Conversion of Arylboronic Acids into Potassium Aryltrifluoroborates: Convenient Precursors of Arylboron Difluoride Lewis Acids

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Reaction of $ArB(OH)_2$ (**3**) with KHF_2 affords crystalline salts $KArBF_3$ (**2**). In the presence of TMSCl in acetonitrile, **2a** reacts to give NMR signals typical of $PhBF_2$ in acetonitrile solution. When the reaction of **2** + TMSCl is performed in the presence of potential Lewis bases, the trivalent borane **1** is intercepted, resulting in organoboron complexes. Thus, the oxazaborolidinones **7**–**10** have been prepared from amino acid-derived amidine carboxylates $NaO_2CCH(R)N{=}CHNMe_2$ (R = H or phenyl). Complexes **11** and **12** derived from 1,3-diketones are also easily prepared. The KHF_2 fluoride exchange coupled with the TMSCl activation method allows *in situ* generation of $ArBF_2$ without having to handle corrosive trivalent boron halides.

We have been interested in the preparation of amino acid-derived oxazaborolidinones as part of our study of crystallization-induced asymmetric transformation.[1] In the early stages of this work, we prepared several oxazaborolidinones from amino acid derivatives by treatment with $PhBF_2$ (**1a**).[2] The trivalent boron reagent was prepared from $PhBCl_2$ according to the published method,[2] but both the starting material and the product were unpleasant to handle. Similar problems have been encountered with other arylboron difluorides.[2,3] Since we anticipated the need to explore several different arylboron environments, experiments were initiated to find a convenient way to generate $ArBF_2$ *in situ*, ideally without using corrosive trivalent boron reagents.

Several strategies have been reported in the literature that circumvent the problem of handling reactive Lewis acids. One option is to use the relatively stable Lewis base complexes (e.g., $BH_3{\cdot}SMe_2$, $R_2HB{\cdot}Me_2NCH_2CH_2NMe_2{\cdot}BHR_2$, $TiCl_4{\cdot}AsPh_3$) as precursors,[4] and another is to employ anionic "ate" species (salts such as $KRBF_3$, $LiBF_4$, $NaBPh_4$, $LiMeBH_3$) as the starting materials.[3,5,6] Under suitable activation conditions, the tetravalent "ate" complexes may function as *in situ* sources of the trivalent borane derivatives. This is illustrated by the reversible dissociation of $LiBF_4$ into BF_3 + LiF at room temperature,[5a] by the acid treatment of $LiMeBH_3$ to generate $MeBH_2$,[5b] or by the conversion of $R_2HB{\cdot}Me_2NCH_2CH_2NMe_2{\cdot}BHR_2$ into R_2BH upon treatment with $BF_3{\cdot}$etherate.[4c] In a more subtle example, $NaBPh_4$ can be used as a replacement for Ph_2BX reagents in the conversion of amino acids into the crystalline and easily isolated 2,2-diphenyl-1,3,2-oxazaborolidin-5-ones, derivatives that can be convenient for purposes of purification. Presumably, hydrolytic cleavage converts the Ph_4B^- ion into a more reactive trivalent intermediate in this case.[6]

In the most relevant prior example, Kaufmann *et al.* showed by ^{11}B NMR that K(ipc)BF_3 liberates (ipc)BF_2 when treated with $BF_3{\cdot}OEt_2$ in acetonitrile (ipc = isopinocampheyl).[3] This experiment demonstrates the possibility of releasing an unstable chiral Lewis acid from a relatively stable alkyltrifluoroborate salt. A literature search also uncovered isolated reports mentioning potassium aryltrifluoroborates[7] and vinyltrifluoroborates,[8,9] structures that might serve as suitable precursors of substituted difluoroboranes. For instance, Stafford prepared $K(CH_2{=}CH)BF_3$ from $(CH_2{=}CH)BF_2$ and KF and demonstrated that it reverts to the starting materials when heated to >250 °C.[8] In contrast to the trivalent vinyldifluoroborane, which hydrolyzes readily to ethylene, the tetravalent "ate" salt potassium vinyltrifluoroborate is stable for days in water. Despite these important observations, the synthetic potential of the alkyl- or aryltrifluoroborate species as *in situ* sources of trivalent boron halide Lewis acids has not attracted much attention. In this paper we report an expedient synthesis of a number of stable salts $KArBF_3$ (**2**) and their facile activation by fluorophiles to give intermediates that function as sources of the corresponding aryldifluoroboranes **1**. In addition, we demonstrate the use of **2** for the preparation of boron heterocycles from amino acid derivatives or 1,3-dicarbonyl compounds.

For our initial studies on the reactivity of the borate salts, $KPhBF_3$ (**2a**) was prepared from $PhBCl_2$ and KF

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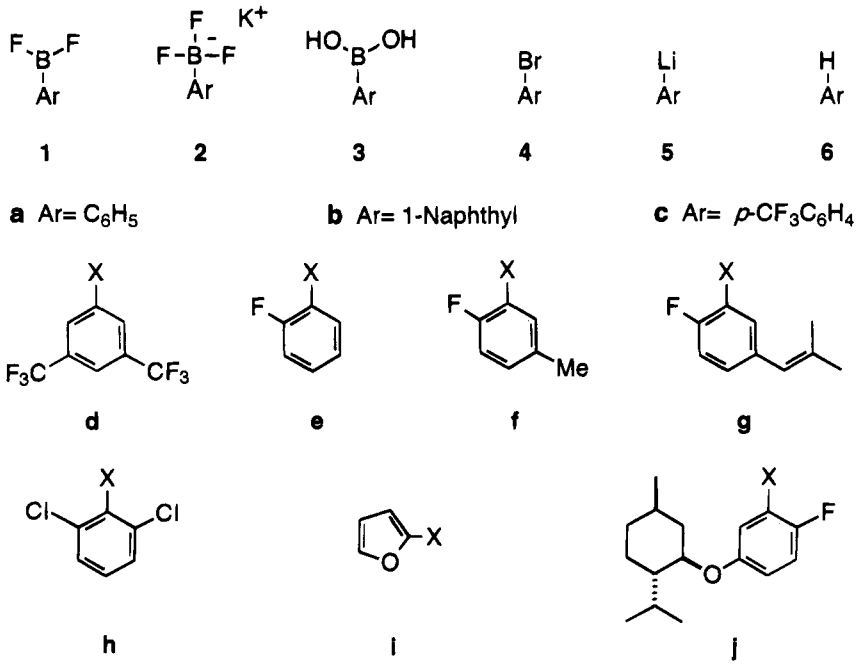
Scheme 1



by analogy to the procedure of Kaufmann et al.[3] Ultimately, however, this approach is not ideal because it still requires dealing directly with the reactive RBX_2 starting material. A far more convenient alternative would be to prepare the desired salts directly from boronic acid precursors that are readily available and air-stable. The potential advantages of this approach were recognized early on,[2] but were frustrated by the sensitivity of arylboronic acids to protodeboronation. A possible solution to the problem was deduced from a literature analogy.[7a] Thus, Thierig and Umland noted that the reaction of the ethanolamine complex of Ph_2BOH (2,2-diphenyl-1,3,2-oxazaborolidine) with aqueous KHF_2 results in formation of KPh_2BF_2. This observation shows that the inexpensive KHF_2 can function as a fluoride ion source, and that it can activate a relatively unreactive boronate structure for ligand exchange under weakly acidic conditions. It also suggests that the diphenyldifluoroborate anion may be thermodynamically more stable under the reaction conditions than is Ph_2BOH (diphenylborinic acid), the initial product expected from "ate" dissociation and hydrolytic cleavage. Thierig and Umland noted that heating the same reactants in glacial acetic acid gave $KPhBF_3$ (**2a**) in unstated yield. While they did not provide experimental details or discuss the mechanism, this transformation would appear to involve intermediates having one B–phenyl and at least one B–oxygen bond, and might well involve phenylboronic acid, the most desirable starting material for direct conversion to the potassium phenyltrifluoroborate salt. A simple, high-yielding procedure for the synthesis of **2a** was devised by extrapolating from these observations as follows. Treatment of a concentrated solution of phenylboronic acid in methanol with saturated aqueous KHF_2 resulted in an exothermic reaction and immediate formation of a precipitate. Collection of the crystals by filtration and recrystallization from acetonitrile afforded an 82% yield of spectroscopically pure $KPhBF_3$ (**2a**). The fluoride exchange did not take place when KF was used in place of KHF_2. The phenyltrifluoroborate salt obtained as described above was not appreciably hygroscopic and could be stored in air for many months without significant decomposition. The structural assignment was confirmed by the ^{11}B NMR spectrum, which has a chemical shift appropriate for tetracoordinate boron (δ 4.1 ppm relative to borontrifluoride etherate)[10] and shows coupling to three equivalent fluorine atoms (^2J = 47 Hz). Aqueous solutions of the salt are somewhat acidic, suggesting the existence of an equilibrium between the tetracoordinated "ate" species and products of hydrolytic cleavage or ligand exchange. The efficient formation of the salt in aqueous methanol must therefore be a consequence of the thermodynamic stability of the phenyltrifluoroborate anion and of the added driving force provided by its low solubility in the reaction medium.

A number of other aryltrifluoroborates have been prepared by this method (Table 1; Scheme 1). The requisite arylboronic acid precursors **3b–d** were synthesized using variants of the method of Snieckus *et al.* and Brown *et al.*[11a,c] Thus, commercially available aryl bromides **4b–d** were converted into the aryllithium reagents **5b–d** by exchange with *n*-butyllithium or *tert*-butyllithium (Table 1; method A). Reaction with $B(OiPr)_3$ or $B(OMe)_3$ and hydrolysis then gave the arylboronic acids **3b–d**. In the other examples (Table 1; method B), the aryllithium reagents were prepared from **6e–j** by direct ortho-metalation of the activated aryl C–H bonds using *n*-butyllithium (**5h,i**) or *sec*-butyllithium (**5e–g,j**). The metalation approach to arylboronic acids has been used extensively, although other activating groups were usually involved.[11a] As before, reaction of **5e–j** with $B(OiPr)_3$ or $B(OMe)_3$ followed by hydrolysis gave arylboronic acids. The crude arylboronic acids were typically used without purification for the conversion to potassium

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Table 1. Preparation of Aryltrifluoroborates 2

entry	starting material	method (RLi)	% yield of 3	$KArBF_3$	% yield of 2
1	$PhB(OH)_2$	–	–	**2a**	80
2	**4b**	A (*n*-BuLi)	84[a]	**2b**	82
3	**4c**	A (*tert*-BuLi)	*b*	**2c**	91[f]
4	**4d**	A (*tert*-BuLi)	*b,c*	**2d**	68[f]
5	**6e**	B (*sec*-BuLi)	81	**2e**	94
6	**6f**	B (*sec*-BuLi)	92	**2f**	93
7	**6g**	B (*sec*-BuLi)	93	**2g**	76
8	**6h**	B (*n*-BuLi)	*b,d*	**2h**	53
9	**6i**	B (*n*-BuLi)	*b*,e	**2i**	48[f]
10	**6j**	B (*sec*-BuLi)	*b*	**2j**	76[f,g]

[a] **3b**: ref 15b. [b] The arylboronic acid **3** was not purified; one-pot conversion into **2**. [c] **3d**: ref 15a. [d] **3h**: ref 15a. [e] **3i**: ref 16. [f] Overall yield based on the indicated starting material (far left column). [g] The starting menthyl *p*-fluorophenyl ether was made by Ullman coupling (ref 17) from *p*-fluorobromobenzene.

aryltrifluoroborate salts **2e–j**. This is feasible because byproducts such as trimeric or oligomeric boronic anhydrides also appear to be reactive in the KHF_2 fluoride exchange procedure. Thus, several aryltrifluoroborates were obtained in good yield using a one-pot approach (Table 1; entries 3, 4, 11). Lower yields in the furan example reflect increased difficulty in the metalation[12] and greater sensitivity of the 2-furylboronic acids to acid-induced protodeboronation.

The best results were obtained with the fluorophenyl or (trifluoromethyl)phenyl substrates. The corresponding fluorine-substituted arylboronic acids are resistant to protodeboronation, and **3e–g** are also relatively well-behaved in the sense that they can be crystallized with relatively minor contamination by boronic anhydrides. However, the relative purity of the fluoroaromatic boronic acids is not the decisive factor in the yield of **2**. As already noted, even a relatively stable ethanolamine-derived "ate" complex of diphenylborinic acid is reactive with KHF_2.[7a] Thus, it seems likely that any aryl-substituted substrate having heteroatom bonds at tetravalent or trivalent boron would be subject to the same conversion into potassium fluoroborate salts **2**, provided that protodeboronation is controlled.

In all of the fluoroaromatic substrates, metalation occurred selectively next to the fluorine substituent using *sec*-BuLi in THF at −78 °C.[13] This result was easily predictable for **6e–g**, but it was not clear that the same preference should be expected in the case of phenyl menthyl ether **6j** (the precursor to **5j** and **2j**). Good selectivity is somewhat surprising in view of prior experience with the metalation of *p*-alkoxyfluorobenzene derivatives.[13] In the absence of strong lithium complexing agents, metalation next to alkoxy oxygen can be competitive or even dominant. However, there is some evidence that the relatively bulky TBS ethers are not effective directing groups in these metalations.[13b] Apparently, the menthyloxy substituent is also too hindered to promote ortho metalation, and the fluorine directing effect dominates.

The isolated yields of aryltrifluoroborate salts were usually in the range of 70% or better, but there were two exceptions. In the furan example (entry 9), yields were low because the intermediate boronic acid **3i** is sensitive to protodeboronation. A different problem was encountered in the boronation of (2,6-dichlorophenyl)lithium case, probably because **5h** decomposes at −50 °C or above.[14] However, the corresponding salt **2h** was stable and easy to handle.

With a variety of aryltrifluoroborates available, attention was turned to the use of these reagents for the *in situ* generation of arylboron difluorides. This conversion requires an agent that can assist in the removal of fluoride from tetrahedral boron. Previous reports indicate that the parent tetrafluoroborate salts $M^+ BF_4^-$ vary greatly in stability, depending on the cation. Thus, $LiBF_4$ is in equilibrium with BF_3 well below room temperature while $NaBF_4$ begins to decompose only above 270 °C and KBF_4 survives to even higher temperatures.[5a] In addition to the difference in kinetic stability, there is a large difference in dissociation enthalpy that strongly favors KBF_4 over KF + BF_3, in contrast to the behavior of $LiBF_4$.[5a] Not surprisingly, it was found that the stability of the aryltrifluoroborate ion is also highly dependent on the identity of the metal counterion. Several potential "fluorophiles" were screened using ^{11}B NMR spectroscopy to monitor the fate of the $PhBF_3^-$ anion. It was found that $KPhBF_3$ rapidly decomposes to phenylboronic acid in the presence of lithium or magnesium cations, presumably via dissociation into $PhBF_2$ and the lithium or magnesium fluorides followed by hydrolysis. This result is consistent with the well-known fact that the addition of organolithium or Grignard reagents to BF_3 results in multiple additions of the organometallic reagent.[2] This occurs because the intermediate ate species can easily dissociate to give LiF or MgF_2, thereby regenerating reactive trivalent boranes. Thus, Mg^{2+} or Li^+ could possibly serve as fluorophiles that convert aryltrifluoroborate species into the arylboron difluorides. However, the complication of having to use anhydrous lithium or magnesium salts to avoid B–F bond hydrolysis prompted us to look for more convenient fluorophiles. We turned our attention to silicon-containing compounds.

The strength of the Si–F bond is the driving force for a number of common reactions, such as the deprotection of trialkylsilyl ethers and the generation of enolates from enol silanes with tetrabutylammonium fluoride. In the present context it is significant that $LiBF_4$ can be used as a reagent for silyl ether deprotection,[17] a transformation that appears to involve the generation of BF_3, Lewis acid activation of oxygen, and ultimately, the transfer of fluoride from the ate complex to silicon. In effect, the silyl ether acts as a fluorophile that drives the kinetically facile dissociation of lithium tetrafluoroborate anion. As expected from this analogy, the relatively electron-deficient trimethylsilyl chloride was found to be an effective fluorophile in the reaction with aryltrifluoroborates. This simple activation technique has proven to be suitable for the generation and trapping of species having the reactivity expected for $ArBF_2$.

The ^{11}B resonance of **2a** in acetonitrile (δ 4.1 ppm) is a quartet due to coupling to three fluorine substituents.

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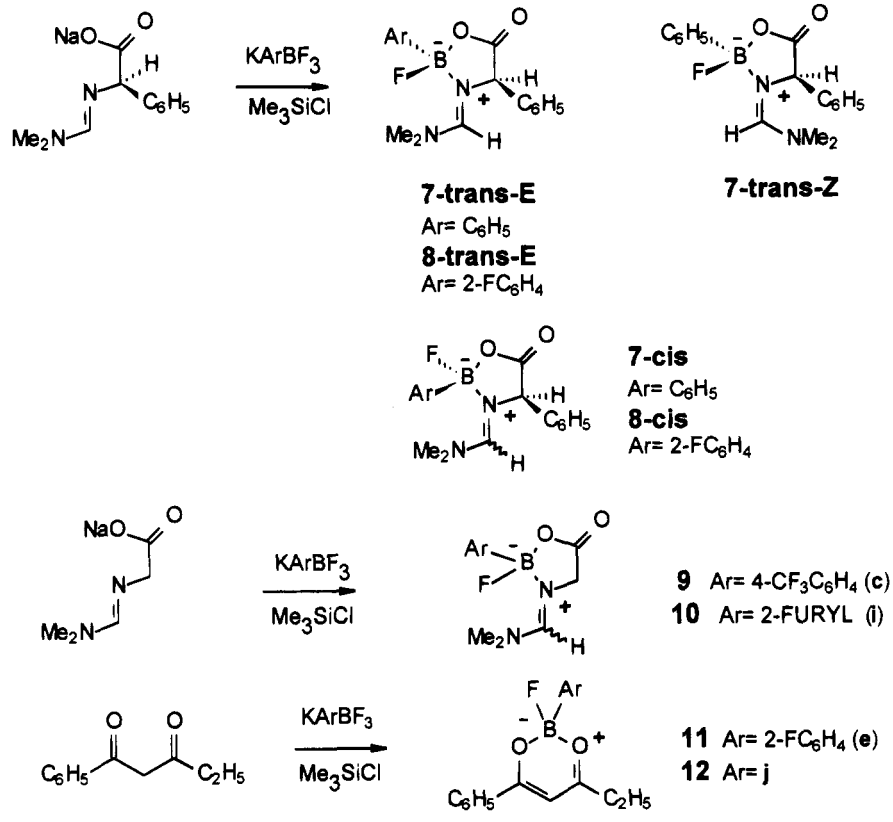
Scheme 2



When a trace of TMSCl (<0.1 equiv) was added to the NMR sample, the coupling vanished and a white precipitate (presumably KCl) appeared. Incremental addition of 1 equiv of TMSCl resulted in a steady downfield progression of the ^{11}B signal to 16 ppm, a chemical shift that corresponds to authentic $PhBF_2$ in acetonitrile. These observations are consistent with the formation of $PhBF_2$ (**1a**) from **2a** and TMSCl, followed by rapid exchange of fluoride between the $PhBF_3^-$ anion and trivalent $PhBF_2$. This process averages the fluorine environment and the ^{11}B chemical shifts, and also collapses the $^{11}B-^{19}F$ splitting pattern. The observed resonance at intermediate ratios of TMSCl and **2a** is therefore a weighted average of the individual ^{11}B signals for the tetravalent **2a**, trivalent **1a**, and acetonitrile-coordinated **1a**. Similar behavior was observed with **2h** (δ 2.82 ppm, q, $^1J_{B-F}$ = 48 Hz) although excess Me_3SiCl (ca. 2 equiv) caused a relatively small change in the chemical shift (to δ ca. 9 ppm), as expected for an equilibrium involving **2h** and **1h**. The presence of the electron-deficient 2,6-dichlorophenyl group should result in increased stability for the anionic ate complex **2h** compared to **1h**. Thus, TMSCl is less effective in converting **2h** into **1h** compared to the analogous experiment with **2a**.

The mechanistic details of the process by which fluoride ion is removed from boron were not studied. However, a spontaneous equilibrium between **2a** or **2h** and KF + $ArBF_2$ (**1**) on the NMR time scale is ruled out by the $^{11}B-^{19}F$ coupling pattern (acetonitrile conditions). Direct interaction between silicon in TMSCl and fluorine in **2** appears obligatory in the activation step, but subsequent events are less clear. No effort was made to isolate **1a** or **1h** because our goal was to avoid handling arylboron difluorides. For simplicity, we shall assume that **1** is released from a silicon-activated intermediate containing a B–F–Si linkage by simple B–F heterolysis, but we cannot exclude other possibilities.

The NMR experiments suggest that **1a** and **1h** can be released from the aryltrifluoroborate salts **2a** and **2h**. To confirm that reactive species equivalent to trivalent **1** are generated in solution, the TMSCl activation method was applied to the preparation of several representative boron heterocycles. Thus, stirring a suspension of the D-phenylglycine- or glycine-derived amidine carboxylates $NaO_2CCHPhN{=}CHNMe_2$ or $NaO_2CCH_2N{=}CHNMe_2$ with the substituted aryltrifluoroborate salts **2a,e,c,i** in THF in the presence of TMSCl gave oxazaborolidinones **7-trans** (78%), **8-trans**, (71%), **9** (79%), or **10** (38%), respectively, after crystallization. The isolation of the *B*-furanyl derivative **10** confirms generation of **1i** or its equivalent from **2i**, but the yield is poor, probably due to the protodeboronation problem mentioned earlier. On the other hand, representative *B*-phenyl derivatives react without complications, as indicated by the good yields of the corresponding oxazaborolidinones.

Structures **7–10** were found to be mixtures of amidine *E/Z* rotamers in solution. In the case of **7** and **8**, the NMR spectra of the crude products were further complicated by the presence of 10–30% of the diastereomers **7-cis** and **8-cis** which also existed as *E/Z* rotamer mixtures. Since the crystallized products are known to have *E*-amidine geometry as shown in **7-trans-E** (X-ray analysis),[1c] it was possible to interpret the NMR spectra by monitoring the signals from variable temperature experiments. Thus, a solution of **7-trans-E** in CD_2Cl_2 prepared at −70 °C was found to contain a single isomer (C_4 methine proton at δ 5.21 ppm). When the solution was allowed to warm to −58 °C over 1 h, traces of a new signal at δ 5.45 ppm were detected. Warming gave a progressively larger signal at δ 5.45 ppm until the equilibrium ratio of amidine rotamers, 3:1 **7-trans-E**:**7-trans-Z**, was

reached at room temperature. Both the δ 5.21 and 5.45 ppm signals were observed as doublets due to fluorine coupling (^4J = 3.7 Hz). Further warming in dichloromethane resulted in the gradual appearance of signals assigned to **7-cis**, but the trans/cis equilibration was more conveniently monitored in CD_3CN. After warming to 70 °C in this solvent, two new signals for **7-cis-E** and **7-cis-Z** appeared (δ 5.68, 5.28 ppm; 1:1 ratio) in addition to the methine signals of **7-trans-E** (δ 5.33 ppm) and **7-trans-Z** (δ 5.62 ppm). In contrast to **7-trans**, the methine signals of **7-cis** were not split appreciably by fluorine (singlets; ^4J = <1 Hz). Attempts to purify **7-cis** invariably gave isomer mixtures due to the facile interconversion of diastereomers.

As already mentioned, the ratio of **7-trans**:**7-cis** at equilibrium was 3:1 at 70 °C. Surprisingly, this product ratio was considerably altered (as high as 99:1 **7-trans**:**7-cis**) after removal of solvent on a rotary evaporator (bath temperature 30–40 °C). This behavior is due to the crystallization-induced asymmetric transformation phenomenon discussed in the accompanying paper[1b] and involves reversible epimerization at boron. The alternative possibility of epimerization at carbon was ruled out by cleavage of **7-trans** to the starting (*R*)-phenylglycine. Thus, **7-trans** was dissolved in warm methanol and ethylenediamine (5 equiv), and a catalytic amount of HCl was added. After solvent removal, (*R*)-phenylglycine was recovered (88%) with no change in optical rotation (>95% ee). This evidence confirms boron epimerization as the mechanism for interconversion of **7-cis** and **7-trans** and also demonstrates that synthesis of **7** using the *in situ* generation of $PhBF_2$ proceeds without racemization of the phenylglycine substrate.

Crystallization-induced asymmetric transformation was not encountered in the *B*-(2-fluorophenyl) series (**8**) derived from **1e**. Conventional chromatography or crystallization could be used to separate the relatively stable diastereomers **8-trans** and **8-cis**. In contrast to the *B*-phenyl analog **7-trans**, the *o*-fluorophenyl derivative **8-trans** did not isomerize, even after heating to 100 °C in toluene. Traces of equilibration did occur when **8-trans** or **8-cis** were heated in acetonitrile, and some decomposition was also observed under these conditions. Attempts to recrystallize **8-cis** may also have encountered minor equilibration, and this isomer could not be obtained completely pure (ca. 5% of **8-trans** contaminant). However, the interconversion of **8-cis** and **8-trans** was considerably slower than the analogous process in the *B*-phenyl series (**7**). This observation is consistent with reversible B–N cleavage as the mechanism for boron epimerization.[1b] The relatively electronegative fluorophenyl group stabilizes the ate complex **8** and prevents boron epimerization via trivalent intermediates.

Conversion of 1,3-dicarbonyl compounds into cyclic boron complexes was also examined briefly using the same TMSCl activation method. Thus, 1-phenylpentane-1,3-dione was stirred with the salts **2e** or **2j** in THF at room temperature with excess TMSCl. Structure **12** was obtained as an inseparable mixture of two diastereomers (two epimers at stereogenic boron relative to stereogenic carbon in the menthyloxy substituent) and did not crystallize. However, no geometrical isomers are possible with **11**. This substance crystallized upon solvent removal and was obtained in nearly quantitative yield.

In summary, we have prepared a variety of $KArBF_3$ salts **2**. The salts are available on multigram scale from arylboronic acids and KHF_2. This method solves an old problem by providing access to reactive arylboron difluorides without resorting to corrosive reagents. The potassium aryltrifluoroborate salts **2** are crystalline, water-resistant materials that can be stored without special precautions. Generation of reactive Lewis acids occurs under mild conditions upon treatment with chlorotrimethylsilane as the fluorophile, and conversion into boron-containing heterocycles is possible in the presence of difunctional reactants.

Experimental Section

Potassium Phenyltrifluoroborate (2a). Phenylboronic acid (20 g, ca. 169 mmol, Aldrich; ca. 80% $PhB(OH)_2$, ca. 20% $(PhBO)_n$) was dissolved in 50 mL of methanol. Excess saturated KHF_2 (125 mL, ca. 4.5 M solution, ca. 563 mmol) was added slowly with vigorous stirring. After 15 min, the precipitated product was collected and washed with cold methanol. Recrystallization from minimal acetonitrile produced 25.5 g (138 mmol, 82%) of pure **2a**, mp 296 °C dec, lit. 290 °C);[7a] anal. calcd: C, 39.16; H, 2.74; found: C, 39.12; H, 3.02; 200 MHz NMR (CD_3CN, ppm) δ 7.44–7.41 (2H, m), 7.22–7.05 (3H, m); 160 MHz ^{11}B NMR (CD_3CN, ppm) δ 4.1 (q, J = 57 Hz); 470 MHz ^{19}F NMR (CD_3CN, ppm vs $CF_3C_6H_5$) δ −79 (1:1:1:1 q, J = 57 Hz).

Potassium 1-Napthyltrifluoroborate (2b). The procedure was similar to that described for **2a**. Pure material (0.221 g, 82% from 0.2 g of 1-naphthylboronic acid[15b]) was obtained by extracting the initial precipitate with hot acetonitrile (2 × 10 mL), evaporation, and recrystallization of the residue from hot acetonitrile, mp 205 °C dec, anal. calcd: C, 51.31; H, 3.01; found: C, 50.99; H, 3.16; 200 MHz NMR (CD_3CN, ppm) δ 8.42–8.39 (1H, m), 7.78–7.71 (1H, m), 7.63 (2H, d, J = 7.7 Hz), 7.40–7.29 (3H, m); 160 MHz ^{11}B NMR (CD_3CN, ppm) δ 4.4 (q, J = 54 Hz).

Potassium 3,5-Bis(trifluoromethyl)phenyltrifluoroborate (2d) by the One-Pot Procedure (Method A). To a solution of 3,5-bis(trifluoromethyl)bromobenzene (4.0 mL, 23.0 mmol) in 20 mL of ether at −78 °C was added dropwise 2 equiv of *tert*-BuLi (1.7 M in pentane, 27 mL, 46.0 mmol). The resulting solution was stirred at −78 °C for 2 h and another 15 min at room temperature. The lithium reagent thus obtained was chilled with a dry ice–acetone bath and dropped into a solution of $B(Oi\text{-}Pr)_3$ (5.3 mL, 23.0 mmol, distilled from sodium) in 100 mL of ether via cannula at −78 °C. After stirring for another 2 h at this temperature, the reaction mixture was allowed to warm to 0 °C and was then quenched by addition of 30 mL of H_2O. After the pH of the aqueous layer was adjusted to 2 with concentrated HCl, the organic phase was separated, and the aqueous phase was extracted with ether (2 × 30 mL). The organic solution was combined, dried ($MgSO_4$), and concentrated to give an oil containing the known boronic acid,[15a] boronic anhydrides, and residual boronic esters due to incomplete hydrolysis. This mixture was satisfactory for the conversion to the potassium aryltrifluoroborate salt in all examples where the arylboronic acid was not purified.

The crude boronic acid obtained above was refluxed with 4.9 g of KHF_2 in 100 mL of MeOH and 20 mL of H_2O for 12 h. The solution was concentrated (rotary evaporator), and the solid residue was extracted with CH_3CN (3 × 20 mL, room temperature). After filtration and evaporation of the acetonitrile, pure material (5.0 g, 68% from 3,5-bis[trifluoromethyl]-bromobenzene) was obtained by recrystallization from ether/hexane, mp 320 °C dec, colorless crystals. Anal. Calcd: C, 30.02; H, 0.94, found: C, 29.70; H, 0.63; IR (KBr, cm^{-1}) 1619, C=C; 1128, C–F; 200 MHz NMR (CD_3CN, ppm) δ 7.96 (2H, s) 7.72 (1H, s).

Potassium 4-(Trifluoromethyl)phenyltrifluoroborate (2c). Method A was used to prepare the arylboronic acid from 4-(trifluoromethyl)bromobenzene (Aldrich, 3.2 mL, 22.8 mmol), *tert*-BuLi (26.9 mL, 1.7M in pentane, 45.6 mmol), and $B(OiPr)_3$ (5.3 mL, 22.8 mmol). After the usual workup, the crude arylboronic acid was dissolved in 100 mL of methanol and 20

mL of water, and 5.9 g of KHF_2 (Aldrich, 75.6 mmol) was added. After refluxing for 36 h, the reaction mixture was concentrated to dryness by aspirator, and the solid residue was extracted with hot acetonitrile (2 × 30 mL). Then the combined acetonitrile solution was concentrated to dryness, and the solid was washed with ether to give essentially pure product (5.3 g, 91% from 4-(trifluoromethyl)bromobenzene). Recrystallization from ethyl acetate/ether gave **2d**, mp 305 °C dec, as colorless crystals. Anal. Calcd: C, 33.36; H, 1.60, found: C, 32.97; H, 1.33; IR (KBr, cm^{-1}) 3091, =C−H; 1331, C−F; 959, B−F; 200 MHz NMR (CD_3CN, ppm) δ 7.60 (2H, d, J = 7.8 Hz), 7.46 (2H, d, J = 7.8 Hz); 160 MHz ^{11}B NMR (CD_3CN, ppm) δ 3.3.

2-Fluoro-5-methylphenylboronic Acid (3f) by Metalation of 6f (Method B). A solution of 4-fluorotoluene (5.0 mL, 45 mmol, Aldrich) in 100 mL of dry THF was chilled in a dry-ice/acetone bath under nitrogen. *sec*-BuLi (48 mL of a 1.0 M solution in cyclohexane, 48 mmol, Aldrich) was added over 10 min, and the resulting yellow solution was allowed to stir for an additional 10 min. Trimethyl borate (Aldrich, 5.4 mL, 48 mmol, distilled over sodium) was added over 1 min, and the solution was allowed to warm to room temperature. The reaction was quenched by the additon of 50 mL of 10% aqueous HCl, and the mixture was diluted with 50 mL of ether. The organic portion was saved and was extracted with 1 N NaOH (2 × 50 mL). The basic extracts were combined and acidified to pH 3 by the addition of 10% aqueous HCl. The mixture was ether extracted (3 × 50 mL), and the organic layer was saved and subsequently concentrated (aspirator) to yield colorless crystals (6.7 g, 96%). Analytical TLC on silica gel, EtOAc, R_f = 0.72. Pure material (6.4 g, 92%) was obtained by crystallization from dichloromethane, mp 168−170 °C dec. Due to the ease of boronic anhydride formation, this material was analyzed after the next step, at the stage of the salt **2f**. Data for **3f**: IR (KBr, cm^{-1}) 3300, O−H; 1400, B−O; 200 MHz NMR ($CDCl_3$, ppm) δ 7.47 (1H, dd, J = 2.1, 6.2 Hz), 7.25 (1H, ddd, J = 2.1, 5.6, 8.6 Hz), 6.94 (1H, dd, J = 8.6, 9.9 Hz), 6.12 (1H, s), 6.11 (1H, s), 2.3 (3H, d, J = 0.5 Hz).

2-Fluorophenylboronic Acid (3e). Method B was used starting with fluorobenzene (5.0 mL, 53 mmol, Aldrich), *sec*-BuLi (56 mL of a 1.0M solution in cyclohexane, 56 mmol, Aldrich), and trimethyl borate (6.6 mL, 59 mmol). After the usual workup, the mixture was ether extracted (3 × 50 mL). The organic solution was allowed to stand, yielding 4.2 g of colorless plates. An additional crop yielded 1.84 g of colorless plates (6.04 g total, 81%). Analytical TLC on silica gel, EtOAc, R_f = 0.77. Nearly pure material was obtained by crystallization from ether, mp 215−217 °C dec. Due to the ease of boronic anhydride formation, this material was analyzed after the next step, at the stage of the salt **2e**. Data for **3e**: IR (KBr, cm^{-1}) 3355, O−H; 1381, B−O; 200 MHz NMR ($CDCl_3$, ppm) δ 7.85 (1H, ddd, J = 1.8, 7.1, 7.3 Hz), 7.45 (1H, dddd, J = 1.8, 6.2, 7.3, 8.2 Hz), 7.20 (1H, dddd, J = 0.8, 0.8, 7.3, 7.3 Hz), 7.05 (1H, ddd, J = 0.8, 8.2, 10.8 Hz), 5.86 (1H, s) 5.82 (1H, s).

Potassium (2-Fluorophenyl)trifluoroborate (2e). To a solution of (2-fluorophenyl)boronic acid (2.0 g, 14.4 mmol) in 20 mL of methanol was added aqueous KHF_2 (14.4 mL of a 3.0M solution in water, 43 mmol). The resulting precipitate was stirred for 20 min, and the solid mass was filtered. The solid was dissolved in 20 mL of hot acetonitrile, filtered, and allowed to stand. Colorless crystals (0.98 g) were filtered, and the mother liquor was allowed to stand to yield an addtional crop (1.23 g, 2.73 g overall or 94%). Analytical TLC on silica gel, EtOAc, R_f = 0.32. Pure material was obtained by crystallization from acetonitrile, mp 304−305 °C, colorless plates. Anal. Calcd: C, 35.67; H, 2.00, found: C, 35.38; H, 2.11; IR (KBr, cm^{-1}) 3080, =C−H; 1189, B−F; 200 MHz NMR (CD_3CN, ppm) δ 7.55−7.42 (1H, m), 7.07 (1H, dddd, J = 7.6, 7.6, 6.6, 2.0 Hz), 6.91 (1H, dd, J = 6.8, 6.6 Hz), 6.80−6.70 (1H, m); ^{11}B NMR (160 MHz, CD_3CN, ppm) δ 3.42 (q, J = 49 Hz).

Potassium (2-Fluoro-5-methylphenyl)trifluoroborate (2f). To a solution of (2-fluoro-5-methylphenyl)boronic acid (5.0 g, 33 mmol) from method B, above, in 40 mL of methanol was added aqueous KHF_2 (33 mL of a 3.0 M solution, 99 mmol). The resulting suspension was stirred for 20 min, and removal of solvent (aspirator) provided a solid mass which was dissolved in hot acetonitrile and suction filtered. The solution was concentrated (aspirator) to yield crystalline material (6.9 g, 97%). Analytical TLC on silica gel, EtOAc, R_f = 0.32. Pure material (6.6 g, 93%) was obtained by crystallization from acetonitrile, mp 265−267 °C as colorless needles. Anal. Calcd: C, 38.91; H, 2.81, found: C, 38.66; H, 3.04; IR (KBr, cm^{-1}) 3042, =C−H; 990, B−F; 200 MHz NMR (CD_3CN, ppm) δ 7.16 (1H, d, J = 2.9 Hz), 6.87 (1H, ddd, J = 2.9, 5.3, 8.7 Hz), 6.66 (1H, dd, J = 8.7, 8.7 Hz), 2.18 (3H, d, J = 0.8 Hz); ^{11}B NMR (160 MHz, CD_3CN, ppm) δ 3.32 (q, J = 49 Hz).

Preparation of 1-(*p*-Fluorophenyl)-2-methyl-1-propene (6g). Step 1. 1-(*p*-Fluorophenyl)-2-methyl-1-propanol. A solution of 4-fluorobenzaldehyde (Aldrich, 20 mL, 186 mmol) in 100 mL of anhydrous ether was chilled in an ice−water bath and to it was added dropwise isopropylmagnesium chloride (Aldrich, 120 mL of a 2 M solution in ether, 240 mmol, 1.3 equiv). The resulting suspension was stirred for 1 h and was allowed to warm to room temperature over 1 h. The suspension was rechilled in an ice−water bath, and 100 mL of saturated aqueous ammonium chloride was added slowly. The organic layer was saved and washed with distilled water (2 × 100 mL) and brine (2 × 100 mL). Removal of solvent (aspirator) yielded a liquid (29.1 g, 93% crude), which was distilled (0.5 torr, 63−65 °C) to provide 28.7 g of the title compound (92% yield), which was sufficiently pure for the next step.

Step 2. 1-(*p*-Fluorophenyl)-2-methyl-1-propene (6g). A solution of 1-(*p*-fluorophenyl)-2-methyl-1-propanol (5.1 g, 30 mmol) and *p*-TsOH·H_2O (0.57 g, 3 mmol) in 80 mL of toluene was refluxed under a Dean−Stark trap for 40 min. After cooling, saturated aqueous sodium bicarbonate (30 mL) was added, the organic layer was extracted with water (2 × 25 mL) and brine (2 × 25 mL) and was dried over Na_2SO_4. The solvent was removed (aspirator) to give 4.3 g of an oil (96%), and short path distillation gave a clear liquid, bp 183−185 °C (740 mm); analytical TLC on silica gel, hexane, R_f = 0.46; molecular ion calcd for $C_{10}H_{11}F$: 150.08447; found m/e = 150.0848, error = 2 ppm; base peak = 135 amu; IR (neat, cm^{-1}) 2970, =C−H; 1506, C=C; 1227, C−F; 200 MHz NMR ($CDCl_3$, ppm) unknown minor impurity, singlets at δ 4.82, 4.70, 3.26, 1.66 ppm; **6g**, δ 7.16 (2H, dd, J = 5.7, 8.5 Hz); 6.97 (2H, dd, J = 8.5, 8.7 Hz), 6.2 (1H, br s), 1.88 (3H, d, J = 1.3 Hz), 1.81 (3H, d, J = 1.3 Hz).

[2-Fluoro-5-(2-methyl-1-propenyl)phenyl]boronic Acid (3g). A solution of 1-(*p*-fluorophenyl)-2-methyl-1-propene (2.0 g, 13.3 mmol) in 40 mL of anhydrous THF was chilled in a dry-ice/acetone bath. To it was added *sec*-BuLi (11.3 mL of a 1.3 M solution in cyclohexane, 14.6 mmol, Aldrich) over 5 min. The reaction was worked up as described for method B to yield crystalline material which was filtered and rinsed with cold ether to yield a white solid (2.01 g, 93%). This material was sufficiently pure for the next step.

Potassium [2-Fluoro-5-(2-methyl-1-propenyl)phenyl]trifluoroborate (2g). To a solution of [2-fluoro-5-(2-methyl-1-propenyl)phenyl]boronic acid (2.01 g, 12.3 mmol) in 15 mL methanol was added aqueous KHF_2 (12.3 mL of a 3.0 M aqueous solution, 36.9 mmol). After stirring for 1 h, the solvent was removed (aspirator) to yield a solid which was dissolved in 30 mL of THF and suction filtered. The solvent was removed to yield a solid (2.55 g, 81%). Pure material (2.4 g, 76% yield from the boronic acid) was obtained by crystallization from tetrahydrofuran, mp 193−193 °C, colorless plates. Analytical TLC on silica gel, EtOAc, R_f = 0.41. Anal. Calcd: C, 46.89; H, 3.94, found: C, 46.48; H, 4.04; IR (KBr, cm^{-1}) 3021, =C−H; 951, B−F; 200 NMR (CD_3CN, ppm) δ 7.22 (1H, dd, J = 2.5, 5.8 Hz), 6.95 (1H, ddd, J = 2.5, 5.8, 8.2 Hz), 6.74 (1H, dd, J = 8.2, 9.0 Hz), 6.18 (1H, s), 1.79 (3H, d, J = 1.3 Hz), 1.75 (3H, d, J = 1.3 Hz); ^{11}B NMR (160 MHz, CD_3CN, ppm) δ 3.31 (q, J = 49 Hz).

Potassium (2,6-Dichlorophenyl)trifluoroborate (2h). Method B was modified to follow ref 14 for metalation of **6h** (1.07 g) with *n*-butyllithium (4.75 mL, 7.27 mmol) at −78 °C (dropwise addition over 30 min). The resulting slurry was stirred 45 min, and $B(OMe)_3$ (2.5 mL; 22mmol) in THF (5 mL) was added over 2 min. The suspension immediately became clear. After 1 h, the mixture was allowed to warm and worked

up as usual. The crude **3h**[15a] (1.17g; ca. 2.3:1 mixture containing the boronic anhydride) was treated with saturated aqueous KHF_2 (5 mL) at room temperature. The thick white precipitate was collected by suction filtration, and the dry solid was extracted with hot THF. Pure material was obtained by recrystallization from acetonitrile, 0.976 g (53%) mp 211 °C dec; anal. calcd: C, 28.49; H, 1.20, found: C, 28.69; H, 1.17; 200 MHz NMR (CD_3CN, ppm) δ 7.14 (2H, J = 7.7 Hz, AB_2 pattern), 6.99 (1H, J = 7.7 Hz, AB_2 pattern); 160 MHz ^{11}B NMR (CD_3CN, ppm) δ 2.82 (q, J = 48 Hz).

Potassium 2-Furyltrifluoroborate (2i). Furan (Aldrich, dried over 3 Å molecular sieves, 5.0 mL, 68.7 mmol) was dissolved in 50 mL of anhydrous THF and treated with 42.0 mL of *n*-BuLi (Aldrich, 1.64 M, 68.9 mmol). After stirring at −5 °C for 3.5 h, the furyllithium was treated with $B(i\text{-}OPr)_3$ as described for [3,4-*bis*(trifluoromethyl)phenyl]lithium. The crude boronic acid, obtained after the usual workup (method B), was dissolved in 200 mL of MeOH and 40 mL of water, and then 3 equiv of KHF_2 (Aldrich, 16 g, 206 mmol) was added. The solution was refluxed overnight. After the same workup as described for potassium [4-(trifluoromethyl)phenyl]trifluoroborate, 5.8 g (48%) of product was obtained as yellow crystals. TLC analysis on silica gel indicated that this compound was readily hydrolyzed to 2-furylboronic acid in wet solvent (*e.g.* CH_3CN). Pure material (5.8 g, 48% from furan) was obtained by recrystallization from anhydrous acetonitrile/ethyl acetate, mp 200 °C dec. Anal. Calcd: C, 27.61%; H, 1.74%, found: C, 27.31%; H, 1.33%; IR (KBr, cm^{-1}) 1575, C=C; 1005, B−F; 970, B−F; 200 MHz NMR (CD_3CN, ppm) δ 7.44−7.33 (1H, m), 6.25−6.17 (1H, m), 6.17−6.10 (1H, m); 160 MHz ^{11}B NMR (CD_3CN, ppm) δ 1.8 (q, J = 49 Hz).

***p*-Fluorophenyl (−)-Menthyl Ether (6j).** The procedure is an adaptation of the method of Whitesides *et al.*[17] To a solution of (−)-menthol (10.3 g, 66 mmol, 1.3 eq, Aldrich) in 75 mL of dry THF chilled in an ice−water bath under nitrogen was added n-BuLi (45 mL of a 1.6 M solution in hexanes, 73 mmol, 1.5 eq, Aldrich) over 20 min. The resulting alkoxide was cannula transferred to a 1 L flask equipped with a reflux condenser charged with anhydrous CuCl (6.6 g, 66 mmol, 1.3 eq, Mallinckrodt). To the resulting dark green solution were added anhydrous pyridine (400 mL) and *p*-bromofluorobenzene (5.5 mL, 50 mmol, Aldrich). The solution was refluxed for 72 h and allowed to cool to room temperature. The reaction was quenched by dropwise addition of 100 mL of 10% aqueous HCl. The mixture was ether extracted (4 × 200 mL), and the combined extracts were washed with distilled water (2 × 100 mL) and brine (2 × 100 mL). Removal of solvent (aspirator) yielded 14.0 g of crude solid, which was fractionally sublimed to yield (−)-menthol (55 °C, 0.1 torr, 4.1 g, 43% recovery) in two fractions and pure *p*-fluorophenylmenthyl ether (75−80 °C, 0.1 torr, 8.9 g, 71%) in the remaining three fractions. Analytical TLC on silica gel, 1:4 ether/hexane, R_f = 0.63. Pure material was obtained by sublimation (75−80 °C, 0.1 torr), mp 47.5−48 °C, colorless needles; *m/e*, calcd for $C_{16}H_{23}FO$ 250.1733; found 250.1720, 1 ppm error; IR (KBr, cm^{-1}) 2967, =C−H; 1208, C-O; 500 MHz NMR ($CDCl_3$, ppm) δ 6.95 (2H, dd, J = 8.2, 9.5 Hz), 6.83 (2H, dd, J = 4.6, 9.5 Hz), 3.91 (1H, ddd, J = 4.1, 10.5, 10.5 Hz), 2.22 (1H, d sept, J = 2.8, 7.0 Hz), 2.10 (1H, dddd, J = 1.9, 3.8, 3.8, 10.9 Hz), 1.73−1.68 (2H, m), 1.48 (1H, dddd, J = 2.8, 2.8, 10.5, 12.5 Hz), 1.46−1.38 (1H, m), 1.13−1.04 (1H, m), 1.03−0.95 (1H, m), 0.92 (3H, d, J = 7.0 Hz), 0.91 (3H, d, J = 7.0 Hz), 0.95−0.91 (1H, m), 0.78 (3H, d, J = 7.0 Hz).

Potassium [2-Fluoro-5-((−)-menthyloxy)phenyl]trifluoroborate (2j). A solution of *p*-fluorophenyl (−)-menthyl ether (0.67 g, 2.7 mmol) in 40 mL of anhydrous THF was chilled in a dry ice/acetone bath. To it was added s-BuLi (3.2 mL of a 1.0 M solution in cyclohexane, 3.2 mmol, Aldrich) over 10 min. The resulting yellow solution was stirred for 70 min and triisopropyl borate (0.74 mL, 3.2 mmol, distilled over sodium, Aldrich) was added in one portion. The mixture was allowed to warm to room temperature and was quenched by the addition of 25 mL of 10% aqueous HCl, followed by dilution with 20 mL of ether. The organic layer was extracted with 1 N NaOH (3 × 50 mL), and the combined basic extracts were acidified to pH = 3 with 10% aqueous HCl. The mixture was ether extracted (3 × 50 mL) and the organic portion was dried over Na_2SO_4 and concentrated (aspirator) to yield a colorless oil weighing 0.67 g in 85% crude yield. The oil was dissolved in 25 mL of methanol, and to the solution were added KHF_2 (0.36 g, 4.6 mmol, Aldrich) and 5 mL of distilled water. The suspension was refluxed for 24 h and cooled to room temperature. The solvent was removed in vacuo to yield a white solid which was dissolved in 10 mL of hot acetonitrile and hot filtered. The solvent was removed to yield 0.64 g of crystalline material in 78% yield. Analytical TLC on silica gel, EtOAc, R_f = 0.46. Pure material (0.62 g, 76%) was obtained by crystallization from ether/hexane, mp 146−147 °C, colorless needles. Anal. Calcd: C, 53.93; H, 6.24, found: C, 53.36; H, 6.39; IR (KBr, cm^{-1}) 2956, =C−H; 2870, C−H; 986, B−F; 270 MHz NMR ($CDCl_3$, ppm) δ 6.93 (1H, d, J = 4.4 Hz), 6.57 (2H, d, J = 7.4 Hz), 3.84 (1H, ddd, J = 3.7, 6.6, 6.6 Hz), 2.3−2.1 (1H, m), 2.1−1.9 (2H, m), 1.62 (2H, d, J = 9.4 Hz), 1.42−1.30 (2H, m), 1.25−0.95 (2H, m), 0.85 (3H, d, J = 6.9 Hz), 0.80 (3H, d, J = 6.4 Hz), 0.69 (3H, d, J = 6.9 Hz); ^{11}B NMR (160 MHz, CD_3CN, ppm) δ 3.19 (q, J = 44 Hz).

(2*R*,4*R*)-3-[(Dimethylamino)methylidene]-2-fluoro-2-phenyl-1,3,2-oxazaborolidin-5-one (7-trans). D-Phenylglycine (Aldrich; 0.914 g, 6.05 mmol) was dissolved in 1 equiv methanolic of NaOMe (8.2 mL, 0.74 M, 6.1 mmol; prepared from Mg-dried methanol and sodium) at room temperature under a nitrogen atmosphere. Dimethylformamide dimethyl acetal (Aldrich; distilled at 1 atm, bp 102−4 °C; 0.762 g, 6.4 mmol) was added, and the solution was stirred for 75 min. Concentration to a white foam (rotary evaporator, 40 °C) followed by trituration with CH_2Cl_2/Et_2O and drying (0.5 mm, 40 °C, 12 h) afforded a white solid, $Me_2NCH{=}NCH(Ph)CO_2$-Na, used without further purification. The crude dry salt (1.38 g, 6.05 mmol) and potassium phenyltrifluoroborate (1.15 g, 6.25 mmol) were suspended in 80 mL anhydrous THF under nitrogen at room temperature and treated with 2.3 equiv of chlorotrimethylsilane (1.75 mL, distilled from polyvinylpyridine) in one portion. After stirring for 2 h, the volatiles were removed by bulb-to-bulb distillation at room temperature under static vacuum (ca. 0.5 mmHg). The resulting white solid was dissolved in 3:1 CH_2Cl_2/H_2O (20 mL), the aqueous layer was washed with additional CH_2Cl_2 (5 mL) and the combined organic extracts were washed with saturated aqueous NaCl, dried ($Na_2SO_4/MgSO_4$), and concentrated to a foam (rotary evaporator, 25 °C). The crude residue after solvent removal at 0.5 mm was washed with water (15 mL) and ether (15 mL) and then dissolved in CH_2Cl_2 (400 mL), dried ($Na_2SO_4/MgSO_4$), and concentrated to a solid (rotary evaporator, 30 °C). The crude product (1.60 g, 85%) consisted of a 99:1 mixture of diastereomers **7-trans**:**7-cis**, as determined by analytical HPLC [5 μm silica gel, 250 mm × 4.6 mm, 25% ethanol/hexane eluent 1.5 mL/min, t_R = 7.5 min (major) and t_R = 10.50 min (minor)]. Crystallization from anhydrous CH_2Cl_2/Et_2O at room temperature produced 1.47 g (three crops, 78% based on starting D-phenylglycine) of pure diastereomer **7-trans**; analytical TLC on silica gel, 2:1 EtOAc/hexane, R_f = 0.26; recrystallization from ether/dichloromethane, mp 217−219 °C dec; $C_{17}H_{18}BFN_2O_2$; *m/e* 312.1433; base peak = 235 amu; IR (CH_2Cl_2, cm^{-1}) 1755, C=O; 1680, C=N; 200 MHz NMR (CD_3CN, ppm; amidine *E*/*Z* rotamers) δ 7.60−7.22 (11H, m) 5.62 (0.25H, d, $^4J_{HF}$ = 3.7 Hz) 5.33 (0.75H, d, $^4J_{HF}$ = 3.7 Hz) 2.89 (0.75H, s) 2.87 (2.25H, s) 2.78 (0.75H, s) 2.78 (2.25H, s); ^{11}B NMR (proton decoupled, CH_2Cl_2, ppm) δ 7.15; ^{19}F NMR (470 MHz, ppm vs $CF_3C_6H_5$ = 0 ppm), δ −86 (*E*, major), −91 (*Z*, minor). The labile (minor) diastereomer **7-cis** could not be obtained pure; analytical TLC on silica gel, 2:1 EtOAc/hexane, R_f = 0.18; 200 MHz NMR (CD_3CN, ppm, partial) δ 5.66 (0.4H, s) 5.28 (0.6H, s) 2.99 (1.8H, s) 2.94 (1.2H, s) 2.83 (1.8H, s) 2.71 (1.2H, s); ^{19}F NMR (470 MHz, ppm vs $CF_3C_6H_5$ = 0 ppm), δ −83 (*E*, major), −89 (*Z*, minor).

(2*R*,4*R*)-3-[(Dimethylamino)methylidene]-2-fluoro-2-(2-fluorophenyl)-1,3,2-oxazaborolidin-5-one (8-trans). To a suspension of sodium (*R*)-*N*-[[(*N'*,*N'*-dimethylamino)methylidene]phenyl]glycine (0.44 g, 1.98 mmol) in THF (30 mL) was added chlorotrimethylsilane (0.50 mL, 3.96 mmol, freshly distilled over CaH_2 and stored over polyvinylpyridine, Aldrich). The suspension cleared to a solution and then became cloudy

over time. The mixture was stirred for 20 min and was chilled in a dry ice/acetone bath. A suspension of potassium (2-fluorophenyl)trifluoroborate (0.40 g, 1.98 mmol) in 20 mL of THF was added over 20 min. The mixture was stirred at −78 °C for 1 h and was allowed to warm to room temperature. After 2 h, ethyl acetate (30 mL) was added, and the mixture was extracted with saturated aqueous $NaHCO_3$ (20 mL), distilled water (2 × 20 mL), and brine (2 × 20 mL). The organic layer was dried over Na_2SO_4, and the solvent was removed (aspirator) to yield **8-trans** as a hygroscopic white solid. A solution enriched in the minor isomer **8-cis** (ca. 1:1 mixture) was stored in dichloromethane−ether to give colorless crystals, mp 207−208 °C; analytical TLC on silica gel, 1:1 EtOAc/hexane, R_f = 0.52; 300 MHz NMR (CD_2Cl_2, 1:1 rotamer mixture, ppm) δ 7.58 (0.5H, s), 7.53−7.43 (0.5H, m), 7.42−7.33 (3.5H, m), 7.27−7.19 (2.5H, m), 7.10−7.05 (1.5H, m), 7.02−6.84 (1.5H, m), 5.5 (0.5H, s), 5.14 (0.5H, s), 3.03 (1.5H, s), 2.86 (1.5H, s), 2.85 (1.5H, s), 2.72 (1.5H, s), 1.75 (br s, H_2O). Traces of the signals of **8-trans** were also present (ca. 5%). ^{11}B NMR (160 MHz, vs BF_3·Et_2O external reference, $CDCl_3$, ppm) δ 6.95, 5.95 (two rotamers). Attempted recrystallization did not remove the contaminant **8-trans**, and decomposition was detected. However, recrystallization of **8-trans** gave a single isomer; analytical TLC on silica gel, dichloromethane, R_f = 0.25; colorless prisms (0.46 g, 71%), hygroscopic; mp 212−213 °C from 10:1 ethyl acetate:acetonitrile; IR (KBr, cm^{-1}) 1741, C=O; B−O; 300 MHz NMR ($CDCl_3$, ppm) δ 7.72 (0.2H, ddd, J = 1.9, 7.0, 7.0 Hz), 7.70 (0.8H, ddd, J = 1.9, 7.0, 7.0 Hz), 7.55−7.12 (8H, m), 6.94 (0.2H, dd, J = 8.2, 9.7 Hz), 6.89 (0.8H, dd, J = 8.2, 9.7 Hz), 5.44 (0.2H, d, J = 3.5 Hz), 5.20 (0.8H, d, J = 3.5 Hz), 3.01 (0.6H, s), 2.99 (2.4H, s), 2.94 (2.4H, s), 2.85 (0.6H, s), 1.60 (br s, H_2O); ^{11}B NMR (160 MHz, BF_3-etherate as external reference) δ 6.06 ppm.

3-[(Dimethylamino)methylidene]-2-fluoro-2-[4-(trifluoromethyl)phenyl]-1,3,2-oxazaborolidin-5-one (9). The sodium salt of *N*-[(*N*′,*N*′-dimethylamino)methylidene]glycine[1a] (150 mg, 1.0 mmol) and potassium [4-(trifluoromethyl)phenyl]-trifluoroborate (250 mg, 1.0 mmol) were suspended in 20 mL anhydrous acetonitrile (distilled from CaH_2, stored over 3 Å molecular sieves) at room temperature under nitrogen. Triethylamine (Aldrich, distilled from CaH_2, 0.071 mL, 1.0 mmol) and TMSCl (Petrarch, distilled from CaH_2, 0.38 mL, 0.10 mmol) were added. After 3 h stirring, more Et_3N (0.1 mmol) and TMSCl (0.05 mmol) were added and stirring was continued 2 h. The mixture was poured into rapidly stirred ice-cold phosphate buffer (pH 7) and ethyl acetate (40 mL). The organic layer was separated, washed with water (3 × 20 mL) and brine (20 mL), dried ($MgSO_4$), and evaporated (aspirator). The residual oil was crystallized from CH_2Cl_2 (25 mL) and ether (30 mL) to give 236 mg of white crystals (first crop) + 4 mg (second crop), 79% combined yield. Analytical TLC on silica gel, EtOAc, R_f = 0.10, mp 164.0−165.5 °C. Formula, $C_{12}H_{13}BF_4N_2O_2$; *m*/*e*, M + 1, 305.1094; error = 3 ppm; IR (KBr, cm^{-1}) 1753, C=O; 1741, C=O; 1681, C=N; 270 MHz NMR ($CDCl_3$, ppm; 2:1 mixture of amidine rotamers) δ 7.60 (1.33H, d, J = 8.1 Hz), 7.56 (1.33H, d, J = 8.1 Hz), 7.52 (1.33H, s), 7.51 (0.33H, br s), 6.96 (0.67H, br s), 4.51 (0.67H, d, J = 17.2 Hz), 4.36 (0.67H, d, J = 17.2 Hz), 4.35 (0.67H, s), 3.27 (2H, s), 3.09 (3H, s), 2.86 (1H, d, J = 1.0 Hz).

3-[(Dimethylamino)methylidene]-2-fluoro-2-(2-furyl)-1,3,2-oxazaborolidin-5-one (10). The usual procedure was used for the preparation of the title compound. Thus, the sodium salt of *N*-[(*N*,*N*-dimethylamino)methylidene]glycine (343 mg, 2.25 mmol) and potassium 2-furyltrifluoroborate (**2i**) (407 mg, 2.34 mmol) were suspended in 25 mL anhydrous acetonitrile under nitrogen and treated with Et_3N (0.35 mL, 2.5 mmol) and TMSCl (0.61 mL, 2.5 mmol). After stirring at room temperature for 4 h, all volatiles were removed by aspirator, and the oily residue was taken up with 20 mL of CH_2Cl_2, washed with ice−water (3 × 15 mL), and dried ($MgSO_4$). Half of the above solution was concentrated to 2 mL, and anhydrous ether was added until cloudiness persisted. Crystallization gave 83 mg of yellow blocks. The mother liquor was concentrated and treated with ether in the same manner, yielding another 15 mg of yellow crystals, combined yield 38%. The amidine group existed as a 2:1 mixture of rotamers in $CDCl_3$. Analytical TLC on silica gel, EtOAc, R_f = 0.12. Analytical material was obtained by filtration through a silica gel plug (0.5 × 2 cm) and subsequent crystallization from ethyl acetate/ether, mp 103.8−104.2 °C, yellow crystals. Molecular ion calcd for $C_9H_{12}BFN_2O_3$: 226.09240; found *m*/*e* = 226.0928, error = 1 ppm; IR (KBr, cm^{-1}) 1747, C=O; 1740, C=O; 1690, C=N; 200 MHz NMR (CD_3CN, ppm) δ 7.55−7.45 (1.33H, br m), 7.17 (0.67H, br s), 6.43 (0.67H, dd, J = 3.1, 0.7 Hz), 6.37 (0.33H, dd, J = 3.1, 0.7 Hz), 6.35−6.30 (1H, br m), 4.45 (0.67H, d, J = 17.3 Hz), 4.35 (0.67H, dd, J = 17.3, 2.8 Hz), 4.18 (0.67H, br s), 3.20 (2H, s), 3.06 (2H, s), 3.04 (1H, s), 2.92 (1H, d, J = 1.3 Hz).

1-Phenyl-1,3-pentanedione Complex 11. Potassium 2-(fluorophenyl)trifluoroborate (**2e**) (0.20 g, 1.0 mmol) and 1-phenyl-1,3-pentanedione (0.17 g, 1.0 mmol) were placed in a 10 mL flask, and the system was purged with nitrogen. Dry acetonitrile (7.0 mL) and chlorotrimethylsilane (0.25 mL, 2.0 mmol, freshly distilled over CaH_2 and stored over polyvinylpyridine, Aldrich) were added sequentially. The mixture was stirred 1 h at room temperature and then diluted with 10 mL of ethyl acetate, washed with distilled water (2 × 20 mL) and brine (2 × 20 mL), and dried over Na_2SO_4. Removal of solvent (aspirator) gave an oily solid which was subjected to plug filtration on silica (3 × 4 cm) with CH_2Cl_2 as eluent, yielding after removal of solvent (aspirator) a white solid (0.297 g, 99%). Analytical TLC on silica gel, EtOAc, R_f = 0.71. Pure material was obtained by crystallization from ether/hexane, mp 69−70 °C, colorless needles. Molecular ion calcd for $C_{17}H_{15}BF_2O_2$: 300.11328; found *m*/*e* = 300.1139, error = 2 ppm; base peak = 205 amu; IR (KBr, cm^{-1}) 1611, C=O; B−O; 2986, C−H; 300 MHz NMR ($CDCl_3$, ppm) δ 8.2−8.0 (2H, m), 7.68 (1H, ddd, J = 7.4, 7.4, 1.9 Hz), 7.63 (1H, dddd, J = 7.4, 7.4, 1.2, 1.2 Hz), 7.4−7.2 (2H, m), 7.28 (1H, dddd, J = 7.4, 7.4, 5.8, 1.9 Hz), 7.13 (1H, dddd, J = 7.4, 7.4, 1.2, 0.8 Hz), 6.95 (1H, ddd, J = 9.4, 7.4, 0.8 Hz), 6.55 (1H, s), 2.63 (2H, q, J = 7.8 Hz), 1.27 (3H, t, J = 7.8 Hz); ^{11}B NMR (160 MHz, BF_3/etherate, CD_3CN, ppm) δ 5.94 (s).

Complex 12 from 2j and 1-Phenyl-1,3-pentanedione. The chiral aryltrifluoroborate **2j** (0.36 g, 0.1 mmol) and 1-phenyl-1,3-pentanedione (0.018 g, 0.1 mmol) were combined in a 10 mL flask. The system was flushed with dry nitrogen, and dry acetonitrile was added (5 mL). To the resulting solution was added chlorotrimethylsilane (26 μL, 0.2 mmol) and a white precipitate immediately formed. The suspension was stirred for 30 min and was quenched with distilled water. The mixture was diluted with 10 mL of ethyl acetate and extracted with distilled water (2 × 20 mL) and brine (2 × 20 mL) and dried over Na_2SO_4. After removal of solvent (aspirator), the residue was purified by preparative layer silica gel (20 × 20 × 0.1 cm), with dichloromethane eluent, to give 0.040 g of **12** in 89% yield as a light yellow oil; analytical TLC on silica gel, dichloromethane, R_f = 0.81. Molecular ion calcd for $C_{27}H_{33}BF_2O_3$: 454.24905; found *m*/*e* = 454.2502, error = 2 ppm; M − 19, 435.2495, error = 3 ppm; base peak = 205 amu; IR (neat, cm^{-1}) 2869, C−H; 1541, C=O; 300 MHz NMR ($CDCl_3$, ppm) δ 8.05 (2H, d, J = 7.8 Hz), 7.65 (1H, dd, J = 7.4, 7.4 Hz), 7.5 (2H, dd, J = 8.2, 7.4 Hz), 7.2 (1H, dd, J = 4.7, 3.1 Hz), 6.85 (1H, dd, J = 8.6, 8.6 Hz), 6.78 (1H, ddd, J = 8.6, 4.7, 3.1 Hz), 6.56 (1H, s), 3.98 (1H, ddd, J = 10.5, 10.5, 3.9 Hz), 2.65 (2H, q, J = 7.4 Hz), 2.3−2.1 (2H, m), 1.72−1.44 (4H, m), 1.31 (3H, t, J = 7.4 Hz), 1.31−0.92 (3H, m), 0.94 (3H, d, J = 7.0 Hz), 0.91 (3H, d, J = 7.0 Hz), 0.80 (3H, d, J = 7.0 Hz); ^{11}B NMR (160 MHz, BF_3/etherate, CD_3CN, ppm) δ 5.90.

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Supplementary Material Available: Copies of ^1H NMR spectra of **6g**, **6j**, **7-trans-E**, **8-trans-E**, and **9**−**12** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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