Full Paper

Applied Organometallic Chemistry

Received: 21 April 2008 Revised: 28 May 2008 Accepted: 28 May 2008 Published online in Wiley Interscience

(www.interscience.com) DOI 10.1002/aoc.1432

# Palladium-catalysed Suzuki cross-coupling of primary alkylboronic acids with alkenyl halides

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**The Suzuki reaction of primary alkylboronic acids with alkenyl halides proceeds nicely using the air-stable catalyst $PdCl(C_3H_5)$(dppb), $Cs_2CO_3$ as base and toluene or xylene as solvent. A minor effect of the substituent position of the alkenyl bromide was observed. Quite similar yields were observed in the presence of $\alpha$- or $\beta$-substituted alkenyl bromides such as 2-bromobut-1-ene or 1-bromo-2-methylprop-1-ene with this catalyst. This reaction proceeded with a variety of alkylboronic acids such as 2-phenylethylboronic acid or *n*-octylboronic acid. Lower yields of coupling products were obtained in the presence of an alkenyl chloride.** 

**Keywords:** palladium; catalysis; alkenyl halide; alkylboronic acids; Suzuki coupling

## Introduction

The palladium-catalysed Suzuki cross-coupling reaction is one of the most powerful methods for the formation of C–C bonds.[1–6] The efficiency of several catalysts for the reaction of aryl or alkenyl halides with aryl or alkenylboronic acid derivatives has been studied in detail. On the other hand, the Suzuki coupling reaction in the presence of alkylboronic acids has attracted less attention.[1] In fact, most of the results described so far with these substrates were obtained in the presence of aryl halides. Relatively few results have been reported in the presence of alkenyl halides.[7–14] Moreover, several reported procedures are not very efficient in terms of substrate : catalyst ratio or substrate scope, or employ toxic or expensive bases. For example, Miyaura and co-workers described the alkylation of a bromocyclohexenone and a bromoacrylate with functionalized alkylboron derivatives using $PdCl_2$(dppf) as catalyst and toxic $Tl_2CO_3$ as base.[7] Another procedure has been employed for the coupling with a (*Z*)-alkenyl iodide; using expensive $Ag_2O$ as additive and $K_2CO_3$ as base with a functionalized primary alkylboronic acid, the corresponding *Z*-alkene was obtained in good yield.[8,9] A iodoalkene bearing a perfluoroalkyl chain has been employed using a quite similar procedure to give a trisubstituted alkene.[10] Bellina and co-workers also described some alkylations of alkenyl bromides using a dibromofuranone and alkylboronic acids such as *n*-butyl or *n*-octylboronic acids. The monoalkylated products were obtained in 69–79% yields.[11] This reaction was performed using $PdCl_2(MeCN)_2$ (5 mol%) associated with $AsPh_3$ (20 mol%) and again with $Ag_2O$ as additive. Air-sensitive electron-rich and bulky phosphane ligands have also been employed for such couplings. For example, the alkylation of a tetrahydroiodopyridine with tri-*n*-butylboroxine was described using Pd associated with $PBu_2Me$.[12] Recently, the butylation of a chlorobenzylidenelactone using another bulky electron-rich ligand has been described.[13] However, the yield of this coupling was quite low. A few examples of coupling reactions of primary alkylboronic acids with alkenyl triflates and of alkyltrifluoroborates with alkenyl halides have also been reported.[14–20]

It should be noted that the coupling of alkenyl halides with alkylboronic acids is more difficult than with arylboronic acids. In some cases, using classical Suzuki-coupling reaction conditions, no formation of the expected products was observed. For example, using (*E*)-bromostilbene and *n*-butyl- or methylboronic acids and $Pd(OAc)_2$–$PPh_3$ as catalyst in absence of additive, the expected products were not obtained.[21] However, using alkylzinc derivatives instead of alkylboronic acids, the reaction proceeded. This difference in reactivity probably comes from a relatively slow transmetallation rate of alkylboronic acids with palladium.

In summary, the alkylation of alkenyl halides with alkylboronic acids proceeds using 3–10 mol% of $PdCl_2$(dppf), $PdCl_2(MeCN)_2$–$AsPh_3$ or $Pd(PBu_2Me)_2$ as catalysts. In several cases, expensive $Ag_2O$ or toxic $Tl_2CO_3$ was added to the reaction mixture. For most of these reactions, alkenyl iodides or bromides were employed. So far, the scope of the reaction for both the alkenyl halide and alkylboronic acids is limited. Therefore, the discovery of more effective conditions, using lower catalyst loading and less toxic and less expensive bases for the coupling of a wider scope of alkylboronic acids and alkenyl halides, is still the subject of significant improvement. In order to further establish the requirements for such Suzuki coupling reactions, we herein report on the reaction of a variety of $\alpha$- and $\beta$-substituted alkenyl bromides and that of an $\alpha$-substituted alkenyl chloride with several primary alkylboronic acids using the commercially available ligand dppb [1,4-bis(diphenylphosphino)butane] and a palladium source.

In the literature, the couplings of alkylboronic acids with aryl bromides or chlorides were generally performed at relatively elevated temperature (up to 110 °C).[1] At these temperatures, a fast decomposition of the palladium complexes associated with monophosphines generally occurs to give so-called 'palladium

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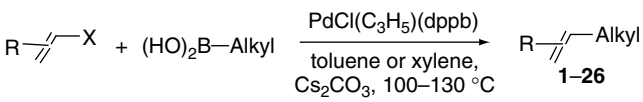
black', which is generally inactive for challenging Suzuki-coupling reactions. In some cases, the use of polydentate ligands seems to increase the stability and longevity of the palladium catalysts. We have already reported that the tetraphosphine ligand, Tedicyp,[22] provides a very powerful catalyst for Suzuki coupling reaction.[22–30] Using Tedicyp–palladium catalyst, the coupling of aryl bromides with primary alkylboronic acids[31] or cyclopropylboronic acid[32] proceeds nicely, indicating that palladium associated with polydentate ligands provides convenient catalysts for the Suzuki coupling of challenging substrates. Thus, we could expect better yield for the coupling of alkylboronic acids and alkenyl halides using palladium associated with bidentate ligands.

For this study, based on previous results,[21] DMAc, DMF, toluene or xylene were chosen as the solvents. The reactions were performed at 80–130 °C in the presence of $PdCl(C_3H_5)$(dppb) as catalyst. This catalyst is air-stable as a solid, but decomposes in solution in the presence of air, especially at elevated temperature. For this reason, the catalytic reactions were performed under argon. We first examined the reactivity of $\beta$-bromostyrene with *n*-octylboronic acid in the presence of 1–2 mol% catalyst (Scheme 1, Tables 1 and 2). Using DMAc as solvent and $K_2CO_3$, $Cs_2CO_3$, KF or AcOK as bases in the presence of 1 mol% catalyst at 100 °C, the product **1** was obtained in very low yield (<20%) together with $\beta$-bromostyrene homo-coupling products (Table 1, entries 1–4). Then we performed the reaction using three solvents: DMAc, DMF and xylene using $K_2CO_3$ as base at 130 °C. High conversions of $\beta$-bromostyrene were observed, but only xylene led to **1** in a relatively high selectivity of 47% and yield of 33% (Table 1, entry 8). The nature of the base has also a huge influence for the reactions performed in xylene. AcONa gave almost no product **1**. On the other hand, $Cs_2CO_3$ led to **1** in a relatively high selectivity of 61% and in 51% isolated yield (Table 1, entry 9). It should be noted that the use of 0.5 $[PdCl(C_3H_5)]_2$/(dppb) as catalyst instead of $PdCl(C_3H_5)$(dppb) using similar reaction conditions gave a very low yield of 6%.

Then, we examined the scope and limitations of this reaction using xylenes or toluene as solvents and $Cs_2CO_3$ as base in the presence of 1–5 mol% of $PdCl(C_3H_5)$(dppb) as catalyst (Tables 2–4). Coupling of (*E*)-$\beta$-bromostyrene with 3-phenylpropylboronic acid also gave stereoselectively the expected (*E*)-2-alkylstyrenes **2** (Table 2, entry 2). Next, we studied the influence of other $\beta$-substitutents on alkenyl bromides for such couplings (Table 2). Two compounds, 1-bromo-2-methylprop-1-ene and (*Z*)-1-bromoprop-1-ene, have been tested. From 1-bromo-2-methylprop-1-ene and 2-phenylethyl-, 3-phenylpropyl-, *n*-octyl- or *n*-dodecylboronic acids, the target coupling products **3**–**6** were obtained selectively in good yields (Table 2, entries 3–6). From (*Z*)-1-bromoprop-1-ene, stereoselective couplings were also observed to give the (*Z*) alk-2-enes **7**–**9** in good yields (Table 2, entries 7–9). In the course of these reactions, no isomerization or migration of the carbon–carbon double bond was detected. Similar stereoselective couplings had already been reported for the cross-coupling of alkylboronic acids with alkenyl halides.[8,9]




**Scheme 1.** Palladium-catalysed alkylation of alkenyl halides.

**Table 1.** Palladium-catalysed coupling of *n*-octylboronic acid with (*E*)-$\beta$-bromostyrene (Scheme 1)

| Entry | Base | Solvent | Temperature (°C) | Yield (%) |
|---|---|---|---|---|
| 1 | $K_2CO_3$ | DMAc | 100 | 18 |
| 2 | $Cs_2CO_3$ | DMAc | 100 | 4 |
| 3 | KOAc | DMAc | 100 | 2 |
| 4 | KF | DMAc | 100 | 17 |
| 5 | $K_2CO_3$ | DMAc | 130 | 3 |
| 6 | $K_2CO_3$ | DMF | 130 | 20 |
| 7 | KOAc | Xylene | 130 | 2 |
| 8 | $K_2CO_3$ | Xylene | 130 | 33 |
| 9 | $Cs_2CO_3$ | Xylene | 130 | 51[a] |

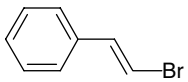
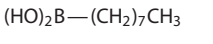
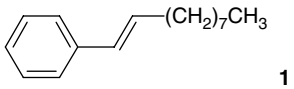
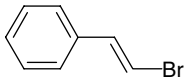
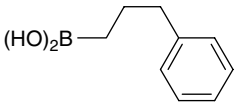
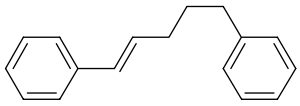
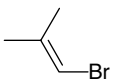
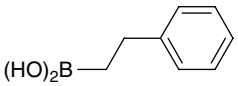
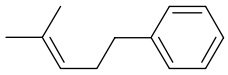
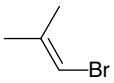
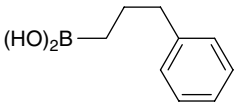
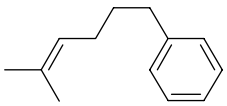
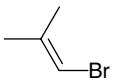
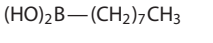
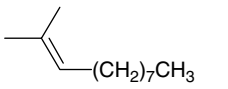
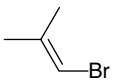
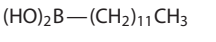
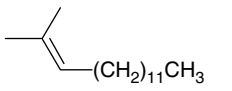
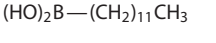
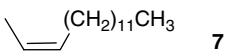
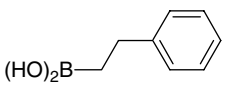
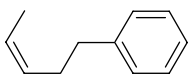
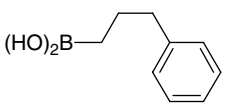
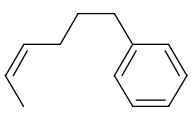
Conditions: $PdCl(C_3H_5)$(dppb) 0.01 mmol; (*E*)-$\beta$-bromostyrene, 1 mmol; *n*octylboronic acid, 2 mmol; base, 2 mmol; 20 h; argon; GC yields.
[a] Isolated yield.

Next, we examined the coupling with $\alpha$-substituted alkenyl bromides (Table 3). The reaction of 2-bromoprop-1-ene with *n*-octyl-, *n*-dodecyl- or 3-phenylpropylboronic acids gave selectively the desired coupling products **10**–**12** in 57–64% yields (Table 3, entries 1–3). These alkylboronic acids were also coupled successfully using 2-bromobut-1-ene, to give **14**–**16** in 60–62% yield (Table 3, entries 5–7). In the course of this reaction, no isomerisation of the alkenyl carbon-carbon double bond was observed. A slightly higher yield of 68% was obtained using 2-phenylethylboronic acid with this alkene (Table 3, entry 4). It should be noted that some unreacted 2-bromoprop-1-ene or 2-bromobut-1-ene was observed, in most cases, at the end of the reaction, when using these reactants. On the other hand, lower yields were obtained using $\alpha$-bromostyrene. This is due to the formation of unidentified side products in the presence of this reactant. However, the target products **17**–**19** were obtained in all cases. Alkenyl chlorides are known to be less reactive than the corresponding alkenyl bromides or iodides due to a slower oxidative addition to palladium. In most cases, the coupling with such substrates has to be performed using palladium associated with electron-rich and sterically congested phosphine ligands.[1] However, the use of such ligands is not very convenient due to their low stability in the presence of air. We observed that methyl 2-chloroacrylate can be coupled with *n*-octyl- or 3-phenylpropylboronic acids using 5 mol% of the air-stable catalyst $PdCl(C_3H_5)$(dppb) to give selectively the acrylates **20** and **21** in moderate yields (Table 3, entries 11 and 12). It should be noted that an incomplete conversion of methyl 2-chloroacrylate was observed. Therefore, on a larger scale, a partial recycling on this reactant should be possible.

Finally, we performed a few reactions using the trisubstituted vinyl bromide: 2-bromo-3-methylbut-2-ene (Table 4). Five alkylboronic acids were employed. As expected, the reactions were very clean, and in all cases, only the formation of the expected products **22**–**26** was observed. Again, no migration of the alkene carbon–carbon double bond was detected. The trisubstitution of the alkenyl bromide does not seem to have a large influence on the oxidative addition rate to palladium. This reaction gives a very simple access to tetrasubstituted alkenes.

In summary, the Suzuki coupling of several alkenyl bromides with primary alkylboronic acid derivatives can be performed with as little as 1–2 mol% of the air-stable $PdCl(C_3H_5)$(dppb) catalyst. The position of the substituents on the alkenyl bromides generally has a minor influence on the yields. On the other hand, lower yields were obtained with the alkenyl chloride, methyl 2-chloroacrylate. This is certainly due to a relatively slow oxidative addition of this alkenyl chloride to palladium. This procedure employing $Cs_2CO_3$

**Table 2.** Palladium-catalysed coupling of alkylboronic acids with 1-bromo-2-methylprop-1-ene, (*Z*)-1-bromoprop-1-ene and (*E*)-$\beta$-bromostyrene (Scheme 1)

| Entry | Alkenyl bromide | Alkylboronic acid | Product | Yield (%) |
|---|---|---|---|---|
| 1 |  |  |  **1** | 51[c] |
| 2 |  |  |  **2** | 47[a,c] |
| 3 |  |  |  **3** | 64[a] |
| 4 |  |  |  **4** | 63[a] |
| 5 |  |  |  **5** | 60 |
| 6 |  |  |  **6** | 63[a,b] |
| 7 |  |  |  **7** | 62[a,b] |
| 8 |  |  |  **8** | 67[a] |
| 9 |  |  |  **9** | 65[a] |

Conditions: $PdCl(C_3H_5)(dppb)$ 0.01 mmol; alkenyl halide, 1 mmol; alkylboronic acid, 2 mmol; $Cs_2CO_3$, 2 mmol; toluene; 100 °C; 20 h; argon; isolated yields. [a] $PdCl(C_3H_5)(dppb)$, 0.02 mmol. [b] 110 °C, xylene. [c] 130 °C, xylene.

as base is less expensive than those using silver salts as additive and more environmentally friendly than those using $Tl_2CO_3$ as base. Moreover, this procedure led to less toxic waste than the Stille reaction, which is often employed for the coupling of alkenyl halides with alkyl chains. In terms of substrate : catalyst ratio, catalyst handling, selectivity, relatively inert wastes and reaction scope, this procedure compares favourably to other reported Suzuki coupling procedures and also to the Stille coupling reaction.

## Experimental Section

### General

All reactions were run under argon in Schlenk tubes using vacuum lines. Xylene or toluene, analytical-grade, were not distilled before use. Cesium carbonate (>99 pure) was used. Commercial alkenyl halides were used without purification. Alkylboronic acids were prepared according to reported procedures by reaction of Mg with alkyl bromides followed by addition of $B(OMe)_3$ at −70 °C, hydrolysis, extraction, drying, evaporation of the solvent and recrystallization. $^1H$ and $^{13}C$ spectra were recorded with a Bruker 200 MHz spectrometer in $CDCl_3$ solutions. Chemical shifts are reported in ppm relative to $CDCl_3$ (7.25 for $^1H$ NMR and 77.0 for $^{13}C$ NMR). Flash chromatography was performed on silica gel (230–400 mesh).

### Preparation of the $PdCl(dppb)(C_3H_5)$ catalyst[33]

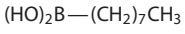
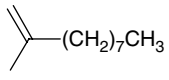
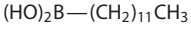
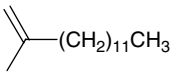
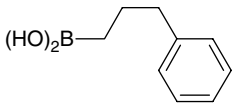
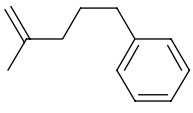
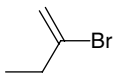
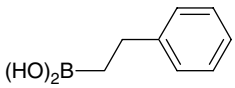
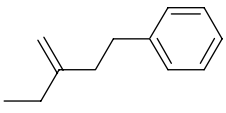
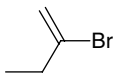
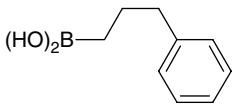
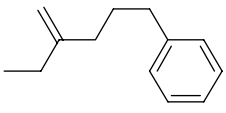
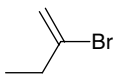
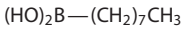
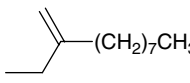
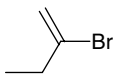
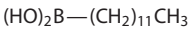
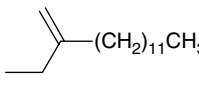
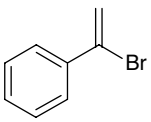
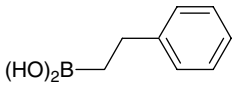
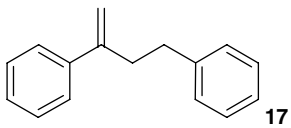
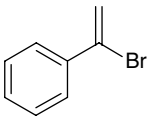
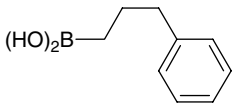
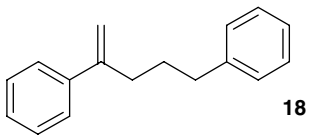
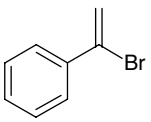
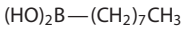
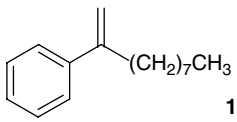
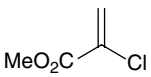
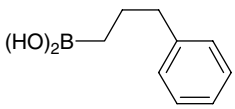
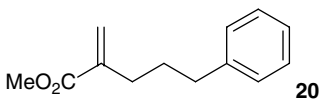
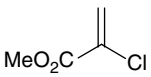
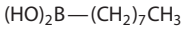
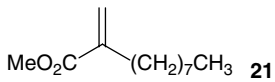
An oven-dried 40 ml Schlenk tube equipped with a magnetic stirring bar under argon atmosphere was charged with $[Pd(C_3H_5)Cl]_2$ (182 mg, 0.5 mmol) and dppb (426 mg, 1 mmol). Anhydrous dichloromethane (10 ml) was added, and the solution was stirred at room temperature for 20 min. The solvent was removed under vacuum. The yellow powder obtained was used without purification. $^{31}P$ NMR (81 MHz, $CDCl_3$) $\delta = 19.3$ (s).

### General procedure for coupling reactions

In a typical experiment, the alkenyl halide (1 mmol), alkylboronic acid derivative (2 mmol), $Cs_2CO_3$ (0.652 g, 2 mmol) and $PdCl(C_3H_5)(dppb)$ (see tables) were dissolved in toluene or xylene (see tables) (5 ml) under an argon atmosphere. The reaction mixture was stirred at 100–130 °C (see tables) for 20 h. The solution was diluted with water (20 ml), then the product was extracted three times with $CH_2Cl_2$. The combined organic layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The product was purified by silica gel column chromatography.

**Table 3.** Palladium-catalysed coupling of alkylboronic acids with 2-bromoprop-1-ene, 2-bromobut-1-ene, α-bromostyrene and methyl 2-chloroacrylate (Scheme 1)

| Entry | Alkenyl bromide | Alkylboronic acid | Product | Yield (%) |
|---|---|---|---|---|
| 1 |  |  |  **10** | 59 |
| 2 |  |  |  **11** | 64[a,b] |
| 3 |  |  |  **12** | 57[a] |
| 4 |  |  |  **13** | 68[a] |
| 5 |  |  |  **14** | 62[a] |
| 6 |  |  |  **15** | 60 |
| 7 |  |  |  **16** | 61[a,b] |
| 8 |  |  |  **17** | 52[a] |
| 9 |  |  |  **18** | 58[a] |
| 10 |  |  |  **19** | 47 |
| 11 |  |  |  **20** | 40[c] |
| 12 |  |  |  **21** | 48[c] |

Conditions: $PdCl(C_3H_5)(dppb)$, 0.01 mmol; alkenyl halide, 1 mmol; alkylboronic acid, 2 mmol; $Cs_2CO_3$, 2 mmol; toluene; 100 °C; 20 h; argon; isolated yields. [a] $PdCl(C_3H_5)(dppb)$, 0.02 mmol. [b] 110 °C, xylene. [c] $PdCl(C_3H_5)(dppb)$, 0.05 mmol.

*(E)-Dec-1-enylbenzene* (**1**)[34]

From β-bromostyrene (0.183 g, 1 mmol), *n*-octylboronic acid (0.316 g, 2 mmol), Pd complex (0.01 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **2** was obtained in 51% (0.111 g) yield.

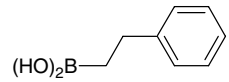
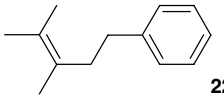
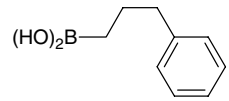
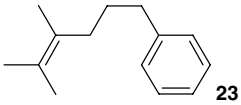
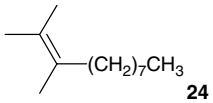
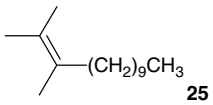
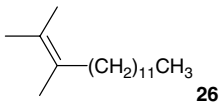
$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.10 (m, 5H), 6.40 (d, $J$ = 16.1 Hz, 1H), 6.27 (dt, $J$ = 16.1 and 7.5 Hz, 1H), 2.30–2.10 (m, 2H), 1.39–1.19 (m, 12H), 0.90 (t, $J$ = 7.5 Hz, 3H).

*(E)-1,5-Diphenylpent-1-ene* (**2**)[35]

From β-bromostyrene (0.183 g, 1 mmol), 3-phenylpropylboronic acid (0.328 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **1** was obtained in 47% (0.105 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.10 (m, 10H), 6.42 (d, $J$ = 16.1 Hz, 1H), 6.22 (dt, $J$ = 16.1 and 7.5 Hz, 1H), 2.71 (t, $J$ = 7.5 Hz, 2H), 2.28 (dt, $J$ = 7.3 and 7.5 Hz, 2H), 1.81 (quint., $J$ = 7.5 Hz, 2H).

**Table 4.** Palladium-catalysed coupling of alkylboronic acids with 2-bromo-3-methylbut-2-ene (Scheme 1)

| Entry | Alkylboronic acid | Product | Yield (%) |
|---|---|---|---|
| 1 |  |  **22** | 68[a] |
| 2 |  |  **23** | 70[a] |
| 3 | $(HO)_2B-(CH_2)_7CH_3$ |  **24** | 62 |
| 4 | $(HO)_2B-(CH_2)_9CH_3$ |  **25** | 67 |
| 5 | $(HO)_2B-(CH_2)_{11}CH_3$ |  **26** | 71[a,b] |

Conditions: $PdCl(C_3H_5)(dppb)$, 0.01 mmol, 2-bromo-3-methylbut-2-ene, 1 mmol; alkylboronic acid, 2 mmol; $Cs_2CO_3$, 2 mmol; toluene; 100 °C; 20 h; argon; isolated yields. [a] $PdCl(C_3H_5)(dppb)$, 0.02 mmol. [b] 110 °C, xylene.

*4-Methylpent-3-enyl)benzene (**3**)*[36]

From 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), 2-phenylethylboronic acid (0.300 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **3** was obtained in 64% (0.102 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.40–7.10 (m, 5H), 5.16 (t, $J$ = 7.3 Hz, 1H), 2.63 (t, $J$ = 7.5 Hz, 2H), 2.30 (dt, $J$ = 7.3 and 7.5 Hz, 2H), 1.68 (s, 3H), 1.56 (s, 3H).

*5-Methylhex-4-enyl)benzene (**4**)*[37]

From 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), 3-phenylpropylboronic acid (0.328 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **4** was obtained in 63% (0.110 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.10 (m, 5H), 5.16 (t, $J$ = 7.3 Hz, 1H), 2.62 (t, $J$ = 7.5 Hz, 2H), 2.05 (dt, $J$ = 7.3 and 7.5 Hz, 2H), 1.71 (s, 3 H), 1.67 (quint., $J$ = 7.5 Hz, 2H), 1.55 (s, 3H).

*2-Methylundec-2-ene (**5**)*[38]

From 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), *n*-octylboronic acid (0.316 g, 2 mmol), Pd complex (0.01 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **5** was obtained in 60% (0.101 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.14 (t, $J$ = 7.3 Hz, 1H), 1.96 (q, $J$ = 7.5 Hz, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.35–1.15 (m, 12H), 0.87 (t, $J$ = 7.5 Hz, 3H).

*2-Methylpentadec-2-ene (**6**)*[39]

From 1-bromo-2-methylprop-1-ene (0.135 g, 1 mmol), *n*-dodecylboronic acid (0.428 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **6** was obtained in 63% (0.141 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.12 (t, $J$ = 7.3 Hz, 1H), 1.96 (q, $J$ = 7.5 Hz, 2H), 1.69 (s, 3 H), 1.60 (s, 3H), 1.68–1.52 (m, 20H), 0.88 (t, $J$ = 7.5 Hz, 3H).

*(Z)-Pentadec-2-ene (**7**)*[40]

From (*Z*)-1-bromoprop-1-ene (0.121 g, 1 mmol), *n*-dodecylboronic acid (0.428 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **7** was obtained in 62% (0.130 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 5.48 (dq, $J$ = 12.5 and 6.4 Hz, 1H), 5.38 (dt, $J$ = 12.5 and 6.4 Hz, 1H), 2.00 (q, $J$ = 6.4 Hz, 2H), 1.60 (d, $J$ = 6.4 Hz, 3H), 1.37–1.17 (m, 20H), 0.90 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 130.9, 123.5, 31.9, 29.5–29.6 (6C), 29.4, 29.3, 26.8, 22.7, 14.1, 12.7.

*(Z)-Pent-3-enylbenzene (**8**)*[41]

From (*Z*)-1-bromoprop-1-ene (0.121 g, 1 mmol), 2-phenylethyl boronic acid (0.300 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **8** was obtained in 67% (0.098 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.22 (m, 5H), 5.48 (dq, $J$ = 12.5 and 6.4 Hz, 1H), 5.40 (dt, $J$ = 12.5 and 6.4 Hz, 1H), 2.66 (t, $J$ = 7.5 Hz, 2H), 2.36 (q, $J$ = 7.5 Hz, 2H), 1.55 (d, $J$ = 6.4 Hz, 3H).

*(Z)-Hex-4-enylbenzene (**9**)*[42]

From (*Z*)-1-bromoprop-1-ene (0.121 g, 1 mmol), 3-phenylpropyl boronic acid (0.328 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **9** was obtained in 65% (0.104 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.40–7.15 (m, 5H), 5.55 (dq, $J$ = 12.5 and 6.4 Hz, 1H), 5.43 (dt, $J$ = 12.5 and 6.4 Hz, 1H), 2.67 (t, $J$ = 7.5 Hz, 2H), 2.12 (q, $J$ = 7.5 Hz, 2H), 1.75 (quint., $J$ = 7.5 Hz, 2H), 1.64 (d, $J$ = 6.4 Hz, 3H).

*2-Methyldec-1-ene (**10**)*[43]

From 2-bromopropene (0.121 g, 1 mmol), *n*-octylboronic acid (0.316 g, 2 mmol), Pd complex (0.01 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **10** was obtained in 59% (0.091 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.67 (s, 2H), 2.01 (t, $J$ = 7.5 Hz, 2H), 1.71 (s, 3H). 1.36–1.16 (m, 12H), 0.88 (t, $J$ = 7.5 Hz, 3H).

*2-Methyltetradec-1-ene (**11**)*[39]

From 2-bromopropene (0.121 g, 1 mmol), *n*-dodecylboronic acid (0.428 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **11** was obtained in 64% (0.135 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.67 (s, 2H), 2.01 (t, $J$ = 7.5 Hz, 2H), 1.71 (s, 3H), 1.36–1.16 (m, 20H), 0.88 (t, $J$ = 7.5 Hz, 3H).

*4-Methylpent-4-enyl)benzene (**12**)*[44]

From 2-bromopropene (0.121 g, 1 mmol), 3-phenylpropylboronic acid (0.328 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **12** was obtained in 57% (0.091 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.20 (m, 5H), 4.73 (s, 1H), 4.71 (s, 1H), 2.61 (t, $J$ = 7.5 Hz, 2H), 2.07 (t, $J$ = 7.5 Hz, 2H), 1.76 (quint., $J$ = 7.5 Hz, 2H), 1.69 (s, 3H).

*3-Ethylbut-3-enyl)benzene* (**13**)[45]

From 2-bromobut-1-ene (0.135 g, 1 mmol), 2-phenylethylboronic acid (0.300 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **13** was obtained in 68% (0.109 g) yield.

$^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 7.30–7.05 (m, 5H), 4.75 (s, 2H), 2.75 (t, $J$ = 7.5 Hz, 2H), 2.35 (t, $J$ = 7.5 Hz, 2H), 2.07 (q, $J$ = 7.5 Hz, 2H), 1.05 (t, $J$ = 7.5 Hz, 3H).

*4-Ethylpent-4-enyl)benzene* (**14**)

From 2-bromobut-1-ene (0.135 g, 1 mmol), 3-phenylpropylboronic acid (0.328 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **14** was obtained in 62% (0.108 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.30–7.05 (m, 5H), 4.73 (s, 2H), 2.63 (t, $J$ = 7.5 Hz, 2H), 2.18–1.98 (m, 4H), 1.77 (quint., $J$ = 7.5 Hz, 2H), 1.02 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 151.2, 142.6, 128.4, 128.2, 125.6, 107.7, 35.8, 35.6, 29.5, 28.7, 12.3. $-C_{13}H_{18}$ ($M$ = 174.3): calcd C 89.59, H 10.41; found C 89.31, H 10.28.

*2-Ethyldec-1-ene* (**15**)[46]

From 2-bromobut-1-ene (0.135 g, 1 mmol), *n*-octylboronic acid (0.316 g, 2 mmol), Pd complex (0.01 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **15** was obtained in 60% (0.101 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.69 (s, 2H), 2.12–1.98 (m, 4H), 1.36–1.16 (m, 12H), 1.02 (t, $J$ = 7.5 Hz, 3H), 0.88 (t, $J$ = 7.5 Hz, 3H).

*2-Ethyltetradec-1-ene* (**16**)[47]

From 2-bromobut-1-ene (0.135 g, 1 mmol), *n*-dodecylboronic acid (0.428 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **16** was obtained in 61% (0.137 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 4.69 (s, 2H), 2.09–1.92 (m, 4H), 1.36–1.16 (m, 20H), 0.99 (t, $J$ = 7.5 Hz, 3H), 0.88 (t, $J$ = 7.5 Hz, 3H).

*2,4-Diphenylbut-1-ene* (**17**)[48]

From $\alpha$-bromostyrene (0.183 g, 1 mmol), 2-phenylethylboronic acid (0.300 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **17** was obtained in 52% (0.108 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.00 (m, 10H), 5.31 (s, 1H), 5.08 (s, 1H), 2.91–2.70 (m, 4H).

*2,5-Diphenylpent-1-ene* (**18**)[49]

From $\alpha$-bromostyrene (0.183 g, 1 mmol), 3-phenylpropylboronic acid (0.328 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **18** was obtained in 58% (0.129 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.00 (m, 10H), 5.31 (s, 1H), 5.10 (s, 1H), 2.67 (t, $J$ = 7.5 Hz, 2H), 2.57 (t, $J$ = 7.5 Hz, 2H), 1.84 (quint., $J$ = 7.5 Hz, 2H).

*Dec-1-en-2-ylbenzene* (**19**)[34]

From $\alpha$-bromostyrene (0.183 g, 1 mmol), *n*-octylboronic acid (0.316 g, 2 mmol), Pd complex (0.01 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **19** was obtained in 47% (0.102 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.50–7.10 (m, 5H), 5.26 (s, 1H), 5.05 (s, 1H), 2.49 (t, $J$ = 7.5 Hz, 2H), 1.40–1.20 (m, 12H), 0.87 (t, $J$ = 7.5 Hz, 3H).

*Methyl 2-methylene-5-phenylpentanoate* (**20**)[50]

From methyl 2-chloroacrylate (0.121 g, 1 mmol), 3-phenylpropylboronic acid (0.328 g, 2 mmol), Pd complex (0.05 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **20** was obtained in 40% (0.082 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.40–7.10 (m, 5H), 6.20 (s, 1H), 5.53 (s, 1H), 3.72 (s, 3H), 2.68 (t, $J$ = 7.5 Hz, 2H), 2.38 (t, $J$ = 7.5 Hz, 2H), 1.82 (quint., $J$ = 7.5 Hz, 3H).

*Methyl 2-methylenedecanoate* (**21**)[51]

From methyl 2-chloroacrylate (0.121 g, 1 mmol), *n*-octylboronic acid (0.316 g, 2 mmol), Pd complex (0.05 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **21** was obtained in 48% (0.095 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 6.12 (s, 1H), 5.52 (s, 1H), 3.75 (s, 3H), 2.29 (t, $J$ = 7.5 Hz, 2H), 1.36–1.16 (m, 12H), 0.87 (t, $J$ = 7.5 Hz, 3H).

*3,4-Dimethylpent-3-enyl)benzene* (**22**)[52]

From 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), 2-phenylethylboronic acid (0.300 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **22** was obtained in 68% (0.119 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.45–7.10 (m, 5H), 2.65 (t, $J$ = 7.5 Hz, 2H), 2.30 (t, $J$ = 7.5 Hz, 2H), 1.70 (s, 3H), 1.66 (s, 3H), 1.60 (s, 3H).

*4,5-Dimethylhex-4-enyl)benzene* (**23**)[53]

From 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), 3-phenylpropylboronic acid (0.328 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **23** was obtained in 70% (0.132 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 7.45–7.10 (m, 5H), 2.65 (t, $J$ = 7.5 Hz, 2H), 2.13 (t, $J$ = 7.5 Hz, 2H), 1.74 (quint., $J$ = 7.5 Hz, 2H), 1.69 (s, 9H).

*2,3-Dimethylundec-2-ene* (**24**)[54]

From 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), *n*-octylboronic acid (0.316 g, 2 mmol), Pd complex (0.01 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **24** was obtained in 62% (0.113 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.97 (t, $J$ = 7.5 Hz, 2H), 1.62 (s, 9H), 1.30–1.10 (m, 12H), 0.88 (t, $J$ = 7.5 Hz, 3H).

*2,3-Dimethyltridec-2-ene* (**25**)

From 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), *n*-decylboronic acid (0.372 g, 2 mmol), Pd complex (0.01 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **25** was obtained in 67% (0.141 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 1.97 (t, $J$ = 7.5 Hz, 2H), 1.62 (s, 9H), 1.30–1.10 (m, 16H), 0.88 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 128.1, 123.6, 34.4, 31.9, 29.7-29.3 (5C), 28.2, 22.7, 20.5, 20.1, 18.3, 14.1. $-C_{15}H_{30}$ (M = 210.4): calcd C 85.63, H 14.37; found C 85.39, H 14.48.

*2,3-Dimethylpentadec-2-ene* (**26**)

From 2-bromo-3-methylbut-2-ene (0.149 g, 1 mmol), *n*-dodecylboronic acid (0.428 g, 2 mmol), Pd complex (0.02 mmol) and $Cs_2CO_3$ (0.652 g, 2 mmol), **26** was obtained in 71% (0.169 g) yield.

$^1$H NMR (200 MHz, $CDCl_3$): $\delta$ = 2.02 (t, $J$ = 7.5 Hz, 2H), 1.66 (s, 9H), 1.39–1.20 (m, 20H), 0.91 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (50 MHz, $CDCl_3$): $\delta$ = 128.0, 123.5, 35.2, 31.9, 29.7-29.3 (7C), 28.2, 22.6, 21.4, 20.8, 18.6, 14.1. – $C_{17}H_{34}$ (M = 238.4): calcd C 85.63, H 14.37; found C 85.45, H 14.38.

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