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Facile preparation of fullerenyl boronic esters

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ABSTRACT

The fullerendiol $C_{60}(OH)_2(OOt\text{-}Bu)_4$ **1** reacts with various arylboronic acids $ArB(OH)_2$ to form fullerene-containing boronic esters $C_{60}(O_2BAr)(OOt\text{-}Bu)_4$ in up to 95% yield depending on the structure of aryl group. Bis(pinacolato)diboron $(B(OCMe_2)_2)_2$ also reacts with **1** to form $C_{60}(O_2BB(OCMe_2)_2)(OOt\text{-}Bu)_4$. The bisboronic ester $C_{60}(O)(O_2BAr)_2(OOt\text{-}Bu)_2$ was also obtained starting from a tetrahydroxyl fullerene derivative $C_{60}(O)(OH)_4(OOt\text{-}Bu)_2$. The fullerenyl boronic esters are moderately stable in air. Single crystal X-ray structure of $C_{60}(O_2BPh)(OOt\text{-}Bu)_4$ was obtained.

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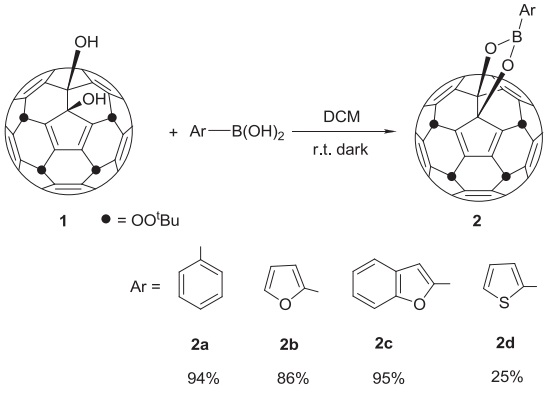
1. Introduction

Numerous fullerene derivatives have been prepared over the past twenty years.[1] Introduction of a suitable addend has limited effect on the π conjugation and cage structure, yet can greatly enhance the solubility in organic solvents or water.[2] Thus fullerene derivatives exhibit improved functional properties in many cases compared to the pristine fullerene.[3] For example, the best known material in fullerene based solar cell is a C_{60} derivative,[4] namely PCBM prepared by addition of an azo compound to C_{60} followed by extrusion of nitrogen under heating.

Among all the reported fullerene derivatives, methano-[5] and pyrrolidinofullerenes[6] are the most intensively investigated fullerene derivatives because of their easy preparation procedure and good stability. Other fullerene derivatives include epimino-,[7] epoxy-,[8] pyrazolino-,[9] lactono-,[10] isoquinolino-,[11] and various [4+2] Diels–Alder adducts.[12] Methods are still being developed in the literature for the preparation of new fullerene derivatives.[13] To the best of our knowledge, fullerene-containing boronic esters remain unknown.[14] We have reported the preparation of fullerene-mixed peroxides.[15] Further investigations have led to a number of cage skeleton modified fullerene derivatives, such as open-cage[16] and azafullerenes.[17] Here we report the preparation of fullerenyl boronic esters through reaction of fullerenol with arylboronic acid.

2. Results and discussion

Boronic esters are widely used in Suzuki–Miyaura coupling reactions.[18] They are readily prepared from boronic acid and alcohol. Vicinal diol esters of alkyl and arylboronic acids, such as pinacol esters are particularly useful because of their enhanced stability. We have reported the fullerene diol **1** through Lewis acid catalyzed hydrolysis of the epoxide precursor $C_{60}(O)(OOt\text{-}Bu)_4$.[19] In an attempt to prepare fullerene-containing boronic esters, we treated **1** with phenylboric acid. The reaction was quite efficient giving the boronic ester **2** in excellent yield after stirring at rt for 50 min (Scheme 1).



Scheme 1. Formation of fullerenyl boronic esters.

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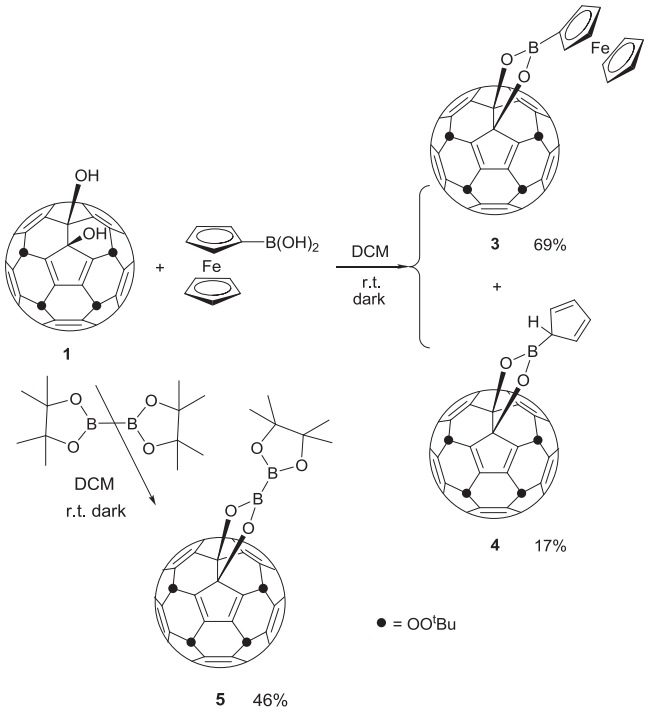
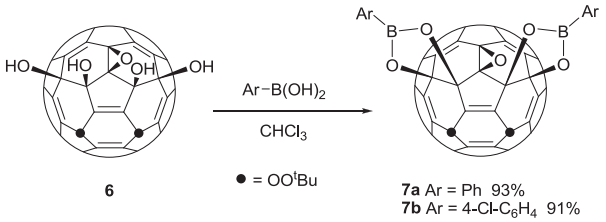
The boronic esterification reaction can be extended to other boronic acids as shown in Scheme 1. Furan-2-ylboronic acids gave good yields, but the thiophen-2-ylboronic acid afforded the corresponding ester in only 25% yield. The major products of the thiophen-2-ylboronic acid reaction with **1** are complex mixtures. Reduction of the peroxo groups in **1** by the thiophen-2-ylboronic acid and subsequent reactions may be responsible for the formation of complex byproducts and low yield of **2d**. In the reaction with ferrocenylboronic acid, a byproduct **4** was also obtained (Scheme 2). Apparently compound **4** was produced from decomposition of the ferrocenyl moiety.[20] The cyclopentadienylboric ester **4** is less polar than the ferrocenylboronic ester **3** and eluted as the first band on silica gel column.



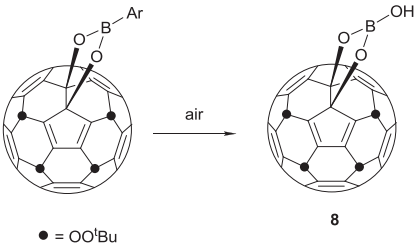
Scheme 2. Reactions with ferrocenylboronic acid and bis(pinacolato)diboron.

The bis(pinacolato)diboron also reacted with **1** smoothly at rt in dichloromethane (Scheme 2). As above no catalyst was needed for the transesterification process. Attempts to replace the second pinacol moiety with **1** failed probably due to steric hindrance. The presence of the four *tert*-butylperoxo groups makes the dumbbell product too crowded. After the successful reactions with the fullerene diol **1**, we then treated the fullerenol **6**[21] with four hydroxyl groups with boronic acids, and obtained the fullerene bisboronic esters **7** (Scheme 3). The yields of compounds **7** are comparable to the diol derivatives **2**.



Scheme 3. Formation of fullerenyl bisboronic esters.

Compared to the analogous 1,3-dioxolane fullerene derivatives,[14a,22] the fullerenyl boronic esters are moderately stable. Upon storage in air for one week, the borate **8** could be detected (Scheme 4). Under nitrogen atmosphere, the fullerenyl boronic esters can be stored for weeks with little change. In our previous study, we have reported the preparation of **8** through treatment of the epoxide precursor $C_{60}(O)(OOt\text{-}Bu)_4$ with BF_3 in the presence of moisture.[14]



Scheme 4. Decomposition of fullerenyl boronic esters.

Spectroscopic data are in agreement with the structures depicted in the Schemes. All the new compounds showed C_s symmetry on the NMR spectra. For compounds **2**–**5**, there are two singlet signals for the four *tert*-butylperoxo groups on the ^{1}H NMR spectra. On the ^{13}C NMR spectra, the 54 sp^2 fullerene cage carbons appeared as 28 signals, two of which are half intensity corresponding to the two unique carbons on the mirror plane. Compounds **7a** and **7b** are slightly different in that they have 52 sp^2 fullerene cage carbons. The HRMS also showed the expected molecular ion signals.

To further confirm the structural assignment, we obtained the single crystal X-ray structure for compound **2a** (Fig. 1). Suitable single crystals were obtained from slow evaporation of a mixture solution $CS_2/CHCl_3$/MeOH. The structure indicates the phenyl ring is almost coplanar with the dioxaborolane ring. The dihedral angle between the two planes is 5.9°. The C–C bond of the dioxaborolane ring is the longest at 1.57 Å. Double bonds on the cyclopentadiene ring are the shortest on the cage (1.33 and 1.34 Å).

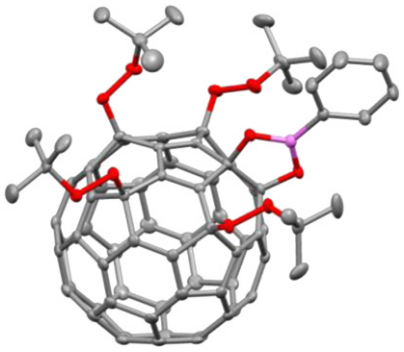


Fig. 1. X-ray structure of **2a**. For clarity hydrogen atoms are not shown. Ellipsoids were drawn at 50% level. Grey-carbon, red-oxygen, purple-boron.

In summary, fullerene-containing boronic esters have been prepared through the reaction between vicinal fullerendiol and arylboronic acid. Yields of the reactions range from moderate to excellent depending on the structure of the aryl group. Preliminary tests indicate that the fullerenyl boronic esters are reactive towards various reagents. Potential applications of fullerenyl boronic esters may include protection of hydroxyl groups in fullerene derivatives and coupling reagents in Suzuki–Miyaura reaction.

3. Experimental section

3.1. General

All reagents were used as received. Dichloromethane (DCM) was distilled from phosphorus pentoxide. Chloroform was treated with

concentrated H_2SO_4, washed with water to remove ethanol, and dried with anhydrous K_2CO_3. Other solvents were used as received. The reactions were carried out in air. The NMR spectra were obtained at 25 °C unless noted. Compounds **1**[19] and **6**[21] were prepared as reported before.

3.2. Caution

A large amount of peroxides is involved in some of the reactions. Care must be taken to avoid possible explosion.

*3.2.1. Compound **2a**.* To a solution of compound **1** (100 mg, 0.09 mmol) in DCM (20 mL) was added phenylboronic acid (55 mg, 0.45 mmol). The resulting solution was stirred at rt in dark for 50 min. The solution was chromatographed on silica gel eluting with toluene to yield the compound **2a** as an orange solid (103 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00–8.06 (m, 2H), 7.40–7.60 (m, 3H), 1.52 (s, 18H), 1.17 (s, 18H). ^{13}C NMR: ($CDCl_3$, 75 MHz, all signals represent 2C except noted): δ 151.23, 150.14, 149.24, 149.21, 148.75, 148.39 (3C), 148.25, 148.11, 147.66, 147.40, 147.36 (4C), 147.01, 145.95, 145.74, 145.44 (4C), 145.21, 144.98, 144.57, 144.30, 143.85, 143.57, 143.30, 143.12, 141.30, 139.59, 135.35, 131.90, 127.87, 91.50, 85.18, 82.37, 82.04, 81.87, 80.86, 26.71 ($6CH_3$), 26.53 ppm ($6CH_3$); FT-IR (microscope): 2980, 2931, 2870, 1393, 1361, 1192, 1095, 1026, 1008, 871, 757, 698 cm^{-1}; ESI-MS: (*m*/*z*, %): 1214 (100) ($M+NH_4^+$), 1235 (30) $(M+K)^+$.

*3.2.2. Crystal data for compound **2a**.* $C_{83}H_{42}BCl_3O_{10}$, T=123(2) K, Monoclinic, space group $P2(1)/n$, Unit cell dimensions: a=15.234(3) Å, b=15.951(3) Å, c=23.808(5) Å, V=5740(2) Å^3. Z=4, ρ_{calcd}=1.523 Mg/m^3. Reflections collected/unique 53,676/13,141 [R(int)=0.05564]. Final R indices [$I>2\sigma(I)$] R_1=0.0672, wR_2=0.1904. CCDC 703261.

*3.2.3. Compound **2b**.* To a solution of compound **1** (85 mg, 0.077 mmol) in DCM (10 mL) was added 2-furanylboronic acid (36 mg, 0.32 mmol). The resulting solution was stirred at rt in dark for 90 min. The solvent was evaporated. The residue was dissolved in about 2 mL $CHCl_3$ and precipitated by adding methanol. The process was repeated three times to remove unreacted 2-furanylboronic acid. The solid was then chromatographed on silica gel eluting with toluene/petroleum ether (bp 60–90 °C)/ethyl acetate (10:10:1) to remove unknown impurities, and then toluene/ethyl acetate (10:7) to yield the compound **2b** as an orange solid (79 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.32 (d, J=2.48 Hz, 1H), 6.53 (s, 1H), 1.48(s, 18H), 1.21(s, 18H). ^{13}C NMR: ($CDCl_3$, 100 MHz, all signals represent 2C except noted): δ 151.09, 149.73, 149.14, 149.13, 148.66, 148.34, 148.30 (1C), 148.16, 148.10, 147.79, 147.58, 147.33, 147.27 (3C), 146.93, 145.63, 145.52, 145.27, 145.24, 145.11, 144.85, 144.44, 144.21, 143.78, 143.50, 143.30, 142.97, 141.22, 139.64, 124.82 (1C), 110.62 (1C), 91.39 (1C), 84.99 (1C), 82.26, 82.00 (*C*-$(CH_3)_3$), 81.98 (*C*-$(CH_3)_3$), 80.87, 26.73 ($6CH_3$), 26.45 ($6CH_3$). FT-IR (microscope): 2980, 2929, 2854, 1578, 1484, 1364, 1338, 1303, 1243, 1231, 1192, 1165, 1122, 1096, 1077, 1042, 1024, 1004 cm^{-1}. HRMS (*m*/*z*): $C_{80}H_{43}BNO_{11}$ ($M+NH_4^+$) calculated: 1204.2936, found: 1204.2937.

*3.2.4. Compound **2c**.* To a solution of compound **1** (95 mg, 0.085 mmol) in DCM (20 mL) was added 2-benzofuranylboronic acid (28 mg, 0.17 mmol). The resulting solution was stirred at rt in dark for 90 min. The solvent was evaporated. The residue was dissolved in about 2 mL $CHCl_3$ and precipitated by adding methanol. The process was repeated three times to remove unreacted 2-benzofuranylboronic acid. The solid was then chromatographed on silica gel eluting with toluene/petroleum ether (bp 60–90 °C)/ethyl acetate (10:10:1) to remove unknown impurities, and then toluene/ethyl acetate (10:7) to yield the compound **2c** as an orange solid (101 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J=7.72 Hz, 1H), 7.67 (d, J=8.80 Hz, 1H), 7.61 (s, 1H), 7.43 (t, J=7.30 Hz, 1H), 7.31 (t, J=3.86 Hz, 1H), 1.50 (s, 18H), 1.20 (s, 18H). ^{13}C NMR: ($CDCl_3$, 100 MHz, all signals represent 2C except noted): δ 150.86, 149.70, 149.16, 148.68, 148.34, 148.31 (1C), 148.17, 148.12, 147.61, 147.34, 147.30 (1C), 147.28, 146.92, 145.63, 145.31, 145.27, 145.25, 145.17, 144.87, 144.47, 144.20, 143.81, 143.51, 143.34, 142.99, 141.20, 139.69, 127.32, 126.38, 122.94, 122.16, 121.06, 112.07, 91.49 (1C), 85.23 (1C), 82.27, 82.03 (4*C*-$(CH_3)_3$), 80.87, 26.76 ($6CH_3$), 26.53 ($6CH_3$). FT-IR (microscope): 2979, 2928, 2854, 1592, 1568, 1474, 1387, 1364, 1331, 1314, 1294, 1258, 1243, 1192, 1167, 1143, 1121, 1105, 1092, 1072, 1042, 1023, 1005 cm^{-1}. ESI-HRMS (*m*/*z*): $C_{84}H_{45}BNO_{11}$ ($M+NH_4^+$), calculated: 1254.3093 found: 1254.3097.

*3.2.5. Compound **2d**.* To a solution of compound **1** (32 mg, 0.029 mmol) in DCM (10 mL) was added 2-thiophenylboronic acid (8.2 mg, 0.064 mmol). The resulting solution was stirred at rt in dark for 50 min. The solution was chromatographed on silica gel eluting with toluene/petroleum ether (bp 60–90 °C) (1:1) to yield the compound **2d** as an orange solid (8.7 mg, 25%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, J=3.08 Hz, 1H), 7.75 (d, J=4.56 Hz, 1H), 7.28 (m, 1H), 1.50 (s, 18H), 1.20 (s, 18H). ^{13}C NMR: ($CDCl_3$, 100 MHz, all signals represent 2C except noted): δ 151.03, 149.99, 149.17, 149.14, 148.68, 148.33, 148.31(1C), 148.19, 148.07, 147.60, 147.34, 147.33 (1C), 147.29, 146.94, 145.70, 145.66, 145.35, 145.32, 145.17, 144.90, 144.48, 144.23, 143.78, 143.50, 143.27, 143.05, 141.23, 139.57, 138.53, 133.49 (1C), 128.28 (1C), 91.43 (1C), 85.16 (1C), 82.34, 82.05 (*C*-$(CH_3)_3$), 81.90 (*C*-$(CH_3)_3$), 80.88, 26.76 ($6CH_3$), 26.51 ($6CH_3$). FT-IR (microscope): 2979, 2924, 2852, 1523, 1464, 1426, 1386, 1364, 1314, 1288, 1261, 1231, 1193, 1142, 1121, 1105, 1092, 1059, 1037, 1024, 1004 cm^{-1}. ESI-HRMS (*m*/*z*): $C_{80}H_{43}BNO_{10}S$ ($M+NH_4^+$) calculated: 1220.2708, found: 1220.2713.

*3.2.6. Compound **3**.* To a solution of compound **1** (305 mg, 0.27 mmol) in DCM (65 mL) was added ferrocenylboronic acid (253 mg, 1.1 mmol). The resulting solution was stirred at rt in dark for 10 h. The solvent was evaporated. The residue was dissolved in about 5 mL $CHCl_3$ and precipitated by adding methanol. The process was repeated three times to remove unreacted ferrocenylboronic acid. The solid was then chromatographed on silica gel eluting with toluene/petroleum ether (bp 60–90 °C) (1:1) to yield the first band as compound **3** (orange solid, 247 mg, 69%), the second red band was eluted as compound **4** (orange solid, 54 mg, 17%). Characterization data for compound **3**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.60 (t, J=1.44 Hz, 2H), 4.48 (t, J=1.54 Hz, 2H), 4.16 (s, 1H), 1.51 (s, 18H), 1.28 (s, 18H). ^{13}C NMR: ($CDCl_3$, 100 MHz, all signals represent 2C except where noted): δ 150.90, 150.13, 149.16, 149.12, 148.64, 148.25 (3C), 148.20, 147.57, 147.53, 147.33, 147.29, 147.28 (1C), 146.91, 145.97, 145.78, 145.63, 145.61, 145.44, 144.99, 144.50, 143.97, 143.60, 143.39, 143.16, 142.99, 141.28, 138.66, 91.24 (1C), 85.11 (1C), 82.96, 82.09 (*C*-$(CH_3)_3$), 82.04 (*C*-$(CH_3)_3$), 80.78, 73.82, 72.22, 68.93 (5C), 67.89 (1C), 26.94 ($6CH_3$), 26.82 ($6CH_3$). FT-IR (microscope): 2979, 2926, 2852, 1483, 1385, 1364, 1319, 1268, 1243, 1192, 1127, 1105, 1092, 1038, 1023, 1005, 870, 816, 752 cm^{-1}. ESI-HRMS (*m*/*z*): $C_{86}H_{45}BFeO_{10}$ ($M+H^+$) calculated: 1304.2465, found: 1304.2444.

*3.2.7. Characterization data for compound **4**.* ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.86 (s, 2H); 4.74 (s, 2H); 1.53 (s, 18H); 1.30 (s, 18H). ^{13}C NMR: ($CDCl_3$, 100 MHz, all signals represent 2C except where noted): δ 150.93, 150.22, 149.17, 149.12, 148.63, 148.27 (3C), 148.21, 147.57 (4C), 147.35, 147.31, 147.29 (1C), 146.93, 146.04, 145.76, 145.66, 145.64, 145.47, 144.99, 144.50, 144.00, 143.61, 143.41, 143.18, 143.00, 141.33, 138.66, 91.34, 85.15, 82.98, 82.05 (*C*-$(CH_3)_3$), 82.01 (*C*-$(CH_3)_3$), 80.81, 74.67, 73.67, 26.98 ($6CH_3$), 26.86 ($6CH_3$). Molecular ion signal was not observed in the Mass spectrum because of unstability.

*3.2.8. Compound **5**.* To a solution of compound **1** (160 mg, 0.14 mmol) in DCM (20 mL) was added bis(pinacolato)diboron (75 mg, 0.25 mmol). The resulting solution was stirred at rt in dark

for 30 min. The solvent was evaporated. The residue was dissolved in about 3 mL $CHCl_3$ and precipitated by adding methanol. The process was repeated three times to remove unreacted bis(pinacolato)diboron. The solid was then chromatographed on silica gel eluting with DCM/petroleum ether (bp 60–90 °C) (1:3) to yield the compound **7** as an orange solid (84 mg, 46%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.45 (s, 18H), 1.38 (s, 18H), 1.32 (s, 12H). ^{13}C NMR: ($CDCl_3$, 100 MHz, all signals represent 2C except noted): δ 150.67, 149.94, 149.12, 149.09, 148.63, 148.31, 148.28 (1C), 148.11, 148.09, 147.56, 147.31, 147.28, 147.23 (1C), 146.89, 145.68, 145.47, 145.43, 145.31, 145.23, 144.87, 144.40, 144.22, 143.74, 143.45, 143.13, 143.06, 141.44, 139.26, 91.45 (1C), 85.10 (1C), 83.88, 82.36 (C-$(CH_3)_3$), 81.86 (C-$(CH_3)_3$), 81.80, 80.85, 26.86 ($6CH_3$), 26.75 ($6CH_3$), 25.00. FT-IR (microscope): 2980, 2929, 2869, 2248, 1465, 1388, 1364, 1292, 1261, 1193, 1169, 1130, 1105, 1043, 1023, 1003, 926, 908, 872, 853, 752, 733 cm^{-1}. ESI-HRMS (m/z): $C_{82}H_{52}B_2NO_2$ ($M+NH_4^+$) calculated: 1264.3676, found: 1264.3693.

3.2.9. Compound ***7a***. To a solution of compound **6** (60 mg, 0.061 mmol) in $CHCl_3$ (12 mL) was added phenylboronic acid (32 mg, 0.26 mmol). The resulting solution was stirred at rt in dark for 20 min. The solution was chromatographed on silica gel eluting with toluene to yield the compound **7a** as an orange solid (66 mg, 93%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 1.26 (s, 18H), 7.52 (t, J=7.50 Hz, 4H), 7.60 (t, J=7.20 Hz, 2H), 8.15 (d, J=7.20 Hz, 4H). ^{13}C NMR: ($CDCl_3$, 150 MHz, all signals represent 2C except noted) δ 149.86, 149.39, 149.00, 148.82, 148.63 (1C), 148.58, 148.43, 148.33, 148.09, 148.01, 147.59, 147.43 (1C), 146.77, 146.34, 146.32, 145.35, 145.18, 145.10 (4C), 144.98, 144.81, 144.78, 144.28, 144.22, 144.19, 139.09, 137.83, 136.03 (4C), 132.64 (2C), 128.36 (4C), 88.16, 87.51, 82.62, 81.05, 75.74 (1C), 64.88 (1C), 27.14 ($6CH_3$). FT-IR (microscope): 3080, 3056, 3023, 2980, 2926, 2852, 1604, 1499, 1439, 1396, 1360, 1260, 1191, 1095, 1029, 1011, 759, 697, 640 cm^{-1}. ESI-HRMS: $C_{80}H_{29}B_2O_9$ ($M+H^+$) calculated: 1155.2015, found: 1155.2021.

3.2.10. Compound ***7b***. To a solution of compound **6** (60 mg, 0.061 mmol) in $CHCl_3$ (12 mL) was added 4-chlorophenylboronic acid (38 mg, 0.24 mmol). The resulting solution was stirred at rt in dark for 5 min. The solution was chromatographed on silica gel eluting with toluene to yield the compound **7b** as an orange solid (68 mg, 91%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (s, 18H), 7.50 (d, J=8.40 Hz, 4H), 8.07 (d, J=8.40 Hz, 4H). ^{13}C NMR: ($CDCl_3$, 100 MHz, all signals represent 2C except noted) δ 149.46, 148.97, 148.56, 148.42, 148.23 (1C), 148.16, 147.99, 147.77, 147.66, 147.57, 147.15, 147.00 (1C), 146.11, 145.83, 145.63, 144.94, 144.77, 144.70, 144.61, 144.47, 144.36, 144.33, 143.81, 143.74, 143.68, 138.67, 138.62, 137.29, 136.93 (4C), 128.37 (4C), 87.77, 87.11, 82.24, 80.57, 75.18 (1C), 64.50 (1C), 26.70 ($6CH_3$). FT-IR (microscope): 3041, 2979, 2930, 2869, 1597, 1395, 1360, 1256, 1190, 1095, 1047, 1017, 961, 921, 825, 760, 724, 642 cm^{-1}. ESI-HRMS: $C_{80}H_{30}B_2Cl_2NO_9$ ($M+NH_4^+$) calculated: 1240.1502, found: 1240.1490.

Acknowledgements

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Supplementary data

Selected spectroscopic data for new compounds and crystallographic data for **2a** including CIF file. Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.03.092.

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