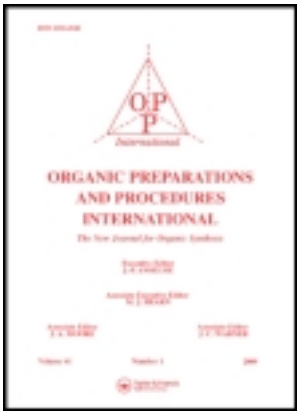


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# Efficient Synthesis of Lupininium, Anabasinium and Quininium Thioselenophosphinates *via* a Multi-component Reaction between Secondary Phosphines, Sulfur, Selenium and Alkaloids

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Thioselenophosphinates [$R_2PSeSM$ (R = aryl or alkyl, M = alkali metal or ammonium)] are key starting compounds for the synthesis of *S*- and *Se*-esters of thioselenophosphinic acids[1,2] as well as versatile ligands for metal complexes.[3–6] The latter are convenient single-source precursors to produce metal selenides nanocrystals having a wide range of unique properties.[7–9] Moreover, thioselenophosphinates represent rare anionic conjugate triads of "S-P-Se" type, possessing of *S,Se*-ambident reactivity, a type of compounds which is nearly unexplored.[1,2]

Conventional syntheses of thioselenophosphinates are multi-step and require air-free manipulations using glove boxes or Schlenk lines due to moisture- and air-sensitive precursors such as chlorophosphines, Grignard and organolithium reagents, as well as 2-(trimethylsilyl)ethanethiol.[10–14] The data on optically active compounds bearing the thioselenophosphinate groups, [$R_2PSeS$], are lacking in the literature, the only exception being triethylammonium *R-tert*-butyl(phenyl)thioselenophosphinate, [*t*-Bu(Ph)PSeS][$HEt_3$].[14]

Very recently, we have reported a convenient one-pot synthesis of alkylammonium thioselenophosphinates *via* a new multi-component, atom-economic reaction between secondary phosphines, selenium, sulfur and aliphatic amines.[15] It should be noted that only some simple amines were used in this reaction.[15]

The aim of this work is to evaluate the scope of this promising reaction. Herein, we have studied the multi-component, atom-economical reaction between secondary phosphines, elemental sulfur, selenium and natural lupinine, anabasine or quinine. The choice of these alkaloids as N-bases is not arbitrary. It is known, that lupinine,[16,17] anabasine[18]

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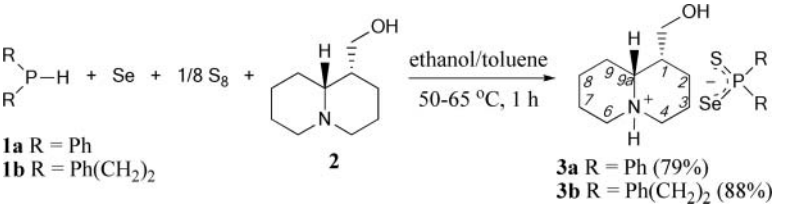
and quinine,[19] as well as their salts, possess a wide spectrum of biological activity and use in various pharmaceuticals, soft drinks and agrochemicals. Thus, one might expect that unknown lupininium, anabasinium and quininium thioselenophosphinates might possess new promising drugs and agrochemicals.

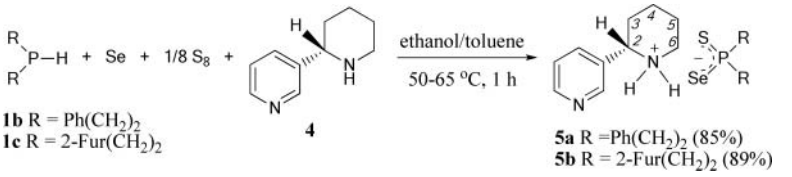
Secondary phosphines **1a**,**b**, elemental selenium, elemental sulfur and natural lupinine (**2**) interact in a multi-component type reaction under mild conditions (50–65°C, ethanol/toluene, 1 h) to afford optically active lupininium thioselenophosphinates **3a**,**b** in good isolated yields (*Scheme 1*).




**Scheme 1**

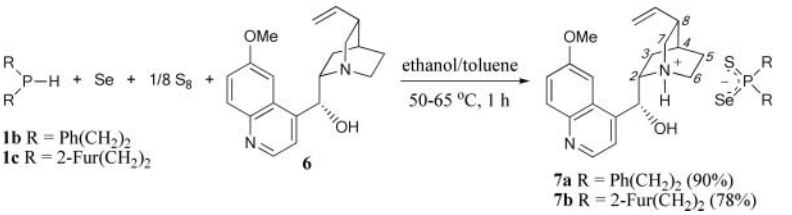
It is noteworthy that red selenium ($Se_8$) may be used in the multi-component reaction instead of amorphous gray selenium.

The atom-economic reaction between secondary phosphines **1b**,**c**, selenium, sulfur and natural anabasine (**4**) proceeds under similar conditions (50–65°C, ethanol/toluene, 1 h) to give thioselenophosphinates **5a**,**b** (according to literature data,[20] including NMR and IR spectra, anabasine is protonated at the piperidine nitrogen) in high yields (*Scheme 2*). The site of protonation in salts **5a**,**b** is supported by their NMR ($^1H$, $^{13}C$) spectra.




**Scheme 2**

The generality and efficacy of the approach elaborated was additionally demonstrated by the synthesis of optically active quininium thioselenophosphinates **7a**,**b** (78–90%) from secondary phosphines **1b**,**c**, selenium, sulfur and free quinine (*Scheme 3*).




**Scheme 3**

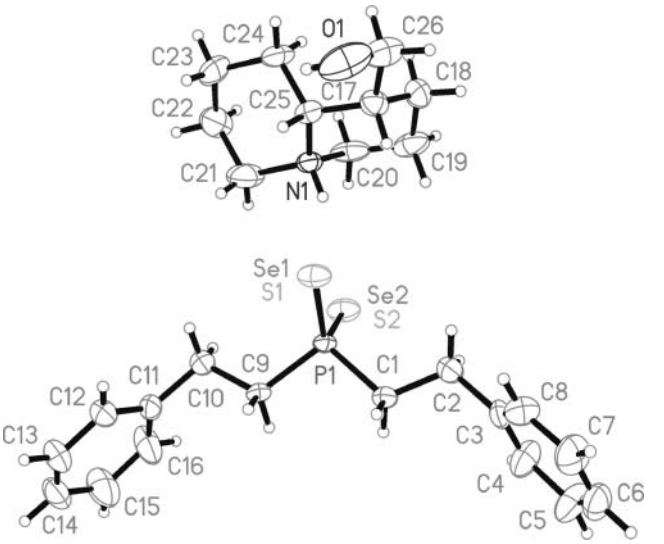
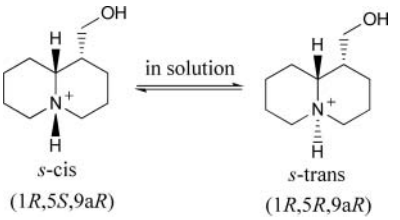



**Figure 1**
Molecular Structure of Lupininium Thioselenophosphinate **3b**

Multinuclear $^{1}$H, $^{13}$C, $^{31}$P, $^{77}$Se and 2D (COSY, HMBC, HSQC) NMR spectroscopy data, as well as X-ray diffraction analysis, and IR investigations of thioselenophosphinates **3**, **5** and **7** are in agreement with their structures. According to X-ray analysis, the absolute configuration of the lupinine skeleton in thioselenophosphinate **3b** was established as 1*R*,5*S*,9a*R* (*Figure 1*). Noteworthy, in the crystal structure of lupinine salt **3b**, the nitrogen atom is of the *S*-configuration. In comparison, the nitrogen atom of lupininium chloride in solid state has *R*-configuration.[21] Both six-membered cycles of the lupininium cation have chair conformations. The phosphorus atom of thioselenophosphinate anion adopts a slightly distorted tetrahedral structure with the bond angles ranging between 101.5° and 116.4°. The sulfur and selenium atoms are disordered and refined with 50% occupancy for both atoms as observed for the similar structures[1,2,9,15] Thus, the molecular structure of compound **3b** is best described as an ion pair of a protonated lupinine and anion of the *bis*(2-phenethyl)thioselenophosphinic acid.

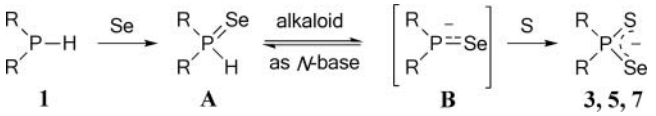
Lupininium cation in solution (unlike in the solid state) exists as equilibrium mixture of the *s*-cis (1*R*,5*S*,9a*R*) and *s*-trans (1*R*,5*R*,9a*R*) forms, which differ in the spatial location of the protons conjugated with nitrogen atom (*Scheme 4*). This is supported by duplication




**Scheme 4**

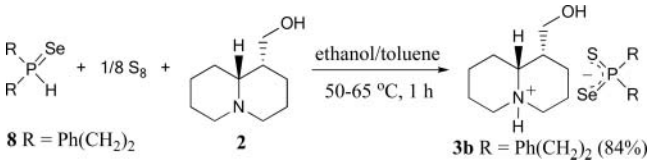
of signals for the carbon atoms of lupinine unit in $^{13}C$ NMR spectra of salts **3a**,**b**. Similar duplication of signals in the $^{13}C$ NMR spectra of lupininium diselenophosphinate[22] or chloride[23] has been reported.

The tentative mechanism of the present multi-component, atom-economic reaction can be rationalized as follows (*Scheme 5*). In the first stage, the secondary phosphine **1** reacts with elemental selenium to give secondary phosphine selenide **A**. The latter is deprotonated by the alkaloid molecule to afford selenophosphinite **B**, which further reacts with elemental sulfur to provide the thioselenophosphinate **3**, **5**, **7**.




**Scheme 5**

The detection of intermediate secondary phosphine selenide **A** in the reaction mixture by $^{31}P$ NMR (singlet at 2 ppm with satellites, $^{1}J_{PSe} = 711$ Hz[24]) supports the above mechanism (*Scheme 5*). In addition, the mechanism proposed is in compliance with our finding that secondary phosphine selenide **8**, preparated from phosphine **1b** and elemental selenium,[24] reacts with sulfur and lupinine (**2**) under the same conditions (50–65°C, ethanol/toluene, 1 h) to form thioselenophosphinate **3b** in 84% yield (*Scheme 6*).




**Scheme 6**

Since starting secondary phosphines are readily available from red phosphorus and styrenes.[25–27] The multi-component assembly presented may be considered as the most concise and expedient approach to the early unknown optically active thioselenophosphinates bearing alkaloid moieties, which are promising pharmaceuticals as well as prospective agrochemicals.

## Experimental Section

$^{1}H$ NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometer (400.13 MHz) in the solvents indicated at room temperature; chemical shifts are expressed with respect to the residual protonated solvent ($\delta$ 7.27 for $CHCl_3$ and 2.05 for DMSO-$d_6$), as an internal standard. $^{13}C$ NMR spectra were recorded on a Bruker DPX 400 (100.61 MHz) instrument; chemical shifts are expressed with respect to the deuterated solvent ($\delta$ 77.00 for $CDCl_3$ and 30.05 for DMSO-$d_6$). $^{1}H$ and $^{13}C$ NMR signals were assigned using 2D NMR methods (COSY, HSQC, HMBC $^{1}H$-$^{13}C$). The $^{31}P$ and $^{77}Se$ NMR spectra were recorded on a Bruker DPX 400 spectrometer (161.98 and 76.31 MHz, respectively) and

referenced to $H_3PO_4$ ($^{31}P$ NMR) and $Me_2Se$ ($^{77}Se$ NMR). Melting points were determined on a Kofler micro hot stage apparatus, and the values given in °C are uncorrected. Fourier transform IR spectra were recorded as films or potassium bromide pellets on a Bruker Vertex 70 spectrometer. The optical activity of the compounds was determined on a Polamat A instrument. All reactions were performed under an argon atmosphere.

Diphenylphosphine (**1a**) was employed as commercial product (Aldrich). Secondary phosphines **1b**,**c** were prepared from styrene or 2-vinylfuran and red phosphorus as described in the literature.[27] *bis*(2-Phenethyl)phosphine selenide (**8**) was prepared by selenation of secondary phosphine **1b** with powdered gray selenium.[24] Commercial ethanol was used in the reaction as a solvent. Diethyl ether and toluene were dried and freshly distilled over metal sodium prior to use.



### *Typical Procedure for the Preparation of Alkaloids Thioselenophosphinates 3, 5 and 7 (Schemes 1–3)*

To a solution of secondary phosphine **1a–c** (1.05 mmol) in ethanol (5 ml) was added amorphous grey selenium (79 mg, 1.0 mmol), and the mixture was stirred (*ca.* 30 min) at 50 °C until dissolution of the residue to give a clear solution. Then a solution of powdered sulfur $S_8$ (32 mg, 0.125 mmol) in toluene (3 ml) and a solution of corresponding alkaloid (lupinine, anabasine or quinine, 1.0 mmol) in ethanol (2 ml) were added consecutively. After stirring for 30 minutes at 65°C, the solvents were removed under reduced pressure, and the residue was triturated and digested with ether (2 × 10 ml). Decantation of the ether left the product (white powder or viscous oil) which was dried *in vacuo* (1 Torr, 40–45°C) to afford the corresponding thioselenophosphinates **3**, **5** or **7**.

### *Procedure for the Preparation of Thioselenophosphinate 3b from Secondary Phosphine Selenide 8, Elemental Sulfur and Lupinine (Scheme 6)*

To a solution of secondary phosphine selenide **8** (321 mg, 1.0 mmol) in ethanol (5 ml), a solution of powdered sulfur $S_8$ (32 mg, 0.125 mmol) in toluene (3 ml) and a solution of lupinine (169 mg, 1.0 mmol) in ethanol (2 ml) were added consecutively. The resultant solution was stirred (30 min) at 65°C. The solvents were removed under reduced pressure, and the residue was digested with ether (2 × 10 ml). Decantation of the ether left a white powder that was dried *in vacuo* (1 Torr, 40°C–45°C) to afford the thioselenophosphinate **3b**, yield: 0.44 g (84%).

**(1*R*,9a*R*)-1-(Hydroxymethyl)octahydro-2*H*-quinolizinium Diphenylthioselenophosphinate (3a)**. Obtained as a white powder. Yield: 0.37 g (79%), mp. > 150°C (dec.). $[\alpha]_D^{23} = -30.7$ (*c* 2.1; $CHCl_3$). FTIR ($cm^{-1}$): 3318 (OH, NH), 558 (P-S), 524 (P-Se). $^1H$ NMR ($CDCl_3$): $\delta$ 1.26–1.40 (m, 1H, H-C8ax), 1.62–2.06 (m, 7H, H-C2,3,7,8eq), 2.22–2.50 (m, 2H, H-C9), 2.56–2.70 (m, 1H, H-C9a), 2.73–2.82 and 3.02–3.12 (m, 2H, H-C4ax,6ax), 3.42–3.68 (m, 2H, $CH_2OH$), 3.55–3.89 (m, 1H, H-C1), 4.01–4.09 and 4.15–4.22 (m, 2H, H-C4eq,6eq), 7.42–7.54 (m, 6H, $C_{m,p}$ in Ph), 8.27–8.39 (m, 4H, $C_o$ in Ph), 9.03 (br s, 1H, NH), 10.00 (br s, 1H, OH). $^{13}C$ NMR (DMSO-$d_6$): $\delta$ 17.2, 18.2 (C-3), 19.6, 19.9 (C-8), 22.3, 23.0 (C-7), 22.7, 23.7 (C-9), 26.1, 28.0 (C-2), 37.6, 39.5 (C-1), 45.1, 53.0 (C-6), 55.0, 59.2 (C-4), 55.9, 60.1 (C-9a), 61.9, 64.7 (C-9a), 127.3 (d, $^2J_{CP} = 12.1$ Hz, $C_o$ in Ph),

128.8 (d, $^4J_{CP} = 2.0$ Hz, $C_p$ in Ph), 131.0 (d, $^3J_{CP} = 10.6$ Hz, $C_m$ in Ph), 145.0 (d, $^1J_{CP} = 67.8$ Hz, $C_{ipso}$ in Ph). $^{31}$P NMR (DMSO-$d_6$): $\delta$ 44.76 (s + d satellites, $^1J_{PSe} = 644$ Hz). $^{77}$Se NMR (DMSO-$d_6$): $\delta$ -8 (d, $^1J_{PSe} = 644$ Hz).

*Anal.* Calcd. for $C_{22}H_{30}NOPSSe$: C, 56.64; H, 6.48; N,3.00; P, 6.64; S, 6.87; Se, 16.93. Found: C, 56.54; H, 6.41; N, 2.91; P, 6.50; S, 6.91; Se, 16.78.

**(1*R*,9a*R*)-1-(Hydroxymethyl)octahydro-2*H*-quinolizinium *bis*(2-phenethyl)thioselenophosphinate (3b)**. Obtained as a white powder. Yield: 0.46 g (88%), mp. 176–178°C (EtOH). $[\alpha]_D{}^{23} = -30.1$ (*c* 2.1; $CHCl_3$). FTIR ($cm^{-1}$): 3352, 3327 (OH, NH), 594 (P-S), 554 (P-Se). $^1$H NMR ($CDCl_3$): $\delta$ 1.14–1.37 (m, 1H, H-C8ax), 1.49–2.04 (m, 7H, H-C2,3,7,8eq), 2.22–2.38 (m, 2H, H-C9), 2.41–2.48 (m, 4H, $CH_2P$), 2.52–2.60 (m, 1H, H-C9a), 2.69–2.79 and 2.83–2.90 (m, 2H, H-C4ax,6ax), 3.07–3.14 (m, 4H, $CH_2Ph$), 3.23-3.78 (m, 3H, H-C1, $CH_2OH$), 3.90–4.15 (m, 2H, H-C4eq,6eq), 7.11–7.30 (m, 10H, Ph). $^{13}$C NMR ($CDCl_3$): $\delta$ 17.0, 17.8 (C-3), 19.2, 19.7 (C-8), 21.7, 22.1 (C-7), 22.5, 22.8 (C-9), 27.3, 27.8 (C-2), 30.0 ($CH_2Ph$), 36.7, 39.3 (C-1), 44.2 (d, $^1J_{CP} = 42.9$ Hz, $CH_2P$), 44.8, 52.6 (C-6), 55.9, 56.5 (C-4), 58.6, 62.1 (C-9a), 61.2, 66.5 (C-9a), 125.3 ($C_p$ in Ph), 127.9 ($C_{o,m}$ in Ph), 142.0 (d, $^3J_{CP} = 17.3$ Hz, $C_{ipso}$ in Ph). $^{31}$P NMR ($CDCl_3$): $\delta$ 48.43 (s + d satellites, $^1J_{PSe} = 610$ Hz). $^{77}$Se NMR ($CDCl_3$), ppm: −78 (d, $^1J_{PSe} = 610$ Hz).

*Anal.* Calcd. for $C_{26}H_{38}NOPSSe$: C, 59.76; H, 7.33; N, 2.68; P, 5.93; S, 6.14; Se, 15.11. Found: C, 59.56; H 7.21; N, 2.51; P, 5.79; S, 6.08; Se, 15.04.

**X-ray Crystallographic Data for Compound 3b** ($C_{26}H_{38}NOPSSe$, $M = 522.56$) monoclinic, space group $P2_1$, $a = 12.2867(10)$ Å, $b = 9.9339(8)$ Å and $c = 12.4158(10)$ Å, $\beta = 116.041(4)$, $V = 1361.56(19)$ Å$^3$, $Z = 2$, $d_{calc} = 1.275$ g/cm$^{-3}$, $\mu(MoK_\alpha) = 1.532$ mm$^{-1}$, $(\theta)_{max} = 30.00°$, data/restraints/parameters: 7654/1/281, *R* indices: $R_1 = 0.0630$ [3847 $I > 2\sigma(I)$], $wR_2$ (all data) = 0.1736. Colorless crystals of **3b** suitable for X-ray analysis were grown from an ethanolic solution. X-ray diffractions studies were carried out on Bruker Kappa Apex II diffractometer at 296 *K* (Mo-$K_\alpha$ radiation). The structure was solved by direct methods and refined by a full matrix least-squares anisotropic procedure using SHELXTL97 programs.[28] The parameters of the hydrogen atoms were given geometrically. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk.conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 808439.

**(*S*)-2-(Pyridin-3-yl)piperidinium *bis*(2-phenethyl)thioselenophosphinate (5a)**. Obtained as a colorless viscous oil. Yield: 0.44 g (85%). $[\alpha]_D{}^{21} = -4.9$ (c 2.0, EtOH). FTIR ($cm^{-1}$): 3435 (NH), 585 (P-S), 553 (P-Se). $^1$H NMR ($CDCl_3$): $\delta$ 1.89–2.11 (m, 6H, H-C3-5 in piperidine ring), 2.26–2.37 (m, 4H, $CH_2P$), 2.85–3.00 (m, 4H, $CH_2Ph$), 3.08 (ddd, 1H, $^2J_{HH} = 12.8$ Hz, $^3J_{HH} = 9.9$ Hz, $^3J_{HH} = 3.1$ Hz, H-C6ax in piperidine ring), 3.82 (d, 1H, $^2J_{HH} = 12.8$ Hz, H-C6eq in piperidine ring), 4.22 (dd, 1H, $^3J_{HH} = 9.7$ Hz, $^3J_{HH} = 12.0$ Hz, H-C2ax in piperidine ring), 7.14-7.28 (m, 11H, Ph, H-C5 in pyridine ring), 8.02 (br. s, 2H, NH), 8.24 (d, 1H, $^3J_{HH} = 8.2$ Hz, H-C4 in pyridine ring), 8.42 (d, 1H, $^3J = 4.1$ Hz, H-C6 in pyridine ring), 8.74 (s, 1H, H-C2 in pyridine ring). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.0 (C-4 in piperidine ring), 22.8 (C-5 in piperidine ring), 30.0 ($CH_2Ph$), 30.4 (C-3 in piperidine ring), 43.8 (d, $^1J_{CP} = 43.3$ Hz, $CH_2P$), 45.4 (C-6 in piperidine ring), 58.5 (C-2 in piperidine ring),

123.9 (C-5 in Py), 125.7 ($C_p$ in Ph), 128.2 ($C_o$ in Ph), 128.2 ($C_m$ in Ph), 132.5 (C-3 in pyridine ring), 136.3 (C-4 in pyridine ring), 141.6 (d, $^3J_{CP}$ = 17.3 Hz, $C_{ipso}$ in Ph), 148.7 (C-2 in pyridine ring), 149.8 (C-6 in pyridine ring). $^{31}$P NMR ($CDCl_3$): $\delta$ 48.56 (s + d satellites $^1J_{PSe}$= 572 Hz). $^{77}$Se NMR ($CDCl_3$), ppm: −71 (d, $^1J_{PSe}$ = 572 Hz).

*Anal*. Calcd. for $C_{26}H_{33}N_2PSSe$: C, 60.57; H, 6.45; N, 5.43; P, 6.01; S, 6.22; Se, 15.32. Found: C, 60.51; C, 6.48; N, 5.54; P, 5.89; S, 6.11; Se, 15.23.

**(*S*)-2-(Pyridin-3-yl)piperidinium *bis*[2-(2-furyl)ethyl]thioselenophosphinate (5b)**. Obtained as a colorless viscous oil. Yield: 0.44 g (89%). $[\alpha]_D^{23}$ = −4.6 (c 2.0, EtOH). FTIR ($cm^{-1}$): 3344 (NH), 599 (P-S), 531 (P-Se). $^1$H NMR ($CDCl_3$): $\delta$ 1.85–2.10 (m, 6H, H-C3-5 in piperidine ring), 2.26–2.32 (m, 4H, $CH_2P$), 2.90–2.97 (m, 4H, $CH_2$Fur), 3.07 (ddd, 1H, $^2J$ = 12.4 Hz, $^3J_{HH}$ = 9.7 Hz, $^3J_{HH}$ = 2.7 Hz, H-C6ax in piperidine ring), 3.71 (d, 1H, $^2J_{HH}$ = 12.4 Hz, HC6eq in piperidine ring), 4.23 (dd, 1H, $^3J_{HH}$ = 9.2 Hz, $^3J_{HH}$ = 13.6 Hz, HC2ax in piperidine ring), 5.94 (d, 2H, $^3J_{HH}$ = 2.4 Hz, H-C4 in furan ring), 6.22 (br. s, 2H, H-C3 in furane ring), 7.24 (br. s, 2H, H-C5 in furan ring), 7.28-7.31 (m, 1H, H-C5 in pyridine ring), 8.18 (d, 1H, $^3J_{HH}$ = 7.8 Hz, H-C4 in pyridine ring), 8.39 (br. s, 2H, NH), 8.45 (d, 1H, $^3J_{HH}$ = 4.1 Hz, H-C6 in pyridine ring), 8.71 (s, 1H, H-C2 in in pyridine ring). $^{13}$C NMR ($CDCl_3$): $\delta$ 22.3 (C-4 in piperidine ring), 22.9 ($CH_2$Fur), 23.0 (C-5 in piperidine ring), 30.7 (C-3 in piperidine ring), 40.0 (d, $^1J_{CP}$ = 44.4 Hz, $CH_2P$), 45.5 (C-6 in piperidine ring), 58.6 (C-2 in piperidine ring), 104.8 (C-3 in furan ring), 110.0 (C-4 in furan ring), 124.0 (C-5 in furan ring), 133.0 (C-3 in furan ring), 136.2 (C-4 in furan ring), 140.8 (C-5 in furan ring), 148.7 (C-2 in furan ring), 149.8 (C-6 in furan ring), 141.6 (d, $^3J_{CP}$ = 20.6 Hz, C-2 in furan ring). $^{31}$P NMR ($CDCl_3$): $\delta$ 47.76 (s + d satellites $^1J_{PSe}$ = 576 Hz). $^{77}$Se NMR ($CDCl_3$): $\delta$ -78 (d, $^1J_{PSe}$ = 576 Hz).

*Anal.* Calcd. for $C_{22}H_{29}N_2O_2PSSe$: C, 53.33; H, 5.90; N, 5.65; P, 6.25; S, 6.47; Se, 15.94. Found: C, 53.16; H, 5.88; N, 5.49; P, 6.10; S, 6.34; Se, 15.78.

**(*R*)-(6-Methoxyquinolin-4-yl)[(2*S*,4*S*,8*R*)-8-vinylquinuclidin-2-yl]methanol *bis*(2-phenethyl)thioselenophosphinate (7a)**. Obtained as a white powder. Yield: 0.61 g (90%), mp. 122–125°C (ether). $[\alpha]_D^{23}$ = −4.9 (c 2.0, EtOH). FTIR ($cm^{-1}$): 3427 (OH), 3082, 3059 and 3024 (NH), 587 (P-S), 528 (P-Se). $^1$H NMR ($CDCl_3$): $\delta$ 1.22–1.27 (m, 1H, H-C3ax in quinuclidine ring), 1.76–1.84 (m, 1H, H-C4 in quinuclidine ring), 1.94–2.00 (m, 1H, H-C5ax in quinuclidine ring), 2.07–2.13 (m, 2H, H-C3eq, 5eq in quinuclidine ring), 2.43–2.50 (m, 4H, $CH_2P$), 2.64–2.71 (m, 1H, H-C8 in quinuclidine ring), 3.05–3.11 (m, 4H, $CH_2$Ph), 3.25–3.31 (m, 1H, H-C7ax in quinuclidine ring), 3.36–3.57 (m, 3H, H-C2,6ax,7eq in quinuclidine ring), 4.01 (s, 3H, MeO), 4.59–4.66 (m, 1H, H-C6eq in quinuclidine ring), 5.00 (d, 1H, $^3J_{HH}$ = 10.5 Hz, $H_2C$=), 5.05 (d, 1H, $^3J_{HH}$ = 17.0 Hz, $H_2C$=), 5.31 (br s, 2H, NH, OH), 5.54 (dddd, 1H, $^3J_{HH}$ = 10.5, 17.0 Hz, HC=), 6.81 (s, 1H, CHOH), 7.11–7.24 (m, 10H, Ph), 7.33 (d, 1H, $^3J_{HH}$ = 9.2 Hz, H-C8 in quinoline ring), 7.47 (d, 1H, $^3J_{HH}$ = 2.2 Hz, H-C5 in quinoline ring), 7.67 (d, 1H, $^3J_{HH}$ = 4.5 Hz, H-C3 in quinoline ring), 7.98 (d, 1H, $^3J_{HH}$ = 9.2 Hz, H-C7 in quinoline ring), 8.72 (d, 1H, $^3J_{HH}$ = 4.5 Hz, H-C2 in quinoline ring). $^{13}$C NMR ($CDCl_3$): $\delta$ 19.3 (C-3 in quinuclidine ring), 24.6 (C-5 in quinuclidine ring), 26.7 (C-4 in quinuclidine ring), 30.2 ($CH_2$Ph), 37.2 (C-8 in quinuclidine ring), 44.0 (d, $^1J_{CP}$ = 43.3 Hz, $CH_2P$), 45.2 (C-6 in quinuclidine ring), 54.8 (C-7 in quinuclidine ring), 57.2 (MeO), 60.0 (C-2 in quinuclidine ring), 65.9 (CHOH), 100.6 (C-5 in quinoline ring), 117.0 (=$CH_2$), 119.1 (C-7 in quinoline ring), 122.3 (C-3 in quinoline ring), 125.7 (C-9 in quinoline ring), 125.8 ($C_p$ in Ph), 128.2–128.3 ($C_{o,m}$ in Ph), 131.5 (C-8 in quinoline ring),

137.3 (HC=), 141.6 (d, $^3J_{CP} = 17.2$ Hz, $C_{ipso}$ in Ph), 143.7 (C-10 in quinoline ring), 143.9 (C-4 in quinoline ring), 147.2 (C-2 in quinoline ring), 158.6 (C-6 in quinoline ring). $^{31}$P NMR ($CDCl_3$): $\delta$ 48.63 (s + d satellites $^1J_{PSe} = 569$ Hz). $^{77}$Se NMR ($CDCl_3$): $\delta$ −73 (d, $^1J_{PSe} = 569$ Hz).

*Anal.* Calcd. for $C_{36}H_{43}N_2O_2PSSe$: C, 63.80; H, 6.40; N, 4.13; P, 4.57; S, 4.73; Se, 11.65. Found: C, 63.71; H, 6.45; N, 4.20; P, 4.46; S, 4.57; Se, 11.57.

**(*R*)-(6-Methoxyquinolin-4-yl)[(2*S*,4*S*,8*R*)-8-vinylquinuclidin-2-yl]methanol *bis*[2-(2-furyl)ethyl]thioselenophosphinate (7b)**. Obtained as colorless viscous oil. Yield: 0.51 g (78%). $[\alpha]_D^{23} = -4.7$ (c 2.0, EtOH). FTIR ($cm^{-1}$): 3236 (OH), 3114, 3083 (NH), 599 (P-S), 529 (P-Se). $^1$H NMR ($CDCl_3$): $\delta$ 1.15–1.25 (m, 1H, H-C3ax in quinuclidine ring), 1.77–1.84 (m, 1H, H-C4 in quinuclidine ring), 1.94-2.00 (dd, 1H, H-C5ax in quinuclidine ring), 2.05–2.14 (m, 2H, H-C3eq, 5eq in quinuclidine ring), 2.41–2.47 (m, 4H, $CH_2P$), 2.64–2.72 (m, 1H, H-C8 in quinuclidine ring), 3.05-3.11 (m, 4H, $CH_2Ph$), 3.22–3.35 (m, 1H, H-C7ax in quinuclidine ring), 3.37–3.53 (m, 3H, H-C2,6ax,7eq in quinuclidine ring), 3.94 (s, 3H, MeO), 4.57–4.64 (m, 1H, H-C6eq in quinuclidine ring), 4.98 (d, 1H, $^3J_{HH} =$ 10.5 Hz, $H_2C$=), 5.03 (d, 1H, $^3J_{HH} = 17.1$ Hz, $H_2C$=), 5.40 (br s, 2H, NH, OH), 5.51 (dddd, 1H, $^3J_{HH} = 10.5$, 17.1 Hz, HC=), 5.93 (br s, 2H, H-C4 in furan), 6.19 (br. s, 2H, H-C3 in furan), 6.75 (s, 1H, CHOH), 7.22 (br. s, 2H, H-C5 in furan), 7.28 (dd, 1H, $^3J_{HH} = 2.4$, 9.1 Hz, H-C8 in quinoline ring), 7.35 (d, 1H, $^3J_{HH} = 2.3$ Hz, H-C5 in quinoline ring), 7.65 (d, 1H, $^3J_{HH} = 4.5$ Hz, H-C3 in quinoline ring), 7.94 (d, 1H, $^3J_{HH} = 9.1$ Hz, H-C7 in quinoline ring), 8.70 (d, 1H, $^3J_{HH} = 4.5$ Hz, H-C2 in quinoline ring). $^{13}$C NMR ($CDCl_3$): $\delta$ 19.2 (C-3 in quinuclidine ring), 23.0 ($CH_2$Fur), 24.5 (C-5 in quinuclidine ring), 26.6 (C-4 in quinuclidine ring), 37.1 (C-8 in quinuclidine ring), 40.1 (d, $^1J_{CP} = 45.0$ Hz, $CH_2P$), 45.2 (C-6 in quinuclidine ring), 54.8 (C-7 in quinuclidine ring), 57.1 (MeO), 59.9 (C-2 in quinuclidine ring), 65.7 (CHOH), 100.5 (C-5 in quinoline ring), 104.9 (C-3 in Fur), 110.0 (C-4 in furan), 117.1 (=$CH_2$), 119.1 (C-7 in quinoline ring), 122.4 (C-3 in quinoline ring), 125.6 (C-9 in quinoline ring), 131.5 (C-8 in quinoline ring), 137.1 (=CH), 140.9 (C-5 in furan), 143.4 (C-10 in quinoline ring), 143.9 (C-4 in quinoline ring), 147.1 (C-2 in quinoline ring), 154.8 (d, $^3J_{CP} = 20.1$ Hz, C-2 in furan), 158.5 (C-6 in quinoline ring). $^{31}$P NMR ($CDCl_3$): $\delta$ 47.87 (s + d satellites $^1J_{PSe} = 573$ Hz). $^{77}$Se NMR ($CDCl_3$pp): $\delta$ −67 (d, $^1J_{PSe} = 573$ Hz).

*Anal.* Calcd. for $C_{32}H_{39}N_2O_4PSSe$: C, 58.44; H, 5.98; N, 4.26; P, 4.71; S, 4.88; Se, 12.01. Found: C, 58.50; H, 5.90; N, 4.21; P, 4.63; S, 4.79; Se, 11.55.



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