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Efficient Palladium-Catalyzed Double Arylation of Phosphonoalkynes and Diarylalkynes in Water: Use of a Dinuclear Palladium(I) Catalyst

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Dedicated to Professor S. S. Krishnamurthy on the occasion of his 70th birthday.

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Abstract: A novel use of the dinuclear palladium(I) catalyst $[(OCH_2CMe_2CH_2O)P\text{-}S\text{-}Pd(PPh_3)]_2$ in aqueous medium for the double arylation of phosphonoalkynes as well as diarylalkynes is reported. This double arylation ***requires*** both the iodoarene and arylboronic acid along with the catalyst. The structures of some key products have been proven by X-ray crystallography.

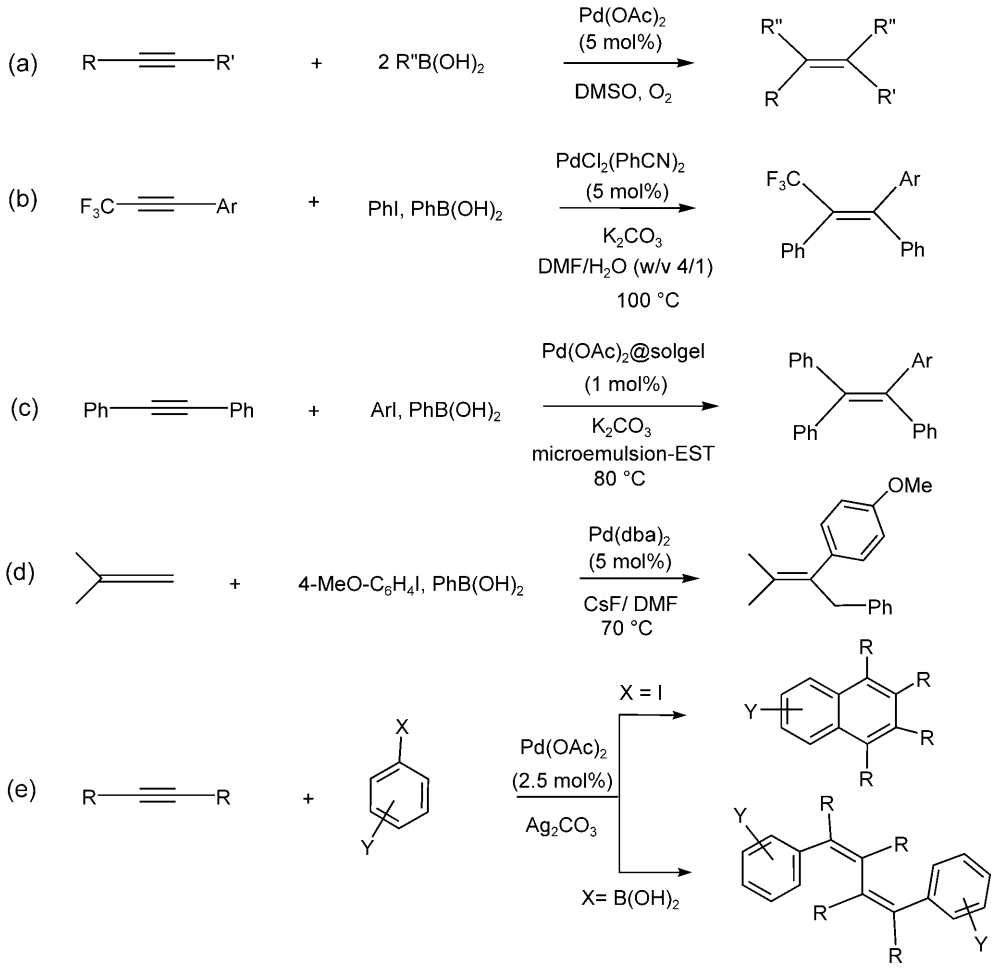
Keywords: diarylalkynes; double arylation; palladium catalysis; phosphonoalkynes; vinylphosphonates; water medium

Introduction

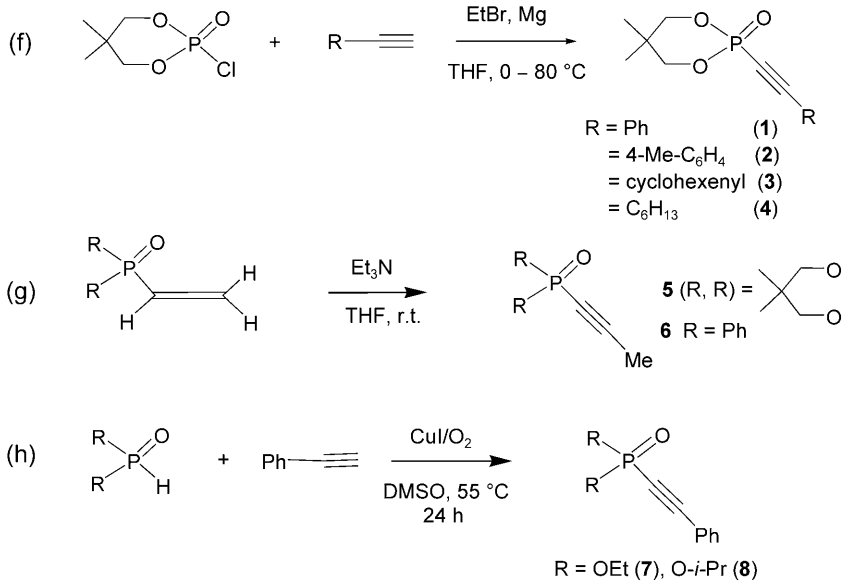
Palladium-catalyzed reactions have been in the forefront of organic synthesis during the last couple of decades.[1] It is known that subtle variations in the catalyst environment can improve the yields dramatically and hence there have been numerous new variations of the known reactions like Heck, Suzuki–Miyaura and Sonogashira couplings. Thus, for the Pd-catalyzed synthesis of tetrasubstituted olefins (including those with internal cyclization) *via* alkynes several modifications have become available; in favorable cases using appropriate stoichiometry, cyclization or multiple-coupling may also be accomplished (Scheme 1).[2] If the alkyne moiety and the iodoaryl entity are in the molecule, cyclization in conjunction with arylation can be accomplished.[3] However, despite all these elegant studies, to the best of our knowledge, phosphonoalkynes as substrates have not been explored to date. These reactions lead to multiply substituted vinylphosphonates (alkenephosphonates) many of which are synthetically useful reagents. Other known synthetic routes to alkenephosphonates with defined stereochemistry involve palladium-catalyzed coupling reaction of alkenyl halides and hydrogen phosphonates $[HP(O)(OR)_2]$,[4] Rh-catalyzed addition of hydrogen phosphonates to alkynes,[5] and Wittig-type reaction with methylenebisphosphonates.[6] In our studies on organophosphonates,[7] we needed vinylphosphonates for our synthetic work and hence wanted to explore phosphonoalkynes as substrates. We also surmised that if our modification is viable for phosphonoalkynes, it should be so for other alkynes and hence have included a few examples using diphenyl- or phenyl(*p*-tolyl)acetylene. We also note that use of the green solvent water for organic synthesis has been one of the thrust areas in recent years.[8] In many cases, due to hydrophobic effects, water can accelerate the reaction rates, even when the reactants are sparingly soluble or insoluble in this medium.[8c] Thus, we planned to perform our palladium-catalyzed reactions in water, which obviously is the most inexpensive and environmentally benign solvent. In this context, we have developed a method for the synthesis of highly substituted alkenephosphonates in aqueous medium by Pd-catalyzed three component coupling of organophosphonylalkynes, arylboronic acids and aryl iodides.

Results and Discussion

The phosphonate/phosphine oxide precursors for this study are prepared by the routes shown in Scheme 2.[9] The dinuclear Pd(I) catalyst **9** (Figure 1)



Scheme 1. Examples of palladium-catalyzed double arylation of alkynes and an allene from the literature.



Scheme 2. Phosphonoalkynes prepared in the present study.

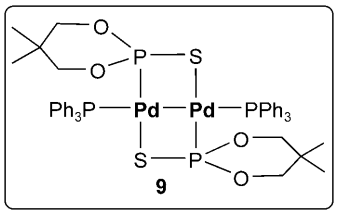


Figure 1. Dinuclear palladium(I) catalyst **9** used in the present study

was prepared by the reaction of $Pd(PPh_3)_4$ with $(OCH_2CMe_2CH_2O)P(S)H$.[10]

Initially we optimized the conditions for the reaction of **1** with iodobenzene and phenylboronic acid (Scheme 3, Table 1) that leads to the vinylphosphonate **10**. As can be seen from the Table 1, in both PEG-400 and water, using the new dinuclear palladium(I) complex **9** (at 1 mol% of Pd), the reaction was quantitative with all the alkyne **1** consumed in 0.5 h (entries 5 and 6). In DMF/H_2O (4:1) mixture, there was no improvement in the rate of reaction compared to water alone as a solvent (75% after 6 h). Although $Pd_2(dba)_3$ also worked well, it needed a longer reaction time (entry 7, *cf.* Figure 2) and at the end of 4 h, there were some other unidentified minor peaks in the ^{31}P NMR spectrum of the reaction mixture. Other Pd catalysts $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$, $Pd(OAc)_2$, or $PdCl_2$ were less effective (entries 8–11). In the case of $PdCl_2$ the reaction was incomplete even after 12 h reflux. Either K_2CO_3 or $KHCO_3$ as a base was better than Na_2CO_3 or $NaHCO_3$. Hence we have used the system **9**/K_2CO_3/water as the medium for the double arylation of several phosphonoalkynes **1**–**8** that led to the products **10**–**28** (Table 2). The yields are quantitative with the only minor limitation being the formation of the biaryls.[11] X-ray structures of the symmetrically double arylated products **18** (Figure 3) and **22** (see Supporting Information; Figure S101) have been determined. As a demonstration of the efficacy of this novel route, we have extended the methodology to include the disubstituted alkynes and obtained the tetrasubstituted alkenes **29**–**34** by double arylation. In these cases also, compounds **29**–**34** were the sole arylated products. The slightly lower isolated yields of the pure products are only because of the nearly same R_f values of the biaryls and **29**–**34**; otherwise, the arylation process was quantitative.

Table 1. Details on optimization studies for double arylation as per Scheme 3.[a]

Entry	Catalyst	Solvent/duration	Yield [%][b]
1	**9**	CH_3CN/0.5 h	n.r.
		CH_3CN/2 h	20
2	**9**	THF/0.5 h	n.r
		THF/2 h	60
3	**9**	dioxane/0.5 h	n.r.
		dioxane/2 h	30
4	**9**	DMF/0.5 h	40
5	**9**	PEG-400/0.5 h	quantitative
6	**9**	**water/0.5 h**	**quantitative**
7	$Pd_2(dba)_3$	water/0.5 h	n.r.
	$Pd_2(dba)_3$	water/2 h	~60
	$Pd_2(dba)_3$	water/4 h	~90[c]
8	$PdCl_2(PPh_3)_2$	water/0.5 h	10
9	$PdCl_2(PhCN)_2$	water/0.5 h	40
10	$Pd(OAc)_2$	water/0.5 h	20
11	$PdCl_2$	water/0.5 h	30
12	**9** + Na_2CO_3[d]	water/0.5 h	80
	9 + $NaHCO_3$[d]	water/0.5 h	80
	9 + $KHCO_3$[d]	water/0.5 h	quantitative

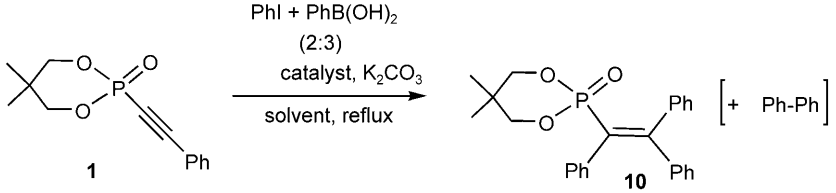
[a] The ratio of alkyne:iodobenzene:arylboronic acid was 1:2:3. Alkyne **1** (0.5 mmol), PhI (1.0 mmol), $PhB(OH)_2$ (1.5 mmol), K_2CO_3 (1.5 mmol), catalyst (0.005 mmol) in solvent (5 mL) under reflux. The isolated yields are in general *ca.* 5% lower than the ^{31}P NMR yields.

[b] There was no reaction in the absence of catalyst; in DMSO and $C_2H_4Cl_2$ in the presence of catalyst **9** also, there was no reaction. Yields were based on ^{31}P NMR spectra.

[c] Although the starting material was absent, there were several minor peaks in the ^{31}P NMR.

[d] Here, Na_2CO_3, $NaHCO_3$ or $KHCO_3$ was used *in lieu* of K_2CO_3.

We have also prepared unsymmetrically double arylated products **35**–**44** by using the above methodology. The yields (^{31}P NMR) were again quantitative with the incoming aryl groups *cis* to each other. In most cases, the isomer with the aryl moiety from the boronic acid entering the position *geminal* to the phosphorus was dominant and the other isomer was the minor product. This assertion is based on (i) a report on double arylation of nonphosphorylated alkynes,[11]



Scheme 3. Palladium(I)-catalyzed symmetrical double arylation of alkyne **1** with PhI and $PhB(OH)_2$.

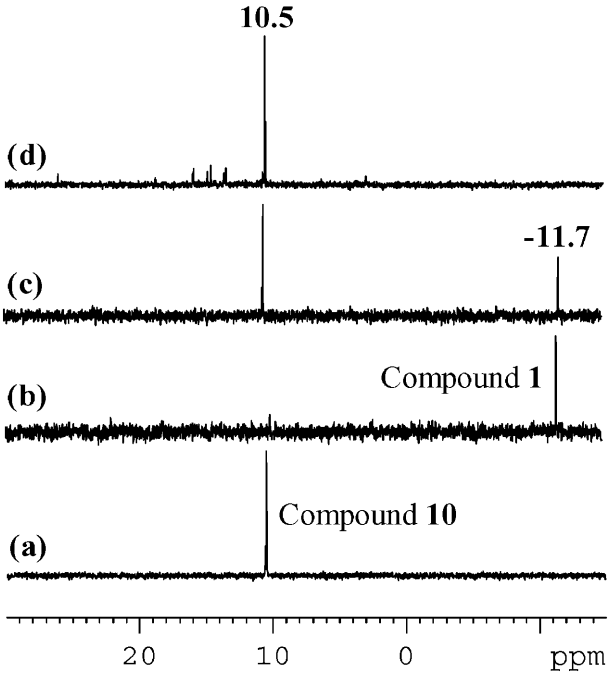
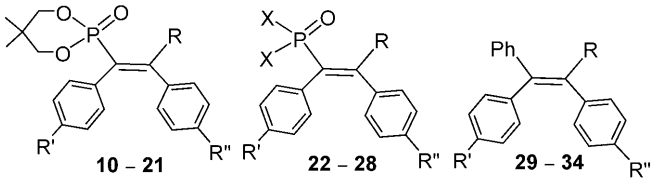


Figure 2. A diagram showing ^{31}P NMR spectra of the reaction shown in Scheme 3 by (**a**) using Pd(I) complex **9** after 0.5 h, (**b**) using $Pd_2(dba)_3$ after 0.5 h, (**c**) using $Pd_2(dba)_3$ after 2 h and (**d**) using $Pd_2(dba)_3$ after 4 h.

and (ii) X-ray structures of the major products **39b** and **40b** (Figure 5). Distinction between the two isomers, we should admit, has not always been easy in the ^{31}P NMR because of the closeness of the chemical shifts; however, the O*C*H$_2$ carbons showed distinct ^{13}C NMR signals in all the cases. For the numbering of compounds obtained as per Scheme 4/Table 3, see Figure 4. These compounds (**35**–**44**) were not separated into individual isomers.

In addition to the above, we also note the following points. (i) Under the conditions employed, there was ***no reaction*** (^{31}P NMR evidence) with the use of only one of the arylating agents, ArI or $PhB(OH)_2$ even after 10 h of reflux. This is to say that it was mandatory to use both ArI and $ArB(OH)_2$ for the disubstitution to occur. It must be noted that in these reactions the monoarylated addition product was not observed in the ^{31}P NMR. (ii) Despite being conducted in a heterogeneous system the reaction works extremely well affording the phosphonate products in high yields (quantitative on the basis of alkyne used, by ^{31}P NMR). (iii) Using our phosphonate precursors, by using $Pd(OAc)_2/O_2$/DMSO in the presence of 4 Å molecular sieves[2c,d] mono- and disubstituted products were formed along with unreacted starting material. Hence this procedure was not adapted in the present work. (iv) There was no reaction of **1** with (a) $PhB(OH)_2$ using $Pd(OAc)_2/Ag_2CO_3$/1-propanol + H_2O (9:1)/120 °C[2b] or (b) PhI using $Pd(OAc)_2$/NaOAc/PPh_3/(n-Bu)$_4$NCl/DMF/100 °C.[12] (v) The monoarene (Ar-H) addition products were obtained exclusively under the conditions shown in Scheme 5. A similar method was reported for the preparation of monoarylated addition product for non-phosphorylated al-

Table 2. Details on the products obtained in double arylation.[a]



Compound	R	R′	R″	δ (^{31}P)[b]	Isolated yield [%]
Symmetrically substituted vinylphosphonates **10–28**					
10	Ph	H	H	10.2	92
11	Ph	Me	Me	10.8	87
12	Ph	OMe	OMe	11.3	85
13	4-Me-C_6H_4	H	H	10.5	86
14	4-Me-C_6H_4	Me	Me	11.1	81
15	4-Me-C_6H_4	OMe	OMe	11.5	81
16	Me	H	H	12.2	79
17	Me	Me	Me	12.8	85
18	Me	OMe	OMe	13.1	84
19	*cyclo*-C_6H_9[c]	H	H	11.7	80
20	*cyclo*-C_6H_9[c]	Me	Me	12.4	82
21	*cyclo*-C_6H_9[c]	OMe	OMe	12.8	79
22	Ph	H	H	15.7	85
23	Ph	OMe	OMe	16.5	84
24	Ph	H	H	13.7	88
25	Ph	OMe	OMe	14.4	82
26	Me	H	H	28.7	79
27	Me	Me	Me	28.9	85
28	Me	OMe	OMe	29.1	80
Tetrasubstituted alkenes **29–34**					
29	Ph	H	H	–	60[d]
30	Ph	Me	Me	–	58[d]
31	Ph	OMe	OMe	–	55[d]
32	4-Me-C_6H_4	H	H	–	66[d]
33	4-Me-C_6H_4	Me	Me	–	62[d]
34	4-Me-C_6H_4	OMe	OMe	–	62[d]

[a] The ratio of alkyne:iodobenzene:arylboronic acid was 1:2:3. Alkyne (0.4 mmol), ArI (0.8 mmol), $ArB(OH)_2$ (1.2 mmol), K_2CO_3 (1.2 mmol), **9** (1.0 mol% based on Pd) in H_2O (5 mL) at 100 °C for 0.5 h.

[b] The variation in chemical shifts was within ±0.3 ppm for the reaction mixture and pure compounds.

[c] Cyclohexenyl group.

[d] Here, although the reaction was quantitative, the isolated yields of the pure products are somewhat lower, mainly because of the closeness of the R_f values for the products and the biaryls. In the literature also a similar problem was encountered; it is reported that the purity of a sample was only ~95%.[11c]

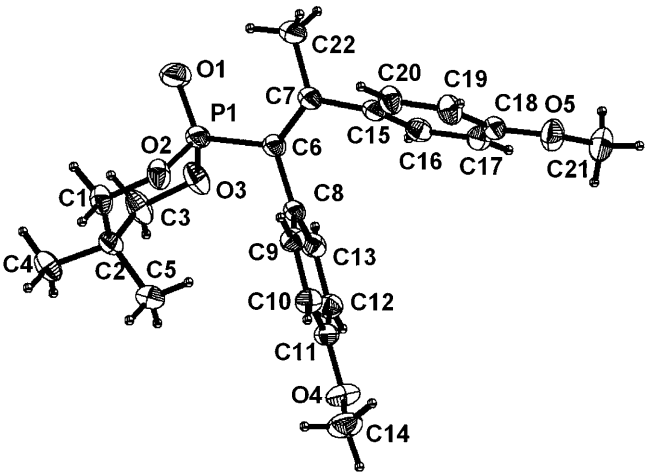
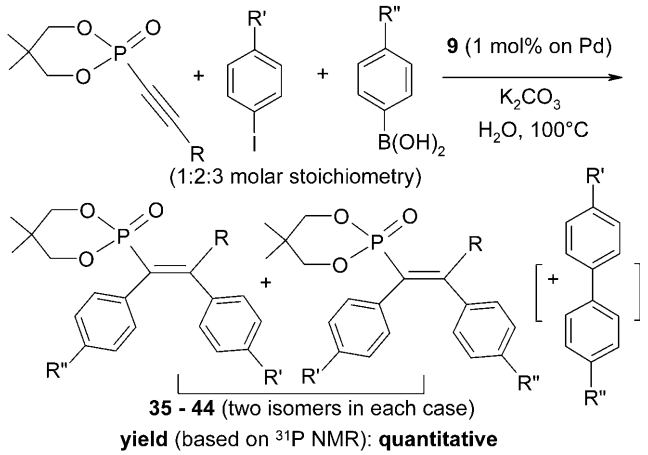
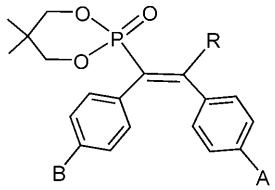


Figure 3. An ORTEP diagram of **18** [P1–O1 1.449(2), P1–O2 1.573(2), P1–O3 1.567(2), P1–C6 1.786(2), C6–C7 1.346(3) Å].

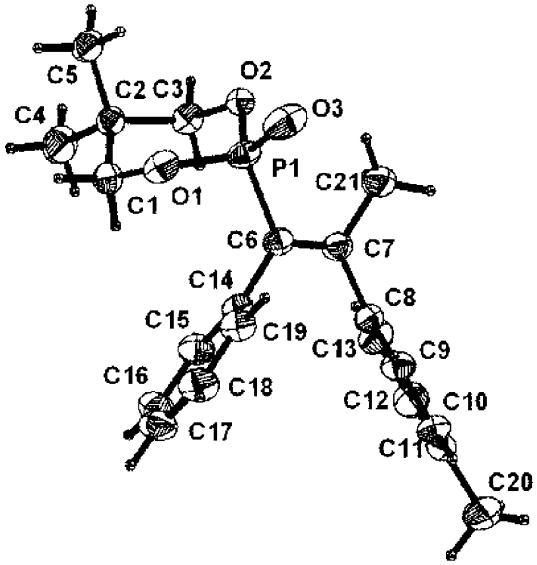


Scheme 4. Palladium-catalyzed unsymmetrical double arylation of phosphonoalkynes with ArI and $ArB(OH)_2$.



R = Ph	A = H, B = Me	(**35a**)
	A = Me, B = H	(**35b**)
	A = H, B = OMe	(**36a**)
	A = OMe, B = H	(**36b**)
R = 4-Me-C_6H_4	A = H, B = Me	(**37a**)
	A = Me, B = H	(**37b**)
	A = H, B = OMe	(**38a**)
	A = OMe, B = H	(**38b**)
R = Me	A = H, B = Me	(**39a**)
	A = Me, B = H	(**39b**)
	A = H, B = OMe	(**40a**)
	A = OMe, B = H	(**40b**)
R = *cyclo*-C_5H_9	A = H, B = Me	(**41a**)
	A = Me, B = H	(**41b**)
	A = H, B = OMe	(**42a**)
	A = OMe, B = H	(**42b**)
R = C_6H_{13}	A = H, B = Me	(**43a**)
	A = Me, B = H	(**43b**)
	A = H, B = OMe	(**44a**)
	A = OMe, B = H	(**44b**)

Figure 4. Structures of the unsymmetrical diarylated vinyl phosphonates **35**–**44**.



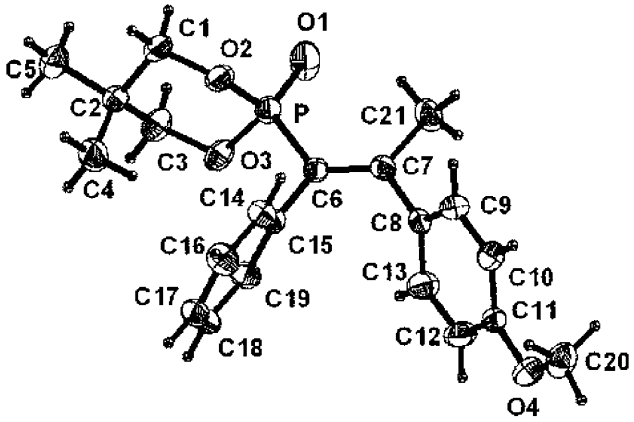


Figure 5. ORTEP diagrams of the major isomers **39b** (entry 10 in Table 3) [*top:* P1–O3 1.455(2), P1–O2 1.5722(17), P1–O1 1.574(2), P1–C6 1.805(2), C6–C7 1.342(3) Å] and **40b** (entry 12 in Table 3) [*bottom:* P–O1 1.456(2), P–O2 1.578(2), P–O3 1.576(2), P–C6 1.789(2), C6–C7 1.344(3 Å].

kynes but by using $NaBPh_4$ in place of phenylboronic acid.[13]

Based on the available literature,[11] for the double arylation, we propose that the Pd complex first reacts with iodoarene and then with arylboronic acid. The aryl group from the iodoarene preferentially goes to the carbon β to the phosphonyl group. As regards the role of the catalyst (or procatalyst) **9**, at least four possible intermediates (**I–IV**, Figure 6) are possible in the initial stages, either by retaining the Pd–Pd bond or by its cleavage[14] leading to the formation of a mononuclear species. In either case, one of the active species should be of the type **V** (Figure 6). In a preliminary experiment, when a solution of the catalyst **9** (1 equiv.) and PhI (2 equiv.) was heated at 100 °C in 1,4-dioxane for 30 min, the color changed from yellow

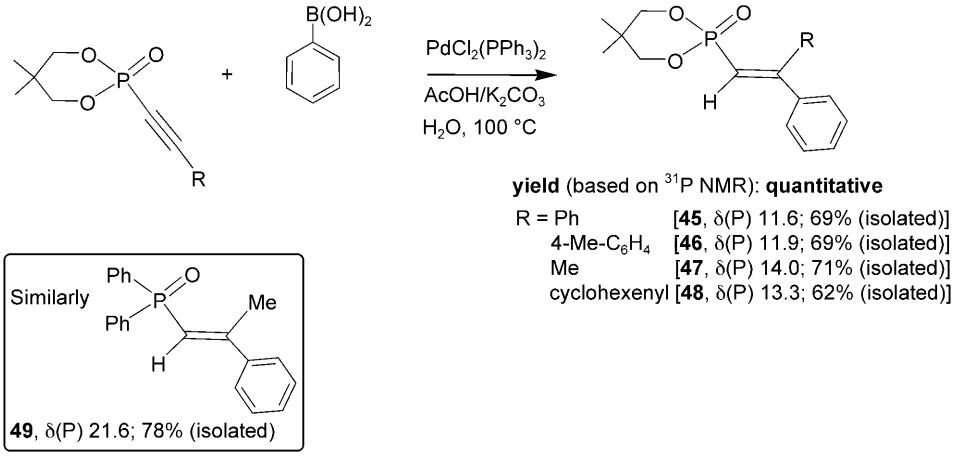
Table 3. Details on the unsymmetrical double arylation products (*cf.* Scheme 4).[a]

Entry	Product	R	R′	R″	δ (^{31}P)[b]	Combined isolated yield [%][c]
	Unsymmetrically substituted vinylphosphonates **29–38**					
1	**35**	Ph	H	Me	10.5_7; 10.6_4	87
2	**35**	Ph	Me	H	same as above	80
3	**36**	Ph	H	OMe	10.7; 10.8	83
4	**36**	Ph	OMe	H	same as above	83
5	**37**	4-Me-C_6H_4	H	Me	10.5; 10.6	93
6	**37**	4-Me-C_6H_4	Me	H	same as above	81
7	**38**	4-Me-C_6H_4	H	OMe	10.8; 10.9	71
8	**38**	4-Me-C_6H_4	OMe	H	same as above	71
9	**39**	Me	H	Me	12.7	75
10	**39**	Me	Me	H	same as above	86
11	**40**	Me	H	OMe	12.8_1; 12.8_5	84
12	**40**	Me	OMe	H	same as above	75
13	**41**	*cyclo*-C_6H_9	H	Me	11.9	87
14	**41**	*cyclo*-C_6H_9	Me	H	same as above	87
15	**42**	*cyclo*-C_6H_9	H	OMe	12.1	90
16	**42**	*cyclo*-C_6H_9	OMe	H	same as above	92
17	**43**	C_6H_{13}	H	Me	12.4	81
18	**43**	C_6H_{13}	Me	H	same as above	87
19	**44**	C_6H_{13}	H	OMe	12.8	86
20	**44**	C_6H_{13}	OMe	H	same as above	84

[a] The molar ratio of alkyne:iodobenzene: arylboronic acid was 1:2:3. Alkyne (0.4 mmol), ArI (0.8 mmol), $ArB(OH)_2$ (1.2 mmol), K_2CO_3 (1.2 mmol), **9** (1.0 mol% based on Pd) in H_2O (5 mL) at 100 °C for 0.5 h. Two entries are there for each compound because of the interchange of the aryl group between the boronic acid and the iodoarene.

[b] In some cases, the $\delta(^{31}P)$ values of the two isomers were the same.

[c] Two isomers are obtained generally in the ratio 7:3 to 9:1 in favor of boronic acid residue geminal to phosphorus moiety. In the case of compound **38** only, both the isomers are formed in nearly equal quantities.



Scheme 5. Synthesis of monosubstituted alkenyl-phosphonates **45**–**48** and the alkenylphosphine oxide **49**.

to dark brown and the peaks corresponding to the catalyst ($\delta = 15.3$ and 148.0) disappeared in the ^{31}P NMR spectrum. New peaks were seen at $\delta = 30.2$ and $\delta = 86.0$; these may be due to the PPh_3 and/or thiophosphorus (P=S) bound ArPdI moiety (**II** or **IV**). Addition of alkyne **1** [1.0 equiv.; $\delta(P) = -12.0$] at this stage did not give any change in the ^{31}P NMR. Upon addition of $PhB(OH)_2$ (3 equiv.) and K_2CO_3 (3 equiv.), the intensity of alkyne (**1**) peak gradually decreased (after 1 h) with the increase in intensity of a peak at $\delta = 10.2$ (^{31}P NMR) due to diarylated product (**10**). In lieu of the peak at $\delta(P) = 86.0$ a new peak appeared at $\delta(P) = 23.0$. After 3 h, the alkyne fully disappeared and the product **10** was formed quantitatively. There was no change in the ^{31}P NMR when Pd catalyst **9** was heated with only $PhB(OH)_2$ under the

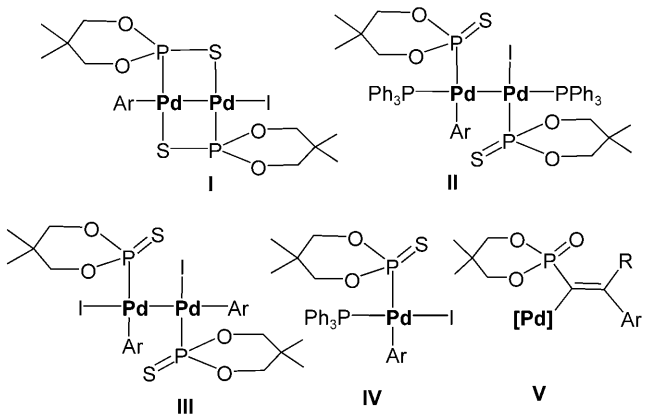
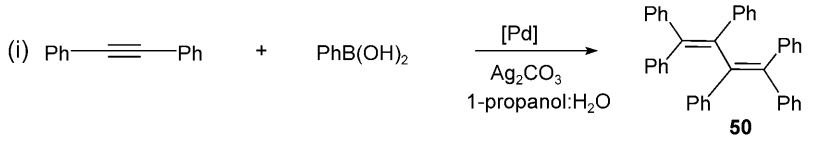


Figure 6. Possible intermediates in the formation of diarylated products.

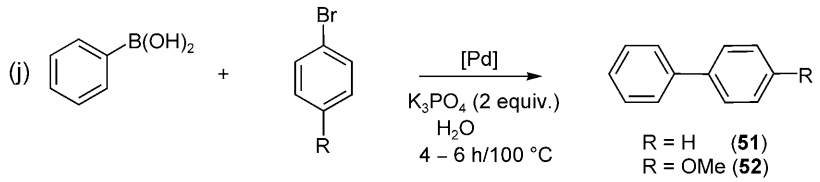
above-mentioned conditions. Attempts towards the isolation of the intermediate/s have not been successful as yet.

To explore the efficacy of our dinuclear palladium(I) catalyst, we have performed a few well known coupling reactions and compared these with the traditional palladium [$Pd(OAc)_2$ and $Pd(PPh_3)_4$] catalyzed reactions[2b,15] as shown in Scheme 6. The results suggest that our catalyst is at least as active as or better than the other catalysts under the similar conditions. The added advantage in the case of **9** is its stability to air. Further work in utilizing the catalyst **9** is underway in our laboratory.[10]



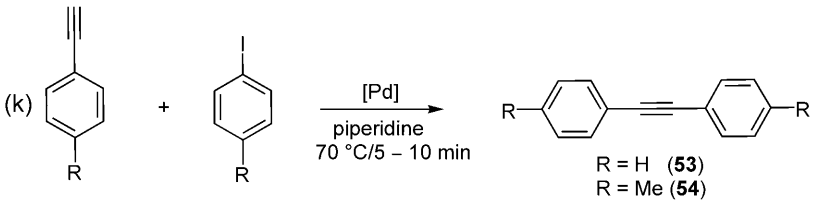
Entry	[Pd] (mol%)	Product	Time [h]	Yield [%][a]
1	**9** (0.5)	**50**	0.5	80
2	$Pd(OAc)_2$ (2.5)	**50**	0.5	67

[a] Isolated yield.



Entry	[Pd] (mol%)	Product	Time [h]	Yield [%][a]
1	**9** (0.5)	**51**	4	82
2	$Pd(PPh_3)_4$ (1.0)	**51**	4	74
3	**9** (0.5)	**52**	6	78
4	$Pd(PPh_3)_4$ (1.0)	**52**	6	76

[a] Isolated yield.



Entry	[Pd] (mol%)	Product	Yield [%][a]
1	**9** (0.5)	**53**	89
2	$Pd(PPh_3)_4$ (1.0)	**53**	87
3	**9** (0.5)	**54**	85
4	$Pd(PPh_3)_4$ (1.0)	**54**	80

[a] Isolated yield.

Scheme 6. Utility of the catalyst **9** in some selected coupling reactions.

Conclusions

A novel Pd-catalyzed protocol for the double arylation of phosphonoalkynes and diarylalkynes in water as the reaction medium has been developed using a new dinuclear Pd(I) catalyst and by the combined use of an aryl iodide and arylboronic acid. The aryl group from the boronic acid preferentially goes to the carbon connected to the phosphonyl group. Despite the heterogeneous nature of the components used, the reaction works well in aqueous medium affording the phosphonate products in yields that are essentially quantitative.

Experimental Section

Chemicals were procured from Aldrich or local manufacturers and were purified when required.[16] ^{1}H, ^{13}C and ^{31}P NMR spectra operating at 400, 100 or 125, and 162 MHz were recorded in $CDCl_3$ solutions, with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). Infrared spectra were recorded neat or by using KBr pellets on an FT/IR spectrometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Microanalyses were performed using a CHNS analyzer. For TLC, glass micro slides were coated with silica gel GF_{254} (mesh size 75μ) and spots were identified using iodine or UV chamber as appropriate. For column chromatography, silica gel of 100–200 mesh size was used. LC-MS data were obtained using electrospray ionization (positive mode) on a C-18 column at a flow rate 0.2 mL min^{-1} using MeOH/water (90:10) as eluent.

Precursors **1–4** were prepared by using a slightly modified version of a literature procedure.[9a] Alkynes $(OCH_2CMe_2CH_2O)P(O)C{\equiv}CCH_3$ (**5**) and $Ph_2P(O)C{\equiv}CCH_3$ (**6**) were synthesized by treatment of corresponding allenes [$(OCH_2CMe_2CH_2O)P(O)CH{=}C{=}CH_2$ and $Ph_2P(O)CH{=}C{=}CH_2$, respectively] with triethylamine (80% yield).[9b] Alkynes **7** and **8** were prepared according to the reported procedure.[9c] The dinuclear palladium(I) catalyst **9** [mp 220 °C (dec); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 15.3$ and 148.0 (d each, $J = 12.2$ Hz)] was prepared by reacting $Pd(PPh_3)_4$ with $(OCH_2CMe_2CH_2O)P(S)H$ in 1:1 molar stoichiometry in 1,4-dioxane at 60 °C.[10,17]

Representative Procedure for the Synthesis of Alkynes 1–4

A solution of phenylacetylene (3.72 g, 36.5 mmol) in THF (5 mL) was added dropwise to a stirred solution of EtMgBr (36.5 mmol) in THF (30 mL) at −10 °C under a nitrogen atmosphere. The contents were stirred further at room temperature for 30 min. To this mixture was added a solution of $(OCH_2CMe_2CH_2O)P(=O)Cl$ (36.5 mmol) in THF (45 mL) dropwise keeping the temperature at −10 °C. After attaining room temperature (25 °C), stirring was continued for further 3 h, the mixture quenched with saturated NH_4Cl solution (10 mL) and extracted with dichloromethane (20 mL). The aqueous layer was washed with dichloromethane (2× 30 mL), the combined organic layer washed thrice (3× 20 mL) with water and brine solution (20 mL), and finally dried over anhydous Na_2SO_4. Removal of the solvent afforded yellow colored gummy material, which was chromatographed (EtOAc/hexane = 3:7) to afford the pure product **1**.

Compounds **2–4** were also synthesized in a manner similar to compound **1** using the same molar quantities.

Compound 1: Isolated yield: 6.10 g (67%); white solid; mp 161–162 °C; IR (KBr): ν = 2975, 2186, 1823, 1489, 1373, 1283, 1055, 1001, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$–7.61 (m, 5H, Ar-*H*), 4.23–4.26 and 3.95–4.04 (2 m, 4H, 2 OCH_2), 1.34 and 0.93 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 132.7$ (d, $J = 2.2$ Hz), 131.0, 128.7, 119.2 (d. $J = 5.4$ Hz, PCC*C*), 100.7 (d, $J = 50.4$ Hz, PC*C*), 77.5, 77.4, 76.5 (d, $J = 287.2$ Hz, P*C*), 32.4 [d, $J = 6.0$ Hz, $C(CH_3)_2$], 22.0, 20.4; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -11.7$; LC/MS: $m/z = 251$ $[M+1]^+$; anal. calcd. for $C_{15}H_{19}O_3P$: C 64.74, H 6.88; found: C 64.82, H 6.87.

Compound 2: Isolated yield: 6.70 g (70%); white solid; mp 172–174 °C; IR (KBr): ν = 2976, 2184, 1605, 1510, 1476, 1372, 1285, 1053, 999, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$ (d, $J = 8.0$, 2H, Ar-*H*), 7.20 (d, $J = 8.0$ Hz, 2H, Ar-*H*), 4.21–4.24 and 3.93–4.01 (2 m, 4H, 2 OCH_2), 2.40 (s, 3H, $C_6H_4CH_3$), 1.33 and 0.91 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 141.7$, 132.7 (d, $J = 2.5$ Hz), 129.5, 116.1 (d, $J = 5.4$ Hz, PCC*C*), 101.3 (d, $J = 51.0$ Hz, PC*C*), 77.4, 77.3, 75.9 (d, $J \sim 295.6$ Hz, P*C*), 32.4 [d, $J = 6.0$ Hz, $C(CH_3)_2$], 21.8, 20.5, 22.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -14.0$; LC/MS: $m/z = 265$ $[M+1]^+$; anal. calcd. for $C_{14}H_{17}O_3P$: C 63.63, H 6.48; found: C 63.49, H 6.53.

Compound 3: Isolated yield: 6.00 g (65%); white solid; mp 125–126 °C; IR (KBr): ν = 2948, 2353, 2168, 1624, 1478, 1373, 1285, 1181, 916, 843 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.48$ [s, 1H, PCC(C=C*H*)], 4.13–4.15 (m, 2H, OCH_2), 3.88–3.96 (m, 2H, OCH_2), 2.17–2.18 [m, 4H, $(CH_2)_2$], 1.62–1.66 [m, 4H, $(CH_2)_2$], 1.30 and 0.90 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 142.6$ (d, $J = 3.1$ Hz), 118.2 (d, $J = 5.7$ Hz, PCC*C*), 103.1 (d, $J = 50.4$ Hz, PC*C*), 77.3, 77.2, 73.8 (d, $J = 290.0$ Hz, P*C*), 32.4 [d, $J = 5.9$ Hz, $C(CH_3)_2$], 28.0, 25.9, 22.0, 21.8, 21.0, 20.5; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -11.1$; LC/MS $m/z = 255$ $[M+1]^+$; anal. calcd. for $C_{13}H_{19}O_3P$: C 61.41, H 7.53; found: C 61.55, H 7.57.

Compound 4: Isolated yield: 6.80 g (72%); brown liquid; IR (neat): ν = 3482, 2932, 2201, 1824, 1634, 1374, 1294, 1188, 1059, 1068, 947, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 4.11$–4.14 and 3.87–3.96 (2 m, 4H, 2 OCH_2), 2.36–2.39 (m, 2H, PCCCH_2), 1.59–1.63 (m, 2H), 1.41–1.44 (m, 2H), 1.29–1.31 (many lines, 7H), 0.89–0.91 (many lines, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 104.9$ (d, $J = 50.7$ Hz, PC*C*), 77.2, 77.1, 68.7 (d, $J = 290.5$ Hz, P*C*), 32.3 [d, $J = 6.0$ Hz, $C(CH_3)_2$], 31.1, 28.5, 27.4_4, 27.4_2, 22.4, 22.0, 20.5, 19.3, 19.2, 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -12.0$; LC/MS $m/z = 259$ $[M+1]^+$; anal. calcd. for $C_{13}H_{23}O_3P$: C 60.45, H 8.98; found: C 60.56, H 9.05.

General Procedure for the Synthesis of Tetrasubstituted Olefins 10–44

A mixture of the alkyne **(1)** (0.10 g, 0.40 mmol), phenylboronic acid (0.15 g, 1.20 mmol), K_2CO_3 (0.17 g, 1.20 mmol), **9** (4.0 mg, 1.0 mol% based on Pd) and iodobenzene (0.16 g,

0.80 mmol) in water (5 mL) was heated under reflux for 0.5 h. The reaction mixture was extracted with EtOAc (2× 20 mL), dried over anhydrous Na_2SO_4, the solvent removed and pure compound **10** was isolated by silica gel column chromatography (EtOAc/hexane = 1:1).

Compounds **11**–**44** were also synthesized similarly by using same molar quantities.

Compound 10: Isolated yield: 0.15 g (92%); white solid; mp 244–246 °C; IR (KBr): ν = 2965, 1591, 1491, 1445, 1372, 1253, 1061, 1013, 980 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.98–7.46 (m, 15H, Ar-*H*), 3.77–3.84 (m, 2H, OCH_2), 3.61 (dd→t, *J* ~10.4 Hz, 2H, OCH_2), 0.99 and 0.70 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 159.4, 141.5, 141.3, 141.1$_3$, 141.0$_6$, 137.4, 137.3, 131.1, 131.0, 129.5, 129.4 (d, $^1J_{P,C}$ = 173.0 Hz), 128.9$_4$, 128.9$_3$, 128.3, 127.8, 127.6, 127.4, 127.1 (d, *J* = 2.0 Hz), 75.7, 75.6, 32.1 [d, *J* = 6.0 Hz, $C(CH_3)_2$], 21.7, 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.2; LC/MS: *m/z* = 405 $[M+1]^+$; anal. calcd. for $C_{25}H_{25}O_3P$: C 74.24, H 6.23; found: C 74.21, H 6.32.

Compound 11: Isolated yield: 0.15 g (87%); white solid; mp 260–262 °C; IR (KBr): ν = 2971, 1589, 1510, 1447, 1252, 1157, 1013, 986 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.45 (m, 2H, Ar-*H*), 7.34–7.35 (m, 3H, Ar-*H*), 7.18 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.00 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.87 (s, 4H, Ar-*H*), 3.72–3.79 (m, 2H, OCH_2), 3.61 (dd→t, *J* ~9.8 Hz, 2H, OCH_2), 2.27 (s, 3H, $C_6H_4CH_3$), 2.19 (s, 3H, $C_6H_4CH_3$), 1.00 and 0.71 (2 s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 158.9, 141.6, 141.5, 138.7, 138.4, 137.2, 136.7, 134.5, 134.4, 130.9, 130.8, 129.6, 129.5, 129.0, 128.3, 128.2, 127.8, 75.7, 75.6, 32.1 [d, *J* = 5.9 Hz, *C*-$(CH_3)_2$], 21.8, 21.2$_1$, 21.1$_5$, 21.1, [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.8; LC/MS: *m/z* = 433 $[M+1]^+$; anal. calcd. for $C_{27}H_{29}O_3P$: C 74.98, H 6.76; found: C 74.81, H 6.91.

Compound 12: Isolated yield: 0.16 g (85%); white solid; mp 216–218 °C; IR (KBr): ν = 2961, 2835, 1611, 1510, 1445, 1252, 1182, 1059, 1009 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.41 (m, 5H, Ar-*H*), 7.21 (d, *J* = 7.2 Hz, 2H, Ar-*H*), 6.88 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.74 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.58 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 3.76–3.83 (m, 5H, $OCH_2 + C_6H_4OCH_3$), 3.69 (s, 3H, $C_6H_4OCH_3$), 3.60 (dd→t, *J* = 10.4 Hz, 2H, OCH_2), 0.98 and 0.71 (2 s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.7, 158.5, 134.0, 133.8, 132.4$_2$, 132.3$_6$, 131.5, 130.1, 130.0, 129.2, 128.2, 127.8, 127.4 (d, *J* = 174.0 Hz, P*C*), 113.5, 113.0, 75.5, 75.4, 55.2, 55.1, 32.1 [d, *J* = 6.0 Hz, $C(CH_3)_2$], 21.7, 21.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.3; LC/MS *m/z* = 465 $[M+1]^+$; anal. calcd. for $C_{27}H_{29}O_5P$: C 69.82, H 6.29; found: C 69.75, H 6.38.

Compound 13: Isolated yield: 0.14 g (86%); white solid; mp 244–246 °C; IR (KBr): ν = 2967, 1586, 1481, 1440, 1250, 1059, 1013, 984 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.28 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.13–7.18 (m, 5H, Ar-*H*), 7.04–7.05 (m, 3H, Ar-*H*), 6.97–6.99 (m, 2H, Ar-*H*), 3.82 (dd→t, *J* ~12.6 Hz, 2H, OCH_2), 3.62 (dd→t, *J* = 10.4 Hz, 2H, OCH_2), 2.36 (s, 3H, $C_6H_4CH_3$), 1.00 and 0.69 (2 s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 159.8, 141.7, 141.5, 138.2, 137.6, 137.5, 131.1, 131.0, 129.7, 129.5, 128.9, 128.6, 128.0, 127.8, 127.6, 127.3, 127.0, 75.6, 75.5, 32.1 [d, *J* = 5.9 Hz, $C(CH_3)_2$], 21.8, 21.4, 21.0, [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.7; LC/MS: *m/z* = 419 $[M+1]^+$; anal. calcd. for $C_{26}H_{27}O_3P$: C 74.62, H 6.50; found: C 74.45, H 6.61.

Compound 14: Isolated yield: 0.14 g (81%); white solid; mp 245–247 °C; IR (KBr): ν = 2961, 1613, 1512, 1404, 1254, 1115, 1063, 1013, 988 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.15–7.18 (m, 4H, Ar-*H*), 6.99 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.86 (br s, 4H, Ar-*H*), 3.78 (dd→t, *J* ~12.8 Hz, 2H, OCH_2), 3.62 (dd→t, *J* = 10.0 Hz, 2H, OCH_2), 2.35 (s, 3H, $C_6H_4CH_3$), 2.26 (s, 3H, $C_6H_4CH_3$), 2.19 (s, 3H, $C_6H_4CH_3$), 1.01 and 0.71 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.5, 159.4, 139.0, 138.8, 138.7, 138.1, 137.2, 136.6, 134.7, 134.6, 131.0, 130.9, 129.7, 129.0, 128.6, 128.5, 128.3, 127.3, 75.7, 75.6, 32.2 (d, *J* = 5.9 Hz, $C(CH_3)_2$), 21.9, 21.4, 21.3, 21.2, 21.1, [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.1; LC/MS: *m/z* = 447 $[M+1]^+$; anal. calcd. for $C_{28}H_{31}O_3P$: C 75.32, H 7.00; found: C 75.36, H 7.12.

Compound 15: Isolated yield: 0.15 g (81%); white solid; mp 208–210 °C; IR (KBr): ν = 2959, 1609, 1512, 1462, 1250, 1181, 1059, 1011, 984 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.15–7.21 (m, 4H, Ar-*H*), 6.87 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 6.73 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 6.57 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 3.74–3.84 (m, 5H, $C_6H_4OCH_3 + OCH_2$), 3.67 (s, 3H, $C_6H_4OCH_3$), 3.61 (dd→t, *J* ~10.6 Hz, 2H, OCH_2), 2.36 (s, 3H, $C_6H_4CH_3$), 0.98 and 0.70 (2 s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 159.1, 158.7, 158.5$_2$, 158.5$_0$, 138.8$_4$,138.7$_7$, 138.0, 134.3, 134.1, 132.4$_4$, 132.3$_9$, 131.5, 130.2, 130.1, 129.2, 128.5, 127.0 (d, *J* = 174.5 Hz), 113.4, 113.0, 75.5, 75.4, 55.1, 55.0, 32.1 [d, *J* = 5.9 Hz, $C(CH_3)_2$], 21.8, 21.4, 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.5; LC/MS: *m/z* = 479 $[M+1]^+$; anal. calcd. for $C_{28}H_{31}O_5P$: C 70.28, H 6.53; found: C 70.41, H 6.52.

Compound 16: Isolated yield: 0.15 g (79%); white solid; mp 192–194 °C; IR (KBr): ν = 2969, 1607, 1441, 1369, 1260, 1213, 1094, 1059, 1005, 982 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.07–7.08 (br m, 8H, Ar-*H*), 6.95 (d, *J* = 6.8 Hz, 2H, Ar-*H*), 3.96 (dd→t, *J* ~12.2 Hz, 2H, OCH_2), 3.56 (dd→t, *J* ~10.2 Hz, 2H, OCH_2), 2.64 (d, *J* = 3.2 Hz, 3H, C≡CCH_3), 1.08 and 0.70 (2 s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 157.4, 142.8, 142.6, 137.6, 137.5, 130.8, 130.7, 128.5, 127.7$_2$, 127.6$_6$, 126.7$_3$, 126.7$_1$, 75.6, 75.5, 32.3 [d, *J* = 6.0 Hz, $C(CH_3)_2$], 24.1 (d, *J* = 7.0 Hz, C≡CCH_3), 21.8, 21.1, [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.2 ; LC/MS: *m/z* = 343 $[M+1]^+$; anal. calcd. for $C_{20}H_{23}O_3P$: C 70.16, H 6.77; found: C 70.32, H 6.82.

Compound 17: Isolated yield: 0.17 g (85%); white solid; mp 179–181 °C; IR (KBr): ν = 2961, 1611, 1510, 1406, 1370, 1258, 1057, 1003, 916 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.83–6.96 (m, 8H, Ar-*H*), 3.87–3.94 (m, 2H, OCH_2), 3.56 (dd→t, *J* ~9.8 Hz, 2H, OCH_2), 2.59 (d, *J* = 3.6 Hz, 3H, C≡CCH_3), 2.23 (s, 3H, $C_6H_4CH_3$), 2.21 (s, 3H, $C_6H_4CH_3$), 1.10 and 0.71 (2 s, 6H, $2CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 156.6, 139.9, 139.6, 136.7, 136.2, 134.6, 134.5, 130.5$_2$, 130.4$_7$, 128.5, 128.4, 127.8, 126.2, 75.7, 75.6, 32.3 [d, *J* = 6.1 Hz, $C(CH_3)_2$], 24.2 (d, *J* = 6.9 Hz, C≡CCH_3), 21.2, 21.1, 21.0, [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 12.8; LC/MS: *m/z* = 372 $[M+1]^+$; anal. calcd. for $C_{22}H_{27}O_3P$: C 71.33, H 7.35; found: C 71.45, H 7.43.

Compound 18: Isolated yield: 0.18 g (84%); white solid; mp 161–163 °C; IR (KBr): ν = 2838, 1605, 1508, 1464, 1291, 1240, 1181, 1059, 1005, 916 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.95–6.98 (m, 2H, Ar-*H*), 6.88 (d, *J* = 8.4 Hz,

2H, Ar-*H*), 6.62–6.67 (m, 4H, Ar-*H*), 3.88–3.94 (m, 2H, OCH_2), 3.72 (s, 3H, $C_6H_4OCH_3$), 3.70 (s, 3H, $C_6H_4OCH_3$), 3.55 (dd→t, J ~10.0 Hz, 2H, OCH_2), 2.58 (d, J=3.6 Hz, 3H, C≡CCH_3), 1.09 and 0.71 (2 s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.4, 158.2$_0$, 158.1$_8$, 156.4, 156.3, 135.1, 134.9, 131.9$_0$, 131.8$_5$, 131.0, 130.0, 129.4, 126.3 (d, $^1J_{P,C}$=173.0 Hz), 113.2$_5$, 113.2$_4$, 113.1, 75.6, 75.5, 55.1, 32.3 [d, J=7.0 Hz, $C(CH_3)_2$], 24.0 (d, J=7.0 Hz, C≡CCH_3), 21.9, 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ=13.1; LC/MS: m/z=403 $[M+1]^+$; anal. calcd. for $C_{22}H_{27}O_5P$: C 65.66, H 6.76; found: C 65.56, H 6.88.

Compound 19: Isolated yield: 0.13 g (80%); white solid; mp 200–202 °C; IR (KBr): ν=2928, 1584, 1489, 1439, 1372, 1252, 1061, 1013, 984 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.03–7.16 (m, 10H, Ar-*H*), 6.09 [br s, 1H, PC=C(C=C*H*)(Ph)], 4.00 (dd→t, J ~11.4 Hz, 2H, OCH_2), 3.60 (dd→t, J=11.4 Hz, 2H, OCH_2), 2.23 (br s, 2H), 2.02 (br s, 2H), 1.63 (br s, 4H), 1.01 and 0.70 (2 s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=163.1, 163.0, 139.1, 138.9, 138.6, 138.4, 137.4, 137.2, 131.2, 129.1, 128.1, 127.5, 127.3, 126.9, 126.3, 75.4, 75.3, 32.2 [d, J=5.3 Hz, $C(CH_3)_2$], 27.5, 25.5, 22.4, 21.7, 21.6, 21.1, [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ=11.7; LC/MS: m/z=409 $[M+1]^+$; anal. calcd. for $C_{25}H_{29}O_3P$: C 73.51, H 7.16; found: C 73.45, H 7.23.

Compound 20: Isolated yield: 0.14 g (82%); white solid; mp 245–247 °C; IR (KBr): ν=2919, 1588, 1510, 1250, 1179, 1061, 1013, 920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.04 (d, J=7.6 Hz, 2H, Ar-*H*), 6.87–6.94 (m, 6H, Ar-*H*), 6.04 [br s, 1H, PC=C(C=C*H*)(*p*-tolyl)], 3.97 (dd→t, J=11.6 Hz, 2H, OCH_2), 3.60 (dd→t, J=10.8 Hz, 2H, OCH_2), 2.21–2.23 (m, 8H, cyclohexenyl CH_2+2$C_6H_4CH_3$), 1.78 (br s, 2H), 1.62 (br s, 4H), 1.02 and 0.71 (2 s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=162.8, 162.6, 138.8, 138.7, 137.2, 136.4, 136.1, 135.9, 134.5, 134.4, 131.2, 131.1, 129.3, 128.4, 128.3, 128.0, 126.5 (d, J=179.3 Hz), 75.4, 75.3, 32.3 [d, J=5.7 Hz, $C(CH_3)_2$], 27.7, 25.6, 21.9, 21.8, 21.3, 22.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ=12.4; LC/MS: m/z=437 $[M+1]^+$; anal. calcd. for $C_{27}H_{33}O_3P$: C 74.29, H 7.62; found: C 74.45, H 7.59.

Compound 21: Isolated yield: 0.15 g (79%); white solid; mp 186–188 °C; IR (KBr): ν=2932, 1607, 1510, 1373, 1248, 1109, 1061, 1011 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.08 (d, J=8.0 Hz, 2H, Ar-*H*), 6.97 (d, J=8.0 Hz, 2H, Ar-*H*), 6.68 (d, J=8.0 Hz, 2H, Ar-*H*), 6.61 (d, J=8.0 Hz, 2H, Ar-*H*), 6.01 [br s, 1H, PC=C(C=C*H*)(*p*-anisyl)], 4.01 (dd→t, J~10.0 Hz, 2H, OCH_2), 3.73 (s, 3H, $C_6H_4OCH_3$), 3.71 (s, 3H, $C_6H_4OCH_3$), 3.59 (dd→t, J=12.0 Hz, 2H, OCH_2), 2.22 (br s, 2H), 1.98 (br s, 2H), 1.63 (br s, 4H), 1.00 and 0.71 (2 s, 6H, 2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=162.5, 162.4, 158.8, 158.3, 138.9, 138.8, 132.6$_3$, 132.5$_8$, 131.2, 130.9, 129.9, 129.8, 128.1$_7$, 128.1$_5$, 125.5 (d, J=181.0 Hz), 113.2, 113.0, 75.2, 75.1, 55.1, 55.0, 32.2 [d, J=6.0 Hz, $C(CH_3)_2$], 27.7, 25.5, 22.5, 21.8, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ=12.8; LC/MS: m/z=469 $[M+1]^+$; anal. calcd. for $C_{27}H_{33}O_5P$: C 69.22, H 7.10; found: C 69.31, H 7.12.

Compound 22: Isolated yield: 0.14 g (86%); white solid; mp 92–94 °C; ^{1}H NMR data are consistent with those reported in the literature;[18] ^{13}C NMR (100 MHz, $CDCl_3$): δ=156.9 (d, J=8.5 Hz), 141.9 (d, J=5.8 Hz), 141.8 (d, J=6.7 Hz), 137.9, 137.8, 134.3, 131.4 (d, J=4.4 Hz), 131.1 (d, J=180.1 Hz), 129.7, 129.4, 127.9, 127.7, 127.6, 127.5, 127.1, 126.9, 61.9$_2$, 61.8$_6$, 16.0$_3$, 15.9$_7$; LC/MS: m/z=393 $[M+1]^+$. See Supporting Information for X-ray structure.

Compound 23: Isolated yield: 0.15 g (84%); white solid; mp 98–100 °C; IR (KBr): ν=2982, 2838, 1605, 1508, 1248, 1179, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.40–7.42 (m, 2H, Ar-*H*), 7.32–7.36 (m, 3H, Ar-*H*), 7.19–7.21 (m, 2H, Ar-*H*), 6.80–6.82 (m, 2H, Ar-*H*), 6.72–6.74 (m, 2H, Ar-*H*), 6.54–6.56 (m, 2H, Ar-*H*), 3.79–3.86 (m, 2H, OCH_2CH_3), 3.75 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.55–3.63 (m, 2H, OCH_2CH_3), 0.98–1.01 (m, 6H, 2 OCH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.5, 158.4, 156.1 (d, J=10.9 Hz), 142.4 (d, J=7.3 Hz), 134.4 (d, J=20.4 Hz), 132.8, 132.7, 131.6, 130.4 (d, J=10.0 Hz), 129.7, 129.2 (d, $^1J_{P,C}$=181.6 Hz, P-*C*), 127.8, 127.6, 113.2, 112.9, 61.8, 61.7, 55.1, 55.0, 16.1, 16.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ=16.5; LC/MS: m/z=453 $[M+1]^+$.

Compound 24: Isolated yield: 0.15 g (88%); gummy material; IR (neat): ν=2978, 2187, 1597, 1491, 1445, 1385, 1238, 1107, 1015 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.45–7.47 (m, 2H, Ar-*H*), 7.29–7.36 (m, 3H, Ar-*H*), 7.24–7.27 (m, 2H, Ar-*H*), 7.10–7.16 (m, 3H, Ar-*H*), 7.00–7.03 (m, 3H, Ar-*H*), 6.91–6.93 (m, 2H, Ar-*H*), 4.37–4.45 [m, 2H, 2 OC*H*$(CH_3)_2$], 1.13 [d, J=6.4 Hz, 6H, OCH$(CH_3)_2$], 0.85 [d, J=6.4 Hz, 6H, OCH$(CH_3)_2$]; ^{13}C NMR (125 MHz, $CDCl_3$): δ=156.3 (d, J=10.0 Hz), 142.5, 142.3, 142.1 (d, J=7.1 Hz), 138.4 (d, J=9.9 Hz), 131.5$_3$, 131.4$_9$, 129.7, 129.6, 128.8, 127.6, 127.5$_4$, 127.4$_7$, 127.4, 127.2 (d, J=10.6 Hz), 126.9, 126.7 (d, J=2.0 Hz), 70.8 (d, J=5.4 Hz), 24.0 (d, J=2.8 Hz), 23.2 (d, J=4.5 Hz), [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ=13.7; LC/MS: m/z=421 $[M+1]^+$.

Compound 25: Isolated yield: 0.16 g (82%); gummy material; IR (neat): ν=2978, 2836, 1605, 1508, 1248, 1179, 1019, 988 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.27–7.40 (m, 4H, Ar-*H*), 7.14–7.20 (m, 2H, Ar-*H*), 7.00–7.02 (m, 1H, Ar-*H*), 6.79–6.90 (m, 3H, Ar-*H*), 6.65–6.72 (m, 2H, Ar-*H*), 6.53–6.55 (m, 1H, Ar-*H*), 4.37–4.46 (m, 2H, 2 OC*H*$(CH_3)_2$), 3.74 and 3.66 (2 s, 6H, OCH_3), 1.11 [d, J=5.6 Hz, 6H, CH-$(CH_3)_2$], 0.89 [d, J=6.8 Hz, 6H, CH$(CH_3)_2$]; ^{13}C NMR (100 MHz, $CDCl_3$): δ=158.4, 156.2, 142.6, 137.5, 135.9, 135.0, 134.8, 132.9, 131.5, 130.8, 129.9, 129.1, 127.5 (d, J=8.7 Hz), 113.5, 113.1, 112.8, 70.8 (d, J=6.7 Hz), 55.1, 55.0, 24.0 (d, J=4.0 Hz), 23.4 (d, J=5.0 Hz), [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ=14.4; LC/MS: m/z=481 $[M+1]^+$.

Compound 26: Isolated yield: 0.13 g (79%); white solid; mp 129–131 °C; IR (KBr): ν=2919, 1589, 1487, 1437, 1192, 1105, 1024, 914 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.62–7.67 (m, 4H, Ar-*H*), 7.31–7.42 (m, 6H, Ar-*H*), 7.01–7.11 (m, 5H, Ar-*H*), 6.79–6.80 (m, 3H, Ar-*H*), 6.71–6.72 (m, 2H, Ar-*H*), 2.53 (d, J=2.8 Hz, 3H, C≡CCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ=157.1, 157.0, 143.4, 143.3, 138.7, 138.6, 134.4, 133.4, 133.3, 132.5, 131.6, 131.5, 131.1$_8$, 131.1$_5$, 130.9, 130.8, 128.2, 128.0, 127.7$_3$, 127.7$_0$, 127.3$_3$, 127.3$_1$, 126.9, 125.9$_3$, 125.9$_1$, 24.6 (d, J=7.0 Hz, C≡CCH_3), [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ=28.7; LC/MS: m/z=395 $[M+1]^+$; anal. calcd. for $C_{27}H_{23}OP$: C 82.21, H 5.88; found: C 82.31, H 5.87.

Compound 27: Isolated yield: 0.15 g (85%); white solid; mp 173–175 °C; IR (KBr): ν=2917, 1894, 1597, 1510, 1435, 1290, 1181, 1113, 1020, 912; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.61–7.63 (m, 4H, Ar-*H*), 7.30–7.41 (m, 6H, Ar-*H*), 6.89–6.91 (m, 4H, Ar-*H*), 6.57–6.62 (m, 4H, Ar-*H*), 2.50 (s, 3H,

C=CCH_3), 2.06 (s, 3H, $C_6H_4CH_3$),1.86 (s, 3H, $C_6H_4CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.8, 156.7, 140.6, 140.5, 136.5, 135.7, 135.6, 135.3$_9$, 135.3$_7$, 134.6, 133.6, 132.8, 131.9, 131.7, 131.6, 131.0$_3$, 131.0$_1$, 130.8, 130.7, 128.4, 128.1, 128.0, 127.8, 24.6 (d, J = 7.0 Hz, C=CCH_3), 21.1, 20.9, [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.9; LC/MS: m/z = 424 $[M+1]^+$; anal. calcd. for $C_{29}H_{27}OP$: C 82.44, H 6.44; found: C 82.51, H 6.41.

Compound 28: Isolated yield: 0.15 g (80%); white solid; mp 120–122 °C; IR (KBr): ν = 3056, 2838, 1750, 1607, 1439, 1377, 1177, 1113, 1032, 910; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.65 (m, 4H, Ar-*H*), 7.32–7.42 (m, 6H, Ar-*H*), 6.96 (d, J = 8.0 Hz, 2H, Ar-*H*), 6.59–6.65 (m, 4H, Ar-*H*), 6.36 (d, J = 8.0 Hz, 2H, Ar-*H*), 3.71 (s, 3H, $C_6H_4OCH_3$), 3.60 (s, 3H, $C_6H_4OCH_3$), 2.50 (s, 3H, C=CCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 157.6, 156.5, 135.8, 135.7, 134.7, 133.6, 132.1, 131.6, 131.5, 131.3, 131.1, 129.3, 128.2, 128.1, 113.1, 112.9, 55.1, 55.0, 24.5 (d, J = 8.0 Hz, C=CCH_3), [the doublet due to $^1J_{P,C}$ was not clear]; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.1; LC/MS: m/z = 455 $[M+1]^+$; anal. calcd. for $C_{29}H_{27}O_3P$: C 76.64, H 5.99; found: C 76.35, H 5.85.

Compound 29: Isolated yield: 0.12 g (60%); white solid; mp 218–220 °C (lit.[2d] mp 222–224 °C); spectral data are consistent with those reported in the literature;[2d] LC/MS: m/z = 333 $[M+1]^+$.

Compound 30: Isolated yield: 0.12 g (58%); white solid; mp 140–142 °C (lit.[2c,19a] mp 143–145 °C); spectral data are consistent with those reported in the literature;[2c,19a] LC/MS: m/z = 361 $[M+1]^+$.

Compound 31: Isolated yield: 0.11 g (55%); white solid; mp 182–184 °C (lit.[19b] mp 186–187 °C); spectral data are consistent with those reported in the literature;[19b] LC/MS: m/z = 393 $[M+1]^+$.

Compound 32: Isolated yield: 0.12 g (66%); white solid; mp 150–152 °C (lit.[11b,19c] mp 146–148 °C; spectral data are consistent with those reported in the literature;[11c,19c] LC/MS: m/z = 347 $[M+1]^+$.

Compound 33: Isolated yield: 0.11 g (62%); white solid; mp 140–142 °C; IR (KBr): ν = 2920, 1904, 1597, 1510, 1443, 1265, 1182, 1111, 1022 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.02–7.09 (m, 5H, Ar-*H*), 6.90–6.91 (m, 12H, Ar-*H*), 2.27 (s, 6H, 2$C_6H_4CH_3$), 2.25 (s, 3H, $C_6H_4CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.4, 141.1$_4$, 141.1$_2$, 140.3, 139.9, 135.8$_1$, 135.7$_9$, 135.7$_6$, 131.4, 131.3, 131.2, 128.3$_4$, 128.2$_8$, 127.6, 126.1, 21.2$_0$, 21.1$_7$; LC/MS: m/z = 375 $[M+1]^+$; anal. calcd. for $C_{29}H_{26}$: C 93.00, H 7.00; found: C 92.85, H 7.06.

Compound 34: Isolated yield: 0.13 g (62%); white solid; mp 139–141 °C; IR (KBr): ν = 2836, 1605, 1508, 1246, 1173, 1107, 1028, 824 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.04–7.26 (m, 5H, Ar-*H*), 6.92–6.99 (m, 8H, Ar-*H*), 6.67 (d, J = 8.0 Hz, 4H, Ar-*H*), 3.77 (s, 6H, 2$C_6H_4OCH_3$), 2.27 (s, 3H, $C_6H_4CH_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9$_3$, 157.8$_8$, 144.5, 141.2, 139.6, 139.2, 136.7, 135.8, 132.5, 131.4, 131.3, 128.3, 127.6, 126.1, 113.1, 55.1, 21.2; LC/MS: m/z = 407 $[M+1]^+$; anal. calcd. for $C_{29}H_{26}O_2$: C 85.68, H 6.45; found: C 85.48, H 6.55.

General Procedure for the Synthesis of Trisubstituted Olefins (45–49)

Alkyne (**1**) (0.10 g, 0.40 mmol), phenylboronic acid (0.05 g, 0.40 mmol), K_2CO_3 (0.06 g, 0.40 mmol), $PdCl_2(PPh_3)_2$ (8.42 mg, 3 mol%) and HOAc (46 μL, 0.80 mmol) in water (2 mL) were refluxed for 2 h. The reaction mixture was extracted with EtOAc (2 × 10 mL), organic layer was dried over anhydrous Na_2SO_4, the solvent removed and pure compound **45** was isolated by silica gel column chromatography (EtOAc/hexane = 1:1).

Compounds **46**–**49**.were synthesized in a manner similar to compound **45** using the same molar quantities.

Compound 45: Isolated yield: 0.09 g (69%); white solid; mp 184–186 °C; IR (KBr): ν = 2974, 1595, 1572, 1471, 1447, 1373, 1263, 1059, 1007, 914 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.42 (m, 10H, Ar-*H*), 6.14 (d, J = 16.0 Hz, 1H, PC*H*=CPh), 3.72–3.82 (m, 4H, OCH_2), 1.13 and 0.85 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 162.1, 141.3, 141.1, 138.3$_3$, 138.2$_6$, 129.8, 129.7, 129.2, 128.4, 128.3, 128.0, 112.3 (d, J = 182.0 Hz), 76.1, 76.0, 32.3 [d, J = 6.2 Hz, $C(CH_3)_2$], 21.8, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.6; LC/MS: m/z = 329 $[M+1]^+$; anal. calcd. for $C_{19}H_{21}O_3P$: C 69.50, H 6.45; found: C 69.71, H 6.31.

Compound 46: Isolated yield: 0.09 g (69%); white solid; mp 180–182 °C; IR (KBr): ν = 2967, 1586, 1508, 1346, 1267, 1059, 1005, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.33 (m, 8H, Ar-*H*), 7.20 (br s, 1H, Ar-*H*), 6.07 (d, J = 16.0 Hz, 1H, PC*H*), 3.75–3.79 (m, 4H, OCH_2), 2.38 (s, 3H, C=C$C_6H_4CH_3$), 1.14 and 0.85 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5$_4$, 162.4$_8$, 141.6, 141.4, 139.3, 135.4$_2$, 135.3$_6$, 129.7, 128.7, 128.4, 128.3, 111.6 (d, J = 181.0 Hz, P*C*H), 76.1, 76.0, 32.3 [d, J = 8.0 Hz, $C(CH_3)_2$], 21.8, 21.4, 21.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.9; LC/MS: m/z = 343 $[M+1]^+$; anal. calcd. for $C_{20}H_{23}O_3P$: C 70.16, H 6.77; found: C 70.35, H 6.69.

Compound 47: Isolated yield: 0.10 g (71%); white solid; mp 88–90 °C; IR (KBr): ν = 2969, 1605, 1572, 1472, 1256, 1055, 999, 947 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.49 (m, 5H, Ar-*H*), 5.95 (d, J = 20.0 Hz, 1H, PC*H*), 4.17 (dd→t, J = 12.0 Hz, 2H, OCH_2), 3.89 (dd→t, J ~10.0 Hz, 2H, OCH_2), 2.55 (s, 3H, C=CCH_3), 1.15 and 1.06 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.2, 141.5 (d, J = 23.0 Hz), 129.0, 128.6 (d, J = 18.0 Hz), 127.1, 126.0, 111.3 (d, J = 186.0 Hz, P*C*H), 75.5$_1$, 75.4$_5$, 32.6 [d, J = 6.0 Hz, *C*-$(CH_3)_2$], 21.6, 21.4, 19.7 (d, J = 7.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 14.0; LC/MS: m/z = 267 $[M+1]^+$; anal. calcd. for $C_{14}H_{19}O_3P$: C 63.15, H 7.19; found: C 63.31, H 7.15.

Compound 48: Isolated yield: 0.08 g (62%); white solid; mp 140–142 °C; IR (KBr): ν = 2934, 1738, 1595, 1263, 1059, 1007, 818 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.45 (m, 2H, Ar-*H*), 7.37–7.38 (m, 3H, Ar-*H*), 6.09 [br s, 1H, PC=C(C=C*H*)(Ph)], 5.79 (d, J = 19.6 Hz, 1H, PC*H*), 4.02–4.09 (m, 2H, OCH_2), 3.88 (dd→t, J ~10.2 Hz, 2H, OCH_2), 2.24 (br s, 2H), 2.00 (br s, 2H), 1.68 (br s, 4H), 1.18 and 0.99 (2 s, 6H, 2 CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 165.8, 139.0, 138.8, 135.6, 135.5, 130.8$_9$, 130.8$_7$, 129.5, 128.5, 127.4, 110.2 (d, J = 186.6 Hz, P*C*H), 75.8$_2$, 75.7$_6$, 32.5 [d, J = 5.8 Hz, $C(CH_3)_2$], 28.0, 25.5, 22.5, 21.8, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ = 13.3. LC/MS: m/z = 333 $[M+1]^+$; anal. calcd. for $C_{19}H_{25}O_3P$: C 68.66, H 7.58; found: C 68.55, H 7.76.

Compound 49: Isolated yield: 0.10 g (77%); white solid; mp 68–70 °C; IR (KBr): ν = 3057, 1595, 1435, 1316, 1231, 1169, 1119, 1101, 995 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77–7.82 (m, 4H, Ar-*H*), 7.36–7.51 (m, 11H, Ar-*H*), 6.14 (d, J = 23.6 Hz, 1H, PC*H*=CCH_3), 2.51 (d, J = 1.2 Hz, 3H, C=

CCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.3_4$, 159.3_2, 142.2, 142.1, 135.3, 134.2, 131.6, 131.5, 131.2, 131.0, 130.9, 129.2, 128.9, 128.6, 128.5, 126.0, 118.4 (d, $J = 103.9$ Hz, P*C*H), 19.7 (d, $J = 7.4$ Hz, CH_3); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 21.6$; LC/MS: $m/z = 317$ $[M-1]^+$; anal. calcd. for $C_{21}H_{19}OP$: C 79.23, H 6.02; found: C 79.35, H 5.88.

Procedure for the Synthesis of Compound 50

A mixture of diphenylacetylene (0.20 g, 1.1 mmol), phenylboronic acid (0.14 g, 1.1 mmol), Ag_2CO_3 (0.31 g, 2.2 mmol), Pd catalyst **9** (6.0 mg, 0.005 mmol) or $Pd(OAc)_2$ (6.5 mg, 0.025 mmol) in 2-propanol/water mixture (2 mL, 9:1) was heated at 120 °C for 0.5 h. The solvent (2-propanol) was removed under vacuum, the mixture extracted with EtOAc (20 mL), dried (Na_2SO_4) and the solvent removed. Pure compound **50** was isolated by silica gel column chromatography (hexane); isolated yield: 0.46 g (80%, by using catalyst **9**), 0.38 g [67%, by using $Pd(OAc)_2$]. Spectral data are consistent with those reported in the literature.[2b]

General Procedure for the Synthesis of Compounds 51 and 52

A mixture of aryl bromide (1.0 mmol), phenylboronic acid (0.15 g, 1.2 mmol), K_3PO_4 (0.44 g, 2.0 mmol), catalyst **9** (5.0 mg, 0.005 mmol) or $Pd(PPh_3)_4$ (12 mg, 0.01 mmol) in water (3 mL) was heated at 100 °C for 4–6 h. The mixture was extracted with diethyl ether (20 mL), dried (Na_2SO_4), the solvent removed and pure compound **51** was isolated by silica gel column chromatography (hexane); isolated yield 0.13 (82%, by using catalyst **9**), 0.11 g [74%, by using $Pd(PPh_3)_4$]. Spectral data are consistent with those reported in the literature.[15a]

Compound 52: Isolated yield: 0.14 g (78%, by using catalyst **9**); 0.13 g [76%, by using $Pd(PPh_3)_4$]. Spectral data are consistent with those reported in the literature.[15a]

General Procedure for the Synthesis of Compounds 53 and 54

A mixture of ArC≡CH (0.5 mmol), aryl iodide (0.6 mmol), Pd catalyst **9** (1.3 mg, 0.0025 mmol) or $Pd(PPh_3)_4$ (2.9 mg, 0.05 mmol) in piperidine (3 mL) was heated at 70 °C for 5–10 min. The reaction mixture was quenched with dil. HCl (5 mL, 10% v/v) and extracted with diethyl ether (2× 20 mL), The combined organic layer was washed with brine solution (10 mL) followed by water (2×10 mL) and dried (Na_2SO_4). The solvent was removed and pure compound **53** was isolated by silica gel column chromatography (hexane); isolated yield: 0.08 g (89%, by using catalyst **9**), 0.078 g [87%, by using $Pd(PPh_3)_4$]. Spectral data are consistent with those reported in the literature.[15b]

Compound 54: Isolated yield: 0.09 g (85%, by using catalyst **9**), 0.08 g [80%, by using $Pd(PPh_3)_4$]. Spectral data are consistent with those reported in the literature.[15c]

Crystal Data

X-ray data for compounds **18**, **22**, **39b** and **40b** were collected on a Bruker AXS SMART or OXFORD diffractometer using Mo-K_α ($\lambda = 0.71073$ Å) radiation. The structures were solved and refined by standard methods.[20] CCDC 78160, CCDC 794596, CCDC 781601 and CCDC 781602 contain the supplementary crystallographic data for the compounds of this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

18: $C_{22}H_{27}O_5P$, $M = 402.41$, triclinic, space group *P-1*, $a = 8.751(2)$, $b = 9.402(2)$, $c = 14.290(3)$ Å, $\alpha = 103.871(3)°$ $\beta = 105.484(3)°$, $\gamma = 101.307(3)°$, $V = 1056.7(4)$ Å^3, $Z = 2$, $m = 0.159$ mm^{-1}, data/restraints/parameters: 5655/0/356, *R* indices $[I > 2\sigma(I)]$: $R1 = 0.0510$ *wR*2 (all data) = 0.1316 [CCDC 781600].

22: $C_{24}H_{25}O_3P$, $M = 392.41$, triclinic, space group *P-1*, $a = 11.2268(12)$, $b = 13.6175(15)$, $c = 15.0322(17)$ Å, $\alpha = 83.132(9)°$ $\beta = 73.282(10)°$, $\gamma = 79.617(9)°$, $V = 2159.4(4)$ Å^3, $Z = 4$, $m = 0.148$ mm^{-1}, data/restraints/parameters: 6211/0/509, *R* indices $[I > 2\sigma(I)]$: $R1 = 0.0688$ *wR*2 (all data) = 0.2017 [CCDC 794596].

39 (major isomer): $C_{21}H_{25}O_3P$, $M = 356.38$, monoclinic, space group *P21/c*, $a = 16.838(5)$, $b = 6.207(2)$, $c = 19.499(6)$ Å, $\beta = 104.944(5)°$, $V = 1969.06(10)$ Å^3, $Z = 4$, $m = 0.155$ mm^{-1}, data/restraints/parameters: 3487/0/230, *R* indices $[I > 2\sigma(I)]$: $R1 = 0.0560$, *wR*2 (all data) = 0.1377 [CCDC 781601].

40 (major isomer): $C_{21}H_{25}O_4P$, $M = 372.38$, monoclinic, space group *P21/c*, $a = 9.309(1)$, $b = 20.331(2)$, $c = 10.625(1)$ Å, $\beta = 99.477(2)°$, $V = 1983.6(3)$ Å^3, $Z = 4$, $m = 0.161$ mm^{-1}, data/restraints/parameters: 3492/0/239, *R* indices $[I > 2\sigma(I)]$: $R1 = 0.0475$, *wR*2 (all data) = 0.1271 [CCDC 781602].

Supporting Information

Spectroscopic and analytical data for compounds **35**–**44**, copies of ^1H and ^{13}C NMR spectra, ORTEP diagram of compound **22**, CIF files (for compounds **18**, **22**, **39b** and **40b**) are available in the Supporting Information.

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