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Photoinduced selective hydrophosphinylation of allylic compounds with diphenylphosphine oxide leading to *γ*-functionalized *P*-ligand precursors

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Abstract

A series of bifunctional phosphine compounds promising as *γ*-functionalized phosphine ligand precursors are conveniently synthesized by the radical addition of diphenylphosphine oxide ($Ph_2P(O)H$) to allylic compounds under photoirradiation. The photoinduced addition proceeds regioselectively in an anti-Markovnikov manner, and phosphines having hydroxy, alkoxy, aryloxy, acyloxy, and thio groups at the *γ*-position can be prepared by simple operation. Interestingly, novel continuous addition of $Ph_2P(O)H$ to two molecules of allylic ethers and related compounds is also observed, although their yields are moderate. The substituent and steric effects of the allylic substituents on the radical addition are discussed in detail.

Keywords Diphenylphosphine oxide · Allylic compound · Radical addition · Anti-Markovnikov addition · Continuous addition

Introduction

Organophosphorus compounds are widely used in catalytic technologies, materials, and pharmaceuticals, so the methods of forming of C–P bonds have received a great deal of attention [1–5]. One of the simplest synthetic methods for C–P bond formation

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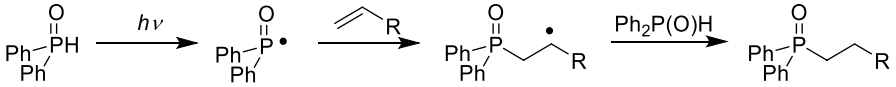
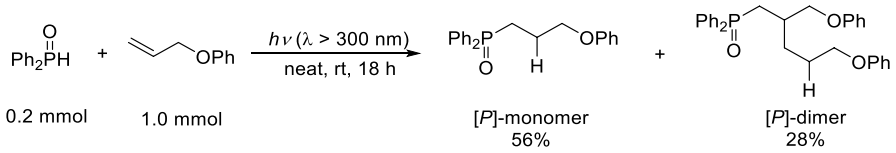


Scheme 1 Photoinduced addition of $Ph_2P(O)H$ to alkenes

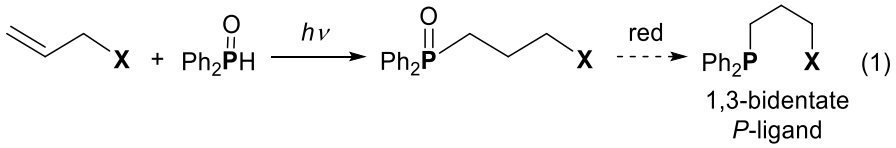


Scheme 2 Photoinduced hydrophosphinylation of allyl phenyl ether with diphenylphosphine oxide

[2–31] is the addition of the secondary phosphine oxides to alkenes [32, 33] due to the low bond dissociation energy (BDEs) of P–H bonds [34]. The mechanism of these reactions has been reported to include radical and/or ionic intermediates [35–40].

In our previous work, we reported the anti-Markovnikov addition of $Ar_2P(O)–H$ to unsaturated bonds [41, 42]. Photoirradiation produces a phosphinoyl radical, which attacks the terminal carbon of alkene [41, 42] to generate a carbon-centered radical. Subsequent hydrogen abstraction from diphenylphosphine oxide yields a hydrophosphinylated product (Scheme 1).

This hydrophosphinylation is very advantageous, because this metal-free method proceeds using no solvent and additives such as base and acid with simple operation. If the photoinduced hydrophosphinylation is applied to allylic heteroatom compounds, a series of 1,3-bidentate phosphorus ligand precursors can conveniently be synthesized (Eq. 1).



(1)

We here report a metal-free photoinduced hydrophosphinylation of a series of allylic compounds with diphenylphosphine oxide leading to γ-heteroatom-functionalized phosphine oxides as 1,3-bidentate *P*-ligand precursors.

Furthermore, when allyl phenyl ether is used for the photoinduced hydrophosphinylation, interestingly, in addition to the desired hydrophosphinylation product (56% yield), namely [*P*]-monomer, a duplicate addition product, namely [*P*]-dimer, is also formed in 28% yield (Scheme 2).

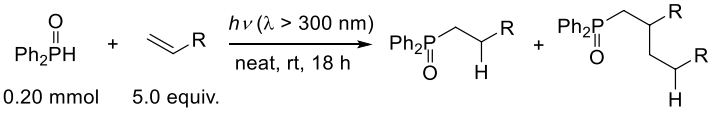
This paper also deals with the insight into the mechanism for the formation of [*P*]-dimer.

Results and discussion

Hydrophosphinylation of alkenes with diarylphosphine oxides is one of the most straightforward methods for introducing phosphorus units into organic molecules, because the addition reactions using air- and moisture-stable pentavalent phosphorus reagents are highly atom-economical by avoiding troublesome treatments of unstable phosphorus reagents [32, 33]. The hydrophosphinylation can proceed via ionic, radical, and transition-metal-catalyzed processes. For ionic hydrophosphinylation, acid- or base-catalyzed addition of $Ar_2P(O)H$ to electron-deficient alkenes is frequently reported to proceed via a conjugate addition to *α,β*-unsaturated carbonyl and cyano compounds [43–46]. The transition-metal-catalyzed hydrophosphinylation is a powerful method for the synthesis of phosphorus compounds, because the regio- and stereoselectivity can be controlled by the selection of catalysts and reaction conditions [47–61]. The radical hydrophosphinylation can be induced by the addition of radical initiators or upon photoirradiation, and it selectively affords anti-Markovnikov adducts [62–66]. Notably, metal-free and additive-free procedures using the radical hydrophosphinylation are much advantageous in view of environmental conservation. In the present photoinduced hydrophosphinylation of allylic compounds, simple operations such as photoirradiation in the absence of solvent have been successfully achieved.

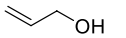
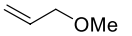
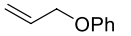
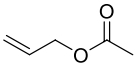
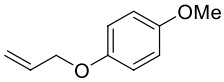
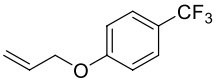
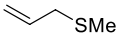
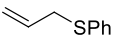
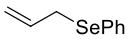
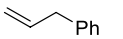
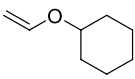
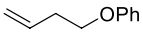
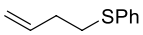
When a mixture of diphenylphosphine oxide **1a** (0.20 mmol) and allyl alcohol **2a** (1.00 mmol) in a NMR tube (Pyrex) was irradiated with a Xe lamp (500 W) at room temperature for 18 h, the desired diphenyl(3-hydroxypropyl)phosphine oxide **3aa** was successfully obtained in 88% yield (Table 1, entry 1). Similarly, allyl methyl ether **2b** underwent regioselective hydrophosphinylation to afford diphenyl(3-methoxypropyl)phosphine oxide **3ab** in 82% yield (entry 2). In the case of allyl phenyl ether **2c**, the corresponding hydrophosphinylation product **3ac** was formed in 56% yield, and interestingly, the duplicate addition of **1a** to two molecules of **2c** took place to give **4ac** in 28% yield (entry 3). Allyl acetate **2d** also exhibited a similar product selectivity, namely single adduct **3ad** and double adduct **4ad** were obtained in 55% and 27% yields, respectively (entry 4). The hydrophosphinylation of allyl aryl ethers **2e** and **2f** was tolerant the electron-donating and electron-withdrawing groups (entries 5 and 6), and single adducts **3ae** and **3af** were formed as the major product along with double adducts **4ae** and **4af** as minor products. In contrast, allyl methyl sulfide **2g** exclusively afforded single adduct **3ag** in good yield without formation of double adduct **4ag** (entry 7). In the case of allyl phenyl sulfide **2h**, adducts **3ah** and **4ah** were generated in 14% and 10% yields, respectively (entry 8). On the other hand, allyl phenyl selenide **2i** did not afford the corresponding adducts **3ai** and **4ai** (entry 9). As PhS and PhSe groups are good leaving groups, the photoinduced reaction of **1a** with **2h** and **2i** might proceed via the elimination of PhS• and PhSe• to provide allyl phosphine oxide and related compounds (Scheme 3).

Table 1 Photoinduced hydrophosphinylation of allylic compounds



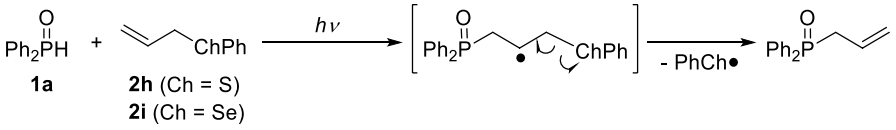
0.20 mmol 5.0 equiv.

1a **2** **3** **4**

Entry	Alkenes		Yield[a]	
			3	**4**
1		**2a**	**3aa**, 88%	**4aa**, 2%
2		**2b**	**3ab**, 82%	**4ab**, 8%
3		**2c**	**3ac**, 56%	**4ac**, 28%
4		**2d**	**3ad**, 55%	**4ad**, 27%
5		**2e**	**3ae**, 50%	**4ae**, 23%
6		**2f**	**3af**, 56%	**4af**, 27%
7		**2g**	**3ag**, 77%	**4ag**, 0%
8		**2h**	**3ah**, 14%	**4ah**, 10%
9		**2i**	**3ai**, 0%	**4ai**, 0%
10		**2j**	**3aj**, 73%	**4aj**, 0%
11		**2k**	**3ak** 92%	**4ak**, 8%
12[b]			**3ak** 84%	**4ak**, 16%
13		**2l**	**3al**, 78%	**4al**, 13%
14		**2m**	**3am**, 80%	**4am**, 0%

[a] Determined by ^{1}H NMR. [b] High-pressure Hg lamp, 35 h.

In the case of allylbenzene **2j**, adduct **3aj** was formed in 73% yield, but there was no adduct **4aj** (entry 10). The reactions of vinyl compounds such as cyclohexyl vinyl ether **2k** with **1a** afforded 92% yield of **3ak** along with small amount of **4ak** (entry 11). It was also acceptable to use a super-high pressure Hg lamp as the light source, and the photoinduced addition of **1a** to **2k** afforded **3ak**



Scheme 3 Photoinduced substitution reaction between allyl phenyl chalcogenides and $Ph_2P(O)H$

and **4ak** in 84% and 16% yields, respectively (entry 12). Homoallyl phenyl ether **2l** provided **3al** and **4al** in 78% and 13% yields, respectively (entry 13). Homoallyl phenyl sulfide **2m** was allowed to react with **1a** to give only adduct **3am** in 80% yield (entry 14).

As can be seen from Table 1, the photoinduced hydrophosphinylation of allylic and related compounds successfully provided a series of 1,3-bidentate *P*-ligand precursors, which can easily be converted to the corresponding trivalent phosphine ligands by the reduction with DIBAL-H [67][1].

In particular, it has been found that allylic compounds bearing an oxygen atom at the allylic position afford duplicate addition products **4** as byproducts. To get insight into the formation of multiple addition products, the reaction of diphenylphosphine oxide **1a** with allyl phenyl ether **2c** was carried out varying the amounts of **2c** (Table 2).

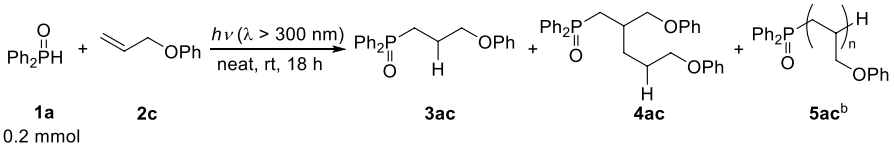
As shown in Table 2, the reaction of **1a** with 1 equiv. of **2c** afforded [*P*]-monomer (**3ac**), [*P*]-dimer (**4ac**), and [*P*]-polymers (**5ac**) in 67%, 6%, and 15% yields, respectively (entry 1). When the amounts of **2c** increased to 3 equiv., the yields of **3ac** and **5ac** decreased to 59% and 5%, respectively and the yield of **4ac** increased to 29% (entry 2). The photoirradiated reactions of **1a** with 5 equiv. of **2c** using a high-pressure mercury lamp or a xenon lamp gave the similar results (entries 3 and 4). When the reactions were conducted in 10 or 15 equiv. of **2c**, the yields of both **3ac** and **4ac** decreased and the yield of **5ac** increased to 18% (entries 5–6). These results indicate that the use of large amounts of allylic compounds resulted in decrease in the formation of [*P*]-monomer.

We next evaluated the influence of P–H compounds on the single/multiple addition using 5 equiv. of **2c** (Table 3).

The addition of diphenylphosphine (Ph_2PH, **1b**) and diphenylphosphine sulfide ($Ph_2P(S)H$, **1c**) to allyl phenyl ether **2c** produced only [*P*]-monomers **3bc** and **3cc** in 62% and 89% yields, respectively (entries 2–3). In both cases, [*P*]-dimers **4bc** and **4cc** were not produced under the condition. In the case of **1b**, the less bulkiness around the phosphorus group might accelerate the hydrogen abstraction of the generated carbon radical from **1b**. The bond dissociation energy (BDE) [34] of the P–H bonds of **1c** is lower than that of **1a** successfully improved the product selectivity to

[1] Upon treating with DIBAL-H, γ-functionalized *P*-ligand precursors, $Ph_2P(O)–CH_2CH_2CH_2–X$, (X = functional group), can be converted to the corresponding phosphines, $Ph_2P–CH_2CH_2CH_2–X$, which are allowed to complex with $Me_2S•BH_3$, followed by purification of thus formed $Ph_2P(BH_3)–CH_2CH_2CH_2–X$ by column chromatography. Then, deprotection using DABCO successfully affords γ-functionalized *P*-ligands, $Ph_2P–CH_2CH_2CH_2–X$.

Table 2 Influence of amounts of allyl ether **2c** on the formation of duplicate and multiplicate addition products **4ac** and **5ac**



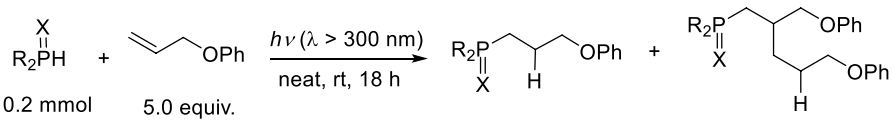
1a 0.2 mmol **2c** **3ac** **4ac** **5ac**[b]

Entry	Amounts of **2c**	Yield[a] (%)		
		3ac	**4ac**	**5ac**
1[c]	1 equiv.	67	6	15
2[c]	3 equiv.	59	29	5
3[c]	5 equiv.	58	33	5
4	5 equiv.	56	28	4
5	10 equiv.	45	21	18
6	15 equiv.	35	16	18

[a]Determined by ^{1}H NMR. [b]$n \geq 3$

[c]High-pressure Hg lamp, 25 h

Table 3 Single/multiple addition using several P–H compounds



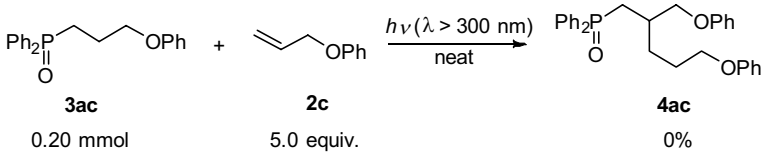
0.2 mmol **1** 5.0 equiv. **2c** **3** **4**

Entry	P source	Yield[a] (%)	
		3	**4**
1	$Ph_2P(O)H$, **1a**	**3ac**, 56%	**4ac**, 28%
2	Ph_2PH, **1b**	**3bc**, 62%	**4bc** 0%
3	$Ph_2P(S)H$, **1c**	**3cc**, 89%	**4cc**, 0%
4	$Ph_2P(Se)H$, **1d**	**3dc**, 96%	**4dc**, 4%
5[b]	$(p\text{-}MeOC_6H_4)_2P(O)H$, **1e**	**3ec**, 36%	**4ec**, 27%
6[b]	$(p\text{-}FC_6H_4)_2P(O)H$, **1f**	**3fc**, 44%	**4fc**, 9%
7[b]	$(EtO)_2P(O)H$, **1g**	**3gc** 0%	**4gc** 0%

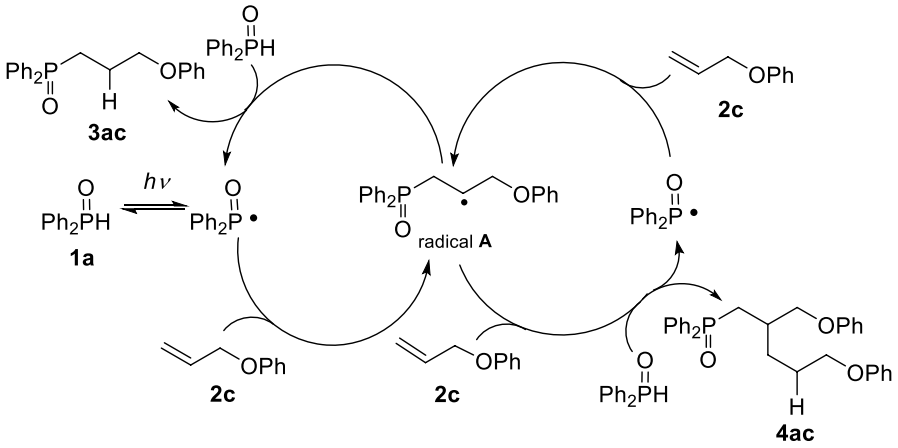
Bold values represents compound numbers

[a]Determined by ^{1}H NMR

[b]High-pressure Hg Lamp, 35 h



Scheme 4 An attempted addition of **3ac** to **2c** under light



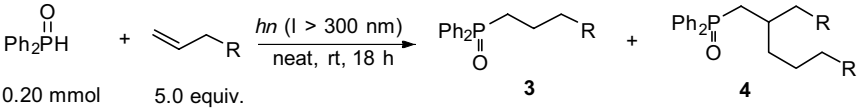
Scheme 5 A proposed mechanism of the radical addition of **1a** to **2c**

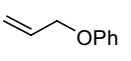
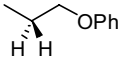
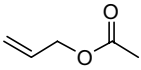
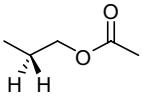
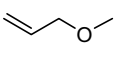
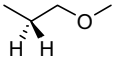
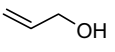
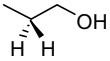
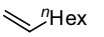
afford only **3cc** in high yield, because the lower BDE of the P–H bond accelerates the hydrogen abstraction of the generated carbon radical from the P–H compounds. The photoinduced reaction of phosphine selenide ($Ph_2P(Se)H$, **1d**) with **2c** afforded the adduct **3dc** in 96% yield along with only 4% of the adduct **4dc** (entry 4). Two other $Ar_2P(O)H$, **1e** and **1f** were also investigated. While $Ar_2P(O)H$ with a methoxy group as an electron-donating group gave **3ec** and **4ec** in 36% and 27% yields, respectively (entry 5), $Ar_2P(O)H$ with a fluoro group as an electron-withdrawing group gave the adducts **3fc** and **4fc** in 44% and 9% yields, respectively (entry 6). However, the hydrophosphinylation with diethyl phosphonate (**1g**) did not produce the corresponding adducts (entry 7). The above results show that the ratios of the adducts **3** and **4** depend on the nature of substituents on the phosphorus atom.

To clarify whether **3ac** is a precursor for **4ac**, the photoinduced reaction of **2c** and **3ac** was conducted as shown in Scheme 4. As the result, no **4ac** was formed, and this fact indicates **3ac** is not a precursor for **4ac**.

A possible pathway is proposed in Scheme 5. Upon photoirradiation, **1a** generates phosphinoyl radical ($Ph_2P(O)\bullet$), which adds to **2c** to afford carbon-centered radical **A**. Hydrogen abstraction by radical **A** from **1a** produces anti-Markovnikov adduct **3ac** [41, 42]. The radical **A** also adds to another **2c** to produce adduct **4ac**. To get some information about the formation of **4**, we estimated the electronic effect of the allylic substituents and the phosphorus substituents by using chemical shifts of allylic protons in ^1H NMR spectra. Table 4 indicates the substituent

Table 4 The reactivity of allylic compounds



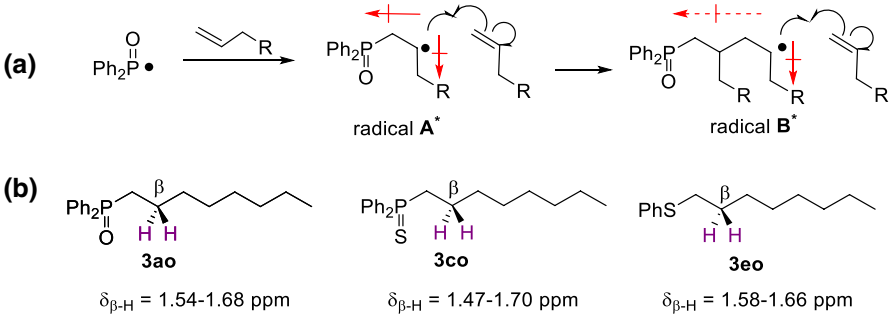
Entry	Allylic compound	Corresponding alkane	$\Delta\delta$ [ppm][a]	Yield[b]	
				3	**4**
1			0.53	56%	28%
2			0.39	55%	27%
3			0.33	82%	8%
4			0.25	88%	2%
5			0	99%	0%

[a]Based on the chemical shift of *n*-octane

[b]Determined by ^{1}H NMR

chemical shift values ($\Delta\delta$), which can be calculated by the shift values of allylic methylene protons of functionalized alkenes toward the methylene chemical shift of *n*-octane. An increase in the electron-withdrawing ability of the allylic substituents results in a downfield shift of the allylic protons, and increasing the $\Delta\delta$ values resulted in increase of the yields of **4**. By referring the $\Delta\delta$ values, the reactivity of the allylic compounds could be predicted. The more reactive allylic compounds led to the higher yields of the adduct **4**. In other words, as the electron-withdrawing ability of the allylic substituent increased, the yield of **3** decreased and the yield of **4** increased.

Electronic effects of the photoinduced multiple addition of **1a** to allylic compounds **2** are summarized in Scheme 6. Scheme 6a indicates the structures of radical intermediates $\mathbf{A}^*$ and $\mathbf{B}^*$, which are generated from the single and duplicate addition, respectively. In these radical intermediates, the location of $Ph_2P(O)$ group against the carbon radical center affects the stability of radical intermediates $\mathbf{A}^*$ and $\mathbf{B}^*$. Since the distance between the $Ph_2P(O)$ group and the carbon-centered radical on the radical $\mathbf{B}^*$ was longer than that on the radical $\mathbf{A}^*$, the radical $\mathbf{B}^*$ was less stable than the radical $\mathbf{A}^*$. The electron-withdrawing ability of the heteroatoms contributed slightly to the stabilization of the radical species, as there was no significant difference in the signal of the protons at the β positions of compounds **3ao**, **3co**, and **3eo** (Scheme 6b). The stability of radical intermediates is affected by many factors



Scheme 6 The substituent effect on the stability of the radicals

including the electronic effect of substituents on both allylic compounds and phosphorus reagents, the steric hindrance, and the distance between $Ph_2P(O)$ group and the carbon radicals generated.

Conclusion

A series of γ-functionalized phosphine ligand precursors, $Ph_2P(O)–CH_2CH_2CH_2–X$, (X = functional group), are conveniently synthesized by the radical addition of diphenylphosphine oxide ($Ph_2P(O)H$) to allylic compounds under photoirradiation. The photoinduced addition proceeds regioselectively in an anti-Markovnikov manner, and organophosphorus compounds having hydroxy, alkoxy, aryloxy, acyloxy, and thio groups at the γ-position can be prepared by simple operation. The stability of carbon radicals contribute to the selectivity of the single/duplicate addition, and it is affected by the electron-withdrawing ability of allylic compounds, the steric hindrance, the nature of phosphorus substituents, and the distance from carbon-centered radicals to $Ph_2P(O)$ group.

Experimental section

General methods

Unless otherwise state, materials were obtained from commercial supplies and purified by distillation. ^1H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) system or JEOL JNM-ECX400 (400 MHz) FT system in $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard. ^{13}C NMR spectra were taken mainly on a JEOL JNM-ECS400 (100 MHz) and JEOL JNM-ECX400 (100 MHz) FT spectrometers in $CDCl_3$. ^{31}P NMR spectra were recorded on JEOL JNM-ECX400 (162 MHz) FT NMR in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. IR spectra were recorded on JASCO FT/IR-680Plus instrument.

High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II ESI(+)/TOF instrument.

General procedure for hydrophosphinylation of alkenes

Under argon atmosphere, diphenylphosphine oxide **1a** (0.20 mmol) and alkene **2** (1.00 mmol) were placed in a Schlenk tube in the absence of solvents. The reaction was irradiated with a Xenon lamp (500 W) at room temperature for 18 h. The products were purified by preparative TLC on silica gel or silica gel column chromatography using *iso*-hexane/methyl acetate as an eluent.

(3-Phenoxypropyl)diphenylphosphine oxide (3ac)

[CAS No. 14580–96-2] [41, 42]: ^{1}H NMR ($CDCl_3$) δ 7.80–7.70 (m, 4H), 7.56–7.43 (m, 6H), 7.26–7.20 (m, 2H), 6.92 (t, J = 7.3 Hz, 1H), 6.83 (d, J = 8.7 Hz, 2H), 3.99 (t, J = 6.0 Hz, 2H), 2.51–2.44 (m, 2H), 2.15–2.06 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 158.6, 132.8 (d, J = 98.7 Hz), 131.8, 130.7 (d, J = 9.5 Hz), 129.4, 128.7 (d, J = 11.5 Hz), 120.8, 114.4, 67.4 (d, J = 14.1 Hz), 26.4 (d, J = 72.7 Hz), 21.8; ^{31}P NMR ($CDCl_3$) δ 33.3.

(5-Phenoxy-2-(phenoxymethyl)pentyl)diphenylphosphine oxide (4ac)

Colorless oil, ^{1}H NMR ($CDCl_3$) δ 7.80–7.73 (m, 4H), 7.50–7.35 (m, 6H), 7.28–7.20 (m, 4H), 6.92 (td, J = 7.3, 3.2 Hz, 2H), 6.83 (d, J = 7.8 Hz, 2H), 6.78 (d, J = 7.8 Hz, 2H), 3.98–87 (m, 4H), 2.72–2.64 (m, 1H), 2.49–2.40 (m, 1H), 1.88–1.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 158.9 (d, J = Hz), 133.5 (d, J = 24.9 Hz), 131.8, 130.8 (dd, J = 13.9, 9.6 Hz), 129.5 (d, J = 3.8 Hz), 128.8 (dd, J = 11.5, 7.7 Hz), 120.7 (d, J = 13.4 Hz), 114.6 (d, J = 5.8 Hz), 69.5 (d, J = 6.7 Hz), 67.7, 33.2 (d, J = 2.9 Hz), 31.3 (d, J = 70.9 Hz), 29.5 (d, J = 8.6 Hz), 26.4; ^{31}P NMR ($CDCl_3$) δ 31.8; IR (KBr, cm^{-1}): 3420, 3057, 2927, 1586, 1496, 1437, 1243, 1173, 1105, 1036, 753, 692, 592, 510; HRMS (ESI+/TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{30}H_{31}NaO_3P$: 493.1909, Found: 493.1918.

(2-(Cyclohexyloxy)ethyl)diphenylphosphine oxide (3ak)

White solid, mp. 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dt, J = 11.8, 1.4 Hz, 2H), 7.73 (dd, J = 11.8, 1.4 Hz, 2H), 7.52–7.42 (m, 6H), 3.80–3.74 (m, 2H), 3.19–3.14 (m, 1H), 2.66–2.59 (m, 2H), 1.74–1.73 (m, 2H), 1.64–1.61 (m, 2H), 1.48–1.43 (m, 1H), 1.18–1.12 (m, 5H, axial position); ^{13}C NMR (100 MHz, $CDCl_3$): 133.3 (d, $J_{C\text{-}P}$ = 99.2 Hz), 131.8 (d, $J_{C\text{-}P}$ = 1.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 77.8, 61.1, 32.1, 31.4 (d, $J_{C\text{-}P}$ = 70.6 Hz), 25.8, 24.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.8; HRMS (ESI+/TOF) *m/z*: $[M+Na]^+$ Calcd. for $C_{20}H_{25}NaO_2P$: 351.1490, Found: 351.1490.

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