Synthesis of Functionalized Borate Building Blocks for the Anionic Derivatization of Neutral Compounds

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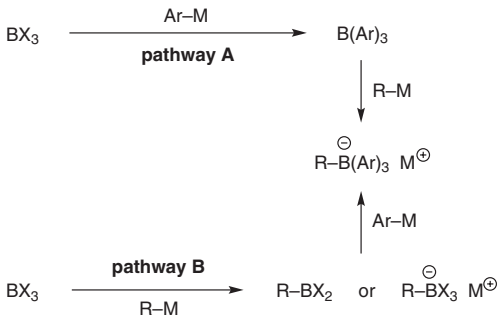
Abstract: Mono- and bifunctional fluorinated borate building blocks were prepared in three to five steps with good to excellent overall yields. Compounds with both nucleophilic and electrophilic functionalities are presented, which can be used for the anionic derivatization of neutral molecules.

Key words: boron, fluorine, organometallic reagents, anions

Fluorinated tetraarylborates constitute an easily accessible class of weakly coordinating anions (WCA),[2] which have found widespread use in the synthesis of highly efficient single-site olefin polymerization catalysts.[3] In addition, they were successfully applied in catalytic asymmetric transformations such as the iridium-catalyzed hydrogenation of unfunctionalized alkenes[4] and Diels–Alder reactions.[5] In most cases, the well-established representatives tetrakis(pentafluorophenyl)borate[6] or tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr^F or TFPB)[7] were employed. Furthermore, related anions with four identical aryl moieties at the boron center have recently been developed.[8] However, there are only a few examples of borates having the composition $[B(C_6F_5)_3(R)]^-$ with different boron substituents, and only simple alkyl derivatives [R = Me, Et, *i*-Pr, *n*-Bu, $CH_2C(CH_3)_3$][9] and the phenyl analogue (R = Ph)[10] have been described in detail.

In principle, the synthesis of $[B(Ar)_3(R)]^-$ species can be accomplished via two synthetic pathways (Scheme 1), differing in the order of steps through which the two substituents at the boron center are introduced.[9,10]



Scheme 1 Two pathways for the preparation of mixed tetraarylborates

If the borane $B(Ar)_3$ is easily accessible, the desired borate can be obtained according to pathway A, in one step, by addition of the appropriate metal organyl compound. Alternatively, a neutral (RBX_2) or anionic intermediate (RBX_3^-) can be generated first and subsequently transformed into the borate by reaction with the corresponding aryl reagent according to pathway B.

In the course of our studies concerning the effect of the counter-ion in iridium-catalyzed asymmetric hydrogenation reactions,[4,11] functionalized borate building blocks were required to prepare anionic derivatives of neutral ligands. In this report, we describe the synthesis of a series of functionalized borates bearing nucleophilic or electrophilic functional groups, which can be used for the anionic functionalization of neutral compounds.

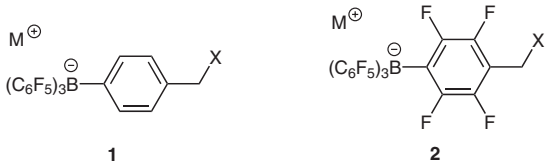


Figure 1 Functionalized borates with two different linkers

Initial attempts to prepare compounds of type **1** with a benzyl linker derived from the commercially available tris(pentafluorophenyl)borane (Figure 1) via pathway A, proved unsuccessful. The intermediate borates suffered from partial decomposition, presumably by proton-induced deborylation of the benzyl moiety, even under only slightly acidic conditions, for example during silica gel chromatography. Therefore, we turned our attention to the corresponding derivatives **2** with perfluorinated linkers. We assumed that the reduced π-basicity of these compounds would slow down the acid-driven cleavage of the carbon–boron bond and thus enable chromatographic purification.

Starting from the known benzylic alcohol **3**,[12] prepared in two steps from pentafluorobenzaldehyde (see experimental section), the silyl ethers **4** and **5** were synthesized (Scheme 2). While the *tert*-butyldimethylsilyl ether **4** was obtained in virtually quantitative yield, protection with *tert*-butyldiphenylsilyl chloride at room temperature furnished the desired aryl bromide **5** in 72% yield after 26 hours along with 27% of re-isolated starting material **3**.

Both silyl ethers **4** and **5** were subsequently metalated at low temperature and the resulting aryllithium compounds

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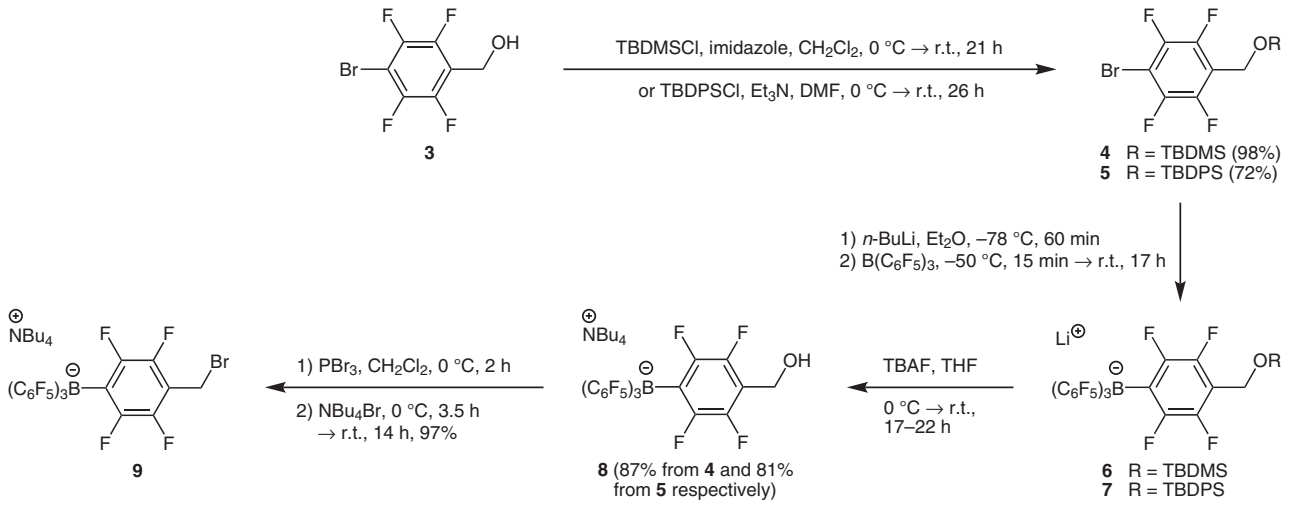


Scheme 2 Synthesis of building blocks derived from tris(pentafluorophenyl)borane

were quenched with tris(pentafluorophenyl)borane. The isolated borates **6** and **7** were contaminated by varying amounts of lithium [tetrakis(pentafluorophenyl)borate], which was easily removed after the next step. This side-product probably resulted from aryl exchange between the product and the borane reagent. The amount of the impurity was dependent on the protecting group and decreased with increasing reaction temperature. However, due to the explosive nature of similar *ortho*-fluorinated aryllithium compounds,[13] the transformations were not performed at temperatures above –50 °C. Under optimized conditions, using *tert*-butyldimethylsilyl ether **4** and slowly adding the electrophile at –50 °C, the ratio of product **6** to lithium [tetrakis(pentafluorophenyl)borate] was found to be 13:1, according to ^{19}F NMR spectroscopy.

The crude silyl ethers **6** and **7** were deprotected and the resulting tetrabutylammonium borate **8** was purified by chromatography on silica gel without any problems. As expected, fluorine substitution of the benzyl linker reduced the acid sensitivity and prevented decomposition during chromatography as observed with compounds **1**. Using the *tert*-butyldimethylsilyl protecting group, the hydroxyl-functionalized borate **8** was readily synthesized in 85% yield over three steps, starting from aryl bromide **3**.

Benzylic bromide **9** was prepared in high yield by treating alcohol **8** with phosphorus tribromide and tetrabutylammonium bromide (TBAB); the reaction without addition of TBAB was less efficient.

Interestingly, borates **6**–**9** showed more than the expected five signals in their ^{19}F NMR spectra. This can be ascribed to hindered rotation of the aryl substituents around the boron–carbon bonds with concomitant collapse of the dynamic C_3-symmetry.[14]

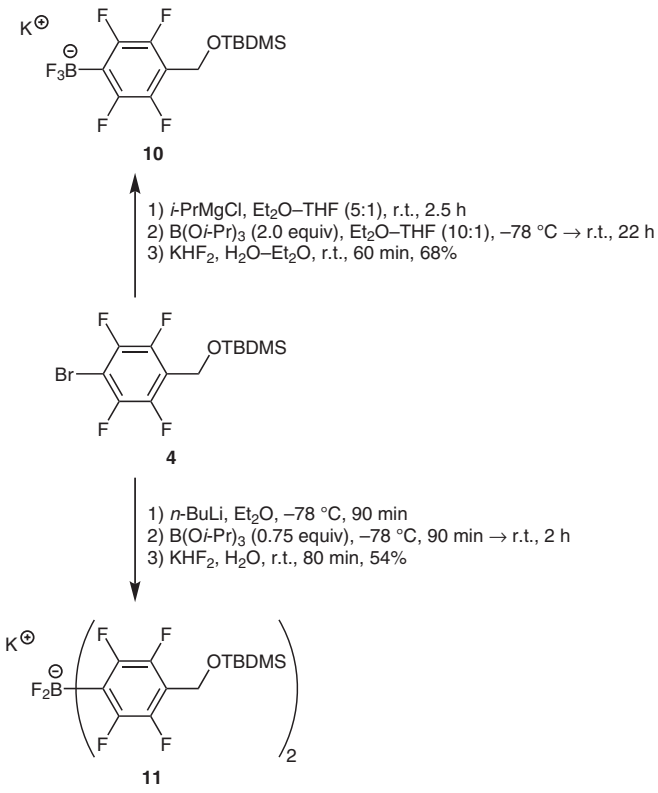
A different route was chosen for the preparation of the corresponding tris[3,5-bis(trifluoromethyl)phenyl]borates **14** and **16**. So far, no practical synthesis of tris[3,5-bis(trifluoromethyl)phenyl]borane has been described in the literature.[15] For this reason, we decided to develop a general reaction sequence according to pathway B in Scheme 1. As an intermediate of type RBX_3^-, the air- and moisture-stable aryltrifluoroborate **10** was chosen (Scheme 3).[16]

Initial attempts to synthesize the desired aryltrifluoroborate **10** from aryl bromide **4**, yielded mainly the corresponding diaryldifluoroborate **11**. Similarly, desired bisarylations of trialkyl borates have been described in the literature for a few cases.[17] However, after careful optimization of the reaction conditions, we were able to obtain both compounds **10** and **11** selectively (Scheme 3).

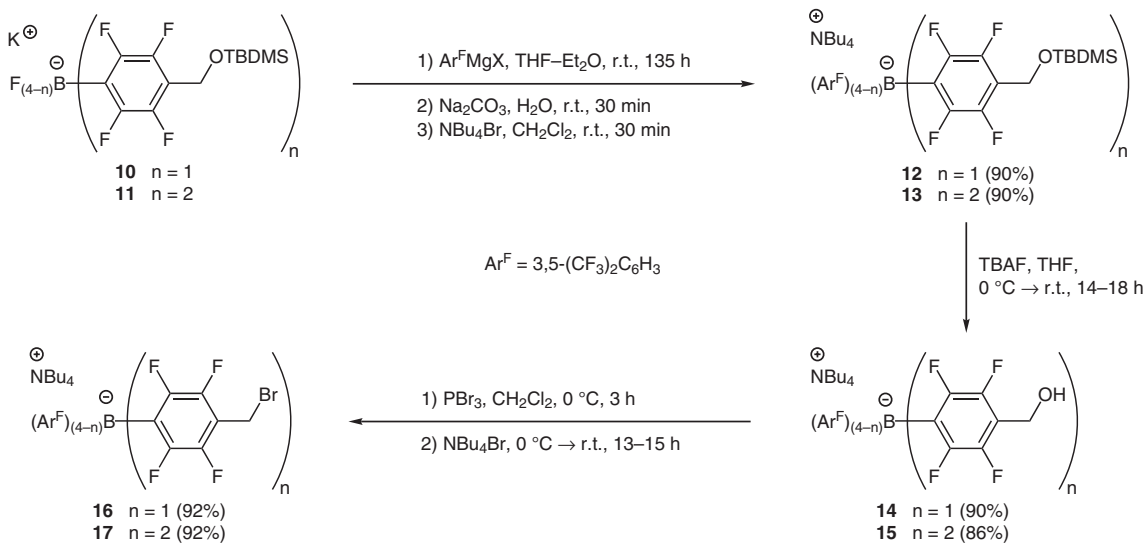
The aryltrifluoroborate **10**, prepared according to Scheme 3, contained about 10% of **11** as a side-product. However, the corresponding mixed tetraarylborates **12** and **13** (Scheme 4) could be easily separated by column chromatography after the next step. Interestingly, the *tert*-butyldimethylsilyl ether proved to be stable under the fluorination conditions,[18] but only if all the tetrahydrofuran present in the reaction mixture was removed before addition of potassium hydrogen difluoride.

Addition of the appropriate arylmagnesium reagent, prepared by halogen-magnesium exchange,[19] to the respective fluoroborates **10** and **11** yielded the mixed tetraarylborates **12** and **13** (Scheme 4). These were subsequently transformed into the bromides **16** and **17** via the corresponding benzylic alcohols **14** and **15**, using the procedures described in Scheme 2. In this way, the hydroxyl- and bromo-functionalized tetraarylborates **14**–**17** were obtained in 81–71% yield over three steps.

In summary, a series of mono- and bifunctional fluorinated borate building blocks have been prepared, containing nucleophilic hydroxyl or electrophilic benzylic bromide functionalities. The compounds are readily accessible in three to five steps with 85–38% overall yield, starting from the literature-known alcohol **3**. The inert nature and lipophilicity, which ensures high solubility in apolar media, are attractive features of the borate unit. Reagents of



Scheme 3 Preparation of arylfluoroborates **10** and **11**



Scheme 4 Synthesis of mono- and bifunctional borates

this type can be used for the anionic derivatization of any neutral compound possessing at least one nucleophilic or electrophilic functional group. Thus they may find use in ESI-MS studies or mechanistic investigations of anion effects. Application of these borate reagents in the synthesis of anionic ligands for metal-catalyzed asymmetric transformations will be reported in due course.

All reactions were performed in flame-dried glassware under argon using Schlenk techniques. Solvents, Et_3N, LiBr and TBAB were dried employing standard procedures.[20] All other commercial reagents were used without further purification. Chromatography was performed on Merck silica gel 60 (Darmstadt, 40–63 nm). For TLC analyses, pre-coated Macherey–Nagel Polygram SIL G/UV_{254} plates were used and the compounds were visualized with the help of UV light. All NMR experiments were performed on Bruker Avance 400 and 500 MHz spectrometers. ^1H and ^{13}C NMR spectra are referenced relative to TMS using the residual solvent peaks and the solvent signals, respectively, as internal standards.[21] The ^{19}F and ^{11}B spectra were calibrated using $CFCl_3$ and $BF_3{\cdot}OEt_2$ as external standards. Mass spectra were measured on VG70-250, Finnigan MAT 95Q (EI) or Finnigan MAT LCQ apparatus (ESI). Elemental

analyses were performed by the Micro Analysis Laboratory of the University of Basel. IR spectra were measured on a Perkin–Elmer 1600 FTIR spectrometer. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Benzylic alcohol **3** was prepared following literature procedures.[12] The abbreviation Ar^F refers to any fluorinated aryl moiety, whilst the abbreviations m_c and dm_c refer to centered multiplet and doublet of centered multiplet, respectively.

4-Bromo-2,3,5,6-tetrafluorobenzaldehyde[12]

A solution of pentafluorobenzaldehyde (11.2 mL, 17.7 g, 90.3 mmol) and dried LiBr (8.90 g, 102 mmol) in anhyd NMP (50 mL) was stirred at 160 °C for 3 h. After the brown mixture had been cooled to r.t., it was filtered through Celite. The filtrate was poured into H_2O (200 mL) and the resulting brownish solid was collected by filtration, washed with H_2O (3 × 20 mL) and dried over P_2O_5 in a desiccator. The filtrate was extracted with Et_2O (5 × 100 mL) and the combined organic phases were dried over $MgSO_4$, filtrated and evaporated under reduced pressure. The remaining sticky solid was washed with H_2O (3 × 10 mL) and dried as described above. The combined crude products were washed with Et_2O (60 mL) and dried. Concentration of the washing solutions to about half volume and isolation of the precipitate formed yielded a second crop of product. Aldehyde **18** was isolated as a pale-yellow solid in total yield of 13.7 g (59%).

Mp 107–108.5 °C (Lit.[12] 105–108 °C); R_f = 0.47 (hexanes–EtOAc, 3:1).

IR (KBr): 2915, 1702, 1636, 1587, 1485, 1415, 1389, 1306, 1273, 1070, 1035, 970, 831, 777, 625, 584 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.30 (s).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 107.5 (tt, J = 22, 2 Hz, Ar-*p*-C), 114.6 (t, J = 10 Hz, Ar-*i*-C), 145.3 (dm_c, J = 251 Hz, Ar-C), 146.8 (dm_c, J = 264 Hz, Ar-C), 182.1 (m_c, CHO).

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –144.2 (m_c, 2 F, Ar-*o*-F), –131.5 (m_c, 2 F, Ar-*m*-F).

MS (EI, 70 eV): *m*/*z* (%) = 257 (100) $[M - H]^+$, 229 (16) $[M - CHO]^+$, 149 (41) $[C_6F_4H^+]$, 99 (28), 79 (10).

Anal. Calcd for C_7HBrF_4O: C, 32.72; H, 0.39. Found: C, 32.67; H, 0.46.

(4-Bromo-2,3,5,6-tetrafluorophenyl)methanol (3)[12]

A solution of 4-bromo-2,3,5,6-tetrafluorobenzaldehyde (18.4 g, 71.6 mmol) in anhyd MeOH (150 mL) was cooled to 0 °C and $NaBH_4$ (2.71 g, 71.6 mmol) was added in portions over a period of 40 min. The mixture was stirred for a further 60 min at 0 °C and then for 3 h at r.t. The solution was poured into cold aqueous HCl (3%, 600 mL) and the resulting suspension was cooled in an ice bath. The yellow solid was collected by filtration, washed with H_2O (4 × 20 mL) and dried over P_2O_5 in a desiccator. The filtrate was concentrated under reduced pressure to a volume of about 100 mL. The resulting precipitate was isolated by filtration, washed with H_2O (3 × 10 mL) and dried as above. The benzylic alcohol **3** was obtained in two crops as a colorless powder (14.3 g, 77%).

Mp 65–66 °C (Lit.[12] 60–62 °C); R_f = 0.24 (hexanes–EtOAc, 3:1).

IR (KBr): 3347, 2980, 2954, 2894, 1637, 1476, 1406, 1370, 1270, 1223, 1044, 1029, 1003, 901, 830, 751, 662, 577, 437 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.96 (t, J = 6.6 Hz, 1 H, OH), 4.82 (d, J = 6.4 Hz, 2 H, CH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 53.0 (CH_2), 100.2 (t, J = 23 Hz, Ar-*p*-C), 118.2 (t, J = 18 Hz, Ar-*i*-C), 144.9 (dm_c, J = 250 Hz, Ar-C), 145.3 (dm_c, J = 251 Hz, Ar-C).

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –143.4 (m_c, 2 F, Ar-*o*-F), –133.3 (m_c, 2 F, Ar-*m*-F).

MS (EI, 70 eV): *m*/*z* (%) = 258 (100) $[M^+]$, 239 (74) $[M - F]^+$, 210 (33), 179 (14) $[M - Br]^+$, 162 (30), 150 (44), 130 (23), 99 (17), 81 (13).

Anal. Calcd for $C_7H_3BrF_4O$: C, 32.46; H, 1.17. Found: C, 32.49; H, 1.23.

(4-Bromo-2,3,5,6-tetrafluorobenzyloxy)-*tert*-butyldimethylsilane (4)

To a solution of benzylic alcohol **3** (1.83 g, 7.05 mmol) and imidazole (959 mg, 14.1 mmol) in anhyd CH_2Cl_2 (20 mL), TBDMSCl (1.59 g, 10.6 mmol) in CH_2Cl_2 (10 mL) was slowly added at 0 °C. After the resulting colorless suspension had been stirred for 21 h (overnight) at r.t., it was poured into aqueous HCl (1 M, 50 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 40 mL). The combined extracts were washed with sat. $NaHCO_3$ (20 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. Purification of the remaining yellow oil by column chromatography (silica gel, 4 × 24 cm, hexanes–EtOAc, 15:1) yielded silyl ether **4** as a colorless, viscous oil, which solidified at –22 °C to a waxy solid (2.57 g, 98%).

R_f = 0.57 (hexanes–EtOAc, 15:1).

IR (NaCl): 2955, 2935, 2891, 2860, 1637, 1487, 1261, 1100, 1051, 917, 837, 780, 717 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.12 [s, 6 H, $Si(CH_3)_2$], 0.90 [s, 9 H, $C(CH_3)_3$], 4.77 (t, J = 1.7 Hz, 2 H, CH_2).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = –5.4 [$Si(CH_3)_2$], 18.5 [$C(CH_3)_3$], 25.9 [$C(CH_3)_3$], 53.4 (CH_2), 99.7 (m_c, Ar-*p*-C), 118.7 (t, J = 18 Hz, Ar-*i*-C), 144.9 (dm_c, J = 243 Hz, Ar-C), 145.4 (dm_c, J = 250 Hz, Ar-C).

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –142.9 (m_c, 2 F, Ar-*o*-F), –133.9 (m_c, 2 F, Ar-*m*-F).

MS (EI, 70 eV): *m*/*z* (%) = 317 (100) $[M - t\text{-Bu}]^+$, 241 (15) $[4\text{-}BrC_6F_4CH_2^+]$, 236 (10), 221 (13), 77 (45).

Anal. Calcd for $C_{13}H_{17}BrF_4OSi$: C, 41.83; H, 4.59. Found: C, 41.76; H, 4.54.

(4-Bromo-2,3,5,6-tetrafluorobenzyloxy)-*tert*-butyldiphenylsilane (5)

To a solution of benzylic alcohol **3** (5.18 g, 20.0 mmol) and anhyd Et_3N (4.18 mL, 30.0 mmol) in anhyd DMF (40 mL), TBDPSCl (6.14 mL, 24.0 mmol) was slowly added at 0 °C. After the mixture had been stirred for 26 h at r.t., it was diluted with Et_2O (150 mL) and poured into aq HCl (0.4 M, 80 mL). The phases were separated and the aqueous phase was extracted with Et_2O (3 × 70 mL). The combined extracts were washed with sat. $NaHCO_3$ (40 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. After purifying the remaining oil by column chromatography (silica gel, 7 × 16 cm, hexanes–EtOAc, 10:1) silyl ether **5** was obtained as colorless, viscous oil (7.14 g, 72%). In addition, some of the starting alcohol **3** was re-isolated (1.39 g, 27%).

R_f = 0.51 (hexanes–EtOAc, 10:1).

IR (NaCl): 3071, 2936, 2893, 2860, 1638, 1487, 1428, 1387, 1270, 1107, 1051, 916, 818, 703 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 9 H, CH_3), 4.78 (s, 2 H, CH_2), 7.41 (m_c, 4 H, Ph-*m*-H), 7.46 (m_c, 2 H, Ph-*p*-H), 7.69 (m_c, 4 H, Ph-*o*-H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 19.4 [$C(CH_3)_3$], 26.8 (CH_3), 54.2 (CH_2), 99.8 (m_c, Ar-*p*-C), 118.4 (t, J = 18 Hz, Ar-*i*-C), 128.0 (Ph-*m*-CH), 130.1 (Ph-*p*-CH), 132.8 (Ph-*i*-C), 135.7 (Ph-*o*-CH), 144.8 (dm_c, J = 248 Hz, Ar-C), 145.4 (dm_c, J = 252 Hz, Ar-C).

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –142.3 (m_c, 2 F, Ar-*o*-F), –134.0 (m_c, 2 F, Ar-*m*-F).

MS (EI, 70 eV): *m*/*z* (%) = 441 (100) [M – *t*-Bu]$^+$, 254 (10), 201 (18).

Anal. Calcd for $C_{23}H_{21}BrF_4OSi$: C, 55.54; H, 4.26. Found: C, 55.70; H, 4.15.

Lithium [4-(*tert*-Butyldimethylsilanyloxymethyl)-2,3,5,6-tetrafluorophenyl]tris(pentafluorophenyl)borate (6)

To a solution of aryl bromide **4** (1.01 g, 2.71 mmol) in anhyd Et_2O (15 mL), *n*-BuLi in hexanes (1.6 M, 1.69 mL, 2.71 mmol) was added dropwise at –78 °C over a period of 12 min (**Caution:** *ortho*-Fluorinated aryllithium reagents are potentially explosive!). After the mixture had been stirred for 60 min at –78 °C, the temperature was raised to –50 °C and $B(C_6F_5)_3$ (1.39 g, 2.71 mmol) in anhyd Et_2O (55 mL) was added slowly within 25 min. The slightly yellow solution was stirred for a further 15 min at –50 °C and then for 17 h (overnight) at r.t. The solution was concentrated under reduced pressure to a volume of about 8 mL and anhyd pentane (50 mL) was added. The mixture was vigorously stirred for 25 min at r.t. and the upper phase was removed. The remaining oil was treated with anhyd pentane (3 × 10 mL) and dried in high vacuum. The colorless, foamy solid obtained consisted of borate **6** and $Li[B(C_6F_5)_4]$ in a ratio of 13:1 according to ^{19}F NMR spectroscopy.

^1H NMR (400 MHz, acetone-d_6): δ = 0.07 [s, 6 H, $Si(CH_3)_2$], 0.87 [s, 9 H, $C(CH_3)_3$], 4.77 (s, 2 H, CH_2).

$^{19}F\{^1H\}$ NMR (375 MHz, acetone-d_6): δ = –167.8 (m_c, 6 F, C_6F_5-*m*-F), –164.0 (t, *J* = 18 Hz, 2 F, C_6F_5-*p*-F), –163.9 (t, *J* = 18 Hz, 1 F, C_6F_5-*p*-F), –149.6 (dd, *J* = 23, 13 Hz, 2 F, Ar-*m*-F), –133.3 (m_c, 2 F, Ar^F-*o*-F), –132.3 (m_c, 2 F, Ar^F-*o*-F), –132.0 (m_c, 2 F, Ar^F-*o*-F), –131.7 (m_c, 2 F, Ar^F-*o*-F).

$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6): δ = –15.8.

MS (ESI): *m*/*z* (%) = 805 (100) $[M – Li]^–$.

Lithium [4-(*tert*-Butyldiphenylsilanyloxymethyl)-2,3,5,6-tetrafluorophenyl]tris(pentafluorophenyl)borate (7)

In analogy to the synthesis of **6**, TBDPS-ether **5** (3.89 g, 7.82 mmol) was reacted with *n*-BuLi in hexanes (1.6 M, 4.89 mL, 7.82 mmol) and $B(C_6F_5)_3$ (4.00 g, 7.82 mmol) in anhyd Et_2O (165 mL in total) for 15 min at –50 °C then for 16 h (overnight) at r.t. A colorless, foamy solid was obtained, which consisted of borate **7** and $Li[B(C_6F_5)_4]$ in a ratio of 9:1 according to ^{19}F NMR spectroscopy.

^1H NMR (400 MHz, acetone-d_6): δ = 1.00 (s, 9 H, CH_3), 4.79 (s, 2 H, CH_2), 7.37–7.49 (m, 6 H, Ph-*m*-H and Ph-*p*-H), 7.70 (d, *J* = 7.3 Hz, 4 H, Ph-*o*-H).

$^{19}F\{^1H\}$ NMR (375 MHz, acetone-d_6): δ = –167.7 (m_c, 6 F, C_6F_5-*m*-F), –164.0 (t, *J* = 20 Hz, 2 F, C_6F_5-*p*-F), –163.9 (t, *J* = 20 Hz, 1 F, C_6F_5-*p*-F), –149.0 (dd, *J* = 23, 13 Hz, 2 F, Ar-*m*-F), –133.2 (m_c, 2 F, Ar^F-*o*-F), –132.3 (m_c, 2 F, Ar^F-*o*-F), –131.9 (m_c, 2 F, Ar^F-*o*-F), –131.6 (m_c, 2 F, Ar^F-*o*-F).

$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6): δ = –15.8.

MS (ESI): *m*/*z* (%) = 929 (100) $[M – Li]^–$.

Tetrabutylammonium (2,3,5,6-Tetrafluoro-4-hydroxymethylphenyl)tris(pentafluorophenyl)borate (8)

To a solution of crude silyl ether **6** in anhyd THF (25 mL), $TBAF·3H_2O$ (2.99 g, 9.47 mmol) was added at 0 °C. After the mixture had been stirred for 17 h (overnight) at r.t., all volatiles were removed under reduced pressure. The remaining yellow oil was redissolved in H_2O (60 mL) and Et_2O (80 mL), the phases were separated and the aqueous phase was extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with H_2O (15 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification of the resulting sticky foam by column chromatography (silica gel, 7 × 14 cm, 1.4 L CH_2Cl_2 then CH_2Cl_2–MeOH, 9:1) yielded benzylic alcohol **8** as a colorless, foamy solid (2.19 g, 87% over two steps).

In an analogous manner, **8** was obtained in 81% yield over two steps using TBDPS-ether **7**. In this case $TBAF·3H_2O$ was added at r.t. and the reaction time was 22 h.

Mp 53–56 °C; R_f = 0.15 (CH_2Cl_2).

IR (KBr): 3626, 3423, 2971, 2882, 1644, 1515, 1461, 1380, 1257, 1089, 977, 924, 885, 766, 694, 661, 626, 609, 575 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 0.98 (t, *J* = 7.3 Hz, 12 H, CH_3), 1.44 (sext, *J* = 7.4 Hz, 8 H, CH_2CH_3), 1.84 (m_c, 8 H, $CH_2CH_2CH_3$), 3.46 (m_c, 8 H, $CH_2CH_2CH_2CH_3$), 4.29 (t, *J* = 6.1 Hz, 1 H, OH), 4.64 (dt, *J* = 6.1, 1.4 Hz, 2 H, CH_2OH).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 13.8 (CH_3), 20.4 (t, *J* = 1 Hz, CH_2CH_3), 24.4 ($CH_2CH_2CH_3$), 52.4 (CH_2OH), 59.4 (t, *J* = 3 Hz, $CH_2CH_2CH_2CH_3$), 116.2 (t, *J* = 19 Hz, Ar-*p*-C), 125.5 (br, C_6F_5-*i*-C and Ar-*i*-C), 137.0 (dm_c, *J* = 244 Hz, C_6F_5-*m*-C), 139.0 (dm_c, *J* = 244 Hz, C_6F_5-*p*-C), 144.9 (dd, *J* = 244, 18 Hz, Ar-*m*-C), 148.9 (dd, *J* = 239, 13 Hz, Ar-*o*-C), 149.1 (dm_c, *J* = 241 Hz, C_6F_5-*o*-C).

$^{19}F\{^1H\}$ NMR (375 MHz, acetone-d_6): δ = –168.0 to –167.6 (m, 6 F, C_6F_5-*m*-F), –164.0 (t, *J* = 20 Hz, 2 F, C_6F_5-*p*-F), –163.9 (t, *J* = 19 Hz, 1 F, C_6F_6-*p*-F), –150.0 (dd, *J* = 22, 14 Hz, 2 F, Ar-*m*-F), –133.5 (m_c, 2 F, Ar^F-*o*-F), –132.3 (m_c, 2 F, Ar^F-*o*-F), –131.9 (m_c, 2 F, Ar^F-*o*-F), –131.7 (m_c, 2 F, Ar^F-*o*-F).

$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6): δ = –15.8.

MS (ESI): *m*/*z* (%) = 691 (100) $[M – NBu_4]^–$.

Anal. Calcd for $C_{41}H_{39}BF_{19}NO$: C, 52.75; H, 4.21; N, 1.50. Found: C, 52.86; H, 4.24; N, 1.52.

Tetrabutylammonium (4-Bromomethyl-2,3,5,6-tetrafluorophenyl)tris(pentafluorophenyl)borate (9)

To a solution of borate **8** (4.67 g, 5.00 mmol) in anhyd CH_2Cl_2 (35 mL), PBr_3 (305 μL, 3.25 mmol) was added dropwise at 0 °C. After the solution had been stirred for 2 h at 0 °C, dried TBAB (2.42 g, 7.50 mmol) was added. The mixture was stirred for a further 3.5 h at 0 °C and then for 14 h (overnight) at r.t. After the resulting colorless solution had been diluted with Et_2O (300 mL), it was successively washed with H_2O (50 mL), half-sat. $NaHCO_3$ (50 mL) and brine (50 mL). The combined aqueous phases were re-extracted with Et_2O (2 × 80 mL) and the combined extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure. Purification of the crude product by column chromatography (silica gel, 4 × 11 cm, CH_2Cl_2) yielded benzylic bromide **9** as a colorless, foamy solid (4.85 g, 97%).

Mp 54–59 °C; $R_f \leq 0.71$ (CH_2Cl_2, tailing).

IR (KBr): 2971, 2881, 1645, 1515, 1483, 1380, 1268, 1219, 1159, 1090, 979, 883, 766, 694, 665, 613, 549 cm^{-1}.

^1H NMR (400 MHz, acetone-d_6): δ = 0.98 (t, *J* = 7.4 Hz, 12 H, CH_3), 1.43 (sext, *J* = 7.4 Hz, 8 H, CH_2CH_3), 1.84 (m_c, 8 H, $CH_2CH_2CH_3$), 3.46 (m_c, 8 H, $CH_2CH_2CH_2CH_3$), 4.63 (s, 2 H, CH_2Br).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = 13.8 (CH_3), 19.1 (CH_2Br), 20.4 (t, *J* = 1 Hz, CH_2CH_3), 24.4 ($CH_2CH_2CH_3$), 59.4 (t, *J* = 3 Hz, $CH_2CH_2CH_2CH_3$), 113.4 (t, *J* = 17 Hz, Ar-*p*-C), 125.0 (br, C_6F_5-*i*-C and Ar-*i*-C), 137.1 (dm_c, *J* = 250 Hz, C_6F_5-*m*-C), 139.0 (dm_c, *J* = 247 Hz, C_6F_5-*p*-C), 144.5 (dd, *J* = 247, 19 Hz, Ar-*m*-C), 149.0 (dm_c, *J* = 238 Hz, C_6F_5-*o*-C and Ar-*o*-C).

$^{19}F\{^1H\}$ NMR (375 MHz, acetone-d_6): δ = –167.8 to –167.5 (m, 6 F, C_6F_5-*m*-F), –163.7 (t, *J* = 20 Hz, 2 F, C_6F_5-*p*-F), –163.5 (t, *J* = 20 Hz, 1 F, C_6F_5-*p*-F), –148.2 (dd, *J* = 22, 13 Hz, 2 F, Ar-*m*-F), –132.6 (m_c, 2 F, Ar^F-*o*-F), –132.3 (m_c, 2 F, Ar^F-*o*-F), –132.0 (m_c, 2 F, Ar^F-*o*-F), –131.8 (m_c, 2 F, Ar^F-*o*-F).

$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6): δ = –15.8.

MS (ESI): *m*/*z* (%) = 753 (100) $[M - NBu_4]^-$.

Anal. Calcd for $C_{41}H_{38}BBrF_{19}N$: C, 49.42; H, 3.84; N, 1.41. Found: C, 49.55; H, 3.85; N, 1.48.

Potassium [4-(*tert*-Butyldimethylsilanyloxymethyl)-2,3,5,6-tetrafluorophenyl]trifluoroborate (10)

To a solution of aryl bromide **4** (1.43 g, 3.82 mmol) in anhyd Et_2O (9 mL), *i*-PrMgCl in THF (2.0 M, 1.91 mL, 3.82 mmol) was added dropwise within 9 min at r.t. The mixture was stirred for 2.5 h and the resulting colorless suspension was diluted with more Et_2O (10 mL) and cooled to –78 °C. $B(O\textit{i}\text{-}Pr)_3$ (1.76 mL, 7.64 mmol) was quickly added and the mixture was stirred for 22 h (overnight) at r.t. To the viscous, colorless suspension, MeOH (100 μL) was added in order to destroy any residual aryllithium reagent. Then all volatiles were removed under reduced pressure. The remaining sticky solid was suspended in Et_2O (30 mL) in a polypropylene vessel and KHF_2 (2.54 g, 32.5 mmol) in H_2O (15 mL) was added dropwise at r.t. The two-phase system was vigorously stirred for 60 min and then evaporated under reduced pressure. The solid residue was extracted with acetone (5 × 10 mL), the combined extracts were filtered and the solvent was removed under reduced pressure. The crude product was suspended in CH_2Cl_2 (6 mL) and the mixture was stirred for 35 min at r.t. and filtered. The solid was washed with CH_2Cl_2 (2 × 2 mL) and dried by suction to yield a colorless powder, which consisted of product **10** and the corresponding difluoroborate **11** in a ratio of 10:1 according to ^{19}F NMR spectroscopy (1.22 g, ~68%). This material was sufficiently pure for use in the next step. Pure aryltrifluoroborate **10** could be obtained by washing this mixture several times with H_2O-saturated Et_2O,[17b] however, this procedure resulted in substantial loss of material.

IR (KBr): 2954, 2934, 2890, 2859, 1654, 1620, 1456, 1393, 1281, 1080, 1037, 979, 906, 842, 809, 781, 719, 678, 638, 599 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 0.11 [s, 6 H, $Si(CH_3)_2$], 0.88 [s, 9 H, $C(CH_3)_3$], 4.78 (t, *J* = 1.4 Hz, 2 H, CH_2).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = –5.3 [$Si(CH_3)_2$], 18.8 [$\textit{C}(CH_3)_3$], 26.1 [$C(\textit{C}H_3)_3$], 53.9 (CH_2), 116.2 (t, *J* = 18 Hz, Ar-*p*-C), 145.1 (dm_c, *J* = 243 Hz, Ar-*m*-C), 148.9 (dm_c, *J* = 244 Hz, Ar-*o*-C). Despite prolonged data acquisition time, the signal for Ar-*i*-C was not detected.

$^{19}F\{^1H\}$ NMR (375 MHz, acetone-d_6): δ = –149.0 (dd, *J* = 24, 15 Hz, 2 F, Ar-*m*-F), –135.9 (m_c, 2 F, Ar-*o*-F), –134.9 (br q, *J* = 41 Hz, 3 F, BF_3^-).

$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6): δ = 2.5 (q, *J* = 43 Hz).

MS (ESI): *m*/*z* (%) = 361 (100) $[M - K]^-$.

Potassium Bis[4-(*tert*-butyldimethylsilanyloxymethyl)-2,3,5,6-tetrafluorophenyl]difluoroborate (11)

To a solution of aryl bromide **4** (1.34 g, 3.58 mmol) in anhyd Et_2O (15 mL), *n*-BuLi in hexanes (1.6 M, 2.24 mL, 3.58 mmol) was added dropwise over a period of 10 min at –78 °C. After the mixture had been stirred for 90 min at this temperature, $B(O\textit{i}\text{-}Pr)_3$ (620 μL, 2.69 mmol) was added within 5 min to the colorless suspension. The mixture was stirred for a further 90 min at –78 °C and then for 2 h at r.t. before being transferred to a polypropylene vessel and KHF_2 (1.12 g, 14.3 mmol) in H_2O (7 mL) was slowly added. The two-phase system was vigorously stirred for 80 min at r.t. and then all volatiles were removed under reduced pressure. The remaining solid was extracted with acetone (5 × 10 mL) and the combined extracts were filtered and evaporated under reduced pressure. The crude product was suspended in CH_2Cl_2 (5 mL), the mixture was stirred for 30 min at r.t. and then filtered. The solid was washed with CH_2Cl_2 (2 × 2 mL) and dried by suction to yield the diaryldifluoroborate **11** as a colorless powder (656 mg, 54%).

IR (KBr): 2956, 2933, 2891, 2860, 1624, 1587, 1455, 1390, 1266, 1104, 1061, 968, 896, 841, 779, 741, 703, 608 cm^{-1}.

^1H NMR (500 MHz, acetone-d_6): δ = 0.10 [s, 12 H, $Si(CH_3)_2$], 0.88 [s, 18 H, $C(CH_3)_3$], 4.77 (t, *J* = 1.4 Hz, 4 H, CH_2).

$^{13}C\{^1H\}$ NMR (125 MHz, acetone-d_6): δ = –5.3 [$Si(CH_3)_2$], 18.8 [$\textit{C}(CH_3)_3$], 26.1 [$C(\textit{C}H_3)_3$], 53.9 (CH_2), 116.1 (t, *J* = 18 Hz, Ar-*p*-C), 145.1 (dd, *J* = 246, 19 Hz, Ar-*m*-C), 148.7 (dt, *J* = 238, 13 Hz, Ar-*o*-C). Despite prolonged data acquisition time, the signal for Ar-*i*-C was not detected.

$^{19}F\{^1H\}$ NMR (375 MHz, acetone-d_6): δ = –149.1 (dd, *J* = 24, 13 Hz, 4 F, Ar-*m*-F), –147.8 (br m_c, 2 F, BF_2^-), –136.7 (m_c, 4 F, Ar-*o*-F).

$^{11}B\{^1H\}$ NMR (160 MHz, acetone-d_6): δ = 5.0 (br t, *J* = 60 Hz).

MS (ESI): *m*/*z* (%) = 635 (100) $[M - K]^-$.

Tetrabutylammonium [4-(*tert*-Butyldimethylsilanyloxymethyl)-2,3,5,6-tetrafluorophenyl]tris[3,5-bis(trifluoromethyl)phenyl]borate (12)

To bromo-3,5-bis(trifluoromethyl)benzene (1.82 mL, 10.5 mmol) in anhyd THF (9 mL), *i*-PrMgCl in THF (2.0 M, 4.86 mL, 9.72 mmol) was added dropwise over a period of 6 min at 0 °C. The mixture was stirred for 60 min at 0 °C and then for 60 min at r.t. This Grignard solution was added to a suspension of aryltrifluoroborate **10** (649 mg, 1.62 mmol) in anhyd Et_2O (28 mL) and the resulting solution was stirred for 135 h at r.t. The mixture was poured into a solution of Na_2CO_3 (4.40 g) in H_2O (55 mL) and the two-phase system was vigorously stirred for 30 min at r.t. The phases were separated and the aqueous phase was extracted with Et_2O (3 × 50 mL). The combined organic extracts were dried over Na_2SO_4, filtered, evaporated under reduced pressure and the remaining oil was re-dissolved in CH_2Cl_2 (30 mL). TBAB (627 mg, 1.94 mmol) in CH_2Cl_2 (10 mL) was added and the suspension was stirred for 30 min at r.t., filtered and concentrated under reduced pressure. Purification of the resulting oil by column chromatography (silica gel, 4 × 11 cm, 240 mL Et_2O then CH_2Cl_2) yielded borate **12** as a colorless solid (1.73 g, 90%).

Mp 89.5–91 °C; $R_f \leq 0.75$ (CH_2Cl_2, tailing).

IR (KBr): 2968, 2885, 1612, 1440, 1359, 1281, 1128, 1037, 941, 888, 842, 785, 728, 681, 624, 586, 448 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.09 [s, 6 H, $Si(CH_3)_2$], 0.87 (t, *J* = 7.3 Hz, 12 H, $CH_2C\textit{H}_3$), 0.89 [s, 9 H, $C(CH_3)_3$], 1.22 (sext, *J* = 7.4 Hz, 8 H, $C\textit{H}_2CH_3$), 1.45 (m_c, 8 H, $C\textit{H}_2CH_2CH_3$), 2.90 (m_c, 8 H, $C\textit{H}_2CH_2CH_2CH_3$), 4.75 (s, 2 H, CH_2O), 7.49 (s, 3 H, Ar^F-*p*-H), 7.77 (s, 6 H, Ar^F-*o*-H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = –5.4 [$Si(CH_3)_2$], 13.2 ($CH_2\textit{C}H_3$), 18.6 [$\textit{C}(CH_3)_3$], 19.5 ($\textit{C}H_2CH_3$), 23.6 ($\textit{C}H_2CH_2CH_3$), 25.9 [$C(\textit{C}H_3)_3$], 53.7 (CH_2O), 58.9 (t, *J* = 3 Hz, $\textit{C}H_2CH_2CH_2CH_3$), 114.8 (t, *J* = 18 Hz, Ar-*p*-C), 117.3 (sept, *J* = 4 Hz, Ar^F-*p*-CH), 124.7 (q, *J* = 272 Hz, CF_3), 128.8 (q, *J* = 31 Hz, Ar^F-*m*-C), 134.1 (Ar^F-*o*-CH), 145.1 (dd, *J* = 246, 17 Hz, Ar-*m*-C), 148.2 (dt, *J* = 238, 12 Hz, Ar-*o*-C), 160.8 (br m_c, Ar^F-*i*-C). Despite prolonged data acquisition time, the signal for Ar-*i*-C was not detected.

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –147.6 (dd, *J* = 25, 14 Hz, 2 F, Ar-*m*-F), –127.2 (dd, *J* = 24, 14 Hz, 2 F, Ar-*o*-F), –62.5 (s, 18 F, CF_3).

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ = –8.5.

MS (ESI): *m*/*z* (%) = 943 (100) $[M - NBu_4]^-$.

Anal. Calcd for $C_{53}H_{62}BF_{22}NOSi$: C, 53.68; H, 5.27; N, 1.18. Found: C, 53.83; H, 5.23; N, 1.22.

Tetrabutylammonium Bis[4-(*tert*-butyldimethylsilanyloxymethyl)-2,3,5,6-tetrafluorophenyl]bis[3,5-bis(trifluoromethyl)phenyl]borate (13)

In analogy to the synthesis of **12**, bromo-3,5-bis(trifluoromethyl)benzene (792 μL, 4.59 mmol) was reacted with *i*-PrMgCl in THF (2.0 M, 2.04 mL, 4.08 mmol) and diaryldifluoroborate **11** (689 mg, 1.02 mmol) in anhyd THF (4 mL) and anhyd Et_2O (12 mL) for 135 h at r.t. After aqueous workup as described above, the magnesium borate was treated with TBAB (395 mg, 1.22 mmol) in CH_2Cl_2 (25 mL) for 30 min at r.t. Purification of the yellow crude product by column chromatography (silica gel, 3 × 12 cm, 140 mL Et_2O then CH_2Cl_2) furnished borate **13** as a colorless, sticky foam (1.16 g, 90%).

$R_f \leq 0.74$ (CH_2Cl_2, tailing).

IR (NaCl): 2962, 2885, 1612, 1443, 1359, 1277, 1128, 1038, 937, 886, 841, 778, 735, 679 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.07 [s, 12 H, $Si(CH_3)_2$], 0.88 [s, 18 H, $C(CH_3)_3$], 0.88 (t, *J* = 7.3 Hz, 12 H, CH_2CH_3), 1.24 (sext, *J* = 7.4 Hz, 8 H, CH_2CH_3), 1.47 (m_c, 8 H, $CH_2CH_2CH_3$), 2.93 (m_c, 8 H, $CH_2CH_2CH_2CH_3$), 4.70 (s, 4 H, CH_2O), 7.47 (s, 2 H, Ar^F-*p*-H), 7.88 (s, 4 H, Ar^F-*o*-H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = –5.4 [$Si(CH_3)_2$], 13.3 (CH_2CH_3), 18.6 [$C(CH_3)_3$], 19.6 (CH_2CH_3), 23.7 ($CH_2CH_2CH_3$), 26.0 [$C(CH_3)_3$], 53.7 (CH_2O), 58.9 ($CH_2CH_2CH_2CH_3$), 113.9 (t, *J* = 18 Hz, Ar-*p*-C), 117.3 (sept, *J* = 4 Hz, Ar^F-*p*-CH), 124.8 (q, *J* = 273 Hz, CF_3), 128.6 (q, *J* = 31 Hz, Ar^F-*m*-C), 133.3 (Ar^F-*o*-CH), 144.7 (dd, *J* = 245, 17 Hz, Ar-*m*-C), 147.7 (dt, *J* = 237, 12 Hz, Ar-*o*-C), 159.3 (br, Ar^F-*i*-C). Despite prolonged data acquisition time the signal for Ar-*i*-C was not detected.

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –148.3 (dd, *J* = 24, 13 Hz, 4 F, Ar-*m*-F), –130.0 (dd, *J* = 24, 13 Hz, 4 F, Ar-*o*-F), –62.3 (s, 12 F, CF_3).

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ = –10.6.

MS (ESI): *m*/*z* (%) = 1023 (100) $[M - NBu_4]^-$.

Tetrabutylammonium (2,3,5,6-Tetrafluoro-4-hydroxymethylphenyl)tris[3,5-bis(trifluoromethyl)phenyl]borate (14)

In analogy to the synthesis of **8**, silyl ether **12** (1.56 g, 1.31 mmol) was treated with TBAF·3H_2O (830 mg, 2.63 mmol) in anhyd THF (15 mL) for 14 h (overnight) at r.t. Purification of the yellowish crude product by column chromatography (silica gel, 3 × 8 cm, 200 mL Et_2O then CH_2Cl_2) yielded benzylic alcohol **14** as a colorless, sticky foam, which gradually solidified to a vitreous solid (1.26 g, 90%).

Mp 120–121 °C; R_f = 0.24 (CH_2Cl_2).

IR (KBr): 3636, 3421, 2973, 2883, 1780, 1612, 1444, 1359, 1281, 1128, 1004, 940, 887, 839, 799, 714, 681, 657, 620, 585, 450 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 12 H, CH_3), 1.26 (sext, *J* = 7.4 Hz, 8 H, CH_2CH_3), 1.48 (m_c, 8 H, $CH_2CH_2CH_3$), 1.88 (br s, 1 H, OH), 2.93 (m_c, 8 H, $CH_2CH_2CH_2CH_3$), 4.75 (s, 2 H, CH_2OH), 7.49 (s, 3 H, Ar^F-*p*-H), 7.79 (s, 6 H, Ar^F-*o*-H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 13.2 (CH_3), 19.5 (CH_2CH_3), 23.6 ($CH_2CH_2CH_3$), 53.2 (CH_2OH), 58.9 (t, *J* = 3 Hz, $CH_2CH_2CH_2CH_3$), 114.4 (t, *J* = 18 Hz, Ar-*p*-C), 117.3 (sept, *J* = 4 Hz, Ar^F-*p*-CH), 124.7 (q, *J* = 272 Hz, CF_3), 128.8 (q, *J* = 31 Hz, Ar^F-*m*-C), 134.0 (Ar^F-*o*-CH), 145.0 (dd, *J* = 247, 18 Hz, Ar-*m*-C), 148.2 (dt, *J* = 239, 13 Hz, Ar-*o*-C), 160.7 (br m_c, Ar^F-*i*-C). Despite prolonged data acquisition time, the signal for Ar-*i*-C was not detected.

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –148.3 (dd, *J* = 24, 14 Hz, 2 F, Ar-*m*-F), –126.7 (dd, *J* = 24, 14 Hz, 2 F, Ar-*o*-F), –62.5 (s, 18 F, CF_3).

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ = 8.4.

MS (ESI): *m*/*z* (%) = 829 (100) $[M - NBu_4]^-$.

Anal. Calcd for $C_{47}H_{48}BF_{22}NO$: C, 52.68; H, 4.51; N, 1.31. Found: C, 52.73; H, 4.42; N, 1.37.

Tetrabutylammonium Bis(2,3,5,6-tetrafluoro-4-hydroxymethylphenyl)bis[3,5-bis(trifluoromethyl)phenyl]borate (15)

In analogy to the synthesis of **8**, silyl ether **13** (1.11 g, 0.878 mmol) was treated with TBAF·3H_2O (1.11 g, 3.51 mmol) in anhyd THF (10 mL) for 18 h (overnight) at r.t. Purification of the yellowish crude product by column chromatography (silica gel, 3 × 12 cm, 300 mL CH_2Cl_2 then CH_2Cl_2–MeOH, 10:1) yielded diol **15** as a colorless, foamy solid (787 mg, 86%).

Mp 67–70 °C; R_f = 0.33 (CH_2Cl_2–MeOH, 10:1).

IR (KBr): 3627, 3386, 2971, 2883, 1612, 1447, 1361, 1279, 1128, 1005, 934, 886, 839, 722, 679, 628 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 12 H, CH_3), 1.25 (sext, *J* = 7.3 Hz, 8 H, CH_2CH_3), 1.48 (m_c, 8 H, $CH_2CH_2CH_3$), 1.92 (br s, 2 H, OH), 2.95 (m_c, 8 H, $CH_2CH_2CH_2CH_3$), 4.68 (s, 4 H, CH_2OH), 7.48 (s, 2 H, Ar^F-*p*-H), 7.91 (s, 4 H, Ar^F-*o*-H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 13.3 (CH_3), 19.5 (CH_2CH_3), 23.7 ($CH_2CH_2CH_3$), 53.2 (CH_2OH), 58.9 ($CH_2CH_2CH_2CH_3$), 113.5 (t, *J* = 18 Hz, Ar-*p*-C), 117.5 (sept, *J* = 4 Hz, Ar^F-*p*-CH), 124.7 (q, *J* = 272 Hz, CF_3), 128.7 (q, *J* = 31 Hz, Ar^F-*m*-C), 133.2 (Ar^F-*o*-CH), 134.3 (br, Ar-*i*-C), 144.5 (dd, *J* = 246, 19 Hz, Ar-*m*-C), 147.6 (dt, *J* = 237, 14 Hz, Ar-*o*-C), 159.0 (br, Ar^F-*i*-C).

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –149.0 (dd, *J* = 24, 13 Hz, 4 F, Ar-*m*-F), –129.7 (dd, *J* = 25, 13 Hz, 4 F, Ar-*o*-F), –62.4 (s, 12 F, CF_3).

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ = –10.6.

MS (ESI): *m*/*z* (%) = 795 (100) $[M - NBu_4]^-$.

Anal. Calcd for $C_{46}H_{48}BF_{20}NO_2$: C, 53.25; H, 4.66; N, 1.35. Found: C, 53.13; H, 4.62; N, 1.36.

Tetrabutylammonium (4-Bromomethyl-2,3,5,6-tetrafluorophenyl)tris[3,5-bis(trifluoromethyl)phenyl]borate (16)

In analogy to the synthesis of **9**, borate **14** (6.13 g, 5.72 mmol) was treated with PBr_3 (403 μL, 4.29 mmol) and subsequently TBAB (2.40 g, 7.44 mmol) in anhyd CH_2Cl_2 (50 mL) at 0 °C for 3 h in total and then for 13 h (overnight) at r.t. Purification of the crude product by column chromatography (silica gel, 5 × 14 cm, CH_2Cl_2) furnished benzylic bromide **16** as a colorless, vitreous solid (5.97 g, 92%).

Mp 89–90 °C; $R_f \leq 0.73$ (CH_2Cl_2, tailing).

IR (KBr): 2973, 2881, 1782, 1612, 1446, 1359, 1281, 1161, 1127, 970, 889, 839, 733, 713, 681, 656, 610 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.3 Hz, 12 H, CH_3), 1.25 (sext, *J* = 7.4 Hz, 8 H, CH_2CH_3), 1.48 (m_c, 8 H, $CH_2CH_2CH_3$), 2.94 (m_c, 8 H, $CH_2CH_2CH_2CH_3$), 4.52 (s, 2 H, CH_2Br), 7.49 (s, 3 H, Ar^F-*p*-H), 7.78 (s, 6 H, Ar^F-*o*-H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 13.2 (CH_3), 18.5 (CH_2Br), 19.6 (CH_2CH_3), 23.7 ($CH_2CH_2CH_3$), 58.9 (t, *J* = 3 Hz, $CH_2CH_2CH_2CH_3$), 112.2 (t, *J* = 17 Hz, Ar-*p*-C), 117.3 (sept, *J* = 4 Hz, Ar^F-*p*-CH), 124.5 (q, *J* = 272 Hz, CF_3), 128.7 (q, *J* = 31 Hz, Ar^F-*m*-C), 133.9 (Ar^F-*o*-CH), 135.5 (br, Ar-*i*-C), 144.7 (dd, *J* = 249, 19 Hz, Ar-*m*-C), 148.2 (dt, *J* = 238, 12 Hz, Ar-*o*-C), 160.5 (br m_c, Ar^F-*i*-C).

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –146.1 (dd, *J* = 23, 13 Hz, 2 F, Ar-*m*-F), –126.2 (dd, *J* = 23, 13 Hz, 2 F, Ar-*o*-F), –62.5 (s, 18 F, CF_3).

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ = –8.4.

MS (ESI): *m*/*z* (%) = 891 (100) $[M - NBu_4]^-$.

Anal. Calcd for $C_{47}H_{47}BBrF_{22}N$: C, 49.76; H, 4.18; N, 1.23. Found: C, 49.63; H, 4.09; N, 1.34.

Tetrabutylammonium Bis(4-bromomethyl-2,3,5,6-tetrafluorophenyl)bis[3,5-bis(trifluoromethyl)phenyl]borate (17)

In analogy to the synthesis of **9**, diol **15** (2.21 g, 2.13 mmol) was treated with PBr_3 (260 μL, 2.77 mmol) and subsequently TBAB (1.71 g, 5.33 mmol) in anhyd CH_2Cl_2 (25 mL) at 0 °C for 3.5 h in total and then for 15 h (overnight) at r.t. Purification of the yellowish crude product by column chromatography (silica gel, 4 × 10 cm, CH_2Cl_2) furnished dibromide **17** as a colorless, foamy solid (2.29 g, 92%).

Mp 57–62 °C; $R_f \leq 0.72$ (CH_2Cl_2, tailing).

IR (KBr): 2971, 2881, 1645, 1612, 1576, 1448, 1360, 1277, 1127, 971, 888, 840, 725, 680, 610, 544 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.3 Hz, 12 H, CH_3), 1.28 (sext, *J* = 7.4 Hz, 8 H, CH_2CH_3), 1.51 (m_c, 8 H, $CH_2CH_2CH_3$), 2.98 (m_c, 8 H, $CH_2CH_2CH_2CH_3$), 4.49 (s, 4 H, CH_2Br), 7.50 (s, 2 H, Ar^F-*p*-H), 7.89 (s, 4 H, Ar^F-*o*-H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 13.3 (CH_3), 18.8 (CH_2Br), 19.6 (CH_2CH_3), 23.7 ($CH_2CH_2CH_3$), 59.1 (t, *J* = 2 Hz, $CH_2CH_2CH_2CH_3$), 111.5 (t, *J* = 17 Hz, Ar-*p*-C), 117.7 (sept, *J* = 4 Hz, Ar^F-*p*-CH), 124.7 (q, *J* = 272 Hz, CF_3), 128.8 (q, *J* = 31 Hz, Ar^F-*m*-C), 133.3 (Ar^F-*o*-CH), 135.4 (br, Ar-*i*-C), 144.2 (dd, *J* = 249, 19 Hz, Ar-*m*-C), 147.7 (dt, *J* = 238, 12 Hz, Ar-*o*-C), 158.5 (br, Ar^F-*i*-C).

$^{19}F\{^1H\}$ NMR (375 MHz, $CDCl_3$): δ = –146.7 (dd, *J* = 22, 11 Hz, 4 F, Ar-*m*-F), –129.3 (dd, *J* = 24, 13 Hz, 4 F, Ar-*o*-F), –62.4 (s, 12 F, CF_3).

$^{11}B\{^1H\}$ NMR (160 MHz, $CDCl_3$): δ = –10.5.

MS (ESI): *m*/*z* (%) = 921 (100) $[M - NBu_4]^-$.

Anal. Calcd for $C_{46}H_{46}BBr_2F_{20}N$: C, 47.49; H, 3.98; N, 1.20. Found: C, 47.46; H, 4.00; N, 1.27.

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