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Radical hydrophosphorylation of alkynes with $R_2P(O)H$ generating alkenylphosphine oxides: scope and limitations

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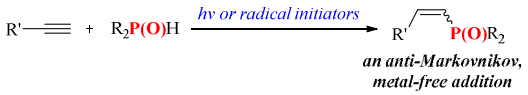


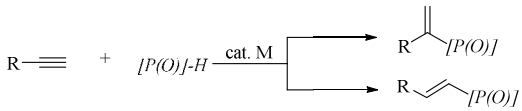
ABSTRACT

Radical hydrophosphorylation of aliphatic terminal alkynes with H-phosphine oxides can produce the corresponding *anti*-Markovnikov alkenylphosphorus adducts in moderate yields. This method is a cleaner way for the preparation of the corresponding alkenylphosphine oxides since it avoids the use of a metal-catalyst that sometimes is difficult to remove from the products.

Organophosphorous compounds are of high importance in organic synthesis, biochemistry and material sciencies.[1] The metal-catalyzed addition of a hydrogen phosphoryl compound P(O)H to an alkyne (hydrophosphorylation) is a powerful method for the preparation of an alkenylphosphoryl compound which is highly useful but difficult to prepare by the conventional method (Scheme 1).[2] One of the remarkable features of this method is the nearly perfect controllable regio- and stereoselectivity of the addition products, i.e., both the α-adduct and the β-adduct can be highly selectively generated, respectively, by employing the right catalyst.[2b] However, despite its novelty, still there are few drawbacks associated with the metal-catalyzed hydrophoshorylations. One of such drawbacks is the difficult removal of the metal-catalyst from the products

because of the strong coordination of the P(O) products to the metals.[3] As a result, the products prepared by the metal-catalyzed hydrophosphorylation, that inherently are colorless oil or white solid when pure, often are yellowish due to the contamination of the metals. This metal-contamination problem can hamper their application as starting materials to electronical materials and pharmaceuticals since "metal-free" clean chemicals are usually required.

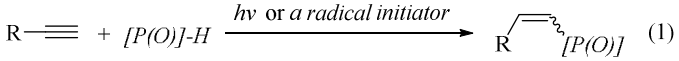
Scheme 1 Metal-catalyzed addition of P(O)H compounds to alkynes.



[P(O)]-H = H-phosphonate, H-phosphinate, H-phosphine oxide

Radical-initiated additions (especially those of the photo-induced ones) of P(O)H compounds to alkynes can avoid the above-mentioned metal-contamination problem. From the literatures, it is expected that both a radical initiator (including oxygen) and light should possibly induce this kind of radical hydrophosphorylation.[4] However, such studies are rather limited, and the scope and limitations of such a radical hydrophosphorylation are not clear. Thus, Russian chemists reported the radical addition of $R_2P(O)H$ to alkynes initiated by dibenzoyl peroxide.[4g] However, the yield was low (ca. 24% yield). Recently, the hydrophosphorylation of terminal alkynes with $(MeO)_2P(O)H$ was conducted under photo-irradiation in the presence of 0.2~0.5 equiv. 2,2-dimethoxy-2-phenylacetophenone (DPAP) as an initiator.[4a-b] However, a large excess amount of $(MeO)_2P(O)H$ (100 equivs) had to be used.

In conjunction with our studies on metal-mediated hydrophosphorylation,[2b,5] we feel it is necessary to have a proper assessment of the radical hydrophosphorylation reactions of alkynes with P(O)H compounds.[4b] Herein we report our studies on the photo-irradiated and radical initiator-induced additions of H-phosphine oxides and related compounds to alkynes (eq 1). As described below, though, in general, far less efficient than that of the metal-mediated hydrophosphorylations, the combination of terminal aliphatic alkynes and H-phosphine oxides can produce the *β*-adducts selectively in moderate to good yields. In particular, propargylic alcohols that could not be used in the palladium-mediated hydrophosphorylations[5] are also applicable.

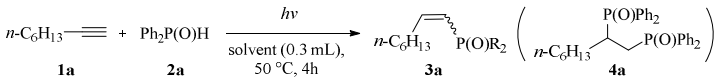


(1)

Light-induced addition of P(O)H compounds to alkynes.

As shown in Table 1, a mixture of 1-octyne **1a** and $Ph_2P(O)H$ **2a** was placed in a Pyrex glass tube[6] under nitrogen atmosphere and irradiated using a high-pressure Hg lamp for 4 h. In the absence of a solvent, an equimolar mixture of **1a** and **2a** produced 49% yield of **3a** as a *Z*- and *E*-isomer mixture (*Z*/*E* = 67/33) (run 1). However, a side product **4a** by the double addition of **2a** to **1a** was also generated in 15% yield based on **2a**.[7] By employing 2 equivs of **2a**, the yield of **3a** increased to 61% (run 2), albeit **4a** also increased to 29% yield. On the other hand, an excess **1a** suppressed the formation of **4a** (runs 3 and 4), although too much of **1a** lowered the yield of **3a** (run 4). The reaction took place more cleanly in a solvent (runs 5-16) since the formation of **4a** could be suppressed. Among the solvents investigated, *i*-PrOH was chosen as the solvent considering both yields and selectivity. As shown in run 11, 70% yield of **3a** (*Z*/*E* = 73/27) could be obtained by using *i*-PrOH as the solvent.

Table 1. Addition of $Ph_2P(O)H$ to 1-octyne under photo-irradiation.[a]



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

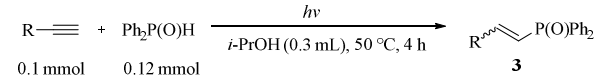
run	**1a** (mmol)	**2a** (mmol)	solvent	**3a** yield (%) (*Z*/*E*)[b]	**4a** yield (%)[c]
1	0.1	0.1	none	49 (67/33)	15
2	0.1	0.2	none	61 (61/39)	29
3	0.2	0.1	none	61(69/31)	10
4	0.5	0.1	none	54(70/30)	trace
5[d]	0.1	0.1	THF	51 (66/34)	trace
6[e]	0.1	0.12	THF	62 (65/35)	trace
7	0.1	0.12	THF	68 (62/38)	trace
8[f]	0.1	0.12	THF	68 (60/40)	trace
9	0.1	0.12	CH_2Cl_2	63 (68/32)	trace
10	0.1	0.12	C_6H_6	61 (54/45)	trace
11	0.1	0.12	*i*-PrOH	70 (73/27)	trace

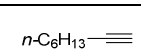
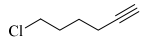
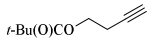
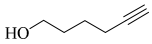
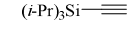
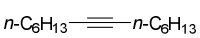
12	0.2	0.1	*i*-PrOH	47 (75/25)	trace
13	0.1	0.15	*i*-PrOH	76 (71/29)	8
14	0.1	0.12	EtOH	47 (80/20)	trace
15	0.1	0.12	*t*-BuOH	58 (80/20)	trace
16[g]	0.1	0.12	*i*-PrOH	42 (58/42)	trace

[a] Reactions conditions: a mixture of **1a** and **2a** was sealed in a Pyrex-tube under dry nitrogen atmosphere and irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ).[6] Yield was calculated based on the less employed starting material. [b]The yield of **3a** and the *Z*/*E* ratio were determined by GC. [c]The yield of **4a** was calculated from ^{31}P NMR spectroscopies. [d]3 h. [e]2 h. [f]6 h. [g]Sealed under air atmosphere.

As shown in Table 2, a variety of alkynes was used to carry out the photo-irradiated additions. Similar to 1-octyne, terminal aliphatic alkynes with an ester group (run 3) or a hydroxyl group (run 4) could react to give the corresponding adducts in good yields. Alkynes with chloro (run 2) group, however, gave low yields of the products. The bulky *t*-butylacetylene (run 5) also produced the corresponding adducts, albeit with the *E*-isomer as the major product due to steric reasons (*vide infra*). A conjugated alkyne (run 6), phenylacetylene (run 7) and internal alkyne (run 16), however, hardly produced the adducts, and most of $Ph_2P(O)H$ remained unreacted.[8] Remarkably, however, the very bulky silylacetylenes (runs 8 and 9) and propargyl alcohols (runs 10-15) all gave the adducts in good yields. An interesting phenomenon is that, being different from *t*-butylacetylene (run 5), both the bulky silylacetylenes and proparlgyl alcohols, all give the *Z*-adduct as the major stereomer, indicating that the R_3Si and OH groups significantly contribute to the reactions (*vide infra*). The efficient reactions with these cheap propargyl alcohols are practically important. Moreover, they are also novel because similar additions by the palladium-catalyzed hydrophosphorylation hardly took place.[5] As expected, under similar conditions, the reaction conducted at 1 mmol scale gave similar results. For example, a mixture of $Ph_2P(O)H$ (242.6 mg, 1.2 mmol) and 2-methyl-3-butyn-2-ol (84.1 mg, 1.0 mmol) in *i*-PrOH (1 mL) under photo-irradiation for 4 h gave 76% yield (*Z*/*E* = 77/23) of **3m** after purification using short column chromatography on silica gel (eluent CH_2Cl_2/MeOH = 100/1).

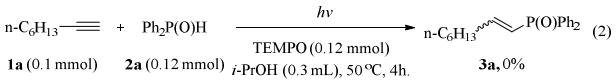
Table 2. Photo-induced addition of $Ph_2P(O)H$ to alkynes.[a]



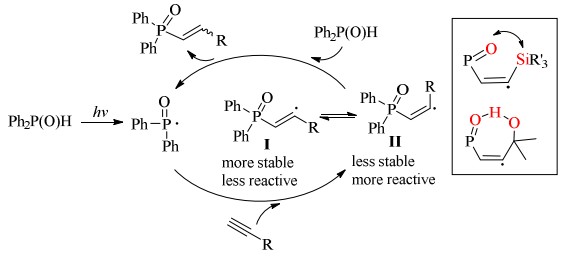
run	alkyne	product	yield (%)[b] (*Z*/*E*)[c]
1		**3a**	65 (73/27)
2		**3b**	33 (55/45)
3		**3c**	54 (64/36)
4		**3d**	71 (70/30)
5		**3e**	42 (37/63)
6		**3f**	trace
7		**3g**	trace
8[d]		**3h**	36 (53/47)
9		**3i**	81 (87/13)
10		**3j**	45 (60/40)
11		**3k**	66 (71/29)
12		**3l**	84 (72/28)
13		**3m**	81 (72/28)
14		**3n**	88 (59/41)
15		**3o**	70 (70/30)
16		**3p**	no addition

[a] Reaction conditions: a *i*-PrOH solution of an alkyne and $Ph_2P(O)H$ in a Pyrex-tube was irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ). The products were isolated using a recycling preparative HPLC (JAI) equipped with a 1H and 2H GPC columns using $CHCl_3$. [b]Isolated yield. [c]The *Z*/*E* ratio was determined for the crude mixture by GC or ^{31}P NMR. [d]Ca. 25% of $Ph_2P(O)CH_2CH_2P(O)Ph_2$ was detected, which was generated by the desilylation of **3i** followed by the addition of $Ph_2P(O)H$.

As shown in eq 2, as expected, the addition reaction did not proceed in the presence of a radical scavenger TEMPO.[4h] A possible mechanism for this photo-induced hydrophosphorylnation is shown in Scheme 2. The phosphoryl radical generated under light[4] adds to alkynes to generate alkenyl radicals which exists in *trans* **I** and *cis* **II** forms with the former being more stable but less reactive and the latter being more reactive but less stable.[9] Subsequent reactions of **I** and **II** with $Ph_2P(O)H$ give the corresponding alkenylphosphine oxides. The *Z*/*E* ratio of the adducts reflects the result of reactions of **I** and **II**. Since **II** is more reactive, usually *Z*-adduct was generated as the major product. However, if R is too bulky (*t*-Bu, for example), the vinyl radical might predominantly exist in the *trans* form **I**, which consequently generates the *E*-adduct as the major isomer. As shown in Scheme 2, it was expected that a silyl group and OH group could interact with the phosphoryl group to stabilize the *cis*-radical **II**. Therefore, different from *t*-butylacetylene, *Z*-adducts were generated from these bulky alkynes.



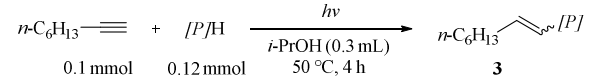
Scheme 2 A possible mechanism for the photo-induced addition of $Ph_2P(O)H$ to alkynes.



Under similar conditions, the reactions of other *[P]*H compounds were investigated (Table 3). The bulky Ph(*t*-Bu)P(O)H (run 1) also produced the corresponding adducts in 45% yield. Aliphatic phosphine oxides (runs 2 and 3) reacted similarly. Ph(EtO)P(O)H could also produce the corresponding adducts. However, additions with $(EtO)_2P(O)H$ hardly proceeded. Therefore, the reactivity of P(O)H compounds roughly follow a decreasing order of H-phosphine oxide > H-phosphinate > H-phosphonate. Finally, diphenylphosphine Ph_2PH could also be used as the

substrate to produce the corresponding alkenylphosphine in good yields (run 6).

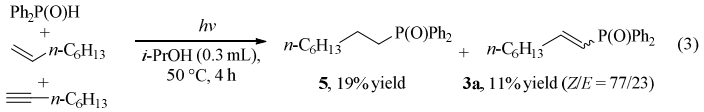
Table 3. Light-induced addition of P(O)H compounds to 1-octyne.[a]



run	*[P]*H	product	yield (%)[b] (*Z*/*E*)[c]
1	Ph(*t*-Bu)P(O)H	**3q**	45 (77/23)
2	$[Ph(CH_2)_4]_2P(O)H$	**3r**	66 (36/64)
3	$Cy_2P(O)H$	**3s**	61 (50/50)
4	Ph(EtO)P(O)H	**3t**	48 (62/38)
5	$(EtO)_2P(O)H$	**3u**	trace
6[b]	Ph_2PH	**3v**	67 (57/43)

[a] Reaction was similarly carried out and the products were isolated as described in Table 2. [b]Isolated yield. [c]The *Z*/*E* ratio was determined for the crude mixture by ^{31}P NMR. [d]Calculated based on ^{31}P NMR after 8 h irradiation with a xenon lamp. Isolated as its corresponding $Ph_2P(O)$ compounds by oxidation with H_2O_2.

Finally, since photo-initiated addition of $Ph_2P(O)H$ to terminal olefins also took place,[4h] to compare the reactivity of a double bond with a triple bond, we carried out a competing reaction of $Ph_2P(O)H$ (0.1 mmol) between 1-octene (0.1 mmol) and 1-octyne (0.1 mmol) (eq 3). As determined by NMR, the ratio of the products from 1-octene **5** *vs* that from 1-octyne **3a** was 63/37, indicating that *an olefin is more reactive (ca. two times faster) than an alkyne*.



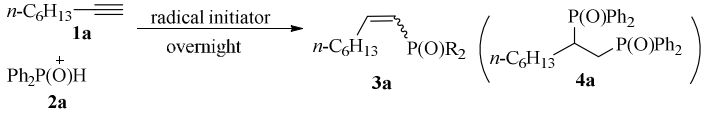
(3)

Radical-initiator-induced addition of P(O)H compounds to alkynes.

As shown in Table 4, $Ph_2P(O)H$ can add to 1-octyne in the presence of a radical initiator. Thus, a mixture of the

two reagents in benzene on heating at 70 °C in the presence of 10 mol% AIBN[10] produced a mixture of the mono-addition product **3a** and the double addition product **4a** in 43% and 29% yields, respectively (run 1). The reaction also took place in THF, although the yield of the double addition product **4a** slightly increased (run 2). The formation **4a** could be negligible by carrying out the reaction in a more diluted solution (runs 3 and 4) or at lower temperatures (runs 5 and 6). Interestingly, the *Z*/*E* selectivity of **3a** could be over 8/2 when carrying out the reaction in EtOH, although the yields were low (runs 7, 8). By conducting the reaction using a radical initiator that decomposes at a low temperature V-70 [2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)],[10] moderate yields of **3a** could be generated selectively (runs 9-11). Moreover, with 20% of an initiator V-601 [dimethyl 2,2'-azobis(isobutyrate)][10], moderate yields of **3a** with high *Z*/*E* selectivities could also be generated (runs 13-16). Since air can initiate the radical addition of P(O)H compounds,[4d] as expected, 58% yield of **3a** could also be generated by conducting the reaction under air (run 17).

Table 4. Addition of $Ph_2P(O)H$ to 1-octyne induced by a radical initiator.[a]



run	solvent	temp. (°C)	**3a** yield (%) (*Z*/*E*)[b]	**4a** yield (%)[c]
1[d]	C_6H_6	70	43 (69/31)	29
2[d]	THF	70	58(67/33)	36
3[d,e]	THF	70	70(67/33)	20
4[d,f]	THF	70	55(66/34)	trace
5[d]	THF	50	53(71/29)	trace
6[d]	THF	35	16(70/30)	trace
7[d]	EtOH	70	36(82/18)	trace
8[d]	EtOH	50	15(84/16)	trace
9[g]	THF	35	49(71/29)	trace

10[g]	THF	50	52(73/27)	trace
11[g, h]	THF	35	59(72/28)	trace
12[g]	EtOH	50	17(88/12)	trace
13[i]	EtOH	50	60(80/20)	trace
14[i]	*i*-PrOH	50	47(82/18)	trace
15[i]	*t*-BuOH	50	45(85/15)	trace
16[j]	*t*-BuOH	50	66 (86/14)	trace
17[k]	EtOH	50	58(89/11)	trace

[a]Reactions conditions: a mixture of **1a** (0.2 mmol), **2a** (0.1 mmol), a radical initiator and a solvent (0.2 mL) was sealed in a Pyrex-tube (1 mL) under nitrogen atmosphere and heated overnight. [b]The yield of **3a** based on **2a** and the *Z*/*E* ratio were determined from crude mixture by GC. [c]The yield of **4a** based on **2a** was estimated from ^{31}P NMR. [d]10 mol% AIBN. [e]0.3 mL. [f]0.5 mL. [g]10 mol% V-70. [h]**1a** (0.1 mmol). [i]20 mol% V-601. [j]40 mol% V-601. [k]The Pyrex tube was sealed with air.

However, similar to the photo-induced radical addition described above, this radical-initiator-induced addition does not apply to phenylacetylenes and other conjugate alkynes related.[8,11] Furthermore, hydrogen phosphonates $(RO)_2P(O)H$ were also hardly applicable to this reaction.

In conclusion, the radical hydrophosphorylation of alkynes with P(O)H compounds by photo-irradiation or radical-initiators have been studied. It appears that *hydrogen phosphonates $(RO)_2P(O)H$ and conjugated alkynes are not applicable to this reaction*. However, with the combination of H-phosphine oxides $R_2P(O)H$ and aliphatic terminal alkynes, moderate yields of the *anti*-Marcovnikov alkenylphosphine oxides could be generated. In particular, propargyl alcohols, which are not applicable to the palladium-catalyzed hydrophosphorylations,[5] can give the corresponding adducts in good yields. Therefore, this metal-free clean radical hydrophosphorylation can serve, to some extent, as a complimentary to the metal-mediated hydrophosphorylation of alkynes.

EXPERIMENTAL SECTION

General information: All materials were purchased and used without further purification. ^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz) FT NMR system in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken on a JEOL JNM-ECS400 (100 MHz) FT NMR system in $CDCl_3$. ^{31}P NMR spectra were taken on a JEOL JNM-ECX400 (162 MHz) FT NMR system in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. Isolation using a preparative HPLC (recycle GPC) was performed on a Japan Analytical Industry LC-908 equipped with JAIGEL-1H and JAIGEL-2H columns using $CHCl_3$. The *Z*- and *E*-isomer configuration of the compounds was assigned on the basis of ^{1}H-NMR spectra by comparing with the reported data and/or the coupling constants of the vinyl protons (J_{HH} and J_{HP}).

General procedures: a mixture of **1** and **2** in a solvent (or neat) was sealed in a Pyrex-tube and was irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ) (Tables 1, 2 and 3). Similarly, were conducted radical-initiated additions except a radical initiator or air was added to the reaction mixture instead of photo-irradiation (Table 4).

(Z)-oct-1-en-1-yldiphenylphosphine oxide [**3a** (*Z*)].[12] White solid; mp 66-67 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75~7.69 (m, 4H), 7.49~7.39 (m, 6H), 6.66 (ddt, J_1 = 7.6 Hz, J_2 = 12.8 Hz, J_3 = 40.4 Hz, 1H), 6.08 (ddt, J_1 = 1.6 Hz, J_2 = 12.8 Hz, J_3 = 25.6 Hz, 1H), 2.54 ~2.48 (m, 2H), 1.36~1.28 (m, 2H), 1.23~1.09 (m, 6H), 0.81 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.2, 134.7 (d, *J* = 103.0 Hz), 131.5 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 9.5 Hz), 128.5 (d, *J* = 11.4 Hz), 121.3 (d, *J* = 100.1 Hz), 31.6, 31.0 (d, *J* = 8.5 Hz), 28.9, 28.8, 22.5, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 21.7.

(*E*)-oct-1-en-1-yldiphenylphosphine oxide [**3a** (*E*)].[13] White solid; mp 69-70 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.64 (m, 4H), 7.52~7.41 (m, 6H), 6.71 (ddt, J_1 = 6.8 Hz, J_2 = 16.8 Hz, J_3 = 19.6 Hz, 1H), 6.20 (ddt, J_1 = 1.6 Hz, J_2 = 16.8 Hz, J_3 = 24.8 Hz, 1H), 2.31~2.25 (m, 2H), 1.50~1.42 (m, 2H), 1.34~1.20 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.0, 133.3 (d, *J* = 103.9 Hz), 131.7 (d, *J* = 2.8 Hz), 131.3 (d, *J* = 9.5 Hz), 128.5 (d, *J* = 12.4 Hz), 121.6 (d, *J* = 102.9 Hz), 34.6 (d, *J* = 16.2 Hz), 31.6, 28.9, 27.9, 22.6, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.3.

(***Z***)**-(6-chlorohex-1-en-1-yl)diphenylphosphine oxide** [**3b** (*Z*)]. White viscous tar. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73~7.68 (m, 4H), 7.50~7.41 (m, 6H), 6.65 (ddt, J_1 = 6.8 Hz, J_2 = 13.2 Hz, J_3 = 40.4 Hz, 1H), 6.13 (dd, J_1

= 13.2 Hz, J_2 = 25.2 Hz, 1H), 3.44 (t, J = 6.8 Hz, 2H), 2.61~2.56 (m, 2H), 1.71~1.64 (m, 2H), 1.55~1.47 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 154.0, 134.4 (d, J = 103.9 Hz), 131.6 (d, J = 1.9 Hz), 130.9 (d, J = 9.5 Hz), 128.6 (d, J = 12.3 Hz), 122.2 (d, J = 100.0 Hz), 44.8, 31.9, 29.9 (d, J = 8.5 Hz), 26.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 21.8. GC-MS (EI, 70 eV) m/z = 320 (M^+, ^{37}Cl, 6), 318 (M^+, ^{35}Cl, 18). Anal. Calcd for $C_{18}H_{20}ClOP$: C, 67.82; H, 6.32. Found: C, 67.60; H, 6.30.

(***E***)**-(6-chlorohex-1-en-1-yl)diphenylphosphine oxide** [**3b** (*E*)]. White solid; mp 80-82 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.63 (m, 4H), 7.51~7.40 (m, 6H), 6.70 (ddt, J_1 = 6.4 Hz, J_2 = 16.8 Hz, J_3 = 19.6 Hz, 1H), 6.24 (dd, J_1 = 16.8 Hz, J_2 = 24.4 Hz, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.34~2.29 (m, 2H), 1.82~1.75 (m, 2H), 1.67~1.59 (m, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 151.6, 133.1 (d, J = 104.8 Hz), 131.8 (d, J = 1.9 Hz), 131.3 (d, J = 10.5 Hz), 128.5 (d, J = 11.5 Hz), 122.4 (d, J = 101.9 Hz), 44.6, 33.6 (d, J = 16.2 Hz), 32.0, 25.2. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.0. GC-MS (EI, 70 eV) m/z = 320 (M^+, ^{37}Cl, 4), 318 (M^+, ^{35}Cl, 11). Anal. Calcd for $C_{18}H_{20}ClOP$: C, 67.82; H, 6.32. Found: C, 67.74; H, 6.33.

4-(Diphenylphosphoryl)but-3-en-1-yl pivalate [**3c** (*E* + *Z*)].[13] White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72~7.63 (m, 4H, *E* + *Z*), 7.50~7.41 (m, 6H, *E* + *Z*), 6.76~6.59 (m, 1H, *E* + *Z*), 6.32 (dd, J_1 = 17.2 Hz, J_2 = 23.6 Hz, 1H, *E*), 6.19 (dd, J_1 = 13.2 Hz, J_2 = 25.6 Hz, 1H, *Z*), 4.18 (t, J = 6.4 Hz, 2H, *E*), 4.09 (t, J = 6.4 Hz, 2H, *Z*), 3.03~2.98 (m, 2H, *Z*), 2.64~2.59 (m, 2H, *E*), 1.13 (s, 9H, *Z*), 1.09 (s, 9H, *E*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 178.4 (*Z*), 178.3 (*E*), 149.6 (*Z*), 147.6 (*E*), 134.0 (d, J = 103.9 Hz, *Z*), 132.7 (d, J = 104.9 Hz, *E*) 131.8 (d, J = 2.8 Hz, *E*), 131.7 (d, J = 2.8 Hz, *Z*), 131.2 (d, J = 10.5 Hz, *E*), 130.9 (d, J = 9.6 Hz, *Z*), 128.6 (d, J = 12.4 Hz, *Z*), 128.5 (d, J = 11.4 Hz, *E*), 124.5 (d, J = 101.1 Hz, *E*), 124.2 (d, J = 98.2 Hz, *Z*), 63.0 (*Z*), 62.0 (*E*), 38.70 (*Z*), 38.67 (*E*), 33.6 (d, J = 17.1 Hz, *E*), 29.8 (d, J = 7.7 Hz, *Z*), 27.14 (*Z*), 27.08 (*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 23.8 (*E*), 22.2 (*Z*).

(*Z*)-(6-hydroxyhex-1-en-1-yl)diphenylphosphine oxide [**3d** (*Z*)]. White solid; mp 94-96 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73~7.68 (m, 4H), 7.51~7.40 (m, 6H), 6.75 (ddt, J_1 = 6.4 Hz, J_2 = 12.8 Hz, J_3 = 40.4 Hz, 1H), 6.10 (dd, J_1 = 12.8 Hz, J_2 = 26.4 Hz, 1H), 3.60 (t, J = 6.4 Hz, 2H), 2.56~2.51 (m, 2H), 2.44 (b, 1H), 1.59~1.48 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 154.9, 134.3 (d, J = 103.9 Hz), 131.6 (d, J = 1.9 Hz), 130.9 (d, J = 9.5 Hz), 128.6 (d, J = 11.5 Hz), 121.5 (d, J = 100.1 Hz), 61.4, 31.3, 29.9 (d, J = 7.6 Hz), 25.3. ^{31}P NMR (162 MHz,

$CDCl_3$): δ (ppm) 22.5. MS (EI, 70 eV) *m*/*z* = 301 ($[M+H]^+$, 5), 300 (M^+, 24). Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05. Found: C, 71.84; H, 7.04.

(*E*)-(6-hydroxyhex-1-en-1-yl)diphenylphosphine oxide [**3d** (*E*)].[14] White solid; mp 66-68 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68~7.63 (m, 4H), 7.51~7.40 (m, 6H), 6.70 (ddt, J_1 = 6.4 Hz, J_2 = 16.8 Hz, J_3 = 19.6 Hz, 1H), 6.22 (dd, J_1 = 16.8 Hz, J_2 = 24.0 Hz, 1H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.33~2.30 (m, 2H), 1.99 (b, 1H), 1.61~1.50 (m, 4H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 152.4, 133.1 (d, *J* = 103.8 Hz), 131.7 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 9.5 Hz), 128.5 (d, *J* = 12.4 Hz), 121.9 (d, *J* = 102.9 Hz), 62.4, 34.3 (d, *J* = 16.2 Hz), 32.2, 24.2. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.2.

(*Z*)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine oxide [**3e** (*Z*)][15]. White solid; mp 116-117 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.64 (m, 4H), 7.41~7.34 (m, 6H), 6.62 (dd, J_1 = 14.8 Hz, J_2 = 43.6 Hz, 1H), 5.90 (dd, J_1 = 14.8 Hz, J_2 = 22.8 Hz, 1H), 1.14 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 164.6, 135.7 (d, *J* = 103.9 Hz), 131.3 (d, *J* = 2.0 Hz), 130.9 (d, *J* = 9.6 Hz), 128.5 (d, *J* = 11.4 Hz), 119.3 (d, *J* = 99.2 Hz), 35.5 (d, *J* = 4.8 Hz), 30.31. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 20.2.

(*E*)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine oxide [**3e** (*E*)].[13] White solid; mp 160-161 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.63 (m, 4H), 7.52~7.41 (m, 6H), 6.75 (dd, J_1 = 17.2 Hz, J_2 = 20.4 Hz, 1H), 6.09 (dd, J_1 = 17.2 Hz, J_2 = 24.0 Hz, 1H), 1.09 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 162.3, 133.4 (d, *J* = 103.9 Hz), 131.7 (d, *J* = 2.9 Hz), 131.3 (d, *J* = 9.6 Hz), 128.5 (d, *J* = 11.5 Hz), 116.5 (d, *J* = 102.9 Hz), 35.3 (d, *J* = 15.3 Hz), 28.7. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 24.8.

(*Z*)-diphenyl(2-(trimethylsilyl)vinyl)phosphine oxide [**3h** (*Z*)].[16] White solid; mp 94-96 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71~7.66 (m, 4H), 7.50~7.40 (m, 6H), 7.08 (dd, J_1 = 17.2 Hz, J_2 = 29.6 Hz, 1H), 6.98 (dd, J_1 = 17.2 Hz, J_2 = 19.2 Hz, 1H), 0.24 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 156.5 (d, *J* = 7.6 Hz), 138.4 (d, *J* = 100.1 Hz), 134.0 (d, *J* = 101.0 Hz), 131.2 (d, *J* = 2.9 Hz), 130.8 (d, *J* = 9.6 Hz), 128.2 (d, *J* = 11.4 Hz), 0.08. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 20.9.

(*E*)-diphenyl(2-(trimethylsilyl)vinyl)phosphine oxide [**3h** (*E*)].[13] White solid; mp 117-119 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.64 (m, 4H), 7.54~7.42 (m, 6H), 7.26 (dd, J_1 = 20.4 Hz, J_2 = 26.0 Hz, 1H), 6.84 (dd, J_1 = 20.4 Hz, J_2 = 31.6 Hz, 1H), 0.14 (s, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.2 (d, *J* = 5.7 Hz), 137.0 (d,

J = 89.6 Hz), 132.7 (d, J = 102.0 Hz), 131.8 (d, J = 2.9 Hz), 131.4 (d, J = 10.4 Hz), 128.6 (d, J = 12.4 Hz), -1.8. ^{31}P-NMR: δ (ppm) 23.5.

(*Z*)-diphenyl(2-(triisopropylsilyl)vinyl)phosphine oxide [**3i** (*Z*)]. White viscous tar. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.71~7.66 (m, 4H), 7.49~7.39 (m, 6H), 7.18 (dd, J_1 = 18.0 Hz, J_2 = 34.4 Hz, 1H), 6.97 (dd, J_1 = 18.0 Hz, J_2 = 50.0 Hz, 1H), 1.61~1.49 (m, 3H), 1.04 (d, J = 7.2 Hz, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 151.7 (d, J = 6.6 Hz), 140.0 (d, J = 101.0 Hz), 134.4 (d, J = 102.0 Hz), 131.4 (d, J = 2.9 Hz), 131.1 (d, J = 9.5 Hz), 128.5 (d, J = 12.4 Hz), 19.3, 12.8. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 19.9. GC-MS (EI, 70 eV) m/z = 342 ($[M+H]^+$ - $CH(CH_3)_2$, 27), 341 (M^+ - $CH(CH_3)_2$, 100). Anal. Calcd for $C_{23}H_{33}OPSi$: C, 71.83; H, 8.65. Found: C, 71.67; H, 8.56.

(*E*)-diphenyl(2-(triisopropylsilyl)vinyl)phosphine oxide [**3i** (*E*)].[16] White viscous tar. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69 ~7.64 (m, 4H), 7.53~7.42 (m, 6H), 7.16 (dd, J_1 = 20.8Hz, J_2 = 30.8 Hz, 1H), 6.92 (dd, J_1 = 20.8 Hz, J_2 = 31.6 Hz, 1H), 1.20~1.10 (m, 3H), 1.04 (d, J = 6.8 Hz, 18H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 150.6 (d, J = 5.7 Hz), 139.5 (d, J = 89.6 Hz), 132.8 (d, J = 102.0 Hz), 131.7 (d, J = 2.9 Hz), 131.4 (d, J = 9.5 Hz), 128.6 (d, J = 12.4 Hz), 18.6, 10.8. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 23.5.

(*Z*)-(3-hydroxyprop-1-en-1-yl)diphenylphosphine oxide [**3j** (*Z*)]. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.69~7.63 (m, 4H), 7.50~7.39 (m, 6H), 6.88 (ddt, J_1 = 4.4 Hz, J_2 = 13.6 Hz, J_3 = 40.0 Hz, 1H), 6.13 (ddt, J_1 = 1.6 Hz, J_2 = 13.6 Hz, J_3 = 24.8 Hz, 1H), 5.61 (b, 1H), 4.42 (b, 2H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.4, 132.7 (d, J = 106.7 Hz), 132.1 (d, J = 1.9 Hz), 131.1 (d, J = 9.6 Hz, 128.7 (d, J = 12.4 Hz), 121.3 (d, J = 97.2 Hz), 61.2 (d, J = 8.6 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.8. GC-MS (EI, 70 eV) m/z = 259 ($[M+H]^+$, 3), 258 (M^+, 16). Anal. Calcd for $C_{15}H_{15}O_2P$: C, 69.76; H, 5.85. Found: C, 69.46; H, 5.78.

(*E*)-(3-hydroxyprop-1-en-1-yl)diphenylphosphine oxide [**3j** (*E*)].[17] White solid, mp: 119-123 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67~7.62 (m, 4H), 7.50~7.38 (m, 6H), 6.76~6.54 (m, 2H), 4.29~4.27 (m, 2H), 3.56 (b, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 152.1, 132.5 (d, J = 105.8 Hz), 131.9 (d, J = 2.8 Hz), 131.3 (d, J = 9.6 Hz), 128.6 (d, J = 12.4 Hz), 119.6 (d, J = 102.9 Hz), 62.8 (d, J = 17.1 Hz). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.1.

(3-Hydroxypent-1-en-1-yl)diphenylphosphine oxide [**3k** (*E* + *Z*)].[18] White solid. ^{1}H-NMR: δ (ppm) 7.68~7.59

(m, 4H, *E* + *Z*), 7.49~7.34 (m, 6H, *E* + *Z*), 6.82~6.67 (m, 1H, *E* + *Z*), 6.49 (ddd, J_1 = 2.0 Hz, J_2 = 16.8 Hz, J_3 = 24.8 Hz, *E*), 6.08 (ddd, J_1 = 1.6 Hz, J_2 = 13.6 Hz, J_3 = 25.2 Hz, *Z*), 5.39 (b, 1H, *Z*), 4.52~4.46 (m, 1H, *Z*), 4.22~4.20 (m, 1H, *E*), 1.66~1.47 (m, 1H, *E* + *Z*), 0.89 (t, *J* = 7.2 Hz, *E* + *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 157.1 (*Z*), 154.0 (*E*), 133.1 (d, *J* = 105.8 Hz *E* + *Z*), 132.9 (d, *J* = 104.9 Hz, *E* + *Z*), 132.0 (d, *J* = 2.9 Hz, *E* + *Z*), 131.9 (d, *J* = 2.9 Hz, *E* + *Z*), 131.3 (d, *J* = 4.8 Hz, *E*), 131.2 (d, *J* = 11.5 Hz, *E* + *Z*), 131.1 (d, *J* = 10.4 Hz, *Z*), 128.7 (d, *J* = 11.5 Hz, *Z*), 128.6 (d, *J* = 15.2 Hz, *E*), 121.2 (d, *J* = 97.2 Hz, *E* + *Z*), 73.2 (d, *J* = 14.3 Hz, *E*), 70.6 (d, *J* = 7.6 Hz, *Z*), 29.9 (*Z*), 29.6 (*E*), 9.9 (*Z*), 9.7 (*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 26.0 (*Z*), 24.8 (*E*).

(3-Hydroxy-3-methylpent-1-en-1-yl)diphenylphosphine oxide [**3l** (*E* + *Z*)]. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68~7.59 (m, 4H, *E* + *Z*), 7.48~7.37 (m, 6H, *E* + *Z*), 6.75 (dd, J_1 = 16.8 Hz, J_2 = 20.0 Hz, 1H, *E*), 6.72 (dd, J_1 = 14.4 Hz, J_2 = 40.4 Hz, 1H, *Z*), 6.46 (dd, J_1 = 16.8 Hz, J_2 = 25.6 Hz, 1H, *E*), 6.32 (b, 1H, *E* + *Z*), 5.93 (dd, J_1 = 14.4 Hz, J_2 = 24.4 Hz, 1H, *Z*), 1.66~1.55 (m, 2H, *E* + *Z*), 1.32 (s, 3H, *Z*), 1.27 (s, 3H, *E*), 0.89 (t, *J* = 7.2 Hz, 3H, *Z*), 0.84 (t, *J* = 7.2 Hz, 3H, *E*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 161.4 (*Z*), 157.3 (*E*), 133.2 (d, *J* = 105.8 Hz, *E* + *Z*), 133.1 (d, *J* = 106.8 Hz, *E* + *Z*), 131.9 (d, *J* = 1.9 Hz, *Z*), 131.8 (d, *J* = 1.9 Hz, *E*), 131.2 (d, *J* = 10.5 Hz, *E* + *Z*), 128.64 (d, *J* = 11.4 Hz, *Z*), 128.60 (d, *J* = 12.3 Hz, *E* + *Z*), 128.58 (d, *J* = 12.4 Hz, *E*), 118.5, (d, *J* = 98.2 Hz, *Z*), 117.8 (d, *J* = 141.0 Hz, *E*), 73.7 (d, *J* = 6.7 Hz, *E* +*Z*), 35.7 (*Z*), 34.6 (*E*), 28.0 (*Z*), 27.5 (*E*), 8.5 (*Z*), 8.1 (*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.3 (*Z*), 24.5 (*E*). GC-MS (EI, 70 eV) **3l** (*Z*) *m*/*z* = 283 ($[M+H]^+$-H_2O, 18), 282 (M^+-H_2O, 72). **3l** (*E*) *m*/*z* = 283 ($[M+H]^+$-H_2O, 5), 282 (M^+-H_2O, 11). Anal. Calcd for $C_{18}H_{21}O_2P$: C, 71.98; H, 7.05. Found: C, 71.98; H, 7.02.

(3-Hydroxy-3-methylbut-1-en-1-yl)diphenylphosphine oxide [**3m** (*E* + *Z*)].[17, 19] White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72~7.64 (m, 4H, *E* + *Z*), 7.53~7.39 (m, 6H, *E* +*Z*), 6.86 (dd, J_1 = 16.8 Hz, J_2 = 19.6 Hz, 1H, *E*), 6.84 (dd, J_1 = 14.0 Hz, J_2 = 40.4 Hz, 1H, *Z*), 6.50 (dd, J_1 = 16.8 Hz, J_2 = 25.2 Hz, 1H, *E*), 6.49 (b, 1H, *E* + *Z*), 5.92 (dd, J_1 = 14.0 Hz, J_2 = 24.0 Hz, 1H, *Z*), 1.43 (s, 6H, *Z*), 1.35 (s, 6H, *E*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 162.0 (*Z*), 158.2 (*E*), 133.1 (d, *J* = 104.8 Hz, *E*), 132.9 (d, *J* = 106.7 Hz, *Z*), 131.9 (d, *J* = 6.1 Hz, *Z*), 131.7 (d, *J* = 1.9 Hz, *E*), 131.24 (d, *J* = 9.5 Hz, *E*), 131.20 (d, *J* = 10.5 Hz, *Z*), 128.7 (d, *J* = 10.5 Hz, *Z*), 128.5 (d, *J* = 10.5 Hz, *E*), 117.83 (d, *J* = 101.0 Hz, *E*), 117.75 (d, *J* = 97.3 Hz, *Z*), 71.9 (d, *J* = 15.3 Hz, *E*), 71.0 (d, *J* = 6.7 Hz, *Z*), 30.3 (*Z*), 29.4 (*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.5 (*Z*), 24.5 (*E*).

(3-Hydroxy-3-phenylbut-1-en-1-yl)diphenylphosphine oxide [**3n** (*E* + *Z*)]. White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75~6.98 (m, 16H, *E* + *Z*), 6.61 (dd, J_1 = 17.2 Hz, J_2 = 24.8 Hz, 1H, *E*), 6.00 (dd, J_1 = 14.0 Hz, J_2 = 23.6 Hz, 1H, *Z*), 1.74 (s, 3H, *Z*), 1.69 (s, 3H, *E*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 161.2 (*Z*), 156.6 (*E*), 146.9 (*Z*), 144.9 (*E*), 132.7 (d, *J* = 106.7 Hz, *E* + *Z*), 132.5 (d, *J* = 105.8 Hz, *E* + *Z*), 132.0 (d, *J* = 2.9 Hz, *E* + *Z*), 131.9 (d, *J* = 2.8 Hz, *E* + *Z*), 131.3 (d, *J* = 10.5 Hz, *E* + *Z*), 131.23 (d, *J* = 9.5 Hz, *E* + *Z*), 131.15 (d, *J* = 10.5 Hz, *E* + *Z*), 128.7 (*E* + *Z*), 128.6 (d, *J* = 12.4 Hz, *E* + *Z*), 128.5 (d, *J* = 12.4 Hz, *E* + *Z*), 128.2 (*E* + *Z*), 126.8 (*E* + *Z*), 125.2 (*E* + *Z*), 118.6 (d, *J* = 96.3 Hz, *E*), 118.2 (d, *J* = 97.2 Hz, *Z*), 75.2 (d, *J* = 13.4 Hz, *E*), 74.7 (d, *J* = 6.7 Hz, *Z*), 31.2 (*Z*), 29.3 (*E*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.2 (*Z*), 24.5 (*E*). GC-MS (EI, 70 eV) **3n** (*Z*) *m*/*z* = 331 ($[M+H]^+$-H_2O, 18), 330 (M^+-H_2O, 72). **3n** (*E*) *m*/*z* = 348 (M^+, 3). Anal. Calcd for $C_{22}H_{21}O_2P$: C, 75.85; H, 6.08. Found: C, 75.62; H, 6.00.

(2-(1-Hydroxycyclopentyl)vinyl)diphenylphosphine oxide [**3o** (*E* + *Z*)].[19] White solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67~7.59 (m, 4H, *E* + *Z*), 7.46~7.35 (m, 6H, *E* + *Z*), 6.82 (dd, J_1 = 14.0 Hz, J_2 = 40.4 Hz, 1H, *Z*), 6.81 (dd, J_1 = 16.8 Hz, J_2 = 19.6 Hz, 1H, *E*), 6.52 (dd, J_1 = 16.8 Hz, J_2 = 25.6 Hz, 1H, *E*), 6.11 (b, 1H, *Z*), 5.93 (dd, J_1 = 14.0 Hz, J_2 = 24.8 Hz, 1H, *Z*), 1.93~1.63 (m, 8H, *E* + *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 160.9 (*Z*), 157.6 (*E*), 133.2 (d, *J* = 104.9 Hz, *E*), 133.1 (d, *J* = 106.8 Hz, *Z*), 131.8 (d, *J* = 1.9 Hz, *Z*), 131.7 (d, *J* = 2.8 Hz, *E*), 131.23 (d, *J* = 9.5 Hz, *E*), 131.18 (d, *J* = 9.5 Hz, *Z*), 128.6 (d, *J* = 12.4 Hz, *Z*), 128.5 (d, *J* = 9.5 Hz, *E*), 118.4 (d, *J* = 98.1 Hz, *Z*), 117.9 (d, *J* = 102.0 Hz, *E*), 82.7 (d, *J* = 15.2 Hz, *E*), 81.5 (d, *J* = 6.7 Hz, *Z*), 41.4 (*Z*), 40.6 (*E*), 24.1 (*E* + *Z*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 27.6 (*Z*), 24.6 (*E*).

(*Z*)-*tert*-butyl(oct-1-en-1-yl)(phenyl)phosphine oxide [**3q** (*Z*)]. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70~7.65 (m, 2H), 7.45~7.35 (m, 3H), 6.62 (ddt, J_1 = 7.6 Hz, J_2 = 12.8 Hz, J_3 = 37.2 Hz, 1H), 6.05 (dd, J_1 = 12.8 Hz, J_2 = 26.0 Hz, 1H), 2.50~2.35 (m, 2H), 1.31~1.04 (m, 17H), 0.75 (t, *J* = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.9, 132.2 (d, *J* = 91.5 Hz), 131.9 (d, *J* = 7.6 Hz), 131.2 (d, *J* = 2.9 Hz), 128.0 (d, *J* = 10.5 Hz), 116.9 (d, *J* = 91.5 Hz), 32.8 (d, *J* = 72.4 Hz), 31.6, 30.8 (d, *J* = 6.6 Hz), 28.9, 24.1, 22.5, 14.1, 1.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 38.1. GC-MS (EI, 70 eV) *m*/*z* = 293 ($[M+H]^+$, 6), 292 (M^+, 30). Anal. Calcd for $C_{18}H_{29}OP$: C, 73.94; H, 10.00. Found: C, 73.99; H, 9.87.

(*E*)-*tert*-butyl(oct-1-en-1-yl)(phenyl)phosphine oxide [**3q** (*E*)].[20] Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ

(ppm) 7.69~7.65 (m, 2H), 7.45~7.35 (m, 3H), 6.82 (ddt, J_1 = 6.8 Hz, J_2 = J_3 = 17.6 Hz, 1H), 6.19 (dd, J_1 = 17.6 Hz, J_2 = 28.0 Hz, 1H), 2.26~2.21 (m, 2H), 1.45~1.37 (m, 2H), 1.29~1.19 (m, 6H), 1.04 (d, J = 14.8 Hz, 9H), 0.81 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.9, 131.9 (d, J = 70.5 Hz), 131.8 (d, J = 8.6 Hz), 131.3 (d, J = 1.9 Hz), 128.1 (d, J = 10.5 Hz), 117.3 (d, J = 92.4 Hz), 34.8 (d, J = 15.3 Hz), 32.6 (d, J = 72.4 Hz), 31.6, 28.9, 24.2, 22.6, 14.1, 1.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 38.2.

Oct-1-en-1-ylbis(4-phenylbutyl)phosphine oxide [**3r** (*E* + *Z*)]. Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21~7.18 (m, 4H, *E* + *Z*), 7.12~7.07 (m, 6H, *E* + *Z*), 6.61 (ddt, J_1 = 6.8 Hz, J_2 = J_3 =17.6 Hz, 1H, *E*), 6.41 (ddt, J_1 = 7.6 Hz, J_2 = 13.2 Hz, J_3 = 38.0 Hz, 1H, *Z*), 5.53 (dd, J_1 = 17.6 Hz, J_2 = 27.6 Hz, 1H, *E*), 5.31 (dd, J_1 = 13.2 Hz, J_2 = 26.8 Hz, 1H, *Z*), 2.57~2.53 (m, 6H, *E*), 2.17~2.11 (m, 6H, *Z*), 1.69~1.53 (m, 12H, *E* + *Z*), 1.37~1.21 (m, 8H, *E* + *Z*), 0.83 (t, J = 6.8 Hz, 3H, *E*), 0.82 (t, J = 6.8 Hz, 3H, *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 154.0 (*Z*), 152.2 (*E*), 141.93 (*Z*), 141.90 (*E*), 128.3 (*E* + *Z*), 125.8 (*E* + *Z*), 121.0 (d, J = 91.5 Hz, *E*), 120.2 (d, J = 89.6 Hz, *Z*), 35.53 (*Z*), 35.46 (*E*), 34.4 (d, J = 15.2 Hz, *E*), 32.9 (d, J = 14.3 Hz, *Z*), 32.8 (d, J = 14.3 Hz, *E*), 30.9 (d, J = 172.5 Hz, *Z*), 30.71 (d, J = 179.2 Hz, *E*), 30.68 (*Z*), 30.2 (d, J = 6.6 Hz, *Z*), 29.2 (d, J = 36.2 Hz, *Z*), 29.0 (d, J = 34.3 Hz, *E*), 28.0 (*E*), 22.6 (*E* + *Z*), 21.5 (d, J = 3.8 Hz, *Z*), 21.3 (d, J = 2.8 Hz, *E*), 14.1 (*E* + *Z*), 1.0 (*E* + *Z*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 39.0 (*Z*), 37.8 (*E*). GC-MS (EI, 70 eV) **3r** (*Z*) *m*/*z* = 425 ($[M+H]^+$, 9) 424 (M^+, 30). **3r** (*E*) *m*/*z* = 425 ($[M+H]^+$, 8), 424 (M^+, 27). Anal. Calcd for $C_{28}H_{41}OP$: C, 79.20; H, 9.73. Found: C, 78.96; H, 9.60.

(*Z*)-dicyclohexyl(oct-1-en-1-yl)phosphine oxide [**3s** (*Z*)]. White viscous tar. ^{1}H-NMR: δ (ppm) 6.55 (ddt, J_1 = 7.2 Hz, J_2 = 12.8 Hz, J_3 = 36.8 Hz, 1H), 5.25 (dd, J_1 = 12.8 Hz, J_2 = 26.0 Hz, 1H), 2.65~2.60 (m, 2H), 1.96~1.93 (m, 2H), 1.80~1.64 (m, 10H), 1.39~1.21 (m, 18H), 0.84 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 155.4, 117.1 (d, J = 84.8 Hz), 36.1 (d, J = 68.6 Hz), 31.7, 30.0 (d, J = 5.7 Hz), 29.5, 29.0, 26.6 (d, J = 12.4 Hz), 26.4 (d, J = 12.4 Hz), 26.0, 25.8 (d, J = 1.9 Hz), 24.7 (d, J = 2.8 Hz), 22.6, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 45.6. GC-MS (EI, 70 eV) *m*/*z* = 325 ($[M+H]^+$, 5), 324 (M^+, 21). Anal. Calcd for $C_{20}H_{37}OP$: C, 74.03; H, 11.49. Found: C, 73.96; H, 11.34.

(*E*)-dicyclohexyl(oct-1-en-1-yl)phosphine oxide [**3s** (*E*)]. White solid; mp 60-62 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 6.66 (ddt, J_1 = 6.4 Hz, J_2 = J_3 = 16.8 Hz, 1H), 5.52 (dd, J_1 = 16.8 Hz, J_2 = 27.2 Hz, 1H), 2.25~2.20

(m, 2H), 1.95~1.92 (m, 2H), 1.80~1.64 (m, 10H), 1.45~1.19 (m 18H), 0.86 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.3, 117.9 (d, J = 86.7 Hz), 35.3 (d, J = 68.6 Hz), 34.6 (d, J = 15.2 Hz), 31.6, 28.8, 28.1, 26.6 (d, J = 12.4 Hz), 26.4 (d, J = 12.4 Hz), 26.0, 25.7 (d, J = 2.9 Hz), 24.7 (d, J = 3.8 Hz), 22.6, 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 43.1. GC-MS (EI, 70 eV) m/z = 325 ($[M+H]^+$, 3), 324 (M^+, 14). Anal. Calcd for $C_{20}H_{37}OP$: C, 74.03; H, 11.49. Found: C, 73.97; H, 11.43.

Ethyl -oct-1-en-1-yl(phenyl)phosphinate [**3t** (*E* + *Z*)].[21] Colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80~7.73 (m, 2H, *E* + *Z*), 7.52~7.40 (m, 3H, *E* + *Z*), 6.74 (ddt, J_1 = 6.4 Hz, J_2 = 16.8 Hz, J_3 = 20.0 Hz, 1H, *E*), 6.44 (ddt, J_1 = 7.6 Hz, J_2 = 12.8 Hz, J_3 = 46.0 Hz, 1H, *Z*), 5.91~5.76 (m, 1H, *E* + *Z*), 4.10~4.00 (m, 1H, *E* + *Z*), 3.98~3.84 (m, 1H, *E* + *Z*), 2.51~2.38 (m, 2H, *Z*), 2.22~2.16 (m, 2H, *E*), 1.32~1.15 (m, 11H, *E* + *Z*), 0.84 (t, J = 6.4 Hz, 3H, *E*), 0.82 (t, J = 6.4 Hz, 3H, *Z*). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 153.8 (d, J = 3.8 Hz, *Z*), 153.1 (d, J = 3.8 Hz, *E*), 132.9 (d, J = 131.5 Hz, *Z*), 132.0 (d, J = 2.8 Hz, *E*), 131.9 (d, J = 2.9 Hz, *Z*), 131.7 (d, J = 134.3 Hz, *E*), 131.4 (d, J = 10.5 Hz, *E*), 131.3 (d, J = 10.5 Hz, *Z*), 128.5 (d, J = 12.4 Hz, *E*), 128.4 (d, J = 13.3 Hz, *Z*), 120.6 (d, J = 136.3 Hz, *E*), 120.5 (d, J = 135.1 Hz, *Z*), 60.6 (d, J = 5.7 Hz, *E*), 60.3 (d, J = 5.7 Hz, *Z*), 34.3 (d, J = 18.1 Hz, *E*), 31.62 (*Z*), 31.59 (*E*), 30.7 (d, J = 8.6 Hz, *Z*), 28.84 (*E* +*Z*), 28.81 (*Z*), 27.8 (*E*), 22.6 (*E* + *Z*), 16.5 (d, J = 6.6 Hz, *E* + *Z*), 14.1 (*E* + *Z*). ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 31.4 (*E*), 30.6 (*Z*).

Octane-1,2-diylbis(diphenylphosphine oxide) (**4a**).[4d] White solid; mp 147-148 ^{o}C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79~7.68 (m, 6H), 7.49~7.32 (m, 14H), 3.02~2.95 (m, 1H), 2.67~2.47 (m, 2H), 1.79~1.63 (m, 1H), 1.49~1.37 (m, 1H), 1.29~1.17 (m, 1H), 1.06~0.97 (m, 2H), 0.94~0.79 (m, 3H), 0.78~0.69 (m, 5H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 133.31 (d, J = 97.3 Hz), 133.25 (d, J = 99.1 Hz), 132.1 (d, J = 91.5 Hz), 132.0 (d, J = 94.3 Hz) 131.8 (d, J = 1.9 Hz), 131.7 (d, J = 2.9 Hz), 131.1 (d, J = 7.6 Hz), 130.9 (d, J = 8.6 Hz), 130.7 (d, J = 8.6 Hz), 130.6 (d, J = 9.6 Hz), 128.8 (d, J = 11.5 Hz), 128.6 (d, J = 11.4 Hz), 128.5 (d, J = 10.5 Hz), 31.3 (dd, J_1 = 2.9 Hz, J_2 = 68.6 Hz), 31.1, 29.2, 28.3, 27.5 (d, J = 68.6 Hz), 27.0 (d, J = 3.8 Hz), 22.4, 14.0. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 37.8 (d, J = 44.9 Hz), 30.8 (d, J = 44.9 Hz).

Octyldiphenylphosphine oxide (**5**).[22] A mixture of diphenylphosphine oxide (24.3 mg, 0.12 mmol), 1-octyne (11.0 mg, 0.1 mmol) and 1-octene (11.2 mg, 0.1 mmol) in *i*-PrOH (0.3 mL) was sealed in a Pyrex-tube under nitrogen and was irradiated using a high-pressure Hg lamp (Ushio, SX-U1501HQ) for 4 h. The reaction mixture

was concentrated under *vacuum*. The crude product was purified by HPLC to obtain the target compound (6.0 mg, 19% yield). White solid; mp 57-58 °C. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74~7.68 (m, 4H), 7.51~7.41 (m, 6H), 2.27~2.20 (m, 2H), 1.65~1.55 (m, 2H), 1.40~1.33 (m, 2H), 1.26~1.20 (m, 8H), 0.83 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 133.2 (d, J = 97.2 Hz), 131.6 (d, J = 2.9 Hz), 130.8 (d, J = 8.5 Hz), 128.6 (d, J = 11.4 Hz), 31.8, 31.0 (d, J = 14.3 Hz), 29.8 (d, J = 71.5 Hz), 22.6, 21.5 (d, J = 3.8 Hz), 14.1. ^{31}P-NMR (162 MHz, $CDCl_3$): δ (ppm) 33.3.

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Notes

The authors declare no competing financial interest.

SUPPORTING INFORMATION

^{1}H, ^{13}C and ^{31}P NMR spectroscopies for products. This material is available free of charge via the internet at http://pubs.acs.org.

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(7) The reaction should not be conducted at a more elevated temperature because the formation of **4a** increased (see ref 4d).

(8) Phenylacetylene was slowly consumed (6% consumed after 4 h, and 12% consumed after 16 h), and the

oligomerization products of phenylacetylene could be detected. However, $Ph_2P(O)H$ remained unchanged even after 16 h.

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(10) Half-life (10 h) temperatures of these radical initiators: AIBN, 65 ^oC; V-601, 66 ^oC; V-70, 30 ^oC.

(11) Only trace amount of the addition products (<5% estimated by ^{31}P NMR) could be detected from the reaction of phenylacetylene (0.2 mmol) with $Ph_2P(O)H$ (0.1 mmol) in THF (0.5 mL) heated at 70 ^oC in the presence of 10mol% AIBN. While some oligomerization of phenylacetylene was observed, most of $Ph_2P(O)H$ remained unchanged.

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