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

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Supporting Information

Experimental

General experimental

$BF_3 \cdot Et_2O$ (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, ^{13}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, $BF_3 \cdot Et_2O$ 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 ($\Phi_f = 0.051$),[1] using the following model:

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

where Φ 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[2] 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.[3] 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.

1. Cui, A;. Peng, X.; Fan, J.; Chen, X.; Wu, Y.; Guo, B. *J. Photochem. Photobiol. A* **2007**, *186*, 85-92.
2. Rohand, T.; Dolusic, E.; Ngo, T.; Maes, W.; Dehaen, W. *Arkivoc* **2007,** 307–324.
3. Groves, B. R.; Crawford, S. M.; Lundrigan, T.; Matta, C. F.; Sowlati-Hashjin, S.; Thompson, A. *Chem. Commun.* **2012**, *49*, 816–818.

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 CH_2Cl_2 (10 mL) under N_2 atmosphere. BCl_3 (1M in CH_2Cl_2, 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).

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ: 21.64, 119.41, 129.49, 130.56, 130.71, 132.23, 133.61, 142.05, 146.16, 147.95.

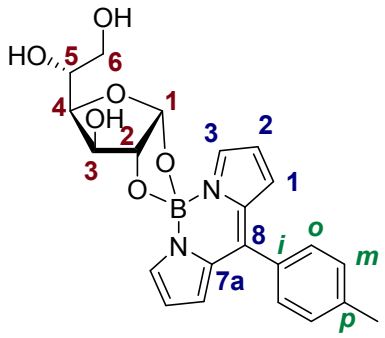
^{11}B NMR (128 MHz, $CDCl_3$): δ: 2.30 (s).

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 N_2 atmosphere. The reaction mixture was stirred for 10 minutes and then quenched with saturated $NaHCO_3$ solution (7 mL). Brine (2 mL) was added to induce phase separation, and the red organic layer was separated and dried with anhydrous Na_2SO_4. 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 CH_2Cl_2 and purified by column chromatography using Brockmann Grade V basic alumina. CH_2Cl_2: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 CH_2Cl_2: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 CH_2Cl_2 and further purified by column chromatography using silica gel. CH_2Cl_2: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 CH_2Cl_2: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)

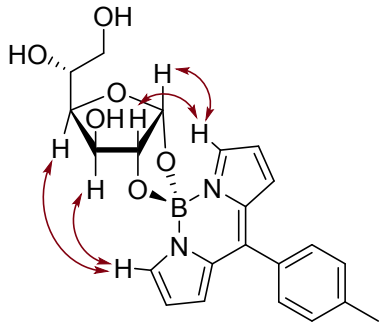


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 7.68 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 7.44 (d, $J_{o,m}$ = 8.1 Hz, 2H, H-*o*), 7.30 (d, $J_{o,m}$ = 8.1 Hz, 2H, H-*m*), 6.91 (dd, J = 3.0, 1.2 Hz, 1H, H-1 BODIPY), 6.90 (dd, J = 3.0, 1.2 Hz, 1H, H-1 BODIPY), 6.50 (dd, J = 4.2, 1.9, 1H, H-2 BODIPY), 6.47 (dd, J = 4.3, 1.9, 1H, H-2 BODIPY), 6.18 (d, $J_{1,2}$ = 2.7 Hz, 1H, H-1), 4.61 (d, $J_{1,2}$ = 3.5 Hz, 1H, H-2), 4.42 (d, $J_{3,4}$ = 2.8 Hz, 1H, H-3), 4.39 (dd, $J_{3,4}$ = 3.0 Hz, $J_{4,5}$ = 6.6 Hz, 1H, H-4), 4.15 (dt, $J_{5,6a}$ = 3.6 Hz, $J_{4,5}$ = $J_{5,6b}$ = 5.9 Hz, 1H, H-5), 3.93 (dd, $J_{5,6a}$ = 3.3 Hz, $J_{6a,6b}$ = 11.4 Hz, 1H, H-6a), 3.83 (dd, $J_{5,6b}$ = 5.7 Hz, $J_{6a,6b}$ = 11.4 Hz, 1H), 3.61 (s, 1H, OH), 3.45 (s, 1H, OH), 2.77 (s, 1H, OH), 2.45 (s, 3H, CH_3-Ph).

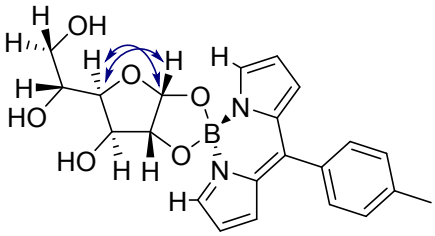
^{13}C NMR (75 MHz, $CDCl_3$) δ 147.3 (C-*i* Ph), 145.2, 144.1 (2 x C-3 BODIPY), 141.0 (C-*p* Ph), 135.5, 135.1 (2 x C-7a BODIPY), 132.1 (C-2 BODIPY), 131.3 (C-8 BODIPY), 131.2 (C-2 BODIPY), 130.7, 129.1 (2 x C-*m* Ph), 118.8, 118.4 (2 x C-*o* Ph), 105.3 (C-1), 85.0 (C-2), 80.3 (C-4), 76.2 (C-3), 70.3 (C-5), 64.5 (C-6), 21.5 (CH_3-Ph).

^{11}B NMR (128 MHz, $CDCl_3$): δ: 5.54 (s).

NOEs:



HMBCs:

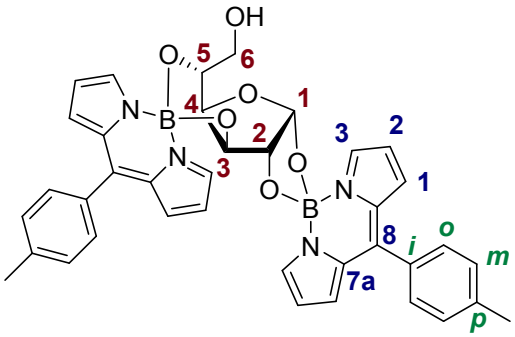


HMBC between H-4/C-1 and H-1/C-4 proves the furanose ring.

$J_{1,2}$ = 2.7 Hz, $J_{2,3}$ = 0 Hz, $J_{3,4}$ = 2.8 Hz, $J_{4,5}$ = 6.6 Hz, $J_{5,6a}$ = 3.6 Hz, $J_{5,6b}$ = 5.9 Hz, $J_{6a,6b}$ = 11.4 Hz fits α-glucofuranoside.

ESI-MS: [(M + Na)$^+$]: found 445.1548, calculated 445.1547 for $C_{22}H_{23}BN_2O_6Na$; [(M + K)$^+$]: found 461.1288, calculated 461.1286 for $C_{22}H_{23}BN_2O_6K$.

1:2 α-glucofuranose BODIPY (2)

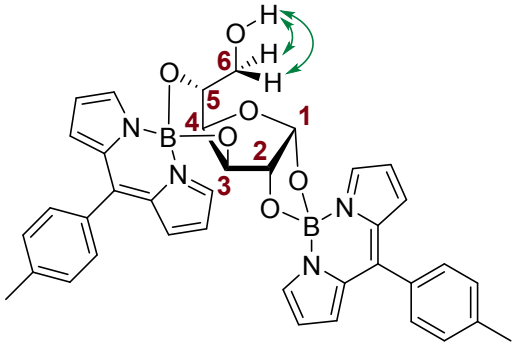


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 8.03 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 7.80 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 7.66 (t, J = 1.3 Hz, 1H, H-3 BODIPY), 7.47 (d, $J_{o,m}$ = 8.3 Hz, 2H, H-*o*), 7.45 (d, $J_{o,m}$ = 8.3 Hz, 2H, H-*o*), 7.311 (d, $J_{o,m}$ = 7.7 Hz, 2H, H-*m*), 7.310 (d, $J_{o,m}$ = 7.7 Hz, 2H, H-*m*), 6.94 (dd, J = 4.3, 1.2 Hz, 1H, H-1 BODIPY), 6.923 (dd, J = 4.1, 1.4 Hz, 1H, H-1 BODIPY), 6.918 (dd, J = 4.0, 1.4 Hz, 1H, H-1 BODIPY), 6.89 (dd, J = 4.2, 1.2 Hz, 1H, H-1 BODIPY), 6.55 (dd, J = 4.2, 1.9 Hz, 1H, H-2 BODIPY), 6.52 (dd, J = 4.3, 1.8 Hz, 1H, H-2 BODIPY), 6.47 (dd, J = 4.3, 2.0 Hz, 1H, H-2 BODIPY), 6.45 (dd, J = 4.2, 2.0 Hz, 1H, H-2 BODIPY), 6.31 (d, $J_{1,2}$ = 2.7 Hz, 1H, H-1), 4.77 (dd, $J_{3,4}$ = 4.1, $J_{4,5}$ = 5.7 Hz, 1H, H-4), 4.74 (d, $J_{1,2}$ = 3.3 Hz, 1H, H-2), 4.54 (d, $J_{3,4}$ = 4.0 Hz, 1H, H-3), 4.11 (ddd, $J_{4,5}$ = 5.6, J = 3.6, J = 5.6 Hz, 1H, H-5), 3.96 (bd, $J_{6a,6b}$ = 10.8 Hz, 1H, H-6a), 3.89 – 3.79 (bm, 1H, H-6b), 2.47 (s, 6H, 2 x CH_3Ph), 2.29 (s, 1H, 6-OH).

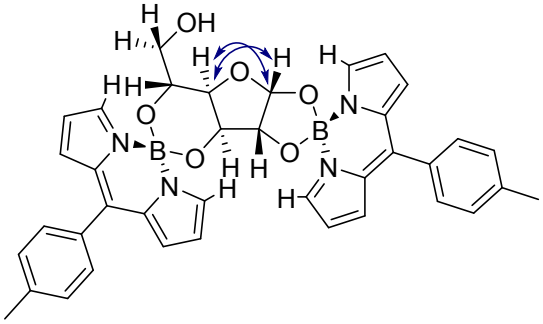
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 147.3 (2 x C-*i* Ph), 145.5, 144.9, 143.8, 143.7 (4 x C-3 BODIPY), 141.2, 141.0 (2 x C-*p* Ph), 135.7, 135.4, 135.3, 135.2 (4 x C-7a BODIPY), 132.0 (C-2 BODIPY), 131.6, 131.5 (2 x C-8 BODIPY), 131.4, 131.2, 131.1 (3 x C-2 BODIPY), 130.8, 130.7 (4 x C-*o* Ph), 129.22, 129.16 (4 x C-*m* Ph), 118.6, 118.2, 117.8 (4 x C-1 BODIPY), 106.2 (C-1), 85.9 (C-2), 80.1 (C-4), 76.5 (C-3), 72.5 (C-5), 65.9 (C-6), 21.6 (2 x CH_3-Ph).

^{11}B NMR (160 MHz, $CDCl_3$) δ 5.67, 1.25.

COSY:



HMBCs:



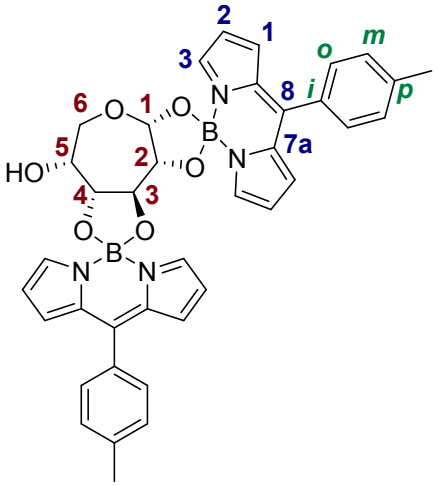
COSY between 6-OH and H-6a/6b shows 6-OH not involved in boron complexation.

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

$J_{1,2}$ = 2.7 Hz, $J_{2,3}$ = 0 Hz, $J_{3,4}$ = 4.1 Hz, $J_{4,5}$ = 5.7 Hz, $J_{5,6a/6b}$ = 3.6/5.6, $J_{6a,6b}$ = 10.8 Hz fits with α-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 α-glucoseptanose BODIPY (3)

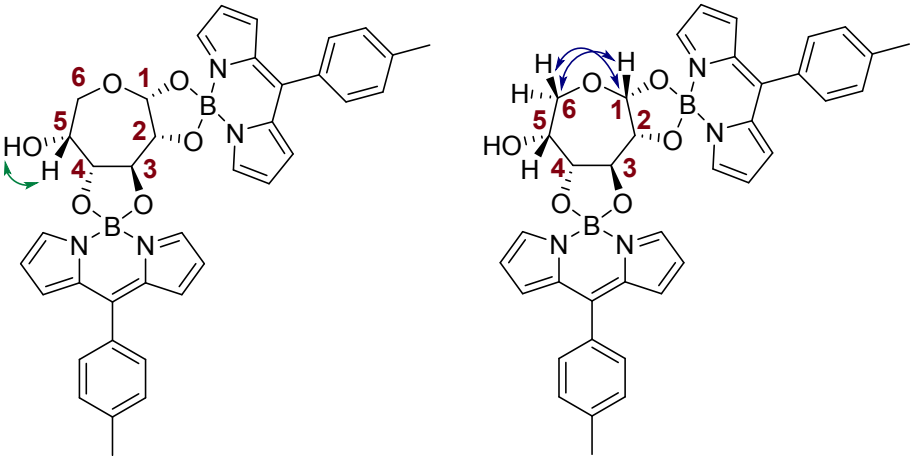


^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (t, *J* = 1.3 Hz, 1H, H-3 BODIPY), 8.08 (t, *J* = 1.3 Hz, 1H, H-3 BODIPY), 7.87 (t, *J* = 1.3 Hz, 1H, H-3 BODIPY), 7.73 (t, *J* = 1.3 Hz, 1H, H-3 BODIPY), 7.422 (d, $J_{o,m}$ = 8.0 Hz, 2H, H-*o*), 7.417 (d, $J_{o,m}$ = 8.0 Hz, 2H, H-*o*), 7.29 (d, $J_{o,m}$ = 7.7 Hz, 2H, H-*m*), 7.28 (d, $J_{o,m}$ = 7.7 Hz, 2H, H-*m*), 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, $J_{2,3}$ = 7.5 Hz, $J_{3,4}$ = 9.3, 1H, H-3), 4.48 (dd, $J_{1,2}$ = 4.0 Hz, $J_{2,3}$ = 7.4, 1H, H-2), 4.42 (dd, $J_{5,6a}$ = 0.4 Hz, $J_{6a,6b}$ = 13.7 Hz, 1H, H-6a), 4.20 – 4.17 (m, 1H, H-5), 4.17 (dd, $J_{4,5}$ = 2.5 Hz, $J_{3,4}$ = 9.3, 1H, H-4), 3.78 (dd, $J_{5,6b}$ = 1.6 Hz, $J_{6a,6b}$ = 14.1, 1H, H-6b), 2.67 (s, 1H, 5-OH), 2.45 (s, 3H, CH_3-Ph), 2.45 (s, 3H, CH_3-Ph).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6 (C-3 BODIPY), 147.2, 146.8 (2 x C-*i* Ph), 145.3, 144.2, 143.6 (3 x C-3 BODIPY), 141.0, 140.9 (2 x C-*p* 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-*o* Ph), 130.4 (C-2 BODIPY), 129.2, 129.1 (4 x C-*m* 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, $CDCl_3$) δ 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 Hz, $J_{2,3}$ = 7.5 Hz, $J_{3,4}$ = 9.3 Hz, $J_{4,5}$ = 2.5 Hz, $J_{5,6a}$ = 0.4 Hz, $J_{5,6b}$ = 1.6 Hz, $J_{6a,6b}$ = 14.0 Hz. Matches oxepane in X-ray, notably pseudo trans-diaxial H-3/H-4 with $J_{3,4}$ = 9.3 Hz, and small couplings for 4,5,6 (all J < 3 Hz) which have near 90° dihedral angles.

ESI-MS: [(M + H)$^+$]: found 665.2710, calculated 665.2743 for $C_{38}H_{35}B_2N_4O_6$; [(M + Na)$^+$]: found 687.2579, calculated 687.2562 for $C_{38}H_{34}B_2N_4O_6Na$.

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_2O and then loaded onto the HPLC column that was pre-eluted with 20:80 MeCN:H_2O. A constant gradient of 26:74 MeCN:H_2O 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_2O and then loaded onto the HPLC column that was pre-eluted with 30:70 MeCN:H_2O. A 30:70 MeCN:H_2O to 90:10 MeCN:H_2O 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_2O and then loaded onto the HPLC column that was pre-eluted with 40:60 MeCN:H_2O. A 30:70 MeCN:H_2O to 90:10 MeCN:H_2O 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)

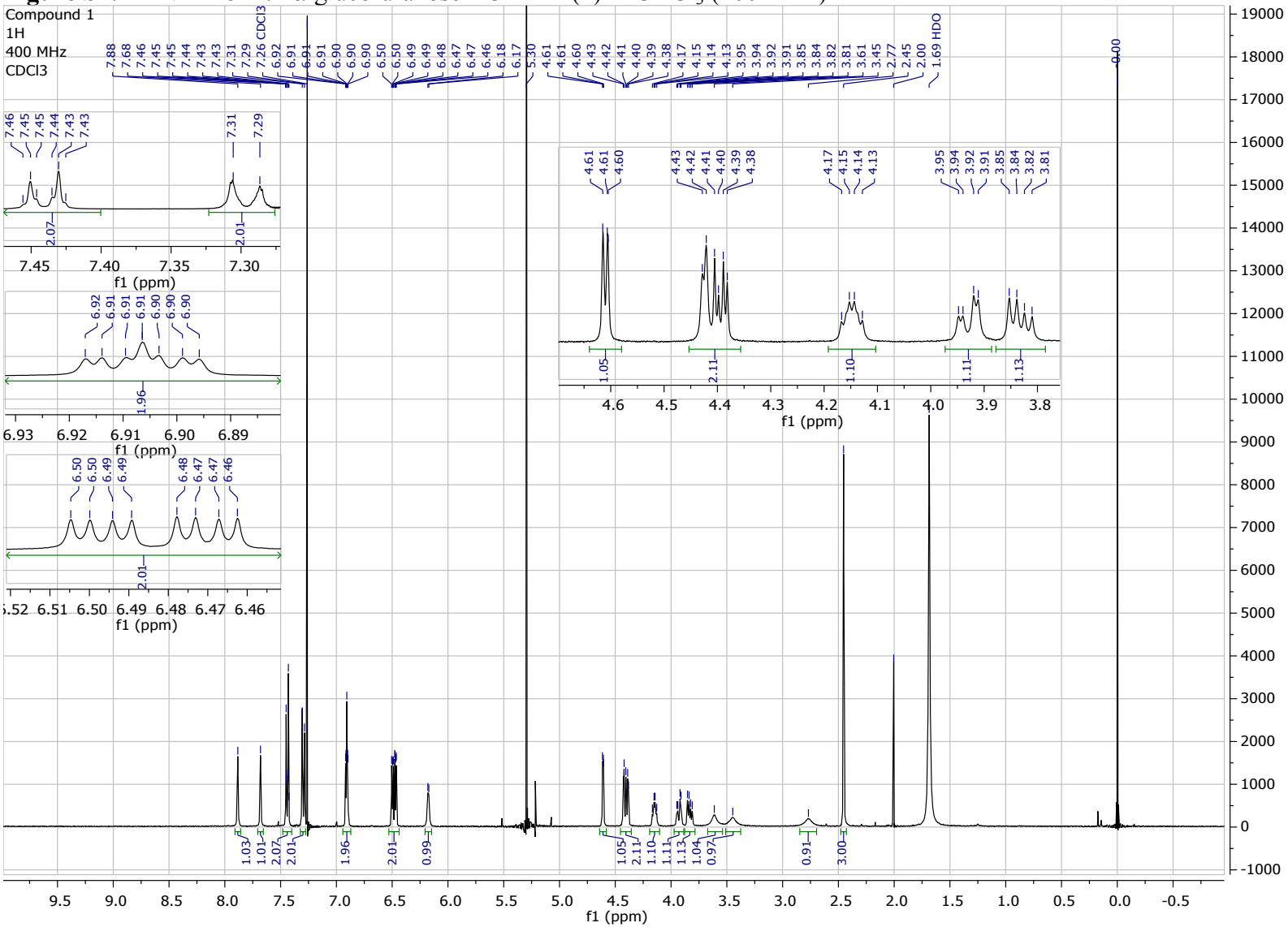


Figure S2: ^{11}B NMR of 1:1 α-glucofuranose BODIPY (**1**) in $CDCl_3$ (128 MHz)

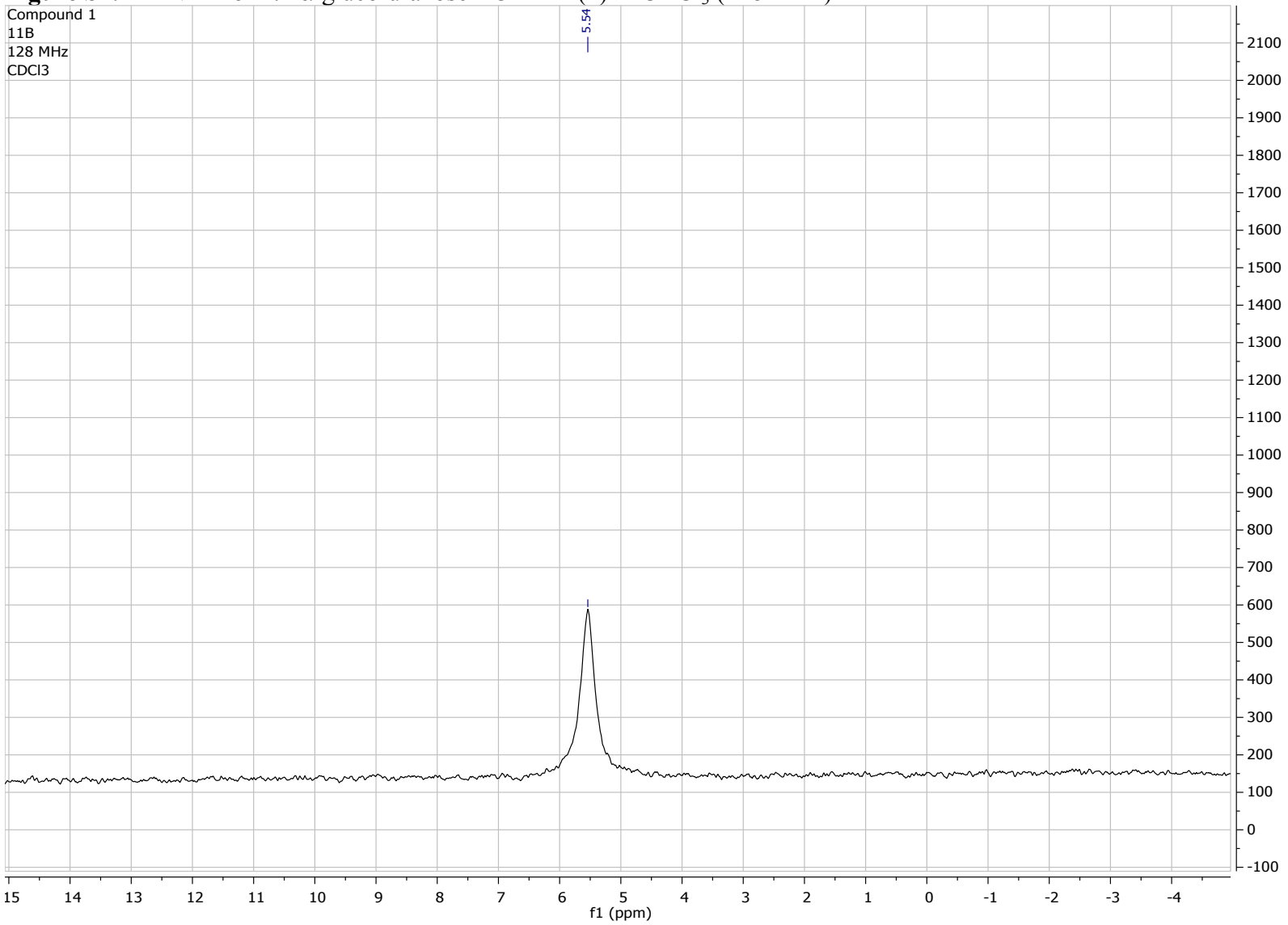


Figure S3: ^{13}C NMR of 1:1 α-glucofuranose BODIPY (**1**) in $CDCl_3$ (75 MHz)

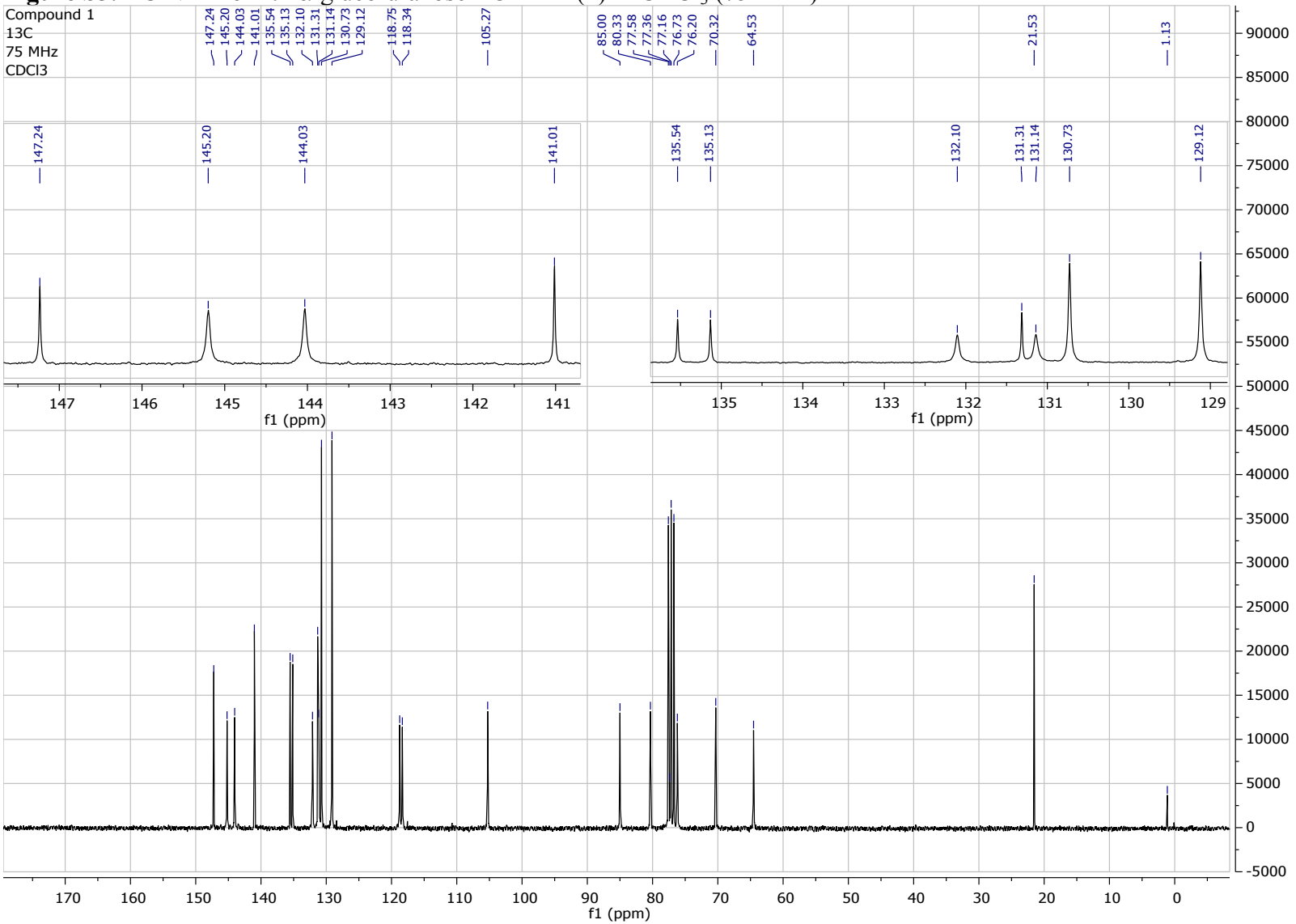


Figure S4: COSY NMR of 1:1 α-glucofuranose BODIPY (**1**) in $CDCl_3$

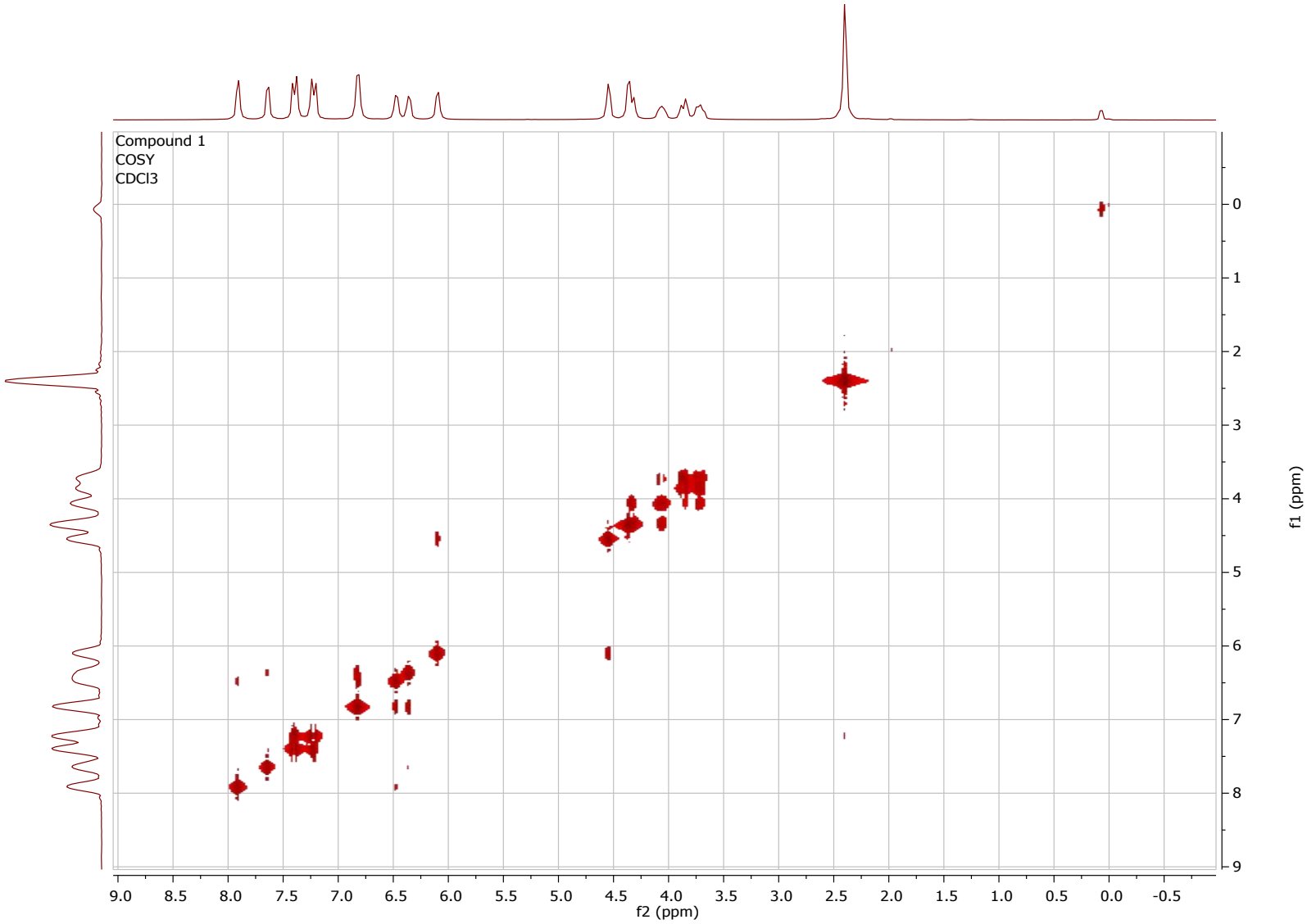


Figure S5: HSQC NMR of 1:1 α-glucofuranose BODIPY (**1**) in $CDCl_3$

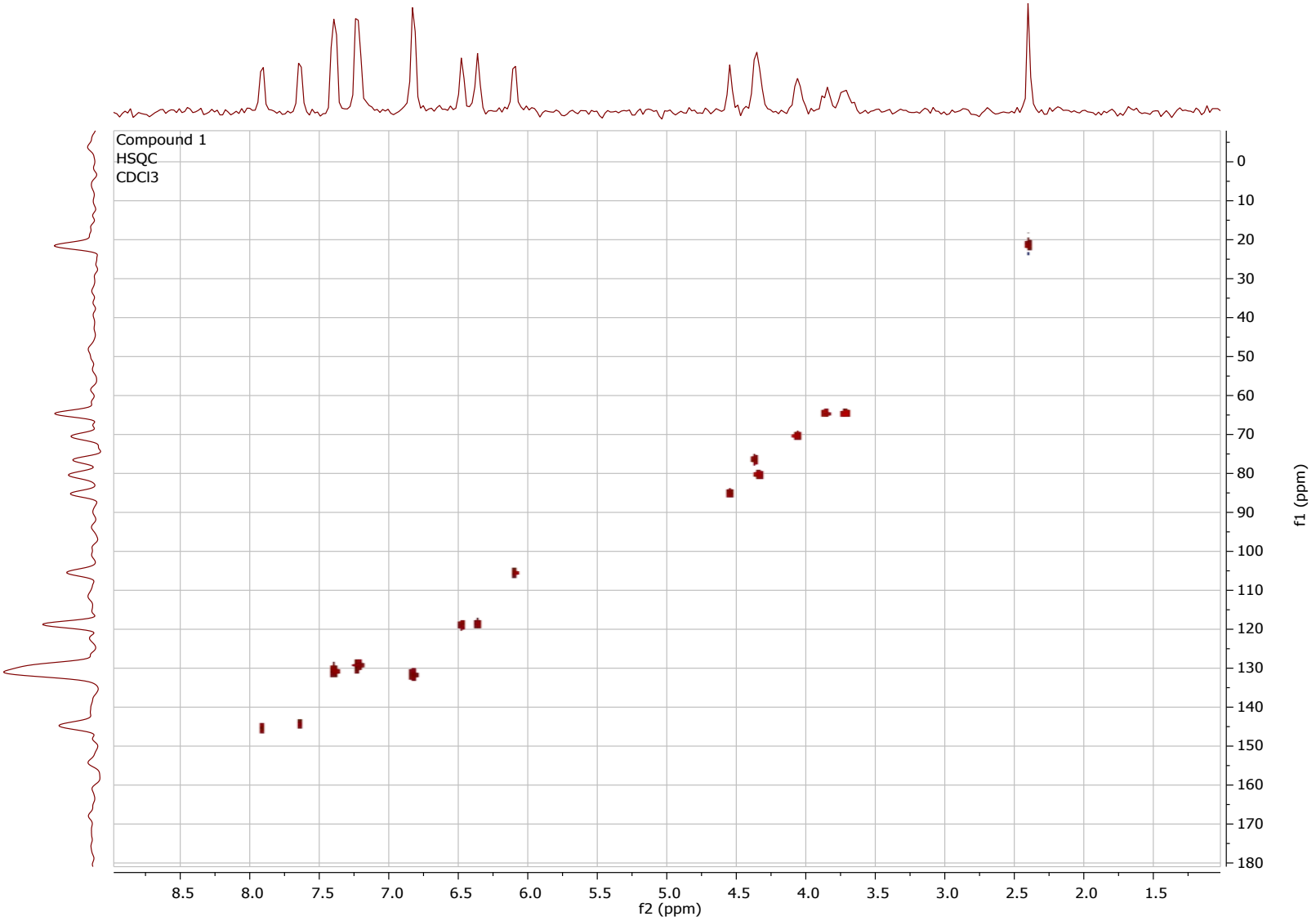


Figure S6: HMBC NMR of 1:1 α-glucofuranose BODIPY (**1**) in $CDCl_3$

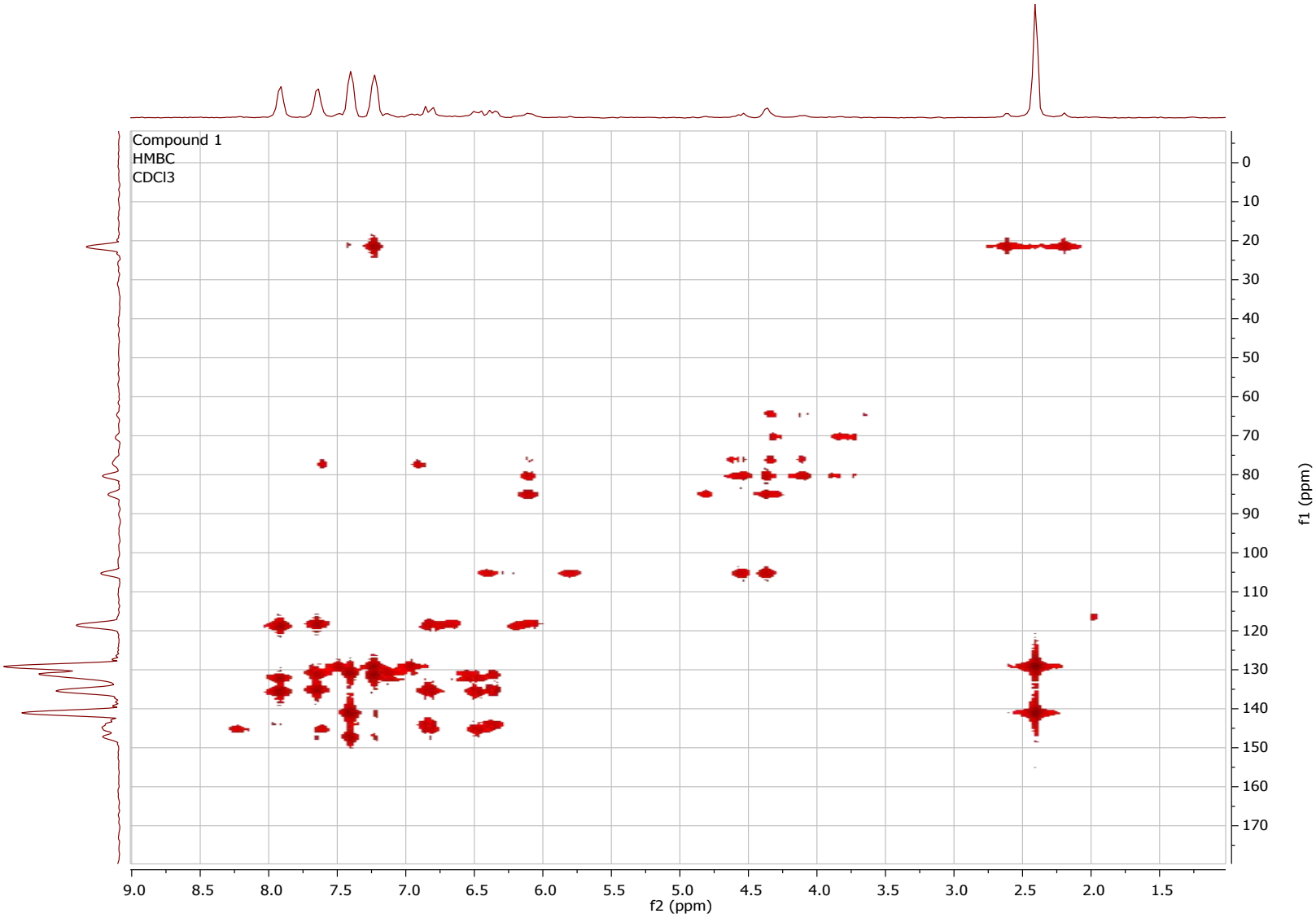


Figure S7: NOESY NMR of 1:1 α-glucofuranose BODIPY (**1**) in $CDCl_3$

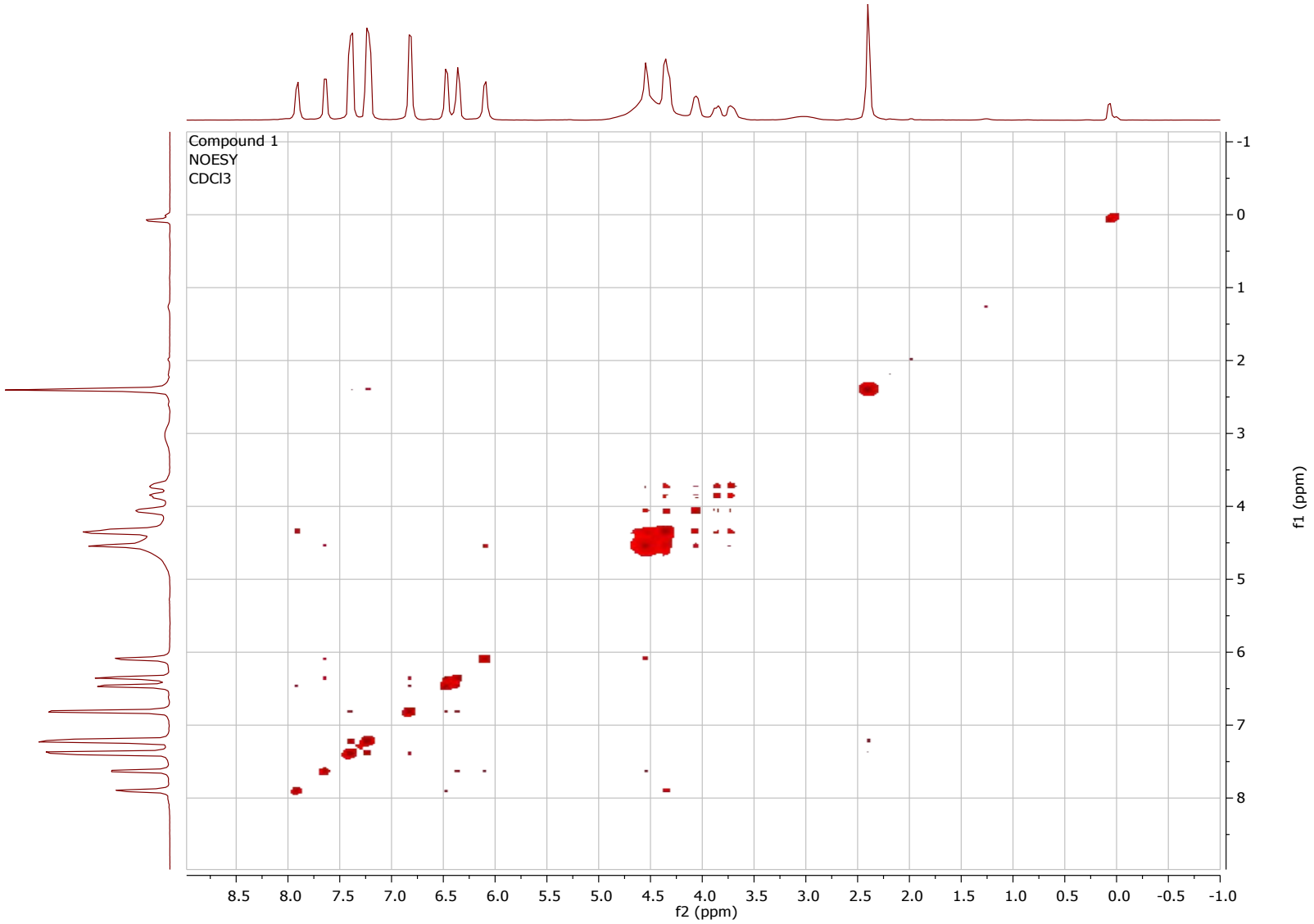


Figure S8: ^{1}H NMR of 1:2 α-glucofuranose BODIPY (**2**) in $CDCl_3$ (500 MHz)

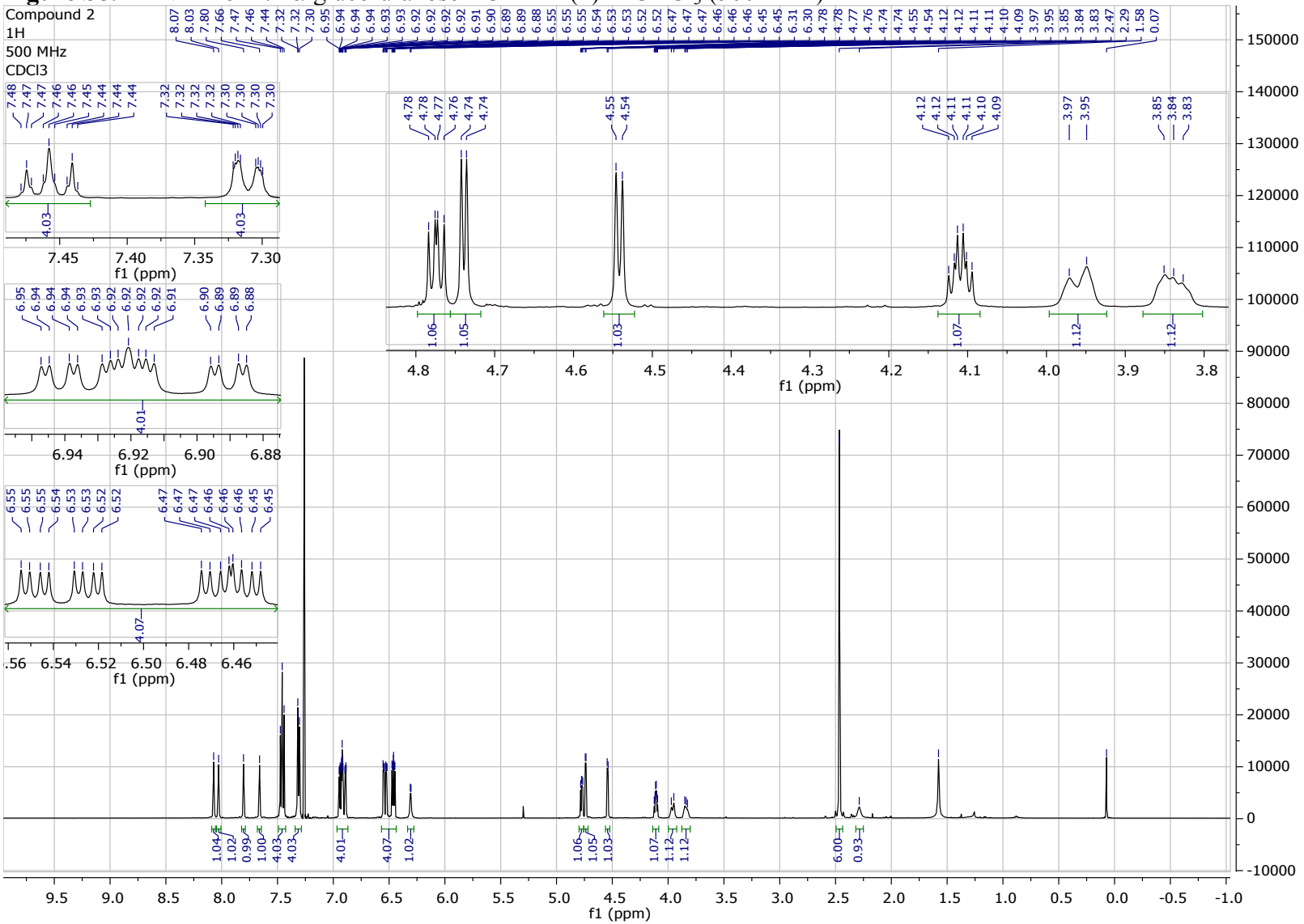


Figure S9: ^{11}B NMR of 1:2 α-glucofuranose BODIPY (**2**) in $CDCl_3$ (160 MHz)

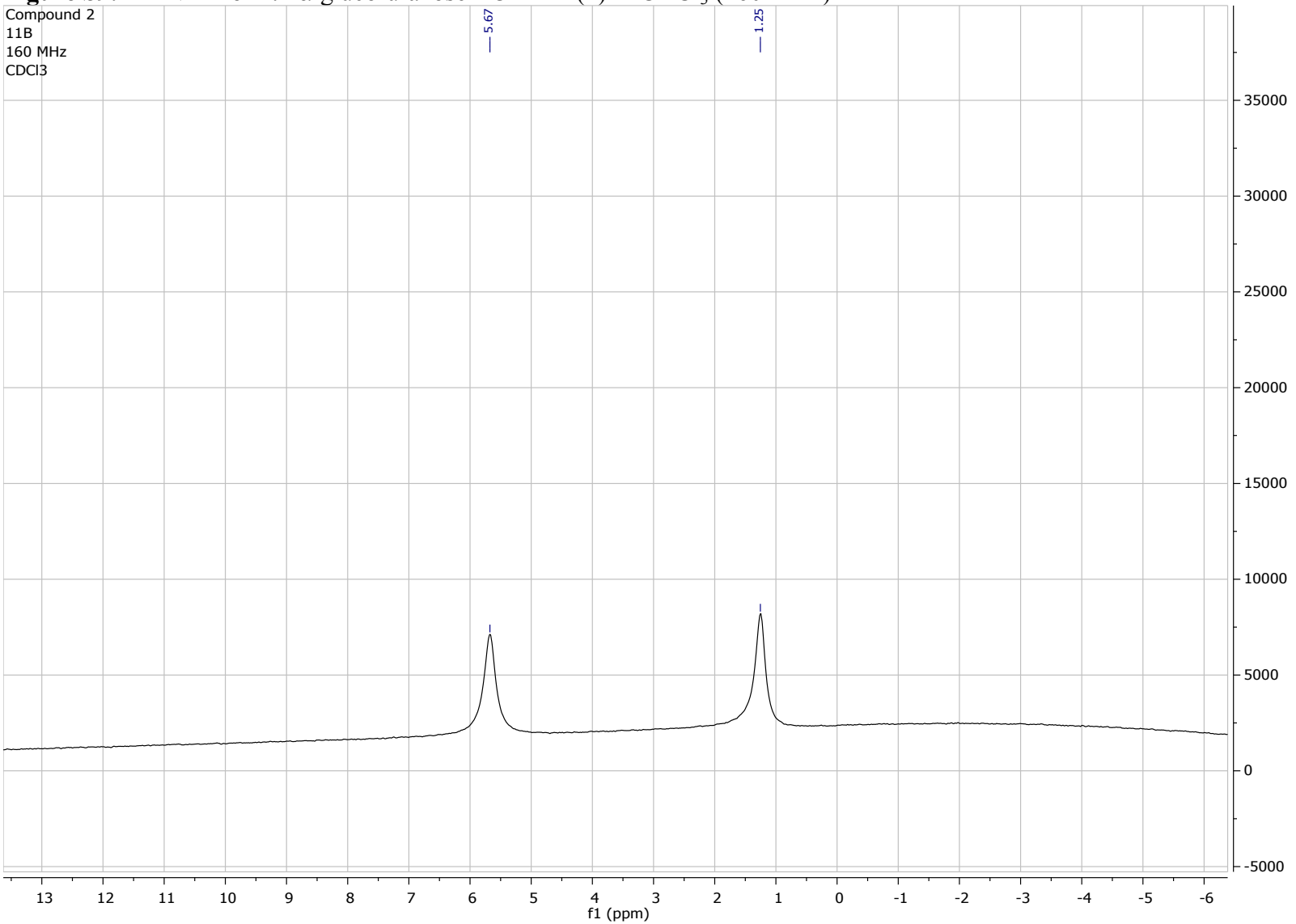


Figure S10: ^{13}C NMR of 1:2 α-glucofuranose BODIPY (**2**) in $CDCl_3$ (125 MHz)

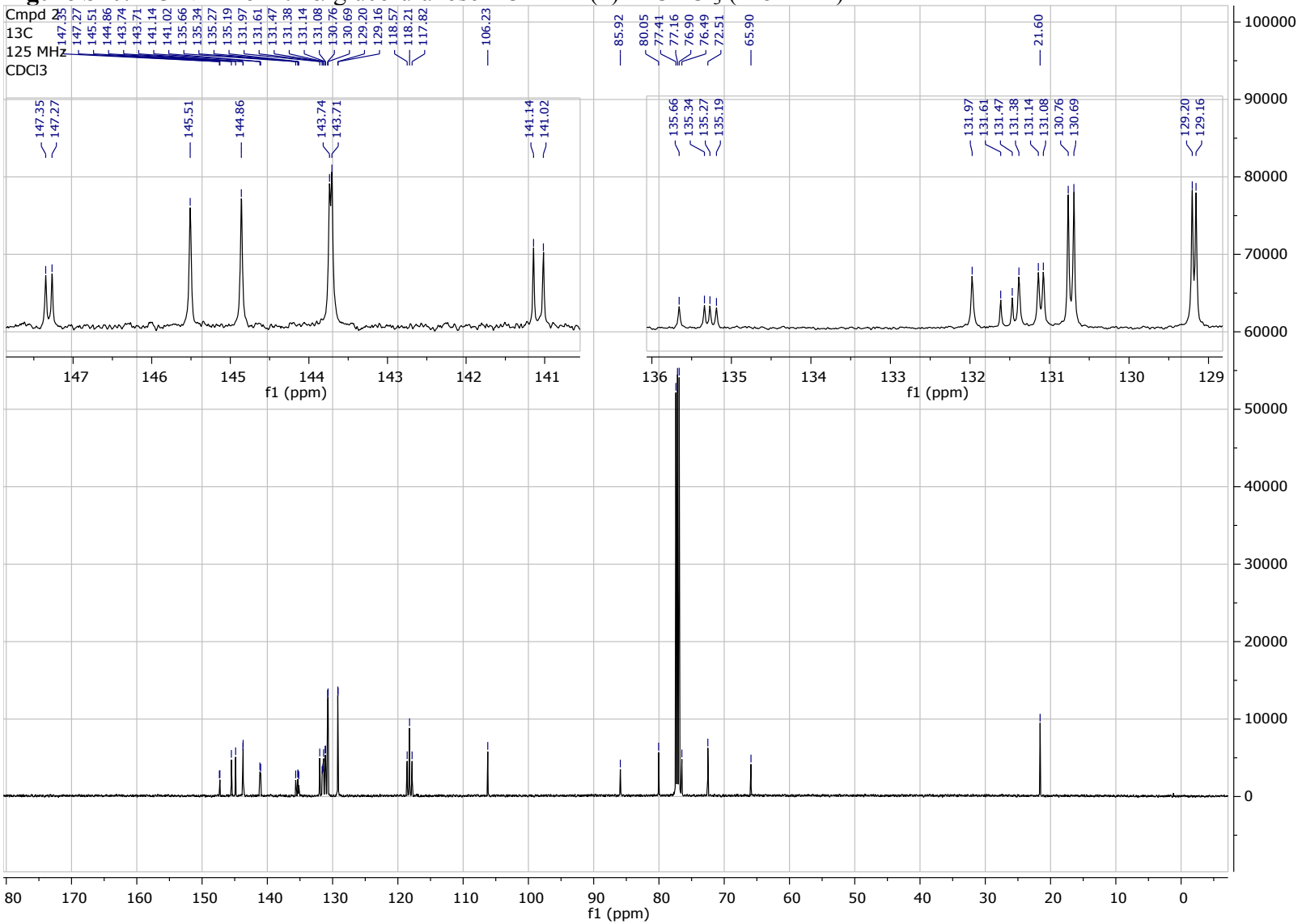


Figure S11: COSY NMR of 1:2 α-glucofuranose BODIPY (**2**) in $CDCl_3$

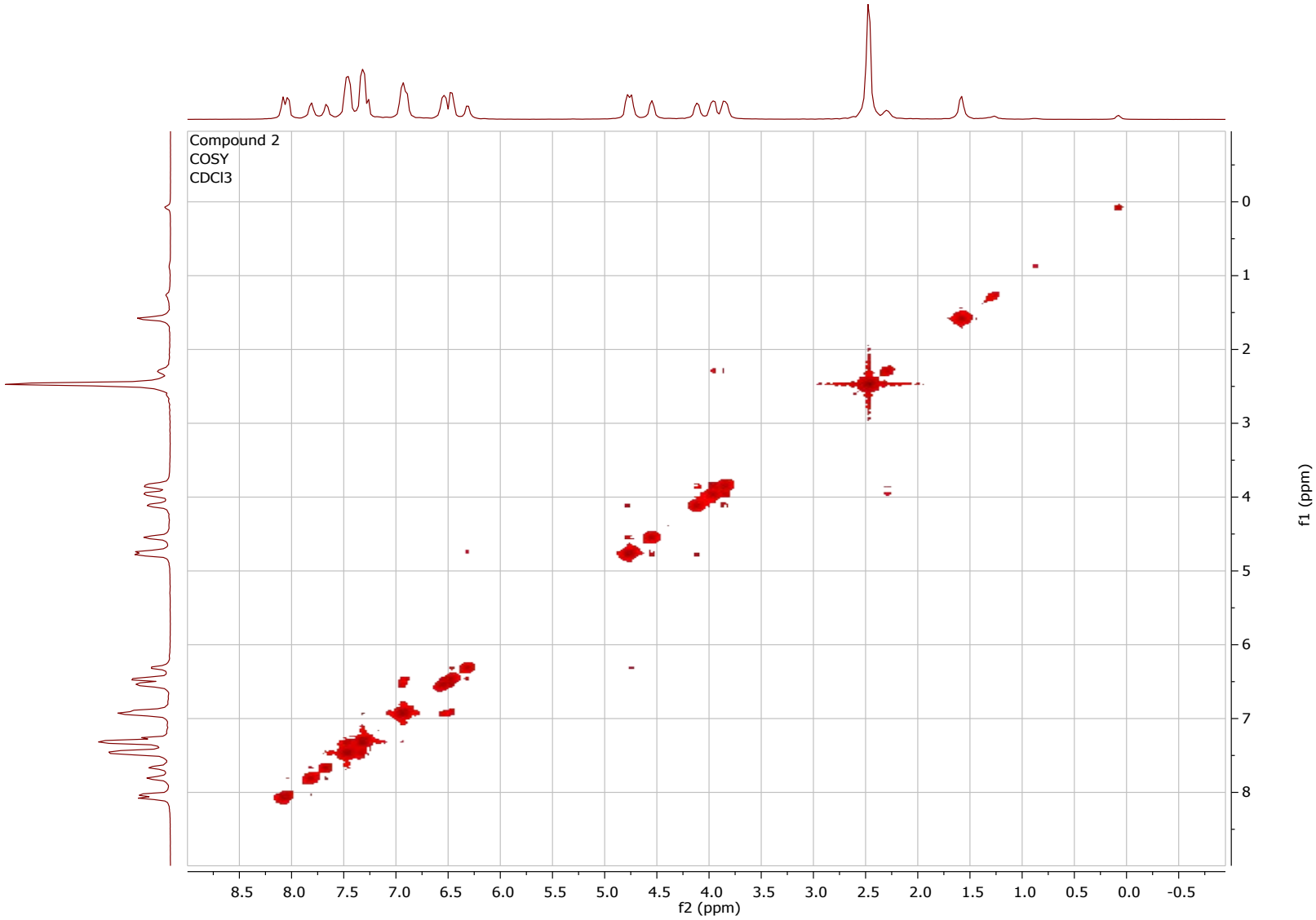


Figure S12: HSQC NMR of 1:2 α-glucofuranose BODIPY (**2**) in $CDCl_3$

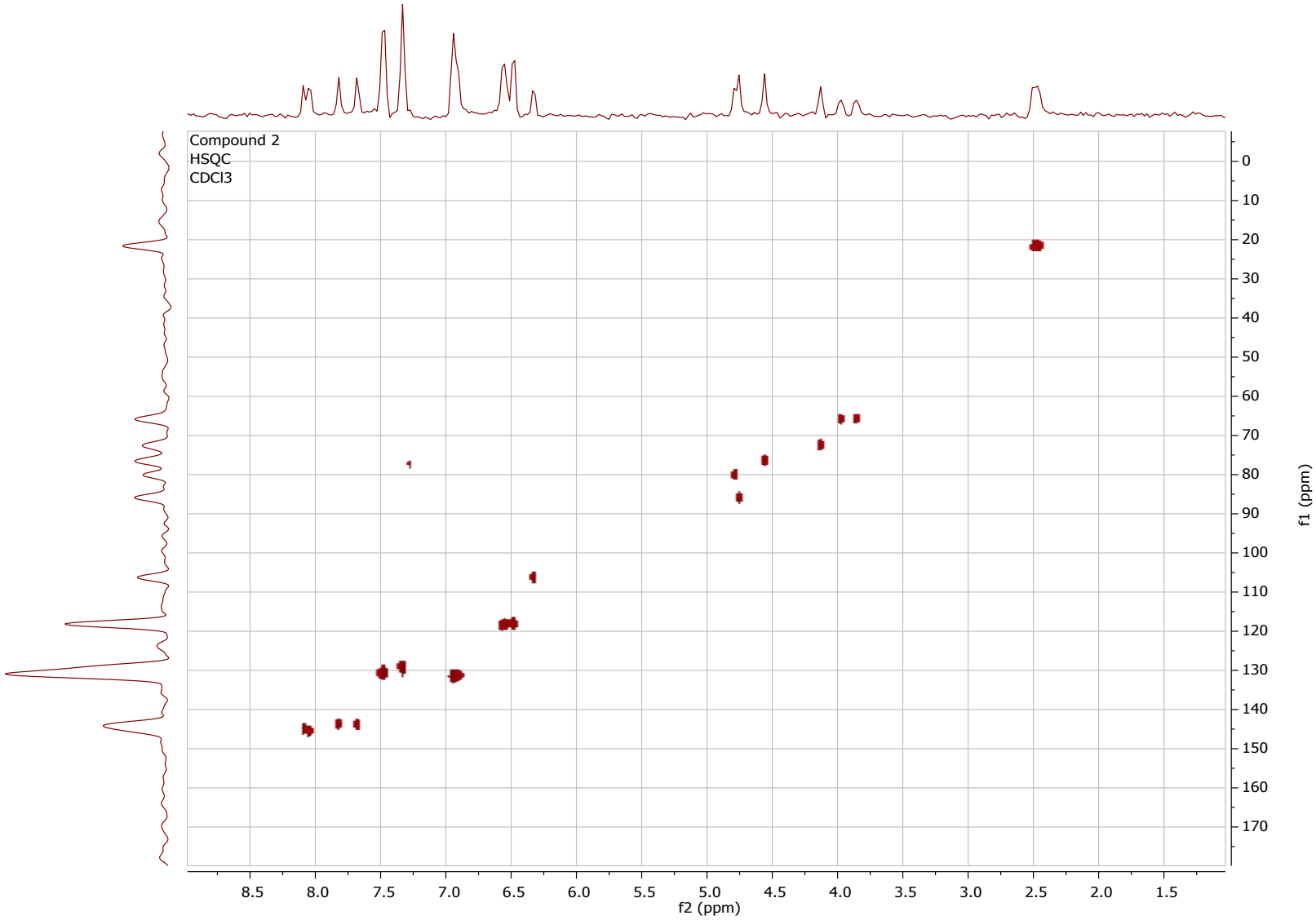


Figure S13: HMBC NMR of 1:2 α-glucofuranose BODIPY (**2**) in $CDCl_3$

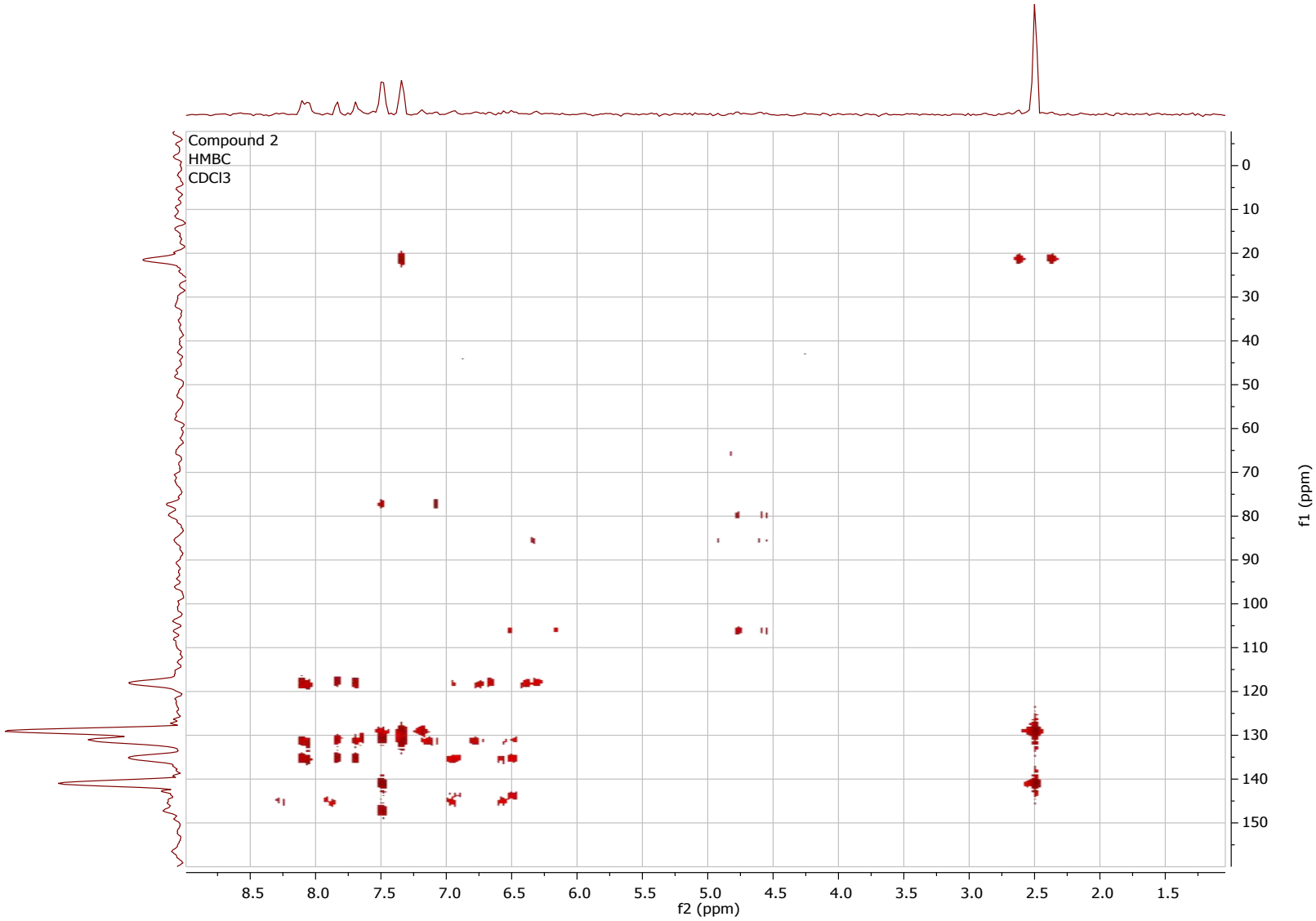


Figure S14: NOESY NMR of 1:2 α-glucofuranose BODIPY (**2**) in $CDCl_3$

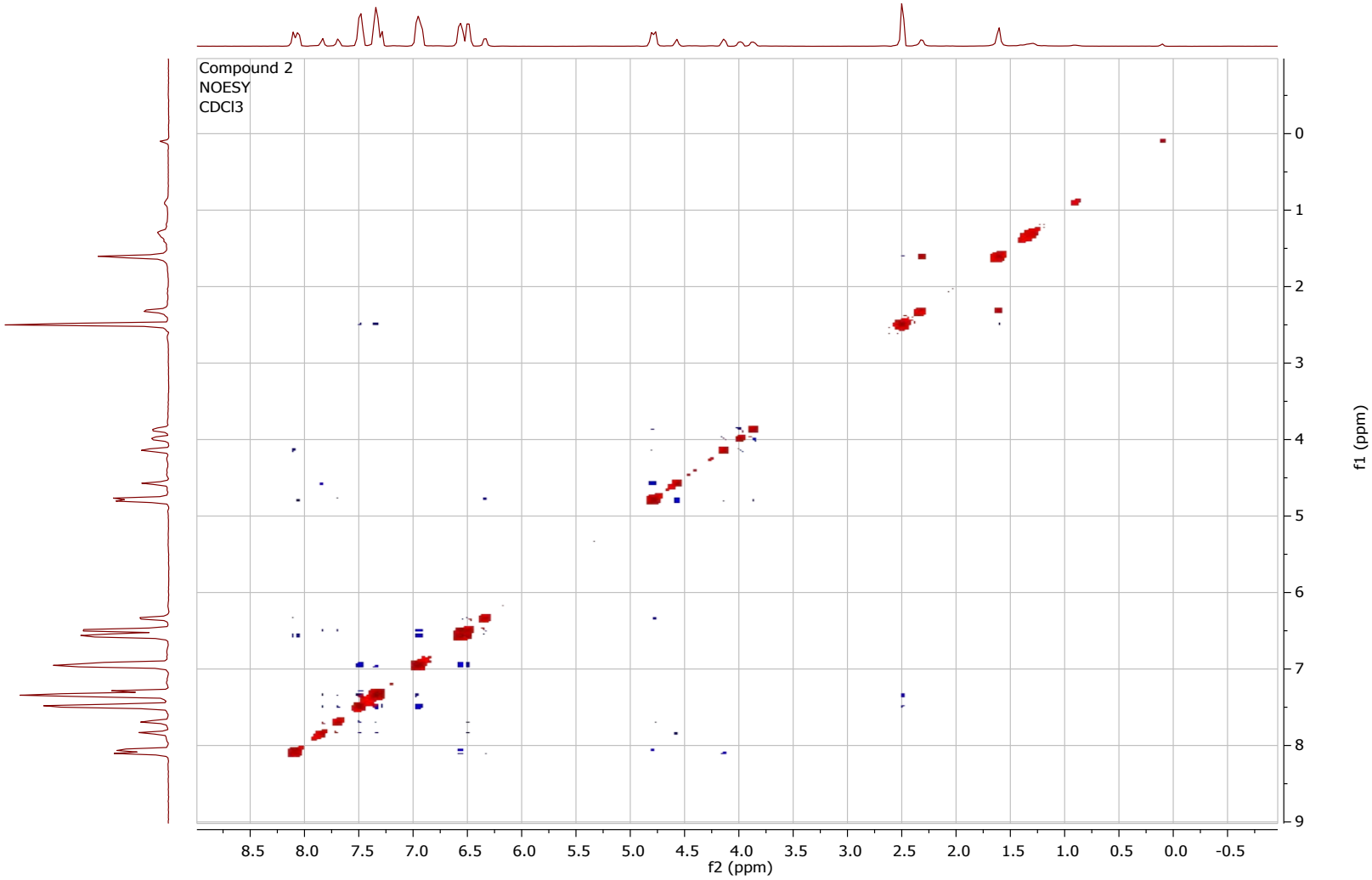


Figure S15: ^{1}H NMR of 1:2 α-glucoseptanose BODIPY (**3**) in $CDCl_3$ (500 MHz)

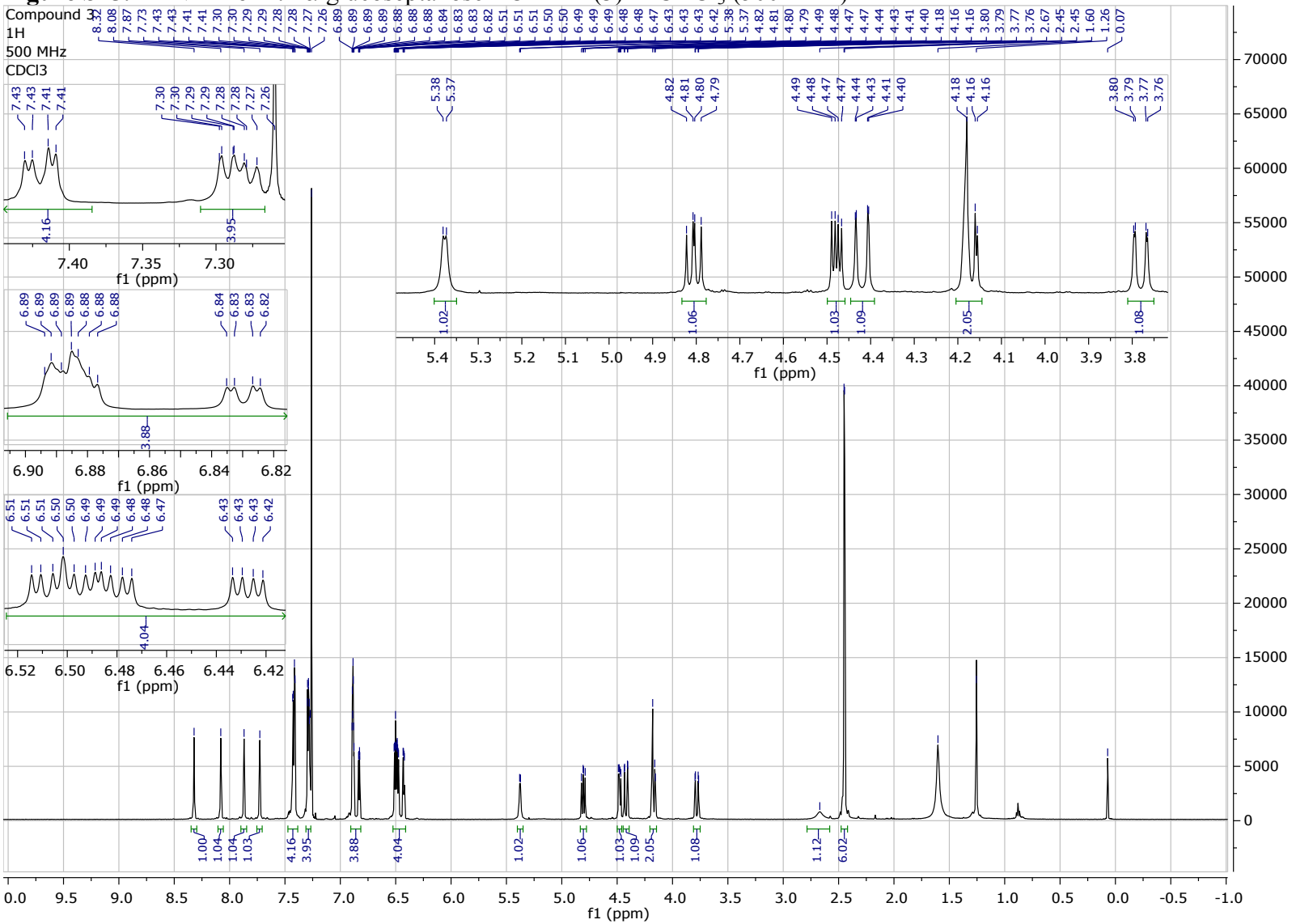


Figure S16: ^{11}B NMR of 1:2 α-glucoseptanose BODIPY (**3**) in $CDCl_3$ (160 MHz)

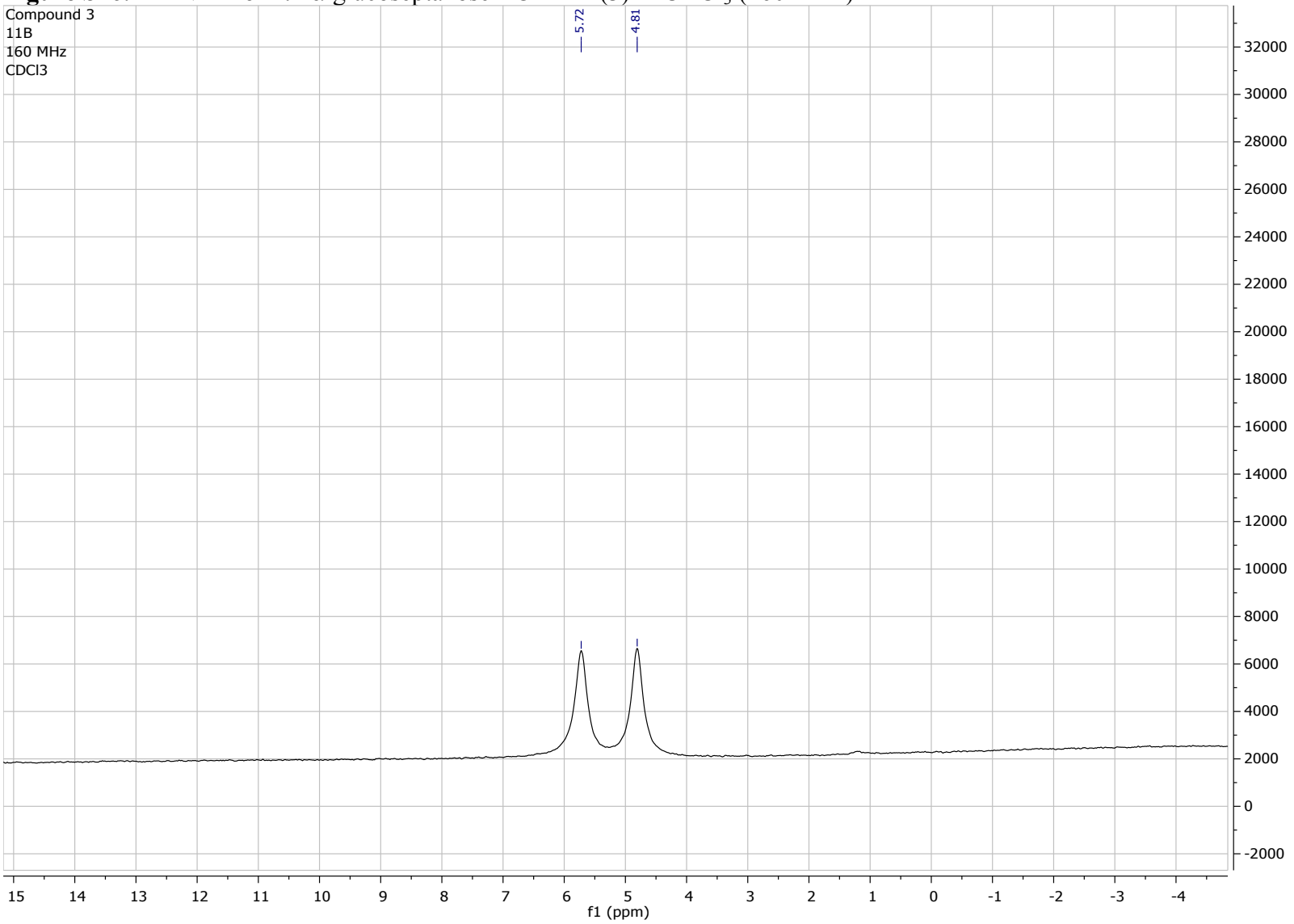


Figure S17: ^{13}C NMR of 1:2 α-glucoseptanose BODIPY (**3**) in $CDCl_3$ (125 MHz)

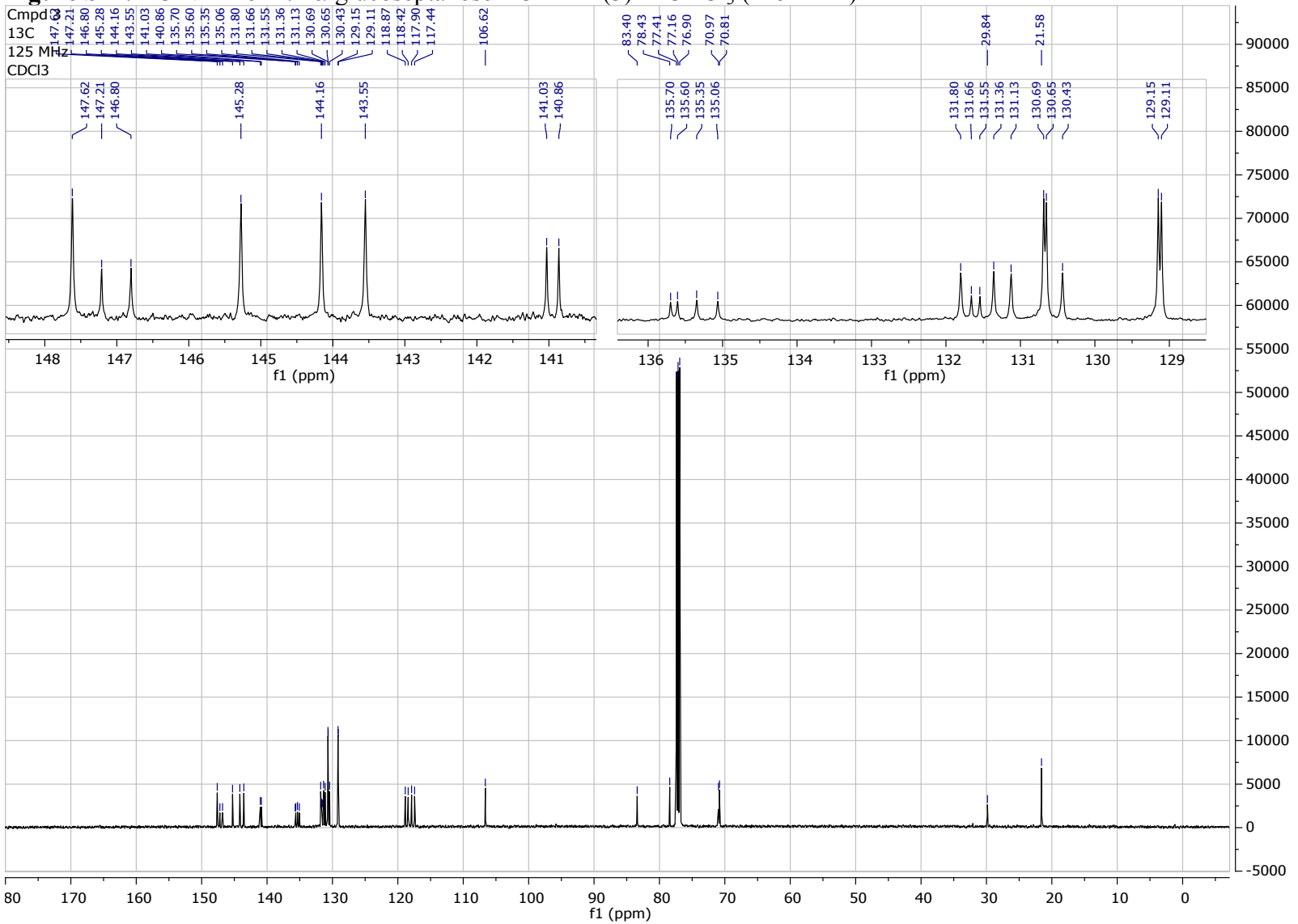


Figure S18: COSY NMR of 1:2 α-glucoseptanose BODIPY (**3**) in $CDCl_3$

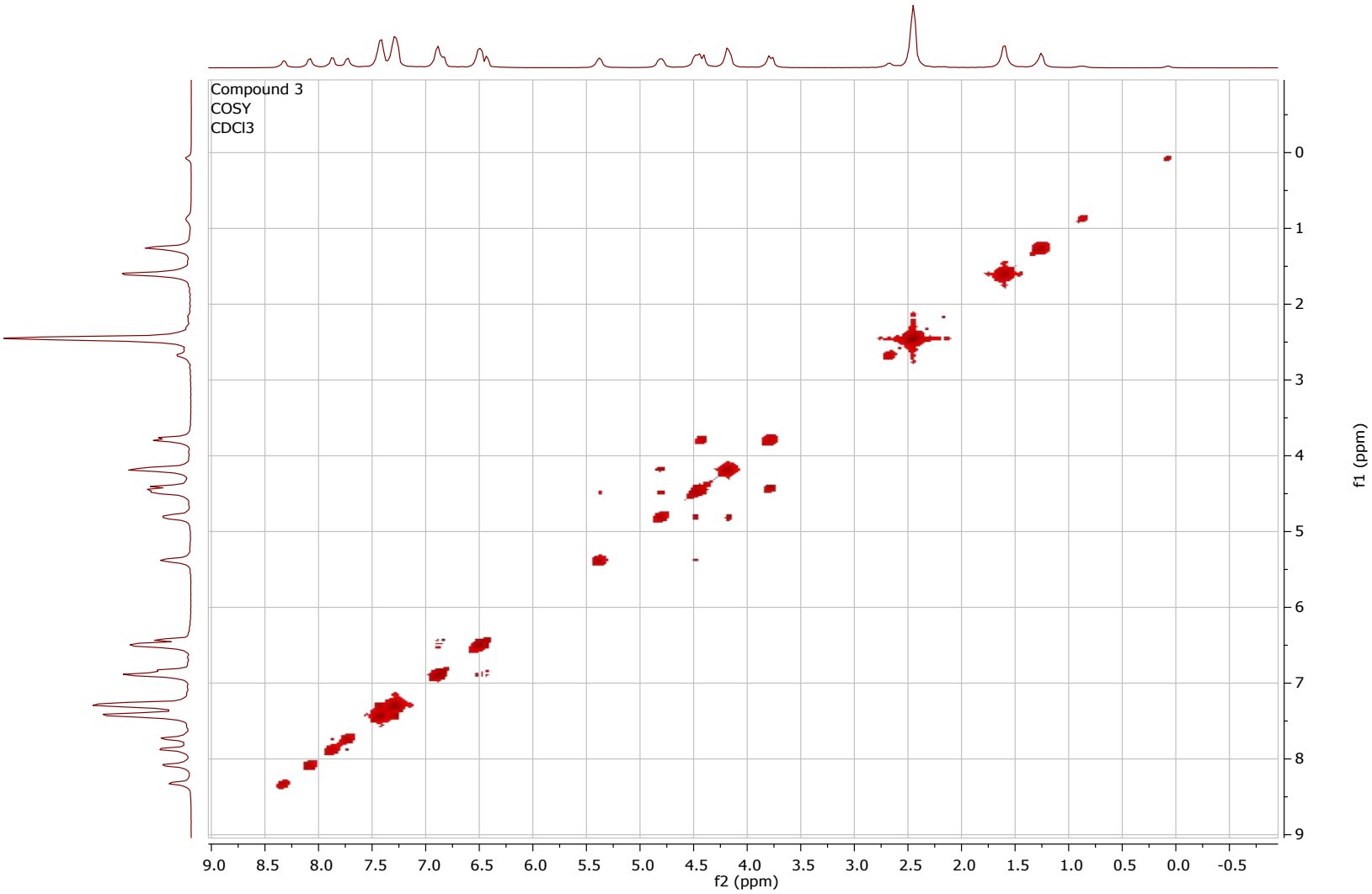


Figure S19: HSQC NMR of 1:2 α-glucoseptanose BODIPY (**3**) in $CDCl_3$

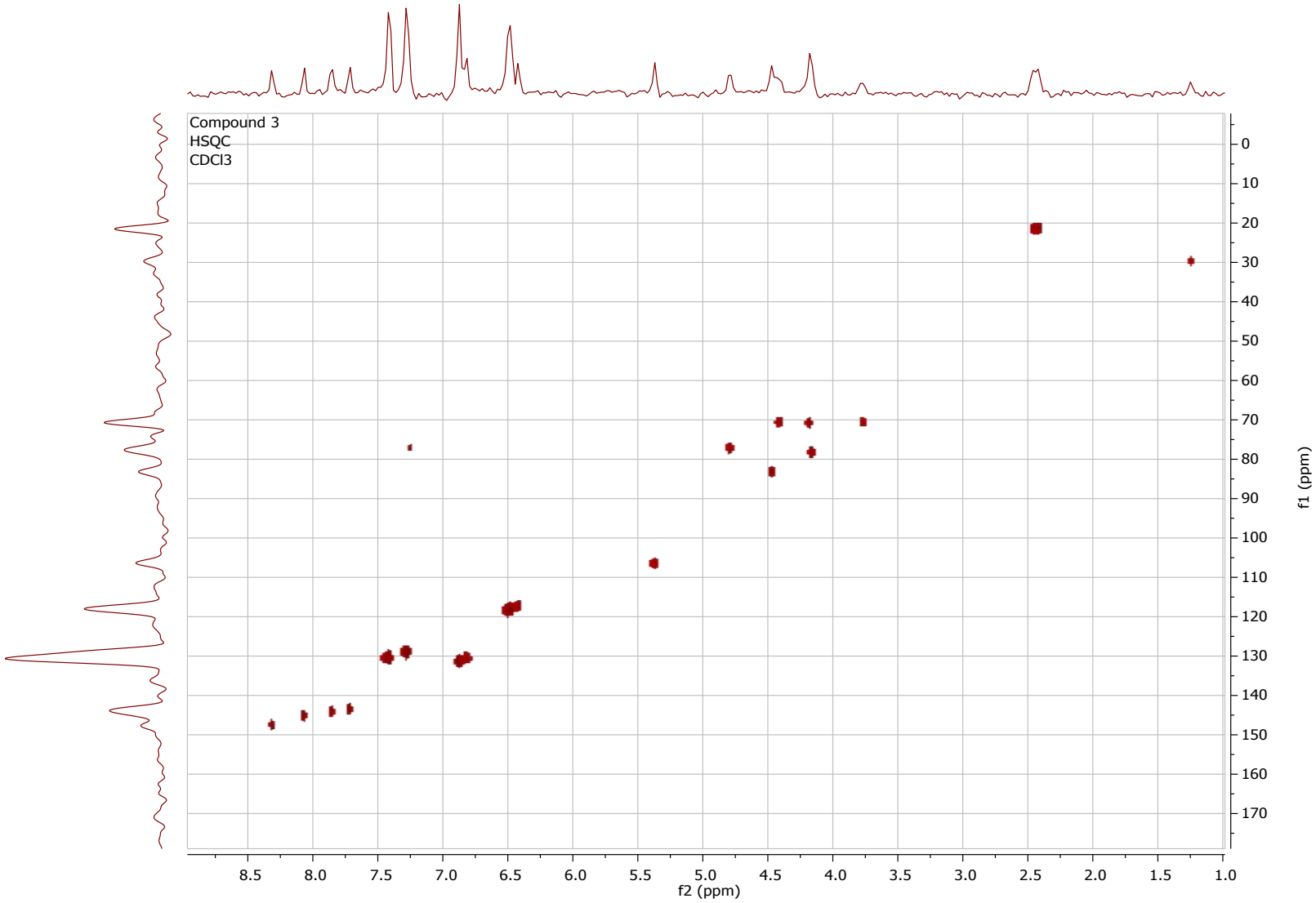


Figure S20: HMBC NMR of 1:2 α-glucoseptanose BODIPY (**3**) in $CDCl_3$

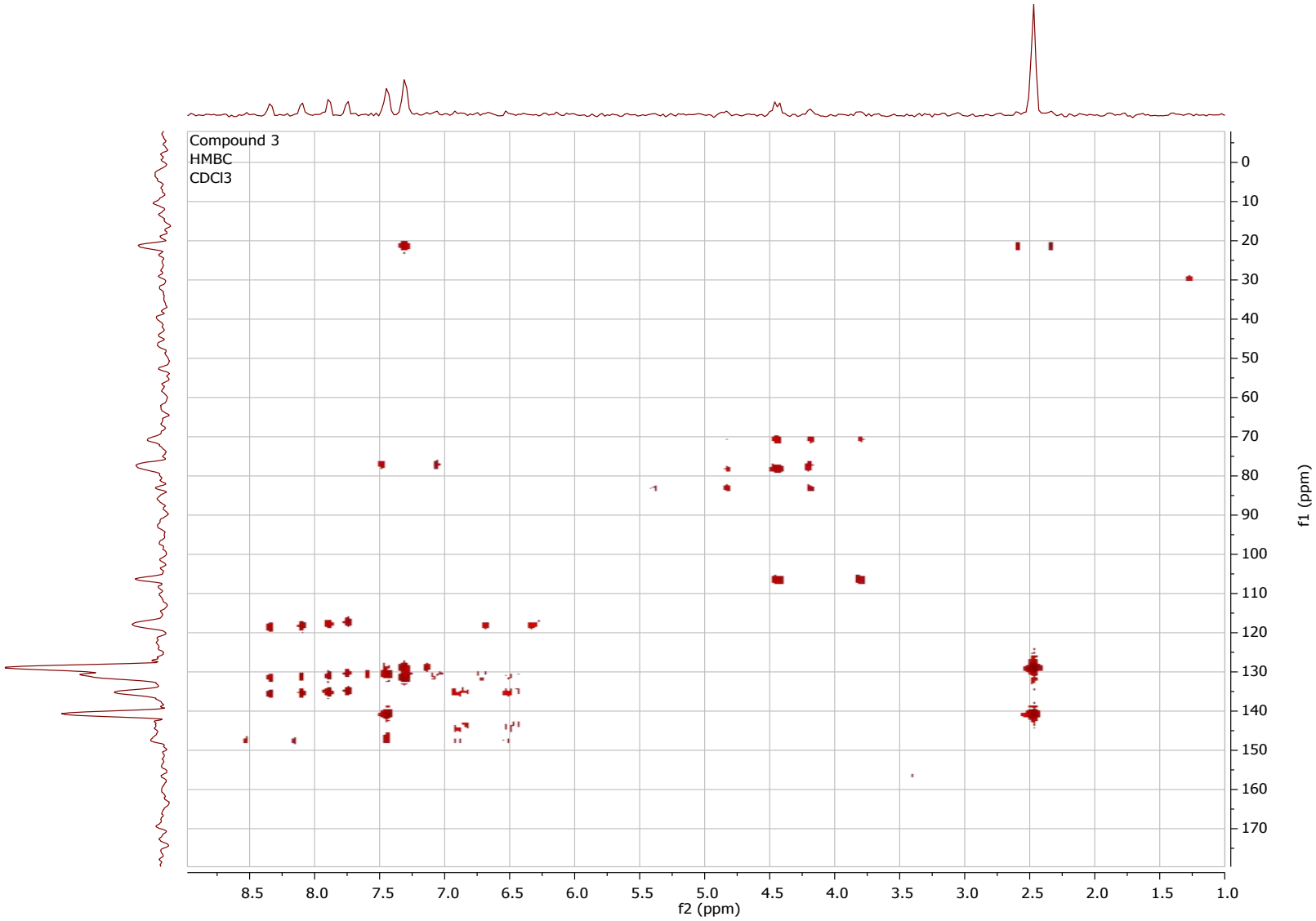


Figure S21: NOESY NMR of 1:2 α-glucoseptanose BODIPY (**3**) in $CDCl_3$

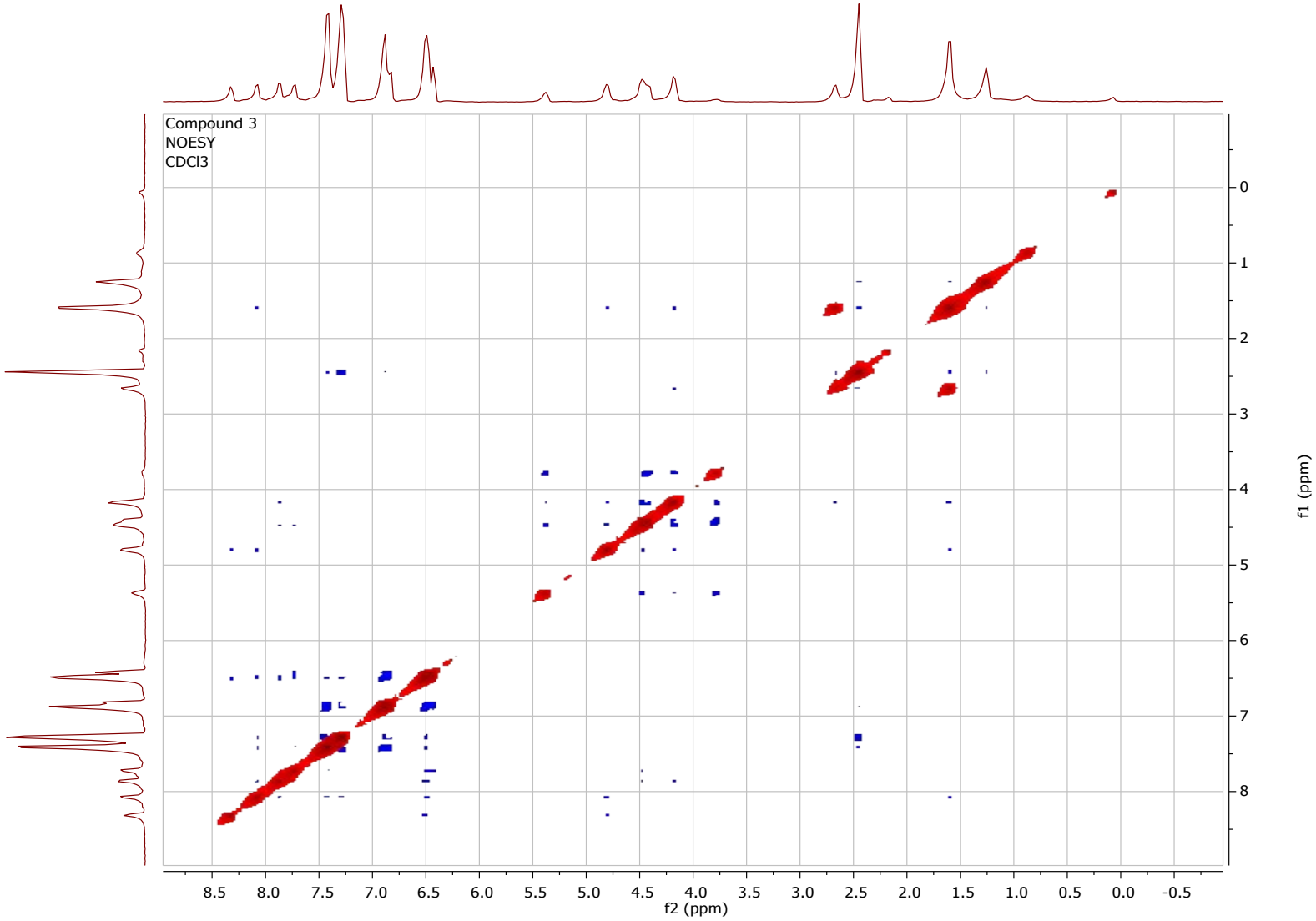
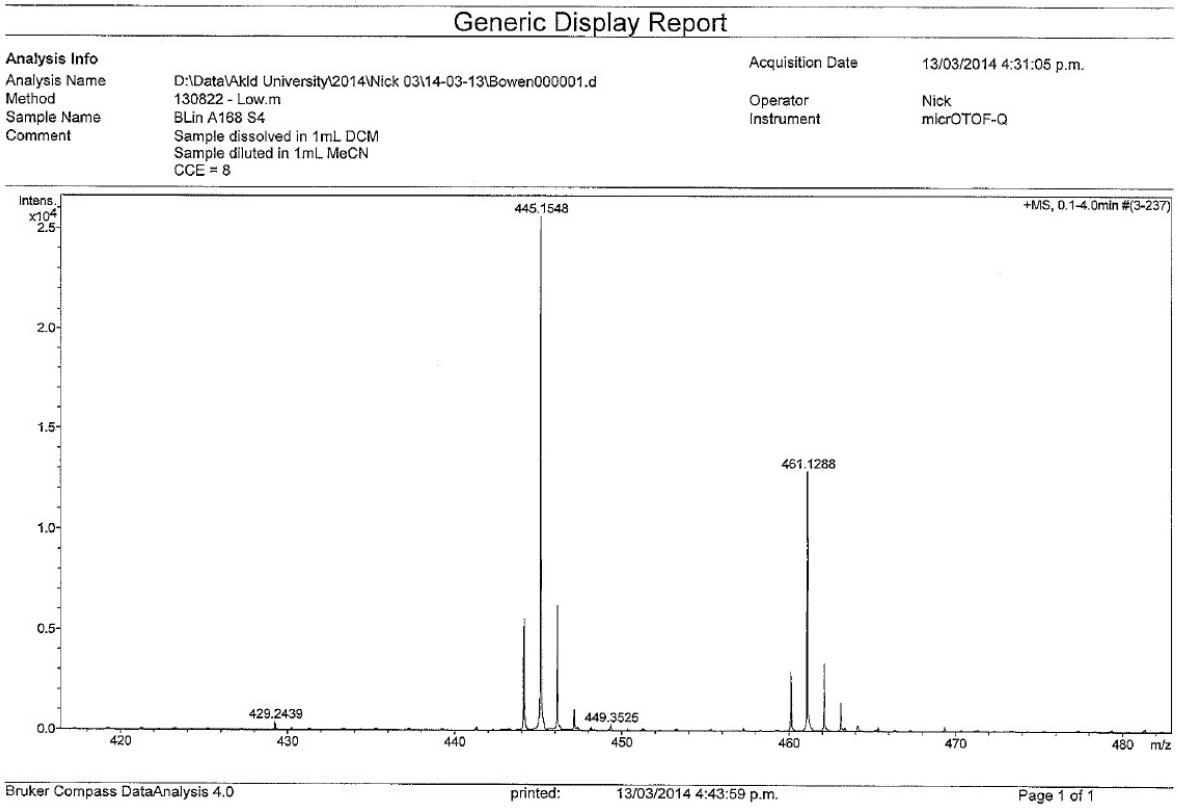


Figure S22: HRMS of 1:1 α-glucofuranose BODIPY (**1**)



Generic Display Report

Analysis Info

Analysis Name	D:\Data\Akld University\2014\Nick 03\14-03-13\Bowen000001.d	Acquisition Date	13/03/2014 4:31:05 p.m.
Method	130822 - Low.m	Operator	Nick
Sample Name	BLin A168 S4	Instrument	micrOTOF-Q
Comment	Sample dissolved in 1mL DCM Sample diluted in 1mL MeCN CCE = 8		

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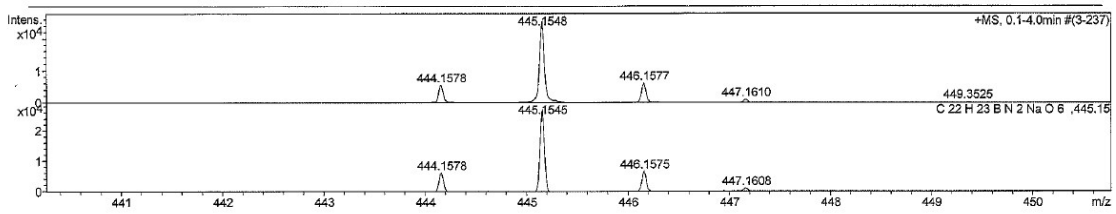
Analysis Info

Analysis Name	D:\Data\Akld University\2014\Nick 03\14-03-13\Bowen000001.d	Acquisition Date	13/03/2014 4:31:05 p.m.
Method	130822 - Low.m	Operator	Nick
Sample Name	BLin A168 S4	Instrument / Ser#	micrOTOF-Q 10191
Comment	Sample dissolved in 1mL DCM Sample diluted in 1mL MeCN CCE = 8		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
445.1548	1	C 22 H 23 B N 2 Na O 6	100.00	445.1545	-0.3	-0.7	8.4	12.5	even	ok
	2	C 22 H 20 B N 5 O 5	79.47	445.1556	0.4	0.8	9.1	16.0	odd	ok

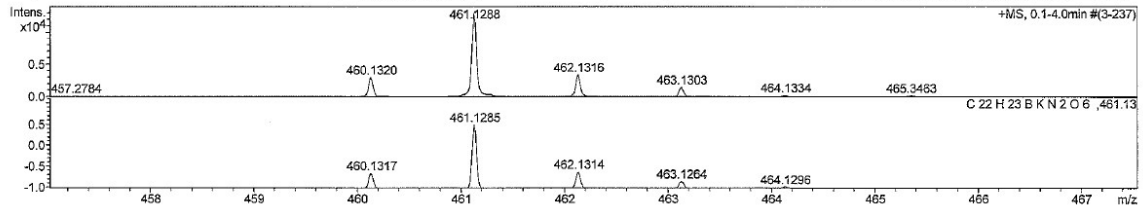
Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Akld University\2014\Nick 03\14-03-13\Bowen000001.d	Acquisition Date	13/03/2014 4:31:05 p.m.
Method	130822 - Low.m	Operator	Nick
Sample Name	BLin A168 S4	Instrument / Ser#	micrOTOF-Q 10191
Comment	Sample dissolved in 1mL DCM Sample diluted in 1mL MeCN CCE = 8		

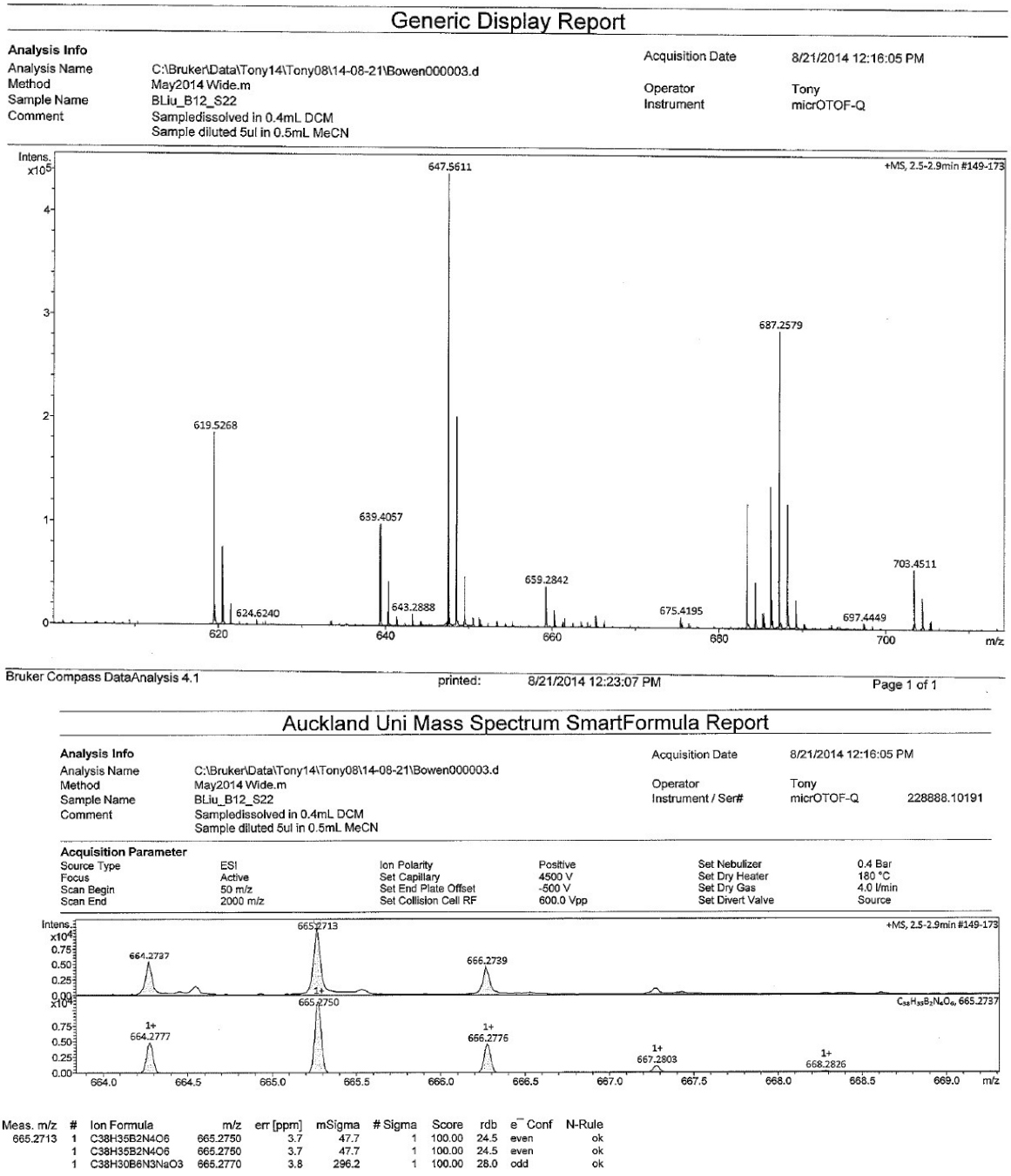
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
461.1288	1	C 22 H 23 B K N 2 O 6	100.00	461.1285	-0.3	-0.7	2.6	12.5	even	ok

Figure S23: HRMS of 1:2 α-glucofuranose BODIPY (**2**)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
665.2713	1	C38H35B2N4O6	665.2750	3.7	47.7	1	100.00	24.5	even	ok
	1	C38H35B2N4O6	665.2750	3.7	47.7	1	100.00	24.5	even	ok
	1	C38H30B6N3NaO3	665.2770	3.8	296.2	1	100.00	28.0	odd	ok

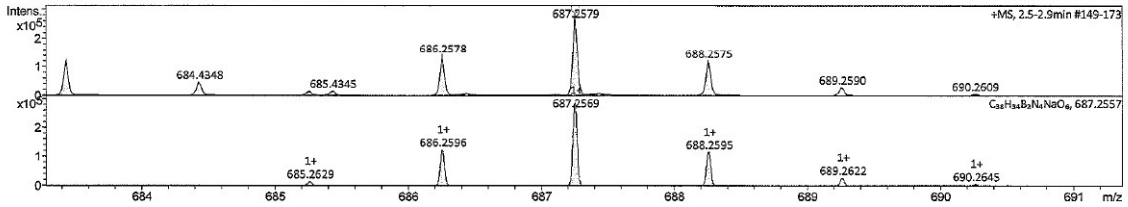
Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Bruker\Data\Tony14\Tony08\14-08-21\Bowen000003.d	Acquisition Date	8/21/2014 12:16:05 PM
Method	May2014 Wide.m	Operator	Tony
Sample Name	BLiu_B12_S22	Instrument / Ser#	micrOTOF-Q 228888.10191
Comment	Sampledissolved in 0.4mL DCM Sample diluted 5ul in 0.5mL MeCN		

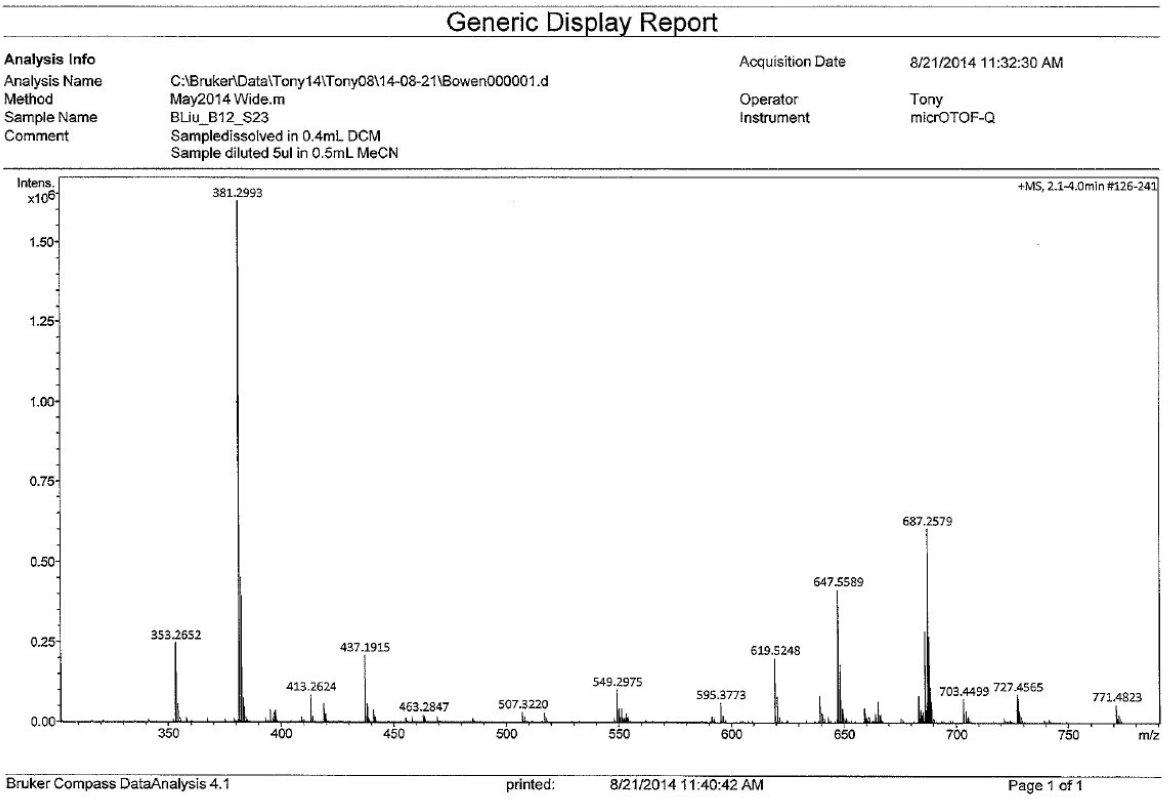
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
687.2579	1	C38H13B16N3	687.2659	2.1	524.3	1	100.00	42.0	odd	ok
	1	C38H13B16N3	687.2659	2.1	524.3	1	100.00	42.0	odd	ok
	1	C38H34B2N4NaO6	687.2569	-3.2	22.7	1	100.00	24.5	even	ok
	2	C38H30B4N5NaO4	687.2586	-2.4	145.6	2	0.63	28.0	odd	ok

Figure S24: HRMS of 1:2 α-glucoseptanose BODIPY (**3**)



Generic Display Report

Analysis Info

Analysis Name	C:\Bruker\Data\Tony14\Tony08\14-08-21\Bowen000001.d	Acquisition Date	8/21/2014 11:32:30 AM
Method	May2014 Wide.m	Operator	Tony
Sample Name	BLiu_B12_S23	Instrument	micrOTOF-Q
Comment	Sampledissolved in 0.4mL DCM Sample diluted 5ul in 0.5mL MeCN		

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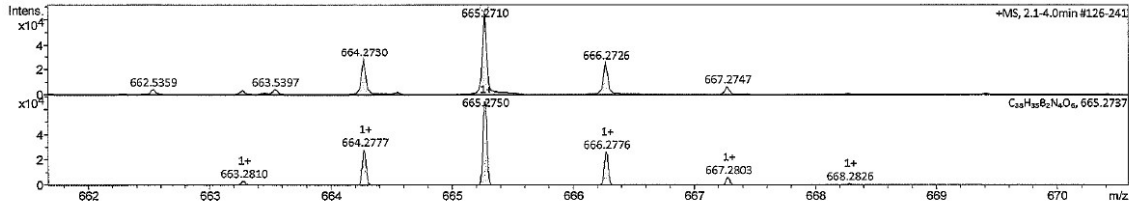
Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Bruker\Data\Tony14\Tony08\14-08-21\Bowen000001.d			Acquisition Date	8/21/2014 11:32:30 AM
Method	May2014 Wide.m			Operator	Tony
Sample Name	BLiu_B12_S23			Instrument / Ser#	micrOTOF-Q 228888.10191
Comment	Sampledissolved in 0.4mL DCM Sample diluted 5ul in 0.5mL MeCN				

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
665.2710	1	C38H35B2N4O6	665.2750	4.0	9.1	1	100.00	24.5	even	ok
	1	C38H35B2N4O6	665.2750	4.0	9.1	1	100.00	24.5	even	ok

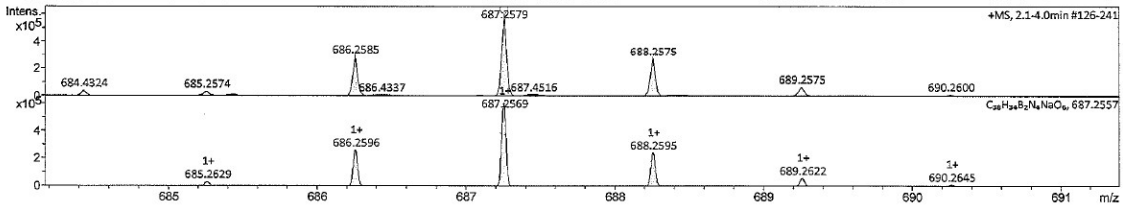
Auckland Uni Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	C:\Bruker\Data\Tony14\Tony08\14-08-21\Bowen000001.d	Acquisition Date	8/21/2014 11:32:30 AM
Method	May2014 Wide.m	Operator	Tony
Sample Name	BLiu_B12_S23	Instrument / Ser#	micrOTOF-Q 228888.10191
Comment	Sampledissolved in 0.4mL DCM Sample diluted 5ul in 0.5mL MeCN		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
687.2579	1	C37H35B2N3O9	687.2566	-3.6	31.5	1	100.00	23.0	odd	ok
	2	C37H31B4N4O7	687.2583	-2.8	149.7	2	0.81	26.5	even	ok
	3	C37H27B6N5O5	687.2597	-2.0	270.3	3	0.00	30.0	odd	ok
	1	C37H35B2N3O9	687.2566	-3.6	31.5	1	100.00	23.0	odd	ok
	2	C37H31B4N4O7	687.2583	-2.8	149.7	2	0.81	26.5	even	ok
	3	C37H27B6N5O5	687.2597	-2.0	270.3	3	0.00	30.0	odd	ok
	1	C38H34B2N4NaO6	687.2569	-3.2	29.6	1	100.00	24.5	even	ok

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

	1	**3**
Formula	$C_{44}H_{46}B_2N_4O_{17}$	$C_{38}H_{34}B_2N_4O_6$
Molecular weight (g mol^{-1})	924.47	664.31
Temperature (K)	100(2)	100(1)
Wavelength (Å)	0.71073	1.54184
Crystal system	Monoclinic	Orthorhombic
Space group	*C*2	$P2_12_12_1$
a (Å)	37.5988(15)	11.3239(5)
b (Å)	14.8713(6)	12.8880(7)
c (Å)	8.2281(3)	25.7528(11)
β (°)	93.381(3)	90
Volume (Å^3)	4592.7(3)	3758.4(3)
Z	4	4
Calculated density (g cm^{-3})	1.337	1.174
Absorption coefficient (mm^{-1})	0.103	0.643
F(000)	1936	1392
Crystal size (mm × mm × mm)	0.25 × 0.15 × 0.10	0.018 x 0.023 x 0.337
2θ (min, max) (°)	1.085, 19.70	3.835, 66.59
Limiting indices	$-35 \le h \le 35$, $-14 \le k \le 14$, $-7 \le l \le 7$	$-13 \le h \le 10$, $-14 \le k \le 15$, $-21 \le l \le 31$
Reflections collected / unique	23480 / 4060 [R(int) = 0.0461]	9143 / 5540 [R(int) = 0.0412]
Completeness to theta max	99.6 %	99.3 %
Data / restraints / parameters	4060 / 267 / 596	5540/0/454
Goodness-of-fit on F^2 [a)]	1.081	0.998
Final R indices [I>2σ(I)] [b)]	R_1 = 0.0871, wR_2 = 0.2318	R_1 = 0.0482, wR_2 = 0.1290
R indices (all data)	R_1 = 0.0920, wR_2 = 0.2389	R_1 = 0.0534, wR_2 = 0.1326
Largest diff. peak and hole (eÅ^{-3})	0.707 and -0.440	0.249 and -0.265

a) GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. b) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.