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# Sodium phenyldiselenophosphonate salts and *Se*-alkyl-*O*-alkylphenyl-phosphonodiselenoates and *Se*,*Se*′-dialkyl-*O*,*O*′-dialkyl-bis(phenylphosphonodiselenoate)s

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A B S T R A C T

The reaction of sodium alkoxides [$R^1ONa$, $R^1 = CH_3$, $CH_3CH_2$, $(CH_3)_2CH$ and $CH_3CH_2CH_2$] with 2,4-diphenyl-1,3-diselenadiphosphetane-2,4-diselenide [PhP(Se)(μ-Se)]$_2$ (Woollins' reagent, **WR**) gave the non-symmetric sodium phenyldiselenophosphonate salts **1a**–**1d**, the latter were further treated with haloalkanes [$R^2X$, $R^2$ = alkyl and aryl; X = Br, Cl and I] or dihaloalkanes [Br-$(CH_2)_n$-Br, $n$ = 1–3 and $BrCH_2C_6H_4CH_2Br$-*p*] to afford a series of new *Se*-alkyl *O*-alkylphenylphosphonodiselenoate esters **2a**–**2k** and *Se*,*Se*′-dialkyl-*O*,*O*′-dialkyl bis(phenylphosphonodiselenoate) esters **3a**–**3j** in good to excellent yields.

## 1. Introduction

The chemistry of selenium-containing diselenophosphates [$(RO)_2PSe_2^-$], diselenophosphonate [$(R)(RO)PSe_2^-$], diselenophosphinates [$R_2PSe_2^-$], and diselenophosphates [$RPSe_3^{2-}$] with $PSe_2$ or $PSe_3$ functional groups has been less well studied compared to their sulfur counterparts [1]. The coordination chemistry of diselenophosphinates [$R_2PSe_2^-$] and diselenophosphates [$RPSe_3^{2-}$] was first described in 1964 [2,3]. Since then, there have been a number of reports of the synthesis and complexation of phosphinodiselenoate and phosphorodiselenoate ligands with a range of metals [4–8]. A varieties of silver and copper containing cluster compound incorporating dialkylphosphorodiselenoate ligands have also been reported [9–15]. However, the reactivity of the diselenophosphates [$(RO)_2PSe_2^-$], diselenophosphonates [$(R)(RO)PSe_2^-$], diselenophosphinates [$R_2PSe_2^-$], and diselenophosphates [$RPSe_3^{2-}$] towards organic substrates remains uninvestigated to date.

2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [PhP(Se)(μ-Se)]$_2$, known as Woollins' reagent, **WR**, is an efficient selenation reagent in synthetic chemistry [16–28] due to its ready preparation and ease of handling in air [29]. Recently, we have reported the synthesis of sodium phosphonodiselenoate salts achieved *via* a ring-opening reaction of **WR**, and their metal complexes [30]. Herein, we report a series of *Se*-alkyl *O*-alkylphenylphosphonodiselenoate esters [$Ph(R^1O)P(Se)SeR^2$, $R^1 = CH_3$, $CH_3CH_2$, $(CH_3)_2CH$ and $CH_3CH_2CH_2$, and $R^2$ = alkyl and aryl] and *Se*,*Se*′-dialkyl-*O*,*O*′-dimethyl bis(phenylphosphonodiselenoate) esters by the reaction of phenyldiselenophosphonate salts with haloalkanes or dihaloalkanes. All new compounds have been characterized by IR, mass spectrometry and multinuclear NMR. To the best of our knowledge this work is the first report of organic derivatives of phosphonodiselenoate salts and provides a valuable addition to the few examples of phosphonodiselenoate ligands known.

## 2. Results and Discussion

Non-symmetric sodium phenyldiselenophosphonates [$Ph(RO)PSe_2Na$] **1a**–**1d** were obtained *via* the cleavage of the four-membered $P_2Se_2$ ring in **WR** by two equivalents of sodium alkoxide [NaOR (R = Me, Et, $^i$Pr and $^n$Pr)] at room temperature as either white or pale yellow solids in high yields [30]. Then, sodium phenyldiselenophosphonates **1a**–**1c** was stirred with one equivalent of haloalkane in tetrahydrofuran at room temperature to yield the corresponding *Se*-alkyl-*O*-alkylphenylphosphonodiselenoate esters **2a**–**2k** as shown in Scheme 1. These new compounds were isolated in high yields as sticky oils or pastes soluble in both chlorinated solvents and tetrahydrofuran. Compounds **2a**–**2k** are stable to air and moisture for months without obvious signals of degradation. It should be noted that **2i**–**2k** bearing bulky $R^1$ groups ($R^1 = CH(CH_3)_2$) were obtained in rather low yields, compared to the compounds **2a**–**2k** bearing small or medium $R^1$ groups

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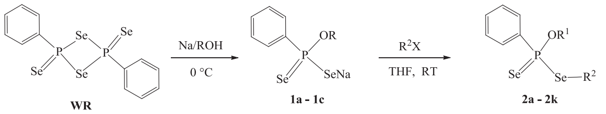
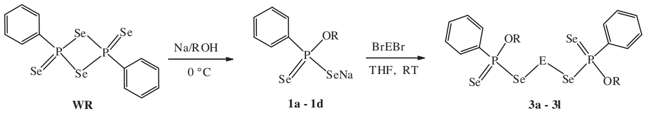


**1a** $R = CH_3$
**1b** $R = CH_3CH_2$
**1c** $R = (CH_3)_2CH$

**2a** $X = Br, R^1 = CH_3, R^2 = 2\text{-}BrC_6H_4CH_2$, 99%
**2b** $X = Br, R^1 = CH_3, R^2 = C_6H_5CH_2$, 93%
**2c** $X = Br, R^1 = CH_3, R^2 = C_6H_5C(O)CH_2$, 89%
**2d** $X = Cl, R^1 = CH_3, R^2 = C_6H_5C(O)$, 99%
**2e** $X = I, R^1 = CH_3, R^2 = CH_3(CH_2)_5CH_2$, 99%
**2f** $X = Cl, R^1 = CH_3, R^2 = C_2H_5OC(O)CH_2C(O)CH_2$, 75%
**2g** $X = Br, R^1 = CH_3CH_2, R^2 = C_6H_5CH_2$, 99%
**2h** $X = Br, R^1 = CH_3CH_2, R^2 = 2\text{-}BrC_6H_4CH_2$, 99%
**2i** $X = Br, R^1 = (CH_3)_2CH, R^2 = 2\text{-}BrC_6H_4CH_2$, 84%
**2j** $X = Br, R^1 = (CH_3)_2CH, R^2 = C_6H_5CH_2$, 83%
**2k** $X = Br, R^1 = (CH_3)_2CH, R^2 = C_6H_4C(O)CH_2$, 83%

**Scheme 1.** Synthesis of *Se*-alkyl-*O*-alkylphenylphosphonodiselenoate esters **2a**–**2k**.



**1a** $R = CH_3$
**1b** $R = CH_3CH_2$
**1c** $R = (CH_3)_2CH$
**1d** $R = CH_3CH_2CH_2$

**3a** $R = CH_3, E = CH_2CH_2CH_2$, 94%
**3b** $R = CH_3, E = H_2CC_6H_4CH_2\text{-}p$, 82%
**3c** $R = CH_3CH_2, E = CH_2$, 72%
**3d** $R = CH_3CH_2, E = CH_2CH_2$, 78%
**3e** $R = CH_3CH_2, E = CH_2CH_2CH_2$, 75%
**3f** $R = CH_3CH_2, E = H_2CC_6H_4CH_2\text{-}p$, 93%
**3g** $R = (CH_3)_2CH, E = CH_2CH_2$, 68%
**3h** $R = (CH_3)_2CH, E = CH_2CH_2CH_2$, 66%
**3i** $R = (CH_3)_2CH, E = H_2CC_6H_4CH_2\text{-}p$, 58%
**3j** $R = CH_3CH_2CH_2, E = H_2CC_6H_4CH_2\text{-}p$, 73%

**Scheme 2.** Synthesis of *Se,Se′*-dialkyl-*O,O′*-dialkyl-bis(phenylphosphonodiselenoate) esters **3a**–**3j**.

($R^1 = CH_3$ or $CH_2CH_3$), suggesting that steric hindrance of $R^1$ groups is important during the formation of the products. Use of haloalkanes with long chain alkyl groups also resulted in slightly lower yields, for example, compound **2f** is the lowest yield (with two stereoisomers present).

Compounds **2a**–**2k** showed the anticipated $[M+H]^+$ or $[M+Na]^+$ peaks in their mass spectra. The accurate mass measurements for all of the compounds were satisfactory. The $^{31}P$ NMR spectra of **2a**–**2k** reveal sharp singlets at $\delta(P)$ in the range of 75.7–85.5 ppm, flanked by two sets of selenium satellites with $^{31}P$–77Se coupling constants in the range of 418–448 and 819–848 Hz (Table 1). The lower magnitude coupling constants are attributed to the P–Se single bonded selenium atoms, and the higher magnitude values to the P═Se double bonded selenium atoms. Meanwhile, the $^{77}Se$ NMR spectra for **2a**–**2k** contain signals arising from exocyclic selenium atoms [$\delta(Se) = -56.1$ to $-106.2$ ppm; $J(P,Se_{exo}) = 819$–$848$ Hz] and endocyclic selenium atoms [$\delta(Se) = 325.6$–$662.5$ ppm; $J(P,Se_{endo}) = 418$–$448$ Hz]. The $^1H$ and $^{13}C$ NMR spectra confirm the presence of the organic substituents on the phosphorus center. The multi-NMR spectra of **2f** reveal a mixture of two stereoisomers with similar $^{31}P$ and $^{77}Se$ NMR spectral patterns. In the IR spectra of **2a**–**2k** the $\nu$(P═Se) vibrations were observed in the narrow region of 543–552 cm$^{-1}$.

Similar reactions were carried out with dihaloalkanes instead of haloalkanes. Thus the dihaloalkane was stirred with two equivalents of sodium phenyldiselenophosphonates **1a**–**1d** in tetrahydrofuran at room temperature to give a series of new *Se,Se′-dialkyl-O,O′*-dialkyl-bis(phenylphosphonodiselenoate) esters **3a**–**3j** as shown in Scheme 2. These new compounds were isolated in high yields as sticky oils or pastes soluble in chloroform, dichloromethane and tetrahydrofuran, and insoluble in diethyl ether and hexane. The $^{31}P$ NMR spectra of **3b**–**3e**, **3g** and **3h** exhibit two sets of double resonances (as a consequence of the stereoisomers present) with two sets of satellites for the endocyclic and exocyclic selenium atoms as shown in Table 2. Detailed $^{31}P$ and $^{77}Se$ NMR spectroscopic analyses reveal the relatively small coupling constants $^3J(P,Se_{endo}) = 19.1$ Hz and $^4J(P,P)] = 4.8$ Hz) in **3c**, $^4J(P,Se_{endo}) = 14.3$ Hz in **3d** and **3g**, confirming the presence of the corresponding P(Se)SeCH$_2$SeP(Se) or P(Se)SeCH$_2$CH$_2$SeP(Se) motif in compounds **3c**, **3d** and **3g**. However, only one major compound was observed for **3a**, **3f**, **3i** and **3j**, and no separate signals assignable to either stereoisomeric forms were observed in their $^1H$, $^{13}C$, $^{31}P$ and $^{77}Se$ NMR spectra The $^{31}P$ and $^{77}Se$ chemical shifts and coupling constants are comparable to the related heterocyclic compounds in the literature [23,31–33].

Satisfactory accurate mass measurements were obtained for **3a–3j**. The IR spectra display $\nu$(P═Se) vibrations in the region of 492–551 cm$^{-1}$.

In conclusion, a convenient and efficient approach to prepare a series of novel *Se*-alkyl *O*-alkylphenylphosphonodiselenoate and *Se,Se′*-dialkyl-*O,O′*-dialkyl bis(phenylphosphonodiselenoate) esters has been developed from the reaction of haloalkane or dihaloalkane with sodium phenyldiselenophosphonates, which were derived from a ring opening reaction of **WR** with the different alkoxides. All of new compounds were fully characterized by IR, mass spectroscopy and multinuclear NMR.

## 3. Experimental

Unless otherwise stated, all reactions were carried out under on 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), $^{31}P$–{1H} (109 MHz) and $^{77}Se$–{1H} (51.4 MHz referenced to external Me$_2$Se) 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. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service

**Table 1**
$^{31}P$ and $^{77}Se$ NMR data for compounds **2a**–**2k**.

| Product | $\delta(P)$ [ppm] | $J(P–Se)/J(P═Se)$ [Hz] | $\delta(Se_{endo})$ [ppm] | $J(Se–P)$ [Hz] | $\delta(Se_{exo})$ [ppm] | $J(Se = P)$ [Hz] |
|---|---|---|---|---|---|---|
| **2a** | 84.3 | 446/826 | 386.3 | 446 | −91.5 | 827 |
| **2b** | 84.3 | 448/848 | 399.7 | 448 | −95.7 | 848 |
| **2c** | 84.5 | 427/833 | 327.1 | 427 | −100.9 | 834 |
| **2d** | 75.7 | 423/840 | 662.5 | 424 | −56.1 | 839 |
| **2e** | 84.8 | 451/826 | 325.6 | 453 | −106.2 | 825 |
| **2f**[a] | 85.5 | 420/832 | 369.6 | 420 | −98.6 | 832 |
|  | 85.1 | 434/837 | 332.6 | 434 | −105.4 | 837 |
| **2g** | 80.0 | 444/824 | 411.8 | 444 | −88.9 | 825 |
| **2h** | 80.1 | 444/822 | 399.4 | 446 | −85.0 | 823 |
| **2i** | 77.3 | 439/819 | 421.5 | 439 | −82.6 | 819 |
| **2j** | 77.1 | 441/822 | 431.9 | 439 | −87.4 | 823 |
| **2k** | 77.6 | 418/826 | 361.0 | 417 | −90.2 | 827 |

[a] Two stereoisomers were found in **2f**.

**Table 2**
$^{31}$P and $^{77}$Se NMR data for **3a**–**3j**.

| Product | δ(P) [ppm] | J(P–Se)/J(P=Se) [Hz] | δ(Se$_{endo}$) [ppm] | J(Se–P) [Hz] | δ(Se$_{exo}$) [ppm] | J(Se = P) [Hz] |
|---|---|---|---|---|---|---|
| **3a** | 84.9 | 440/829 | 321.6 | 440 | −108.8 | 829 |
| **3b** | 84.4 | 448/827 | 401.3 | 448 | −95.4 | 827 |
| | 84.3 | 446/827 | 402.4 | 446 | −94.2 | 827 |
| **3c** | 81.4 | 420/832 | 410.8 | 420 | −69.8 | 832 |
| | 81.2 | 422/832 | 409.8 | 422 | −97.1 | 832 |
| **3d** | 80.6 | 432/829 | 387.4 | 432 | −99.0 | 827 |
| | 80.5 | 432/829 | 386.9 | 432 | −99.2 | 827 |
| **3e** | 80.9 | 437/826 | 340.1 | 437 | −101.3 | 825 |
| | 80.6 | 437/826 | 335.1 | 437 | −101.6 | 825 |
| **3f** | 80.2 | 444/825 | 414.2 | 444 | −88.5 | 825 |
| **3g** | 77.6 | 427/826 | 406.8 | 427 | −94.2 | 826 |
| | 77.5 | 427/826 | 399.7 | 427 | −94.4 | 826 |
| **3h** | 77.9 | 434/822 | 359.7 | 434 | −96.5 | 822 |
| | 77.6 | 434/822 | 359.5 | 434 | −96.7 | 822 |
| **3i** | 77.1 | 439/819 | 433.1 | 439 | −87.1 | 819 |
| **3j** | 80.2 | 446/825 | 412.9 | 444 | −88.1 | 825 |

Centre, Swansea and the University of St. Andrews Mass Spectrometry Service.

### *3.1. General procedure for the synthesis of compounds **2a**–**2k***

A solution of haloalkane (2.0 mmol) and sodium phenyldiselenophosphonates (2.0 mmol) was stirred in dry tetrahydrofuran (50 cm$^3$) at room temperature under nitrogen gas for 20 h. Upon filtering to remove insoluble solid, the filtrate was dried in vacuum. The residue was purified by column chromatography (silica gel, eluent dichloromethane) to give the corresponding products **2a**–**2k**.

#### *3.1.1. O-Methylphenyl-Se-2-bromobenzylphosphonodiselenoate (**2a**)*

1.875 g as a colorless oil in 99% yield. Selected IR (KBr, cm$^{-1}$): 1472(m), 1437(s), 1105(s), 1023(vs), 779(m), 747(s), 713(m), 688(m), 548(vs P=Se), 499(s). $^1$H NMR ($CD_2Cl_2$, δ), 7.96–7.88 (m, 2H, ArH), 7.52–7.50 (m, 3H, ArH), 7.23–7.04 (m, 4H, ArH), 4.07 (d, J(P,H) = 11.6 Hz, 3H, $OCH_3$), 3.68 (d, J(P,H) = 16.3 Hz, 2H, $SeCH_2$) ppm. $^{13}$C NMR ($CD_2Cl_2$, δ), 133.0, 132.4 (d, J(P,C) = 3.1 Hz), 130.9, 130.5, 130.3, 129.1, 128.7, 128.5, 127.7, 124.7, 52.7, 36.5 ppm. $^{31}$P NMR ($CD_2Cl_2$, δ), 84.3 (s, J(P,Se$_{endo}$) = 446 Hz, J(P,Se$_{exo}$) = 826 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, δ), 386.3 (d, J(P,Se$_{endo}$) = 446 Hz), −91.5 (d, J(P,Se$_{exo}$) = 827 Hz) ppm. MS (CI$^+$, m/z), 467 [M+H]$^+$. Accurate mass measurement [CI$^+$MS, m/z]: 468.8377 [M+H]$^+$, calculated mass for $C_{14}H_{15}BrOPSe_2$: 468.8378.

#### *3.1.2. O-Methylphenyl-Se-benzylphosphonodiselenoate (**2b**)*

0.718 g as a colorless oil in 93% yield. Selected IR (KBr, cm$^{-1}$): 1493(m), 1437(m), 1179(m), 1022(vs), 779(m), 746(m), 691(s), 547(vs P=Se), 499(s). $^1$H NMR ($CD_2Cl_2$, δ), 7.97–7.88 (m, 4H, ArH), 7.53–7.48 (m, 2H, ArH), 7.24–7.18 (m, 4H, ArH), 3.97 (d, J(P,H) = 11.8 Hz, 3H, $OCH_3$), 3.65 (d, J(P,H) = 16.3 Hz, 2H, $SeCH_2$) ppm. $^{13}$C NMR ($CD_2Cl_2$, δ), 132.4 (d, J(P,C) = 3.1 Hz), 130.4, 130.3, 129.1, 128.7, 128.5, 127.3, 52.8, 36.1 ppm. $^{31}$P NMR ($CD_2Cl_2$, δ), 84.3 (s, J(P,Se$_{endo}$) = 448 Hz, J(P,Se$_{exo}$) = 848 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, δ), 399.7 (d, J(P,Se$_{endo}$) = 448 Hz), −95.7 (J(P,Se$_{exo}$) = 848 Hz) ppm. MS (CI$^+$, m/z), 391 [M+H]$^+$. Accurate mass measurement [CI$^+$MS, m/z]: 390.9267 [M+H]$^+$, calculated mass for $C_{14}H_{16}OPSe_2$: 390.9269.

#### *3.1.3. O-Methyl-Se-2-oxo-2-phenylethyl phenylphosphonodiselenoate (**2c**)*

0.741 g as a slightly yellow oil in 89% yield. Selected IR (KBr, cm$^{-1}$): 1595(m), 1579(m), 1438(m), 1272(s), 1180(s), 1106(m), 1020(s), 782(m), 746(s), 712(s), 687(s), 550(s, P=Se), 499(m). $^1$H NMR ($CD_2Cl_2$, δ), 7.99–7.85 (m, 4H, ArH), 7.58–7.42 (m, 6H, ArH), 4.18 (d, J(P,H) = 11.6 Hz, 2H, $SeCH_2$), 4.17 (d, J(P,H) = 11.6 Hz, 2H, $SeCH_2$), 3.76 (d, J(P,H) = 16.5 Hz, 3H, $OCH_3$), 3.75 (d, J(P,H) = 16.5 Hz, 3H, $OCH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, δ), 193.8 (C = O), 135.4, 135.0, 133.7, 132.7, 132.6, 130.4 (d, J(P,C) = 12.5 Hz), 128.8, 128.6, 128.5, 128.3, 126.0, 53.2, 38.0 ppm. $^{31}$P NMR ($CD_2Cl_2$, δ), 84.5 (s, J(P,Se$_{endo}$) = 427 Hz, J(P,Se$_{exo}$) = 833 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, δ), 327.1 (d, J(P,Se$_{endo}$) = 427 Hz), −100.9 (d, J(P,Se$_{exo}$) = 834 Hz) ppm. MS (CI$^+$, m/z), 417 [M+H]$^+$. Accurate mass measurement [CI$^+$MS, m/z]: 416.9226 [M+H]$^+$, calculated mass for $C_{15}H_{17}O_2PSe_2$: 416.9226.

#### *3.1.4. Benzoic (O-methyl phenylphosphonoselenoic) selenoanhydride (**2d**)*

0.800 g as an yellow oil in 99% yield. Selected IR (KBr, cm$^{-1}$): 1735(m), 1687(s), 1580(w), 1438(s), 1196(s), 1172(s), 1105(m), 1024(s), 866(s), 686(s), 666(m), 543(s, P=Se). $^1$H NMR ($CD_2Cl_2$, δ), 8.15–8.03 (m, 2H, ArH), 7.76 (d, J(H,H) = 7.2 Hz, 2H, ArH), 7.60 (m, 6H, ArH), 3.90, (d, J(P,H) = 16.8 Hz, 3H, $OCH_3$) ppm. $^{13}$C NMR (toluene-d$_8$, δ), 137.2, 133.8, 132.2, 132.1, 131.6, 131.4, 128.9, 128.6, 128.2, 128.0, 127.8, 127.7, 127.3, 125.2, 124.8, 124.5, 52.7 (d, $^2$J(P,C) = 6.2 Hz, $OCH_3$) ppm. $^{31}$P NMR (toluene-d$_8$, δ), 75.7 (s, J(P,Se$_{endo}$) = 423 Hz, J(P,Se$_{exo}$) = 840 Hz) ppm. $^{77}$Se NMR (toluene-d$_8$, δ), 662.5 (d, J(P,Se$_{endo}$) = 424 Hz), −56.1 (d, J(P,Se$_{exo}$) = 839 Hz) ppm. MS (CI$^+$, m/z), 403 [M+H]$^+$. Accurate mass measurement [CI$^+$MS, m/z]: 403.0039 [M+H]$^+$, calculated mass for $C_{18}H_{20}FePS_2$: 403.0037.

#### *3.1.5. O-Methyl-Se-heptyl phenylphosphonodiselenoate (**2e**)*

0.810 g as a colorless oil in 99% yield. Selected IR (KBr, cm$^{-1}$): 1437(m), 1106(m), 1024(vs), 777(m), 745(m), 714(m), 689(m), 552(vs P=Se), 502(m). $^1$H NMR ($CD_2Cl_2$, δ), 7.96–7.88 (m, 2H, ArH), 7.51–7.48 (m, 4H, ArH), 3.90 (d, (d, J(P,H) = 15.9 Hz, 3H, $OCH_3$), 1.96–1.54 (m, 5H, $CH_2$), 1.27–1.22 (m, 9H, $CH_2$), 0.86 (t, J(H,H) = 6.3 Hz, 3H, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, δ), 132.3, 132.1, 130.2 (d, J(P,C) = 12.5 Hz), 128.4 (d, J(P,C) = 12.5 Hz), 14.4 Hz), 52.7 ($OCH_3$), 32.9, 31.8, 30.5, 29.7, 28.5, 25.6, 22.7, 13.9 ppm. $^{31}$P NMR ($CD_2Cl_2$, δ), 84.8 (s, J(P,Se$_{endo}$) = 451 Hz and J(P,Se$_{exo}$) = 826 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, δ), 325.6 (d, J(P,Se$_{endo}$) = 453 Hz), −106.2 (d, J(P,Se$_{exo}$) = 825 Hz) ppm. MS (CI$^+$, m/z), 411 [M+H]$^+$. Accurate mass measurement [CI$^+$MS, m/z]: 411.0061 [M+H]$^+$, calculated mass for $C_{15}H_{26}OPSe_2$: 411.0059.

#### *3.1.6. Ethyl 4-(methoxy(phenyl)phosphoroselenoylselanyl)-3-oxobutanoate (**2f**)*

0.640 g as a colorless oil in 75% yield. Selected IR (KBr, cm$^{-1}$): 1744(vs), 1630)(w), 1439(w), 1405(w), 1321(m), 1239(w), 1182(w), 1106(m), 1024(s), 783(m), 748(m), 714(m), 690(m), 551(vs), 501(m). Two diasteroisomers in 10:1 ratio were found in multi-NMR spectra.

$^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.96–7.87 (m, 2H × 2, ArH), 7.59–7.44 (m, 3H × 2, ArH), 4.27 (s, 2H × 2, CH$_2$), 4.14 (q, $J$(H,H) = 7.2 Hz, 2H × 2, CH$_2$), 3.76 (d, $J$(P,H) = 16.3 Hz, 3H, CH$_3$O), 3.73 (d, $J$(P,H) = 16.3 Hz, 3H, CH$_3$O), 3.60 (d, $J$(P,H) = 2.2 Hz, 2H, CH$_2$), 3.51 (d, $J$(P,H) = 2.2 Hz, 2H, CH$_2$), 1.24 (t, $J$(H,H) = 7.2 Hz, 3H × 2, CH$_3$) ppm $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 196.9, 195.2, 172.4 (d, $J$(P,C) = 15.6 Hz), 166.5 (d, $J$(P,C) = 16.6 Hz), 135.6 (d, $J$(P,C) = 15.6 Hz), 132.8 (d, $J$(P,C) = 3.1 Hz), 132.6 (d, $J$(P,C) = 3.1 Hz), 130.4 (d, $J$(P,C) = 12.5 Hz), 128.7 (d, $J$(P,C) = 14.5 Hz), 128.6 (d, $J$(P,C) = 14.5 Hz), 61.8, 61.6, 53.6, 53.3, 53.1, 53.0, 40.6 (d, $J$(P,C) = 3.1 Hz), 40.2 (d, $J$(P,C) = 3.1 Hz), 14.1, 14.0 ppm. $^{31}$P NMR (CD$_2$Cl$_2$, $\delta$), 85.5 (s, $J$(P,Se$_{endo}$) = 420 Hz and $J$(P,Se$_{exo}$) = 832 Hz); 85.1 (s, $J$(P,Se$_{endo}$) = 434 Hz and $J$(P,Se$_{exo}$) = 837 Hz) ppm. $^{77}$Se NMR (CD$_2$Cl$_2$, $\delta$), 369.6 (d, $J$(P,Se$_{endo}$) = 434 Hz), 332.6 (d, $J$(P,Se$_{endo}$) = 434 Hz), −98.6 ($J$(P,Se$_{exo}$) = 832 Hz), −105.4 (d, $J$(P,Se$_{endo}$) = 437 Hz) ppm. Mass spectrum (ES$^{+}$, $m/z$): 451 [M+Na]$^{+}$. Accurate mass measurement [CI$^{+}$MS, $m/z$]: 426.9277 [M+H]$^{+}$, calculated mass for $C_{13}H_{18}O_4PSe_2$: 426.9276.

### 3.1.7. *O-Ethyl-Se-benzylphenylphosphonodiselenoate (**2g**)*

0.800 g as a red oil in 99% yield. Selected IR (KBr, cm$^{-1}$): 1437(m), 1104(m), 1020(s), 943(s), 745(m), 692(s), 545(s, P=Se), 497(m). $^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.96–7.87 (m, 2H, ArH), 7.52–7.48 (m, 3H, ArH), 7.23–7.20 (m, 5H, ArH), 4.28–4.14 (m, 2H, OCH$_2$), 4.01–3.95 (m, 2H, SeCH$_2$), 1.33 (t, $J$(H,H) = 7.2 Hz, 3H, CH$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 132.3, 130.4, 130.3, 129.1, 128.7, 128.5, 128.2, 127.3, 63.1 (d, $J$(P,C) = 6.2 Hz), 35.9, 15.5 (d, $J$(P,C) = 9.4 Hz) ppm. $^{31}$P NMR (CD$_2$Cl$_2$, $\delta$), 80.0 (s, $J$(P,Se$_{endo}$) = 444 Hz and $J$(P,Se$_{exo}$) = 824 Hz) ppm. $^{77}$Se NMR (CD$_2$Cl$_2$, $\delta$), 411.8 (d, $J$(P,Se$_{endo}$) = 444 Hz), −88.9 ($J$ (P,Se$_{exo}$) = 825 Hz) ppm. MS (CI$^{+}$, $m/z$), 403 [M+H]$^{+}$. Accurate mass measurement [CI$^{+}$MS, $m/z$]: 402.9434 [M+H]$^{+}$, calculated mass for $C_{15}H_{18}OPSe_2$: 402.9433.

### 3.1.8. *O-Ethyl-Se-2-bromobenzylphenylphosphonodiselenoate (**2h**)*

0.960 g as a slightly yellow oil in 99% yield. Selected IR (KBr, cm$^{-1}$): 1438(m), 1104(m), 1023(vs), 943(s), 753(s), 713(m), 688(m), 548(vs P=Se), 496(m). $^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.97–7.88 (m, 2H, ArH), 7.52–7.44 (m, 3H, ArH), 7.21–7.04 (m, 4H, ArH), 4.31–4.16 (m, 2H, OCH$_2$), 4.12–3.95 (m, 2H, SeCH$_2$), 1.35 (t, $J$(H,H) = 7.2 Hz, 3H, CH$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 132.9, 132.4 (d, $J$(P,C) = 3.1 Hz), 131.0, 130.5, 130.3, 129.1, 128.7, 128.5, 127.7, 63.2 (d, $J$(P,C) = 6.2 Hz), 36.4, 15.6 (d, $J$(P,C) = 9.4 Hz) ppm. $^{31}$P NMR (CD$_2$Cl$_2$, $\delta$), 80.1 (s, $J$(P,Se$_{endo}$) = 444 Hz and $J$(P,Se$_{exo}$) = 822 Hz) ppm. $^{77}$Se NMR (CD$_2$Cl$_2$, $\delta$), 399.4 (d, $J$(P,Se$_{endo}$) = 446 Hz), −85.0 (d, $J$(P,Se$_{exo}$) = 823 Hz) ppm. MS (CI$^{+}$, $m/z$), 483 [M+H]$^{+}$. Accurate mass measurement [CI$^{+}$MS, $m/z$]: 482.8518 [M+H]$^{+}$, calculated mass for $C_{15}H_{17}BrOPSe_2$: 482.8523.

### 3.1.9. *O-Isopropyl-Se-2-bromobenzylphenylphosphonodiselenoate (**2i**)*

0.415 g as a pale yellow oil in 84% yield. Selected IR (KBr, cm$^{-1}$): 1473(m), 1438(m), 1372(m), 1100(s), 1024(m), 962(vs), 753(s), 688(m), 547(vs P=Se), 495(m). $^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.94–7.85 (m, 2H, ArH), 7.52–7.47 (m, 4H, ArH), 7.15–7.04 (m, 3H, ArH), 5.03–4.90 (m, 1H, CH), 4.20–4.01 (m, 2H, SeCH$_2$), 1.36 (d, $J$(H,H) = 6.3 Hz, 6H, CH$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 137.6, 132.9, 132.2, 131.0, 130.5, 130.3, 129.0, 128.6, 128.4, 127.6, 73.3 (d, $J$(P,C) = 6.2 Hz, O–C), 36.5 (CH$_3$), 23.5 (d, $J$(P,C) = 37.0 Hz, Se–C) ppm. $^{31}$P NMR (CD$_2$Cl$_2$, $\delta$), 77.3 (s, $J$(P,Se$_{endo}$) = 439 Hz and $J$(P,Se$_{exo}$) = 819 Hz) ppm. $^{77}$Se NMR (CD$_2$Cl$_2$, $\delta$), 421.5 (d, $J$(P,Se$_{endo}$) = 439 Hz), −82.6 (d, $J$(P,Se$_{exo}$) = 820 Hz) ppm. MS (ES$^{+}$, $m/z$), 519 [M+Na]$^{+}$. Accurate mass measurement (ES$^{+}$MS): 518.8509 [M+Na]$^{+}$, calculate mass for [$C_{16}H_{18}BrOPSe_2Na$]: 518.8506.

### 3.1.10. *O-Isopropyl-Se-benzylphenylphosphonodiselenoate (**2j**)*

0.346 g as a colorless oil in 83% yield. Selected IR (KBr, cm$^{-1}$): 1494(m), 1453(m), 1437(m), 1372(m), 1178(m), 1100(s), 962(vs), 742(m), 692(s), 545(s, P=Se), 496(m). $^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.96–7.88 (m, 2H, ArH), 7.50–7.32 (m, 4H, ArH), 7.20–7.18 (m, 4H, ArH), 5.02–4.92 (m, 1H, CH), 4.11–3.93 (m, 2H, SeCH$_2$), 1.36 (d, $J$(H,H) = 6.3 Hz, 6H, CH$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 138.1, 137.7, 132.1 (d, $J$(P,C) = 3.1 Hz), 130.3 (d, $J$(P,C) = 11.4 Hz), 129.1, 128.8, 128.6, 128.5, 127.3, 73.3 (d, $J$(P,C) = 7.3 Hz, O–C), 36.0, 35.9, 23.6 (d, $J$(P,C) = 35.3 Hz, Se–C), 23.5 (d, $J$(P,C) = 35.3 Hz, Se–C) ppm. $^{31}$P NMR (CD$_2$Cl$_2$, $\delta$), 77.1 (s, $J$(P,Se$_{endo}$) = 441 Hz and $J$(P,Se$_{exo}$) = 822 Hz) ppm. $^{77}$Se NMR (CD$_2$Cl$_2$, $\delta$), 431.9 (d, $J$(P,Se$_{endo}$) = 439 Hz), −87.4 (d, $J$(P,Se$_{exo}$) = 823 Hz) ppm MS (ES$^{+}$, $m/z$), 441 [M+Na]$^{+}$. Accurate mass measurement (ES$^{+}$MS): 440.9408 [M+Na]$^{+}$, calculate mass for [$C_{16}H_{19}OPSe_2Na$]: 440.9403.

### 3.1.11. *O-Isopropyl-Se-2-oxo-2-phenylethylphenylphosphonodiselenoate (**2k**)*

0.372 g as a colorless oil in 83% yield. Selected IR (KBr, cm$^{-1}$): 1675(s), 1596(m), 1580(m), 1448(m), 1373(m), 1272(s), 1180(m), 1100(s), 962(vs), 746(s), 688(s), 549(s, P=Se), 496(m). $^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.97–7.83 (m, 4H, ArH), 7.66–7.41 (m, 6H, ArH), 5.07–4.93 (m, 1H, CH), 4.19 (d, $J$(P,H) = 10.7 Hz, SeCH$_2$), 1.38 (dd, $J$(P,H) = 10.2 Hz, $J$(H,H) = 6.3 Hz, 6H, CH$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 193.9(C = O), 134.0, 133.7, 132.5, 130.4 (d, $J$(P,C) = 12.5 Hz), 129.0, 128.8, 128.7, 128.4, 73.7 (d, $J$(P,C) = 7.3 Hz, O–C), 38.0 (CH$_3$), 23.6 (d, $J$(P,C) = 29.1 Hz, Se–C) ppm. $^{31}$P NMR (CD$_2$Cl$_2$, $\delta$), 77.6 (s, $J$(P,Se$_{endo}$) = 418 Hz and $J$(P,Se$_{exo}$) = 826 Hz) ppm. $^{77}$Se NMR (CD$_2$Cl$_2$, $\delta$), 361.0 (d, $J$(P,Se$_{endo}$) = 417 Hz), −90.2 (d, $J$(P,Se$_{exo}$) = 827 Hz) ppm. MS (ES$^{+}$, $m/z$), 468 [M+Na]$^{+}$. Accurate mass measurement (ES$^{+}$MS): 467.9515 [M+Na]$^{+}$, calculate mass for [$C_{17}H_{20}NOPSe_2Na$]: 467.9511.

## 3.2. *General procedure for the synthesis of compounds **3a**–**3i***

A mixture of dihaloalkane (1.0 mmol) and sodium phenyldiselenophosphonates (2.0 mmol) in 50 cm$^{3}$ of dry tetrahydrofuran was stirred at room temperature under nitrogen gas for 20 h. Upon filtering to remove insoluble solid, the filtrate was concentrated to approximate 5 cm$^{3}$ in vacuum and purified by column chromatography (silica gel, eluented by dichloromethane) to afford the corresponding products **3a**–**3i**.

### 3.2.1. *O,O′-Dimethyl-Se,Se′-propane-1,3-diylbis(phenylphosphonodiselenoate) (**3a**)*

0.600 g as a colorless oil in 94% yield. Selected IR (KBr, cm$^{-1}$): 1435(s), 1291(w), 1238(s), 1106(m), 1022(vs), 778(m), 747(m), 713(m),689(m), 551(vs P=Se), 502(s, P=Se). $^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.96–7.87 (m, 4H, ArH), 7.56–7.45 (m, 6H, ArH), 3.75 (d, $J$(P,H) = 16.3 Hz, 6H, OCH$_3$), 3.55 (t, $J$(H,H) = 7.2 Hz, 4H, SeCH$_2$), 2.37–2.30 (m, 2H, CH$_2$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 136.3 (d, $J$(P,C) = 101 Hz), 132.5 (d, $J$(P,C) = 3.1 Hz), 130.3 (d, $J$(P,C) = 12.5 Hz), 128.6 (d, $J$(P,C) = 14.5 Hz), 52.9, 35.0, 32.9, 30.7 (d, $J$(P,C) = 3.1 Hz) ppm. $^{31}$P NMR (CD$_2$Cl$_2$, $\delta$), 84.9 (s, $J$(P,Se$_{endo}$) = 440 Hz, $J$(P,Se$_{exo}$) = 829 Hz) ppm. $^{77}$Se NMR (CD$_2$Cl$_2$, $\delta$), 321.6 (d, $J$(P,Se$_{endo}$) = 440 Hz), −108.8 (d, $J$(P,Se$_{exo}$) = 829 Hz) ppm. MS (CI$^{+}$, $m/z$), 641 [M+H]$^{+}$. Accurate mass measurement (CI$^{+}$MS): 640.7833 [M+H]$^{+}$, calculate mass for [$C_{17}H_{22}O_2P_2Se_4H$]: 640.7838.

### 3.2.2. *O,O′-Dimethyl-Se,Se″-1,4-phenylenebis(methylene)bis(phenylphosphonodiselenoate) (**3b**)*

0.570 g as a colorless oil in 82% yield. Selected IR (KBr, cm$^{-1}$): 1509(m), 1477(m), 1435(s), 1178(s), 1105(s), 1020(vs), 778(s), 745(s), 712(m), 688(s), 548(vs P=Se), 498(s, P=Se). Two isomers were found in *ca.* 10:1 intensity ratio in multi-NMR spectra. $^{1}$H NMR (CD$_2$Cl$_2$, $\delta$), 7.92 (d, $J$(H,H) = 7.4 Hz, 4H × 2, ArH), 7.52–7.47 (m, 6H × 2, ArH), 7.07 (d, $J$(H,H) = 7.4 Hz, 4H × 2, ArH), 3.95 (d, $J$(P,H) = 12.1 Hz, 4H, CH$_2$), 3.93 (d, $J$(P,H) = 12.1 Hz, 4H, CH$_2$), 3.65 (d, $J$(P,H) = 16.5 Hz, 6H, CH$_3$), 3.64 (d, $J$(P,H) = 16.5 Hz, 6H, CH$_3$) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, $\delta$), 137.0, 136.9, 135.5, 132.7 (d, $J$(P,C) = 3.1 Hz), 132.5 (d, $J$(P,C) = 3.1 Hz), 130.3 (d, $J$(P,C) = 12.5 Hz), 129.5, 129.4, 128.6 (d, $J$(P,C) = 14.5 Hz), 52.8, 52.7, 35.8, 35.7 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 84.4 (s, $J$(P,Se$_{\text{endo}}$) = 448 Hz, $J$(P,Se$_{\text{exo}}$) = 827 Hz), 84.3 (s, $J$(P,Se$_{\text{endo}}$) = 446 Hz, $J$(P,Se$_{\text{exo}}$) = 827 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 402.4 (d, $J$(P,Se$_{\text{endo}}$) = 446 Hz), 401.3 (d, $J$(P,Se$_{\text{endo}}$) = 448 Hz), −94.2 (d, $J$(P,Se$_{\text{exo}}$) = 827 Hz), −95.4 (d, $J$(P,Se$_{\text{exo}}$) = 827 Hz) ppm. MS (ES$^+$, $m/z$), 723 [M+Na]$^+$. Accurate mass measurement (ES$^+$MS): 722.7803 [M+Na]$^+$, calculate mass for $[C_{22}H_{24}O_2P_2Se_4Na]$: 722.7824.

### 3.2.3. *O,O′-Diethyl-Se,Se′-methylenebis(phenylphosphonodiselenoate) (**3c**)*

0.460 g as a colorless oil in 72% yield. Selected IR (KBr, cm$^{-1}$): 1474(m), 1436(s), 1385(m), 1104(s), 1027(vs), 943(s), 744(s), 687(s), 546(vs P=Se), 492(s, P=Se). Two isomers were found in *ca.* 1:1 intensity ratio in multi-NMR spectra. $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.92–7.88 (m, 4H × 2, ArH), 7.51–7.750 (m, 6H × 2, ArH), 4.274.23 (m, 2H × 2, $CH_2$), 4.14–3.92 (m, 4H × 2, $CH_2$), 1.41 (t, $J$(H,H) = 6.9 Hz, 6H × 2, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 136.1 (d, $J$(P,C) = 100 Hz), 132.6, 130.3 (d, $J$(P,C) = 12.5 Hz), 128.8, 128.5, 63.5, 63.4, 28.7, 28.5, 27.6, 27.5, 15.7, 15.5 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 81.4 (s, $J$(P,Se$_{\text{endo}}$) = 420 Hz, $J$(P,Se$_{\text{exo}}$) = 832 Hz), 81.2 (s, $J$(P,Se$_{\text{endo}}$) = 422 Hz, $J$(P,Se$_{\text{exo}}$) = 832 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 410.8 (d, $J$(P,Se$_{\text{endo}}$) = 420 Hz), 409.8 (d, $J$(P,Se$_{\text{endo}}$) = 422 Hz), −69.8 (d, $J$(P,Se$_{\text{exo}}$) = 832 Hz), −97.1 (d, $J$ (P,Se$_{\text{exo}}$) = 832 Hz) ppm. MS (CI$^+$, $m/z$), 641 [M+H]$^+$. Accurate mass measurement (CI$^+$MS): 640.7831 [M+H]$^+$, calculate mass for $[C_{17}H_{23}O_2P_2Se_4]$: 640.7838.

### 3.2.4. *O,O′-Diethyl-Se,Se′-ethane-1,2-diylbis(phenylphosphonodiselenoate) (**3d**)*

0.610 g as an yellow oil in 93% yield. Selected IR (KBr, cm$^{-1}$): 1436(s), 1385(m), 1162(m), 1103(s), 1018(vs), 943(s), 745(s), 689(s), 547(vs P=Se), 496(s, P=Se). Two isomers were found in *ca.* 3:2 intensity ratio in multi-NMR spectra. $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.82–7.74 (m, 4H × 2, ArH), 7.60–7.32 (m, 6H × 2, ArH), 4.16–3.92 (m, 4H × 2, $OCH_2$), 3.01–2.88 (m, 4H × 2, $SeCH_2$), 1.43–1.18 (m, 6H × 2, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 136.8 (d, $J$(P,C) = 99.7 Hz), 132.4 (d, $J$(P,C) = 3.1 Hz), 130.3 (d, $J$(P,C) = 12.5 Hz), 128.5 (d, $J$(P,C) = 14.5 Hz), 63.2 (d, $J$(P,C) = 6.2 Hz), 32.0, 15.7, 15.6 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 80.6 (s, $J$(P,Se$_{\text{endo}}$) = 432 Hz, $J$(P,Se$_{\text{exo}}$) = 829 Hz), 80.5 (s, $J$(P,Se$_{\text{endo}}$) = 432 Hz, $J$(P,Se$_{\text{exo}}$) = 829 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 387.4 (d, $J$(P,Se$_{\text{endo}}$) = 432 Hz), 386.9 (d, $J$(P,Se$_{\text{endo}}$) = 432 Hz), −99.0 (d, $J$(P,Se$_{\text{exo}}$) = 827 Hz), −99.2 (d, $J$(P,Se$_{\text{exo}}$) = 827 Hz) ppm. MS (ES$^+$, $m/z$), 677 [M+Na]$^+$. Accurate mass measurement (ES$^+$MS): 676.7804 [M+Na]$^+$, calculate mass for $[C_{18}H_{24}O_2P_2Se_4Na]$: 676.7810.

### 3.2.5. *O,O′-Diethyl-Se,Se′-propane-1,3-diyl bis(phenylphosphonodiselenoate) (**3e**)*

0.490 g as an yellow oil in 75% yield. Selected IR (KBr, cm$^{-1}$): 1476(m), 1436(s), 1386(m), 1104(s), 1020(s), 942(s), 745(s), 712(m), 689(s), 549(vs P=Se), 497(s, P=Se). Two isomers were found in *ca.* 8:1 intensity ratio in multi-NMR spectra. $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.98–7.85 (m, 4H × 2, ArH), 7.53–7.45 (m, 6H × 2, ArH), 4.28–4.10 (m, 4H × 2, $OCH_2$), 2.96–2.70 (m, 4H × 2, $SeCH_2$), 2.13–1.88 (m, 2H × 2, $CH_2$), 1.42–1.27 (m, 6H × 2, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 136.8 (d, $J$(P,C) = 99.7 Hz), 132.3 (d, $J$(P,C) = 3.1 Hz), 130.3 (d, $J$(P,C) = 11.4 Hz), 128.5 (d, $J$(P,C) = 14.5 Hz), 63.1, 63.0, 32.0 (d, $J$(P,C) = 3.1 Hz), 30.5 (d, $J$(P,C) = 3.1 Hz), 22.7, 22.6, 15.7, 15.6 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 80.9 (s, $J$(P,Se$_{\text{endo}}$) = 437 Hz, $J$(P,Se$_{\text{exo}}$) = 826 Hz), 80.6 (s, $J$(P,Se$_{\text{endo}}$) = 437 Hz, $J$(P,Se$_{\text{exo}}$) = 826 Hz) ppm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 340.1 (d, $J$(P,Se$_{\text{endo}}$) = 437 Hz), 335.1 (d, $J$(P,Se$_{\text{endo}}$) = 437 Hz), −101.3 (d, $J$(P,Se$_{\text{exo}}$) = 825 Hz), −101.6 (d, $J$(P,Se$_{\text{exo}}$) = 825 Hz) ppm. MS (ES$^+$, $m/z$), 691 [M+Na]$^+$. Accurate mass measurement (ES$^+$MS): 690.7960 [M+Na]$^+$, calculate mass for $[C_{19}H_{26}O_2P_2Se_4Na]$: 690.7967.

### 3.2.6. *O,O′-Diethyl-Se,Se′-1,4-phenylenebis(methylene)bis(phenylphosphonodiselenoate) (**3f**)*

0.560 g as a colorless oil in 77% yield. Selected IR (KBr, cm$^{-1}$): 1510(w), 1476(m), 1436(m), 1386(m), 1104(m), 1019(vs), 943(s), 744(s), 687(m), 548(vs P=Se), 496(s, P=Se). $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.96–7.88 (m, 4H, ArH), 7.56–7.45 (m, 6H, ArH), 7.07 (d, $J$(H,H) = 7.4 Hz, 4H, ArH), 4.28–4.11 (m, 4H, $OCH_2$), 4.12–3.92 (m, 4H, $SeCH_2$), 1.34 (t, $J$(H,H) = 6.9 Hz, 6H, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 136.9 (d, $J$(P,C) = 4.2 Hz), 136.6 (d, $J$(P,C) = 100.7 Hz), 132.4 (d, $J$(P,C) = 3.1 Hz), 130.4 (d, $J$(P,C) = 12.5 Hz), 129.4, 128.6 (d, $J$(P,C) = 14.5 Hz), 63.1 (d, $J$(P,C) = 6.2 Hz, O–C), 35.6 (d, $J$(P,C) = 4.2 Hz, Se–C), 15.9 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 80.2 (s, $J$(P,Se$_{\text{endo}}$) = 444 Hz, $J$(P,Se$_{\text{exo}}$) = 825 Hz) pm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 414.2 (d, $J$(P,Se$_{\text{endo}}$) = 444 Hz), −88.5 (d, $J$(P,Se$_{\text{exo}}$) = 825 Hz) ppm. MS (ES$^+$, $m/z$), 753 [M+Na]$^+$. Accurate mass measurement (ES$^+$MS): 752.8114 [M+Na]$^+$, calculate mass for $[C_{24}H_{28}O_2P_2Se_4Na]$: 752.8123.

### 3.2.7. *O,O′-Diisopropyl-Se,Se′-ethane-1,2-diylbis(phenylphosphonodiselenoate) (**3g**)*

0.460 g as a pale yellow oil in 68% yield. Selected IR (KBr, cm$^{-1}$): 1436(m), 1372(m), 1174(m), 1099(s), 962(vs), 885(m), 741(m), 688(m), 547(vs P=Se), 495(s, P=Se). Two isomers were found in *ca.* 3:2 intensity ratio in multi-NMR spectra. $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.90–7.88 (m, 4H, ArH), 7.60–7.48 (m, 6H, ArH), 4.96–4.93 (m, 2H, OCH), 3.01–2.98 (m, 4H, $SeCH_2$), 1.50–1.31 (m, 12H, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 137.5 (d, $J$(P,C) = (d, $J$(P,C) = 100.7 Hz), 132.3 (d, $J$(P,C) = 3.1 Hz), 130.2 (d, $J$(P,C) = 12.5 Hz), 128.5 (d, $J$(P,C) = 14.5 Hz), 73.3 (d, $J$(P,C) = 6.2 Hz, O–C), 31.9, 30.5, 23.7 (d, $J$(P,C) = 18.7 Hz), 23.6 (d, $J$(P,C) = 18.7 Hz) ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 77.6 (s, $J$(P,Se$_{\text{endo}}$) = 427 Hz, $J$(P,Se$_{\text{exo}}$) = 826 Hz), 77.5 (s, $J$(P,Se$_{\text{endo}}$) = 427 Hz, $J$(P,Se$_{\text{exo}}$) = 826 Hz) pm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 406.8 (d, $J$(P,Se$_{\text{endo}}$) = 427 Hz), 399.7 (d, $J$(P,Se$_{\text{endo}}$) = 427 Hz), −94.2 (d, $J$(P,Se$_{\text{exo}}$) = 826 Hz), −94.4 (d, $J$(P,Se$_{\text{exo}}$) = 826 Hz) ppm. MS (CI$^+$, $m/z$), 681 [M+H]$^+$. Accurate mass measurement (CI$^+$MS): 680.8313 [M+H]$^+$, calculate mass for $[C_{20}H_{28}O_2P_2Se_4H]$: 680.8317.

### 3.2.8. *O,O′-Diisopropyl-Se,Se′-propane-1,3-diylbis(phenylphosphonodiselenoate) (**3h**)*

0.455 g as a reddish yellow oil in 66% isolated yield. Selected IR (KBr, cm$^{-1}$): 1436(m), 1371(m), 1100(s), 961(vs), 885(m), 741(s), 689(m), 548(vs P=Se), 496(s, P=Se). Two isomers were found in *ca.* 6:1 intensity ratio in multi-NMR spectra. $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.95–7.87 (m, 4H, ArH), 7.50–7.44 (m, 6H, ArH), 7.05 (d, $J$(H,H) = 7.4 Hz, 4H, ArH), 4.19–3.80 (m, 8H, $OCH_2$+$SeCH_2$), 1.76–1.65 (m, 4H, $CH_2$), 1.00–0.94 (m, 6H, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 137.6 (d, $J$(P,C) = 99.7 Hz), 137.5 (d, $J$(P,C) = 99.7 Hz), 132.2 (d, $J$(P,C) = 3.1 Hz), 130.2 (d, $J$(P,C) = 12.5 Hz), 128.4 (d, $J$(P,C) = 14.5 Hz), 73.1 (d, $J$(P,C) = 6.2 Hz, O–C), 32.9 (d, $J$(P,C) = 3.1 Hz, Se–C), 31.9(d, $J$(P,C) = 3.1 Hz, Se–C), 30.8, 30.5, 23.7 (d, $J$(P,C) = 19.7 Hz, $CH_3$), 23.6 (d, $J$(P,C) = 20.8 Hz, $CH_3$) ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 77.9 (s, $J$(P,Se$_{\text{endo}}$) = 434 Hz, $J$(P,Se$_{\text{exo}}$) = 822 Hz), 77.6 (s, $J$(P,Se$_{\text{endo}}$) = 434 Hz, $J$(P,Se$_{\text{exo}}$) = 822 Hz) pm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 359.8 (d, $J$(P,Se$_{\text{endo}}$) = 434 Hz), 359.5 (d, $J$(P,Se$_{\text{endo}}$) = 434 Hz), −96.5 (d, $J$(P,Se$_{\text{exo}}$) = 822 Hz), −96.7 (d, $J$(P,Se$_{\text{exo}}$) = 822 Hz) ppm. MS (CI$^+$, $m/z$), 695 [M+H]$^+$. Accurate mass measurement (CI$^+$MS): 694.8473 [M+H]$^+$, calculate mass for $[C_{21}H_{30}O_2P_2Se_4H]$: 694.8474.

### 3.2.9. *O,O′-Diisopropyl-Se,Se′-1,4-phenylenebis(methylene) bis(phenylphosphonodiselenoate) (**3i**)*

0.435 g as a bright yellow oil in 58% isolated yield. Selected IR (KBr, cm$^{-1}$): 1509(w), 1435(m), 1371(m), 1099(s), 961(vs), 885(m), 740(m), 688(m), 547(vs P=Se), 495(s, P=Se). $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.89–7.82 (m, 4H, ArH), 7.50–7.47 (m, 6H, ArH), 7.02 (d, $J$(H,H) = 7.4 Hz, 4H, ArH), 4.94–4.80 (m, 2H, OCH), 4.13–3.80 (m, 4H, $SeCH_2$), 1.54–0.88 (m, 12H, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$,

$\delta$), 137.2 (d, $J$(P,C) = 99.7 Hz), 136.8 (d, $J$(P,C) = 4.1 Hz), 132.2 (d, $J$(P,C) = 3.1 Hz), 130.3 (d, $J$(P,C) = 12.5 Hz), 129.3, 128.5 (d, $J$(P,C) = 14.5 Hz), 73.2 (d, $J$(P,C) = 6.2 Hz, O–C), 35.6, 23.7 (d, $J$(P,C) = 33.2 Hz, $CH_3$), 23.6 (d, $J$(P,C) = 33.3 Hz, $CH_3$) ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 77.1 (s, $J$(P,$Se_{endo}$) = 439 Hz, $J$(P,$Se_{exo}$) = 819 Hz) pm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 433.1 (d, $J$(P,$Se_{endo}$) = 439 Hz), −87.1 (d, $J$(P,$Se_{exo}$) = 819 Hz) ppm. MS (CI$^+$, $m/z$), 774 [M+$NH_4$]$^+$. Accurate mass measurement (CI$^+$MS): 773.8894 [M+$NH_4$]$^+$, calculate mass for [$C_{26}H_{32}O_2P_2Se_4NH_4$]: 773.8898.

### *3.2.10. O,O′-Dipropyl-Se,Se′-1,4-phenylenebis(methylene)bis(phenylphosphonodiselenoate) (**3j**)*

To dried propanol solution (20 cm$^3$) at room temperature under nitrogen was added a small piece of sodium (46 mg, 2.0 mmol). The mixture was stirred for 2 h and became clear colorless solution. Then, Woollins' reagent (0.54 g, 1.0 mmol) was added and the mixture was stirred at room temperature for 2 h. Then 1,3-dibromopropane (0.264 g, 1.0 mmol) was added and the mixture was continued stirring for 20 h. After filtered to remove unreacted solid, the crude product obtained on removal of solvent and purified by column chromatography, eluted with dichloromethane to give colorless oil (0.550 g, 73% yield). Selected IR (KBr, cm$^{-1}$): 1510(w), 1476(m), 1436(m), 1385(m), 1104(m), 979(vs), 833(m), 745(m), 688(m), 551(vs), 498(s). $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.95–7.87 (m, 4H, Ar-H), 7.50–7.44 (m, 6H, Ar-H), 7.05 (d, $J$(H,H) = 7.4 Hz, 4H, Ar-H), 4.19–3.80 (m, 8H, $OCH_2$ + $SeCH_2$), 1.76–1.65 (m, 4H, $CH_2$), 1.00–0.94 (m, 6H, $CH_3$) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 136.9 (d, $J$(P,C) = 4.2 Hz), 136.6 (d, $J$(P,C) = 99.7 Hz), 132.4 (d, $J$(P,C) = 3.1 Hz), 130.3 (d, $J$(P,C) = 12.5 Hz), 129.3, 128.6 (d, $J$(P,C) = 14.5 Hz), 68.3 (d, $J$(P,C) = 6.2 Hz, O–C), 35.6 (d, $J$(P,C) = 4.2 Hz, Se–C), 23.3 (d, $J$(P,C) = 9.3 Hz, $CH_2$), 10.3 ($CH_3$) ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 80.2 (s, $J$(P,$Se_{endo}$) = 446 Hz, $J$(P,$Se_{exo}$) = 825 Hz) pm. $^{77}$Se NMR ($CD_2Cl_2$, $\delta$), 412.9 (d, $J$(P,$Se_{endo}$) = 444 Hz), −88.1 (d, $J$(P,$Se_{exo}$) = 825 Hz) ppm. MS (CI$^+$, $m/z$), 774 [M+$NH_4$]$^+$. Accurate mass measurement (CI$^+$MS): 773.8894 [M+$NH_4$]$^+$, calculate mass for [$C_{26}H_{32}O_2P_2Se_4NH_4$]: 773.8898.

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## References

[1] T.S. Lobana, J.C. Wang, C.W. Liu, Coord. Chem. Rev. 251 (2007) 91.
[2] W. Kuchen, B. Knop, Angew. Chem., Int. Ed. 3 (1964) 507.
[3] W. Kuchen, B. Knop, Angew. Chem., Int. Ed. 4 (1965) 244.
[4] R.P. Davies, M.G. Martinelli, Inorg. Chem. 41 (2002) 348.
[5] R.P. Davies, M.G. Martinelli, A.E.H. Wheatley, A.J.P. White, D.J. Williams, Eur. J. Inorg. Chem. (2003) 3409.
[6] R.P. Davies, C.V. Francis, A.P.S. Jurd, M.G. Martinelli, A.J.P. White, D.J. Williams, Inorg. Chem. 43 (2004) 4802.
[7] B.K. Santra, B.J. Liaw, C.M. Hung, C.W. Liu, Inorg. Chem. 42 (2003) 8866.
[8] C.W. Liu, H.C. Chen, J.C. Wang, T.C. Keng, Chem. Commun. (1998) 1831.
[9] C.W. Liu, H.C. Chen, J.C. Wang, T.C. Keng, Chem. Commun. (1999) 995.
[10] C.W. Liu, C.M. Hung, H.C. Chen, J.C. Wang, T.C. Keng, K. Guo, Chem. Commun. 2000 (1897).
[11] C.W. Liu, I.J. Shang, C.M. Hung, J.C. Wang, T.C. Keng, J. Chem. Soc., Dalton Trans. (2002) 1974.
[12] C.W. Liu, C.M. Hung, J.C. Wang, T.C. Keng, J. Chem. Soc., Dalton Trans. (2002) 3482.
[13] C.W. Liu, C.M. Hung, B.K. Santra, J.C. Wang, H.M. Kao, Z. Lin, Inorg. Chem. 42 (2003) 8551.
[14] C.W. Liu, C.M. Hung, B.K. Santra, H.C. Chen, H.H. Hsueh, J.C. Wang, Inorg. Chem. 42 (2003) 3216.
[15] C.W. Liu, C.M. Hung, H.C. Haia, B.J. Liau, L.S. Liou, Y.F. Tsai, J.C. Wang, Chem. Commun. (2003) 976.
[16] G. Hua, J.D. Woollins, Angew. Chem., Int. Ed. 48 (2009) 1368.
[17] C.J.A. Gomez, R.M. Romano, H. Beckers, H. Willner, V.C.O. Della, Inorg. Chem. 49 (2010) 9972.
[18] G. Hua, A.L. Fuller, Y. Li, A.M.Z. Slawin, J.D. Woollins, New J. Chem. 34 (2010) 1565.
[19] M. Abdo, Y. Zhang, V.L. Schramm, Org. Lett. 12 (2010) 2982.
[20] Y. Huang, G. Jahreis, C. Luecke, D. Wildemann, G. Fischer, J. Am. Chem. Soc. 132 (2010) 7578.
[21] G. Hua, A.L. Fuller, A.M.Z. Slawin, J.D. Woollins, Eur. J. Org. Chem. (2010) 2607.
[22] G. Hua, J.B. Henry, Y. Li, A.R. Mount, A.M.Z. Slawin, J.D. Woollins, Org. Biomol. Chem. 8 (2010) 1655.
[23] G. Hua, Q. Zhang, Y. Li, A.M.Z. Slawin, J.D. Woollins, Tetrahedron 65 (2009) 6074.
[24] G. Hua, Y. Li, A.L. Fuller, A.M.Z. Slawin, J.D. Woollins, Eur. J. Org. Chem. (2009) 1612.
[25] G. Hua, A.L. Fuller, A.M.Z. Slawin, J.D. Woollins, Polyhedron 30 (2011) 805.
[26] G. Hua, A.L. Fuller, A.M.Z. Slawin, J.D. Woollins, Eur. J. Org. Chem. (2011) 3067.
[27] G. Hua, J.M. Griffin, S.E. Ashbrook, A.M.Z. Slawin, J.D. Woollins, Angew. Chem., Int. Ed. 50 (2011) 4123.
[28] G. Hua, D.B. Cordes, Y. Li, A.M.Z. Slawin, J.D. Woollins, Tetrahedron Lett. 52 (2011) 3311.
[29] I.P. Gray, P. Bhattacharyya, A.M.Z. Slawin, J.D. Woollins, Chem. Eur. J. 11 (2005) 6221.
[30] I.P. Gray, A.M.Z. Slawin, J.D. Woollins, Dalton Trans. (2005) 2188.
[31] P. Kilian, P. Bhattacharyya, A.M.Z. Slawin, J.D. Woollins, Eur. J. Inorg. Chem. (2003) 1461.
[32] K. Karaghiosoff, K. Eckstein, Phosphorus, Sulfur Silicon Relat. Elem. 75 (1993) 257.
[33] M.J. Pilkington, A.M.Z. Slawin, D.J. William, D.J. Woollins, Heteroatom. Chem. 1 (1990) 351.