Chemoselective Reactions of Secondary Phosphine Chalcogenides with Vinyloxyalkylamines: Synthesis of a Novel Family of Functional Phosphinochalcogenoic Amides

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Abstract: The reactions of secondary phosphine chalcogenides with vinyloxyalkylamines proceed chemoselectively in triethylamine–carbon tetrachloride under mild conditions to give the corresponding phosphinochalcogenoic amides bearing vinyloxy moieties in 78–95% yields.

Key words: amines, amides, chalcogenides, chemoselective, cross-coupling

Phosphinic, phosphinothioic and phosphinoselenoic amides find wide application in the design of multi-purpose metal complexes.[1,2] For example, complexes of phosphinochalcogenoic amides with zirconium and lanthanides were shown to be effective precatalysts for intramolecular alkene hydroaminations.[1] Amides with phosphinochalcogenoic moieties were used to generate active palladium catalysts for the Suzuki–Miyaura reaction.[2h] Phosphinochalcogenoic amides were also employed as catalysts for the asymmetric N,O-acetalization of aldehydes.[2i] Complexes of di(*tert*-butyl)selenophosphinic amides with transition metals (Ti,[2a] Zn, Cd,[2b] Cr, Mn, Fe, Co, Ni[2f]) are popular single-source precursors for the preparation of nano-sized metal selenides possessing unique semiconductor and magneto-optical properties. Moreover, phosphinochalcogenoic amides have attracted interest as intermediates for drug design,[3] and as building blocks for organic and element-organic synthesis.[3a,4] Diphenylphosphinothioic and diphenylphosphinoselenoic amides can function as acetylcholinesterase inhibitors,[3c] while several derivatives of diphenylphosphinic amide display high fungicidal activity.[3a] Functional phosphinochalcogenoic amides bearing, for example, vinyloxy moieties as attractive building blocks and monomers/comonomers deserve particular attention in view of the rich and diverse chemistry of vinyl ethers.[5] To the best of our knowledge, the literature lacks any data on such functional phosphinochalcogenoic amides.

Herein, we report a convenient approach to a novel family of phosphinochalcogenoic amides possessing vinyloxy substituents based on the chemoselective reaction of vinyloxyalkylamines with secondary phosphine chalcogenides, which recently became available via one-pot syntheses from red phosphorus and styrenes.[6] The choice of vinyloxyalkylamines as substrates is appropriate as these compounds are produced by industrially feasible direct vinylation of amino alcohols with ethyne.[7]

The outcomes of the reactions of vinyloxyalkylamines with secondary phosphine chalcogenides are not always predictable. Theoretically, this reaction can proceed by way of oxidative cross-coupling of secondary phosphine chalcogenides with the NH groups of the vinyloxyalkylamines in the triethylamine–carbon tetrachloride (Et_3N–CCl_4) system,[8] or via addition of the secondary phosphine chalcogenide to the double bond of the vinyloxy moiety.[9] Furthermore, it is known that vinyl ethers are able to react with carbon tetrachloride under certain conditions.[10]

As our experiments showed, secondary phosphine oxide **1**, phosphine sulfides **2** and **3** and phosphine selenides **4**–**6** reacted with vinyloxyalkylamines **7**–**9** in the triethylamine–carbon tetrachloride system, under mild conditions (r.t., 0.5–1.5 h, argon), to afford chemoselectively, phosphinochalcogenoic amides **10a**–**m** in 78–95% yield (Table 1).

The reaction was found to be general in character. Secondary phosphine chalcogenides **1**–**6**, possessing aryl and arylalkyl substituents, as well as various primary (**7** and **8**) and secondary (**9**) amines participated readily in this process. The obtained results showed that the reactivity of the secondary phosphine chalcogenides in reactions with amines **7**–**9** decreased in the following order: secondary phosphine selenides ≥ secondary phosphine sulfides > secondary phosphine oxides (Table 1, compare entries 1, 4 and 9), which is in agreement with previously published data.[11]

The mechanism of the reaction is likely triggered by deprotonation of the secondary phosphine chalcogenide by triethylamine to give P,X-ambident chalcogenophosphinite anion **A**. The latter takes part in one-electron transfer with carbon tetrachloride (oxidizer) to afford the free radical of the secondary phosphine chalcogenide, **B** and anion radical **C**, the interaction of which leads to

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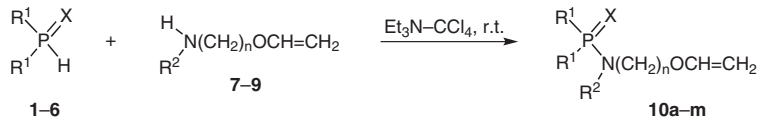
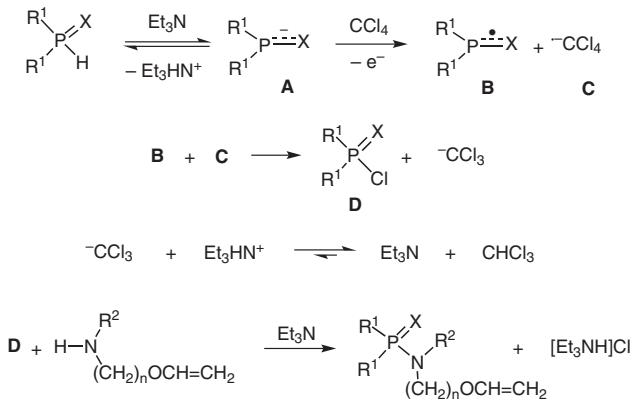
Table 1 Oxidative Cross-Coupling of Secondary Phosphine Chalcogenides with Amines for the Synthesis of Phosphinochalcogenoic Amides[a]



Entry	$(R^1)_2P(X)H$	X	R^1	Amine	R^2	n	Time (h)	Product	Yield (%)
1	**1**	O	$Ph(CH_2)_2$	**7**	H	2	1.5	**10a**	78
2	**2**	S	Ph	**7**	H	2	0.5	**10b**	84
3	**2**	S	Ph	**8**	H	3	0.5	**10c**	87
4	**3**	S	$Ph(CH_2)_2$	**7**	H	2	0.5	**10d**	90
5	**3**	S	$Ph(CH_2)_2$	**8**	H	3	0.5	**10e**	88
6	**3**	S	$Ph(CH_2)_2$	**9**	Me	2	1	**10f**	79
7	**4**	Se	Ph	**7**	H	2	0.5	**10g**	80
8	**4**	Se	Ph	**8**	H	3	0.5	**10h**	87
9	**5**	Se	$Ph(CH_2)_2$	**7**	H	2	0.5	**10i**	92
10	**5**	Se	$Ph(CH_2)_2$	**8**	H	3	0.5	**10j**	90
11	**5**	Se	$Ph(CH_2)_2$	**9**	Me	2	1.5	**10k**	80
12	**6**	Se	$PhCH(Me)CH_2$	**7**	H	2	0.5	**10l**	89
13	**6**	Se	$PhCH(Me)CH_2$	**8**	H	3	0.5	**10m**	95

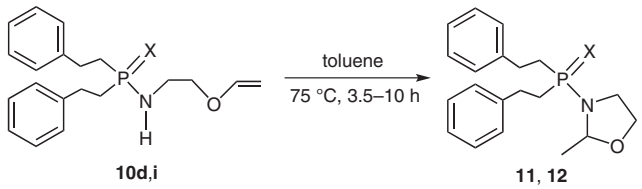
[a] Reaction conditions: phosphine chalcogenide **1**–**6** (1 mmol), amine **7**–**9** (1 mmol), Et_3N (1 mmol), CCl_4 (4 mL), r.t., 0.5–1.5 h.

phosphinochalcogenoic chloride **D** and a carbanion ($^-CCl_3$). This step is followed by protonation of the carbanion with a triethylammonium cation to regenerate triethylamine and to form chloroform. The reaction between chloride **D** and a vinyloxyalkylamine in the presence of triethylamine furnishes the target phosphinochalcogenoic amide product and triethylammonium chloride (Scheme 1). In support of this mechanism, triethylammonium chloride was consistently isolated from the reaction mixture (by filtration) and the presence of chloroform was confirmed by GC–MS.



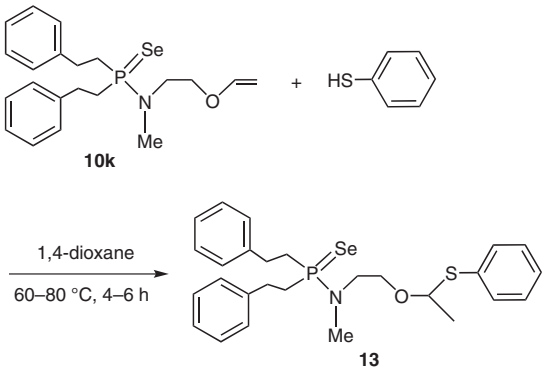
Scheme 1 A tentative mechanism for the formation of phosphinochalcogenoic amides **10**

The synthesized amides bearing reactive vinyloxy groups represent promising building blocks for organic synthesis. Thus, we have shown that amides **10d**,**i** readily, and almost quantitatively, cyclize on heating in an intramolecular fashion to afford oxazolidines **11** and **12** (Scheme 2).



Scheme 2 Synthesis of 3-(diphenethylphosphorochalcogenoyl)-2-methyl-1,3-oxazolidines **11** and **12**

In the case of compound **10k**, it was discovered that benzenethiol adds to the vinyloxy group at 60–80 °C (4–6 h, 1,4-dioxane) to give Markovnikov adduct **13** in up to 70% yield (Scheme 3). This reaction is the subject of further study and the experimental details will be published elsewhere.



Scheme 3 Regioselective addition of benzenethiol to *P*,*P*-diphenethyl-*N*-methyl-*N*-[2-(vinyloxy)ethyl]phosphinoselenoic amide (**10k**)

In summary, an efficient route to a series of phosphinochalcogenoic amides functionalized with vinyloxy groups has been developed using the chemoselective reaction of secondary phosphine chalcogenides with vinyloxyalkylamines. The cross-coupling proceeds easily at ambient temperature in the triethylamine–carbon tetrachloride system to afford the target compounds in high yields. The products are prospective monomers and potentially highly reactive building blocks for target organic synthesis, ligands for the preparation of metal complexes, promising intermediates for the production of conducting nanomaterials and precursors for the design of biologically and pharmaceutically important compounds.

All reactions were carried out under an argon atmosphere. All solvents were dried and/or purified according to standard procedures.[12] Secondary phosphine chalcogenides **1**, **3**, **5** and **6** were prepared from styrene or α-methylstyrene and elemental phosphorus as previously reported.[6] Diphenylphosphine sulfide (**2**) and diphenylphosphine selenide (**4**) were prepared by oxidation of commercially available diphenylphosphine (Aldrich) with elemental sulfur or gray selenium.[13] Vinyloxyalkylamines **7**–**9** were synthesized via direct vinylation of the corresponding hydroxyalkylamines with ethyne.[14] The reactions were monitored by ^{31}P NMR spectroscopy by following the disappearance of the signals due to the starting secondary phosphine chalcogenides **1**–**6** and the appearance of new resonances corresponding to *N*-[(vinyloxy)alkyl]phosphinochalcogenoic amides **10a**–**m**. Melting points were recorded on a Stuart melting point apparatus and are uncorrected. IR spectra were obtained using a Bruker Vertex 70 spectrometer. ^{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, 100.61, 40.56, 161.98 and 76.31 MHz, respectively) in $CDCl_3$ and referenced to TMS (^{1}H NMR, ^{13}C NMR), $MeNO_2$ (^{15}N NMR), H_3PO_4 (^{31}P NMR) and Me_2Se (^{77}Se NMR). The ^{15}N chemical shifts of the products were determined to within 0.1 ppm using 2D ^{1}H–^{15}N NMR HMBC. Mass spectra (EI, 70 eV) were obtained on a Shimadzu GCMS–QP5050 A (quadruple mass analyzer, the range of detected mass was from 34 to 650 Da); capillary column SPB–5ms (60 m × 0.25 mm × 0.25 μm), gas carrier helium, flow rate 0.7 mL/min, temperature of injector and ion source 250 °C, pressure 100 kPa; temperature programming from 50 to 250°C, 10 °C/min. The C, H and N elemental analyses were performed with a Flash E112 Thermo Finnigan Elemental Analyzer. The P elemental analyses were obtained with a Specoll 11 spectrophotometer.

N-[2-(Vinyloxy)alkyl]phosphinochalcogenoic Amides 10a–m; General Procedure

A mixture of secondary phosphine chalcogenide **1**–**6** (1.0 mmol) and Et_3N (101 mg, 139 μL, 1.0 mmol) in CCl_4 (4 mL) was stirred at 20–22 °C for 10 min. The vinyloxyalkylamine **7**–**9** (1.0 mmol) was added, and the resulting mixture stirred at 20–22 °C for 0.5–1.5 h (see Table 1). The solvent was removed under reduced pressure, and 1,4-dioxane (3 mL) was added. The precipitated white solid, $[Et_3NH]Cl$, was removed by filtration and the 1,4-dioxane was evaporated. The residue obtained was rinsed with hot hexane (2 × 3 mL), and the hexane soln was allowed to stand for 12 h at –8 °C. The soln was decanted from the precipitate and the solvent was evaporated under vacuum. The residue was dried under vacuum to give phosphinochalcogenoic amides **10a**,**d**–**f**,**i**–**m**. With amides **10b**,**c**,**g**,**h**, the residues (after evaporation of 1,4-dioxane under vacuum) were re-precipitated from Et_2O into hexane to afford the pure products.

P,*P*-Diphenethyl-*N*-[2-(vinyloxy)ethyl]phosphinic Amide (10a)

Yield: 268 mg (78%); white powder; mp 80–81 °C (Et_2O–hexane, 1:1).

IR (KBr): 3187 (NH), 1637 (OC=C), 1619, 1161 (P=O), 1031 (P–N–C), 699 cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.00–2.07 (m, 4 H, CH_2P), 2.74 (br s, 1 H, NH), 2.88–2.94 (m, 4 H, $PhCH_2$), 3.22 (m, 2 H, NCH_2), 3.73 (t, $^{3}J_{HH}$ = 5.1 Hz, 2 H, OCH_2), 4.05 (dd, $^{3}J_{HH}$ = 6.7 Hz, $^{2}J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 4.21 (dd, $^{3}J_{HH}$ = 14.3 Hz, $^{2}J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 6.45 (dd, $^{3}J_{HH}$ = 14.3 Hz, $^{3}J_{HH}$ = 6.7 Hz, 1 H, OCH=), 7.19–7.24 (m, 6 H, H_o, H_p, Ph), 7.30 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 7.2 Hz, 4 H, H_m, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 28.2 (d, $^{2}J_{PC}$ = 3.0 Hz, $PhCH_2$), 30.6 (d, $^{1}J_{PC}$ = 82.6 Hz, CH_2P), 39.3 (NCH_2), 68.7 (d, $^{3}J_{PC}$ = 4.8 Hz, CH_2O), 87.3 (=CH_2), 126.0 (C_p), 128.1 (C_o), 128.7 (C_m), 141.1 (d, $^{3}J_{PC}$ = 13.6 Hz, C_i), 151.4 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 44.4.

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –338.0.

Anal. Calcd for $C_{20}H_{26}NO_2P$: C, 69.95; H, 7.63; N, 4.08; P, 9.02. Found: C, 69.67; H, 7.59; N, 4.03; P, 8.78.

P,*P*-Diphenyl-*N*-[2-(vinyloxy)ethyl]phosphinothioic Amide (10b)

Yield: 254 mg (84%); white powder; mp 83–85 °C (hexane).

IR (KBr): 3192 (NH), 1637 (OC=C), 1621, 1094 (P–N–C), 694, 613 (P=S) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.92 (br s, 1 H, NH), 3.28 (dt, $^{3}J_{PH}$ = 16.2 Hz, $^{3}J_{HH}$ = 5.0 Hz, 2 H, NCH_2), 3.82 (t, $^{3}J_{HH}$ = 5.0 Hz, 2 H, CH_2O), 4.03 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{2}J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 4.20 (dd, $^{3}J_{HH}$ = 14.6 Hz, $^{2}J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 6.46 (dd, $^{3}J_{HH}$ = 14.6 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1 H, OCH=), 7.45–7.51 (m, 6 H, H_m, H_p, Ph), 8.01 (dd, $^{3}J_{PH}$ = 13.6 Hz, $^{3}J_{HH}$ = 7.3 Hz, 4 H, H_o, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 40.5 (NCH_2), 67.9 (d, $^{3}J_{PC}$ = 8.4 Hz, CH_2O), 87.5 (=CH_2), 128.6 (d, $^{3}J_{PC}$ = 12.8 Hz, C_m), 131.6 (d, $^{2}J_{PC}$ = 11.0 Hz, C_o), 131.8 (d, $^{4}J_{PC}$ = 3.3 Hz, C_p), 132.9 (d, $^{1}J_{PC}$ = 102.0 Hz, C_i), 151.4 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 60.7.

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –336.3.

Anal. Calcd for $C_{16}H_{18}NOPS$: C, 63.35; H, 5.98; N, 4.62; P, 10.21; S, 10.57. Found: C, 62.99; H, 5.96; N, 4.61; P, 9.89; S, 10.49.

P,*P*-Diphenyl-*N*-[3-(vinyloxy)propyl]phosphinothioic Amide (10c)

Yield: 276 mg (87%); white powder; mp 66–67 °C (hexane).

IR (KBr): 3240 (NH), 1632 (OC=C), 1614, 1100 (P–N–C), 693, 611 (P=S) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.88 (m, 2 H, NCH_2CH_2), 2.79 (br s, 1 H, NH), 3.05–3.10 (m, 2 H, NCH_2), 3.77 (t, $^3J_{HH}$ = 5.7 Hz, 2 H, CH_2O), 3.99 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 4.15 (dd, $^3J_{HH}$ = 14.4 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 6.40 (dd, $^3J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, OCH=), 7.41–7.49 (m, 6 H, H_m, H_p, Ph), 7.96 (dd, $^3J_{PH}$ = 13.4 Hz, $^3J_{HH}$ = 6.9 Hz, 4 H, H_o, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 30.5 (d, $^3J_{PC}$ = 8.8 Hz, NCH_2CH_2), 39.1 (NCH_2), 66.1 (CH_2O), 86.9 (=CH_2), 128.5 (d, $^3J_{PC}$ = 12.5 Hz, C_m), 131.6 (C_p), 131.7 (C_o), 134.1 (d, $^1J_{PC}$ = 102.1 Hz, C_i), 151.6 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 60.2.

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –331.9.

Anal. Calcd for $C_{17}H_{20}NOPS$: C, 64.33; H, 6.35; N, 4.41; P, 9.76; S, 10.11. Found: C, 63.93; H, 6.35; N, 4.38; P, 9.27; S, 10.02.

_P_,_P_-Diphenethyl-_N_-[2-(vinyloxy)ethyl]phosphinothioic Amide (10d)

Yield: 323 mg (90%); waxy solid.

IR (neat): 3369, 3278 (NH), 1636 (OC=C), 1619, 1117 (P–N–C), 1083 (sh), 698, 617 (P=S) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.14–2.24 (m, 4 H, CH_2P), 2.87–3.05 (m, 4 H, $PhCH_2$), 3.16–3.19 (m, 2 H, CH_2N), 3.68 (t, $^3J_{HH}$ = 5.1 Hz, 2 H, CH_2O), 4.04 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 4.18 (dd, $^3J_{HH}$ = 14.2 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 6.43 (dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, OCH=), 7.19–7.30 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 28.7 (d, $^2J_{PC}$ = 1.9 Hz, $PhCH_2$), 35.6 (d, $^1J_{PC}$ = 63.4 Hz, CH_2P), 40.5 (NCH_2), 68.3 (d, $^3J_{PC}$ = 6.4 Hz, CH_2O), 87.4 (=CH_2), 126.5 (C_p), 128.4 (C_o), 128.8 (C_m), 140.9 (d, $^3J_{PC}$ = 14.5 Hz, C_i), 151.4 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 71.9.

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –341.5.

Anal. Calcd for $C_{20}H_{26}NOPS$: C, 66.83; H, 7.29; N, 3.90; P, 8.62; S, 8.91. Found: C, 66.77; H, 7.28; N, 3.88; P, 8.46; S, 8.87.

_P_,_P_-Diphenethyl-_N_-[3-(vinyloxy)propyl]phosphinothioic Amide (10e)

Yield: 329 mg (88%); waxy solid.

IR (neat): 3367, 3268 (NH), 1636 (OC=C), 1617, 1096 (P–N–C), 698, 615 (P=S) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.82 (m, 2 H, NCH_2CH_2), 2.16 (m, 1 H, NH), 2.17–2.25 (m, 4 H, CH_2P), 2.95–3.05 (m, 6 H, $PhCH_2$, NCH_2), 3.75 (t, $^3J_{HH}$ = 5.9 Hz, 2 H, OCH_2), 4.04 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HH}$ = 2.1 Hz, 1 H, =CH_2), 4.20 (dd, $^3J_{HH}$ = 14.4 Hz, $^2J_{HH}$ = 2.1 Hz, 1 H, =CH_2), 6.45 (dd, $^3J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, OCH=), 7.23–7.34 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 29.2 (d, $^2J_{PC}$ = 2.4 Hz, $PhCH_2$), 30.9 (d, $^3J_{PC}$ = 7.6 Hz, NCH_2CH_2), 34.8 (d, $^1J_{PC}$ = 63.1 Hz, CH_2P), 38.8 (d, $^2J_{PC}$ = 2.4 Hz, NCH_2), 65.5 (CH_2O), 87.0 (=CH_2), 126.5 (C_p), 128.4 (C_o), 128.7 (C_m), 140.5 (d, $^3J_{PC}$ = 14.8 Hz, C_i), 151.5 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 71.2.

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –336.1 (d, $^1J_{NH}$ = 87.8 Hz).

Anal. Calcd for $C_{21}H_{28}NOPS$: C, 67.53; H, 7.56; N, 3.75; P, 8.29; S, 8.59. Found: C, 66.90; H, 7.67; N, 3.65; P, 8.18; S, 8.43.

_P_,_P_-Diphenethyl-_N_-methyl-_N_-[2-(vinyloxy)ethyl]phosphinothioic Amide (10f)

Yield: 295 mg (79%); waxy solid.

IR (neat): 1635 (OC=C), 1618, 1073 (P–N–C), 698, 605 (P=S) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.13–2.20 and 2.31–2.37 (m, 4 H, CH_2P), 2.74 (d, $^3J_{PH}$ = 10.2 Hz, 3 H, NMe), 2.85–2.93 and 3.01–3.11 (m, 4 H, $PhCH_2$), 3.41 (dt, $^3J_{PH}$ = 10.8 Hz, $^3J_{HH}$ = 5.3 Hz, 2 H, CH_2N), 3.82 (t, $^3J_{HH}$ = 5.3 Hz, 2 H, OCH_2), 4.06 (dd, $^3J_{HH}$ = 6.7 Hz, $^2J_{HH}$ = 2.3 Hz, 1 H, =CH_2), 4.23 (dd, $^3J_{HH}$ = 14.2 Hz, $^2J_{HH}$ = 2.3 Hz, 1 H, =CH_2), 6.49 (dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 6.7 Hz, 1 H, OCH=), 7.17–7.29 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 28.4 (d, $^2J_{PC}$ = 2.8 Hz, $PhCH_2$), 34.1 (d, $^1J_{PC}$ = 63.1 Hz, CH_2P), 35.0 (NMe), 48.2 (NCH_2), 67.6 (CH_2O), 87.1 (=CH_2), 126.4 (C_p), 128.3 (C_o), 128.8 (C_m), 141.2 (d, $^3J_{PC}$ = 15.2 Hz, C_i), 151.5 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 78.8.

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –355.9.

Anal. Calcd for $C_{21}H_{28}NOPS$: C, 67.53; H, 7.56; N, 3.75; P, 8.29; S, 8.59. Found: C, 67.49; H, 7.53; N, 3.71; P, 8.14; S, 8.56.

_P_,_P_-Diphenyl-_N_-[2-(vinyloxy)ethyl]phosphinoselenoic Amide (10g)

Yield: 280 mg (80%); beige powder; mp 115–117 °C (Et_2O–hexane, 1:1).

IR (KBr): 3165 (NH), 1637 (OC=C), 1621, 1094 (P–N–C), 694, 546 (P=Se) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.81 (br s, 1 H, NH), 3.24 (dt, $^3J_{PH}$ = 16.2 Hz, $^3J_{HH}$ = 5.2 Hz, 2 H, NCH_2), 3.82 (t, $^3J_{HH}$ = 5.2 Hz, 2 H, CH_2O), 4.03 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HH}$ = 1.8 Hz, 1 H, =CH_2), 4.18 (dd, $^3J_{HH}$ = 14.4 Hz, $^2J_{HH}$ = 1.8 Hz, 1 H, =CH_2), 6.43 (dd, $^3J_{HH}$ = 14.4 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, OCH=), 7.44–7.49 (m, 6 H, H_m, H_p, Ph), 7.97 (dt, $^3J_{PH}$ = 13.8 Hz, $^3J_{HH}$ = 6.9 Hz, 4 H, H_o, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 41.5 (NCH_2), 67.6 (d, $^3J_{PC}$ = 8.5 Hz, CH_2O), 87.4 (=CH_2), 128.6 (d, $^3J_{PC}$ = 12.9 Hz, C_m), 131.8 (d, $^2J_{PC}$ = 11.4 Hz, C_o), 131.9 (d, $^4J_{PC}$ = 2.9 Hz, C_p), 133.7 (d, $^1J_{PC}$ = 91.4 Hz, C_i), 151.4 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 58.3 (s) (+ d satellite, $^1J_{PSe}$ = 783 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –338.8.

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –268.5 (d, $^1J_{PSe}$ = 783 Hz).

Anal. Calcd for $C_{16}H_{18}NOPSe$: C, 54.87; H, 5.18; N, 4.00; P, 8.84; Se, 22.54. Found: C, 54.78; H, 5.11; N, 4.04; P, 8.39; Se, 22.79.

_P_,_P_-Diphenyl-_N_-[3-(vinyloxy)propyl]phosphinoselenoic Amide (10h)

Yield: 317 mg (87%); white powder; mp 75–76 °C (hexane).

IR (KBr): 3213 (NH), 1637 (OC=C), 1617, 1621, 1068 (P–N–C), 694, 555 (P=Se) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.93 (quin, $^3J_{HH}$ = 6.2 Hz, 2 H, NCH_2CH_2), 2.64 (br s, 1 H, NH), 3.06 (m, 2 H, NCH_2), 3.77 (t, $^3J_{HH}$ = 5.9 Hz, 2 H, CH_2O), 4.00 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 4.15 (dd, $^3J_{HH}$ = 14.3 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 6.40 (dd, $^3J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, OCH=), 7.28–7.44 (m, 6 H, H_m, H_p, Ph), 7.97 (dd, $^3J_{PH}$ = 13.0 Hz, $^3J_{HH}$ = 6.7 Hz, 4 H, H_o, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 30.0 (d, $^3J_{PC}$ = 9.2 Hz, NCH_2CH_2), 39.9 (NCH_2), 65.9 (CH_2O), 86.7 (=CH_2), 128.3 (d, $^3J_{PC}$ = 12.8 Hz, C_m), 131.5 (C_p), 131.6 (C_o), 133.5 (d, $^1J_{PC}$ = 94.7 Hz, C_i), 151.3 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 56.4 (s) (+ d satellite, $^1J_{PSe}$ = 750 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –333.9 (d, $^1J_{NH}$ = 78.8 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –265.5 (d, $^1J_{PSe}$ = 750 Hz).

Anal. Calcd for $C_{17}H_{20}NOPSe$: C, 56.05; H, 5.53; N, 3.85; P, 8.50; Se, 21.68. Found: C, 55.82; H, 5.51; N, 3.83; P, 8.39; Se, 21.51.

_P_,_P_-Diphenethyl-_N_-[2-(vinyloxy)ethyl]phosphinoselenoic Amide (10i)

Yield: 374 mg (92%); waxy solid.

IR (neat): 3362, 3257 (NH), 1637 (OC=C), 1619, 1115 (P–N–C), 1082 (sh), 698, 579 (P=Se) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.25–2.34 (m, 4 H, CH_2P), 2.42 (br s, 1 H, NH), 2.94–2.99 (m, 4 H, $PhCH_2$), 3.15 (m, 2 H, CH_2N), 3.67 (t, $^3J_{HH}$ = 5.0 Hz, 2 H, CH_2O), 4.04 (dd, $^3J_{HH}$ = 6.7 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 4.18 (dd, $^3J_{HH}$ = 14.3 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 6.42 (dd, $^3J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 6.7 Hz, 1 H, OCH=), 7.18–7.30 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 29.1 ($PhCH_2$), 35.8 (d, $^1J_{PC}$ = 54.3 Hz, CH_2P), 41.2 (NCH_2), 67.7 (d, $^3J_{PC}$ = 6.8 Hz, CH_2O), 87.2 (=CH_2), 126.4 (C_p), 128.2 (C_o), 128.6 (C_m), 140.4 (d, $^3J_{PC}$ = 14.8 Hz, C_i), 151.1 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 65.1 (s) (+ d satellite, $^1J_{PSe}$ = 731 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –343.5.

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –325.5 (d, $^1J_{PSe}$ = 731 Hz).

Anal. Calcd for $C_{20}H_{26}NOPSe$: C, 59.11; H, 6.45; N, 3.45; P, 7.62; Se, 19.43. Found: C, 59.08; H, 6.42; N, 3.41; P, 7.48; Se, 19.39.

_P_,_P_-Diphenethyl-_N_-[3-(vinyloxy)propyl]phosphinoselenoic Amide (10j)
Yield: 378 mg (90%); waxy solid.

IR (neat): 3361, 3250 (NH), 1636 (OC=C), 1617, 1090 (P–N–C), 698, 579 (P=Se) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.82 (m, 2 H, NCH_2), 2.09 (m, 1 H, NH), 2.25–2.36 (m, 4 H, CH_2P), 2.95–3.04 (m, 6 H, $PhCH_2$, NCH_2CH_2), 3.75 (t, $^3J_{HH}$ = 5.9 Hz, 2 H, OCH_2), 4.04 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 4.20 (dd, $^3J_{HH}$ = 14.2 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 6.45 (dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, OCH=), 7.20–7.35 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 29.2 ($PhCH_2$), 30.7 (d, $^2J_{PC}$ = 7.6 Hz, NCH_2), 35.6 (d, $^1J_{PC}$ = 54.3 Hz, CH_2P), 39.6 (d, $^3J_{PC}$ = 3.6 Hz, NCH_2CH_2), 65.4 (CH_2O), 87.1 (=CH_2), 126.5 (C_p), 128.4 (C_o), 128.7 (C_m), 140.6 (d, $^3J_{PC}$ = 14.4 Hz, C_i), 151.5 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 65.2 (s) (+ d satellite, $^1J_{PSe}$ = 744 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –337.9 (d, $^1J_{NH}$ = 82 Hz).

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –320.3 (d, $^1J_{PSe}$ = 744 Hz).

Anal. Calcd for $C_{21}H_{28}NOPSe$: C, 60.00; H, 6.71; N, 3.33; P, 7.37; Se, 18.78. Found: C, 60.23; H, 6.64; N, 3.34; P, 7.29; Se, 18.73.

_P_,_P_-Diphenethyl-_N_-methyl-_N_-[2-(vinyloxy)ethyl]phosphinoselenoic Amide (10k)
Yield: 336 mg (80%); waxy solid.

IR (neat): 1636 (OC=C), 1618, 1121 (P–N–C), 1077 (sh), 698, 579 (P=Se) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.25–2.28 and 2.48–2.53 (m, 4 H, CH_2P), 2.74 (d, $^3J_{PH}$ = 10.5 Hz, 3 H, NMe), 2.89–2.93 and 3.02–3.09 (m, 4 H, $PhCH_2$), 3.40 (dt, $^3J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 5.3 Hz, 2 H, NCH_2), 3.82 (t, $^3J_{HH}$ = 5.3 Hz, 2 H, OCH_2), 4.07 (dd, $^3J_{HH}$ = 7.0 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 4.24 (dd, $^3J_{HH}$ = 14.2 Hz, $^2J_{HH}$ = 2.2 Hz, 1 H, =CH_2), 6.49 (dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 7.0 Hz, 1 H, OCH=), 7.22–7.35 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 29.1 ($PhCH_2$), 34.7 (d, $^1J_{PC}$ = 54.7 Hz, CH_2P), 35.3 (NMe), 49.5 (NCH_2), 67.4 (d, $^3J_{PC}$ = 3.2 Hz, CH_2O), 87.2 (=CH_2), 126.4 (C_p), 128.5 (C_o), 128.8 (C_m), 140.8 (d, $^3J_{PC}$ = 15.6 Hz, C_i), 151.5 (OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 75.2 (s) (+ d satellite, $^1J_{PSe}$ = 763 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –358.5.

^{77}Se NMR (76.31 Hz, $CDCl_3$): δ = –353.0 (d, $^1J_{PSe}$ = 763 Hz).

Anal. Calcd for $C_{21}H_{28}NOPSe$: C, 60.00; H, 6.71; N, 3.33; P, 7.37; Se, 18.78. Found: C, 60.07; H, 6.54; N, 3.13; P, 7.31; Se, 18.69.

_P_,_P_-Bis(2-phenylpropyl)-_N_-[2-(vinyloxy)ethyl]phosphinoselenoic Amide (10l)
Yield: 387 mg (89%); waxy solid.

IR (neat): 3366, 3266 (NH), 1636 (OC=C), 1619, 1112 (sh, P–N–C), 1086, 701, 561 (P=Se) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.14, 1.23 and 1.31 (3 d, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.6 Hz, 6 H, *Me*CH, respectively), 1.56–1.60 (m, 1 H, NH), 1.82–1.90, 1.95–2.03, 2.06–2.12 and 2.15–2.28 (m, 4 H, CH_2P), 2.49–2.54, 2.59–2.64, 2.70–2.78 and 2.88–2.94 (m, 2 H, NCH_2), 3.15 (t, $^2J_{HH}$ = $^3J_{HH}$ = 5.1 Hz, 1 H, OCH_2), 3.20–3.29 and 3.30–3.36 (m, 2 H, C*H*Me), 3.43 (t, $^2J_{HH}$ = $^3J_{HH}$ = 5.1 Hz, 1 H, OCH_2), 3.90, 3.91 and 3.93 (3 dd, $^3J_{HH}$ = 6.9 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 4.00, 4.01 and 4.05 (3 dd, $^3J_{HH}$ = 14.2 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 6.20, 6.23 and 6.28 (3 dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 6.9 Hz, 1 H, OCH=), 7.09–7.26 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 24.0, 24.1 and 24.6 (3 d, $^3J_{PC}$ = 12.5 Hz, $^3J_{PC}$ = 12.9 Hz, $^3J_{PC}$ = 14.0 Hz, *Me*CH, respectively), 34.6, 35.0, 35.5 and 35.7 (4 d, $^2J_{PC}$ = 2.2 Hz, $^2J_{PC}$ = 2.6 Hz, $^2J_{PC}$ = 1.5 Hz, $^2J_{PC}$ = 1.8 Hz, Me*C*H, respectively), 40.3, 40.4 and 40.7 (3 s, NCH_2), 41.0, 42.4, 43.1 and 43.8 (4 d, $^1J_{PC}$ = 53.8 Hz, $^1J_{PC}$ = 52.7 Hz, $^1J_{PC}$ = 56.0 Hz, $^1J_{PC}$ = 56.4 Hz, CH_2P, respectively), 66.9, 67.1 and 67.4 (3 d, $^3J_{PC}$ = 8.1 Hz, $^3J_{PC}$ = 7.7 Hz, $^3J_{PC}$ = 7.7 Hz, OCH_2, respectively), 86.5, 86.6 and 86.7 (3 s, =CH_2), 126.37, 126.41 and 126.5 (3 s, C_p), 126.8, 126.9 and 127.0 (3 s, C_m), 128.3, 128.4 and 128.5 (3 s, C_o), 145.5–145.8 (m, C_i), 150.9 and 151.0 (2 s, OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 66.4 (s) (+ d satellites, $^1J_{PSe}$ = 727.4 Hz), 66.5 (s) (+ d satellites, $^1J_{PSe}$ = 724.5 Hz), 66.7 (s) (+ d satellites, $^1J_{PSe}$ = 723 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –343.3, –340.7.

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –313.1 (d, $^1J_{PSe}$ = 726.7 Hz), –295.3 (d, $^1J_{PSe}$ = 726.7 Hz), –292.3 (d, $^1J_{PSe}$ = 726.7 Hz).

Anal. Calcd for $C_{22}H_{30}NOPSe$: C, 60.83; H, 6.96; N, 3.22; P, 7.13; Se, 18.18. Found: C, 60.88; H, 6.94; N, 3.26; P, 7.09; Se, 18.12.

_P_,_P_-Bis(2-phenylpropyl)-_N_-[3-(vinyloxy)propyl]phosphinoselenoic Amide (10m)
Yield: 426 mg (95%); waxy solid.

IR (neat): 3364, 3256 (NH), 1636 (OC=C), 1617, 1119 (sh, P–N–C), 1085, 701, 561 (P=Se) cm^{-1}.

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.21, 1.32 and 1.38 (3 d, $^3J_{HH}$ = 6.9 Hz, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 7.1 Hz, 6 H, *Me*CH, respectively), 1.42–1.46 (m, 1 H, NCH_2CH_2), 1.56 (quin, $^3J_{HH}$ = 6.2 Hz, 1 H, NCH_2CH_2), 1.88, 1.90, 1.91 and 1.94 (4 d, $^2J_{PH}$ = 4.8 Hz, 1 H, NH), 1.99–2.32 (m, 4 H, CH_2P), 2.36–2.46, 2.59–2.67 and 2.77–2.84 (m, 2 H, NCH_2), 3.14–3.20 and 3.38–3.46 (m, 2 H, C*H*Me), 3.46–3.48 and 3.54–3.57 (m, 2 H, OCH_2), 3.99, 4.00, 4.02 and 4.06 (4 dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 4.10, 4.12, 4.15 and 4.23 (4 dd, $^3J_{HH}$ = 14.2 Hz, $^2J_{HH}$ = 2.0 Hz, 1 H, =CH_2), 6.37, 6.39, 6.42 and 6.51 (4 dd, $^3J_{HH}$ = 14.2 Hz, $^3J_{HH}$ = 6.8 Hz, 1 H, OCH=), 7.18–7.32 (m, 10 H, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 24.3, 24.4, 24.7 and 24.8 (4 d, $^3J_{PC}$ = 12.8 Hz, $^3J_{PC}$ = 12.8 Hz, $^3J_{PC}$ = 14.8 Hz, $^3J_{PC}$ = 13.6 Hz, *Me*CH, respectively), 30.0, 30.2 and 30.4 (3 d, $^3J_{PC}$ = 9.2 Hz, $^3J_{PC}$ = 8.8 Hz, $^3J_{PC}$ = 8.4 Hz, NCH_2CH_2, respectively), 34.9, 35.3, 35.8 and 36.1 (4 d, $^2J_{PC}$ = 2.8 Hz, $^2J_{PC}$ = 3.6 Hz, $^2J_{PC}$ = 0.4 Hz, $^2J_{PC}$ = 2.4 Hz, *C*HMe, respectively), 38.1–38.8 (4 s, NCH_2), 40.3, 42.1, 42.9 and 43.3 (4 d, $^1J_{PC}$ = 53.1 Hz, $^1J_{PC}$ = 53.1 Hz, $^1J_{PC}$ = 55.5 Hz, $^1J_{PC}$ = 57.5 Hz, CH_2P, respectively), 65.1, 65.2 and 65.4 (3 s, CH_2O), 86.6, 86.7 and 86.8 (3 s, =CH_2), 126.7–126.8, 127.3–127.4 and 128.7–128.8 (m, C_o, C_m, C_p), 145.9–146.2 (m, C_i), 151.3, 151.5 and 151.6 (3 s, OCH=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 65.2 (s) (+ d satellites, $^1J_{PSe}$ = 723.2 Hz), 66.8 (s) (+ d satellites; $^1J_{PSe}$ = 723.2 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –335.8.

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –309.2 (d, $^1J_{PSe}$ = 722.2 Hz), –292.9 (d, $^1J_{PSe}$ = 721.1 Hz), –289.1 (d, $^1J_{PSe}$ = 715.9 Hz).

Anal. Calcd for $C_{23}H_{32}NOPSe$: C, 61.60; H, 7.19; N, 3.12; P, 6.91; Se, 17.61. Found: C, 61.53; H, 7.17; N, 3.08; P, 6.89; Se, 17.55.

3-(Diphenethylphosphorochalcogenoyl)-2-methyl-1,3-oxazolidines 11 and 12; General Procedure

A soln of *N*-[2-(vinyloxy)alkyl]phosphinochalcogenoic amide **10d** or **10i** (0.6 mmol) in toluene (2.3 mL), in a sealed ampoule, was stirred at 75 °C (10 h for phosphinothioic amide **10d**, 3.5 h for phosphinoselenoic amide **10i**). The progress of the reaction was monitored using ^{31}P NMR spectroscopy by following the disappearance of the signal due to the starting phosphinochalcogenoic amide (at ca. 65–72 ppm) and the appearance of a new resonance in the region of 68–72 ppm for the product. The mixture was filtered through a layer of Al_2O_3 (activity level II, 1.5 cm, eluent: toluene). The solvent was removed by distillation under reduced pressure to give 2-methyl-1,3-oxazolidine **11** or **12**.

3-(Diphenethylphosphorothioyl)-2-methyl-1,3-oxazolidine (11)

Yield: 174 mg (80%); waxy product.

IR (neat): 2978 ($COCH_2$), 1602 (C=C, Ph), 1161 (P–N–C), 698, 619 (P=S) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.32 (d, $^3J_{HH}$ = 5.2 Hz, 3 H, Me), 2.06–2.25 (m, 4 H, $PhCH_2$), 2.80–3.02 (m, 4 H, CH_2P), 3.08–3.16 and 3.40–3.48 (m, 2 H, NCH_2), 3.76–3.82 and 3.96–4.00 (m, 2 H, CH_2O), 5.42 (dq, $^3J_{PH}$ = 10.0 Hz, $^3J_{HH}$ = 5.2 Hz, 1 H, C*H*Me), 7.12–7.22 (m, 6 H, H_o, H_p, Ph), 7.24 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 7.2 Hz, 4 H, H_m, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.8 (d, $^3J_{PC}$ = 3.6 Hz, Me), 28.3 and 28.5 (2 d, $^2J_{PC}$ = 2.4 Hz, $^2J_{PC}$ = 2.8 Hz, $PhCH_2$, respectively), 34.2 and 34.6, (2 d, $^1J_{PC}$ = 61.1 Hz, $^1J_{PC}$ = 64.3 Hz, PCH_2, respectively), 44.8 (NCH_2), 65.8 (d, $^3J_{PC}$ = 4.0 Hz, OCH_2), 87.4 (d, $^2J_{PC}$ = 3.2 Hz, *C*Me), 126.3 (C_p), 128.1 (d, $^4J_{PC}$ = 6.0 Hz, C_o), 128.5 (d, $^5J_{PC}$ = 0.8 Hz, C_m), 140.4 (d, $^3J_{PC}$ = 15.2 Hz, C_i).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 72.1.

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –317.9.

Anal. Calcd for $C_{20}H_{26}NOPS$: C, 66.83; H, 7.29; N, 3.90; P, 8.62; S, 8.92. Found: C, 66.79; H, 7.23; N, 3.87; P, 8.59; S, 8.88.

3-(Diphenethylphosphoroselenoyl)-2-methyl-1,3-oxazolidine (12)

Yield: 219 mg (90%); waxy solid.

IR (neat): 2978 ($COCH_2$), 1603 (C=C, Ph), 1157 (P–N–C), 698, 580 (P=Se) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.22 (d, $^3J_{HH}$ = 5.1 Hz, 3 H, Me), 2.30–2.43 (m, 4 H, $PhCH_2$), 2.91–3.05 (m, 4 H, CH_2P), 3.16–3.19 and 3.51–3.53 (m, 2 H, NCH_2), 3.30–3.89 and 4.04–4.05 (m, 2 H, CH_2O), 5.38 (dq, $^3J_{PH}$ = 10.1 Hz, $^3J_{HH}$ = 5.1 Hz, 1 H, C*H*Me), 7.19–7.26 (m, 6 H, H_o, H_p, Ph), 7.31 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 7.1 Hz, 4 H, H_m, Ph).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.8 (d, $^3J_{PC}$ = 4.8 Hz, Me), 29.2 and 29.3 (2 s, $PhCH_2$), 35.0 and 35.5 (2 d, $^1J_{PC}$ = 55.8 Hz, $^1J_{PC}$ = 53.1 Hz, PCH_2, respectively), 45.6 (NCH_2), 65.9 (d, $^3J_{PC}$ = 4.0 Hz, OCH_2), 88.1 (d, $^2J_{PC}$ = 2.8 Hz, *C*Me), 126.4 (C_p), 128.2 (d, $^4J_{PC}$ = 6.0 Hz, C_o), 128.7 (C_m), 140.4 (d, $^3J_{PC}$ = 15.2 Hz, C_i).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 68.2 (s) (+ d satellite, $^1J_{PSe}$ = 742 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –320.8.

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –334.7 (d, $^1J_{PSe}$ = 742 Hz).

Anal. Calcd for $C_{20}H_{26}NOPSe$: C, 59.11; H, 6.45; N, 3.45; P, 7.62; Se, 19.43. Found: C, 59.02; H, 6.47; N, 3.43; P, 7.56; Se, 19.38.

***N*-Methyl-*P*,*P*-diphenethyl-*N*-{2-[1-(phenylsulfanyl)ethoxy]ethyl}phosphinoselenoic Amide (13)**

A mixture of *P*,*P*-diphenethyl-*N*-methyl-*N*-[2-(vinyloxy)ethyl]phosphinoselenoic amide (**10k**; 210 mg, 0.50 mmol) and benzenethiol (68 mg, 0.62 mmol) in dioxane (2 mL) was stirred at 75 °C for 5.5 h. The solvent was removed under reduced pressure. The residue obtained was washed with hexane (5 × 0.2 mL), the solvent was removed by decantation, and the residue was dried under vacuum to give product **13**.

Yield: 186 mg (70%); waxy solid.

IR (neat): 3060 (CH_3), 1107, 698, 578 (P=Se) cm^{-1}.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.51 (d, $^3J_{HH}$ = 6.2 Hz, 3 H, Me), 2.23–2.30 and 2.41–2.49 (m, 4 H, CH_2P), 2.72 (d, $^3J_{PH}$ = 11.2 Hz, 3 H, NMe), 2.49–2.87 and 2.93–3.04 (m, 4 H, $PhCH_2$), 3.22–3.29 and 3.31–3.40 (m, 2 H, NCH_2), 3.55–3.60 and 3.97–4.02 (m, 2 H, CH_2O), 4.36 (q, $^3J_{HH}$ = 6.2 Hz, 1 H, C*H*Me), 7.20–7.24 and 7.27–7.32 (m, 10 H, Ph), 7.47 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, C_o, SPh), 7.48 (m, 2 H, C_m, SPh), 7.52 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, C_p, SPh).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 22.6 (Me), 29.3 ($PhCH_2$), 34.7 (d, $^1J_{PC}$ = 54.7 Hz, CH_2P), 35.0 (NMe), 49.8 (NCH_2), 66.4 (CH_2O), 85.1 (CHS), 126.4 (C_p), 127.6 (C_p, PhS), 128.3 (C_o), 128.6 (C_m), 128.8 (C_m, PhS), 129.5 (C_i, PhS), 133.6 (C_o, PhS), 140.9 (d, $^3J_{PC}$ = 15.6 Hz, C_i).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 74.7 (s) (+ d satellite, $^1J_{PSe}$ = 736 Hz).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –358.0.

^{77}Se NMR (76.31 MHz, $CDCl_3$): δ = –349.3 (d, $^1J_{PSe}$ = 736 Hz).

Anal. Calcd for $C_{27}H_{34}NOPSSe$: C, 61.12; H, 6.46; N, 2.64; P, 5.84; S, 6.04; Se, 14.88. Found: C, 61.07; H, 6.44; N, 2.62; P, 5.79; S, 6.01; Se, 14.85.

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