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An *ortho*-lithiated derivative of protected phenylboronic acid: an approach to *ortho*-functionalized arylboronic acids and 1,3-dihydro-1-hydroxybenzo[c][2,1]oxaboroles

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2-(2′-Bromophenyl)-6-butyl-[1,3,6,2]dioxazaborocan, prepared readily by the esterification of 2-bromophenylboronic acid with *N*-butyldiethanolamine (BDEA), undergoes Br/Li exchange using BuLi/THF at −78 °C. A resulting intermediate proved useful in synthesis of various *ortho*-functionalized arylboronic acids. Specifically, reactions with benzaldehydes provide a convenient access to 1,3-dihydro-1-hydroxy-3-arylbenzo[c][2,1]oxaboroles that exhibit a remarkably high rotational barrier around the C–aryl bond. In addition, the molecular structure of sterically hindered 1,3-dihydro-1-hydroxy-3-(2′, 6′-dimethoxyphenyl)benzo[c][2,1]oxaborole is reported. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: arylboronic acids; benzo[c][2,1]oxaboroles; halogen–lithium exchange; boron–lithium reagents; protective groups

INTRODUCTION

Arylboronic acids and esters are important synthetic intermediates. They are synthesized by classical routes involving transmetalation of aryllithium[1,2] or arylmagnesium[3] compounds with trialkyl borates. Pd-catalyzed coupling of aryl halides with diboron derivatives or hydroboranes[4–6] became an alternative in the 1990s. In all of these methods the introduction of boronic group constitutes the last step before a final product isolation. More recently, alternative methods based on the protection of a boronic acid group followed by derivatization of another reactive substituent have been developed. One of them involves immobilization of substituted (X = CHO, CH_2Br, COOH, NH_2) arylboronic acids onto diethanolaminomethyl polystyrene.[7] The use of analogous protocol for the introduction of lithium to a boronated aromatic ring is limited to a few examples,[8–10] although there are many examples of synthesis and use of boron–lithium and other mixed boron-containing bimetallic derivatives of alkanes[11] and alkenes.[12] The lithiation of *N*-methyldiethanolamine esters of 3- and 4-bromophenylboronic acids was used as a key step in synthesis of boronated nucleoside derivatives,[8] functionalized quinuclidines,[9] *meta*- and *para*-boronated sulfamides,[10] but an approach to *ortho*-isomers failed.[10] Very, recently the Br/Li exchange in potassium 3-and 4-bromophenyltrifluoroboranes[13] and the preparation of magnesiated arylboronic pinacol esters have been reported.[14] Our continuous interest in *ortho*-functionalized arylboronic acids as versatile reagents (especially in molecular recognition processes) has prompted us to attempt the preparation and reactivity of an *ortho*-lithiated derivative of protected phenylboronic acid.

RESULTS AND DISCUSSION

Protection of 2-bromophenylboronic acid

As a modification of previously reported procedures[8–10] we used *N*-butyldiethanolamine (BDEA), instead of *N*-methyldiethanolamine, as a protective reagent for the boronic group, as we assumed that the longer alkyl chain will increase solubility of arylboronic azaester. In our protocol, a mixture of

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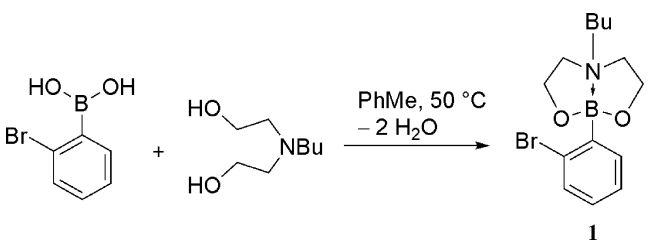
a 2-bromophenylboronic acid (1 equiv.), BDEA (1 equiv.) and toluene was heated for ca. 1 h at 50 °C. The resultant mixture was subjected to concentration to remove water (by product) and the major amount of toluene until a clear solution was obtained. Well-defined, air-stable and crystalline 2-(2′-bromophenyl)-6-butyl[1.3.6.2]dioxazaborocan **1** precipitated upon addition of hexane with 92% yield. The tetrahedral boron environment in **1** with the B–N dative bond was established directly by ^{11}B NMR analysis showing a single resonance at 7 ppm. Compound **1** is insoluble in hexane and diethyl ether but well soluble in THF (Scheme 1).

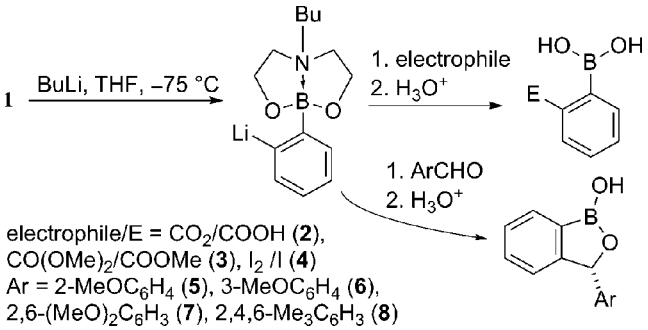
Br/Li exchange and subsequent reactions with electrophiles

The reaction of **1** with BuLi was performed as follows: a solution of **1** in THF was added to a precooled (−80 °C, internal temperature) solution of BuLi in THF (ca. 0.6 M). It is advisable to use a slight excess of BuLi (1.1–1.2 equiv.) followed by stirring for ca. 15–20 min at ca. −75 °C to complete the interconversion. A resultant lithiated intermediate precipitates gradually to give a white slurry. It was sufficiently stable under these conditions and some decomposition resulting in lowering product yields was observed above −70 °C. The quench with electrophiles [CO_2, $(MeO)_2CO$, I_2] followed by aqueous acidic hydrolysis and subsequent workup afforded functionalized arylboronic acids **2**–**4** in good yield for 10–50 mmol scale reactions (Scheme 2). The protection was readily cleaved upon acidic hydrolysis at room temperature. It should be noted that the synthesis of the important 2-carboxyphenylboronic acid **2** by the classical oxidation of 2-methylphenylboronic acid with $KMnO_4$ has long remained problematic; it has been optimized only recently[15] but our method seems to be a useful alternative. In general, various *ortho* substituted arylboronic acids, especially those bearing reactive functional groups, can potentially be synthesized using the approach based on a temporal protection of the boronic group.

A range of electrophiles was extended by employing benzaldehydes. Additions to a carbonyl group also proceed smoothly in the case of sterically hindered benzaldehydes such as 2,6-dimethoxybenzaldehyde and 2,4,6-trimethylbenzaldehyde to produce well-defined 1,3-dihydro-1-hydroxy-3-arylbenzo[c][2,1]oxaboroles. Interestingly, a room temperature ^{1}H NMR spectrum of compound



Scheme 1. Protection of 2-bromophenylboronic acid with BDEA.



Scheme 2. Synthesis of *ortho*-functionalized arylboronic acids and 1,3-dihydro-1-hydroxybenzo[c][2,1]oxaboroles via an *ortho*-lithiated derivative of protected phenylboronic acid.

7 exhibits two broad resonances of OMe groups, which coalesce above ca. 310 K. Accordingly, resonances of aryl hydrogens *ortho* to OMe groups are also broadened (their coalescence is observed at 293 K). These facts indicate clearly that rotation of the 2,6-dimethoxyphenyl group in **7** is retarded. The rotation barrier was calculated to be ca. 53 kJ mol^{-1} by means of VT NMR line shape analysis. A similar behavior was observed for **8** although the rotation barrier for the mesityl group was slightly higher (56 kJ mol^{-1}). This is in accord with previous results showing greater rotational restrictions for mesityl groups when compared with 2,6-dimethoxyphenyl group.[16,17] We suppose that the structural rigidification upon formation of the boraheterocycle may account for the significant rotational restriction in **7**. In a related phenyl(2,6-dimethoxyphenyl)methanol (i.e. the carbon analogue of **7**) two methoxy groups give one signal. In this case the 2,6-dimethoxyphenyl group is not attached to a cyclic system and accordingly its rotation is rapid on the NMR time scale under comparable conditions.[18] In addition, it should be noted that the ^{1}H NMR chemical shift of one of methoxy resonances is only 3.3 ppm, i.e. it is significantly shifted upfield (by ca. 0.5 ppm) when compared with δ values typical of aryloxy bound methyl hydrogen atoms; a similar effect is observed for one *ortho*-Me group in **8** ($\delta = 1.70$ ppm).

Crystal structure of 7

The molecular structure of **7** is shown in Fig. 1. The metric features of the benzo[c][2,1]oxaborole heterocycle are similar to those reported for other analogues;[19–24] the fused ring system is essentially planar. Both methoxy groups possess an *exo* orientation with respect to the benzo[c][2,1]oxaborole system; the O19 atom being located over the five-membered heterocyclic ring. The molecules form centrosymmetric dimers (as a pair of *R* and *S* enantiomers, Fig. 2) due to intermolecular bifurcated[25] hydrogen bonds, the major component being formed between BOH groups and the methoxy O19 atoms. The interactions between BOH groups and ring O3 atoms of the partner molecule are significantly weaker, also in comparison with known structures of analogous compounds.[20–22]

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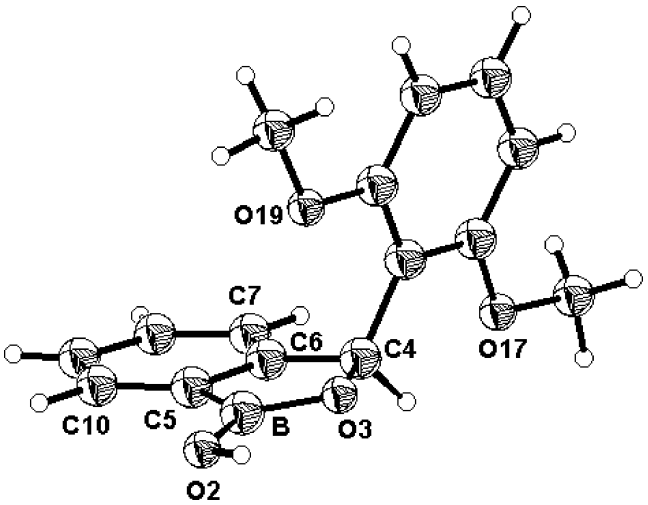


Figure 1. The molecular structure of **7**. Selected geometric parameters: B–O2 1.3468(13), B–O3 1.3887(12); B1–C5 1.5540(14), O3–C4 1.4486(11) Å; O2–B–O3 123.12(9), O2–B–C5 127.99(9), O3–B–C5 108.86(8), B–O3–C4 110.23(7), O3–C4–C6 105.46(7), B–C5–C10 135.86(9), O2–B–C5–C10 5.15(18), O3–B–C5–C10 −176.80(10)°.

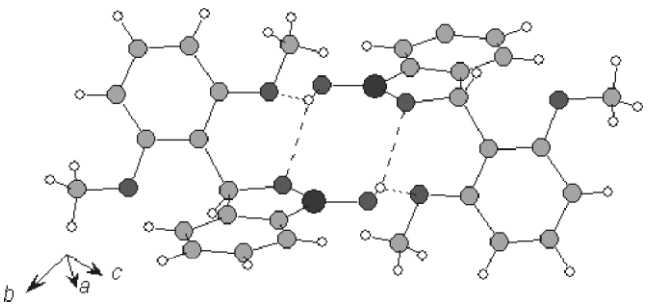


Figure 2. The dimeric structure of **7**. Bifurcated hydrogen bonds are marked by dashed lines. O2–H2O···O19^{i}, 2.127(19) Å; O2···O19^{i}, 2.9278(10) Å; ∠(O2–H2O···O19^{i}), 150°; O2–H2O···O3^{i}, 2.337(18) Å; O2···O3^{i}, 3.0273(10) Å; ∠(O2–H2O···O3^{i}), 135°; i: 1 − *x*, −*y*, −*z*.

Regioselectivity of the Br/Li exchange

We were interested to determine if the protected boronic group exhibits some *ortho*-directing properties due to the precomplexation of BuLi by oxygen lone pairs. For this purpose, the regioselectivity of halogen–lithium exchange was studied using 2-(2′,5′-dibromophenyl)-6-butyl[1,3,6,2]dioxazaborocan (**9**). However, reaction of **9** with 1 equiv of BuLi followed by DMF quench afforded a mixture of 5-bromo-2-formyl- and 2-bromo-5-formylphenylboronic acids, **10** and **11**, in a ratio of ca. 3:7, respectively, which means that the major product comes from the lithiation *meta* to the protected boronic moiety (Scheme 3). Hence, this group is unable to provide an effective *ortho*-assistance for approaching lithium, which would kinetically favour the Br/Li exchange at the 2-position. It seems that such a product distribution is caused primarily by electron-donating properties of this substituent as it is similar to that observed in lithiation of 2,5-dibromotoluene, which occurs preferentially in a 5-position, too.[25]

In conclusion, the bimetallic compound prepared via halogen–lithium exchange from **1** is a versatile synthetic intermediate in boronic acid chemistry, as demonstrated by reactions with selected electrophiles. We are undertaking work on the synthesis of other boron-containing bimetallic reagents using lithium–metal interconversion.

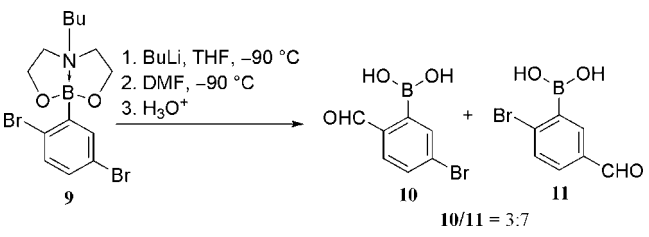
EXPERIMENTAL

General comments

All reactions involving air- and moisture-sensitive reagents were carried out under an argon atmosphere. Solvents were stored over sodium wire before use. Key reagents including arylboronic acids, BDEA, BuLi (10 M solution in hexanes), dimethyl carbonate and benzaldehydes were received from Aldrich and used without additional purification. The NMR chemical shifts are given relative to TMS using known chemical shifts of residual proton (^{1}H) or carbon (^{13}C) solvent resonances. In the ^{13}C NMR spectra the resonances of carbon atoms bound to boron were not observed due to their broadening by quadrupolar boron nucleus. The spectra were recorded at room temperature unless otherwise noted.

*2-(2′-Bromophenyl)-6-butyl[1,3,6,2]dioxazaborocan (**1**)*

A mixture of 2-bromophenylboronic acid (20.1 g, 0.1 mol), *N*-butyldiethanolamine (17.0 g, 0.105 mol) and toluene (100 ml) was heated with stirring for 1 h at 50 °C. The mixture was concentrated under reduced pressure to remove water (by product) and the majority of the toluene. To a remaining viscous solution hexane (100 ml) was added to precipitate a crystalline material. It was filtered, washed with diethyl ether (2 × 25 ml) and dried to give the title compound.Yield: 31.0 g (95%), m.p. 91–93 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) $\delta = 7.77$ (dd, $J = 8.0$, 1.5 Hz, 1H, Ph), 7.47 (dd, $J = 8.0$, 1.0 Hz, 1H, Ph), 7.20 (td, $J = 8.0$, 1.0 Hz, 1H, Ph), 7.06 (td, $J = 8.0$, 1.5 Hz, 1H, Ph), 4.18–4.06 (m, 4H, CH_2O), 3.30–3.23 (m, 2H, CH_2CH_2O), 3.04–2.99 (m, 2H, CH_2CH_2O), 2.62–2.58 (m, 2H,



Scheme 3. The non-selective Br/Li exchange for **9** followed by DMF quench.

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$NCH_2CH_2CH_2CH_3$), 1.55–1.47 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.19–1.10 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.81 (t, $J = 7.0$ Hz, 3H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) $\delta = 136.8, 133.2, 129.4, 129.2, 126.2, 62.9, 58.17, 58.11, 26.8, 20.1, 13.6$ ppm. ^{11}B NMR ($CDCl_3$, 64.16 MHz) $\delta = 7$ ppm. IR (KBr) 2959, 2872, 1188, 1112, 838, 752 cm^{-1}. $C_{14}H_{21}BBrNO_2$ (326.04): calcd C 51.57, H 6.49, N 4.29; found C 51.52, H 6.44, N 4.22.

*2-(2′,5′-Dibromophenyl)-6-butyl[1,3,6,2] dioxazaborocan (**9**)*

This compound has been prepared as described for **1** starting with 2,5-dibromophenylboronic acid. Yield: 30.8 g (91%), m.p. 95–98 °C. ^1H NMR ($CDCl_3$, 400 MHz) $\delta = 7.93$ (d, $J = 3.0$ Hz, 1 H, Ph), 7.35 (d, J 8.0 Hz, 1H, Ph), 7.20 (dd, $J = 8.0$, 3.0 Hz, 1H, Ph), 4.20–4.08 (m, 4 H, CH_2O), 3.32–3.26 (m, 2H, CH_2CH_2O), 3.10–3.03 (m, 2H, CH_2CH_2O), 2.65–2.60 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.60–1.52 (m, 2H, $NCH_2CH_2CH_2CH_3$), 1.24–1.15 (m, 2H, $NCH_2CH_2CH_2CH_3$), 0.86 (t, $J = 7.0$ Hz, 3H, $NCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 139.3, 134.7, 132.1, 127.8, 121.3, 63.0, 58.42, 58.31, 26.9, 20.1, 13.7 ppm. IR (KBr) 2962, 2874, 1178, 1109, 842 cm^{-1}. ^{11}B NMR ($CDCl_3$, 64.16 MHz) $\delta = 7$ ppm. $C_{14}H_{20}BBr_2NO_2$ (404.94) calcd: C 41.53, H 4.98, N, 3.46; found C 42.04, H 5.03, N 3.53.

*2-Carboxyphenylboronic acid (**2**)*

BuLi (10 M solution in hexanes, 6 mL, 60 mmol) was added to THF (160 mL) at −70 °C and a solution was cooled to ca. −90 °C. Then a solution of **1** (16.3 g, 50 mmol) in THF (50 ml) was added during ca. 5 min. After the addition the temperature increased to −75 °C. A mixture was stirred for 20 min at −75 °C and cooled to −90 °C followed by passing an excess of gaseous carbon dioxide while maintaining the temperature below −85 °C. A mixture was stirred for 30 min and hydrolyzed with aqueous HCl (6 M, 20 ml). The organic phase was separated and solvents were evaporated under reduced pressure. The viscous residue was triturated with Et_2O to give a solid, which was filtered and washed with cold water (2 × 10 ml) and ether (2 × 5 ml). Drying *in vacuo* afforded the title compound as a white powder; yield: 5.5 g (66%), m.p. 158–160 °C (Tao *et al.*; m.p. 159–162 °C) ^1H NMR (acetone-d_6, 400 MHz) $\delta = 7.81$ (d, $J = 8.0$ Hz, 1H, Ph), 7.55–7.35 (m, 3H, Ph) ppm. ^{11}B NMR (acetone-$d_6 + D_2O$, 64.16 MHz) $\delta = 30$ ppm.

*2-(Methoxycarbonyl)phenylboronic acid (**3**)*

1 (3.26 g, 10 mmol) was lithiated as described for **2** followed by a rapid addition of dimethyl carbonate (1.80 g, 20 mmol) to a precooled solution (−95 °C). A mixture was stirred for 30 min and hydrolyzed with aqueous sulfuric acid (1.5 M, 15 ml). The organic phase was separated and solvents were evaporated under reduced pressure. The solid residue was filtered and washed consecutively with water (2 × 2 ml), ether (2 × 2 ml) and hexane (5 ml). Drying in vacuo afforded the title compound as a white powder; yield: 1.12 g (60%), m.p. 102–104 °C. ^1H NMR (acetone-d_6, 400 MHz) $\delta = 7.89$ (dt, $J = 8.0$, 1.0 Hz, 1H, Ph), 7.54–7.52 (m, 2H, Ph), 7.43–7.39 (m, 1H, Ph), 7.22 (broad, 1H), 3.83 (s, 3H, COOMe), 3.09 (s, 1H) ppm. ^{13}C NMR (acetone-d_6, 100.6 MHz) $\delta = 169.0$, 133.4, 132.8, 129.4, 128.8, 52.2 ppm. ^{11}B NMR (acetone-d_6, 64.16 MHz) $\delta = 30$ ppm. IR (KBr) 3440, 3324, 3272, 1692, 1364, 1136, 764 cm^{-1}. $C_8H_9BO_4$ (179.97): calcd C 53.39, H 5.04; found C 53.31, H 5.15.

*2-Iodophenylboronic acid (**4**)*

1 (3.26 g, 10 mmol) was lithiated as described for **2** followed by a dropwise addition of a solution of iodine (2.54 g, 10 mmol) in THF (10 ml) at −80 °C. A mixture was stirred for 30 min and hydrolyzed. Subsequent workup afforded a brown residue that was washed with water (10 ml) and redissolved in Et_2O (30 ml). A solution was washed with aqueous $Na_2S_2O_3$ (10 wt%, 20 ml) and water (20 ml). Ether was removed to leave a crystalline solid, which was washed with water (5 ml) and recrystallized from toluene (10 ml). Yield: 1.52 g (62%), m.p. 128–130 °C. ^1H NMR (acetone-d_6, 400 MHz) $\delta = 7.76$ (d, J 8.0 Hz, 1H), 7.45 (s, 1H), 7.38–7.31 (m, 2H), 7.06 (m, 1H), 3.09 (s, 1H). ^{13}C NMR (acetone-d_6, 100.6 MHz) $\delta = 139.1, 134.6, 131.1, 127.7, 99.3$. ^{11}B NMR (acetone-d_6, 64.16 MHz) $\delta = 29$ ppm. IR (KBr) 3300, 1582, 1352, 1000, 753. $C_6H_6BIO_2$ (247.82): calcd C 29.08, H 2.44; found C 29.45, H 2.83.

*1,3-Dihydro-1-hydroxy-3-(2′-methoxyphenyl) benzo[c][2,1]oxaborole (**5**)*

1 was lithiated as described for **2** followed by a dropwise addition of a solution of 2-methoxybenzaldehyde (1.50 g, 11 mmol) in Et_2O (10 ml) at −80 °C. A mixture was stirred for 30 min and hydrolyzed. Subsequent workup was performed as described for **2**; a crude product was washed with water (2 × 2 ml), hexane (5 ml) and dried. Yield 1.88 g (78%), m.p. 130–133 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 7.5$ Hz, 1H, Ph), 7.43 (td, $J = 7.5$, 2.0 Hz, 1H, Ph), 7.35 (t, $J = 7.5$ Hz, 1H, Ph), 7.30–7.26 (m, 2H, Ph), 7.03–6.96 (m, 2H, Ph), 6.88 (t, $J = 7.5$ Hz, 1H, Ph), 6.75 (s, 1H, C*H*), 6.10 (broad, 1H, BO*H*), 3.95 (s, 3H, OMe) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 157.0, 156.9, 131.1, 130.3, 129.2, 128.5, 127.3, 126.8, 122.3, 120.7, 110.7, 78.0, 55.5$ ppm. ^{11}B NMR (64.3 MHz, $CDCl_3$): $\delta = 28$ ppm. $C_{14}H_{13}BO_3$ (240.07): calcd C 70.04, H 5.46; found C 69.78, H 5.33.

*1,3-Dihydro-1-hydroxy-3-(3′-methoxyphenyl) benzo[c][2,1]oxaborole (**6**)*

This compound has been prepared as described for **5** starting with 3-methoxybenzaldehyde. Yield 1.80 g (75%), m.p. 111–113 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 7.5$ Hz, 1H, Ph), 7.42 (td, $J = 7.5$, 2.0 Hz, 1H, Ph), 7.35 (t, $J = 7.5$ Hz, 1H, Ph), 7.26 (t, $J = 7.5$ Hz, 1H, Ph), 7.18 (dd, $J = 7.5$, 1.0 Hz, 1H, Ph), 6.89–6.80 (m, 3H, Ph), 6.16 (s, 1 H, CH), 3.76 (s, 3H, OMe) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$): $\delta = 159.7$, 156.4, 141.6, 131.35, 130.4, 129.7, 127.6, 122.2, 119.1, 113.7, 112.3, 83.6, 55.2 ppm. ^{11}B NMR (64.3 MHz,

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$CDCl_3$): $\delta = 28$ ppm. $C_{14}H_{13}BO_3$ (240.07): calcd C 70.04, H 5.46; found C 70.09, H 5.55.

*1,3-Dihydro-1-hydroxy-3-(2′,6′-dimethoxyphenyl) benzo[c][2,1]oxaborole (**7**)*

This compound has been prepared as described for **5** starting with 2,6-dimethoxybenzaldehyde. Yield 1.91 g (71%), m.p. 132–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.73$ (d, $J = 7.5$, Hz, 1H, Ph), 7.35 (td, $J = 7.5$, 1.0 Hz, 1H, Ph), 7.30 (t, $J = 7.5$ Hz, 1H, Ph), 7.22 (t, $J = 7.5$ Hz, 1H, Ph), 7.09 (dd, $J = 7.5$, 1.0 Hz, 1H, Ph), 6.87 (s, 1H, C*H*), 6.53 (broad, 2 H, Ph), 5.23 (s, 1H, BO*H*), 6.08 (broad, 1H, BO*H*), 3.90 (broad, 3H, OMe), 3.40 (broad, 3H, OMe) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$, 213 K): $\delta = 159.1$, 157.75, 156.3, 130.5, 129.7, 129.63, 126.4, 120.8, 113.9, 104.6, 103.05, 75.4, 55.8, 55.4 ppm. ^{11}B NMR (64.3 MHz, $CDCl_3$): $\delta = 28$ ppm. $C_{15}H_{15}BO_4$ (270.09): calcd C 66.70, H 5.60; found C 66.56, H 5.54.

*1,3-Dihydro-1-hydroxy-3-(2′,4′,6′-trimethylphenyl) benzo[c][2,1]oxaborole (**8**)*

This compound was prepared as described for **5** starting with 2,4,6-trimethylbenzaldehyde. Yield 1.75 g (69%), m.p. 127–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J =$ 7.5 Hz, 1H, Ph), 7.39 (t, $J = 7.5$ Hz, 1H, Ph), 7.33 (t, $J = 7.5$ Hz, 1H, Ph), 7.04 (d, $J = 7.5$ Hz, 1H, Ph), 6.93 (s, 1H, Mes), 6.70 (s, 1H, Mes), 6.67 (s, 1H, CH), 6.08 (broad, 1H, BO*H*), 2.57 (s, 3H, 2′-Me), 2.25 (s, 3H, 4′-Me), 1.70 (s, 3H, 6′-Me) ppm. ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): $\delta = 156.6$, 137.8, 137.7, 132.7, 132.5, 131.6, 131.4, 131.25, 130.3, 129.3, 127.2, 121.4, 80.5, 20.9, 20.85, 20.0 ppm. ^{11}B NMR (64.3 MHz, $CDCl_3$): $\delta = 28$ ppm. $C_{16}H_{17}BO_2$ (252.12): calcd C 76.22, H 6.80; found C 76.10, H 6.97.

Crystal structure of 7

Data were collected at 100(2) K on a KM4CCD κ-axis diffractometer with graphite-monochromated MoK_α radiation. $C_{15}H_{15}BO_4$, $M = 270.08$, monoclinic, $P2_1/c$, $a =$ 9.0075(3), $b = 16.6916(7)$, $c = 9.2463(3)$ Å, $\beta = 106.676(3)°$, $V = 1331.71(9)$ Å, $Z = 4$, 3254 unique reflecions, $\theta_{max} = 28.6°$, R $[I > 2\sigma(I)] = 0.032$, wR (all data) = 0.092. Programs used: CrysAlisCCD & CrysAlisRED,[27] SHELXL97[28] and DIAMOND.[29] CCDC deposition number: 630348.

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