

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

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Reaction of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [Woollins' reagent, **WR**] with four equivalents of primary/secondary amines led to a series of ammonium phenylphosphonamidodiselenoates or phenylphosphonamidodiselenoic diamides **1a-n**, the latter further reacted *in situ* with either two equivalents of haloalkanes or equimolar amount of dihaloalkanes resulting in the corresponding *Se*-alkylphenyl-

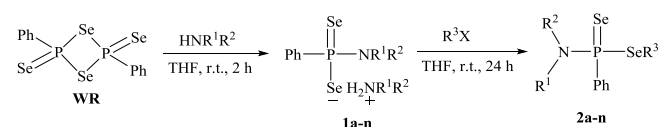
Se-alkylphenyl-phosphonamidodiselenoates **2a-n** and alkane bis(*N*-alkyl-*P*-phenylphosphonamidodiselenoate)s **3a-n** in good to excellent yields. All new compounds have been characterized spectroscopically including multi-NMR (¹H, ¹³C, ³¹P and ⁷⁷Se), IR and mass spectroscopy. Two representative X-ray structures are also described.

Introduction

Organophosphorus chemistry has been attracted huge attention in both academic and industrial research for several decades.¹⁻³ A wide range of applications have been documented in different fields such as coordination chemistry, material science, homogeneous catalysis, development of biologically active compounds or pesticides, and additives for polymers such as lubricants and antioxidants.⁴⁻¹⁰ 2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [$\{\text{PhP}(\text{Se})(\mu\text{-Se})\}_2$] (Woollins' reagent, **WR**), a selenium counterpart of the well-known Lawesson's reagent (**LR**), has been well developed as an efficient phosphorus-selenium containing building block or selenation reagent in organic synthetic chemistry in recent years.¹¹ The reactions of **WR** with various organic substrates exhibit a diverse spectrum ranging 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 recently have reported the synthesis of a series of ammonium phenylphosphonamidodiselenoates and phenylphosphonamidodiselenoic diamides from the reaction of **WR** with primary or secondary amines,²⁶ and the formation of a series of organo phosphorus-selenium heteroatom derivatives from the selenation of alkenyl or arynyl-diamines.²⁷ As a part of our continuous exploration into the reactivity of **WR** towards different organic nucleophiles, herein, we report the synthesis of a series of novel *Se*-alkylphenylphosphonamidodiselenoates and alkane bis(*N*-alkyl-*P*-phenylphosphonamidodiselenoate)s *via* the reaction of **WR** with primary/secondary amines, followed by the *in situ* treatment with haloalkanes or dihaloalkanes. We also report two representative X-ray structures.

Results and Discussion

Treatment of **WR** with four molar equivalents of primary or secondary amine in dry THF at ambient temperature for 2 h proceeded with the cleavage of the four-membered ring in **WR** leading to the corresponding ammonium salts of phenylphosphonamidodiselenoates and phenylphosphonamidodiselenoic 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*-alkylphenylphosphonamidodiselenoates **2a-n** as depicted in Scheme 1. These new heteroatom compounds were isolated in good to excellent yields (41% - 93%) (Table 1) as sticky oils or pastes which are soluble in both chlorinated solvents and tetrahydrofuran. It should be noted that products **2e-l** bearing the strong electron-withdrawing group R³ (R³ = *p*-BrC₆H₄COCH₂) were obtained in rather high yields (55% - 93%), meanwhile, products **2b** and **2c** bearing less electron-withdrawing group R³ (R³ = CH₃(CH₂)₁₀ or CH₃(CH₂)₆) were isolated in the lowest yields (41% and 42%). Thus, it appears that a strong electron-withdrawing group R³ is hugely beneficial for the formation of the reaction products. Compounds **2a-n** are stable to air or moisture for months without any obvious signals of degradation.



Scheme 1 Synthesis of *Se*-alkylphenylphosphonamidodiselenoates **2a-n** (the R groups are defined in Table 1 below)

2a-n were characterised by ¹H, ¹³C, ³¹P and ⁷⁷Se 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. Two isomers were found in the NMR spectra of **2f**. The ³¹P 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 ³¹P-⁷⁷Se coupling constants in the range

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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 $\delta = 299.8 - 384.0$ ppm and from the P=Se selenium in the range of $\delta = -104.8 - -26.1$ ppm, respectively with matching ^{31}P - ^{77}Se coupling constants as shown in Table 1.

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 [($J_{\text{P,Se}}$), Hz]	δ_{Se} , ppm [($J_{\text{P,Se}}$), Hz]
Cl	c- Hexyl	H	C ₆ H ₅ COCH 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 ₆ H ₄ COCH ₂	2e	82	46.9 [355/794]	384.0 [355] -53.0 [792]
Br	^t Bu	H	1,4- BrC ₆ H ₄ COCH ₂	2f*	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 ₆ H ₄ COCH ₂	2g	81	58.0 [370/794]	321.2 [370] -100.4 [794]
Br	c- Hexyl	H	1,4- BrC ₆ H ₄ COCH ₂	2h	56	54.5 [369/794]	347.7 [369] -100.7 [794]
Br	c- Pentyl	H	1,4- BrC ₆ H ₄ COCH ₂	2i	81	55.8 [369/791]	338.8 [369] -95.3 [791]
Br	ⁱ Pr	H	1,4- BrC ₆ H ₄ COCH ₂	2j	88	54.6 [369/794]	345.3 [370] -102.4 [794]
Br	ⁱ Pr	ⁱ Pr	1,4- BrC ₆ H ₄ COCH ₂	2k	55	62.5 [366/789]	311.7 [367] -26.1 [789]
Br	^t Bu	^t Bu	1,4- BrC ₆ H ₄ COCH ₂	2l	67	78.4 [362/798]	299.8 [362] -93.5 [799]
Br	ⁱ Pr	ⁱ Pr	1,2- (HOCH ₂) ₂ C ₆ H ₄ CH ₂	2m	44	59.9 [387/777]	361.4 [388] -26.4 [777]
Br	B _n	H	1,4- BrC ₆ H ₄ COCH ₂	2n	47	58.3 [376/798]	324.8 [376] -103.4 [798]

* Two diastereomers were found in compound **2f**.

The molecular structures of **2e** and **2i** were confirmed by single-crystal X-ray diffraction studies as shown in Figures 1²⁸ and 2.²⁹ The transparent, and colourless cubic crystals of **2e** and **2i** were grown from dichloromethane solution with slow diffusion of hexane. Compound **2e** crystallizes in the triclinic space group *P*-*I*, meanwhile, compound **2i** in the monoclinic space group *P*2₁/*c* with two independent molecules per unit cell. In compound **2e** the two phenyl rings are inclined 56.85° to one another. The P(1)-Se(1) of 2.103(3) Å and P(1)-Se(2) bondlengths of 2.0954(13) Å in **2e** and P(1)-Se(1) of 2.097(4) [2.103(4)] and P(1)-Se(2) of 2.281(4) [2.208(4)] Å 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 other similar compounds.^{25,30,31}

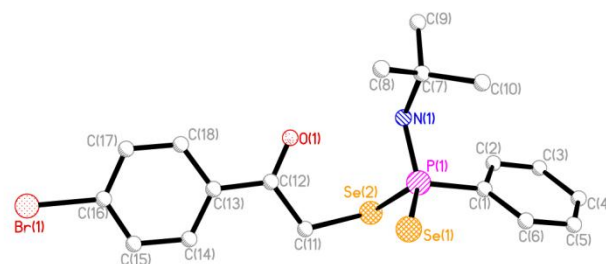


Figure 1. X-ray structure of compound **2e** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses): Se(1)-P(1) 2.103(3), Se(2)-P(1) 2.257(3), Se(2)-C(11) 1.948(9), P(1)-C(1) 1.807(8), P(1)-N(1) 1.666(6), N(1)-C(7) 1.488(9); P(1)-Se(2)-C(11) 99.3(3), Se(1)-P(1)-Se(2) 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).

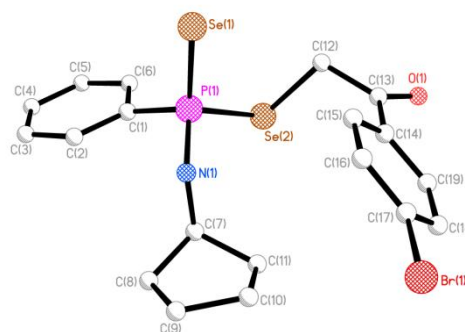
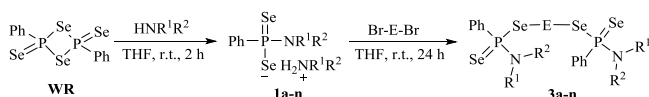


Figure 2. X-ray structure of compound **2i** (Hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°) (esds in parentheses) (Dimensions for second independent molecule in square parentheses): Se(1)-P(1) 2.097(4) [2.103(4)], Se(2)-P(1) 2.281(4) [2.208(4)], Se(2)-C(12) 1.950(11) [1.972(10)], 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)].

We also carried out the analogous reactions by using dihaloalkanes instead of mono-haloalkanes. 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-alkylphenylphosphonamidodiselenoates **3a-n**, as shown in Scheme 2. These new compounds were isolated in moderate to good yields (51 to 80%) as listed in Table 2 as sticky oils or pastes or solids soluble in chloroform, dichloromethane and tetrahydrofuran, and insoluble in diethyl ether and hexane.

The characterisation of **3a-n** was performed by ^1H , ^{13}C , ^{31}P and ^{77}Se NMR, IR spectroscopy and mass spectrometry. All new compounds showed the anticipated $[\text{M}+\text{H}]^+$ or $[\text{M}+\text{Na}]^+$ 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 inasmuch, meanwhile, interestingly, the ^{31}P NMR spectra of **3i**, **3m** and **3n** display four sets of double resonances and three sets of double resonances was found in **3k**, as a consequence of the stereoisomers present (Table 2). Normally, two phosphorus atoms are potentially stereogenic centres in compounds **3a-n**, thus, being stereotopic with (*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 of $\delta(\text{p}) = 52.4 - 54.9$ ppm, flanked by two sets of satellites for the endocyclic and exocyclic selenium atoms [$J(\text{P}, \text{Se}_{\text{endo}})$ coupling constants being in the range of 371 – 387 Hz and $J(\text{P}, \text{Se}_{\text{exo}})$ coupling constants in the range of 784 – 794 Hz] though we are not able to assign them specifically to (*R, R*), (*S, S*), (*S, R*) and (*R, S*) stereoisomers. However, four phosphorus signals with very similar chemical shifts and different intensity ratio (*see experimental section*) were found in the ^{31}P NMR spectra of compound **3i**, **3m** and **3n**, meanwhile, three similar phosphorus signals with different intensity ratio (*see experimental section*) were also observed in the ^{31}P NMR spectrum of compound **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 big $\text{Ph}(\text{NR}^1\text{R}^2)\text{P}(\text{Se})\text{CH}_2$ groups from *ortho* or *meta* position in the bridged linkage benzene backbone in compounds of **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 centers exist. Detailed ^{31}P and ^{77}Se NMR spectroscopic analyses reveal the relatively small coupling constant $^3J(\text{P}, \text{Se}) = 17.0$ Hz and $^4J(\text{P}, \text{P}) = 4.2$ Hz in **3a**, $^4J(\text{P}, \text{Se}) = 12.3$ Hz in **3b** and **3f**, supporting the presence of the $\text{P}(\text{Se})\text{SeCH}_2\text{SeP}(\text{Se})$ or $\text{P}(\text{Se})\text{SeCH}_2\text{CH}_2\text{SeP}(\text{Se})$ linkage in compounds **3a**, **3b** and **3f**. The ^{31}P and ^{77}Se chemical shifts and coupling constants are comparable to phosphorus-selenium compounds in the literature.³²⁻³⁵



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

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 [(<i>J</i> _{Se}), Hz]	δ_{ss} , ppm [(<i>J</i> _{Se}), Hz]
3a	<i>c</i> -Hexyl	H	CH ₃	79	54.9 [374/791] 54.8 [371/791]	398.6 [371], -91.9 [791] 395.5 [374], -92.7 [791]
3b	<i>c</i> -Hexyl	H	CH ₂ CH ₃	80	52.5 [384/789] 52.4 [386/786]	378.5 [384], -90.1 [784] 375.6 [386], -94.7 [786]
3c	<i>c</i> -Hexyl	H	CH ₂ CH ₂ CH ₃	70	53.7 [384/789] 53.6 [386/786]	325.1 [384], -102.8 [789] 324.8 [386], -103.5 [786]
3d	<i>c</i> -Hexyl	H	CH ₂ CH ₂ CH ₂ CH ₃ H ₂	78	53.5 [384/789] 53.4 [386/786]	326.7 [386], -105.0 [789] 326.3 [388], -105.2 [786]
3e	<i>c</i> -Hexyl	H	1,2- CH ₂ C ₆ H ₄ CH ₂	77	53.9 [386/789] 53.8 [386/789]	395.9 [386], -96.7 [789] 395.1 [386], -96.8 [789]
3f	^{<i>t</i>} Pr	H	CH ₂ CH ₃	65	53.0 [383/786] 52.7 [385/784]	514.7 [385], -248.5 [784] 514.5 [383], -248.7 [786]
3g	^{<i>t</i>} Pr	H	CH ₂ CH ₂ CH ₃	55	53.9 [385/789] 53.8 [385/789]	323.4 [385], -164.2 [789] 323.0 [385], -173.8 [789]
3h	^{<i>t</i>} Pr	H	1,2- CH ₂ C ₆ H ₄ CH ₂	56	54.2 [385/786] 54.1 [385/786]	392.7 [385], -99.5 [786] 392.1 [385], -99.7 [786]
3i	^{<i>t</i>} Bu	^{<i>t</i>} Bu	1,2- CH ₂ C ₆ H ₄ CH 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>t</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	^{<i>t</i>} Bu	H	1,3- CH ₂ C ₆ H ₄ CH 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	^{<i>t</i>} Bu	H	1,2- CH ₂ C ₆ H ₄ CH ₂	51	46.0 [376/789] 45.9 [378/786]	438.8 [378], -50.3 [789] 438.1 [385], -50.4 [789]
3m	^{<i>t</i>} Bu	H	1,2- CH ₂ C ₆ H ₄ CH 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	^{<i>t</i>} Bu	H	1,3-	60	55.0 [390/789]	406.4 [390], -97.1 [789]

		CH ₂ C ₆ H ₄ CH ₂		54.9 [390/789] 54.6 [390/789] 54.5 [390/789]	406.2 [390], -97.5 [789] 406.1 [390], -99.1 [789] 405.7 [390], -99.5 [789]
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Conclusions

In conclusion, an efficient route has been developed to prepare a series of new *Se*-alkylphenylphosphonamidodiselenoates and alkane bis(*N*-alkyl-*P*-phenylphosphonamidodiselenoate)s in moderate to good yields from the reaction of ammonium phenylphosphonamidodiselenoates or phenylphosphonamidodiselenoic diamides, which were derived from **WR** with primary/secondary amines, with either two molar equivalents of haloalkanes or one molar equivalent of dibromoalkanes. All new compounds were fully elucidated by means of IR, mass spectroscopy and multinuclear NMR in conjunction with single crystal X-ray crystallography of two structures.

Experimental Section

Unless otherwise stated, all reactions were carried out under an oxygen free nitrogen atmosphere using pre-dried 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 - $\{^1\text{H}\}$ (109 MHz) and ^{77}Se - $\{^1\text{H}\}$ (51.4 MHz) referenced to external Me_2Se NMR spectra were recorded at 25 °C (unless stated otherwise) on a JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000-250 cm^{-1} on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Microanalysis was performed by the University of St-Andrews microanalysis service. 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** was collected using a Rigaku SCXMini Mercury CCD system. Intensity data were collected 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 semi-empirical 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. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk. CCDC **2e** 944056; **2i** 944057.

General procedure for synthesis of compounds 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 haloalkanes (2.0 mmol) was added and the mixture was allowed to stir 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 using dichloromethane/hexane (1:1) as eluent to give the compounds **2a-n**.

***N*-Cyclohexyl *Se*-(2-oxo-2-phenylethyl) phenylphosphonamidodiselenoate (**2a**):** 0.519 g as a yellow oil in 54% yield. Selected IR (KBr, cm^{-1}): 1670(vs), 1596(m), 1579(m), 1448(s), 1274(vs), 1180(m), 1005(m), 798(m), 748(m), 709(s), 688(s), 605(m). ^1H NMR (CD_2Cl_2 , δ): 8.06-7.91 (m, 4H, Ar-H), 7.61-7.41 (m, 6H, Ar-H), 4.75 (d, 2H, SeCH_2), 4.37-4.12 (m, 1H, cyclohexyl-H), 3.32-3.20 (m, 1H, NH), 1.96-0.85 (m, 10H,

cyclohexyl-H) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 194.9 (C=O), 136.1 (d, $J(\text{P,C}) = 91.3$ Hz), 134.0, 133.1, 132.2 (d, $J(\text{P,C}) = 3.1$ Hz), 130.9 (d, $J(\text{P,C}) = 12.5$ Hz), 128.8, 128.7, 128.5 (d, $J(\text{P,C}) = 13.5$ Hz), 53.0, 37.5, 35.4 (d, $J(\text{P,C}) = 19.7$ Hz), 35.3 (d, $J(\text{P,C}) = 18.7$ Hz), 25.1 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 53.7 (s, $J(\text{P,Se}) = 371$ Hz, $J(\text{P,Se}) = 792$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 345.4 (d, $J(\text{P,Se}) = 371$ Hz), -102.0 (d, $J(\text{P,Se}) = 792$ Hz) ppm. Mass spectrum [CI^+ , m/z]: 486 [$\text{M}+\text{H}^+$]. Accurate mass measurement (CI^+): 485.9994, calculate mass for $\text{C}_{20}\text{H}_{24}\text{NOPSe}_2\text{H} [\text{M}+\text{H}]^+$: 486.0002.

***N*-Cyclohexyl *Se*-undecyl phenylphosphonamidodiselenoate (2b):** 0.433 g as a pale yellow oil in 42% yield. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.05-7.97 (m, 2H, Ar-H), 7.49-7.45 (m, 3H, Ar-H), 3.40 (dt, $J(\text{H,H}) = 7.4$ Hz, 1H, cyclohexyl-H), 3.22-3.12 (m, 2H, cyclohexyl-H), 2.92-2.84 (m, $J(\text{P,H}) = 13.2$ Hz, $J(\text{H,H}) = 7.4$ Hz, 2H, SeCH_2), 2.71 (t, $J(\text{H,H}) = 7.4$ Hz, 2H, CH_2), 1.96 (d, $J(\text{H,H}) = 9.4$ Hz, 1H, NH), 1.71-1.19 (m, 24H, cyclohexyl-H + CH_2), 0.87 (t, $J(\text{H,H}) = 6.6$ Hz, 3H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 137.3 (d, $J(\text{P,C}) = 87.2$ Hz), 131.9 (d, $J(\text{P,C}) = 3.1$ Hz), 130.8 (d, $J(\text{P,C}) = 12.5$ Hz), 128.4 (d, $J(\text{P,C}) = 13.5$ Hz), 52.8, 35.7 (d, $J(\text{P,C}) = 5.2$ Hz), 35.6 (d, $J(\text{P,C}) = 5.2$ Hz), 32.9, 32.0, 30.5 (d, $J(\text{P,C}) = 3.1$ 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, $J(\text{P,Se}) = 391$ Hz, $J(\text{P,Se}) = 786$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 323.6 (d, $J(\text{P,Se}) = 391$ Hz), -104.5 (d, $J(\text{P,Se}) = 786$ Hz) ppm. Mass spectrum [CI^+ , m/z]: 522 [$\text{M}+\text{H}^+$]. Accurate mass measurement (CI^+): 522.1299, calculate mass for $\text{C}_{23}\text{H}_{40}\text{NPS}_2\text{H} [\text{M}+\text{H}]^+$: 522.1303.

***N*-Cyclohexyl *Se*-nonyl phenylphosphonamidodiselenoate (2c):** 0.405 g as a colourless oil in 41% yield. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.05-7.97 (m, 2H, Ar-H), 7.49-7.45 (m, 3H, Ar-H), 3.40 (dt, $J(\text{H,H}) = 7.4$ Hz, 1H, cyclohexyl-H), 3.22-3.12 (m, 2H, cyclohexyl-H), 2.92-2.84 (m, $J(\text{P,H}) = 13.2$ Hz, $J(\text{H,H}) = 7.4$ Hz, 2H, SeCH_2), 2.72 (t, $J(\text{H,H}) = 7.4$ Hz, 2H, CH_2), 1.96 (d, $J(\text{H,H}) = 9.4$ Hz, 1H, NH), 1.71-1.18 (m, 20H, cyclohexyl-H + CH_2), 0.87 (t, $J(\text{H,H}) = 6.6$ Hz, 3H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 137.3 (d, $J(\text{P,C}) = 86.2$ Hz), 131.8 (d, $J(\text{P,C}) = 3.1$ Hz), 130.8 (d, $J(\text{P,C}) = 12.5$ Hz), 128.3 (d, $J(\text{P,C}) = 13.5$ Hz), 52.8, 35.6 (d, $J(\text{P,C}) = 5.2$ Hz), 35.5 (d, $J(\text{P,C}) = 5.2$ Hz), 32.9, 31.9, 30.5 (d, $J(\text{P,C}) = 3.1$ 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, $J(\text{P,Se}) = 390$ Hz, $J(\text{P,Se}) = 786$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 323.6 (d, $J(\text{P,Se}) = 390$ Hz), -104.6 (d, $J(\text{P,Se}) = 786$ Hz) ppm. Mass spectrum [CI^+ , m/z]: 494 [$\text{M}+\text{H}^+$]. Accurate mass measurement (CI^+): 494.0892, calculate mass for $\text{C}_{21}\text{H}_{36}\text{NPS}_2\text{H} [\text{M}+\text{H}]^+$: 494.0990.

***N*-Cyclohexyl *Se*-heptyl phenylphosphonamidodiselenoate (2d):** 0.272 g as a colourless oil in 59% yield. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.06-7.97 (m, 2H, Ar-H), 7.50-7.45 (m, 3H, Ar-H), 3.17-3.12 (m, 1H, cyclohexyl-H), 2.89 (dt, $J(\text{P,H}) = 13.2$ Hz, $J(\text{H,H}) = 7.4$ Hz, 2H, SeCH_2), 2.72 (t, $J(\text{H,H}) = 7.4$ Hz, 2H, CH_2), 1.96 (d, $J(\text{H,H}) = 9.4$ Hz, 1H, NH), 1.69-1.09 (m, 18H, cyclohexyl-H + CH_2), 0.86 (t, $J(\text{H,H}) = 6.6$ Hz, 3H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 137.2 (d, $J(\text{P,C}) = 87.2$ Hz), 131.9 (d, $J(\text{P,C}) = 3.1$ Hz), 130.8 (d, $J(\text{P,C}) = 12.5$ Hz), 128.4 (d, $J(\text{P,C}) = 13.5$ Hz), 52.9, 35.7 (d, $J(\text{P,C}) = 5.2$ Hz), 35.6 (d, $J(\text{P,C}) = 5.2$ Hz), 32.9, 31.7, 30.5 (d, $J(\text{P,C}) = 3.1$ Hz), 29.9, 28.8, 25.3, 22.7, 13.9 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 53.2 (s, $J(\text{P,Se}) = 390$ Hz, $J(\text{P,Se}) = 786$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 323.6 (d, $J(\text{P,Se}) = 391$ Hz), -104.4 (d, $J(\text{P,Se}) = 786$ Hz) ppm. Mass spectrum [ES^+ , m/z]: 488 [$\text{M}+\text{Na}^+$]. Accurate mass measurement (ES^+): 488.0500, calculate mass for $\text{C}_{19}\text{H}_{32}\text{NNaPS}_2 [\text{M}+\text{Na}]^+$: 488.0500.

***N*-tert-Butyl *Se*-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphinodiselenoate (2e):** 0.440 g as a pale yellow paste in 82% yield. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.12-8.04 (m, 2H, Ar-H), 7.84 (d, $J(\text{H,H}) = 8.8$ Hz, 2H, Ar-H), 7.60 (d, $J(\text{H,H}) = 8.8$ Hz, 2H, Ar-H), 7.51-7.43 (m, 3H, Ar-H), 4.37 (d, $J(\text{P,H}) = 13.2$ Hz, 2H, SeCH_2), 2.54 (d, $J(\text{H,H}) = 9.5$ Hz, 1H, NH), 1.30 (s, 9H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 194.3 (C=O), 137.7 (d, $J(\text{P,C}) = 91.3$ 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, $J(\text{P,Se}) = 355$ Hz, $J(\text{P,Se}) = 794$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 384.0 (d, $J(\text{P,Se}) = 355$ Hz), -53.0 (d, $J(\text{P,Se}) = 792$ Hz) ppm. Mass spectrum [ES^+ , m/z]: 560 [$\text{M}+\text{Na}^+$]. Accurate mass measurement (ES^+): 559.8767, calculate mass for $\text{C}_{18}\text{H}_{21}\text{BrNONaPS}_2 [\text{M}+\text{Na}]^+$: 559.8772.

***N*-sec-Butyl *Se*-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2f):** 0.500 g as a reddish yellow sticky oil in 93% yield. Two stereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.04-7.94 (m, 2x2H, Ar-H), 7.81-7.75 (m, 2x2H, Ar-H), 7.61-7.54 (m, 2x2H, Ar-H), 7.49-7.45 (m, 3H, Ar-H), 4.27-3.91 (m, 2x1H, CH), 3.51-3.05 (m, 2x2H, SeCH_2), 2.54 (d, $J(\text{H,H}) = 9.5$ Hz, 2x1H, NH), 1.59-1.41 (m, 2x2H, CH_2), 1.13 (dd, $J(\text{H,H}) = 6.6$ Hz, $J(\text{P,H}) = 3.3$ Hz, 3H, CH_3), 1.12 (dd, $J(\text{H,H}) = 6.6$ Hz, $J(\text{P,H}) = 3.3$ Hz, 3H, CH_3), 0.88 (t, $J(\text{H,H}) = 7.4$ Hz, 3H, CH_3), 0.85 (t, $J(\text{H,H}) = 7.4$ Hz, 3H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 194.4 (C=O), 136.3 (d, $J(\text{P,C}) = 89.4$ Hz), 136.2 (d, $J(\text{P,C}) = 90.6$ Hz), 134.6, 134.5, 132.6 (d, $J(\text{P,C}) = 3.1$ Hz), 132.5 (d, $J(\text{P,C}) = 3.1$ 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, $J(\text{P,C}) = 18.9$ Hz), 51.4 (d, $J(\text{P,C}) = 18.7$ Hz), 38.1, 37.5, 31.8 (d, $J(\text{P,C}) = 23.6$ Hz), 31.7 (d, $J(\text{P,C}) = 22.1$ Hz), 22.2 (d, $J(\text{P,C}) = 21.4$ Hz), 22.1 (d, $J(\text{P,C}) = 20.5$ Hz), 10.5, 10.4 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 56.0 (s, $J(\text{P,Se}) = 366$ Hz, $J(\text{P,Se}) = 796$ Hz), 54.8 (s, $J(\text{P,Se}) = 373$ Hz, $J(\text{P,Se}) = 782$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 348.5 (d, $J(\text{P,Se}) = 374$ Hz), 346.1 (d, $J(\text{P,Se}) = 367$ Hz), -101.9 (d, $J(\text{P,Se}) = 794$ Hz), -104.8 (d, $J(\text{P,Se}) = 784$ Hz) ppm. Mass spectrum [ES^+ , m/z]: 560 [$\text{M}+\text{Na}^+$]. Accurate mass measurement (ES^+): 559.8762, calculate mass for $\text{C}_{18}\text{H}_{21}\text{BrNONaPS}_2 [\text{M}+\text{Na}]^+$: 559.8772.

***N*-Butyl *Se*-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2g):** 0.434 g as a yellow sticky oil in 81% yield. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.00-7.92 (m, 2H, Ar-H), 7.81 (d, $J(\text{H,H}) = 6.9$ Hz, 2H, Ar-H), 7.61 (d, $J(\text{H,H}) = 6.9$ Hz, 2H, Ar-H), 7.50-7.47 (m, 3H, Ar-H), 4.31-4.15 (m, 2H, NHCH_2), 3.18 (ws, 1H, NH), 2.91 (d, 2H, SeCH_2), 1.62-1.28 (m, 4H, cyclohexyl-H), 0.87 (t, $J(\text{H,H}) = 7.4$ Hz, 3H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 194.4 (C=O), 135.4 (d, $J(\text{P,C}) = 89.9$ Hz), 134.5, 132.8 (d, $J(\text{P,C}) = 3.1$ Hz), 132.4, 131.1 (d, $J(\text{P,C}) = 12.5$ Hz), 130.7, 129.1 (d, $J(\text{P,C}) = 13.5$ Hz), 43.5 (d, $J(\text{P,C}) = 3.7$ Hz), 37.2, 33.3 (d, $J(\text{P,C}) = 9.5$ Hz), 20.4, 13.9 ppm. ^{31}P NMR (CD_2Cl_2 , δ), 58.0 (s, $J(\text{P,Se}) = 370$ Hz, $J(\text{P,Se}) = 794$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 321.2 (d, $J(\text{P,Se}) = 370$ Hz), -100.4 (d, $J(\text{P,Se}) = 794$ Hz), ppm. Mass spectrum [ES^+ , m/z]: 560 [$\text{M}+\text{Na}^+$]. Accurate mass measurement (ES^+): 559.8771, calculate mass for $\text{C}_{18}\text{H}_{21}\text{NONaBrPS}_2 [\text{M}+\text{Na}]^+$: 559.8772.

***N*-Cyclohexyl *Se*-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2h):** 0.630 g as a brown paste in 56% yield. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.02-7.97 (m, 2H, Ar-H), 7.80-7.78 (m, 2H, Ar-H), 7.62-7.58 (m, 2H, Ar-H), 7.50-7.43 (m, 3H, Ar-H), 4.30-4.14 (m, 1H, cyclohexyl-H), 3.23 (ws,

1H, NH), 2.59-2.52 (d, 2H, SeCH₂), 2.05-0.86 (m, 10H, cyclohexyl-H) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, δ), 54.5 (s, J(P,Se) = 369 Hz, J(P,Se) = 794 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 347.7 (d, J(P,Se) = 369 Hz), -100.7 (d, J(P,Se) = 794 Hz) ppm. Mass spectrum [CI⁺, m/z]: 564 [M+H]⁺. Accurate mass measurement (CI⁺): 563.9111, calculate mass for C₂₀H₂₃BrNOPSe₂H [M+H]⁺: 563.9109.

N-Cyclopentyl Se-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2i): 0.445 g as a greyish yellow paste in 81% yield. Selected IR (KBr, cm⁻¹): 1658(s), 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). ¹H NMR (CD₂Cl₂, δ), 8.02-7.93 (m, 2H, Ar-H), 7.81 (d, J(H,H) = 6.9 Hz, 2H, Ar-H), 7.58 (d, J(H,H) = 6.9 Hz, 2H, Ar-H), 7.52-7.42 (m, 3H, Ar-H), 4.32-4.12 (m, 1H, cyclopentyl-H), 3.31 (dd, 1H, NH), 2.54 (d, 2H, SeCH₂), 1.94-1.45 (m, 8H, cyclopentyl-H) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, δ), 55.8 (s, J(P,Se) = 369 Hz, J(P,Se) = 791 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 338.8 (d, J(P,Se) = 369 Hz), -95.3 (d, J(P,Se) = 791 Hz) ppm. Mass spectrum [ES⁺, m/z]: 572 [M+Na]⁺. Accurate mass measurement (ES⁺): 571.8766, calculate mass for C₁₉H₂₁NONaBrPSe₂ [M+Na]⁺: 571.8772.

N-Isopropyl Se-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2j): 0.460 g as a light yellow paste in 88% yield. Selected IR (KBr, cm⁻¹): 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). ¹H NMR (CD₂Cl₂, δ), 8.01 (dd, J(P,H) = 14.9 Hz, J(H,H) = 8.0 Hz, 2H, Ar-H), 7.80 (d, J(H,H) = 8.5 Hz, 2H, Ar-H), 7.60 (d, J(H,H) = 8.5 Hz, 2H, Ar-H), 7.52-7.43 (m, 3H, Ar-H), 4.31-4.08 (m, 1H, CH), 3.65-3.52 (m, 2H, SeCH₂), 3.19 (w, 1H, NH), 1.15 (d, J(H,H) = 6.1 Hz, 6H, CH₃) ppm. ¹³C NMR (CD₂Cl₂, 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, CH₃), 24.6 (d, J(P,C) = 5.2 Hz, CH₃) ppm. ³¹P NMR (CD₂Cl₂, δ), 54.6 (s, J(P,Se) = 369 Hz, J(P,Se) = 794 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 345.3 (d, J(P,Se) = 370 Hz), -102.4 (d, J(P,Se) = 794 Hz) ppm. Mass spectrum [CI⁺, m/z]: 524 [M+H]⁺. Accurate mass measurement (CI⁺): 523.8791, calculate mass for C₁₇H₁₉BrNOPSe₂H [M+H]⁺: 523.8789.

N,N-Diisopropyl Se-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2k): 0.310 g as a yellow paste in 55% yield. Selected IR (KBr, cm⁻¹): 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). ¹H NMR (CD₂Cl₂, δ), 7.82-7.80 (m, 2H, Ar-H), 7.78 (d, J(H,H) = 6.9 Hz, 2H, Ar-H), 7.61 (d, J(H,H) = 6.9 Hz, 2H, Ar-H), 7.58-7.54 (m, 3H, Ar-H), 4.39-4.34 (m, 2H, CH), 2.54 (d, 2H, SeCH₂), 1.46 (d, J(H,H) = 6.4 Hz, 12H, CH₃) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, δ), 62.5 (s, J(P,Se) = 366 Hz, J(P,Se) = 789 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 311.7 (d, J(P,Se) = 367 Hz), -26.1 (d, J(P,Se) = 789 Hz) ppm. Mass spectrum [CI⁺, m/z]: 566 [M+H]⁺. Accurate mass measurement (CI⁺): 565.9269, calculate mass for C₂₀H₂₄BrNOPSe₂H [M+H]⁺: 565.9266.

N,N-Diisobutyl Se-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2l): 0.398 g as a reddish yellow sticky oil in 67% yield. Selected IR (KBr, cm⁻¹): 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). ¹H NMR (CD₂Cl₂, δ), 8.02 (dd, J(P,H) = 14.6 Hz, J(H,H) = 6.6 Hz, 2H, Ar-H), 7.81 (d, J(H,H) = 6.9 Hz, 2H, Ar-H), 7.59 (d, J(H,H) = 6.9 Hz, 2H, Ar-H), 7.51-7.42 (m, 3H, Ar-H), 4.27 (d, J(P,H) = 10.8 Hz, 2H, SeCH₂), 2.94-2.81 (m, 4H, NCH₂), 1.89-1.81 (m, 2H, CH), 0.81 (d, J(H,H) = 6.6 Hz, 6H, CH₃), 0.75 (d, J(H,H) = 6.6 Hz, 6H, CH₃) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, δ), 78.4 (s, J(P,Se) = 362 Hz, J(P,Se) = 798 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 299.8 (d, J(P,Se) = 362 Hz), -93.5 (d, J(P,Se) = 799 Hz) ppm. Mass spectrum [ES⁺, m/z]: 616 [M+Na]⁺. Accurate mass measurement (ES⁺): 615.9409, calculate mass for C₂₂H₂₉NONaBrPSe₂ [M+Na]⁺: 615.9398.

N,N-Diisopropyl Se-[2-(hydroxymethyl)benzyl] phenylphosphonamidodiselenoate (2m): 0.215 g as a yellow paste in 44% yield. Selected IR (KBr, cm⁻¹): 1486(m), 1453(m), 1435(m), 1172(m), 1040(m), 759(s), 711(m), 550(s), 507(m), 442(m). ¹H NMR (CD₂Cl₂, δ), 8.01-7.94 (m, 2H, Ar-H), 7.35-7.22 (m, 7H, Ar-H), 4.67 (d, J(H,H) = 15.4 Hz, 2H, CH₂), 3.96-3.85 (m, 2H, CH), 3.70 (t, 1H, OH), 2.59 (d, 2H, SeCH₂), 1.29 (dd, 12H, CH₃) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, δ), 59.9 (s, J(P,Se) = 387 Hz, J(P,Se) = 777 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 361.4 (d, J(P,Se) = 388 Hz), -26.4 (d, J(P,Se) = 777 Hz) ppm. Mass spectrum [CI⁺, m/z]: 490 [M+H]⁺. Accurate mass measurement (CI⁺): 490.0308, calculate mass for C₂₀H₂₈NONaBrPSe₂H [M+H]⁺: 490.0315.

N-Benzyl Se-[2-(4-bromophenyl)-2-oxoethyl] phenylphosphonamidodiselenoate (2n): 0.534 g as a yellow paste in 47% yield. Selected IR (KBr, cm⁻¹): 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). ¹H NMR (CD₂Cl₂, δ), 8.03 (d, J(H,H) = 8.26 Hz, 2H, Ar-H), 7.81-7.77 (m, 2H, Ar-H), 7.60-7.47 (m, 5H, Ar-H), 7.36-7.26 (m, 5H, Ar-H), 4.31-4.01 (m, 4H, CH₂), 3.68-3.60 (m, 1H, NH) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, δ), 58.3 (s, J(P,Se) = 376 Hz, J(P,Se) = 798 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 324.8 (d, J(P,Se) = 376 Hz), -103.4 (d, J(P,Se) = 798 Hz) ppm. Mass spectrum [ES⁺, m/z]: 594 [M+Na]⁺. Accurate mass measurement (CI⁺): 571.8787, calculate mass for C₂₁H₁₉NONaBrPSe₂H [M+H]⁺: 571.8790.

General procedure for synthesis of compounds 3a-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 dihaloalkane (1.0 mmol) was added and the mixture was allowed to stir 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 using dichloromethane as eluent to give the compounds **3a-n**.

Methylene bis(N-cyclohexyl-P-phenylphosphonamidodiselenoate) (3a): 0.585 g as a pale yellow oil in 79% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm⁻¹): 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). ¹H NMR (CD₂Cl₂, δ), 8.01-7.88 (m, 2x4H, Ar-H), 7.60-7.39 (m, 2x6H,

Ar-H), 4.42-4.20 (m, 2x2H, Cyclohexyl-H), 3.21 (d, 2H, SeCH₂), 3.05 (d, 2H, SeCH₂), 1.96-0.83 (m, 2x20H, NH + Cyclohexyl-H) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, 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. ⁷⁷Se NMR (CD₂Cl₂, 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. Mass spectrum [Cl⁺, m/z]: 745 [M+H]⁺. Accurate mass measurement (Cl⁺MS): 744.9099, calculate mass for C₂₅H₃₇N₂P₂Se₄ [M+H]: 744.9101.

Ethane-1,2-diyl bis(N-cyclohexyl-P-phenylphosphonamidodiselenoate) (3b): 0.604 g as a pale yellow oil in 80% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm⁻¹): 1434(m), 1405(m), 1077(s), 994(m), 878(m), 745(m), 688(s), 519(s), 479(m), 443(m). ¹H NMR (CD₂Cl₂, δ), 8.12-7.90 (m, 2x4H, Ar-H), 7.50-7.43 (m, 2x6H, Ar-H), 4.36-4.06 (dd, 2x2H, Cyclohexyl-H), 3.20-3.08 (m, 2x4H, CH₂Se), 2.28-1.17 (m, 2x22H, NH + Cyclohexyl-H) ppm. ¹³C NMR (CD₂Cl₂, δ), 135.7 (d, J(P,C) = 90.3 Hz), 135.6 (d, J(P,C) = 90.3 Hz), 132.2 (d, J(P,C) = 3.1 Hz), 132.5 (d, J(P,C) = 3.1 Hz), 130.9 (d, J(P,C) = 12.5 Hz), 130.8 (d, J(P,C) = 12.5 Hz), 128.6 130.9 (d, J(P,C) = 13.5 Hz), 53.0, 52.9, 35.7, 35.6, 32.1, 30.9, 25.4, 25.3 ppm. ³¹P NMR (CD₂Cl₂, δ), 52.5 (s, J(P,Se) = 384 Hz, J(P,Se) = 784 Hz), 52.4 (s, J(P,Se) = 386 Hz, J(P,Se) = 786 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 378.5 (d, J(P,Se) = 384 Hz), 375.6 (d, J(P,Se) = 386 Hz), -90.1 (d, J(P,Se) = 784 Hz), -94.7 (d, J(P,Se) = 786 Hz) ppm. Mass spectrum [Cl⁺, m/z]: 759 [M+H]⁺. Accurate mass measurement (Cl⁺MS): 758.9260, calculate mass for C₂₆H₃₉N₂P₂Se₄ [M+H]: 758.9256.

Propane-1,3-diyl bis(N-cyclohexyl-P-phenylphosphonamidodiselenoate) (3c): 0.540 g as a pale yellow paste in 70% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm⁻¹): 1435(m), 1403(m), 1289(m), 1229(m), 1078(vs), 994(m), 878(m), 745(s), 689(s), 568(s), 520(s), 489(m). ¹H NMR (CD₂Cl₂, δ), 8.03-7.95 (m, 2x4H, Ar-H), 7.53-7.451 (m, 2x6H, Ar-H), 3.28-3.11 (m, 2x2H, Cyclohexyl-H), 2.96-2.76 (m, 2x6H, SeCH₂ + NH), 2.14-1.07 (m, 2x22H, Cyclohexyl-H) ppm. ¹³C NMR (CD₂Cl₂, δ), 137.1 (d, J(P,C) = 88.2 Hz), 132.0 (d, J(P,C) = 3.1 Hz), 130.8 (d, J(P,C) = 12.5 Hz), 128.5 (d, J(P,C) = 13.5 Hz), 53.0, 35.6, 32.3, 31.2, 25.4, 25.3 ppm. ³¹P NMR (CD₂Cl₂, δ), 53.7 (s, J(P,Se) = 384 Hz, J(P,Se) = 789 Hz), 53.6 (s, J(P,Se) = 386 Hz, J(P,Se) = 786 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 325.1 (d, J(P,Se) = 384 Hz), 324.8 (d, J(P,Se) = 386 Hz), -102.8 (d, J(P,Se) = 789 Hz), -103.5 (d, J(P,Se) = 786 Hz) ppm. Mass spectrum [Cl⁺, m/z]: 773 [M+H]⁺. Accurate mass measurement (Cl⁺MS): 772.9416, calculate mass for C₂₇H₄₁N₂P₂Se₄ [M+H]: 772.9421.

Butane-1,4-diyl bis(N-cyclohexyl-P-phenylphosphonamidodiselenoate) (3d): 0.610 g as a pale green paste in 48% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm⁻¹): 1436(m), 1396(m), 1078(s), 997(m), 886(m), 746(s), 688(s), 572(m), 519(s), 485(m). ¹H NMR (CD₂Cl₂, δ), 7.98-7.96 (m, 2x4H, Ar-H), 7.47-7.42 (m, 2x6H, Ar-H), 3.96-3.79 (m, 2x4H, SeCH₂), 2.81-1.15 (m, 2x28H, NH + Cyclohexyl-H) ppm. ¹³C NMR (CD₂Cl₂, δ), 137.1 (d, J(P,C) = 86.2 Hz), 132.7 (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, 33.4, 25.9, 25.1, 24.5 ppm. ³¹P NMR (CD₂Cl₂, δ), 53.5 (s, J(P,Se) = 384 Hz, J(P,Se) = 789 Hz), 53.4 (s, J(P,Se) = 386 Hz, J(P,Se) = 786 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 326.7 (d, J(P,Se) = 386 Hz), 326.3 (d, J(P,Se) = 388 Hz), -105.0 (d, J(P,Se) = 789 Hz), -105.2 (d, J(P,Se) = 786 Hz) ppm. Mass spectrum [Cl⁺, m/z]: 789 [M+H]⁺. Accurate mass measurement (Cl⁺MS): 788.9556, calculate mass for C₂₈H₄₃N₂P₂Se₄ [M+H]: 788.9562.

1,2-Phenylenebis(methylene) bis(N-cyclohexyl-P-phenylphosphonamidodiselenoate) (3e): 0.642 g as a milky green solid in 77% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm⁻¹): 1435(m), 1401(m), 1290(w), 1072(m), 1076(s), 993(m), 877(m), 745(s), 688(s), 567(m), 519(s), 489(m), m436(m). ¹H NMR (CD₂Cl₂, δ), 7.94-7.88 (m, 2x4H, Ar-H), 7.38-7.22 (m, 2x6H, Ar-H), 7.21-6.99 (m, 2x4H, Ar-H), 4.38-4.18 (m, 2x2H, Cyclohexyl-H), 3.11-2.76 (m, 2x6H, SeCH₂ + NH), 1.86-1.12 (m, 2x20H, Cyclohexyl-H) ppm. ¹³C NMR (CD₂Cl₂, 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. ³¹P NMR (CD₂Cl₂, δ), 53.9 (s, J(P,Se) = 386 Hz, J(P,Se) = 789 Hz), 53.8 (s, J(P,Se) = 386 Hz, J(P,Se) = 789 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 395.9 (d, J(P,Se) = 386 Hz), 395.1 (d, J(P,Se) = 386 Hz), -96.7 (d, J(P,Se) = 789 Hz), -96.8 (d, J(P,Se) = 789 Hz) ppm. Mass spectrum [Cl⁺, m/z]: 835 [M+H]⁺. Accurate mass measurement (Cl⁺MS): 834.9569, calculate mass for C₃₂H₄₃N₂PSe₄ [M+H]: 834.9580.

Ethane-1,2-diyl bis(N-isopropyl-P-phenylphosphonamidodiselenoate) (3f): 0.440 g as a reddish pink paste in 55% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 2 : 3 intensity ratio. Selected IR (KBr, cm⁻¹): 1436(s), 1398(m), 1160(m), 1130(s), 1027(s), 946(m), 890(m), 747(s), 692(s), 586(s), 537(s). ¹H NMR (CD₂Cl₂, δ), 7.88-7.79 (m, 2x4H, Ar-H), 7.50-7.43 (m, 2x6H, Ar-H), 4.25-4.05 (m, 2x2H, CH), 3.60-3.57 (m, 2x4H, SeCH₂), 3.19-3.16 (m, 2x2H, NH), 1.38-1.34 (m, 2x12H, CH₃) ppm. ¹³C NMR (CD₂Cl₂, δ), 137.1, 136.5, 131.6 (d, J(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. ³¹P NMR (CD₂Cl₂, δ), 53.0 (s, J(P,Se) = 383 Hz, J(P,Se) = 786 Hz), 52.7 (s, J(P,Se) = 385 Hz, J(P,Se) = 784 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 514.7 (d, J(P,Se) = 385 Hz), 514.5 (d, J(P,Se) = 383 Hz), -248.5 (d, J(P,Se) = 784 Hz), -248.7 (d, J(P,Se) = 786 Hz) ppm. Mass spectrum [Cl⁺, m/z]: 679 [M+H]⁺. Accurate mass measurement (Cl⁺MS): 678.8625, calculate mass for C₂₀H₃₁N₂PSe₄ [M+H]: 678.8631.

Propane-1,3-diyl bis(N-isopropyl-P-phenylphosphonamidodiselenoate) (3g): 0.380 g as a reddish yellow paste in 55% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm⁻¹): 163(w), 1435(m), 1285(m), 1114(m), 1029(s), 893(s), 806(s), 747(m), 691(s), 542(m). ¹H NMR (CD₂Cl₂, δ), 8.03-7.94 (m, 2x4H, Ar-H), 7.54-7.47 (m, 2x6H, Ar-H), 3.90-3.52 (m, 2x2H, CH), 3.30-3.24 (m, 2x4H, SeCH₂), 2.98-2.88 (m, 2x2H, NH), 1.52-1.37 (m, 2x2H, CH₂), 1.17-1.12 (m, 2x12H, CH₃) ppm. ¹³C NMR (CD₂Cl₂, δ), 136.8, 136.2, 135.5, 135.1, 132.6 (d, J(P,C) = 3.1 Hz), 132.1 (d, J(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. ³¹P NMR (CD₂Cl₂, δ), 53.9 (s, J(P,Se) = 385 Hz, J(P,Se) = 789 Hz), 53.8 (s, J(P,Se) = 385 Hz, J(P,Se) = 789 Hz) ppm. ⁷⁷Se NMR (CD₂Cl₂, δ), 323.4 (d, J(P,Se) = 385 Hz), 323.0 (d, J(P,Se) = 385 Hz), -164.2 (d, J(P,Se) = 789 Hz), -173.8 (d, J(P,Se) = 786 Hz) ppm. Mass spectrum [Cl⁺, m/z]: 693 [M+H]⁺. Accurate mass measurement (Cl⁺MS): 692.8779, calculate mass for C₂₁H₃₃N₂PSe₄ [M+H]: 692.8788.

1,2-Phenylenebis(methylene) bis(N-isopropyl-P-phenylphosphonamidodiselenoate) (3h): 0.495 g as a pale green paste in 66% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 3 : 2 intensity ratio. Selected IR (KBr, cm⁻¹): 1434(m), 1362(m), 1124(m), 1096(m), 1007(s), 881(s), 744(s), 688(s), 532(s). ¹H NMR (CD₂Cl₂, δ), 8.04-7.94 (m, 2x4H, Ar-H), 7.52-7.47 (m, 2x6H, Ar-H), 7.15-7.06 (m, 2x4H, Ar-H), 4.27-4.20 (m, 2x2H, CH), 3.92-3.83 (m, 2x4H, SeCH₂), 2.74-2.68 (m, 2x2H, NH), 1.15-1.08 (m, 2x12H, CH₃) ppm. ¹³C NMR (CD₂Cl₂, δ), 137.6, 137.1, 136.6, 135.8, 132.2 (d, J(P,C) = 3.1 Hz), 131.0 (d, J(P,C) = 12.5 Hz), 130.9 (d, J(P,C) = 12.5 Hz), 128.6 (d, J(P,C) = 13.5 Hz), 127.8 (d, J(P,C) = 13.5 Hz), 46.3, 33.7, 24.9, 24.8 ppm. ³¹P NMR (CD₂Cl₂, δ), 54.2 (s, J(P,Se) = 385 Hz, J(P,Se) = 786

Hz), 54.1 (s, $J(\text{P,Se}) = 385$ Hz, $J(\text{P,Se}) = 786$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 392.7 (d, $J(\text{P,Se}) = 385$ Hz), 392.1 (d, $J(\text{P,Se}) = 385$ Hz), -99.5 (d, $J(\text{P,Se}) = 786$ Hz), -99.7 (d, $J(\text{P,Se}) = 786$ Hz) ppm. Mass spectrum [Cl^+ , m/z]: 755 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement (Cl^+MS): 692.8779, calculate mass for $\text{C}_{26}\text{H}_{35}\text{N}_2\text{PSe}_4$ [$\text{M}+\text{H}$]: 692.8788.

1,2-Phenylenebis(methylene) bis(*N,N*-diisobutyl-*P*-phenylphosphonamidodiselenoate) (3i): 0.475 g as a pale green paste in 53% yield. Four diastereoisomers were found in multi-NMR spectra in *ca.* 1 : 1 : 3 : 3 intensity ratio. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.09-7.97 (m, 4x4H, Ar-H), 7.47-7.38 (m, 4x6H, Ar-H), 7.15-7.04 (m, 4x4H, Ar-H), 4.30-3.80 (m, 4x8H, CH_2), 2.96-2.82 (m, 4x4H, SeCH_2), 1.91-1.81 (m, 4x4H, CH), 0.85-0.75 (m, 4x24H, CH_3) ppm. ^{13}C NMR (CD_2Cl_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_2Cl_2 , δ), 77.1 (s, $J(\text{P,Se}) = 386$ Hz, $J(\text{P,Se}) = 792$ Hz), 76.8 (s, $J(\text{P,Se}) = 386$ Hz, $J(\text{P,Se}) = 794$ Hz), 76.2 (s, $J(\text{P,Se}) = 386$ Hz, $J(\text{P,Se}) = 794$ Hz), 76.1 (s, $J(\text{P,Se}) = 386$ Hz, $J(\text{P,Se}) = 792$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 357.1 (d, $J(\text{P,Se}) = 386$ Hz), 354.1 (d, $J(\text{P,Se}) = 386$ Hz), 350.5 (d, $J(\text{P,Se}) = 386$ Hz), 350.1 (d, $J(\text{P,Se}) = 386$ Hz), -95.6 (d, $J(\text{P,Se}) = 792$ Hz), -96.7 (d, $J(\text{P,Se}) = 794$ Hz), -98.4 (d, $J(\text{P,Se}) = 794$ Hz), -99.1 (d, $J(\text{P,Se}) = 792$ Hz) ppm. Mass spectrum [Cl^+ , m/z]: 895 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement (Cl^+MS): 895.0498, calculate mass for $\text{C}_{36}\text{H}_{55}\text{N}_2\text{PSe}_4$ [$\text{M}+\text{H}$]: 895.0520.

Biphenyl-4,4'-diylbis(methylene) bis(*N*-isopropyl-*P*-phenylphosphonamidodiselenoate) (3j): 0.445 g as a reddish yellow solid in 54% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 2 intensity ratio. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.01-7.93 (m, 2x4H, Ar-H), 7.45-7.29 (m, 2x14H, Ar-H), 4.20-4.17 (m, 2x4H, SeCH_2), 3.91-3.78 (m, 2x2H, CH), 2.65-2.55 (m, 2x2H, NH), 1.30-1.11 (m, 2x12H, CH_3) ppm. ^{13}C NMR (CD_2Cl_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_2Cl_2 , δ), 54.0 (s, $J(\text{P,Se}) = 387$ Hz, $J(\text{P,Se}) = 789$ Hz), 53.9 (s, $J(\text{P,Se}) = 387$ Hz, $J(\text{P,Se}) = 789$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 408.5 (d, $J(\text{P,Se}) = 386$ Hz), 408.4 (d, $J(\text{P,Se}) = 386$ Hz), -99.1 (d, $J(\text{P,Se}) = 789$ Hz), -99.3 (d, $J(\text{P,Se}) = 789$ Hz) ppm. Mass spectrum [Cl^+ , m/z]: 831 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement (Cl^+MS): 830.9254, calculate mass for $\text{C}_{32}\text{H}_{39}\text{N}_2\text{P}_2\text{Se}_4$ [$\text{M}+\text{H}$]: 830.9257.

1,3-Phenylenebis(methylene) bis(*N*-tert-butyl-*P*-phenylphosphonamidodiselenoate) (3k): 0.460 g as a pale yellow paste in 59% yield. Three diastereoisomers were found in multi-NMR spectra in *ca.* 1 : 2 : 2 intensity ratio. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.09-8.00 (m, 3x4H, Ar-H), 7.51-7.44 (m, 3x6H, Ar-H), 7.23-7.07 (m, 3x4H, Ar-H), 4.26-4.09 (m, 3x4H, SeCH_2), 2.78 (very wide, 3x2H, NH), 1.30-1.21 (m, 3x18H, CH_3) ppm. ^{13}C NMR (CD_2Cl_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_2Cl_2 , δ), 46.1 (s, $J(\text{P,Se}) = 374$ Hz, $J(\text{P,Se}) = 794$ Hz), 45.9 (s, $J(\text{P,Se}) = 367$ Hz, $J(\text{P,Se}) = 789$ Hz), 45.8 (s, $J(\text{P,Se}) = 377$ Hz, $J(\text{P,Se}) = 789$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 450.7 (d, $J(\text{P,Se}) = 374$ Hz), 447.8 (d, $J(\text{P,Se}) = 377$ Hz), 447.2 (d, $J(\text{P,Se}) = 367$ Hz), -49.2 (d, $J(\text{P,Se}) = 789$ Hz), -49.8 (d, $J(\text{P,Se}) = 789$ Hz), -50.4 (d, $J(\text{P,Se}) = 794$ Hz) ppm. Mass spectrum [Cl^+ , m/z]: 783 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement (Cl^+MS): 782.9250, calculate mass for $\text{C}_{28}\text{H}_{39}\text{N}_2\text{P}_2\text{Se}_4$ [$\text{M}+\text{H}$]: 782.9257.

1,2-Phenylenebis(methylene) bis(*N*-tert-butyl-*P*-phenylphosphonamidodiselenoate) (3l): 0.396 g as a greenish yellow solid in 51% yield. A pair of diastereoisomers was found in multi-NMR spectra in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.10-8.01 (m, 2x4H, Ar-H), 7.49-7.44 (m, 2x6H, Ar-H), 7.36-7.31 (m, 2x2H, Ar-H), 7.16-7.08 (m, 2x2H, Ar-H), 4.41-4.19 (m, 2x4H, SeCH_2), 2.83 (wide, 2x2H, NH), 1.28 (s, 18H, CH_3), 1.26 (s, 18H, CH_3) ppm. ^{13}C NMR (CD_2Cl_2 , δ), 138.4 (d, $J(\text{P,C}) = 109$ Hz), 137.3 (d, $J(\text{P,C}) = 108$ Hz), 133.3 (d, $J(\text{P,C}) = 3.1$ Hz), 131.8 (d, $J(\text{P,C}) = 3.1$ 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_2Cl_2 , δ), 46.0 (s, $J(\text{P,Se}) = 376$ Hz, $J(\text{P,Se}) = 789$ Hz), 45.9 (s, $J(\text{P,Se}) = 378$ Hz, $J(\text{P,Se}) = 786$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 438.8 (d, $J(\text{P,Se}) = 378$ Hz), 438.1 (d, $J(\text{P,Se}) = 376$ Hz), -50.3 (d, $J(\text{P,Se}) = 789$ Hz), -50.4 (d, $J(\text{P,Se}) = 789$ Hz) ppm. Mass spectrum [Cl^+ , m/z]: 783 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement (Cl^+MS): 782.9238, calculate mass for $\text{C}_{28}\text{H}_{39}\text{N}_2\text{P}_2\text{Se}_4$ [$\text{M}+\text{H}$]: 782.9257.

1,2-Phenylenebis(methylene) bis(*N*-sec-butyl-*P*-phenylphosphonamidodiselenoate) (3m): 0.420 g as a yellow paste in 54% yield. Four diastereoisomers were found in multi-NMR spectra in *ca.* 1.0 : 1.0 : 1.2 : 1.0 intensity ratio. Selected IR (KBr, cm^{-1}): 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). ^1H NMR (CD_2Cl_2 , δ), 8.15-7.90 (m, 4x4H, Ar-H), 7.56-7.30 (m, 4x6H, Ar-H), 7.27-7.05 (m, 4x4H, Ar-H), 4.23-4.05 (m, 4x4H, SeCH_2), 3.95-3.86 (m, 4x2H, CH), 2.69-2.66 (m, 4x2H, NH), 1.62-1.28 (m, 4x4H, CH_2), 1.15-1.09 (m, 4x6H, CH_3), 0.85-0.83 (m, 4x6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_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_2Cl_2 , δ), 55.2 (s, $J(\text{P,Se}) = 384$ Hz, $J(\text{P,Se}) = 789$ Hz), 55.1 (s, $J(\text{P,Se}) = 384$ Hz, $J(\text{P,Se}) = 789$ Hz), 54.8 (s, $J(\text{P,Se}) = 384$ Hz, $J(\text{P,Se}) = 789$ Hz), 54.7 (s, $J(\text{P,Se}) = 387$ Hz, $J(\text{P,Se}) = 789$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 395.9 (d, $J(\text{P,Se}) = 384$ Hz), 395.2 (d, $J(\text{P,Se}) = 384$ Hz), 394.8 (d, $J(\text{P,Se}) = 384$ Hz), 391.4 (d, $J(\text{P,Se}) = 387$ Hz), -99.0 (d, $J(\text{P,Se}) = 789$ Hz), -99.5 (d, $J(\text{P,Se}) = 789$ Hz), -101.1 (d, $J(\text{P,Se}) = 789$ Hz), -101.4 (d, $J(\text{P,Se}) = 789$ Hz) ppm. Mass spectrum [Cl^+ , m/z]: 783 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement (Cl^+MS): 782.9249, calculate mass for $\text{C}_{28}\text{H}_{39}\text{N}_2\text{P}_2\text{Se}_4$ [$\text{M}+\text{H}$]: 782.9257.

1,3-Phenylenebis(methylene) bis(*N*-sec-butyl-*P*-phenylphosphonamidodiselenoate) (3n): 0.470 g as a yellow paste in 60% yield. Four diastereoisomers were found in multi-NMR spectra in *ca.* 1.1 : 1.0 : 1.0 : 1.2 intensity ratio. Selected IR (KBr, cm^{-1}): 1602(m), 1485(m), 1435(s), 1396(m), 1184(m), 1133(m), 1097(s), 1-38(m), 1008(m), 951(m), 744(s), 692(vs), 535(vs), 487(m). ^1H NMR (CD_2Cl_2 , δ), 8.15-7.96 (m, 4x4H, Ar-H), 7.51-7.46 (m, 4x6H, Ar-H), 7.14-6.90 (m, 4x4H, Ar-H), 4.10-4.04 (m, 4x4H, SeCH_2), 3.82-3.61 (m, 4x2H, CH), 2.69-2.64 (m, 4x2H, NH), 1.45-1.38 (m, 4x4H, CH_2), 1.19-1.10 (m, 4x6H, CH_3), 0.98-0.83 (m, 4x6H, CH_3) ppm. ^{13}C NMR (CD_2Cl_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_2Cl_2 , δ), 55.0 (s, $J(\text{P,Se}) = 390$ Hz, $J(\text{P,Se}) = 789$ Hz), 54.9 (s, $J(\text{P,Se}) = 390$ Hz, $J(\text{P,Se}) = 789$ Hz), 54.6 (s, $J(\text{P,Se}) = 390$ Hz, $J(\text{P,Se}) = 789$ Hz), 54.5 (s, $J(\text{P,Se}) = 390$ Hz, $J(\text{P,Se}) = 789$ Hz) ppm. ^{77}Se NMR (CD_2Cl_2 , δ), 406.4 (d, $J(\text{P,Se}) = 390$ Hz), 406.2 (d, $J(\text{P,Se}) = 390$ Hz), 406.1 (d, $J(\text{P,Se}) = 390$ Hz), 405.7 (d, $J(\text{P,Se}) = 390$ Hz), -97.1 (d, $J(\text{P,Se}) = 789$ Hz), -97.5 (d, $J(\text{P,Se}) = 789$ Hz), -99.1 (d, $J(\text{P,Se}) = 789$ Hz), -99.5 (d, $J(\text{P,Se}) = 789$ Hz) ppm. Mass spectrum [Cl^+ , m/z]: 783 [$\text{M}+\text{H}$] $^+$. Accurate mass measurement (Cl^+MS): 782.9246, calculate mass for $\text{C}_{28}\text{H}_{39}\text{N}_2\text{P}_2\text{Se}_4$ [$\text{M}+\text{H}$]: 782.9257.

Acknowledgments

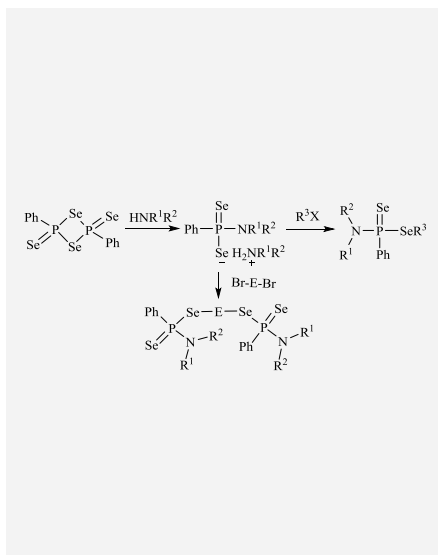
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- [28] Crystallographic data for compound **2e**. C₁₈H₂₀BrNOPSe₂, *M* = 535.16, Triclinic, space group *P*-1, *a* = 8.176(8) Å, *b* = 10.242(10) Å, *c* = 12.652(13) Å, α = 81.19(3)°, β = 79.35(3)°, γ = 75.78(3)°, *U* = 999.6(17) Å³, *Z* = 2, μ = 5.7896 mm⁻¹, 8488 reflections, 3516 unique (*R*_{int} = 0.0827); *R*₁ = 0.0522, *wR*₂ = 0.1329.
- [29] Crystallographic data for compound **2i**. C₁₉H₂₀BrNOPSe₂, *M* = 547.17, Monoclinic, space group *P*2_{1/c}, *a* = 6.956(6) Å, *b* = 17.86(2) Å, *c* = 32.53(3) Å, β = 92.038(11)°, *U* = 4040(6) Å³, *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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Entry for the Table of Contents

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



Organo Phosphorus-Selenium Chemistry

*Guoxiong Hua, Kasun S. A. Arachchige, Alexandra M. Z. Slawin, and J. Derek Woollins** Page No. ... Page No.

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

Keywords: *Woollins' reagent / Selenation / Phosphorus-Selenium Compounds / Amines / Haloalkanes*