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Functionalization of Dihalophenylboronic Acids by Deprotonation of Their *N*-Butyldiethanolamine Esters

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Deprotonative lithiation of various 6-butyl-2-(dihalophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocanes (*N*-butyldiethanolamine esters of dihalophenylboronic acids) was investigated. It was found that selective transformations can be best achieved by use of LDA as the lithiating reagent. The reactivities of these compounds vary significantly, depending on the natures and positions of the halogen atoms. The resultant boron-lithium bimetallic intermediates were subjected to reactions with electrophiles to afford functionalized halogenated arylboronic acids.

Introduction

Arylboronic acids and esters have recently become very important reagents in modern organic synthesis; they have also found applications in other fields.[1] Ongoing interest in novel functionalized arylboronic acid derivatives stimulates work on the development of new simple general synthetic routes to these compounds. Classically, they can be obtained by transmetallation of aryllithium[2] or arylmagnesium[3] compounds with trialkylborates, although aryl derivatives of silicon, mercury, tin or thallium have also been used in combination with borane or tribromoborane.[4] More recent approaches involve Pd-[5] and CuI-catalysed[6] coupling of aryl halides with diboron derivatives or hydroboranes.

Alternative strategies based on the structural modification of protected arylboronic acids have also been developed.[7] One of these is based on the generation of bimetallic boron-metal intermediates. Besides magnesiated arylboronic pinacol esters,[8] the syntheses and reactivities of a few types of boron-lithium bimetallic reagents have been reported. Examples include potassium (3- and 4-lithiophenyl)trifluoroborates,[9] as well as closely related lithium (lithiophenyl)triisopropoxyborates.[10] The conversion of arylboronic acids into 6-alkyl-2-aryl-(*N*–*B*)-1,3,6,2-dioxazaborocanes (for simplicity designated throughout this paper by the ad hoc term "arylboronic azaesters") has also been used for the introduction of lithium into the boronated aromatic ring.[11] All of these bimetallic reagents were generated by means of halogen-lithium exchange from the corresponding bromine- or iodine-containing precursors. In this work we report for the first time on the application of deprotonative metallation for the functionalization of related arylboron derivatives.

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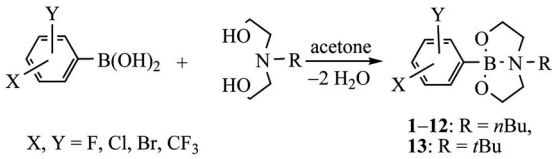
Results and Discussion

Protection of Dihalophenylboronic Acids

In a modification of previously reported procedures[11a–11c] and by our reported protocol[11d] we used *N*-butyldiethanolamine (BDEA) instead of *N*-methyldiethanolamine, because we assumed that the longer alkyl chain should increase the solubilities of arylboronic azaesters and (at least to some extent) the resistance of the boronic moiety to nucleophilic attack, due to the better steric protection. In our protocol, a mixture of a dihalophenylboronic acid (50–100 mmol), BDEA (50–100 mmol) and anhydrous $MgSO_4$ in acetone was stirred for ca. 1 h at 35–40 °C. The resulting mixture was filtered and subjected to concentration to remove acetone. Upon addition of diethyl ether the precipitated material was filtered off. In all cases well-defined, air-stable and crystalline 6-butyl-2-haloaryl-(*N*–*B*)-1,3,6,2-dioxazaborocanes **1**–**12** were obtained in high yields, in general exceeding 90% (Table 1). In addition, 6-*tert*-butyl-2-(3′,5′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (**13**) was also prepared from 3,5-difluorophenylboronic acid and *N*-*tert*-butyldiethanolamine. The tetrahedral boron environment with the B–N dative bond was established directly by ^{11}B NMR analyses, which in all cases showed single resonances at $\delta \approx 7$–8 ppm. Compounds **1**–**12** are insoluble in hexane and diethyl ether but very soluble in THF. On the other hand, compound **13** is only sparingly soluble in THF and exhibits fluxional behaviour in $CDCl_3$ solution at room temperature, manifested in the strong broadening of the resonances of the methylene protons bonded to the nitrogen atom.

Table 1. Preparation of 6-butyl-2-(dihalophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocanes.



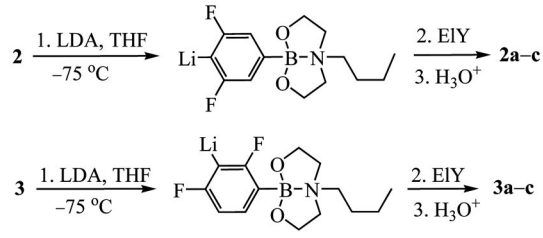
Product	X, Y	% Yield
1	4-F, H	98
2	3-F, 5-F	97
3	2-F, 4-F	98
4	2-F, 3-F	94
5	3-F, 4-F	92
6	2-F, 5-F	96
7	3-Cl, 5-Cl	97
8	3-Cl, 4-Cl	97
9	2-Cl, 3-Cl	96
10	3-Br, 5-Br	96
11	3-Br, 5-F	96
12	2-F, 5-CF_3	96
13	3-F, 5-F	99

Lithiation of Dihalophenylboronic Azaesters

We started our work with an attempted metallation of 6-butyl-2-(4′-fluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (**1**). Unfortunately, this compound proved essentially resistant against deprotonation with LDA and LDA/*t*BuOK. Even the stronger alkyllithium bases *n*BuLi, *n*BuLi/PMDTA and *s*BuLi were not effective. It should be noted that simple fluorobenzene is readily lithiated with *s*BuLi,[12] whereas *n*BuLi/PMDTA has been successfully used for deprotonation of fluoroanisoles *ortho* to fluorine.[13] It seems that the reduced reactivity of **1** is the result of the electronic influence of the borocanyl group on the fluorophenyl ring. This group acts as a σ-donor, and hence the increased electron density in the aromatic ring makes the *ortho*-fluoro hydrogen atoms much less susceptible to abstraction.

We next turned our attention to more acidic substrates containing two halogen atoms in the aromatic ring. The acidities of isomeric dihalobenzenes depend on the positions of the two halogens atoms with respect to each other, 1,3-dihalobenzene being more acidic than the 1,2- and 1,4-isomers because of the cooperating effects of two *ortho*-halogens.[14] We hence expected that 6-butyl-2-(3′,5′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (**2**) should be sufficiently reactive. Indeed, the lithiation of **2** with LDA in THF at ca –75 °C (Scheme 1) proved feasible. The formation of the resultant 4′-lithio intermediate **2-Li** was indicated by its precipitation from the solution.

Subsequent derivatization of **2-Li** with selected electrophiles afforded 3,5-difluorophenylboronic acids functionalized at their 4-positions (Table 2), including the interesting fluorinated 1,4-phenylenediboronic acid **2c**. For comparison, the isomeric *tert*-butyl azaester **13** gave a mixture of products; these contained some borinic derivatives, which suggested that the boron atom in **13** is protected less effectively than in **2**. It is plausible that the increased



Scheme 1.

susceptibility of the boron atom to nucleophilic attack is due to the fluxional behaviour of the azaester moiety in **13**.

In addition, a competition experiment was performed to assess the impact of boronation on the reactivity of the 1,3-difluorobenzene system towards lithiation. For this purpose, a mixture of 1,3-difluorobenzene (1 equiv.) and **2** (1 equiv.) was treated with LDA (1 equiv.). Subsequent trapping with Me_3SiCl (1 equiv.), followed by hydrolysis, gave a mixture of 1,3-difluoro-2-(trimethylsilyl)benzene and 3,5-difluorophenylboronic acid, which indicates that the proton abstraction from the boronated 1,3-difluorobenzene derivative is strongly retarded relative to that from the parent compound.

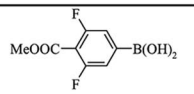
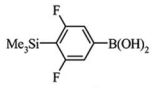
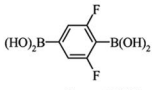
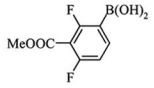
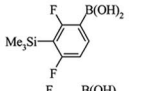
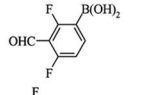
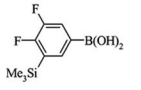
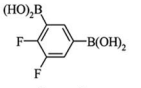
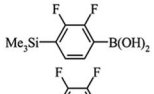
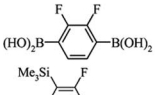
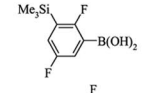
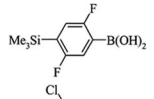
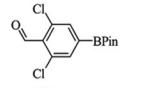
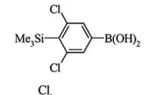
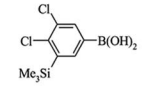
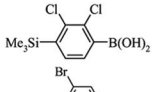
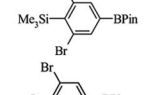
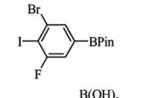
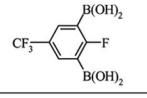
An approach similar to that optimized for **2** also proved useful in the lithiation of the closely related 6-butyl-2-(2′,4′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (**3**, Scheme 1). Again, lithiation proceeded effectively at low temperature, and subsequent treatment with electrophiles gave 3-substituted 2,4-difluorophenylboronic acids in good yields.

These results encouraged us to investigate the metallation of azaesters of other isomeric difluorophenylboronic acids. However, we observed that the lithiation of 6-butyl-2-(3′,4′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (**4**) does not occur under the conditions successfully applied for substrates **2** and **3**. Treatment of the reaction mixture with DMF, followed by the hydrolytic workup, simply afforded recovered 3,4-difluorophenylboronic acid, and no incorporation of the formyl group onto the aromatic ring was observed.

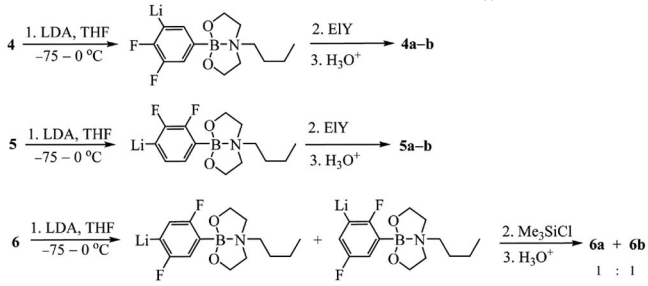
In the next attempt we added Me_3SiCl as an electrophile and the reaction mixture was allowed to warm up slowly to 0 °C. Me_3SiCl is known to co-exist with bulky lithium amides such as LTMP and LDA in solution but reacts quite rapidly even with some sterically hindered aryllithiums,[15] so we assumed that this electrophile should effectively trap the lithiated azaester, thus preventing its plausible degradation at higher temperature (e.g., by an aryne mechanism). Indeed, the workup of the resulting mixture cleanly gave 3,4-difluoro-5-(trimethylsilyl)phenylboronic acid (**4a**), which indicates that of the two potential metallation sites *ortho* to fluorine, lithium goes selectively to the less hindered one (Scheme 2).

In a similar way, the boronation of **4** was performed with LTMP/B(O*i*Pr)$_3$. It had previously been demonstrated that B(O*i*Pr)$_3$ is compatible with bulky lithium amides in the in situ quench technique.[16] Unfortunately, an attempted stannylation with LTMP/Bu_3SnCl did not proceed cleanly. Be-

Table 2. The preparation of functionalized dihaloarylboronic acids through deprotonation of dihalophenylboronic BDEA azaesters with LDA.

Starting material	Temp. [°C]	Electrophile	Product		% Yield
2	−75	$(MeO)_2CO$		**2a**	88
		Me_3SiCl		**2b**	85
		$B(OiPr)_3$		**2c**	90
3	−75	$(MeO)_2CO$		**3a**	83
		Me_3SiCl		**3b**	90
		DMF		**3c**	83
4	0	Me_3SiCl[a]		**4a**	90
	0	$B(OiPr)_3$[a]		**4b**	85
5	0	Me_3SiCl[a]		**5a**	80
	0	$B(OiPr)_3$[a]		**5b**	90
6	0 °C	Me_3SiCl[a]		**6a**	86[b]
				**6b**	
7	−75	DMF		**7a**	87
		Me_3SiCl		**7b**	95
8	0	Me_3SiCl[a]		**8a**	10[c]
9	0	Me_3SiCl[a]		**9a**	8[c]
10	−75	Me_3SiCl		**10a**	55
11	−75	I_2		**11a**	73
12	0	$B(OiPr)_3$[a]		**12a**	83

[a] In situ quenching. [b] Total yield, see Scheme 2. [c] Poor conversion of the substrate.



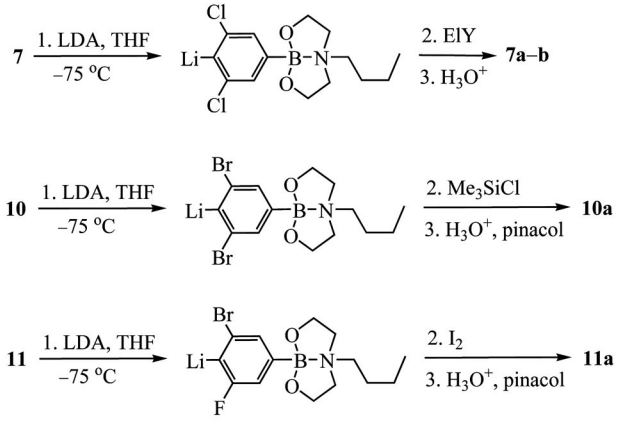
Scheme 2.

cause the low-temperature metallation of 6-butyl-2-(2′,3′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (**5**) was also unsuccessful, we also employed the lithiation/silylation and lithiation/boronation protocols described above for **4** for this substrate. Again, we succeeded in the isolation of the silylated boronic acid **5a**, as well as the diboronic acid **5b**. In a similar approach, treatment of **6** with LDA/Me_3-SiCl gave an almost equimolar mixture of 2,5-difluoro-3-(trimethylsilyl)phenylboronic acid (**6a**) and 2,5-difluoro-4-(trimethylsilyl)phenylboronic acid (**6b**). In this case lithiation at the position between fluorine and the borocanyl function is apparently hampered by steric congestion. On the other hand, this function does not exhibit any appreciable long-range electronic effects, which should result in some preference in the formation of acids **6a** or **6b**.

The lower reactivities of azaesters **4**–**6** with respect to **2**–**3** correlate with different relative reactivities of the parent difluorobenzenes. 1,3-Difluorobenzene is more reactive than both 1,2- and 1,4-difluorobenzene, although all these compounds are readily deprotonated with LDA at –75 °C. Boronation significantly decreases the reactivities of all difluorobenzenes, but nevertheless, azaesters **2** and **3** derived from 1,3-difluorobenzene can be lithiated at –75 °C. This is no longer the case, however, for **4**–**6**, derived from less acidic difluorobenzenes, because they require higher temperatures for effective proton abstraction. One interpretation, assuming the operation of a CIPE-based mechanism,[17] would involve better precoordination of the base close to the metallation site flanked by two heteroatoms. However, this alternative seems to be less likely, because fluorine (in fluoroarenes) is recognized as a weak donor for lithium, in sharp contrast with the oxygen in the solvent (THF). There is indeed no spectroscopic evidence, for instance, for Li···F interaction between fluorobenzene and *n*BuLi in toluene.[18] The *ortho*-directing ability of fluorine is hence due only to its inductive effect, resulting in the enhancement of both thermodynamic and kinetic acidities. Accordingly, the cumulative *ortho*-acidifying effect at the position between two fluorines is responsible for the higher reactivities of **2**–**3** with respect to **4**–**6**.

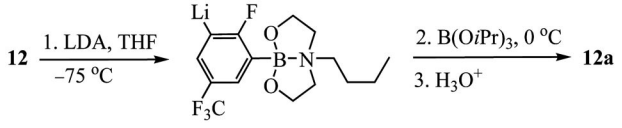
We extended our research by using selected heavier halogen analogues of **2**–**6**. Azaesters of three isomeric dichlorophenylboronic acids **7**–**9** were prepared and their behaviour towards LDA was studied. Compound **7** undergoes lithiation readily at –75 °C (Scheme 3), as confirmed by the high-yield formation of pinacol ester **7a** and acid **7b**. Azaes-

ters **8** and **9**, however, proved to be less reactive than their fluorinated counterparts **4** and **5**, because under similar lithiation/silylation conditions they gave only small amounts of the corresponding silylated dichlorophenylboronic acids **8a** and **9a**, whereas simple dichlorophenylboronic acids resulting from hydrolysis of the starting azaesters were found as major products. The degree of conversion was higher with LTMP as the lithiating agent in the case of **8**, but it was still rather poor (ca 50%) from the point of view of preparative utility.



Scheme 3.

The lithiation of the two bromine-containing azaesters **10** and **11** was also accomplished (Scheme 3). Again, the cumulated *ortho*-acidifying effects of two halogen atoms allowed for the proton abstraction at –75 °C. Finally, metallation of the CF_3-substituted azaester **12** was performed under the conditions applied for **4**–**6**, but with $B(OiPr)_3$ as the electrophile (Scheme 4). This approach resulted in the clean formation of diboronic acid **12a**, because lithiation occurs only *ortho* to fluorine, whereas CF_3 activates this position through its potent long-range activating effect.[19]

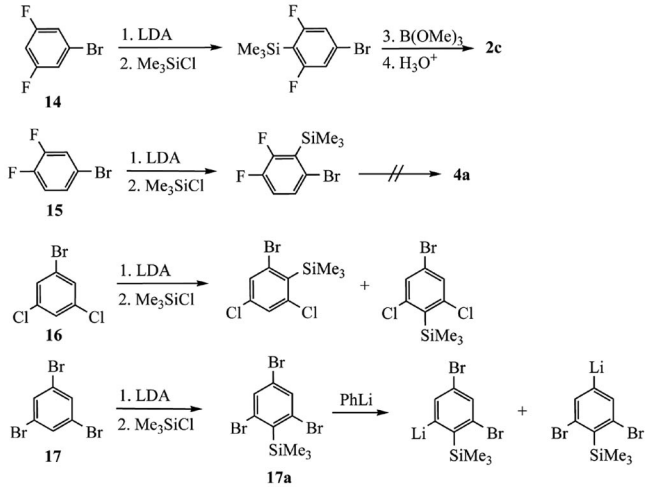


Scheme 4.

In addition, we performed several competition experiments to assess the relative reactivities of selected azaesters. In the first of these, a mixture of **2** (1 equiv.) and **3** (1 equiv.) was added at ca –75 °C to LDA (1 equiv.) in THF, followed by quenching with Me_3SiCl (1 equiv.). A mixture containing comparable amounts of acids **2b** and **3b** was formed (together with the two difluorophenylboronic acids resulting from the hydrolysis of unreacted azaesters). This indicates that the position of the borocanyl moiety with respect to the metallation site (*meta* vs. *para*) does not have a significant influence on the reactivity.

A different situation was observed when a mixture of **2** and **7** was subjected to a similar experiment. In this case, **2** was preferentially deprotonated and only a small amount of 3,5-difluorophenylboronic acid and traces of the acid **7b** (resulting from the lithiation/silylation of **7**) were detected in the reaction mixture. This result confirmed the observations described above concerning the weaker reactivities of chlorinated azaesters relative to their fluorinated analogues.

It should be stressed that the route to arylboronic acids described in this study, through the reversed approach involving first the introduction of the functional group and then boronation, would not be trivial in most cases. The acid **2b** could potentially be prepared from the commercially available 1-bromo-3,5-fluorobenzene (**14**) by lithiation/silylation with LDA/Me_3SiCl,[20] followed by Br–Li exchange and boronation (Scheme 5). However, the isomeric acid **4a** is not easily accessible by the same route from 1-bromo-3,4-fluorobenzene (**15**), because this substrate deprotonates between Br and F[21] rather than at the 5-position. Another problematic example would be the synthesis of **7a** and **7b** starting with deprotonation of 1-bromo-3,5-dichlorobenzene (**16**), because this reaction would be expected to be unselective, due to the similar *ortho*-directing abilities of chlorine and bromine.[22] On the other hand, (2,4,6-tribromophenyl)trimethylsilane (**17a**) can be cleanly obtained from 1,3,5-tribromobenzene (**17**),[23] but it cannot serve as an optimal substrate for **10a** because it preferentially undergoes Br–Li interconversion *ortho* to the $SiMe_3$ group.[24] Finally, the synthesis of the diboronic acids **2c**, **4b**, **5b**, or **12a** from the corresponding halogenated dilithiobenzenes by double boronation would seem to be the simplest option. Unfortunately, such dilithiated intermediates are not easily accessible and so our protocol becomes the only real alternative.



Scheme 5.

Conclusions

In conclusion, the generation of bimetallic boron-lithium reagents by deprotonation of halogenated arylboronic azaesters is possible with non-nucleophilic lithium amides such as LDA, provided that the aryl hydrogens are sufficiently activated. This can readily be achieved when two fluorine

atoms are attached to the aryl ring, whereas some dichlorinated analogues exhibit lower reactivities. The resulting lithiated azaesters can be subsequently derivatized by treatment with appropriate electrophiles, which provides access to various functionalized halogenated arylboronic acids in most cases not easily accessible by other methods.

Experimental Section

General: All reactions involving air- or moisture-sensitive reagents were carried out under argon. Et_2O and THF were stored over sodium wire before use. All halogenated phenylboronic acids used as starting materials are commercially available from Aldrich. This is also the case for *N*-butyldiethanolamine and other important reagents including *n*BuLi (10 M solution in hexanes), diisopropylamine, 2,2,6,6-tetramethylpiperidine, chlorotrimethylsilane, chlorotributyltin, dimethyl carbonate, dimethylformamide, iodine and triisopropoxyborane, which were used as received. The NMR chemical shifts are given relative to TMS with the aid of known chemical shifts of residual proton (^1H) or carbon (^{13}C) solvent resonances. In the ^{13}C NMR spectra the resonances of boron-bound carbon atoms were not observed in most cases, due to their broadening by quadrupolar boron nuclei.

6-Butyl-2-(4′-fluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (1): A mixture of 4-fluorophenylboronic acid (7.0 g, 0.05 mol), *N*-butyldiethanolamine (8.5 g, 0.052 mol), anhydrous $MgSO_4$ (5 g) and acetone (50 mL) was stirred for 1 h at 35 °C. The mixture was filtered and concentrated under reduced pressure. Et_2O (25 mL) was added to the remaining solid residue, followed by filtration of the resulting slurry. The crystalline product was washed with diethyl ether (2 × 20 mL) and dried to give the title compound, yield 13.0 g (98%), m.p. 146–148 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.54 (t, J = 8.5 Hz, 2 H, Ph), 6.92 (t, J = 8.5 Hz, 2 H, Ph), 4.15–4.03 (m, 4 H, CH_2O), 3.03–2.91 (m, 4 H, CH_2N), 2.23–2.19 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.47–1.39 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.12–1.02 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.77 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 162.9 (d, J = 243.0 Hz), 134.8 (d, J = 243.0 Hz), 113.8 (d, J = 19.0 Hz), 62.9, 59.7, 57.2, 26.7, 20.0, 13.6 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 8 ppm. $C_{14}H_{21}BFNO_2$ (265.14): calcd. C 63.42, H 7.98, N 5.28; found C 63.25, H 8.01, N 5.33.

6-Butyl-2-(3′,5′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (2): Yield 13.7 g (97%), m.p. 112–114 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.06 (dt, J = 7.0, 2.0 Hz, 2 H, Ph), 6.61 (tt, J = 7.0, 2.0 Hz, 1 H, Ph), 4.13–4.02 (m, 4 H, CH_2O), 3.05–2.91 (m, 4 H, CH_2N), 2.27–2.22 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.48–1.40 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.13–1.04 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.78 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 162.6 (dd, J = 248.5, 11.0 Hz), 114.9 (dd, J = 16.1, 4.5 Hz), 102.4 (t, J = 26.0 Hz), 63.0, 59.6, 57.3, 26.6, 20.0, 13.5 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BF_2NO_2$ (283.13): calcd. C 59.39, H 7.12, N 4.95; found C 59.25, H 7.10, N 5.03.

6-Butyl-2-(2′,4′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (3): Yield 13.8 g (98%), m.p. 119–121 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.61 (q, J = 8.0 Hz, 1 H, Ph), 6.76 (dt, J = 8.5, 2.5 Hz, 1 H, Ph), 6.64 (dt, J = 10.0, 2.5 Hz, 1 H, Ph), 4.14–4.02 (m, 4 H, CH_2O), 3.14–3.00 (m, 4 H, CH_2N), 2.56–2.51 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.55–1.47 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.20–1.10 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.81 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 166.4 (dd, J = 244.5, 11.0 Hz), 163.2 (dd, J = 247.5, 12.5 Hz), 136.7 (dd, J = 12.5, 8.5 Hz), 110.2 (dd, J = 18.5, 3.0 Hz), 102.8 (dd, J = 30.0, 23.5 Hz), 62.6, 58.0, 57.3, 26.7, 20.0, 13.6 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BF_2NO_2$ (283.13): calcd. C 59.39, H 7.12, N 4.95; found C 59.26, H 6.97, N 4.98.

6-Butyl-2-(3′,4′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (4): Yield 13.2 g (94%), m.p. 75–78 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.34 (m, 1 H, Ph), 7.26 (m, 1 H, Ph), 7.00 (m, 1 H, Ph), 4.12–4.00 (m, 4 H, CH_2O), 3.05–2.91 (m, 4 H, CH_2N), 2.24–2.20 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.48–1.40 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.12–1.03 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.76 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 150.0 (dd, J = 248.5, 15.0 Hz), 149.8 (dd, J = 250.5, 15.0 Hz), 129.1 (dd, J = 6.0, 3.5 Hz), 121.3 (d, J = 13.5 Hz), 115.9 (d, J = 15.5 Hz), 62.9, 59.8, 57.3, 26.6, 20.0, 13.5 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BF_2NO_2$ (283.13): calcd. C 59.39, H 7.12, N 4.95; found C 59.12, H 7.04, N 5.02.

6-Butyl-2-(2′,3′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (5): Yield 13.0 g (92%), m.p. 86–88 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.37 (m, 1 H, Ph), 7.06–6.94 (m, 2 H, Ph), 4.16–4.04 (m, 4 H, CH_2O), 3.18–3.11 (m, 2 H, CH_2N), 3.09–3.02 (m, 2 H, CH_2N), 2.60–2.55 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.57–1.50 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.21–1.12 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.82 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 153.4 (dd, J = 241.5, 10.5 Hz), 150.5 (dd, J = 246.5, 16.0 Hz), 130.2 (dd, J = 9.0, 4.0 Hz), 123.5 (m), 116.5 (d, J = 17.5 Hz), 62.7, 58.0, 57.4, 26.8, 20.1, 13.6 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BF_2NO_2$ (283.13): calcd. C 59.39, H 7.12, N 4.95; found C 59.22, H 7.19, N 4.91.

6-Butyl-2-(2′,5′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (6): Yield 13.5 g (96%), m.p. 71–74 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.32–7.26 (m, 1 H, Ph), 7.85–6.81 (m, 2 H, Ph), 4.12–4.00 (m, 4 H, CH_2O), 3.14–3.00 (m, 4 H, CH_2N), 2.58–2.54 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.54–1.46 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.18–1.09 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.80 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 162.0 (d, J = 237.5 Hz), 158.7 (d, J = 241.5 Hz) 121.3 (dd, J = 21.5, 11.5 Hz), 115.8–115.3 (m, 2 × C_{arom}), 62.6, 57.9, 57.4, 26.6, 20.0, 13.5 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BF_2NO_2$ (283.13): calcd. C 59.39, H 7.12, N 4.95; found C 58.98, H 7.24, N 5.33.

6-Butyl-2-(3′,5′-dichlorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (7): Yield 15.3 g (97%), m.p. 137–139 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.44 (d, J = 2.0 Hz, 2 H, Ph), 7.21 (t, J = 2.0 Hz, 1 H, Ph), 7.20 (td, J = 8.0, 1.0 Hz, 1 H, Ph), 7.06 (td, J = 8.0, 1.5 Hz, 1 H, Ph), 4.16–4.05 (m, 4 H, CH_2O), 3.07–2.95 (m, 4 H, CH_2N), 2.30–2.25 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.51–1.43 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.17–1.08 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.81 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 134.0, 131.3, 127.4, 63.1, 59.8, 57.5, 26.8, 20.0, 13.7 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BCl_2NO_2$ (316.04): calcd. C 53.21, H 6.38, N 4.43; found C 53.03, H 6.43, N 4.47.

6-Butyl-2-(3′,4′-dichlorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (8): Yield 15.3 g (97%), m.p. 118–120 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.64 (d, J = 1.5 Hz, 1 H, Ph), 7.38 (dd, J = 8.0, 1.5 Hz, 1 H, Ph), 7.30 (d, J = 8.0 Hz, 1 H, Ph), 4.13–4.01 (m, 4 H, CH_2O), 3.04–2.91 (m, 4 H, CH_2N), 2.25–2.20 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.48–1.40 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.13–1.04 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.78 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 135.0, 132.6, 131.3, 131.1, 129.3, 63.9, 59.9, 57.4, 26.7, 20.0, 13.6 ppm. ^{11}B NMR

($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BCl_2NO_2$ (316.04): calcd. C 53.21, H 6.38, N 4.43; found C 53.10, H 6.18, N 4.52.

6-Butyl-2-(2′,3′-dichlorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (9): Yield 15.1 g (96%), m.p. 147–148 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71 (dd, J = 7.5, 1.5 Hz, 1 H, Ph), 7.34 (dd, J = 7.5, 1.5 Hz, 1 H, Ph), 7.10 (t, J = 7.5 Hz, 1 H, Ph), 4.18–4.07 (m, 4 H, CH_2O), 3.29–3.22 (m, 2 H, CH_2N), 3.07–3.02 (m, 2 H, CH_2N), 2.62–2.58 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.57–1.49 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.20–1.11 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.82 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 136.6, 134.6, 132.9, 130.0, 126.6, 62.9, 58.1, 58.0, 26.9, 20.1, 13.7 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BCl_2NO_2$ (316.04): calcd. C 53.21, H 6.38, N 4.43; found C 53.15, H 6.23, N 4.54.

6-Butyl-2-(3′,5′-dibromophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (10): Yield 19.5 g (96%), m.p. 140–142 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (d, J = 2.0 Hz, 2 H, Ph), 7.53 (t, J = 2.0 Hz, 1 H, Ph), 4.17–4.07 (m, 4 H, CH_2O), 3.10–2.96 (m, 4 H, CH_2N), 2.32–2.28 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.54–1.46 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.20–1.11 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.84 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 134.7, 132.9, 122.6, 63.1, 59.9, 57.5, 26.9, 20.1, 13.7 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{14}H_{20}BBr_2NO_2$ (404.94): calcd. C 41.53, H 4.98, N 3.46; found C 41.67, H 4.75, N 3.49.

2-(3′-Bromo-5′-fluorophenyl)-6-butyl-(*N*–*B*)-1,3,6,2-dioxazaborocane (11): Yield 16.5 g (96%), m.p. 119–121 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.49 (d, J = 2.0 Hz, 1 H, Ph), 7.21 (dd, J = 9.0, 2.0 Hz, 1 H, Ph), 7.08 (dt, J = 8.0, 2.0 Hz, 1 H, Ph), 4.15–4.04 (m, 4 H, CH_2O), 3.07–2.94 (m, 4 H, CH_2N), 2.29–2.24 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.50–1.42 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.16–1.07 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.80 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 162.4 (d, J = 250.5 Hz), 131.7 (d, J = 2.5 Hz), 121.8 (d, J = 8.5 Hz), 118.2 (d, J = 18.0 Hz), 117.8 (d, J = 25.0 Hz), 63.0, 59.8, 57.4, 26.8, 20.0, 13.6 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 8 ppm. $C_{14}H_{20}BBrFNO_2$ (344.03): calcd. C 48.88, H 5.86, N 4.07; found C 48.70, H 5.67, N 4.12.

6-Butyl-2-[2′-fluoro-5′-(trifluoromethyl)phenyl]-(*N*–*B*)-1,3,6,2-dioxazaborocane (12): Yield 16.0 g (96%), m.p. 107–108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.94 (m, 1 H, Ph), 7.46 (m, 1 H, Ph), 6.97 (t, J = 9.0 Hz, 1 H, Ph), 4.13–4.02 (m, 4 H, CH_2O), 3.16–3.02 (m, 4 H, CH_2N), 2.56–2.52 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.54–1.46 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 1.16–1.07 (m, 2 H, $NCH_2CH_2CH_2CH_3$), 0.81 (t, J = 7.0 Hz, 3 H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 168.1 (d, J = 246.5 Hz), 133.4 (m), 126.9 (m), 125.5 (q, J = 31.0 Hz), 124.4 (d, J = 271.5 Hz), 115 ppm. 1 (d, J = 28.0 Hz), 62.7, 58.1, 57.5, 26.6, 20.0, 13.4 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 7 ppm. $C_{15}H_{20}BF_4NO_2$ (333.13): calcd. C 54.08, H 6.05, N 4.20; found C 53.85, H 5.92, N 4.26.

6-*tert*-Butyl-2-(3′,5′-difluorophenyl)-(*N*–*B*)-1,3,6,2-dioxazaborocane (13): Yield 14.0 g (99%), m.p. 212–215 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.24 (dt, J = 7.0, 2.0 Hz, 2 H, Ph), 6.66 (tt, J = 9.0, 2.5 Hz, 1 H, Ph), 4.16 (t, J = 6.0 Hz, 4 H, CH_2O), 3.10 (br., 4 H, CH_2N), 1.14 (s, 9 H, *t*Bu) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 162.4 (dd, J = 245.5, 11.0 Hz), 116.4 (dd, J = 14.0, 4.5 Hz), 102.7 (t, J = 26.0 Hz), 63.1, 61.7, 53.5, 26.4 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 8 ppm. $C_{14}H_{20}BF_2NO_2$ (283.13): calcd. C 59.39, H 7.12, N 4.95; found C 59.17, H 7.00, N 5.04.

3,5-Difluoro-4-(methoxycarbonyl)phenylboronic Acid (2a): A solution of **2** (2.84 g, 10 mmol) in THF (20 mL) was added at –75 °C to a stirred solution of LDA, freshly prepared from diisopropylamine (1.52 g, 15 mmol) and *n*BuLi (10 M, 1.5 mL, 15 mmol) in THF (20 mL). After ca 30 min stirring at ca –75 °C (internal temperature) a mixture containing the lithiate **2-Li** was quenched with dimethyl carbonate (2.7 g, 30 mmol). The mixture was stirred for 30 min at –75 °C and was then hydrolysed with aq. H_2SO_4 (2 M, 10 mL). The water phase was separated, followed by extraction with diethyl ether (2×15 mL). The extracts were added to the organic phase, which was concentrated under reduced pressure. A solid residue was filtered and washed consecutively with water (2×10 mL), toluene (5 mL) and hexane (5 mL). Drying in vacuo afforded the title compound as a white powder, m.p. 148–151 °C (dec), yield 1.9 g (88%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.69 [br, 2 H, $B(OH)_2$], 7.48 (d, J = 9.0 Hz, 2 H, Ph), 3.92 (s, 3 H, OMe) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 162.4, 160.5 (dd, J = 255.0, 5.5 Hz), 117.5 (dd, J = 19.0, 5.0 Hz), 113.0 (t, J = 19.0 Hz), 53.1 ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_8H_7BF_2O_4$ (215.95): calcd. C 44.50, H 3.27; found C 44.80, H 3.08.

3,5-Difluoro-4-(trimethylsilyl)phenylboronic Acid Anhydride (2b): This compound was prepared as described for **2a** with use of Me_3SiCl (2.17 g, 20 mmol, excess) dissolved in THF (5 mL) as electrophile. White powder, m.p. 160–163 °C, yield 1.8 g (85%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.31 (d, J = 9.0 Hz, 2 H, Ph), 0.33 (t, J = 1.0 Hz, 9 H, $SiMe_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 167.4 (dd, J = 241.5, 14.5 Hz), 116.6 (d, J = 26.0 Hz), 115.7 (t, J = 34.0 Hz), 0.2 ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_9H_{11}BF_2OSi$ (212.08): calcd. C 50.97, H 5.23; found C 51.08, H 5.18.

2,6-Difluoro-1,4-phenylenediboronic Acid Monohydrate (2c): This compound was prepared as described for **2a**, with $B(OiPr)_3$ (2.17 g, 12 mmol) as electrophile. White powder, m.p. > 350 °C, yield 2.0 g (90%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.84 [br, 2 H, $B(OH)_2$], 7.54 [br, 2 H, $B(OH)_2$], 7.31 (dd, J = 7.5 Hz, 2 H, Ph), 3.29 (br., 2 H, H_2O) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 165.5 (dd, J = 244.0, 14.0 Hz), 139.7 (br), 116.3 (dd, J = 20.0, 5.5 Hz), 114.4 (br) ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_6H_6B_2F_2O_4 \cdot H_2O$ (219.75): calcd. C 32.80, H 3.67; found C 33.04, H 3.59.

2,4-Difluoro-3-(methoxycarbonyl)phenylboronic Acid (3a): This compound was prepared as described for **2a**, starting with azaester **3**. White powder, m.p. 220–225 °C, yield 1.8 g (83%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.89 (q, J = 8.0 Hz, 1 H, Ph), 7.12 (td, J = 8.0, 1.0 Hz, 1 H, Ph), 3.91 (s, 3 H, OMe) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 164.6 (dd, J = 254.0, 6.5 Hz), 162.6, 162.3 (dd, J = 255.0, 7.0 Hz), 140.2 (t, J = 11.0 Hz), 112.4 (dd, J = 10.5, 3.0 Hz), 53.1 ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_8H_7BF_2O_4$ (215.95): calcd. C 44.50, H 3.27; found C 44.71, H 3.12.

2,4-Difluoro-3-(trimethylsilyl)phenylboronic Acid (3b): This compound was prepared as described for **2b**, starting with azaester **3**. White powder, m.p. 88–90 °C, yield 2.1 g (90%). ^{1}H NMR ([D$_6$]-acetone, 400 MHz): δ = 7.80 (q, J = 8.0 Hz, 1 H, Ph), 7.20 [d, J = 2.5 Hz, 2 H, $B(OH)_2$], 6.91 (t, J = 8.0 Hz, 1 H, Ph), 0.36 (t, J = 1.5 Hz, 9 H, $SiMe_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 172.2 (dd, J = 243.5, 15.0 Hz), 169.4 (dd, J = 245.0, 17.0 Hz), 140.1 (t, J = 10.5 Hz), 113.1 (dd, J = 38.0, 34.0 Hz), 111.7 (dd, J = 25.0, 3.5 Hz), 0.3 (t, J = 3.0 Hz) ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_9H_{13}BF_2O_2Si$ (230.09): calcd. C 46.98, H 5.69; found C 47.16, H 5.46.

2,4-Difluoro-3-formylphenylboronic Acid (3c): This compound was prepared as described for **3a**, with Me_2NCHO as electrophile.

White powder, m.p. 225–230 °C, yield 1.8 g (83%). ^{1}H NMR ([D$_6$]-acetone, 400 MHz): δ = 10.31 (s, 1 H, CHO), 8.02 (q, J = 8.0 Hz, 1 H, Ph), 7.50 [br, 2 H, B(OH)$_2$], 7.12 (td, J = 8.0, 1.0 Hz, 1 H, Ph) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 185.2, 167.9 (dd, J = 254.0, 4.5 Hz), 164.9 (dd, J = 264.5, 6.0 Hz), 143.7 (t, J = 12.0 Hz), 114.4 (t, J = 13.0 Hz), 113.0 (d, J = 20.0 Hz), 53.1 ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_7H_5BF_2O_3$ (185.92): calcd. C 45.22, H 2.71; found C 45.24, H 2.64.

3,4-Difluoro-5-(trimethylsilyl)phenylboronic Acid (4a): This compound was prepared as described for **2b**, starting with azaester **4**, except that the reaction mixture was allowed to warm to 0 °C after the addition of Me_3SiCl. White powder, m.p. 165–167 °C, yield 2.1 g (90%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.73 (m, 1 H, Ph), 7.68 (m, 1 H, Ph), 0.31 (d, J = 1.0 Hz, 9 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 156.4 (dd, J = 242.0, 11.5 Hz), 150.3 (dd, J = 248.0, 16.0 Hz), 136.8 (dd, J = 10.5, 4.0 Hz), 128.6 (d, J = 24.0 Hz), 124.3 (d, J = 15.0 Hz), –1.0 ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_9H_{13}BF_2O_2Si$ (230.09): calcd. C 46.98, H 5.69; found C 46.79, H 5.59.

4,5-Difluoro-1,3-phenylenediboronic Acid (4b): This compound was prepared as described for **4a**, with B(OiPr)$_3$ (2.17 g, 12 mmol) as electrophile. White powder, m.p. > 400 °C, yield 1.7 g (85%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.98 (d, J = 5.0 Hz, 1 H, Ph), 7.71 (m, 1 H, Ph), 7.42 [br, 2 H, B(OH)$_2$], 7.37 [br, 2 H, B(OH)$_2$] ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 156.1 (dd, J = 250.0, 11.5 Hz), 150.5 (dd, J = 246.0, 14.5 Hz), 137.8 (dd, J = 7.5, 4.0 Hz), 131.3 (br), 124.7 (d, J = 15.0 Hz), 123.6 (br) ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_6H_6B_2F_2O_4$ (201.73): calcd. C 35.72, H 3.00; found C 35.74, H 2.73.

2,3-Difluoro-4-(trimethylsilyl)phenylboronic Acid (5a): This compound was prepared as described for **4a**, starting with azaester **5**. White powder, m.p. 63–66 °C, yield 1.8 g (80%). ^{1}H NMR ([D$_6$]-acetone, 400 MHz): δ = 7.46 (dd, J = 7.5, 5.0 Hz, 1 H, Ph), 7.41 [br, 2 H, B(OH)$_2$], 7.18 (ddd, J = 7.5, 4.5, 1.0 Hz, 1 H, Ph), 0.32 (d, J = 1.0 Hz, 9 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 154.8 (dd, J = 240.0, 13.0 Hz), 154.2 (dd, J = 247.0, 14.0 Hz), 131.6 (d, J = 26.0 Hz), 131.1 (dd, J = 6.0, 3.0 Hz), 129.9 (dd, J = 9.0, 4.0 Hz), –1.1 ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_9H_{13}BF_2O_2Si$ (230.09): calcd. C 46.98, H 5.69; found C 47.35, H 5.43.

2,3-Difluoro-1,4-phenylenediboronic Acid (5b): This compound was prepared as described for **5a**, with B(OiPr)$_3$ (2.17 g, 12 mmol) as electrophile. White powder, m.p. > 400 °C, yield 1.8 g (90%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.41 (t, J = 1.5 Hz, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 154.2 (dd, J = 246.0, 16.0 Hz), 130.4 (t, J = 6.0 Hz), 126.2 (br) ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_6H_6B_2F_2O_4$ (201.73): calcd. C 35.72, H 3.00; found C 35.86, H 2.62.

2-(3′,5′-Dichloro-4′-formylphenyl)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (7a): This compound was prepared by starting from **7** as described for **3c**. The crude boronic acid was mixed with pinacol (1.18 g, 10 mmol) and $MgSO_4$ (1.0 g) in Et_2O (30 mL). After filtration the solvent was removed in vacuo. Recrystallization of the residue from hexane (20 mL) at –30 °C afforded the title compound as pale yellow crystals, m.p. 130–132 °C, yield 2.6 g (87%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 10.44 (s, 1 H, CHO), 7.72 (s, 2 H, Ph), 1.30 (s, 12 H, Me) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ = 188.9, 135.9, 135.2, 131.9, 84.9, 24.7 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 27 ppm. $C_{13}H_{15}BCl_2O_3$ (300.98): calcd. C 51.88, H 5.02; found C 51.84, H 5.04.

3,5-Dichloro-4-(trimethylsilyl)phenylboronic Acid Anhydride (7b): This compound was prepared by starting with azaester **7** as described for **2b**. White powder, m.p. 285–290 °C, yield 2.3 g (95%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 7.72 (s, 2 H, Ph), 0.48 (s, 9 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 141.8, 138.6, 134.7, 2.9 ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_9H_{11}BCl_2OSi$ (244.99): calcd. C 44.12, H 4.53; found C 44.52, H 4.35.

2-[3′,5′-Dibromo-4′-(trimethylsilyl)phenyl]-4,4,5,5-tetramethyl[1,3,2]-dioxaborolane (10a): This compound was prepared by starting with azaester **10** as described for **7b**. The crude boronic acid was mixed with pinacol (1.18 g, 10 mmol) and $MgSO_4$ (1.0 g) in Et_2O (30 mL). After filtration the solvent was removed in vacuo. Recrystallization of the residue from hexane (20 mL) at –30 °C afforded the title compound as a white powder, m.p. 140–143 °C, yield 2.4 g (55%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88 (s, 2 H, Ph), 1.32 (s, 12 H, Me), 0.55 (s, 9 H, SiMe$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ = 143.8, 138.5, 130.7, 84.4, 24.8, 3.8 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 27 ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz): δ = 28 ppm. $C_{15}H_{23}BBr_2O_2Si$ (434.05): calcd. C 41.51, H 5.34; found C 41.90, H 5.26.

2-{3′-Bromo-5′-fluoro-4′-iodophenyl}-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (11a): This compound was prepared by starting with **11** as described for **2a**, with iodine (2.8 g, 11 mmol) as electrophile dissolved in THF (10 mL) at –80 °C. After hydrolysis with aq. sulfuric acid (1.5 M, 10 mL) the organic phase was consecutively separated and concentrated under reduced pressure. The dark oily residue was dissolved in Et_2O (30 mL) and washed with aq. $Na_2S_2O_3$ (20 wt.-%, 20 mL). After removal of ether the residue was washed with water and hexane and dried. The crude boronic acid was mixed with pinacol (1.18 g, 10 mmol) and $MgSO_4$ (1.0 g) in Et_2O (30 mL). After filtration the solvent was removed in vacuo. Recrystallization of the residue from hexane (20 mL) at –20 °C afforded the title compound as colourless crystals, m.p. 92–94 °C, yield 3.1 g (73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 1 H, Ph), 7.34 (dd, J = 8.0, 1.0 Hz 1 H, Ph), 1.33 (s, 12 H, Me) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ = 162.2 (d, J = 248 Hz), 133.9 (d, J = 2.5 Hz), 130.7, 119.0 (d, J = 23.0 Hz), 94.2 (d, J = 27.0 Hz), 84.6, 24.8 ppm. ^{11}B NMR (64.2 MHz, $CDCl_3$): δ = 25.3 ppm. $C_{12}H_{14}BBrFIO_2$ (426.86): calcd. C 33.77, H 3.31; found C 34.12, H 3.00.

2-Fluoro-5-(trifluoromethyl)-1,3-phenylenediboronic Acid (12a): This compound was prepared by starting with azaester **12** as described for **2c**, except that the reaction mixture was allowed to warm to 0 °C after the addition of B(OiPr)$_3$. White powder, dec. >350 °C, yield 2.1 g (83%). ^{1}H NMR ([D$_6$]acetone, 400 MHz): δ = 8.06 (d, J = 4.0 Hz, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR ([D$_6$]acetone, 100.6 MHz): δ = 173.1 (d, J = 251.0 Hz), 136.0 (d, J = 7.5 Hz), 126.1 (q, J = 32.0 Hz), 125.3 (q, J = 271.5 Hz), 122.3 (br) ppm. ^{11}B NMR ([D$_6$]acetone, 64.16 MHz): δ = 28 ppm. $C_7H_6B_2F_4O_4$ (251.74): calcd. C 33.40, H 2.40; found C 33.56, H 2.37.

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