsF. The mixture was stirred for 12 h then 76 mg (2 mmol) of sodium borohydride was added immediately followed by 5 mL of methanol, and the resulting mixture stirred for 1 h. At this time, 5 mL of water was added and the mixture concentrated under reduced pressure. The residue was dissolved in 15 mL of methylene chloride and the resulting solution washed with water (2 X 10 mL), dried (Na_2SO_4), filtered and evaporated. The residue was purified by column chromatography (silica gel; hexane/ethylacetate/triethylamine: 30:20:1) to isolate product. Physical and spectral properties are given below.

2-Diethylamino-4*H*-1,3-benzoselenazine (11a)

Yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (t, *J* = 7.1 Hz, 6 H), 3.49 (q, *J* = 7.1 Hz, 4 H), 4.43 (s, 2 H), 7.24-7.34 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 43.9, 53.8, 126.3, 126.8. 126.9, 127.1, 131.8, 135.6, 156.0. Anal. Calcd for $C_{12}H_{16}N_2Se$: C, 53.93; H, 6.03; N, 10.48. Found: C, 54.05; H, 5.99; N, 10.57.

2-Diethylamino-5,8-dimethoxy-4*H*-1,3-benzoselenazine (11b)

Yellow crystals (hexane/$CHCl_3$) mp: 68 - 69^{O}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72 (t, *J* = 7.5 Hz, 6 H), 3.49 (q, *J* = 7.5 Hz, 4 H), 3.81 (s, 3 H), 3.51 (s, 3 H), 4.49 (s, 2 H), 6.71 (d, *J* = 8.1 Hz, 1 H), 6.76 (d, *J* = 8.1 Hz, 1 H); (100 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 44.5, 55.8, 61.2, 56.1, 108.1, 109.0, 120.5, 125.0, 150.3, 150.3, 154.5. Anal. Calcd for $C_{14}H_{20}N_2O_2Se$: C, 51.38; H, 6.16; N, 8.56. Found: C, 51.44; H, 6.22; N, 8.60.

2-Diethylamino-5,6-dimethoxy-4*H*-1,3-benzoselenazine (11c)

Viscous yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, *J* = 7.1 Hz, 6 H), 3.40 (q, *J* = 7.1 Hz, 4 H), 4.44 (s, 2 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 6.77 (d, *J*= 8.4 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 44.5, 50.3, 55.8, 61.2, 111.3, 121.8, 124.7, 129.9, 146.0, 151.8, 155.4. Anal. Calcd for $C_{14}H_{20}N_2O_2Se$: C, 51.38; H, 6.16; N, 8.56. Found: C, 51.44; H, 6.20; N, 8.66.

2-Diethylamino-5-methoxy-4*H*-1,3-benzoselenazine (11d)

Yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (t, *J* = 6.9 Hz, 6H), 3.49 (q, *J* = 6.9 Hz, 4 H), 3.86 (s, 3 H), 4.51 (s, 2 H), 6.81(d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1 H), 7.14-7.18 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 45.2, 50.1, 56.0, 109.6, 122.3, 125.0, 128.0, 132.7, 155.1, 156.5.

Anal. Calcd for $C_{13}H_{18}N_2OSe$: C, 52.53; H, 6.10; N, 9.42. Found: C, 52.58; H, 6.21; N, 9.60. X-Ray Crystallographic Data: formula $C_{13}H_{18}N_2OSe$, formula weight 297.26, orthorhombic, space group $P2_12_12$, a = 8.2709(5), b = 23.7582(15), c = 6.7579(4) Å, v = 1327.9(1) Å^3, z = 4, d = 1.547 Mg/m^3, μ = 2.818 mm^{-1}. Data were collected on a Bruker APEX diffractometer at 100 ^{o}K, MoKα, 2θ 3.42 − 56.58^{o}. Reflection collected 16212, independent 3229 [R(int) = 0.025]]. The structure was solved by direct-methods and subsequent difference Fourier syntheses using SHELXTL program package.[9] Semi-

empirical absorption study was applied. The structure was refined with full-matrix least-squares on F^2. The final indices R_1 [$I > 2\sigma(I)$] = 0.021, wR_2 [all data] = 0.049. Selected bond lengths (Å) and angles (^{O}): Se – C(2) 1.9565(17), Se(1) – C(9) 1.9079(16), C(2) – N(3) 1.273(2), N(3) – C(4) 1.467(2), C(4) – C(10) 1.509(2), C(9) – C(10) 1.391(2); C(2) – Se(1) – C(9) 93.56 (7), Se(1) – C(2) – N(3) 121.86(13), C(2) – N(3) – C(4) 118.74(15), N(3) – C(4) – C(10) 113.56(13), C(4) – C(10) – C(9) 119.06(14), and Se(1) – C(9) – C(10) 117.92 (13).

2-Diethylamino-6,7-difluoro-4*H*-1,3-benzoselenazine (11e)

Light brown solid (hexane/$CHCl_3$), mp: 77 - 78 ºC. ^{1}H NMR (400 MHz, $CDCl_3$); δ 1.63 (t, *J* = 7.0 Hz, 6 H), 3.47 (q, *J* = 7.0 Hz, 4 H), 4.30 (s, 2 H), 7.17-7.22 (m, 1 H), 7.29-7.33 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 45.4, 57.3, 117.1 (d, $^2J_{C\text{-}8F\text{-}7}$ = 171 Hz), 118.6 (d, $^2J_{C\text{-}5F\text{-}6}$ 186 Hz), 125.8 (d, ^3J = 3.7 Hz). 133.1 (d, ^3J = 4.4 Hz), 149.7 (dd, $^1J_{CF}$ = 244 Hz, $^2J_{CF}$ = 14.5 Hz), 150.1 (dd, $^1J_{CF}$ = 250 Hz, $^2J_{CF}$ = 14.6 Hz), 156.0. Anal. Calcd for $C_{12}H_{14}N_2F_2Se$: C, 47.53; H, 4.66; N, 9.24. Found: C, 47.62; H, 4.80; N, 9.31.

2-Pyrrolidin-1-yl-4*H*-1,3-benzoselenazine (11f)

Yellow crystals (hexane/$CHCl_3$), mp: 77 – 78ºC. ^{1}H NMR(400 MHz, $CDCl_3$): δ 1.91-1.94 (m, 4 H), 3.49 (t, *J* = 6.0 Hz, 4 H), 4.38 (s, 2 H), 7.20-7.27 (m, 2 H), 7.35 (d *J* = 7.3 Hz, 1 H), 7.47 (d, *J* = 7.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8, 25.7, 49.6, 57.5, 126.9, 127.0, 129.6, 130.4, 135.8, 156.7. Anal. Calcd for $C_{12}H_{14}N_2Se$: C, 54.34; H, 5.32; N, 10.56. Found: C, 54.44; H, 5.40; N, 10.66.

5,8-Dimethoxy-2-pyrrolidin-1-yl-4*H*-1,3-benzoselenazine (11g)

Yellow crystals (hexane/$CHCl_3$), mp: 105 – 106^{O}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91-1.93 (m, 4 H), 3.51 (t, *J* = 6.0 Hz, 4 H), 3.80 (s, 3H), 3.85 (s, 3 H), 4.5 (s, 2 H), 6.70 (d, *J* = 8.8 Hz, 1 H), 6.76 (d, *J* = 8.8. Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.0, 48.8, 49.3, 56.156.1, 108.2, 109.4, 120.4, 124.5. 150.2, 150.6, 152.8. Anal. Calcd for $C_{14}H_{20}N_2O_2Se$: C, 51.70; H, 5.58; N, 8.60. Found: C, 51.77; H, 5.64; N, 8.66.

5,6-Dimethoxy-2-pyrrolidin-1-yl-4*H*-1,3-benzoselenazine (11h)

Viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (m, 4 H), 3.51 (m, 4 H), 3.87 (s, 3 H), 3.87 (s, 3 H), 4.50 (s, 2 H), 6.83 (d, *J* = 8.4 Hz, 1 H), 7.17 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.5, 49.7, 56.5, 61.8, 112.0, 122.2, 130.0, 146.8, 152.5, 154.2. Anal. Calcd for $C_{14}H_{20}N_2O_2Se$: C, 51.70; H, 5.58; N, 8.61. Found: C, 51.77; H, 5.49; N, 8.68.

5-Methoxy-2-pyrrolidin-1-yl-4*H*-1,3-benzoselenazine (11i)

Yellow crystals (hexane/$CHCl_3$), mp: 96 - 97ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.94 (m, 4H), 3.51 (m, 4 H), 3.85 (s, 3 H), 4.51 (s, 2 H), 6.81(d, *J* = 8.0 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1 H), 7.14-7.18 (m, 1 H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 25.5, 49.5, 49.9, 56.1, 109.6, 122.2, 124.5, 128.0, 132.4, 153.4, 156.6. Anal. Calcd for $C_{13}H_{16}N_2OSe$: C, 52.89; H, 5.46; N, 9.49. Found: C, 52.84; H, 5.40; N, 9.54.

6,7-Difluoro-2-pyrrolidin-1-yl-4*H*-1,3-benzoselenazine (11j)

Yellow solid (hexane/$CHCl_3$), mp: 142 - 143 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$): 25.5, 49.6, 57.2, 116.2 (d, *J* = 160 Hz), 118.5 (d, *J* = 181 Hz), 125.5 (d, *J* = 34 Hz), 132.5 (d, *J* = 38 Hz), 150.1 (dd, *J* = 250 Hz, 14.3 Hz), 150.3 (dd, *J*= 255 Hz, 15 Hz), 152.7. Anal. Calcd for $C_{12}H_{12}N_2F_2Se$: C, 47.85; H, 4.02; N, 9.30. Found: C, 47.88; H, 3.98; N, 9.38.

2-Piperidin-1-yl-4*H*-1,3-benzoselenazine (11k) Yellow crystals (hexane/$CHCl_3$), mp: 72 - 73ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (m, 6 H), 3.52 (m, 4 H), 4.40 (s, 2 H), 7.21 (m, 2 H), 7.36 (d= 7.2 Hz, 1 H), 7.49 (d, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.8. 25.6, 50.0, 57.5, 126.9, 127.0, 129.6, 130.4, 135.8, 156.7. Calcd for $C_{13}H_{16}N_2Se$: C, 55.92; H, 5.78; N, 10.03. Found: C, 55.96; H, 5.88; N, 10.14.

5,8-Dimethoxy-2-piperidin-1-yl-4*H*-1,3-benzoselenazine (11l)

Viscous liquid. ^{1}H NMR (400 Mz, $CDCl_3$): δ 1.60 (m, 6 H), 3.54 (m, 4 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 4.51 (s, 2 H), 6.71 (d, *J* = 8.8 Hz, 1 H), 6.76 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$): δ 24.9, 25.7, 49. 6, 56.2, 56.3, 108.3, 109.3, 120.7, 125.0, 150.5, 150.57, 157.3. Anal. Calcd for $C_{15}H_{20}N_2O_2Se$: C, 53.10; H, 5.94; N, 8.26. Found: C, 53.02; H, 6.02; N, 8.25.

5,6-Dimethoxy-2-piperidin-1-yl-4*H*-1,3-benzoselenazine (11m)

Viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (m, 6 H), 2.62 (m, 4 H), 3.85 (s, 3 H), 3.87 (s, 3 H), 4.51 (s, 2 H), 6.83 (d, *J* = 8.8. Hz, 1 H), 7.27 (d, *J* = 8.8 Hz 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.1, 44.7, 50.1, 50.9, 56.5, 61.9, 112.1, 122.3, 125.4, 130.3, 146.5, 152.5, 158.8. Anal. Calcd for $C_{15}H_{20}N_2O_2Se$: C, 53.10; H, 5.94; N, 8.26. Found: 53.21; H, 6.02; N, 8.30.

5-Methoxy-2-piperidin-1-yl-4*H*-1,3-benzoselenazine (11n)

Colorless solid (hexane/$CHCl_3$), mp: 101 - 102ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.57 (m, 6H), 3.52 (m, 4 H), 3.86 (s, 3 H), 4.52 (s, 2 H), 6.81(d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.0 Hz, 1 H), 7.14-7.18 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.4, 26.1. 50.1, 50.2, 56.0, 109.6, 1.4, 124.9, 128.0, 132.7, 156.6, 157.8. Anal. Calcd for $C_{14}H_{18}N_2OSe$: C, 54.37; H, 5.87; N, 9.06. Found: C, 54.44; H, 5.88; N, 9.13.

6,7-Difluoro-2- piperidin-1-yl-4*H*-1,3-benzoselenazine (11o)

Yellow crystals (hexane/$CHCl_3$), mp: 103 - 104ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (m, 6H), 3.51 (m, 4 H), 4.32 (s, 2 H), 7.18 (m, 1 H), 7.29 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.3, 26.0, 50.3, 57.3, 116.1 (d, $^2J_{CF}$ = 171 Hz,) 118.6 (d, $^2J_{C\text{-}8,\ F\text{-}7}$ = 17.1 Hz, $^2J_{C\text{-}6,F\text{-}6}$), 132.9 (d, ^3J = 3.7 Hz), 133.1 (d, ^3J = 4.4 Hz), 148.5 (dd, $^1J_{CF}$ = 250 Hz, $^2J_{CF}$ = 15.3 Hz), 151.0 (dd, $^1J_{CF}$ = 248 Hz, $^2J_{CF}$ = 14.5 Hz), 156.0. Anal. Calcd for $C_{13}H_{14}N_2F_2Se$: C, 49.53; H, 4.48; F, 12.05. Found: C, 49.60; H, 4.63; N, 12.16.

Synthesis of 4-deuterio-2-diethylamino-5,6-dimethoxy-4*H*-1,3-benzoselenazine (11p)

Compound (**11p**) was prepared in similar manner as described above and treated with selenazine (**10d**) with the exception that $NaBD_4$ was used in place of $NaBH_4$. Viscous oil. ^1H NMR ($CDCl_3$): δ 1.17 (t, *J* = 7.1 Hz, 6 H), 3.49 (q, *J* = 7.1 Hz, 4 H), 3.86 (s, 3 H), 3.90 (s, 3 H), 4.40 (s, 1 H), 6.82 (d, *J*= 8.4 Hz, 1 H), 7.18 (d, *J* = 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 13.7, 44.7, 50.0, 56.0, 61.4, 111.5, 122.0, 124.8, 130.1, 146.2, 152.1, 155.6.

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