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Oxidative cross-coupling of secondary phosphine chalcogenides with amino alcohols and aminophenols: aspects of the reaction chemoselectivity†

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Secondary phosphine chalcogenides react with primary amino alcohols under mild conditions (room temperature, molar ratio of the initial reagents 1 : 1) in a CCl_4/Et_3N oxidizing system to chemoselectively deliver amides of chalcogenophosphinic acids with free OH groups. Under similar conditions, mono-cross-coupling between secondary phosphine chalcogenides and 1,2- or 1,3-aminophenols proceeds only with the participation of phenolic hydroxyl to give aminophenylchalcogenophosphinic *O*-esters. The yields of the synthesized functional amides or esters are 60–85%.

Introduction

In organoelement chemistry, the synthesis of fundamentally new molecules and materials, including organophosphorus ones, is becoming increasingly topical. Organophosphorus compounds bearing P–N or P–O bonds are attracting growing interest thanks to a wide range of their applications.[1–6] Some of these compounds, namely amides and esters of chalcogenophosphinic acids, find application in the directed synthesis of biologically active molecules,[1] such as chemotherapeutic agents against Chagas disease,[1a] acetylcholinesterase[1b] or HIV-1 non-nucleoside reverse transcriptase[1c] inhibitors, and anticancer drugs,[1e] and as ligands for metal complex catalysts,[2] intermediates for the design of semiconductor nanomaterials,[3] fluorescent labels for mercury ion determination,[4] flame retardants,[5] and agrochemicals.[6]

Traditional methods for the synthesis of chalcogenophosphinic acid derivatives are not environmentally friendly because of the use of toxic phosphoryl halides sensitive to moisture and air oxygen.[2c,7] Therefore, the development of a new general and efficient methodology for the synthesis of chalcogenophosphinic acid derivatives, including functional ones, is an urgent challenge. A simple and convenient approach to the preparation of chalcogenophosphinic acids amides and esters is based on the Atherton–Todd reaction, phosphorylation of amines with dialkyl phosphites in the presence of bases and CCl_4.[8] This reaction still draws attention of synthetic chemists as evidenced by numerous publications.[9] In recent decades, the oxidative cross-coupling of secondary phosphine chalcogenides with various HN-, HO- and HS-compounds has been successfully implemented and studied.[10] At the same time, the data on the interaction of secondary phosphine chalcogenides with compounds containing simultaneously different XH groups (where X = N, O, S) are limited to the publication on the cross-coupling of diphenylphosphine oxide with 2-aminoethanol or 3-aminopropanol[11] in CCl_4/CH_2Cl_2 medium affording chalcogenophosphinic amides. The reaction occurs in the presence of 30–50% aq. NaOH that is unacceptable for secondary phosphine sulfides and phosphine selenides because of their disproportionation under the alkaline conditions.[12] Besides, we have recently received signal information on the interaction of available (obtained from red phosphorus and styrene[13]) bis(2-phenylethyl)phosphine chalcogenides with 2-aminophenol in the CCl_4/Et_3N system chemoselectively leading to aminophenylchalcogenophosphinic *O*-esters.[14]

Herein, for the first time we have conducted and studied the reaction of secondary phosphine sulfides and phosphine selenides with amino alcohols in the CCl_4/Et_3N system, determined its chemoselectivity and synthesized new functional derivatives of chalcogenophosphinic acids. In addition, to determine the generality and peculiarities of similar cross-couplings, we have carried out this reaction involving various secondary phosphine oxides, phosphine sulfides, phosphine selenides and 1,2- and 1,3-aminophenols, including functional ones.

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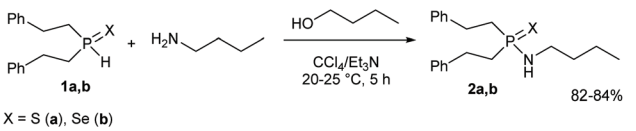
Results and discussion

To obtain preliminary data on the possible direction of the studied cross-coupling, we conducted a competitive reaction among aliphatic amine, alcohol and secondary phosphine chalcogenide. It turned out that stirring a mixture of 1-butylamine, 1-butanol and bis(2-phenylethyl)phosphine sulfide **1a** or bis(2-phenylethyl)phosphine selenide **1b** (all three reagents were taken in an equal molar ratio) at room temperature (5 h, CCl_4/Et_3N system) leads to the chemoselective formation of the corresponding chalcogenophosphinic amides **2a** and **2b** (^{31}P NMR data). In this case, 1-butylamine completely wins the competition for phosphine chalcogenide (Scheme 1), the yields of amides **2a** and **2b** being 82–84%.

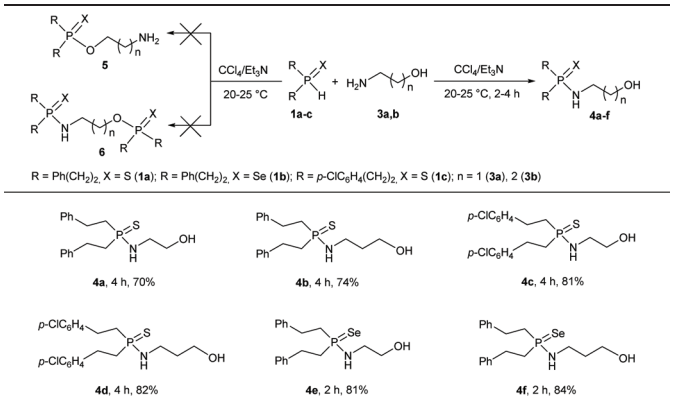
The oxidative cross-coupling between secondary phosphine chalcogenides **1a–c** and primary amino alcohols **3a** and **3b** also proceeds chemoselectively under mild conditions (20–25 °C, 2–4 h, CCl_4/Et_3N, **1 : 3** molar ratio = 1 : 1) to give only chalcogenophosphinic amides **4a–f** in up to 84% yield (Table 1). Possible chalcogenophosphinic *O*-esters **5** and the corresponding *N*,*O*-dichalcogenophosphinates **6** are not formed under the reaction conditions.

Hereinafter, the reactions were monitored by ^{31}P NMR spectroscopy until complete disappearance of peaks of the initial secondary phosphine chalcogenides. In almost all cases, by-products of these reactions were chalcogenophosphinic anhydrides **7** (up to 5%) formed from secondary phosphine chalcogenides **1** according to the known data[15] (Scheme 2).

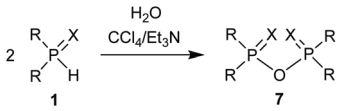


Scheme 1 A competitive reaction of 1-butylamine and 1-butanol with a secondary phosphine chalcogenide.

Table 1 Reaction of secondary phosphine chalcogenides with primary amino alcohols[a]



[a] Reagents and conditions: phosphine chalcogenides **1a–c** (1.0 mmol), amino alcohols **3a** and **3b** (1.0 mmol), Et_3N (1.0 mmol), CCl_4 (3 mL), 20–25 °C.

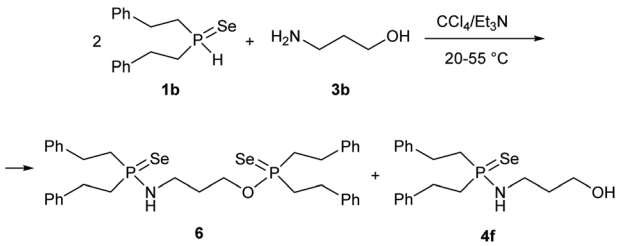


Scheme 2 Formation of chalcogenophosphinic anhydride **7**.

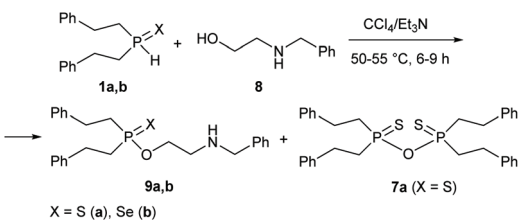
In the example of bis(2-phenylethyl)phosphine selenide **1b** we have shown that a change in the ratio of the initial reagents (secondary phosphine selenide : amino alcohol = 2 : 1, r.t. or 50–55 °C) allows carrying out the cross-coupling simultaneously on both functional groups of amino alcohol to obtain the corresponding *N*,*O*-diselenophosphinate **6** in a 28–32% yield (^{31}P NMR data). However, along with *N*,*O*-diselenophosphinate **6**, selenophosphinic amide **4f** (20–39%) was detected in the reaction mixture (Scheme 3).

To expand the substrate scope of the studied reaction, we tried to transfer this cross-coupling to secondary amino alcohols. However, the interaction between secondary phosphine chalcogenides **1a** and **1b** and 2-(benzylamino)-1-ethanol **8** (50–55 °C, 6–9 h, CCl_4/Et_3N), instead of the expected chalcogenophosphinic amides, delivered chalcogenophosphinic *O*-esters **9a** and **9b**. This reaction with phosphine selenide **1b** proceeded quite efficiently to give ester **9b** in 73% yield. In the case of phosphine sulfide **1a**, which is less reactive in this cross-coupling process, the yield of the target ester **9a** was 46%; a by-product, bis(2-phenylethyl)thiophosphinic anhydride **7a**, was formed in a comparable amount (≈50%, ^{31}P NMR data) (Scheme 4).

To further define the scope and chemoselectivity of this protocol, we subjected aromatic compounds to oxidative cross-coupling with secondary phosphine chalcogenides. To start



Scheme 3 Reaction of secondary phosphine chalcogenide **1b** with amino alcohol **3b** (**1b** : **3b** molar ratio = 2 : 1).

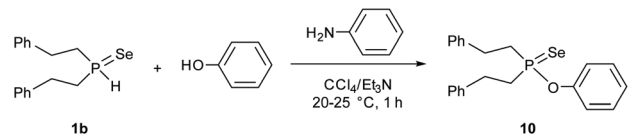


Scheme 4 Reaction of secondary phosphine chalcogenides with a secondary amino alcohol.

with, we conducted a competitive reaction between aniline, phenol and secondary phosphine chalcogenide **1b** (rt, 1 h, CCl_4/Et_3N, molar ratio of the reagents is 1 : 1 : 1).

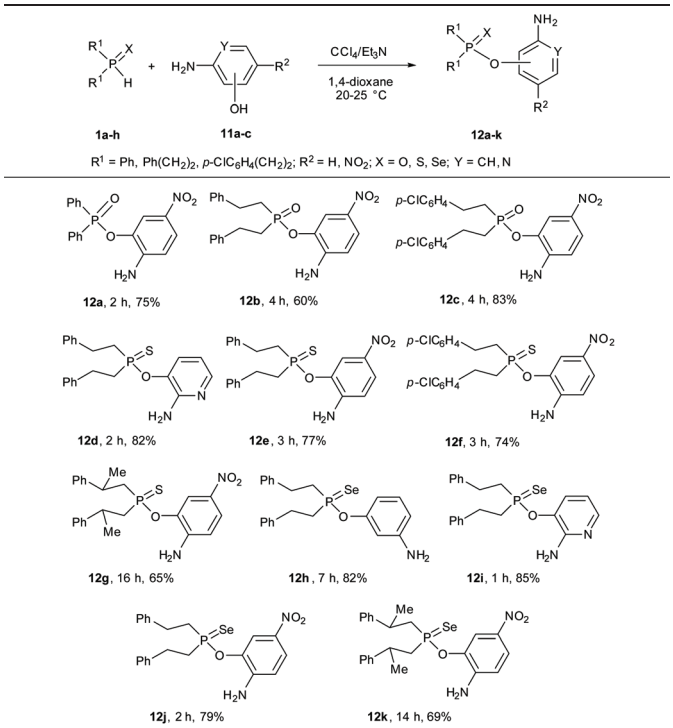
To our surprise, only phenol reacted with phosphine selenide **1b** to yield the corresponding selenophosphinic *O*-ester **10** (Scheme 5), which was identified in the reaction mixture by ^1H, ^{13}C, and ^{31}P NMR using an authentic sample.[10c] Even no traces of amide, the product of the possible reaction of aniline with selenide **1b**, were formed (^{31}P NMR data).

Next, we implemented phosphorylation of 3-aminophenol **11a**, 2-amino-5-nitrophenol **11b**, and 2-amino-3-pyridinol **11c** by secondary phosphine chalcogenides **1a–h** in the CCl_4/Et_3N system. The oxidative cross-coupling of the initial reagents proceeded under mild conditions (20–25 °C, molar ratio **1 : 11** = 1 : 1). The reaction turned out to be strictly chemoselective: only the OH function of aminophenols underwent phosphorylation to furnish the corresponding aminophenyl esters of diorganylchalcogenophosphinic acids **12a–k** in 60–85% yields (Table 2).



Scheme 5 A competitive reaction of phenol and aniline with a secondary phosphine chalcogenide.

Table 2 The scope of the chemoselective phosphorylation of aminophenols[a]



[a] Reagents and conditions: phosphine chalcogenides **1a–h** (1.0 mmol), aminophenols **11a–c** (1.0 mmol), Et_3N (1.0 mmol), CCl_4 (3 mL), 1,4-dioxane (1 mL), 20–25 °C.

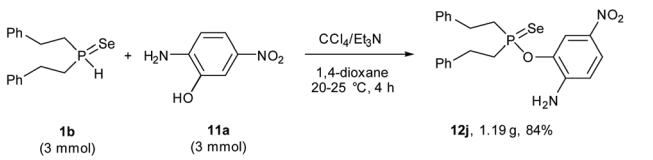
The high chemoselectivity of this reaction also remained intact when a two-fold molar excess of secondary phosphine chalcogenide with respect to aminophenol was used: neither products of the oxidative cross-coupling at the amino group nor dicoupling products (*N*,*O*-derivatives of chalcogenophosphinic acid) were detected in the reaction mixture (^{31}P NMR data) under similar conditions (20–25 °C, CCl_4/Et_3N).

To confirm the practicability and scalability of the process, the gram-scale synthesis of compound **12j** was successfully performed (Scheme 6). Phosphine selenide **1b** (3 mmol) and aminophenol **11a** (3 mmol) reacted facilely under the above conditions without any loss in the efficiency and chemoselectivity.

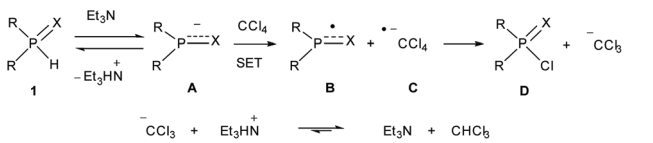
Apparently,[16] the reaction of secondary phosphine chalcogenides with amino alcohols and aminophenols starts with deprotonation of secondary phosphine chalcogenide **1** by triethylamine (Scheme 7). According to the calculations (see also the ESI, Table S2†), the barrier for this stage is +94–114 kcal mol^{-1}, so this is probably the rate-limiting step. The resulting *P*,*X*-ambident chalcogenophosphinite-anion **A** participates in single electron transfer (SET) with a molecule of CCl_4 to give the free radical of secondary phosphine chalcogenide **B** and the anion radical **C**. The interaction of species **B** and **C** leads to *in situ* generation of chalcogenophosphoryl chloride **D** and $^-CCl_3$ carbanion and does not affect the reaction rate, since it proceeds in the cell and is energetically favorable in general (ΔE −7.6–30.7 kcal mol^{-1}, see Fig. 1).

The trichloromethanide anion is protonated by the triethylammonium cation to regenerate Et_3N and form chloroform. Chalcogenophosphoryl chloride **D** and chloroform have been identified in the reaction mixture by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

The reaction between chloride **D** and primary amino alcohol **3** in the presence of Et_3N results in the target amides **4** (Scheme 8). The chemoselective formation of chalcogenophosphinic amides **4** at an equimolar ratio of the starting reagents can be explained by a higher *N*-nucleophilicity of primary



Scheme 6 Gram-scale synthesis of **12j**.



Scheme 7 A plausible reaction mechanism.

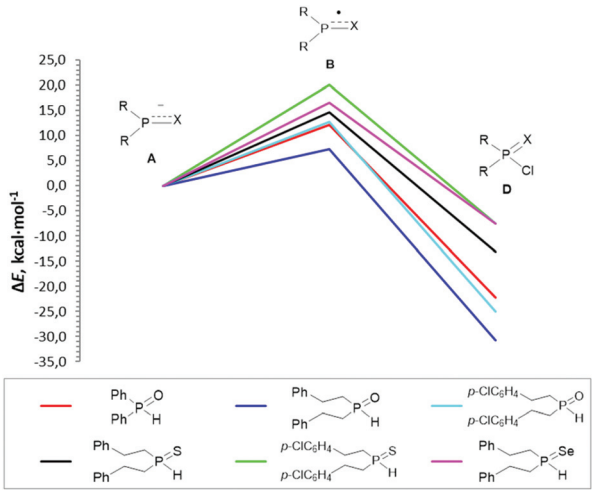
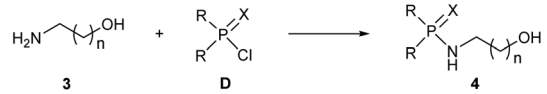


Fig. 1 Energy profiles for the formation of chlorides **D**.

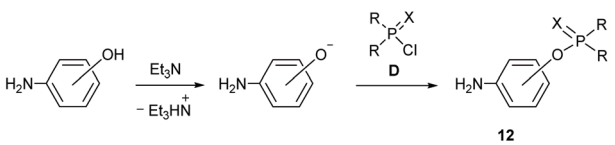


Scheme 8 Formation of chalcogenophosphinic amides **4**.

amino alcohols compared to their *O*-nucleophilicity (similar to the competitive reaction of 1-butylamine and 1-butanol with secondary phosphine chalcogenide, Scheme 1). The observed lower reactivity of the secondary amino group is apparently due to the electron-withdrawing effect of the benzyl group and steric hindrance created by bulky substituents at the nitrogen atom in secondary amino alcohol **8** that decreases its *N*-nucleophilicity.

The change in the cross-coupling chemoselectivity upon replacement of primary amino alcohols with aminophenols is probably due to deprotonation of aminophenols by Et_3N under the reaction conditions (Scheme 9). The resulting phenolate anion has a considerably higher nucleophilicity than an aromatic amino group[17] that allows directing the process exclusively to the formation of *O*-esters **12**.

The proposed reaction mechanism including the generation of the free radical of secondary phosphine chalcogenide **B** (Scheme 7) has been confirmed experimentally. So, while stirring bis(2-phenylethyl)phosphine selenide **1b**, Et_3N and TEMPO (their molar ratio being 1 : 1 : 1) in CCl_4 at r.t. (10 min), TEMPO quantitatively trapped selenophosphoryl radicals of type **B** to deliver the corresponding adduct, 1-{[bis(2-phenylethyl)phosphoroselenoyl]oxy}-2,2,6,6-tetramethylpiperidine, thus completely preventing the formation of chloride **D** (see also the ESI† for the experiment details).



Scheme 9 Formation of chalcogenophosphinic esters **12**.

As observed from Tables 1, 2 and Scheme 4, the reaction rate considerably depends on the nature of the chalcogen in secondary phosphine chalcogenides. For secondary phosphine oxides, in comparison with phosphine sulfides and selenides, the barrier for the formation of radical **B** from anion **A** (ΔE +7–20 kcal mol^{-1}) is smaller and the energetic effect of the formation of chloride **D** is greater (Fig. 1).

However, despite the fact that the stage of the formation of chalcogenophosphoryl chloride is thermodynamically more favorable for phosphine oxides, analogous phosphine sulfides and especially phosphine selenides turned out to be more reactive in the studied process (*e.g.*, compare Table 2, **12b**, **12e**, and **12j**). Apparently, the rate-determining step of the oxidative cross-coupling is the stage of nucleophilic substitution of the halogen atom at the phosphorus atom of the chalcogenophosphoryl group in chloride **D** (Schemes 8 and 9). Extended calculations for this stage are in progress and will be published later.

It is noteworthy that the reactivity order for secondary phosphine chalcogenides observed in this work (Table 2, Se > S > O) is inverse to that previously published.[16d] This is probably due to differences in the nature of the substrates used in both works.

Substituents at the phosphorus atom also have a significant effect on the reaction progress. Bulkier (and less acidic[18]) bis(2-phenylethyl)phosphine oxide turned out to be less reactive than diphenylphosphine oxide (compare Table 2, **12a** and **12b**). The longest reaction time (14 and 16 h) was observed for phosphine chalcogenides with the bulkiest substituent, PhCH(Me)CH_2 (Table 2, **12g,k**), which clearly indicates the importance of steric shielding of the phosphorus atom.

Among the studied aminophenols, 2-amino-3-pyridinol **11c** was the most active (Table 2, **12d,i**) which is in accordance with Scheme 9. Since pyridinols seem to be more acidic than the corresponding phenols,[19] they should generate phenolate anions in a higher concentration.

Conclusions

In conclusion, we have developed a convenient protocol for the directed highly chemoselective synthesis of new prospective functional derivatives of chalcogenophosphinic acids, amides with a free hydroxyl function and esters with an amino group, thus opening a way to their further modification, including with pharmacophore groups.

Experimental

General information

All reactions were carried out under an argon atmosphere. Amino alcohols, aminophenols, 1-butylamine, 1-butanol, and

diphenylphosphine oxide **1d** are commercial reagents (Aldrich). Secondary phosphine chalcogenides **1a–c,e–h** were prepared from styrene, 4-chlorostyrene, α-methylstyrene and elemental phosphorus as previously described.[20] The reaction was monitored using ^{31}P NMR spectra by the disappearance of peaks of the initial secondary phosphine chalcogenides.

The ^{1}H, ^{13}C, ^{15}N, ^{31}P, and ^{77}Se NMR spectra were recorded on Bruker DPX 400 and Bruker AV-400 spectrometers (400.13, 100.62, 40.56, 161.98, and 76.31 MHz, respectively) in $CDCl_3$, DMSO-d_6, and acetone-d_6 solutions and referenced to HMDS (^{1}H, ^{13}C), $MeNO_2$ (^{15}N), H_3PO_4 (^{31}P), and Me_2Se (^{77}Se). The assignment of signals in ^{1}H spectra was performed using the 2D homonuclear correlation method COSY. The resonance signals of ^{13}C were assigned with the application of 2D heteronuclear correlation methods HSQC and HMBC. The values of δ ^{15}N were measured through the 2D ^{1}H–^{15}N HMBC experiment. FT-IR spectra were obtained with a Varian 3100 FT-IR spectrometer. The C, H, N microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The Cl, P, S, and Se contents were determined by the combustion method. The optimized geometries and energies of the reactants were calculated at the B3LYP/6-311++G(d,p) level of theory using the Gaussian 09 program.[21]

Typical procedure and analytical data

A competitive reaction of 1-butylamine and 1-butanol with secondary phosphine chalcogenides 1a and 1b: general procedure. To a solution of secondary phosphine chalcogenide **1a** or **1b** (1.0 mmol) in CCl_4 (3 mL), Et_3N (101 mg, 1.0 mmol) was added. The mixture was stirred at 20–25 °C for 10 min. Then, a solution of 1-butylamine (1.0 mmol) and 1-butanol (1.0 mmol) in CCl_4 (1 mL) was added, and the reaction mixture was stirred at 20–25 °C for 5 h. After the completion of the reaction (^{31}P NMR monitoring), the solvent was removed under reduced pressure. The residue was purified by column chromatography on SiO_2, eluent – toluene/Et_2O (10 : 1). The obtained crude product was dried under vacuum to give amides **2a** and **2b**.

***N*-Butyl-bis(2-phenylethyl)phosphinothioic amide (2a).** Yield: 283 mg (82%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.95 (t, 3H, Me, $^{3}J_{HH}$ = 7.2 Hz); 1.33–1.38 (m, 2H, $NCH_2CH_2C\underline{H}_2$); 1.42–1.47 (m, 2H, $NCH_2C\underline{H}_2$); 1.98 (br s, 1H, NH); 2.16–2.27 (m, 4H, CH_2P); 2.82–2.89 (m, 2H, CH_2N); 2.97–3.07 (m, 4H, $PhC\underline{H}_2$); 7.24–7.35 (m, 10H, Ph). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 13.7 (Me); 19.8 ($NCH_2CH_2\underline{C}H_2$); 28.5 (d, $Ph\underline{C}H_2$, $^{2}J_{PC}$ = 2.9 Hz); 33.8 (d, $NCH_2\underline{C}H_2$, $^{3}J_{PC}$ = 7.3 Hz); 34.6 (d, CH_2P, $^{1}J_{PC}$ = 62.9 Hz); 41.0 (d, CH_2N, $^{2}J_{PC}$ = 3.4 Hz); 126.2 (C_p); 128.2 (C_m); 128.5 (C_o); 140.8 (d, C_i, $^{3}J_{PC}$ = 14.4 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −334.9. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 70.5. IR (neat): ν_{max} = 3060, 3026, 2953, 2928, 2865, 1602, 1496, 1454, 1400, 1211, 1123, 1089, 1031, 950, 906, 846, 749, 699, 611, 554, 496 cm^{-1}. Anal. calcd for $C_{20}H_{28}NPS$: C 69.53; H 8.17; N 4.05; P 8.97; S 9.28. Found: C 69.71; H 8.25; N 4.12; P 8.73; S 9.07.

***N*-Butyl-bis(2-phenylethyl)phosphinoselenoic amide (2b).** Yield: 329 mg (84%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.93 (t, 3H, Me, $^{3}J_{HH}$ = 7.3 Hz); 1.29–1.38 (m, 2H, $NCH_2CH_2C\underline{H}_2$); 1.40–1.47 (m, 2H, $NCH_2C\underline{H}_2$); 1.95 (br s, 1H, NH); 2.22–2.43 (m, 4H, CH_2P); 2.79–2.86 (m, 2H, CH_2N); 2.93–3.09 (m, 4H, $PhC\underline{H}_2$); 7.22–7.34 (m, 10H, Ph). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 13.7 (Me); 19.8 ($NCH_2CH_2\underline{C}H_2$); 29.1 (d, $Ph\underline{C}H_2$, $^{2}J_{PC}$ = 2.3 Hz); 33.5 (d, $NCH_2\underline{C}H_2$, $^{3}J_{PC}$ = 7.7 Hz); 34.9 (d, CH_2P, $^{1}J_{PC}$ = 54.7 Hz); 41.8 (d, CH_2N, $^{2}J_{PC}$ = 4.2 Hz); 126.4 (C_p); 128.3 (C_m); 128.6 (C_o); 140.5 (d, C_i, $^{3}J_{PC}$ = 14.6 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −334.7. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 64.2 (+d-satellites, $^{1}J_{PSe}$ = 723.8 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −316.2 (d, $^{1}J_{PSe}$ = 723.8 Hz). IR (neat): ν_{max} = 3061, 3026, 2955, 2929, 2866, 1602, 1494, 1453, 1399, 1212, 1129, 1087, 1031, 950, 908, 845, 748, 700, 579, 477 cm^{-1}. Anal. calcd for $C_{20}H_{28}NPSe$: C 61.22; H 7.19; N 3.57; P 7.89; Se 20.12. Found: C 61.43; H 7.30; N 3.49; P 7.72; Se 19.95.

Reaction of secondary phosphine chalcogenides 1a–c with amino alcohols 3a and 3b and 8: general procedure. To a solution of secondary phosphine chalcogenides **1a–c** (1.0 mmol) in CCl_4 (3 mL), Et_3N (101 mg, 1.0 mmol) was added. The mixture was stirred at 20–25 °C for 10 min. Then, amino alcohols **3a** or **3b** or **8** (1.0 mmol) were added and the reaction mixture was stirred at 20–25 °C for 2–6 h (see also Table 1 and Scheme 4). After the completion of the reaction (^{31}P NMR monitoring), the solvent was removed under reduced pressure. The residue was purified by column chromatography on SiO_2, eluent – toluene/Et_2O (10 : 1). The obtained crude product was dried under vacuum to give amides **4a–f** and **9a** and **9b**.

***N*-(2-Hydroxyethyl)-bis(2-phenylethyl)phosphinothioic amide (4a).** Yield: 233 mg (70%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.17–2.25 (m, 4H, CH_2P); 2.41, 2.43 (br s, 2H, OH, NH); 2.93–3.06 (m, 6H, $PhC\underline{H}_2$, NCH_2); 3.66 (t, 2H, OCH_2, $^{3}J_{HH}$ = 5.2 Hz); 7.20–7.23 (m, 6H, $H_{o,p}$); 7.28–7.32 (m, 4H, H_m). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 28.8 (d, $Ph\underline{C}H_2$, $^{2}J_{PC}$ = 2.9 Hz); 35.3 (d, CH_2P, $^{1}J_{PC}$ = 63.3 Hz); 43.5 (d, NCH_2, $^{2}J_{PC}$ = 2.4 Hz); 63.0 (d, OCH_2, $^{3}J_{PC}$ = 6.2 Hz); 126.6 (C_p); 128.4 (C_o); 128.8 (C_m); 140.8 (d, C_i, $^{3}J_{PC}$ = 14.2 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −338.6. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 72.0. IR (neat): ν_{max} = 3287, 3059, 3026, 2924, 2863, 1603, 1495, 1451, 1400, 1208, 1109, 1055, 952, 756, 700, 608, 553, 494 cm^{-1}. Anal. calcd for $C_{18}H_{24}NOPS$: C 64.84; H 7.26; N 4.20; P 9.29; S 9.62. Found: C 64.99; H 7.32; N 4.25; P 9.07; S 9.39.

***N*-(3-Hydroxypropyl)-bis(2-phenylethyl)phosphinothioic amide (4b).** Yield: 257 mg (74%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.69 (quintet, 2H, $-CH_2-$, $^{3}J_{HH}$ = 5.9 Hz); 2.18–2.31 (m, 6H, CH_2P, OH, NH); 2.96–3.09 (m, 6H, $PhC\underline{H}_2$, NCH_2); 3.74 (t, 2H, OCH_2, $^{3}J_{HH}$ = 5.7 Hz); 7.24–7.27 (m, 6H, $H_{o,p}$); 7.30–7.36 (m, 4H, H_m). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 28.7 (d, $Ph\underline{C}H_2$, $^{2}J_{PC}$ = 2.8 Hz); 33.8 (d, $-CH_2-$, $^{3}J_{PC}$ = 6.4 Hz); 35.0 (d, CH_2P, $^{1}J_{PC}$ = 63.0 Hz); 38.2 (d, NCH_2, $^{2}J_{PC}$ = 2.6 Hz); 59.9 (OCH_2); 126.5 (C_p); 128.4 (C_o); 128.7 (C_m); 140.8 (d, C_i, $^{3}J_{PC}$ = 14.4 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −335.2. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 71.3. IR (neat): ν_{max} = 3284, 3060, 3027, 2929, 2870, 1602, 1493, 1450, 1402, 1209, 1092, 1072, 1006, 950, 859, 752, 700, 608, 554, 496 cm^{-1}. Anal. calcd for $C_{19}H_{26}NOPS$: C 65.68; H 7.54; N 4.03; P 8.91; S 9.23. Found: C 65.90; H 7.61; N 4.11; P 8.69; S 9.01.

***N*-(2-Hydroxyethyl)-bis[2-(4-chlorophenyl)ethyl]phosphinothioic amide (4c).** Yield: 326 mg (81%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.13–2.23 (m, 4H, CH_2P); 2.88–3.00 (m, 6H, PhC$\underline{H}_2$, OH, NH); 3.06–3.11 (m, 2H, NCH_2); 3.69 (t, 2H, OCH_2, $^{3}J_{HH}$ = 4.9 Hz); 7.13–7.15 (m, 4H, H_o); 7.26–7.28 (m, 4H, H_m). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 28.0 (d, Ph$\underline{C}H_2$, $^{2}J_{PC}$ = 2.6 Hz); 34.8 (d, CH_2P, $^{1}J_{PC}$ = 63.0 Hz); 43.4 (d, NCH_2, $^{2}J_{PC}$ = 2.9 Hz); 62.7 (d, OCH_2, $^{3}J_{PC}$ = 6.3 Hz); 128.8 (C_o); 129.3 (C_m); 132.2 (C_p); 139.0 (d, C_i, $^{3}J_{PC}$ = 14.9 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −340.1. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 71.5. IR (neat): ν_{max} = 3299, 3097, 3035, 2928, 2869, 1648, 1491, 1445, 1404, 1210, 1097, 1057, 1015, 953, 811, 772, 732, 655, 593, 512 cm^{-1}. Anal. calcd for $C_{18}H_{22}Cl_2NOPS$: C 53.74; H 5.51; Cl 17.62; N 3.48; P 7.70; S 7.97. Found: C 53.91; H 5.60; Cl 17.47; N 3.57; P 7.48; S 7.73.

***N*-(3-Hydroxypropyl)-bis[2-(4-chlorophenyl)ethyl]phosphinothioic amide (4d).** Yield: 341 mg (82%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.81 (quintet, 2H, –CH_2–, $^{3}J_{HH}$ = 5.4 Hz); 2.18–2.33 (m, 4H, CH_2P); 2.50, 2.60 (br s, 2H, NH, OH); 2.97–3.19 (m, 6H, PhC$\underline{H}_2$, NCH_2); 3.85 (t, 2H, OCH_2, $^{3}J_{HH}$ = 5.3 Hz); 7.24–7.26 (m, 4H, H_o); 7.37–7.39 (m, 4H, H_m). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 28.1 (d, Ph$\underline{C}H_2$, $^{2}J_{PC}$ = 2.6 Hz); 33.8 (d, –CH_2–, $^{3}J_{PC}$ = 6.5 Hz); 34.8 (d, CH_2P, $^{1}J_{PC}$ = 63.0 Hz); 38.4 (d, NCH_2, $^{2}J_{PC}$ = 2.8 Hz); 59.9 (OCH_2); 128.8 (C_o); 129.7 (C_m); 132.3 (C_p); 139.2 (d, C_i, $^{3}J_{PC}$ = 14.8 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −335.6. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 70.7. IR (neat): ν_{max} = 3278, 3092, 3032, 2928, 2871, 1644, 1490, 1443, 1405, 1210, 1092, 1011, 950, 914, 811, 773, 732, 655, 593, 513 cm^{-1}. Anal. calcd for $C_{19}H_{22}Cl_2NOPS$: C 54.81; H 5.81; Cl 17.03; N 3.36; P 7.44; S 7.70. Found: C 55.01; H 5.89; Cl 16.90; N 3.43; P 7.28; S 7.49.

***N*-(2-Hydroxyethyl)-bis(2-phenylethyl)phosphinoselenoic amide (4e).** Yield: 308 mg (81%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.26–2.36 (m, 4H, CH_2P); 2.68 (br s, 1H, OH); 2.88–3.03 (m, 7H, PhC$\underline{H}_2$, NCH_2, NH); 3.63 (t, 2H, OCH_2, $^{3}J_{HH}$ = 4.9 Hz); 7.19–7.21 (m, 6H, $H_{o,p}$); 7.26–7.30 (m, 4H, H_m). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 29.2 (d, Ph$\underline{C}H_2$, $^{2}J_{PC}$ = 2.3 Hz); 35.5 (d, CH_2P, $^{1}J_{PC}$ = 54.4 Hz); 44.1 (d, NCH_2, $^{2}J_{PC}$ = 3.1 Hz); 62.4 (d, OCH_2, $^{3}J_{PC}$ = 6.7 Hz); 126.4 (C_p); 128.3 (C_o); 128.6 (C_m); 140.4 (d, C_i, $^{3}J_{PC}$ = 14.8 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −340.4. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 66.5 (+d-satellites, $^{1}J_{PSe}$ = 718.9 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −302.9 (d, $^{1}J_{PSe}$ = 718.9 Hz). IR (neat): ν_{max} = 3273, 3060, 3026, 2925, 2862, 1602, 1495, 1450, 1398, 1208, 1107, 1054, 952, 913, 875, 750, 701, 577, 471 cm^{-1}. Anal. calcd for $C_{18}H_{24}NOPSe$: C 56.84; H 6.36; N 3.68; P 8.14; Se 20.76. Found: C 57.02; H 6.44; N 3.75; P 7.92; Se 20.61.

***N*-(3-Hydroxypropyl)-bis(2-phenylethyl)phosphinoselenoic amide (4f).** Yield: 331 mg (84%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.68 (quintet, 2H, –CH_2–, $^{3}J_{HH}$ = 5.9 Hz); 2.24–2.42 (m, 6H, CH_2P, OH, NH); 2.96–3.07 (m, 6H, PhC$\underline{H}_2$, NCH_2); 3.73 (t, 2H, OCH_2, $^{3}J_{HH}$ = 5.7 Hz); 7.24–7.35 (m, 10H, Ph). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 29.3 (d, Ph$\underline{C}H_2$, $^{2}J_{PC}$ = 2.3 Hz); 33.6 (d, –CH_2–, $^{3}J_{PC}$ = 6.9 Hz); 35.5 (d, CH_2P, $^{1}J_{PC}$ = 54.6 Hz); 39.2 (d, NCH_2, $^{2}J_{PC}$ = 3.2 Hz); 59.9 (OCH_2); 126.6 (C_p); 128.4 (C_o); 128.8 (C_m); 140.5 (d, C_i, $^{3}J_{PC}$ = 14.5 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −337.1. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 65.2 (+d-satellites, $^{1}J_{PSe}$ = 719.0 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −315.0 (d, $^{1}J_{PSe}$ = 719.0 Hz). IR (neat): ν_{max} = 3261, 3062, 3027, 2927, 2864, 1602, 1494, 1452, 1400, 1207, 1074, 1005, 911, 866, 738, 650, 577, 475 cm^{-1}. Anal. calcd for $C_{19}H_{26}NOPSe$: C 57.87; H 6.65; N 3.55; P 7.85; Se 20.02. Found: C 58.04; H 6.72; N 3.62; P 7.66; Se 19.87.

***O*-[2-(Benzylamino)ethyl]-bis(2-phenylethyl)phosphinothioate (9a).** Yield: 195 mg (46%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.17–2.31 (m, 4H, CH_2P); 2.86 (t, 2H, $NC\underline{H}_2CH_2$, $^{3}J_{HH}$ = 5.2 Hz); 2.93–3.02 (m, 5H, $PhC\underline{H}_2CH_2$, NH); 3.84 (s, 2H, $NC\underline{H}_2Ph$); 4.11 (dt, 2H, OCH_2, $^{3}J_{HH}$ = 5.2 Hz, $^{2}J_{PH}$ = 9.3 Hz); 7.18–7.34 (m, 15H, Ph). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 28.8 (d, $Ph\underline{C}H_2CH_2$, $^{2}J_{PC}$ = 3.1 Hz); 36.2 (d, CH_2P, $^{1}J_{PC}$ = 67.5 Hz); 48.9 (d, $N\underline{C}H_2CH_2$, $^{3}J_{PC}$ = 7.1 Hz); 53.4 ($N\underline{C}H_2Ph$); 64.0 (d, OCH_2, $^{2}J_{PC}$ = 6.5 Hz); 126.5 (C_p, $\underline{Ph}CH_2CH_2$); 127.3 (C_p, $NCH_2\underline{Ph}$); 128.31 (C_o, $NCH_2\underline{Ph}$); 128.34 (C_o, $\underline{Ph}CH_2CH_2$); 128.6 (C_m, $NCH_2\underline{Ph}$); 128.7 (C_m, $\underline{Ph}CH_2CH_2$); 139.4 (C_i, $NCH_2\underline{Ph}$); 140.6 (d, C_i, $\underline{Ph}CH_2CH_2$, $^{3}J_{PC}$ = 14.9 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −343.7. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 104.1. Anal. calcd for $C_{25}H_{30}NOPS$: C 70.89; H 7.14; N 3.31; P 7.31; Se 7.57. Found: C 70.72; H 7.06; N 3.16; P 7.12; S 7.33.

***O*-[2-(Benzylamino)ethyl]-bis(2-phenylethyl)phosphinoselenoate (9b).** Yield: 343 mg (73%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.36–2.46 (m, 4H, CH_2P); 2.88 (t, 2H, $NC\underline{H}_2CH_2$, $^{3}J_{HH}$ = 5.0 Hz); 2.93–3.03 (m, 5H, $PhC\underline{H}_2CH_2$, NH); 3.86 (s, 2H, $NC\underline{H}_2Ph$); 4.13 (dt, 2H, OCH_2, $^{3}J_{HH}$ = 5.0 Hz, $^{2}J_{PH}$ = 9.8 Hz); 7.20–7.38 (m, 15H, Ph). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 29.3 (d, $Ph\underline{C}H_2CH_2$, $^{2}J_{PC}$ = 2.6 Hz); 37.4 (d, CH_2P, $^{1}J_{PC}$ = 57.7 Hz); 48.7 (d, $N\underline{C}H_2CH_2$, $^{3}J_{PC}$ = 7.2 Hz); 53.4 ($N\underline{C}H_2Ph$); 65.4 (d, OCH_2, $^{2}J_{PC}$ = 6.7 Hz); 126.6 (C_p, $\underline{Ph}CH_2CH_2$); 127.4 (C_p, $NCH_2\underline{Ph}$); 128.40 (C_o, $NCH_2\underline{Ph}$); 128.42 (C_o, $\underline{Ph}CH_2CH_2$); 128.6 (C_m, $NCH_2\underline{Ph}$); 128.8 (C_m, $\underline{Ph}CH_2CH_2$); 139.3 (C_i, $NCH_2\underline{Ph}$); 140.4 (d, C_i, $\underline{Ph}CH_2CH_2$, $^{3}J_{PC}$ = 15.2 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −343.3. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 104.5 (+d-satellites, $^{1}J_{PSe}$ = 776.2 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −300.6 (d, $^{1}J_{PSe}$ = 776.2 Hz). IR (neat): ν_{max} = 3155, 3064, 3029, 2924, 2854, 2251, 2221, 1636, 1604, 1495, 1455, 1213, 1134, 1031, 910, 735, 650, 581, 465 cm^{-1}. Anal. calcd for $C_{25}H_{30}NOPSe$: C 63.83; H 6.43; N 2.98; P 6.58; Se 16.78. Found: C 63.99; H 6.50; N 3.05; P 6.42; Se 16.63.

Reaction of secondary phosphine chalcogenides 1a–h with aminophenols 11a–c: general procedure. To a solution of secondary phosphine chalcogenides **1a–h** (1.0 mmol) in a mixture of CCl_4 (3 mL) and 1,4-dioxane (1 mL), Et_3N (101 mg, 1.0 mmol) was added. The mixture was stirred at 20–25 °C for 10 min. Then, aminophenols **11a–c** (1.0 mmol) were added, and the reaction mixture was stirred at 20–25 °C for 2–4 h (see also Table 2). After the completion of the reaction (^{31}P NMR monitoring), the solvent was removed under reduced pressure, and 1,4-dioxane (3 mL) was added to the residue. The precipitated white solid (triethylammonium chloride) was filtered, and the solvent was removed from the filtrate under reduced pressure. The residue obtained was reprecipitated from $CHCl_3$ to hexane (for compounds **12b,e,g,h,j,k**) or washed with Et_2O

(2 mL × 7) (for **12a,c,d,f,i**), and then dried under vacuum to give esters **12a–k**.

Gram-scale synthesis of compound 12j. To a solution of secondary phosphine selenide **1b** (964 mg, 3.0 mmol) in a mixture of CCl_4 (9 mL) and 1,4-dioxane (3 mL), Et_3N (304 mg, 3.0 mmol) was added. The mixture was stirred at 20–25 °C for 10 min. Then, aminophenol **11a** (462 mg, 3.0 mmol) was added, and the reaction mixture was stirred at 20–25 °C for 4 h (see also Scheme 6). After the completion of the reaction (^{31}P NMR monitoring), the solvent was removed under reduced pressure, and 1,4-dioxane (9 mL) was added to the residue. The precipitated white solid (triethylammonium chloride) was filtered, and the solvent was removed from the filtrate under reduced pressure. The residue obtained was reprecipitated from $CHCl_3$ to hexane, and then dried under vacuum to give ester **12j** (yield: 1.19 g, 84%).

2-Amino-5-nitrophenyl diphenylphosphinate (12a). Yield: 266 mg (75%); yellow powder, mp 205–206 °C (washed with Et_2O). ^{1}H NMR (400.13 MHz, DMSO-d_6): δ 6.68 (br s, 2H, NH_2); 6.78 (d, 1H, H_3, OPh, $^3J_{HH}$ = 8.9 Hz); 7.56–7.64 (m, 6H, $H_{m,p}$, PhP); 7.79 (d, 1H, H_4, OPh, $^3J_{HH}$ = 8.9 Hz); 7.96–8.00 (m, 4H, H_o, PhP); 8.22 (s, 1H, H_6, OPh). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6): δ 113.7 (C_4, OPh); 116.5 (d, C_6, OPh, $^3J_{PC}$ = 3.8 Hz); 122.5 (C_3, OPh); 128.9 (d, C_m, PhP, $^3J_{PC}$ = 13.3 Hz); 130.0 (d, C_i, PhP, $^1J_{PC}$ = 136.2 Hz); 131.5 (d, C_o, PhP, $^2J_{PC}$ = 10.7 Hz); 133.0 (d, C_p, PhP, $^4J_{PC}$ = 2.9 Hz); 134.9 (C_5, OPh); 135.4 (d, C_2, OPh, $^3J_{PC}$ = 7.8 Hz); 147.1 (d, C_1, OPh, $^2J_{PC}$ = 4.7 Hz). ^{15}N NMR (40.56 MHz, DMSO-d_6): δ −307.6 (NH_2); −11.4 (NO_2). ^{31}P NMR (161.98 MHz, DMSO-d_6): δ 34.0. IR (KBr): ν_{max} = 3189, 3058, 2734, 1637, 1593, 1519, 1481, 1439, 1306, 1219, 1193, 1133, 1088, 963, 900, 860, 821, 736, 694, 569, 528 cm^{-1}. Anal. calcd for $C_{18}H_{15}N_2O_4P$: C 61.02; H 4.27; N 7.91; P 8.74. Found: C 61.21; H 4.35; N 7.98; P 8.58.

2-Amino-5-nitrophenyl bis(2-phenylethyl)phosphinate (12b). Yield: 246 mg (60%); yellow powder, mp 139–141 °C (reprecipitated from $CHCl_3$ to hexane). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.14–2.23 (m, 4H, CH_2P); 2.90–2.99 (m, 4H, PhC$\underline{H}_2$); 3.10 (br s, 2H, NH_2); 6.74 (d, 1H, H_3, OPh, $^3J_{HH}$ = 8.8 Hz); 7.16 (d, 4H, H_o, $\underline{Ph}CH_2$, $^3J_{HH}$ = 8.2 Hz); 7.21–7.25 (m, 4H, H_m, $\underline{Ph}CH_2$); 7.28–7.33 (m, 2H, H_p, $\underline{Ph}CH_2$); 7.93 (dd, 1H, H_4, OPh, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.6 Hz); 7.97 (dd, 1H, H_6, OPh, $^4J_{HH}$ = 2.6 Hz, $^4J_{HH}$ = 1.4 Hz). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 28.0 (d, PhC$\underline{H}_2$, $^2J_{PC}$ = 3.0 Hz); 29.9 (d, CH_2P, $^1J_{PC}$ = 85.5 Hz); 115.1 (C_4, OPh); 118.0 (d, C_6, OPh, $^3J_{PC}$ = 4.0 Hz); 122.9 (C_3, OPh); 126.9 (C_p, $\underline{Ph}CH_2$); 128.2 (C_o, $\underline{Ph}CH_2$); 128.9 (C_m, $\underline{Ph}CH_2$); 136.4 (d, C_2, OPh, $^3J_{PC}$ = 9.7 Hz); 138.3 (C_5, OPh); 140.0 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 13.7 Hz); 146.0 (d, C_1, OPh, $^2J_{PC}$ = 2.8 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −316.6 (NH_2); −10.8 (NO_2). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 60.7. IR (neat): ν_{max} = 3202, 3065, 3027, 2923, 1629, 1595, 1512, 1495, 1452, 1401, 1312, 1199, 1082, 1028, 965, 907, 858, 786, 740, 703, 641, 495, 451 cm^{-1}. Anal. calcd for $C_{22}H_{23}N_2O_4P$: C 64.38; H 5.65; N 6.83; P 7.55. Found: C 64.56; H 5.72; N 6.89; P 7.37.

2-Amino-5-nitrophenyl bis[2-(4-chlorophenyl)ethyl]phosphinate (12c). Yield: 398 mg (83%); brown powder, mp 131–133 °C (washed with Et_2O). ^{1}H NMR (400.13 MHz, DMSO-d_6): δ 2.24–2.32 (m, 4H, CH_2P); 2.76–2.89 (m, 4H, PhC$\underline{H}_2$); 6.73 (br s, 2H, NH_2); 6.79 (d, 1H, H_3, OPh, $^3J_{HH}$ = 9.1 Hz); 7.26 (d, 4H, H_o, $\underline{Ph}CH_2$, $^3J_{HH}$ = 8.1 Hz); 7.33 (d, 4H, H_m, $\underline{Ph}CH_2$, $^3J_{HH}$ = 8.1 Hz); 7.87 (d, 1H, H_4, OPh, $^3J_{HH}$ = 9.1 Hz); 8.08 (s, 1H, H_6, OPh). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6): δ 26.3 (d, PhC$\underline{H}_2$, $^2J_{PC}$ = 3.2 Hz); 29.0 (d, CH_2P, $^1J_{PC}$ = 85.1 Hz); 113.2 (C_4, OPh); 116.7 (C_6, OPh); 123.5 (C_3, OPh); 128.3 (C_o, $\underline{Ph}CH_2$); 130.0 (C_m, $\underline{Ph}CH_2$); 130.8 (C_p, $\underline{Ph}CH_2$); 135.1 (C_5, OPh); 135.3 (d, C_2, OPh, $^3J_{PC}$ = 8.7 Hz); 140.0 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 15.6 Hz); 147.6 (C_1, OPh). ^{15}N NMR (40.56 MHz, DMSO-d_6): δ −306.1 (NH_2); −9.6 (NO_2). ^{31}P NMR (161.98 MHz, DMSO-d_6): δ 60.1. IR (KBr): ν_{max} = 3181, 3060, 1633, 1593, 1511, 1403, 1315, 1220, 1193, 1047, 1087, 1012, 964, 902, 851, 806, 742, 685, 655, 514 cm^{-1}. Anal. calcd for $C_{22}H_{21}Cl_2N_2O_4P$: C 55.13; H 4.42; Cl 14.79; N 5.84; P 6.46. Found: C 55.30; H 4.47; Cl 14.63; N 5.90; P 6.29.

***O*-(2-Aminopyridin-3-yl) bis(2-phenylethyl)phosphinothioate (12d).** Yield: 314 mg (82%); white powder, mp 139–142 °C (washed with Et_2O). ^{1}H NMR (400.13 MHz, acetone-d_6 + DMSO-d_6): δ 2.53–2.63 (m, 4H, CH_2P); 2.93–3.05 (m, 4H, PhC$\underline{H}_2$); 5.69 (br s, 2H, NH_2); 6.57 (dd, 1H, H_5, OPh, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 4.8 Hz); 7.18–7.31 (m, 10H, $H_{o,m,p}$, $\underline{Ph}CH_2$); 7.63 (d, 1H, H_6, OPh, $^3J_{HH}$ = 7.8 Hz); 7.80 (d, 1H, H_4, OPh, $^3J_{HH}$ = 4.8 Hz). ^{13}C{^{1}H} NMR (100.62 MHz, acetone-d_6 + DMSO-d_6): δ 29.3 (d, PhC$\underline{H}_2$, $^2J_{PC}$ = 2.2 Hz); 36.7 (d, CH_2P, $^1J_{PC}$ = 65.6 Hz); 112.9 (C_5, OPh); 127.0 (C_p, $\underline{Ph}CH_2$); 128.7 (d, C_6, OPh, $^3J_{PC}$ = 4.0 Hz); 129.0 (C_m, $\underline{Ph}CH_2$); 129.3 (C_o, $\underline{Ph}CH_2$); 134.3 (d, C_2, OPh, $^3J_{PC}$ = 10.0 Hz); 141.7 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 16.5 Hz); 144.4 (C_4, OPh); 153.8 (d, C_1, OPh, $^2J_{PC}$ = 2.9 Hz). ^{15}N NMR (40.56 MHz, acetone-d_6 + DMSO-d_6): δ −312.9 (NH_2); −104.8 (N). ^{31}P NMR (161.98 MHz, acetone-d_6 + DMSO-d_6): δ 109.4. IR (KBr): ν_{max} = 3136, 3063, 3029, 2960, 2930, 2864, 1630, 1601, 1561, 1482, 1449, 1395, 1273, 1182, 1129, 1072, 1028, 925, 843, 783, 757, 696, 613, 500, 425 cm^{-1}. Anal. calcd for $C_{21}H_{23}N_2OPS$: C 65.95; H 6.06; N 7.32; P 8.10; S 8.38. Found: C 66.11; H 6.13; N 7.38; P 7.94; S 8.11.

***O*-(2-Amino-5-nitrophenyl) bis(2-phenylethyl)phosphinothioate (12e).** Yield: 328 mg (77%); yellow powder, mp 127–129 °C (reprecipitated from $CHCl_3$ to hexane). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.38–2.46 (m, 4H, CH_2P); 2.94–3.04 (m, 4H, PhC$\underline{H}_2$); 4.57 (br s, 2H, NH_2); 6.70 (d, 1H, H_3, OPh, $^3J_{HH}$ = 8.8 Hz); 7.15–7.30 (m, 10H, $H_{o,m,p}$, $\underline{Ph}CH_2$); 7.90 (dd, 1H, H_4, OPh, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.3 Hz); 8.02 (dd, 1H, H_6, OPh, $^4J_{HH}$ = 2.3 Hz, $^4J_{HH}$ = 1.6 Hz). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 29.1 (d, PhC$\underline{H}_2$, $^2J_{PC}$ = 2.6 Hz); 36.5 (d, CH_2P, $^1J_{PC}$ = 63.3 Hz); 114.8 (C_3, OPh); 118.2 (d, C_6, OPh, $^3J_{PC}$ = 3.9 Hz); 122.8 (C_4, OPh); 126.9 (C_p, $\underline{Ph}CH_2$); 128.4 (C_o, $\underline{Ph}CH_2$); 129.0 (C_m, $\underline{Ph}CH_2$); 136.5 (d, C_2, OPh, $^3J_{PC}$ = 10.1 Hz); 138.4 (C_5, OPh); 139.8 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 14.7 Hz); 146.2 (d, C_1, OPh, $^2J_{PC}$ = 3.3 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −316.3 (NH_2); −11.4 (NO_2). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 108.2. IR (neat): ν_{max} = 3202, 3064, 3027, 2923, 2857, 1620, 1588, 1513, 1455, 1397, 1309, 1199, 1150, 1083, 1030, 960, 899, 843, 752, 700, 620 cm^{-1}. Anal. calcd for $C_{22}H_{23}N_2O_3PS$: C 61.96; H 5.44; N 6.57; P 7.26; S 7.52. Found: C 62.15; H 5.51; N 6.64; P 7.08; S 7.35.

***O*-(2-Amino-5-nitrophenyl) bis[2-(4-chlorophenyl)ethyl]phosphinothioate (12f).** Yield: 366 mg (74%); yellow powder, mp

196–198 °C (washed with Et_2O). ^{1}H NMR (400.13 MHz, DMSO-d_6): δ 2.53–2.67 (m, 4H, CH_2P); 2.79–2.98 (m, 4H, PhC$\underline{H}_2$); 6.67 (br s, 2H, NH_2); 6.80 (d, 1H, H_3, OPh, $^3J_{HH}$ = 9.0 Hz); 7.28 (d, 4H, H_o, $\underline{Ph}CH_2$, $^3J_{HH}$ = 8.2 Hz); 7.35 (d, 4H, H_m, $\underline{Ph}CH_2$, $^3J_{HH}$ = 8.2 Hz); 7.87 (dd, 1H, H_4, OPh, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.6 Hz); 8.16 (dd, 1H, H_6, OPh, $^4J_{HH}$ = 2.6 Hz, $^4J_{HH}$ = 1.5 Hz). ^{13}C{^{1}H} NMR (100.62 MHz, acetone-d_6 + DMSO-d_6): δ 28.4 (d, Ph$\underline{C}H_2$, $^2J_{PC}$ = 2.6 Hz); 36.0 (d, CH_2P, $^1J_{PC}$ = 65.4 Hz); 114.3 (C_3, OPh); 118.6 (d, C_6, OPh, $^3J_{PC}$ = 4.3 Hz); 123.0 (C_4, OPh); 129.1 (C_o, $\underline{Ph}CH_2$); 130.8 (C_m, $\underline{Ph}CH_2$); 132.0 (C_p, $\underline{Ph}CH_2$); 136.1 (d, C_2, OPh, $^3J_{PC}$ = 9.7 Hz); 136.3 (C_5, OPh); 140.5 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 16.7 Hz); 148.7 (d, C_1, OPh, $^2J_{PC}$ = 3.5 Hz). ^{15}N NMR (40.56 MHz, DMSO-d_6): δ −310.1 (NH_2); −9.9 (NO_2). ^{31}P NMR (161.98 MHz, DMSO-d_6): δ 108.6. IR (KBr): ν_{max} = 3200, 3033, 2933, 2858, 1619, 1589, 1505, 1491, 1442, 1408, 1306, 1192, 1147, 1087, 1016, 955, 839, 809, 745, 655, 514 cm^{-1}. Anal. calcd for $C_{22}H_{21}Cl_2N_2O_3PS$: C 53.34; H 4.27; Cl 14.31; N 5.66; P 6.25; S 6.47. Found: C 53.54; H 4.33; Cl 14.17; N 5.73; P 6.08; S 6.28.

***O*-(2-Amino-5-nitrophenyl) bis(2-phenylpropyl)phosphinothioate (12g).** Yield: 295 mg (65%); waxy product. The product is a mixture of three stereoisomers in a ratio of 9.3 : 8.9 : 1 (^{1}H and ^{31}P NMR data). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.15, 1.24, 1.32, 1.42 (4 d, Me, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 6.9 Hz); 1.44–1.50, 1.98–2.06, 2.18–2.44 (3 m, 4H, CH_2P); 3.14–3.22, 3.29–3.42 (2 m, 2H, PhC$\underline{H}$); 4.03 (br s, 2H, NH_2); 6.55, 6.61 (2 d, 1H, H_3, OPh, $^3J_{HH}$ = 8.7 Hz); 7.13–7.35 (m, 10H, $H_{o,m,p}$, $\underline{Ph}CH$); 7.84, 7.85, 7.87 (3 dd, 1H, H_4, OPh, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.0 Hz); 7.98–8.01 (m, 1H, H_6, OPh). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 24.5, 24.6, 25.0, 25.2 (4 d, Me, $^3J_{PC}$ = 13.6 Hz, $^3J_{PC}$ = 15.3 Hz, $^3J_{PC}$ = 14.5 Hz, $^3J_{PC}$ = 13.5 Hz); 34.8, 35.4, 35.6, 35.9 (3 d, s, Ph$\underline{C}H$, $^2J_{PC}$ = 4.2 Hz, $^2J_{PC}$ = 3.5 Hz, $^2J_{PC}$ = 2.2 Hz); 42.3, 43.0, 43.8, 44.0 (4 d, CH_2P, $^1J_{PC}$ = 66.6 Hz, $^1J_{PC}$ = 63.4 Hz, $^1J_{PC}$ = 62.6 Hz, $^1J_{PC}$ = 64.6 Hz); 114.0, 114.2, 114.4 (C_4, OPh); 117.9, 118.2 (3 d, C_6, OPh, $^3J_{PC}$ = 3.9 Hz, $^3J_{PC}$ = 4.0 Hz); 122.3, 122.4 (C_3, OPh); 126.8, 127.0 (C_p, $\underline{Ph}CH$); 127.2, 127.3, 127.5 (C_o, $\underline{Ph}CH$); 128.8, 128.9, 129.0 (C_m, $\underline{Ph}CH$); 136.2, 136.4 (2 d, C_2, OPh, $^3J_{PC}$ = 10.3 Hz); 138.1, 138.3 (C_5, OPh); 145.1, 145.2, 145.9, 146.0 (4 d, C_i, $\underline{Ph}CH$, $^3J_{PC}$ = 14.1 Hz, $^3J_{PC}$ = 15.5 Hz, $^3J_{PC}$ = 12.9 Hz, $^3J_{PC}$ = 15.3 Hz); 145.9, 146.0 (2 d, C_1, OPh, $^2J_{PC}$ = 3.8 Hz, $^2J_{PC}$ = 4.8 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −318.9 (NH_2); −11.4 (NO_2). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 105.7, 107.9, 108.6. IR (neat): ν_{max} = 3202, 3065, 3028, 2964, 2924, 2874, 1619, 1589, 1510, 1453, 1395, 1309, 1200, 1154, 1086, 1051, 1005, 963, 908, 846, 764, 737, 703, 635, 623, 536 cm^{-1}. Anal. calcd for $C_{24}H_{27}N_2O_3PS$: C 63.42; H 5.99; N 6.16; P 6.81; S 7.05. Found: C 63.62; H 6.06; N 6.23; P 6.64; S 6.86.

***O*-(3-Aminophenyl) bis(2-phenylethyl)phosphinoselenoate (12h).** Yield: 351 mg (82%); waxy product. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.49–2.61 (m, 4H, CH_2P); 2.95–3.14 (m, 4H, PhC$\underline{H}_2$); 3.89 (br s, 2H, NH_2); 6.53 (d, 1H, H_4, OPh, $^3J_{HH}$ = 8.0 Hz); 6.57 (s, 1H, H_2, OPh); 6.58 (d, 1H, H_6, OPh, $^4J_{HH}$ = 8.2 Hz); 7.12 (dd, 1H, H_5, OPh, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.2 Hz); 7.22–7.29 (m, 6H, $H_{o,p}$, $\underline{Ph}CH_2$); 7.32–7.36 (m, 4H, H_m, $\underline{Ph}CH_2$). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 29.5 (d, Ph$\underline{C}H_2$, $^2J_{PC}$ = 2.5 Hz); 37.6 (d, CH_2P, $^1J_{PC}$ = 56.3 Hz); 108.6 (d, C_3, OPh, $^3J_{PC}$ = 4.5 Hz); 111.5 (d, C_6, OPh, $^3J_{PC}$ = 4.4 Hz); 112.2 (C_4, OPh); 126.7 (C_p, $\underline{Ph}CH_2$); 128.4 (C_o, $\underline{Ph}CH_2$); 128.8 (C_m, $\underline{Ph}CH_2$); 130.2 (C_5, OPh); 140.3 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 15.8 Hz); 147.8 (C_2, OPh); 151.8 (d, C_1, OPh, $^2J_{PC}$ = 9.9 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −322.0 (NH_2). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 103.8 (+d-satellites, $^1J_{PSe}$ = 798.0 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −243.4 (d, $^1J_{PSe}$ = 798.0 Hz). IR (neat): ν_{max} = 3216, 3059, 3027, 2923, 2855, 1611, 1491, 1458, 1398, 1316, 1280, 1210, 1146, 1072, 970, 909, 849, 742, 695, 580, 466 cm^{-1}. Anal. calcd for $C_{22}H_{24}NOPSe$: C 61.68; H 5.68; N 3.27; P 7.23; Se 18.43. Found: C 61.90; H 5.75; N 3.35; P 7.09; Se 18.29.

***O*-(2-Aminopyridin-3-yl) bis(2-phenylethyl)phosphinoselenoate (12i).** Yield: 365 mg (85%); purple powder, mp 150–152 °C (washed with Et_2O). ^{1}H NMR (400.13 MHz, DMSO-d_6): δ 2.64–2.79 (m, 4H, CH_2P); 2.83–3.00 (m, 4H, PhC$\underline{H}_2$); 6.05 (br s, 2H, NH_2); 6.53 (dd, 1H, H_5, OPh, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.9 Hz); 7.19–7.32 (m, 10H, $H_{o,m,p}$, $\underline{Ph}CH_2$); 7.57 (d, 1H, H_6, OPh, $^3J_{HH}$ = 7.6 Hz); 7.77 (d, 1H, H_4, OPh, $^3J_{HH}$ = 4.9 Hz). ^{13}C{^{1}H} NMR (100.62 MHz, DMSO-d_6): δ 28.7 (d, Ph$\underline{C}H_2$, $^2J_{PC}$ = 2.2 Hz); 36.2 (d, CH_2P, $^1J_{PC}$ = 54.8 Hz); 111.6 (C_5, OPh); 126.3 (C_p, $\underline{Ph}CH_2$); 127.9 (d, C_6, OPh, $^3J_{PC}$ = 4.3 Hz); 128.3 (C_m, $\underline{Ph}CH_2$); 128.5 (C_o, $\underline{Ph}CH_2$); 132.9 (d, C_2, OPh, $^3J_{PC}$ = 10.3 Hz); 140.4 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 17.1 Hz); 143.6 (C_4, OPh); 152.9 (C_1, OPh). ^{15}N NMR (40.56 MHz, DMSO-d_6): δ −312.7 (NH_2); −104.7 (N). ^{31}P NMR (161.98 MHz, DMSO-d_6): δ 111.2 (+d-satellites, $^1J_{PSe}$ = 805.2 Hz). ^{77}Se NMR (76.31 MHz, DMSO-d_6): δ −249.0 (d, $^1J_{PSe}$ = 805.2 Hz). IR (KBr): ν_{max} = 3134, 3029, 2958, 2930, 2867, 1629, 1555, 1481, 1452, 1393, 1337, 1271, 1178, 1128, 1072, 1026, 926, 842, 754, 725, 703, 670, 575, 470 cm^{-1}. Anal. calcd for $C_{21}H_{23}N_2OPSe$: C 58.75; H 5.40; N 6.52; P 7.21; Se 18.39. Found: C 58.96; H 6.47; N 6.58; P 7.03; Se 18.25.

***O*-(2-Amino-5-nitrophenyl) bis(2-phenylethyl)phosphinoselenoate (12j).** Yield: 374 mg (79%); yellow powder, mp 136–138 °C (reprecipitated from $CHCl_3$ to hexane). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 2.55–2.63 (m, 4H, CH_2P); 2.99–3.09 (m, 4H, PhC$\underline{H}_2$); NH_2 was not detected due to broadening; 6.74 (d, 1H, H_3, OPh, $^3J_{HH}$ = 8.9 Hz); 7.20–7.34 (m, 10H, $H_{o,m,p}$, $\underline{Ph}CH_2$); 7.95 (dd, 1H, H_4, OPh, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 2.4 Hz); 8.05 (dd, 1H, H_6, OPh, $^4J_{HH}$ = 2.4 Hz, $^4J_{HH}$ = 1.7 Hz). ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): δ 29.7 (d, Ph$\underline{C}H_2$, $^2J_{PC}$ = 2.4 Hz); 37.8 (d, CH_2P, $^1J_{PC}$ = 53.8 Hz); 114.9 (C_3, OPh); 118.3 (d, C_6, OPh, $^3J_{PC}$ = 3.9 Hz); 122.9 (C_4, OPh); 127.0 (C_p, $\underline{Ph}CH_2$); 128.5 (C_o, $\underline{Ph}CH_2$); 129.0 (C_m, $\underline{Ph}CH_2$); 136.7 (d, C_2, OPh, $^3J_{PC}$ = 10.1 Hz); 138.5 (C_5, OPh); 139.6 (d, C_i, $\underline{Ph}CH_2$, $^3J_{PC}$ = 14.7 Hz); 146.1 (d, C_1, OPh, $^2J_{PC}$ = 3.5 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −317.3 (NH_2); −10.8 (NO_2). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 108.3 (+d-satellites, $^1J_{PSe}$ = 809.0 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −237.4 (d, $^1J_{PSe}$ = 809.0 Hz). IR (neat): ν_{max} = 3198, 3064, 3027, 2922, 2858, 1619, 1589, 1510, 1451, 1397, 1310, 1268, 1198, 1151, 1085, 1005, 960, 905, 842, 750, 701, 640, 581, 467 cm^{-1}. Anal. calcd for $C_{22}H_{23}N_2O_3PSe$: C 55.82; H 4.90; N 5.92; P 6.54; Se 16.68. Found: C 55.99; H 4.96; N 5.98; P 6.36; Se 16.53.

***O*-(2-Amino-5-nitrophenyl) bis(2-phenylpropyl)phosphinoselenoate (12k).** Yield: 346 mg (69%); waxy product. The product

is a mixture of three stereoisomers in a ratio of 2.5 : 1.6 : 1 (^{1}H and ^{31}P NMR data). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.16, 1.25, 1.32, 1.44 (4 d, Me, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 7.0 Hz, $^3J_{HH}$ = 7.0 Hz); 1.49–1.55, 2.07–2.16, 2.34–2.71 (3 m, 4H, CH_2P); 3.17–3.26, 3.33–3.50 (2 m, 2H, PhC<u>H</u>); 3.69, 3.93, 4.22 (3 br s, 2H, NH_2); 6.52, 6.55, 6.61 (3 d, 1H, H_3, OPh, $^3J_{HH}$ = 8.8 Hz); 7.16–7.37 (m, 10H, $H_{o,m,p}$, <u>Ph</u>CH); 7.83, 7.85, 7.87, 7.88 (4 dd, 1H, H_4, OPh, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.5 Hz); 7.93, 8.02, 8.04 (3 dd, 1H, H_6, OPh, $^4J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR (100.62 MHz, $CDCl_3$): δ 24.4, 24.5, 25.0, 25.2 (4 d, Me, $^3J_{PC}$ = 13.9 Hz, $^3J_{PC}$ = 15.2 Hz, $^3J_{PC}$ = 13.5 Hz, $^3J_{PC}$ = 14.2 Hz); 35.4, 36.0, 36.1, 36.3 (4 d, Ph<u>C</u>H, $^2J_{PC}$ = 4.0 Hz, $^2J_{PC}$ = 3.2 Hz, $^2J_{PC}$ = 1.5 Hz, $^2J_{PC}$ = 1.0 Hz); 43.1, 44.2, 44.9, 45.1 (4 d, CH_2P, $^1J_{PC}$ = 56.5 Hz, $^1J_{PC}$ = 52.9 Hz, $^1J_{PC}$ = 52.1 Hz, $^1J_{PC}$ = 54.3 Hz, $^1J_{PC}$ = 64.6 Hz); 114.0, 114.2, 114.4 (C_4, OPh); 116.6, 117.8, 118.1 (3 d, C_6, OPh, $^3J_{PC}$ = 5.0 Hz, $^3J_{PC}$ = 4.2 Hz, $^3J_{PC}$ = 4.4 Hz); 122.2, 122.4 (C_3, OPh); 126.9, 127.1, 127.2, 128.4 (C_p, <u>Ph</u>CH); 127,2. 127.3, 127.5 (C_o, <u>Ph</u>CH); 128.9, 129.0, 129.1 (C_m, <u>Ph</u>CH); 136.2, 136.5 (2 d, C_2, OPh, $^3J_{PC}$ = 9.9 Hz); 137.8, 138.0 (C_5, OPh); 144.9, 145.1 (2 d, C_1, OPh, $^2J_{PC}$ = 4.3 Hz, $^2J_{PC}$ = 5.3 Hz); 145.6, 145.7, 145.9, 146.0 (4 d, C_i, <u>Ph</u>CH, $^3J_{PC}$ = 14.5 Hz, $^3J_{PC}$ = 14.1 Hz, $^3J_{PC}$ = 12.3 Hz, $^3J_{PC}$ = 15.7 Hz). ^{15}N NMR (40.56 MHz, $CDCl_3$): δ −316.6 (NH_2); −9.6 (NO_2). ^{31}P NMR (161.98 MHz, $CDCl_3$): δ 106.2 (+d-satellites, $^1J_{PSe}$ = 804.6 Hz); 109.7 (+d-satellites, $^1J_{PSe}$ = 807.9 Hz); 110.0 (+d-satellites, $^1J_{PSe}$ = 804.1 Hz). ^{77}Se NMR (76.31 MHz, $CDCl_3$): δ −227.9 (d, $^1J_{PSe}$ = 807.9 Hz); −217.3 (d, $^1J_{PSe}$ = 804.6 Hz); −211.2 (d, $^1J_{PSe}$ = 804.1 Hz). IR (neat): ν_{max} = 3198, 3065, 3027, 2964, 2924, 2874, 1618, 1588, 1508, 1452, 1393, 1309, 1198, 1153, 1086, 1051, 1005, 962, 908, 845, 759, 736, 704, 643, 530, 487 cm^{-1}. Anal. calcd for $C_{24}H_{27}N_2O_3PSe$: C 57.49; H 5.43; N 5.59; P 6.18; Se 15.75. Found: C 57.68; H 5.50; N 5.66; P 6.00; Se 15.59.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*a*) E. L. Ravaschino, R. Docampo and J. B. Rodriguez, *J. Med. Chem.*, 2006, **49**, 426–435; (*b*) S. Dehghanpour, Y. Rasmi and M. Bagheri, *Mol. Divers.*, 2007, **11**, 47–57; (*c*) F.-R. Alexandre, A. S. Amador, S. Bot, C. T. Caillet, T. Convard, J. Jakubik, C. Musiu, B. Poddesu, L. Vargiu, M. Liuzzi, A. Roland, M. Seifer, D. Standring, R. Storer and C. B. Dousson, *J. Med. Chem.*, 2011, **54**, 392–395; (*d*) Ł. Joachimiak and K. M. Błażewska, *J. Med. Chem.*, 2018, **61**, 8536–8562; (*e*) Á. Tajti and G. Keglevich, in *Organophosphorus Chemistry*, ed. G. Keglevich, Boston: De Gruyter, Berlin, 2018, pp. 53–65.

2 (*a*) Y. K. Kim, T. Livinghouse and Y. Horino, *J. Am. Chem. Soc.*, 2003, **125**, 9560–9561; (*b*) D. Cauzzi, C. Graiff, R. Pattacini, G. Predieri, A. Tiripicchio, S. Kahlal and J.-Y. Saillard, *Eur. J. Inorg. Chem.*, 2004, 1063–1072; (*c*) D. B. G. Williams, S. J. Evans, H. de Bod, M. S. Mokhadinyana and T. Hughes, *Synthesis*, 2009, 3106–3112; (*d*) C. Popovici, I. Fernández, P. Oña-Burgos, L. Roces, S. García-Granda and F. López Ortiz, *Dalton Trans.*, 2011, **40**, 6691–6703.

3 (*a*) X. Song and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 2689–2692; (*b*) P. Oña Burgos, I. Fernández, M. J. Iglesias, S. García-Granda and F. López Ortiz, *Org. Lett.*, 2008, **10**, 537–540; (*c*) R. H. Crampton, S. El Hajjaji, M. E. Fox and S. Woodward, *Tetrahedron: Asymmetry*, 2009, **20**, 2497–2503.

4 B. Tang, B. Ding, K. Xu and L. Tong, *Chem. – Eur. J.*, 2009, **15**, 3147–3151.

5 (*a*) C.-S. Cho, S.-C. Fu, L.-W. Chen and T.-R. Wu, *Polym. Int.*, 1998, **47**, 203–209; (*b*) Z. Jiang, D. Xu, X. Ma, J. Liu and P. Zhu, *Cellulose*, 2019, **26**, 5783–5796.

6 (*a*) F. Orsini, G. Sello and M. Sisti, *Curr. Med. Chem.*, 2010, **17**, 264–289; (*b*) P. Jeschke, *Pest Manag. Sci.*, 2016, **72**, 210–225.

7 (*a*) D. V. Aleksanyan, V. A. Kozlov, Y. V. Nelyubina, K. A. Lyssenko, L. N. Puntus, E. I. Gutsul, N. E. Shepel, A. A. Vasil’ev, P. V. Petrovskii and I. L. Odinets, *Dalton Trans.*, 2011, **40**, 1535–1546; (*b*) G. M. Dobrikov, V. Valcheva, M. Stoilova-Disheva, G. Momekov, P. Tzvetkova, A. Chimov and V. Dimitrov, *Eur. J. Med. Chem.*, 2012, **48**, 45–56; (*c*) G. Bianchini, G. Strukul, D. F. Wass and A. Scarso, *RSC Adv.*, 2015, **5**, 10795–10798.

8 F. R. Atherton, H. T. Openshaw and A. R. Todd, *J. Chem. Soc.*, 1945, 660–663.

9 (*a*) S. S. Le Corre, M. Berchel, H. Couthon-Gourvès, J.-P. Haelters and P.-A. Jaffrès, *Beilstein J. Org. Chem.*, 2014, **10**, 1166–1196; (*b*) Y. Ou, Y. Huang, Z. He, G. Yu, Y. Huo, X. Li, Y. Gao and Q. Chen, *Chem. Commun.*, 2020, **56**, 1357–1360.

10 (*a*) G. Wang, R. Shen, Q. Xu, M. Goto, Y. Zhao and L.-B. Han, *J. Org. Chem.*, 2010, **75**, 3890–3892; (*b*) N. K. Gusarova, P. A. Volkov, N. I. Ivanova, L. I. Larina and B. A. Trofimov, *Tetrahedron Lett.*, 2011, **52**, 2367–2369; (*c*) N. K. Gusarova, P. A. Volkov, N. I. Ivanova, L. I. Larina and B. A. Trofimov, *Synthesis*, 2011, 3723–3729; (*d*) S. Wagner, M. Rakotomalala, Y. Bykov, O. Walter and M. Dőring, *Heteroat. Chem.*, 2012, **23**, 216–222; (*e*) N. K. Gusarova, P. A. Volkov, N. I. Ivanova, L. I. Larina and B. A. Trofimov, *Heteroat. Chem.*, 2012, **23**, 322–328; (*f*) N. K. Gusarova, P. A. Volkov, N. I. Ivanova, Y. V. Gatilov and B. A. Trofimov, *Tetrahedron Lett.*, 2013, **54**, 3543–3545; (*g*) P. A. Volkov, N. I. Ivanova, N. K. Gusarova and B. A. Trofimov, *J. Sulfur Chem.*, 2014, **35**, 237–247; (*h*) X. Yu,

S. Zhang, Z. Jiang, H.-S. Zhang and T. Wang, *Eur. J. Org. Chem.*, 2020, 3110–3113; (*i*) X. Dong, R. Wang, W. Jin and C. Liu, *Org. Lett.*, 2020, **22**, 3062–3066.

11 N. A. Bondarenko, A. V. Kharlamov and A. G. Vendilo, *Russ. Chem. Bull.*, 2009, **58**, 1872–1885.

12 B. A. Trofimov, A. V. Artem'ev, S. F. Malysheva and N. K. Gusarova, *Dokl. Chem.*, 2009, **428**, 225–227.

13 B. A. Trofimov and N. K. Gusarova, *Mendeleev Commun.*, 2009, **19**, 295–302.

14 K. O. Khrapova, P. A. Volkov, N. I. Ivanova, A. A. Telezhkin, N. K. Gusarova and B. A. Trofimov, *Russ. J. Gen. Chem.*, 2018, **88**, 2223–2226.

15 N. K. Gusarova, P. A. Volkov, N. I. Ivanova, L. I. Larina and B. A. Trofimov, *Heteroat. Chem.*, 2012, **23**, 322–328.

16 (*a*) N. K. Gusarova, P. A. Volkov, N. I. Ivanova, B. G. Sukhov, L. I. Larina, O. N. Kazheva, G. G. Alexandrov, O. A. D′ yachenko and B. A. Trofimov, *Tetrahedron Lett.*, 2013, **54**, 6772–6775; (*b*) P. A. Volkov, N. N. Pogodaeva, N. I. Ivanova, K. O. Khrapova, L. I. Larina, B. G. Sukhov, Y. V. Gatilov, N. K. Gusarova and B. A. Trofimov, *Tetrahedron Lett.*, 2014, **55**, 4927–4929; (*c*) P. A. Volkov, N. I. Ivanova, N. K. Gusarova, B. G. Sukhov, K. O. Khrapova, L. E. Zelenkov, V. I. Smirnov, T. N. Borodina, T. I. Vakul'skaya, S. S. Khutsishvili and B. A. Trofimov, *Heteroat. Chem.*, 2015, **26**, 329–334; (*d*) P. A. Volkov, K. B. Petrushenko, N. I. Ivanova, K. O. Khrapova, L. I. Larina, N. K. Gusarova and B. A. Trofimov, *Tetrahedron Lett.*, 2017, **58**, 1992–1995.

17 (*a*) F. Brotzel, Y. C. Chu and H. Mayr, *J. Org. Chem.*, 2007, **72**, 3679–3688; (*b*) R. J. Mayer, M. Breugst, N. Hampel, A. R. Ofial and H. Mayr, *J. Org. Chem.*, 2019, **84**, 8837–8858.

18 D. Semenzin, G. Etemad-Moghadam, D. Albouy, O. Diallo and M. Koenig, *J. Org. Chem.*, 1997, **62**, 2414–2422.

19 (*a*) A. Albert and J. N. Phillips, *J. Chem. Soc.*, 1956, 1294–1304; (*b*) T. Nam, S. J. Nara, I. Zagol-Ikapitte, T. Cooper, L. Valgimigli, J. A. Oates, N. A. Porter, O. Boutaud and D. A. Pratt, *Org. Biomol. Chem.*, 2009, **7**, 5103–5112.

20 (*a*) N. K. Gusarova and B. A. Trofimov, *Russ. Chem. Rev.*, 2020, **89**, 225–249; (*b*) A. V. Artem'ev, S. F. Malysheva, N. K. Gusarova, A. O. Korocheva, L. V. Timokhina and B. A. Trofimov, *Russ. Chem. Bull.*, 2013, **62**, 2495–2497.

21 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09, Revision C.01*, Gaussian Inc., Wallingford, CT, 2016.

