Pd-Catalyzed Oxidative Arylation of Cinnamylphosphonates: An Efficient Synthesis of (*Z*)-Alkenylphosphonates

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Various alkenylphosphonates were prepared *via* the palladium-catalyzed oxidative arylation of cinnamylphosphonates with arenes. The regioselectivity during the β-H elimination of the corresponding alkylpalladium intermediate was governed most likely by steric factors.

Key Words : Palladium, Oxidative arylation, Cinnamylphosphonate, Alkenylphosphonates, Morita-Baylis-Hillman adducts

Introduction

A palladium-catalyzed chelation-assisted arylation of olefins has been studied extensively for the purpose of stereo- and regiocontrol, and multiple arylations.[1-3] Various functional groups such as ester, ketone, amide, imide and amines have been known to act as a directing group (DG), which stabilizes the palladium intermediate by chelation.[1-3] Very recently, we also reported an efficient palladium-catalyzed chelation-assisted oxidative arylation of methyl cinnamates bearing a directing group (DG) at the α-position such as ester, amide, and imide.[3] We were interested in whether the oxygen atom of a phosphonate moiety could chelate with an electrophilic palladium center and stabilize the palladium intermediate or not.

Results and Discussion

The reaction of Morita-Baylis-Hillman (MBH) acetate and triethyl phosphite readily afforded a cinnamylphosphonate *via* the Arbuzov reaction.[4] Thus we selected a cinnamylphosphonate **2a** as a representative model substrate, as shown in Scheme 1. When we examined the reaction of **2a** and benzene in the presence of Pd(TFA)$_2$/AgOAc/PivOH,[5] alkenylphosphonate **4a** was obtained as a major product (69%) along with a low yield (9%) of cinnamylphosphonate **3a**. Alkenylphosphonates are valuable compounds due to their widespread applications in organic synthesis.[6,7] Thus, there have been reported numerous synthetic approaches of alkenylphosphonates[6,7] including a palladium-catalyzed arylation of alkenylphosphonates.[8] In addition, many alkenylphosphonates showed interesting biological properties.[9]

Thus we decided to examine the synthesis of alkenylphosphonates *via* the palladium-catalyzed oxidative arylation from cinnamylphosphonates which derived easily from the acetates of MBH adducts.

According to the palladium-catalyzed chelation-assisted arylation mechanism,[1-3] compound **3a** could be formed as a major product (*vide infra*). Thus, we speculated that compound **4a** might be formed by AgOAc-mediated isomerization process of an initially formed **3a**. However, the reaction of **3a** and AgOAc in benzene (reflux, 24 h) did not produce any trace amount of **4a**, as shown in Scheme 2. The reaction of **4a** and AgOAc also did not produce **3a**. Instead, a treatment of **4a** with DBU (0.2 equiv) in toluene (reflux, 2 h) produced **3a** in high yield (94%),[10] and the result stated that compound **3a** would be thermodynamically more stable than **4a**. From these experiments, we concluded that both compounds **3a** and **4a** must be formed directly from the Pd-catalyzed arylation reaction.
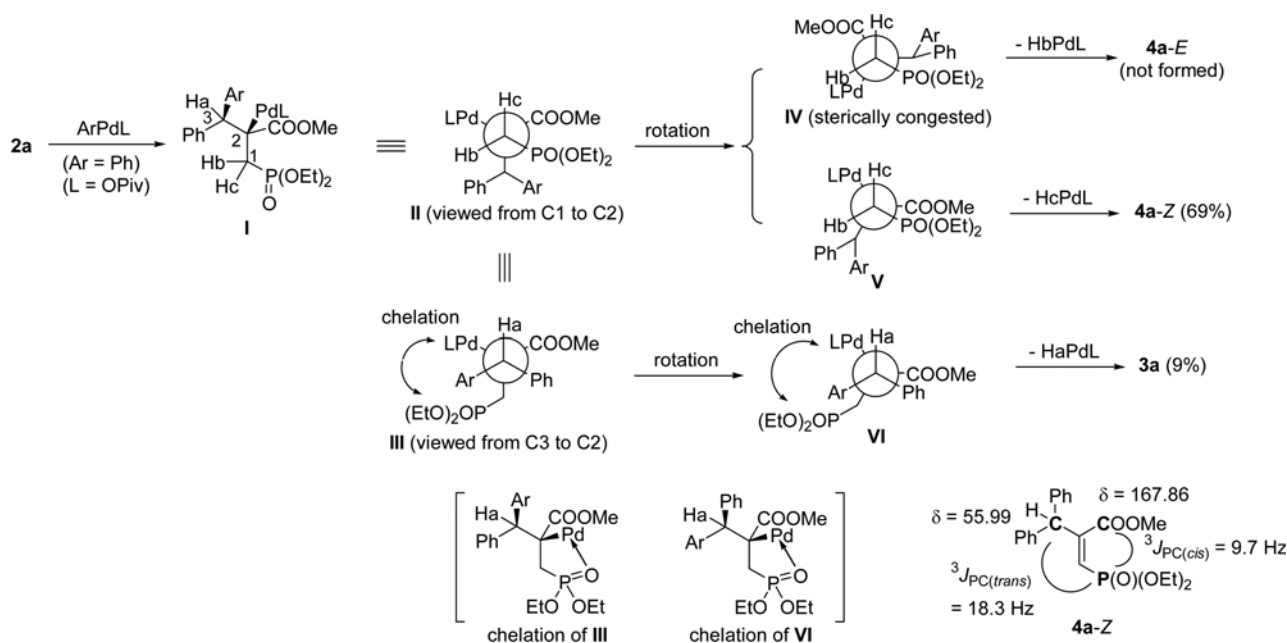
The above results (Schemes 1 and 2) stated that the regioselectivity for β-H elimination was governed by the steric factor rather than the chelation effect between the Pd center and the phosphonate moiety, as shown in Scheme 3. In the arylation reaction of **2a**, three plausible conformers
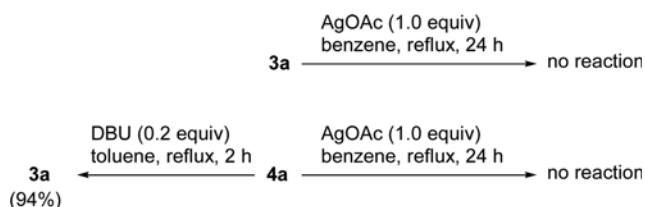
Scheme 2
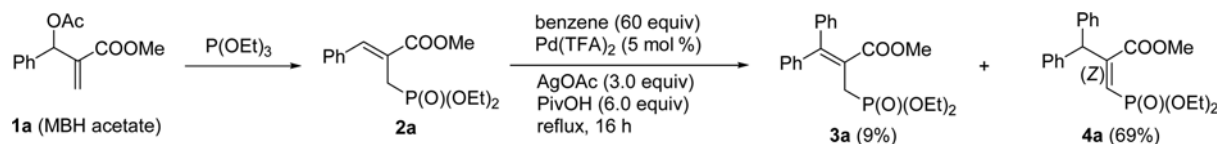
Scheme 1

Scheme 3

IV-VI leading to **4a**-*E*, **4a**-*Z* and **3a** could be suggested after *syn*-carbopalladation of ArPd(OPiv). Compound **4a**-*E* could be formed *via* the β-H$_b$ elimination; however, the corresponding conformer **IV** was sterically too congested to form **4a**-*E*. Actually, compounds **4a**-*Z* and **3a** were formed by - H$_c$Pd(OPiv) *via* **V** and -H$_a$Pd(OPiv) *via* **VI**, respectively. Compound **3a** could be formed as a major product, after rotation around C-C single bond and subsequent β-H$_a$ elimination process, if the chelation effect is strong between the palladium center and the oxygen atom of a phosphonate moiety, as in our previous paper.[3] However, such a chelation effect between palladium and phosphonate seemed relatively weak based on the experimental results. Thus the regioselectivity for β-H elimination was governed by the steric factor rather than the chelation effect, as noted above. The stereochemistry of **4a**-*Z* could be easily deduced by comparison of the coupling constant J_{CP} of **4a** with the reported data.[6c,m] The three-bond coupling constant between the carbonyl carbon (δ = 167.86 ppm) and phosphorous atom is small ($^3J_{PC}$ = 9.7 Hz), and this stated their *cis*-relationship, as shown in Scheme 3. While the *trans* three-bond coupling constant between the benzylic carbon (δ = 55.99 ppm) and the phosphorous atom is large ($^3J_{PC}$ = 18.3 Hz).

Encouraged by the results, we examined the synthesis various alkenylphosphonates **4b-g**, and the results are summarized in Table 1. The reaction of **2a** and *m*-xylene afforded **4b** and **3b** in 47% and 11%, respectively (entry 2). The reaction with *o*-xylene showed a similar result (entry 3) while the reaction of *p*-xylene (entry 4) failed completely presumably due to increased steric hindrance caused by the *ortho*-methyl group.[3,5f,j] The reaction with *o*-dichlorobenzene (entry 5) showed a similar result to that of *o*-xylene. The reactions of **2b** and **2c** with benzene (entries 6 and 7) produced the corresponding alkenylphosphonates **4e** and **4f** in good yields (63% and 68%), respectively. The corresponding cinnamylphosphonates **3e** and **3f** were observed on TLC at the right position in low yield; however, we failed to separate them. The reaction of diisopropylphosphonate derivative **2d** (entry 8) produced **4g** (60%) and **3g** (6%).

The stereochemistry of minor cinnamylphosphonates **3b-d** was *Z*, and the counter stereoisomer (*E*-form) was not formed in the reaction. The result stated that compounds **3b-d** must be formed in a stereoselective manner *via* the chelation-assisted stabilized palladium intermediates **III** and **VI**, as shown in Scheme 3 (*vide supra*). In a sharp contrast, a base (DBU)-mediated isomerization of **4d**, as an example, produced a mixture of *E/Z* isomers, as shown in Scheme 4. The *Z* stereochemistry of **3d**, as an example, was confirmed by NOE experiment, as shown in Scheme 4.

In summary, various alkenylphosphonates were prepared *via* the palladium-catalyzed oxidative arylation of cinnamylphosphonates with arenes. The regioselectivity during the β-H elimination of the corresponding alkylpalladium intermediate was governed most likely by steric factors.

Experimental Section

The preparation of cinnamylphosphonates **2a-d** was carried out according to the literature,[4a-c] and the spectroscopic data of unknown compound **2d** are as follows.

Compound 2d. 87%; colorless oil; IR (film) 1719, 1269, 1007, 985 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.18 (d, *J* = 6.3 Hz, 6H), 1.22 (d, *J* = 6.3 Hz, 6H), 3.13 (d, J_{PH} = 22.5 Hz, 2H), 3.77 (s, 3H), 4.56-4.71 (m, 2H), 7.21-7.36 (m, 3H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.69 (d, J_{PH} = 5.7 Hz, 1H); ^{13}C NMR

Table 1. Synthesis of alkenylphosphonates

| Entry	Substrate	Conditions[a]	Products (%)	
1	**2a**	benzene reflux, 16 h	**4a** (69)	**3a** (9)
2	**2a**	*m*-xylene 110 °C, 20 h Pd(TFA)₂ (8%)	**4b** (47)[b]	**3b** (11)[b]
3	**2a**	*o*-xylene 110 °C, 16 h Pd(TFA)₂ (8%)	**4c** (46)[c]	**3c** (13)[c]
4	**2a**	*p*-xylene 110 °C, 40 h	no reaction	
5	**2a**	ODCB 110 °C, 18 h Pd(TFA)₂ (8%)	**4d** (37)[d]	**3d** (14)[d]
6	**2b**[e]	benzene reflux, 12 h	**4e** (63)[e]	**3e**[e,f]
7	**2c**[g]	benzene reflux, 16 h	**4f** (68)[g]	**3f**[f,g]
8	**2d**	benzene reflux, 16 h	**4g** (60)	**3g** (6)

[a]Conditions: Arenes (60 equiv), Pd(TFA)₂ (5 mol %), AgOAc (3.0 equiv), PivOH (6.0 equiv). [b]Ar¹ is 3,5-dimethylphenyl. [c]Ar² is 3,4-dimethylphenyl. [d]Ar³ is 3,4-dichlorophenyl. [e]Ar⁴ is 4-methylphenyl. [f]Failed to isolate. [g]Ar⁵ is 4-methoxyphenyl.

(CDCl₃, 75 MHz) δ 23.74 (d, J_{PC} = 5.2 Hz), 23.96 (d, J_{PC} = 4.1 Hz), 27.44 (d, J_{PC} = 141.4 Hz), 52.15, 70.63 (d, J_{PC} = 6.9 Hz), 124.19 (d, J_{PC} = 12.0 Hz), 128.43, 128.81, 129.49, 134.80, 140.97 (d, J_{PC} = 10.9 Hz), 168.12; ESIMS *m/z* 341 [M+H]⁺. Anal. Calcd. For $C_{17}H_{25}O_5P$: C, 59.99; H, 7.40. Found: C, 60.12; H, 7.27.

Typical Procedure for the Synthesis of 3a and 4a. A stirred mixture of **2a** (156 mg, 0.5 mmol), Pd(TFA)₂ (8 mg, 0.025 mmol), AgOAc (250 mg, 1.5 mmol) and PivOH (306 mg, 3.0 mmol) in benzene (2.35 g, 30 mmol) was heated to reflux under nitrogen atmosphere for 16 h. After cooling to room temperature, the reaction mixture was filtered over a pad of Celite and washed with CH₂Cl₂ (100 mL). The filtrates were washed with a saturated solution of NaHCO₃ (20 mL × 3), and the organic layer was dried over MgSO₄. After removal of solvent and column chromatographic purification process (hexanes/acetone, 3:1) compound **3a** (17 mg, 9%) and **4a** (134 mg, 69%) were isolated as colorless oils. Other compounds were synthesized similarly, and the spectroscopic data of **4a-g**, **3a-c**, **3d-Z**, **3d-E**, and **3g** are as follows.

Compound 4a. 69%; colorless oil; IR (film) 1734, 1624, 1495, 1450, 1435, 1261, 1213, 1052, 1025, 966 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 1.29 (t, *J* = 7.2 Hz, 6H), 3.67 (s, 3H), 4.01-4.14 (m, 4H), 5.34 (t, J_{PH} = 2.1 Hz, J_{HH} = 2.1 Hz, 1H), 5.42 (dd, J_{PH} = 14.1 Hz, J_{HH} = 2.1 Hz, 1H), 7.14-7.18 (m, 4H), 7.21-7.34 (m, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 16.25 (d, J_{PC} = 6.3 Hz), 52.38, 55.99 (d, J_{PC} = 18.3 Hz), 62.02 (d, J_{PC} = 5.8 Hz), 122.56 (d, J_{PC} = 184.9 Hz), 127.25, 128.62, 129.24, 139.11, 155.56 (d, J_{PC} = 4.1 Hz), 167.86 (d, J_{PC} = 9.7 Hz); ³¹P NMR (CDCl₃, 202 MHz) δ 14.25; ESIMS *m/z* 389 [M+H]⁺. Anal. Calcd. For $C_{21}H_{25}O_5P$: C, 64.94; H, 6.49. Found: C, 64.76; H, 6.71.

Compound 4b. 47%; colorless oil; IR (film) 1734, 1260, 1213, 1053, 1025, 966 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 1.22 (t, *J* = 7.2 Hz, 6H), 2.18 (s, 6H), 3.60 (s, 3H), 3.95-4.06 (m, 4H), 5.18 (t, J_{PH} = 2.1 Hz, J_{HH} = 2.1 Hz, 1H), 5.35 (dd, J_{PH} = 14.1 Hz, J_{HH} = 2.1 Hz, 1H), 6.69 (s, 2H), 6.80 (s, 1H),

Scheme 4
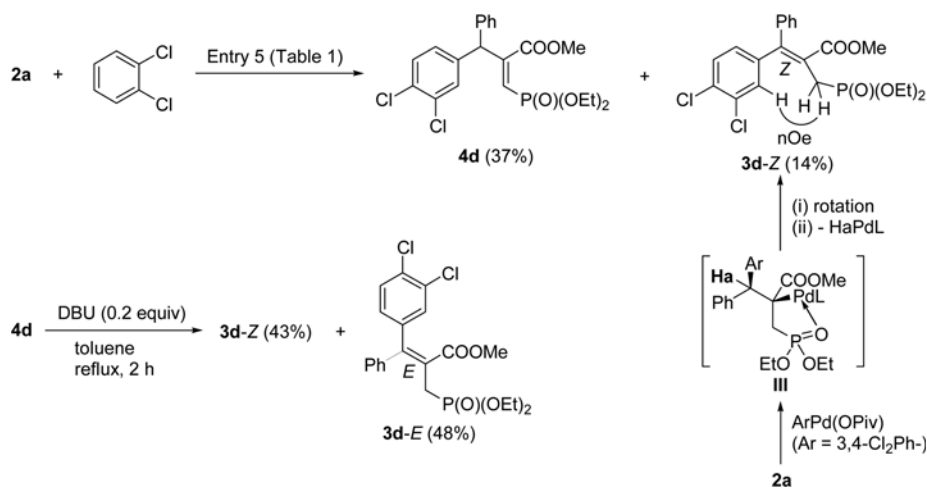
7.06-7.10 (m, 2H), 7.13-7.26 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.23 (d, J_{PC} = 6.3 Hz), 21.25, 52.36, 55.91 (d, J_{PC} = 17.8 Hz), 62.02 (d, J_{PC} = 5.2 Hz), 122.27 (d, J_{PC} = 185.5 Hz), 127.03, 127.14, 128.56, 128.93, 129.23, 138.04, 138.89, 139.29, 155.82 (d, J_{PC} = 4.0 Hz), 167.94 (d, J_{PC} = 9.8 Hz); ESIMS *m/z* 417 [M+H]$^+$. Anal. Calcd. For C$_{23}$H$_{29}$O$_5$P: C, 66.33; H, 7.02. Found: C, 66.28; H, 7.24.

Compound 4c. 46%; colorless oil; IR (film) 1734, 1261, 1214, 1053, 1025, 966 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.30 (t, J = 7.2 Hz, 6H), 2.21 (s, 3H), 2.23 (s, 3H), 3.68 (s, 3H), 4.03-4.14 (m, 4H), 5.28 (t, J_{PH} = 1.8 Hz, J_{HH} = 1.8 Hz, 1H), 5.44 (dd, J_{PH} = 14.1 Hz, J_{HH} = 1.8 Hz, 1H), 6.89 (d, J = 7.8 Hz, 1H), 6.92 (s, 1H), 7.07 (d, J = 7.8 Hz, 1H), 7.14-7.18 (m, 2H), 7.21-7.34 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.27 (d, J_{PC} = 5.7 Hz), 19.35, 19.78, 52.38, 55.69 (d, J_{PC} = 17.8 Hz), 62.05 (d, J_{PC} = 5.7 Hz), 122.15 (d, J_{PC} = 185.4 Hz), 126.50, 127.13, 128.59, 129.22, 129.82, 130.52, 135.57, 136.40, 136.83, 139.46, 155.97 (d, J_{PC} = 4.0 Hz), 168.00 (d, J_{PC} = 9.7 Hz); ESIMS *m/z* 417 [M+H]$^+$. Anal. Calcd. For C$_{23}$H$_{29}$O$_5$P: C, 66.33; H, 7.02. Found: C, 66.51; H, 7.19.

Compound 4d. 37%; colorless oil; IR (film) 1735, 1259, 1215, 1052, 1028, 967 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.22 (t, J = 7.2 Hz, 6H), 3.62 (s, 3H), 3.96-4.07 (m, 4H), 5.21 (t, J_{PH} = 1.8 Hz, J_{HH} = 1.8 Hz, 1H), 5.36 (dd, J_{PH} = 13.2 Hz, J_{HH} = 1.8 Hz, 1H), 6.96 (dd, J = 8.4 and 2.1 Hz, 1H), 7.03-7.06 (m, 2H), 7.18-7.34 (m, 5H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.26 (d, J_{PC} = 6.3 Hz), 52.59, 54.97 (d, J_{PC} = 17.8 Hz), 62.20 (d, J_{PC} = 5.7 Hz), 123.43 (d, J_{PC} = 186.0 Hz), 127.75, 128.53, 128.92, 129.08, 130.59, 131.12, 131.55, 132.81, 138.01, 139.49, 154.20 (d, J_{PC} = 4.6 Hz), 167.47 (d, J_{PC} = 9.8 Hz); ESIMS *m/z* 457 [M+H]$^+$, 459 [M+H+2]$^+$, 461 [M+H+4]$^+$. Anal. Calcd. For C$_{21}$H$_{23}$Cl$_2$O$_5$P: C, 55.16; H, 5.07. Found: C, 55.45; H, 4.96.

Compound 4e. 63%; colorless oil; IR (film) 1734, 1260, 1215, 1053, 1025, 966 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.21 (t, J = 7.2 Hz, 6H), 2.24 (s, 3H), 3.59 (s, 3H), 3.94-4.06 (m, 4H), 5.22 (t, J_{PH} = 1.8 Hz, J_{HH} = 1.8 Hz, 1H), 5.34 (dd, J_{PH} = 13.8 Hz, J_{HH} = 1.8 Hz, 1H), 6.95-7.09 (m, 6H), 7.12-7.28 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.20 (d, J_{PC} = 6.3 Hz), 20.94, 52.32, 55.61 (d, J_{PC} = 17.8 Hz), 61.97 (d, J_{PC} = 5.8 Hz), 122.18 (d, J_{PC} = 185.4 Hz), 127.12, 128.54, 129.04, 129.14, 129.29, 135.97, 136.84, 139.29, 155.81 (d, J_{PC} = 4.1 Hz), 167.89 (d, J_{PC} = 9.8 Hz); ESIMS *m/z* 403 [M+H]$^+$. Anal. Calcd. For C$_{22}$H$_{27}$O$_5$P: C, 65.66; H, 6.76. Found: C, 65.58; H, 6.94.

Compound 4f. 68%; colorless oil; IR (film) 1734, 1257, 1214, 1052, 1028, 966 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.21 (t, J = 7.2 Hz, 6H), 3.59 (s, 3H), 3.70 (s, 3H), 3.94-4.07 (m, 4H), 5.21 (t, J_{PH} = 1.8 Hz, J_{HH} = 1.8 Hz, 1H), 5.33 (dd, J_{PH} = 14.1 Hz, J_{HH} = 1.8 Hz, 1H), 6.76 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 7.05-7.09 (m, 2H), 7.15-7.26 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.21 (d, J_{PC} = 6.3 Hz), 52.33, 55.12, 55.22 (d, J_{PC} = 17.8 Hz), 61.98 (d, J_{PC} = 5.7 Hz), 113.98, 122.05 (d, J_{PC} = 185.5 Hz), 127.14, 128.56, 129.10, 130.25, 131.03, 139.41, 155.97 (d, J_{PC} = 4.0 Hz), 158.64, 167.93 (d, J_{PC} = 9.8 Hz); ESIMS *m/z* 419 [M+H]$^+$. Anal. Calcd. For C$_{22}$H$_{27}$O$_6$P: C, 63.15; H, 6.50. Found: C, 63.46; H, 6.82.

Compound 4g. 60%; colorless oil; IR (film) 1735, 1260, 1215, 1006, 983 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.17 (d, J = 6.3 Hz, 6H), 1.22 (d, J = 6.3 Hz, 6H), 3.59 (s, 3H), 4.52-4.68 (m, 2H), 5.26 (t, J_{PH} = 1.8 Hz, J_{HH} = 1.8 Hz, 1H), 5.32 (dd, J_{PH} = 13.5 Hz, J_{HH} = 1.8 Hz, 1H), 7.07-7.10 (m, 4H), 7.14-7.27 (m, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 23.71 (d, J_{PC} = 4.6 Hz), 23.98 (d, J_{PC} = 4.0 Hz), 52.32, 55.97 (d, J_{PC} = 17.7 Hz), 70.67 (d, J_{PC} = 5.7 Hz), 123.87 (d, J_{PC} = 184.9 Hz), 127.22, 128.59, 129.27, 139.25, 154.80 (d, J_{PC} = 4.6 Hz), 168.09 (d, J_{PC} = 9.8 Hz); ESIMS *m/z* 417 [M+H]$^+$. Anal. Calcd. For C$_{23}$H$_{29}$O$_5$P: C, 66.33; H, 7.02. Found: C, 66.16; H, 7.39.

Compound 3a. 9%; colorless oil; IR (film) 1718, 1261, 1156, 1053, 1026, 965 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.24 (t, J = 7.2 Hz, 6H), 2.96 (d, J_{PH} = 21.9 Hz, 2H), 3.38 (s, 3H), 3.98-4.08 (m, 4H), 7.02-7.05 (m, 2H), 7.16-7.32 (m, 8H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.27 (d, J_{PC} = 6.3 Hz), 30.41 (d, J_{PC} = 140.8 Hz), 51.56, 61.96 (d, J_{PC} = 6.2 Hz), 123.17 (d, J_{PC} = 10.3 Hz), 127.67, 127.89, 128.11, 128.15, 128.42, 129.41, 139.77, 141.88, 149.44 (d, J_{PC} = 13.2 Hz), 170.08; ^{31}P NMR (CDCl$_3$, 202 MHz) δ 25.67; ESIMS *m/z* 389 [M+H]$^+$. Anal. Calcd. For C$_{21}$H$_{25}$O$_5$P: C, 64.94; H, 6.49. Found: C, 65.05; H, 6.34.

Compound 3b. 11%; colorless oil; IR (film) 1718, 1256, 1109, 1054, 1026 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 2.21 (s, 6H), 2.96 (d, J_{PH} = 21.9 Hz, 2H), 3.38 (s, 3H), 3.98-4.08 (m, 4H), 6.87 (s, 1H), 6.89 (s, 2H), 7.03-7.06 (m, 2H), 7.15-7.23 (m, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.36 (d, J_{PC} = 6.3 Hz), 21.20, 30.48 (d, J_{PC} = 140.8 Hz), 51.57, 61.93 (d, J_{PC} = 6.3 Hz), 122.95 (d, J_{PC} = 10.3 Hz), 127.01, 127.61, 127.88, 128.39, 129.78, 137.71, 139.74, 141.95, 149.86 (d, J_{PC} = 13.1 Hz), 170.19; ESIMS *m/z* 417 [M+H]$^+$. Anal. Calcd. For C$_{23}$H$_{29}$O$_5$P: C, 66.33; H, 7.02. Found: C, 66.54; H, 7.07.

Compound 3c. 13%; colorless oil; IR (film) 1718, 1265, 1053, 1026, 965 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 2.16 (s, 3H), 2.18 (s, 3H), 2.99 (d, J_{PH} = 21.6 Hz, 2H), 3.37 (s, 3H), 3.99-4.08 (m, 4H), 7.02-7.06 (m, 5H), 7.16-7.21 (m, 3H)HHh; ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.35 (d, J_{PC} = 6.3 Hz), 19.50, 19.65, 30.54 (d, J_{PC} = 140.4 Hz), 51.54, 61.96 (d, J_{PC} = 6.2 Hz), 122.68 (d, J_{PC} = 9.8 Hz), 126.97, 127.59, 127.87, 128.48, 129.41, 130.53, 136.38, 136.73, 137.39, 142.19, 149.86 (d, J_{PC} = 12.6 Hz), 170.30; ESIMS *m/z* 417 [M+H]$^+$. Anal. Calcd. For C$_{23}$H$_{29}$O$_5$P: C, 66.33; H, 7.02. Found: C, 66.39; H, 6.89.

Compound 3d-Z. 14%; colorless oil; IR (film) 1720, 1271, 1052, 1028, 967 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.26 (t, J = 7.2 Hz, 6H), 2.93 (d, J_{PH} = 22.2 Hz, 2H), 3.39 (s, 3H), 4.00-4.10 (m, 4H), 6.99-7.03 (m, 2H), 7.17-7.24 (m, 4H), 7.36 (d, J = 8.1 Hz, 1H), 7.48 (d, J = 2.1 Hz, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.36 (d, J_{PC} = 6.3 Hz), 30.64 (d, J_{PC} = 141.4 Hz), 51.78, 62.23 (d, J_{PC} = 6.8 Hz), 124.58 (d, J_{PC} = 10.3 Hz), 128.20 (2C), 128.48, 129.07, 130.30, 131.42, 132.50, 132.56, 139.63, 140.93, 146.95 (d, J_{PC} = 12.6 Hz), 169.70; ESIMS *m/z* 457 [M+H]$^+$, 459 [M+H+2]$^+$, 461 [M+H+4]$^+$. Anal. Calcd. For C$_{21}$H$_{23}$Cl$_2$O$_5$P: C, 55.16; H,

5.07. Found: C, 55.34; H, 5.22.

Compound 3d-*E*. 48%; colorless oil; IR (film) 1721, 1269, 1053, 1028, 966 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.25 (t, J = 7.2 Hz, 6H), 2.95 (d, J_{PH} = 21.9 Hz, 2H), 3.48 (s, 3H), 3.98-4.08 (m, 4H), 6.89 (dd, J = 8.4 and 2.1 Hz, 1H), 7.13 (d, J = 2.1 Hz, 1H), 7.25-7.30 (m, 6H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 16.33 (d, J_{PC} = 6.3 Hz), 30.51 (d, J_{PC} = 140.9 Hz), 51.92, 62.12 (d, J_{PC} = 6.3 Hz), 124.72 (d, J_{PC} = 10.3 Hz), 127.87, 128.49, 128.62, 129.37, 129.96, 130.33, 131.94, 132.23, 138.82, 141.78, 147.00 (d, J_{PC} = 12.6 Hz), 169.37; ESIMS *m/z* 457 [M+H]$^+$, 459 [M+H+2]$^+$, 461 [M+H+4]$^+$. Anal. Calcd. For C$_{21}$H$_{23}$Cl$_2$O$_5$P: C, 55.16; H, 5.07. Found: C, 55.43; H, 5.31.

Compound 3g. 6%; colorless oil; IR (film) 1719, 1259, 1006, 984 cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.22 (d, J = 6.3 Hz, 6H), 1.25 (d, J = 6.3 Hz, 6H), 2.92 (d, J_{PH} = 22.2 Hz, 2H), 3.38 (s, 3H), 4.57-4.72 (m, 2H), 7.02-7.05 (m, 2H), 7.14-7.35 (m, 8H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 23.85 (d, J_{PC} = 4.6 Hz), 24.01 (d, J_{PC} = 4.0 Hz), 31.84 (d, J_{PC} = 142.5 Hz), 51.52, 70.65 (d, J_{PC} = 6.9 Hz), 123.72 (d, J_{PC} = 10.4 Hz), 127.59, 127.90, 128.04, 128.09, 128.49, 129.62, 139.85, 142.07, 148.75 (d, J_{PC} = 12.6 Hz), 170.11; ESIMS *m/z* 417 [M+H]$^+$. Anal. Calcd. For C$_{23}$H$_{29}$O$_5$P: C, 66.33; H, 7.02. Found: C, 66.17; H, 7.34.

References and Notes

1. For some selected Pd-catalyzed chelation-assisted arylation of olefins with arenes, see: (a) Li, Z.; Zhang, Y.; Liu, Z.-Q. *Org. Lett.* **2012**, *14*, 74. (b) Zhang, Y.; Li, Z.; Liu, Z.-Q. *Org. Lett.* **2012**, *14*, 226. (c) Shang, X.; Xiong, Y.; Zhang, L.; Liu, Z.-Q. *Synlett* **2012**, 259. (d) Pan, D.; Yu, M.; Chen, W.; Jiao, N. *Chem. Asian J.* **2010**, *5*, 1090. (e) Pan, D.; Jiao, N. *Synlett* **2010**, 1577 and further references cited therein.

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