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Highly Selective Synthesis of [(*Z*)-3-Chloro-2-(phenylselanyl)-1-alkenyl]phosphonates and 2-Ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxides by Electrophilic Reaction of 1,2-Alkadienylphosphonates with PhSeCl

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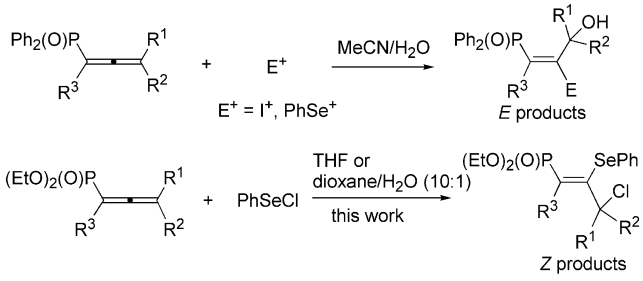
The reactions of monosubstituted 1,2-alkadienylphosphonates with PhSeCl in THF or dioxane/H_2O (10:1) at 70 °C afforded the selenochlorination products [(*Z*)-3-chloro-2-(phenylselanyl)-1-alkenyl]phosphonates with very high chemo- and stereoselectivity, whereas the same reaction with di- and trisubstituted allenylphosphonates afforded 2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-oxides exclusively. It was interesting to note that the stereoselctivity for the selenochlorination reaction is opposite to that of the iodo- and selenohydroxylation reactions of (allenyl)diphenylphosphane oxides with Cl^- acting as the nucleophile. The stereoselectivity of the cyclization reaction is clearly different from that of the selenochlorination reaction.

Introduction

Recently, we observed that in the halo- and selenohydroxylation reactions of allenylphosphane oxides,[1–3] the electrophilic moiety was added to the central carbon atom of the allene moiety with the hydroxy group always attached to the 3-position with respect to the phosphorus atom; the excellent regio- and (*E*) stereoselectivity of the reactions has been rationalized in terms of the neighbouring-group participation ability of phosphane oxide.[1,2] However, when 1,2-alkadienylphosphonates were used, the chemistry was different: Angelov and co-workers reported that the reactions of allenylphosphonates with RSeCl led to (*E*)/(*Z*) mixtures of [2-(alkyl- or phenylseleno)-3-chloro-1-alkenyl]-phosphonates.[4] Macomber et al. reported that dimethyl (propa-1,2-dienyl)phosphonate reacted with 1.0 equiv. PhSeCl in anhydrous chloroform to afford dimethyl [(*E*)-3-chloro-2-(phenylselanyl)-1-propenyl]phosphonate.[5] In this paper, we wish to report the unexpected reactions of 1- and 3-monosubstituted allenylphosphonates[6–9] with PhSeCl, which afforded [(*Z*)-3-chloro-2-(phenylselanyl)-1-alkenyl]-phosphonates with (*Z*) stereoselectivity and the chloro substituent at the 3-position of the starting phosphonates instead of the usual hydroxy group, which opens up new opportunities for the introduction of other nucleophiles with different stereoselectivity in this type of transformation (Scheme 1).[10]



Scheme 1.

Results and Discussion

The reaction of diethyl hepta-1,2-dienylphosphonate (**1a**) with 2.0 equiv. of PhSeCl was conducted in CH_3CN/H_2O (40:1) at room temperature and afforded diethyl [(*Z*)-3-chloro-2-(phenylselanyl)-1-heptenyl]phosphonate [(*Z*)-**2a**] in 33% isolated yield, unexpectedly together with the electrophilic cyclization reaction product, that is, 5-(*n*-butyl)-2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-oxide (**3a**; Entry 1, Table 1).[4,5,11] The reaction in MeCN/H_2O (3:1) afforded the cyclization product **3a** with a much higher selectivity (Entry 2, Table 1). Further studies revealed that in CH_3CN/H_2O (10:1) the products were formed with an interesting (*Z*)-**2a**/**3a** selectivity. The reac-

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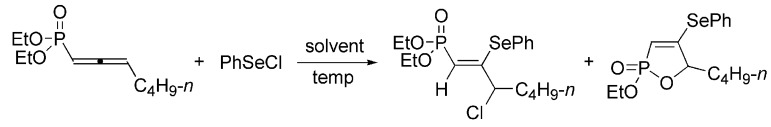
Table 1. Selenochlorination of diethyl hepta-1,2-dienylphosphonate (**1a**) with PhSeCl.[a]



1a *Z*-**2a** **3a**

Entry	PhSeCl [equiv.]	Solvent/H_2O (ratio)	Temp. [°C]	Time [h]	Isolated yield of (*Z*)-**2a**/**3a** [%]	(*Z*)-**2a**/**3a**[b]
1	2.0	MeCN (40:1)	r.t.	2.3	33:36	48:52
2	2.0	MeCN (3:1)	r.t.	2	18:49	27:73
3	2.0	MeCN (10:1)	r.t.	23	37:3	>92:8[c]
4	1.5	MeCN (10:1)	70	3.5	42:6	>88:12[c]
5	2.0	MeCN (10:1)	50	11.3	44:0	99:1
6	1.5	dioxane (10:1)	70	4	69:0	99:1
7	1.5	DMF (10:1)	70	4	48:28	>63:37[c]
8	1.5	MeOH (10:1)	70	2	15:20	>43:57[c]
9	1.2	THF (10:1)	70	2	62:0	99:1
10	1.5	THF (10:1)	70	2.5	69:0	99:1
11	2.0	THF (10:1)	70	2	64:0	99:1

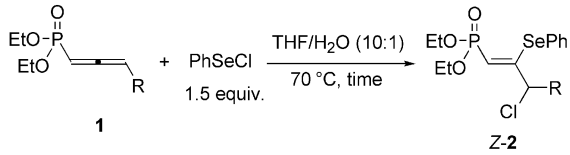
[a] The reaction was carried out by using 0.2 mmol of **1a** and 1.5–2.0 equiv. of PhSeCl in 4.0 mL of solvent. [b] The ratio of (*Z*)-**2a**/**3a** was determined by isolation. [c] Another impurity was formed in this reaction, which could not be separated from **3a**.

tion in CH_3CN/H_2O (10:1) at 50 °C afforded (*Z*)-**2a** exclusively in an isolated yield of 44% (Entry 5, Table 1), whereas the reaction in aqueous DMF or CH_3OH was poor (Entries 7 and 8, Table 1). However, the reaction in THF/H_2O (10:1) or dioxane/H_2O (10:1) at 70 °C with 1.5 equiv. of PhSeCl afforded (*Z*)-**2a** exclusively in yields of 69% (Entries 6 and 10, Table 1). After screening for the effect of the amount of PhSeCl on the reaction, we finally chose THF/H_2O (10:1) or dioxane/H_2O (10:1) as the best media for the selenochlorination reaction (Entries 6 and 10, Table 1).

Although the yield in dioxane was the same as that in THF, due to the lower boiling point of THF, the reactions of the diethyl (3-monosubstituted alka-1,2-dienyl)phosphonates **1a**–**1g** and diethyl propa-1,2-dienylphosphonate (**1h**) were conducted in THF. The yields of (*Z*)-**2** ranged from 52 to 81% (Table 2).

To further confirm the stereochemistry of this selenochlorination reaction, the reaction of diethyl propa-1,2-dienylphosphonate with 4-BrC_6H_4SeCl was conducted. However, the corresponding product (*Z*)-**2i** was a liquid [Equation (1), Scheme 2]. Thus, the cyclic phosphonate **1j** was prepared and its reaction with 4-BrC_6H_4SeCl afforded (*Z*)-**2j**, which is fortunately a solid with a melting point of 125.9–126.4 °C. The configuration of the carbon–carbon double bond in **2j** was then determined by its X-ray diffraction study (Figure 1).[12] Note that Macomber et al. assigned the stereochemistry of dimethyl [3-chloro-(2-phenylselanyl)-1-propenyl]phosphonate formed from the reaction of dimethyl propa-1,2-dienylphosphonate and 1.0 equiv. of PhSeCl in anhydrous chloroform to an (*E*) configuration based on the allylic ^1H-^1H coupling and its similarity with certain sulfur analogues.[5] However, when we conducted the reaction of dimethyl propa-1,2-dienylphosphonate with PhSeCl under both our conditions and those of Macomber et al., the same product (*Z*)-**2k** was isolated. Thus, we reasoned that (*Z*)-**2k** was misassigned as (*E*)-**2k** in the literature (Scheme 2).[5]

Table 2. Selenochlorination of diethyl (3-monosubstituted 1,2-alkadienyl)phosphonates with PhSeCl.[a]



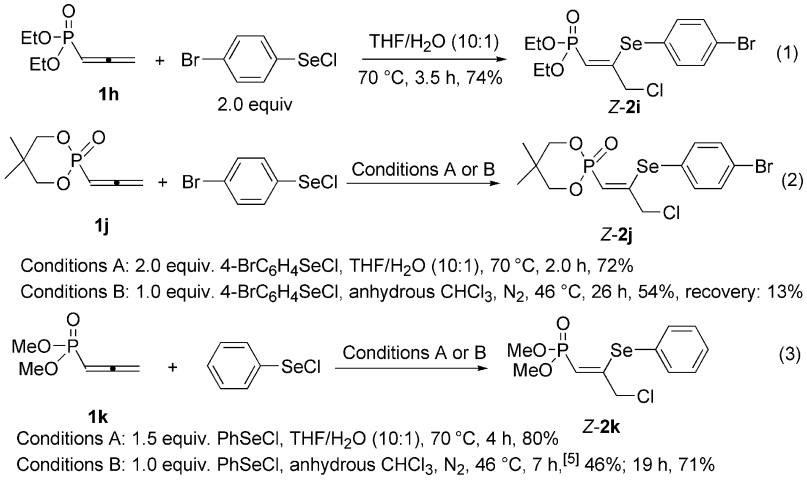
1 *Z*-**2**

Entry	R	Time [h]	Isolated yield of (*Z*)-**2** [%]
1	*n*-C_4H_9 (**1a**)	2.5	69 (**2a**)
2[b]	*n*-C_4H_9 (**1a**)	4.0	69 (**2a**)
3	Me (**1b**)	1.0	52 (**2b**)
4[b]	Me (**1b**)	5.0	53 (**2b**)
5	*n*Pr (**1c**)	1.5	64 (**2c**)
6	*n*-C_5H_{11} (**1d**)	1.0	66 (**2d**)
7	*n*-C_6H_{13} (**1e**)	1.0	68 (**2e**)
8	*i*Pr (**1f**)	1.5	74 (**2f**)
9	Bn (**1g**)	3.3	78 (**2g**)
10	H (**1h**)	3.0	81 (**2h**)

[a] The reactions were carried out by using 0.3 mmol of **1** and 0.45 mmol of PhSeCl in 6.0 mL of THF and 0.6 mL of H_2O. [b] Dioxane/H_2O (10:1) was used as the solvent.

The reaction may be easily extended to a scale of 4.8 or 5.5 mmol of the substrates **1a** and **1j** (Scheme 3).

For the diethyl (1-monosubstituted alka-1,2-dienyl)phosphonates, dioxane/H_2O is clearly superior to THF/H_2O (compare Entries 1 and 2 in Table 3). All the selenochlorination reactions proceeded smoothly to afford the products (*Z*)-**2m**–(*Z*)-**2o** in moderate yields. The configuration of the C=C bond in these products was determined by the NOE study of (*Z*)-**2m** (Figure 2). Note that the electrophilic cyclization products 2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-oxides **3m**–**3o** were also formed in 6–12% yields. However, the selenochlorination reaction became complicated when diethyl (1-phenyl- and 3-phenylpropa-



Scheme 2.

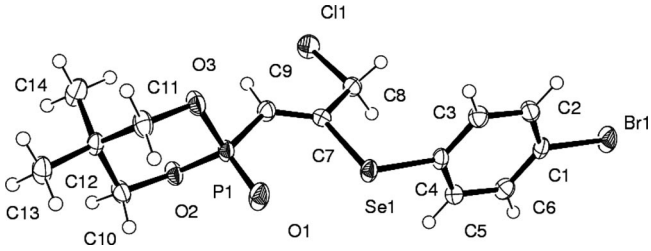


Figure 1. ORTEP representation of (*Z*)-**2j**.

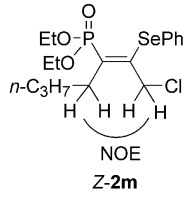
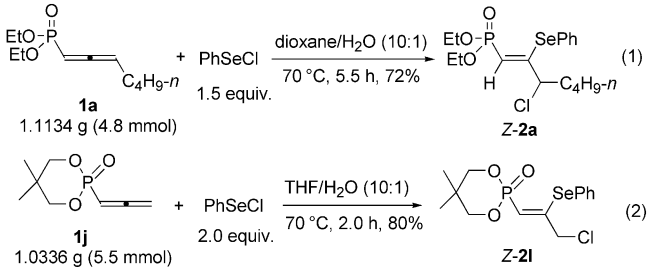


Figure 2. NOE study of (*Z*)-**2m**.

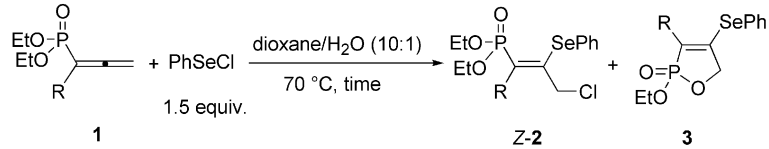


Scheme 3.

1,2-dienyl)phosphonate were subjected to the optimum conditions with 1.5 equiv. of PhSeCl in THF/H_2O (10:1) at 70 °C.

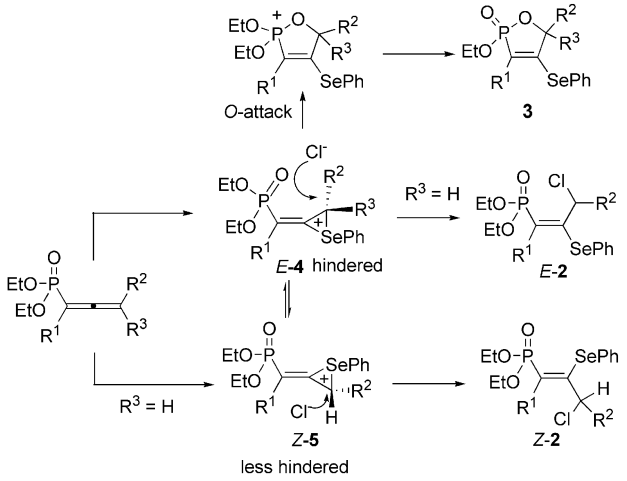
It is interesting to observe that the stereoselectivity is different from that of the iodo- and selenohydroxylation reactions of (1,2-alkadienyl)diphenylphosphane oxides.[1,2] In our previous studies of the halohydroxylation reaction we also observed (*Z*) stereoselectivity, which was rationalized in terms of a steric effect[13] or a soft Lewis acid/base interaction.[14] It is proposed that the reaction proceeds through an equilibrium between the three-membered selenonium intermediates (*E*)-**4** and (*Z*)-**5**. Owing to the steric repulsion between the relatively bulky Cl^- and the $PO(OEt)_2$ group and the carbon atom with R^2 and R^3 in (*E*)-**4**, intermediate **5** is more favored in the nucleophilic attack of Cl^- than intermediate (*E*)-**4**. Thus, the (*Z*) selenochlorination products (*Z*)-**2** were formed with high stereoselectivity (Scheme 4).[15]

Table 3. Selenochlorination of diethyl (1-substituted 1,2-alkadienyl)phosphonates with PhSeCl.[a]



Entry	R	Time [h]	Isolated yield of (*Z*)-**2** [%]	Isolated yield of **3** [%]
1	*n*-C_4H_9 (**1m**)	3.0	74 (**2m**)	12 (**3m**)
2[b]	*n*-C_4H_9 (**1m**)	2.0	57 (**2m**)	7 (**3m**)
3	Me (**1n**)	3.0	63 (**2n**)	6 (**3n**)
4	*n*-C_7H_{15} (**1o**)	3.0	69 (**2o**)	9 (**3o**)

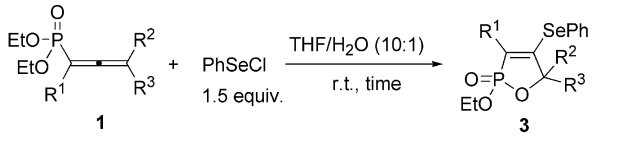
[a] The reaction was carried out by using 0.3 mmol of **1** and 0.45 mmol of PhSeCl in 6.0 mL of dioxane and 0.6 mL of H_2O. [b] THF/H_2O (10:1) was used as the solvent.



Scheme 4.

The reactions of (1,3-di-, 3,3-di-, and fully substituted allenyl)phosphonates under the standard conditions all afforded the cyclic 2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-oxides **3p**–**3r** as the only products (Entries 1–3, Table 4), as reported previously.[4,5,11] Interestingly, these cyclic products must be formed by *O*-attack of intermediate (*E*)-**4**, which indicates the coexistence of both intermediates (*E*)-**4** and (*Z*)-**5** in this transformation (Scheme 4).

Table 4. Reaction of multisubstituted diethyl allenylphosphonates with PhSeCl.[a]



Entry	R^1	R^2	R^3	Time [h]	Isolated yield of **3** [%]
1	H	Me	Me (**1p**)	3.0	55 (**3p**)
2[b]	*n*-C_4H_9	H	Et (**1q**)	0.3	92 (**3q**)
3	*n*-C_4H_9	Me	Me (**1r**)	4.0	87 (**3r**)

[a] The reaction was carried out by using 0.3 mmol of **1**, 0.45 mmol of PhSeCl, 6.0 mL of THF, and 0.6 mL of H_2O. [b] The reaction was conducted at 70 °C.

Conclusions

We have developed a convenient and practical method for the synthesis of [(*Z*)-3-chloro-2-(phenylselanyl)-1-alkenyl]phosphonates with high regio- and (*Z*) stereoselectivity from (1- and 3-monosubstituted 1,2-allenyl)phosphonates. 2-Ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-oxides were formed from (1,3-di-, 3,3-di-, and fully substituted allenyl)phosphonates. As a result of the presence of a carbon–carbon double bond, carbon–selenium bond, and a carbon–phosphorus bond, these compounds will be useful in organic synthesis.[16–19] The unique stereoselectivity observed also provides new information on the control of selectivity in this type of transformation. Further studies in this area are being conducted in our laboratory.

Experimental Section

Starting Materials: Compounds **1a**–**d**, **1f**, **1h**–**p**, **1r** and new compounds **1e**, **1g**, and **1q** were prepared according to the reported procedure.[20]

Diethyl Nona-1,2-dienylphosphonate (1e). Typical Procedure I: An oven-dried three-necked round-bottomed flask was charged with non-1-yn-3-ol (2.0943 g, 15 mmol), triethylamine (2.80 mL, *d* = 0.7275 g/mL, 2.04 g, 20 mmol), and THF (60 mL). After cooling the mixture to –78 °C in a dry ice/acetone bath, a solution of diethyl chlorophosphite (3.5282 g, 22.5 mmol) in THF (15 mL) was added dropwise at –78 °C with stirring over 15 min. Then the resulting mixture was warmed up naturally to room temperature and heated at reflux. After complete conversion of the propargylic alcohol, as monitored by TLC (petroleum/ethyl acetate, 2:1), the mixture was quenched with water (20 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL) and dried with anhydrous Na_2SO_4. After filtration and evaporation of the solvent, chromatography of the crude product on silica gel (petroleum ether/ethyl acetate, 2:1) afforded **1e** (2.8568 g, 73%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.43–5.32 (m, 1 H), 5.27–5.20 (m, 1 H), 4.11–3.99 (m, 4 H), 2.09–1.96 (m, 2 H), 1.44–1.33 (m, 2 H), 1.33–1.15 (m, 12 H), 0.82 (t, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 211.8, 92.3 (d, J_{PC} = 16.3 Hz), 79.8 (d, J_{PC} = 198.5 Hz), 62.2 (d, J_{PC} = 6.0 Hz), 31.5, 28.8 (d, J_{PC} = 3.5 Hz), 28.6, 27.3 (d, J_{PC} = 6.6 Hz), 22.5, 16.2 (d, J_{PC} = 6.3 Hz), 14.0 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.2 ppm. MS (ESI): *m*/*z* (%) = 543 [2 M + Na]$^+$ (15.06), 522 [2 M + H]$^+$ (26.78), 521 [2 M + H]$^+$ (100), 261 [M + 1]$^+$ (5.02). IR (neat): $\tilde{\nu}$ = 2958, 2929, 2858, 1956, 1459, 1388, 1259, 1164, 1098, 1028 cm^{-1}. HRMS: calcd. for $C_{13}H_{26}O_3P^+$ [M + H]$^+$ 261.1614; found 261.1619.

The following compounds were also prepared according to Typical Procedure I.

Diethyl (4-Phenylbuta-1,2-dienyl)phosphonate (1g): The reaction of 1-phenylbut-3-yn-2-ol (1.1690 g, 8.0 mmol), Et_3N (1.65 mL, *d* = 0.7275 g/mL, 1.20 g, 11.9 mmol), THF (30 mL), and $ClP(OEt)_2$ (1.9000 g, 12.1 mmol)/THF (5 mL) afforded **1g** (1.0919 g, 46%; purity: 91%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.18 (m, 5 H), 5.69–5.56 (m, 1 H), 5.35–5.28 (m, 1 H), 4.13–3.91 (m, 4 H), 3.51–3.32 (m, 2 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.30 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 212.1, 138.6 (d, J_{PC} = 4.7 Hz), 128.5, 128.4, 126.5, 91.7 (d, J_{PC} = 15.7 Hz), 80.4 (d, J_{PC} = 196.4 Hz), 62.1 (d, J_{PC} = 7.0 Hz), 33.7 (d, J_{PC} = 6.4 Hz), 16.2 (d, J_{PC} = 1.7 Hz), 16.1 (d, J_{PC} = 2.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 266 [M]$^+$ (0.62), 128 (100). IR (neat): $\tilde{\nu}$ = 3028, 2983, 2906, 1956, 1603, 1496, 1454, 1390, 1256, 1221, 1164, 1098 cm^{-1}. HRMS: calcd. for $C_{14}H_{19}O_3P$ [M]$^+$ 266.1072; found 266.1080.

Diethyl Nona-3,4-dien-5-ylphosphonate (1q): The reaction of non-4-yn-3-ol (1.3951 g, 10.0 mmol), Et_3N (2.0 mL, *d* = 0.7275 g/mL, 1.46 g, 14.4 mmol), THF (40 mL), and $ClP(OEt)_2$ (2.3572 g, 15.0 mmol)/THF (10 mL) afforded **1q** (1.7718 g, 68%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.44–5.31 (m, 1 H), 4.10–3.91 (m, 4 H), 2.13–1.94 (m, 4 H), 1.46–1.17 (m, 10 H), 1.02–0.91 (m, 3 H), 0.88–0.76 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

207.9 (d, J_{PC} = 5.0 Hz), 94.8 (d, J_{PC} = 16.0 Hz), 94.4 (d, J_{PC} = 186.9 Hz), 61.9, 61.8, 30.1 (d, J_{PC} = 6.8 Hz), 28.0 (d, J_{PC} = 7.5 Hz), 22.0, 21.0 (d, J_{PC} = 7.9 Hz), 16.14 (d, J_{PC} = 2.1 Hz), 16.08 (d, J_{PC} = 2.0 Hz), 13.7, 13.1 (d, J_{PC} = 4.1 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 20.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 260 $[M]^+$ (1.42), 43 (100). IR (neat): $\tilde{\nu}$ = 2963, 2933, 2873, 1951, 1458, 1391, 1247, 1164, 1098, 1059, 1028 cm^{-1}. HRMS: calcd. for $C_{13}H_{25}O_3P$ $[M]^+$ 260.1541; found 260.1545.

Reaction of Diethyl (3-Substituted allenyl)phosphonates with PhSeCl

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-heptenyl]phosphonate [(*Z*)-2a]. Typical Procedure II: H_2O (0.4 mL) was added to a solution of PhSeCl (57.0 mg, 0.3 mmol) in THF (3.0 mL) at room temperature. Then a solution of **1a** (46.4 mg, 0.2 mmol) in THF (1.0 mL) was added, and the resulting mixture was stirred at 70 °C for 2.5 h. The mixture was quenched with H_2O (5 mL) and extracted with diethyl ether (3 × 20 mL), washed with brine (5 mL), and dried with anhydrous Na_2SO_4. Filtration, concentration, and flash chromatography on silica gel (petroleum ether/ethyl acetate, 2:1) afforded (*Z*)-**2a** (58.8 mg, 69%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.57 (m, 2 H), 7.43–7.28 (m, 3 H), 6.54 (d, *J* = 12.9 Hz, 1 H), 4.27–4.08 (m, 5 H), 2.00–1.86 (m, 1 H), 1.75–1.60 (m, 1 H), 1.40–1.22 (m, 1 H), 1.36 (t, *J* = 7.2 Hz, 6 H), 1.20–1.00 (m, 3 H), 0.79 (t, *J* = 7.0 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5 (d, J_{PC} = 5.6 Hz), 136.0, 129.5, 129.1, 126.7, 117.6 (d, J_{PC} = 195.8 Hz), 63.2 (d, J_{PC} = 20.8 Hz), 62.3 (d, J_{PC} = 5.4 Hz), 61.8 (d, J_{PC} = 5.5 Hz), 38.0 (d, J_{PC} = 1.1 Hz), 28.2, 21.7, 16.4, 16.3, 13.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 429 $[M(^{82}Se^{37}Cl) + 1]^+$ (0.23), 428 $[M(^{82}Se^{37}Cl)]^+$ (1.23), 427 $[M(^{82}Se^{35}Cl) + 1]^+$ or $[M(^{80}Se^{37}Cl) + 1]^+$ (1.90), 426 $[M(^{82}Se^{35}Cl)]^+$ or $[M(^{80}Se^{37}Cl)]^+$ (9.09), 425 $[M(^{80}Se^{35}Cl) + 1]^+$ or $[M(^{78}Se^{37}Cl) + 1]^+$ (4.21), 424 $[M(^{80}Se^{35}Cl)]^+$ or $[M(^{78}Se^{37}Cl)]^+$ or $[M(^{77}Se^{37}Cl) + 1]^+$ (20.21), 423 $[M(^{77}Se^{37}Cl)]^+$ or $[M(^{78}Se^{35}Cl) + 1]^+$ or $[M(^{76}Se^{37}Cl) + 1]^+$ (3.01), 422 $[M(^{78}Se^{35}Cl)]^+$ or $[M(^{76}Se^{37}Cl)]^+$ or $[M(^{77}Se^{35}Cl) + 1]^+$ (9.76), 421 $[M(^{77}Se^{35}Cl)]^+$ or $[M(^{76}Se^{35}Cl) + 1]^+$ or $[M(^{74}Se^{37}Cl) + 1]^+$ (3.44), 420 $[M(^{76}Se^{35}Cl)]^+$ or $[M(^{74}Se^{37}Cl)]^+$ (3.36), 418 $[M(^{74}Se^{35}Cl)]^+$ (0.33), 267 (100). IR (neat): $\tilde{\nu}$ = 3057, 2959, 2931, 2872, 1576, 1476, 1439, 1391, 1368, 1250, 1163, 1097, 1053, 1025 cm^{-1}. HRMS: calcd. for $C_{17}H_{27}{}^{35}ClO_3P^{80}Se$ $[M + H]^+$ 425.0552; found 425.0548.

Reaction in Dioxane/H_2O. Typical Procedure III: H_2O (0.4 mL) was added to a solution of PhSeCl (58.2 mg, 0.3 mmol) in dioxane (3.0 mL) at room temperature. Then a solution of **1a** (45.5 mg, 0.2 mmol) in dioxane (1.0 mL) was subsequently added, and the resulting mixture was stirred at 70 °C for 4 h. The mixture was quenched with H_2O (5 mL) and extracted with diethyl ether (3 × 20 mL), washed with brine (5 mL), and dried with anhydrous Na_2SO_4. Filtration, concentration, and flash chromatography on silica gel (petroleum ether/ethyl acetate, 2:1) afforded (*Z*)-**2a** (57.6 mg, 69%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.57 (m, 2 H), 7.43–7.28 (m, 3 H), 6.54 (dd, J_1 = 12.9, J_2 = 0.8 Hz, 1 H), 4.27–4.09 (m, 5 H), 2.00–1.85 (m, 1 H), 1.75–1.60 (m, 1 H), 1.40–1.22 (m, 1 H), 1.37 (t, *J* = 7.2 Hz, 6 H), 1.20–1.00 (m, 3 H), 0.80 (t, *J* = 7.1 Hz, 3 H) ppm.

Larger Scale Reaction of 1a: H_2O (2.4 mL) was added to a solution of PhSeCl (1.3802 g, 7.2 mmol) in dioxane (36 mL) at room temperature. Then a solution of **1a** (1.1134 g, 4.8 mmol) in dioxane (12 mL) was subsequently added dropwise over 3 min, and the resulting mixture was stirred at 70 °C for 5.5 h. The mixture was quenched with H_2O (10 mL) and extracted with diethyl ether (3 × 30 mL), washed with brine (10 mL), and dried with anhydrous Na_2SO_4. Filtration, concentration, and flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1 to 2:1) afforded (*Z*)-**2a** (1.4637 g, 72%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64–7.57 (m, 2 H), 7.43–7.28 (m, 3 H), 6.54 (d, *J* = 12.9 Hz, 1 H), 4.27–4.08 (m, 5 H), 2.00–1.86 (m, 1 H), 1.75–1.60 (m, 1 H), 1.40–1.22 (m, 1 H), 1.36 (t, *J* = 7.2 Hz, 6 H), 1.20–1.00 (m, 3 H), 0.79 (t, *J* = 7.0 Hz, 3 H) ppm.

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-heptenyl]phosphonate [(*Z*)-2a] and 5-(*n*-Butyl)-2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (3a): H_2O (1.6 mL) was added to a solution of PhSeCl (115.4 mg, 0.6 mmol) in MeCN (3.3 mL) at room temperature. Then a solution of **1a** (70.6 mg, 0.3 mmol) in MeCN (1.5 mL) was subsequently added, and the resulting mixture was stirred at room temp. for 2 h. The mixture was worked up with H_2O (5 mL) and extracted with diethyl ether (3 × 20 mL), washed with brine (5 mL), and dried with anhydrous Na_2SO_4. Filtration, concentration, and flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1) afforded (*Z*)-**2a** (22.8 mg, 18%) and **3a** (53.3 mg, 49%). **3a**: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.55 (m, 2 H), 7.48–7.33 (m, 3 H), [5.42 (dd, J_1 = 29.5, J_2 = 1.6, 0.34 H), 5.40 (dd, J_1 = 29.5, J_2 = 1.6 Hz, 0.64 H), *dr* = 35:65], 4.97–4.85 (m, 1 H), 4.14–3.93 (m, 2 H), 1.97–1.81 (m, 1 H), 1.77–1.21 (m, 8 H), 0.90 (t, *J* = 7.2 Hz, 3 H) ppm. MS (EI, 70 eV): *m*/*z* (%) = 362 $[M(^{82}Se)]^+$ (3.7), 360 $[M(^{80}Se)]^+$ (22.1), 358 $[M(^{78}Se)]^+$ or $[M(^{77}Se) + 1]^+$ (12.1), 357 $[M(^{77}Se)]^+$ or $[M(^{76}Se) + 1]^+$ (5.1), 356 $[M(^{76}Se)]^+$ (4.8), 361 $[M(^{80}Se) + 1]^+$ (4.8), 359 $[M(^{78}Se) + 1]^+$ (2.6), 355 $[M(^{74}Se) + 1]^+$ (1.9), 93 (100). IR (neat): $\tilde{\nu}$ = 3057, 2957, 2932, 2871, 1558, 1476, 1439, 1389, 1328, 1262, 1200, 1163, 1041, 1002 cm^{-1}. $C_{15}H_{21}O_3PSe$ (359.26): calcd. C 50.15, H 5.89; found C 50.15, H 5.92.

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-butenyl]phosphonate [(*Z*)-2b]: According to the typical procedure III, the reaction of **1b** (57.8 mg, 0.30 mmol) and PhSeCl (86.1 mg, 0.45 mmol) in H_2O (0.6 mL) and dioxane (6 mL) at 70 °C for 5 h afforded (*Z*)-**2b** (62.0 mg, 53%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.55 (m, 2 H), 7.41–7.28 (m, 3 H), 6.57 (dd, J_1 = 12.9, J_2 = 0.6 Hz, 1 H), 4.33 (q, *J* = 6.7 Hz, 1 H), 4.24–4.09 (m, 4 H), 1.55 (d, *J* = 6.6 Hz, 3 H), 1.35 (t, *J* = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3 (d, J_{PC} = 5.4 Hz), 135.7, 129.6, 129.1, 126.8, 117.8 (d, J_{PC} = 195.0 Hz), 62.4 (d, J_{PC} = 5.7 Hz), 61.9 (d, J_{PC} = 6.4 Hz), 58.3 (d, J_{PC} = 21.4 Hz), 25.6, 16.4, 16.3 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 384 $[M(^{82}Se^{35}Cl)]^+$ or $[M(^{80}Se^{37}Cl)]^+$ (0.68), 383 $[M(^{80}Se^{35}Cl) + 1]^+$ or $[M(^{78}Se^{37}Cl) + 1]^+$ (3.57), 382 $[M(^{80}Se^{35}Cl)]^+$ or $[M(^{78}Se^{37}Cl)]^+$ or $[M(^{77}Se^{37}Cl) + 1]^+$ (1.87), 381 $[M(^{77}Se^{37}Cl)]^+$ or $[M(^{78}Se^{35}Cl) + 1]^+$ or $[M(^{76}Se^{37}Cl) + 1]^+$ (9.84), 380 $[M(^{78}Se^{35}Cl)]^+$ or $[M(^{76}Se^{37}Cl)]^+$ or $[M(^{77}Se^{35}Cl) + 1]^+$ (0.74), 379 $[M(^{77}Se^{35}Cl)]^+$ or $[M(^{76}Se^{35}Cl) + 1]^+$ or $[M(^{74}Se^{37}Cl) + 1]^+$ (3.95), 378 $[M(^{76}Se^{35}Cl)]^+$ or $[M(^{74}Se^{37}Cl)]^+$ (0.30), 377 $[M(^{74}Se^{35}Cl) + 1]^+$ (1.57), 133 (100). IR (neat): $\tilde{\nu}$ = 3057, 2982, 2930, 2901, 1576, 1477, 1439, 1391, 1368, 1248, 1163, 1097, 1051, 1024 cm^{-1}. HRMS: calcd. for $C_{14}H_{20}{}^{35}ClO_3P^{80}Se$ $[M]^+$ 382.0004; found 382.0010.

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-butenyl]phosphonate [(*Z*)-2b]: According to the typical procedure II, the reaction of **1b** (56.4 mg, 0.30 mmol) and PhSeCl (86.4 mg, 0.45 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 1 h afforded (*Z*)-**2b** (58.6 mg, 52%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.55 (m, 2 H), 7.41–7.28 (m, 3 H), 6.58 (d, *J* = 12.8 Hz, 1 H), 4.33 (q, *J* = 6.6 Hz, 1 H), 4.24–4.09 (m, 4 H), 1.55 (d, *J* = 6.6 Hz, 3 H), 1.34 (t, *J* = 7.1 Hz, 6 H) ppm.

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-hexenyl]phosphonate [(*Z*)-2c]: According to the typical procedure II, the reaction of **1c** (64.9 mg, 0.30 mmol) and PhSeCl (86.8 mg, 0.45 mmol) in H_2O

(0.6 mL) and THF (6 mL) at 70 °C for 1.5 h afforded (*Z*)-**2c** (77.7 mg, 64%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.6 Hz, 2 H), 7.40–7.28 (m, 3 H), 6.52 (d, J = 12.8 Hz, 1 H), 4.24–4.09 (m, 5 H), 1.91–1.81 (m, 1 H), 1.71–1.60 (m, 1 H), 1.40–1.25 (m, 1 H), 1.34 (t, J = 7.4 Hz, 6 H), 1.16–1.04 (m, 1 H), 0.67 (t, J = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6 (d, J_{PC} = 5.5 Hz), 136.0, 129.5, 129.1, 126.6, 117.4 (d, J_{PC} = 194.8 Hz), 62.8 (d, J_{PC} = 20.5 Hz), 62.3 (d, J_{PC} = 5.5 Hz), 61.8 (d, J_{PC} = 5.6 Hz), 40.1, 19.3, 16.34, 16.28, 12.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 378 [M(^{82}Se^{35}Cl) + 1 – ^{35}Cl]$^+$ or [M(^{80}Se^{37}Cl) + 1 – ^{35}Cl]$^+$ (0.75), 377 [M(^{82}Se^{35}Cl) – ^{35}Cl]$^+$ or [M(^{80}Se^{37}Cl) – ^{35}Cl]$^+$ (3.96), 376 [M(^{80}Se^{35}Cl) + 1 – ^{35}Cl]$^+$ or [M(^{78}Se^{37}Cl) + 1 – ^{35}Cl]$^+$ (4.61), 375 [M(^{80}Se^{35}Cl) – ^{35}Cl]$^+$ or [M(^{78}Se^{37}Cl) – ^{35}Cl]$^+$ or [M(^{77}Se^{37}Cl) + 1 – ^{35}Cl]$^+$ (18.61), 374 [M(^{77}Se^{37}Cl) – ^{35}Cl]$^+$ or [M(^{78}Se^{35}Cl) + 1 – ^{35}Cl]$^+$ or [M(^{76}Se^{37}Cl) + 1 – ^{35}Cl]$^+$ (2.11), 373 [M(^{78}Se^{35}Cl) – ^{35}Cl]$^+$ or [M(^{76}Se^{37}Cl) – ^{35}Cl]$^+$ or [M(^{77}Se^{35}Cl) + 1 – ^{35}Cl]$^+$ (11.32), 372 [M(^{77}Se^{35}Cl) – ^{35}Cl]$^+$ or [M(^{76}Se^{35}Cl) + 1 – ^{35}Cl]$^+$ or [M(^{74}Se^{37}Cl) + 1 – ^{35}Cl]$^+$ (4.23), 371 [M(^{76}Se^{35}Cl) – ^{35}Cl]$^+$ or [M(^{74}Se^{37}Cl) – ^{35}Cl]$^+$ (4.24), 79 (100). IR (neat): $\tilde{\nu}$ = 3056, 2962, 2933, 2873, 1576, 1476, 1439, 1391, 1250, 1163, 1097, 1053, 1023 cm^{-1}. $C_{16}H_{24}ClO_3PSe$ (409.75): calcd. C 46.90, H 5.90; found C 46.86, H 5.93.

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-octenyl]phosphonate [(*Z*)-2d]: According to the typical procedure II, the reaction of **1d** (74.4 mg, 0.30 mmol) and PhSeCl (85.5 mg, 0.45 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 1 h afforded (*Z*)-**2d** (87.8 mg, 66%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (d, J = 7.2 Hz, 2 H), 7.40–7.28 (m, 3 H), 6.51 (d, J = 13.2 Hz, 1 H), 4.27–4.08 (m, 5 H), 1.94–1.84 (m, 1 H), 1.70–1.58 (m, 1 H), 1.34 (t, J = 7.0 Hz, 6 H), 1.34–1.25 (m, 1 H), 1.22–1.10 (m, 2 H), 1.10–0.97 (m, 3 H), 0.78 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6 (d, J_{PC} = 5.6 Hz), 136.0, 129.5, 129.1, 126.6, 117.4 (d, J_{PC} = 196.5 Hz), 63.1 (d, J_{PC} = 20.6 Hz), 62.2 (d, J_{PC} = 5.4 Hz), 61.8 (d, J_{PC} = 5.4 Hz), 38.2, 30.6, 25.7, 22.2, 16.32, 16.26, 13.8 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.1 ppm. MS (EI, 70 eV): *m*/*z* (%) = 441 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (1.50), 440 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (6.90), 439 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (3.97), 438 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (15.28), 436 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (7.63), 435 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (3.35), 434 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (2.73), 281 (100). IR (neat): $\tilde{\nu}$ = 2930, 2860, 1576, 1476, 1439, 1391, 1368, 1249, 1164, 1097, 1024 cm^{-1}. HRMS: calcd. for $C_{18}H_{28}{}^{35}ClO_3P^{80}Se$ [M]$^+$ 438.0630; found 438.0639.

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-nonenyl]phosphonate [(*Z*)-2e]: According to the typical procedure II, the reaction of **1e** (51.6 mg, 0.20 mmol) and PhSeCl (58.0 mg, 0.30 mmol) in H_2O (0.4 mL) and THF (4 mL) at 70 °C for 1 h afforded (*Z*)-**2e** (60.7 mg, 68%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.57 (m, 2 H), 7.40–7.29 (m, 3 H), 6.53 (d, J = 13.2 Hz, 1 H), 4.24–4.09 (m, 5 H), 1.95–1.86 (m, 1 H), 1.73–1.61 (m, 1 H), 1.35 (d, J = 7.2 Hz, 6 H), 1.35–1.25 (m, 1 H), 1.25–0.95 (m, 7 H), 0.83 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7 (d, J_{PC} = 5.4 Hz), 136.1, 129.5, 129.2, 126.7, 117.6 (d, J_{PC} = 196.1 Hz), 63.2 (d, J_{PC} = 20.6 Hz), 62.3 (d, J_{PC} = 6.5 Hz), 61.8 (d, J_{PC} = 5.3 Hz), 38.3 (d, J_{PC} = 1.6 Hz), 31.4, 28.2, 26.0, 22.4, 16.4, 16.3, 13.9 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.3 ppm. MS (ESI) *m*/*z* (%) = 457 [M(^{82}Se^{37}Cl) + 1]$^+$ (4.08), 456 [M(^{82}Se^{37}Cl)]$^+$ (9.39), 455 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (44.49), 454 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (19.18), 453 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (100), 452 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (13.88), 451 [M(^{77}Se^{37}Cl)]$^+$ or [M(^{78}Se^{35}Cl) + 1]$^+$ or [M(^{76}Se^{37}Cl) + 1]$^+$ (48.16), 450 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (14.69), 449 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (16.73). IR (neat): $\tilde{\nu}$ = 2961, 2956, 2929, 2858, 1577, 1477, 1439, 1386, 1249, 1158, 1095, 1053, 1024 cm^{-1}. HRMS: calcd. for $C_{19}H_{31}{}^{35}ClO_3P^{80}Se$ [M + H]$^+$ 453.0859; found 453.0856.

Diethyl [(*Z*)-3-Chloro-4-methyl-2-(phenylselanyl)-1-pentenyl]phosphonate [(*Z*)-2f]: According to the typical procedure II, the reaction of **1f** (64.1 mg, 0.30 mmol) and PhSeCl (85.9 mg, 0.45 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 1.5 h afforded (*Z*)-**2f** (89.6 mg, 74%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.56 (m, 2 H), 7.39–7.29 (m, 3 H), 6.50 (d, J = 13.6 Hz, 1 H), 4.24–4.08 (m, 5 H), 2.31–2.20 (m, 1 H), 1.334 (t, J = 7.2 Hz, 3 H), 1.332 (t, J = 7.2 Hz, 3 H), 0.79 (d, J = 7.0 Hz, 3 H), 0.73 (d, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2 (d, J_{PC} = 6.0 Hz), 136.0, 129.5, 129.1, 126.6, 118.4 (d, J_{PC} = 194.1 Hz), 69.6 (d, J_{PC} = 20.1 Hz), 62.3 (d, J_{PC} = 5.4 Hz), 61.7 (d, J_{PC} = 5.5 Hz), 32.4, 20.6, 16.34, 16.27, 15.1 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.0 ppm. MS (EI, 70 eV): *m*/*z* (%) = 412 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (10.56), 411 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (5.21), 410 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (23.50), 408 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (12.07), 407 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (4.41), 406 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (4.15), 253 (100). IR (neat): $\tilde{\nu}$ = 3055, 2974, 2932, 2905, 2873, 1575, 1473, 1440, 1389, 1368, 1250, 1164, 1097, 1053, 1024 cm^{-1}. HRMS: calcd. for $C_{16}H_{24}{}^{35}ClO_3P^{80}Se$ [M]$^+$ 410.0317; found 410.0321.

Diethyl [(*Z*)-3-Chloro-4-phenyl-2-(phenylselanyl)-1-butenyl]phosphonate [(*Z*)-2g]: According to the typical procedure II, the reaction of **1g** (54.1 mg, 0.20 mmol, purity: 91%) and PhSeCl (59.1 mg, 0.30 mmol) in H_2O (0.4 mL) and THF (4 mL) at 70 °C for 3.3 h afforded (*Z*)-**2g** (66.1 mg, 78%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67–7.60 (m, 2 H), 7.47–7.36 (m, 3 H), 7.23–7.14 (m, 3 H), 6.86–6.79 (m, 2 H), 6.56 (d, J = 12.6 Hz, 1 H), 4.51 (dd, J_1 = 9.0, J_2 = 3.9 Hz, 1 H), 4.23–4.08 (m, 4 H), 3.34 (dd, J_1 = 14.4, J_2 = 3.9 Hz, 1 H), 2.86 (dd, J_1 = 14.4, J_2 = 9.0 Hz, 1 H), 1.38 (t, J = 6.9 Hz, 3 H), 1.37 (t, J = 6.9 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6 (d, J_{PC} = 6.0 Hz), 136.4, 136.3, 129.8, 129.4, 129.2, 128.1, 126.9, 126.6, 118.1 (d, J_{PC} = 194.4 Hz), 63.5 (d, J_{PC} = 20.9 Hz), 62.3 (d, J_{PC} = 5.6 Hz), 61.9 (d, J_{PC} = 5.5 Hz), 44.2 (d, J_{PC} = 1.4 Hz), 16.4, 16.3 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 461 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (1.72), 460 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (7.38), 459 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (4.23), 458 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (16.45), 456 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (8.20), 455 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (3.27), 454 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (2.81), 128 (100). IR (neat): $\tilde{\nu}$ = 3060, 2982, 2930, 2905, 1574, 1476, 1439, 1391, 1249, 1163, 1097, 1024 cm^{-1}. HRMS: calcd. for $C_{20}H_{24}{}^{35}ClO_3P^{80}Se$ [M]$^+$ 458.0317; found 458.0315.

Diethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-propenyl]phosphonate [(*Z*)-2h]: According to the typical procedure II, the reaction of **1h** (52.6 mg, 0.30 mmol) and PhSeCl (85.5 mg, 0.45 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 3 h afforded (*Z*)-**2h** (89.2 mg, 81%) as a liquid.[4a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.62 (m, 2 H), 7.44–7.28 (m, 3 H), 6.46 (dt, J_1 = 13.2, J_2 = 1.6 Hz, 1 H), 4.23–4.10 (m, 4 H), 3.96 (t, J = 1.6 Hz, 2 H), 1.36 (t, J = 7.0 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5 (d, J_{PC} = 6.4 Hz), 136.7, 129.44, 129.38, 125.4, 116.5 (d, J_{PC} = 194.5 Hz), 62.0 (d, J_{PC} = 5.6 Hz), 48.4 (d, J_{PC} = 22.7 Hz), 16.3 (d,

J_{PC} = 6.3 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.8 ppm. MS (EI, 70 eV): *m/z* (%) = 372 [M(^{82}Se^{37}Cl)]$^+$ (0.80), 371 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (1.00), 370 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (5.38), 369 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (2.43), 368 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (11.70), 367 [M(^{77}Se^{37}Cl)]$^+$ or [M(^{78}Se^{35}Cl) + 1]$^+$ or [M(^{76}Se^{37}Cl) + 1]$^+$ (1.84), 366 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (5.26), 365 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (1.98), 364 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (2.05), 211 (100). IR (neat): $\tilde{\nu}$ = 3054, 2982, 2937, 2905, 1576, 1477, 1439, 1391, 1246, 1163, 1097, 1021 cm^{-1}.

Diethyl [(*Z*)-2-(4-Bromophenylselanyl)-3-chloro-1-propenyl]phosphonate [(*Z*)-2i]: According to the typical procedure II, the reaction of **1h** (52.3 mg, 0.30 mmol) and *p*-bromophenylselanyl chloride (163.1 mg, 0.60 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 3.5 h afforded (*Z*)-**2i** (98.6 mg, 74%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.41 (m, 4 H), 6.45 (dt, J_1 = 12.6, J_2 = 1.4 Hz, 1 H), 4.22–4.07 (m, 4 H), 3.95 (t, J = 1.4 Hz, 2 H), 1.35 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.9 (d, J_{PC} = 5.9 Hz), 138.2, 132.7, 124.41, 124.37, 117.5 (d, J_{PC} = 194.3 Hz), 62.2 (d, J_{PC} = 5.7 Hz), 48.3 (d, J_{PC} = 22.8 Hz), 16.4 (d, J_{PC} = 6.4 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 15.4 ppm. MS (EI, 70 eV): *m/z* (%) = 450 [M(^{82}Se^{81}Br^{35}Cl)]$^+$ or [M(^{82}Se^{79}Br^{37}Cl)]$^+$ or [M(^{80}Se^{81}Br^{37}Cl)]$^+$ (2.85), 448 [M(^{82}Se^{79}Br^{35}Cl)]$^+$ or [M(^{80}Se^{81}Br^{35}Cl)]$^+$ or [M(^{80}Se^{79}Br^{37}Cl)]$^+$ or [M(^{78}Se^{81}Br^{37}Cl)]$^+$ (7.67), 446 [M(^{80}Se^{79}Br^{35}Cl)]$^+$ or [M(^{78}Se^{79}Br^{37}Cl)]$^+$ or [M(^{78}Se^{81}Br^{35}Cl)]$^+$ or [M(^{76}Se^{81}Br^{37}Cl)]$^+$ (7.27), 444 [M(^{78}Se^{79}Br^{35}Cl)]$^+$ or [M(^{76}Se^{81}Br^{35}Cl)]$^+$ or [M(^{76}Se^{79}Br^{37}Cl)]$^+$ or [M(^{74}Se^{81}Br^{37}Cl)]$^+$ (2.98), 447 [M(^{80}Se^{79}Br^{35}Cl) + 1]$^+$ or [M(^{78}Se^{79}Br^{37}Cl) + 1]$^+$ or [M(^{78}Se^{81}Br^{35}Cl) + 1]$^+$ or [M(^{76}Se^{81}Br^{37}Cl) + 1]$^+$ (1.74), 445 [M(^{78}Se^{79}Br^{35}Cl) + 1]$^+$ or [M(^{76}Se^{81}Br^{35}Cl) + 1]$^+$ or [M(^{76}Se^{79}Br^{37}Cl) + 1]$^+$ or [M(^{74}Se^{81}Br^{37}Cl) + 1]$^+$ (1.36), 211 (100). IR (neat): $\tilde{\nu}$ = 2982, 2936, 2904, 1585, 1568, 1467, 1441, 1381, 1245, 1163, 1095, 1051, 1024, 1007 cm^{-1}. HRMS: calcd. for $C_{13}H_{17}{}^{79}Br^{35}ClO_3P^{80}Se$ [M]$^+$ 445.8952; found 445.8954.

2-[(1*Z*)-2-(4-Bromophenylselanyl)-3-chloro-1-propenyl]-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-Oxide [(*Z*)-2j]: According to the typical procedure II, the reaction of **1j** (56.5 mg, 0.30 mmol) and *p*-bromophenylselanyl chloride (161.9 mg, 0.60 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 2 h afforded (*Z*)-**2j** (99.6 mg, 72%) as a white solid; m.p. 125.9–126.4 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.49 (m, 2 H), 7.48–7.42 (m, 2 H), 6.53 (dt, J_1 = 15.0, J_2 = 1.5 Hz, 1 H), 4.19–4.08 (m, 2 H), 3.98 (t, J = 1.5 Hz, 2 H), 3.96–3.85 (m, 2 H), 1.13 (s, 3 H), 1.04 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.0 (d, J_{PC} = 7.3 Hz), 138.3, 132.8, 124.5, 124.1, 115.1 (d, J_{PC} = 191.0 Hz), 75.9, 75.8, 48.3 (d, J_{PC} = 22.9 Hz), 32.4 (d, J_{PC} = 6.0 Hz), 21.5, 21.3 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 10.3 ppm. MS (EI, 70 eV): *m/z* (%) = 462 [M(^{82}Se^{81}Br^{35}Cl)]$^+$ or [M(^{82}Se^{79}Br^{37}Cl)]$^+$ or [M(^{80}Se^{81}Br^{37}Cl)]$^+$ (3.30), 460 [M(^{82}Se^{79}Br^{35}Cl)]$^+$ or [M(^{80}Se^{81}Br^{35}Cl)]$^+$ or [M(^{80}Se^{79}Br^{37}Cl)]$^+$ or [M(^{78}Se^{81}Br^{37}Cl)]$^+$ (8.15), 458 [M(^{80}Se^{79}Br^{35}Cl)]$^+$ or [M(^{78}Se^{79}Br^{37}Cl)]$^+$ or [M(^{78}Se^{81}Br^{35}Cl)]$^+$ or [M(^{76}Se^{81}Br^{37}Cl)]$^+$ (9.17), 457 [M(^{78}Se^{79}Br^{35}Cl) + 1]$^+$ or [M(^{76}Se^{81}Br^{35}Cl) + 1]$^+$ or [M(^{76}Se^{79}Br^{37}Cl) + 1]$^+$ or [M(^{74}Se^{81}Br^{37}Cl) + 1]$^+$ (3.41), 456 [M(^{78}Se^{79}Br^{35}Cl)]$^+$ or [M(^{76}Se^{81}Br^{35}Cl)]$^+$ or [M(^{76}Se^{79}Br^{37}Cl)]$^+$ or [M(^{74}Se^{81}Br^{37}Cl)]$^+$ (4.21), 223 (100). IR (KBr): $\tilde{\nu}$ = 3067, 2958, 2883, 1568, 1466, 1379, 1255, 1228, 1061, 1053 cm^{-1}. $C_{14}H_{17}BrClO_3PSe$ (458.57): calcd. C 36.67, H 3.74; found C 36.95, H 3.88.

Reaction of 1j and *p*-BrC_6H_4SeCl in Anhydrous Chloroform:[5] Compound **1j** (75.4 mg, 0.40 mmol), followed by anhydrous chloroform (1.3 mL), was placed in a dried Schlenk tube under nitrogen at room temperature. A solution of *p*-bromophenylselanyl chloride (108.5 mg, 0.40 mmol) in anhydrous chloroform (1.1 mL) was then added dropwise to the reaction mixture at room temp. within 5 min. Then the resulting mixture was stirred at 46 °C for 26 h. After evaporation and flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:2), (*Z*)-**2j** (98.7 mg, 54%) was obtained as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.50 (m, 2 H), 7.49–7.43 (m, 2 H), 6.54 (dt, J_1 = 15.0, J_2 = 1.5 Hz, 1 H), 4.20–4.09 (m, 2 H), 3.99 (t, J = 1.5 Hz, 2 H), 3.96–3.86 (m, 2 H), 1.13 (s, 3 H), 1.05 (s, 3 H) ppm. 13% of **1j** was recovered, as determined by ^{1}H NMR analysis of the crude product.

Dimethyl [(*Z*)-3-Chloro-2-(phenylselanyl)-1-propenyl]phosphonate [(*Z*)-2k]: According to the typical procedure II, the reaction of **1k** (59.5 mg, 0.40 mmol) and PhSeCl (114.8 mg, 0.60 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 4 h afforded (*Z*)-**2k** (108.9 mg, 80%) as a liquid.[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.62 (m, 2 H), 7.44–7.29 (m, 3 H), 6.44 (dt, J_1 = 13.5, J_2 = 1.5 Hz, 1 H), 3.96 (t, J = 1.5 Hz, 2 H), 3.82 (s, 3 H), 3.78 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.7 (d, J_{PC} = 6.9 Hz), 136.8, 129.5, 125.2, 115.0 (d, J_{PC} = 195.1 Hz), 52.6 (d, J_{PC} = 5.8 Hz), 48.4 (d, J_{PC} = 23.9 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 18.5 ppm. MS (EI, 70 eV): *m/z* (%) = 345 [M(^{82}Se^{37}Cl) + 1]$^+$ (0.07), 344 [M(^{82}Se^{37}Cl)]$^+$ (0.48), 343 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (0.45), 342 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (3.76), 341 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (1.16), 340 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (8.67), 339 [M(^{77}Se^{37}Cl)]$^+$ or [M(^{78}Se^{35}Cl) + 1]$^+$ or [M(^{76}Se^{37}Cl) + 1]$^+$ (1.03), 338 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (4.16), 337 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (1.35), 336 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (1.43), 183 (100). IR (neat): $\tilde{\nu}$ = 3055, 2992, 2951, 2849, 1585, 1576, 1470, 1439, 1414, 1249, 1183, 1028 cm^{-1}. HRMS: calcd. for $C_{11}H_{14}{}^{35}ClO_3P^{80}Se$ [M]$^+$ 339.9534; found 339.9524.

Reaction of 1k and PhSeCl in Anhydrous Chloroform:[5] Compound **1k** (103.3 mg, 0.70 mmol), followed by anhydrous chloroform (2.0 mL), was placed in a dried Schlenk tube under nitrogen at room temperature. A solution of phenylselanyl chloride (134.8 mg, 0.70 mmol) in anhydrous chloroform (2.4 mL) was then added dropwise to the reaction mixture at room temp. within 5 min. Then the resulting mixture was stirred at 46 °C for 19 h. After concentration and flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:1 to 2:1), (*Z*)-**2k** (167.5 mg, 71%) was obtained as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66–7.60 (m, 2 H), 7.42–7.28 (m, 3 H), 6.43 (dt, J_1 = 13.5, J_2 = 1.5 Hz, 1 H), 3.95 (t, J = 1.5 Hz, 2 H), 3.80 (s, 3 H), 3.76 (s, 3 H) ppm.

2-[(1*Z*)-3-Chloro-2-(phenylselanyl)-1-propenyl]-5,5-dimethyl-1,3,2-dioxaphosphorinane 2-Oxide [(*Z*)-2l]. Large-Scale Reaction: According to the typical procedure II, the reaction of **1j** (1.0336 g, 5.5 mmol)/THF (13 mL), PhSeCl (2.1070 g, 11.0 mmol)/THF (39 mL), and H_2O (5.2 mL) at 70 °C for 2 h afforded (*Z*)-**2l** (1.6716 g, 80%) as a white solid; m.p. 126.6–127.4 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.60 (m, 2 H), 7.45–7.29 (m, 3 H), 6.52 (d, J = 15.0 Hz, 1 H), 4.13 (dd, J_1 = 13.8, J_2 = 11.1 Hz, 2 H), 3.99 (t, J = 1.5 Hz, 2 H), 3.92 (t, J = 10.4 Hz, 2 H), 1.14 (s, 3 H), 1.04 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.6 (d, J_{PC} = 7.4 Hz), 136.8, 129.6, 129.5, 125.0, 114.0 (d, J_{PC} = 190.7 Hz), 75.9, 75.8, 48.4 (d, J_{PC} = 22.7 Hz), 32.4 (d, J_{PC} = 6.5 Hz), 21.5, 21.2 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 10.6 ppm. MS (EI, 70 eV): *m/z* (%) = 385 [M(^{82}Se^{37}Cl) + 1]$^+$ (0.13), 384 [M(^{82}Se^{37}Cl)]$^+$ (0.86), 383 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (1.09), 382 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$

(6.59), 381 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (2.54), 380 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (15.37), 378 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (7.48), 377 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (2.45), 376 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (2.51), 374 [M(^{74}Se^{35}Cl)]$^+$ (0.24), 223 (100). IR (KBr): $\tilde{\nu}$ = 3072, 3012, 2971, 2894, 1575, 1471, 1439, 1262, 1057, 1008 cm^{-1}. $C_{14}H_{18}ClO_3PSe$ (379.68): calcd. C 44.29, H 4.78; found C 44.35, H 4.89.

Reaction of Diethyl (1-Substituted allenyl)phosphonates with PhSeCl

Diethyl [(*Z*)-1-Chloro-2-(phenylselanyl)-2-hepten-3-yl]phosphonate [(*Z*)-2m] and 3-(*n*-Butyl)-2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (3m): According to the typical procedure III, the reaction of PhSeCl (85.5 mg, 0.45 mmol) and **1m** (69.2 mg, 0.30 mmol) in H_2O (0.6 mL) and dioxane (6.0 mL) at 70 °C for 3 h afforded a mixture of (*Z*)-**2m** and **3m**, which was separated by double chromatography on silica gel to afford (*Z*)-**2m** (93.3 mg, 74%) and **3m** (12.6 mg, 12%) [petroleum ether/ethyl acetate, 5:1 (first round) to 4:1 (second round)]. (*Z*)-**2m**: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.63 (m, 2 H), 7.42–7.28 (m, 3 H), 4.26–4.10 (m, 4 H), 4.00 (s, 2 H), 2.50–2.35 (m, 2 H), 1.58–1.44 (m, 2 H), 1.44–1.28 (m, 2 H), 1.36 (t, J = 7.1 Hz, 6 H), 0.91 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9 (d, J_{PC} = 9.2 Hz), 136.5, 134.1 (d, J_{PC} = 178.3 Hz), 129.2, 129.0, 128.0 (d, J_{PC} = 1.3 Hz), 62.1 (d, J_{PC} = 6.4 Hz), 42.4 (d, J_{PC} = 20.2 Hz), 32.3 (d, J_{PC} = 9.2 Hz), 32.0 (d, J_{PC} = 1.4 Hz), 22.8, 16.3 (d, J_{PC} = 6.4 Hz), 13.7 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.8 ppm. MS (EI, 70 eV): *m*/*z* (%) = 429 [M(^{82}Se^{37}Cl) + 1]$^+$ (0.13), 428 [M(^{82}Se^{37}Cl)]$^+$ (0.50), 427 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (0.84), 426 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (3.29), 425 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (2.04), 424 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (7.08), 423 [M(^{77}Se^{37}Cl)]$^+$ or [M(^{78}Se^{35}Cl) + 1]$^+$ or [M(^{76}Se^{37}Cl) + 1]$^+$ (1.40), 422 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (3.50), 421 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (1.35), 420 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (1.21), 419 [M(^{74}Se^{35}Cl) + 1]$^+$ (0.10), 418 [M(^{74}Se^{35}Cl)]$^+$ (0.11), 267 (100). IR (neat): $\tilde{\nu}$ = 3057, 2959, 2930, 2872, 1560, 1476, 1438, 1390, 1247, 1220, 1163, 1097, 1051, 1022 cm^{-1}. HRMS: calcd. for $C_{17}H_{26}{}^{35}ClO_3P^{74}Se$ [M]$^+$ 418.0533; found 418.0531. **3m**: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.55 (m, 2 H), 7.45–7.29 (m, 3 H), 4.34–4.27 (m, 2 H), 4.16–4.04 (m, 2 H), 2.56–2.26 (m, 2 H), 1.68–1.52 (m, 2 H), 1.47–1.31 (m, 2 H), 1.33 (t, J = 7.1 Hz, 3 H), 0.95 (t, J = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.0 (d, J_{PC} = 33.8 Hz), 136.0 (d, J_{PC} = 4.5 Hz), 129.7, 129.5, 127.0 (d, J_{PC} = 154.9 Hz), 123.4, 71.4 (d, J_{PC} = 9.7 Hz), 63.0 (d, J_{PC} = 7.0 Hz), 30.1 (d, J_{PC} = 2.1 Hz), 27.2 (d, J_{PC} = 13.4 Hz), 22.6, 16.5 (d, J_{PC} = 5.1 Hz), 13.8 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 39.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 363 [M(^{82}Se) + 1]$^+$ (0.73), 361 [M(^{80}Se) + 1]$^+$ (3.38), 359 [M(^{78}Se) + 1]$^+$ (2.09), 357 [M(^{77}Se)]$^+$ or [M (^{76}Se) + 1]$^+$ (2.89), 362 [M(^{82}Se)]$^+$ (3.22), 360 [M(^{80}Se)]$^+$ (15.05), 358 [M(^{78}Se)]$^+$ or [M (^{77}Se) + 1]$^+$ (7.86), 356 [M(^{76}Se)]$^+$ (3.01), 93 (100). IR (neat): $\tilde{\nu}$ = 3056, 2958, 2931, 2872, 1601, 1578, 1464, 1440, 1388, 1344, 1264, 1163, 1100, 1044, 1009 cm^{-1}. HRMS: calcd. for $C_{15}H_{21}O_3P^{80}Se$ [M]$^+$ 360.0394; found 360.0396.

Diethyl [(*Z*)-1-Chloro-2-(phenylselanyl)-2-hepten-3-yl]phosphonate [(*Z*)-2m] and 3-(*n*-Butyl)-2-ethoxy-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (3m): According to the typical procedure II, the reaction of **1m** (68.8 mg, 0.30 mmol) and PhSeCl (86.5 mg, 0.45 mmol) in THF (6 mL) and H_2O (0.6 mL) at 70 °C for 2 h afforded a mixture of (*Z*)-**2m** and **3m**, which were separated by repeated chromatography on silica gel (petroleum ether/ethyl acetate, 5:1, twice) to afford pure (*Z*)-**2m** (72.2 mg, 57%) and **3m** (7.5 mg, 7%). (*Z*)-**2m**: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.65 (m, 2 H), 7.44–7.28 (m, 3 H), 4.28–4.12 (m, 4 H), 4.03 (s, 2 H), 2.52–2.38 (m, 2 H), 1.60–1.46 (m, 2 H), 1.43–1.30 (m, 2 H), 1.38 (t, J = 7.1 Hz, 6 H), 0.93 (t, J = 7.2 Hz, 3 H) ppm. **3m**: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.55 (m, 2 H), 7.45–7.29 (m, 3 H), 4.34–4.27 (m, 2 H), 4.16–4.04 (m, 2 H), 2.52–2.30 (m, 2 H), 1.68–1.52 (m, 2 H), 1.47–1.31 (m, 2 H), 1.33 (t, J = 7.1 Hz, 3 H), 0.96 (t, J = 7.5 Hz, 3 H) ppm.

Diethyl [(*Z*)-1-Chloro-2-(phenylselanyl)-2-buten-3-yl]phosphonate [(*Z*)-2n] and 2-Ethoxy-3-methyl-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (3n): According to the typical procedure III, the reaction of **1n** (57.7 mg, 0.30 mmol) and PhSeCl (86.5 mg, 0.45 mmol) in H_2O (0.6 mL) and dioxane (6.0 mL) at 70 °C for 3 h afforded a mixture of (*Z*)-**2n** and **3n**, which were separated by repeated chromatography on silica gel (petroleum ether/ethyl acetate, 2:1, twice) to afford pure (*Z*)-**2n** (72.9 mg, 63%) and **3n** (5.7 mg, 6%). (*Z*)-**2n**: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73–7.65 (m, 2 H), 7.43–7.28 (m, 3 H), 4.24–4.08 (m, 4 H), 4.02 (s, 2 H), 2.06 (d, J = 13.5 Hz, 3 H), 1.38 (t, J = 6.9 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.0 (d, J_{PC} = 9.5 Hz), 136.8, 129.2, 129.1, 127.7, 127.2 (d, J_{PC} = 181.8 Hz), 62.1 (d, J_{PC} = 5.9 Hz), 42.6 (d, J_{PC} = 21.1 Hz), 17.8 (d, J_{PC} = 9.3 Hz), 16.3 (d, J_{PC} = 6.1 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 18.2 ppm. MS (EI, 70 eV): *m*/*z* (%) = 386 [M(^{82}Se^{37}Cl)]$^+$ (0.49), 385 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (0.77), 384 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (3.38), 383 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (1.43), 382 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (7.53), 381 [M(^{77}Se^{37}Cl)]$^+$ or [M(^{78}Se^{35}Cl) + 1]$^+$ or [M(^{76}Se^{37}Cl) + 1]$^+$ (1.18), 380 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (3.72), 379 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (1.37), 378 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (1.31), 225 (100). IR (neat): $\tilde{\nu}$ = 3056, 2980, 2930, 2905, 1569, 1475, 1440, 1391, 1247, 1192, 1162, 1096, 1049 cm^{-1}. HRMS: calcd. for $C_{14}H_{20}{}^{35}ClO_3P^{80}Se$ [M]$^+$ 382.0004; found 382.0018. **3n**: Liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.55 (m, 2 H), 7.45–7.30 (m, 3 H), 4.38–4.31 (m, 2 H), 4.18–4.04 (m, 2 H), 1.99 (dt, J_1 = 14.4, J_1 = 2.0 Hz, 3 H), 1.34 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9 (d, J_{PC} = 33.3 Hz), 135.9, 129.8, 129.5, 123.4, 122.6 (d, J_{PC} = 158.2 Hz), 71.8 (d, J_{PC} = 8.9 Hz), 63.2 (d, J_{PC} = 6.5 Hz), 16.6 (d, J_{PC} = 5.3 Hz), 11.7 (d, J_{PC} = 14.3 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 39.6 ppm. MS (EI, 70 eV): *m*/*z* (%) = 321 [M(^{82}Se) + 1]$^+$ (2.69), 319 [M(^{80}Se) + 1]$^+$ (14.40), 317 [M(^{78}Se) + 1]$^+$ (10.27), 320 [M(^{82}Se)]$^+$ (19.09), 318 [M(^{80}Se)]$^+$ (100), 316 [M(^{78}Se)]$^+$ or [M (^{77}Se) + 1]$^+$ (50.29), 315 [M(^{77}Se)]$^+$ or [M(^{76}Se) + 1]$^+$ (19.40), 314 [M(^{76}Se)]$^+$ (19.40), 312 [M(^{74}Se)]$^+$ (1.92). IR (neat): $\tilde{\nu}$ = 3056, 2979, 2928, 2877, 2853, 1609, 1577, 1476, 1439, 1390, 1344, 1261, 1198, 1162, 1097, 1045, 1024 cm^{-1}. HRMS: calcd. for $C_{12}H_{15}O_3P^{80}Se$ [M]$^+$ 317.9924; found 317.9915.

Diethyl [(*Z*)-1-Chloro-2-(phenylselanyl)-2-decen-3-yl]phosphonate [(*Z*)-2o] and 2-Ethoxy-3-(*n*-heptyl)-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (3o): According to the typical procedure III, the reaction of **1o** (81.6 mg, 0.30 mmol) and PhSeCl (85.7 mg, 0.45 mmol) in H_2O (0.6 mL) and dioxane (6 mL) at 70 °C for 3 h afforded a mixture of (*Z*)-**2o** and **3o**, which were separated by repeated chromatography on silica gel (petroleum ether/ethyl acetate, 5:1, twice) to afford pure (*Z*)-**2o** (95.5 mg, 69%) and **3o** (11.0 mg, 9%). (*Z*)-**2o**: Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71–7.65 (m, 2 H), 7.42–7.28 (m, 3 H), 4.26–4.07 (m, 4 H), 4.01 (s, 2 H), 2.49–2.35 (m, 2 H), 1.57–1.44 (m, 2 H), 1.39–1.19 (m, 8 H), 1.37 (t, J = 7.2 Hz, 6 H), 0.87 (t, J = 6.6 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9 (d, J_{PC} = 9.1 Hz), 136.6, 134.3 (d, J_{PC} = 178.9 Hz), 129.2, 129.0, 128.1, 62.1 (d, J_{PC} = 5.1 Hz),

42.5 (d, J_{PC} = 20.3 Hz), 32.7 (d, J_{PC} = 9.4 Hz), 31.7, 29.9, 29.7, 28.9, 22.6, 16.4 (d, J_{PC} = 5.8 Hz), 14.1 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.9 ppm. MS (EI, 70 eV): *m*/*z* (%) = 470 [M(^{82}Se^{37}Cl)]$^+$ (0.47), 469 [M(^{82}Se^{35}Cl) + 1]$^+$ or [M(^{80}Se^{37}Cl) + 1]$^+$ (0.72), 468 [M(^{82}Se^{35}Cl)]$^+$ or [M(^{80}Se^{37}Cl)]$^+$ (2.66), 467 [M(^{80}Se^{35}Cl) + 1]$^+$ or [M(^{78}Se^{37}Cl) + 1]$^+$ (1.66), 466 [M(^{80}Se^{35}Cl)]$^+$ or [M(^{78}Se^{37}Cl)]$^+$ or [M(^{77}Se^{37}Cl) + 1]$^+$ (6.12), 465 [M(^{77}Se^{37}Cl)]$^+$ or [M(^{78}Se^{35}Cl) + 1]$^+$ or [M(^{76}Se^{37}Cl) + 1]$^+$ (1.23), 464 [M(^{78}Se^{35}Cl)]$^+$ or [M(^{76}Se^{37}Cl)]$^+$ or [M(^{77}Se^{35}Cl) + 1]$^+$ (3.16), 463 [M(^{77}Se^{35}Cl)]$^+$ or [M(^{76}Se^{35}Cl) + 1]$^+$ or [M(^{74}Se^{37}Cl) + 1]$^+$ (1.18), 462 [M(^{76}Se^{35}Cl)]$^+$ or [M(^{74}Se^{37}Cl)]$^+$ (1.05), 309 (100). IR (neat): $\tilde{\nu}$ = 3056, 2956, 2927, 2856, 1560, 1469, 1439, 1390, 1248, 1197, 1163, 1097, 1051, 1024 cm^{-1}. HRMS: calcd. for $C_{20}H_{32}{}^{35}ClO_3P^{80}Se$ [M]$^+$ 466.0943; found 466.0966. **3o**: Colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62–7.55 (m, 2 H), 7.45–7.30 (m, 3 H), 4.38–4.25 (m, 2 H), 4.17–4.04 (m, 2 H), 2.58–2.28 (m, 2 H), 1.70–1.55 (m, 2 H), 1.43–1.20 (m, 11 H), 0.90 (t, *J* = 6.3 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.9 (d, J_{PC} = 33.6 Hz), 136.0, 129.7, 129.5, 127.1 (d, J_{PC} = 154.4 Hz), 123.5, 71.5 (d, J_{PC} = 9.1 Hz), 63.0 (d, J_{PC} = 7.1 Hz), 31.8, 29.6 (d, J_{PC} = 13.5 Hz), 29.0, 28.0 (d, J_{PC} = 2.1 Hz), 27.5 (d, J_{PC} = 12.6 Hz), 22.6, 16.5 (d, J_{PC} = 6.3 Hz), 14.1 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 39.4 ppm. MS (EI, 70 eV): *m*/*z* (%) = 405 [M(^{82}Se) + 1]$^+$ (1.04), 403 [M(^{80}Se) + 1]$^+$ (6.43), 401 [M(^{78}Se) + 1]$^+$ (4.59), 404 [M(^{82}Se)]$^+$ (4.97), 402 [M(^{80}Se)]$^+$ (24.04), 400 [M(^{78}Se)]$^+$ or [M (^{77}Se) + 1]$^+$ (11.82), 399 [M(^{77}Se)]$^+$ or [M(^{76}Se) + 1]$^+$ (5.35), 398 [M(^{76}Se)]$^+$ (4.79), 245 (100). IR (neat): $\tilde{\nu}$ = 3057, 2927, 2855, 1601, 1577, 1456, 1439, 1390, 1343, 1265, 1163, 1106, 1044 cm^{-1}. HRMS: calcd. for $C_{18}H_{27}O_3P^{80}Se$ [M]$^+$ 402.0863; found 402.0874.

Reaction of Diethyl (Multisubstituted allenyl)phosphonates with PhSeCl: The reactions of **1p** and **1r** with PhSeCl at 70 °C according to the typical procedure II are complicated. Thus, an alternative approach was used.

2-Ethoxy-4-(phenylselanyl)-2,5-dihydro-5,5-dimethyl-1,2-oxaphosphole 2-Oxide (3p). Typical Procedure IV: H_2O (0.6 mL) was added to a solution of PhSeCl (87.6 mg, 0.45 mmol) in THF (4.5 mL) at room temperature. Then a solution of **1p** (62.9 mg, 0.3 mmol) in THF (1.5 mL) was added and the resulting mixture was stirred at room temp. for 3 h. The mixture was quenched with H_2O (5 mL) and extracted with diethyl ether (3 × 20 mL), washed with brine (5 mL), and dried with anhydrous Na_2SO_4. Filtration, concentration, and flash chromatography on silica gel (petroleum ether/ethyl acetate, 3:2) afforded **3p** (55.7 mg, 55%) as a liquid.[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63–7.57 (m, 2 H), 7.48–7.35 (m, 3 H), 5.25 (d, *J* = 28.2 Hz, 1 H), 4.12–3.94 (m, 2 H), 1.64 (s, 3 H), 1.58 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9 (d, J_{PC} = 23.3 Hz), 136.5, 130.1, 129.9, 125.3, 109.2 (d, J_{PC} = 161.9 Hz), 87.2 (d, J_{PC} = 8.3 Hz), 62.8 (d, J_{PC} = 6.4 Hz), 29.1 (d, J_{PC} = 2.9 Hz), 28.4 (d, J_{PC} = 1.9 Hz), 16.4 (d, J_{PC} = 5.9 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 34.7 ppm. MS (EI, 70 eV): *m*/*z* (%) = 335 [M(^{82}Se) + 1]$^+$ (4.08), 333 [M(^{80}Se) + 1]$^+$ (12.64), 329 [M(^{77}Se)]$^+$ or [M (^{76}Se) + 1]$^+$ (20.13), 334 [M(^{82}Se)]$^+$ (20.41), 332 [M(^{80}Se)]$^+$ (98.89), 330 [M(^{78}Se)]$^+$ or [M(^{77}Se) + 1]$^+$ (56.92), 328 [M(^{76}Se)]$^+$ (20.10), 326 [M(^{74}Se)]$^+$ (2.43), 223 (100). IR (neat): $\tilde{\nu}$ = 3059, 2981, 2931, 1558, 1475, 1440, 1387, 1368, 1268, 1186, 1141, 1096, 1041 cm^{-1}.

3-(*n*-Butyl)-2-ethoxy-5-ethyl-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (3q): According to the typical procedure IV, the reaction of **1q** (77.4 mg, 0.3 mmol) and PhSeCl (86.8 mg, 0.45 mmol) in H_2O (0.6 mL) and THF (6 mL) at 70 °C for 0.3 h afforded **3q** (106.5 mg, 92%) (petroleum/ethyl acetate, 5:1 to 3:1) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.46 (m, 2 H), 7.37–7.25 (m, 3 H), 4.57–4.47 (m, 1 H), 4.23–4.03 (m, 2 H), 2.59–2.30 (m, 2 H), 1.93–1.82 (m, 1 H), 1.62–1.44 (m, 3 H), 1.40–1.28 (m, 5 H), 0.94–0.87 (m, 3 H), 0.87–0.78 (m, 3 H) ppm. MS (EI, 70 eV): *m*/*z* (%) = 390 [M(^{82}Se)]$^+$ (3.37), 388 [M(^{80}Se)]$^+$ (13.22), 386 [M(^{78}Se)]$^+$ or [M (^{77}Se) + 1]$^+$ (7.35), 384 [M(^{76}Se)]$^+$ (2.39), 389 [M(^{80}Se) + 1]$^+$ (5.42), 387 [M(^{78}Se) + 1]$^+$ (2.76), 385 [M(^{77}Se)]$^+$ or [M (^{76}Se) + 1]$^+$ (3.21), 189 (100). IR (neat): $\tilde{\nu}$ = 3057, 2961, 2932, 2873, 1597, 1577, 1477, 1439, 1386, 1324, 1262, 1163, 1141, 1097, 1039 cm^{-1}. $C_{17}H_{25}O_3PSe$ (387.31): calcd. C 52.72, H 6.51; found C 52.69, H 6.60.

3-(*n*-Butyl)-2-ethoxy-5,5-dimethyl-4-(phenylselanyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (3r): According to the typical procedure IV, the reaction of **1r** (77.9 mg, 0.3 mmol) and PhSeCl (86.6 mg, 0.45 mmol) in H_2O (0.4 mL) and THF (4 mL) at room temp. for 4 h afforded **3r** (101.2 mg, 87%) (petroleum/ethyl acetate, 5:2) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 2 H), 7.28–7.22 (m, 3 H), 4.18–4.08 (m, 2 H), 2.40–2.17 (m, 2 H), 1.49 (s, 3 H), 1.46 (s, 3 H), 1.42–1.34 (m, 2 H), 1.32 (t, *J* = 7.0 Hz, 3 H), 1.23–1.17 (m, 2 H), 0.79 (t, *J* = 7.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.7 (d, J_{PC} = 31.1 Hz), 134.8 (d, J_{PC} = 145.0 Hz), 132.2, 129.5, 128.5 (d, J_{PC} = 1.5 Hz), 127.7, 87.9 (d, J_{PC} = 8.1 Hz), 62.7 (d, J_{PC} = 7.8 Hz), 29.6 (d, J_{PC} = 1.4 Hz), 28.3 (d, J_{PC} = 11.7 Hz), 28.1 (d, J_{PC} = 2.8 Hz), 27.4, 22.6, 16.5 (d, J_{PC} = 6.1 Hz), 13.6 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 34.5 ppm. MS (EI, 70 eV): *m*/*z* (%) = 390 [M(^{82}Se)]$^+$ (2.69), 388 [M(^{80}Se)]$^+$ (12.86), 386 [M(^{78}Se)]$^+$ or [M (^{77}Se) + 1]$^+$ (5.35), 384 [M(^{76}Se)]$^+$ (2.09), 389 [M(^{80}Se) + 1]$^+$ (4.58), 387 [M(^{78}Se) + 1]$^+$ (1.03), 121 (100). IR (neat): $\tilde{\nu}$ = 3059, 2980, 2958, 2932, 2871, 1597, 1577, 1477, 1460, 1439, 1365, 1267, 1224, 1144, 1041 cm^{-1}. HRMS: calcd. for $C_{17}H_{25}O_3P^{80}Se$ [M]$^+$ 388.0707; found 388.0712.

Supporting Information (see footnote on the first page of this article): ^{1}H, ^{13}C, and ^{31}P NMR spectra of all compounds.

Acknowledgments

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