

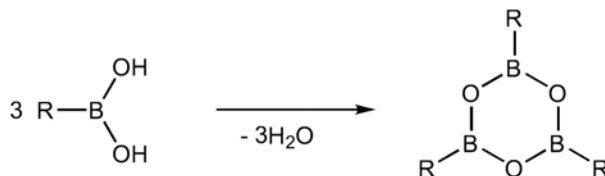
Boronic acids and their derivatives are among the most useful classes of organoboron molecules. Unlike many organometallic derivatives and most organoboranes, boronic acids are usually stable to air and moisture, and are of relatively low toxicity and environmental impact. The reactions of boronic acids can be divided into two categories according to whether the boron-oxygen or the carbon-boron bonds are involved.

## Reactions involving the B-O bonds

### Boroxine formation

Most boronic acids readily undergo dehydration to form cyclic trimeric anhydrides (boroxines) (Scheme 1). This tends to occur spontaneously at room temperature, so that it is difficult to obtain the acid free from the anhydride. Since in almost all cases, both will undergo the required reaction, they can usually be regarded as equivalent.

#### Scheme 1



### Boronate formation

The ease with which boronic acids react with diols, with loss of water, to give cyclic boronic esters (boronates) has led to their application in a number of areas, especially in the carbohydrate field.

### Protection of diols

One of the main applications of boronic acids has been as reagents for protection and derivatization of 1,2- and 1,3-diols as boronates (1,3,2-dioxaborolanes and 1,3,2-dioxaborinanes), particularly in carbohydrate chemistry.<sup>1</sup> These have been widely used as volatile derivatives for GC and GC-MS purposes. The boronate derivatives are formed simply by stirring the boronic acid and diol together at ambient temperature, by warming, or, if necessary, with azeotropic removal of water. Usually cleavage occurs readily under hydrolytic conditions, by exchange with a glycol,<sup>2</sup> or by treatment with hydrogen peroxide.<sup>3</sup> Hindered boronic esters, such as those of pinacol, may be relatively stable to hydrolysis, and can often be purified by chromatography. A useful application of boronate protection is in the osmium tetroxide catalysed cis-dihydroxylation of alkenes under anhydrous conditions in the presence of a boronic acid.<sup>3b,4</sup> Further information on the applications of boronic acids as derivatizing and protecting agents can be found in various reviews<sup>5,6</sup> and monographs.<sup>7-9</sup>

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## Other applications in carbohydrate chemistry

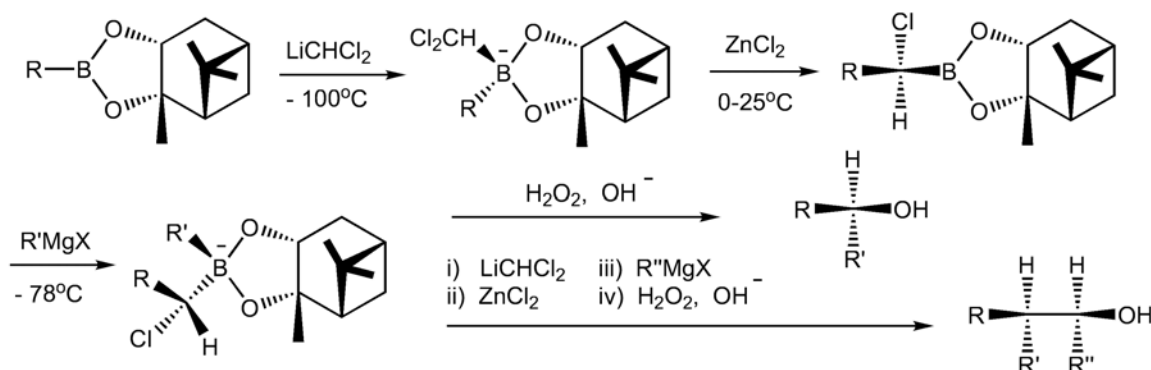
The formation of boronates with carbohydrate molecules has been utilized in numerous other applications, including the selective transport of sugars in lipophilic environments,<sup>10,11</sup> and the design of artificial receptors, as discussed in several reviews.<sup>12-15</sup>

## Boronic acids and esters in asymmetric synthesis

### Chiral boronates

Matteson has carried out extensive work on cyclic boronates,<sup>16,17</sup> formed from chiral diols such as (1S,2S,3R,5S)-2,3-pinandediol or (R,R)-(-)-2,3-butanediol, which undergo carbon insertion with  $\text{LiCHCl}_2$  in the presence of zinc chloride in up to 99% diastereomeric excess (de). Treatment of the resulting  $\alpha$ -chloro boronic esters with various nucleophiles leads to  $\alpha$ -substituted boronic esters which can be deprotected with hydrogen peroxide, or the sequence can be repeated to introduce a second chiral center, as illustrated in Scheme 2.

### Scheme 2



### Oxazaborolidines

Reaction of various boronic acids with chiral amino alcohols gives oxazaborolidines, which were introduced by Corey as excellent catalysts for enantioselective borane reduction of ketones with very high ee.<sup>18</sup> The reagents derived from  $\alpha,\alpha$ -diphenylprolinol have received the most attention, although the use of other amino alcohols has also been reported.<sup>19,20</sup> For further details, reaction scheme and references, see under (S)-(-)- $\alpha,\alpha$ -Diphenylprolinol, (S)-2-Methyl-CBS-oxazaborolidine monohydrate and n-Butylboronic acid in the main Catalogue. Reviews on the use of oxazaborolidines as enantioselective catalysts,<sup>21,22</sup> and the asymmetric reduction of ketones<sup>23,24</sup> are available.

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## Diels-Alder reactions

Boronic acids form stable chiral acyloxyborane (CAB) catalysts with tartaric acid derivatives, which have been developed by Yamamoto as catalysts for asymmetric Diels-Alder<sup>25</sup> and hetero Diels-Alder<sup>26</sup> reactions, for example between aldehydes and Danishefsky's Diene [1-methoxy-3-(trimethylsiloxy)-1,3-butadiene; L06100, L14672], to give enantioselectively, dihydro-4-pyrone derivatives.<sup>27</sup>

For the use of a boronic acid template in stereocontrolled Diels-Alder reactions,<sup>28</sup> see under Benzenboronic acid in the main section of the Catalogue.

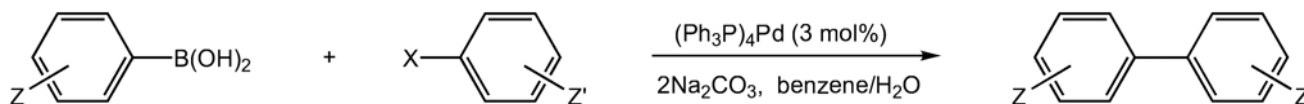
## Reactions involving cleavage of the C-B bond

In these reactions, displacement of boron by an electrophilic species takes place with formation of a new carbon-carbon or carbon-heteroatom bond.

### C-C bond forming reactions: Suzuki biaryl coupling

The discovery by Suzuki and Miyaura<sup>29</sup> that arylboronic acids undergo palladium-catalyzed cross-coupling with aryl halides in the presence of a base (Scheme 3) has stimulated enormous interest in the application of this (the Suzuki reaction), and variants developed subsequently, to the synthesis of unsymmetrical biaryls and related compounds.

#### Scheme 3



Many of the methods previously employed for such syntheses involve the direct coupling of highly-reactive organometallic reagents (Grignard, organolithium, etc.) with aryl halides in the presence of various catalysts. Such reactions are of limited utility, since the presence of many functional groups interferes. Boronic acids, on the other hand, which are air-stable materials of relatively low toxicity, will undergo the Suzuki reaction in the presence of a wide variety of functional groups. The highly versatile Stille coupling reaction,<sup>30</sup> by comparison,<sup>31</sup> involves toxic organotin species. Under the standard coupling conditions, aryl bromides are most frequently used as the electrophilic species, but iodides are more reactive. The successful coupling of the more readily available, but normally unreactive aryl chlorides has been achieved under modified conditions, using either palladium<sup>32</sup> or nickel<sup>33</sup> catalysts. A catalytic cycle for the Suzuki reaction<sup>34,35</sup> is outlined in Scheme 4. A detailed mechanistic study has also been published.<sup>36</sup>

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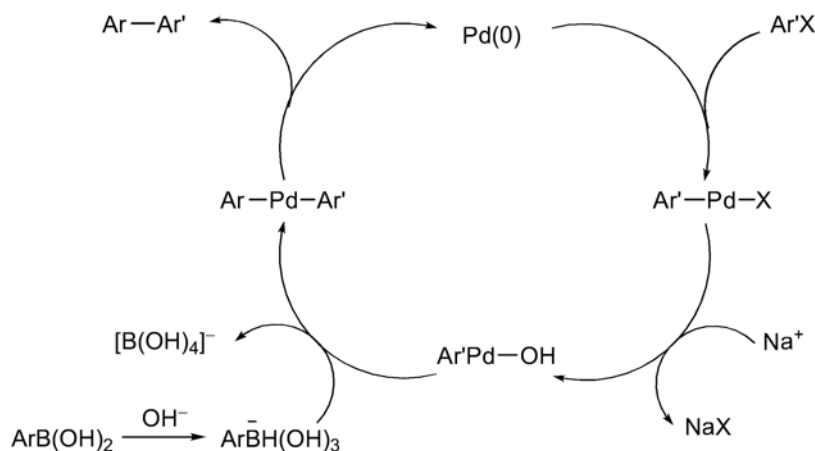
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**Scheme 4**



Alternative illustrative experimental procedures for the biaryl synthesis have been reported in *Organic Syntheses*.<sup>37</sup> Useful reviews of the Suzuki and related reactions have been published by Suzuki and Miyaura<sup>38,39</sup> and by Martin and Yang,<sup>35</sup> and of biaryl synthesis via cross-coupling reactions by Stanforth.<sup>40</sup> The more recent literature has been reviewed by Kotha *et al.*<sup>88</sup>

## Related coupling reactions

A variety of heterocyclic halides have been coupled with boronic acids, including thiophenes,<sup>41</sup> furans, thiazoles,<sup>42</sup> isoxazoles,<sup>43</sup> pyridines,<sup>44,45</sup> pyrimidines<sup>42,44</sup> and pyrazines.<sup>44,45</sup> Aryl or vinyl triflates can undergo palladium-catalyzed boronic acid coupling, which usefully extends the scope of the reaction to phenols or enols.<sup>46-48</sup> Coupling of boronate derivatives with aryl mesylates, catalyzed by nickel complexes, has also been reported,<sup>49,50</sup> as has palladium-catalyzed coupling with sulfonium salts.<sup>51</sup> Arenediazonium tetrafluoroborates have been found to undergo coupling with arylboronic acids in dioxane or methanol, catalyzed by palladium acetate in the absence of both added base and phosphine ligand.<sup>52</sup> This has been extended to the coupling of arenediazonium tetrafluoroborates with potassium aryltrifluoroborates,<sup>53</sup> which are more nucleophilic than the corresponding arylboronic acids, and also with potassium vinyl trifluoroborates,<sup>54</sup> which are air-stable crystalline solids, more readily prepared and isolated than the corresponding vinylboronate esters. Alkenyl and aryl trifluoroborates have also been reported by Molander to couple with aryl halides, which greatly extends their usefulness.<sup>89</sup>

Coupling of arylboronic acids with, for example vinylic halides,<sup>55,56</sup> or allenyl methyl carbonate,<sup>57</sup> have also been described.

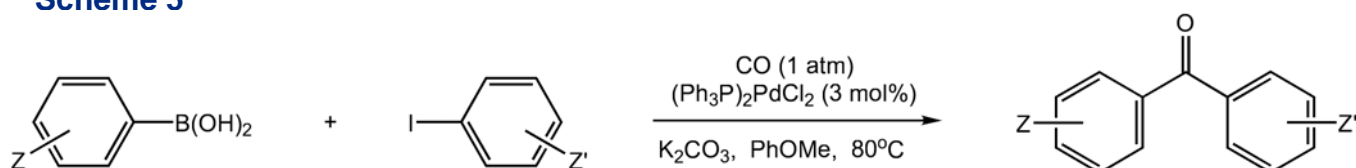
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Coupling reactions involving alkylboronic acids were reported to be difficult to accomplish.<sup>90</sup> However, Molander has described conditions under which primary alkylboronic acids could be coupled efficiently with aryl halides and triflates.<sup>91</sup>

A further useful variation of the Suzuki reaction, shown in Scheme 5, is the carbonylative cross-coupling of arylboronic acids with aryl iodides in the presence of carbon monoxide at atmospheric pressure, to give substituted benzophenones.<sup>58</sup>

## Scheme 5



Unsymmetrical ketones have also subsequently been prepared by cross-coupling of arylboronic acids with acyl chlorides, catalyzed either by (Ph<sub>3</sub>P)<sub>4</sub>Pd,<sup>59</sup> or Pd(OAc)<sub>2</sub> with no added ligand.<sup>60</sup>

Tetrakis(triphenylphosphine)palladium(0) was the catalyst originally employed for the biaryl coupling,<sup>29</sup> and is still the most popular. A wide variety of alternative catalysts have been reported for Suzuki and related couplings, including: (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>,<sup>43,58</sup> dppbPdCl<sub>2</sub>,<sup>44,61</sup> "Pd(dba)<sub>2</sub>",<sup>62</sup> Pd(OAc)<sub>2</sub>,<sup>52,63</sup> Pd(OAc)<sub>2</sub>/(o-tol)<sub>3</sub>P,<sup>45,64</sup> Pd(OAc)<sub>2</sub>/dppf,<sup>45</sup> (PhCN)<sub>2</sub>PdCl<sub>2</sub>/Ph<sub>3</sub>As,<sup>56</sup> (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub>,<sup>58</sup> Pd-C,<sup>65</sup> (Ph<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>,<sup>50</sup> and the palladacycle complex trans-di-μ-acetatobis[2-(di-o-tolylphosphino)-benzyl]dipalladium(II).<sup>66</sup>

Alternative bases to sodium carbonate include: NaHCO<sub>3</sub>,<sup>43,67</sup> K<sub>2</sub>CO<sub>3</sub>,<sup>54</sup> Cs<sub>2</sub>CO<sub>3</sub>,<sup>32b</sup> K<sub>3</sub>PO<sub>4</sub>,<sup>49</sup> Et<sub>3</sub>N,<sup>45,64a</sup> Ag<sub>2</sub>O,<sup>56</sup> Ba(OH)<sub>2</sub>,<sup>68</sup> good for sterically-hindered biaryls, and CsF,<sup>69</sup> compatible with readily-hydrolyzed functionality, such as esters. Suzuki and Miyaura<sup>29</sup> reported that stronger bases such as ethoxide or hydroxide gave poorer yields than carbonate; sodium acetate was also found to be ineffective.

The palladium-catalyzed coupling of boron compounds with aryl halides has been extended by Miyaura's group to the cleavage of a boron-boron bond in the one-step conversion of aryl halides to boronic esters using the novel reagent **Bis(pinacolato) diboron** (L16088),<sup>70</sup> allowing access to boronic acid derivatives without protection of functionalities such as ester, ketone, cyano or nitro groups. For reaction scheme and further uses of this reagent, see text entry in main section of the Catalogue.

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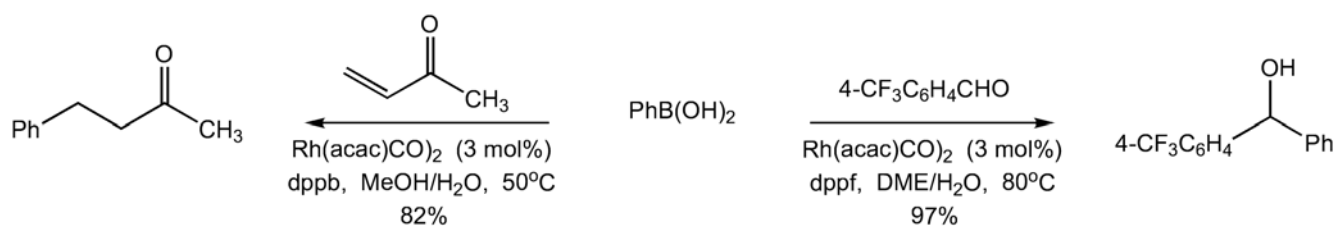
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## 1,2- and 1,4-additions to carbonyl compounds

Miyaura has also described the conjugate addition of arylboronic acids to enones, in the presence of a rhodium catalyst and a chelating phosphine, to give good yields of saturated ketones.<sup>71</sup> Under similar conditions, both aryl- and alkenylboronic acids can add to aldehydes to give secondary alcohols in high yield (Scheme 6).<sup>72</sup>

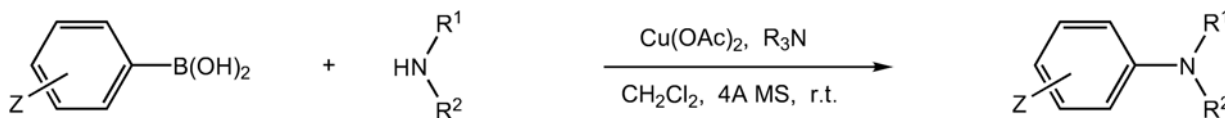
### Scheme 6



## C-O, C-N and C-S bond-forming reactions

One of the simplest reactions of arylboronic acids is their oxidative cleavage, usually with hydrogen peroxide,<sup>74</sup> to give phenols. Other oxidative reactions with NBS or NIS to give aryl halides are known.<sup>75</sup> More usefully, arylboronic acids undergo Ullmann-type C-O and C-N coupling reactions with phenols,<sup>76,77</sup> amines, amides and imides,<sup>77,78</sup> ureas, sulfonamides and carbamates,<sup>75</sup> and N-heteroaromatics<sup>79</sup> in the presence of copper(II) acetate (Scheme 7) to give the corresponding diaryl ethers, arylamines or N-aryl heterocycles.

### Scheme 7



Formation of unsymmetrical thioethers from arylboronic acids and thiols, mediated by copper(II) acetate has also been reported.<sup>80</sup>

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## Other reactions of boronic acids

Many other examples of boronic acid chemistry have been reported:

For ortho-specific  $\alpha$ -hydroxyalkylation of phenols by aldehydes,<sup>81</sup> see under Benzeneboronic acid in the main section of the Catalogue.

With lead(IV) acetate, catalysed by mercury(II) acetate, arylboronic acids are transmetalated to the aryllead triacetate, used *in situ* for electrophilic arylation, for example of active methylene compounds,<sup>82</sup> or with sodium azide in DMSO for the preparation of aryl azides, providing a useful two-step route for the preparation of these from aryl halides.<sup>83</sup>

Arylboronic acids have been converted, via the N-methyldiethanolamine cyclic esters, to aryl fluorides using cesium fluoroxysulfate.<sup>84</sup>

Boronic acids undergo a Mannich-type reaction with aldehydes and secondary amines.<sup>85</sup> For asymmetric boronic acid Mannich reaction with aldehydes,<sup>86</sup> see under Furan-2-boronic acid.

Certain arylboronic acids have also been shown to be effective catalysts for amidation of carboxylic acids.<sup>87</sup>

## Product Listings

### Alkenylboronic acids and esters

- |  |   |
|--|---|
| <b>L19700</b> 3-Acetoxy-1-propenylboronic acid pinacol ester             | <b>L19648</b> (E)-1-Pentene-1,2-diboronic acid bis(pinacol) ester           |
| <b>L19579</b> 3-Diethoxy-1-propenylboronic acid pinacol ester            | <b>L19701</b> 5-Phenyl-1-pentenylboronic acid pinacol ester                 |
| <b>L19649</b> (E)-1-Heptene-1,2-diboronic acid bis(pinacol ester)        | <b>L19652</b> (E)-Stilbenediboronic acid bis(pinacol ester)                 |
| <b>L19650</b> (E)-1-Hexene-1,2-diboronic acid bis(pinacol ester)         | <b>L19573</b> cis-Stilbeneboronic acid diethanolamine ester                 |
| <b>L19704</b> 4-Methyl- $\beta$ -styrylboronic acid diethanolamine ester | <b>L19576</b> cis-Stilbeneboronic acid pinacol ester                        |
| <b>L19698</b> 4-Methyl- $\beta$ -styrylboronic acid pinacol ester        | <b>L19651</b> (E)- $\alpha,\beta$ -Styrenediboronic acid bis(pinacol ester) |
| <b>L19697</b> 1-Octenylboronic acid pinacol ester                        | <b>L19571</b> $\beta$ -Styrylboronic acid diethanolamine ester              |
| <b>L19705</b> 4-Octenylboronic acid diethanolamine ester                 | <b>L19529</b> $\beta$ -Styrylboronic acid pinacol ester                     |
| <b>L19699</b> 4-Octenylboronic acid pinacol ester                        | <b>L19577</b> 2-(Trimethylsilyl)vinylboronic acid pinacol ester             |
| <b>L19677</b> 1-Pentenylboronic acid                                     | <b>L19811</b> Vinylboronic acid pinacol ester                               |

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## Alkylboronic acids and esters

- L16232** Allylboronic acid pinacol ester  
**A13725** n-Butylboronic acid  
**L19575** 2-(9H-Carbazolyl)ethylboronic acid diethanolamine ester  
**L19580** 2-(9H-Carbazolyl)ethylboronic acid pinacol ester  
**L19957** n-Decylboronic acid  
**L19532** 3,3-Diethoxy-1-propylboronic acid pinacol ester  
**L19533** 2-(1,3-Dioxolan-2-on-4-yl)-1-ethylboronic acid pinacol ester  
**L19703** 2,2-Diphenyl-1-ethylboronic acid diethanolamine ester  
**L19958** n-Dodecylboronic acid  
**L19959** Ethylboronic acid  
**B22446** n-Hexylboronic acid
- L19574** 2-Indanylboronic acid diethanolamine ester  
**L19535** 2-Indanylboronic acid pinacol ester  
**L19962** Isopropylboronic acid  
**L15589** Methylboronic acid  
**L19964** n-Octylboronic acid  
**L19871** 2-Phenylethyl-1-boronic acid  
**L19706** 2-Phenylethyl-1-boronic acid diethanolamine ester  
**L19530** 2-Phenylethyl-1-boronic acid pinacol ester  
**L19965** n-Propylboronic acid  
**L19966** n-Tetradecylboronic acid  
**L19572** 2-Trimethylsilyl-1-ethylboronic acid diethanolamine ester  
**L19534** 2-Trimethylsilyl-1-ethylboronic acid pinacol ester

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**L19580** 2-(9H-Carbazolyl)ethylboronic acid pinacol ester  
**L19957** n-Decylboronic acid  
**L19532** 3,3-Diethoxy-1-propylboronic acid pinacol ester  
**L19533** 2-(1,3-Dioxolan-2-on-4-yl)-1-ethylboronic acid pinacol ester  
**L19703** 2,2-Diphenyl-1-ethylboronic acid diethanolamine ester  
**L19958** n-Dodecylboronic acid  
**L19959** Ethylboronic acid  
**B22446** n-Hexylboronic acid
- L19574** 2-Indanylboronic acid diethanolamine ester  
**L19535** 2-Indanylboronic acid pinacol ester  
**L19962** Isopropylboronic acid  
**L15589** Methylboronic acid  
**L19964** n-Octylboronic acid  
**L19871** 2-Phenylethyl-1-boronic acid  
**L19706** 2-Phenylethyl-1-boronic acid diethanolamine ester  
**L19530** 2-Phenylethyl-1-boronic acid pinacol ester  
**L19965** n-Propylboronic acid  
**L19966** n-Tetradecylboronic acid  
**L19572** 2-Trimethylsilyl-1-ethylboronic acid diethanolamine ester  
**L19534** 2-Trimethylsilyl-1-ethylboronic acid pinacol ester

## Alkenyltrifluoroborate salts

- L17973** Potassium 4-methyl- $\beta$ -styryltrifluoroborate  
**L17971** Potassium  $\beta$ -styryltrifluoroborate
- L17970** Potassium vinyltrifluoroborate

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## Arylboronic acids

- B23833** 3-Acetamidobenzeneboronic acid  
**B23478** 3-Acetylbenzeneboronic acid  
**B23234** 4-Acetylbenzeneboronic acid  
**A17240** 3-Aminobenzeneboronic acid hemisulfate  
**L18069** 2-Aminobenzeneboronic acid  
**A18189** 3-Aminobenzeneboronic acid monohydrate  
**L19630** 9-Anthraceneboronic acid  
**A14257** Benzeneboronic acid  
**L19459** Benzeneboronic acid, polymer-supported  
**B24903** 1,4-Benzenediboronic acid  
**L20100** 2-Benzyloxybenzeneboronic acid  
**L17474** 3-Benzyloxybenzeneboronic acid  
**B24351** 4-Benzyloxybenzeneboronic acid  
**L17547** 2-Biphenylboronic acid  
**L17552** 3-Biphenylboronic acid  
**B23703** 4-Biphenylboronic acid  
**L13328** 4,4'-Biphenyldiboronic acid  
**L18161** 2,4-Bis(trifluoromethyl)benzeneboronic acid  
**L19952** 2,6-Bis(trifluoromethyl)benzeneboronic acid  
**A11373** 3,5-Bis(trifluoromethyl)benzeneboronic acid  
**L18581** 2-Bromobenzeneboronic acid  
**L16354** 3-Bromobenzeneboronic acid  
**L01565** 4-Bromobenzeneboronic acid  
**L18516** 4-Bromo-2,3-difluorobenzeneboronic acid  
**L17468** 4-Bromo-2-fluorobenzeneboronic acid  
**L18514** 4-Bromo-3-fluorobenzeneboronic acid  
**L20102** 3-(Bromomethyl)benzeneboronic acid  
**L19953** 4-(Bromomethyl)benzeneboronic acid  
**L15584** 4-n-Butylbenzeneboronic acid  
**B24408** 4-tert-Butylbenzeneboronic acid  
**L16301** 2-Carboxybenzeneboronic acid  
**B25315** 3-Carboxybenzeneboronic acid  
**B20954** 4-Carboxybenzeneboronic acid  
**L17485** 4-(2-Carboxyethyl)benzeneboronic acid  
**L16368** 2-(2-Carboxyvinyl)benzeneboronic acid  
**L16369** 3-(2-Carboxyvinyl)benzeneboronic acid  
**L15586** 4-(2-Carboxyvinyl)benzeneboronic acid  
**B23324** 2-Chlorobenzeneboronic acid  
**B24444** 3-Chlorobenzeneboronic acid  
**A15657** 4-Chlorobenzeneboronic acid  
**B22755** 3-Chloro-4-fluorobenzeneboronic acid  
**B23688** 4-Chloro-2-methylbenzeneboronic acid  
**B23179** 4-Chloro-3-methylbenzeneboronic acid  
**L20103** 2-Chloro-4-(trifluoromethyl)benzeneboronic acid  
**L20104** 2-Chloro-5-(trifluoromethyl)benzeneboronic acid  
**L20105** 4-Chloro-3-(trifluoromethyl)benzeneboronic acid  
**L19676** 2-Cyanobenzeneboronic acid  
**L19635** 3-Cyanobenzeneboronic acid  
**L18007** 4-Cyanobenzeneboronic acid  
**L19955** 4-(Cyanomethyl)benzeneboronic acid  
**L18076** 4-Cyclohexylbenzeneboronic acid  
**B23863** 3,5-Dibromobenzeneboronic acid  
**B22781** 2,3-Dichlorobenzeneboronic acid  
**L01563** 2,4-Dichlorobenzeneboronic acid  
**B22984** 2,5-Dichlorobenzeneboronic acid  
**B24292** 3,4-Dichlorobenzeneboronic acid  
**B22765** 3,5-Dichlorobenzeneboronic acid  
**L18012** 2,3-Difluorobenzeneboronic acid  
**B23821** 2,4-Difluorobenzeneboronic acid  
**B24113** 2,5-Difluorobenzeneboronic acid  
**B22805** 2,6-Difluorobenzeneboronic acid  
**B24305** 2,6-Dimethoxybenzeneboronic acid  
**B22799** 3,4-Difluorobenzeneboronic acid  
**L17425** 3,5-Difluorobenzeneboronic acid  
**L19773** 3,5-Difluoro-2-methoxybenzeneboronic acid  
**B24125** 2,3-Dimethoxybenzeneboronic acid  
**B24374** 2,4-Dimethoxybenzeneboronic acid  
**B24571** 2,5-Dimethoxybenzeneboronic acid  
**B24305** 2,6-Dimethoxybenzeneboronic acid  
**B22799** 3,4-Difluorobenzeneboronic acid  
**B23942** 2,3-Dimethylbenzeneboronic acid  
**B23076** 2,4-Dimethylbenzeneboronic acid  
**B23740** 2,5-Dimethylbenzeneboronic acid  
**B24613** 2,6-Dimethylbenzeneboronic acid  
**L17461** 3,4-Dimethylbenzeneboronic acid  
**B23434** 3,5-Dimethylbenzeneboronic acid  
**L17814** 4-(Ethanesulfonyl)benzeneboronic acid  
**B23644** 2-Ethoxybenzeneboronic acid  
**B24485** 3-Ethoxybenzeneboronic acid  
**B23683** 4-Ethoxybenzeneboronic acid  
**L17719** 2-Ethylbenzeneboronic acid  
**B24656** 4-Ethylbenzeneboronic acid  
**L20296** 3,4-(Ethylenedioxy)benzeneboronic acid  
**L17623** 4-(Ethylthio)benzeneboronic acid  
**B23103** 2-Fluorobenzeneboronic acid  
**B21247** 3-Fluorobenzeneboronic acid  
**A15991** 4-Fluorobenzeneboronic acid

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## Arylboronic acids con't

- L15634** 2-Fluorobiphenyl-4-boronic acid  
**L17851** 3-Fluoro-4-formylbenzeneboronic acid  
**L17808** 4-Fluoro-3-formylbenzeneboronic acid  
**L19655** 2-Fluoro-3-methoxybenzeneboronic acid  
**L19960** 2-Fluoro-4-methoxybenzeneboronic acid  
**L19818** 3-Fluoro-4-methoxybenzeneboronic acid  
**B24512** 3-Fluoro-4-methylbenzeneboronic acid  
**B24117** 4-Fluoro-2-methylbenzeneboronic acid  
**L18753** 4-Fluoro-3-methylbenzeneboronic acid  
**L19819** 5-Fluoro-2-methylbenzeneboronic acid  
**B25434** 2-Formylbenzeneboronic acid  
**B25437** 3-Formylbenzeneboronic acid  
**B25199** 4-Formylbenzeneboronic acid  
**L17850** 3-Formyl-4-methoxybenzeneboronic acid  
**L19059** 5-Formyl-2-methoxybenzeneboronic acid  
**L19400** 2-Hydroxybenzeneboronic acid  
**L19061** 3-Hydroxybenzeneboronic acid  
**L15594** 4-Hydroxybenzeneboronic acid  
**L15192** 2-(Hydroxymethyl)benzeneboronic acid hemiester  
**L15193** 3-(Hydroxymethyl)benzeneboronic acid  
**L15194** 4-(Hydroxymethyl)benzeneboronic acid  
**L20110** 2-Isopropylbenzeneboronic acid  
**L15530** 3-Isopropylbenzeneboronic acid  
**L17459** 4-Isopropylbenzeneboronic acid  
**L17460** 5-Isopropyl-2-methoxybenzeneboronic acid  
**L17865** 4-(Methanesulfinyl)benzeneboronic acid  
**L17720** 4-(Methanesulfonyl)benzeneboronic acid  
**B21071** 2-Methoxybenzeneboronic acid  
**B24412** 3-Methoxybenzeneboronic acid  
**A14462** 4-Methoxybenzeneboronic acid  
**L17958** 2-(Methoxycarbonyl)benzeneboronic acid  
**L19820** 4-Methoxy-3,5-dimethylbenzeneboronic acid  
**L20112** 4-Methoxy-2-methylbenzeneboronic acid  
**L19821** 4-Methoxy-3-methylbenzeneboronic acid  
**L19060** 6-Methoxy-2-naphthaleneboronic acid  
**B23154** 2-Methylbenzeneboronic acid  
**B23025** 3-Methylbenzeneboronic acid  
**A13347** 4-Methylbenzeneboronic acid  
**B24217** 3,4-(Methylenedioxy)benzeneboronic acid  
**L17456** 2-(Methylthio)benzeneboronic acid  
**L20250** 3-(Methylthio)benzeneboronic acid  
**B23454** 4-(Methylthio)benzeneboronic acid  
**B21219** 1-Naphthaleneboronic acid  
**B24157** 2-Naphthaleneboronic acid  
**L17988** 2-Nitrobenzeneboronic acid  
**A13336** 3-Nitrobenzeneboronic acid  
**L17004** trans-4-( $\beta$ -Nitrovinyl)benzeneboronic acid  
**L17753** 4-n-Nonylbenzeneboronic acid  
**B22922** 2,3,4,5,6-Pentafluorobenzeneboronic acid  
**L18011** 4-n-Pentylbenzeneboronic acid  
**L19824** 2,3,4,5-Tetrafluorobenzeneboronic acid  
**L19825** 2,3,4,6-Tetrafluorobenzeneboronic acid  
**L19826** 2,3,5,6-Tetrafluorobenzeneboronic acid  
**L19827** 2,3,4-Trifluorobenzeneboronic acid  
**L17511** 2,3,5-Trichlorobenzeneboronic acid  
**L19402** 2,4,6-Trifluorobenzeneboronic acid  
**L18519** 3,4,5-Trifluorobenzeneboronic acid  
**L19774** 2-(Trifluoromethoxy)benzeneboronic acid  
**L19775** 3-(Trifluoromethoxy)benzeneboronic acid  
**B23233** 4-(Trifluoromethoxy)benzeneboronic acid  
**B24343** 2-(Trifluoromethyl)benzeneboronic acid  
**B21661** 3-(Trifluoromethyl)benzeneboronic acid  
**B22374** 4-(Trifluoromethyl)benzeneboronic acid  
**B22891** 2,4,6-Triisopropylbenzeneboronic acid  
**L19838** 2,3,4-Trimethoxybenzeneboronic acid  
**L19837** 2,4,6-Trimethoxybenzeneboronic acid  
**L15191** 3,4,5-Trimethoxybenzeneboronic acid  
**B24060** 2,4,6-Trimethylbenzeneboronic acid  
**L19828** 2-Vinylbenzeneboronic acid  
**L19829** 3-Vinylbenzeneboronic acid  
**B23709** 4-Vinylbenzeneboronic acid

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## Arylboronic esters

- L19951** 2-Aminobenzeneboronic acid pinacol ester  
**L16187** 1,4-Benzenediboronic acid bis(neopentyl glycol) ester  
**L17605** 4,4'-Biphenyldiboronic acid bis(neopentyl glycol) ester  
**L19653** 4-(Boc-amino)benzeneboronic acid pinacol ester  
**L17796** 3-Bromobenzeneboronic acid N-methyl-diethanolamine ester  
**L17775** 4-Bromobenzeneboronic acid N-methyl-diethanolamine ester  
**L17455** 4-Bromobenzeneboronic acid neopentyl glycol ester  
**L19954** 4-(Bromomethyl)benzeneboronic acid pinacol ester

## Aryltrifluoroborate salts

- L17966** Potassium 3-bromophenyltrifluoroborate  
**L17967** Potassium 4-bromophenyltrifluoroborate  
**L17655** Potassium 4-fluorophenyltrifluoroborate  
**L17968** Potassium 2-formylphenyltrifluoroborate

## Heterocyclic boronic acids

- L15221** 5-Acetylthiophene-2-boronic acid  
**B23676** Benzo[b]furan-2-boronic acid  
**B22835** Benzo[b]thiophene-2-boronic acid  
**L19915** 5-Bromo-2-fluoropyridine-3-boronic acid  
**L20084** 5-Bromopyridine-3-boronic acid  
**L20085** 6-Bromopyridine-3-boronic acid  
**L20327** 2-Bromoquinoline-3-boronic acid  
**L20303** 2-Chloropyridine-3-boronic acid  
**L20329** 2-Chloroquinoline-3-boronic acid  
**B23193** 5-Chlorothiophene-2-boronic acid  
**L18523** 5-Cyanothiophene-2-boronic acid  
**L19830** Dibenzofuran-4-boronic acid  
**L19831** Dibenzothiophene-4-boronic acid  
**L20389** 2,6-Dimethoxypyridine-3-boronic acid  
**L20398** 6-Ethoxypyridine-3-boronic acid  
**L20108** 2-Fluoropyridine-3-boronic acid hydrate  
**L20387** 6-Fluoropyridine-3-boronic acid  
**L20341** 2-Fluoroquinoline-3-boronic acid

## Heterocyclic boronic esters

- L17779** 5-Formyl-4-methylthiophene-2-boronic acid 1,3-propanediol ester  
**L18366** Furan-2-boronic acid pinacol ester

- L19956** 4-(Cyanomethyl)benzeneboronic acid pinacol ester  
**L17266** 3,5-Difluorobenzeneboronic acid neopentyl glycol ester  
**L17670** 3-Isopropylbenzeneboronic acid ethylene glycol ester  
**L19563** 4-Methylbenzeneboronic acid neopentyl glycol ester  
**L17612** 1-Naphthaleneboronic acid neopentyl glycol ester  
**L19963** 2-Nitrobenzeneboronic acid pinacol ester  
**L17232** 2,4,6-Trimethylbenzeneboronic acid neopentyl glycol ester

- L17969** Potassium 4-formylphenyltrifluoroborate  
**L17604** Potassium 4-methylphenyltrifluoroborate  
**L17568** Potassium phenyltrifluoroborate

- L15198** 3-Formylfuran-2-boronic acid  
**L17920** 5-Formylfuran-2-boronic acid  
**L15195** 2-Formylthiophene-3-boronic acid  
**L15196** 3-Formylthiophene-2-boronic acid  
**B23842** Furan-2-boronic acid  
**L19834** Furan-3-boronic acid  
**L20430** Isoquinoline-4-boronic acid  
**L20094** 2-Methoxypyridine-3-boronic acid  
**L20087** 6-Methoxypyridine-3-boronic acid  
**B23138** 5-Methylthiophene-2-boronic acid  
**L15040** Pyridine-3-boronic acid  
**L15179** Pyridine-4-boronic acid hydrate  
**L20088** Quinoline-3-boronic acid  
**L19639** Quinoline-5-boronic acid  
**L19640** Quinoline-8-boronic acid  
**L19833** Thianthrene-1-boronic acid  
**B23071** Thiophene-2-boronic acid  
**B23637** Thiophene-3-boronic acid

- L19654** Pyrazole-4-boronic acid pinacol ester  
**L17010** Pyridine-3-boronic acid 1,3-propanediol ester  
**L17854** Pyridine-4-boronic acid pinacol ester

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## Other products of interest

The following products from the Catalogue have relevance to the chemistry described in the foregoing sections of this Appendix:

## Oxazaborolidine reagents

- L07705** Borane dimethyl sulfide complex  
**L13961** Borane tetrahydrofuran complex  
**L09218** (R)-(+)- $\alpha,\alpha$ -Diphenylprolinol  
**L09217** (S)-(-)- $\alpha,\alpha$ -Diphenylprolinol  
**L14582** (R)-2-Methyl-CBS-oxazaborolidine  
**L09230** (R)-2-Methyl-CBS-oxazaborolidine monohydrate  
**L14583** (S)-2-Methyl-CBS-oxazaborolidine  
**L09219** (S)-2-Methyl-CBS-oxazaborolidine monohydrate

## Boronation reagents

- L18675** Bis(neopentyl glycolato)diboron  
**L16088** Bis(pinacolato)diboron  
**L14998** Catecholborane  
**L17278** 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane  
**L19056** 2-Methoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane  
**L17558** Pinacolborane

## Coupling catalysts

- 39288** (Acetylacetonato)bis(ethylene)rhodium(I)  
**39295** (Acetylacetonato)dicarbonylrhodium(I)  
**10002** Bis(acetonitrile)dichloropalladium(II)  
**10006** trans-Bis(benzonitrile)dichloro-palladium(II)  
**12764** Bis(dibenzylideneacetone)palladium(0)  
**96588** [1,1'-Bis(diphenylphosphino)ferrocene]-palladium(II) chloride  
**41225** [1,1'-Bis(diphenylphosphino)ferrocene]-palladium(II) chloride, complex with dichloromethane  
**96586** Diacetato[1,3-bis(diphenylphosphino)-butane]palladium(II)  
**13930** Dichlorobis(triphenylphosphine)nickel(II)  
**10491** trans-Dichlorobis(triphenylphosphine)-palladium(II)  
**A16203** Copper(II) acetate monohydrate  
**L16948** trans-Di- $\mu$ -acetatobis[2-(di-*o*-tolylphosphino)benzyl]dipalladium(II)  
**96587** Dichloro[1,4-bis(diphenylphosphino)-butane]palladium(II)  
**18779** Dichloro[bis(1,2-diphenylphosphino)ethane]-palladium(II)  
**30167** Dichloro[bis(1,3-diphenylphosphino)propane]-nickel(II)  
**44844** Dichlorobis(tricyclohexylphosphine)-palladium(II)  
**96590** Dichlorobis(tri-*o*-tolylphosphine)palladium(II)  
**A12623** Palladium, 5% on carbon  
**A12012** Palladium, 10% on carbon  
**L19015** Palladium, polymer-supported, ca 2% wt. on Deloxan<sup>®</sup> resin  
**10516** Palladium(II) acetate, trimer  
**11034** Palladium(II) chloride  
**10517** Palladium(II) 2,4-pentanedionate  
**44446** Palladium tri-*tert*-butylphosphine bromide, dimer  
**11886** Sodium tetrachloropalladate(II)  
**10548** Tetrakis(triphenylphosphine)palladium(0)  
**10549** Tetrakis(triphenylphosphine)platinum(0)  
**12760** Tris(dibenzylideneacetone)dipalladium(0)  
**L15980** Tris(dibenzylideneacetone)dipalladium(0) chloroform adduct

## Phosphine ligands

- B21122** 1,4-Bis(diphenylphosphino)butane [dppb]  
**B21166** 1,1'-Bis(diphenylphosphino)ferrocene [dppf]  
**A12931** 1,3-Bis(diphenylphosphino)propane [dppp]  
**L19477** Diphenylmethylphosphine, polymersupported  
**10178** Tri-*tert*-butylphosphine  
**L19752** Tri-*tert*-butylphosphonium tetrafluoroborate  
**41952** Tricyclohexylphosphine  
**L03616** Triphenylarsine  
**L02502** Triphenylphosphine, powder  
**A14089** Triphenylphosphine, flake  
**L19478** Triphenylphosphine, polymer-supported  
**A12093** Tri(*o*-tolyl)phosphine

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