Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsrp20

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Published online: 02 Nov 2011.

To cite this article: Alexander V. Artem'ev, Svetlana F. Malysheva, Anastasiya O. Korocheva, Yuriy V. Gatilov, Victor I. Mamatyuk & Nina K. Gusarova (2011) Novel atom-economic synthesis of thioselenophosphinates via three-component reaction between secondary phosphine sulfides, elemental selenium, and amines, Journal of Sulfur Chemistry, 32:6, 599-610, DOI: 10.1080/17415993.2011.628993

To link to this article: http://dx.doi.org/10.1080/17415993.2011.628993

Journal of Sulfur Chemistry
Vol. 32, No. 6, December 2011, 599–610

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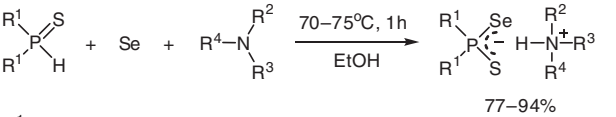
(*Received 18 August 2011; final version received 19 September 2011*)

An efficient, general, and atom-economic synthesis of organoammonium thioselenophosphinates has been developed by exploiting a three-component reaction between secondary phosphine sulfides, elemental selenium, and various amines. The reaction proceeds under mild conditions (70–75 °C, 1 h, EtOH) to afford thioselenophosphinates in 77–94% yields.



R^1 = aryl, arylalkyl, hetarylalkyl

R^2, R^3, R^4 = H, Et, Bu, Bn, All, Ph, $HO(CH_2)_2$, (*R*)-$CH_2CH(OH)Et$

Keywords: amines; secondary phosphine sulfides; elemental selenium; thioselenophosphinates; three-component reaction

1. Introduction

The salts of thioselenophosphinic acids are convenient models for the investigation of S,Se-ambident dual reactivity (almost unexplored so far (*1*)), which is specific for the conjugate anionic triads of "S−X−Se" type [X = carbon (*2*) or phosphorus (*3*)]. Furthermore, thioselenophosphinates are employed as key starting compounds for access to both S- and Se-esters of thioselenophosphinic acids (*1*) as well as versatile S-and/or Se-donor ligands for the design of metal complexes (*4*). The latter are high-potential single-source precursors for the fabrication

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ISSN 1741-5993 print/ISSN 1741-6000 online

http://dx.doi.org/10.1080/17415993.2011.628993
http://www.tandfonline.com

of nanosized semiconducting metal sulfides and/or selenides, having a wide range of remarkable properties (*5*).

The most conventional approach to the synthesis of thioselenophosphinates is based on two mutually complementary reactions (Scheme 1): condensation of selenophosphinic chlorides $R_2P(Se)Cl$ with sodium hydrosulfide (*4*c,d, *6*) (Pathway a) or interaction of thiophosphinic chlorides $R_2P(S)Cl$ with sodium hydroselenide (*6*) (Pathway b).

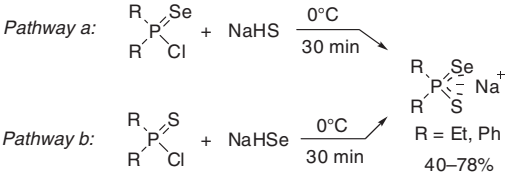
Also, sodium diethylthioselenophosphinate was synthesized by the reaction of tetraethyldiphosphine disulfide with sodium selenide and elemental selenium in low yield (*6b*) (Scheme 2).

Alternative synthesis of thioselenophosphinic acid salts involves the reaction of primary or secondary amines with *S*-(thioacyl)thioselenophosphinates prepared from diphenylselenophosphinic chloride and cesium dithiocarboxylates (*7*) (Scheme 3).

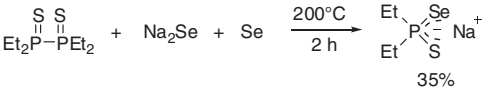
A more modern route to thioselenophosphinates includes the following procedure (*1*) (Scheme 4), which involves as the key step the reaction of tetraalkylammonium fluoride with *S*-2-(trimethylsilyl)ethyl thioselenophosphinates. The latter were prepared in several steps from phenyldichlorophosphine, Grignard reagents, elemental selenium, and lithium 2-(trimethylsilyl)ethanethiolate (*1*).

Clearly, the aforementioned methods have significant drawbacks such as the multistage character, difficulty in preparing starting compounds, the need for anhydrous conditions, low temperatures, and long reaction times.

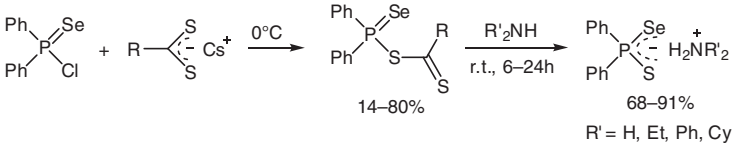
Currently, the most convenient approach to thioselenophosphinates is their one-pot synthesis from secondary phosphines, selenium, sulfur, and aliphatic amines (*8*) (Scheme 5). This method is triggered by the oxidation of secondary phosphines by elemental selenium to give secondary phosphine selenides. The latter, without isolation, interact with elemental sulfur and amines in a three-component-type reaction to afford the target thioselenophosphinates. It should be noted that only very simple amines were used in this reaction (*8*).



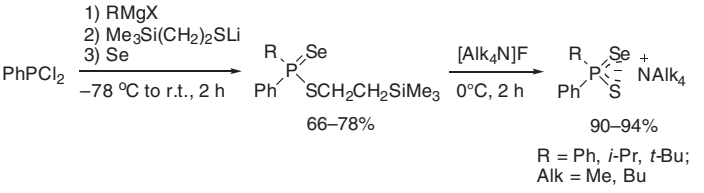
Scheme 1. Synthesis of thioselenophosphinates via condensation of chalcophosphinic chlorides with sodium hydrochalcogenides.



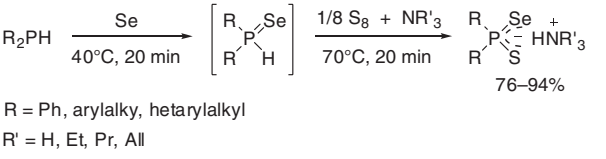
Scheme 2. Synthesis of sodium diethylthioselenophosphinate from tetraethyldiphosphine disulfide, sodium selenide and elemental selenium.



Scheme 3. Multi-step synthesis of organoammonim thioselenophosphinates.



Scheme 4. Multi-step synthesis of tetraalkylammonium thioselenophosphinates.



Scheme 5. One-pot synthesis of thioselenophosphinates from secondary phosphines, elemental selenium, sulfur, and amines.

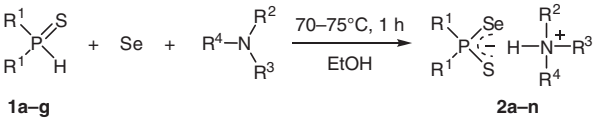
Herein, we report on a new general and efficient synthesis of organoammonium thioselenophosphinates via a three-component reaction between secondary phosphine sulfides, elemental selenium, and diverse amines. This reaction, apart from its fundamental importance, has a practical value because the application of secondary phosphine sulfides are experimentally more convenient than that of secondary phosphines, especially in the cases when the latter demonstrate propensity to oxidize upon exposure to air. It should be noted that the secondary phosphine sulfides as starting materials are now easily accessible (*9*) in one step from cheap red phosphorus, elemental sulfur, and vinylarenes or vinylhetarenes, *e.g.* styrenes, vinylpyridines, or 2-vinylfurane.

2. Results and discussion

Our experiments have shown that secondary phosphine sulfides **1a**–**g** react readily with elemental selenium and various amines in the molar ratio 1:1:1.1 (70–75 °C, 1 h, ethanol) to afford thioselenophosphinates **2a**–**n** in 77–94% yields (Scheme 6, Table 1).

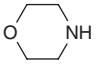
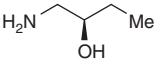
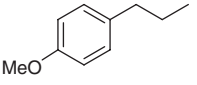
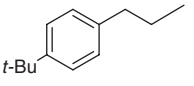
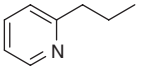
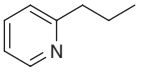
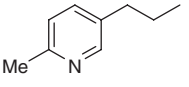
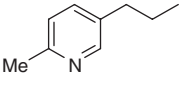
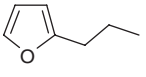
The generality of the three-component reaction is illustrated with respect to various secondary phosphine sulfides and includes a wide range of functionally unsaturated and optically active amines. In addition, the reaction occurs under mild and eco-friendly conditions, which are amenable to scale-up.

Significantly, the three-component reaction of bis(pyridylethyl)phosphine sulfides **1d** and **e** with elemental selenium and allylamine or diethylamine (Entries 8–11, Table 1) proceeds chemoselectively to give exclusively salts **2h**–**k**, *i.e.* the pyridine moiety as an alternative *N*-base remains intact.



Scheme 6. Efficient atom-economic synthesis of organoammonium thioselenophosphinates via a three-component reaction between secondary phosphine sulfides, elemental selenium, and amines.

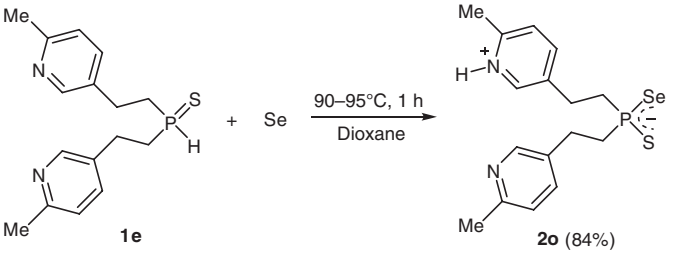
Table 1. Synthesis of thioselenophosphinates from secondary phosphine sulfides, elemental selenium, and amines.

Entry	Phosphine sulfide	R^1	Amine	Product	Yield (%)[a]
1	**1a**	$Ph(CH_2)_2$	Et_2NH	**2a**	94
2	**1a**	$Ph(CH_2)_2$		**2b**	82
3	**1a**	$Ph(CH_2)_2$	$HO(CH_2)_2NH_2$	**2c**	77
4	**1a**	$Ph(CH_2)_2$		**2d**	79
5	**1a**	$Ph(CH_2)_2$	$PhNH_2$	**2e**	85
6	**1b**		Et_2NH	**2f**	88
7	**1c**		Pr_2NH	**2g**	78
8	**1d**		$AllNH_2$	**2h**	82
9	**1d**		Et_2NH	**2i**	77
10	**1e**		$AllNH_2$	**2j**	84
11	**1e**		Et_2NH	**2k**	88
12	**1f**		Bn_2NH	**2l**	87
13	**1g**	Ph	Bu_2NH	**2m**	82
14	**1g**	Ph	Et_3N	**2n**	85

Note: [a]Isolated yield.

At same time, we have found that secondary phosphine sulfide **1e** reacts with elemental selenium in a 1:1 molar ratio to form salt **2o** in 84% yield, which is the first representative of zwitterionic thioselenophosphinates (Scheme 7). This two-component reaction proceeds under harsher conditions (90–95 °C, 1 h, dioxane) than required in the three-component reactions discussed above (Table 1).

The newly synthesized thioselenophosphinates **2a–o** are air-stable colorless crystalline powders soluble in polar solvents. Their structures have been proved by multinuclear NMR (^1H, ^{13}C, ^{31}P, and ^{77}Se) and IR spectroscopy. In addition, one of thioselenophosphinates, namely diethylammonium salt **2a**, was structurally characterized by single-crystal X-ray crystallography. Figure 1 shows a molecular structure of compound **2a**, which crystallized in the orthorhombic crystal system with space group Pna_1. In thioselenophosphinate anion, the phosphorus atom is attached to the selenium and sulfur atoms in a distorted tetrahedral geometry. As expected, sulfur and selenium atoms are disordered over two positions (0.620:0.380). It should be noted that such disorder of chalcogen atoms is specific for many thioselenophosphinates (*1*,*8*,*10*), except for tellurium



Scheme 7. Atom-economic synthesis of zwitterionic thioselenophosphinate **2o**.

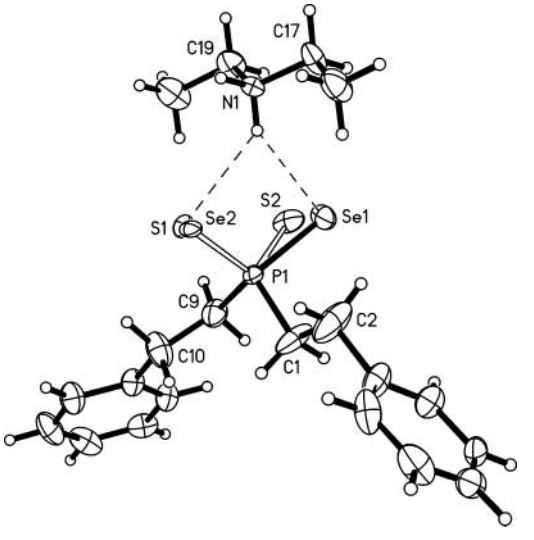
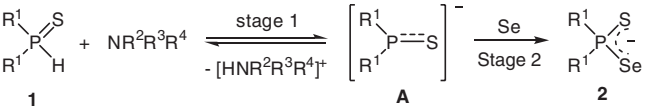


Figure 1. X-ray crystal structure of thioselenophosphinate **2a** showing the hydrogen bonding interactions of N −H · · · S(Se). The sulfur and selenium atoms are disordered over two positions (0.620:0.380).

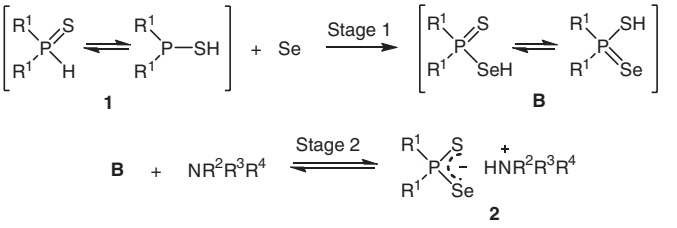
(*11a*) and thallium (*11b*) diethylthioselenophosphinates. The values of the P−S and P−Se bond lengths in **2a** are similar to literature ones (*3*,*8*,*10*). In the solid state of diethylammonium salt **2a**, there is an N−H· · · Ch (Ch = S, Se) hydrogen bonding interaction (Figure 1), with the H· · · Ch bond distances equal to 2.44–2.71 Å.

One of the tentative pathways of thioselenophosphinate **2a**–**n** formation (Scheme 8) includes the deprotonation of the starting secondary phosphine sulfide **1** by the amine to generate the *P*, *S*-ambident thiophosphinite anion **A** (stage 1), which further reacts (as an *P*-nucleophile) with elemental selenium to provide thiselenophosphinate **2** (Stage 2).

Alternatively, this three-component reaction (Scheme 9) might start from the oxidation of secondary phosphine sulfide **1**, existing in two tautomeric forms, by elemental selenium to give

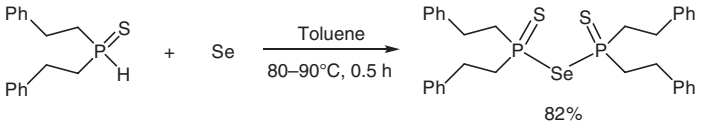


Scheme 8. Plausible pathway for the three-component reaction between secondary phosphine sulfides, amines, and selenium.



1 B 2

Scheme 9. Alternative mechanism of the three-component reaction via thioselenophosphinic acid **B** formation.



Scheme 10. Chemoselective reaction between secondary phosphine sulfide and elemental selenium.

thioselenophosphinic acid **B** (Stage 1). The latter is deprotonated by the corresponding amine to afford salt **2** (Stage 2).

However, it has been found that secondary phosphine sulfides react with elemental selenium (1:1 molar ratio, toluene, 80–90 °C, 0.5 h) to furnish bis[diorganothiophosphoryl]selenides in high yield instead of the anticipated acids **B** (Scheme 10). The results of the unprecedented chemoselective reaction will be published elsewhere.

But despite of this, the mechanism of three-component reaction still needs to be elucidated. At the moment, due to the lack of additional experimental data, it is impossible to assess with any confidence that the tentative pathway presented in Scheme 8 is correct.

3. Conclusion

In summary, we have developed a novel general and efficient atom-economic synthesis of diverse organoammonium thioselenophosphinates via three-component reaction between secondary phosphine sulfides, elemental selenium, and amines. The reaction readily proceeds in ethanol ("green" solvent) at 70–75 °C within 1 h, the product yields reaching 94%. The resulting thioselenophosphinates are prospective ligands for the design of metal complexes as well as highly reactive building blocks for numerous chemical transformations in organic synthesis. The results represent a novel principal contribution to both theoretical and synthetic chemistry of secondary phosphine sulfides and thioselenophosphinates.

4. Experimental

4.1. *General*

Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The optical activity of salt **2d** was determined on a Polamat A instrument. Fourier transform IR spectra were run on a Bruker Vertex 70 instrument. The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker AV-400

spectrometer (400.13, 100.61, 161.98, and 76.31 MHz, respectively) and referenced to H_3PO_4 (^{31}P NMR) and Me_2Se (^{77}Se NMR). Chemical shifts (δ) are expressed in ppm downfield from hexamethyldisiloxane, $CHCl_3$, or DMSO-d_6 as internal standards. All steps of the experiment were carried out in argon atmosphere.

Brand ethanol (96%) was used in the reaction as a solvent. Diethyl ether and dioxane were distilled over metal sodium before use. Secondary phosphine sulfides **1a–f** were prepared from red phosphorus, elemental sulfur, and styrene (*9a*), 4-methoxystyrene, 4-*tert*-butylstyrene (*9c*), 2-vinylpyridine (*9a*), 5-vinyl-2-methylpyridine (*9b*), or 2-vinylfurane as described in the literature. Diphenylphosphine sulfide (**1g**) was prepared by the oxidation of commercial diphenylphosphine (Aldrich) with powdered sulfur in ethanol. Amines were distilled over powdered potassium hydroxide prior to use. Optically activity (*R*)-1-aminobutano-2-ol was employed as the commercial product (Aldrich) without further purification. Room temperature refers to 20–25 °C.

4.2. *X-ray crystallography of compound 2a*

Single crystals of thioselenophosphinate **2a** suitable for X-ray diffraction were obtained by slow evaporation of its ethanol solution at 3–5 °C. X-ray data were measured at 150(2) K on a Bruker Kappa Apex II diffractometer with graphite monochromated MoKα radiation using φ, ω scans ($\theta < 30°$). A correction for absorption was made using SADABS program (transmission 0.25–0.34). The structure was solved by direct methods and refined by a full matrix least-squares anisotropic procedure using SHELXTL97 programs (*12*). The parameters of the hydrogen atoms were given geometrically. The final indexes are $wR_2 = 0.1178$, $S = 1.081$ for all 6348 F^2 and $R_1 = 0.0427$ for 4924 $F_o > 4\sigma$ (239 parameters, 1 restrains, racemic twinning 17(1)%). CCDC-832002 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data and structural refinement for ***2a***: $[C_{16}H_{18}PSSe]^-$, $[C_4H_{12}N]^+$, $M = 426.44$, crystal class orthorhombic, space group $Pna2_1$, $a = 15.1349(13)$, $b = 22.694(2)$, $c = 6.3965(5)$ Å, $V = 2197.0(3)$ Å^3, $Z = 4$, $d_c = 1.289$ g/cm^3, μ(MoKa) = 1.879 mm^{-1}, crystal size $0.05 \times 0.09 \times 0.45$ mm. Selected bond lengths (Å): Se1–P1 2.1206(9), Se2–P1 2.030(6), S1–P1 2.115(9), S2–P1 2.034(2), P1–C1 1.793(3), P1–C9 1.835(3). The sulfur and selenium atoms are disordered over two positions (0.620:0.380).

4.3. *General procedure for the synthesis of thioselenophosphinate 2a–n*

The amine (1.1 mmol) was added to a suspension of powdered gray selenium (0.079 g, 1.0 mmol) in a solution of secondary phosphine sulfide **1a–g** (1.0 mmol) in EtOH (10 ml) at room temperature. The suspension was stirred at 70–75 °C until dissolution of selenium (~1 h) to give a transparent solution. The solvents were removed under reduced pressure and the residue was washed with ether (2×10 ml) and dried *in vacuo* (1 Torr, 45 °C) to afford the corresponding thioselenophosphinate **2a–n**.

4.3.1. *Diethylammonium bis(2-phenethyl)thioselenophosphinate (**2a**)*

White powder; yield: 0.40 g (94%); m.p. 154–156 °C. IR (KBr, ν, cm^{-1}): 3449, 3057, 3024, 2937, 2841, 2788, 2495, 1949, 1806, 1600, 1536, 1496, 1451, 1400, 1384, 1332, 1266, 1195, 1159, 1124, 1063, 1047, 1019, 950, 934, 903, 872, 764, 750, 723, 697, 588, 552, 495, 477, 434. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.55$ (t, $^3J_{HH} = 7.4$ Hz, 6 H, Me), 2.45–2.52 (m, 4 H, CH_2P),

3.09–3.16 (m, 4 H, CH_2Ph), 3.18–3.24 (m, 4 H, CH_2N), 7.19–7.33 (m, 10 H, Ph), 8.77 (br. s, 2 H, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 11.4$ (Me), 30.2 (CH_2Ph), 41.2 (CH_2N), 43.9 (d, $^1J_{CP} = 42.9$ Hz, CH_2P), 125.9 (p-C_{Ph}), 128.3 (o,m-C_{Ph}), 141.7 (d, $^3J_{CP} = 17.2$ Hz, i-C_{Ph}). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 48.14$ (s, $^1J_{PSe} = 565$ Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): $\delta = -72$ (d, $^1J_{PSe} = 565$ Hz). Anal. Calcd for $C_{20}H_{30}NPSSe$: C, 56.33; H, 7.09; P, 7.26; S, 7.52; Se, 18.52. Found: C, 56.28; H, 7.18; P, 7.21; S, 7.37; Se, 18.41.

4.3.2. *Morpholin-4-ium bis(2-phenethyl)thioselenophosphinate (**2b**)*

White powder; yield: 0.36 g (82%); m.p. 143–145 °C. IR (KBr, ν, cm^{-1}): 3450, 3082, 3061, 2999, 2975, 2926, 2864, 2807, 2703, 2639, 2473, 1951, 1813, 1600, 1581, 1496, 1453, 1442, 1392, 1371, 1304, 1231, 1206, 1179, 1166, 1127, 1103, 1066, 1041, 1020, 946, 911, 871, 828, 769, 742, 729, 707, 698, 592, 559, 500, 438, 421. ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.30$–2.37 (m, 4 H, CH_2P), 2.91–2.98 (m, 4 H, CH_2Ph), 3.27–3.30 (m, 4 H, CH_2N), 3.88–3.90 (m, 4 H, CH_2O), 7.06–7.19 (m, 10 H, Ph), 8.40 (br. s, 2 H, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 30.5$ (CH_2Ph), 43.3 (CH_2N), 43.6 (d, $^1J_{CP} = 42.1$ Hz, CH_2P), 64.0 (CH_2O), 126.1 (p-C_{Ph}), 128.3 (o-C_{Ph}), 128.5 (m-C_{Ph}), 141.2 (d, $^3J_{CP} = 16.5$ Hz, i-C_{Ph}). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 48.70$ (s, $^1J_{PSe} = 558$ Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): $\delta = -70$ (d, $^1J_{PSe} = 558$ Hz). Anal. Calcd for $C_{20}H_{28}NOPSSe$: C, 54.54; H, 6.41; N, 3.18; P, 7.03; S, 7.28; Se, 17.93. Found: C, 54.46; H, 6.51; N, 3.04; P, 6.84; S, 7.19; Se, 18.03.

4.3.3. *(2-Hydroxyethyl)ammonium bis(2-phenethyl)thioselenophosphinate (**2c**)*

White powder; yield: 0.32 g (77%); m.p. 112–114 °C. IR (KBr, ν, cm^{-1}): 3449, 3289, 3061, 3025, 2999, 2930, 2893, 1955, 1880, 1813, 1661, 1602, 1582, 1495, 1453, 1398, 1321, 1261, 1207, 1155, 1094, 1067, 1029, 1007, 945, 912, 846, 752, 699, 574, 508, 480, 415, 397. ^1H NMR (400.13 MHz, DMSO-d_6): $\delta = 2.09$–2.15 (m, 4 H, CH_2P), 2.83–2.86 (m, 2 H, CH_2N), 2.91–2.97 (m, 4 H, CH_2Ph), 3.54–3.58 (m, 2 H, CH_2O), 5.10 (br. s, 1 H, OH), 7.12–7.26 (m, 10 H, Ph), 7.64 (br. s, 3 H, HN). ^{13}C NMR (100.61 MHz, DMSO-d_6): $\delta = 30.7$ (CH_2Ph), 41.7 (CH_2N), 45.6 (d, $^1J_{CP} = 42.7$ Hz, CH_2P), 57.9 (CH_2O), 126.0 (p-C_{Ph}), 128.6 (o-C_{Ph}), 128.8 (m-C_{Ph}), 143.3 (d, $^3J_{CP} = 16.0$ Hz, i-C_{Ph}). ^{31}P NMR (161.98 Hz, DMSO-d_6): $\delta = 48.93$ (s, $^1J_{PSe} = 590$ Hz). ^{77}Se NMR (76.31 Hz, DMSO-d_6): $\delta = -55$ (d, $^1J_{PSe} = 590$ Hz). Anal. Calcd for $C_{18}H_{26}NOPSSe$: C, 52.17; H, 6.32; N, 3.38; P, 7.47; S, 7.74; Se, 19.05. Found: C, 51.58; H, 6.25; N, 3.27; P, 7.29; S, 7.69; Se, 19.12.

4.3.4. *(R)-2-Hydroxybut-1-ylammonium bis(2-phenethyl)thioselenophosphinate (**2d**)*

White powder; yield: 0.35 g (79%); >160 °C decomp.; $[\alpha]_D^{24} = -6.94$ (c 0.025, EtOH). IR (KBr, ν, cm^{-1}): 3422, 3192, 3055, 3024, 2967, 2927, 2593, 1804, 1749, 1601, 1580, 1494, 1474, 1453, 1374, 1323, 1260, 1245, 1213, 1192, 1155, 1122, 1055, 1036, 1022, 1000, 962, 947, 908, 837, 776, 761, 741, 715, 698, 594, 569, 557, 497, 439. ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.02$ (t, $^3J_{HH} = 7.5$ Hz, 3 H, Me), 1.69–1.90 (m, 2 H, CH_2Me), 2.39–2.46 (m, 4 H, CH_2P), 2.97–3.04 (m, 4 H, CH_2Ph), 3.39–3.45 (m, 1 H, CHOH), 3.78–3.83 (m, 1 H, CH_2N), 3.90–3.99 (m, 1 H, CH_2N), 6.45 (br. s, 4 H, HN, OH), 7.14–7.27 (m, 10 H, Ph). ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 10.2$ (Me), 23.0 (CH_2Me), 30.4 (CH_2Ph), 43.4 (d, $^1J_{CP} = 41.6$ Hz, CH_2P), 55.7 (CH_2N), 60.8 (CHOH), 126.1 (p-C_{Ph}), 128.3 (o-C_{Ph}), 128.5 (m-C_{Ph}), 141.2 (d, $^3J_{CP} = 16.4$ Hz, i-C_{Ph}). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.52 (s, $^1J_{PSe}$ = 557 Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): $\delta = -60$ (d, $^1J_{PSe} = 557$ Hz). Anal. Calcd for $C_{20}H_{30}NOPSSe$: C, 54.29; H, 6.83; N, 3.17; P, 7.00; S, 7.25; Se, 17.85. Found: C, 54.20; H, 6.77; N, 3.08; P, 7.13; S, 7.06; Se, 17.80.

4.3.5. *Anilinium bis(2-phenethyl)thioselenophosphinate (**2e**)*

White powder; yield: 0.38 g (85%); m.p. 115–117 °C. IR (KBr, ν, cm^{-1}): 3546, 3476, 3415, 3104, 3083, 3057, 3024, 2924, 2901, 2843, 1602, 1536, 1514, 1494, 1452, 1434, 1396, 1205, 1140, 1024, 941, 893, 829, 756, 739, 729, 709, 700, 687, 588, 573, 553, 526, 499, 476, 467, 431. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.42$–2.51 (m, 4 H, CH_2P), 2.95–3.05 (m, 4 H, CH_2Ph), 5.90 (br. s, 3 H, HN), 7.13–7.35 (m, 15 H, Ph). ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 30.0$ (CH_2Ph), 42.4 (d, $^{1}J_{CP} = 38.9$ Hz, CH_2P), 122.1 (*o*-C_{Ph}), 126.1 and 127.3 (*p*-C, Ph), 128.2 (*o*-C_{Ph}), 128.4 and 129.9 (*m*-C_{Ph}), 140.7 (*i*-C_{Ph}), 140.8 (d, $^{3}J_{CP} = 17.7$ Hz, *i*-C_{Ph}). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 50.35$ (br. s). ^{77}Se NMR (76.31 Hz, $CDCl_3$): $\delta = -60$ (d, $^{1}J_{PSe} = 595$ Hz). Anal. Calcd for $C_{22}H_{26}NPSSe$: C, 59.19; H, 5.87; N, 3.14; P, 6.94; S, 7.18; Se, 17.69. Found: C, 59.07; H, 5.76; N, 3.20; P, 6.71; S, 7.12; Se, 17.52.

4.3.6. *Diethylammonium bis[2-(4-methoxyphenyl)ethyl)]thioselenophosphinate (**2f**)*

White powder; yield: 0.43 g (88%); m.p. 199–201 °C. IR (KBr, ν, cm^{-1}): 2978, 2952, 2937, 2884, 2835, 2800, 2719, 1611, 1582, 1513, 1463, 1444, 1403, 1385, 1372, 1301, 1247, 1176, 1160, 1128, 1063, 1036, 1013, 949, 933, 872, 818, 786, 769, 754, 728, 577, 550, 528, 466, 449, 424. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.49$ (t, 6 H, $^{3}J_{HH} = 7.3$ Hz, *Me*CH_2), 2.35–2.42 (m, 4 H, CH_2P), 2.98–3.04 (m, 4 H, C*H*$_2$Ar), 3.13–3.18 (m, 4 H, CH_2N), 3.76 (s, 6 H, MeO), 6.80, and 7.13 (m, 8 H, Ar), 7.25 (s, 2 H, HN). ^{13}C NMR (100.61 Hz, $CDCl_3$): $\delta = 12.3$ (*Me*CH_2), 30.28 (*C*H_2Ar), 42.1 (CH_2N), 45.1 (d, $^{1}J_{CP} = 42.6$ Hz, CH_2P), 56.1 (MeO), 114.7 ($C2_{Ar}$, $C6_{Ar}$), 130.2 ($C3_{Ar}$, $C5_{Ar}$), 134.7 (d, $^{3}J_{CP} = 17.2$ Hz, $C1_{Ar}$), 158.8 ($C4_{Ar}$). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 48.41$ (s, $^{1}J_{PSe} = 576$ Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): $\delta = -84$ (d, $^{1}J_{PSe} = 576$ Hz). Anal. Calcd for $C_{22}H_{34}NO_2PSSe$: C, 54.31; H, 7.04; N, 2.88; P, 6.37; S, 6.59; Se, 16.23. Found: C, 54.46; H, 7.19; N, 2.72; P, 6.24; S, 6.42; Se, 16.35.

4.3.7. *Dipropylammonium bis[(4-tert-butyl)phenethyl]thioselenophosphinate (**2g**)*

White powder; yield: 0.44 g (78%); m.p. 202–204 °C. IR (KBr, ν, cm^{-1}): 3436, 3023, 2964, 2936, 2876, 2775, 2515, 1901, 1790, 1634, 1574, 1517, 1466, 1458, 1401, 1393, 1364, 1331, 1293, 1268, 1202, 1192, 1133, 1108, 1069, 1046, 1019, 951, 850, 837, 815, 767, 756, 730, 667, 579, 559, 518, 499, 456, 407. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.08$ (t, $^{3}J_{HH} = 7.5$ Hz, 6 H, *Me*CH_2), 1.31 (s, 18 H, Me_3C), 1.92–1.98 (m, 4 H, C*H*$_2$Me), 2.40–2.47 (m, 4 H, CH_2P), 3.01–3.10 (m, 8 H, C*H*$_2$Ar, CH_2N), 7.18–7.32 (m, 8 H, Ar), 8.56 (s, 2 H, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 11.6$ (*Me*CH_2), 19.7 (*C*H_2Me), 29.9 (*C*H_2Ar), 31.6 (*Me*$_3$C), 34.6 (*C*Me$_3$), 44.1 (d, $^{1}J_{CP} = 42.7$ Hz, CH_2P), 48.3 (CH_2N), 125.5 ($C2_{Ar}$, $C6_{Ar}$), 128.3 ($C3_{Ar}$, $C5_{Ar}$), 139.0 (d, $^{3}J_{CP} = 17.2$ Hz, $C1_{Ar}$), 148.9 ($C4_{Ar}$). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 48.10$ (s, $^{1}J_{PSe} = 576$ Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): $\delta = -82$ (d, $^{1}J_{PSe} = 576$ Hz). Anal. Calcd for $C_{30}H_{50}NPSSe$: C, 63.58; H, 8.89; N, 2.47; P, 5.47; S, 5.66; Se, 13.93. Found: C, 63.64; H, 8.97; N, 2.33; P, 5.27; S, 5.51; Se, 14.01.

4.3.8. *Allylammonium bis[2-(pyrid-2-yl)ethyl]thioselenophosphinate (**2h**)*

White powder; yield: 0.34 g (82%); m.p. 87–89 °C. IR (KBr, ν, cm^{-1}): 3354, 3006, 2925, 2618, 2104, 1671, 1646, 1593, 1568, 1474, 1435, 1403, 1310, 1267, 1223, 1194, 1150, 1125, 1083, 1052, 993, 944, 890, 850, 759, 633, 602, 570, 507, 441. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.49$–2.55 (m, 4 H, CH_2P), 3.26–3.32 (m, 4 H, CH_2Py), 3.84 (d, $^{3}J_{HH} = 5.9$ Hz, 2 H, CH_2N), 5.38 (d, $^{3}J_{HH} = 10.4$ Hz, 1 H, $=CH_2$), 5.47 (d, $^{3}J_{HH} = 17.1$ Hz, 1 H, $=CH_2$), 6.09–6.19 (m, 1 H, =CH), 7.13 (t, $^{3}J_{HH} = 5.8$ Hz, 2 H, Py), 7.22 (d, $^{3}J_{HH} = 7.7$ Hz, 2 H, Py), 7.62 (t, $^{3}J_{HH} = 7.3$ Hz, 2 H,

Py), 8.46 (d, $^3J_{HH}$ = 4.1 Hz, 2 H, Py), 8.71 (br. s, 3 H, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 32.4 (CH_2Py), 41.7 (CH_2N), 42.7 (d, $^1J_{CP}$ = 43.6 Hz, CH_2P), 121.4 (=CH_2, C-5 in Py), 123.4 ($C3_{Py}$), 130.1 (=CH), 137.1 ($C4_{Py}$), 148.6 ($C6_{Py}$), 161.4 (d, $^3J_{CP}$ = 17.0 Hz, $C2_{Py}$). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 49.48 (s, $^1J_{PSe}$ = 580 Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = −76 (d, $^1J_{PSe}$ = 580 Hz). Anal. Calcd for $C_{17}H_{24}N_3PSSe$: C, 49.51; H, 5.87; N, 10.19; P, 7.51; S, 7.78; Se, 19.15. Found: C, 49.60; H, 5.75; N, 10.01; P, 7.34; S, 7.87; Se, 19.21.

4.3.9. *Diethylammonium bis[2-(pyrid-2-yl)ethyl]thioselenophosphinate (**2i**)*

White powder; yield: 0.33 g (77%); m.p. 109–110 °C. IR (KBr, ν, cm^{-1}): 3497, 2976, 2882, 2717, 2495, 1631, 1585, 1567, 1471, 1432, 1404, 1384, 1333, 1308, 1268, 1217, 1186, 1160, 1148, 1120, 1063, 1046, 1007, 992, 948, 883, 849, 758, 628, 590, 570, 562, 498, 431. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.18 (t, $^3J_{HH}$ = 7.3 Hz, 6 H, Me), 2.54–2.61 (m, 4 H, CH_2P), 3.19–3.24 (m, 4 H, CH_2N), 3.26–3.33 (m, 4 H, CH_2Py), 7.07–7.10 (t, $^3J_{HH}$ = 5.8 Hz, 2 H, Py), 7.22 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, Py), 7.62 (t, $^3J_{HH}$ = 7.3 Hz, 2 H, Py), 8.46 (d, $^3J_{HH}$ = 4.1 Hz, 2 H, Py), 9.34 (br. s, 2 H, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 11.4 (Me), 32.7 (CH_2Py), 41.8 (CH_2N), 43.8 (d, $^1J_{CP}$ = 44.3 Hz, CH_2P), 121.1 ($C5_{Py}$), 123.0 ($C3_{Py}$), 136.5 ($C4_{Py}$), 148.8 ($C6_{Py}$), 161.5 (d, $^3J_{CP}$ = 17.7 Hz, $C2_{Py}$). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 49.06 (s, $^1J_{PSe}$ = 578 Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = −71 (d, $^1J_{PSe}$ = 578 Hz). Anal. Calcd for $C_{18}H_{28}N_3PSSe$: C, 50.46; H, 6.59; N, 9.81; P, 7.23; S, 7.48; Se, 18.43. Found: C, 50.38; H, 6.46; N, 9.71; P, 7.09; S, 7.34; Se, 18.47.

4.3.10. *Allylammonium bis[2-(2-methylpyrid-5-yl)ethyl]thioselenophosphinate (**2j**)*

White powder; yield: 0.37 g (84%); m.p. 79–82 °C. IR (KBr, ν, cm^{-1}): 3432, 2922, 1603, 1568, 1491, 1445, 1391, 1298, 1244, 1197, 1136, 1035, 991, 940, 855, 826, 775, 722, 652, 584, 540, 490, 410. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.33–2.40 (m, 4 H, CH_2P), 2.49 (s, 6 H, Me), 3.00–3.07 (m, 4 H, CH_2Py), 3.80 (d, $^3J_{HH}$ = 5.9 Hz, 2 H, CH_2N), 5.35 (d, $^3J_{HH}$ = 10.3 Hz, 1 H, =CH_2), 5.47 (d, $^3J_{HH}$ = 17.0 Hz, 1 H, =CH_2), 6.02–6.11 (m, 1 H, =CH), 7.04 (d, 2 H, Py), 7.45 (d, 2 H, Py), 8.41 (br. s, 5 H, Py, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 23.6 (Me), 27.2 (CH_2Py), 41.8 (CH_2N), 43.5 (d, $^1J_{CP}$ = 42.9 Hz, CH_2P), 121.4 (=CH_2), 123.5 ($C3_{Py}$), 130.0 (HC=), 134.7 (d, $^3J_{CP}$ = 17.0 Hz, $C5_{Py}$), 137.3 ($C4_{Py}$), 148.2 ($C6_{Py}$), 155.2 ($C2_{Py}$). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.18 (s, $^1J_{PSe}$ = 575 Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = −65 (d, $^1J_{PSe}$ = 575 Hz). Anal. Calcd for $C_{19}H_{28}N_3PSSe$: C, 51.81; H, 6.41; N, 9.54; P, 7.03; S, 7.28; Se, 17.93. Found: C, 51.72; H, 6.33; N, 9.37; P, 6.89; S, 7.20; Se, 17.76.

4.3.11. *Diethylammonium bis[2-(2-methylpyrid-5-yl)ethyl]thioselenophosphinate (**2k**)*

White powder; yield: 0.40 g (88%); m.p. 112–114 °C. IR (KBr, ν, cm^{-1}): 3459, 3001, 2950, 2787, 2717, 1600, 1567, 1492, 1446, 1396, 1385, 1305, 1277, 1247, 1195, 1160, 1145, 1064, 1030, 936, 850, 829, 778, 747, 723, 704, 645, 609, 584, 544, 532, 491, 440. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.14 (t, $^3J_{HH}$ = 7.3 Hz, 6 H, *Me*CH_2), 2.30–2.37 (m, 4 H, CH_2P), 2.44 (s, 6 H, *Me*Py), 3.01–3.09 (m, 4 H, CH_2Py), 3.14–3.20 (m, 4 H, CH_2N), 7.02 (d, 2 H, Py), 7.47 (d, 2 H, Py), 8.43 (br. s, 5 H, Py, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 11.9 (*Me*CH_2), 23.7 (*Me*Py), 27.3 (CH_2Py), 42.0 (CH_2N), 43.3 (d, $^1J_{CP}$ = 42.5 Hz, CH_2P), 123.4 ($C3_{Py}$), 134.7 (d, $^3J_{CP}$ = 17.1 Hz, $C5_{Py}$), 137.2 ($C4_{Py}$), 148.1 ($C6_{Py}$), 155.2 ($C2_{Py}$). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.11 (s, $^1J_{PSe}$ = 577 Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = −68 (d, $^1J_{PSe}$ = 577 Hz). Anal. Calcd for $C_{20}H_{32}N_3PSSe$: C, 52.62; H, 7.07; N, 9.21; P, 6.79; S, 7.02; Se, 17.30. Found: C, 52.55; H, 7.01; N, 9.12; P, 6.67; S, 7.19; Se, 17.22.

4.3.12. *Dibenzylammonium bis[2-(2-furyl)ethyl]thioselenophosphinate (**2l**)*

White powder; yield: 0.46 g (87%); m.p. 145–148 °C. IR (KBr, ν, cm^{-1}): 3449, 3034, 2975, 2856, 2746, 2691, 2588, 2397, 1951, 1597, 1505, 1458, 1446, 1416, 1330, 1284, 1227, 1213, 1169, 1145, 1073, 1031, 1003, 956, 937, 910, 883, 842, 793, 756, 727, 692, 640, 598, 571, 482, 460, 444. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 2.42$–2.49 (m, 4 H, CH_2P), 3.06–3.12 (m, 4 H, CH_2Fur), 4.11 (s, 4 H, CH_2N), 6.03, 6.27 and 7.29 (m, 6 H, Fur), 7.40–7.51 (m, 10 H, Ph), 9.98 (br. s, 2 H, HN). ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 23.0$ (CH_2Fur), 39.9 (d, $^1J_{CP} = 44.7$ Hz, CH_2P), 47.6 (CH_2N), 105.1 ($C3_{Fur}$), 110.2 ($C4_{Fur}$), 129.5, 129.8 and 130.0 (Ph), 141.0 ($C5_{Fur}$), 155.2 (d, $^3J_{CP} = 19.9$ Hz, $C2_{Fur}$). ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 48.54$ (s, $^1J_{PSe} = 560$ Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): $\delta = -55$ (d, $^1J_{PSe} = 560$ Hz). Anal. Calcd for $C_{26}H_{30}NO_2PSSe$: C, 58.86; H, 5.70; N, 2.64; P, 5.84; S, 6.04; Se, 14.88. Found: C, 58.91; H, 5.76; N, 2.55; P, 5.72; S, 6.12; Se, 14.79.

4.3.13. *Dibutylammonium diphenylthioselenophosphinate (**2m**)*

White powder; yield: 0.35 g (82%); m.p. 192–194 °C. IR (KBr, ν, cm^{-1}): 3490, 2968, 2848, 1813, 1674, 1571, 1537, 1477, 1453, 1434, 1391, 1333, 1303, 1271, 1179, 1152, 1130, 1093, 1068, 1026, 998, 974, 935, 890, 873, 801, 780, 750, 694, 649, 627, 608, 599, 562, 543, 522, 483, 456, 436. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 0.98$ (t, $^3J_{HH} = 7.4$ Hz, 6 H, Me), 1.40–1.45 (m, 4 H, CH_2Me), 1.67–1.80 (m, 4 H, CH_2Et), 3.09–3.20 (m, 4 H, CH_2N), 6.87–6.95 and 7.68–7.73 (m, 10 H, Ph), 10.14 (s, 2 H, HN). ^{13}C NMR (100.61 Hz, $CDCl_3$): $\delta = 10.2$ (Me), 17.2 (*C*H_2Me), 26.8 (*C*H_2Et), 54.6 (*C*H_2N), 127.3 (d, $^2J_{CP} = 12.9$ Hz, *i*-C_{Ph}), 129.2 (d, $^4J_{CP} = 2.0$ Hz, *p*-C_{Ph}), 130.7 (d, $^3J_{CP} = 11.8$ Hz, $\mathcal{M}$-C_{Ph}), 142.0 (d, $^1J_{CP} = 72.0$ Hz, *i*-C_{Ph}). ^{31}P NMR (161.98 MHz, $CDCl_3$): $\delta = 44.53$ (s, $^1J_{PSe} = 602$ Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): $\delta = 0$ (d, $^1J_{PSe} = 602$ Hz). Anal. Calcd for $C_{20}H_{30}NPSSe$: C, 56.33; H, 7.09; N, 3.28; P, 7.26; S, 7.52; Se, 18.52. Found: C, 56.25; H, 7.14; N, 3.40; P, 7.19; S, 7.44; Se, 18.50.

4.3.14. *Triethylammonium diphenylthioselenophosphinate (**2n**)*

White powder; yield: 0.34 g (85%); m.p. 201–205 °C. IR (KBr, ν, cm^{-1}): 3064, 3043, 2972, 2938, 2806, 2788, 2745, 2652, 2512, 2480, 1639, 1468, 1455, 1437, 1387, 1306, 1285, 1172, 1159, 1089, 1067, 1054, 1028, 1011, 997, 980, 896, 837, 804, 788, 770, 757, 698, 631, 603, 525, 481, 420. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 1.29$ (t, $^3J_{HH} = 7.4$ Hz, 9 H, Me), 3.21–3.27 (m, 6 H, CH_2N), 7.25–7.31 and 8.10–8.15 (m, 10 H, Ph), 10.06 (s, 1 H, HN). ^{13}C NMR (100.61 Hz, $CDCl_3$): $\delta = 8.3$ (Me), 45.7 (CH_2N), 127.3 (d, $^2J_{CP} = 12.5$ Hz, *i*-C_{Ph}), 129.1 (d, $^4J_{CP} = 2.7$ Hz, *p*-C_{Ph}), 130.6 (d, $^3J_{CP} = 11.4$ Hz, $\mathcal{M}$-C_{Ph}), 142.7 (d, $^1J_{CP} = 70.9$ Hz, *i*-C_{Ph}). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 44.43$ (s, $^1J_{PSe} = 606$ Hz). ^{77}Se NMR (76.31 Hz, $CDCl_3$): $\delta = 1.9$ (d, $^1J_{PSe} = 606$ Hz). Anal. Calcd for $C_{18}H_{26}NPSSe$: C, 54.26; H, 6.58; N, 3.52; P, 7.77; S, 8.05; Se, 19.82. Found: C, 54.35; H, 6.61; N, 3.69; P, 7.60; S, 7.91; Se, 19.90.

4.4. *Synthesis of zwitterionic thioselenophosphinate 2o*

The powdered gray selenium (0.079 g, 1.0 mmol) was added to a solution of secondary phosphine sulfide **1e** (1.0 mmol) in dioxane (10 ml) at room temperature. The suspension was stirred at 90–95 °C until dissolution of selenium (~1 h) to give a transparent solution. The solvents were removed under reduced pressure and the residue was washed with ether (2 × 10 ml) and dried *in vacuo* (1 Torr, 45 °C) to afford the zwitterionic thioselenophosphinate **2o**.

4.4.1. *2-(2-methylpyrid-5-yl)ethyl[2-(2-methylpyrid-inium-5-yl)ethyl]thio- selenophosphinate (**2o**)*

White powder, yield: 0.32 g (84%); m.p. 201–205 °C with decomp. IR (KBr, ν, cm^{-1}): 3444, 3096, 3029, 3006, 2919, 2855, 1639, 1601, 1568, 1491, 1445, 1402, 1334, 1300, 1247, 1213, 1197, 1147, 1029, 1017, 969, 952, 930, 910, 865, 836, 789, 764, 755, 739, 729, 714, 646, 616, 562, 542, 489, 411. ^{1}H NMR (400.13 MHz, DMSO-d_6): $\delta = 2.35$–2.41 (m, 4 H, CH_2P), 2.41 (s, 6 H, *Me*Py), 3.10–3.19 (m, 4 H, CH_2Py), 7.11 (d, 2 H, Py), 7.61 (d, 2 H, Py), 8.54 (br. s, 3 H, Py, HN). ^{13}C NMR (100.61 MHz, DMSO-d_6): $\delta = 24.1$(*Me*Py), 27.9 (CH_2Py), 43.4 (d, $^1J_{CP} = 41.5$ Hz, CH_2P), 123.1 ($C3_{Py}$), 135.1 (d, $^3J_{CP} = 17.0$ Hz, $C5_{Py}$), 137.3 ($C4_{Py}$), 149.1 ($C6_{Py}$), 155.4 ($C2_{Py}$). ^{31}P NMR (161.98 Hz, DMSO-d_6): $\delta = 49.01$ (s, $^1J_{PSe} = 577$ Hz). ^{77}Se NMR (76.31 Hz, DMSO-d_6): $\delta = -76$ (d, $^1J_{PSe} = 577$ Hz). Anal. Calcd for $C_{16}H_{21}N_2PSSe$: C, 50.13; H, 5.52; N, 7.31; P, 8.08; S, 8.36; Se, 20.60. Found: C, 50.17; H, 5.66; N, 7.35; P, 7.95; S, 8.42; Se, 20.48.

Acknowledgement

This work was supported by the Russian Foundation for Basic Research (grant no. 11-03-92003-HHC_a) and the President of the Russian Federation [programs for the support of leading scientific schools (grant NSh-3230.2010.3) and young Russian scientists (grant MK-629-2010.3)].

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