Efficient General Synthesis of Alkylammonium Diselenophosphinates via Multicomponent One-Pot Reaction of Secondary Phosphines with Elemental Selenium and Amines

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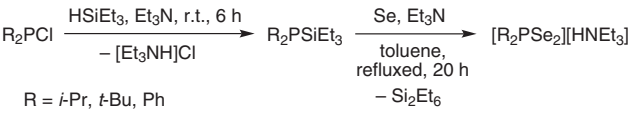
Abstract: The multicomponent reaction between secondary phosphines, elemental selenium, and primary, secondary, or tertiary amines is accomplished efficiently in ethanol (60 °C, 0.5 h) to give the corresponding mono-, di-, or trialkylammonium diselenophosphinates in high yield (up to 97%).

Key words: secondary phosphines, elemental selenium, amines, three-component reaction, diselenophosphinates

In recent years, the chemistry of diselenophosphinates has received special attention due to their potential and practical applications as SSPs (single-source precursors) of magneto-optical and semiconducting nanomaterials,[1] ligands for metal complexes,[2] building blocks for organic and elemento-organic synthesis,[3] promising extractants of heavy elements,[4] and prospective pharmaceutical compounds.[5] For example, heavy metal diselenophosphinates are now employed as efficient SSPs for the preparation of metal phosphide or selenide nanoparticles possessing many unique properties.[6] Nickel and cobalt dialkyldiselenophosphinates are used for the synthesis of phosphide or selenide nanoparticles with good electrical, semiconductive, and magnetic properties.[7] Silver diselenophosphinate is employed as an SSP to obtain silver selenide nanofilms.[8] Europium diselenophosphinates are actively applied to design europium selenide nanocrystals showing remarkable magneto-optical properties.[9] Nanorods of zinc selenide exhibiting semiconductive properties have been synthesized from zinc diselenophosphinate.[10] In 2010, P. O'Brien et. al. developed the efficient synthesis of $CoSe_2$, CoP, or Co_2P nanoparticles from cobalt diselenophosphinates, $[Co(Se_2PR_2)_2]$.[11]

The convenient syntheses of the aforementioned heavy metal diselenophosphinates are based on the reaction of alkylammonium diselenophosphinates with heavy metal halides.[7–11] In addition, alkylammonium diselenophosphinates are key intermediates in the synthesis of *Se*-esters of diselenophosphinic acids.[3] The latter represent efficient iniferters[12] and prospective pesticides.[13] One might expect that alkylammonium diselenophosphinates will also possess features typical for ammonium compounds, including those applied in pharmaceutics as well as protonic ionic liquids.[14]

At the same time, the conventional synthesis of alkylammonium diselenophosphinates is multistep and laborious and requires aggressive and poisonous phosphorus halides and flammable unstable organometallic reactants.[10] Triethylammonium diselenophosphinates were prepared by the multistep reaction of toxic and unavailable monochlorophosphines R_2PCl with triethylsilane, triethylamine, and selenium in toluene by reflux for period of ca. 20 hours.[10] Furthermore, the reaction resulted in some byproducts together with the target compounds (Scheme 1).



Scheme 1 Preparation of triethylammonium diselenophosphinates from R_2PCl, triethylsilane, triethylamine and selenium[10]

Recently, a facile synthesis of alkylammonium diselenophosphinates from secondary phosphine selenides, $R_2P(Se)H$, elemental selenium, and amines was reported.[15] Secondary phosphine selenides were obtained by the oxidation of secondary phosphines R_2PH by elemental selenium. The data on the possible variation in the secondary phosphines in this reaction are limited in the short communication which covers only the reaction of bis(2-phenylethyl)phosphine with selenium and diethylamine or diisopropylamine.[16] Therefore, the scope and synthetic importance of this synthesis have not been examined. In particular, it is unclear what amines and secondary phosphines can be employed in this synthesis.

Thus, the aim of this work is to evaluate the true generality of this promising reaction. We have systematically studied the reaction of various secondary phosphines with elemental selenium and primary, secondary, or tertiary amines.

The experiments have shown that the three-component reaction between secondary phosphines **1**–**8**, elemental selenium, and amines proceeds under mild conditions (60

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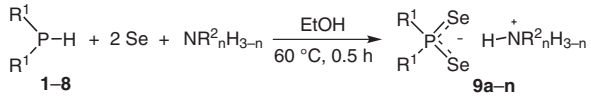
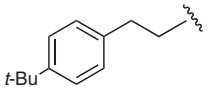
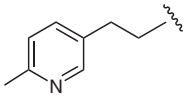
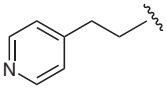
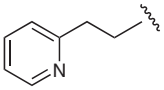
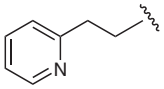
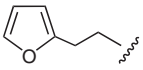
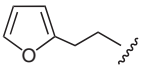
Table 1 One-Pot Synthesis of Alkylammonium Diselenophosphinates from Secondary Phosphines, Elemental Selenium, and Amines



Entry	Phosphine	R^1	Amine, $NR^2_nH_{3-n}$	Product	Yield[a] (%)
1	**1**	Ph	Et_3N	**9a**	92
2	**1**	Ph	allylNH_2	**9b**	97
3	**2**	$(CH_2)_2Ph$	Et_3N	**9c**	88
4	**2**	$(CH_2)_2Ph$	Et_2NH	**9d**	91
5	**2**	$(CH_2)_2Ph$	*i*-Pr_2NH	**9e**	94
6	**2**	$(CH_2)_2Ph$	allylNH_2	**9f**	85
7	**3**	$CH_2CH(Me)Ph$	*i*-Pr_2NH	**9g**	87
8	**4**		Et_3N	**9h**	85
9	**5**		Pr_2NH	**9i**	94
10	**6**		Et_3N	**9j**	91
11	**7**		Et_3N	**9k**	89
12	**7**		allylNH_2	**9l**	94
13	**8**		Et_3N	**9m**	87
14	**8**		allylNH_2	**9n**	96

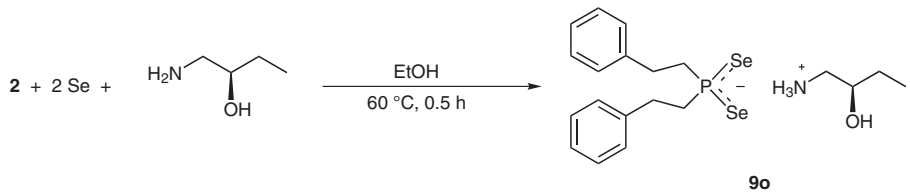
[a] All yields refer to isolated products.

°C, 0.5 h) in ethanol to afford diselenophosphinates **9a**–**n** in 85–97% yields (Table 1).

As seen from Table 1, the reaction was found to be of general character. Various secondary phosphines with aryl, arylalkyl, and hetarylalkyl substituents as well as primary, secondary, and tertiary amines including an unsaturated one participate readily in this three-component reaction.

The general character of the reaction is additionally supported by the fact that chiral and functional amines can also be employed in this reaction. For example, secondary phosphine **2** easily reacts with elemental selenium and optically active (*R*)-1-aminobutan-2-ol (EtOH, 60 °C, 0.5 h) to furnish diselenophosphinate **9o** in 86% yield (Scheme 2).

The choice of initial secondary phosphines **2**–**8** is not arbitrary since these phosphines are now easily prepared



Scheme 2 Synthesis of optically active diselenophosphinate **9o**

from red phosphorus and vinylarenes or vinylhetarenes (e.g., styrenes,[17] vinylpyridines,[18] 2-vinylfuran[17]) in one step.

The synthesized salts are crystalline colorless compounds that are soluble in most organic solvents (acetone, MeCN, $CHCl_3$, DMSO, EtOH, MeOH), but they are insoluble in water. Their structure unambiguously follows from X-ray analysis data and ^{31}P, ^{77}Se, ^{1}H, and ^{13}C NMR spectra.

X-ray diffraction studies of diselenophosphinates **9d**,**e** have shown that the molecular structure of these salts is formed by the anion of the bis(2-phenylethyl)diselenophosphinic acid and cation of diethylammonium or diisopropylammonium, respectively (Figure 1 and Figure 2). The geometry of the anion in compounds **9d**,**e** is characterized by high symmetry relative to the phosphorus atom. The coordination geometry around phosphorus is a distorted tetrahedral with the bond angles ranging between 102.4 and 114.46°. The P–Se bond lengths of 2.130–2.158 Å are intermediate between those expected for P–Se single (2.26 Å)[19] and P=Se (2.09 Å)[20] bonds and it is indicative of delocalization of the negative charge across the PSe_2 unit and a P–Se bond order of 1.5. This delocalization can also be observed in solution using ^{31}P NMR spectroscopy from the $^{1}J_{PSe}$ coupling constant (556–621 Hz), which is midway between the expected values for P–Se (200–600 Hz) and P=Se (800–1200 Hz) bonds.[21] In the ^{77}Se NMR spectra, the doublet with $^{1}J_{SeP}$ = 556–621 Hz at δ = 24–(–76) confirms also the chemical equivalency of both selenium atoms of the PSe_2 fragment. The IR spectrum of the compounds synthesized shows strong absorptions at 530–560 and 460–470 cm^{-1} which can be assigned to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the PSe_2 groups. The elemental analysis of all the compounds isolated corresponds to their structures.

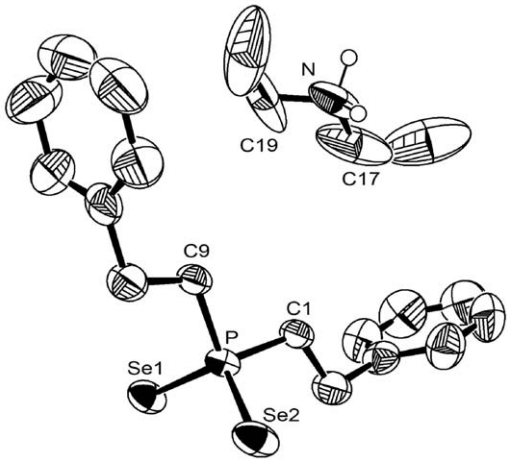
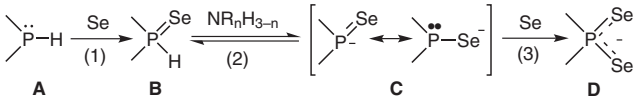


Figure 1 Thermal ellipsoid plot (50% probability) of the structure of **9d**

The tentative mechanism of the formation of diselenophosphinates can be rationalized as follows (Scheme 3). In the first stage (1), the secondary phosphine **A** reacts with one equivalent of elemental selenium to give secondary phosphine selenide **B**. The latter is deprotonated by the amine to afford selenophosphinite anion **C** (stage 2), which further reacts with a second equivalent of elemental selenium to provide the diselenophosphinate anion **D** (stage 3).



Scheme 3 Probable mechanism of alkylammonium diselenophosphinates formation

To summarize, a general and efficient operationally convenient protocol of the multicomponent reaction between various secondary phosphines, elemental selenium, and aliphatic amines to give mono-, di-, or trialkylammonium diselenophosphinates ensembles has been elaborated. The reaction proceeds under mild conditions (EtOH, 60 °C, 0.5 h) affording the target diselenophosphinates in high yields. The diselenophosphinates that have now become available due to the methodology developed herein represent highly potent precursors for the preparation of magneto-optical and semiconducting nanomaterials,[1] ligands for design of coordination structures,[2] and promising building blocks for elemento-organic synthesis.[3]

All steps of the experiment were carried out under a dry inert atmosphere (argon). Brand EtOH was used in the reaction as a solvent without additional purification. Ph_2PH (**1**) was employed as commercial product (Aldrich). Secondary phosphines **2–8** were prepared from styrene,[17a] α-methylstyrene,[17a] 4-*tert*-butylstyrene,[17b] 2-vinylpyridine,[18] 4-vinylpyridine,[18] 2-methyl-5-vinylpyridine,[18] or 2-vinylfuran[17a] and red phosphorus as described in the literature. The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 and 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). IR spectra were run on a Bruker IFS 25 in-

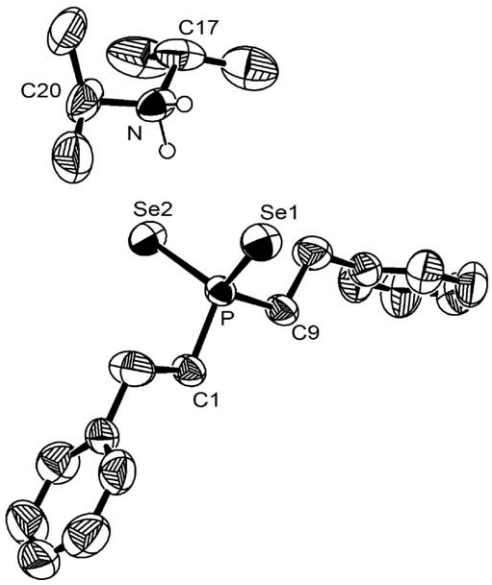


Figure 2 Thermal ellipsoid plot (50% probability) of the structure of **9e**

strument. Melting points were measured on a Kofler micro hot stage apparatus.

X-ray Crystallography of 9d,e

X-ray diffractions studies were carried out with an Xcalibur Oxford Diffraction diffractometer. The crystal structure was solved by direct methods followed with Fourier synthesis using SHELXS-97.[22] All non-hydrogen atoms were refined using anisotropic full-matrix approximation using SHELXL-97.[22] The coordinates of the hydrogen atoms were calculated from geometrical positions.[23]

Crystal data and structural refinement for **9d***:* $C_{20}H_{30}NPSe_2$, $M = 473.34$, $T = 302$ K, orthorhombic, $P2_12_12_1$, $a = 9.7085(3)$ Å, $b = 12.7313$ Å, $c = 18.8589(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2330.99(13)$ Å^3, $Z = 4$, $D_{calc} = 1.349$ g·cm^{-3}, $\mu = 3.243$ mm^{-1}, $(2\theta)_{max} = 26.37°$, reflections measured 8939, reflections independent 4760, 224 parameters refined, final R indices [$I > 2\sigma(I)$] $R1 = 0.0281$, w$R2 = 0.0496$. Selected bond lengths (Å): C1–P: 1.804(3), C9–P: 1.820(3), P–Se1: 2.1432(9), P–Se2: 2.1478(8), N–H: 0.91(4), 0.99(4). Selected bond angles (°): Se1–P–C9: 109.84(10), Se1–P–C1: 108.83(10), Se2–P–C9: 110.37(10), Se2–P–C1: 109.80(10), Se1–P–Se2: 116.12(3), C1–P–C9: 100.77(13).

Crystal data and structural refinement for **9e***:* $C_{22}H_{34}NPSe_2$, $M = 501.39$, $T = 302$ K, monoclinic, $P2_1/c$, $a = 12.668(3)$ Å, $b = 6.4258(8)$ Å, $c = 30.342(8)$ Å, $\alpha = 90°$, $\beta = 91.16(3)°$, $\gamma = 90°$, $V = 2469.4(9)$ Å^3, $Z = 4$, $D_{calc} = 1.349$ g·cm^{-3}, $\mu = 3.065$ mm^{-1}, $(2\theta)_{max} = 26.37°$, reflections measured 9304, reflections independent 4983, 245 parameters refined, final R indices [$I > 2\sigma(I)$] $R1 = 0.0629$, w$R2 = 0.1275$. Selected bond lengths (Å): C1–P: 1.822(5), C9–P: 1.812(5), P–Se1: 2.1303(14), P–Se2: 2.1582(15), N–H: 0.83(6), 1.06(6). Selected bond angles (°): Se1–P–C9: 110.46(19), Se1–P–C1: 110.65(18), Se2–P–C9: 109.0(2), Se2–P–C1: 109.14(19), Se1–P–Se2: 114.46(6), C1–P–C9: 102.4(2).

Alkylammonium Diselenophosphinates 9a–o; General Procedure

Amorphous gray selenium (0.158 g, 2.00 mmol) was added to a mixture of secondary phosphine **1**–**8** (1.00 mmol) and the aliphatic amine (1.10 mmol) in EtOH (10 mL) at r.t. under argon. The suspension was stirred at 60 °C until full dissolution of selenium (~0.5 h) to give a colorless, transparent soln. The solvents were removed under reduced pressure, the residue was washed with Et_2O (2 × 10 mL), and dried in vacuo (45 °C/1.33 mbar) to afford the salt **9a–o**.

Triethylammonium Diphenyldiselenophosphinate (9a)

White powder; yield: 0.41 g (92%); mp 97–100 °C (EtOH).

IR (KBr): 3063, 3042, 2970, 2937, 2783, 2744, 2653, 2477, 1468, 1454, 1436, 1387, 1356, 1307, 1283, 1173, 1159, 1106, 1085, 1052, 1028, 1011, 997, 896, 837, 804, 769, 756, 697, 622, 547, 522, 476, 442, 418 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.21 (t, $^3J_{HH}$ = 7.4 Hz, 9 H, CH_3), 3.11–3.16 (m, 6 H, NCH_2), 8.11–8.16 (m, 10 H, Ph), 10.11 (br s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.53 (NCH_2CH_3), 45.82 (NCH_2CH_3), 127.40 (d, $^2J_{CP}$ = 12.1 Hz, *o*-C), 129.30 (d, $^4J_{CP}$ = 3.0 Hz, *p*-C), 131.10 (d, $^3J_{CP}$ = 12.0 Hz, *m*-C), 141.63 (d, $^1J_{CP}$ = 62.8 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 22.07 (s + d satellites: $^1J_{PSe}$ = 603 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = 24 (d, $^1J_{PSe}$ = 603 Hz).

Anal. Calcd for $C_{18}H_{26}NPSe_2$: C, 48.55; H, 5.89; N, 3.15; P, 6.96; Se, 35.46. Found: C, 48.50; H, 5.88; N, 3.23; P, 7.06; Se, 35.41.

Allylammonium Diphenyldiselenophosphinate (9b)

White powder; yield: 0.39 g (97%); mp 110–112 °C (EtOH–hexane).

IR (KBr): 3453, 3046, 2980, 2885, 2667, 2585, 1576, 1477, 1433, 1422, 1356, 1331, 1300, 1178, 1156, 1126, 1087, 1066, 1025, 997, 981, 941, 924, 876, 853, 746, 704, 688, 637, 618, 541, 514, 467 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.23 (d, $^3J_{HH}$ = 5.9 Hz, 2 H, NCH_2), 5.03 (d, $^3J_{HH}$ = 10.3 Hz, 1 H, =CH_2), 5.09 (d, $^3J_{HH}$ = 17.1 Hz, 1 H, =CH_2), 5.51–5.60 (m, 1 H, CH=), 7.24–7.30, 8.04–8.09 (m, 10 H, Ph), 7.67 (br s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 41.43 (NCH_2CH=), 121.67 (CH=CH_2), 127.67 (d, $^2J_{CP}$ = 12.4 Hz, *o*-C), 128.45 (*C*H=CH_2), 129.80 (d, $^4J_{CP}$ = 2.2 Hz, *p*-C), 131.00 (d, $^3J_{CP}$ = 11.7 Hz, *m*-C), 140.21 (d, $^1J_{CP}$ = 62.5 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 22.20 (s + d satellites: $^1J_{PSe}$ = 584 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = 10 (d, $^1J_{PSe}$ = 584 Hz).

Anal. Calcd for $C_{15}H_{18}NPSe_2$: C, 44.90; H, 4.52; N, 3.49; P, 7.72; Se, 39.36. Found: C, 44.81; H, 4.58; N, 3.40; P, 7.51; Se, 39.41.

Triethylammonium Bis(2-phenylethyl)diselenophosphinate (9c)

White powder; yield: 0.44 g (88%); mp 91–92 °C (EtOH).

IR (KBr): 3061, 3028, 2977, 2928, 2754, 2651, 2485, 1601, 1494, 1467, 1454, 1397, 1360, 1308, 1209, 1190, 1176, 1156, 1136, 1122, 1058, 1033, 1009, 951, 935, 919, 833, 807, 790, 770, 759, 733, 707, 620, 575, 495, 479 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.42 (t, $^3J_{HH}$ = 7.0 Hz, 9 H, CH_3), 2.54–2.61 (m, 4 H, PCH_2), 3.11–3.17 (m, 4 H, CH_2Ph), 3.31–3.36 (m, 6 H, NCH_2), 7.17–7.27 (m, 10 H, Ph), 8.86 (br s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.48 (CH_3), 30.86 (*C*H_2Ph), 44.22 (d, $^1J_{CP}$ = 36.4 Hz, PCH_2), 45.83 (NCH_2), 125.69 (*p*-C), 128.24 (*o*-C), 128.36 (*m*-C), 141.87 (d, $^3J_{CP}$ = 17.6 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 24.84 (s + d satellites: $^1J_{PSe}$ = 575 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –49 (d, $^1J_{PSe}$ = 575 Hz).

Anal. Calcd for $C_{22}H_{34}NPSe_2$: C, 52.70; H, 6.83; N, 2.79; P, 6.18; Se, 31.50. Found: C, 52.73; H, 6.52; N, 2.70; P, 6.03; Se, 31.41.

Diethylammonium Bis(2-phenylethyl)diselenophosphinate (9d)

White powder; yield: 0.43 g (91%); mp 192–194 °C (EtOH).

IR (KBr): 3445, 3058, 3024, 2968, 2837, 2785, 2715, 1601, 1531, 1496, 1452, 1431, 1397, 1385, 1372, 1332, 1266, 1195, 1160, 1137, 1123, 1063, 1047, 1019, 949, 933, 905, 870, 850, 820, 749, 737, 720, 696, 576, 491, 478 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.54 (t, $^3J_{HH}$ = 7.3 Hz, 6 H, CH_3), 2.55–2.61 (m, 4 H, PCH_2), 3.08–3.15 (m, 4 H, CH_2Ph), 3.19–3.24 (m, 4 H, NCH_2), 7.19–7.31 (m, 10 H, Ph), 8.58 (br s, 2 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 11.52 (CH_3), 30.96 (*C*H_2Ph), 41.18 (*C*H_2CH_3), 43.96 (d, $^1J_{CP}$ = 36.7 Hz, PCH_2), 126.08 (*p*-C), 128.55 (*o*,*m*-C), 141.72 (d, $^3J_{CP}$ = 17.1 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 25.42 (s + d satellites: $^1J_{PSe}$ = 562 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –67 (d, $^1J_{PSe}$ = 562 Hz).

Anal. Calcd for $C_{20}H_{30}NPSe_2$: C, 50.75; H, 6.39; N, 2.96; P, 6.54; Se, 33.36. Found: C, 52.73; H, 6.52; N, 2.70; P, 6.43; Se, 33.41.

Diisopropylammonium Bis(2-phenylethyl)diselenophosphinate (9e)

White powder; yield: 0.47 g (94%); mp 190–192 °C (EtOH).

IR (KBr): 3454, 3058, 3021, 2822, 2755, 2707, 1601, 1582, 1524, 1496, 1462, 1392, 1377, 1332, 1269, 1189, 1183, 1144, 1124, 1099, 1086, 1030, 1007, 971, 942, 911, 823, 761, 750, 734, 697, 490, 475 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.55 (d, $^3J_{HH}$ = 6.5 Hz, 12 H, CH_3), 2.51–2.58 (m, 4 H, PCH_2), 3.06–3.13 (m, 4 H, CH_2Ph), 3.43–3.50 (m, 2 H, NCH), 7.16–7.27 (m, 10 H, Ph), 8.63 (br s, 2 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.13 (CH_3), 30.42 (CH_2Ph), 43.71 (d, $^1J_{CP}$ = 37.1 Hz, CH_2P), 48.31 [*C*H(CH_3)$_2$], 125.59 (*p*-C), 128.11 (*o*-C), 128.18 (*m*-C), 141.52 (d, $^3J_{CP}$ = 17.3 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 25.02 (s + d satellites: $^1J_{PSe}$ = 569 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –63 (d, $^1J_{PSe}$ = 569 Hz).

Anal. Calcd for $C_{22}H_{34}NPSe_2$: C, 52.70; H, 6.83; N, 2.79; P, 6.18; Se, 31.50. Found: C, 52.73; H, 6.52; N, 2.70; P, 6.03; Se, 31.41.

Allylammonium Bis(2-phenylethyl)diselenophosphinate (9f)

White powder; yield: 0.39 g (85%); mp 115–116 °C (EtOH).

IR (KBr): 3021, 2924, 2861, 2776, 2586, 2345, 1948, 1806, 1648, 1599, 1582, 1495, 1474, 1451, 1441, 1424, 1402, 1330, 1313, 1284, 1261, 1212, 1196, 1154, 1135, 1119, 1076, 1028, 1008, 987, 959, 939, 929, 906, 893, 869, 845, 833, 758, 733, 725, 709, 694, 668, 638, 579, 563, 543, 503, 473, 413 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.48–2.55 (m, 4 H, PCH_2), 2.97–3.04 (m, 4 H, CH_2Ph), 3.82 (d, $^3J_{HH}$ = 6.2 Hz, 2 H, NCH_2), 5.34 (d, $^3J_{HH}$ = 10.5 Hz, 1 H, =CH_2), 5.51 (d, $^3J_{HH}$ = 17.2 Hz, 1 H, =CH_2), 6.02–6.12 (m, 1 H, CH=), 7.15–7.28 (m, 10 H, Ph), 8.31 (br s, 3 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 31.14 (CH_2Ph), 41.99 (N*C*H_2CH=), 43.43 (d, $^1J_{CP}$ = 35.0 Hz, PCH_2), 122.75 (CH=*C*H_2), 126.36 (*p*-C), 126.16 (*C*H=CH_2), 128.57 (*o*-C), 128.70 (*m*-C), 141.13 (d, $^3J_{CP}$ = 16.7 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 24.83 (s + d satellites: $^1J_{PSe}$ = 556 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –59 (d, $^1J_{PSe}$ = 556 Hz).

Anal. Calcd for $C_{19}H_{26}NPSe_2$: C, 49.90; H, 5.73; N, 3.06; P, 6.77; Se, 34.53. Found: C, 49.91; H, 5.70; N, 2.91; P, 6.60; Se, 34.41.

Diisopropylammonium Bis(2-phenylpropyl)diselenophosphinate (9g)

White powder; yield: 0.46 g (87%); mp 98–99 °C (EtOH).

IR (KBr): 3059, 3024, 2976, 2821, 2715, 2535, 2395, 2345, 1941, 1868, 1799, 1743, 1601, 1582, 1573, 1531, 1491, 1463, 1450, 1393, 1377, 1337, 1316, 1299, 1235, 1195, 1181, 1171, 1144, 1100, 1087, 1071, 1043, 1030, 999, 973, 943, 906, 875, 819, 796, 772, 762, 729, 699, 587, 573, 527, 491, 454, 402, 376 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.33, 1.38 [d, $^3J_{HH}$ = 7.1 Hz, 6 H, CH(C*H*$_3$)Ph], 1.52 [d, $^3J_{HH}$ = 6.5 Hz, 12 H, NCH(C*H*$_3$)$_2$], 2.18–2.32, 2.38–2.50 (m, 4 H, PCH_2), 3.39–3.52 (m, 4 H, CHPh, NCH), 7.08–7.25 (m, 10 H, Ph), 8.91 (br s, 2 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 20.45 [NCH(*C*H$_3$)$_2$], 23.86, 24.30 [d, $^3J_{CP}$ = 7.6 Hz, CH(*C*H$_3$)Ph], 37.39 (d, $^2J_{CP}$ = 25.4 Hz, CHPh), 48.59 (NCH), 50.78 (d, $^1J_{CP}$ = 34.8 Hz, CH_2P), 125.97 (*p*-C), 127.41 (*o*-C), 128.37 (*m*-C), 148.04, 148.08 (d, $^3J_{CP}$ = 9.6 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 24.23 and 25.17 (s + d satellites: $^1J_{PSe}$ = 567 Hz and $^1J_{PSe}$ = 563 Hz, respectively).

^{77}Se NMR(76.31 MHz, $CDCl_3$): δ = –35 (d, $^1J_{PSe}$ = 563 Hz), –11 (d, $^1J_{PSe}$ = 567 Hz), 10 (d, $^1J_{PSe}$ = 565 Hz).

Anal. Calcd for $C_{24}H_{38}NPSe_2$: C, 54.44; H, 7.23; N, 2.65; P, 5.85; Se, 29.83. Found: C, 54.37; H, 7.42; N, 2.64; P, 5.60; Se, 29.80.

Triethylammonium Bis[2-(4-*tert*-butylphenyl)ethyl]diselenophosphinate (9h)

White powder; yield: 0.52 g (85%); mp 107–109 °C (EtOH).

IR (KBr): 3090, 3053, 3018, 2959, 2902, 2866, 2778, 2704, 2664, 2607, 2474, 1638, 1516, 1508, 1463, 1437, 1412, 1390, 1363, 1314, 1293, 1267, 1200, 1184, 1161, 1137, 1108, 1067, 1016, 935, 876, 851, 835, 817, 771, 753, 737, 710, 682, 661, 559, 516, 498, 467, 456 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.34 [s, 18 H, C(CH_3)$_3$], 1.46 (t, $^3J_{HH}$ = 7.4 Hz, 9 H, CH_2CH_3), 2.55–2.62 (m, 4 H, PCH_2), 3.11–3.17 (m, 4 H, $CH_2C_6H_4$), 3.36–3.42 (m, 6 H, NCH_2), 7.22–7.34 (m, 8 H, C_6H_4), 9.76 (br s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.55 (CH_2CH_3), 30.41 ($CH_2C_6H_4$), 31.40 [C(*C*H$_3$)$_3$], 34.33 [*C*(CH$_3$)$_3$], 44.29 (d, $^1J_{CP}$ = 36.3 Hz, PCH_2), 45.86 (NCH_2), 125.25 ($C2_{Ar}$, $C6_{Ar}$), 128.16 ($C3_{Ar}$, $C5_{Ar}$), 138.87 (d, $^3J_{CP}$ = 17.2 Hz, $C1_{Ar}$), 148.58 ($C4_{Ar}$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 25.23 (s + d satellites: $^1J_{PSe}$ = 572 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –48 (d, $^1J_{PSe}$ = 572 Hz).

Anal. Calcd for $C_{30}H_{50}NPSe_2$: C, 58.72; H, 8.21; N, 2.28; P, 5.05; Se, 25.74. Found: C, 58.70; H, 8.18; N, 2.39; P, 5.10; Se, 25.68.

Dipropylammonium Bis[2-(6-methyl-3-pyridyl)ethyl]diselenophosphinate (9i)

White powder; yield: 0.50 g (94%); mp 170–171 °C (EtOH).

IR (KBr): 3030, 3002, 2969, 2920, 2881, 2768, 2506, 2487, 1657, 1600, 1568, 1535, 1490, 1466, 1450, 1396, 1320, 1302, 1246, 1200, 1189, 1143, 1118, 1094, 1066, 1029, 1007, 949, 855, 829, 788, 761, 743, 728, 720, 645, 537, 476, 422, 406, 383 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.04 (t, $^3J_{HH}$ = 7.4 Hz, 6 H, CH_3), 1.90–1.99 (m, 4 H, CH_2CH_3), 2.48–2.54 (m, 10 H, PCH_2, CH_3), 3.06–3.12 (m, 8 H, CH_2Py, NCH_2), 7.06 (d, 2 H, Py), 7.46 (d, 2 H, Py), 8.38 (s, 2 H, Py), 8.87 (br s, 2 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 11.37 (CH_3), 19.44 (CH_2CH_3), 23.94 (CH_3), 27.64 (CH_2Py), 43.59 (d, $^1J_{CP}$ = 36.6 Hz, PCH_2), 48.49 (NCH_2), 123.11 ($C5_{Py}$), 134.00 (d, $^3J_{CP}$ = 16.2 Hz, $C1_{Py}$), 136.54 ($C6_{Py}$), 148.86 ($C2_{Py}$), 155.74 ($C4_{Py}$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 24.28 (s + d satellites: $^1J_{PSe}$ = 574 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –59 (d, $^1J_{PSe}$ = 574 Hz).

Anal. Calcd for $C_{22}H_{36}N_3PSe_2$: C, 49.72; H, 6.83; N, 7.91; P, 5.83; Se, 29.72. Found: C, 49.60; H, 7.08; N, 7.89; P, 6.02; Se, 29.83.

Triethylammonium Bis[2-(4-pyridyl)ethyl]diselenophosphinate (9j)

White powder; yield: 0.46 g (91%); mp >200 °C dec.

IR (KBr): 3490, 3068, 3043, 2979, 2953, 2894, 2849, 2162, 2068, 1976, 1615, 1556, 1506, 1413, 1393, 1316, 1276, 1248, 1230, 1207, 1169, 1139, 1085, 1065, 1014, 956, 938, 923, 888, 810, 763, 737, 702, 658, 526, 489 cm^{-1}.

^1H NMR (400.13 MHz, DMSO-d_6): δ = 1.17 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3), 2.30–2.36 (m, 4 H, CH_2P), 3.03–3.13 (m, 10 H, CH_2Py, NCH_2), 7.35, 8.47 (d, 8 H, Py).

^{31}P NMR (161.98 MHz, DMSO-d_6): δ = 23.35 (s + d satellites: $^1J_{PSe}$ = 621 Hz).

Anal. Calcd for $C_{20}H_{32}N_3PSe_2$: C, 47.72; H, 6.41; N, 8.35; P, 6.15; Se, 31.37. Found: C, 47.60; H, 6.32; N, 8.45; P, 6.02; Se, 31.51.

Triethylammonium Bis[2-(2-pyridyl)ethyl]diselenophosphinate (9k)

White powder; yield: 0.45 g (89%); mp >200 °C dec.

IR (KBr): 3425, 3062, 3005, 2976, 2905, 2862, 2774, 2662, 2474, 1627, 1593, 1567, 1551, 1473, 1435, 1400, 1388, 1340, 1321, 1300, 1266, 1224, 1198, 1179, 1156, 1130, 1094, 1069, 1051, 1012, 992, 944, 930, 895, 843, 817, 770, 760, 732, 713, 640, 628, 618, 595, 584, 513, 501, 484, 403 cm^{-1}.

^1H NMR (400.13 MHz, DMSO-d_6): δ = 1.18 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3), 2.37–2.44 (m, 4 H, PCH_2), 3.09–3.18 (m, 10 H, CH_2Py, NCH_2), 7.18–7.35 (m, 4 H, $H3_{Ph}$, $H5_{Py}$), 7.68–7.72 (m, 2 H, $H4_{Py}$), 8.46–8.47 (m, 2 H, $H6_{Py}$), 8.87 (br s, 1 H, NH).

^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 9.67 (CH_3), 33.97 (CH_2Py), 43.85 (d, $^1J_{CP}$ = 37.9 Hz, PCH_2), 46.80 (NCH_2), 122.21 ($C5_{Py}$), 123.75 ($C3_{Py}$), 137.84 ($C4_{Py}$), 149.51 ($C6_{Py}$), 162.50 (d, $^3J_{CP}$ = 17.4 Hz, $C2_{Py}$).

^{31}P NMR (161.98 MHz, DMSO-d_6): δ = 24.57 (s + d satellites: $^1J_{PSe}$ = 612 Hz).

^{77}Se NMR (76.31 MHz, DMSO-d_6): δ = –70 (d, $^1J_{PSe}$ = 612 Hz).

Anal. Calcd for $C_{20}H_{32}N_3PSe_2$: C, 47.72; H, 6.41; N, 8.35; P, 6.15; Se, 31.37. Found: C, 47.64; H, 6.33; N, 8.31; P, 6.02; Se, 31.45.

Allylammonium Bis[2-(2-pyridyl)ethyl]diselenophosphinate (9l)

White powder; yield: 0.43 g (94%); mp >200 °C dec.

IR (KBr): 3450, 2951, 2853, 2794, 2698, 2071, 1647, 1627, 1591, 1566, 1473, 1433, 1404, 1328, 1310, 1292, 1265, 1229, 1192, 1150, 1123, 1080, 1051, 1002, 989, 940, 925, 897, 883, 842, 781, 763, 742, 719, 699, 634, 589, 555, 512, 484 cm^{-1}.

^1H NMR (400.13 MHz, DMSO-d_6): δ = 2.37–2.43 (m, 4 H, PCH_2), 3.11–3.17 (m, 4 H, CH_2Py), 3.49 (d, $^3J_{HH}$ = 5.8 Hz, 2 H, NCH_2), 5.30 (d, $^3J_{HH}$ = 10.7 Hz, 1 H, $=CH_2$), 5.37 (d, $^3J_{HH}$ = 17.4 Hz, 1 H, $=CH_2$), 5.82–5.92 (m, 1 H, CH=), 7.15–7.26 (m, 4 H, $H3_{Py}$, $H5_{Py}$), 7.65–7.69 (m, 2 H, $H4_{Py}$), 7.90 (s, 3 H, NH), 8.44–8.45 (m, 2 H, $H6_{Py}$).

^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 33.48 (CH_2Py), 41.37 (NCH_2CH=), 43.18 (d, $^1J_{CP}$ = 37.9 Hz, PCH_2), 120.28 (CH=CH_2), 121.49 ($C5_{Py}$), 123.01 ($C3_{Py}$), 131.16 (CH=CH_2), 136.89 ($C4_{Py}$), 149.19 ($C6_{Py}$), 162.02 (d, $^3J_{CP}$ = 17.8 Hz, $C2_{Py}$).

^{31}P NMR (161.98 MHz, DMSO-d_6): δ = 24.70 (s + d satellites: $^1J_{PSe}$ = 610 Hz).

^{77}Se NMR (76.31 MHz, DMSO-d_6): δ = –76 (d, $^1J_{PSe}$ = 610 Hz).

Anal. Calcd for $C_{17}H_{24}N_3PSe_2$: C, 44.46; H, 5.27; N, 9.15; P, 6.74; Se, 34.38. Found: C, 44.60; H, 5.20; N, 9.23; P, 6.52; Se, 34.21.

Triethylammonium Bis[2-(2-furyl)ethyl]diselenophosphinate (9m)

White powder; yield: 0.42 g (87%); mp 171–173 °C (EtOH–hexane).

IR (KBr): 3444, 3140, 3099, 2977, 2931, 2850, 2763, 2740, 2704, 2636, 2472, 1653, 1589, 1507, 1487, 1469, 1437, 1415, 1395, 1359, 1333, 1288, 1272, 1232, 1213, 1167, 1142, 1086, 1071, 1029, 1001, 967, 937, 926, 910, 884, 873, 834, 811, 794, 748, 727, 676, 598, 511, 424, 404 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.41 (t, $^3J_{HH}$ = 7.3 Hz, 9 H, CH_3), 2.52–2.59 (m, 4 H, PCH_2), 3.10–3.17 (m, 4 H, CH_2Fur), 3.30–3.36 (m, 6 H, NCH_2), 6.01, 6.25, 7.27 (m, 6 H, Fur), 9.61 (br s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 8.49 (CH_3), 23.73 (CH_2Fur), 40.47 (d, $^1J_{CP}$ = 38.2 Hz, PCH_2), 45.92 (NCH_2), 104.84 ($C3_{Fur}$), 110.04 ($C4_{Fur}$), 140.82 ($C5_{Fur}$), 155.25 (d, $^3J_{CP}$ = 20.2 Hz, $C2_{Fur}$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 23.06 (s + d satellites: $^1J_{PSe}$ = 580 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –55 (d, $^1J_{PSe}$ = 580 Hz).

Anal. Calcd for $C_{18}H_{30}NO_2PSe_2$: C, 44.92; H, 6.28; N, 2.91; P, 6.44; Se, 32.81. Found: C, 44.78; H, 6.10; N, 2.89; P, 6.22; Se, 32.71.

Allylammonium Bis[2-(2-furyl)ethyl]diselenophosphinate (9n)

White powder; yield: 0.42 g (96%); mp 152–154 °C (EtOH–hexane).

IR (KBr): 3457, 2968, 2930, 2856, 2780, 1994, 1586, 1505, 1474, 1443, 1424, 1402, 1383, 1330, 1285, 1232, 1213, 1167, 1072, 1038, 1007, 986, 939, 912, 883, 869, 790, 771, 730, 677, 641, 597, 545, 497, 479, 438 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.47–2.54 (m, 4 H, PCH_2), 2.99–3.05 (m, 4 H, CH_2Fur), 3.83 (d, $^3J_{HH}$ = 5.7 Hz, 2 H, NCH_2), 5.40 (d, $^3J_{HH}$ = 10.2 Hz, 1 H, $=CH_2$), 5.54 (d, $^3J_{HH}$ = 17.2 Hz, 1 H, $=CH_2$), 6.02–6.13 (m, 3 H, CH=, Fur), 6.24, 7.26 (m, 4 H, Fur), 8.15 (br s, 1 H, NH).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 23.74 (CH_2Fur), 39.42 (d, $^1J_{CP}$ = 36.8 Hz, PCH_2), 41.79 (NCH_2CH=), 105.32 ($C3_{Fur}$), 110.18 ($C4_{Fur}$), 122.50 (CH=CH_2), 128.67 (CH=CH_2), 141.05 ($C5_{Fur}$), 154.15 (d, $^3J_{CP}$ = 19.01 Hz, $C2_{Fur}$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 25.01 (s + d satellites: $^1J_{PSe}$ = 561 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –58 (d, $^1J_{PSe}$ = 561 Hz).

Anal. Calcd for $C_{15}H_{22}NO_2PSe_2$: C, 41.20; H, 5.07; N, 3.20; P, 7.08; Se, 36.12. Found: C, 41.34; H, 5.14; N, 3.10; P, 7.19; Se, 36.17.

(*R*)-2-Hydroxybutylammonium Bis(2-phenylethyl)diselenophosphinate (9o)

White powder; yield: 0.42 g (86%); mp >150 °C dec.

$[\alpha]_D^{23}$ –6.88 (*c* 0.025, EtOH).

IR (KBr): 3412, 3266, 3102, 3082, 3060, 3024, 2974, 2960, 2931, 2895, 2843, 2767, 2729, 2657, 2606, 2517, 2024, 2004, 1972, 1949, 1892, 1613, 1601, 1580, 1494, 1481, 1467, 1453, 1433, 1412, 1390, 1368, 1345, 1329, 1297, 1274, 1262, 1237, 1202, 1178, 1157, 1125, 1082, 1069, 1042, 1031, 1015, 988, 945, 927, 910, 860, 822, 771, 759, 750, 740, 718, 699, 660, 622, 570, 557, 515, 496, 481, 448, 423 cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.00 (t, $^3J_{HH}$ = 7.5 Hz, 3 H, CH_3), 1.67–1.80 (m, 2 H, CH_2CH_3), 2.49–2.56 (m, 4 H, PCH_2), 2.99–3.05 (m, 4 H, CH_2Ph), 3.32–3.38 (m, 1 H, CHOH), 3.72–3.77 (m, 1 H, NCH_2), 3.91–3.94 (m, 1 H, NCH_2), 6.27 (br s, 4 H, NH, OH), 7.14–7.26 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 10.36 (CH_3), 23.66 (CH_2CH_3), 31.02 (CH_2Ph), 43.45 (d, $^1J_{CP}$ = 35.1 Hz, PCH_2), 55.42 (NCH_2), 61.47 (CHOH), 126.15 (*p*-C), 128.40 (*o*-C), 128.55 (*m*-C), 141.15 (d, $^3J_{CP}$ = 16.6 Hz, *ipso*-C).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 25.82 (s + d satellites: $^1J_{PSe}$ = 560 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –51 (d, $^1J_{PSe}$ = 560 Hz).

Anal. Calcd for $C_{20}H_{30}NOPSe_2$: C, 49.09; H, 6.18; N, 2.86; P, 6.33; Se, 32.27. Found: C, 49.30; H, 6.08; N, 2.89; P, 6.12; Se, 32.04.

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