Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Chemoenzymatic Synthesis of Complex *N*-Glycans of the Parasite *S. mansoni* to Examine the Importance of Epitope Presentation on DC-SIGN recognition

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SUPPORTING INFORMATION

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1. Chemical synthesis

1.1 General methods: Reactions were performed using flame-dried glassware with anhydrous solvents under an atmosphere of argon unless otherwise noted. Proton nuclear magnetic resonance (^{1}H -NMR) spectra were recorded with Varian 400 (at 400 MHz) or Bruker 600 (at 600 MHz) spectrometers. Multiplicities are assigned as singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet of doublets (td), triplet (t), quartet (q) or multiplet (m). Carbon nuclear magnetic resonance (^{13}C) spectra were recorded with Varian 400 (at 101 MHz) or Bruker 600 (at 151 MHz) spectrometers. Spectra were assigned using gCOSY and multiplicity-edited gHSQC experiments. Tetramethylsilane (TMS) was used as an internal standard in all ^{1}H and ^{13}C spectra (δ = 0 ppm) when applicable. Mass spectra was recorded using high resolution Shimadzu LCMS-IT-TOF or Kratos Analytical Maxima-CFR MALDI-TOF system. Column chromatography was performed on silica gel G60 (Silicycle, 60-200 µm, 60 Å). Thin layer chromatography (TLC) analysis was conducted on Silicagel 60 F254 (EMD Chemicals Inc.) coated aluminum sheets. Plates were visualized by UV light (254 nm) and by charring with 10% sulfuric acid in ethanol and/or Hanessian's stain. Size exclusion chromatography was carried out on bio-beads S-X1 (40-80 µm) or bio-gel P2 (45-90 µm). Acid washed molecular sieves (4 Å) were flame activated under vacuum prior to reactions.

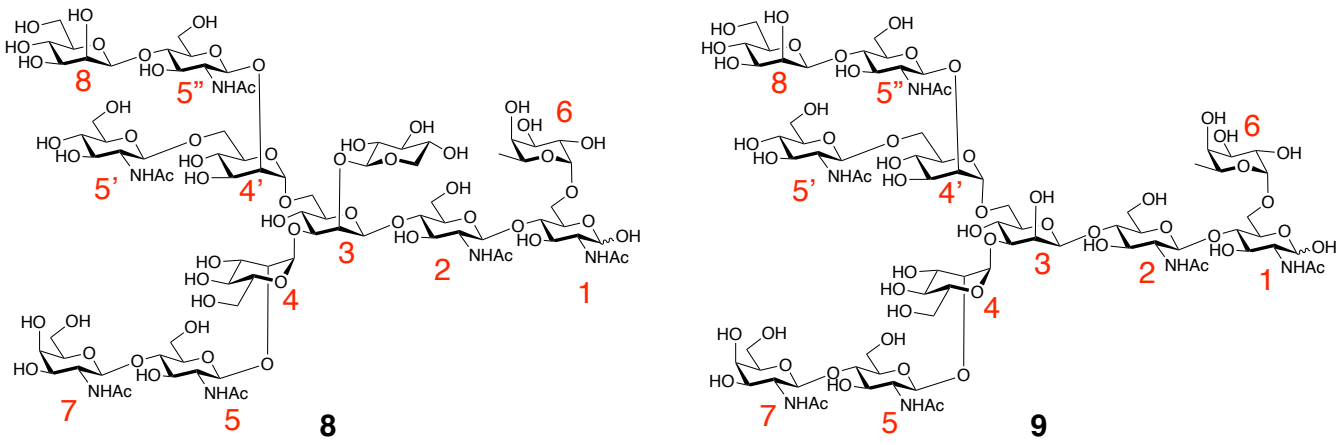
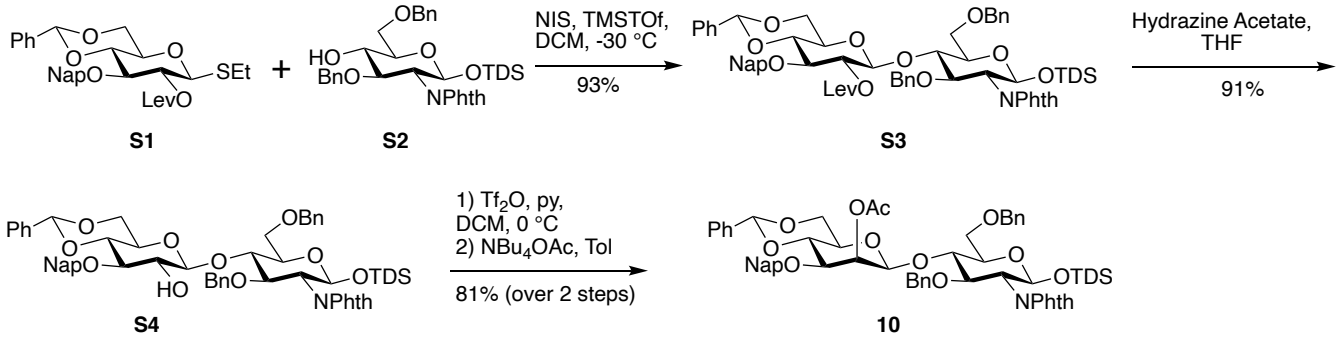


Figure S1. Monosaccharide nomenclature system for NMR assignments.

For the simpler building blocks, the monosaccharides were denoted with their known abbreviations, for eg., Glucose (Glc), *N*-acetyl glucosamine (GlcN), Mannose (Man), *N*-acetyl galactosamine (GalN), Fucose (Fuc), etc. For the oligosaccharide glycans, the individual monosaccharides have been labeled from the reducing end of the glycans as shown in Fig. S1. For eg., the *N*-acetyl glucosamine residues from the reducing end of the glycans were labeled as GlcN-1 and GlcN-2 respectively; the *β*- mannoside of the core pentasaccharide is labeled as Man-3, the α-3 and α-6 mannosides were labeled as Man-4 and Man-4' respectively. The mannose moeity of the unnatural Man-β-(1→4)-GlcNAc terminus was labeled as Man-8;The *N*-acetylglucosamine residues as GlcNAc-5, 5', 5". The *N*-acetyl galactosamine of the GalN-β-(1→4)-GlcN terminus was denoted as GalN-7.



Scheme S1: Synthesis of building block **10.**

Dimethylthexylsilyl [4,6-*O*-benzylidene-2-*O*-levulenoyl-3-*O*-(2-methylnaphthyl)-β-D-glucopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S3): Donor **S1** (24.6 g, 44.8 mmol) and acceptor **S2** (23.5 g, 37.3 mmol), were dissolved in DCM (300 mL) and stirred with pre-activated molecular sieves (50 g) for 20 min. The mixture was then cooled down to -30 ºC, followed by the addition of NIS (10.5 g, 46.7 mmol) and TfOH (692 μL, 7.5 mmol). The reaction mixture was warmed up to -10 ºC over a period of 30 min, after which it was quenched with Et_3N (5 mL). The mixture was diluted by DCM (200 mL) and washed with 10% $Na_2S_2O_3$ (200 mL). The organic phase was dried over $MgSO_4$ and the filtrate was concentrated *in vacuo* to give the crude product as a brown syrup. Silica gel column chromatography with Tol: EtOAc (9.5: 0.5, v: v to 8: 2, v: v) yielded the product as white amorphous powder (38.8 g, 93%). R_f = 0.59 (Tol: EtOAc, 9: 1 v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 to 6.82 (26H, m, H-Ar), 5.48 (1H, s, PhC<u>H</u> of benzylidene), 5.30 (1H, d, H-1 GlcN, *J* = 7.9 Hz), 5.01 (2H, m, H-2 Glc, PhC<u>H</u>H), 4.82 (1H, d, PhCH<u>H</u>, *J* = 12.2 Hz), 4.74 (2H, m, C<u>H</u>$_2$ of Nap), 4.63 (1H, d, *J* =8.1 Hz), 4.45 (2H, m, PhC<u>H</u>$_2$), 4.24 (2H, m, H-6b Glc, H-3 GlcN), 4.06 (2H, m, H-2 GlcN, H-3 Glc), 3.82 (1H, m, H-6b GlcN), 3.66 (3H, m, H-6a GlcN, H-5 GlcN, H-4 Glc), 3.50 (2H, m, H-6a Glc, H-4 GlcN), 3.26 (1H, m, H-5 Glc), 2.62 (2H, m, C<u>H</u>$_2$COCH$_3$ of Lev), 2.42 (2H, m, COOC<u>H</u>$_2$ of Lev), 2.10 (3H, s, CH$_2$COC<u>H</u>$_3$ of Lev), 1.35 [1H, m, C<u>H</u>(CH$_3$)$_2$ of TDS], 0.56 [12H, m, C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], 0.09 to -0.08 (6H, 2s, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.53, 206.10, 172.60, 171.21, 138.69, 138.10, 137.84, 137.24, 135.79, 133.22, 133.15, 133.08, 132.93, 132.09, 129.01, 128.93, 128.65, 128.51, 128.48, 128.45, 128.43, 128.36, 128.31, 128.29, 128.26, 128.20, 128.14, 128.00, 127.96, 127.89, 127.87, 127.84, 127.81, 127.73, 127.68, 127.66, 127.38, 127.29, 126.98, 126.52, 126.43, 126.28, 126.24, 126.06, 125.98, 125.92, 125.85, 125.80, 125.28, 101.22, 101.04, 100.65, 93.38, 93.28, 81.71, 78.54, 78.46, 78.03, 77.33, 77.02, 76.70, 76.37, 74.87, 74.48, 74.25, 74.10, 73.76, 73.71, 73.62, 73.56, 68.63, 67.94, 66.62, 65.91, 57.74, 57.38, 37.92, 37.76, 37.67, 33.87, 33.83, 29.87, 29.82, 28.02, 27.80, 24.47, 21.45, 19.89, 19.85, 19.71, 19.66, 18.28, 18.16, -1.82, -3.81, -3.88. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{65}H_{73}NO_{14}SiNa$, 1142.4698; found 1142.4762.

Dimethylthexylsilyl [4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-β-D-glucopyranosyl]- (1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S4): Compound **S3** (38.5 g, 34.4 mmol) was dissolved in THF (200 mL), followed by the addition of hydrazine acetate (4.8 g, 51.6 mmol), and stirred for 3 h after which the solvent was evaporated *in vacuo* and the residue was diluted by DCM (300 mL) and washed with water (200 mL) and brine (100 mL). The organic fractions were then dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using Pet. Ether: EtOAc (8: 2, v: v to 6: 4, v: v) gave the product as a white amorphous powder. (32.2 g, 91%). R_f = 0.56 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 to 6.74 (26H, m, H-Ar), 5.48 (1H, s, PhC<u>H</u> of benzylidene), 5.30 (1H, d, C<u>H</u>H of Nap, *J* = 10.7 Hz), 4.94 (1H, d, CH<u>H</u> of Nap, *J* = 10.7 Hz), 4.72 (3H, m, H-1 Glc, PhCH<u>H</u>, PhCH<u>H</u>), 4.59 (1H, d, PhC<u>H</u>H, *J* = 12.3 Hz), 4.38 (2H, m, H-3 GlcN, PhC<u>H</u>H), 4.12 (3H, m, H-2 GlcN, H-6b Glc, H-3 Glc), 4.02 (1H, m, H-6a Glc), 3.74 (1H, d, H-6b GlcN, *J* = 11.1 Hz), 3.58 (5H, m, H-6a GlcN, H-4 GlcN, H-4 Glc, H-5 GlcN, H-2 Glc), 3.23 (2H, m, H-5 Glc, O<u>H</u>), 1.35 [1H, m, C<u>H</u>$(CH_3)_2$ of TDS], 0.57 [12H, m, C($C\underline{H}_3$)$_2$, CH($C\underline{H}_3$)$_2$ of TDS], 0.08 to -0.10 (6H, 2s, 2x $C\underline{H}_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.51, 138.30, 137.74, 137.31, 135.90, 133.35, 133.27, 132.99, 132.91, 132.32, 128.95, 128.88, 128.71, 128.47, 128.44, 128.40, 128.31, 128.26, 128.22, 128.13, 127.96, 127.93, 127.89, 127.85, 127.80, 127.77, 127.68, 127.64, 127.39, 127.34, 127.28, 127.08, 126.70, 126.60, 126.47, 126.16, 126.07, 126.06, 126.04, 125.99, 125.96, 125.87, 125.81, 125.40, 125.13, 103.62, 101.24, 93.47, 93.38, 81.26, 80.30, 78.92, 77.95, 77.32, 77.00, 76.68, 75.43, 75.15, 74.67, 74.55, 74.35, 74.06, 73.76, 73.60, 68.65, 68.41, 66.28, 65.46, 60.37, 57.89, 57.40, 33.86, 33.83, 24.48, 21.03, 19.86, 19.67, 18.28, 18.16, 14.18, -1.81, -1.85, -3.80, -3.88. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{60}H_{67}NO_{12}SiNa$, 1044.4330; found 1044.4125.

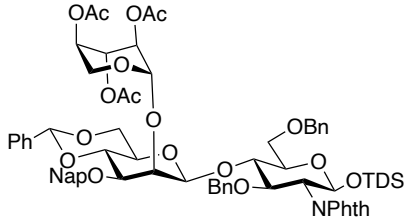
Dimethylthexylsilyl [2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (10): Compound **S4** (32.0 g, 31.3 mmol) was dissolved in anhydrous DCM (200 mL) and the mixture was cooled down to 0 °C. This was followed by the addition of anhydrous pyridine (7.6 mL, 93.9 mmol) and Tf_2O (10.5 mL, 62.2 mmol) and the mixture was stirred at this temperature for 1 h after which it was diluted by DCM (300 mL) and washed with sat. $NaHCO_3$ (200 mL). The organic fractions were then dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*, resulting in crude product as a yellow syrup. The crude product was then dissolved in dry Toluene (300 mL) followed by the addition of tetrabutylammonium acetate (47.1 g, 156.5 mmol). The suspension was sonicated under Ar atmosphere for 3 h, after which the solvent was evaporated *in vacuo*, and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (9: 1, v: v to 6: 4, v: v) which provided the product as a white amorphous powder. (27.1 g, 81% over two steps). R_f = 0.53 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 to 6.82 (26H, m, H-Ar), 5.55 (1H, s, PhC<u>H</u> of benzylidene), 5.53 (1H, d, H-2 Man, *J* = 3.3 Hz), 5.31 (1H, d, H-1 GlcN, *J* = 8.1 Hz), 4.83 (2H, m, PhC<u>H</u>H, C<u>H</u>H of Nap), 4.71 (3H, m, H-1 Man, CH<u>H</u> of Nap, PhCH<u>H</u>), 4.45 (2H, dd, Ph$C\underline{H}_2$, *J* = 12.1 Hz, 3.6 Hz), 4.28 (1H, dd, H-3 GlcN, *J* = 10.8 Hz, 8.5 Hz), 4.13 (3H, m, H-2 GlcN, H-6b Man, H-4 GlcN), 3.92 (1H, t, H-4 Man, *J* = 9.7 Hz), 3.81 (1H, m, H-6a Man), 3.61 (4H, m, H-6a GlcN, H-3 Man, H-5 GlcN, H-6b GlcN), 3.18 (1H, m, H-5 Man), 2.19 (3H, s, $C\underline{H}_3$ of Ac), 1.36 [1H, m, C<u>H</u>$(CH_3)_2$ of TDS], 0.60 [12H, m, C($C\underline{H}_3$)$_2$, CH($C\underline{H}_3$)$_2$ of TDS], 0.10 to -0.06 (6H, 2s, 2x $C\underline{H}_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.32, 138.66, 137.90, 137.46, 135.27, 133.66, 133.29, 132.97, 131.67, 128.96, 128.45, 128.21, 128.10, 127.95, 127.93, 127.89, 127.80, 127.74, 127.73,

127.61, 127.13, 126.19, 126.17, 126.01, 125.83, 125.39, 123.04, 101.57, 99.51, 93.42, 79.23, 77.88, 77.34, 77.23, 77.03, 76.75, 76.71, 75.75, 74.40, 74.32, 73.47, 71.49, 69.19, 68.62, 68.47, 66.98, 57.77, 33.87, 24.49, 21.07, 20.14, 19.88, 19.71, 18.58, 18.28, 18.17, -0.01, -1.46, -1.84, -3.80. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{62}H_{69}NO_{13}SiNa$, 1086.4436; found 1086.4643.

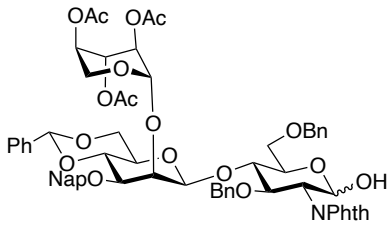
Benzyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (12): Compound was synthesized according to reported literature[1] (20.1 g, 22.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 to 6.69 (29H, m, H-Ar), 5.12 (1H, m, H-1 GlcN), 4.99 (1H, d, PhC<u>H</u>H, *J* = 12.1 Hz), 4.80 (8H, m, PhC<u>H</u>H, 3x Ph<u>CH</u>$_2$, H-1 Fuc), 4.46 (2H, m, PhCH<u>H</u>, PhCH<u>H</u>), 4.18 (2H, m, H-2 GlcN, H-3 GlcN), 4.11 (1H, m, H-2 Fuc), 4.03 (2H, m, H-5 Fuc, H-4 GlcN), 3.90 (3H, m, H-6a GlcN, H-6b GlcN, H-3 Fuc), 3.79 (1H, O<u>H</u>), 3.70 (1H, s, H-4 Fuc), 3.57 (1H, m, H-5 GlcN), 1.14 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.77, 138.55, 138.51, 138.45, 138.36, 138.08, 137.65, 137.11, 133.61, 131.67, 128.48, 128.43, 128.41, 128.38, 128.36, 128.33, 128.30, 128.26, 128.23, 128.21, 128.19, 128.11, 128.10, 128.03, 128.00, 127.94, 127.91, 127.88, 127.83, 127.78, 127.73, 127.68, 127.65, 127.64, 127.60, 127.56, 127.53, 127.52, 127.47, 127.26, 127.21, 123.17, 100.14, 98.61, 97.37, 97.31, 91.80, 84.34, 83.71, 81.28, 79.30, 79.11, 78.01, 77.63, 77.50, 77.39, 77.28, 77.08, 76.76, 76.51, 76.40, 75.10, 74.94, 74.76, 74.62, 74.22, 74.19, 73.72, 73.44, 73.15, 72.99, 72.92, 72.43, 70.80, 70.70, 68.50, 66.87, 66.61, 55.62, 55.39, 16.79, 16.64, 15.59, 0.03. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{55}H_{55}NO_{11}Na$, 928.3673; found 928.3342.

Dimethylthexylsilyl [4,6-*O*-benzylidine-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl]- (1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (15): Compound **10** (17.0 g, 15.9 mmol), was dissolved in DCM (200 mL), followed by the addition of 0.1M NaOMe in MeOH (20 mL), and stirred for 3 h after which the reaction was quenched by AcOH (5 mL). The solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (8: 2, v: v to 6: 4, v: v) gave the product as a white amorphous powder. (14.4 g, 88%). R_f = 0.54 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 to 6.74 (26H, m, H-Ar), 5.52 (1H, s, PhC<u>H</u> of benzylidene), 5.31 (1H, d, H-1 GlcN, *J* = 8.0 Hz), 4.85 (3H, m, PhCH<u>H</u>, C<u>H</u>$_2$ of Nap), 4.66 (2H, m, PhC<u>H</u>H, H-1 Man), 4.45 (2H, m, PhC<u>H</u>$_2$), 4.38 (1H, dd, H-3 GlcN, *J* = 10.7 Hz, 8.6 Hz), 4.09 (5H, m, H-2 GlcN, H-2 Man, H-3 Man, H-4 Man, H-6b Man), 3.79 (1H, dd, H-6a Man, *J* = 11.4 Hz, 3.1 Hz), 3.63 (3H, m, H-5 GlcN, H-6a GlcN, H-6b GlcN), 3.53 (1H, dd, H-4 GlcN, *J* = 9.6 Hz, 3.1 Hz), 3.19 (1H, m, H-5 Man), 2.63(1H, O<u>H</u>), 1.35 [1H, m, C<u>H</u>(CH$_3$)$_2$ of TDS], 0.58 [12H, m,C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], -0.08 to 0.09 (6H, 2s, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.12, 138.48, 137.85, 137.49, 135.41, 133.68, 133.22, 133.02, 131.66, 129.11, 128.92, 128.44, 128.38, 128.28, 128.24, 128.21, 128.20, 127.93, 127.91, 127.80, 127.70, 127.67, 127.10, 127.00, 126.56, 126.23, 126.12, 126.11, 126.05, 125.94, 125.74, 125.65, 123.05, 101.53, 100.80, 93.43, 78.93, 78.72, 78.21, 77.39, 77.33, 77.21, 77.01, 76.95, 76.80, 76.69, 74.53, 74.35, 73.61, 73.38, 72.35, 69.61, 68.85, 68.68, 68.53, 66.83, 60.37, 57.84, 53.41, 33.87, 24.48, 21.03, 20.22, 19.87, 19.69, 18.28, 18.16, 14.18, -0.02, -1.85, -3.79. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{60}H_{67}NO_{12}SiNa$, 1044.4330 ; found 1044.4541.

Dimethylthexylsilyl [2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidine-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (16): Imidate donor **11** (9.4 g, 21.1 mmol) and acceptor **15** (14.4 g, 14.1 mmol), were dissolved in DCM (250 mL) and stirred with pre-activated molecular sieves (30 g) for 20 min. The mixture was then cooled down to -20 ºC, followed by the addition of TMSTOf (1.15 mL, 6.3 mmol). The reaction mixture was warmed up to -10 ºC over a period of 30 min, after which it was quenched with Et_3N (5 mL). The sieves were filtered off and the mixture was concentrated *in vacuo* to give the crude product as a brown syrup. Silica gel column chromatography with Tol: EtOAc (9.5: 0.5, v: v to 8: 2, v: v) yielded the product as white amorphous powder. (16.3 g, 90%). R_f = 0.50 (Tol: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 to 6.79 (26H, m, H-Ar), 5.48 (1H, s, PhC<u>H</u> of benzylidene), 5.35 (1H, d, H-1 GlcN, *J* = 8.1 Hz), 5.15 (1H, d, H1-Xyl, *J* = 3.7 Hz), 5.10 (1H, t, H-3 Xyl, *J* = 5.6 Hz), 5.04 (1H, m, H-4 Xyl), 4.85 (4H, m, H-2 Xyl, C<u>H</u>$_2$ of Nap, PhCH<u>H</u>), 4.58 (3H, m, H-5b Xyl, PhC<u>H</u>H, H-1 Man), 4.35 (3H, m, H-3 GlcN, PhC<u>H</u>$_2$), 4.11 (3H, m, H-2 GlcN, H-6b GlcN, H-2 Man), 3.95 (2H, m, H-4 Man, H-3 Man), 3.61 (3H, m, H-4 GlcN, H-6a Man, H-6b Man), 3.47 (3H, m, H-5a Xyl, H-6a GlcN, H-5 GlcN), 3.15 (1H, m, H-5 Man), 2.09 to 2.00 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.36 [1H, m, C<u>H</u>(CH$_3$)$_2$ of TDS], 0.60 [12H, m, C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], 0.09 to -0.06 (6H, 2s, 2xC<u>H</u>$_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.90, 169.91, 169.37, 169.00, 138.81, 137.75, 137.47, 135.68, 133.62, 133.25, 132.94, 131.67, 129.00, 128.92, 128.43, 128.24, 128.19, 128.06, 127.86, 127.83, 127.79, 127.67, 127.56, 127.43, 126.88, 126.13, 126.11, 126.07, 125.85, 125.44, 125.27, 123.03, 102.30, 101.53, 99.17, 93.39, 80.92, 78.26, 77.34, 77.23, 77.03, 76.96, 76.76, 76.71, 74.72, 74.58, 74.32, 73.53, 71.95, 68.98, 68.68, 68.56, 68.35, 67.34, 60.26, 57.77, 33.88, 30.89, 24.49, 21.43, 20.98, 20.92, 20.80, 19.88, 19.70, 18.28, 18.17, -0.02, -1.84, -3.46, -3.74. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{71}H_{81}NO_{19}SiNa$, 1302.5070; found 1302.5166.

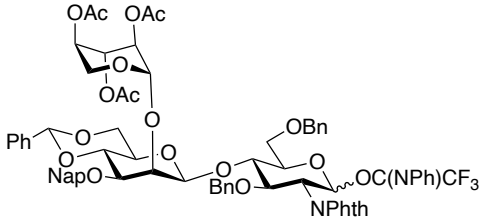


2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidine-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-α/β-D-glucopyranoside (S5): Compound **16** (16.2 g, 12.7 mmol) was dissolved in pyridine (150 mL) followed by dropwise addition of HF in pyridine (70% HF, 30% pyridine; 25 mL). The mixture was stirred for 15 h after which it was quenched by solid $NaHCO_3$ (50 g), till all CO_2 bubbling stopped. The salts were filtered off, the solvent was evaporated *in vacuo*, and the residue was re-dissolved in DCM, followed by washing with water (300 mL) and saturated $NaHCO_3$ (300 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated, and the residue was purified using silica gel column chromatography (Pet. Ether: EtOAc, 8: 2, v: v to Pet: EtOAc, 4: 6, v: v), which provided the product as a white foamy solid. (12.2 g, 84 %). R_f = 0.34 (Pet. Ether: EtOAc, 1: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 to 6.71 (26H, m, H-Ar), 5.45 (1H, s, PhC<u>H</u> of benzylidene), 5.34 (1H, d, H-1 GlcN, *J* = 8.9 Hz), 5.03 (3H, m, H-4 Xyl, H-3 Xyl, H-1 Xyl), 4.82 (4H, m, H-2 Xyl, C<u>H</u>$_2$ of Nap, PhCH<u>H</u>), 4.60 (2H, m, H-5b Xyl, PhC<u>H</u>H), 4.44 (2H, m, H-3 GlcN, H-1 Man), 4.30 (2H, m, PhC<u>H</u>$_2$), 4.07 (3H, m, H-2 GlcN, H-6b GlcN, H-2 Man), 3.89 (2H, m, H-4 Man, H-3 Man), 3.66 (3H, m, H-4 GlcN, H-6a Man, H-6b Man), 3.40 (3H, m, H-5a Xyl, H-6a GlcN, H-5 GlcN), 3.09 (1H, m, H-5 Man), 2.16 to 1.92 (9H, 3s, 3x C<u>H</u>$_3$ of Ac); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.94, 169.27, 168.97, 168.10, 155.37, 138.74, 137.42, 137.37, 135.64, 133.76, 133.24, 132.93, 131.55, 128.96, 128.49, 128.20, 128.09, 128.00, 127.83, 127.66, 127.31, 126.98, 126.91, 126.13,

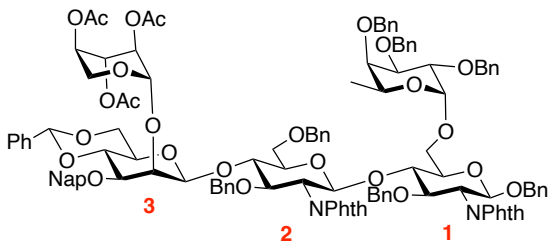


126.03, 125.88, 125.34, 123.28, 101.94, 101.54, 99.05, 92.99, 80.42, 78.23, 77.33, 77.21, 77.01, 76.88, 76.69, 75.04, 74.59, 74.51, 73.56, 71.90, 68.57, 68.29, 68.09, 67.20, 59.95, 57.54, 55.75, 20.98, 20.93, 20.79, 14.17, -0.02. MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{63}H_{63}NO_{19}Na$, 1160.3892; found 1160.3767.

(*N*-Phenyl)-2,2,2-trifluoroacetimidate 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidine-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy- 2-phthalimido-α/β-D-glucopyranoside (17): Compound **S5** (12.2 g, 10.7 mmol) was dissolved in DCM (150 mL), followed by the addition of 2,2,2- Trifluoro-*N*-phenylacetimidoyl chloride (2.7 mL, 12.8 mmol) and DBU (1.6 mL, 10.7 mmol). The reaction mixture was stirred for 30 min, after which the solvent was evaporated and the residue was purified using silica gel column chromatography (Pet. Ether: EtOAc, 9: 1, v: v to Pet. Ether: EtOAc, 1: 1, v: v), which provided the product as an off-white foamy powder. (12.5 g, 87%). R_f = 0.61 (Pet. Ether: EtOAc, 1: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 to 6.55 (31H, m, H-Ar), 5.45 (1H, s, PhC<u>H</u> of benzylidene), 5.34 (1H, d, H-1 GlcN$^\beta$, *J* = 8.5 Hz), 5.29 (1H, d, H-1 GlcN$^\alpha$, *J* = 3.3 Hz), 5.17 to 4.90 (4H, m, H-3 Xyl, H-4 Xyl, H-1 Xyl, PhC<u>H</u>H), 4.89 to 4.70 (4H, m, H-2 Xyl, C<u>H</u>$_2$ of Nap, PhCH<u>H</u>), 4.62 (2H, m, H-5b Xyl, PhC<u>H</u>H), 4.54 to 4.33 (3H, m, H-2 GlcN$^\alpha$, H-3 GlcN, H-1 Man), 4.33 to 4.20 (2H, m, PhC<u>H</u>H, PhCH<u>H</u>), 4.16 to 3.93 (4H, m, H-2 GlcN$^\beta$, H-6b GlcN, H-2 Man, H-3 Man), 3.86 (1H, m, H-4 Man), 3.63 (3H, m, H-4 GlcN, H-6a Man, H-6b Man), 3.48 (1H, m, H-5a Xyl), 3.37 (2H, m, H-6a GlcN, H-5 GlcN), 3.08 (1H, m, H-5 Man), 2.18 to 1.92 (9H, 3s, 3x C<u>H</u>$_3$ of Ac); ^{13}C NMR (101 MHz, $CDCl_3$): δ170.00, 169.97, 169.30, 169.18, 169.01, 168.11, 138.96, 138.69, 137.39, 137.30, 135.58, 135.07, 134.18, 133.79, 133.24, 132.94, 131.54, 129.35, 129.00, 128.51, 128.21, 128.12, 128.09, 128.06, 128.05, 127.86, 127.85, 127.83, 127.77, 127.67, 127.32, 126.99, 126.94, 126.89, 126.33, 126.14, 126.13, 126.05, 125.99, 125.90, 125.34, 125.30, 123.59, 123.30, 120.42, 104.98, 101.93, 101.56, 101.28, 99.16, 99.04, 93.01, 92.90, 80.37, 78.23, 77.31, 76.99, 76.84, 76.67, 76.00, 75.07, 74.61, 74.49, 74.15, 73.58, 71.92, 71.79, 69.99, 68.55, 68.27, 68.07, 67.98, 67.70, 67.21, 66.97, 59.94, 59.48, 57.53, 55.72, 21.07, 20.98, 20.95, 20.93, 20.79, -0.03. Compound was unstable under MALDI-TOF-MS conditions.

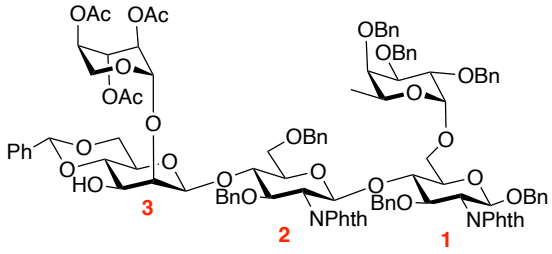


Benzyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidine-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (18): Donor **17** (12.5 g, 9.5 mmol) and acceptor **12** (10.3 g, 11.4 mmol), were dissolved in DCM (100 mL) and stirred with pre-activated molecular sieves (25 g) for 20 min. The mixture was then cooled down to -60 ºC, followed by the addition of TMSTOf (619 μL, 3.4 mmol). The reaction mixture was warmed up to -40 ºC over a period of 45 min, after which it was quenched with Et_3N (5 mL). The sieves were filtered off and the mixture was concentrated *in vacuo* to give the crude product as a brown syrup. Silica gel column chromatography with DCM: Acetone (9.9: 0.1, v: v to 9: 1, v: v) yielded the product as white amorphous powder. (16.5 g, 85 %). R_f = 0.58 (DCM: Acetone, 9.5: 0.5, v: v). ^{1}H NMR (400 MHz,



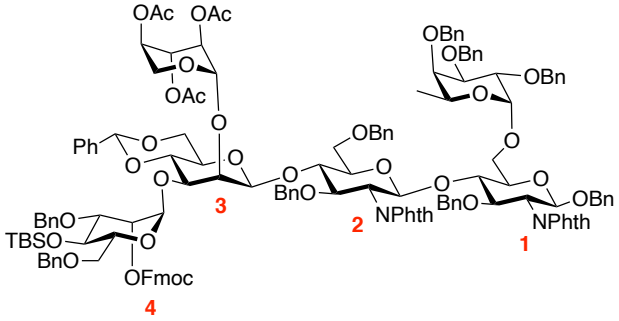
$CDCl_3$): δ 7.94 to 6.61 (60H, m, H-Ar), 5.48 (1H, d, H-1 GlcN-2, *J* = 8.4 Hz), 5.44 (1H, s, PhC<u>H</u> of benzylidene), 5.02 (1H, d, H-1 Xyl, *J* = 3.4 Hz), 4.95 (4H, m, H-4 Xyl, H-3 Xyl, H-1 GlcN-1, C<u>H</u>H of Nap), 4.80 (9H, m, H-2 Xyl, H-1 Fuc, 3x PhC<u>H</u>$_2$, CH<u>H</u> of Nap), 4.55 (4H, m, PhCH<u>H</u>, PhC<u>H</u>H, PhCH<u>H</u>, H-1 Man-3), 4.38 (5H, m, H-5b Xyl, PhC<u>H</u>H, PhC<u>H</u>$_2$, H-3 GlcN-1), 4.22 (4H, m, H-2 GlcN-2, PhC<u>H</u>H, PhCH<u>H</u>, H-3 GlcN-2), 4.09 (5H, m, H-2 GlcN-1, H-6b GlcN-1, H-2 Man-3, H-4 Fuc, H-2 Fuc), 3.92 (4H, m, H-5 Fuc, H-3 Fuc, H-4 Man-3, H-3 Man-3), 3.67 (4H, m, H-6b GlcN-2, H-6b Man-3, H-5 GlcN-2, H-4 GlcN-2), 3.41 (4H, m, H-6a GlcN-2, H-6a GlcN-1, H-6a Man-3, H-5 GlcN-1), 3.23 (2H, m, H-5a Xyl, H-4 GlcN-1), 3.03 (1H, m, H-5 Man-3), 2.09 to 1.73 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 0.99 (1H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.85, 169.25, 169.02, 167.63, 138.97, 138.84, 138.73, 138.62, 137.53, 137.50, 137.04, 135.67, 133.92, 133.81, 133.48, 133.27, 132.94, 131.62, 131.39, 128.91, 128.52, 128.47, 128.43, 128.40, 128.37, 128.35, 128.28, 128.17, 128.16, 128.12, 128.05, 128.03, 127.91, 127.86, 127.84, 127.74, 127.66, 127.60, 127.56, 127.54, 127.46, 127.44, 127.42, 127.33, 127.32, 126.94, 126.82, 126.16, 126.15, 126.10, 125.85, 125.39, 123.58, 123.07, 101.79, 101.54, 98.87, 97.03, 96.84, 96.63, 80.00, 79.44, 78.19, 77.59, 77.44, 77.12, 76.88, 76.80, 76.73, 76.42, 75.56, 75.13, 74.73, 74.46, 74.33, 74.08, 73.86, 73.81, 73.16, 73.07, 72.59, 71.63, 69.94, 69.41, 69.02, 68.55, 68.46, 68.14, 67.44, 66.00, 64.34, 60.27, 56.59, 55.78, 29.65, 20.91, 20.75, 20.52, 16.61, 16.43, 14.19. MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{118}H_{116}N_2O_{29}Na$, 2047.7561; found 2048.7192.

Benzyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidine-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (19): Compound **18** (16.1 g, 7.9 mmol) was dissolved in the solvent system DCM (200 mL) and H_2O (20 mL), followed by the addition of DDQ (3.6 g, 15.8 mmol) and β-pinene (3.7 mL, 23.7 mmol). The mixture was stirred in dark for 48 h after which reaction did not proceed any further. The solvent was evaporated *in vacuo* and the residue was diluted by DCM (300 mL) and washed with water (200 mL) and sat. $NaHCO_3$ (300 mL). The organic phase was dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography and using Tol: EtOAc (9: 1, v: v to 7: 3, v: v). The recovered starting material was re-subjected to the above reaction conditions, and purification by silica gel column chromatography gave the combined product as yellow amorphous solid. (9.7 g, 64%). R_f = 0.47 (Tol: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 to 6.67 (48H, m, H-Ar), 5.59 (1H, d, H-1 GlcN-2, *J* = 8.2 Hz), 5.42 (1H, s, PhC<u>H</u> of benzylidene), 4.93 (9H, m, H-1 Fuc, H-1 GlcN-1, H-2 Xyl, H-4 Xyl, H-3 Xyl, 2x PhC<u>H</u>$_2$), 4.75 (4H, m, PhC<u>H</u>H, PhC<u>H</u>$_2$, H-1 Xyl), 4.61 (5H, m, PhCH<u>H</u>, H-1 Man-3, PhC<u>H</u>$_2$, PhCH<u>H</u>), 4.48 (3H, m, PhC<u>H</u>$_2$, H-3 GlcN-1), 4.33 (3H, m, H-2 GlcN-2, PhC<u>H</u>H, H-3 GlcN-2), 4.20 (3H, m, H-2 GlcN-1, H-3 Man-3, H-2 Fuc), 4.02 (6H, m, H-5b Xyl, H-5 Fuc, H-6b GlcN-2, H-2 Man-3, H-3 Fuc, H-4 Fuc), 3.88 (2H, m, H-6b Man-3, H-4 Man-3), 3.75 (1H, d, H-6b GlcN-1, *J* = 11.2 Hz), 3.60 (4H, m, H-5 GlcN-1, H-5 GlcN-2, H-6a Man-3, H-4 GlcN-2), 3.37 (3H, m, H-6a GlcN-1, H-6a GlcN-2, H-4 GlcN-1), 3.13 (1H, m, H-5 Man-3), 3.03 (1H, bs, O<u>H</u>), 2.86 (1H, dd, H-5a Xyl, *J* = 11.8 Hz, 8.9 Hz), 2.07 to 1.79 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.02 (1H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) : δ 171.10, 169.72, 169.68, 169.55, 169.45, 169.29, 168.44, 167.68, 138.86, 138.80, 138.73, 138.57, 138.43, 137.58, 137.25, 137.02, 133.95, 133.61, 133.30, 131.64, 129.06, 128.68, 128.64, 128.57, 128.47, 128.41, 128.38, 128.32, 128.26, 128.22, 128.20, 128.15, 128.10, 128.07, 128.01, 127.99, 127.92, 127.91, 127.85, 127.83, 127.80, 127.67, 127.63, 127.57, 127.54, 127.51, 127.47, 127.39, 127.37, 127.29, 127.21, 127.19, 126.96, 126.37, 126.34, 126.20, 123.68, 123.18, 102.04,

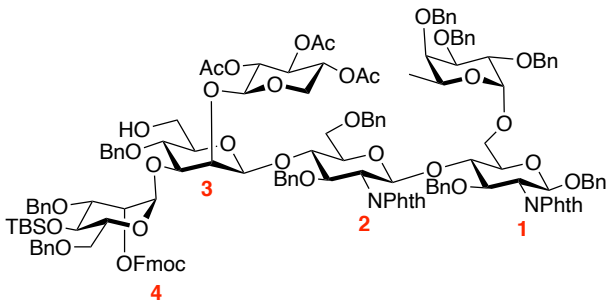


101.52, 99.92, 97.00, 96.71, 96.64, 79.87, 79.48, 79.07, 77.59, 77.55, 77.43, 77.23, 77.05, 76.92, 76.15, 75.21, 74.89, 74.77, 74.38, 74.34, 73.83, 73.77, 73.45, 73.08, 72.58, 70.95, 70.92, 70.66, 70.12, 69.98, 68.44, 68.38, 67.95, 67.43, 66.08, 64.13, 61.58, 60.38, 56.36, 55.83, 21.05, 21.05, 20.77, 20.72, 20.68, 20.66, 16.43, 14.23. MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{107}H_{108}N_2O_{29}Na$, 1884.7038; found 1885.6401.

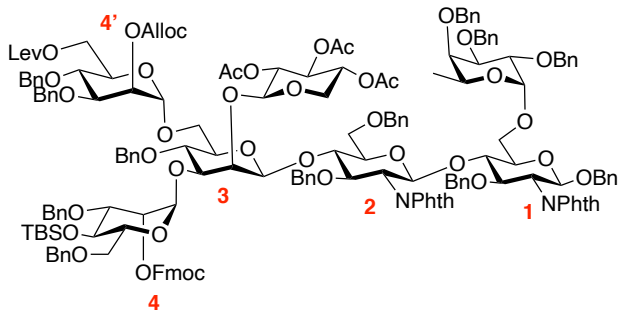
Benzyl [3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-*O*-fluorenylmethoxycarbonyl-α-D-mannopyranosyl]-(1→3)-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4,6-*O*-benzylidine-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (20): A mixture of acceptor **19** (9.3 g, 4.9 mmol) and donor **13** (7.8 g, 9.9 mmol), was stirred in DCM (100 mL) with pre-activated molecular sieves (20 g) for 20 min. The mixture was then cooled down to -30 ºC, followed by the sequential addition of NIS (2.22 g, 9.9 mmol) and TMSTOf (717 μL, 3.96 mmol). The reaction mixture was warmed up to -20 ºC over a period of 30 min, after which it was quenched with pyridine (10 mL). The sieves were filtered off, the mixture was diluted by DCM (200 mL) and washed with 5% $Na_2S_2O_3$ (100 mL) and sat. $NaHCO_3$ (200 mL). The mixture was concentrated *in vacuo* to give the crude product as a brown syrup. Silica gel column chromatography with Tol: EtOAc (9: 1, v: v to 7: 3, v: v) yielded the product as an off-white amorphous powder. (9.7 g, 77 %). R_f = 0.51 (Tol: EtOAc, 8: 2, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 to 6.65 (77H, m, H-Ar), 5.46 (1H, d, H-1 GlcN-2, *J* = 8.6 Hz), 5.40 (2H, m, PhC<u>H</u> of benzylidene, H-2 Man-4), 5.27 (1H, s, H-1 Man-4), 4.96 (7H, m, H-1 Xyl, H-2 Xyl, H-1 GlcN-1, H-4 Xyl, H-3 Xyl), 4.82 (5H, m, H-1 Fuc, 2x PhC<u>H</u>$_2$), 4.72 (2H, m, PhC<u>H</u>$_2$), 4.64 to 4.39(10H, m, C<u>H</u>$_2$ of Fmoc, PhC<u>H</u>$_2$ protons, H-1 Man-3), 4.31 (5H, m, H-3 GlcN-1, PhC<u>H</u>$_2$ protons), 4.16 (8H, m, C<u>H</u> of Fmoc, H-2 GlcN-1, H-2 GlcN-2, H-3 GlcN-2, H-2 Man-3, PhC<u>H</u>$_2$), 4.01 (4H, m, H-4 Man-3, H-3 Man-3, H-2 Fuc, H-4 Fuc), 3.91 (2H, m, H-5 Fuc, H-3 Fuc), 3.77 (6H, m, H-6b GlcN-1, H-6a Man-4, H-6b Man-4, H-3 Man-4, H-5 GlcN-1, H-4 GlcN-2), 3.63 (4H, m, H-4 Man-4, H-5 Man-4, H-5 GlcN-2, H-6b GlcN-2), 3.50 (1H, dd, H-6b Man-3, *J* = 11.2 Hz, 2.9 Hz), 3.29 (4H, m, H-5a Xyl, H-6a GlcN-2, H-6a GlcN-1, H-6a Man-3), 2.96 (1H, m, H-5 Man-3), 2.08 to 1.78 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 0.99 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.5 Hz), 0.80 (9H, s, 3x C-C<u>H</u>3 of TBS), 0.03 to -0.02 (6H, d, 2x C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$) : δ 169.58, 169.36, 167.71, 154.51, 143.65, 143.39, 143.34, 141.27, 141.24, 138.97, 138.95, 138.83, 138.69, 138.63, 138.41, 137.91, 137.87, 137.78, 137.24, 137.11, 134.00, 133.54, 131.71, 129.07, 128.72, 128.65, 128.59, 128.51, 128.46, 128.44, 128.42, 128.35, 128.27, 128.18, 128.11, 128.08, 127.98, 127.91, 127.87, 127.84, 127.76, 127.73, 127.66, 127.61, 127.56, 127.53, 127.51, 127.49, 127.44, 127.40, 127.31, 127.22, 127.13, 126.92, 125.98, 125.38, 125.34, 123.15, 120.01, 101.71, 101.20, 99.59, 98.84, 97.24, 97.13, 96.70, 79.48, 79.33, 78.06, 77.76, 77.46, 77.34, 77.14, 76.82, 76.61, 76.03, 75.69, 75.29, 74.79, 74.61, 74.45, 74.02, 73.82, 73.53, 73.35, 73.26, 73.13, 72.62, 71.58, 70.96, 70.65, 70.41, 70.25, 69.99, 69.66, 68.64, 68.34, 68.08, 67.99, 67.27, 66.07, 64.49, 61.17, 56.46, 55.83, 46.57, 30.93, 26.05, 26.01, 21.50, 20.84, 20.81, 20.72, 18.20, 16.49, -3.87, -4.95, -5.25. MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{148}H_{154}N_2O_{36}SiNa$, 2585.9948; found 2586.1830.



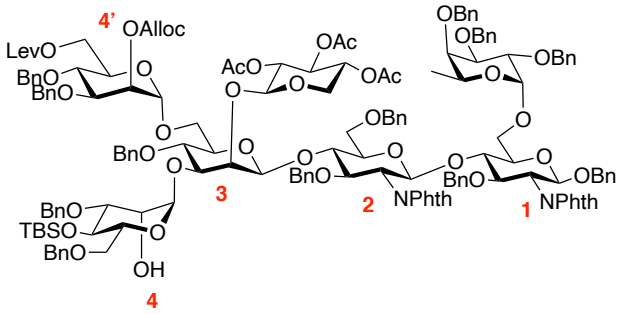
Benzyl [3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-*O*-fluorenylmethoxycarbonyl-α-D-mannopyranosyl-(1→3)-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (21): Compound **20** (9.7 g, 3.8 mmol) was dissolved in DCM (150 mL) and stirred with pre-activated molecular sieves (30 g) for 30 min, after which the temperature was brought down to -70 °C. The mixture was stirred at this temperature for another 30 min after which Et_3SiH (1.2 mL, 7.6 mmol) and $PhBCl_2$ (1.5 mL, 11.4 mmol). The mixture was stirred at this temperature for 20 min after which it was quenched with pyridine (20 mL). The mixture was further diluted by DCM (200 mL), the sieves were filtered off, and the mixture was washed with sat. $NaHCO_3$ (200 mL). The organic phase was dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 7: 3, v: v) gave the product as yellow amorphous powder. (7.1 g, 72%). R_f = 0.27 (Tol: EtOAc, 8: 2, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 to 6.59 (80H, m, H-Ar), 5.37 (1H, d, H-1 GlcN-2, *J* = 8.3 Hz), 5.25 (1H, s, H-2 Man-4), 5.16 (1H, s, H-1 Man-4), 5.03 to 4.80 (9H, m, H-4 Xyl, H-3 Xyl, H-2 Xyl, H-1 Fuc, H-1 GlcN-1, H-1 Xyl, PhC$\underline{H}_2$ protons), 4.70 (5H, m, H-1 Man-3, PhC$\underline{H}_2$, C$\underline{H}_2$ of Fmoc), 4.53 (6H, m, PhC$\underline{H}_2$ protons), 4.39 (4H, m, H-3 GlcN-1, PhC$\underline{H}_2$ protons), 4.18 (10H, m, C$\underline{H}$ of Fmoc, H-2 GlcN-2, H-2 GlcN-1, H-5b Xyl, H-4 Man-4, H-3 GlcN-2, H-2 Man-3, PhC$\underline{H}_2$ protons), 3.92 (4H, m, H-5 Fuc, H-3 Man-3, H-2 Fuc, H-4 Fuc), 3.70 (6H, m, H-6b GlcN-2, H-6b Man-3, H-6a Man-4, H-6b Man-4, H-4 GlcN-2, H-3 Fuc), 3.50 (5H, m, H-6b GlcN-1, H-6a Man-3, H-4 GlcN-1, H-5 GlcN-2, H-5 GlcN-1), 3.28 (4H, m, H-5a Xyl, H-6a GlcN-2, H-6a GlcN-1, H-4 Man-3), 2.92 (1H, m, H-5 Man-3), 2.09 to 1.72 (9H, 3s, 3x C$\underline{H}_3$ of Ac), 0.94 (3H, d, C$\underline{H}_3$ of Fuc, *J* = 6.5 Hz), 0.79 (9H, s, 3x C-C$\underline{H}$3 of TBS), 0.01 to -0.02 (6H, d, 2x C$\underline{H}_3$-Si of TBS; ^{13}C NMR (151 MHz, $CDCl_3$) : δ 169.68, 169.62, 169.42, 167.68, 154.55, 143.58, 143.34, 141.29, 141.27, 138.97, 138.83, 138.70, 138.58, 138.42, 137.91, 137.79, 137.73, 137.11, 134.15, 133.84, 133.48, 131.69, 130.35, 129.08, 128.58, 128.55, 128.47, 128.44, 128.42, 128.27, 128.23, 128.21, 128.19, 128.17, 128.10, 128.04, 127.95, 127.89, 127.86, 127.81, 127.71, 127.67, 127.58, 127.56, 127.54, 127.51, 127.43, 127.39, 127.31, 127.23, 126.89, 126.86, 125.45, 125.35, 123.15, 120.03, 100.99, 99.89, 98.89, 97.23, 97.18, 96.67, 79.77, 79.58, 79.25, 77.75, 77.43, 77.30, 77.09, 76.88, 76.74, 76.22, 75.71, 75.67, 75.34, 75.20, 74.78, 74.74, 74.48, 74.21, 74.03, 73.88, 73.46, 73.27, 73.17, 73.14, 72.56, 72.29, 71.34, 70.32, 70.23, 70.12, 69.98, 69.66, 68.31, 67.99, 67.90, 66.04, 64.49, 61.83, 60.72, 56.52, 55.81, 46.58, 30.96, 26.04, 21.50, 20.86, 20.79, 20.72, 18.17, 16.48, 0.05, -3.83, -4.94. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{148}H_{156}N_2O_{36}SiNa$, 2588.0105; found 2589.5942.



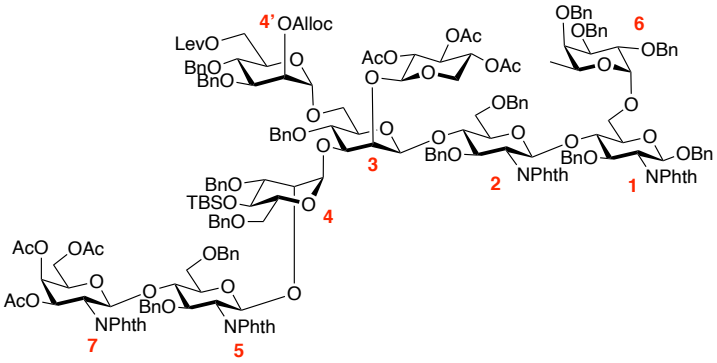
Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-levulenoyl-α-D-mannopyranosyl]-(1→6) -3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-*O*-fluorenylmethoxycarbonyl-α-D- mannopyranosyl-(1→3)-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (4a): A mixture of acceptor **21** (7.1 g, 2.8 mmol) and donor **14** (7.9 g, 11.1 mmol), was stirred in DCM (100 mL) with pre-activated molecular sieves (20 g) for 20 min. The mixture was then cooled down to -30 ºC, followed by the addition of TMSTOf (603 μL, 3.33 mmol). The reaction mixture was warmed up to -15 ºC over a period of 30 min, after which it was quenched with pyridine (10 mL). The sieves were filtered off and the mixture was concentrated *in vacuo.* The residue was purified by silica gel column chromatography using DCM to DCM: Acetone (95: 5, v: v) which yielded the product as a white amorphous powder. (6.6 g, 75 %). R_f = 0.64 (DCM: Acetone, 9.5: 0.5, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 to 6.59 (85H, m, H-Ar), 5.78 (1H, m, C<u>H</u>=CH_2 of alloc), 5.33 (2H, m, H-2 Man-4, H-1 GlcN-2), 5.19 (4H, m, H-2 Man-4', H-1 Man-4, CH=C<u>H</u>$_2$ of alloc), 5.07 (2H, m, H-4 Xyl, H-3 Xyl), 4.88 (2H, m, H-1 GlcN-1, PhCH<u>H</u>), 4.97 (1H, m, H-2 Xyl), 4.84 to 4.71 (10H, m, H-1 Fuc, H-1 Man-4', H-1 Xyl, PhC<u>H</u>$_2$ protons), 4.64 (4H, m, H-1 Man-3, PhC<u>H</u>H, PhC<u>H</u>$_2$ protons), 4.58 to 4.37 (14H, PhC<u>H</u>$_2$ protons, C<u>H</u>$_2$ of Fmoc, OC<u>H</u>$_2$ of alloc), 4.34 (2H, m, H-3 GlcN-1, PhCH<u>H</u>), 4.30 to 4.13 (8H, m, C<u>H</u> of Fmoc, H-2 GlcN-1, H-2 GlcN-2, H-5b Xyl, H-3 GlcN-2, PhC<u>H</u>$_2$ protons), 4.12 to 3.95 (8H, m, H-6a Man-4', H-6b Man-4', H-2 Man-3, H-4 Man-4, H-2 Fuc, H-3 Man-3), 3.93 to 3.76 (7H, m, H-6b Man-3, H-5 Fuc, H-5 Man-4, H-5 Man-4' , H-3 Man-4', H-4 Fuc), 3.67 (3H, m, H-6a Man-4, H-6b Man-4, H-3 Fuc), 3.59 (6H, m, H-6b GlcN-2, H-6b GlcN-1, H-6a Man-3, H-4 GlcN-2, H-5 GlcN-1, H-3 Man-4), 3.49 (3H, m, H-6a GlcN-2, H-4 GlcN-1, H-5 GlcN-2), 3.26 (2H, m, H-6a GlcN-1, H-4 Man-3), 3.04 (2H, m, H-5a Xyl, H-5 Man-3), 2.56 (2H, t, COOC<u>H</u>$_2$C<u>H</u>$_2$ of Lev, *J* = 6.6 Hz), 2.40 (2H, t, COOC<u>H</u>$_2$C<u>H</u>$_2$ of Lev, *J* = 6.6 Hz), 2.07 (3H, s, CH2COC<u>H</u>$_3$ of Lev), 2.04 to 1.69 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 0.91 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.5 Hz), 0.76 (9H, s, 3x C-C<u>H</u>$_3$ of TBS), 0.03 to -0.07 (6H, d, 2x -C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.01, 206.46, 172.31, 169.81, 169.49, 169.41, 167.65, 154.49, 154.34, 143.62, 143.31, 141.26, 141.23, 138.96, 138.92, 138.83, 138.60, 138.44, 138.37, 138.31, 138.13, 137.91, 137.84, 137.08, 133.49, 131.59, 128.59, 128.51, 128.47, 128.42, 128.39, 128.28, 128.26, 128.24, 128.19, 128.15, 128.07, 127.99, 127.97, 127.91, 127.85, 127.79, 127.67, 127.61, 127.54, 127.52, 127.50, 127.47, 127.39, 127.37, 127.32, 127.29, 127.26, 127.20, 127.11, 126.85, 125.38, 125.35, 123.15, 119.99, 118.87, 101.97, 100.28, 99.44, 97.38, 97.27, 97.08, 96.59, 80.58, 79.37, 78.74, 77.79, 77.72, 77.49, 77.27, 77.06, 76.96, 76.85, 76.61, 76.14, 75.56, 75.06, 75.02, 74.87, 74.72, 74.63, 74.56, 74.51, 74.07, 73.66, 73.30, 73.06, 72.99, 72.57, 72.20, 71.92, 71.88, 71.36, 71.31, 71.25, 70.29, 69.92, 69.88, 69.71, 69.27, 68.61, 68.00, 66.12, 65.97, 64.53, 63.15, 62.02, 56.39, 55.77, 53.46, 46.54, 37.87, 30.96, 29.81, 27.88, 26.03, 20.74, 20.51, 18.19, 16.44, 0.03, -3.91, -5.02. MALTI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{177}H_{188}N_2O_{45}SiNa$, 3112.2151; found 3113.0973.



Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-levulenoyl-α-D-mannopyranosyl-(1→6)-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl-(1→3)-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (22): Compound **4a** (6.6 g, 2.1 mmol) was dissolved in DCM (80 mL) followed by the addition of Et_3N (10 mL). The mixture was stirred for 3 h after which it was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using solvent gradient DCM to DCM: Acetone (9.5: 0.5, v: v) which afforded the product as an off-white amorphous powder. (4.9 g, 81%). R_f = 0.51 (DCM: Acetone, 9.5: 0.5, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 to 6.55 (65H, m, H-Ar), 5.80 (1H, m, C<u>H</u>=CH_2 of alloc), 5.35 (1H, d, H-1 GlcN-2, *J* = 8.5 Hz), 5.31 to 4.94 (10H, m, H-2 Xyl, H-4 Xyl, H-3 Xyl, H-2 Man-4', H-1 Man-4, CH=C<u>H_2</u> of alloc), 4.94 to 4.71 (11H, m, H-1 Fuc, H-1 Man-4', H-1 Xyl, H-1 GlcN-1, PhC<u>H_2</u> protons), 4.67 (3H, m, H-1 Man-3, PhC<u>H_2</u>), 4.66 to 4.36 (16H, m, PhC<u>H_2</u> protons, OC<u>H_2</u> of alloc), 4.28 (3H, m, PhC<u>H_2</u>, H-3 GlcN-1), 4.20 to 4.02 (8H, m, H-2 GlcN-2, H-2 GlcN-1, H-5b Xyl, H-6a Man-4, H-6b Man-4', H-3 Man-4', H-3 Man-3, H-3 GlcN-2), 3.99 to 3.74 (9H, m, H-6b Man-3, H-5 Fuc, H-4 Man-4, H-3 Man-4, H-5 Man-4, H-5 Man-4', H-2 Fuc, H-2 Man-3, H-3 Man-4'), 3.72 to 3.42 (12H, m, H-6a GlcN-2, H-6b GlcN-2, H-6b GlcN-1, H-6a Man-3, H-4 GlcN-1, H-6a Man-4, H-6b Man-4, H-3 Fuc, H-4 GlcN-2, H-5 GlcN-1, H-5 GlcN-2, H-2 Man-4), 3.27 (2H, m, H-6a GlcN-1, H-4 Man-3), 3.06 (2H, m, H-5a Xyl, H-5 Man-3), 2.58 (2H, t, COOC<u>H_2</u>CH_2 of Lev, *J* = 6.6 Hz), 2.42 (2H, t, COOCH_2C<u>H_2</u> of Lev, *J* = 6.6 Hz), 2.09 (3H, s, CH_2COC<u>H</u>3 of Lev), 2.04 to 1.68 (9H, 3s, 3x C<u>H_3</u> of Ac), 0.92 (3H, d, C<u>H_3</u> of Fuc, *J* = 6.5 Hz), 0.79 (9H, s, 3x C-C<u>H</u>3 of TBS), 0.00 to -0.05 (6H, d, 2x C<u>H_3</u>-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 206.38, 172.25, 169.70, 169.50, 169.35, 167.59, 154.29, 138.90, 138.86, 138.79, 138.56, 138.42, 138.27, 138.25, 138.18, 137.86, 137.84, 137.03, 133.41, 131.63, 131.53, 128.52, 128.49, 128.45, 128.41, 128.38, 128.36, 128.33, 128.20, 128.17, 128.13, 128.11, 128.09, 128.04, 128.01, 127.99, 127.96, 127.92, 127.89, 127.82, 127.73, 127.60, 127.53, 127.50, 127.47, 127.46, 127.44, 127.42, 127.39, 127.38, 127.31, 127.27, 127.03, 126.78, 123.06, 118.81, 102.05, 101.37, 99.99, 97.34, 97.22, 97.09, 96.56, 80.62, 79.97, 79.29, 77.84, 77.72, 77.34, 77.23, 77.03, 76.88, 76.71, 76.18, 75.52, 75.11, 75.03, 74.77, 74.68, 74.54, 74.40, 74.05, 73.71, 73.25, 73.02, 72.94, 72.50, 71.90, 71.78, 71.69, 71.44, 71.16, 69.87, 69.80, 69.66, 69.26, 68.56, 68.05, 67.53, 66.23, 65.93, 64.54, 63.09, 61.90, 59.51, 56.36, 55.72, 53.42, 50.77, 38.13, 37.82, 37.08, 32.73, 31.91, 31.22, 30.01, 29.76, 29.71, 29.68, 29.64, 29.34, 27.85, 27.07, 25.98, 25.84, 22.68, 20.71, 20.69, 20.50, 18.09, 16.39, 14.11, 13.42, 0.40, -0.01, -3.88, -5.03. MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{162}H_{178}N_2O_{43}SiNa$, 2890.1470; found 2890.5249.

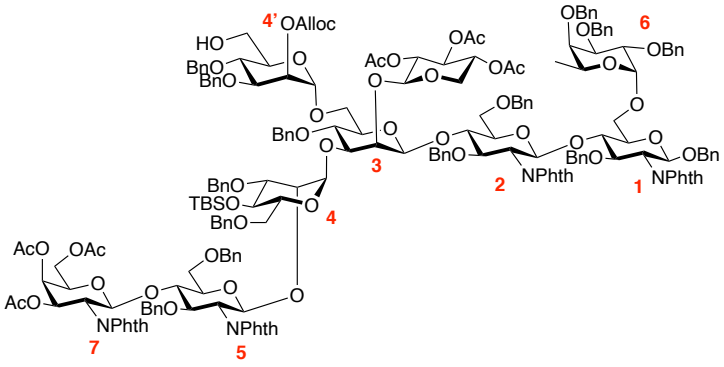


Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-levulenoyl-α-D-mannopyranosyl-(1→6)]-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside-(1→2)-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl-(1→3)]-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (23): A mixture of acceptor **22** (4.8 g, 1.7 mmol) and donor **5** (5.4 g, 5.1 mmol), was stirred in DCM (50 mL) with pre-activated molecular sieves (10 g) for 20 min, after which the mixture was cooled down to -40 ºC, followed by the addition of TfOH (137 μL, 1.53 mmol). The mixture was warmed up to -20 ºC over a period of 30 min, after which it was quenched with Et_3N (1 mL). The sieves were filtered off and the mixture was concentrated *in vacuo.* The residue was purified by silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 1:1, v: v) which afforded the product as an off-white amorphous powder. (5.1 g, 80%). R_f = 0.46 (Tol: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 to 6.61 (86H, m, H-Ar), 6.03 (1H, m, C<u>H</u>=CH_2 of alloc), 5.94 (1H, d, H-3 GalN-7, *J* = 11.1 Hz), 5.57 (1H, d, H-1 GlcN-2, *J* = 8.3 Hz), 5.49 (3H, m, H-2 Man-4', H-1 GlcN-5, CH=C<u>H</u>H of alloc), 5.35 (2H, m, H-4 GalN-7, CH=CH<u>H</u> of alloc), 5.25 (1H, t, H-4 Xyl, *J* = 8.8 Hz), 5.20 to 5.00 (9H, m, H-2 Xyl, H-3 Xyl, H-1 Man-4, 3x PhC<u>H</u>$_2$ protons), 4.99 to 4.89 (5H, m, H-1 Xyl, H-1 GlcN-1, PhC<u>H</u>$_2$ protons), 4.85 (3H, m, H-1 GalN-7, H-1 Man-4', PhC<u>H</u>H), 4.81 to 4.62 (11H, m, H-2 GalN-7, H-2 GlcN-5, H-1 Fuc-6, PhC<u>H</u>$_2$ protons, OC<u>H</u>$_2$ of alloc), 4.61 to 4.43 (9H, m, H-1 Man-3, H-3 GlcN-1, PhC<u>H</u>$_2$ protons), 4.41 to 4.24 (9H, m, H-2 GlcN-2, H-2 GlcN-1, H-3 GlcN-2, H-3 GlcN-5, PhC<u>H</u>$_2$ protons), 4.24 to 4.01 (12H, m, H-6a GalN-7, H-6b GalN-7, H-6a Man-4', H-6b Man-4', H-5a Xyl, H-4 GlcN-1, H-4 GlcN-2, H-4 GlcN-5, H-3 Fuc-6, H-2 Fuc-6, H-4 Man-3, H-3 Man-4), 3.93 (4H, m, H-5 Fuc-6, H-2 Man-4, H-5 GalN-7, PhCH<u>H</u>), 3.79 (5H, m, H-6a GlcN-2, H-6a Man-4, H-2 Man-3, H-5 Man-4', H-5 Man-4), 3.68 (3H, m, H-6a Man-3, H-4 Man-4', H-3 Man-4'), 3.57 (5H, m, H-4 Man-4, H-6b Man-4, H-6a GlcN-5, H-3 Man-3, H-4 Fuc-6), 3.45 (4H, m, H-6b GlcN-2, H-6b Man-3, H-5 GlcN-2, H-5 GlcN-1), 3.16 (2H, m, H-5b Xyl, H-6a GlcN-1), 3.08 (1H, m, H-6b GlcN-1), 2.78 (3H, m, COOC<u>H</u>$_2$CH$_2$ of Lev, H-5 Man-3), 2.54 (3H, m, COOCH$_2$C<u>H</u>$_2$ of Lev, H-6b GlcN-5), 2.33 (3H, s, CH2COC<u>H</u>3 of Lev), 2.23 to 1.86 (19H, m, 6x C<u>H</u>$_3$ of Ac, H-5 GlcN-5), 1.13 (3H, d, C<u>H</u>$_3$ of Fuc-6, *J* = 6.3 Hz), 0.82 (9H, s, 3x C-C<u>H</u>3 of TBS), 0.11 to -0.06 (6H, d, 2x C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 206.42, 172.30, 172.22, 170.30, 170.26, 169.77, 169.69, 169.41, 169.33, 168.09, 167.57, 167.40, 154.34, 138.96, 138.90, 138.82, 138.53, 138.46, 138.43, 138.34, 138.26, 138.17, 138.09, 137.94, 137.82, 137.11, 133.51, 131.96, 131.57, 131.54, 129.12, 129.06, 128.91, 128.78, 128.64, 128.53, 128.48, 128.44, 128.42, 128.39, 128.37, 128.32, 128.31, 128.26, 128.22, 128.19, 128.15, 128.08, 128.00, 127.94, 127.93, 127.90, 127.87, 127.83, 127.78, 127.75, 127.71, 127.66, 127.62, 127.60, 127.54, 127.51, 127.43, 127.37, 127.35, 127.29, 127.25, 127.13, 127.02, 126.87, 125.60, 125.34, 123.87, 123.50, 123.11, 118.91, 101.13, 100.27, 97.33, 97.25, 96.66, 79.27, 77.70, 77.57, 77.45, 77.25, 76.93, 76.49, 75.73, 75.20, 75.00, 74.72, 74.23, 74.02, 73.63, 73.25, 72.92, 72.81, 72.70, 72.56, 71.99, 71.80, 71.61, 71.27, 70.48, 69.95, 69.70, 68.60, 68.07, 67.90, 66.67, 65.97, 60.87, 56.30, 55.78, 55.62, 52.07, 37.85, 31.94, 31.48, 30.24, 29.83, 29.82, 29.70, 29.38, 27.85, 26.05, 26.02, 25.95, 22.72, 21.49, 20.76, 20.71, 20.66, 20.62, 20.53, 20.51,



18.14, 18.06, 17.83, 16.45, 14.19, 0.08, -3.81, -5.26, -5.38. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{210}H_{222}N_4O_{58}SiNa$, 3778.4212; found 3778.5018.

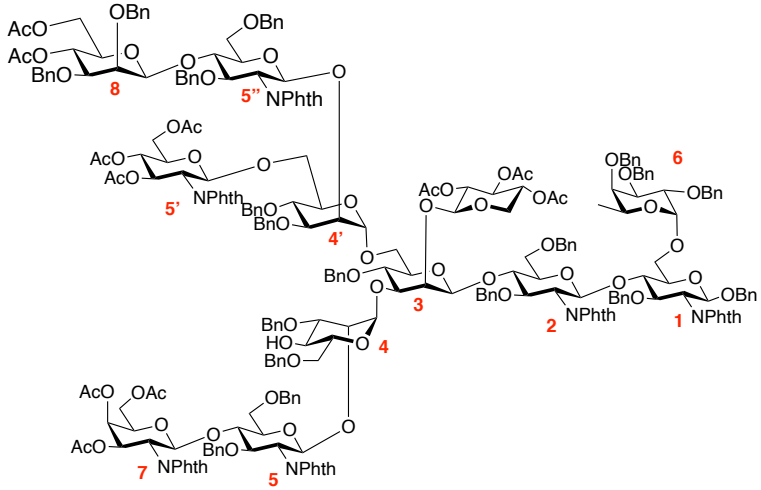
Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside-(1→2)-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D- mannopyranosyl-(1→3)]-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (24): Compound **23** (2.5 g, 0.66 mmol) was dissolved in DCM (20 mL) and MeOH (10 mL), followed by the addition of solid hydrazine acetate (304 mg, 3.3 mmol). The mixture was stirred for 1 h after which it was concentrated *in vacuo* and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (8: 2, v: v to 1:1, v: v) which afforded the product as a white foamy solid. (1.6 g, 66%). R_f = 0.49 (Tol: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 to 6.35 (86H, m, H-Ar), 5.83 (1H, m, C<u>H</u>=CH$_2$ of alloc), 5.74 (1H, dd, H-3 GalN-7, *J* = 11.8 Hz, 3.6 Hz), 5.38 (1H, d, H-1 GlcN-2, *J* = 8.1 Hz), 5.33 (1H, d, H-2 Man-4', *J* = 3.6 Hz), 5.28 (2H, m, H-1 GlcN-5, CH=C<u>H</u>H of alloc), 5.18 (1H, m, CH=CH<u>H</u> of alloc), 5.12 (1H, m, H-4 GalN-7), 5.04 (1H, t, H-4 Xyl, *J* = 8.9 Hz), 4.98 to 4.71 (14H, m, H-2 Xyl, H-3 Xyl, H-1 Man-4, H-1 Xyl, H-1 GlcN-1, PhC<u>H</u>$_2$ protons), 4.65 (4H, m, H-1 GalN-7, H-1 Man-4', PhC<u>H</u>$_2$), 4.60 to 4.41 (11H, m, H-2 GalN-7, H-1 Fuc-6, PhC<u>H</u>$_2$ protons, OC<u>H</u>$_2$ of alloc), 4.41 to 4.24 (7H, m, H-1 Man-3, H-3 GlcN-1, PhC<u>H</u>$_2$ protons), 4.25 to 4.08 (7H, m, H-2 GlcN-2, H-2 GlcN-1, H-2 GlcN-5, H-3 GlcN-2, H-3 GlcN-5, PhC<u>H</u>H protons), 4.07 to 3.81 (9H, m, H-6a GalN-7, H-6b GalN-7, H-5a Xyl, H-4 GlcN-1, H-4 GlcN-2, H-4 GlcN-5, H-3 Fuc-6, H-2 Fuc-6, H-4 Man-3), 3.77 (4H, m, H-5 Fuc-6, H-2 Man-4, H-5 GalN-7, PhCH<u>H</u>), 3.69 to 3.49 (5H, m, H-6a GlcN-2, H-6a Man-4, H-2 Man-3, H-5 Man-4', H-5 Man-4), 3.49 to 3.31 (8H, m, H-6a Man-4', H-6b Man-4', H-6a Man-3, H-4 Man-4, H-6b Man-4, H-6a GlcN-5, H-3 Man-3, H-3 Man-4', H-4 Man-4'), 3.26 (5H, m, H-6b GlcN-2, H-6b Man-3, H-4 Fuc-6, H-5 GlcN-2, H-5 GlcN-1), 2.97 (3H, m, H-5b Xyl, H-6a GlcN-1, H-6b GlcN-1), 2.38 (2H, m, H-5 Man-3, H-6b GlcN-5), 2.11 to 1.67 (19H, m, 6x C<u>H</u>$_3$ of Ac, H-5 GlcN-5), 0.93 (3H, d, C<u>H</u>$_3$ of Fuc-6, *J* = 6.5 Hz), 0.63 (9H, s, 3x C-C<u>H</u>3 of TBS), -0.07 to -0.20 (6H, d, 2x C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$, signals from edited HSQCAD experiment): δ 123.82, 123.64, 134.68, 123.19, 133.57, 123.35, 127.96, 133.56, 128.33, 126.01, 128.19, 76.97, 127.86, 127.95, 127.93, 127.74, 125.64, 127.67, 125.67, 127.87, 127.47, 127.84, 127.84, 126.97, 131.69, 67.86, 96.81, 96.71, 66.63, 97.27, 118.95, 71.95, 71.83, 71.16, 96.64, 69.29, 74.68, 72.64, 74.95, 97.46, 72.94, 100.17, 97.30, 71.42, 73.02, 94.85, 69.98, 74.87, 68.65, 73.66, 52.04, 71.43, 74.85, 74.73, 101.18, 70.52, 72.94, 76.62, 69.96, 72.86, 75.47, 55.72, 76.96, 76.65, 60.94, 60.89, 75.21, 75.60, 79.46, 77.88, 72.84, 71.09, 66.00, 73.41, 73.97, 70.50, 68.39, 64.59, 76.07, 77.80, 61.87, 65.97, 74.20, 67.61, 70.74, 71.89, 74.13, 64.63, 78.27, 61.84, 68.02, 74.07, 70.81, 20.75, 20.69, 25.06, 20.73, 20.54, 17.30, 73.34, 18.01, 20.55, 16.47, 26.03, 24.50, 26.02, 0.02, -5.23, -3.80, -5.35. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{205}H_{216}N_4O_{56}SiNa$, 3680.3844; found 3680.4160.



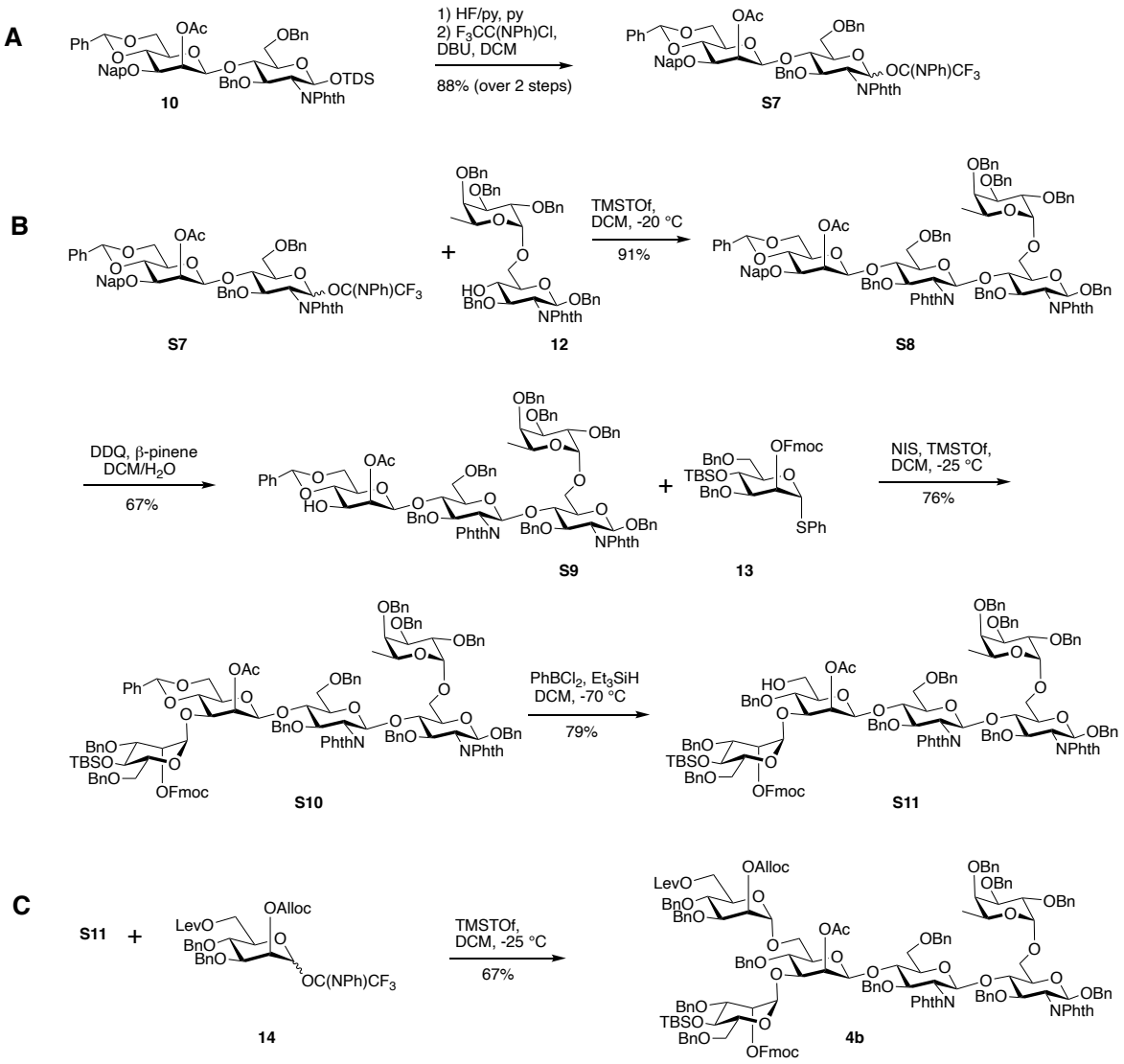
Benzyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→6)-2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl-(1→6)]-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside-(1→2)-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl-(1→3)]-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-β-D-mannopyranosyl- (1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)- 3-*O*-benzyl-2-deoxy- 2-phthalimido-β-D-glucopyranoside (25): A mixture of acceptor **24** (1.6 g, 0.44 mmol) and donor **6** (1.07 g, 1.76 mmol), was stirred in DCM (15 mL) with pre-activated molecular sieves (3 g) for 10 min, after which the mixture was cooled down to -40 ºC, followed by the addition of TfOH (16 μL, 0.18 mmol). The mixture was warmed up to -10 ºC over a period of 30 min, after which it was quenched with Et_3N (150 μL). The sieves were filtered off and the mixture was concentrated *in vacuo.* The residue was purified by silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 6: 4, v: v) and then passed through BioGel SX-1 column using Tol: Acetone (1: 1, v: v) as mobile phase, which afforded the product as an off-white amorphous powder. (1.19 g, 65%). R_f = 0.57 (Tol: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 to 6.41 (90H, m, H-Ar), 5.85 (1H, m, C<u>H</u>=CH_2 of alloc), 5.74 (2H, m, H-3 GalN-7, H-3 GlcN-5'), 5.39 (1H, d, H-1 GlcN-2, *J* = 8.7 Hz), 5.34 (1H, d, H-2 Man-4', *J* = 3.1 Hz), 5.29 (2H, m, H-1 GlcN-5, CH=C<u>H</u>H of alloc), 5.21 (2H, m, H-1 GlcN-5', CH=CH<u>H</u> of alloc), 5.07 (2H, m, H-4 GlcN-5', H-4 GalN-7), 5.00 (1H, m, H-4 Xyl), 4.96 to 4.82 (7H, m, H-2 Xyl, H-3 Xyl, H-1 Man-4, PhC<u>H</u>$_2$ protons), 4.82 to 4.71 (4H, m, H-1 Xyl, H-1 GlcN-1, PhC<u>H</u>$_2$ protons), 4.71 to 4.57 (5H, m, H-1 GalN-7, PhC<u>H</u>$_2$ protons), 4.56 to 4.41 (10H, m, H-2 GalN-7, H-1 Fuc-6, PhC<u>H</u>$_2$ protons, OC<u>H</u>$_2$ of alloc), 4.41 to 4.30 (7H, m, H-1 Man-4', H-1 Man-3, PhC<u>H</u>$_2$ protons), 4.26 (5H, m, H-2 GlcN-5', H-6a GlcN-5', PhC<u>H</u>$_2$, H-3 GlcN-1), 4.20 to 4.05 (10H, m, H-2 GlcN-1, H-2 GlcN-2, H-2 GlcN-5, H-6b GlcN-5', H-3 GlcN-2, H-3 GlcN-5, PhC<u>H</u>$_2$ protons), 4.04 to 3.87 (8H, m, H-6a GalN-7, H-6b GalN-7, H-5a Xyl, H-4 GlcN-1, H-4 GlcN-2, H-4 GlcN-5, H-3 Fuc-6, H-2 Fuc-6), 3.84 to 3.69 (7H, m, H-5 Fuc-6, H-6a GlcN-1, H-2 Man-4, PhCH<u>H</u>, H-5 GalN-7, H-3 Man-4, H-5 Man-4'), 3.66 to 3.48 (6H, m, H-6a Man-4', H-6a Man-4, H-2 Man-3, H-5 GlcN-5', H-5 Man-4, H-4 Man-4'), 3.44 to 3.19 (11H, m, H-6b Man-4', H-6a GlcN-2, H-4 Man-4, H-6b Man-4, H-6b GlcN-1, H-6a GlcN-5, H-3 Man-3, H-3 Man-4', H-5 GlcN-2, H-4 Fuc-6, H-5 GlcN-1), 2.99 (2H, m, H-5b Xyl, H-6a Man-3), 2.91 (1H, d, H-6b Man-3, *J* = 10.6 Hz), 2.79 (1H, d, H-6b GlcN-2, *J* = 10.7 Hz), 2.43 (1H, m, H-5 Man-3), 2.29 (1H, m, H-6b GlcN-5), 2.09 to 1.65 (28H, m, 9x C<u>H</u>$_3$ of Ac, H-5 GlcN-5), 0.93 (3H, d, C<u>H</u>$_3$ of Fuc-6, *J* = 6.5 Hz), 0.62 (9H, s, 3x C-CH3 of TBS), -0.09 to -0.28 (6H, d, 2x C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$, signals from edited HSQCAD experiment): δ 123.91, 123.63, 134.85, 123.22, 133.61, 123.47, 128.02, 123.33, 133.54, 128.18, 126.09, 128.21, 128.13, 76.96, 127.99, 125.80, 128.06, 127.76, 127.72, 124.08, 125.61, 127.79, 127.96, 128.05, 127.50, 127.81, 127.83, 126.79, 131.70, 67.87, 70.70, 96.77, 66.65, 118.82, 97.29, 118.82, 98.55, 118.81, 68.98, 71.93, 71.47, 96.62, 71.16, 69.23, 74.69, 72.57, 97.41, 97.80, 72.88, 100.07, 73.18, 70.78, 94.80, 70.02, 74.72, 74.03, 52.07, 68.54, 74.75, 70.89, 72.90, 97.45, 70.58, 101.34, 72.98, 72.96, 69.98, 69.97, 76.59, 54.42, 62.03, 72.89, 75.63, 72.91, 55.82, 77.05, 62.00, 76.71, 60.92, 75.91, 60.86, 69.71, 79.29, 75.27, 79.34, 80.03, 72.66, 66.01, 73.76, 71.10, 69.12, 73.43, 77.19, 70.52, 71.69, 68.33, 64.62, 76.13, 77.83, 74.02, 68.46, 70.85, 69.12, 67.77, 74.02, 66.36, 74.14, 64.60, 78.46, 70.34, 68.02, 61.92, 68.00, 66.38, 73.86, 70.81, 22.89, 20.73, 19.18, 20.69, 20.73, 20.54, 19.00, 73.33, 20.53, 29.68, 16.47, 10.21, 24.52, 26.02, 0.04, -5.20, -

3.80, -6.87, -5.35. MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{225}H_{235}N_5O_{65}SiNa$, 4097.4904; found 4097.6391.

Benzyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→6)-4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-D-mannopyranosyl]-(1→6)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside-(1→2)-3,6-di-*O*-benzyl-α-D-mannopyranosyl-(1→3)]-2,3,4-tri-*O*-acetyl-β-D-xylopyranosyl-(1→2)-4-*O*-benzyl-β-D-mannopyranosyl- (1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)- 3-*O*-benzyl-2-deoxy- 2-phthalimido-β-D-glucopyranoside (S6): Compound **25** (1.1 g, 0.27 mmol) was dissolved in THF (30 mL) and H_2O (3 mL), followed by the addition of tetrakis(triphenylphosphine)palladium (62 mg, 0.054 mmol) and morpholine (95 μL, 1.08 mmol). The mixture was stirred for 2 h after which it was concentrated *in vacuo* and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (8: 2, v: v to 3:7, v: v) which afforded the product as a white amorphous solid. (850 mg, 79%). R_f = 0.41 (Tol: EtOAc, 7: 3, v: v). A mixture of acceptor **24** (850 mg, 0.21 mmol) and donor **7** (926 mg, 0.85 mmol), was stirred in DCM (10 mL) with pre-activated molecular sieves (2 g) for 10 min, after which the mixture was cooled down to -40 ºC, followed by the addition of TfOH (7.6 μL, 0.085 mmol). The mixture was warmed up to -20 ºC over a period of 30 min, after which it was quenched with Et_3N (100 μL). The sieves were filtered off and the mixture was concentrated *in vacuo.* The residue was purified by silica gel column chromatography using Tol: EtOAc (8: 2, v: v to 1: 1, v: v) and then passed through BioGel SX-1 column using Tol: Acetone (1: 1, v: v) as mobile phase, which afforded the product **25** as an off-white amorphous powder (774mg, 76%). To a suspension of **25** (774 mg, 0.161 mmol) in pyridine (10 mL) was added HF in pyridine (70% HF, 30% pyridine; 1.0 mL) dropwise. The mixture was stirred for 6 h at 60 °C, after which it was quenched by solid $NaHCO_3$ 10 g), till all CO_2 bubbling stopped. The salts were filtered off, the solvent was evaporated *in vacuo*, and the residue was re-dissolved in DCM, followed by successive washing with water (50 mL) and saturated $NaHCO_3$ 50 mL). The residue was passed through BioGel SX-1, providing intermediate compound **S6** (602 mg, 78%). R_f = 0.39 (Tol: EtOAc, 6: 4, v: v). ^1H NMR (600 MHz, $CDCl_3$): δ 8.11 to 6.41 (104H, m, H-Ar), 5.78 (1H, dd, H-3 GalN, *J* = 11.5 Hz, 3.3 Hz), 5.42 (1H, m, H-3 GlcN-5'), 5.35 (3H, m, H-1 GlcN-2, H-1 GlcN-5, H-4 Man-8), 5.25 (1H, m, H-4 GlcN-5'), 5.05 to 4.71 (15H, m, H-4 GalN-7, H-4 Xyl, H-1 GlcN-5', H-1 GlcN-5", H-2 Xyl, H-3 Xyl, H-1 Man-4, H-1 Man-8, PhC$\underline{H}_2$ protons), 4.70 to 4.38 (19H, m, H-2 GalN-7, H-1 Xyl, H-1 GlcN-1, H-1 Fuc-6, H-1 GalN-7, PhC$\underline{H}_2$ protons), 4.38 to 4.20 (8H, m, H-3 GlcN-1, H-1 Man-4', H-1 Man-3, PhC$\underline{H}_2$ protons), 4.20 to 3.98 (16H, m, H-2 GlcN-5', H-2 GlcN-5, H-2 GlcN-2, H-2 GlcN-1, H-5 Man-8, H-3 GlcN-2, H-3 GlcN-5", H-3 GlcN-5, H-6a GalN-7, H-6a Man-8, H-6b Man-8, H-6a GlcN-5', H-3 Man-8, PhC$\underline{H}_2$ protons), 3.98 to 3.76 (13H, m, H-2 GlcN-5", H-6b GalN-7, H6b GlcN-5', H-5a Xyl, H-5 Fuc-6, H-5 GlcN-5', H-4 GlcN-1, H-4 GlcN-2, H-4 GlcN-5, H-4 GlcN-5", PhC$\underline{H}_2$ protons), 3.75 to 3.48 (8H, m, H-6a Man-4', H-6a GlcN-1, H-5 GalN-7, H-4 Man-4, H-3 Fuc-6, H-3 Man-3, H-3 Man-4', H-2 Fuc-6), 3.47 to 3.15 (15H, m, H-6b Man-

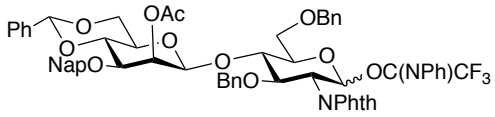


4', H-2 Man-4', H-6a GlcN-2, H-6b GlcN-1, H-6a GlcN-5", H-6b GlcN-5", H-6a Man-4, H-6a GlcN-5, H-4 Fuc-6, H-2 Man-3, H-2 Man-4, H-5 Man-4', H-5 Man-4, H-4 Man-3, H-4 Man-4'), 3.11 (1H, m, H-5 GlcN-2), 2.98 (4H, m, H-6a Man-3, H-6b Man-3, H-5 GlcN-5", H-5 GlcN-1), 2.82 (1H, m, H-5b Xyl), 2.69 (2H, m, H-6b GlcN-2, H-6b Man-4), 2.58 (1H, m, H-6b GlcN-5), 2.47 (1H, m, H-5 Man-3), 2.09 to 1.65 (34H, m, 11x $C\underline{H}_3$ of Ac, H-5 GlcN-5), 0.94 (3H, d, $C\underline{H}_3$ of Fuc-6, J = 6.3 Hz); ^{13}C NMR (151 MHz, $CDCl_3$, signals from edited HSQCAD experiment): δ 123.94, 123.69, 135.04, 123.32, 133.66, 128.05, 123.25, 127.88, 128.32, 125.80, 128.08, 76.95, 127.97, 127.99, 127.84, 127.94, 127.63, 127.80, 127.84, 126.90, 67.87, 67.82, 70.64, 96.59, 66.67, 68.08, 71.86, 96.62, 68.74, 74.12, 97.64, 72.89, 73.18, 70.77, 98.39, 99.88, 95.02, 70.03, 74.75, 52.06, 101.50, 73.58, 72.91, 71.34, 101.63, 97.07, 73.21, 75.03, 55.74, 76.96, 76.84, 74.83, 62.85, 71.74, 61.02, 73.10, 62.88, 61.06, 79.40, 75.16, 73.16, 54.40, 71.98, 61.76, 65.98, 80.55, 74.80, 71.31, 76.15, 76.97, 70.57, 64.52, 64.44, 77.76, 66.71, 71.05, 68.70, 72.50, 74.07, 64.51, 79.58, 66.18, 68.01, 70.36, 61.73, 66.22, 30.95, 29.42, 20.76, 20.74, 20.86, 20.75, 20.66, 20.54, 73.39, 20.61, 30.33, 59.68, 30.28, 22.68, 31.50, 28.12, 29.70, 31.98, 31.27, 16.46, 14.17, 25.98, 0.03. MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{267}H_{268}N_6O_{76}Na$, 4796.7188; found 4797.0277.

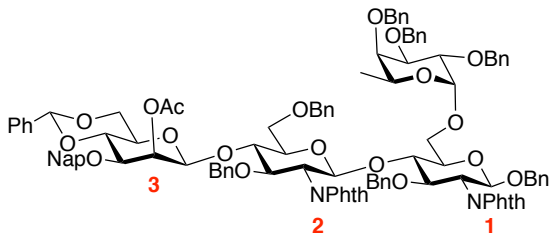


Scheme S2: Synthesis of core fucosylated hexasaccharide with orthogonal protecting groups.

***N*-phenyltrifluoracetimidate [2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S7):** Compound **10** (10.0 g, 9.4 mmol) was dissolved in pyridine (100 mL) followed by dropwise addition of HF in pyridine (70% HF, 30% pyridine; 15 mL). The mixture was stirred for 15 h after which it was quenched by solid $NaHCO_3$ (20 g) till all CO_2 bubbling stopped. The salts were filtered off, the solvent was evaporated *in vacuo*, and the residue was re-dissolved in DCM, followed by washing with water (150 mL) and saturated $NaHCO_3$ (200 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated, affording compound with silyl group removed as a white foamy solid, which was used for the next reaction without further purification. This crude compound (7.7 g, 8.4 mmol) was dissolved in DCM (100 mL), followed by the addition of 2,2,2- Trifluoro-*N*-phenylacetimidoyl chloride (2.1 mL, 10.1 mmol) and DBU (1.2 mL, 8.4 mmol). The reaction mixture was stirred for 30 min, after which the solvent was evaporated and the residue was purified using silica gel column chromatography (Tol to Tol: EtOAc, 8: 2, v: v), which provided the product as an off-white foamy powder. (9.1 g, 88.3% over two steps). R_f = 0.63 (Tol: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 to 6.48 (31H, m, H-Ar), 5.54 (1H, s, PhC<u>H</u> of benzylidene), 5.46 (1H, s, H-2 Man), 4.83 (2H, m, PhC<u>H</u>H, C<u>H</u>H of Nap), 4.67 (3H, m, H-1 Man, CH<u>H</u> of Nap, PhCH<u>H</u>), 4.40 (3H, m, PhC<u>H</u>$_2$, H-2 GlcN), 4.18 (3H, m, H-3 GlcN, H-4 GlcN, H-6b Man), 3.90 (1H, t, H-4 Man, *J* = 9.6 Hz), 3.73 (2H, bd, H-6a GlcN, H-6b GlcN), 3.58 (1H, m, H-6a Man), 3.48 (1H, m, H-3 Man), 3.13 (1H, m, H-5 Man), 2.18 (3H, s, C<u>H</u>$_3$ of Ac); ^{13}C NMR (101 MHz, $CDCl_3$): δ170.30, 167.60, 143.00, 138.35, 137.54, 137.51, 135.32, 134.02, 133.37, 133.05, 131.44, 129.09, 128.66, 128.61, 128.31, 128.21, 128.16, 128.13, 128.07, 128.02, 127.83, 127.70, 127.60, 127.37, 126.28, 126.19, 126.13, 125.95, 125.40, 124.51, 123.51, 119.37, 101.68, 99.30, 93.43, 78.18, 77.87, 77.34, 77.12, 76.91, 76.56, 75.67, 75.15, 74.71, 73.51, 71.48, 69.10, 68.48, 67.67, 67.02, 60.43, 54.80, 53.50, 21.11. Compound was unstable under MALDI-TOF-MS conditions.

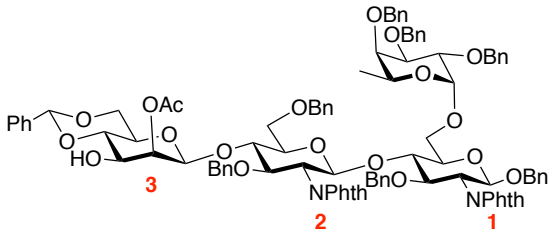


Benzyl [2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S8): Donor **S7** (7.7 g, 7.1 mmol) and Acceptor **12** (5.6 g, 6.1 mmol), were dissolved in DCM (50 mL) and stirred with pre-activated molecular sieves (12 g) for 20 min. The mixture was then cooled down to -40 ºC, followed by the addition of TMSTOf (386 μL, 2.1 mmol). The reaction mixture was warmed up to -20 ºC over a period of 45 min, after which it was quenched with Et_3N (1 mL). The mixture was concentrated *in vacuo* to give the crude product as a brown syrup. Silica gel column chromatography with Tol: EtOAc (9.5: 0.5, v: v to 8: 2, v: v) yielded the product as white amorphous powder. (10.2 g, 91 %). R_f = 0.48 (Tol: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 to 6.63 (55H, m, H-Ar), 5.51 (3H, m, H-1 GlcN-2, PhC<u>H</u> of benzylidene, H-2 Man-3), 4.99 to 4.73 (9H, m, H-1 GlcN-1, H-1 Fuc, 3x PhC<u>H</u>$_2$ protons, PhC<u>H</u>H of Nap), 4.64 (4H, m, PhC<u>H</u>$_2$, PhCH<u>H</u> of Nap, H-1 Man-3), 4.51 (2H, m, PhC<u>H</u>$_2$), 4.40 (2H, m, PhC<u>H</u>$_2$), 4.30 (3H, m, H-3 GlcN-1, PhC<u>H</u>$_2$), 4.25 to 4.05 (6H, m, H-3 GlcN-2, H-2 GlcN-2, H-3 Fuc, H-6a Man-3, H-2 GlcN-1, H-4 GlcN-1), 4.00 (3H, m, H-5 Fuc, H-4 GlcN-2, H-2 Fuc), 3.84 (1H, t, H-4 Man, *J* = 9.5 Hz),

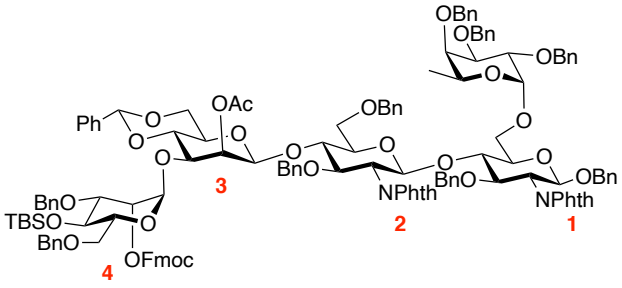


3.74 (3H, m, H-6a GlcN-2, H-6a GlcN-1, H-4 Fuc), 3.64 (2H, m, H-6b GlcN-1, H-5 GlcN-1), 3.50 (2H, m, H-6b Man-3, H-3 Man-3), 3.36 (1H, m, H-6b GlcN-2), 3.23 (1H, m, H-5 GlcN-2), 3.09 (1H, m, H-5 Man-3), 1.84 (3H, s, C$\underline{H}_3$ of Ac), 0.97 (3H, d, C$\underline{H}_3$ of Fuc, J = 6.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.99, 168.23, 167.65, 139.23, 138.96, 138.78, 138.72, 138.64, 137.76, 137.47, 137.04, 135.31, 133.48, 133.30, 132.96, 131.82, 131.66, 131.44, 129.03, 128.95, 128.49, 128.45, 128.42, 128.37, 128.21, 128.16, 128.12, 128.10, 128.07, 128.03, 127.96, 127.92, 127.77, 127.71, 127.66, 127.64, 127.61, 127.55, 127.48, 127.46, 127.34, 127.15, 126.84, 126.19, 126.11, 126.00, 125.82, 125.36, 125.29, 123.57, 123.15, 101.52, 99.35, 96.96, 96.75, 96.59, 79.69, 79.40, 77.78, 77.61, 77.34, 77.03, 76.91, 76.71, 76.09, 75.76, 75.22, 75.10, 74.71, 74.60, 74.35, 73.98, 73.62, 73.34, 73.16, 72.78, 71.33, 69.81, 68.87, 68.42, 68.01, 66.83, 65.96, 63.60, 56.46, 55.80, 20.45, 16.39, -0.00. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{109}H_{104}N_2O_{23}Na$, 1831.6928; found 1831.6942.

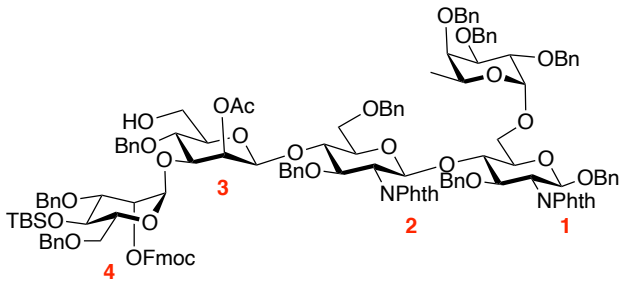
Benzyl [2-*O*-acetyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S9): Compound **S8** (10.1 g, 5.6 mmol) was dissolved in the solvent system DCM (200 mL) and H_2O (20 mL), followed by the addition of DDQ (2.6 g, 11.1 mmol) and β-pinene (3.5 mL, 22.1 mmol). The mixture was stirred in dark for 36 h after which the solvent was evaporated *in vacuo* and the residue was diluted by DCM (300 mL) and washed with water (100 mL) and sat. $NaHCO_3$ (150 mL). The organic phase was dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 7: 3, v: v) gave the product as yellow amorphous solid. (6.2 g, 67%). R_f = 0.32 (Tol: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 to 6.54 (48H, m, H-Ar), 5.51(1H, d, H-1 GlcN-2, J = 8.2 Hz), 5.43 (1H, s, PhC$\underline{H}$ of benzylidene), 5.28 (1H, s, H-2 Man-3), 4.92 (2H, m, PhCH$\underline{H}$, H-1 GlcN-1), 4.84 (6H, m, PhC$\underline{H}$H, H-1 Fuc, 2x PhC$\underline{H}_2$), 4.74 (2H, m, PhC$\underline{H}$H, H-1 Man-3), 4.57 (4H, m, PhCH$\underline{H}$, PhC$\underline{H}_2$, PhCH$\underline{H}$), 4.41 (2H, m, PhC$\underline{H}_2$), 4.30 (3H, m, PhC$\underline{H}$H, H-3 GlcN-2, H-3 GlcN-1), 4.22 to 4.05 (5H, m, H-2 GlcN-2, H-2 GlcN-1, H-6a Man-3, H-4 GlcN-1, H-3 Fuc), 3.98 (3H, m, H-5 Fuc, H-4 GlcN-2, H-2 Fuc), 3.81 to 3.60 (7H, m, H-6a GlcN-2, H-6a GlcN-1, H-6b GlcN-1, H-3 Man-3, H-4 Fuc, H-5 GlcN-1, H-4 Man-3), 3.49 (1H, t, H-6b Man-3, J = 10.1 Hz), 3.35 (1H, m, H-6b GlcN-2), 3.22 (1H, m, H-5 GlcN-2), 3.12 (1H, m, H-5 Man-3), 1.81 (3H, s, C$\underline{H}_3$ of Ac), 0.96 (3H, d, C$\underline{H}_3$ of Fuc, J = 6.5 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.29, 167.62, 139.20, 138.88, 138.76, 138.68, 138.64, 137.86, 137.03, 133.49, 131.66, 129.20, 129.01, 128.52, 128.47, 128.43, 128.41, 128.38, 128.28, 128.20, 128.09, 128.05, 127.91, 127.86, 127.77, 127.70, 127.67, 127.64, 127.53, 127.46, 127.43, 127.40, 127.36, 127.32, 127.14, 126.83, 126.20, 125.27, 123.57, 123.14, 101.99, 99.36, 96.90, 96.70, 96.59, 79.66, 78.49, 77.63, 77.33, 77.22, 77.01, 76.90, 76.70, 76.12, 75.19, 75.16, 74.69, 74.58, 74.35, 73.99, 73.62, 73.40, 73.27, 72.71, 71.13, 69.88, 69.80, 68.38, 67.95, 66.56, 65.95, 63.58, 56.50, 55.80, 20.37, 16.38. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{98}H_{96}N_2O_{23}Na$, 1691.6302; found 1691.6331.



Benzyl [3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-*O*-fluorenylmethoxycarbonyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4,6-*O*-benzylidene-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S10): A mixture of acceptor **S9** (4.9 g, 2.9 mmol) and donor **13** (2.8 g, 3.5 mmol), was stirred in DCM (30 mL) with pre-activated molecular sieves (8 g) for 20 min. The mixture was then cooled down to -25 ºC, followed by the sequential addition of NIS (983 mg, 4.3 mmol) and TMSTOf (160 μL, 0.88 mmol). The reaction mixture was warmed up to -5 ºC over a period of 25 min, after which it was quenched with pyridine (5 mL). The sieves were filtered off, the mixture was diluted by DCM (200 mL), and washed with 5% $Na_2S_2O_3$ (100 mL) and sat. $NaHCO_3$ (120 mL). The mixture was concentrated *in vacuo* to give the crude product as a brown syrup. Silica gel column chromatography with Tol: EtOAc (9: 1, v: v to 7: 3, v: v) yielded the product as an off-white amorphous powder. (5.2 g, 76 %). R_f = 0.63 (Tol: EtOAc, 8: 2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 to 6.62 (66H, m, H-Ar), 5.43 (3H, m, H-1 GlcN-2, PhC<u>H</u> of benzylidene, H-2 Man-4), 5.30 (1H, d, H-1 Man-4, *J* = 1.3 Hz), 5.24 (1H, s, H-2 Man-3), 4.97 to 4.76 (10H, m, H-1 GlcN-1, H-1 Fuc, 4x PhC<u>H</u>$_2$ protons), 4.71 (1H, m, PhC<u>H</u>H), 4.76 to 4.46 (H-1 Man-3, PhC<u>H</u>$_2$ protons, C<u>H</u>$_2$ of Fmoc), 4.37 (4H, m, PhC<u>H</u>$_2$ protons, H-3 GlcN-1), 4.27 (3H, m, H-3 GlcN-2, PhCH<u>H</u>), 4.18 (5H, m, C<u>H</u> of Fmoc, H-2 GlcN-1, H-2 GlcN-2, H-4 GlcN-1, H-3 Fuc), 4.13 to 3.86 (8H, m, H-5 Fuc, H-6a Man-3, H-4 Man-4, H-4 GlcN-2, H-2 Fuc, H-5 Man-4, H-3 Man-3), 3.77 (5H, m, H-6a GlcN-2, H-6a GlcN-1, H-6a Man-4, H-6b Man-4, H-3 Man-4), 3.59 (4H, m, H-6b GlcN-1, H-4 Fuc, H-4 Man-3, H-5 GlcN-1), 3.44 (1H, m, H-6b Man-3), 3.31 (1H, m, H-6b GlcN-2), 3.22 (1H, m, H-5 GlcN-2), 3.01 (1H, m, H-5 Man-3), 1.82 (3H, s, C<u>H</u>$_3$ of Ac), 0.95 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.5 Hz), 0.84 (9H, s, 3x C-C<u>H</u>$_3$ of TBS), 0.04 to -0.03 (6H, d, 2x C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.49, 166.94, 153.81, 142.86, 142.55, 140.51, 140.48, 138.48, 138.21, 138.10, 138.04, 137.97, 137.78, 137.18, 137.15, 136.39, 136.36, 133.13, 132.78, 130.98, 130.74, 128.06, 127.85, 127.79, 127.75, 127.70, 127.63, 127.52, 127.42, 127.36, 127.29, 127.25, 127.12, 127.07, 127.03, 126.89, 126.85, 126.77, 126.74, 126.71, 126.63, 126.60, 126.55, 126.49, 126.44, 126.13, 125.22, 124.63, 124.59, 122.89, 122.45, 119.25, 100.50, 98.47, 97.44, 96.21, 95.91, 78.72, 78.16, 78.06, 77.07, 77.02, 76.66, 76.54, 76.34, 76.20, 76.02, 75.58, 74.83, 74.68, 74.02, 73.79, 73.38, 73.01, 72.93, 72.64, 72.56, 72.37, 72.20, 72.04, 71.03, 70.37, 70.18, 69.82, 69.51, 69.11, 68.67, 67.64, 67.05, 66.86, 65.59, 65.26, 62.98, 55.84, 55.10, 45.79, 25.29, 25.19, 19.66, 17.51, 15.70, -4.56, -5.59. MALDI-TOF-MS (*m/z*): [M+Na]$^+$ calculated for $C_{139}H_{142}N_2O_{30}SiNa$, 2369.9314; found 2369.9405.

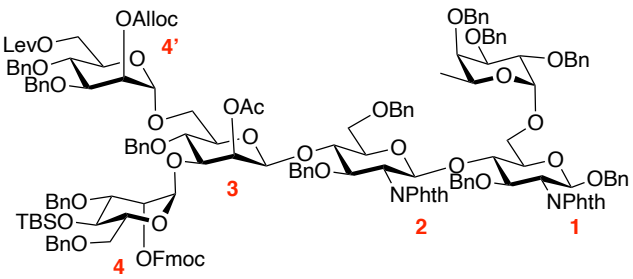


Benzyl [3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-*O*-fluorenylmethoxycarbonyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S11): Compound **S10** (4.5 g, 1.9 mmol) was dissolved in DCM (100 mL) and stirred with pre-activated molecular sieves (20 g) for 30 min, after which the temperature was brought down to -70 °C. The mixture was stirred at this temperature for another 30 min after which Et_3SiH (611 μL, 3.8 mmol) and $PhBCl_2$ (743 μL, 5.7 mmol). The mixture was stirred at

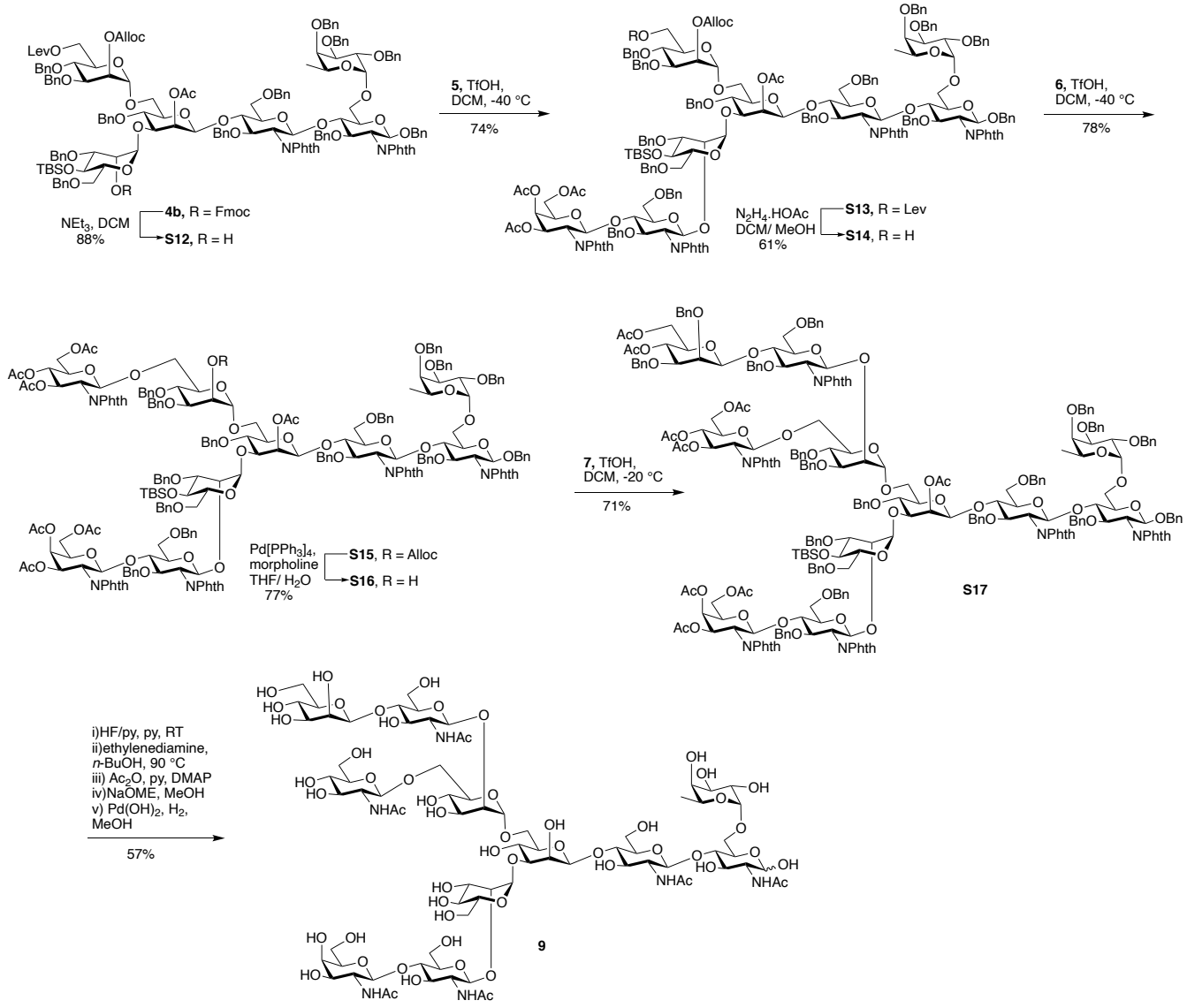


this temperature for 20 min after which it was quenched with pyridine (10 mL). The mixture was further diluted by DCM (200 mL), the sieves were filtered off, and the mixture was washed with sat. $NaHCO_3$ (150 mL). The organic phase was dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 6: 4, v: v) gave the product as yellow amorphous powder. (3.6 g, 79%). R_f = 0.35 (Tol: EtOAc, 8: 2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 to 6.63 (66H, m, H-Ar), 5.42 (2H, m H-2 Man-4, H-1 GlcN-2), 5.25 (1H, s, H-1 Man-4), 5.21 (1H, s, H-2 Man-3), 4.99 to 4.78 (8H, m, H-1 GlcN-1, H-1 Fuc, $PhCH_2$ protons), 4.70 (3H, m, PhCHH, $PhCH_2$), 4.65 to 4.36 (12H, m, PhCHH, $PhCH_2$ protons, CH_2 of Fmoc), 4.29 (5H, m, H-3 GlcN-1, $PhCH_2$ protons), 4.18 (4H, m, CH of Fmoc, H-2 GlcN-2, H-2 GlcN-1, H-3 GlcN-2), 4.09 (4H, m, H-4 Man-4, H-4 GlcN-1, H-3 Fuc, H-4 GlcN-2), 3.97 (3H, m, H-5 Fuc, H-5 Man-4, H-2 Fuc), 3.76 (3H, m, H-6a Man-4, H-6b Man-4, H-3 Man-4), 3.72 to 3.56 (7H, m, H-6a GlcN-2, H-6a GlcN-1, H-6a Man-3, H-4 Fuc, H-4 Man-3, H-5 GlcN-1), 3.51 (2H, m, H-6b Man-3, H-3 Man-3), 3.39 (1H, m, H-6b GlcN-2), 3.27 (2H, m, H-6b GlcN-1, H-5 GlcN-2), 2.97 (1H, m, H-5 Man-3), 1.88 (3H, s, CH_3 of Ac), 0.96 (3H, d, CH_3 of Fuc, J = 6.3 Hz), 0.86 (9H, s, 3x C-CH_3 of TBS), 0.03 to -0.01 (6H, d, 2x CH_3-Si of TBS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.36, 167.92, 154.82, 143.76, 143.55, 141.47, 139.44, 139.21, 139.08, 138.95, 138.80, 138.08, 137.94, 137.33, 134.28, 133.70, 131.96, 129.83, 128.79, 128.70, 128.64, 128.61, 128.59, 128.45, 128.38, 128.32, 128.26, 128.09, 128.00, 127.97, 127.80, 127.72, 127.65, 127.59, 127.54, 127.50, 127.46, 127.05, 125.58, 123.37, 120.22, 115.61, 99.37, 98.45, 97.32, 97.17, 96.89, 79.60, 78.36, 78.07, 77.93, 77.62, 77.50, 77.30, 76.98, 76.77, 76.08, 75.88, 75.43, 75.33, 75.27, 75.00, 74.89, 74.60, 74.37, 74.03, 73.60, 73.52, 73.36, 73.03, 72.39, 71.38, 71.04, 70.54, 70.10, 69.49, 68.00, 67.68, 66.24, 64.00, 61.81, 56.78, 56.08, 46.78, 26.22, 20.80, 18.44, 16.67, -3.58, -4.70. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{139}H_{144}N_2O_{30}SiNa$, 2371.9471; found 2371.9453.

Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-levulenoyl-α-D-mannopyranosyl]-(1→6) [3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-*O*-fluorenylmethoxycarbonyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (4b): A mixture of acceptor **S11** (3.6 g, 1.5 mmol) and donor **14** (4.3 g, 6.0 mmol), was stirred in DCM (50 mL) with pre-activated molecular sieves (10 g) for 20 min. The mixture was then cooled down to -45 ºC, followed by the addition of TMSTOf (108 µL, 0.60 mmol). The reaction mixture was warmed up to -25 ºC over a period of 30 min, after which it was quenched with pyridine (2 mL). The sieves were filtered off and the mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using DCM to DCM: Acetone (95: 5, v: v) which yielded the product as a white amorphous powder. (2.9 g, 67 %). R_f = 0.62 (DCM: Acetone, 9.7: 0.3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 to 6.59 (76H, m, H-Ar), 5.66 (1H, m, 5.78, CH=CH_2 of alloc), 5.44 (1H, d, H-2 Man-4', J = 2.4 Hz), 5.33 (1H, d, H-1 GlcN-2, J = 8.3 Hz), 5.27 (1H, m, H-2 Man-4), 5.23 (1H, d, H-1 Man-4', J = 1.4 Hz), 5.13 (3H, m, H-2 Man-3, CH=CH_2 of alloc), 5.04 (1H, d, H-1 Man-4, J = 1.6 Hz),



4.91 (3H, m, H-1 GlcN-1, PhC$\underline{H}_2$), 4.83 (7H, m, H-1 Fuc, PhC$\underline{H}_2$ protons, C$\underline{H}_2$ of Fmoc), 4.72 (2H, m, PhC$\underline{H}_2$ protons), 4.65 (4H, m, H-1 Man-3, PhC$\underline{H}_2$ protons) 4.62 to 4.51 (6H, m, PhC$\underline{H}_2$ protons, OC$\underline{H}_2$ of alloc), 4.50 to 4.24 (11H, m, PhC$\underline{H}_2$ protons), 4.20 (2H, m, C$\underline{H}$ of Fmoc, PhC$\underline{H}$H), 4.17 to 4.04 (10H, m, H-2 GlcN-1, H-2 GlcN-2, H-6a Man-4', H-6b Man-4', H-4 Man-4, PhCH$\underline{H}$, H-3 GlcN-1, H-3 GlcN-2, H-3 Fuc, H-3 Man-4'), 3.98 (2H, m, H-4 GlcN-1, H-4 GlcN-2), 3.91 (2H, m, H-5 Fuc, H-2 Fuc), 3.85 (1H, dd, H-4 Man-3, *J* = 8.9 Hz, 3.1 Hz), 3.81 to 3.69 (8H, m, H-6a Man-4, H-6b Man-4, H-6a Man-3, H-6b Man-3, H-5 Man-4, H-3 Man-4, H-6a GlcN-1, H-5 Man-4'), 3.67 to 3.58 (3H, m, H-6a GlcN-2, H-3 Man-3, H-4 Man-4'), 3.55 (2H, m, H-6b GlcN-1, H-5 GlcN-1), 3.42 (1H, m, H-4 Fuc), 3.20 (2H, m, H-6b GlcN-2, H-5 GlcN-2), 3.03 (1H, m, H-5 Man-3), 2.62 (2H, t, COOC$\underline{H}_2$CH$_2$ of Lev, *J* = 6.6 Hz), 2.46 ((2H, t, COOCH$_2$C$\underline{H}_2$ of Lev, *J* = 6.6 Hz), 2.09 (3H, s, CH2COC$\underline{H}$3 of Lev), 1.96 (3H, s, C$\underline{H}_3$ of Ac), 0.93 (3H, d, C$\underline{H}_3$ of Fuc, *J* = 6.5 Hz), 0.86 (9H, s, 3x C-C$\underline{H}_3$ of TBS), 0.04 to -0.01 (6H, d, 2x C$\underline{H}_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 207.01, 206.54, 172.34, 169.46, 167.75, 167.55, 154.61, 154.20, 143.56, 143.31, 141.24, 139.17, 139.03, 138.86, 138.71, 138.55, 138.08, 137.96, 137.89, 137.69, 137.09, 133.72, 133.49, 131.40, 129.06, 128.54, 128.48, 128.46, 128.40, 128.35, 128.30, 128.25, 128.19, 128.14, 128.10, 128.08, 128.01, 128.00, 127.96, 127.87, 127.76, 127.73, 127.71, 127.65, 127.61, 127.56, 127.47, 127.42, 127.38, 127.33, 127.28, 127.24, 126.78, 125.38, 123.44, 123.21, 119.99, 118.74, 99.27, 99.22, 97.75, 96.92, 96.82, 96.57, 79.45, 79.24, 78.14, 78.00, 77.85, 77.50, 77.26, 77.05, 76.84, 76.62, 75.77, 75.71, 75.24, 74.95, 74.74, 74.63, 74.13, 73.90, 73.86, 73.81, 73.41, 73.31, 72.93, 72.66, 72.04, 71.90, 71.44, 71.09, 71.03, 70.33, 69.97, 69.80, 69.24, 68.48, 67.85, 67.40, 65.92, 65.50, 63.74, 63.16, 56.60, 55.78, 53.45, 46.53, 37.91, 30.96, 29.83, 27.94, 25.99, 20.59, 18.22, 16.41, 0.02, -3.83, -4.97. MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{168}H_{176}N_2O_{39}SiNa$, 2896.1517; found 2896.1744.



Scheme S3: Synthetic Scheme for extension of core hexasaccharide **4b**.

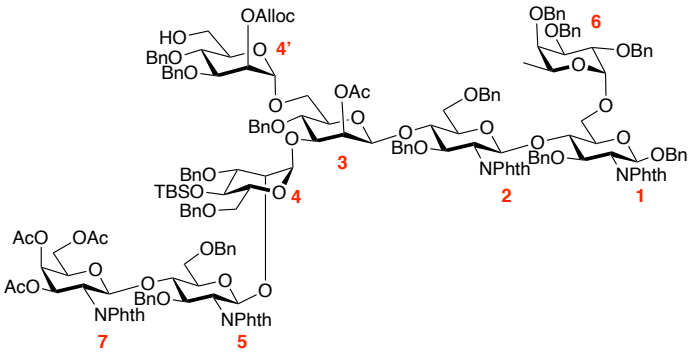
Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-levulenoyl-α-D-mannopyranosyl]-(1→6) [3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S12): Compound **4b** (2.9 g, 1.1 mmol) was dissolved in DCM (100 mL) followed by the addition of Et_3N (5 mL). The mixture was stirred for 3 h after which it was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using solvent gradient DCM to DCM: Acetone (9.5: 0.5, v: v) which afforded the product as an off-white amorphous powder. (2.6 g, 88%). R_f = 0.54 (DCM: Acetone, 9.7: 0.3,

v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 to 6.50 (68H, m, H-Ar), 5.70 (1H, m, C<u>H</u>=CH_2 of alloc), 5.43 (1H, d, H-2 Man-4', *J* = 3.1 Hz), 5.36 (1H, d, H-1 GlcN-2, *J* = 8.2 Hz), 5.15 (4H, m, CH=C<u>H</u>$_2$ of alloc, H-2 Man-3, H-1 Man-4'), 5.05 (1H, d, H-1 Man-4, *J* = 1.3 Hz), 4.94 (3H, m, H-1 GlcN-1, PhC<u>H</u>$_2$ protons), 4.89 to 4.69 (9H, H-1 Fuc, PhC<u>H</u>$_2$ protons), 4.66 (1H, H-1 Man-3), 4.63 to 4.25 (20H, m, PhC<u>H</u>$_2$ protons, OC<u>H</u>$_2$ of alloc)), 4.20 to 4.06 (8H, m, H-2 GlcN-2, H-2 GlcN-1, H-6a Man-4', H-6b Man-4', H-3 GlcN-1, H-3 GlcN-2, H-3 Man-4', H-3 Fuc), 4.0 (2H, m, H-4 Man-4, H-4 GlcN-1), 3.96 to 3.81 (5H, m, H-5 Fuc, H-2 Man-4, H-4 GlcN-2, H-2 Fuc, H-4 Man-3), 3.79 to 3.62 (9H, m, H-6a Man-3, H-6b Man-3, H-6a GlcN-1, H-6a Man-4, H-6b Man-4, H-5 Man-4', H-5 Man-4, H-4 Man-4', H-3 Man-4), 3.57 (4H, m, H-6a GlcN-2, H-6b GlcN-1, H-3 Man-3, H-5 GlcN-1), 3.47 (1H, d, H-4 Fuc), 3.23 (2H, m, H-6b GlcN-2, H-5 GlcN-2), 3.07 (1H, m, H-5 Man-3), 2.64 (2H, t, COOC<u>H</u>$_2$CH$_2$ of Lev, *J* = 6.6 Hz), 2.49 (2H, t, COOCH$_2$C<u>H</u>$_2$ of Lev, *J* = 6.6 Hz), 2.12 (3H, s, CH2COC<u>H</u>3 of Lev), 1.94 (3H, s, C<u>H</u>$_3$ of Ac), 0.96 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.6 Hz), 0.89 (9H, s, 3x C-C<u>H</u>$_3$ of TBS), 0.05 to 0.03 (6H, d, 2x C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 206.47, 172.31, 169.35, 167.76, 167.64, 167.52, 154.22, 139.17, 139.02, 138.97, 138.86, 138.74, 138.71, 138.60, 138.54, 138.47, 138.09, 137.98, 137.94, 137.79, 137.73, 137.10, 133.68, 133.45, 131.81, 131.69, 131.51, 131.41, 131.39, 129.04, 128.69, 128.52, 128.45, 128.43, 128.38, 128.35, 128.33, 128.29, 128.28, 128.26, 128.23, 128.17, 128.15, 128.12, 128.09, 128.05, 127.98, 127.92, 127.83, 127.79, 127.77, 127.74, 127.71, 127.68, 127.65, 127.63, 127.57, 127.54, 127.48, 127.46, 127.44, 127.41, 127.39, 127.34, 127.32, 127.18, 127.13, 126.77, 125.31, 123.41, 123.12, 118.76, 118.33, 101.53, 99.45, 97.70, 96.90, 96.87, 96.59, 80.36, 79.67, 79.26, 78.98, 77.88, 77.70, 77.38, 77.26, 77.06, 76.74, 76.60, 75.90, 75.73, 75.60, 75.25, 74.95, 74.72, 74.69, 74.57, 74.20, 73.97, 73.86, 73.82, 73.40, 73.30, 73.30, 73.16, 72.94, 72.66, 71.91, 71.44, 71.23, 69.97, 69.79, 69.10, 68.74, 68.50, 67.86, 66.87, 65.92, 65.65, 63.81, 63.13, 56.60, 55.78, 53.81, 53.45, 37.89, 30.92, 29.80, 29.29, 27.93, 25.98, 25.96, 21.46, 20.55, 18.16, 16.39, 0.01, -3.80. MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{153}H_{166}N_2O_{37}SiNa$, 2674.0836; found 2674.1021.

Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-levulenoyl-α-D-mannopyranosyl]-(1→6)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-(1→2)-[3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S13): A mixture of acceptor **S12** (2.5 g, 0.94 mmol) and imidate donor **5** (3.5 g, 3.3 mmol), was stirred in DCM (20 mL) with pre-activated molecular sieves (5 g) for 20 min, after which the mixture was cooled down to -40 ºC, followed by the addition of TfOH (30 μL, 0.33 mmol). The mixture was warmed up to -20 ºC over a period of 30 min, after which it was quenched with Et_3N (200 μL). The sieves were filtered off and the mixture was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 1:1, v: v) which afforded the product as an off-white amorphous powder. (2.5 g, 74%). R_f = 0.39 (Tol: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16 to 6.49 (86H, m, H-

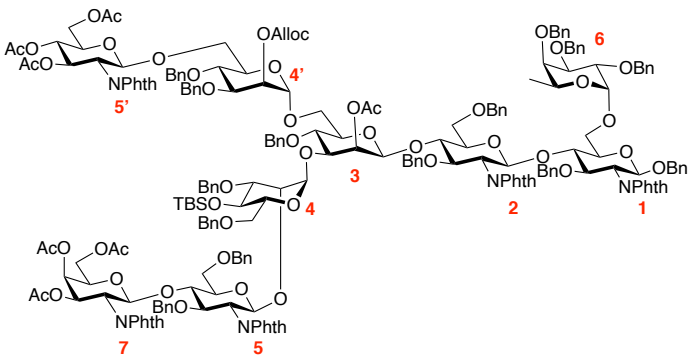
Ar), 5.73 (1H, d, H-3 GalN-7, *J* = 11.3 Hz), 5.66 (1H, m, C<u>H</u>=CH$_2$ of alloc), 5.37 (1H, d, H-1 GlcN-2, *J* = 8.2 Hz), 5.31 (2H, m, H-4 GalN-7, H-1 Man-4'), 5.22 (1H, d, H-1 Man-4', *J* = 7.1 Hz), 5.13 (3H, m, H-2 Man-4', CH=C<u>H</u>$_2$ of alloc), 5.02 (1H, s, H-2 Man-3), 4.92 to 4.76 (11H, m, H-1 Man-4, H-1 GlcN-5, H-1 GalN-7, H-1 GlcN-1, PhC<u>H</u>$_2$ protons), 4.70 (3H, m, H-1 Fuc-6, PhC<u>H</u>$_2$ protons), 4.65 to 4.54 (5H, m, PhC<u>H</u>$_2$ protons), 4.51 (5H, m, H-2 GalN-7, PhC<u>H</u>$_2$ protons), 4.46 to 4.19 (13H, m, H-1 Man-3, PhC<u>H</u>$_2$ protons, OC<u>H</u>$_2$ of alloc), 4.17 to 3.98 (14H, m, H-2 GlcN-2, H-2 GlcN-1, H-2 GlcN-5, H-6a GalN-7, H-6a Man-4', H-6b Man-4', H-3 GlcN-1, H-3 GlcN-2, H-3 GlcN-5, PhC<u>H</u>$_2$ protons), 3.98 to 3.87 (6H, m, H-6b GalN-7, H-4 GlcN-1, H-4 GlcN-2, H-3 Fuc, H-2 Fuc, PhC<u>H</u>$_2$ protons), 3.81 (3H, m, H-5 Fuc-6, H-2 Man-4, H-4 Man-3), 3.73 to 3.49 (9H, m, H-6a GlcN-2, H-6a Man-3, H-6b Man-3, H-5 Man-4, H-4 Man-4', H-5 GalN-7, H-4 GlcN-5, H-3 Man-4', H-3 Man-4), 3.45 (3H, m, H-4 Man-4, H-6a Man-4, H-3 Man-3), 3.36 (2H, m, H-6a GlcN-5, H-5 GlcN-1), 3.31 (1H, m, H-6b Man-4), 3.18 (3H, m, H-6b GlcN-2, H-4 Fuc-6, H-5 GlcN-2), 3.04 (2H, m, H-6a GlcN-1, H-6b GlcN-1), 2.63 (2H, t, COOC<u>H</u>$_2$CH$_2$ of Lev, *J* = 6.6 Hz), 2.58 (2H, m, H-6b GlcN-5, H-5 Man-3), 2.46 (2H, t, COOCH$_2$C<u>H</u>$_2$ of Lev, *J* = 6.6 Hz), 2.13 (3H, s, CH$_2$COC<u>H</u>$_3$ of Lev), 2.08 to 1.81 (13H, m, 4x C<u>H</u>$_3$ of Ac, H-5 GlcN-5), 0.91 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.4 Hz), 0.75 (9H, s, 3x C-C<u>H</u>$_3$ of TBS), -0.11 to -0.19 (6H, d, 2x C<u>H</u>$_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$, signals from edited HSQCAD experiment): δ 123.87, 123.63, 134.73, 123.35, 123.23, 133.55, 123.34, 133.58, 133.53, 128.02, 123.19, 128.04, 128.24, 126.08, 77.00, 125.86, 125.71, 128.02, 128.02, 124.12, 125.66, 127.50, 125.91, 125.57, 127.95, 125.83, 127.72, 128.08, 127.84, 67.89, 131.47, 96.85, 96.75, 66.70, 53.72, 97.28, 118.80, 118.78, 70.99, 118.77, 71.74, 74.79, 74.81, 97.28, 74.33, 73.07, 96.79, 75.27, 72.70, 73.38, 95.23, 73.94, 73.94, 74.78, 74.82, 69.87, 73.70, 73.72, 52.10, 75.28, 71.42, 74.23, 74.54, 72.77, 98.70, 69.89, 69.92, 55.60, 75.55, 63.10, 72.79, 55.89, 77.10, 68.47, 56.62, 76.55, 72.90, 60.94, 60.90, 75.82, 72.78, 79.08, 65.93, 70.98, 73.75, 77.88, 73.36, 70.50, 73.80, 69.98, 63.79, 65.86, 77.97, 68.10, 67.36, 74.59, 70.61, 76.78, 68.06, 73.86, 63.77, 68.27, 68.26, 28.01, 37.99, 74.03, 70.61, 38.09, 28.03, 29.92, 28.40, 19.17, 20.72, 73.54, 20.54, 19.02, 28.62, 40.99, 30.42, 31.51, 29.74, 31.98, 23.94, 20.90, 20.66, 14.47, 16.48, 14.25, 0.08, -3.64, -6.64, -5.12. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{201}H_{210}N_4O_{52}SiNa$, 3562.3578; found 3562.3604.

Benzyl [2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl]-(1→6)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl]-(1→2)-[3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S14): Compound **S13** (2.3 g, 0.65 mmol) was dissolved in DCM (20 mL) and MeOH (10 mL), followed by the addition of solid hydrazine acetate (299 mg, 3.25 mmol). The mixture was stirred for 1 h after which it was concentrated *in vacuo* and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (8: 2, v: v to 1:1, v: v) which afforded the product as a white foamy solid. (1.4 g, 61%). R_f = 0.34 (Pet. Ether: EtOAc, 1:1, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 to 6.72 (86H, m, H-Ar), 5.93 (1H, d, H-3 GalN-7, *J* = 11.2 Hz), 5.77 (1H, m, C<u>H</u>=CH$_2$ of alloc), 5.56 (1H, d, H-1 GlcN-2, *J* = 8.3 Hz), 5.52 (1H, s, H-4 GalN-7), 5.40 (1H, d, Man-4', *J* = 6.8 Hz), 5.27 (5H, m, H-2 Man-4', H-2 Man-3, H-1 Man-4, CH=C<u>H</u>$_2$ of alloc), 5.14 to 4.96 (10H, m, H-1 GalN-7, H-1 GlcN-5, H-1 GlcN-1, PhC<u>H</u>$_2$ protons), 4.87 (4H,



m, H-1 Fuc-6, PhC$\underline{H}_2$ protons), 4.79 to 4.37 (18H, m, H-2 GalN-7, H-1 Man-3, PhC$\underline{H}_2$ protons, OC$\underline{H}_2$ of alloc), 4.36 to 4.07 (19H, m, H-2 GlcN-1, H-2 GlcN-2, H-2 GlcN-5, H-6a GalN-7, H-6b GalN-7, H-3 GlcN-1, H-3 GlcN-2, H-3 GlcN-5, H-4 GlcN-2, H-4 GlcN-1, H-3 Fuc-6, H-2 Fuc-6), 4.00 (3H, m, H-5 Fuc-6, H-2 Man-4, H-4 Man-3), 3.93 to 3.76 (6H, m, H-6a Man-4', H-6b Man-4', H-6a Man-3, H-5 GalN-7, H-5 Man-4, H-4 Man-4'), 3.75 to 3.58 (7H, m, H-6a GlcN-2, H-6b Man-3, H-4 Man-4, H-6a Man-4, H-3 Man-3, H-5 Man-4', H-3 Man-4), 3.54 (2H, m, H-6a GlcN-5, H-5 GlcN-1), 3.44 (1H, m, H-6b Man-4), 3.38 (1H, m, H-4 Fuc), 3.30 (2H, m, H-6b GlcN-2, H-5 GlcN-2), 3.24 (2H, m, H-6a GlcN-1, H-6b GlcN-1), 2.74 (2H, m, H-6b GlcN-5, H-5 Man-3), 2.27 to 1.98 (13H, m, 4x C$\underline{H}_3$ of Ac, H-5 GlcN-5), 1.11 (3H, d, C$\underline{H}_3$ of Fuc, J = 6.4 Hz), 0.93 (9H, s, 3x C-C$\underline{H}_3$ of TBS), 0.01 to -0.01 (6H, d, 2x C$\underline{H}_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$, signals from edited HSQCAD experiment): δ 123.89, 123.65, 134.71, 123.50, 123.19, 123.25, 123.37, 133.59, 133.55, 133.59, 127.93, 126.33, 123.20, 127.92, 126.30, 128.29, 128.38, 128.24, 126.12, 76.96, 127.93, 125.77, 125.65, 127.90, 124.15, 127.49, 125.92, 128.04, 125.53, 127.85, 125.83, 127.45, 128.06, 127.90, 67.94, 131.36, 96.79, 66.65, 53.74, 97.24, 70.94, 118.79, 118.77, 118.76, 72.08, 97.30, 74.81, 96.60, 97.88, 73.34, 96.67, 75.34, 73.07, 95.18, 73.90, 70.05, 74.84, 75.21, 69.84, 71.58, 73.71, 52.10, 73.69, 72.83, 98.63, 69.93, 98.33, 55.56, 60.41, 75.58, 72.80, 55.79, 77.10, 76.64, 56.52, 68.44, 60.88, 72.97, 60.88, 75.93, 78.31, 72.80, 79.01, 65.94, 71.01, 74.16, 77.84, 77.78, 73.86, 61.90, 70.54, 64.68, 61.91, 63.65, 77.93, 72.27, 74.30, 68.04, 64.74, 67.29, 74.46, 70.64, 76.71, 74.33, 67.98, 73.88, 73.62, 63.62, 68.24, 70.62, 74.55, 20.79, 19.21, 33.91, 19.26, 73.51, 20.50, 18.96, 28.53, 40.99, 30.34, 29.00, 17.36, 30.33, 22.77, 31.39, 29.69, 28.12, 31.98, 14.24, 23.92, 20.88, 16.43, 17.46, 14.22, 7.98, 19.78, 24.43, 25.96, -3.67, -6.69, -5.16. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{196}H_{204}N_4O_{50}SiNa$, 3464.3210; found 3464.3224.

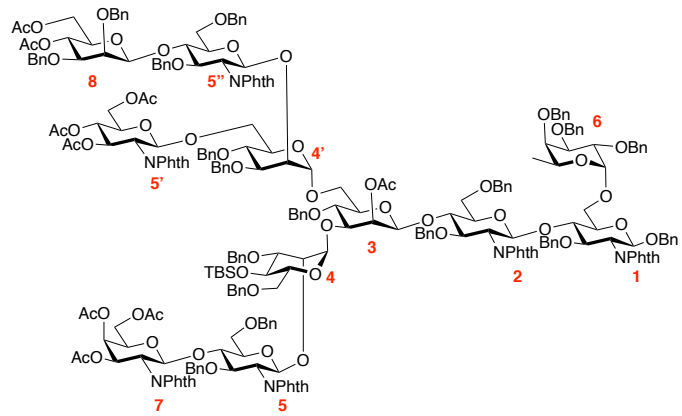
Benzyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-α-D-mannopyranosyl]-(1→6)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S15): A mixture of acceptor **S14** (1.4 g, 0.41 mmol) and donor **6**



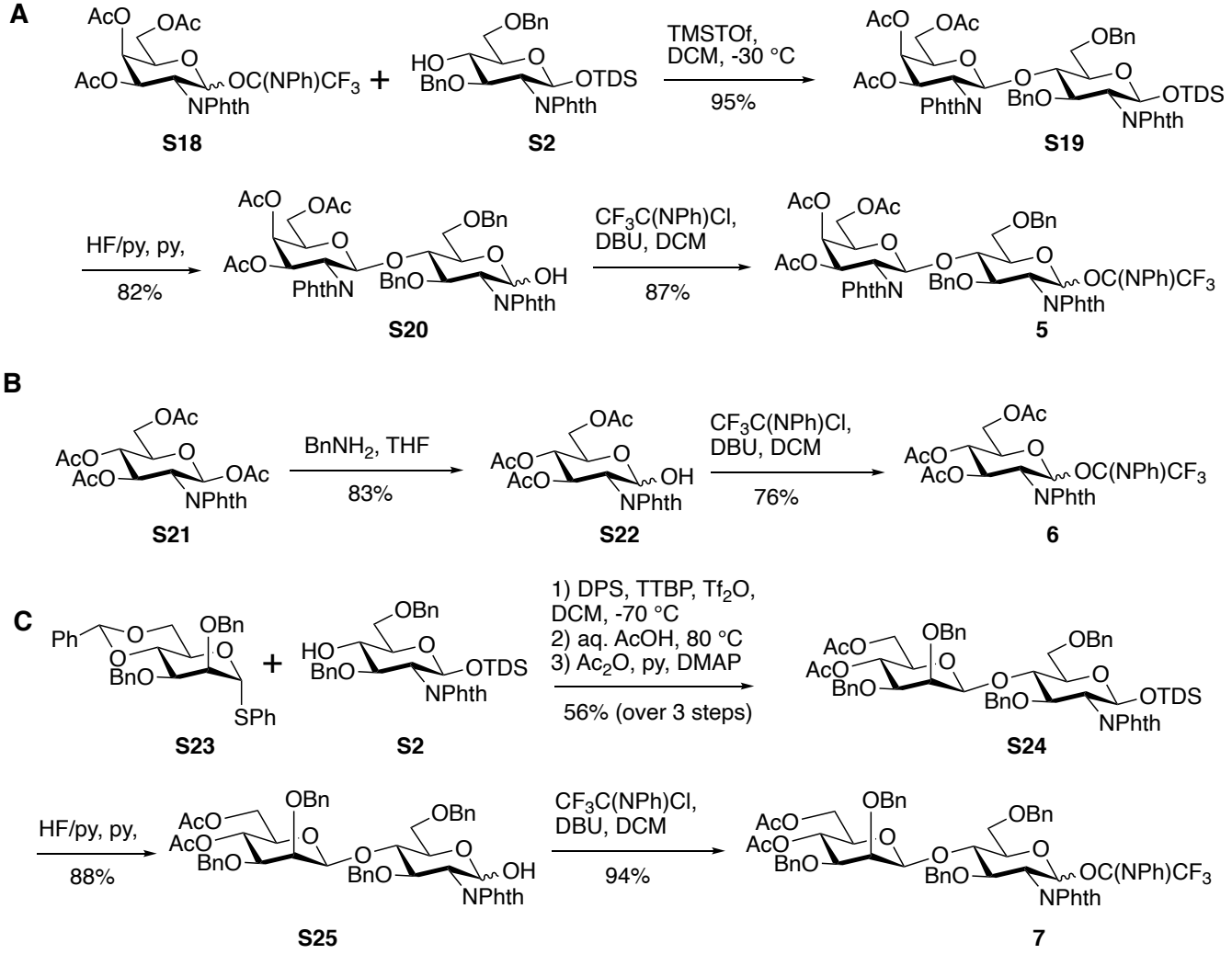
(986 mg, 1.6 mmol), was stirred in DCM (10 mL) with pre-activated molecular sieves (2 g) for 10 min, after which the mixture was cooled down to -40 ºC, followed by the addition of TfOH (15 μL, 0.16 mmol). The mixture was warmed up to -20 ºC over a period of 30 min, after which it was quenched with Et_3N (150 μL). The sieves were filtered off and the mixture was concentrated *in vacuo.* The residue was purified by silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 6: 4, v: v) and then passed through BioGel SX-1 column using Tol: Acetone (1: 1, v: v) as mobile phase, which afforded the product as an off-white amorphous powder. (1.25 g, 78%). R_f = 0.37 (Tol: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09 to 6.53 (90H, m, H-Ar), 5.81 (1H, t, H-3 GlcN-5', J = 9.7 Hz), 5.74 (1H, d, H-3 GalN-7, J = 11.3 Hz), 5.62 (1H, m, C$\underline{H}$=CH$_2$ of alloc), 5.38 (1H, d, H-1 GlcN-2, J = 8.1 Hz), 5.31 (2H, m, H-4 GalN-7, H-1 Man-4'), 5.19 (1H, d, H-1 GlcN-5, J = 7.7 Hz), 5.13 (4H, m, H-2 Man-4', H-4 GlcN-5', CH=C$\underline{H}_2$ of alloc), 4.98 to 4.78 (9H, m, H-2 Man-3, H-1 Man-4, H-1 GalN-7, H-1 GlcN-5', PhC$\underline{H}_2$ protons), 4.69 (3H, m, H-1 GlcN-1, PhC$\underline{H}_2$ protons), 4.56 (7H, m, H-2 GalN-7, H-1 Fuc,

PhC$\underline{H}_2$ protons), 4.48 to 4.20 (16H, m, H-2 GlcN-5', H-1 Man-3, H-6a GlcN-5', PhC$\underline{H}_2$ protons, OC$\underline{H}_2$ of alloc), 4.19 to 3.98 (13H, m, H-2 GlcN-1, H-2 GlcN-2, H-2 GlcN-5, H-6b GlcN-5', H-6a GalN-7, H-3 GlcN-1, H-3 GlcN-2, H-3 GlcN-5, PhC$\underline{H}_2$ protons), 3.98 to 3.76 (11H, m, H-6b GalN-7, H-5 Fuc-6, H-6a Man-3, H-2 Man-4, H-4 Man-4', H-4 GlcN-1, H-4 GlcN-2, H-4 GlcN-5, H-3 Fuc-6, H-2 Fuc-6, PhC$\underline{H}_2$ protons), 3.64 (3H, m, H-5 GalN-7, H-5 Man-4, H-5 GlcN-5'), 3.53 (2H, m, H-6a Man-4', H-3 Man-4), 3.45 (4H, m, H-4 Man-4, H-6b Man-3, H-6a Man-4, H-3 Man-3), 3.39 to 3.26 (6H, m, H-6a GlcN-2, H-6b Man-4, H-6a GlcN-5, H-5 Man-4', H-3 Man-4', H-5 GlcN-1), 3.20 (1H, m, H-4 Fuc-6), 3.15 to 2.98 (5H, m, H-6b GlcN-2, H-6b Man-4', H-6a GlcN-1, H-6b GlcN-1, H-5 GlcN-2), 2.54 (1H, m, H-6b GlcN-5), 2.46 (1H, m, H-5 Man-3), 2.10 to 1.75 (22H, m, 7x C$\underline{H}_3$ of Ac, H-5 GlcN-5), 0.92 (3H, d, C$\underline{H}_3$ of Fuc, J = 6.4 Hz), 0.74 (9H, s, 3x C-C$\underline{H}_3$ of TBS), -0.12 to -0.19 (6H, d, 2x C$\underline{H}_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$, signals from edited HSQCAD experiment): δ 123.91, 123.62, 128.01, 134.75, 123.42, 123.26, 133.59, 123.37, 126.32, 133.69, 127.98, 123.19, 128.05, 128.52, 128.08, 76.97, 128.26, 125.85, 127.44, 128.09, 125.66, 127.49, 127.89, 127.45, 128.53, 127.83, 70.65, 67.97, 131.49, 65.60, 96.77, 66.64, 98.37, 97.43, 118.54, 70.93, 69.07, 118.48, 74.83, 96.58, 71.44, 97.88, 73.02, 96.70, 73.06, 95.12, 74.83, 69.88, 73.80, 52.07, 97.98, 71.21, 74.87, 74.92, 72.84, 62.06, 98.39, 54.45, 69.91, 74.97, 68.28, 75.57, 61.99, 72.81, 55.77, 77.37, 76.69, 56.45, 74.62, 73.09, 60.85, 60.86, 75.80, 69.14, 72.86, 78.84, 65.89, 68.34, 71.03, 71.80, 73.29, 70.58, 77.53, 77.49, 63.68, 77.91, 68.81, 70.87, 67.31, 70.68, 76.80, 65.93, 68.06, 74.33, 73.93, 73.57, 63.67, 68.22, 65.89, 74.09, 30.97, 29.89, 20.74, 20.75, 19.22, 20.50, 29.86, 16.43, 24.40, 25.93, 0.02, -3.67, -5.19. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{216}H_{223}N_5O_{59}SiNa$, 3881.4270; found 3881.4741.

Benzyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,4-di-*O*-benzyl-α-D-mannopyranosyl]-(1→6)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→2)-3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-α-D-mannopyranosyl]-(1→3)-[2-*O*-acetyl-4-*O*-benzyl-β-D-mannopyranosyl]-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→4)-2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→6)-3-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S17): Compound **S15** (1.2 g, 0.31 mmol) was dissolved in THF (30 mL) and H_2O (3 mL), followed by the addition of tetrakis(triphenylphosphine)palladium (72 mg, 0.062 mmol) and morpholine (108 μL, 1.24 mmol). The mixture was stirred for 2 h after which it was concentrated *in vacuo* and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (8: 2, v: v to 3:7, v: v) which afforded the product as a white amorphous solid. (918 mg, 77%). R_f = 0.32 (Tol: EtOAc, 7:3, v: v). A mixture of acceptor **S16** (900 mg, 0.24 mmol) and donor **7** (1.0 g, 0.95 mmol), was stirred in DCM (10 mL) with pre-activated molecular sieves (2 g) for 10 min, after which the mixture was cooled down to -40 ºC, followed by the addition of TfOH (8.5 μL, 0.095 mmol). The mixture was warmed up to -20 ºC over a period of 30 min, after which it was quenched with Et_3N (100 μL). The sieves were filtered off and the mixture was concentrated *in vacuo.* The residue was purified by silica gel column chromatography using Tol: EtOAc (8: 2, v: v to 1: 1, v: v) and then passed through BioGel SX-1 column



using Tol: Acetone (1: 1, v: v) as mobile phase, which afforded the product as an off-white amorphous powder. (823 mg, 71%). R_f = 0.35 (Tol: EtOAc, 6: 4, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 to 6.44 (1140H, m, H-Ar), 5.76 (1H, dd, H-3 GalN-7, *J* = 11.5 Hz, 3.4 Hz), 5.35 (3H, m, H-4 GalN-7, H-3 GlcN-5', H-1 GlcN-2), 5.26 (2H, m, H-4 Man-8, H-1 Man-4'), 5.13 (1H, d, H-4 GlcN-5', *J* = 3.3 Hz), 4.95 to 4.82 (9H, m, H-2 Man-3, H-1 Man-4, H-1 GlcN-5, PhC$\underline{H}_2$ protons), 4.81 to 4.71 (6H, m, H-1 GalN-7, H-1 GlcN-5", H-1 GlcN-1, H-1 GlcN-5', PhC$\underline{H}_2$), 4.70 to 4.50 (10H, m, H-2 GalN-7, H-1 Fuc-6, PhC$\underline{H}_2$ protons), 4.49 to 4.22 (13H, m, H-1 Man-8, H-1 Man-3, PhC$\underline{H}_2$ protons), 4.21 to 4.03 (13H, m, H-2 GlcN-1, H-2 GlcN-2, H-2 GlcN-5, H-2 GlcN-5', H-6a GalN-7, H-6a Man-8, H-6a GlcN-5', H-3 GlcN-1, H-3 GlcN-2, H-3 GlcN-5, H-3 GlcN-5", PhC$\underline{H}_2$ protons), 4.03 to 3.90 (7H, m, H-6b GalN-7, H-6b GlcN-5', H-4 GlcN-1, H-4 GlcN-2, H-4 GlcN-5, H-4 GlcN-5", PhC$\underline{H}$H), 3.90 to 3.75 (8H, m, H-2 GlcN-5", H-6b Man-8, H-5 Fuc-6, H-4 Man-4', H-2 Man-4, H-3 Fuc-6, H-2 Fuc-6, PhCH$\underline{H}$), 3.70 (2H, m, H-5 Man-4, H-2 Man-4'), 3.64 to 3.51 (5H, m, H-6a GlcN-5", H-6a GlcN-5, H-5 GalN-7, H-5 Man-8, H-5 GlcN-5'), 3.50 to 3.28 (11H, m, H-4 Man-4, H-6b GlcN-5, H-6a Man-4, H-6a GlcN-1, H-6a Man-3, H-2 Man-8, H-5 Man-4', H-3 Man-3, H-3 Man-8, H-3 Man-4'), 3.21 (5H, m, H-6b GlcN-5", H-6a Man-4', H-6b Man-4, H-4 Man-3, H-3 Man-4), 3.13 (1H, m, H-5 GlcN-1), 3.04 (1H, m, H-5 GlcN-5"), 2.97 (1H, m, H-6a GlcN-2), 2.86 (2H, m, H-6b GlcN-2, H-6b Man-3), 2.68 (1H, m, H-6b Man-4'), 2.54 (4H, m, H-6b GlcN-1, H-5 Man-3, H-4 Fuc-6, H-5 GlcN-2), 2.10 to 1.81 (30H, 9x CH_3 of Ac, H-5 GlcN-5), 0.92 (3H, d, CH_3 of Fuc-6, *J* = 6.3 Hz), 0.74 (9H, s, 3x C-C$\underline{H}_3$ of TBS), -0.13 to -0.20 (6H, d, 2x C$\underline{H}_3$-Si of TBS); ^{13}C NMR (151 MHz, $CDCl_3$) δ 123.98, 123.62, 135.11, 123.49, 123.36, 133.66, 133.70, 133.58, 128.18, 126.55, 123.15, 127.90, 126.30, 128.22, 128.19, 76.95, 127.78, 125.80, 127.74, 128.08, 125.34, 127.95, 126.27, 127.92, 125.90, 128.02, 124.31, 125.88, 127.53, 125.99, 127.91, 127.85, 125.33, 127.11, 67.82, 70.68, 96.57, 66.65, 96.90, 68.10, 71.00, 96.60, 68.65, 74.31, 97.86, 97.05, 72.99, 94.98, 98.62, 73.38, 69.88, 74.22, 69.70, 52.02, 74.14, 73.78, 101.44, 71.46, 72.83, 72.78, 99.28, 69.90, 97.30, 69.29, 73.23, 55.83, 76.36, 62.93, 60.98, 72.83, 76.94, 73.10, 62.95, 60.88, 75.57, 72.78, 54.39, 79.16, 65.98, 61.67, 71.21, 75.07, 73.33, 70.54, 76.50, 64.06, 67.87, 77.96, 67.21, 70.90, 73.82, 67.93, 77.42, 68.91, 76.73, 72.51, 66.05, 68.89, 64.04, 79.64, 73.91, 74.33, 70.53, 68.14, 68.09, 70.94, 66.04, 70.96, 73.72, 70.42, 73.15, 19.98, 21.52, 30.98, 29.43, 20.80, 20.77, 19.24, 20.90, 20.76, 20.55, 19.02, 20.33, 73.43, 29.81, 14.88, 16.42, 24.42, 25.96, 0.03, -3.71, -5.16. MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{264}H_{270}N_6O_{70}SiNa$, 4694.7419; found 4694.7738.

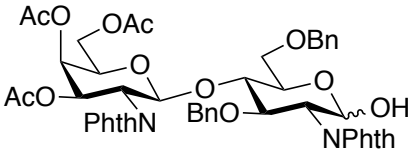


Scheme S4: Synthesis of Epitopes for extension at orthogonal sites.

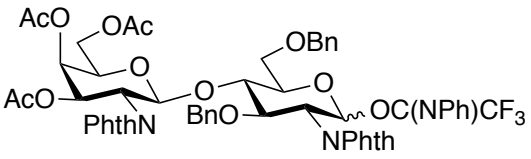
Dimethylthexylsilyl 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S19): A mixture of *N*-phenyltrifluoroimidate donor **S18** (6.2 g, 10.3 mmol) and acceptor **S2** (5.0 g, 7.9 mmol), was stirred with pre-activated molecular sieves (50 g) in DCM (50 mL) for 20 min. The mixture was then cooled down to -30 ºC, followed by the addition of TMSTOf (373 μL, 2.1 mmol). The reaction mixture was warmed up to -10 ºC over a period of 30 min, after which it was quenched with Et_3N (5 mL). The sieves were filtered off, and the mixture was concentrated *in vacuo* to give the crude product as a yellow syrup. Silica gel column chromatography with Tol: EtOAc (9.5: 0.5, v: v to 7: 3, v: v) yielded the product as white amorphous powder (7.9 g, 95%). R_f = 0.44 (Tol: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 to 6.85 (18H, m, H-Ar), 5.80 (1H, dd, H-3 GalN, *J* = 11.8 Hz, 2.6 Hz), 5.51 (1H, d, H-1 GalN, *J* = 8.5 Hz), 5.38 (1H, s, H-4 GalN), 5.18 (1H, d, H-1 GlcN, *J* = 8.4 Hz), 4.85 (1H, d, PhCHH, *J* = 12.6 Hz), 4.51 (3H, m, PhCHH, PhCHH, H-2 GalN), 4.44 (1H, d, PhCHH, *J* = 11.2 Hz), 4.25 (1H, t, H-3 GlcN, *J* = 8.8 Hz), 4.16 (1H, m, H-5 GalN), 4.12 to 3.94 (3H, m, H-2 GlcN, H-6a GalN, H-6b GalN), 3.80 (1H, t, H-4 GlcN, *J* = 6.7 Hz), 3.49 to 3.30 (3H, m, H-5 GlcN, H-6a GlcN, H-6b GlcN), 2.11 to 1.78 (9H,

3s, 3x C<u>H</u>$_3$ of Ac), 1.31 [1H, m, C<u>H</u>(CH$_3$)$_2$ of TDS] , 0.54 [12H, m, C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], 0.01 to -0.21 (6H, 2s, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.21, 172.14, 171.64, 170.21, 169.42, 140.66, 140.25, 136.32, 136.26, 135.57, 133.61, 133.34, 133.31, 130.94, 130.18, 130.13, 129.84, 129.60, 129.29, 129.21, 128.92, 125.71, 125.39, 125.05, 99.34, 95.16, 79.16, 79.02, 78.95, 78.80, 78.74, 78.58, 78.33, 76.38, 75.71, 74.67, 72.52, 69.85, 69.75, 68.54, 62.90, 59.65, 53.98, 35.76, 26.36, 22.60, 22.56, 22.42, 21.75, 21.58, 20.18, 20.06, 1.92, 0.00, -1.99. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{56}H_{64}N_2O_{16}SiNa$, 1071.3923; found 1071.3985.

3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20): Compound **S19** (7.5 g, 7.1 mmol) was dissolved in pyridine (100 mL) followed by dropwise addition of HF in pyridine (70% HF, 30% pyridine; 10 mL). The mixture was stirred for 15 h after which it was quenched by solid $NaHCO_3$, till all CO_2 bubbling stopped. The salts were filtered off, the solvent was evaporated *in vacuo*, and the residue was re-dissolved in DCM, followed by washing with water (150 mL) and saturated $NaHCO_3$ (150 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated. The residue was purified by silica gel column chromatography with Pet. Ether: EtOAc (8: 2, v: v to 1:1, v: v) as eluent to give the affording the product as a white foamy solid. (5.3 g, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 to 6.85 (18H, m, H-Ar), 5.76 (1H, dd, H-3 GalN, *J* = 11.5 Hz, 3.3 Hz), 5.44 (1H, d, H-1 GalN, *J* = 8.5 Hz), 5.36 (1H, s, H-4 GalN), 5.18 (1H, d, H-1 GlcN, *J* = 8.6 Hz), 4.87 (1H, d, PhCH<u>H</u>, *J* = 12.6 Hz), 4.47 (4H, m, PhC<u>H</u>H, PhC<u>H</u>H, H-2 GalN, PhCH<u>H</u>), 4.27 (1H, t, H-3 GlcN, *J* = 10.0 Hz), 4.19 (1H, m, H-5 GalN), 4.07 to 3.95 (3H, m, H-2 GlcN, H-6a GalN, H-6b GalN), 3.69 (1H, t, H-4 GlcN, *J* = 6.8 Hz), 3.57 to 3.37 (3H, m, H-5 GlcN, H-6a GlcN, H-6b GlcN), 2.09 to 1.79 (9H, 3s, 3x C<u>H</u>$_3$ of Ac); ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.34, 170.30, 169.81, 168.45, 168.39, 168.10, 167.52, 138.75, 138.54, 138.20, 138.08, 134.55, 134.50, 134.27, 133.84, 131.54, 131.39, 131.36, 131.30, 129.05, 128.40, 128.37, 128.25, 127.96, 127.95, 127.76, 127.62, 127.59, 127.50, 127.18, 127.13, 123.90, 123.61, 123.57, 123.31, 97.13, 96.97, 92.79, 92.55, 77.36, 77.15, 76.94, 76.44, 75.89, 75.86, 74.38, 74.26, 74.07, 73.60, 72.89, 72.83, 70.60, 70.57, 69.77, 68.24, 68.10, 67.79, 67.76, 66.60, 66.57, 60.85, 60.46, 57.37, 55.77, 52.02, 31.93, 29.70, 28.95, 22.71, 21.07, 20.69, 20.64, 20.62, 20.51. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{48}H_{46}N_2O_{16}Na$, 929.2745; found 929.2819.

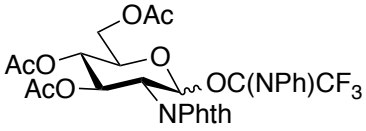


(*N*-Phenyl)-2,2,2-trifluoroacetimidate 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (5): Compound **S20** (5.3 g, 5.8 mmol) was dissolved in DCM (50 mL), followed by the addition of 2,2,2-Trifluoro-*N*-phenylacetimidoyl chloride (1.5 mL, 7.5 mmol) and DBU (867 μL, 5.8 mmol). The reaction mixture was stirred for 30 min, after which the solvent was evaporated *in vacuo* and the residue was purified using silica gel column chromatography (Pet. Ether: EtOAc, 9: 1, v: v to 7: 3, v: v), which provided the product as an off-white foamy powder. (5.5 g, 87%). R_f = 0.63 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 to 6.81 (22H, m, H-Ar), 6.53 (1H, br s, H-1 GlcN), 5.79 (1H, dd, H-3 GalN, *J* = 11.2 Hz, 2.9 Hz), 5.48 (1H, d, H-1 GalN, *J* = 8.5 Hz), 5.36 (1H, d, H-4 GalN, *J* = 2.6 Hz), 4.89 (1H, d, PhCH<u>H</u>, *J* = 10.6 Hz), 4.47 (4H, m, PhC<u>H</u>H, PhC<u>H</u>H, H-2 GalN, PhCH<u>H</u>), 4.34 (2H, m, H-3 GlcN, H-2 GlcN) 4.11 to 3.98 (2H, m, H-6a GalN, H-6b GalN), 3.70 (1H, t, H-4 GlcN, *J* = 6.9 Hz), 3.63 to 3.35 (3H, m, H-5 GlcN, H-6a GlcN, H-6b GlcN), 2.09 to 1.79 (9H, 3s, 3x C<u>H</u>$_3$ of Ac); ^{13}C NMR

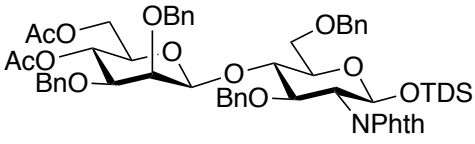


(151 MHz, $CDCl_3$): δ 171.18, 170.31, 170.24, 169.77, 168.39, 167.51, 142.97, 138.31, 138.06, 134.56, 134.51, 134.01, 131.42, 131.41, 131.35, 128.52, 128.40, 128.03, 127.88, 127.65, 127.54, 127.26, 124.25, 123.89, 123.54, 123.50, 119.20, 97.13, 77.33, 77.12, 76.91, 76.36, 75.34, 75.22, 74.26, 72.73, 70.66, 67.77, 66.58, 60.91, 60.41, 54.58, 51.99, 49.78, 23.42, 21.07, 20.71, 20.65, 20.53, 14.22. Compound was unstable under MALDI-TOF-MS conditions.

(*N*-Phenyl)-2,2,2-trifluoroacetimidate 3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-D-glucopyranoside (6): To a solution of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose **S21** (28.7 g, 60.2 mmol) in anhydrous THF was added benzylamine (4.7 mL, 43.1 mmol), and the reaction mixture was stirred for 10 h, after which the solvent was removed in vacuo, the residue was dissolved in DCM (300 mL), and washed with 1N HCl (200 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo* to afford compound **S22** as a yellow oil. This residue was purified by silica gel column chromatography with Pet. Ether: EtOAc (8: 2, v: v to 4: 6, v: v). To a solution of 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose **S22** in DCM (150 mL) was added 2,2,2- Trifluoro-*N*-phenylacetimidoyl chloride (15 mL, 72.2 mmol) and DBU (9.5 mL, 45.9 mmol) at 0 °C. The reaction mixture was stirred at this temperature for 1 h, after which it was concentrated *in vacuo* and purified by silica gel column chromatography with Pet. Ether: EtOAc (9: 1, v: v to 1: 1, v: v) as eluent to give the imidate as a light-yellow foam. (25.2 g, 76% over two steps). R*f* = 0.62 (Pet. Ether: EtOAc, 6: 4, v: v). NMR data corresponds to reported literature.[2]

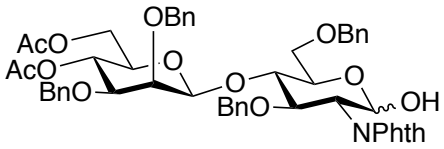


Dimethylthexylsilyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S24): A mixture of phenyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-*α*-D-mannopyranoside donor **S23** (8.5 g, 15.8 mmol), diphenyl sulfoxide (3.2 g, 15.8 mmol), TTBP (3.9 g, 15.8 mmol) and pre-activated molecular sieves was stirred in DCM (40 mL) for 20 min. The mixture was then cooled to -70 ºC, followed by the addition of Tf_2O (2.6 mL, 15.8 mmol) along the wall of the flask. After 10 min at -70 ºC, a solution of **S2** (5.0 g, 7.9 mmol) in dry DCM (15 mL) was slowly added along the wall of the flask. The reaction was stirred for additional 30 min at -70 ºC, after which it was gradually warmed to -50 ºC, and then quenched with Et_3N (15 mL). The sieves were filtered off, the filtrate was diluted with DCM (100 mL) and washed with sat. $NaHCO_3$ (50 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo* to give the crude product, which was directly dissolved in 80% aq. AcOH (150 mL) and the resulting solution was heated at 80 °C for 3 h. The mixture was concentrated *in vacuo*, and the residue was re-dissolved in DCM and washed with sat. $NaHCO_3$ (100 mL). The organic phase was dried over $MgSO_4$, filtered, the filtrate was concentrated and co-evaporated with toluene thrice. The residue was further dissolved in pyridine (100 mL), followed by the addition of DMAP (500 mg, cat.) and Ac_2O (50 mL). The mixture was stirred for 2 h, after which it was quenched with methanol (1 mL) and concentrated. The resulting syrup was then dissolved in DCM (20 mL) and washed with 1 M HCl (50 mL) after which the solvent was evaporated, and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (8: 2, v: v to 1: 1, v: v) as eluent giving the pure compound as a white foamy powder. (4.7 g, 56% over three steps). R*f* = 0.64 (Pet. Ether: EtOAc, 6: 4, v: v). ^{1}H NMR

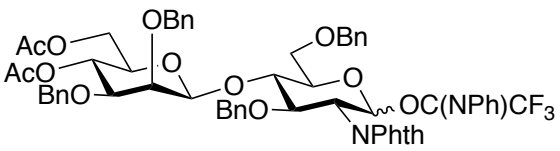


(600 MHz, $CDCl_3$): δ 7.71 to 6.64 (24H, m, H-Ar), 5.22 (2H, m, H-4 Man, H-1 GlcN), 4.76 (3H, m, PhC$\underline{H}_2$, PhC$\underline{H}$H), 4.57 (1H, d, PhCH$\underline{H}$, *J* = 11.8 Hz), 4.50 (1H, s, H-1 Man), 4.42 to 4.32 (3H, m, PhCH$\underline{H}$, PhCH_2), 4.22 (1H, d, PhC$\underline{H}$H, *J* = 11.8 Hz), 4.16 (1H, dd, H-3 GlcN, *J* = 10.7 Hz, 8.8 Hz), 4.02 (2H, m, H-2 GlcN, H-6a Man), 3.91 (2H, m, H-6b Man, H-4 GlcN), 3.71 (1H, d, H-2 Man, *J* = 2.5 Hz), 3.55 (2H, m, H-6a GlcN, H-6b GlcN), 3.45 (1H, m, H-5 GlcN), 3.31 (1H, m, H-5 Man), 3.21 (1H, dd, H-3 Man, *J* = 9.8 Hz, 2.8 Hz), 1.94 to 1.81 (6H, 2s, 2x C$\underline{H}_3$ of Ac), 1.27 [1H, m, C$\underline{H}(CH_3)_2$ of TDS] , 0.50 [12H, m, C(C$\underline{H}_3)_2$, CH(C$\underline{H}_3)_2$ of TDS], 0.03 to -0.20 (6H, 2s, 2x C$\underline{H}_3$-Si of TDS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.76, 171.54, 170.04, 169.46, 140.72, 140.41, 139.90, 139.73, 135.54, 135.40, 133.57, 133.42, 130.34, 130.23, 130.19, 130.16, 129.98, 129.92, 129.86, 129.74, 129.63, 129.58, 129.56, 129.53, 129.47, 129.25, 129.16, 129.13, 128.68, 124.89, 124.77, 103.37, 95.24, 81.38, 81.26, 79.18, 78.97, 78.76, 78.66, 76.45, 76.17, 76.07, 75.83, 75.36, 74.43, 74.30, 73.21, 70.64, 69.89, 64.78, 59.62, 35.70, 33.74, 31.50, 26.31, 22.74, 22.68, 22.55, 22.18, 21.71, 21.54, 20.45, 20.12, 20.01, 16.03, 0.24, 0.00, -1.99, -2.09. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{60}H_{71}NO_{14}SiNa$, 1080.4542; found 1080.4505.

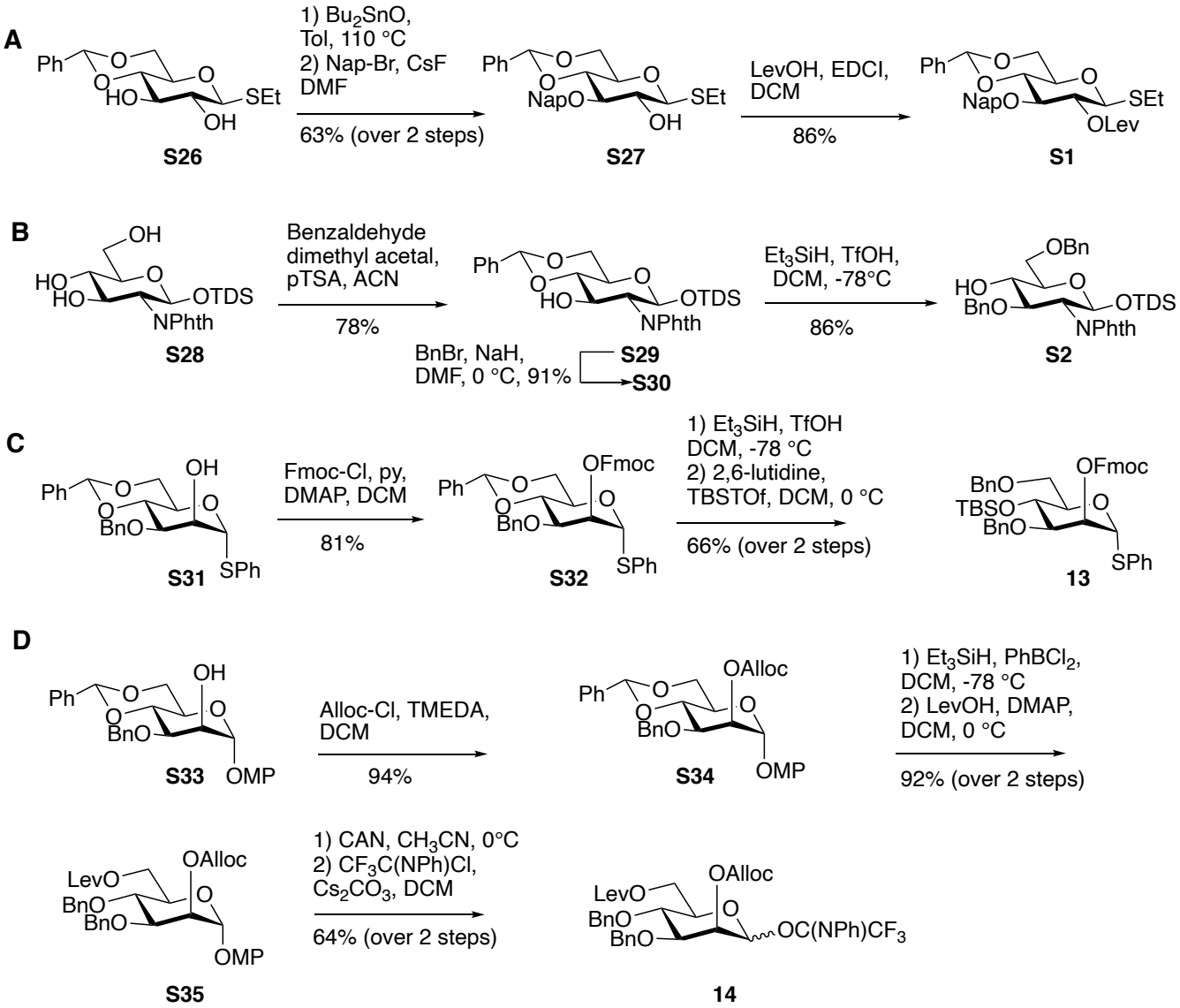
4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S25): Compound **S24** (4.5 g, 4.2 mmol) was dissolved in pyridine (70 mL) followed by dropwise addition of HF in pyridine (70% HF, 30% pyridine; 6 mL). The mixture was stirred for 12 h after which it was quenched by solid $NaHCO_3$ (20 g), till all CO_2 bubbling stopped. The salts were filtered off, the solvent was evaporated *in vacuo*, and the residue was re-dissolved in DCM (50 mL), followed by successive washing with water (100 mL) and saturated $NaHCO_3$ (100 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated. The residue was purified by silica gel column chromatography with Pet. Ether: EtOAc (8: 2, v: v to 1:1, v: v) as eluent to give the affording the product as a white foamy powder. (3.7 g, 88%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 to 6.67 (24H, m, H-Ar), 5.30 (2H, m, H-4 Man, H-1 GlcN), 4.93 to 4.79 (3H, m, PhC$\underline{H}_2$, PhC$\underline{H}$H), 4.66 (1H, d, PhCH$\underline{H}$, *J* = 11.9 Hz), 4.52 to 4.38 (4H, m, H-1 Man, PhCH$\underline{H}$, PhC$\underline{H}_2$), 4.31 (2H, m, PhC$\underline{H}$H, H-3 GlcN), 4.15 to 3.98 (4H, m, H-2 GlcN, H-6a Man, H-6b Man, H-4 GlcN), 3.73 (1H, d, H-2 Man, *J* = 2.8 Hz), 3.68 (1H, m, H-6a GlcN), 3.59 (2H, m, H-6b GlcN, H-5 GlcN), 3.36 (1H, m, H-5 Man), 3.23 (1H, dd, H-3 Man, *J* = 9.7 Hz, 2.6 Hz), 2.02 to 1.92 (6H, 2s, 2x C$\underline{H}_3$ of Ac); ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.95, 169.70, 168.11, 138.82, 138.53, 137.93, 137.76, 133.78, 131.61, 128.61, 128.45, 128.18, 128.00, 127.97, 127.86, 127.79, 127.78, 127.50, 127.29, 126.91, 123.29, 101.41, 93.01, 79.43, 79.23, 77.26, 77.05, 76.84, 74.66, 74.54, 74.37, 74.08, 73.61, 72.43, 71.42, 68.56, 68.02, 62.91, 60.45, 57.57, 20.95, 20.74, 0.03. MALDI-TOF-MS (*m/z*): [M+ Na]$^+$ calculated for $C_{52}H_{53}NO_{14}Na$, 938.3364; found 938.3771.



(*N*-Phenyl)-2,2,2-trifluoroacetimidate 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (7): Compound **S25** (3.7 g, 4.0 mmol) was dissolved in DCM (50 mL), followed by the addition of 2,2,2- Trifluoro-*N*-phenylacetimidoyl chloride (1.1 mL, 5.3 mmol) and DBU (598 μL, 4.0 mmol). The reaction mixture was stirred for 30 min, after which the solvent was evaporated *in vacuo* and the residue was purified using silica gel column chromatography (Pet. Ether: EtOAc, 9: 1, v: v to 6: 4, v: v), which provided the product as an off-white amorphous powder. (4.1 g, 94%). R_f = 0.58 (Pet. Ether: EtOAc, 6: 4, v: v). ^{1}H NMR (400



MHz, $CDCl_3$): δ 7.92 to 6.72 (28H, m, H-Ar), 6.63 (1H, br s, H-1 GlcN), 5.29 (1H, t, H-4 Man, *J* = 9.8 Hz), 4.84 (3H, m, PhC$\underline{H}_2$, PhCH$\underline{H}$), 4.68 (1H, d, PhC$\underline{H}$H, *J* = 12.1 Hz), 4.52 (1H, s, H-1 Man), 4.48 to 4.27 (5H, m, 2x PhC$\underline{H}_2$, PhCH$\underline{H}$), 4.17 to 3.95 (3H, m, H-6a Man, H-3 GlcN, H-6b Man), 3.74 (1H, d, H-2, Man, *J* = 2.7 Hz), 3.36 (1H, m, H-5 Man), 3.25 (1H, dd, H-3, Man, *J* = 9.8 Hz, 2.8 Hz), 2.12 to 1.84 (3H, 2s, C$\underline{H}_3$ of Ac); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.86, 169.64, 142.98, 138.56, 138.45, 137.88, 137.69, 133.85, 131.43, 128.57, 128.40, 128.14, 127.97, 127.91, 127.85, 127.83, 127.77, 127.74, 127.47, 127.26, 126.94, 124.36, 123.38, 119.30, 101.25, 79.44, 78.58, 77.45, 77.03, 76.66, 76.60, 75.37, 74.59, 74.32, 74.03, 73.50, 72.45, 71.46, 68.02, 62.90, 54.71, 30.90, 20.90, 20.70. Compound was unstable under MALDI-TOF-MS conditions.



Scheme S5: Synthesis of building blocks.

Ethane 4,6-*O*-benzylidene-3-*O*-(2-methylnaphthyl)-1-thio-β-D-glucopyranoside (S27): To a suspension of diol compound **S26** (34.0 g, 109 mmol) in anhydrous toluene (200 mL) was added Bu_2SnO (40.7 g, 163.5 mmol) and the mixture was refluxed at 110 °C for 2 h, till the solution became clear. The mixture was then cooled to room temperature and solvent was evaporated *in vacuo.* The residue was dissolved in DMF (200 mL), followed by the addition of 2-(bromomethyl)naphthalene (28.9 g, 130.7 mmol) and CsF (33g, 217.9 mmol). The mixture was stirred overnight after which it was concentrated *in vacuo*. The residue was dissolved in DCM (400 mL) and washed with sat. $NaHCO_3$ (500 mL). The organic phase was then filtered over Buchner funnel to remove the precipitated salts, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 6:4, v: v) which afforded the product as a white foamy solid. (31.2 g, 63%). R_f = 0.53 (Tol: EtOAc, 8:2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 to 7.21 (12H, m, H-Ar), 5.58 (1H, s, PhC<u>H</u> of benzylidene), 5.12 (1H, d, CH<u>H</u> of Nap, *J* = 11.9 Hz), 4.99 (1H, d, C<u>H</u>H of Nap, *J* = 11.9 Hz), 4.45 (1H, d, H-1, *J* = 9.7 Hz), 4.35 (1H, q, H-6a), 3.74 (3H, m, H-6b, H-3, H-4), 3.61 (1H, m, H-2), 3.48 (1H, m, H-5), 2.73 (2H, m, SC<u>H</u>$_2$CH$_3$), 1.31 (3H, t, SCH$_2$C<u>H</u>$_3$, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 197.50, 137.22, 136.95, 135.71, 133.25, 133.02, 129.02, 128.33, 128.27, 128.21, 127.93, 127.69, 127.66, 126.82, 126.26, 126.06, 126.03, 125.97, 125.87, 101.89, 101.34, 86.63, 81.39, 81.17, 80.35, 77.34, 77.23, 77.03, 76.71, 74.66, 73.21, 73.11, 71.04, 70.75, 68.64, 53.42, 24.58, 15.24, -0.00. MALDI-TOF-MS (*m/z*): [M + Na]$^+$: calculated for $C_{26}H_{28}O_5SNa$, 475.1555; found 475.1607.

Ethane 4,6-*O*-benzylidene-2-*O*-levulenoyl-3-*O*-(2-methylnaphthyl)-1-thio-β-D-glucopyranoside (S1): Compound **S27** (30.0 g, 66.3 mmol) was dissolved in DCM (200 mL) and the mixture was cooled down to 0 °C. This was followed by the addition of LevOH (10.2 mL, 99.5 mmol) and EDCI (15.4 g, 99.5 mmol). The mixture was stirred for 6 h, during which the temperature was warmed to room temperature. The mixture was then diluted with DCM (200 mL) and washed with sat. $NaHCO_3$ (100 mL). The organic phase was dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 7: 3, v: v) which afforded the product as a white foamy solid. (31.4 g, 86%). R_f = 0.47 (Tol: EtOAc, 8:2, v: v). ^{1}H NMR (400MHz, $CDCl_3$): δ 7.90 to 7.21 (12H, m, H-Ar), 5.59 (1H, s, PhC<u>H</u> of benzylidene), 5.08 (1H, m, H-2), 5.02 (1H, d, CH<u>H</u> of Nap, *J* = 12.0 Hz), 4.89 (1H, d, C<u>H</u>H of Nap, *J* = 12.0 Hz), 4.44 (1H, d, H-1, *J* = 10.1 Hz), 4.37 (1H, q, H-6a), 3.78 (3H, m, H-6b, H-3, H-4), 3.47 (1H, m, H-5), 2.66 (4H, m, SC<u>H</u>$_2$CH$_3$, C<u>H</u>$_2$COCH$_3$), 2.51 (2H, m, COOC<u>H</u>$_2$), 2.10 (3H, s, Lev CH$_2$COC<u>H</u>$_3$), 1.24 (3H, t, SCH$_2$C<u>H</u>$_3$, *J* = 7.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.11, 171.41, 137.18, 135.66, 133.20, 133.01, 132.98, 129.06, 128.33, 128.30, 128.10, 128.02, 127.92, 127.67, 126.82, 126.79, 126.14, 126.11, 126.06, 126.04, 125.88, 101.29, 84.17, 81.45, 79.46, 77.44, 77.31, 77.12, 76.80, 74.33, 73.47, 71.67, 70.64, 68.57, 53.48, 37.75, 37.67, 29.76, 28.00, 27.77, 24.02, 14.87. MALDI-TOF-MS (*m/z*): [M + Na]$^+$: calculated for $C_{31}H_{34}O_7SNa$, 573.1923; found 573.1960.

Dimethylthexylsilyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (S29): To a suspension of triol **S28** (42.0 g, 93.1 mmol) in anhydrous acetonitrile (200 mL) was added benzaldehyde dimethyl acetal (18.2 mL, 121.0 mmol) and *p*-Toluenesulfonic acid monohydrate (3.5 g, 18.6 mmol). The mixture was stirred

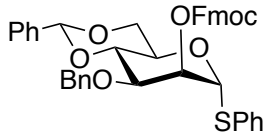
for 6 h, after which it was quenched with NEt_3 (20 mL). The solvent was concentrated *in vacuo* and the residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (9: 1, v: v to 7: 3, v: v), which afforded the target compound as a white amorphous solid, (39.2 g, 78%). R_f = 0.47 (Pet. Ether: EtOAc, 8: 2 v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 to 7.32 (9H, m, H-Ar), 5.55 (1H, s, PhC<u>H</u> of benzylidene), 5.47 (1H, d, H-1, *J* = 8.4 Hz), 4.62 (1H, dd, H-3, *J* = 10.5 Hz, 8.6 Hz), 4.31 (1H, q, H-6b), 4.19 (1H, dd, H-2, *J* = 10.5 Hz, 8.2 Hz), 3.81(1H, m, H-6a), 3.61(2H, m, H-4, H-5), 1.38 [1H, m, C<u>H</u>$(CH_3)_2$ of TDS], 0.62 [12H, m, C($C\underline{H}_3)_2$, CH($C\underline{H}_3)_2$ of TDS], 0.09 to -0.04 (6H, 2s, 2x $C\underline{H}_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.03, 134.05, 131.69, 129.31, 128.35, 126.32, 123.27, 101.95, 93.88, 82.40, 77.31, 77.00, 76.68, 68.74, 68.44, 66.20, 58.64, 33.79, 24.47, 19.79, 19.60, 18.29, 18.16, -0.02, -1.86, -3.82. MALDI-TOF-MS (*m/z*): $[M + Na]^+$: calculated for $C_{29}H_{37}NO_7SiNa$, 562.2237; found 562.2313.

Dimethylthexylsilyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranoside (S30): A solution of **S29** (39.0 g, 72.3 mmol) in DMF (200 mL) was cooled down to 0 ºC, followed by the sequential addition of BnBr (12.9 mL, 108.4 mmol) and NaH (5.8 g, 144.6 mmol, 60% dispersion in oil). The mixture was stirred at this temperature for two h, after which it was quenched with AcOH (50 mL). The solvent was evaporated *in vacuo* and the residue was diluted with DCM (200 mL), washed with saturated $NaHCO_3$ (500 mL) and water (500 mL) and dried over $MgSO_4$. The organic phase was filtered, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography using Pet. Ether: EtOAc (9: 1, v: v to 7: 3, v: v), which afforded the target compound as a transparent sticky syrup. (41.6 g, 91%). R_f = 0.66 (Pet. Ether: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 to 6.75 (14H, m, H-Ar), 5.60 (1H, s, PhC<u>H</u> of benzylidene), 5.41 (1H, d, H-1, *J* = 8.4 Hz), 4.77 (1H, d, PhC<u>H</u>H, *J* = 12.2 Hz), 4.50 (1H, d, PhCH<u>H</u>, *J* = 12.2 Hz), 4.42 (1H, dd, H-3, *J* = 10.6 Hz, 9.1 Hz), 4.33 (1H, q, H-6b), 4.16 (1H, dd, H-2, *J* = 10.6 Hz, 8.2 Hz), 3.63 (1H, m, H-5), 3.83 (2H, m, H-6a, H-4), 1.35 [1H, m, C<u>H</u>$(CH_3)_2$ of TDS], 0.60 [12H, m, C($C\underline{H}_3)_2$, CH($C\underline{H}_3)_2$ of TDS], 0.06 to -0.09 (6H, 2s, 2x $C\underline{H}_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 38.05, 137.42, 133.76, 131.67, 128.97, 128.55, 128.25, 128.04, 128.00, 127.31, 126.08, 123.13, 101.33, 93.92, 83.23, 77.31, 76.99, 76.67, 74.36, 73.92, 68.85, 66.22, 57.91, 33.77, 24.47, 19.77, 19.61, 18.26, 18.15, -0.03, -1.88, -3.87. MALDI-TOF-MS (*m/z*): $[M + Na]^+$: calculated for $C_{29}H_{37}NO_7SiNa$, 562.2237; found 562.2313.

Dimethylthexylsilyl 3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S2): A solution of compound **S30** (41.5 g, 65.9 mmol) was stirred with pre-activated molecular sieves (100 g) in DCM (300 mL) for 30 min. The mixture was cooled down to -78 ºC, followed by the sequential addition of triethylsilane (21.1 mL, 131.8 mmol) and trifluoromethanesulfonic acid (9.9 mL, 112.1 mmol). The mixture was stirred at this temperature for half an hour, after which it was quenched with a mixture of Et_3N: MeOH (40 mL, 1:1, v: v). The mixture was warmed to room temperature, the molecular sieves were filtered off and the filtrate was diluted by DCM (200 mL) and washed with sat. $NaHCO_3$ (300 mL) and dried over $MgSO_4$. The organic phase was filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using Pet. Ether: EtOAc (9: 1, v: v to 7: 3, v: v) yielded the product as an off-white semi-solid. (35.6 g, 86%). R_f = 0.28 (Pet. Ether: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 to 6.88 (14H, m, H-Ar), 5.35 (1H, d, H-1, *J* = 8.0 Hz), 4.71 (1H, d, PhC<u>H</u>H, *J* = 12.2 Hz), 4.60 (2H, m, PhC$\underline{H}_2$), 4.53 (1H, d, PhCH<u>H</u>, *J* = 12.2 Hz), 4.42 (1H, dd, H-3, *J* = 10.9 Hz, 8.4 Hz), 4.10 (1H, dd, H-2, *J* = 10.9 Hz, 8.1 Hz),

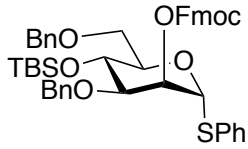
3.78 (3H, m, H-6a, H-6b H-4), 3.63 (1H, m, H-5), 2.84 (1H, d, OH, *J* = 2.5 Hz), 1.34 [1H, m, CH(CH$_3$)$_2$ of TDS], 0.57 [12H, m, C(CH$_3$)$_2$, CH(CH$_3$)$_2$ of TDS], 0.08 to -0.07 (6H, 2s, 2x CH$_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.30, 137.71, 133.73, 128.47, 128.14, 127.86, 127.81, 127.68, 127.38, 93.38, 78.47, 77.31, 77.19, 76.99, 76.67, 74.47, 74.05, 73.77, 73.55, 70.97, 57.38, 33.82, 24.45, 19.83, 19.64, 18.26, 18.14, -0.03, -1.82, -3.89. MALDI-TOF-MS (*m/z*): [M + Na]$^+$: calculated for $C_{36}H_{45}NO_7SiNa$, 654.2863; found 654.2988.

Phenyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-fluorenylmethoxycarbonyl-1-thio-α-D-mannopyranoside (S32): To a solution of **S31** (30.0 g, 66.6 mmol) in DCM (200 mL) was added DMAP (500 mg, cat), pyridine (60 mL) and Fmoc-Cl (34.5 g, 133.2 mmol) and the mixture was stirred for 2 h.



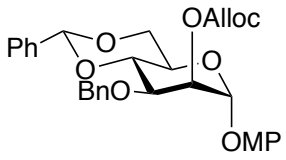
After that time, a second portion of Fmoc-Cl (8.6 g, 33.3 mmol) was added and stirring was continued for another 30 min, upon which TLC (Pet. Ether: EtOAc, 7: 3) showed the full consumption of starting material. The mixture was then diluted by DCM (200 mL) and washed with 1 N HCl (100 mL). The organic phase was dried ($MgSO_4$), filtered and the filtrate was concentrated. The residue was purified by silica gel column chromatography with Pet. Ether: EtOAc (9:1, v: v to 6:4, v: v) as eluent which gave the desired product as a white foam. (36.3 g, 81%). R*f* = 0.69 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 to 7.15 (22H, m, H-Ar), 5.71 (s, 1H, PhCH of benzylidene), 5.60 (1H, d, H-1, *J* = 1.5 Hz), 5.48 (1H, dd, H-2, *J* = 3.4 Hz, 1.5 Hz), 4.80 (2H, s, CH$_2$ of Fmoc), 4.52 to 4.30 (3H, m, PhCHH, H-5, PhCHH), 4.32 to 4.21 (3H, m, H-6a, H-4, CH of Fmoc), 4.08 (1H, dd, H-3, *J* = 9.8 Hz, 3.4 Hz), 3.95 (1H, t, H-6b, *J* = 10.2 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.62, 143.41, 143.10, 141.29, 141.24, 137.79, 137.38, 132.87, 132.21, 129.25, 129.00, 128.37, 128.23, 128.12, 127.92, 127.89, 127.74, 127.68, 127.22, 127.19, 126.13, 125.29, 125.16, 120.05, 101.65, 86.92, 78.51, 77.46, 77.03, 76.61, 75.56, 74.06, 72.56, 70.45, 68.40, 65.26, 46.66. MALDI-TOF-MS (*m/z*): [M + Na]$^+$: calculated for $C_{41}H_{36}O_7SNa$, 695.2079; found 695.2103.

Phenyl 3,6-di-*O*-benzyl-4-*O*-*t*-butyldimethylsilyl-2-*O*-fluorenylmethoxycarbonyl-1-thio-α-D-mannopyranoside (13): A solution of compound **S32** (36.3 g, 54.0 mmol) was stirred with pre-activated molecular sieves (70 g) in DCM (300 mL) for 30 min. The mixture was cooled down to -78 ºC, followed by the sequential addition of Et_3SiH (17.3 mL, 108.0 mmol) and trifluoromethanesulfonic acid (8.1 mL, 91.8 mmol). The mixture was stirred at this temperature for half an hour, after which it was quenched with a mixture of Et_3N: MeOH (40 mL, 1:1, v: v). The mixture was warmed to room temperature, the molecular sieves were filtered off and the filtrate was diluted by DCM (200 mL) and washed with sat. $NaHCO_3$ and dried over $MgSO_4$. The organic phase was filtered, and the filtrate was concentrated *in vacuo* to give the crude product as an oil. This crude product was dissolved in anhydrous DCM (200 mL), and cooled down to 0 °C, followed by the addition of 2,6-lutidine (9.1 mL, 77.9 mmol), and TBSOTf (14.3 mL, 62.3 mmol), and stirring was continued for 1 h, after which the mixture was diluted by DCM and washed with sat. $NaHCO_3$ (200 mL) and 1 N HCl (200 mL). The organic phase was then dried over MgSO4, filtered and filtrate was concentrated to afford the crude product as a clear oil. Silica gel column chromatography with Pet. Ether: EtOAc (9: 1, v: v to 6: 4, v: v) afforded the product a transparent oil. (28.4 g, 66% over two steps). R_f = 0.33 (Pet. Ether: EtOAc, 8: 2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 to 7.09 (23H, m, H-Ar), 5.61 (1H, d, H-1, *J* = 1.4 Hz), 5.45 (1H, m, H-2), 4.72 (1H,

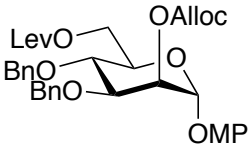


d, PhCHH, *J* = 11.3 Hz), 4.60 (2H, s, CH_2 of Fmoc), 4.53 (1H, d, PhCHH, *J* = 11.3 Hz), 4.43 to 4.20 (4H, m, PhCHH, CH of Fmoc, PhCHH, H-5), 4.08 (1H, t, H-4, *J* = 8.8 Hz), 3.91 to 3.80 (2H, m, H-6a, H-6b), 3.75 (1H, dd, H-3, *J* = 8.9 Hz, 3.1 Hz), 0.87 (9H, s, 3x C-CH_3 of TBS), 0.07 (6H, d, 2x CH_3-Si of TBS *J* = 12.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.66, 154.57, 143.41, 143.36, 143.24, 141.33, 141.24, 141.23, 138.45, 137.52, 136.48, 133.50, 132.32, 131.88, 131.85, 129.05, 128.99, 128.36, 128.26, 128.22, 128.13, 128.01, 127.91, 127.87, 127.85, 127.77, 127.72, 127.61, 127.49, 127.47, 127.39, 127.35, 127.24, 127.19, 127.13, 125.28, 125.18, 120.11, 120.09, 120.00, 86.02, 85.33, 78.62, 77.34, 77.22, 77.02, 76.70, 74.03, 73.79, 73.67, 73.20, 72.20, 71.28, 70.31, 69.91, 69.53, 68.14, 46.78, 46.55, 25.95, 25.77, 25.65, 24.51, 18.19, 17.97, 0.00, -3.57, -3.82, -4.26, -4.81, -4.94. MALDI-TOF-MS (*m/z*): $[M + Na]^+$: calculated for $C_{47}H_{52}O_7SSiNa$, 811.3101; found 811.3420.

4-Methoxyphenyl 2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-1-thio-α-D-mannopyranoside (S34): To a solution of compound **S33** (16 g, 34.5 mmol) in DCM (100 mL) was added TMEDA (7.7 mL, 51.7 mmol), followed by Alloc-Cl (4.4 mL, 41.4 mmol), and the reaction mixture was left stirring for 30 min, after which a second portion of TMEDA (1.5 mL, 11.14 mmol) and Alloc-Cl (1.3 mL, 11.14 mmol) were added, and stirring was continued for another 30 min. The mixture was diluted with DCM (200 mL) and washed with 1 N HCl (100 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated to give the crude product. The crude product was purified by silica gel column chromatography with Pet. Ether: EtOAc (9:1, v: v to 1:1, v: v) as eluent to give the desired product as a transparent oil. (17.8 g, 94%). R*f* = 0.65 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 to 6.75 (14H, m, H-Ar), 5.92 (1H, m, CH=CH_2 of alloc), 5.63 (1H, s, PhCH of benzylidene), 5.48 (1H, d, H-1, *J* = 1.5 Hz), 5.38 (2H, m, H-2, CH=CHH of alloc), 5.26 (1H, dd, CH=CHH of alloc, *J* = 10.5 Hz, 1.2 Hz), 4.78 (2H, s, PhCH_2), 4.65 (2H, m, OCH_2 of alloc), 4.18 (3H, m, H-6a, H-4, H-3), 4.00 (1H, m, H-5), 3.83 (1H, t, H-6b, *J* = 10.2 Hz), 3.76 (3H, s, OCH_3); ^{13}C NMR (101 MHz, $CDCl_3$): δ 126.08, 127.91, 128.29, 128.25, 128.17, 117.90, 117.88, 114.69, 101.59, 97.56, 119.28, 73.54, 119.28, 119.27, 119.28, 70.75, 72.47, 73.58, 71.36, 69.02, 68.50, 73.71, 78.20, 78.21, 64.43, 68.51, 53.92, 55.62, 54.51, 56.73. MALDI-TOF-MS (*m/z*): $[M + Na]^+$: calculated for $C_{31}H32O9Na$, 571.1944; found 571.2296.

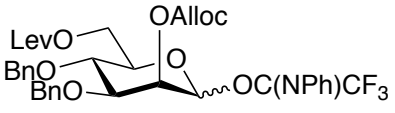


4-Methoxyphenyl 2-*O*-allyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-levulenoyl-1-thio-α-D-mannopyranoside (S35): A mixture of **S34** (17.8 g, 32.5 mmol), Et_3SiH (7.8 mL, 48.7 mmol) and pre-activated molecular sieves was stirred in DCM (150 mL) for 30 min. The solution was cooled to -78 ºC, after which $PhBCl_2$ (5.5 mL, 42.3 mmol) was added, and the reaction was stirred at -78 ºC for 15 min after which it was quenched with Et_3N (20 mL). The mixture was then diluted with DCM (200 mL) and washed with sat. $NaHCO_3$ (100 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo* to give the crude product as a transparent oil. This was used in the next step without further purification. A solution of the crude product in DCM (200 mL) was cooled to 0 °C, followed by the addition of LevOH (5.6 mL, 48.7 mmol), DMAP (500 mg, cat) and EDCI (10.1 g, 65.0 mmol). The reaction mixture was left stirring for 3 h, after which it was diluted with DCM (200 mL) and washed with sat. $NaHCO_3$ (200 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo*. Chromatography on silica gel with Pet. Ether: EtOAc (8: 2, v: v to 1: 1, v: v) as eluent gave the desired product as a transparent oil. (19.4 g, 92%). R*f* = 0.54 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz,



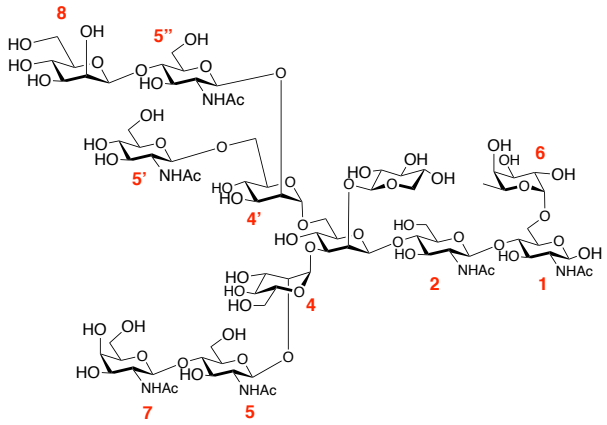
$CDCl_3$): δ 7.47 to 6.69 (14H, m, H-Ar), 5.93 (1H, m, C<u>H</u>=CH_2 of alloc), 5.48 (1H, d, H-1, *J* = 1.8 Hz), 5.40 to 5.32 (2H, m, H-2, CH=CH<u>H</u> of alloc), 5.27 (1H, dd, CH=C<u>H</u>H of alloc, *J* = 10.5 Hz, 1.2 Hz), 4.93 (1H, d, PhC<u>H</u>H, *J* = 10.9 Hz), 4.82 ((1H, d, PhC<u>H</u>H, *J* = 11.4 Hz), 4.66 (3H, m, O<u>CH_2</u> of alloc, PhCH<u>H</u>), 4.59 (1H, d, PhCH<u>H</u>, *J* = 10.9 Hz), 4.30 (2H, m, H-6a, H-6b), 4.19 (1H, dd, H-3, *J* = 9.2 Hz, 3.2 Hz), 3.97 (1H, m, H-5), 3.83 (1H, t, H-4, *J* = 9.6 Hz), 3.76 (3H, s, O<u>CH_3</u>), 2.69 (2H, m, $COOCH_2$<u>CH_2</u> of Lev), 2.55 (2H, m, COO<u>CH_2</u>CH_2 of Lev), 2.15 (3H, s, CH_2CO<u>CH_3</u> of Lev); ^{13}C NMR (151 MHz, $CDCl_3$): δ 206.49, 172.38, 155.30, 154.60, 149.74, 137.98, 137.89, 137.78, 131.34, 129.06, 128.47, 128.44, 128.25, 128.14, 128.01, 127.88, 127.85, 125.32, 119.28, 117.88, 114.62, 96.59, 77.95, 77.27, 77.06, 76.85, 75.40, 73.90, 72.23, 72.04, 70.37, 69.00, 63.15, 55.65, 37.90, 29.83, 27.95, 21.49, 0.03. MALDI-TOF-MS (*m/z*): $[M + Na]^+$: calculated for $C_{31}H_{32}O_9Na$, 571.1944; found 571.2296.

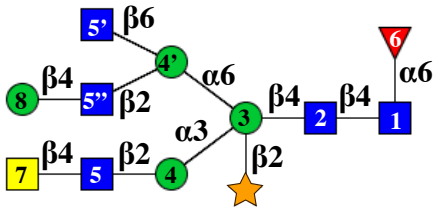
(*N*-Phenyl)-2,2,2-trifluoroacetimidate-3,4-di-*O*-benzyl-6-*O*-levulenoyl-D-mannopyranoside (14):



To a solution of compound **S35** (19.4 g, 29.9 mmol) in acetonitrile (200 mL) was added ceric ammonium nitrate (49.1 g, 89.7 mmol) at 0 °C, and the reaction mixture was stirred for 2 h, after which the solvent was evaporated *in vacuo*. The residue was diluted with EtOAc (300 mL) and successively washed with water (200 mL) and sat. $NaHCO_3$ (200 mL). The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo* to afford a residue, which was chromatographed with Pet. Ether: EtOAc (7: 3, v: v to 1: 1, v: v) as eluent to give the lactol as an orangish foamy solid. To a solution of this hemiacetal in anhydrous DCM (150 mL), was added $CF_3C(NPh)Cl$ (7.4 mL, 35.9 mmol) and Cs_2CO_3 (29.2 g, 89.7 mmol). The reaction mixture was stirred for 3 h, after which it was diluted by DCM (200 mL) and the salts were filtered off. The mixture was concentrated, and the residue was purified by silica gel column chromatography with Pet. Ether: EtOAc (8: 2, v: v to 1: 1, v: v) as eluent to give the imidate product as an off-white foamy powder. (13.6 g, 64%, over two steps). R*f* = 0.7 (Pet. Ether: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 to 6.72 (15H, m, H-Ar), 6.26 (1H, br s, H-1), 5.95 (1H, m, C<u>H</u>=CH_2 of alloc), 5.62 (1H, s, H-2), 5.38 (2H, m, CH=C<u>H</u>H of alloc), 5.27 (2H, m, CH=CH<u>H</u> of alloc), 4.92 (1H, m, PhCH<u>H</u>), 4.77 (1H, m, PhCH<u>H</u>), 4.72 to 4.54 (4H, m, PhC<u>H</u>H, O<u>CH_2</u> of alloc, PhC<u>H</u>H), 4.35 (2H, m, H-6a, H-6b), 4.04 (1H, dd, H-3, *J* = 9.1 Hz, 3.2 Hz), 3.81 (2H, m, H-4, H-5), 2.74 (2H, m, $COOCH_2$<u>CH_2</u> of Lev), 2.61 (1H, t, COO<u>CH_2</u>CH_2 of Lev, *J* = 6.6 Hz, 2H, Lev), 2.17 (3H, s, CH_2CO<u>CH_3</u> of Lev); ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.47, 172.30, 154.85, 137.66, 137.33, 137.12, 131.27, 131.16, 128.80, 128.49, 128.46, 128.23, 128.16, 128.13, 127.99, 127.96, 124.53, 119.36, 119.30, 119.05, 93.96, 79.28, 77.45, 77.36, 77.02, 76.60, 75.54, 75.30, 74.36, 73.38, 73.24, 72.30, 71.80, 71.04, 70.18, 69.12, 69.03, 62.82, 37.88, 29.78, 27.99, 27.94. Compound was unstable under MALDI-TOF-MS conditions.

2. Deprotection conditions to yield glycan 8





To a suspension of **27** (600 mg, 0.125 mmol) in *n*BuOH (10 mL) was added ethylenediamine (10 mL) and the resulting clear solution was heated at 90 °C for 16 h. The mixture was concentrated *in vacuo*, co-evaporated with toluene 5 times, and the resulting residue was dissolved in pyridine: Ac_2O (20 mL, 1: 1, v: v), after which DMAP (50 mg, cat) was added. The reaction was left stirring for 2 h, after which TLC (Tol: Acetone, 7: 3, v: v) showed the presence of one major product. The mixture was concentrated *in vacuo*, and the resulting crude product was briefly chromatographed with (Tol: Acetone, 7: 3, v: v) as eluent to give product which was additionally passed through BioGel SX-1 column (Tol: Acetone, 1: 1, v: v) as mobile phase to provide the acetylated intermediate as a clear syrup. This material was then dissolved in MeOH, after which 1 M NaOMe (500 µl) was added and the deacetylation was left proceeding at for 2 h. The reaction was neutralized with the Amberlite 120 H^+ resin, filtered and the filtrate was concentrated *in vacuo*. This syrup was dissolved in MeOH: H_2O (10 mL, 1: 1), followed by adding $Pd(OH)_2$ (150 mg, 20%, Degussa type) and the reaction mixture was left stirring under the atmosphere of hydrogen for 48 h, after which MALDI showed the product peak. The mixture was then filtered to remove catalyst, and the filtrate was concentrated *in vacuo*, passed through the BioGel P-4 column and lyophilized to give the desired glycan as a white cotton-like solid. (144 mg, 53% over four steps). The glycan was additionally purified (in batches of 15 to 20 mg) by HPLC with a semi-preparative amide HILIC column (10 x 250 mm, Waters Inc.) by the gradient solvent system CH_3CN: H_2O (9: 1, v: v to 1: 1, v: v) with the UV (210 nm) detector to afford analytically pure glycan used for further enzymatic reactions.

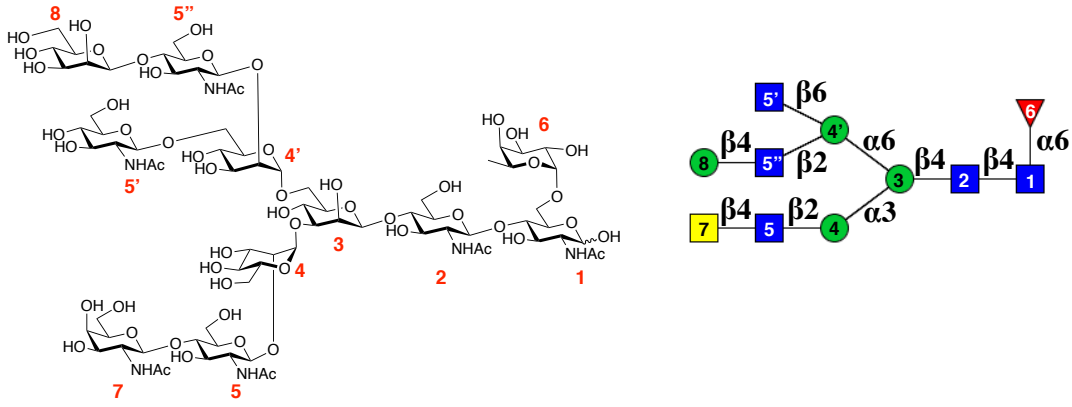
^1H NMR (600 MHz, D_2O):

8	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.07 (d, *J* = 2.6 Hz)	3.80	3.89	3.66	NA	NA	–
Man-4	5.03	4.05	3.81	3.42	NA	3.80, 3.51	–
Man-3	4.75	4.17	3.79	3.71	3.75	3.85, 3.60	–
Man-4'	4.74	3.99	3.75	3.31	3.68	4.09, 3.46	–
Man-8	4.65	3.97	3.55	NA	NA	NA	–
GlcNAc-1β	4.58	3.63	3.65	NA	NA	NA	–
GlcNAc-2	4.55	3.69	3.67	3.54	NA	NA	–
GlcNAc-5"	4.46	3.64	3.53	3.63	3.39	NA	–

	(d, *J* = 7.8 Hz)						
GlcNAc-5'	4.42	3.66	3.55	3.62	3.39	NA	–
GlcNAc-5	4.40	3.66	3.46	3.64	3.40	NA	–
GalNAc-7	4.40	3.84	3.63	3.85	NA	NA	–
Xyl (core)	4.32 (d, *J* = 7.6 Hz)	3.28	3.35	NA	3.14, 3.89	–	–
Fuc-6 (core) α,β	4.78	3.69	3.79	NA	3.99, 4.02	–	1.10

MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{78}H_{130}N_6O_{55}Na$, 2053.7458; found 2053.8128.

3. Deprotection conditions to yield glycan 9



To a suspension of **S17** (815 mg, 0.17 mmol) in pyridine (10 mL) was added HF in pyridine (70% HF, 30% pyridine; 1.0 mL) dropwise. The mixture was stirred for 6 h at 60 °C, after which it was quenched by solid $NaHCO_3$, till all CO_2 bubbling stopped. The salts were filtered off, the solvent was evaporated *in vacuo*, and the residue was re-dissolved in DCM, followed by successive washing with water and saturated $NaHCO_3$. The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated. To a suspension of the residue in *n*BuOH (10 mL) was added ethylenediamine (10 mL) and the resulting clear solution was heated at 90 °C for 16 h. The mixture was concentrated *in vacuo*, co-evaporated with toluene 5 times, and the resulting residue was dissolved in pyridine: Ac_2O (20 mL, 1: 1, v: v), after which DMAP (50 mg, cat) was added. The reaction was left stirring for 2 h, after which TLC (Tol: Acetone, 7: 3, v: v) showed the presence of one major product. The mixture was concentrated *in vacuo*, and the resulting crude product was briefly chromatographed with (Tol: Acetone, 7: 3, v: v) as eluent to give product which was additionally passed through BioGel SX-1 column (Tol: Acetone, 1: 1, v: v) as mobile phase to provide the acetylated intermediate as a clear syrup. This material was then dissolved in MeOH, after which 1 M NaOMe (500 µl) was added and the deacetylation was left proceeding at for 2 h. The reaction was neutralized with the Amberlite 120 H^+ resin, filtered and the filtrate was concentrated *in vacuo*. This syrup was dissolved in MeOH: H_2O (10 mL, 1: 1), followed by adding $Pd(OH)_2$ (150 mg, 20%, Degussa type) and the reaction mixture was left stirring under the atmosphere of hydrogen for 48 h, after which MALDI showed the product peak. The mixture was then filtered to remove catalyst, and the filtrate was concentrated *in vacuo*, passed through the BioGel P-4 column and lyophilized to give the desired glycan as a white cotton-like solid. (203 mg, 57% over five steps). The glycan was additionally

purified (in batches of 15 to 20 mg) by HPLC with a semi-preparative amide HILIC column (10 x 250 mm, Waters Inc.) by the gradient solvent system CH_3CN: H_2O (9: 1, v: v to 1: 1, v: v) with the UV (210 nm) detector to afford analytically pure glycan used for further enzymatic reactions.

^{1}H NMR (600 MHz, D_2O)

9	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.07 (d, *J* = 3.0 Hz)	3.78	3.89	3.69	NA	3.73, 3.60	–
Man-4	5.00 (s)	4.07	3.80	3.38	3.47	3.82, 3.50	–
Man-4'	4.75	3.97	3.76	3.29	3.71	4.09, 3.47	–
Man-3	4.65	4.13	3.67	3.71	3.46	3.81, 3.63	–
Man-8	4.65	3.96	3.55	3.62	3.34	NA	–
GlcNAc-1β	4.58 (d, *J* = 8.2 Hz)	3.59	3.63	NA	NA	NA	–
GlcNAc-2	4.55	3.67	3.65	3.50	NA	NA	–
GlcNAc-5"	4.48 (d, *J* = 7.3 Hz)	3.62	3.38	3.61	3.38	NA	–
GlcNAc-5	4.44	3.62	3.47	3.61	3.39	NA	–
GlcNAc-5'	4.42	3.61	3.48	3.62	3.39	NA	
GalNAc-7	4.40	3.82	3.60	3.82	NA	NA	–
Fuc-6 (core) (α, β)	4.78	3.68	3.81	3.68	3.98, 4.02	–	1.10

MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{78}H_{130}N_6O_{55}Na$, 2053.7458; found 2053.8128.

4. Enzymatic reactions

4.1 General methods

All enzymatic reactions were performed in aqueous buffers with an appropriate pH for each enzyme. B3GNT2 [β-(1→3)-glucosaminyltransferase], FUT5 [α-(1→3)-fucosyltransferase] and B4GalT1 [β-(1→4)-galactosyltransferase] were provided by Dr. K. W. Moremen (Complex Carbohydrate Research Center, Athens, GA, USA). *Helix pomatia* β-mannosidase and Alkaline phosphatase from calf intestine (CIAP) was purchased from Sigma-Aldrich. Uridine 5'-diphospho-*N*-acetylglucosamine (UDP-GlcNAc) was purchased from Sigma-Aldrich; uridine 5'-diphosphogalactose (UDP-Gal) were purchased from Roche Diagnostic Corporation (Indianapolis, IN); guanosine 5'-diphospho-L-fucose (GDP-Fuc) was synthesized chemically using reported procedures.[3] All enzymatic reactions, unless otherwise stated, were monitored by mass spectrometry, and recorded on a Shimadzu Biotech Axima-CFR MALDI-TOF using dihydroxybenzoic acid or 4- hydroxycinnamic acid as matrices. Gel filtration chromatography was

performed using a column (30 cm x 1.5 cm) packed with BioGel P-4 or P-6 (GE Healthcare), eluted with deionized water. Glycans were purified by HPLC using HILIC column (XBridge® Amide 5 µm, 10 mm x 250 mm, Waters) HPLC grade Acetonitrile and de-ionised water as eluents under UV detection (210 nm). Glycans were lyophilized by dissolving the compound in water and freezing using liquid nitrogen. All enzymatic reactions were driven to full completion by adding excess of glycosyltransferases until all starting material was consumed, as detected by MALDI-TOF-MS. This approach enabled efficient product isolation and purification. All nuclear magnetic resonance (NMR) spectra were acquired on 400, 500 or 600, MHz Varian/Agilent Direct Drive, operating at 25 °C unless otherwise stated. Data were collected using standard pulse programs from the spectrometer library. Samples were dissolved in 99.96% D_2O. Chemical shifts were referenced to the residual HOD signal at 4.79 ppm.

4.2 Expression and purification of human glycosyl transferses

The catalytic domains of all human glycosyl transferases were expressed as a soluble secreted fusion protein for production in mammalian (HEK293) suspension cultures.[4] The coding regions were amplified from Mammalian Gene Collection clones using primers that appended a tobacco etch virus (TEV) protease cleavage site[5] to the NH2-terminal end of the coding region and attL1 and attL2 Gateway adaptor sites were extended on the 5' and 3' terminal ends of the coding region during transfer to pDONR221 vector backbone.[4b] The pDONR221 clones were then recombined via LR clonase reaction into a custom Gateway adapted version of the pGEn2 mammalian expression vector[4b] to assemble a recombinant coding region comprised of a 25 amino acid NH_2-terminal signal sequence from the *T. cruzi* lysosomal α-mannosidase[6] followed by an 8xHis tag, 17 amino acid AviTag,[7] "superfolder" GFP,[8] the nine amino acid sequence encoded by attB1 recombination site, followed by the TEV protease cleavage site and the respective glycosyltransferase catalytic domain coding region.

Suspension culture HEK293 cells (Freestyle 293-F cells, Life Technologies, Grand Island, NY) were transfected as previously described[4] and the culture supernatant was subjected to Ni^{2+} -NTA superflow chromatography (Qiagen, Valencia, CA). Enzyme preparations were eluted with 300 mM imidazole, concentrated by ultrafiltration, and subjected to gel filtration on a Superdex 75 column (GE Healthcare) preconditioned with a buffer containing 20 mM HEPES, pH 7.0, 100 mM NaCl, 10% glycerol, 0.05% Na azide. Peak fractions were pooled and concentrated to ~1 mg/mL using an ultrafiltration pressure cell membrane (Millipore, Billerica, MA) with a 10 kDa molecular weight cutoff.

Enzyme	Amino Acid residues	Uniprot ID
B3GNT2	35-397	Q9NY97
B4GalT1	63-398	P15291
FUT5	40-374	Q11128

Table S1. Enzyme expression details

4.3 General procedures for enzymatic reactions

General procedure for α(1→3) fucosylation. Glycan and GDP-Fucose (2 eq per fucose) were dissolved in Tris buffer (50 mM, pH~7.3) containing $MnCl_2$ (10 mM), CIAP (10 mU). Recombinant α(1,3)-Fuctosyltransferase FUT5 (6.6 mU/µmol of substrate) was added to achieve a final concentration of 4 mmol. The resulting mixture was incubated at 37 ºC for 12 h. In case MALDI-TOF-MS showed the remaining starting material additional GDP-Fucose (1 or 2 eq), CIAP (10 mU) and enzyme FUT5 was

added and incubation at 37 ºC was continued until no more starting material could be detected. The reaction mixture was quenched by adding methanol (10 μL), after which it was passed through Biogel P-4 or P-6 column. Fractions containing product were identified using TLC (dipping into the anisaldehyde stain followed by charring at 150 ºC), combined and lyophilized to give the product.

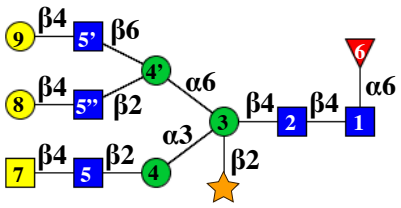
General procedure for β(1→4) galactosylation. Glycans and UDP-Gal (2 eq per galactoside) were dissolved in Tris buffer (50 mM, pH~7.5) containing BSA (0.1%) and $MnCl_2$ (20 mM). CIAP (10 mU) and B4GalT1 (3.4 mU/μmol) were added to achieve a final concentration of 4 mmol. The reaction mixture was then incubated at 37 ºC for 10 h. The reaction mixture was quenched by adding methanol (10 μL) and passed through Biogel P-4 or P-6 column. Fractions containing product were identified using TLC (dipping into the anisaldehyde stain followed by charring at 150 ºC), combined and lyophilized to give the respective products as white fluffy solids.

General procedure for installation of β(1→3) *N*-acetylglucosamine moieties. Glycans and UDP-GlcNAc (2 eq) were dissolved in HEPES buffer (50 mM, pH~7.3) containing KCl (25 mM), $MgCl_2$ (2 mM), and DTT (1 mM). To this, CIAP (10 mU) and B3GNT2 (6.0 mU/μmol) were added to achieve a final concentration of glycan at 4 mM. The resulting mixture was then incubated at 37 ºC for 12 h. The reaction mixture was quenched by adding methanol (10 μL) and passed through Biogel P-4 or P-6 column. Fractions containing product were identified using TLC (dipping into the anisaldehyde stain followed by charring at 150 ºC), combined and lyophilized to give the respective products as white fluffy solids.

General procedure for β-mannose removal with subsequent installation of a β-galactose moiety. Glycan was dissolved in 100 mM NaOAc buffer (500 μL, pH~5.0) followed by adding 10 mM deoxyfuconojirimycin hydrochloride and the appropriate amounts of the *Helix pomatia* β-mannosidase the reaction mixture was then incubated at 37 ºC for 6 h. In case MALDI-TOF-MS showed the remaining starting material, additional portion of the enzyme was added and incubated at 37 ºC until no more starting material could be detected. After this time the reaction mixture was heated at 100 ºC for 10 min, centrifuged, the supernatant was lyophilized, and the resulting product was desalted using the BioGel P-2 column. Fractions containing the product were combined and lyophilized. This glycan and UDP-Gal (1.5 - 2 eq per galactoside) were dissolved in Tris buffer (50 mM, pH~7.5) containing BSA (0.1%) and $MnCl_2$ (20 mM). CIAP (10 mU) and B4GalT1 (3.4 mU/μmol) were added to achieve a final concentration of 4 mM. The reaction mixture was then incubated at 37 ºC for 10 h. The reaction mixture was quenched by adding methanol (10 μL), after which it was passed through Biogel P-4 or P-6 column. Fractions containing product were identified using TLC (dipping into the anisaldehyde stain followed by charring at 150 ºC), were combined and lyophilized to give products as a white cotton-like solid.

4.4 Enzymatic reactions on glycans

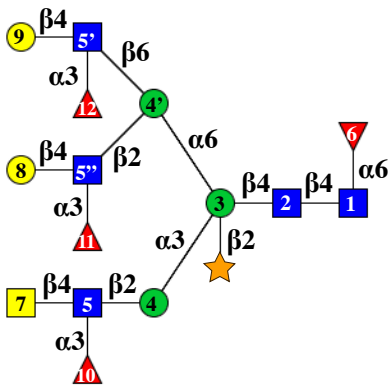
Glycan 29: Glycan **8** (5.0 mg) was dissolved in 100 mM NaOAc buffer (500 µL, pH~5.0) followed by adding 10 mM deoxyfuconojirimycin hydrochloride (20 µL) and *Helix pomatia* β-mannosidase (10 µL) the reaction mixture was then incubated at 37 ºC for 12 h. After this time the reaction mixture was heated at 100 ºC for 10 min, centrifuged, the supernatant was lyophilized, and the resulting product was desalted using the BioGel P-2 column. Fractions containing the product were combined and lyophilized. This glycan **28** and UDP-Gal (4 eq) were dissolved in Tris buffer (50 mM, pH~7.5) containing BSA (0.1%) and $MnCl_2$ (20 mM). CIAP (10 mU) and B4GalT1 (3.4 mU/µmol) were added to achieve a final concentration of 4 mM. The reaction mixture was then incubated at 37 ºC for 10 h. The reaction mixture was quenched by adding methanol (10 µL), after which it was passed through Biogel P-4 column. Fractions containing product were combined and lyophilized to give the product **29** as a white fluffy solid (5.4 mg). MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{89}H_{148}N_6O_{64}Na$, 2347.8409; found 2348.1302.



29	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.06 (d, *J* = 3.1 Hz)	3.78	3.88	3.66	NA	NA	–
Man-4	5.03	4.02	3.78	3.39	NA	3.79, 3.49	–
Man-3	4.75	4.14	3.76	3.69	3.76	3.83, 3.58	–
Man-4'	4.74	3.97	3.74	3.30	3.68	4.10, 3.46	–
GlcNAc-1β	4.57 (d, *J* = 8.2 Hz)	3.59	3.61	NA	NA	NA	–
GlcNAc-2	4.55	3.65	3.64	3.51	NA	NA	–
GlcNAc-5"	4.46	3.62	3.52	3.61	3.37	NA	–
GlcNAc-5'	4.43 (d, *J* = 8.3 Hz)	3.68	3.52	3.62	3.37	NA	–
GlcNAc-5	4.40	3.66	3.45	3.62	3.38	NA	–
GalNAc-7	4.40	3.82	3.62	3.83	NA	NA	–
Gal-8	4.37	3.42	3.56	3.81	NA	NA	–
Gal-9	4.35	3.42	3.55	3.80	NA	NA	–
Xyl (core)	4.32 (d, *J* = 7.4 Hz)	3.27	3.33	NA	3.13, 3.89	–	–
Fuc-6 (core) α,β	4.78	3.67	3.78	NA	3.98, 4.02	–	1.10

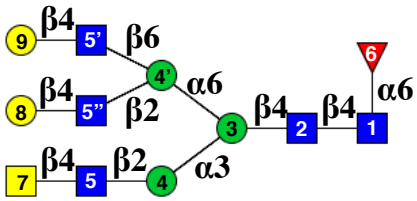
SUPPORTING INFORMATION

Glycan 1: Glycan **29** (5.4 mg) and GDP-Fucose (6 eq) were dissolved in Tris buffer (50 mM, pH~7.3) containing $MnCl_2$ (10 mM), CIAP (10 mU). Recombinant α(1,3)-Fuctosyltransferase FUT5 (6.6 mU/μmol of substrate) was added to achieve a final concentration of 4 mmol. The resulting mixture was incubated at 37 ºC for 12 h. After this time, additional GDP-Fucose (2 eq), CIAP (10 mU) and enzymes were added and incubation at 37 ºC was continued until no more starting material could be detected by MALDI-TOF. The reaction mixture was quenched by adding methanol (10 μL), after which it was passed through Biogel P-6 column. Fractions containing the product were combined and lyophilized to give the product as a white fluffy solid. This product was put for HPLC purification using HILIC column, using solvent gradient ACN: H_2O (90: 10, v: v to 50: 50, v: v). The fractions containing the product were concentrated and lyophilized yielding the purified glycan **1** as a white cotton like fluffy solid (3.0 mg). MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{107}H_{178}N_6O_{76}Na$, 2786.0146; found 2786.7738.



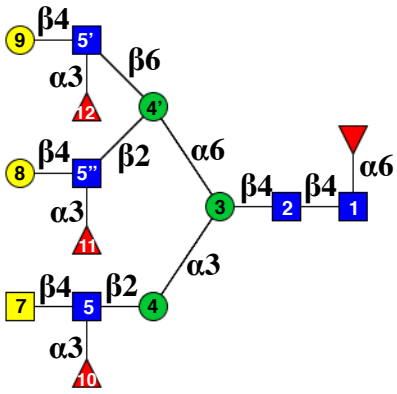
1	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.10 (d, *J* = 3.1 Hz)	3.81	3.90	3.67	NA	NA	–
Man-4	5.06	4.05	3.81	3.42	3.47	3.84, 3.51	–
Man-3	4.79	4.18	3.80	3.69	3.78	3.83, 3.60	–
Man-4'	4.76	4.00	3.77	3.32	3.69	4.12, 3.48	–
GlcNAc-1β	4.61 (d, *J* = 8.3 Hz)	3.63	3.66	NA	NA	NA	–
GlcNAc-2	4.59	3.68	3.67	3.53	NA	NA	–
GlcNAc-5"	4.52	3.65	3.56	3.62	3.43	NA	–
GlcNAc-5'	4.48 (d, *J* = 7.1 Hz)	3.72	3.56	3.63	3.42	NA	–
GlcNAc-5	4.43 (d, *J* = 8.3 Hz)	3.69	3.48	3.63	3.43	NA	–
GalNAc-7	4.38	3.85	3.64	3.85	NA	NA	–
Gal-8	4.37	3.44	3.57	3.82	NA	NA	–
Gal-9	4.37	3.43	3.56	3.80	NA	NA	–
Xyl (core)	4.36	3.32	3.32	NA	3.17, 3.93	–	–
Fuc-6 (core) α,β	4.82	3.71	3.82	NA	4.02, 4.06	–	1.14
Fuc-10	5.04	3.88	3.86	3.67	4.77	–	1.10
Fuc-11	5.04	3.84	3.82	3.65	4.80	–	1.18
Fuc-12	5.03	3.85	3.79	3.64	4.80	–	1.17

Glycan 31: Glycan **9** (5.0 mg) was dissolved in 100 mM NaOAc buffer (500 µL, pH~5.0) followed by adding 10 mM deoxyfuconojirimycin hydrochloride (20 µL) and *Helix pomatia* β-mannosidase (10 µL) the reaction mixture was then incubated at 37 ºC for 12 h. After this time the reaction mixture was heated at 100 ºC for 10 min, centrifuged, the supernatant was lyophilized, and the resulting product was desalted using the BioGel P-2 column. Fractions containing the product were combined and lyophilized. This glycan **30** and UDP-Gal (4 eq) were dissolved in Tris buffer (50 mM, pH~7.5) containing BSA (0.1%) and $MnCl_2$ (20 mM). CIAP (10 mU) and B4GalT1 (3.4 mU/µmol) were added to achieve a final concentration of 4 mM. The reaction mixture was then incubated at 37 ºC for 10 h. The reaction mixture was quenched by adding methanol (10 µL), after which it was passed through Biogel P-4 column. Fractions containing product were combined and lyophilized to give the product as a white fluffy solid (5.5 mg). MALDI-TOF-MS (*m/z*): $[M+Na]^+$ calculated for $C_{84}H_{140}N_6O_{60}Na$, 2215.7458; found 2215.9522.



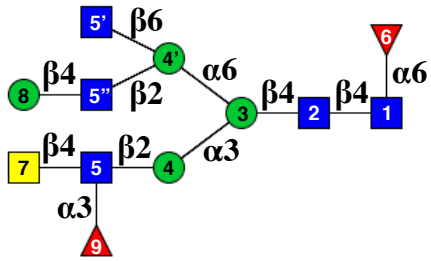
31	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.07 (d, *J*= 3.1 Hz)	3.78	3.88	3.69	NA	3.72, 3.60	–
Man-4	5.00	4.07	3.80	3.38	3.44	3.81, 3.49	–
Man-4'	4.76	3.97	3.75	3.29	3.70	4.09, 3.46	–
Man-3	4.65	4.14	3.67	3.71	3.43	3.81,3.63	–
GlcNAc-1β	4.58 (d, *J*= 8.0 Hz)	3.59	3.63	NA	NA	NA	–
GlcNAc-2	4.54	3.67	3.65	3.50	NA	NA	–
GlcNAc-5"	4.48 (d, *J*= 7.5 Hz)	3.66	3.38	3.61	3.38	NA	–
GlcNAc-5	4.44	3.64	3.47	3.61	3.39	NA	–
GlcNAc-5'	4.43	3.61	3.48	3.62	3.39	NA	
GalNAc-7	4.40 (d, *J*= 8.5 Hz)	3.82	3.60	3.82	NA	NA	
Gal-8	4.37	3.44	3.55	3.83	3.53	NA	–
Gal-9	4.35	3.42	3.54	3.83	3.52	NA	
Fuc-6 (core) α, β	4.78	3.69	3.81	3.68	3.98, 4.02	–	1.10

Glycan 2: Glycan **31** (5.5 mg) and GDP-Fucose (6 eq) were dissolved in Tris buffer (50 mM, pH~7.3) containing $MnCl_2$ (10 mM), CIAP (10 mU). Recombinant α(1,3)-Fuctosyltransferase FUT5 (6.6 mU/μmol of substrate) was added to achieve a final concentration of 4 mmol. The resulting mixture was incubated at 37 ºC for 12 h. After this time, additional GDP-Fucose (2 eq), CIAP (10 mU) and enzymes were added and incubation at 37 ºC was continued until no more starting material could be detected by MALDI-TOF. The reaction mixture was quenched by adding methanol (10 μL), after which it was passed through Biogel P-6 column. Fractions containing the product were combined and lyophilized to give the product as a white fluffy solid. This product was put for HPLC purification using HILIC column, using solvent gradient ACN: H_2O (90: 10, v: v to 50: 50, v: v). The fractions containing the product were concentrated and lyophilized yielding the purified glycan **2** as a white cotton like fluffy solid (3.0 mg). MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{102}H_{170}N_6O_{72}Na$, 2653.9723; found 2654.01917.



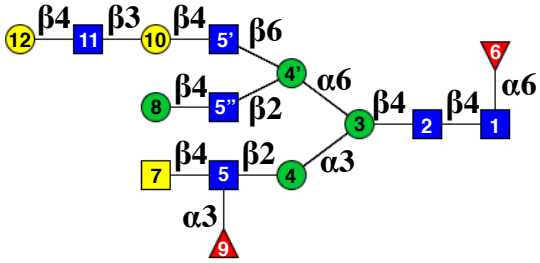
2	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.06 (d, *J* = 2.9 Hz)	3.77	3.86	3.69	NA	3.72, 3.61	–
Man-4	5.00	4.05	3.78	3.39	3.44	3.81, 3.48	–
Man-4'	4.74	3.96	3.74	3.30	3.69	4.09, 3.46	–
Man-3	4.65	4.14	3.67	3.71	3.46	3.81, 3.65	–
GlcNAc-1β	4.48 (d, *J* = 8.1 Hz)	3.58	3.62	NA	NA	NA	–
GlcNAc-2	4.54	3.66	3.65	3.51	NA	NA	–
GlcNAc-5"	4.48	3.71	3.41	3.65	NA	NA	–
GlcNAc-5	4.45	3.72	3.43	3.66	NA	NA	–
GlcNAc-5'	4.43	3.76	3.46	3.63	3.38	NA	–
GalNAc-7	4.35	3.85	3.63	3.82	NA	NA	–
Gal-8	4.33	3.53	3.55	3.85	3.52	NA	–
Gal-9	4.33	3.56	3.59	3.89	3.55	NA	–
Fuc-6 (core) α, β	4.77	3.68	3.81	3.68	3.98, 4.01	–	1.10
Fuc-10	5.01	3.83	3.82	3.64	4.76	–	1.15
Fuc-11	5.00	3.80	3.78	3.62	4.72	–	1.06
Fuc-12	4.98	3.82	3.75	3.61	4.73	–	1.06

Glycan 32: Glycan **9** (7.0 mg) and GDP-Fucose (2 eq) were dissolved in Tris buffer (50 mM, pH~7.3) containing $MnCl_2$ (10 mM), CIAP (10 mU). Recombinant α(1,3)-Fuctosyltransferase FUT5 (6.6 mU/μmol of substrate) was added to achieve a final concentration of 4 mmol. The resulting mixture was incubated at 37 ºC for 12 h. The reaction mixture was quenched by adding methanol (10 μL), after which it was passed through Biogel P-4 column. Fractions containing the product were combined and lyophilized to give the product as a white fluffy solid (7.0 mg). MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{84}H_{140}N_6O_{59}Na$, 2199.8037; found 2200.0307.



32	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.07 (d, *J* = 2.2 Hz)	3.78	3.88	3.69	NA	3.72, 3.60	–
Man-4	4.99	4.06	3.80	3.38	3.43	3.81, 3.49	–
Man-4'	4.75	3.98	3.76	3.28	3.70	4.10, 3.47	–
Man-3	4.65	4.14	3.67	3.72	3.41	3.80, 3.63	–
Man-8	4.65	3.96	3.55	NA	NA	NA	–
GlcNAc-1β	4.58 (d, *J* = 8.2 Hz)	3.59	3.63	NA	NA	NA	–
GlcNAc-2	4.55	3.66	3.65	3.50	NA	NA	–
GlcNAc-5"	4.48 (d, *J* = 6.5 Hz)	3.61	3.38	3.61	3.38	NA	–
GlcNAc-5	4.44	3.63	3.46	3.60	3.39	NA	–
GlcNAc-5'	4.41	3.60	3.47	3.61	3.39	NA	–
GalNAc-7	4.33 (d, *J* = 8.4 Hz)	3.86	3.62	3.82	NA	NA	–
Fuc-6 (core) (α, β)	4.78	3.68	3.81	3.68	3.98, 4.02	–	1.10
Fuc-9	5.02 (d, *J* = 3.4 Hz)	3.84	3.82	3.66	4.75	–	1.15

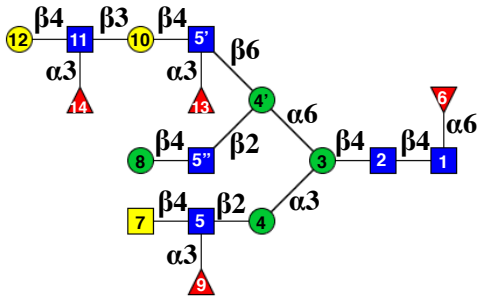
Glycan 34: Glycan **32** (7.0 mg) and UDP-Gal (2 eq) were dissolved in Tris buffer (50 mM, pH~7.5) containing BSA (0.1%) and $MnCl_2$ (20 mM). CIAP (10 mU) and B4GalT1 (3.4 mU/μmol) were added to achieve a final concentration of 4 mM. The reaction mixture was then incubated at 37 ºC for 10 h. The reaction mixture was quenched by adding methanol (10 μL), after which it was passed through Biogel P-4 column. Fractions containing product were combined and lyophilized to give the glycan **33** (7.5 mg). This glycan and UDP-GlcNAc (2 eq) were dissolved in HEPES buffer (50 mM,



pH~7.3) containing KCl (25 mM), $MgCl_2$ (2 mM), and DTT (1 mM). To this, CIAP (10 mU) and B3GNT2 (6.0 mU/μmol) were added to achieve a final concentration of glycan at 4 mM. The resulting mixture was then incubated at 37 ºC for 12 h. The reaction mixture was quenched by adding methanol (10 μL) and passed through Biogel P-6 column. The fractions containing product were combined and lyophilized to give the intermediate glycan, which was again put for galactosylation reaction using the conditions described above, yielding glycan **34** (8.0 mg). This product was put for HPLC purification using HILIC column, using solvent gradient ACN: H_2O (90: 10, v: v to 50: 50, v: v). The fractions containing the product were concentrated and lyophilized yielding the purified glycan as a white cotton like fluffy solid (5.0 mg). MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{104}H_{173}N_7O_{74}Na$, 2726.9887; found 2727.1029.

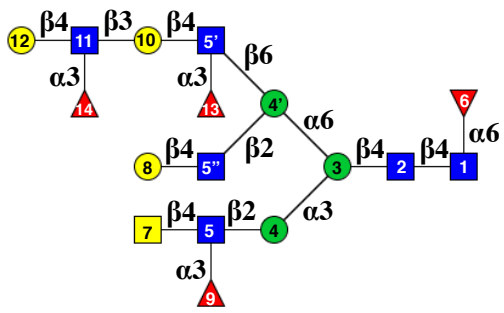
34	**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**Fuc-CH_3**
GlcNAc-1α	5.10 (d, *J* = 3.0 Hz)	3.80	3.93	3.72	NA	3.73, 3.59	–
Man-4	5.02	4.09	3.82	3.41	3.45	3.83, 3.52	–
Man-4'	4.79	3.99	3.79	3.32	3.73	4.12, 3.50	–
Man-3	4.67	4.17	3.68	3.75	3.43	3.83, 3.66	–
Man-8	4.68	3.98	3.56	NA	NA	NA	–
GlcNAc-11	4.62	3.71	3.57	3.70	NA	NA	–
GlcNAc-1β	4.60	3.62	3.65	NA	NA	NA	–
GlcNAc-2	4.58	3.69	3.67	3.53	NA	NA	–
GlcNAc-5"	4.51 (d, *J* = 7.2 Hz)	3.64	3.40	3.65	3.42	NA	–
GlcNAc-5	4.46	3.65	3.48	3.63	3.41	NA	–
GlcNAc-5'	4.46	3.67	3.54	3.66	3.42	NA	–
GalNAc-7	4.39	3.89	3.64	3.85	NA	NA	–
Gal-10	4.38	3.50	3.59	3.88	3.57	NA	–
Gal-12	4.36	3.46	3.58	3.88	3.55	NA	–
Fuc-6 (core) (α, β)	4.81	3.72	3.84	3.72	4.01, 4.05	–	1.13
Fuc-9	5.05 (d, *J* = 3.8 Hz)	3.86	3.85	3.68	4.79	–	1.18

Glycan 35: Glycan **34** (5.0 mg) and GDP-Fucose (4 eq) were dissolved in Tris buffer (50 mM, pH~7.3) containing $MnCl_2$ (10 mM), CIAP (10 mU). Recombinant α(1,3)-Fuctosyltransferase FUT5 (6.6 mU/μmol of substrate) was added to achieve a final concentration of 4 mmol. The resulting mixture was incubated at 37 ºC for 12 h. After this time, additional GDP-Fucose (2 eq), CIAP (10 mU) and FUT5 enzyme was added and incubation at 37 ºC was continued until no more starting material could be detected by MALDI-TOF. The reaction mixture was quenched by adding methanol (10 μL), after which it was passed through Biogel P-6 column. Fractions containing the product were combined and lyophilized to give the product as a white fluffy solid (5.6 mg). MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{116}H_{193}N_7O_{82}Na$, 3019.1045; found 3019.4936.



35	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.07 (d, *J* = 3.1 Hz)	3.78	3.90	3.69	NA	3.72, 3.58	–
Man-4	4.99	4.05	3.79	3.38	3.43	3.81, 3.49	–
Man-4'	4.78	3.96	3.75	3.29	3.69	4.09, 3.47	–
Man-3	4.66	4.14	3.66	3.73	3.42	3.81, 3.65	–
Man-8	4.65	3.95	3.54	NA	NA	NA	–
GlcNAc-11	4.59	3.74	3.59	3.72	NA	NA	–
GlcNAc-1β	4.58	3.60	3.63	NA	NA	NA	–
GlcNAc-2	4.55	3.65	3.64	3.51	NA	NA	–
GlcNAc-5"	4.48 (d, *J* = 7.4 Hz)	3.60	3.38	3.63	NA	NA	–
GlcNAc-5	4.44	3.71	3.43	3.59	3.38	NA	–
GlcNAc-5'	4.43	3.76	3.52	3.63	3.39	NA	–
GalNAc-7	4.34	3.86	3.61	3.83	NA	NA	–
Gal-10	4.34	3.54	3.56	3.85	3.53	NA	–
Gal-12	4.33	3.55	3.60	3.91	3.56	NA	–
Fuc-6 (core) (α, β)	4.75	3.69	3.81	3.68	3.97, 4.02	–	1.09
Fuc-9	5.02	3.82	3.80	3.64	4.75	–	1.15
Fuc-13	5.02	3.80	3.78	3.61	4.72	–	1.06
Fuc-14	4.99	3.77	3.76	3.60	4.71	–	1.04

Glycan 3: Glycan **35** (5.6 mg) was dissolved in 100 mM NaOAc buffer (500 µL, pH~5.0) followed by adding 10 mM deoxyfuconojirimycin hydrochloride (20 µL) and *Helix pomatia* β-mannosidase (10 µL) the reaction mixture was then incubated at 37 ºC for 12 h. After this time the reaction mixture was heated at 100 ºC for 10 min, centrifuged, the supernatant was lyophilized, and the resulting product was desalted using the BioGel P-2 column. Fractions containing the product were combined and lyophilized. This glycan **36** and UDP-Gal (2 eq) were dissolved in Tris buffer (50 mM, pH~7.5) containing BSA (0.1%) and $MnCl_2$ (20 mM). CIAP (10 mU) and B4GalT1 (3.4 mU/µmol) were added to achieve a final concentration of 4 mM. The reaction mixture was then incubated at 37 ºC for 10 h. The reaction mixture was quenched by adding methanol (10 µL), after which it was passed through Biogel P-4 column. Fractions containing product were combined and lyophilized to give the product as a white fluffy solid (5.0 mg). This product was put for HPLC purification using HILIC column, using solvent gradient ACN: H_2O (90: 10, v: v to 50: 50, v: v). The fractions containing the product were concentrated and lyophilized yielding the purified glycan **3** as a white cotton like fluffy solid (2.5 mg). MALDI-TOF-MS (*m/z*): $[M+ Na]^+$ calculated for $C_{116}H_{193}N_7O_{82}Na$, 3019.1045; found 3019.3130.



3	H1	H2	H3	H4	H5	H6	Fuc-CH_3
GlcNAc-1α	5.06 (d, *J* = 2.8 Hz)	3.78	3.90	3.69	NA	3.71, 3.58	–
Man-4	4.99	4.05	3.79	3.38	3.43	3.81, 3.48	–
Man-4'	4.78	3.97	3.74	3.29	3.69	4.09, 3.47	–
Man-3	4.65	4.14	3.66	3.73	3.41	3.81, 3.65	–
GlcNAc-11	4.59	3.75	3.58	3.72	NA	NA	–
GlcNAc-1β	4.58	3.59	3.63	NA	NA	NA	–
GlcNAc-2	4.55	3.66	3.63	3.50	NA	NA	–
GlcNAc-5"	4.48 (d, *J* = 6.9 Hz)	3.60	3.38	3.63	NA	NA	–
GlcNAc-5	4.45	3.71	3.44	3.59	3.39	NA	–
GlcNAc-5'	4.43	3.76	3.52	3.63	3.38	NA	–
Gal-8	4.36	3.44	3.54	3.81	NA	NA	–
GalNAc-7	4.34	3.87	3.62	3.83	NA	NA	–
Gal-10	4.33	3.54	3.55	3.85	3.51	NA	–
Gal-12	4.33	3.55	3.60	3.91	3.55	NA	–
Fuc-6 (core) (α, β)	4.75	3.69	3.81	3.68	3.99, 4.02	–	1.10
Fuc-9	5.02	3.83	3.81	3.64	4.76	–	1.15
Fuc-13	5.02	3.80	3.78	3.61	4.72	–	1.06
Fuc-14	4.98	3.77	3.76	3.60	4.71	–	1.04

5. Molecular interaction studies by NMR

5.1 Protein expression and purification. The extracellular domain of DC-SIGN was obtained as previously described.[9] The carbohydrate recognition domain of DC-SIGN in its ^{15}N labelled form was obtained as previously described.[10]

5.2 ^{1}H Saturation transfer difference (STD) NMR. The samples for saturation-transfer difference (STD) NMR experiments were prepared using the extracellular domain of DC-SIGN at 10 μM concentration in 25 mM Tris-d11, 150 mM NaCl, 4 mM $CaCl_2$ in D_2O (pD 8) using lectin/ligand ratios of 1:50. The temperature was set to 298 K. STD experiments were performed at 600 MHz Bruker spectrometer, using standard Bruker pulse sequences with water suppression by using the excitation sculpting and without protein spin-lock filter. Protein saturation was achieved with a Gaussian-shaped pulse of 49 ms (Gauss 1.1000, with a power of $1e^{-05}$ W). Different irradiation frequencies for only the ligand and in presence of the protein (Fig. S2 a and b, respectively) were tested. We found that the irradiation at 0.4 ppm was the best compromise between optimal protein saturation and minimal ligand direct irradiation. Thus, the on-resonance frequency was set at aliphatic regions (0.4 ppm) and the off-resonance frequency at 100 ppm. Blank STD experiments of the ligands alone were acquired in the same conditions. The results of blank ^{1}H-STD NMR experiments for ligands **1-3** are shown in Figs S3, S4 and S5 respectively.

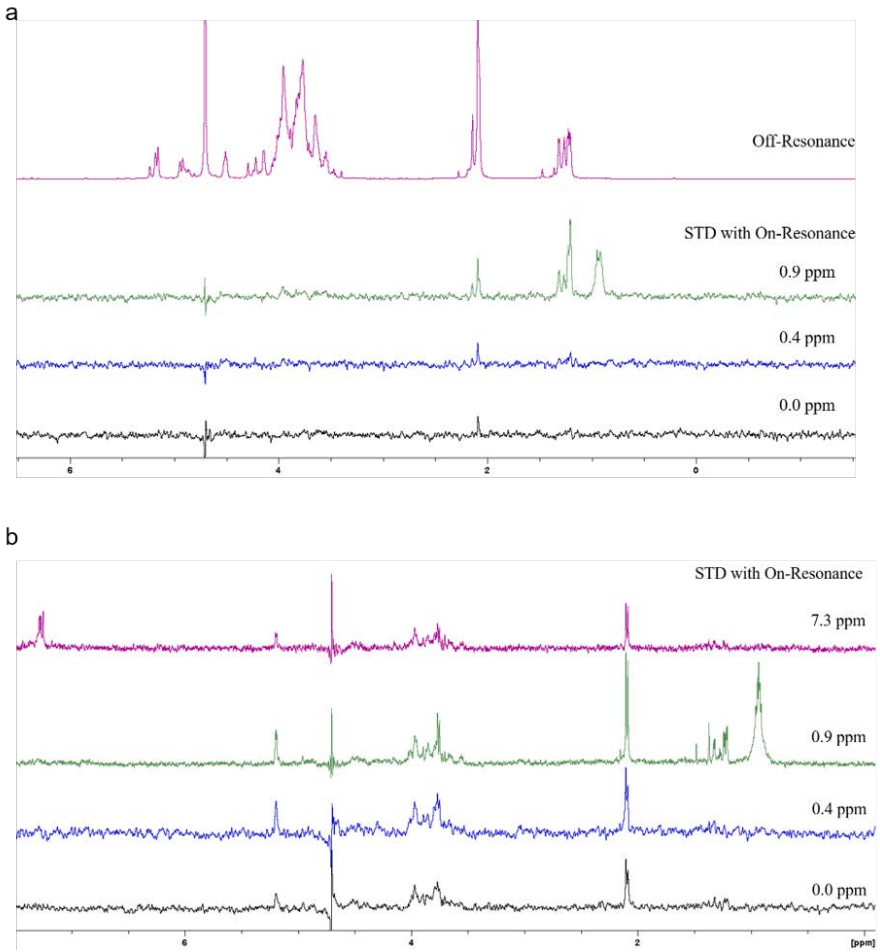


Figure S2. Different irradiation frequency tested for ^{1}H-STD NMR experiments. (a) Only the ligand. (b) In the presence of the protein.

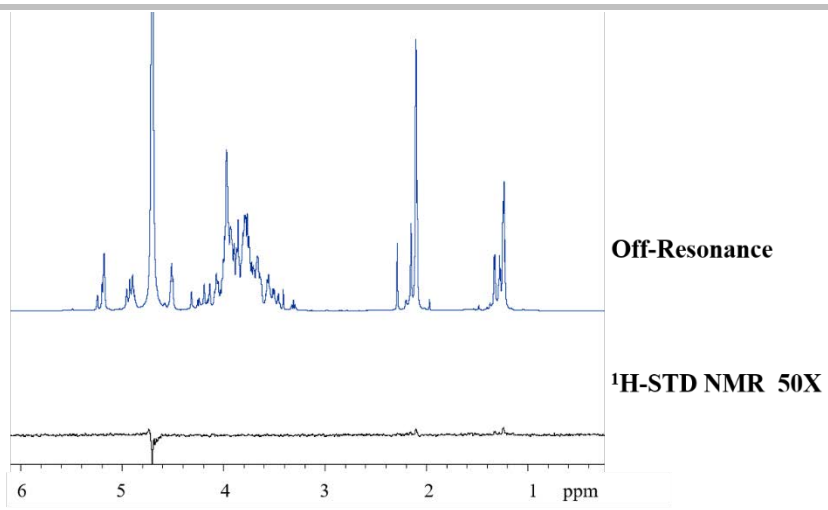


Figure S3. Blank ^{1}H-STD experiment of the free ligand **1**. Ligand concentration is 500 μM in D_2O.

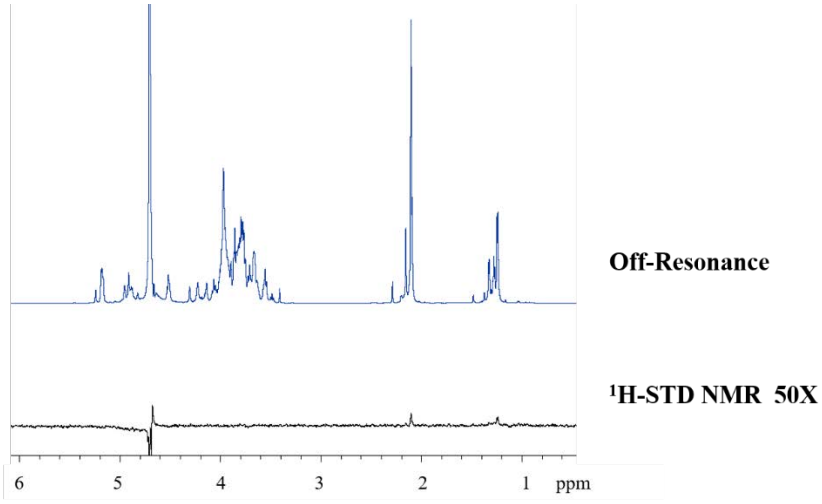


Figure S4. Blank ^{1}H-STD experiment of the free ligand **2**. Ligand concentration is 500 μM in D_2O.

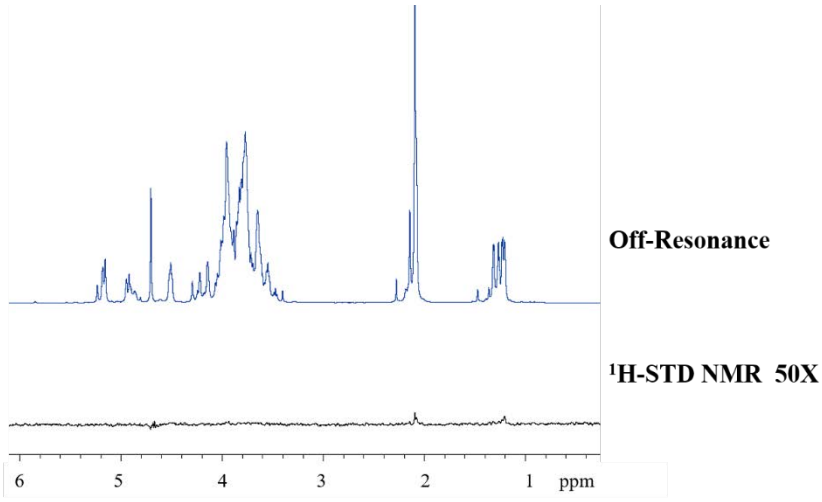


Figure S5. Blank ^{1}H-STD experiment of the free ligand **3**. Ligand concentration is 500 μM in D_2O.

5.3 ^{19}F CPMG NMR. ^{19}F CPMG spectra were acquired in a 600 MHz spectrometer equipped with a Bruker selective ^{19}F–^{1}H decoupling (SEF) probe at 298 K, on samples containing 8 μM of DC-SIGN ECD, the concentration is calculated with respect to the tetramer, and 0.8 mM of the fluorinated probes (2-fluoro-Fucose). Competitors glycans **1-3** were successively added to the sample at a final concentration of 0.4 mM. All samples were measured in buffer 25 mM Tris-d11, 150 mM NaCl, 4 mM $CaCl_2$ in H_2O or D_2O (pH/D 8). The standard CPMG Bruker pulse sequence was modified as described.[11] Twenty four (24) points were acquired with total echo times from 8 to 5200 ms, with τ = 2 ms. Data were analyzed with the T1T2 relaxation module of Topspin3.5.

5.4 Chemical shift perturbation analysis. ^{1}H-^{15}N-HSQC-based experiments were performed using ^{15}N-labeled CRD DC-SIGN at 50 μM, with 2 mM DTT-d10, at 800 MHz Bruker spectrometer equipped with a cryoprobe, at 310 K. Five titration points were acquired for ligands **1-3**, with ligand concentrations varying from 0.0 to 1.0 mM. Averaged chemical shift perturbation (CSP) was calculated using the CcpNmr Analysis 2.4.2.3. The chemical shift perturbation analysis was performed based on the protein backbone assignment deposited in the BMRB database with the code 27854.

5.5 Receptor-based NMR experiments. The CSPs induced on the ^{15}N labeled DC-SIGN (CRD) cross peaks by titration with compound (**1-3**) were compared (Fig. S6). The observed perturbations took place at the primary carbohydrate binding site, which is composed by residues in an extended loop and in β-strand-4 (from W343 to D355 and from N363 to D367, respectively) and at the secondary binding region (from E356 to G361).

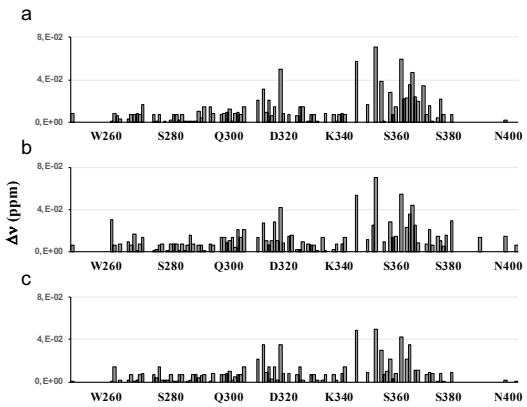


Figure S6. Average chemical shift perturbation (CSPs) produced on the ^{1}H-^{15}N resonances of the DC-SIGN (CRD) upon the addition of 20 eq. of (a) glycan (**1**), (b) glycan (**2**) and (c) glycan (**3**).

6. Molecular modeling

6.1 Molecular dynamic simulations. Initial geometries of ligands **1-3** were built in the Glycam web (http://glycam.org). The MD simulations were performed using the Amber16 program4 with the GLYCAM_06h force field parameters. Thereafter, the starting 3D geometries were placed into a 10 Å octahedral box of explicit TIP3P waters, and counterions were added to maintain electroneutrality. Two consecutive minimization stages were performed involving (1) only the water molecules and ions and (2) the whole system with a higher number of cycles, using the steepest descent algorithm. The system was

subjected to two rapid molecular dynamic simulations (heating and equilibration) before starting the real dynamic simulation. The equilibrated structures were the starting points for the final MD simulations at constant temperature (300 K) and pressure (1 atm). 100 ns Molecular dynamics simulations without constraints were recorded, using an NPT ensemble with periodic boundary conditions, a cut-off of 10 Å, and the particle mesh Ewald method. A total of 50 000 000 molecular dynamics steps were run with a time step of 1 fs per step. Coordinates and energy values were recorded every 50000 steps (50 ps) for a total of 1 000 MD models. The detailed analysis of the glycosidic linkages for glycans **1-3** was performed along the MD trajectory using the cpptraj module included in Amber-Tools 16 package.

6.2 Conformational analysis. We performed molecular modelling studies to determine the main conformational distribution of the synthetized glycans **1**, **2** and **3**. Molecular dynamic (MD) simulation were performed for each compound during 100 ns. The short MD trajectory satisfactory explored the expected conformational distribution of triantennary glycans, with the main flexibility at the O5C5C6O6 ω dihedral angles. All the ϕ dihedral angles respected the *exo*-anomeric effect, while the ψ dihedral angles showed the expected wider distribution (data not shown). The distribution of the ω dihedral angles along the MD trajectory of compound **1** is shown in Fig. S7. The presence of the xylose ring does not hamper the expected flexibility of branched glycans. Both dihedral angles mainly populate the gt and gg conformations, giving rise to four main conformers. The four main conformers (gg;gt), (gt;gt), (gg;gg) and (gt;gg) are represented for compounds **1** and **3** in Fig. S8.

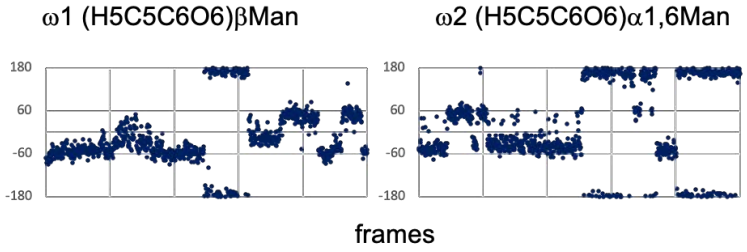


Figure S7. Map of the ω dihedral angles for glycan **1** as generated by analysis along the 100 ns MD simulation.

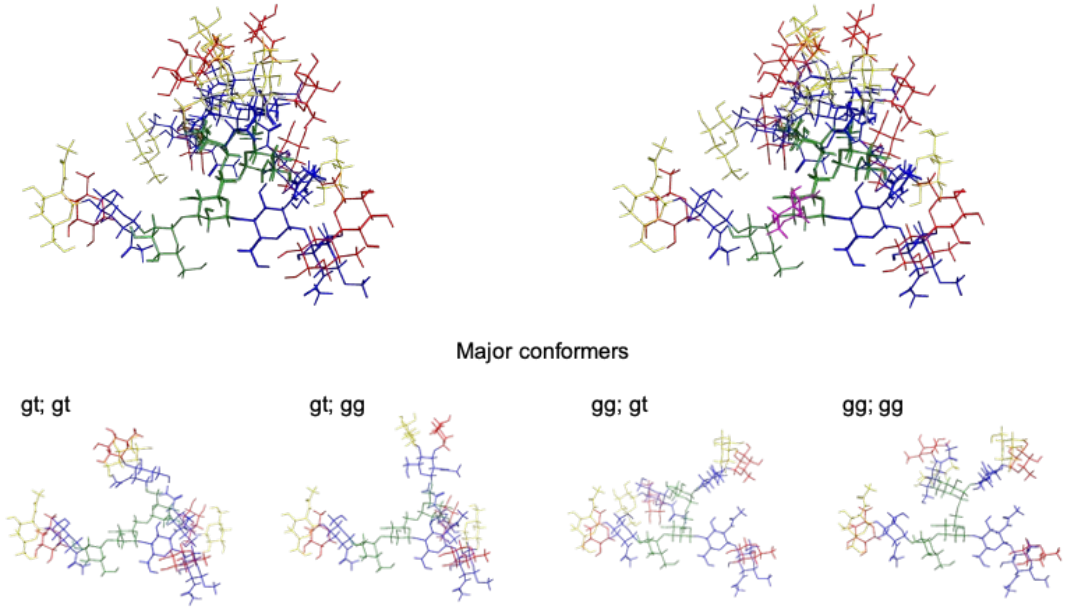


Figure S8. Representation of the average conformational distribution for glycan **1** (right) and **2** (left). The main conformers are defined as gt;gt (ω1 -60, ω2 -60), gt;gg (ω1 -60, ω2 ±180), gg;gt (ω1 ±180, ω2 -60) and gg;gg (ω1 ±180, ω2 ±180). The structures are derived from MD simulations study.

6.3 Modelling of the bound states. The initial pdb coordinates for CRD of DC-SIGN were derived from the crystal structure Protein Database (PDB) 1SL5, while the model of DC-SIGN ECD was generated as previously described.[12] Briefly, to build the model of the protein's head, the DC-SIGN CRD (PDB code 1sl5) was superimposed on the mannose-binding protein CRD (PDB code 1hup), which represents the prototype of the C-type family of lectin and for which an oligomeric structure is available. Four copies of DC-SIGN CRD in this orientation were generated. To model the neck, 8 repeating units of 23 residues (PDB code 3JQH) were linearly assembled and four of those were arranged as the four α-helices observed in the structure of the tetramer of DC-SIGNR CRDs (PDB code 1xar). We underline that our model for the DC-SIGN ECD tetramer is an approximation. However, the generated model satisfactorily resembles the one previously described, which is derived from SAXS data and nicely fits the apo DC-SIGN structure as visualized by negative-stain technique. To generate protein/ ligand complexes, the fucose pyranose rings of the Le^x and LDN-F motives of glycans **1-3** were manually superimposed onto the corresponding sugar in the deposited 1sl5 structure. Glycans structures used to model the binding poses were derived from the above-described conformational study. All alternative binding poses were generated for each ligand and are represented in Fig. S9. To further explore the two alternative binding poses proposed for ligand 3, we performed MD simulations on the bound state. Both, the terminal and the internal LeX moieties were manually superimposed onto the corresponding trisaccharide in the x-ray structure (pdb 1sl5) giving rise to the first and second binding pose, respectively. The two structures were submitted to MD simulations during 100 ns. MD simulations support the experimental results, evidencing that both binding poses are possible and stable along the simulation. The last frames of the simulations are represented in Fig. S9c.

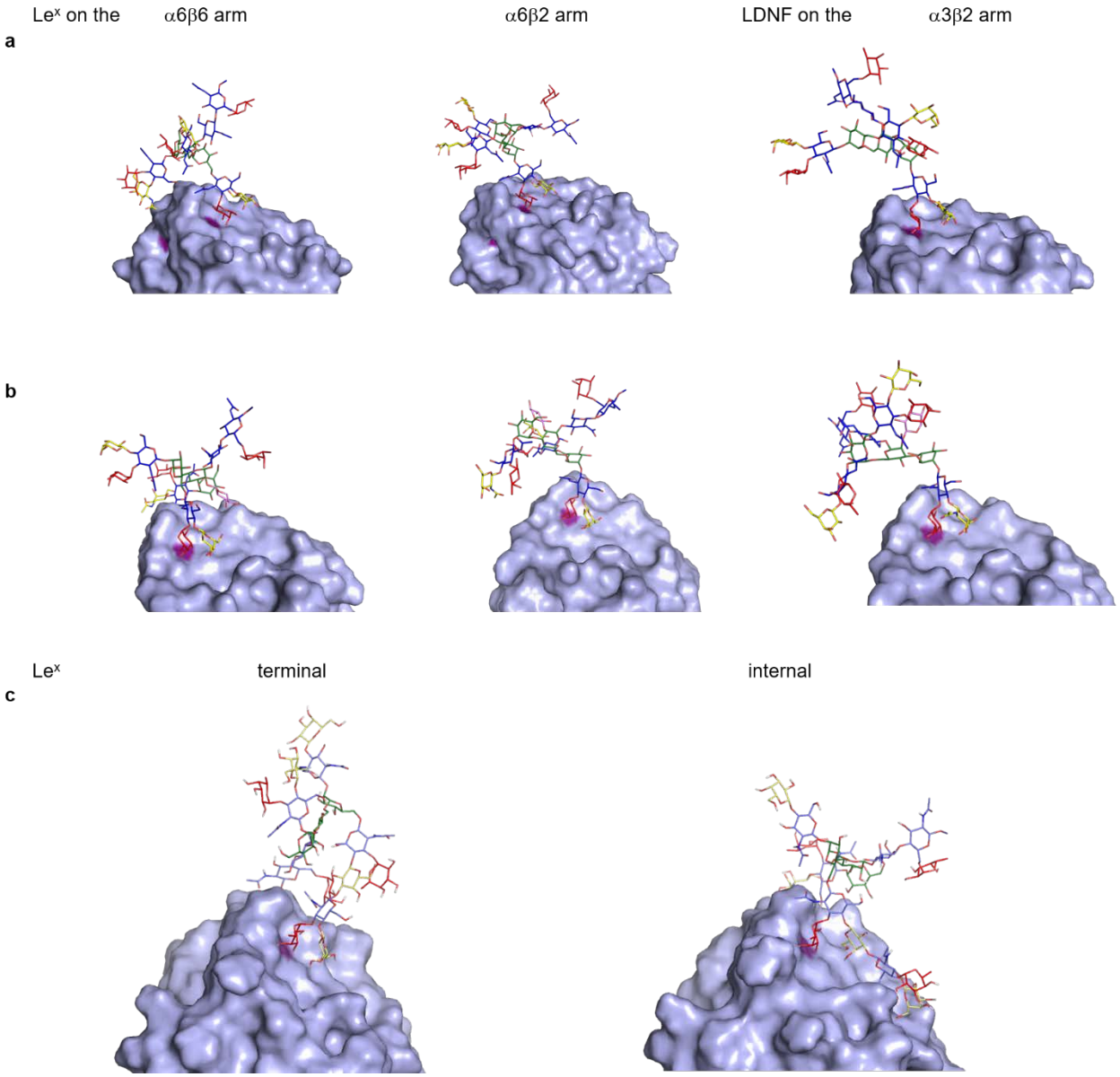


Figure S9. Models of the binding mode for the complex between CRD DC-SIGN and the glycans (a) **2**, (b) **1** and (c) **3**. All possible binding models are represented for compounds **1** and **3**, each corresponding to a different arm of the triantennary glycans. Two alternative binding modes are presented for the glycan **3**, one in which the terminal Le^x motif is recognized and the second in which the internal Le^x is into the binding pocket.

7. EM sample preparation and TEM data collection

The apo DC-SIGN sample (4 µL at 1.5 mg/mL) and the samples of DC-SIGN in presence of the ligands **1** and **2**, at 1 to 50 molar ratio (4 µL at 1.5 mg/mL protein and 1.4 mg/mL ligand) were pipetted onto plasma-cleaned 200-mesh Quantifoil R 2/2 Cu 200. The grids were vitrified using the climate-controlled plunge-freezing device Vitrobot (Mark III-FEI). Different blot pad position and blotting times were tested with offset number 0 and 3 s blotting giving satisfactory results in terms of ice thickness relative to particle's size. All samples were prepared in triplicate and the grids were inspected under low dose condition on a JEM-2200FS/CR (JEOL, Ltd.) electron microscope operating at 200kV and equipped with an omega in-column energy filter. About 50 cryo-images were recorded on an UltraScan 4000 SP (4008x4008 pixels) cooled slow-scan CCD camera (GATAN) at defocus of -2.5/ -3.0 micron with a total dose of 20 e–/Å² at a nominal magnification of ×50,000, producing a pixel size at the specimen of 2.0 Å. For negative-stain EM the DC-SIGN sample was applied to glow-discharged carbon-coated copper grids and stained with 2% (w/v) uranyl acetate. Micrographs were collected on a JEOL JEM-1230 LaB6 transmission electron microscope operated at 100 kV and equipped with an Orius SC1000 CCD camera with a nominal magnification of 40,000 (1.78 Å per pixel). A set of 1,086 particles were manually selected and extracted. This set of particles was subjected to an iterative reference-free two-dimensional alignment and classification procedure using the Relion software within the Scipion package.[13] The three class-averages shown in Fig. 6c (from left to right) are composed of 85, 187 and 332 class members, respectively.

Both sample preparation and TEM analysis were performed at the EM facility at the CIC bioGUNE.

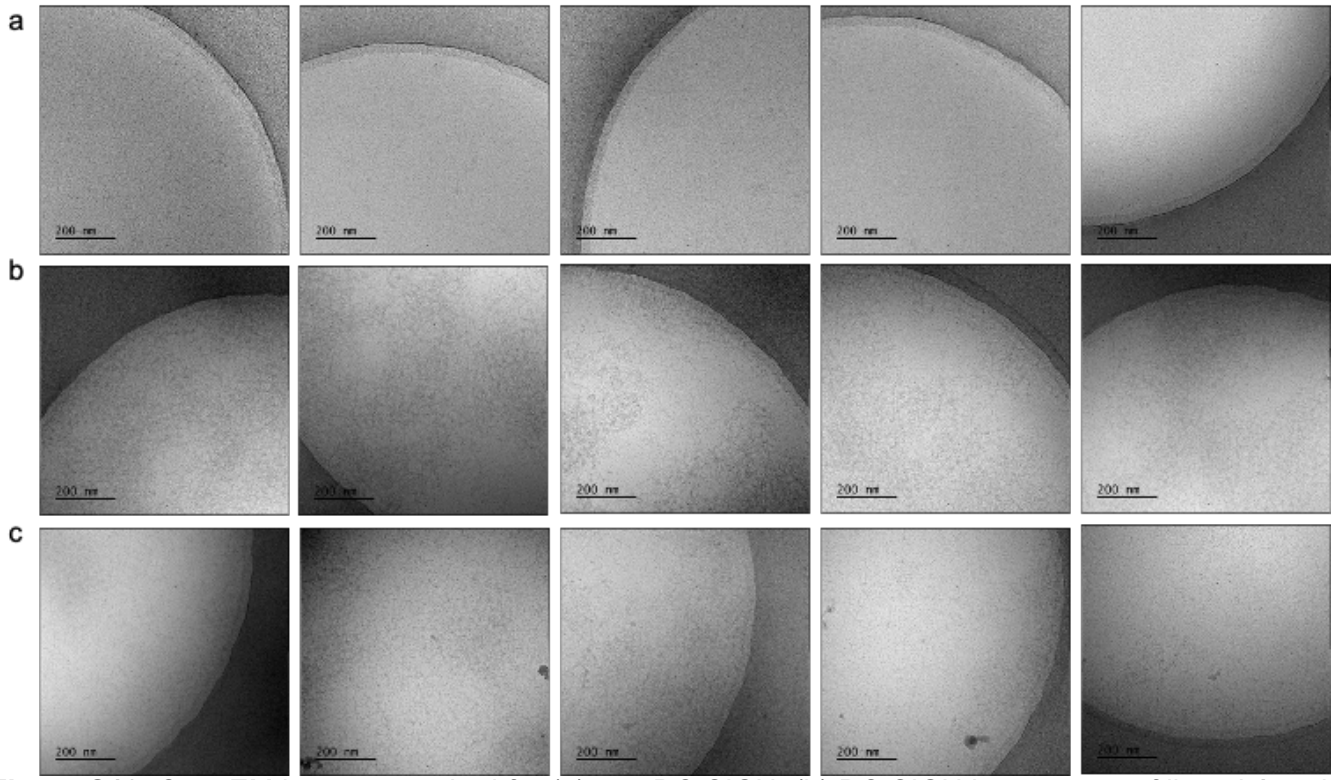


Figure S10. Cryo-EM images acquired for (a) apo DC-SIGN, (b) DC-SIGN in presence of ligand **1** and (c) ligand **2**. Nominal magnification is ×50,000.

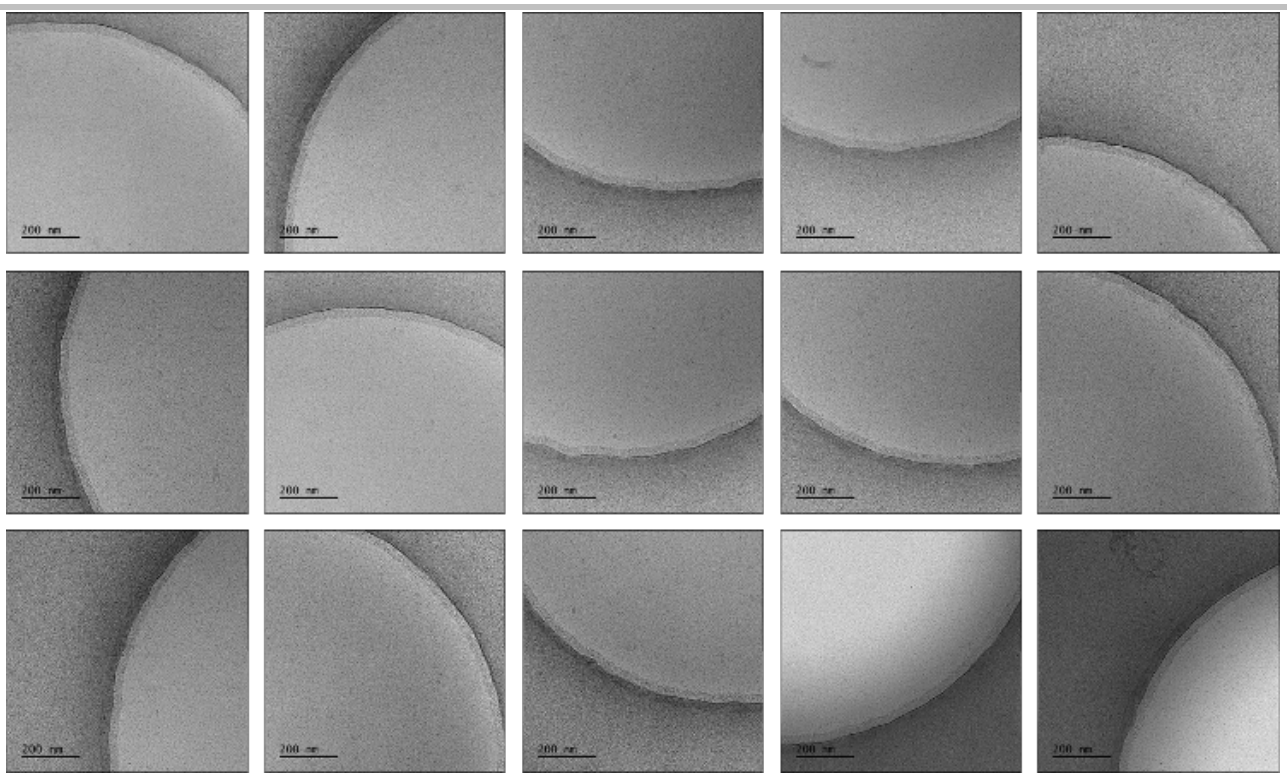


Figure S11. Cryo-EM images acquired for *apo* DC-SIGN. Nominal magnification is ×50,000.

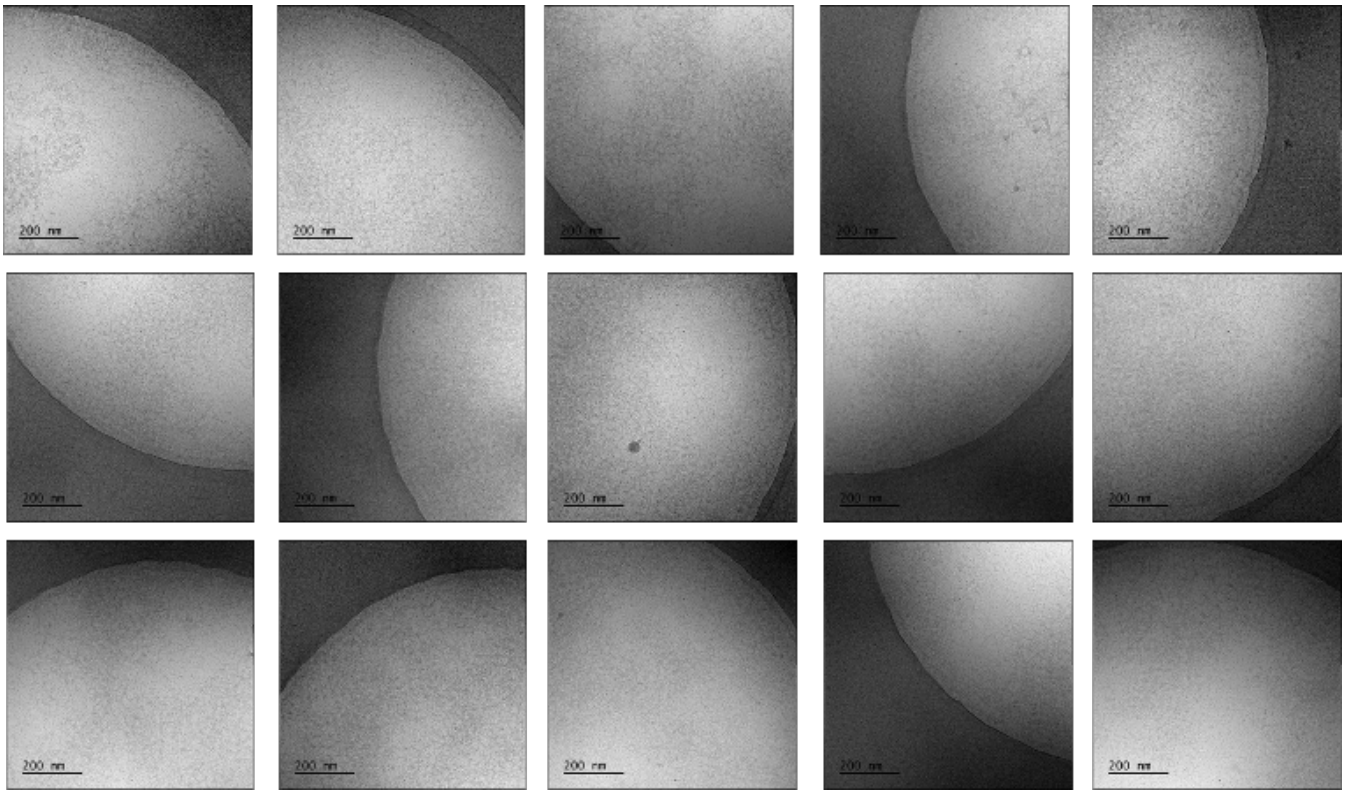


Figure S12. Cryo-EM images acquired for DC-SIGN in complex with ligand **1**. Nominal magnification is ×50,000.

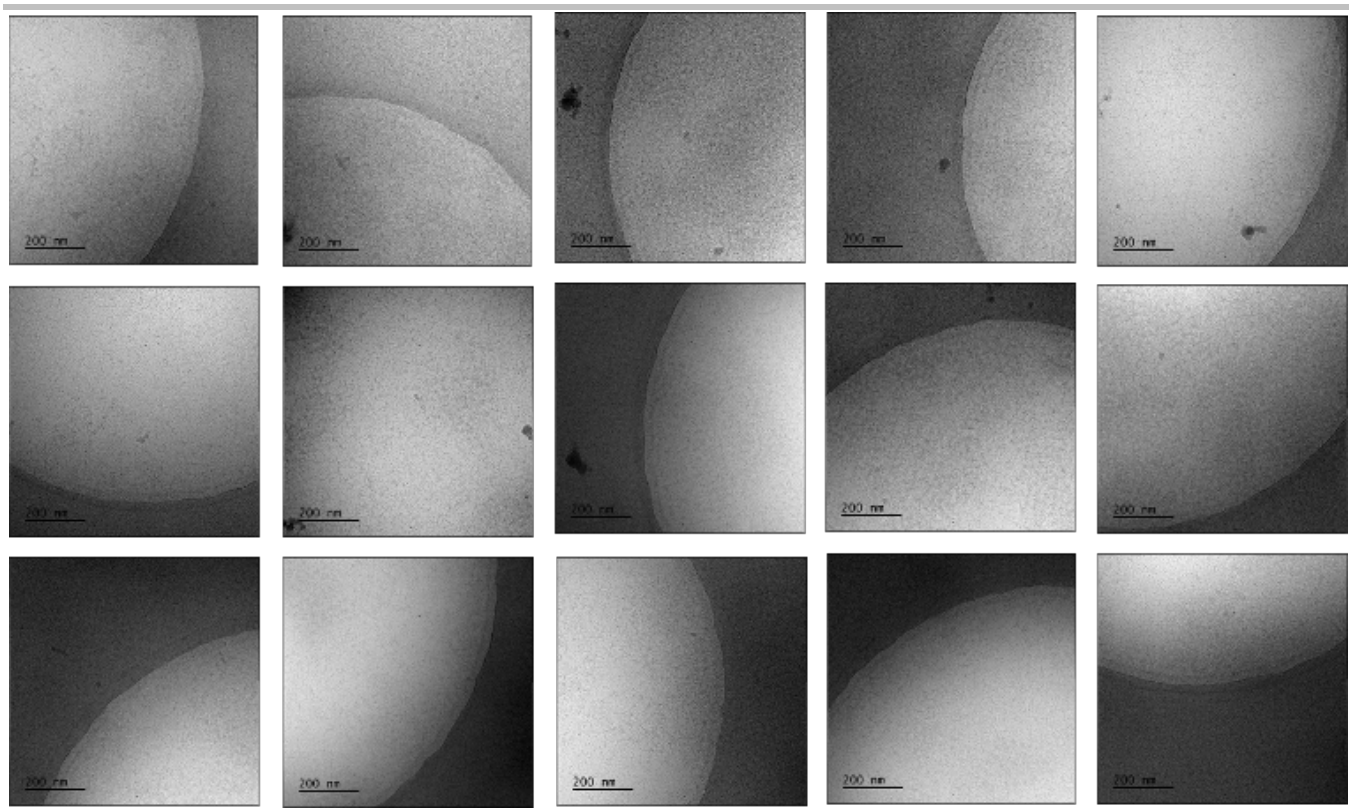


Figure S13. Cryo-EM images acquired for DC-SIGN in complex with ligand **2**. Nominal magnification is ×50,000.

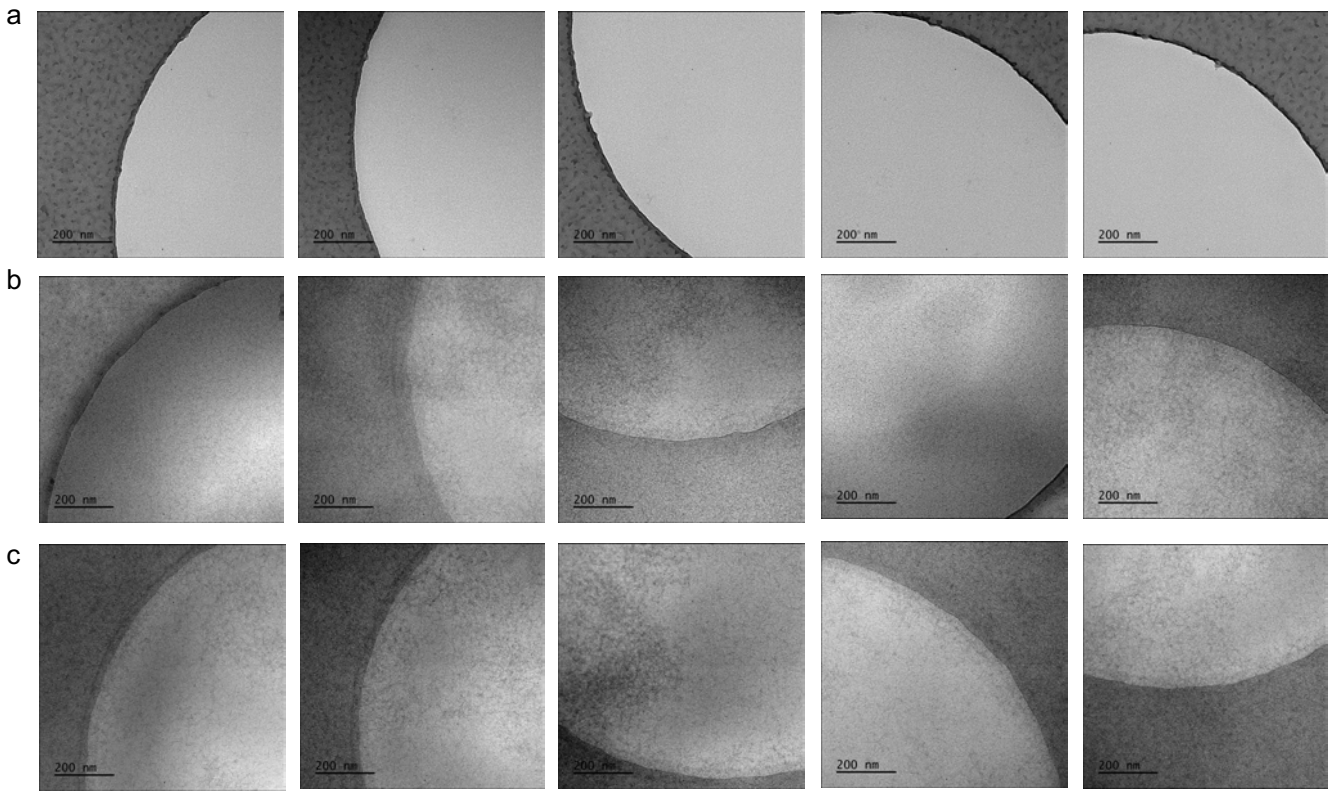


Figure S14. Cryo-EM images acquired using Quantifoil grids coated with a carbon layer (a) apo DC-SIGN, (b) DC-SIGN in presence of ligand **1** and (c) ligand **2**. Nominal magnification is ×50,000.

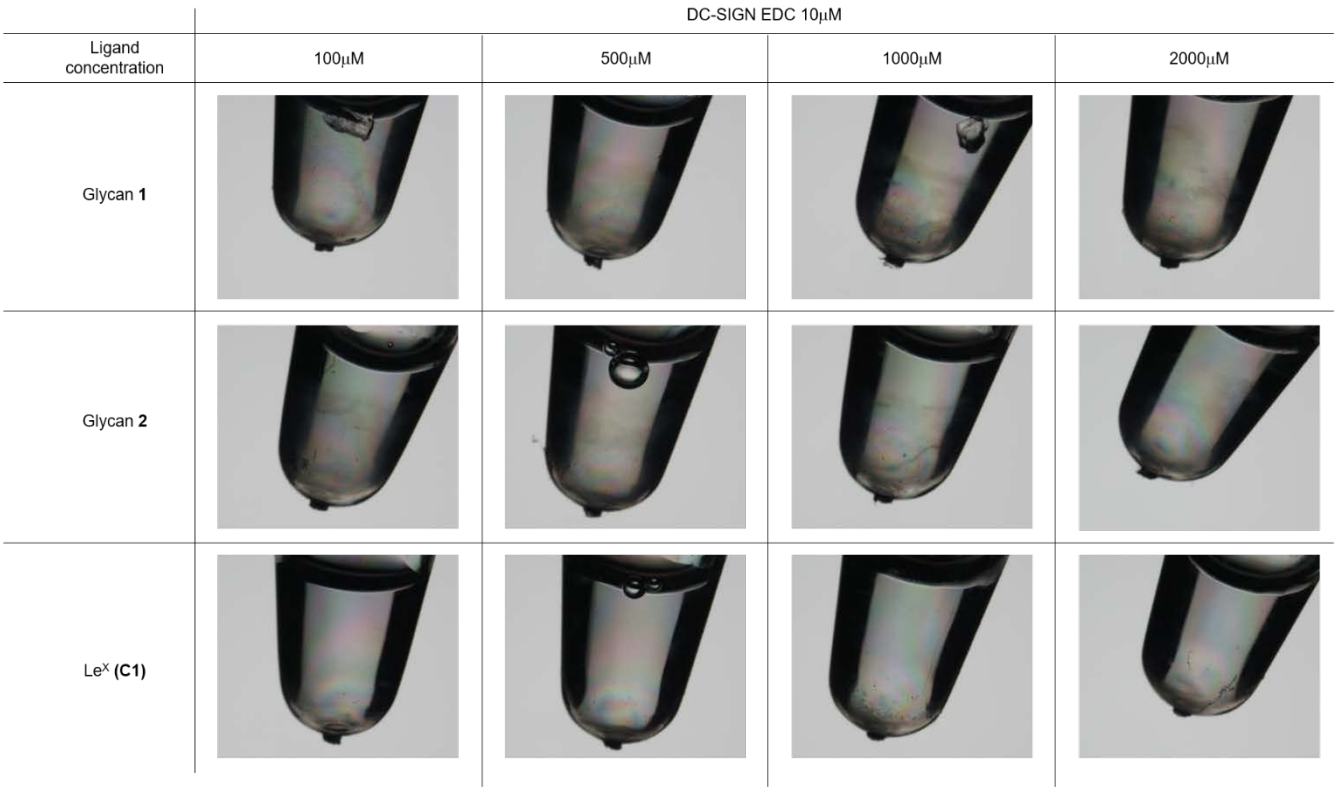


Figure S15. Pictures of the samples containing DC-SIGN (ECD) in the presence of different concentrations of ligands **1**, **2** and **C1**. The presence of aggregates is visible for ligands **1** and **2**, but not for ligand **C1**.

Table S2. Absorbance at 600 nm.

DC-SIGN EDC 10 μM	**Absorbance at 600 nM**			
Ligand Concentration	100 μM	500 μM	1000 μM	2000 μM
Glycan **1**	0.27	0.25	0.17	0.18
Glycan **2**	0.27	0.20	0.18	0.16
Le^X (**C1**)	0.04	0.00	0.04	0.06

8. References

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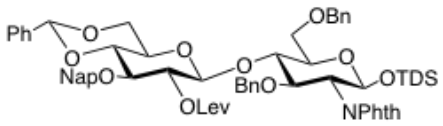
9. Author contributions

A.D.S., L.U. and G.J.B. conceived the study and wrote the paper; A.D.S., M.B. and I.A.G. performed chemical synthesis; A.D.S. performed enzymatic transformations; L.U and A.A. performed NMR experiments; N.G.A.A. and S.D. performed cryo-EM studies; all authors contributed reviewing the manuscript.

10. Copies of NMR spectra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1.00
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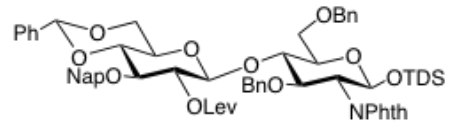
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S3

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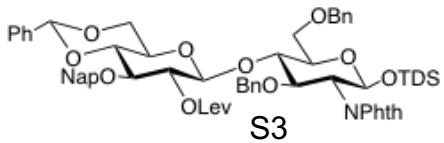

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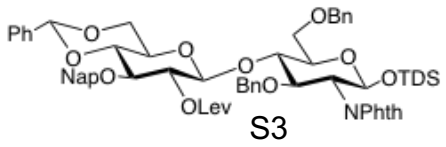
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S3

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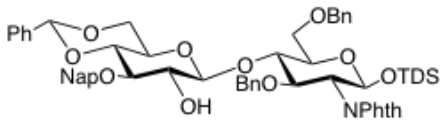
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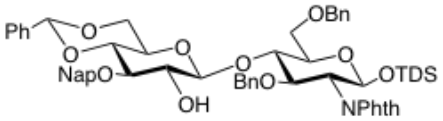

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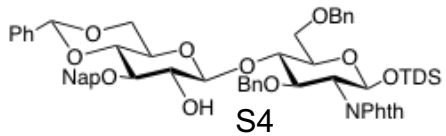
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S4

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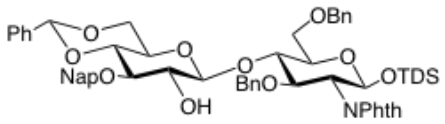
f1 (ppm)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S4

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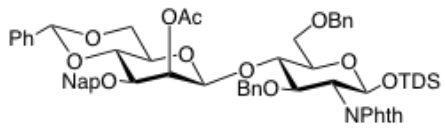

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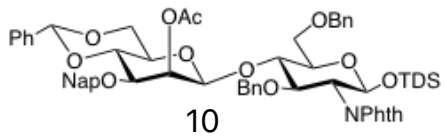

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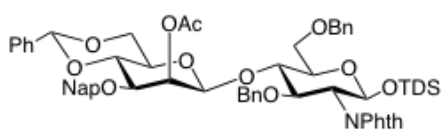
f2 (ppm)

f1 (ppm)



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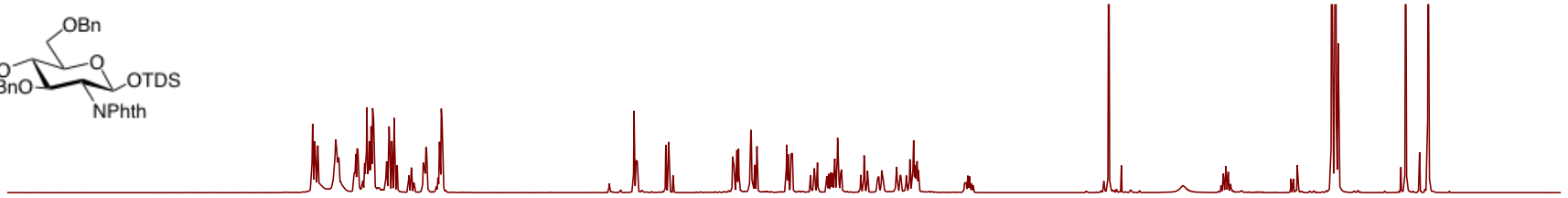

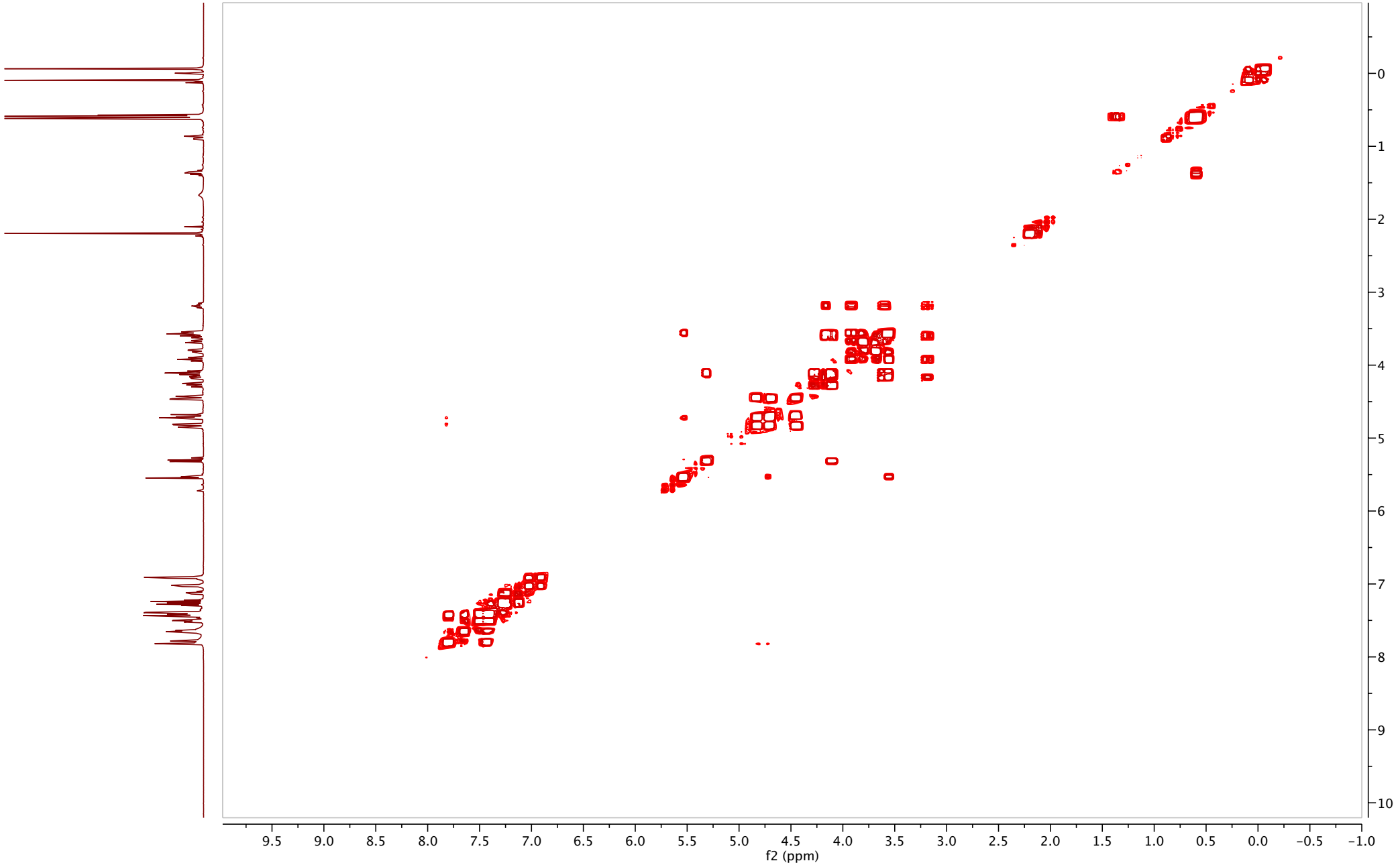

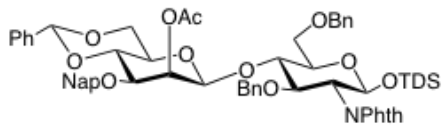

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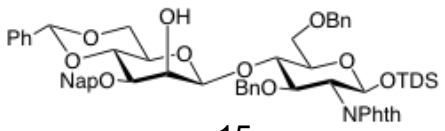
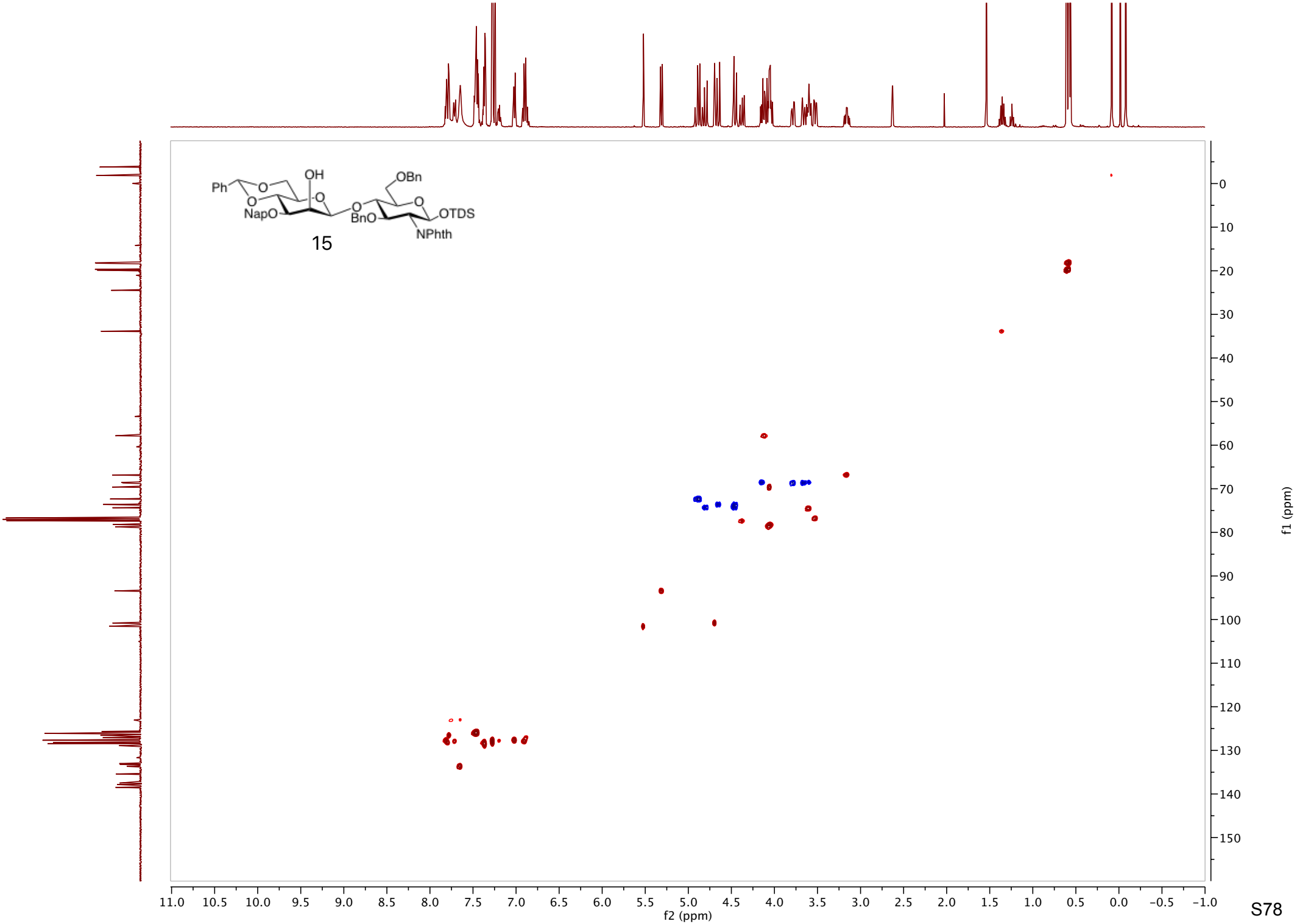
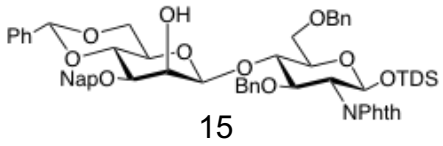

Ph
O
OH
O
O
NapO
O
BnO
OBn
O
OTDS
NPhth

15

23.31
1.02
1.00
2.99
1.81
1.74
1.00
4.57
1.05
2.88
1.06
1.08
0.91
1.03
11.05
6.02
f1 (ppm)

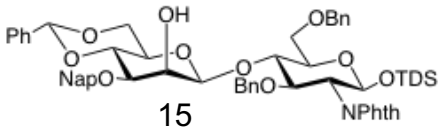

Ph
O
OH
O
O
NapO
O
BnO
OBn
O
OTDS
NPhth
15
f2 (ppm)
f1 (ppm)



15

f2 (ppm)

f1 (ppm)



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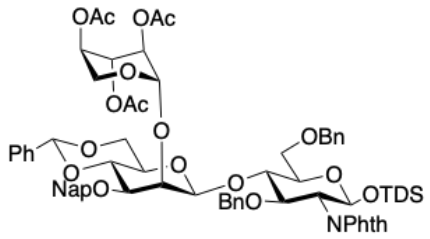
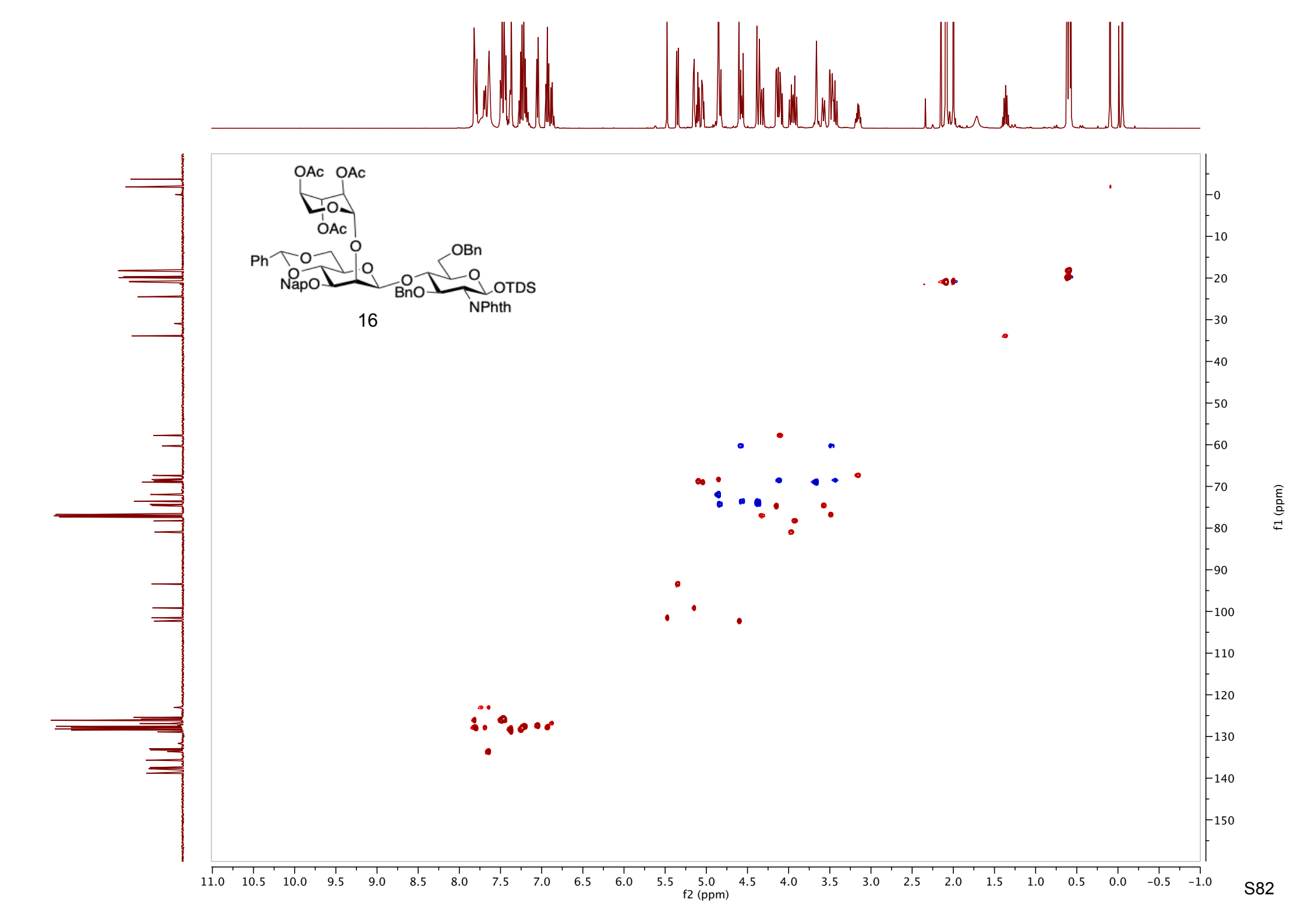
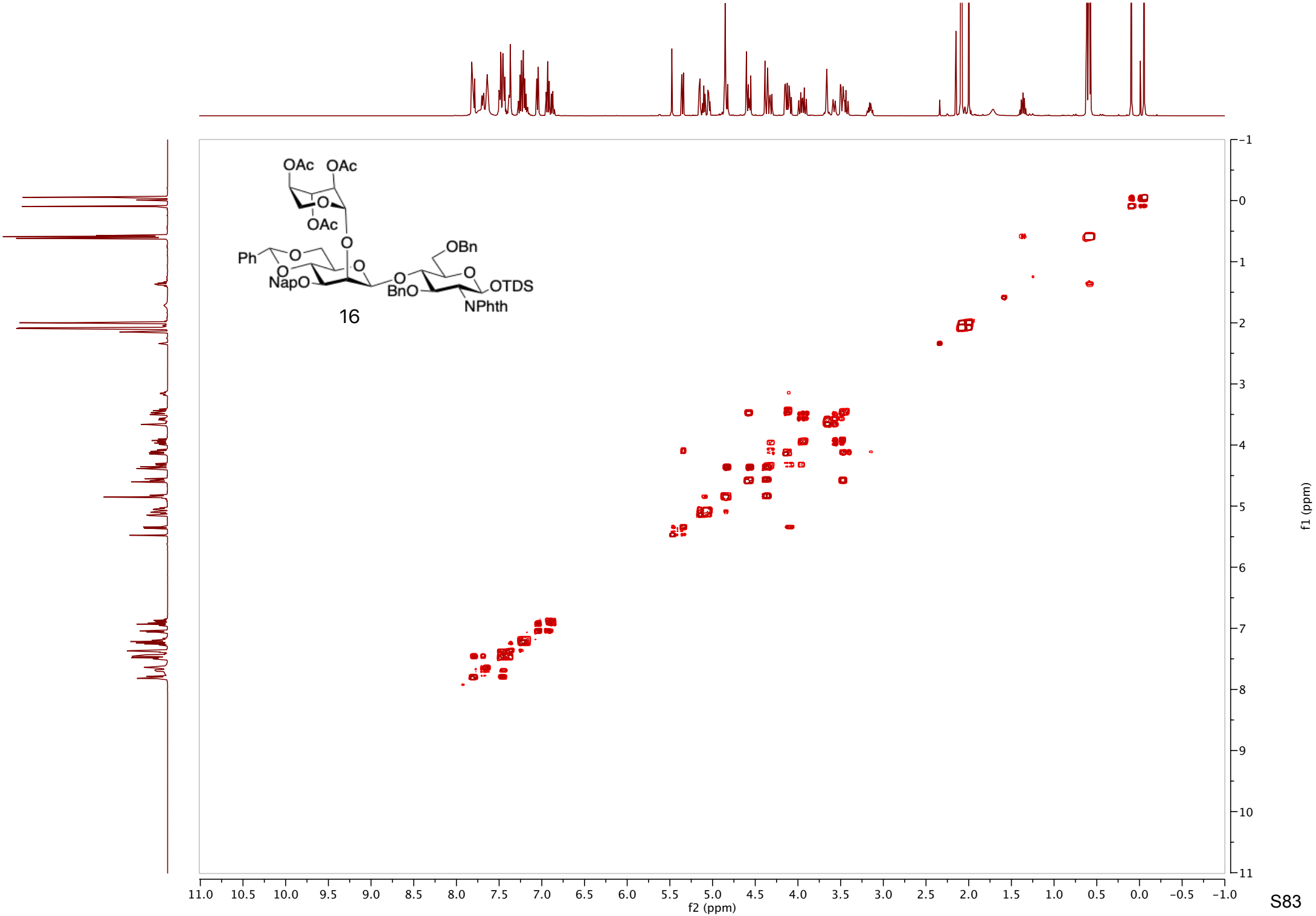
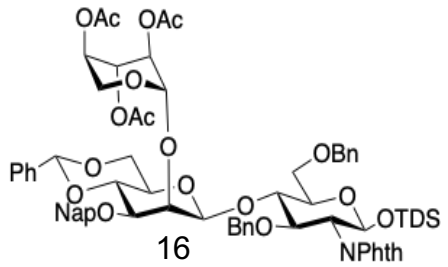

OAc
OAc
OAc
O
Ph
O
O
NapO
O
O
BnO
OBn
O
OTDS
NPhth

16

26.27
0.88
1.00
1.00
1.08
1.10
4.01
3.21
3.18
2.99
2.26
3.36
3.24
1.15
9.60
1.25
12.23
6.93
f1 (ppm)

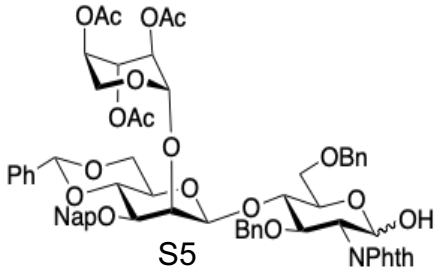

OAc
OAc
OAc
O
Ph
O
O
NapO
O
O
BnO
OBn
O
OTDS
NPhth
16
f2 (ppm)
f1 (ppm)


OAc
OAc
OAc
O
Ph
O
O
NapO
O
O
BnO
OBn
O
OTDS
NPhth
16
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)
−1
0
1
2
3
4
5
6
7
8
9
10
11
f1 (ppm)


OAc
OAc
O
OAc
O
Ph
O
O
NapO
O
O
BnO
OBn
O
OTDS
NPhth

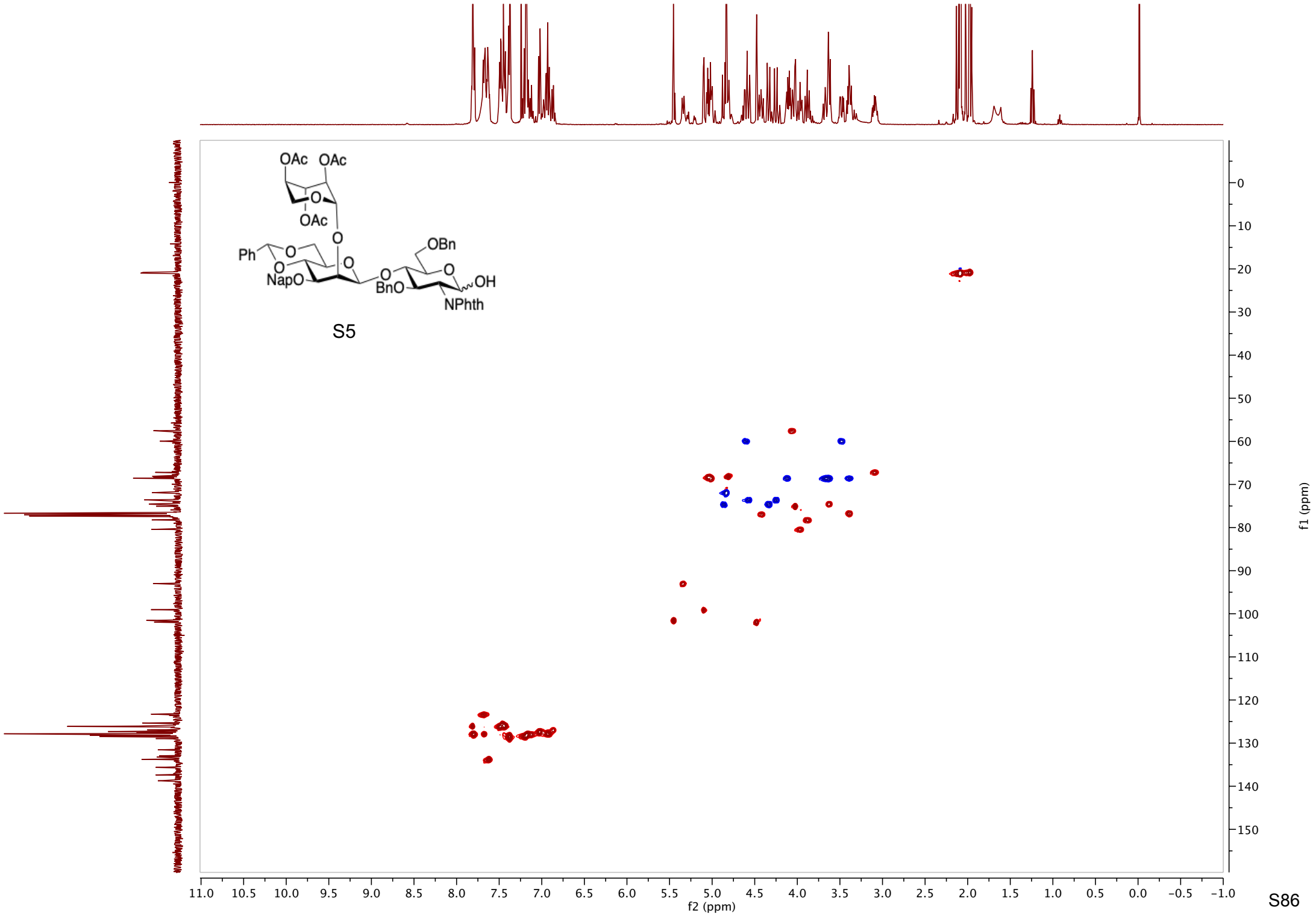
16

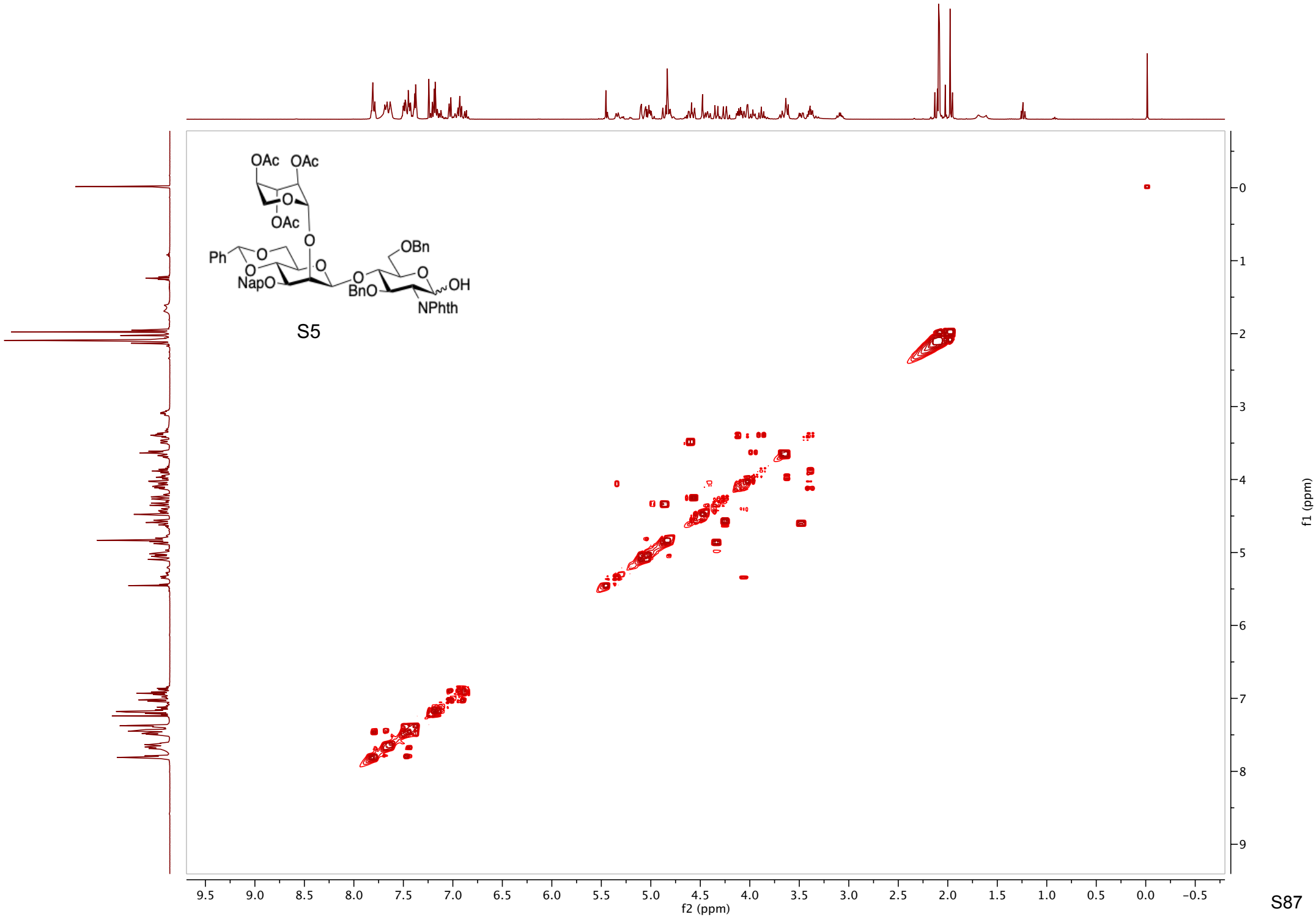
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

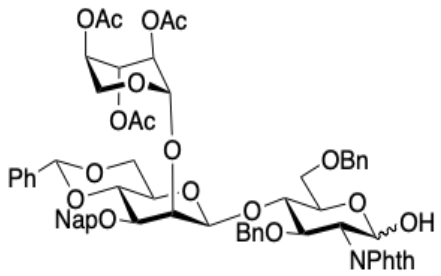

OAc
OAc
O
OAc
Ph
O
O
NapO
O
O
OBn
O
BnO
OH
NPhth

S5

26.76
1.00
1.07
3.36
4.09
2.13
2.21
2.22
3.47
2.21
3.04
1.13
2.36
1.23
9.29
f1 (ppm)

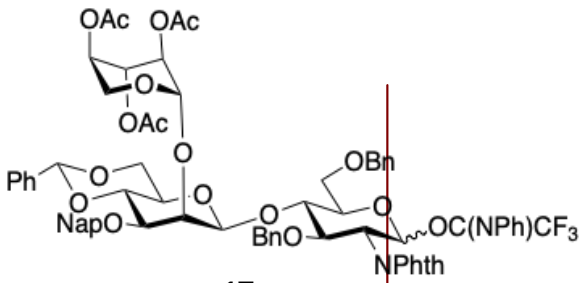

OAc
OAc
OAc
O
Ph
O
O
NapO
O
O
BnO
OBn
O
OH
NPhth
S5
f2 (ppm)
f1 (ppm)


OAc
OAc
OAc
O
Ph
O
O
NapO
O
O
BnO
OBn
O
OH
NPhth
S5
f1 (ppm)
f2 (ppm)


OAc
OAc
OAc
O
Ph
O
O
NapO
O
O
OBn
O
BnO
OH
NPhth

S5

26
24
22
20
18
16
14
12
10
8
6
4
2
0
−2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



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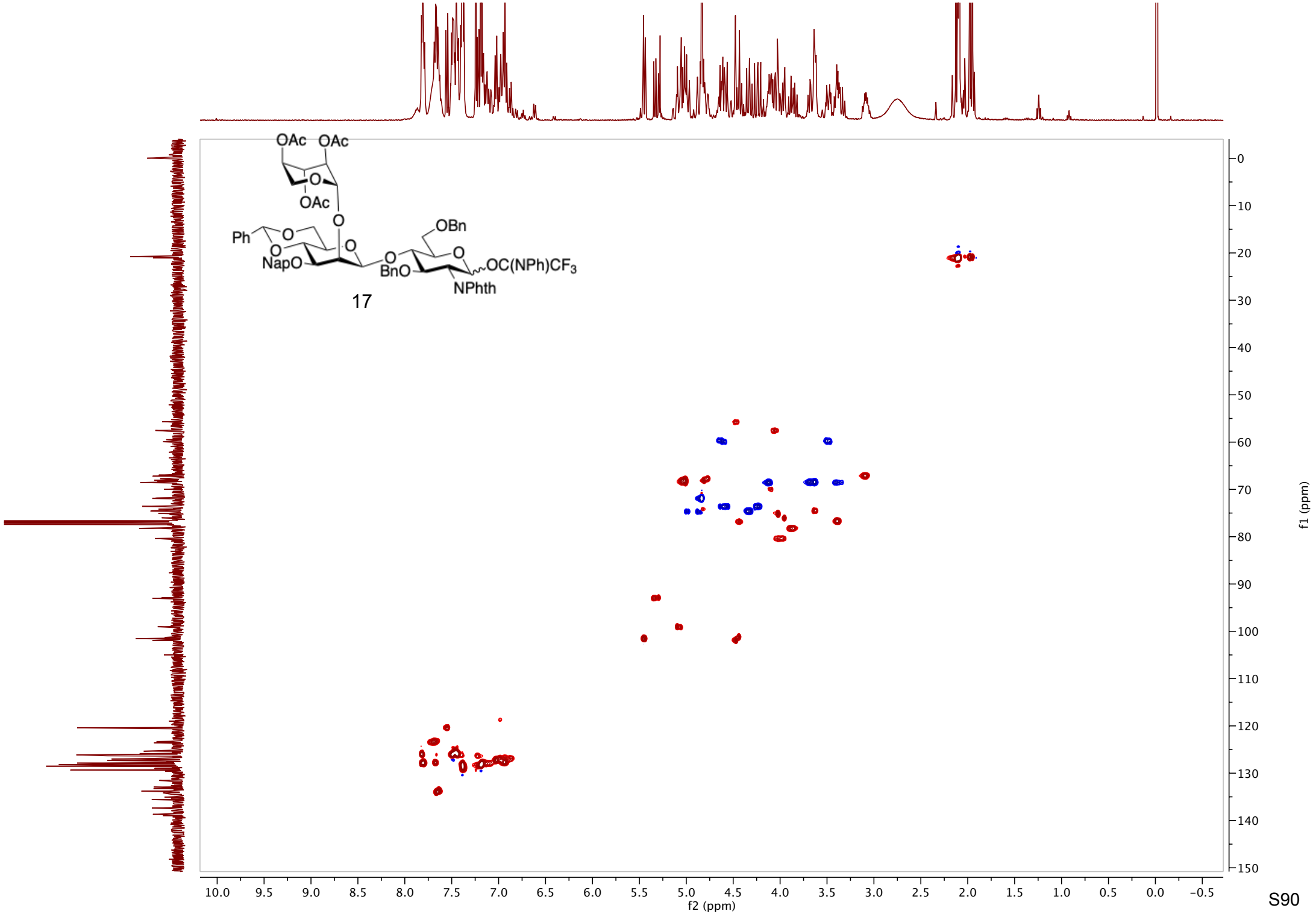
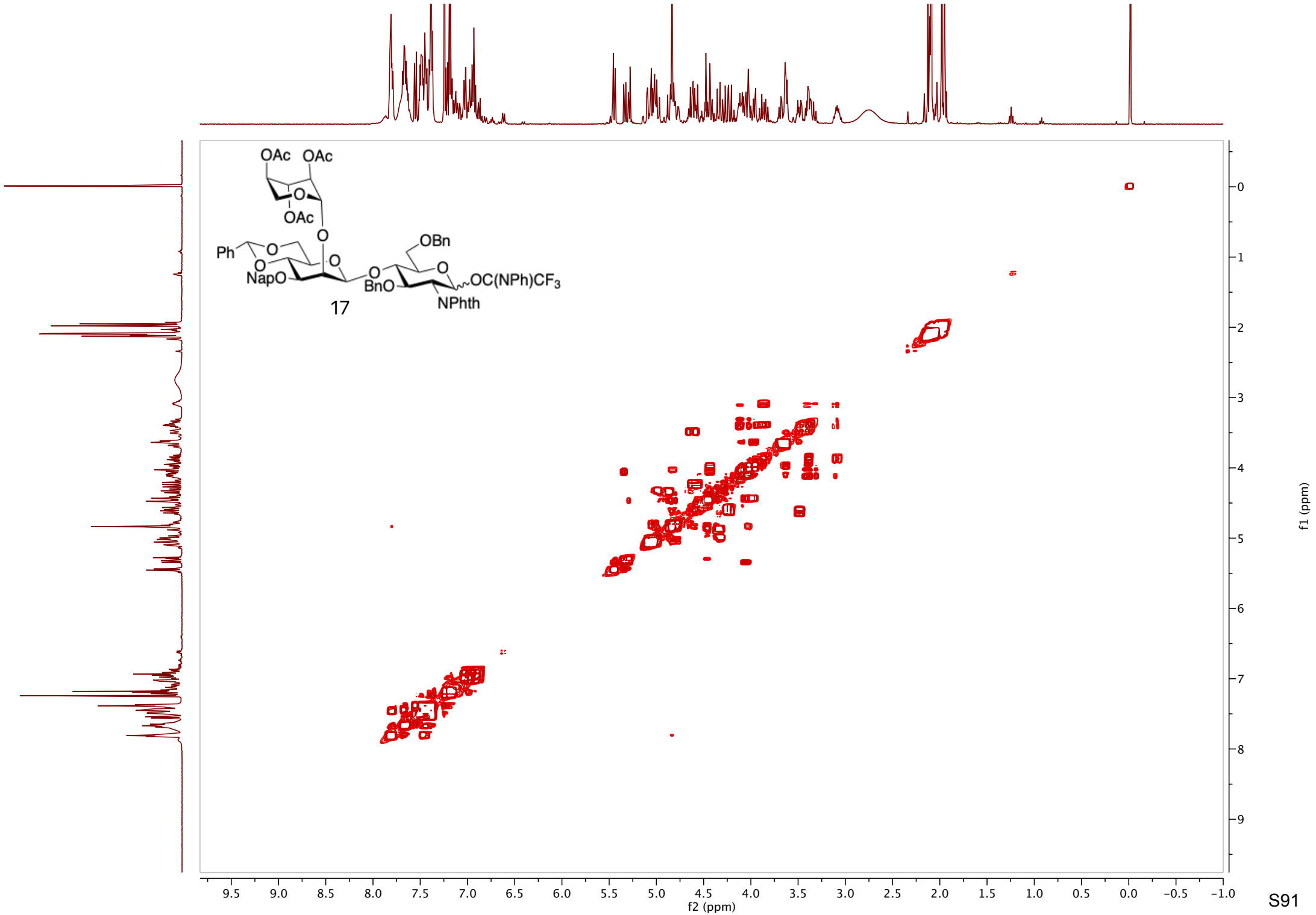
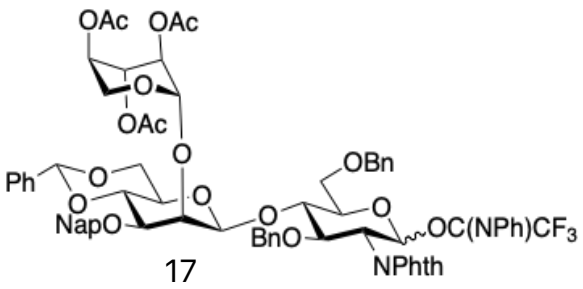
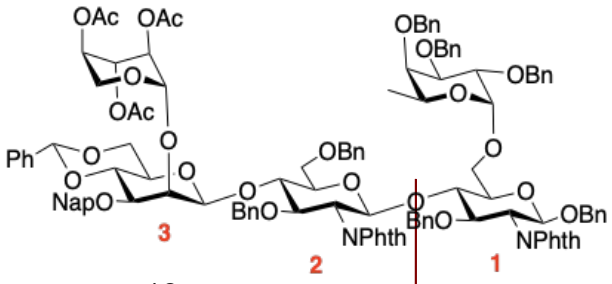

OAc
OAc
OAc
O
Ph
O
O
NapO
O
O
O
BnO
OBn
O
OC(NPh)CF3
NPhth
17
f2 (ppm)
f1 (ppm)


OAc
OAc
OAc
O
Ph
O
O
NapO
O
BnO
OBn
O
OC(NPh)CF3
NPhth
17
f2 (ppm)
f1 (ppm)

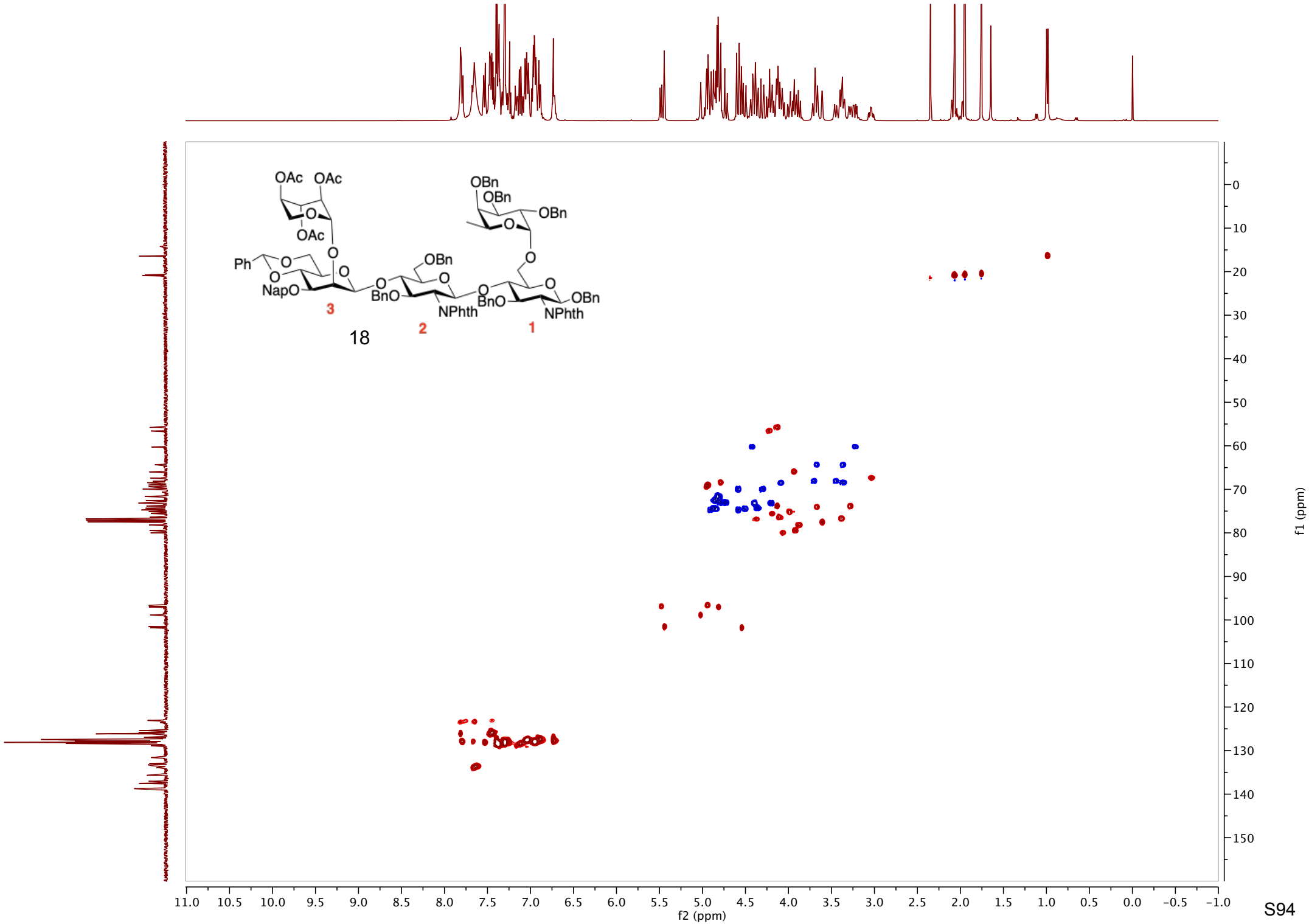


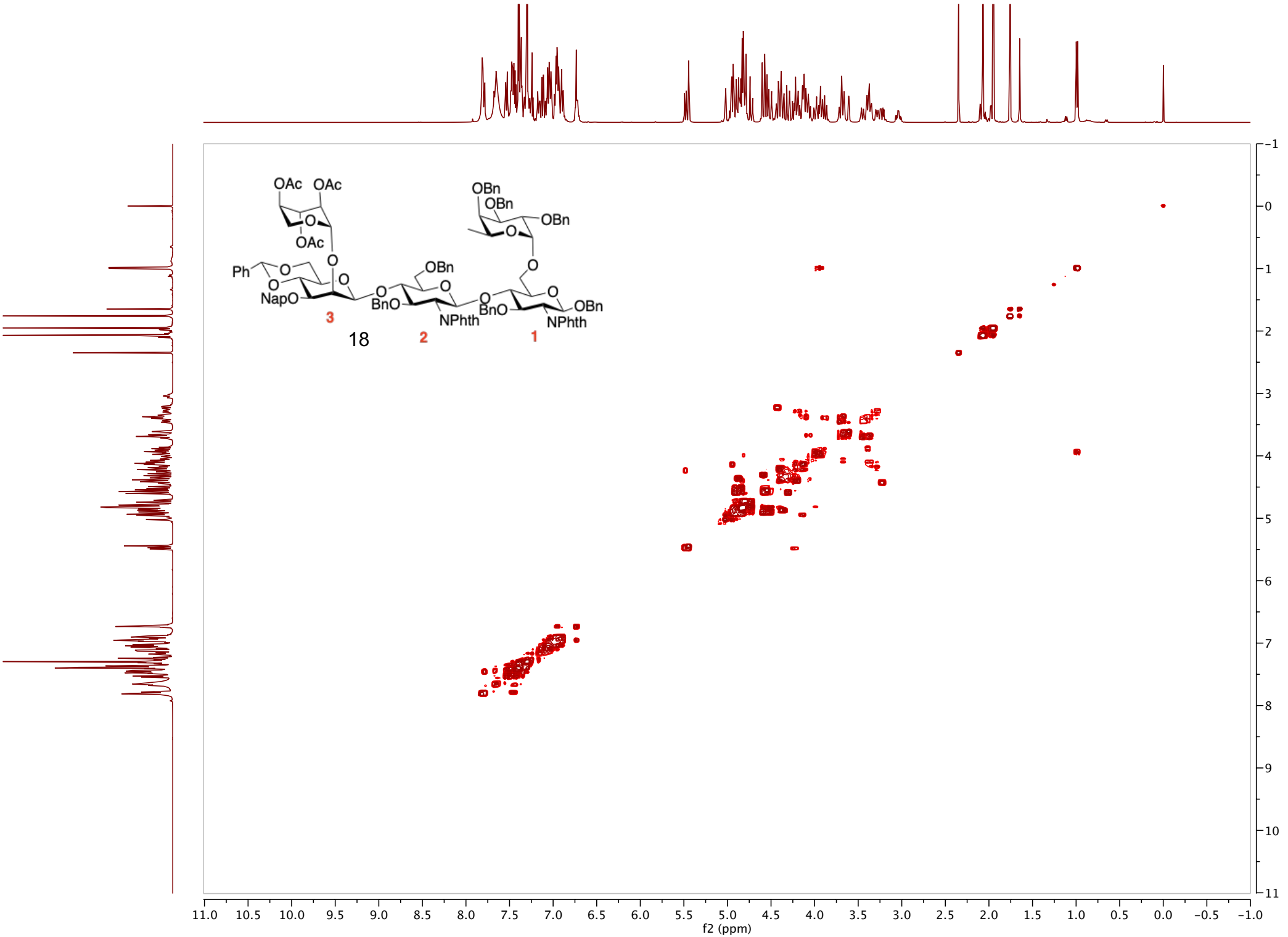
17

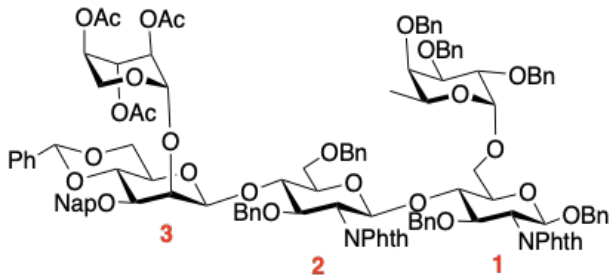

OAc
OAc
OAc
O
Ph
O
O
NapO
O
3
O
OBn
O
BnO
NPhth
2
O
OBn
OBn
OBn
O
O
O
BnO
OBn
NPhth
1

18

62.42
1.00
1.17
1.14
3.59
10.88
1.31
4.88
5.97
3.68
5.48
4.51
4.34
4.46
2.49
1.06
9.74
3.03
f1 (ppm)

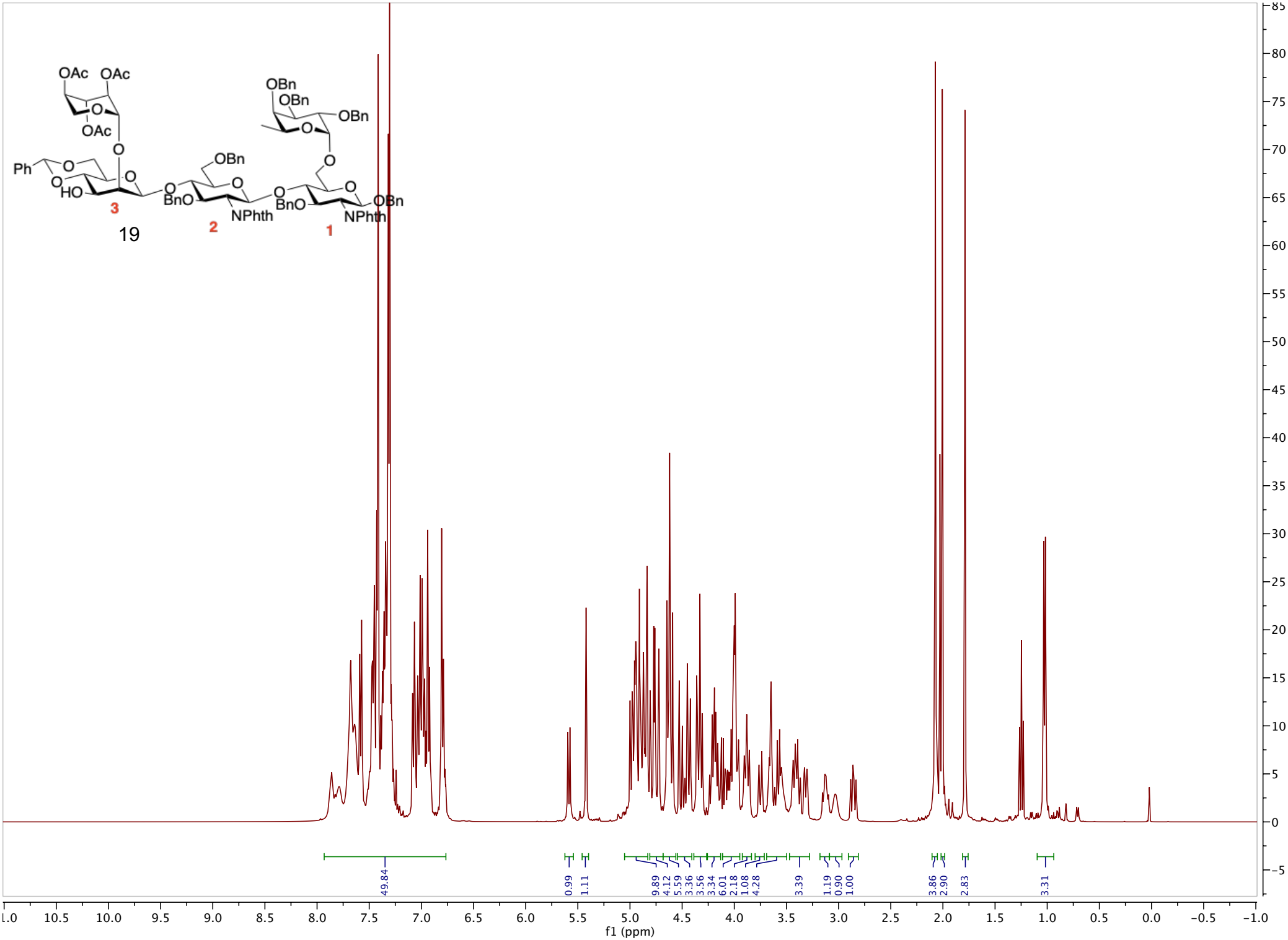

OAc
OAc
OAc
O
Ph
O
O
NapO
3
O
OBn
O
BnO
NPhth
2
O
OBn
OBn
OBn
O
O
BnO
NPhth
1
OBn
18
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

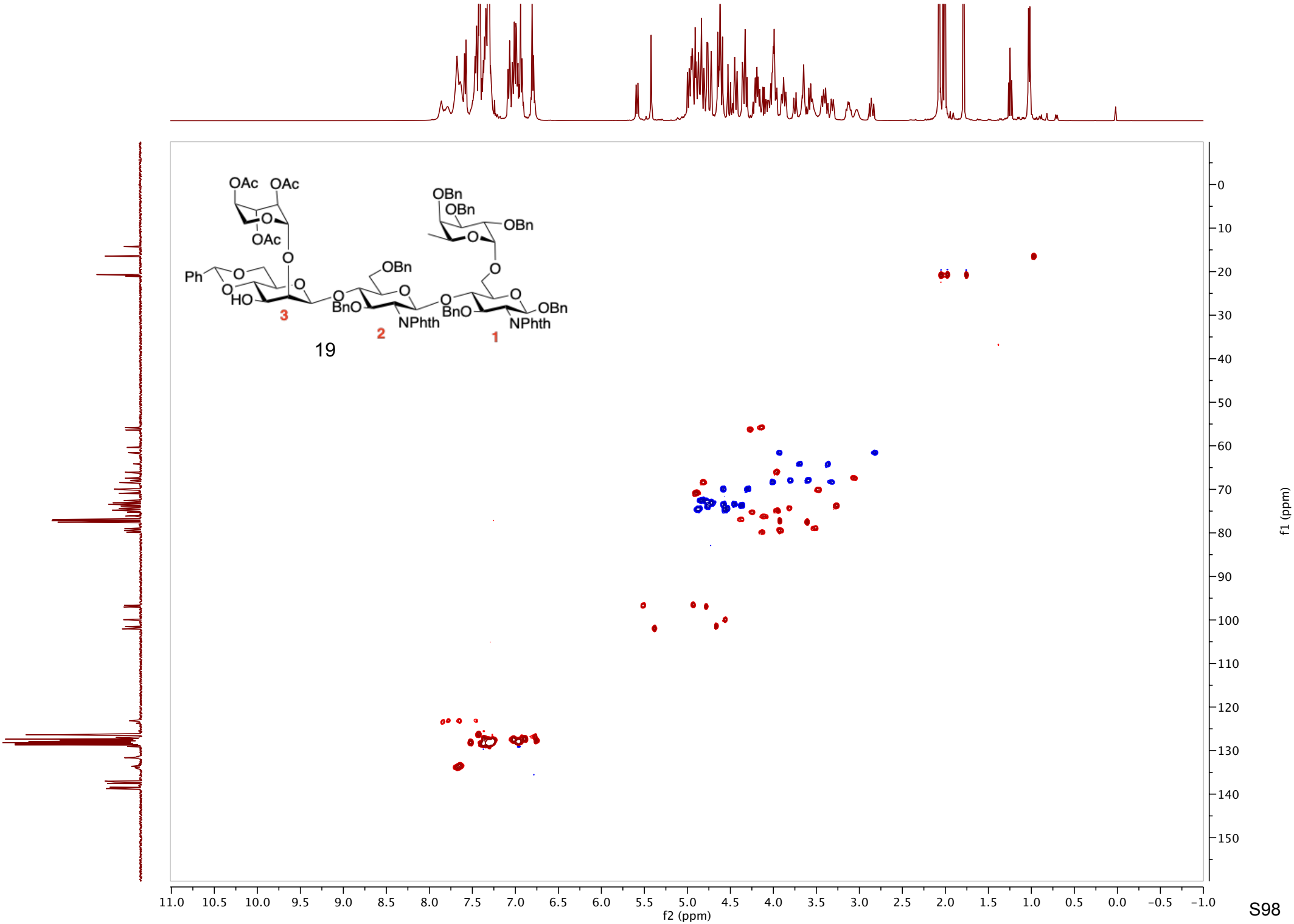

OAc
OAc
OAc
Ph
NapO
OBn
BnO
NPhth
OBn
OBn
OBn
BnO
NPhth
OBn
3
2
1
18
f2 (ppm)
f1 (ppm)

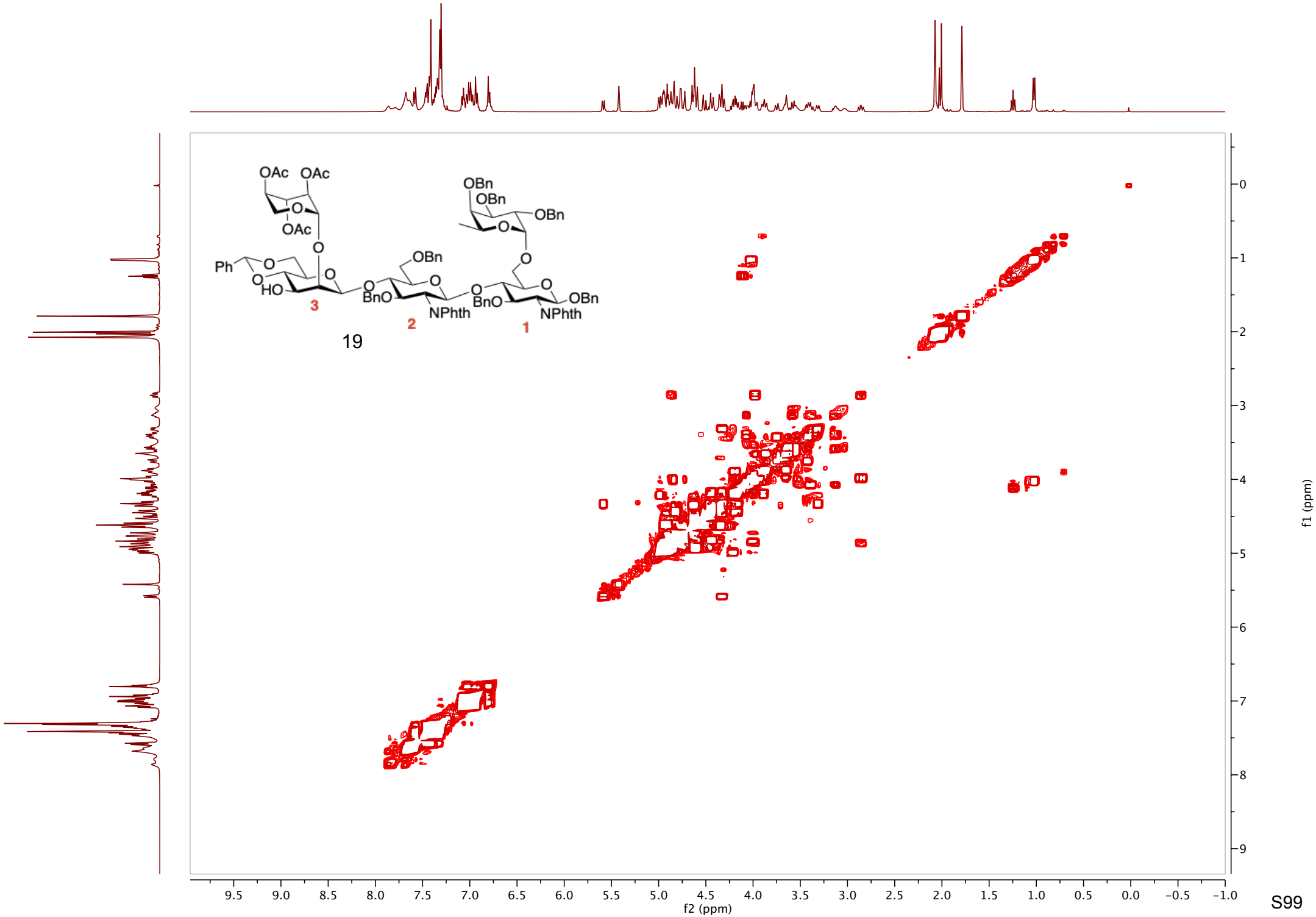

OAc
OAc
OAc
O
Ph
O
O
NapO
3
O
OBn
O
BnO
NPhth
2
O
OBn
OBn
OBn
O
O
BnO
OBn
NPhth
1

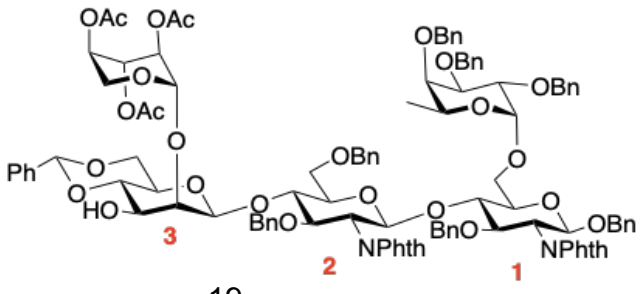
18

40
35
30
25
20
15
10
5
0
−5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OAc
OAc
OAc
O
Ph
O
O
HO
3
O
O
BnO
OBn
O
NPhth
2
O
OBn
OBn
OBn
O
O
BnO
OBn
NPhth
1
19
49.84
0.99
1.11
9.89
4.12
5.59
3.36
3.56
3.34
6.01
2.18
1.08
4.28
3.39
1.19
0.90
1.00
3.86
2.90
2.83
3.31
f1 (ppm)

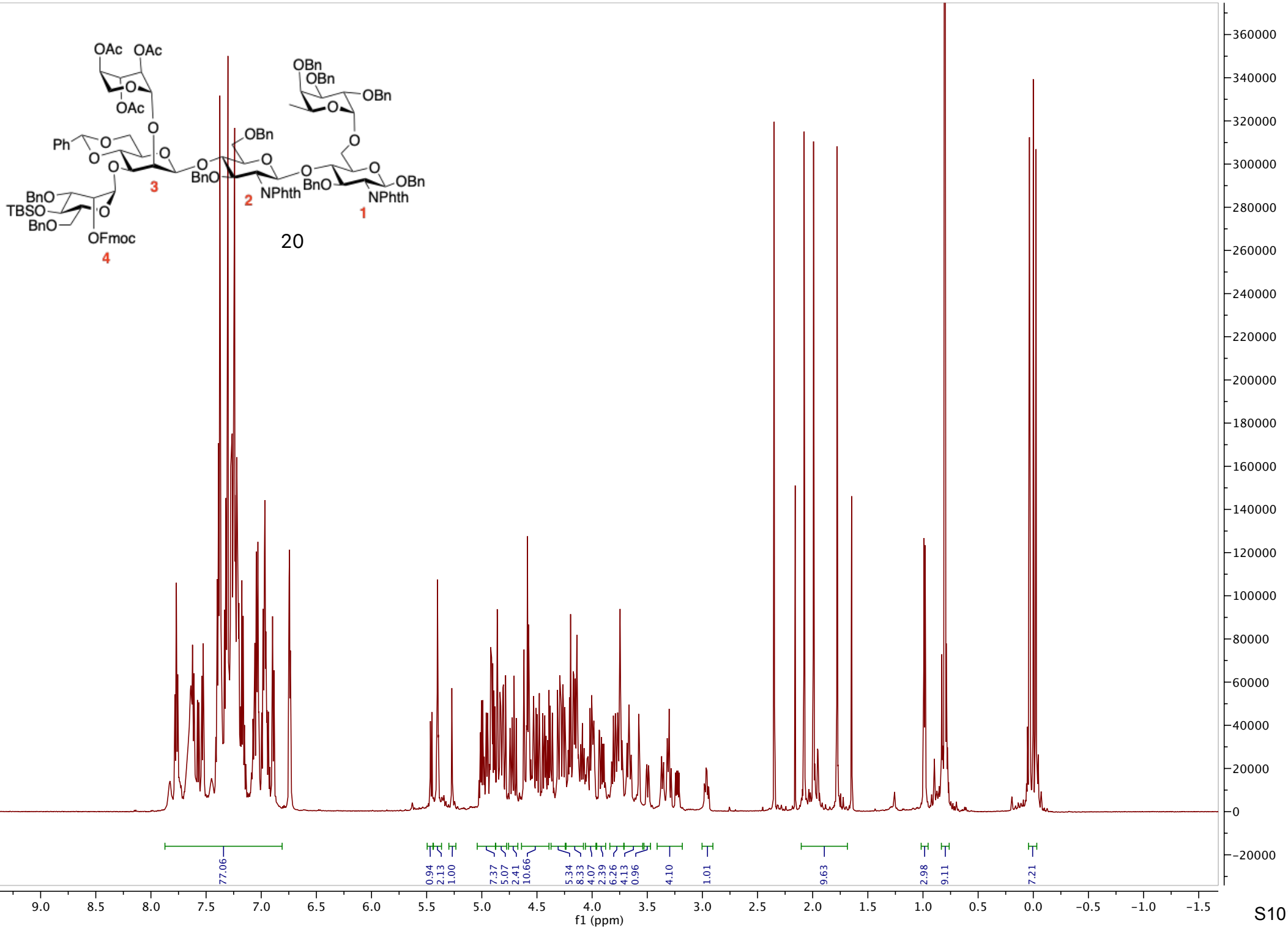

OAc
OAc
OAc
O
Ph
O
O
HO
3
O
BnO
OBn
O
NPhth
2
O
BnO
OBn
OBn
OBn
O
O
OBn
NPhth
1
19
f2 (ppm)
f1 (ppm)

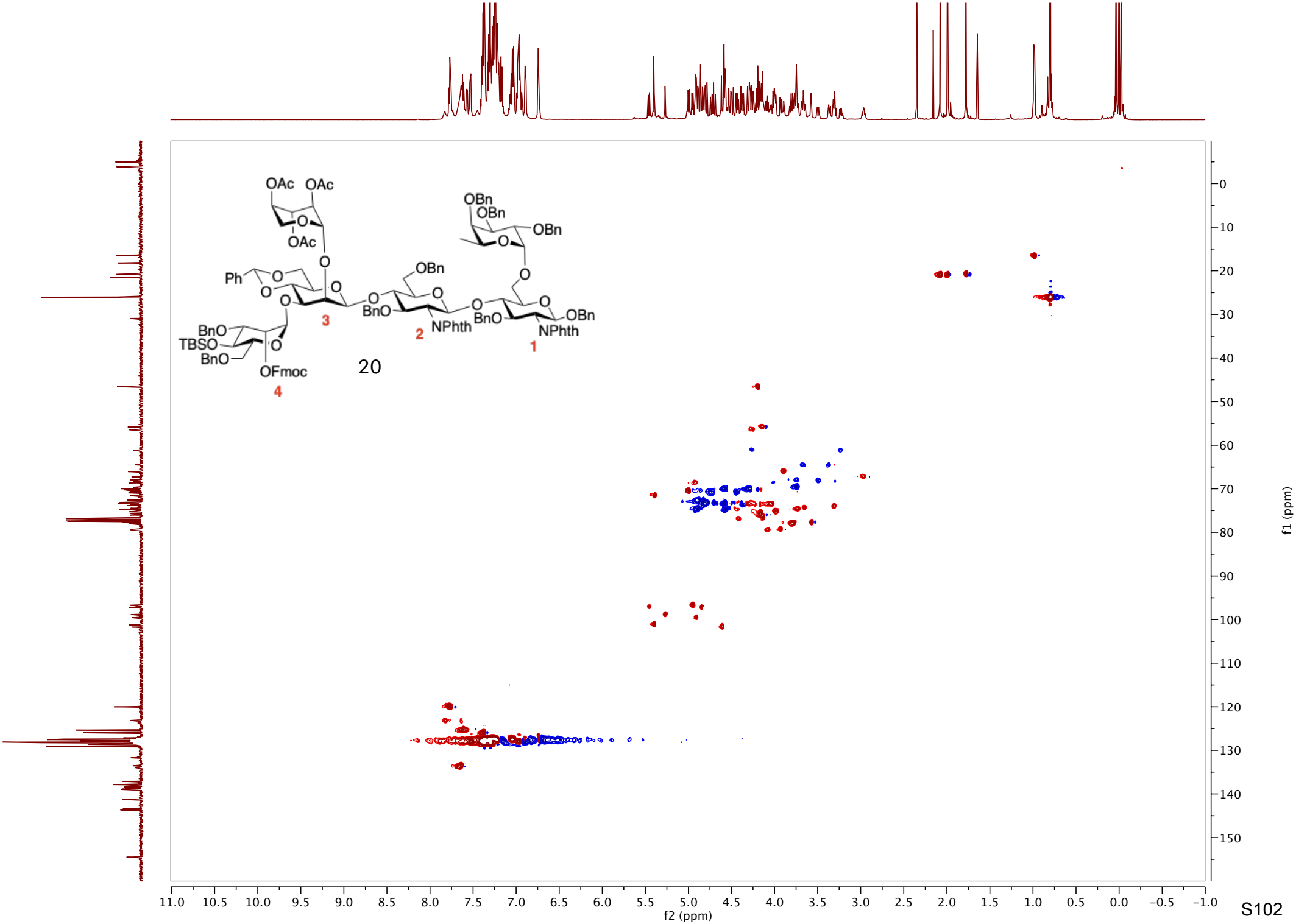

OAc
OAc
OAc
O
Ph
O
O
HO
3
OBn
O
BnO
2
NPhth
OBn
OBn
OBn
O
O
BnO
1
NPhth
OBn
19
f2 (ppm)
f1 (ppm)

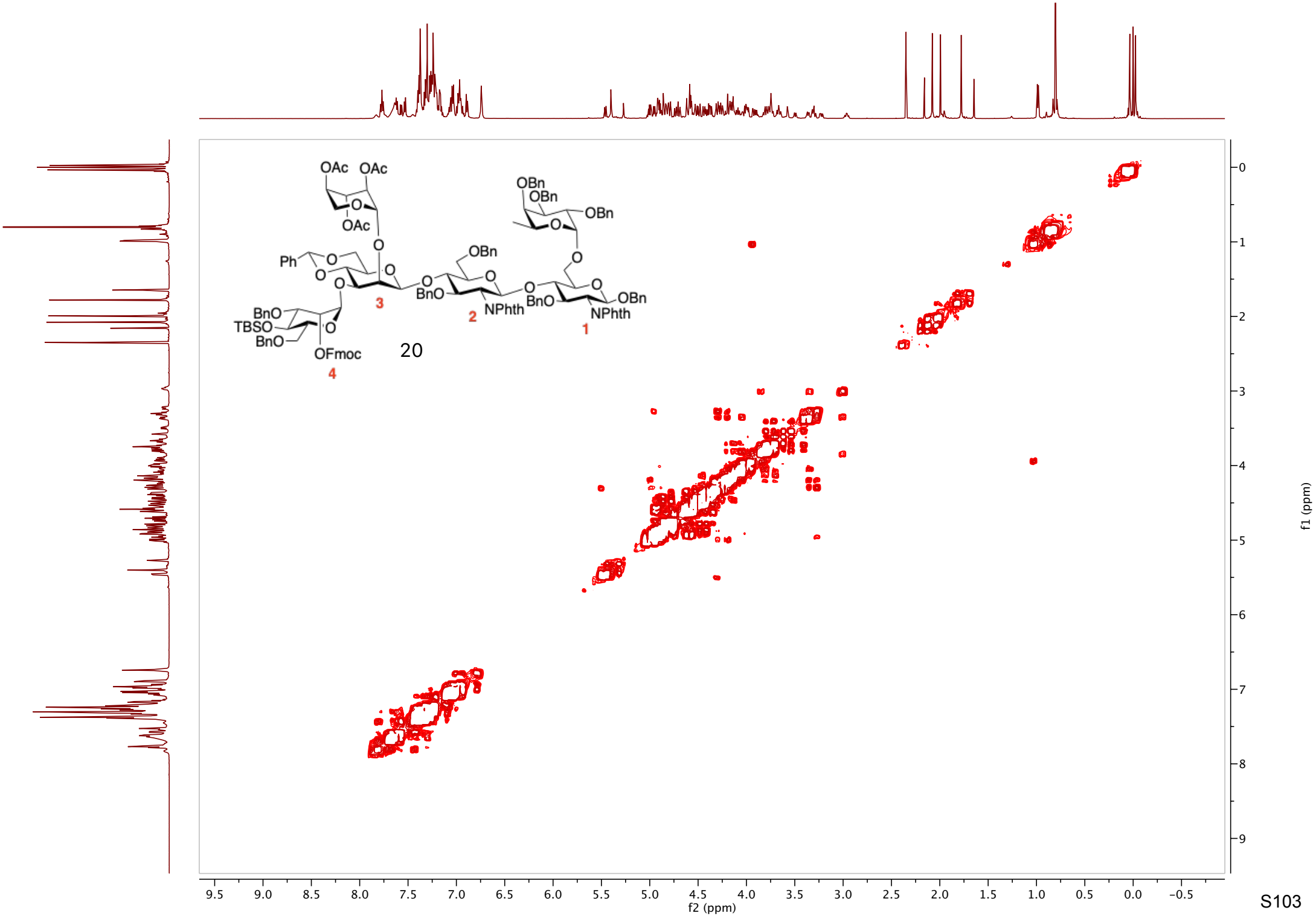

OAc
OAc
OAc
O
Ph
O
O
HO
3
O
O
BnO
OBn
O
NPhth
2
O
BnO
OBn
OBn
OBn
O
O
NPhth
1

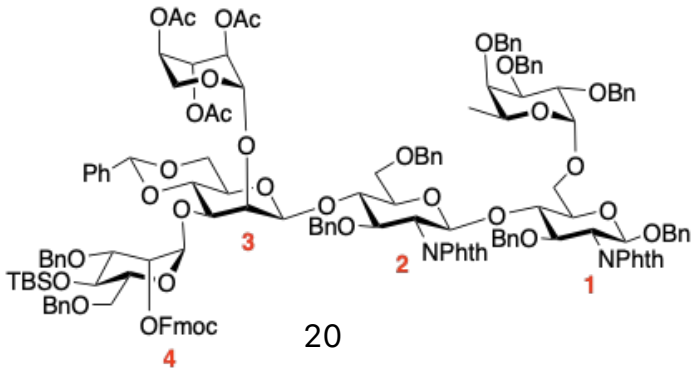
19

65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OAc
OAc
OAc
O
Ph
O
O
O
3
BnO
TBSO
BnO
O
OFmoc
4
OBn
OBn
OBn
O
BnO
O
O
2
NPhth
BnO
O
O
1
NPhth
OBn
20
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
77.06
0.94
2.13
1.00
7.37
5.07
2.41
10.66
5.34
8.33
4.07
2.39
6.26
4.13
0.96
4.10
1.01
9.63
2.98
9.11
7.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

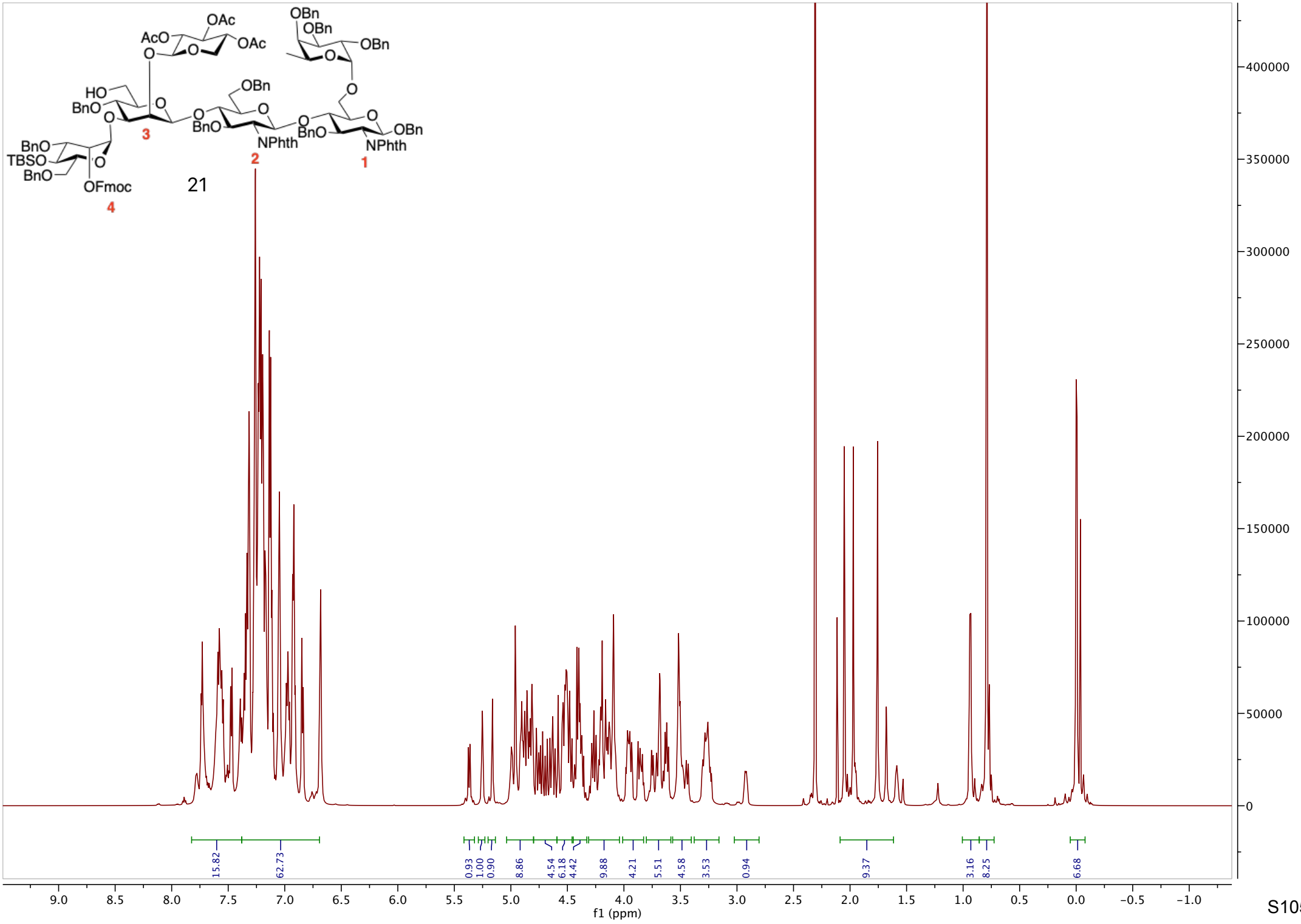

OAc
OAc
OAc
O
Ph
O
O
O
3
BnO
TBSO
BnO
OFmoc
4
OBn
O
BnO
NPhth
2
OBn
OBn
OBn
O
BnO
NPhth
1
20
f2 (ppm)
f1 (ppm)

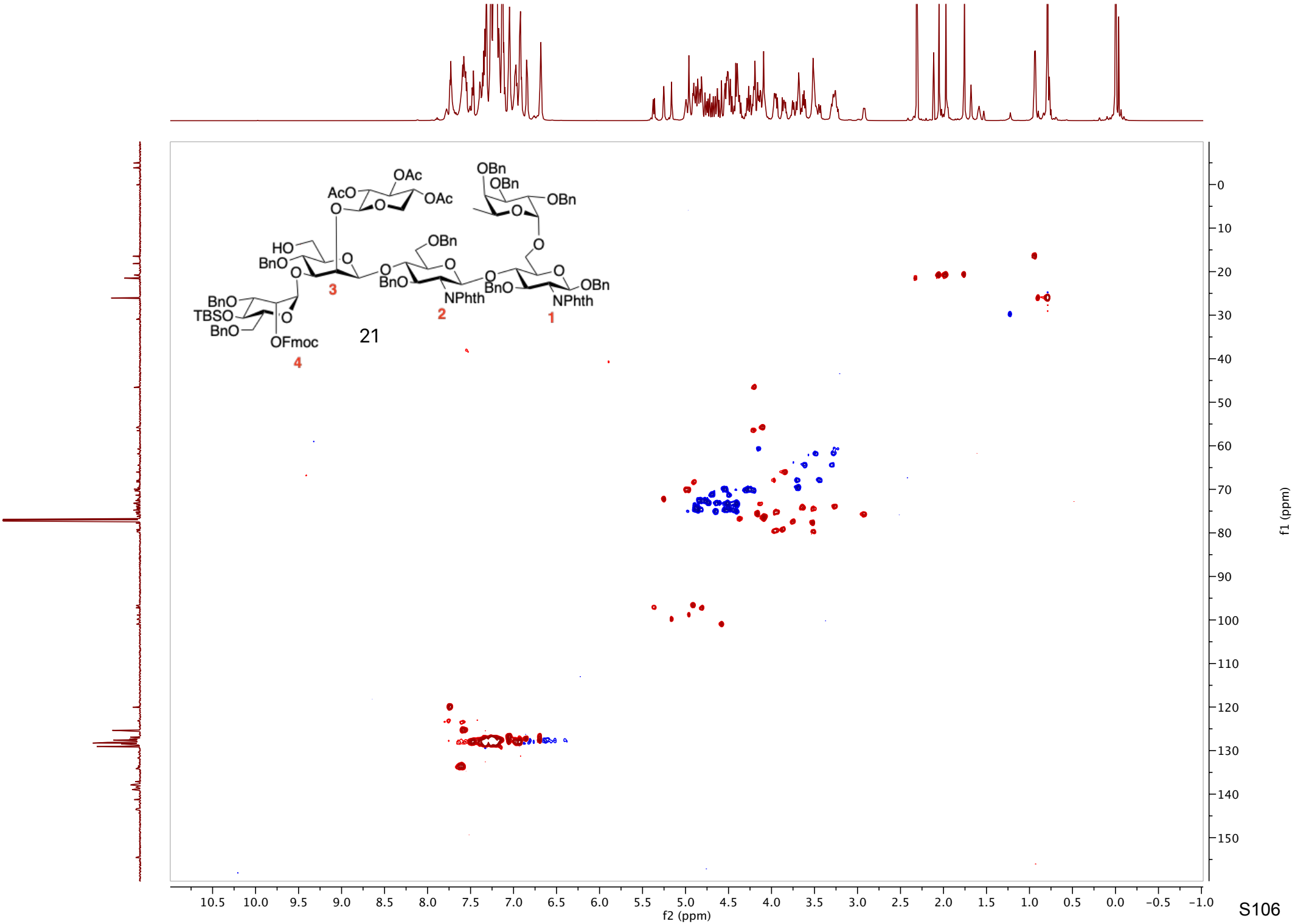

OAc
OAc
OAc
O
Ph
O
O
O
3
BnO
TBSO
BnO
O
OFmoc
4
O
BnO
O
2
NPhth
OBn
OBn
OBn
O
O
BnO
O
1
NPhth
OBn
20
f2 (ppm)
f1 (ppm)

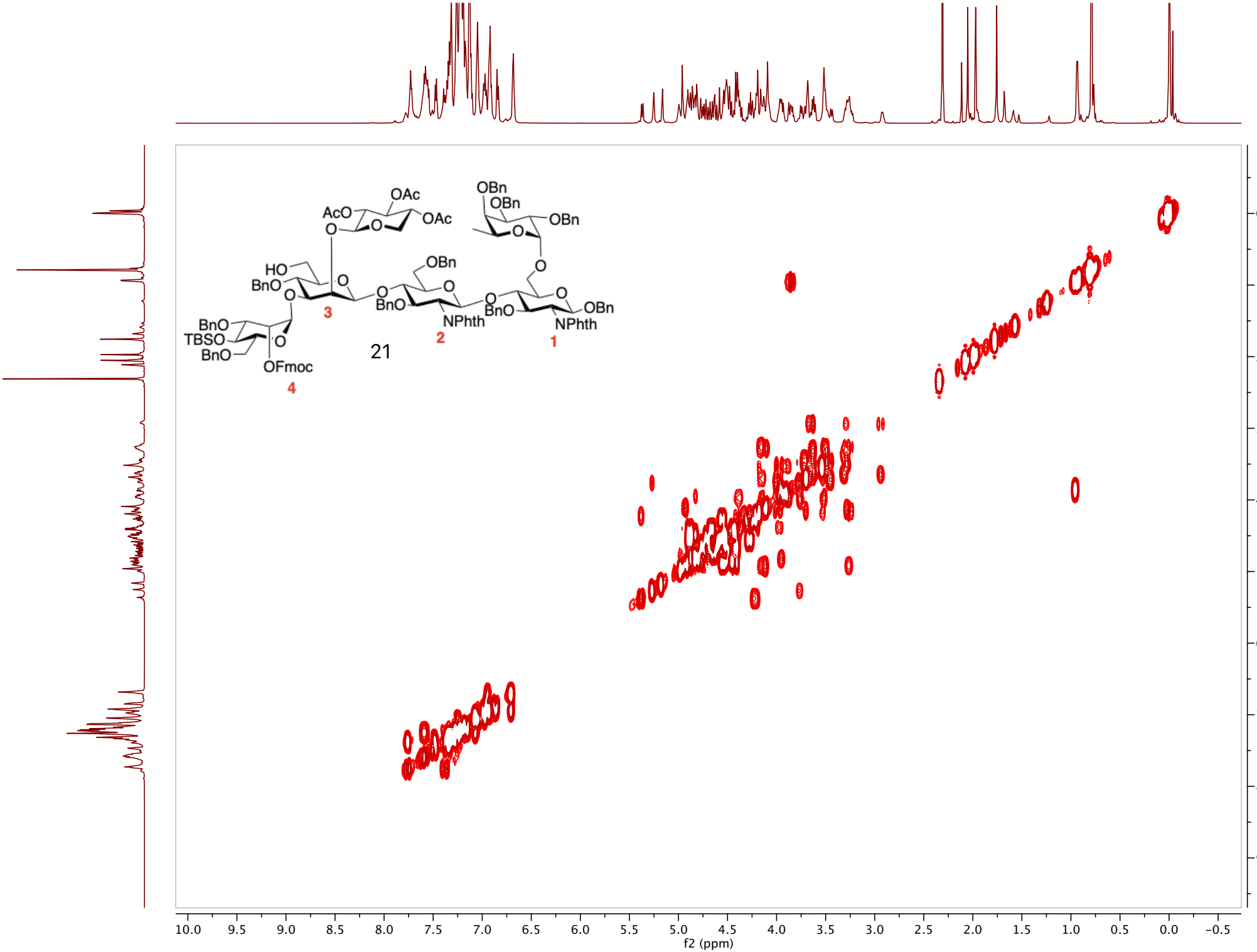

OAc
OAc
OAc
O
Ph
O
O
O
3
BnO
TBSO
BnO
OFmoc
4
O
BnO
OBn
O
NPhth
2
OBn
OBn
OBn
O
O
BnO
O
NPhth
1
OBn

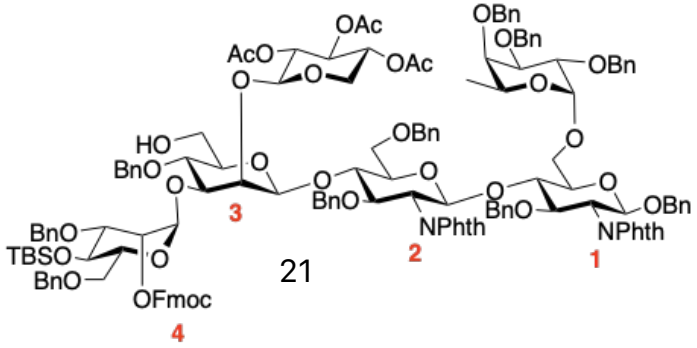
20

25
20
15
10
5
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


OAc
AcO
OAc
OBn
OBn
OBn
HO
BnO
OBn
BnO
BnO
NPhth
BnO
OBn
NPhth
BnO
TBSO
BnO
OFmoc
3
2
1
4
21
400000
350000
300000
250000
200000
150000
100000
50000
0
15.82
62.73
0.93
1.00
0.90
8.86
4.54
6.18
4.42
9.88
4.21
5.51
4.58
3.53
0.94
9.37
3.16
8.25
6.68
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


OAc
AcO
OAc
OBn
OBn
OBn
HO
BnO
OBn
BnO
BnO
NPhth
BnO
OBn
NPhth
BnO
TBSO
BnO
OFmoc
3
2
1
4
21
f2 (ppm)
f1 (ppm)


OAc
AcO
OAc
OBn
OBn
OBn
HO
BnO
OBn
BnO
BnO
NPhth
BnO
NPhth
OBn
BnO
TBSO
BnO
OFmoc
3
2
1
4
21
f2 (ppm)
f1 (ppm)

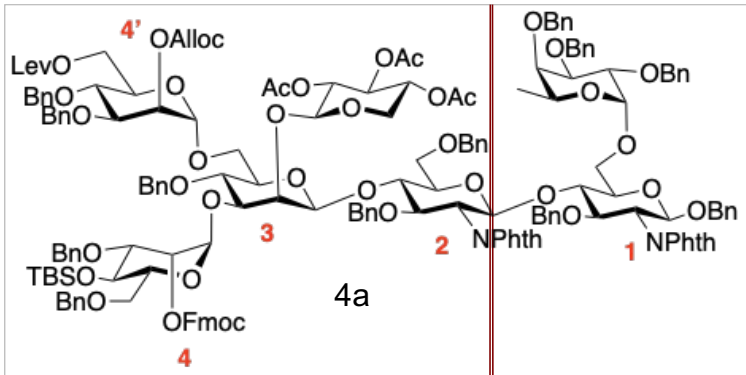


21

650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000

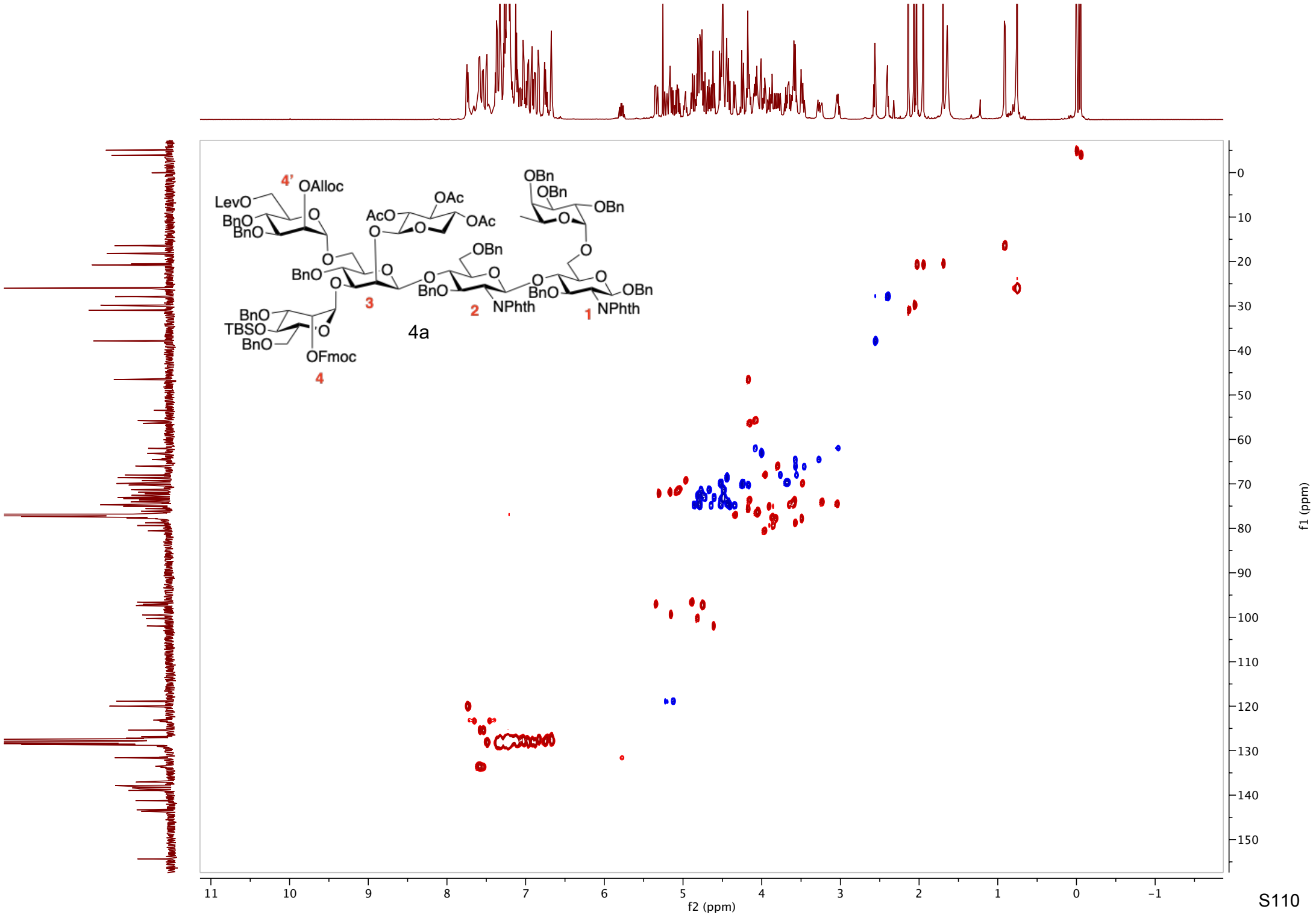
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10

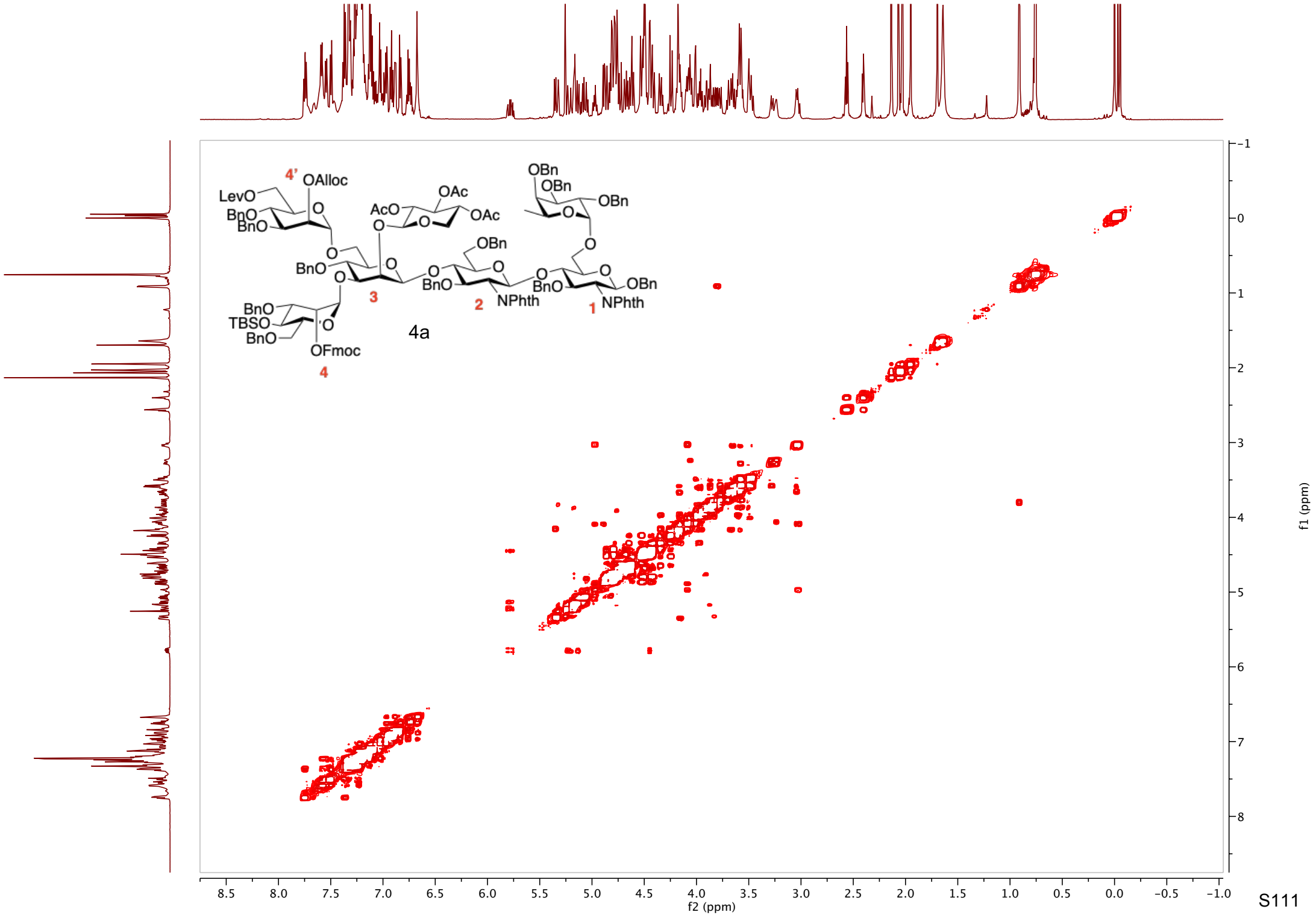
f1 (ppm)

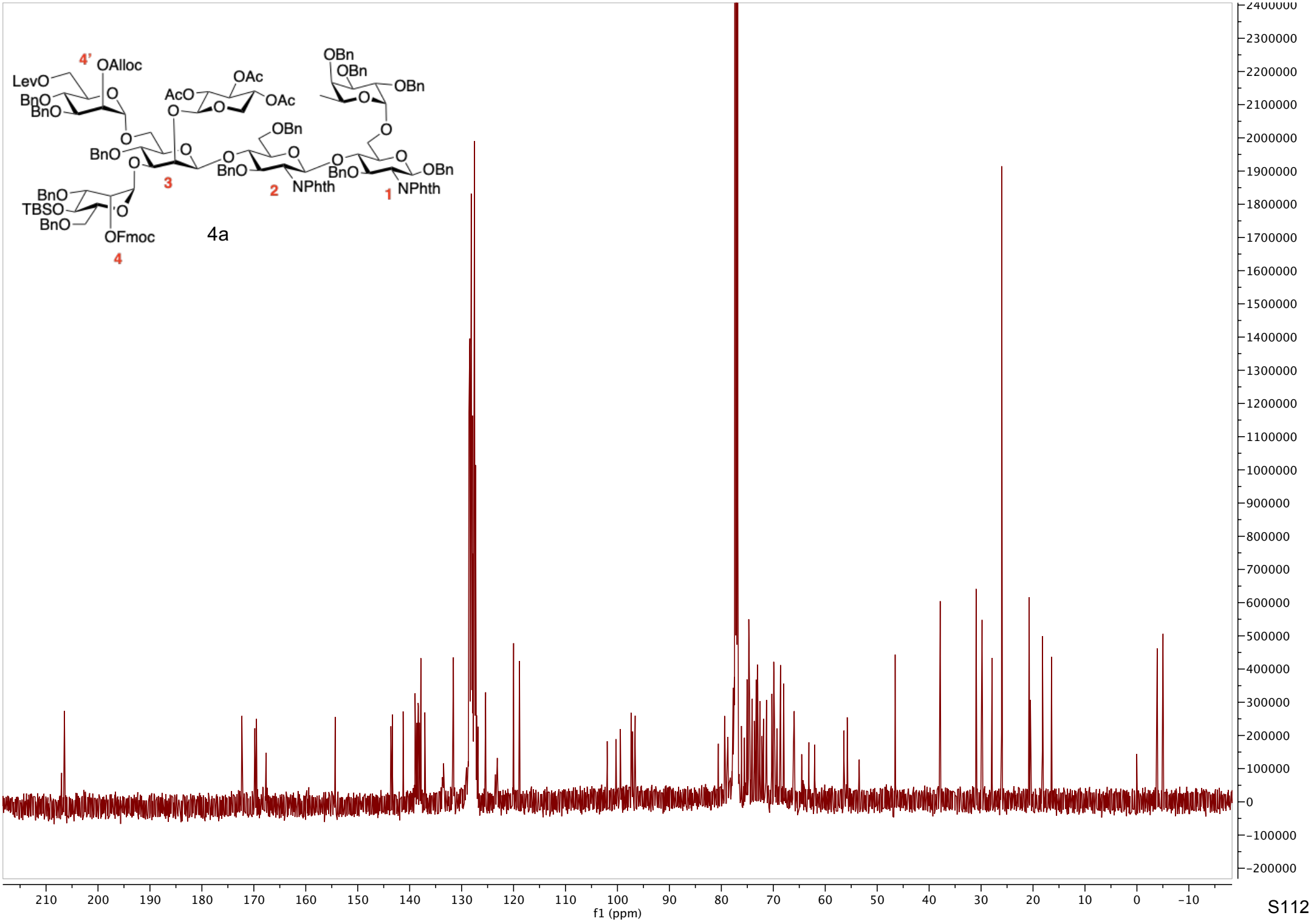

4'
OAlloc
LevO
BnO
BnO
O
AcO
OAc
OAc
O
OBn
OBn
OBn
O
BnO
O
O
O
OBn
BnO
O
O
BnO
O
O
OBn
3
2
NPhth
1
NPhth
BnO
TBSO
BnO
O
OFmoc
4

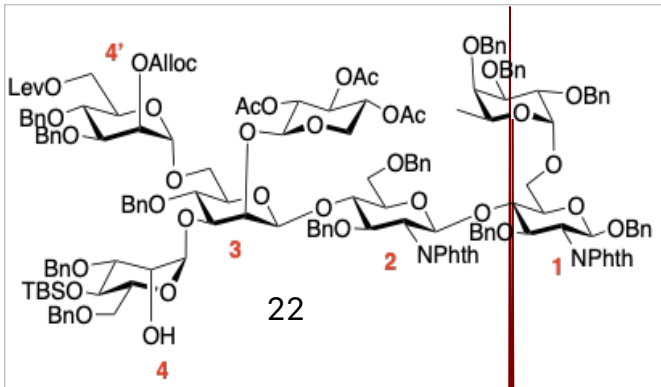
4a

1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
84.48
0.99
2.08
5.02
2.05
1.26
2.34
10.38
4.64
14.30
2.25
7.91
8.68
6.85
3.33
5.97
3.09
2.19
1.95
2.24
1.99
3.27
6.55
3.18
3.17
9.29
7.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


4'
OAlloc
LevO
BnO
BnO
AcO
OAc
OAc
OBn
OBn
OBn
BnO
3
BnO
2
NPhth
BnO
1
NPhth
OBn
BnO
TBSO
BnO
OFmoc
4
4a
f2 (ppm)
f1 (ppm)

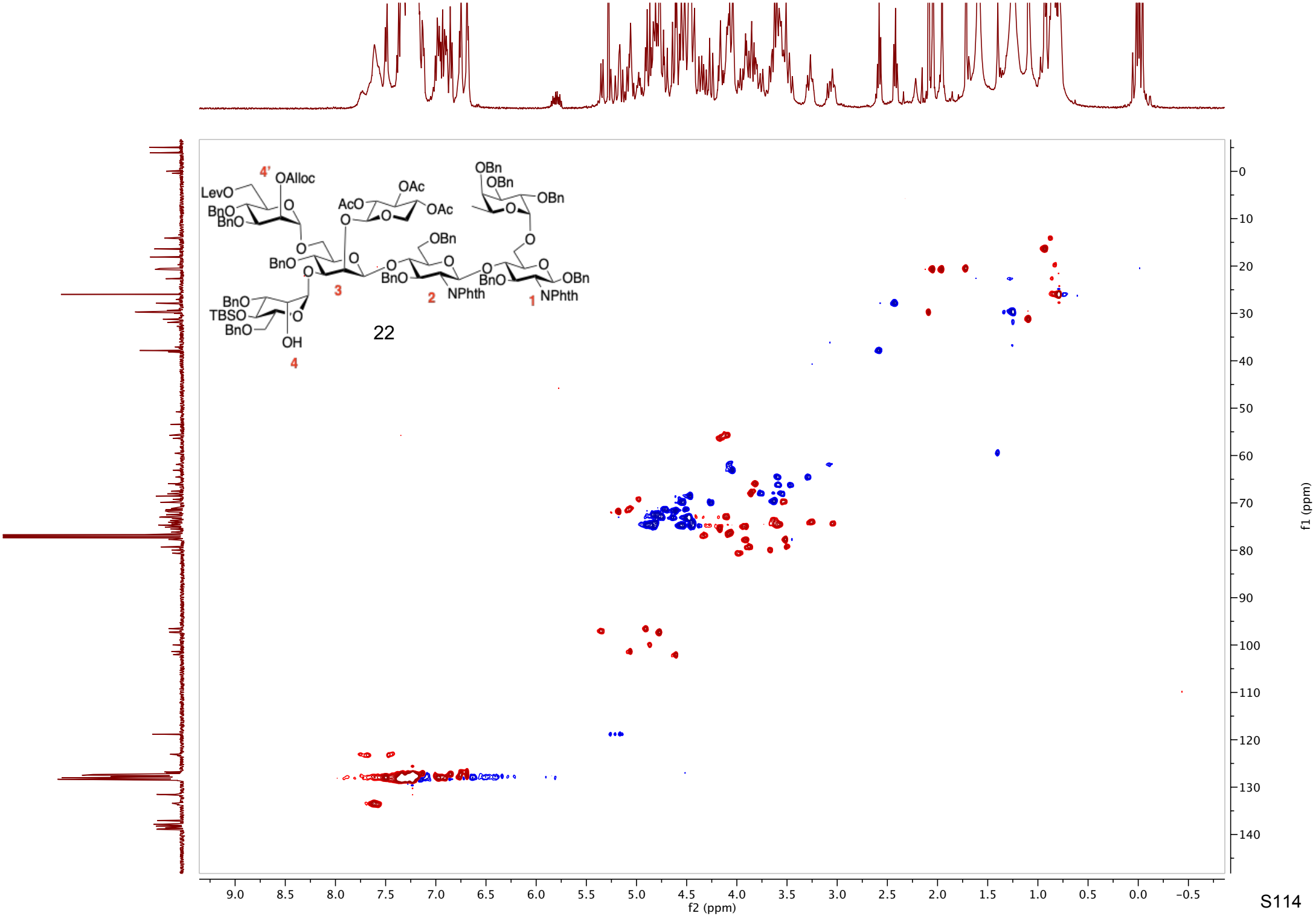

4' OAlloc
LevO
BnO
BnO
AcO
OAc
OAc
OBn
OBn
OBn
BnO
BnO
BnO
OBn
BnO
TBSO
BnO
OFmoc
NPhth
NPhth
1
2
3
4
4a
f2 (ppm)
f1 (ppm)

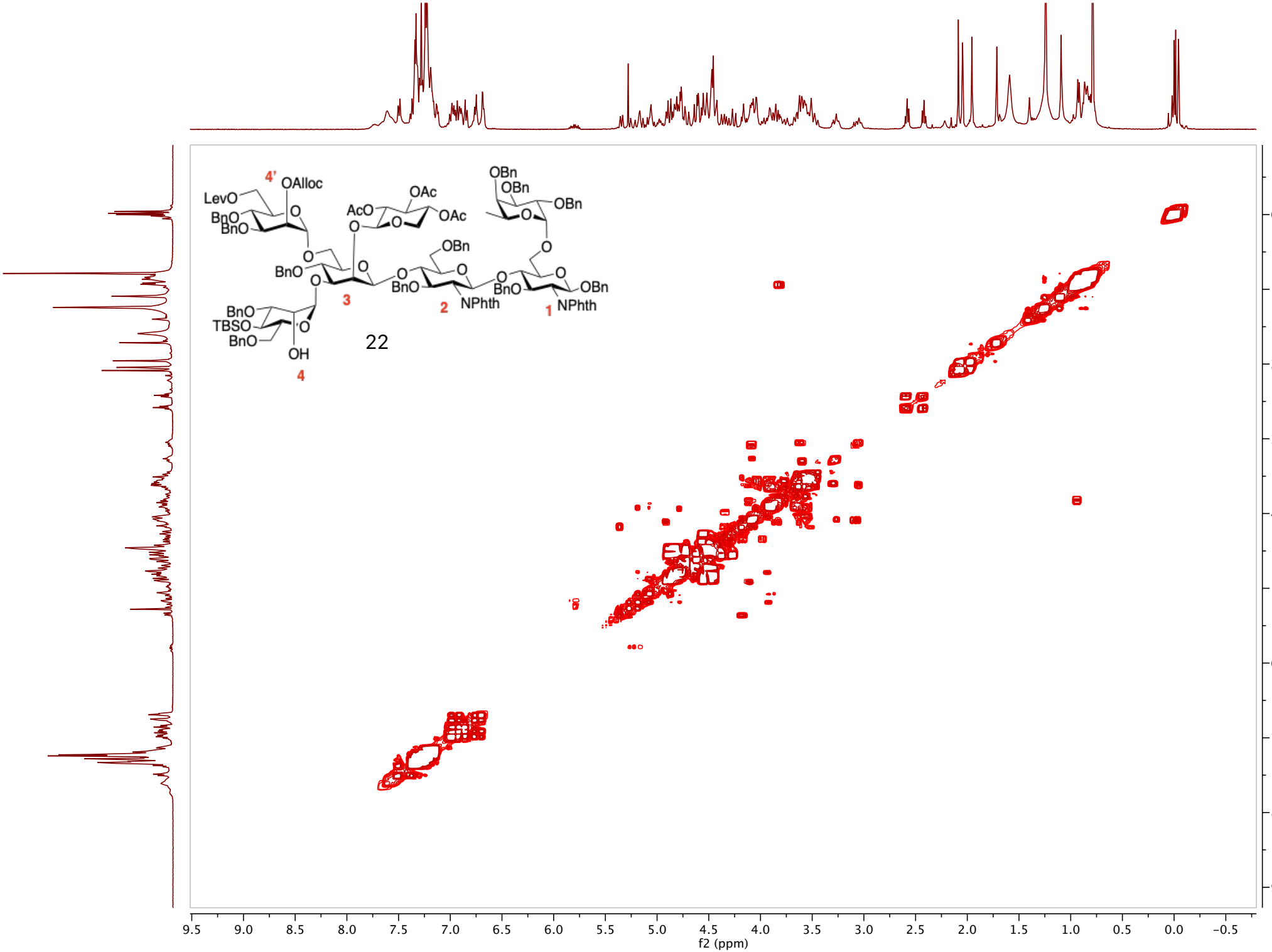

4' OAlloc
LevO
BnO
BnO
AcO
OAc
OAc
OBn
OBn
OBn
BnO
BnO
BnO
NPhth
NPhth
OBn
BnO
TBSO
BnO
OFmoc
1
2
3
4
4a
f1 (ppm)

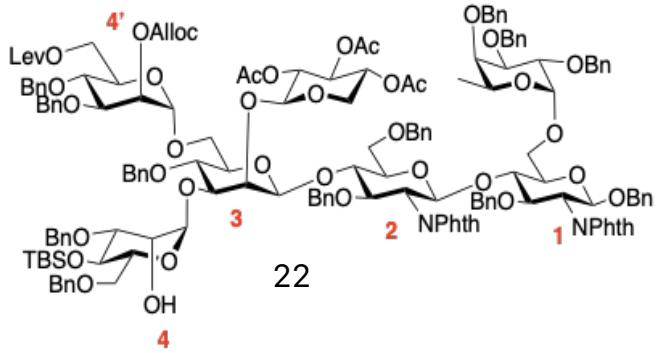

4'
OAlloc
LevO
BnO
BnO
OAc
AcO
OAc
OBn
OBn
OBn
BnO
BnO
OBn
BnO
BnO
OBn
BnO
TBSO
BnO
OH
4
3
2
NPhth
1
NPhth

22

65.38
1.56
1.00
10.74
11.26
2.61
15.89
3.27
8.84
9.15
12.34
2.78
2.40
2.33
1.98
3.50
6.71
2.97
3.71
8.57
6.15
f1 (ppm)

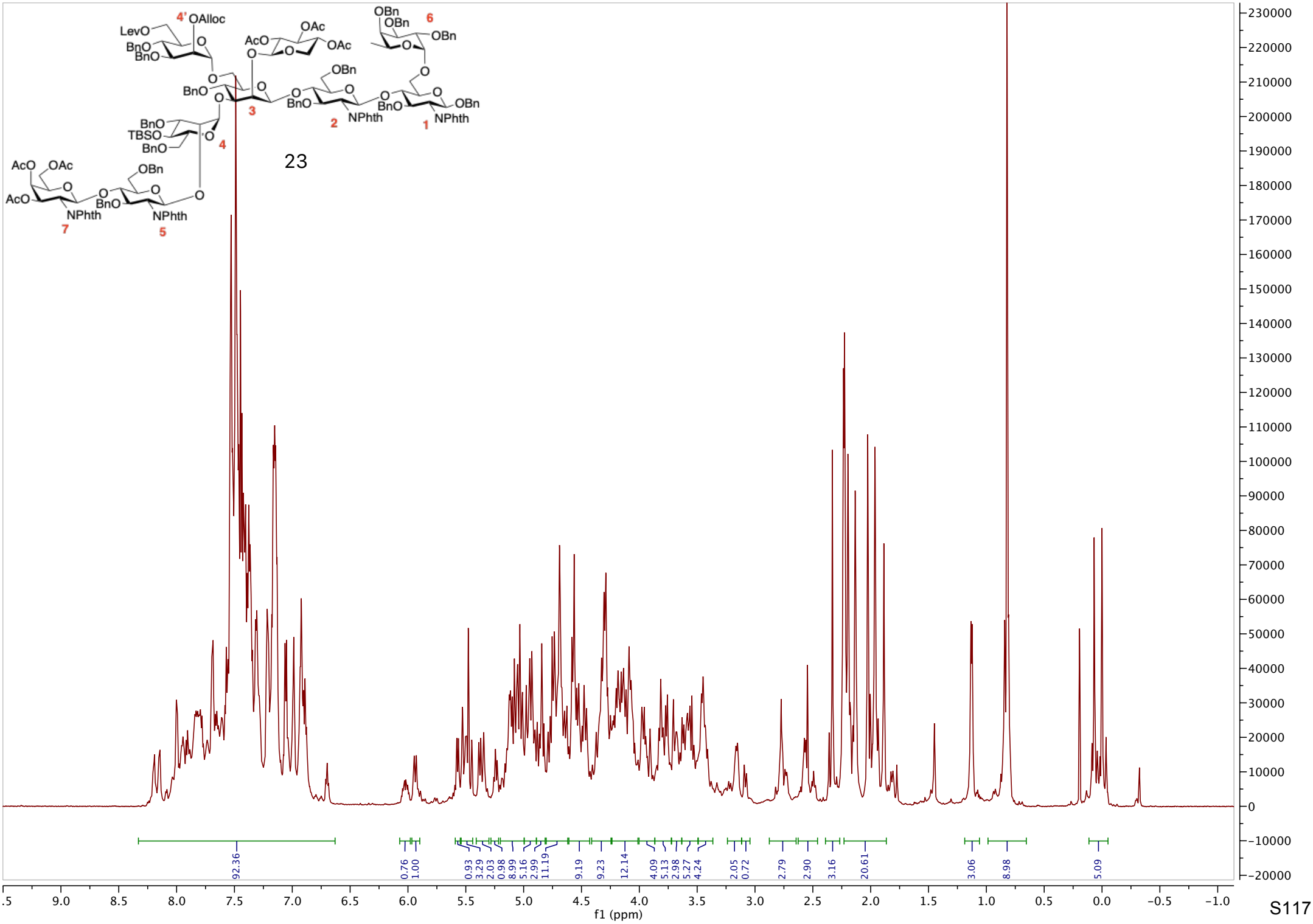

4'
OAlloc
LevO
BnO
BnO
O
OAc
AcO
OAc
O
OBn
OBn
OBn
O
BnO
O
O
BnO
O
OBn
3
2
NPhth
BnO
O
1
NPhth
BnO
TBSO
BnO
OH
4
22
f2 (ppm)
f1 (ppm)

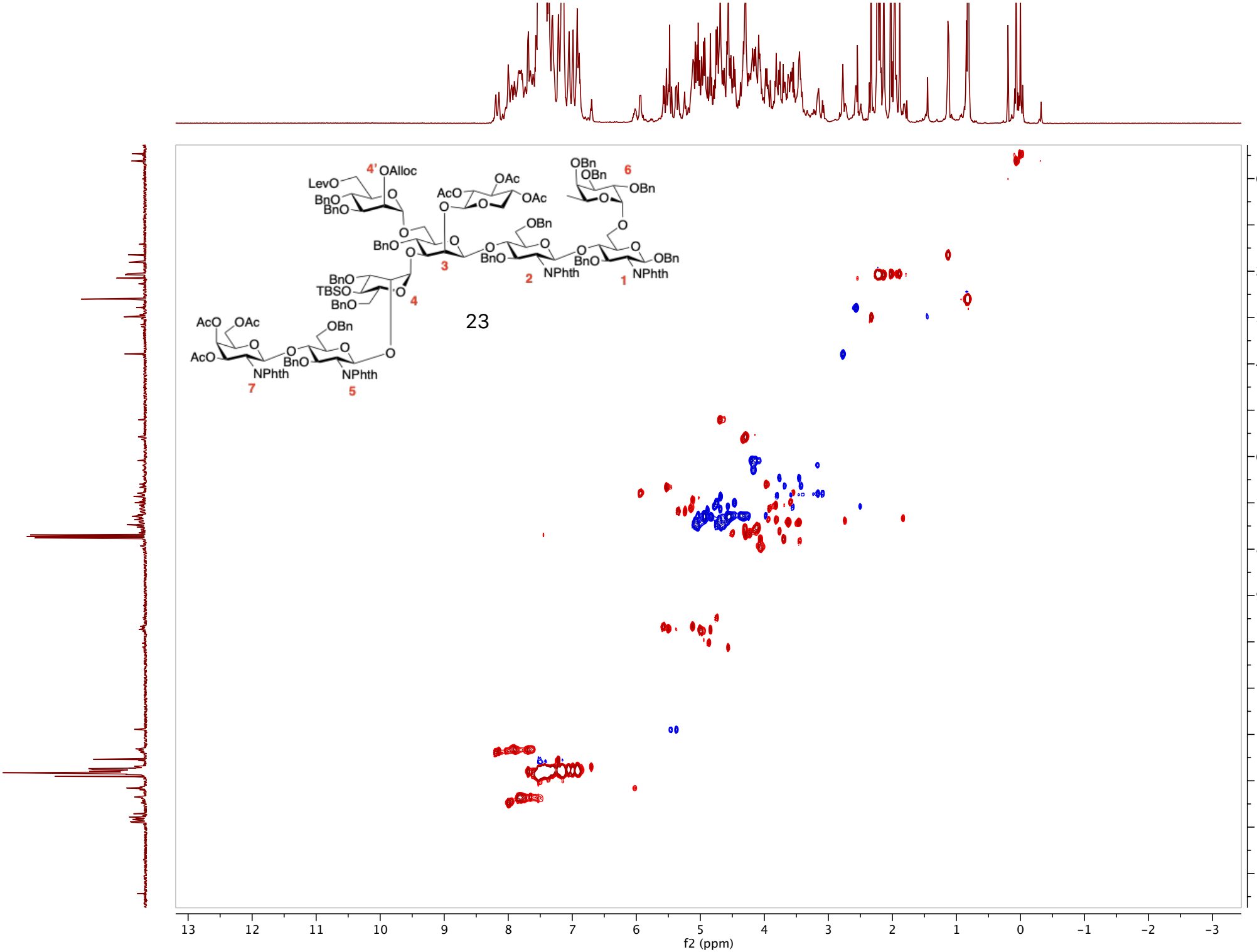

4'
OAlloc
LevO
BnO
BnO
OAc
AcO
OAc
OBn
OBn
OBn
BnO
3
BnO
2
NPhth
BnO
1
NPhth
OBn
BnO
TBSO
BnO
OH
4
22
f2 (ppm)
f1 (ppm)

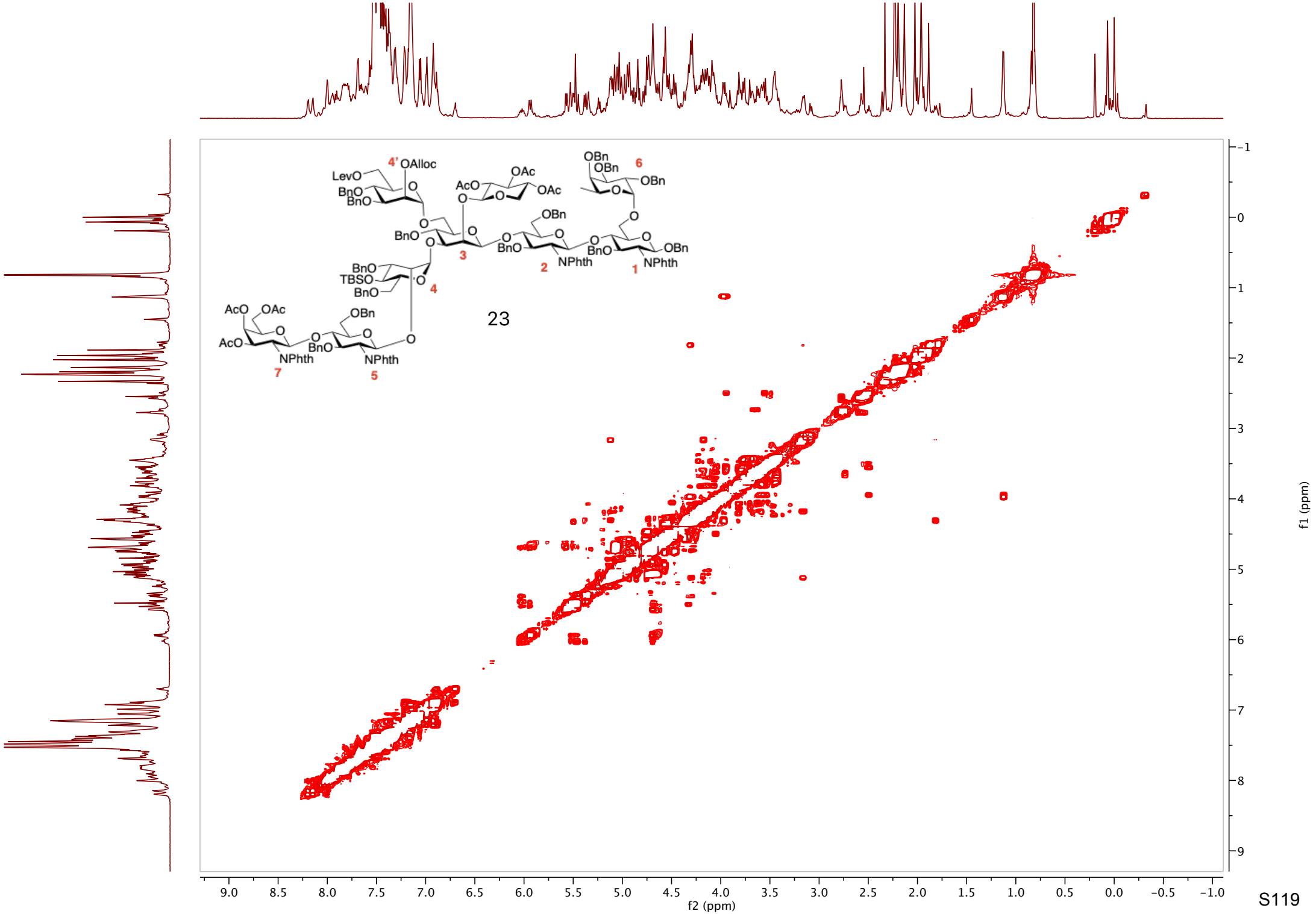

4'
OAlloc
LevO
BnO
BnO
AcO
OAc
OAc
OBn
OBn
OBn
BnO
BnO
OBn
BnO
TBSO
BnO
OH
NPhth
NPhth
1
2
3
4

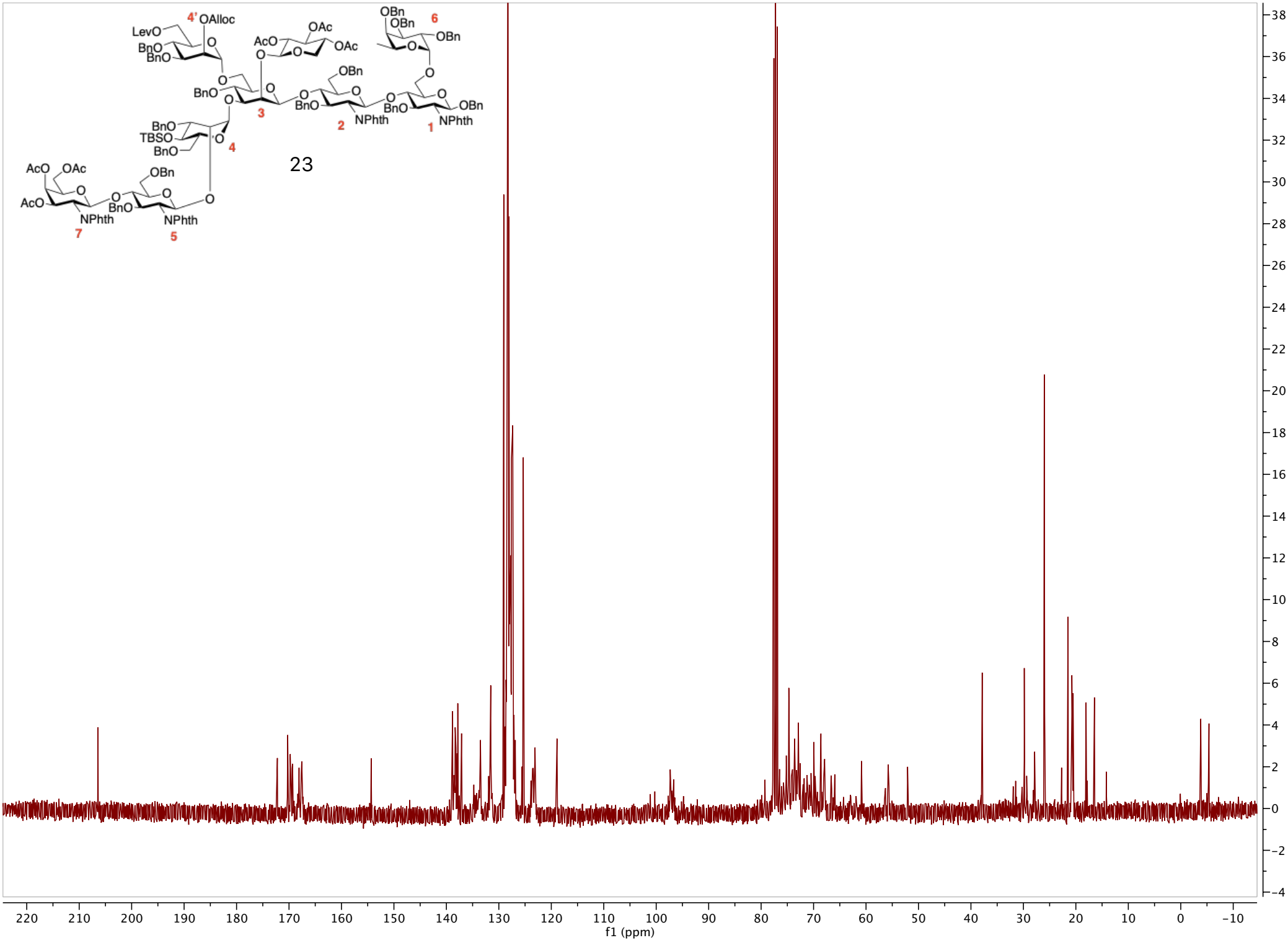
22

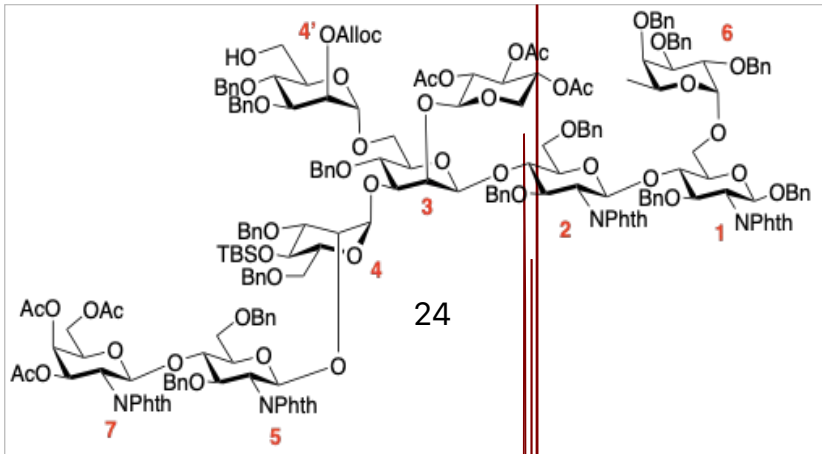
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
55 50 45 40 35 30 25 20 15 10 5 0 −5


23
f1 (ppm)


23
f2 (ppm)
f1 (ppm)

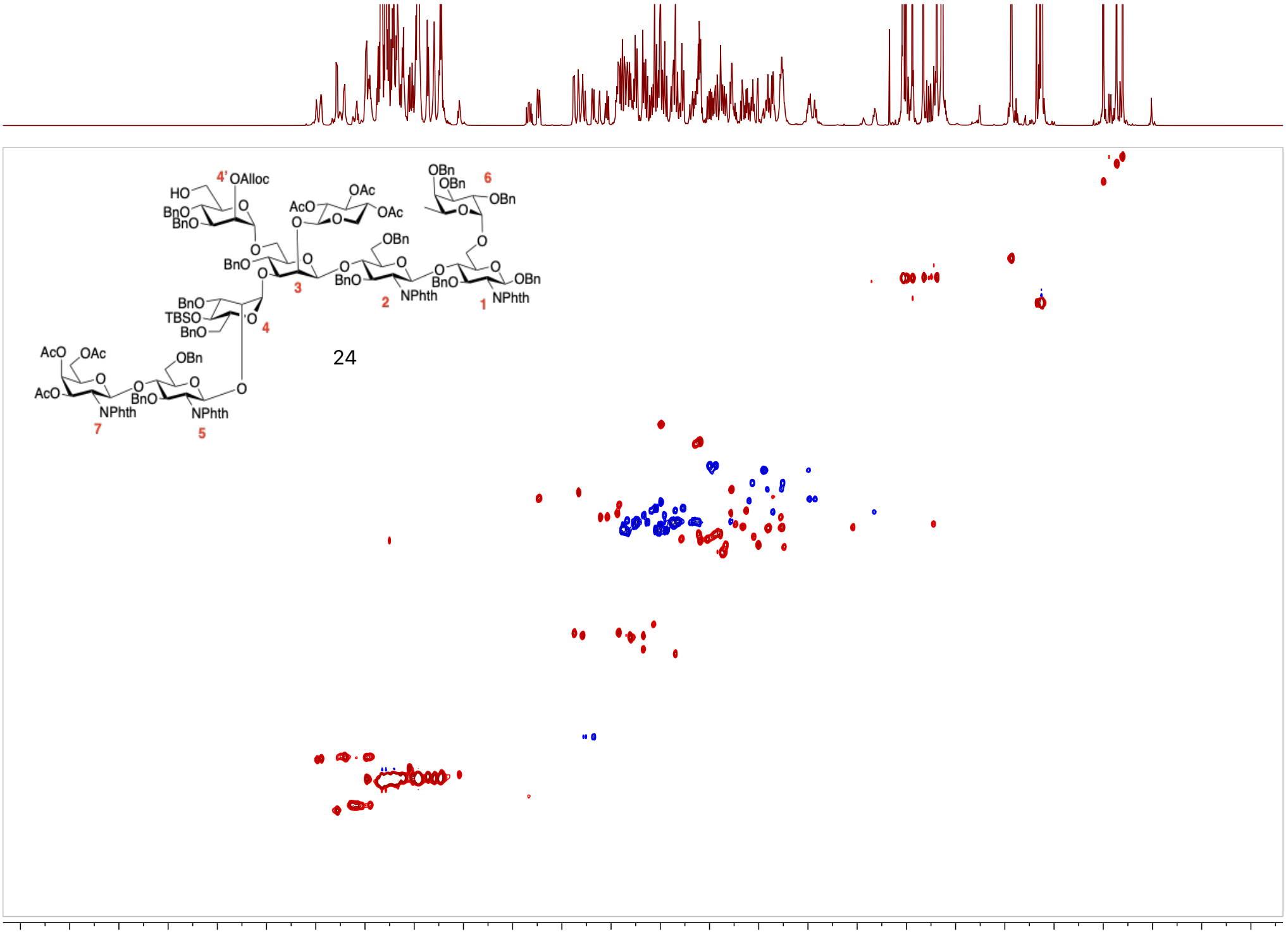

4' OAlloc
LevO
BnO
BnO
AcO
OAc
OAc
OBn
OBn
6
OBn
BnO
3
BnO
2
NPhth
BnO
1
NPhth
OBn
BnO
TBSO
BnO
4
AcO
OAc
AcO
NPhth
7
OBn
BnO
NPhth
5
23
f2 (ppm)
f1 (ppm)

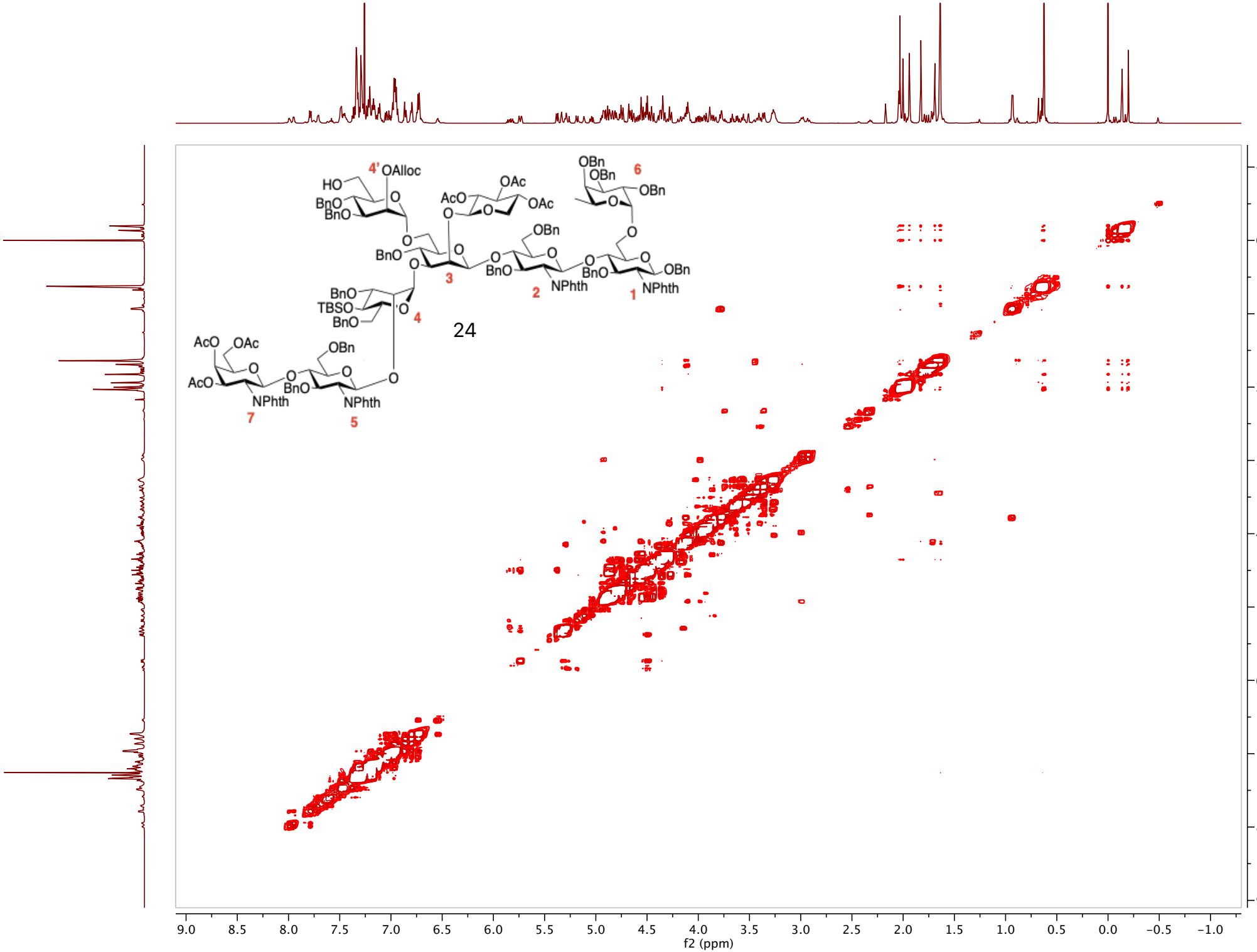

4' OAlloc
LevO
BnO
BnO
AcO
OAc
OAc
OBn
OBn
6
OBn
BnO
3
BnO
2
NPhth
BnO
1
NPhth
OBn
BnO
TBSO
BnO
4
23
AcO
OAc
AcO
OBn
BnO
NPhth
7
NPhth
5
38
36
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
−2
−4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

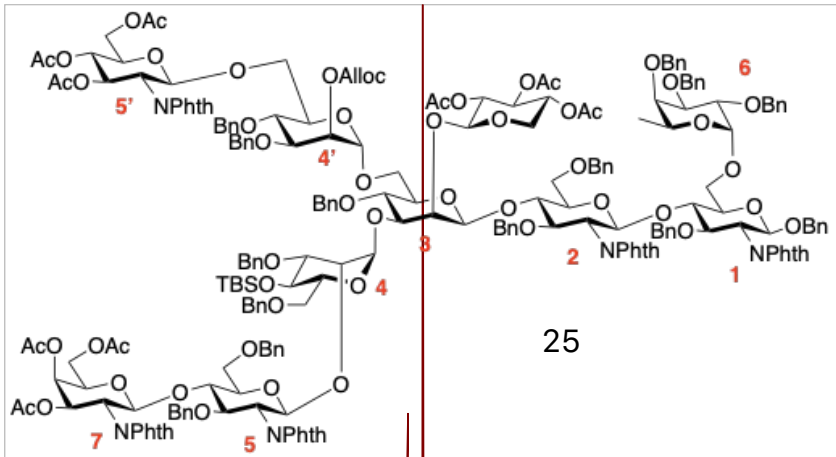

4' OAlloc
HO
BnO
BnO
O
AcO
OAc
OAc
OBn
OBn
6
OBn
BnO
3
BnO
2
NPhth
BnO
1
NPhth
BnO
TBSO
BnO
4
AcO
OAc
AcO
NPhth
7
OBn
BnO
NPhth
5

24

800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
79.93
0.86
1.00
1.01
1.13
1.91
1.01
0.84
0.98
14.15
3.85
10.24
7.25
7.10
7.62
3.15
4.86
4.97
4.80
3.16
1.09
23.78
11.49
2.98
9.32
6.58
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)

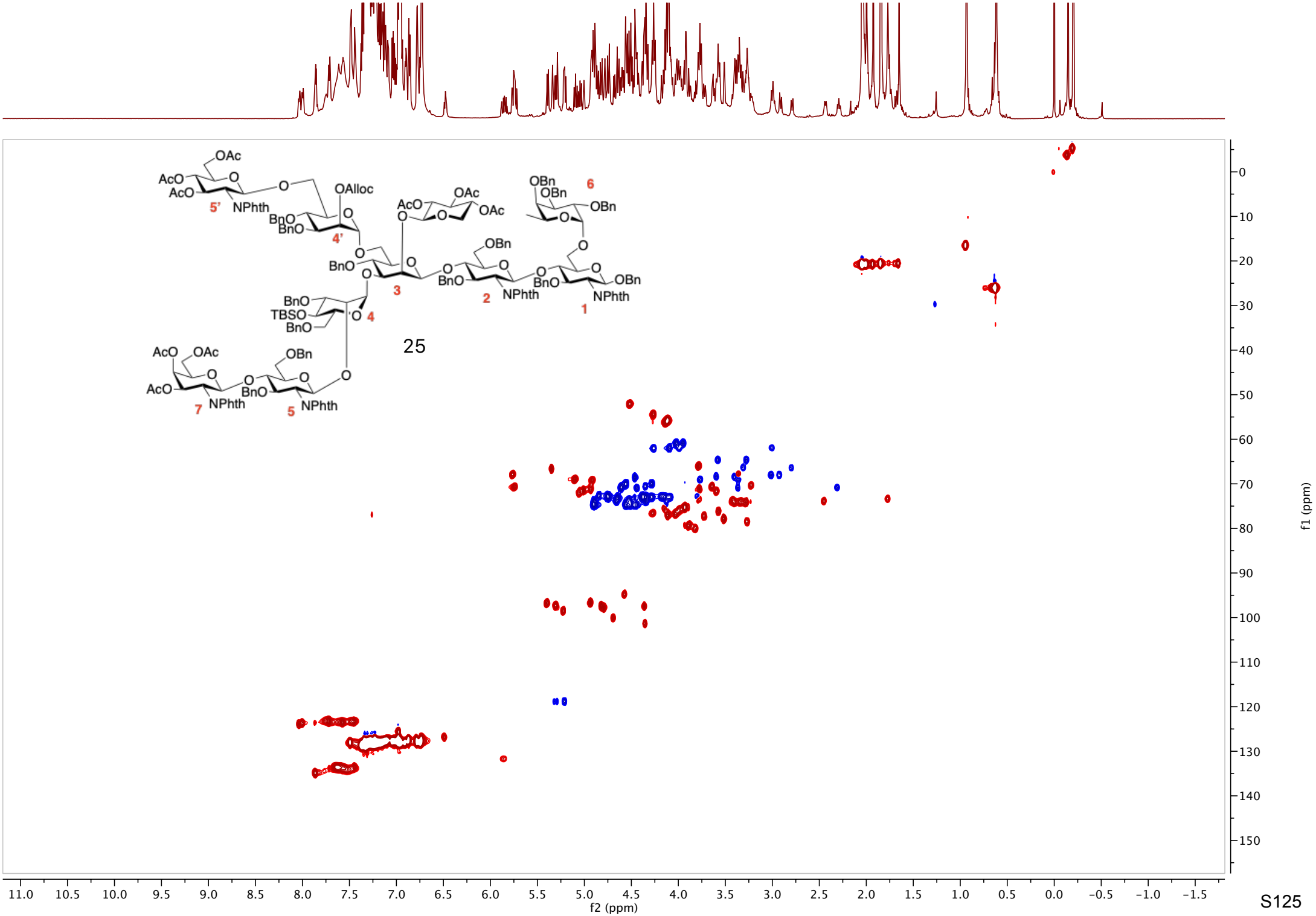

4' OAlloc
HO
BnO
BnO
AcO
OAc
OAc
OBn
OBn
6
OBn
BnO
3
BnO
2
NPhth
BnO
1
NPhth
OBn
BnO
TBSO
BnO
4
24
AcO
OAc
AcO
OBn
BnO
NPhth
NPhth
7
5
f2 (ppm)
f1 (ppm)

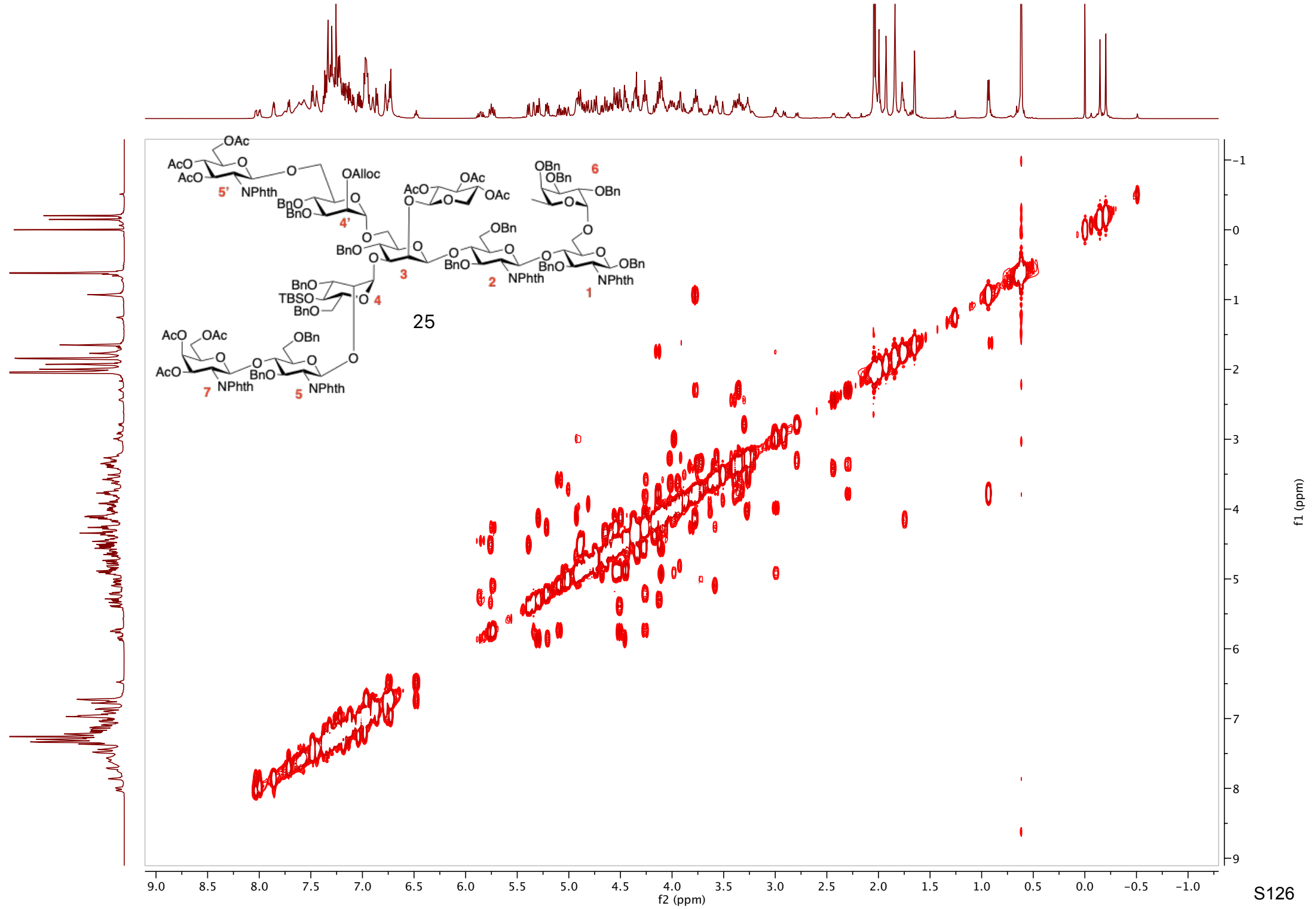

4' OAlloc
HO
BnO
BnO
AcO
OAc
OAc
O
BnO
3
OBn
BnO
2
NPhth
OBn
OBn
6
OBn
BnO
1
NPhth
BnO
TBSO
BnO
4
24
AcO
OAc
AcO
NPhth
7
OBn
BnO
NPhth
5
f2 (ppm)
f1 (ppm)

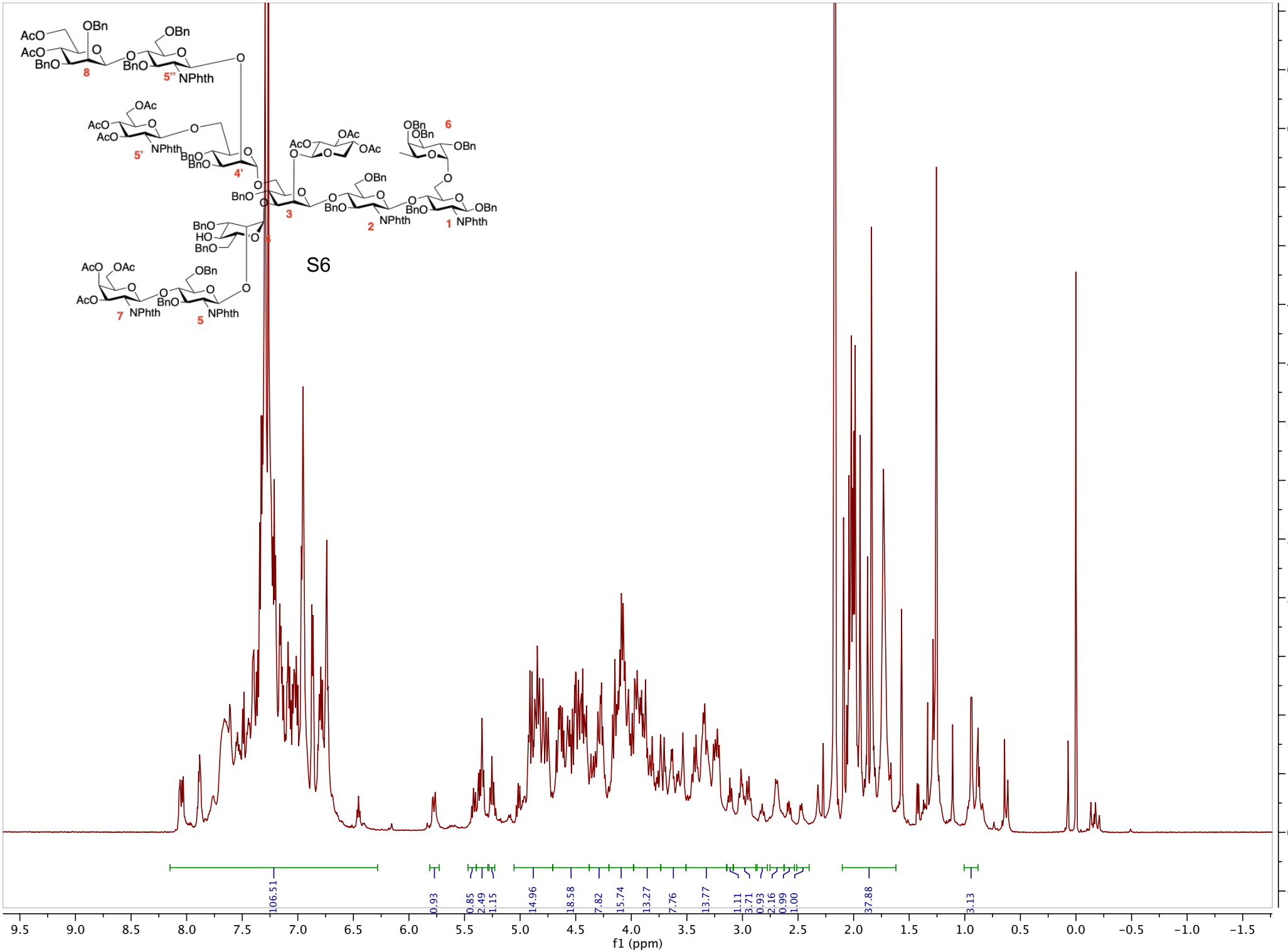

OAc
AcO
AcO
5'
NPhth
OAlloc
BnO
BnO
4'
AcO
OAc
OAc
OBn
OBn
6
OBn
BnO
3
BnO
2
NPhth
BnO
OBn
NPhth
1
BnO
TBSO
BnO
4
AcO
OAc
OBn
AcO
BnO
7
NPhth
5
NPhth

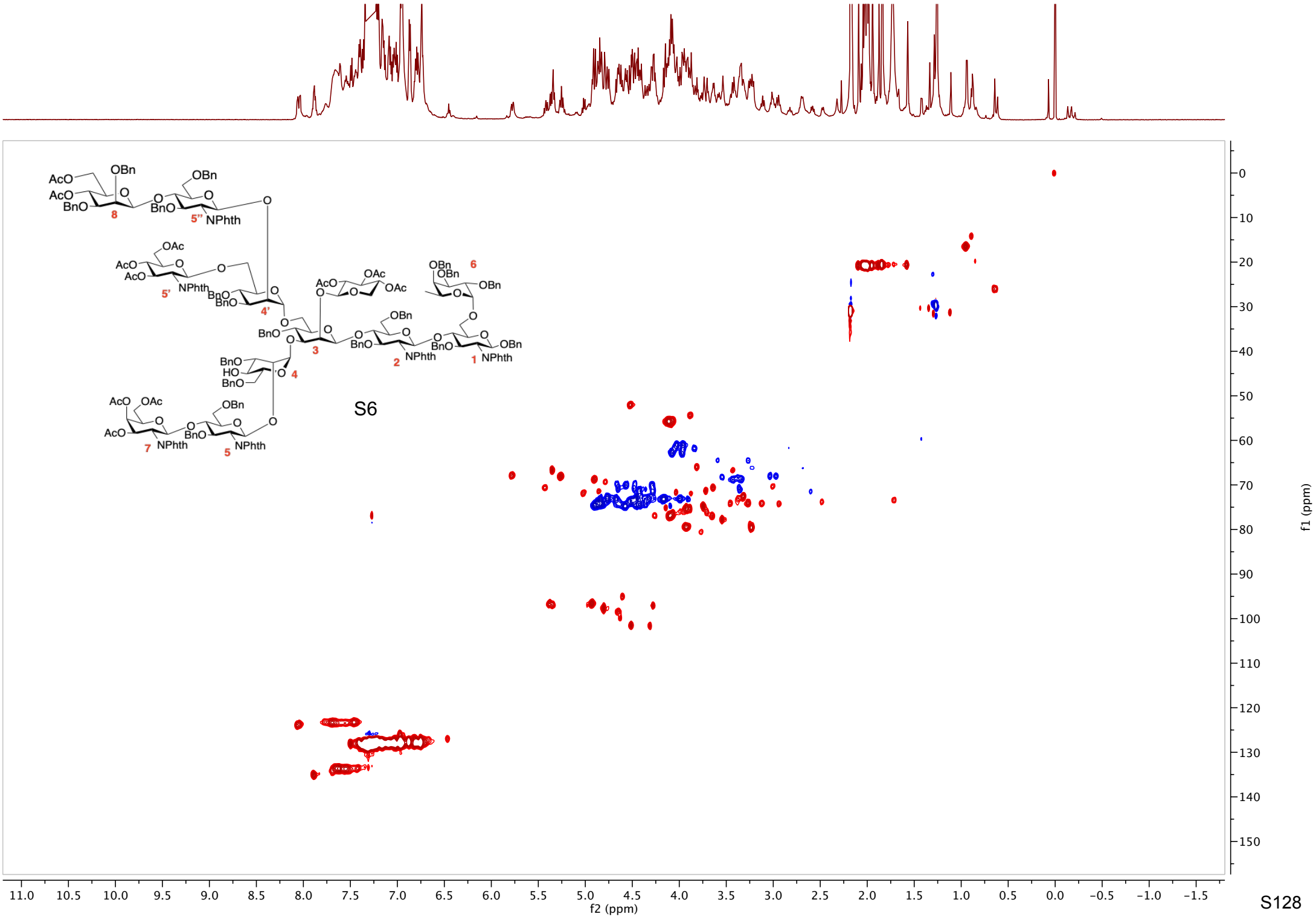
25

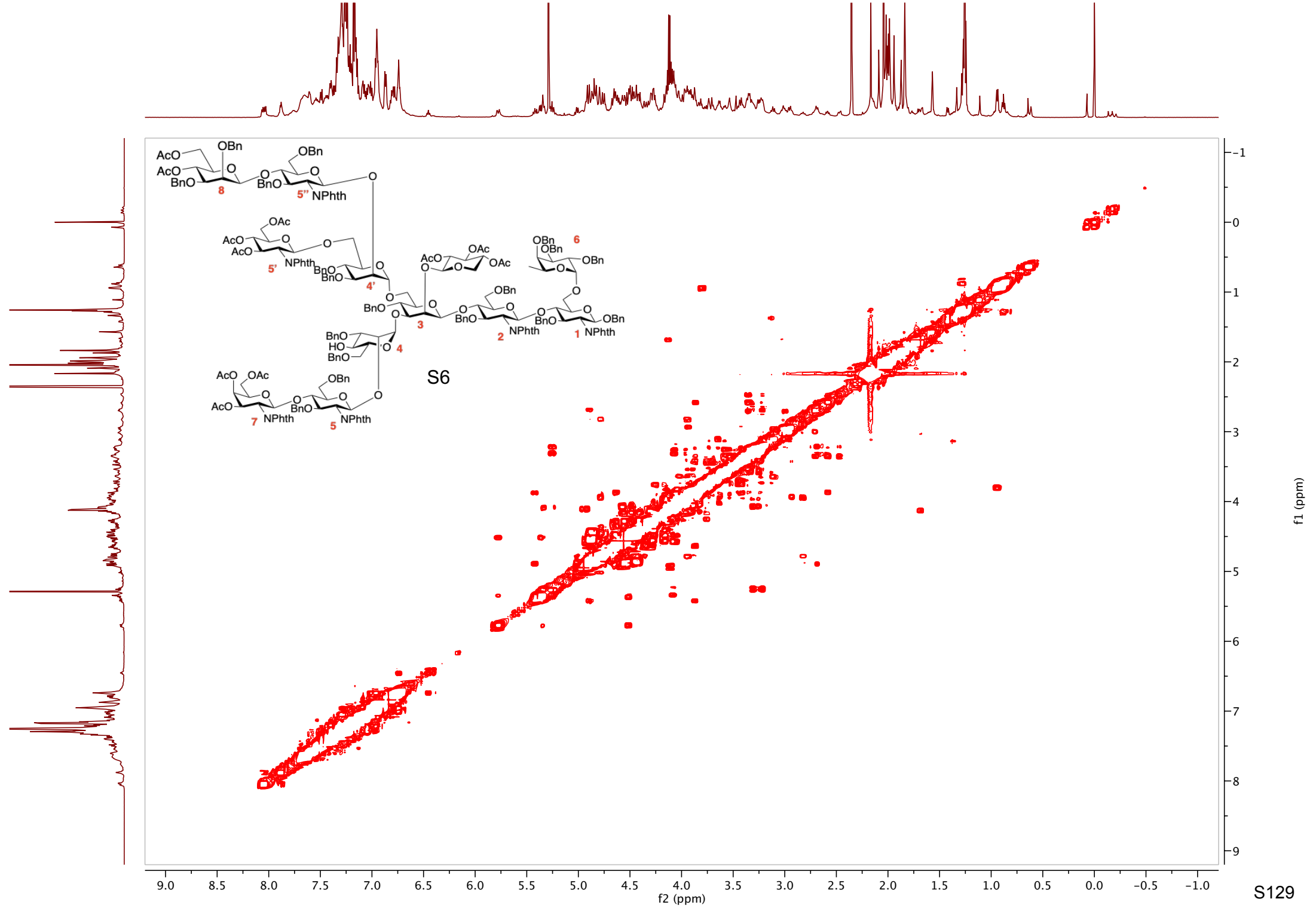
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
94.58
1.04
1.86
1.00
0.97
1.98
2.04
2.20
0.98
7.01
4.67
5.22
10.29
7.11
5.08
10.06
8.71
7.07
6.43
11.20
1.91
0.90
0.74
0.80
0.83
29.61
3.08
8.93
5.37
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

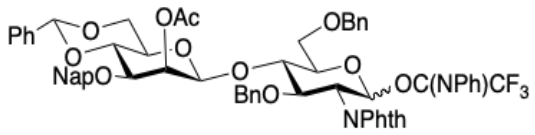

25
f2 (ppm)
f1 (ppm)


25
f2 (ppm)
f1 (ppm)

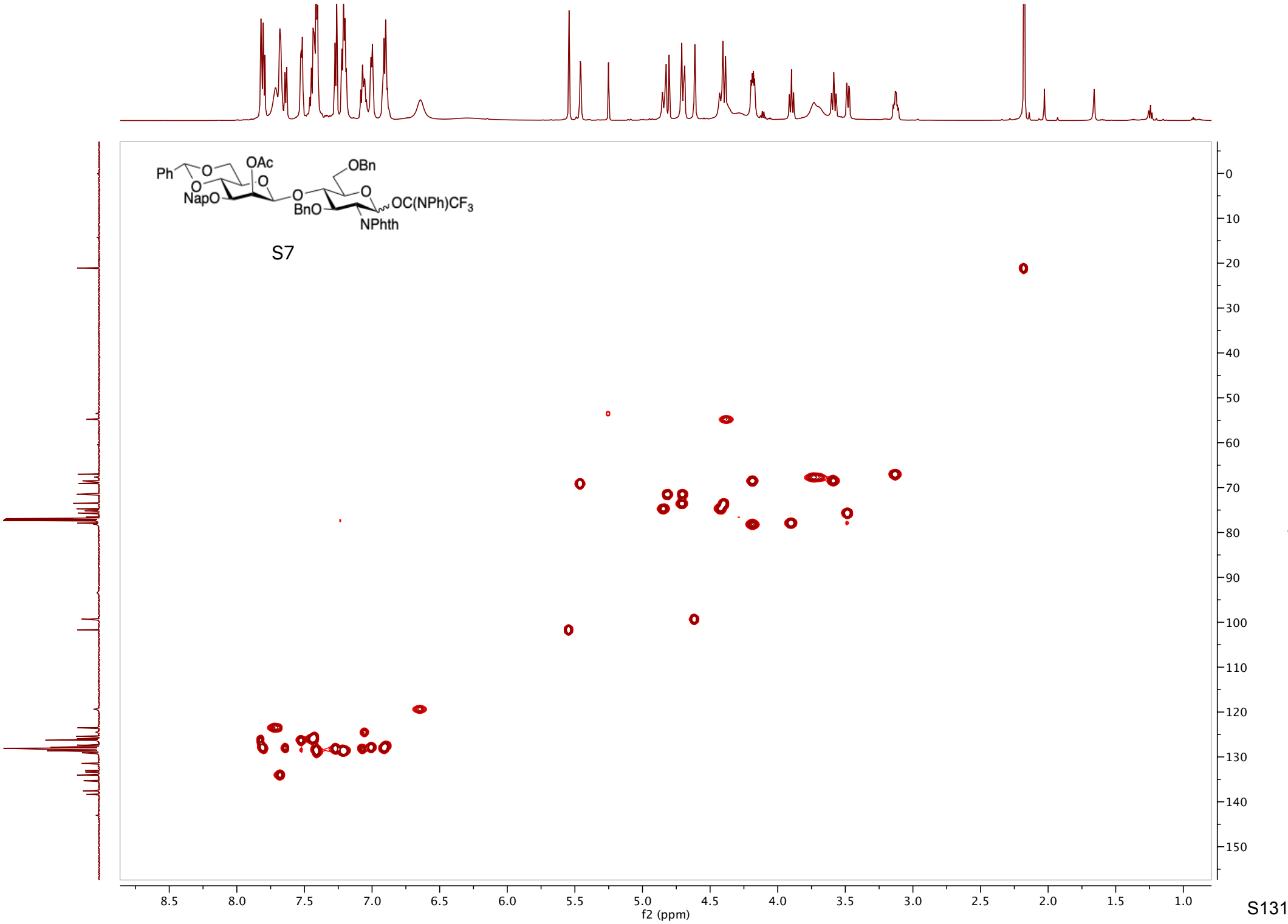

S6
f1 (ppm)

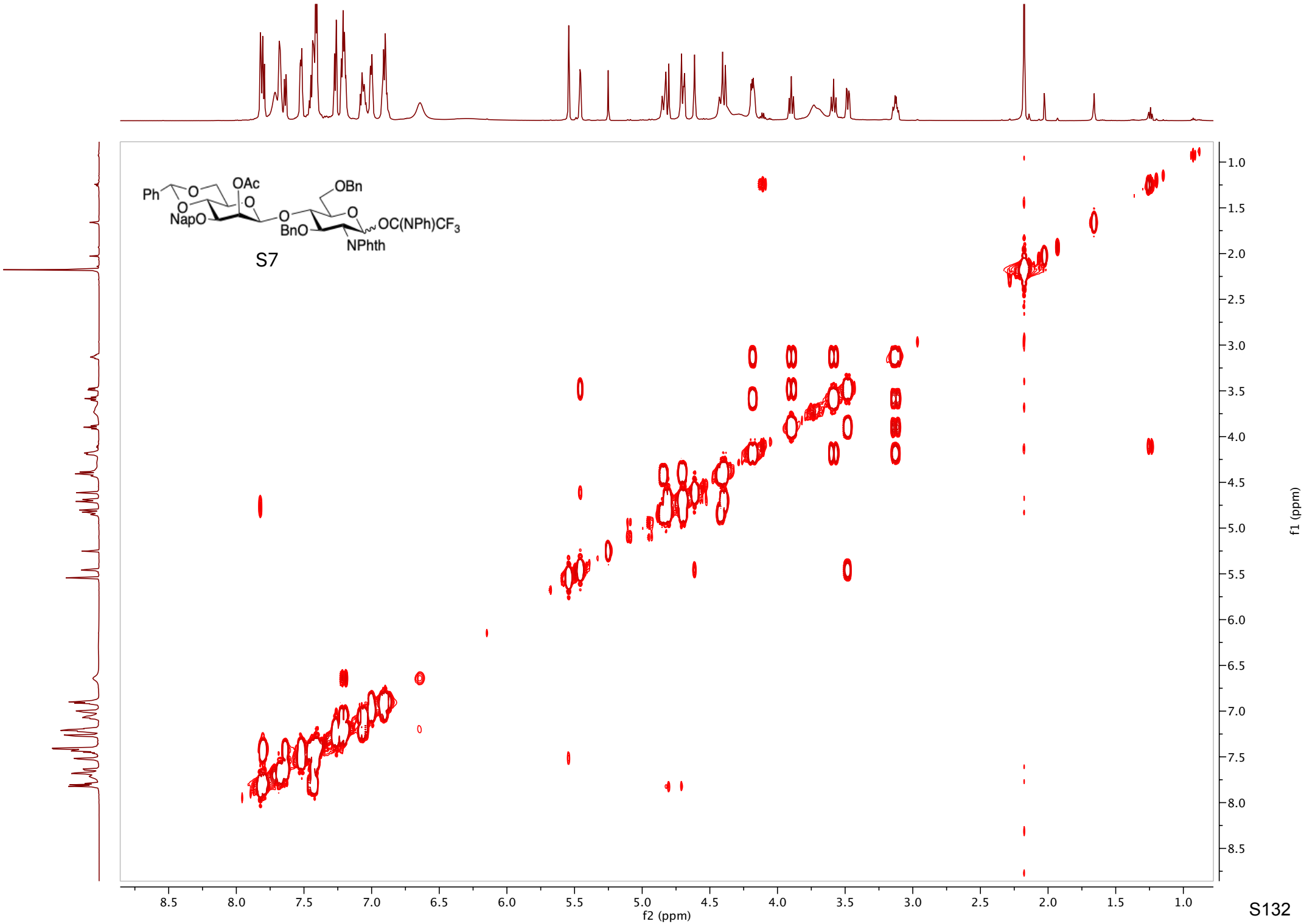

S6
f2 (ppm)
f1 (ppm)

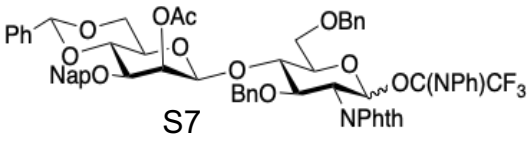

S6
f2 (ppm)
f1 (ppm)



S7

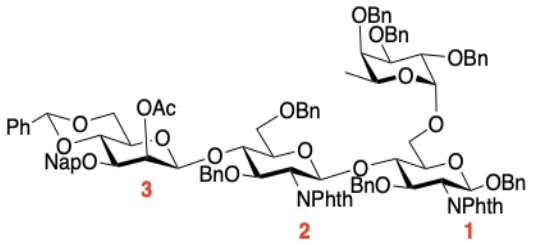

Ph
OAc
OBn
NapO
BnO
OC(NPh)CF3
NPhth
S7
f2 (ppm)
f1 (ppm)


Ph
O
OAc
O
OBn
O
NapO
O
O
BnO
OC(NPh)CF3
NPhth
S7
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f2 (ppm)
f1 (ppm)


Ph
O
OAc
O
NapO
O
OBn
O
BnO
OC(NPh)CF3
NPhth

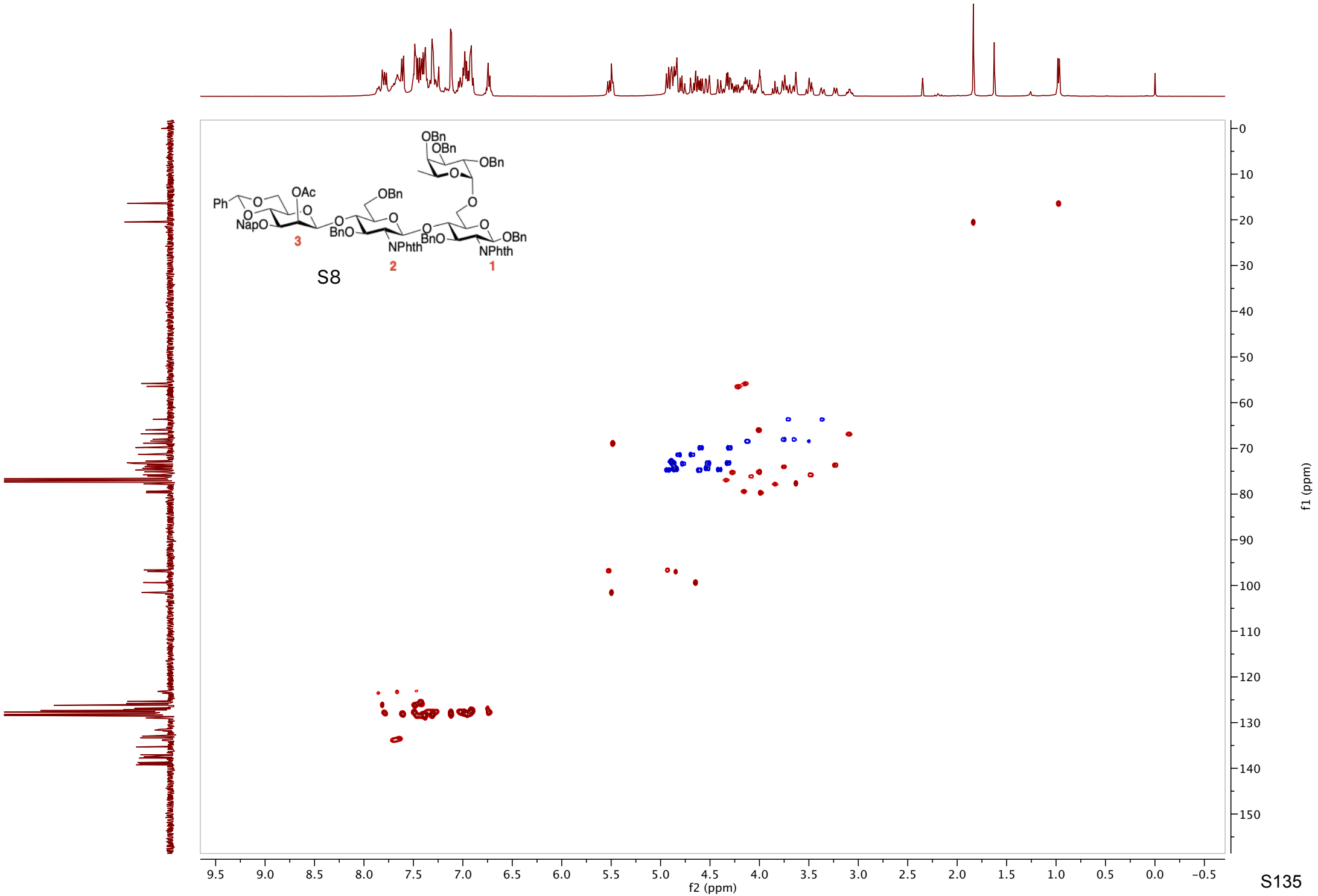
S7

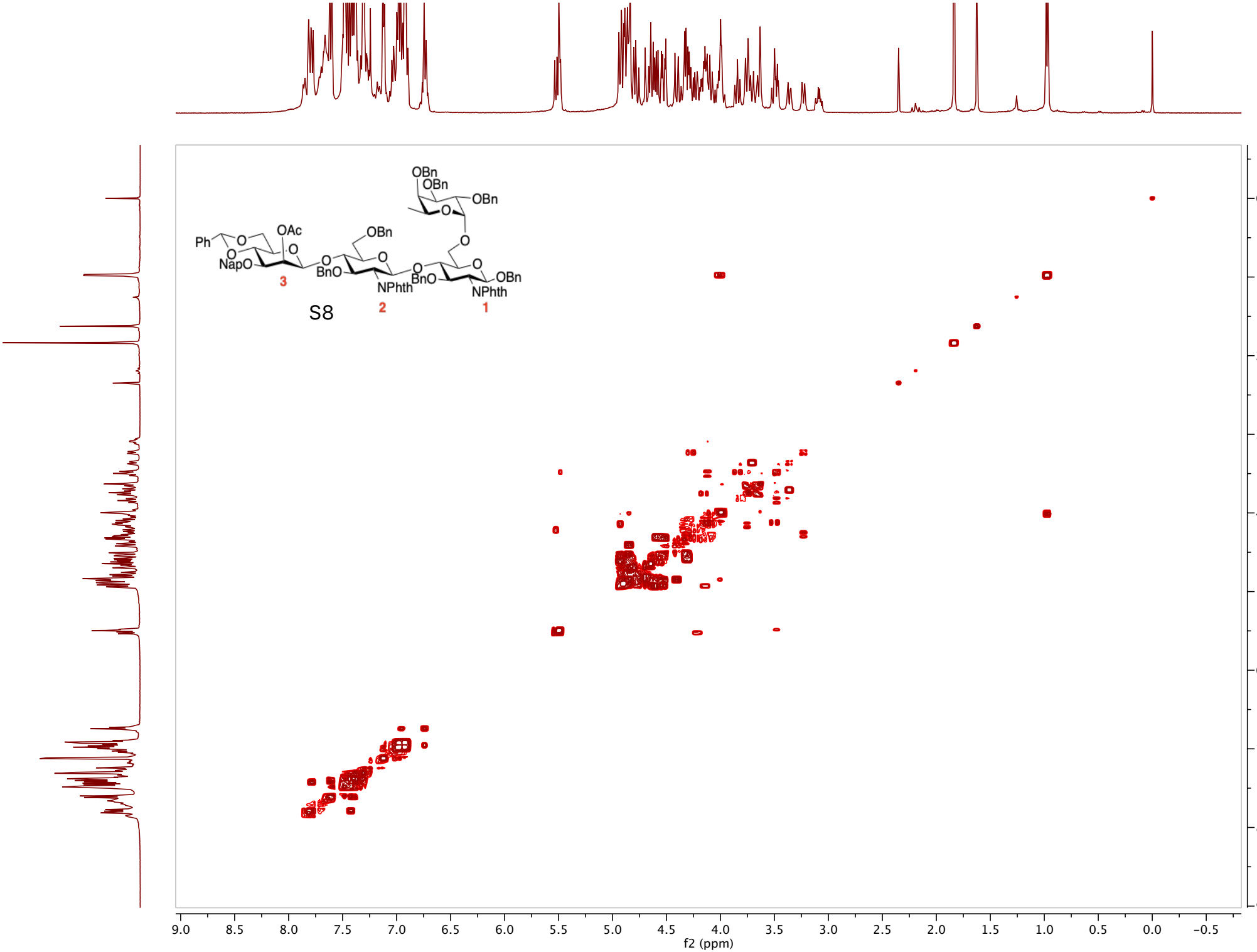
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

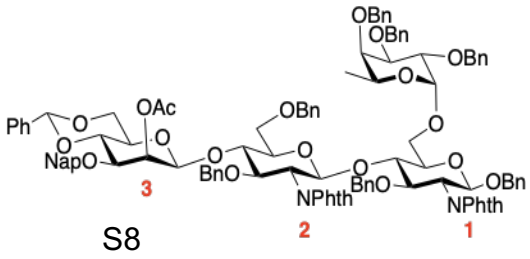

OBn
OBn
OBn
O
O
Ph
O
OAc
O
O
NapO
3
O
BnO
O
OBn
NPhth
2
O
BnO
O
O
OBn
NPhth
1

S8

49.96
3.08
8.95
4.34
2.26
1.89
2.97
5.43
3.07
1.35
3.04
2.09
2.18
1.20
1.08
1.25
2.74
2.72
f1 (ppm)

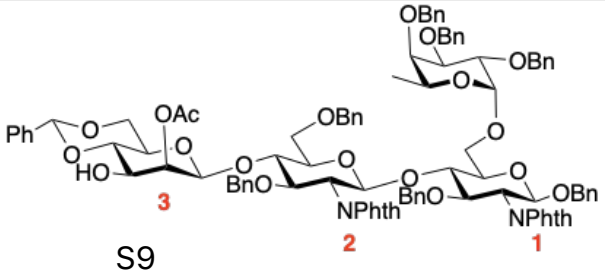

OBn
OBn
OBn
O
O
Ph
O
OAc
O
NapO
3
O
BnO
OBn
O
NPhth
2
O
BnO
O
OBn
NPhth
1
S8
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f2 (ppm)


OBn
OBn
OBn
O
O
Ph
O
OAc
O
OBn
O
O
NapO
O
BnO
O
O
BnO
O
OBn
3
NPhth
2
NPhth
1
S8
f2 (ppm)
f1 (ppm)


OBn
OBn
OBn
O
O
Ph
O
OAc
OBn
O
O
O
O
NapO
O
BnO
O
O
BnO
O
OBn
NPhth
NPhth
3
2
1

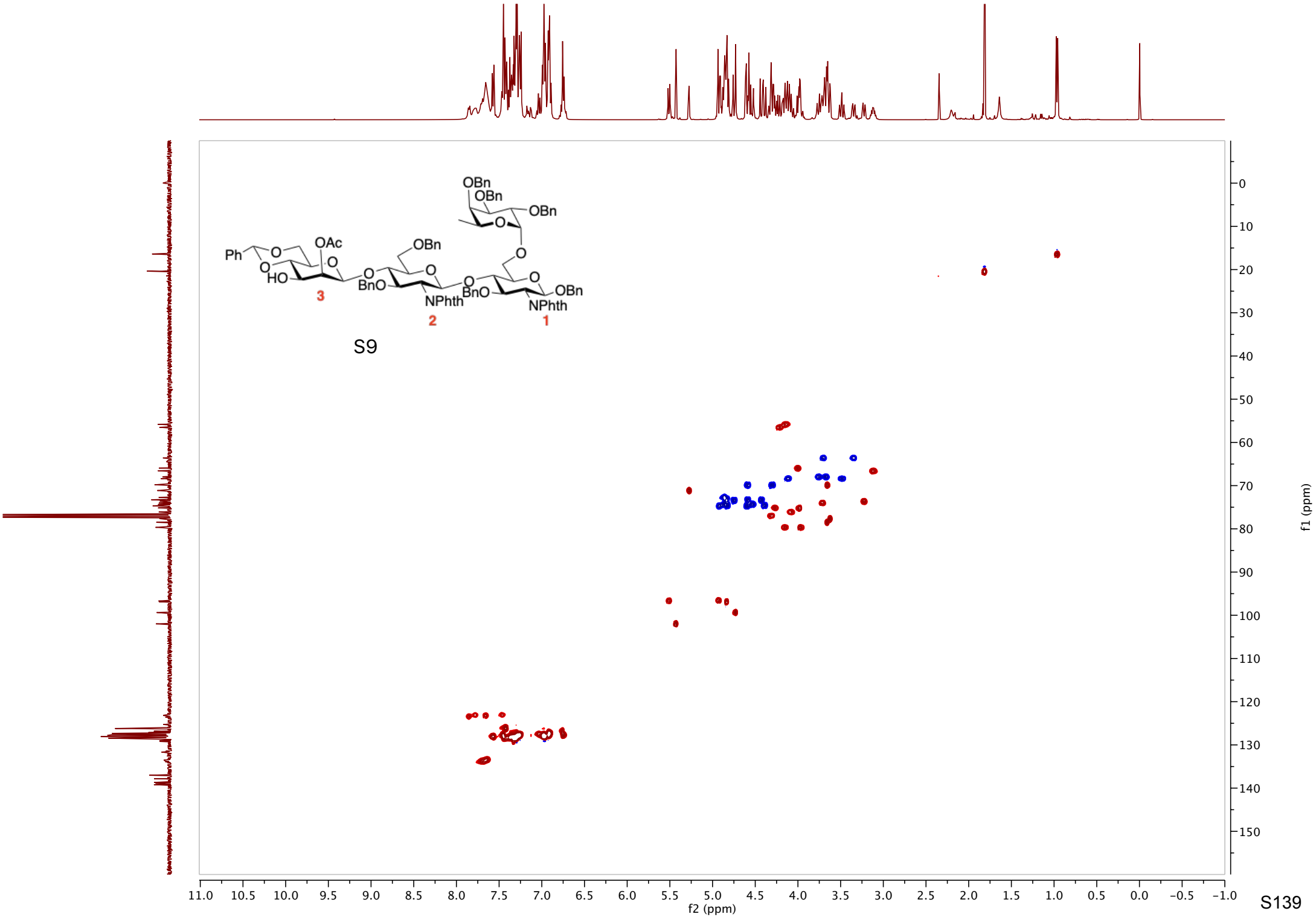
S8

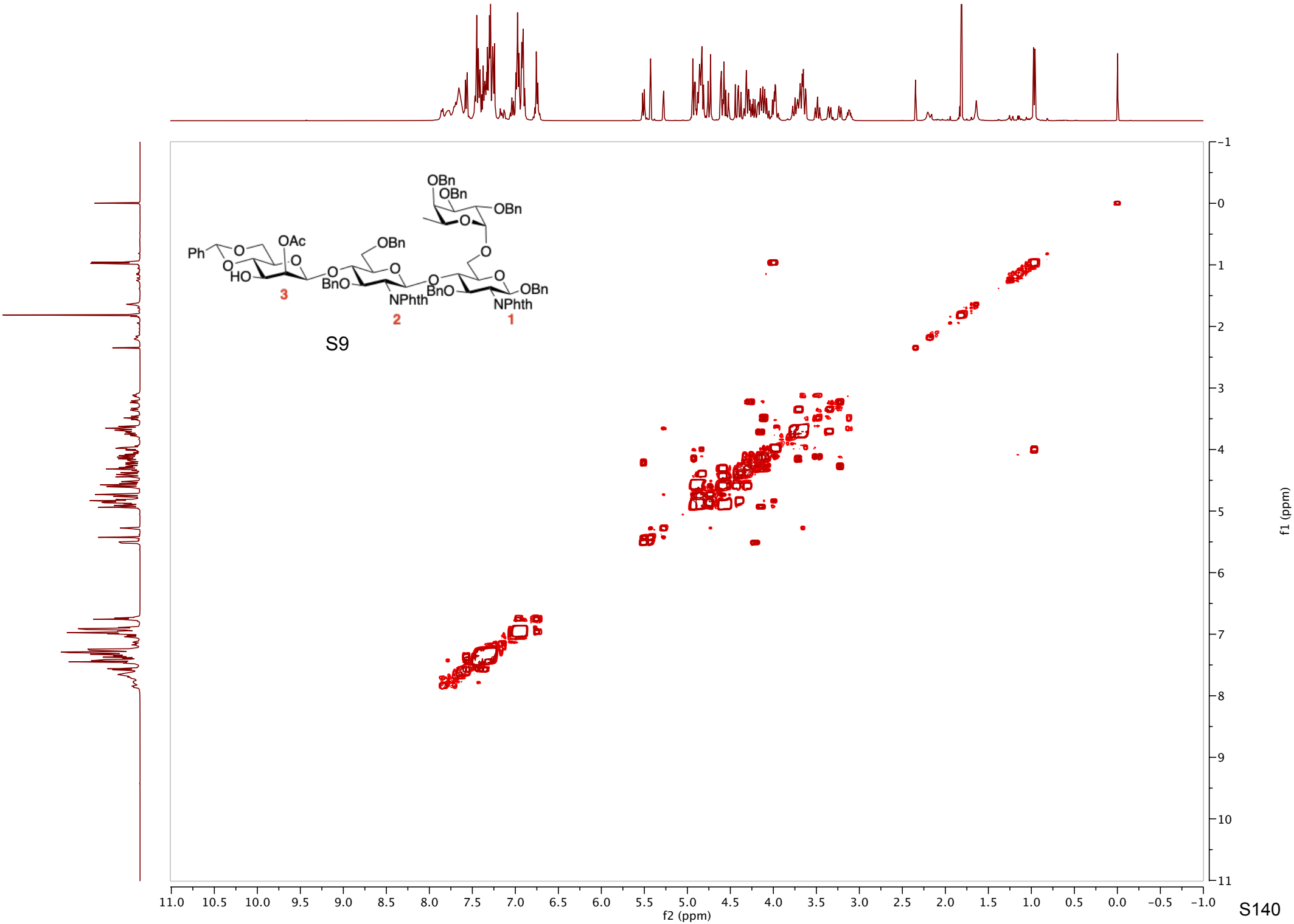
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

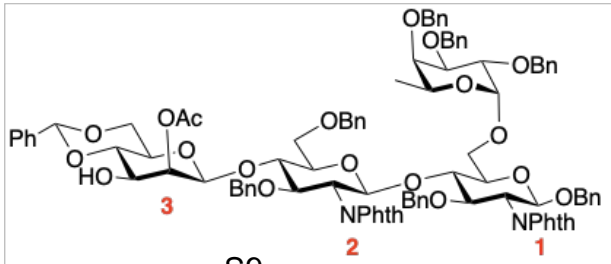

OBn
OBn
OBn
OAc
OBn
Ph
O
O
HO
O
BnO
O
NPhth
BnO
O
O
OBn
NPhth
3
2
1

S9

51.03
1.12
1.00
0.90
2.36
6.54
2.16
4.24
2.29
3.14
5.27
2.98
7.39
1.11
1.09
1.07
1.05
2.91
2.89
f1 (ppm)

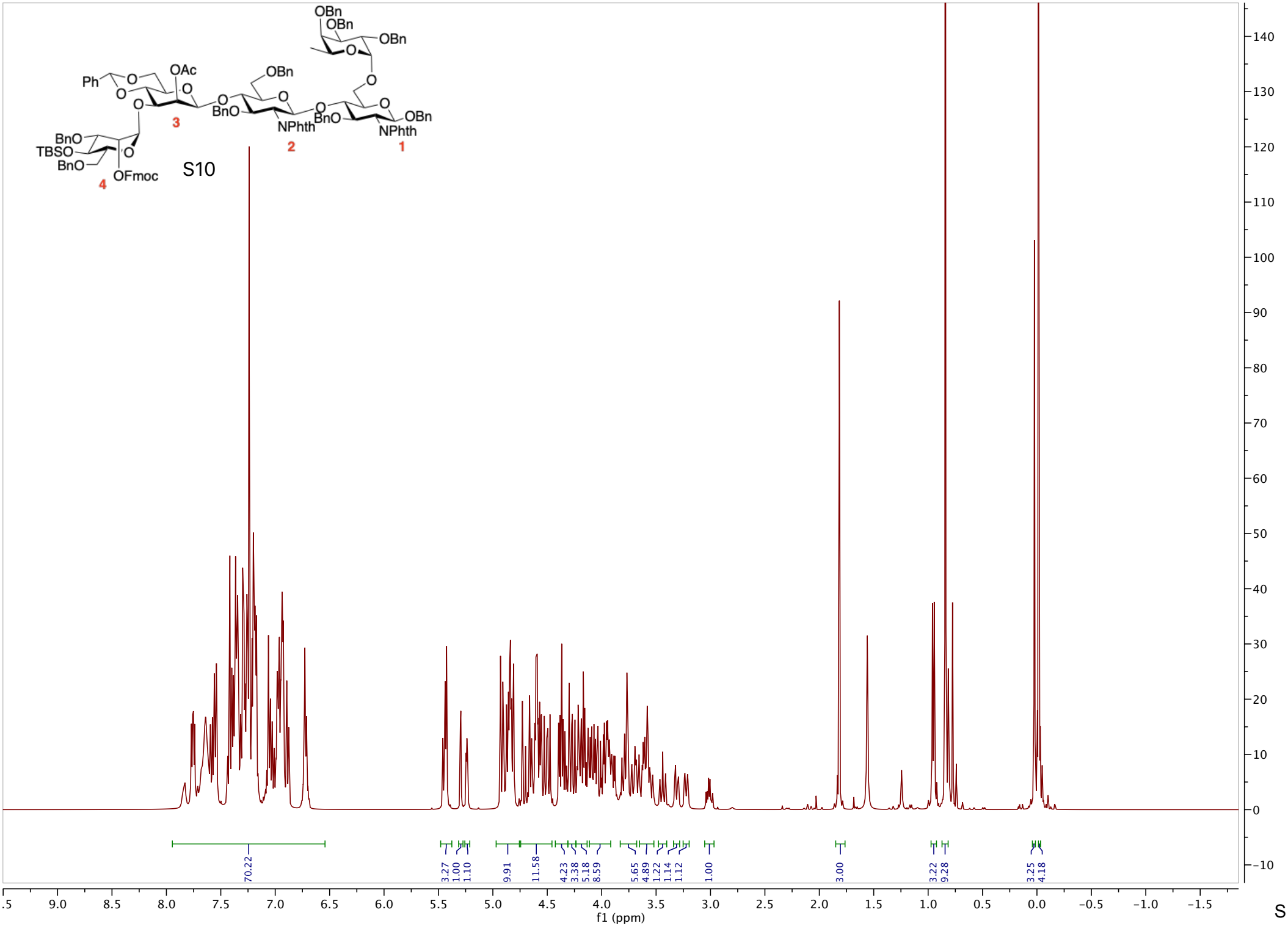

OBn
OBn
OBn
O
O
Ph
O
OAc
O
O
HO
3
O
BnO
OBn
O
NPhth
2
O
BnO
O
O
OBn
NPhth
1
S9
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

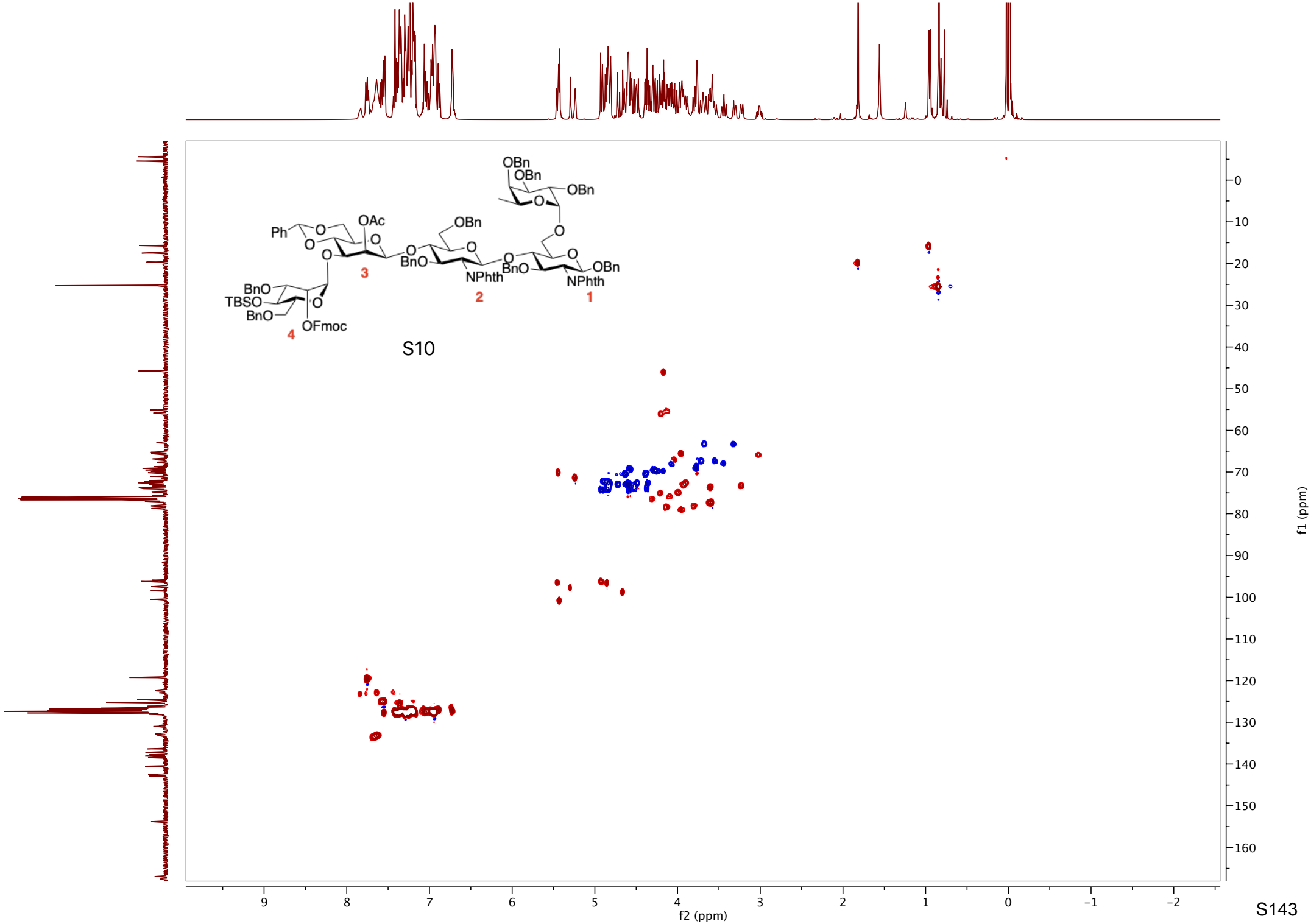

OBn
OBn
OBn
O
O
Ph
O
OAc
O
OBn
O
O
HO
O
BnO
O
O
BnO
O
OBn
NPhth
NPhth
3
2
1
S9
f2 (ppm)
f1 (ppm)

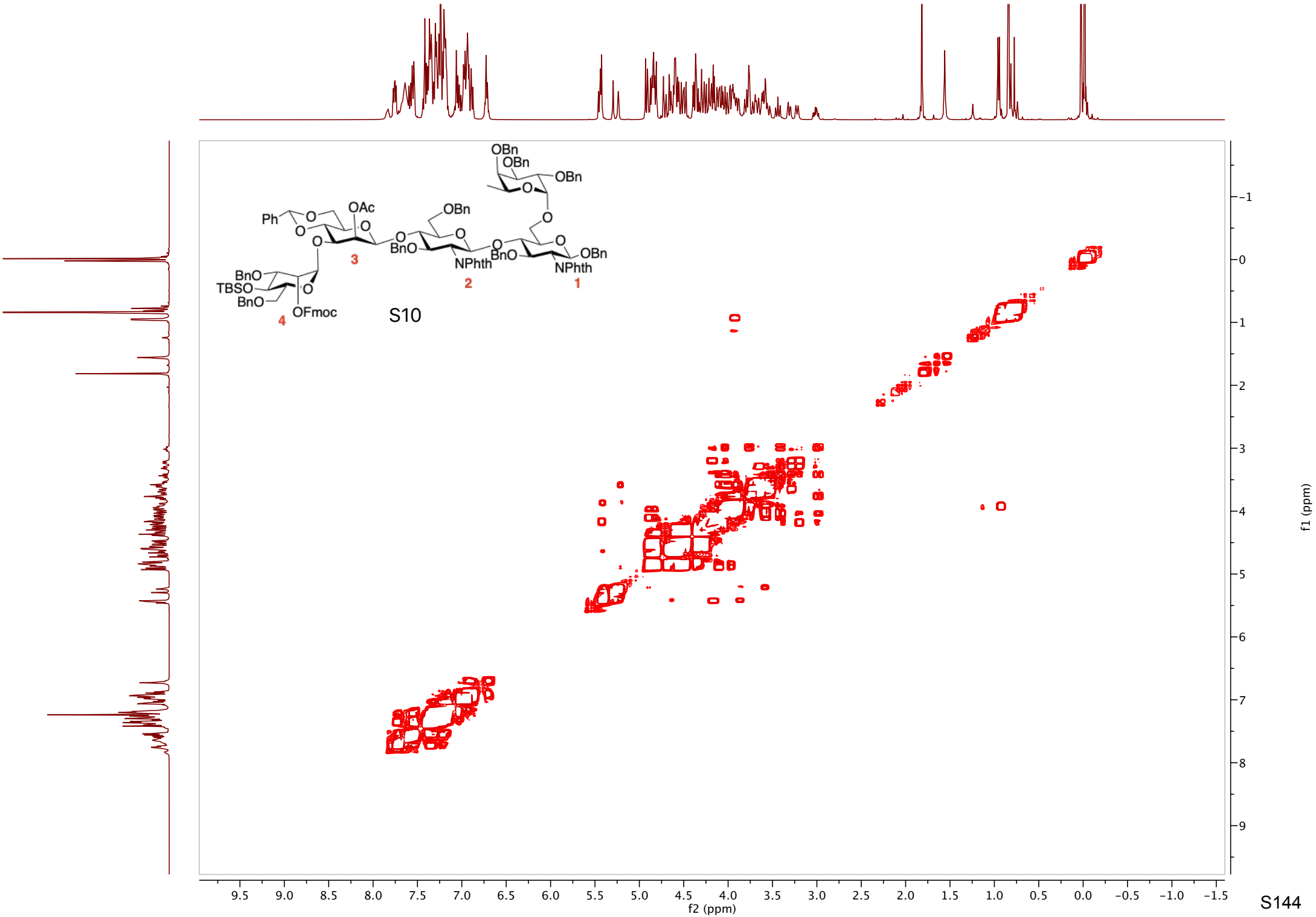

OBn
OBn
OBn
O
O
Ph
O
OAc
O
OBn
O
O
HO
O
BnO
O
O
BnO
O
OBn
NPhth
NPhth
3
2
1

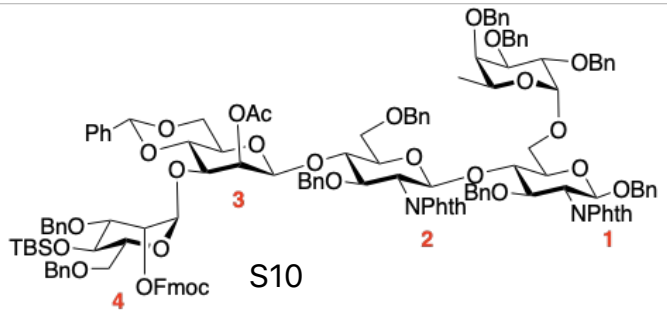
S9

24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OBn
OBn
OBn
Ph
OAc
OBn
BnO
NPhth
BnO
NPhth
OBn
BnO
TBSO
BnO
OFmoc
3
2
1
4
S10
f1 (ppm)

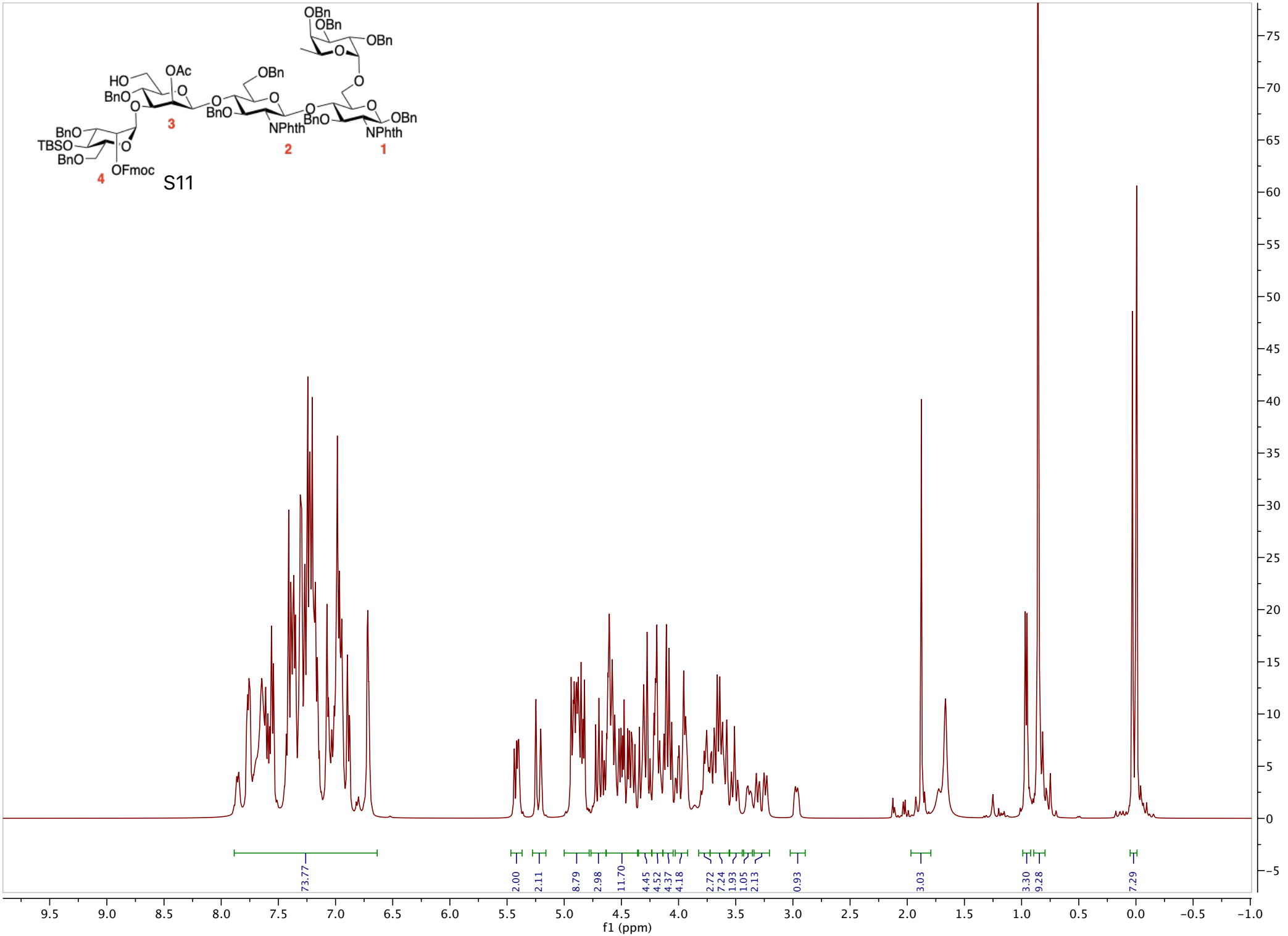

OBn
OBn
OBn
O
O
Ph
O
O
OAc
O
O
3
OBn
O
BnO
O
NPhth
2
BnO
O
O
OBn
NPhth
1
BnO
TBSO
BnO
O
4
OFmoc
S10
f2 (ppm)
f1 (ppm)

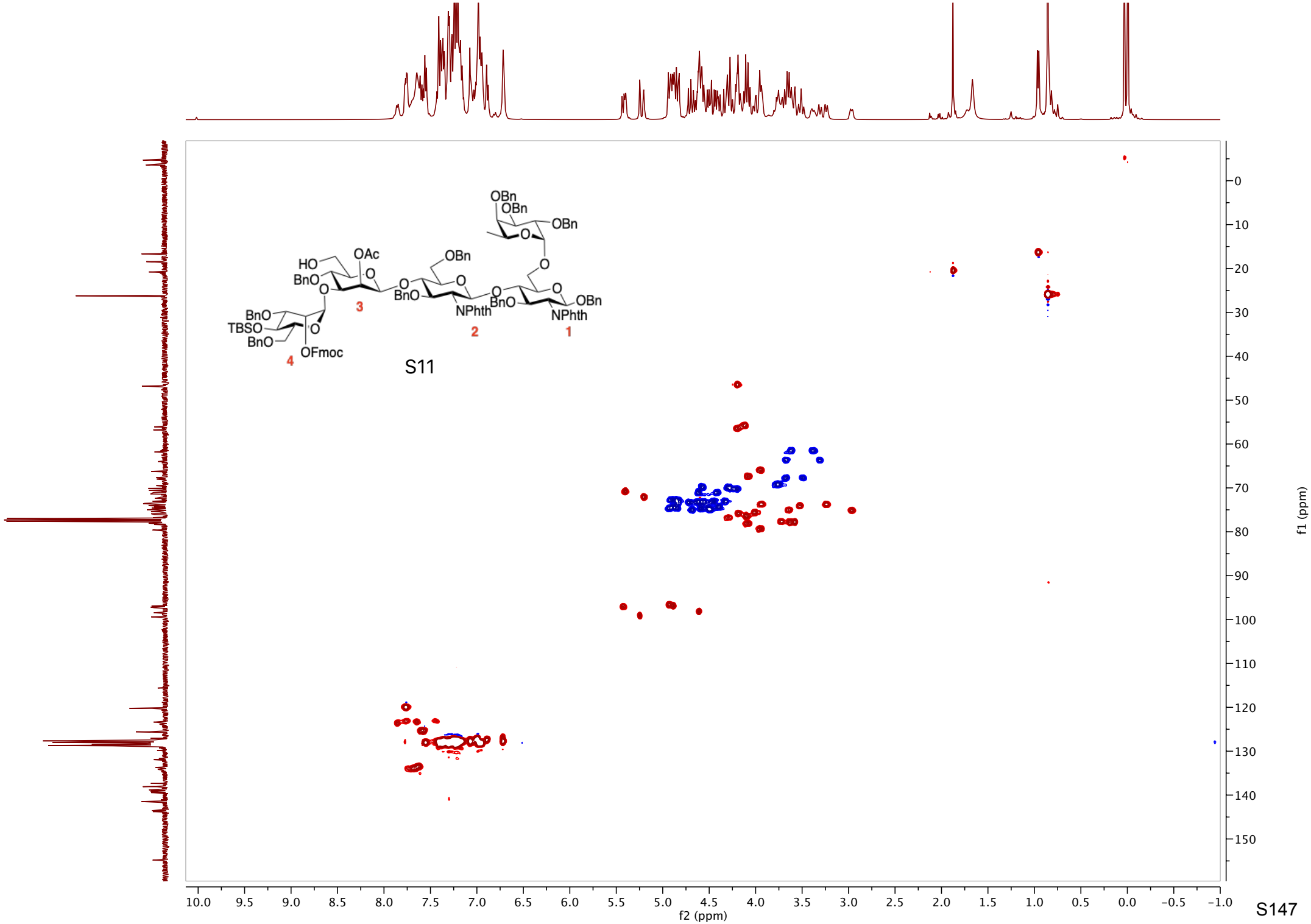

OBn
OBn
OBn
O
Ph
O
OAc
O
O
3
OBn
O
BnO
O
NPhth
2
O
BnO
O
NPhth
1
OBn
BnO
TBSO
BnO
O
4
OFmoc
S10
f2 (ppm)
f1 (ppm)

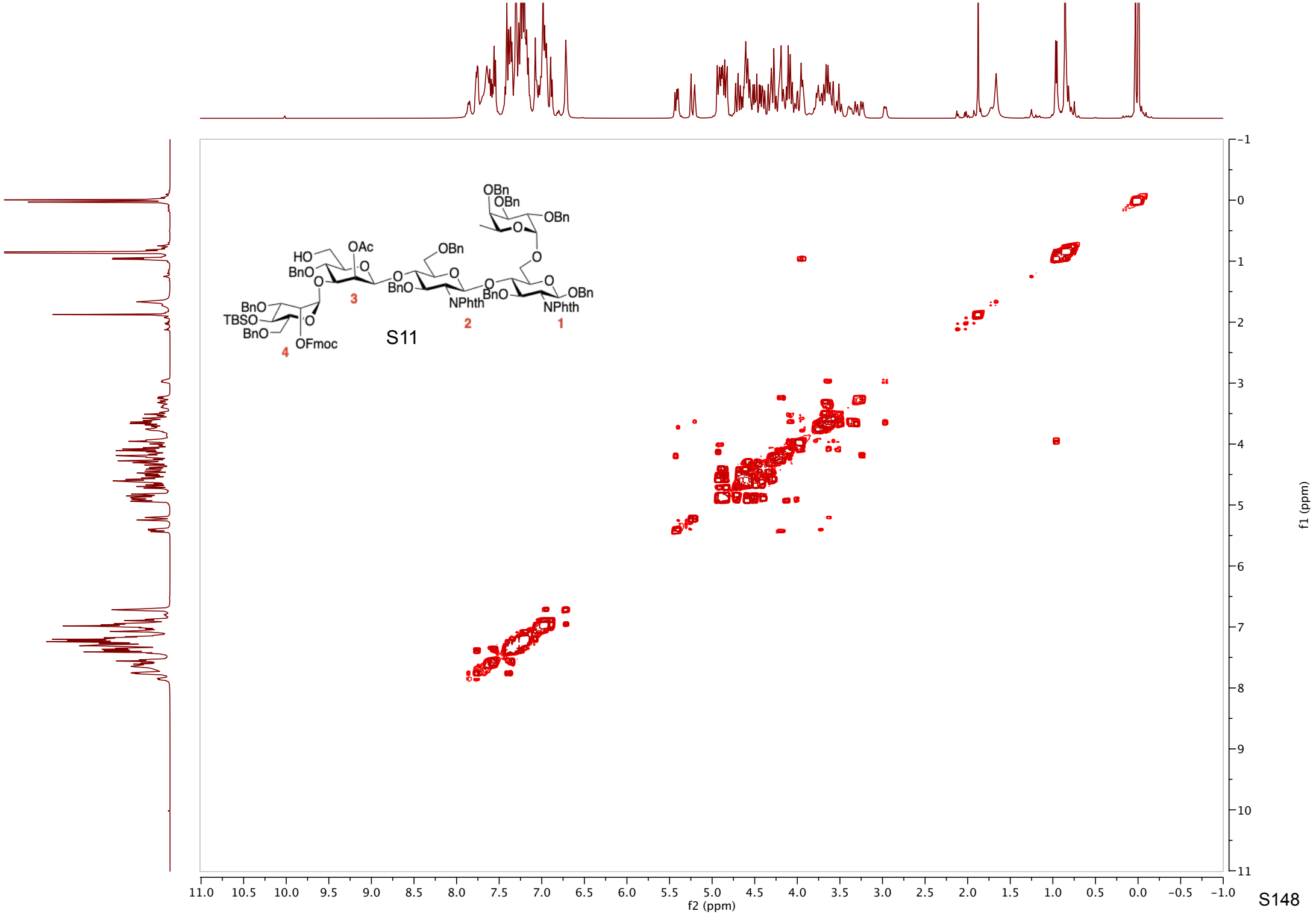

OBn
OBn
OBn
O
O
Ph
O
OAc
O
O
3
O
BnO
O
OBn
NPhth
2
O
BnO
O
O
OBn
NPhth
1
BnO
TBSO
BnO
O
4
OFmoc

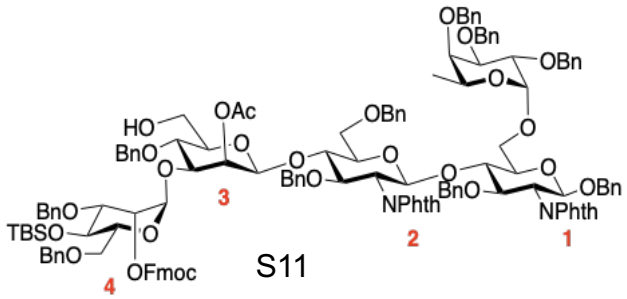
S10

70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OBn
OBn
OBn
O
HO
OAc
O
BnO
O
O
BnO
OBn
O
NPhth
BnO
O
O
OBn
NPhth
3
2
1
BnO
TBSO
BnO
O
OFmoc
4
S11
73.77
2.00
2.11
8.79
2.98
11.70
4.45
4.52
4.37
4.18
2.72
7.24
1.93
1.05
2.13
0.93
3.03
3.30
9.28
7.29
f1 (ppm)

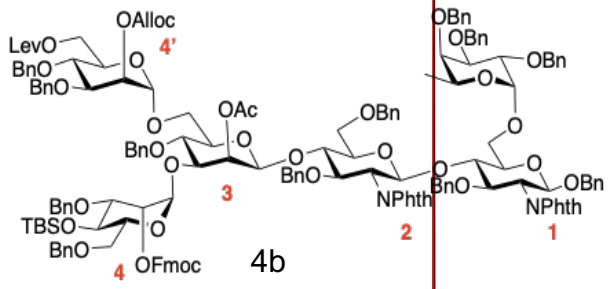

OBn
OBn
OBn
O
O
HO
OAc
BnO
O
O
OBn
BnO
O
O
O
BnO
NPhth
BnO
OBn
BnO
TBSO
O
NPhth
BnO
OFmoc
3
2
1
4
S11
f2 (ppm)
f1 (ppm)


OBn
OBn
OBn
O
HO
OAc
OBn
BnO
O
O
O
O
O
BnO
O
BnO
NPhth
BnO
OBn
3
2
1
BnO
TBSO
BnO
O
NPhth
4
OFmoc
S11
f2 (ppm)
f1 (ppm)


OBn
OBn
OBn
O
O
HO
OAc
BnO
O
O
OBn
O
BnO
O
O
BnO
NPhth
BnO
NPhth
OBn
3
2
1
BnO
TBSO
BnO
O
OFmoc
4

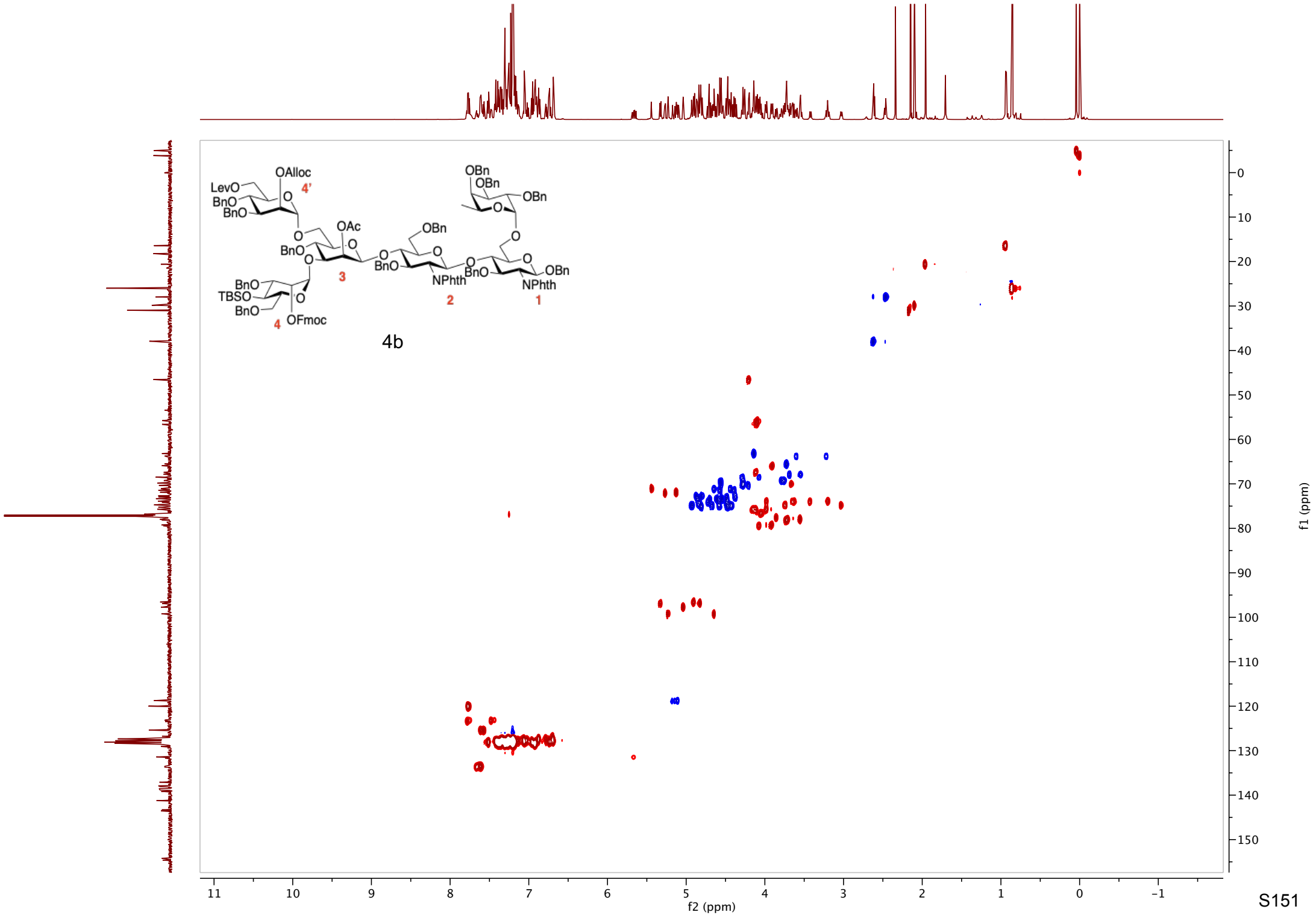
S11

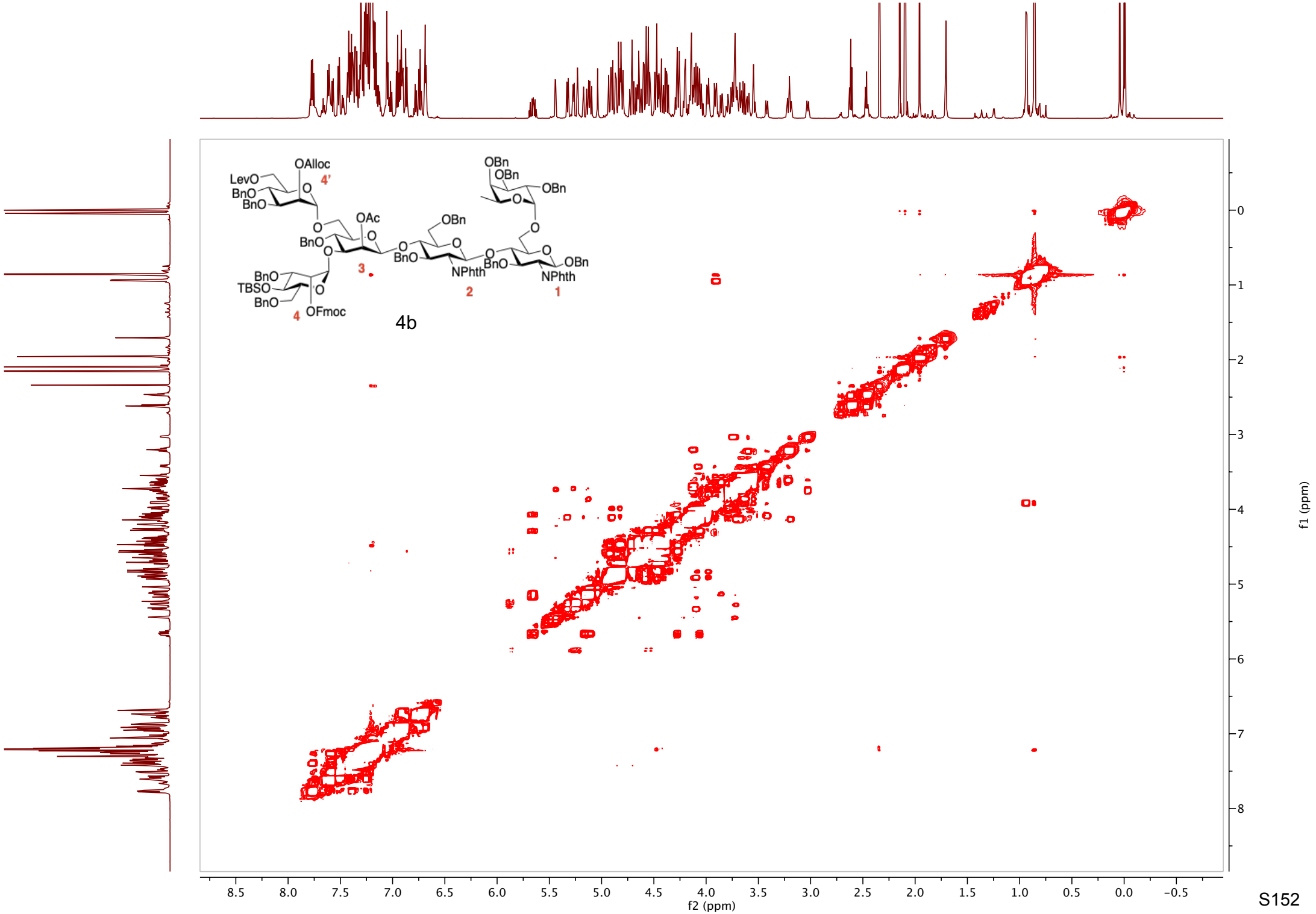
40
35
30
25
20
15
10
5
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

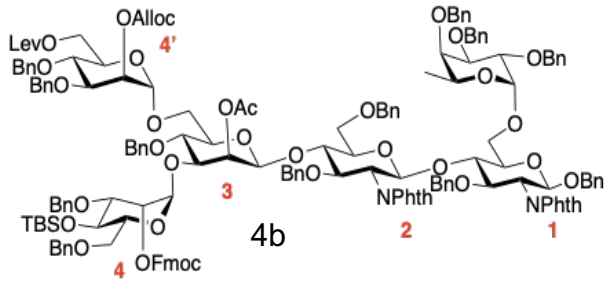

OAlloc
4'
LevO
BnO
BnO
O
OAc
O
BnO
O
3
BnO
TBSO
BnO
4
OFmoc
OBn
OBn
OBn
O
O
BnO
O
BnO
NPhth
2
O
O
BnO
OBn
NPhth
1

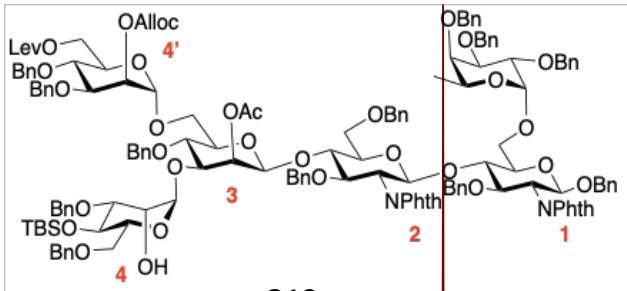
4b

2400000
2300000
2200000
2100000
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
-200000
90.58
1.15
1.19
1.14
1.26
1.03
3.50
0.99
3.19
6.99
2.19
3.83
6.56
13.30
2.23
10.58
2.24
2.16
1.09
8.53
3.18
2.18
1.02
2.15
1.00
2.26
2.23
3.84
2.97
3.79
9.46
6.59
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


OAlloc
LevO
BnO
BnO
4'
O
OAc
OBn
OBn
OBn
OBn
BnO
BnO
BnO
NPhth
BnO
OBn
NPhth
BnO
TBSO
BnO
3
2
1
4
OFmoc
4b
f2 (ppm)
f1 (ppm)

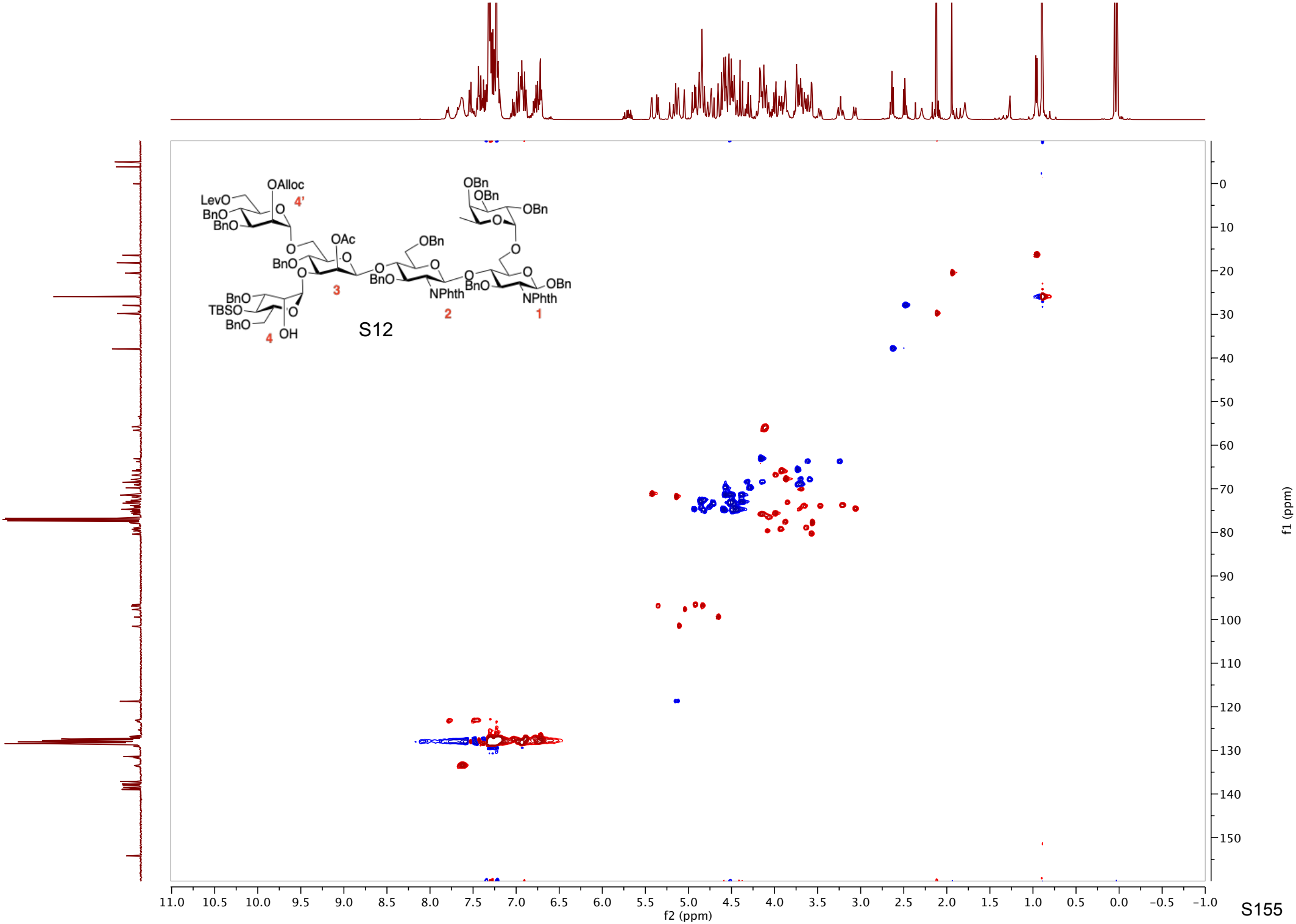

LevO
BnO
BnO
OAlloc
4'
O
O
BnO
OAc
O
O
BnO
O
3
BnO
TBSO
BnO
O
4
OFmoc
OBn
O
BnO
NPhth
2
OBn
OBn
OBn
O
O
BnO
O
NPhth
1
4b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

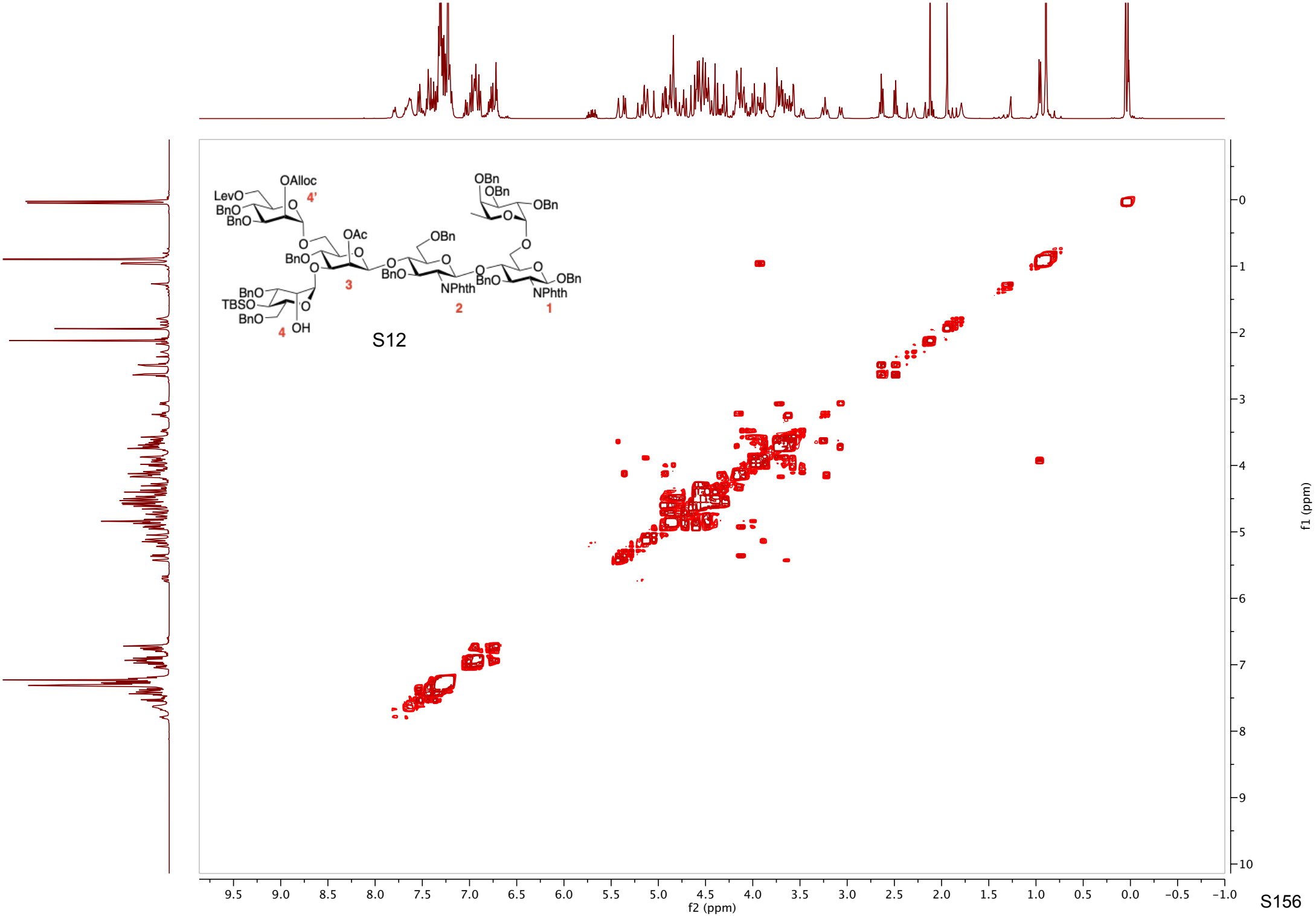

OAlloc
4'
LevO
BnO
BnO
OAc
OBn
OBn
OBn
OBn
BnO
BnO
BnO
NPhth
BnO
OBn
NPhth
BnO
TBSO
BnO
OFmoc
3
2
1
4
4b

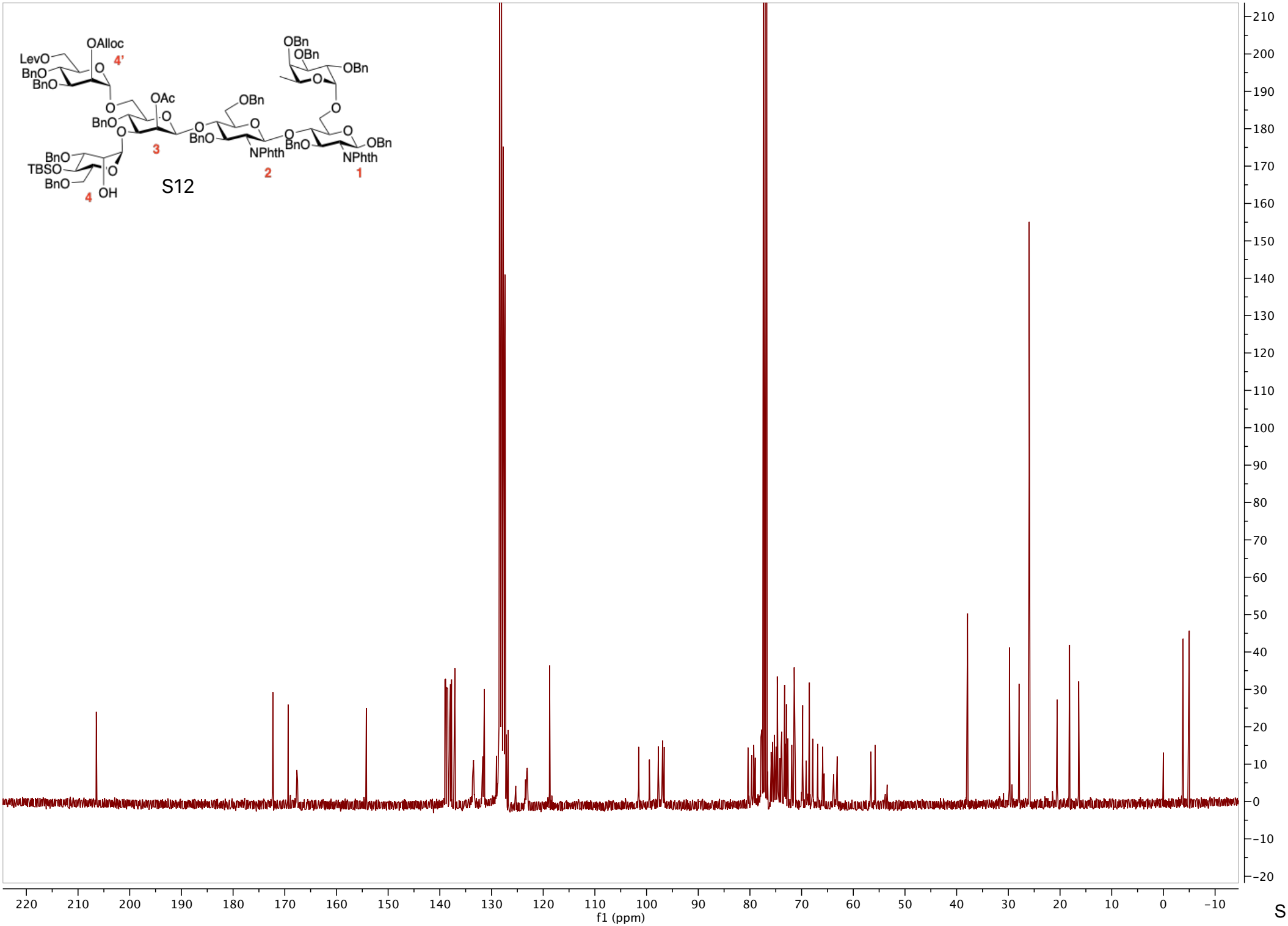

OAlloc
LevO
BnO
BnO
4'
O
OAc
BnO
O
OBn
O
BnO
O
O
BnO
NPhth
2
OBn
OBn
OBn
O
O
BnO
OBn
NPhth
1
BnO
TBSO
BnO
O
3
4
OH

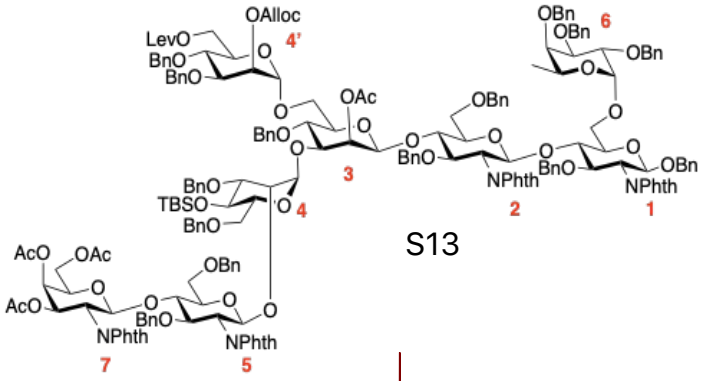
S12

62.57
0.89
0.95
1.19
4.17
0.96
2.87
9.05
0.99
19.75
8.20
2.46
5.03
8.49
3.74
1.01
2.12
1.00
2.31
2.04
3.46
2.78
3.24
10.12
7.43
f1 (ppm)


OAlloc
LevO
BnO
BnO
4'
O
OAc
BnO
O
3
BnO
TBSO
BnO
4
OH
OBn
OBn
OBn
O
BnO
NPhth
2
BnO
OBn
NPhth
1
S12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
f1 (ppm)

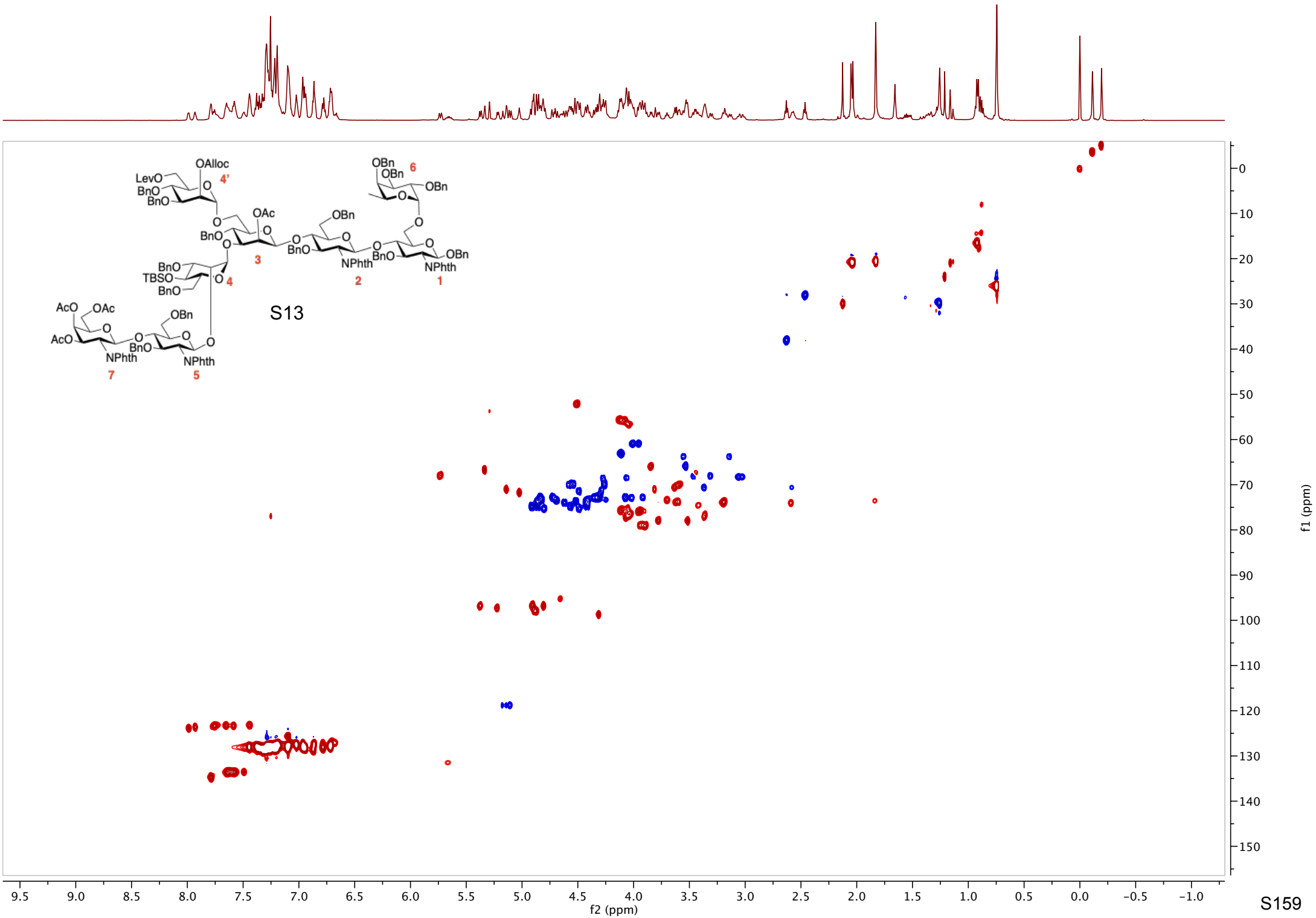

OAlloc
LevO
BnO
BnO
4'
OAc
OBn
OBn
OBn
OBn
BnO
BnO
BnO
NPhth
BnO
OBn
NPhth
BnO
TBSO
BnO
3
2
1
4
OH
S12
f2 (ppm)
f1 (ppm)

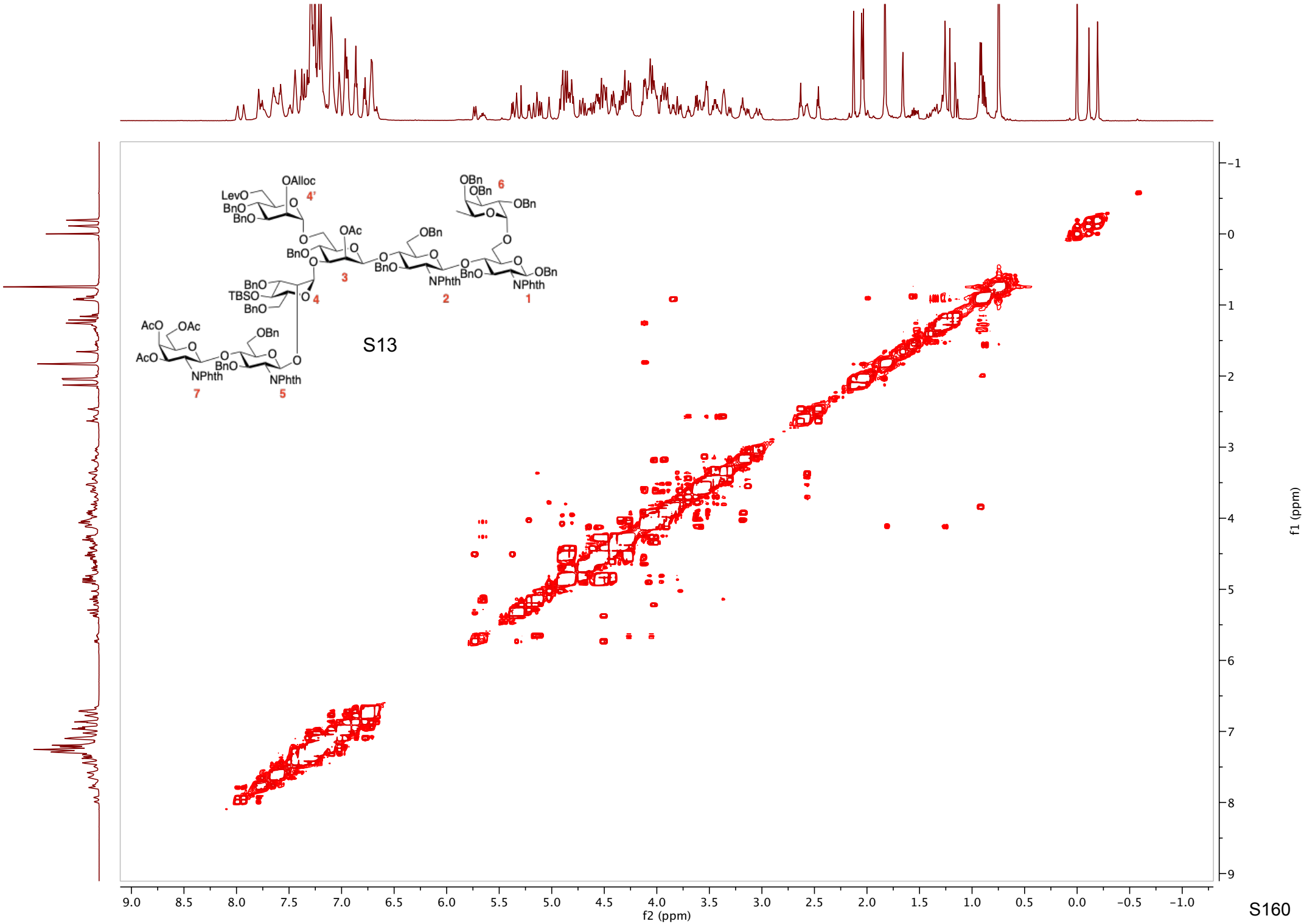

OAlloc
LevO
BnO
BnO
4'
O
OAc
O
BnO
O
3
BnO
TBSO
BnO
4
OH
O
OBn
BnO
NPhth
2
OBn
OBn
OBn
O
O
BnO
O
OBn
NPhth
1
S12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

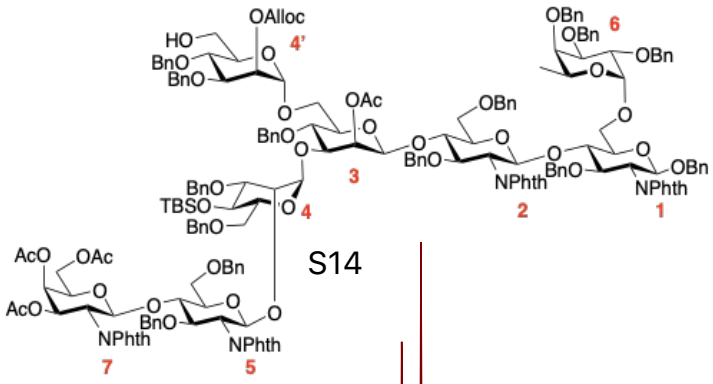

OAlloc
LevO
BnO
BnO
4'
OAc
BnO
3
OBn
BnO
NPhth
2
OBn
OBn
6
OBn
BnO
NPhth
1
BnO
TBSO
BnO
4
AcO
OAc
AcO
NPhth
7
OBn
BnO
NPhth
5

S13

1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
96.78
1.00
1.05
1.09
2.14
1.06
3.14
1.05
11.16
2.96
4.87
5.05
13.39
14.63
6.51
3.51
9.23
3.47
2.50
1.11
3.27
2.02
2.04
2.09
2.06
3.22
6.61
5.51
3.57
8.67
5.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

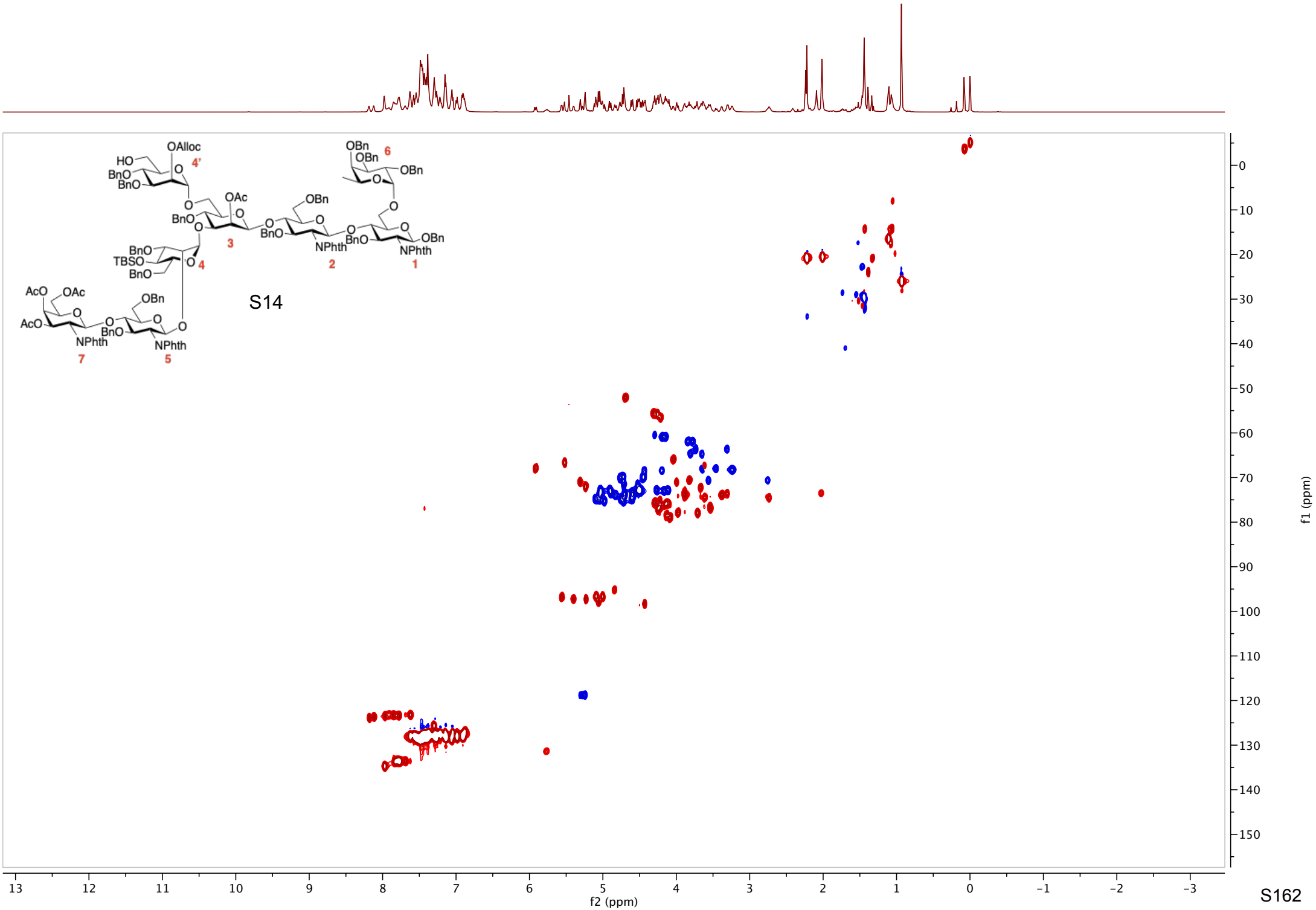

S13
f2 (ppm)
f1 (ppm)

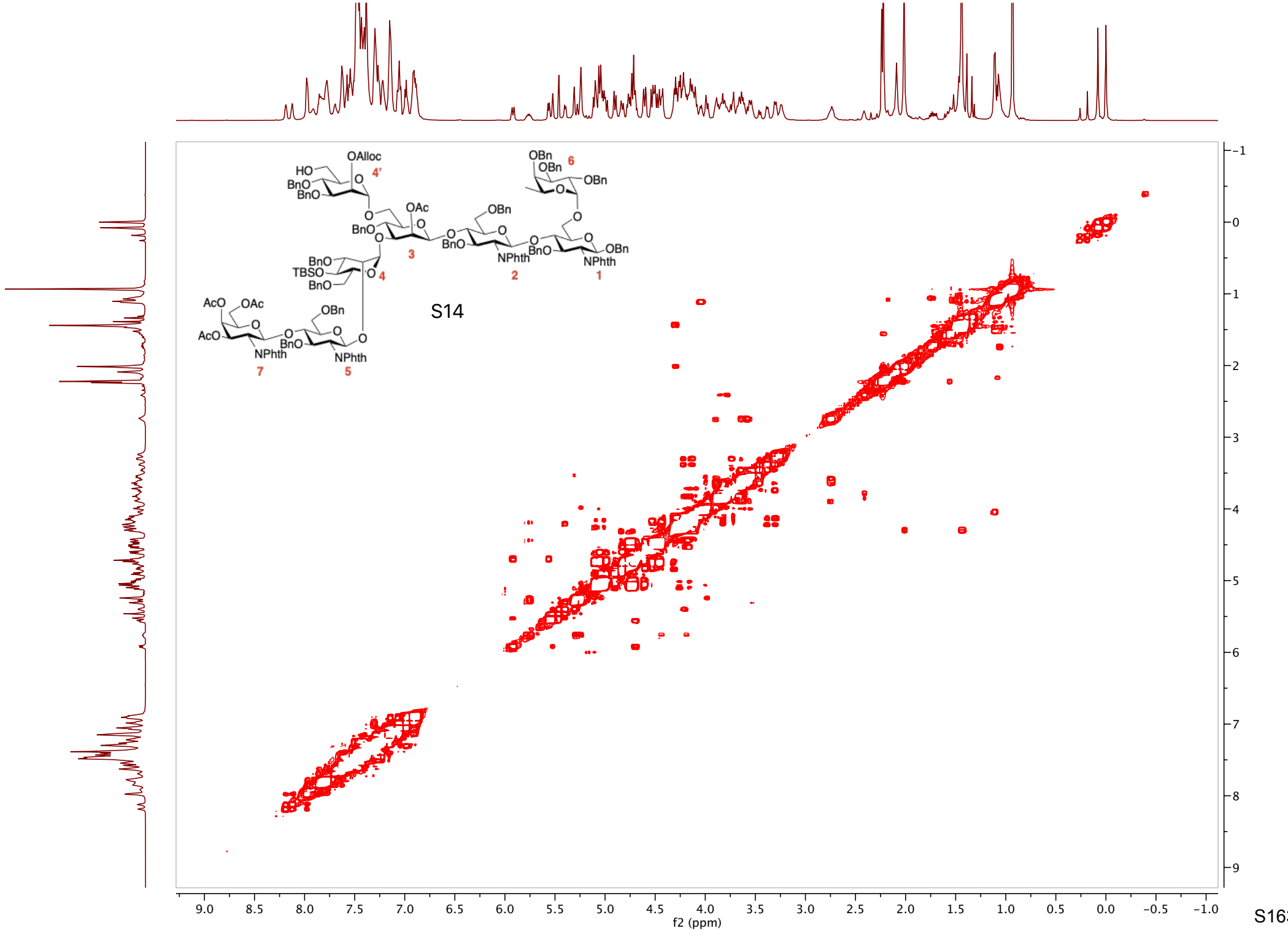

S13
f2 (ppm)
f1 (ppm)

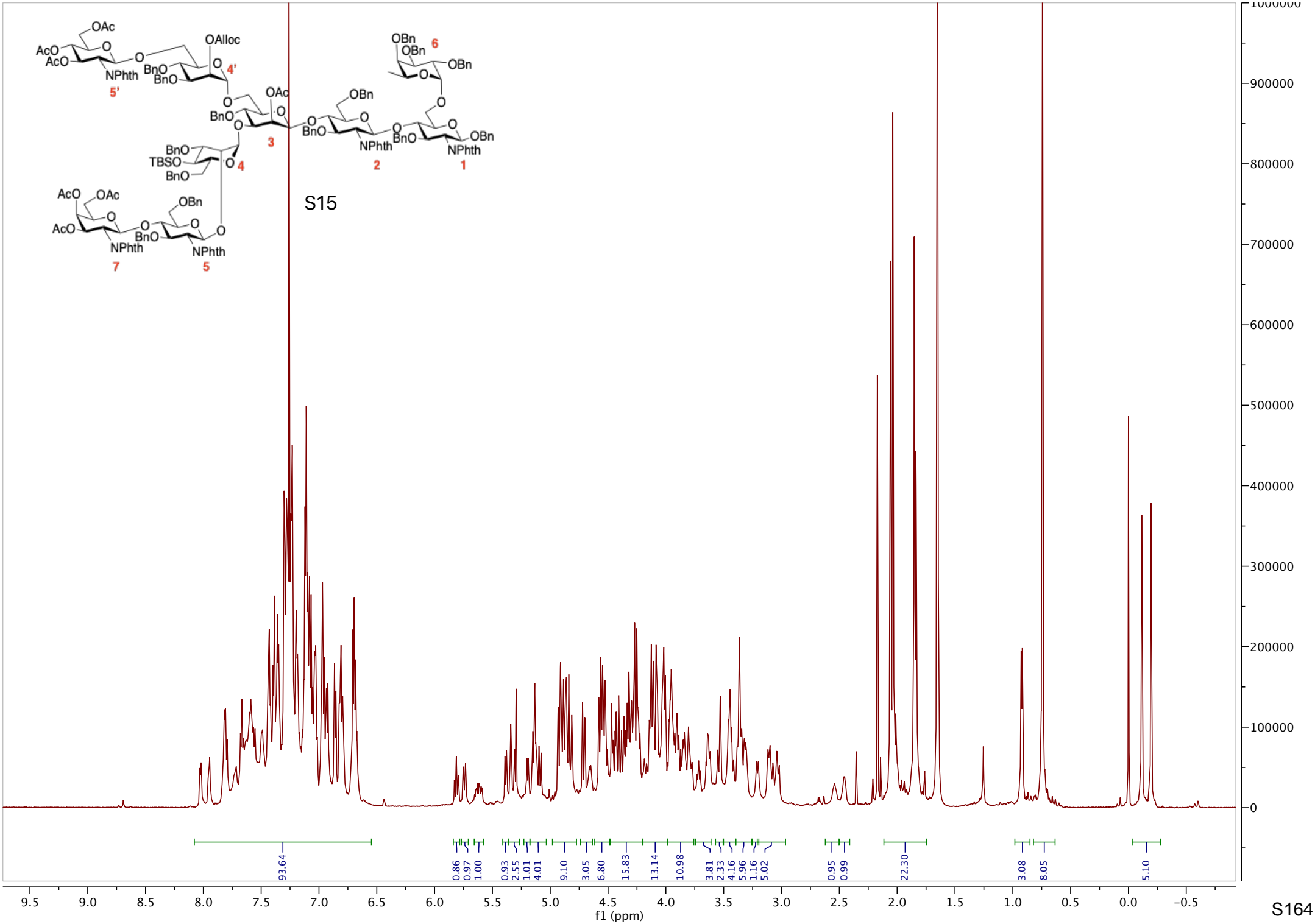

OAlloc
HO
BnO
BnO
4'
OAc
BnO
OBn
BnO
NPhth
BnO
OBn
NPhth
OBn
OBn
6
OBn
3
2
1
BnO
TBSO
BnO
4
AcO
OAc
AcO
OBn
BnO
NPhth
NPhth
7
5

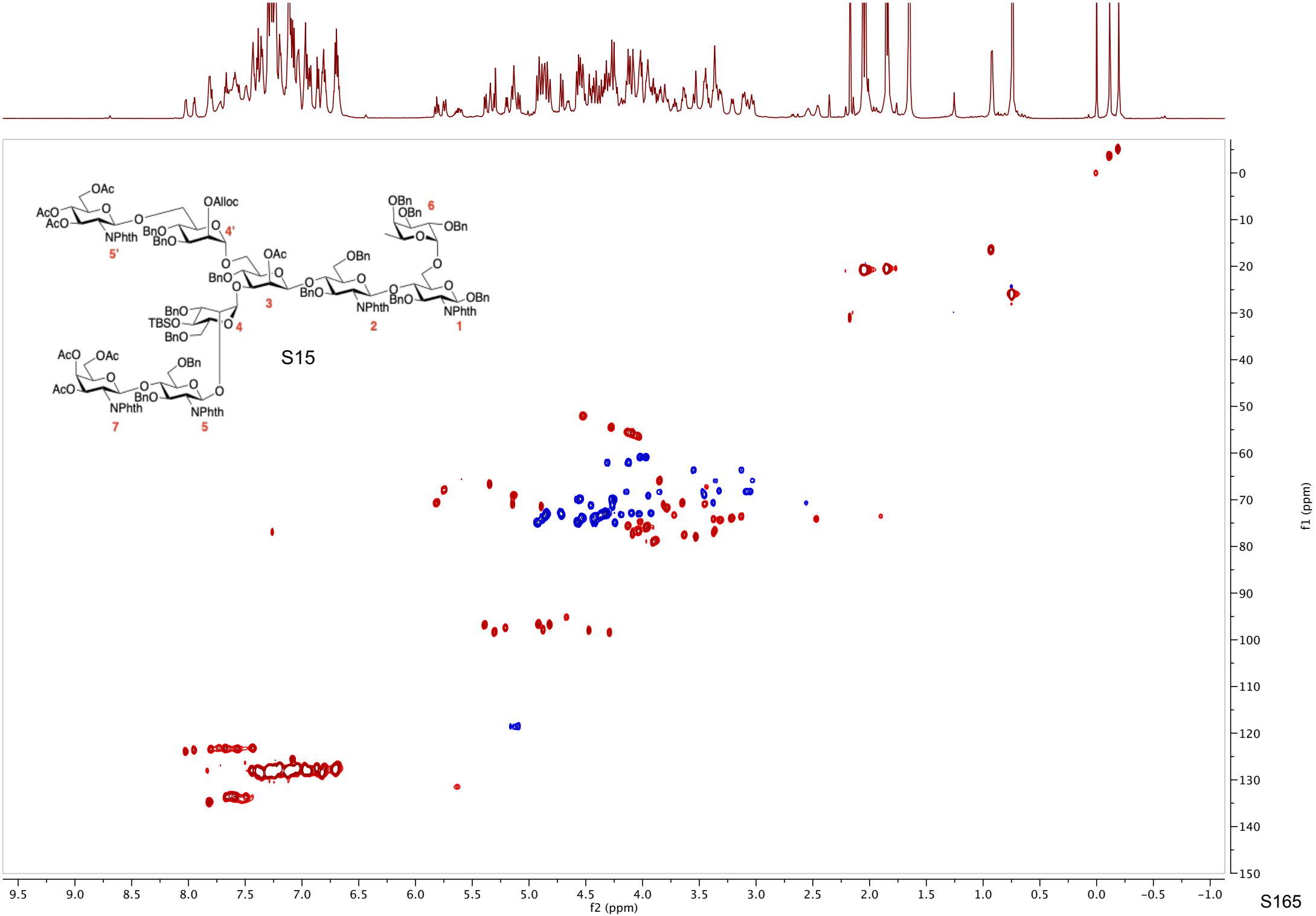
S14

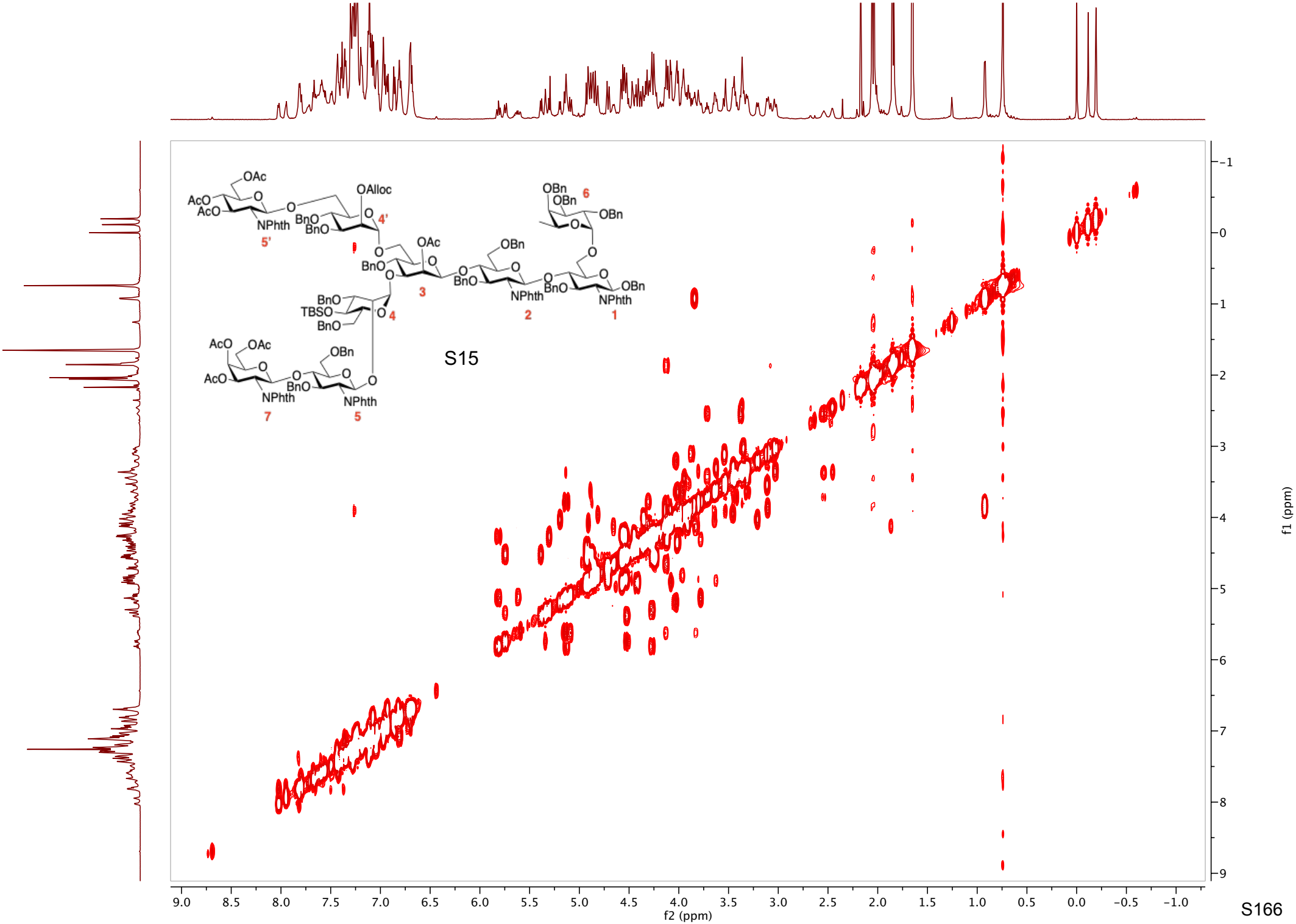
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
102.32
1.00
0.85
0.98
1.16
1.09
5.14
10.18
3.88
18.46
18.92
3.34
6.09
7.20
2.35
0.80
1.25
1.84
1.90
1.91
7.50
6.14
4.52
8.41
5.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

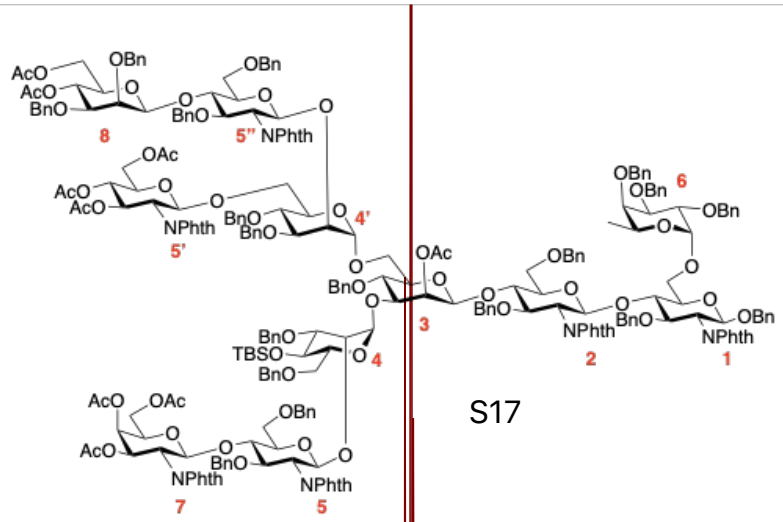

S14
f2 (ppm)
f1 (ppm)


S14
f2 (ppm)
f1 (ppm)


S15
f1 (ppm)


S15
f2 (ppm)
f1 (ppm)

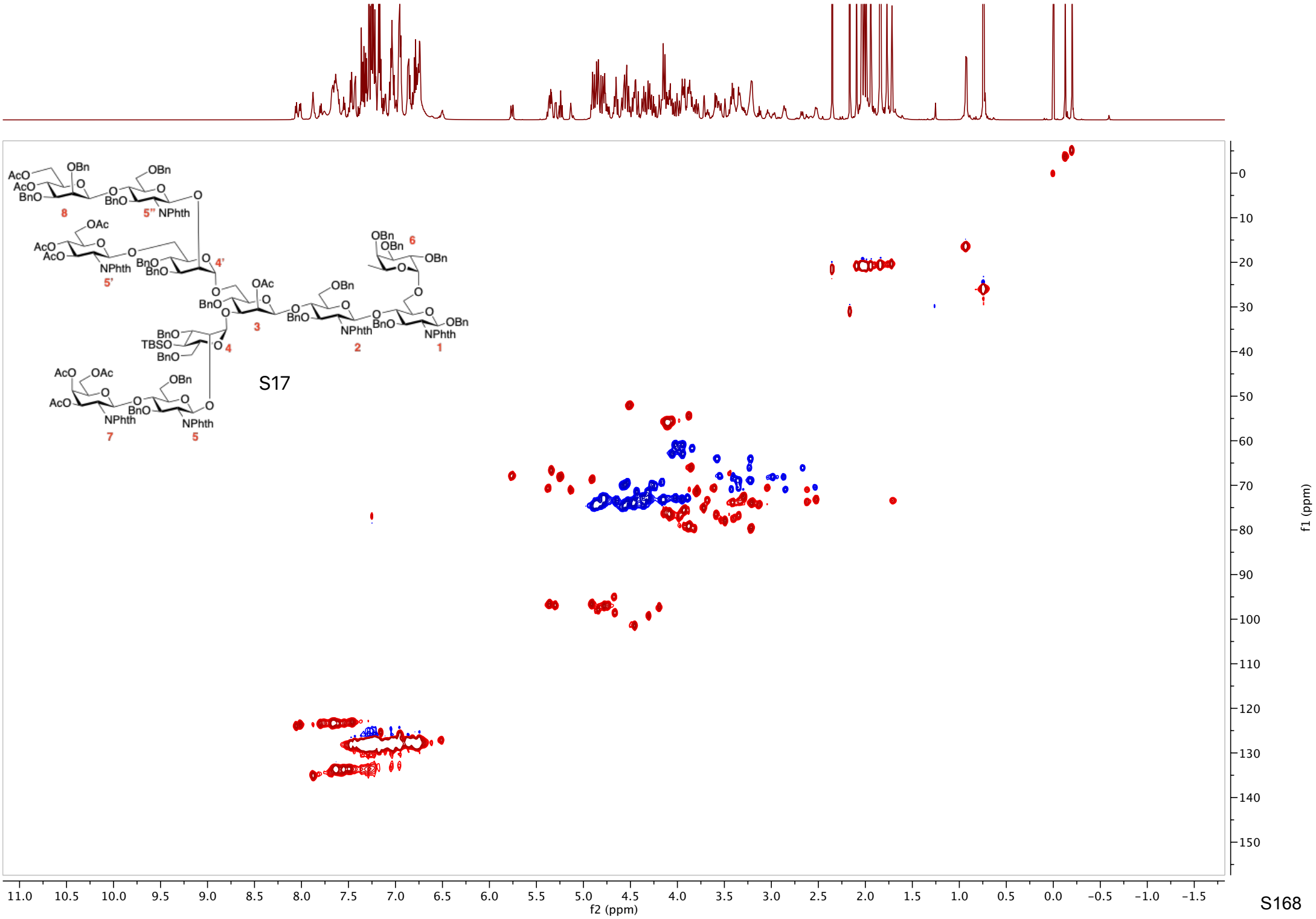

S15
f2 (ppm)
f1 (ppm)

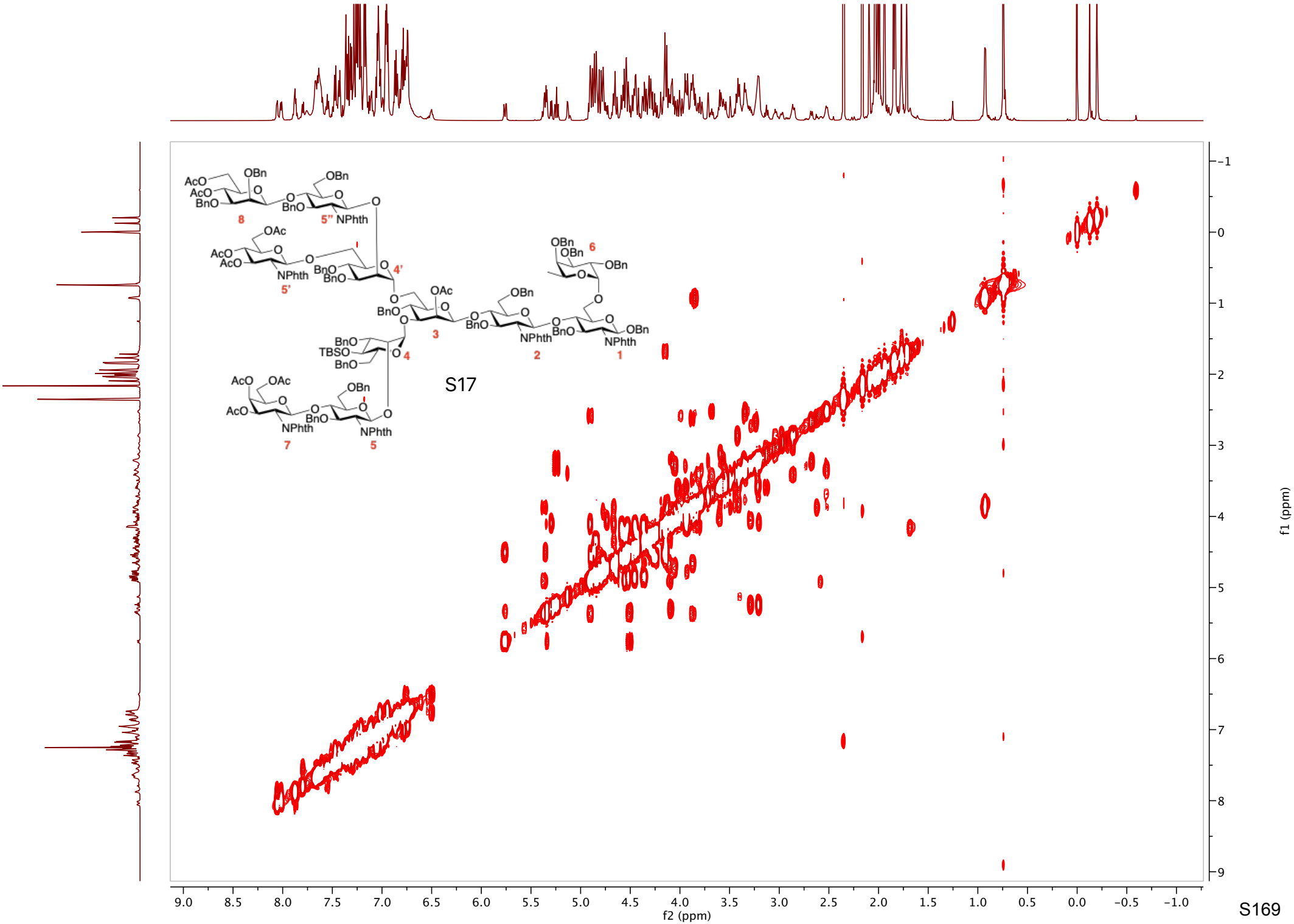


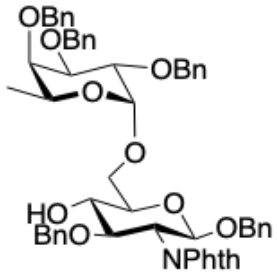
S17

f1 (ppm)

S167

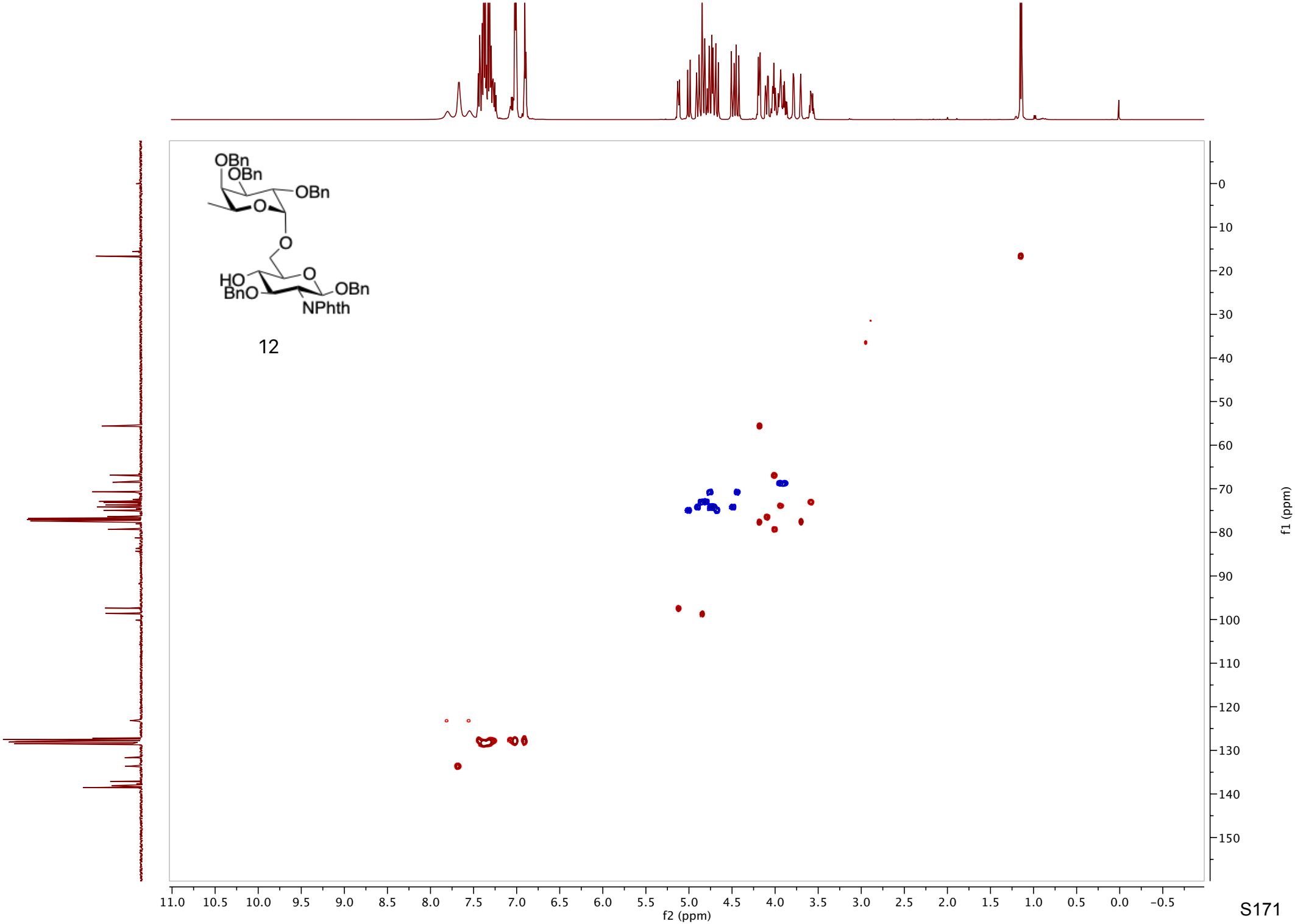

S17
f2 (ppm)
f1 (ppm)

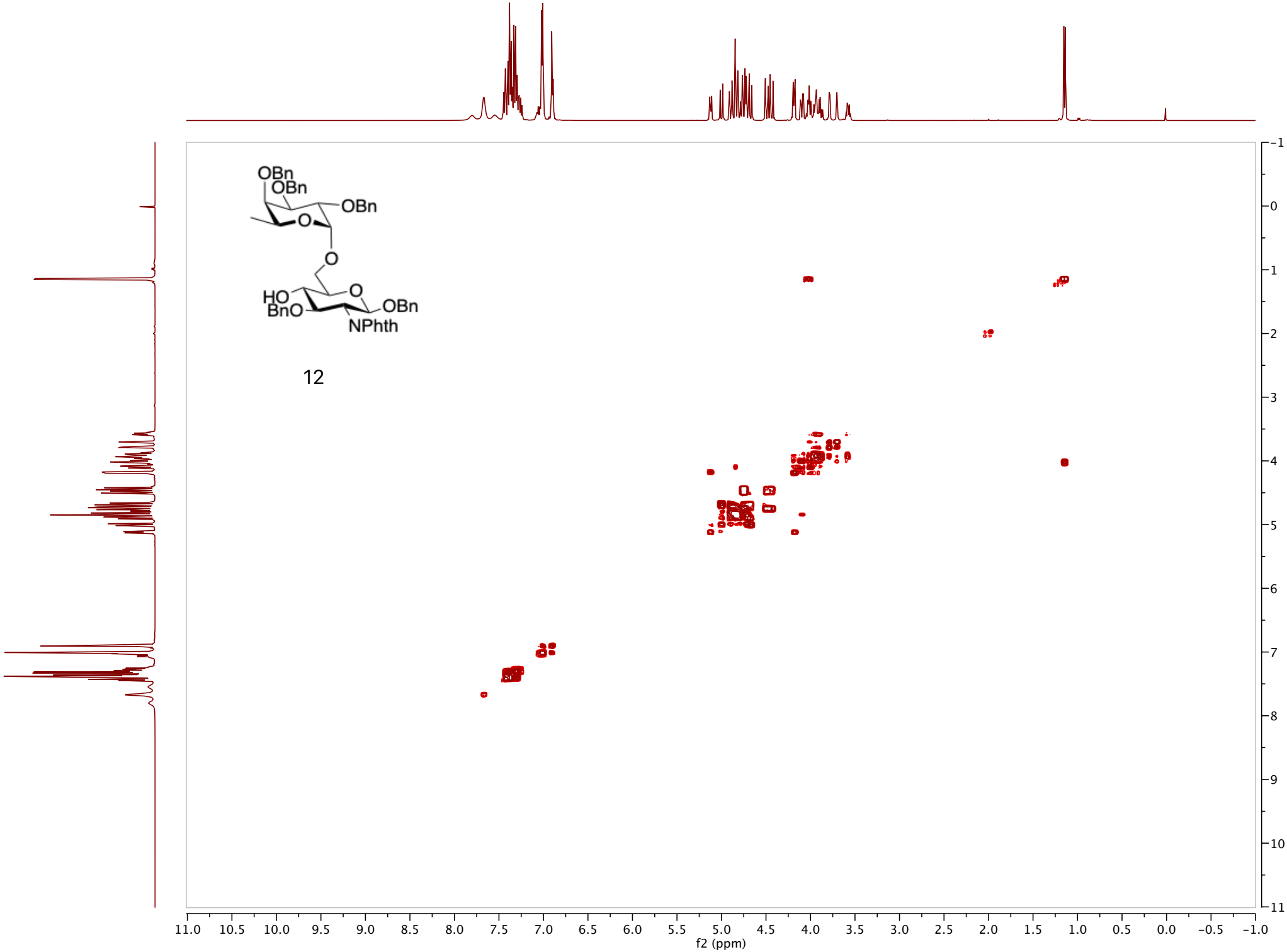

S17
f2 (ppm)
f1 (ppm)

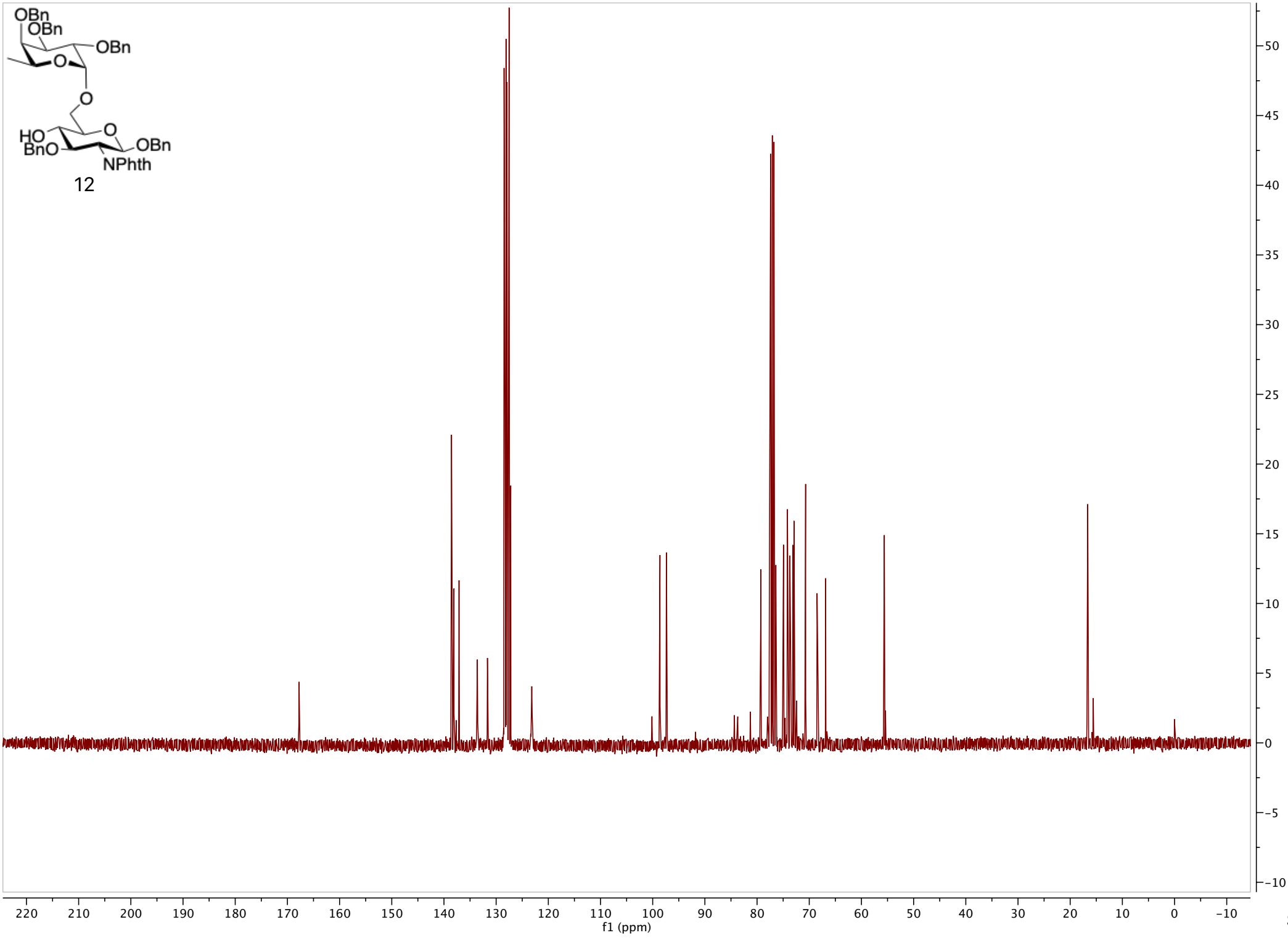

OBn
OBn
OBn
O
O
HO
BnO
O
OBn
NPhth

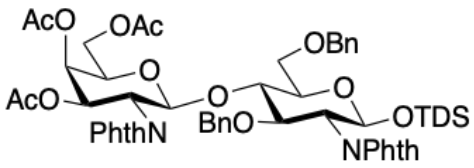
12

27.08
0.94
1.03
3.91
4.68
2.29
1.83
1.13
2.05
2.96
0.96
0.97
1.00
2.90
f1 (ppm)


OBn
OBn
OBn
O
O
HO
BnO
O
OBn
NPhth
12
f2 (ppm)
f1 (ppm)

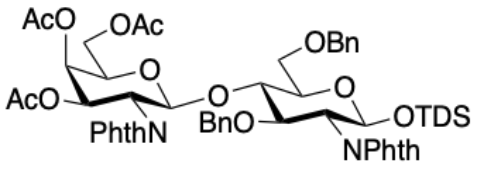

OBn
OBn
OBn
O
O
HO
BnO
O
OBn
NPhth
12
f2 (ppm)
f1 (ppm)


OBn
OBn
OBn
O
O
HO
BnO
O
OBn
NPhth
12
50
45
40
35
30
25
20
15
10
5
0
−5
−10
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

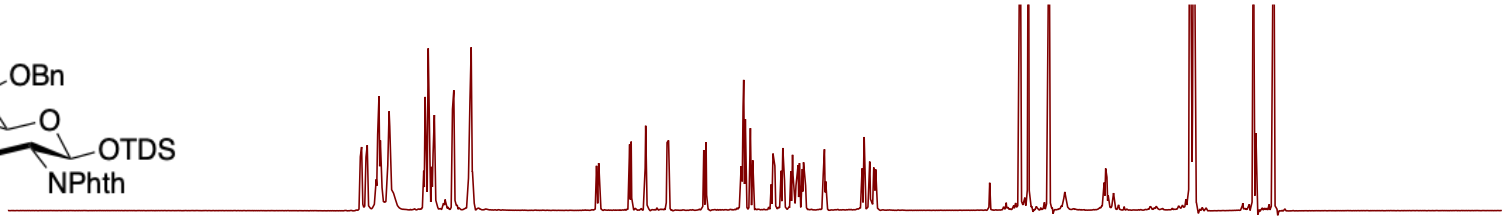

AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OTDS
NPhth

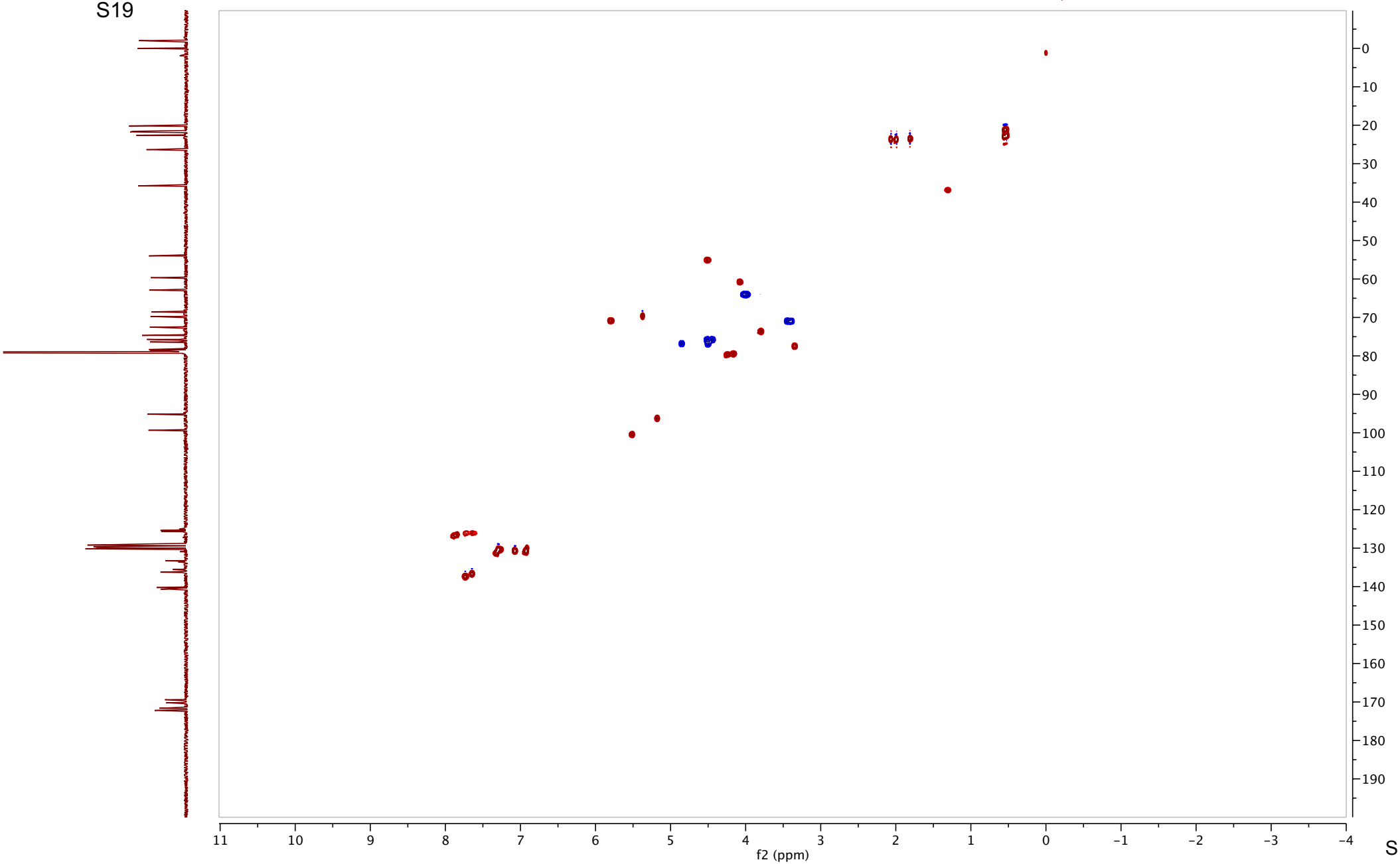
S19

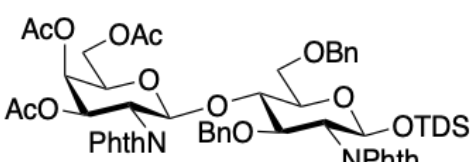
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
19.17
1.00
1.01
0.98
0.98
1.01
2.92
1.03
1.10
1.07
3.10
1.00
2.97
9.29
1.17
11.81
6.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
f1 (ppm)


AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OTDS
NPhth

S19



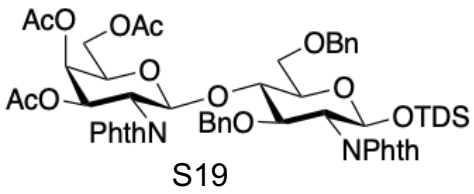

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
−4
f2 (ppm)



S19

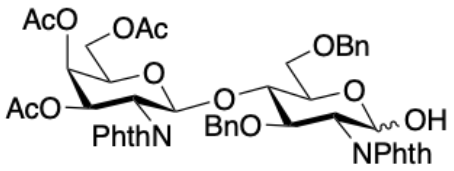
f2 (ppm)

f1 (ppm)


AcO
OAc
O
AcO
O
PhthN
BnO
OBn
O
OTDS
NPhth

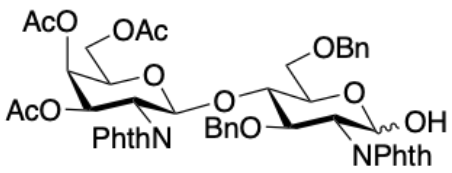
S19

1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

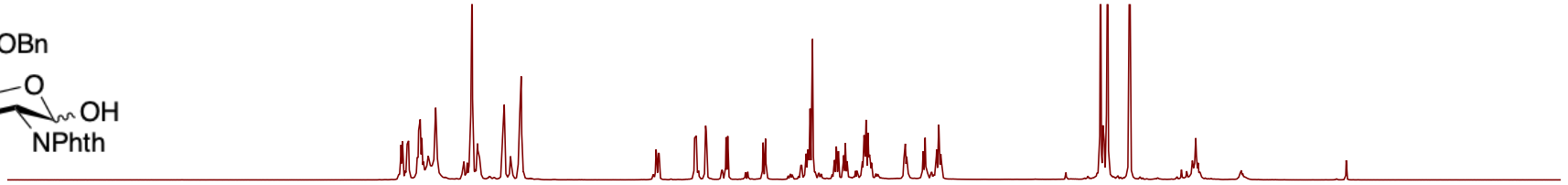

AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OH
NPhth

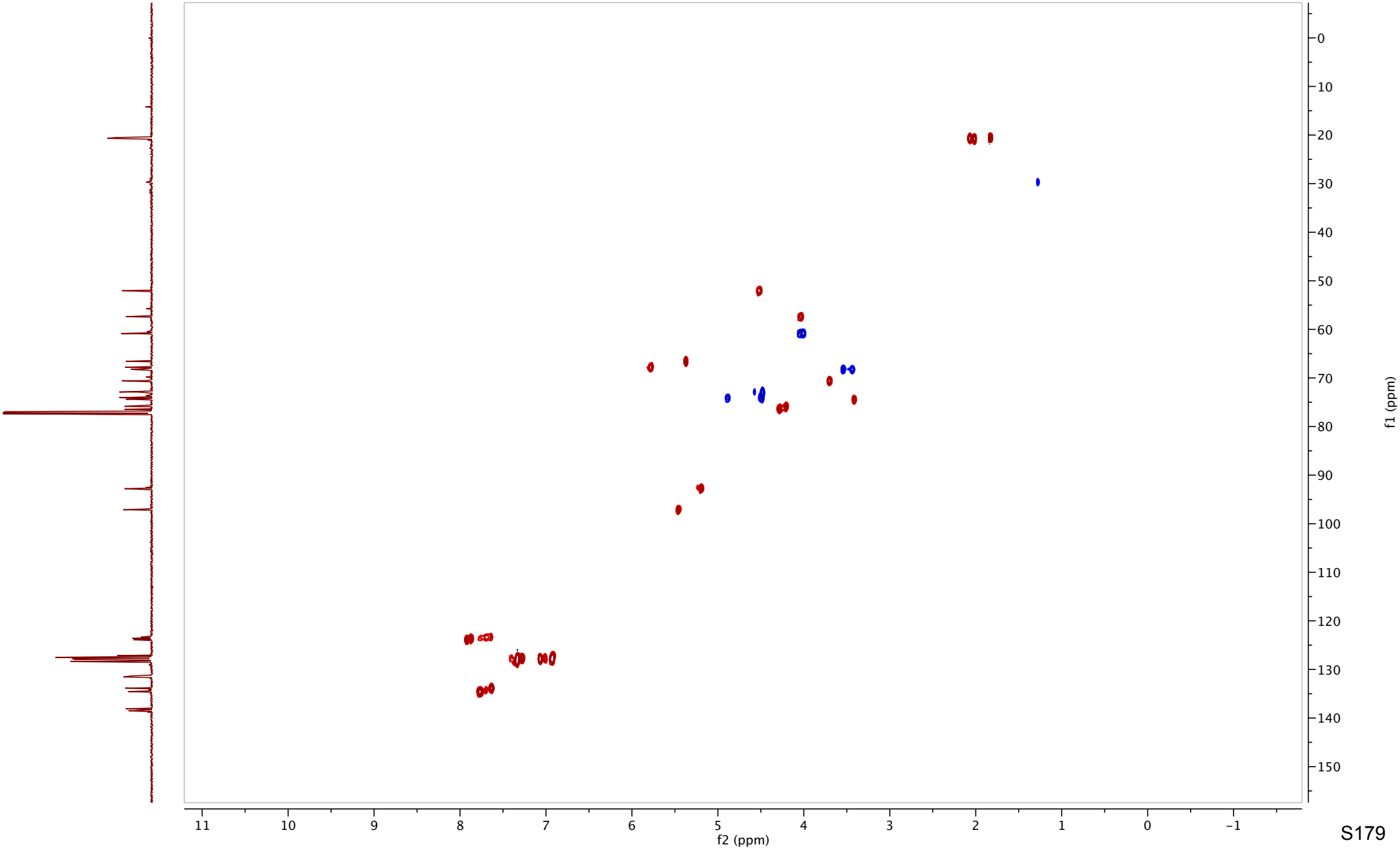
S20

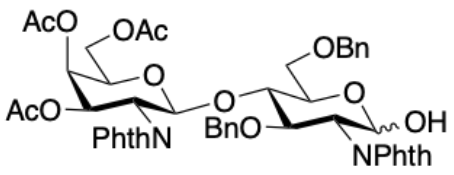
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
21.42
1.00
1.11
1.09
0.95
1.01
4.25
1.20
1.07
3.36
1.24
3.40
10.71
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)


AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OH
NPhth

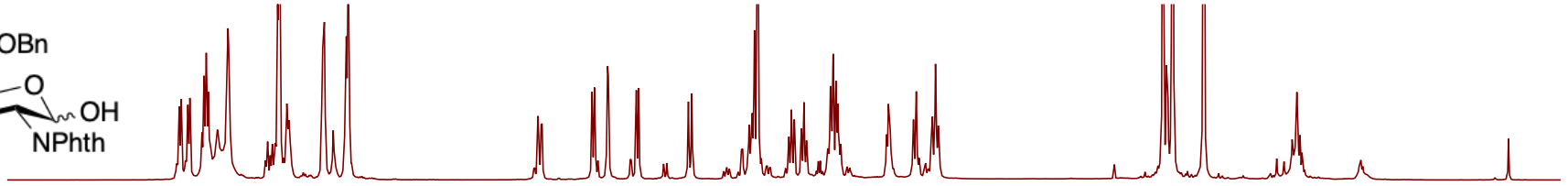
S20

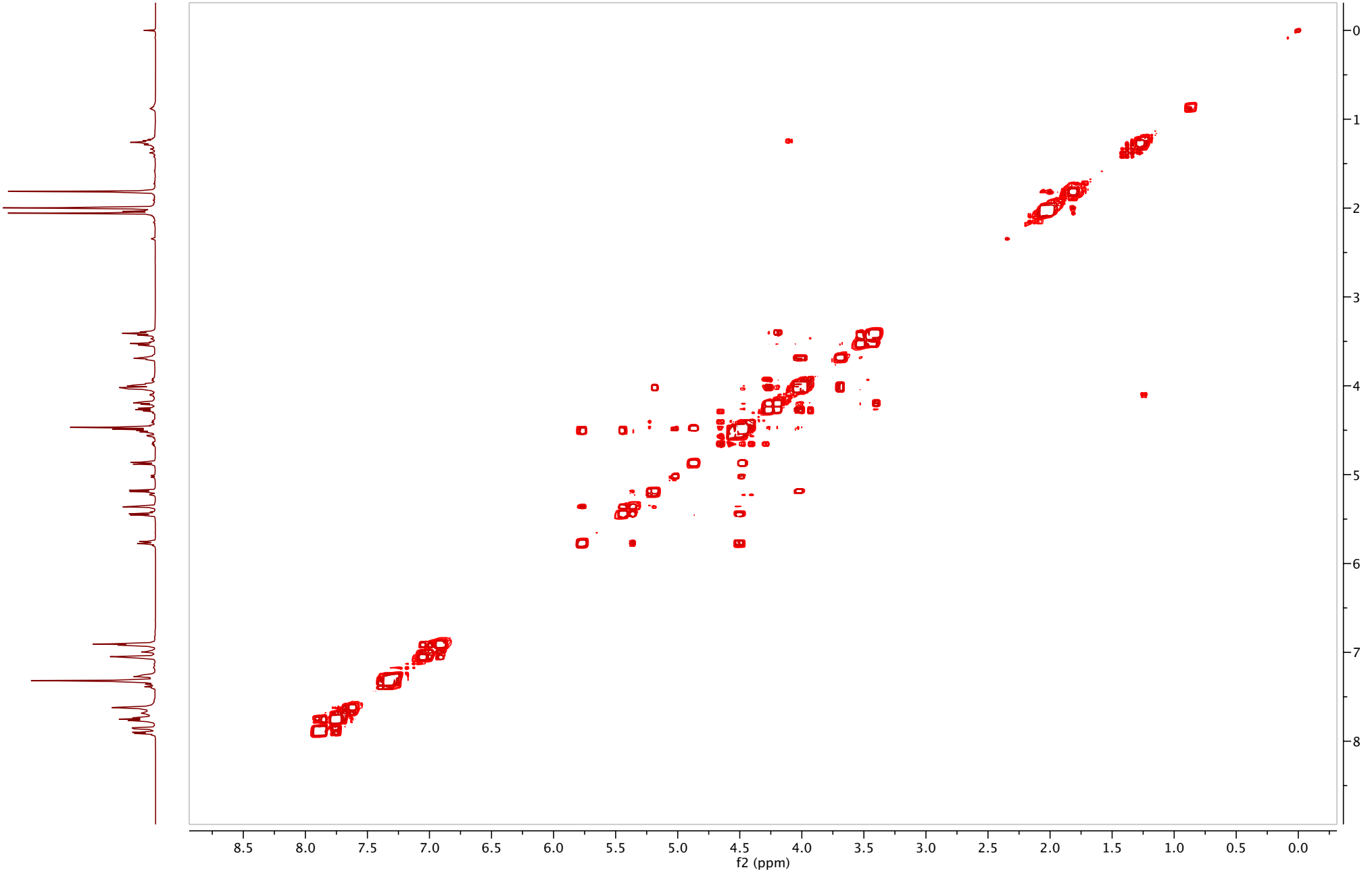


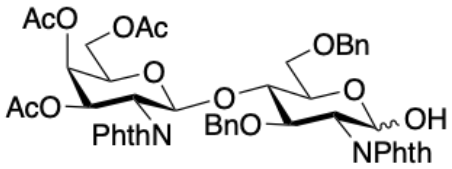

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
11
10
9
8
7
6
5
4
3
2
1
0
−1
f2 (ppm)


AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OH
NPhth

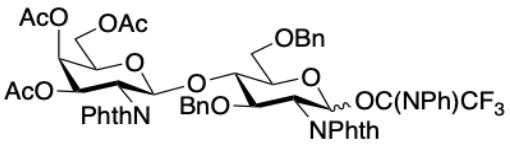
S20




8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)

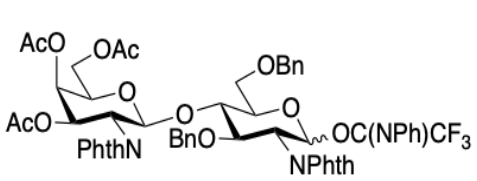


S20


AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OC(NPh)CF3
NPhth

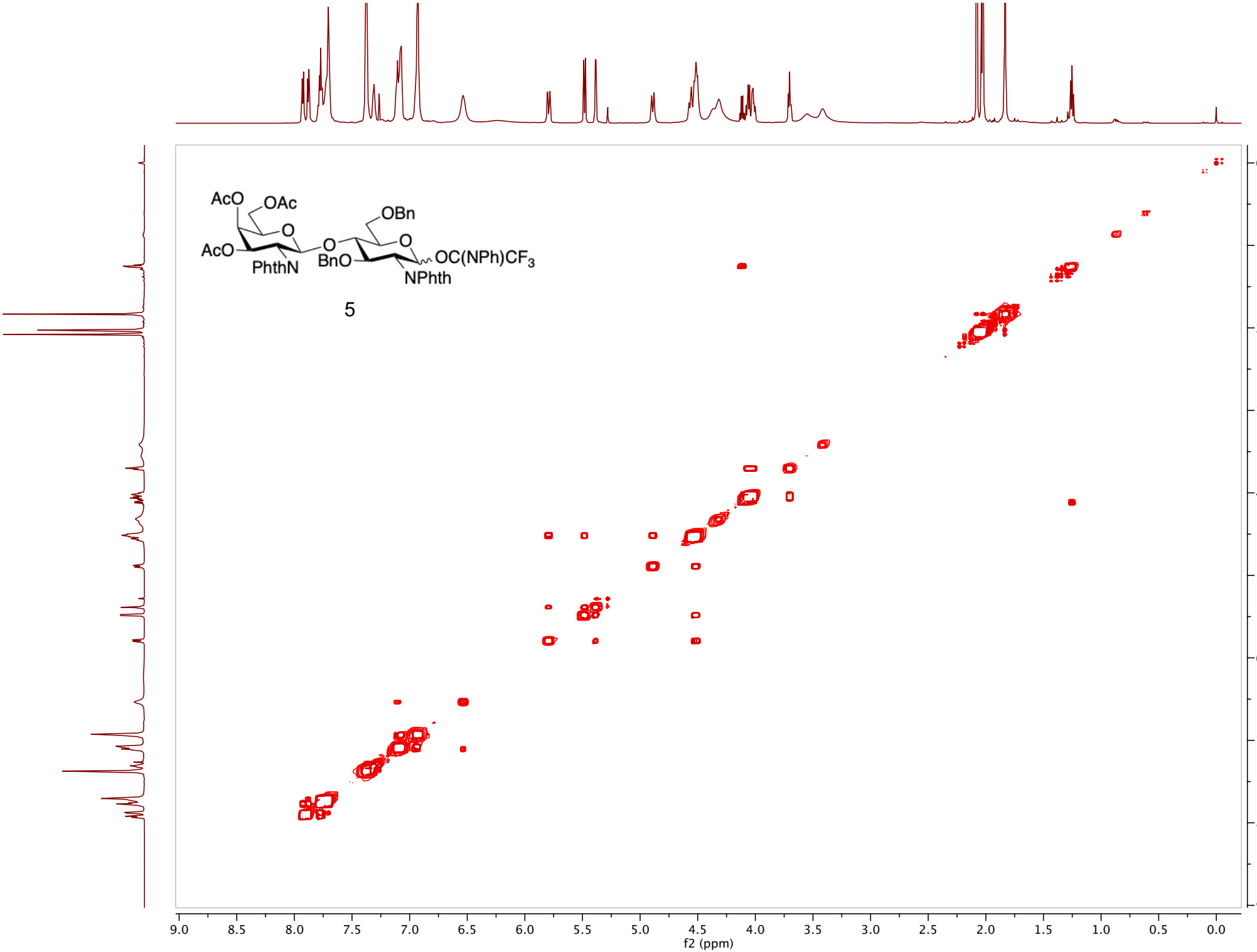
5

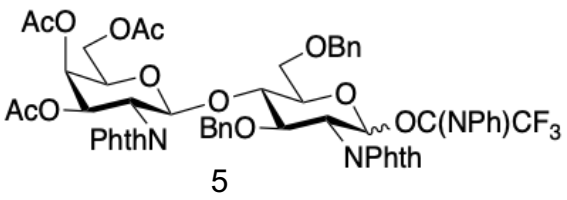
22.59
1.76
1.00
1.00
0.99
1.00
3.97
2.80
2.21
1.06
2.73
10.57
f1 (ppm)


AcO
OAc
AcO
O
PhthN
O
BnO
OBn
O
NPhth
OC(NPh)CF3

5

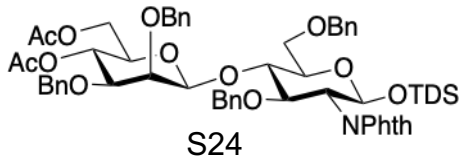
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)


AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OC(NPh)CF3
NPhth
5
f2 (ppm)
f1 (ppm)


AcO
OAc
O
AcO
PhthN
O
BnO
OBn
O
OC(NPh)CF3
NPhth

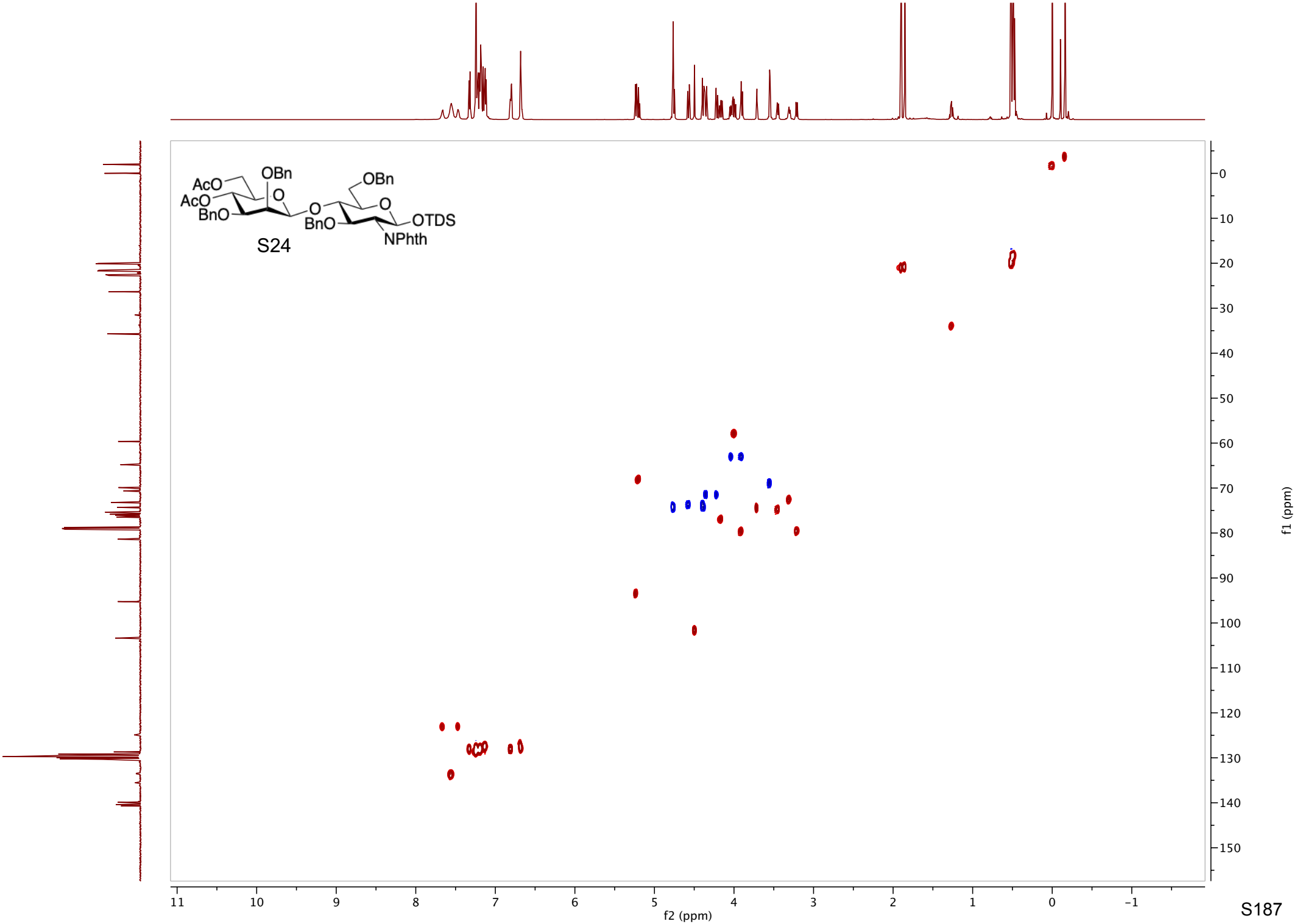
5

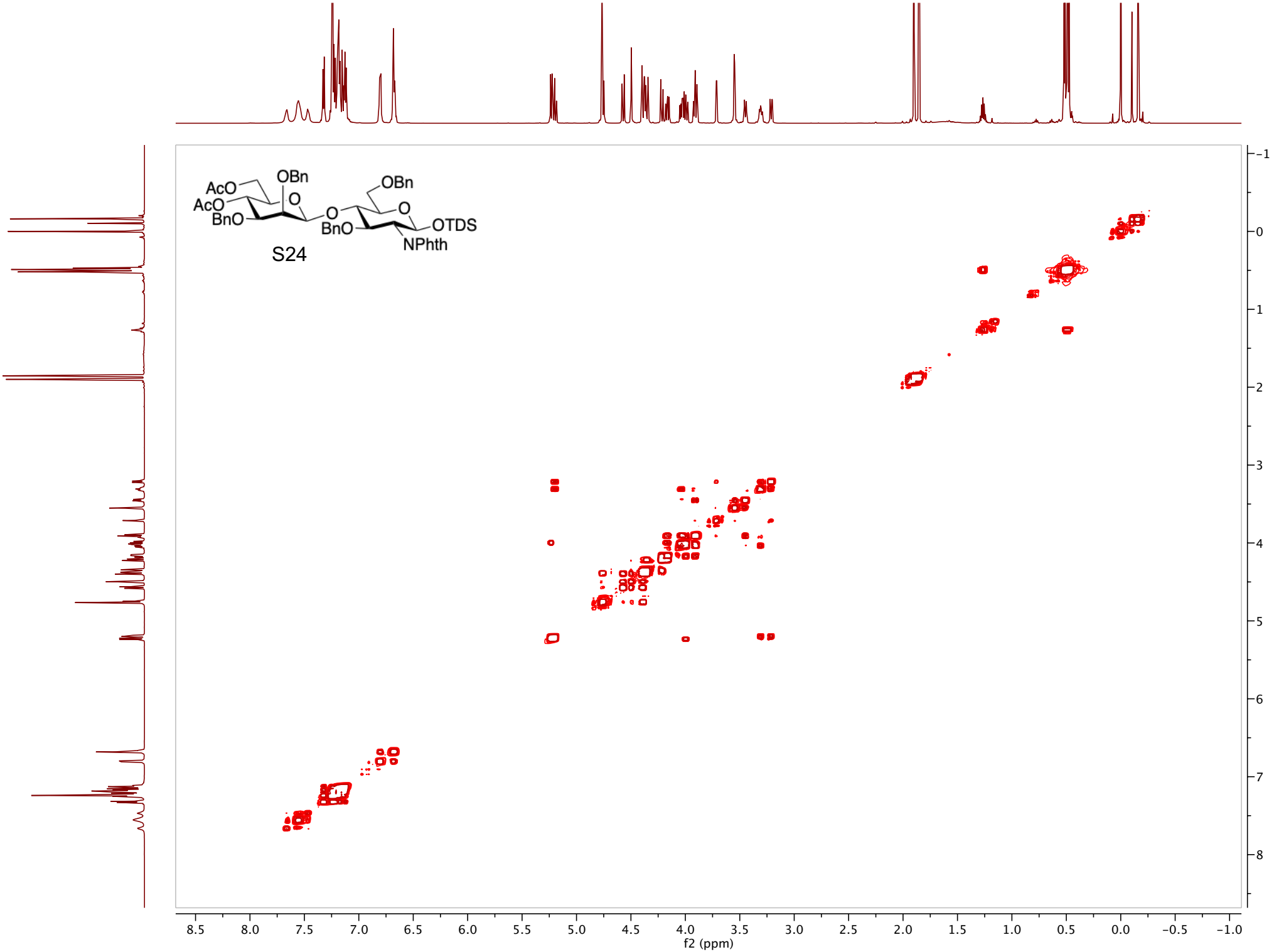
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

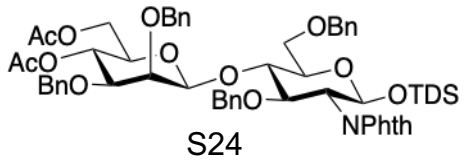

AcO
AcO
BnO
OBn
O
O
BnO
OBn
O
OTDS
NPhth

S24

6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
−500000
27.04
2.08
2.99
1.00
1.04
3.30
1.02
1.07
2.13
1.95
0.96
1.77
1.04
1.07
0.99
6.04
1.18
12.10
7.16
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

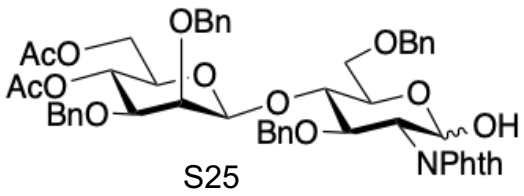

AcO
AcO
BnO
OBn
O
O
BnO
OBn
O
OTDS
NPhth
S24
f2 (ppm)
f1 (ppm)


AcO
AcO
BnO
OBn
O
O
BnO
OBn
O
OTDS
NPhth
S24
f2 (ppm)
f1 (ppm)


AcO
AcO
BnO
OBn
O
O
BnO
OBn
O
OTDS
NPhth

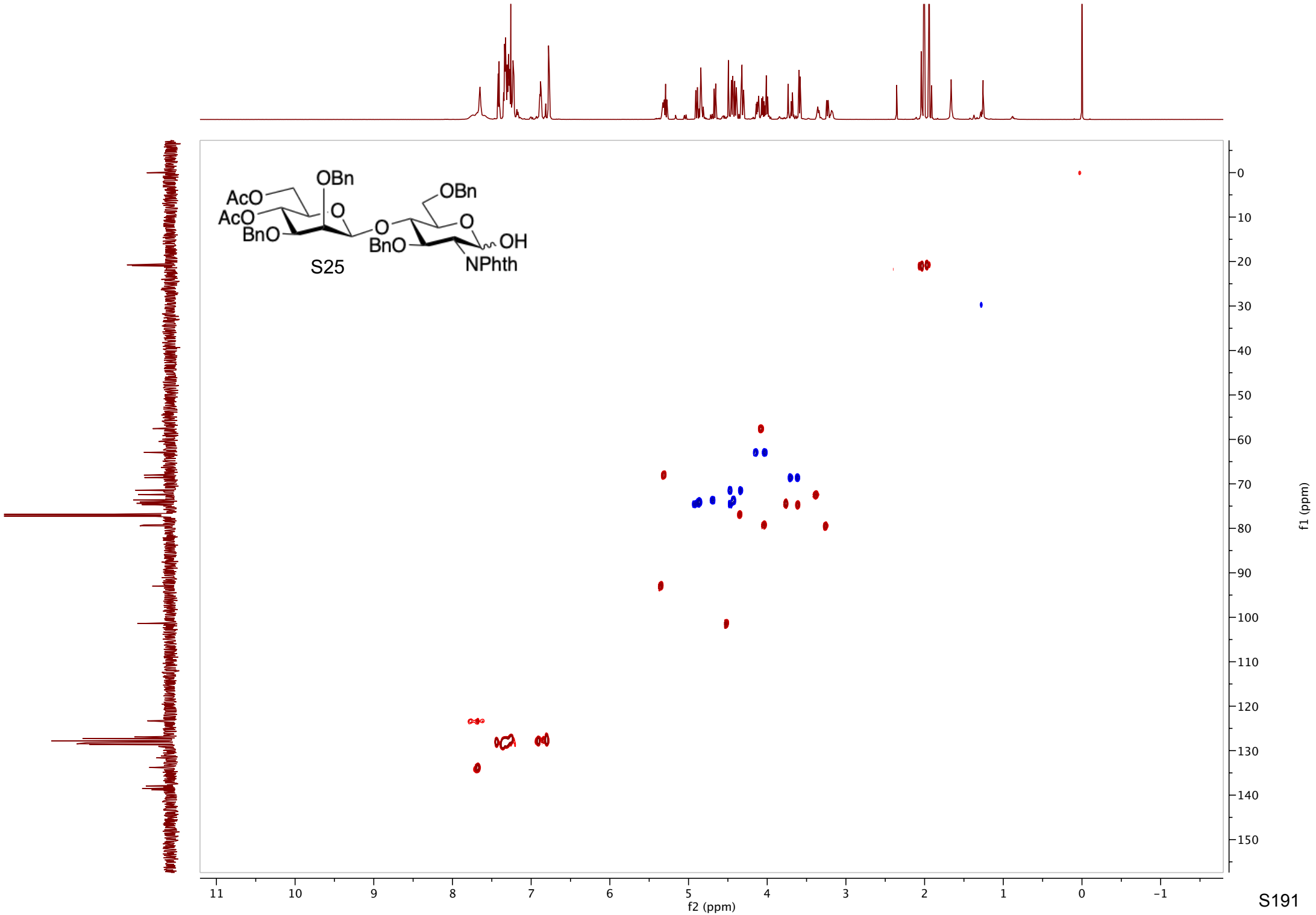
S24

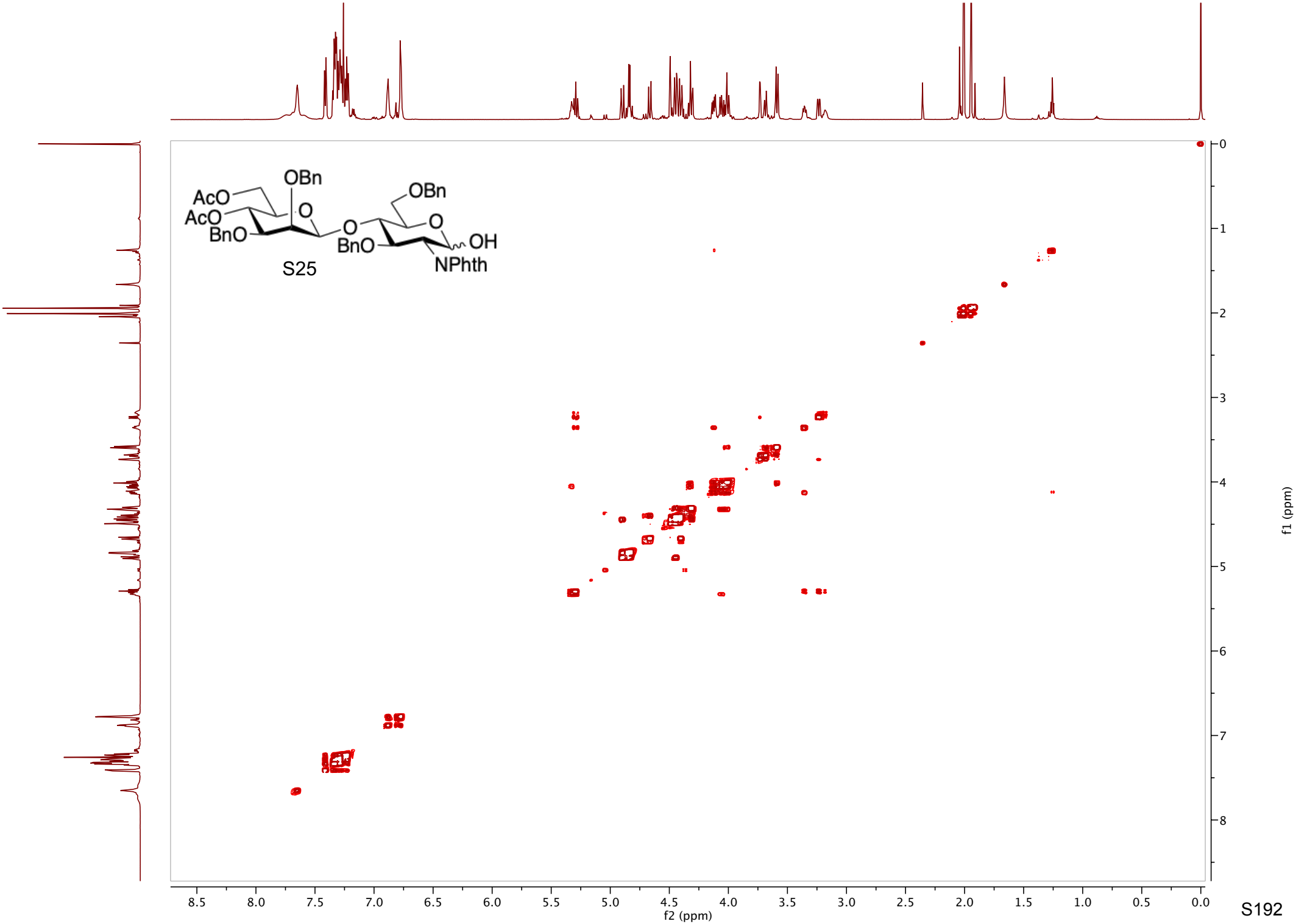
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

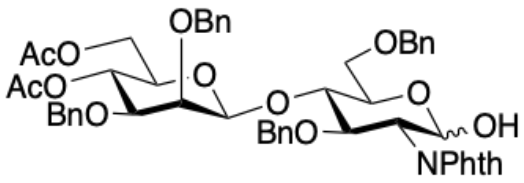

OBn
AcO
AcO
BnO
O
O
OBn
O
BnO
OH
NPhth

S25

29.55
2.33
3.29
1.00
4.54
1.94
4.70
1.11
1.00
1.93
1.03
1.02
6.05
f1 (ppm)

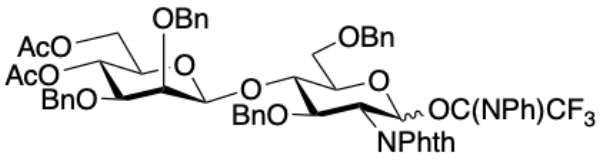

OBn
AcO
AcO
BnO
O
O
OBn
O
BnO
OH
NPhth
S25
f2 (ppm)
f1 (ppm)


OBn
AcO
AcO
BnO
O
O
OBn
O
BnO
OH
NPhth
S25
f2 (ppm)
f1 (ppm)


OBn
AcO
AcO
O
BnO
O
OBn
O
BnO
OH
NPhth

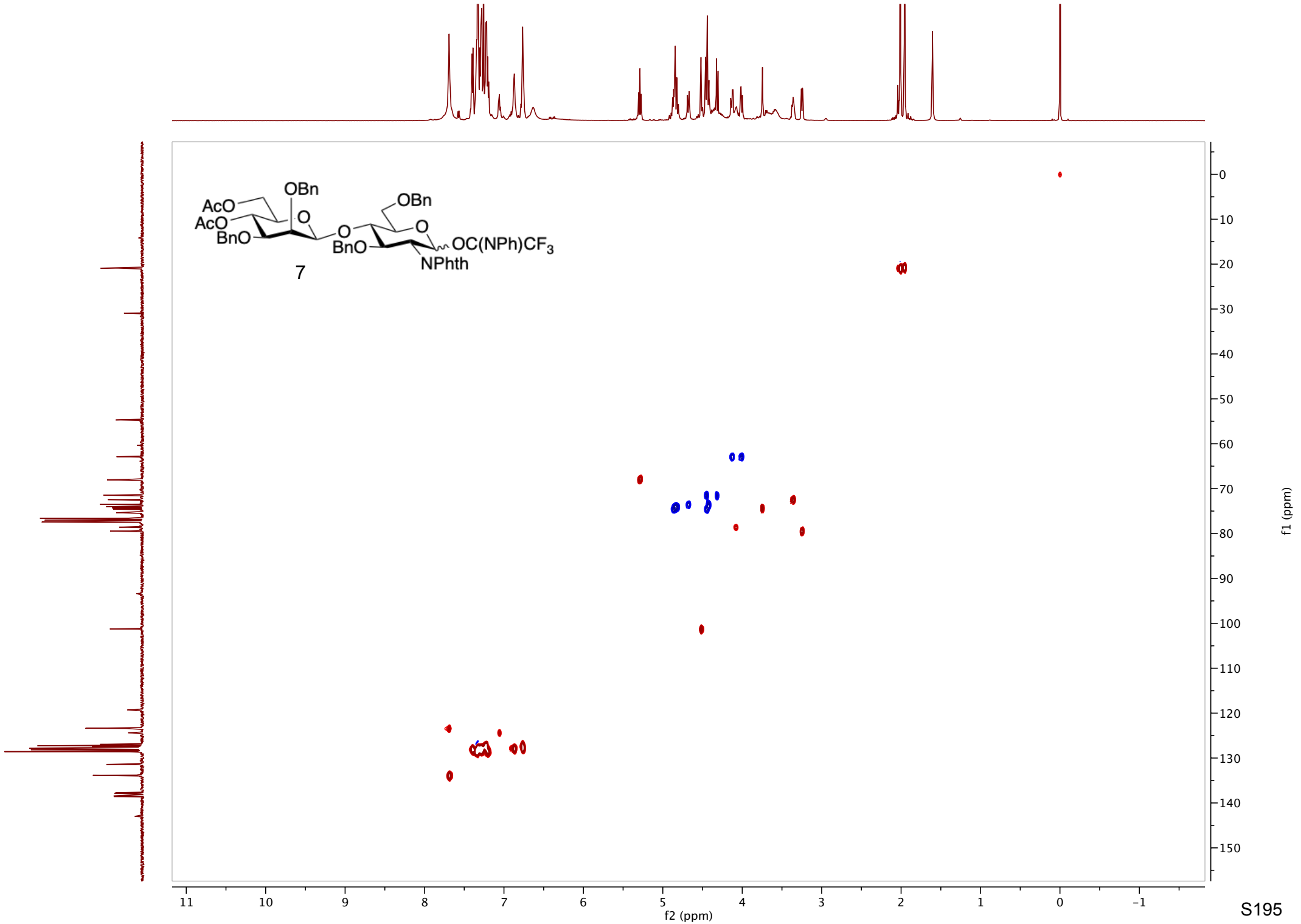
S25

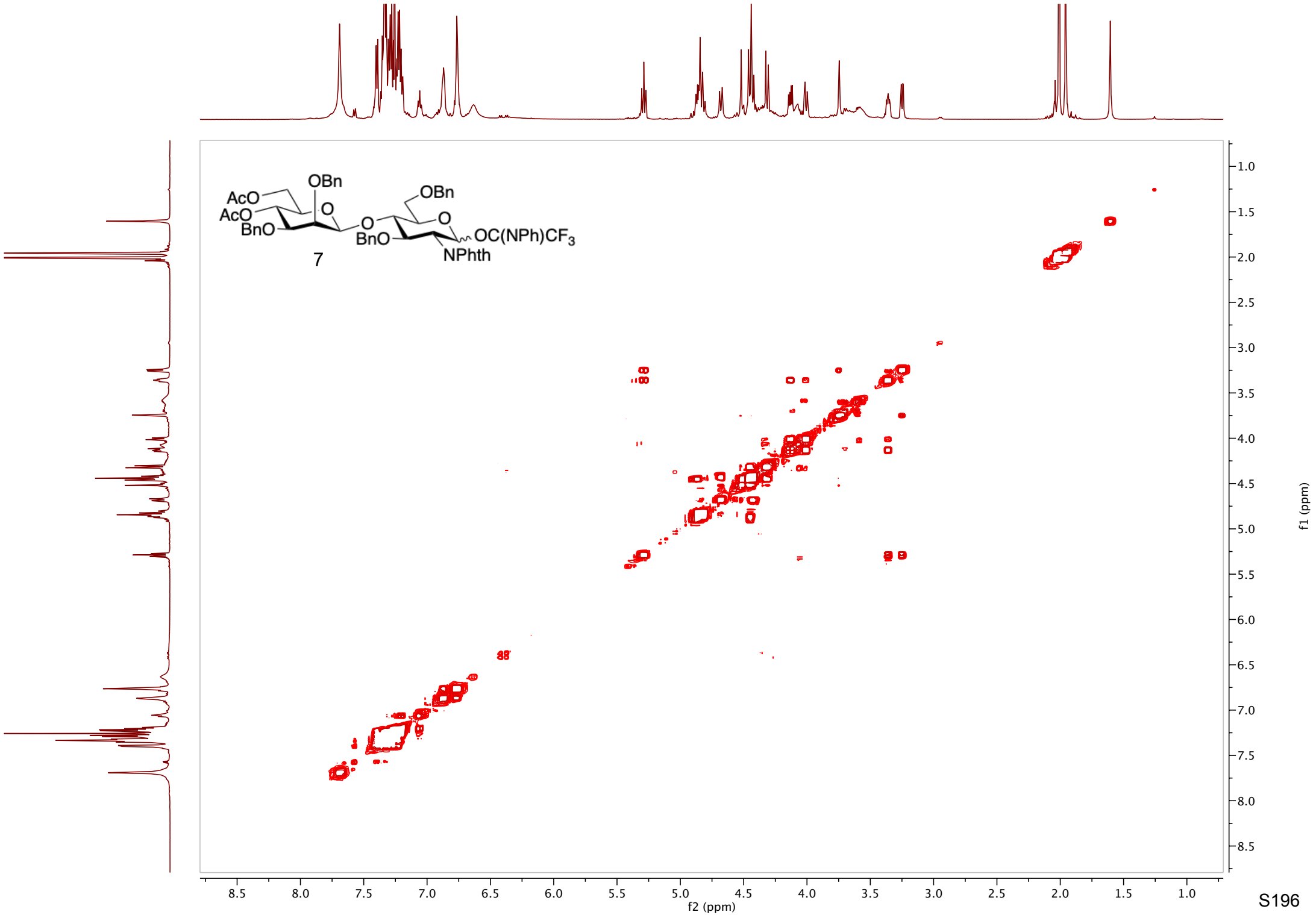
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
−20000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

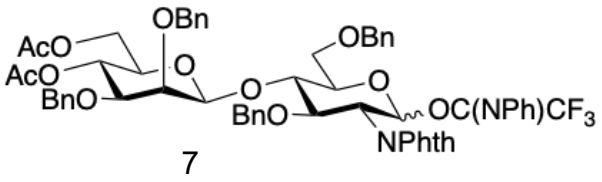

AcO
AcO
BnO
OBn
O
O
BnO
OBn
O
OC(NPh)CF3
NPhth

7

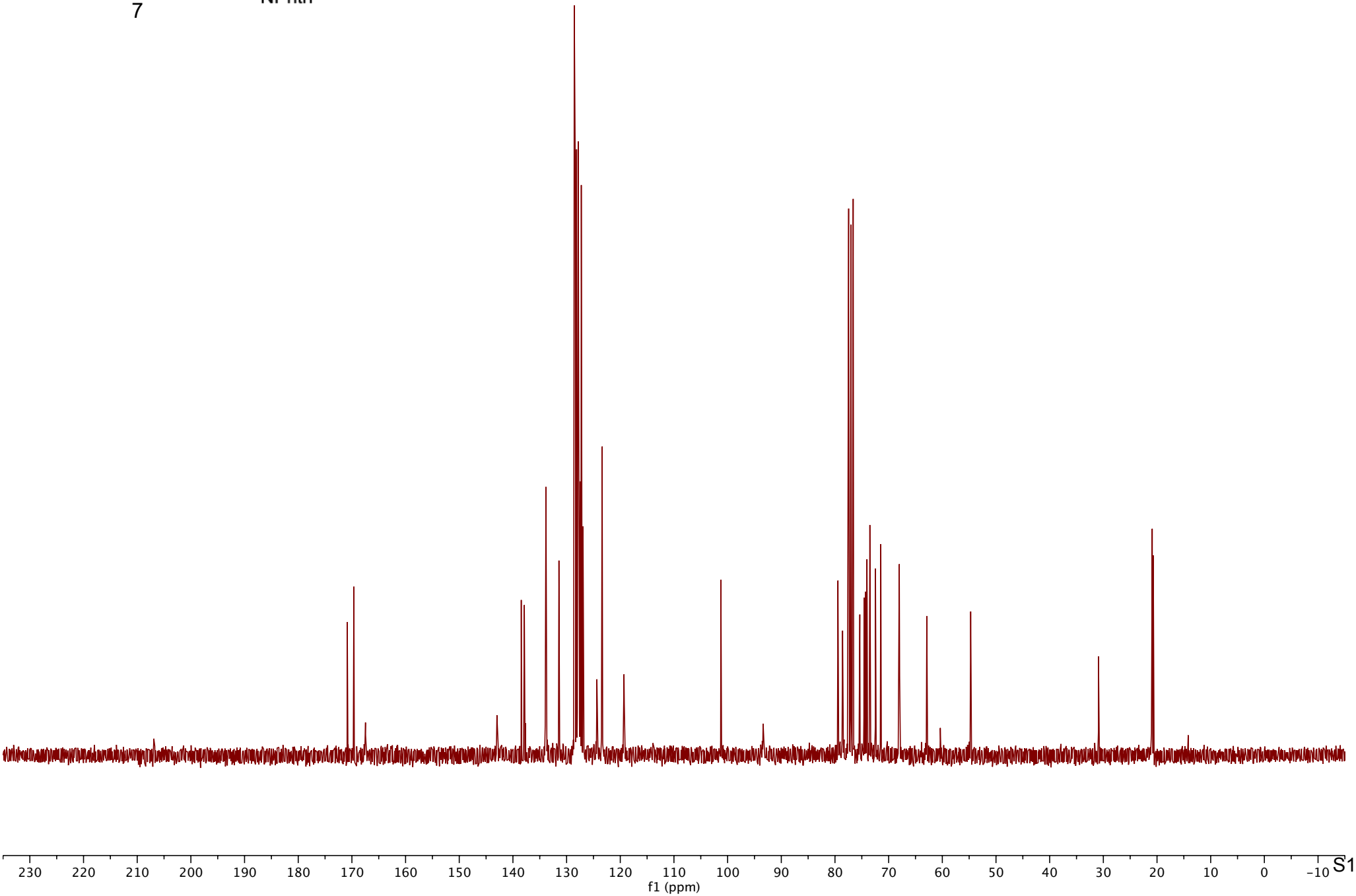
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
28.06
1.32
1.00
2.72
0.95
0.88
5.25
3.14
1.04
1.01
0.93
6.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

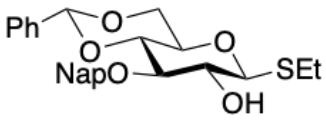

AcO
AcO
BnO
OBn
O
O
BnO
OBn
O
OC(NPh)CF3
NPhth
7
f2 (ppm)
f1 (ppm)


OBn
AcO
AcO
BnO
O
O
OBn
O
BnO
OC(NPh)CF3
NPhth
7
f2 (ppm)
f1 (ppm)


AcO
AcO
BnO
OBn
O
O
BnO
OBn
O
OC(NPh)CF3
NPhth

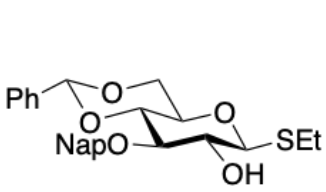
7


230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Ph
O
O
O
NapO
SEt
OH

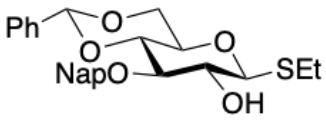
S27

11.38
1.00
0.96
0.97
1.00
1.01
3.13
1.01
1.12
1.97
3.05
f1 (ppm)

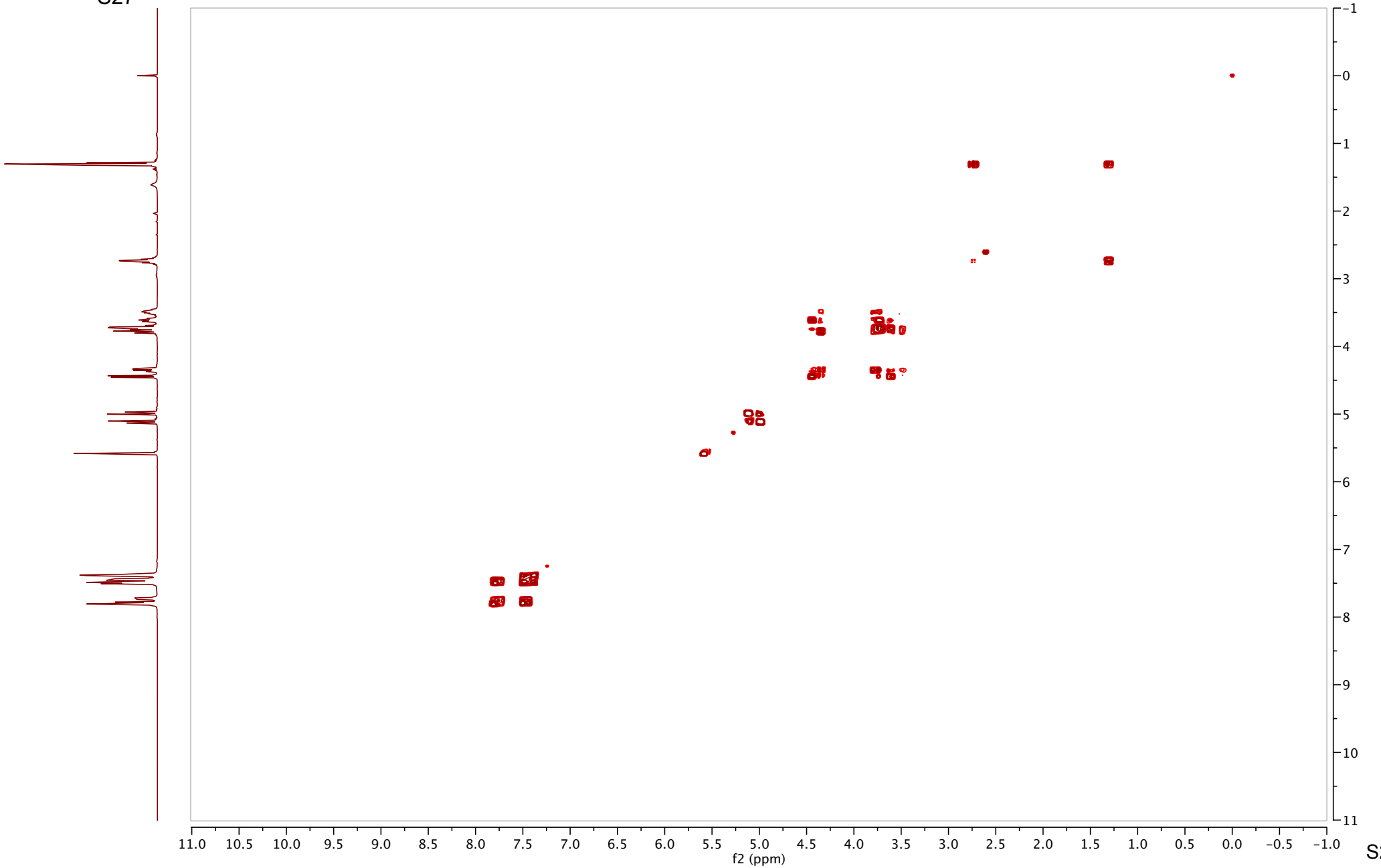

Ph
O
O
O
NapO
SEt
OH

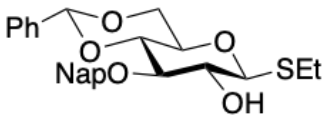
S27

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)

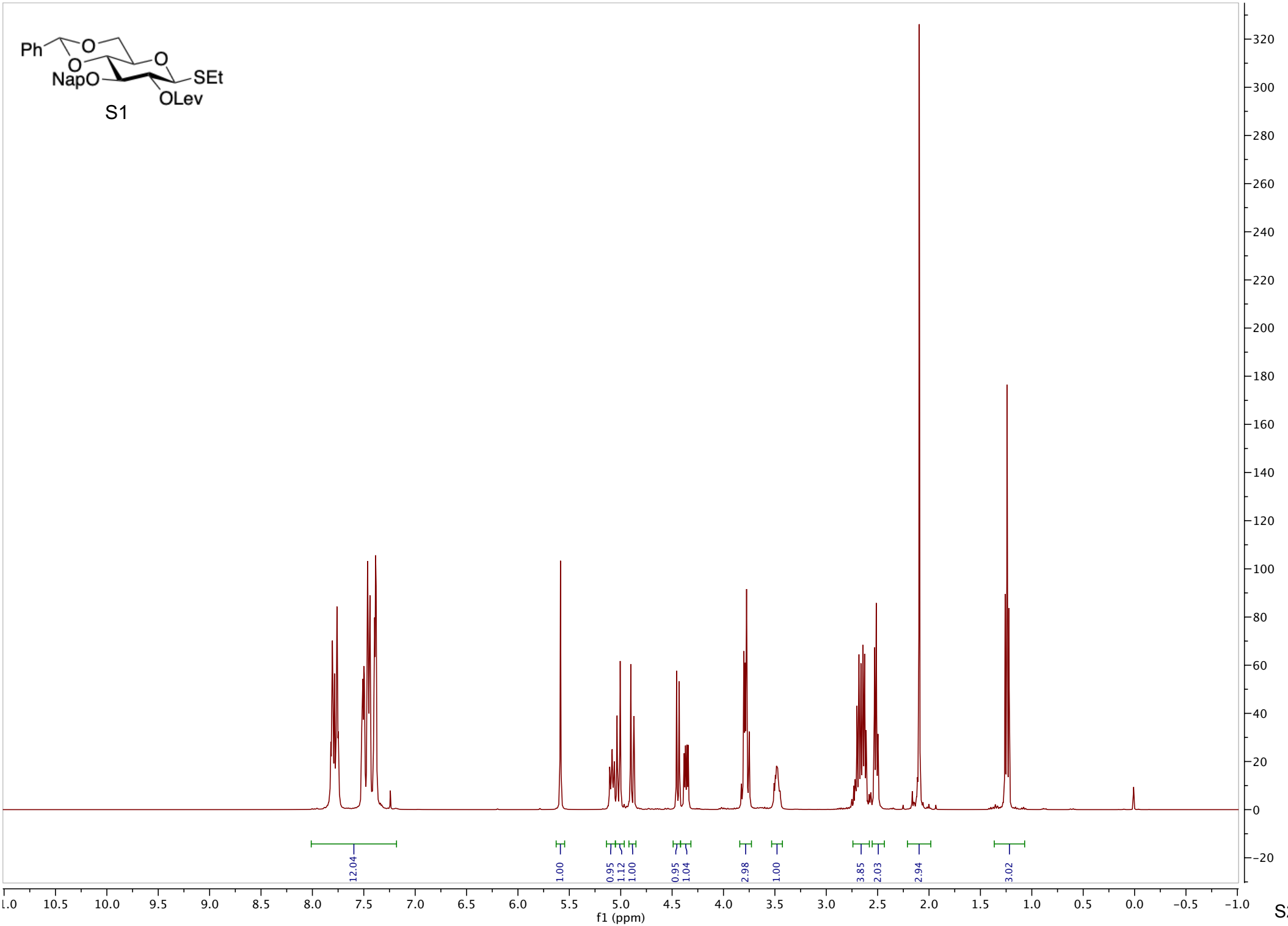


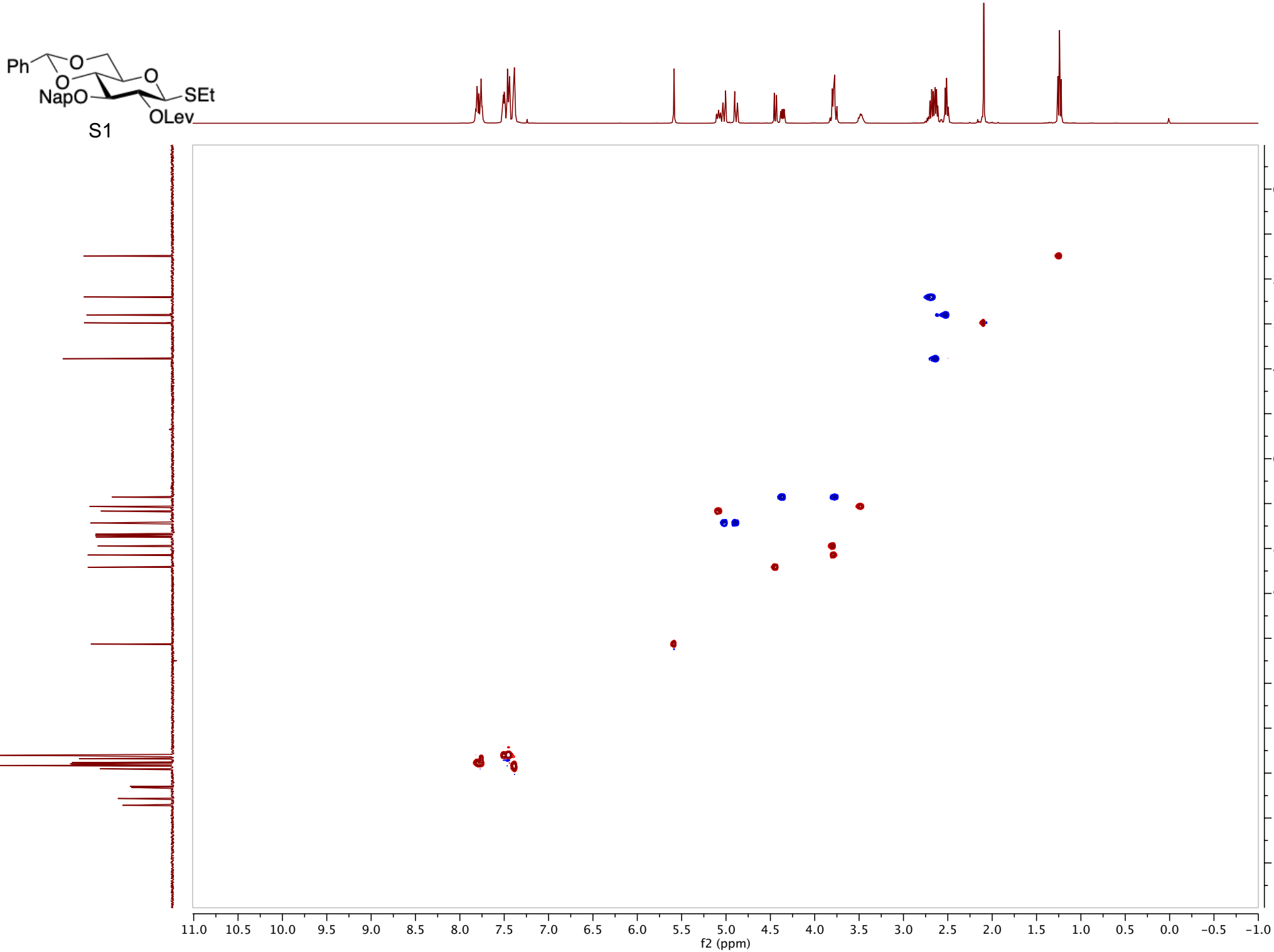
S27

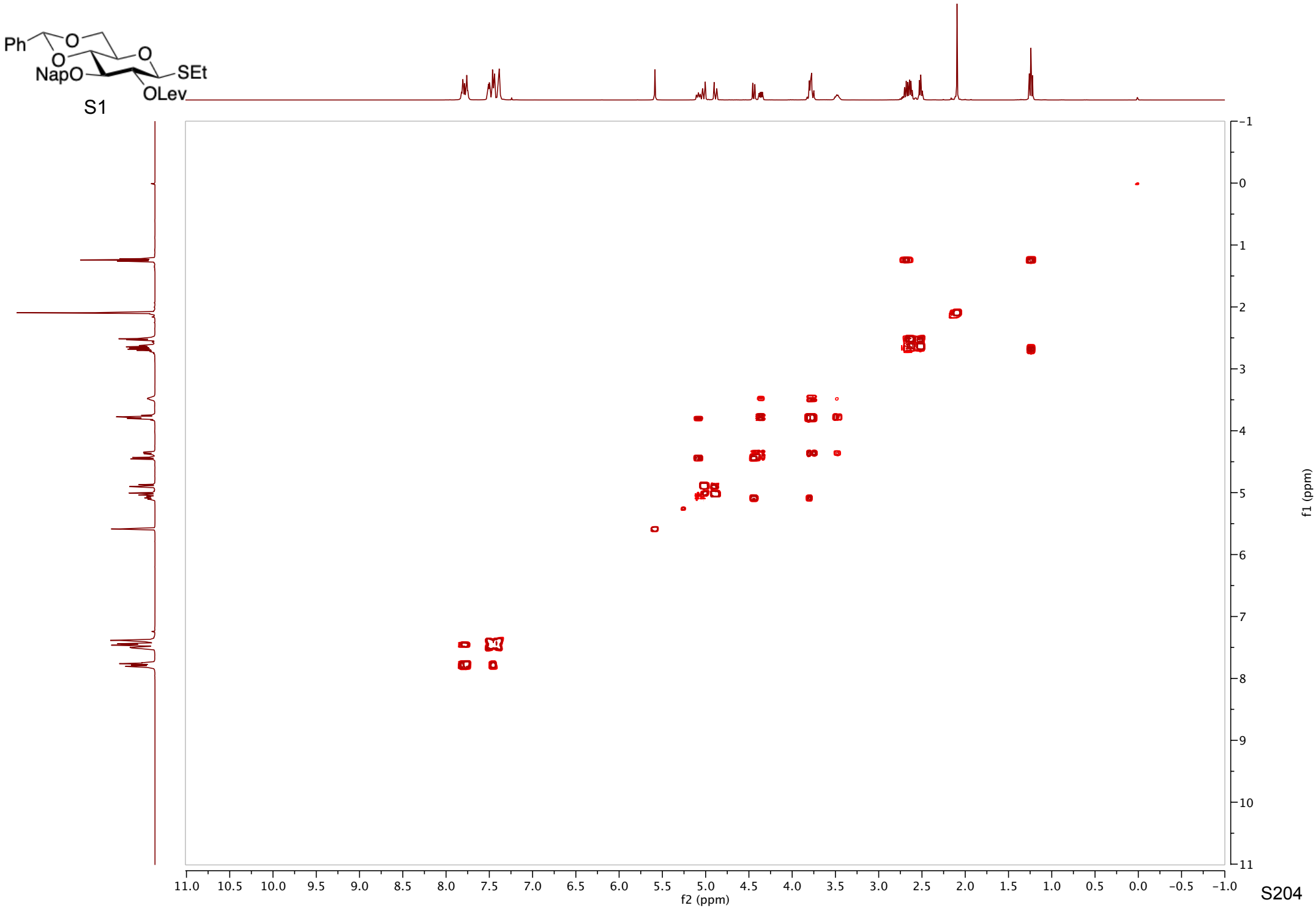


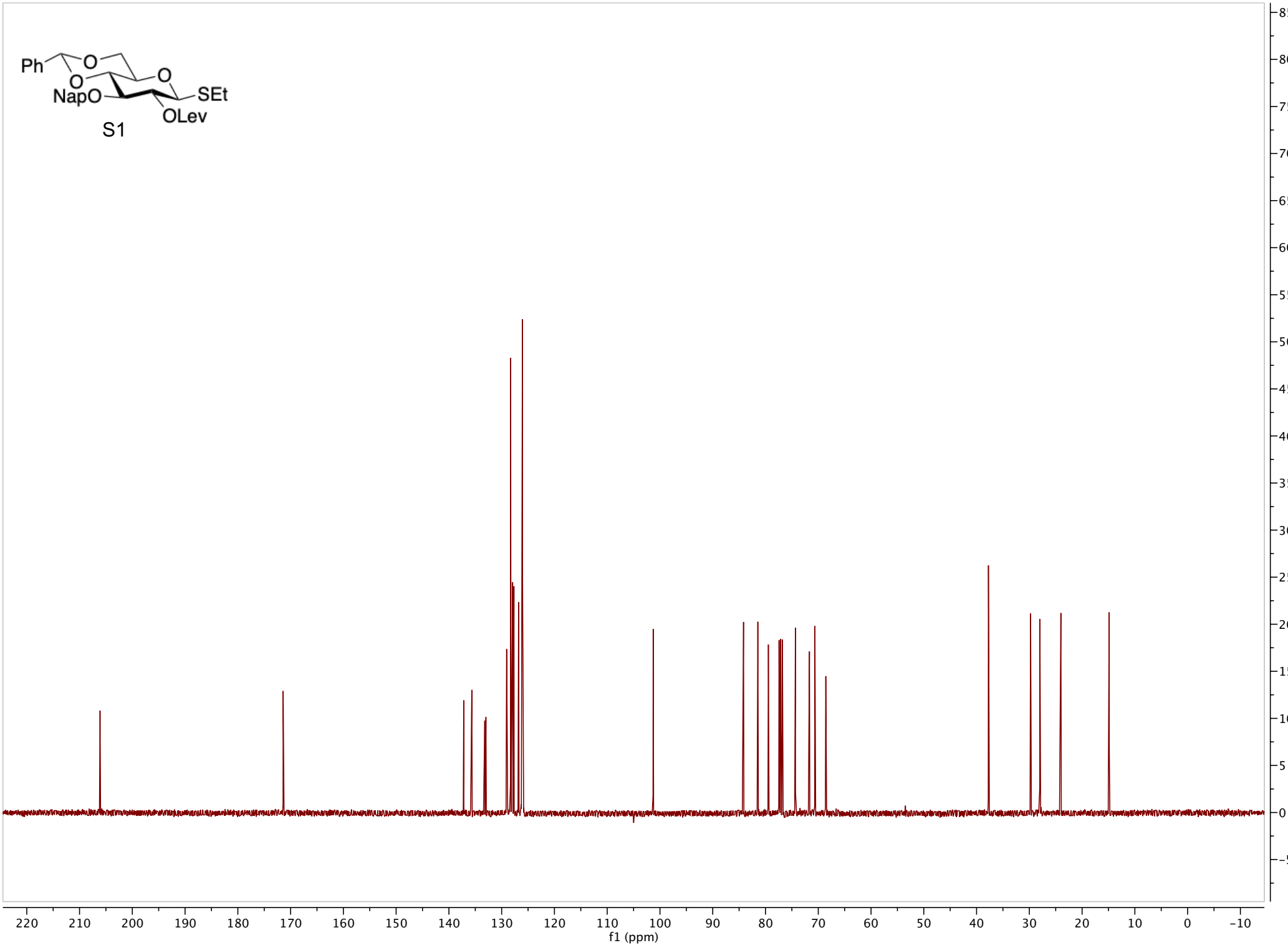


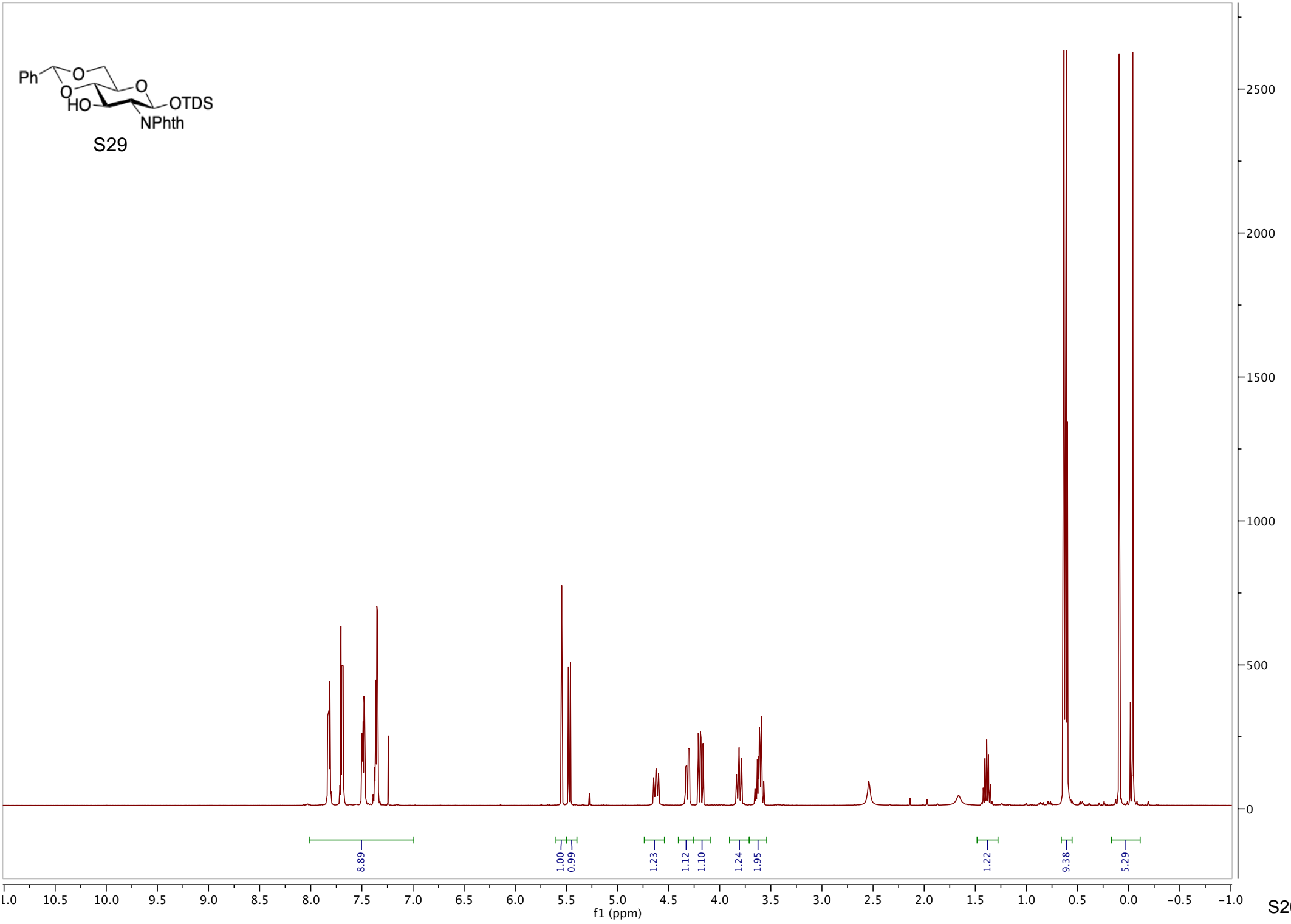
S27

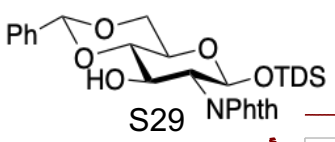

Ph
O
O
O
NapO
SEt
OLev
S1
12.04
1.00
0.95
1.12
1.00
0.95
1.04
2.98
1.00
3.85
2.03
2.94
3.02
f1 (ppm)


Ph
O
O
O
NapO
SEt
OLev
S1
f2 (ppm)
f1 (ppm)

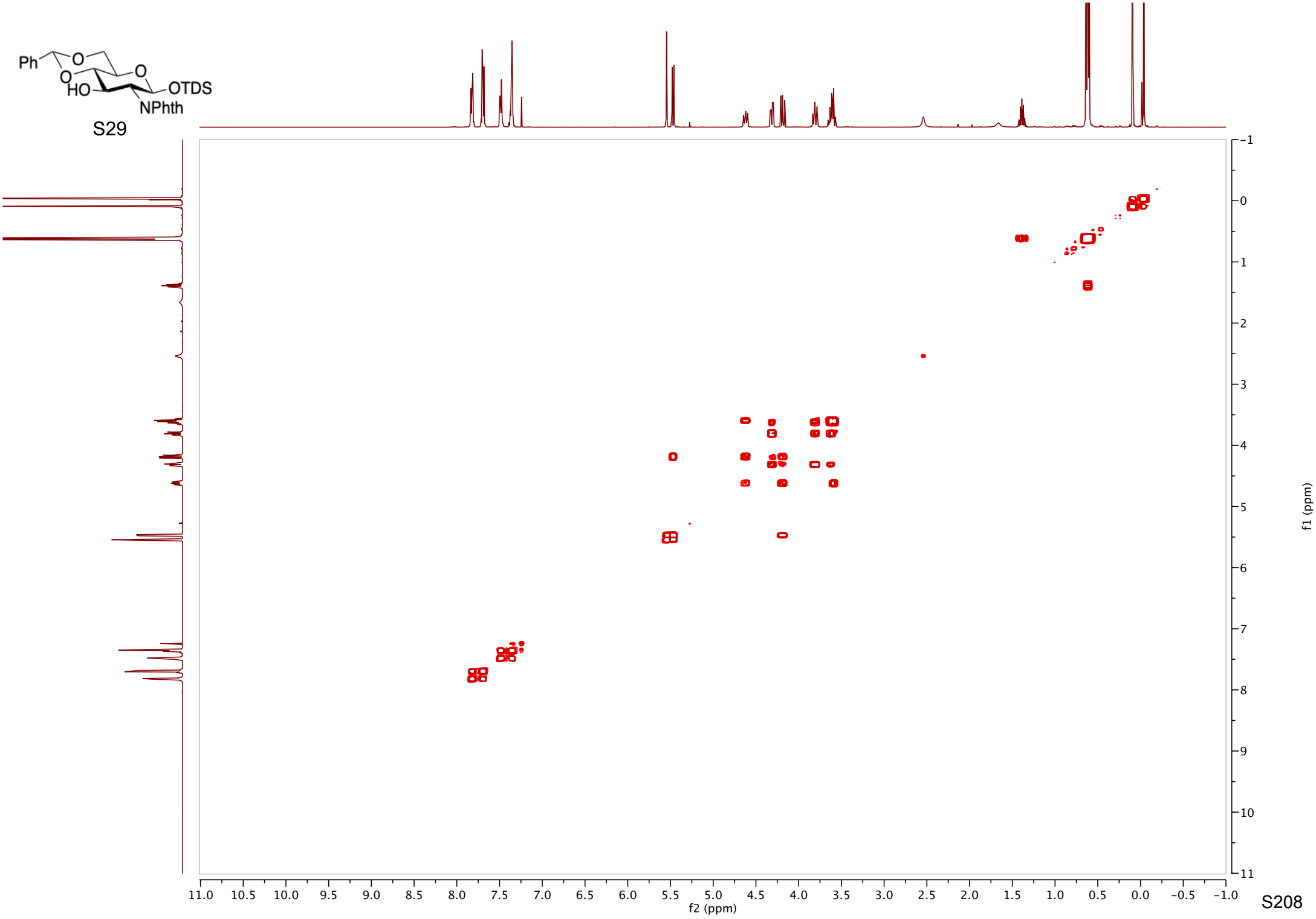

Ph
O
O
O
NapO
SEt
OLev
S1
f2 (ppm)
f1 (ppm)

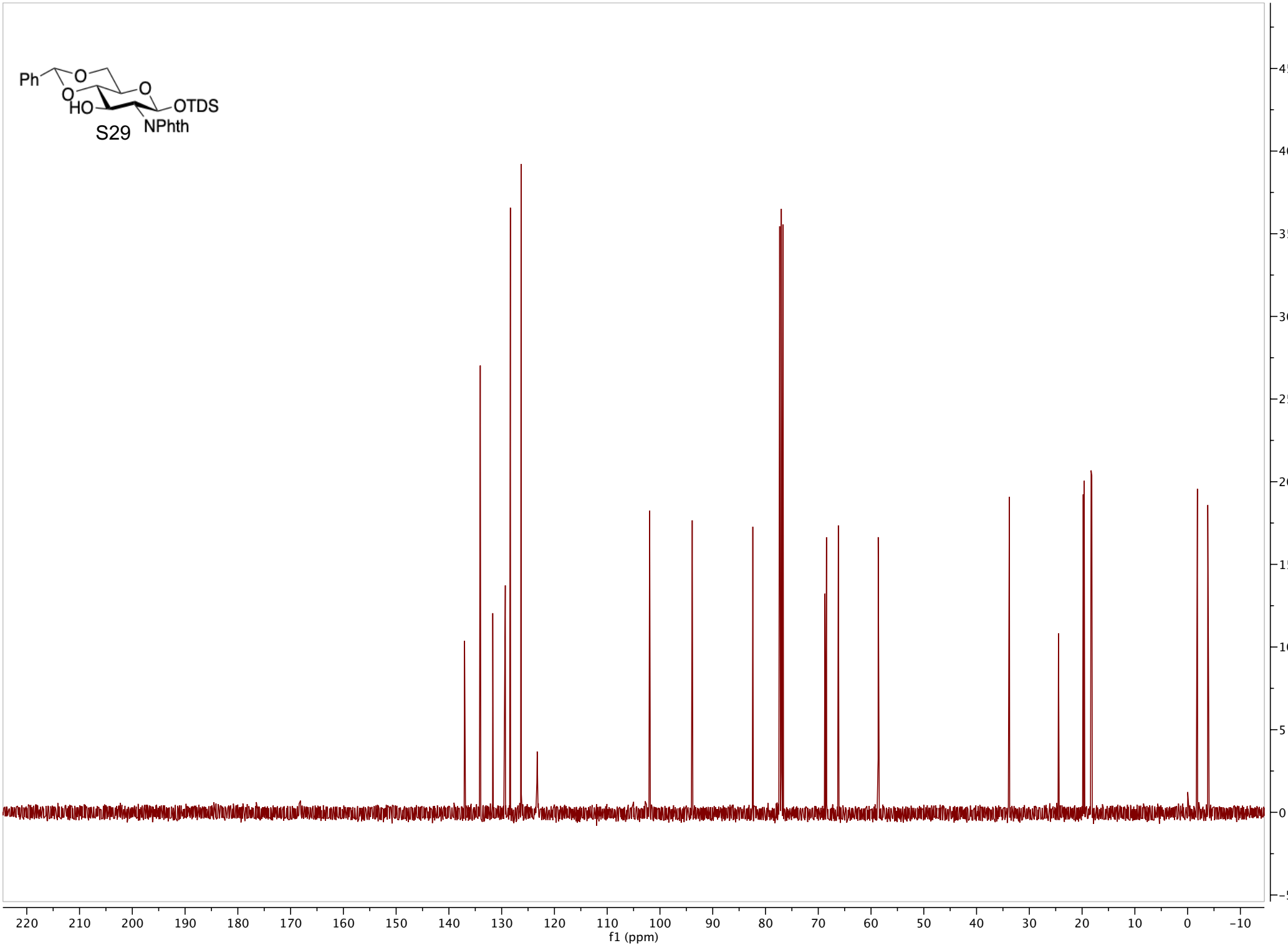

Ph
O
O
O
NapO
SEt
OLev
S1
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

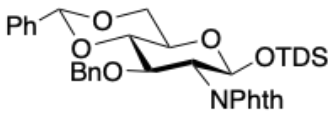

Ph
O
O
O
HO
OTDS
NPhth
S29
2500
2000
1500
1000
500
0
8.89
1.00
0.99
1.23
1.12
1.10
1.24
1.95
1.22
9.38
5.29
f1 (ppm)



S29

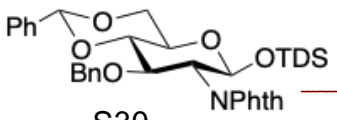

Ph
O
O
O
HO
OTDS
NPhth
S29
f2 (ppm)
f1 (ppm)


Ph
O
O
O
HO
OTDS
NPhth
S29
45
40
35
30
25
20
15
10
5
0
−5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

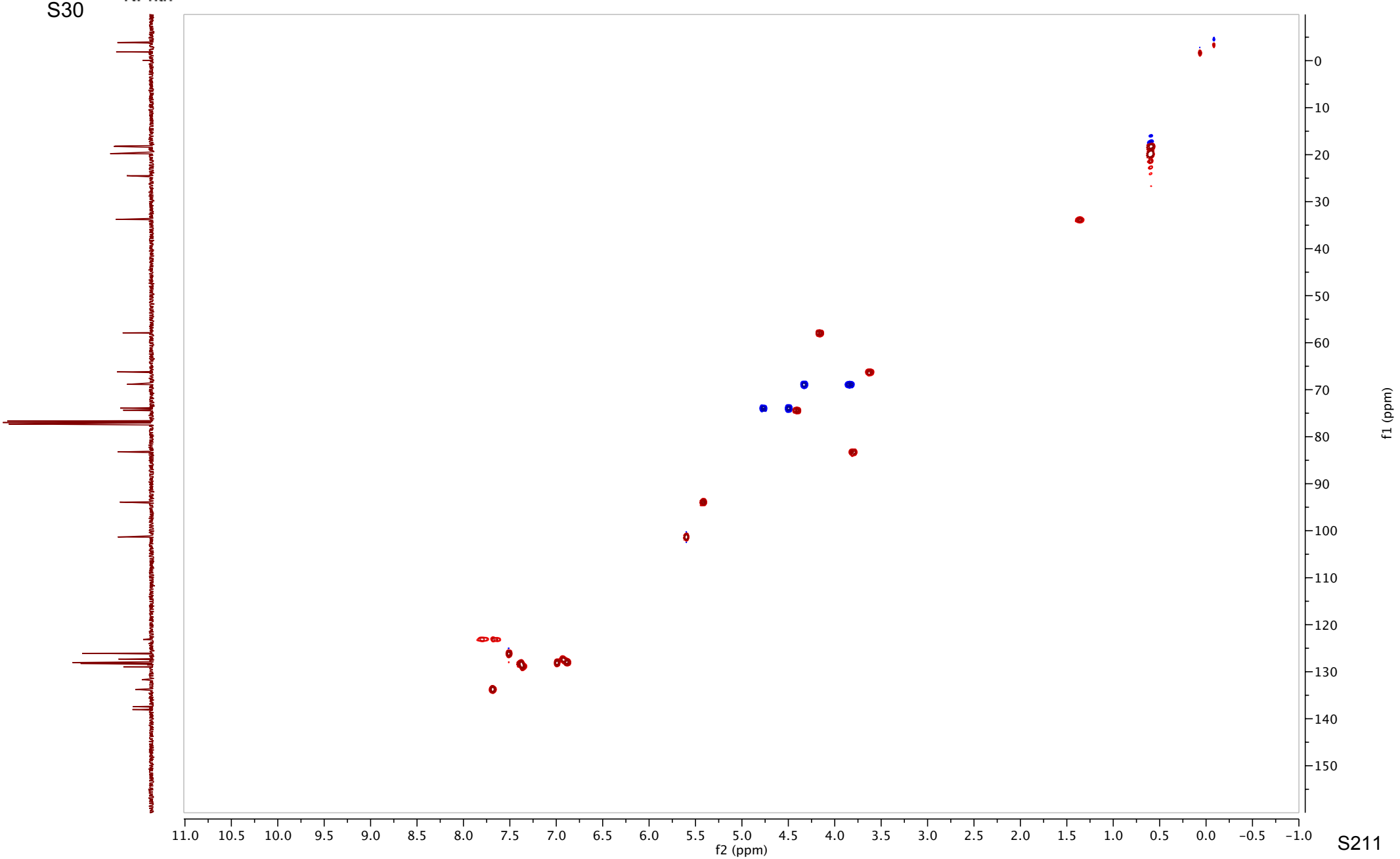

Ph
O
O
O
BnO
OTDS
NPhth

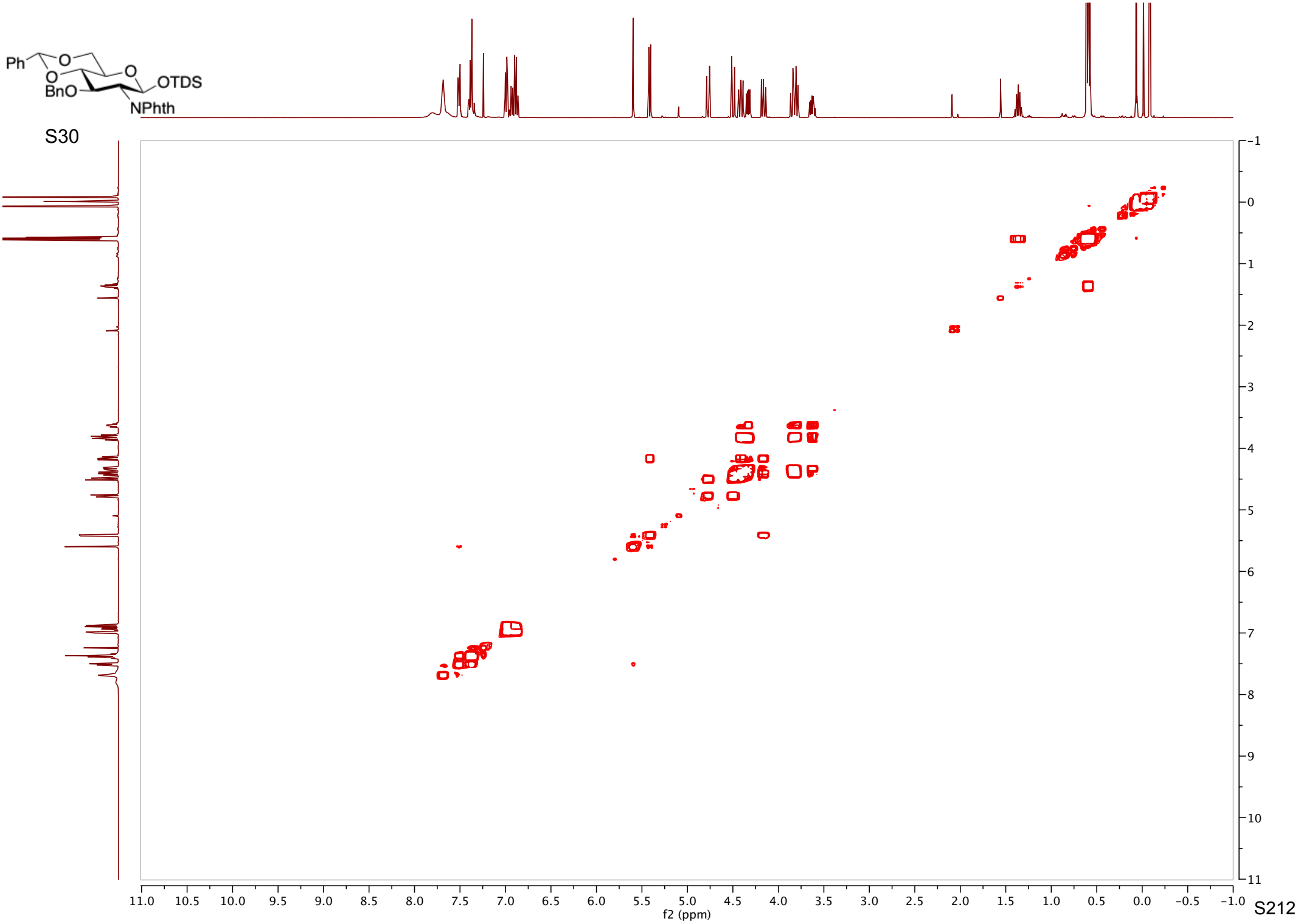
S30

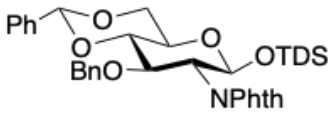
13.92
0.87
0.93
1.00
0.94
0.98
0.98
0.93
1.83
1.02
1.10
9.95
5.79
f1 (ppm)


Ph
O
O
O
BnO
OTDS
NPhth

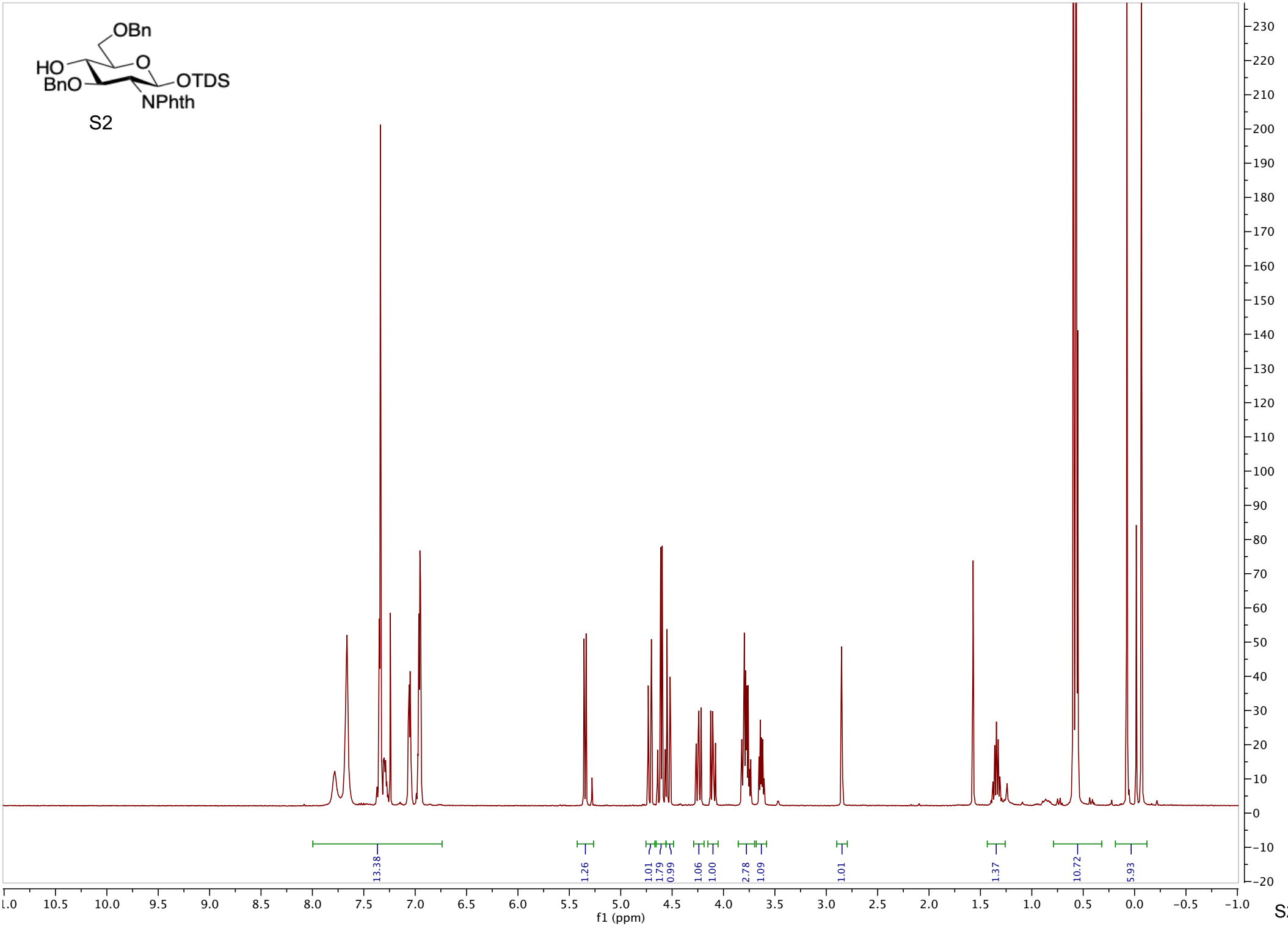
S30

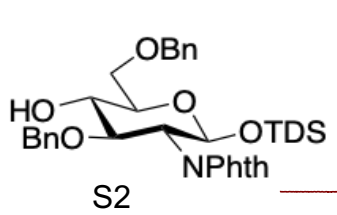

11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)


Ph
O
O
O
BnO
OTDS
NPhth
S30
f2 (ppm)
S212

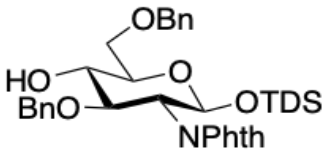


S30

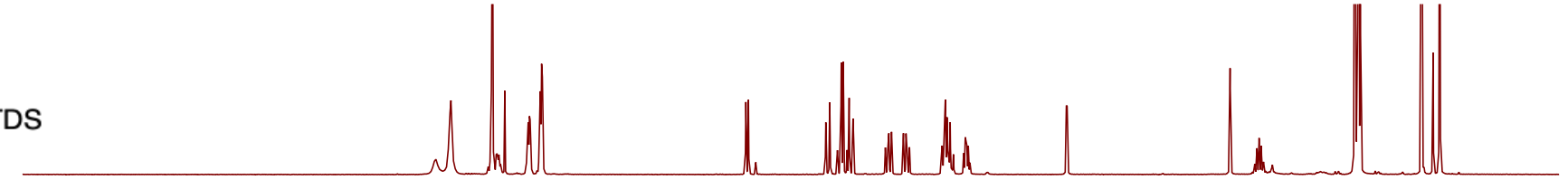

OBn
HO
O
BnO
OTDS
NPhth
S2
13.38
1.26
1.01
1.79
0.99
1.06
1.00
2.78
1.09
1.01
1.37
10.72
5.93
f1 (ppm)

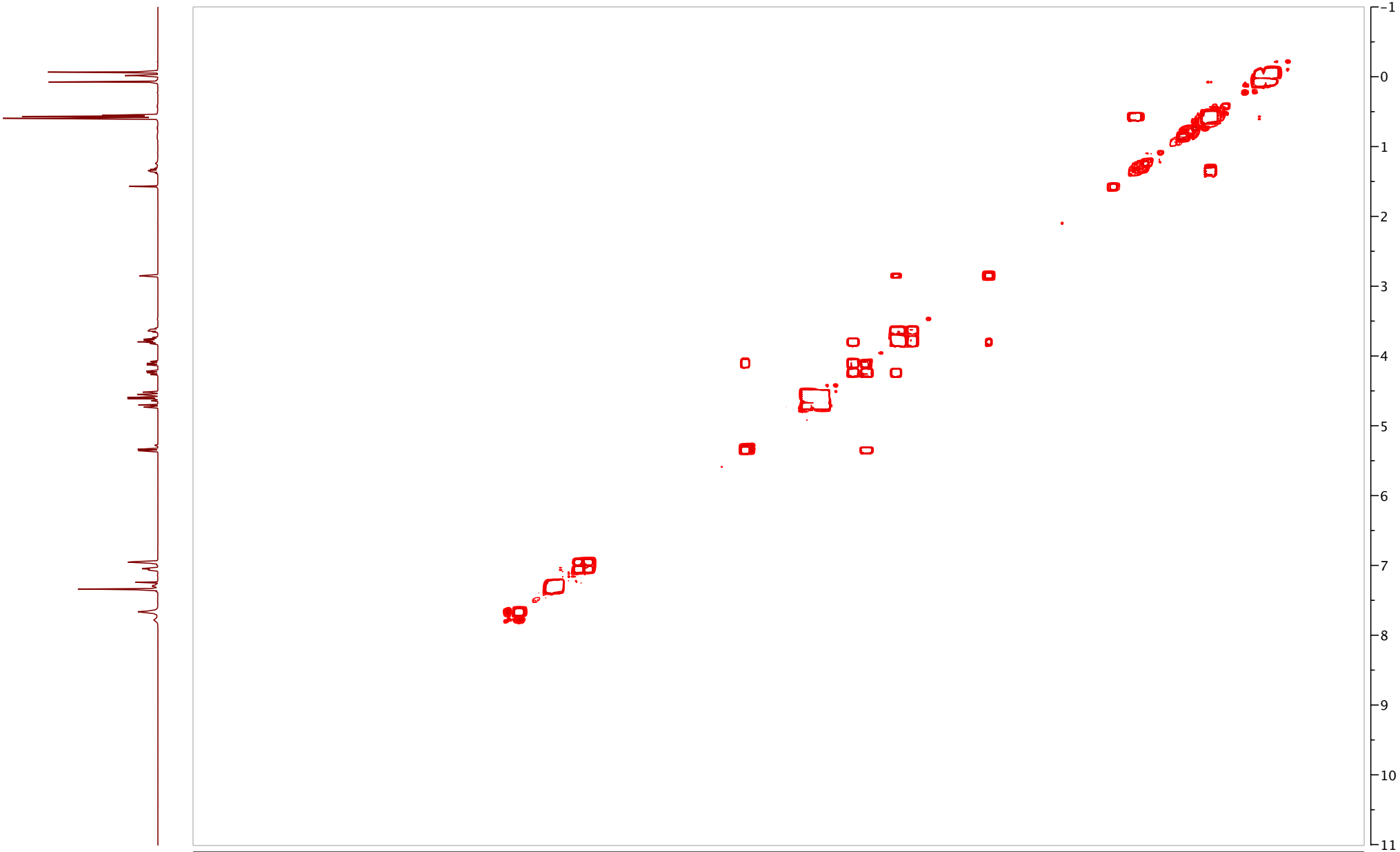


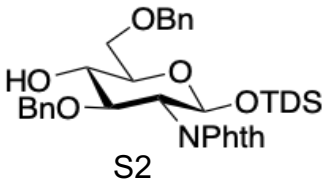
S2


OBn
HO
O
BnO
OTDS
NPhth

S2

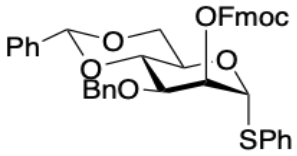



11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9 10 11
f1 (ppm)

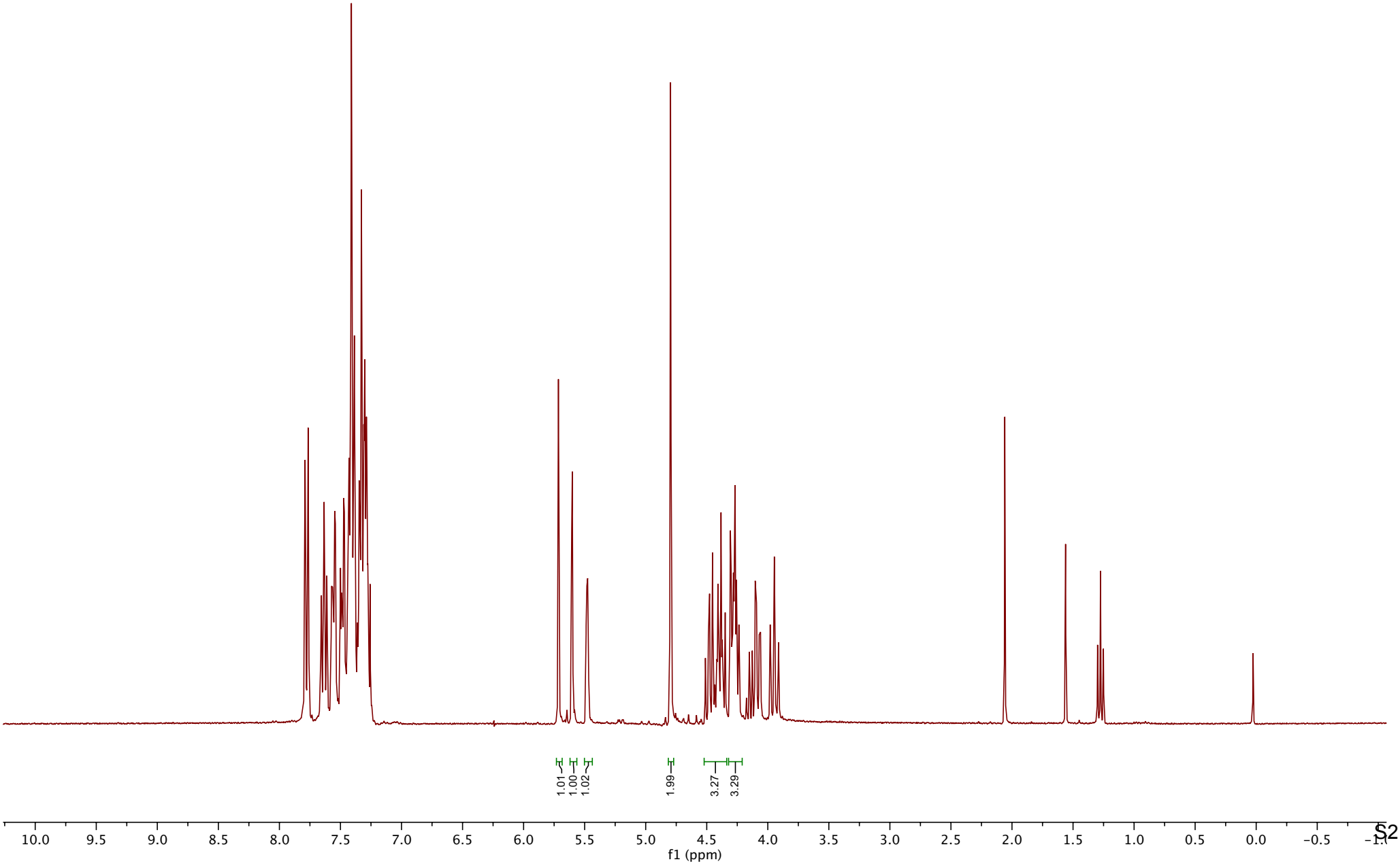

OBn
HO
O
BnO
OTDS
NPhth

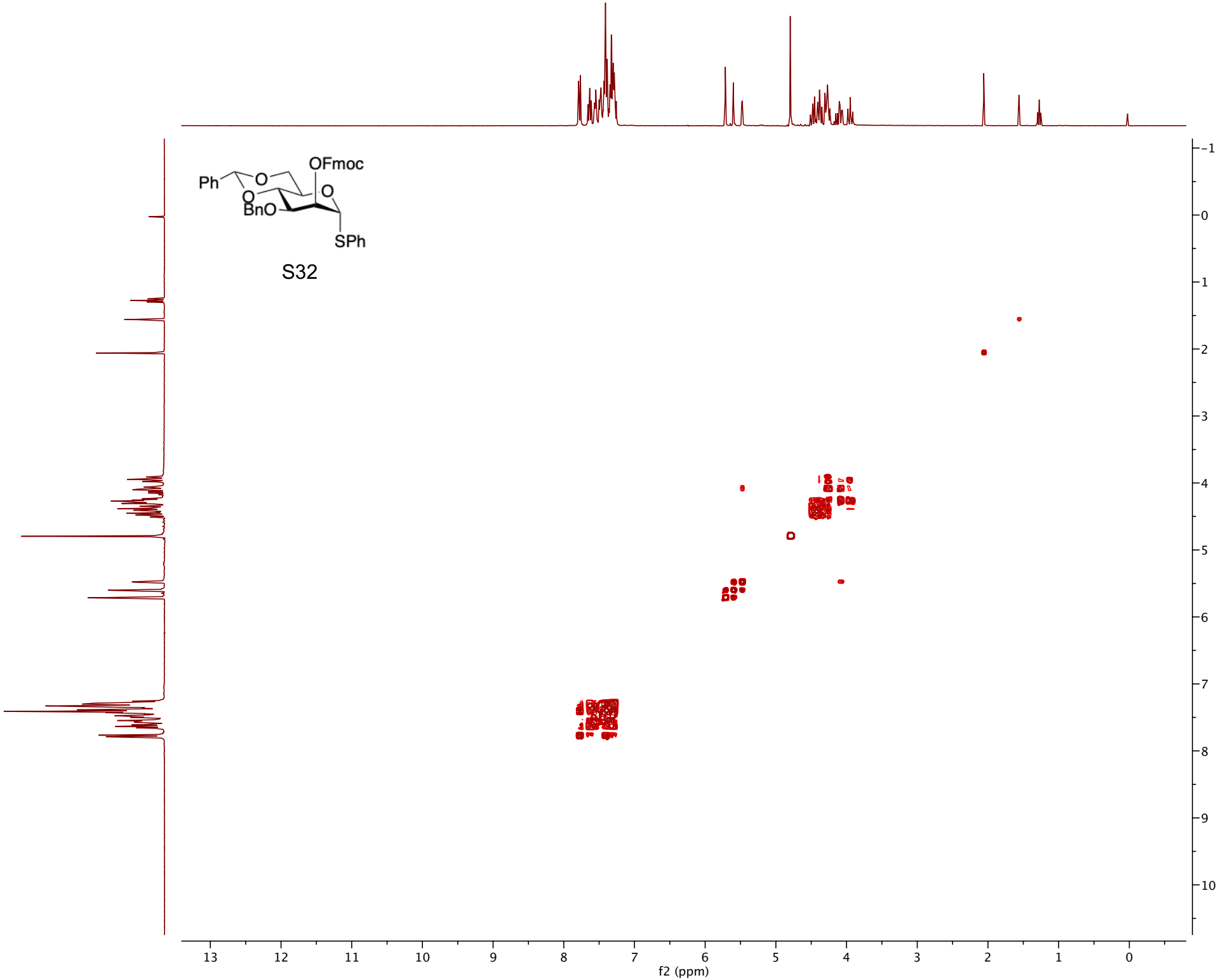
S2

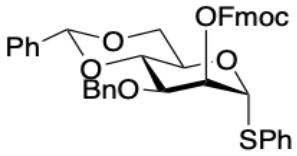
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


OFmoc
Ph
O
O
O
BnO
SPh

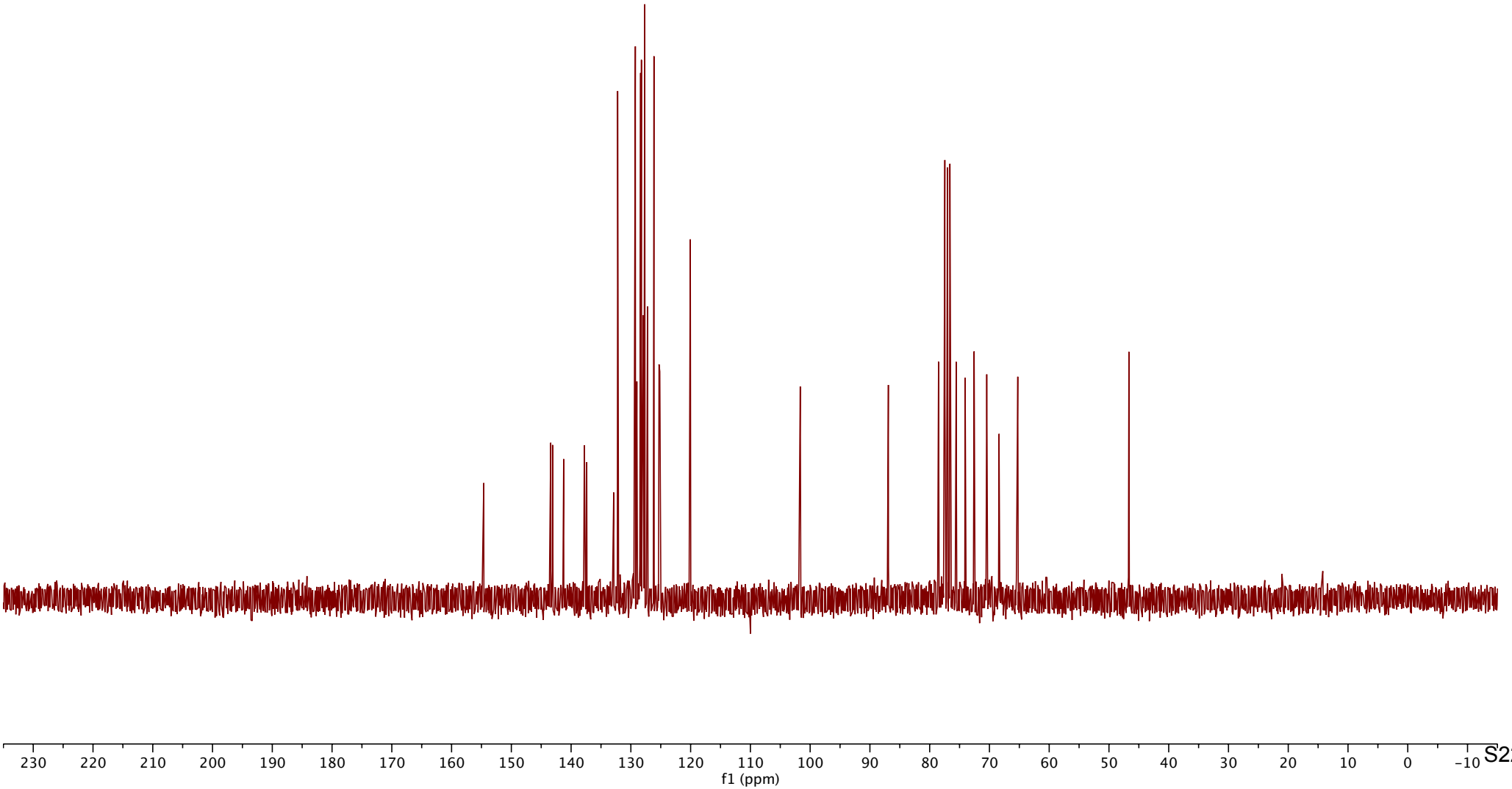
S32

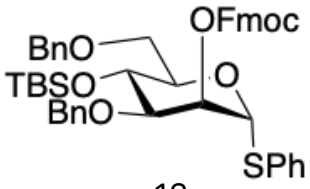

1.01
1.00
1.02
1.99
3.27
3.29
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


OFmoc
Ph
O
O
O
BnO
SPh
S32
f2 (ppm)
f1 (ppm)

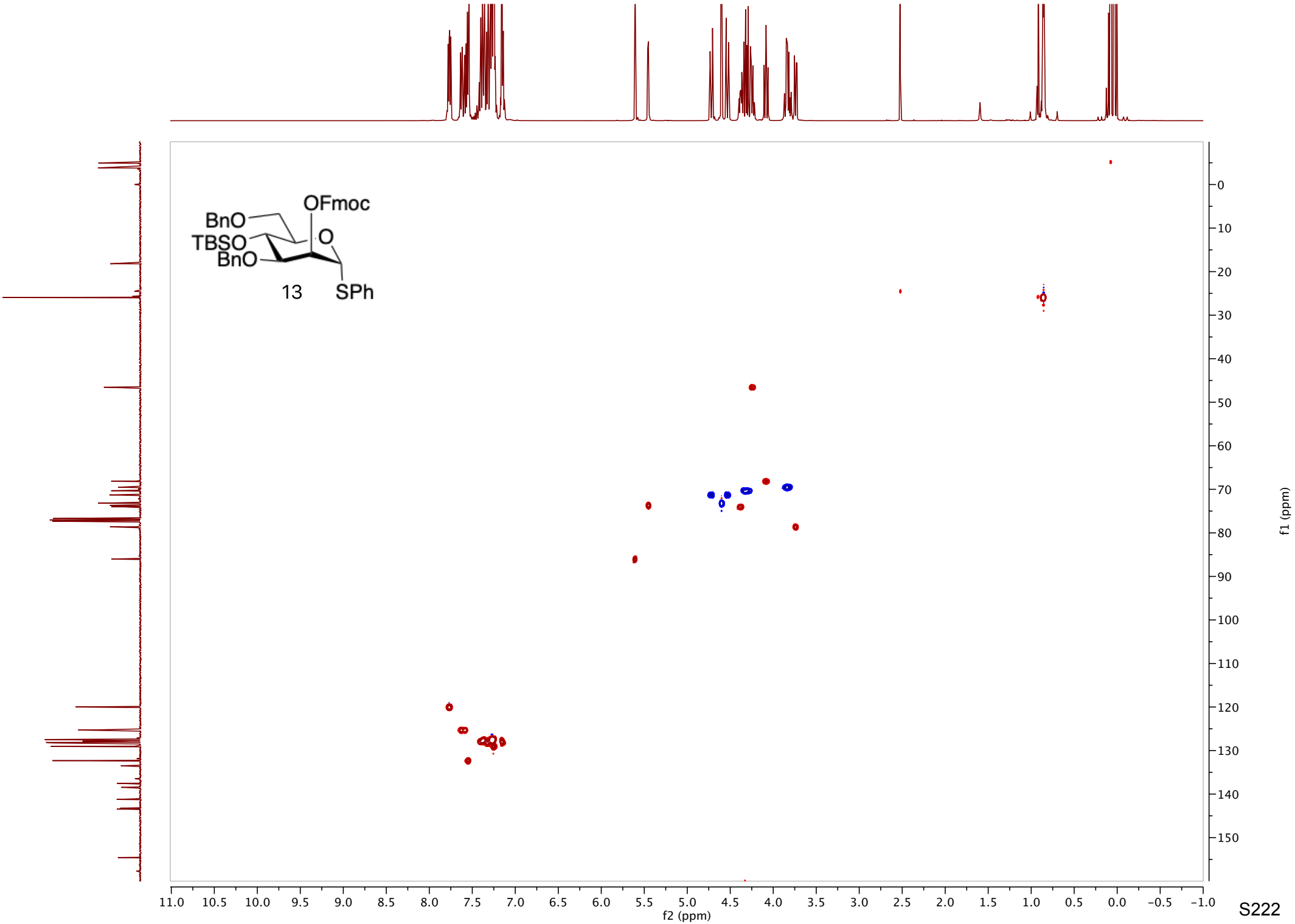

OFmoc
Ph
O
O
O
BnO
SPh

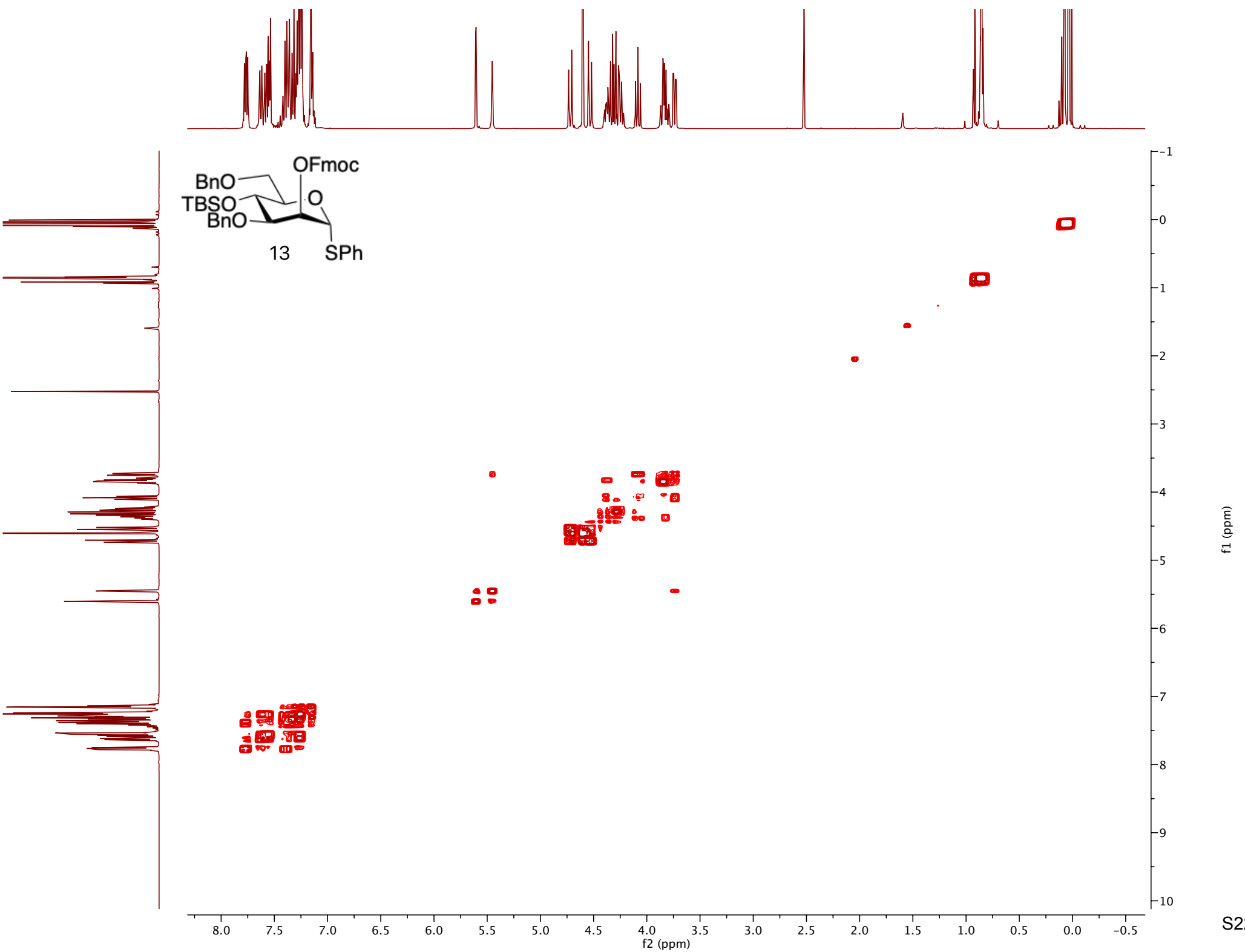
S32

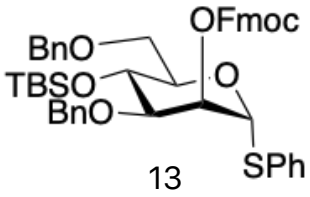

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



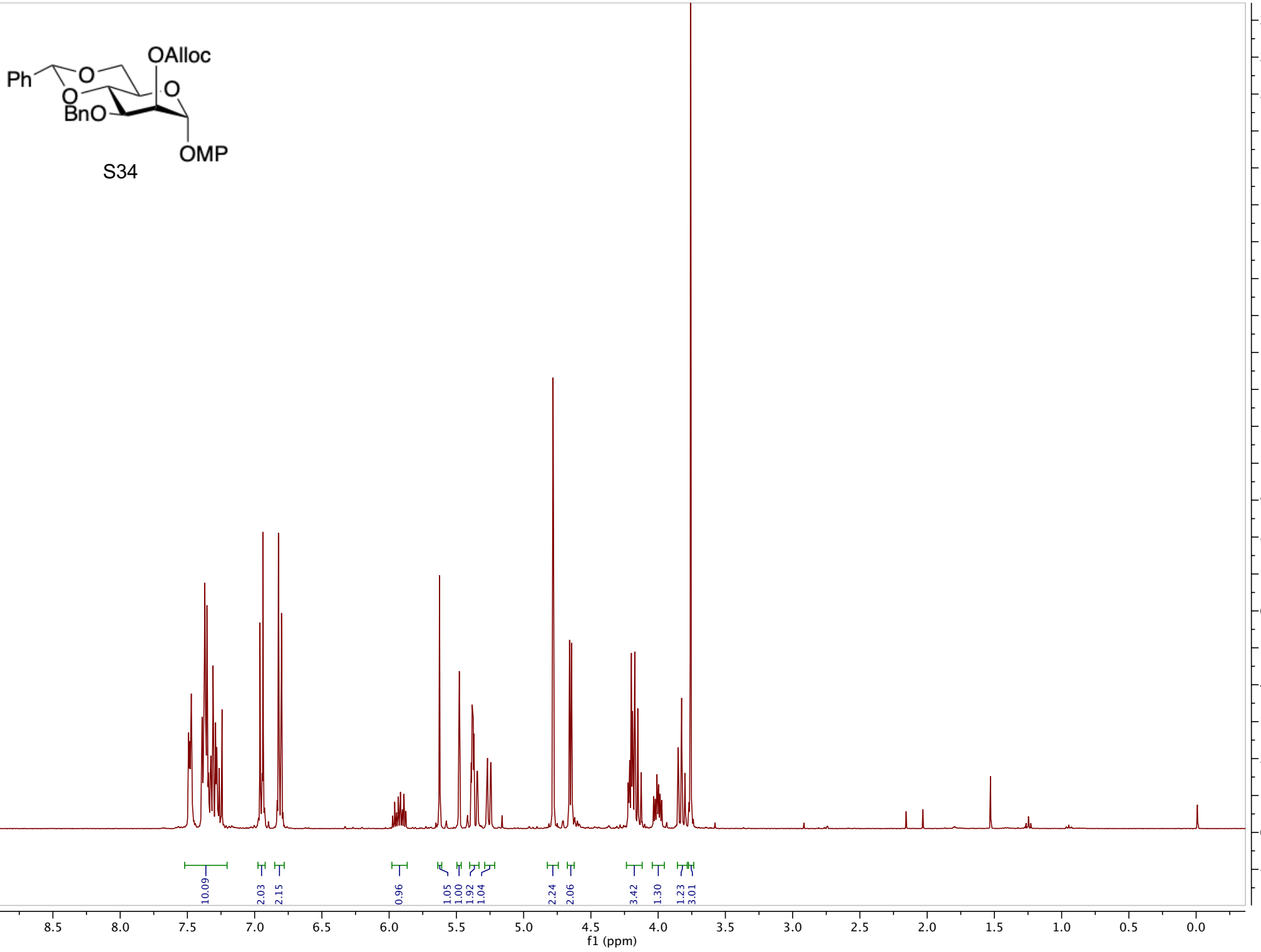
13

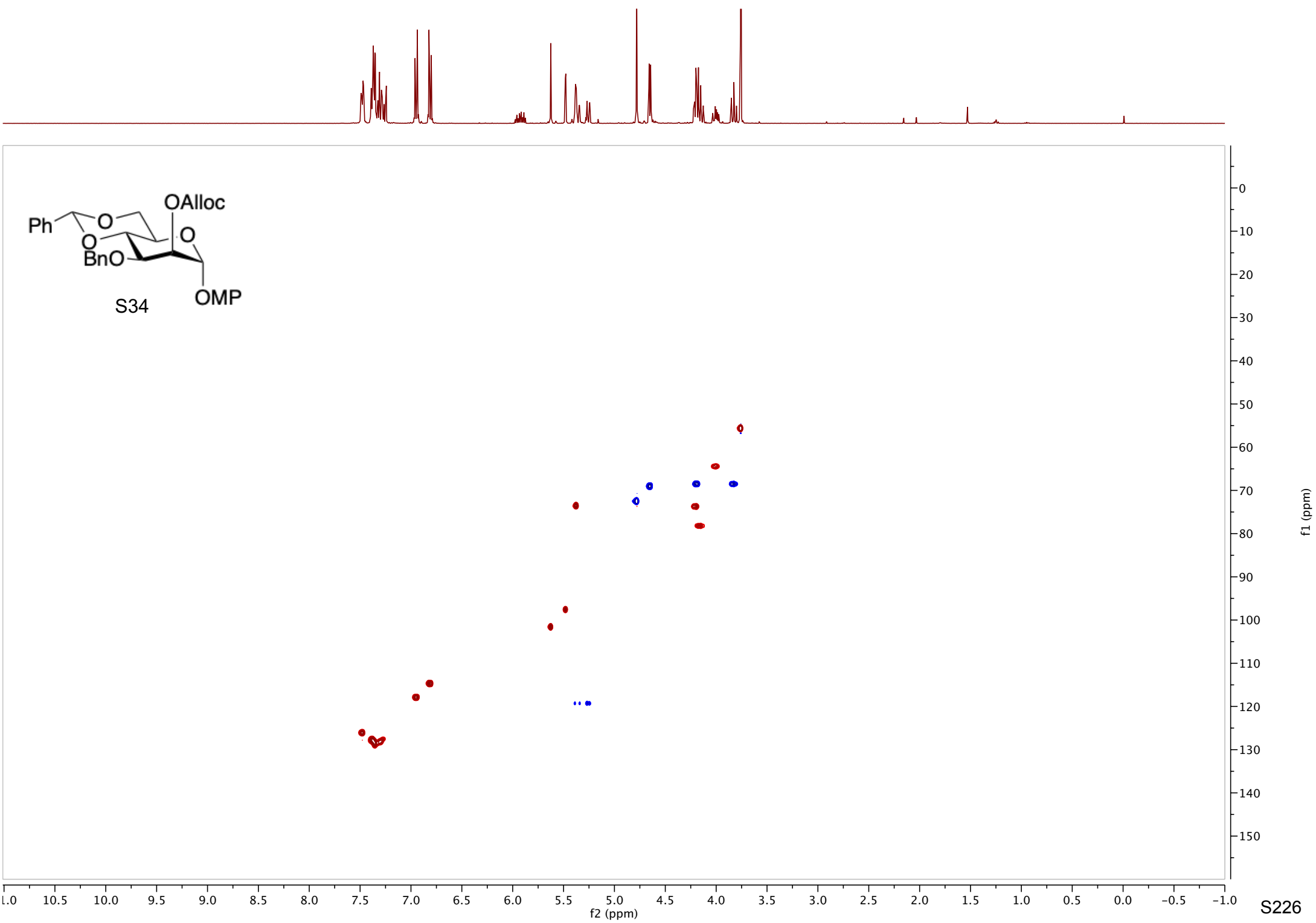

OFmoc
BnO
TBSO
BnO
O
13
SPh
f2 (ppm)
f1 (ppm)

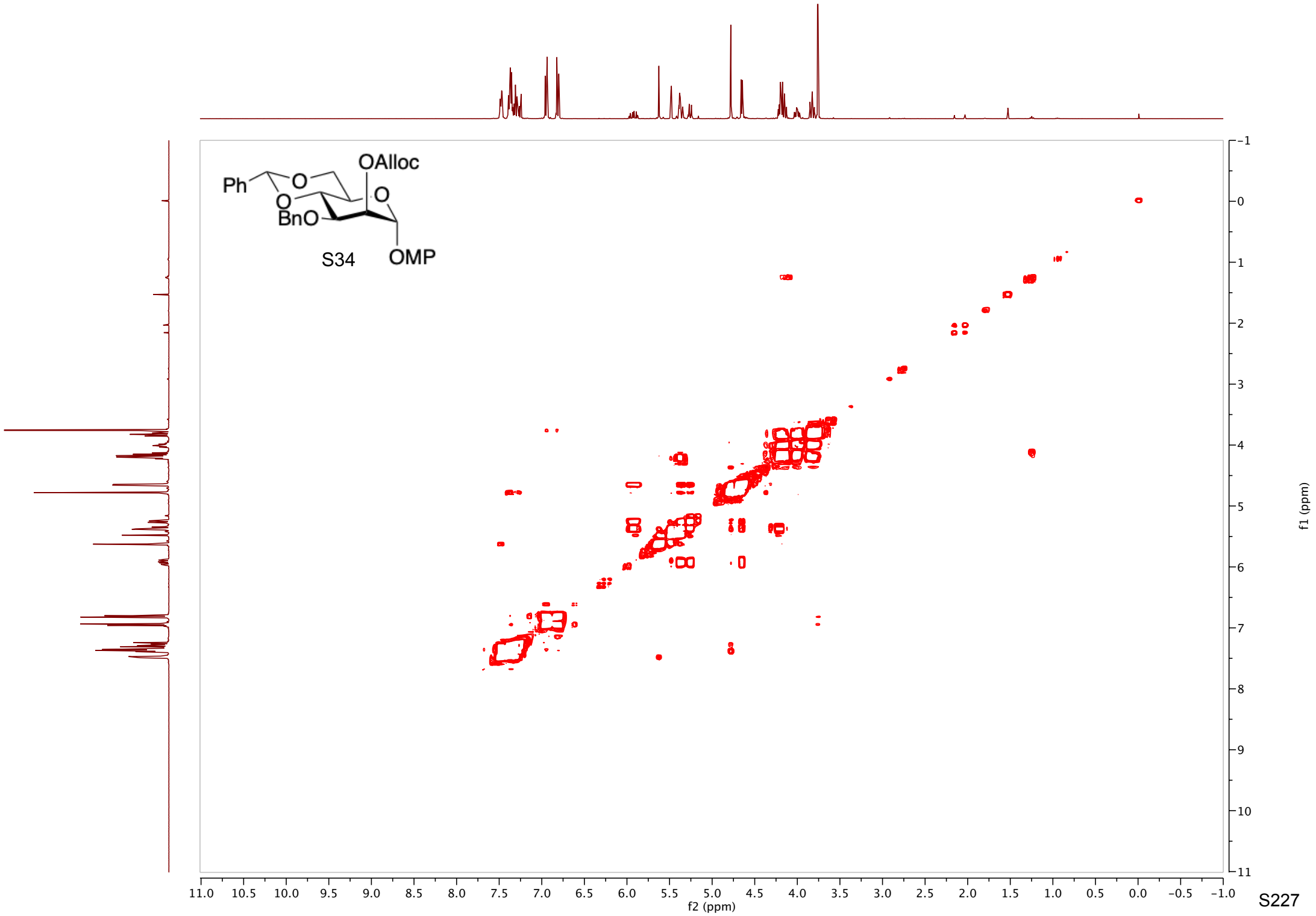

OFmoc
BnO
TBSO
BnO
O
13
SPh
f2 (ppm)
f1 (ppm)

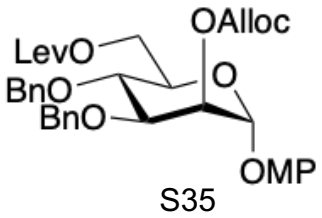


13


OAlloc
Ph
O
O
O
BnO
OMP
S34
10.09
2.03
2.15
0.96
1.05
1.00
1.92
1.04
2.24
2.06
3.42
1.30
1.23
3.01
f1 (ppm)

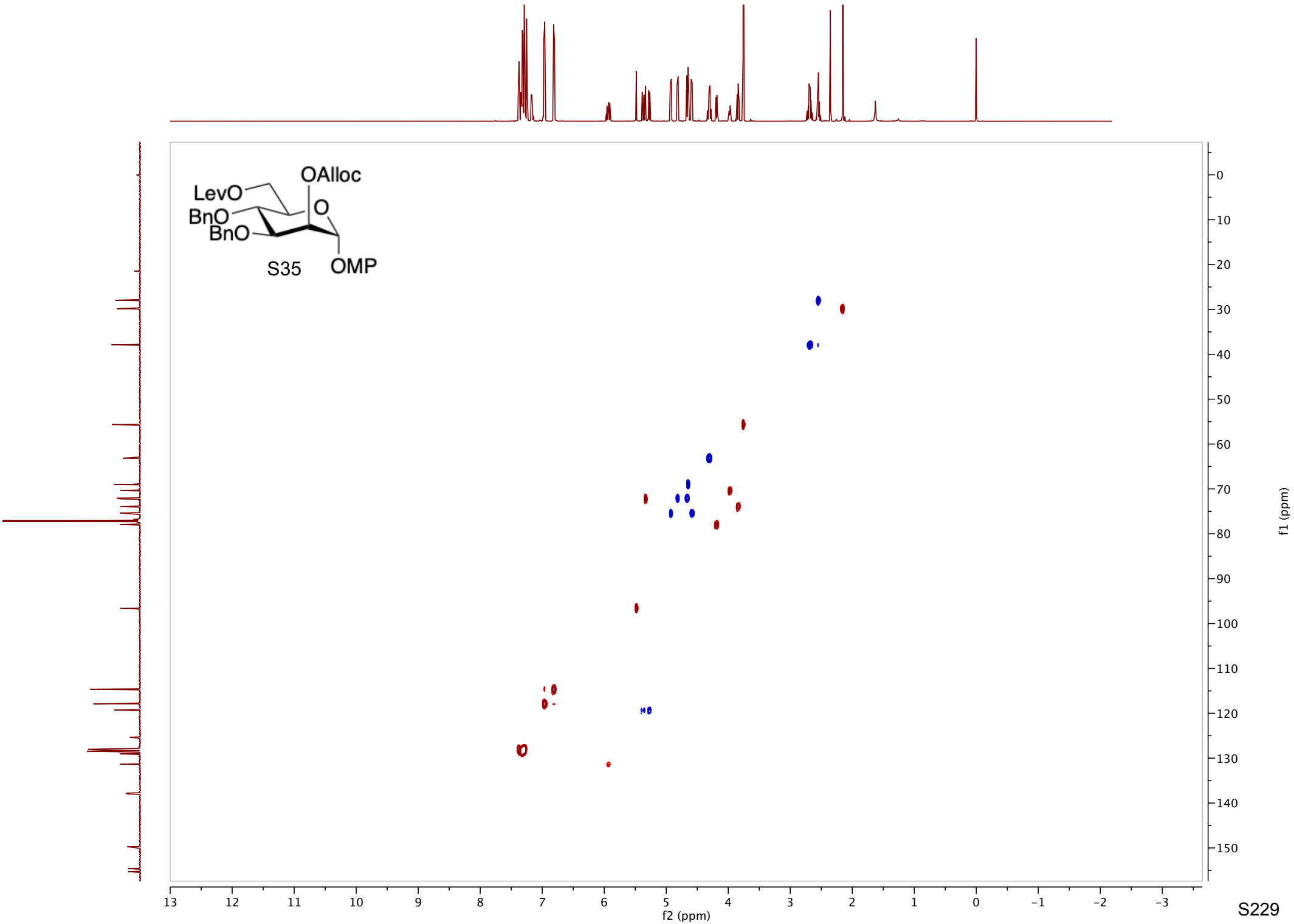

OAlloc
Ph
O
O
BnO
O
OMP
S34
f2 (ppm)
f1 (ppm)

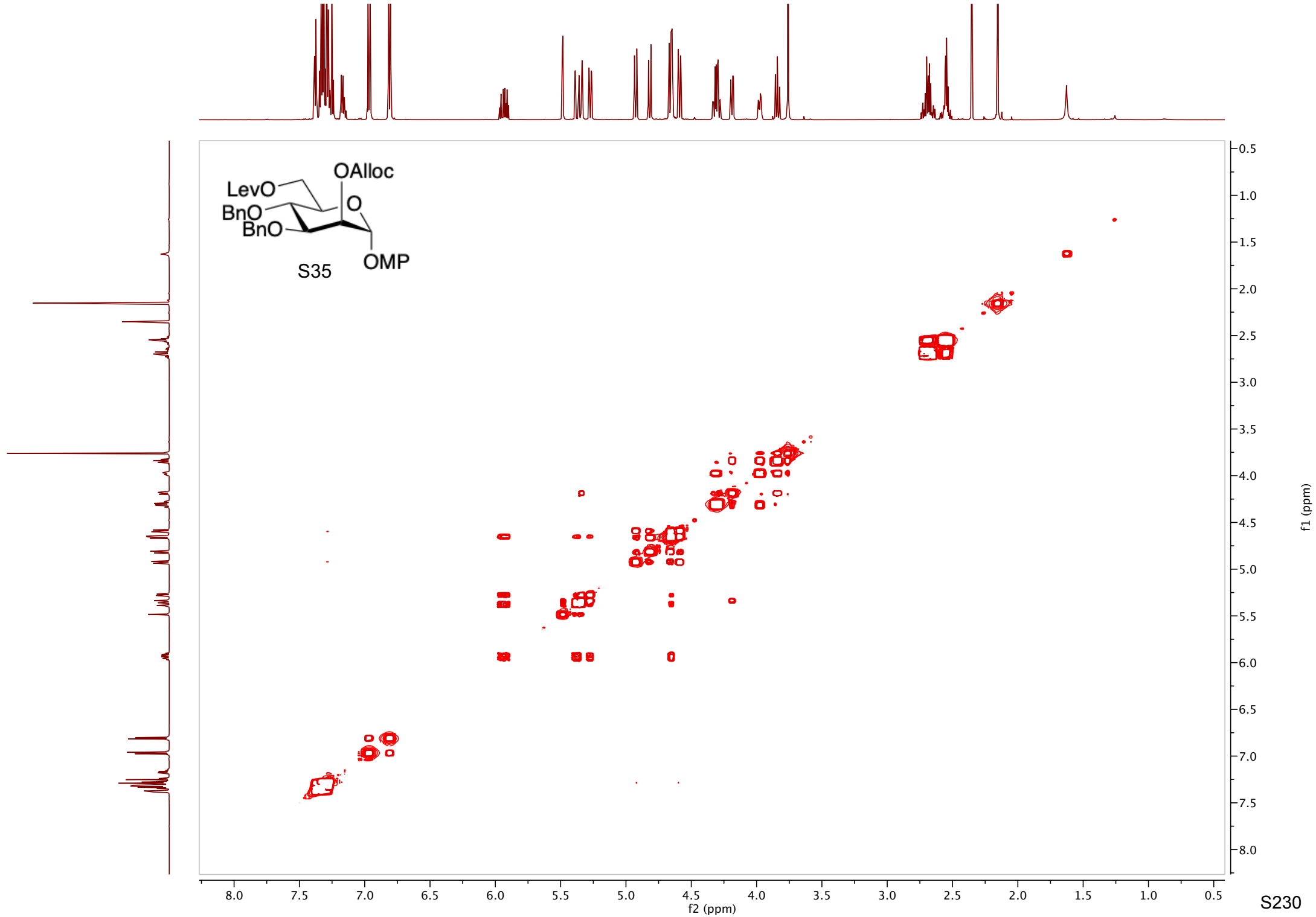

OAlloc
Ph
O
O
O
BnO
S34
OMP
f2 (ppm)
f1 (ppm)

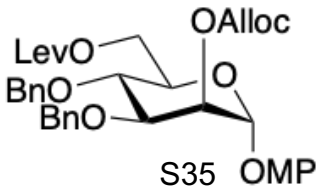

OAlloc
LevO
O
BnO
BnO
OMP

S35

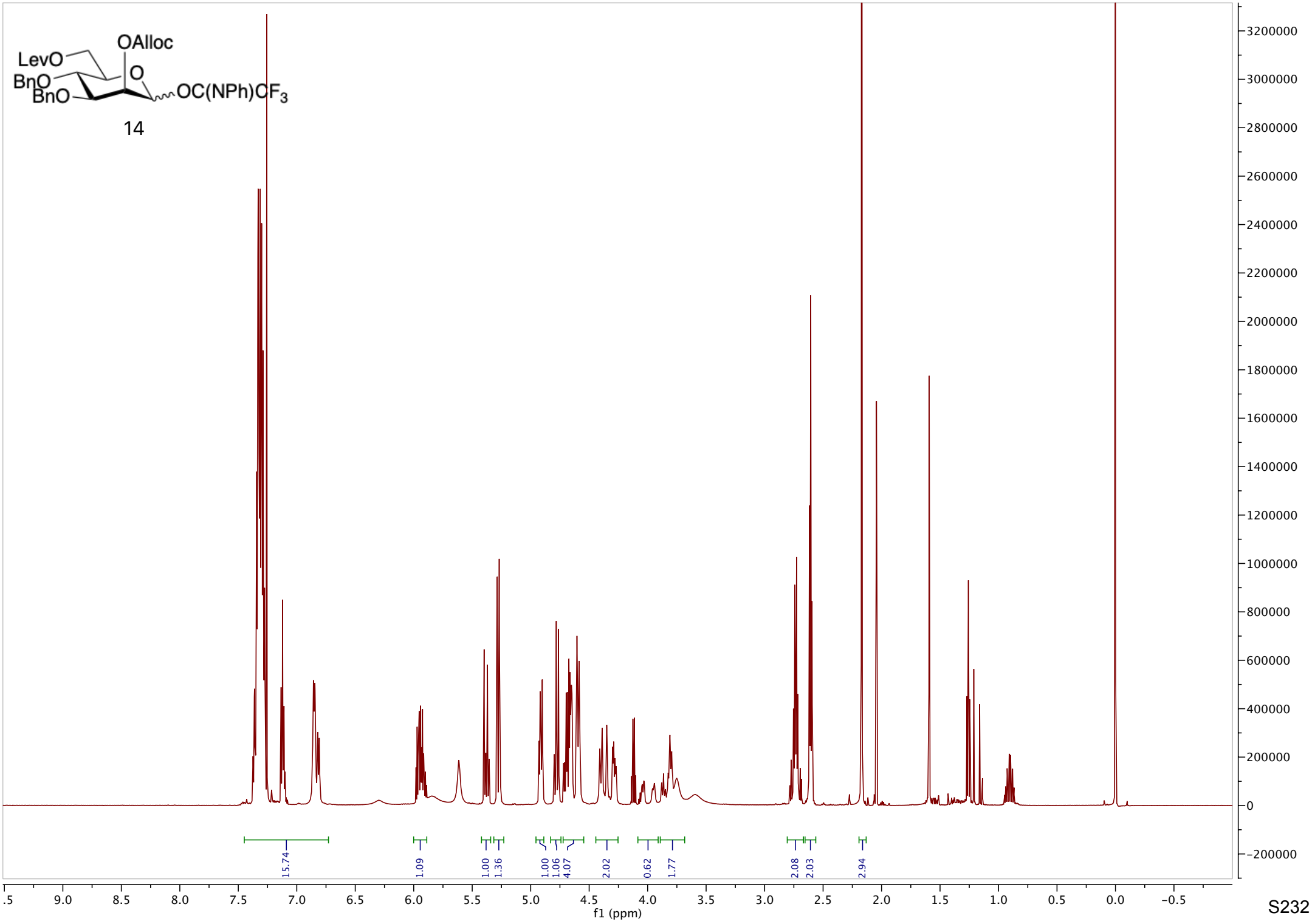
16.83
0.95
1.00
2.01
0.99
0.99
1.01
2.99
1.04
2.01
1.01
1.01
1.01
3.00
2.05
2.01
2.93
f1 (ppm)

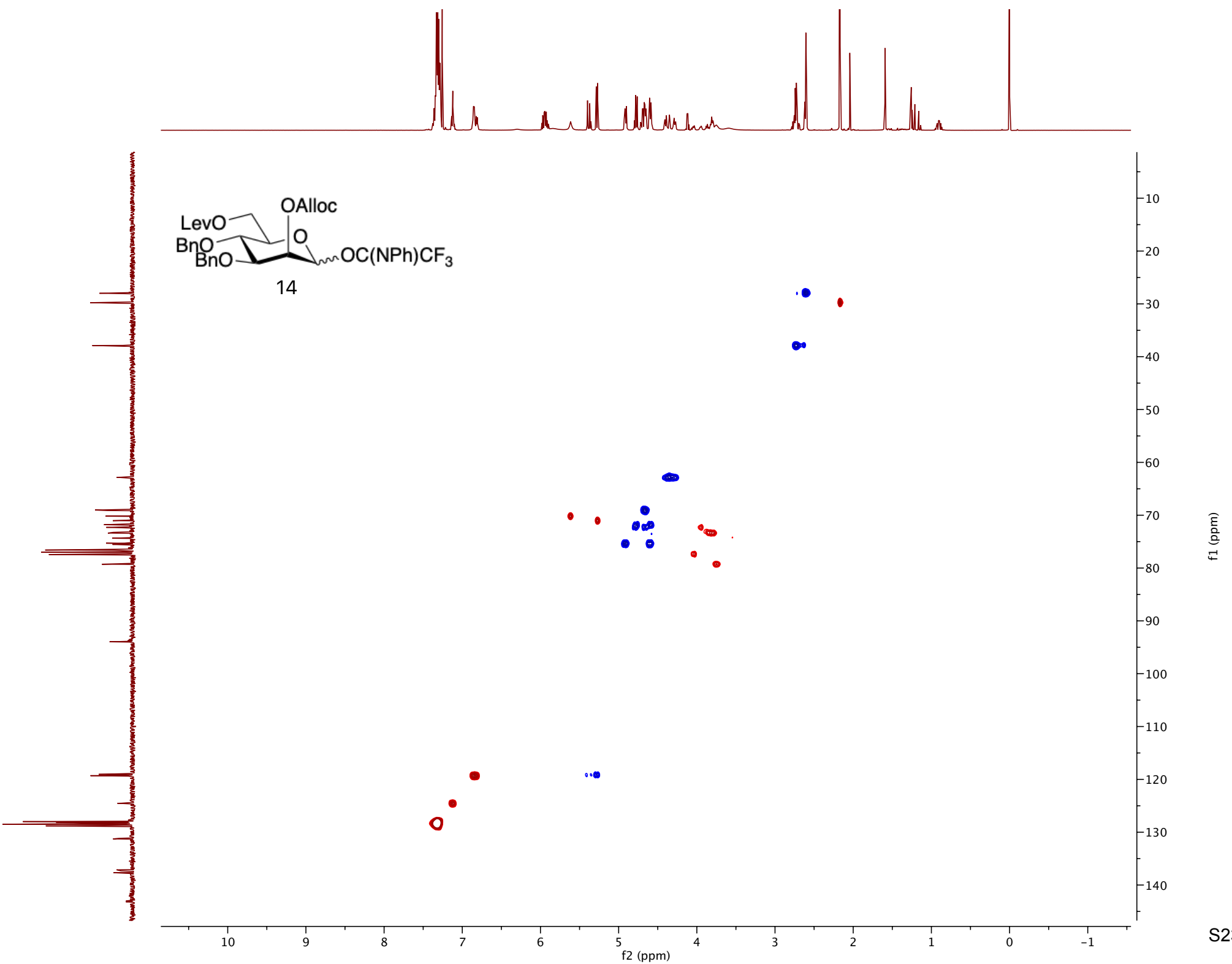

OAlloc
LevO
O
BnO
BnO
S35
OMP
f2 (ppm)
f1 (ppm)

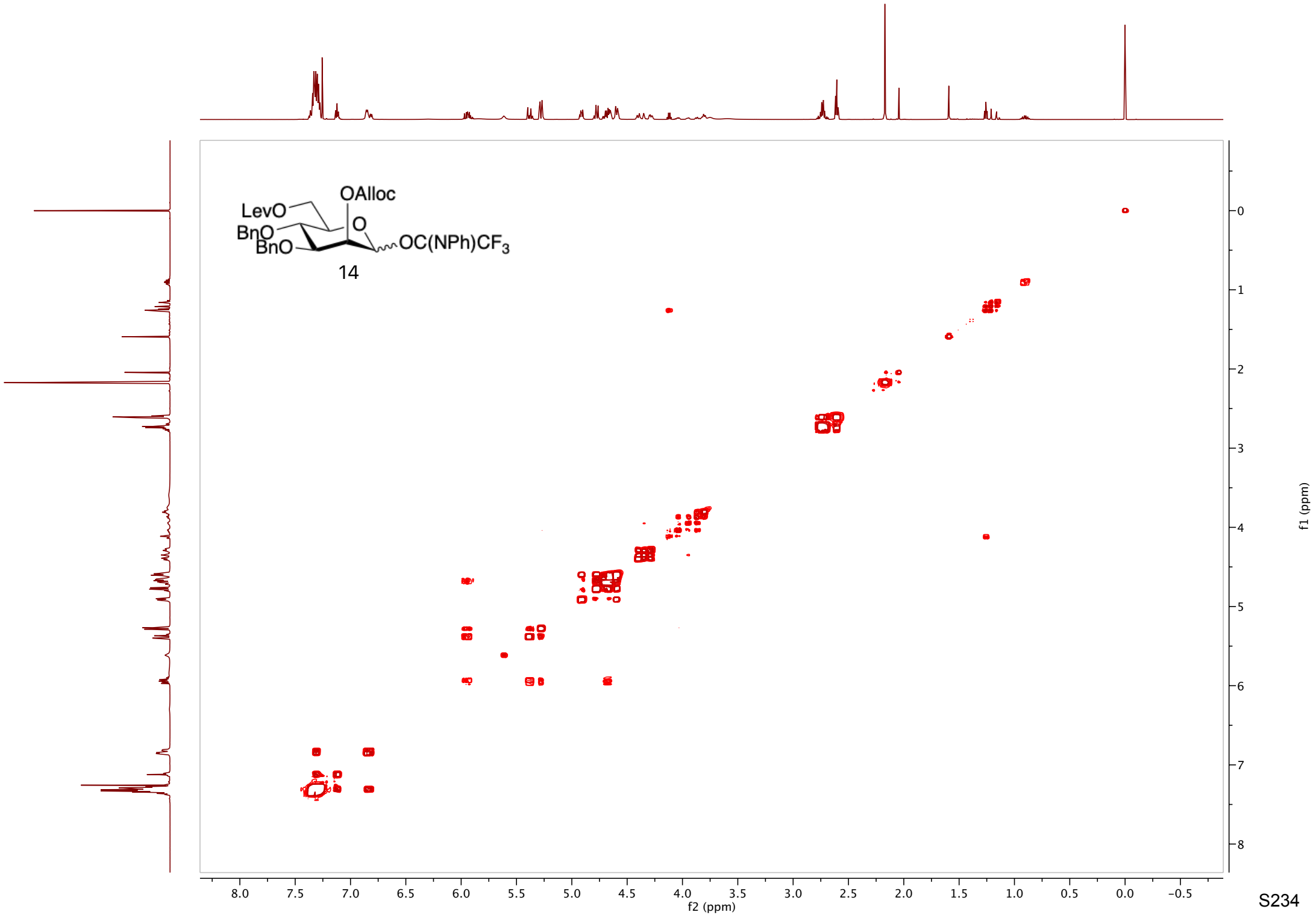

OAlloc
LevO
O
BnO
BnO
OMP
S35
f2 (ppm)
f1 (ppm)

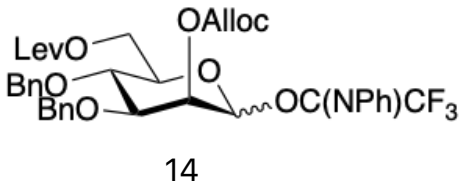


S35 OMP


OAlloc
LevO
BnO
BnO
O
OC(NPh)CF3
14
15.74
1.09
1.00
1.36
1.00
1.06
4.07
2.02
0.62
1.77
2.08
2.03
2.94
f1 (ppm)

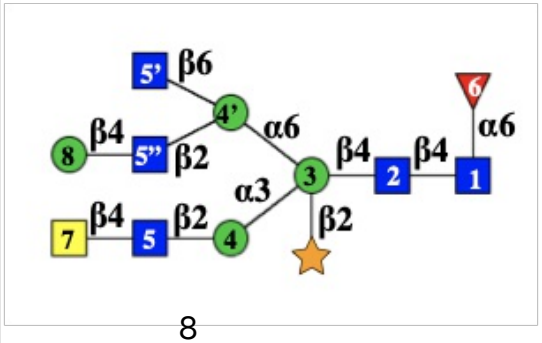

OAlloc
LevO
O
BnO
BnO
OC(NPh)CF3
14
f2 (ppm)
f1 (ppm)


OAlloc
LevO
O
BnO
BnO
OC(NPh)CF3
14
f2 (ppm)
f1 (ppm)

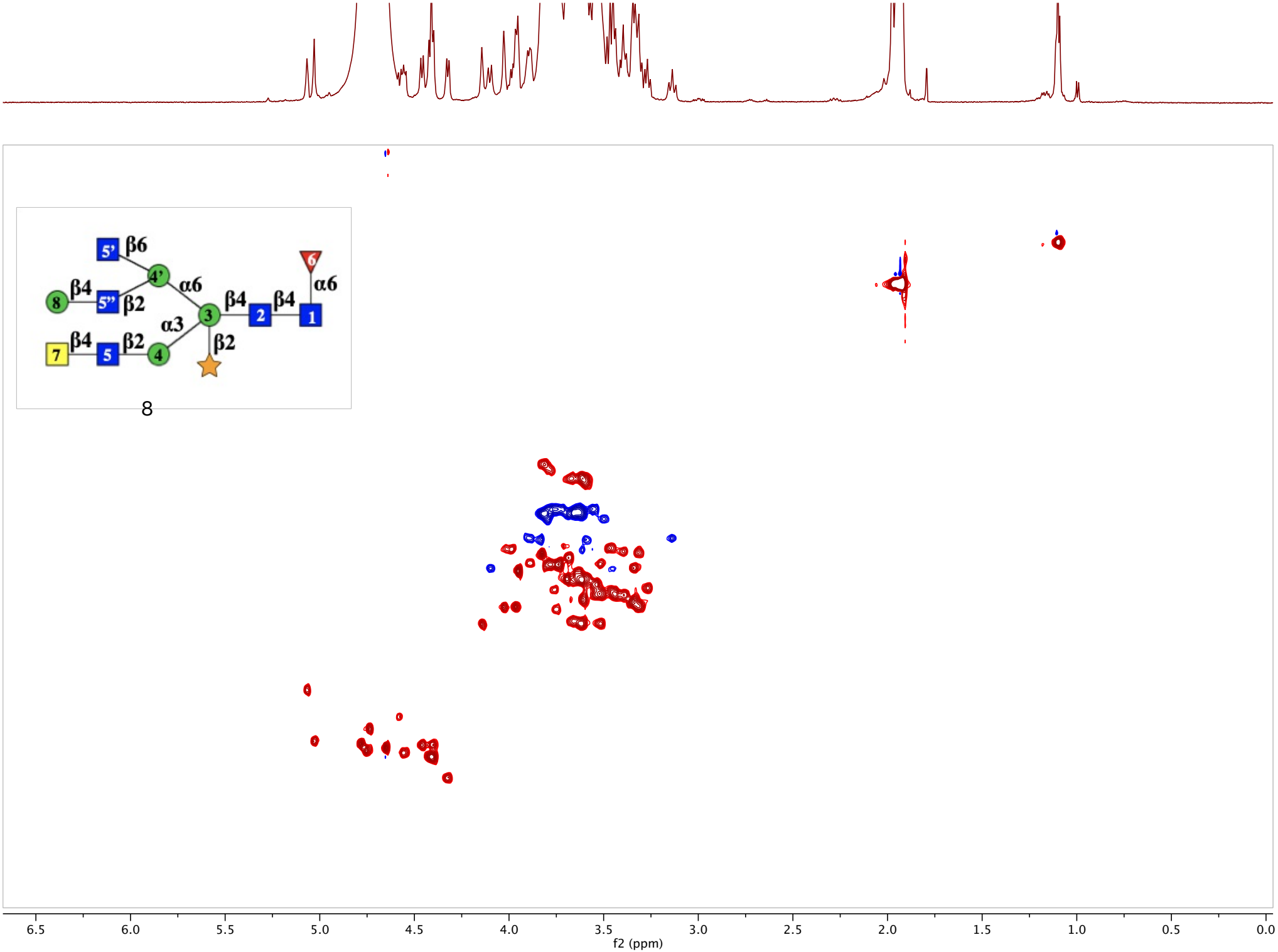

OAlloc
LevO
O
BnO
BnO
OC(NPh)CF3

14

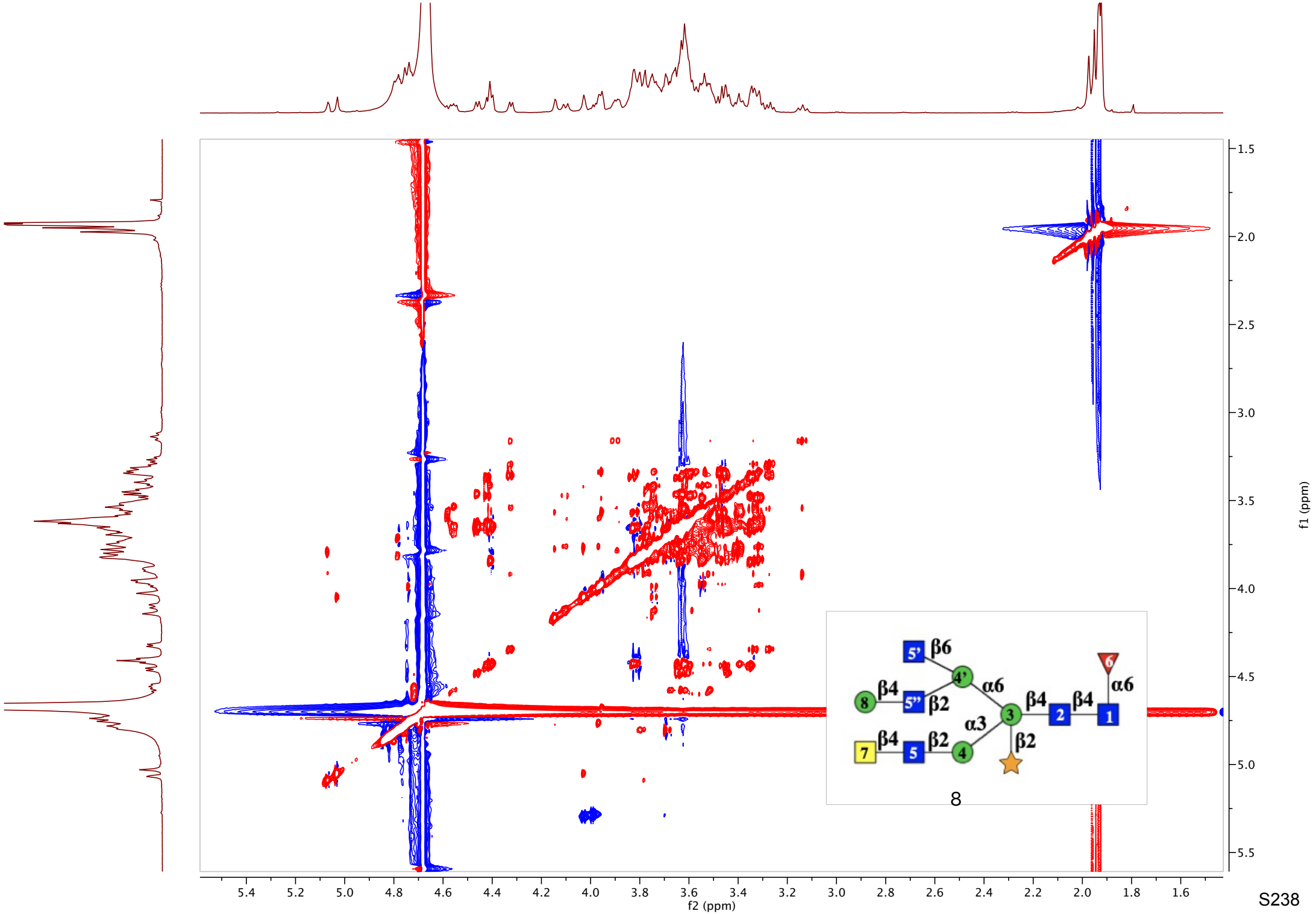
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



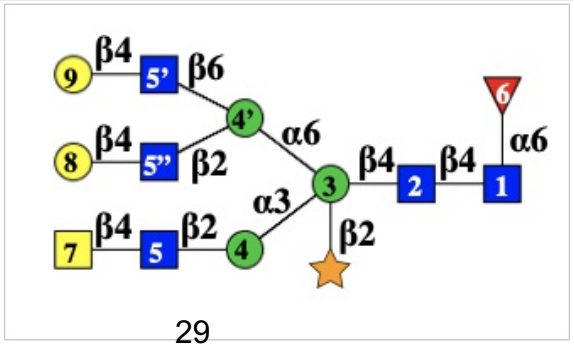
8



8

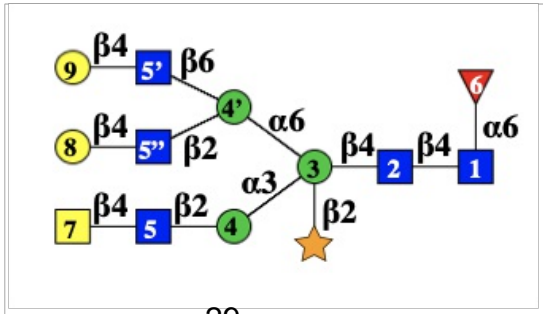

f2 (ppm)
f1 (ppm)
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
5'
β6
4'
α6
8
β4
5"
β2
3
β4
2
β4
1
α6
6
α3
7
β4
5
β2
4
β2

8


β4
β6
9
5'
4'
α6
6
α6
β4
β4
8
5''
β2
3
2
1
α3
β4
β2
β2
7
5
4

29

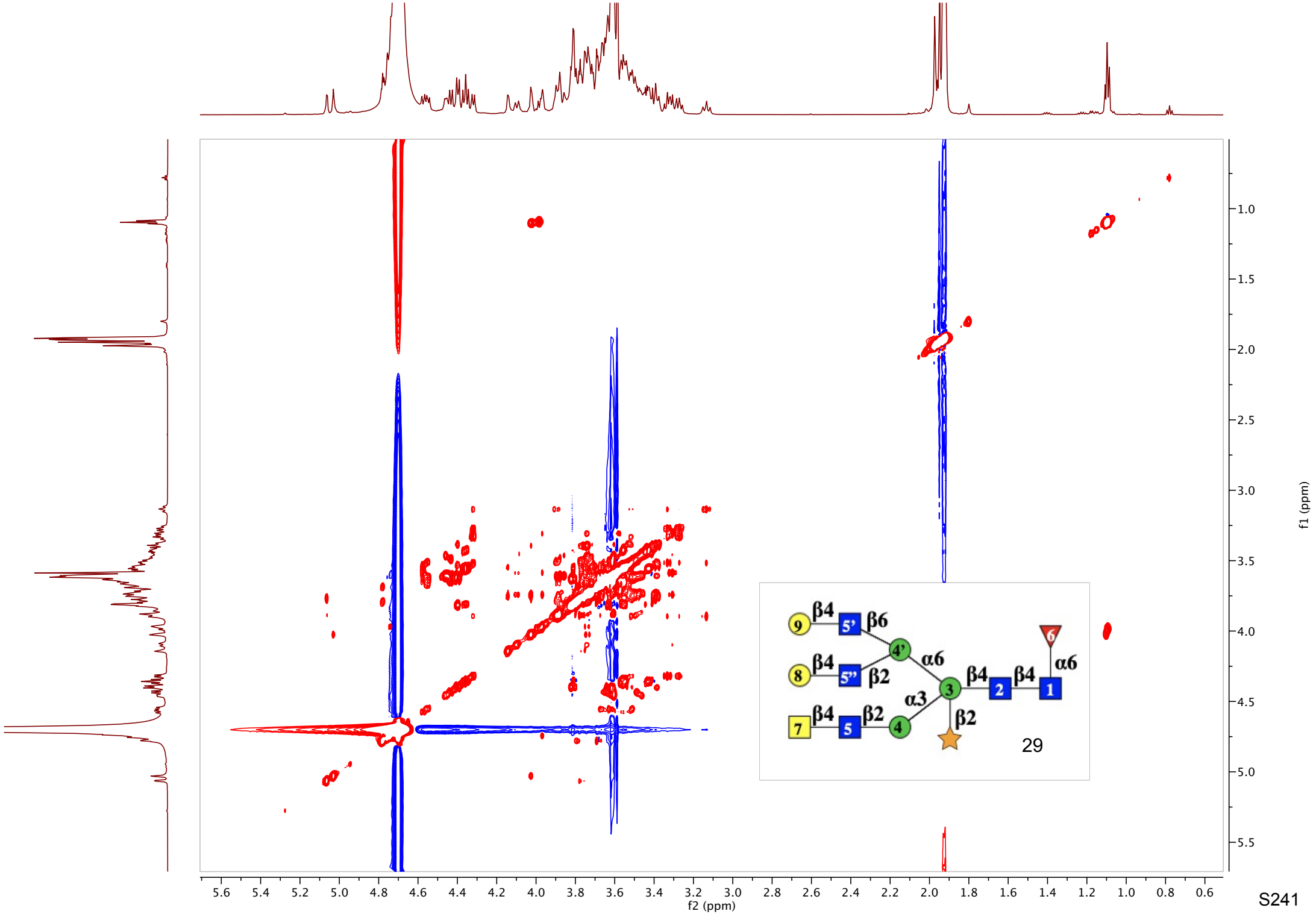
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

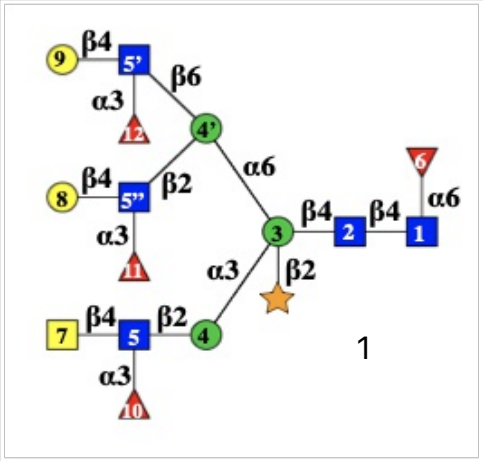


29

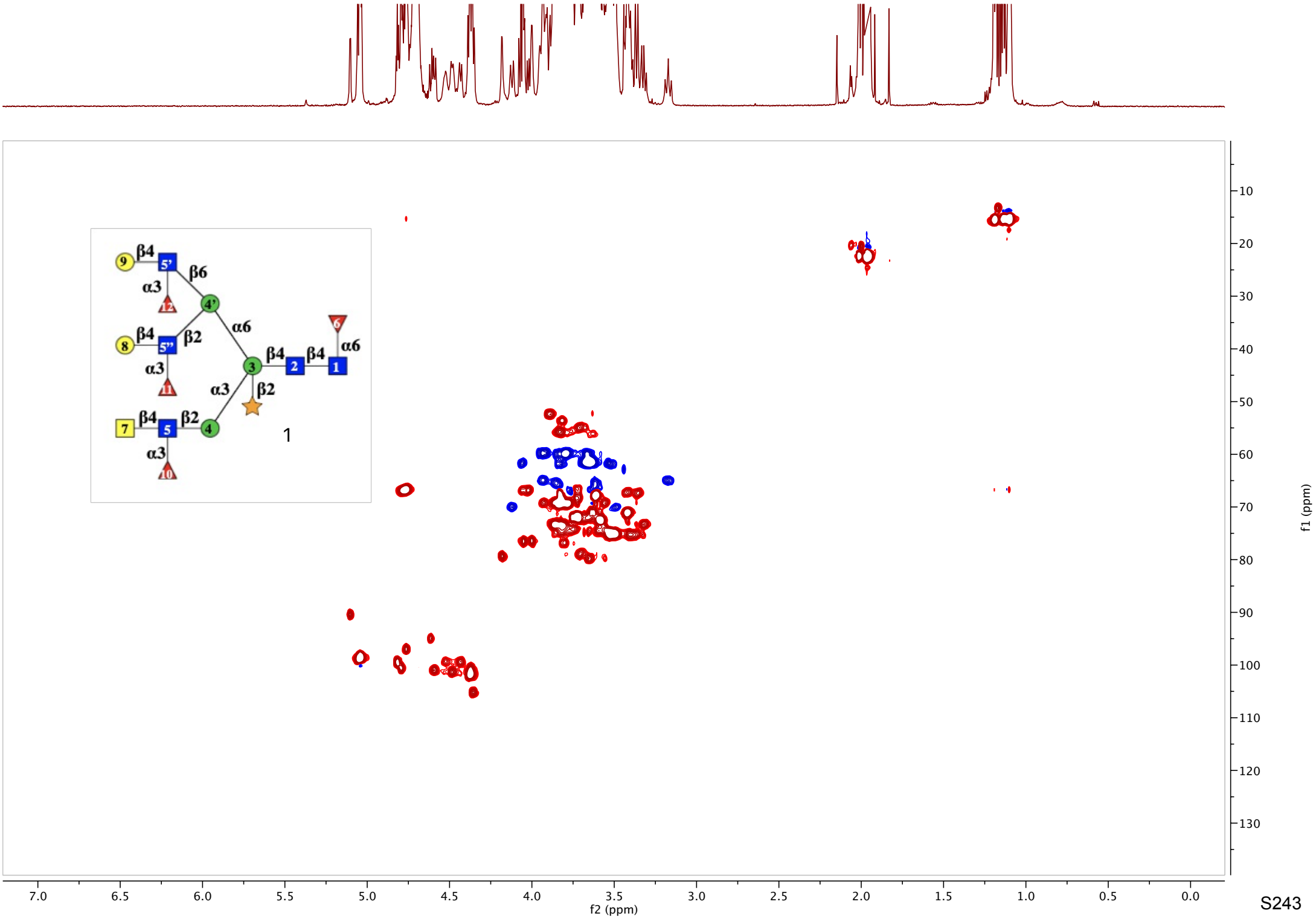
f2 (ppm)

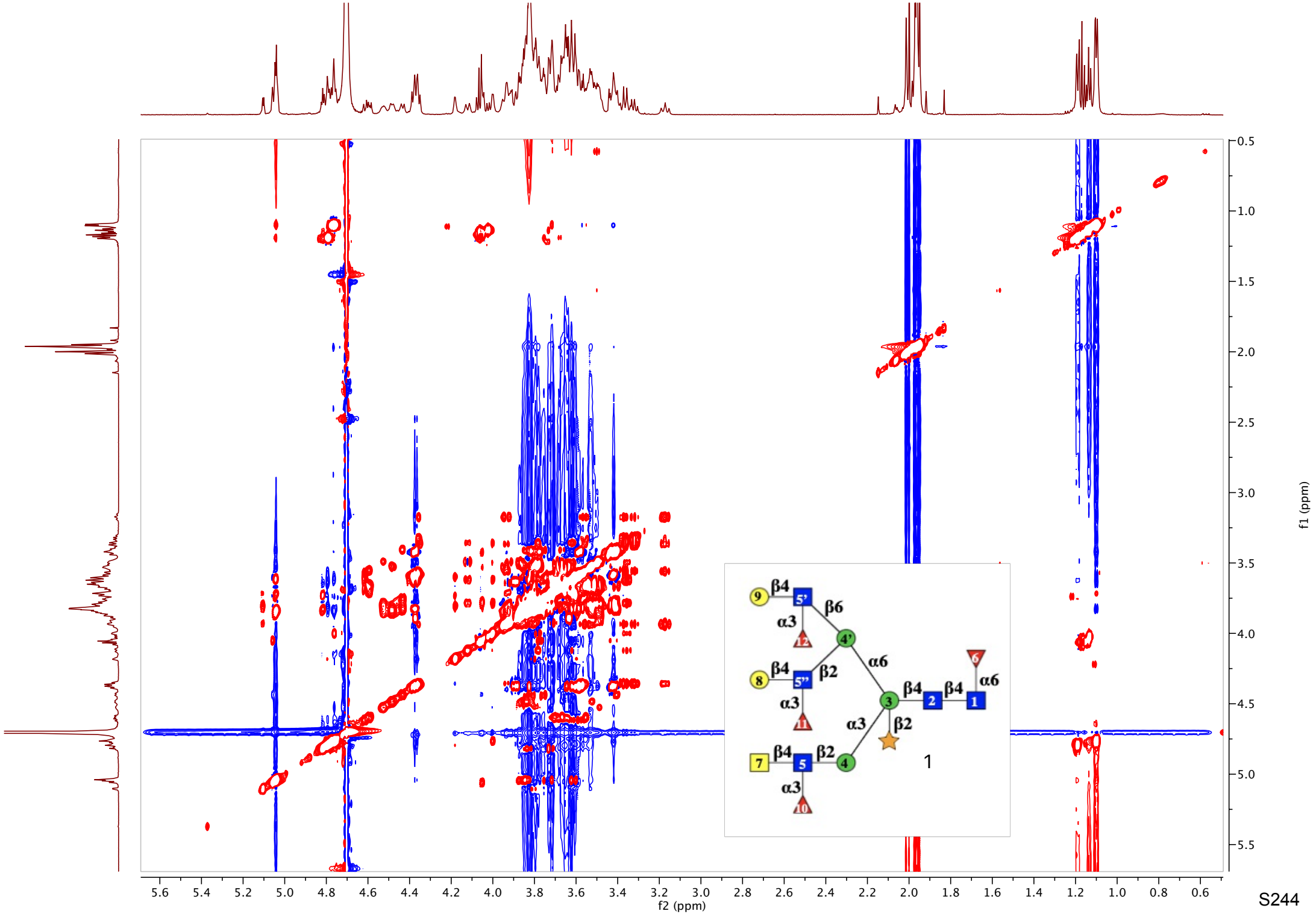
f1 (ppm)

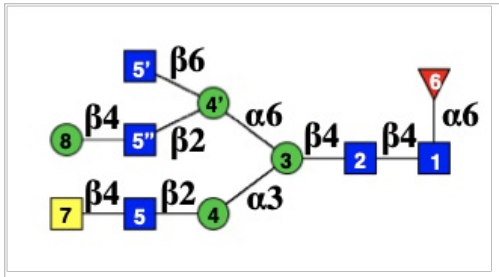

f2 (ppm)
f1 (ppm)
29


9
β4
5'
β6
α3
12
4'
6
α6
8
β4
5''
β2
α3
11
3
β4
2
β4
1
α6
α3
β2
7
β4
5
β2
4
α3
10
1

500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

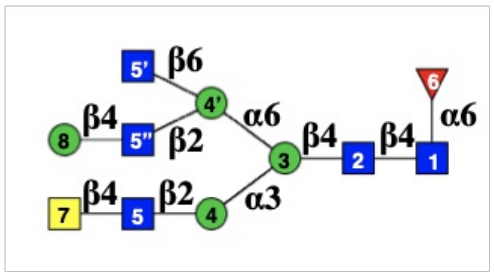

β4
9
5'
β6
α3
12
4'
α6
6
β4
8
5''
β2
α6
α3
11
3
β4
2
β4
1
α3
β2
β4
7
5
β2
4
α3
10
1
f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)
5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6
0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
β4 β6 α3 α6 β2 β4 β4 α6 α3 β2 α3 β4 β2 α3
1


5'
β6
4'
α6
6
α6
β4
8
5''
β2
3
β4
2
β4
1
7
β4
5
β2
4
α3

9

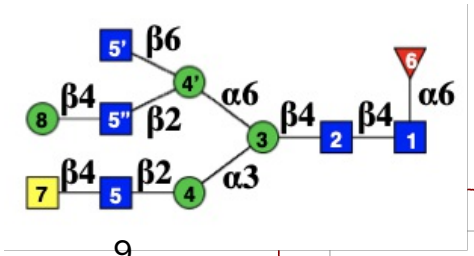
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



9

f2 (ppm)

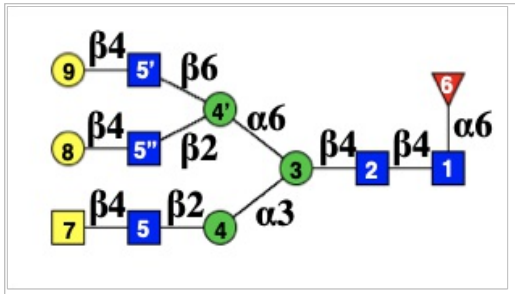
f1 (ppm)



9

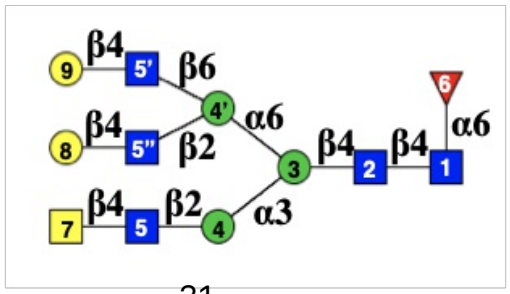
f2 (ppm)

f1 (ppm)

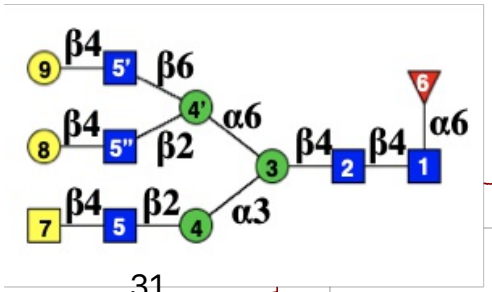

β4
9
5'
β6
4'
α6
6
β4
8
5''
β2
3
β4
2
β4
1
α6
β4
7
5
β2
4
α3

31

650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



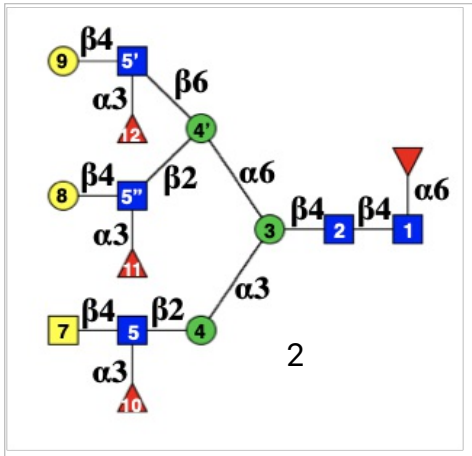
31



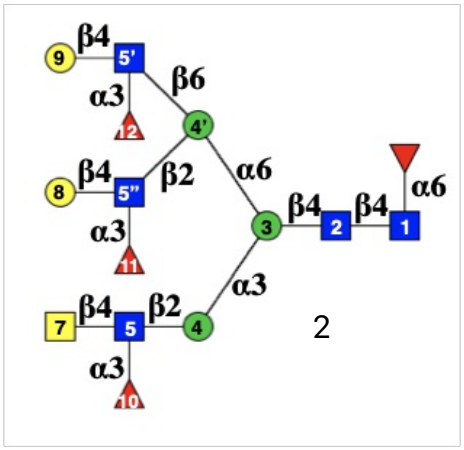
31

f2 (ppm)

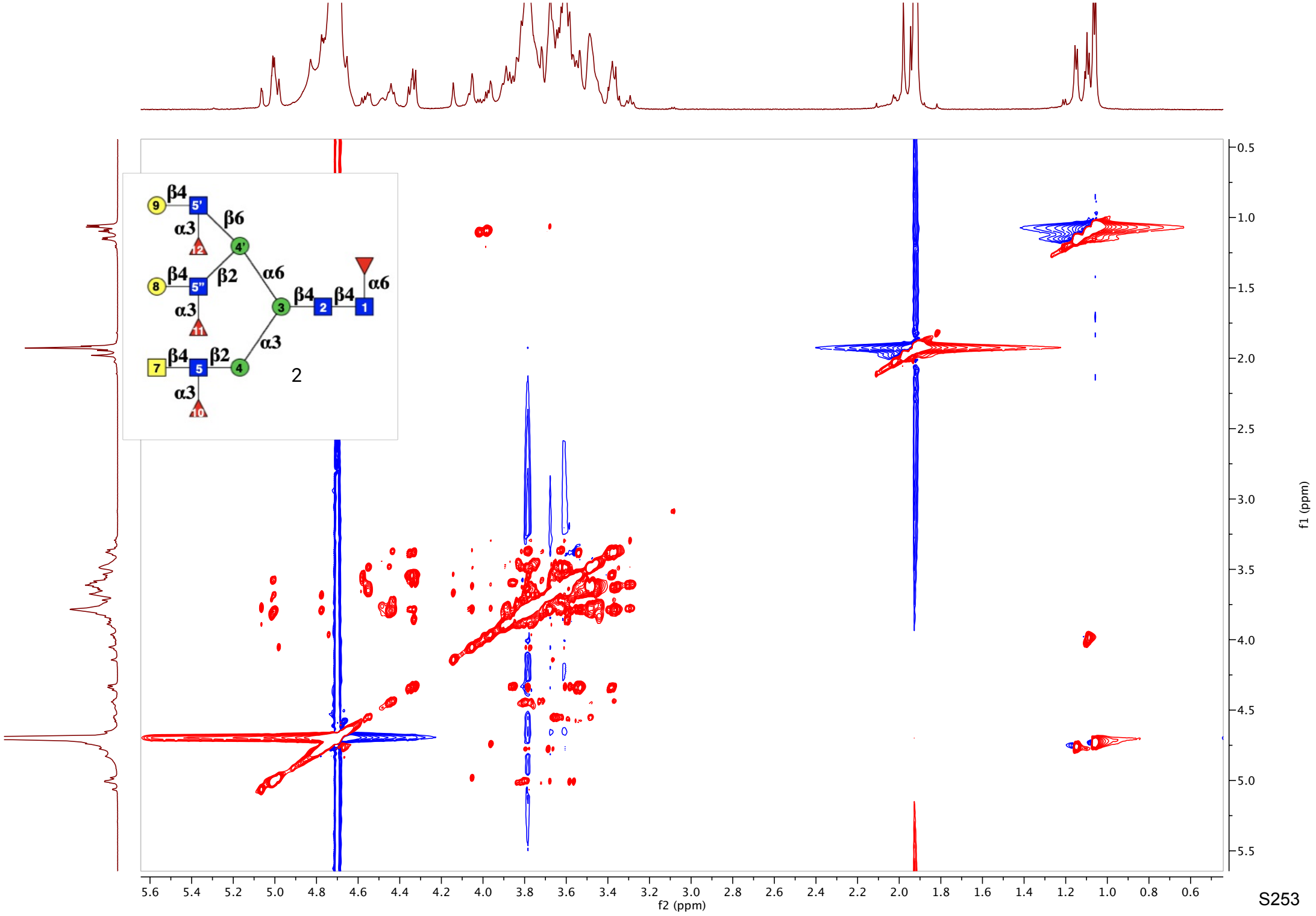
f1 (ppm)

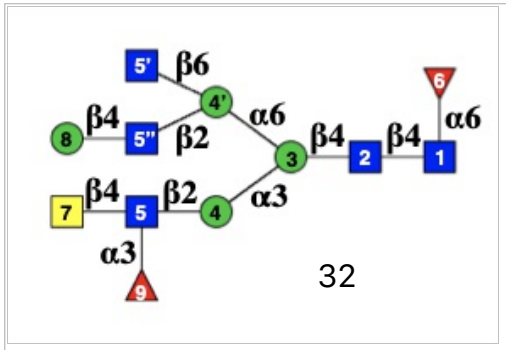

β4
9
5'
β6
α3
12
4'
β4
8
5"
β2
α6
α3
11
3
2
β4
β4
1
α6
β4
7
5
β2
4
α3
α3
10
2

380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


β4
9
5'
β6
α3
12
4'
β4
8
5''
β2
α6
α3
11
3
β4
2
β4
1
α6
α3
β4
7
5
β2
4
α3
10
2

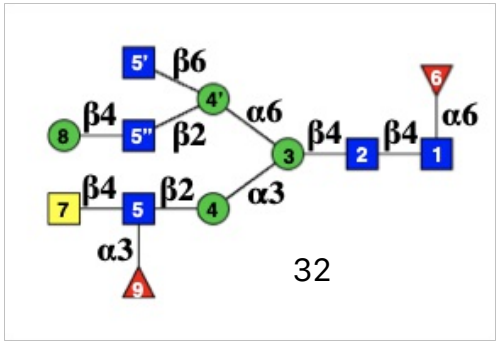
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
f1 (ppm)


β4
9
5'
β6
α3
12
4'
β4
8
5''
β2
α6
α3
11
3
β4
2
β4
1
α6
β4
7
5
β2
4
α3
α3
10
2
f2 (ppm)
f1 (ppm)


5'
β6
4'
α6
6
β4
8
5''
β2
3
β4
2
β4
1
α6
β4
β2
7
5
4
α3
α3
9

32

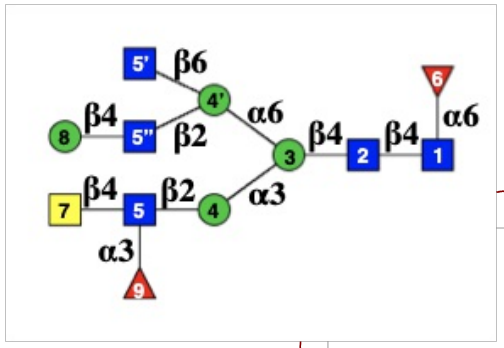
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



32

f2 (ppm)

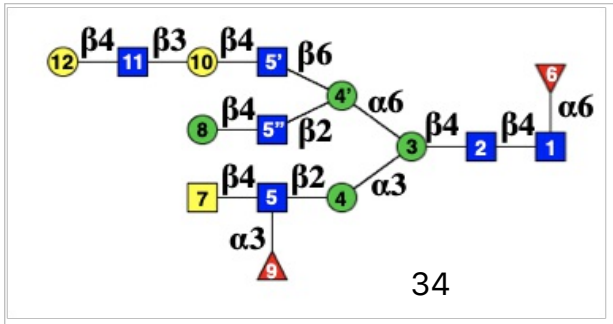
f1 (ppm)



32

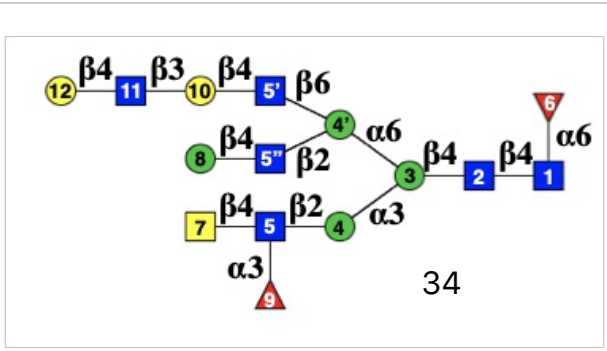
f2 (ppm)

f1 (ppm)

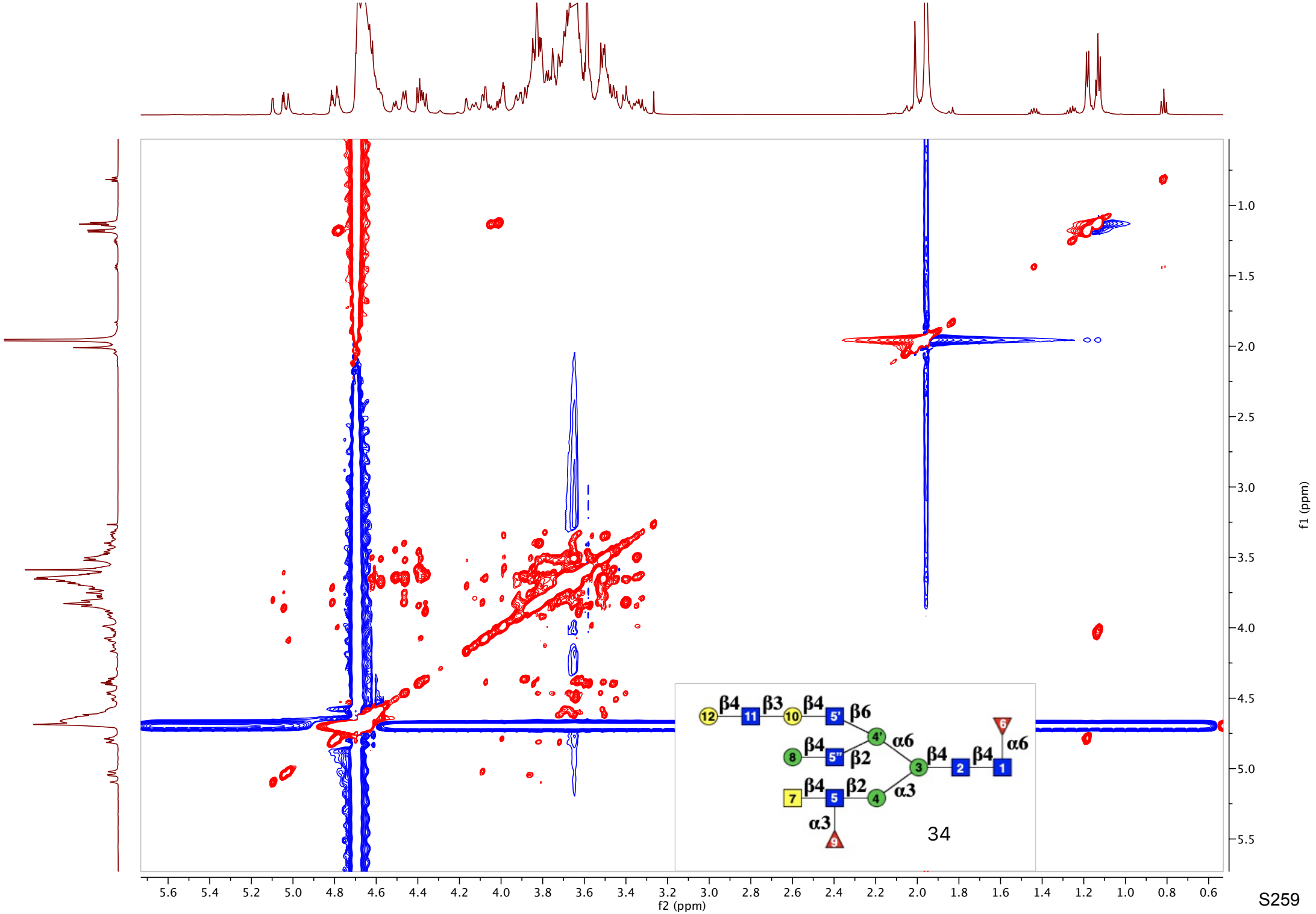

β4
β3
β4
β6
α6
β4
β4
α6
β4
β2
β4
β2
α3
α3
12
11
10
5'
4'
8
5''
3
2
1
6
7
5
4
9

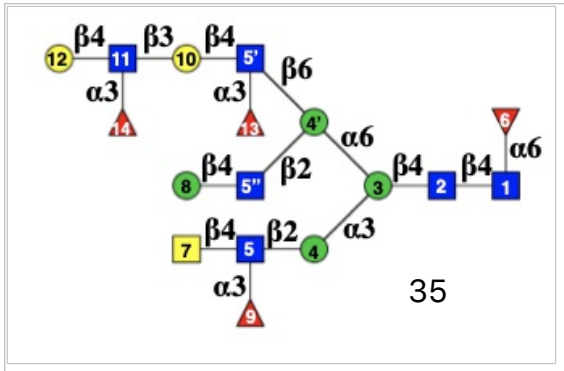
34

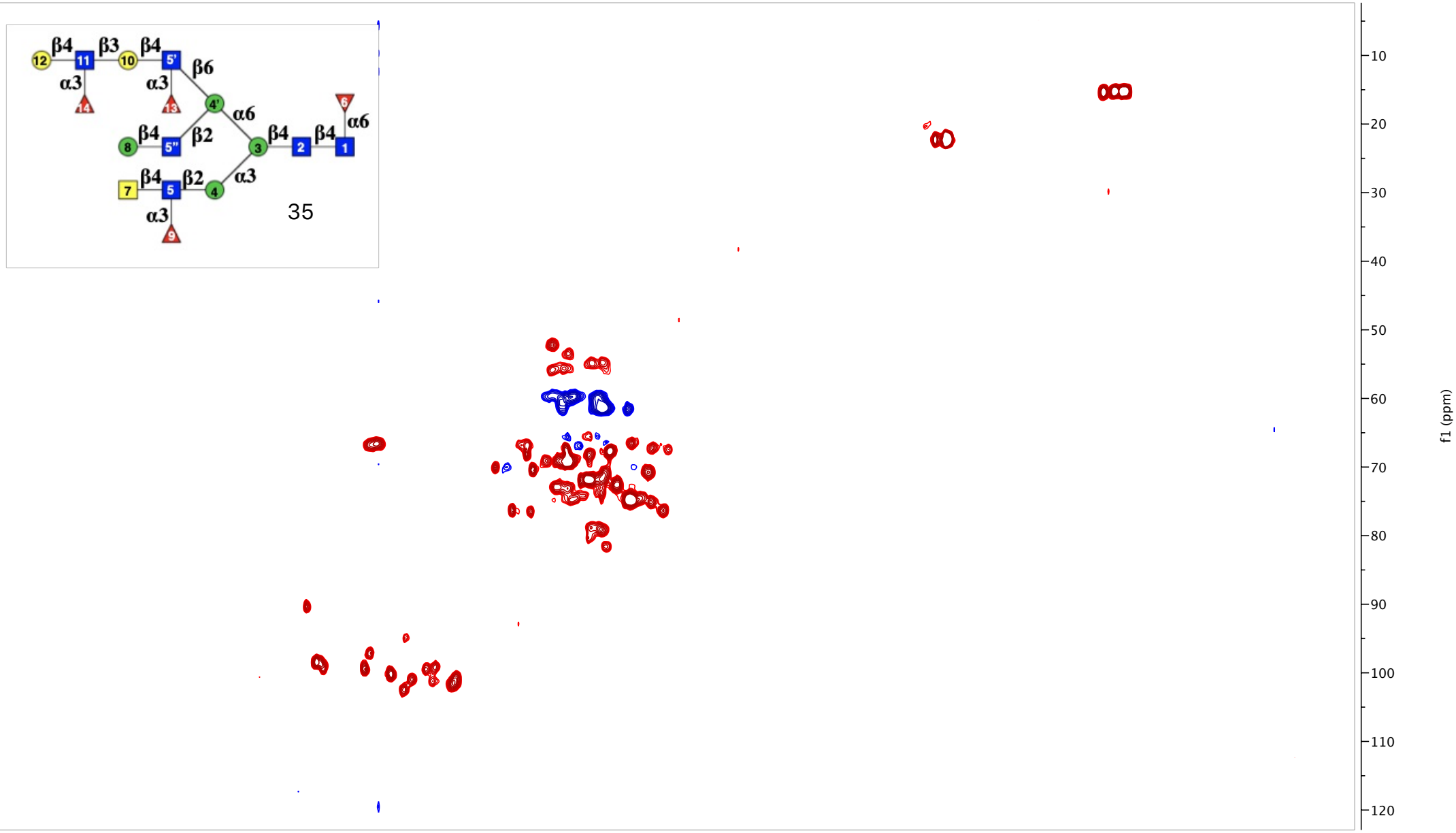
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
18.78
7.23
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

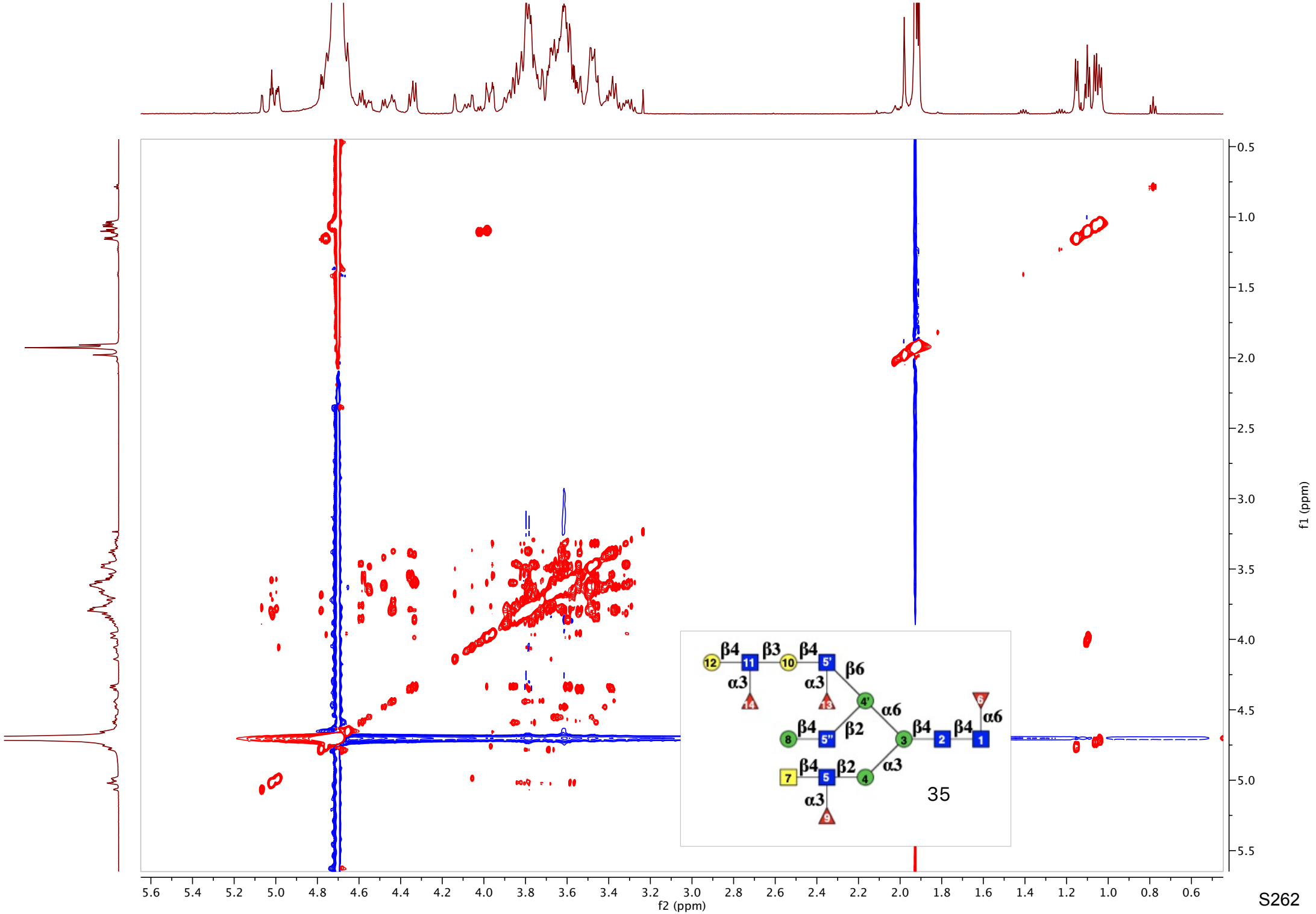

β4
β3
β4
β6
α6
β4
β2
β4
β4
α6
β4
β2
α3
α3
12
11
10
5'
4'
8
5''
3
2
1
6
7
5
4
9
34

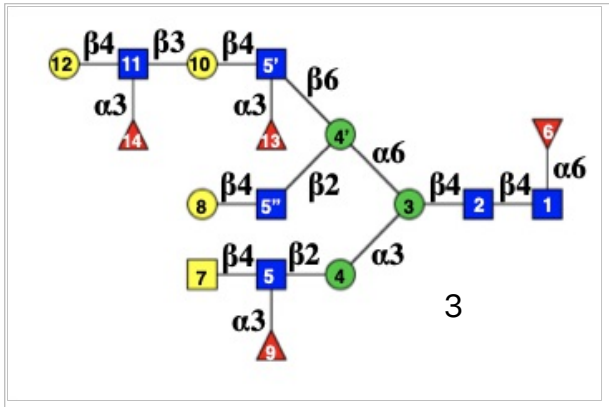
f2 (ppm)
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
10
20
30
40
50
60
70
80
90
100
110


f2 (ppm)
f1 (ppm)
34


β4
β3
β4
β6
α3
α3
α6
β4
β2
β4
β4
α6
β4
β2
α3
α3
35

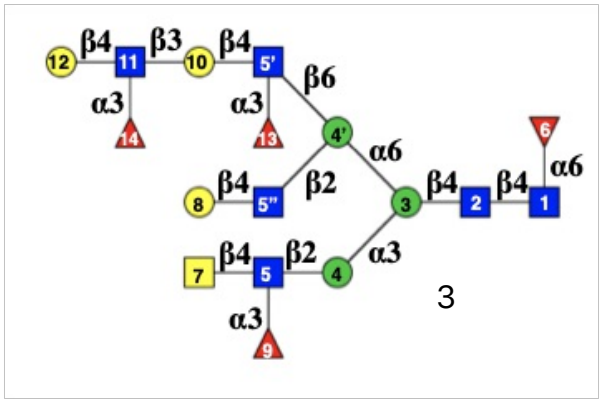

β4
β3
β4
β6
α3
α3
α6
β4
β2
β4
β4
α6
β4
β2
α3
α3
35
f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)
35


β4
β3
β4
β6
α3
α3
α6
β4
β2
β4
β4
α6
β4
β2
α3
α3
12
11
10
5'
4'
6
14
13
8
5"
3
2
1
7
5
4
9

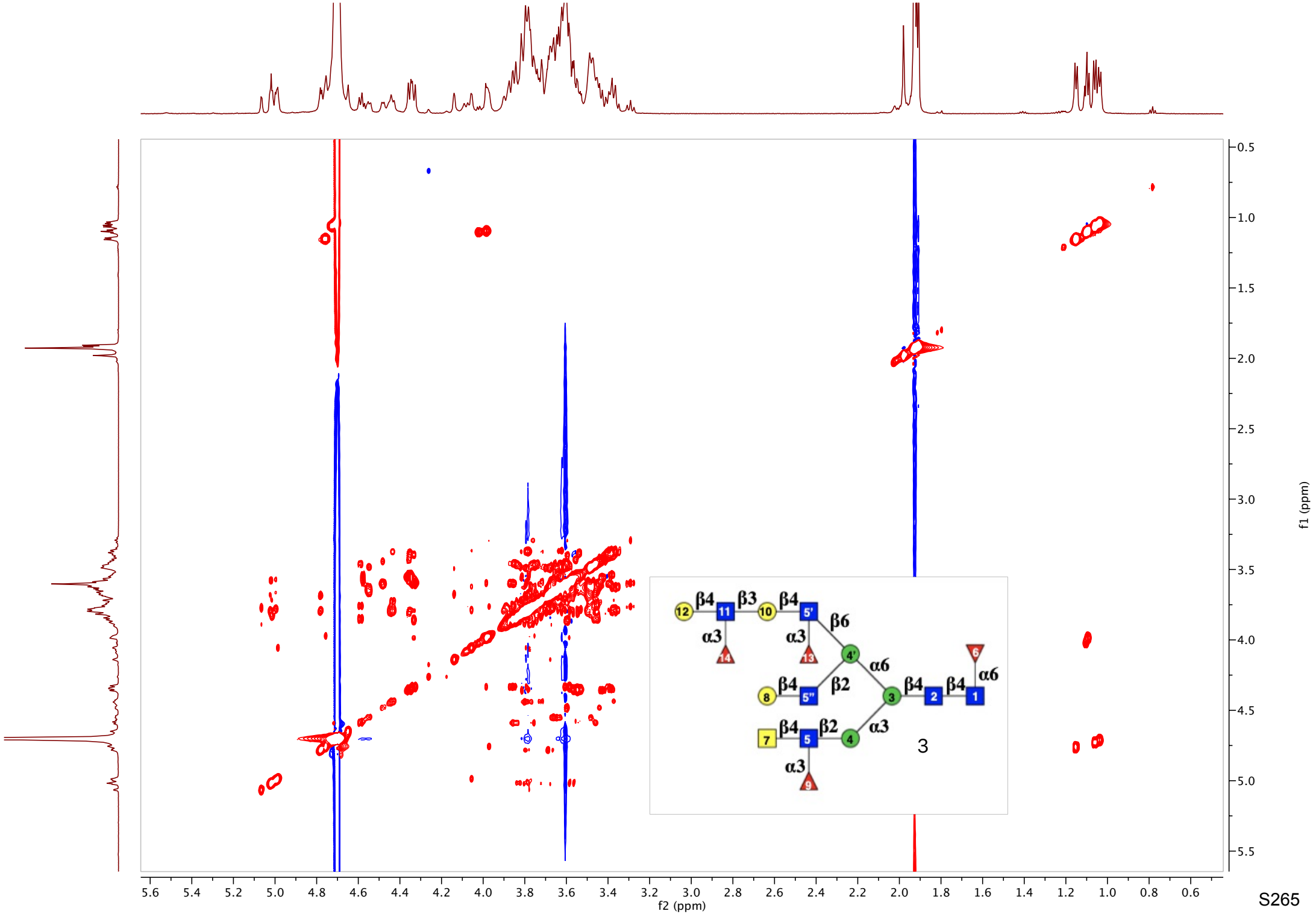
3

420000
400000
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



f2 (ppm)

f1 (ppm)


f2 (ppm)
f1 (ppm)
3