Three-Component Reaction between Vinyl Ethers, Secondary Phosphines, and Elemental Selenium: One-Pot Synthesis of 1-(Alkoxy)ethyl and 1-(Aryloxy)ethyl Phosphinodiselenoates

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Abstract: A family of previously unknown phosphinodiselenoic esters containing a selenoacetal moiety, $R^2_2P(=Se)SeCH(Me)OR^1$ (R^1, R^2 = alkyl, aryl, etc.), were synthesized by means of a three-component reaction between the elemental selenium and the corresponding vinyl ether and secondary phosphine. The reaction proceeds readily in 1,4-dioxane at 90 °C for 1–1.5 hours and gives the phosphinodiselenoic esters quantitatively and in an entirely atom-economic manner. The reaction proceeds through electrophilic addition to the electron-rich double bond of the phosphinodiselenoic acids generated in situ.

Key words: phosphines, multicomponent reactions, phosphorus, selenium, phosphinodiselenoate esters

A recently discovered three-component reaction between aryl- or hetarylalkenes, secondary phosphines, and elemental selenium provides an expedient route to novel family of phosphinodiselenoic esters.[1] Compounds of this type are currently attracting an increasing degree of attention as potential candidates for the design of pharmaceuticals[2] or pesticides,[3] as prospective capping agents and selenium sources for the fabrication of selenium-containing nanocrystals,[4,5] as building blocks for organic synthesis,[6] and as selenium-donating ligands for the design of metal complexes (including catalysts).[7] Furthermore, phosphinodiselenoic esters are efficient reagents for living reversible addition–fragmentation chain-transfer (RAFT) polymerization of vinyl monomers.[8] Therefore, the further elaboration of fundamental and practical aspects of this promising multicomponent reaction is a logical step in organoselenophosphorus chemistry.

The aim of this work was to extend the scope of the reaction to vinyl ethers, another large family of functional alkenes of theoretical and synthetic importance, thereby opening a shortcut to hitherto unknown functional phosphinodiselenoic esters containing selenoacetal moieties. The selenoacetals are known to be useful intermediates and building blocks in total syntheses of several biologically significant compounds.[9]

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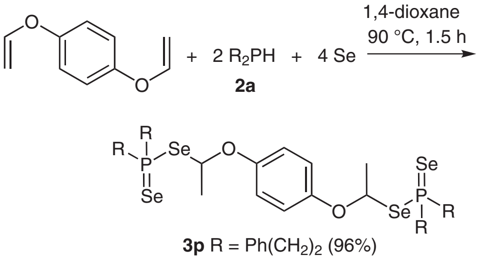
In this context, we studied the reaction of vinyl esters with secondary phosphines and elemental selenium. The choice of vinyl ethers as functional alkenes was partially motivated by their ready availability.[10]

The three-component reaction between vinyl ethers **1a**–**i**, secondary phosphines **2a**–**d**, and elemental selenium proceeded practically quantitatively when the reactants were mixed in a **1**/**2**/Se ratio of 1.05:1:2 in 1,4-dioxane and heated at 90 °C for 1–1.5 h, giving the 1-(alkoxy)ethyl and 1-(aryloxy)ethyl phosphinodiselenoates **3a**–**o** (Table 1). Numerous combinations of various vinyl ethers and secondary phosphines reacted effectively to give the corresponding phosphinodiselenoic esters, demonstrating the general character of the synthesis. Note that vinyl ethers bearing electron-donating substituents and those bearing electron-withdrawing substituents both participated successfully in the three-component reaction.

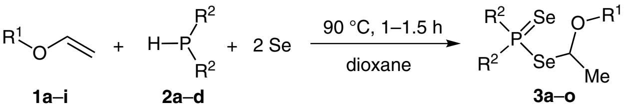
The preparation of bis-ester **3p** in 96% yield from 1,4-bis(vinyloxy)benzene, phosphine **2a**, and elemental selenium under the same conditions provided an additional demonstration of the general nature of this reaction by showing that divinyl ethers participate readily in the synthesis (Scheme 1).



Scheme 1 Synthesis of bisphosphinodiselenoic ester **3p**

The experimental protocol that we developed was also shown to be also applicable to the synthesis of optically active phosphinodiselenoic esters (for example, **3q**) by using vinyl ethers of carbohydrates and their derivatives, such as the vinyl ether of di-*O*-isopropylidene-α-D-glucofuranose **1j**[11] (Scheme 2). It is worth emphasizing that the reaction proceeded chemoselectively at the vinyloxy group of ether **1j**; in other words, both the acetal and sugar moieties tolerate the reaction conditions.

Table 1 Phosphinodiselenoic Esters **3a**–**o** from Vinyl Esters **1a**–**i**, Secondary Phosphines **2a**–**d**, and Elemental Selenium

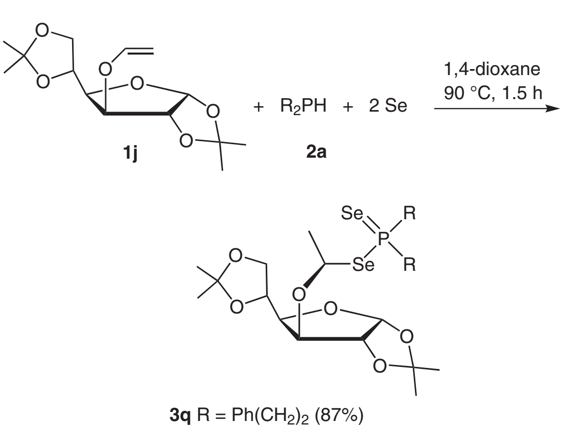


Entry[a]	Ether	R^1	Phosphine	R^2	Product	Yield (%)[b]
1	**1a**	Bu	**2a**	$(CH_2)_2Ph$	**3a**	96
2	**1b**	$(CH_2)_4Me$	**2a**	$(CH_2)_2Ph$	**3b**	94
3	**1c**	CH_2CHEt_2	**2a**	$(CH_2)_2Ph$	**3c**	92
4	**1d**	$CH_2(CF_2)_2H$	**2a**	$(CH_2)_2Ph$	**3d**	97
5	**1e**	$CH_2(CF_2)_4H$	**2a**	$(CH_2)_2Ph$	**3e**	99
6	**1f**	2-furylmethyl	**2a**	$(CH_2)_2Ph$	**3f**	90
7	**1g**	Ph	**2a**	$(CH_2)_2Ph$	**3g**	98
8	**1h**	3-Tol	**2a**	$(CH_2)_2Ph$	**3h**	99
9	**1i**	2,6-$Me_2C_6H_3$	**2a**	$(CH_2)_2Ph$	**3i**	97
10	**1e**	$CH_2(CF_2)_4H$	**2b**	$(CH_2)_2$-4-$MeOC_6H_4$	**3j**	95
11	**1h**	3-Tol	**2b**	$(CH_2)_2$-4-$MeOC_6H_4$	**3k**	91
12	**1g**	Ph	**2c**	2-(2-furyl)ethyl	**3l**	96
13	**1h**	3-Tol	**2c**	2-(2-furyl)ethyl	**3m**	94
14	**1e**	$CH_2(CF_2)_4H$	**2d**	Ph	**3n**	98
15	**1g**	Ph	**2d**	Ph	**3o**	90

[a] Reaction conditions: vinyl ether (**1a**–**i**) (2.1 mmol), secondary phosphine (**2a**–**d**) (2.0 mmol), elemental Se (4.0 mmol), 1,4-dioxane (8 mL), 90 °C, 1–1.5 h. According to the ^{31}P NMR spectra, yields of the compounds **3a**–**o** were near quantitative.

[b] Isolated yields based on phosphines **2a**–**d**.

The synthesized phosphinodiselenoic esters are air- and moisture-stable viscous oils with a shelf life of several months in a closed vessel and they have a particular odor. They are readily soluble in hydrocarbons, diethyl ether, chlorinated solvents, or 1,4-dioxane, but barely soluble in ethanol. Esters **3a**–**q** were characterized by means of their ^1H, ^{13}C, ^{31}P, and ^{77}Se NMR and IR spectra.



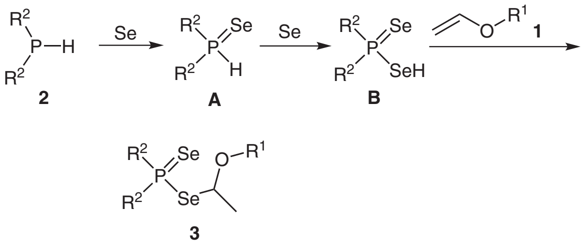
Scheme 2 Synthesis of an optically active phosphinodiselenoic ester **3q**

In the ^1H NMR spectra of products **3a**–**q**, doublets of the methyl protons of the selenoacetal moieties, $SeCH(Me)OR^1$, were observed at $\delta = 1.79–2.17$ ppm with a $^3J_{HH}$ coupling constant of 5.6–6.2 Hz. The multiplets in the region $\delta = 5.41–6.07$ ppm were assigned to the methyne protons of the selenoacetal moieties. In the ^{13}C NMR spectra, the methyl group gave a signal in the region $\delta = 25.3–26.9$ ppm with a $^3J_{CP}$ coupling constant of 2.2–2.9 Hz, whereas the methyne carbon atom resonated at $\delta = 87.4–95.2$ ppm.

Each of the ^{31}P NMR spectra of the synthesized esters showed a sharp singlet at $\delta = 37.51–49.82$ ppm which was accompanied by two sets of ^{77}Se satellites: $^1J_{PSe} = 344–370$ and $^1J_{PSe} = 738–768$ Hz. The couplings with the lower magnitude were assigned to the P–Se single bond, and those of a higher magnitude were assigned to the P=Se double bond.

The ^{77}Se NMR spectra of the phosphinodiselenoates showed two distinct signals: a doublet at $\delta = –237$ to $–156$ ppm with a $^1J_{PSe}$ coupling constant of 738–768 Hz, and a doublet at 310–427 ppm with a $^1J_{PSe}$ coupling constant of 344–370 Hz. These were assigned to the P=Se and P–Se bonds, respectively.

A plausible pathway for the three-component reaction is shown in Scheme 3. The first step involves oxidation of the secondary phosphine **2** with elemental selenium to form the secondary phosphine selenide **A**, which reacts with a second equivalent of elemental selenium to generate the phosphinodiselenoic acid **B**. Subsequent electrophilic addition of the latter to the electron-rich double bond of vinyl ether **1** affords the expected Markovnikov-type adduct, the phosphinodiselenoic ester **3**.



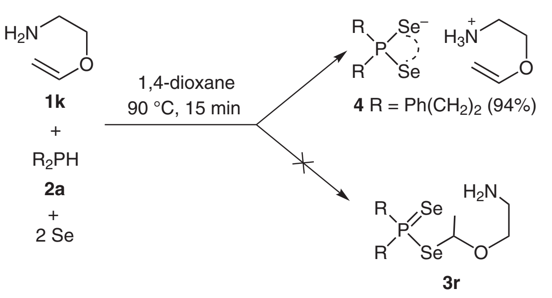
Scheme 3 A plausible mechanism for the three-component reaction between vinyl ethers **1**, secondary phosphines **2**, and elemental selenium

The formation of secondary phosphine selenides **A** from phosphines **2a–d** and elemental selenium has been reported previously.[12] The presence of a secondary phosphine selenide **A** [$R^2 = (CH_2)_2Ph$] in the reaction mixture has been detected by ^{31}P NMR as a singlet at δ = 2 ppm with a $^1J_{PSe}$ coupling constant of 710 Hz,[12a] thus confirms the initial step of the mechanism shown above. The absence of anti-Markovnikov-type adducts in the reaction mixture (^{1}H and ^{31}P NMR data) implies that homolytic addition of the intermediary phosphinodiselenoic acid **B** to vinyl ethers (which might be initiated by the first two redox steps in Scheme 3) does not take place under our conditions. To the best of our knowledge, there are no published reports of electrophilic addition of Se–H acids (either C–SeH or P–SeH acids) to vinyl ethers.

Phosphinodiselenoic acids cannot add directly to vinyl ethers because of the instability of these acids.[13,14] An attempt to synthesize free phosphinodiselenoic acids by oxidation of secondary phosphines with two equivalents of elemental selenium did not give the expected result.[14] Furthermore, acidolysis of alkali metal salts of these acids leads to a mixture of a bis(selenophosphoryl)monoselenide [$Se(Se{=}PR_2)_2$] and -triselenide [$Se_3(Se{=}PR_2)_2$].[13]

Besides, the suggested generation of the intermediary phosphinodiselenoic acids (step two) is in keeping with the result obtained for 2-(vinyloxy)ethylamine (**1k**), which formed salt **4** in 94% yield instead of the expected vinyl-group adduct **3r** (Scheme 4).

Esters **3a–q** are stable up to 120 °C. The expected[10c] elimination of alcohols from these esters to afford the corresponding vinyl esters of the phosphinodiselenoic acids did not take place even at 150 °C in vacuo (10 mmHg) in the presence or the absence of small amount (5 mol%) of 4-toluenesulfonic acid. In the presence of the acid, at least 17 diverse organophosphorus compounds were detectable (^{31}P NMR) in the reaction mixture.



Scheme 4 Synthesis of organoammonium salt **4** bearing a vinyloxy moiety

In conclusion, a three-component reaction of vinyl ethers, secondary phosphines, and elemental selenium was discovered and developed. The reaction can be applied to vinyl ethers containing alkyl, polyfluoroalkyl, aryl, or hetaryl substituents, as well as vinyl ethers of optically active sugar derivatives. The secondary phosphines can be substituted with aryl, arylalkyl, or hetarylalkyl groups.

The reaction provides a general, straightforward, and atom-economic route to a novel family of phosphinodiselenoic esters bearing rare selenoacetal moieties. The synthesized phosphinodiselenoic esters may be useful as capping agents for the preparation of metal selenide nanoparticles, as ligands for metallocomplexes with a range of applications, or as building blocks for drug and pesticide design. The results contribute to the fundamental chemistry of vinyl ethers, organic phosphines, and elemental selenium, as well as to the synthesis of organoselenophosphorus compounds by means of multicomponent reactions.

All reactions were performed under an atmosphere of dry argon. 1,4-Dioxane and Et_2O were dried and freshly distilled from metallic Na before use. Vinyl ethers **1a–c**,[15] **1d**,**e**,[16] **1f**,[17] and **1k**[18] were prepared according to the published methods. Vinyl ethers **1g–i** and the 1,4-bis(vinyloxy)benzene were synthesized by direct vinylation of the corresponding phenol or hydroquinone with acetylene in KOH–DMSO suspension (unpublished data). The optically active vinyl ether **1j** was obtained by direct vinylation of commercial 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose with acetylene.[11] Diphenylphosphine (**2d**) was a commercial product (Aldrich). Secondary phosphines **2a–c** were prepared by a known procedure from red phosphorus and styrene, 4-methoxystyrene, or 2-vinylfuran, respectively.[19] The ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 spectrometer or a Bruker AV-400 spectrometer (400.13, 100.62, 161.98, and 76.31 MHz, respectively) and are referenced to H_3PO_4 (^{31}P NMR) or Me_2Se (^{77}Se NMR). Chemical shifts (δ) are expressed in ppm downfield from HMDS as an internal standard. Fourier-transform IR spectra were recorded on a Bruker Vertex 70 spectrometer. Optical rotations were measured on a Polamat A polarimeter at 23 °C. Microanalyses were performed on a Flash EA 1112 Series elemental analyzer.

Phosphinodiselenoate Esters 3a–o; General Procedure

Vinyl ester **1a–i** (2.1 mmol) and powdered gray Se (316 mg, 4.0 mmol) were added consecutively to a soln of secondary phosphine **2a–d** (2.0 mmol) in 1,4-dioxane (8 mL) at r.t. The suspension was stirred at 90 °C until the Se residue dissolved (~1–1.5 h) to give a clear yellow soln. The solvent was removed under reduced pressure (50–60 °C, 1 Torr), and the residue was purified by flash chromatography [alumina (3 cm), hexane]; yield: 90–99%.

The bisphosphinodiselenoic diester **3p** was synthesized by the same protocol from 1,4-bis(vinyloxy)benzene (162.2 mg, 1.0 mmol).

1-(Butoxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3a)

Yield: 961 mg (96%); colorless oil.

IR (film): 3105, 3085, 3062, 3027, 2927, 2870, 1602, 1584, 1496, 1453, 1396, 1374, 1331, 1288, 1254, 1222, 1198, 1178, 1154, 1119, 1094, 1072, 1047, 1030, 1006, 965, 945, 907, 882, 874, 836, 747, 698, 613, 577 (P=Se), 556 (P–Se), 467 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 0.91 (t, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, 3 H, *Me*CH$_2$), 1.41 (m, 2 H, C*H*$_2$Me), 1.59 (m, 2 H, C*H*$_2$Et), 1.98 (d, $^{3}J_{\mathrm{HH}}$ = 6.0 Hz, 3 H, *Me*CH), 2.46–2.53 (m, 4 H, CH$_2$P), 2.99–3.26 (m, 4 H, C*H*$_2$Ph), 3.64 and 3.91 (dt, $^{3}J_{\mathrm{HH}}$ = 6.4 and 6.6 Hz, $^{2}J_{\mathrm{HH}}$ = 16.0 Hz, 2 H, CH$_2$O), 5.84 (m, 1 H, CHSe), 7.14–7.30 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 13.5 (*Me*CH$_2$), 19.1 (*C*H$_2$Me), 26.4 (d, $^{3}J_{\mathrm{PC}}$ = 2.9 Hz, *Me*CH), 29.9 and 30.2 (*C*H$_2$Ph), 31.1 (*C*H$_2$Et), 39.8 and 40.2 (d, $^{1}J_{\mathrm{PC}}$ = 38.7 and 37.0 Hz, CH$_2$P), 69.5 (CH$_2$O), 95.2 (CHSe), 126.1, 126.2, 127.3, 127.5, 128.3, 128.4 (*o-, m-, p*-C, Ph), 140.7 (d, $^{3}J_{\mathrm{PC}}$ = 13.2 Hz, *i*-C, Ph).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 45.38 (s, $^{1}J_{\mathrm{P–Se}}$ = 361 Hz, $^{1}J_{\mathrm{P=Se}}$ = 755 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –230 (d, $^{1}J_{\mathrm{P=Se}}$ = 755 Hz), 390 (d, $^{1}J_{\mathrm{P–Se}}$ = 361 Hz).

Anal. Calcd for $C_{22}H_{31}OPSe_2$: C, 52.81; H, 6.24; P, 6.19; Se, 31.56. Found: C, 52.74; H, 6.19; P, 6.11; Se, 31.63.

1-(Pentyloxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3b)

Yield: 967 mg (94%); yellowish oil.

IR (film): 3106, 3085, 3062, 3028, 2950, 2926, 2873, 1603, 1585, 1490, 1453, 1394, 1335, 1276, 1254, 1223, 1203, 1174, 1156, 1121, 1095, 1057, 1003, 962, 872, 835, 746, 699, 614, 575 (P=Se), 554 (P–Se), 467 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 0.87 (t, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, 3 H, *Me*CH$_2$), 1.27–1.37 (m, 4 H, (C*H*$_2$)$_2$Me), 1.48–1.55 (m, 2 H, C*H*$_2$Pr), 1.93 (d, $^{3}J_{\mathrm{HH}}$ = 6.1 Hz, 3 H, *Me*CH), 2.50–2.69 (m, 4 H, CH$_2$P), 2.87–3.15 (m, 4 H, C*H*$_2$Ph), 3.53 and 3.91 (dt, $^{3}J_{\mathrm{HH}}$ = 6.8 and 6.6 Hz, $^{2}J_{\mathrm{HH}}$ = 15.9 Hz, 2 H, CH$_2$O), 5.43 (m, 1 H, CHSe), 7.14–7.30 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 13.3 (*Me*CH$_2$), 21.7 (*C*H$_2$Me), 23.4 (*C*H$_2$Et), 26.4 (d, $^{3}J_{\mathrm{PC}}$ = 2.8 Hz, *Me*CH), 29.7 and 30.2 (*C*H$_2$Ph), 31.3 (*C*H$_2$Pr), 40.0 and 40.5 (d, $^{1}J_{\mathrm{PC}}$ = 38.0 and 37.6 Hz, CH$_2$P), 69.7 (CH$_2$O), 94.9 (CHSe), 125.5, 125.6, 127.9, 128.1, 128.4 (*o-, m-, p*-C, Ph), 140.6 (d, $^{3}J_{\mathrm{PC}}$ = 14.7 Hz, *i*-C, Ph).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 46.85 (s, $^{1}J_{\mathrm{P–Se}}$ = 362 Hz, $^{1}J_{\mathrm{P=Se}}$ = 751 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –237 (d, $^{1}J_{\mathrm{P=Se}}$ = 751 Hz), 387 (d, $^{1}J_{\mathrm{P–Se}}$ = 362 Hz).

Anal. Calcd for $C_{23}H_{33}OPSe_2$: C, 53.70; H, 6.47; P, 6.02; Se, 30.70. Found: C, 54.12; H, 6.51; P, 5.83; Se, 30.86.

1-(2-Ethylbutoxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3c)

Yield: 972 mg (92%); yellowish oil.

IR (film): 3107, 3086, 3064, 3028, 2961, 2926, 2875, 1603, 1585, 1486, 1395, 1379, 1338, 1262, 1237, 1225, 1211, 1169, 1122, 1098, 1054, 963, 915, 901, 863, 839, 747, 698, 633, 576 (P=Se), 554 (P–Se), 466 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 0.88 (t, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, 6 H, *Me*CH$_2$), 1.34–1.50 [m, 5 H, C*H*(C*H*$_2$Me)$_2$], 1.94 (d, $^{3}J_{\mathrm{HH}}$ = 6.1 Hz, 3 H, *Me*CH), 2.55–2.64 (m, 4 H, CH$_2$P), 2.92–3.06 (m, 4 H, C*H*$_2$Ph), 3.50 and 3.66 (dt, $^{3}J_{\mathrm{HH}}$ = 5.0 and 5.9 Hz, $^{2}J_{\mathrm{HH}}$ = 9.4 Hz, 2 H, CH$_2$O), 5.41 (m, 1 H, CHSe), 7.20–7.28 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 11.5 (Me), 23.7 (*C*H$_2$Me), 26.3 (d, $^{3}J_{\mathrm{PC}}$ = 2.7 Hz, *Me*CH), 29.3 and 29.5 (*C*H$_2$Ph), 39.8 and 40.5 (d, $^{1}J_{\mathrm{PC}}$ = 38.7 and 37.0 Hz, CH$_2$P), 41.1 (*C*HEt), 72.5 (CH$_2$O), 93.7 (CHSe), 126.6, 126.7, 127.67, 127.7, 128.8, and 128.9 (*o-, m-, p*-C, Ph), 140.8 (d, $^{3}J_{\mathrm{PC}}$ = 12.8 Hz, *i*-C, Ph).

^{31}P NMR (100.62 MHz, CDCl$_3$): δ = 47.01 (s, $^{1}J_{\mathrm{P–Se}}$ = 364 Hz, $^{1}J_{\mathrm{P=Se}}$ = 749 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –232 (d, $^{1}J_{\mathrm{P=Se}}$ = 749 Hz), 386 (d, $^{1}J_{\mathrm{P–Se}}$ = 364 Hz).

Anal. Calcd for $C_{24}H_{35}OPSe_2$: C, 54.55; H, 6.68; P, 5.86; Se, 29.88. Found: C, 54.52; H, 6.51; P, 5.63; Se, 30.06.

1-(2,2,3,3-Tetrafluoropropoxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3d)

Yield: 1180 mg (97%); yellowish oil.

IR (film): 3085, 3062, 3027, 2926, 2856, 1646, 1603, 1587, 1496, 1453, 1400, 1379, 1276, 1231, 1203, 1104, 1003, 943, 895, 874, 835, 746, 699, 613, 575 (P=Se), 554 (P–Se), 467 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.93 (d, $^{3}J_{\mathrm{HH}}$ = 6.1 Hz, 3 H, *Me*CH), 2.53–2.65 (m, 4 H, CH$_2$P), 2.85–3.03 (m, 4 H, C*H*$_2$Ph), 4.18 (m, 2 H, CH$_2$O), 5.47 (m, 1 H, CHSe), 5.86 (tt, $^{2}J_{\mathrm{HF}}$ = 53.3 Hz, $^{3}J_{\mathrm{HH}}$ = 5.4 Hz, 1 H, CF$_2$H), 7.16–7.28 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 25.8 (*Me*CH), 30.0 and 30.1 (*C*H$_2$Ph), 39.5 and 40.4 (d, $^{1}J_{\mathrm{PC}}$ = 36.6 and 37.2 Hz, CH$_2$P), 65.9 (t, $^{2}J_{\mathrm{CF}}$ = 28.8 Hz, CH$_2$O), 92.8 (CHSe), 109.0 (tt, $^{1}J_{\mathrm{CF}}$ = 248.0 Hz, $^{2}J_{\mathrm{CF}}$ = 34.3 Hz, CF$_2$H), 114.4 (tt, $^{1}J_{\mathrm{CF}}$ = 256.50 Hz, $^{2}J_{\mathrm{CF}}$ = 29.85 Hz, CF$_2$), 126.6, 126.6, 128.3, and 128.7 (*o-, m-, p*-C, Ph), 139.8 (d, $^{3}J_{\mathrm{PC}}$ = 17.0 Hz, *i*-C, Ph).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 48.61 (s, $^{1}J_{\mathrm{P–Se}}$ = 349 Hz, $^{1}J_{\mathrm{P=Se}}$ = 748 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –225 (d, $^{1}J_{\mathrm{P=Se}}$ = 748 Hz), 323 (d, $^{1}J_{\mathrm{P–Se}}$ = 349 Hz).

Anal. Calcd for $C_{22}H_{25}F_6OPSe_2$: C, 43.44; H, 4.14; F, 18.74; P, 5.09; Se, 25.96. Found: C, 43.52; H, 4.51; F, 18.80; P, 5.23; Se, 25.86.

1-[(2,2,3,3,4,4,5,5-Octafluoropentyl)oxy]ethyl Bis(2-phenylethyl)phosphinodiselenoate (3e)

Yield: 1303 mg (99%); yellowish oil.

IR (film): 3087, 3064, 3028, 2928, 2860, 1603, 1585, 1497, 1454, 1400, 1379, 1360, 1325, 1287, 1228, 1204, 1173, 1131, 1096, 1044, 1031, 991, 956, 946, 904, 876, 838, 809, 748, 698, 631, 614, 576, 567 (P=Se), 548 (P–Se), 466 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.97 (d, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, 3 H, *Me*CH), 2.51–2.71 (m, 4 H, CH$_2$P), 2.82–3.13 (m, 4 H, C*H*$_2$Ph), 4.12–4.20 (m, 2 H, CH$_2$O), 5.50 (m, 1 H, CHSe), 6.02 (tt, $^{2}J_{\mathrm{HF}}$ = 51.9 Hz, $^{3}J_{\mathrm{HH}}$ = 5.4 Hz, 1 H, CF$_2$H), 7.16–7.31 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 25.7 (d, $^{1}J_{\mathrm{PC}}$ = 2.6 Hz, *Me*CH), 29.9 and 30.0 (*C*H$_2$Ph), 39.3 and 40.3 (d, $^{1}J_{\mathrm{PC}}$ = 37.2 and 36.8 Hz, CH$_2$P), 65.7 (t, $^{3}J_{\mathrm{CF}}$ = 26.0 Hz, CH$_2$O), 93.0 (CHSe), 107.5 (tt, $^{1}J_{\mathrm{CF}}$ = 255.40 Hz, $^{2}J_{\mathrm{CF}}$ = 29.85 Hz, CF$_2$H), 109.7–113.5 (m, CF$_2$CF$_2$), 114.8 (tt, $^{1}J_{\mathrm{CF}}$ = 256.50 Hz, $^{2}J_{\mathrm{CF}}$ = 29.85 Hz, CF$_2$), 126.5, 126.6, 128.2, 128.2, 128.6, and 128.6 (*o*-, *m*-, *p*-C, Ph), 139.6 (d, $^{3}J_{\mathrm{PC}}$ = 16.6 Hz, *i*-C, Ph).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 49.30 (s, $^1J_{\text{P–Se}}$ = 344 Hz, $^1J_{\text{P=Se}}$ = 754 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –237 (d, $^1J_{\text{P=Se}}$ = 754 Hz), 327 (d, $^1J_{\text{P–Se}}$ = 344 Hz).

Anal. Calcd for $C_{23}H_{25}F_8OPSe_2$: C, 41.96; H, 3.83; F, 23.09; P, 4.70; Se, 23.99. Found: C, 41.54; H, 3.68; F, 22.89; P, 4.78; Se, 23.65.

1-(2-Furylmethyloxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3f)

Yield: 944 mg (90%); yellowish oil.

IR (film): 3109, 3084, 3061, 3026, 2923, 2860, 1603, 1497, 1453, 1396, 1377, 1328, 1267, 1223, 1150, 1100, 1016, 945, 921, 902, 852, 816, 745, 699, 599 (P=Se), 575 (P–Se), 467 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.99 (d, $^3J_{\text{HH}}$ = 6.2 Hz, 3 H, *Me*CH), 2.61–2.73 (m, 4 H, CH$_2$P), 2.97–3.11 (m, 4 H, C*H*$_2$Ph), 4.63 and 4.76 (d, $^2J_{\text{HH}}$ = 12.4 Hz, 2 H, CH$_2$O), 5.62 (m, 1 H, CHSe), 6.35 (dd, $^3J_{\text{HH}}$ = 1.9 Hz, $^3J_{\text{HH}}$ = 3.1 Hz, 1 H, H^4 in Fur), 6.44 (d, $^3J_{\text{HH}}$ = 3.1 Hz, 1 H, H^3 in Fur), 7.14–7.30 (m, 10 H, Ph), 7.37 (s, 1 H, H^5 in Fur).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 26.4 (d, $^3J_{\text{PC}}$ = 2.9 Hz, *Me*CH), 29.8 and 30.1 (*C*H$_2$Ph), 39.6 and 39.7 (d, $^1J_{\text{PC}}$ = 36.5 and 37.2 Hz, CH$_2$P), 63.3 (CH$_2$O), 92.7 (CHSe), 110.0, 110.2 (C^{3,4} in Fur), 126.4, 128.2, 128.5 (o-, *m*-, *p*-C, Ph), 139.8 (d, $^3J_{\text{PC}}$ = 17.3 Hz, *i*-C, Ph), 142.9 and 150.0 (C^{2,5} in Fur).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 47.30 (s, $^1J_{\text{P–Se}}$ = 358 Hz, $^1J_{\text{P=Se}}$ = 750 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –228 (d, $^1J_{\text{P=Se}}$ = 750 Hz), 310 (d, $^1J_{\text{P–Se}}$ = 358 Hz).

Anal. Calcd for $C_{23}H_{27}O_2PSe_2$: C, 52.68; H, 5.19; P, 5.91; Se, 30.12. Found: C, 52.45; H, 5.28; P, 5.78; Se, 30.20.

1-Phenoxyethyl Bis(2-phenylethyl)phosphinodiselenoate (3g)

Yield: 1020 mg (98%); yellowish oil.

IR (film): 3085, 3061, 3027, 2922, 2853, 1592, 1495, 1454, 1395, 1377, 1334, 1291, 1234, 1213, 1174, 1154, 1092, 1072, 1028, 1005, 929, 908, 874, 836, 796, 753, 695, 613, 576, 565 (P=Se), 512 (P–Se), 466 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.13 (d, $^3J_{\text{HH}}$ = 6.1 Hz, 3 H, *Me*CH), 2.34–2.40, 2.51–2.56 (m, 4 H, CH$_2$P), 2.71–3.07 (m, 4 H, C*H*$_2$Ph), 6.04 (m, 1 H, CHSe), 7.05 (m, 3 H, PhO), 7.17–7.33 (m, 12 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 26.2 (d, $^3J_{\text{PC}}$ = 2.9 Hz, *Me*CH), 29.6 and 29.8 (*C*H$_2$Ph), 38.6 and 39.6 (d, $^1J_{\text{PC}}$ = 37.6 and 35.8 Hz, CH$_2$P), 89.1 (CHSe), 117.9, 122.8 (*o*-, *p*-C, PhO), 126.1, 126.2, 127.9, 128.0, 128.2, and 128.4 (*o*-, *m*-, *p*-C, Ph), 129.1 (*m*-C, PhO), 139.7 (d, $^3J_{\text{PC}}$ = 17.0 Hz, *i*-C, Ph), 155.65 (*i*-C, PhO).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 48.59 (s, $^1J_{\text{P–Se}}$ = 354 Hz, $^1J_{\text{P=Se}}$ = 744 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –233 (d, $^1J_{\text{P=Se}}$ = 744 Hz), 326 (d, $^1J_{\text{P–Se}}$ = 354 Hz).

Anal. Calcd for $C_{24}H_{27}OPSe_2$: C, 55.40; H, 5.23; P, 5.95; Se, 30.35. Found: C, 55.70; H, 5.11; P, 6.27; Se, 30.56.

1-(3-Methylphenoxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3h)

Yield: 1058 mg (99%); yellowish oil.

IR (film): 3060, 3027, 2965, 2922, 2859, 2735, 2676, 2603, 1947, 1891, 1806, 1735, 1603, 1587, 1492, 1452, 1396, 1377, 1337, 1288, 1256, 1217, 1086, 1011, 948, 894, 871, 745, 696, 619, 571 (P=Se), 548 (P–Se), 467 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.16 (d, $^3J_{\text{HH}}$ = 6.1 Hz, 3 H, *Me*CH), 2.36 (s, 3 H, *Me*C$_6$H$_4$), 2.38–2.41 and 2.56–2.59 (m, 4 H, C*H*$_2$Ph), 2.78–3.09 (m, 4 H, CH$_2$P), 6.07 (m, 1 H, CHSe), 6.86 (d, ^3J = 7.4 Hz, 1 H, H^4 in C$_6$H$_4$), 7.02 (d, ^3J = 8.1 Hz, 1 H, H^5 in C$_6$H$_4$), 7.06–7.10 (m, 2 H, H^{2,6} in C$_6$H$_4$), 7.29–7.35 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 20.9 (*Me*C$_6$H$_4$), 26.0 (d, $^3J_{\text{PC}}$ = 2.6 Hz, *Me*CH), 29.5 and 29.7 (d, $^3J_{\text{PC}}$ = 2.6 and 2.2 Hz, *C*H$_2$Ph), 38.4 and 39.3 (d, $^1J_{\text{PC}}$ = 37.7 and 35.4 Hz, CH$_2$P), 88.9 (CHSe), 114.7, 118.4, and 123.5 (C^{2,4,6} in C$_6$H$_4$), 125.9, 126.1, 127.8, 127.9, 128.1, and 128.2 (*o*-, *m*-, *p*-C, Ph), 128.7, 139.0 (C^{3,5} in C$_6$H$_4$), 139.7 (d, $^3J_{\text{PC}}$ = 11.4 Hz, *i*-C, Ph), 155.4 (C^1 in C$_6$H$_4$).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 47.10 (s, $^1J_{\text{P–Se}}$ = 358 Hz, $^1J_{\text{P=Se}}$ = 744 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –233 (d, $^1J_{\text{P=Se}}$ = 744 Hz), 325 (d, $^1J_{\text{P–Se}}$ = 358 Hz).

Anal. Calcd for $C_{25}H_{29}OPSe_2$: C, 56.19; H, 5.47; P, 5.80; Se, 29.55. Found: C, 56.02; H, 5.58; P, 5.90; Se, 29.42.

1-(2,6-Dimethylphenoxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3i)

Yield: 1064 mg (97%); yellowish oil.

IR (film): 3084, 3061, 3026, 2951, 2921, 2857, 1602, 1495, 1473, 1453, 1397, 1375, 1327, 1261, 1240, 1190, 1129, 1082, 1030, 1000, 945, 918, 837, 815, 769, 747, 699, 579 (P=Se), 546 (P–Se), 524, 467 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.17 (d, $^3J_{\text{HH}}$ = 6.1 Hz, 3 H, *Me*CH), 2.28–2.58 (m, 10 H, CH$_2$P, 2,6-*Me*$_2$C$_6$H$_3$), 2.88–3.04 (m, 4 H, C*H*$_2$Ph), 5.93 (m, 1 H, CHSe), 6.81 (d, ^3J = 7.5 Hz, 1 H, H^4 in C$_6$H$_3$), 6.95 (d, ^3J = 7.5 Hz, 2 H, H^{3,5} in C$_6$H$_3$), 7.16–7.32 (m, 10 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 17.5 (*Me*C$_6$H$_3$), 26.2 (*Me*CH), 29.7 (*C*H$_2$Ph), 37.8 and 37.9 (d, $^1J_{\text{PC}}$ = 38.3 and 34.9 Hz, CH$_2$P), 93.7 (CHSe), 124.6 and 126.3 (C^{3,4,5} in C$_6$H$_3$), 128.2, 128.4, 128.5 and 129.0 (*o*-, *m*-, *p*-C, Ph), 130.7 (C^{2,6} in C$_6$H$_3$), 139.9 (t, ^3J = 17.3 Hz, *i*-C, Ph), 153.1 (C^1 in C$_6$H$_3$).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 49.82 (s, $^1J_{\text{P–Se}}$ = 360 Hz, $^1J_{\text{P=Se}}$ = 738 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –231 (d, $^1J_{\text{P=Se}}$ = 738 Hz), 328 (d, $^1J_{\text{P–Se}}$ = 360 Hz).

Anal. Calcd for $C_{26}H_{31}OPSe_2$: C, 56.94; H, 5.70; P, 5.65; Se, 28.80. Found: C, 56.45; H, 5.88; P, 5.72; Se, 28.75.

1-[(2,2,3,3,4,4,5,5-Octafluoropentyl)oxy]ethyl Bis[2-(4-Methoxyphenyl)ethyl]phosphinodiselenoate (3j)

Yield: 1368 mg (95%); yellowish oil.

IR (film): 3080, 3062, 2999, 2932, 2838, 1612, 1584, 1513, 1462, 1445, 1401, 1300, 1247, 1175, 1130, 1097, 1036, 992, 954, 901, 874, 816, 734, 635, 579 (P=Se), 549 (P–Se), 480 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.94 (d, $^3J_{\text{HH}}$ = 5.6 Hz, 3 H, *Me*CH), 2.46–2.56 (m, 4 H, CH$_2$P), 2.79–2.96 (m, 4 H, C*H*$_2$Ph), 3.74 (s, 6 H, MeO), 4.12–4.17 (m, 2 H, CH$_2$O), 5.48 (m, 1 H, CHSe), 6.00 (tt, $^2J_{\text{HF}}$ = 52.2 Hz, $^3J_{\text{HH}}$ = 5.4 Hz, 1 H, HCF$_2$), 6.79 (m, 4 H, H^{2,6} in C$_6$H$_4$), 6.08 (m, 4 H, H^{3,5} in C$_6$H$_4$).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 25.7 (*Me*CH), 29.2 (*C*H$_2$C$_6$H$_4$), 39.5 and 40.3 (d, $^1J_{\text{PC}}$ = 36.1 Hz, CH$_2$P), 55.2 (MeO), 65.7 (t, $^3J_{\text{CF}}$ = 25.8 Hz, *C*H$_2$CF$_2$), 92.8 (CHSe), 107.6 (tt, $^1J_{\text{CF}}$ = 253.1 Hz, $^2J_{\text{CF}}$ = 30.5 Hz, CF$_2$H), 108.1–114.1 (m, CF$_2$CF$_2$), 115.2 (tt, $^1J_{\text{CF}}$ = 256.5 Hz, $^2J_{\text{CF}}$ = 30.9 Hz, CF$_2$), 114.1, 129.2 (C^{2,3,5,6} in C$_6$H$_4$), 131.6, 131.8 (d, $^3J_{\text{PC}}$ = 16.6 Hz, C^1 in C$_6$H$_4$), 158.3 (C^4 in C$_6$H$_4$).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 48.38 (s, $^1J_{\text{P–Se}}$ = 348 Hz, $^1J_{\text{P=Se}}$ = 746 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –225 (d, $^1J_{P=Se}$ = 746 Hz), 323 (d, $^1J_{P–Se}$ = 348 Hz).

Anal. Calcd for $C_{25}H_{29}F_8O_3PSe_2$: C, 41.80; H, 4.07; F, 21.16; P, 4.31; Se, 21.98. Found: C, 41.53; H, 4.12; F, 21.45; P, 4.15; Se, 21.62.

1-(3-Methylphenoxy)ethyl Bis[2-(4-methoxyphenyl)ethyl]phosphinodiselenoate (3k)

Yield: 1082 mg (91%); yellowish oil.

IR (film): 3029, 2995, 2951, 2927, 2854, 2835, 1610, 1586, 1512, 1490, 1458, 1445, 1377, 1300, 1247, 1176, 1159, 1129, 1085, 1035, 949, 871, 820, 781, 732, 692, 614, 550 (P=Se), 519 P–Se), 495, 477, 449 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.07 (d, $^3J_{HH}$ = 5.6 Hz, 3 H, *Me*CH), 2.27 (s, 3 H, *Me*C$_6$H$_4$), 2.27–2.29 and 2.40–2.44 (m, 4 H, CH$_2$P), 2.57–2.66 (m, 1 H, C*H*$_2$C$_6$H$_4$), 2.74–2.98 (m, 3 H, C*H*$_2$C$_6$H$_4$), 3.74 (s, 6 H, MeO), 5.98 (m, 1 H, CHSe), 6.79–7.08 (m, 12 H, Ar).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 21.3 (*Me*C$_6$H$_4$), 26.4 (d, $^3J_{PC}$ = 2.2 Hz, *Me*CH), 29.0 and 29.2 (*C*H$_2$C$_6$H$_4$), 39.4 and 40.2 (d, $^1J_{PC}$ = 36.8 and 34.6 Hz, CH$_2$P), 55.2 (MeO), 89.0 (CHSe), 113.9, 114.0, 115.1, 118.8, 123.8, 129.1, and 129.2 (Ar), 132.04 (d, $^3J_{PC}$ = 16.9 Hz, *i*-C, C$_6$H$_4$), 139.4, 155.9, and 158.1 (Ar).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 46.99 (s, $^1J_{P–Se}$ = 357 Hz, $^1J_{P=Se}$ = 742 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –230 (d, $^1J_{P=Se}$ = 742 Hz), 325 (d, $^1J_{P–Se}$ = 357 Hz).

Anal. Calcd for $C_{27}H_{33}O_3PSe_2$: C, 54.55; H, 5.60; P, 5.21; Se, 26.57. Found: C, 54.62; H, 5.58; P, 5.26; Se, 26.71.

1-Phenoxyethyl Bis[2-(2-furyl)ethyl]phosphinodiselenoate (3l)

Yield: 961 mg (96%); yellowish oil.

IR (film): 3149, 3114, 3061, 3040, 2967, 2921, 2854, 1720, 1655, 1593, 1505, 1490, 1437, 1398, 1378, 1333, 1290, 1232, 1213, 1174, 1147, 1091, 1073, 1007, 917, 886, 850, 798, 753, 733, 692, 638, 599 (P=Se), 564 (P–Se), 512, 479, 419 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.05 (d, $^3J_{HH}$ = 6.1 Hz, 3 H, *Me*CH), 2.29–2.35 and 2.43–2.54 (m, 4 H, CH$_2$P), 2.64–2.75 and 2.80–3.07 (m, 4 H, C*H*$_2$Fur), 5.90 (d, ^3J = 3.1 Hz, 1 H, H^3 in Fur), 5.93 (m, 1 H, CHSe), 6.00 (d, $^3J_{HH}$ = 2.9 Hz, 1 H, H^3 in Fur), 6.22 and 6.25 (s, 2 H, H^4 in Fur), 7.01 (t, ^3J = 7.3 Hz, 1 H, H^4 in Ph), 7.10 (d, ^3J = 7.3 Hz, 2 H, H^4 in Ph), 7.12–7.29 (m, 4 H, Ph, H^5 in Fur).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 22.8 (d, $^3J_{PC}$ = 19.4 Hz, *C*H$_2$Fur), 26.3 (*Me*CH) 35.1 and 36.1 (d, $^1J_{PC}$ = 40.1 and 37.6 Hz, CH$_2$P), 89.6 (CHSe), 105.9, 105.9, 110.3 and 110.3 (C^{3,4} in Fur), 118.3, 123.2, and 129.4 (*o*-, *m*-, *p*-C, Ph), 141.3 and 141.4 (C^5 in Fur), 153.0 and 153.2 (C^{2,5} in Fur), 155.9 (*i*-C, Ph).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 47.38 (s, $^1J_{P–Se}$ = 356 Hz, $^1J_{P=Se}$ = 754 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –237 (d, $^1J_{P=Se}$ = 754 Hz), 323 (d, $^1J_{P–Se}$ = 356 Hz).

Anal. Calcd for $C_{20}H_{23}O_3PSe_2$: C, 48.02; H, 4.63; P, 6.19; Se, 31.57. Found: C, 48.33; H, 4.35; P, 6.15; Se, 31.62.

1-(3-Methylphenoxy)ethyl Bis[2-(2-furyl)ethyl]phosphinodiselenoate (3m)

Yield: 968 mg (94%); yellowish oil.

IR (film): 3145, 3115, 3035, 2969, 2921, 2857, 1589, 1506, 1489, 1438, 1399, 1378, 1333, 1288, 1257, 1230, 1217, 1171, 1151, 1086, 1009, 950, 915, 885, 856, 796, 782, 732, 691, 638, 599 (P=Se), 567 (P–Se), 499, 479 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.03 (d, $^3J_{HH}$ = 6.1 Hz, 3 H, *Me*CH), 2.28 (s, 3 H, *Me*C$_6$H$_4$), 2.25–2.31 and 2.41–2.51 (m, 4 H, CH$_2$P), 2.61–2.72 and 2.80–3.06 (m, 4 H, C*H*$_2$Fur), 5.88–5.91 (m, 2 H, CHSe, H^3 in Fur), 5.99 (d, $^3J_{HH}$ = 1.8 Hz, 1 H, H^3 in Fur), 6.20–6.24 (m, 2 H, H^4 in Fur), 6.80 (d, $^3J_{HH}$ = 7.5 Hz, 1 H, H^4 in C$_6$H$_4$), 6.88 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, H^6 in C$_6$H$_4$), 6.94 (s, 1 H, H^2 in C$_6$H$_4$), 7.13 (t, ^3J = 7.5 Hz, 1 H, H^5 in C$_6$H$_4$), 7.23 and 7.26 (s, 2 H, H^5 in Fur).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 21.1 (*Me*C$_6$H$_4$), 22.5 and 22.7 (*C*H$_2$Fur), 26.2 (d, $^3J_{PC}$ = 2.6 Hz, *Me*CH), 34.8 and 35.8 (d, $^1J_{PC}$ = 39.8 and 37.6 Hz, CH$_2$P), 89.5 (CHSe), 105.5, 105.7, 110.0 and 110.1 (C^{3,4} in Fur), 115.0, 118.6, 123.7, 128.9, and 139.2 (C^{2,3,4,5,6} in C$_6$H$_4$), 141.1 and 141.2 (C^5 in Fur), 152.7, 152.9 (C^2 in Fur), 155.5 (C^1 in C$_6$H$_4$).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 46.13 (s, $^1J_{P–Se}$ = 361 Hz, $^1J_{P=Se}$ = 746 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –236 (d, $^1J_{P=Se}$ = 746 Hz), 324 (d, $^1J_{P–Se}$ = 361 Hz).

Anal. Calcd for $C_{21}H_{25}O_3PSe_2$: C, 49.04; H, 4.90; P, 6.02; Se, 30.70. Found: C, 49.23; H, 4.85; P, 6.12; Se, 30.68.

1-[(2,2,3,3,4,4,5,5-Octafluoropentyl)oxy]ethyl Diphenylphosphinodiselenoate (3n)

Yield: 1179 mg (98%); yellowish oil.

IR (film): 3145, 3056, 2972, 2928, 2883, 2859, 1479, 1437, 1403, 1378, 1331, 1308, 1287, 1228, 1173, 1131, 1092, 1044, 1029, 996, 958, 902, 809, 747, 691, 618, 575 (P=Se), 542 (P–Se), 502, 475, 420 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.89 (d, $^3J_{HH}$ = 5.8 Hz, 3 H, *Me*CH), 3.93 (t, $^3J_{HH}$ = 13.8 Hz, 2 H, CH$_2$O), 5.57 (m, 1 H, CHSe), 6.00 (tt, $^2J_{HF}$ = 52.2 Hz, $^3J_{HH}$ = 5.4 Hz, 1 H, HCF$_2$), 7.48 (m, 6 H, H^{3,4,5} in Ph), 7.87 (m, 2 H, H^6 in Ph), 7.99 (m, 2 H, H^2 in Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 25.3 (*Me*CH), 65.9 (t, $^3J_{CF}$ = 26.2 Hz, CH$_2$O), 92.0 (CHSe), 107.5 (tt, $^1J_{CF}$ = 254.7 Hz, $^2J_{CF}$ = 30.6 Hz, CF$_2$H), 110.3–114.1 (m, CF$_2$CF$_2$), 114.74 (tt, $^1J_{CF}$ = 256.5 Hz, $^2J_{CF}$ = 29.8 Hz, CF$_2$), 128.7, 131.7, 132.0 (*o*-, *m*-, *p*-C, Ph), 133.7 (d, $^3J_{PC}$ = 41.3 Hz, *i*-C, Ph), 134.4 (d, $^3J_{PC}$ = 43.1 Hz, *i*-C, Ph).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 39.05 (s, $^1J_{P–Se}$ = 361 Hz, $^1J_{P=Se}$ = 768 Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –164 (d, $^1J_{P=Se}$ = 768 Hz), 419 (d, $^1J_{P–Se}$ = 361 Hz).

Anal. Calcd for $C_{19}H_{17}F_8OPSe_2$: C, 37.89; H, 2.85; F, 25.24; P, 5.14; Se, 26.22. Found: C, 37.94; H, 2.72; F, 25.44; P, 5.35; Se, 26.08.

1-(Phenoxy)ethyl Diphenylphosphinodiselenoate (3o)

Yield: 836 mg (90%); yellowish oil.

IR (film): 3086, 3050, 2975, 2923, 2852, 2799, 2720, 1591, 1490, 1481, 1435, 1378, 1331, 1306, 1233, 1212, 1174, 1157, 1090, 1026, 998, 929, 889, 874, 845, 795, 749, 691, 617, 573 P=Se), 541 (P–Se), 515, 502, 475, 421 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.00 (d, $^3J_{HH}$ = 6.0 Hz, 3 H, *Me*CH), 6.07 (m, 1 H, CHSe), 6.95 (t, $^3J_{HH}$ = 8.4 Hz, 1 H, H^4 in Ph), 7.12 (d, $^3J_{HH}$ = 8.6 Hz, 2 H, H^{2,6} in Ph), 7.31 (m, 2 H, H^{3,5} in Ph), 7.48 (m, 6 H, H^{3,4,5} in Ph), 7.87 (m, 2 H, H^6 in Ph), 7.99 (m, 2 H, H^2 in Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 26.2 (*Me*CH), 87.4 (CHSe), 117.2, 122.6, 127.5, 127.6, 128.5, 128.6, 129.3, and 131.2 (*o*-, *m*-, *p*-C, Ph), 133.8 (d, $^3J_{PC}$ = 33.2 Hz, *i*-C, Ph), 134.6 (d, $^3J_{PC}$ = 34.7 Hz, *i*-C, Ph), 155.9 (*i*-C, PhO).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 37.91 (s, $^1J_{\mathrm{P-Se}} = 370$ Hz, $^1J_{\mathrm{P=Se}} = 764$ Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –168 (d, $^1J_{\mathrm{P=Se}} = 764$ Hz), 425 (d, $^1J_{\mathrm{P-Se}} = 370$ Hz).

Anal. Calcd for $C_{20}H_{19}OPSe_2$: C, 51.74; H, 4.13; P, 6.67; Se, 34.02. Found: C, 51.82; H, 4.24; P, 6.62; Se, 34.11.

1,4-Phenylenebis(oxyethane-1,1-diyl) Bis[bis(2-phenylethyl)(phosphinodiselenoate)] (3p)

Yield: 924 mg (96%); yellowish oil.

IR (film): 3060, 3028, 2959, 2917, 2853, 1953, 1877, 1810, 1731, 1641, 1600, 1500, 1447, 1381, 1240, 1205, 1120, 1083, 1003, 930, 877, 939, 747, 702, 568 (P=Se), 548 (P–Se), 471 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.06, 2.08, 2.11, and 2.13 (d, $^3J_{\mathrm{HH}} = 5.9$ Hz, 6 H, *Me*CH), 2.24–2.60 (m, 8 H, CH$_2$P), 2.65–3.12 (m, 8 H, C*H*$_2$Ph), 5.88–6.03 (m, 2 H, CHSe), 7.07–7.32 (m, 24 H, Ar).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 26.1 (d, $^3J_{\mathrm{PC}} = 2.5$ Hz, *Me*CH), 29.3, 29.6, 29.8, and 30.0 (*C*H$_2$Ph), 38.6, 38.7, 39.3, and 39.5 (d, $^1J_{\mathrm{PC}}$ = 38.1, 37.5, 38.4, and 38.8 Hz, CH$_2$P), 89.7, 89.9, 90.0, and 90.3 (CHSe), 117.6 (C^{2,3,5,6} in C$_6$H$_4$), 126.1, 126.2, 126.4, 127.9, 128.0, 128.3, 128.4, and 128.5 (*o*-, *m*-, *p*-C, Ph), 139.5, 139.6, and 137.7 (d, $^3J_{\mathrm{PC}}$ = 16.5, 16.9, and 16.5 Hz, *i*-C, Ph), 151.3 (C^{1,4} in C$_6$H$_4$).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 48.65, 48.84, and 49.15 (s, $^1J_{\mathrm{P-Se}} = 354$ Hz, $^1J_{\mathrm{P=Se}}$ = 747, 746, and 747 Hz) in the ratio 1:2.2:1.8.

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –232, –230, and –231 (d, $^1J_{\mathrm{P=Se}}$ = 747, 746, and 747 Hz), 320, 321, and 322 (d, $^1J_{\mathrm{P-Se}} = 354$ Hz).

The presence of several signals in the ^{1}H, ^{13}C, ^{31}P, and ^{77}Se NMR spectra of bisphosphinodiselenoate **3p** might be due to the existence of two asymmetric carbon atoms in the molecule.

Anal. Calcd for $C_{42}H_{48}O_2P_2Se_4$: C, 52.40; H, 5.03; P, 6.44; Se, 32.81. Found: C, 52.47; H, 4.93; P, 6.36; Se, 32.70.

1-(1,2:5,6-Di-*O*-isopropylidene-d-glucofuranosyloxy)ethyl Bis(2-phenylethyl)phosphinodiselenoate (3q)

1,2:5,6-Di-*O*-isopropylidene-3-*O*-vinyl-α-D-glucofuranose (**1j**; 573 mg, 2.0 mmol) and powdered gray Se (316 mg, 4.0 mmol) were added consecutively to a soln of secondary phosphine **2a** (485 mg, 2.0 mmol) in 1,4-dioxane (8 mL) at r.t. The suspension was stirred at 90 °C until the Se residue dissolved (~1.5 h) to give a clear yellowish soln. The solvent was then removed under reduced pressure (50–60 °C, 1 Torr) and the residue was washed sequentially with EtOH (2 × 5 mL) and hexane (2 × 5 mL) then dried in vacuo (40–45 °C, 1 Torr) to give a yellowish oil; yield: 1195 mg (87%). The NMR spectra suggest that this phosphinodiselenoate was obtained as a mixture of two diastereomers; $[\alpha]_D^{23}$ –21.3 (*c* 2, CHCl$_3$).

IR (film): 3053, 2985, 2933, 2890, 2854, 1478, 1453, 1436, 1373, 1330, 1308, 1254, 1216, 1164, 1107, 1074, 1021, 956, 918, 873, 849, 793, 747, 692, 637, 615, 576 (P=Se), 541 (P–Se), 501, 475, 421 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 1.22, 1.27, 1.31, 1.32, 1.41, 1.43 (s, 12 H, MeC), 1.79 (d, $^3J_{\mathrm{HH}} = 5.9$ Hz, 3 H, *Me*CH), 2.50–2.71 (m, 4 H, CH$_2$P), 2.87–3.18 (m, 4 H, C*H*$_2$Ph), 3.89–3.98 (m, 2 H, H^{4,6}), 4.05–4.20 (m, 3 H, H^{3,5,6}), 4.45–4.50 (m, 1 H, H^2), 5.54–5.67 (m, 1 H, CHSe), 5.78–5.93 (m, 1 H, H^1), 7.44 (m, 6 H, Ph), 7.85–7.97 (m, 4 H, Ph).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 25.1–26.3 (m, *Me*C), 26.6–26.9 (m, *Me*CH), 29.6–30.4 (m, *C*H$_2$Ph), 39.1–40.3 (m, CH$_2$P), 66.5, 67.0, 67.5, and 67.6 (m, C^6), 72.7, 72.8, 73.3, and 75.0 (m, C^5), 80.1, 80.2, 81.1, 82.0, 82.4, and 83.2 (m, C^{2,3,4}), 91.6, 94.1 (CHSe), 105.1, 105.2, and 105.3 (C^1), 108.7, 109.2, 111.9, and 112.0 (m, OCO), 126.4, 126.5, 126.7, 128.3, 128.5, and 128.6 (*o*-, *m*-, *p*-C, Ph), 139.9, 140.0, and 140.1 (*i*-C, Ph).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 37.51 and 38.65 (s, $^1J_{\mathrm{P-Se}}$ = 370 and 367 Hz, $^1J_{\mathrm{P=Se}}$ = 768 and 764 Hz) in a 1:2 ratio.

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –161 and –156 (d, $^1J_{\mathrm{P=Se}}$ = 764 and 768 Hz), 406 and 427 (d, $^1J_{\mathrm{P-Se}}$ = 367 and 370 Hz).

Anal. Calcd for $C_{30}H_{41}O_6PSe_2$: C, 52.48; H, 6.02; P, 4.51; Se, 23.00. Found: C, 52.61; H, 6.09; P, 4.65; Se, 23.18.

[2-(Vinyloxy)ethyl]ammonium bis(2-phenylethyl)phosphinodiselenoate (4)

[2-(Vinyloxy)ethyl]amine (**1k**; 183 mg, 2.1 mmol) and powdered gray Se (316 mg, 4.0 mmol) were added consecutively to a soln of bis(2-phenylethyl)phosphine (**2a**; 485 mg, 2.0 mmol) in 1,4-dioxane (8 mL) at r.t. The suspension was stirred at 90 °C until the Se residue dissolved (~15 min) to give a clear colorless soln. The solvent was removed under reduced pressure (30–40 °C, 1 Torr) and the residue was washed with Et$_2$O (2 × 10 mL) and dried in vacuo (40 °C, 1 Torr); yield: 916 mg (94%); mp 78–87 (dec).

IR (film): 3163, 3050, 2933, 2849, 2702, 1641, 1620, 1600, 1578, 1495, 1478, 1453, 1396, 1365, 1320, 1270, 1198, 1123, 1064, 1021, 994, 967, 945, 829, 761, 743, 698, 571 (P–Se), 489, 421 cm^{-1}.

^{1}H NMR (400.13 MHz, CDCl$_3$): δ = 2.44–2.50 (m, 4 H, CH$_2$P), 2.93–3.00 (m, 4 H, C*H*$_2$Ph), 3.51 (t, $^3J_{\mathrm{HH}} = 4.5$ Hz, 2 H, CH$_2$N), 4.00 (m, 3 H, CH$_2$O, H$_2$C=), 4.13 (dd, $^3J_{\mathrm{HH}} = 14.4$ Hz, $^2J_{\mathrm{HH}} = 1.8$ Hz, 1 H, H$_2$C=), 6.32 (dd, $^3J_{\mathrm{HH}}$ = 6.8 and 14.4 Hz, 1 H, HC=), 7.13–7.21 (m, 10 H, Ph), 7.86 (s, 3 H, HN).

^{13}C NMR (100.62 MHz, CDCl$_3$): δ = 30.6 (*C*H$_2$Ph), 38.7 (CH$_2$N), 43.0 (d, $^1J_{\mathrm{PC}} = 35.3$ Hz, CH$_2$P), 62.5 (CH$_2$O), 88.3 (=CH$_2$), 125.5 (*p*-C, Ph), 128.2 and 128.3 (*o*-, *m*-C, Ph), 140.7 (d, $^3J_{\mathrm{PC}} = 17.2$ Hz, *i*-C, Ph), 149.9 (=CH).

^{31}P NMR (161.98 MHz, CDCl$_3$): δ = 25.70 (s, $^1J_{\mathrm{P-Se}} = 558$ Hz).

^{77}Se NMR (76.31 MHz, CDCl$_3$): δ = –67 (d, $^1J_{\mathrm{PSe}} = 558$ Hz).

Anal. Calcd for $C_{20}H_{28}NOPSe_2$: C, 49.29; H, 5.79; P, 6.36; Se, 32.40. Found: C, 49.44; H, 5.81; P, 6.12; Se, 32.34.

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References

(1) Gusarova, N. K.; Artem'ev, A. V.; Malysheva, S. F.; Tarasova, O. A.; Trofimov, B. A. *Tetrahedron Lett.* **2011**, *52*, 6985.

(2) For details of the biological significance and pharmacological activity of organoselenium compounds, see: (a) National Research Council Subcommittee on Selenium *Selenium in Nutrition, Revised Edition*; National Academy Press: Washington (DC, USA), **1983**. (b) Mugesh, G.; du Mont, W.-W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125. (c) Parker, J. N.; Parker, P. M. *Selenium: A Medical Dictionary, Bibliography, and Annotated Research Guide to Internet References*; Icon Health Publications: San Diego, **2004**. (d) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255. (e) Reilly, C. *Selenium in Food and Health*; Springer: New York, **2006**. (f) *Selenium: Its Molecular Biology and Role in Human Health: Hatfield*

D. L., Berry M. J., Gladyshev V. N., 2nd ed.; Springer: New York, **2006**. (g) Divac, V. M.; Bugarčić, Z. M. *Synthesis* **2009**, 3684. (h) Ganesh, V.; Chandrasekaran, S. *Synthesis* **2009**, 3267. (i) Ren, K.; Wang, M.; Liu, P.; Wang, L. *Synthesis* **2010**, 1078. (j) Kálai, T.; Bagi, N.; Jekö, J.; Berente, Z.; Hideg, K. *Synthesis* **2010**, 1702. (k) Braga, A. L.; Wessjohann, L. A.; Taube, P. S.; Galetto, F. Z.; de Andrade, F. M. *Synthesis* **2010**, 3131.

(3) (a) Mel'nikov, N. N.; Novozhilov, K. V.; Pylova, T. N. *The Pesticide Chemistry* **Moscow**, 1980;. (b) Matolcsy, G.; Nádasy, M.; Andriska, V. *Pesticide Chemistry*; Elsevier: Amsterdam, **1988**.

(4) For recent examples of the use of P–Se compounds as capping agents and selenium sources for syntheses of selenium-containing nanomaterials, see: (a) Hsu, Y.-J.; Hung, C.-M.; Lin, Y.-F.; Liaw, B.-J.; Lobana, T. S.; Lu, S.-Y.; Liu, C. W. *Chem. Mater.* **2006**, *18*, 3323. (b) Lin, Y.-F.; Chang, H.-W.; Lu, S.-Y.; Liu, C. W. *J. Phys. Chem. C.* **2007**, *111*, 18538. (c) Chang, H.-W.; Sarkar, B.; Liu, C. W. *Cryst. Growth Des.* **2007**, *7*, 2691. (d) Ahmad, K.; Afzaal, M.; O'Brien, P.; Hua, G.; Woollins, J. D. *Chem. Mater.* **2010**, *22*, 4619. (e) Malik, M. A.; Afzaal, M.; O'Brien, P. *Chem. Rev.* **2010**, *110*, 4417. (f) Owen, J. S.; Chan, E. M.; Liu, H.; Alivisatos, A. P. *J. Am. Chem. Soc.* **2010**, *132*, 18206. (g) Cossairt, B. M.; Owen, J. S. *Chem. Mater.* **2011**, *23*, 3114.

(5) For applications of phosphinodiselenoates in the preparation of nanomaterials, see: (a) Nguyen, C. Q.; Afzaal, M.; Malik, M. A.; Helliwell, M.; Raftery, J.; O'Brien, P. *J. Organomet. Chem.* **2007**, *692*, 2669. (b) Kawai, T.; Hasegawa, Y.; Adachi, T. WO 2007102271, **2007**; *Chem. Abstr.* **2007**, *147*, 368034. (c) Panneerselvam, A.; Nguyen, C. Q.; Waters, J.; Malik, M. A.; O'Brien, P.; Raftery, J.; Helliwell, M. *Dalton Trans.* **2008**, 4499. (d) Hasegawa, Y.; Adachi, T.; Tanaka, A.; Afzaal, M.; O'Brien, P.; Doi, T.; Hinatsu, Y.; Fujita, K.; Tanaka, K.; Kawai, T. *J. Am. Chem. Soc.* **2008**, *130*, 5710. (e) Maneeprakorn, W.; Nguyen, C. Q.; Malik, M. A.; O'Brien, P.; Raftery, J. *Dalton Trans.* **2009**, 2103. (f) Panneerselvam, A.; Nguyen, C. Q.; Malik, M. A.; O'Brien, P.; Raftery, J. *J. Mater. Chem.* **2009**, *19*, 419. (g) Tanaka, A.; Adachi, T.-a.; Hasegawa, Y.; Kawai, T. *J. Alloys Compd.* **2009**, *488*, 538. (h) Maneeprakorn, W.; Malik, M. A.; O'Brien, P. *J. Mater. Chem.* **2010**, *20*, 2329.

(6) (a) Murai, T.; Kimura, T. *Curr. Org. Chem.* **2006**, *10*, 1963. (b) Davies, R. In *Handbook of Chalcogen Chemistry: New Perspectives in Sulfur, Selenium and Tellurium*; Devillanova, F. A., Ed.; Royal Society of Chemistry: Cambridge, **2007**, Chap. 5, 286. (c) Sarkar, B.; Fang, C.-S.; You, L.-Y.; Wang, J.-C.; Liu, C. W. *New J. Chem.* **2009**, *33*, 626. (d) *Selenium and Tellurium Chemistry: From Small Molecules to Biomolecules and Materials*; Woollins, J. D.; Laitinen, R. S., Eds.; Springer: Heidelberg, **2011**. (e) Artem'ev, A. V.; Gusarova, N. K.; Malysheva, S. F.; Trofimov, B. A. *Org. Prep. Proced. Int.* **2011**, *43*, 381. (f) Artem'ev, A. V.; Chernysheva, N. A.; Gusarova, N. K.; Malysheva, S. F.; Yas'ko, S. V.; Albanov, A. I.; Trofimov, B. A. *Synthesis* **2011**, 1309.

(7) For applications of P–Se compounds as selenium-donating ligands, see: (a) Shi, M.; Wang, C.-J.; Zhang, W. *Chem. Eur. J.* **2004**, *10*, 5507. (b) Gray, I. P.; Slawin, A. M. Z.; Woollins, J. D. *Dalton Trans.* **2005**, 2188. (c) Lobana, T. S.; Wang, J.-C.; Liu, C. W. *Coord. Chem. Rev.* **2007**, *251*, 91. (d) Liu, C. W.; Sarkar, B.; Huang, Y.-J.; Liao, P.-K.; Wang, J.-C.; Saillard, J.-Y.; Kahlal, S. *J. Am. Chem. Soc.* **2009**, *131*, 11222. (e) Davies, R. P.; Martinelli, M. G.; Patel, L.; White, A. J. P. *Inorg. Chem.* **2010**, *49*, 4626. (f) Liu, C. W.; Chang, H.-W.; Sarkar, B.; Saillard, J.-Y.; Kahlal, S.; Wu, Y.-Y. *Inorg. Chem.* **2010**, *49*, 468. (g) You, H.-J.; Fang, C.-S.; Lin, J.-L.; Sun, S.-S.; Liu, C. W. *Inorg. Chem.* **2010**, *49*, 7641. (h) Hua, G.; Randall, R. A. M.; Slawin, A. M. Z.; Woollins, J. D. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1800.

(8) (a) Moon, J.; Nam, H.; Kim, S.; Ryu, J.; Han, C.; Lee, C.; Lee, S. *Tetrahedron Lett.* **2008**, *49*, 5137. (b) Song, E.; Jo, Y.; Bae, G.; Oh, I.-K.; Jung, H. M.; Lee, S. *Bull. Korean Chem. Soc.* **2009**, *30*, 2129.

(9) (a) Krief, A.; Bousbaa, J. *Tetrahedron Lett.* **1997**, *38*, 6291. (b) Sasaki, M.; Inoue, M.; Noguchi, T.; Takeichi, A.; Tachibana, K. *Tetrahedron Lett.* **1998**, *39*, 2783. (c) Delouvrié, B.; Fensterbank, L.; Lacôte, E.; Malacria, M. *J. Am. Chem. Soc.* **1999**, *121*, 11395. (d) Shimada, K.; Kikuta, Y.; Koganebuchi, H.; Yonezawa, F.; Aoyagi, S.; Takikawa, Y. *Tetrahedron Lett.* **2000**, *41*, 4637. (e) Sasaki, M.; Noguchi, T.; Tachibana, K. *J. Org. Chem.* **2002**, *67*, 3301. (f) Deleuze, A.; Sollogoub, M.; Blériot, Y.; Marrot, J.; Sinaÿ, P. *Eur. J. Org. Chem.* **2003**, 2678. (g) Tsuchii, K.; Doi, M.; Hirao, T.; Ogawa, A. *Angew. Chem. Int. Ed.* **2003**, *42*, 3490. (h) Davidson, J. E. P.; Gilmour, R.; Ducki, S.; Davies, J. E.; Green, R.; Burton, J. W.; Holmes, A. B. *Synlett* **2004**, 1434. (i) Tsuchii, K.; Doi, M.; Ogawa, I.; Einaga, Y.; Ogawa, A. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1534. (j) Yamamoto, T.; Moriura, E.; Sawa, A.; Yoshimatsu, M. *Chem. Lett.* **2008**, *37*, 1046. (k) Frankie Mak, S. Y.; Chiang, G. C. H.; Davidson, J. E. P.; Davies, J. E.; Burton, J. W.; Holmes, A. B.; Ayscough, A.; Pain, G. *Tetrahedron: Asymmetry* **2009**, *20*, 921.

(10) For details on the accessibility of vinyl ethers, see: (a) Trofimov, B. A. *Curr. Org. Chem.* **2002**, *6*, 1121. (b) Trofimov, B. A.; Gusarova, N. K. *Russ. Chem. Rev.* **2007**, *76*, 507. (c) Winternheimer, D. J.; Shade, R. E.; Merlic, C. A. *Synthesis* **2010**, 2497.

(11) Trofimov, B. A.; Parshina, L. N.; Oparina, L. A.; Tantsyrev, A. P.; Khil'ko, M. Yu.; Vysotskaya, O. V.; Stepanov, A. V.; Gusarova, N. K.; Henkelmann, J. *Tetrahedron* **2007**, *63*, 11661.

(12) (a) Sukhov, B. G.; Gusarova, N. K.; Ivanova, N. I.; Bogdanova, M. V.; Kazheva, O. N.; Alexandrov, G. G.; D'yachenko, O. A.; Sinegovskaya, L. M.; Malysheva, S. F.; Trofimov, B. A. *J. Struct. Chem.* **2005**, *46*, 1066. (b) Dornhaus, F.; Lerner, H.-W.; Michael, B. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2007**, *63*, o4917.

(13) (a) Kuchen, W.; Knop, B. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 244. (b) Kuchen, W.; Knop, B. *Chem. Ber.* **1966**, *99*, 1663.

(14) Artem'ev, A. V.; Gusarova, N. K.; Malysheva, S. F.; Ushakov, I. A.; Trofimov, B. A. *Tetrahedron Lett.* **2010**, *51*, 2141.

(15) Oparina, L. A.; Shaikhudinova, S. I.; Parshina, L. N.; Vysotskaya, O. V.; Preiss, T. h.; Henkelmann, J.; Trofimov, B. A. *Russ. J. Org. Chem.* **2005**, *41*, 656.

(16) Trofimov, B. A.; Khil'ko, M. Ya.; Nedolya, N. A.; Demanov, Yu. K.; Vyalykh, E. P. *Zh. Org. Khim.* **1982**, *18*, 744; *Chem. Abstr.* **1982**, *97*, 55265.

(17) Oparina, L. A.; Vysotskaya, O. V.; Stepanov, A. V.; Gusarova, N. K.; Trofimov, B. A. *Russ. J. Org. Chem.* **2009**, *45*, 134.

(18) Lavrov, V. I.; Oparina, L. A.; Parshina, L. N.; Vins, V. V.; Trofimov, B. A. *Russ. J. Appl. Chem.* **1990**, *63*, 835.

(19) Trofimov, B. A.; Brandsma, L.; Arbuzova, S. N.; Malysheva, S. F.; Gusarova, N. K. *Tetrahedron Lett.* **1994**, *35*, 7647.