Lighting up sugars: fluorescent BODIPY-gluco-furanose and -septanose conjugates linked by direct B-O-C bonds

Bowen Liu, a Nina Novikova, a,b M. Cather Simpson, a,b Mattie S. M. Timmer, c Bridget L. Stocker, c Tilo Söhnel, a David C. Ware, a and Penelope J. Brothers* a,b

a School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland 1142, New Zealand
b School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington 6140, New Zealand
c The MacDiarmid Institute for Advanced Materials and Nanotechnology

Supporting Information

Experimental

General experimental
Syntheses

Figure S1: 1H NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl3 (400 MHz)
Figure S2: 11B NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl3 (128 MHz)
Figure S3: 13C NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl3 (75 MHz)
Figure S4: COSY NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl3
Figure S5: HSQC NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl3
Figure S6: HMBC NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl3
Figure S7: NOESY NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl3
Figure S8: 1H NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl3 (500 MHz)
Figure S9: 11B NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl3 (160 MHz)
Figure S10: 13C NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl3 (125 MHz)
Figure S11: COSY NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl3
Figure S12: HSQC NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl3
Figure S13: HMBC NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl3
Figure S14: NOESY NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl3
Figure S15: 1H NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl3 (500 MHz)
Figure S16: 11B NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl3 (160 MHz)
Figure S17: 13C NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl3 (125 MHz)
Figure S18: COSY NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl3
Figure S19: HSQC NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl3
Figure S20: HMBC NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl3
Figure S21: NOESY NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl3
Figure S22: HRMS of 1:1 α-glucofuranose BODIPY (1)
Figure S23: HRMS of 1:2 α-glucofuranose BODIPY (2)
Figure S24: HRMS of 1:2 α-glucoseptanose BODIPY (3)

Table S1. Details of collected X-ray data for compounds 1 and 3
**Experimental**

**General experimental**

BF$_3$·Et$_2$O (Aldrich) and N,N’-diisopropylethyl amine (Aldrich) were distilled prior to use. All other reagents were used as received (Aldrich, Fluka). Silica (DAVISIL® LC150A 35-70 µm) was used for flash chromatography. Brockmann Grade I basic alumina, deactivated using standard procedures to Grade V was used to purify the complexes. $^1$H, $^1$C, $^{11}$B, COSY and NOESY spectra were recorded on Bruker Avance AV 300, Bruker Avance AVIII 400 or Bruker Avance AVIII-HD 500 spectrometers at 298 K. Spectra were recorded in CDCl$_3$ and referenced to TMS or residual solvent peaks. For $^{11}$B NMR, BF$_3$·Et$_2$O was used as external reference. Accurate mass calculations were referenced to polyethyleneglycol (PEG). ESI and LDI-TOF mass spectra were recorded on Bruker microTOF-QII and Waters Micromass MALDI micro MX, respectively, mass spectrometers. HPLC was performed on a Dionex Ultimate 3000 using a Phenomenex Gemini C18 semi-preparative column (250 × 10 mm, 5 µ, 110Å), eluted at a flow rate of 5 mL/min with detection at 210, 230, 254 and 280 nm.

The UV/Vis absorption measurements were obtained using a Shimadzu UV-Vis-NIR Spectrophotometer UV-3600 Plus and the software package UVProbe 2.50. The fluorescence measurements were obtained using a Shimadzu RF10-AXL Fluorescence Detector and Shimadzu LC Solution v1.25 SP2 software. The fluorescence quantum yields were calculated using 4,4-difluoro-8-(p-tolyl)-3a,4a-diaza-s-indacene (BODIPY) as a standard ($\Phi_f = 0.051$), using the following model:

$$\Phi_x = \Phi_s (A_{std}/A_x)(F_{std}/F_x)$$

where $\Phi$ is fluorescence quantum yield, $A$ is absorption at the excitation wavelength, $F$ is the area under the curve of the emission signal, and where std represents a standard and x the unknown compound. All measurements were done using 440 nm excitation wavelength in spectroscopic grade anhydrous dichloromethane from Sigma-Aldrich used as received.

The meso-p-tolyldipyrromethane was synthesized by a modified procedure in which p-tolualdehyde was reacted with an excess of pyrrole under acidic conditions for three hours. The dipyrromethane was then converted into F-BODIPY (4,4-difluoro-8-p-tolyl-4-bora-3a,4a-diaza-s-indacene) using a modified literature procedure. Initial oxidation of the dipyrromethane with DDQ followed by treatment with BF$_3$.OEt$_2$ in the presence of DIPEA afforded F-BODIPY as a red powder after purification.

Syntheses

**Cl-BODIPY** (4,4-dichloro-8-p-tolyl-4-bora-3a,4a-diaza-s-indacene)

*F*-BODIPY (0.050 g, 0.177 mmol) was dissolved in anhydrous CH₂Cl₂ (10 mL) under N₂ atmosphere. BCl₃ (1M in CH₂Cl₂, 0.25 mL, 0.250 mmol) was added dropwise, and the reaction mixture rapidly became darker red and significantly more fluorescent under long wave UV light (365 nm). The mixture was stirred for 15 minutes, and then the solvent was removed under reduced pressure over a period of 10 minutes to result in a shiny pink solid (quantitative yield).

**¹H NMR (400 MHz, CDCl₃):** δ: 2.48 (s, 3H), 6.60 (m, J = 4.5 Hz, 2.0 Hz, 2H), 7.00 (m, J = 4.2 Hz, 1.0 Hz, 2H), 7.35 (m, J = 8.0 Hz, 2H), 7.49 (m, J = 8.0 Hz, 2H), 8.14 (br s, 2H).

**¹³C NMR (100 MHz, CDCl₃):** δ: 21.64, 119.41, 129.49, 130.56, 130.71, 132.23, 133.61, 142.05, 146.16, 147.95.

**¹¹B NMR (128 MHz, CDCl₃):** δ: 2.30 (s).

Glucose BODIPY esters (1-3)

Cl-BODIPY (0.104 g, 0.330 mmol) and anhydrous D-glucose (0.059 g, 0.330 mmol) were dissolved in anhydrous acetonitrile (5 mL) under N₂ atmosphere. The reaction mixture was stirred for 10 minutes and then quenched with saturated NaHCO₃ solution (7 mL). Brine (2 mL) was added to induce phase separation, and the red organic layer was separated and dried with anhydrous Na₂SO₄. The mixture was filtered and the solvent was removed under reduced pressure to result in a red oily solid. The crude product was dissolved in minimum CH₂Cl₂ and purified by column chromatography using Brockmann Grade V basic alumina. CH₂Cl₂:acetonitrile (50:1) was used to elute all the non-polar orange components, which consists of the decomplexed dipyrrin species, 1:2 α-glucofuranose BODIPY (2), and 1:2 α-glucoseptanose BODIPY (3). Then CH₂Cl₂:acetonitrile (50:5) was used to elute the next orange component, which consists of dihydroxy-BODIPY produced from unreacted Cl-BODIPY. Finally, acetonitrile:water (50:3) was used to elute the remaining orange component, which consists of 1:1 α-glucofuranose BODIPY (1). This was dried under reduced pressure to result in a red solid (yield 24.2%).

The first non-polar orange component that contained 1:2 α-glucofuranose BODIPY (2), and 1:2 α-glucoseptanose BODIPY (3) was dried under reduced pressure (combined yield 9.8%). It was then dissolved in minimum CH₂Cl₂ and further purified by column chromatography using silica gel. CH₂Cl₂:acetonitrile (5:1) was used to elute the first orange component, which consists of the 1:2 α-glucofuranose BODIPY (2). This was dried under reduced pressure to result in a red solid. Then CH₂Cl₂:acetonitrile (5:3) was used to elute the second orange component, which consists of 1:2 α-glucoseptanose BODIPY (3). This was dried under reduced pressure to result in a bright orange solid.
1:1 α-glucofuranose BODIPY (1)

1H NMR (400 MHz, CDCl₃) δ = 7.88 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 7.68 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 7.44 (d, Jₒ,m = 8.1 Hz, 2H, H-o), 7.30 (d, Jₒ,m = 8.1 Hz, 2H, H-m), 6.91 (dd, J = 3.0, 1.2 Hz, 1H, H-1 BODIPY), 6.90 (dd, J = 3.0, 1.2 Hz, 1H, H-1 BODIPY), 6.50 (dd, J = 4.2, 1.9, 1H, H-2 BODIPY), 6.47 (dd, J = 4.3, 1.9, 1H, H-2 BODIPY), 6.18 (d, J₁₂ = 2.7 Hz, 1H, H-1), 4.61 (d, J₁₂ = 3.5 Hz, 1H, H-2), 4.42 (d, J₃₄ = 2.8 Hz, 1H, H-3), 4.39 (dd, J₃₄ = 3.0 Hz, J₄₅ = 6.6 Hz, 1H, H-4), 4.15 (dt, J₅₆ₐ = 3.6 Hz, J₄₅ = J₆₆ᵦ = 5.9 Hz, 1H, H-5), 3.93 (dd, J₅₆ₐ = 3.3 Hz, J₆₆ᵦ = 11.4 Hz, 1H, H-6a), 3.83 (dd, J₅₆ₐ = 5.7 Hz, J₆₆ᵦ = 11.4 Hz, 1H), 3.61 (s, 1H, OH), 3.45 (s, 1H, OH), 2.77 (s, 1H, OH), 2.45 (s, 3H, CH₃-Ph).

13C NMR (75 MHz, CDCl₃) δ 147.3 (C-i Ph), 145.2, 144.1 (2 x C-3 BODIPY), 141.0 (C-p Ph), 135.5, 135.1 (2 x C-7a BODIPY), 132.1 (C-2 BODIPY), 131.3 (C-8 BODIPY), 131.2 (C-2 BODIPY), 130.7, 129.1 (2 x C-m Ph), 118.8, 118.4 (2 x C-o Ph), 105.3 (C-1), 85.0 (C-2), 80.3 (C-4), 76.2 (C-3), 70.3 (C-5), 64.5 (C-6), 21.5 (CH₃-Ph).

11B NMR (128 MHz, CDCl₃): δ: 5.54 (s).

NOEs: HMBCs:

HMBC between H-4/C-1 and H-1/C-4 proves the furanose ring.

J₁₂ = 2.7 Hz, J₂₃ = 0 Hz, J₃₄ = 2.8 Hz, J₄₅ = 6.6 Hz, J₅₆ₐ = 3.6 Hz, J₅₆ᵦ = 5.9 Hz, J₆₆ᵦ = 11.4 Hz fits α-glucofuranoside.

ESI-MS: [(M + Na)⁺]: found 445.1548, calculated 445.1547 for C₂₂H₂₁BN₂O₆Na; [(M + K)⁺]: found 461.1288, calculated 461.1286 for C₂₂H₂₁BN₂O₆K.
1:2 α-glucofuranose BODIPY (2)

\[ \text{COSY:} \]

\[ \text{HMBCs:} \]

\[ \text{COSY between 6-OH and H-6a/6b shows 6-OH not involved in boron complexation.} \]

\[ \text{HMBC between both H-1/C-4 and H-4/C-1 proves the furanose configuration.} \]
$J_{1,2} = 2.7 \text{ Hz}, J_{2,3} = 0 \text{ Hz}, J_{3,4} = 4.1 \text{ Hz}, J_{4,5} = 5.7 \text{ Hz}, J_{5,6a/6b} = 3.6/5.6, J_{6a,6b} = 10.8 \text{ Hz}$ fits with $\alpha$-glucofuranoside.

ESI-MS: [(M + H)$^+$]: found 665.2713, calculated 665.2743 for $C_{38}H_{35}B_2N_4O_6$; [(M + Na)$^+$]: found 687.2579, calculated 687.2562 for $C_{38}H_{34}B_2N_4O_6Na$.

1:2 $\alpha$-glucoseptanose BODIPY (3)

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.32 (t, $J = 1.3$ Hz, 1H, H-3 BODIPY), 8.08 (t, $J = 1.3$ Hz, 1H, H-3 BODIPY), 7.87 (t, $J = 1.3$ Hz, 1H, H-3 BODIPY), 7.73 (t, $J = 1.3$ Hz, 1H, H-3 BODIPY), 7.422 (d, $J_{o,m} = 8.0$ Hz, 2H, H-1), 7.417 (d, $J_{o,m} = 8.0$ Hz, 2H, H-1), 7.29 (d, $J_{o,m} = 7.7$ Hz, 2H, H-1), 7.28 (d, $J_{o,m} = 7.7$ Hz, 2H, H-1), 6.90 – 6.87 (m, 3H, 3 x H-1 BODIPY), 6.83 (dd, $J = 4.2, 1.1$ Hz, 1H, H-1 BODIPY), 6.51 (dd, $J = 4.3, 1.9, 1H, H-2 BODIPY), 6.49 (dd, $J = 4.3, 1.9, 1H, H-2 BODIPY), 6.48 (dd, $J = 4.3, 1.9, 1H, H-2 BODIPY), 6.43 (dd, $J = 4.2, 1.9$ Hz, 1H, H-2 BODIPY), 5.38 (d, $J = 3.2$ Hz, 1H, H-1), 4.81 (dd, $J = 4.0$ Hz, 1H, H-5), 4.79 (dd, $J = 4.0$ Hz, 1H, H-5), 4.48 (dd, $J = 4.0$ Hz, 1H, H-5), 4.47 (dd, $J = 4.0$ Hz, 1H, H-5), 4.42 (dd, $J = 4.0$ Hz, 1H, H-5), 4.41 (dd, $J = 4.0$ Hz, 1H, H-5), 4.39 (dd, $J = 4.0$ Hz, 1H, H-5), 3.78 (dd, $J = 4.0$ Hz, 1H, H-5), 3.74 (dd, $J = 4.0$ Hz, 1H, H-5).

$^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 147.6 (C-3 BODIPY), 147.2, 146.8 (2 x C-1 Ph), 145.3, 144.2, 143.6 (3 x C-3 BODIPY), 141.0, 140.9 (2 x C-2 Ph), 135.7, 135.6, 135.4, 135.1 (4 x C-7a BODIPY), 131.8 (C-2 BODIPY), 131.7, 131.6 (2 x C-8 BODIPY), 131.4, 131.1 (2 x C-2 BODIPY), 130.70, 130.67 (4 x C-8 Ph), 130.4 (C-2 BODIPY), 129.2, 129.1 (4 x C-1 Ph), 118.9, 118.4, 117.9, 117.4 (4 x C-1 BODIPY), 106.6 (C-1), 83.4 (C-2), 78.4 (C-4), 77.4 (C-3), 71.0 (C-5), 70.8 (C-6), 21.6 (2 x CH$_3$-Ph).

$^{11}$B NMR (160 MHz, CDCl$_3$) $\delta$ 5.72, 4.80.
COSY: HMBCs:

COSY between 5-OH and H-5 shows 5-OH not involved in boron complexation.
HMBC between H-6a/6b and C-1 proves oxepane ring.

\[ J_{1,2} = 3.2 \text{ Hz}, \quad J_{2,3} = 7.5 \text{ Hz}, \quad J_{3,4} = 9.3 \text{ Hz}, \quad J_{4,5} = 2.5 \text{ Hz}, \quad J_{5,6a} = 0.4 \text{ Hz}, \quad J_{5,6b} = 1.6 \text{ Hz}, \quad J_{6a,6b} = 14.0 \text{ Hz}. \]

Matches oxepane in X-ray, notably pseudo trans-diaxial H-3/H-4 with \( J_{3,4} = 9.3 \text{ Hz} \), and small couplings for 4,5,6 (all \( J < 3 \text{ Hz} \)) which have near 90° dihedral angles.

ESI-MS: \([\text{M} + \text{H}]^+\): found 665.2710, calculated 665.2743 for \( \text{C}_{38}\text{H}_{35}\text{B}_{2}\text{N}_{4}\text{O}_{6} \); \([\text{M} + \text{Na}]^+\): found 687.2579, calculated 687.2562 for \( \text{C}_{38}\text{H}_{34}\text{B}_{2}\text{N}_{4}\text{O}_{6}\text{Na} \).

**HPLC purification**

Compound 1 (1:1 glucofuranose BODIPY): 10 mg of material, which was previously purified by a conventional column as described in the experimental method, was dissolved in 3 mL AR MeCN. The solution was diluted with 12 mL of milliQ H\(_2\)O and then loaded onto the HPLC column that was pre-eluted with 20:80 MeCN:H\(_2\)O. A constant gradient of 26:74 MeCN:H\(_2\)O was used. The main peak was collected and then lyophilized overnight.

Compound 2 (1:2 glucofuranose BODIPY): 1.3 mg of material, which was previously purified by a conventional column, was dissolved in 3 mL AR MeCN. The solution was diluted with 7 mL milliQ H\(_2\)O and then loaded onto the HPLC column that was pre-eluted with 30:70 MeCN:H\(_2\)O. A 30:70 MeCN:H\(_2\)O to 90:10 MeCN:H\(_2\)O gradient was set, with a 1% increase in MeCN per minute. The main peak was collected and then lyophilized overnight.

Compound 3 (1:2 glucoseptanose BODIPY): 1 mg of material, which was previously purified by a conventional column, was dissolved in 4 mL AR MeCN. The solution was diluted with 6 mL milliQ H\(_2\)O and then loaded onto the HPLC column that was pre-eluted with 40:60 MeCN:H\(_2\)O. A 30:70 MeCN:H\(_2\)O to 90:10 MeCN:H\(_2\)O gradient was set, with a 1% increase in MeCN per minute. The main peak was collected and then lyophilized overnight.
Figure S1: $^1$H NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl$_3$ (400 MHz)
Figure S2: $^{11}$B NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl₃ (128 MHz)

Compound 1

$^{11}$B

128 MHz

CDCl₃
Figure S3: $^{13}$C NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl$_3$ (75 MHz)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{13}$C (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>142.02, 141.01</td>
</tr>
<tr>
<td>13C</td>
<td>135.54, 135.13</td>
</tr>
<tr>
<td>CDCl$_3$</td>
<td>129.12, 130.73</td>
</tr>
</tbody>
</table>
Figure S4: COSY NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl$_3$
Figure S5: HSQC NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl$_3$
Figure S6: HMBC NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl₃
**Figure S7**: NOESY NMR of 1:1 α-glucofuranose BODIPY (1) in CDCl$_3$
Figure S8: $^1$H NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl$_3$ (500 MHz)
Figure S9: $^{11}$B NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl$_3$ (160 MHz)
Figure S10: $^{13}$C NMR of 1:2 $\alpha$-glucofuranose BODIPY (2) in CDCl$_3$ (125 MHz)
Figure S11: COSY NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl₃
Figure S12: HSQC NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl₃
Figure S13: HMBC NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl₃
Figure S14: NOESY NMR of 1:2 α-glucofuranose BODIPY (2) in CDCl₃
Figure S15: $^1$H NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl$_3$ (500 MHz)
Figure S16: $^{11}$B NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl$_3$ (160 MHz)
Figure S17: $^{13}$C NMR of 1:2 α-glucosanose BODIPY (3) in CDCl$_3$ (125 MHz)
Figure S18: COSY NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl₃
Figure S19: HSQC NMR of 1:2 α-glucosptanose BODIPY (3) in CDCl₃
Figure S20: HMBC NMR of 1:2 α-glucoseptanose BODIPY (3) in CDCl₃
Figure S21: NOESY NMR of 1:2 α-glucosptanose BODIPY (3) in CDCl$_3$
Figure S22: HRMS of 1:1 α-glucofuranose BODIPY (1)
Figure S23: HRMS of 1:2 α-glucofuranose BODIPY (2)
### Auckland Uni Mass Spectrum SmartFormula Report

**Analysis Info**
- **Analyst Name**: C. Wrick
- **Sample Name**: AUU XZ02_022
- **Comment**: Sample dissolved in 0.6 mL DCM
- **Acquisition Date**: 5/11/2014 12:18:05 PM
- **Instrument**: Orbitrap Q-TOF
- **Operator**: Tony

**Acquisition Parameters**
- **Source Type**: ESI
- **Ion Polarity**: Positive
- **Scan Type**: Mono伊斯
- **Scan Range**: 2000 m/z
- **Source Temp**: 350 °C
- **CapHeight**: -400 V
- **Capillary Voltage**: 3.5 kV
- **HPR**: 0.6 Bar

### Mass List

<table>
<thead>
<tr>
<th>Meas. m/z</th>
<th>m/z</th>
<th>err (ppm)</th>
<th>m/z/leu</th>
<th>leu</th>
<th>_Sigma</th>
<th>Score</th>
<th>nbb</th>
<th>_Conf</th>
<th>N-Meta</th>
<th>N-Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>687.2870</td>
<td>687.2863</td>
<td>2.1</td>
<td>334.3</td>
<td>1</td>
<td>100.00</td>
<td>42.0</td>
<td>0.00</td>
<td>uk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>C2H13O8NiH2O2</td>
<td>687.2863</td>
<td>2.1</td>
<td>334.3</td>
<td>1</td>
<td>100.00</td>
<td>42.0</td>
<td>0.00</td>
<td>uk</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>C2H13O8NiH2O2</td>
<td>687.2858</td>
<td>3.3</td>
<td>22.7</td>
<td>1</td>
<td>100.00</td>
<td>56.0</td>
<td>even</td>
<td>uk</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C2H13O8NiH2O2</td>
<td>687.2525</td>
<td>-4.4</td>
<td>140.6</td>
<td>2</td>
<td>0.50</td>
<td>25.0</td>
<td>0.00</td>
<td>uk</td>
<td></td>
</tr>
</tbody>
</table>

![Mass Spectrum Diagram](image)
Figure S24: HRMS of 1:2 α-glucoseptanose BODIPY (3)
Table S1. Details of collected X-ray data for compounds 1 and 3

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{44}H_{46}B_{2}N_{4}O_{7}</td>
<td>C_{38}H_{34}B_{2}N_{4}O_{6}</td>
</tr>
<tr>
<td>Molecular weight (g mol⁻¹)</td>
<td>924.47</td>
<td>664.31</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>100(2)</td>
<td>100(1)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>0.71073</td>
<td>1.54184</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2</td>
<td>P2₁2₁2₁</td>
</tr>
<tr>
<td>a (Å)</td>
<td>37.5988(15)</td>
<td>11.3239(5)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.8713(6)</td>
<td>12.8880(7)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.2281(3)</td>
<td>25.7528(11)</td>
</tr>
<tr>
<td>β (°)</td>
<td>93.381(3)</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>4592.7(3)</td>
<td>3758.4(3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Calculated density (g cm⁻³)</td>
<td>1.337</td>
<td>1.174</td>
</tr>
<tr>
<td>Absorption coefficient (mm⁻¹)</td>
<td>0.103</td>
<td>0.643</td>
</tr>
<tr>
<td>F(000)</td>
<td>1936</td>
<td>1392</td>
</tr>
<tr>
<td>Crystal size (mm × mm × mm)</td>
<td>0.25 × 0.15 × 0.10</td>
<td>0.018 x 0.023 x 0.337</td>
</tr>
<tr>
<td>20 (min, max) (°)</td>
<td>1.085, 19.70</td>
<td>3.835, 66.59</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-35 ≤ h ≤ 35, -14 ≤ k ≤ 14, -7 ≤ l ≤ 7,</td>
<td>-35 ≤ h ≤ 10, -14 ≤ k ≤ 15, -21 ≤ l ≤ 31,</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>23480 / 4060 [R(int) = 0.0461]</td>
<td>9143 / 5540 [R(int) = 0.0412]</td>
</tr>
<tr>
<td>Completeness to theta max</td>
<td>99.6 %</td>
<td>99.3 %</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4060 / 267 / 596</td>
<td>5540/0/454</td>
</tr>
<tr>
<td>Goodness-of-fit on F² a)</td>
<td>1.081</td>
<td>0.998</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)] b)</td>
<td>R₁ = 0.0871, wR₂ = 0.2318</td>
<td>R₁ = 0.0482, wR₂ = 0.1290</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁ = 0.0920, wR₂ = 0.2389</td>
<td>R₁ = 0.0534, wR₂ = 0.1326</td>
</tr>
<tr>
<td>Largest diff. peak and hole (eÅ⁻³)</td>
<td>0.707 and -0.440</td>
<td>0.249 and -0.265</td>
</tr>
</tbody>
</table>

a) GOF = (Σ[w(F_o² - F_c²)²]/(n - p))¹/², where n is the number of reflections and p is the total number of parameters refined. b) R₁ = Σ|F_o| - |F_c|/Σ|F_o|. wR₂ = (Σ[w(F_o² - F_c²)²]/Σ[w(F_o²)])¹/².