# Facile Atom-Economic Synthesis of Ammonium Diselenophosphinates via Three-Component Reaction of Secondary Phosphines, Elemental Selenium, and Ammonia

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**Abstract:** The three-component reaction between secondary phosphines, $R_2PH$ [R = $Ph(CH_2)_2$, PhCHMeCH$_2$, PhCH$_2$CHMe, 4-*t*-BuC$_6$H$_4$(CH$_2$)$_2$, 4-MeOC$_6$H$_4$(CH$_2$)$_2$, 2-furyl(CH$_2$)$_2$, 4-pyridyl(CH$_2$)$_2$, 6-Me-3-pyridyl(CH$_2$)$_2$, Ph], elemental selenium, and ammonia proceeds under mild conditions (EtOH–H$_2$O, 53–55 °C or EtOH, r.t., 10 min) without the formation of byproducts to give the first representatives of ammonium diselenophosphinates in high yields (up to 96%).

**Key words:** secondary phosphines, elemental selenium, ammonia, three-component reaction, diselenophosphinates, ammonium salts, phosphinodiselenoic acid

At present, only salts of alkali metals [$M(Se_2PR_2)$] (M = Li,[1] Na,[2] K,[3,4] Li-Cs[5]) and alkylammonium [$(alkyl)_nNH_{4-n}(Se_2PR_2)$] (n = 3,[6] 1–3[7]) are known as the starting source for diselenophosphinate anions. The latter represent convenient intermediates for the synthesis of heavy metal diselenophosphinates, which are intensively used as single-source precursors (SSPs) for the preparation of nano-sized metal phosphides or selenides (Zn, Cd, Ni, Co, Ag, In, Eu, etc.) possessing unique magneto-optical, electrical, and other properties.[8] For example, nickel phosphides ($Ni_2P$ and $Ni_{12}P_5$) or nickel selenide (NiSe) nanoparticles were prepared from nickel(II) dialkyldiselenophosphinates, [$Ni(Se_2PR_2)_2$], by thermolysis in trioctylphosphine as a coordinating solvent.[9] Silver diselenophosphinate, [Ag(Se$_2$P*i*-Pr$_2$)], was employed as a SSP to obtain silver selenide ($Ag_2Se$) nanofilms via aerosol-assisted chemical vapor deposition.[10] Europium diselenophosphinate, [$Eu(Se_2PPh_2)_3$], was used for the synthesis of europium selenide (EuSe) nanocrystals, the starting block for the design of novel remarkable magneto-optical nanomaterials.[3] Nanorods of zinc selenide (ZnSe) exhibiting semiconductive properties were synthesized from zinc diselenophosphinate, [Zn(Se$_2$P*i*-Pr$_2$)$_2$].[6]

In addition, the diselenophosphinates of alkali metals and alkylammoniums are ligands for metal complexes,[11] promising extractants of heavy, rare, and transuranium elements,[12] potential biologically active compounds,[13] as well as the building blocks for organic and elementoorganic synthesis.[14] For instance, alkylation of diselenophosphinates represents a facile route to the corresponding *Se*-esters of diselenophosphinates[14a] [$R^1_2P(Se)SeR^2$], showing the properties of efficient reversible addition fragmentation transfer polymerization (RAFT) agents.[15]

At the same time, the data on ammonium salts of diselenophosphinic acids [phosphinodiselenoic acids, $NH_4(Se_2PR_2)$] are absent in literature. One can expect that ammonium diselenophosphinates would be more convenient reagents compared to alkylammonium or alkali metals salts. For example, ammonium diselenophosphinates might be employed as efficient synthetic equivalents of the corresponding diselenophosphinic acids [$R_2P(Se)SeH$], because the gaseous ammonia evolved (unlike amines or alkali metal hydroxides) is readily removed from the reaction mixture.

Here, we report an atom-economic synthesis of the first representatives of ammonium diselenophosphinates via the three-component reaction of secondary phosphines with elemental selenium and ammonia.

The initial secondary phosphines are readily available from the reaction of red phosphorus and arylethenes or hetarylethenes (styrenes,[16] vinylpyridines,[17] or 2-vinylfuran[16a]) in one preparative step.

As our experiments have showed, secondary phosphines **1**–**9** react readily with elemental selenium and aqueous ammonia solution (EtOH–H$_2$O, 53–55 °C, 10 min, Method A) or with liquid ammonia (EtOH, r.t., 10 min, Method B) to afford ammonium diselenophosphinates **10a**–**i** in high yields (76–96%) (Table 1).

The reaction involves no formation of byproducts and, hence, is completely atom-economic and 'green' (ethanol, a nontoxic recoverable solvent, is used).

The tentative mechanism of the formation of diselenophosphinates can be presented as follows (Scheme 1). 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 ammonia to afford *P*,*Se*-ambident selenophosphinite anion **C** (stage 2), which further reacts with second equivalent of elemental selenium to provide the diselenophosphinate anion **D** (stage 3).

The synthesized salts **10a**–**i** are powders, stable under an argon blanket, and well soluble in organic solvents (alco-

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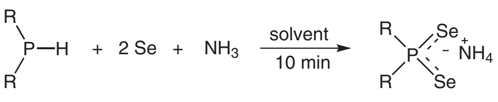
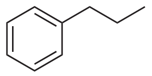
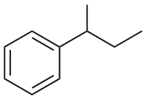
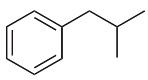
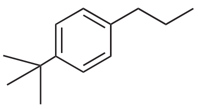
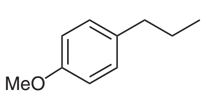
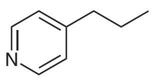
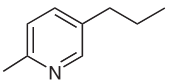
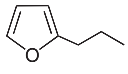
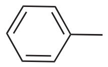
**Table 1** Synthesis of Ammonium Diselenophosphinates from Secondary Phosphines, Elemental Selenium, and Ammonia[a]



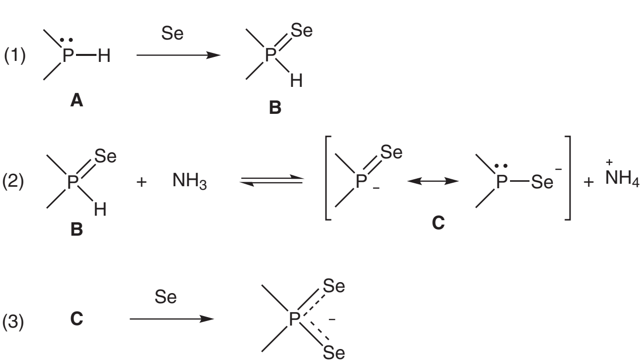
**1–9** **10a–i**

| Entry | Phosphine | R | Method[b] | Product | Yield[c] (%) |
|---|---|---|---|---|---|
| 1 | **1** |  | A<br>B | **10a** | 94<br>96 |
| 2 | **2** |  | A<br>B | **10b** | 87<br>85 |
| 3 | **3** |  | A | **10c** | 76 |
| 4 | **4** |  | B | **10d** | 88 |
| 5 | **5** |  | A<br>B | **10e** | 89<br>88 |
| 6 | **6** |  | A | **10f** | 95 |
| 7 | **7** |  | A<br>B | **10g** | 93<br>95 |
| 8 | **8** |  | A<br>B | **10h** | 92<br>92 |
| 9 | **9** |  | A<br>B | **10i** | 94<br>89 |

[a] The ratio of phosphine **1–9**/Se/$NH_3$ was 1:2:1.6.

[b] Method A: 25% aq $NH_3$ soln, EtOH–$H_2O$, 53–55 °C; Method B: liquid $NH_3$, EtOH, r.t.

[c] All yields refer to isolated products.



**Scheme 1** Probable mechanism of formation of ammonium diselenophosphinates

hols, dioxane, THF, DMSO). In addition, these salts can be easily prepared as crystals by recrystallization from ethanol, diethyl ether, or hexane.

The structures of compounds **10a–i** were identified by multinuclear ($^1H$, $^{13}C$, $^{31}P$, and $^{77}Se$) NMR and their composition was confirmed by elemental analysis data. Equivalency of selenium atoms in salts **10a–i** follows from $^{77}Se$ and $^{31}P$ NMR data. For example, in the $^{77}Se$ NMR spectra, a doublet ($^1J_{PSe}$ = 564–640 Hz) is present; in the $^{31}P$ NMR spectra, a singlet with one typical satellite pair is observed ($^1J_{PSe}$ = 564–640 Hz). The $^1J_{PSe}$ value (564–640 Hz) is intermediate between the coupling constant values for P–Se and P=Se moieties (200–600 and 800–1200 Hz, respectively[18]), thus corresponds to the 1.5 order of the phosphorus–selenium bond.

In summary, a novel three-component reaction between secondary phosphines, elemental selenium, and ammonia affords cleanly the corresponding ammonium salts of diselenophosphinic acids (a new family of diselenophosphinates) in high yields. The generality and preparative efficiency of the atom-economic ('green') method developed has been demonstrated by the synthesis of ammonium salts of diselenophosphinic acids bearing aralkyl-, hetaralkyl-, and aryl substituents. The salts synthesized are promising intermediates in the production of conducting nanomaterials and SSPs of semiconducting thin films and precursors for the design of bioactive products, as well as building blocks for diverse phosphorus–selenium organic compounds.

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. Secondary phosphines **1–8** were prepared from styrene,[16a] α-methylstyrene,[16a] β-methylstyrene, 4-*tert*-butylstyrene,[16b] 4-methoxystyrene, 4-vinylpyridine,[17] 2-methyl-5-vinylpyridine,[17] or 2-vinylfuran[16a] and red phosphorus as described in the literature. Diphenylphosphine (**9**) was employed as commercial product (Aldrich, 2009). The $^1H$, $^{13}C$, $^{31}P$, and $^{77}Se$ NMR spectra were recorded on Bruker DPX 400 and Bruker AV-400 spectrometers (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 instrument. Melting points were measured on a Kofler micro hot stage apparatus.

### Ammonium Diselenophosphinates 10a–c,e–i; General Procedure (Method A)

To a soln of the secondary phosphine **1–3**, **5–9** (1.0 mmol) in EtOH (10 mL), 25% aq $NH_3$ soln (~0.12 mL, 1.6 mmol) and amorphous grey selenium (0.158 g, 2.0 mmol) were consecutively added at r.t. under argon. The suspension was vigorously stirred at 53–55 °C until the selenium had dissolved completely (~10 min). The colorless transparent soln formed was filtered, EtOH and $H_2O$ were removed under reduced pressure, and the residue was ground in hexane (10 mL). The latter was decanted, the white powder formed was washed with hexane (10 mL) and dried in vacuo (35–40 °C/1.33 mbar) to afford the corresponding salt **10a–c**,**e–i**.

### Ammonium Diselenophosphinates 10a,b,d,e,g–i; General Procedure (Method B)

To a soln of the secondary phosphine **1**, **2**, **4**, **5**, **7–9** (1.0 mmol) in EtOH (10 mL), liquid $NH_3$ (~0.04 mL, 1.6 mmol) and amorphous grey selenium (0.158 g, 2.0 mmol) were consecutively added at r.t.

under argon. The suspension was vigorously stirred at r.t. until the selenium had dissolved completely (~10 min). The colorless transparent soln formed was filtered, the solvent was removed under reduced pressure, and the residue was ground in hexane (10 mL). The latter was decanted, the white powder formed was washed with hexane (10 mL) and dried in vacuo (35–40 °C/1.33 mbar) to afford the corresponding salt **10a**,**b**,**d**,**e**,**g**–**i**.

### Ammonium Bis(2-phenylethyl)diselenophosphinate (10a)

White powder; yield: 0.400 g (96%); mp 217–219 °C ($Et_2O$).

IR (KBr): 3060, 3023, 2944, 2789, 1949, 1876, 1810, 1752, 1633, 1601, 1495, 1453, 1397, 1265, 1208, 1193, 1156, 1137, 1126, 1068, 1028, 1008, 958, 938, 909, 832, 810, 751, 736, 697, 620, 566, 517, 606, 481, 413 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 2.26–2.31 (m, 4 H, $CH_2Ph$), 2.95–3.02 (m, 4 H, $CH_2P$), 7.15–7.28 (m, 14 H, Ph, $NH_4$).

$^{13}C$ NMR (DMSO-$d_6$): δ = 30.58 (d, $^2J_{PC}$ = 1.8 Hz, $CH_2Ph$), 44.84 (d, $^1J_{PC}$ = 36.9 Hz, $CH_2P$), 125.50 (*p*-C), 128.09 (*o*-C), 128.25 (*m*-C), 142.50 (d, $^3J_{PC}$ = 16.4 Hz, *ipso*-C).

$^{31}P$ NMR (DMSO-$d_6$): δ = 24.29 (s + d satellites: $^1J_{PSe}$ = 616 Hz).

$^{77}Se$ NMR (DMSO-$d_6$): δ = –36 (d, $^1J_{PSe}$ = 616 Hz).

Anal. Calcd for $C_{16}H_{22}NPSe_2$: C, 46.06; H, 5.31; N, 3.36; P, 7.42; Se, 37.85. Found: C, 46.10; H, 5.29; N, 3.31; P, 7.31; Se, 37.75.

### Ammonium Bis(2-phenylpropyl)diselenophosphinate (10b)

White powder; yield: 0.387 g (87%); mp 154–156 °C ($Et_2O$).

IR (KBr): 3250, 3080, 3060, 2957, 2867, 2765, 1947, 1880, 1806, 1638, 1601, 1582, 1493, 1451, 1392, 1306, 1283, 1234, 1196, 1182, 1148, 1086, 1075, 1047, 1027, 1005, 995, 911, 847, 829, 763, 747, 732, 699, 584, 562, 544, 532, 488, 462, 404 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 1.27–1.35 (m, 6 H, Me), 2.04–2.24 (m, 4 H, $CH_2P$), 3.36–3.52 (m, 2 H, CH), 7.08–7.22 (m, 14 H, Ph, $NH_4$).

$^{13}C$ NMR (DMSO-$d_6$): δ = 23.98, 24.37 (d, $^3J_{PC}$ = 5.2 Hz, Me), 37.02, 37.40 (CHPh), 52.22, 52.63 (d, $^1J_{PC}$ = 34.0, 35.0 Hz, $CH_2P$), 125.01 (*p*-C), 127.52, 127.54 (*o*-C), 128.30 (*m*-C), 149.48, 149.60 (d, $^3J_{PC}$ = 12.4 Hz, *ipso*-C).

$^{31}P$ NMR (DMSO-$d_6$): δ = 22.94 (s + d satellites: $^1J_{PSe}$ = 607 Hz), 24.14 (satellites: $^1J_{PSe}$ = 612 Hz), the ratio of intensities is 52:48.

$^{77}Se$ NMR (DMSO-$d_6$): δ = –23.2, 23 (d, $^1J_{PSe}$ = 607 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, 5.77; N, 3.11; P, 6.69; Se, 35.43.

### Ammonium Bis(1-methyl-2-phenylethyl)diselenophosphinate (10c)

White powder; yield: 0.338 g (76%); mp 178–181 °C ($Et_2O$).

IR (KBr): 3251, 3078, 3060, 2955, 2864, 2760, 1947, 1880, 1805, 1635, 1604, 1580, 1493, 1450, 1390, 1306, 1284, 1233, 1195, 1181, 1148, 1085, 1074, 1047, 1028, 1005, 996, 912, 848, 829, 763, 747, 735, 701, 584, 560, 545, 530, 489, 460, 405 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.19 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{PH}$ = 7.8 Hz, 6 H, Me), 2.51–2.57 (m, 2 H, CHP), 3.43–3.53 (m, 4 H, $CH_2Ph$), 7.16–7.28 (m, 14 H, Ph, $NH_4$).

$^{13}C$ NMR ($CDCl_3$): δ = 13.22, 14.74 (Me), 36.79 ($CH_2h$), 39.68, 40.07 (d, $^1J_{PC}$ = 40.5, 41.5 Hz, CHP), 125.61 (*p*-C), 127.86 (*o*-C), 128.90, 129.02 (*m*-C), 139.46, 139.71 (d, $^3J_{PC}$ = 15.9, 17.1 Hz, *ipso*-C).

$^{31}P$ NMR (EtOH): δ = 63.51, 63.85 (s + d satellites: $^1J_{PSe}$ = 585 Hz), the ratio of intensities is 40:60.

$^{77}Se$ NMR (EtOH): δ = –160, –158, –156 (d, $^1J_{PSe}$ = 584 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, 48.53; H, 5.97; N, 3.08; P, 6.61; Se, 35.27.

### Ammonium Bis[2-(4-*tert*-butylphenylethyl]diselenophosphinate (10d)

White powder; yield: 0.466 g (88%); mp 190–194 °C (hexane).

IR (KBr): 3451, 3092, 3055, 3023, 2961, 2903, 2865, 1905, 1793, 1627, 1516, 1495, 1462, 1439, 1393, 1363, 1268, 1202, 1136, 1108, 1067, 1018, 943, 875, 853, 839, 813, 770, 738, 663, 563, 517, 495 $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ = 1.35 (s, 18 H, Me), 2.59–2.66 (m, 4 H, $CH_2P$), 3.05–3.11 (m, 4 H, $CH_2C_6H_4$), 7.13 (s, 4 H, $NH_4$), 7.23–7.35 (m, 8 H, $C_6H_4$).

$^{13}C$ NMR ($CDCl_3$): δ = 30.05 ($CH_2C_6H_4$), 31.43 ($Me_3C$), 34.39 ($CMe_3$), 43.15 (d, $CH_2P$, $^1J_{PC}$ = 35.4 Hz), 125.45 ($C2_{Ar}$, $C6_{Ar}$), 128.32 ($C3_{Ar}$, $C5_{Ar}$), 138.03 (d, $^3J_{PC}$ = 16.2 Hz, $C1_{Ar}$), 148.96 ($C4_{Ar}$).

$^{31}P$ NMR ($CDCl_3$): δ = 26.75 (s + d satellites: $^1J_{PSe}$ = 640 Hz).

$^{77}Se$ NMR ($CDCl_3$): δ = –48 (d, $^1J_{PSe}$ = 640 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, 54.31; H, 7.29; N, 2.72; P, 5.80; Se, 29.75.

### Ammonium Bis[2-(4-methoxyphenyl)ethyl)]diselenophosphinate (10e)

White powder; yield: 0.425 g (89%); mp 180–184 °C ($Et_2O$).

IR (KBr): 3285, 3024, 2992, 2834, 2044, 1877, 1649, 1609, 1583, 1511, 1464, 1442, 1396, 1318, 1299, 1265, 1244, 1196, 1176, 1128, 1026, 951, 937, 876, 848, 812, 774, 736, 723, 709, 691, 638, 548, 520, 502, 484, 454, 421, 404 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 2.19–2.26 (m, 4 H, $CH_2P$), 2.86–2.93 (m, 4 H, $CH_2C_6H_4$), 3.70 (s, 6 H, OMe), 6.81–7.11 (m, 12 H, $C_6H_4$, $NH_4$).

$^{13}C$ NMR (DMSO-$d_6$): δ = 30.28 ($CH_2C_6H_4$), 45.60 (d, $^1J_{PC}$ = 36.2 Hz, $CH_2P$), 55.55 (OMe), 114.31 ($C2_{Ar}$, $C6_{Ar}$), 129.60 ($C3_{Ar}$, $C5_{Ar}$), 134.89 (d, $^3J_{PC}$ = 16.6 Hz, $C1_{Ar}$), 157.86 ($C4_{Ar}$).

$^{31}P$ NMR (DMSO-$d_6$): δ = 24.04 (s + d satellites: $^1J_{PSe}$ = 608 Hz).

$^{77}Se$ NMR (DMSO-$d_6$): δ = –35 (d, $^1J_{PSe}$ = 608 Hz).

Anal. Calcd for $C_{18}H_{26}NO_2PSe_2$: C, 45.30; H, 5.49; N, 2.93; P, 6.49; Se, 33.09. Found: C, 45.15; H, 5.54; N, 2.90; P, 6.44; Se, 32.98.

### Ammonium Bis[2-(4-pyridyl)ethyl]diselenophosphinate (10f)

Yellow powder; yield: 0.400 g (95%); mp >200 °C (dec.).

IR (KBr): 3452, 2991, 2893, 2610, 2225, 2152, 2111, 1923, 1709, 1675, 1609, 1557, 1503, 1456, 1452, 1425, 1395, 1316, 1282, 1246, 1222, 1212, 1198, 1189, 1140, 1093, 1071, 1030, 1007, 948, 936, 880, 831, 802, 763, 748, 736, 703, 665, 585, 572, 519, 482, 423 $cm^{-1}$.

$^1H$ NMR (DMSO-$d_6$): δ = 2.27–2.34 (m, 4 H, $CH_2P$), 2.99–3.05 (m, 4 H, $CH_2Py$), 7.08 (s, 4 H, $NH_4$), 7.25 (d, 4 H, Py), 8.42 (d, 4 H, Py).

$^{13}C$ NMR (DMSO-$d_6$): δ = 30.54 ($CH_2Py$), 43.94 (d, $^1J_{PC}$ = 37.5 Hz, $CH_2P$), 124.27, 149.79 (Py), 152.12 (d, $^3J_{PC}$ = 16.7 Hz, Py).

$^{31}P$ NMR (DMSO-$d_6$): δ = 24.20 (s + d satellites: $^1J_{PSe}$ = 616 Hz).

$^{77}Se$ NMR (DMSO-$d_6$): δ = –51 (d, $^1J_{PSe}$ = 616 Hz).

Anal. Calcd for $C_{14}H_{20}N_3PSe_2$: C, 40.11; H, 4.81; N, 10.02; P, 7.39; Se, 37.67. Found: C, 40.04; H, 4.86; N, 10.11; P, 7.13; Se, 37.49.

### Ammonium Bis[2-(6-methyl-3-pyridyl)ethyl]diselenophosphinate (10g)

Yellowish powder; yield: 0.425 g (95%); mp 178–180 °C ($Et_2O$).

IR (KBr): 3450, 3001, 2920, 2861, 2115, 1955, 1890, 1678, 1657, 1639, 1604, 1569, 1495, 1473, 1441, 1393, 1325, 1298, 1278, 1246, 1207, 1189, 1171, 1139, 1113, 1094, 1037, 1011, 979, 950, 916, 856, 831, 790, 775, 741, 729, 717, 672, 652, 826, 543, 519, 512, 501, 484, 417 $cm^{-1}$.

$^1$H NMR ($D_2O$): $\delta$ = 2.12–2.19 (m, 10 H, $CH_2P$, Me), 2.62–2.68 (m, 4 H, $CH_2Py$), 6.87 (d, 2 H, Py), 7.26 (d, 2 H, Py), 7.93 (s, 2 H, Py).

$^{13}$C NMR ($D_2O$): $\delta$ = 22.14 (Me), 27.31 ($CH_2Py$), 42.22 (d, $^1J_{PC}$ = 35.9 Hz, $CH_2P$), 123.88 (Py), 134.13 (d, $^3J_{PC}$ = 15.8 Hz, Py), 137.95, 147.09, 155.24 (Py).

$^{31}$P NMR ($D_2O$): $\delta$ = 26.36 (s + d satellites: $^1J_{PSe}$ = 564 Hz).

$^{77}$Se NMR ($D_2O$): $\delta$ = –63 (d, $^1J_{PSe}$ = 564 Hz).

Anal. Calcd for $C_{16}H_{24}N_3PSe_2$: C, 42.96; H, 5.41; N, 9.39; P, 6.92; Se, 35.31. Found: C, 42.93; H, 5.34; N, 9.21; P, 6.73; Se, 35.19.

### Ammonium Bis[2-(2-furyl)ethyl]diselenophosphinate (10h)

White powder; yield: 0.365 g (92%); mp 147–150 °C ($Et_2O$).

IR (KBr): 3288, 3106, 3058, 2933, 2898, 2759, 1716, 1643, 1597, 1505, 1435, 1384, 1327, 1276, 1225, 1204, 1195, 1170, 1143, 1122, 1108, 1069, 1031, 1007, 964, 947, 936, 914, 903, 883, 815, 790, 778, 725, 677, 641, 600, 492, 418, 402 $cm^{-1}$.

$^1$H NMR (DMSO-$d_6$): $\delta$ = 2.24–2.31 (m, 4 H, $CH_2P$), 2.97–3.03 (m, 4 H, $CH_2Fur$), 6.08–6.31, 7.47 (m, 6 H, $H3_{furyl}$, $H4_{furyl}$, $H5_{furyl}$), 7.13 (s, 4 H, $NH_4$).

$^{13}$C NMR (DMSO-$d_6$): $\delta$ = 23.26 ($CH_2$furyl), 41.02 (d, $^1J_{PC}$ = 38.0 Hz, $CH_2P$), 104.73 ($C3_{furyl}$), 110.30 ($C4_{furyl}$), 141.11 ($C5_{furyl}$), 155.50 (d, $^3J_{PC}$ = 20.2 Hz, $C2_{furyl}$).

$^{31}$P NMR (DMSO-$d_6$): $\delta$ = 23.01 (s + d satellites: $^1J_{PSe}$ = 607 Hz).

$^{77}$Se NMR (DMSO-$d_6$): $\delta$ = –42 (d, $^1J_{PSe}$ = 607 Hz).

Anal. Calcd for $C_{12}H_{18}NO_2PSe_2$: C, 36.29; H, 4.57; N, 3.53; P, 7.80; Se, 39.76. Found: C, 36.32; H, 4.51; N, 3.60; P, 7.68; Se, 39.85.

### Ammonium Diphenyldiselenophosphinate (10i)

White powder; yield: 0.340 g (94%); mp 201–203 °C ($Et_2O$).

IR (KBr): 3048, 2930, 2787, 1958, 1919, 1895, 1816, 1770, 1633, 1570, 1476, 1433, 1395, 1373, 1333, 1305, 1178, 1156, 1127, 1089, 1068, 1024, 997, 973, 923, 849, 742, 689, 618, 536, 516, 472, 444, 428 $cm^{-1}$.

$^1$H NMR (DMSO-$d_6$): $\delta$ = 7.13 (s, 4 H, $NH_4$), 7.21–7.23 (m, 2 H, Ph), 7.25–7.29 (m, 4 H, Ph), 8.01–8.06 (m, 4 H, Ph).

$^{13}$C NMR (DMSO-$d_6$): $\delta$ = 126.66 (d, $^2J_{PC}$ = 11.5 Hz, *o*-C), 128.28 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C), 130.72 (d, $^3J_{PC}$ = 11.0 Hz, *m*-C), 143.30 (d, $^1J_{PC}$ = 59.3 Hz, *ipso*-C).

$^{31}$P NMR (DMSO-$d_6$): $\delta$ = 23.64 (s + d satellites: $^1J_{PSe}$ = 631 Hz).

$^{77}$Se NMR (DMSO-$d_6$): $\delta$ = 15 (d, $^1J_{PSe}$ = 631 Hz).

Anal. Calcd for $C_{12}H_{14}NPSe_2$: C, 39.91; H, 3.91; N, 3.88; P, 8.58; Se, 43.73. Found: C, 39.84; H, 3.96; N, 3.71; P, 8.33; Se, 43.75.

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