Concise Synthesis of Diborylxanthenes

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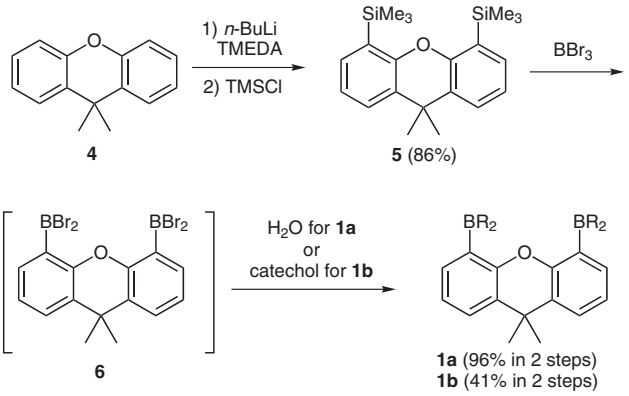
Abstract: A simple and efficient synthesis of a series of bidentate diborylxanthene derivatives is described.

Key words: boron, cross-coupling, Lewis acids, *ipso*-substitution, xanthene

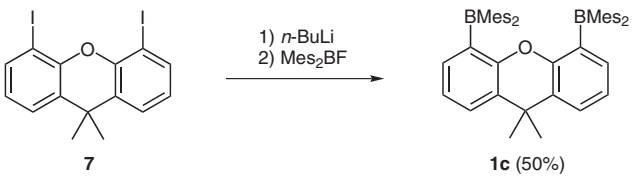
Bidentate organoboron Lewis acids[1] have been widely investigated and utilized as complexing agents for various anions and bases. Diborylethanes[2] and diborylnaphthalenes[3] bind with small anions such as fluoride, alkoxides and hydride. Bidentate organoboranes with dibenzofuran[4] and an anthracene spacer[5] have also been prepared. On the other hand, few bidentate boronic acids with a xanthene framework have been reported in the literature.[6,7] In this paper, we report the concise synthesis of a series of bidentate organoboron compounds with a xanthene backbone as the spacer (Figure 1).

The results of the synthesis of **1a–c** are summarized in Scheme 1 and Scheme 2. We synthesized **1a** in three steps as shown in Scheme 1. By Ogino's method,[8] silylation was accomplished in high yield by the reaction of chlorotrimethylsilane with dilithiated xanthene. Subsequently, diborylxanthene **6** was synthesized by the *ipso*-substitution[9] of **5** with boron tribromide and the hydrolysis of **6** gave the boronic acid **1a**. The pure product was isolated through these simple procedures in much higher yield (96%) than those obtained through the reported procedure (50% yield).[7] The reaction of catechol with **6** was also carried out to afford **1b** (Scheme 1).



Scheme 1

Gabbaï and co-workers reported the synthesis of **1c** by the reaction of **4** with *n*-BuLi-TMEDA and the subsequent borylation of the lithiated compound with Mes_2BF and noted that the product was not isolated in pure form.[4] Though we, too, were unable to isolate **1c** by carrying out a similar reaction, we succeeded in the synthesis of **1c** by the lithiation of **7**[10] and the subsequent addition of Mes_2BF to the reaction mixture (Scheme 2). The result suggests that the presence of TMEDA prevents the isolation of **1c** in pure form. Although compound **1b** was not stable toward moisture, the decomposition of **1a** or **1c** was not observed after exposing the compounds to air for several months.



Scheme 2

We introduced spacers between the boron centers and the xanthene framework which could modulate the steric and electronic nature of the boron centers. First, phenyl spac-

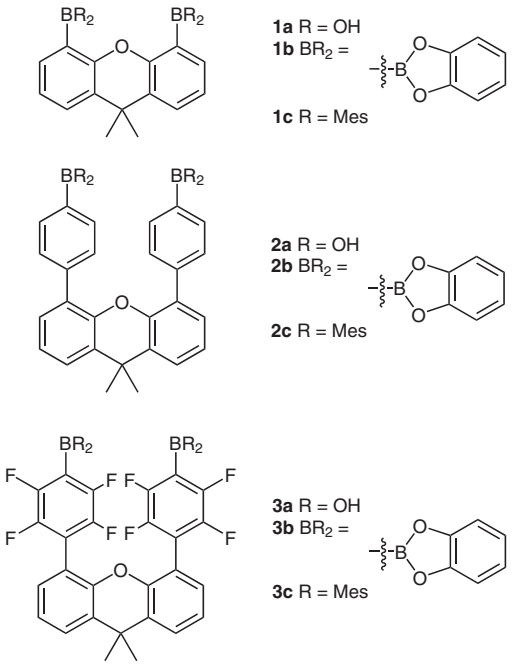


Figure 1

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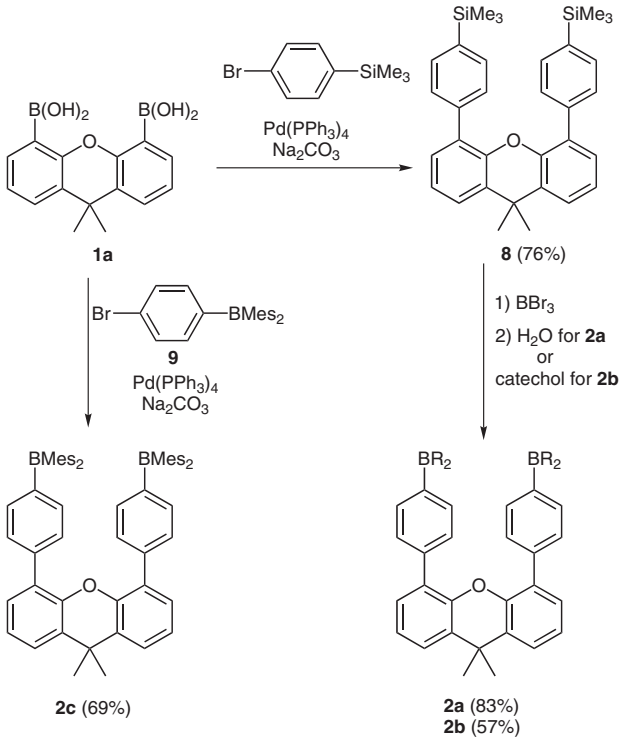
ers were introduced, and the syntheses of **2a–c** are summarized in Scheme 3. Diboronic acid **1a** reacted with 4-bromotrimethylsilylbenzene in the presence of $Pd(PPh_3)_4$ to give **8**.[11] *Ipso*-substitution of **8** with boron tribromide was carried out and the bis(dibromoboryl) derivative was hydrolyzed to afford **2a**. Compound **2b** was synthesized by a similar method. The reaction of **1a** with 4-bromophenyldimesitylborane (**9**) in the presence of $Pd(PPh_3)_4$ afforded **2c** in moderate yield.

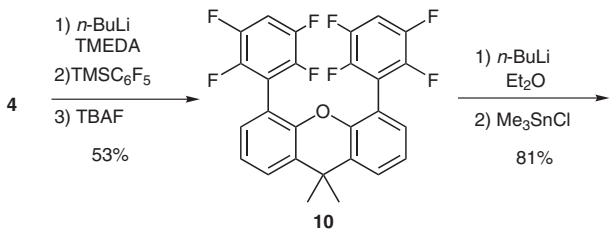


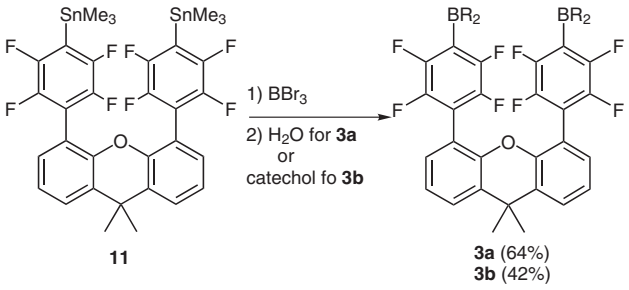
Scheme 3

Expecting the acidity of the boron centers to be enhanced by the introduction of electron-withdrawing groups, fluorinated spacers were introduced. Compound **10** was isolated by the nucleophilic substitution of lithiated **4** with trimethylsilylpentafluorobenzene,[12,13] followed by desilylation, in good yield. Subsequently, stannylation was accomplished by the lithiation of **10** followed by the addition of trimethyltin chloride.[14] The stannyl compound **11** was reacted with BBr_3,[15,16] and the product was hydrolyzed to afford **3a** (Scheme 4).[17] Compound **3b** was also synthesized in a similar manner.[18]

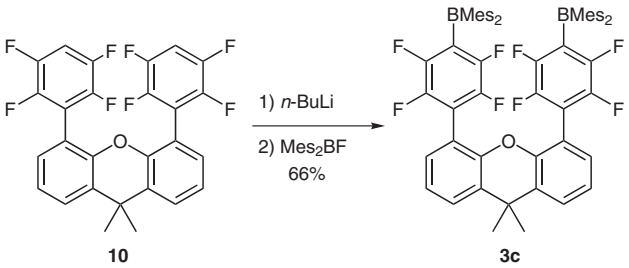
Unlike other compounds, the mesitylated borane **3c** was synthesized directly from **10**; the reaction of lithiated **10** with dimesitylboron fluoride proceeded smoothly and compound **3c** was isolated in 66% yield (Scheme 5).

In summary, we have developed a concise and efficient method for the synthesis of diborylxanthenes. The acidity and bulkiness of the boron centers could be modulated by introducing various boryl groups to the xanthene framework. The compounds are promising candidates for chelation of various anions and bases.





Scheme 4



Scheme 5

N,*N*,*N*′,*N*′-Tetramethylethylenediamine (TMEDA) and chlorotrimethylsilane (TMSCl) were distilled over CaH_2 prior to use. 9,9-Dimethylxanthene (**4**),[19] 4,5-diiodo-9,9-dimethylxanthene (**7**),[10] 1-bromo-4-trimethylsilylbenzene,[20] and tetrakis(triphenylphosphine)palladium[21] were prepared according to literature procedures. Trimethylsilylpentafluorobenzene[22] was prepared by the reaction of pentafluorophenyllithium[23] with TMSCl, and purified by distillation under reduced pressure from P_4O_{10}. Anhydrous Et_2O, anhydrous hexane, anhydrous CH_2Cl_2 and anhydrous toluene were purchased from Kanto Kagaku Co., Ltd. Other reagents were commercially available and used without further purification. NMR spectra were recorded on a Jeol JNM-EX270L FT NMR system (270 MHz), a Jeol JNM-EX300L FT NMR system (300 MHz), a Bruker AV400M (400 MHz), Jeol JNM-LA500 FT NMR system (500 MHz), or a Bruker AM600 (600 MHz). Chemical shifts are reported in delta units (δ) relative to $CDCl_3$ (7.24 ppm for ^1H NMR and 77.0 ppm for ^{13}C NMR), benzene-d_6 (7.15 ppm for ^1H NMR, 128.0 ppm for ^{13}C NMR), CD_3OD (3.75 ppm for ^1H NMR, 49.3 ppm for ^{13}C NMR), C_6F_6 (–162.9 ppm for ^{19}F NMR), or $BF_3{\cdot}OEt_2$ (0 ppm for ^{11}B NMR).[24,25] IR spectra were recorded on a Jasco FT/IR-410 (FT-IR). Elemental analyses were carried out on a Yanaco CHN corder MT-6. High-resolution mass spectra were measured on a Jeol SX102A (EI) or a Bruker Daltonics microTOF focus (ESI). Column chromatography was performed with silica gel 60N (spherical, neutral, 63–210 μm, purchased from Kanto Kagaku Co., Ltd). Gel permeation chromatography (GPC) was carried out on a Japan Analytical Industry LC-928 Recycling Preparative HPLC, equipped with JAIGEL-1H and JAIGEL-2H columns. Thin layer chromatography (TLC) was performed on Merck silica gel 60F-254

plates. All manipulations were carried out under anhydrous and anaerobic conditions unless otherwise noted.

4,5-Bis(trimethylsilyl)-9,9-dimethylxanthene (5)

To a solution of 9,9-dimethylxanthene (**4**; 25 g, 120 mmol) and TMEDA (36 mL, 240 mmol) in a mixture of anhyd Et_2O (480 mL) and anhyd hexane (360 mL) at r.t., was added *n*-BuLi (1.6 M in hexane, 180 mL, 288 mmol) diluted with anhyd hexane (360 mL) over 10 min, and the mixture was heated to 40 °C for 3 h. The deep-red solution was cooled to 0 °C and TMSCl (37 mL, 288 mmol) in anhyd hexane (240 mL) was added over 10 min. The mixture was warmed to r.t. and a colorless precipitate was formed. After stirring for 13 h, H_2O (200 mL) was added and the organic layer was separated. The aqueous layer was extracted with hexane (2 × 50 mL) and the combined organic layer was dried over $MgSO_4$ and concentrated. The residue was subjected to short column chromatography (silica gel; hexane), and further purified by recrystallization from EtOH to afford **5**.

Yield: 36 g (86%); colorless crystals; mp 84.5–84.8 °C.

IR (KBr): 3058, 2963, 2899, 1605, 1567, 1385, 1247, 1216, 1194, 1145, 1124, 953, 841, 787, 758, 745, 682, 629, 484 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.40 (s, 18 H), 1.61 (s, 6 H), 7.08 (t, *J* = 7.2 Hz, 2 H), 7.36 (dd, *J* = 7.2, 1.8 Hz, 2 H), 7.46 (dd, *J* = 7.2, 1.8 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.9, 32.8, 34.1, 122.6, 126.3, 127.6, 129.6, 134.0, 155.6.

Anal. Calcd for $C_{21}H_{30}OSi_2$: C, 71.12; H, 8.53. Found: C, 70.95; H, 8.35.

9,9-Dimethylxanthene-4,5-diboronic Acid (1a)

To a solution of **5** (3.5 g, 10 mmol) in anhyd CH_2Cl_2 (30 mL) was added BBr_3 (2.3 mL, 24 mmol), and the mixture was stirred at r.t. overnight. To the resulting solution of **6** was added H_2O (3 mL), and a colorless precipitate was formed. The precipitate was collected by filtration and washed with H_2O (3 × 30 mL) and CH_2Cl_2 (10 mL). The product was dried under reduced pressure to afford **1a** (2.9 g, 96%) as a colorless solid. ^1H NMR and ^{13}C NMR were in good agreement with the literature.[7]

^{11}B NMR (96 MHz, DMSO-d_6): δ = 20.8.

4,5-Bis(1,3,2-dioxaborolyl)-9,9-dimethylxanthene (1b)

To a solution of **5** (3.5 g, 10 mmol) in anhyd CH_2Cl_2 (30 mL) at r.t., was added BBr_3 (2.3 mL, 24 mmol). The solution turned yellow. After stirring at r.t. overnight, all volatiles were removed under reduced pressure and the yellow-white residue was dissolved in anhyd toluene (100 mL). Catechol (2.2 g, 20 mmol) was added and the mixture was stirred under reflux for 4 h. The solvents were removed under reduced pressure and the resulting residue was extracted with hot hexane (100 mL). The filtrate was concentrated and the residue was recrystallized from toluene–hexane to afford **1b**.

Yield: 1.8 g (41%); colorless crystals; mp 184–185 °C.

IR (KBr): 3530, 3336, 3059, 2979, 2954, 1622, 1473, 1415, 1396, 1370, 1336, 1239, 756, 736 cm^{-1}.

^1H NMR (300 MHz, C_6D_6): δ = 1.36 (s, 6 H), 6.74–6.81 (m, 8 H), 6.94 (t, *J* = 7.4 Hz, 2 H), 7.23 (dd, *J* = 7.4, 1.7 Hz, 2 H), 7.83 (dd, *J* = 7.4, 1.7 Hz, 2 H).

^{13}C NMR (75 MHz, C_6D_6): δ = 31.7, 34.3, 112.9, 122.7, 123.4, 129.8, 130.4, 134.9, 149.2, 155.5.

^{11}B NMR (96 MHz, C_6D_6): δ = 31.8.

HRMS-EI: *m*/*z* [M^+] calcd for $C_{27}H_{20}B_2O_5$: 446.1497; found: 446.1505.

4,5-Bis(dimesitylboryl)-9,9-dimethylxanthene (1c)

To a solution of diiodoxanthene **7**[10] (0.46 g, 1.0 mmol) in anhyd THF (3 mL) was added *n*-BuLi (1.5M in hexane, 1.3 mL, 2.0 mmol) at 0 °C, and the mixture was stirred for 30 min. The solution was cooled to –78 °C and dimesitylboron fluoride (0.54 g, 2.0 mmol) in anhyd THF (5 mL) was added to the solution. The mixture was slowly warmed to r.t. and stirred overnight. The solvent was removed under reduced pressure and Et_2O (30 mL) was added. The solution was washed with H_2O (30 mL) and dried over $MgSO_4$. The filtrate was concentrated to ~3 mL and the precipitate was collected by filtration to afford **1c** (0.17 g, 24%) as colorless crystals. The residue was purified by column chromatography (silica gel; hexane–CH_2Cl_2, 10:1) to afford **1c** (0.18 g, 26%).

Colorless solid; mp 289.0–291.5 °C.

IR (KBr): 2965, 2915, 1604, 1445, 1396, 1223, 846 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 1.62 (s, 24 H), 1.68 (s, 6 H), 2.23 (s, 12 H), 6.82 (dd, *J* = 7.2, 1.2 Hz, 2 H), 6.95 (t, *J* = 7.2 Hz, 2 H), 7.48 (dd, *J* = 7.2, 1.2 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.3, 23.3 (br), 33.7, 34.2, 123.2, 128.0, 128.4 (br), 129.9, 133.6, 137.2, 138.9 (br), 141.4 (br), 153.8.

Anal. Calcd for $C_{51}H_{56}B_2O$: C, 86.69; H, 7.99. Found: C, 86.87; H, 8.06.

4,5-Bis(4-trimethylsilylphenyl)-9,9-dimethylxanthene (8)

A mixture of diboronic acid **1a** (1.5 g, 5.0 mmol), 1-bromo-4-trimethysilylbenzene (2.1 mL, 11 mmol), tetrakis(triphenylphosphine)palladium (0.35 g, 0.30 mmol) and Na_2CO_3 (1.2 g, 11 mmol) was dissolved into toluene (25 mL), EtOH (minimum volume to dissolve diboronic acid **1a**, ~5 mL) and H_2O (5.5 mL). After refluxing for 30 h, the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic solution was dried over $MgSO_4$ and concentrated. The residue was subjected to short column chromatography (silica gel; hexane–CH_2Cl_2, 20:1), and the product was recrystallized from hexane to afford **8**.

Yield: 1.9 g (76%); colorless crystals; mp 170.0–170.2 °C.

IR (KBr): 2954, 2894, 1422, 1246, 875, 851, 825, 788, 749 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 0.29 (s, 18 H), 1.69 (s, 6 H), 7.13 (t, *J* = 7.8 Hz, 2 H), 7.18 (dd, *J* = 7.8, 3.0 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 4 H), 7.39 (d, *J* = 8.3 Hz, 4 H), 7.42 (dd, *J* = 7.8, 3.0 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = –0.8, 31.3, 34.7, 123.1, 124.5, 129.1, 129.8, 131.5, 132.9, 138.3, 138.4, 148.4.

Anal. Calcd for $C_{33}H_{38}OSi_2$: C, 78.20; H, 7.56. Found: C, 78.31; H, 7.57.

4,5-Bis(4-dihydroxyborylphenyl)-9,9-dimethylxanthene (2a)

To a solution of **8** (253 mg, 0.50 mmol) in CH_2Cl_2 (3 mL) was added BBr_3 (0.12 mL, 1.2 mmol), and the mixture was stirred at r.t. overnight. All volatiles were removed under reduced pressure then H_2O (1 mL) was added to the residue. After stirring the suspension for 1 h, the precipitate was collected by filtration and washed with CH_2Cl_2 (2 × 5 mL) to afford **2a**.

Yield: 187 mg (83%); colorless solid; mp >300 °C.

IR (KBr): 3245, 2962, 1714, 1430, 1367, 1244, 1203, 1102, 1017 cm^{-1}.

^1H NMR (600 MHz, CD_3OD): δ = 2.15 (s, 6 H), 7.60–7.66 (m, 6 H), 7.80 (br, 4 H), 7.95–7.96 (m, 4 H).

^{13}C NMR (150 MHz, CD_3OD): δ = 32.1, 36.1, 124.6, 126.3, 129.2, 130.0, 130.3, 130.8, 131.7, 133.0, 134.8, 149.6.

^{11}B NMR (96 MHz, CD_3OD): δ = 31.0.

HRMS-ESI: *m/z* [M + Na]$^+$ calcd for $C_{27}H_{24}B_2O_5Na$: 473.1711; found: 473.1710.

4,5-Bis[4-(1,3,2-dioxaborolyl)phenyl]-9,9-dimethylxanthene (2b)

To a solution of **8** (0.50 g, 1.0 mmol) in CH_2Cl_2 (3 mL) was added BBr_3 (0.23 mL, 2.4 mmol) and the mixture was stirred at r.t. overnight. A colorless precipitate formed. All volatiles were removed under reduced pressure and the residue was suspended in toluene (10 mL). Catechol (0.22 g, 2 mmol) was added to the suspension and the mixture was stirred under reflux for 4 h. The mixture was cooled to r.t. and the precipitate was collected by filtration. The precipitates were washed with toluene and hexane to afford **2b**.

Yield: 0.34 g (57%); colorless wool-like solid; mp 269.5–270.0 °C.

IR (KBr): 1611, 1474, 1427, 1395, 1378, 1337, 1240, 728, 658 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.73 (s, 6 H), 6.82–6.88 (m, 8 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.21 (dd, *J* = 7.8, 1.2 Hz, 2 H), 7.33 (d, *J* = 7.8 Hz, 4 H), 7.46 (dd, *J* = 7.8, 1.2 Hz, 2 H), 7.75 (d, *J* = 7.8 Hz, 4 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.4, 34.8, 112.1, 122.4, 123.2, 125.2, 128.6, 129.3, 129.9, 131.2, 134.5, 141.5, 147.9, 148.3.

^{11}B NMR (96 MHz, $CDCl_3$): δ = 32.6.

HRMS-EI: *m/z* [M$^+$] calcd for $C_{39}H_{28}B_2O_5$: 598.2123; found: 598.2122.

4-Bromophenyldimesitylborane (9)

To a solution of 1,4-dibromobenzene (0.94 g, 4.0 mmol) in anhyd Et_2O (10 mL) was added *n*-BuLi (1.6 M in hexane, 2.4 mL, 4 mmol) at –78 °C. After stirring for 1 h at r.t., the solution was cooled to –78 °C then dimesitylboron fluoride (1.07 g, 4.4 mmol) in anhyd Et_2O (5 mL) was added. The mixture was stirred for 17 h at r.t. then the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2 (3 × 10 mL) and the organic layer was dried over $MgSO_4$. The filtrate was concentrated and the product was purified by column chromatography (silica gel; hexane–CH_2Cl_2, 30:1) to afford **9**.

Yield: 619 mg (84%); colorless crystals; mp 180.0–182.5 °C.

IR(KBr): 2912, 1605, 1573, 1422, 1213, 1067, 1010, 848, 812 cm^{-1}.

^{1}H NMR (270 MHz, $CDCl_3$): δ = 1.96 (s, 12 H), 2.28 (s, 6 H), 6.80 (s, 4 H), 7.34 (d, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.2, 23.4, 127.4, 128.2, 131.3, 137.8, 138.9, 140.7.

^{11}B NMR (96 MHz, $CDCl_3$): d = 74.2.

Anal. Calcd for $C_{24}H_{26}BBr$: C, 71.14; H, 6.47. Found: C, 71.14; H, 6.25.

4,5-Bis[4-(dimesitylboryl)phenyl]-9,9-dimethylxanthene (2c)

A mixture of **1a** (298 mg, 1.0 mmol), **9** (891 mg, 2.2 mmol), $Pd(PPh_3)_4$ (69 mg, 0.06 mmol) and Na_2CO_3 (233 mg, 2.2 mmol) was dissolved in toluene (5 mL), EtOH (minimum volume to dissolve **1a**, ~1 mL) and H_2O (1.1 mL). The solution was heated to reflux and stirred for 28 h. H_2O (10 mL) was added and the product was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was dried over $MgSO_4$ and the filtrate was concentrated. The product was purified by recrystallization from toluene–hexane to afford **2c**.

Yield: 593 mg (69%); colorless crystals; mp >300 °C.

IR (KBr): 2972, 1604, 1420, 1387, 1240, 1209 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.71 (s, 6 H), 1.87 (s, 24 H), 2.31 (s, 12 H), 6.76 (s, 8 H), 7.14 (t, *J* = 7.2 Hz, 2 H), 7.20 (dd, *J* = 7.2, 1.2 Hz, 2 H), 7.27 (d, *J* = 7.8 Hz, 4 H), 7.44–7.46 (m, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.3, 23.7, 32.1, 34.5, 123.2, 125.2, 128.1, 129.2, 129.5, 130.7, 131.1, 135.8, 138.6, 141.1, 141.7, 141.8, 144.7, 148.0.

Anal. Calcd for $C_{63}H_{64}B_2O$: C, 88.11; H, 7.51. Found: C, 87.82; H, 7.52.

4,5-Bis(2,3,5,6-tetrafluorophenyl)-9,9-dimethylxanthene (10)

To a solution of 9,9-dimethylxanthene (**4**; 3.2 g, 15 mmol) and TMEDA (4.5 mL, 30 mmol) in a mixture of anhyd Et_2O (60 mL) and anhyd hexane (45 mL), was added *n*-BuLi (1.6 M in hexane, 23 mL, 36 mmol) diluted with anhyd hexane (45 mL) over 10 min. The mixture was heated to 40 °C for 3 h, then the deep-red solution was cooled to 0 °C and trimethylsilylpentafluorobenzene (7.3 mL, 38 mmol) in anhyd hexane (40 mL) was added. The mixture was warmed to r.t. and stirred for 2 h then TBAF (1 M in THF, 76 mL, 76 mmol) was added and the mixture was stirred for 1 h. H_2O (100 mL) was added and the organic layer was separated and washed with aq HCl (2M, 100 mL), dried over $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography (silica gel; hexane–CH_2Cl_2, 20:1) to afford **10**.

Yield: 4.0 g (53%); colorless solid; mp 149.5–151.0 °C.

IR (KBr): 3064, 1502, 1464, 1448, 1426, 1391, 1288, 1248, 1174, 1147, 952, 940, 910, 886, 845, 793, 750, 699 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.71 (s, 6 H), 6.92–6.98 (m, 2 H), 7.13 (br d, *J* = 6.6 Hz, 2 H), 7.19 (t, *J* = 7.8 Hz, 2 H), 7.54 (dt, *J* = 7.8, 1.2 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 31.9, 34.6, 104.8 (t, J_{C-F} = 21.8 Hz), 115.3, 117.6 (t, J_{C-F} = 17.6 Hz), 123.2, 127.4, 129.5, 130.8, 142.8–143.0 (m), 144.5–144.8 (m), 146.3–146.4 (m), 147.7.

^{19}F NMR (470 MHz, C_6D_6): δ = –141.0 (m, 2 × F), –139.5 (m, 2 × F).

Anal. Calcd for $C_{27}H_{14}F_8O$: C, 64.04; H, 2.79; F, 30.01. Found: C, 64.05; H, 2.91; F, 30.04.

4,5-Bis(4-trimethylstannyl-2,3,5,6-tetrafluorophenyl)-9,9-dimethylxanthene (11)

To a solution of **10** (1.5 g, 3.0 mmol) in anhyd Et_2O (15 mL) was added *n*-BuLi (1.6 M in hexane, 3.8 mL, 6 mmol) at –78 °C. After stirring for 2 h at –78 °C, trimethyltin chloride (1.2 g, 6.0 mmol) in anhyd Et_2O (10 mL) was added. The mixture was slowly warmed to r.t. and stirred overnight. The precipitate was removed by filtration and the filtrate was concentrated by rotary evaporation. The residue was purified by recrystallization from toluene–hexane to afford **11**.

Yield: 2.0 g (81%); colorless crystals; mp 181.0–183.0 °C.

IR (KBr): 2982, 2958, 2919, 1418, 1358, 1292, 1281, 1121, 1087, 948, 892, 881, 781, 754, 700, 542, 515 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.49 [s, ^{117}Sn (7.7%) and ^{119}Sn (8.4%) satellites, ^2J = 58.2 Hz, 18 H], 1.70 (s, 6 H), 7.10 (d, *J* = 7.2 Hz, 2 H), 7.17 (t, *J* = 7.2 Hz, 2 H), 7.53 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = –7.1 [^{117}Sn (7.7%) and ^{119}Sn (8.4%) satellites, *J* = 378, 362 Hz], 31.7, 34.6, 116.2 [^{117}Sn (7.7%) and ^{119}Sn (8.4%) satellites, *J* = 93.4 Hz], 118.0 (t, J_{C-F} = 18.5 Hz), 123.0, 126.9, 130.3, 131.1, 143.1 (ddd, J_{C-F} = 247.8, 17.6, 8.1 Hz), 147.7–147.9 (m), 148.3, 149.3–149.5 (m).

^{19}F NMR (470 MHz, C_6D_6): δ = –139.2 (m, 2 × F), –123.3 (m, 2 × F).

Anal. Calcd for $C_{33}H_{30}F_8OSn_2$: C, 47.64; H, 3.63. Found: C, 47.69; H, 3.50.

4,5-Bis(4-dihydroxyboryl-2,3,5,6-tetrafluorophenyl)-9,9-dimethylxanthene (3a)

A mixture of **11** (416 mg, 0.50 mmol) and BBr_3 (0.95 mL, 10 mmol) was stirred for 11 h. All volatiles were removed under reduced pressure and the organotin compounds were removed by sublimation under reduced pressure. H_2O (1 mL) was added to the residue and the mixture was stirred for 1 h. The precipitate was collected by filtration and washed with CH_2Cl_2 (2 × 5 mL) to afford **3a**.

Yield: 190 mg (64%); colorless solid; mp >300 °C.

IR (KBr): 3388, 2970, 1652, 1472, 1424, 1346, 1252, 1040, 961 cm^{-1}.

^1H NMR (300 MHz, CD_3OD): δ = 1.79 (s, 6 H), 7.23 (br d, *J* = 6.9 Hz, 2 H), 7.31 (t, *J* = 7.8 Hz, 2 H), 7.74 (dd, *J* = 7.8, 1.8 Hz, 2 H).

^{13}C NMR (150 MHz, CD_3OD): δ = 32.5, 36.0, 117.0, 119.7 (t, J_{C-F} = 17.6 Hz), 124.9, 131.1, 132.7, 143.4 (dd, J_{C-F} = 247.7, 16.3 Hz), 147.5 (br), 149.1 (br), 149.3.

^{19}F NMR (470 MHz, CD_3OD): δ = –140.4 (br s, 2 × F), –132.1 (br s, 2 × F).

^{11}B NMR (96 MHz, CD_3OD): δ = 28.1.

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{27}H_{16}B_2F_8O_6Na$: 617.0958; found: 617.0949.

4,5-Bis[4-(1,3,2-benzodioxaborolyl)-2,3,5,6-tetrafluorophenyl]-9,9-dimethylxanthene (3b)

Compound **11** (0.42 g, 0.50 mmol) was dissolved in BBr_3 (0.47 mL, 5.0 mmol) and the mixture was stirred at r.t. overnight. All volatiles were removed under reduced pressure and the residue was washed with hexane (2 × 5 mL). The residue was dissolved in toluene (4 mL) and catechol (0.11 g, 1.0 mmol) was added. The mixture was heated to reflux for 4 h then cooled to r.t. and the precipitate was collected by filtration and washed with toluene (5 mL) and hexane (2 × 5 mL) to afford **1c**.

Yield: 160 mg (42%); colorless wool-like solid; mp 242.5–243.0 °C.

IR (KBr): 1469, 1428, 1399, 1362, 1330, 1279, 1239, 976, 966, 809, 737 cm^{-1}.

^1H NMR (600 MHz, C_6D_6): δ = 1.28 (s, 6 H), 6.54–6.57 (m, 4 H), 6.64–6.66 (m, 4 H), 6.90 (t, *J* = 7.2 Hz, 2 H), 7.01 (d, *J* = 7.2 Hz, 2 H), 7.10 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (150 MHz, C_6D_6): δ = 28.4, 31.6, 109.8, 112.6, 112.7, 118.2, 118.8 (t, J_{C-F} = 17.6 Hz), 120.2, 120.7, 126.6, 128.8, 141.4 (dd, J_{C-F} = 243.5, 14.3 Hz), 145.03, 146.2–146.4 (m), 147.9–148.1 (m).

^{19}F NMR (470 MHz, C_6D_6): δ = –140.4 (dd, *J* = 23.0, 14.1 Hz, 2 × F), –121.3 (dd, *J* = 21.6, 15.0 Hz, 2 × F).

^{11}B NMR (96 MHz, C_6D_6): δ = 30.8.

HRMS-EI: *m/z* $[M^+]$ calcd for $C_{39}H_{20}B_2F_8O_5$: 742.1369; found: 742.1368.

4,5-Bis(4-dimesitylboryl-2,3,5,6-tetrafluorophenyl)-9,9-dimethylxanthene (3c)

To a solution of **10** (506 mg, 1.0 mmol) in anhyd Et_2O (10 mL), was added *n*-BuLi (1.6 M in hexane, 1.3 mL, 2 mmol) at –78 °C and the mixture was stirred for 2 h. Mes_2BF (563 mg, 2.1 mmol) in anhyd Et_2O (10 mL) was added to the solution at –78 °C. The mixture was warmed to r.t. and stirred for 19 h. H_2O (30 mL) was added and the product was extracted with Et_2O (2 × 10 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The product was purified by column chromatography (silica gel; hexane–EtOAc, 50:1) to afford **3c**.

Yield: 663 mg (66%); colorless amorphous solid; mp 132.0–133.0 °C.

IR (KBr): 2962, 2920, 1606, 1450, 1419, 1306, 1244 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 1.70 (s, 6 H), 1.99 (s, 24 H), 2.25 (br, 12 H), 6.73 (br, 8 H), 7.08 (br d, *J* = 7.2 Hz, 2 H), 7.16 (t, *J* = 7.8 Hz, 2 H), 7.54 (dd, *J* = 7.8, 1.2 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.3, 22.7, 32.8, 34.5, 115.5, 119.9 (t, J_{C-F} = 18.7 Hz), 123.0, 124.2 (t, J_{C-F} = 24.1 Hz), 127.6, 128.5, 130.8, 131.2, 140.1 (br), 141.0 (br), 141.7 (br), 143.8 (dd, J_{C-F} = 250.2, 16.4 Hz), 146.2 (dt, J_{C-F} = 246.0, 12.1 Hz), 147.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –141.4 (dd, *J* = 23.3, 12.4 Hz, 2 × F), –132.1 (dd, *J* = 21.5, 12.0 Hz, 2 × F).

HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_{63}H_{56}B_2F_8ONa$: 1025.4301; found: 1025.4301.

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(15) Since the silicon–boron exchange reaction did not take place on silylpolyfluoroarenes, the use of the stannylpolyfluoroarene was essential. See: Frohn, H.-J.; Franke, H.; Fritzen, P.; Bardin, V. V. *J. Organomet. Chem.* **2000**, *598*, 127.

(16) We chose the trimethylstannyl group instead of the more common tributylstannyl group as the substituent, since the removal of the organotin derivatives, which were formed by the borylation reaction, could be easily achieved by sublimation. See: Britovsek, G. J. P.; Ugolotti, J.; White, A. J. P. *Organometallics* **2005**, *24*, 1685.

(17) The boronic acid **3a** was also prepared in 35% yield by the lithiation (*n*-BuLi) of **10**, the reaction of the aryllithium with $B(OMe)_3$ and the hydrolysis of the aryltrimethoxyborate. See: Frohn, H.; Adnin, N. Y.; Bardin, V. V.; Starichenko, V. F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2827; the solubility of **3a**, however, was very low in common organic solvents and

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