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Tetrahedron

Tetrahedron 62 (2006) 2511-2519

Ytterbium-catalyzed dual intermolecular hydrophosphination: synthesis of bis(phosphinyl)dienes and bis(alkenyl)phosphine oxides

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Received 19 November 2005; revised 17 December 2005; accepted 21 December 2005

Available online 18 January 2006

Abstract—Dual intermolecular hydrophosphination of conjugated diynes with 2 equiv of diphenylphosphine was catalyzed by ytterbium complexes, $Yb(\eta^2-Ph_2CNPh)(hmpa)_3$ (1) and $Yb[N(SiMe_3)_2]_3(hmpa)_2$ (2), to give the corresponding 1,4-bis(diphenylphosphinyl)buta-1,3-dienes in high yields after oxidative work-up. Distribution of the four possible stereoisomers sharply depended on substituents of the substrates. (*Z*,*Z*)-Isomers were predominantly obtained from the disubstituted diynes, together with minor (*Z*,*E*)-isomers. On the other hand, the reaction of the terminal diynes provided major (*E*,*Z*) and minor (*E*,*E*)-butadienes. 1,4-Di-*tert*-butylbuta-1,3-diyne was exclusively converted to an allenic compound. Moreover, the dual hydrophosphination using phenyphosphine was also performed with 1 and 2. Thus, the reaction of 2 equiv of aromatic alkynes with PhPH₂ and subsequent oxidation gave bis(alkenyl)phosphine oxides in preference of the (*Z*,*Z*)-stereoisomers.

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1. Introduction

α,β-Unsaturated phosphorus compounds are useful building blocks in organic synthesis.¹ Of their synthetic methods, addition reaction of (RO)₂P(O)H and R₂P(O)H to alkynes through oxidative addition of groups 9 and 10 catalysts to P–H bond has been recognized as the most promising and atom-economical process.² When this methodology was applied to the reaction of R₂PH, instead of pentavalent phosphorus, harsh conditions were necessary to promote the reaction, because of strong affinity of the late transition metals with the trivalent phosphines.³ On the other hand, interaction between hard lanthanide metals and the soft phosphines could be so weak, and thus efficient intramolecular hydrophosphination of alkynyl and alkenylphosphines has been explored with lanthanocenes.⁴

Previously, we reported that a divalent ytterbium-imine complex, $Yb(\eta^2-Ph_2CNPh)(hmpa)_3$ (1), and a trivalent silylamide complex, $Yb[N(SiMe_3)_2]_3(hmpa)_2$ (2), served as highly effective precatalysts for intermolecular hydrophosphination of alkynes with diphenylphosphine and that

Keywords: Rare-earth catalysts; Dual hydrophosphination; Diynes.

the active species generated in situ were ytterbium phosphides, $\overline{Yb}(PPh_2)_2$ and $Yb(PPh_2)_3$, which exhibited similar regio- and stereoselectivity irrespective of their valence state.⁵ Based on this work, we intended to develop a simple method for the synthesis of potentially useful phosphorus compounds 3-5. Diphenylphosphinyldienes 3 have been already prepared by the Y[N(SiMe₃)₂]₃-catalyzed dimerization of terminal alkynes, followed by hydrophosphination of the resulting enynes with Ph₂PH in one-pot.⁶ Compound 4 would be synthesized with dual hydrophosphination of conjugated divnes with 2 equiv of Ph₂PH. However, two preliminary examples revealed that 4 was formed from primary alkyldiyne, but in contrast, tertiary alkyldiyne gave an allenic product.⁵ Bis(alkeny)phosphines and their oxide 5 would be also prepared using PhPH₂, though it has been never used in the present system. To confirm these possibilities, we investigated the dual intermolecular hydrophosphination leading to 4 and 5.



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2. Results and discussion

When hexadeca-7,9-divne (6a) was treated with 2 equiv of Ph₂PH in the presence of 1 (10 mol%) in THF at room temperature for 1 h, 7,10-bis(diphenylphosphinyl)hexadeca-7.9-diene (4a) was obtained in 80% total yield as a mixture of two stereoisomers (61:39) after oxidation with H_2O_2 (Table 1, run 1).⁷ The major product showed one olefinic signal at 7.74 ppm with 34.8 Hz of *trans*- ${}^{3}J_{P-H}$ in ${}^{1}H$ NMR and one signal at 29.53 ppm in ³¹P NMR. On the other hand, two olefinic signals at 6.83 ($cis^{-3}J_{P-H}=20.6$ Hz) and 7.13 ppm ($trans^{-3}J_{P-H}=35.0$ Hz) in ¹H NMR and two signals at 28.18 and 33.58 ppm in ³¹P NMR were observed for the minor. Therefore, the major product was definitely assigned to the (Z,Z)-isomer, and the minor to the (Z,E)isomer. The stereoselectivity was increased a little with decreasing temperature (run 2). The reaction was also conducted with the silylamide 2 effectively (run 3). Two cyclohexyl substituents in 6c did not change the reaction mode, though its reactivity was somewhat decreased (run 5). Arylalkyldiynes **6d** and **6e** gave the (Z,Z) and (Z,E)-dienes 4d and 4e; in the latter substrate, a small amount of the (E,Z)-isomer was contaminated in the mixture (runs 6–9). 1,4-Diphenylbuta-1,3-diene (6f) was so reactive that no phosphinylated product **4f** was obtained with **1**, other than polymers even at -78 °C (run 10). In the absence of Ph₂PH, 6f was recovered unchanged by the treatment with 1 at room temperature. Use of milder precatalyst 2 afforded (E,E)-4f in low yield (run 11). The reaction of terminal diynes 6g and 6h gave the expected products 4g and 4h, but their stereochemistry was drastically altered, (E,Z) and (E,E)isomers being major and minor, respectively (runs 12-15).

Table 1. Dual hydrophosphination of conjugated diynes with diphenylphosphine

Aromatic terminal diyne 6i was exclusively polymerized with both 1 and 2, because of its higher reactivity (run 16).

The behavior of di-*tert*-butyldiyne **6j** seems to be very different from that of others. Thus, the reaction with **1** at -35 °C gave bis(diphenylphosphinyl)allene **7** and (*Z*,*Z*)-diene **4j** in 71 and 12% yields, respectively (Eq. 1). When the reaction was performed at room temperature with **1** and **2**, the allene **7** was exclusively obtained in high yields.



Then, single hydrophosphination of unsymmetrical diynes **6d** and **6g** was carried out using equimolar amounts of Ph₂PH to learn the reaction process (Eq. 2). Apparently, the first reaction in **6d** took place at the α -alkyne carbon attached to the Ph group, with high selectivity for *anti*-addition, to yield (Z)-**8d**. This result contrasts well with the regio- and stereoselectivity observed for simple aromatic alkynes, in which *syn*-addition of Ph₂P occurred at the β -alkyne carbon to the aryl substituents, giving rise to

	R1-===		2 Ph ₂ PH	i) 1 or 2 (10 mol%) THF, 1 h ii) H ₂ O ₂				
	RÎ Ph ₂ (O)P	P(O) (<i>Z,Z</i>)- 4	Ph ₂ + Ph ₂ (C	(Z,E)-4	$R^{2} \xrightarrow{Ph_{2}(O)P} R^{2} \xrightarrow{+} R^{1}$ $P(O)Ph_{2} \qquad (E,Z)$	P(0)Pł R ²	¹ ² Ph ₂ (O)P + R ¹ (<i>E</i> , <i>E</i>)- 4	$\left< \begin{smallmatrix} R^2 \\ P(O)Ph_2 \end{smallmatrix} \right.$
Run	6	R^1	R^2	Precatalyst	Temperature (°C)	4	Total yield (%) ^a	Ratio of isomers (Z,Z) : (Z,E) : (E,Z) : (E,E)
1 2 3	6a	"Hex	"Hex	1 1 2	rt 	4 a	80 82 82	61:39:—:0 74:26:—:0 61:39:—:0
4	6b	ⁿ Bu	ⁿ Bu	1	-15	4b	92	67:33:—:0
5	6c	c-CeH11	c-CeH11	1	-15	4c	74	86:14::0
6 7	6d	Ph	"Hex	1 2	-15 -15	4d	98 95	73:27:0:0 72:28:0:0
8 9	6e	4-MeOPh	"Hex	1 2	-15 -15	4e	85 65	73:19:8:0 74:18:8:0
10 11	6f	Ph	Ph	1 2	78 78	4f	0 28	Polymerization 0:0:—:100
12 13	6g	Н	"Hex	1 2	—78 ^ь —78 ^ь	4g	80 89	0:0:61:39 6:0:75:19
14 15	6h	Н	"Bu	1 2	$-78^{\rm b}$ $-78^{\rm b}$	4h	89 72	16:0:64:20 7:0:61:32
16	6i	Н	Ph	1 or 2	-78	4i	0	Polymerization

^a NMR yield.

^b -78 °C for 1 h then room temperature for 2 h.

(*E*)-products.⁵ In the reaction of the terminal diyne 6g, enyne compound (*Z*)-8g was formed as a single isomer through *anti*-addition to the terminal position.



Combining these results with the reaction mechanism for the hydrophosphination of simple alkynes,⁵ the process of the present system would be accounted for as follows (Scheme 1). At first, bis or tris(diphenylphosphino)ytterbium species, [Yb]-PPh₂, was generated in situ from the precatalysts 1 or 2 as previously proved. *anti*-Addition of the phosphide complex to the diyne 6 gave the intermediate **A**, which was readily protonated with Ph₂PH to yield the enyne compound **8** and regenerate the active phosphide species. The enyne **8** reacted further with the phosphide in a manner similar to the first cycle to yield the diene **4** via dienylytterbium **B**.



Scheme 1.

Regiochemistry was independent of the substituents of the diyne **6**, that is, two Ph_2P were introduced to the 1- and 4-position of the butadiyne moiety, whereas stereochemistry was significantly variable. As proposed in Scheme 1,

repeated anti-addition of the Yb-phosphide complex could produce (Z,Z)-4, which is the case of the internal divises 6a-6e. In general, the overall stereoselectivity would be rationalized by the isomerization of the intermediate **B** formed by the second addition, which proceeds through allenic species C (Scheme 2). In the case of the terminal divnes $\hat{6g}$ and $\hat{6h}$, \hat{B} (R¹=H) changes readily to other dienylytterbium **D** to avoid the steric repulsion between Ph_2P and Yb in the structure of **B**, giving rise to (E,Z)-4g and 4h as major products. Moreover, it is likely that all four stereoisomeric dienvlytterbiums such as **B** and **D** are interconvertible via C, but the equilibrium would not be attained completely, because of the rapid protonation of the intermediates with Ph₂PH. Therefore, stereoselectivity of the present reaction would be a reflection of both kinetic and thermodynamic factors.

Formation of the allene 7 from di-*tert*-butyldiyne **6j** substantiates the scenario described above. In this case, two tertiary substituents caused severe steric crowding in the form of a dienylytterbium species, and thus the allenic C should be the most stable intermediate, giving rise to 7 exclusively at room temperature. However, when the reaction was carried out at lower temperature, the (Z,Z)-diene **4j** derived from **B** was included as a minor product. Thus, **4j** and 7 could be kinetic and thermodynamic products, respectively.

Next, we studied the dual hydrophosphination with phenylphosphine for the synthesis of bis(alkenyl)phosphines and their oxides 5. The reaction of 1-phenylprop-1-yne (9a) (2 equiv) with $PhPH_2$ using the imine complex 1 (10 mol%) was slower than that with Ph₂PH, and required heating (Table 2, runs 1 and 2). After oxidative work-up with H_2O_2 , three isomers of bis(β -methylstyryl)phenylphosphine oxide (5a) were formed in 43% total yield (run 2). The silvlamide precatalyst 2 gave better yield, which was further increased to 64% yield, though still non-selective, by addition of 20 mol% of aniline (runs 3 and 4). The reaction using equimolar amounts of the alkyne 9a and PhPH₂ gave an intractable mixture, in which bis(1-methyl-2-phenylethyl)phenylphosphine oxide, a reduced product of 5a, was mainly detected. In the reaction of phenylacetylene (9b), the aniline additive showed a significant effect for improvement of the selectivity as well as total yield of **5b** (run 5 vs 6). Thus, the (Z,Z)- and (Z,E)-isomers were obtained in 80 and 20% yields, respectively. Similarly, various aromatic alkynes 9c-9f were converted to the expected products **5c–5f** in high yields (runs 7–10).

Unfortunately, this method was not applicable to the reaction of aliphatic alkynes, which resulted in recovery of the starting materials or exclusive consumption of $PhPH_2$ under various conditions. Moreover, the reaction of diphenylacetylene (**9g**) gave cyclic phosphine oxide **10**



Table 2. Dual hydrophosphination of alkynes with phenylphosphine

			$2 R^{1} - R^{2} + PhPH_{2} \xrightarrow{i) 1 \text{ or } 2 (10 \text{ mol}\%) \\ PhNH_{2} (20 \text{ mol}\%) \\ \hline THF, 4 \text{ h} \\ ii) H_{2}O_{2} \\ \end{array}$										
			R ¹ Pr (<i>Z,Z</i>)-	R^2 R^2 R^2 R^1 + R^2 S	$R^{1} \xrightarrow{P^{0}}_{P^{1}} + R^{2}$	$R^{1} \xrightarrow{R^{2}} O$ $Ph \xrightarrow{R^{2}} R^{2}$ $(E,E)-5$	R ¹						
Run	9	\mathbb{R}^1	R ²	Precatalyst	Temperature (°C)	5	Total yield (%) ^a	Ratio of isomers (Z,Z) : (Z,E) : (E,E)					
1 2 3 4	9a	Ph	Me	1 ^b 1 ^b 2 ^b 2	rt ^c Reflux Reflux Reflux	5a	7 43 59 64	100:0:0 37:37:26 46:34:20 36:34:30					
5 6	9b	Ph	Н	2 ^b 2	rt rt	5b	75 Quant	48:52:0 80:20:0					
7 8 9 10	9c 9d 9e 9f	4-MeOPh 4-MePh 4-CIPh 4-BrPh	H H H H	2 2 2 2	rt rt rt rt	5c 5d 5e 5f	Quant 97 89 89	82:18:0 89:11:0 78:22:0 81:19:0					

^a NMR yield.

^b In the absence of PhNH₂.

^c Reaction period is 15 h.

unexpectedly in low yields, together with small amounts of *trans*-stilbene (Eq. 3).⁸



The present reaction would proceed in a mechanism analogous to that with diphenylphosphine as shown in Scheme 3. Addition of phenylphosphinoytterbium, [Yb]-PHPh, to aromatic alkyne 9, followed by intramolecular proton transfer would yield alkenylphosphide species \mathbf{F} , which reacts further with the second molecule of 9 to give bis(alkenyl)phosphine 5 through the intermediate \mathbf{G} .





The regiochemistry was in agreement with that observed for the reaction with Ph_2PH , whereas the stereochemistry was reversed. Since isomerization of the intermediates and products is less likely in the present system, *anti*-addition of the phosphide species would take place preferentially to afford the (*Z*,*Z*)-isomers. The high (*Z*)-selectivity may be caused by a radical mechanism instead of the process proposed in Scheme 3.⁹ However, this possibility was completely ruled out. Thus, the reaction of 2 equiv of 1-decene with PhPH₂ did not occur with **2**, but in contrast, addition product **11** was quantitatively formed under radical conditions (Eq. 4). Alternatively, the (*Z*)-selectivity would be attributed to the amine additive, which has been known to change the activity of the lanthanide catalysts and product selectivity in various reactions as a proton source and ligand.^{6,10} In fact, aliphatic amines like amylamine decreased the yield and selectivity in contrast to aniline. However, the reason for the difference between the reaction with PhPH₂ and Ph₂PH is still unclear at present.

$$2 \ ^{n}\text{Oct} \checkmark + \text{PhPH}_{2} \ \frac{\text{i) } 2 \text{ or AIBN (10 mol%)}}{\text{THF, reflux, 24 h}} \ \text{PhP(O)(^{n}\text{C}_{10}\text{H}_{21})_{2}} \\ \text{ii) } \text{H}_{2}\text{O}_{2} \qquad \text{no reaction with } 2 \\ \text{quantitative with AIBN}$$
(4)

In summary, dual intermolecular hydrophosphination of conjugated diynes with 2 equiv of Ph_2PH has been achieved using ytterbium (II) and (III) precatalysts 1 and 2 to give bis(diphenylphosphinyl)dienes 4 in high yields. Addition reaction of the active species, Yb–phosphide, was found to proceed in an anti-fashion, but the resulting intermediates could isomerize via an allenic species. Thus, the stereo-chemistry of the products 4 was determined both kinetically and thermodynamically, depending on their substituents. Moreover, bis(alkenyl)phosphine oxides 5 were effectively obtained from 2 equiv of aromatic alkynes and PhPH₂ by the dual reaction in the presence of an aniline additive.

3. Experimental

3.1. General

¹H, ¹³C, and ³¹P NMR spectra were recorded at 396, 99, and 160 MHz, respectively. IR spectra were taken on an FT-IR spectrophotometer. Mass spectra (EI) were obtained at 70 eV on a GC-MS apparatus. MALDI-TOF mass spectra were acquired using 1,8,9-trihydroxyanthracene as the matrix. Microanalyses were performed at our analytical laboratory. Melting points are uncorrected. All reactions were carried out under argon. THF was distilled from sodium/benzophenone ketyl immediately prior to use. HMPA was distilled from CaH₂ and stored over molecular sieves. The Yb-imine precatalyst 1 was generated in situ from Yb metal, $Ph_2C = NPh$, and HMPA (6 equiv) in THF as previously reported.⁵ The silylamide precatalyst **2** was also generated by treatment of $Yb[N(SiMe_3)_2]_3(thf)_2^{11}$ with HMPA (2 equiv) in THF. Symmetrical divnes 6a-6c and **6f**,¹² unsymmetrical divnes **6d** and **6e**,¹³ and terminal divnes $6g-6i^{14}$ were prepared according to the literature methods. All other materials were commercially available and were used after drying and distillation.

3.2. Dual hydrophosphination of the conjugated diynes 6 with diphenylphosphine

 Ph_2PH (2.0 mmol) was added to a solution of 1 or 2 (0.1 mmol) in THF (1 mL) and the mixture was stirred for 30 min at room temperature. After cooling the mixture to the appropriate temperature indicated in Table 1, divne 6 (1.0 mmol) was added to the solution and stirring was continued for 1 h at this temperature. In the case of terminal diynes, the mixture was stirred for 1 h at -78 °C, and then for 2 h at room temperature to ensure the completion of the reaction. The reaction was quenched with H₂O (1 mL) and HCl solution (1 M, 1 mL), and the mixture was oxidized with H_2O_2 (30%, 1 mL) at 0 °C. Dimethyl terephthalate was added to the mixture as an internal standard. The reaction mixture was extracted with CHCl₃, washed with brine, dried over MgSO₄, and concentrated in vacuo. The product yield and ratio were determined by ¹H and ³¹P NMR spectra of the crude mixture. Analytically pure compounds 4 were isolated by column chromatography on silica gel with chloroform-acetone eluent.

For determination of the stereochemistry of the products, the coupling constants between the olefinic protons and Ph₂P(O) in ¹H NMR are informative; *trans*-³J_{P-H} (ca. 35 Hz), *cis*-³J_{P-H} (ca. 19 Hz), and ²J_{P-H} (ca. 22 Hz). In addition, ³¹P NMR signals of the olefinic (*Z*)-Ph₂P(O) always appear in higher field than those of the (*E*).⁹ For examples, (alkyl)[P(O)]C=CHR appears at ca. 29 (*Z*) and 33 ppm (*E*), (aryl)[P(O)]C=CHR at ca. 26 (*Z*) and 31 ppm (*E*), (H)[P(O)]C=CHR at ca. 22 (*Z*) and 25 ppm (*E*).

3.2.1. 7,10-Bis(diphenylphosphinyl)hexadeca-7,9-diene (**4a).** (*Z*,*Z*)-Isomer: white solid; mp 137–140 °C; IR (KBr) 1180 cm⁻¹; MS (MALDI) *m*/*z* 619.99 (M⁺ – 2); MS *m*/*z* 622 (M⁺), 551 (M⁺ – C₅H₁₁), 421 (M⁺ – Ph₂PO), 201 (Ph₂PO⁺); ¹H NMR (CDCl₃) δ 0.75 (6H, t, *J*=7.2 Hz), 0.83–0.97 (12H, m), 1.00–1.09 (4H, m), 1.86–1.97 (4H, m), 7.45–7.55 (12H, m), 7.64–7.69 (8H, m), 7.76 (2H, d, J=35.0 Hz); ¹³C NMR (CDCl₃) δ 13.9, 22.3, 28.6, 29.3 (d, J=3.7 Hz), 31.2, 35.7 (d, J=12.3 Hz), 128.5 (d, J=8.3 Hz), 131.7 (d, J = 2.5 Hz), 131.8 (d, J = 10.7 Hz), 133.2 (d, J=101.7 Hz), 137.6 (d, J=86.2 Hz), 140.9 (dd, J=10.3, 3.7 Hz); ³¹P NMR (CDCl₃) δ 29.53. Anal. Calcd for C₄₀H₄₈O₂P₂: C, 77.15; H, 7.77. Found: C, 77.03; H, 7.74. (Z,E)-Isomer: yellow oil; IR (neat) 1178 cm⁻¹; MS (MALDI) m/z 621.17 (M⁺-1); ¹H NMR (CDCl₃) δ 0.81 (3H, t, J=7.0 Hz), 0.84 (3H, t, J=7.0 Hz), 1.09–1.37 (16H, m), 2.21 (2H, dt, J=13.8, 6.9 Hz), 2.50 (2H, dt, J=16.1, 7.7 Hz), 6.83 (1H, dd, J = 20.6, 11.8 Hz), 7.13 (1H, ddd, J =35.0, 11.8, 1.2 Hz), 7.27–7.53 (20H, m); ¹³C NMR (CDCl₃) δ 13.9, 14.0, 22.4, 22.5, 28.7, 29.3, 29.5 (d, *J*=4.1 Hz), 30.5 (d, J=1.7 Hz), 31.3, 31.4, 36.4 (d, J=1.7 Hz), 36.5 (d, J=1.6 Hz), 128.3 (d, J=11.4 Hz), 128.5 (d, J=12.3 Hz), 131.1 (d, J = 101.7 Hz), 131.5 (d, J = 9.8 Hz), 131.62 (d, J =10.7 Hz), 131.63 (d, J=10.1 Hz), 131.8 (d, J=9.0 Hz), 132.7 (d, J = 101.7 Hz), 136.7 (dd, J = 19.7, 5.7 Hz), 136.9 (dd, J=14.0, 9.8 Hz), 140.1 (dd, J=96.0, 2.1 Hz), 140.9(d, J = 86.1 Hz); ³¹P NMR (CDCl₃) δ 28.18, 33.58.

3.2.2. 5,8-Bis(diphenyphophinyl)dodeca-5,7-diene (4b). (Z,Z)-Isomer: white solid; mp 162–163 °C; IR (KBr) 1180 cm⁻¹; MS (MALDI) m/z 564.81 (M⁺-2); ¹H NMR $(CDCl_3) \delta 0.56 (6H, t, J = 6.9 Hz), 0.85 - 0.92 (8H, m), 1.92$ (4H, dt, J=13.5, 6.7 Hz), 7.44–7.55 (12H, m), 7.64–7.69 (8H, m), 7.76 (2H, d, J=34.8 Hz); ¹³C NMR (CDCl₃) δ 13.4, 21.9, 31.2, 35.3 (d, J=12.3 Hz), 128.4 (d, J=12.3 Hz), 131.72, (d, J=9.8 Hz), 131.73, 133.1 (d, J=100.9 Hz), 137.5 (dd, J=88.2, 2.1 Hz), 140.8 (dd, J=9.8, 4.1 Hz); ³¹P NMR (CDCl₃) δ 29.57. Anal. Calcd for C₃₆H₄₀O₂P₂: C, 76.31; H, 7.12. Found: C, 76.51; H, 7.08. (Z,E)-Isomer: yellow oil; IR (neat) 1182 cm⁻¹; MS (MALDI) m/z 564.86 (M⁺-2); ¹H NMR (CDCl₃) δ 0.74 (3H, t, J=7.2 Hz), 0.83 (3H, t, J=7.1 Hz), 1.14–1.37 (8H, m), 2.21 (2H, dt, J=13.7, 6.6 Hz), 2.53 (2H, dt, J=15.4, 7.6 Hz), 6.81 (1H, dd, J = 20.6, 11.4 Hz), 7.13 (1H, dd, J =35.0, 11.4 Hz), 7.34–7.50 (20H, m); ¹³C NMR (CDCl₃) δ 13.5, 13.6, 22.1, 22.7, 27.2 (d, J=9.0 Hz), 31.6 (d, J=4.1 Hz), 32.6, 36.1 (d, J = 10.6 Hz), 128.3 (d, J = 12.3 Hz), 128.4 (d, J = 12.3 Hz), 131.1 (d, J = 102.5 Hz), 131.4 (d, J =9.8 Hz), 131.61 (d, J=9.8 Hz), 131.62 (d, J=9.8 Hz), 131.7 (d, J = 9.8 Hz), 132.6 (d, J = 101.7 Hz), 136.5 (dd, J =19.7, 6.5 Hz), 136.8 (dd, J = 14.7, 9.8 Hz), 140.0 (dd, J =96.8, 2.1 Hz), 140.9 (d, J=87.6 Hz); ³¹P NMR (CDCl₃) δ 28.25, 33.71.

3.2.3. 1,4-Bis(diphenylphosphinyl)-1,4-dicyclohexylbuta-1,3-diene (4c). (*Z*,*Z*)-Isomer: white solid; mp 238–239 °C; IR (KBr) 1174 cm⁻¹; MS (MALDI) *m*/*z* 616.76 (M⁺ – 2); ¹H NMR (CDCl₃) δ 0.68–0.74 (10H, m), 1.25–1.43 (10H, m), 2.00 (2H, quin, *J*=11.5 Hz), 7.43–7.55 (14H, m), 7.63– 7.67 (8H, m); ¹³C NMR (CDCl₃) δ 25.4, 26.3, 33.0 (d, *J*= 10.6 Hz), 44.2 (d, *J*=10.6 Hz), 128.3 (d, *J*=12.3 Hz), 131.56, (d, *J*=9.8 Hz), 131.57, 133.4 (d, *J*=100.9 Hz), 138.2 (dd, *J*=10.7, 4.1 Hz), 143.0 (dd, *J*=87.0, 2.4 Hz); ³¹P NMR (CDCl₃) δ 29.61. Anal. Calcd for C₄₀H₄₄O₂P₂: C, 77.65; H, 7.17. Found: C, 77.77; H, 7.21. (*Z*,*E*)-Isomer: isolated as a mixture with (*Z*,*Z*)-isomer; MS (MALDI) *m*/*z* 617.46 (M⁺ – 1); ¹H NMR (CDCl₃) (clearly assignable peaks) δ 6.69 (1H, dd, *J*=22.1, 11.7 Hz); ¹³C NMR (CDCl₃) δ 25.80, 25.83, 26.6, 26.9, 32.3 (d, *J*=3.3 Hz), 33.9 (d, *J*= 4.1 Hz), 40.1 (d, *J*=9.0 Hz), 42.0 (d, *J*=11.5 Hz), 128.2 (d, J=11.5 Hz), 128.5 (d, J=12.3 Hz), 131.4 (d, J=2.4 Hz), 131.5 (d, J=42.7 Hz), 131.64 (d, J=9.8 Hz), 131.65 (d, J=2.4 Hz), 131.9 (d, J=9.8 Hz), 132.9 (d, J=101.7 Hz), 135.1 (dd, J=20.9, 5.3 Hz), 136.9 (dd, J=15.6, 9.8 Hz), 144.0 (dd, J=93.5, 1.6 Hz), 145.1 (d, J=86.1, 1.6 Hz); ³¹P NMR (CDCl₃) δ 29.92, 35.16.

3.2.4. 1,4-Bis(diphenylphosphinyl)-1-phenyldeca-1,3diene (4d). (Z,Z)-Isomer: white solid; mp 124–126 °C; IR (KBr) 1180 cm⁻¹; MS (MALDI) m/z 613.77 (M⁺-1); ¹H NMR (CDCl₃) δ 0.77 (3H, t, J = 7.4 Hz), 0.87–1.00 (6H, m), 1.07 (2H, quint, J=7.1 Hz), 1.95–2.00 (2H, m), 6.69 (2H, d, J=7.0 Hz), 6.94 (2H, t, J=7.4 Hz), 7.01 (1H, t, J=7.3 Hz), 7.32-7.68 (20H, m), 7.82 (1H, dd, J=35.5, 11.0 Hz), 7.89 (1H, dd, J=33.9, 11.0 Hz); ¹³C NMR (CDCl₃) (clearly assignable peaks) δ 13.9, 22.2, 28.6, 29.1 (d, J=4.1 Hz), 31.1, 35.6 (d, J = 11.5 Hz), 132.8 (d, J = 101.7 Hz), 133.5 (d, J = 102.5 Hz), 138.5 (dd, J = 90.2, 2.1 Hz), 139.5 (d, J =9.8 Hz), 140.3 (dd, J = 87.4, 2.0 Hz); ³¹P NMR (CDCl₃) δ 26.13, 29.43. Anal. Calcd for C40H40O2P2: C, 78.16; H, 6.56. Found: C, 78.03; H, 6.68. (Z,E)-Isomer: colorless oil; IR (neat) 1182 cm⁻¹; MS (MALDI) m/z 613.04 (M⁺-1); ¹H NMR (CDCl₃) δ 0.80 (3H, t, J=7.3 Hz), 1.09–1.45 (8H, m), 2.54 (2H, dd, J = 16.0, 8.0 Hz), 6.99–7.01 (2H, m), 7.07-7.18 (4H, m), 7.27-7.53 (21H, m); ¹³C NMR (CDCl₃) (clearly assignable peaks) δ 13.9, 22.4, 27.5 (d, J=9.0 Hz), 29.2, 30.4, 31.2, 136.5 (dd, J=14.8, 9.1 Hz), 139.9 (dd, J= 9.9, 1.7 Hz), 141.8 (dd, J=88.6, 1.6 Hz), 143.0 (dd, J=95.2, 1.7 Hz); ³¹P NMR (CDCl₃) δ 25.52, 33.38.

3.2.5. 1,4-Bis(diphenylphosphinyl)-1-(4-methoxyphenyl)deca-1,3-diene (4e). (Z,Z)-Isomer: white solid; mp 113–115 °C; IR (KBr) 1178 cm⁻¹; MS (MALDI) m/z643.88 (M⁺-1); ¹H NMR (CDCl₃) δ 0.77 (3H, t, J= 7.2 Hz), 0.79-1.12 (8H, m), 1.91-2.00 (2H, m), 3.67 (3H, s), 6.48 (2H, d, J=8.2 Hz), 6.59 (2H, d, J=8.2 Hz), 7.35-7.68 (20H, m), 7.78 (1H, dd, J=35.3, 12.1 Hz), 7.83 (1H, dd, J=34.5, 12.1 Hz); ¹³C NMR (CDCl₃) δ 14.0, 22.3, 28.7, 29.2 (d, J=3.3 Hz), 31.2, 35.7 (d, J=10.7 Hz), 55.1, 113.1, 128.3 (d, J = 12.3 Hz), 128.5 (d, J = 11.5 Hz), 129.9 (d, J =4.9 Hz), 131.5 (d, J=2.4 Hz), 131.6 (d, J=9.8 Hz), 131.7 (d, J=9.8 Hz), 131.8 (d, J=2.4 Hz), 132.1 (d, J=10.7 Hz),133.0 (d, J = 101.7 Hz), 133.7 (d, J = 102.5 Hz), 138.0 (dd, J=90.7, 2.1 Hz, 140.0 (dd, J=87.4, 2.1 Hz), 140.4 (dd, J=8.6, 4.5 Hz), 140.9 (dd, J=9.4, 5.3 Hz), 158.8; ³¹P NMR (CDCl₃) & 26.18, 29.41. Anal. Calcd for C₄₁H₄₂O₃P₂: C, 76.38; H, 6.57. Found: C, 75.96; H, 6.52. (Z,E)-Isomer: isolated as a mixture of (Z,E) and (E,Z)-isomer (65:35): yellow oil; MS (MALDI) m/z 643.88 (M⁺-1); ¹H NMR (CDCl₃) δ 0.81 (3H, t, J=7.1 Hz), 0.99–1.39 (8H, m), 2.49– 2.57 (2H, m), 3.72 (3H, s), 6.65 (2H, d, J=8.7 Hz), 6.93 (2H, d, J=8.7 Hz), 7.07 (1H, dd, J=20.4, 11.7 Hz), 7.28-7.57 (21H, m); ³¹P NMR (CDCl₃) δ 25.69, 33.58. (E,Z)-Isomer: ¹H NMR (CDCl₃) (clearly assignable peaks) δ 0.77 (3H, t, J=7.4 Hz), 2.06–2.11 (2H, m), 3.75 (3H, s), 6.81 (2H, d, J=8.7 Hz), 7.22 (2H, d, J=8.9 Hz); ³¹P NMR (CDCl₃) δ 28.33, 31.37.

3.2.6. (*E*,*E*)-1,4-Bis(diphenylphosphinyl)-1,4-diphenylbuta-1,3-diene (4f). White solid; mp 267–270 °C; IR (KBr) 1182 cm⁻¹; MS (MALDI) m/z 605.67 (M⁺-1); ¹H NMR (CDCl₃) δ 6.76 (2H, d, J=16.9 Hz), 7.04–7.16 (10H, m), 7.27–7.43 (12H, m), 7.53–7.58 (8H, m); ¹³C

NMR (CDCl₃) δ 128.1 (d, J=30.4 Hz), 128.2 (d, J= 2.4 Hz), 128.3 (d, J=2.4 Hz), 129.5 (d, J=2.4 Hz), 130.7 (d, J=104.2 Hz), 131.78 (d, J=9.0 Hz), 131.82 (d, J= 7.4 Hz), 134.1 (d, J=4.5 Hz), 137.9 (d, J=14.4 Hz), 142.8 (dd, J=94.3, 1.4 Hz); ³¹P NMR (CDCl₃) δ 29.97. Anal. Calcd for C₄₀H₃₂O₂P₂: C, 79.20; H, 5.32. Found: C, 79.13; H, 5.02.

3.2.7. 1,4-Bis(diphenylphosphinyl)deca-1,3-diene (4g). (Z,Z)-Isomer: white solid; mp 174–176 °C; IR (KBr) 1195, 1176 cm⁻¹; MS (MALDI) m/z 536.73 (M⁺-2); ¹H NMR $(CDCl_3) \delta 0.76 (3H, t, J=7.1 Hz), 0.91-1.14 (8H, m), 1.98-$ 2.05 (2H, m), 6.12 (1H, dd, J=24.6, 12.3 Hz), 7.45-7.53 (12H, m), 7.64–7.74 (8H, m), 8.15 (1H, dd, J=34.8, 12.3 Hz), 8.27 (1H, dt, J=37.4, 12.3 Hz); ¹³C NMR $(CDCl_3) \delta 13.8, 22.2, 28.6, 29.2 (d, J=4.1 Hz), 31.0, 35.7$ (d, J = 11.5 Hz), 124.0 (dd, J = 96.8, 1.6 Hz), 124.4 (d, J =6.6 Hz), 128.5 (d, J=7.6 Hz) 130.9 (d, J=9.8 Hz), 131.6 (d, J=2.4 Hz), 131.7 (d, J=9.8 Hz), 131.8 (d, J=3.3 Hz),132.5 (d, J=102.6 Hz), 133.8 (d, J=105.0 Hz), 140.9 (dd, J = 10.2, 4.5 Hz, 141.0 (dd, J = 84.5, 2.1 Hz), 144.7 (dd, J=9.4, 2.9 Hz); ³¹P NMR (CDCl₃) δ 22.32, 30.73. Anal. Calcd for C₃₄H₃₆O₂P₂: C, 75.82; H, 6.74. Found: C, 75.46; H, 6.71. (E,Z)-Isomer: colorless oil; IR (neat) 1182 cm⁻¹; MS (MALDI) m/z 538.13 (M⁺); ¹H NMR (CDCl₃) δ 0.81 (3H, t, J=7.1 Hz), 1.05-1.24 (6H, m), 1.32 (2H, quin, J=7.5 Hz), 2.20 (2H, dt, J=12.7, 7.5 Hz), 6.33 (1H, t, J=16.7 Hz), 6.91 (1H, dd, J = 34.9, 11.4 Hz), 7.16 (1H, td, J =16.7, 11.4 Hz), 7.37–7.43 (8H, m), 7.48–7.55 (12H, m); ¹³C NMR (CDCl₃) δ 13.9, 22.3, 28.7, 29.4 (d, J = 3.3 Hz), 31.2, 35.9 (d, J=9.8 Hz), 128.4 (d, J=12.3 Hz), 128.5, (d, J=11.5 Hz), 128.6 (br d, J = 103.3 Hz) 131.3 (d, J = 97.6 Hz), 131.4 (d, J=9.8 Hz), 131.5 (d, J=9.9 Hz), 131.8 (d, J=6.5 Hz), 132.4 (d, J=102.6 Hz), 141.5 (dd, J=22.5, 5.6 Hz), 142.7 (br d, J=86.1 Hz), 143.0 (dd, J=9.5, 6.2 Hz); ³¹P NMR (CDCl₃) δ 26.31, 28.25. Anal. Calcd for C₃₄H₃₆O₂P₂: C, 75.82; H, 6.74. Found: C, 75.64; H, 6.53. (E,E)-Isomer: white solid; mp 212–214 °C; IR (KBr) 1186 cm^{-1} ; MS (MALDI) m/z 537.94 (M⁺-1); ¹H NMR $(CDCl_3) \delta 0.78 (3H, t, J = 7.2 Hz), 0.96 - 1.17 (8H, m), 2.32 -$ 2.40 (2H, m), 6.53 (1H, dd, J=22.6, 17.0 Hz), 6.84 (1H, dd, J = 19.3, 11.2 Hz), 7.37 (1H, td, J = 17.0, 11.2 Hz), 7.46– 7.57 (13H, m), 7.65–7.72 (7H, m); 13 C NMR (CDCl₃) δ 13.9, 22.4, 28.9 (d, J=9.8 Hz), 29.3, 30.6, 31.2, 128.5 (d, J = 11.5 Hz, 128.6 (d, J = 12.3 Hz), 129.5 (d, J = 100.9 Hz) 131.2 (d, J = 102.5 Hz), 131.3 (d, J = 9.9 Hz), 131.9 (d, J =9.9 Hz), 132.0 (d, J=2.4 Hz), 132.4 (d, J=67.3 Hz), 139.5 (dd, J=20.5, 10.7 Hz), 140.5 (dd, J=18.4, 3.7 Hz), 142.6(br d, J=91.9 Hz); ³¹P NMR (CDCl₃) δ 23.77, 31.68.

3.2.8. 1,4-Bis(diphenylphosphinyl)octa-1,3-diene (4h). (*Z*,*Z*)-Isomer: isolated as a mixture of (*Z*,*Z*) and (*E*,*E*)-isomer (52:48); white solid; IR (KBr) 1178 cm⁻¹; MS (MALDI) *m*/*z* 509.78 (M⁺ – 1); ¹H NMR (CDCl₃) δ 0.60 (3H, t, *J*=7.2 Hz), 0.94–1.10 (4H, m), 1.97–2.04 (2H, m), 6.12 (1H, dd, *J*=25.3, 12.4 Hz), 7.44–7.73 (20H, m), 8.14 (1H, dd, *J*=34.6, 12.4 Hz), 8.26 (1H, dt, *J*=37.8, 12.4 Hz); ³¹P NMR (CDCl₃) δ 22.41, 30.82. (*E*,*Z*)-Isomer: isolated as a mixture of (*E*,*Z*) and (*E*,*E*)-isomer (57:43); white solid; MS (MALDI) *m*/*z* 510.25 (M⁺); ¹H NMR (CDCl₃) δ 0.71 (3H, t, *J*=7.2 Hz), 1.05–1.32 (4H, m), 2.16–2.23 (2H, m), 6.31 (1H, t, *J*=17.3 Hz), 6.89 (1H, dd, *J*=34.8, 11.1 Hz), 7.11 (1H, td, *J*=17.3, 11.1 Hz), 7.34–7.54 (16H, m),

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7.63–7.70 (4H, m); ³¹P NMR (CDCl₃) δ 26.71, 28.41. Anal. Calcd for C₃₂H₃₂O₂P₂: C, 75.28; H, 6.32. Found: C, 75.43; H, 6.30. (*E,E*)-Isomer: ¹H NMR (CDCl₃) (clearly assignable peaks) δ 0.66 (3H, t, *J*=7.2 Hz), 2.32–2.39 (2H, m), 6.53 (1H, dd, *J*=22.4, 16.8 Hz), 6.83 (1H, dd, *J*=19.5, 11.2 Hz), 7.36 (1H, td, *J*=16.8, 11.2 Hz); ³¹P NMR (CDCl₃) δ 23.71, 31.70.

3.2.9. (*Z*,*Z*)-3,6-Bis(diphenylphosphinyl)-2,2,7,7-tetramethylocta-3,5-diene (4j). White solid; IR (Nujol) 1188 cm⁻¹; MS (EI) m/z 566 (M⁺); ¹H NMR (CDCl₃) δ 0.85 (18H, s), 7.35–7.53 (14H, m), 7.68 (4H, tm, *J* = 8.8 Hz), 7.90 (4H, tm, *J*=8.8 Hz); ¹³C NMR (CDCl₃) (clearly assignable peaks) δ 29.7, 36.7. Anal. Calcd for C₃₆H₄₀O₂P₂: C, 76.31; H, 7.11. Found: C, 76.80; H, 7.47.

3.3. Dual hydrophosphination of aromatic alkynes 9 with phenylphosphine

The reaction was carried out in a manner similar to that of the diynes **6** described above, using the aromatic alkynes **9** (2.0 mmol), PhPH₂ (1.0 mmol), and **1** or **2** (0.1 mmol) in THF (1 mL). In the reaction with aniline, this additive and PhPH₂ were successively added to a solution of **1** or **2**, and the mixture was stirred for 30 min at room temperature.

3.3.1. Bis(β -methylstyryl)phenylphosphine oxide (5a). (Z,Z)-Isomer: IR (Nujol) 1178 cm⁻¹; MS (EI) m/z 358 (M^+) ; ¹H NMR (CDCl₃) δ 1.96 (6H, dd, J = 12.2, 1.5 Hz), 7.03 (2H, dd, J=37.0, 1.5 Hz), 7.17–7.19 (6H, m), 7.28– 7.40 (7H, m), 7.66–7.71 (2H, m); ¹³C NMR (CDCl₃) δ 23.9 (d, J=13.1 Hz), 127.3, 127.9, 128.1, 128.4 (d, J=50.9 Hz), 129.5 (d, J=1.6 Hz), 131.1 (d, J=3.2 Hz), 131.5 (d, J=9.0 Hz), 132.5 (d, J=99.9 Hz), 136.0 (d, J=6.5 Hz), 144.6 (d, J = 6.5 Hz); ³¹P NMR (CDCl₃) δ 27.52. Anal. Calcd for C₂₄H₂₃OP: C, 80.43; H, 6.47. Found: C, 80.29; H, 6.51. (*Z*,*E*)-Isomer: MS (EI) m/z 358 (M⁺); ¹H NMR (CDCl₃) δ 1.75 (3H, dd, J=14.0, 1.0 Hz), 2.09 (3H, dd, J=12.0, 1.2 Hz), 7.05–7.49 (15H, m), 7.66–7.71 (2H, m); ¹³C NMR (CDCl₃) δ 14.4 (d, J=11.4 Hz), 23.8 (d, J=12.3 Hz), 127.3, 127.5, 127.9 (d, J=12.6 Hz), 128.1, 128.2 (d, J=11.5 Hz), 128.8 (d, J=90.9 Hz), 129.2, 129.5 (d, J=1.6 Hz), 131.0 (d, J = 81.1 Hz), 131.1 (d, J = 3.3 Hz), 131.3 (d, J=21.5 Hz), 132.0 (d, J=84.4 Hz), 135.8 (d, J=5.7 Hz), 136.0 (d, J=18.9 Hz), 141.3 (d, J=9.8 Hz), 145.4 (d, J=7.3 Hz); ³¹P NMR (CDCl₃) δ 29.81. (*E*,*E*)-Isomer: MS (EI) m/z 358 (M⁺); ¹H NMR (CDCl₃) δ 2.17 (6H, dd, *J*=13.2, 1.2 Hz), 7.25–7.57 (15H, m), 7.80–7.85 (2H, m); ¹³C NMR (CDCl₃) δ 15.0 (d, J=9.8 Hz), 128.3, 128.4, 128.68, 128.71 (d, J=29.5 Hz), 129.4, 129.6 (d, J=41.7 Hz), 131.4 (d, J=92.6 Hz), 132.0 (d, J=9.8 Hz), 135.9 (d, J = 18.0 Hz), 142.4 (d, J = 10.6 Hz); ³¹P NMR (CDCl₃) δ 38.40.

3.3.2. Bis(styryl)phenylphosphine oxide (5b). (*Z*,*Z*)-Isomer: white solid; mp 78–80 °C; IR (KBr) 1178 cm⁻¹; MS (EI) m/z 330 (M⁺); ¹H NMR (CDCl₃) δ 6.07 (2H, dd, *J*= 19.5, 14.0 Hz), 7.18–7.32 (11H, m), 7.65–7.72 (6H, m); ¹³C NMR (CDCl₃) δ 123.9 (d, *J*=100.0 Hz), 127.8, 128.0, 129.1, 130.0, 130.7 (d, *J*=9.8 Hz), 131.0 (d, *J*=2.5 Hz), 133.7 (d, *J*=107.5 Hz), 135.2 (d, *J*=7.4 Hz), 148.0; ³¹P NMR (CDCl₃) δ 15.03. Anal. Calcd for C₂₂H₁₉OP: C, 79.98; H, 5.80. Found: C, 79.87; H, 5.81. (*Z*,*E*)-Isomer:

white solid; MS (EI) m/z 330 (M⁺); ¹H NMR (CDCl₃) δ 6.22 (1H, dd, J=19.0, 13.9 Hz), 6.41 (1H, dd, J=22.9, 17.4 Hz), 7.11–7.54 (13H, m), 7.68–7.79 (4H, m); ¹³C NMR (CDCl₃) δ 120.3 (d, J=105.0 Hz), 122.5 (d, J=100.1 Hz), 127.3, 127.8, 128.3, 128.5 (d, J=9.0 Hz), 129.2, 129.6, 129.8 (d, J=1.6 Hz), 130.4 (d, J=9.8 Hz), 131.3 (d, J= 3.3 Hz), 133.5 (d, J=107.5 Hz), 134.9 (d, J=7.4 Hz), 135.1 (d, J=18.0 Hz), 146.0 (d, J=3.3 Hz), 148.9; ³¹P NMR (CDCl₃) δ 17.56.

3.3.3. Bis(4-methoxystyryl)phenylphosphine oxide (5c). (Z,Z)-Isomer: IR (neat) 1180 cm⁻¹; MS (EI) m/z 390 (M⁺); ¹H NMR (CDCl₃) δ 3.76 (6H, s), 5.92 (2H, dd, J = 19.5, 14.0 Hz), 6.75-6.79 (4H, m), 7.17 (2H, dd, J=40.5, 14.0 Hz), 7.26–7.34 (3H, m), 7.70–7.76 (6H, m); ¹³C NMR (CDCl₃) δ 55.2, 113.4, 121.1 (d, J=100.9 Hz), 128.07 (d, J = 18.9 Hz), 128.09, 130.8 (d, J = 9.8 Hz), 131.0 (d, J=3.3 Hz), 132.1 (d, J=1.6 Hz), 134.3 (d, J=106.6 Hz), 147.5 (d, J = 1.6 Hz), 160.4; ³¹P NMR (CDCl₃) δ 15.91. Anal. Calcd for C₂₄H₂₃O₃P: C, 73.83; H, 5.94. Found: C, 73.43; H, 5.98. (Z,E)-Isomer: MS (EI) m/z 390 (M^+) ; ¹H NMR (CDCl₃) δ 3.72 (3H, s), 3.80 (3H, s), 6.04 (1H, dd, J = 19.4, 13.8 Hz), 6.30 (1H, dd, J = 22.6, 17.2 Hz),6.74-6.85 (4H, m), 7.29-7.48 (7H, m), 7.64-7.80 (4H, m); ¹³C NMR (CDCl₃) δ 55.2, 55.3, 113.4, 114.1, 117.8 (d, J =107.5 Hz), 119.7 (d, J = 100.9 Hz), 127.9 (d, J = 7.4 Hz), 128.2, 128.4 (d, J = 12.3 Hz), 129.1, 130.6 (d, J = 9.8 Hz), 131.3 (d, J=2.4 Hz), 132.0, 134.2 (d, J=107.5 Hz), 145.5 (d, J=4.2 Hz), 148.4, 160.5, 160.9; ³¹P NMR (CDCl₃) δ 18.57.

3.3.4. Bis(4-methylstyryl)phenylphosphine oxide (5d). (Z,Z)-Isomer: white solid; mp 98–99 °C; IR (KBr) 1178 cm⁻¹; MS (EI) m/z 358 (M^+); ¹H NMR (CDCl₃) δ 2.29 (6H, s), 6.00 (2H, dd, J=19.8, 14.0 Hz), 7.04-7.32 (10H, m), 7.61–7.72 (5H, m); ¹³C NMR (CDCl₃) δ 21.3, 122.8 (d, J = 100.9 Hz), 127.9 (d, J = 11.5 Hz), 128.7, 130.2 (d, J = 1.6 Hz), 130.8 (d, J = 9.8 Hz), 130.9 (d, J = 3.3 Hz), 132.5 (d, J=7.4 Hz), 134.2 (d, J=107.5 Hz), 139.4, 147.9 (d, J = 1.6 Hz); ³¹P NMR (CDCl₃) δ 15.29. Anal. Calcd for C₂₄H₂₃OP: C, 80.43; H, 6.47. Found: C, 80.21; H, 6.43. (Z,E)-Isomer: MS (EI) m/z 358 (M⁺); ¹H NMR (CDCl₃) δ 2.24 (3H, s), 2.33 (3H, s), 6.14 (1H, dd, J=19.0, 14.0 Hz),6.35 (1H, dd, J=22.8, 17.2 Hz), 6.92–7.79 (15H, m): ¹³C NMR (CDCl₃) δ 21.2, 21.3, 119.3 (d, J = 105.8 Hz), 121.5 (d, J = 100.1 Hz), 127.4, 128.4 (d, J = 12.3 Hz), 128.7, 129.3, 130.1, 130.6 (d, J=9.8 Hz), 131.3 (d, J=3.3 Hz), 132.4 (d, J=7.4 Hz), 132.7 (d, J=18.9 Hz), 134.0 (d, J=107.5 Hz), 139.5, 139.9, 145.9 (d, J=3.3 Hz), 148.9; ³¹P NMR (CDCl₃) δ 18.09.

3.3.5. Bis(4-chlorostyryl)phenylphosphine oxide (5e). (*Z*,*Z*)-Isomer: white solid; mp 111–112 °C; IR (CHCl₃) 1175 cm⁻¹; MS (EI) *m*/*z* 398 (M⁺); ¹H NMR (CDCl₃) δ 6.09 (2H, dd, *J*=19.6, 14.0 Hz), 7.15–7.39 (9H, m), 7.64–7.68 (6H, m); ¹³C NMR (CDCl₃) δ 124.4 (d, *J*=100.0 Hz), 128.1, 128.3, 130.7 (d, *J*=9.8 Hz), 131.39, 131.44 (d, *J*= 3.2 Hz), 133.2 (d, *J*=106.5 Hz), 133.5 (d, *J*=8.2 Hz), 135.3, 147.0; ³¹P NMR (CDCl₃) δ 14.78. Anal. Calcd for C₂₂H₁₇Cl₂OP: C, 66.18; H, 4.29. Found: C, 66.12; H, 4.01. (*Z*,*E*)-Isomer: white solid; mp 150–151 °C; IR (CHCl₃) 1180 cm⁻¹; MS (EI) *m*/*z* 398 (M⁺); ¹H NMR (CDCl₃) δ 6.25 (1H, dd, *J*=19.1, 13.8 Hz), 6.40 (1H, dd, *J*=22.7,

17.1 Hz), 7.20–7.50 (11H, m), 7.64–7.77 (4H, m); ³¹P NMR (CDCl₃) δ 17.21. Anal. Calcd for C₂₂H₁₇Cl₂OP: C, 66.18; H, 4.29. Found: C, 66.19; H, 4.16.

3.3.6. Bis(4-bromostyryl)phenylphosphine oxide (5f). (Z,Z)-Isomer: white solid; mp 117-118 °C; IR (CHCl₃) 1180 cm⁻¹; MS (EI) m/z 486 (M⁺); ¹H NMR (CDCl₃) δ 6.10 (2H, dd, J=19.7, 14.0 Hz), 7.20 (2H, dd, J=40.1, 14.0 Hz), 7.27–7.39 (7H, m), 7.58–7.68 (6H, m); ¹³C NMR $(CDCl_3)$ δ 123.8, 124.6 (d, J=99.2 Hz), 128.2 (d, J= 12.3 Hz), 130.7 (d, J = 9.8 Hz), 131.2, 131.5 (d, J = 2.5 Hz), 131.6 (d, J = 1.2 Hz), 133.2 (d, J = 107.3 Hz), 134.0 (d, J =7.4 Hz), 147.1; ³¹P NMR (CDCl₃) δ 12.14. Anal. Calcd for C₂₂H₁₇Br₂OP: C, 54.13; H, 3.51. Found: C, 54.18; H, 3.51. (Z,E)-Isomer: white solid; MS (EI) m/z 486 (M⁺); ¹H NMR $(CDCl_3) \delta 6.25 (1H, dd, J=19.1, 14.0 Hz), 6.40 (1H, 14.$ J=23.0, 17.4 Hz), 7.19–7.76 (15H, m); ¹³C NMR (CDCl₃) δ 121.0 (d, J=104.9 Hz), 123.4 (d, J=99.2 Hz), 124.1, 128.7 (d, J = 12.2 Hz), 128.9, 129.1, 130.5 (d, J = 10.7 Hz), 131.2, 131.6, 131.8, 132.0, 133.1 (d, J=112.0 Hz), 133.98, 134.03 (d, J=25.4 Hz), 145.1 (d, J=3.3 Hz), 147.8; ³¹P NMR (CDCl₃) δ 14.61.

3.3.7. 3.6-Bis(diphenylphosphinyl)-2,2,7,7-tetramethylocta-3,4-diene (7). White solid; mp 202–204 °C; IR (KBr) 1203, 1186 cm⁻¹; MS (MALDI) m/z 564.01 (M⁺-2); MS m/z 566 (M⁺), 509 (M⁺- t Bu), 452 $(M^+ - 2^t Bu)$, 365 $(M^+ - Ph_2PO)$, 308 $(365^{-t}Bu^+)$, 201 (Ph₂PO⁺); ¹H NMR (CDCl₃) δ 1.16 (9H, s), 1.33 (9H, s), 2.81 (1H, ddd, J = 7.7, 5.9, 4.3 Hz), 5.30 (1H, ddd, J = 16.7,11.6, 7.7 Hz), 6.94–7.76 (20H, m); 13 C NMR (CDCl₃) δ 29.8 (d, J=5.7 Hz), 29.9 (d, J=4.1 Hz), 37.5 (d, J=6.6 Hz), 37.8 (d, J=5.7 Hz), 45.3 (dd, J=70.6, 4.9 Hz), 90.6 (d, J=13.9 Hz), 107.8 (d, J=96.8 Hz), 127.9 (d, J= 11.5 Hz), 128.1 (d, J=100.9 Hz), 128.7, 130.2 (d, J=1.6 Hz), 130.8 (d, J=9.8 Hz), 130.9 (d, J=12.3 Hz), 128.3 (d, J=11.5 Hz), 128.4 (d, J=11.5 Hz), 130.0 (d, J=9.1 Hz), 130.5 (d, J=8.2 Hz), 130.7 (d, J=2.5 Hz), 131.1 (d, J=3.3 Hz), 131.4 (d, J=2.5 Hz), 131.5 (d, J=3.3 Hz),131.6 (d, J=9.0 Hz), 132.0 (d, J=10.7 Hz), 132.9 (d, J=100.9 Hz), 134.0 (d, J=96.0 Hz), 135.6 (d, J=95.2 Hz), 137.8 (d, J = 108.3 Hz), 207.1 (d, J = 26.3 Hz); ³¹P NMR $(CDCl_3) \delta 28.78 (d, J = 5.9 Hz), 31.68 (d, J = 5.9 Hz).$ Anal. Calcd for C₃₆H₄₀O₂P₂: C, 76.31; H, 7.11. Found: C, 76.53; H, 7.11.

3.3.8. 1-Diphenylphosphinyl-1-phenyldec-1-en-3-yne (**8d**). Isolated as a mixture of (*Z*) and (*E*)-isomer (91:9); yellow oil; IR (neat) 1190 cm⁻¹; MS (EI) *m*/*z* 412 (M⁺); ¹H NMR (CDCl₃) δ (*Z*)-isomer: 0.84 (3H, t, *J*=6.9 Hz), 1.14– 1.56 (8H, m), 2.53–2.61 (2H, m), 6.52 (1H, d, *J*=36.2 Hz), 6.87 (2H, d, *J*=7.0 Hz), 7.15–7.57 (9H, m), 7.70–7.86 (4H, m); (*E*)-isomer: 6.22 (d, *J*=18.1 Hz); ¹³C NMR (CDCl₃) δ (*Z*)-isomer: 14.0, 22.4, 28.7, 29.4 (d, *J*=3.2 Hz), 31.5, 34.9 (d, *J*=8.2 Hz), 86.7 (d, *J*=10.6 Hz), 99.8 (d, *J*=1.6 Hz), 120.8 (d, *J*=6.5 Hz), 127.9, 128.3 (d, *J*=12.3 Hz), 128.5, 131.3, 131.73, 131.76 (d, *J*=10.7 Hz), 131.8, 132.5 (d, *J*= 103.4 Hz), 146.8 (d, *J*=90.5 Hz); ³¹P NMR (CDCl₃) δ (*Z*)isomer: 27.76, (*E*)-isomer: 31.77. Anal. Calcd for C₂₈H₂₉OP: C, 81.53; H, 7.09. Found: C, 81.56; H, 7.22.

3.3.9. (*Z*)-1-Diphenylphosphinyldec-1-en-3-yne (8g). Yellow oil; IR (neat) 1188 cm^{-1} ; MS (EI) *m/z* 336 (M⁺);

¹H NMR (CDCl₃) δ 0.86 (3H, t, *J*=7.1 Hz), 1.15–1.27 (8H, m), 1.97–2.00 (2H, m), 6.47 (1H, dd, *J*=18.7, 13.2 Hz), 6.53 (1H, ddt, *J*=35.8, 13.2, 2.4 Hz), 7.43–7.53 (6H, m), 7.76–7.81 (4H, m); ¹³C NMR (CDCl₃) δ 14.0, 19.6, 22.4, 27.7, 28.4, 31.2, 77.3 (d, *J*=12.3 Hz), 104.8, 128.3 (d, *J*=12.3 Hz), 128.4 (d, *J*=1.6 Hz), 131.26 (d, *J*=9.8 Hz), 131.30 (d, *J*=99.3 Hz), 131.6 (d, *J*=3.5 Hz), 133.0 (d, *J*=105.8 Hz); ³¹P NMR (CDCl₃) δ 21.46. Anal. Calcd for C₂₂H₂₅OP: C, 78.55; H, 7.49. Found: C, 78.60; H, 7.58.

3.3.10. 1,2,3,4,5-Pentaphenyl-1-phosphacyclopent-2-ene 1-oxide (10). Isolated as a single isomer with unknown stereochemistry; white solid; mp 295–297 °C; IR (KBr) 1215 cm⁻¹; MS (MALDI) *m*/*z* 482.60 (M⁺); ¹H NMR (CDCl₃) δ 3.98 (1H, dd, *J*=10.1, 8.2 Hz), 4.96 (1H, dd, *J*= 27.3, 8.2 Hz), 7.01–7.39 (23H, m), 7.67–7.72 (2H, m); ¹³C NMR (CDCl₃) δ 51.0 (d, *J*=69.7 Hz), 59.7 (d, *J*=7.3 Hz), 126.7, 127.0, 127.4, 127.7, 128.1, 128.27, 128.34, 128.40 (d, *J*=10.6 Hz), 128.85, 128.90, 129.7, 130.8 (d, *J*=7.5 Hz), 131.5 (d, *J*=9.8 Hz), 131.6 (d, *J*=2.4 Hz), 133.1 (d, *J*= 119.6 Hz), 133.7 (d, *J*=1.0 Hz), 133.9, 134.0, 136.1 (d, *J*= 92.6 Hz), 136.6 (d, *J*=15.5 Hz), 137.2, 157.9 (d, *J*=25.4 Hz); ³¹P NMR (CDCl₃) δ 52.06. Anal. Calcd for C₃₄H₂₇OP: C, 84.63; H, 5.64. Found: C, 84.44; H, 5.68.

3.3.11. Di(decyl)phenylphosphine oxide (11). White solid; mp 56–57 °C; IR (KBr) 1165 cm⁻¹; MS (EI) *m*/*z* 406 (M⁺); ¹H NMR (CDCl₃) δ 0.86 (6H, t, *J*=6.7 Hz), 1.21–2.17 (36H, m), 7.47–7.52 (3H, m), 7.66–7.71 (2H, m); ¹³C NMR (CDCl₃) δ 14.1, 21.4 (d, *J*=4.1 Hz), 22.7, 29.1, 29.3, 29.4, 29.5 30.0 (d, *J*=68.1 Hz), 31.0 (d, *J*=13.8 Hz), 31.9, 128.6 (d, *J*=11.4 Hz), 130.4 (d, *J*=8.2 Hz), 131.4 (d, *J*=3.2 Hz), 132.3 (d, *J*=91.8 Hz); ³¹P NMR (CDCl₃) δ 40.72. Anal. Calcd for C₂₆H₄₇OP: C, 76.80; H, 11.65. Found: C, 76.84; H, 11.65.

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