Boronic Acids

Properties and Applications





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Boronic Acids

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Within the field of organoboron chemistry, boronic acids have emerged in a leading role, with applications in synthesis, catalysis, analytical chemistry and in biological systems. The discovery of a wealth of new chemistry, in particular the Suzuki-Miyaura cross-coupling reaction, combined with their accessibility and ease of handling, have established boronic acids and boronates among the most frequently-encountered of intermediates. Nearly thirty years ago, Lancaster Synthesis, now incorporated in the Alfa Aesar group, pioneered the commercial production of a range of boronic acids for use in research and development. Since then, the astonishing growth of interest in the chemistry of these molecules has been paralleled by an enormous increase in the diversity of examples available from commercial sources, among which Alfa Aesar continues to hold a leading position. We can provide outstanding synthetic and analytical expertise in boronic acids, esters and related products. This publication outlines the chemical properties and highlights the main synthetic uses of these versatile molecules.

1. Introduction

Elemental boron is rather difficult to isolate in a pure state, in which it is usually obtained as an extremely hard, dark brown or black powder, mp 2075°C. Its properties, such as electronegativity (Table 1), are those of a non-metal or metalloid, although organoboron compounds are often classed as organometallics, since they have certain similarities to compounds of some metallic elements.

Table 1: Electronegativities (Pauling) of representative elements¹

	-		
Н	2.20	Li	0.98
Be	1.57	Mg	1.31
В	2.04	AI	1.61
С	2.55	Si	1.90
Ν	3.04	Р	2.19
0	3.44	S	2.58
F	3.98	CI	3.16
Zn	1.65	Pd	2.20
Cu	1.90	Sn	1.96

Table 2 shows a representative selection of bond strengths involving boron, along with data for related elements for comparison.

Table 2: Typical covalent bond energies^{1,2}

Bond	Bond energy			
	kJ mol⁻¹	kcal mol ⁻¹		
B–H	375	90		
B–C	323	77		
B–O	544	130		
B–F	659	158		
B–Cl	456	109		
B–B	286	68		
C–C	358	85		
Li–C	126	30		
Si–C	301	72		
Sn–C	225	54		

Organoboron compounds³ tend to be air-sensitive, and in some cases pyrophoric materials. In work predating Mendeleev's periodic classification of the elements, Frankland⁴ reported in 1859 the reaction of pyrophoric diethylzinc with triethyl borate to form a new pyrophoric product, triethylborane, readily oxidized by air to diethylborinic acid Et₂BOH. A second, slow oxidation step gave a more stable, crystalline product, identified as ethylboronic acid EtB(OH)₂. This sequence, the first known synthesis of a boronic acid, is inconvenient and of limited scope, but half a century elapsed before the publication of Khotonsky and Melamed's preparation of benzeneboronic acid from phenylmagnesium bromide and trimethyl borate,⁵ which was to become the basis of the most generally useful route to boronic acids. The procedure was improved in the 1930s by Johnson,⁶ and in the 1950s by Washburn.⁷ Further details can be found in Section 4.

Although organoboron chemistry became a focus of attention in the second half of the 20th century, mainly due to the work of H. C. Brown, boronic acid chemistry continued to be a relative backwater over 100 years after Frankland's initial disclosure, but from the 1970s onwards, the level of interest has increased dramatically, as new applications have come to light. Whereas the chemistry of boronic acids could be covered by a 47-page review in 1964,⁸ a recent comprehensive monograph on the subject runs to well over 500 pages.⁹

Most boronic acids are crystalline solids, easily handled in the presence of air and moisture. They are usually stable to long-term storage, but may undergo dehydration (see below) or, in some cases, are prone to air oxidation or gradual degradation. Where these may present a problem, either the corresponding boronate ester (Section 2) or trifluoroborate salt (Section 3) usually offers a satisfactory alternative which can undergo many of the reactions of the boronic acid itself. Such evidence as exists indicates that the boronic acid moiety is of relatively low intrinsic toxicity.¹⁰ Recent applications in medicine support this view.¹¹ From an environmental perspective, boronic acids will degrade ultimately to the relatively benign boric acid, although the fate of the rest of the molecule will depend on the nature of any substituents.

Chemical character

Since the electron-deficient boron atom has a vacant porbital, boronic acids behave as mild Lewis acids, which can coordinate to Lewis bases. Hence, in water they tend to coordinate an OH group to form the tetrahedral anionic species, rather than acting as Brønsted acids by losing a proton (Scheme 1).¹² The measured acidity of arylboronic acids is comparable to phenols (benzeneboronic acid: pK_a 8.9 in water); alkylboronic acids are weaker. Electronwithdrawing substituents on the aryl group increase acidity, and electron-releasing groups decrease it.¹³

$$R \xrightarrow{OH}_{OH} + H_{2}O \xrightarrow{H}_{R} \xrightarrow{O^{-}}_{OH} + H_{3}O^{+}$$

$$R \xrightarrow{OH}_{OH} + 2H_{2}O \xrightarrow{OH}_{R} \xrightarrow{OH}_{H} + H_{3}O^{+}$$

$$R \xrightarrow{OH}_{OH} + 2H_{2}O \xrightarrow{I}_{OH} + H_{3}O^{+}$$

$$Scheme 1$$

In this review, the reactions of boronic acids are divided into two broad categories, according to whether they involve retention or cleavage of the boron-carbon bond, which are discussed in Sections 2 and 3 respectively. Section 4 outlines some of the preparative methods used for boronic acids and boronates.

2. Reactions in which the B–C bond is retained

Boroxine formation

Most boronic acids readily undergo dehydration (Scheme 2) to form the cyclic trimeric anhydride (boroxine; 1,3,5,2,4,6-trioxatriborinane). This often tends to occur spontaneously at room temperature, or in the course of drying, so that it may be difficult to obtain the acid free from the anhydride. Apart from difficulties in characterization (variable analyses and unreproducible melting points), this is rarely a serious problem, since in many applications, the acid and the anhydride are essentially indistinguishable.



However, if required, conversion of the boronic acid to a boronate ester with a suitable diol (see below) will prevent the dehydration reaction.

Boronate formation: protection of diols

Boronic acids react with alcohols, with loss of water, to form boronic esters (boronates). With simple alcohols, the products are very susceptible to hydrolysis, but with 1,2and 1,3-diols, the resulting cyclic boronates (1,3,2dioxaborolanes and 1,3,2-dioxaborinanes) are stable enough to be isolated.

The main early application was for protection and derivatization of 1,2- and 1,3-diols, particularly in carbohydrate chemistry.¹⁴ These boronates have been widely used as volatile derivatives for GC and GC-MS purposes. They may be formed simply by stirring the boronic acid and diol together at ambient temperature, by warming, or, if necessary, with azeotropic removal of water. A detailed examination of boronic acid-diol complexation has been published.¹⁵ Usually cleavage occurs readily under hydrolytic conditions, by exchange with a glycol,¹⁶ or by treatment with hydrogen peroxide.¹⁷ Hindered boronic esters, such as those of pinacol (2,3dimethyl-2,3-butanediol), may be relatively stable to hydrolysis, and can often be purified by chromatography. A useful application of boronate protection is in the osmium(VIII) oxide catalyzed cis-dihydroxylation of alkenes under anhydrous conditions in the presence of a boronic acid (Scheme 3).^{17b,18}



Further information on the applications of boronic acids as derivatizing and protecting agents can be found in various reviews¹⁹⁻²¹ and monographs.²²⁻²⁴

Other applications of diol boronates

The formation of boronic esters with polymer-bound diols has been utilized as a linker system for solid phase synthesis, enabling modification of the polymer-bound boronic acid, followed by mild deprotection with methanol.²⁵

Many other uses of boronates formed with carbohydrate molecules have been developed, including the selective transport of sugars in lipophilic environments,^{26,27} and the design of artificial receptors, as discussed in several reviews.²⁸⁻³²

Boronic derivatives as activating and directing groups

The mild Lewis acidity of boronic acids, along with the ease of exchange around oxygen or nitrogen atoms attached to boron, has led to the application of the acids and their derivatives as catalysts or temporary scaffolds in a variety of regio-, stereo- and enantioselective syntheses. Arylboronic acids can behave as water-, acid-, and basetolerant, thermally stable Lewis acids. Yamamoto has found that a boronic acid with electron withdrawing substituents, in particular 3,4,5-trifluorobenzeneboronic acid [Alfa Aesar product code **L18519**] can be an effective catalyst for amidation and esterification of carboxylic acids.³³ The reaction is thought to involve a 6-membered cyclic intermediate (Scheme 4).



The amidation reaction has been extended to ureas.³⁴ 3,4,5-Trifluorobenzeneboronic acid also catalyzes the onepot synthesis of acyl azides from carboxylic acids and sodium azide,³⁵ and the one-pot reduction of carboxylic acids to alcohols with sodium borohydride.³⁶ In some reactions, 3-nitrobenzeneboronic acid may be an effective catalyst, as in the transesterification of β -keto esters.³⁷ The use of arylboron compounds as acid catalysts was reviewed by Ishihara and Yamamoto.³⁸

Benzeneboronic acid mediates the *ortho*-specific α -hydroxyalkylation of phenols by aldehydes.³⁹ The key intermediate is a cyclic boronate, formed via a [3,3] sigmatropic rearrangement. This process was utilized in the mild syntheses of benzo-fused heterocycles, including tetrahydrocannabinoids,^{39b} and 2*H*-chromenes (Scheme 5).⁴⁰



Chiral boronates

Matteson has carried out extensive work on cyclic boronates,^{41,42} formed from chiral diols, which undergo carbon insertion with LiCHCl₂ in the presence of zinc chloride in up to 99% diastereomeric excess (de). Treatment of the resulting α -chloro boronic esters with various nucleophiles leads to α -substituted boronic esters which can be oxidatively cleaved with hydrogen peroxide, or the sequence can be repeated to introduce a second chiral carbon atom, as illustrated in Scheme 6.



Further aspects of this area of boronic ester chemistry have since been reviewed by Matteson.⁴³

Oxazaborolidines

The reaction of a boronic acid with a chiral 2-amino alcohol gives an oxazaborolidine. These derivatives were introduced by Corey, Bakshi and Shibata⁴⁴ ("CBS" reagents) as excellent catalysts for enantioselective borane reduction of prochiral ketones (Scheme 7) with very high yield and enantiomeric excess (ee).



The reagents derived from (R)- and (S)- α , α diphenylprolinol [product codes **L09218** and **L09217**], usually with methylboronic acid: (R)- and (S)-2-methyl-CBS-oxazaborolidine **[L09230, L14582, L09219, L14583**], have received the most attention, although the use of other amino alcohols has been reported.^{45,46} Reviews on the use of oxazaborolidines as enantioselective catalysts,^{47,48} and the asymmetric reduction of ketones^{49,50} are available.

Diels-Alder reactions

Boronic acids can form stable chiral acyloxyborane (CAB) catalysts with tartaric acid derivatives. These compounds have been developed by Yamamoto as catalysts for asymmetric Diels-Alder⁵¹ and hetero Diels-Alder⁵² reactions, for example between aldehydes and Danishefsky's diene [1-methoxy-3-(trimethylsiloxy)-1,3-butadiene; [product codes **L06100** (94%) and **L14672** (98+%)], to give, enantioselectively, dihydro-4-pyrone derivatives (Scheme 8).⁵³



Benzeneboronic acid itself can be used as a template for Diels-Alder reactions by forming boronate linkages with a hydroxy diene and a hydroxy dieneophile,⁵⁴ an approach which was applied successfully by Nicolaou to synthesize the fully functionalized CD ring system of Taxol (Scheme 9).⁵⁵



The use of boron acids as protective agents and catalysts in synthesis has been reviewed by Duggan and Tyndall.²¹

3. Reactions involving B–C bond cleavage

In the reactions described in the following sections, displacement of boron takes place with formation of a new carbon-carbon or carbon-heteroatom bond.

C–C bond-formation: the Suzuki-Miyaura crosscoupling reaction

In comparison with typical organometallic compounds of lithium, magnesium or the transition metals, the difference in electronegativity between boron and carbon is relatively small, and the boron-carbon bond strong (see Tables 1,2). Organoboron compounds, therefore, in the absence of a catalyst, normally exhibit very low reactivity towards electrophiles such as organic halides. In 1979, Suzuki and Miyaura reported the successful coupling of alkenylboranes and catecholyl boronates, in the presence of a Pd(0) catalyst and a base,⁵⁶ with alkenyl and alkynyl,⁵⁷ aryl⁵⁸ allyl and benzyl⁵⁹ halides. However, it was their discovery, published in 1981,60 that stable, easily-handled arylboronic acids undergo palladium-catalyzed crosscoupling with aryl bromides and iodides in the presence of a base (Scheme 10), which stimulated the greatest interest in the application of this reaction. As a result, a plethora of applications and variants have subsequently been developed leading to the synthesis of unsymmetrical biaryls and many other types of coupled products.



Scheme 10

Earlier methods employed for such syntheses generally involve the direct coupling of highly-reactive, usually moisture- and air-sensitive organometallic reagents (Grignard, organolithium, organozinc, etc.) with aryl halides, generally in the presence of a transition metal catalyst. Such reactions normally require strictly anhydrous conditions and an inert atmosphere, and are of limited scope, since the presence of many functional groups interferes. In contrast, Suzuki and Miyaura carried out the cross-coupling of boronic acids under aqueous conditions, and the reaction tolerates a wide variety of functional groups. The widely-used Stille cross-coupling reaction,⁶¹ by comparison,⁶² is also extremely versatile, and in some ways complementary to the boronic coupling, but involves toxic, environmentally hazardous organotin species.

Since its first disclosure, the cross-coupling reaction of boronic acids (usually known as the Suzuki or Suzuki-Miyaura reaction) has been developed in scope to become a cornerstone of modern synthetic organic chemistry. Under the standard coupling conditions, aryl bromides are most frequently used as the electrophilic species, but iodides may be preferred since they are more reactive. The successful coupling of the often more readily available and lower cost, but less reactive, aryl chlorides has been achieved under modified conditions, using a variety of palladium⁶⁴⁻⁶⁹ or nickel^{70,71} catalysts. Because of its versatility and the mild reaction conditions, the Suzuki coupling has been widely adopted for solid-phase synthesis on polymer supports.^{72,73}

A proposed catalytic cycle for the reaction^{74,75} is shown in Scheme 11. A detailed mechanistic study has also been published.⁷⁶



Suzuki and Miyaura's initial publication was followed by a series of papers by Gronowitz *et al*,⁷⁷ who showed that the

deboronylation found as a side reaction, particularly with electron-rich boronic acids, could be minimized by using dimethoxyethane (DME) as solvent in conjunction with aqueous Na₂CO₃. This system was found to be applicable to a variety of aryl and heteroaryl substrates, and has been widely adopted by other workers. Alternative illustrative experimental procedures are described in Organic Syntheses.⁷⁸ Useful reviews of the Suzuki-Miyaura and related reactions have been published by Suzuki and Miyaura,^{79,80} by Martin and Yang,⁷⁵ with particular emphasis on heteroaryl systems, and by Stanforth⁸¹ on biaryl synthesis via cross-coupling reactions. The more recent literature on the Suzuki-Miyaura cross-coupling has been reviewed by Kotha et al.82 A review of palladiumcatalyzed coupling reactions of aryl chlorides, majoring on recent improvements, is also available,⁸³ as is a general review of aryl-aryl bond formation.⁸⁴

Related coupling reactions

In early extensions of the biaryl coupling reaction, aryland heterorarylboronic acids were coupled with a variety of heterocyclic halides, including thiophenes,⁸⁵ furans, thiazoles,⁸⁶ isoxazoles,⁸⁷ pyridines,^{64,88-90} quinolines,⁸⁸ pyrimidines,^{86,89} and pyrazines.^{89,90} Many further examples have subsequently been published.

Aryl^{91,92} or vinyl⁹³ triflates also undergo boronic acid coupling, which usefully extends the scope of the reaction to phenols or enols. The relative reactivity of leaving groups is normally in the order I⁻ > OTf⁻ > Br⁻ >> Cl⁻. Cross-coupling of boronate derivatives with aryl mesylates,^{94,95} and tosylates,⁹⁶ catalyzed by nickel complexes, has also been described, as has palladium-catalyzed coupling with sulfonium salts.⁹⁷ Coupling of arylboronic acids with heteroaryl thioethers has been brought about with a palladium catalyst, mediated by a Cu(I) carboxylate,⁹⁸ while nickel-catalyzed coupling with aryl quaternary ammonium salts has also been reported.⁹⁹ Other substrates (Pd-catalyzed) for arylboronic acid cross-coupling include: benzyl bromides,¹⁰⁰ α -bromo esters,¹⁰¹ vinyl halides,¹⁰²⁻¹⁰⁴ allylic bromides¹⁰⁵ or acetates,¹⁰⁶ allenic alcohols,¹⁰⁷ propargylic alcohols,¹⁰⁸ and allylic alcohols (Pd-catalyzed¹⁰⁹ or Rh-catalyzed¹¹⁰).

As already stated, Suzuki and Miyaura's earliest papers on the cross-coupling reaction related to alkenylboranes and boronic esters of catechol,^{57,58} and, although the use of free boronic acids now predominates, aryl and enol boronates, particularly with pinacol (2,3-dimethyl-2,3-butanediol), still find use in the reaction, particularly in examples where they are more accessible via coupling or hydroboration methods (see Section 4), or more stable, than the corresponding free boronic acids. This is frequently an advantage in complex, multi-step syntheses, where the boronate substituent can be introduced under mild conditions, and may then be utilized to form a C–C bond with a preformed electrophilic fragment. Scheme 12 illustrates examples of boronate coupling.^{111,112}



There are relatively few accounts of boronic acids coupling with unactivated alkyl halides, although these have begun to appear, mainly due to the work of Fu, who has described conditions for Pd-catalyzed coupling of aryl-, alkenyl- or alkylboronic acids with primary alkyl halides, in the presence of hindered phosphines, such as tricyclohexylphosphine or particularly P(t-Bu)₂Me,¹¹³ and also of the Ni-catalyzed coupling of aryl- and alkenylboronic acids with secondary alkyl bromides and iodides, in the presence of a phenathroline ligand.¹¹⁴

Improved syntheses and availability from commercial sources, including Alfa Aesar, of boronic acids derived from electron-deficient hetereroaryl systems (e.g. pyridines) make their use more attractive. There are several reviews on the chemistry of these molecules.¹¹⁵⁻¹¹⁸

Coupling reactions of organotrifluoroborate salts

Darses and Genêt showed that the cross-coupling of arylboronic acids with arenediazonium tetrafluoroborates, catalyzed by palladium acetate in dioxane or methanol, needed neither added base nor phosphine ligand.¹¹⁹ They applied similar conditions to the coupling of diazonium tetrafluoroborates with potassium aryl trifluoroborates,¹²⁰ which are air-stable crystalline solids readily prepared from arylboronic acids and KHF₂, and potassium vinyl trifluoroborates,¹²¹ which are also readily isolable crystalline solids, more stable than the corresponding vinylboronic acids. The cross-coupling of potassium aryl and heteroaryl trifluoroborates with aryl and heteroaryl halides was subsequently described by Molander.¹²² For aryl and electron-rich heteroaryl (e.g. thiophene) trifluoroborates, these reactions proceed in the presence of Pd(OAc)₂ under ligandless conditions. However he found that for electron-deficient heteroaryl (e.g. pyridine) trifluoroborates, the use of a liganded catalyst, [1,1'bis(diphenylphosphino)-ferrocene]palladium(II) chloride, was necessary to give satisfactory yields.^{122b} Conditions for coupling potassium aryl and heteroaryl trifluoroborates with aryl and heteroaryl triflates have also been reported.¹²³ In general, trifluoroborate salts are more nucleophilic than the equivalent boronic acids.^{120,124} Furthermore, they are often more crystalline and more stable to long-term storage.

Molander has also demonstrated the coupling of potassium alkenyl trifluoroborates with aryl halides and triflates (Scheme 13), greatly extending the usefulness of these intermediates.¹²⁵ In the case of potassium vinyltrifluoroborate [**L17970**], high yields of Suzuki coupling products are obtained free from the products of Heck coupling observed with vinylboronic esters (see Section 4).¹²⁶



Scheme 13

Potassium alkenyl trifluoroborates also couple with alkenyl bromides, affording, 1,3-dienes with retention of double-bond geometry.¹²⁷

Alkylboron couplings

Suzuki-Miyaura coupling of alkylboronic acids was described as difficult to accomplish and limited in scope.¹²⁸ However, Molander subsequently reported conditions under which primary alkylboronic acids can be coupled efficiently with aryl halides and triflates (Scheme 14).¹²⁹



This has been extended to the coupling of potassium alkyl trifluoroborates with aryl halides and triflates, catalyzed by (dppf)PdCl₂.¹³⁰

Formation of carbonyl compounds

Suzuki and Miyaura reported a variation of the biaryl coupling reaction, shown in Scheme 15, in which carbonylative cross-coupling of arylboronic acids with aryl iodides occurs in the presence of carbon monoxide at atmospheric pressure, to give unsymmetrical substituted benzophenones.¹³¹



Scheme 15

In contrast, Uemura found that, in the absence of an aryl halide, carbonylation of an aryl- or alkenylboronic acid, with a Pd(0) catalyst in THF, leads to the corresponding symmetrical ketone. In methanol without added base, a mixture of the ketone and the methyl aryl or alkenyl carboxylic ester is formed, whereas in the presence of sodium acetate, the methyl ester is the major product.¹³² Unsymmetrical ketones were later prepared by reaction of arylboronic acids with acyl chlorides, catalyzed either by (Ph₃P)₄Pd,¹³³ (Ph₃P)₂PdCl₂,¹³⁴ or Pd(OAc)₂ with no added ligand,¹³⁵ and also with anhydrides, catalyzed by rhodium complexes.¹³⁶ A route to esters and amides is available via the coupling of arylboronic acids with chloroformates (Scheme 16).¹³⁷



Scheme 16

Similarly, tertiary amides have been prepared by reaction of arylboronic acids¹³⁷ or arylboronates¹³⁸ with N,N-dialkylcarbamoyl chlorides.

Coupling reactions of arylboronic acids with S-phenyl trifluorothioacetate, with $Pd_2(dba)_3$ and a Cu(I) cocatalyst,¹³⁹ or with phenyl trifluoroacetate, or the phenyl ester of another perfluoroalkanoic acid, catalyzed by $Pd(OAc)_2^{140}$ (Scheme 17), have been used to prepare the corresponding aryl perfluoroalkyl ketones.



Catalyst systems

In the original biaryl coupling work, Suzuki and Miyaura⁶⁰ employed the readily-available complex tetrakis(triphenylphosphine)palladium(0), which continues to be the preferred catalyst in most routine syntheses. An extremely wide variety of alternative catalyst and ligand systems have been reported, with advantages in cost, efficiency or selectivity for particular applications. Examples include: selectivity for particular applications. Examples include: $(Ph_3P)_2PdCl_2$, ^{87,131} (dppb)PdCl_2, ^{89,141} Pd(dba)_n^{115,142} Pd(OAc)₂, ^{119,143} Pd(OAc)₂/(o-tol)₃P, ^{90,144} Pd(OAc)₂/dppf, ⁹⁰ PdCl₂/pyridine, ¹⁴⁵ (dppf)PdCl₂, ^{101,104,111,112,129,130,146} (PhCN)₂PdCl₂/Ph₃As, ¹⁰³ (CH₃CN)₂PdCl₂, ¹³¹ palladium on carbon, ^{65,88,147,149} palladium on a polymer support, ^{64,150} (Ph₃P)₂NiCl₂, ^{70,95} NiCl₂.6H₂O, ⁷¹ and the palladacycle trans-di-µ-acetatobis[2-(di-o-tolylphosphino)complex benzyl]dipalladium(II).¹⁵¹ Low-cost trialkyl phosphites have also been successfully used as ligands in palladium-^{152,153} and nickel-¹⁵² catalyzed couplings. As an alternative phosphorus(III) derivatives, inexpensive 1,4to diazabicyclo[2.2.2]octane (Dabco), in the presence of Pd(OAc)₂ has been found to be an effective ligand.^{154,155}

 $Pd_2(dba)_3/(t-Bu)_3P$,¹²⁰ and the air-stable equivalent $Pd_2(dba)_3/[(t-Bu)_3PH]BF_4$,¹²¹ developed by Fu's group, as well as Buchwald's biphenylphosphine systems, e.g. $Pd(OAc)_2/2$ -(di-*tert*-butylphosphino)biphenyl.⁶⁹ are good for coupling difficult substrates, including aryl chlorides, under mild conditions (Scheme 18).



The use of tetrakis(triphenylphosphine)platinum(0) instead of the palladium(0) complex permits selective coupling with an aryl iodide in the presence of an aryl bromide.¹⁵⁶

A comprehensive range of coupling catalyst systems, including most of those mentioned above and some more specialized systems, is available from Johnson Matthey Catalysts. These products are offered in research quantities through Alfa Aesar, and are listed in the Product section of this publication. Further technical information on the uses of these catalysts is available on request.

Bases

In contrast to the coupling reactions of organotin or organozinc reagents, Suzuki and Miyaura found that the arylboronic acid coupling requires 2 equivalents of a base, originally aqueous sodium carbonate.^{56,60} They also reported that the stronger bases ethoxide or hydroxide gave poorer yields than carbonate, and that sodium acetate was ineffective, although its use under modified conditions has since been reported.¹⁵⁷ Many alternative bases have been introduced for these reactions, some of which offer advantages for particular substrates; examples include: NaHCO₃,^{87,158} K₂CO₃,^{92,111} Cs₂CO₃,^{63b} K₃PO₄,⁹⁴ Et₃N/DMF,⁹⁰ Ag₂O,¹⁰³ Ba(OH)₂,^{112,159} good for sterically-hindered biaryls, and CsF,¹⁶⁰ compatible with readily-hydrolyzed functionality, such as esters.

Other reaction conditions

Many Suzuki-Miyaura biaryl coupling reactions described in the literature use an aqueous mixed solvent with a water-miscible component such as DME or 1,4-dioxane. Examples have appeared of the use of poly(ethylene glycol)^{155,161,162} or poly(ethylene oxide)¹⁶³ as co-solvent, potentially replacing volatile organic solvents, and facilitating recycling of the catalyst system.

The coupling reaction of arylboronic acids with aryl bromides is dramatically accelerated by using the ionic liquid, 1-*n*-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] as the reaction medium; improved yields with reduced catalyst loading of $(Ph_3P)_4Pd$ are claimed.¹⁶⁴ 4-Iodophenol immobilized on Wang resin undergoes accelerated coupling with the same catalyst in [bmim][BF₄].⁷³ The application of ultrasound, also in [bmim][BF₄], with ligand-free Pd(OAc)₂ as catalyst and NaOAc as base, has been found to promote rapid coupling

at ambient temperature under extremely mild conditions.¹⁵⁷ Water dramatically accelerates the Pd(OAc)₂-catalyzed coupling of aryl halides in [bmim][BF₄] and [bmim][PF₆], enabling multiple recycling of the catalyst system.¹⁶⁵ A short review article on palladium-catalyzed C-C coupling reactions in ionic liquids is available.¹⁶⁶

Arylboronic acids also undergo *rhodium*-catalyzed, copper-mediated coupling with allylic alcohols in [bmim][PF₆].¹¹⁶ At elevated temperatures, the simple phase-transfer catalyst tetra-n-butylammonium bromide (TBAB) behaves as an ionic liquid; mixtures with water have been utilized by Bedford for the ligand-free Pd(OAc)₂-catalyzed cross-coupling of aryl chlorides.⁶⁶

Leadbeater studied the accelerating effect of microwaves on ligand-free Pd(OAc)₂-catalyzed Suzuki-type couplings in water, with or without TBAB.¹⁶⁷ He also demonstrated Suzuki coupling of aryl chlorides using palladium on carbon catalyst in water with microwave heating and simultaneous cooling.¹⁶⁸ Yu has reported improved yields with aryl chlorides using a Pd-phosphine complex in aqueous media.¹⁶⁹ Leadbeater's claim¹⁷⁰ to have achieved microwave-promoted, transition metal-free coupling was later retracted, with the detection of traces of palladium in the sodium carbonate base.¹⁷¹ Microwaves also enable cross-coupling of organotrifluoroborates with ultra-low (ppm) catalyst loadings.¹⁷² "Environmentally friendly" Suzuki reactions have been reviewed.¹⁷³

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

Palladium-catalyzed reactions

Uemura reported palladium-catalyzed 1,4-addition of arylboronic acids to enones,¹⁷⁴ but yields were generally poor. Ohta has since found that 1,2-addition of arylboronic acids to aldehydes, catalyzed by Pd(0), can be effected, but only in the presence of chloroform.^{175a} Organoboronic acids also undergo 1,4-addition to α , β -unsaturated ketones with a Pd phosphine complex and chloroform.^{175b}

Rhodium-catalyzed reactions

Miyaura and Hayashi described the conjugate addition of arylboronic acids to enones, catalyzed by a rhodium(I) complex and a chelating phosphine, to give good yields of saturated ketones.¹⁷⁶ Under similar conditions, both aryland alkenylboronic acids can add to aldehydes to give secondary alcohols in high yield (Scheme 19).¹⁷⁷



An extension of these reactions to the addition of potassium alkenyl- and aryltrifluoroborates to aldehydes and enones has been described.^{178,179} Miyaura and Hayashi utilized the Rh(I)-catalyzed 1,4-addition reaction of boronic acids to α , β -unsaturated ketones,¹⁸⁰ esters¹⁸¹ or amides,¹⁸² in the presence of a chiral BINAP ligand, in enantioselective syntheses of the corresponding saturated ketones and esters. This area was reviewed by Hayashi.¹⁸³ Further investigations of the 1,4-addition reactions have led to improved results under milder conditions (Scheme 20).¹⁸⁴ New results in this field continue to appear on a regular basis.¹⁸⁵



Mizoroki-Heck and other transition metalcatalyzed reactions with alkenes and alkynes

Uemura reported the Pd(OAc)₂-catalyzed cross-coupling of arylboronic and alkenylboronic acids with alkenes in acetic acid to give aryl-substituted alkenes and conjugated dienes respectively, by oxidative addition of the B-C bond to an *in situ* formed Pd(0) species.¹⁸⁶ Subsequently, Mori described a Pd(II)-catalyzed pathway, employing catalytic Pd(OAc)₂ with Cu(OAc)₂ as stoichiometric co-oxidant.¹⁸⁷ Treatment of a variety of alkenes with arylboronic acids thus affords β-arylated products in good yield (Scheme 21). The reaction conditions were also adapted to permit the coupling of sodium tetraphenylborate alkenylboronates.



Jung has demonstrated the palladium-catalyzed oxygenpromoted coupling of a number of aryl and heteroaryl boronic acids and boronates with a variety of olefins in good yields under mild conditions (Scheme 22).¹⁸⁶



In contrast, with electron-rich olefins (vinyl ethers and Nvinylamides), the use of a phenanthroline ligand, promotes Pd-catalyzed Heck arylation at the internal (heteroatomsubstituted) position.¹⁸⁹ Arylboronic acids also undergo aerobic Pd-catalyzed Heck-type coupling with phenyl vinyl sulfones¹⁹⁰ and vinylphosphonates.¹⁹¹

Conditions for Heck-type reactions of arylboronic acids with acrylate esters to give cinnamic esters have been described by Brown, with a ruthenium catalyst in the presence of a Cu(II) oxidant,¹⁹² and by Zou, with a rhodium catalyst.¹⁹³

Lautens has investigated the rhodium catalyzed coupling of boronic acids with alkenes and alkynes in aqueous systems. In the presence of [Rh(COD)Cl]₂ and a watersoluble phosphine ligand, arylboronic acids undergo a Heck-type reaction with styrenes to give trans-stilbenes, whereas, with vinyl-substituted pyridines, quinolines or pyrazine, hydroarylation of the olefinic bond gives the heterocycle.194 saturated 2-arylethyl Alkynyl heteroaromatic compounds under analogous conditions also undergo hydroarylation to 2-arylvinyl derivatives.¹⁹⁵ Stereoselective rhodium-catalyzed hydroarylation of internal alkynes had previously been demonstrated by Hayashi.¹⁹⁶ Terminal alkynes with a palladium catalyst can undergo either hydroarylation by arylboronic acids, reported by Oh,¹⁹⁷ or Heck-type coupling under oxidative conditions, by Zou (see Scheme 23).¹⁹⁸ The regioselectivity of palladium-catalyzed hydroarylation of unsymmetrical internal alkynes has been studied by Oh.¹⁹⁹



Internal alkynes undergo addition with arylboronic acids, affording tetrasubstituted olefins.²⁰⁰

The Boron-Mannich (Petasis) reaction

Petasis initially described the Mannich-type reaction of alkenylboronic acids with paraformaldehyde and secondary amines,²⁰¹ affording allylamines in good yield with retention of double-bond geometry. Subsequently, he developed the three-component Mannich reaction of an alkenylboronic acid with glyoxylic acid and an amine to give β , γ -unsaturated α -amino acid derivatives,²⁰² which was extended to the synthesis α -aryl and α -heteroaryl glycines from the corresponding boronic acids,²⁰³ as shown in Scheme 24.



Harwood and co-workers demonstrated the use of a chiral secondary amine as a template in a diastereo-controlled Mannich reaction with furan-2-boronic acid [**L15297**], to give substituted furfurylamines with high de.²⁰⁴ The Petasis reaction has been investigated with one of the three components anchored to a polymer support, and found to give satisfactory results in most cases.²⁰⁵ The reaction has also been successfully extended to pinacolyl boronic esters,²⁰⁶ with chiral induction achievable via a homochiral boronic ester.²⁰⁷

Petasis has reported an analogous stereocontrolled threecomponent condensation, involving a boronic acid, an amine and an α -hydroxy aldehyde, to yield the *anti*- β amino alcohol.²⁰⁸ This route has been adapted to give the product enantioselectively with high ee.²⁰⁹

The Petasis reaction has been extended to the more reactive potassium organotrifluoroborates (aryl, vinyl and allyl), which undergo a Mannich-type condensation with an aldehyde and an amine, in the presence of a Lewis acid.²¹⁰ Alkenyl, aryl and heteroaryl pinacol boronates react slowly or not at all in the Petasis reaction in aprotic solvents. In alcohols such as methanol or hexafluoroisopropanol, the reaction proceeds well to give amino acid derivatives, mostly in high yield.²¹¹

Allylation reactions

Allylboronic esters can add stereoselectively to aldehydes, in the absence of a catalyst, to give homoallylic alcohols.^{41c} Ishiyama and Miyaura have shown that the reaction of pinacolyl allylboronates is dramatically accelerated, and the chemoselectivity increased, by a catalytic amount of a Lewis acid (Scheme 25).²¹² The potential for modest enantioselectivity was demonstrated in the presence of a BINOL co-catalyst.



C–O, C–N and C–S bond forming reactions

Oxidative cleavage of organoboron compounds to give alcohols or phenols is well known. In the case of boronic acids and esters, conditions utilizing hydrogen peroxide^{17,213} or Oxone^{® 214} have been described.

More useful synthetic reactions are the C–O and C–N coupling of arylboronic acids with phenols,^{215,216} N-hydroxyphthalimide,²¹⁷ amines,^{216,218} amides and imides,^{216,219} ureas, sulfonamides and carbamates,²¹⁵ and N-heteroaromatics,²²⁰ mediated by copper(II) acetate, to give the corresponding diaryl ethers, arylamines or N-aryl heterocycles. The C–N coupling reaction has been applied to solid-phase synthesis of N-heterocycles.²²¹ The formation of unsymmetrical thioethers from arylboronic acids and thiols, mediated by Cu(OAc)₂ has been reported.²²² Alkyl and aryl sulfinic acid salts also react with arylboronic acids, in the presence of Cu(OAc)₂, to give good yields of aryl sulfones.²²³

As originally described, these reactions required stoichiometric amounts of Cu(II). Buchwald reported a catalytic procedure for amination utilizing molecular oxygen as reoxidant for copper,²²⁴ and Batey has since developed improved oxygen-mediated catalytic procedures for the formation of ethers from trifluoroborate salts (or, in reduced yield, boronic acids) and aliphatic alcohols,²²⁵ and also for amination of both boronic acids and trifluoroborates (Scheme 26).²²⁶



Scheme 26

Arylboronic acids undergo reductive amination with arylnitroso compounds, mediated by Cu(I), providing a route to unsymmetrical diarylamines.²²⁷

Unsymmetrical diaryl or aryl heteroaryl sulfones have been prepared via a ligand-free, palladium chloride-catalyzed coupling of arylboronic acids with arylsulfonyl chlorides.²²⁸

Miscellaneous displacement reactions of boronic acids

Many other examples can be found of boronic acid chemistry involving displacement of boron:

Reaction of arylboronic acids with copper(II) chloride or bromide to give the corresponding aryl halide with loss of boron has long been known.²²⁹ More recently, ipsobromination or -iodination of arylboronic acids with NBS or NIS in acetonitrile has been described.²³⁰ The reaction has been further developed utilizing 1,3-dibromo-5,5dimethylhydantoin and the dichloro analogue, providing convenient access to "abnormally" substituted bromo and chloro aromatics.²³¹ A catalytic amount of sodium methoxide was found to minimize side reactions, affording high yields of the required products. Potassium aryltrifluoroborates salts undergo ipso-iodinations using a combination of sodium iodide and Chloramine-T.232 Arylboronic acids have been converted, via the Nmethyldiethanolamine cyclic esters, to aryl fluorides using cesium fluoroxysulfate.²³³ Widdowson and co-workers²³⁴ have demonstrated the facile conversion of arylboronic acids to diaryliodonium triflates in the presence of PhI(OAc)₂/TfOH. Diaryl and heteroaryl (phenyl)iodonium tosylates can also be readily prepared from the corresponding boronic acid and Koser's reagent [PhI(OH)OTs]. This approach is preferable to the previous route via toxic stannanes. The displacement reaction of iodonium salts with fluoride ion provides a mild synthesis of aryl fluorides, including ¹⁸F labelled derivatives, which can be employed in positron emission tomography.

Vinylboronic acids can be converted to vinyl halides, with retention of double-bond configuration, using NCS, NBS or NIS.²³⁵ Vinyl and alkynyl trifluoroborates can be iodinated with sodium iodide/ Chloramine-T.²³⁶ Fluorination of vinylboronic acids occurs with 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) [Selectfluor®; **L17003**], but better results have been obtained starting from the corresponding potassium alkenyl trifluoroborates.²³⁷

Arylboronic acids undergo *ipso*-nitration with ammonium nitrate/ trifluoroacetic anhydride²³⁸ (Crivello's reagent: *in situ* trifluoroacetyl nitrate), or, more selectively, with a nitrate salt and TMS chloride,²³⁹ to give the boron-free aryl nitro compound, in contrast to conventional nitration which tends to give mainly the *m*-nitrobenzeneboronic acid.

With lead(IV) acetate, catalyzed by mercury(II) acetate, arylboronic acids are transmetallated to the aryllead triacetates, used *in situ* for electrophilic arylation, for example of active methylene compounds,²⁴⁰ 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.²⁴¹

Transmetallation of an arylboronic acid to an arylzinc species *in situ* has been achieved with diethyzinc.²⁴²

4. Preparative routes to boronic acids and esters

Boronylation of organometallics

Boronic acids are most often prepared from the corresponding organomagnesium or organolithium reagent and a trialkyl borate, followed by acidic hydrolysis of the resulting dialkyl boronate. The original conditions of Kotinsky and Melamed,⁵ addition of trimethyl borate to an ether solution of phenylmagnesium bromide, were by Gilman,²⁴³ who claimed yields of repeated benzeneboronic acid as high as 86%. However, most other workers were unable to reproduce this, and often obtained only very low yields, mainly due to the formation of large amounts of diphenylborinic acid. Johnson subsequently used a reverse-addition technique, adding the ethereal phenyl Grignard to trimethyl borate at -12°C (ca 30% vield),^{6a} or to tributyl borate at -70 to -75°C, (50-60%) vield).^{6b} Washburn later undertook a more detailed study of the synthesis of benzeneboronic acid from phenylmagnesium bromide and trimethyl borate,⁷ confirming that the yield of boronic acid is much improved by carrying out the boronylation of the Grignard at low temperatures (generally below -50° C). As the reaction temperature approaches ambient, increasing amounts of the ester of diphenylborinic acid are formed by further attack of the Grignard on the intermediate dimethyl benzeneboronate. He also demonstrated that simultaneous addition of the borate and Grignard to a vessel containing ether stirred at low temperature tended to minimize formation of diphenylborinic acid. In a second key paper²⁴⁴ Washburn discussed further experimental and mechanistic aspects of the reaction of phenyl- and substituted phenylmagnesium halides with trialkyl borates. His optimal procedure for benzeneboronic acid is detailed in *Organic Syntheses.*²⁴⁵ The results of other workers indicate that the use of triisopropyl borate²⁴⁶ or isopropyl pinacol borate (2-isopropoxy-4,4,5,5-tetramethyl-1,3,2dioxaborolane)²⁴⁷ [L17278] instead of trimethyl borate may have advantages in particular cases.

Snieckus has developed directed metallation²⁴⁸ routes to boronic acids. His initial publication²⁴⁹ described *ortho*lithiation of N,N-dialkyl benzamides, followed by boronylation with trimethyl borate. In a subsequent paper,²⁵⁰ better results for a range of substrates were claimed by an *ortho*-lithiation-silylation-*ipso*-borodesilylation²⁵¹ sequence with boron tribromide (Scheme 27).



Other workers²⁵² have utilized *ipso*-borodesilylation with either BBr₃ or BCl₃ in the formation of boronic acids and esters. Neopentyl esters have been *ortho*-lithiated with LDA and reacted with triisopropyl borate *in situ* to give good yields of arylboronic acids, isolated via the diethanolamine esters.²⁵³

Hydroboration methods

Hydroboration of alkenes with catecholborane to give alkylboronic esters²⁵⁴ usually requires forcing conditions. Improved results can be obtained by catalysis with LiBH₄,²⁵⁵ or with $Rh(I)^{256,257}$ or $Ir(I)^{257}$ complexes. Hydroboration of alkynes with catecholborane occurs somewhat more readily, affording alkenylboronic esters, often regio- and stereoselectively.254 Nevertheless, catalysis with, for example Rh(I),²⁵⁶ Ni(II)²⁵⁸ or Pd(II)²⁵⁹ complexes, may permit reaction under milder conditions, with greater selectivity. Alkenes can undergo Rh(I)catalyzed hydroboration with pinacolborane [L17558], to give the alkylboronate,²⁶⁰ or, with a phosphine-free Rh(I) complex, the alkenylboronate²⁶¹ by dehydrogenative boronylation. Vinylboronates are also formed from alkynes and pinacolborane (2 eq.) under mild conditions.²⁶² High yields are obtained with 1 eq. of the reagent in the presence of Rh or Ni catalysts²⁶⁰ (Scheme 28).



Transition metal catalyzed B-C coupling

As well as the need for low temperatures, the use of reactive organometallics, RMgX or RLi, as boronic acid precursors is generally limited to substrates lacking functional groups which could react with the organometallic species. A major advance in the synthesis of arylboronic esters came with the publication by Miyaura²⁶³ of the palladium-catalyzed coupling of aryl halides with diboron esters, especially bis(pinacolato)diboron [L16088], by cleavage of the B-B bond, enabling access to boronic acid derivatives without protection of functionalities such as ester, ketone, cyano or nitro groups (Scheme 29).



Aryl triflates are also converted to pinacol arylboronates under similar conditions,²⁶⁴ as are arenediazonium salts.²⁶⁵ The reaction has been adapted to boronylation of polymersupported aryl iodides, allowing *in situ* coupling to give unsymmetrical biaryls.²⁶⁶ Microwave irradiation has been found to offer dramatic rate enhancements and improved yields in the formation of otherwise difficult electron-rich boronates.²⁶⁷ In a further detailed examination of the boronylation reaction, Zhang has shown that ligandless Pd(OAc)₂ is a highly effective catalyst with advantages of lower cost, ease of work-up, and the ability to couple the boronate *in situ* with a suitable electrophile.²⁶⁸

The preparation of pinacolyl arylboronates by palladiumcatalyzed coupling of aryl iodides, triflates or, less readily, bromides with pinacolborane has been described by Masuda.²⁶⁹ In this method, the arene, formed by reduction of the aryl halide, was often found as a significant byproduct. This method has been adapted to a one-pot conversion of aryl bromides to unsymmetrical biaryls via the pinacol boronates.²⁷⁰ Aryl iodides can also be converted to the pinacol boronates in accepatble yield in a Pd-free, CuI catalyzed reaction, along with a strong base, preferably NaH.²⁷¹ Masuda has reported the Pt(0)catalyzed regio- and stereoselective synthesis of allylboronates from allyl halides and pinacolborane.²⁷²

Boronylation with bis(pinacolato)diboron, catalyzed by Pd complexes, has been extended to alkenyl halides and triflates,^{273,274} benzyl halides^{275,276} and allyl acetates.²⁷⁷ Miyaura has also reported coupling with allyl halides, mediated by copper(I) chloride.²⁷⁸

The reaction with alkynes, catalyzed by Pt(0) affords *cis*bis-boryl alkenes.^{279,280} Cu(I)-mediated 1,2-addition to terminal alkynes has also been described.²⁷⁸ Stereoselective Pt(0)-catalyzed addition to 1,3-dienes gives 1,4-bis-boryl 2-alkenes,²⁸¹ (Scheme 30).



Scheme 30

A detailed discussion of diboration reactions with diboron derivatives has been published by Marder and Norman.²⁸²

Marder and Norman first reported 1,4-addition of bis(pinacolato)diboron to enones, catalyzed by a Pt(0) complex.²⁸³ Other authors have described a variety

conditions for this type of reaction, promoted by Pt(0),²⁸⁴ $Cu(I)^{278,285}$ or $Rh(I)^{286}$ systems (Scheme 31).



Alkylbenzenes can be boronylated on the side-chain with either bis(pinacolato)diboron or pinacolborane, in the presence of Pd/C catalyst, providing a direct route to benzylboronates.²⁸⁷ Direct boronylation of aromatic rings has been achieved with pinacolborane in the presence of a rhodium complex,²⁸⁸ or with bis(pinacolato)diboron with an iridium(I) complex (Scheme 32).²⁸⁹



Vinylboronate reactions

Vinylboronic acid polymerizes too readily for convenient isolation. The pinacol ester [**L19811**], on the other hand, is stable enough to be stored, and can undergo a variety of useful reactions. Whiting has shown that palladium-catalyzed cross-coupling with halides can take place in either Suzuki (loss of boron) or Heck (retention of boron) modes.¹²⁶ However, use of the more nucleophilic vinyltrifluoroborate salt [**L17970**] in the Suzuki coupling may be preferable (see Section 3).¹²⁵ With the pinacol ester, Whiting has developed reaction conditions which favor the Heck coupling, providing a route to styryl and other 2-substituted vinylboronates (Scheme 33).^{290,291}



Scheme 33

Homologated alkenylboronates are available via ruthenium-catalyzed cross-metathesis with terminal alkenes.²⁹² The olefinic double bond of a vinylboronate can also undergo cycloaddition reactions with 1,3-dipoles, such as isoxazolines from nitrile oxides,^{293,294} and various free-radical reactions,²⁹⁵⁻²⁹⁷ leading to substituted boronates.

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The Alfa Aesar range of boronics

Arylboronic acids

3-Acetamidok	benzeneboronic acid, 98%		Benzeneboro	nic acid, polymer-supported	, 2.6-
B23833 [78887-39-5]	HN CH ₃	1g 5g 25g	3.2 mmol/g L19459	B(OH) ₂	1g 5g 25g
3-Acetylbenz	eneboronic acid. 97%		1,3-Benzened	liboronic acid, 97%	
B23478 [204841-19-0]	B(OH) ₂ OCH ₃	1g 5g 25g	B24903 [4612-28-6]	B(OH) ₂ B(OH) ₂	1g 5g 25g
4 Acotylbonz	anabaranic acid 08+%		1,4-Benzened	liboronic acid, 96%	
B23234 [149104-90-5]	CH ₃ CH ₃ B(OH) ₂	1g 5g 25g	B24064 [4612-26-4]	(HO) ₂ B	1g 5g 25g
	ö		2-Benzyloxyb	enzeneboronic acid, 96%	
2-Aminobenz L18069 [5570-18-3]	eneboronic acid, 96%	100mg 1g 5g	L20100 [190661-29-1]	B(OH) ₂	1g 5g
			3-Benzyloxyb	enzeneboronic acid, 98+%	
3-Aminobenz A18189 [206658-89-1]	eneboronic acid monohyd	rate , 97% 1g 5g 25g	L17474 [156682-54-1]	B(OH) ₂	1g 5g
	NH ₂		4-Benzyloxyb	enzeneboronic acid, 97%	
3-Aminobenz	eneboronic acid hemisulfa	ite , 98+%	B24351	B(OH) ₂	250mg
A17240 [66472-86-4]	B(OH) ₂	1g 5g 25g	[146631-00-7]		1g 5g
	$NH_2 . {}^{1}/_2 H_2SO_4$		4-Benzyloxy-2	2-fluorobenzeneboronic acid	, 96%
3-Amino-4-me L17695 [22237-12-3]	ethylbenzeneboronic acid, CH ₃ CH ₃ B(OH) ₂	98% 1g 5g	L18521 [166744-78-1]	F F	250mg 1g 5g
	ŃH ₂		4-Benzyloxy-	3-fluorobenzeneboronic acid	, 98%
9-Anthracene L19630 [100622-34-2]	B(OH) ₂	100mg 500mg	L18520 [133057-83-7] 2-Binbenylbo	F B(UH) ₂	250mg 1g
Benzeneboro	nic acid, 98+%		1 17547	(HO) ₂ B	10
A14257 [98-80-6]	B(OH) ₂	10g 50g 250g	[4688-76-0]		'9

3-Biphenylk	oronic acid, 98%		4-Bromo-2-flu	orobenzeneboronic acid	, 95%
L17552 [5122-95-2]	B(OH) ₂	1g 5g	L17468 [216393-64-5]	Br F	250mg 1g
4-Biphenylb	oronic acid, 98+%		4-Bromo-3-flu	orobenzeneboronic acid	, 98+%
B23703 [156682-54-1]	B(OH)2	1g 5g 25g	L18514 [374790-97-3]	Br F B(OH) ₂	1g 5g
4,4'-Biphen	yldiboronic acid, 97%		3-(Bromometh	hvl)benzeneboronic acid	95%
L13328 [4151-80-8]	(HO) ₂ B	1g 5g	L20102 [51323-43-4]	B(OH) ₂	1g 5g 25g
2,4-Bis(trifl 97%	ioromethyl)benzeneboronic a	acid,		Br	
L18161 [153254-09-2]	CF3 CF3 B(OH)2	1g 5g	4-(Bromometh L19953 [68162-47-04]	hyl)benzeneboronic acid, Br	94% 1g 5g
2,6-Bis(triflu	oromethyl)benzeneboronic	acid,			
97%			4- <i>n</i> -Butylbenz	ceneboronic acid, 98%	4.
L19952	B(OH) ₂ CF ₃	250mg 1g 5g	L15584 [145240-28-4]	CH ₃ B(OH) ₂	1g 5g
2 E Dia/trifl	oromothyllbonzonohoronia	aaid	B24408	B(OH)2	1a
3, 5-DIS (IIIII) 98%	loromethyl)benzeneborometa	aciu,	[123324-71-0]	CH.	5g
A11373 [73852-19-4]	CF ₃ CF ₃ CF ₃	1g 5g 25g	5-tert-Butyl-2-	-methoxybenzeneboronic	acid
	Ŭ		L20415	CH ₃ CH ₃	250mg
2-Bromober	nzeneboronic acid, 98%		[128733-85-7]	CH ₃ B(OH) ₂	ig
L18581 [244205-40-1]	B(OH) ₂ Br	1g 5g	2 Carboxybor	OCH ₃	
0 Durana har			L 16301		250mg
L16354 [89598-96-9]		1g 5g 25g	[149105-19-1]	ОН	1g 5g
	Br		3-Carboxyben	zeneboronic acid, 98%	
4-Bromober	zeneboronic acid, 98+%		B25315	B(OH) ₂	1g
L01565 [5467-74-3]	Br B(OH) ₂	1g 5g 25g	[25487-66-5]	ООН	bg
4-Bromo-2,	B-difluorobenzeneboronic aci	d	4-Carboxyben	zeneboronic acid, 95%	
L18516 [374790-99-5]	Br F F	250mg 1g	B20954 [14047-29-1]	HO O	1g 5g 25g

4-(2-Carboxy	ethyl)benzeneboronic acid,	97%	2-Chloro-4-(tr	ifluoromethyl)benzeneboro	onic
L17485 [166316-48-9]	HO B(OH) ₂	1g 5g	acid, 96% L20103 [254993-59-4]	CF ₃ CF ₃ B(OH) ₂ Cl	1g 5g
2-(2-Carboxy	vinyl)benzeneboronic acid,	98%	2-Chloro-5-(tr	ifluoromethyl)benzeneboro	onic
L16368 [374105-86-9]	B(OH) ₂ OH	50mg 250mg	acid, 96% L20104 [182344-18-9]	CF ₃ CI	1g 5g
3-(2-Carboxy	vinyl)benzeneboronic acid,	97%	4-Chloro-3-(tr	ifluoromethyl)benzeneboro	onic
L16369 [216144-91-1]	HO B(OH) ₂	250mg 1g	acid, 96% L20105 [176976-42-4]	CI CF ₂ B(OH) ₂	1g 5g
4-(2-Carboxy	vinyl)benzeneboronic acid,	95%		U U	
L15586	B(OH) ₂	250mg	2-Cyanobenze	eneboronic acid, 98%	
[151169-68-5]	HO	1g 5g	L19676 [138642-62-3]	B(OH) ₂ CN	1g 5g
2-Chlorobenz	zeneboronic acid, 97%		3-Cyanobenze	eneboronic acid, 98+%	
B23324 [3900-89-8]	B(OH) ₂	1g 5g 25g	L19635 [150255-96-2]	B(OH) ₂	250mg 1g 5g
3-Chiorobenz			4-Cvanobenze	eneboronic acid. 98%	
B24444 [63503-60-6]	CI B(OH) ₂	1g 5g 25g	L18007 [126747-14-6]	NC B(OH) ₂	1g 5g
4-Chlorobenz	zeneboronic acid, 98+%		4-(Cyanometh	yl)benzeneboronic acid, 98	3%
A15657 [1679-18-1]	CI B(OH)2	1g 5g 25g	L19955 [91983-26-5]	NC B(OH)2	1g 5g
3-Chloro-4-flu	uorobenzeneboronic acid, 9	9%	4-Cyclohexylk	penzeneboronic acid, 98%	
B22755 [144432-85-9]	F B(OH) ₂	1g 5g 25g	L18076 [374538-04-2]	B(OH)2	250mg 1g 5g
	CI		3,5-Dibromob	enzeneboronic acid, 97%	
4-Chloro-2-m B23688 [209919-30-2]	ethylbenzeneboronic acid, s CI	98% 1g 5g	B23863 [117695-55-3]	Br Br	1g 5g 25g
4-Chloro-3-m	ethylbenzeneboronic acid,	98%	2,3-Dichlorob	enzeneboronic acid, 98+%	
B23179 [161950-10-3]	CI CH ₃ B(OH) ₂	1g 5g	B22781 [151169-74-3]	CI CI	1g 5g 25g

2,4-Dichlorob	enzeneboronic acid, 98+%		3,5-Difluoro-2-	methoxybenzeneboronic ac	id,
L01563	B(OH) ₂	1g	97%	5 5/010	
[68716-47-2]		5g	L19773	F B(OH) ₂	250mg
				OCH3	5g
2,5-Dichlorob	enzeneboronic acid, 98+%			F	
B22984	CI B(OH)2	1g	2.2 Dimetheve	henzeneberenie seid 000/	
[135145-90-3]		5g	2,3-Dimethoxy		4
	CI		B24125	B(OH) ₂	1g 5a
3.4-Dichlorob	enzeneboronic acid. 97%		[40972-00-9]	OCH3	25g
B24292	→ B(OH) ₂	1α		OCH3	
[151169-75-4]		5g			
	CI	25g	2,4-Dimethoxy	benzeneboronic acid, 98%	
	ĊI		B24374	B(OH) ₂	1g 5g
3,5-Dichlorob	enzeneboronic acid, 98+%		[133730-34-4]	CH ₃ O OCH ₃	25g
B22765	CIB(OH) ₂	1g			
[67492-50-6]	l I	5g	2,5-Dimethoxy	benzeneboronic acid, 98%	
		25g	B24571	CH ₃ O B(OH) ₂	1g
	CI		[107099-99-0]		5g 25g
2,3-Difluorob	enzeneboronic acid, 98%				209
L18012	B(OH) ₂	1g	2,6-Dimethoxy	benzeneboronic acid, 98%	
[121219-16-7]		5g	B24305	OCH ₃	1g
	Ť.	zəy	[23112-96-1]	B(OH) ₂	5g
	F				25g
2,4-Difluorob	enzeneboronic acid, 97%			 ✓ OCH₃ 	
B23821	B(OH) ₂	1g	3,4-Dimethoxy	denzeneboronic acid, 98%	
[144025-03-6]		5g 25g	B24240	B(OH)2	1g 5g
	F ~ F	209	[122775-35-3]	CH ₃ O	25g
2,5-Difluorob	enzeneboronic acid, 96%			OCH3	
B24113	FB(OH) ₂	1g	2.2 Dimethylk	ennensherenis said 000/	
[193353-34-3]		5g	2,3-Dimethylbo		4
	→ F	259	BZ394Z [183158-34-1]		1g 5g
2,6-Difluorob	enzeneboronic acid, 98%			CH3	25g
B22805	Ę	1g		\dot{CH}_3	
[162101-25-9]	B(OH) ₂	5g	2.4 Dimothylb	onzonoboronic acid 07%	
		25g	2,4-Dimetryio		10
	~ F		D23070 [55499-44-0]		5g
3,4-Difluorob	enzeneboronic acid, 98%		[00.000.11.0]	CH3 CH3	25g
B22799	B(OH) ₂	1g			
[168267-41-2]		5g	2,5-Dimethylbo	enzeneboronic acid, 95%	
	F´ \	259	B23740	CH ₃ B(OH) ₂	1g 5g
	F		[85199-06-0]	CH3	25g
3,5-Difluorob	enzeneboronic acid, 98+%			- 0	-
L17425	FB(OH) ₂	1g	2,6-Dimethylbe	enzeneboronic acid, 97%	
[156545-07-2]		5g	B24613	CH ₃	1g
	Ĭ F		[100379-00-8]	B(OH) ₂	5g
	,				209
				013	

3,4-Dimethylb	enzeneboronic acid, 98+%		3-Fluorobenze	eneboronic acid, 97%	
L17461 [55499-43-9]	CH ₃ CH ₃ CH ₃ CH ₃	1g 5g	B21247 [768-35-4]	F B(OH) ₂	1g 5g 25g
3,5-Dimethylb	enzeneboronic acid, 98%		4-Fluorobenze	eneboronic acid, 98%	
B23434 [172975-69-8]	CH ₃ CH ₃ CH ₃ B(OH) ₂	1g 5g 25g	A15991 [1765-93-1]	F B(OH) ₂	1g 5g 25g
4-(Ethanesulfo	onvl)benzeneboronic acid	98+%	2-Fluorobiphe	nyl-4-boronic acid, 97%	
L17814 [352530-24-6]	CH ₃ O ^S O ^{B(OH)₂}	250mg 1g	L15634 [178305-99-2]	B(OH) ₂	1g 5g
2-Ethoxybenz	eneboronic acid 98%		3-Fluoro-4-for	mylbenzeneboronic acid, 9	8%
B23644 [213211-69-9		1g 5g 25g	L17851 [248270-25-9]	H F B(OH)2	1g
3-Ethoxybenz	eneboronic acid		4-Fluoro-3-for	mylbenzeneboronic acid, 9	8+%
B24485 [90555-66-1]	B(OH) ₂ O_CH ₃	1g 5g 25g	L17808 [374538-01-9]	F H O	250mg 1g
4-Ethoxybenze	eneboronic acid, 98%		2-Fluoro-3-me	thoxybenzeneboronic acid	, 97%
L23683 [22237-13-4]	CH ₃ O	1g 5g 25g	L19655 [352303-67-4]	F OCH ₃	1g 5g
2-Ethylbenzen	eboronic acid, 98+%		3 Eluoro 4 ma	thoxybonzonoboronic acid	08+%
L17719 [90002-36-1]	CH ₃	1g 5g	L19818 [149507-26-6]		, 90+ 78 1g 5g
4-Ethylbenzen	eboronic acid, 97%			F	
B24656 [63139-21-9]	CH ₃ B(OH) ₂	1g 5g 25g	3-Fluoro-4-me	thylbenzeneboronic acid, 9	98% 1g
2 4 (Etherland		070/	[168267-99-0]		5g
3,4-(Ethylened L20296 [164014-95-3]		1, 97% 1g 5g	4 Elucare 0 ma	CH ₃ F	25g
	0		4-Fluoro-2-me		18%
4-(Ethylthio)be	enzeneboronic acid, 98%		B24117 [139911-29-8]	B(OH)2	1g 5g
L17623 [145349-76-4]	CH ₃ SB(OH) ₂	1g 5g	4 Elucare 2 ma	F CH ₃	25g
			4-FIUORO-3-Me	enyipenzeneboronic acid, 9	10%
2-Fluorobenze B23103 [1993-03-9]	B(OH) ₂	1g 5g 25g	L18/53 [139911-27-6]	F CH ₃	1g 5g

5-Fluoro-2-m	nethylbenzeneboronic acid, s	99%	3-(Hydroxyme	ethyl)benzeneboronic ac	d , 94%
L19819 [163517-62-2]	F B(OH) ₂ CH ₃	1g 5g	L15193 [87199-15-3]	B(OH) ₂ OH	1g 5g
2-Formylben	izeneboronic acid, 97%		A (11)	4. N	
B25434	B(OH) ₂	1g 5g	4-(Hydroxyme	etnyi)benzeneboronic aci	id , 98%
[40138-16-7]	U H	°9	L15194 [59016-93-2]	HO B(OH)2	1g 5g 25g
3-Formylben	zeneboronic acid, 98%		2-Isopropylbe	enzeneboronic acid, 97%	
B25437 [87199-16-4]	B(OH) ₂	1g 5g 25g	L20110 [89787-12-2]	B(OH) ₂ CH ₃ CH ₃	250mg 1g 5g
4-Formylben	zeneboronic acid, 97%		3-Isopropylbe	enzeneboronic acid, 99%	
B25199 [87199-17-5]	H O O B(OH) ₂	1g 5g 25g	L15530 [216019-28-2]	CH ₃ CH ₃ B(OH) ₂	250mg 1g 5g
3-Formyl-4-r	nethoxybenzeneboronic aci	d , 98%	4-Isopropylbe	enzeneboronic acid, 98+%	6
L17850 [121124-97-8]	CH ₃ O H	1g 5g	L17459 [16152-51-5]	CH ₃ CH ₃ CH ₃	1g 5g
5-Formyl-2-r	nethoxybenzeneboronic aci	d , 98%	5-IsopropyI-2-	-methoxybenzeneboroni	c acid,
L19059		250mg	98+%		
[127972-02-5]	H B(OH) ₂ OCH ₃	1g 5g	L17460 [216393-63-4]	CH ₃ CH ₃ B(OH) ₂ OCH ₃	1g 5g
2-Hydroxybe	enzeneboronic acid, 97%		A (Mothanosu	lfinyl)bonzonoboronic ac	id 0.8%
L19400	B(OH) ₂	1g	4-(International		100mg
[89466-08-0]	ОН	5g	[166386-48-7]	CH ₃ S	1g
3-Hydroxybe	enzeneboronic acid, 97%			0	
L19061	B(OH) ₂	1g	4-(Methanesu	lfonyl)benzeneboronic a	cid , 98%
[87199-18-6]	OH OH	5g	L17720 [149104-88-1]	CH3 B(OH)2 O S O	250mg 1g 5g
		10	2-Methoxyber	zeneboronic acid 97%	
[71597-85-8]	HO HO PARABADORONIC acid	5g	B21071 [5720-06-9]	B(OH) ₂ OCH ₃	1g 5g 25g
hemiester. 9	8+%		3-Methoxyber	zeneboronic acid 97%	
L15192 [5735-41-1]	ОН	250mg 1g	B24412 [10365-98-7]	B(OH) ₂ OCH ₃	1g 5g 25g

4-Methoxybe	nzeneboronic acid, 98%		4-Methyl-3-n	itrobenzeneboronic acid, 9	8%
A14462 [5720-07-0]	CH ₃ O	1g 5g 25g	L17052 [80500-27-2]	CH ₃ NO ₂ B(OH) ₂	1g 5g
2-(Methoxyca	arbonyl)benzeneboronic a	cid , 97%			
L17958	B(OH) ₂	250mg	2-(Methylthic	o)benzeneboronic acid, 98+	+%
[374538-03-1]	OCH3	1g 5g	L1/456 [168618-42-6]	SCH3	1g 5g
4-Methoxy-3 ,	5-dimethylbenzeneboronio	c acid,	3-(Methylthic	o)benzeneboronic acid, 97%	%
L19820 [301699-39-8]	CH ₃ CH ₃ O CH ₃ O CH ₃	1g 5g	L20250 [128312-11-8]	SCH ₃	250mg 1g 5g
A Matheway 9		id 000/	4-(Methylthic	o)benzeneboronic acid, 97%	%
4-methoxy-2-		10, 98%	B23454	B(OH) ₂	1g 5a
[208399-66-0]	CH ₃ O CH ₃	5g	[96340-31-1]		25g
4-Methoxy-3-	methylbenzeneboronic ac	id, 98+%	R21219		10
L19821 [175883-62-2]	CH ₃ O CH ₂ B(OH) ₂	1g 5g	[13922-41-3]		5g 25g
	0113		2-Naphthale	neboronic acid, 97%	
6-Methoxy-2-	naphthaleneboronic acid,	95%	B24157	B(OH) ₂	1g
L19060 [156641-98-4]	CH ₃ O	1g 5g	[32316-92-0]		25g
			2-Nitrobenze		10
2-Methylbenz	zeneboronic acid, 98%		[5570-19-4]		5g
B23154 [16419-60-6]	B(OH) ₂	1g 5g 25g		NO ₂	
	013	0	3-Nitrobenze	eneboronic acid, 98%	4
3-Methylbenz	zeneboronic acid, 97%		[13331-27-6]		1g 5g
B23025 [17933-03-8]	B(OH) ₂	1g 5g 25g		NO ₂	25g
	ĊH ₃		<i>trans</i> -4-(β-Ni	trovinyl)benzeneboronic ad	cid , 97%
4-Methylbenz	zeneboronic acid, 99%		L17004	B(OH)2	250mg 1g
A13347	B(OH) ₂	1g 5g	[210004 04 0]	O ₂ N	0
	CH ₃	25g	4-n-Nonylbe	nzeneboronic acid, 98+%	
3 4-(Mothylor	adioxy)benzenehoronic a	cid 08%	L17753		^{B(OH)} ² 1g
B24217		1a	[256383-45-6]	CH ₃	J
[94839-07-3]		5g			

2,3,4,5,6-Pent	afluorobenzeneboronic aci	d , 97%	2-(Trifluoromet	thoxy)benzeneboronic a	cid , 98%
B22922 [1582-24-7]	F F F F	5g 25g	L19774 [175676-65-0]	B(OH) ₂ OCF ₃	250mg 1g
4-n-Pentylber	nzeneboronic acid, 97%		3-(Trifluoromet	thoxy)benzeneboronic a	cid , 98%
L18011 [121219-12-3]	CH ₃ B(OH) ₂	250mg 1g 5g	L19775 [179113-90-7]	OCF ₃ B(OH) ₂	1g 5g
2,3,4,5-Tetraf	luorobenzeneboronic acid,	98%	4-(Trifluoromet	thoxy)benzeneboronic a	cid , 98%
L19824 [179923-32-1]	F F F	250mg 1g	B23233 [139301-27-2]	CF ₃ O ^{B(OH)} 2	1g 5g 25g
2,3,4,6-Tetraf	luorobenzeneboronic acid		2-(Trifluoromet	thyl)benzeneboronic aci	d , 97%
L19825	F F F F	250mg 1g	B24343 [1423-27-4] 3-(Trifluoromet	CF ₃	1g 5g 25g d 98%
0 0 5 6 Tatuat	luana hannana hanania aaid d	000/	B21661	B(OH) ₂	1a
2,3,5,6-Tetraf		99% 1g	[1423-26-3]	CF3	5g 25g
	F F		4-(Trifluoromet	thyl)benzeneboronic aci	d , 98%
4-(Tetrahydro acid	-2H-pyran-2-yloxy)benzene	boronic	B22374 [128796-39-4]	CF3	1g 5g 25g
H5U445		250mg 1g			0.000
[::==::::=]			2,4,6-1 riisopro		, 98%
2,3,5-Trichlor	obenzeneboronic acid, 98%	•	B22891		1g 5g
L17511 [212779-19-6]	CI CI CI	1g 5g	[1040403050]	CH ₃ CH ₃ CH ₃ CH ₃ CH ₃ CH ₃	25g
2,3,4-Trifluoro	obenzeneboronic acid		2,3,4-Trimetho	xybenzeneboronic acid,	98%
L19827 [226396-32-3]	F F F	250mg 1g	L19838 [118062-05-8]	CH ₃ O OCH ₃	1g 5g
0 / 0 7 ·//			2,4,6-Trimetho	xybenzeneboronic acid,	98%
L19402 [182482-25-3]	F F F F F	1g 5g	L19837 [135159-25-0]	CH ₃ O ^{OCH₃} B(OH) ₂ CH ₃ O ^{OCH₃}	1g 5g
3 / 5 Trifluor	henzenehoronic soid 070/		3,4,5-Trimetho	xybenzeneboronic acid,	98+%
5,4,5-1111000 L18519 [143418-49-9]	F = F = F = F	250mg 1g	L15191 [182163-96-8]	CH ₃ O CH ₃ O OCH ₃	1g 5g



2,4,6-Trimethylb glycol ester, 99%	enzeneboronic acid neo ⁄₀	pentyl	Heteroary	l boronic acids	
L17232	,CH₃	1g	5-Acetvlthionh	nene-2-horonic acid 98%	
[214360-78-8] C	CH ₃ CH ₃ CH ₃ CH ₃	5g	L15221 [206551-43-1]	CH ₃ O B(OH) ₂	1g 5g 25g
			Benzo[b]furan	1-2-boronic acid, 98%	
			B23676		1g
Aryltrifluo	roborate salts		[98437-24-2]	B(OH) ₂	5g 25g
Potassium 3-br	omophenvltrifluorobora	te . 97%	Benzo[b]thiop	hene-2-boronic acid, 98%	/ 0
L17966 [374564-34-8]	BF ₃ ⁺ K [−]	1g 5g	B22835 [98437-23-1]	B(OH) ₂	1g 5g 25g
	 Br		1-Boc-indole-2	2-boronic acid, 95%	
Potassium 4-br	omophenyltrifluorobora	te , 97%	L18009 [213318-44-6]	B(OH)2	250mg 1g
L 17967 [374564-35-9]	BF ₃ ⁺ K [−]	1g 5g		CH ₃ CH ₃	5g
Potassium 4-flu	uorophenyltrifluoroborat	e , 98%	5-Bromo-2-flu	oropyridine-3-boronic ac	id , 98%
L 17655 [192863-35-7]	F BF3 ⁺ K [−]	1g 5g	L19915 [501435-91-2]	Br N F	250mg 1g 5g
Potassium 2-fo	rmylphenyltrifluoroborat	te	5-Bromopyrid	ine-3-boronic acid, 95%	
L17968 [192863-39-1]	BF ₃ ⁺ K [−] H	1g	L20084 [452972-09-7]	Br B(OH) ₂	250mg 1g 5g
D. 4	-		6-Bromopyrid	ine-3-boronic acid, 95%	
Potassium 4-fo L17969 [374564-36-0]	rmyipnenyitrifiuoroborat	1g 5g	L20085 [223463-14-7]	Br N B(OH)2	250mg 1g 5g
	Ň		2-Bromoquino	oline-3-boronic acid, 97%	
Dotoooium 4 m	othy link ony litrifly or ohoro	to 089/	L20327	B(OH) ₂	250mg
L17604		1g		N Br	1g 5g
[210434-02-1]	CH ₃	- 5	2-Chloropyrid	ine-3-boronic acid, 96%	
			L20303	B(OH) ₂	1g
Potassium 2-ph	nenyethyltrifluoroborate,	, 98%	[381248-04-0]	L CI	Jy
H25930 [329976-74-1]	BF3 ⁺ K ⁻	1g 5g	6-Chloropyrid	ine-3-boronic acid, 96%	
			L20388	B(OH) ₂	250mg
Potassium phe L17568	nyltrifluoroborate, 98%	1g	[444120-91-6]		1g 5g
[153766-81-5]		5g	2-Chloroquino	oline-3-boronic acid, 97%	
	*				

5-Chlorothiop	hene-2-boronic acid, 97%		5-Formyl-4-me
B23193 [162607-18-3]	CI S B(OH) ₂	1g 5g 25g	H25947 [352530-25-7]
5-Cyanothioph	nene-2-boronic acid, 98%		
L18523 [305832-67-1]	NC S B(OH)2	250mg 1g	2-Formylthiopl L15195
Dibenzofuran-	4-boronic acid, 98+%		[4347-31-3]
L19830 [100124-06-9]	B(OH)2	1g 5g	3-Formylthiopl L15196
Dibenzothioph	ene-4-boronic acid		[17303-83-2]
L19831 [108847-20-7]	S S S	1g 5g	-
	B(OH) ₂		Furan-2-boron
2,6-Dimethoxy	pyridine-3-boronic acid, 9	5%	B23842
L20389	B(OH) ₂	250mg	[13331-23-2]
[444120-91-6]	CH ₃ O N OCH ₃	1g 5g	Furan-3-boron
6 Ethoxyovridi	ing 2 horonic acid 0.8%		L19834
		250mg	[00002-70-0]
[612845-44-0]	CH ₃ ON	1g 5g	Isoquinoline-4
2-Fluoropyridi	ne-3-boronic acid, 97%		[192182-56-2]
L20108 [174669-73-9]	B(OH) ₂	1g 5g	
a F i	e i i i i o o o o i		2-Methoxypyri
6-Fluoropyridi L20387 [351019-18-6]	F N B(OH) ₂	250mg 1g 5g	L20094 [163105-90-6]
			6-Methoxypyri
2-Fluoroquino	line-3-boronic acid, 97%		L20087
L20341 [745784-10-5]	N F	250mg 1g 5g	[163105-89-3]
2 Earmulfuran	2 horonic soid 070/		5-weurynmopr
		10	D23130 [162607-20-7]
[27339-38-4]	B(OH) ₂	1g 5g	Pyridine-3-bor L15040 [1692-25-7]
5-Formylfuran		055	
L17920 [27329-70-0]	H B(OH) ₂	250mg 1g 5g	Pyridine-4-bor L15179 [1692-15-5]

5-Formyl-4-meth	ylthiophene-2-boronic	acid
H25947 352530-25-7]	H O B(OH) ₂	
2-Formylthiophe	ne-3-boronic acid, 97%	/ 0
_15195 4347-31-3]	B(OH) ₂ S H	1g 5g
3-Formylthiophe	ne-2-boronic acid, 97%	/ 0
_15196 17303-83-2]	H B(OH) ₂	1g 5g
uran-2-boronic	acid, 97%	
323842 13331-23-2]	B(OH)2	1g 5g 25g
uran-3-boronic	acid, 97%	
_19834 55552-70-0]	B(OH) ₂	1g 5g
soquinoline-4-b	oronic acid, 97%	
_20430 192182-56-2]	B(OH) ₂	250mg 1g 5g
2-Methoxypyridi	ne-3-boronic acid, 98%)
_20094 163105-90-6]	B(OH) ₂ NOCH ₃	1g 5g
6-Methoxypyridi	ne-3-boronic acid, 98%)
_20087 163105-89-3]	CH ₃ O N B(OH) ₂	250mg 1g 5g
5-Methylthiophe	ne-2-boronic acid, 98%)
323138 162607-20-7]	CH ₃ S B(OH) ₂	1g 5g
Pyridine-3-boror	nic acid	
_15040 1692-25-7]	B(OH) ₂	1g 5g
Pyridine-4-boror	nic acid hydrate	
_15179 1692-15-5]	B(OH) ₂ .xH ₂ O	1g 5g

Quinoline-3-bor	onic acid, 95%		2-(4-Boc-1-pip	erazino)pyridine-3-boronic a	acid
L20088	B(OH) ₂	250mg	pinacol ester	CHo	4 -
[191162-39-7]		5g	H50058		1g 5g
				B O CH ₃	
Quinoline-5-bor		250mm		N N N	
L19639 [355386-94-6]		250mg 1g			
				O CH_3	
	N/N/		6-(4-Boc-1-pip	erazino)pyridine-3-boronic a	acid
Quinoline-8-bor	onic acid, 99%		pinacol ester		
L19640		250mg	H50145	CH ₃ CH ₃	250mg
[86-58-8]		1g	[496786-98-2]		ig
	B(OH) ₂		CF		
Thionthrops 1 h	arania acid tash 00%				
I manthrene-1-D		10			
L 19033 [108847-76-3]	S S	5g	5 Durante 0 me		
			pinacol ester	ethoxypyriaine-3-boronic aci	a
	∽ `s´ ∽		H50064	CH _{3 CH₃}	250mg
Thiophene-2-bo	ronic acid, 98+%			OCH3	1g
B23071		1g		Br B-O CH ₃	
[6165-68-0]	S B(OH) ₂	5g 25g		N OCH3	
Thiophone-3-bo	ronic acid 08%	=9		ine 2 herenie eeld vineeel e	-1
B23637	B(OH) ₂	10	в-втотторупа		
[6165-69-1]		5g	[214360-62-0]	O-CH3	5g
	s			B O CH ₃	
				Br	
			2-Chioropyria		ster
			H50053 [452972-11-1]	O CH3	1g 5g
•• •			[B-O CH ₃	
Hetero	aryl boronic este	rs			
7-Azaindole-5-bo	pronic acid pinacol este	•			- 4
H50015	CH ₃ , CH ₃	250mg	2-Chloropyrid		ster
[754214-56-7]	CH3 O	1g	H50070 [458532-84-8]		1g 5g
	CH ₃ O ^{-B}		[100002 01 0]	ÓBÝÓ	0
	N H				
2-(Boc-amino)py	vridine-3-boronic acid pi	nacol			
ester		inuooi			
H50094	CH ₃ CH ₃	250mg	6-Chloropyrid		ster
		1g	H500071 [444120-94-9]	O-CH3	1g 5g
	°O CH ₃		[20-04-0]	B-O CH ₃	5
	N NH CH ₃ ↓ ↓ CH ₃				
	0 CH3			2	





H50015 [532391-30-3]



Alkenylboronic acid

1-Pentenylboronic acid, 98%			
L19677 [104376-24-1]	CH ₃ B(OH) ₂	250mg 1g 5g	

Alkenylboronic esters

3-Acetoxy-1 97%	-propenylboronic acid pinacol	ester,
L19700 [161395-97-7]	CH_3	250mg 1g
3,3-Diethox ester, 97%	y-1-propenylboronic acid pina	col
L19579 [153737-25-8]	$\begin{array}{c} CH_3\\ O\\ CH_3\\ CH_3\\ CH_3\end{array}$	250mg 1g
(E)-1-Hepter ester, 98%	ne-1,2-diboronic acid bis(pinac	col)
L19649 [307531-74-4]	$CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 $	1g 5g
(E)-1-Hexen ester, 98%	e-1,2-diboronic acid bis(pinace	ol)
L19650 [185427-48-9]	$CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 CH_3 $	1g 5g

4-Methyl-β-s ester, 98+%	styrylboronic acid diethanolan	nine
L19704 [608534-31-2]	CH ₃	100mg
4-Methyl-β-s	styrylboronic acid pinacol este	e r , 98%
L19698	CH ₃ CH ₃	250mg
[149777-84-4]	CH ₃	Ig
1-Octenylbo	pronic acid pinacol ester, 97%	
L19697	CH ₃ CH ₃	250mg
[170942-79-7]	CH ₃	1g
	CH3 CH3 CH3	
4-Octenylbo	pronic acid diethanolamine est	er,
1 19705	ų	100ma
[608534-40-3]		
	O-B-O	
	CH3 CH3	
_		
4-Octenylbo	pronic acid pinacol ester, 98%	
L19699	$CH_3 CH_3$ $CH_3 CH_3 CH_3$	250mg
[177949-95-0]	0, 0	ig
	B	
	CH ₃ CH ₃	
(E)-1-Penter	ne-1,2-diboronic acid bis(pinad	col)
	CH ₃ CH ₃	10
[177949-95-0]	CH ₃ CH ₃ CH ₃	5g
[
	CH ₃ CH ₃ CH ₃	
5-Phenyl-1- 96%	pentenylboronic acid pinacol o	ester,
L19701	CH ₃ CH ₃	250mg
[154820-97-0]	CH ₃	1g
	B-O CH ₃	
(E)-Stilbene 98%	diboronic acid bis(pinacol est	er),
L19652	CH ₃ CH ₃	1g
[151416-94-3]	$\left[\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	by
	~ ~ ~ O CH ₃	
	B-O CH ₃	
	CH ₃ CH ₃	

cis-Stilbeneboronic acid diethanolamine ester, 98%

L19573 100mg [501014-42-2] cis-Stilbeneboronic acid pinacol ester, 99% L19576 250mg CH_3 0 -ČH₃ 1g [264144-59-4] CH₃ ĊH₃ (*E*)- α , β -Styrenediboronic acid bis(pinacol) ester, 98% CH₂ CH_3 L19651 1g CH-CH₃ 5g [173603-23-1] CH_{3CH3} CHβ-Styrylboronic acid diethanolamine ester, 99% L19571 100mg [411222-52-1] β-Styrylboronic acid pinacol ester, 99% CH₃ CH₃ L19529 250mg 1g [78782-27-1] O CH₃ ℃H₃ 2-(Trimethylsilyl)vinylboronic acid pinacol ester, 95% CH_3 250mg L19577 ,CH₃ 1ġ [126688-99-1] CH₃ CH₃ CH₃ CH₃ L CH₃ Alkenyltrifluoroborate salts Potassium 4-methyl-β-styryltrifluoroborate L17973 BF₃+ K⁻ 1g 5g [219718-86-2] CH₃ Potassium β-styryltrifluoroborate L17971 BF3⁺ K⁻ 1g

5g

[201852-49-5]

Potassium vinyltrifluoroborate, 97%

L17970 [13682-77-4] 1g 5g

Alkylboronic acids

n-Butylbor	onic acid, 96%	
A13725 [4426-47-5]	CH ₃ B(OH) ₂	1g 5g 25g
n-Decylbor	onic acid	
L19957 [24464-63-9]	CH ₃ B(OH) ₂	1g 5g 25g
n-Dodecyll	poronic acid	
L19958 [24464-63-9]	CH ₃ B(OH) ₂	1g 5g 25g
Ethylboror	ni c acid , 98%	
L19959 [4433-63-0]	CH ₃ B(OH) ₂	1g 5g 25g
<i>n</i> -Hexylbor	onic acid, 98%	
B22446 [16343-08-1]	CH ₃ B(OH) ₂	1g 5g 25g
Isopropylb	oronic acid, 98%	
L19962 [80041-89-0]	CH ₃ CH ₃ B(OH) ₂	1g 5g 25g
Methylbor	onic acid, 97%	
L15589 [13061-96-6]	CH ₃ B(OH) ₂	1g 5g
n-Octylbor	onic acid, 97%	
L19964 [28741-08-4]	CH ₃ B(OH) ₂	1g 5g 25g
n-Propylbo	pronic acid, 98%	
L19965 [17745-45-8]	CH ₃ B(OH) ₂	1g 5g 25g
n-Tetradec	ylboronic acid	
L19966 [100888-40-2]	B(OH) ₂ CH ₃	1g 5g 25g





100mg

100mg

250mg

100mg

250mg

1g

1g

CH₃

сн₃

CH₃ CH₃

CH3 CH-

O

-ČH

CH₃

2-Trimethylsilyl-1-ethylboronic acid pinacol CH₃

250mg 1g CH₃ CH

Other products

Selected Alfa Aesar products with applications in boronic acid chemistry. Most are referred to in the text of this publication.



Bis(ethylene)(2,4-pentanedionato)rhodiur	n(l)
39288 [12082-47-2]	CH ₃ CH ₃ CH ₃	250mg 1g
Chloro(1,5-cyc	clooctadiene)iridium(I) dime	r
12749 [12112-67-3]		250mg 1g 5g
Chloro(1,5-cyc	clooctadiene)rhodium(I) dim	ner
10466 [12092-47-6]	Cl Cl	250mg 1g
Chlorotris(trip	henylphosphine)rhodium(l)	
10468 [14694-95-2]	(Ph ₃ P) ₃ RhCl	250mg 1g 5g
Copper(II) ace	tate monohydrate	
A16203 [6046-93-1]	(CH ₃ COO) ₂ Cu .H ₂ O	100g 500g 2.5kg
(1,5-Cycloocta (tricyclohexyl) hexafluoropho 42057 [64536-78-3]	adiene)(pyridine) phosphine)iridium(I) psphate, Crabtree's catalyst, ir_{PCy_3} PF_6^-	99% 50mg 250mg 1g
Diacetato[1,3-	bis(diphenylphosphino)pro	pane]
palladium(II)		
44970 [149796-59-8]	Ph P P Pd(OCOCH ₃) ₂ P P Ph Ph	1g 5g
trans-Di-μ-ace	tatobis[2-(di-o-	
tolylphosphin	o)benzyl]dipalladium(II), 989	%
L16948 [172418-32-5]	(o-Tol) (o-Tol) Pd Pd Pd Pd Pd CH ₃ (o-Tol) (o-Tol) CH ₃	250mg 1g
Dibromobis(tr	i-o-tolylphosphine)palladiu	n(ll)
44979 [24554-43-6]	[(o-Tol) ₃ P] ₂ PdBr ₂	1g 5g
Dicarbonyl(2,4	I-pentanedionato)rhodium(I), 99%
39295 [14874-82-9]	CH ₃ CH ₃ CH ₃ O Rh(CO) ₂	250mg 1g 5g

Dichlorobis(1,4 palladium(II)	-diphenylphosphinobut	ane)
44971 [29964-62-3]	Ph P-Ph PdCl ₂ P-Ph Ph Ph	1g 5g
Dichlorobis(2-d palladium(II)	liphenylphosphinophen	yl ether)
44977 [205319-06-8]	Ph P-Ph O PdCl ₂ P-Ph Ph	1g 5g
Dichlorobis(1,3 nickel(II)	-diphenylphosphinopro	pane)
30167 [15629-92-2]	Ph I P P NiCl ₂ P P Ph Ph	2g 10g
Dichlorobis(tric	cyclohexylphoshine)pall	adium(II)
44844 [29934-17-6]	$[Cy_3P]_2PdCl_2$	1g
Dichlorobis(trip	henylphosphine)nickel	(II)
13930 [14220-64-5]	$(Ph_3P)_2NiCl_2$	5g 25g 100g
trans-Dichlorob	bis(triphenylphosphine)	
10491 [13965-03-2]	Ph ₃ P、CI Pd CI PPh ₃	1g 5g 25g
Dichlorobis(tri-	o-tolylphosphine)pallad	ium(II)
44976 [40691-33-6]	[(o-Tol) ₃ P] ₂ PdCl ₂	1g 5g
Palladium, 5% of	on carbon powder, dry	
A12623		10g 50g
Palladium, 5% or reduced, 50% w	on carbon powder, standa ater wet	ırd,
38300		5g 25g 100g
Palladium, 5% of unreduced, 50%	on carbon powder, standa water wet	ırd,
38301		5g 25g 100g
Palladium, 10%	on carbon powder, dry	
A12012		2g 10g 50g

Palladium , 10% on carbon powder, standard, reduced, 50% water wet			
38304		5g 25g 100g	
Palladium, 5% unreduced, 50%	on carbon powder, standard, % water wet		
38305		5g 25g 100g	
Palladium(II) a	cetate, trimer		
10516 [3375-31-3]	$[(CH_3COO)_2Pd]_3$	1g 2g 10g	
Palladium(II) c	hloride		
11034 [7647-10-1]	PdCl ₂	1g 5g 25g	
Palladium(II) 2	,4-pentanedionate		
10517 [14024-61-4]	CH ₃ Pd CH ₃ O CH ₃ O CH ₃ CH ₃ CH ₃	1g 5g	
Palladium tri-te	ert-butylphosphine bromide	, dimer	
44446 [185812-86-6]	$\{[(CH_3)_3C]_3PPdBr\}_2$	100mg 500mg 2g	
Sodium tetrac	hloropalladate(II) hydrate		
11886 [13820-53-6]	Na ₂ PdCl ₄ .xH ₂ O	1g 5g	
Tetrakis(triphe	enylphosphine)palladium(0)		
10548 [14221-01-3]	$(Ph_3P)_4Pd$	1g 5g 25g	
Tetrakis(triphe	enylphosphine)platinum(0),	98%	
10549 [14221-02-4]	(Ph ₃ P) ₄ Pt	1g 5g	
Tris(dibenzylic	deneacetone)dipalladium(0		
12760 [51364-51-3]	$\begin{bmatrix} Ph_{Ph}_{Ph_{Ph_{Ph_{Ph_{Ph}_{Ph_{Ph_{Ph}_{Ph}_{Ph}_{Ph_{Ph}_{Ph}_{Ph}_{Ph}_{Ph}_{Ph}_{Ph}_$	1g 5g	
Tris(dibenzylic complex with cl	deneacetone)dipalladium(0) hloroform, 98%		
L15980 [52522-40-4]	$\begin{bmatrix} Ph & Ph \\ & O \end{bmatrix} \overset{Ph}{\underset{3}{\overset{Pl}{\underset{3}{\overset{P}{\underset{3}{\overset{P}{\underset{3}{\overset{P}{\underset{3}{\atop}}}{\overset{P}{\underset{1}{\overset{P}{\underset{1}{\overset{P}{\underset{1}{\overset{P}{\underset{1}{\overset{P}{\underset{1}{\underset{1}{\atop\atop1}{\underset{1}{\underset{1}{\atop\atop1}{\underset{1}{$	250mg 1g 5g	

Phosphine ligands

1,1'-Bis(di-tert-b	utylphosphino)ferrocene	e , 98%	
L19759 [84680-95-5]	C(CH ₃) ₃ C(CH ₃) ₃ C(CH ₃) ₃ C(CH ₃) ₃ C(CH ₃) ₃	500mg 2g	
(R)-(+)-2,2'-Bis(d binaphthyl, 98%	iphenylphosphino)-1,1'-		
B23785 [76189-55-4]	PPh2 PPh2	100mg 250mg 1g	
(S)-(-)-2,2'-Bis(di binaphthyl, 97%	phenylphosphino)-1,1'-		
B23872 [76189-55-4]	PPh ₂	100mg 250mg 1g	
1,4-Bis(diphenyl	phosphino)butane, 98%		
B21122 [100959-19-1]	Ph ₂ P	1g 5g 25g	
1,1'-Bis(dipheny	Iphosphino)ferrocene, 9	7%	
B21166 [12150-46-8]	Fe PPh ₂	1g 5g 25g	
Bis[(2-diphenylp	hosphino)phenyl ether,	98%	
L18481 [166330-10-5]	PPh ₂ PPh ₂	1g 5g	
1,3-Bis(diphenyl	phosphino)propane, 97%	6	
A12931 [6737-42-4]	Ph ₂ P PPh ₂	5g 25g 100g	
2-(Di-tert-butylph	nosphino)biphenyl, 99%		
L19758 [224311-51-7]	(CH ₃) ₃ C-P C(CH ₃) ₃	500mg 2g 10g	
Diphenylmethylphosphine, polymer-supported,			
0.9-1.4 mmol/g or	n polystyrene		
L194 <i>11</i>	P ^{-r} " Ph	1g 5g 25g	

Tri-tert-butylpho	osphine, 96%	
10178 [13716-12-6]	$\begin{array}{c} CH_3 \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \end{array}$	1g 5g
Tri-tert-butylpho	osphonium tetrafluoro	borate , 98%
L19752 [131274-22-1]	$\begin{array}{c} CH_3 \\ H \\ CH_3 \\ H \\ CH_3 \end{array} BF_4^-$	1g 5g
Tricyclohexylph	osphine, 97%	
30386 [2622-14-2]		1g 5g 25g
Tri(2-furyl)phos	phine, 97%	
L13329	$\sqrt{-}$	1g
[5518-52-5]		5g
	00 0/	
Triphenylarsine	, 98%	-
L03616 [603-32-7]	Ph I Ph ² As Ph	5g 25g
Triphenylphosp	hine, powder, 99%	
L02502 [603-32-7]	Ph I Ph ^P Ph	50g 250g 1kg
Triphenylphosp	hine , flake, 99%	
A14089 [603-32-7]		250g 1kg 5kg
Triphenylphosp	hine, polymer-suppor	ted, 1.4-2.0
mmoi/g on polyst	yrene	4
L19478		1g 5g 25g
Tri(o-tolyl)phos	ohine, 98+%	
A12093 [6163-58-2]	CH ₃ P CH ₃ CH ₃	1g 5g 25g

Boronylation reagents

	-		
Bis(neopen	tyl glycolato)diboron, 97%		
L18675	CH ₃ O CH ₃	250mg	
[201733-56-4]	CH ₃ B-B CH ₃	1g	
		Sy	
Bis(pinacol	ato)diboron, 99%		
L16088	CH_3 CH_3	1g	
[73183-34-3]		5g	
	CH ₃ O CH ₃	zəy	
Catecholbo	rane, 97%		
L14998		5g	
[274-07-7]	ВН	25g	
	\sim 0		
2-Isopropo	xy-4,4,5,5-tetramethyl-1,3,2-		
dioxaborola	ane, 98%		
L17278	CH_3	1g	
[61676-62-8]	B-O	5g 25g	
	CH ₃ O CH ₃	259	
	CH ₃ CH ₃		
2-Methoxy-	4.4.5.5-tetramethvl-1.3.2-		
dioxaborola	ane, 97%		
L19056	CH ₃	5g	
[1195-66-0]		25g	
	CH ₃ O		
	CH ₃		
Pinacolbora	ane, 97%		
L17558	CH ₃	5a	
[25015-63-8]	CH ₃ O	25g	
	CH ₃ O		
	CH ₃		
Tri-n-butyl	borate, 98%		
A19322	OCH ₂ CH ₂ CH ₂ CH ₃	25mL	
[688-74-4]		100mL	
		500mL	
Triisopropy	/l borate , 98+%		
Δ17592	OCH(CH ₃) ₂	100ml	
[5419-55-6]	B B B B B B B B B B B B B B B B B B B	500mL	
[3.10.00.0]	$(CH_3)_2$ CHO OCH $(CH_3)_2$	2.5L	
Trimethyl horate 99%			
D2024E	OCH-	250ml	
D2U213	I B	250mL 11	
[121-43-7]	CH ₃ O OCH ₃		

Boronic Acids

Properties and Applications

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