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Polyfluorinated arylboranes as catalysts in organic synthesis

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The review analyzes actual data on the use of polyfluorinated triarylboranes, diarylborinic and arylboronic acids as catalysts for organic reactions, *e.g.*, hydrogenation of unsaturated bonds and alkylation of aromatic compounds.
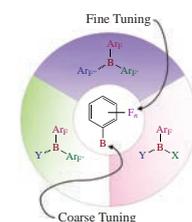
Introduction

Fluorinated organic compounds of the three-coordinated boron are unique acid catalysts, whose activity is regulated by the two main fine-tuning tools. Firstly, this can be achieved by changing the number of electron-withdrawing fluorine atoms in the aromatic ring and their location relative to the boron atom, which determines the electronic and steric properties of the aryl moiety. Secondly, changing the rest of the coordination environment of boron is also employed since the electronic nature and steric requirements of the ligands significantly affect the coordination ability of boron with electron donor groups.

In this review article, we consider triarylboranes, diarylborinic and arylboronic acids. In the case of triarylboranes, we settled on frustrated Lewis pairs (FLP) formed with their participation. These pairs are formed as a result of the interaction of fluorinated arylboranes with Lewis bases when the formation of a stable adduct is impossible due to steric hindrances. The emerging 'quasimetastable' state is capable of suddenly releasing the strain energy in the subsequent stage of bond activation. This feature of FLP actually allowed the elements of the main groups (B, O, N, P) to emulate the coordinated acting donor–acceptor properties of transition metals and significantly expanded the possibilities of bifunctional cooperative catalysis. First of all, the discovery of FLP contributed to the development of hydrogenation methods for unsaturated compounds without the use of transition metals.[1,2]

Two types of FLP are currently distinguished, classified according to their electronic structures. Each of them is additionally subdivided according to the nature of their constituent bases (oxygen, nitrogen, phosphorus, or carbene-containing bases). The first type is intramolecular FLP, in which the Lewis acid/Lewis base (LA/LB) components are part of a single molecule. The reaction centers in them are covalently bonded to each other, and the distances LA–LB are close to those in classical Lewis adducts.[2–4]

The second type of FLP is intermolecular, in which the centers of LA and LB are located in two different molecules. It is assumed that upon contact in solution, two separate components (LA and LB) form a complex through secondary weak interactions, mainly dispersion attraction. The most attractive feature of intermolecular FLP is the possibility of wide varying

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Lewis acids and bases. As a rule, to optimize the selected reaction, the acidity and basicity of the FLP components must be adjusted by electronical modifying their molecular structures. Since both properties can be changed independently, there are great opportunities for the chemical construction of catalytic structures.
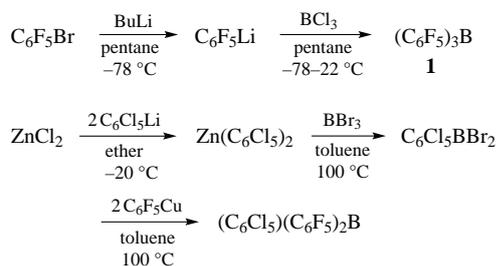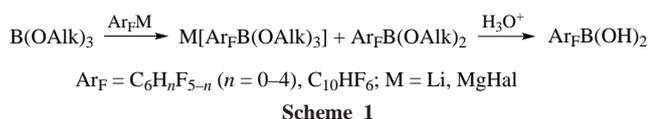
The simplest way to change the properties of intermolecular FLP is to replace the base in the classical system $(C_6F_5)_3B/Bu^t_3P$.[5] In the examples below, we consider an alternative method where the Lewis acidity of LA component was changed. From a large set of data on the use of $Ar_{F3}B$ as electrophilic catalysts, here we consider only those where FLP is a key intermediate.

Arylboronic and diarylborinic acids are widely used in organic chemistry as components for cross-coupling reactions to form a C–C bond. Preparation, physicochemical properties and many aspects of their reactivity are well described in a book.[6] Information has recently been updated by a review.[7]

It should be noted that the nature of the catalytic activity of arylboronic and diarylborinic acids is associated not with Brønsted acidity, but with Lewis one. The coordination of the boron atom with H_2O and the subsequent protonation of the second water molecule lead to the formation of a hydroxonium cation and an aryltrihydroxyborate anion. In the similar manner, they interact with carboxylic acids to form semiesters which can be truly reactive. Another way of catalytic action is to coordinate the *n*-electron-donor reagent with the vacant boron orbital, and the formed species can be further transformed. The mechanisms of catalysis by arylboronic acids are discussed in more detail in a review.[7]

Preparation of catalysts

Tris(pentafluorophenyl)borane **1** and a number of fluorine-containing phenylboronic acids are commercially available. We will briefly dwell on some methods of their preparation. The main methods are based on the reaction of a polyfluorinated organometallic reagent with a suitable boron-containing electrophile. Some examples of such syntheses are given in Schemes 1 and 2.[3,4,8–17]

$$B(OAlk)_3 \xrightarrow{Ar_FM} M[Ar_FB(OAlk)_3] + Ar_FB(OAlk)_2 \xrightarrow{H_3O^+} Ar_FB(OH)_2$$

$$Ar_F = C_6H_nF_{5-n} \ (n = 0-4), C_{10}HF_6; M = Li, MgHal$$

Scheme 1

$$C_6F_5Br \xrightarrow[\text{pentane} \\ -78\,°C]{BuLi} C_6F_5Li \xrightarrow[\text{pentane} \\ -78-22\,°C]{BCl_3} (C_6F_5)_3B \quad \mathbf{1}$$

$$ZnCl_2 \xrightarrow[\text{ether} \\ -20\,°C]{2\,C_6Cl_5Li} Zn(C_6Cl_5)_2 \xrightarrow[\text{toluene} \\ 100\,°C]{BBr_3} C_6Cl_5BBr_2$$

$$\xrightarrow[\text{toluene} \\ 100\,°C]{2\,C_6F_5Cu} (C_6Cl_5)(C_6F_5)_2B$$

Scheme 2

It is necessary to mention the particular method of producing alkylbis(polyfluorophenyl)boranes based on the addition of bis(pentafluorophenyl)borane **2**, $HB(C_6F_5)_2$ (the Pierce borane), to multiple bonds of alkenes and alkynes (Scheme 3).[18] In this way, fluorinated alkenyl and alkyldiarylboranes including ones with chiral centers in the alkyl chain can be accessed.[19–29]

Scheme 3
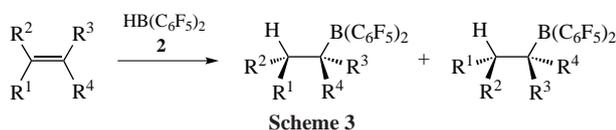
Some properties of polyfluorinated triarylboranes, arylboronic and diarylborinic acids

Tris(pentafluorophenyl)borane is a thermally stable compound tolerant to oxygen (135 °C, 1 h), it does not form C_6F_5H with water at 22 °C over a period of 18 h and easily forms complexes with O-, N-, P- and S-bases.[8,30] The relative acidity of boranes is important for our purposes, and we give here data which was determined by the Beckett–Gutmann method with Et_3PO as base.[31–34] The LA of $(C_6F_5)_3B$ was taken as 100%. The relative LA of **1**, $(4-HC_6F_4)_3B$ **3**, $(2-HC_6F_4)_3B$ **4**,[35] $(2,6-F_2C_6H_3)_2(2,6-Cl_2C_6H_3)B$ **5** and $(2,6-F_2C_6H_3)_3B$ **6** are 100, 98, 95, 78 and 82%,[36] respectively.

An important feature of polyfluorinated arylboronic acids in comparison with their less fluorinated analogues would undergo hydrodeboration by bases. Pentafluorophenylboronic acid **7** is converted to pentafluorobenzene even on contact with MeOH within a few minutes. The reaction with pyridine proceeds exothermally with the same result. The less fluorinated phenylboronic acids are more tolerant to bases but at 100 °C decompose in aqueous pyridine within several hours. 2,4-Difluorophenylboronic acid and 3,4,5-trifluorophenylboronic acid **8** display the higher stability under these conditions.[37]

The acidity constants pK_a of all isomers of fluorine-substituted phenylboronic acids have been determined by both spectrophotometric and potentiometric methods, and their values lie in the range of 6–8. The estimated pK_a values of $C_6F_5B(OH)_2$ (7.4) and $2,3,5,6-F_4C_6HB(OH)_2$ **9** (8.5) were found to be unreliable.[38,39] Certainly, the presence of fluorine in the aromatic ring enhances the Lewis acidity of boronic acids depending on the position and number of fluorine substituents, although there is no simple correlation between the pK_a and the decomposition rate under basic conditions. The kinetic studies of hydrodeboration in 50% aqueous dioxane at pH > 13 displayed the dramatic difference of the half-lives of species $[ArB(OH)_3]^-$ from 6.5 months (Ar = $3-FC_6H_4$) to 2.6 ms (Ar = C_6F_5).[40]

Using changes in chemical shifts in the ^{31}P NMR spectra during the complexation of Lewis acids with Et_3PO, the activation of hydrogen bonds was measured for many organocatalysts.[41] It was found that $\Delta\delta_P$ in ^{31}P NMR spectra and acceptor numbers correlate well with catalytic activity based on the relative rates of the Friedel–Crafts alkylation reaction of indole with nitrostyrene (model reaction). A detailed investigation of a wide range of arylboronic acids confirmed that hydrogen-bonding interactions non-binding to the Lewis acidic boron center is the primary activation mode that accounts for the observed binding and catalytic activity for these acids. However, this conclusion seems dubious in relation to studied fluorinated arylboronic acids. Indeed, the k_{rel} values for the model reaction are 2.49 (Ar = $2,6-F_2C_6H_3$), 6.98 (Ar = C_6H_5), 9.74 (Ar = $4-FC_6H_4$), 14.96 (Ar = $3-FC_6H_4$), and 18.79 (Ar = $3,5-F_2C_6H_3$). This order is not in agreement with many other data on the catalytic activity of $Ar_FB(OH)_2$ and, probably, conclusion is specific for this model.

Bis(pentafluorophenyl)borinic acid **10** is both Lewis and Brønsted relatively strong acids and also contains a Lewis basic site within the same molecule. In contrast to pentafluorophenylboronic acid, acid **10** is more tolerant to bases. In non-polar or weakly polar solvents (toluene, CCl_4, $CHCl_3$, CH_2Cl_2) it exists as equilibrium of monomers and trimers.[42,43] Titration of acid **10** with THF in CD_2Cl_2 leads to the formation of the complex stable at 10 °C, however, species $[(C_6F_5)_2B(OH_2)_2]^+[(C_6F_5)_6B_3O_3H_2]^-$ was also detected.[44] In the presence of molecular sieves, acid **10** undergoes esterification with MeOH to give $(C_6F_5)_2BOMe$ in nearly quantitative yield.[45] Freshly prepared solution of **10** in nitriles RCN (R = Me, Et, Ph) does not contain complexes (^{11}B NMR), but within several hours

the formation of $(C_6F_5)_2BOCR=NH·(C_6F_5)_2BOH$ proceeds, which exists as the stable cyclic structure.[46] In the presence of stoichiometric DMAN [1,8-bis(dimethylamino)naphthalene, 'the proton sponge'] in CD_2Cl_2, acid **10** was converted at –100 °C into a mixture of two boroxinate anions, $[(C_6F_5)_6B_3O_3H_2]^-$ and $[(C_6F_5)_5B_3O_3H]^-$. The good Brønsted basicity (pK_a = 12.1) and negligible Lewis basicity favour deprotonation of borinic acid without formation of Lewis acid–base adducts with the boron atom. At room temperature, the further hydrodeboration leads to C_6HF_5 and $[(C_6F_5)_4B_3O_3]^-$.[47] It is of note that the stronger Lewis and Brønsted base, pyridine, forms the stable complex $(C_6F_5)_2B(OH)·Py$. The latter was isolated and characterized by multinuclear NMR spectra as well as the X-ray data. No hydrodeboration of compound **10** occurs in the presence of pyridine in CD_2Cl_2 at room temperature.[48]

FLP catalysts

Relatively few intramolecular FLP are known, due to the difficulties of their synthesis. The first fluorinated organoboron compound capable of reversibly activating molecular hydrogen was phosphino borane $(Mes)_2PC_6F_4B(C_6F_5)_2$ **11** obtained from borane **1** and dimesitylphosphine.[49] The intramolecular *ansa*-amino borane N-TMP-$CH_2C_6H_4B(C_6F_5)_2$ **12** (TMP is 2,2,6,6-tetramethylpiperidin-1-yl) is resistant to moisture and air.[3] Structurally being an intramolecular FLP, it is capable of reversible activating molecular hydrogen. Due to the rigid geometry, this *ansa*-amino borane reacts with hydrogen in toluene at 20 °C forming an ammonium *ansa*-borane with a short hydrogen–hydrogen bond (1.78 Å) in the N–H···H–B fragment. When heated above 100 °C, coordinated hydrogen is released. *ansa*-Amino boranes with structural fragments of other sterically hindered amines possess similar properties.[13] This ability of *ansa*-amino boranes N–R–$CH_2C_6H_4B(C_6F_5)_2$ **13**–**15** to absorb hydrogen at 20 °C and to lose it above 100 °C was used for catalytic reduction of sterically hindered amines and enamines.[3,13]

11 **12** **13** **14** **15**
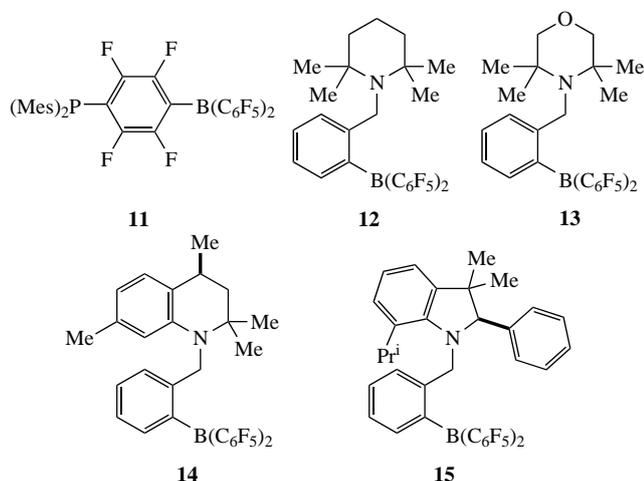
Noteworthy, when amino groups are chiral, the imines undergo asymmetric hydrogenation.[13] The chiral phosphonium hydride borate zwitterion obtained from camphor as a result of five-stage synthesis has been successfully used in the enantioselective hydrogenation of imines with selectivity up to 76%.[23] Intermolecular FLPs are readily prepared from available Lewis acids and bases. For illustration of their catalytic activity, the typical examples of FLP-catalyzed hydrogenation are shown in Scheme 4.

One of the first modifications of the classical $(C_6F_5)_3B/Bu^t_3P$ system was the replacement of $(C_6F_5)_3B$ **1** with tris(tetrafluorophenyl)boranes.[5] Later some FLP with other
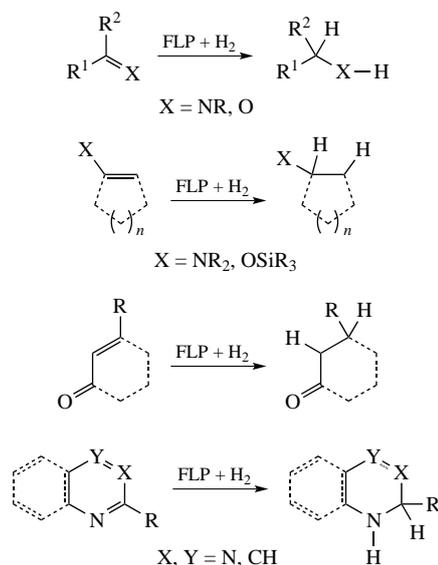

Scheme 4

phosphines PR_3 (R = Cy, *o*-Tol) were obtained.[15] Although the Lewis acidity of boranes **3** and **4** is only slightly (2–3%) lower than that of borane **1**,[35] this does not prevent the activation of molecular hydrogen by the **4**/P(*o*-Tol)$_3$ system at 20 °C.[15] Moreover, in contrast to **1**, these boranes are not susceptible to nucleophilic phosphodefluorination with phosphines, which makes it possible to construct FLP with a wide range of phosphines that cannot be used in combination with **1**.[50]

The use of polyfluorinated triarylboranes in catalysis of homogeneous hydrogenation is favored by the fact that Lewis base partners can be reactants to be reduced and/or electron-donating solvents (THF, dioxane). For example, hydrogenating of 2,3-disubstituted quinoxalines with hydrogen proceeds *via* the key FLP formed by borane **3** and the nitrogen atom of quinoxalines.[51]

Illustrative examples of the regulation of the electronic properties of triarylboranes with a fixed steric accessibility of the boron atom were reported.[12,52] Successively replacement of the *meta*- and *para*-hydrogen atoms in triphenylborane with fluorine or chlorine atoms provides a series of triarylboranes X_2YB.


R^1 = Me, Cl; R^2 = H, Cl;
R^3 = H, Me; R^4 = H, Cl;
X = H, F; Y = H, F
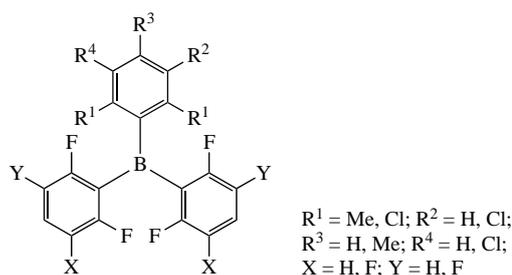
These boranes are used as the catalysts for the hydrogenation of carbonyl compounds[12] and imines[52] in THF or dioxane. The authors established a relationship between the Lewis acidity of triarylboranes and the catalytic properties of FLP in these reactions. Thus, the replacement of hydrogen with fluorine in the *meta*-positions of the phenyl group led to a significant increase in Lewis acidity and catalytic activity of borane.[12] The effect of the similar replacement of H by Cl is essentially lower.[12]

The decrease in the Lewis acidity of borane $(2,6-F_2C_6H_3)_3B$ **6** enables the production of FLP with Bu^t_3P and 2,2,6,6-tetra-methylpiperidine capable of reversible activating hydrogen at room temperature. Pyridine derivatives in combination with

borane **6** represent highly active catalysts for the reduction of nitroalkenes and acrylates.[36]

Useful method for the conversion of carboxamides to amines by hydrogenation in the presence of **6** and oxalyl chloride was proposed.[53] Here, the real partner base in FLP is not an amide or intermediate imidoyl chloride, but a chloride anion. The reaction proceeds under mild conditions (50–70 °C, 80 bar) and gives the desired products in good yields. Target compounds are obtained as ammonium chlorides, which facilitates their isolation (Scheme 5).

Scheme 5
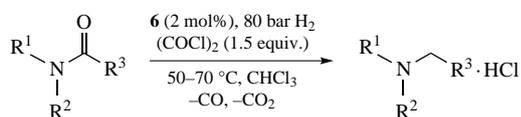
The successive replacement of pentafluorophenyl groups with their perchlorinated analogues allows one to smoothly decrease the Lewis acidity of boranes $(C_6Cl_5)_n(C_6F_5)_{3-n}B$ by increasing n.[16] The combination of reduced Lewis acidity with additional steric shielding of the boron atom in borane $(C_6Cl_5)(C_6F_5)_2B$ **16** made it possible to obtain FLP with THF capable of catalyzing hydrogenation of imines[54] and acetone.[55] A decrease in Lewis acidity in boranes $CyB(C_6F_5)_2$ **17** and $PhCH_2CH_2B(C_6F_5)_2$ **18** to 15 and 10%, respectively (relative to **1**), opened the possibility of obtaining FLP with 2,2,6,6-tetra-methyl- and 1,2,2,6,6-pentamethylpiperidanes. These FLP absorb hydrogen at room temperature and lose it when heated.[25] Replacing one of the pentafluorophenyl groups in borane **1** with chiral organic substituents reduces the Lewis acidity of boranes, and on their basis a series of catalysts for enantioselective hydrogenation of imines was obtained.[26,29]

Among the intermolecular FLP capable of catalyzing the hydrogenation of imines with enantioselectivity of 83% *ee*, there was a catalyst formed from Bu^t_3P and chiral borane **19**. This borane was obtained in several steps from camphor where one of the last steps was the addition of borane $HB(C_6F_5)_2$ **2** at C=C bond of unsaturated camphor derivative.[26] Amino borane **20** was obtained similarly and became the basis of the catalyst for enantioselective hydrosilylation of aromatic imines. It allowed one to obtain chiral amines with a selectivity of more than 80%

ee after hydrolysis.[24] Liu *et al.*[29] proposed to generate chiral diboranes *in situ* from the corresponding dienes **21** and borane **2**. The resulting catalysts provide the enantioselective hydrogenation of aromatic imines with a selectivity of up to 89% *ee*. However, an attempt to asymmetrically hydrogenate bis-imine **22** using a chiral borane catalyst (10 mol%) formed *in situ* by hydroboration of the chiral diene **23** with **2** was unsuccessful.[56] With almost complete conversion of the starting bis-imine, the enantio-selectivity of the reaction did not exceed 10% *ee*. Using hydroboration reactions of C_2-symmetric spiro-bicyclic dienes with **2** and $HB(4\text{-}HC_6F_4)_2$ **24**, another series of spiro-bicyclic bis-borane catalysts **25** was obtained and used for enantioselective hydrogenation of quinolines. These catalysts have good stability (up to 460 rpm) and provide excellent yields with an enantiomeric selectivity of up to 98%.[19]

Hydrogenation of compounds with multiple bonds catalyzed by transition metals is one of the most frequently used transformations in organic chemistry, used both in laboratory practice and in industry. However, the production of pharmaceutical intermediates requires the almost complete removal of transition metals because of their toxicity. Along with the high cost of such catalysts (mainly, noble transition metals), this leads to a significant increase in the cost of the target products, which often eliminates all the obvious advantages of catalytic methods for producing amines. A promising alternative to transition metals is catalytic systems based on FLP. The discovery of hydrogen activation using FLP has become an important milestone in modern chemistry, opening up new possibilities and new applications.

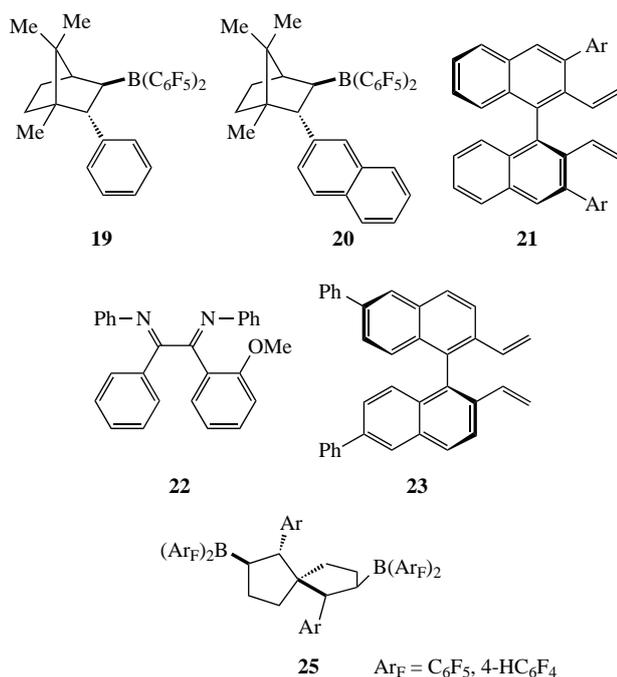## Catalysis with polyfluorinated arylboronic and diarylborinic acids

In 1963 Letsinger *et al.*[57] reported the first application of arylboronic acids as catalysts for hydrolysis and alcoholysis of chlorine-containing alcohols. However, their practical applications became possible after they became commercially available.
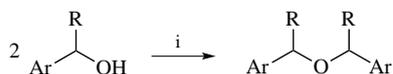
The most popular route from carboxylic acids to esters or amides is the conversion of the acid into its chloride and subsequent nucleophilic substitution resulting in the replacement of the C–Cl bond by C–O or C–N ones. It is very attractive to exclude the intermediate step, *e.g.*, to perform the catalytic esterification or amidation. It turned out that these reactions can be carried out using fluorinated arylboronic acids as catalysts. Thus, 4-phenylbutanoic acid reacts with aliphatic alcohols in the presence of $3,4,5\text{-}F_3C_6H_2B(OH)_2$ **8** to give esters in good yields (Scheme 6).[58]
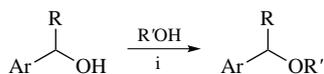
Alk = Me, Pr, Bu

Scheme 6
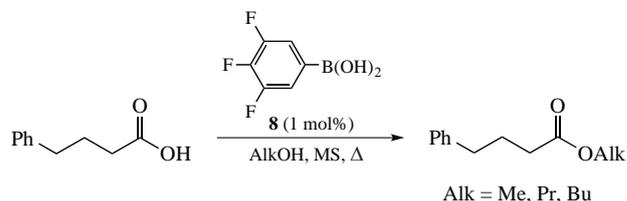
Also, benzylic alcohols can be the electrophilic component. In combination with a second molecule of alcohol as nucleophile the intermolecular dehydrative substitution occurs to give ethers. Reaction proceeds in the presence of pentafluorophenylboronic acid **7** and oxalic acid.[59] It is important that the intermolecular cross-etherification also proceeded resulting in the corresponding asymmetric ethers in a good yield (Scheme 7).

Under the same conditions, the intramolecular etherification gave tetrahydrofuran and tetrahydropyran derivatives (Scheme 8).
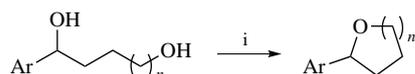
19   **20**   **21**   **22**   **23**

25 $Ar_F = C_6F_5, 4\text{-}HC_6F_4$

$$2 \quad \underset{Ar}{\overset{R}{\underset{\quad}{\bigvee}}} OH \xrightarrow{\quad i \quad} \underset{Ar}{\overset{R}{\bigvee}} O \underset{\quad}{\overset{R}{\bigvee}} Ar$$

Ar = Ph, 2-BrC$_6$H$_4$, 3-MeC$_6$H$_4$, 4-XC$_6$H$_4$ (X = Me, F, Cl, Br)
R = H, Ph

$$\underset{Ar}{\overset{R}{\underset{\quad}{\bigvee}}} OH \xrightarrow[i]{\quad R'OH \quad} \underset{Ar}{\overset{R}{\underset{\quad}{\bigvee}}} OR'$$

Ar = Ph; R = Ph; R′ = Me, Et, Bu, Pr^i, CF$_3$CH$_2$, Et(Me)CH,
CH$_2$=CH(CH$_2$)$_3$CH$_2$, HC≡CCH$_2$CH$_2$, EtOCOCH$_2$
Ar = Ph; R = Me, Pr^i, Bu^t, HC≡C; R′ = CH$_2$=CH(CH$_2$)$_3$CH$_2$

Scheme 7 *Reagents ans conditions*: i, C$_6$F$_5$B(OH)$_2$ **7** (5 mol%), (COOH)$_2$ (10 mol%), MeNO$_2$.

$$\underset{Ar}{\overset{OH}{\bigvee}}\underset{\quad}{\overset{\quad}{\bigvee}} \overset{OH}{\underset{(\quad)_n}{}} \xrightarrow{\quad i \quad} \underset{Ar}{\overset{O}{\bigvee}} \overset{}{\underset{n}{}}$$

Ar = Ph, 4-XC$_6$H$_4$ (X = Me, MeO, CF$_3$, Cl, Br)
n = 1, 2

Scheme 8 *Reagents and conditions*: i, C$_6$F$_5$B(OH)$_2$ **7** (5 mol%), (COOH)$_2$ (10 mol%), MeNO$_2$, 40–90 °C.

No reaction took place when $n = 0$. Seven-membered heterocycle formed from 6-phenylhexane-1,6-diol in 30% yield after heating at 40 °C for 48 h. To understand the role of oxalic acid, the authors of ref. 59 performed additional experiments and isolated complex (Figure 1) which was characterized by NMR spectroscopy and X-ray analysis. This complex was supposed to be a competent precatalyst for the reaction, which likely acted as a strong Brønsted acid. Protonation of a benzylic alcohol and subsequent dissociation (or polarization) of C–O bond accelerated the coupling with nucleophile R′OH to yield ether and to release boronate species.
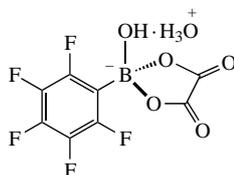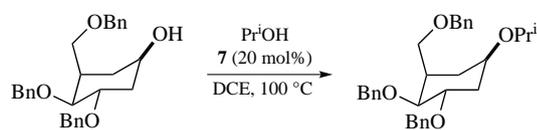
Figure 1 Complex of C$_6$F$_5$B(OH)$_2$ **7** with oxalic acid.

The catalytic ability of a series of arylboronic acids was tested in esterification of hemiacetal **26** with propan-2-ol. Phenylboronic acid displayed the low activity, whereas acid **7** and its the more Lewis acidic catechol ester were significantly more effective catalysts[60] (Scheme 9).

Scheme 9

The nucleophilicity of amines is higher than that of alcohols, hence, arylboronic acid-catalyzed amidation proceeds faster. Amidation of carboxylic acids with primary and secondary amines displayed the higher efficiency of acid **8** as the catalyst with respect to phenylboronic acid (Scheme 10). However, the presence of several fluorine atoms in the aromatic moiety does not automatically entail an increase in acid activity. Thus, 2,4,6-F$_3$C$_6$H$_2$B(OH)$_2$ showed the same result as C$_6$H$_5$B(OH)$_2$, while 2,3,4,5-tetrafluorophenylboronic acid **27** was the worst catalyst among those tested.[58]

$$R^1COOH + R^2R^3NH \xrightarrow{\quad i \quad} R^1CONR^2R^3$$
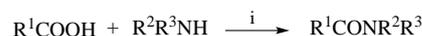
R^1 = Ph(CH$_2$)$_4$, c-C$_6$H$_{11}$; R^2 = H; R^3 = Ph, PhCH$_2$, Ph(CH$_2$)$_2$
R^1 = Ph, Ph(CH$_2$)$_4$, PhCH=CH; R^{2}R^{3}NH = Bu$_2$NH, 3,5-dimethylpiperidine
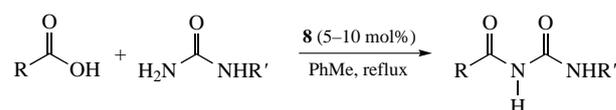
Scheme 10 *Reagents and conditions*: i, 3,4,5-F$_3$C$_6$H$_2$B(OH)$_2$ **8** (1 mol%), toluene, xylene or mesitylene, 3 or 4 Å MS, reflux.

Arylboronic acids can be used as catalysts for the direct amidation of amino acid analogues to form simple amide derivatives with reasonable efficiency and generally with retention of the amino acid absolute configuration with good enantio- or diastereoselectivity.[61] Reflux of N-Boc-phenylalanine with PhCH$_2$NH$_2$ and catalytic amount of 3,4,5-F$_3$C$_6$H$_2$B(OH)$_2$ **8** in fluorobenzene leads to the corresponding benzylamide in 37–54% yield. Moreover, it is possible to couple N-terminal to C-terminal protected amino acids without racemization. The access to dipeptide derivatives synthesis by direct amidation under similar conditions is shown in Scheme 11.
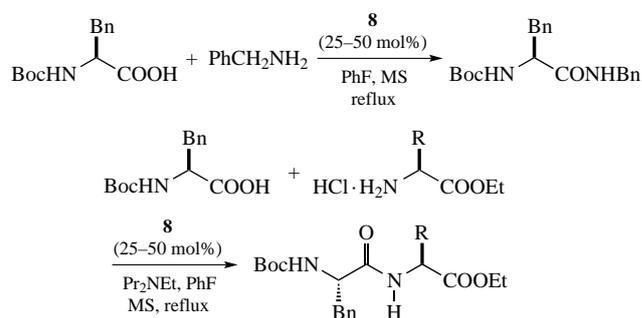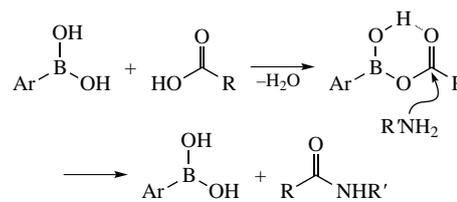
Scheme 11

Aliphatic carboxylic acids react with ureas in the presence of strong acids or *via* intermediate conversion to anhydride or acyl chloride.[62,63] The alternative method based on catalytic effect of **8** allows one to perform monoamidation of these compounds in high yield under mild conditions (Scheme 12).

$$\underset{R}{\overset{O}{\bigvee}} OH + \underset{H_2N}{\overset{O}{\bigvee}} NHR' \xrightarrow[PhMe, reflux]{\textbf{8} (5–10 mol\%)} \underset{R}{\overset{O}{\bigvee}} \underset{H}{N} \overset{O}{\bigvee} NHR'$$

R = Ph(CH$_2$)$_4$, c-C$_6$H$_{11}$, 1-adamantyl
R′ = H, Bn, Bn(Me)CH

Scheme 12

The accepted mechanism of catalytic action of arylboronic and diarylborinic acids in amidation involves the intermediate formation of mixed ester and subsequent attack of the carbonyl atom by N-nucleophile (Scheme 13).[7] The related scheme was offered for catalysis with diarylborinic acids.[64]
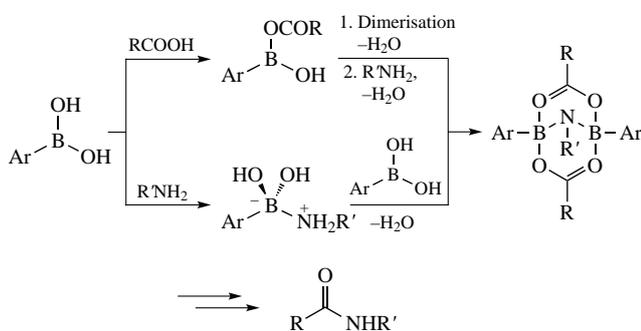
Scheme 13

Recently the mechanism of catalytic amidation was thoroughly re-investigated using multiple techniques.[65] Interaction of several diarylborinic acids (including **8**) with RNH$_2$ leads to the formation of the complex with tetra-
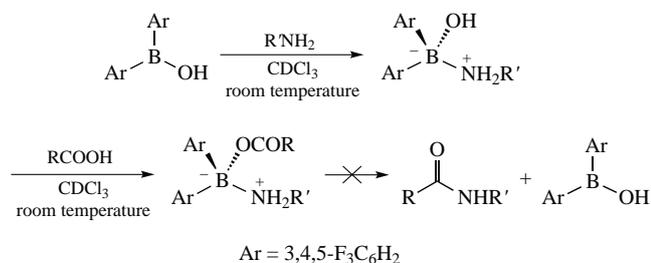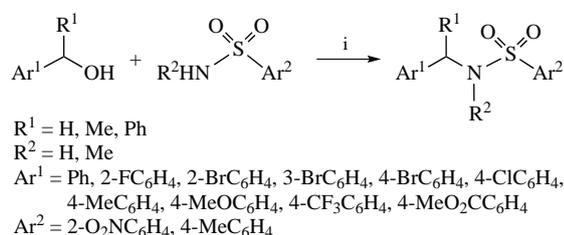
Scheme 14

coordinated boron. Treatment with RCOOH results in zwitter-ion which does not convert to amide (Scheme 14).

The further study allowed one to conclude that in the course of the reaction borinic acids underwent protodeboronation to boronic acids and the real key intermediate was the cyclic analogue of boronic acid that caused downstream amidation catalysis. Having applied to arylboronic acid, the alternative mechanism is displayed in Scheme 15.[65]
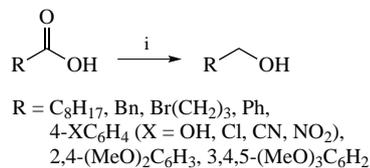

Scheme 15

All the above reactions represent the formal replacement of the hydroxy group by the amino one. In this sense, the recently described sulfonamidation of benzylic alcohols with sulfonamides is the extension of this preparative method of amidation for the synthesis of N-substituted sulfonamides.[66] Reaction of benzylic alcohols and arenesulfonamides proceeds in a mixture of hexafluoropropan-2-ol and nitromethane in the presence of polyfluorinated phenylboronic acids **7** or 2,3,4,5-tetrafluorophenylboronic acid **27**. However, for the successful preparation of the desired product, catalytic amounts of oxalic acid should be added, which is not required in the case of esterification or amidation of carboxylic acids (Scheme 16).

$R^1 = H, Me, Ph$
$R^2 = H, Me$
$Ar^1 = Ph, 2\text{-}FC_6H_4, 2\text{-}BrC_6H_4, 3\text{-}BrC_6H_4, 4\text{-}BrC_6H_4, 4\text{-}ClC_6H_4,$
    $4\text{-}MeC_6H_4, 4\text{-}MeOC_6H_4, 4\text{-}CF_3C_6H_4, 4\text{-}MeO_2CC_6H_4$
$Ar^2 = 2\text{-}O_2NC_6H_4, 4\text{-}MeC_6H_4$

Scheme 16 *Reagents and conditions*: i, $2,3,4,5\text{-}F_4C_6HB(OH)_2$ **27** (10 mol%), $(COOH)_2 \cdot 2H_2O$ (10 mol%), $(CF_3)_2CHOH$, $MeNO_2$, room temperature.
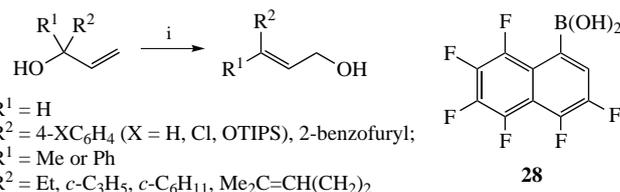
A specific type of nucleophilic substitution of hydroxy group is reduction of carboxylic acids to alcohols[67] proceeding, apparently, *via* the intermediate aldehydes (Scheme 17). Interestingly, boronic acid-catalyzed reduction of aldehydes is not reported so far.

$R = C_8H_{17}, Bn, Br(CH_2)_3, Ph,$
    $4\text{-}XC_6H_4 (X = OH, Cl, CN, NO_2),$
    $2,4\text{-}(MeO)_2C_6H_3, 3,4,5\text{-}(MeO)_3C_6H_2$

Scheme 17 *Reagents and conditions*: i, $NaBH_4$, $3,4,5\text{-}F_3C_6H_2B(OH)_2$ **8** (1 mol%), THF, room temperature.

The Oppenauer-type oxidation of primary and secondary allylic and benzylic alcohols with pivalaldehyde under catalysis with bis(pentafluorophenyl)borinic acid **10** (1–2 mol%) is reported.[68] The reaction is carried out in the presence of $MgSO_4$ as the water scavenger in toluene. For this transformation, acid **8** was the less effective whereas acid **7** was not active. Aliphatic alcohols $C_{13}H_{27}OH$ and 4-*tert*-butylcyclohexanol also underwent oxidation, however, their conversions and yields of target products were unsatisfactory.

The ability of arylboronic acids to readily form esters with alcohols is used in a number of reactions in which these acids serve as homogeneous catalysts. Allylic and propargylic alcohols undergo the 1,3-isomerisation under the mild condition in the presence of fluorinated arylboronic acids. Using 1-phenylprop-2-en-1-ol as a model alcohol, Hall *et al.*[69] evaluated several acids to accelerate the allylic rearrangements. Acids $PhB(OH)_2$, $2\text{-}FC_6H_4B(OH)_2$, $2,6\text{-}F_2C_6H_3B(OH)_2$, **7** and **8** were ineffective. Acid $2,3,5,6\text{-}F_4C_6HB(OH)_2$ **9** showed the moderate acceleration of rearrangement, while 3,4,5,6,7,8-hexafluoronaphthalen-1-ylboronic acid **28** was the most effective (Scheme 18).

$R^1 = H$
$R^2 = 4\text{-}XC_6H_4 (X = H, Cl, OTIPS), 2\text{-benzofuryl};$
$R^1 = Me$ or Ph
$R^2 = Et, c\text{-}C_3H_5, c\text{-}C_6H_{11}, Me_2C{=}CH(CH_2)_2$

Scheme 18 *Reagents and conditions*: i, **9** or **28** (50 mol%), toluene, 22–80 °C, 12–48 h.

The closely related processes were attributed to series of propargylic alcohols (Scheme 19).

$R^1 = H; R^2 = Ph; R^3 = H, OEt, N(Ts)Bn$
$R^1 = R^2 = Ph; R^3 = H, C_6H_{13}, SMe$
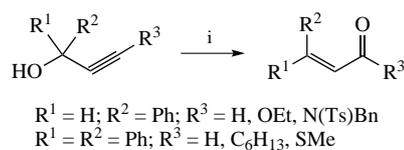
Scheme 19 *Reagents and conditions*: i, **9** or **28** (50 mol%), toluene, 22–50 °C, 0.3–24 h.

The role of arylboronic acid consists in the formation of ester ArB(OH)–OR with the strongly polarized O–R bond. This leads to increase in the positive charge on a carbon atom and subsequent interaction with potential nucleophilic center in this or the other molecule. One of such processes is the Nazarov cyclization of divinyl ketones to cyclopentenones. Thus, 2,4-dimethyl-1,3,5-triphenylpenta-1,4-dien-3-ol was converted to dimethyltriphenylcyclopentadienes upon stirring with acid **9** in CH_2Cl_2 at room temperature.[70] When reaction was performed in the presence of maleic anhydride or phenylmaleimide as dienophiles, the Diels–Alder adducts were obtained (Scheme 20).

Hall *et al.*[71] reported a typical example of the Diels–Alder cycloaddition catalyzed by *ortho*-substituted phenylboronic acids. The most active catalysts were iodo-, bromo-, chloro- and

X = O; R = Me, Bu, Ph, CH$_2$=CHCH$_2$, PhC≡C, CH$_2$=CH
X = NPh; R = Me, Bu, Ph, CH$_2$=CHCH$_2$
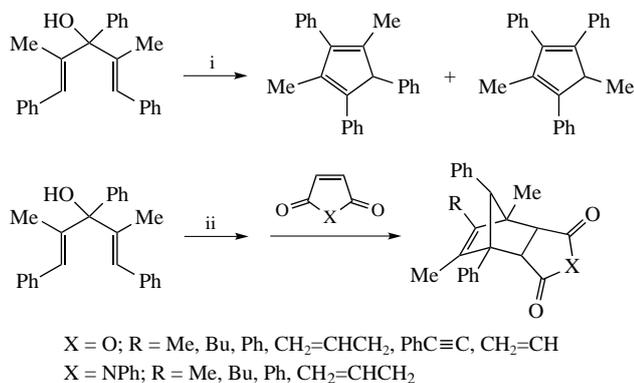
Scheme 20 *Reagents and conditions*: i, 2,3,5,6-F$_4$C$_6$HB(OH)$_2$ **9** (20 mol%), CH$_2$Cl$_2$, room temperature, 48 h; ii, **9** (20 mol%), MeNO$_2$, 50 °C, 16 h.
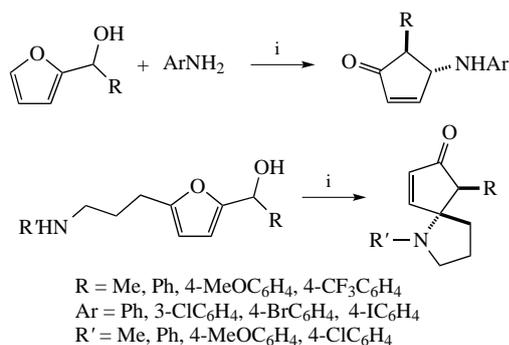
nitro-derivatives although 2-fluorophenylboronic acid showed the moderate activity. Unfortunately, optimization was limited by the screening of only these acids and the highly fluorinated phenylboronic acids were not tested.

There are several arylboronic acid-catalyzed reactions of benzylic and allylic alcohols, which lead to the formation of carbocycles. Benzofuran-2-yl(phenyl)methanol reacted with 1,3-butadiene in CH$_2$Cl$_2$ in the presence of 2,3,4,5-F$_4$C$_6$HB(OH)$_2$ **27** to give substituted cyclohepta[*b*]benzofuran. The proposed mechanism of this [4+3] reaction includes esterification of acid **9**. The formation of ionic pair 'allyl carbocation– aryltri(hydroxy) borate' is possible, which would undergo concerted [4+3] reaction or stepwise cycloaddition (Scheme 21).[72]
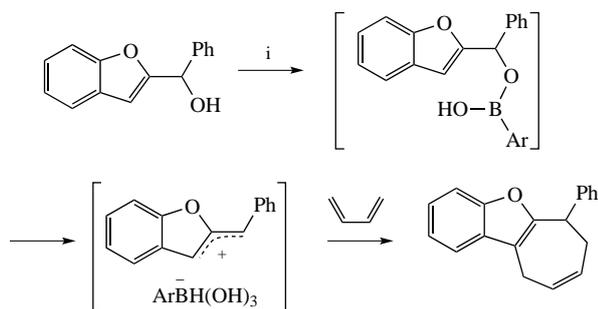
Scheme 21 *Reagents and conditions*: i, 2,3,4,5-F$_4$C$_6$HB(OH)$_2$ **27** (20 mol%), CH$_2$Cl$_2$, 50 °C.

trans-4,5-Disubstituted cyclopentenones were prepared by the reaction of 2-furyl(aryl)methanol with both primary and secondary anilines in the presence of acid **9**.[73] The intramolecular version of reaction using 5-ω-aminopropyl-2-furyl(aryl)-methanol, gave a number of substituted 1-azaspiro[4.4]non-8-en-7-ones (Scheme 22). The first step of process is similar to the

R = Me, Ph, 4-MeOC$_6$H$_4$, 4-CF$_3$C$_6$H$_4$
Ar = Ph, 3-ClC$_6$H$_4$, 4-BrC$_6$H$_4$, 4-IC$_6$H$_4$
R′ = Me, Ph, 4-MeOC$_6$H$_4$, 4-ClC$_6$H$_4$

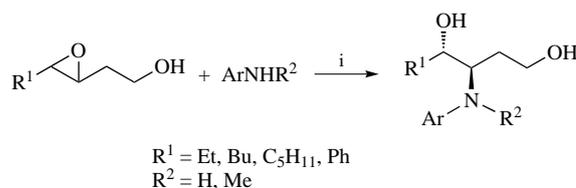**Scheme 22** *Reagents and conditions*: i, 2,3,5,6-F$_4$C$_6$HB(OH)$_2$ **9** (20 mol%), MeCN, 60–100 °C.

abovementioned one (see Scheme 21) and leads to furfuryl cation. The trapping of that with aniline and subsequent rearrangements afford a hydroxycyclopentenyl aryltri(hydroxy)-borate which converts to aminocyclopentenone and releases acid **9**.

The next example of the related cyclization is synthesis of 2*H*-chromenes from phenols and α,β-unsaturated aldehydes and ketones.[74] As above, the catalytic step is esterification of arylboronic acid with phenol, the intramolecular alkylation leading to benzodioxaborinine intermediate followed by fragmentation to an *ortho*-quinone methide and electrocyclic ring closure. For the better yield of the product, condensation should be provided in the presence of Brønsted acid of medium strength (Scheme 23). When 1- and 2-naphthol were involved, the corresponding of 2*H*-naphtho[1,2-*b*]- and 2*H*-naphtho[2,1-*b*]-pyrans, respectively, were prepared.

R^1 = Me, Ph; R^2 = Me, Pr, Ph; R^3 = H, Me, Ph
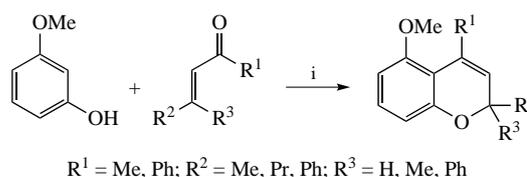
Scheme 23 *Reagents and conditions*: i, C$_6$F$_5$B(OH)$_2$ **7** (20 mol%), Ph$_2$PO$_2$H (20 mol%), heptane, 100 °C.

Aminolysis of 3,4-epoxyhomoallylic alcohols with anilines catalyzed by Lewis acids proceeded as the regio-, dia- and enantiospecific hydroxyl-directed ring opening leading to amino diols.[75] In general, the catalytic properties of a number of Lewis acids were tested and displayed satisfactory to good yields of desired products, while the best result was achieved with acid 3,4,5-F$_3$C$_6$H$_2$B(OH)$_2$ **8**. In model reaction of *trans*-3,4-epoxyhexan-1-ol with *o*-anisidine, the yields of amino diol exceeded 90% in solvents of different types (DCE, THF, MeCN, toluene, HFIP). Catalysis with acid C$_6$F$_5$B(OH)$_2$ **7** provided slightly lower yield (74%). In case of electron-rich anilines the products were obtained in excellent yields, whereas anilines containing electron-withdrawing substituent in *para*-position were slightly less reactive. Derivatives of *N*-methylaniline and indole were prepared in good yields. However, an attempted aminolysis with piperidine gave amino diol in only 18% yield. Evaluation of the substrate scope of C-3 selective aminolysis by varying the structure of the epoxides did not reveal sensitivity of reaction to the nature of substituent at the position 4 of substrate although introduction of two methyl groups at position 1 led to a remarkable decrease in yield (Scheme 24). It is noteworthy that substrates with one CH$_2$ unit between oxirane ring and hydroxy group give the products in significantly lower yield, while 5,6-epoxyheptan-1-ol with (CH$_2$)$_5$ chain did not undergo aminolysis.
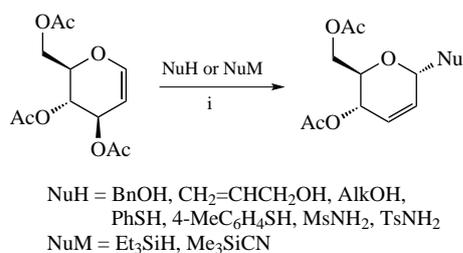

R^1 = Et, Bu, C$_5$H$_{11}$, Ph
R^2 = H, Me

Scheme 24 *Reagents and conditions*: i, 3,4,5-F$_3$C$_6$H$_2$B(OH)$_2$ **8** (15–25 mol%), toluene or (CF$_3$)$_2$CHOH, 40–60 °C, 24 h.

However, under the same conditions the reaction of *trans*-3,4-epoxyhexan-1-ol with 4-methoxythiophenol resulted in the low yields (15–27%) of expected 3-(4-methoxyphenylthio)hexane-1,4-diol, whereas the best yield (98%) was obtained using

3-nitrophenylboronic acid.[76] Unfortunately, authors did not comment such a result.

The synthesis of 2,3-unsaturated C-, O-, N- and S-linked glycosides (enosides) using pentaflurophenylboronic acid as a catalyst was performed *via* the Ferrier rearrangement. Optimal conditions were found using reaction of 3,4,6-tri-*O*-acetyl-D-glucal with benzyl alcohol in the presence of 20 mol% of $C_6F_5B(OH)_2$ **7** in different solvents. The best result was obtained in nitromethane, whereas in MeCN the yield was reduced, and in CH_2Cl_2 or THF no reaction occurred. In this way, derivatization of D-glucals and L-rhamnals with various C-, O-, N- and S-nucleophiles was accomplished to prepare a wide range of glycosides with mainly α-anomeric selectivity[77] (Scheme 25).

NuH = BnOH, CH_2=$CHCH_2OH$, AlkOH,
     PhSH, $4-MeC_6H_4SH$, $MsNH_2$, $TsNH_2$
NuM = Et_3SiH, Me_3SiCN

Scheme 25 *Reagents and conditions*: i, $C_6F_5B(OH)_2$ **7** (20 mol%), $MeNO_2$, 40 °C, 6 h.

The same authors reported pentafluorophenylboronic acid-catalyzed α-stereoselective direct addition of alcohols to deactivated peracetylated D-galactal to prepare 2-deoxy-galactosides as well as disaccharides containing 2-deoxygalactose moiety.[78] 4-Fluorophenylboronic acid displayed no catalytic activity. Along with the results of the previous work[77] (see Scheme 25), the strong influence of conformation factor of the starting glycal but not the reaction temperature on the structure of final product was revealed (Scheme 26).

ROH = phenols, alcohols, glucoses, mannoses, ribose, arabinose
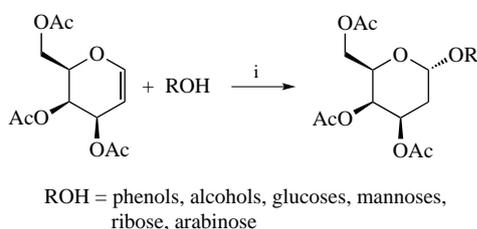
Scheme 26 *Reagents and conditions*: i, $C_6F_5B(OH)_2$ **7** (20 mol%), $MeNO_2$, 40 °C, 6 h.

The ability of arylboronic acids to generate C-electrophilic centers in reaction with alcohols was employed in the Friedel–Crafts alkylation of arenes and hetarenes. (The depiction of carbocations in schemes is an exaggeration to illustrate the mechanism of the process. Actually, this is only the polarization of the carbon–oxygen bond.) In 2010, McCubbin *et al.*[79] presented the alkylation of electron-rich arenes and furans with various allylic alcohols catalyzed with acid **7** (Scheme 27).
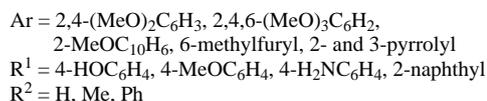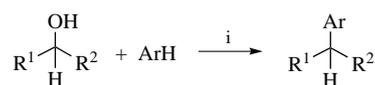
Ar = $4-MeC_6H_4$, $2-MeOC_{10}H_6$, 2- and 3-pyrrolyl, 3-indolyl
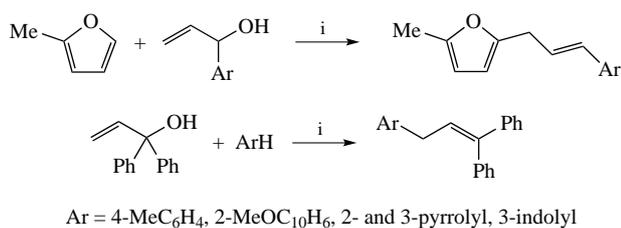
Scheme 27 *Reagents and conditions*: i, $C_6F_5B(OH)_2$ **7** (20 mol%), CH_2Cl_2, MS, room temperature, 16 h.

The further optimization of this process led to application of acid **27** and 2,3-difluoro-4-dihydroxyboryl-1-methylpyridinium chloride (**29**) as catalysts in addition to acid **7**. Moreover, the use of a 4:1 mixture of hexafluoroisopropanol and nitromethane at room temperature allowed one to abandon the use of molecular sieves as a dehydrating agent. Presumably, this polar solvent mixture is preferable due to its high ionizing ability, which favors the stabilization of carbocations or the closely related transition state. This combination 'catalyst–solvent' was successful in alkylation of toluene, *m*-xylene, substituted anisoles, dimethylnaphthalene and pyrene with a number of allylic alcohols (Scheme 28).[80]

R^1 = Me, Ar; R^2 = H, Alk, Ph; R^3 = H, Me

X = Ph, I; R = Ph, Alk
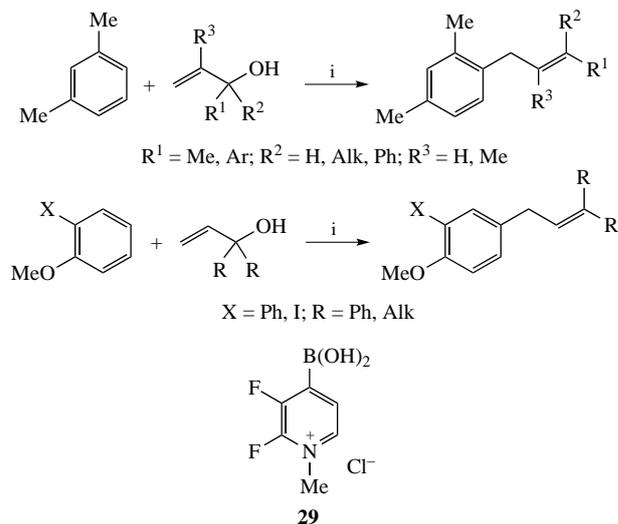
Scheme 28 *Reagents and conditions*: i, $2,3,4,5-F_4C_6HB(OH)_2$ **27** or **29** (10–20 mol%), CH_2Cl_2, $(CF_3)_2CHOH$–$MeNO_2$ (4:1), room temperature.

These reactions were extended to the closely related benzylic alcohols.[81] Arylalkylation proceeded in refluxing DCE or toluene, *i.e.*, at temperatures higher than in cases of allylic alcohols to afford products in more than 80–90% yield (Scheme 29). However, triphenylmethanol alkylated only high electron-rich substrates such as 2-methylfuran, pyrrole and indole.

Ar = $2,4-(MeO)_2C_6H_3$, $2,4,6-(MeO)_3C_6H_2$,
     $2-MeOC_{10}H_6$, 6-methylfuryl, 2- and 3-pyrrolyl
R^1 = $4-HOC_6H_4$, $4-MeOC_6H_4$, $4-H_2NC_6H_4$, 2-naphthyl
R^2 = H, Me, Ph

Scheme 29 *Reagents and conditions*: i, $C_6F_5B(OH)_2$ **7** (10 mol%), DCE or PhMe, MS, reflux.

Later this procedure was significantly improved by application of perfluoropinacol additive as a co-catalyst.[82] Likely, it forms an electrophilic boronic ester which is the actual catalyst (Scheme 30). This assumption was supported by ^{11}B NMR measurements as well ESI mass spectrometry in the negative mode. It is noteworthy that other tested additives (oxalic acid, 2,2-difluoropropane-1,3-diol, 2,2,3,3-tetrafluorobutane-1,4-diol and tetrabromocatehol) were less effective or even useless.

Obviously, additives of 1,2-dihydroxy compounds can enhance the catalytic activity of arylboronic acids because the corresponding esters seem to be stronger Lewis acids than the acids themselves. Moran *et al.*[83] studied the influence of several additives on the catalytic activity of fluorinated phenylboronic acids in the alkylation of mesitylene with 4-methoxybenzylic
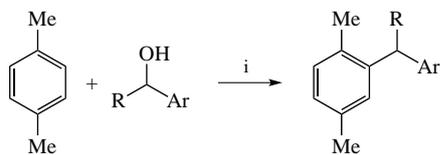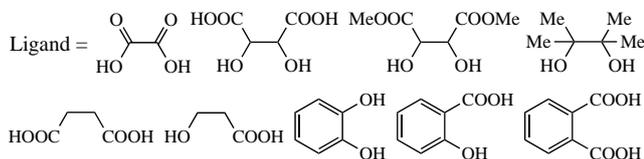
R = H; Ar = 4-XC₆H₄ (X = H, Br, CF₃, CO₂Me, SO₂Me, NO₂)
R = Ph; Ar = Ph, 4-BrC₆H₄, 3,5-(CF₃)₂C₆H₃
R = Ar = 4-XC₆H₄ (X = F, Cl)

Scheme 30 *Reagents and conditions*: i, C₆F₅B(OH)₂ **7** (10 mol%), (CF₃)₂C(OH)₂ (10 mol%), (CF₃)₂CHOH–MeNO₂ (4:1), 80 °C, 24 h.
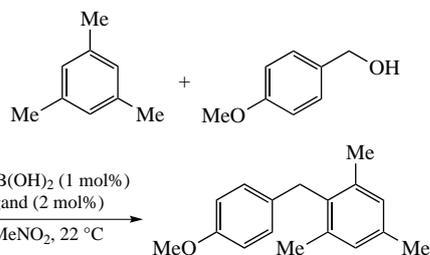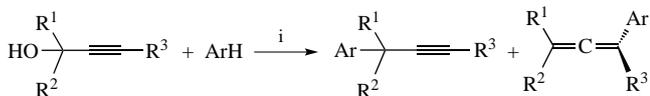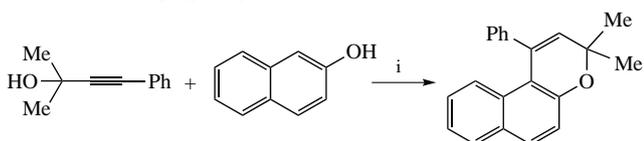

Scheme 31

alcohol (Scheme 31). They found that combination of acid **7** with oxalic acid was the most effective catalytic system, although acid **27** and (COOH)₂ showed the comparative activity too.

Taking into account the abovementioned results, the successful alkylation of activated aromatics, furans and pyrroles with propargylic alcohols under catalysis with acid **7** is not surprising (Scheme 32). Under these conditions, isomeric allenes were also formed, whose fraction depended on the structure of reactants.[84] Furthermore, the intramolecular cyclization of intermediate obtained from 2-naphthol and propargylic alcohols allowed one to prepare substituted naphthofurans (see Scheme 32).


Ar = 2,4-(MeO)₂C₆H₃, 2,4,6-(MeO)₃C₆H₂,
2-MeOC₁₀H₆, 5-methylfuryl, 2- and 3-pyrrolyl
R¹ = H, Me, Ph; R² = 4-XC₆H₄ (X = H, F, OH, OMe, CF₃)
R³ = Ph, C₆H₁₃, Me₃Si

Scheme 32 *Reagents and conditions*: i, C₆F₅B(OH)₂ **7** (10 mol%), CH₂Cl₂, MS, room temperature, 16 h.

The interesting development of boronic acid-catalyzed Friedel–Crafts alkylation is intramolecular cyclization of allylic alcohols (Scheme 33).[85] Under optimal conditions a number of 4-alkenylchromanes and alkenyltetralines was obtained in good yields. All tested catalysts, acids **27**, **28** and **29** (as iodide), displayed satisfactory and nearly equal activity, although
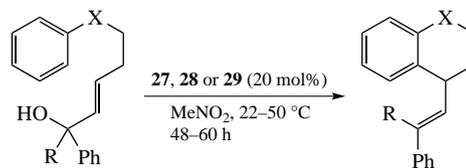

X = O, CH₂; R = H, Ph

Scheme 33

commercially available 2,3,4,5-C₆F₄HB(OH)₂ **27** is the most attractive one.

When this approach was extended to long-chain aliphatic allylic alcohols, the intramolecular heterocyclization with diols and amino alcohols was successfully performed (Scheme 34). In the presence of acid **27**, derivatives of tetrahydrofuran, pyran, oxepane, pyrrolidine and piperidine were obtained in high yields (Scheme 34).
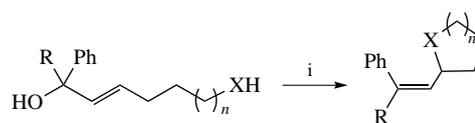
X = O, TsN; R = H, Ph; n = 1–3

Scheme 34 *Reagents and conditions*: i, 2,3,4,5-F₄C₆HB(OH)₂ **27** (10 mol%), MeNO₂, 25–50 °C, 16–48 h.

The synthetic potential of such cyclizations was exemplified by polycyclization and spiroketalization (Scheme 35).
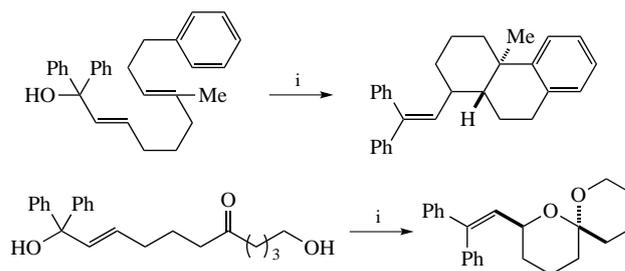
Scheme 35 *Reagents and conditions*: i, 2,3,4,5-F₄C₆HB(OH)₂ **27** (20 mol%), MeNO₂, 25–50 °C, 16–48 h.

Conclusions

Fluorinated arylboranes are unique compounds. The existing and constantly improving methods for their preparation are convenient tools for adjusting the basic properties of these compounds, which determine their ability to participate in the transformations of other organic molecules. For instance, the methods for constructing the ligand environment of a boron atom can be compared with coarse tuning tools that determine such basic properties of arylboranes as Lewis and Brønsted acidity, steric availability of boron atom, and the presence of specific groups (for example, chiral ones). The type and measure of acidity affect the catalytic activity of arylboranes. The steric availability of the boron atom is important for control of the selectivity of the catalytic process. The presence of chiral groups makes it possible to use arylboranes in the synthesis of chiral organic compounds.

The change in the number of fluorine atoms in the aromatic ring and their position relative to the boron atom can be attributed to fine-tuning tools. A decrease in the number of fluorine atoms in the aromatic ring allows one to reduce the acidity of the boron atom. By varying the mutual arrangement of fluorine atoms in the aromatic ring, it is also possible to change the acidic and chemical properties of arylboranes. The combination of the

steric isolation of the boron atom with the high acidity of fluorinated triarylboranes has become an objective prerequisite for the emergence of a new direction in chemistry – the chemistry of uncompensated sterically hindered Lewis pairs (FLP), capable of activating such small molecules as H_2, CO and CO_2.

The individual examples presented above demonstrate the high potential of fluorinated arylboranes as effective homogeneous catalysts for various types of reactions of organic compounds. Of particular interest is the use of polyfluorotriarylboranes in catalytic hydrogenation, since it opens up the possibility of excluding transition metals from the synthesis of biologically active substances, in particular pharmaceutical preparations.

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