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Organophosphorus-Selenium Heteroatom Derivatives from Selenation of Primary/Secondary Amines and Haloalkanes/Dihaloalkanes

Guoxiong Hua,[a] Kasun S. A. Arachchige,[a] Alexandra M. Z. Slawin,[a] and J. Derek Woollins*[a]

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Reaction of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide (Woollins' reagent) with four equivalents of primary/secondary amines led to a series of ammonium phenylphosphonamido-diselenoates or phenylphosphonamido-diselenoic diamides **1a**–**n**, the latter further reacted in situ with either two equivalents of haloalkanes or an equimolar amount of dihaloalkane, resulting in formation of the corresponding *Se*-alkylphenyl-*Se*-alkylphenyl-phosphonamidodiselenoates **2a**–**n** and alkane bis(*N*-alkyl-*P*-phenylphosphonamido-diselenoate) derivatives **3a**–**n** in good to excellent yields. All new compounds have been characterized spectroscopically including multinuclear NMR (^{1}H, ^{13}C, ^{31}P and ^{77}Se), IR and mass spectroscopy. Two representative X-ray structures are also described.

Introduction

Organophosphorus chemistry has attracted huge attention in both academic and industrial research for several decades.[1–3] A wide range of applications have been documented in fields such as coordination chemistry, material science, homogeneous catalysis, the synthesis of biologically active agents or pesticides, and additives for polymers such as lubricants and antioxidants.[4–10] 2,4-Bis(phenyl)-1,3-diselenadiphosphethane-2,4-diselenide [$\{PhP(Se)(\mu\text{-}Se)\}_2$] (Woollins' reagent, WR), a selenium counterpart of the well-known Lawesson's reagent (LR), has been well-developed in recent years as an efficient phosphorus-selenium-containing building block or selenation reagent for organic synthetic chemistry.[11] The reactions of WR with various organic substrates ranges from simple oxygen–selenium exchange to the formation of complex phosphorus-selenium heterocycles as well as the formation of surprising phosphorus-selenium-free products.[12–25] We have recently reported the synthesis of a series of ammonium phenylphosphonamido-diselenoates and phenylphosphonamido-diselenoic diamides from the reaction of WR with primary or secondary amines,[26] and the formation of a series of organophosphorus-selenium heteroatom derivatives from the selenation of alkenyl or arynyl-diamines.[27] As a part of our continuing exploration into the reactivity of WR towards different organic nucleophiles, herein, we report the synthesis of a series of novel *Se*-alkylphenylphosphonamido-diselenoate and alkane bis(*N*-alkyl-*P*-phenylphosphonamido-diselenoate) derivatives through the reaction of WR with primary/secondary amines, followed by treatment with haloalkanes or dihaloalkanes in situ. We also report two representative X-ray structures.

Results and Discussion

Treatment of WR with four molar equivalents of primary or secondary amine in anhydrous tetrahydrofuran (THF) at ambient temperature for 2 h proceeded with cleavage of the four-membered ring in WR, leading to formation of the corresponding ammonium salts of phenylphosphonamido-diselenoates and phenylphosphonamido-diselenoic diamides **1a**–**n** in almost quantitative yields.[26] These ammonium salts were further reacted in situ with two equivalents of haloalkanes at ambient temperature for 24 h to give the corresponding *Se*-alkylphenylphosphonamido-diselenoates **2a**–**n**, as depicted in Scheme 1. These new heteroatom compounds were isolated in good to excellent yields (41–93%; Table 1) as either sticky oils or pastes that were soluble in both chlorinated solvents and tetrahydrofuran. It should be noted that products **2e**–**l**, bearing a strong electron-withdrawing group R^3 (p-$BrC_6H_4COCH_2$), were obtained in rather high yields (55–93%), whereas products **2b** and **2c**, bearing a less electron-withdrawing group R^3 [$CH_3(CH_2)_{10}$ or $CH_3(CH_2)_6$], were isolated in the lowest yields (41 and 42%, respectively). Thus, it appears that a strong electron-withdrawing group R^3 is hugely beneficial for the formation of the reaction products. Compounds **2a**–**n** are stable to air and moisture for months without any clear signs of degradation.

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[a] EaStCHEM School of Chemistry, University of St Andrews,
St Andrews, Fife, Scotland, KY16 9ST, UK
E-mail: jdw3@st-and.ac.uk
http://www.st-andrews.ac.uk/chemistry/

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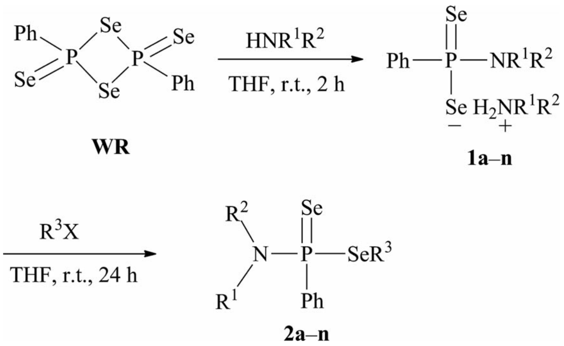
Table 1. *Se*-Alkylphenylphosphonamidodiselenoates **2a**–**n** and their ^{31}P and ^{77}Se NMR spectra.

X	R^1	R^2	R^3	Product	Yield (%)	δ_P (ppm) [($J_{P,Se}$), Hz]	δ_{Se} (ppm) [($J_{P,Se}$), Hz]
Cl	*c*-Hexyl	H	$C_6H_5COCH_2$	**2a**	54	53.7 [371/792]	345.4 [371] –102.0 [792]
Br	*c*-Hexyl	H	$CH_3(CH_2)_{10}$	**2b**	42	53.2 [391/786]	323.6 [391] –104.5 [786]
Br	*c*-Hexyl	H	$CH_3(CH_2)_8$	**2c**	41	53.2 [390/786]	323.6 [390] –104.6 [786]
Br	*c*-Hexyl	H	$CH_3(CH_2)_6$	**2d**	59	53.2 [390/786]	323.6 [391] –104.4 [786]
Br	*t*Bu	H	$1,4-BrC_6H_4COCH_2$	**2e**	82	46.9 [355/794]	384.0 [355] –53.0 [792]
Br	*s*Bu	H	$1,4-BrC_6H_4COCH_2$	**2f**[a]	93	56.0 [366/796] 54.8 [373/782]	346.1 [367] –101.9 [794] 348.5 [374] –104.8 [784]
Br	*n*Bu	H	$1,4-BrC_6H_4COCH_2$	**2g**	81	58.0 [370/794]	321.2 [370] –100.4 [794]
Br	*c*-Hexyl	H	$1,4-BrC_6H_4COCH_2$	**2h**	56	54.5 [369/794]	347.7 [369] –100.7 [794]
Br	*c*-Pentyl	H	$1,4-BrC_6H_4COCH_2$	**2i**	81	55.8 [369/791]	338.8 [369] –95.3 [791]
Br	*i*Pr	H	$1,4-BrC_6H_4COCH_2$	**2j**	88	54.6 [369/794]	345.3 [370] –102.4 [794]
Br	*i*Pr	*i*Pr	$1,4-BrC_6H_4COCH_2$	**2k**	55	62.5 [366/789]	311.7 [367] –26.1 [789]
Br	*i*Bu	*i*Bu	$1,4-BrC_6H_4COCH_2$	**2l**	67	78.4 [362/798]	299.8 [362] –93.5 [799]
Br	*i*Pr	*i*Pr	$1,2-(HOCH_2)C_6H_4CH_2$	**2m**	44	59.9 [387/777]	361.4 [388] –26.4 [777]
Br	B$_n$	H	$1,4-BrC_6H_4COCH_2$	**2n**	47	58.3 [376/798]	324.8 [376] –103.4 [798]

[a] Two diastereomers were found in compound **2f**.



Scheme 1. Synthesis of *Se*-alkylphenylphosphonamidodiselenoates **2a**–**n** (R groups defined in Table 1).

Compounds **2a**–**n** were characterised by IR and ^1H, ^{13}C, ^{31}P and ^{77}Se NMR spectroscopy and by mass spectrometry. All new compounds showed the anticipated $[M + H]^+$ or $[M + Na]^+$ peak in their mass spectra and satisfactory accurate mass measurements. Two isomers were found in the NMR spectra of **2f**. The ^{31}P NMR spectra of **2a**–**n** display sharp singlets in the range of 46.9–78.4 ppm, flanked by two pairs of selenium satellites with ^{31}P–^{77}Se coupling constants in the range of 355–391 Hz and 777–798 Hz, indicating the presence of P–Se single bonds and P=Se double bonds in each compound. This was further substantiated by the ^{77}Se NMR spectra of **2a**–**n**, which contain signals arising from SeR in the range of δ = 299.8–384.0 ppm and from P=Se in the range of δ = –104.8 to –26.1 ppm, respectively, with matching ^{31}P–^{77}Se coupling constants (Table 1).

The molecular structures of **2e** and **2i** were confirmed by single-crystal X-ray diffraction analysis, which are shown in Figure 1[28] and Figure 2.[29] The transparent, colourless cubic crystals of **2e** and **2i** were grown from dichloromethane solution with slow diffusion of hexane. Compound **2e** crystallized in the triclinic space group $P\bar{1}$, whereas compound **2i** crystallized in the monoclinic space group $P2_{1/c}$ with two independent molecules per unit cell. In compound

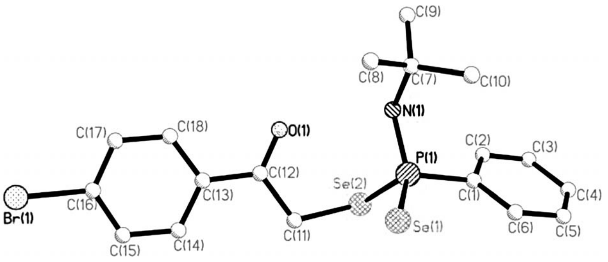


Figure 1. X-ray structure of **2e** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles (°) (esds in parentheses): Se(1)–P(1) 2.103(3), Se(2)–P(1) 2.257(3), Se(2)–C(11) 1.948(9), P(1)–C(1) 1.807(8), P(1)–N(1) 1.666(6), N(1)–C(7) 1.488(9); P(1)–Se(2)–C(11) 99.3(3), Se(1)–P(1)–Se(2) 113.48(11), Se(1)–P(1)–N(1) 120.7(2), Se(1)–P(1)–C(1) 113.0(3), Se(2)–P(1)–N(1) 100.8(3), Se(2)–P(1)–C(1) 100.4(3), N(1)–P(1)–C(1) 106.0(4), P(1)–N(1)–C(7) 124.9(5).

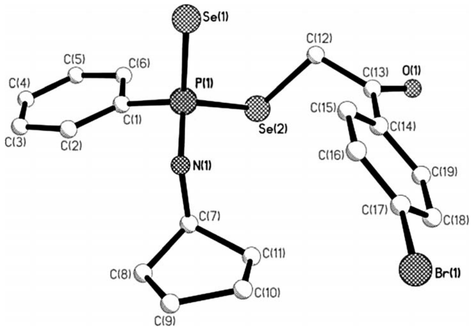
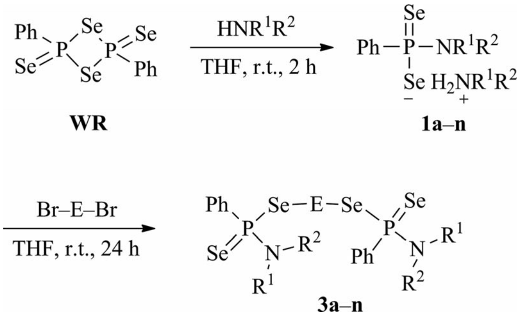


Figure 2. X-ray structure of **2i** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles (°) (esds in parentheses) (dimensions for second independent molecule in square parentheses): Se(1)–P(1) 2.097(4) [2.103(4)], Se(2)–P(1) 2.281(4) [2.208(4)], Se(2)–C(12) 1.950(11) [1.972(10)], P(1)–C(1) 1.791(10) [1.838(10)], P(1)–N(1) 1.666(6) [1.644(9)], N(1)–C(7) 1.483(12) [1.513(12)]; P(1)–Se(2)–C(11) 99.4(3) [101.3(3)], Se(1)–P(1)–Se(2) 114.09(12) [114.29(12)], Se(1)–P(1)–N(1) 113.3(3) [111.2(4)], Se(1)–P(1)–C(1) 113.7(4) [113.3(4)], Se(2)–P(1)–N(1) 109.4(3) [110.1(3)], Se(2)–P(1)–C(1) 101.3(4) [100.6(4)], N(1)–P(1)–C(1) 106.4(5) [106.6(5)], P(1)–N(1)–C(7) 119.2(6) [121.1(7)].

2e, the two phenyl rings are inclined 56.85° to one another. The P(1)–Se(1) [2.103(3) Å] and P(1)–Se(2) [2.0954(13) Å] bond lengths in **2e** and the P(1)–Se(1) [2.097(4)/2.103(4)] and P(1)–Se(2) [2.281(4)/2.208(4) Å] bond lengths in **2i** are consistent with P–Se single bonds (2.2–2.3 Å) and P=Se double bonds (2.08–2.12 Å) in similar compounds.[25,30,31]

We also carried out analogous reactions by using dihaloalkanes instead of monohaloalkanes. Thus, ammonium phenyldiselenophosphonates **1a**–**n** were further reacted in situ with one molar equivalent of dibromoalkanes in tetrahydrofuran at ambient temperature for 24 h to give the corresponding *Se*-alkylphenylphosphonamido-diselenoates **3a**–**n**, as shown in Scheme 2. These new compounds were isolated in moderate to good yields (51–80 %; Table 2) as sticky



Scheme 2. Synthesis of *Se*-alkylphenylphosphonamidodiselenoates **3a**–**n** (R and E groups are defined in Table 2).

Table 2. *Se*-Alkylphenylphosphonamidodiselenoates **3a**–**n** and their ^{31}P and ^{77}Se NMR spectra.

Product	R^1	R^2	E	Yield (%)	δ_P (ppm) [($J_{P,Se}$), Hz]	δ_{Se} (ppm) [($J_{P,Se}$), Hz]
3a	*c*-Hexyl	H	CH_2	79	54.9 [374/791] 54.8 [371/791]	398.6 [371], –91.9 [791] 395.5 [374], –92.7 [791]
3b	*c*-Hexyl	H	CH_2CH_2	80	52.5 [384/789] 52.4 [386/786]	378.5 [384], –90.1 [784] 375.6 [386], –94.7 [786]
3c	*c*-Hexyl	H	$CH_2CH_2CH_2$	70	53.7 [384/789] 53.6 [386/786]	325.1 [384], –102.8 [789] 324.8 [386], –103.5 [786]
3d	*c*-Hexyl	H	$CH_2CH_2CH_2CH_2$	78	53.5 [384/789] 53.4 [386/786]	326.7 [386], –105.0[789] 326.3 [388], –105.2 [786]
3e	*c*-Hexyl	H	1,2-$CH_2C_6H_4CH_2$	77	53.9 [386/789] 53.8 [386/789]	395.9 [386], –96.7 [789] 395.1 [386], –96.8 [789]
3f	*i*Pr	H	CH_2CH_2	65	53.0 [383/786] 52.7 [385/784]	514.7 [385], –248.5 [784] 514.5 [383], –248.7 [786]
3g	*i*Pr	H	$CH_2CH_2CH_2$	55	53.9 [385/789] 53.8 [385/789]	323.4 [385], –164.2 [789] 323.0 [385], –173.8 [789]
3h	*i*Pr	H	1,2-$CH_2C_6H_4CH_2$	56	54.2 [385/786] 54.1 [385/786]	392.7 [385], –99.5 [786] 392.1 [385], –99.7 [786]
3i	*i*Bu	*i*Bu	1,2-$CH_2C_6H_4CH_2$	53	77.1 [386/792] 76.8 [386/794] 76.2 [386/794] 76.1 [386/792]	357.1 [386], –95.6 [792] 354.1 [386], –96.7 [794] 350.5 [386], –98.4 [794] 350.1 [386], –99.1 [792]
3j	*i*Pr	H	biphenyl-4,4′-diylbis(methylene)	54	54.0 [387/789] 53.9 [387/789]	408.5 [386], –99.1 [789] 408.4 [385], –99.3 [789]
3k	*t*Bu	H	1,3-$CH_2C_6H_4CH_2$	59	46.1 [374/794] 45.9 [367/789] 45.8 [377/789]	450.7 [374], –49.2 [789] 447.8 [377], –49.8 [789] 447.2 [367], –50.4 [789]
3l	*t*Bu	H	1,2-$CH_2C_6H_4CH_2$	51	46.0 [376/789] 45.9 [378/786]	438.8 [378], –50.3 [789] 438.1 [385], –50.4 [789]
3m	*s*Bu	H	1,2-$CH_2C_6H_4CH_2$	54	55.2 [384/789] 55.1 [384/789] 54.8 [384/789] 54.7 [387/789]	395.9 [384], –99.0 [789] 395.2 [384], –99.5 [789] 394.8 [384], –101.2 [789] 391.4 [387], –101.4 [789]
3n	*s*Bu	H	1,3-$CH_2C_6H_4CH_2$	60	55.0 [390/789] 54.9 [390/789] 54.6 [390/789] 54.5 [390/789]	406.4 [390], –97.1 [789] 406.2 [390], –97.5 [789] 406.1 [390], –99.1 [789] 405.7 [390], –99.5 [789]

oils, pastes or solids that were soluble in chloroform, dichloromethane and tetrahydrofuran, and insoluble in diethyl ether and hexane.

The characterisation of **3a**–**n** was made on the basis of ^1H, ^{13}C, ^{31}P and ^{77}Se NMR, IR spectroscopy and mass spectrometry. All new compounds showed the anticipated $[M + H]^+$ or $[M + Na]^+$ peak in their mass spectra and satisfactory accurate mass measurements were obtained for all compounds. The ^{31}P NMR spectra of **3a**–**h**, **3j** and **3l** exhibit two sets of double resonances (as a consequence of the stereoisomers present) with two sets of satellites, whereas, interestingly, the ^{31}P NMR spectra of **3i**, **3m** and **3n** displayed four sets of double resonances, and three sets of double resonances were found in **3k**, as a consequence of the stereoisomers present (Table 2). The two phosphorus atoms constitute potential stereogenic centres in compounds **3a**–**n**, thus, stereotopic (*R*,*R*), (*S*,*S*), (*S*,*R*) and (*R*,*S*) stereoisomers are possible. Not surprisingly, in the ^{31}P NMR spectra of **3a**–**h**, **3j** and **3l**, two phosphorus signals with different intensity ratio (see experimental section) were observed in the range δ = 52.4–54.9 ppm, flanked by two sets of satellites for the endocyclic and exocyclic selenium atoms [$J(P,Se_{endo})$ coupling constants being in the range of 371–387 Hz and $J(P,Se_{exo})$ coupling constants in the range of 784–794 Hz], although we were not able to assign them specifically to particular stereoisomers. However, four phosphorus signals with very similar chemical shifts and different intensity ratio were found in the ^{31}P NMR spectra of compound **3i**, **3m** and **3n**, whereas three similar phosphorus signals with different intensity ratio were also observed in the ^{31}P NMR spectrum of **3k**, and all of these signals were flanked by two sets of satellites for the endocyclic and exocyclic selenium atoms (see Table 2). The results indicate the presence of some spatial hindrance effects in compounds **3i**, **3k**, **3m** and **3n**, compared with compounds **3a**–**h**, **3j** and **3l**. The hindered rotation of two large $Ph(NR^1R^2)P(Se)CH_2$ groups from the *ortho* or *meta* position in the bridged linkage benzene backbone in **3i**, **3k**, **3m** and **3n** may result in three or four magnetically different phosphorus environments rather than three or four chemically different phosphorus environments when two potential stereogenic centres exist. Detailed ^{31}P and ^{77}Se NMR spectroscopic analyses reveal the relatively small coupling constant $^3J_{P,Se}$ = 17.0 Hz and $^4J_{P,P}$ = 4.2 Hz in **3a**, $^4J_{P,Se}$ = 12.3 Hz in **3b** and **3f**, supporting the presence of the $P(Se)SeCH_2SeP(Se)$ or $P(Se)SeCH_2CH_2SeP(Se)$ linkage in compounds **3a**, **3b** and **3f**. The ^{31}P and ^{77}Se NMR chemical shifts and coupling constants are comparable to those of previously reported phosphorus-selenium compounds.[32–35]

Conclusions

An efficient route has been developed to prepare a series of new *Se*-alkylphenylphosphonamido-diselenoate and alkane bis(*N*-alkyl-*P*-phenylphosphonamido-diselenoate) derivatives in moderate to good yields from the reaction of ammonium phenylphosphonamido-diselenoates or phenylphosphonamido-diselenoic diamides, which were derived from the reaction of WR with primary/secondary amines, with either two molar equivalents of haloalkanes or one molar equivalent of dibromoalkanes. All new compounds were fully characterised by means of IR, mass spectroscopy and multinuclear NMR analysis in conjunction with single-crystal X-ray crystallography of two structures.

Experimental Section

General: Unless otherwise stated, all reactions were carried out under on oxygen-free nitrogen atmosphere by using predried solvents and standard Schlenk techniques; subsequent chromatographic and work up procedures were performed in air. ^1H (270 MHz), ^{13}C (67.9 MHz), $^{31}P\{^1H\}$ (109 MHz) and $^{77}Se\{^1H\}$ (51.4 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise) with a JEOL GSX 270 instrument. IR spectra were recorded as KBr pellets in the range of 4000–250 cm^{-1} with a Perkin–Elmer 2000 FTIR/Raman spectrometer. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St Andrews Mass Spectrometry Service. X-ray crystal data for **2e** and **2j** were collected with a Rigaku SCXMini Mercury CCD system. Intensity data were collected by using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semiempirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 by using the program SHELXTL.[36] Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries.

CCDC-944056 (for **2e**) and -944057 (for **2i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for the Synthesis of 2a–n: A mixture of amine (4.0 mmol) and WR (0.54 g, 1.0 mmol) in tetrahydrofuran (60 mL) was stirred at room temperature for 2 h (the brown suspension disappeared and a pale-yellow suspension formed). To the mixture, the appropriate haloalkane (2.0 mmol) was added and the mixture was stirred at room temperature for 24 h. After filtering to remove insoluble solid and drying in vacuo, the residue was dissolved in dichloromethane (ca. 2.0 mL) and purified by column chromatography on silica gel (dichloromethane/hexane, 1:1) to give the product **2a**–**n**.

***N*-Cyclohexyl *Se*-(2-Oxo-2-phenylethyl) Phenylphosphonamidodiselenoate (2a):** Yield 0.519 g (54%); yellow oil. IR (KBr): $\tilde{\nu}$ = 1670 (vs), 1596 (m), 1579 (m), 1448 (s), 1274 (vs), 1180 (m), 1005 (m), 798 (m), 748 (m), 709 (s), 688 (s), 605 (m) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 8.06–7.91 (m, 4 H, Ar-H), 7.61–7.41 (m, 6 H, Ar-H), 4.75 (d, $J\{^{31}P\text{-}^1H\}$ = 13.5 Hz, 2 H, $SeCH_2$), 4.37–4.12 (m, 1 H, cyclohexyl-H), 3.32–3.20 (m, 1 H, NH), 1.96–0.85 (m, 10 H, cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.9 (C=O), 136.1 (d, $J_{P,C}$ = 91.3 Hz), 134.0, 133.1, 132.2 (d, $J_{P,C}$ = 3.1 Hz], 130.9 (d, $J_{P,C}$ = 12.5 Hz), 128.8, 128.7, 128.5 (d, $J_{P,C}$ = 13.5 Hz), 53.0, 37.5, 35.4 (d, $J_{P,C}$ = 19.7 Hz), 35.3 (d, $J_{P,C}$ = 18.7 Hz), 25.1 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.7 (s, $J_{P,Se}$ = 371 Hz, $J_{P,Se}$ = 792 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 345.4 (d, $J_{P,Se}$ = 371 Hz), –102.0 (d, $J_{P,Se}$ = 792 Hz) ppm. MS (CI+): m/z = 486 $[M + H]^+$. HRMS (CI+): calcd for $C_{20}H_{24}NOPSe_2H$ $[M + H]^+$ 486.0002; found 485.9994.

***N*-Cyclohexyl *Se*-Undecyl Phenylphosphonamidodiselenoate (2b):** Yield 0.433 g (42%); pale-yellow oil. IR (KBr): $\tilde{\nu}$ = 1446 (m), 1436 (m), 1403 (m), 1292 (m), 1231 (m), 1136 (m), 1081 (s), 994 (m), 877 (m), 745 (s), 690 (s), 560 (s), 524 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.05–7.97 (m, 2 H, Ar-H), 7.49–7.45 (m, 3 H, Ar-H), 3.40 (dt, $J_{H,H}$ = 7.4 Hz, 1 H, cyclohexyl-H), 3.22–3.12 (m, 2 H, cyclohexyl-H), 2.92–2.84 (m, $J_{P,H}$ = 13.2 Hz, $J_{H,H}$ = 7.4 Hz, 2 H, $SeCH_2$), 2.71 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 1.96 (d, $J_{H,H}$ = 9.4 Hz, 1 H, NH), 1.71–1.19 (m, 24 H, cyclohexyl-H, CH_2), 0.87 (t, $J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2: δ = 137.3 (d, $J_{P,C}$ = 87.2 Hz), 131.9 (d, $J_{P,C}$ = 3.1 Hz), 130.8 (d, $J_{P,C}$ = 12.5 Hz), 128.4 (d, $J_{P,C}$ = 13.5 Hz), 52.8, 35.7 (d, $J_{P,C}$ = 5.2 Hz), 35.6 (d, $J_{P,C}$ = 5.2 Hz), 32.9, 32.0, 30.5 (d, $J_{P,C}$ = 3.1 Hz), 29.9, 29.6, 29.5, 29.4, 29.1, 25.5, 25.2, 22.8, 14.0 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.2 (s, $J_{P,Se}$ = 391 Hz, $J_{P,Se}$ = 786 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 323.6 (d, $J_{P,Se}$ = 391 Hz), –104.5 (d, $J_{P,Se}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 522 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{23}H_{40}NPSe_2H$ [M + H]$^+$ 522.1303; found 522.1299.

***N*-Cyclohexyl *Se*-Nonyl Phenylphosphonamidodiselenoate (2c):** Yield 0.405 g (41%); colourless oil. IR (KBr): $\tilde{\nu}$ = 1447 (m), 1436 (m), 1404 (m), 1293 (m), 1231 (m), 1142 (m), 1081 (s), 994 (m), 878 (m), 746 (s), 690 (s), 569 (s), 524 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.05–7.97 (m, 2 H, Ar-H), 7.49–7.45 (m, 3 H, Ar-H), 3.40 (dt, $J_{H,H}$ = 7.4 Hz, 1 H, cyclohexyl-H), 3.22–3.12 (m, 2 H, cyclohexyl-H), 2.92–2.84 (m, $J_{P,H}$ = 13.2 Hz, $J_{H,H}$ = 7.4 Hz, 2 H, $SeCH_2$), 2.72 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 1.96 (d, $J_{H,H}$ = 9.4 Hz, 1 H, NH), 1.71–1.18 (m, 20 H, cyclohexyl-H, CH_2), 0.87 (t, $J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 137.3 (d, $J_{P,C}$ = 86.2 Hz), 131.8 (d, $J_{P,C}$ = 3.1 Hz), 130.8 (d, $J_{P,C}$ = 12.5 Hz), 128.3 (d, $J_{P,C}$ = 13.5 Hz), 52.8, 35.6 (d, $J_{P,C}$ = 5.2 Hz), 35.5 (d, $J_{P,C}$ = 5.2 Hz), 32.9, 31.9, 30.5 (d, $J_{P,C}$ = 3.1 Hz), 29.9, 29.5, 29.4, 29.3, 25.5, 25.2, 22.8, 14.0 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.2 (s, $J_{P,Se}$ = 390 Hz, $J_{P,Se}$ = 786 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 323.6 (d, $J_{P,Se}$ = 390 Hz), –104.6 (d, $J_{P,Se}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 494 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{21}H_{36}NPSe_2H$ [M + H]$^+$ 494.0990; found 494.0892.

***N*-Cyclohexyl *Se*-Heptyl Phenylphosphonamidodiselenoate (2d):** Yield 0.272 g (59%); colourless oil. IR (KBr): $\tilde{\nu}$ = 1450 (m), 1436 (m), 1404 (m), 1293 (m), 1231 (m), 1140 (m), 1081 (vs), 994 (m), 878 (m), 746 (s), 690 (s), 570 (s), 523 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.06–7.97 (m, 2 H, Ar-H), 7.50–7.45 (m, 3 H, Ar-H), 3.17–3.12 (m, 1 H, cyclohexyl-H), 2.89 (dt, $J_{P,H}$ = 13.2 Hz, $J_{H,H}$ = 7.4 Hz, 2 H, $SeCH_2$), 2.72 (t, $J_{H,H}$ = 7.4 Hz, 2 H, CH_2), 1.96 (d, $J_{H,H}$ = 9.4 Hz, 1 H, NH), 1.69–1.09 (m, 18 H, cyclohexyl-H, CH_2), 0.86 (t, $J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 137.2 (d, $J_{P,C}$ = 87.2 Hz], 131.9 (d, $J_{P,C}$ = 3.1 Hz), 130.8 (d, $J_{P,C}$ = 12.5 Hz), 128.4 (d, $J_{P,C}$ = 13.5 Hz), 52.9, 35.7 (d, $J_{P,C}$ = 5.2 Hz), 35.6 (d, $J_{P,C}$ = 5.2 Hz), 32.9, 31.7, 30.5 (d, $J_{P,C}$ = 3.1 Hz), 29.9, 28.8, 25.3, 22.7, 13.9 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.2 (s, $J_{P,Se}$ = 390 Hz, $J_{P,Se}$ = 786 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 323.6 (d, $J_{P,Se}$ = 391 Hz), –104.4 (d, $J_{P,Se}$ = 786 Hz) ppm. MS (ES$^+$): *m*/*z* = 488 [M + Na]$^+$. HRMS (ES$^+$): calcd for $C_{19}H_{32}NNaPSe_2$ [M + Na]$^+$ 488.0500; found 488.0500.

***N*-*tert*-Butyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2e):** Yield 0.440 g (82%); pale-yellow paste. IR (KBr): $\tilde{\nu}$ = 1669 (s), 1582 (s), 1564 (m), 1474 (m), 1437 (m), 1385 (m), 1363 (m), 1270 (m), 1222 (m), 1188 (s), 1095 (m), 1070 (m), 983 (s), 804 (m), 747 (s), 691 (s), 546 (m), 528 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.12–8.04 (m, 2 H, Ar-H), 7.84 (d, $J_{H,H}$ = 8.8 Hz, 2 H, Ar-H), 7.60 (d, $J_{H,H}$ = 8.8 Hz, 2 H, Ar-H), 7.51–7.43 (m, 3 H, Ar-H), 4.37 (d, $J_{P,H}$ = 13.2 Hz, 2 H, $SeCH_2$), 2.54 (d, $J_{H,H}$ = 9.5 Hz, 1 H, NH), 1.30 (s, 9 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.3 (C=O), 137.7 (d, $J_{P,C}$ = 91.3 Hz), 134.4, 132.1, 131.2, 131.0, 130.4, 128.6, 128.4, 58.0, 38.5, 31.1 ppm. ^{31}P NMR (CD_2Cl_2): δ = 46.9 (s, $J_{P,Se}$ = 355 Hz, $J_{P,Se}$ = 794 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 384.0 (d, $J_{P,Se}$ = 355 Hz), –53.0 (d, $J_{P,Se}$ = 792 Hz) ppm. MS (ES$^+$): *m*/*z* = 560 [M + Na]$^+$. HRMS (ES$^+$): calcd for $C_{18}H_{21}BrNONaPSe_2$ [M + Na]$^+$ 559.8772; found 559.8767.

***N*-*sec*-Butyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2f):** Yield 0.500 g (93%); reddish yellow sticky oil. Two stereoisomers were found in ca. 1:1 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1671 (s), 1583 (s), 1435 (m), 1397 (s), 1273 (s), 1178 (s), 1098 (m), 1070 (s), 1004 (s), 838 (m), 746 (s), 689 (m), 538 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.04–7.94 (m, 2×2 H, Ar-H), 7.81–7.75 (m, 2×2 H, Ar-H), 7.61–7.54 (m, 2×2 H, Ar-H), 7.49–7.45 (m, 3 H, Ar-H), 4.27–3.91 (m, 2×1 H, CH), 3.51–3.05 (m, 2×2 H, $SeCH_2$), 2.54 (d, $J_{H,H}$ = 9.5 Hz, 2×1 H, NH), 1.59–1.41 (m, 2×2 H, CH_2), 1.13 (dd, $J_{H,H}$ = 6.6 Hz, $J_{P,H}$ = 3.3 Hz, 3 H, CH_3), 1.12 (dd, $J_{H,H}$ = 6.6 Hz, $J_{P,H}$ = 3.3 Hz, 3 H, CH_3), 0.88 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 0.85 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.4 (C=O), 136.3 (d, $J_{P,C}$ = 89.4 Hz), 136.2 (d, $J_{P,C}$ = 90.6 Hz), 134.6, 134.5, 132.6 (d, $J_{P,C}$ = 3.1 Hz), 132.5 (d, $J_{P,C}$ = 3.1 Hz), 132.4, 132.3, 132.2, 131.5, 131.4, 131.3, 131.2, 130.7, 130.6, 129.1, 129.0, 128.3, 128.7, 51.7 (d, $J_{P,C}$ = 18.9 Hz), 51.4 (d, $J_{P,C}$ = 18.7 Hz), 38.1, 37.5, 31.8 (d, $J_{P,C}$ = 23.6 Hz), 31.7 (d, $J_{P,C}$ = 22.1 Hz), 22.2 (d, $J_{P,C}$ = 21.4 Hz), 22.1 (d, $J_{P,C}$ = 20.5 Hz), 10.5, 10.4 ppm. ^{31}P NMR (CD_2Cl_2): δ = 56.0 (s, $J_{P,Se}$ = 366 Hz, $J_{P,Se}$ = 796 Hz), 54.8 (s, $J_{P,Se}$ = 373 Hz, $J_{P,Se}$ = 782 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 348.5 (d, $J_{P,Se}$ = 374 Hz), 346.1 (d, $J_{P,Se}$ = 367 Hz), –101.9 (d, $J_{P,Se}$ = 794 Hz), –104.8 (d, $J_{P,Se}$ = 784 Hz) ppm. MS (ES$^+$): *m*/*z* = 560 [M + Na]$^+$. HRMS (ES$^+$): calcd for $C_{18}H_{21}BrNONaPSe_2$ [M + Na]$^+$ 559.8772; found 559.8762.

***N*-Butyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2g):** Yield 0.434 g (81%); yellow sticky oil. IR (KBr): $\tilde{\nu}$ = 1657 (s), 1585 (s), 1435 (m), 1396 (m), 1279 (s), 1100 (m), 1085 (m), 1069 (m), 1004 (s), 841 (m), 752 (s), 705 (m), 689 (m), 567 (s), 441 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.00–7.92 (m, 2 H, Ar-H), 7.81 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.61 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.50–7.47 (m, 3 H, Ar-H), 4.31–4.15 (m, 2 H, $NHCH_2$), 3.18 (br. s, 1 H, NH), 2.91 (d, 2 H, $SeCH_2$), 1.62–1.28 (m, 4 H, cyclohexyl-H), 0.87 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.4 (C=O), 135.4 (d, $J_{P,C}$ = 89.9 Hz), 134.5, 132.8 (d, $J_{P,C}$ = 3.1 Hz), 132.4, 131.1 (d, $J_{P,C}$ = 12.5 Hz), 130.7, 129.1 (d, $J_{P,C}$ = 13.5 Hz), 43.5 (d, $J_{P,C}$ = 3.7 Hz), 37.2, 33.3 (d, $J_{P,C}$ = 9.5 Hz), 20.4, 13.9 ppm. ^{31}P NMR (CD_2Cl_2): δ = 58.0 (s, $J_{P,Se}$ = 370 Hz, $J_{P,Se}$ = 794 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 321.2 (d, $J_{P,Se}$ = 370 Hz), –100.4 (d, $J_{P,Se}$ = 794 Hz) ppm. MS (ES$^+$): *m*/*z* = 560 [M + Na]$^+$. HRMS (ES$^+$): calcd for $C_{18}H_{21}NONaBrPSe_2$ [M + Na]$^+$ 559.8772; found 559.8771.

***N*-Cyclohexyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2h):** Yield 0.630 g (56%); brown paste. IR (KBr): $\tilde{\nu}$ = 1673 (s), 1584 (s), 1483 (m), 1435 (m), 1396 (m), 1270 (s), 1178 (m), 1071 (s), 1004 (s), 836 (m), 747 (s), 689 (m), 519 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.02–7.97 (m, 2 H, Ar-H), 7.80–7.78 (m, 2 H, Ar-H), 7.62–7.58 (m, 2 H, Ar-H), 7.50–7.43 (m, 3 H, Ar-H), 4.30–4.14 (m, 1 H, cyclohexyl-H), 3.23 (br. s, 1 H, NH), 2.59–2.52 (d, 2 H, $SeCH_2$), 2.05–0.86 (m, 10 H, cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.3 (C=O), 136.3 (d, $J_{P,C}$ = 90.0 Hz), 134.5, 132.6 (d, $J_{P,C}$ = 3.1 Hz), 132.4, 131.1 (d, $J_{P,C}$ = 12.5 Hz), 130.7, 129.1 (d, $J_{P,C}$ = 13.5 Hz), 53.1 (d, $J_{P,C}$ = 18.1 Hz), 37.8, 35.8, 29.0, 25.3 ppm. ^{31}P NMR (CD_2Cl_2): δ = 54.5 (s, $J_{P,Se}$ = 369 Hz, $J_{P,Se}$ = 794 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 347.7 (d, $J_{P,Se}$ = 369 Hz), –100.7 (d, $J_{P,Se}$ = 794 Hz) ppm. MS (CI$^+$): *m*/*z* = 564 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{20}H_{23}BrNOPSe_2H$ [M + H]$^+$ 563.9109; found 563.9111.

***N*-Cyclopentyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2i):** Yield 0.445 g (81%); greyish yellow paste. IR (KBr): ṽ = 1658 (s)m, 1581 (s), 1434 (m), 1416 (m), 1395 (m), 1278 (s), 1177 (m), 1093 (m), 1068 (m), 1004 (s), 840 (s), 752 (s), 704 (m), 687 (m), 621 (m), 555 (s), 463 (s), 418 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.02–7.93 (m, 2 H, Ar-H), 7.81 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.58 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.52–7.42 (m, 3 H, Ar-H), 4.32–4.12 (m, 1 H, cyclopentyl-H), 3.31 (dd, 1 H, NH), 2.54 (d, 2 H, $SeCH_2$), 1.94–1.45 (m, 8 H, cyclopentyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.1 (d, $J_{P,C}$ = 3.4 Hz, C=O), 135.6 (d, $J_{P,C}$ = 90.3 Hz), 134.2, 132.4 (d, $J_{P,C}$ = 3.1 Hz), 132.0, 130.9 (d, $J_{P,C}$ = 12.5 Hz), 130.4, 128.7 (d, $J_{P,C}$ = 13.5 Hz), 55.8 (d, $J_{P,C}$ = 4.2 Hz), 37.2, 34.8 (d, $J_{P,C}$ = 6.2 Hz), 23.3 (d, $J_{P,C}$ = 7.3 Hz) ppm. ^{31}P NMR (CD_2Cl_2): δ = 55.8 (s, $J_{P,Se}$ = 369 Hz, $J_{P,Se}$ = 791 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 338.8 (d, $J_{P,Se}$ = 369 Hz), –95.3 (d, $J_{P,Se}$ = 791 Hz) ppm. MS (ES$^+$): *m/z* = 572 [M + Na]$^+$. HRMS (ES$^+$): calcd for $C_{19}H_{21}NONaBrPSe_2$ [M + Na]$^+$ 571.8772; found 571.8766.

***N*-Isopropyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2j):** Yield 0.460 g (88%); light-yellow paste. IR (KBr): ṽ = 1656 (s), 1580 (s), 1563 (m), 1413 (s), 1277 (s), 1124 (m), 1094 (m), 1068 (m), 1029 (m), 1004 (s), 748 (s), 703 (m), 687 (m), 622 (m), 565 (s), 473 (m), 585 (m), 420 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.01 (dd, $J_{P,H}$ = 14.9 Hz, $J_{H,H}$ = 8.0 Hz, 2 H, Ar-H), 7.80 (d, $J_{H,H}$ = 8.5 Hz, 2 H, Ar-H), 7.60 (d, $J_{H,H}$ = 8.5 Hz, 2 H, Ar-H), 7.52–7.43 (m, 3 H, Ar-H), 4.31–4.08 (m, 1 H, CH), 3.65–3.52 (m, 2 H, $SeCH_2$), 3.19 (br., 1 H, NH), 1.15 (d, $J_{H,H}$ = 6.1 Hz, 6 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.0 (C=O), 135.8 (d, $J_{P,C}$ = 90.3 Hz, Ar-C), 134.2 (Ar-C), 132.3 (d, $J_{P,C}$ = 3.1 Hz, Ar-C), 132.1 (Ar-C), 130.9 (d, $J_{P,C}$ = 12.5 Hz, Ar-C), 130.4 (Ar-C), 128.6 (d, $J_{P,C}$ = 13.5 Hz, Ar-C), 46.2 (N-C), 37.4 (Se-C), 25.0 (d, $J_{P,C}$ = 5.2 Hz, CH_3), 24.6 (d, $J_{P,C}$ = 5.2 Hz, CH_3) ppm. ^{31}P NMR (CD_2Cl_2): δ = 54.6 (s, $J_{P,Se}$ = 369 Hz, $J_{P,Se}$ = 794 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 345.3 (d, $J_{P,Se}$ = 370 Hz), –102.4 (d, $J_{P,Se}$ = 794 Hz) ppm. MS (CI$^+$): *m/z* = 524 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{17}H_{19}BrNOPSe_2H$ [M + H]$^+$ 523.8789; found 523.8791.

***N,N*-Diisopropyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2k):** Yield 0.310 g (55%); yellow paste. IR (KBr): ṽ = 1682 (s), 1585 (s), 1434 (m), 1394 (s), 1362 (m), 1266 (s), 1174 (m), 1105 (m), 1071 (s), 1007 (s), 821 (s), 747 (s), 588 (m), 559 (m), 496 (m), 454 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.82–7.80 (m, 2 H, Ar-H), 7.78 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.61 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.58–7.54 (m, 3 H, Ar-H), 4.39–4.34 (m, 2 H, CH), 2.54 (d, 2 H, $SeCH_2$), 1.46 (d, $J_{H,H}$ = 6.4 Hz, 12 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 194.1 (C=O), 133.5 (d, $J_{P,C}$ = 112.1 Hz), 132.1, 131.9, 131.6 (d, $J_{P,C}$ = 3.1 Hz), 131.2 (d, $J_{P,C}$ = 12.5 Hz), 130.5, 130.2, 128.3 (d, $J_{P,C}$ = 13.5 Hz), 50.0, 39.3, 22.8 ppm. ^{31}P NMR (CD_2Cl_2): δ = 62.5 (s, $J_{P,Se}$ = 366 Hz, $J_{P,Se}$ = 789 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 311.7 (d, $J_{P,Se}$ = 367 Hz), –26.1 (d, $J_{P,Se}$ = 789 Hz) ppm. MS (CI$^+$): *m/z* = 566 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{20}H_{24}BrNOPSe_2H$ [M + H]$^+$ 565.9266; found 565.9269.

***N,N*-Diisobuyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2l):** Yield 0.398 g (67%); reddish yellow sticky oil. IR (KBr): ṽ = 1683 (s), 1585 (s), 1465 (m), 1434 (m), 1394 (m), 1267 (s), 1177 (m), 1156 (m), 1094 (s), 1070 (s), 1009 (s), 876 (m), 819 (m), 745 (s), 704 (m), 690 (m), 575 (s), 490 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.02 (dd, $J_{P,H}$ = 14.6 Hz, $J_{H,H}$ = 6.6 Hz, 2 H, Ar-H), 7.81 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.59 (d, $J_{H,H}$ = 6.9 Hz, 2 H, Ar-H), 7.51–7.42 (m, 3 H, Ar-H), 4.27 (d, $J_{P,H}$ = 10.8 Hz, 2 H, $SeCH_2$), 2.94–2.81 (m, 4 H, NCH_2), 1.89–1.81 (m, 2 H, CH), 0.81 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 0.75 (d, $J_{H,H}$ = 6.6 Hz, 6 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 193.9 (C=O), 135.2 (d, $J_{P,C}$ = 112.1 Hz), 132.3, 132.1, 132.0 (d, $J_{P,C}$ = 3.1 Hz), 131.9, 130.2 (d, $J_{P,C}$ = 12.5 Hz), 129.5, 128.3 (d, $J_{P,C}$ = 13.5 Hz), 55.3, 38.9, 26.8, 20.3 ppm. ^{31}P NMR (CD_2Cl_2): δ = 78.4 (s, $J_{P,Se}$ = 362 Hz, $J_{P,Se}$ = 798 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 299.8 (d, $J_{P,Se}$ = 362 Hz), –93.5 (d, $J_{P,Se}$ = 799 Hz) ppm. MS (ES$^+$): *m/z* = 616 [M + Na]$^+$. HRMS (ES$^+$): calcd for $C_{22}H_{29}NONaBrPSe_2$ [M + Na]$^+$ 615.9398; found 615.9409.

***N,N*-Diisopropyl *Se*-[2-(Hydroxymethyl)benzyl] Phenylphosphonamidodiselenoate (2m):** Yield 0.215 g (44%); yellow paste. IR (KBr): ṽ = 1486 (m), 1453 (m), 1435 (m), 1172 (m), 1040 (m), 759 (s), 711 (m), 550 (s), 507 (m), 442 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.01–7.94 (m, 2 H, Ar-H), 7.35–7.22 (m, 7 H, Ar-H), 4.67 (d, $J_{H,H}$ = 15.4 Hz, 2 H, CH_2), 3.96–3.85 (m, 2 H, CH), 3.70 (t, 1 H, OH), 2.59 (d, 2 H, $SeCH_2$), 1.29 (dd, 12 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 139.2, 136.7, 133.5, 131.5, 131.2, 131.0, 130.3, 128.8, 127.7, 127.3, 62.6, 50.0, 29.9, 22.8 ppm. ^{31}P NMR (CD_2Cl_2); δ = 59.9 (s, $J_{P,Se}$ = 387 Hz, $J_{P,Se}$ = 777 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 361.4 (d, $J_{P,Se}$ = 388 Hz), –26.4 (d, $J_{P,Se}$ = 777 Hz) ppm. MS (CI$^+$): *m/z* = 490 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{20}H_{28}NOPSe_2H$ [M + H]$^+$ 490.0315; found 490.0308.

***N*-Benzyl *Se*-[2-(4-Bromophenyl)-2-oxoethyl] Phenylphosphonamidodiselenoate (2n):** Yield 0.534 g (47%); yellow paste. IR (KBr): ṽ = 1693 (vs), 1580 (s), 1479 (m), 1453 (m), 1434 (m), 1394 (m), 1274 (m), 1189 (m), 1100 (m), 1056 (s), 984 (s), 801 (s), 731 (s), 686 (s), 555 (s), 492 (m), 475 (m), 445 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.03 (d, $J_{H,H}$ = 8.26 Hz, 2 H, Ar-H), 7.81–7.77 (m, 2 H, Ar-H), 7.60–7.47 (m, 5 H, Ar-H), 7.36–7.26 (m, 5 H, Ar-H), 4.31–4.01 (m, 4 H, CH_2), 3.68–3.60 (m, 1 H, NH) ppm. ^{13}C NMR (CD_2Cl_2): δ = 193.9 (C=O), 138.7, 138.5, 134.8 (d, $J_{P,C}$ = 91.3 Hz), 132.6 (d, $J_{P,C}$ = 3.1 Hz), 132.1, 130.9 (d, $J_{P,C}$ = 12.5 Hz), 130.4 (d, $J_{P,C}$ = 13.5 Hz), 129.9, 128.9, 128.7, 128.1, 127.6, 46.9, 37.2 ppm. ^{31}P NMR (CD_2Cl_2): δ = 58.3 (s, $J_{P,Se}$ = 376 Hz, $J_{P,Se}$ = 798 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 324.8 (d, $J_{P,Se}$ = 376 Hz), –103.4 (d, $J_{P,Se}$ = 798 Hz) ppm. MS (ES$^+$): *m/z* = 594 [M + Na]$^+$. HRMS (CI$^+$): calcd for $C_{21}H_{19}NOPSe_2BrH$ [M + H]$^+$ 571.8790; found 571.8787.

General Procedure for the Synthesis of 3a–n: A mixture of amine (4.0 mmol) and WR (0.54 g, 1.0 mmol) in THF (60 mL) was stirred at room temperature for 2 h (the brown suspension disappeared and a pale-yellow suspension formed). To the mixture, the appropriate dihaloalkane (1.0 mmol) was added and the mixture was stirred at room temperature for 24 h. After filtering to remove insoluble solid and drying in vacuo, the residue was dissolved in dichloromethane (ca. 2.0 mL) and purified by column chromatography on silica gel (dichloromethane) to give the product **3a**–**n**.

Methylene Bis(*N*-cyclohexyl-*P*-phenylphosphonamidodiselenoate) (3a): Yield 0.585 g (79%); pale-yellow oil. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:1 intensity ratio. IR (KBr): ṽ = 1435 (s), 1403 (m), 1292 (m), 1231 (m), 1139 (m), 1077 (vs), 994 (s), 902 (s), 879 (s), 745 (s), 688 (s), 567 (s), 518 (vs), 490 (s), 438 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.01–7.88 (m, 2 × 4 H, Ar-H), 7.60–7.39 (m, 2 × 6 H, Ar-H), 4.42–4.20 (m, 2 × 2 H, cyclohexyl-H), 3.21 (d, 2 H, $SeCH_2$), 3.05 (d, 2 H, $SeCH_2$), 1.96–0.83 (m, 2 × 20 H, NH, cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 136.2 (d, $J_{P,C}$ = 88.2 Hz), 132.3 (d, $J_{P,C}$ = 3.1 Hz), 130.9 (d, $J_{P,C}$ = 12.5 Hz), 128.6 (d, $J_{P,C}$ = 13.5 Hz), 53.1 (d, $J_{P,C}$ = 9.5 Hz), 35.6, 29.1, 25.4, 25.2 ppm. ^{31}P NMR (CD_2Cl_2): δ = 54.9 (s, $J_{P,Se}$ = 374 Hz, $J_{P,Se}$ = 791 Hz), 54.8 (s, $J_{P,Se}$ = 371 Hz, $J_{P,Se}$ = 791 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 398.6 (d, $J_{P,Se}$ = 371 Hz), 395.5 (d, $J_{P,Se}$ = 374 Hz), –91.9 (d, $J_{P,Se}$ = 791 Hz), –92.7 (d, $J_{P,Se}$ = 791 Hz) ppm. MS (CI$^+$): *m/z* = 745 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{25}H_{37}N_2P_2Se_4$ [M + H] 744.9101; found 744.9099.

Ethane-1,2-diyl Bis(*N*-cyclohexyl-*P*-phenylphosphonamidodiselenoate) (3b): Yield 0.604 g (80%); pale-yellow oil. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:1 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1434 (m), 1405 (m), 1077 (s), 994 (m), 878 (m), 745 (m), 688 (s), 519 (s), 479 (m), 443 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.12–7.90 (m, 2×4 H, Ar-H), 7.50–7.43 (m, 2×6 H, Ar-H), 4.36–4.06 (dd, 2×2 H, cyclohexyl-H), 3.20–3.08 (m, 2×4 H, CH_2Se), 2.28–1.17 (m, 2×22 H, NH, cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 135.7 (d, $J_{\mathrm{P,C}}$ = 90.3 Hz), 135.6 (d, $J_{\mathrm{P,C}}$ = 90.3 Hz), 132.2 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 132.5 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 130.9 (d, $J_{\mathrm{P,C}}$ = 12.5 Hz), 130.8 (d, $J_{\mathrm{P,C}}$ = 12.5 Hz), 128.6, 130.9 (d, $J_{\mathrm{P,C}}$ = 13.5 Hz), 53.0, 52.9, 35.7, 35.6, 32.1, 30.9, 25.4, 25.3 ppm. ^{31}P NMR (CD_2Cl_2): δ = 52.5 (s, $J_{\mathrm{P,Se}}$ = 384 Hz, $J_{\mathrm{P,Se}}$ = 784 Hz), 52.4 (s, $J_{\mathrm{P,Se}}$ = 386 Hz, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 378.5 (d, $J_{\mathrm{P,Se}}$ = 384 Hz), 375.6 (d, $J_{\mathrm{P,Se}}$ = 386 Hz), –90.1 (d, $J_{\mathrm{P,Se}}$ = 784 Hz), –94.7 (d, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 759 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{26}H_{39}N_2P_2Se_4$ [M + H] 758.9256; found 758.9260.

Propane-1,3-diyl Bis(*N*-cyclohexyl-*P*-phenylphosphonamidodiselenoate) (3c): Yield 0.540 g (70%); pale-yellow paste. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:1 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1435 (m), 1403 (m), 1289 (m), 1229 (m), 1078 (vs), 994 (m), 878 (m), 745 (s), 689 (s), 568 (m), 520 (s), 489 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.03–7.95 (m, 2×4 H, Ar-H), 7.53–7.451 (m, 2×6 H, Ar-H), 3.28–3.11 (m, 2×2 H, cyclohexyl-H), 2.96–2.76 (m, 2×6 H, $SeCH_2$, NH), 2.14–1.07 (m, 2×22 H, cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 137.1 (d, $J_{\mathrm{P,C}}$ = 88.2 Hz), 132.0 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 130.8 (d, $J_{\mathrm{P,C}}$ = 12.5 Hz), 128.5 (d, $J_{\mathrm{P,C}}$ = 13.5 Hz), 53.0, 35.6, 32.3, 31.2, 25.4, 25.3 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.7 (s, $J_{\mathrm{P,Se}}$ = 384 Hz, $J_{\mathrm{P,Se}}$ = 789 Hz), 53.6 (s, $J_{\mathrm{P,Se}}$ = 386 Hz, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 325.1 (d, $J_{\mathrm{P,Se}}$ = 384 Hz), 324.8 (d, $J_{\mathrm{P,Se}}$ = 386 Hz), –102.8 (d, $J_{\mathrm{P,Se}}$ = 789 Hz), –103.5 (d, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 773 [M + H]$^+$. HRMS (CI$^+$): calcd for $C_{27}H_{41}N_2P_2Se_4$ [M + H] 772.9421; found 772.9416.

Butane-1,4-diyl Bis(*N*-cyclohexyl-*P*-phenylphosphonamidodiselenoate) (3d): Yield 0.610 g (48%); pale-green paste. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:1 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1436 (m), 1396 (m), 1078 (s), 997 (m), 886 (m), 746 (s), 688 (s), 572 (m), 519 (s), 485 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.98–7.96 (m, 2×4 H, Ar-H), 7.47–7.42 (m, 2×6 H, Ar-H), 3.96–3.79 (m, 2×4 H, $SeCH_2$), 2.81–1.15 (m, 2×28 H, NH, cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 137.1 (d, $J_{\mathrm{P,C}}$ = 86.2 Hz), 132.7 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 130.8 (d, $J_{\mathrm{P,C}}$ = 12.5 Hz), 128.4 (d, $J_{\mathrm{P,C}}$ = 13.5 Hz), 52.9, 35.7, 33.4, 25.9, 25.1, 24.5 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.5 (s, $J_{\mathrm{P,Se}}$ = 384 Hz, $J_{\mathrm{P,Se}}$ = 789 Hz), 53.4 (s, $J_{\mathrm{P,Se}}$ = 386 Hz, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 326.7 (d, $J_{\mathrm{P,Se}}$ = 386 Hz), 326.3 (d, $J_{\mathrm{P,Se}}$ = 388 Hz), –105.0 (d, $J_{\mathrm{P,Se}}$ = 789 Hz), –105.2 (d, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 789 [M + H]$^+$. HRMS (C|I$^+$): calcd for $C_{28}H_{43}N_2PSe_4$ [M + H] 788.9562; found 788.9556.

1,2-Phenylenebis(methylene) Bis(*N*-cyclohexyl-*P*-phenylphosphonamidodiselenoate) (3e): Yield 0.642 g (77%); milky green solid. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:1 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1435 (m), 1401 (m), 1290 (w), 1072 (m), 1076 (s), 993 (m), 877 (m), 745 (s), 688 (s), 567 (m), 519 (s), 489 (m), 436 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.94–7.88 (m, 2×4 H, Ar-H), 7.38–7.22 (m, 2×6 H, Ar-H), 7.21–6.99 (m, 2×4 H, Ar-H), 4.38–4.18 (m, 2×2 H, cyclohexyl-H), 3.11–2.76 (m, 2×6 H, $SeCH_2$, NH), 1.86–1.12 (m, 2×20 H, cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 137.3, 136.6, 136.1, 132.0, 130.9, 130.8, 128.6, 128.4, 127.8, 53.1, 52.7, 35.6, 33.8, 33.4, 25.4, 25.2 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.9 (s, $J_{\mathrm{P,Se}}$ = 386 Hz, $J_{\mathrm{P,Se}}$ = 789 Hz), 53.8 (s, $J_{\mathrm{P,Se}}$ = 386 Hz, $J_{\mathrm{P,Se}}$ = 789 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 395.9 (d, $J_{\mathrm{P,Se}}$ = 386 Hz), 395.1 (d, $J_{\mathrm{P,Se}}$ = 386 Hz), –96.7 (d, $J_{\mathrm{P,Se}}$ = 789 Hz), –96.8 (d, $J_{\mathrm{P,Se}}$ = 789 Hz) ppm. MS (CI$^+$): *m*/*z* = 835 [M + H]$^+$. HRMS (C|I$^+$): calcd for $C_{32}H_{43}N_2PSe_4$ [M + H] 834.9580; found 834.9569.

Ethane-1,2-diyl Bis(*N*-isopropyl-*P*-phenylphosphonamidodiselenoate) (3f): Yield 0.440 g (55%); reddish pink paste. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 2:3 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1436 (s), 1398 (m), 1160 (m), 1130 (s), 1027 (s), 946 (m), 890 (m), 747 (s), 692 (s), 586 (s), 537 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.88–7.79 (m, 2×4 H, Ar-H), 7.50–7.43 (m, 2×6 H, Ar-H), 4.25–4.05 (m, 2×2 H, CH), 3.60–3.57 (m, 2×4 H, $SeCH_2$), 3.19–3.16 (m, 2×2 H, NH), 1.38–1.34 (m, 2×12 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 137.1, 136.5, 131.6 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 130.8, 130.6, 128.3, 128.1, 61.9, 61.8, 45.3, 44.7, 25.2, 24.7 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.0 (s, $J_{\mathrm{P,Se}}$ = 383 Hz, $J_{\mathrm{P,Se}}$ = 786 Hz), 52.7 (s, $J_{\mathrm{P,Se}}$ = 385 Hz, $J_{\mathrm{P,Se}}$ = 784 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 514.7 (d, $J_{\mathrm{P,Se}}$ = 385 Hz), 514.5 (d, $J_{\mathrm{P,Se}}$ = 383 Hz), –248.5 (d, $J_{\mathrm{P,Se}}$ = 784 Hz), –248.7 (d, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 679 [M + H]$^+$. HRMS (C|I$^+$): calcd for $C_{20}H_{31}N_2PSe_4$ [M + H] 678.8631; found 678.8625.

Propane-1,3-diyl Bis(*N*-isopropyl-*P*-phenylphosphonamidodiselenoate) (3g): Yield 0.380 g (55%); reddish yellow paste. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:1 intensity ratio. IR (KBr): $\tilde{\nu}$ = 163 (w), 1435 (m), 1285 (m), 1114 (m), 1029 (s), 893 (s), 806 (s), 747 (m), 691 (s), 542 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.03–7.94 (m, 2×4 H, Ar-H), 7.54–7.47 (m, 2×6 H, Ar-H), 3.90–3.52 (m, 2×2 H, CH), 3.30–3.24 (m, 2×4 H, $SeCH_2$), 2.98–2.88 (m, 2×2 H, NH), 1.52–1.37 (m, 2×2 H, CH_2), 1.17–1.12 (m, 2×12 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 136.8, 136.2, 135.5, 135.1, 132.6 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 132.1 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 131.1, 130.9, 130.7, 130.5, 129.1, 128.9, 18.6, 128.4, 46.2, 45.8, 29.1, 29.0, 25.0, 24.5, 20.9 ppm. ^{31}P NMR (CD_2Cl_2): δ = 53.9 (s, $J_{\mathrm{P,Se}}$ = 385 Hz, $J_{\mathrm{P,Se}}$ = 789 Hz), 53.8 (s, $J_{\mathrm{P,Se}}$ = 385 Hz, $J_{\mathrm{P,Se}}$ = 789 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 323.4 (d, $J_{\mathrm{P,Se}}$ = 385 Hz), 323.0 (d, $J_{\mathrm{P,Se}}$ = 385 Hz), –164.2 (d, $J_{\mathrm{P,Se}}$ = 789 Hz), –173.8 (d, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 693 [M + H]$^+$. HRMS (C|I$^+$): calcd for $C_{21}H_{33}N_2PSe_4$ [M + H] 692.8788; found 692.8779.

1,2-Phenylenebis(methylene) Bis(*N*-isopropyl-*P*-phenylphosphonamidodiselenoate) (3h): Yield 0.495 g (66%); pale-green paste. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 3:2 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1434 (m), 1362 (m), 1124 (m), 1096 (m), 1007 (s), 881 (s), 744 (s), 688 (s), 532 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.04–7.94 (m, 2×4 H, Ar-H), 7.52–7.47 (m, 2×6 H, Ar-H), 7.15–7.06 (m, 2×4 H, Ar-H), 4.27–4.20 (m, 2×2 H, CH), 3.92–3.83 (m, 2×4 H, $SeCH_2$), 2.74–2.68 (m, 2×2 H, NH), 1.15–1.08 (m, 2×12 H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2): δ = 137.6, 137.1, 136.6, 135.8, 132.2 (d, $J_{\mathrm{P,C}}$ = 3.1 Hz), 131.0 (d, $J_{\mathrm{P,C}}$ = 12.5 Hz), 130.9 (d, $J_{\mathrm{P,C}}$ = 12.5 Hz), 128.6 (d, $J_{\mathrm{P,C}}$ = 13.5 Hz), 127.8 (d, $J_{\mathrm{P,C}}$ = 13.5 Hz), 46.3, 33.7, 24.9, 24.8 ppm. ^{31}P NMR (CD_2Cl_2): δ = 54.2 (s, $J_{\mathrm{P,Se}}$ = 385 Hz, $J_{\mathrm{P,Se}}$ = 786 Hz), 54.1 (s, $J_{\mathrm{P,Se}}$ = 385 Hz, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. ^{77}Se NMR (CD_2Cl_2): δ = 392.7 (d, $J_{\mathrm{P,Se}}$ = 385 Hz), 392.1 (d, $J_{\mathrm{P,Se}}$ = 385 Hz), –99.5 (d, $J_{\mathrm{P,Se}}$ = 786 Hz), –99.7 (d, $J_{\mathrm{P,Se}}$ = 786 Hz) ppm. MS (CI$^+$): *m*/*z* = 755 [M + H]$^+$. HRMS (C|I$^+$): calcd for $C_{26}H_{35}N_2PSe_4$ [M + H] 692.8788; found 692.8779.

1,2-Phenylenebis(methylene) Bis(*N*,*N*-diisobutyl-*P*-phenylphosphonamidodiselenoate) (3i): Yield 0.475 g (53%); pale-green paste. Four diastereoisomers were found in multinuclear NMR spectra in ca. 1:1:3:3 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1616 (w), 1509 (w), 1436 (m), 1396 (m), 1216 (s), 1138 (s), 1026 (m), 897 (s), 747 (m), 715 (m), 692 (s), 541 (s), 487 (m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.09–

7.97 (m, 4×4 H, Ar-H), 7.47–7.38 (m, 4×6 H, Ar-H), 7.15–7.04 (m, 4×4 H, Ar-H), 4.30–3.80 (m, 4×8 H, CH$_2$), 2.96–2.82 (m, 4×4 H, SeCH$_2$), 1.91–1.81 (m, 4×4 H, CH), 0.85–0.75 (m, 4×24 H, CH$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 137.8, 137.5, 137.4, 136.7, 136.4, 136.0, 135.9, 135.1, 132.2, 132.1, 131.8, 131.7, 131.0, 130.8, 130.5, 128.4, 128.2, 127.6, 127.5, 55.5, 34.5, 34.3, 30.3, 27.0, 26.9, 20.5, 20.3 ppm. ^{31}P NMR (CD$_2$Cl$_2$): δ = 77.1 (s, $J_{P,Se}$ = 386 Hz, $J_{P,Se}$ = 792 Hz), 76.8 (s, $J_{P,Se}$ = 386 Hz, $J_{P,Se}$ = 794 Hz), 76.2 (s, $J_{P,Se}$ = 386 Hz, $J_{P,Se}$ = 794 Hz), 76.1 (s, $J_{P,Se}$ = 386 Hz, $J_{P,Se}$ = 792 Hz) ppm. ^{77}Se NMR (CD$_2$Cl$_2$): δ = 357.1 (d, $J_{P,Se}$ = 386 Hz), 354.1 (d, $J_{P,Se}$ = 386 Hz), 350.5 (d, $J_{P,Se}$ = 386 Hz), 350.1 (d, $J_{P,Se}$ = 386 Hz), –95.6 (d, $J_{P,Se}$ = 792 Hz), –96.7 (d, $J_{P,Se}$ = 794 Hz), –98.4 (d, $J_{P,Se}$ = 794 Hz), –99.1 (d, $J_{P,Se}$ = 792 Hz) ppm. MS (CI$^+$): *m*/*z* = 895 [M + H]$^+$. HRMS (C|I$^+$): calcd for C$_{36}$H$_{55}$N$_2$PSe$_4$ [M + H] 895.0520; found 895.0498.

Biphenyl-4,4′-Diylbis(methylene) Bis(*N*-isopropyl-*P*-phenylphosphonamidodiselenoate) (3j): Yield 0.445 g (54%); reddish yellow solid. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:2 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1580 (w), 1495 (s), 1433 (m), 1396 (s), 1160 (s), 1094 (s), 1002 (m), 814 (s), 741 (s), 687 (s), 508 (s), 486 (s), 409 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.01–7.93 (m, 2×4 H, Ar-H), 7.45–7.29 (m, 2×14 H, Ar-H), 4.20–4.17 (m, 2×4 H, SeCH$_2$), 3.91–3.78 (m, 2×2 H, CH), 2.65–2.55 (m, 2×2 H, NH), 1.30–1.11 (m, 2×12 H, CH$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 139.5, 139.4, 138.4, 137.6, 132.0, 131.0, 130.8, 130.0, 129.7, 129.5, 128.6, 128.4, 127.1, 126.9, 46.2, 35.7, 24.9 ppm. ^{31}P NMR (CD$_2$Cl$_2$): δ = 54.0 (s, $J_{P,Se}$ = 387 Hz, $J_{P,Se}$ = 789 Hz), 53.9 (s, $J_{P,Se}$ = 387 Hz, $J_{P,Se}$ = 789 Hz) ppm. ^{77}Se NMR (CD$_2$Cl$_2$): δ = 408.5 (d, $J_{P,Se}$ = 386 Hz), 408.4 (d, $J_{P,Se}$ = 386 Hz), –99.1 (d, $J_{P,Se}$ = 789 Hz), –99.3 (d, $J_{P,Se}$ = 789 Hz) ppm. MS (CI$^+$): *m*/*z* = 831 [M + H]$^+$. HRMS (C|I$^+$): calcd for C$_{32}$H$_{39}$N$_2$P$_2$Se$_4$ [M + H] 830.9257; found 830.9254.

1,3-Phenylenebis(methylene) Bis(*N*-*tert*-butyl-*P*-phenylphosphonamidodiselenoate) (3k): Yield 0.460 g (59%); pale-yellow paste. Three diastereoisomers were found in multinuclear NMR spectra in ca. 1:2:2 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1602 (m), 1483 (m), 1435 (s), 1364 (s), 1217 (s), 1209 (s), 1094 (s), 993 (s), 840 (m), 794 (m), 745 (m), 691 (s), 529 (vs), 429 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.09–8.00 (m, 3×4 H, Ar-H), 7.51–7.44 (m, 3×6 H, Ar-H), 7.23–7.07 (m, 3×4 H, Ar-H), 4.26–4.09 (m, 3×4 H, SeCH$_2$), 2.78 (br., 3×2 H, NH), 1.30–1.21 (m, 3×18 H, CH$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 140.0, 139.7, 139.2, 139.0, 138.2, 137.9, 132.7, 132.2, 131.8, 131.1, 130.9, 130.5, 130.4, 130.3, 130.1, 129.9, 129.1, 128.9, 128.7, 128.5, 128.3, 128.2, 128.1, 127.9, 127.7, 56.0, 55.9, 31.4, 31.3, 27.8 ppm. ^{31}P NMR (CD$_2$Cl$_2$): δ = 46.1 (s, $J_{P,Se}$ = 374 Hz, $J_{P,Se}$ = 794 Hz), 45.9 (s, $J_{P,Se}$ = 367 Hz, $J_{P,Se}$ = 789 Hz), 45.8 (s, $J_{P,Se}$ = 377 Hz, $J_{P,Se}$ = 789 Hz) ppm. ^{77}Se NMR (CD$_2$Cl$_2$): δ = 450.7 (d, $J_{P,Se}$ = 374 Hz), 447.8 (d, $J_{P,Se}$ = 377 Hz), 447.2 (d, $J_{P,Se}$ = 367 Hz), –49.2 (d, $J_{P,Se}$ = 789 Hz), –49.8 (d, $J_{P,Se}$ = 789 Hz), –50.4 (d, $J_{P,Se}$ = 794 Hz) ppm. MS (CI$^+$): *m*/*z* = 783 [M + H]$^+$. HRMS (C|I$^+$): calcd for C$_{28}$H$_{39}$N$_2$P$_2$Se$_4$ [M + H] 782.9257; found 782.9250.

1,2-Phenylenebis(methylene) Bis(*N*-*tert*-butyl-*P*-phenylphosphonamidodiselenoate) (3l): Yield 0.396 g (51%); greenish yellow solid. A pair of diastereoisomers was found in multinuclear NMR spectra in ca. 1:1 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1434 (s), 1363 (s), 1217 (s), 1194 (s), 1093 (s), 990 (s), 838 (m), 746 (m), 725 (m), 688 (s), 529 (vs), 485 (m), 432 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.10–8.01 (m, 2×4 H, Ar-H), 7.49–7.44 (m, 2×6 H, Ar-H), 7.36–7.31 (m, 2×2 H, Ar-H), 7.16–7.08 (m, 2×2 H, Ar-H), 4.41–4.19 (m, 2×4 H, SeCH$_2$), 2.83 (br., 2×2 H, NH), 1.28 (s, 18 H, CH$_3$), 1.26 (s, 18 H, CH$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 138.4 (d, $J_{P,C}$ = 109 Hz), 137.3 (d, $J_{P,C}$ = 108 Hz), 133.3 (d, $J_{P,C}$ = 3.1 Hz), 131.8 (d, $J_{P,C}$ = 3.1 Hz), 131.2, 131.0, 130.8, 130.4, 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 56.0, 55.9, 34.5, 31.4, 31.3 ppm. ^{31}P NMR (CD$_2$Cl$_2$): δ = 46.0 (s, $J_{P,Se}$ = 376 Hz, $J_{P,Se}$ = 789 Hz), 45.9 (s, $J_{P,Se}$ = 378 Hz, $J_{P,Se}$ = 786 Hz) ppm. ^{77}Se NMR (CD$_2$Cl$_2$): δ = 438.8 (d, $J_{P,Se}$ = 378 Hz), 438.1 (d, $J_{P,Se}$ = 376 Hz), –50.3 (d, $J_{P,Se}$ = 789 Hz), –50.4 (d, $J_{P,Se}$ = 789 Hz) ppm. MS (CI$^+$): *m*/*z* = 783 [M + H]$^+$. HRMS (C|I$^+$): calcd for C$_{28}$H$_{39}$N$_2$P$_2$Se$_4$ [M + H] 782.9257; found 782.9238.

1,2-Phenylenebis(methylene) Bis(*N*-*sec*-butyl-*P*-phenylphosphonamidodiselenoate) (3m): Yield 0.420 g (54%); yellow paste. Four diastereoisomers were found in multinuclear NMR spectra in ca. 1.0:1.0:1.2:1.0 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1453 (m), 1434 (s), 1398 (m), 1131 (m), 1096 (s), 1038 (m), 1007 (m), 949 (m), 852 (m), 744 (s), 688 (s), 534 (vs), 490 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.15–7.90 (m, 4×4 H, Ar-H), 7.56–7.30 (m, 4×6 H, Ar-H), 7.27–7.05 (m, 4×4 H, Ar-H), 4.23–4.05 (m, 4×4 H, SeCH$_2$), 3.95–3.86 (m, 4×2 H, CH), 2.69–2.66 (m, 4×2 H, NH), 1.62–1.28 (m, 4×4 H, CH$_2$), 1.15–1.09 (m, 4×6 H, CH$_3$), 0.85–0.83 (m, 4×6 H, CH$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 137.6, 137.2, 136.5, 135.9, 133.3, 132.0, 131.7, 131.1, 130.9, 130.5, 128.6, 128.4, 127.8, 127.7, 51.3, 51.2, 33.9, 32.4, 31.5, 30.2, 22.0, 10.2 ppm. ^{31}P NMR (CD$_2$Cl$_2$): δ = 55.2 (s, $J_{P,Se}$ = 384 Hz, $J_{P,Se}$ = 789 Hz), 55.1 (s, $J_{P,Se}$ = 384 Hz, $J_{P,Se}$ = 789 Hz), 54.8 (s, $J_{P,Se}$ = 384 Hz, $J_{P,Se}$ = 789 Hz), 54.7 (s, $J_{P,Se}$ = 387 Hz, $J_{P,Se}$ = 789 Hz) ppm. ^{77}Se NMR (CD$_2$Cl$_2$): δ = 395.9 (d, $J_{P,Se}$ = 384 Hz), 395.2 (d, $J_{P,Se}$ = 384 Hz), 394.8 (d, $J_{P,Se}$ = 384 Hz), 391.4 (d, $J_{P,Se}$ = 387 Hz), –99.0 (d, $J_{P,Se}$ = 789 Hz), –99.5 (d, $J_{P,Se}$ = 789 Hz), –101.1 (d, $J_{P,Se}$ = 789 Hz), –101.4 (d, $J_{P,Se}$ = 789 Hz) ppm. MS (CI$^+$): *m*/*z* = 783 [M + H]$^+$. HRMS (C|I$^+$): calcd for C$_{28}$H$_{39}$N$_2$P$_2$Se$_4$ [M + H] 782.9257; found 782.9249.

1,3-Phenylenebis(methylene) Bis(*N*-*sec*-butyl-*P*-phenylphosphonamidodiselenoate) (3n): Yield 0.470 g (60%); yellow paste. Four diastereoisomers were found in multinuclear NMR spectra in ca. 1.1:1.0:1.0:1.2 intensity ratio. IR (KBr): $\tilde{\nu}$ = 1602 (m), 1485 (m), 1435 (s), 1396 (m), 1184 (m), 1133 (m), 1097 (s), 1038 (m), 1008 (m), 951 (m), 744 (s), 692 (vs), 535 (vs), 487 (m) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 8.15–7.96 (m, 4×4 H, Ar-H), 7.51–7.46 (m, 4×6 H, Ar-H), 7.14–6.90 (m, 4×4 H, Ar-H), 4.10–4.04 (m, 4×4 H, SeCH$_2$), 3.82–3.61 (m, 4×2 H, CH), 2.69–2.64 (m, 4×2 H, NH), 1.45–1.38 (m, 4×4 H, CH$_2$), 1.19–1.10 (m, 4×6 H, CH$_3$), 0.98–0.83 (m, 4×6 H, CH$_3$) ppm. ^{13}C NMR (CD$_2$Cl$_2$): δ = 139.7, 138.7, 137.1, 135.9, 132.1, 131.1, 130.9, 130.2, 130.0, 129.8, 128.9, 128.6, 128.4, 128.0, 127.9, 127.6, 51.3, 51.1, 50.1, 36.1, 35.9, 32.4, 31.5, 28.0, 27.4, 22.0, 18.2, 10.2 ppm. ^{31}P NMR (CD$_2$Cl$_2$): δ = 55.0 (s, $J_{P,Se}$ = 390 Hz, $J_{P,Se}$ = 789 Hz), 54.9 (s, $J_{P,Se}$ = 390 Hz, $J_{P,Se}$ = 789 Hz), 54.6 (s, $J_{P,Se}$ = 390 Hz, $J_{P,Se}$ = 789 Hz), 54.5 (s, $J_{P,Se}$ = 390 Hz, $J_{P,Se}$ = 789 Hz) ppm. ^{77}Se NMR (CD$_2$Cl$_2$): δ = 406.4 (d, $J_{P,Se}$ = 390 Hz), 406.2 (d, $J_{P,Se}$ = 390 Hz), 406.1 (d, $J_{P,Se}$ = 390 Hz), 405.7 (d, $J_{P,Se}$ = 390 Hz), –97.1 (d, $J_{P,Se}$ = 789 Hz), –97.5 (d, $J_{P,Se}$ = 789 Hz), –99.1 (d, $J_{P,Se}$ = 789 Hz), –99.5 (d, $J_{P,Se}$ = 789 Hz) ppm. MS (CI$^+$): *m*/*z* = 783 [M + H]$^+$. HRMS (C|I$^+$): calcd for C$_{28}$H$_{39}$N$_2$P$_2$Se$_4$ [M + H] 782.9257; found 782.9246.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra of the new compounds.

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[28] Crystallographic data for compound **2e**: $C_{18}H_{20}BrNOPSe_2$; M = 535.16; triclinic; space group $P\bar{1}$; a = 8.176(8) Å, b = 10.242(10) Å, c = 12.652(13) Å, α = 81.19(3)°, β = 79.35(3)°, γ = 75.78(3)°; U = 999.6(17) Å^3; Z = 2; μ = 5.7896 mm^{-1}; 8488 reflections, 3516 unique (R_{int} = 0.0827); R_1 = 0.0522, wR_2 = 0.1329.

[29] Crystallographic data for compound **2i**: $C_{19}H_{20}BrNOPSe_2$; M = 547.17; monoclinic; space group $P2_{1/c}$; a = 6.956(6) Å, b = 17.86(2) Å, c = 32.53(3) Å, β = 92.038(11)°; U = 4040(6) Å^3; Z = 8; μ = 5.7318 mm^{-1}; 33067 reflections, 7116 unique (R_{int} = 0.01636); R_1 = 0.0659, wR_2 = 0.1445.

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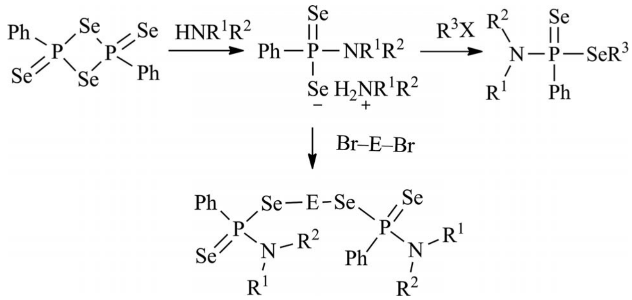

Woollins' reagent has been applied as a highly efficient building block for the synthesis of organo selenium-phosphorus heteroatom compounds.

G. Hua, K. S. A. Arachchige, A. M. Z. Slawin, J. D. Woollins* 1–10

Organophosphorus-Selenium Heteroatom Derivatives from Selenation of Primary/Secondary Amines and Haloalkanes/Dihaloalkanes

Keywords: Woollins' reagent / Selenium / Phosphorus / Amines / Haloalkanes