Direct Synthesis of Functionalized Allylic Boronic Esters from Allylic Alcohols and Inexpensive Reagents and Catalysts

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Received 8 May 2008

This paper is dedicated to Professor Reinhard Hoffman, one of the leaders in the field of stereocontrolled synthesis, on the occasion of his 75th birthday.

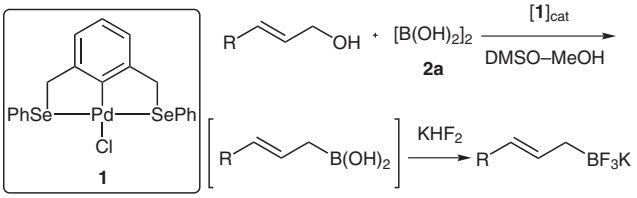
Abstract: A remarkably simple and effective system for the direct conversion of allylic alcohols into high value allylic boronic esters using commercially available reagents and catalysts is described.

Key words: allylation, palladium, palladacycles, transition metal

Allylic boranes and boronic esters are extremely important intermediates in organic synthesis, providing very high levels of stereoselectivity in their reactions with aldehydes,[1] ketones[2a–c] and imines,[2d–f] and being effective partners in a range of cross-coupling reactions.[2f–h] Recent landmark contributions from Hall[3] have extended the range of allylic boronic esters available[4] and improved the selectivity of these reagents further.[5] Because of the significance of these reagents in organic synthesis, their ready availability and ease of synthesis is crucial. They have been prepared from reactions of allylic Grignards with borates[6] and from reactions of pinacol borane with allylic halides catalysed by $Pt(dba)_2$.[7] However, the most common method involves the reaction of allylic acetates or carbonates with bis(pinacolato)diboron using $Pd(OAc)_2$[8] or Cu(I) as catalysts.[9] However, dimerization occasionally competes leading to 1,5-dienes which not only consume the substrate but also cause product inhibition by complexation with the metal catalyst.[8a] Very recently the direct conversion of allylic alcohols into allylic boronic acids using diboronic acid and palladium pincer complex **1** was reported (Scheme 1).[10,11] The allylic boronic acids were unstable and were therefore isolated as their trifluoroborate salts[10] or were reacted directly with aldehydes and imines.[11]

We are thus very close to the ideal synthesis of allylic boronic esters from simple starting materials. In this paper we report the direct conversion of allylic alcohols into allylic boronic esters using both commercially available bis(pinacolato)diboron (**2b**) and palladium catalyst **3**, which we believe fulfils this ideal.

We began our investigations with geraniol **4a** and the diboron reagent **2b** employing dimethyl sulfoxide–methanol with 5 mol% *p*-toluenesulfonic acid (TSOH) as these conditions had been effective in coupling the diboronic acid **2a**.[10] Concerning the choice of catalyst, we decided to investigate palladacycle **3** because it bears significant structural similarity to the pincer complex **1** and is also commercially available.[12] We were pleased to find that this combination of boronic ester **2b** and palladium catalyst **3** was effective in the borylation reaction (Table 1, entry 1). The use of just 5% TSOH was crucial to the success of the borylation process. Without TSOH, only unreacted starting material was recovered (entry 2), whilst stoichiometric amounts of TSOH caused extensive decomposition of the product instead (presumably through protodeborination) (entry 3). Increasing the stoichiometry of bis(pinacolato)diboron (**2b**) led to a dramatic increase in yield and this allowed a reduction in palladium loading down to 1.25 mol% without negative consequences (Entries 4 to 6). However, increased temperatures (80 °C) were deleterious to the reaction (Entry 7).



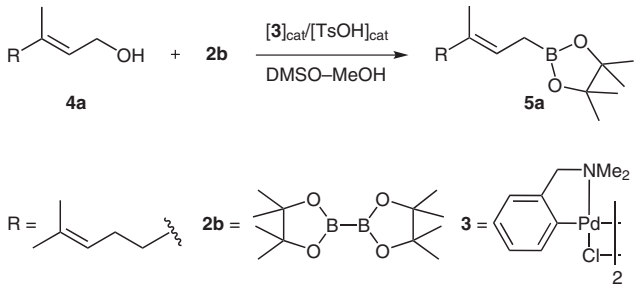
Scheme 1 Direct borination of allylic alcohols

The optimum conditions found (Table 1, entry 4) provided a general borylation process that was applicable to a broad range of allylic alcohols **4** (Table 2). The olefin of the allylic alcohol **4** could be mono-, di- or tri-substituted (in the case of di-substituted olefins, *E* and *Z* isomers of 1,1- and 1,2 substituted substrates were accepted) and gave *E* allylic boronates **5** in all cases, except in the case of **5a** (93:7, *E*:*Z*).[13]

The alcohol **4** could be primary, secondary or tertiary leading to linear (less substituted) boronic esters **5** in all cases. The reaction tolerated ester functionality (entry 5) and vinyl silanes (entry 8), providing usefully functionalized allylic boronic esters, thus demonstrating the enhanced scope of the process. The reaction shown in entry 1 was uneventfully scaled up (25 mmol) to give a similar yield of the boronic ester **5a**.

SYNTHESIS 2008, No. 14, pp 2293–2297
Advanced online publication: 18.06.2008
DOI: 10.1055/s-2008-1067144; Art ID: C02308SS

Table 1 Optimization of Conditions[a]



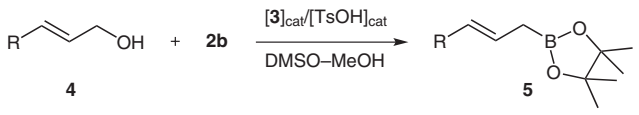
Entry	**2b** (equiv)	**3** (%)	Temp (°C)	TSOH (%)	Yield **5a** (%)[b]
1	1.2	2.5	50	5	53
2	1.2	2.5	50	0	0
3	1.2	2.5	50	100	11
4	2.0	2.5	50	5	87
5	2.0	1.25	50	5	83
6	2.0	0.5	50	5	59
7	2.0	2.5	80	5	14

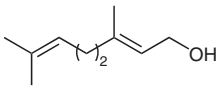
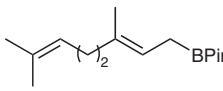
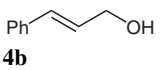
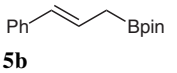
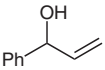
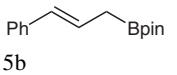
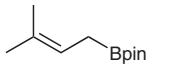
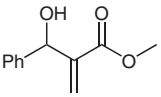
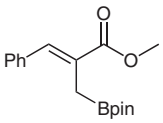
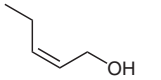
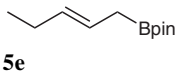
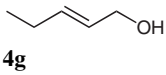
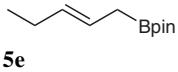
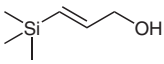
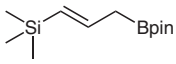
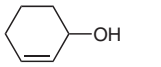
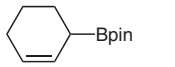
[a] Unless otherwise stated, the reactions were conducted with geraniol (0.5 mmol) overnight in a 1:1 mixture of DMSO/MeOH (2 mL).
[b] Isolated yield.

Monitoring the progress of the catalytic reactions by ^{1}H NMR under a variety of conditions (Figure 1) revealed some intriguing mechanistic aspects and favourable properties for the new catalyst **3**. The rate of formation of cinnamyl boronate **5b** from cinnamyl alcohol **4b** was found to be dependent on the presence of acid, the diboronate source (**2a** or **2b**) and the palladium catalyst employed (**1** or **3**). Key findings were:
(1) Acid promotes the reaction. The fastest borylation reaction took place with $B_2(OH)_4$ (**2a**) as the boron source in the presence of 5 mol% TSOH (conditions A). The same reaction using B_2pin_2 (**2b**) in place of **2a** was the next fastest (condition B). Without TSOH the borylation reaction still took place with **2a** (conditions E; bisboronic acid present), albeit more slowly, however, no reaction occurred with B_2pin_2 (**2b**; conditions G and H).
(2) The newly developed catalyst **3** was considerably faster in effecting the borylation reactions than the pincer complex **1** (compare conditions A/C, B/F, G/H; D/E were similar).

A broad mechanistic rationale for this intriguing reaction is described below (Scheme 2). Decoordination of chloride followed by transmetallation with B_2pin_2 **2b**, by analogy with the mechanism advanced for palladium-catalyzed diboration of alkenes,[14] would give the palladium complex **B**. Subsequent reaction with a boron-activated allylic alcohol **C** would then furnish the allylic boronic ester **5** and return the palladium catalyst **A** for further transformations. The precise order of events and intermediates involved in the latter process have not yet been identified. The role of the acid is believed to be to promote formation of the boron-activated allylic alcohol **C** through (partial) transesterification processes.

Table 2 Palladium-Catalysed Direct Boronation of Allylic Alcohols[a]



Entry	Substrate	Product	Yield (%)[b]
1	 **4a**[c]	 **5a**[c]	87 77[d] 85[d,e]
2	 **4b**	 **5b**	81 91[e]
3	 **4c**	 5b	76 96[e]
4	 **4d**	 **5c**	81
5	 **4e**	 **5d**	92
6	 **4f**	 **5e**	79 88[e]
7	 **4g**	 **5e**	91
8	 **4h**	 **5f**	57
9	 **4i**	 **5g**	46 71[e]

[a] Unless otherwise stated, the reactions were conducted with allylic alcohol **4** (0.5 mmol) in the presence of **2b** (2.0 equiv), **3** (2.5 mol%) and TSOH (5 mol%) at 50 °C overnight in a 1:1 mixture of DMSO/MeOH (2 mL).
[b] Isolated yield.
[c] Obtained as a 93:7 ratio of *E*:*Z* isomers.
[d] The reaction was performed on 25 mmol scale.
[e] 3.0 equiv of **2b** was used.

In conclusion, we have discovered a remarkably simple and effective system for the direct conversion of allylic alcohols **4** into allylic boronic esters **5** using commercially available reagents and catalysts [bis(pinacalato)diboron (**2b**) and palladium catalyst **3**]. Because of the importance of allylic boronic esters in synthesis, this novel, scalable process, with broad substrate scope, will no doubt find wide application.

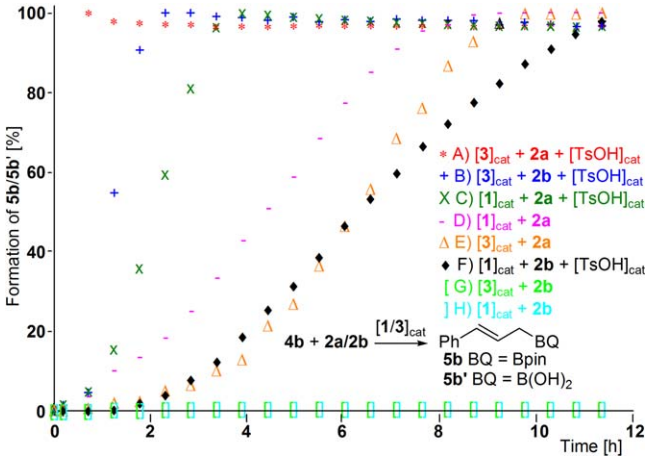
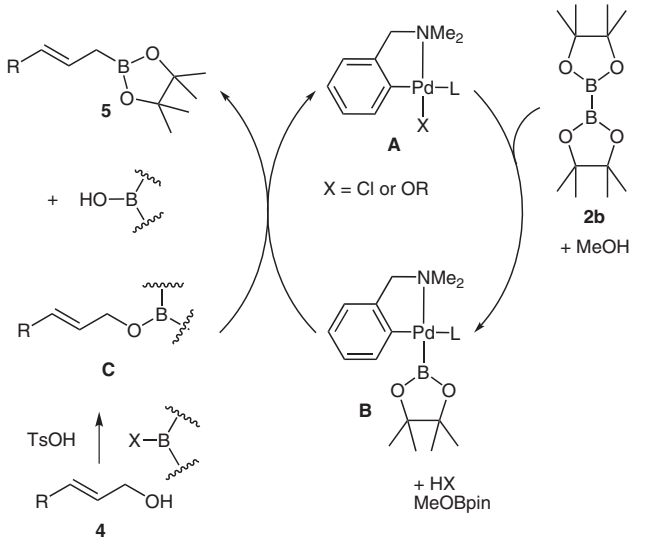


Figure 1 Competitive borylation of cinnamyl alcohol with **2a** $[B_2(OH)_4]$ or **2b** (B_2pin_2) in the presence of 5 mol% of Pd-catalyst (i.e. 5 mol% of **1** or 2.5 mol% of **3**) in DMSO/MeOH (3:1) at 55 °C. The reactions were carried out in the presence (5 mol%) or in the absence of TsOH. Conditions A–H are given in the legends.



Scheme 2 Mechanistic rationale

All reactions were carried out in flame-dried Schlenk tubes under an argon atmosphere employing standard manifold techniques. Solvents were dried by standard methods. NMR spectra were recorded on JEOL 270 MHz, JEOL 400 MHz or Eclipse 300 MHz spectrometers using TMS as the internal standard (δ = 0.00 ppm). $CDCl_3$ was used as an internal standard for ^{13}C NMR spectra (δ = 77.0 ppm). CI mass spectra were obtained using a VG Platform mass spectrometer. All IR data were obtained on a Perkin–Elmer Spectrum One FT-IR spectrometer. All MS were recorded on Agilent Technologies GC-MS Spectrum equipped with a 6890 Series GC system, 7683 Series injector and 5973 Network Mass Selective detector. Analytical TLC was done on aluminium backed plates (1.5 × 5 cm) precoated (0.25 mm) with silica gel (Merck, Silica Gel 60 F_{254}). Compounds were visualised by exposure to UV light or by dipping the plates in a solution of 5% $(NH_4)_2Mo_7O_{24}{\cdot}4H_2O$ in 95% EtOH (w/v) followed by heating. Flash chromatography was done on silica gel (Merck Kieselgel 60). Bis(pinacolato)diboron was purchased from AK Scientific Inc., di-μ-chlorobis{2-[(dimethylamino)methyl]phenyl-C,N}dipalladium(II) from Aldrich Chemical Company, TsOH and anhydrous MeOH from Acros Chemical Company and were used without further purification. DMSO was purchased from Aldrich and distilled over CaH_2 prior to use. Petroleum ether (PE), where used, had a boiling range of 40–60 °C.

Synthesis of Allylic Pinacol Boronic Esters from Allylic Alcohols; General Procedure

To a solution of allylic alcohol (0.50 mmol, 1 equiv) in anhydrous DMSO (1 mL) and anhydrous MeOH (1 mL) at r.t. was added TSOH (4.5 mg, 0.025 mmol, 0.05 equiv), di-μ-chlorobis{2-[(dimethylamino)methyl]phenyl-C,N}dipalladium(II) (**3**; 7.0 mg, 0.0125 mmol, 0.025 equiv) and bis(pinacolato)diboron (**2b**; 254 mg, 1.00 mmol, 2 equiv). The mixture was stirred at 50 °C overnight then cooled to r.t. and H_2O (5 mL) was added. Et_2O (10 mL) was then added and the layers were separated. The aqueous layer was extracted with Et_2O (2 × 10 mL) and the combined organic layers were dried ($MgSO_4$), filtered on a thin silica pad and concentrated in vacuo. The crude product was purified by flash chromatography.

(*E*)-2-(3,7-Dimethylocta-2,6-dienyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a) from Geraniol (4a)

This compound was prepared according to the above general procedure. The crude product was purified by flash chromatography (Et_2O–PE, 2%) to yield **5a**.

Yield: 114 mg (87%); colourless oil; R_f = 0.5 (Et_2O–PE, 2%).

IR (neat): 2978, 2924, 1370, 1322, 1145 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.27–5.24 (m, 1 H), 5.13–5.09 (m, 1 H), 2.08–1.98 (m, 4 H), 1.70–1.57 (3 × s + m, 11 H), 1.25 (s, 12 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.1, 131.1, 124.4, 118.5, 83.0, 39.7, 26.8, 25.4, 24.7, 24.5, 17.7, 15.9.

^{11}B NMR ($CDCl_3$, 96 MHz): δ = 35.4.

Anal. Calcd for $C_{16}H_{29}BO_2$: C, 72.73; H, 11.06. Found: C, 72.39; H, 10.88.

GC-MS analysis (on supelco SLBTM-5ms, 15 m × 0.25 mm × 0.25 μm, injector 250 °C, starts at 70 °C for 2 min, ramps at 25 °C/min to 150 °C, ramps at 45 °C/min to 250 °C) shows a 93:7 ratio of geometrical isomers [retention times: 6.3 min (*Z*) and 6.4 min (*E*)].

2-Cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b) from Cinnamyl Alcohol (4b)

This compound was prepared according to the above general procedure except that bis(pinacolato)diboron (**2b**; 3 equiv) was added. The crude product was purified by flash chromatography (Et_2O–PE, 2%) to yield **5b**.

Yield: 111 mg (91%); colourless oil; R_f = 0.2 (Et_2O–PE, 2%).

IR (neat): 3025, 2978, 2932, 1357, 1323, 1142, 963, 850, 693 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.35–7.13 (m, 5 H), 6.37 (d, *J* = 15.8 Hz, 1 H), 6.29 (dt, *J* = 15.8, 7.1 Hz, 1 H), 1.87 (d, *J* = 7.1 Hz, 2 H), 1.26 (s, 12 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 138.2, 130.2, 128.3, 126.5, 126.3, 125.8, 83.3, 24.8, 24.2.

^{11}B ($CDCl_3$, 96 MHz): δ = 32.2.

Anal. Calcd for $C_{15}H_{21}BO_2$: C, 73.79; H, 8.67. Found: C, 73.49; H, 8.74.

2-Cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5b) from 1-Phenylprop-2-en-1-ol (4c)

This compound was prepared according to the above general procedure except that bis(pinacolato)diboron (**2b**; 3 equiv) was added, yielding **5b** (96%). See above for analytical data.

4,4,5,5-Tetramethyl-2-(3-methylbut-2-enyl)-1,3,2-dioxaborolane (5c) from 2-Methyl-3-buten-2-ol (4d)

This compound was prepared according to the above general procedure. The crude product was purified by flash chromatography (Et_2O–PE, 2%) to yield **5c**.

Yield: 79 mg (81%); colourless oil; R_f = 0.4 (Et_2O–PE, 2%).

IR (neat): 2978, 2933, 1372, 1346, 1141, 850, 672 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.21 (m, 1 H), 1.67 (s, 3 H), 1.57 (m, 5 H), 1.23 (s, 12 H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 131.4, 118.4, 83.0, 25.6, 24.7, 17.6, 17.5.

^{11}B NMR ($CDCl_3$, 96 MHz): δ = 32.4.

Anal. Calcd for $C_{11}H_{21}BO_2$: C, 67.37; H, 10.79. Found: C, 67.19; H, 10.61.

(*E*)-Methyl 3-Phenyl-2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]acrylate (5d) from Methyl 2-[Hydroxyl(phenyl)methyl]acrylate (4e)

This compound was prepared according to the above general procedure. The crude product was purified by flash chromatography (Et_2O–PE, 10%; R_f = 0.3) to yield an inseparable mixture of **5d** and **2b** (304 mg, 1:1.4 mixture of **5b/2b**, 92%). All spectral data were in accordance with literature values.

IR (neat): 3421, 2978, 2924, 1708, 1372, 1346, 1323, 1142, 1123, 848 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.68 (s, 1 H), 7.40–7.25 (m, 5 H), 3.81 (s, 3 H), 2.15 (s, 2 H), 1.27 (s, 12 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.1, 137.5, 136.2, 131.3, 129.3, 128.3, 128.0, 83.4, 51.9, 24.7, 24.6.

^{11}B NMR ($CDCl_3$, 96 MHz): δ = 29.8.

HRMS (EI^+): *m/z* calcd for $C_{17}H_{23}BO_4$: 302.1689; found: 302.1687.

(*E*)-4,4,5,5-Tetramethyl-2-(pent-2-enyl)-1,3,2-dioxaborolane (5e) from (*Z*)-Pent-2-en-1-ol (4f)

This compound was prepared according to the above general procedure except that bis(pinacolato)diboron (**2b**; 3 equiv) was added. The crude product was purified by flash chromatography (Et_2O–PE, 2%) to yield **5e**.

Yield: 96 mg (98%); colourless oil; R_f = 0.5 (Et_2O–PE, 2%).

IR (neat): 2978, 2933, 1358, 1323, 1143, 966, 846 cm^{-1}.

^1H NMR ($CDCl_3$, 270 MHz): δ = 5.45–5.43 (m, 2 H), 2.05–1.97 (m, 2 H), 1.65 (d, *J* = 3.2 Hz, 2 H), 1.26 (s, 12 H), 0.96 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.7, 123.7, 83.1, 25.8, 24.8, 24.7, 14.1.

^{11}B NMR ($CDCl_3$, 96 MHz): δ = 32.2.

Anal. Calcd for $C_{11}H_{21}BO_2$: C, 67.37; H, 10.79. Found: C, 67.06; H, 10.56.

(*E*)-4,4,5,5-Tetramethyl-2-(pent-2-enyl)-1,3,2-dioxaborolane (5e) from (*E*)-Pent-2-en-1-ol (4g)

This compound was prepared according to the above general procedure, yielding **5e** (91%). See above for analytical data.

(*E*)-Trimethyl[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-enyl]silane (5f) from (*E*)-3-(Trimethylsilyl)prop-2-en-1-ol (4h)

This compound was prepared according to the above general procedure. The crude product was purified by flash chromatography (Et_2O–PE, 2%) to yield **5f**. All spectral data were in accordance with literature values.

Yield: 68 mg (57%); colourless oil; R_f = 0.6 (Et_2O–PE, 2%).

IR (neat): 2978, 2931, 1438, 1326, 1145, 982, 836, 672 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.08 (dt, *J* = 18.3, 7.1 Hz, 1 H), 5.63 (dt, *J* = 18.3, 1.5 Hz, 1 H), 2.36 (br d, *J* = 7.1 Hz, 2 H), 1.25 (s, 12 H), 0.00 (s, 9 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.1, 130.7, 83.2, 24.8, 24.7, –1.1.

^{11}B NMR ($CDCl_3$, 96 MHz): δ = 31.9.

Anal. Calcd for $C_{12}H_{25}BO_2Si$: C, 60.00; H, 10.49. Found: C, 59.89; H, 10.33.

2-(Cyclohex-2-enyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5g) from Cyclohex-2-enol (4i)

This compound was prepared according to the above general procedure except that bis(pinacolato)diboron (**2b**; 3 equiv) were added. The crude product was purified by flash chromatography (Et_2O–PE, 2%) to yield **5g**. All spectral data were in accordance with literature values.

Yield: 74 mg (71%); colourless oil; R_f = 0.4 (Et_2O–PE, 2%).

IR (neat): 2976, 2929, 1370, 1285, 1123, 1110, 847 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.74–5.65 (m, 2 H), 2.01–1.98 (m, 2 H), 1.84–1.58 (m, 5 H), 1.25 (s, 12 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 127.7, 126.2, 83.7, 25.1, 24.9, 24.8, 24.2, 22.6.

^{11}B NMR ($CDCl_3$, 96 MHz): δ = 32.4.

Competitive Boronation of Cinnamyl Alcohol (4b; Figure 1)

In an NMR tube, cinnamyl alcohol **4b** (0.020 g, 0.15 mmol) was dissolved in a mixture of DMSO-d_6 and MeOH-d_4 (0.3/0.1 mL) followed by addition of diboronate **2a** or **2b** (0.18 mmol) and palladium catalyst **1** or **3** (5 mol% Pd). The reactions were conducted in a NMR tube at 55 °C for 11 h. The progress of the reaction was monitored by ^1H NMR spectroscopy. The ^1H NMR spectrum of allyl boronic acid product was determined from the crude mixture.

^1H NMR (DMSO-d_6/CD_3OD, 400 MHz): δ = 7.29 (d, *J* = 7.4 Hz, 2 H), 7.23 (t, *J* = 7.4 Hz, 2 H), 7.11 (t, *J* = 7.4 Hz, 1 H), 6.31 (dt, *J* = 7.0, 15.6 Hz, 1 H), 6.23 (d, *J* = 15.6 Hz, 1 H), 1.76 (d, *J* = 7.0 Hz, 2 H).

Acknowledgment

We thank the EPSRC and the Swedish Research Council for support of this work. VKA thanks the Royal Society for a Wolfson Research Merit Award and the EPSRC for a Senior Research Fellowship.

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