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Palladium-catalyzed cross-coupling of aryl and alkenyl boronic acids with alkenes via oxidative addition of a carbon–boron bond to palladium(0)

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Abstract

Arylboronic acids react with alkenes in acetic acid at 25°C in the presence of a catalytic amount of palladium(II) acetate together with sodium acetate to give the corresponding aryl-substituted alkenes in high yields. Alkenylboronic acids react with alkenes under similar conditions to give the corresponding conjugated dienes stereospecifically, but the product yields are lower, compared with those from arylboronic acids. Similar treatment of sodium tetraphenylborate ($NaBPh_4$) with alkenes also affords the corresponding phenylated alkenes in high yields together with biphenyl and benzene as side products. Oxidative addition of a carbon–boron bond to palladium(0), formed *in situ*, to give an organopalladium(II) species is assumed to be the key step of these cross-coupling reactions.

Key words: Boronic acid; Aryl; Alkenyl; Alkene; Palladium; Oxidative addition

1. Introduction

Palladium-catalyzed cross-coupling reactions of aryl- and vinyl boron compounds with aryl- and vinyl halides (Br, I) and aryl triflates have been recognized as a very important and useful synthetic tool [1]. Thus, the reaction has been effectively applied to the synthesis of natural products and their related compounds such as *trans* (C_{10})-allofarnesene [2], pheromone bombykol [3], 5-arylnicotinates [4], trisporol B [5], isoflavones [6], and 9-demethylretinoids [7]. In contrast to the above reports, although Dieck and Heck partly investigated the stereospecific cross-coupling reactions of vinylboronic acids with alkenes in the presence of a stoichiometric amount of palladium(II) acetate [8], relatively little is known about the transition metal catalyzed cross-coupling of the organoboronic acids with alkenes to give the arylated and alkenylated alkenes (Heck-type reaction). On the other hand, one of us reported recently that tetrakis(triphenylphosphine)palladium(0) catalyzed the carbonylation of aryl- and alkenyl borates and -boronic acids and predicted that the reaction proceeded via oxidative addition of a carbon–boron bond to palladium(0) [9], this prediction having so far been made only for certain limited examples [10]. We here report [11] the palladium(0)-catalyzed cross-coupling reactions of aryl- and alkenyl boronic acids or tetraphenylborate anion with alkenes as another example of a putative oxidative addition of a carbon–boron bond to Pd^0.

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2. Results and discussion

2.1. Cross-coupling of arylboronic acids with alkenes

Treatment of benzeneboronic acid (1 mmol) with styrene (1.2 mmol) in acetic acid (10 ml) in the presence of a catalytic amount of palladium(II) acetate (0.05 mmol) and sodium acetate (4 mmol) at 25°C for 20 h afforded *trans*-stilbene (0.99 mmol, 99% yield based on $PhB(OH)_2$) together with a trace amount of *cis*-isomer, while the stilbene was obtained only in 10% yield in the absence of sodium acetate. The reaction also proceeded using other bases such as lithium acetate, sodium ethoxide, and potassium carbonate in place of sodium acetate, but the product yield was

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generally lower (26–51%) even at 85°C and for 5–20 h. Even in the presence of sodium acetate, bis(triphenylphosphine)palladium(II) dichloride and palladium(II) chloride were almost ineffective for this cross-coupling (0–6%). Many solvents other than acetic acid such as methanol, tetrahydrofuran, acetonitrile, dimethylformamide, and benzene were ineffective, the yield of stilbene being lower (14–16%) with biphenyl (1–16%) being formed as a side product. The reaction can be applied to various alkenes (**2**) such as 4-methylstyrene, 1,1-diphenylethylene, methyl and ethyl acrylates, and *trans*-stilbene, and also to various easily available arylboronic acids (**1**), the stereochemistry of the arylated alkenes (**3**) being always almost *trans* (Scheme 1). The presence of an electron-withdrawing group such as Cl and NO_2 on aromatic ring of the boronic acid (**1**) lowered the product yield. Typical results are summarized in Table 1.

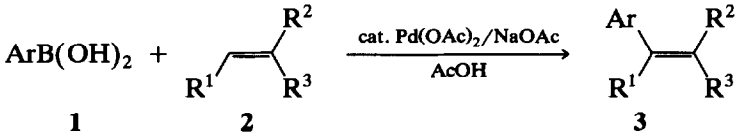
Cross-coupling reaction of benzeneboronic acid (**1a**) with 2-substituted propenes (**4**) gave the double phenylated product (**7**) together with the expected mono-phenylation compounds **5** and **6** as has been observed in Pd^{II}-catalyzed phenylation with $NaBPh_4$ [12] (Scheme 2). The ratio of compounds **5**, **6**, and **7** was dependent on the nature of the alkenes as well as on the molar ratio between both substrates as shown in Table 2. Since it was not possible to separate these three compounds, the total yield and the product distribution were analyzed from the intensity of the clearly separated protons in the ^1H NMR spectrum (see Experimental section). The use of a larger amount of the boronic acid favoured the formation of the compound **7** as expected which will be derived from the compound **5** (*vide infra*). With 2,3,3-trimethyl-1-butene (**4d**), the compound **6d** was the main product and the compound **5d** as well as the double phenylation product **7d** were formed only slightly. **6d** seems to be thermodynamically far more stable than **5d** because of resonance stabilization in the former.

TABLE 1. Palladium(0)-catalyzed cross-coupling of arylboronic acids (**1**) with alkenes (**2**) [a]

Arylboronic acid	Alkene (mmol)	Reaction time (h)	Product and yield (%) [b]
1a	**2g** (1.2)	20	**3ag** 99
1a	**2h** (1)	20	**3ah** 99
1a	**2i** (1)	20	**3ai** 98, 88 [c]
1a	**2j** (1)	27	**3aj** 69
1a	**2k** (1.2)	20	**3ak** 73
1a	**2l** (1)	20	**3al** 63
1b	**2g** (1.2)	20	**3bg** 86
1c	**2g** (1.2)	20	**3cg** 97
1d	**2g** (1.2)	24	**3dg** 39 [c]
1e [d]	**2g** (1.2)	24	**3eg** 64 [c]
1f	**2g** (1.2)	20	**3fg** 63 [c,e]

[a] All reactions were carried out with arylboronic acid (1 mmol), $Pd(OAc)_2$ (0.05 mmol), and NaOAc (4 mmol) in AcOH (10 ml) at 25°C. [b] GLC yield based on **1**. Products are almost all *trans*. [c] Isolated yield. [d] AcOH (20 ml). [e] Other product; naphthalene (13%).

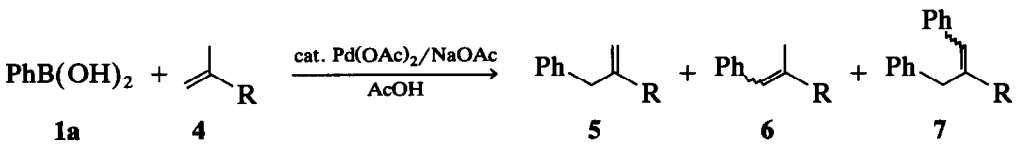
In the reaction of benzeneboronic acid with allyl acetate, the expected cinnamyl acetate was obtained in only 5% yield together with a trace amount of allylbenzene. Here, the main product was benzene (*ca.* 50%). The formation of benzene is due to the protodeboronation of benzeneboronic acid as has been clarified by Kuivila and Nahabedian [13]. It may be conceivable that the formation of stable π-allylpalladium(II) acetate complex (**8**) by oxidative addition of allyl acetate to Pd^0, formed *in situ*, hinders the cross-coupling to give cinnamyl acetate. Although Suzuki *et al.* reported that 1-alkenylboranes cross-coupled with π-allylpalladium(II) complexes [1e], we confirmed in a separate experiment that benzeneboronic acid did not cross-couple with **8** under our reaction conditions (Scheme 3). With allyl bromide, the product was only allylbenzene (23%) as has been observed in the palladium(II)-catalyzed reaction with phenylmercury(II) compound [14], diphenyltellurium(IV) compound [15], and sodium tetraphenylborate [12]. In this case the



1 **2** **3**

a; Ar = Ph
b; Ar = 4-MeC_6H_4
c; Ar = 4-$MeOC_6H_4$
d; Ar = 4-ClC_6H_4
e; Ar = 3-$NO_2C_6H_4$
f; Ar = 1-naphthyl
g; $R^1 = R^2 = H$, $R^3 = Ph$
h; $R^1 = R^2 = H$, R^3 = 4-MeC_6H_4
i; $R^1 = H$, $R^2 = R^3 = Ph$
j; $R^1 = R^2 = Ph$, $R^3 = H$
k; $R^1 = R^2 = H$, $R^3 = CO_2Me$
l; $R^1 = R^2 = H$, $R^3 = CO_2Et$

Scheme 1.



1a 4 5 6 7

a; R = CO_2Et
b; R = CO_2Me
c; R = Ph
d; R = $C(CH_3)_3$

Scheme 2.

amount of benzene, which might be formed as well, was not determined.

2.2. Cross-coupling of alkenylboronic acids with alkenes

We then examined the cross-coupling reaction of alkenylboronic acids with alkenes by taking account of previous results (Scheme 4). Treatment of an equimolar amount of (*E*)-2-phenylethenylboronic acid (**9a**) with ethyl acrylate (**10c** = **2l**) under the conditions similar to the arylboronic acid case afforded the cross-coupling product (**12ac**), ethyl (2*E*,4*E*)-5-phenyl-2,4-pentadienoate, stereospecifically in 16% yield together with the homo-coupling product (**13a**), (1*E*,3*E*)-1,4-diphenyl-1,3-butadiene (14% yield), and styrene (**11a**) (25% yield). Here, styrene was clearly produced by protodeboronation of **9a**, because protonolysis of alkenylboron compounds with acetic acid has been well known [16*]. With a longer reaction time (44 h) the yield of **12ac** was not improved. Although it was reported that the acid **9a** homo-coupled effectively in the presence of palladium(II) salt [17], under our reaction system the homo-coupling seemed to proceed between **9a** and styrene, *i.e.* by a cascade reaction. In order to confirm this prediction and also to avoid formation of the homo-coupling product, the reaction by use of 10 equiv of alkene to the boronic acid was carried out. As a result, the formation of **13a** was almost undetected. When the reaction was carried out at 50°C, the yield of **12** increased. Typical results are summarized in Table 3. Alkenylboronic acids **9** evidently did not cross-couple so effectively with alkenes, compared with arylboronic acids as coupling partners. One reason for low yield of the expected **12** seems to be a facile protodeboronation of the starting **9**. The isolation, however, of the cross-coupling product **12** in a pure form was facile.

2.3. Plausible reaction pathway

Although the reaction mechanism is still obscure and no spectroscopic evidence for the intermediate species is obtained, one plausible reaction pathway seems to be that shown in Scheme 5. Oxidative addition of a carbon–boron bond of aryl- and alkenylboronic acids to a naked palladium(0), formed *in situ* by reduction of palladium(II) acetate, gives an aryl- or alkenyl-palladium(II) species [$ArPdB(OH)_2$] which adds to a carbon–carbon double bond. This is followed by elimination of the Pd-B species with vicinal hydrogen to give aryl- or alkenyl-substituted alkenes regenerating palladium(0) (Heck-type reaction). The double phenylated compound **7** may be formed by addition of phenylpalladium(II) species to the initially produced **5** as shown in Scheme 6. In the case of allyl acetate, formation of the palladium complex **8** is much faster than the oxidative addition of the boronic acid to palladium(0). With allyl bromide, the formation of allylbenzene can be explained by Scheme 7.

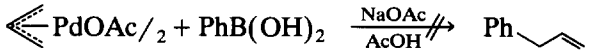
The following experimental observations are worth noting as evidence for the formation and/or presence of palladium(0) species in our catalytic system. When iodobenzene was employed in place of benzeneboronic acid in the reaction with styrene, *trans*-stilbene was obtained in 7% yield. Although the yield is low, this is a clear evidence for oxidative addition of a C–I bond to Pd^0. This result also shows that the addition of a carbon–boron bond to Pd^0 is much faster than that of

TABLE 2. Palladium(0)-catalyzed cross-coupling of phenylboronic acid (**1a**) with 2-substituted propenes (**4**) [a]

Alkene	$PhB(OH)_2$ (mmol)	$Pd(OAc)_2$ (mmol)	Reaction time (h)	Products and yield(%) [b] [5:6 [c]:7 [c]]
4a	1	0.05	38	33 [45:42:13]
4a	1.5	0.1	24	80 [20:45:35]
4b	1.5	0.1	24	72 [43:42:15 [d]]
4c	1.5	0.1	24	80 [14:49 [e]:37 [f]]
4d	1.5	0.1	24	69 [4:90:6]

[a] All reactions were carried out with alkene (**4**) (1 mmol) and NaOAc (4 mmol) in AcOH (10 ml) at 25°C. [b] Isolated yield based on alkene (**4**): isomer distribution was determined by ^{1}H-NMR (270 MHz). [c] Only *E*-isomer was formed except otherwise mentioned. [d] *E*/*Z* = 96/4. [e] *E*/*Z* = 95/5. [f] *E*/*Z* = 85/15.

* Reference number with asterisk indicates a note in the list of references.

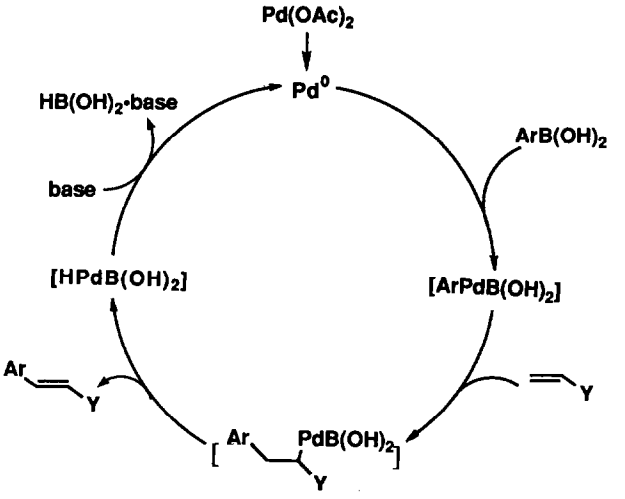


8

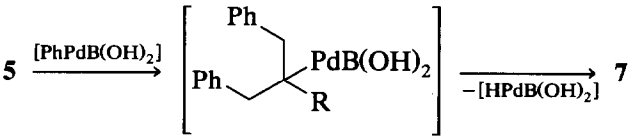
Scheme 3.

a carbon–halogen bond under the reaction conditions employed (no stilbene was obtained from bromobenzene). Further, a similar reaction using tris(dibenzylideneacetone)dipalladium(0) in place of $Pd(OAc)_2$/NaOAc afforded *trans*-stilbene in 12% yield.

On the other hand, similar palladium-catalyzed reactions between benzeneboronic acid and styrene in the presence of triphenylphosphine (0.2 ~ 1 mmol) or carbon monoxide (1 atm) did not give any *trans*-stilbene. These results indicate that the naked Pd^0 might be deactivated by coordination with such a ligand and the oxidative addition to a carbon–boron bond becomes slow. In fact, the catalytic reaction using $Pd(PPh_3)_4$ did not afford any *trans*-stilbene under our reaction conditions [18*].



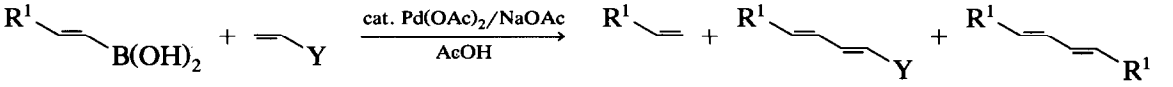
Scheme 5.



Scheme 6.

2.4. *Cross-coupling of sodium tetraphenylborate with alkenes*

Recently, we found that sodium tetraphenylborate ($NaBPh_4$) reacted with alkenes to give the corresponding phenylated alkenes in the presence of a catalytic amount of palladium(II) acetate together with silver acetate as a reoxidant [12]. Application of the borate to our newly developed reaction system also resulted in formation of the corresponding phenylated alkenes in high yield (Scheme 8). The reaction could be applied to various alkenes and typical results are summarized in



9 **10** **11** **12** **13**

a; R^1 = Ph
b; $R^1 = (CH_2)_5CH_3$

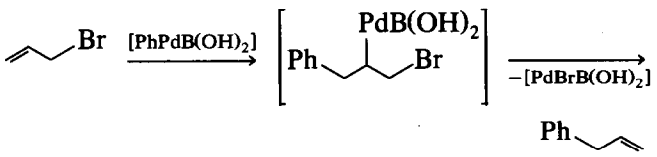
c; Y = CO_2Et
d; Y = CO_2Me
e; Y = Ph

Scheme 4.

TABLE 3. Palladium(0)-catalyzed cross-coupling of alkenylboronic acids (**9**) with alkenes (**10**) [a]

Alkenylboronic acid (1 mmol)	Alkene [b] (mmol)	Reaction time (h)	Reaction temp (°C)	Products and yield (%) [c]		
				11	**12** [d]	**13** [d]
9a	**10c** (1)	20	25	25	16	14
9a	**10c** (10)	21	25	26	18	trace
9a	**10c** (10)	15	50	29	34(29)	trace
9a	**10c** (10)	5	80	41	29	trace
9a	**10d** (10)	20	50	34	34(26)	trace
9a	**10e** (5)	20	50	–	49	–
9b	**10c** (10)	20	50	12	39(22)	– [e]
9b	**10d** (10)	20	50	8	36(21)	– [e]

[a] All reactions were carried out with $Pd(OAc)_2$ (0.1 mmol) and NaOAc (4 mmol) in AcOH (10 ml). [b] **10c** = **2l**, **10d** = **2k**, **10e** = **2g**. [c] GLC yield based on compound **9**. Isolated yield is shown in parentheses. [d] (*E*,*E*)-isomer. [e] Not determined. Even if it is present, its amount is a trace.

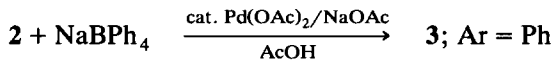


Scheme 7.

Table 4. In this reaction with borate, some different phenomena were noted, compared with the benzeneboronic acid reaction. In all cases, biphenyl was formed in less than 5% yield as a side product by homo-coupling and a large amount of benzene (1.31–3.03 mmol) was also produced. In the reaction with allyl acetate, allylbenzene was obtained in 6% yield together with cinnamyl acetate (5% yield). It has been known that palladium(0) catalyzes the phenyl substitution reaction of allylic acetates with sodium tetraphenylborate to give allylbenzene [19].

In the palladium(II) reaction system, we have proposed that a putative phenylpalladium intermediate [PhPdZ] was generated from the interaction of Pd^{II} salt with both sodium tetraphenylborate itself and triphenylboron(Ph_3B) [Scheme 9; (a) and (b)] and the species reacted with alkenes [Scheme 9; (c)].

In contrast, in the present Pd^0-catalyzed reactions, triphenylboron may be considered to be the main phenylating agent [Scheme 9; (d) and (e)], because it has been known that tetraphenylborate anion was dissociated to triphenylboron and benzene in an acidic medium [20], and in fact, we observed the formation of benzene in high yield by dissolving $NaBPh_4$ in acetic acid [21*]. It is also well known that Ph_3B reacts with an organic acid to give benzene via protodeboronation [20]. When we treated styrene (1.2 mmol) with triphenylboron (1 mmol) under the conditions shown in Scheme 8, *trans*-stilbene (1.16 mmol) and biphenyl (0.06 mmol) were obtained together with benzene (1.03 mmol). This result indicates that a carbon–boron bond of triphenylboron may add to Pd^0 and also that at least two phenyl groups out of three in triphenylboron can be used for the phenyl transfer.



Scheme 8.

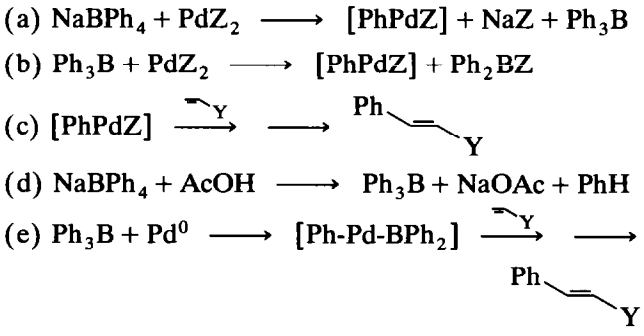
TABLE 4. Palladium(0)-catalyzed cross-coupling of sodium tetraphenylborate with alkenes (2) [a]

Alkene (mmol)	Reaction time (h)	Products and yield (%) [b]	PhPh
2g (1.2)	20	**3ag** 79	1
2h (1)	20	**3ah** 87	trace
2i (1)	20	**3ai** 99	1
2j (1)	24	**3aj** 66	3
2k (1.2)	24	**3ak** 69	5
2l (1.2)	20	**3al** 49	4
4a (1) [c]	24	**6a** 26 **7a** 52	5
allyl bromide (1.2)	20	allylbenzene 31	1
allyl acetate (1.2)	24	cinnamyl acetate 5 allylbenzene 6	1

[a] All reactions were carried out with $NaBPh_4$ (1 mmol), $Pd(OAc)_2$ (0.05 mmol), and NaOAc (4 mmol) in AcOH (10 ml) at 25°C except otherwise mentioned. [b] GLC yield based on $NaBPh_4$. Products are all *trans*. A large amount of benzene (1.31–3.03 mmol) was always formed. [c] $NaBPh_4$ (1.5 mmol) and $Pd(OAc)_2$ (0.1 mmol).

3. Experimental details

^1H (270 MHz) and ^{13}C (67.8 MHz) NMR spectra were measured with a JEOL GSX-270 spectrometer using TMS as an internal standard in $CDCl_3$. Chemical shifts are reported in δ units downfield from TMS. Mass spectra were obtained on a Shimadzu QP-2000 spectrometer. Melting points were determined on a Yanaco MP-J3 micro melting point apparatus and were uncorrected. GLC analyses were carried out with a Shimadzu GC-14A with flame ionization detectors equipped with a CBP10-S25-050 column (Shimadzu, fused silica capillary column, 0.33 mm × 25 m, 0.5 μm film thickness) using nitrogen as the carrier gas. GLC yields were determined using suitable hydrocarbons as internal standards. The isolation of pure products was carried out with column chromatography (Wakogel C-200, 100–200 mesh, Wako Pure Chemical Ind. Ltd.) or



Scheme 9.

thin-layer chromatography (silica gel 60 HF 254, Merck).

Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by standard methods before use. The products such as (*E*)-4-methylstilbene (**3bg**) and (*E*)-4-methoxystilbene (**3cg**) were prepared separately by the reported method [22] and used as authentic samples for GLC determination. Except for benzeneboronic acid (**1a**) and 3-nitrobenzeneboronic acid (**1e**), which were purchased from Nacalai Tesque Inc. and Aldrich Chemical Co., respectively, the boronic acids such as 4-methylbenzeneboronic acid (**1b**), 4-methoxybenzeneboronic acid (**1c**), 4-chlorobenzeneboronic acid (**1d**), and 1-naphthaleneboronic acid (**1f**) were prepared by the reported method [23*]. (*E*)-2-Phenylethenylboronic acid (**9a**) and (*E*)-1-octenylboronic acid (**9b**) were prepared by hydroboration of the corresponding alkynes with catecholborane followed by hydrolysis [24]. Di-μ-acetatodiallyldipalladium(II) complex (**8**) was prepared by the treatment of the corresponding chloro complex [25] with silver acetate [26].

3.1. General procedure for the arylation of alkenes with arylboronic acid

A mixture of arylboronic acid (1 mmol), alkene (1–1.2 mmol), palladium(II) acetate (0.011 g, 0.05 mmol), sodium acetate (0.328 g, 4 mmol), and an appropriate amount of internal standard (generally 1,2-diphenylethane) was stirred in acetic acid (10 ml) at 25°C for an appropriate time. The precipitated black solid was filtered off and the filtrate was poured into a saturated aqueous NaCl solution (100 ml), extracted with methylene chloride (50 ml × 2), and washed with aqueous $NaHCO_3$. The extracts were washed with water, dried over anhydrous Na_2SO_4, and analyzed by GLC. The reaction of an alkene with sodium tetraphenylborate was similarly carried out as above. Some arylated products were isolated by column or thin-layer chromatography using ethyl acetate-hexane as eluent. (*E*)-4-Chlorostilbene (**3dg**): a white solid, m.p. 128–129°C (lit. [27] 128.5–129.5°C); (*E*)-3-Nitrostilbene (**3eg**): a yellow solid, m.p. 110–111°C (lit. [28] 110.8–111.8°C); (*E*)-1-(2-Phenylethenyl)naphthalene (**3fg**): white needles, m.p. 69–69.5°C (lit. [29] 70–71°C).

3.2. General procedure for the phenylation of 2-substituted propenes with benzeneboronic acid

A mixture of benzeneboronic acid (0.183 g, 1.5 mmol), 2-substituted propene (1 mmol), palladium(II) acetate (0.023 g, 0.1 mmol), and sodium acetate (0.328 g, 4 mmol) was stirred in acetic acid (10 ml) at 25°C for 24 h. The precipitate black solid was filtered off and the filtrate was poured into a saturated aqueous NaCl solution (100 ml), extracted with methylene chloride (50 ml × 2), and washed with aqueous $NaHCO_3$. The extracts were washed with water, dried over anhydrous Na_2SO_4, and filtered and the solvent was removed under reduced pressure. Phenylated alkenes were separated as a pale yellow oil of the mixture of three compounds by column chromatography or preparative TLC using ethyl acetate-hexane as eluent. The molar ratio was determined from the peak areas of the clearly separated protons such as vinylic, allylic methyl, and benzylic in the ^1H NMR spectrum. Typical spectroscopic data are as follows.

A mixture of **5a**, **6a**, and **7a**. ^1H NMR: **5a** δ 3.62 (2H, s, benzylic), 5.42 (1H, q, $J = 1.47$ Hz, vinylic), 6.22 (1H, d, $J = 0.74$ Hz, vinylic); **6a** 2.11 (3H, d, $J = 1.47$ Hz, allylic CH_3), 7.69 (1H, q, $J = 1.47$ Hz, vinylic); **7a** 3.95 (2H, s, benzylic), 7.93 (1H, s, vinylic). ^{13}C NMR: δ 14.08 (**6a**, allylic CH_3), 14.05, 14.14, 14.32 ($-OCH_2$ CH_3), 33.17 (**7a**, benzylic), 38.08 (**5a**, benzylic), 60.81, 60.84, 60.92 ($-OCH_2-$), 166.86, 168.09, 168.62 (C=O). MS *m/z* (rel. intensity): **5a** 190 (M^+, 31), 145 (25), 144 (30), 117 (70), 91 (34), 58 (20), 39 (22); **6a** 190 (M^+, 52), 161 (20), 145 (64), 117 (100), 116 (87), 115 (91), 91 (33), 40 (24), 39 (22); **7a** 266 (M^+, 28), 220 (42), 193 (37), 192 (100), 191 (37), 159 (25), 115 (73), 91 (47).

A mixture of **5b**, **6b**, and **7b**. ^1H NMR: **5b** δ 3.63 (2H, s, benzylic), 3.72 (3H, s, $-OCH_3$), 5.46 (1H, q, $J = 1.47$ Hz, vinylic), 6.23 (1H, d, $J = 0.74$ Hz, vinylic); **6b** 2.12 (3H, d, $J = 1.47$ Hz, allylic CH_3), 3.81 (3H, s, $-OCH_3$), 7.69 (1H, q, $J = 1.47$ Hz, vinylic); **7b** 3.74 (3H, s, $-OCH_3$), 3.95 (2H, s, benzylic), 7.93 (1H, s, vinylic). ^{13}C NMR: δ 14.08 (**6b**, allylic CH_3), 33.17 (**7b**, benzylic), 38.07 (**5b**, benzylic), 51.88, 52.07, 52.10 ($-OCH_3$), 167.37, 168.62, 169.15 (C=O). MS *m/z* (rel. intensity): **5b** 176 (M^+, 39), 145 (18), 144 (33), 117 (47), 116 (100), 115 (71), 91 (30), 39 (25), 15 (21); **6b** 176 (M^+, 65), 145 (35), 144 (24), 117 (80), 116 (100), 115 (97), 91 (36), 39 (35), 15 (40); (*E*)-**7b** 252 (M^+, 29), 221 (15), 220 (45), 193 (36), 192 (100), 191 (39), 115 (69), 91 (36), 65 (15), 39 (10), 15 (16); (*Z*)-**7b** 252 (M^+, 21), 221 (13), 220 (32), 193 (26), 192 (100), 191 (40), 149 (22), 115 (75), 91 (47), 65 (22), 39 (19), 15 (26).

A mixture of **5c**, **6c**, and **7c**. ^1H NMR: **5c** δ 3.82 (2H, s, benzylic), 5.00 (1H, q, $J = 1.47$ Hz, vinylic), 5.48 (1H, d, $J = 1.10$ Hz, vinylic); (*E*)-**6c** 2.27 (3H, d, $J = 1.10$ Hz, allylic CH_3); (*Z*)-**6c** 2.19 (3H, d, $J = 1.47$ Hz, allylic CH_3); (*E*)-**7c** 4.12 (2H, s, benzylic); (*Z*)-**7c** 3.77 (2H, s, benzylic). ^{13}C NMR: δ 17.46 [(*E*)-**6c**, allylic CH_3], 27.09 [(*Z*)-**6c**, allylic CH_3], 36.13 [(*E*)-**7c**, benzylic], 41.63 (**5c**, benzylic), 46.94 [(*Z*)-**7c**, benzylic], 114.54 (**5c**, $=CH_2$]. MS *m/z* (rel. intensity): **5c** 194 (M^+, 64), 179 (48), 116 (56), 103 (100), 91 (24), 77 (49); (*E*)-**6c** 194 (M+, 100), 179 (89), 178 (43), 115 (29), 103 (13), 91 (11), 77 (10); (*Z*)-**6c** 194 (M^+, 100), 179 (90), 178 (53),

115 (30), 103 (14), 91 (13), 77 (11); (*E*)-**7c** 270 (M^+, 100), 192 (99), 191 (38), 179 (74), 178 (89), 115 (25), 91 (39), 77 (8); (*Z*)-**7c** 270 (M^+, 100), 192 (94), 191 (30), 179 (63), 178 (84), 115 (24), 91 (35), 77 (9).

A mixture of **5d**, **6d**, and **7d**. ^{1}H NMR: **5d** δ 3.38 (2H, s, benzylic), 4.40 (1H, d, J = 1.10 Hz, vinylic), 4.97 (1H, t, J = 1.47 Hz, vinylic); **6d** 1.82 (3H, d, J = 1.46 Hz, allylic CH_3), 6.35 (1H, s, vinylic); **7d** 3.74 (2H, s, benzylic), 6.75 (1H, s, vinylic). MS m/z (rel. intensity): **5d** 174 (M^+, 64), 159 (13), 117 (100), 91 (32), 83 (51), 57 (22), 55 (45), 41 (48), 18 (65); **6d** 174 (M^+, 49), 159 (94), 117 (100), 91 (26), 57 (14), 43 (37), 41 (32), 29 (25); **7d** 250 (M^+, 16), 193 (42), 159 (100), 117 (63), 115 (35), 91 (87), 57 (28), 43 (21), 41 (24), 29 (21).

3.3. Typical procedure for the vinylation of alkenes with alkenylboronic acid

A mixture of (*E*)-2-phenylethenylboronic acid (**9a**) (0.148 g, 1 mmol), ethyl acrylate (1.001 g, 10 mmol), palladium(II) acetate (0.023 g, 0.1 mmol), and sodium acetate (0.328 g, 4 mmol) was stirred in acetic acid (10 ml) at 50°C for 15 h. The precipitated black solid was filtered off and the filtrate was poured into a saturated aqueous NaCl solution (100 ml), extracted with methylene chloride (50 ml × 2), and washed with aqueous $NaHCO_3$. The extracts were washed with water, dried over anhydrous Na_2SO_4, and filtered. Removal of the solvent under reduced pressure left a pale yellow oil which was separated by TLC using ethyl acetate/n-hexane (1/10 v/v%) as eluent to give ethyl (2*E*,4*E*)-5-phenyl-2,4-pentadienoate (0.058 g, 29%). The same reaction was also carried out separately for GLC analysis. The dienes prepared by the above procedure were fully characterized spectroscopically as shown below. The dienes were also prepared separately by Heck reaction using a stoichiometric amount of $Pd(OAc)_2$ [8] as authentic samples for GLC determination (only *E*,*E*-isomer).

3.3.1. Ethyl (2E,4E)-5-phenyl-2,4-pentadienoate (12ac)

A pale yellow semisolid, ^{1}H NMR: δ 1.31 (3H, t, J = 6.96 Hz), 4.22 (2H, q, J = 6.96 Hz), 5.98 (1H, d, J = 15.4 Hz), 6.85 (1H, dd, J = 19.6 and 15.4 Hz), 6.87 (1H, s), 7.26–7.49 (6H, m). ^{13}C NMR: δ 14.31 ($-CH_3$), 60.30 ($-OCH_2-$), 121.33, 126.22, 127.17, 128.78, 129.00, 136.03, 140.33, 144.51, 166.99 (C=O). MS m/z (rel. intensity): 202 (M^+, 20), 157 (22), 129 (100), 128 (60), 127 (19), 77 (13), 64 (13), 63 (11), 51 (19), 29 (24), 27 (16).

3.3.2. Methyl (2E,4E)-5-phenyl-2,4-pentadienoate (12ad)

A white solid, mp. 68°C (lit. [30] 71°C), ^{1}H NMR δ 3.77 (3H, s), 6.00 (1H, d, J = 15.4 Hz), 6.87 (1H, dd, J = 20.5 and 15.4 Hz), 6.89 (1H, s), 7.27–7.50 (6H, m). ^{13}C NMR: δ 51.57 ($-OCH_3$), 120.82, 126.19, 127.20, 128.81, 129.07, 136.00, 140.55, 144.83, 167.48 (C=O). MS m/z (rel. intensity) 188 (M^+, 22), 157 (19), 129 (100), 128 (69), 127 (22), 77 (15), 64 (22), 63 (18), 51 (27), 39 (11), 15 (18).

3.3.3. Methyl (2E,4E)-2,4-undecadienoate (12bd)

A pale yellow oil, ^{1}H NMR: δ 0.88 (3H, t, J = 6.97 Hz), 1.28–1.45 (8H, m), 2.13–2.20 (2H, m), 3.73 (3H, s), 5.79 (1H, d, J = 15.4 Hz), 6.06–6.23 (2H, m), 7.22–7.31 (1H, m). ^{13}C NMR: δ 14.07, 22.59, 28.68, 28.87, 31.65, 33.02, 51.59 ($-OCH_3$), 118.65, 128.31, 145.02, 145.44, 167.78 (C=O).

3.3.4. Ethyl (2E,4E)-2,4-undecadienoate (12bc)

A pale yellow oil, ^{1}H NMR: δ 0.88 (3H, t, J = 6.96 Hz), 1.26–1.44 (11H, m), 2.13–2.20 (2H, m), 4.20 (2H, q, J = 6.96 Hz), 5.78 (1H, d, J = 15.4 Hz), 6.06–6.22 (2H, m), 7.21–7.31 (1H, m). ^{13}C NMR: δ 14.05, 14.22, 22.58, 28.69, 28.86, 31.65, 33.00, 60.19 ($-OCH_2-$), 119.14, 128.34, 144.82, 145.16, 167.39 (C=O).

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