Nickel-Catalyzed Allylboration of Aldehydes

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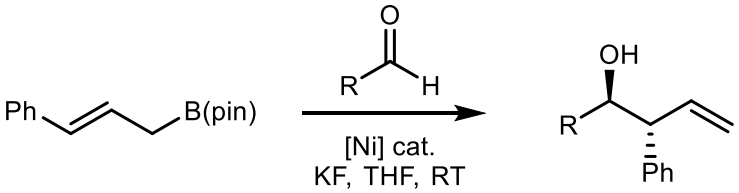

up to >19:1 d.r.
59-95% yield

- *26 examples*
- *Allylation through a cyclic transition state.*
- *Ni acts as a Lewis acid catalyst.*

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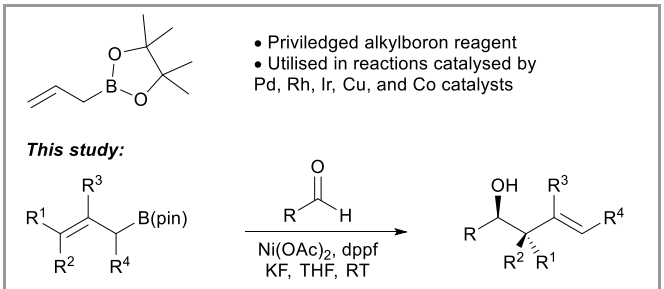
Abstract A nickel catalyst for the allylboration of aldehydes is reported, facilitating the preparation of homoallylic alcohols in high diastereoselectivity. The observed diasteroselectivities and NMR experiments suggest that allylation occurs through well-defined 6-membered transition state, with nickel acting as a Lewis acid.

Key words allylboration, boronic esters, catalysis, homoallylic alcohols, nickel

The use of aryl boron reagents in combination of transition metal catalysis enables wide range of C-C and C-heteroatom bond forming reactions.[1] However, reactions involving the corresponding alkylboronic esters[2] are underdeveloped despite recent growth in methods to make these valuable reagents.[3] Allylboron reagents are a privileged exception, with catalysts based on metals such as palladium,[4] rhodium,[5] iridium,[6] copper,[7] and cobalt[8] reported to promote reactions, including cross-couplings and allylborations. In comparison, Ni-catalyzed transformations of allylboron reagents are rare.[9,10] The ability to develop nickel catalysts which promote the functionalization of alkylboron reagents is desirable. This is both due to nickel's higher abundance and lower cost compared with many precious metals, but also the opportunity to exploit its diverse reactivity in the development of new transformations.[11]

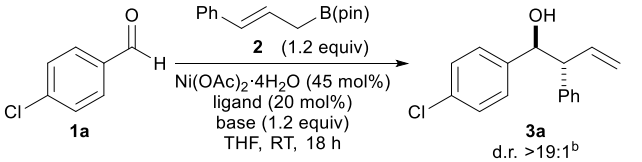
As part of a programme aimed at the development of metal-catalyzed transformations of alkylboronic esters,[12] we report a Ni-catalyzed allylboration.[10,13] Previously, isolated allylnickel species have been shown to be nucleophilic, and stoichiometric reactions with aldehydes give homoallylic alcohols as products.[14,] Our results also complement reports of Ni-catalyzed reductive allylations of carbonyls[15] and the Ni-catalzyed allylation via double bond transposition of alkenyl borates.[16]



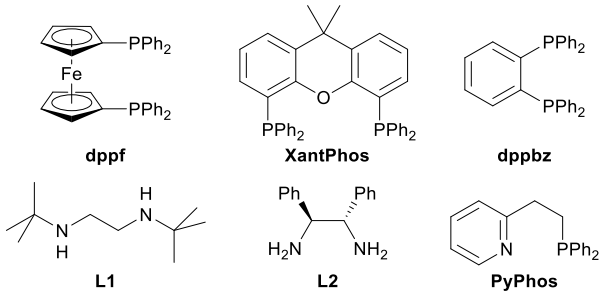
Scheme 1 Allylboronic ester and its use with transition metal catalysts.

We started by investigating the effect of adding $Ni(OAc)_2$ and a variety of ligands on the yield of allylboration of aldehyde **1a** with boronic ester **2** (Table 1).[17] In the absence of Ni, there was a modest background reaction after 18 h, with 41% yield of homoallylic alcohol **3a** obtained (entry 1). The addition of $Ni(OAc)_2$ provided little improvement. However, a combination of $Ni(OAc)_2$ and dppf in a 2.2:1 ratio led to an increased in yield (entry 2). Addition of KF as a base was beneficial (entry 3), though Cs_2CO_3 led to a reduced yield (entry 4). From a survey of ligands, addition of dppf led to the most active catalyst. Other ligand classes including diamines and P,N-ligands led to moderate yields at best (entries 5-9). Using dppf, the loading of catalyst could be reduced. Though 76% of **3a** was obtained within 5 h using 37% $Ni(OAc)_2$ and 15 mol% dppf, similar yields were only obtained with 12 mol% $Ni(OAc)_2$ and 5.5 mol% dppf after 24 h. In the interests of reducing the overall cost of reagents, we chose the lower Ni loading to explore the scope of the reaction. These conditions could be scaled up, with 85% of alcohol **3a** isolated as a single diastereomer (entry 10).

Table 1 Evaluation on effect of the reaction conditions on the yield of allylboration.



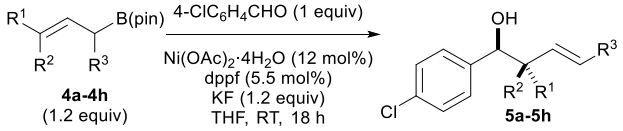
Entry	Ligand	Base	Yield[c]
1[d]	-	-	41%
2	dppf	-	70%
3	dppf	KF	84%
4	dppf	Cs_2CO_3	45%
5	XantPhos	KF	78%
6	dppbz	KF	82%
7	**L1**	KF	68%
8	**L2**	KF	54%
9	PyPhos	KF	52%
10[e]	dppf	KF	84%

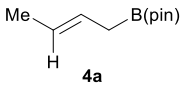
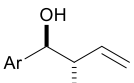
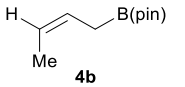
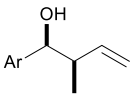
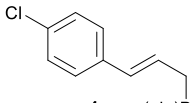
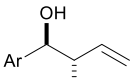
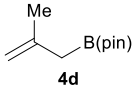
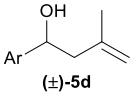
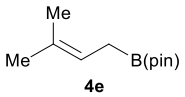
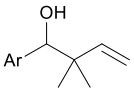
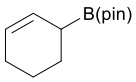
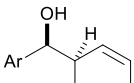
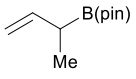
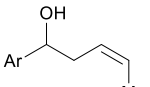
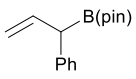
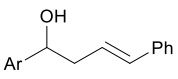


[a] 0.044 mmol scale. [b] d.r. determined by ^{1}H NMR analysis of the crude reaction mixture. [c] yield determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [d] without $Ni(OAc)_2.6H_2O$. [e] 12 mol% $Ni(OAc)_2$ and 5.5 mol% dppf; 0.33 mmol scale; isolated yield.

Next, we explored the scope with respect to the allylboronic ester reagent (Table 2). *E*- and *Z*-crotyl boronic esters reacted to give the *anti* and *syn* homoallylic alcohols **5a** and **5b** respectively. This is consistent with allylboration occurring through a well-defined cyclic transition state. In both cases, the E/Z-ratio of the allylboron matched the d.r. of the product. This suggests that isomerisation of the allyl nucleophile does not occur on the time scale of the reaction. Further boronic esters tested included aryl chloride **4c** and 2-substituted boronic ester 4**d**, both of which reacted smoothly. The reaction of trisubstituted allyl boronic ester **4e** demonstrated that formation of a quaternary centre is possible, and that 1,3-allylic transposition does not occur prior to allylation.

Table 2 Allylboration of primary and secondary boronic esters[a]



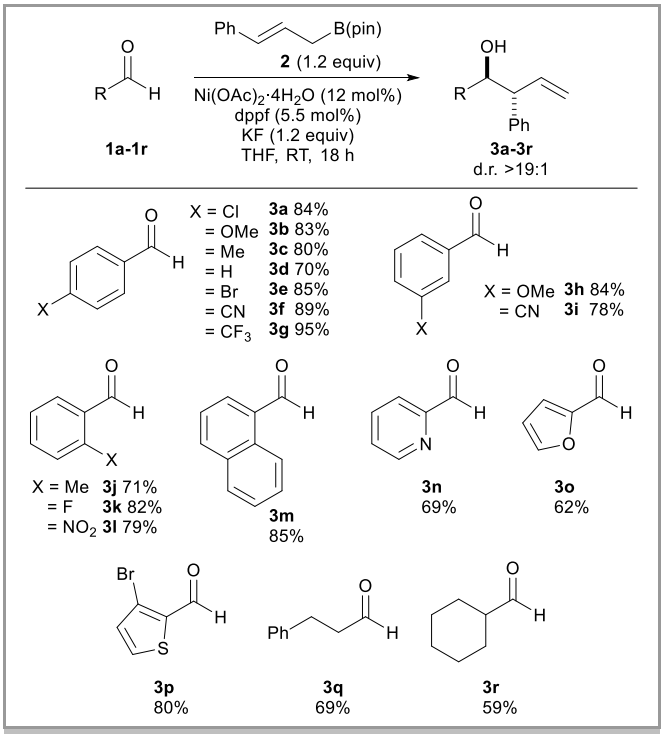
Boronic Ester	Product	Yield[b]	d.r.[c]
 **4a** *E*:*Z* = 4:1	 **(±)-5a**	65%	4:1
 **4b**	 **(±)-5b**	99%	>19:1
 **4c**	 **(±)-5c**	89%	>19:1
 **4d**	 **(±)-5d**	95%	n/a
 **4e**	 **(±)-5e**	79%	n/a
 **(±)-4f**	 **(±)-5f**	69%	>9:1
 **(±)-4g**	 **(±)-5g**	75%	1:3 (E/Z)
 **(±)-4h**	 **(±)-5h**	76%[d]	9:1 (E/Z)

[a] 0.33 mmol scale. [b] Isolated yield. [c] d.r. determined by ^{1}H NMR analysis of the crude reaction mixture. [d] 0.29 mmol scale. Ar = 4-Cl-C_6H_4

The method was also successful with secondary allylboronic esters **4f**-**4h** (Table 2). Cyclic boronic ester **4f** reacted to give *syn*-homoallylic alcohol **5f** in high yield as a single diastereomer. Acyclic boronic ester **4g** reacted to give alkene **5g** in a modest 3:1 Z:E ratio, consistent with previous allylborations using secondary pinacol allylboronic esters.[18] Instead, **4h** reacted to give the corresponding *E*-alkene **5h** in good stereochemical control. Usually a sterically unhindered allylboron reagent is needed to obtain *E*-selectivity for the homoallylic alcohol product.[19] However, it has been observed previously that aryl-substituted secondary allyl boronic esters react to give *E*-homoallylic alcohols preferentially.[20] The *E*-selectivity could be accounted for by Ni acting as a Lewis acid catalyst, as a moderate switch from *Z*- to *E*-selectivity has also been observed using Lewis acid catalysts.[21]

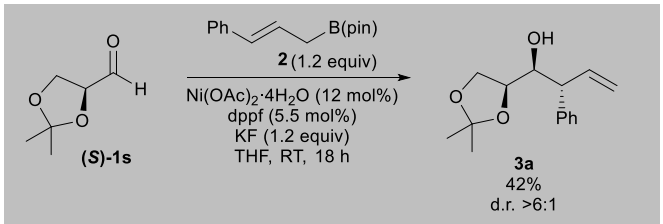
We next explored the scope of aldehydes tolerated in the Ni-catalyzed allylboration. Boronic ester **2** reacted with a range of benzaldehyde derivatives to give *anti*-homoallylic alcohols **3a-3r** in good to excellent yield (Scheme 2). The relative configuration

of **3f** was confirmed by x-ray crystallography.[22] The remainder of the products were assigned through comparison with literature data or by analogy to **3f**. Functional groups tolerated include aryl halides, nitrile, nitro, and trifluormethyl groups. Substitution at the ortho-position position did not lower the reaction efficiency. Heteroaromatic pyridyl-, furyl- and thiophenyl-derived aldehydes also reacted in good yield. The reaction conditions were also successful with aliphatic aldehydes **1q** and **1r**.



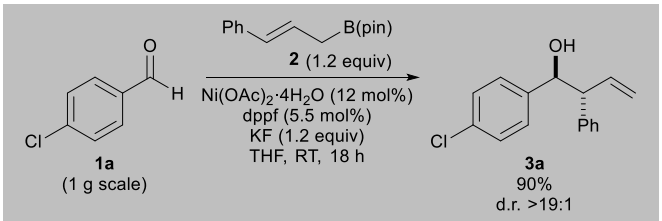
Scheme 2 Scope of Ni-catalyzed allylboration with respect to carbonyl electrophile. Reactions were performed on 0.33 mmol scale. Diastereomeric ratios were determined by ^{1}H NMR analysis of the crude reaction mixture. Isolated yields are reported.

The reaction of **(*S*)-1s** provided homoallylic alcohol **(S,S,R)-3s**, the syn,anti diasteromer, which was isolated as a single diastereomer (eq 1). The absolute configuration was confirmed by X-ray crystallography.[22] The diastereoselectivity observed (>6:1) is greater than for the corresponding reaction of aldehyde **1s** with boronic ester **4a** as described by Roush and co-workers, which gave a 1:1 mixture of syn,anti and anti,anti products.[23] The syn diastereoselectivity is consistent with a chelate controlled anti-Cram addition to aldehyde **(*S*)-1s**.[24]



Equation 1 Nickel-catalyzed allylboration of aldehyde **(*S*)-1s**.

The Ni-catalyzed allylboration reaction could also be carried out on the gram scale without decrease in reaction efficiency (eq 2).



Equation 2 Nickel-catalyzed allylboration on gram-scale.

To give insight to the role of the Ni catalyst, we performed a series of ^{11}B NMR experiments (Figure 1). First we analysed a solution containing $Ni(OAc)_2$, dppf, KF and boronic ester **2** in THF. A characteristic peak for a boronic ester was observed at 33 ppm. This signal remained unchanged over a 3 h period. Next, 1 equivalent of benzaldehyde was added to the solution and the mixture was reanalysed. Within 30 minutes, a new peak was observed by boron NMR at 22 ppm, which is consistent with a borate, presumably structure **6** formed through allylboration. This suggests that the Ni catalyst is unlikely to undergo transmetallation with the boronic ester, as an AcO-B(pin) by-product was not observed before addition of the aldehyde. Instead, the data are more consistent with Ni acting as a Lewis acid catalyst.

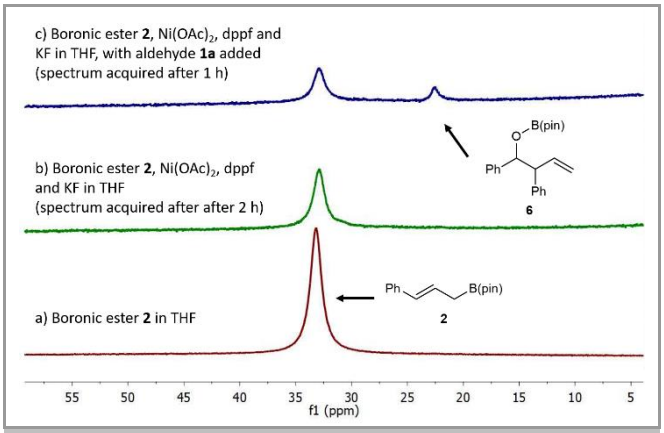


Figure 1 Overlaid ^{11}B NMR spectra for a) boronic ester **2**, b) boronic ester **2** in the presence of the Ni catalyst, c) boronic ester **2** in the presence of the Ni catalyst with aldehyde **1a** added after 3 h.

In summary, we have developed a Ni-catalyzed allylboration of aldehydes with allylboronic esters. The high diastereoselectivities obtained are consistent with allylation occurring through a cyclic transition state. A NMR study suggests that the role of the Ni-catalyst is likely to be as a Lewis acid.

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All reagents and solvents used were supplied by commercial sources without further purification unless specified. All air-sensitive reactions were carried out under a nitrogen atmosphere using oven-dried apparatus. Anhydrous Et_2O and THF were dried and purified by passage through activated alumina columns using a solvent purification system. All petroleum ether used was 40-60 °C petroleum ether. Thin layer chromatography (TLC) was performed on aluminium-backed plates pre-coated with silica. Compounds were visualised by exposure to UV light or by dipping the plates into solutions of vanillin followed by heating. All flash chromatography was carried out using silica gel mesh 40-63. Infra-red spectra were recorded on a Perkin Elmer 100 FT instrument on the neat compound. NMR spectra were recorded on Bruker Advance 400 and 500 instruments at the indicated 101, 128, 126, 377 and 400 MHz as dilute

solutions in the indicated deuterated solvent at ambient temperature. All chemical shifts (δ) reported in parts per million (ppm) relative to residual protio solvent (δH: $CHCl_3$ = 7.27 ppm) or the solvent itself (δC: $CDCl_3$ = 77.0 ppm). All multiplets are designated by the following abbreviations: s = singlet, br s = broad singlet, d = doublet, dt = doublet triplet, td = triplet doublet, ddd = doublet of doublets of doublets, q = quartet, br q = broad quartet, m = multiplet. All coupling constants (*J*) are reported in Hertz (Hz). ^{13}C NMR spectra were acquired DEPT-Q experiments as standard; standard ^{13}C NMR experiments were acquired when quaternary carbons were hard to distinguish by DEPT-Q. ^{19}F NMR spectra acquired as decoupled spectra. High-resolution mass spectra were recorded using either electrospray ionization (ESI) or electron ionisation (EI) by the Mass Spectrometry Service at the Department of Chemistry, University of Sheffield. Melting points were measured using Linkam HFs91 heating stage, used in conjunction with a TC92 controller and are uncorrected. Single crystal X-ray intensity data was collected at 100 K on a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS detector using a CuKα microfocus X-ray source from crystals mounted in fomblin oil on a MiTiGen microloop and cooled in a stream of cold N_2.

Procedures

1,3,2-Dioxaborolane-4,4,5,5-tetramethyl-2[(2E)-3-phenyl-2-propen-1-yl (2)

Using a modification of the procedure by Singaram and co-workers,[25] a flask containing magnesium turnings (0.583 g, 24.0 mmol) was purged with nitrogen and charged with anhydrous THF (30 mL) followed by HB(pin) (3.0 mL, 20 mmol). Cinnamyl chloride (2.8 mL, 20 mmol) was added dropwise over 5 min at room temperature. The mixture was stirred for 1 h, and another portion of cinnamyl chloride (1.4 mL, 10.0 mmol) was added. After 5 h of stirring at room temperature the magnesium turnings were fully consumed. The reaction was diluted with hexanes (20 mL) and quenched with aqueous HCl (0.1 M, 60 mL) (Caution! Hydrogen evolution). The mixture was extracted with hexanes (2 × 20 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (2% Et_2O/petroleum ether) to give boronic ester **2** (1.29 g, 26%) as a colourless solid. The data were consistent with the literature.[26]

Rf = 0.06 (2% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29-7.17 (m, 4H, Ar**H**), 7.12-7.09 (t, *J* = 7.2 Hz, 1H, Ar**H**), 6.30 (d, *J* = 15.8 Hz, 1H, PhC**H**=C), 6.20 (dt, *J* = 15.8, 7.2, Hz, 1H, PhCH=C**H**), 1.86 (d, *J* = 7.2 Hz, 2H, C**H$_2$**), 1.24 (s, 12H, 4 × C**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 138.2 (C), 130.2 (CH), 128.4 (2 ×CH), 126.5 (CH), 126.3 (CH), 125.8 (2 × CH), 83.4 (2 × OC), 24.8 (4 × CH_3).

^{11}B NMR ($CDCl_3$, 128 MHz) δ 32.9.

2-(2*E*)-2-Buten-1-yl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4a)

Using a modification of the procedure by Morken and co-workers[27] a flask containing $Pd_2(dba)_3$ (66.3 mg, 0.075 mmol) and bis(pinacolto)diboron (3.80 g, 15.0 mmol) was purged with nitrogen and charged with anhydrous THF (7 mL) followed by crotyl bromide (1.50 mL, 15.0 mmol). The mixture was stirred at 60 °C for 18 h. The mixture was cooled to r.t., concentrated *in vacuo* and purified by flash chromatography (2% Et_2O/pentane), to give the boronic ester **4a** (905 mg, 34%, *E*/*Z* = 4:1) as a colourless oil. The data were consistent with the literature.[26]

Rf = 0.07 (2% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.57-5.40 (m, 2H, **H**C=C**H**), 1.67-1.65 (m, 3H, CHC**H$_3$**), 1.62-1.60 (m, 2H, C**H$_2$**), 1.24 (s, 12H, 4 × CC**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 125.9 (CH), 125.3 (CH), 83.1 (2 × OC), 24.8 (4 × CH_3), 18.1 (CH_3). Characteristic signals for *Z* isomer: 125.0 (CH), 123.8 (CH), 14.3 (CH_3).

^{11}B NMR ($CDCl_3$, 128 MHz) 32.7.

4,4,5,5-Tetramethyl-2-[(2E)-3-(4-chlorophenyl)prop-2-en-1-yl]-1,3,2-dioxaborolane (4c)

Using a modification of the procedure by Morken and co-workers,[4i] an oven-dried flask containing aldehyde (2.00 g, 14.0 mmol) was purged under nitrogen. THF (70 mL) was added and the mixture was cooled to −78 °C. Vinyl magnesium bromide (0.7 M in THF, 25 mL, 17.0 mmol) was added and the mixture was warmed to room temperature and stirred for 3 h. Saturated aqueous ammonium chloride (40 mL) was added, and the mixture was extracted with Et_2O (3 × 30 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give 1-(4-chlorophenyl)prop-2-en-1-ol (2.40 g) as an orange oil. The material was used without further purification.

An oven-dried round bottom flask containing 1-(4-chlorophenyl)prop-2-en-1-ol (1.00 g, 6.00 mmol) was purged under nitrogen. CH_2Cl_2 (10 mL) was added and the mixture was cooled to 0 °C. $SOCl_2$ (1.29 mL, 17.9 mmol) was added, and the mixture was stirred at 0 °C for 3 h and then at room temperature for 2 h. The mixture was quenched with ice water (30 mL), and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give 1-chloro-4-[(1E)-3-chloroprop-1-en-1-yl]benzene (1.11 g) as a brown solid. The material was used without further purification.

Using a modification of the procedure by Singaram and co-workers,[25] a round bottom flask containing magnesium turnings (127 mg, 5.29 mmol) was purged with nitrogen. Anhydrous THF (15 mL) was added followed by HB(pin) (0.60 mL, 4.4 mmol). 1-Chloro-4-[(1E)-3-chloroprop-1-en-1-yl]benzene (0.83 g, 4.4 mmol) was added dropwise over 5 min at room temperature. The mixture was stirred for 1 h, another 0.5 equiv of allyl chloride **S2** (0.41 g, 2.2 mmol) was added. After stirring at room temperature overnight the magnesium turnings were fully consumed. The mixture was diluted with hexanes (10 mL) and quenched with aqueous HCl (0.1 M, 30 mL) (Caution! Hydrogen evolution). The mixture was extracted with hexanes (3 × 10 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography (2% Et_2O/petroleum ether) to give boronic ester **4c** (94.4 mg, 5%) as a pale yellow oil. The data were consistent with the literature.[28]

Rf = 0.23 (2% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27-7.20 (m, 4H, Ar**H**), 6.29-6.26 (m, 2H, **H**C=C**H**), 1.86 (d, *J* = 6.5 Hz, 2H, C**H$_2$**), 1.23 (s, 12H, 4 × C**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 136.6 (C), 132.0 (C), 129.1 (CH), 128.5 (2 × CH), 127.1 (2 × CH), 127.0 (CH), 83.5 (2 × C), 24.8 (4 × CH_3).

^{11}B NMR ($CDCl_3$, 128 MHz) δ 32.7.

4,4,5,5-Tetramethyl-2-(2-methylprop-2-en-1-yl)-1,3,2-dioxaborolane (4d)

Using a modification of the procedure by Singaram and co-workers,[25] a flask containing magnesium turnings (0.583 g, 24.0 mmol) was purged with nitrogen and charged with anhydrous THF (30 mL) followed by HB(pin) (3.0 mL, 20 mmol). 3-Chloro-2-methyl-1-propene (2.0 mL, 20 mmol) was added dropwise over 5 min at room temperature. The mixture was stirred for 1 h, and another portion of 3-chloro-2-methyl-1-propene (2.0 mL, 20.0 mmol) was added. After 18 h of stirring at room temperature the magnesium turnings were fully consumed. The reaction was diluted with hexanes (20 mL) and quenched with aqueous HCl (0.1 M, 60 mL) (Caution! Hydrogen evolution). The mixture was extracted with hexanes (3 × 20 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated in *vacuo*. The residue was purified by flash column chromatography (2% Et_2O/petroleum ether) to give boronic ester **4d** (1.02 g, 27%) as a colourless oil. The data were consistent with the literature.[29]

Rf = 0.40 (2% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.66 (d, *J* = 7.2 Hz, 2H, C=CH_2), 1.76 (s, 3H, CH_2=CCH_3), 1.71 (s, 2H, BCH_2), 1.24 (s, 12H, 4 × CH_3).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.9 (C), 110.2 (CH_2), 83.2 (2 × OC), 24.7 (4 × CH_3), 24.5 (CH_3).

^{11}B NMR ($CDCl_3$, 128 MHz) 32.7.

4,4,5,5-Tetramethyl-2-(3-methylbut-2-en-1-yl)-1,3,2-dioxaborolane (4e)

Using a modification of the procedure by Morken and co-workers,[27] a flask containing $Pd_2(dba)_3$ (0.024 g, 0.027 mmol) and B_2Pin_2 (0.768 g, 5.3 mmol) was purged with nitrogen and charged with anhydrous THF (5 mL). 1-Bromo-3-methyl but-2-ene (0.9 mL, 5.3 mmol) was added. The mixture was stirred at 60 °C for 18 h. The mixture was concentrated *in vacuo* and purified by flash chromatography (2% EtOAc/petroleum ether) to give the boronic ester **4e** (699 mg, 88%) as a pale yellow oil. The data were consistent with the literature.[30]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.23 (ddd, *J* = 7.6, 4.7, 1.5 Hz, 1H, C**H**), 1.70 (s, 3H, C**H$_3$**), 1.60 (m, 5H, C**H$_3$** and C**H$_2$**), 1.25 (m, 12H, 4 × CC**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 131.5 (C), 118.5 (CH), 83.1 (2 × OC), 25.7 (CH_3), 24.8 (4 × CH_3), 17.6 (CH_3).

^{11}B NMR ($CDCl_3$, 128 MHz) δ 32.8.

(±)-2-(Cyclohex-2-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4f)

Using a modification of the procedure by Marder and co-workers,[31] a solution of $CuCl_2$ (8.0 mg, 0.060 mmol), IMes (20.0 mg, 0.060 mmol), KOMe (252 mg, 3.60 mmol) in THF (12 mL) was stirred for 10 min. B_2Pin_2 (1.83 g, 7.2 mmol) and KOMe (252 mg, 3.60 mmol) were added and the mixture was stirred for 10 min. 3-Bromocyclohexene (0.69 mL, 6.0 mmol) was added and the mixture was stirred overnight. The mixture was diluted with Et_2O (20 mL), filtered through a plug of celite, and concentrated *in vacuo*. The residue was purified by flash chromatography (5% Et_2O/petroleum ether), to give the boronic ester **4f** (844 mg, 68%) as a colourless oil. The data were consistent with the literature.[31]

Rf = 0.50 (5% Et_2O/petroleum ether)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.86-5.56 (m, 2H, **H**C=C**H**), 2.11-1.94 (m, 2H, C**H$_2$**), 1.87-1.72 (m, 2H, C**H$_2$**), 1.71-1.54 (m, 3H, C**H$_2$**C**H**), 1.24 (s, 12H, 4 × C**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 127.6 (CH), 126.1 (CH), 83.1 (2 × C), 25.0 (CH_2), 24.8 (2 × CH_3), 24.7 (2 × CH_3), 24.1 (CH_2), 22.5 (CH_2).

^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.4.

(±)-4,4,5,5-Tetramethyl-2-(1-methyl-2-propen-1-yl)-1,3,2-dioxaborolane (4g)

Using a modification of the procedure by Singaram and co-workers,[25] a flask containing magnesium turnings (0.516 g, 21.2 mmol) was purged with nitrogen and charged with anhydrous THF (30 mL) followed by HB(pin) (2.5 mL, 17.7 mmol). Crotyl bromide (1.5 mL, 17.7 mmol) was added dropwise over 5 min at room temperature. The mixture was stirred for 1 h, and another portion of crotyl bromide (1.5 mL, 17.7 mmol) was added. After 5 h of stirring at room temperature the magnesium turnings were fully consumed. The reaction was diluted with hexanes (20 mL) and quenched with aqueous HCl (0.1 M, 60 mL) (Caution! Hydrogen evolution). The mixture was extracted with hexanes (2 × 20 mL) and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The residue was purified by flash chromatography (2% Et_2O/petroleum ether) to give boronic ester **4g** (1.60 g, 59%) as a colourless oil. The data were consistent with the literature.[25]

Rf = 0.20 (2% Et_2O/petroleum ether)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.93 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H, C**H**=CH_2), 4.96 (dt, *J* = 17.3, 1.7 Hz, 1H, CH=C**H$_A$**H$_B$), 4.91 (dt, *J* = 10.3, 1.7 Hz, 1H, CH=CH$_A$**H$_B$**), 1.97-1.81 (m, 1H, C**H**), 1.23 (s, 12H, 4 × CC**H$_3$**), 1.08 (d, *J* = 5.8 Hz, 3H, CHC**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.8 (2 × CH), 111.9 (CH_2), 83.1 (2 × C), 24.6 (4 × CH_3), 14.0 (CH_3).

^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.2.

(±)-2-(1-Phenyl-2-propen-1-yl)-4,4,5,5-tetramethyl-1,3,2-Dioxaborolane (4h)

Using a modification of the procedure by Aggarwal and co-workers,[32] a Schlenck flask containing benzyl *N*,*N*-diisopropylcarbamate[12] (1.16 g, 4.97 mmol) was backfilled with nitrogen three times. TMEDA (0.74 mL, 4.97 mmol) and anhydrous Et_2O (12 mL, 0.2 M) were added and the mixture was cooled to −78 °C. *s*-BuLi (1.3 M in hexanes, 3.80 mL, 4.67 mmol) was added dropwise and the mixture was stirred at **−**78 °C for 4 h. 2-Vinyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.5 mL, 2.9 mmol) was added dropwise, and the mixture was stirred at **−**78 °C for 1 h. A solution of $MgBr_2$ in Et_2O (2.50 mL, 8.77 mmol; freshly prepared from Mg turnings (0.210 g, 8.75 mmol), Et_2O (3 mL) and 1,2-dibromoethane (0.75 mL, 8.75 mmol)) was added dropwise and the mixture was stirred at 34 °C for 18 h. The mixture was cooled to room temperature, and NH_4Cl (20 mL) and Et_2O (15 mL) were added. The mixture was extracted with Et_2O (3 × 15 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The mixture was purified by flash chromatography (2% Et_2O/petroleum ether), to give the boronic ester **4h** (451 mg, 64%) as a colourless oil. There is only partial data available in the literature.[33]

***Rf* =** 0.20 (2% Et_2O/petroleum ether)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31-7.11 (m, 5H, Ar**H**), 6.10 (ddd, *J* = 17.1, 10.2, 8.2 Hz, 1H, C**H**=CH_2), 5.02-5.00 (m, 2H, C**H$_2$**), 3.23 (d, *J* = 8.2 Hz, 1H, ArC**H**), 1.21 (s, 12H, 4 × C**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 141.1 (C), 138.7 (CH), 128.4 (4 × CH), 125.5 (CH), 114.5 (CH_2), 83.6 (2 × C), 24.6 (4 × CH_3).

^{11}B NMR ($CDCl_3$, 128 MHz) δ 32.2.

HRMS (EI) Exact mass calculated for $C_{15}H_{21}BO_2$ [M+]: 244.1634, found 244.1629.

General Procedure 1: Preparative Scale Nickel Catalyzed Allylboration. An oven-dried flask was charged with an aldehyde (0.330 mmol), $Ni(OAc)_2.4H_2O$ (10.0 mg, 0.040 mmol), KF (21.0 mg, 0.390 mmol) and dppf (9.5 mg, 0.017 mmol) and purged under nitrogen for 1 h. Boronic ester (0.390 mmol, 1.2 equiv) and THF (3 mL) was added, and the mixture stirred at room temperature for 18 h. Water (10 mL) was added and the mixture was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and dried *in vacuo*. The crude material was purified by flash chromatography.

(±)-*anti*-1-(4-Chlorophenyl)-2-phenyl-but-3-en-1-ol (3a)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (45.3 mg, 0.332 mmol) and boronic ester **2** (99.3 mg, 0.407 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give alcohol **3a** (70.4 mg, 84%) as a colourless oil. The data were consistent with the literature.[34]

Rf = 0.18 (10% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25-7.15 (m, 5H, Ar**H**), 7.07-7.03 (m, 4H, Ar**H**), 6.24 (ddd, *J* = 17.1, 10.2, 9.6 Hz, 1H, C**H**=CH_2), 5.28 (dd, *J* = 10.2, 1.2 Hz, 1H, CH=C**H$_A$**H$_B$), 5.24 (dd, *J* = 17.1, 1.2 Hz, 1H, CH=CH$_A$**H$_B$**), 4.81 (d, *J* = 7.9 Hz, 1H, HOC**H**), 3.48 (dd, *J* = 9.6, 7.9 Hz, 1H, C=CC**H**), 2.39 (d, *J* = 2.2 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.3 (C), 140.1 (C), 137.5 (CH), 133.0 (C), 128.4 (2 × CH), 128.2 (2 × CH), 128.0 (4 × CH), 126.7 (CH), 118.7 (CH_2), 76.5 (CH), 59.3 (CH).

(±)-*anti*-1-(4-Chlorophenyl)-2-phenyl-but-3-en-1-ol (3a) (Gram Scale)

An oven-dried flask was charged with 4-chlorobenzaldehyde (1.01 g, 7.21 mmol), $Ni(OAc)_2.4H_2O$ (0.219 g, 0.880 mmol), KF (0.535 g,

9.21 mmol) and dppf (0.198 mg, 0.357 mmol) and purged under nitrogen for 1 h. Boronic ester **2** (2.09 g, 8.55 mmol) and THF (12 mL) was added, and the mixture stirred at room temperature for 18 h. Water (20 mL) was added and the mixture was extracted with Et_2O (3 × 20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and dried in *vacuo*. The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **3a** (1.67 g, 90%) as a pale yellow oil. The data were consistent with the literature.[34] See above for NMR data.

(±)-*anti*-1-(4-Chlorophenyl)-3-methyl-but-3-en-1-ol (5a)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (48.3 mg, 0.344 mmol) and boronic ester **4a** (72.8 g, 0.400 mmol). The crude material was purified by flash chromatography (10% Et_2O/pentane) to give alcohol **5a** (44.2 mg, 65%) as a pale yellow oil. The data were consistent with the literature.[35]

Rf = 0.19 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ *anti* isomer: 7.35-7.23 (m, 4H, Ar**H**), 5.82-5.68 (m, 1H, C=C**H**), 5.23-5.22 (m, 2H, CH=C**H$_2$**), 4.36 (d, *J* = 7.8 Hz, 1H, HOC**H**), 2.45-2.41 (m, 1H, C=CC**H**), 2.16 (s, 1H, O**H**), 0.88 (d, *J* = 6.8 Hz, 3H, C**H$_3$**). Characteristic signals from the minor diastereoisomer were observed at: 5.11-4.99 (m, 1H, CH=C**H$_2$**), 4.62 (d, *J* = 5.4 Hz, 1H, HOC**H**), 2.59-2.59 (m, 1H, C=CC**H**), 1.93 (s, 1H, O**H**), 1.00 (d, *J* = 6.8 Hz, 1H, C**H$_3$**).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.8 (C), 140.2 (CH), 133.3 (C), 128.4 (2 × CH), 128.2 (2 × CH), 117.3 (CH_2), 76.5 (CH), 46.4 (CH), 16.4 (CH_3). Characteristic signals from the minor diastereoisomer were observed at: 140.9 (C), 139.8 (CH), 133.0 (C), 127.8 (2 × CH), 116.0 (CH_2), 77.1 (CH), 44.6 (CH), 13.8 (CH_3).

(±)-*syn*-1-(4-Chlorophenyl)-3-methylbut-3-en-1-ol (5b)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (42.3 mg, 0.301 mmol) and boronic ester **4b** (73.6 mg, 0.404 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **5b** (59.0 mg, 99%) as a colourless oil. The data were consistent with the literature.[35]

Rf = 0.16 (10% Et_2O/hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.29 (m, 2H, Ar**H**), 7.27-7.24 (, m, 2H Ar**H**), 5.75 (ddd, *J* = 17.3, 10.6, 7.0 Hz, 1H, C=C**H**), 5.13-5.02 (m, 2H, CH=C**H$_2$**), 4.62 (d, *J* = 5.4 Hz, 1H, HOC**H**), 2.56 (qd, *J* = 6.8, 5.4 Hz, 1H, C=CC**H**), 1.92, (s, 1H, O**H**), 1.00 (d, *J* = 6.8 Hz, 3H, C**H$_3$**).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 141.0 (C), 139.9 (CH), 133.0 (C), 128.2 (2 × CH), 127.9 (2 × CH), 116.0 (CH_2), 76.5 (CH), 44.6 (CH), 13.8 (CH_3).

(±)-*anti*-1,2-bis(4-chlorophenyl) but-3-en-1-ol (5c)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (47.1 mg, 0.335 mmol) and boronic ester **4c** (111 mg, 0.379 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give *alcohol* **5c** (87.4 mg, 89%) as a colourless oil.

Rf = 0.09 (10% Et_2O/hexane).

IR (ATR) **3**418 (O-H), 2904, 1596, 1490, 1090, 1013, 923, 820.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22-7.16 (m, 4H, Ar**H**), 7.06 (dd, *J* = 8.7, 2.1 Hz, 2H, Ar**H**), 7.00-6.90 (m, 2H, Ar**H**), 6.18 (ddd, *J* = 17.1, 10.1, 8.9 Hz, 1H, C**H**=CH_2), 5.31 (dd, *J* = 10.1, 0.8 Hz, 1H, CH=C**H$_A$H$_B$**), 5.24 (dd, *J* = 17.1, 0.8 Hz, 1H, CH=CH_A**H$_B$**), 4.76 (dd, *J* = 7.9, 2.2 Hz, 1H, HOC**H**), 3.48 (dd, *J* = 8.9, 7.9 Hz, 1H,C=CC**H**), 2.32 (d, *J* = 2.2 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.0 (C), 138.7 (C), 137.1 (CH), 133.3 (C), 132.6 (C), 129.6 (2 × CH), 128.6 (2 × CH), 128.2 (2 × CH), 128.0 (2 × CH), 119.1 (CH_2), 76.5 (CH), 58.6 (CH).

HRMS (ESI) Exact mass calculated for $C_{16}H_{14}O^{35}Cl_2Na$ [M+Na$^+$]: 315.0319, found 315.0322.

(±)-1-(4-Chlorophenyl)-3-methylbut-3-en-1-ol (5d)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (46.7 mg, 0.332 mmol) and boronic ester **4d** (77.6 mg, 0.426 mmol). The crude material was purified by flash column chromatography on silica gel (10% Et_2O/*n*-hexane) to give alcohol **5d** (61.8 mg, 95%) as a pale yellow oil. The data were consistent with the literature.[34]

Rf = 0.16 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (s, 4H, ArH), 4.95 (d, *J* = 1.4 Hz, 1H, C=C**H$_A$**H$_B$), 4.87 (d, *J* = 1.4 Hz, 1H, C=CH$_A$**H$_B$**), 4.80 (ddd, *J* = 7.8, 5.6, 2.2 Hz, 1H, HOC**H**), 2.48-2.33 (m, 2H, CHC**H$_2$**), 2.16 (d, *J* = 2.2 Hz, 1H, O**H**), 1.81 (s, 3H, C**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.5 (C), 142.0 (C), 133.1 (C), 128.5 (2 × CH), 127.1 (2 × CH), 114.5 (CH_2), 70.7 (CH), 48.4 (CH_2), 22.3 (CH_3).

(±)-1-(4-Chlorophenyl)-2,2-dimethylbut-3-en-1-ol (5e)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (47.8 mg, 0.340 mmol) and boronic ester **4e** (81.4 mg, 0.415 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **xx** (56.7 mg, 79%) as a colourless oil. The data were consistent with the literature.[36]

Rf = 0.2 (10% Et_2O/hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.25 (m, 4H, Ar**H**), 5.91 (dd, *J* = 17.5, 10.8 Hz, 1H, C**H**=CH_2), 5.19 (dd, *J* = 10.8, 1.1 Hz, 1H, CH=C**H$_A$**CH_B), 5.11 (dd, *J* = 17.5, 1.1 Hz, 1H, CH=CH_AC**H$_B$**), 4.44 (s, 1H, C**H**OH), 2.06 (d, *J* = 2.1 Hz, 1H, O**H**), 1.02 (s, 3H, C**H$_3$**), 0.97 (s, 3H, C**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 144.7 (CH), 139.1 (C), 133.1 (C), 129.1 (2 × CH), 127.6 (2 × CH), 114.4 (CH_2), 79.9 (CH), 42.3 (C), 24.4 (CH_3), 20.7 (CH_3).

(±)-*syn*-(4-Chlorophenyl)(cyclohex-2-en-1-yl)methanol (5f)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (49.9 mg, 0.355 mmol) and boronic ester **4f** (85.3 mg, 0.409 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give *alcohol* **5f** (54.9 mg, 69%) as a colourless oil. The data were consistent with the literature.[37]

Rf = 0.16 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32-7.26 (m, 4H, Ar**H**), 5.83 (ddd, *J* = 10.0, 6.1, 3.5 Hz, 1H, CHCH=C**H**), 5.37 (dd, *J* = 10.0, 1.9 Hz, 1H, CHC**H**=CH), 4.57 (d, *J* = 6.2 Hz, 1H, HOC**H**), 2.54-2.45 (m, 1H, CH=CHC**H**), 2.20-1.93 (m, 2H, CH=CHC**H$_2$**), 1.92 (s, 1H, O**H**), 1.75 (ddd, *J* = 14.7, 9.2, 4.8 Hz, 1H, CHC**H$_A$**H_B), 1.61 (ddd, *J* = 17.0, 9.4, 5.5 Hz, 1H, $CHCH_2$C**H$_A$H$_B$**), 1.54-1.45 (m, 2H, $CHCH_2CH_A$**H$_B$** + $CHCH_A$**H$_B$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 141.2 (C), 133.0 (C), 130.9 (CH), 128.3 (2 × CH), 127.8 (2 × CH), 127.6 (CH), 76.6 (CH), 43.0 (CH), 25.2 (CH_2), 23.5 (CH_2), 21.0 (CH_2).

(±)-(*Z*)-1-(4-Chlorophenyl)-pent-3-en-1-ol (5g)

The title compound was prepared according to General Procedure 1 from 4-chlorobenzaldehyde (45.2 mg, 0.321 mmol) and boronic ester **4g** (72.5 mg, 0.398 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **5g** (47.3 mg, 75%) as a colourless oil.

The literature data for the ***E*-5g** and ***Z*-5g** isomers has inconsistencies. Based on reference 18b we have assigned the major isomer as **Z-5g**.

Rf = 0.23 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ ^{1}H NMR (CDCl3, 400 MHz) δ 7.36-7.29 (m, 4H, Ar**H**), 5.70-5.66 (m, 1H, C=C**H**), 5.45-5.38 (m, 1H, C=C**H**), 4.74-4.71 (m, 1H, HOC**H**), 2.64-2.34 (m, 2H, C**H$_2$**), 1.96 (br s, 1H, O**H**), 1.62 (d, *J* = 7.4 Hz, 3H,

C**H**$_3$). Characteristic signals from **(*E*)-5g** were observed at: 4.68-4.66 (m, 1H, HOC**H**), 1.71 (d, *J* = 6.4 Hz, 3H, C**H**$_3$).

^{13}C NMR ($CDCl_3$, 101 MHz) *E* isomer: δ 142.5 (C), 133.1 (C), 128.5 (2 × CH), 128.1 (CH), 127.2 (2 × CH), 125.2 (CH), 73.1 (CH), 37.0 (CH_2), 13.0 (CH_3). Characteristic signals from **(*E*)-5g** were observed at: 133.0 (C), 130.0 (C), 127.8 (2 × CH), 127.2 (2 × CH), 126.3 (CH), 72.7 (CH) 42.8 (CH_2) 18.1 (CH_3).

Data from reference 18b

Z-isomer:

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.32 (m, 4H, Ar**H**), 5.69-5.62 (m, 1H, C**H**=CH), 5.36-5.43 (m, 1H, CH=C**H**), 4.70 (br t, *J* = 6.4 Hz, 1H, ArC**H**), 2.58-2.50 (m, 1H, C**H**$_A$CH$_B$), 2.47-2.40 (m, 1H, CH$_A$C**H**$_B$), 2.02 (br s, 1H, O**H**), 1.59 (dt, *J* = 6.8, 0.8 Hz, 3H, C**H**$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.5 (C), 133.1 (C), 128.4 (CH), 128.1 (CH), 127.2 (CH), 125.1 (CH), 73.1 (CH), 37.0 (CH_2), 13.0 (CH_3).

Data from reference 38

E-isomer:

^{1}H NMR ($CDCl_3$, 400 MHz): 7.33-7.27 (4H, m), 5.70-5.56 (1H, m,), 5.43-5.36 (1H, m), 4.72-4.68 (1H, m), 2.58-2.31 (2H, m), 2.05 (1H, s), 1.60 (3H, d, *J* = 6.0 Hz).

13C NMR ($CDCl_3$, 100 MHz,) δ 142.57, 133.11, 128.49, 128.49,128.05, 127.24, 127.24, 125.21, 73.14, 36.95, 12.96.

Z-isomer:

^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.67-4.64 (1H, m), 2.10 (1H, s), 1.69 (3H, d, *J* = 6.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz,): δ 142.53, 133.02, 129.91, 128.47,128.47, 127.20, 127.20, 126.31, 72.74, 42.81, 18.02.

(±)-(*E*)-1-(4-Chlorophenyl)4-phenylbut-3-en-1-ol (5h)

The title compound was prepared using a modification of General Procedure 1 from 4-chlorobenzaldehyde (40.8 mg, 0.290 mmol), boronic ester **4h** (82.9 mg, 0.340 mmol), $Ni(OAc)_2.4H_2O$ (8.9 mg, 0.036 mmol), KF (19.6 mg, 0.338 mmol) and dppf (7.9 mg, 0.014 mmol) THF (3 mL). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **5h** (57.2 mg, 76%) as a white solid. The data were consistent with the literature.[39]

Rf = 0.30 (10% Et_2O/*n*-hexane).

m.p. 123-125 °C (Petroleum ether). No literature data available.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38-7.21 (m, 9H, Ar**H**), 6.51 (d, *J* = 15.9 Hz, 1H, CH=C**H**Ph), 6.27-6.12 (m, 1H, C**H**=CHPh), 4.81 (ddd, *J* = 8.1, 5.2, 3.2 Hz, 1H, HOC**H**), 2.73-2.58 (m, 2H, C**H**$_2$), 2.08 (d, *J* = 3.2 Hz, 1H, O**H**). Characteristic signals from **(*Z*)-5h** were observed at: 6.60 (d, *J* = 12.4 Hz, 1H, CH=C**H**Ar), 5.79-5.65 (m, 1H, C**H**=CHPh), 2.88-2.80 (m, 2H, C**H**$_2$), 1.97 (d, *J* = 3.51 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) *E* isomer: δ 142.3 (C), 137.0 (C), 133.9 (CH), 133.2 (C), 128.6 (2 × CH), 128.6 (2 × CH), 127.5 (CH), 127.2 (2 × CH), 126.2 (2 × CH), 125.3 (CH), 73.0 (CH), 43.1 (CH_2). Characteristic signals from **(*Z*)-5h** were observed at: 132.1 (C), 128.7 (2 × CH), 128.2 (2 × CH), 127.3 (2 × CH), 126.9 (CH), 73.5 (CH), 38.2 (CH_2).

(±)-*anti*-1-(4-Methoxyphenyl)-2-phenyl-but-3-en-1-ol (3b)

The title compound was prepared according to General Procedure 1 from *p*-anisaldehyde (45.5 mg, 0.334 mmol) and boronic ester **2** (97.5 mg, 0.399 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give alcohol **3b** (70.4 mg, 83%) as a colourless oil. The data were consistent with the literature.[40]

Rf = 0.04 (10% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24-7.19 (m, 2H, Ar**H**), 7.17-7.13 (m, 1H, Ar**H**), 7.10-7.05 (m, 4H, Ar**H**), 6.77-6.69 (m, 2H, Ar**H**), 6.27 (ddd, *J* = 17.0, 10.2, 9.0 Hz, 1H, C**H**=CH_2), 5.30-5.23 (m, 2H, CH=C**H**$_2$), 4.81 (d, *J* = 7.9 Hz, 1H, HOC**H**), 3.76 (s, 3H, C**H**$_3$), 3.55 (dd, *J* = 9.0, 7.9 Hz, 1H, C=CC**H**), 2.32 (s, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 158.8 (C), 140.7 (C), 138.2 (CH), 134.0 (C), 128.3 (4 × CH), 127.8 (2 × CH), 126.5 (CH), 118.2 (CH_2), 113.3 (2 × CH), 76.8 (CH), 59.3 (CH), 55.1 (CH_3).

(±)-*anti*-1-(4-Methylphenyl)2-phenyl-but-3-en-1-ol (3c)

The title compound was prepared according to General Procedure 1 from *p*-tolualdehyde (42.3 mg, 0.352 mmol) and boronic ester **2** (99.7 mg, 0.408 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give *alcohol* **3c** (67.4 mg, 80%) as a colourless oil.

Rf = 0.16 (10% Et_2O/n-hexane).

IR (ATR) 3437 (O-H), 3025, 1636, 1492, 1178, 915, 755.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25-7.14 (m, 3H, Ar**H**), 7.09-7.01 (m, 6H, Ar**H**), 6.26 (ddd, *J* = 17.1, 10.2, 9.1 Hz, 1H, C**H**=CH_2), 5.28 (d, *J* = 10.2 Hz, 1H, CH=C**H**$_A$H$_B$), 5.22 (d, *J* = 17.1 Hz, 1H, CH=CH$_A$**H**$_B$), 4.84 (d, *J* = 7.8 Hz, 1H, HOC**H**), 3.57 (dd, *J* = 9.1, 7.8 Hz, 1H, C=CC**H**), 2.29 (s, 3H, C**H**$_3$).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.8 (C), 138.8 (C), 138.0 (CH), 137.0 (C), 128.6 (2 × CH), 128.3 (3 × CH), 126.6 (2 × CH), 126.5 (2 × CH), 118.2 (CH_2), 77.0 (CH), 59.1 (CH), 21.1 (CH_3).

HRMS (ESI) Exact mass calculated for $C_{17}H_{18}ONa$ [M+Na$^+$]: 261.1250, found 261.1246.

(±)-*anti*-1,2-Diphenyl-but-3-en-1-ol (3d).

The title compound was prepared according to General Procedure 1 from benzaldehyde (37.0 mg, 0.349 mmol) and boronic ester **2** (101 mg, 0.414 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give alcohol **3d** (54.4 mg, 70%) as a colourless oil. The data were consistent with the literature.[41]

Rf = 0.16 (10% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25-7.14 (m, 8H, Ar**H**), 7.08-7.06 (m, 2H, Ar**H**), 6.27 (ddd, *J* = 17.2, 10.3, 8.4 Hz, 1H, C**H**=CH_2), 5.30-5.22 (m, 2H, CH=C**H**$_2$), 4.87 (d, *J* = 7.8 Hz, 1H, HOC**H**), 3.57 (dd, *J* = 8.4, 7.8 Hz, 1H, C=CC**H**), 2.30 (d, *J* = 2.3 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 141.8 (C), 140.6 (C), 137.8 (CH), 128.3 (2 × CH), 128.3 (2 × CH), 127.9 (2 × CH), 127.4 (CH), 126.7 (2 × CH), 126.6 (CH), 118.4 (CH_2), 77.2 (CH), 59.2 (CH).

(±)-*anti*-1-(4-Bromophenyl)-2-phenylbut-3-en-1-ol (3e)

The title compound was prepared according to General Procedure 1 from 4-bromobenzaldehyde (62.9 mg, 0.344 mmol) and boronic ester **2** (99.4 mg, 0.407 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **3e** (88.3 mg, 85%) as a pale yellow oil. The data were consistent with the literature.[41]

Rf = 0.16 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36-7.30 (m, 2H, Ar**H**), 7.24-7.16 (m, 3H, Ar**H**), 7.05-7.00 (m, 4H, Ar**H**), 6.23 (ddd, *J* = 17.0, 10.1, 9.1 Hz, 1H, C**H**=CH_2), 5.32-5.24 (m, 2H, CH=C**H**$_2$), 4.80 (dd, *J* = 8.3, 2.3 Hz, 1H, HOC**H**), 3.48 (dd, *J* = 9.1, 8.3 Hz, 1H, C=CC**H**), 2.36 (d, *J* = 2.3 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.7 (C), 140.1 (C), 137.5 (CH), 131.0 (2 × CH), 128.5 (2 × CH), 128.4 (2 × CH), 128.2 (2 × CH), 126.8 (CH), 121.2 (C), 118.8 (CH_2), 76.6 (CH), 59.3 (CH).

(±)-*anti*-1-(4-Cyanophenyl)-2-phenyl-but-3-en-1-ol (3f)

The title compound was prepared according to General Procedure 1 from 4-cyanobenzaldehyde (42.7 mg, 0.326 mmol) and boronic ester **2** (96.1 mg, 0.394 mmol). The crude material was purified by flash

chromatography (10% Et_2O/petroleum ether) to give alcohol **3f** (72.0 mg, 89%) as a white solid. The data were consistent with the literature.[42]

Rf = 0.05 (10% Et_2O/petroleum ether).

m.p. 98-100 °C (petroleum ether), literature: 93-94 °C (CCl_4).[43]

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50-7.48 (m, 2H, Ar**H**) 7.26-7.19 (m, 5H, Ar**H**), 7.04-7.02 (m, 2H, Ar**H**), 6.23 (dt, *J* = 17.1, 9.7 Hz, 1H, C**H**=CH_2), 5.34-5.25 (m, 2H, CH=C**H$_2$**), 4.87 (d, *J* = 7.9 Hz, 1H, HOC**H**), 3.46 (dd, *J* = 9.7, 7.9 Hz, 1H, C=CC**H**), 2.48 (s, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 147.1 (C), 139.6 (C), 136.9 (CH), 131.7 (2 × CH), 128.7 (2 × CH), 128.1 (2 × CH), 127.3 (2 × CH), 127.1 (CH), 119.4 (CH_2), 118.8 (C), 111.1 (C), 76.6 (CH), 59.5 (CH).

For X-ray crystallography data, see the Supporting Information.

(±)-*anti*-1-(4-Trifluoromethyl)-2-phenylbut-3-en-1-ol (3g)

The title compound was prepared according to General Procedure 1 from 4-(trifluoromethyl)benzaldehyde (55.2 mg, 0.317 mmol) and boronic ester **2** (104 mg, 0.426 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **3g** (88.3 mg, 95%) as a pale yellow oil. The data were consistent with the literature.[41]

Rf = 0.16 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, *J* = 8.1 Hz, 2H, Ar**H**), 7.27-7.19 (m, 5H, Ar**H**), 7.10-7.05 (m, 2H, Ar**H**), 6.25 (ddd, *J* = 17.1, 10.2, 9.0 Hz, 1H, C**H**=CH_2), 5.36-5.21 (m, 2H, CH=C**H$_2$**), 4.91 (dd, *J* = 7.7, 2.1 Hz, 1H, HOC**H**), 3.52 (dd, *J* = 9.0, 7.7 Hz, 1H, C=CC**H**), 2.40 (d, *J* = 2.1 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 145.7 (C), 145.7 (C), 139.9 (CH), 137.2 (CH), 129.5 (C, q, J_F = 32.3 Hz), 128.6 (2 × CH), 128.2 (2 × CH), 127.0 (2 × CH), 124.8 (2 × CH, q, J_F = 3.8 Hz), 123.7 (CF_3, br q, J_F = 272.4 Hz), 119.1 (CH_2), 76.6 (CH), 59.3 (CH).

(±)-*anti*-1-(3-Methoxyphenyl)-2-phenylbut-3-en-1-ol (3h)

The title compound was prepared according to General Procedure 1 from *m*-anisaldehyde (44.7 mg, 0.328 mmol) and boronic ester **2** (101.0 mg, 0.414 mmol). The crude material was purified by flash chromatography (10% Et_2O/*n*-hexane) to give alcohol **3h** (70.5 mg, 84%) as a colourless oil. The data were consistent with the literature.[41]

Rf = 0.07 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23-7.16 (m, 2H, Ar**H**), 7.12-7.08 (m, 4H, Ar**H**), 6.75-6.70 (m, 3H, Ar**H**), 6.26 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H, C**H**=CH_2), 5.30-5.21 (m, 2H, CH=C**H$_2$**), 4.84 (dd, *J* = 7.6, 2.5 Hz, 1H, HOC**H**), 3.71 (s, 3H, C**H$_3$**), 3.54 (dd, *J* = 8.9, 7.6 Hz, 1H, C=CC**H**), 2.29 (d, *J* = 2.5 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 159.2 (C), 143.5 (C), 140.6 (C), 137.8 (CH), 128.9 (CH), 128.3 (4 × CH), 126.6 (CH), 119.0 (CH), 118.4 (CH_2), 113.2 (CH), 111.9 (CH), 77.3 (CH), 59.1 (CH), 55.1 (CH_3).

(±)-*anti*-1-(3-Cyanophenyl)-2-phenyl-but-3-en-1-ol (3i)

The title compound was prepared according to General Procedure 1 from 3-cyanobenzaldehyde (45.3 mg, 0.345 mmol) and boronic ester **2** (99.3 mg, 0.407 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give *alcohol* **3i** (67.3 mg, 78%) as a colourless oil.

Rf = 0.08 (10% Et_2O/petroleum ether).

IR (ATR) 3450 (O-H), 2230 (C≡N), 1600, 1493, 920, 799.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49-7.45 (m, 2H, Ar**H**) 7.31-7.22 (m, 5H, Ar**H**), 7.04-7.02 (m, 2H, Ar**H**), 6.23 (dt, *J* = 17.1, 9.7 Hz, 1H, C**H**=CH_2), 5.35-5.25 (m, 2H, CH=C**H$_2$**), 4.86 (d, *J* = 7.9 Hz, 1H, HOC**H**), 3.46 (dd, *J* = 9.7, 7.9 Hz, 1H, C=CC**H**), 2.46 (s, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 143.2 (C), 139.5 (C), 136.9 (CH), 131.1 (CH), 131.1 (CH), 130.3 (CH), 128.7 (2 × CH), 128.6 (CH), 128.1 (2 × CH), 127.1 (CH), 119.5 (CH_2), 118.8 (C), 111.9 (C), 76.3 (CH), 59.6 (CH).

HRMS (ESI) Exact mass calculated for $C_{17}H_{16}NO$ $[M+H]^+$: 250.1226, found 250.1231.

(±)-*anti*-1-(2-Methyl phenyl)-2-phenyl-but-3-en-1-ol (3j)

The title compound was prepared according to General Procedure 1 from *o*-tolualdehyde (41.3 mg, 0.344 mmol) and boronic ester **2** (97.8 mg, 0.401 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give *alcohol* **3j** (58.0 mg, 71%) as a colourless oil.

Rf = 0.16 (10% Et_2O/petroleum ether).

IR (ATR) 3416 (O-H), 2920, 1600, 1452, 1178, 918, 760.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (d, *J* = 7.7 Hz, 1H, Ar**H**), 7.23-7.16 (m, 7H, Ar**H**), 6.99 (d, *J* = 7.5 Hz, 1H, Ar**H**), 6.35 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H, C**H**=CH_2), 5.30 (dd, *J* = 10.2, 1.2 Hz, 1H, CH=C**H$_A$**H$_B$), 5.20 (dd, *J* = 17.1, 1.2 Hz, 1H, CH=CH$_A$**H$_B$**), 5.12 (d, *J* = 7.1 Hz, 1H, HOC**H**), 3.62 (dd, *J* = 8.9, 7.1 Hz, 1H, C=CC**H**), 2.06 (s, 3H, C**H$_3$**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 140.8 (C), 140.2 (C), 137.3 (CH), 135.1 (C), 130.0 (CH), 128.3 (4 × CH), 127.2 (CH), 126.6 (CH), 126.5 (CH), 125.8 (CH), 118.6 (CH_2), 73.1 (CH), 57.7 (CH), 19.1 (CH_3).

HRMS (ESI) Exact mass calculated for $C_{17}H_{18}ONa$ $[M+Na]^+$: 261.1250, found 261.1250.

(±)-anti-1-(2-Fluorophenyl)-2-phenyl-but-3-en-1-ol (3k)

The title compound was prepared according to General Procedure 1 from 2-fluorobenzaldehyde (41.3 mg, 0.333 mmol) and boronic ester **2** (97.2 mg, 0.398 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give *alcohol* **3k** (66.4 mg, 82%) as a pale yellow oil.

Rf = 0.16 (10% Et_2O/petroleum ether).

IR (ATR) 3411 (O-H), 2915, 1489, 1221, 1030, 918, 796.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (td, *J* = 13.2, 2.7 Hz, 1H, Ar**H**), 7.24-7.19 (m, 6H, Ar**H**), 7.08 (td, *J* = 7.5, 2.5 Hz, 1H, ArH), 6.91-6.87 (m, 1H, Ar**H**), 6.29-6.23 (m, 1H, C**H**=CH_2), 5.26-5.23 (m, 2H, CH=C**H$_A$**H$_B$ and HOC**H**), 5.16 (dd, *J* = 17.7 and 1.7 Hz, 1H, CH=CH$_A$**H$_B$**), 3.69 (dd, *J* = 8.2, 7.8 Hz, 1H, C=CC**H**), 2.25 (br s, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 159.8 (d, J_F = 245.6 Hz, C), 140.5 (C), 137.2 (C), 129.1 (d, J_F = 12.8 Hz, CH), 128.9 (d, J_F = 8.4 Hz, CH), 128.4 (2 × CH), 128.3 (d, J_F = 4.4 Hz, CH), 128.2 (2 × CH) 126.7 (CH), 123.9 (d, J_F = 3.4 Hz, CH), 118.5 (CH_2), 115.0 (d, J_F = 22.1 Hz, CH), 71.2 (CH), 57.5 (CH).

^{19}F NMR ($CDCl_3$, 377 MHz) δ −118.5 (s).

HRMS (EI) Exact mass calculated for $C_{16}H_{15}FO$ [M+]: 242.1101, found 242.1112.

(±)-*anti*-1-(2-Nitrophenyl)-2-phenylbut-3-en-1-ol (3l)

The title compound was prepared according to General Procedure 1 from 2-nitrobenzaldehyde (50.2 mg, 0.332 mmol) and boronic ester **2** (98.6 mg, 0.404 mmol). The crude material was purified by flash chromatography (10% Et_2O/n-hexane) to give alcohol **3l** (70.4 mg, 79%) as a colourless oil. The data were consistent with the literature.[41]

Rf = 0.23 (10% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (dd, *J* = 8.2, 1.2 Hz, 1H, Ar**H**), 7.76-7.75 (m, 1H, Ar**H**), 7.58 (dd, *J* = 11.0, 4.2 Hz, 1H, Ar**H**), 7.40-7.34 (m, 1H, Ar**H**), 7.31-7.20 (5H, m, Ar**H**), 6.37-6.28 (1H, m, CH=C**H**), 5.64 (1H, d, *J* = 5.3 Hz, HOC**H**), 5.20 (dd, *J* = 10.2, 1.0 Hz, 1H, CH=C**H$_A$**H$_B$), 5.03 (dd, *J* = 17.1, 1.0 Hz, 1H, CH=CH$_A$**H$_B$**), 3.75 (dd, *J* = 9.2, 5.3 Hz, 1H, C=CC**H**), 2.38 (s, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 148.0 (C), 140.7 (C), 137.3 (C), 135.7 (CH), 132.8 (CH), 129.4 (CH), 128.7 (2 × CH), 128.1 (3 × CH), 127.0 (CH), 124.3 (CH), 119.1 (CH_2), 72.6 (CH), 56.7 (CH).

(±)-*anti*-1-(1-Naphthyl)-2-phenyl-but-3-en-1-ol (3m)

The title compound was prepared according to General Procedure 1 from 1-napthaldehyde (50.5 mg, 0.324 mmol) and boronic ester **2** (99.0 mg, 0.406 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give alcohol **3m** (75.8 mg, 85%) as a pale yellow oil. The data were consistent with the literature.[44]

Rf = 0.16 (10% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, *J* = 7.7 Hz, 1H, ArH), 7.87-7.85 (m, 1H, Ar**H**), 7.75 (d, *J* = 8.1 Hz, 1H, Ar**H**), 7.56-7.40 (m, 4H, Ar**H**), 7.27-7.23 (m, 4H, Ar**H**), 7.20-7.16 (m, 1H, Ar**H**), 6.37-6.28 (m, 1H, C**H**=CH_2), 5.73-5.71 (m, 1H, HOC**H**), 5.22 (d, *J* = 10.3 Hz, 1H, CH=C**H**$_A$H$_B$), 5.00 (d, *J* = 17.2 Hz, 1H, CH=CH$_A$**H$_B$**), 3.94 (dd, *J* = 8.4, 5.5 Hz, 1H, C=CC**H**), 2.30 (d, *J* = 3.2 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 141.6 (C), 137.7 (CH), 136.7 (C), 133.7 (C), 130.5 (C), 128.9 (CH), 128.5 (2 × CH), 128.2 (2 × CH), 128.0 (CH), 126.7 (CH), 125.9 (CH), 125.3 (CH), 125.0 (CH), 124.5 (CH), 123.1 (CH), 118.6 (CH_2), 74.2 (CH), 56.6 (CH).

(±)-*anti*-2-phenyl-1-(Pyridine-2-yl) but-3-en-1-ol (3n)

The title compound was prepared according to General Procedure 1 from 2-pyridinecarboxaldehyde (35.7 mg, 0.333 mmol) and boronic ester **2** (95.0 mg, 0.389 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give *alcohol* **3n** (52.0 mg, 69%) as a pale yellow oil.

Rf = 0.10 (10% Et_2O/petroleum ether).

m.p. 75-77 °C (petroleum ether).

IR (ATR) 3250 (O-H), 3080, 1598, 1433, 1066, 928, 756, 698.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.55 (d, *J* = 4.5 Hz, 1H, Ar**H**), 7.60-7.56 (m, 1H, Ar**H**), 7.29-7.19 (m, 6H, Ar**H**), 6.98 (d, *J* = 7.9 Hz, 1H, Ar**H**), 6.24 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H, C**H**=CH_2), 5.16-5.13 (dd, *J* = 10.3 1.2 Hz, 1H, HOC**H**), 5.07-5.01 (m, 2H, CH=C**H$_2$**), 4.25 (br s, 1H, O**H**), 3.78-3.71 (m, 1H, C=CC**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 160.0 (CH), 148.2 (C), 141.2 (C), 137.1 (CH), 136.1 (CH), 128.5 (2 × CH), 128.4 (2 × CH), 126.6 (CH), 122.4 (CH), 121.5 (CH), 117.6 (CH_2), 76.2 (CH), 57.8 (CH).

HRMS (ESI) Exact mass calculated for $C_{15}H_{16}NO$ $[M+H]^+$: 226.1226, found 226.1230.

(±)-*anti*-1-(Furan-2-yl)-2-phenyl-but-3-en-1-ol (3o)

The title compound was prepared according to General Procedure 1 from furaldehyde (35.8 mg, 0.372 mmol) and boronic ester **2** (96.2 mg, 0.394 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give alcohol **3o** (49.1 mg, 62%) as a pale yellow oil. The data were consistent with the literature.[44]

Rf = 0.16 (10% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33-7.15 (m, 6H, Ar**H**), 6.25-6.20 (m, 2H, Ar**H**), 6.06 (ddd, *J* = 17.2, 10.2, 8.3 Hz, 1H, C**H**=CH_2), 5.31-5.25 (m, 2H, CH=C**H$_2$**), 4.90 (d, *J* = 8.3 Hz, 1H, HOC**H**), 3.85 (t, *J* = 8.3 Hz, 1H, C=CC**H**), 2.27 (s, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 101 MHz) 154.2 (C), 141.8 (CH), 140.4 (C), 137.6 (CH), 128.4 (2 × CH), 128.1 (2 × CH), 126.8 (CH), 118.5 (CH_2), 110.1 (CH), 107.6 (CH), 71.0 (CH), 55.9 (CH).

(±)-*anti*-1-(3-Bromothiophen-2-yl)-2-phenylbut-3-en-1-ol (3p)

The title compound was prepared according to General Procedure 1 from 3-bromothiophene-2-carboxaldehyde (63.9 mg, 0.334 mmol) and boronic ester **2** (100.6 mg, 0.412 mmol). The crude material was purified by flash chromatography (10% Et_2O/pentane) to give *alcohol* **3p** (83.0 mg, 80%) as a colourless oil.

Rf = 0.33 (10% Et_2O/pentane).

IR (ATR) 3414 (O-H), 3038, 2904, 1601, 1494, 920, 870, 698.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29-7.20 (m, 6H, Ar**H**), 6.81 (d, *J* = 5.3 Hz, 1H, Ar**H**), 6.31 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H, C**H**=CH_2), 5.30-5.28 (m, 2H, C=C**H$_A$**CH$_B$ + HOC**H**), 5.26-5.21 (m, 1H, C=CH$_A$C**H$_B$**), 3.78-3.70 (m, 1H, C=CC**H**), 2.44 (d, *J* = 2.9 Hz, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 140.3 (C), 139.9 (C), 136.8 (CH), 129.5 (CH), 128.5 (2× CH), 128.2 (2 × CH), 126.9 (CH), 125.1 (CH), 119.0 (CH_2), 108.6 (C), 72.4 (CH), 57.9 (CH).

HRMS (ESI) Exact mass calculated for $C_{14}H_{13}{}^{81}BrOSNa$ $[M+Na]^+$: 332.9742, found: 332.9742.

(±)-*anti*-1,4-Diphenylhex-5-en-3-ol (3q)

The title compound was prepared according to General Procedure 1 from 3-phenylpropionaldehyde (44.2 mg, 0.329 mmol) and boronic ester **2** (97.3 mg, 0.399 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give alcohol **3q** (57.2 mg, 69%) as a colourless oil. The data were consistent with the literature.[45]

Rf = 0.23 (10% Et_2O/petroleum ether).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (t, *J* = 7.3 Hz, 2H, Ar**H**), 7.27-7.22 (m, 3H, Ar**H**), 7.18-7.17 (m, 3H, Ar**H**), 7.12 (d, *J* = 7.0 Hz, 2H, Ar**H**), 6.16-6.07 (m, 1H, C**H**=CH_2), 5.25 (dd, *J* = 10.2, 1.1 Hz, 1H, CH=C**H$_A$**H$_B$), 5.22 (dd, *J* = 17.4, 1.1 Hz, 1H, CH=CH$_A$**H$_B$**), 3.83- 3.76 (m, 1H, HOC**H**), 3.30-3.26 (m, 1H, C=CC**H**), 2.88-2.81 (m, 1H, PhC**H$_A$**H$_B$), 2.67-2.59 (m, 1H, PhCH$_A$**H$_B$**), 1.88-1.86 (m, 1H, PhCH$_2$C**H$_A$**H$_B$), 1.70-1.61 (m, 1H, PhCH$_2$CH$_A$**H$_B$**), 1.58 (s, 1H, O**H**).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 142.0 (C), 141.4 (C), 138.3 (CH), 128.7 (2 × CH), 128.4 (2 × CH), 128.3 (2 × CH), 128.0 (2 × CH), 126.7 (CH), 125.7 (CH), 118.0 (CH_2), 73.2 (CH), 57.5 (CH), 36.0 (CH_2), 32.0 (CH_2).

(±)-*anti*-1-Cyclohexyl-2-phenylbut-3-en-1-ol (3r)

The title compound was prepared according to General Procedure 1 from cyclohexane carboxaldehyde (38.9 mg, 0.347 mmol) and boronic ester **2** (99.6 mg, 0.408 mmol). The crude material was purified by flash column chromatography on silica gel (10% Et_2O/*n*-hexane) to give alcohol **3r** (47.2 mg, 59%) as a colourless oil. The data were consistent with the literature.[46]

Rf = 0.10 (10% Et_2O/*n*-hexane).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.32 (m, 2H, Ar**H**), 7.27-7.22 (m, 3H, Ar**H**), 6.15 (dd, *J* = 17.0, 9.7, 8.7 Hz, 1H, C**H**=CH_2), 5.24-5.18 (m, 2H, CH=C**H$_2$**), 3.60-3.58 (m, 1H, HOC**H**), 3.47 (dd, *J* = 8.7, 7.8 Hz, 1H, C=CC**H**), 1.83-1.82 (m, 1H, Cy), 1.73-1.59 (m, 4H, Cy), 1.27-1.01 (m, 6H, Cy).

^{13}C NMR ($CDCl_3$, 101 MHz) δ 142.1 (C), 138.4 (CH), 128.7 (2 × CH), 127.9 (2 × CH), 126.5 (CH), 117.7 (CH_2), 78.1 (CH), 53.7 (CH), 39.5 (CH), 30.2 (CH_2), 26.5 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 26.0 (CH_2).

(1S,2R)-1-[(4*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-phenylbut-3-en-1-ol (3s)

The title compound was prepared according to General Procedure 1 from 2,3-O-Isopropylidene-D-glyceraldehyde 50% w/w in dichloromethane (175.5 mg, 0.674 mmol) and boronic ester **2** (196.6 mg, 0.805 mmol). The crude material was purified by flash chromatography (10% Et_2O/petroleum ether) to give *alcohol* **3s** (70.6 mg, 42%) as a pale yellow solid.

$[\alpha]^{20}_D$ +82° (c = 0.22, $CHCl_3$)

m.p. 54-56 °C (pentane)

IR 3484 (O-H), 2993, 1455, 1221, 1061, 698.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (2H, m, Ar**H**), 7.26-7.24 (3H, m, Ar**H**), 6.25 (1H, ddd, *J* = 17.2, 10.2, 8.5 Hz, C**H**=CH_2), 5.21 (1H, d, *J* = 9.6 Hz, CH=C**H**$_A$H$_B$), 5.15 (1H, d, *J* = 17.1 Hz, CH=CH$_A$**H$_B$**), 3.92 (1H, td, *J* = 6.7, 4.8 Hz, 1H), 3.77-3.70 (2H, m, *J* = 14.6, 7.9, 5.8 Hz, 1H), 3.62 (1H, t, *J* = 7.6 Hz, 1H), 3.39 (1H, t, *J* = 8.1 Hz, 1H), 2.31 (1H, d, *J* = 5.8 Hz, O**H**), 1.44 (3H, s, C**H$_3$**), 1.31 (3H, s, C**H$_3$**).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8 (C), 138.1 (CH), 128.7 (2 × CH), 128.3 (2 × CH), 126.9 (CH), 117.2 (CH_2), 109.1 (C), 76.5 (CH), 74.4 (CH), 66.1 (CH_2), 54.1 (CH), 26.5 (CH_3), 25.3 (CH_3).

HRMS (Q-TOF) Exact mass calculated for $C_{15}H_{20}O_3$[M+H$^+$]: 249.1446, found 249.1485.

For X-ray crystallography data, see the Supporting Information.

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Supporting Information

YES (this text will be updated with links prior to publication)

Primary Data

YES (this text will be updated with links prior to publication)

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