Supplementary Information for

Facile access to boryltetralins and borylnaphthalenes via a cycloaddition using o-quinodimethanes

Hiroto Yoshida,* Masashi Mukae and Joji Ohshita

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Contents

General Remarks S2

Materials S2

Experimental Procedures and Characterization Data of Products S3

References S16

1H and 13C NMR Spectra of New Compounds
**General remarks.**

All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (\(^1\)H, 270 MHz; \(^{13}\)C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (\(^1\)H, 400 MHz; \(^{13}\)C, 99.5 MHz) spectrometer using residual chloroform (\(^1\)H, \(\delta = 7.26\)), or CDCl\(_3\) (\(^{13}\)C, \(\delta = 77.0\)) as an internal standard. \(^1\)H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, quint = quintet, sext = sextet, br = broad, m = multiplet), coupling constants (Hz), integration. High-resolution mass spectra were obtained with a JEOL JMS-SX102A spectrometer. Preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (chloroform or toluene as an eluent). Unless otherwise noted, commercially available reagents were used without purification. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h. Dioxane was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide.

**Materials.**

\(\text{o-Quinodimethane precursors (1a–1e)}^1\) and borylalkenes (2a–2l)\(^2\) were prepared according to literature procedures. Other borylalkenes (2m and 2n) were purchased from Aldrich.
[4+2] Cycloaddition between o-QDMs and borylalkenes: a general procedure.
A dioxane solution (1 mL) of 1 (0.30 mmol), 2 (0.20 mmol), 18-crown-6 (0.33 mmol) and KF (0.33 mmol) was stirred at 100 °C for the period as specified in Table 1, Scheme 4 and eqn. 1. The mixture was diluted with ethyl acetate and washed with cold brine. The organic layer was dried over MgSO₄ and concentrated in vacuo. Preparative recycling gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

4,4,5,5-Tetramethyl-2-[3-(phenyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-[1,3,2]dioxaborolane (3aa)

A pale yellow solid: ¹H NMR (CDCl₃): δ 0.97 (s, 6H, CH₃), 0.99 (s, 6H, CH₃), 1.74 (td, J = 10.9, 6.3 Hz, 1H, BCH), 2.88-3.06 (m, 5H, ArCH₂ and ArCH), 7.06-7.13 (m, 4H, ArH), 7.16-7.24 (m, 1H, ArH), 7.29-7.31 (m, 4H, ArH); ¹³C NMR (CDCl₃): δ 24.35, 24.43, 31.6, 39.1, 42.9, 76.5, 125.4, 125.6, 126.2, 127.6, 128.2, 128.6, 128.9, 136.4, 136.8, 146.4.

4,4,5,5-Tetramethyl-2-[3-(1-naphthyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ab)

A yellow solid: ¹H NMR (CDCl₃): δ 0.74 (s, 6H, CH₃), 0.86 (s, 6H, CH₃), 1.97 (td, J = 11.5, 5.3 Hz, 1H, BCH), 1.91-2.02 (m, 4H, ArCH₂), 3.93 (td, J = 11.2, 4.6 Hz, 1H, ArCH), 7.03-7.17 (m, 4H, ArH), 7.41-7.52 (m, 4H, ArH), 7.70 (dd, J = 6.9, 2.3 Hz, 1H, ArH), 7.84 (dd, J = 6.3, 2.6 Hz, 1H, ArH), 8.23 (dd, J = 8.2, 2.0 Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 24.19, 24.21, 29.7, 31.8, 39.0, 82.9, 123.6, 125.3, 125.5, 125.56, 125.59, 125.7, 126.5, 128.65, 128.70, 128.9, 131.7, 133.8, 136.5, 136.9, 143.0.

4,4,5,5-Tetramethyl-2-[3-(biphenyl-4-yl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ac)
A white solid: $^1$H NMR (CDCl$_3$): δ 0.98 (s, 6H, CH$_3$), 1.02 (s, 6H, CH$_3$), 1.76 (td, $J = 10.9, 6.3$ Hz, 1H, BCH), 2.94-3.12 (m, 5H, ArCH$_2$ and ArCH), 7.12-7.16 (m 4H, ArH), 7.33-7.57 (m, 9H, ArH); $^{13}$C NMR (CDCl$_3$): δ 24.3, 24.4, 31.6, 39.0, 42.5, 83.0, 125.5, 125.6, 127.0, 128.1, 128.6, 128.7, 129.0, 136.4, 136.7, 139.2, 141.2, 145.6.

4,4,5,5-Tetramethyl-2-[3-(4-n-butylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ad)

A pale yellow oil: $^1$H NMR (CDCl$_3$): δ 0.93 (t, $J = 6.8$ Hz, 3H, CH$_3$CH$_2$), 0.96 (s, 6H, CH$_3$), 1.00 (s, 6H, CH$_3$), 1.35 (sext, $J = 7.8$ Hz, 2H, CH$_2$), 1.57 (quint, $J = 7.7$ Hz, 2H, CH$_2$), 1.71 (td, $J = 11.6, 5.8$ Hz, 1H, BCH), 2.59 (t, $J = 7.7$ Hz, 2H, ArCH$_2$CH$_2$), 2.90-3.03 (m, 5H, ArCH$_2$ and ArCH), 7.06-7.13 (m, 6H, ArH), 7.21 (d, $J = 8.7$ Hz, 2H, ArH); $^{13}$C NMR (CDCl$_3$): δ 13.9, 22.2, 24.3, 24.4, 31.7, 33.8, 35.2, 39.1, 42.5, 82.9, 125.4, 125.5, 127.5, 128.3, 128.6, 129.0, 136.4, 136.9, 140.7, 143.5.

4,4,5,5-Tetramethyl-2-[3-(2,5-dimethoxyphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ae)

A yellow oil: $^1$H NMR (CDCl$_3$): δ 0.99 (s, 6H, CH$_3$), 1.02 (s, 6H, CH$_3$), 1.83 (td, $J = 11.2, 5.6$ Hz, 1H, BCH), 2.77-3.06 (m, 4H, ArCH$_2$), 3.46 (td, $J = 11.5, 4.9$ Hz, 1H, ArCH), 3.77 (s, 3H, OCH$_3$), 3.79 (s, 3H, OCH$_3$), 6.68-6.84 (m, 3H, ArH), 7.07-7.11 (m 4H, ArH); $^{13}$C
NMR (CDCl₃): δ 24.3, 24.4, 31.7, 36.0, 53.5, 55.7, 56.4, 82.8, 111.5, 112.1, 114.0, 125.3, 125.4, 128.6, 128.9, 136.1, 136.5, 137.1, 151.6, 153.7.

4,4,5,5-Tetramethyl-2-[3-(4-trifluoromethylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3af)

A white solid: ¹H NMR (CDCl₃): δ 0.98 (s, 6H, CH₃), 1.00 (s, 6H, CH₃), 1.73 (td, J = 10.9, 6.6 Hz, 1H, BCH), 2.83-3.15 (m, 5H, ArCH₂ and ArCH), 7.05-7.14 (m, 4H, ArH), 7.41 (d, J = 8.4 Hz, 2H, ArH), 7.57 (d, J = 8.4 Hz, 2H, ArH); ¹³C NMR (CDCl₃): δ 24.30, 24.34, 31.4, 38.7, 42.8, 83.1, 125.06, 125.11, 125.17, 125.22, 125.6, 125.8, 128.0, 128.3, 128.6, 128.9, 136.1, 136.2, 150.66, 150.68.

4,4,5,5-Tetramethyl-2-[3-(4-bromophenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ag)

A white solid: ¹H NMR (CDCl₃): δ 1.01 (s, 6H, CH₃), 1.02 (s, 6H, CH₃), 1.65-1.72 (m, 1H, BCH), 2.79-3.01 (m, 5H, ArCH₂ and ArCH), 7.06-7.13 (m, 4H, ArH), 7.18 (d, J = 8.7 Hz, 2H, ArH), 7.43 (d, J = 7.7 Hz, 2H, ArH); ¹³C NMR (CDCl₃): δ 24.39, 24.41, 31.4, 38.9, 42.3, 83.0, 119.8, 125.5, 125.7, 128.6, 128.9, 129.4, 131.2, 136.2, 136.3.

4,4,5,5-Tetramethyl-2-[3-(4-ethynylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ah)
A white solid: $^1$H NMR (CDCl$_3$): $\delta$1.00 (s, 6H, CH$_3$), 1.01 (s, 6H, CH$_3$), 1.71 (td, $J = 11.6$, 6.8 Hz, 1H, BCH), 2.85-3.06 (m, 6H, CH, ArCH$_2$ and ArCH), 7.07-7.13 (m, 4H, ArH), 7.26 (d, $J = 7.8$ Hz, 2H, ArH), 7.45 (d, $J = 7.8$ Hz, 2H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.39, 24.40, 31.4, 38.8, 42.7, 76.5, 83.0, 83.9, 119.8, 125.5, 125.7, 127.6, 128.6, 128.9, 132.0, 136.2, 136.4, 147.5.

4,4,5,5-Tetramethyl-2-[3-(1-octynylphenyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ai)

A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.92 (t, $J = 6.7$ Hz, 3H, CH$_3$CH$_2$), 1.00 (s, 6H, CH$_3$), 1.01 (s, 6H, CH$_3$), 1.34-1.71 (m, 9H, BCH and C$_2$H$_2$), 2.41 (t, $J = 6.7$ Hz, 2H, C=CCH$_2$), 2.80-3.00 (m, 5H, ArCH$_2$ and ArCH), 7.06-7.12 (m, 4H, ArH), 7.21 (d, $J = 7.7$ Hz, 2H, ArH), 7.34 (d, $J = 7.7$ Hz, 2H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 14.0, 19.4, 22.5, 24.4, 25.1, 28.6, 28.8, 31.3, 31.5, 38.9, 42.6, 80.7, 83.0, 89.6, 121.8, 125.5, 125.6, 127.5, 128.5, 128.9, 131.4, 136.3, 136.5, 146.0.

4,4,5,5-Tetramethyl-2-[3-(2-thienyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3aj)

A colorless oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.07 (s, 6H, CH$_3$), 1.09 (s, 6H, CH$_3$), 1.70 (td, $J = 11.1$, 6.1 Hz, 1H, BCH), 2.89-3.02 (m, 3H, ArCH$_2$ and ArCH), 3.14 (dd, $J = 16.4$, 5.1 Hz, 1H, ArCH$_2$), 3.38 (td, $J = 11.1$, 5.1 Hz, 1H, (thiophene)CH), 6.91-6.93 (m, 2H, ArH), 7.06-7.14 (m, 5H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.4, 24.5, 31.2, 37.7, 39.5, 83.1, 122.6, 123.4, 125.5, 125.7, 126.3, 128.5, 128.8, 136.0, 136.1, 150.3.

4,4,5,5-Tetramethyl-2-[3-((tetrahydro-2H-pyran-2-yl)oxy)methyl)-1,2,3,4-tetrahydro-naphthalen-2-yl]-[1,3,2]dioxaborolane (3ak)

S6
A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.20-1.29 (m, 2H, $CH_2$), 1.24 (s, 12H, $CH_3$), 1.52-1.85 (m, 6H, $BCH$ and $CH_2$), 2.15-2.27 (m, 1H, $CHCH_2$O), 2.62-2.68 (m, 1H, $ArCH_2$), 2.80-2.83 (m, 2H, $ArCH_2$), 2.98 (td, $J = 16.4, 5.8$ Hz, 1H, $ArCH_2$), 3.31 (dd, $J = 9.8, 7.2$ Hz, 1H, $OCH_2$), 3.49 (dd, $J = 9.7, 4.9$ Hz, 1H, $OCH_2$), 3.62 (t, $J = 9.7$ Hz, 1H, $OCH_2$), 3.81-3.89 (m, 1H, Ar$H$), 4.61 (dt, $J = 10.6, 3.8$ Hz, 1H, $OCHO$), 7.07 (brs, 4H, Ar$H$); $^{13}$C NMR (CDCl$_3$): $\delta$ 19.4, 20.8, 24.6, 24.71, 24.74, 24.8, 25.5, 30.20, 30.24, 30.3, 30.6, 30.65, 32.70, 32.9, 33.1, 33.2, 35.4, 35.5, 61.5, 61.8, 71.6, 71.9, 83.08, 83.12, 97.7, 98.25, 98.33, 99.1, 99.7, 124.5, 125.2, 125.5, 128.0, 128.1, 128.3, 128.8, 129.1, 136.5, 136.6, 137.0, 137.1.

4,4,5,5-Tetramethyl-2-(3-n-hexyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-[1,3,2]dioxaborolane (3al)

A colorless oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.89 (t, $J = 6.8$, 3H, $CH_3CH_2$), 1.13-1.51 (m, 23H, $CH_3$, $CH_2$ and $CH$), 1.83-1.92 (m, 1H, $BCH$), 2.39 (dd, $J = 16.4, 9.7$ Hz, 1H, $ArCH_2$), 2.79-2.82 (m, 2H, $ArCH_2$), 2.90 (dd, $J = 16.4, 4.8$ Hz, 1H, $ArCH_2$), 7.06 (brs, 4H, Ar$H$); $^{13}$C NMR (CDCl$_3$): $\delta$ 14.1, 22.7, 24.7, 24.8, 26.5, 29.5, 30.8, 31.8, 34.9, 35.0, 36.4, 83.0, 125.2, 125.3, 128.2, 128.9, 136.9, 137.1.

4,4,5,5-Tetramethyl-2-(3-cyclopropyl-1,2,3,4-tetrahydro-naphthalen-2-yl)-[1,3,2]dioxaborolane (3am)

A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.13-0.18 (m, 1H), 0.29-0.38 (m, 1H), 0.42-0.50 (m, 2H), 0.65-0.74 (m, 1H), 1.01-1.23 (m 1H), 1.24-1.38 (m, 1H, $BCH$), 1.29 (s, 12H, $CH_3$), 2.60 (dd, $J = 16.4, 10.6$ Hz, 1H, $ArCH_2$), 2.82 (d, 7.7 Hz, 2H, $ArCH_2$), 2.90 (dd, $J = 7.7$ Hz, 2H, $ArCH_2$), 2.90 (dd, $J = 7.7$ Hz, 2H, $ArCH_2$).
16.4, 4.8 Hz, 1H, ArCH$_2$), 7.07 (brs, 4H, ArH). $^{13}$C NMR (CDCl$_3$): δ 3.4, 5.3, 17.3, 24.8, 25.1, 31.2, 36.2, 40.9, 83.0, 125.3, 128.3, 128.9, 136.8, 136.9.

A mixture of 2-(3,4-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba) and 2-(1,3-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3’ba) (3ba:3’ba = 93:7)

A yellow solid: $^1$H NMR (CDCl$_3$): δ 0.67-0.97 (m, CH$_3$), 1.99-2.11 (m, BCH), 3.00-3.09 (m, ArCH$_2$), 3.47 (dd, J = 12.5, 4.8 Hz, PhCH), 4.07-4.27 (m, ArCHPh), 6.47 (d, J = 6.8 Hz, ArH), 6.71-7.36 (m, ArH). $^{13}$C NMR (CDCl$_3$): δ 24.08, 24.11, 24.15, 24.23, 24.3, 31.4, 32.3, 40.2, 43.9, 47.0, 51.3, 51.9, 55.0, 82.8, 82.88, 82.92, 125.6, 125.7, 125.9, 126.0, 126.1, 126.5, 126.9, 127.3, 127.71, 127.73, 128.2, 128.3, 128.4, 129.0, 129.4, 129.5, 130.3, 130.7, 130.8, 136.4, 136.8, 137.1, 139.6, 140.3, 140.4, 142.5, 143.5, 144.2, 145.4, 145.5.

A mixture of 4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3,4-tetrahydro-1,1’-binaphthyl-3-yl)-1,3,2-dioxaborolane (3ca) and 4,4,5,5-tetramethyl-2-(3-phenyl-1,2,3,4-tetrahydro-1,1’-binaphthyl-2-yl)-1,3,2-dioxaborolane (3’ca) (3ca:3’ca = 89:11)

A pale yellow oil: $^1$H NMR (CDCl$_3$): δ 0.84-0.97 (m, CH$_3$), 2.13-2.33 (m, BCH), 3.21 (d, J = 8.77 Hz, ArCH$_2$), 3.64 (dd, J = 12.6, 5.8 Hz, PhCH), 5.33 (d, J = 5.8 Hz, ArCHAr), 6.57-7.78 (m, ArH). $^{13}$C NMR (CDCl$_3$): δ 17.6, 24.0, 24.07, 24.14, 24.2, 24.26, 24.33, 24.4, 31.4, 32.3, 44.0, 44.1, 44.3, 47.3, 82.7, 82.8, 82.9, 123.5, 124.3, 124.56, 124.61, 124.63, 125.1, 125.5, 125.8, 125.9, 126.0, 126.4, 126.5, 127.0, 127.6, 127.7, 127.8, 127.9, 128.3, 128.5, 128.9, 129.5, 129.6, 130.8, 132.7, 133.2, 136.6, 139.6, 140.7, 143.0, 145.5.

A mixture of 2-(3,8-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3da) and 2-(3,5-diphenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3’da) (3da:3’da = 68:32)
A yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.92-0.94 (m, CH$_3$), 0.98-1.01 (m, CH$_3$), 1.64 (td, $J$ = 11.6, 3.8 Hz, BC$_3$H), 1.78 (td, $J$ = 10.6, 6.7 Hz, BC$_3$H), 2.71-3.18 (m, ArCH$_2$ and PhCH), 7.07-7.46 (m, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.31, 24.34, 24.4, 30.2, 32.3, 37.7, 39.7, 42.7, 43.3, 77.2, 82.88, 82.89, 125.28, 125.33, 126.1, 126.2, 126.6, 126.7, 127.3, 127.4, 127.6, 127.7, 127.8, 127.88, 127.94, 128.0, 128.1, 128.2, 128.3, 129.1, 129.2, 134.0, 134.3, 136.7, 137.2, 141.7, 141.8, 141.9, 142.1, 146.4.

A mixture of 4,4,5,5-tetramethyl-2-(3-phenyl-1,2,3,4-tetrahydrophenanthren-2-yl)-1,3,2-dioxaborolane (3ea) and 4,4,5,5-tetramethyl-2-(2-phenyl-1,2,3,4-tetrahydrophenanthren-3-yl)-1,3,2-dioxaborolane (3’ea) (3ea:3’ea = 50:50)

A yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.98-1.02 (m, CH$_3$), 1.82 (td, $J$ = 11.6, 4.8 Hz, BC$_3$H), 3.01-3.20 (m), 3.43 (dd, $J$ = 17.4, 4.8 Hz), 3.54 (dd, $J$ = 15.5, 2.9 Hz), 7.18-7.51 (m, ArH), 7.63 (d, $J$ = 3.9 Hz, ArH), 7.65 (d, $J$ = 2.9 Hz, ArH), 7.79-7.82 (m, ArH), 7.89 (d, $J$ = 7.7 Hz, ArH), 8.01 (d, $J$ = 8.7 Hz, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.37, 24.43, 24.5, 28.0, 32.6, 35.7, 40.0, 42.5, 43.0, 82.99, 83.03, 122.7, 123.0, 124.7, 125.7, 125.79, 125.82, 126.27, 126.32, 127.66, 127.71, 127.8, 128.0, 128.25, 128.33, 128.36, 128.38, 130.9, 131.2, 132.0, 132.1, 132.2, 132.3, 133.8, 134.1, 146.3, 146.6.

A mixture of anti- and syn-4,4,5,5-tetramethyl-2-(4-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (3bo) (anti:syn = 62:38)

A colorless oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.21 (s, CH$_3$), 1.22 (s, CH$_3$), 1.43-1.58 (m), 1.70-2.31 (m), 2.80-3.00 (m, ArCH$_2$), 4.05 (dd, $J$ = 11.9, 4.0 Hz, ArCHPh), 4.25 (dd, $J$ = 5.8, 2.9 Hz, ArCHPh), 6.77-7.31 (m, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.67, 24.74, 24.8, 30.6, 31.4, 33.2,
A mixture of anti- and syn-4,4,5,5-tetramethyl-2-(1-phenyl-1,2,3,4-tetrahydronaphthalen-2-yl)-1,3,2-dioxaborolane (3’bo) (anti:syn = 84:16)

A colorless oil: ¹H NMR (CDCl₃): δ 1.02-1.12 (m, CH₃), 1.58 (td, J = 10.6, 2.9 Hz, BCH), 1.79-1.87 (m, CH₂), 1.96-2.02 (m, CH₂), 2.88-2.95 (m, ArCH₂), 4.16 (d, J = 10.6 Hz, ArCHPh), 4.41 (d, J = 4.0 Hz, ArCHPh) 6.75 (d, J = 7.8 Hz, ArH), 6.93-7.27 (m, ArH);
¹³C NMR (CDCl₃): δ 14.1, 19.1, 23.0, 23.5, 24.0, 24.5, 24.6, 24.7, 25.1, 25.8, 29.6, 30.0, 37.7, 45.1, 47.3, 83.0, 83.1, 121.3, 125.4, 125.5, 125.6, 125.7, 125.86, 125.91, 127.6, 128.1, 128.8, 129.0, 129.3, 129.7, 129.9, 137.15, 137.19, 140.5, 147.0.

Aromatization of boryltetralins: a general procedure.

**Method A:** A benzene (6 mL) solution of 3 (0.10 mmol), NBS (0.50 mmol), sodium methoxide (0.30 mmol) and AIBN (5.0 µmol) was stirred at reflux temperature in the dark for the period as specified in Schemes 3 and 4. The mixture was diluted with hexane before filtration with Celite pad. Preparative recycling gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

**Method B:** A toluene (0.5 mL) solution of 3 (0.10 mmol) and DDQ (0.25 mmol) was stirred at 100 °C for the period as specified in Scheme 3. The mixture was diluted with benzene before filtration with Celite pad. Preparative recycling gel permeation chromatography (chloroform as an eluent) gave the corresponding product.

4,4,5,5-Tetramethyl-2-(3-phenyl-naphthalen-2-yl)-[1,3,2]dioxaborolane (4aa)
A yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.26 (s, 12H, $CH_3$), 7.37-7.53 (m, 7H, ArH), 7.83-7.92 (m, 3H, ArH), 8.29 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 23.7, 83.8, 125.8, 126.8, 127.1, 127.5, 127.8, 128.1, 129.3, 131.6, 134.2, 135.8, 143.1, 143.6; HRMS Calcd for C$_{22}$H$_{23}$BO$_2$: M$^+$, 330.1791. Found: m/z 330.1776.

4,4,5,5-Tetramethyl-2-[3-(1-naphthyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ab)

![Structure of 4ab](image)

A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.69 (s, 6H, $CH_3$), 0.97 (s, 6H, $CH_3$), 7.34 (t, $J = 6.8$ Hz, 1H, ArH), 7.44 (t, $J = 6.8$ Hz, 1H, ArH), 7.51-7.61 (m, 5H, ArH), 7.97 (d, $J = 7.7$ Hz, 1H, ArH), 8.37 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.0, 24.4, 83.3, 84.1, 124.9, 125.2, 125.3, 125.7, 125.8, 125.9, 126.3, 126.7, 127.0, 127.09, 127.14, 127.4, 127.7, 127.76, 127.79, 128.0, 128.2, 128.3, 128.4, 131.9, 133.2, 133.4, 134.5, 135.3, 141.5, 142.3; HRMS Calcd for C$_{26}$H$_{27}$BO$_2$: M$^+$, 380.1948. Found: m/z 380.1942.

4,4,5,5-Tetramethyl-2-[3-(biphenyl-4-yl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ac)

![Structure of 4ac](image)

A white solid: $^1$H NMR (CDCl$_3$): $\delta$ 1.28 (s, 12H, $CH_3$), 7.38 (t, $J = 8.7$ Hz, 1H, ArH), 7.47-7.70 (m, 10H, ArH), 7.85-7.92 (m, 3H, ArH), 8.31 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.6, 83.9, 125.9, 126.6, 127.10, 127.12, 127.2, 127.5, 127.8, 128.1, 128.8, 129.75, 129.83, 131.7, 134.3, 136.0, 139.6, 141.1, 142.2, 143.2; HRMS Calcd for C$_{28}$H$_{27}$BO$_2$: M$^+$, 406.2104. Found: m/z 406.2089.

4,4,5,5-Tetramethyl-2-[3-(4-n-butylphenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ad)

S11
A yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.96 (t, $J = 7.7$ Hz, 3H, CH$_3$CH$_2$), 1.26 (s, 12H, CH$_3$), 1.40 (sext, $J = 7.7$ Hz, 2H, CH$_2$), 1.66 (qunt, $J = 7.7$ Hz, 2H, CH$_2$), 2.69 (t, $J = 7.7$ Hz, 2H, ArCH$_2$), 7.23 (d, $J = 7.7$ Hz, 2H, ArH), 7.41 (d, $J = 7.7$ Hz, 2H, ArH) 7.47 (t, $J = 7.7$ Hz, 3H, ArH), 7.51 (t, $J = 6.8$ Hz, 1H, ArH), 7.82 (s, 1H, ArH), 7.83 (d, $J = 8.7$ Hz, 1H, ArH), 7.89 (d, $J = 6.8$ Hz, 1H, ArH), 8.26 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 14.0, 22.2, 24.6, 33.8, 35.3, 83.8, 127.2, 127.3, 127.8, 127.9, 128.1, 129.0, 129.2, 131.6, 134.2, 135.6, 135.7, 140.5, 141.4, 143.6; HRMS Calcd for C$_{26}$H$_{31}$BO$_2$: M$^+$, 386.2417. Found: m/z 386.2415.

4,4,5,5-Tetramethyl-2-[3-(2,5-dimethoxyphenyl)naphthalen-2-yl]-[1,3,2]dioxaborolane (4ae)

A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.23 (s, 12H, CH$_3$), 3.62 (s, 3H, OCH$_3$), 3.83 (s, 3H, OCH$_3$), 6.82-6.97 (m, 3H, ArH), 7.45-7.51 (m, 2H, ArH), 7.76 (s, 1H, ArH) 7.82 (d, $J = 7.7$ Hz, 1H, ArH), 7.89 (d, $J = 8.7$ Hz 1H, ArH), 8.39 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.7, 55.7, 56.5, 83.4, 112.6, 113.0, 116.6, 125.7, 126.3, 126.7, 127.8, 128.0, 128.1, 131.8, 133.7, 134.4, 135.0, 140.0, 151.4, 153.7; HRMS Calcd for C$_{24}$H$_{27}$BO$_4$: M$^+$, 390.2002. Found: m/z 390.2000.

4,4,5,5-Tetramethyl-2-[3-(4-trifluoromethylphenyl)naphthalen-2-yl]-[1,3,2]dioxaborolane (4af)
A yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.27 (s, 12H, CH$_3$), 7.50-7.68 (m, 6H, ArH), 7.79-7.93 (m, 3H, ArH), 8.34 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.6, 84.0, 124.5, 124.6, 126.3, 126.9, 127.4, 127.7, 127.9, 128.3, 129.1, 129.7, 130.2, 131.4, 131.9, 134.1, 136.5, 136.9, 142.4, 146.8; HRMS Calcd for C$_{23}$H$_{22}$BF$_3$O$_2$: M$,^+$, 398.1665. Found: m/z 398.1654.

$^{4,4,5,5}$-Tetramethyl-2-[3-(4-bromophenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ag)

![4,4,5,5-Tetramethyl-2-[3-(4-bromophenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane](image)

A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.27 (s, 12H, CH$_3$), 7.36 (d, $J = 8.7$ Hz, 2H, ArH), 7.47-7.57 (m, 4H, ArH), 7.77 (s, 1H, ArH), 7.83 (d, $J = 7.7$ Hz, 1H, ArH), 7.90 (d, $J = 7.7$ Hz, 1H, ArH), 8.31 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.6, 83.9, 121.0, 126.1, 127.3, 127.5, 127.8, 128.1, 130.7, 131.0, 131.8, 134.2, 136.4, 142.1, 142.5; HRMS Calcd for C$_{22}$H$_{22}$BBrO$_2$: M$,^+$, 408.0896. Found: m/z 408.0901.

$^{4,4,5,5}$-Tetramethyl-2-[3-(4-ethynylphenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4ah)

![4,4,5,5-Tetramethyl-2-[3-(4-ethynylphenyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane](image)

A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.26 (s, 12H, CH$_3$), 3.14 (s, 1H, CH), 7.45-7.55 (m, 6H, ArH), 7.79 (s, 1H, ArH), 7.84 (d, $J = 7.7$ Hz, 1H, ArH), 7.90 (d, $J = 8.7$ Hz, 1H, ArH), 8.30 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.6, 77.2, 84.0, 120.4, 126.1, 127.28, 127.31, 127.6, 127.8, 128.1, 129.4, 131.6, 131.8, 132.5, 134.2, 136.3, 142.8, 143.8; HRMS Calcd for C$_{24}$H$_{23}$BO$_2$: M$,^+$, 354.1791. Found: m/z 354.1798.

$^{4,4,5,5}$-Tetramethyl-2-[3-(2-thienyl)-naphthalen-2-yl]-[1,3,2]dioxaborolane (4aj)
A yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 1.31 (s, 12H, CH$_3$), 7.08 (t, J = 3.9 Hz, 1H, ArH-thiophene), 7.18 (d, J = 4.8 Hz, 1H, ArH-thiophene), 7.33 (d, J = 3.9 Hz, 1H, ArH-thiophene), 7.46-7.53 (m, 2H, ArH), 7.84 (dd, J = 18.3, 7.7 Hz, 2H, ArH), 7.91 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.7, 84.0, 125.1, 126.1, 126.4, 127.0, 127.2, 127.8, 128.07, 128.14, 132.0, 134.1, 135.6, 135.8, 145.0; HRMS Calcd for C$_{20}$H$_{21}$BO$_2$S: M$^+$, 336.1355. Found: m/z 336.1353.

4,4,5,5-Tetramethyl-2-(3-n-hexyl-naphthalen-2-yl)-[1,3,2]dioxaborolane (4al)

A pale yellow oil: $^1$H NMR (CDCl$_3$): $\delta$ 0.89 (t, J = 7.7 Hz, 3H, CH$_3$CH$_2$), 1.27-1.39 (m, 18H, CH$_3$ and CH$_2$), 1.61 (quint, J = 7.8 Hz, 2H, CH$_2$), 3.00 (t, J = 7.8 Hz, 2H, ArCH$_2$), 7.38 (t, J = 7.7 Hz, 1H, ArH), 7.46 (t, J = 7.7 Hz, 1H, ArH), 7.58 (s, 1H, ArH), 7.74 (d, J = 7.7 Hz, 1H, ArH), 7.83 (d, J = 7.7 Hz, 1H, ArH), 8.32 (s, 1H, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 14.1, 22.7, 24.9, 29.5, 31.9, 33.4, 36.1, 83.5, 124.8, 126.7, 126.9, 127.0, 128.2, 131.1, 134.9, 137.5, 145.6; HRMS Calcd for C$_{22}$H$_{31}$BO$_2$: M$^+$, 338.2417. Found: m/z 338.2415.

A mixture of 2-(3,4-diphenyl-naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4ba) and 2-(1,3-diphenyl-naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4’ba) (4ba:4’ba = 93:7)

A yellow solid: $^1$H NMR (CDCl$_3$): $\delta$ 1.14 (s, CH$_3$), 7.11-7.28 (m, ArH), 7.37-7.55 (m, ArH), 7.68 (d, J = 8.6 Hz, ArH), 7.94 (d, J = 7.6 Hz, ArH), 8.19 (s, ArH), 8.26 (s, ArH); $^{13}$C NMR (CDCl$_3$): $\delta$ 24.5, 24.9, 83.6, 83.8, 125.5, 125.8, 126.3, 126.7, 126.9, 127.5, 127.7, 128.2, 130.1, 130.5, 131.2, 131.9, 133.4, 134.3, 137.6, 139.1, 141.9, 142.5; HRMS Calcd for C$_{28}$H$_{27}$BO$_2$: M$^+$, 406.2104. Found: m/z 406.2107.
A mixture of 4,4,5,5-tetramethyl-2-(2-phenyl-1,1'-binaphthyl-3-yl)-1,3,2-dioxaborolane (4ca) and 4,4,5,5-tetramethyl-2-(3-phenyl-1,1'-binaphthyl-2-yl)-1,3,2-dioxaborolane (4’ca) (4ca:4’ca = 89:11)

A pale yellow oil: ¹H NMR (CDCl₃): δ 1.07-1.17 (m, C₇H₃), 6.96-7.48 (m, ArH), 7.71-7.86 (m, ArH), 7.99 (d, J = 7.8 Hz, ArH), 8.27 (s, ArH), 8.35 (s, ArH), 8.40 (d, J = 7.8 Hz, ArH); ¹³C NMR (CDCl₃): δ 24.3, 24.4, 24.5, 24.7, 83.7, 83.9, 125.0, 125.4, 125.56, 125.62, 125.8, 126.7, 126.8, 126.9, 127.0, 127.2, 127.9, 128.2, 128.3, 129.0, 131.7, 133.0, 133.4, 133.9, 134.6, 134.7, 135.6, 136.9, 142.4, 142.9; HRMS Calcd for C₃₂H₂₉BO₂: M⁺, 456.2261. Found: m/z 456.2247.

2-(3,8-Diphenylnaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4da)

A yellow oil: ¹H NMR (CDCl₃): δ 1.27 (s, 12H, C₇H₃), 7.32-7.54 (m, 12H, ArH), 7.92 (s, 1H, ArH), 7.93 (d, J = 8.7 Hz, 1H, ArH), 8.36 (s, 1H, ArH); ¹³C NMR (CDCl₃): δ 24.6, 83.8, 125.3, 125.5, 126.7, 127.2, 127.7, 128.3, 128.3, 129.3, 130.0, 132.0, 132.3, 136.3, 140.2, 140.5, 143.3, 143.8; HRMS Calcd for C₂₈H₂₇BO₂: M⁺, 406.2104. Found: m/z 406.2095.

2-(3,5-Diphenylnaphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4’da)

A yellow oil: ¹H NMR (CDCl₃): δ 1.17 (s, 12H, C₇H₃), 7.37-7.57 (m, 12H, ArH), 7.86 (d, J = 7.7 Hz, 1H, ArH), 7.89 (s, 1H, ArH), 8.32 (s, 1H, ArH); ¹³C NMR (CDCl₃): δ 24.5, 83.8, 126.5, 126.8, 127.1, 127.2, 127.6, 127.7, 127.9, 128.2, 129.2, 129.7, 130.2, 133.3, 134.6,
A mixture of 4,4,5,5-tetramethyl-2-(3-phenylphenanthren-2-yl)-1,3,2-dioxaborolane (4ea) and 4,4,5,5-tetramethyl-2-(2-phenylphenanthren-3-yl)-1,3,2-dioxaborolane (4’ea) (4ea:4’ea = 50:50)

A yellow oil: 1H NMR (CDCl₃): δ 1.27 (s, CH₃), 1.29 (s, CH₃), 7.38-7.91 (m, ArH), 8.30 (s, ArH), 8.65 (s, ArH), 8.27 (d, J = 6.7 Hz, ArH), 8.82 (d, J = 7.8 Hz, ArH), 9.09 (s, ArH); 13C NMR (CDCl₃): δ 24.6, 24.7, 83.91, 83.92, 122.90, 122.91, 126.46, 126.50, 126.7, 126.82, 126.84, 126.88, 126.89, 126.93, 127.8, 127.9, 128.16, 128.22, 128.3, 128.4, 128.5, 128.6, 129.4, 129.5, 130.0, 130.1, 130.2, 131.4, 132.0, 132.7, 133.2, 136.0, 143.0, 143.5, 144.97, 145.01; HRMS Calcd for C₂₈H₂₇BO₂: M⁺, 406.2104. Found: m/z 406.2119.

References
2 S. Pereira and M. Srebnik, Organometallics, 1995, 14, 3127.
Supplementary Material (ESI) for Chemical Communications
This journal is (c) The Royal Society of Chemistry 2010
1H

3ca + 3'ca

13C

3ca + 3'ca
PhB(pin) + PhB(pin) = 3ea + 3'ea

1H

δ / ppm

13C

δ / ppm
PhB(pin) Ph

4ba + 4'ba

1H

δ / ppm

PhB(pin) Ph

4ba + 4'ba

13C

δ / ppm
**Supplementary Material (ESI) for Chemical Communications**

This journal is (c) The Royal Society of Chemistry 2010

4ca + 4'ca

**1H**

4ca + 4'ca

**13C**
Ph
B(pin)
Ph

4ea + 4'ea

Ph
B(pin)
Ph

4ea + 4'ea