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Diselenophosphinates of lupinine or anabasine via a new three-component reaction of secondary phosphines, elemental selenium, and amines

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ABSTRACT

Secondary phosphines, elemental selenium, and the natural alkaloids, lupinine and anabasine, interact in a three-component-type reaction under mild conditions (70 °C, 1–1.5 h, EtOH) without the formation of any by-products to give diselenophosphinates of the above-mentioned alkaloids (in almost quantitative yields) with the retention of their intrinsic optical activity. Thus, the developed synthesis represents an atom-economic route to new selenophosphorus derivatives of alkaloids.

The alkaloids lupinine and anabasine, which can be easily extracted from natural products,[1] possess a wide spectrum of biological activity[2,3] and are used as precursors for drug design and pesticide preparation. For example, anabasine hydrochloride is employed in medicine as an antismoking agent,[4] anabasine sulfate is an efficient insecticide,[5] and lupicaine (a lupinine derivative) exhibits anesthetic action.[6] Among the phosphorylated derivatives of lupinine and anabasine are compounds showing antitumor, antituberculosis, hepatoprotective, antiviral, antibacterial, antifungal, anticholinesterase, anthelmintic, and other activities.[7,8] Examples of lupinine and anabasine derivatives containing a diselenophosphinate group (Se_2PR_2) are lacking in the literature.

It should be emphasized that selenium itself is a biologically important element and occurs as a key active factor in several drugs.[9] Therefore, combination of these pharmacophore functions with molecules of lupinine and anabasine should allow promising new drug candidates and/or precursors to be developed. Thus, the synthesis and investigations of lupinine and anabasine derivatives functionalized with diselenophosphinate moieties represent an interesting research area.

In this Letter, we report on the direct one-pot synthesis of derivatives of lupinine **1a** and anabasine **1b** containing a diselenophosphinate group via a recently discovered[10] three-component reaction between secondary phosphines, elemental selenium, and amines.

We found that lupinine **1a** reacts with secondary phosphines **2a**,**b** and elemental selenium under mild conditions (70 °C, 1 h, EtOH) quantitatively (^{31}P NMR) to give the diselenophosphinates of lupinine, **3a**,**b** in 91% and 89% isolated yields, respectively[11] (Scheme 1).

The reaction of natural anabasine **1b**, secondary phosphines **2a**,**c**, and elemental selenium proceeds under similar conditions (70 °C, 1.5 h, EtOH) to afford salts **3c**,**d** (according to literature data,[12] including X-ray analysis, anabasine is regiospecifically protonated at the piperidine nitrogen) in high yields[11] (Scheme 2).

The site of protonation in salts **3c**,**d** is supported by their ^{13}C NMR spectra: the chemical shifts of the pyridine carbon atoms of salts **3c**,**d** are close to those of free anabasine **1b**.[12]

Owing to the mild reaction conditions the intrinsic optical activity of the starting natural alkaloids is retained. The value of the specific rotation for lupinine released from salt **3a** under the action of NaOH (rt, EtOH) was the same as for authentic lupinine ($[\alpha]_D^{24}$ −1.77, *c* 4.0% in EtOH).

The secondary phosphines **2** employed in this work are readily available from the reaction of elemental phosphorus with the corresponding electrophiles (styrene,[13] 4-*t*-butylstyrene[14] or 2-vinylfuran[13]) in superbase systems.

The reactions described herein (Schemes 1 and 2) are not accompanied by the formation of any by-products and hence are

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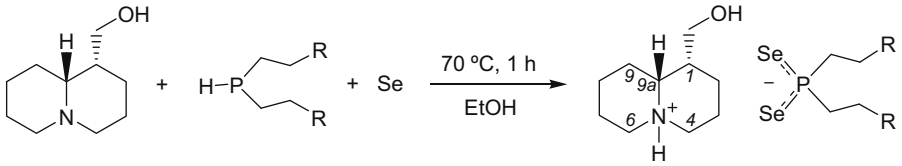
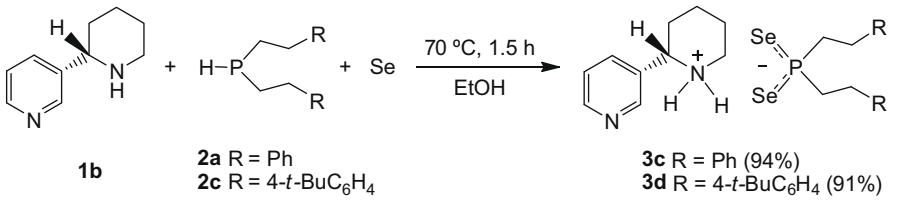


Scheme 1.



Scheme 2.

atom-economic and 'green' (ethanol, a non-toxic recoverable solvent is used).

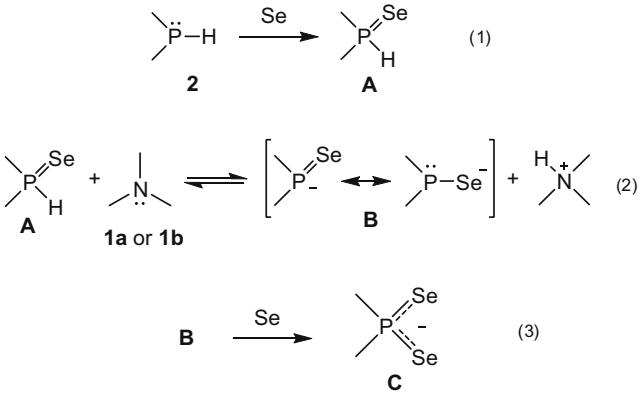
A probable mechanism for the formation of diselenophosphinates **3** is shown in Scheme 3. In the first stage (1), the secondary phosphine **2** reacts with one equivalent of elemental selenium to give secondary phosphine selenide **A**. The latter is deprotonated by the nitrogen base (lupinine **1a** or anabasine **1b**) to afford P,Se-ambident selenophosphinite anion **B** (stage 2), which reacts with a second equivalent of elemental selenium to provide the diselenophosphinate anion **C** (stage 3).

All the compounds synthesized are stable to air, are poorly soluble in water and highly soluble in organic solvents (EtOH, THF, DMSO). Lupininium salts **3a**,**b** are crystalline solids, whereas anabasinium salts **3c**,**d** are oils. Their structures have been established by single-crystal X-ray diffraction analysis and/or multinuclear (^{1}H, ^{13}C, ^{31}P and ^{77}Se) NMR spectroscopy.

The molecular structure of the salt **3a** consists of an anion of the bis(2-phenethyl)diselenophosphinic acid and a protonated lupinine cation (Fig. 1).[15] The geometry of the anion is characterized by high symmetry with respect to the phosphorus atom and differs substantially from that of the same anion in the salt, 4-aza-1-azoniabicyclo[2.2.2]octane bis(2-phenethyl)diselenophosphinate, studied previously.[16]

Torsion angles in the anion are PC(11)C(12)C(15) = 171.7(8)°; PC(13)C(14)C(21) = 177.1(7)°; C(13)PC(11)C(12) = 173.4(8)°. The dihedral angle between the six-membered rings is equal to 86.3(3)°. Maximum deviations out of the plane of the six-membered rings are 0.01 Å for C(20) of the C(15)C(16)···C(20) ring and 0.01 Å for C(26) of the C(21)C(22)···C(26) ring. The bond distances are as follows: P–Se(1) = 2.136(3) Å, P–Se(2) = 2.153(3) Å, P–C(11) = 1.800(4) Å, P–C(13) = 1.799(4) Å. The angles at the P atom are: C(11)–P–C(13) = 102.0(5)°, C(13)–P–Se(1) = 111.5(4)°, C(11)–P–Se(1) = ···110(4)°, C(13)–P–Se(2) = 109.1(4)°, C(11)–P–Se(2) = 106.5(4)°, Se(1)–P–Se(2) = 116.57(15)°. The values of the P–Se(1) and P–Se(2) bond distances in the anion are similar which can indicate to delocalization of the double bond, as has been observed for analogous compounds of four-coordinated phosphorus. Both six-membered rings of the lupinine cation adopt a chair conformation. The cation is significantly distorted unlike neutral lupinine,[17] and is similar to the methyl-substituted cation in iodomethylate salts.[18]

A fragment of the crystal structure of compound **3a** is shown in Figure 2. The cations and anions are bound by short intermolecular bonding O(1)···Se(2) 3.26(1) Å and N(1)···Se(2) 3.360(8) (sum of van der Waals radii: O···Se = 3.40 Å, N···Se = 3.50 Å[19]).



Scheme 3.

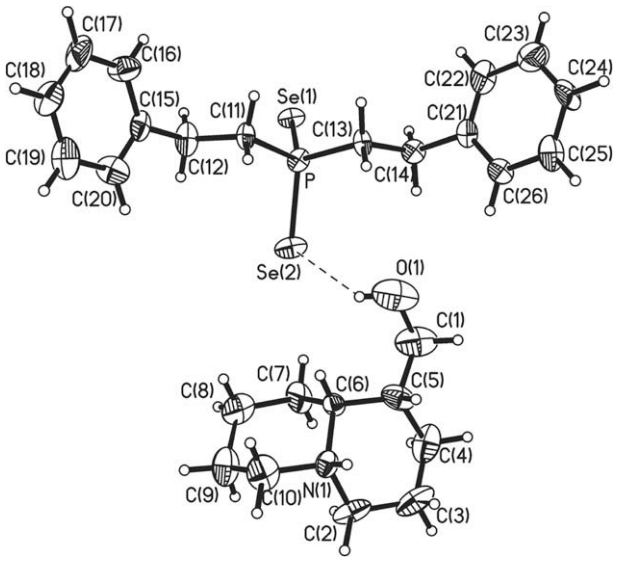


Figure 1. ORTEP diagram of **3a**.

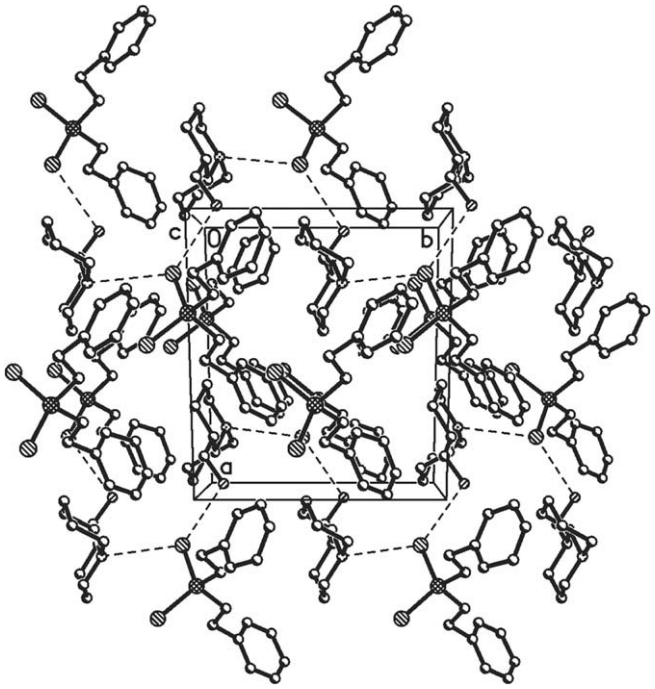


Figure 2. Packing diagram of the structure of **3a**.

In conclusion, a three-component reaction between secondary phosphines, elemental selenium, and natural lupinine or anabasine has been shown to be a convenient one-pot, atom-economic route to optically active diselenophosphinates of alkaloids, as potential drug candidates and/or precursors for the synthesis of pharmaceutically important compounds.

Acknowledgments

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11. *Experimental procedure*: Amorphous grey selenium (0.158 g, 2 mmol) was added to a solution of phosphine **2** (1.1 mmol) in EtOH (5 mL) at 70 °C under argon. Lupinine **1a** (0.169 g, 1 mmol) or anabasine **1b** (0.162 g, 1 mmol) in EtOH (2 mL) was added to the stirred suspension which was stirred until complete dissolution of selenium (ca. 1–1.5 h) at 70 °C; this gave a colorless, transparent soln. The solvent was removed under reduced pressure and the residue was washed with cold Et_2O (6 mL × 1) and dried in vacuo (1 Torr, rt) to give salts **3**.
Compound **3a**: *(1R,9aR)-1-(hydroxymethyl)octahydro-2H-quinolizinium bis(2-phenylethyl)diselenophosphinate*: colorless crystalline powder, yield 0.518 g (91%), mp 164–167 °C (EtOH), $[\alpha]_D^{21}$ −19.1 (*c* 2.0, EtOH). IR (KBr, ν/cm^{-1}): 3335, 3083, 3061, 2943, 2865, 2838, 2727, 1601, 1583, 1496, 1451, 1432, 1425, 1408, 1396, 1378, 1362, 1348, 1334, 1314, 1298, 1270, 1260, 1212, 1198, 1188, 1158, 1124, 1106, 1076, 1056, 1047, 1024, 1013, 986, 968, 946, 930, 906, 894, 877, 859, 834, 825, 808, 764, 751, 735, 713, 695, 596, 579, 509, 481, 382. ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm), δ: 1.15–1.25 (m, 1H, H-C^8), 1.61–1.93 (m, 10H, H-C$^{2,3,4ax,7-9}$), 2.20–2.53 (m, 1H, H-C^{6ax}), 2.55–2.62 (m, 4H, CH_2P), 2.68–2.73 (m, 1H, H-C^1), 2.90–2.97 (m, 1H, H-C^{9a}), 3.11–3.17 (m, 4H, CH_2Ph), 3.35–3.40 (m, 1H, H-C^{6eq}), 3.50–3.70 (m, 1H, H-C^{4eq}), 3.78–4.16 (m, 2H, CH_2OH), 7.16–7.37 (m, 10H, Ph), 9.50 (s, 2H, NH, OH). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm), δ: 17.77 and 18.53 (C-3), 19.92 and 20.49 (C-8), 22.46 and 22.85 (C-7), 23.19 and 23.50 (C-9), 28.03 and 28.75 (C-2), 31.27 (CH_2Ph), 37.27 and 40.07 (C-1), 44.53 (d, $^1J_{P,C}$ = 36.4 Hz, CH_2P), 45.65 and 53.53 (C-6), 56.61 and 57.20 (C-4), 59.45 (C-10), 62.05 (C-9a), 62.85 (C-10), 67.27 (C-9a), 126.10 (C-*p* in Ph), 128.63, 128.69 (C-*o*,*m* in Ph), 142.17 (d, $^3J_{P,C}$ = 17.2 Hz, C-*i* in Ph). ^{31}P NMR (161.98 MHz, $CDCl_3$, ppm), δ: 25.13 (satellites $^1J_{P,Se}$ = 573 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$, ppm), δ: −59.40 (d, $^1J_{P,Se}$ = 573 Hz). Calcd for $C_{26}H_{38}NOPSe_2$ (%): C, 54.84; H, 6.73; N, 2.46; P, 5.44; Se, 27.73. Found (%): C, 54.90; H, 6.76; N, 2.40; P, 5.38; Se, 27.70. In the ^{13}C NMR spectra of salts **3a**,**b**, the presence of two signals for all the carbon atoms in the lupinine unit is due to the equilibrium (in solution) between two protonated forms of this alkaloid (s-*cis* and s-*trans*), which differ in the spatial location of the proton conjugated with nitrogen atom. Similar duplication of signals in the ^{13}C NMR spectra of known salts of lupinine (for example, in the ^{13}C NMR spectrum of lupinine hydrochloride) has been reported.[20]
Compound **3b**: *(1R,9aR)-1-(hydroxymethyl)octahydro-2H-quinolizinium bis[2-(2-furyl)ethyl]diselenophos-phinate*: colorless crystalline powder, yield 0.489 g (89%), mp 90–92 °C (EtOH), $[\alpha]_D^{21}$ −9.6 (*c* 2.0, EtOH). IR (KBr, ν/cm^{-1}): 3332, 2927, 2889, 2855, 2720, 2700, 2653, 2590, 1727, 1656, 1638, 1628, 1588, 1543, 1506, 1472, 1448, 1410, 1371, 1357, 1338, 1330, 1312, 1282, 1265, 1230, 1218, 1166, 1147, 1128, 1105, 1074, 1059, 1048, 1024, 1008, 969, 947, 932, 910, 883, 858, 844, 825, 807, 793, 756, 743, 732, 696, 678, 598, 584, 548, 499, 478, 455. ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm), δ: 1.15–1.25 (m, 1H, H-C^8), 1.40–2.08 (m, 10H, H-C$^{2,3,4ax,7-9}$), 2.16–2.40 (m, 1H, H-C^{6ax}), 2.51–2.60 (m, 4H, CH_2P), 2.61–2.69 (m, 1H, H-C^1), 2.98–3.06 (m, 1H, H-C^{9a}), 3.10–3.16 (m, 4H, CH_2Fur), 3.25–3.50 (m, 1H, H-C^{6eq}), 3.60–3.75 (m, 1H, H-C^{4eq}), 3.78–4.10 (m, 2H, CH_2OH), 6.01–6.02 (m, 2H, H-C^2 in Fur), 6.25–6.26 (m, 2H, H-C^3 in Fur), 7.28–7.29 (m, 2H, H-C^4 in Fur), 9.30 (s, 2H, NH, OH). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm), δ: 17.35 and 18.13 (C-3), 19.50 and 20.06 (C-8), 22.04 and 22.43 (C-7), 22.73 and 23.12 (C-9), 23.68 (CH_2 Fur), 27.65 and 28.23 (C-2), 36.62 and 39.72 (C-1), 40.30 (d, $^1J_{P,C}$ = 38.1 Hz, CH_2P), 45.78 and 53.13 (C-6), 56.15 and 56.71 (C-4), 59.08 (C-10), 61.73 (C-9a), 62.35 (C-10), 66.78 (C-9a), 104.76 (C-2 in Fur), 109.99 (C-3 in Fur), 140.70 (C-4 in Fur), 155.10 (d, $^3J_{P,C}$ = 20.3 Hz, C-1 in Fur). ^{31}P NMR (161.98 MHz, $CDCl_3$, ppm), δ: 23.60 (satellites $^1J_{P,Se}$ = 581 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$, ppm), δ: −60.10 (d, $^1J_{P,Se}$ = 581 Hz). Calcd for $C_{22}H_{34}NO_3PSe_2$ (%): C, 48.09; H, 6.24; N, 2.55; P, 5.64; Se, 28.74. Found (%): C, 48.11; H, 6.26; N, 2.56; P, 5.50; Se, 28.63.
Compound **3c**: *(S)-2-(pyridin-3-yl)piperidinium bis(2-phenylethyl)diselenophosphinate*: colorless oil, yield: 0.529 g (94%), $[\alpha]_D^{21}$ −4.9 (*c* 2.0, EtOH). IR (film, ν/cm^{-1}): 3354, 3083, 3025, 2922, 2851, 2352, 2197, 1951, 1881, 1811, 1751, 1602, 1581, 1496, 1454, 1434, 1326, 1298, 1280, 1263, 1206, 1193, 1153, 1126, 1102, 1077, 1049, 1029, 944, 910, 835, 807, 757, 663, 643, 631, 618, 574, 507, 478, 444. ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm), δ: 1.75–2.05 (m, 6H, H-C$^{3-5}$), 2.03–2.37 (m, 4H, CH_2P), 2.83–2.90 (m, 4H, CH_2Ph), 3.02 (ddd, 1H, ^2J = 12.8 Hz, ^3J = 9.6 Hz, ^3J = 2.9 Hz, H$_{ax}$C^6), 3.67 (d, 1H, ^2J = 12.8 Hz, H$_{eq}$C^6), 4.22 (d, 1H, ^3J = 10.5 Hz, H$_{ax}$C^2), 7.05–7.15 (m, 11H in Ph, H-C^5 in Py), 8.13 (d, 1H, ^3J = 8.2 Hz, H-C^4 in Py), 8.29 (d, 1H, ^3J = 4.7 Hz, H-C^6 in Py), 8.69 (s, 1H, H-C^2 in Py), 9.08 (s, 2H, NH). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm), δ: 22.35 (C-4), 23.05 (C-5), 30.85 (CH_2Ph, C-3), 44.79 (d, $^1J_{P,C}$ = 36.5 Hz, CH_2P), 45.52 (C-6), 58.63 (C-2), 124.06 (C-5 in Py), 125.94 (C-*p* in Ph), 128.38 (C-*o* in Ph), 128.41 (C-*m* in Ph), 133.12 (C-3 in Py), 136.34 (C-4 in Py), 141.61 (d, $^3J_{P,C}$ = 17.2 Hz, C-*i* in Ph), 148.92 (C-2 in Py), 149.86 (C-6 in Py). ^{31}P NMR (161.98 MHz, $CDCl_3$, ppm), δ: 25.49 (satellites $^1J_{P,Se}$ = 573 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$, ppm), δ: −68.56 (d, $^1J_{P,Se}$ = 573 Hz). Calcd for $C_{26}H_{33}N_2PSe_2$ (%): C, 55.52; H, 5.91; N, 4.98; P, 5.51; Se, 28.08. Found (%): C, 55.58; H, 6.00; N, 4.94; P, 5.39; Se, 28.04.
Compound **3d**: *(S)-2-(pyridin-3-yl)piperidinium bis[2-(4-tertbutylphenyl)ethyl] -diselenophosphinate*: colorless oil, yield: 0.614 g (91%), $[\alpha]_D^{21}$ −4.1 (*c* 2.0, EtOH). IR (film, ν/cm^{-1}): 3443, 2959, 2904, 2864, 2804, 2774, 2705, 1633, 1596, 1577, 1516, 1463, 1444, 1432, 1416, 1363, 1326, 1294, 1268, 1201, 1132, 1108, 1077, 1048, 1017, 1008, 941, 910, 875, 853, 838, 812, 769, 730, 710, 661, 631, 616, 563, 526, 493, 443. ^{1}H NMR (400.13 MHz, $CDCl_3$, ppm), δ: 1.28 (s, 18H, Me), 1.90–2.15 (m, 6H, H-C$^{3-5}$), 2.39–2.45 (m, 4H, CH_2P), 2.90–2.96 (m, 4H, CH_2Ph), 3.10 (t, 1H, ^2J = 11.2 Hz, H$_{ax}$C^6), 3.84 (d, 1H, ^2J = 11.2 Hz, H$_{eq}$C^6), 4.27 (d, 1H, ^3J = 12.0 Hz,

$H_{ax}C^2$), 7.11–7.27 (m, 9H in C_6H_4, H-C^5 in Py), 8.26 (d, 1H, ^3J = 7.5 Hz, H-C^4 in Py), 8.45 (d, 1H, ^3J = 3.8 Hz, H-C^6 in Py), 8.55 (s, 2H, NH), 8.76 (s, 1H, H-C^2 in Py). ^{13}C NMR (100.62 MHz, $CDCl_3$, ppm), δ: 22.19 (C-4), 22.97 (C-5), 30.21 (CH_2Ph), 30.66 (C-3), 31.29 (Me), 34.21 (*C*Me), 43.74 (d, $^1J_{P,C}$ = 39.4 Hz, CH_2P), 45.41 (C-6), 58.60 (C-2), 123.92 (C-5 in Py), 125.15 (C-*o* in C_6H_4), 127.97 (C-*m* in C_6H_4), 132.78 (C-3 in Py), 136.29 (C-4 in Py), 138.46 (d, $^3J_{P,C}$ = 18.9 Hz, C-*i* in C_6H_4), 148.57 (C-2 in Py), 148.87 (C-*p* in C_6H_4), 149.87 (C-6 in Py). ^{31}P NMR (161.98 MHz, $CDCl_3$, ppm), δ: 25.95 (satellites $^1J_{P,Se}$ = 570 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$, ppm), δ: −69.51 (d, $^1J_{P,Se}$ = 570 Hz). Calcd for $C_{34}H_{49}N_2PSe_2$ (%): C, 60.53; H, 7.32; N, 4.15; P, 4.59; Se, 23.41. Found (%): C, 60.58; H, 7.20; N, 4.10; P, 4.40; Se, 23.44.

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15. *X-ray crystallographic data for compound* **3a**. $C_{26}H_{38}NOPSe_2$, M_r = 569.48, monoclinic, space group $P2_1$, a = 12.278(2), b = 9.879(2) and c = 12.307(2), β = 115.465(3)°, V = 1347.8(4) Å^3, Z = 2, d_{calc} = 1.40 g cm^{-3}, μ(MoK$_\alpha$) = 2.820 mm^{-1}. X-ray diffraction studies were carried out using a Bruker SMART APEX2 CCD diffractometer at 200 *K* (Mo-K$_\alpha$ radiation). The number of measured reflections = 10,289, the number of independent reflections = 4524, the number of refined parameters = 280, R-factor 0.110 for 2277 reflections with [$F_0 > 4\sigma(F_0)$]. The crystal structure was solved by direct methods followed with Fourier synthesis using SHELX-97.[21] The structure was refined using full-matrix least-square anisotropic approximation for all non-hydrogen atoms with SHELXL-97.[21] Coordinates of hydrogen atoms were defined experimentally and refined isotropically. 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 754636.
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