Tetrahedron 65 (2009) 4877–4889

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Studies on highly regio- and stereoselective selenohydroxylation reaction of 1,2-allenyl phosphine oxides with PhSeCl

Guangke He [a], Hao Guo [b], Rong Qian [c], Yinlong Guo [c], Chunling Fu [a,*], Shengming Ma [a,b,*]

[a] Laboratory of Molecular Recognition and Synthesis, Department of Chemistry, Zhejiang University, Hangzhou 310027, Zhejiang, PR China
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, PR China
[c] Shanghai Mass Spectrometry Center, Shanghai Institute of Organic Chemistry Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, PR China

ARTICLE INFO

Article history:
Received 6 December 2008
Received in revised form 4 April 2009
Accepted 7 April 2009
Available online 16 April 2009

ABSTRACT

The selenohydroxylation of readily available 1,2-allenyl phosphine oxides with PhSeCl in MeCN/H_2O afforded 3-hydroxy-2-phenylselanyl-1(*E*)-alkenyl diphenyl phosphine oxides in good yields with very high regio- and stereoselectivities including the high efficiency of the axial chirality transfer. The *E*-stereoselectivity is believed to be determined by the neighboring group participation effect of the diphenyl phosphine oxide functionality.

1. Introduction

Phosphorous-containing compounds show important biological activity.[1] In addition to the biological potential, this type of compounds also plays an important role in organic synthesis.[2] On the other hand, 1-alkenyl selenides are important organic intermediates,[3a,b] particularly in synthesizing carbonyl compounds[3c,d] and stereoselective preparation of functionalized alkenes.[3e,f] Thus, development of new methods for the highly selective synthesis of 2-phosphoryl-1-alkenyl selenides is highly desired.

Recently, we have developed the halohydroxylation of 1,2-allenyl sulfides,[4,5] selenides,[6] sulfoxides,[7] sulfones,[8] phosphine oxides,[9] and 3-aryl-1,2-allenes.[10] In all the cases, the halogen atom has been introduced to the center carbon atom of the allene moiety while the hydroxyl group is connected to the 3-position of the starting allenes referring to the carbon atom connected to the heteroatom. The stereoselectivity depends on the nature of the functional group: for sulfides and selenides the *Z*-products were formed[4–6] while for other cases *E*-products were produced.[7–9] Recently, we also studied the selenolactonization of 2,3-allenoic acids[11] and 2,3-allenoates.[12,13] Similarly, the reaction of 1,2-allenylic phosphonates, phosphinates, phosphoric acids with RSeCl and RSeBr was also reported to afford 4-selenyl-2,5-dihydro-1,2-oxaphosphole 2-oxides.[14–20] Furthermore, the selenohydroxylation of 1,2-allenylic sulfoxides with PhSeCl has been reported by this group.[21] Due to the similarity between the phosphine oxides and sulfoxides or sulfones, we show interest in the selenohydroxylation of 1,2-allenylic phosphine oxides. Herein, we wish to report the realization of selenohydroxylation of 1,2-allenyl diphenyl phosphine oxides affording (*E*)-3-hydroxy-2-phenylselanyl alkenyl diphenyl phosphine oxides with high regio- and stereoselectivity.

2. Results and discussion

After some screening, it is observed that the reaction of **1a** with 1.5 equiv of PhSeCl in CH_2Cl_2 at rt afforded the expected product *E*-**2a** as the only stereoisomer in 41% yield (entry 1, Table 1). The reaction in CH_3NO_2 afforded *E*-**2a** in 62% yield (entry 2, Table 1). The solvent effect is obvious: the yields for the reaction in toluene, ethyl acetate, and MeCN are much higher (entries 3–5, Table 1). Since the formed hydroxyl group may have something to do with the water present in the reaction media, H_2O was added as the cosolvent to MeCN and the yields were improved to 96% (entries 6–10, Table 1). With 1.2 equiv of PhSeCl, the yield is lower (entry 10, Table 1). No reaction was observed in aqueous acetone while the reaction in aqueous THF, EtOH, or DMF afforded the product *E*-**2a** in 82–90% yields (entries 12–14, Table 1).

With the optimized reaction conditions in hand (entry 7, Table 1), the scope of this selenohydroxylation reaction was demonstrated (Table 2). The reaction is very general: for 3-monosubstituted diphenyl phosphine oxide, the yield is good (entries 2 and 3, Table 2); the reaction of 3,3-disubstituted substituted (entries 4–6, Table 2), 1-monosubstituted (entries 7 and 8, Table 2), 1,3-disubstituted (entries 9 and 10, Table 2), and fully substituted (entry 11, Table 2) 1,2-allenyl diphenyl phosphine oxides all worked smoothly and cleanly to afford the corresponding *E*-selenohydroxylation products. The regio- and stereochemical outcome was further established by the X-ray diffraction study of *E*-**2b** (Fig. 1).[22]

* Corresponding authors.
E-mail addresses: fud@zju.edu.cn (C. Fu), masm@mail.sioc.ac.cn (S. Ma).

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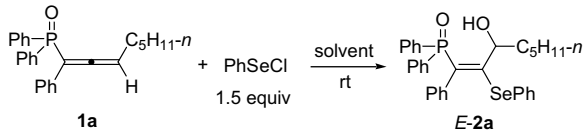
doi:10.1016/j.tet.2009.04.023

Table 1
Selenohydroxylation of 1-phenylocta-1,2-dienyl diphenyl phosphine oxide (**1a**) with PhSeCl[a]

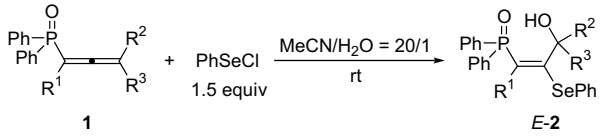


Entry	Solvent	*T* (h)	Yield of ***E*-2a**[b]
1	CH_2Cl_2	3.5	41
2	CH_3NO_2	1.2	62
3	Toluene	30.2	75
4	Ethyl acetate	30.4	82
5	MeCN	12	82
6	MeCN/H_2O=40/1	0.65	92
7	MeCN/H_2O=20/1	0.25	96
8	MeCN/H_2O=10/1	0.6	87
9	MeCN/H_2O=5/1	12	80
10[c]	MeCN/H_2O=20/1	0.6	84
11	Acetone/H_2O=20/1	44.5	0[d]
12	THF/H_2O=20/1	16	90
13	EtOH/H_2O=20/1	28	82
14	DMF/H_2O=20/1	17	85

[a] The reaction was carried out using 0.2 mmol of **1a**, 0.3 mmol of PhSeCl, and 4.0 mL of organic solvent.
[b] NMR yield based on **1a** using CH_2Br_2 as the internal standard.
[c] PhSeCl (1.2 equiv) was used.
[d] Compound **1a** (91%) was recovered.

However, in the case of R^1=R^2=H, R^3=alkyl group (except for methyl group), the reaction is not clean, i.e., 3-chloro-2-phenylselanyl-1(*Z*)-alkenyl diphenyl phosphine oxides were formed as the by-product (entries 12–16, Table 2). In addition, it is interesting to

Table 2
Selenohydroxylation of differently substituted 1,2-propadienyl diphenyl phosphine oxides **1** with PhSeCl[a]



Entry	R^1	R^2	R^3	*T* (min)	Isolated yield of *E*-**2** (%)
1	Ph	H	*n*-C_5H_{11} (**1a**)	14	91 (**2a**)
2	H	H	Me (**1b**)	12	82 (**2b**)
3	H	H	Ph (**1c**)	28	85 (**2c**)
4	H	Me	Me (**1d**)	19	89 (**2d**)
5	H	*n*-Pr	*n*-Pr (**1e**)	18	80 (**2e**)
6	H	$(CH_2)_5$ (**1f**)		10	84 (**2f**)
7	*n*-C_4H_9	H	H (**1g**)	16	67 (**2g**)
8	Ph	H	H (**1h**)	14	80 (**2h**)
9	Et	H	Me (**1i**)	10	90 (**2i**)
10	Ph	H	Et (**1j**)	5	88 (**2j**)
11	*n*-C_4H_9	Me	Me (**1k**)	10	65 (**2k**)
12	H	H	*i*-Pr (**1l**)	20	76 (**2l**)[b]
13	H	H	H (**1m**)	16	13 (**2m**)[c]
14	H	H	Et (**1n**)	20	82.5 (**2n**)[d]
15	H	H	*n*-C_6H_{13} (**1o**)	30	64 (**2o**)[e]
16	H	H	Bn (**1p**)	15	64 (**2p**)[f]

[a] The reaction was carried out using 0.3 mmol of **1a**, 0.45 mmol of PhSeCl, 6.0 mL of MeCN, and 0.3 mL of H_2O.
[b] The reaction also afforded 3-chloro-4-methyl-2-phenylselanyl-1(*Z*)-pentenyl diphenyl phosphine oxide (*Z*-**3l**) in 7% isolated yield.
[c] The reaction also afforded 3-chloro-2-phenylselanyl-1(*Z*)-propenyl diphenyl phosphine oxide (*Z*-**3m**) in 61.5% isolated yield.
[d] The reaction also afforded 3-chloro-4,-2-phenylselanyl-1(*Z*)-pentenyl diphenyl phosphine oxide (*Z*-**3n**) in 6% isolated yield.
[e] The reaction also afforded 3-chloro-2-phenylselanyl-1(*Z*)-nonenyl diphenyl phosphine oxide (*Z*-**3o**) in 6% isolated yield.
[f] The reaction also afforded 3-chloro-4-phenyl-2-phenylselanyl-1(*Z*)-butenyl diphenyl phosphine oxide (*Z*-**3p**) in 14% isolated yield.

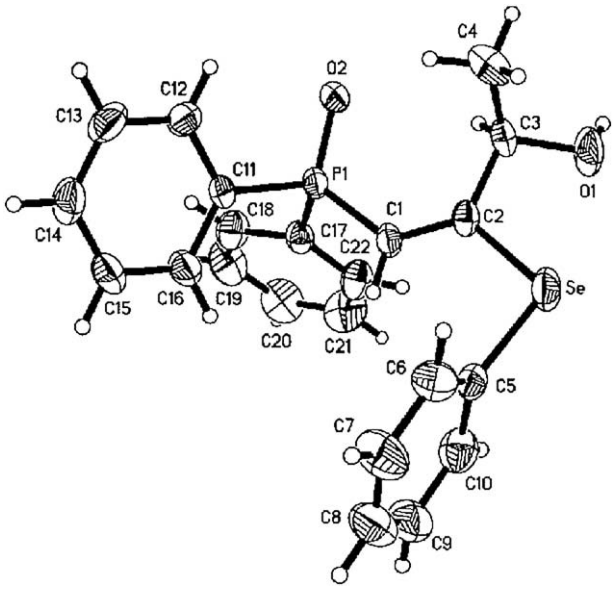


Figure 1. ORTEP representation of *E*-**2b**.

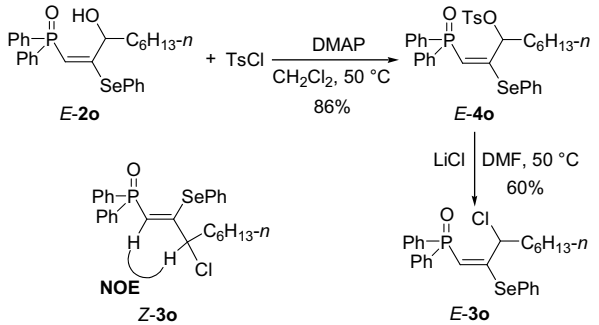
observe that the stereochemistry for the formation of the chlorides **3l**–**p** is different from that for the selenohydroxylation product *E*-**2**.

In order to further confirm this difference, *E*-**3o** was prepared from the sequential tosylation[23] and chlorination[24] of *E*-**2o** (Scheme 1). It is still not clear why the formed allylic chloride is in *Z*-configuration. After further screening, it was observed that when reaction of **1l** was conducted in MeCN/H_2O (2:1) at 70 °C, the yield of *E*-**2l** and the ratio of *E*-**2l**/*Z*-**3l** is much higher (compare entries 1–6, Table 3).

Some typical results of selenohydroxylation of 3-monosubstituted or the simple allenyl phosphine oxides under this new set of reaction conditions are summarized in Table 4.

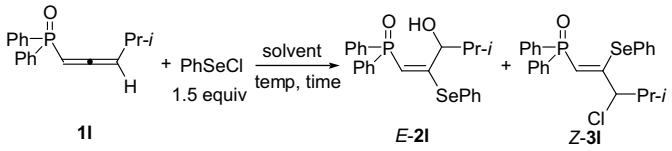
As optically active 1,2-allenyl phosphine oxides are easily available from the corresponding optically active propargylic alcohols,[25,26] we also investigated the possibility of synthesizing optically active selenohydroxylation product by means of the present method. The experimental results showed that the axial chirality in allenyl phosphine oxides could be transferred to the central chirality of the products with high efficiency (Scheme 2). The absolute configuration of the products was determined by X-ray diffraction analysis of *S*-(*E*)-**2b** by using the selenium atom in the molecule as a reference (Fig. 2).[27]

In order to study the reaction mechanism, we carried out this selenohydroxylation reaction of **1h** using water and ^{18}O-labeled water. The normal product *E*-**2h** and the ^{18}O-labeled product *E*-**2h*** were isolated and studied by ESI-MS technique



Scheme 1.

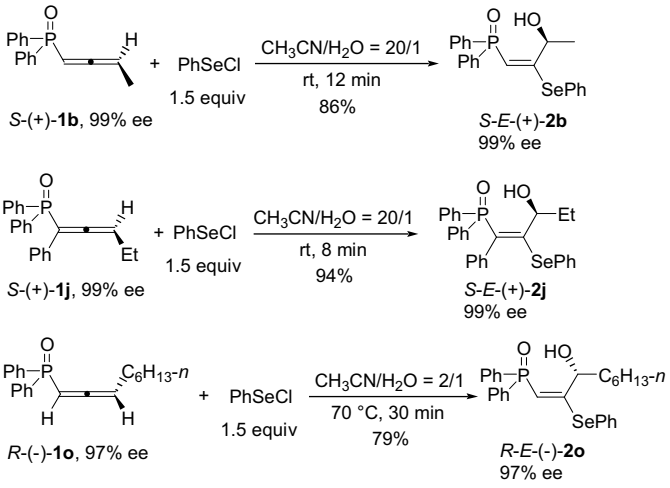
Table 3
Selenohydroxylation of 4-methylpenta-1,2-dienyl diphenyl phosphine oxide (**1l**) with PhSeCl



1l *E*-**2l** *Z*-**3l**

Entry	Solvent ($MeCN/H_2O$)	Temp (°C)	*T* (h)	Yield of *E*-**2l** (%)[a]	Ratio of *E*-**2l**/*Z*-**3l**[b]
1	20/1	rt	0.50	64	90/10
2	10/1	rt	0.37	76	91/9
3	5/1	rt	0.60	84	94/6
4	2/1	rt	13.4	89	97/3
5	1/1	rt	65.7	77	98/2
6	2/1	70	0.57	82	97/3

[a] NMR yield based on **1l** using CH_2Br_2 as the internal standard.
[b] The ratio of *E*-**2l**/*Z*-**3l** was determined by ^1H NMR analysis of the crude product.



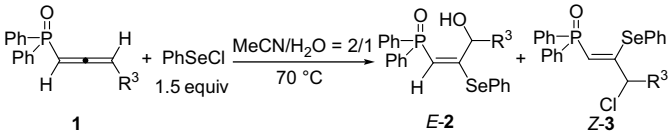
Scheme 2.

(Figs. 3 and 4). The ESI-MS/MS spectra showed that the $[M+H]^+$ ion of *E*-**2h** at *m*/*z*=491 fragmented to yield the daughter ion at *m*/*z*=473 (Fig. 3c). While that of *E*-**2h*** at *m*/*z*=493 displayed the same fragmentation chemistry to yield the corresponding daughter ion at *m*/*z*=475 (Fig. 4c). These results indicated that ^{18}O atom was bound to phosphorous, and the oxygen atom of the hydroxyl group comes from the phosphine oxide functionality in the starting allene. Similarly, the reactions of **1c** and **1e** with PhSeCl in the presence of $H_2^{18}O$ were also conducted with the results being summarized in Scheme 3 (for the MS spectra, see Supplementary data).

Based on these results, a possible mechanism was proposed[9] (Scheme 4). In the first step, the selenium intermediate **5** is afforded by the reaction of the relatively electron-rich carbon–carbon double bond with $PhSe^+$. Subsequently, a five-membered cyclic intermediate **6** is formed via neighboring group participation of the oxygen atom of the diphenyl phosphine oxide functionality, which is similar with what was observed in the iodohydroxylation of allenylic sulfoxides[7b] and phosphine oxides[9] or the bromohydroxy lation of allenylic sulfones.[8a] Finally, the $H_2^{18}O$ molecule attacks at the positively charged phosphorous atom to cleave the P–O bond, which forms the final product *E*-**2*** (Scheme 4). Of course, it is difficult to exclude other possibilities since the ^{18}O incorporation is still low (69.5%) for *E*-**2e***.

This reaction mechanism may also be used to explain the chirality transfer observed in Scheme 2 (Scheme 5).

Table 4
Selenohydroxylation of differently 3-monosubstituted 1,2-allenyl diphenyl phosphine oxides with PhSeCl



1 *E*-**2** *Z*-**3**

Entry	R^3	Time (min)	Isolated yield of *E*-**2** (%)	Ratio of *E*-**2**/*Z*-**3**[a]
1	*i*-Pr	34	82 (**2l**)	97/3
2[b]	H	540	52.5 (**2m**)	79/21
3	Et	21	78 (**2n**)	>99/1
4[b]	*n*-C_6H_{13}	70	74 (**2o**)	98/2
5	Bn	105	77 (**2p**)	96.5/3.5

[a] The ratio of *E*-**2**/*Z*-**3** was determined by ^1H NMR analysis of the crude product.
[b] The ratio of $MeCN/H_2O$ in the solvent was 1/1.

3. Conclusions

In conclusion, we have established an effective and practical method to synthesize 3-hydroxy-2-phenylselanyl-1(*E*)-alkenyl diphenyl phosphine oxides with high regio- and stereoselectivity and observed the neighboring group participation effect of the diphenylphosphinyl group by ESI-MS using $H_2^{18}O$ as the probe. Due to the presence of carbon–carbon double bond, carbon–selenium bond, and the hydroxyl group, this reaction will be useful in organic synthesis. Further studies in this area including the factors determining the stereoselectivity for the formation of *Z*-**3o** are currently being carried out in our laboratory.

4. Experimental

4.1. Starting materials

Known compounds **1b–d**, **1f**, **1h**, **1i**, and **1n** were prepared according to the known procedures.[28] New compounds **1e**, **1g**, **1j**, **1k**, and **1p** were also prepared according to this procedure.[28] Due to

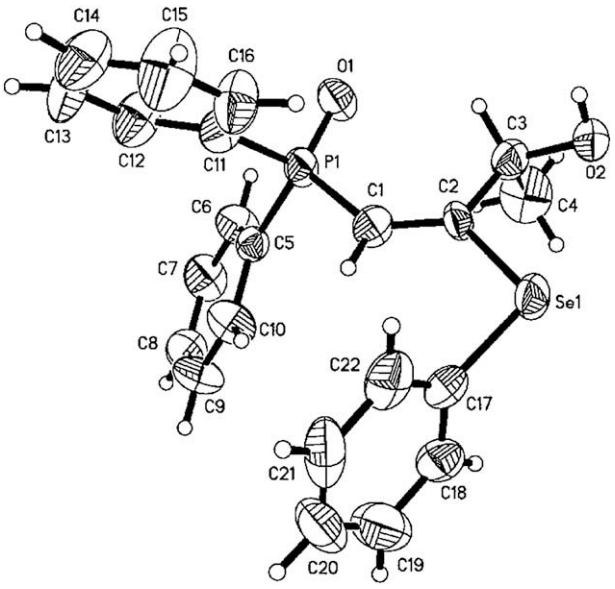


Figure 2. ORTEP representation of *S*-*E*-**2b**.

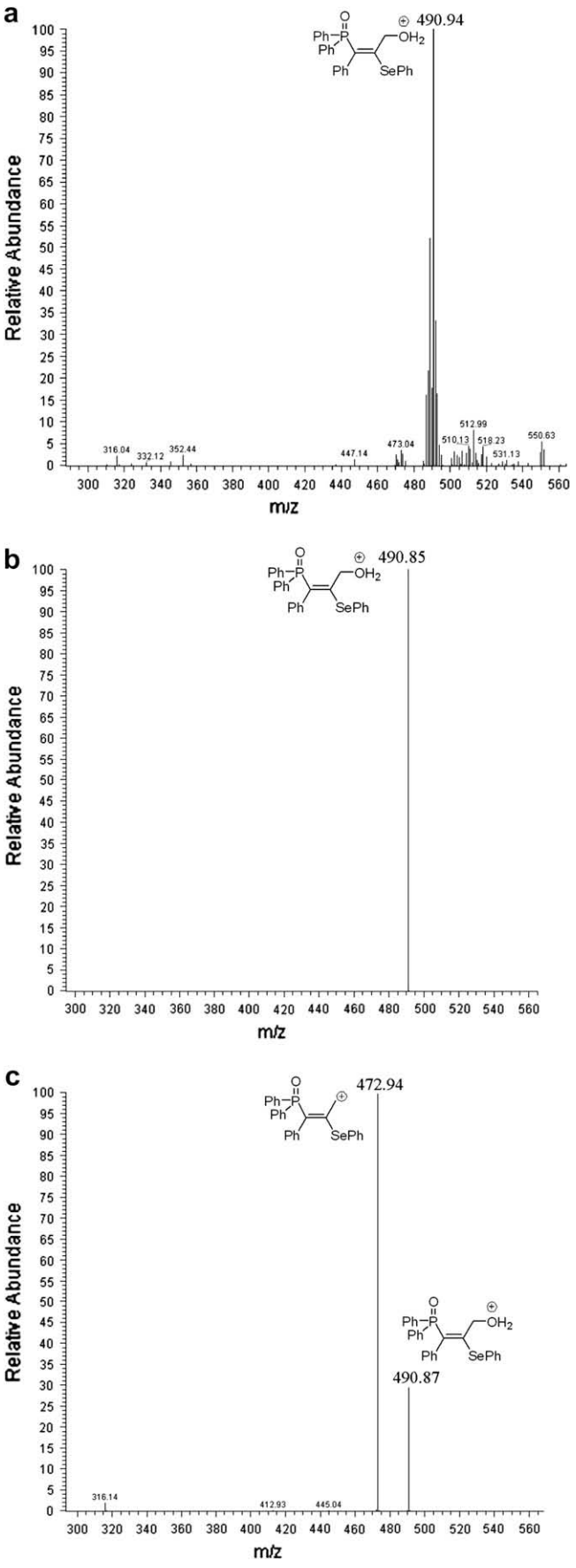


Figure 3. (a) ESI-MS spectrum for *E*-**2h**, (b) ESI-SIM-MS spectrum for the precursor ion of *E*-**2h** at *m*/*z*=491, and (c) ESI-MS/MS spectrum for the precursor ion of *E*-**2h** at *m*/*z*=491.

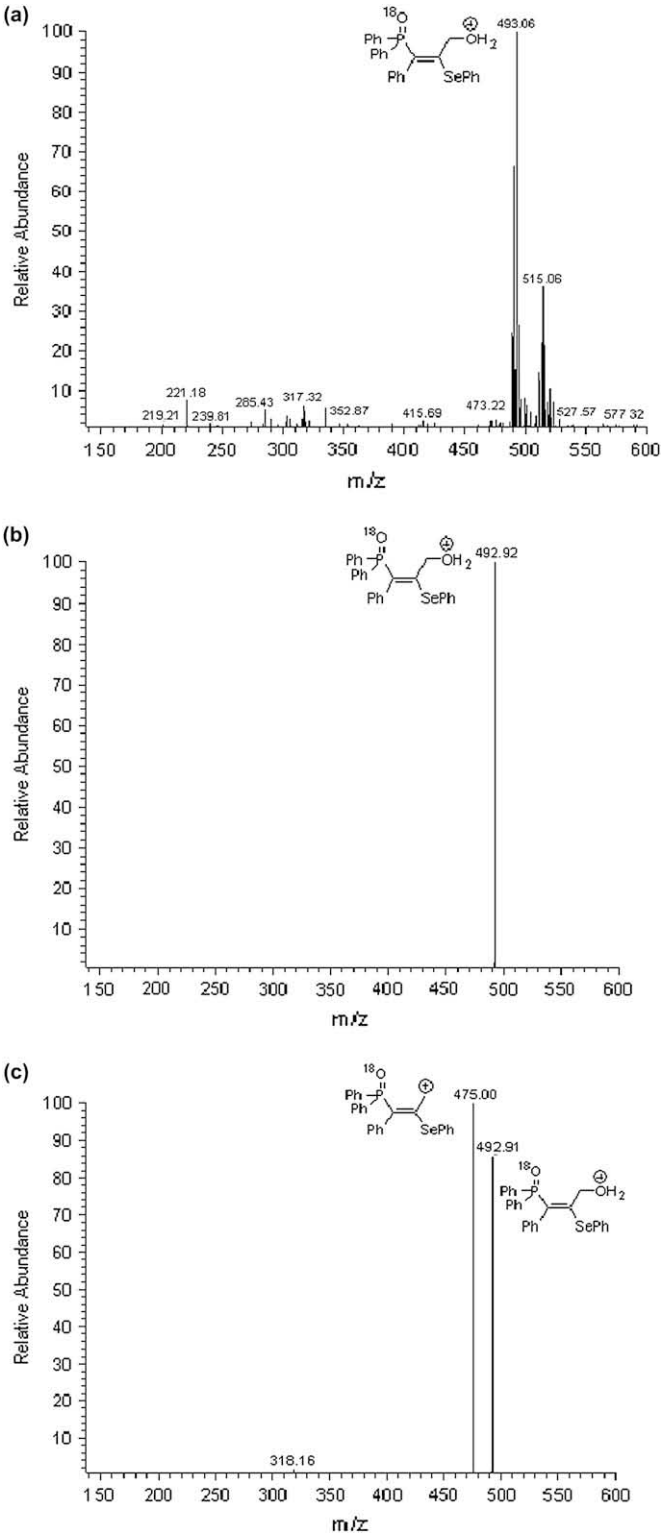
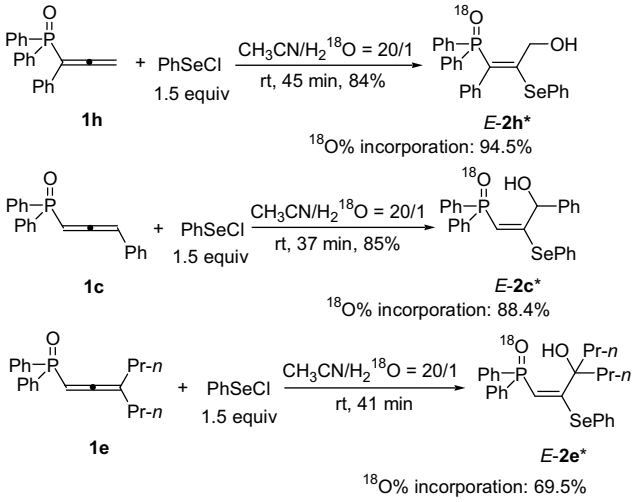


Figure 4. (a) ESI-MS spectrum for *E*-**2h**$^{+}$, (b) ESI-SIM-MS spectrum for the precursor ion of *E*-**2h**$^{+}$ at *m*/*z*=493, and (c) ESI-MS/MS spectrum for the precursor ion of *E*-**2h**$^{+}$ at *m*/*z*=493.

the coupling between ^{13}C and ^{31}P, the ^{13}C NMR is very complicated and the spectra are provided in Supplementary data.

4.1.1. 1-Phenylpenta-1,2-dienyl diphenyl phosphine oxide (**1j**)

General Procedure I. To a dried three-necked round-bottom flask were added with 1-phenylpent-1-yn-3-ol (2.4336 g, 15 mmol),



Scheme 3. Reactions conducted in the presence of $H_2^{18}O$.

Et_3N (2.10 mL, d=0.73 g/mL, 1.53 g, 15 mmol), and 40 mL of CH_2Cl_2. A solution of chlorodiphenylphosphine (2.80 mL, d=1.20 g/mL, 3.36 g, 15 mmol) in 5 mL of CH_2Cl_2 was then added dropwise at −64 °C within 30 min. After being warmed up naturally to room temperature, the reaction was monitored by TLC (petroleum ether/ethyl acetate=1:1). Upon complete conversion of the alcohol, the reaction was quenched with 20 mL of water. The organic layer was separated and the aqueous layer was extracted with 20×3 mL of CH_2Cl_2. The combined organic layer was washed with 20 mL of brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, chromatography on silica gel (eluent: CH_2Cl_2/ethyl acetate=10:1) of the crude product afforded **1j** (2.1617 g, 41%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.67 (m, 4H), 7.59 (d, J=7.6 Hz, 2H), 7.45–7.30 (m, 6H), 7.18 (t, J=7.4 Hz, 2H), 7.09 (t, J=7.2 Hz, 1H), 5.28 (dt, J_1=10.8 Hz, J_2=6.6 Hz, 1H), 1.85–1.71 (m, 2H), 0.74 (t, J=7.6 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.2; MS (EI, 70 eV) m/z (%) 345 (M^++1, 12.26), 344 (M^+, 47.54), 201 (100); IR ν (neat, cm^{-1}) 1939, 1593, 1493, 1437, 1304, 1190, 1117. Anal. Calcd for $C_{23}H_{21}OP$: C, 80.21; H, 6.15. Found: C, 80.25; H, 6.19.

The following compounds were prepared according to *General Procedure I*.

4.1.2. 3-Propylhexa-1,2-dienyl diphenyl phosphine oxide (**1e**)

The reaction of 3-propylhex-1-yn-3-ol (2.1020 g, 15 mmol), Et_3N (2.10 mL, d=0.73 g/mL, 1.53 g, 15 mmol), and Ph_2PCl (2.80 mL, d=1.20 g/mL, 3.36 g, 15 mmol) in 45 mL of CH_2Cl_2 was conducted at −64 °C according to *General Procedure I*. After warming up to rt, the reaction mixture was heated to reflux within 30 min and kept under reflux for 30 h to afford **1e** (1.3731 g, 28%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.65 (m, 4H), 7.50–7.37 (m, 6H), 5.81–5.70 (m, 1H), 1.84–1.64 (m, 4H), 1.30–1.12 (m, 4H), 0.77 (t, J=5.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 132.8 (d, J_{pc}=104.3 Hz), 131.4 (d, J_{pc}=2.6 Hz), 131.2 (d, J_{pc}=9.6 Hz), 128.0 (d, J_{pc}=11.9 Hz), 106.2 (d, J_{pc}=13.7 Hz), 85.3 (d, J_{pc}=107.6 Hz), 33.3 (d, J_{pc}=5.9 Hz), 20.3 (d, J_{pc}=1.4 Hz), 13.6; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.8; MS (EI, 70 eV) m/z (%) 325 (M^++1, 1.45), 324 (M^+, 3.08), 202 (100); IR ν (neat, cm^{-1}) 1949, 1591, 1437, 1380, 1199, 1119. HRMS calcd for $C_{21}H_{25}OP$: 324.1643. Found: 324.1645.

4.1.3. Hepta-1,2-dien-3-yl diphenyl phosphine oxide (**1g**)

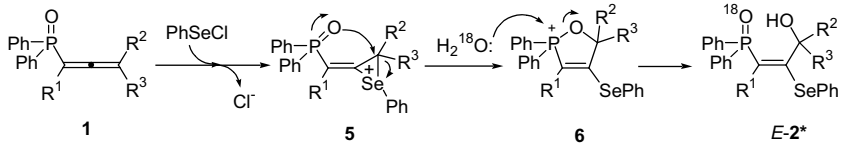
The reaction of hept-2-yn-1-ol (1.6865 g, 15 mmol), Et_3N (2.10 mL, d=0.73 g/mL, 1.53 g, 15 mmol), and Ph_2PCl (2.75 mL, d=1.20 g/mL, 3.30 g, 15 mmol) in 45 mL of CH_2Cl_2 for 7.5 h afforded **1g** (2.6667 g, 60%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.63 (m, 4H), 7.52–7.46 (m, 2H), 7.45–7.38 (m, 4H), 4.67 (dt, J_1=11.2 Hz, J_2=3.2 Hz, 2H), 2.28–2.15 (m, 2H), 1.53–1.40 (m, 2H), 1.35–1.24 (m, 2H), 0.82 (t, J=7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0 (d, J_{pc}=7.1 Hz), 131.8 (d, J_{pc}=103.9 Hz), 131.7 (d, J_{pc}=5.0 Hz), 131.6 (d, J_{pc}=8.9 Hz), 128.2 (d, J_{pc}=11.9 Hz), 97.6 (d, J_{pc}=99.9 Hz), 77.4, 30.2 (d, J_{pc}=5.5 Hz), 26.8 (d, J_{pc}=6.1 Hz), 22.1, 13.7; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 29.5; MS (EI, 70 eV) m/z (%) 297 (M^++1, 3.53), 296 (M^+, 12.30), 201 (100); IR ν (neat, cm^{-1}) 1937, 1590, 1483, 1466, 1438, 1379, 1310, 1193, 1118, 1102. HRMS calcd for $C_{19}H_{21}OP$: 296.1330. Found: 296.1331.

4.1.4. 2-Methylocta-2,3-dien-4-yl diphenyl phosphine oxide (**1k**)

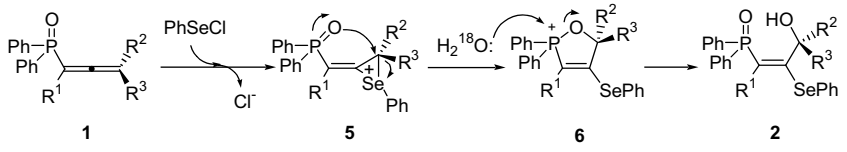
The reaction of 2-methyloct-3-yn-2-ol (2.0734 g, 15 mmol), Et_3N (2.10 mL, d=0.73 g/mL, 1.53 g, 15 mmol), and Ph_2PCl (2.80 mL, d=1.20 g/mL, 3.36 g, 15 mmol) in 45 mL of CH_2Cl_2 for 15 h afforded **1k** (2.1277 g, 44%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.60 (m, 4H), 7.50–7.35 (m, 6H), 2.23–2.13 (m, 2H), 1.48–1.35 (m, 8H), 1.35–1.20 (m, 2H), 0.85–0.78 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.4 (d, J_{pc}=6.4 Hz), 132.5 (d, J_{pc}=102.6 Hz), 131.4, 131.3, 128.0 (d, J_{pc}=11.8 Hz), 98.4 (d, J_{pc}=14.6 Hz), 96.4 (d, J_{pc}=102.2 Hz), 30.4 (d, J_{pc}=6.2 Hz), 27.1 (d, J_{pc}=8.4 Hz), 22.1, 19.1 (d, J_{pc}=5.9 Hz), 13.8; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 31.9; MS (EI, 70 eV) m/z (%) 325 (M^++1, 5.97), 324 (M^+, 3.35), 282 (100); IR ν (neat, cm^{-1}) 1955, 1590, 1483, 1437, 1376, 1193, 1118. HRMS calcd for $C_{21}H_{25}OP$: 324.1643. Found: 324.1645.

4.1.5. 4-Phenylbuta-1,2-dienyl diphenyl phosphine oxide (**1p**)

The reaction of 4-phenylbut-1-yn-3-ol (2.1919 g, 15 mmol), Et_3N (2.20 mL, d=0.73 g/mL, 1.61 g, 15 mmol), and Ph_2PCl (2.80 mL, d=1.20 g/mL, 3.36 g, 15 mmol) in 45 mL of CH_2Cl_2 for 12 h afforded



Scheme 4. The proposed mechanism.



Scheme 5. Rationale for the axial chirality transfer observed in Scheme 2.

1p (2.3521 g, 47%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68–7.57 (m, 4H), 7.55–7.46 (m, 2H), 7.46–7.37 (m, 4H), 7.25–7.18 (m, 3H), 6.97–6.90 (m, 2H), 5.87–5.79 (m, 1H), 5.44 (dq, J_1=10.8 Hz, J_2=6.8 Hz, 1H), 3.30–3.20 (m, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.5; MS (EI, 70 eV) *m*/*z* (%) 331 (M^++1, 8.27), 330 (M^+, 33.90), 201 (100); IR ν (neat, cm^{-1}) 1954, 1494, 1452, 1437, 1383, 1174. HRMS calcd for $C_{22}H_{19}OP$: 330.1174. Found: 330.1175.

4.2. Compounds 1a, 1l, 1o, *S*-(+)-1j, and *R*-(+)-1o

These compounds were prepared according to a known procedure described as *General Procedure II*.[29] It should be noted that conducting the preparation of *R*-(+)-**1o** according to *General Procedure I* led to an ee value of *R*-(+)-**1o** at the level of 60% from the optically active propargylic alcohol (99% ee).

4.2.1. 1-Phenylocta-1,2-dienyl diphenyl phosphine oxide (*1a*)

General Procedure II. To a dried three-necked round-bottom flask was charged with 1-phenyloct-1-yn-3-ol (3.0038 g, 15 mmol), triethylamine (3.3 mL, *d*=0.73 g/mL, 2.41 g, 22.5 mmol), and 50 mL of THF. A solution of chlorodiphenylphosphine (4.30 mL, *d*=1.20 g/mL, 5.18 g, 22.5 mmol) in 10 mL of THF was then added dropwise at −64 °C within 22 min. After being warmed up naturally to room temperature, the reaction was monitored by TLC (petroleum ether/ethyl acetate=1:1). Upon complete conversion of the alcohol, the reaction was quenched with 20 mL of water. The organic layer was separated and the aqueous layer was extracted with 30×3 mL of Et_2O. The combined organic layer was washed with 15 mL of brine and dried over anhydrous Na_2SO_4. After evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether/ethyl acetate=5:1 to 2:1) of the crude product afforded **1a** (4.1912 g, 73%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84–7.67 (m, 4H), 7.61 (d, *J*=7.8 Hz, 2H), 7.54–7.35 (m, 6H), 7.31–7.10 (m, 3H), 5.30 (dt, J_1=10.5 Hz, J_2=7.1 Hz, 1H), 1.92–1.70 (m, 2H), 1.30–1.02 (m, 6H), 0.84 (t, *J*=7.1 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.1; MS (EI, 70 eV) *m*/*z* (%) 387 (M^++1, 6.83), 386 (M^+, 25.81), 201 (100); IR ν (neat, cm^{-1}) 1940, 1595, 1492, 1438, 1387, 1319, 1190, 1182. Anal. Calcd for $C_{26}H_{27}OP$: C, 80.80; H, 7.04. Found: C, 80.80; H, 7.09.

4.2.2. S-1-Phenylpenta-1,2-dienyl diphenyl phosphine oxide (*S*-*1j*)[25,26]

The reaction of *S*-(−)-1-phenylpent-1-yn-3-ol (0.6390 g, 4.0 mmol, 99% ee), Et_3N (0.83 mL, *d*=0.73 g/mL, 0.61 g, 6.0 mmol), and Ph_2PCl (1.10 mL, *d*=1.20 g/mL, 1.32 g, 6.0 mmol) in 25 mL of THF for 2.0 h afforded *S*-(+)-**1j** (0.6290 g, 46%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84–7.68 (m, 4H), 7.61 (d, *J*=7.5 Hz, 2H), 7.55–7.33 (m, 6H), 7.28–7.12 (m, 3H), 5.33 (dt, J_1=10.5 Hz, J_2=6.3 Hz, 1H), 1.93–1.75 (m, 2H), 0.79 (t, *J*=7.4 Hz, 3H); HPLC conditions: Chiralcel OD-H, hexane/*i*-PrOH=95:5, 0.7 mL/min, *n*=230 nm, t_R 14.8 (major), 16.3 (minor); $[\alpha]_D^{20}$ +20.72 (*c* 0.74, $CHCl_3$).

4.2.3. 4-Methylpenta-1,2-dienyl diphenyl phosphine oxide (*1l*)

The reaction of 4-methylpent-1-yn-3-ol (2.0619 g (contaminated with THF, purity: 95%), 20 mmol), Et_3N (4.20 mL, *d*=0.73 g/mL, 3.07 g, 30 mmol), and Ph_2PCl (5.50 mL, *d*=1.20 g/mL, 6.60 g, 30 mmol) in 55.5 mL of THF for 12 h afforded **1l** (2.4698 g, 44%) as a solid. Mp 63–64 °C (Et_2O). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.70 (m, 4H), 7.55–7.41 (m, 6H), 5.91–5.84 (m, 1H), 5.24 (dt, J_1=10.8 Hz, J_2=6.4 Hz, 1H), 2.27–2.15 (m, 1H), 0.81 (d, *J*=6.8 Hz, 3H), 0.80 (d, J_2=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.3, 132.6 (d, J_{pc}=105.9 Hz), 132.3 (d, J_{pc}=105.9 Hz), 131.6 (d, J_{pc}=2.7 Hz), 131.4 (d, J_{pc}=8.8 Hz), 131.3 (d, J_{pc}=9.7 Hz), 128.2 (d, J_{pc}=1.5 Hz), 128.1 (d, J_{pc}=1.8 Hz), 99.8 (d, J_{pc}=13.5 Hz), 86.4 (d, J_{pc}=105.9 Hz), 27.2 (d, J_{pc}=5.2 Hz), 22.1 (d, J_{pc}=3.6 Hz), 21.8 (d, J_{pc}=2.6 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.9; MS (EI, 70 eV) *m*/*z* (%) 283 (M^++1, 6.22), 282 (M^+, 25.02), 201 (100); IR ν (KBr, cm^{-1}) 1945, 1592, 1464, 1440, 1284, 1189, 1120. Anal. Calcd for $C_{18}H_{19}OP$: C, 76.58; H, 6.78. Found: C, 76.56; H, 6.74.

4.2.4. Nona-1,2-dienyl diphenyl phosphine oxide (*1o*)

The reaction of non-1-yn-3-ol (2.1046 g, 15 mmol), Et_3N (3.20 mL, *d*=0.73 g/mL, 2.34 g, 22.5 mmol), and Ph_2PCl (4.20 mL, *d*=1.20 g/mL, 5.04 g, 22.5 mmol) in 45 mL of THF for 3.5 h afforded **1o** (3.0060 g, 62%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.66 (m, 4H), 7.56–7.36 (m, 6H), 5.83–5.74 (m, 1H), 5.29–5.17 (m, 1H), 1.88–1.80 (m, 2H), 1.32–1.07 (m, 8H), 0.89–0.77 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 132.6 (d, J_{pc}=105.8 Hz), 132.5 (d, J_{pc}=105.5 Hz), 131.6 (d, J_{pc}=2.6 Hz), 131.3 (d, J_{pc}=9.7 Hz), 128.2 (d, J_{pc}=12.2 Hz), 92.8 (d, J_{pc}=13.5 Hz), 85.1 (d, J_{pc}=105.9 Hz), 31.4, 28.7 (d, J_{pc}=3.2 Hz), 28.5, 27.1 (d, J_{pc}=5.3 Hz), 22.3, 13.9; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.2; MS (EI, 70 eV) *m*/*z* (%) 325 (M^++1, 2.06), 324 (M^+, 3.15), 201 (100); IR ν (neat, cm^{-1}) 1949, 1590, 1483, 1465, 1437, 1379, 1311, 1189, 1120, 1104. HRMS calcd for $C_{21}H_{25}OP$: 324.1643. Found: 324.1645.

4.2.5. R-Nona-1,2-dienyl diphenyl phosphine oxide (*R*-*1o*)

The reaction of *R*-(+)-1-nonyn-3-ol (0.9757 g, 7.0 mmol, 99% ee), Et_3N (1.45 mL, *d*=0.73 g/mL, 1.06 g, 10.5 mmol), and Ph_2PCl (1.95 mL, *d*=1.20 g/mL, 2.34 g, 10.5 mmol) in 25 mL of THF for 3.0 h afforded *R*-(+)-**1o** (1.2900 g, 57%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81–7.66 (m, 4H), 7.56–7.36 (m, 6H), 5.83–5.74 (m, 1H), 5.29–5.17 (m, 1H), 1.94–1.80 (m, 2H), 1.32–1.07 (m, 8H), 0.85 (t, *J*=6.3 Hz, 3H); HPLC conditions: Chiralcel OD-H, hexane/*i*-PrOH=90:10, 0.7 mL/min, *n*=230 nm, t_R 10.1 (major), 13.1 (minor); $[\alpha]_D^{20}$ −123.8 (*c* 1.21, $CHCl_3$).

4.3. Reaction of multi-substituted allenyl phosphine oxides with PhSeCl

4.3.1. 3-Hydroxy-1-phenyl-2-phenylselanyl-1(E)-octenyl diphenyl phosphine oxide (*E*-*2a*)

General Procedure III. To a solution of PhSeCl (58.1 mg, 0.3 mmol) in 3 mL of MeCN was added 0.2 mL of H_2O. Then a solution of **1a** (77.7 mg, 0.2 mmol) in 1 mL of MeCN was added and the resulting mixture was stirred at room temperature for 14 min. After complete consumption of the starting material as monitored by TLC (eluent: petroleum ether/ethyl acetate=2:1), the mixture was quenched with 5 mL of H_2O, extracted with 20×3 mL of diethyl ether, washed with 5 mL of brine, and dried over anhydrous Na_2SO_4. Filtration, evaporation, and flash chromatography on silica gel (petroleum ether/ethyl acetate=3:1 to 2:1) afforded *E*-**2a** (102.3 mg, 91%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.73 (m, 2H), 7.61–7.50 (m, 3H), 7.49–7.40 (m, 3H), 7.40–7.24 (m, 7H), 7.16–7.08 (m, 2H), 7.00–6.92 (m, 1H), 6.92–6.83 (m, 1H), 6.78 (d, *J*=10.8 Hz, 1H), 6.52 (d, *J*=7.6 Hz, 1H), 4.37 (t, *J*=9.8 Hz, 1H), 2.22–2.03 (m, 1H), 1.91–1.76 (m, 1H), 1.54–1.37 (m, 1H), 1.29–1.14 (m, 2H), 1.12–0.95 (m, 3H), 0.83 (t, *J*=7.4 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 32.4; MS (ESI) *m*/*z* (%) 561 (M^+(^{80}Se)+1, 3.49), 546 (M^+(^{82}Se)+1−OH, 6.10), 544 (M^+(^{80}Se)+1−OH, 45.35), 542 (M^+(^{78}Se)+1−OH, 16.86), 545 (M^+(^{82}Se)−OH, 27.33), 543 (M^+(^{80}Se)−OH, 100), 541 (M^+(^{78}Se)−OH or M^+(^{77}Se)+1−OH, 56.40), 540 (M^+(^{77}Se)−OH or M^+(^{76}Se)+1−OH, 24.42), 539 (M^+(^{76}Se)−OH, 30.23); IR ν (neat, cm^{-1}) 3280, 1560, 1473, 1437, 1168. Anal. Calcd for $C_{32}H_{33}O_2PSe$: C, 68.69; H, 5.94. Found: C, 68.67; H, 5.91.

The following compounds were prepared according to *General Procedure III*.

4.3.2. 3-Hydroxy-2-phenylselanyl-1(E)-butenyl diphenyl phosphine oxide (*E*-*2b*)

The reaction of **1b** (77.0 mg, 0.30 mmol) and PhSeCl (87.1 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 12 min afforded

E-**2b** (106.3 mg, 82%) as a solid. Mp 145–146 °C (hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.27 (m, 15H), 5.98 (d, J=7.2 Hz, 1H), 5.59 (d, J=20.4 Hz, 1H), 5.05–4.92 (m, 1H), 1.55 (d, J=5.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 136.7, 133.4 (d, J_{pc}=105.4 Hz), 133.1 (d, J_{pc}=105.1 Hz), 131.62 (d, J_{pc}=4.3 Hz), 131.59 (d, J_{pc}=4.5 Hz), 130.7 (d, J_{pc}=10.0 Hz), 130.6 (d, J_{pc}=9.8 Hz), 129.7, 129.2, 128.4 (d, J_{pc}=12.0 Hz), 127.5, 112.8 (d, J_{pc}=96.1 Hz), 69.9 (d, J_{pc}=6.7 Hz), 23.5; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.7; MS (EI, 70 eV) *m*/*z* (%) 386 (M^+(^{82}Se)+1−CH_3CHOH, 1.68), 384 (M^+(^{80}Se)+1−CH_3CHOH, 2.32), 382 (M^+(^{78}Se)+1−CH_3CHOH, 1.92), 380 (M^+(^{76}Se)+1−CH_3CHOH or M^+(^{77}Se)−CH_3CHOH, 0.75), 385 (M^+(^{82}Se)−CH_3CHOH, 4.83), 383 (M^+(^{80}Se)−CH_3CHOH, 5.09), 381 (M^+(^{78}Se)−CH_3CHOH, or M^+(^{77}Se)+1−CH_3CHOH, 2.16), 379 (M^+(^{76}Se)−CH_3CHOH, 0.58), 271 (100); IR ν (KBr, cm^{-1}) 3300, 1591, 1566, 1477, 1436, 1360, 1273, 1172, 1119, 1104. Anal. Calcd for $C_{22}H_{21}O_2PSe$: C, 61.83; H, 4.95. Found: C, 61.85; H, 4.96.

4.3.3. 3-Hydroxy-3-phenyl-2-phenylselanyl-1(*E*)-propenyl diphenyl phosphine oxide (*E*-**2c**)

The reaction of **1c** (94.9 mg, 0.30 mmol) and PhSeCl (87.1 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 28 min afforded *E*-**2c** (125.5 mg, 85%) as a solid. Mp 163–164 °C (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60–7.23 (m, 20H), 6.33 (d, J=6.6 Hz, 1H), 6.00 (d, J=5.4 Hz, 1H), 5.80 (d, J=19.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 140.7, 136.7, 133.1 (d, J_{pc}=106.0 Hz), 133.0 (d, J_{pc}=107.0 Hz), 131.76 (d, J_{pc}=12.4 Hz), 131.72 (d, J_{pc}=12.0 Hz), 130.9 (d, J_{pc}=14.9 Hz), 130.7 (d, J_{pc}=16.1 Hz), 129.8, 129.3, 128.6 (d, J_{pc}=12.0 Hz), 128.5 (d, J_{pc}=12.2 Hz), 128.2, 128.1, 127.8, 127.0, 115.6 (d, J_{pc}=96.2 Hz), 74.9 (d, J_{pc}=7.1 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.8; MS (ESI) *m*/*z* (%) 492 (M^+(^{82}Se), 9.30), 491 (M^+(^{80}Se)+1, 43.72), 489 (M^+(^{78}Se)+1, 20.35), 476 (M^+(^{82}Se)+1−OH, 6.98), 474 (M^+(^{80}Se)+1−OH, 29.94), 472 (M^+(^{78}Se)+1−OH, 12.79), 470 (M^+(^{77}Se)−OH or M^+(^{76}Se)+1−OH, 19.19), 475 (M^+(^{82}Se)−OH, 26.74), 473 (M^+(^{80}Se)−OH, 100), 471 (M^+(^{78}Se)−OH or M^+(^{77}Se)+1−OH, 51.16), 469 (M^+(^{76}Se)−OH, 14.83); IR ν (KBr, cm^{-1}) 3275, 1592, 1571, 1493, 1474, 1439, 1274, 1186, 1173, 1118. Anal. Calcd for $C_{27}H_{23}O_2PSe$: C, 66.26; H, 4.74. Found: C, 66.25; H, 4.77.

4.3.4. 3-Hydroxy-3-methyl-2-phenylselanyl-1(*E*)-butenyl diphenyl phosphine oxide (*E*-**2d**)

The reaction of **1d** (81.0 mg, 0.30 mmol) and PhSeCl (86.4 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 19 min afforded *E*-**2d** (118.6 mg, 89%) as a solid. Mp 103–104 °C (hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J=7.2 Hz, 2H), 7.47–7.24 (m, 13H), 7.02 (s, 1H), 5.47 (d, J=18.0 Hz, 1H), 1.65 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 136.9, 133.1 (d, J_{pc}=106.5 Hz), 131.5 (d, J_{pc}=2.5 Hz), 130.8 (d, J_{pc}=9.0 Hz), 129.9, 129.3, 128.9, 128.4 (d, J_{pc}=12.3 Hz), 113.0 (d, J_{pc}=96.6 Hz), 75.0 (d, J_{pc}=5.7 Hz), 29.8; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.9; MS (ESI) *m*/*z* (%) 445 (M^+(^{82}Se)+1, 21.43), 443 (M^+(^{80}Se)+1 or M^+(^{82}Se)−1, 100), 441 (M^+(^{78}Se)+1 or M^+(^{80}Se)−1, 48.41), 440 (M^+(^{77}Se)+1 or M^+(^{78}Se), 18.25), 439 (M^+(^{76}Se)+1 or M^+(^{77}Se) or M^+(^{78}Se)−1, 15.87), 444 (M^+(^{82}Se), 24.60), 442 (M^+(^{80}Se), 14.29); IR ν (KBr, cm^{-1}) 3242, 1583, 1568, 1438, 1358, 1190, 1160, 1117, 1097. Anal. Calcd for $C_{23}H_{23}O_2PSe$: C, 62.59; H, 5.25. Found: C, 62.54; H, 5.31.

4.3.5. 3-Hydroxy-2-phenylselanyl-3-propyl-1(*E*)-hexenyl diphenyl phosphine oxide (*E*-**2e**)

The reaction of **1e** (97.3 mg, 0.30 mmol) and PhSeCl (85.5 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 18 min afforded *E*-**2e** (119.7 mg, 80%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J=6.8 Hz, 2H), 7.47–7.36 (m, 7H), 7.35–7.28 (m, 6H), 6.53 (s, 1H), 5.71 (d, J=18.4 Hz, 1H), 1.90–1.70 (m, 4H), 1.53–1.32 (m, 4H), 0.91 (t, J=7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 137.2, 134.0 (d, J_{pc}=107.2 Hz), 131.2 (d, J_{pc}=2.4 Hz), 130.7 (d, J_{pc}=9.3 Hz), 129.9, 129.3, 128.6, 128.2 (d, J_{pc}=11.8 Hz), 115.8 (d, J_{pc}=97.4 Hz), 80.7 (d, J_{pc}=5.4 Hz), 44.4, 16.6, 14.4; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.9; MS (ESI) *m*/*z* (%) 484 (M^+(^{82}Se)+1−OH, 14.91), 482 (M^+(^{80}Se)+1−OH, 58.19), 480 (M^+(^{78}Se)−OH+1, 28.65), 478 (M^+(^{76}Se)+1−OH or M^+(^{77}Se)−OH, 46.78), 476 (M^+(^{74}Se)+1−OH, 1.75), 483 (M^+(^{82}Se)−OH, 47.37), 481 (M^+(^{80}Se)−OH, 100), 479 (M^+(^{78}Se)−OH or M^+(^{77}Se)+1−OH, 83.63), 477 (M^+(^{76}Se)−OH or M^+(^{77}Se)−H_2O, 39.18), 475 (M^+(^{74}Se)−OH, 4.68); IR ν (neat, cm^{-1}) 3212, 1571, 1473, 1435, 1313, 1168, 1121, 1099. Anal. Calcd for $C_{27}H_{31}O_2PSe$: C, 65.19; H, 6.28. Found: C, 65.28; H, 6.21.

4.3.6. 3-Hydroxy-3,3-pentamethylene-2-phenylselanyl-1(*E*)-propenyl diphenyl phosphine oxide (*E*-**2f**)

The reaction of **1f** (93.3 mg, 0.30 mmol) and PhSeCl (87.5 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 10 min afforded *E*-**2f** (122.9 mg, 84%) as a solid. Mp 134–135 °C (hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J=7.8 Hz, 2H), 7.48–7.24 (m, 13H), 6.68 (s, 1H), 5.45 (d, J=18.3 Hz, 1H), 2.04–1.76 (m, 6H), 1.76–1.54 (m, 3H), 1.32–1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6 (d, J_{pc}=2.1 Hz), 136.9, 133.3 (d, J_{pc}=107.5 Hz), 131.4 (d, J_{pc}=2.3 Hz), 130.7 (d, J_{pc}=9.8 Hz), 129.8, 129.2, 129.1, 128.3 (d, J_{pc}=12.1 Hz), 113.0 (d, J_{pc}=97.2 Hz), 76.2 (d, J_{pc}=5.4 Hz), 36.6, 25.3, 21.5; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 26.1; MS (EI, 70 eV) *m*/*z* (%) 402 (M^+(^{77}Se)−C_6H_5 or M^+(^{78}Se)−C_6H_5−1, 2.82), 401 (M^+(^{76}Se)−C_6H_5, 9.01), 386 (M^+(^{82}Se)+1−$C_6H_{10}OH$, 0.77), 384 (M^+(^{80}Se)+1−$C_6H_{10}OH$, 4.41), 382 (M^+(^{78}Se)+1−$C_6H_{10}OH$, 1.30), 381 (M^+(^{77}Se)+1−$C_6H_{10}OH$ or M^+(^{78}Se)−$C_6H_{10}OH$, 1.57), 380 (M^+(^{76}Se)+1−$C_6H_{10}OH$ or M^+(^{77}Se)−$C_6H_{10}OH$, 0.87), 385 (M^+(^{82}Se)−$C_6H_{10}OH$, 1.90), 383 (M^+(^{80}Se)−$C_6H_{10}OH$, 8.00), 201 (100); IR ν (KBr, cm^{-1}) 3182, 1561, 1543, 1443, 1435, 1168, 1155, 1117, 1097. Anal. Calcd for $C_{26}H_{27}O_2PSe$: C, 64.87; H, 5.65. Found: C, 64.87; H, 5.66.

4.3.7. 1-Hydroxy-2-phenylselanyl-2(*E*)-hepten-3-yl diphenyl phosphine oxide (*E*-**2g**)

The reaction of **1g** (88.9 mg, 0.30 mmol) and PhSeCl (86.6 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 16 min afforded *E*-**2g** (94.6 mg, 67%) as a solid. Mp 113–114 °C (hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.43 (m, 12H), 7.41–7.28 (m, 3H), 5.61 (t, J=7.5 Hz, 1H), 4.22 (d, J=7.5 Hz, 2H), 2.37–2.15 (m, 2H), 1.10–0.90 (m, 4H), 0.60 (t, J=6.5 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 32.9; MS (ESI) *m*/*z* (%) 473 (M^+(^{82}Se)+1, 19.25), 471 (M^+(^{80}Se)+1 or M^+(^{82}Se)−1, 100), 469 (M^+(^{78}Se)+1 or M^+(^{80}Se)−1, 49.37), 468 (M^+(^{77}Se)+1 or M^+(^{78}Se), 20.08), 467 (M^+(^{76}Se)+1 or M^+(^{77}Se) or M^+(^{78}Se)−1, 21.76), 472 (M^+(^{82}Se), 25.94), 470 (M^+(^{80}Se), 30.13), 466 (M^+(^{76}Se) or M^+(^{77}Se)−1, 19.25); IR ν (KBr, cm^{-1}) 3307, 1577, 1548, 1466, 1440, 1167, 1145. Anal. Calcd for $C_{25}H_{27}O_2PSe$: C, 63.97; H, 5.80. Found: C, 63.98; H, 5.82.

4.3.8. 3-Hydroxy-1-phenyl-2-phenylselanyl-1(*E*)-propenyl diphenyl phosphine oxide (*E*-**2h**)

The reaction of **1h** (95.3 mg, 0.30 mmol) and PhSeCl (88.6 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 14 min afforded *E*-**2h** (117.9 mg, 80%) as a solid. Mp 138–139 °C (hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.52 (m, 6H), 7.51–7.42 (m, 2H), 7.41–7.29 (m, 7H), 7.18–7.06 (m, 3H), 6.84 (d, J=8.0 Hz, 2H), 5.94 (br s, 1H), 4.40 (s, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.5; MS (ESI) *m*/*z* (%) 493 (M^+(^{82}Se)+1, 16.23), 491 (M^+(^{80}Se)+1 or M^+(^{82}Se)−1, 100), 489 (M^+(^{78}Se)+1 or M^+(^{80}Se)−1, 52.27), 488 (M^+(^{77}Se)+1 or M^+(^{78}Se), 21.75), 487 (M^+(^{76}Se)+1 or M^+(^{77}Se) or M^+(^{78}Se)−1, 16.23), 492 (M^+(^{82}Se), 33.44), 490 (M^+(^{80}Se), 17.86); IR ν (KBr, cm^{-1}) 3325, 1576, 1558, 1474, 1440, 1160. Anal. Calcd for $C_{27}H_{23}O_2PSe$: C, 66.26; H, 4.74. Found: C, 66.24; H, 4.79.

4.3.9. 5-Hydroxy-4-phenylselanyl-3(*E*)-hexen-3-yl diphenyl phosphine oxide (*E*-**2i**)

The reaction of **1i** (90.3 mg, 0.30 mmol) and PhSeCl (87.1 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 10 min afforded

E-**2i** (130.6 mg, 90%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.62 (m, 4H), 7.62–7.41 (m, 8H), 7.36–7.27 (m, 3H), 6.62 (br s, 1H), 4.64–4.52 (m, 1H), 2.55–2.21 (m, 2H), 1.49 (d, J=6.6 Hz, 3H), 0.44 (t, J=7.2 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 33.7; MS (ESI) m/z (%) 459 ($M^+(^{82}Se)$+1, 21.01), 457 ($M^+(^{80}Se)$+1 or $M^+(^{82}Se)$−1, 100), 455 ($M^+(^{78}Se)$+1 or $M^+(^{80}Se)$−1, 54.62), 454 ($M^+(^{77}Se)$+1 or $M^+(^{78}Se)$, 17.65), 453 ($M^+(^{76}Se)$+1 or $M^+(^{77}Se)$ or $M^+(^{78}Se)$−1, 18.49), 458 ($M^+(^{82}Se)$, 26.89), 456 ($M^+(^{80}Se)$, 14.29), 452 ($M^+(^{76}Se)$ or $M^+(^{77}Se)$−1, 21.01), 439 ($M^+(^{80}Se)$−OH, 13.87); IR ν (neat, cm^{-1}) 3240, 1576, 1557, 1476, 1437, 1363, 1167, 1117. Anal. Calcd for $C_{24}H_{25}O_2PSe$: C, 63.30; H, 5.53. Found: C, 63.33; H, 5.57.

4.3.10. 3-Hydroxy-1-phenyl-2-phenylselanyl-1(E)-pentenyl diphenyl phosphine oxide (*E*-**2j**)

The reaction of **1j** (103.7 mg, 0.30 mmol) and PhSeCl (87.8 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 5 min afforded *E*-**2j** (137.8 mg, 88%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, J_1=12.5 Hz, J_2=7.4 Hz, 2H), 7.61–7.22 (m, 13H), 7.16–7.07 (m, 2H), 7.01–6.90 (m, 1H), 6.90–6.79 (m, 1H), 6.74 (d, J=11.4 Hz, 1H), 6.51 (d, J=7.2 Hz, 1H), 4.22 (t, J=9.5 Hz, 1H), 2.22–2.01 (m, 1H), 1.98–1.82 (m, 1H), 0.80 (t, J=7.4 Hz, 3H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 32.3; MS (ESI) m/z (%) 504 ($M^+(^{82}Se)$+1−OH, 8.77), 502 ($M^+(^{80}Se)$+1−OH or $M^+(^{82}Se)$−H_2O, 56.14), 500 ($M^+(^{78}Se)$+1−OH or $M^+(^{80}Se)$−H_2O, 42.69), 503 ($M^+(^{82}Se)$−OH, 38.60), 501 ($M^+(^{80}Se)$−OH, 100), 499 ($M^+(^{78}Se)$−OH or $M^+(^{77}Se)$+1−OH, 72.81), 498 ($M^+(^{77}Se)$−OH or $M^+(^{76}Se)$+1−OH or $M^+(^{78}Se)$−H_2O, 43.27), 497 ($M^+(^{76}Se)$−OH or $M^+(^{77}Se)$−H_2O, 35.07), 495 ($M^+(^{74}Se)$−OH, 2.92); IR ν (neat, cm^{-1}) 3422, 1560, 1550, 1473, 1437, 1380, 1160, 1116, 1098. Anal. Calcd for $C_{29}H_{27}O_2PSe$: C, 67.31; H, 5.26. Found: C, 67.27; H, 5.28.

4.3.11. 2-Hydroxy-2-methyl-3-phenylselanyl-3(E)-octen-4-yl diphenyl phosphine oxide (*E*-**2k**)

The reaction of **1k** (95.5 mg, 0.30 mmol) and PhSeCl (86.2 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 10 min afforded *E*-**2k** (94.7 mg, 65%) as a liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.61 (m, 4H), 7.56–7.49 (m, 2H), 7.48–7.40 (m, 6H), 7.34 (s, 1H), 7.30–7.20 (m, 3H), 2.25–2.12 (m, 2H), 1.65 (s, 6H), 1.05–0.95 (m, 2H), 0.85–0.73 (m, 2H), 0.51 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, J_{pc}=4.6 Hz), 136.1 (d, J_{pc}=78.8 Hz), 133.4 (d, J_{pc}=1.9 Hz), 132.8 (d, J_{pc}=104.2 Hz), 132.1 (d, J_{pc}=10.1 Hz), 131.8 (d, J_{pc}=2.6 Hz), 129.9, 129.3, 128.3 (d, J_{pc}=12.0 Hz), 126.6, 77.2 (d, J_{pc}=4.9 Hz), 38.1 (d, J_{pc}=14.9 Hz), 31.3, 30.4, 22.5, 13.3; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 37.3; MS (ESI) m/z (%) 484 ($M^+(^{82}Se)$+1−OH, 17.58), 482 ($M^+(^{80}Se)$+1−OH or $M^+(^{82}Se)$−H_2O, 72.73), 483 ($M^+(^{82}Se)$−OH, 61.82), 481 ($M^+(^{80}Se)$−OH, 100), 479 ($M^+(^{78}Se)$−OH or $M^+(^{77}Se)$+1−OH, 91.82), 477 ($M^+(^{76}Se)$−OH or $M^+(^{77}Se)$−H_2O, 57.58), 475 ($M^+(^{74}Se)$−OH, 5.45); IR ν (neat, cm^{-1}) 3209, 1576, 1534, 1476, 1437, 1354, 1186, 1164, 1116, 1095. Anal. Calcd for $C_{27}H_{31}O_2PSe$: C, 65.19; H, 6.28. Found: C, 65.21; H, 6.30.

4.3.12. 3-Hydroxy-4-methyl-2-phenylselanyl-1(E)-pentenyl diphenyl phosphine oxide (*E*-**2l**) and 3-chloro-4-methyl-2-phenylselanyl-1(Z)-pentenyl diphenyl phosphine oxide (*Z*-**3l**)

The reaction of **1l** (422.6 mg, 1.5 mmol) and PhSeCl (431.8 mg, 2.25 mmol) in 1.0 mL of H_2O and 20 mL of MeCN afforded a crude mixture, which was purified by flash chromatography on silica gel (eluent: CH_2Cl_2/ethyl acetate=40:1 to 3:1) to yield *E*-**2l** (525.5 mg, 76%) and *Z*-**3l** (less polar, 52.1 mg, 7%). *E*-**2l**/*Z*-**3l**=92:8. Compound *E*-**2l**: solid. Mp 149–150 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.52 (m, 2H), 7.52–7.27 (m, 13H), 5.71 (d, J=7.6 Hz, 1H), 5.65 (d, J=20.4 Hz, 1H), 4.60 (t, J=7.2 Hz, 1H), 2.22–2.10 (m, 1H), 1.07 (d, J=6.4 Hz, 3H), 0.92 (d, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 136.8, 133.7 (d, J_{pc}=105.9 Hz), 133.5 (d, J_{pc}=105.8 Hz), 131.4, 130.6 (d, J_{pc}=6.5 Hz), 130.5 (d, J_{pc}=6.5 Hz), 129.7, 129.2, 128.32 (d, J_{pc}=12.7 Hz), 128.30 (d, J_{pc}=11.6 Hz), 127.7, 113.9 (d, J_{pc}=96.8 Hz), 78.5 (d, J_{pc}=5.3 Hz), 34.6, 19.7, 18.5; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 22.6; MS (ESI) m/z (%) 482 ($M^+(^{82}Se)$+Na+1, 5.88), 480 ($M^+(^{80}Se)$+Na+1, 25.21), 478 ($M^+(^{78}Se)$+Na+1, 12.61), 481 ($M^+(^{82}Se)$+Na, 21.85), 479 ($M^+(^{80}Se)$+Na, 100), 477 ($M^+(^{78}Se)$+Na or $M^+(^{77}Se)$+Na+1, 51.68), 476 ($M^+(^{77}Se)$+Na or $M^+(^{76}Se)$+Na+1, 15.97), 475 ($M^+(^{76}Se)$+Na, 9.24), 459 ($M^+(^{82}Se)$+1, 8.40), 457 ($M^+(^{80}Se)$+1, 36.13), 455 ($M^+(^{78}Se)$+1, 17.23), 458 ($M^+(^{82}Se)$, 11.76), 456 ($M^+(^{80}Se)$, 3.36), 454 ($M^+(^{78}Se)$ or $M^+(^{77}Se)$+1, 9.66), 453 ($M^+(^{77}Se)$ or $M^+(^{76}Se)$+1, 8.40); IR ν (KBr, cm^{-1}) 3299, 1592, 1578, 1570, 1437, 1288, 1172. Anal. Calcd for $C_{24}H_{25}O_2PSe$: C, 63.30, H, 5.53. Found: C, 63.34; H, 5.54. Compound *Z*-**3l**: liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93–7.83 (m, 2H), 7.83–7.73 (m, 2H), 7.60–7.43 (m, 6H), 7.43–7.23 (m, 5H), 7.10 (dd, J_1=21.3 Hz, J_2=0.9 Hz, 1H), 4.28 (dd, J_1=3.2 Hz, J_2=0.9 Hz, 1H), 2.49–2.31 (m, 1H), 0.87 (d, J=6.6 Hz, 3H), 0.82 (d, J=6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.0 (d, J_{pc}=1.4 Hz), 136.0, 134.1 (d, J_{pc}=106.2 Hz), 133.1 (d, J_{pc}=105.8 Hz), 131.7 (d, J_{pc}=2.8 Hz), 131.6 (d, J_{pc}=2.7 Hz), 131.3 (d, J_{pc}=10.1 Hz), 130.8 (d, J_{pc}=9.5 Hz), 129.4, 129.1, 128.6 (d, J_{pc}=12.5 Hz), 128.4 (d, J_{pc}=12.2 Hz), 126.9, 123.5 (d, J_{pc}=105.9 Hz), 70.3 (d, J_{pc}=14.3 Hz), 32.7, 20.7, 15.3; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.5; MS (ESI) m/z (%) 479 ($M^+(^{82}Se^{37}Cl)$+1, 4.20), 477 ($M^+(^{82}Se^{35}Cl)$+1 or $M^+(^{80}Se^{37}Cl)$+1, 39.50), 475 ($M^+(^{80}Se^{35}Cl)$+1 or $M^+(^{78}Se^{37}Cl)$+1, 100), 471 ($M^+(^{77}Se^{35}Cl)$ or $M^+(^{76}Se^{35}Cl)$+1 or $M^+(^{74}Se^{37}Cl)$+1, 13.45), 478 ($M^+(^{82}Se^{37}Cl)$, 10.08), 476 ($M^+(^{82}Se^{35}Cl)$ or $M^+(^{80}Se^{37}Cl)$, 25.21), 474 ($M^+(^{80}Se^{35}Cl)$ or $M^+(^{78}Se^{37}Cl)$, 15.13), 473 ($M^+(^{77}Se^{37}Cl)$ or $M^+(^{78}Se^{35}Cl)$+1 or $M^+(^{76}Se^{37}Cl)$+1, 43.70), 472 ($M^+(^{76}Se^{37}Cl)$ or $M^+(^{78}Se^{35}Cl)$, 12.61); IR ν (neat, cm^{-1}) 3056, 2967, 2929, 2871, 1560, 1476, 1437, 1195. Anal. Calcd for $C_{24}H_{24}ClOPSe$: C, 60.84; H, 5.11; Cl, 7.48. Found: C, 60.86; H, 5.13; Cl, 7.31.

4.3.13. 3-Hydroxy-2-phenylselanyl-1(E)-propenyl diphenyl phosphine oxide (*E*-**2m**) and 3-chloro-2-phenylselanyl-1(Z)-propenyl diphenyl phosphine oxide (*Z*-**3m**)

The reaction of **1m** (71.8 mg, 0.3 mmol) and PhSeCl (86.6 mg, 0.45 mmol) in 0.3 mL of H_2O and 6.0 mL of MeCN afforded *E*-**2m** (15.7 mg, 13%) and *Z*-**3m** (less polar, 79.4 mg, 61.5%). *E*-**2m**/*Z*-**3m**=17.5:82.5. Compound *E*-**2m**: solid. Mp 136.7–137.6 °C (petroleum/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.31 (m, 15H), 6.11 (t, J=7.2 Hz, 1H), 5.79 (d, J=21.0 Hz, 1H), 4.52 (d, J=5.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 136.4, 132.9 (d, J_{pc}=106.1 Hz), 131.8 (d, J_{pc}=3.1 Hz), 130.7 (d, J_{pc}=10.4 Hz), 129.8, 129.4, 128.5 (d, J_{pc}=12.1 Hz), 127.3, 114.6 (d, J_{pc}=95.8 Hz), 64.3 (d, J_{pc}=6.8 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 25.1; MS (ESI) m/z (%) 417 ($M^+(^{82}Se)$+1, 19.83), 415 ($M^+(^{80}Se)$+1 or $M^+(^{82}Se)$−1, 100), 413 ($M^+(^{78}Se)$+1 or $M^+(^{80}Se)$−1, 6.47), 416 ($M^+(^{82}Se)$, 18.53), 414 ($M^+(^{80}Se)$, 14.22), 412 ($M^+(^{78}Se)$ or $M^+(^{77}Se)$+1, 17.24), 411 ($M^+(^{77}Se)$ or $M^+(^{78}Se)$−1 or $M^+(^{76}Se)$+1, 15.52), 410 ($M^+(^{76}Se)$ or $M^+(^{77}Se)$−1, 14.66); IR ν (KBr, cm^{-1}) 3231, 1567, 1439, 1279, 1169, 1121, 1105, 1076. Anal. Calcd for $C_{21}H_{19}O_2PSe$: C, 61.03; H, 4.63. Found: C, 61.11; H, 4.55. Compound *Z*-**3m**: liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89–7.74 (m, 4H), 7.60–7.42 (m, 8H), 7.40–7.24 (m, 3H), 7.02 (dt, J_1=21.0 Hz, J_2=1.7 Hz, 1H), 4.06 (t, J=1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6 (d, J_{pc}=2.0 Hz), 136.7, 133.2 (d, J_{pc}=106.0 Hz), 131.8 (d, J_{pc}=2.9 Hz), 131.1 (d, J_{pc}=9.3 Hz), 129.4, 129.3, 128.6 (d, J_{pc}=12.0 Hz), 125.8, 121.2 (d, J_{pc}=105.1 Hz), 48.7 (d, J_{pc}=16.4 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 22.1; MS (ESI) m/z (%) 437 ($M^+(^{82}Se^{37}Cl)$+1, 5.88), 436 ($M^+(^{82}Se^{37}Cl)$, 7.56), 435 ($M^+(^{82}Se^{35}Cl)$+1 or $M^+(^{80}Se^{37}Cl)$+1, 42.86), 434 ($M^+(^{82}Se^{35}Cl)$ or $M^+(^{80}Se^{37}Cl)$, 18.49), 433 ($M^+(^{80}Se^{35}Cl)$+1 or $M^+(^{78}Se^{37}Cl)$+1, 100), 431 ($M^+(^{77}Se^{37}Cl)$ or $M^+(^{78}Se^{35}Cl)$+1 or $M^+(^{76}Se^{37}Cl)$+1, 45.38), 430 ($M^+(^{76}Se^{37}Cl)$ or $M^+(^{78}Se^{35}Cl)$, 18.49), 429 ($M^+(^{77}Se^{35}Cl)$ or $M^+(^{76}Se^{35}Cl)$+1 or $M^+(^{74}Se^{37}Cl)$+1, 16.81); IR ν (neat, cm^{-1}) 3054, 1589, 1560, 1475, 1437, 1261, 1183, 1118. Anal. Calcd for $C_{21}H_{18}ClOPSe$: C, 58.42; H, 4.20; Cl, 8.21. Found: C, 58.31; H, 4.25; Cl, 8.08.

4.3.14. 3-Hydroxy-2-phenylselanyl-1(E)-pentenyl diphenyl phosphine oxide (E-**2n**) and 3-chloro-2-phenylselanyl-1(Z)-pentenyl diphenyl phosphine oxide (Z-**3n**)

The reaction of **1n** (321.0 mg, 1.2 mmol) and PhSeCl (345.3 mg, 1.8 mmol) in 0.9 mL of H_2O and 18.0 mL of MeCN afforded *E*-**2n** (436.1 mg, 82.5%) and *Z*-**3n** (less polar, 33.9 mg, 6%). *E*-**2n**/*Z*-**3n**=93:7. Compound *E*-**2n**: solid. Mp 146.5–147.5 °C (hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.31 (m, 15H), 5.71 (d, J=9.0 Hz, 1H), 5.64 (d, J=20.1 Hz, 1H), 4.67–4.51 (m, 1H), 2.00–1.80 (m, 2H), 1.01 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 136.7, 133.5 (d, J_{pc}=106.4 Hz), 133.2 (d, J_{pc}=105.8 Hz), 131.6, 130.7 (d, J_{pc}=8.6 Hz), 130.6 (d, J_{pc}=9.8 Hz), 129.7, 129.3, 128.4 (d, J_{pc}=11.9 Hz), 127.6, 113.3 (d, J_{pc}=96.9 Hz), 75.4 (d, J_{pc}=5.3 Hz), 30.6, 10.7; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.6; MS (ESI) *m*/*z* (%) 468 (M^+(^{82}Se)+Na+1, 4.17), 466 (M^+(^{80}Se)+Na+1, 20.00), 464 (M^+(^{78}Se)+Na+1, 7.08), 467 (M^+(^{82}Se)+Na, 20.00), 465 (M^+(^{80}Se)+Na, 100), 463 (M^+(^{78}Se)+Na or M^+(^{77}Se)+Na+1, 50.83), 462 (M^+(^{77}Se)+Na or M^+(^{76}Se)+Na+1, 18.75), 461 (M^+(^{76}Se)+Na, 18.33), 445 (M^+(^{82}Se)+1, 10.00), 443 (M^+(^{80}Se)+1, 41.67), 441 (M^+(^{78}Se)+1, 25.42), 439 (M^+(^{77}Se) or M^+(^{76}Se)+1, 6.67), 444 (M^+(^{82}Se), 14.58), 442 (M^+(^{80}Se), 4.58), 440 (M^+(^{78}Se) or M^+(^{77}Se)+1, 6.25); IR ν (KBr, cm^{-1}) 3342, 3072, 3049, 1605, 1584, 1568, 1435, 1302, 1274, 1173, 1117, 1098. Anal. Calcd for $C_{23}H_{23}O_2PSe$: C, 62.59; H, 5.25. Found: C, 62.61; H, 5.26. Compound *Z*-**3n**: liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94–7.83 (m, 2H), 7.83–7.72 (m, 2H), 7.58–7.44 (m, 6H), 7.44–7.24 (m, 5H), 7.12 (d, J=21.0 Hz, 1H), 4.25 (dd, J_1=8.0 Hz, J_2=3.5 Hz, 1H), 2.14–2.01 (m, 1H), 1.90–1.73 (m, 1H), 0.87 (t, J=7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 135.9, 134.0 (d, J_{pc}=105.9 Hz), 133.2 (d, J_{pc}=106.0 Hz), 131.7 (d, J_{pc}=2.8 Hz), 131.6 (d, J_{pc}=2.7 Hz), 131.4 (d, J_{pc}=9.5 Hz), 130.9 (d, J_{pc}=9.5 Hz), 129.5, 129.1, 128.6 (d, J_{pc}=11.6 Hz), 128.5 (d, J_{pc}=12.2 Hz), 127.1, 123.1 (d, J_{pc}=105.2 Hz), 65.4 (d, J_{pc}=14.0 Hz), 31.7, 10.5; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.6; MS (ESI) *m*/*z* (%) 465 (M^+(^{82}Se^{37}Cl)+1, 6.03), 464 (M^+(^{82}Se^{37}Cl), 11.21), 463 (M^+(^{82}Se^{35}Cl)+1 or M^+(^{80}Se^{37}Cl)+1, 44.83), 462 (M^+(^{82}Se^{35}Cl) or M^+(^{80}Se^{37}Cl), 25.86), 461 (M^+(^{80}Se^{35}Cl)+1 or M^+(^{78}Se^{37}Cl)+1, 100), 459 (M^+(^{77}Se^{37}Cl) or M^+(^{78}Se^{35}Cl)+1 or M^+(^{76}Se^{37}Cl)+1, 50.86), 458 (M^+(^{76}Se^{37}Cl) or M^+(^{78}Se^{35}Cl) or M^+(^{77}Se^{35}Cl)+1, 16.81), 457 (M^+(^{77}Se^{35}Cl) or M^+(^{76}Se^{35}Cl)+1 or M^+(^{74}Se^{37}Cl)+1, 15.95); IR ν (neat, cm^{-1}) 3055, 1567, 1476, 1458, 1437, 1381, 1306, 1194, 1118. HRMS calcd for $C_{23}H_{22}ClNaOPSe^+$ $(M+Na)^+$: 483.0162. Found: 483.0139.

4.3.15. 3-Hydroxy-2-phenylselanyl-1(E)-nonenyl diphenyl phosphine oxide (E-**2o**) and 3-chloro-2-phenylselanyl-1(Z)-nonenyl diphenyl phosphine oxide (Z-**3o**)

The reaction of **1o** (649.3 mg, 2.0 mmol) and PhSeCl (575.4 mg, 3.0 mmol) in 1.5 mL of H_2O and 30 mL of CH_3CN for 30 min afforded *E*-**2o** (642.2 mg, 64%) and *Z*-**3o** (less polar, 61.2 mg, 6%). *E*-**2o**/*Z*-**3o**=91:9. Compound *E*-**2o**: solid. Mp 104–105 °C (hexane/ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.43 (m, 8H), 7.42–7.31 (m, 7H), 5.75 (br s, 1H), 5.64 (d, J=20.0 Hz, 1H), 4.70–4.58 (m, 1H), 1.95–1.75 (m, 2H), 1.60–1.48 (m, 1H), 1.41–1.17 (m, 7H), 0.85 (t, J=7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 136.7, 133.6 (d, J_{pc}=105.1 Hz), 133.3 (d, J_{pc}=107.6 Hz), 131.6, 130.8 (d, J_{pc}=10.0 Hz), 130.7 (d, J_{pc}=9.1 Hz), 129.8, 129.3, 128.5 (d, J_{pc}=12.3 Hz), 127.7, 113.4 (d, J_{pc}=97.0 Hz), 74.3 (d, J_{pc}=6.2 Hz), 37.4, 31.7, 28.9, 26.1, 22.5, 14.0; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.3; MS (ESI) *m*/*z* (%) 501 (M^+(^{82}Se)+1, 13.45), 499 (M^+(^{80}Se)+1 or M^+(^{82}Se)-1, 68.13), 497 (M^+(^{78}Se)+1 or M^+(^{80}Se)-1, 31.87), 500 (M^+(^{82}Se), 26.32), 498 (M^+(^{80}Se), 10.23), 496 (M^+(^{78}Se) or M^+(^{77}Se)+1, 10.06), 495 (M^+(^{77}Se) or M^+(^{76}Se)+1 or M^+(^{78}Se)-1, 8.48), 484 (M^+(^{82}Se)+1−OH, 15.20), 482 (M^+(^{80}Se)+1−OH or M^+(^{82}Se)−H_2O, 65.79), 480 (M^+(^{78}Se)+1−OH or M^+(^{80}Se)−H_2O, 32.16), 483 (M^+(^{82}Se)−OH, 53.22), 481 (M^+(^{80}Se)−OH, 100), 479 (M^+(^{78}Se)−OH or M^+(^{77}Se)+1−OH, 70.76), 478 (M^+(^{77}Se)−OH or M^+(^{76}Se)+1−OH or M^+(^{78}Se)−H_2O, 27.19), 477 (M^+(^{76}Se)−OH or M^+(^{77}Se)−H_2O, 23.10); IR ν (KBr, cm^{-1}) 3330, 1590, 1560, 1437, 1187, 1118. Anal. Calcd for $C_{27}H_{31}O_2PSe$: C, 65.19; H, 6.28. Found: C, 65.21; H, 6.19. Compound *Z*-**3o**: liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93–7.73 (m, 4H), 7.58–7.23 (m, 11H), 7.11 (d, J=21.0 Hz, 1H), 4.29 (dd, J_1=9.0 Hz, J_2=3.3 Hz, 1H), 2.08–1.96 (m, 1H), 1.82–1.66 (m, 1H), 1.47–1.32 (m, 1H), 1.31–1.02 (m, 7H), 0.85 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5 (d, J_{pc}=1.3 Hz), 136.0, 133.9 (d, J_{pc}=106.1 Hz), 133.1 (d, J_{pc}=105.8 Hz), 131.7 (d, J_{pc}=2.6 Hz), 131.6 (d, J_{pc}=2.9 Hz), 131.3 (d, J_{pc}=9.9 Hz), 130.9 (d, J_{pc}=9.7 Hz), 129.4, 129.1, 128.6 (d, J_{pc}=9.7 Hz), 128.5 (d, J_{pc}=10.4 Hz), 127.0, 122.5 (d, J_{pc}=105.5 Hz), 63.9 (d, J_{pc}=14.9 Hz), 38.6 (d, J_{pc}=1.6 Hz), 31.4, 28.2, 26.1, 22.4, 14.0; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.7; MS (ESI) *m*/*z* (%) 556 (M^+(^{80}Se^{35}Cl)+K^+ or M^+(^{78}Se^{37}Cl)+K^+, 3.35), 535 (M^+(^{80}Se^{35}Cl)+NH_4^+ or M^+(^{78}Se^{37}Cl)+NH_4^+, 8.37), 533 (M^+(^{77}Se^{37}Cl) or M^+(^{78}Se^{35}Cl)+NH_4^+ or M^+(^{76}Se^{37}Cl)+NH_4^+, 16.74), 521 (M^+(^{82}Se^{37}Cl)+1, 4.60), 519 (M^+(^{82}Se^{35}Cl)+1 or M^+(^{80}Se^{37}Cl)+1, 53.56), 517 (M^+(^{80}Se^{35}Cl)+1 or M^+(^{78}Se^{37}Cl)+1, 100), 515 (M^+(^{77}Se^{37}Cl) or M^+(^{78}Se^{35}Cl)+1 or M^+(^{76}Se^{37}Cl)+1, 50.21), 513 (M^+(^{77}Se^{35}Cl) or M^+(^{76}Se^{35}Cl)+1 or M^+(^{74}Se^{37}Cl)+1, 14.23), 520 (M^+(^{82}Se^{37}Cl), 13.81), 518 (M^+(^{82}Se^{35}Cl) or M^+(^{80}Se^{37}Cl), 15.06), 516 (M^+(^{80}Se^{35}Cl) or M^+(^{78}Se^{37}Cl), 18.41), 514 (M^+(^{76}Se^{37}Cl) or M^+(^{78}Se^{35}Cl), 16.32); IR ν (neat, cm^{-1}) 3055, 1567, 1476, 1437, 1196, 1118, 1104. Anal. Calcd for $C_{27}H_{30}ClOPSe$: C, 62.86; H, 5.86. Found: C, 62.88; H, 5.77.

4.3.16. 3-Hydroxy-4-phenyl-2-phenylselanyl-1(E)-butenyl diphenyl phosphine oxide (E-**2p**) and 3-chloro-4-phenyl-2-phenylselanyl-1(Z)-butenyl diphenyl phosphine oxide (Z-**3p**)

The reaction of **1p** (200.2 mg, 0.60 mmol) and PhSeCl (172.2 mg, 0.90 mmol) in 0.6 mL of H_2O and 12 mL of CH_3CN for 15 min afforded *E*-**2p** (196.4 mg, 64%) and *Z*-**3p** (less polar, 43.5 mg, 14%). *E*-**2p**/*Z*-**3p**=82:18. Compound *E*-**2p**: solid. Mp 177–178 °C (ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.36 (m, 15H), 7.35–7.17 (m, 5H), 5.71 (d, J=19.8 Hz, 1H), 5.52 (d, J=8.1 Hz, 1H), 5.15–5.04 (m, 1H), 3.31–3.14 (m, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.3; MS (ESI) *m*/*z* (%) 507 (M^+(^{82}Se)+1, 23.03), 505 (M^+(^{80}Se)+1 or M^+(^{82}Se)−1, 100), 503 (M^+(^{78}Se)+1 or M^+(^{80}Se)−1, 50.91), 506 (M^+(^{82}Se), 28.48), 504 (M^+(^{80}Se), 15.15), 502 (M^+(^{78}Se) or M^+(^{77}Se)+1, 20.00), 501 (M^+(^{77}Se) or M^+(^{76}Se)+1 or M^+(^{78}Se)−1, 16.36); IR ν (KBr, cm^{-1}) 3209, 1564, 1496, 1437, 1306, 1177, 1119. Anal. Calcd for $C_{28}H_{25}O_2PSe$: C, 66.80; H, 5.01. Found: C, 66.86; H, 5.01. Compound *Z*-**3p**: liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89–7.79 (m, 2H), 7.75–7.64 (m, 2H), 7.58–7.41 (m, 8H), 7.41–7.35 (m, 1H), 7.35–7.27 (m, 2H), 7.22–7.15 (m, 3H), 7.07 (d, J=20.7 Hz, 1H), 6.90–6.82 (m, 2H), 4.56 (dd, J_1=8.7 Hz, J_2=3.9 Hz, 1H), 3.41 (dd, J_1=14.7 Hz, J_2=3.9 Hz, 1H), 2.92 (dd, J_1=14.4 Hz, J_2=8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.9 (d, J_{pc}=1.3 Hz), 136.4, 136.2, 133.7 (d, J_{pc}=106.1 Hz), 133.0 (d, J_{pc}=105.2 Hz), 131.8 (d, J_{pc}=2.7 Hz), 131.7 (d, J_{pc}=2.8 Hz), 131.3, 131.2, 130.9 (d, J_{pc}=9.6 Hz), 129.7, 129.3, 129.2, 128.6 (d, J_{pc}=11.8 Hz), 128.5 (d, J_{pc}=12.4 Hz), 128.2, 126.9 (d, J_{pc}=2.3 Hz), 123.4 (d, J_{pc}=104.9 Hz), 64.0 (d, J_{pc}=14.0 Hz), 44.2 (d, J_{pc}=1.3 Hz); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 21.9; MS (ESI) *m*/*z* (%) 539 (M^+(^{77}Se^{37}Cl)+NH_4^+ or M^+(^{78}Se^{35}Cl)+NH_4^+ or M^+(^{76}Se^{37}Cl)+NH_4^+, 10.88), 527 (M^+(^{82}Se^{37}Cl)+1, 8.37), 525 (M^+(^{82}Se^{35}Cl)+1 or M^+(^{80}Se^{37}Cl)+1, 34.31), 523 (M^+(^{80}Se^{35}Cl)+1 or M^+(^{78}Se^{37}Cl)+1, 100), 521 (M^+(^{77}Se^{37}Cl) or M^+(^{78}Se^{35}Cl)+1 or M^+(^{76}Se^{37}Cl)+1, 31.80), 519 (M^+(^{77}Se^{35}Cl) or M^+(^{76}Se^{35}Cl)+1 or M^+(^{74}Se^{37}Cl)+1, 11.30), 526 (M^+(^{82}Se^{37}Cl), 6.69), 524 (M^+(^{82}Se^{35}Cl) or M^+(^{80}Se^{37}Cl), 22.18), 522 (M^+(^{80}Se^{35}Cl) or M^+(^{78}Se^{37}Cl), 16.74), 520 (M^+(^{76}Se^{37}Cl) or M^+(^{78}Se^{35}Cl), 8.37); IR ν (neat, cm^{-1}) 3056, 1565, 1495, 1476, 1437, 1307, 1195, 1118. HRMS calcd for $C_{28}H_{25}ClOPSe^+$ (M^++H): 523.0480. Found: 523.0491.

4.3.17. Synthesis of 3-chloro-2-phenylselanyl-1(E)-nonenyl diphenyl phosphine oxide (E-**3o**)

4.3.17.1. 3-Tosyloxy-2-phenylselanyl-1(E)-nonenyl diphenyl phosphine oxide (E-**4o**).[23] To a solution of *E*-**2o** (152.7 mg, 0.31 mmol),

p-TsCl (235.0 mg, 1.24 mmol) in 1.0 mL of anhydrous CH_2Cl_2 was added dropwise 4-dimethylaminopyridine (225.5 mg, 1.86 mmol) in 1.0 mL of anhydrous CH_2Cl_2 under the atmosphere of N_2. Then the resulting mixture was refluxed at 50 °C for 2.5 h. After evaporation, purification by flash chromatography on silica gel (petroleum ether/ethyl acetate=3:1 to 2:1) afforded *E*-**4o** (172.2 mg, 86%) as a solid. Mp 130–131 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J=8.4 Hz, 2H), 7.58–7.29 (m, 15H), 7.17 (d, J=8.1 Hz, 2H), 6.66 (dd, J_1=8.4 Hz, J_2=4.2 Hz, 1H), 5.47 (d, J=19.8 Hz, 1H), 2.37 (s, 3H), 2.01–1.86 (m, 1H), 1.80–1.66 (m, 1H), 1.31–0.93 (m, 8H), 0.81 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 144.4, 137.1, 133.7 (d, J_{pc}=104.1 Hz), 133.6 (d, J_{pc}=105.4 Hz), 133.1, 131.6 (d, J_{pc}=2.7 Hz), 131.5 (d, J_{pc}=2.8 Hz), 130.9 (d, J_{pc}=9.5 Hz), 130.5 (d, J_{pc}=9.6 Hz), 129.8, 129.45, 129.41, 128.49, 128.47 (d, J_{pc}=14.9 Hz), 128.43 (d, J_{pc}=14.3 Hz), 126.9, 115.8 (d, J_{pc}=93.9 Hz), 80.6 (d, J_{pc}=6.3 Hz), 36.3, 31.5, 28.5, 24.8, 22.3, 21.6, 14.0; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 20.8; MS (ESI) m/z (%) 694 (M^+(^{82}Se)+K+1, 7.55), 692 (M^+(^{80}Se)+K+1, 16.55), 690 (M^+(^{78}Se)+K+1, 9.71), 693 (M^+(^{82}Se)+K, 22.66), 691 (M^+(^{80}Se)+K, 51.08), 689 (M^+(^{78}Se)+K or M^+(^{77}Se)+K+1, 32.37), 688 (M^+(^{77}Se)+K or M^+(^{76}Se)+K+1, 9.35), 687 (M^+(^{76}Se)+K, 8.63), 678 (M^+(^{82}Se)+Na+1, 10.07), 676 (M^+(^{80}Se)+Na+1, 34.17), 674 (M^+(^{78}Se)+Na+1, 19.78), 677 (M^+(^{82}Se)+Na, 28.78), 675 (M^+(^{80}Se)+Na, 100), 673 (M^+(^{78}Se)+Na or M^+(^{77}Se)+Na+1, 50.36), 672 (M^+(^{77}Se)+Na or M^+(^{76}Se)+Na+1, 24.10), 671 (M^+(^{76}Se)+Na, 17.63), 655 (M^+(^{82}Se)+1, 25.90), 653 (M^+(^{80}Se)+1, 87.77), 651 (M^+(^{78}Se)+1, 41.01), 650 (M^+(^{78}Se) or M^+(^{77}Se)+1, 20.86), 649 (M^+(^{77}Se) or M^+(^{76}Se)+1, 8.63), 654 (M^+(^{82}Se), 26.62), 652 (M^+(^{80}Se), 15.11); IR ν (KBr, cm^{-1}) 3060, 1595, 1572, 1440, 1361, 1311, 1283, 1190, 1175, 1118. Anal. Calcd for $C_{34}H_{37}O_4PSSe$: C, 62.67; H, 5.72. Found: C, 62.74; H, 5.75.

*4.3.17.2. 3-Chloro-2-phenylselanyl-1(E)-nonenyl diphenyl phosphine oxide (E-**3o**).*[24] To a solution of tosylate *E*-**4o** (80.4 mg, 0.15 mmol) in 1.5 mL of anhydrous DMF was added anhydrous LiCl (53.7 mg, 1.20 mmol) at the atmosphere of N_2. Then the resulting mixture was stirred at 50 °C for 29 h and quenched with 5 mL of water. The aqueous layer was extracted with 20×3 mL of Et_2O. The combined organic layer was washed with 5 mL of H_2O, 5 mL of 5% diluted aqueous HCl and 5 mL of saturated brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, chromatography on silica gel (eluent: petroleum ether/ethyl acetate=3:1) of the crude product afforded *E*-**3o** (38.1 mg, 60%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.56 (m, 2H), 7.56–7.31 (m, 13H), 6.24–6.15 (m, 1H), 5.70 (d, J=19.8 Hz, 1H), 2.10–1.94 (m, 2H), 1.57–1.41 (m, 1H), 1.37–1.12 (m, 7H), 0.86 (t, J=6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 137.0, 133.6 (d, J_{pc}=105.2 Hz), 133.5 (d, J_{pc}=105.5 Hz), 131.7 (d, J_{pc}=2.7 Hz), 131.6 (d, J_{pc}=2.8 Hz), 130.7 (d, J_{pc}=12.4 Hz), 130.6 (d, J_{pc}=11.6 Hz), 129.9, 129.4, 128.55 (d, J_{pc}=12.4 Hz), 128.46 (d, J_{pc}=12.0 Hz), 127.5, 118.5 (d, J_{pc}=93.2 Hz), 60.5 (d, J_{pc}=6.9 Hz), 39.0, 31.5, 28.6, 26.5, 22.4, 14.1; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 20.4; MS (ESI) m/z (%) 559 (M^+(^{82}Se^{37}Cl)+K, 4.66), 557 (M^+(^{82}Se^{35}Cl)+K or M^+(^{80}Se^{37}Cl)+K, 21.51), 555 (M^+(^{80}Se^{35}Cl)+K or M^+(^{78}Se^{37}Cl)+K, 46.59), 553 (M^+(^{76}Se^{37}Cl)+K or M^+(^{78}Se^{35}Cl)+K, 19.35), 551 (M^+(^{76}Se^{35}Cl)+K or M^+(^{74}Se^{37}Cl)+K, 6.09), 558 (M^+(^{82}Se^{35}Cl)+K+1 or M^+(^{80}Se^{37}Cl)+K+1, 5.73), 556 (M^+(^{80}Se^{35}Cl)+K+1 or M^+(^{78}Se^{37}Cl)+K+1, 13.26), 554 (M^+(^{77}Se^{37}Cl)+K or M^+(^{78}Se^{35}Cl)+K+1 or M^+(^{76}Se^{37}Cl)+K+1, 8.60), 552 (M^+(^{77}Se^{35}Cl)+K or M^+(^{76}Se^{35}Cl)+K+1 or M^+(^{74}Se^{37}Cl)+K+1, 7.53), 543 (M^+(^{82}Se^{37}Cl)+Na, 3.58), 541 (M^+(^{82}Se^{35}Cl)+Na or M^+(^{80}Se^{37}Cl)+Na, 20.43), 539 (M^+(^{80}Se^{35}Cl)+Na or M^+(^{78}Se^{37}Cl)+Na, 41.94), 537 (M^+(^{76}Se^{37}Cl)+Na or M^+(^{78}Se^{35}Cl)+Na, 22.58), 535 (M^+(^{76}Se^{35}Cl)+Na or M^+(^{74}Se^{37}Cl)+Na, 7.17), 542 (M^+(^{82}Se^{35}Cl)+Na+1 or M^+(^{80}Se^{37}Cl)+Na+1, 5.38), 540 (M^+(^{80}Se^{35}Cl)+Na+1 or M^+(^{78}Se^{37}Cl)+Na+1, 11.47), 538 (M^+(^{77}Se^{37}Cl)+Na or M^+(^{78}Se^{35}Cl)+Na+1 or M^+(^{76}Se^{37}Cl)+Na+1, 7.89), 536 (M^+(^{77}Se^{35}Cl)+Na or M^+(^{76}Se^{35}Cl)+Na+1 or M^+(^{74}Se^{37}Cl)+Na+1, 7.89), 521 (M^+(^{82}Se^{37}Cl)+1, 6.45), 519 (M^+(^{82}Se^{35}Cl)+1 or M^+(^{80}Se^{37}Cl)+1, 41.58), 517 (M^+(^{80}Se^{35}Cl)+1 or M^+(^{78}Se^{37}Cl)+1, 78.85), 515 (M^+(^{77}Se^{37}Cl) or M^+(^{78}Se^{35}Cl)+1 or M^+(^{76}Se^{37}Cl)+1, 32.26), 513 (M^+(^{77}Se^{35}Cl) or M^+(^{76}Se^{35}Cl)+1 or M^+(^{74}Se^{37}Cl)+1, 11.47), 520 (M^+(^{82}Se^{37}Cl), 10.75), 518 (M^+(^{82}Se^{35}Cl) or M^+(^{80}Se^{37}Cl), 22.94), 516 (M^+(^{80}Se^{35}Cl) or M^+(^{78}Se^{37}Cl), 13.62), 514 (M^+(^{76}Se^{37}Cl) or M^+(^{78}Se^{35}Cl), 14.70), 506 (M^+(^{82}Se)+Na−Cl, 2.15), 504 (M^+(^{80}Se)+Na−Cl, 10.39), 502 (M^+(^{78}Se)+Na−Cl, 6.45), 505 (M^+(^{82}Se)+Na−HCl, 7.89), 503 (M^+(^{80}Se)+Na−HCl, 42.29), 501 (M^+(^{78}Se)+Na−HCl or M^+(^{77}Se)+Na−Cl, 20.07), 500 (M^+(^{77}Se)+Na−HCl or M^+(^{76}Se)+Na−Cl, 6.45), 499 (M^+(^{76}Se)+Na−HCl, 8.24), 484 (M^+(^{82}Se)+1−Cl, 3.58), 482 (M^+(^{80}Se)+1−Cl, 21.51), 480 (M^+(^{78}Se)+1−Cl, 14.70), 483 (M^+(^{82}Se)−Cl, 19.00), 481 (M^+(^{80}Se)−Cl, 100), 479 (M^+(^{78}Se)−Cl or M^+(^{77}Se)+1−Cl, 50.18), 478 (M^+(^{77}Se)−Cl or M^+(^{76}Se)+1−Cl, 19.00), 477 (M^+(^{76}Se)−Cl, 14.70); IR ν (neat, cm^{-1}) 3057, 1585, 1574, 1466, 1437, 1274, 1195, 1117. Anal. Calcd for $C_{27}H_{30}ClOPSe$: C, 62.86; H, 5.86. Found: C, 62.85; H, 5.89.

*4.3.18. Synthesis of ^{18}O-labeled 3-hydroxy-1-phenyl-2-phenylselanyl-1(E)-propenyl diphenyl phosphine oxide (E-**2h***)*

The starting material **1h** was dried in vacuo over P_2O_5 for one day. MeCN was firstly heated with CaH_2 under reflux in an argon atmosphere for 24 h. Then the distilled MeCN was treated with P_2O_5 under reflux in an argon atmosphere for another 24 h. After distillation, the generated anhydrous MeCN was stored in a bottle with molecular sieves and placed in the glove box under nitrogen atmosphere. $H_2^{18}O$ (96%) was bought from J&K Chemical LTD. All the operation was carried out in the glove box under nitrogen atmosphere.

A solution of PhSeCl (87.1 mg, 0.45 mmol) in anhydrous CH_3CN (2.0 mL) and $H_2^{18}O$ (0.1 mL) was stirred at rt for 262 min. Then a solution of **1h** (95.1 mg, 0.30 mmol) in anhydrous CH_3CN (2.0 mL) and $H_2^{18}O$ (0.2 mL), which had been stirred at rt for 259 min, was added subsequently. Anhydrous CH_3CN (1.0 mL×2) was used to wash the container for **1h** and transferred into the reaction mixture. After being stirred at rt for 10 min, the reaction mixture was directly purified with flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate=2:1) to afford 124.8 mg (84%) of *E*-**2h*** (94.5% of ^{18}O incorporation) as a solid. Mp 142.5–143.3 °C (*n*-hexane/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68–7.52 (m, 6H), 7.51–7.42 (m, 2H), 7.41–7.29 (m, 7H), 7.18–7.06 (m, 3H), 6.87–6.81 (m, 2H), 5.97 (t, J=7.6 Hz, 1H), 4.39 (dd, J_1=7.6 Hz, J_2=0.9 Hz, 2H); ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 30.6; MS (ESI) m/z (%) 518 (M^+(^{82}Se)+Na+1, 5.02), 516 (M^+(^{80}Se)+Na+1, 10.60), 514 (M^+(^{78}Se)+Na+1, 7.10), 512 (M^+(^{77}Se)+Na or M^+(^{76}Se)+Na+1, 8.27), 517 (M^+(^{82}Se)+Na, 9.52), 515 (M^+(^{80}Se)+Na, 36.16), 513 (M^+(^{78}Se)+Na or M^+(^{77}Se)+Na+1, 20.01), 511 (M^+(^{76}Se)+Na, 8.07), 495 (M^+(^{82}Se)+1, 22.58), 493 (M^+(^{80}Se)+1, 100), 491 (M^+(^{78}Se)+1, 56.66), 489 (M^+(^{77}Se) or M^+(^{76}Se)+1, 20.64), 494 (M^+(^{82}Se), 28.07), 492 (M^+(^{80}Se), 18.08), 490 (M^+(^{78}Se) or M^+(^{77}Se)+1, 21.55); IR ν (KBr, cm^{-1}) 3431, 3055, 3022, 2926, 1577, 1560, 1474, 1439, 1388, 1311, 1252, 1138, 1116, 1088, 1064, 1021. HRMS calcd for $C_{27}H_{24}O^{18}OPSe^+$ (M^++1): 493.07161. Found: 493.07115.

According to the MS spectrum of this product (page S113, in Supplementary data), the relative abundances of 489.05, 490.06, 491.04, 492.06, 493.02, 494.04, 495.02 are 20.64, 21.55, 56.66, 18.08, 100, 28.07, 22.58; according to the simulated MS spectrum of *E*-**2h*** with 100% of ^{18}O (page S112, in Supplementary data), their relative abundances should be 18.561, 20.515, 52.147, 14.585, 100, 29.099, 21.547; according to the simulated MS spectrum of *E*-**2h** (page S111, in Supplementary data) their relative abundances should be 52.134, 14.631, 100, 29.134, 21.739, 5.580, 0.837. If x and y represent the amount of *E*-**2h*** and *E*-**2h**, respectively, then

$$0.2064 = 0.18561x + 0.52134y$$

$$0.2155 = 0.20515x + 0.14631y$$

$$0.5666 = 0.52147x + 1.00000y$$

$$0.1808 = 0.14585x + 0.29134y$$

$$1.0000 = 1.00000x + 0.21739y$$

$$0.2807 = 0.29099x + 0.05580y$$

$$0.2258 = 0.21547x + 0.00837y$$

which can be written as

$$\begin{bmatrix} 0.2064 \\ 0.2155 \\ 0.5666 \\ 0.1808 \\ 1.0000 \\ 0.2807 \\ 0.2258 \end{bmatrix} = \begin{bmatrix} 0.18561 & 0.52134 \\ 0.20515 & 0.14631 \\ 0.52147 & 1.00000 \\ 0.14585 & 0.29134 \\ 1.00000 & 0.21739 \\ 0.29099 & 0.05580 \\ 0.21547 & 0.00837 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

By using MATLAB 5.3 (by the MathWorks), we know that x=0.9873, y=0.0573. Thus, the incorporation of ^{18}O % in the product=$x/(x+y)$=0.945.

The following compounds were prepared according to this procedure.

*4.3.19. Synthesis of ^{18}O-labeled 3-hydroxy-3-phenyl-2-phenylselanyl-1(E)-propenyl diphenyl phosphine oxide (E-**2c***)*

The reaction of **1c** (94.8 mg, 0.30 mmol) and PhSeCl (87.2 mg, 0.45 mmol) in 0.3 mL of $H_2^{18}O$ and 6 mL of anhydrous CH_3CN for 37 min afforded 126.0 mg (85%) of *E*-**2c**** (88.4% of ^{18}O incorporation) as a solid. Mp 163.2–163.6 °C (ethyl acetate). ^1H NMR (300 MHz, $CDCl_3$) δ 7.51–7.09 (m, 20H), 6.00 (s, 1H), 5.79 (br, 1H), 5.68 (d, J=20.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 140.7, 136.7, 133.0 (d, J_{pc}=105.4 Hz), 132.9 (d, J_{pc}=107.9 Hz), 131.8 (d, J_{pc}=2.5 Hz), 131.6 (d, J_{pc}=2.9 Hz), 130.8 (d, J_{pc}=14.9 Hz), 130.7 (d, J_{pc}=15.6 Hz), 129.8, 129.3, 128.5 (d, J_{pc}=11.8 Hz), 128.4 (d, J_{pc}=12.2 Hz), 128.1, 128.0, 127.8, 127.0, 115.3 (d, J_{pc}=94.3 Hz), 74.7; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 23.9; MS (ESI) m/z (%) 515 ($M^+(^{80}Se)$+Na, 20.60), 513 ($M^+(^{78}Se)$+Na or $M^+(^{77}Se)$+Na+1, 14.05), 511 ($M^+(^{76}Se)$+Na, 11.07), 512 ($M^+(^{77}Se)$+Na or $M^+(^{76}Se)$+Na+1, 8.61), 495 ($M^+(^{82}Se)$+1, 23.14), 493 ($M^+(^{80}Se)$+1, 100), 491 ($M^+(^{78}Se)$+1, 63.09), 489 ($M^+(^{77}Se)$ or $M^+(^{76}Se)$+1, 25.10), 494 ($M^+(^{82}Se)$, 28.85), 492 ($M^+(^{80}Se)$, 19.78), 490 ($M^+(^{78}Se)$ or $M^+(^{77}Se)$+1, 22.01), 476 ($M^+(^{80}Se)$+1−OH, 6.07), 475 ($M^+(^{80}Se)$−OH, 20.55), 473 ($M^+(^{78}Se)$−OH or $M^+(^{77}Se)$+1−OH, 14.54); IR ν (KBr, cm^{-1}) 3274, 1592, 1571, 1474, 1439, 1332, 1274, 1157, 1147, 1117, 1093, 1047. HRMS calcd for $C_{27}H_{24}O^{18}OPSe^+$ (M^++1): 493.07161. Found: 493.07085.

According to the MS spectrum of this product (page S119, in Supplementary data), the relative abundances of 488.96, 489.98, 490.93, 491.98, 492.91, 493.94, 494.93 are 25.10, 22.01, 63.09, 19.78, 100, 28.85, 23.14; according to the simulated MS spectrum of *E*-**2c**** with 100% of ^{18}O (page S118, in Supplementary data), their relative abundances should be 18.561, 20.515, 52.147, 14.585, 100, 29.099, 21.547; according to the simulated MS spectrum of *E*-**2c** (page S117, in Supplementary data) their relative abundances should be 52.134, 14.631, 100, 29.134, 21.739, 5.580, 0.837. If x and y represent the amount of *E*-**2c**** and *E*-**2c**, respectively, then

$$0.2510 = 0.18561x + 0.52134y$$

$$0.2201 = 0.20515x + 0.14631y$$

$$0.6309 = 0.52147x + 1.00000y$$

$$0.1978 = 0.14585x + 0.29134y$$

$$1.0000 = 1.00000x + 0.21739y$$

$$0.2885 = 0.29099x + 0.05580y$$

$$0.2314 = 0.21547x + 0.00837y$$

Similarly, by using MATLAB 5.3 (by the MathWorks), we know that x=0.9759, y=0.1282. Thus incorporation of ^{18}O % in the product=$x/(x+y)$=0.884.

*4.3.20. Synthesis of ^{18}O-labeled 3-hydroxy-2-phenylselanyl-3-propyl-1(E)-hexenyl diphenyl phosphine oxide (E-**2e***)*

The reaction of **1e** (97.2 mg, 0.30 mmol) and PhSeCl (85.9 mg, 0.45 mmol) in 0.3 mL of $H_2^{18}O$ and 6 mL of anhydrous CH_3CN for 41 min afforded 127.7 mg (85%) of *E*-**2e**** (69.5% of ^{18}O incorporation) as a liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.52–7.42 (m, 2H), 7.42–7.20 (m, 13H), 5.75 (br, 1H), 5.62 (d, J=18.3 Hz, 1H), 1.85–1.58 (m, 4H), 1.47–1.23 (m, 4H), 0.83 (t, J=7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.2 (d, J_{pc}=1.4 Hz), 137.2, 134.0 (d, J_{pc}=107.4 Hz), 131.2 (d, J_{pc}=2.9 Hz), 130.7 (d, J_{pc}=9.7 Hz), 129.9, 129.3, 128.6, 128.2 (d, J_{pc}=11.9 Hz), 115.7 (d, J_{pc}=98.0 Hz), 80.7 (d, J_{pc}=5.5 Hz), 44.4, 16.7, 14.4; ^{31}P NMR (121.5 MHz, $CDCl_3$) δ 24.9; MS (ESI) m/z (%) 503 ($M^+(^{82}Se)$+1, 19.12), 501 ($M^+(^{80}Se)$+1, 100), 499 ($M^+(^{78}Se)$+1, 86.67), 497 ($M^+(^{77}Se)$ or $M^+(^{76}Se)$+1, 37.28), 495 ($M^+(^{74}Se)$+1, 9.41), 502 ($M^+(^{82}Se)$, 28.34), 500 ($M^+(^{80}Se)$, 27.52), 498 ($M^+(^{78}Se)$ or $M^+(^{77}Se)$+1, 25.25), 496 ($M^+(^{76}Se)$, 8.78), 483 ($M^+(^{82}Se)$−OH, 8.88), 481 ($M^+(^{80}Se)$−OH, 13.03), 479 ($M^+(^{78}Se)$−OH or $M^+(^{77}Se)$+1−OH, 5.58), 482 ($M^+(^{80}Se)$+1−OH, 3.65); IR ν (neat, cm^{-1}) 3336, 1580, 1556, 1462, 1437, 1376, 1337, 1306, 1274, 1154, 1140, 1115, 1088, 1067, 1021. HRMS calcd for $C_{27}H_{32}O^{18}OPSe^+$ (M^++1): 501.13421. Found: 501.13349.

According to the MS spectrum of this product (page S125, in Supplementary data), the relative abundances of 495.04, 496.06, 497.02, 498.04, 498.99, 500.03, 500.98, 502.00, 502.98 are 9.41, 8.78, 37.28, 25.25, 86.67, 27.52, 100, 28.34, 19.12; according to the simulated MS spectrum of *E*-**2e**** with 100% of ^{18}O (page S124, in Supplementary data), their relative abundances should be 1.755, 0.520, 18.559, 20.529, 52.158, 14.631, 100.00, 29.187, 21.571; according to the simulated MS spectrum of *E*-**2e** (page S123, in Supplementary data) their relative abundances should be 18.542, 20.514, 52.146, 14.677, 100.00, 29.222, 21.763, 5.999, 0.842. If x and y represent the amount of *E*-**2e**** and *E*-**2e**, respectively, then

$$0.0941 = 0.01755x + 0.18542y$$

$$0.0878 = 0.00520x + 0.20514y$$

$$0.3728 = 0.18559x + 0.52146y$$

$$0.2525 = 0.20529x + 0.14677y$$

$$0.8667 = 0.52158x + 1.00000y$$

$$0.2752 = 0.14631x + 0.29222y$$

$$1.0000 = 1.00000x + 0.21763y$$

$$0.2834 = 0.29187x + 0.05999y$$

$$0.1912 = 0.21571x + 0.00842y$$

Similarly, by using MATLAB 5.3 (by the MathWorks), we know that x=0.9100, y=0.3994. Thus incorporation of ^{18}O %=x/(x+y)=0.695.

4.4. Reaction of mono-substituted 1,2-allenyl phosphine oxides with PhSeCl

*4.4.1. 3-Hydroxy-4-methyl-2-phenylselanyl-1(E)-pentenyl diphenyl phosphine oxide (E-**2l**)*

Typical procedure IV. To a solution of PhSeCl (55.6 mg, 0.2 mmol) in 2 mL of MeCN and 1.5 mL of H_2O was added a solution of **1l** (57.3 mg, 0.3 mmol) in 1 mL of MeCN at room temperature. Then the resulting mixture was stirred at 70 °C for 34 min. After complete consumption of the starting material as monitored by TLC (eluent: dichloromethane/ethyl acetate=10:1), the mixture was quenched with 5 mL of H_2O, extracted with 20×3 mL of diethyl ether, washed with 5 mL of brine, and dried over anhydrous Na_2SO_4. Filtration and evaporation afforded the crude product, which was analyzed by ^1H NMR study to show an *E*-**2l**/*Z*-**3l** ratio of 97:3. Flash chromatography on silica gel (dichloromethane/ethyl acetate=10:1, then 5:1) afforded *E*-**2l** (73.8 mg, 82%) (*E*-**2l**/*Z*-**3l**=97:3).

*4.4.2. 3-Hydroxy-2-phenylselanyl-1(E)-propenyl diphenyl phosphine oxide (E-**2m**)*

The reaction of **1m** (72.5 mg, 0.30 mmol) and PhSeCl (86.4 mg, 0.45 mmol) in 3.0 mL of H_2O and 3.0 mL of CH_3CN at 70 °C for 9 h afforded *E*-**2m** (65.6 mg, 52.5%) and *Z*-**3m** (17.8 mg, 14%) (*E*-**2m**/*Z*-**3m**=79:21 by ^1H NMR analysis of the crude product).

*4.4.3. 3-Hydroxy-2-phenylselanyl-1(E)-pentenyl diphenyl phosphine oxide (E-**2n**)*

The reaction of **1n** (81.1 mg, 0.30 mmol) and PhSeCl (86.8 mg, 0.45 mmol) in 1.5 mL of H_2O and 3 mL of CH_3CN at 70 °C for 21 min afforded *E*-**2n** (104.6 mg, 78%) as a solid (*E*-**2n**/*Z*-**3n**>99:1 by ^1H NMR analysis of the crude product).

*4.4.4. 3-Hydroxy-2-phenylselanyl-1(E)-nonenyl diphenyl phosphine oxide (E-**2o**)*

The reaction of **1o** (96.8 mg, 0.30 mmol) and PhSeCl (85.5 mg, 0.45 mmol) in 1.5 mL of H_2O and 3 mL of CH_3CN at 70 °C for 70 min afforded *E*-**2o** (110.6 mg, 74%) (*E*-**2o**/*Z*-**3o**=98:2 by ^1H NMR analysis of the crude product).

*4.4.5. 3-Hydroxy-4-phenyl-2-phenylselanyl-1(E)-butenyl diphenyl phosphine oxide (E-**2p**)*

The reaction of **1p** (101.0 mg, 0.30 mmol) and PhSeCl (87.4 mg, 0.45 mmol) in 2.3 mL of H_2O and 2.3 mL of CH_3CN at 70 °C for 105 min afforded *E*-**2p** (118.1 mg, 77%) (*E*-**2p**/*Z*-**3p**=96.5:3.5 by ^1H NMR analysis of the crude product).

4.5. Reaction of optically active 1,2-allenyl phosphine oxides with PhSeCl

*4.5.1. S-3-Hydroxy-2-phenylselanyl-1(E)-butenyl diphenyl phosphine oxide (S-**2b**)*

The reaction of *S*-(+)-**1b** (76.2 mg, 0.30 mmol) and PhSeCl (86.7 mg, 0.45 mmol) in 0.3 mL of H_2O and 6 mL of CH_3CN for 12 min afforded *S*-(+)-**2b** (110.5 mg, 86%) as a solid. Mp 150–151 °C (*n*-hexane/ethyl acetate). ^1H NMR (300 MHz, $CDCl_3$) δ 7.62–7.28 (m, 15H), 5.88 (d, J=8.4 Hz, 1H), 5.62 (d, J=20.1 Hz, 1H), 4.96–4.82 (m, 1H), 1.58 (d, J=6.6 Hz, 3H); HPLC conditions: Chiralcel AD-H, hexane/*i*-PrOH=80:20, 0.8 mL/min, n=230 nm, t_R 12.6 (major), 17.3 (minor); $[\alpha]_D^{20}$ +22.5 (c 1.01, $CHCl_3$).

*4.5.2. S-3-Hydroxy-1-phenyl-2-phenylselanyl-1(E)-pentenyl diphenyl phosphine oxide (S-**2j**)*

The reaction of *S*-(+)-**1j** (103.8 mg, 0.30 mmol, 99% ee) and PhSeCl (88.5 mg, 0.45 mmol) of in 0.3 mL of H_2O and 6 mL of CH_3CN for 8 min afforded *S*-(+)-**2j** (146.8 mg, 94%, 99% ee) as a liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (dd, J_1=12.3 Hz, J_2=7.2 Hz, 2H), 7.54 (dd, J_1=17.1 Hz, J_2=6.9 Hz, 3H), 7.48–7.22 (m, 10H), 7.16–7.07 (m, 2H), 7.00–6.90 (m, 1H), 6.89–6.80 (m, 1H), 6.75 (d, J=11.4 Hz, 1H), 6.52 (d, J=6.9 Hz, 1H), 4.24 (t, J=9.8 Hz, 1H), 2.22–2.05 (m, 1H), 1.98–1.83 (m, 1H), 0.80 (t, J=7.2 Hz, 3H); HPLC conditions: Chiralcel AD-H, hexane/*i*-PrOH=90:10, 0.7 mL/min, n=230 nm, t_R=25.7; $[\alpha]_D^{20}$ +103.1 (c 0.96, $CHCl_3$).

*4.5.3. R-3-Hydroxy-2-phenylselanyl-1(E)-nonenyl diphenyl phosphine oxide (R-**2o**)*

The reaction of *R*-(−)-**1o** (97.6 mg, 0.30 mmol, 97% ee) and PhSeCl (86.9 mg, 0.45 mmol) in 1.5 mL of H_2O and 3 mL of CH_3CN at 70 °C for 30 min afforded *R*-(−)-**2o** (118.2 mg, 79%, 97% ee) as a liquid. ^1H NMR (300 MHz, $CDCl_3$) δ 7.64–7.31 (m, 15H), 5.78–5.57 (m, 2H), 4.70–4.58 (m, 1H), 1.97–1.73 (m, 2H), 1.66–1.45 (m, 1H), 1.44–1.13 (m, 7H), 0.86 (t, J=6.2 Hz, 3H); HPLC conditions: Chiralcel OD-H, hexane/*i*-PrOH=95:5, 0.7 mL/min, n=230 nm, t_R 11.7 (major), 13.5 (minor); $[\alpha]_D^{20}$ −25.15 (c 1.05, $CHCl_3$).

Acknowledgements

Financial support from the National Natural Science Foundation of China (No. 20572093) and the Major State Basic Research Development Program (Grant No. 2009CB825300) is greatly appreciated. S.M. is a Qiu Shi Adjunct Professor at Zhejiang University. We thank Bo Lü in our research group for reproducing the results presented in entries 7 and 12 in Table 2, entry 4 in Table 4, and the second equation in Scheme 2.

Supplementary data

The ^1H, ^{13}C, ^{31}P spectra for all the new compounds, the MS spectra for *E*-**2h***, *E*-**2c***, and *E*-**2e***, the simulated MS spectra for *E*-**2h***, *E*-**2c***, and *E*-**2e*** and the simulated MS spectra for *E*-**2h**, *E*-**2c**, and *E*-**2e** are included in Supplementary data. This material is available free of charge via the Internet. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.04.023.

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