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Preparation, properties and synthetic potentials of fluorous boronates

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Abstract—A fluorous approach to the chemistry of boronic acids and its application in fluorous-phase techniques are described. Treatment of fluorous bromosilane **2** with allyl Grignard reagent followed by dihydroxylation provided fluorous diol **1**. A series of boronic acids were attached to **1** by esterification. The formed fluorous boronates **4** were moisture sensitive and thus their synthetic potentials were limited. Thus a fluorous pinacol, **5**, was designed and synthesized by treatment of fluorous bromosilane **2** with excess 2,3-dimethyl-2-butyenylmagnesium bromide **9** to afford fluorous tetramethyl ethene **8**, and was dihydroxylated. Compound **5** was successfully used to prepare fluorous boronates in a one-pot process from organic bromides. We have demonstrated that olefin cross-metathesis can be carried out in a fluorous version. It is noteworthy that all of the fluorinated compounds reported in this paper were purified by simple liquid extraction.
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1. Introduction

Since the pioneering work of Harváth and Rábai,[1] the fluorous property of highly fluorinated compounds has been exploited to influence phase behavior and thereby simplify separations in organic synthesis. With the expansion and generalization of fluorous concepts, fluorous phase oriented synthesis is developing into a viable alternative to solid-phase techniques in organic synthesis.[2] Fluorous synthesis performed in homogeneous media overcomes some drawbacks of heterogeneous reactions associated with solid-phase synthesis. In principle, any solid-phase synthetic technology has a counterpart in fluorous synthesis. In this context, we were interested in examining how the fluorous phase approach could be applied to boron chemistry. Boronic acids are important intermediates in organic synthesis and are useful for the development of biologically active agents. For example, boronic acids are widely used in Suzuki cross-coupling reactions[3] and for the development of sensors for carbohydrates and amino acids.[4] However, the isolation and purification of compounds containing a boronic acid functionality by conventional methods prove to be notoriously troublesome due to their amphiphilic character. To facilitate the synthesis and separation of functionalized boronic acids, several groups have recently reported the preparation of several kinds of polymer-bound diols that be used as linkers to immobilize boronic acids.[5–9]

In this paper we report the synthesis of fluorous boronates, along with a assessment of their application in fluorous phase techniques.[10]

2. Results and discussion

Boronic acids rapidly and reversibly form cyclic esters with diols in basic aqueous media. In light of this known reaction, it seems promising to use fluorous diols for the immobilization of boronic acids in the fluorocarbon phase via a boronate linkage. Accordingly, we have first prepared fluorous diol **1** as shown in Scheme 1. As usual, fluorous bromosilane **2**[11] was employed as a fluorous phase label. Treatment of **2** with excess allyl Grignard reagent afforded fluorous allylsilane **3** in 98% yield. The dihydroxylation of **2** with *N*-methylmorpholine-*N*-oxide (NMNO) and catalytic osmium tetraoxide in aqueous acetone provided the desired fluorous diol, **1**, in quantitative yield. As the only fluorous product, compound **1** was obtained in high purity by simple extractive workup (FC-77/aqueous acetone). Subsequently, experiments were conducted to test the effectiveness of fluorous diol **1** to immobilize boronic acid templates. Encouraging results showed that compound **1** could couple with 1.0 equiv. or a slight excess of arylboronic acids in quantitative yields. Depending on the solubility of boronic acids, the reaction time may vary. Nevertheless, the formation of fluorous boronates **4** was highly favored in anhydrous solvents like THF, ether, pentane or benzotrifluoride (BTF), and total conversion of **1** was achieved

Keywords: fluorous boronates; organic synthesis; boronic acids.

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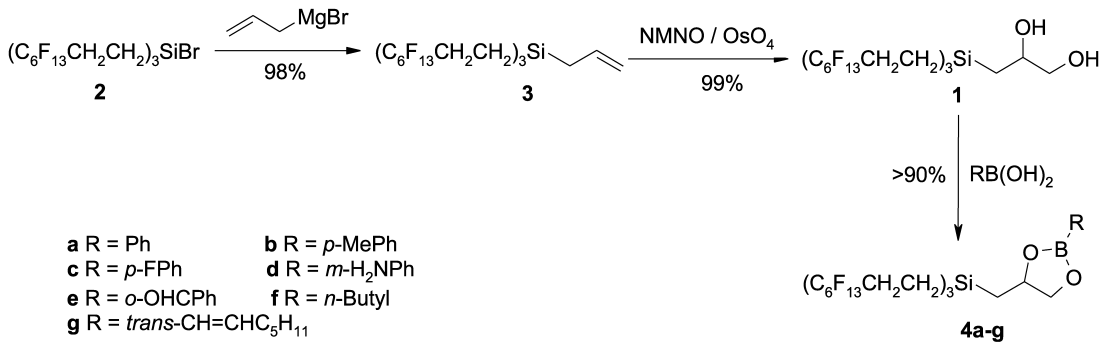


Scheme 1.

Table 1. Partition coefficients of fluorous boronate **4a** (K_D=*C*(fluorous solvent)/*C*(organic solvent))

Organic solvents	K_D	Organic solvents	K_D
Acetonitrile	13.3	Ethyl acetate	0.88
Dichloromethane	7.53	Acetone	2.73
Chloroform	5.43	Toluene	7.69
Hexane	6.50	Tetrahydrofuran	2.91

The fluorous solvent is FC-77.

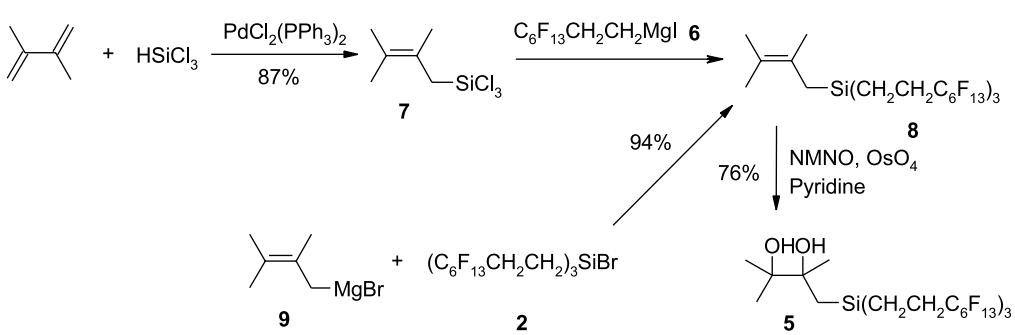
with the aid of 4 Å MS. The fluorous boronates **4**, purified by FC-77/CH_3CN extraction if necessary, were provided in high purity without contaminating by any diol components. As shown in Scheme 1, this reaction is applicable to a wide variety of electron rich and electron-poor arylboronic acids. It is noteworthy that fluorous diol **1** could also couple with alkenylboronic acid, as well as air sensitive alkylboronic acids as effectively as arylboronic acids.

To assess the fluorous affinity of these boronates, we chose compound **4a** as a representative fluorous boronate, and determined its partition coefficient K_D in several fluorous biphasic solvent combinations. As shown in Table 1, boronate **4a** behaves as a "fluorous compound" for most solvent pairs. With the appropriate selection of organic solvents, the K_D values are high enough for effective fluorous extraction.

Fluorous boronates **4** were quickly hydrolyzed with the release of free boronic acids in an acidic aqueous medium of THF/HOAc/H_2O. The released boronic acids were recovered intact by liquid–liquid extraction in reasonable yields. Meanwhile, fluorous diol **1**, which was partitioned into FC-77, could be recycled without additional treatment.

Fluorous boronates **4** were moisture sensitive and easily hydrolyzed in air and thus their synthetic potentials were limited. Since the pinacol protected boronic acids (pinacolboranates) display excellent aqueous and chromatographic stability, they are highly valuable synthetic intermediates,[12] particularly with regards to carbon–carbon bond formation. Moreover, pinacol can coordinate with Os,[13] Si,[14] As,[15] P[16] and protect carbonyl groups.[17] The preparation of fluorous pinacol **5** and its application in the synthesis of fluorous boronates were investigated.

An initial attempt to synthesize fluorous pinacol **5** was carried out by the treatment of Grignard reagent **6** with 1-trichlorosilyl-2,3-dimethyl-2-butene **7** (Scheme 2), which was prepared from the reaction of 2,3-dimethyl-1,3-butadiene with trichlorosilane in the presence of $PdCl_2$-$(PPh_3)_2$.[18] The reaction failed to give the expected product **8**. Therefore, an alternative route was investigated (Scheme 2). Fluorous bromosilane **2** was employed as a fluorous label. Treatment of **2** with excess 2,3-dimethyl-2-butenylmagnesium bromide **9** afforded fluorous tetramethyl ethene **8** in excellent yield. Compound **8** was obtained in high purity by simple extractive workup (FC-77/CH_2Cl_2). It is known that the dihydroxylation of tetrasubstituted double bond is so difficult, it cannot be achieved by traditional reaction conditions (*N*-methylmorpholine *N*-oxide and OsO_4). Noting that pyridine catalyzed the formation[19] and basic conditions favor the hydrolysis[20] of osmate esters, we used pyridine as solvent for the dihydroxylation reaction. Treatment of **8** with *N*-methylmorpholine *N*-oxide (NMNO, 3.0 equiv.) and catalytic osmium tetraoxide (5 mol%) in pyridine at 65°C for 24 h provided the desired fluorous pinacol **5** in 75% yield. It is noteworthy that the dihydroxylation was carried out in two phases and the



Scheme 2.

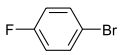
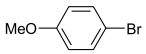
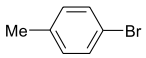
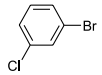
termination of the reaction was indicated by the color change of the fluorous phase. At the beginning of the reaction, the fluorous phase was black; when the reaction was completed it became colorless.

With the fluorous diol **5** in hand, the preparation of fluorous boronic esters was investigated, since arylboronic esters have been used as a substitute of arylboronic acids to efficiently couple with aryl halides or aryl triflates in the presence of catalytic palladium. More recently, the preparation of arylboronic esters from aryl bromides in a one-pot process was reported.[21] We planned to use fluorous pinacol **5** to prepare fluorous boronates in a one-pot procedure. As shown in Scheme 3, the Grignard reagent (C_6H_5MgBr) formed from bromobenzene and magnesium in THF was added into a solution of trimethyl borate (2 equiv.) at −78°C. After stirring 2 h at −78°C, the reaction mixture was warmed to room temperature and stirred for 2 h. Instead of quenching the reaction mixture with acidic aqueous solution, the solvent and excess $B(OMe)_3$ were removed by a rotary evaporator under reduced pressure to give a yellow white powder. Then the solid was dissolved in anhydrous ethylene glycol. The fluorous pinacol **5** solved in FC-77 was added to the resulting ethylene glycol solution and heated to reflux overnight. Because the reaction was carried out in a biphasic system, the formed fluorous boronate **10a** was transferred to the fluorous phase (FC-77), and the separation process automatically drives the reaction. Finally, the FC-77 layer was separated and concentrated to afford fluorous boronate **10a** in 98% yield as a single product. These reaction conditions were utilized for the synthesis of a diverse set of fluorous boronates (**10a**–**i**). As summarized in Table 2, the isolated yields of fluorous arylboronates were usually excellent (entries 1–6). Moreover, the fluorous vinyl and alkyl boronic esters were isolated in excellent yield (entries 8–9). However, the fluorous heteroaryl boronate was obtained in only 45% yield (entry 7). It is noteworthy that these fluorous boronates display excellent stability under aqueous conditions.

Scheme 3.

After the successful preparation of fluorous boronates, their applications in fluorous synthesis were further investigated. As olefin cross-metathesis has been used to prepare vinyl boronic esters,[22] and the alkenylboronic esters and acids are highly valuable synthetic intermediates, we chose the fluorous vinyl boronate **10h** as a model substrate for the olefin cross-metathesis reaction. Our approach is as shown in Scheme 4. Much to our delight, upon treatment of **10h** with styrene and *N*-heterocyclic carbene-containing catalyst **11**[23] in benzotrifluoride (BTF), the new fluorous alkenylboronate **12** was furnished in 78% yield as a single *E*-isomer in high purity through simple extraction. To our best knowledge, this is the first example that the olefin metathesis reaction was carried out in a fluorous version. The cyclopropanation of **12** with diazomethane-palladium

Table 2. Preparation of fluorous boronates **10** in a one-pot procedure

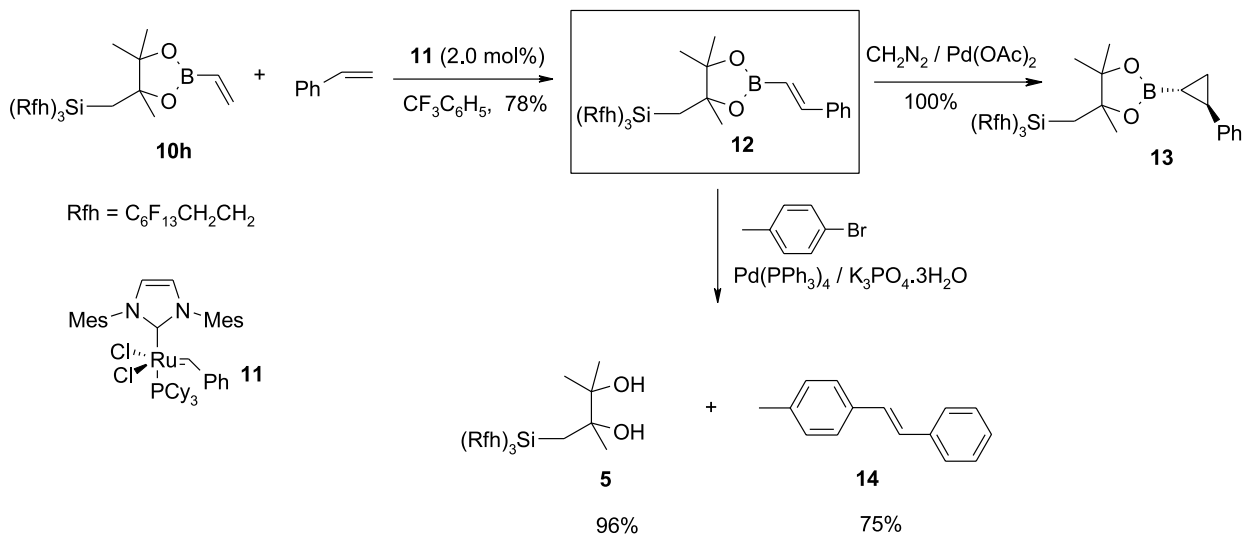
Entry	R–X	Fluorous boronates **10**	Yield (%)[a]
1		**10a**	98
2		**10b**	96
3		**10c**	95
4		**10d**	96
5		**10e**	95
6		**10f**	93
7		**10g**	45
8		**10h**	94
9	n-$C_8H_{17}Br$	**10i**	95

All reactions were carried out in multiple steps R–Br/$B(OMe)_3$/**5**=4:8:1, all the products were isolated by FC-77 extraction, without further purification before analysis.
[a] The yield is based on fluorous pinacol **5**.

(II) acetate provided fluorous cyclopropylboronate **13** in quantitative yield.

As a robust and general method for carbon–carbon bond formation, the Suzuki reaction has emerged as an important tool in parallel synthesis and combinatorial chemistry.[3,24] In consideration of this fact, we sought to use the Suzuki reaction as a detagging process. In comparison with simple hydrolysis to provide novel boronic acids, we believe this synthesis would be of more interest to combinatorial chemistry. Compound **12** reacted smoothly with 4-bromotoluene under standard Suzuki reaction conditions in dioxane. Although fluorous boronates were used in this case, we did not find any retarding effect for the Suzuki coupling reaction by the perfluoroalkyl chains. Fluorous pinacol **5**, which was distributed into FC-77, was completely recovered from repeated FC-77/CH_2Cl_2 extractions. Finally, 4-methylstilbene **14** was obtained in 75% yield by the concentration of the CH_2Cl_2 layer and flash chromatography.

In summary, we have designed and synthesized fluorous diols **1** and **5**. A series of boronic acids were attached to fluorous diol **1** by esterification. The formed fluorous boronates **4** were moisture sensitive and thus their synthetic potentials were limited. Fluorous pinacol **5** was used for the preparation of fluorous boronates **10** in a one-pot process. The formed fluorous boronates **10** display excellent aqueous stability. Functional transformation of fluorous boronate **10h** illustrated its usefulness in fluorous-phase techniques. We have demonstrated that the cross-metathesis can be carried out in a fluorous version. We have also engaged the Suzuki coupling reaction as the detagging process in fluorous synthesis.



Scheme 4.

3. Experimental

3.1. General

All purchased chemicals and reagents were used as received. All reactions were carried out under argon in pre-dried glassware. NMR spectra were acquired in $CDCl_3$ at 300 MHz for ^1H NMR and 282 MHz for ^{19}F NMR. Chemical shifts (δ) in ppm are relative to TMS for ^1H NMR and to $CFCl_3$ for ^{19}F NMR (high field is negative).

3.1.1. Allyl-*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (3). To freshly prepared allyl Grignard reagent (30 mmol) in ether (40 mL), was added an ethereal solution of fluorous bromosilane **2** (7.4 mmol) under an argon atmosphere. The reaction mixture was allowed to reflux overnight. After cooling to room temperature, the reaction was quenched with aqueous NH_4Cl. The aqueous phase was extracted with ether, and the combined organic phases were dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by FC-77/CH_2Cl_2 extraction afforded pure fluorous allylsilane **3** (8.6 g, 98%). ^1H NMR ($CDCl_3$) δ 5.67–5.81 (m, 1H), 4.96–5.02 (m, 2H), 2.00–2.15 (m, 6H), 1.70 (d, J=8.1 Hz, 2H), 0.88–0.94 (m, 6H); ^{19}F NMR ($CDCl_3$) δ −81.27 to −81.33 (m, 9F), −116.52 to −116.63 (m, 6F), −122.34 (s, 6F), −123.32 (s, 6F), −123.76 (s, 6F), −126.57 to −126.67 (m, 6F); IR (thin film): 1635, 1363, 1240, 1208, 1146, 1074, 908 cm^{-1}; MS (EI, 70 eV, *m/z*): 639 (0.9), 309 (98), 289 (75), 239 (100); Anal. Calcd for $C_{27}H_{17}F_{39}Si$: C 29.20; H 1.54; Found: C 29.18; H 1.55.

3.1.2. 3-[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctylsilanyl)propane-1,2-diol (1). In a three-necked flask, NMNO (1.48 g, 11 mmol) and allylsilane **3** (8.5 g, 7.7 mmol) were dissolved in acetone (20 mL) and H_2O (2 mL). The mixture was cooled to 0–5°C, and 4% aqueous solution of OsO_4 (0.64 mL) was added via syringe. After stirring for an hour, the mixture was warmed to room temperature, and stirring was continued until TLC indicated complete conversion of **3** to diol **1**, about 8 h. After removal of solvent in vacuo, the residue was dissolved in FC-77 (10 mL), washed with H_2O, and evaporated to give pure compound **1** (8.7 g, 99%). ^1H NMR ($CDCl_3$) δ 3.85–3.91 (m, 1H), 3.68 (dd, J_1=10.5 Hz, J_2=3.0 Hz, 1H), 3.38 (dd, J_1=10.5 Hz, J_2=8.0 Hz, 1H), 2.01–2.19 (m, 6H), 1.93 (br, 2H), 0.75–0.98 (m, 8H); ^{19}F NMR δ −78.66 (t, J=8.5 Hz, 9F), −113.90 (t, J=14.4 Hz, 6F), −119.76 (s, 6F), −120.71 (s, 6F), −121.12 (s, 6F), −123.98 (s, 6F); IR (thin film): 3383, 2949, 1443, 1240, 1208, 1145, 904, 707 cm^{-1}; MS (EI, 70 eV, *m/z*): 721 (0.81), 289 (15), 239 (28), 69 (14); Anal. Calcd for $C_{27}H_{19}O_2F_{39}Si$: C 28.33; H 1.67; Found: C 28.36; H 1.73.

3.2. General procedure for the preparation of fluorous boronates (4)

To a mixture of 4 Å MS (0.3 g) and aryl boronic acid (0.45 mmol), was added a solution of compound **1** (0.40 mmol) in anhydrous ether (2 mL) under an argon atmosphere. Then pentane (8 mL) was added, and the mixture was stirred at room temperature. When the reaction was completed as detected by TLC, the mixture was filtered, concentrated in vacuo, and dissolved in FC-77 (5 mL). The fluorous solution was washed twice with acetonitrile (1 mL), and evaporated to afford the fluorous boronates **4** (>90%).

3.2.1. 2-Phenyl-4-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (4a). ^1H NMR ($CDCl_3$) δ 7.73 (d, J=8.1 Hz, 2H), 7.45–7.52 (m, 1H), 7.36 (t, J=8.1 Hz, 2H), 4.68–4.74 (m, 1H), 4.54 (t, J=8.1 Hz, 1H), 3.92 (t, J=8.1 Hz, 1H), 2.06–2.20 (m, 6H), 1.13–1.17 (m, 2H), 1.01–1.10 (m, 6H); IR (thin film): 2908, 1605, 1502, 1443, 1240, 1212, 1145, 1096, 904, 746 cm^{-1}; MS (EI, 70 eV, *m/z*): 1230 (M^+, 5), 527 (3), 367 (32), 227 (75); Anal. Calcd for $C_{33}H_{22}O_2F_{39}SiB$: C 32.21; H 1.80; Found: C 32.42; H 1.92.

3.2.2. 2-*p*-Tolyl-4-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (4b). ^1H NMR ($CDCl_3$) δ 7.63 (d, J=8.1 Hz, 2H), 7.17 (d, J=8.1 Hz, 2H), 4.67–4.72 (m, 1H), 4.52 (t, J=8.1 Hz, 1H), 3.90 (t, J=8.1 Hz, 1H), 2.36 (s, 3H), 2.06–2.20 (m, 6H), 1.12–1.16 (m, 2H), 1.00–1.06 (m, 6H); IR (thin film): 2908,

1616, 1520, 1372, 1239, 1211, 1145, 1093, 814, 707 cm^{-1}; MS (EI, 70 eV, *m/z*): 1244 (M^+, 3), 241 (23), 41 (100); Anal. Calcd for $C_{34}H_{24}O_2F_{39}SiB$: C 32.82; H 1.94; Found: C 32.60; H 1.84.

3.2.3. 2-(4-Fluorophenyl)-4-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (4c). ^1H NMR ($CDCl_3$) δ 7.74 (dd, J_1=18.1 Hz, J_2=6.0 Hz, 2H), 7.01–7.10 (m, 2H), 4.68–4.75 (m, 1H), 4.53 (t, J=8.1 Hz, 1H), 3.91 (t, J=8.1 Hz, 1H), 2.05–2.19 (m, 6H), 0.89–1.21 (m, 8H); IR (thin film): 2910, 1604, 1240, 1145, 1093, 904, 837, 707 cm^{-1}; MS (EI, 70 eV, *m/z*): 1248 (M^+, 5), 239 (34), 69 (10), 41 (100); Anal. Calcd for $C_{33}H_{21}O_2F_{40}SiB$: C 31.73; H 1.69; Found: C 31.98; H 1.81.

3.2.4. 2-(3-Aminophenyl)-4-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (4d). ^1H NMR ($CDCl_3$) δ 7.17–7.23 (m, 2H), 7.10 (d, J=2.7 Hz, 1H), 6.82–6.86 (m, 1H), 4.67–4.76 (m, 1H), 4.52–4.57 (m, 1H), 3.90–3.95 (m, 1H), 3.22 (br, 2H), 2.09–2.19 (m, 6H), 0.80–1.23 (m, 8H); IR (thin film): 3381 (NH_2), 2909, 1625, 1585, 1448, 1372, 1239, 1145, 1072, 904, 707 cm^{-1}; MS (EI, 70 eV, *m/z*): 1245 (M^+, 62), 1244 (100), 41 (20); Anal. Calcd for $C_{33}H_{23}O_2NF_{39}SiB$: C 31.83; H 1.86; N 1.12; Found: C 31.88; H 1.96; N 1.04.

3.2.5. 2-(2-Formylphenyl)-4-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (4e). ^1H NMR (acetone-d_6) δ 10.40 (s, 1H), 7.96 (dd, J_1=4.8 Hz, J_2=3.6 Hz, 1H), 7.80 (dd, J_1=4.8 Hz, J_2=3.0 Hz, 1H), 7.64–7.67 (m, 2H), 4.95–5.04 (m, 1H), 4.63 (t, J=8.7 Hz, 1H), 4.04 (t, J=8.7 Hz, 1H), 2.36–2.42 (m, 6H), 1.45–1.55 (m, 2H), 1.00–1.20 (m, 6H); IR (thin film): 2908, 1694, 1596, 1364, 1239, 1145, 1075, 904, 707 cm^{-1}; MS (EI, 70 eV, *m/z*): 1258 (M^+, 5), 910 (24), 582 (10), 159 (100); Anal. Calcd for $C_{34}H_{22}O_3F_{39}SiB$: C 32.45; H 1.76; Found: C 32.15; H 1.91.

3.2.6. 2-Butyl-4-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (4f). ^1H NMR ($CDCl_3$) δ 4.47–4.52 (m, 1H), 4.35 (dd, J_1=8.4 Hz, J_2=7.8 Hz, 1H), 3.73 (dd, J_1=8.4 Hz, J_2=7.8 Hz, 1H), 2.01–2.19 (m, 6H), 1.28–1.39 (m, 4H), 0.94–1.05 (m, 6H), 0.77–0.90 (m, 7H); IR (thin film): 2964, 1443, 1396, 1240, 1208, 1145, 1072, 904, 707 cm^{-1}; MS (EI, 70 eV, *m/z*): 417 (0.5), 69 (16), 57 ($C_4H_9^+$, 5), 41 (100); Anal. Calcd for $C_{31}H_{26}O_2F_{39}SiB$: C 30.76; H 2.17; Found: C 31.01; H 2.14.

3.2.7. 2-Styryl-4-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (4g). ^1H NMR ($CDCl_3$) δ 6.64 (dt, J_1=18.0, 6.3 Hz, 1H), 5.2 (dt, J_1=18.3 Hz, J_2=1.5 Hz, 1H), 4.52–4.57 (m, 1H), 4.38 (dd, J_1=9.0 Hz, J_2=7.5 Hz, 1H), 3.77 (dd, J_1=9.0 Hz, J_2=7.5 Hz, 1H), 2.03–2.18 (m, 6H), 1.25–1.43 (m, 6H), 0.94–1.05 (m, 10H), 0.90 (t, J=6.9 Hz, 3H); IR (thin film): 2936, 1640, 1442, 1399, 1373, 1241, 1210, 1145, 1073, 905, 707 cm^{-1}; MS (EI, 70 eV, *m/z*): 1249 (3), 289 (13), 69 (31), 41 (100); Anal. Calcd for $C_{34}H_{30}O_2F_{39}SiB$: C 32.66; H 2.42; Found: C 32.64; H 2.68.

3.2.8. 1-Trichlorosilyl-2,3-dimethyl-2-butene (7). [18]Trichlorosilane (4.5 g, 33 mmol), 2,3-dimethyl-1,3-butadiene (4.9 g, 60 mmol) and $PdCl_2(PPh_3)_2$ (12 mg, 1.7 mmol) were heated in a sealed glass ampoule at 80°C for 6 h. Then the reaction mixture was distilled to give **7** (6.4 g, 86%). ^1H NMR δ 2.42 (s, 2H), 1.78 (s, 3H), 1.70 (s, 6H); MS (EI, 70 eV, *m/z*): 202 (M^+-15, 2), 161 (5), 91 (10), 83 (58), 55 (65), 41 (100).

3.2.9. (2,3-Dimethylbut-2-enyl)-tris-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane (8). Bromo-tris-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silane **2** (14 mmol) was added at 0°C to a freshly prepared 2,3-dimethyl-2-butenylmagnesium bromide **9** (50 mmol) formed from 1-bromo-2,3-dimethylbut-2-ene with magnesium in THF at 0°C. The reaction mixture was stirred at 0°C for 4 h, and then warmed to room temperature and stirred for another 10 h. The reaction mixture was quenched with aqueous NH_4Cl. The aqueous phase was further extracted with ether, and the combined organic layers were dried over $MgSO_4$, and concentrated in vacuo. The crude product was purified by repeated extraction with FC-77/CH_2Cl_2 to afford pure titled compound **8** as a colorless oil (15.2 g, 94%). ^1H NMR δ 1.95–2.13 (m, 6H), 1.69 (s, 3H), 1.66 (s, 3H), 1.63 (s, 3H), 1.58 (s, 3H), 0.86–0.92 (m, 6H); ^{19}F NMR δ −81.33 (t, J=11.3 Hz, 9F), −116.81 (t, J=15.2 Hz, 6F), −122.45 (s, 6F), −123.43 (s, 6F), −123.89 (s, 6F), −126.68 (s, 6F); IR (thin film): 2929, 1443, 1362, 1240, 1209, 1145, 1070, 904 cm^{-1}; MS (EI, 70 eV, *m/z*): 1152 (M^+, 1), 497 (1), 289 (8), 83 (100); Anal. Calcd for $C_{30}H_{23}F_{39}Si$: C 31.26, H 2.01; Found: C 31.52, H 2.27.

3.2.10. 2,3-Dimethyl-1-[tris-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]-butane-2,3-diol (5). A 4% aqueous solution of OsO_4 (1.2 mL, 0.2 mmol) was added via syringe at 0–5°C to a mixture of NMNO (1.4 g, 8.6 mmol), compound **8** (2.8 g, 2.4 mmol) and pyridine (16 mL). After stirring for 1 h, the reaction mixture was warmed to 65°C and stirred for 20 h. The reaction mixture was extracted thrice with ether (10 mL). The combined organic phases were washed with aqueous NH_4Cl, brine, dried over $MgSO_4$, and concentrated in vacuo. Purification of the residue by flash column chromatography (silica gel, hexane/EtOAc 10:1) afforded pure fluorous pinacol **5** as a colorless oil (2.2 g, 76%). ^1H NMR δ 2.03–2.17 (m, 6H), 1.72 (br, 2H), 1.44 (d, J=14.7 Hz, 1H), 1.26 (s, 9H), 0.85–1.05 (m, 6H), 0.82 (d, J=14.7 Hz, 1H); ^{19}F NMR δ −80.96 to −81.04 (m, 9F), −116.17 to −116.29 (m, 6F), −122.08 (s, 6F), −123.05 (s, 6F), −123.42 (s, 6F), −126.27 to −126.38 (m, 6F); MS (ESI, *m/z*): 1225 ($M+K^+$, 8), 1209 ($M+Na^+$, 100), 1204 ($M+NH_4^+$, 63); IR (thin film): 3454, 2986, 1443, 1240, 1209, 1145, 1072, 903 cm^{-1}; Anal. Calcd for $C_{30}H_{25}F_{39}O_2Si$: C 30.37, H 2.12; Found: C 30.52, H 2.30.

3.3. General procedure for the preparation of fluorous boronic esters (10)

Organo magnesium bromide (1.0 mmol) prepared from organic bromides (1.0 mmol) and magnesium turnings (1.1 mmol) in 5 mL THF was added dropwise to a solution of trimethyl borate (2.0 mmol) in THF at −78°C. The reaction mixture was warmed to room temperature and concentrated to dryness by rotary evaporation under reduced pressure. Then a mixture of ethylene glycol

(3 mL), FC-77 (4 mL) and pinacol **5** (0.25 mmol) was added to the resulting solid. The reaction mixture was refluxed overnight. The FC-77 layer was separated and concentrated in vacuo to give the corresponding pure boronates **10**.

3.3.1. 2-Phenyl-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (10a). White waxy solid. Mp 48.5–51.0°C. ^{1}H NMR δ 7.72 (d, J=7.4 Hz, 2H), 7.47 (t, J=7.5 Hz, 1H), 7.25 (t, J=7.2 Hz, 2H), 2.02–2.22 (m, 6H), 1.40 (d, J=14.7 Hz, 1H), 1.37 (s, 9H), 1.00–1.08 (m, 6H), 0.87 (d, J=14.7 Hz, 1H); ^{19}F NMR δ −80.94 (t, J=7.61 Hz, 9F), −116.11 (t, J=16.5 Hz, 6F), −122.02 (s, 6F), −122.97 (s, 6F), −123.30 (s, 6F), −126.20 to −126.27 (m, 6F); MS (EI, 70 ev, *m/z*): 1273 (M+1$^+$, 3), 1272 (M$^+$, 3), 926 (3), 493 (4), 105 (38), 83 (100); IR (neat): 2985, 1606, 1501, 1442, 1363, 1240, 1207, 1145, 1070, 903 cm^{-1}; Anal. Calcd for $C_{36}H_{28}F_{39}O_2BSi$: C 33.98, H 2.22; Found: C 33.95, H 2.36.

3.3.2. 2-(4-Fluorophenyl)-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]-methyl}-[1,3,2]dioxaborolane (10b). White waxy solid. Mp 58.5–60.5°C. ^{1}H NMR δ 7.71 (t, J=6.6 Hz, 2H), 7.03 (t, J=9.0 Hz, 2H), 2.00–2.18 (m, 6H), 1.40 (d, J=15.3 Hz, 1H), 1.36 (s, 9H), 0.96–1.05 (m, 6H), 0.89 (d, J=15.3 Hz, 1H); ^{19}F NMR δ −81.29, −81.41 (m, 9F), −108.19, −108.30 (m, 1F), −116.48, −116.70 (m, 6F), −122.48 (s, 6F), −123.45 (s, 6F), −123.78 (s, 6F), −126.66, −126.78 (m, 6F); IR (neat): 2989, 1605, 1364, 1239, 1208, 1143, 1068, 903 cm^{-1}; Anal. Calcd for $C_{36}H_{27}F_{40}O_2BSi$: C 33.51, H 2.11; Found: C 33.67, H 2.41.

3.3.3. 2-(4-Methoxyphenyl)-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]-methyl}-[1,3,2]dioxaborolane (10c). Colorless syrup. ^{1}H NMR δ 7.68 (d, J=7.7 Hz, 2H), 6.88 (d, J=7.7 Hz, 2H), 3.82 (s, 3H), 2.02–2.20 (m, 6H), 1.40 (d, J=14.4 Hz, 1H), 1.36 (s, 9H), 1.00–1.06 (m, 6H), 0.88 (d, J=14.4 Hz, 1H); ^{19}F NMR δ −81.25 to −81.37 (m, 9F), −116.46 to −116.67 (m, 6F), −122.47 (s, 6F), −123.43 (s, 6F), −123.74 (s, 6F), −126.64, −126.77 (m, 6F); IR (thin film): 2983, 1608, 1364, 1243, 1208, 1145, 1070, 904 cm^{-1}; Anal Calcd for $C_{37}H_{30}F_{39}O_3BSi$: C 34.12, H 2.32; Found: C 34.22, H 2.18.

3.3.4. 2-*p*-Tolyl-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (10d). Colorless syrup. ^{1}H NMR δ 7.62 (d, J=7.5 Hz, 2H), 7.17 (d, J=7.5 Hz, 2H), 2.36 (s, 3H), 2.05–2.19 (m, 6H), 1.40 (d, J=14.7 Hz, 1H), 1.36 (s, 9H), 0.99–1.05 (m, 6H), 0.88 (d, J=14.7 Hz, 1H); ^{19}F NMR δ −80.88 (t, J=11.6 Hz, 9F), −116.05 (t, J=15.4 Hz, 6F), −121.98 (s, 6F), −122.94 (s, 6F), −123.26 (s, 6F), −126.15, −126.28 (m, 6F); IR (thin film): 2984, 1616, 1502, 1399, 1363, 1240, 1208, 1145, 1072, 904 cm^{-1}; Anal. Calcd for $C_{37}H_{30}F_{39}O_2BSi$: C 34.54, H 2.35; Found: C 34.71, H 2.20.

3.3.5. 2-(3-Chlorophenyl)-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]-methyl}-[1,3,2]dioxaborolane (10e). Colorless syrup. ^{1}H NMR δ 7.70 (t, J=7.1 Hz, 1H), 7.58 (d, J=7.2 Hz, 1H), 7.42–7.46 (m, 1H), 7.26–7.30 (m, 1H), 2.19–2.04 (m, 6H), 1.40 (d, J=15.6 Hz, 1H), 1.37 (s, 9H), 1.00–1.06 (m, 6H), 0.89 (d, J=15.6 Hz, 1H); ^{19}F NMR δ −80.90 to −80.79 (m, 9F), −115.98 to −116.20 (m, 6F), −121.99 (s, 6F), −122.96 (s, 6F), −123.30 (s, 6F), −126.19 to −126.33 (m, 6F); IR (thin film): 2985, 1600, 1564, 1357, 1363, 1241, 1208, 1145, 1071, 903 cm^{-1}; Anal. Calcd for $C_{36}H_{27}F_{39}ClO_2BSi$: C 33.09; H 2.08; Found: C 33.17; H 2.14.

3.3.6. 2-Naphthalen-1-yl-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]-methyl}-[1,3,2]dioxaborolane (10f). Colorless syrup. ^{1}H NMR δ 8.68 (d, J=8.5 Hz, 1H), 7.99 (d, J=4.5 Hz, 1H), 7.94 (d, J=8.4 Hz, 1H), 7.83 (d, J=4.3 Hz, 1H), 7.01–7.51 (m, 1H), 2.02–2.17 (m, 6H), 1.48 (d, J=15.0 Hz, 1H), 1.46 (s, 9H), 1.00–1.07 (m, 6H), 0.94 (d, J=15.0 Hz, 1H); ^{19}F NMR δ −81.33 (t, J=9.9 Hz, 9F), −116.52 to −116.75 (m, 6F), −122.48 (s, 6F), −123.44 (s, 6F), −123.80 (s, 6F), −126.64 to −126.74 (m, 6F); IR (thin film): 2984, 1579, 1511, 1344, 1240, 1207, 1145, 1070, 903 cm^{-1}; Anal Calcd for $C_{40}H_{30}F_{39}O_2BSi$: C 36.33, H 2.29; Found: C 36.51, H 2.24.

3.3.7. 2-Thiophen-2-yl-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]-methyl}-[1,3,2]dioxaborolane (10g). White waxy solid. Mp 50.5–53.0°C. ^{1}H NMR δ 7.65 (d, J=4.2 Hz, 1H), 7.59 (d, J=3.6 Hz, 1H), 7.18 (dd, J_1=3.6 Hz, J_2=4.2 Hz, 1H), 2.03–2.15 (m, 6H), 1.40 (d, J=15.3 Hz, 1H), 1.37 (s, 9H), 1.00–1.05 (m, 6H), 0.88 (d, J=15.3 Hz, 1H); ^{19}F NMR δ −80.87 to −80.94 (m, 9F), −116.00 to −116.16 (m, 6F), −121.99 (s, 6F), −122.26 (s, 6F), −123.27 (s, 6F), −126.18 to −126.30 (m, 6F); IR (neat): 2985, 1525, 1440, 1430, 1367, 1240, 1209, 1145, 1121, 1069, 904 cm^{-1}; Anal. Calcd for $C_{34}H_{26}F_{39}O_2BSSi$: C 31.94, H 2.05; Found: C 32.02, H 2.08.

3.3.8. 2-Vinyl-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl} -[1,3,2]dioxaborolane (10h). White waxy solid. ^{1}H NMR δ 6.12 (dd, J_1=4.2 Hz, J_2=19.5 Hz, 1H), 6.03 (dd, J_1=4.2 Hz, J_2=13.8 Hz, 1H), 5.80 (dd, J_1=13.8 Hz, J_2=18.9 Hz, 1H), 2.04–2.18 (m, 6H), 1.33 (d, J=14.4 Hz, 1H), 1.31 (s, 9H), 0.96–1.05 (m, 6H), 0.82 (d, J=14.4 Hz, 1H); ^{19}F NMR δ −80.95 (s, 9F), −116.21 (s, 6F), −122.02 (s, 6F), −123.02 (s, 6F), −123.40 (s, 6F), −126.26 (s, 6F); IR (neat): 3076, 2984, 1621, 1442, 1241, 1208, 1145, 1072, 904 cm^{-1}; Anal. Calcd for $C_{32}H_{26}F_{39}O_2BSi$: C 31.44, H 2.14; Found: C 31.39, H 2.15.

3.3.9. 2-Octyl-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (10i). Colorless syrup. ^{1}H NMR δ 2.03–2.17 (m, 6H), 1.24–1.32 (m, 22H), 0.94–1.01 (m, 6H), 0.84–0.91 (m, 3H), 0.70–0.77 (m, 3H); ^{19}F NMR δ −81.43 (t, J=10.0 Hz, 9F), −116.69 (t, J=16.5 Hz, 6F), −122.52 (s, 6F), −123.48 (s, 6F), −123.84 (s, 6F), −126.71 to −126.81 (m, 6F); IR (thin film): 2933, 2861, 1442, 1377, 1241, 1208, 1145, 1072, 904 cm^{-1}; Anal. Calcd for $C_{38}H_{40}F_{39}O_2BSi$: C 34.88, H 3.08; Found: C 35.03, H 3.01.

3.3.10. 2-Styryl-4,4,5-trimethyl-5-{[*tris*-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]methyl}-[1,3,2]dioxaborolane (12). Catalyst **11** (8.4 mg, 0.01 mmol) was added to a solution of **10h** (578 mg, 0.47 mmol) and styrene (104 mg, 1.0 mmol) in trifluoromethylbenzene (6 mL). The reaction mixture was refluxed

overnight. Evaporation of the solvent and extraction with FC-77/CH_2Cl_2 gave the desired product **12** as a colorless oil (478 mg, 78%). ^{1}H NMR δ 7.44–7.47 (m, 2H), 7.41 (d, J=17.7 Hz, 1H), 7.30–7.34 (m, 3H), 6.09 (d, J=18.6 Hz, 1H), 2.06–2.21 (m, 6H), 1.41 (d, J=15.3 Hz, 1H), 1.34 (s, 9H), 0.92–1.00 (m, 6H), 0.88 (d, J=14.4 Hz, 1H); ^{19}F NMR δ −81.36 to −81.68 (s, 9F), −116.53 to −116.74 (m, 6F), −122.51 (s, 6F), −123.49 (s, 6F), −123.77 (s, 6F), −126.75 to −126.95 (m, 6F); IR (thin film): 3031, 2983, 1626, 1580, 1356, 1239, 1145, 1072, 904 cm^{-1}; MS (EI, 70 eV, *m/z*): 1298 (M^+, 11), 83 (100). Anal. Calcd for $C_{38}H_{30}F_{39}O_2BSi$: C 35.15, H 2.33; Found: C 35.28, H 2.55.

3.3.11. 2-(2-Phenylcyclopropyl)-4,4,5-trimethyl-5-{[tris-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silanyl]-methyl}-[1,3,2]dioxaborolane (13). Dioxaborolane **12** (1.1 g, 0.85 mmol) was dissolved in diethyl ether (5 mL) and 5 mol% palladium (II) acetate was added. After cooling the mixture to 0°C, diazomethane (20 mL, 0.5 M solution in diethyl ether) was slowly added over 20 min. The reaction mixture was stirred vigorously at room temperature for 2 h. Then the mixture was filtered through celite. The filtrate was concentrated under reduced pressure. The residue was extracted by FC-77/CH_2Cl_2 to give analytically pure titled compound **13** (1.12 g, 100 %) from the FC-77 as pale yellow oil. ^{1}H NMR δ 7.20–7.24 (m, 2H), 7.13–7.16 (m, 1H), 7.04 (d, J=7.2 Hz, 2H), 2.03–2.14 (m, 6H), 1.23–1.34 (m, 10H), 1.08–1.13 (m, 1H), 0.96–1.05 (m, 6H), 0.78–0.91 (m, 3H), 0.23–0.28 (m, 1H); ^{19}F NMR δ −81.10 (s, 9F), −116.40 (s, 6F), −122.31 (s, 6F), −123.26 (s, 6F), −123.58 (s, 6F), −126.54 (s, 6F); IR (thin film): 2984, 2947, 1607, 1421, 1360, 1239, 1208, 1145, 1071, 903 cm^{-1}; MS (EI, 70 eV, *m/z*): 1312 (M^+, 24), 1194 (8), 821 (0.5), 83 (100); Anal. Calcd for $C_{39}H_{32}F_{39}O_2BSi$: C 35.69, H 2.46; Found: C 35.94, H 2.48.

3.4. The Suzuki cross coupling reaction of (12)

$Pd(PPh_3)_4$ (7 mg, 0.006 mmol), and $K_3PO_4{\cdot}3H_2O$ (160 mg, 0.6 mmol) were added to a solution of **12** (264 mg, 0.2 mmol) and 4-bromotoluene (38 mg, 0.22 mmol) in dioxane. The reaction mixture was heated to reflux for 8 h. Then H_2O (10 mL), CH_2Cl_2 (6 mL) and FC-77 (6 mL) were added to the reaction mixture. Fluorous pinacol **5** (248 mg, 96 %) was recovered from FC-77 and 4-methyl-stilbene **14** (29 mg, 75%) was obtained from the CH_2Cl_2 phase after flash chromatography. **14**: MS (EI, 70 eV, *m/z*): 194 (M^+, 51), 180 (52), 179 (100), 178 (82), 115 (8), 51 (7).

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