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# Facile Method for Conversion of 2-(Chloroseleno)benzoyl Chloride into 2-Substituted 3-Hydroxybenzo[b]selenophenes

Rafał Lisiak [a] & Jacek Młochowski [a]
[a] Department of Organic Chemistry, Faculty of Chemistry, Wrocław University of Technology, Wrocław, Poland
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# Facile Method for Conversion of 2-(Chloroseleno)benzoyl Chloride into 2-Substituted 3-Hydroxybenzo[*b*]selenophenes

**Rafał Lisiak and Jacek Młochowski**
Department of Organic Chemistry, Faculty of Chemistry, Wrocław University of Technology, Wrocław, Poland

**Abstract:** The easily accessible 2-(chloroseleno)benzoyl chloride has broad application in the synthesis of benzizoselenazol-3(2*H*)-ones and benzo[*b*]selenophen-3(2*H*)-ones. Treatment of 2-acylbenzo[*b*]selenophen-3(2*H*)-ones with nitrogen nucleophiles such as hydrazines and hydroxylamine resulted in formation of 2-substituted 3-hydroxybenzo[*b*]selenophenes in 72–98% yield.

**Keywords:** Benzo[*b*]selenophenes, 2-(chloroseleno)benzoyl chloride, hydrazines, selenaheterocycles

During the past decade, a growing interest in the methodology of the synthesis of selenaheterocycles has been observed.[1] Some of them (particularly those having a selenenamide moiety) play an important role in medicinal biology as biological response modifiers, gluthathione peroxidase mimetics, and promising anti-inflammatory agents.[2] On the other hand, they can be used as oxygen-transfer catalysts for hydroperoxide oxidation of various organic functional groups.[1–4] We focus our attention on the selenophenes and their benzologs (e.g., benzoselenophenes) because of their growing importance in material engineering as stable organic semiconductors for high-performance, field-effect transistors.[3,5,6] Although the benzo[*b*]selenophene moiety so far has not been

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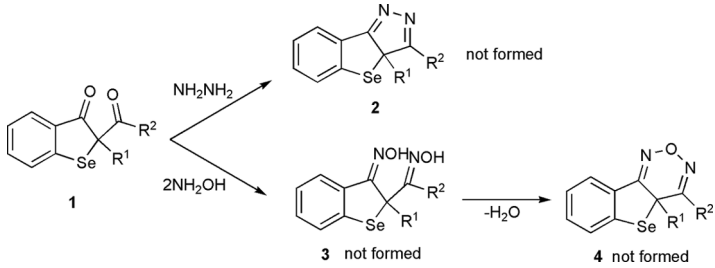
Address correspondence to Rafał Lisiak, Department of Organic Chemistry, Faculty of Chemistry, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. E-mail: rafal.lisiak@pwr.wroc.pl

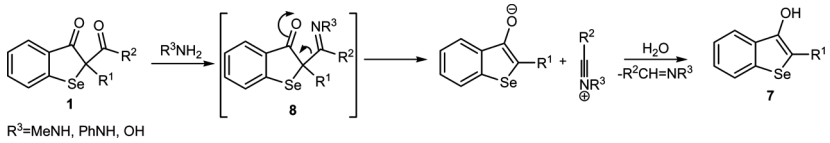
detected in natural products, they are considered bioisosteric with benzene, thiophene, and pyrrole [e.g., 2-amino-3-(benzo[*b*]selenophen-3-yl)propionic acid of the analog of the proteinogenic amino acid tryptophan].[7] The biological activity of benzo[*b*]selenophenes and their synthetic applications have been presented in literature.[8] In comparison with other selenaheterocycles, the works devoted to the synthesis of benzo[*b*]selenophenes are limited to a few published papers.[9] The oldest reported methods involved higher temperatures and gaseous reagents such as acetylene, action of potassium hexacyanoferrate(III), on *o*-selenocinnamic acids, or reaction of selenium dioxide with styrene in the presence of chromic oxide on aluminium oxide.[10] The yields of benzo[*b*]selenophenes were usually poor. Reaction of selenophenols with bromoacetaldehyde dimethyl acetal and oxidative cyclization of the formed selenides with phosphorous pentoxide could lead to benzo[*b*]selenophenes substituted in only the benzene ring.[11] As reagents for preparation of benzo[*b*]selenophenes with more than 50% yield, the α,β-unsaturated aldehydes can be used in thermal gas-phase reaction with diorganyl diselenides.[10] 2,3-Disubstituted benzo[*b*]selenophenes have been obtained by cyclization of 1-(1-alkynyl)-2-(methylseleno)arenes by treatment with electrophiles such as bromine, N-bromosuccinimide (NBS), and benzeneselenenyl chloride.[12]

First, we focused our attention on the synthesis of a new class of selenium-containing heterocycles **2** and **4** based on the 2,3-dihydrobenzo[*b*]selenophene system. For this purpose, we needed the substrates bearing the 1,3-diketone moiety, which would give the pyrazole ring on treatment with hydrazines. In a previous paper, we reported the reactions of 2-(chloroseleno)benzoyl chloride **5** with C-H acids **6** having an activated methylene group with two hydrogen atoms leading to benzo[*b*]selenophen-3(2*H*)-ones formation.[13,14] We expected that 2,2-disubstituted benzo[*b*]selenophen-3(2*H*)-ones **1** with acyl groups as one of substituents present in the α-position would behave typically as 1,3-diketones and should form products with three condensed rings, **2**, when treated with hydrazines. Neither expected tricyclic products **2**,**4** nor dioxime of 1,3-diketone **3** (when hydroxylamine was a reagent) have been isolated from the reaction mixture (Scheme 1).

On the other hand, spontaneous deacylation was observed earlier for some of 2,2-diacyl benzo[*b*]selenophen-3(2*H*)-ones, especially in case of acetylacetone derivatives, which could be explained by their hydrolyses during isolation.[13] In other cases, the 2,2-disubstituted benzo[*b*]selenophen-3(2*H*)-ones **1** remained stable. In the present study, we found that deacylation of 2,2-disubstituted benzo[*b*]selenophen-3(2*H*)-ones **1** occured readily during treatment with hydrazines, regardless of the kind of substituent, $R^1$ and $R^2$. We suggest the unstable hydrazone **8** is an



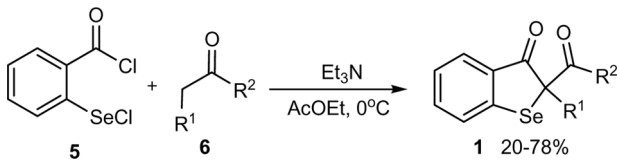

***Scheme 1.*** The expected products of reaction **1** with hydrazine or hydroxylamine.




***Scheme 2.*** A plausible mechanism of 2-substituted 3-hydroxybenzo[*b*]selenophenes formation.

intermediate formed in the first stage of the reaction. The 2-substituted 3-hydroxybenzo[*b*]selenophenes **7** and corresponding hydrazones and oximes were the only products (Scheme 2). The described protocols are very useful for synthesis of the 2-substituted 3-hydroxybenzo[*b*] selenophenes because the method is simple, more efficient, and general in comparison with those reported earlier.

The results of the reaction of 2-(chloroseleno)benzoyl chloride **5** with C-H acids **6** [i.e., benzoylacetonitrile, α-nitroacetophenone, ethyl benzoylacetate, dibenzoylmethane, 1-phenyl-1,3-butanedione, 2,4-pentanedione, diethyl (2-oxo-2-phenylethyl)phosphonate, and diethyl (2-oxopropyl)-phosphonate] to give 2,2-disubstituted benzo[*b*]selenophen-3(2*H*)-ones **1** (Scheme 3) are presented in Table 1. The cyclization was carried out with a 1:1 molar ration of **5** and **6**; triethylamine was used in excess. Yields of **1a** and **1d** were satisfactory and comparable with Ref.[13] The poor yield




***Scheme 3.*** Synthesis of benzo[*b*]selenophen-3(2*H*)-ones.

**Table 1.** 2,2-Disubstituted benzo[*b*]selenophen-3(2*H*)-ones **1**

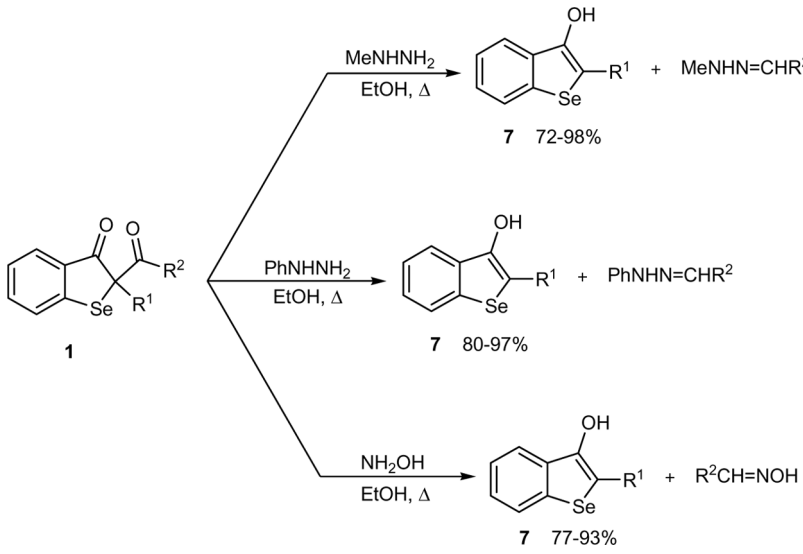
| **1**[a] | $R^1$ | $R^2$ | Yield (%) |
|---|---|---|---|
| **a** | CN | Ph | 70 |
| **b** | COOEt | Ph | 75 |
| **c** | COPh | Ph | 78 |
| **d** | COMe | Ph | 49 |
| **e** | $NO_2$ | Ph | 72 |
| **f** | $PO_3Et_2$ | Ph | 70 |
| **g** | $PO_3Et_2$ | Me | 68 |
| **h** | COMe | Me | 20 |

[a]Some benzo[*b*]selenophen-3(2*H*)-ones **1** have been reported earlier: **1a**,[13] **1d**,[14] and **1h**.[13]



of compounds **1h** is due to formation of macromolecular by-products, which were difficult to characterize. The phosphonates **1f–g**, nitro **1e**, and dibenzoyl **1c** derivatives have not been reported thus far.

To prepare the 3-hydroxybenzo[*b*]selenophene **7**, the mixture of **1** with phenyl- or methylhydrazine (or hydroxylamine hydrochloride with the presence of triethylamine) was heated under reflux in ethanol for 3 h. All used substrates were easily converted into benzo[*b*]selenophenes **7**, and yields did not depend on the *N*-nucleophile used (Scheme 4, Table 2).




***Scheme 4.*** Synthesis of 3-hydroxybenzo[*b*]selenophenes.

**Table 2.** 3-Hydroxybenzo[*b*]selenophenes **7**

| Benzo[*b*] selenophenone **1** | Benzo[*b*] selenophene[a] **7** | $R^1$ | Yield[b] (%) of **7** | Yield[c] (%) of **7** | Yield[d] (%) of **7** |
|---|---|---|---|---|---|
| **a** | **a** | CN | 76 | 81 | 77 |
| **b** | **b** | COOEt | 85 | 83 | 79 |
| **c** | **c** | COPh | 87 | 86 | 78 |
| **d** | **d** | COMe | 72 | 80 | 77 |
| **e** | **e** | $NO_2$ | 79 | 84 | 80 |
| **f** | **f** | $PO_3Et_2$ | 94 | 90 | 91 |
| **g** | **f** | $PO_3Et_2$ | 98 | 96 | 89 |
| **h** | **d** | COMe | 98 | 97 | 93 |

[a]Some benzo[*b*]selenophenes **7** have been reported earlier: **7b**[13] (yield 59%), **7c**[13] (yield 28%), and **7d**[13,14] (yield 58%).
[b]Yields of **7** with $MeNHNH_2$ as reagent.
[c]Yields of **7** with $PhNHNH_2$ as reagent.
[d]Yields of **7** with $NH_2OH$ as reagent.

When position 2 in benzo[*b*]selenophen-3(2*H*)-one was occupied by two different acyl groups (e.g., benzoyl and acetyl, **1d**), only one product of the reaction more resistant to elimination of substituent (**7d**, $R^1 = COMe$) in the 2-position was observed. The easier leaving group (COPh) was eliminated in the form of hydrazone (or oxime).

3-Hydroxybenzo[*b*]selenophene **7f** was hydrolyzed to phosphonic acid **7g**. For this purpose, the solution of **7f** in dry dichloromethane was treated with an excess of trimethylbromosilane (Scheme 5). As a result, we obtained 3-hydroxybenzo[*b*]selenophen-2-ylphosphonic acid **7g**, which was stable in organic solvents but in the presence of water slowly decomposed to elementary selenium.

The carbonyl groups of selenophen-3(2*H*)-one ring of **1** shows a strong absorption band above 1715 $cm^{-1}$ in the IR spectra characteristic for ring strain cycloalkanones. Acyl groups at position 2 absorb below 1700 $cm^{-1}$. In the IR spectra of compounds **7**, broad bands of the hydroxyl group are localized at 3142–3479 $cm^{-1}$, which suggests the intramolecular hydrogen bond stabilizing the enol form.


**7f** **7g** 78%

***Scheme 5.*** Synthesis of 3-hydroxybenzo[*b*]selenophen-2-ylphosphonic acid.

In the $^{77}$Se NMR spectra of **7**, the chemical shift of selenium nuclei depends on the character of the substituent present in the position 2. The resonance signal of cyano derivative **7a** is observed at $\delta = 487$ ppm, whereas the chemical shift of acetyl derivative **7d** is $\delta = 406$ ppm. In all phosphonate derivatives (**1f–g**, **7f–g**), the resonance signal of $^{77}$Se nuclei appears as a doublet ($J = 20$–$50$ Hz) because of the coupling of selenium and phosphorous nuclei.

## EXPERIMENTAL

### General Methods

The reaction products were identified by their melting points (Digital Melting Points Apparatus Electrothermal IA 911000), by analysis of their $^{1}$H and $^{31}$P NMR data [(δ, ppm, $CDCl_3$ or dimethylsulfoxide (DMSO)-$d_6$, tetramethylsilane (TMS), $H_3PO_4$, Bruker DRX 300-MHz spectrometer)], $^{77}$Se NMR data (δ, ppm, $CDCl_3$ or DMSO-$d_6$, $Me_2Se$ as external $^{77}$Se standard, Bruker Avance 600-MHz spectrometer), and by analysis of IR spectra (Perkin-Elmer 2000FT spectrometer). Substrates, solvents, thin-layer chromatography (TLC) plates, and silica gel for column chromatography (70–230 mesh) were purchased from Aldrich and Fluka.

2-(Chloroseleno)benzoyl chloride **5** was prepared from anthranilic acid according to the known procedure.[15,16]

### Synthesis of 2,2-Disubstituted Benzo[*b*]selenazol-3(2*H*)-ones (1)

A solution of compound **2** (1 mmol) and triethylamine (2.8 mmol) in dry ethyl acetate (30 ml) was cooled in an ice bath while 2-(chloroseleno)benzoyl chloride **5** (0.25 g, 1 mmol) dissolved in dry ethyl acetate (20 ml) was added dropwise. After the addition was completed, the mixture was allowed to reach room temperature. Stirring was continued for an additional 24 h, and the precipitate was filtered. The filtrate was concentrated, and the product was isolated from the residue by crystallization from ethanol (for **1a–e**) or column chromatography on silica gel using dichloromethane–hexane 1:1 (for **1h**) or ethyl acetate (for **1f–g**) as eluent.

### Data

2-Benzoyl-3-oxo-2,3-dihydrobenzo[*b*]selenophene-2-carbonitrile (**1a**)

Colorless crystals, yield 0.22 g (70%), mp 138–139°C (140–142°C[13]).

Ethyl 2-Benzoyl-3-oxo-2,3-dihydrobenzo[*b*]selenophene-2-carboxylate (**1b**)

Yellow needles, yield 0.28 g (75%), mp 110–112°C; $^1$H NMR (300 MHz, $CDCl_3$): δ, 1.17 (t, 3H, $J = 7.12$ Hz, $CH_3$), 4.29 (q, 2H, $J = 7.10$ Hz, $CH_2$), 7.36 (t, 1H, $J = 7.44$ Hz, ArH), 7.42–7.50 (m, 3H, ArH), 7.55–7.62 (m, 2H, ArH), 7.85 (dt, 3H, $J = 8.69$ Hz and $J = 1.12$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 469; IR (KBr): 3063, 2981, 1736, 1699, 1675, 1671, 1233, 766 cm$^{-1}$. Anal. calcd. for $C_{18}H_{14}O_4Se$ (373.26): C, 57.92; H, 3.78. Found: C, 57.90; H, 3.73.

2,2-Dibenzoylbenzo[*b*]selenophen-3(2*H*)-one (**1c**)

Yellow crystals, yield 0.32 g (78%), mp 143–145°C; $^1$H NMR (300 MHz, $CDCl_3$): δ, 7.34–7.43 (m, 5H, ArH), 7.47–7.53 (m, 3H, ArH), 7.63 (dt, 1H, $J = 8.05$ Hz and $J = 7.91$ Hz and $J = 1.32$ Hz, ArH), 7.81–7.84 (m, 4H, ArH), 7.91–7.94 (m, 1H, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 471; IR (KBr): 3069, 3027, 1715, 1661, 1444, 1224, 687 cm$^{-1}$. Anal. calcd. for $C_{22}H_{14}O_3Se$ (405.30): C, 65.19; H, 3.48. Found: C, 65.13, H, 3.49.

2-Acetyl-2-benzoylbenzo[*b*]selenophen-3(2*H*)-one (**1d**)

Orange needles, yield 0.17 g (49%), mp 158–162°C (oil[13]).

2-Benzoyl-2-nitrobenzo[*b*]selenophen-3(2*H*)-one (**1e**)

Yellow prisms, yield 0.25 g (72%), mp 174–176°C; $^1$H NMR (300 MHz, $CDCl_3$): δ, 7.41 (dt, 1H, $J = 7.52$ Hz and $J = 0.97$ Hz, ArH), 7.55 (t, 3H, $J = 8.03$ Hz, ArH), 6.65–7.71 (m, 2H, ArH), 7.94 (dd, 1H, $J = 7.69$ Hz and $J = 1.35$ Hz, ArH), 8.13 (dd, 2H, $J = 8.40$ Hz and $J = 1.29$ Hz, ArH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 409; IR (KBr): 3068, 1758, 1697, 1236, 1008, 697 cm$^{-1}$. Anal. calcd. for $C_{15}H_9NO_4Se$ (346.20): C, 52.04; H, 2.62; N, 4.05. Found: C, 51.94; H, 2.56; N, 4,00.

Diethyl 2-Benzoyl-3-oxo-2,3-dihydrobenzo[*b*]selenophen-2-ylphosphonate (**1f**)

Colorless crystals, yield 0.30 g (70%), mp 75–80°C; $^1$H NMR (300 MHz, $CDCl_3$): δ, 0.99 (t, 3H, $J = 7.07$ Hz, $CH_3$), 1.24 (t, 3H, $J = 7.08$ Hz, $CH_3$), 4.05–4.12 (m, 2H, $CH_2$), 4.24–4.54 (m, 2H, $CH_2$), 7.21 (dd, 2H, $J = 8.35$ Hz and $J = 7.52$ Hz, ArH), 7.34 (t, 1H, $J = 7.41$ Hz, ArH),

7.39–7.41 (m, 1H, ArH), 7.53 (d, 1H, $J = 7.75$ Hz, ArH), 7.56–7.59 (m, 1H, ArH), 7.61 (dd, 2H, $J = 8.49$ Hz and $J = 1.16$ Hz, ArH), 7.83 (dd, 1H, $J = 7.76$ Hz and $J = 0.70$ Hz, ArH); $^{31}$P NMR (300 MHz, $CDCl_3$): δ, 14.6; $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 447 (d, $J = 20.30$ Hz); IR (KBr): 3095, 2979, 1715, 1686, 1662, 1238, 1010, 776 cm$^{-1}$. Anal. calcd. for $C_{19}H_9O_5PSe$ (437.28): C, 52.19; H, 4.38. Found: C, 52,08; H, 4.30.

Diethyl 2-Acetyl-3-oxo-2,3-dihydrobenzo[*b*]selenophen-2-ylphosphonate (**1g**)

Waxy solid, yield 0.25 g (68%); $^1$H NMR (300 MHz, $CDCl_3$): δ, 1.20 (t, 3H, $J = 7.06$ Hz, $CH_3$), 1.34 (t, 3H, $J = 7.08$ Hz, $CH_3$), 2.42 (s, 3H, $COCH_3$), 4.16–4.34 (m, 4H, $2CH_2$), 7.34 (ddd, 1H, $J = 8.01$ Hz and $J = 6.92$ Hz and $J = 1.24$ Hz, ArH), 7.53 (d, 1H, $J = 7.35$ Hz, ArH), 7.56–7.62 (m, 1H, ArH), 7.84 (dd, 1H, $J = 7.80$ Hz and $J = 0.60$ Hz, ArH); $^{31}$P NMR (300 MHz, $CDCl_3$): δ, 14.6; $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 463 (d, $J = 51.0$ Hz); IR (film): 3069, 2984, 1715, 1688, 1256, 1019, 791 cm$^{-1}$. Anal. calcd. for $C_{14}H_{17}O_5PSe$ (375.22): C, 44.81; H, 4.57. Found: C, 44.77; H, 4.51.

2,2-Diacetylbenzo[*b*]selenophen-3(2*H*)-one (**1h**)

Orange solid, yield 0.06 g (20%), mp 106–110°C (109–111°C[14]).

## Synthesis of 2-Substituted 3-Hydroxybenzo[*b*]selenophenes (7)

2,2-Disubstituted benzo[*b*]selenazol-3(2*H*)-one **1** (1 mmol) was dissolved in warm ethanol (40 ml) and corresponding alkyl- or arylhydrazine (1 mmol) or hydroxylamine hydrochloride (1 mmol) was added in one portion. When hydroxylamine hydrochloride was used, addition of triethylamine (1.1 mmol) was needed. The mixture was refluxed for 3 h. After cooling, the hydrazones **5** crystallized. Then the solvent was evaporated, and the product was isolated by column chromatography on silica gel (DCM was an eluent for **7a**–**e** and **7g**, ethyl acetate for **7f**).

## Data

3-Hydroxybenzo[*b*]selenophene-2-carbonitrile (**7a**)

Colorless crystals, yield 0.17–0.18 g (76–81%), mp 147–148°C; $^1$H NMR (300 MHz, DMSO-$d_6$): δ, 7.58 (quin., 2H, $J = 7.10$ Hz and $J = 1.08$ Hz,

ArH), 8.05 (dd, 1H, $J = 8.10$ Hz and $J = 1.24$ Hz, ArH), 8.17 (dd, 1H, $J = 7.80$ Hz and $J = 1.17$ Hz, ArH), 12.12 (s, 1H, OH); $^{77}$Se NMR (600 MHz, DMSO-$d_6$): δ, 487; IR (KBr): 3142, 2205, 1268, 768 $cm^{-1}$. Anal. calcd. for $C_9H_5NOSe$ (222.10): C, 48.67; H, 2.27; N, 6.31. Found: C, 48.64; H, 2.22; N, 6.25.

Ethyl 3-Hydroxybenzo[*b*]selenophene-2-carboxylate (**7b**)

Yellow crystals, yield 0.21–0.23 g (79–85%), mp 86–87°C (87–88°C[13]).

2-Benzoyl-3-hydroxybenzo[*b*]selenophene (**7c**)

Yellow needles, yield 0.23–0.26 g (78–87%), mp 107–109°C (109–111°C[13]).

2-Acetyl-3-hydroxybenzo[*b*]selenophene (**7d**)

Violet prisms, yield 0.17–0.19 g (72–80%), mp 76–77°C (76–78°C[14]).

3-Hydroxy-2-nitrobenzo[*b*]selenophene (**7e**)

Yellow crystals, yield 0.19–0.20 g (79–84%), mp 155–157°C; $^1$H NMR (300 MHz, $CDCl_3$): δ, 7.33–7.38 (m, 1H, ArH), 7.53 (ddd, 1H, $J = 7.83$ Hz and $J = 1.05$ and $J = 0.57$ Hz, ArH), 7.62 (ddd, 1H, $J = 7.82$ Hz and $J = 7.23$ Hz and $J = 1.45$ Hz, ArH), 7.89 (ddd, 1H, $J = 7.69$ Hz and $J = 1.42$ Hz and $J = 0.55$ Hz, ArH), 9.99 (s, 1H, OH); $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 435; IR (KBr): 3147, 3087, 2984, 1687, 1284, 997, 732 $cm^{-1}$. Anal. calcd. for $C_8H_5NO_3Se$ (242.09): C, 39.69; H, 2.08; N, 5.79. Found: C, 39.54; H, 1.98; N, 5.58.

Diethyl 3-Hydroxybenzo[*b*]selenophen-2-ylphosphonate (**7f**)

Colorless oil, yield 0.29–0.33 g (89–98%); $^1$H NMR (300 MHz, DMSO-$d_6$): δ, 1.35 (t, 6H, $J = 7.06$ Hz, $2CH_3$), 4.08–4.20 (m, 4H, $2CH_2$), 7.41–7.47 (m, 2H, ArH), 7.82 (dd, 1H, $J = 6.18$ Hz and $J = 2.84$ Hz, ArH), 7.96 (dd, 1H, $J = 6.24$ Hz and $J = 3.06$ Hz, ArH), 10.46 (s, 1H, OH); $^{31}$P NMR (300 MHz, DMSO-$d_6$): δ, 14.6; $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 465 (d, $J = 45.5$ Hz); IR (film): 3389, 3062, 2984, 1574, 1526, 1020, 731 $cm^{-1}$. Anal. calcd. for $C_{12}H_{15}O_4PSe$ (333.18): C, 43.26; H, 4.54. Found: C, 43.14; H, 4.39.

3-Hydroxybenzo[*b*]selenophen-2-ylphosphonic Acid (**7g**)

Diethyl 3-hydroxybenzo[*b*]selenophen-2-ylphosphonate **7f** (0.33 g, 1 mmol) was dissolved in dry DCM (10 ml) and trimethylbromosilane (0.6 g, 0.52 ml, 4 mmol) was added under a slow stream of nitrogen. The mixture was stirred for 24 h, and then the solvent was evaporated. The silyl esters were decomposed by treatment with methanol (10 ml). After evaporation the solvent, the product was isolated from the residue by crystallization from ethanol. Yield 0.22 g (78%), pale orange crystals, mp 158–160°C; $^{1}$H NMR (300 MHz, DMSO-$d_6$): δ, 7.45 (dd, 2H, $J = 6.03$ Hz and $J = 3.19$ Hz, ArH), 7.79–7.82 (m, 1H, ArH), 8.04–8.07 (m, 1H, ArH), 11.11 (s, 1H, OH); $^{31}$P NMR (300 MHz, DMSO-$d_6$): δ, 13.2; $^{77}$Se NMR (600 MHz, $CDCl_3$): δ, 462 (d, $J = 51.23$ Hz); IR (KBr): 3394, 3083, 2935, 1651, 735 $cm^{-1}$. Anal. calcd. for $C_8H_7O_4PSe$ (277.07): C, 34.68; H, 2.55. Found: C, 34.59; H, 2.44.

## ACKNOWLEDGMENT

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