The Reaction of Acetic Acid 2-Selenoxo-2*H*-pyridin-1-yl Esters with Benzynes: A Convenient Route to Benzo[*b*]seleno[2,3-*b*]pyridines

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Benzyne and its 3,4,5,6-tetraphenyl, 3- and 4-methyl, 3-methoxy and 4,5-difluoro derivatives react with acetic acid 2-selenoxo-2*H*-pyridin-1-yl esters **4a-e** to give benzo[*b*]seleno[2,3-*b*]pyridines **10-15** in modest yields. The benzynes were generated by one or more of the following methods: diazotization of anthranilic acids **5a-g** with isoamyl nitrate; mild thermal decomposition of 2-diazoniobenzenecarboxylate hydrochlorides **6a-d**; treatment of (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate (**7**) with tetrabutylammonium fluoride; and treatment of 2-trimethylsilylphenyl triflates **8a-c** with cesium fluoride. In all the reactions, the corresponding 2-(methylselenenyl)pyridines **16a-d** were also obtained suggesting that these reactions may involve selenium addition to benzyne *via* a SET (single electron transfer).

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Introduction.

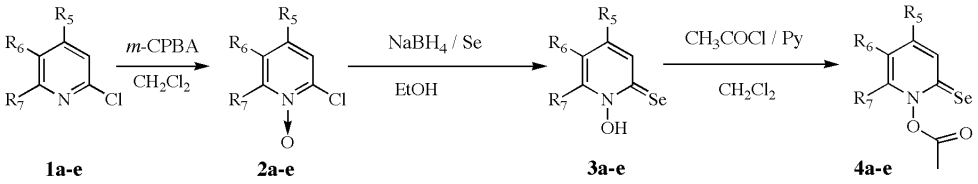
We [1] have recently reported the synthesis of benzo[4,5]thieno[2,3-*b*]pyridines and naphtho[2',3':4,5]-thieno[2,3-*b*]pyridines by the reaction of Barton esters (acetic acid 2-thioxo-2*H*-pyridin-1-yl ester) with benzyne, 3,4,5,6-tetraphenylbenzyne, 2,3-dehydronaphthalene, and 3-methylbenzyne. The benzyne intermediates were prepared by diazotization of the appropriate anthranilic acid with isoamyl nitrite in refluxing dichloromethane (40°) in the presence of the Barton ester . The first three aforementioned symmetric benzynes gave a single benzyne product, while the unsymmetric 4-methylbenzyne gave a 1:1 isomeric mixture of 7- and 8-methyl regioisomers. Attempts to generate 3,4-difluoro- or 3,4-dimethoxybenzyne under similar conditions failed. Although no direct evidence for free-radical addition of Barton esters to benzyne was found, such an addition appears likely based on the well-known nucleophilicity of sulfur. These esters could react with benzynes by SET (single electron transfer) to give a radical intermediate, which could subsequently undergo intramolecular cyclization to give the product *via* a tricyclic ring radical.

Okuma and coworkers [2] recently showed that the reaction of benzyne with thiones, which gives 2*H*-benzothietes, could be extended to the preparation of 2*H*-benzoselenates by the reaction of benzyne with 2-selones. This benzyne synthesis and the recently reported novel ring transformation of dihydroselenines to selenabicyclo[3.1.0]hexenes [3] are the only significant examples in the literature involving the addition of an organoselenium reagent to benzyne. Additionally, the only reported synthesis of benzoseleno[2,3-*b*]pyridines involves a multi-step reaction that requires starting materials that are not readily available [4]. These results prompted us to investigate the possibility of synthesizing benzo[*b*]seleno[2,3-*b*]pyridines by the reaction of acetic acid 2-selenoxo-2*H*-pyridin-1-yl esters (hereafter referred to as Barton 2-selenoxo esters) with benzynes. Such a study should allow ready access to these relatively under-investigated selenium heterocycles and could provide additional information on the nature of selenium addition to benzynes.

Results and Discussion

As shown in Scheme 1, the Barton 2-selenoxo esters **4a-e** were prepared from the corresponding 2-chloropyridines **1a-e** by a previously described method [5]. The percentage yields of the pyridine *N*-oxide **2a-e**, *N*-hydroxy-2-selenones **3a-e**, and Barton 2-selenoxo esters **4a-e** are listed in Table 1. Unfortunately, the nitro ester **4e** decomposed rapidly during the esterification of **3e**, thus negating its use in this study. In actual practice, the esters **4a-d** were prepared by esterification of the *N*-hydroxy-2-selopyridones **3a-d** just prior to use.

Scheme 1



Preparation of Barton 2-Selenoxo Esters **4a-e**

Table 1

Yields of Compounds **2a-e**-**4a-e**

	2	**3**	4
a	97	90	98
b	96	95	82
c	94	81	85
d	99	98	79
e	92	74	0

Since Barton 2-selenoxo esters are thermally labile and base sensitive, we sought readily available benzyne precursors that would be capable of generating benzynes under mild, aprotic, and non-basic conditions. Four types of benzyne precursor met these conditions and were selected for study. They include: anthranilic acids **5** [6], 2-diazoniobenzenecarboxylate hydrochlorides **6** [7], (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflates **7** [8], and 2-(trimethylsilyl)phenyl triflate (**8**) [9]. The structures of the individual members in each group and the benzynes **9** generated from these precursors are shown in Figures 1 and 2 respectively.

As shown in Scheme 2, the reaction of benzynes **9**, generated from the precursors **5-8**, with Barton 2-selenoxo esters **4** gave benzo[*b*]seleno[2,3-*b*]pyridines **10-15** along with 2-(methylselanyl)pyridines **16** as side products. The structures of **10-15** and **16** are shown in Figures 3 and 4, respectively. The yields of the desired seleno[2,3-*b*]pyridines **10-15**, which are shown in Table 2, depend upon the nature of the benzyne precursors and the conditions used in generating the benzyne intermediates. Thus, the reaction ofbenzyne (**9a**) generated from 1 equivalent of the benzyne precursors **5a,**

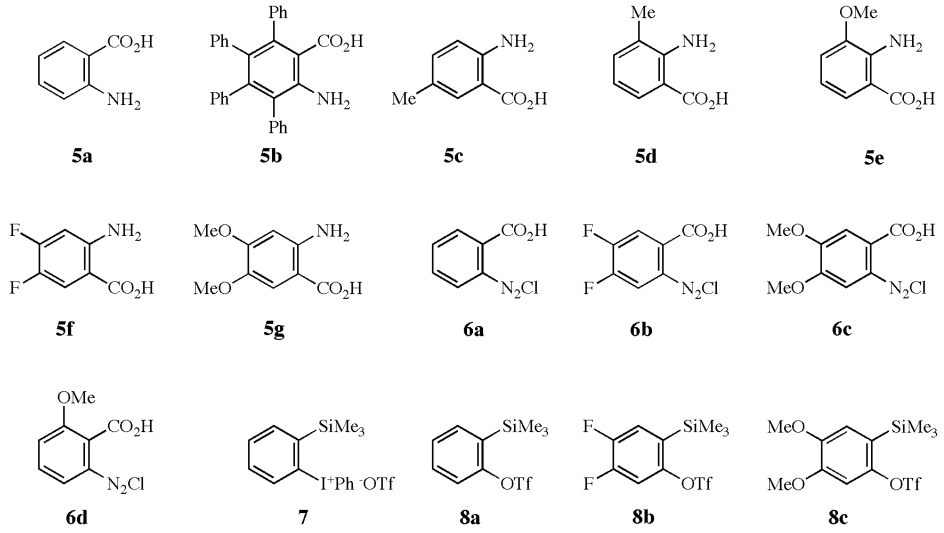


Figure 1 Benzyne Precursors **5-8** Used

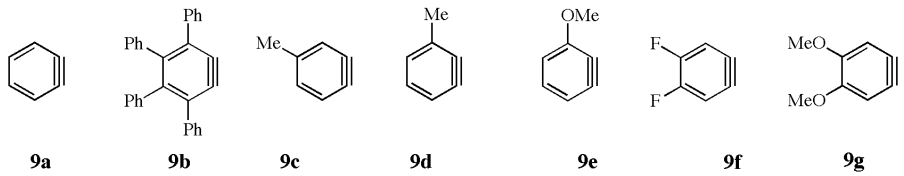
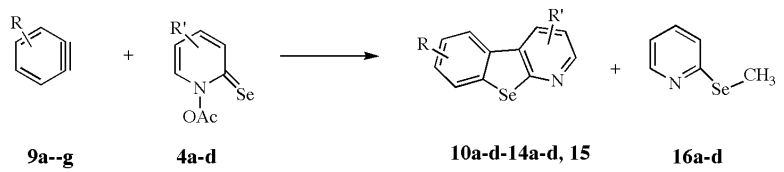


Figure 2 Benzynes **9** Used.

Scheme 2



Reaction of Benzynes **9a-g** with Barton 2-Selenoxo Esters **4a-e**

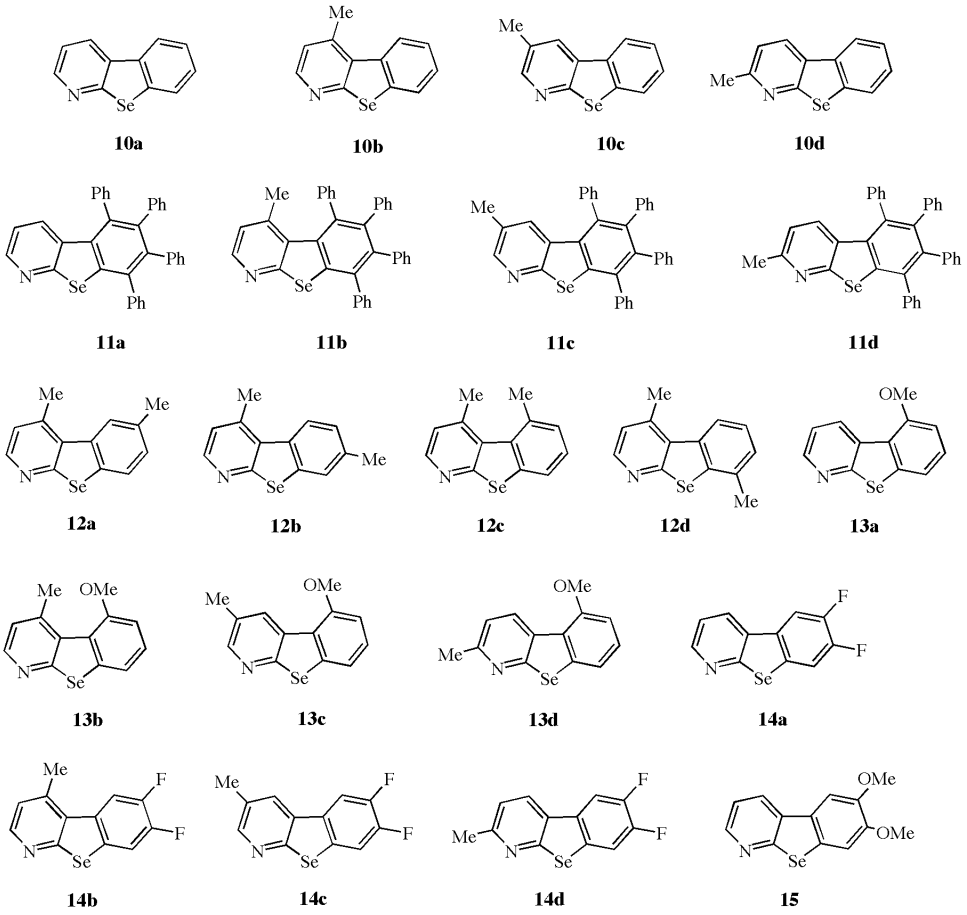


Figure 3. Acetic Acid 2-Selenoxo-2*H*-pyridin-1-yl Esters **10-15**.

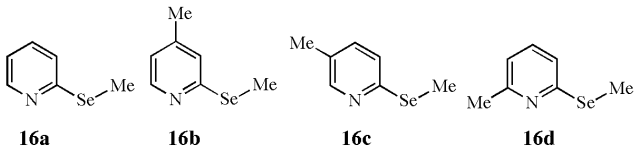


Figure 4. 2-(Methylselenenyl)pyridines **16a-d**.

6a, 7 and **8a** in the presence of 1.1 equivalents of the Barton 2-selenoxo esters **4a-d** (entries 5-8) gave the corresponding benzo[*b*]seleno[2,3-*b*]pyridines **10a-d**. Compounds **10a-d** were obtained in highest yields (51-67%) when benzyne (**9a**) was generated from 2-diazoniobenzenecarboxylate hydrochloride salts **6a** in tetrahydrofuran at 45°. Slightly lower yields of **10a-d** were obtained when **9a** was generated from anthranilic acid (**5a**) and isoamyl nitrite in refluxing dichloromethane (entries 1-4, 41-51%) and from the reaction of **8a** with cesium fluoride (entries 13-16, 43-54%) in acetonitrile. The products **10a-d** were obtained in low yields (20-35%) from the reaction of the Barton 2-selenoxo esters **4a-d** with benzyne (**9a**) generated from (phenyl)-[*o*-(trimethylsilyl)phenyl]iodonium triflate (**7**) with tetrabutylammonium fluoride at room temperature (entries 9-12). On the other hand, the reaction of **7** carried out at room temperature using 5 equivalents of **4a-d** per equivalent of **7** gave **10a-d** in increased yields of 42-49%. Attempts to improve the yield of compounds **10a-d** by performing the reaction of **7** with **4a-d** in refluxing dichloromethane afforded complex mixtures of selenium decomposition products.

The proposed structures of **10a-d** are consistent with their ^{1}H and ^{13}C nmr spectra. The structure of the 4-methyl derivative **14b** was further verified by single crystal X-ray crystallographic analysis.

The reactions of substituted benzynes **9b-9g** with the Barton 2-selenoxo esters **4a-d** were next studied. The benzynes were initially generated by diazotization of the commercially or readily available anthranilic acids **5b-f**. Of these, anthranilic acids **5b-d** formed benzyne (**9a**), 3,4,5,6-tetraphenylbenzyne (**9b**), 4-methyl- (**9c**), and 3-methylbenzyne (**9d**), which reacted with Barton 2-selenoxo esters **4a-d** to give the desired products. For example, the tetraphenyl compounds **11a-d** were formed in yields ranging from 20-29% (entries 19-22). The low yields probably reflect a steric effect of the phenyl groups. The reaction of the unsymmetrical benzynes **9c** and **9d** with 4-methyl Barton 2-selenoxo ester **4b** gave a 1:1 inseparable mixture of

Table 2

Reaction of Benzynes **9a-g** with Barton 2-selenoxo Esters **4a-d**

Entry No.	Benzyne Precursor	Benzyne	Method	Ester **4**	Product **10-15**	Yield, % [e]	Product **16**	Yield, %
1	**5a**	**9a**	A [a]	**a**	**10a**	51	**16a**	20
2	**5a**	**9a**	A	**b**	**10b**	46	**16b**	25
3	**5a**	**9a**	A	**c**	**10c**	45	**16c**	29
4	**5a**	**9a**	A	**d**	**10d**	41	**16d**	28
5	**6a**	**9a**	B [b]	**a**	**10a**	51	**16a**	32
6	**6a**	**9a**	B	**b**	**10b**	62	**16b**	26
7	**6a**	**9a**	B	**c**	**10c**	67	**16c**	35
8	**6a**	**9a**	B	**d**	**10d**	64	**16d**	24
9	**7**	**9a**	C [c]	**a**	**10a**	30 [f] (45)[g]	**16a**	16 [f] (38)[g]
10	**7**	**9a**	C	**b**	**10b**	35 [f] (49)[g]	**16b**	18 [f] (39)[g]
11	**7**	**9a**	C	**c**	**10c**	20 [f] (42)[g]	**16c**	15 [f] (35)[g]
12	**7**	**9a**	C	**d**	**10d**	26 [f] (47)[g]	**16d**	15 [f] (33)[g]
13	**8a**	**9a**	D [d]	**a**	**10a**	54	**16a**	19
14	**8a**	**9a**	D	**b**	**10b**	48	**16b**	20
15	**8a**	**9a**	D	**c**	**10c**	52	**15c**	17
16	**8a**	**9a**	D	**d**	**10d**	43	**16d**	14
17	**5d**	**9f**	C	**a**	**14a**	<2%	**16a**	_
18	**5e**	**9g**	C	**b**	**15**	<2%	**16a**	_
19	**5b**	**9b**	A	**a**	**11a**	29	**16a**	30
20	**5b**	**9b**	A	**b**	**11b**	24	**16b**	33
21	**5b**	**9b**	A	**c**	**11c**	20	**16c**	36
22	**5b**	**9b**	A	**d**	**11d**	22	**16d**	36
23	**5e**	**9c**	A	**b**	**12a,b**	26,26	**16b**	31
24	**5f**	**9d**	A	**b**	**12c,d**	16,32	**16b**	27
25	**6d**	**9e**	B	**a**	**13a**	56	**16a**	29
26	**6d**	**9e**	B	**b**	**13b**	49	**16b**	21
27	**6d**	**9e**	B	**c**	**13c**	64	**16c**	28
28	**6d**	**9e**	B	**d**	**13d**	56	**16d**	22
29	**8b**	**9f**	D	**a**	**14a**	56	**16a**	15
30	**8b**	**9f**	D	**b**	**14b**	49	**16b**	13
31	**8b**	**9f**	D	**c**	**14c**	64	**16c**	16
32	**8b**	**9f**	D	**d**	**14d**	56	**16d**	18

[a] Method A; isoamyl nitrite/dichloromethane/40°; [b] Method B; tetrahydrofuran/45°; [c] Method C; tetrabutylammonium fluoride/dichloromethane/room temperature; [d] Method D; cesium fluoride/ acetonitrile/room temperature; [e] Unless indicated otherwise, 1 equivalent of **1** and 1.1 equivalents of **4** were used; [f] refluxing dichloromethane resulted in decomposition of **1** and **4** as indicated by gcms; [g] one equivalent of **1** and **5** equivalents of **4** were used.

4,6-dimethyl **12a** and 4,7-dimethyl products **12b** (entry 23) and a 1:2 mixture of the 5-methyl- **12c** and 8-methyl derivatives **12d** (entry 24), respectively. The product ratios were obtained by gcms analysis and integration of the methyl signals in ^{1}H nmr spectrum of the reaction mixtures. The lack of selectivity in the ester addition to 4-benzyne **9d** is expected since the 4-methyl group is located at a remote location relative to the "triple bond" where its steric and electronic effects are weak. On the other hand, some degree of regioselectivity was obtained in the reaction of 3-methylbenzyne (**9d**) with **4b** since the weakly electron-releasing 3-methyl group is located at a site adjacent to the "triple bond". A similar products distribution for addition to 3-methylbenzyne has been previously observed [12].

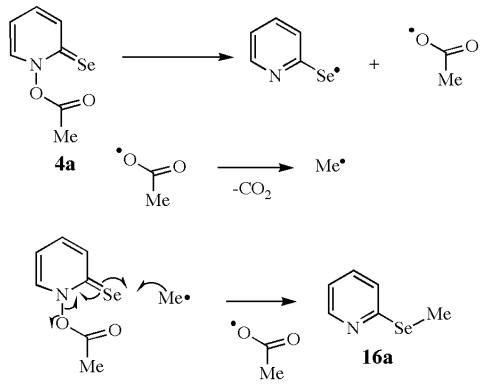
However, the reaction of the 3,4-difluoro- **5f** and 3,4-dimethoxyanthranilic acids **5g** with the Barton 2-selenoxo ester **4a** gave complex reaction mixtures (entries 17 and 18) in which the desired products **14a** and **15** were present in <2% yields as determined by gcms analysis of the reaction mixtures. Similar treatment of 3-methoxyanthranilic acid (**5e**) and Barton 2-selenoxo ester **4a** gave no detectible amount of **13a**. That the benzynes **9e-g** are not readily formed in these reactions could be a consequence of an alternate decomposition mode [10]. In such cases, Wege [10] has shown that this pathway can be avoided by using diazonium carboxylate hydrochloride salts. Subsequently we were able to generate 3-methoxybenzyne (**9e**) from the hydrochloride salt **6d** to which the Barton 2-selenoxo esters **4a-d** added regioselectively to give 7-methoxybenzo[*b*]seleno[2,3-*b*]pyridines **13a-d** in modest yields (entries 29-32, 49-64%). An analytically pure sample of 5-methoxy-2-methylbenzo[*b*]seleno[2,3-*b*]pyridine

(**13d**) could not be obtained. However, the ^{1}H nmr spectrum of **13c** was useful in assigning the position of the 5-methoxy group. For example, the chemical shift of the 4-H singlet in the 5-methoxy-3-methyl derivative **13c** is shifted upfield to δ 7.2 from the 4-H chemical shift in the 3-methyl derivative **10c**. Additionally, the ^{1}H nmr of the 4-methyl derivative **13b** showed that the 4-methyl group resonance occurred at 1.3 ppm, which is upfield by 0.9 ppm from the corresponding signal in **10b**. However, the majority of the spectrum consisted of highly complex multiplets. The methyl upfield shift observed in **13c** is probably due to the electronic shielding provided by the lone pair of electrons on the oxygen atom of the 5-methoxy group.

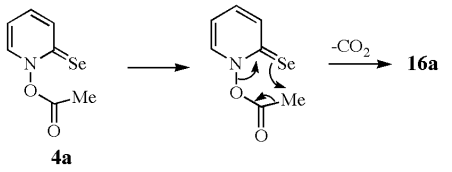
Attempts to extend this method to the synthesis of the dimethoxy **15** and difluoro**14a-d** derivatives by heating the respective benzyne precursors **6c** and **6b** in a variety of refluxing solvents failed. Under these conditions, the esters decomposed rapidly to yield complex mixtures of selenium side products. 2-Trimethylsilylphenyl triflates have recently been shown to generate a wide variety of substituted benzynes including 4,5-difluorobenzyne (**9f**) [11]. We subsequently were able to prepare the difluoro products **14a-d** in 49-64% yields (entries 28-32) by treating the Barton 2-selenoxo esters **4a-d** with 4,5-difluorobenzyne (**9f**), which was generated from the reaction of cesium fluoride and 4,5-difluoro triflate **8b** at room temperature. To date, we have not been able to prepare 4,5-dimethoxy triflate **8c**.

As previously mentioned 2-(methylselanyl)pyridines **16a-d** were obtained as side products in these reactions. There are at least two possible mechanisms for the formation of **16**. Scheme 3 shows a free-radical chain mechanism based on that proposed by Barton [5] for the rearrangement of the sulfur ester to **16**. However, Barton was not able to trap carbon radicals formed in the rearrangement as they were able to do so with radicals derived from the Barton sulfur esters. He thus concluded that the 2-selenoxo esters must be considered either as better "traps" for carbon radicals than the sulfur esters or as undergoing rearrangement *via* a "tight" radical cage. An alternate mechanism for the formation of **16**, which was not considered by Barton, is shown in Scheme 4 that involves a pericyclic rearrangement of the Barton ester **4a** with loss of carbon dioxide.

Scheme 3



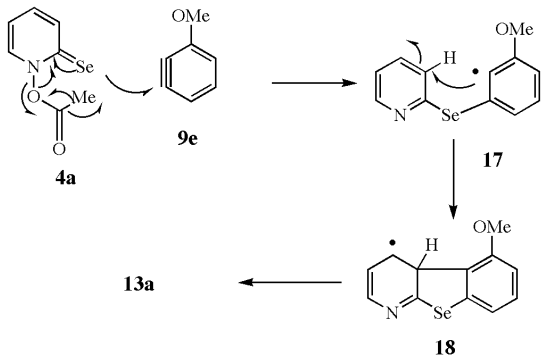
Scheme 4



Pericyclic Rearrangement

We cannot offer evidence to challenge or support either pathway. However, it would be difficult to account for the formation of the benzo[*b*]seleno[2,3-*b*]pyridines **10-14** if selenium free radicals were not involved. For example, attempts to carryout reactions of benzynes **9a-c** with 2-selenone **3a** at room temperature failed. Thus the *N*-acetyloxy group in **4a** appears to be a necessary requirement for the benzyne reaction. A tentative explanation for a possible mechanism of the synthesis of **10-14** is given in Scheme 5 using the observed regioselective addition of the Barton 2≠selenoxo ester **4a** to 3-methoxybenzyne (**9e**). As shown, initial attack by the selenium atom onto **9e** *via* SET gives the radical adduct **17** that then cyclizes to the tricyclic ring **18** which eventually is converted to product **13a**.

Scheme 5



Possible Pathway for the Formation of **13a** From **4a** and **9e**.

The isomer distributions shown in Table 2 are dictated by both steric and electronic factors . One such factor may be the inherent stabilities of the intermediate radicals formed after selenium addition (**17** in Scheme 5). Table 3 lists the relative energies for the isomers in both the $CH_3C_6H_4$• and $CH_3OC_6H_4$• radical systems derived from *ab initio* molecular orbital calculations. The calculations show that the energies of both the anisole and toluene radicals increase in the order, *o*- < *m*- < *p*-, with the greatest energy differences

found in the anisole system. These results are consistent with the data shown in Table 2. The increased stability of the *o*-anisole over its *m*-isomer would favor the formation of compounds **13a-d** in the reaction of **9e** with the Barton esters. Since the methyl group of the anisole ether can be rotated away form the ester, steric factors should not play a significant role in determining the site of selenium attack, and electronic factors should determine the isomer distribution. On the other hand, steric factors seem to play a dominant role in the reactions with toluene radicals. Table 3 shows that there is very little difference between the energies of the *o*- and *m*-radicals (~1.1 kJ/mol) or between the *m*- and *p*-radical (~1.3 kJ/mol). Therefore the equal molar ratio of products **12a** and **12b** in the reaction of the ester **4b** with **9c** is not unexpected. On the other hand, the

Table 3

Relative Energies Calculated for Arene Radicals [a,b]

Radical	ΔE [c]	Radical	ΔE [c]
o-$CH_3OC_6H_4$•	0	*o*-$CH_3C_6H_4$•	0
m-$CH_3OC_6H_4$•	4.6	*m*-$CH_3C_6H_4$•	1.1
p-$CH_3OC_6H_4$•	6.2	*p*-$CH_3C_6H_4$•	2.4

[a] Geometries optimized and energies calculated at the UHF/6-31G** level of theory using the SPARTAN series of programs; [b] SPARTAN version 5.0, © 1997 Wavefunction, Inc.; 18401 Von Karman Ave., #370; Irvine, CA 92715; [c] ΔE (kJ/mol) values are relative to the ortho-radical.

preponderance of **12d** over **12c** can be traced to steric factors. *Ab initio* molecular orbital calculations show that the relative energies of **12a-d**, in kJ/mol, are: 5.4 (**12a**); 3.6 (**12b**); 54.7 (**12c**); and 0.0 (**12d**). The near energy equivalence of **12a** and **12b**, as well as their respective precursor radicals is quite consistent with the results in Table 3. On the other hand, **12c** lay some 54.7 kJ/mol in energy above **12d**, which would favor production of latter compound. In addition, the dihedral angle between the pyridine and benzene rings was calculated to be 27° for **12c**, compared to 0° in the other compounds.

In conclusion, we have shown that Barton 2-selenoxo esters can react with benzynes generated from a variety of commercially or readily available benzyne precursors to give benzo[*b*]seleno[2,3-*b*]pyridines in modest yields. This method is superior to the best non-benzyne method previously reported [4], which requires several steps.

EXPERIMENTAL

General Data.

Melting points were taken on a capillary melting point apparatus, and are uncorrected with respect to stem correction. The ^1H and ^{13}C nmr spectra were recorded on a multi-nuclear nmr spectrometer; chemical shifts were referenced to TMS as internal standard. Elemental analyses were obtained from SMU Analytical Services Laboratories. The anthranilic acids **5a,c,d** and 2-(trimethylsilyl)phenyl triflate (**8a**) were obtained from commercial sources. 5,6,7,8-Tetraphenylanthranilic acid (**5b**) [13], 2-diazoniobenzenecarboxylate hydrochloride salts **6a-d** [7], 4,5-difluoro- (**8b**) and 4,5-dimethoxy-(2-trimethylsilyl)phenyl triflate (**8c**) [11] were prepared by literature procedures. All benzyne reactions were carried out under an atmosphere of dry O_2-free N_2 *via* balloon and under subdued lighting.

Preparation of Acetic Acid 2-Selenoxo-*2H*-pyridin-1-yl Esters **4a-d**.

These compounds were prepared by the Barton method [5]. Physical and spectral data are given below.

Acetic Acid 2-Selenoxo-2*H*-pyridin-1-yl Ester (**4a**).

This compound was obtained as a viscous liquid; ^1H nmr (deuteriochloroform): δ 2.5 (s, 3 H), 6.87 (td, J = 6.9, 1.7 Hz, 1 H), 7.25 (td, J = 8.6, 1.4 Hz, 1 H), 7.77 (dd, J = 6.9, 1.4 Hz, 1 H), 8.08 (dd, J = 8.6, 1.7 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 18.7, 115.4, 132.7, 138.8, 141.7, 165.6, 173.5.

Acetic Acid 4-Methyl-2-selenoxo-2*H*-pyridin-1-yl Ester (**4b**).

This compound was obtained as a viscous liquid; ^1H nmr (deuteriochloroform): δ 2.19 (s, 3 H), 2.47 (s, 3 H), 6.67 (dd, J = 7.0, 2.1 Hz, 1 H), 7.62 (d, J = 7.0 Hz, 1 H), 7.92 (d, J = 2.1 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 18.4, 20.4, 117.5, 137.5, 140.0, 145.6, 165.5, 171.4.

Acetic Acid 5-Methyl-2-selenoxo-2*H*-pyridin-1-yl Ester (**4c**).

This compound was obtained as a viscous liquid; ^1H nmr (deuteriochloroform): δ 2.21 (s, 3 H), 2.49 (s, 3 H), 7.09 (d, J = 8.6 Hz, 1 H), 7.58 (s, 1 H), 7.95 (d, J = 8.6 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 17.3, 18.8, 126.3, 135.6, 136.9, 140.7, 165.7, 170.2.

Acetic Acid 6-Methyl-2-selenoxo-2*H*-pyridin-1-yl Ester (**4d**).

This compound was obtained as a viscous liquid; ^1H nmr (deuteriochloroform): δ 2.42 (s, 3 H), 2.51 (s, 3 H), 6.68 (d, J = 8.2 Hz, 1 H), 7.12 (dd, J = 8.2, 6.1 Hz, 1 H), 7.93 (d, J = 6.1 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 18.2, 18.5, 116.0, 133.2, 138.3, 148.9, 165.1, 172.9.

General Procedure for the Benzyne Reactions.

Using Anthranilic Acids **5a-g** to Generate Benzyne Precursors.

Method A.

A solution containing 1.1 mmol of anthranilic acid **5a-g** dissolved in 5 mL acetone was added dropwise over 45-60 minutes to a refluxing mixture of 1 mmol or 5 mmol of *O*-ester **4a-d** and isoamyl nitrite in dichloromethane. After the resulting solution was refluxed for an additional 3 hours it was cooled to room temperature and the solvent evaporated to give a crude product mixture. The residue was separated on a silica gel column, prepacked in hexane. The desired products were eluted off the column with hexane:ethyl acetate (95:5 v/v).

Using 2-Diazoniobenzenecarboxylate Hydrochlorides **6a-c** as Benzyne Precursors.

Method B.

A stirred mixture containing 0.325 mmol of the diazonium salt **6** and 0.355 mmol of ester **4** in 20 mL of tetrahydrofuran was gradually warmed to 45° and kept there for 3 hours. The mixture

was then cooled to room temperature and the solvent evaporated to give crude product residue. The residue was separated on a silica gel column, prepacked in hexane. The desired products were eluted off the column with hexane:ethyl acetate (95:5 v/v).

Using (Phenyl)[*o*-(trimethylsilyl)phenyl]iodonium Triflate (**7**) as Benzyne Precursor.

Method C.

The reactions were similar to that described using anthranilic acid as benzyne precursor with the following exceptions. To a solution of compound **7** (251 mg, 0.5 mmol) and 5 mL anhydrous dichloromethane was added the Barton 2-selenoxo ester **4a-d** (0.55 mmol or 2.5 mmol in 5 mL) and the resulting solution cooled to 0° under an ice bath. After the dropwise addition of tetrabutylammonium fluoride (0.75 mL of 1.0 *M* solution in tetrahydrofuran) the ice-bath was removed and the reaction mixture was allowed to warm to room temperature where it was stirred for 3 hours. An additional 10 mL of dichloromethane was then added to the reaction mixture and the resulting solution was washed with water (2 X 10 mL), dried (sodium sulfate) and evaporated to give an oily residue. The residue was separated on a silica gel column prepacked in hexane. The desired products were eluted from the column with hexane:ethyl acetate (95:5 v/v).

Using 2-(Trimethylsilyl)phenyl Triflates **8a-c** as Benzyne Precursor.

Method D.

To a mixture of cesium fluoride (0.152 g, 1 mmol) and ester **4a-d** in acetonitrile (10 mL) was added the appropriate benzyne precursor (0.50 mmol) and the resulting mixture was stirred at room temperature for 5 hours. Ethyl acetate (10 mL) was added to the mixture and the resulting solution was washed with water. The reaction mixture dried (sodium sulfate) and evaporated to give an oily residue. The residue was separated on a silica gel column prepacked in hexane. The desired products were eluted off the column with hexane:ethyl acetate (95:5 v/v). The spectral and analytical data for the benzyne products **10-15** are shown below.

Benzo[*b*]seleno[2,3-*b*]pyridine (**10a**).

This compound was obtained as a colorless solid, mp 61-63°; R_f (hexane:ethyl acetate [9:1 v/v]) 0.35; ^{1}H nmr (deuteriochloroform): δ 7.42-7.54 (m, 3 H), 7.96 (dd, J = 7.9, 1.5 Hz, 1 H), 8.14 (dd, J = 7.5, 1.6 Hz, 1 H), 8.35 (dd, J = 8.0, 1.4 Hz, 1 H), 8.63 (dd, J = 4.2, 1.4 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 119.9, 123.1, 125.2, 126.3, 127.7, 129.6, 135.3, 138.8, 148.2, 163.7; ms: m/z 233, (M^+, 100), 153 (40), 126 (10); hrms: [M^+] Calcd. for $C_{11}H_7N^{80}Se$: 232.9744, found: 232.9746.

Anal. Calcd. for $C_{11}H_7NS$: C, 56.91; H, 3.04; N, 6.03. Found: C, 56.99; H, 3.06; N, 6.10.

4-Methylbenzo[*b*]seleno[2,3-*b*]pyridine (**10b**).

This compound was obtained as a colorless solid, mp 160-162° [lit [4a] 158 - 162°]; Rf (hexane:ethyl acetate [9:1 v/v]) 0.28; ^{1}H nmr (deuteriochloroform): δ 2.90 (s, 3 H), 7.18 (d, J = 4.7 Hz, 1 H), 7.44-7.52 (m, 2 H), 7.95 (dd, J = 7.4, 2.2 Hz, 1 H), 8.30 (dd, J = 7.7, 2.2 Hz, 1 H), 8.43 (d, J = 4.7 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 22.4, 122.9, 125.0, 126.3, 126.7, 126.9, 131.5, 136.7, 138.8, 144.2, 147.1, 164.1; ms: m/z 247 (M^+, 100); hrms: [M^+]: Calcd. for $C_{12}H_9N^{80}Se$: 246.9900, found: 246.9995.

3-Methylbenzo[*b*]seleno[2,3-*b*]pyridine (**10c**).

This compound was obtained as a colorless solid, mp 174-176°; R_f (hexane:ethyl acetate [9:1 v/v]) 0.47; ^{1}H nmr (deuteriochloroform): δ 2.51 (s, 3 H), 7.44-7.49 (m, 2 H), 7.90 (dd, J = 7.9, 1.5 Hz, 1 H), 8.09 (dd, J = 7.5, 1.6 Hz, 1 H), 8.13 (d, J = 1.4 Hz, 1 H), 8.45 (d, J = 1.4 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 18.8, 123.4, 125.5, 126.8, 127.9, 129.9, 130.6, 133.1, 135.6, 139.6, 149.6, 160.8; ms: m/z 247 (M^+, 100), 219 (10), 167 (15), 139 (20).

Anal. Calcd. for $C_{12}H_9NSe$: C, 58.55; H, 3.69; N, 5.69. Found : C, 58.52; H, 3.55; N, 5.61.

2-Methylbenzo[*b*]seleno[2,3-*b*]pyridine(**10d**).

This compound was obtained as a colorless solid, mp 78-79° (lit.,[4a] mp 79 - 80°); R_f (hexane:ethyl acetate [9:1 v/v]) 0.40; ^{1}H nmr (deuteriochloroform) δ 2.71 (s, 3 H), 7.25 (d, J = 8.0 Hz, 1 H), 7.42-7.48 (m, 2 H), 7.91 (dd, J = 7.0, 1.2 Hz, 1 H), 8.06 (dd, J = 7.9, 1.1 Hz, 1 H), 8.19 (d, J = 8.0 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 24.5, 119.8, 122.7, 125.1, 126.3, 127.2, 129.9, 130.3, 135.6, 138.4, 157.8, 163.3; ms: m/z 247 (M^+, 100); hrms: Calcd. for $C_{12}H_9N^{80}Se$: 246.9900, found: 246.9901.

5,6,7,8-Tetraphenylbenzo[*b*]seleno[2,3-*b*]pyridine (**11a**).

This compound was obtained as a colorless solid, mp 302-304°; R_f (hexane:ethyl acetate [9:1 v/v]) 0.37; ^{1}H nmr (deuteriochloroform): δ 6.69 (dd, J = 8.3, 1.6 Hz, 1 H), 6.89 - 6.91 (m, 11 H), 7.23 - 7.36 (m, 10 H), 8.42 -8.44 (dd, J = 4.6 Hz, 1.6 Hz,1 H); ^{13}C nmr (deuteriochloroform): δ 119.0, 125.5, 125.7, 126.5, 126.7, 127.2, 127.4, 128.2, 128.5, 129.5, 129.9, 131.1, 131.3, 132.3, 133.4, 134.2, 138.2, 139.0, 139.3 139.4, 139.5, 139.6, 139.6, 139.9, 141.2, 141.5, 147.2; hrms: [M^+] Calcd. for $C_{35}H_{23}N^{80}Se$: 537.0096, found: 537.1006.

Anal. Calcd for $C_{35}H_{23}N^{80}Se$: C, 73.35; H, 4.32; N, 2.61. Found: C, 73.47; H, 4.30; N, 2.69.

4-Methyl-5,6,7,8-tetraphenylbenzo[*b*]seleno[2,3-*b*]pyridine (**11b**).

This compound was obtained as a colorless solid, mp 265–267°; R_f ([hexane:ethyl acetate (9:1 v/v]) 0.40; ^{1}H nmr (deuteriochloroform): δ 1.43 (s, 3 H), 6.75-7.32 (m, 21 H), 8.39 (d, J = 4.3 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 22.8, 122.3, 125.4, 125.6, 126.4, 126.5, 126.7, 126.9, 127.4, 127.6, 128.2, 129.8, 130.9, 130.9, 131.4, 131.5, 131.7, 131.7, 133.8, 134.1, 137.1, 139.1, 139.6, 139.7, 139.7, 140.0, 141.5, 141.7, 146.0, 146.6; hrms: [M^+] Calcd. for $C_{36}H_{25}N^{80}Se$ 551.1152, found: 551.1160.

Anal. Calcd. for $C_{36}H_{25}N^{80}Se$: C, 78.54; H, 4.58; N, 2.54. Found: C, 78.44; H, 4.66; N, 2.51.

3-Methyl-5,6,7,8-tetraphenylbenzo[*b*]seleno[2,3-*b*]pyridine (**11c**).

This compound was obtained as a colorless solid, mp 280-282°; R_f (hexane: ethyl acetate [9:1 v/v]) 0.31; ^{1}H nmr (deuteriochloroform): δ 2.36 (s, 3 H), 6.38 (d, J = 1.3 Hz, 1 H), 6.86-6.89 (m, 10 H), 7.21 - 7.36 (m, 10 H), 8.26 (d, J = 1.3 Hz, 1 H); hrms: [M^+] Calcd. for $C_{36}H_{25}N^{80}Se$: 551.1152, found: 551.1148.

Anal. Calcd. for $C_{36}H_{25}N^{80}Se$: C, 78.54; H, 4.58; N, 2.54. Found: C, 78.57; H, 4.56; N, 2.48.

2-Methyl-5,6,7,8-tetraphenylbenzo[*b*]seleno[2,3-*b*]pyridine (**11d**).

This compound was obtained as a colorless solid, mp 295-298°; R_f (hexane:ethyl acetate [9:1 v/v]) 0.28; ^{1}H nmr (deuterio-

chloroform): δ 2.55 (s, 3 H), 6.56 (d, J = 7.9 Hz, 1 H), 6.78 (d, J = 7.9 Hz, 1 H), 6.87-6.89 (m, 11 H), 7.22 - 7.34(m, 9 H); ^{13}C nmr (deuteriochloroform): δ 24.5, 119.5, 128.8, 126.0, 126.9, 127.1, 127.3, 127.5, 127.7, 127.9, 128.6, 128.8, 130.0, 130.2, 130.47, 130.6, 131.6, 137.6, 131.7, 131.9, 133.0, 134.0, 138.6, 138.9, 139.3, 139.9, 140.0, 140.1, 140.2, 141.2, 142.0, 157.0, 164.8; hrms: [M$^+$] Calcd. for $C_{36}H_{25}N^{80}Se$: 551.1152, found: 551.1155.

Anal. Calcd. for $C_{36}H_{25}N^{80}Se$: C, 78.54; H, 4.58; N, 2.54. Found: C, 78.40; H, 4.68; N, 2.55.

5-Methoxybenzo[*b*]seleno[2,3-*b*]pyridine (**13a**).

This compound was obtained as a viscous liquid; ^{1}H nmr (deuteriochloroform): δ 3.82 (s, 3 H), 6.95 (m, 1 H), 7.05 (dd, J = 6.4, 1.2 Hz, 1 H), 7.30 (dd, J = 7.2, 2.0 Hz, 1 H), 7.33 (t, J = 5.7 Hz, 1 H). 7.44 (m, 1 H). 8.46 (d, J = 4.5 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 55.7, 115.3, 120.8, 121.5, 124.8, 128.6, 129.0, 130.8, 137.0, 150.3, 159.1, 160.5; lcms: m/z 266 (M$^+$, 100), 264 (52), 263 (30), 246 (10), 242 (15).

Anal. Calcd. for $C_{12}H_9NO^{80}Se$: C, 54.98; H, 3.46; N, 5.34. Found: C, 54.95; H, 3.44; N, 5.32.

5-Methoxy-4-methylbenzo[*b*]seleno[2,3-*b*]pyridine(**13b**).

This compound was obtained as a viscous liquid; ^{1}H nmr (deuteriochloroform): δ 1. 27 (s, 3 H), 3.83 (s, 3 H), 6.87 (m, 1 H), 6.96 (dd, J = 6.4, 1.2 Hz, 1 H), 7.33 (m, 2 H). 8.32 (d, J = 4.5 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 21.3, 55.7, 115.2, 121.3, 122.3, 125.7, 128.5, 129.2. 130.7, 148.5, 149.9, 158.4, 160.5; lcms: m/z 280 (M$^+$,100), 278 (70), 276 (25), 264 (10).

Anal. Calcd. for $C_{13}H_{11}NO^{80}Se$: C, 56.53; H, 4.01; N, 5.07. Found: C, 56.51; H, 3.98; N, 5.02.

5-Methoxy-3-methylbenzo[*b*]seleno[2,3-*b*]pyridine (**13c**).

This compound was obtained as a liquid; ^{1}H nmr (deuteriochloroform): δ 2. 27 (s, 3 H), 3.81 (s, 3 H), 6.91 (d, J = 7.3 Hz 1 H), 7.03 (dd, J = 7.3, 2.1 Hz, 1 H), 7.25-7.29 (m, 2 H), 8.32 (d, J = 1.1 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 18.2, 55.7, 115.0, 121.0, 125.1, 128.1, 129.7, 130.7, 137.9, 150.7, 154.7, 160.5; lcms: m/z 280 (M$^+$, 100) 278 (60), 276 (30), 254 (15).

Anal. Calcd. for $C_{13}H_{11}NO^{80}Se$: C, 56.53; H, 4.01; N, 5.07. Found: C, 56.50; H, 3.96; N, 5.01

5-Methoxy-2-methylbenzo[*b*]seleno[2,3-*b*]pyridine (**13d**).

This compound was obtained as a liquid; ^{1}H nmr (deuteriochloroform) : δ 2. 54 (s, 3 H), 3.82 (s, 3 H), 6.81-6.97 (m, 2 H), 7.29 - 7.32 (m, 3 H), ^{13}C nmr (deuteriochloroform): δ 30.7, 55.7, 114.88, 115.3, 120.4, 121.7, 128.6, 129.3, 130.8, 137.2, 158.4, 159.3 160.5; lcms: m/z 280(M$^+$, 100), 276 (40), 263 (15). A pure compound could not be obtained for elemental analysis.

6,7-Difluorobenzo[*b*]seleno[2,3-*b*]pyridine (**14a**).

This compound was obtained as a colorless solid, mp 184°: R_f (hexane:ethyl acetate [9:1 v/v]) 0.34; ^{1}H nmr (deuteriochloroform): δ 7.43 (dd, J = 7.9, 4.7 Hz, 1 H), 7.71 (dd, J = 9.4, 7.3 Hz, 1 H), 7.88 (dd, J = 9.4, 7.3 Hz, 1 H), 8.21 (dd, J = 7.9, 1.6 Hz, 1 H), 8.61 (dd, J = 4.7, 1.6 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 111.2 (d, J = 19.5 Hz), 114.5, (d, J = 20.1Hz), 120.1, 129.8, 133.1 (dd, J = 7.2, 2.8Hz) 134.5 (dd, J = 6.9, 3.0 Hz), 148.4, 149.0 (dd, J = 247.4, 14.6 Hz), 150.0 (dd, J = 245.2, 14.6 Hz), 164.1; hrms: [M$^+$] Calcd. for $C_{11}H_5F_2N^{80}Se$: 268.9550, found: 268.9555.

*Ana*l. Calcd. for $C_{11}H_5F_2N^{80}Se$: C, 49.28; H, 1.88; N, 5.22. Found: C, 49.32; H, 1.93; N, 5.26.

6,7-Difluoro-4-methylbenzo[*b*]seleno[2,3-*b*]pyridine (**14b**).

This compound was obtained as a colorless solid, mp 170°; R_f (hexane:ethyl acetate [9:1 v/v]) 0.27; ^{1}H nmr (deuteriochloroform): δ 2.87 (s, 3 H), 7.24 (d, 4.8 Hz, 1 H), 7.73 (dd, J = 9.3, 7.6 Hz, 1 H), 8.12 (dd, J = 11.9, 7.4 Hz, 1 H), 8.46 (d, J = 4.8 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 21. 9, 114.1 (d, J = 19.7 Hz), 114.8 (d, J = 20.0 Hz), 123.1, 130.5, 132.7 (dd, J = 7.0, 3.1 Hz), 133.7 (dd, J = 6.8, 2.7 Hz), 143.9, 147.3, 148.8 (dd, J = 243.2, 13.4 Hz), 149.3 (dd, J = 251.1, 14.3 Hz), 164.4; hrms: [M$^+$] Calcd. for $C_{12}H_7F_2N^{80}Se$: 282.9712, found: 282.9712.

Anal. Calcd. for $C_{12}H_7F_2N^{80}Se$: C, 51.08; H, 2.50; N, 4.96. Found: C 51.15; H, 2.75; N, 5.10.

6,7-Difluoro-3-methylbenzo[*b*]seleno[2,3-*b*]pyridine (**14c**).

This compound was obtained as a colorless solid, mp 192–193^0: R_f (hexane:ethyl acetate [9:1 v/v]) 0.30; ^{1}H nmr (deuteriochloroform): δ 2.50 (s, 3 H), 7.66 (dd, J = 9.2, 7.5 Hz, 1 H), 7.82 (dd, J = 10.4, 7.4 Hz, 1 H), 7.98 (s, 1 H), 8.44 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 18. 3, 111.1 (d, J = 18.7 Hz), 114. 5 (d, J = 20.2 Hz), 129.8, 130.2, 131.5 (dd, J = 6.4, 3.3 Hz), 133.7 (dd, J = 6.8, 2.8 Hz), 149.6 (dd, J = 245.3, 14.1 Hz), 150.9, (dd, J = 250.9, 14.4 Hz), 160.7; hrms: [M+] Calcd. for.$C_{12}H_7F_2N^{80}Se$: 282.9712, found: 282.9711.

Anal. Calcd. for $C_{12}H_7F_2NSe$: C, 51.08; H, 2.50; N, 4.96. Found: C, 51.13; H, 2.61; N, 5.01

6,7-Difluoro-2-methylbenzo[*b*]seleno[2,3-*b*]pyridine (**14d**).

This compound was obtained as a colorless solid, mp 125-127°: R_f (hexane:ethyl acetate [9:1 v/v]) 0.39; ^{1}H nmr (deuteriochloroform): δ 2.71 (s, 3 H), 7.28 (d, J = 7.9 Hz, 1 H), 7.68 (dd, J = 9.4, 7.3, 1 H), 8.30 (dd, J =10.3, 7.3 Hz, 1 H), 8.08 (d, J = 7.9 Hz, 1 H); hrms [M$^+$] Calcd. for $C_{12}H_7F_2N^{80}Se$: 282.9712, found: 282.9711.

Anal. Calcd. for $C_{12}H_7F_2N^{80}Se$: C, 51.08; H, 2.50; N, 4.96. Found: C, 51.04; H, 2.55; N, 5.03.

2-(Methylselenenyl)pyridine (**16a**).

This compound was obtained a pale yellow oil; R_f (hexane:ethyl acetate [9:1 v/v]) 0.63; ^{1}H nmr (deuteriochloroform): δ 2.09 (s, 3 H), 6.84 (dd, J = 8.1, 4.1 Hz, 1 H), 7.12 (dd, J = 7.8, 2.1 Hz, 1 H), 7.54 (dd, J = 8.1, 7.8 Hz, 1 H), 8.46 (dd, J = 4.1, 1.8 Hz, 1 H); ms: m/z 173 (M$^+$, 30), 93 (100), 78 (30), 51(20).

4-Methyl-2-(methylselenenyl)pyridine (**16b**).

This compound was obtained as a pale yellow oil; R_f (hexane:ethyl acetate [9:1 v/v]) 0.66; ^{1}H nmr (deuteriochloroform): δ 2.19 (s, 3 H), 2.47 (s, 3 H), 6.82 (dd, J = 4.9, 1.6 Hz, 1 H), 7.15 (d, J = 1.6 Hz, 1 H), 8.33 (d, J = 4.9 Hz, 1 H); ms: m/z 187 (M$^+$, 40), 107 (100), 93 (40), 65 (30).

Anal. Calcd. for $C_7H_9N^{80}Se$: C, 45.17; H, 4.87; N, 7.53. Found: C, 45.27; H, 4.92; N, 7.50.

5-Methyl-2-(methylselenenyl)pyridine (**16c**).

This compound was isolated as a pale yellow oil; R_f (hexane:ethyl acetate [9:1 v/v] 0.65; ^{1}H nmr (deuteriochloroform): δ 2.28 (s, 3 H), 2.46 (s, 3 H), 7.22 (d, J = 8.1 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 1 H), 8.32 (s, 1 H); ^{13C} nmr (deuteriochloroform): δ 5.62, 17.84, 124.13, 129.53, 136.81, 150.34, 152.04; ms: m/z 187 (M$^+$, 30), 107 (100), 93 (25).

Anal. Calcd. for $C_7H_9N^{80}Se$: C, 45.17; H, 4.87; N, 7.53. Found: C, 45.10; H, 4.80; N, 7.58.

6-Methyl-2-(methylselenenyl)pyridine (**16d**).

This compound was obtained as a pale yellow oil; R_f (hexane:ethyl acetate [9:1 v/v]) 0.63; ^{1}H nmr (deuteriochloroform): δ 2.46 (s, 3 H), 2.53 (s, 3 H), 6.89 (dd, J = 7.5, 1.7 Hz, 1 H), 7.11 (dd, J = 7.8, 1.7 Hz, 1 H), 7.36 (dd, J = 7.8, 7.5 Hz, 1 H); ^{13}C nmr (deuteriochloroform): δ 5.45, 13.99, 119.29, 121.05, 135.99, 154.95, 158.74; ms: m/z 187 (M^+, 100), 107 (40), 92 (50).

Anal. Calcd. for $C_7H_9N^{80}Se$: C, 45.17; H, 4.87; N, 7.53. Found: C, 45.33; H, 4.90; N, 7.45.

X-ray Analysis of Compound **14c**.

Crystal data are as follows. $C_{12}H_7F_2NSe$, formula weight 282.15, triclinic, space group a P?1, a = 8.371(2), b = 11.217(3), c = 11.820(3) Å, α = 94.18(2), β = 96.35(2), γ= 109.42(2)^o, v = 1033.2(5) Å^3, z = 4, d = 1.814 g/cm, μ = 3.630 mm^{-1}. Data were collected on a Bruker-AXS P4 diffractometer, MoKα, 2θ 3.5 − 50.0°. Data were corrected for Lorentz and polarization effects, as well as for absorption. The structure was solved by direct-methods and refined with SHELX97 [14]. There are two independent molecules in an asymmetric unit. H atoms are located in calculated positions. The final refinement converged at R_1 = 0.065, wR_2 (all data) = 0.183.

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