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Supporting Information

Mono- and Di-Fucosylated Glycans of the Parasitic Worm *S. mansoni* are Recognized Differently by the Innate Immune Receptor DC-SIGN

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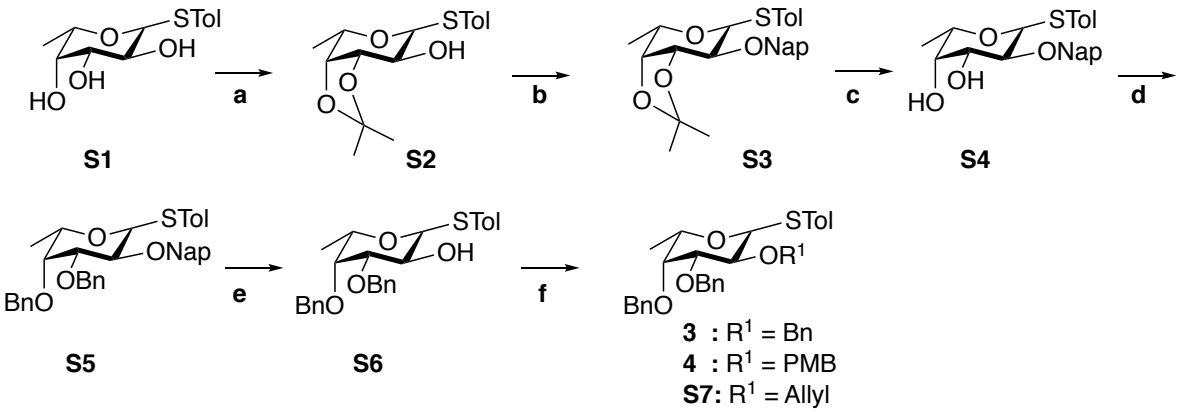
Table of Contents

1. Chemical Synthesis of Building Blocks for Optimization Reactions

1.1 General Methods

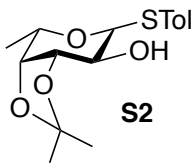
Reactions were performed using flame-dried glassware with anhydrous solvents under an atmosphere of argon unless otherwise noted. Proton nuclear magnetic resonance (^{1}H -NMR) spectra were recorded with Varian 400 (at 400 MHz) or Bruker 600 (at 600 MHz) spectrometers. Multiplicities are assigned as 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. The final compounds were purified by HPLC using HILIC column (XBridge® Amide 5 μm, 10 mm x 250 mm, Waters) using UV detection (210 nm) and lyophilized by dissolving the compound in water and freezing using liquid nitrogen.

1.2 Scheme S1: Synthesis of Fucose Donors



Reagents and Conditions **: a)** 2,2-dimethoxy propane, p-tolunesulfonic acid, DMF, R.T., 12h, 96% ; **b)** NapBr, NaH, DMF, R.T., 15 mins, 83% ; **c)** *p*-TSA, MeOH, DCM, R.T. 24h, 89% ; **d)** BnBr, NaH, DMF, R.T, 1h, 92% ; **e)** DDQ, DCM, H_2O, R.T, 1h, 86% **f) NaH,** PMB-Cl or Bn-Br or Allyl-Cl, DMF, 0°C, 1h, 85 to 90%

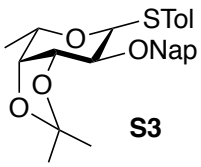
4-methylphenyl 3,4-*O*-isopropylidine-1-thio-β-L-fucopyranoside (S2):



S2

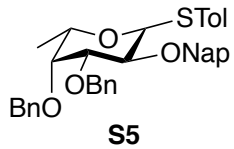
Triol **S1** (8.0 g, 29.5 mmol) was dissolved in DMF (80 mL) under argon atmosphere, followed by the addition of 2,2-dimethoxy propane (7.3 mL, 59.0 mmol) and *p*-toluenesulfonic acid monohydrate (1.1 g, 5.9 mmol). The reaction mixture was stirred overnight, after which the TLC (petroleum ether (PE): EtOAc, 7: 3, v: v, R_f = 0.56) showed the completion of reaction. The reaction was quenched with NEt_3 (10 mL) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography using PE: EtOAc (9: 1, v: v to 8:2, v: v) which gave the desired product as a transparent sticky syrup, as majority beta product. (8.8 g, 96%). R_f = 0.62 (PE: EtOAc, 7: 3, v: v). For NMR studies and subsequent reactions, the beta product was isolated and used. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 to 7.09 (4H, m, H-Ar), 4.34 (1H, d, H-1, *J* = 10.2 Hz), 4.01 (2H, m, H-3, H-4), 3.82 (1H, m, H-5), 3.49 (1H, dd, H-2, *J* = 10.2 Hz, 6.3 Hz), 2.31 (3H, s, C$\underline{H}_3$ of STol), 1.40 to 1.32 (9H, m, 2x C$\underline{H}_3$ of iso-propylidene, C$\underline{H}_3$ of Fuc); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.23 to 128.25 (C-Ar), 88.14 (C-1), 79.05 (C-3), 77.32, 77.20, 77.00, 76.68 (C-4), 72.76 (C-5), 71.28 (C-2), 28.08 and 26.32 (C$\underline{H}_3$ of iso-propylidene), 21.10 (C$\underline{H}_3$ of STol), 16.90 (C$\underline{H}_3$ of Fuc). ESI (*m/z*): $[M + NH_4]^+$ calculated for $C_{16}H_{22}O_4S$, 328.1583; found 328.1587.

4-methylphenyl 3,4-*O*-isopropylidine-2-*O*-(2-methylnaphthyl)-1-thio-β-L-fucopyranoside (S3): Compound **S2** (8.0 g, 25.8 mmol) was dissolved in DMF (50 mL) followed by the addition of NaH (2.0 g, 51.6 mmol, 60% dispersion in oil) and NapBr (8.5 g, 38.7 mmol). The reaction mixture was stirred for 30 min, after which it was quenched with AcOH (10 mL) and solvent was evaporated *in vacuo*. The residue was diluted with DCM (100 mL) and washed successively with water and saturated $NaHCO_3$. The organic phase was dried over $MgSO_4$, filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 8: 2, v: v) afforded the product as a transparent oil. (9.8 g, 84%). R_f = 0.59 (PE: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 to 7.04 (11H, m, H-Ar), 4.97 (1H, CHH of Nap, *J* = 11.5 Hz), 4.83 (1H, d, CHH of Nap, *J* = 11.5 Hz), 4.54 (1H, d, H-1, *J* = 9.8 Hz), 4.24 (1H, t, H-3, *J* = 6.1 Hz), 4.03 (1H, dd, H-4, *J* = 5.6 Hz, 2.1 Hz), 3.79 (1H, m, H-5), 3.51 (1H, dd, H-2, *J* = 9.5 Hz, 6.5 Hz), 2.30 (3H, s, CH_3 of STol), 1.38 (3H, d, *J* = 6.7 Hz, CH_3 of Fuc), 1.37 to 1.35 (6H, 2s, 2x CH_3 of iso-propylidene); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.51 to 125.76 (C-Ar), 86.47 (C-1), 79.90 (C-4), 78.02 (C-2), 77.31, 76.99, 76.67, 76.44 (C-3), 73.43 (CH_2 of Nap), 72.37 (C-5), 27.84 and 26.38 (CH_3 of iso-propylidene), 21.09 (CH_3 of STol), 16.87 (CH_3 of Fuc). ESI (*m/z*): $[M + NH_4]^+$ calculated for $C_{27}H_{30}O_4S$, 468.2209; found 468.2218.



S3

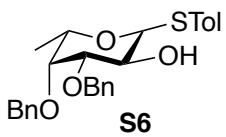
4-methylphenyl 3,4-di-*O*-benzyl-2-*O*-(2-methylnaphthyl)-1-thio-β-L-fucopyranoside (S5): Compound **S3** (9.5 g, 21.1 mmol) was dissolved in the solvent system DCM (50 mL) and MeOH (50 mL), followed by the addition of *p*-toluenesulfonic acid monohydrate (665 mg, 3.5 mmol) and stirred for 24 h, after which the iso-propylidine ring fell off to give the desired diol. The reaction mixture was quenched with NEt_3 (5 mL), following which the solvent was evaporated *in vacuo* giving the crude mixture as a white foamy powder. This crude residue was used in further reaction without any purification. R_f = 0.42 (DCM: MeOH, 9: 1, v: v). The crude diol **S4** (6.2 g, 15.1 mmol) was dissolved in anhydrous DMF (100 mL), followed by the addition of NaH (2.4 g, 59.9 mmol, 60% dispersion in oil) and BnBr (5.3 mL, 45.0 mmol). The



S5

reaction mixture was stirred for one h, after which it was quenched with AcOH (10 mL) and solvent was evaporated *in vacuo*. The residue was diluted with DCM and washed successively with water and saturated $NaHCO_3$ solution. The organic phase was dried over $MgSO_4$, filtered and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 7: 3, v: v) afforded the product as a white amorphous powder. (7.9 g, 90%). R_f = 0.51 (PE: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 to 6.89 (21H, m, H-Ar), 4.96 (3H, m, PhC<u>H</u>H, PhCH<u>H</u>, CH<u>H</u> of Nap), 4.76 (2H, s, PhC<u>H</u>H, PhCH<u>H</u>), 4.68 (1H, d, C<u>H</u>H of Nap, *J* = 11.7 Hz), 4.59 (1H, d, H-1, *J* = 9.6 Hz), 3.96 (1H, t, H-2, *J* = 9.4 Hz), 3.63 (2H, m, H-3, H-4), 3.52 (1H, m, H-5), 2.30 (3H, s, C<u>H</u>$_3$ of STol), 1.28 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.75 to 125.72 (C-Ar), 87.89 (C-1), 84.60 (C-4), 77.31 (C-2), 77.17, 76.99, 76.67, 76.64 (C-3), 75.53 (Ph<u>C</u>H$_2$), 74.58 (C-5), 74.56 (<u>C</u>H$_2$ of Nap), 72.81 (Ph<u>C</u>H$_2$), 21.08 (<u>C</u>H$_3$ of STol), 17.30 (<u>C</u>H$_3$ of Fuc). ESI (*m/z*): $[M + NH_4]^+$ calculated for $C_{38}H_{38}O_4S$, 608.2835; found 608.2832.

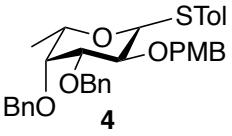
4-methylphenyl 3,4-di-*O*-benzyl-1-thio-β-L-fucopyranoside (S6): Compound **S5** (7.0 g, 11.8 mmol) was dissolved in DCM: H_2O (100 mL, 9: 1, v: v) followed by the addition of DDQ (5.8 g, 23.7 mmol). The reaction mixture was stirred in dark for 2 h, following which the TLC showed full conversion of starting material to product. R_f = 0.44 (PE: EtOAc, 7: 3, v: v). The mixture was diluted by DCM (100 mL) and washed successively with saturated $NaHCO_3$ and water. The organic phase was dried over $MgSO_4$, filtered and the filtrate was concentrated *in vacuo*. Silica gel column chromatography with PE: EtOAc (8: 2, v: v to 6: 4, v: v) afforded the product as a yellowish amorphous powder. (4.7 g, 88.6%). R_f = 0.44 (PE: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 to 6.93 (14H, m, H-Ar), 4.92 (1H, d, PhCH<u>H</u>), 4.72 (2H, s, PhC<u>H</u>H, PhCH<u>H</u>), 4.62 (1H, d, PhC<u>H</u>H, *J* = 11.4 Hz), 4.42 (1H, d, H-1, *J* = 9.7 Hz), 3.93 (1H, t, H-2, *J* = 9.3 Hz), 3.61 (1H, d, H-4, *J* = 2.6 Hz), 3.54 (1H, m, H-5), 3.45 (1H, dd, H-3, *J* = 9.4 Hz, 2.7 Hz), 2.29 (3H, s, C<u>H</u>$_3$ of STol), 1.26 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.64 to 127.36 (C-Ar), 88.73 (C-1), 83.54 (C-3),



S6

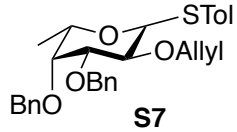
77.29, 77.17, 76.97 (C-4), 76.65, 76.37, 74.95 (C-5), 74.52 (Ph<u>C</u>H$_2$), 72.55 (Ph<u>C</u>H$_2$), 68.89 (C-2), 21.09 (<u>C</u>H$_3$ of STol), 17.27 (<u>C</u>H$_3$ of Fuc). ESI (*m/z*): [M + NH$_4$]$^+$ calculated for $C_{27}H_{30}O_4S$, 468.2209; found 468.2212.

4-methylphenyl 3,4-di-*O*-benzyl-2-*O*-*p*-methoxybenzyl-1-thio-β-L-fucopyranoside (4): Compound **S6** (2.0 g, 4.4 mmol) was dissolved in DMF (20 mL), followed by the addition of NaH (280 mg, 7.0 mmol, 60% dispersion in oil) and 4-methoxybenzyl chloride (710 μL, 5.2 mmol). The reaction mixture was stirred for 1 h, after which it was quenched with AcOH (2 mL). The solvent was evaporated *in vacuo* and the residue was diluted with DCM (50 mL) and washed successively with water and saturated NaHCO$_3$ solution. The organic layers were collected, dried over MgSO$_4$ and concentrated *in vacuo*. Silica gel column chromatography using PE: EtOAc (9: 1, v: v) afforded the required product as a colorless syrup. (2.2 g, 88%). R_f = 0.53 (PE: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 to 6.71 (18H, m, H-Ar), 4.99 (1H, d, PhCH<u>H</u>, *J* = 11.7 Hz), 4.68 (5H, m, PhC<u>H</u>H, 2x Ph-C<u>H</u>$_2$), 4.52 (1H, d, H-1, *J* = 9.7 Hz), 3.86 (1H, t, H-2, *J* = 9.3 Hz), 3.78 (3H, s, OC<u>H</u>$_3$ of PMB), 3.61 (1H, d, H-4, *J* = 2.4 Hz), 3.55 (1H, dd, H-3, *J* = 9.2 Hz, 2.7 Hz), 3.48 (1H, m, H-5), 2.28 (3H, s, C<u>H</u>$_3$ of STol), 1.26 (3H, d, C<u>H</u>$_3$ of Fuc, *J* = 6.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.22 to 113.71 (C-Ar), 87.89 (C-1), 84.56 (C-3), 77.31, 76.99, 76.86 (C-2), 76.67 (C-4), 76.62, 75.15 (Ph<u>C</u>H$_2$), 74.51 (C-5), 72.84 (Ph<u>C</u>H$_2$), 55.27 (O<u>C</u>H$_3$ of PMB), 21.09 (<u>C</u>H$_3$ of STol), 17.28 (<u>C</u>H$_3$ of Fuc). ESI (*m/z*): [M + NH$_4$]$^+$ calculated for $C_{35}H_{38}O_5S$, 588.2784; found 588.2781.



4

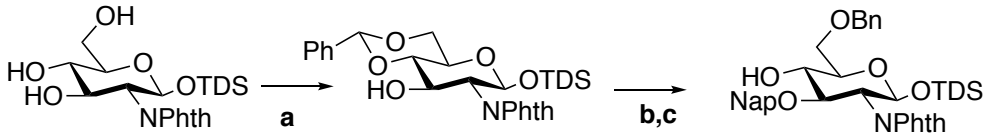
4-methylphenyl 2-*O*-allyl-3,4-di-*O*-benzyl-1-thio-β-L-fucopyranoside (S7): Compound **S6** (2.0 g, 4.4 mmol) was dissolved in DMF (20 mL), followed by the addition of NaH (280 mg, 7.0 mmol, 60% dispersion in oil) and allyl bromide (571 μL, 6.6 mmol). The mixture was stirred for 1 h, after which it was quenched with AcOH (2 mL). The solvent was evaporated *in vacuo*,



S7

the residue was diluted with DCM (50 mL) and washed successively with water and saturated $NaHCO_3$ solution. The organic phase was dried over $MgSO_4$, filtered and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using PE: EtOAc (9: 1, v: v) afforded the required product as a colorless syrup. (1.6 g, 74%), R_f = 0.49 (PE: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 to 6.89 (14H, m, H-Ar), 5.97 (1H, m, $OCH_2C\underline{H}=CH_2$ of Allyl), 5.18 (2H, m, $OCH_2CH=C\underline{H}_2$ of Allyl), 4.96 (1H, d, PhC$\underline{H}$H, *J* = 11.8 Hz), 4.71 (2H, m, PhC$\underline{H}$H, PhC$\underline{H}$H), 4.64 (1H, d, PhC$\underline{H}$H, *J* = 11.8 Hz), 4.46 (1H, d, H-1, *J* = 9.4 Hz), 4.26 (2H, m, $OC\underline{H}_2CH=CH_2$ of Allyl), 3.74 (1H, t, H-2, *J* = 9.3 Hz), 3.59 (1H, d, H-4, *J* = 2.8 Hz), 3.49 (2H, m, H-5, H-3), 2.29 (3H, s, $C\underline{H}_3$ of STol), 1.23 (3H, d, $C\underline{H}_3$ of Fuc, *J* = 6.4 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.76 to 136.99 (C-Ar), 135.07 ($OCH_2\underline{C}H=CH_2$ of Allyl), 132.10 to 127.37 (C-Ar), 116.89 ($OCH_2CH=\underline{C}H_2$ of Allyl), 87.85 (C-1), 84.40 (C-3), 77.30, 77.04, 76.98, 76.70 (C-2), 76.67 (C-4), 74.55 ($Ph\underline{C}H_2$), 74.48 (H-5), 74.33 ($O\underline{C}H_2CH=CH_2$ of Allyl), 72.90 ($Ph\underline{C}H_2$), 21.06 ($\underline{C}H_3$ of STol), 17.23 ($\underline{C}H_3$ of Fuc). ESI (*m/z*): $[M + NH_4]^+$ calculated for $C_{30}H_{34}O_4S$, 508.2522; found 508.2513.

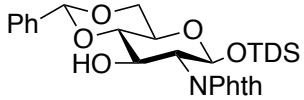
1.3 Scheme S2: Synthesis of Acceptor S10



S8 **S9** **S10**

Reagents and Conditions **: a)** Benzaldehyde dimethyl acetal, p-tolunesulfonic acid, ACN, R.T., 2h, 85% ; **b)** NapBr, NaH, DMF, 0ºC, 2h **c)** TfOH, Et_3SiH, DCM, mol. sieves, -60ºC, 30 mins, 76% over two steps

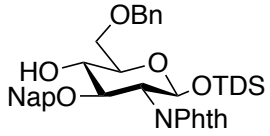
Dimethylthexylsilyl 4,6-*O*-benzylidine-2-deoxy-2-phthalimido-β-D-glucopyranoside (S9): To a suspension of triol **S8** (10.0 g, 22.2 mmol) in dry acetonitrile (100 mL) was added benzaldehyde dimethyl acetal (4.0 mL, 26.6 mmol) and *p*-toluenesulfonic acid monohydrate (764 mg, 4.4 mmol). The reaction mixture was stirred at room temperature for 6 h, after



S9

which it was quenched with NEt_3 (5 mL). The solvent was concentrated *in vacuo* and the residue was purified by silica gel column chromatography using PE: EtOAc (9: 1, v: v to 7: 3, v: v), which afforded the target compound as a white amorphous solid, (10.1 g, 85%). R_f = 0.47 (PE: 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, CHPh 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, m, 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, $CH(CH_3)_2$ of TDS], 0.62 [12H, m, $C(CH_3)_2$, $CH(CH_3)_2$ of TDS], 0.09 to -0.04 (6H, 2s, 2x CH_3-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.03 to 123.27 (C-Ar), 101.95 (CHPh of benzylidene), 93.88 (C-1), 82.40 (C-4), 77.31, 77.00, 76.68, 68.74 (C-6), 68.44 (C-3), 66.20 (C-5), 58.64 (C-2), 33.79 ($CH(CH_3)_2$ of TDS), 19.79 to 18.16 (4x CH_3 of TDS), -0.02 to -1.86 (2x CH_3-Si of TDS). ESI (*m/z*): $[M+ Na]^+$ calculated for $C_{29}H_{37}NO_7Si$, 562.2237; found 562.2233.

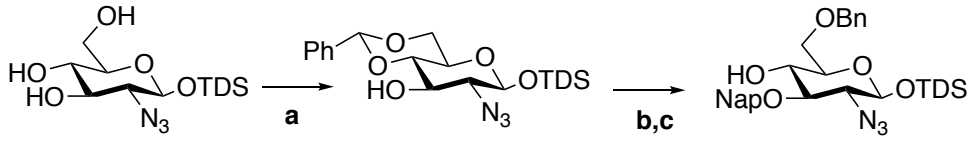
Dimethylthexylsilyl 6-*O*-benzyl-3-*O*-(2-methylnaphthyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (S10): A solution of **S9** (10.0 g, 18.5 mmol) in DMF (100 mL) was cooled down to 0 ºC, followed by the sequential addition of NapBr (5.3 g, 24.1 mmol) and NaH (1.1 g, 27.8 mmol, 60% dispersion in oil). The reaction mixture was stirred at this temperature for 2 h, after which it was quenched with AcOH (5 mL). The solvent was evaporated *in vacuo* and the residue was diluted with DCM, washed with saturated $NaHCO_3$ and water and dried over $MgSO_4$. The organic phase was filtered, and the filtrate was concentrated *in vacuo* and was used in the next step without purification. The residue was stirred with pre-activated molecular sieves (20 g) in 100 mL DCM for 30 min. The mixture was cooled down to -60 ºC, followed by the sequential addition of triethylsilane (4.2 mL, 26.5 mmol) and trifluoromethanesulfonic acid (1.8 mL, 19.9 mmol). The reaction mixture was stirred at this temperature for 30 min, after which it was quenched with a mixture of NEt_3: MeOH (5 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 and washed with saturated $NaHCO_3$ and dried over $MgSO_4$. The organic phase was filtered, and the filtrate was concentrated



S10

in vacuo. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 7: 3, v: v) yielded the product as a pale-yellow powder. (6.9 g, 76% over two steps). R_f = 0.53 (PE: EtOAc, 8: 2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 to 7.09 (16H, m, H-Ar), 5.32 (1H, d, H-1, *J* = 8.2 Hz), 4.93 (1H, d, CHH of Nap, *J* = 12.6 Hz), 4.64 (3H, m, CHH of Nap, PhCHH, PhCHH), 4.32 (1H, dd, H-3, *J* = 10.6 Hz, 8.0 Hz), 4.08 (1H, dd, H-2, *J* = 10.0 Hz, 8.0 Hz), 3.81 (3H, m, H-6a, H-4, H-6b), 3.65 (1H, m, H-5), 2.98 (1H, d, OH, *J* = 2.4 Hz), 1.31 [1H, m, $CH(CH_3)_2$ of TDS], 0.54 [12H, m, $C(CH_3)_2$, $CH(CH_3)_2$ of TDS], 0.06 to -0.11 (6H, 2s, 2x CH_3-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.67 to 125.49 (C-Ar), 93.36 (C-1), 78.93 (C-3), 77.29, 77.18, 76.98, 76.66, 74.79 (CH_2 of Nap), 74.61 (C-4), 73.79 ($PhCH_2$), 73.46 (C-5), 71.05 (C-6), 57.38 (C-2), 33.79 ($CH(CH_3)_2$ of TDS), 24.42, 19.80 to 18.10 (4x CH_3 of TDS), -1.85 to -3.92 (2x CH_3-Si of TDS). ESI (*m/z*): $[M+ NH_4]^+$ calculated for $C_{40}H_{47}NO_7Si$, 699.3466; found 699.3460.

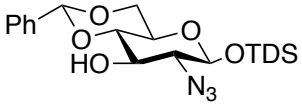
1.4 Scheme S3: Synthesis of Acceptor 2



S11 **S12** **2**

Reagents and Conditions **: a)** Benzaldehyde dimethyl acetal, p-tolunesulfonic acid, ACN, R.T., 6h, 77% ; **b)** NapBr, NaH, DMF, 0ºC, 2h **c)** TfOH, Et_3SiH, DCM, mol. sieves, -60ºC, 30 mins, 73% over two steps

Dimethylthexylsilyl 2-deoxy-2-azido-4,6-*O*-benzylidine-β-D-glucopyranoside (S12):

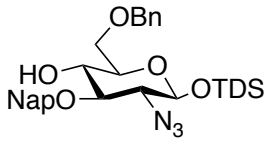


S12

To a suspension of triol **S11**, (10.6 g, 30.5 mmol) in dry acetonitrile (100 mL) was added benzaldehyde dimethyl acetal (5.5 mL, 36.6 mmol) and *p*-toluenesulfonic acid monohydrate (1.2 g, 6.1 mmol) and the reaction mixture was stirred at room temperature for 6 h after which the TLC (PE: EtOAc, 7: 3, v: v) showed the reaction had gone to completion. The reaction mixture was quenched with NEt_3 (5 mL) and concentrated *in vacuo*. Silica gel column chromatography

using PE: EtOAc (8: 2, v: v) afforded the target compound as a transparent syrup, (10.3 g, 78%). R_f = 0.59 (PE: EtOAc, 8: 2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 to 7.20 (5H, m, Ar-H), 5.51 (1H, s, C<u>H</u>Ph of benzylidene), 4.60 (1H, d, H-1, *J* = 7.5 Hz), 4.26 (1H, dd, H-6b, *J* = 10.5 Hz, 5.1 Hz), 3.75 (1H, t, H-6a, *J* = 10.1 Hz), 3.57 (2H, m, H-3, H-4), 3.37 (1H, m, H-5), 3.29 (1H, dd, H-2, *J* = 9.4 Hz, 7.7 Hz), 1.65 [1H, m, C<u>H</u>$(CH_3)_2$ of TDS], 0.89 [12H, m, C($C\underline{H}_3)_2$, CH($C\underline{H}_3)_2$ of TDS], 0.19 (6H, d, 2x $C\underline{H}_3$-Si of TDS, *J* = 8.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.86 to 126.22 (C-Ar), 101.96 (<u>C</u>HPh of benzylidene), 97.36 (C-1), 80.74 (C-3), 77.32 , 77.21, 77.00, 76.69, 71.88 (C-4), 69.11 (C-2), 68.54 (C-6), 66.23 (C-5), 34.14 (<u>C</u>H$(CH_3)_2$ of TDS), 19.91 to 18.36 (4x <u>C</u>H_3 of TDS), -0.03 to -3.23 (2x <u>C</u>H_3-Si of TDS). ESI (*m/z*): $[M+ NH_4]^+$ calculated for $C_{21}H_{33}N_3O_5Si$, 453.2533; found 453.2531.

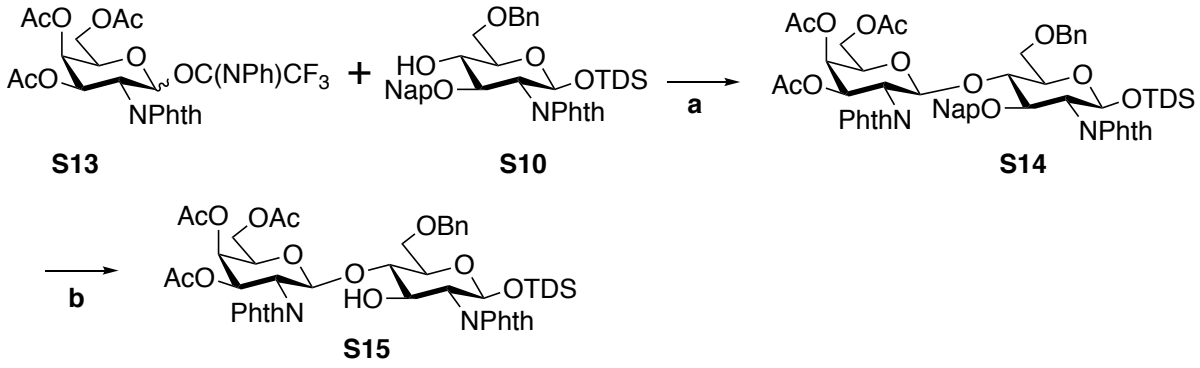
Dimethylthexylsilyl 2-deoxy-2-azido-6-*O*-benzyl-3-*O*-(2-methylnaphthyl)-β-D-glucopyranoside (2): A solution of **S12** (10.1 g, 23.2 mmol) in DMF (100 mL) was cooled down to 0 ºC, followed by the sequential addition of NapBr (6.1 g, 27.6 mmol) and NaH (1.4 g, 34.5 mmol, 60% dispersion in oil). The reaction mixture was stirred at this temperature for 2 h, after which it was quenched with AcOH (5 mL). The solvent was evaporated *in vacuo*, the residue was diluted with DCM, and washed with $NaHCO_3$ and water. The organic phase was dried over $MgSO_4$, filtered and the filtrate was concentrated *in vacuo*. The residue was used in further step without purification. The residue was stirred with pre-activated molecular sieves (20 g) in DCM (100 mL) for 30 min after which it was cooled down to -60 ºC, followed by the sequential addition of triethylsilane (8.2 mL, 51.0 mmol) and trifluoromethanesulfonic acid (2.2 mL, 25.5 mmol). The reaction mixture was stirred at this temperature for 30 min, after which it was quenched with a mixture of NEt_3: MeOH (5 mL, 1: 1, v: v). The molecular sieves were filtered off, the filtrate was diluted by DCM and washed with saturated $NaHCO_3$ 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 PE: EtOAc (8: 2, v: v to 6: 4 v: v), which yielded the product



2

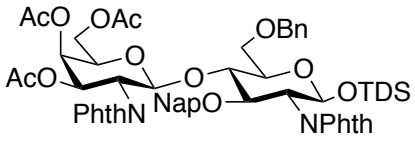
as a transparent sticky syrup, (7.5 g, 73% over two steps). R_f = 0.54 (PE: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 to 7.23 (12H, m, H-Ar), 5.06 (1H, d, CHH of Nap, *J* = 11.5 Hz), 4.93 (1H, d, CHH of Nap, *J* = 11.5 Hz), 4.56 (2H, m, PhCHH, PhCHH), 4.51 (1H, d, H-1, *J* = 7.7 Hz), 3.69 (3H, m, H-4, H-6a, H-6b), 3.34 (3H, m, H-2, H-5, H-3), 1.67 [1H, m, CH$(CH_3)_2$ of TDS], 0.89 [12H, m, C$(CH_3)_2$, CH$(CH_3)_2$ of TDS], 0.19 (6H, d, 2x CH_3-Si of TDS, *J* = 6.0 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.74 to 125.89 (C-Ar), 97.03 (C-1), 82.34 (C-3), 77.31, 77.00, 76.68, 74.99 (CH_2 of Nap), 73.88 ($PhCH_2$), 73.70 (C-5), 72.16 (C-4), 70.43 ($PhCH_2$), 68.27 (C-2), 33.89 (CH$(CH_3)_2$ of TDS), 19.96 to 18.38 (4x CH_3 of TDS), -0.02 to -3.28 (2x CH_3-Si of TDS). ESI (*m/z*): $[M+ NH_4]^+$ calculated for $C_{32}H_{43}N_3O_5Si$, 595.3316; found 595.3313.

1.5 Scheme 4: Synthesis of LDN acceptor S15



Reagents and Conditions **: a)** TMSTOf, DCM, -30 °C, 92% ; **b)** DDQ, DCM/H_2O = 9:1, 88%

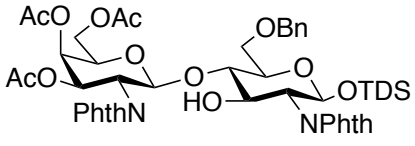
Dimethylthexylsilyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl]-(1→4)-6-*O*-benzyl-3-*O*-(2-methylnaphthyl)-2-deoxy-2-phthalimido-β-D-glucopyranoside (S14): *N*-phenyltrifluoroimidate donor **S13** (5.2 g, 8.6 mmol), with acceptor **S10** (4.5 g, 6.6 mmol) was dissolved in DCM (50 mL) and stirred with pre-activated molecular sieves (10 g) for 30 min. The mixture was then cooled



S14

down to -30 ºC, followed by the addition of TMSTOf (240 μL, 1.3 mmol). The reaction was quenched after 20 min with NEt_3 (500 μL). The mixture was warmed up to room temperature and then concentrated *in vacuo*. Silica gel column chromatography with PE: EtOAc (9: 1, v: v to 7: 3, v: v) yielded the product as white amorphous powder (6.7 g, 92%). R_f = 0.58 (PE: EtOAc, 6: 4 v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 to 6.98 (20H, m, H-Ar), 5.83 (1H, dd, H-3 GalN, *J* = 11.4 Hz, 3.5 Hz), 5.56 (1H, d, H-1 GalN, *J* = 8.4 Hz), 5.40 (1H, d, H-4 GalN, *J* = 3.4 Hz), 5.14 (1H, d, H-1 GlcN, *J* = 8.4 Hz), 4.98 (1H, d, CH<u>H</u> of Nap, *J* = 12.6 Hz), 4.65 (1H, d, C<u>H</u>H of Nap, *J* = 12.6 Hz), 4.51 (3H, m, PhC<u>H</u>H, PhCH<u>H</u>, H-2 GalN), 4.32 (1H, dd, H-3 GlcN, *J* = 11.0 Hz, 8.7 Hz), 4.11 (4H, m, H-2 GlcN, H-6a GalN, H-6b GalN, H-5 GalN), 3.87 (1H, t, H-4 GlcN, *J* = 6.7 Hz), 3.41 (3H, m, H-5 GlcN, H-6a GlcN, H-6b GlcN), 2.05 to 1.82 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.26 [1H, m, C<u>H</u>$(CH_3)_2$ of TDS] , 0.49 [12H, m, C$(C\underline{H}_3)_2$, CH$(C\underline{H}_3)_2$ of TDS], -0.02 to -0.22 (6H, 2s, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.35 to 168.29 (3x <u>C</u>OCH_3 of Ac), 138.30 to 123.48 (C-Ar), 97.58 (C-1 GalN), 93.17 (C-1 GlcN), 77.32, 77.20, 77.18, 77.00, 76.79 (C-3 GlcN), 76.68 (C-5 GalN), 74.43 (C-5 GlcN), 74.40 (<u>C</u>H$_2$ of Nap), 72.74 (Ph<u>C</u>H$_2$), 70.65 (C-4 GlcN), 67.90 (C-6 GlcN), 67.83 (C-3 GalN), 66.64 (C-4 GalN), 61.09 (C-6 GalN), 57.70 (C-2 GlcN), 52.10 (C-2 GalN), 33.77 (<u>C</u>H$(CH_3)_2$ of TDS), 20.67 to 20.49 (3x <u>C</u>H$_3$ of Ac), 19.76 to 18.07 (4x <u>C</u>H$_3$ of TDS), -0.02 to -3.99 (2x <u>C</u>H$_3$-Si of TDS). ESI (*m/z*): [M+ $NH_4]^+$ calculated for $C_{60}H_{66}N_2O_{16}Si$, 1116.4525; found 1116.4527.

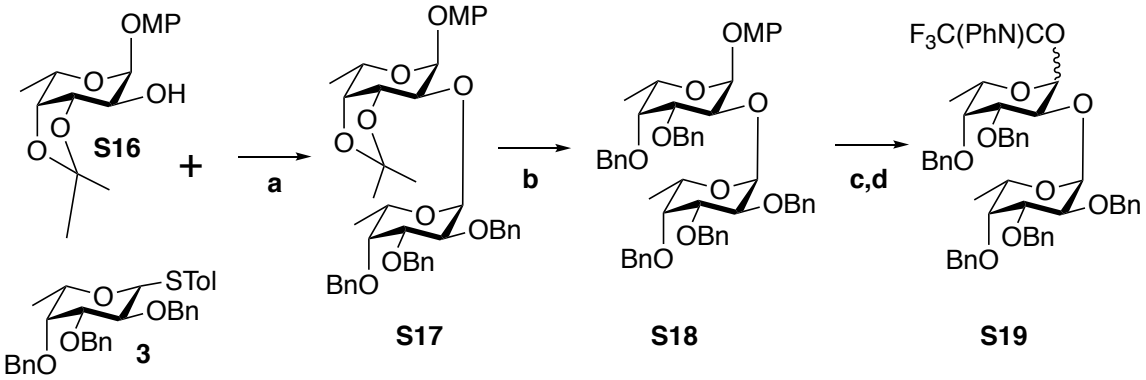
Dimethylthexylsilyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl]-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S15): Compound **S14** (6.7 g, 6.1 mmol) was dissolved in the solvent system DCM: H_2O (100 mL, 9: 1, v: v), followed by the addition of DDQ (2.8 g, 12.2 mmol), and allowed to stir in the dark for 3 h after which it was diluted by DCM and washed with saturated $NaHCO_3$ and water. The organic fractions were then dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using PE: EtOAc (8: 2, v: v to 6: 4, v: v) gave the product as a



S15

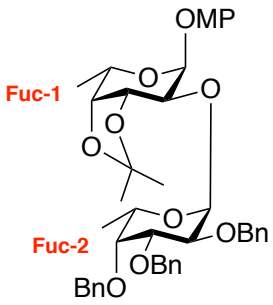
white amorphous powder. (5.2 g, 88%). R_f = 0.48 (PE: EtOAc, 6: 4, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 to 6.98 (13H, m, H-Ar), 5.83 (1H, dd, H-3 GalN, *J* = 11.4 Hz, 3.5 Hz), 5.44 (2H, m, H-4 GalN, H-1 GalN), 5.32 (1H, d, H-1 GlcN, *J* = 8.1 Hz), 4.55 (1H, dd, H-2 GalN, *J* = 11.4 Hz, 8.5 Hz), 4.42 (1H, m, H-3 GlcN), 4.17 (1H, d, H-5 GalN, *J* = 1.8 Hz), 4.09 (5H, m, H-2 GlcN, H-6a GalN, H-6b GalN, PhC<u>H</u>H, PhCH<u>H</u>), 3.68 (1H, t, H-4 GlcN, *J* = 9.0 Hz), 3.49 (1H, m, H-5 GlcN), 3.21 (2H, m, H-6a GlcN, H-6b GlcN), 2.16 to 1.82 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.36 [1H, m, C<u>H</u>(CH$_3$)$_2$ of TDS], 0.59 [12H, m, C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], 0.02 to -0.10 (6H, 2s, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.44 to 167.37 (3x <u>C</u>OCH$_3$ of Ac), 138.04 to 123.62 (C-Ar), 99.33 (C-1 GalN), 93.20 (C-1 GlcN), 82.60 (C-4 GlcN), 77.32 , 77.20, 77.00, 76.68, 73.86 (C-5 GlcN), 72.81 (Ph<u>C</u>H$_2$), 71.20 (C-5 GalN), 69.71 (C-3 GlcN), 68.00 (C-6 GlcN), 67.61 (C-3 GalN), 66.40 (C-4 GalN), 61.85 (C-6 GalN), 57.97 (C-2 GlcN), 51.32 (C-2 GalN), 33.91 (<u>C</u>H(CH$_3$)$_2$ of TDS), 20.64 to 20.23 (3x <u>C</u>H$_3$ of Ac), 19.86 to 18.15 (4x <u>C</u>H$_3$ of TDS), -0.03 to -3.90 (2x <u>C</u>H$_3$-Si of TDS). ESI (*m/z*): [M+ Na]$^+$ calculated for $C_{49}H_{58}N_2O_{16}Si$, 981.3453; found 981.3456.

1.6 Scheme 5: Synthesis of disaccharide Fucose-α-1,2-Fucose Donor



Reagents and Conditions **: a)** NS/TMSTOf, DCM, -20 to -5°C, DCM:DMF=1:1, 86% ; **b)** i) pTSA, MeOH, DCM ; ii) BnBr, NaH, DMF, 84% (over two steps); **c)** CAN, ACN:H_2O= 4:1 **d)** N-phenylimidate, DBU, DCM, 71% (over two steps)

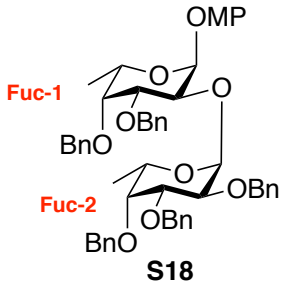
***p*-methoxyphenyl [2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→2)-3,4-*O*-isopropylidine-α-L-fucopyranoside (S17):** Acceptor **S16** (5.0 g, 16.1 mmol) and donor



S17

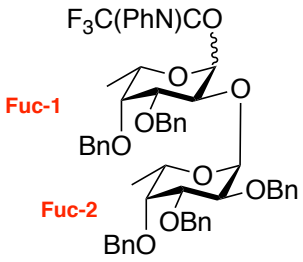
3 (9.6 g, 17.8 mmol), were dissolved in the solvent system DCM: DMF (100 mL, 1: 1, v: v) and stirred with pre-activated molecular sieves (15.0 g) for 30 min, after which the temperature was brought down to -20 ºC. This was followed by the sequential addition of NIS (4.3 g, 19.35 mmol) and TMSTOf (2.3 mL, 12.9 mmol). The reaction mixture was warmed up to -5 ºC over a period of 1 h, after which the TLC showed complete consumption of acceptor. The reaction mixture was quenched with NEt_3 (10 mL) and warmed up to room temperature. The sieves were filtered off, and the filtrate was concentrated *in vacuo*. The residue was diluted by DCM and washed with saturated $NaHCO_3$ solution and 5% sodium thiosulphate solution respectively. The organic phase was dried over MgSO4 and filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using (PE: EtOAc (9: 1, v: v to 7: 3, v: v) yielded the product as transparent syrup. (10.1 g, 86%). R_f = 0.51 (PE: EtOAc, 8: 2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 to 6.69 (19H, m, H-Ar), 5.46 (1H, d, H-1 Fuc-2, *J* = 3.4 Hz), 4.97 (2H, m, H-1 Fuc-1, PhCHH), 4.72 (5H, m, PhCHH, 2x PhCHH, 2x PhCHH), 4.49 (1H, dd, H-3 Fuc-2, *J* = 8.0 Hz, 5.4 Hz), 4.23 (2H, m, H-5 Fuc-2, H-5 Fuc-1), 4.12 (2H, m H-2 Fuc-1, H-4 Fuc-2), 4.02 (1H, dd, H-3 Fuc-1, *J* = 10.1 Hz, 3.6 Hz), 3.94 (1H, dd, H-2 Fuc-2, *J* = 8.1 Hz, 3.4 Hz), 3.74 (4H, m, H-4 Fuc-1, OCH_3 of OMP), 1.53 to 1.37 (6H, 2s, 2x CH_3 of iso-propylidine), 1.32 (3H, d, CH_3 of Fuc-1, *J* = 6.7 Hz), 1.12 (3H, d, CH_3 of Fuc-2, *J* = 6.6 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.97 to 114.60 (C-Ar), 94.84 (C-1 Fuc-2), 94.76 (C-1 Fuc-1), 79.29 (C-2 Fuc-1), 77.60 (C-4 Fuc-1), 77.34, 77.02, 76.71, 76.04 (C-4 Fuc-2), 75.79 (C-3 Fuc-1), 74.86 ($PhCH_2$), 74.71 (C-3 Fuc-2), 73.03 ($PhCH_2$), 72.90 ($PhCH_2$), 72.58 (C-2 Fuc-2), 66.27 (C-5 Fuc-1), 63.69 (C-5 Fuc-2), 55.64 (OCH_3 of OMP), 28.54 to 26.46 (2x CH_3 of iso-propylidine), 16.50 (CH_3 Fuc-1), 16.33 (CH_3 Fuc-2). ESI (*m/z*): $[M + NH_4]^+$ calculated for $C_{43}H_{50}O_{10}$, 744.3748; found 744.3709.

p-methoxyphenyl [2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→2)-3,4-di-*O*-benzyl-α-L-fucopyranoside (S18): The disaccharide **S17** (10.1 g, 13.9 mmol) was dissolved in the solvent system DCM (70 mL) and MeOH (50 mL), followed by the addition of *p*-toluenesulfonic acid monohydrate (665 mg, 3.5 mmol) and stirred overnight, after which the isopropylidine ring fell off to give the desired diol. The solvent was removed *in vacuo*, the residue was diluted by DCM and washed with saturated $NaHCO_3$. The organic fractions were dried over $MgSO_4$ and filtered. The filtrate was concentrated, and the residue was dried on high vacuum for 2 h. This was further used for benzylation without purification. The residue was dissolved in dry DMF (100 mL) and cooled down to 0 °C. This was followed by the addition of NaH (1.6 g, 40.8 mmol, 60% dispersion in oil) and BnBr (4.8 mL, 40.8 mmol), and the reaction mixture was stirred at this temperature for 30 min after which it was quenched with AcOH (5 mL) and the solvent was removed *in vacuo.* Silica gel column chromatography using at first pure PE and then increasing the polarity to PE: EtOAc (9: 1, v: v), gave the product as a white amorphous powder. (9.1 g, 76% over two steps). R_f = 0.54 (PE: EtOAc, 9: 1, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 to 6.66 (29H, m, H-Ar), 5.42 (1H, d, H-1 Fuc-2, *J* = 3.7 Hz), 4.97 (2H, m, H-1 Fuc-1, PhCHH), 4.70 (5H, m, PhCHH, 2x PhCHH, 2x PhCHH), 4.11 (4H, m, H-2 Fuc-1, H-5 Fuc-1, H-5 Fuc-2, H-2 Fuc-2), 3.95 (1H, dd, H-3 Fuc-2, *J* = 10.1 Hz, 2.8 Hz), 3.85 (2H, m, H-3 Fuc-1, H-4 Fuc-2), 3.70 (4H, m, H-4 Fuc-1, OCH_3 -OMP), 1.28 (3H, d, CH_3 of Fuc-1, *J* = 6.6 Hz), 1.14 (3H, d, CH_3 of Fuc-2, *J* = 6.3 Hz); ^{13}C NMR (101 MHz, $CDCl_3$): δ 155.11 to 114.47 (C-Ar), 98.47 (C-1 Fuc-1), 98.12 (C-1 Fuc-2), 78.70 (C-3 Fuc-2), 78.23 (C-3 Fuc-1), 77.46, 77.30 (C-4 Fuc-1), 77.19, 76.99, 76.67 (C-2 Fuc-1), 75.87 ($PhCH_2$), 74.91 ($PhCH_2$), 73.16 to 73.10 (3x $PhCH_2$), 71.38 (C-4 Fuc-2), 68.93 (C-2 Fuc-1), 67.79 (C-2 Fuc-2), 66.31 (C-5 Fuc-1), 55.63 (C-5 Fuc-2), 16.58 (CH_3 of Fuc-2), 16.10 (CH_3 of Fuc-2). ESI (*m/z*): $[M + NH_4]^+$ calculated for $C_{54}H_{58}O_{10}$, 884.4374; found 844.4381.



S18

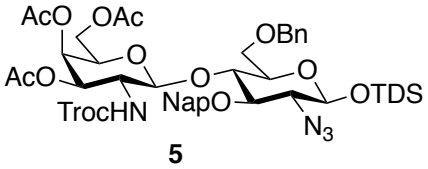
(*N*-Phenyl)-2,2,2-trifluoroacetimidate [2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→2)-3,4-di-*O*-benzyl-α/β-L-fucopyranoside (S19): Compound **S18** (4.0 g, 4.6 mmol) was dissolved in acetonitrile (40 mL) and water (10 mL) was added. This was followed by the addition of ceric ammonium nitrate (5.1 g, 9.2 mmol). The reaction mixture was stirred under argon, in the dark, for 2 h, after which TLC (PE: EtOAc = 6: 4, v: v) showed complete consumption of starting material. The solvent was evaporated *in vacuo*, and the residue was dissolved in DCM, and washed with water and saturated $NaHCO_3$ and the organic phase was dried over $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* and dried over high vacuum over a period of 2 h. This residue was then used further without purification. The residue was dissolved in DCM followed by the addition of DBU (344 μl, 2.3 mmol) and 2,2,2- Trifluoro-*N*-phenylacetimidoyl chloride (1.4 mL, 6.9 mmol). The reaction mixture was stirred for 30 min. After this time, the solvent was evaporated, and the residue was quickly purified using PE: EtOAc (9: 1, v: v to 6: 4, v: v). The product was dried over high vacuum for 30 min. This afforded the disaccharide as a colorless syrup. (3.1 g, 71 % over two steps). R_f = 0.61 (PE: EtOAc, 7: 3, v: v). The imidate product showed hydrolysis when dissolved in $CDCl_3$, hence NMR and mass were not recorded as the product was unstable and used for next reaction immediately.



S19

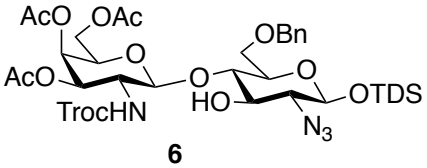
2. Final Synthesis of LDN-F and LDN-DF Epitopes

Dimethylthexylsilyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2,-trichloroethoxy) carbonylamino-β-D-galactopyranosyl]-(1→4)-2-deoxy-2-azido-6-*O*-benzyl-3-*O*-(2-methylnaphthyl)-β-D-glucopyranoside (5): *N*-phenyltrifluoroimidate donor **1** (9.4 g, 14.5 mmol) with acceptor **2** (7.0 g, 12.1 mmol) were dissolved in DCM (50 mL), and allowed to stir with pre-activated molecular sieves for 30 min. The mixture was then cooled down to -30 ºC, followed by the addition of TMSTOf (657 μL, 3.6 mmol). The reaction was quenched after 10 min with NEt_3 (2 mL). Concentration of mixture *in vacuo* and silica gel column chromatography with PE: EtOAc (9: 1, v: v to 6: 4, v: v) yielded the product as white solid. (10.9 g, 93%). R_f = 0.48 (PE: EtOAc, 7: 3, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 to 7.27 (12H, m, H-Ar), 5.20 (1H, d, H-4 GalN, *J* = 3.2 Hz), 5.12 (1H, d, CHH of Nap, *J* = 10.3 Hz), 4.83 (2H, m, CHH of Nap, PhCHH), 4.68 (3H, m, CH_2 of Troc, H-3 GalN), 4.40 (3H, m, PhCHH, H-1 GlcN, H-1 GalN), 3.98 (2H, m, H-5 GalN, H-6b GalN), 3.78 (3H, m, H-2 GalN, H-6a GlcN, H-6a GalN), 3.58 (2H, m, H-4 GlcN, H-6b GlcN), 3.31 (3H, m, H-5 GlcN, H-3 GlcN, H-2 GlcN), 2.01 to 1.94 (9H, 3s, 3x CH_3 of Ac), 1.65 [1H, m, $CH(CH_3)_2$ of TDS] , 0.88 [12H, m, $C(CH_3)_2$, $CH(CH_3)_2$ of TDS], 0.17 (6H, d, 2x CH_3-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.13 to 170.10 (3x $COCH_3$ of Ac), 154.06 ($COOCH_2$ of Troc), 137.40 to 125.67 (C-Ar), 100.69 (C-1 GalN), 97.05 (C-1 GlcN), 80.72 (C-3 GlcN), 77.30, 76.98, 76.66 (C-5 GalN), 74.93 (CH_2 of Nap), 74.42 (CH_2 of Troc), 74.18 (C-5 GlcN), 73.81 ($PhCH_2$), 70.36 (C-3 GalN), 70.21 (C-4 GlcN), 68.42 (C-2 GlcN), 67.74 (C-6 GlcN), 66.08 (C-4 GalN), 60.79 (C-6 GalN), 52.76 (C-2 GalN), 33.90 ($CH(CH_3)_2$ of TDS), 20.83 to 20.55 (3x CH_3 of Ac), 19.97 to 18.37 (4x CH_3 of TDS), -0.03 to -3.27 (2x CH_3-Si of TDS). ESI (*m/z*): $[M+ NH_4]^+$ calculated for $C_{47}H_{61}Cl_3N_4O_{14}Si$, 1056.3363; found 1056.3351.



5

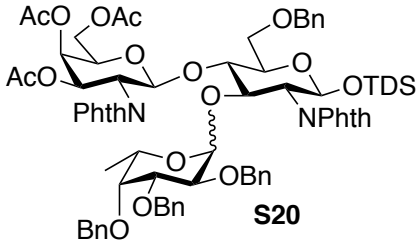
Dimethylthexylsilyl [3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy) carbonylamino-β-D-galactopyranosyl]-(1→4)-2-deoxy-2-azido-6-*O*-benzyl-β-D-glucopyranoside (6): Compound **5** (10.9 g, 11.3 mmol) was dissolved in DCM: H_2O (100 mL, 9: 1, v: v), followed by the addition of DDQ (2.8 g, 12.2 mmol), and stirred in the dark for 3 h, after which it was diluted by DCM and washed with saturated $NaHCO_3$ and water. The organic fractions were dried over $MgSO_4$, filtered, and the filtrate was then concentrated. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 7: 3, v: v) gave the product as a pale-yellow amorphous powder. (9.0 g, 88%). R_f = 0.52 (PE: EtOAc, 7.5: 2.5, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 to 7.16 (5H, Ar-H), 5.27 (1H, d, H-4 GalN, *J* = 3.2 Hz), 4.81 (1H, d, PhCHH, *J* = 11.8 Hz), 4.66 (3H, m, H-3 GalN, CH_2 of Troc), 4.44 (1H, d, H-1 GlcN, *J* = 7.9 Hz), 4.37 (1H, d, PhCHH, *J* = 11.8 Hz), 4.12 (4H, m, H-1 GalN, H-6a GalN, H-6b GalN, NH of Troc), 3.87 (2H, m, H-5 GalN, H-2 GalN), 3.68 (2H, m, H-3 GlcN, H-6b GlcN), 3.50 (2H, m, H-4 GlcN, H-6a GlcN), 3.33 (1H, m, H-5 GlcN), 3.22 (1H, dd, H-2 GlcN, *J* = 9.7 Hz, 7.6 Hz), 2.12 to 1.95 (9H, 3s, 3x CH_3 of Ac), 1.66 [1H, m, $CH(CH_3)_2$ of TDS], 0.88 [12H, m, $C(CH_3)_2$, $CH(CH_3)_2$ of TDS], 0.17 (6H, d, 2x CH_3-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.59 to 170.05 (3x $COCH_3$ of Ac), 154.12 ($COOCH_2$ of Troc), 137.98 to 127.33 (C-Ar), 102.06 (C-1 GalN), 96.65 (C-1 GlcN), 81.17 (C-3 GlcN), 77.35, 77.24, 77.04, 76.72, 74.57 (CH_2 of Troc), 73.56 ($PhCH_2$), 73.49 (C-5 GlcN), 73.25 (C-4 GlcN), 71.17 (C-5 GalN), 70.08 (C-3 GalN), 68.05 (C-2 GlcN), 67.45 (C-6 GlcN), 66.24 (C-4 GalN), 61.63 (C-6 GalN), 52.03 (C-2 GalN), 33.88 ($CH(CH_3)_2$ of TDS), 20.57 to 20.48 (3x CH_3 of Ac), 19.97 to 18.39 (4x CH_3 of TDS) , -0.03 to -3.25 (2x CH_3-Si of TDS).



6

ESI (*m/z*): $[M+ NH_4]^+$ calculated for $C_{36}H_{53}Cl_3N_4O_{14}Si$; 916.2737; found 916.2726.

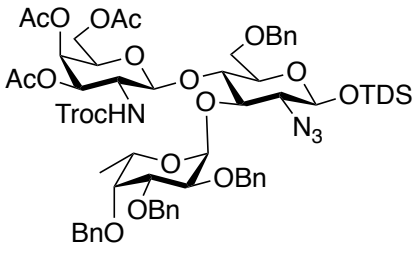
Dimethylthexylsilyl [2,3,4-tri-*O*-benzyl-α/β-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-galactopyranosyl]-(1→4)-6-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (S20) : Donor **3** (1.0 g, 1.8 mmol), DPS (748 mg, 3.7 mmol) and TTBP (1.1 g, 4.6 mmol) were dissolved in DCM (10 mL) and allowed to stir with pre-activated molecular sieves (2 g) for 30 min. The temperature was brought down to -70 ºC, followed by the addition of Tf_2O (620 μl, 3.7 mmol). After 10 min, a solution of acceptor **S15** (886 mg, 0.925 mmol) in anhydrous DCM (5 mL) was added dropwise along the wall of the flask, and the reaction mixture was stirred for 2 h, during which the temperature was slowly raised to -40º C. The TLC (PE: EtOAc, 7: 3, v: v) showed complete consumption of acceptor, at which point, the reaction was quenched using NEt_3 (1 mL). The molecular sieves were filtered off, and the solvent was removed *in vacuo*. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 6: 4, v: v) gave the product as a white amorphous powder in an inseparable α: β ratio of 8: 2. (1.1 g, 88%). R_f = 0.52 (PE: EtOAc, 7: 3, v: v). For the NMR analysis, the proton signals for alpha and beta product are assigned with superscript ($^{\alpha}$ or $^{\beta}$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 to 6.83 (32H, m, H-Ar), 5.83 (H-3 GalN$^{\beta}$), 5.75 (1H, dd, H-3 GalN$^{\alpha}$, *J* = 11.6 Hz, 3.5 Hz), 5.58 (1H, d, H-1 GalN$^{\alpha}$, *J* = 8.5 Hz), 5.43 (H-4 GalN$^{\beta}$, H-1 GalN$^{\beta}$), 5.34 (1H, d, H-4 GalN$^{\alpha}$, *J* = 3.3 Hz), 5.21 (1H, d, H-1 GlcN$^{\alpha}$, *J* = 8.1 Hz), 5.16 (H-1 GlcN$^{\beta}$), 4.87 (1H, d, H-1 Fuc$^{\alpha}$, *J* = 3.3 Hz), 4.80 (1H, d, PhC<u>H</u>H, *J* = 11.8 Hz), 4.58 (5H, m, PhCH<u>H</u> , 2x PhC<u>H</u>H, 2x PhCH<u>H</u> , H-5 GalN$^{\alpha}$), 4.47 (1H, m, H-5 Fuc$^{\alpha}$), 4.39 (2H, m, PhC<u>H</u>H, H-2 GalN$^{\alpha}$), 4.22 (3H, m, H-6b GalN$^{\alpha}$, H-4 Fuc$^{\alpha}$, H-2 GlcN$^{\alpha}$), 4.11 (1H, d, PhCH<u>H</u>, *J* = 12.6 Hz), 4.01 (H-6a Gal$^{\beta}$), 3.88 (2H, m, H-3 GlcN$^{\alpha}$, H-6a GalN$^{\alpha}$), 3.76 (2H, m, H-2 Fuc$^{\alpha}$, H-4 GlcN$^{\alpha}$), 3.65 (1H, s, H-3 Fuc$^{\alpha}$), 3.55 (2H, m, H-6a GlcN$^{\alpha}$, H-6b GlcN$^{\alpha}$), 3.37 (1H, m, H-5 GlcN$^{\alpha}$), 3.28 (H-5 GlcN$^{\beta}$), 1.92 to 1.77 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.31 [4H, m, C<u>H</u>(CH$_3$)$_2$ of TDS, C<u>H</u>$_3$ of Fuc], 0.55 [12H, m, C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], 0.01 to -0.18 (6H, 2s, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.14 to 167.25 (3x <u>C</u>OCH$_3$ of Ac), 138.97 to 123.09 (C-Ar), 97.99 (C-1 Fuc$^{\alpha}$), 96.90 (C-1 GalN$^{\alpha}$), 92.99 (C-1 GlcN$^{\alpha}$), 79.51 (C-3 GlcN$^{\alpha}$), 77.76 (C-3 Fuc$^{\alpha}$), 77.30 , 76.99,



S20

76.67, 75.02 (C-2 Fuc$^{\alpha}$), 74.95 (C-4 Fuc$^{\alpha}$), 74.70 (C-5 GlcN$^{\alpha}$), 74.44 ($PhCH_2$), 74.38 (C-5 GalN$^{\alpha}$), 72.71 ($Ph\underline{C}H_2$), 72.61 ($Ph\underline{C}H_2$), 72.46, 70.67, 68.13 (C-6 GlcN$^{\alpha}$), 67.81 (C-3 GalN$^{\alpha}$), 66.90 (C-5 Fuc$^{\alpha}$), 66.56 (C-4 GalN$^{\alpha}$), 60.67 (C-6 GalN$^{\alpha}$), 58.39 (C-2 GlcN$^{\alpha}$), 51.86 (C-2 GalN$^{\alpha}$), 33.82 ($\underline{C}H(CH_3)_2$ of TDS), 20.60 to 20.42 (3x $\underline{C}H_3$ of Ac), 19.83 to 18.13 (4x $\underline{C}H_3$ of TDS), 16.84 ($\underline{C}H_3$ of Fuc$^{\alpha}$), -1.97 to -3.80 (2x $\underline{C}H_3$-Si of TDS). ESI (*m/z*): $[M+ Na]^+$ calculated for $C_{76}H_{86}N_2O_{20}Si$; 1397.5441; found 1397.5450.

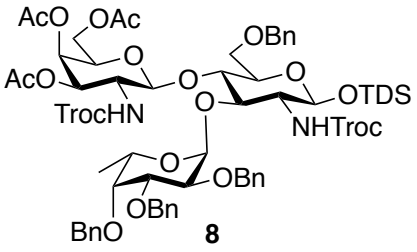
Dimethylthexylsilyl [2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-galactopyranosyl]-(1→4)-2-deoxy-2-azido-6-*O*-benzyl-β-D-glucopyranoside (7): Donor **3** (2.1 g, 4.4 mmol), DPS (900 mg, 4.4 mmol) and DTBMP (912 mg, 4.4 mmol) were dissolved in DCM (20 mL) and stirred with pre-activated molecular sieves (2 g) for 30 min. After this time, the temperature was brought down to -60 ºC, followed by the addition of Tf_2O (750 μL, 4.4 mmol). After 10 min at this temperature, a solution of acceptor **6** (1.0 g, 1.1 mmol) in anhydrous DCM (5 mL), was added dropwise along the wall of the flask and the reaction mixture was stirred for 1 h, during which the temperature was slowly raised to -40 ºC. The TLC (PE: EtOAc, 7: 3, v: v) showed complete consumption of acceptor, at which point, the reaction was quenched with NEt_3 (2 mL). The molecular sieves were filtered off, and DCM was removed *in vacuo*. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 7: 3, v: v) gave the product as a white amorphous powder. (1.0 g, 68%); R_f = 0.55 (PE: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 to 7.03 (20H, m, H-Ar), 5.34 (1H, d, H-1 Fuc, *J* = 3.5 Hz), 5.03 (1H, d, H-4 GalN, *J* = 3.4 Hz), 4.80 to 4.54 (7H, m, 3x PhCH$\underline{H}$, 3x PhC$\underline{H}$H, PhCH$\underline{H}$), 4.49 (3H, m, H-5 Fuc, C$\underline{H}_2$ of Troc), 4.36 (1H, m, H-3 GalN), 4.33 (1H, d, H-1 GlcN, *J* = 7.8 Hz), 4.22 (2H, m, PhC$\underline{H}$H, H-1 GalN), 3.93 (2H, m, H-2 Fuc, H-6b GalN), 3.75 (3H, m, H- 6a GalN, H-3 Fuc, H-5 GalN), 3.54 (2H, m, H-6b GlcN, H-3 GlcN), 3.43 (2H, m, H-2 GalN, H-4 GlcN), 3.36 (2H, m, H-6a GlcN, H-4 Fuc), 3.27 (1H, dd, H-2 GlcN, *J* = 9.9 Hz, 7.7 Hz), 3.08 (1H, m, H-5 GlcN), 1.83



7

to 1.55 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.49 [1H, m, C<u>H</u>(CH$_3$)$_2$ of TDS], 1.06 (3H, C<u>H</u>$_3$ of Fuc), 0.70 [12H, m, C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], 0.00 (6H, d, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.22 to 169.80 (3x <u>C</u>OCH$_3$ of Ac), 154.04 (<u>C</u>OOCH$_2$ of Troc), 139.15 to 126.97 (C-Ar), 100.43 (C-1 GalN), 97.40 (C-1 GlcN), 97.21 (C-1 Fuc), 79.80 (C-3 Fuc), 77.34, 77.22, 77.02, 76.98 (C-3 GlcN), 75.60 (C-2 Fuc), 74.64 (C-5 GalN), 74.57 (C-4 Fuc), 74.27 (C-5 GlcN), 74.04 to 72.61 (4x Ph<u>C</u>H$_2$), 70.56 (C-3 GalN), 70.24 (C-4 GlcN), 68.71 (C-2 GlcN), 68.22 (C-6 GlcN), 66.08 (C-5 Fuc), 65.83 (C-4 GalN), 60.15 (C-6 GalN), 52.20 (C-2 GalN), 33.95 (<u>C</u>H(CH$_3$)$_2$ of TDS), 20.64 to 20.35 (3x <u>C</u>H$_3$ of Ac), 20.01, 19.98 to 18.36 (4x <u>C</u>H$_3$ of TDS), 16.82 (<u>C</u>H$_3$ of Fuc), -2.09 to -3.02 (2x <u>C</u>H$_3$-Si of TDS). ESI (*m/z*): [M+ Na]$^+$ calculated for $C_{63}H_{81}Cl_3N_4O_{18}Si$, 1337.4278; found 1337.4285.

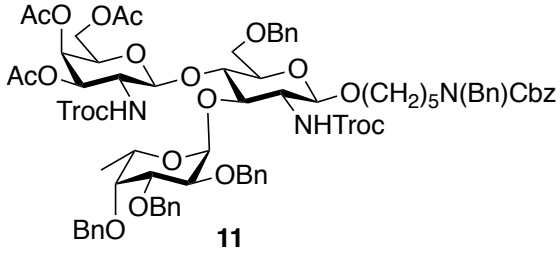
Dimethylthexylsilyl [2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-galactopyranosyl]-(1→4)-[6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)]carbonylamino-β-D-glucopyranoside (8): Compound **7** (1.0 g, 0.76 mmol) was dissolved in THF (20 mL) and water (4 mL) was added. This was followed by the addition of trimethylphosphine (1.7 mL, 17.2 mmol). The reaction mixture was stirred under argon for 2 h, following which the solvent was evaporated *in vacuo* and co-evaporated with toluene twice. The residue (800 mg, 0.6 mmol) was dissolved in DCM (20 mL), followed by the addition of 2,2,2- trichloroethyl chloroformate (170 μL, 1.24 mmol) and triethylamine (173 μL, 1.24 mmol). The reaction mixture was stirred for 1 h after which it was diluted by DCM (100 mL) and washed with water. The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 7: 3, v: v) afforded the product as a yellowish amorphous solid. (700.0 mg, 77%); R_f = 0.58 (PE: EtOAc, 7: 3 v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 to 7.07 (20H, m, H-Ar), 5.22 (1H, d, N<u>H</u> of Troc, *J* = 7.1 Hz), 5.19 (1H, d, H-4 GalN, *J* = 3.1 Hz), 5.09 (1H, d, H-1 Fuc, *J* = 2.8 Hz), 5.01 (1H, d, H-1 GlcN, *J* = 7.4 Hz), 4.76 (11H, m, 2x C<u>H</u>$_2$ of Troc, 3x PhCH<u>H</u>, 3x PhC<u>H</u>H), 4.53



8

(2H, m, H-5 Fuc, PhCH<u>H</u>), 4.46 (1H, d, H-1 GalN, *J* = 9.0 Hz), 4.37 (1H, d, PhC<u>H</u>H, *J* = 11.7 Hz), 4.07 (3H, m, H-6b GalN, H-2 Fuc, H-3 GlcN), 3.85 (3H, m, H-3 Fuc, H-6a GalN, H-5 GalN), 3.67 (2H, m, H-6b GlcN, H-4 Fuc), 3.58 (2H, m, H-2 GalN, H-4 GlcN), 3.50 (1H, d, H-6a GlcN, *J* = 10.1 Hz), 3.32 (1H, m, H-5 GlcN), 2.94 (1H, m, H-2 GlcN), 1.97 to 1.76 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.51 [1H, m, C<u>H</u>(CH$_3$)$_2$ of TDS], 1.17 (3H, C<u>H</u>$_3$ of Fuc), 0.77 [12H, m, C(C<u>H</u>$_3$)$_2$, CH(C<u>H</u>$_3$)$_2$ of TDS], 0.03 (6H, d, 2x C<u>H</u>$_3$-Si of TDS); ^{13}C NMR (151 MHz, $CDCl_3$): δ 172.08 to 171.87 (3x <u>C</u>OCH$_3$ of Ac), 155.92 to 155.33 (2x <u>C</u>OOCH$_2$ of Troc), 140.84 to 128.99 (C-Ar), 101.87 (C-1 GalN), 99.52 (C-1 Fuc), 96.15 (C-1 GlcN), 81.81 (C-3 Fuc), 79.17, 79.04 (C-3 GlcN), 78.96 (C-4 Fuc), 78.85, 78.75, 77.06 (C-5 GalN), 76.63 (C-2 Fuc), 76.37 to 76.15 (2x Ph<u>C</u>H$_2$), 75.95 (C-5 GlcN), 75.88 to 74.53 (2x Ph<u>C</u>H$_2$), 72.13 (C-4 GlcN), 70.39 (C-6 GlcN), 68.14 (C-5 Fuc), 67.99 (C-4 GalN), 63.44 (C-2 GlcN), 62.31 (C-6 GalN), 54.29 (C-2 GalN), 35.97 (<u>C</u>H(CH$_3$)$_2$ of TDS), 22.59 to 22.06 (3x <u>C</u>H$_3$ of Ac), 21.89 to 19.22 (4x <u>C</u>H$_3$ of TDS), 18.84 (<u>C</u>H$_3$ of Fuc), -0.01 to -1.58 (2x <u>C</u>H$_3$-Si of TDS). ESI (*m/z*): [M+ NH$_4$]$^+$ calculated for $C_{66}H_{84}Cl_6N_2O_{20}Si$, 1480.3862; found 1480.3878.

5-(*N*-Benzyloxycarbonyl,*N*-Benzyl)aminopentyl [2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-galactopyranosyl]-(1→4)-[6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)] carbonylamino-β-D-glucopyranoside (11): Compound **8** (700 mg, 0.47 mmol) was dissolved in the solvent system DCM: pyridine (30 mL, 1: 2, v: v), followed by dropwise addition of HF in pyridine (70% HF, 30% pyridine; 5 mL). The reaction mixture was stirred at room temperature for 12 h, after which it was quenched with 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 and saturated $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered and the filtrate was concentrated and put for the next stage without further

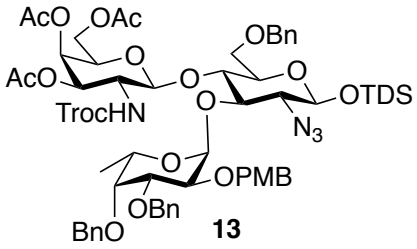


11

purification. The residue (554 mg, 0.42 mmol) was dissolved in DCM (20 mL), followed by the addition of 2,2,2- trifluoro-*N*-phenylacetimidoyl chloride (130 μL, 0.63 mmol) and DBU (62 μL, 0.42 mmol). The reaction was stirred for 30 min, after which the solvent was evaporated and product was purified using silica gel column chromatography (PE to PE: EtOAc, 7: 3, v: v). The product was dried over high vacuum for 30 min, and immediately put for glycosylation reaction. The imidate donor (570 mg, 0.38 mmol) and 5-(*N*-benzyloxycarbonyl,*N*-benzyl)aminopentyl linker (626 mg, 1.91 mmol) were dissolved in DCM (10 mL), and stirred with pre-activated molecular sieves (1.5 g), under argon for 30 min. The reaction mixture was cooled down to -50 °C, followed by the addition of TfOH (6.8 μL, 0.076 mmol). The temperature was slowly warmed up to -30 °C, after which the TLC showed complete consumption of donor and a new product spot formed. The reaction mixture was quenched with NEt_3 (100 μl), the sieves were filtered off, and the solvent was evaporated. Silica gel column chromatography using PE: EtOAc (9: 1, v: v to 7: 3, v: v) afforded the product as a transparent syrup (509 mg, 66% over 3 steps). R_f = 0.52 (PE: EtOAc, 7: 3, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 to 6.96 (30H, m, H-Ar), 5.24 (1H, d, H-4 GalN, *J* = 3.1 Hz), 5.15 (3H, m, C<u>H</u>$_2$ of Cbz of N(Bn)Cbz Linker, H-1 Fuc), 4.99 to 4.66 (9H, m, 3x PhC<u>H</u>H, 3xPhCH<u>H</u>, H-1 GlcN, CH_2 of Troc), 4.60 (3H, m, H-5 Fuc, H-3 GalN, PhCH<u>H</u>), 4.43 (4H, m, C<u>H</u>$_2$ of Bn of N(Bn)Cbz Linker, PhC<u>H</u>H, H-1 GalN), 4.16 (3H, m, H-6a GalN, H-3 GlcN, H-2 Fuc), 3.92 (3H, m, H-3 Fuc, H-5 GalN, H-6b GalN), 3.75 (3H, m, H-6b GlcN, OCH<u>H</u>$(CH_2)_4$N(Bn)Cbz, H-4 Fuc), 3.60 (3H, m, H-2 GalN, H-6a GlcN, H-4 GlcN), 3.37 (2H, m, OC<u>H</u>H$(CH_2)_4$N(Bn)Cbz, H-5 GlcN), 3.17 (3H, m, O$(CH_2)_4$C<u>H</u>$_2$N(Bn)Cbz Linker, H-2 GlcN), 2.01 to 1.81 (9H, 3s, 3x C<u>H</u>$_3$ of Ac), 1.48 (4H, m, 2x C<u>H</u>$_2$ of linker), 1.22 (5H, m, C<u>H</u>$_3$ of Fuc, C<u>H</u>$_2$ of linker); ^{13}C NMR (151 MHz, $CDCl_3$): δ 171.38 to 170.01 (3x <u>C</u>OCH$_3$ of Ac), 156.81 to 153.68 (2x <u>C</u>OOCH$_2$ of Troc), 138.97 to 128.28 (C-Ar), 100.23 (C-1 GalN), 99.98 (C-1 GlcN), 97.61 (C-1 Fuc), 79.94 (C-3 Fuc), 77.51, 77.29 (C-4 Fuc), 77.08, 76.60 (C-2 Fuc), 74.89 (C-5 GalN), 74.49 (C-3 GlcN), 74.38 (Ph<u>C</u>H$_2$), 74.25 (C-5 GlcN), 73.83 to 72.64 (2x Ph<u>C</u>H$_2$), 70.19 (C-3 GalN), 69.68 (C-4 GlcN), 68.25 (C-6 GlcN), 67.24 (<u>C</u>H$_2$ of Cbz of N(Bn)Cbz Linker), 66.43 (C-5 Fuc), 66.02 (C-4 GalN), 64.42, 60.47, 60.42 (C-6 GalN), 58.74 (C-2 GlcN), 54.19, 52.35 (C-2 GalN), 50.54, 50.32 (<u>C</u>H$_2$ of Bn of N(Bn)Cbz), 47.24, 46.18 (O$(CH_2)_4$<u>C</u>H$_2$N(Bn)Cbz

Linker), 40.98, 33.86, 31.96, 30.66, 30.39, 29.73, 29.69, 29.15, 29.03, 28.50, 27.90 to 27.33 (2x CH_2) of linker, 24.02, 23.14, 22.74, 21.11, 21.07, 20.99, 20.69 to 20.61 (3x $\underline{C}H_3$ of Ac), 19.17, 17.62, 17.37, 16.96 ($\underline{C}H_3$ of Fuc). ESI (*m/z*): $[M+ Na]^+$ calculated for $C_{78}H_{89}Cl_6N_3O_{22}$, 1652.3967; found 1652.3955.

Dimethylthexylsilyl [3,4-di-*O*-benzyl-2-*O*-p-methoxybenzyl-α-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-galactopyranosyl]-(1→4)-2-deoxy-2-azido-6-*O*-benzyl-β-D-glucopyranoside (13):

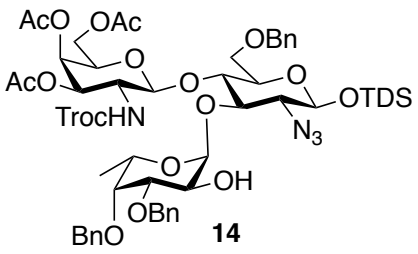


13

Donor **4** (4.0 g, 7.0 mmol), DPS (1.4 g, 7.0 mmol) and TTBP (1.74 g, 7.0 mmol) were dissolved in DCM (25 mL) and stirred with pre-activated molecular sieves (6.0 g) for 30 min, after which the temperature was brought down to -60 ºC, followed by the addition of Tf_2O (1.2 mL, 7.0 mmol). After 10 min, a solution of acceptor **6** (1.6 g, 1.7 mmol) in anhydrous DCM (6 mL) was added dropwise along the wall of the flask, and the reaction mixture was stirred for 1 h, during which the temperature was slowly raised to -40 ºC. After TLC (Tol: EtOAc, 8.5: 1.5, v: v) showed complete consumption of acceptor, the reaction was quenched using NEt_3 (5 mL). The molecular sieves were filtered off, and the solvent was removed *in vacuo*. Silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 7: 3, v: v) gave the product as a white amorphous powder. (1.8 g, 73%). R_f = 0.49 (Tol: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 to 6.67 (19H, m, H-Ar), 5.48 (1H, d, H-1 Fuc, *J* = 3.8 Hz), 5.21 (1H, d, H-4 GalN, *J* = 3.2 Hz), 4.92 (2H, m, PhC$\underline{H}$H, PhC$\underline{H}$H), 4.81 (3H, m, CH_2 of Troc, PhCH$\underline{H}$), 4.67 (6H, m, H-3 GalN, H-5 Fuc, 3x PhCH$\underline{H}$, PhC$\underline{H}$H), 4.50 (1H, d, H-1 GlcN, *J* = 7.6 Hz), 4.40 (2H, m, PhC$\underline{H}$H, H-1 GalN), 4.11 (2H, m, H-2 Fuc, H-6b GalN), 3.92 (3H, m, H- 6a GalN, H-3 Fuc, H-5 GalN), 3.76 (5H, m, H-6b GlcN, H-3 GlcN, *O*CH_3 of PMB), 3.58 (4H, m, H-6a GlcN, H-4 Fuc, H-2 GalN, H-4 GlcN), 3.46 (1H, m, H-2 GlcN), 3.26 (1H, m, H-5 GlcN), 2.00 to 1.74 (9H, 3s, 3x C$\underline{H}_3$ of Ac), 1.67 [1H, m, C$\underline{H}$(CH_3)$_2$ of TDS], 1.22 (3H, d, C$\underline{H}_3$ of Fuc, *J* = 7.1 Hz), 0.88 [12H, m, C(C$\underline{H}_3$)$_2$, CH(C$\underline{H}_3$)$_2$ of TDS], 0.18 (6H, d, 2x C$\underline{H}_3$-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.04 to 169.75

(3x $\underline{C}OCH_3$ of Ac), 153.89 ($\underline{C}OOCH_2$ of Troc), 139.08 to 113.39 (C-Ar), 100.38 (C-1 GalN), 97.36 (C-1 GlcN), 97.30 (C-1 Fuc), 79.88 (C-3 Fuc), 77.31, 76.99 (C-3 GlcN), 76.67, 75.03, 74.54 (C-2 Fuc), 74.40 (C-5 GalN), 74.02 (C-4 Fuc), 73.92 (C-5 GlcN), 72.80 to 72.71 ($Ph\underline{C}H_2$), 70.10 (C-4 GlcN), 68.75 (C-2 GlcN), 68.12 (C-6 GlcN), 66.02 (C-5 Fuc), 65.79 (C-4 GalN), 60.11 (C-6 GalN), 55.21 ($O\underline{C}H_3$ of PMB), 52.17 (C-2 GalN), 33.85 ($\underline{C}H(CH_3)_2$ of TDS), 20.63 to 20.46 (3x $\underline{C}H_3$ of Ac), 19.97 to 18.35 (4x $\underline{C}H_3$ of TDS), 16.82 ($\underline{C}H_3$ of Fuc), -0.03 to -3.03 (2x $\underline{C}H_3$-Si of TDS). ESI (*m/z*): $[M+ Na]^+$ calculated for $C_{64}H_{83}Cl_3N_4O_{19}Si$; 1367.4384; found 1367.4367.

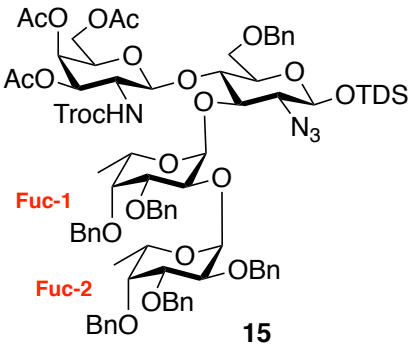
Dimethylthexylsilyl [3,4-di-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-galactopyranosyl]-(1→4)-6-*O*-benzyl-2-deoxy-2-azido-β-D-glucopyranoside (14): Trisaccharide **13** (1.5 g, 1.11 mmol) was dissolved in DCM: H2O (20 mL, 9: 1, v: v) followed by the addition of DDQ (506 mg, 2.2 mmol), and was stirred for 2 h, after which the TLC showed full conversion of starting material to product. The reaction mixture was then diluted by DCM and washed with water and saturated $NaHCO_3$. The organic layer 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 (8: 2, v: v) which gave the product as a white amorphous solid. (1.0 g, 74%). R_f = 0.47 (Tol: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.65 to 7.06 (15H, m, H-Ar), 5.46 (1H, d, H-1 Fuc, *J* = 4.2 Hz), 5.22 (1H, d, H-4 GalN, *J* = 3.5 Hz), 4.95 to 4.61 (6H, m, CH_2 of Troc, 2x PhCH$\underline{H}$, 2x PhC$\underline{H}$H), 4.54 (2H, m, H-5 Fuc, H-3 GalN), 4.47 (1H, d, H-1 GlcN, *J* = 7.8 Hz), 4.41 (2H, m, H-1 GalN, PhC$\underline{H}$H), 4.21 (1H, m, H-2 Fuc), 4.09 (1H, m, H-6b GalN), 3.90 (2H, m, H-6a GalN, H-3 Fuc), 3.72 (2H, m, H-6b GlcN, H-5 GalN), 3.63 (3H ,m, H-2 GalN, H-4 GlcN, H-3 GlcN), 3.54 (2H, m, H-6a GlcN, H-4 Fuc), 3.30 (2H, m, H-5 GlcN, H-2 GlcN), 2.03 to 1.76 (9H, 3s, 3x $C\underline{H}_3$ of Ac), 1.67 [1H, m, $C\underline{H}(CH_3)_2$ of TDS] , 1.22 (3H, d, $C\underline{H}_3$ of Fuc, *J* = 6.2 Hz), 0.88 [12H, m, $C(C\underline{H}_3)_2$, $CH(C\underline{H}_3)_2$ of TDS], 0.17 (6H, d, 2x $C\underline{H}_3$-Si of TDS); ^{13}C NMR (151



14

MHz, $CDCl_3$): δ 170.04 to 169.78 (3x $\underline{C}OCH_3$ of Ac), 153.91 ($\underline{C}OOCH_2$ of Troc), 138.68 to 127.12 (C-Ar), 100.07 (C-1 GalN), 98.41(C-1 Fuc), 97.22 (C-1 GlcN), 80.63 (C-5 GalN), 77.30 , 77.18, 76.98, 76.66, 76.09 (C-3 GlcN), 75.14 (C-4 Fuc), 74.39 (C-5 GlcN), 74.37, 73.98 (C-3 Fuc), 73.90 to 70.36 (3x $Ph\underline{C}H_2$), 70.12 $\underline{C}H_2$ of Troc), 69.29 (C-4 GlcN), 69.13 (C-5 Fuc), 68.94 (C-2 Fuc), 68.55 (C-2 GlcN), 67.96 (C-3 GalN), 67.72 (C-6 GlcN), 65.91 (C-4 GalN), 60.44 (C-6 GalN), 52.15 (C-2 GalN), 33.84 ($\underline{C}H(CH_3)_2$ of TDS), 20.67 to 20.46 (3x $\underline{C}H_3$ of Ac), 19.97 to 18.34 (4x $\underline{C}H_3$ of TDS), 16.90 ($\underline{C}H_3$ of Fuc), -0.04 to -3.19 (2x $\underline{C}H_3$-Si of TDS). ESI (*m/z*): $[M+ Na]^+$ calculated for $C_{56}H_{75}Cl_3N_4O_{18}Si$, 1247.3809; found 1247.3815.

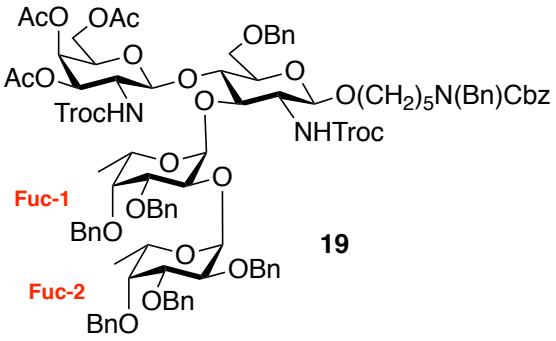
Dimethylthexylsilyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-[3,4-di-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-galactopyranosyl]-(1→4)-2-azido-2-deoxy-6-*O*-benzyl-β-D-glucopyranoside (15): Acceptor **14** (800 mg, 0.65 mmol) and donor **3** (625 mg, 1.3 mmol), were dissolved in the solvent system DCM (5 mL) and DMF (5 mL) and stirred with pre-activated molecular sieves (2 g) for 30 min, after which the temperature was brought down to -30 ºC. This was followed by the sequential addition of NIS (293 mg, 1.3 mmol) and TMSTOf (118 µl, 0.65 mmol). The reaction mixture was warmed up to +5 ºC over a period of one h, after which the TLC showed complete consumption of acceptor. The reaction mixture was quenched with NEt_3 (1 mL). The solvent was removed *in vacuo*, the residue was diluted by DCM and washed with saturated $NaHCO_3$ and 5% sodium thio-sulphate respectively. The organic phase was dried over $MgSO_4$ and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified using silica gel column chromatography (Tol: EtOAc, 9: 1, v: v to 7: 3, v: v) yielded the product as a pale-yellow amorphous powder. (890 mg, 83%). R_f = 0.61 (Tol: EtOAc, 8: 2, v: v). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 to 6.98 (30H, Ar-H), 5.69 (1H, d, H-1 Fuc-2, *J* = 3.6 Hz), 5.31 (1H, d, H-1 Fuc-1, *J* = 3.3 Hz), 5.23 (1H, d, H-4 GalN, *J* = 3.2



15

Hz), 4.73 to 5.02 (8H, m, CH_2 of Troc, 3x PhCHH, PhCHH), 4.64 (4H, m, H-3 GalN, H-5 Fuc-1, PhCHH, PhCHH), 4.49 (4H, m, H-1 GalN, H-1 GlcN, PhCHH, PhCHH), 4.43 (3H, m, H-2 Fuc-2, PhCHH, PhCHH), 4.20 (2H, m, H-6b GalN, H-5 Fuc-2), 4.07 (2H, m, H-6a GalN, H-2 Fuc-1), 3.96 (1H, m, H-5 GalN), 3.80 (2H, m H-4 Fuc-2, H-3 Fuc-1), 3.69 (3H, m, H-6b GlcN, H-4 GlcN, H-3 GlcN), 3.59 (2H, m, H-4 Fuc-1, H-2 GalN), 3.47 (1H, m, H-6a GlcN), 3.22 (3H, m, H-5 GlcN, H-2 GlcN, H-3 Fuc-2), 1.97 to 1.79 (9H, 3s, 3x CH_3 of Ac), 1.60 [1H, m, $CH(CH_3)_2$ of TDS], 1.24 (3H, m, CH_3 of Fuc-1), 1.01 (3H, d, CH_3 of Fuc-2, J = 6.6 Hz), 0.83 [12H, m, $C(CH_3)_2$, $CH(CH_3)_2$ of TDS], 0.13 (6H, d, 2x CH_3-Si of TDS); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.23 to 169.74 (3x $COCH_3$ of Ac), 153.93 ($COOCH_2$ of Troc), 139.24 to 126.13 (C-Ar), 100.50 (C-1 GalN), 97.14 (C-1 GlcN), 94.80 (C-1 Fuc-2), 93.25 (C-1 Fuc-1), 79.63 (C-4 Fuc-2), 78.27 (C-5 GalN), 77.49 (C-4 GlcN), 77.31, 77.19 (C-3 Fuc-2), 77.08, 76.99, 76.67, 76.07 (C-2 Fuc-1), 74.82 (C-3 Fuc-1), 74.70 ($PhCH_2$), 74.43 ($PhCH_2$), 74.38 (C-5 GlcN), 74.10 to 74.01 (2x ($PhCH_2$), 73.63 (C-4 Fuc-1), 72.54 to 72.46 (2x$PhCH_2$, CH_2 of Troc), 70.36 (C-3 GlcN), 70.23 (C-3 GalN), 69.17 (C-2 Fuc-2), 68.40 (C-6 GlcN), 67.69 (C-2 GlcN), 65.98 (C-4 GalN), 65.90 (C-5 Fuc-1), 65.82 (C-5 Fuc-2), 60.49 (C-6 GalN), 52.30 (C-2 GalN), 33.69 ($CH(CH_3)_2$ of TDS), 31.90, 29.67, 29.24, 20.68 to 20.51 (3x CH_3 of Ac), 19.94 to 18.31 (4x CH_3 of TDS), 16.78 (CH_3 of Fuc-1), 16.14 (CH_3 of Fuc-2), -0.03 to -3.01 (2x CH_3-Si of TDS). ESI (*m/z*): $[M+ Na]^+$ calculated for $C_{83}H_{103}Cl_3N_4O_{22}Si$, 1663.5797; found 1663.5792.

5-(*N*-Benzyloxycarbonyl,*N*-Benzyl)aminopentyl 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl-(1→2)-[3,4-di-*O*-benzyl-α-L-fucopyranosyl]-(1→3)-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2,-trichloroethoxy)carbonylamino-β-D-galactopyranosyl]-(1→4)-6-*O*-benzyl-2-deoxy-2-(2,2,2-trichloroethoxy)carbonylamino-β-D-glucopyranoside (19): Compound **15** (850 mg, 0.53 mmol) was dissolved in THF (9 mL) and H_2O (1 mL), followed by the addition of Trimethyl phosphine (283 μL, 2.7 mmol). The reaction mixture was stirred under argon for 2 h. After this time, the solvent was evaporated, and the residue was co-evaporated with toluene thrice. The residue was used further without purification. The residue was dissolved in DCM (10 mL), followed by the addition of 2,2,2-Trichloroethyl chloroformate (136 μL, 0.99 mmol) and NEt_3 (138 μL, 0.99 mmol). The reaction mixture was then allowed to stir for 1 h, after which the TLC (R_f = 0.58, Tol: EtOAc, 8: 2, v: v) showed installation of Troc group at the free amine of C-2 of GlcN. The solvent was evaporated, the residue was dissolved in DCM, and washed with water and 1M HCl. The organic layer was dried over $MgSO_4$, filtered, and the filtrate was concentrated and used for next step. The Troc installed compound **16** (500 mg, 0.28 mmol) was dissolved in DCM (5 mL) and pyridine (10 mL), followed by dropwise addition of HF in pyridine (70% HF, 30% pyridine; 3 mL). The reaction mixture was stirred for 12 h, after which it was quenched with 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 and saturated $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and the filtrate was concentrated, affording compound **17** and put for the next stage without further purification. Compound **17** (370 mg, 0.224 mmol) was dissolved in DCM (20 mL), followed by the addition of 2,2,2- Trifluoro-*N*-phenylacetimidoyl chloride (70 μL, 0.337 mmol) and DBU (334 μL, 0.224 mmol). The reaction was stirred for 30 min, after which the solvent was evaporated and product was purified using silica gel column chromatography (Tol to Tol: EtOAc, 8: 2, v: v). The product **18** was dried over high vacuum for 30 min, and immediately put for glycosylation reaction. The imidate donor **18**

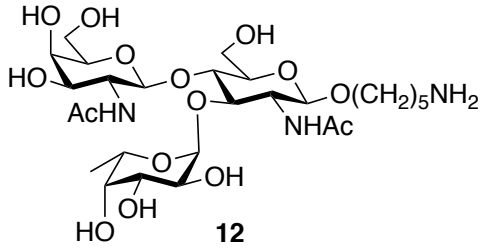


19

(350 mg, 0.19 mmol) and 5-(*N*-Benzyloxycarbonyl,*N*-Benzyl)aminopentyl linker (316 mg, 0.98 mmol) were dissolved in DCM (5 mL), and stirred with pre-activated molecular sieves (500 mg), under argon for 30 min. The mixture was cooled down to -50 °C, followed by the addition of TfOH (6.0 μL, 0.069 mmol). The temperature was slowly warmed up to -30 °C, after which the TLC showed complete consumption of donor and a new product spot formed. The reaction mixture was quenched with NEt_3 (50 μL), the sieves were filtered off, and the solvent was evaporated. Silica gel column chromatography using Tol: EtOAc (9: 1, v: v to 7: 3, v: v) afforded the product **19** as a transparent syrup (312.0 mg, 31% over 5 steps). R_f = 0.62 (Tol: EtOAc, 8.5: 1.5, v: v). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 to 7.05 (40H, m, H-Ar), 5.26 (1H, d, H-4 GalN, *J* = 3.3 Hz), 5.14 (3H, m, C$\underline{H}_2$ of Cbz of N(Bn)Cbz linker, H-1 Fuc-1, H-1 Fuc-2), 4.96 (3H, m, H-1 GlcN, PhC$\underline{H}$H, PhCH$\underline{H}$), 4.86 (4H, m, 2x PhC$\underline{H}$H, 2x PhCH$\underline{H}$), 4.67 (9H, m, PhC$\underline{H}$H, H-5 Fuc-1, H-3 GalN, 2x C$\underline{H}_2$ of Troc, PhC$\underline{H}$H, PhCH$\underline{H}$), 4.51 (2H, m, PhC$\underline{H}$H, PhCH$\underline{H}$), 4.40 (5H, m, C$\underline{H}_2$ of Bn of N(Bn)Cbz linker, H-2 Fuc-2, PhCH$\underline{H}$, H-1 GalN), 4.25 (1H, m, H-5 Fuc-2), 4.11 (4H, m, H-6a GalN, H-6b GalN, H-2 Fuc-1, H-3 GlcN), 3.95 (2H, m, H-4 Fuc-2, H-5 GalN), 3.81 (1H, m, H-3 Fuc-1), 3.71 (3H, m, H-6b GlcN, H-4 Fuc-1, OCH$\underline{H}$(CH$_2$)$_4$N(Bn)Cbz), 3.58 (3H, m, H-6a GlcN, H-2 GalN, H-4 GlcN), 3.33 (3H, m, OC$\underline{H}$H(CH$_2$)$_4$N(Bn)Cbz, H-5 GlcN, H-3 Fuc-2), 3.08 (3H, m, O(CH$_2$)$_4$C$\underline{H}_2$N(Bn)Cbz, H-2 GlcN), 2.05 to 1.84 (9H, 3s, 3x C$\underline{H}_3$ of Ac), 1.40 (4H, m, 2x C$\underline{H}_2$ of Linker), 1.24 (5H, m, C$\underline{H}_3$ of Fuc-1, C$\underline{H}_2$ of Linker), 0.81 (3H, d, C$\underline{H}_3$ of Fuc-2); ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.23 to 169.95 (3x $\underline{C}$OCH$_3$ of Ac), 153.99 to 153.33 (2x $\underline{C}$OOCH$_2$ of Troc) 138.80 to 127.20 (C-Ar), 100.00 (C-1 GalN), 99.73 (C-1 GlcN), 95.82 (C-1 Fuc-1), 95.69 (C-1 Fuc-2), 80.74 (C-4 Fuc-2), 78.49 (C-5 GalN), 77.37 (C-4 Fuc-1), 77.15, 76.94 (C-5 GlcN), 75.65 (C-2 Fuc-1), 74.61 (C-3 Fuc-1), 74.52 (Ph$\underline{C}$H$_2$), 74.37 (C-3 GlcN), 74.14 (Ph$\underline{C}$H$_2$), 74.06 (C-3 Fuc-2), 73.99 to 72.10 (4x Ph$\underline{C}$H$_2$, 2x CH$_2$ of Troc), 71.23 (C-2 Fuc-2), 70.21 (C-3 GalN), 70.21 (C-4 GlcN), 69.78 (O$\underline{C}$H$_2$(CH$_2$)$_4$N(Bn)Cbz), 68.09 (C-6 GlcN), 67.20 ($\underline{C}$H$_2$ of Cbz of N(Bn)Cbz linker), 66.34 (C-5 Fuc-1), 66.11 (C-4 GalN), 65.95 (C-5 Fuc-2), 60.31 (C-6 GalN), 59.13 (C-2 GlcN), 52.29 (C-2 GalN), 50.51 ($\underline{C}$H$_2$ of Bn of N(Bn)Cbz linker), 50.19, 47.14, 46.21, 40.93, 33.85, 31.97, 30.37, 29.74, 29.40, 29.31, 28.47, 27.96, 27.46, 23.94, 23.16, 22.74, 20.90,

20.70 to 20.59 (3x $\underline{C}H_3$ of Ac), 17.57, 17.35, 16.84 ($\underline{C}H_3$ of Fuc-1), 16.15 ($\underline{C}H_3$ of Fuc-2). ESI (*m/z*): $[M+ NH_4]^+$ calculated for $C_{98}H_{111}Cl_6N_3O_{26}$, 1959.6610; found 1959.1591.

5-aminopentyl α-L-fucopyranosyl-(1→3)-[2-deoxy-2-acetamido)-β-D-galactopyranosyl]-(1→4)-2-deoxy-2-acetamido-β-D-glucopyranoside (12):



12

Compound **11** (500 mg, 0.3 mmol) was dissolved in THF (20 mL). To this solution, was added zinc (Zn) dust (1.0 g, pre-activated with 1N HCl), Acetic anhydride (1.0 mL) and acetic acid (250 μL). The reaction mixture was stirred for 30 min, after which, TLC (Tol: acetone, 9: 1, v: v), showed complete consumption of starting material. The Zn dust was filtered off, and the residue was co-evaporated with toluene. The residue was dissolved in DCM (10 mL) and MeOH (10 mL), followed by the addition of 1M NaOMe (250 μL). After 2 h, the reaction mixture was quenched Amberlite® IR 120 hydrogen form resin. The resin was filtered off, solvent was evaporated *in vacuo* and the residue was dried over high vacuum. This was used for the next reaction without any purification. The residue was dissolved in solvent system MeOH (5 mL) and water (5 mL), followed by the addition of palladium hydroxide (Degussa type, 100 mg), and AcOH (50 μL). The reaction mixture was stirred under hydrogen for 24 h, after which MALDI showed that the product had completely formed. The catalyst was carefully filtered off using celite, the solvent was evaporated *in vacuo*, and the residue was purified over P-2 Biogel using 50 mM ammonium bicarbonate as eluent. The compound was further purified using HILIC HPLC, using a gradient solvent system ACN: 50 mM NH_4HCO_3 (95: 5, v: v to 80: 20, v: v). The resulting product was a white cotton-like solid after lyophilization (89.3 mg, 45 % over three steps).

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

12	H1	H2	H3	H4	H5	H6	Fuc-CH_3	NHAc
GlcNAc	4.33, d, *J* = 8.3 Hz	3.77	3.82	3.71	3.39	3.45, 3.77	-	1.92
GalNAc	4.37 d, *J* = 8.4 Hz	3.85	3.79	3.76	3.46	3.62, 3.80	-	1.94
Fuc	4.99 d, *J* = 3.8 Hz	3.57	3.59	3.72	4.74	N.A.	1.14, d, *J* = 6.6 Hz	-

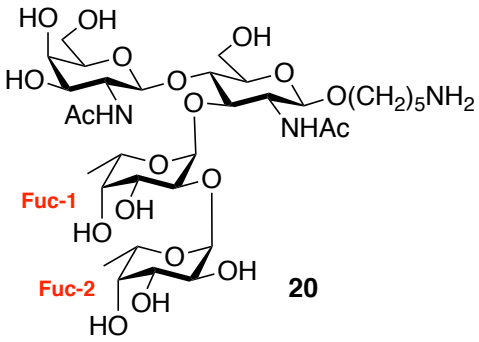
^{13}C NMR (151 MHz, D_2O)

12	C1	C2	C3	C4	C5	C6	**C**OCH_3 of NHAc	CO**C**H_3 of NHAc
GlcNAc	100.91	55.59	67.29	71.94	75.39	70.11	174.80	22.13
GalNAc	100.69	52.30	69.10	73.29	74.80	59.95	174.07	22.07
Fuc	98.42	67.64	70.65	74.61	66.89	15.31	-	-

Linker Peak	^{1}H Signal	^{13}C Signal
OCH_2CH_2**CH_2**$CH_2CH_2NH_2$	1.27	22.21
$OCH_2CH_2CH_2$**CH_2**CH_2NH_2	1.47	26.33
OCH_2**CH_2**$CH_2CH_2CH_2NH_2$	1.55	28.02
$OCH_2CH_2CH_2CH_2$**CH_2**NH_2	2.86	39.25
O**CH_2**$CH_2CH_2CH_2CH_2NH_2$	3.62	61.42

ESI (*m/z*): [M+ Na^+] calculated for $C_{27}H_{49}N_3O_{15}$, 678.3061; found 678.3076

5-aminopentyl α-L-fucopyranosyl-(1→2)-α-L-fucopyranosyl-(1→3)-[2-deoxy-2-acetamido-β-D-galactopyranosyl]-(1→4)-2-deoxy-2-acetamido-β-D-glucopyranoside (20): Compound **19** (310 mg, 0.16 mmol) was dissolved in THF (15 mL). To this solution was added Zn dust (800 mg, pre-activated with 1N HCl), acetic anhydride (800 μL) and acetic acid (200 μL). The reaction mixture was stirred for 30 min, after which, TLC (Tol: acetone, 9: 1, v: v), showed complete consumption of starting material. The Zn dust was filtered off, and the residue was co-evaporated with toluene. The residue was dissolved in DCM (10 mL) and MeOH (10 mL), followed by the addition of 1M NaOMe (200 μL). After 2 h, the reaction mixture was quenched with Amberlite® IR 120 hydrogen form resin. The resin was filtered off, solvent was evaporated *in vacuo* and the residue was dried over high vacuum. This was used for the next reaction without any purification. The residue was dissolved in solvent system MeOH (5 mL) and water (5 mL), followed by the addition of palladium hydroxide (Degussa type, 80 mg), and AcOH (50 μL). The reaction mixture was stirred under hydrogen for 24 h, after which MALDI showed that the product had completely formed. The catalyst was filtered off using celite, the solvent was evaporated, and the residue was purified over P-2 gel using 50 mM ammonium bicarbonate as eluent. The compound was further purified using HILIC HPLC, using a gradient solvent system ACN: 50 mM NH_4HCO_3 (95: 5, v: v to 75: 25, v: v). The resulting product was a white cotton-like solid after lyophilization. (47.8 mg, 38% over three steps).



20

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

20	H1	H2	H3	H4	H5	H6	Fuc-CH_3	NHAc
GlcNAc	4.36	3.71	3.87	3.77	3.37	3.44, 3.79	-	1.92
GalNAc	4.36	3.84	3.80	4.03, dd, *J* = 10.4, 3.3 Hz	3.46	3.62, 3.82	-	1.94
Fuc-1	4.74	3.66	3.59	3.75	4.67	N.A.	1.15, d, *J* = 6.5 Hz	-
Fuc-2	5.34, d, *J* = 3.5 Hz	3.64	3.93	3.68	4.11	N.A.	1.10, d, *J* = 6.7 Hz	-

^{13}C NMR (151 MHz, D_2O)

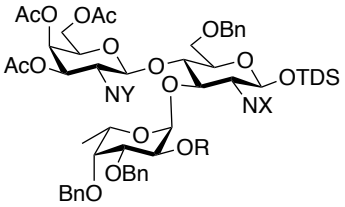
12	C1	C2	C3	C4	C5	C6	**C**OCH_3 of NHAc	CO**C**H_3 of NHAc
GlcNAc	100.70	56.15	68.93	71.58	75.22	70.17	174.75	22.46
GalNAc	101.07	52.34	67.84	67.22	75.14	59.85	174.50	22.26
Fuc-1	95.12	71.65	70.49	71.50	66.81	15.23	-	-
Fuc-2	94.14	72.99	73.12	71.81	66.88	15.27	-	-

Linker Peak	^{1}H Signal	^{13}C Signal
OCH_2CH_2**CH_2**$CH_2CH_2NH_2$	1.25	22.15
$OCH_2CH_2CH_2$**CH_2**CH_2NH_2	1.46	27.77
OCH_2**CH_2**$CH_2CH_2CH_2NH_2$	1.51	28.28
$OCH_2CH_2CH_2CH_2$**CH_2**NH_2	2.75	39.25
O**CH**$HCH_2CH_2CH_2CH_2NH_2$,	3.60	61.44
OCH**H**$CH_2CH_2CH_2CH_2NH_2$	3.70	-

ESI (*m/z*): [M+ Na^+] calculated for $C_{33}H_{59}N_3O_{19}$, 824.3640; found 824.3663.

3. Tables of Optimization of Synthesis Protocols

Table S1: Trial Reactions for Assembly of LDN-F Trisaccharide



NX and NY are different N-ptotecting groups

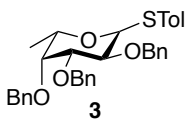
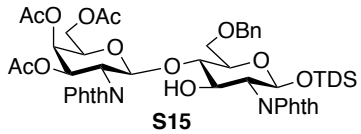
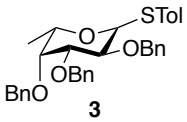
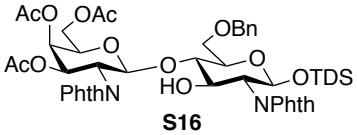
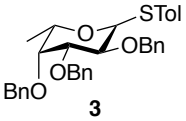
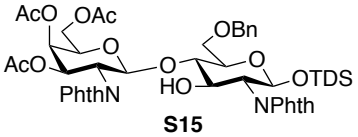
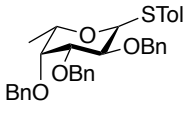
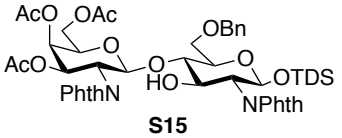
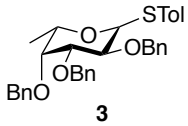
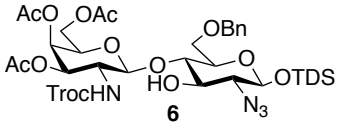
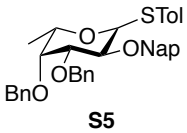
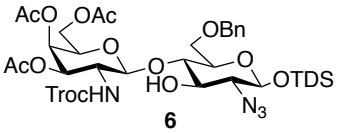
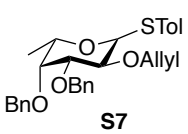
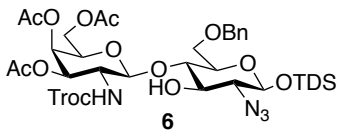
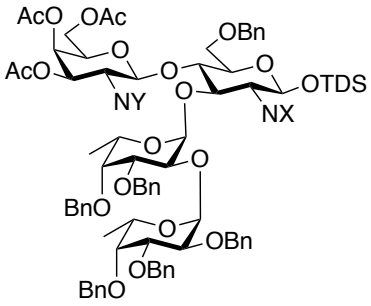
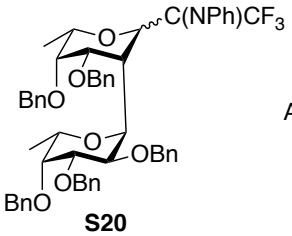
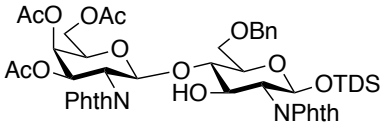
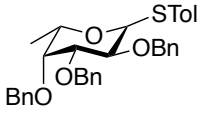
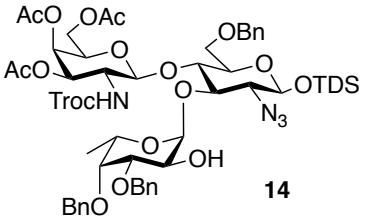
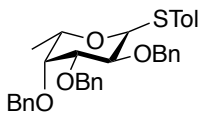
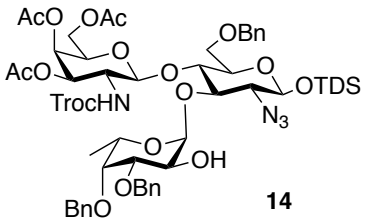
Donor	Acceptor	Promoter	Result
 **3**	 **S15**	NIS/TMSTOf;DCM; -40 to -20 °C	Donor hydrolysis, acceptor unreacted
 **3**	 **S16**	MeOTf, DMTST, 0°C	Donor hydrolysis, acceptor unreacted
 **3**	 **S15**	$CuBr_2$/TBAB, 0°C to R.T., 2h	Donor hydrolysis, acceptor unreacted
 **3**	 **S15**	DPS/ Tf_2O ; DCM -70 to -40 °C	88% product; α:β = 8:2, inseparable mixture **S20**
 **3**	 **6**	DPS/ Tf_2O ; DCM -70 to -40 °C	68% only α product; **7**
 **S5**	 **6**	DPS/ Tf_2O ; DCM -70 to -40 °C	No reaction, acceptor starts degrading beyond -40 °
 **S7**	 **6**	DPS/ Tf_2O ; DCM -70 to -40 °C	Donor degradation

Table S2: Trial Reactions for Assembly of LDN-DF Tetrasaccharide



NX and NY are different N-ptotecting groups

Donor	Acceptor	Promoter	Result
 **S20**	 **S15**	TMSTOf; DCM; -40 to -20 °C	Donor hydrolysis, acceptor unreacted
 **3**	 **14**	NIS/TMSTOf; DCM -20 to -5 °C	Product is α:β mixture = 1:1; Reaction does not go to completion, acceptor recovered
 **3**	 **14**	$CuBr_2$/ TBAB, DCM: DMF= 1:1 0 °C to R.T.	Trace product; hydrolysed donor

4. NMR and Molecular Modeling Studies

Protein expression and purification. The extracellular domain of DC-SIGN was obtained as previously described.[1] The carbohydrate recognition domain of DC-SIGN in its ^{15}N labeled form was obtained as previously described.[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-d_{11}, 150 mM NaCl, 4 mM $CaCl_2$ in D_2O (pD 8) using lectin/ligand ratios of 1:60. The temperature was set to 298 K. STD experiments were performed at 600 MHz Bruker spectrometer, using standard Bruker pulse sequences without water suppression nor protein spin-lock filter. Protein saturation was achieved with a Gaussian-shaped pulse of 49 ms. The on-resonance frequency was set at aliphatic regions (0.76 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 **12** and **20** are shown in Figures S1 and S2 respectively.

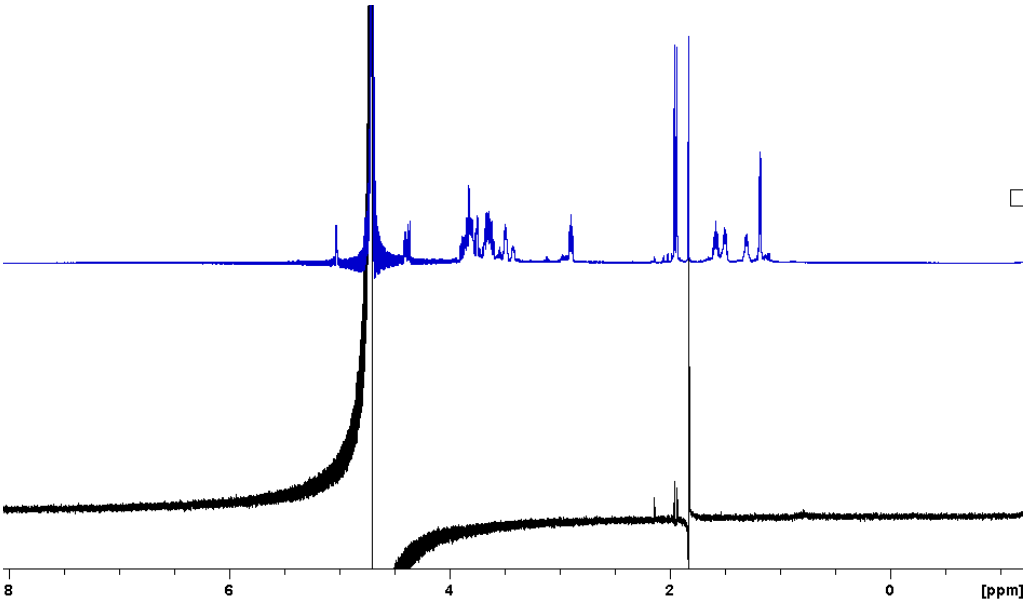


Figure S1. Blank ^{1}H-STD experiment of the free LDN-F. Ligand concentration is 780 μM in D_2O.

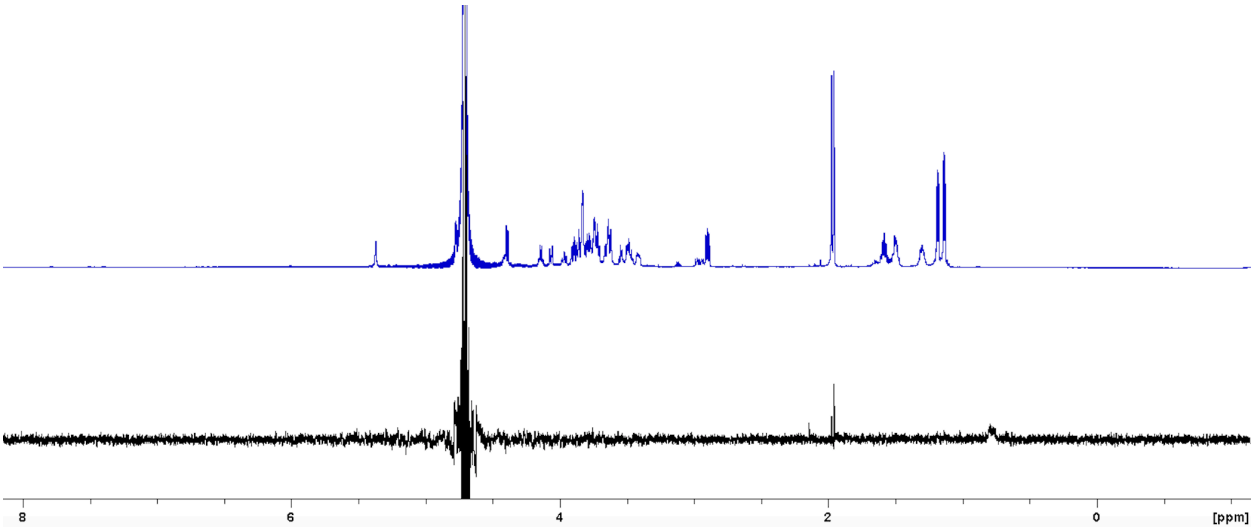


Figure S2. Blank ^{1}H-STD experiment of the free LDN-DF. Ligand concentration is 780 μM in D_2O.

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-d_{10}, at 800 MHz Bruker spectrometer equipped with a cryoprobe, at 310 K. Eight and ten titration points were acquired for ligands **12** and **20** respectively, with ligand concentrations varying from 0.0 to 0.5 mM for the former and from 0.0 to 1.5 mM for latter. Averaged chemical shift perturbation (CSP) and dissociation constants (k_D) were 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. The results from this analysis are shown in Figure S3.

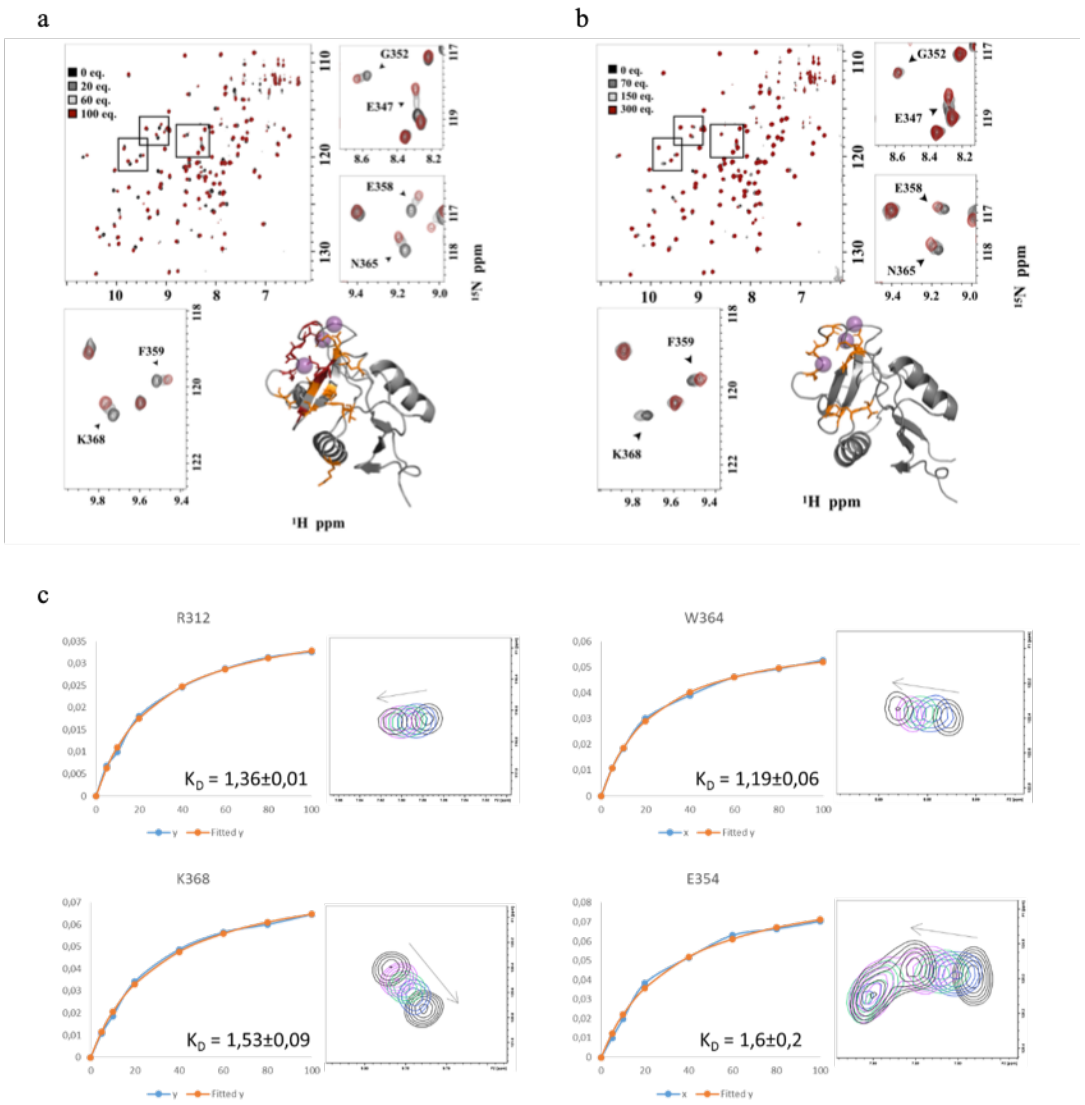


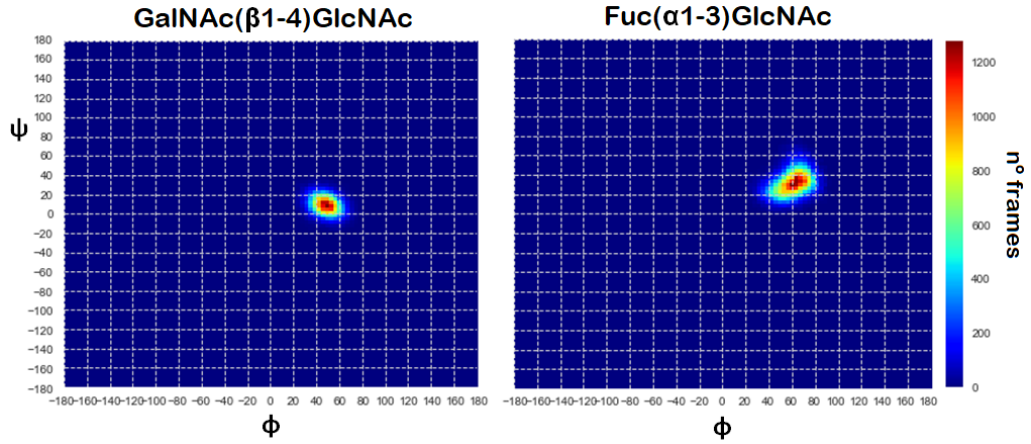
Figure S3. Superimposition of ^{1}H-^{15}N HSQC spectra (black, apo DC-SIGN; from dark gray to red, in the presence of increasing equiv. of LDN-F (a) and LDN-DF (b), respectively. Some regions of the spectra are enlarged in boxes. Perturbed residues are mapped onto the protein (cartoon representation). Most affected residues are in red, while less ones are in orange. c) Average chemical shift perturbation *versus* protein/ligand ratio for selected amino acids for the determination of the k_D for the binding of LDN-F ligand.

Transferred NOESY spectrum for glycan **12**, was acquired at 800 MHz Bruker spectrometer equipped with a cryoprobe in the presence of 0.2 equivalents of DC-SIGN (180 μM of protein), with a mixing time of 400 ms, at 298 K.

Molecular modeling. Initial geometries of ligands **12** and **20** were built in the Glycam web (http://glycam.org). Proton-proton distances derived from NOESY spectra (using the isolated spin-pair approximation) were used to check the goodness of the minimized structures. The initial pdb coordinates for CRD of DC-SIGN were derived from the crystal structure Protein Database (PDB) 1SL5. The magnesium ion was replaced by calcium, and the fucose pyranose ring of glycans **12** and **20** was superimposed onto the corresponding sugar in the deposited 1SL5 structure. The resulting binding poses were used as starting points for molecular dynamics (MD) simulations. The MD simulations were performed using the Amber16 program[4] with the ff99SB force field parameters for protein and GLYCAM_06h for the saccharides. Thereafter, the starting 3D geometries were placed into a 12 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). 500 ns Molecular dynamics simulations without constraints were recorded, using an NPT ensemble with periodic boundary conditions, a cutoff of 10 Å, and the particle mesh Ewald method. A total of 250 000 000 molecular dynamics steps were run with a time step of 1 fs per step. Coordinates and energy values were recorded every 10000 steps (10 ps) for a total of 25 000 MD models. A detailed analysis of the glycosydic linkages for glycans **12** and **20** was performed along the MD trajectory using the cpptraj module included in Amber-Tools 16 package and are represented in Figure S4.

MD 500 ns

LDN-F:



LDN-DF:

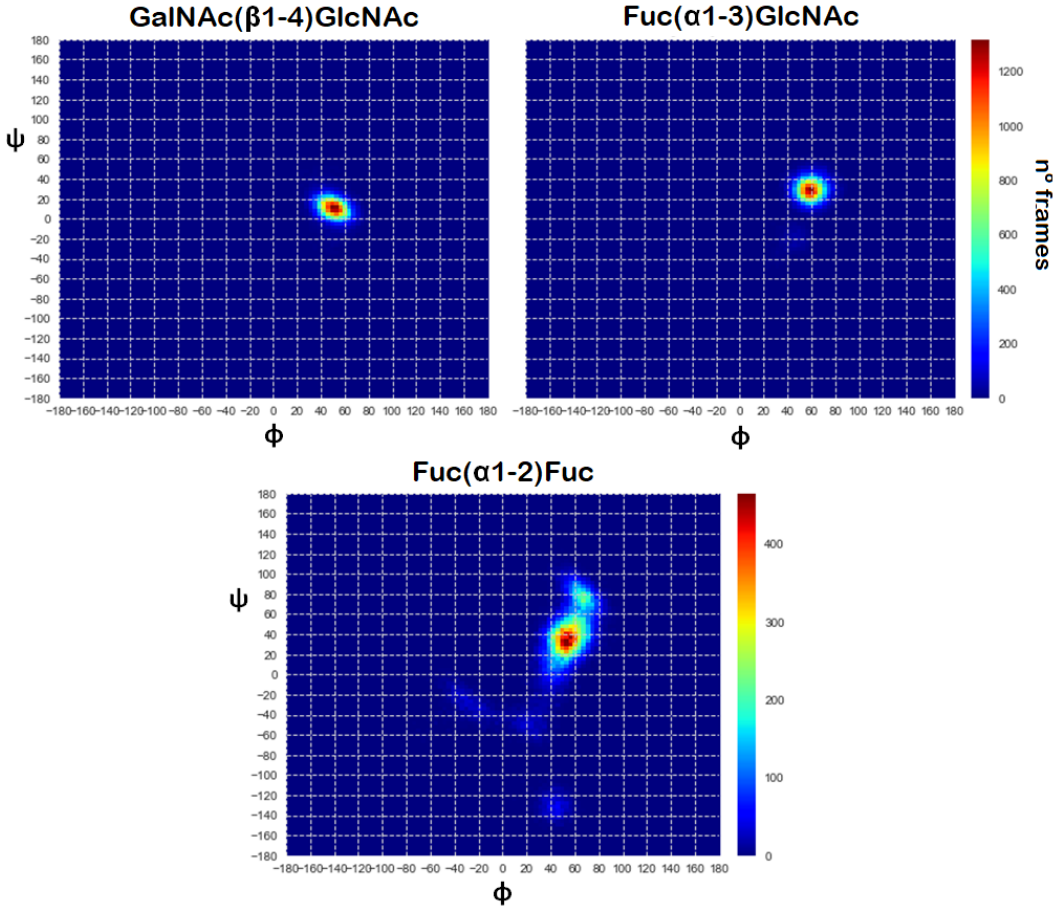


Figure S4. Glycans conformation analysis. Phi and Psi dihedral angles are monitored for the glycosidic linkages of **12** (top) and **20** (bottom) along 500 ns of MD simulation in complex with DC-SIGN.

Corcema-ST calculation. Corcema-ST matlab scripts were applied to the modeled structures of the complexes obtained by molecular dynamics calculations. Average structures from MD simulations for both ligands were selected and were analyzed by Corcema-ST.[5] The input parameters used in the calculations were: 2 s saturation time; amino acid in a radius of 10 Å around the ligand; direct irradiation on methyl groups of Ile, Leu, Val, Thr and Ala (as an approximation to 0.76 ppm experimental irradiation frequency); experimental k_D dissociation constants, 1.0 mM for **12** and 6.0 mM for **20** and experimental ligands/protein concentrations. An optimal k_{on} of 10^4 L mol^{-1} s^{-1} was determined by fitting the theoretical absolute STDs with the experimental one. Correlation times of 0.5 and 67ns for the ligands in the free and bound forms, respectively, were estimated following an empirical approximation and considering a 160.855 kDa tetramer form for the DC-SIGN. The comparison between the experimental STD NMR intensities and the CORCEMA-ST calculated profiles are represented in Figure S5.

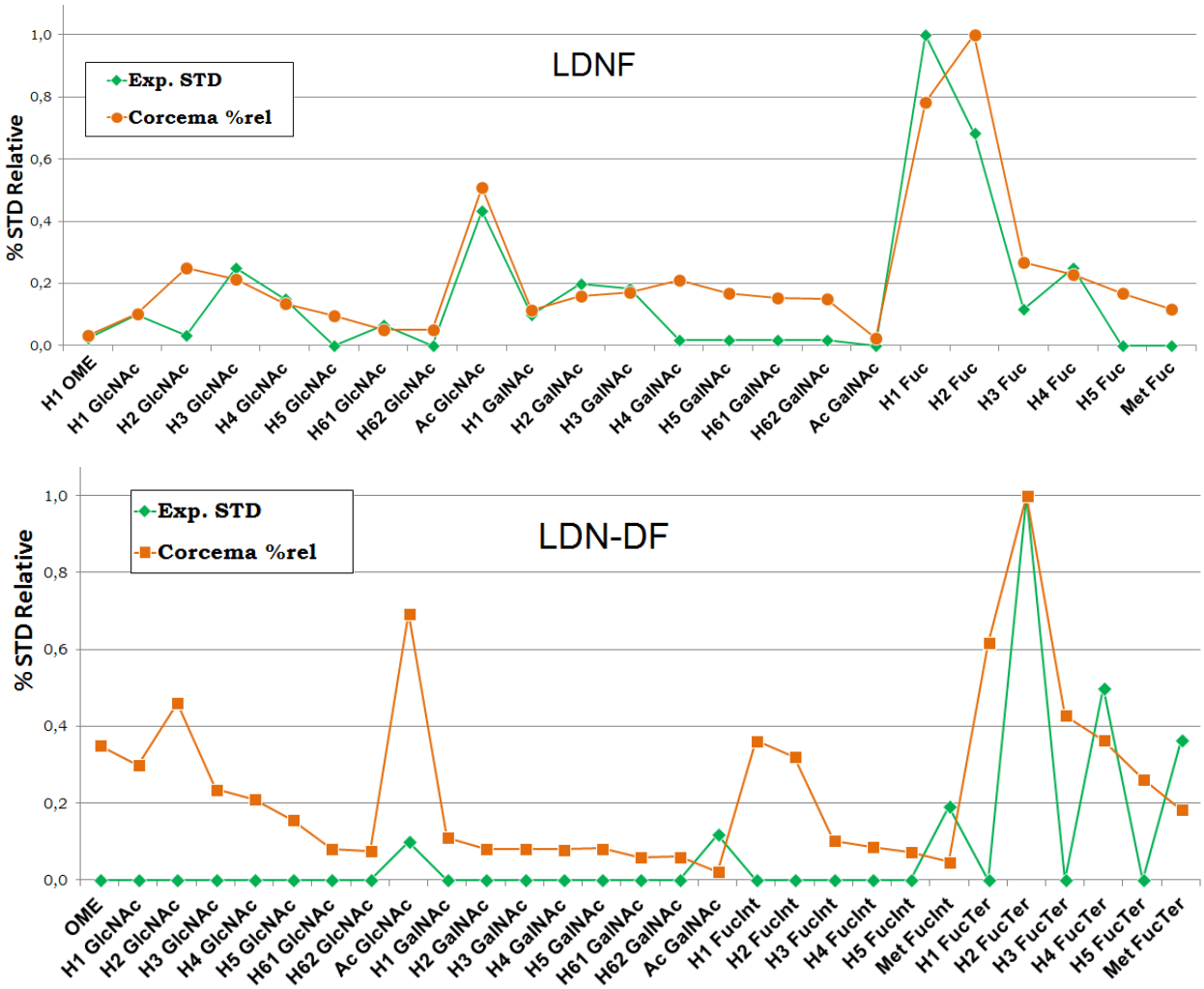


Figure S5. Comparison between the experimental STD intensities and the CORCEMA-ST profiles obtained from the MD simulations. The CORCEMA values were estimated using 50 frames randomly selected and the following parameters were set: 60 eq of ligand, k_{on} = 10^4 M^{-1} s^{-1}, t_{sat} = 2 sec, Δ_{sat} = Aliphatic (I, L, V, A, T), K_a = 10^3 M^{-1}, B_0 = 600 MHz, $\tau_{free\ lig}$ = 0,5 ns, $\tau_{bound\ lig}$ = 67 ns, $\tau_{internal}$ = 0,01 ns, rholeak = 0.1.

5. Microarray Studies

Glycan array printing. The synthetic compounds (100 μM in sodium phosphate (250 mM), pH 8.5 buffer) were printed on activated glass slides (Nexterion Slide H, Schott Inc) by piezoelectric non-contact printing (sciFLEXARRAYER S3, Scienion Inc) with a drop volume of ~400 pL and 1 drop per spot at 50% relative humidity. Compounds were printed as replicates of 6, 32x25 spots per subarray, and 24 subarrays (3x8) per slide. After overnight incubation in a saturated NaCl chamber (75% relative humidity), the remaining activated esters were quenched with ethanolamine (50 mM) in TRIS (100 mM), pH 9.0. Next, slides were rinsed with DI water, dried by centrifugation, and stored in a desiccator at RT.

Screening. To validate printing sub-arrays were incubated at RT with 50 μL of a mixture of biotinylated *Aleuria aurantia* lectin (AAL; Vector Labs, B-1395) and Streptavidin-AlexaFluor635 (5 μg/mL; ThermoFisher Scientific, S32364) in TSM binding buffer (20 mM Tris Cl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween, 1% BSA) for 1 h followed by 4 successive washes of the whole slide with TSM wash buffer (20 mM Tris Cl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$, 0.05% Tween-20) - TSM buffer (20 mM Tris Cl, pH 7.4, 150 mM NaCl, 2 mM $CaCl_2$, 2 mM $MgCl_2$) - 2x deionized H_2O with each 5 min soak time.

Recombinant human DC-SIGN--Fc Chimera (R&D systems, 161-DC) was assayed at the indicated concentrations premixed with anti-IgG Fc-biotin (5 μg/mL; ThermoFisher Scientific, A18833) and Streptavidin-AlexaFluor635 (5 μg/mL) in TSM binding buffer and washed were performed as described above.

Analyses. Washed arrays were dried by centrifugation and immediately scanned for fluorescence on a GenePix 4000 B microarray scanner (Molecular Devices). The detection gain was adjusted to avoid saturation of the signal. The data were processed with GenePix Pro 7 software and further analyzed using our home written Microsoft Excel macro. After removal of the lowest and highest value of the 6 replicates, the mean fluorescent intensities (corrected for mean background) and standard deviations (SD)

were calculated (n=4). Data were fitted using Prism software (GraphPad Software, Inc). Bar graphs represent the mean ± SD for each compound.

Printing validation. *Aleuria aurantia* lectin (AAL) binds to fucose linked (α-1,2, α-1,3, and α-1,6) structures. As expected all glycans show binding to AAL (Fig. S6).

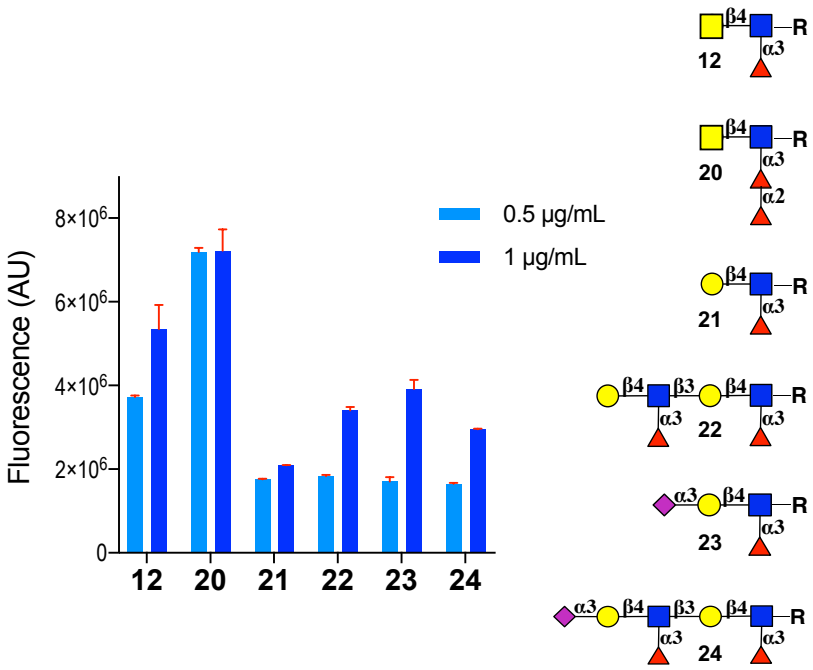


Figure S6. Microarray results of the glycan library at 100 μM for binding to AAL (0.5 and 1 μg/mL). Bars represent the mean ± SD.

6. References

[1] J. D. Martínez, P. Valverde, S. Delgado, C. Romanò, B. Linclau, N. C. Reichardt, S. Oscarson, A. Ardá, J. Jiménez-Barbero, F. J. Cañada, *Molecules* **2019**, *24*, E2337.

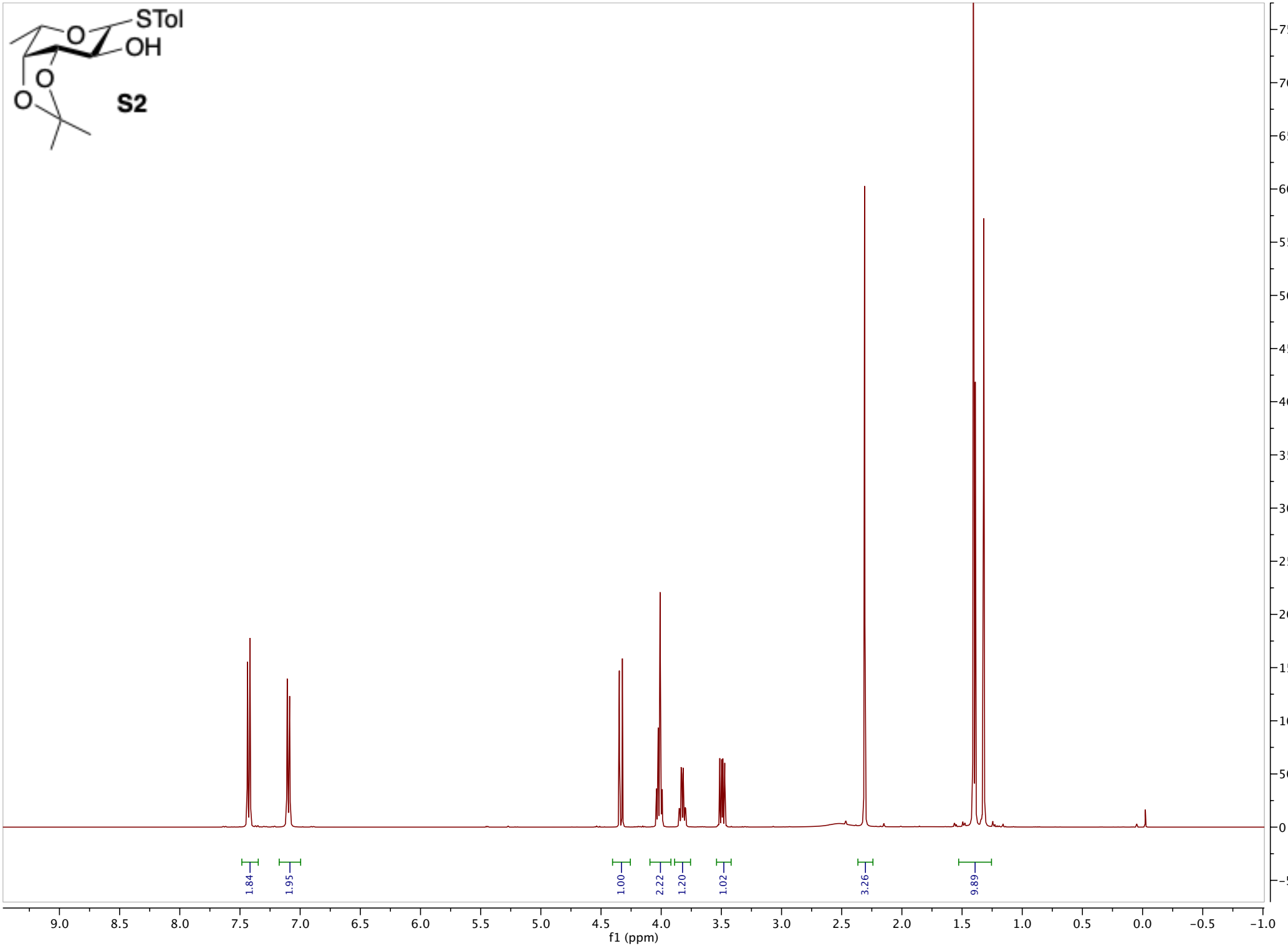
[2] P. Valverde, S. Delgado, J. D. Martínez, J. B. Vendeville, J. Malassis, B. Linclau, N. C. Reichardt, F. J. Cañada, J. Jiménez-Barbero, A. Arda, *ACS Chem. Biol.* **2019**, *14*, 1660-1671.

[3] W. F. Vranken, W. Boucher, T. J. Stevens, R. H. Fogh, A. Pajon, M. Llinas, E. L. Ulrich, J. L. Markley, J. Ionides, E. D. Laue, *Proteins* **2005**, *59*, 687-696.

[4] D. A. Case, R. M. Betz, D. S. Cerutti, T. E. Cheatham III, T. A. Darden, R. E. Duke, T. J. Giese, H. Gohlke, A. W. Goetz, N. Homeyer, S. Izadi, P. Janowski, J. Kaus, A. Kovalenko, T. S. Lee, S. LeGrand, P. Li, C. Lin, T. Luchko, R. Luo, B. Madej, D. Mermelstein, K. M. Merz, G. Monard, H. Nguyen, H. T. Nguyen, I. Omelyan, A. Onufriev, D. R. Roe, A. Roitberg, C. Sagui, C. L. Simmerling, W. M. Botello-Smith, J. Swails, R. C. Walker, J. Wang, R. M. Wolf, X. Wu, L. Xiao, P. A. Kollman in *AMBER 2016*, *Vol.* University of California, San Francisco, **2016**.

[5] N. R. Krishna, V. Jayalakshmi, *Top. Curr. Chem.* **2008**, *273*, 15-54.

7. NMR Spectra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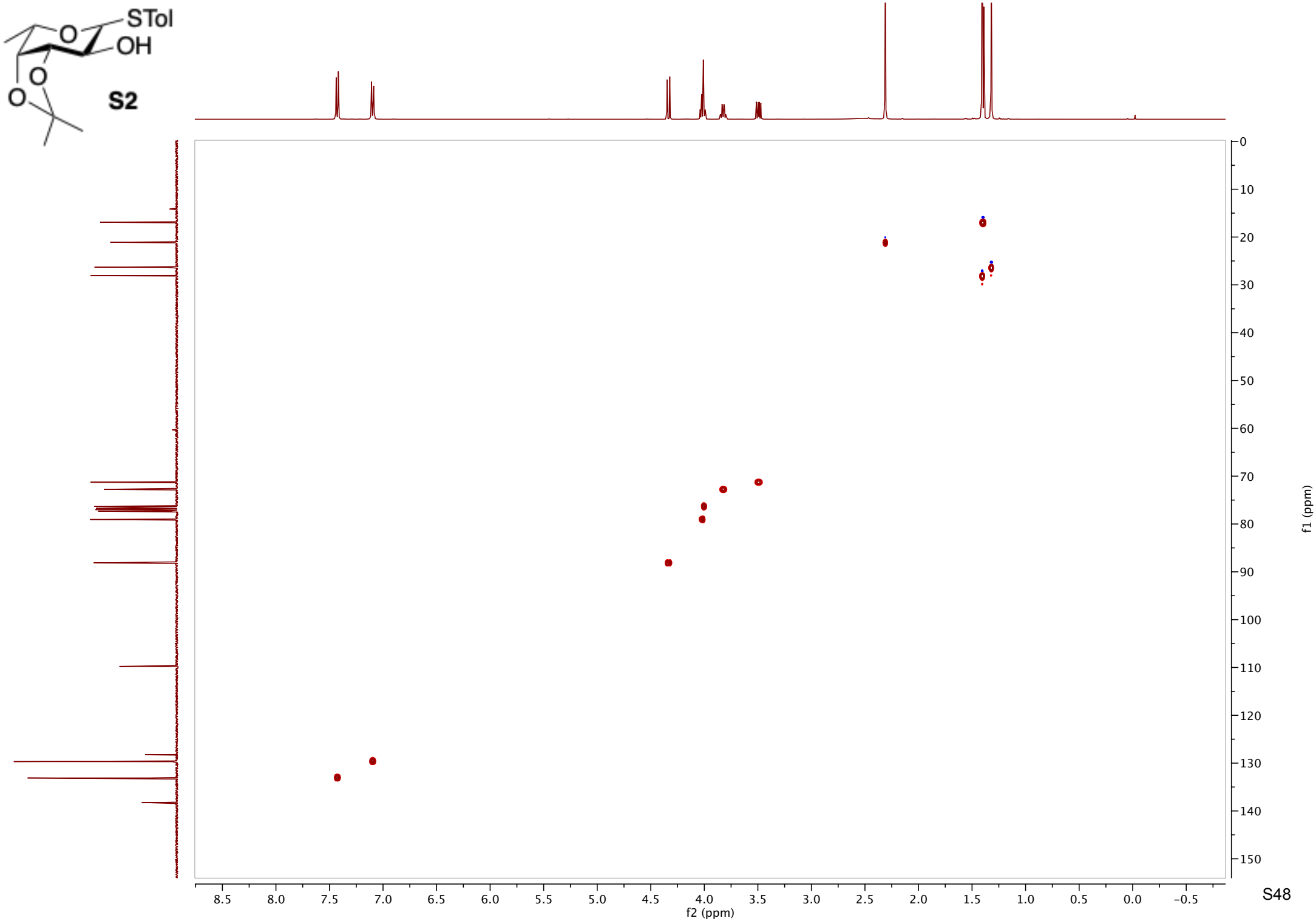
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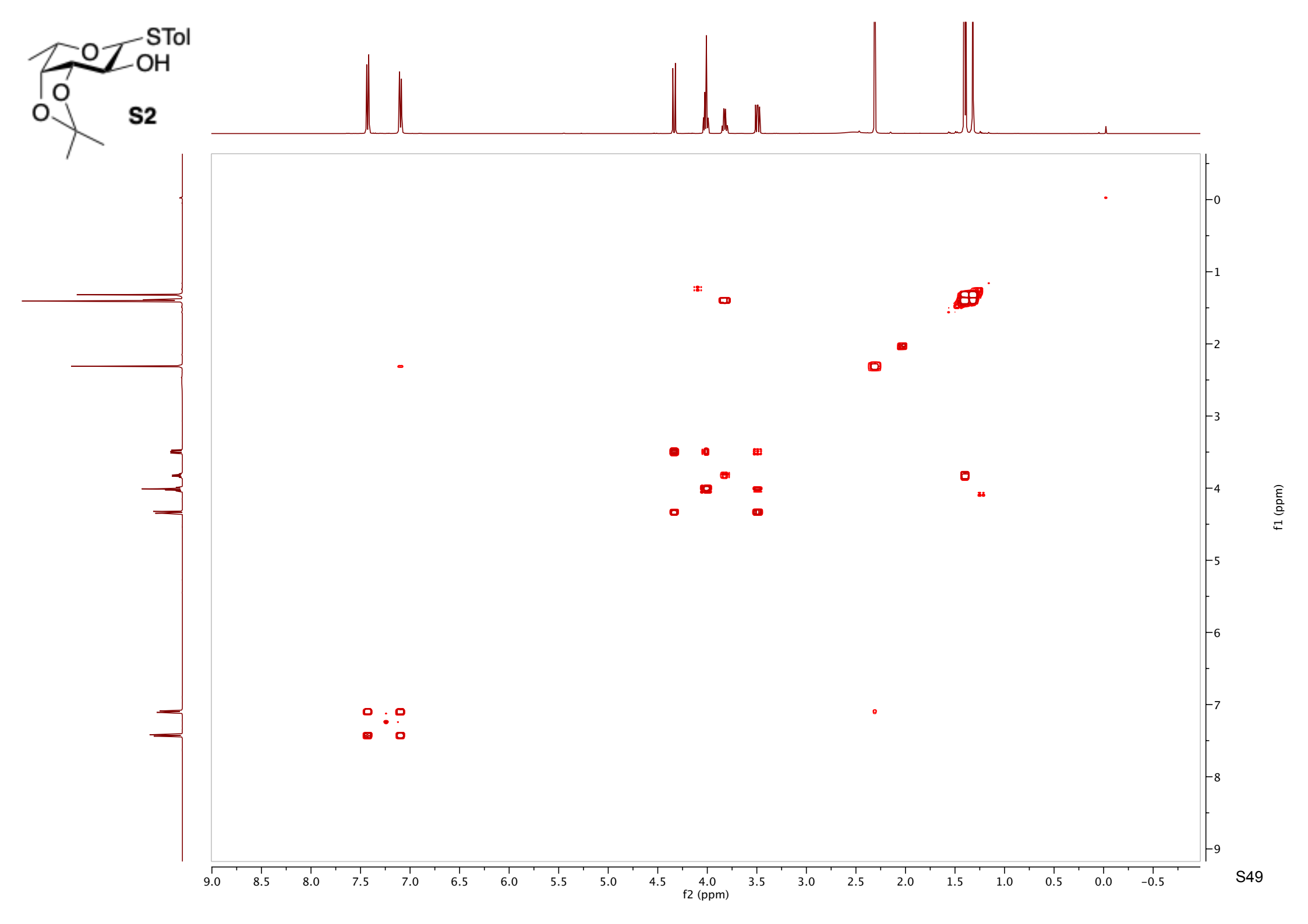
O
S2
f2 (ppm)
f1 (ppm)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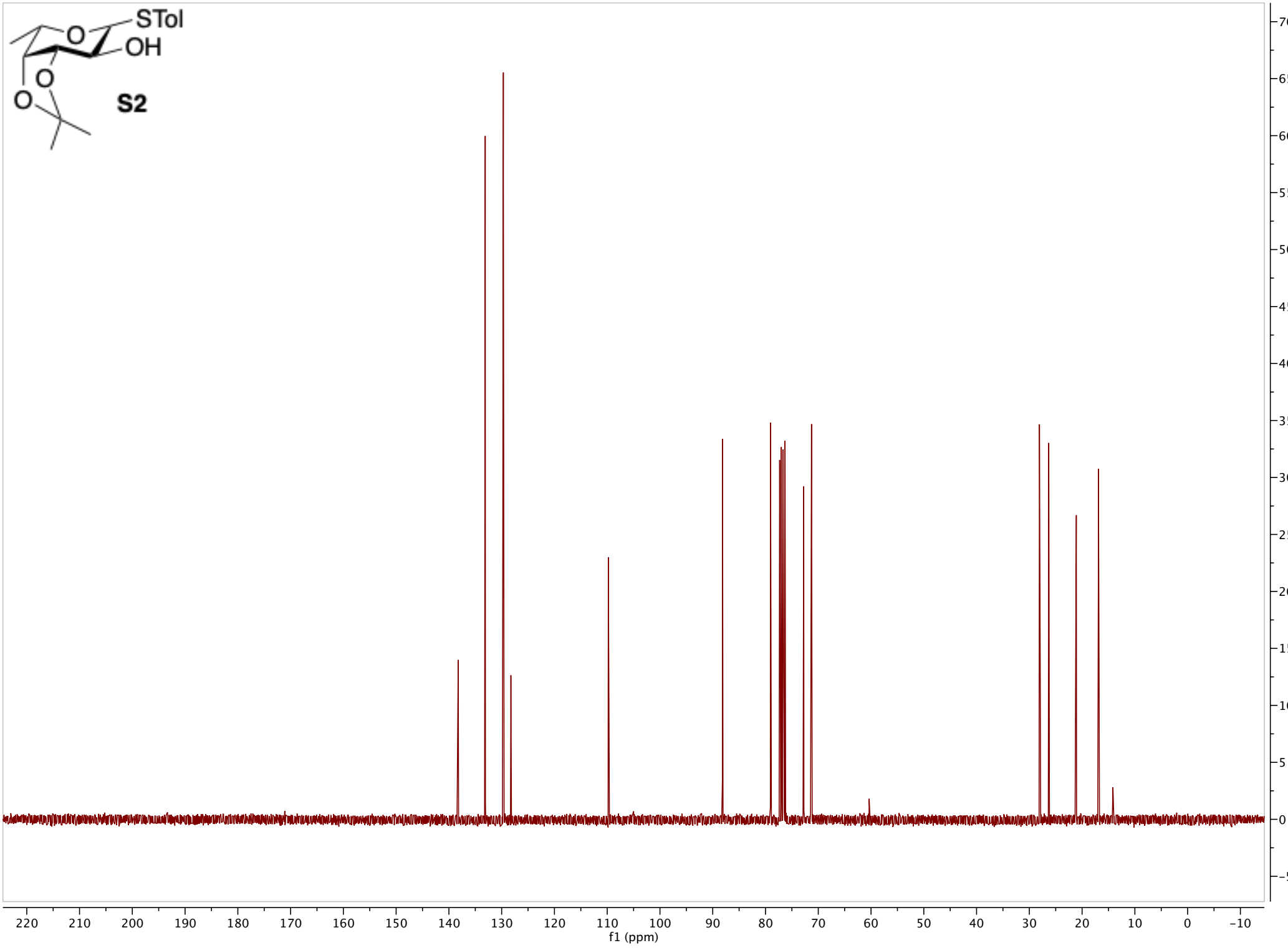
OH
O
O
O
S2
f2 (ppm)
f1 (ppm)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O
O
S2
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55
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45
40
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30
25
20
15
10
5
0
−5
220
210
200
190
180
170
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150
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110
100
90
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60
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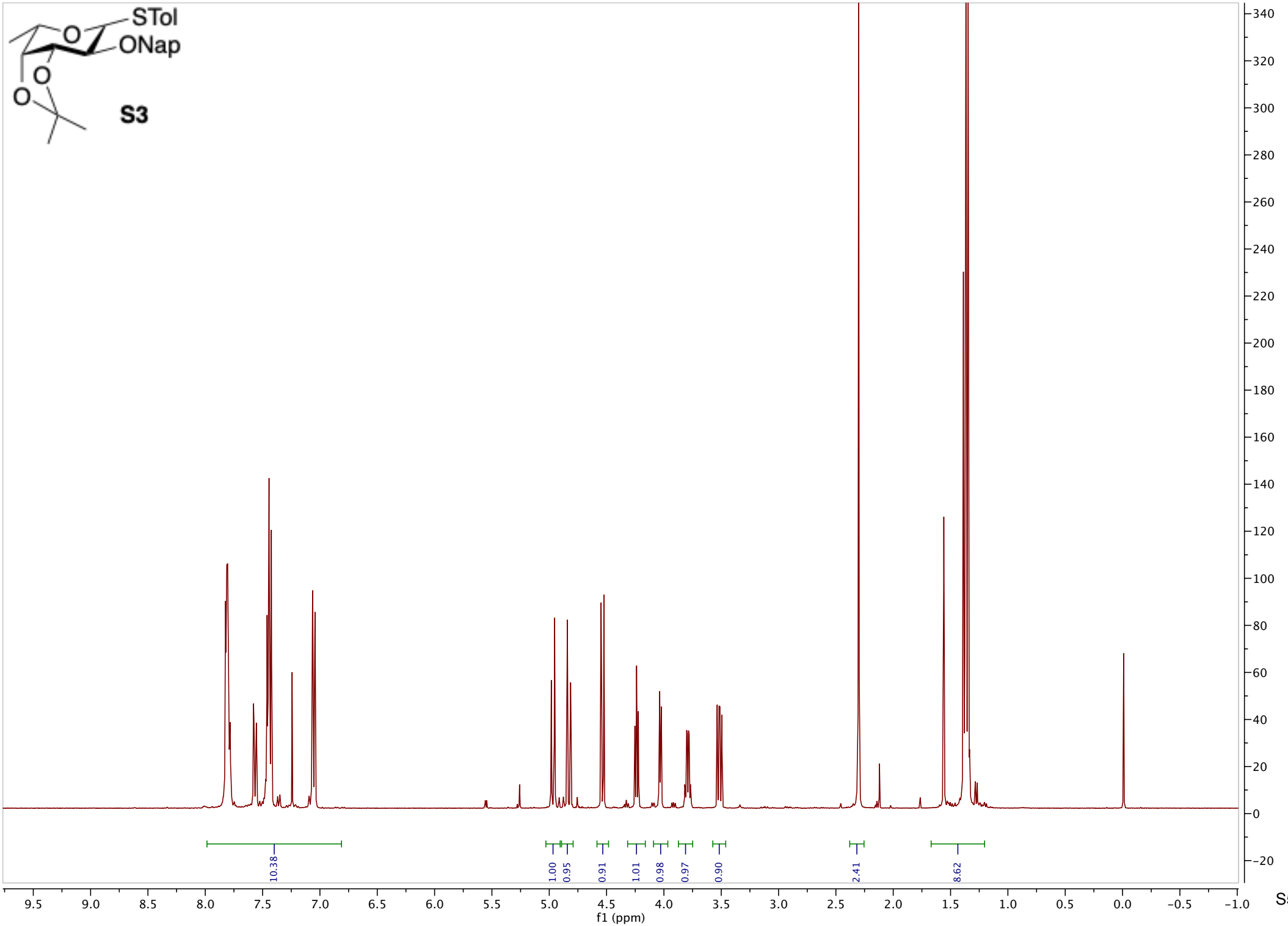
40
30
20
10
0
−10
f1 (ppm)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8.62
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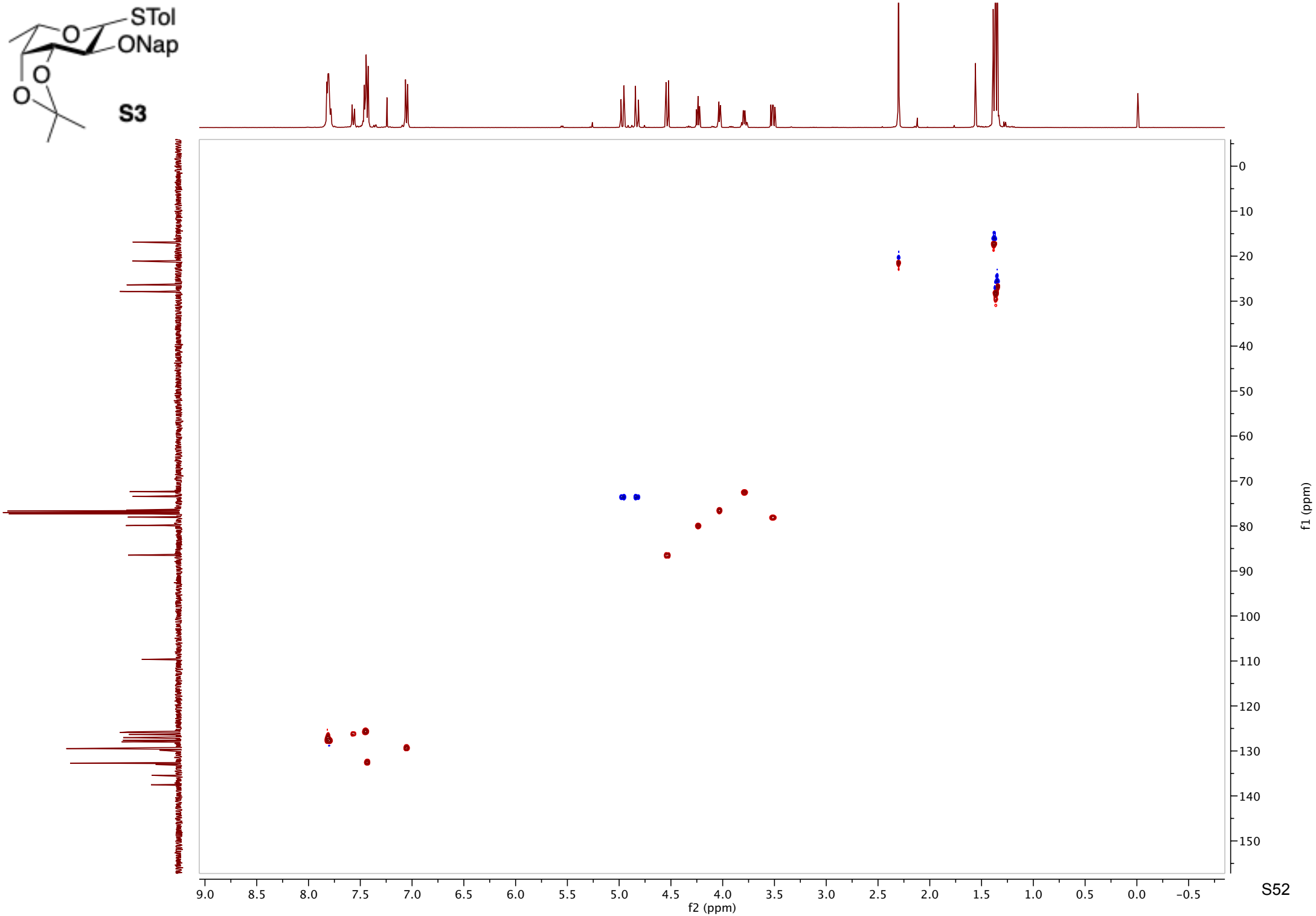
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ONap
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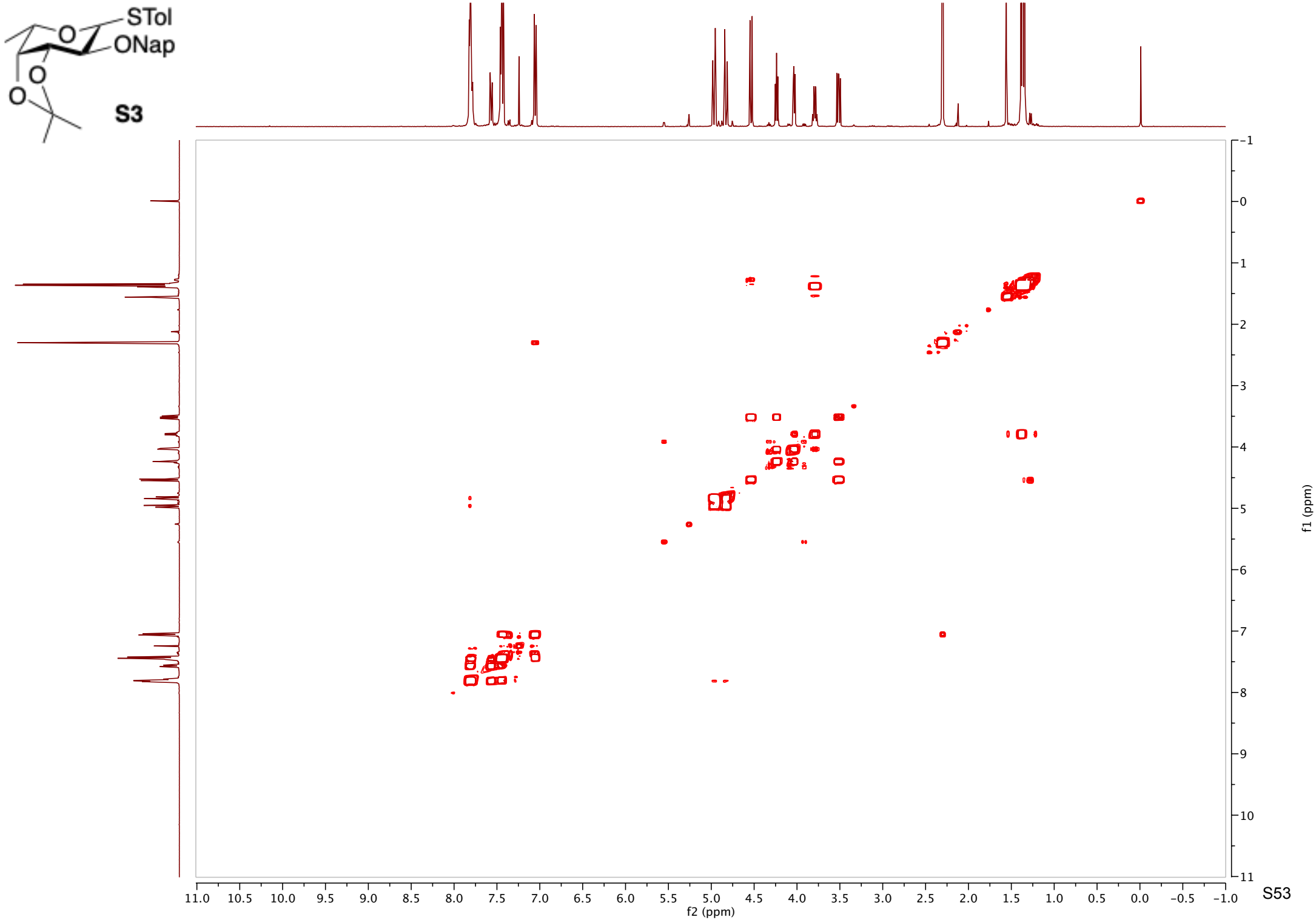
O
O
S3
f2 (ppm)
f1 (ppm)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ONap
O
O
O
S3
f2 (ppm)
f1 (ppm)
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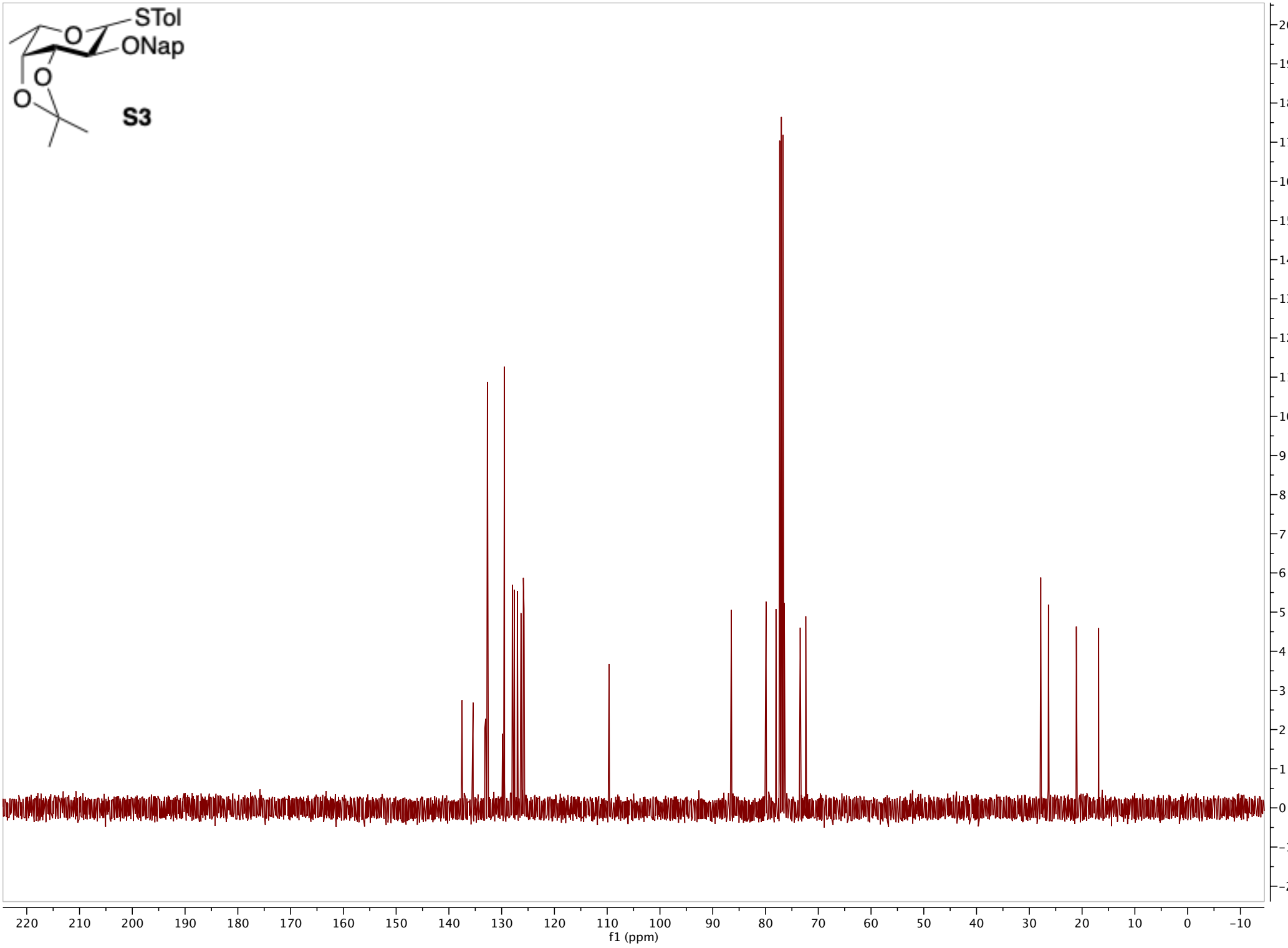
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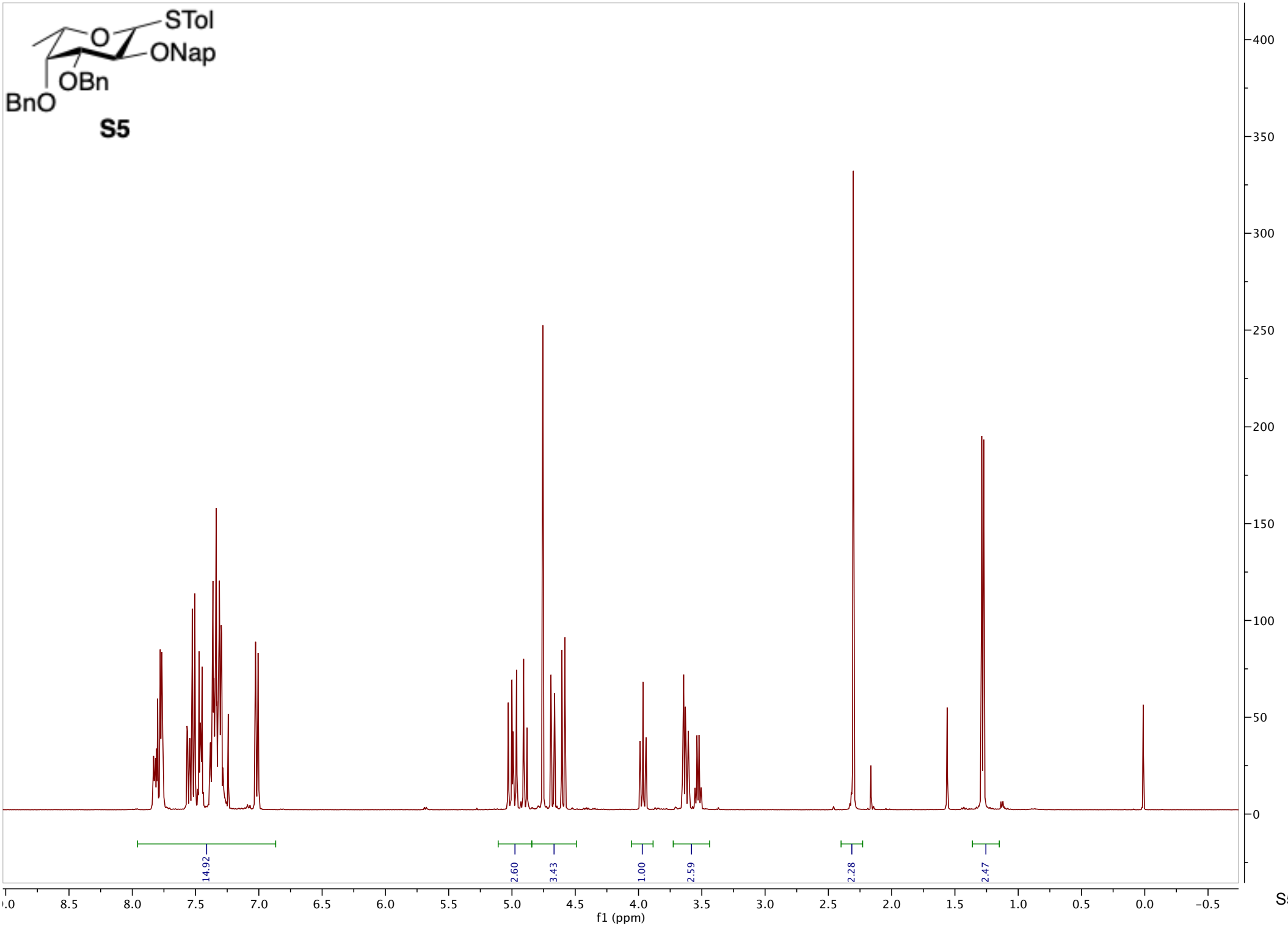
S3
f1 (ppm)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1.00
2.59
2.28
2.47
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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2.0
1.5
1.0
0.5
0.0
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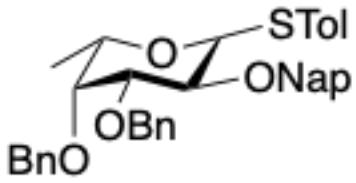
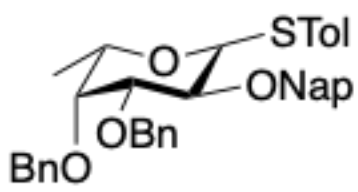
f1 (ppm)



S5



S5

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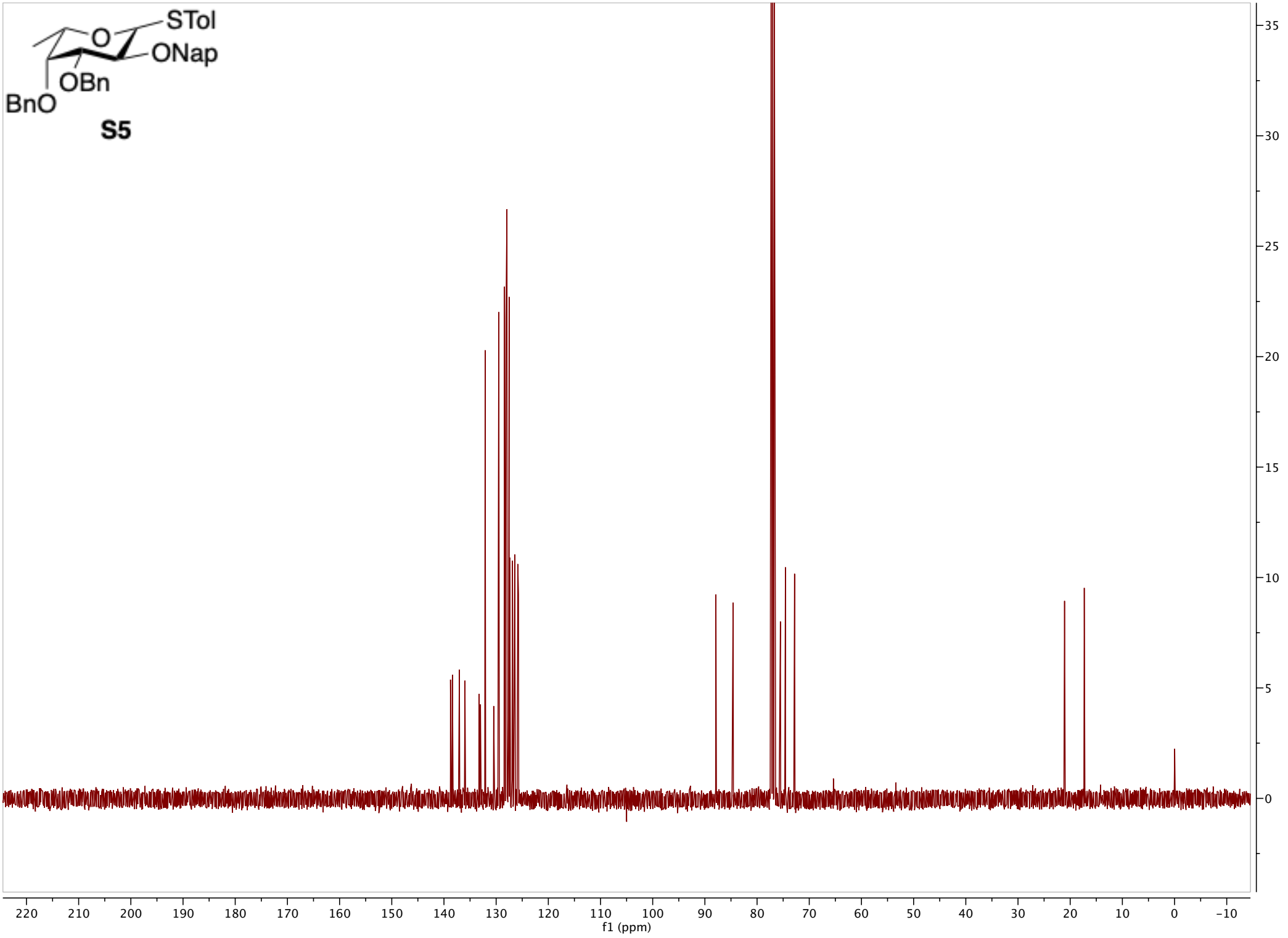
f1 (ppm)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O
ONap
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BnO
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35
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25
20
15
10
5
0
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190
180
170
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150
140
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120
110
100
90
80
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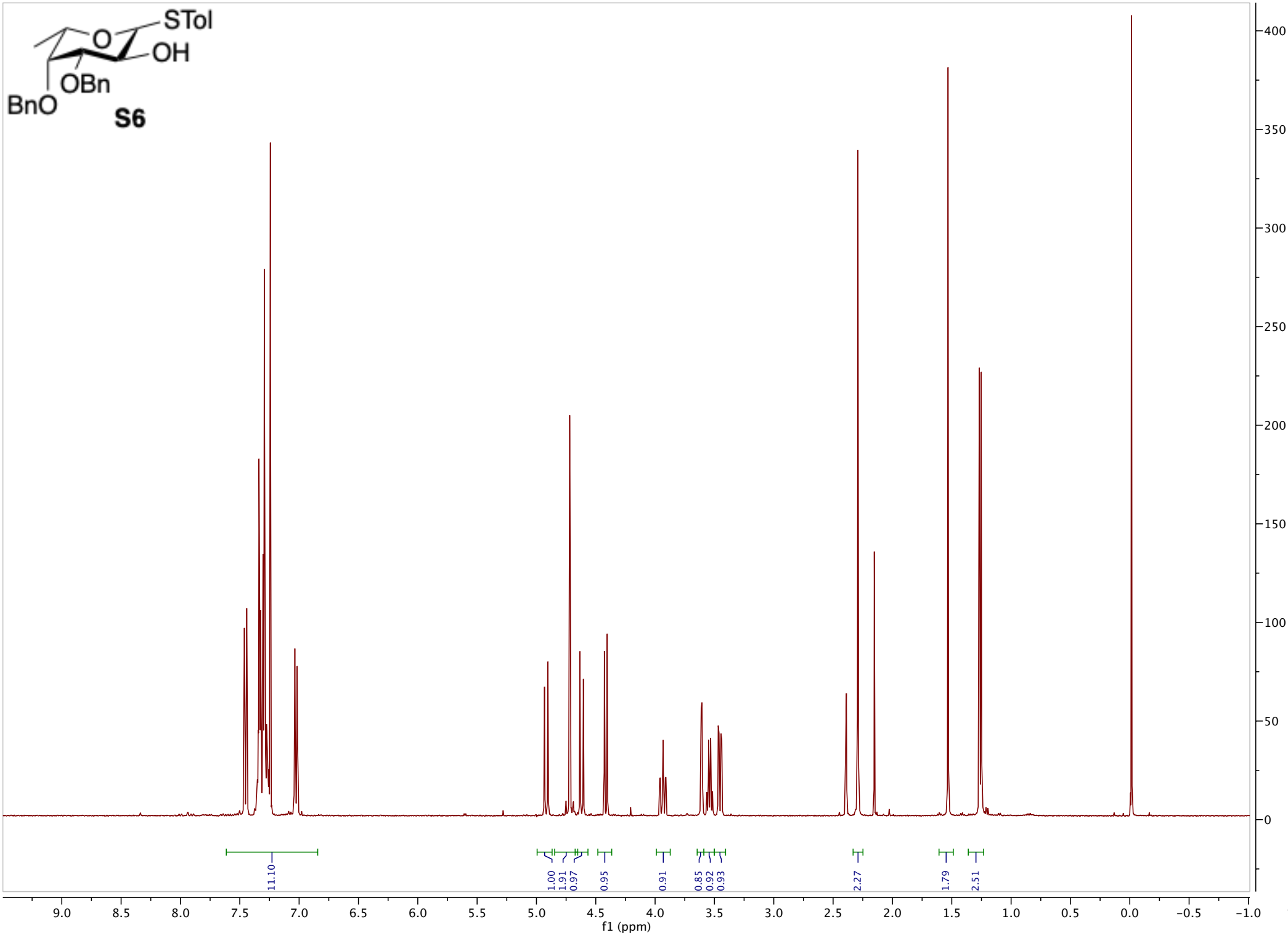
60
50
40
30
20
10
0
−10
f1 (ppm)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BnO
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0.92
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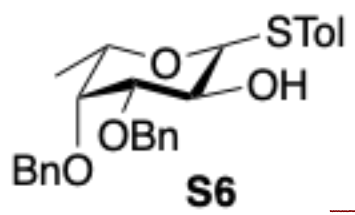
2.51
f1 (ppm)



S6

f2 (ppm)

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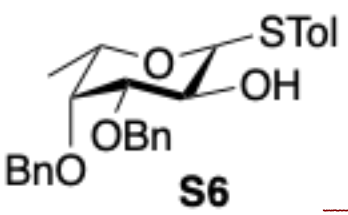
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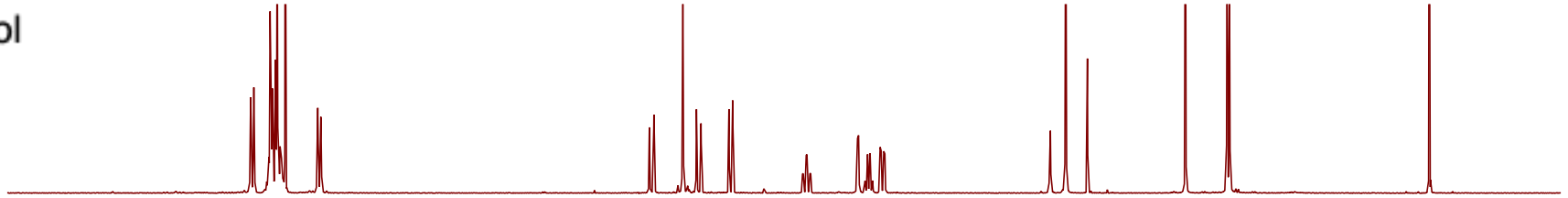
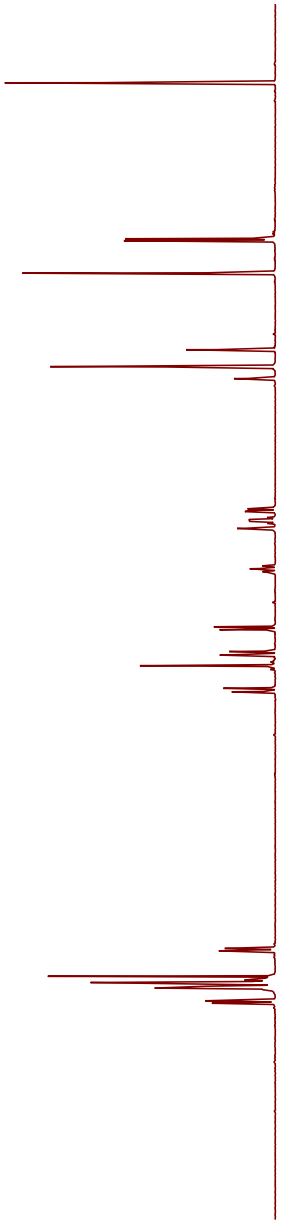
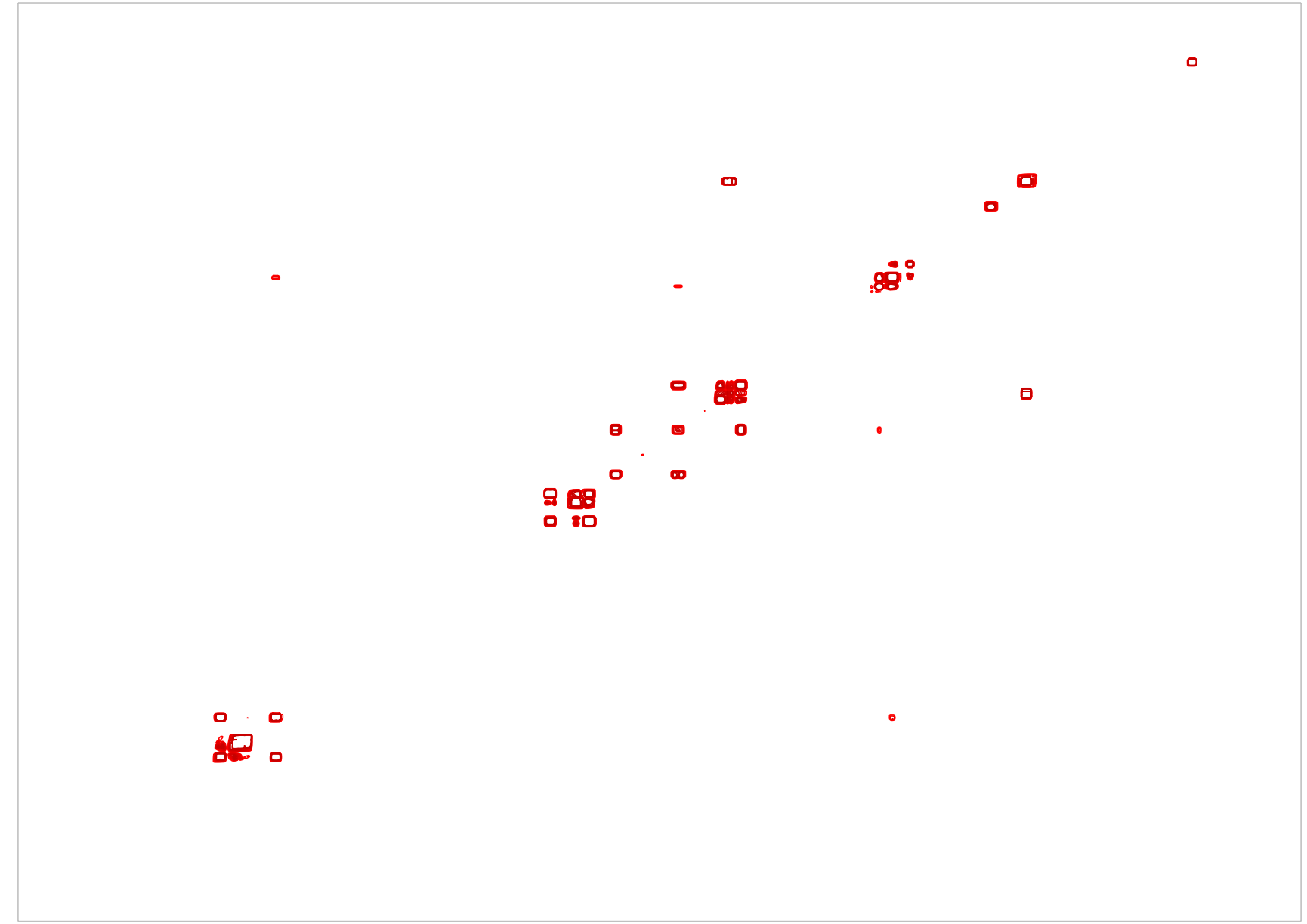
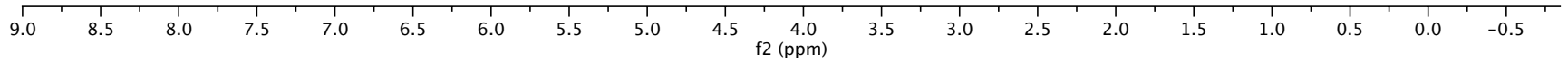
O
OH
OBn
BnO

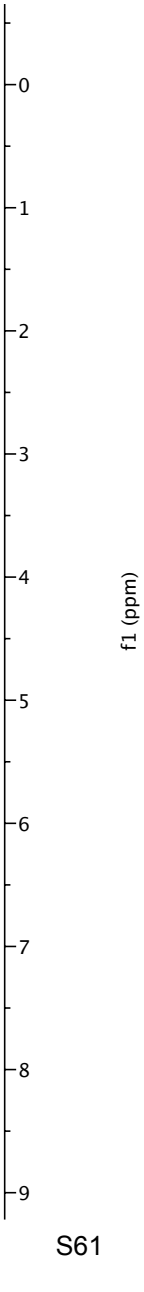
S6

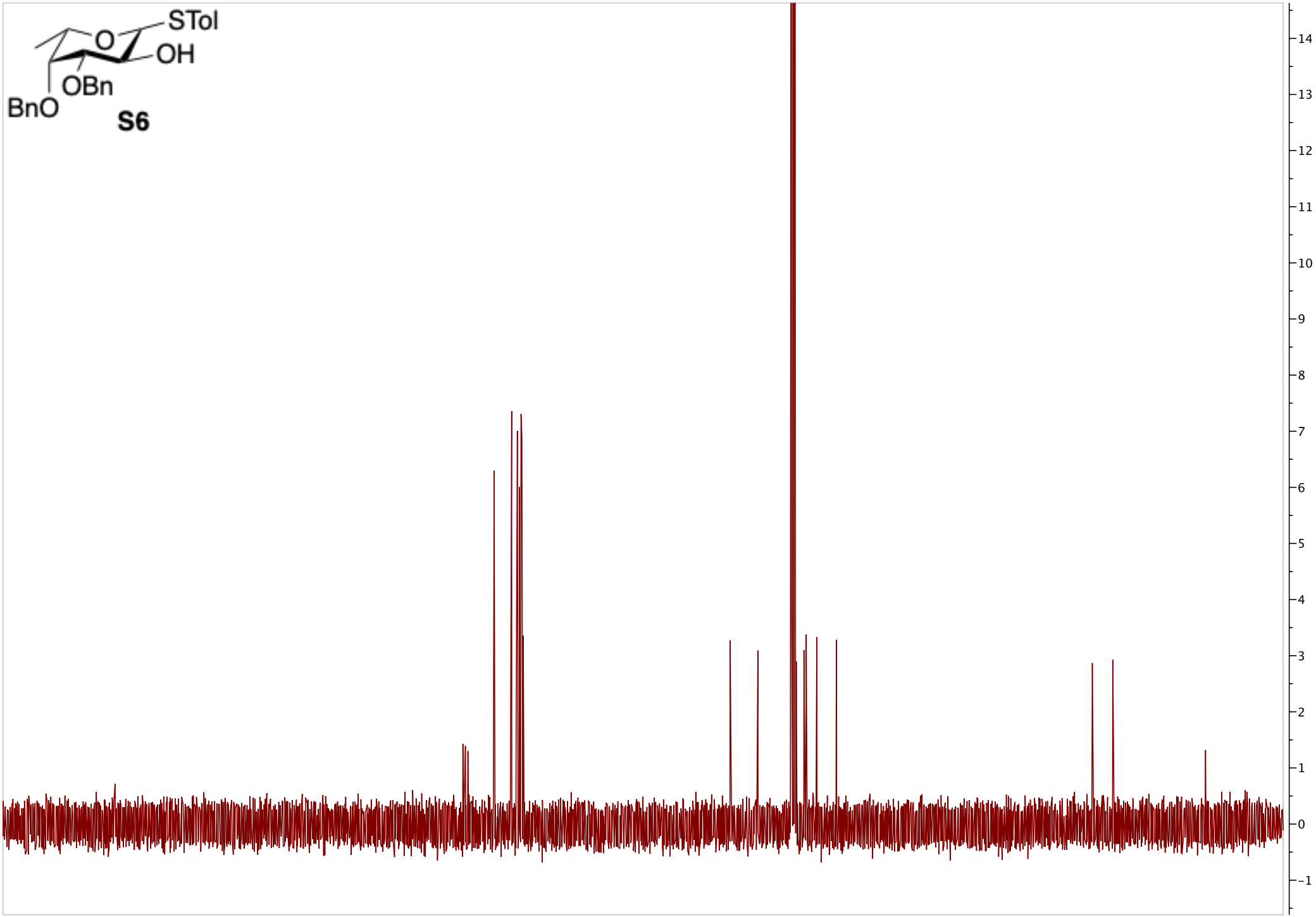


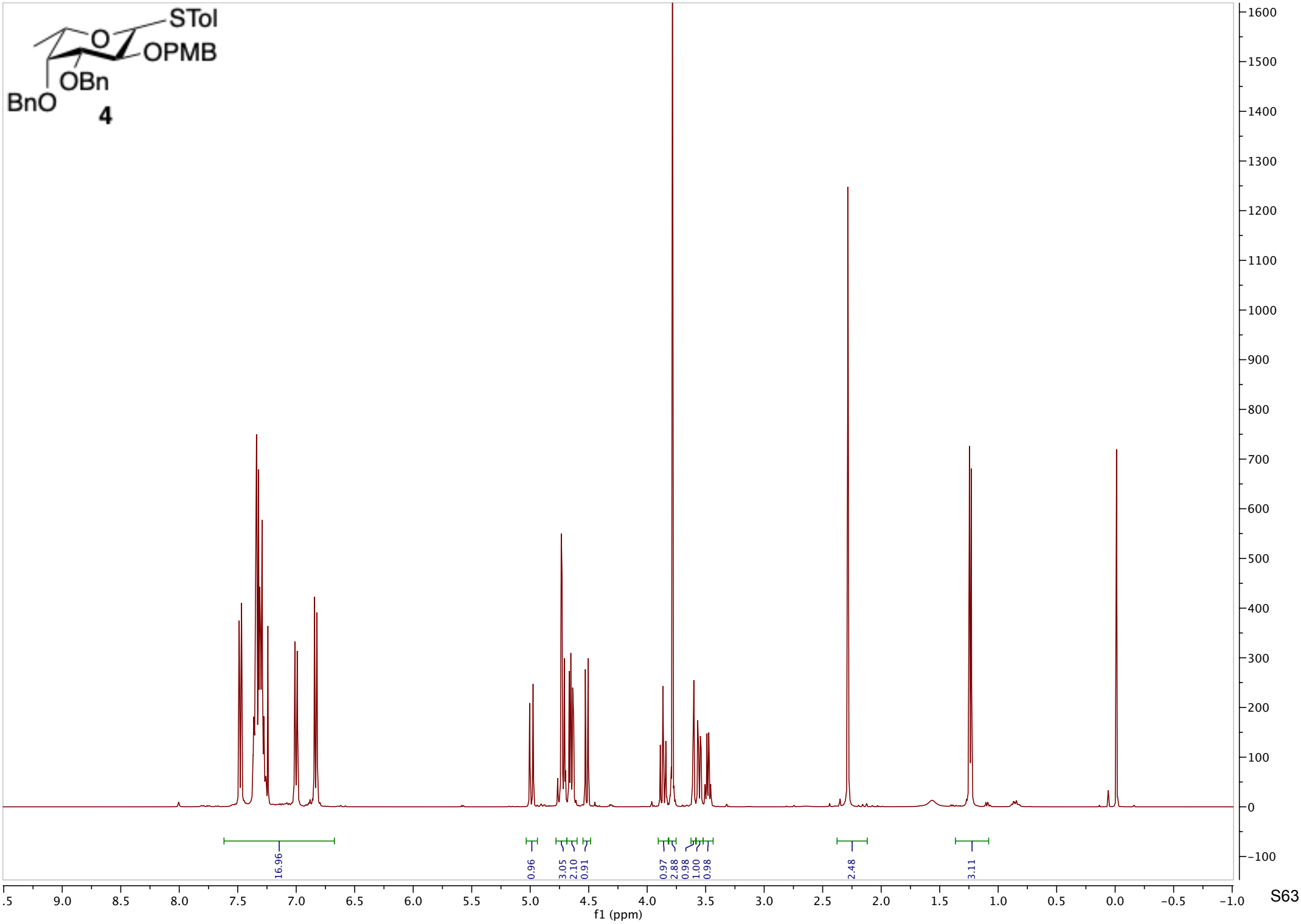


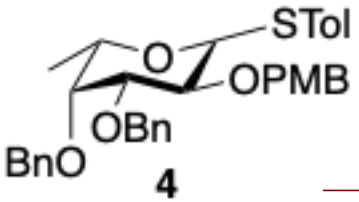


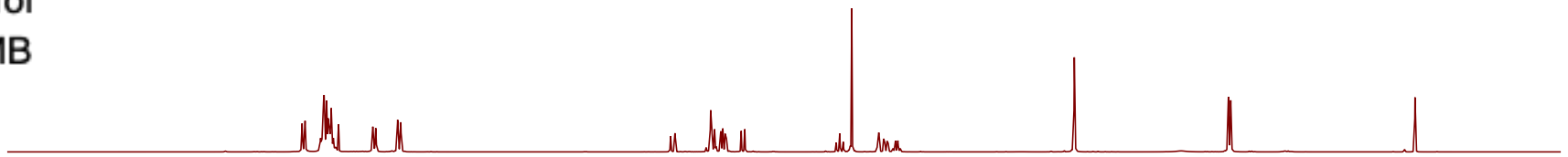

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

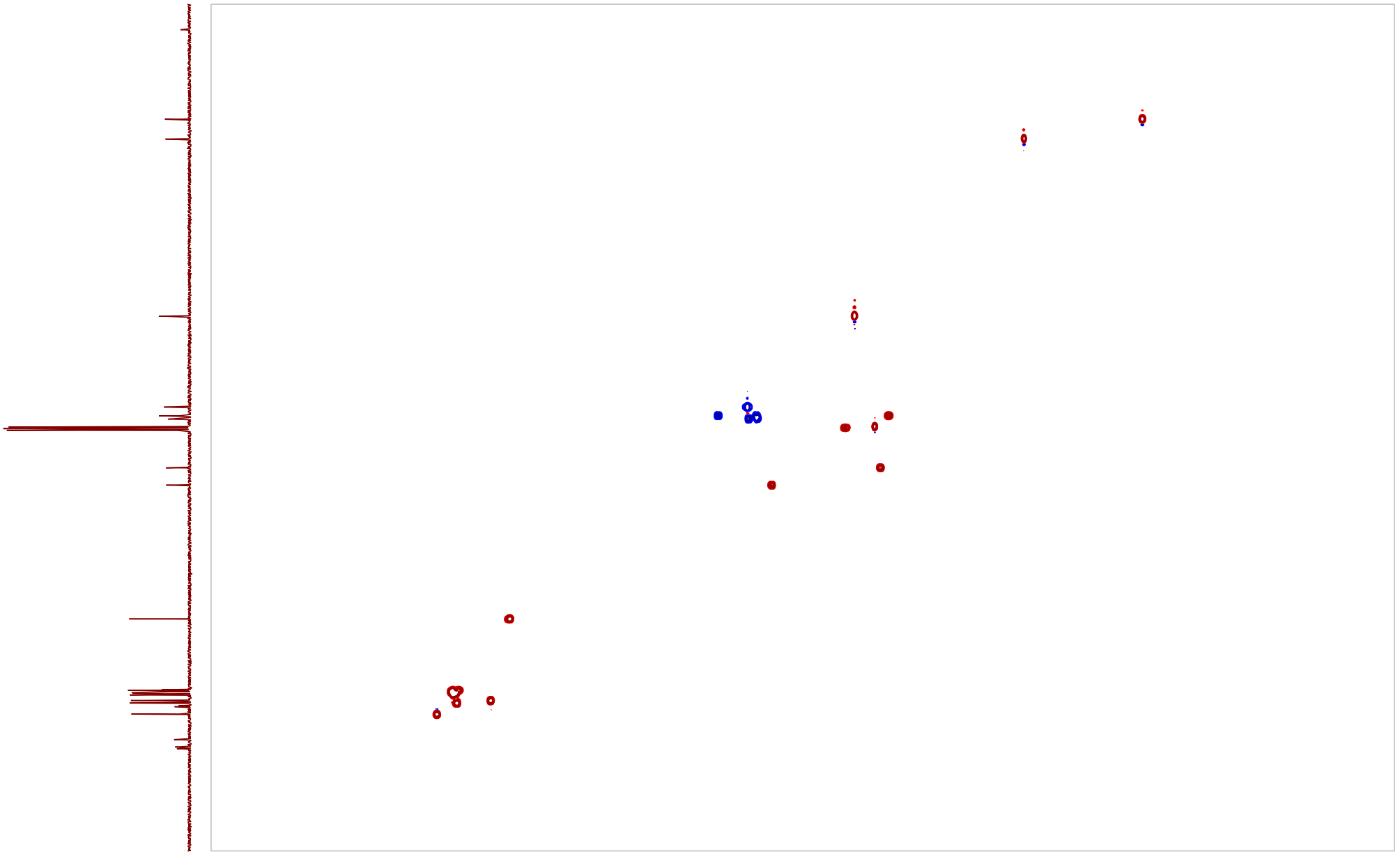

0
1
2
3
4
5
6
7
8
9
f1 (ppm)

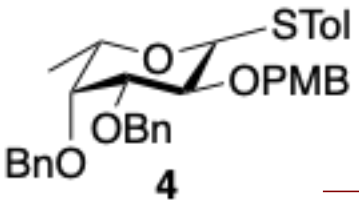

STol
O
OH
OBn
BnO
S6
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

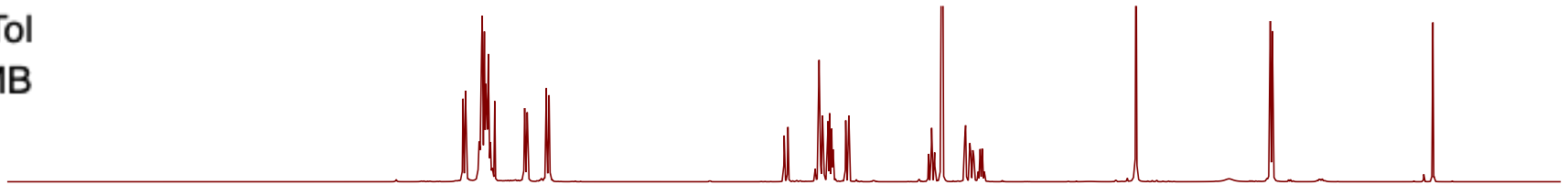

STol
O
OPMB
OBn
BnO
4
16.96
0.96
3.05
2.10
0.91
0.97
2.88
0.98
1.00
0.98
2.48
3.11
f1 (ppm)

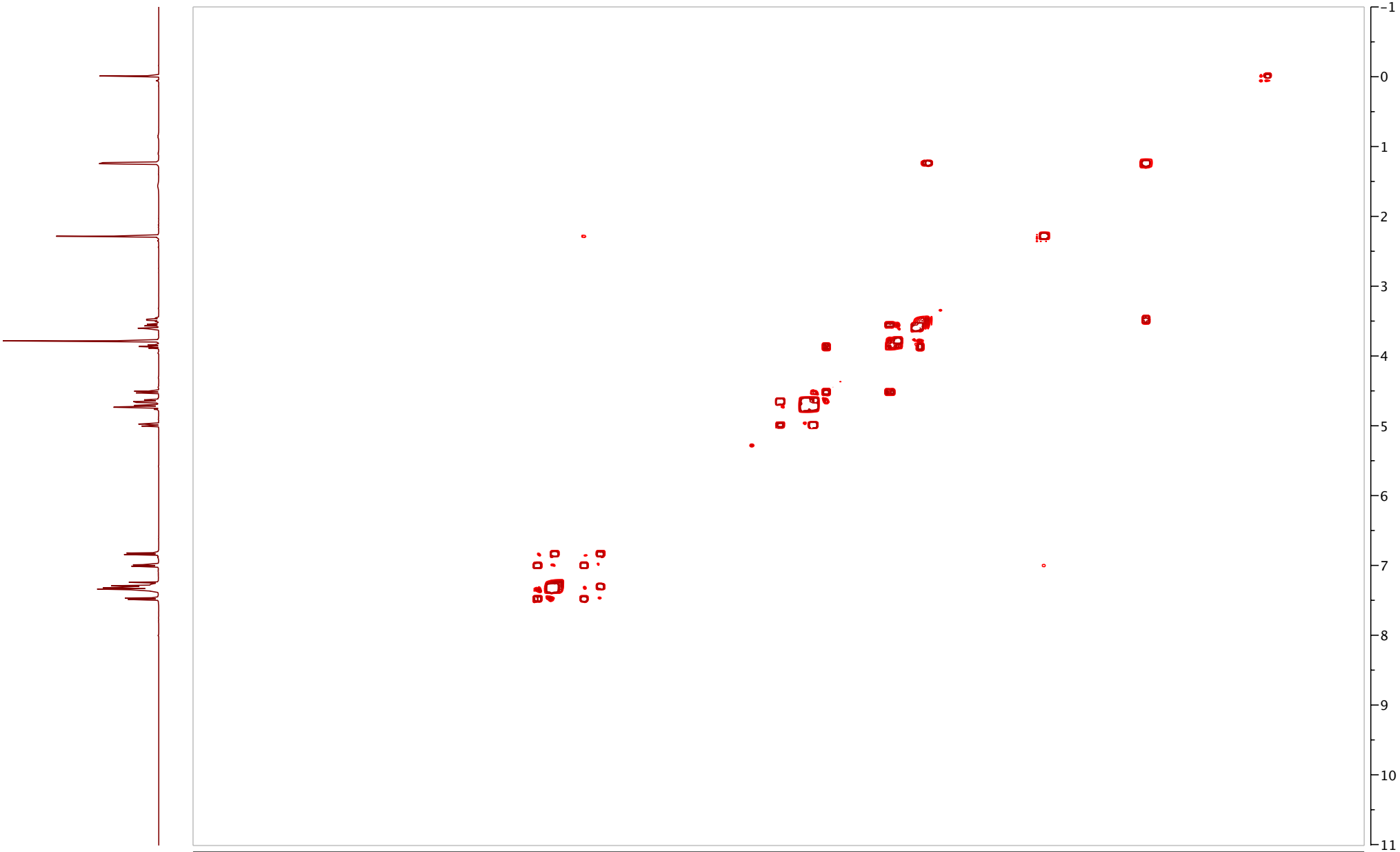

STol
O
OPMB
OBn
BnO
4

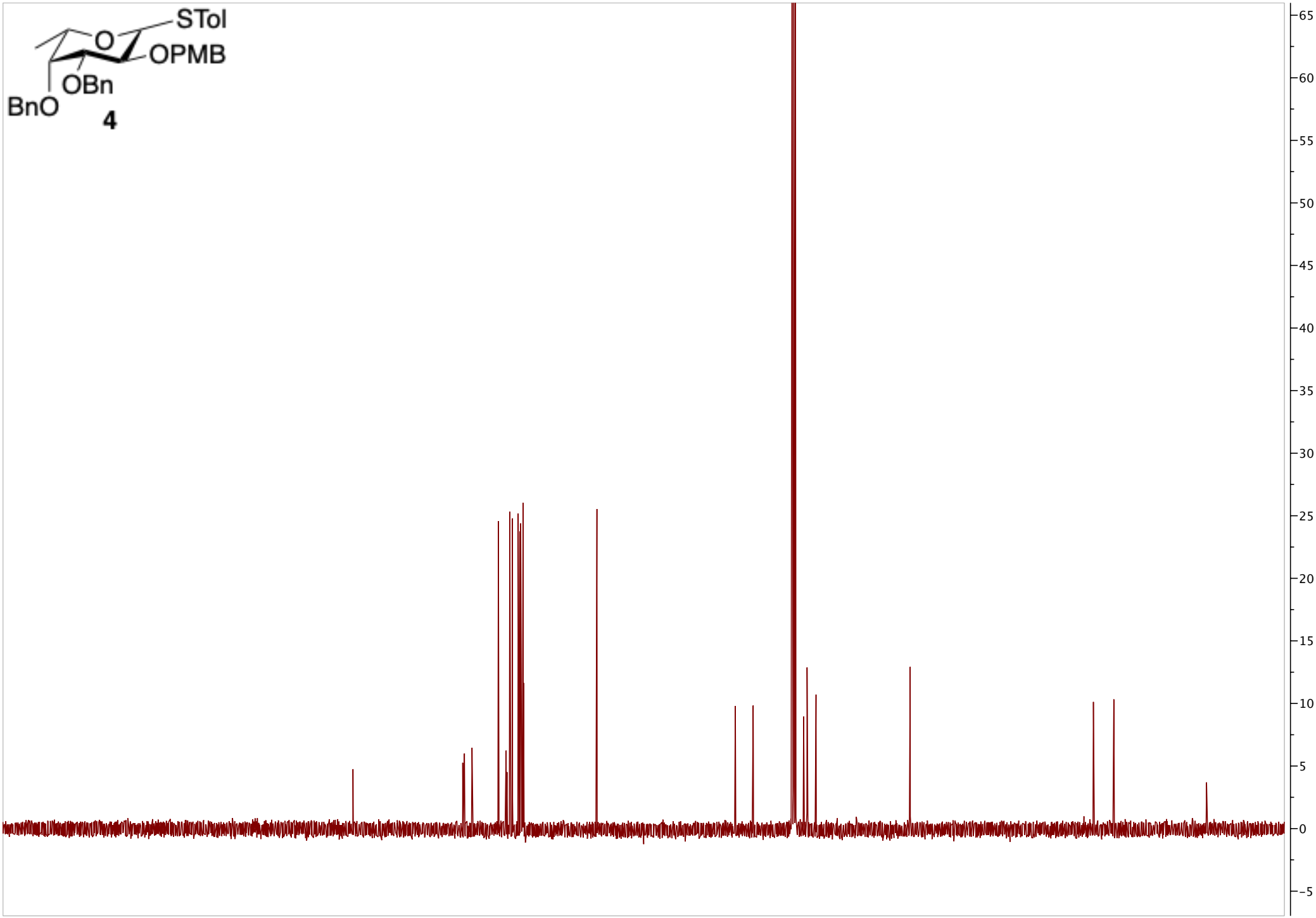


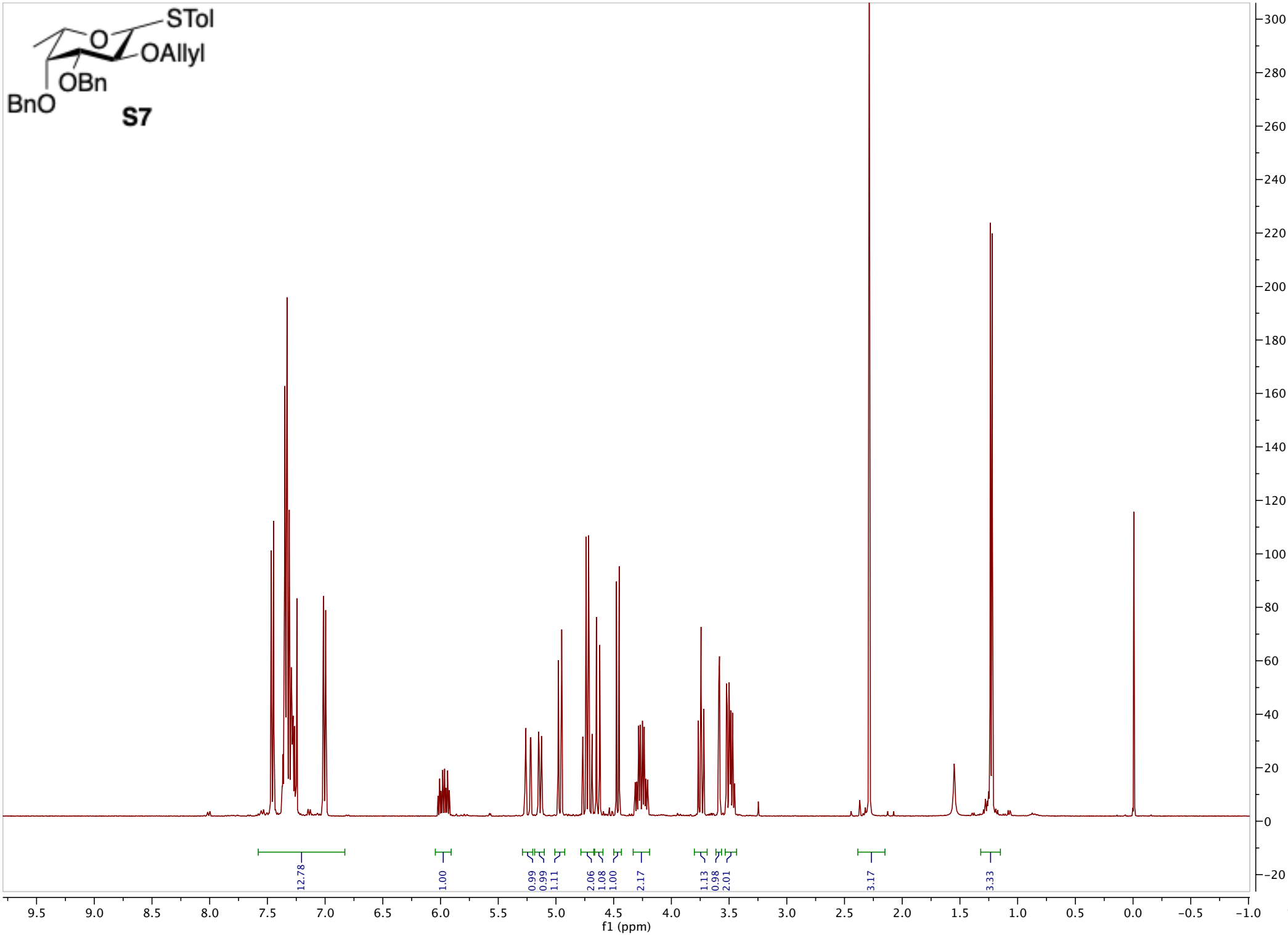

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

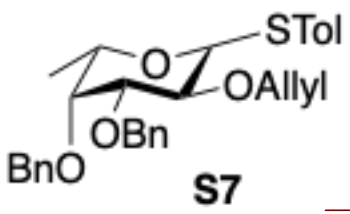

STol
O
OPMB
OBn
BnO
4



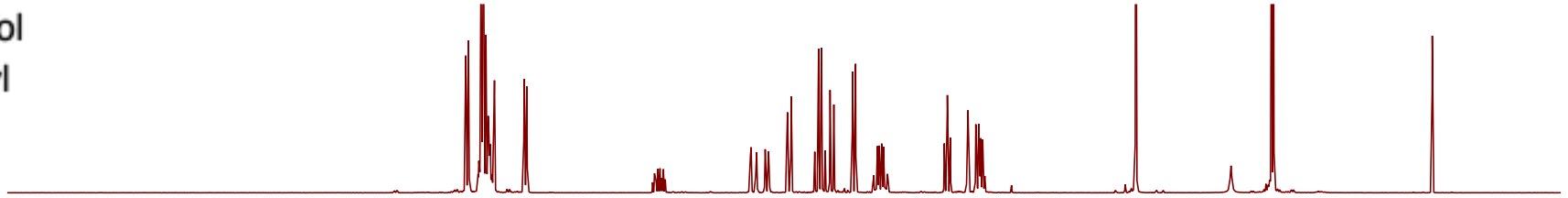

f1 (ppm)
f2 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
-1 0 1 2 3 4 5 6 7 8 9 10 11

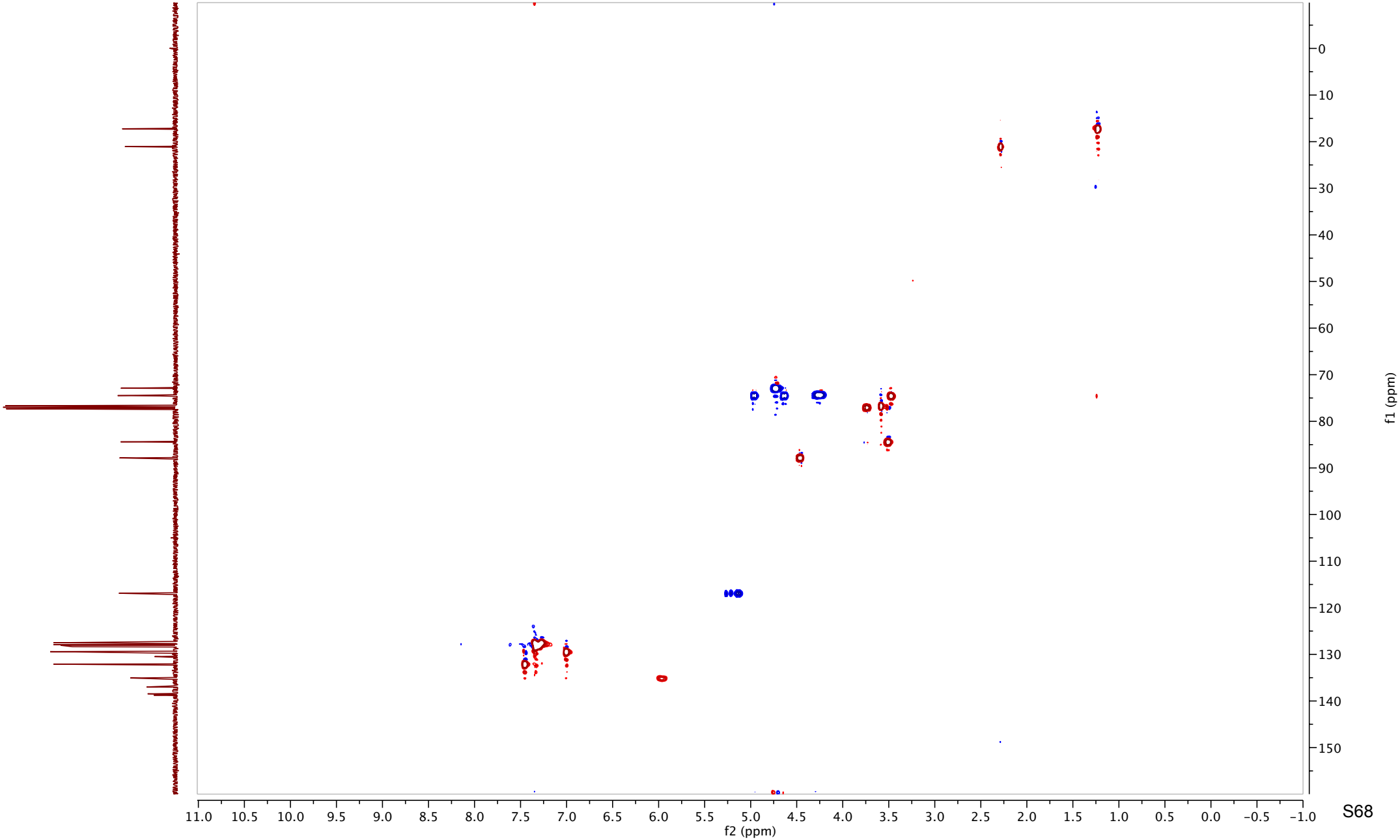

STol
O
OPMB
OBn
BnO
4
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

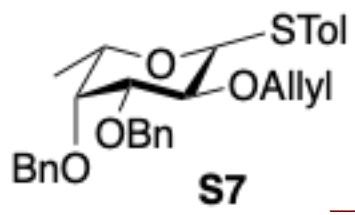

STol
O
OAllyl
OBn
BnO
S7
12.78
1.00
0.99
0.99
1.11
2.06
1.08
1.00
2.17
1.13
0.98
2.01
3.17
3.33
f1 (ppm)


STol
O
OAllyl
OBn
BnO

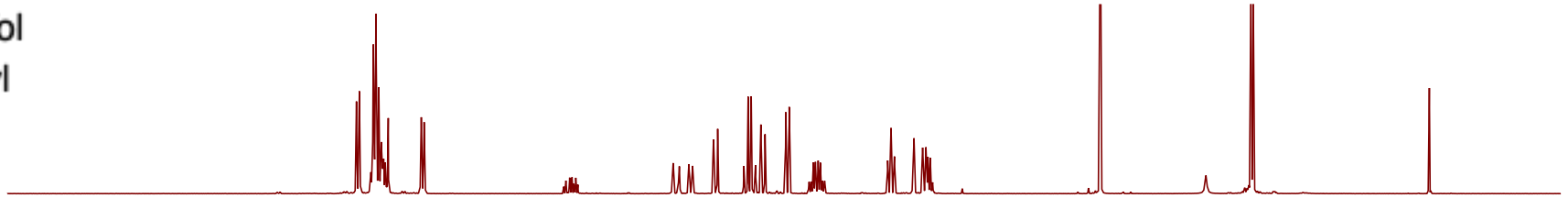
S7

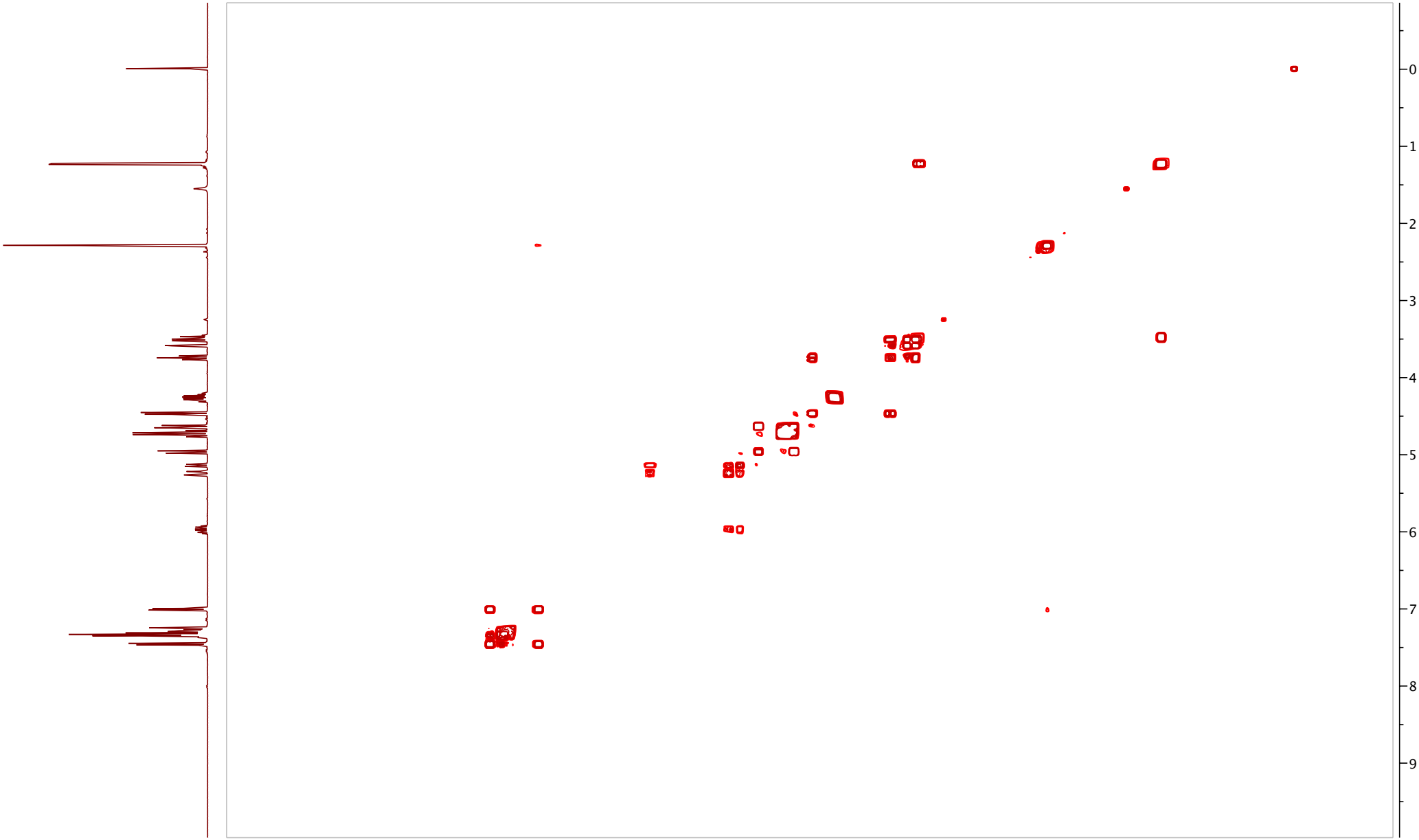


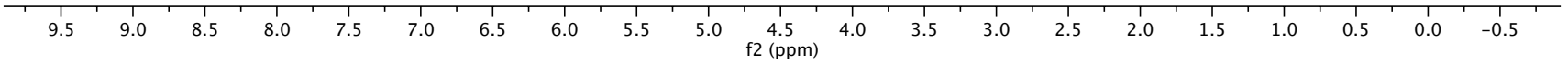

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)

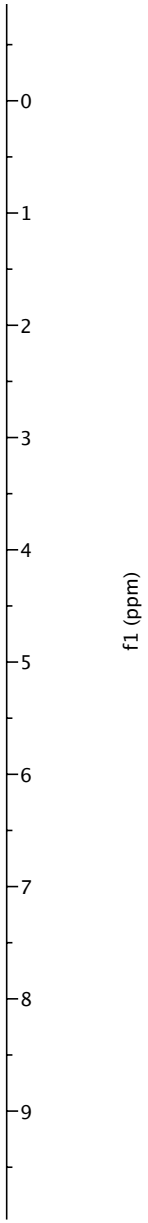

STol
O
OAllyl
OBn
BnO

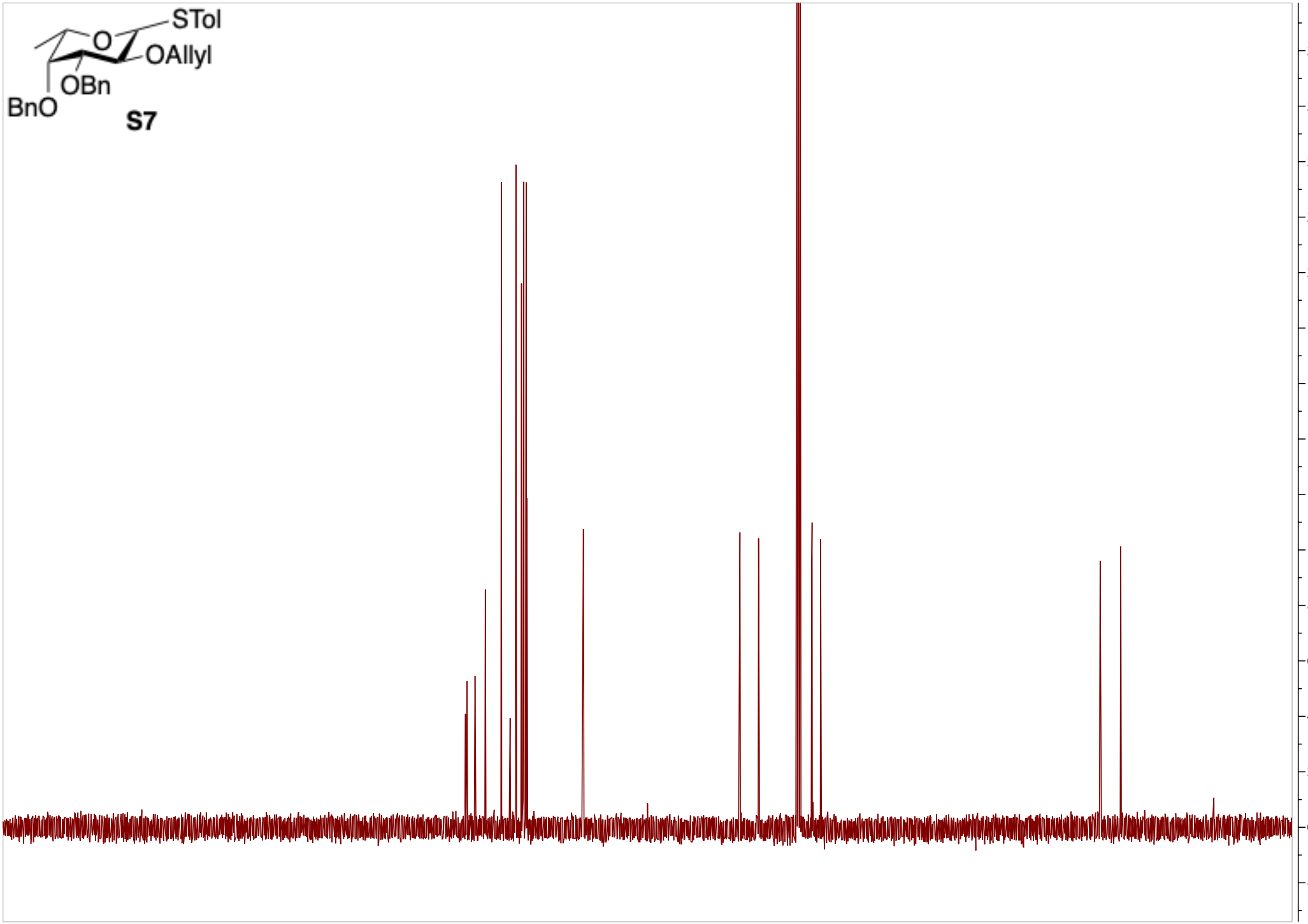
S7

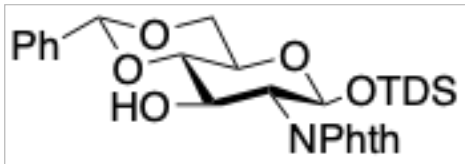





9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

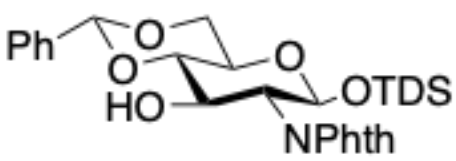

0
1
2
3
4
5
6
7
8
9
f1 (ppm)


STol
O
OAllyl
OBn
BnO
S7
28
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)

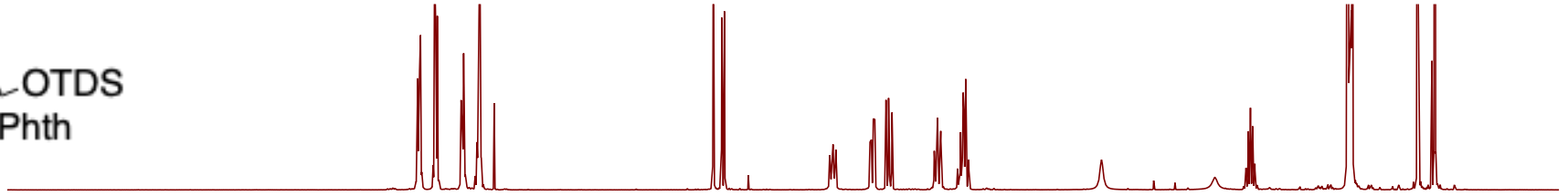

Ph
O
O
O
HO
OTDS
NPhth

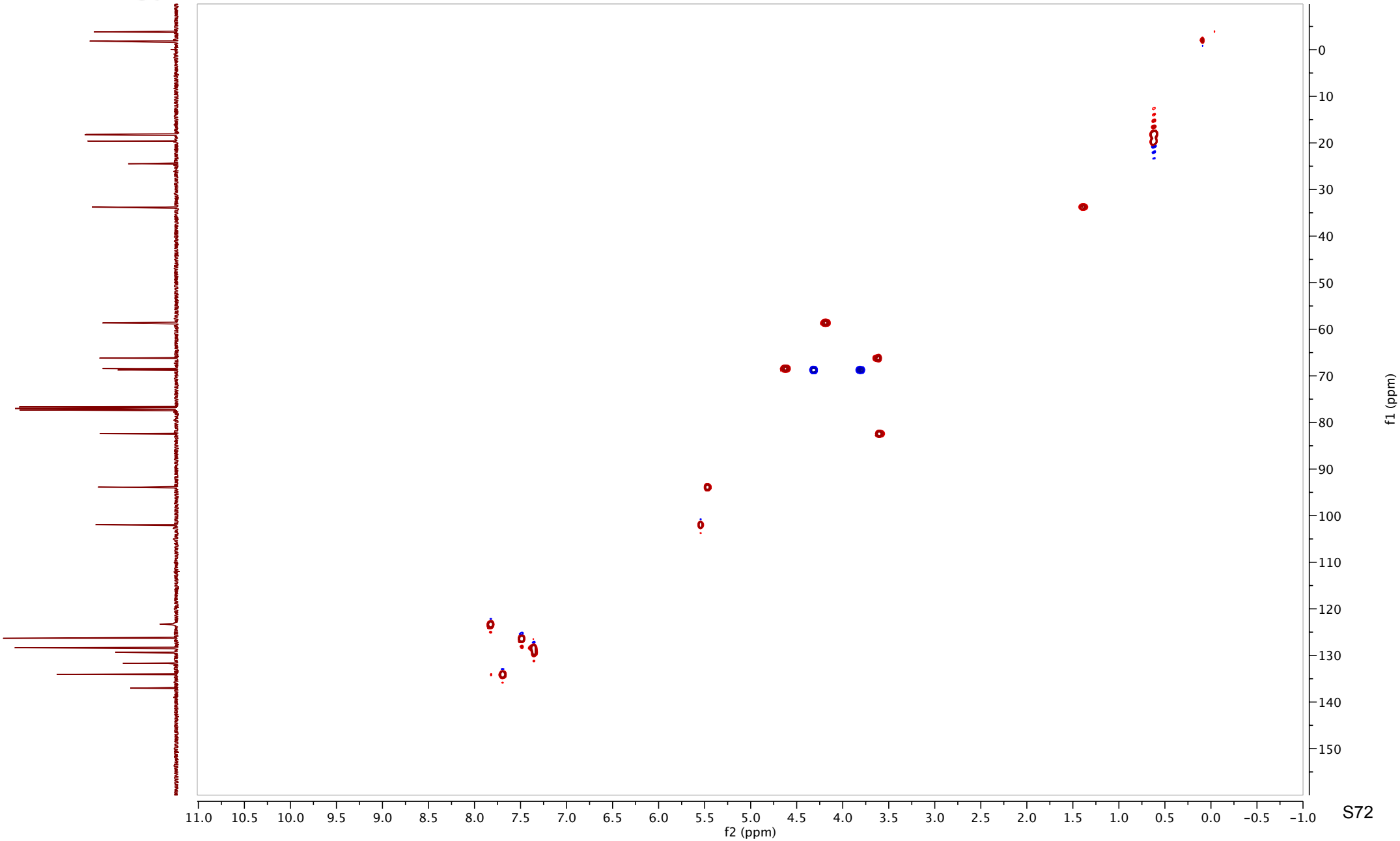
S9

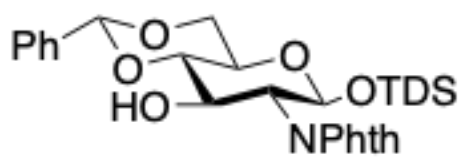
8.57
1.00
0.94
1.10
1.04
1.06
1.01
1.90
1.22
9.67
5.31
f1 (ppm)


Ph
O
O
O
HO
OTDS
NPhth

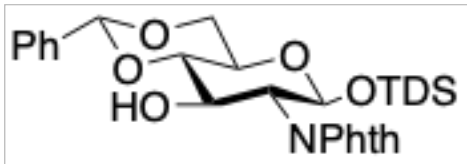
S9




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)

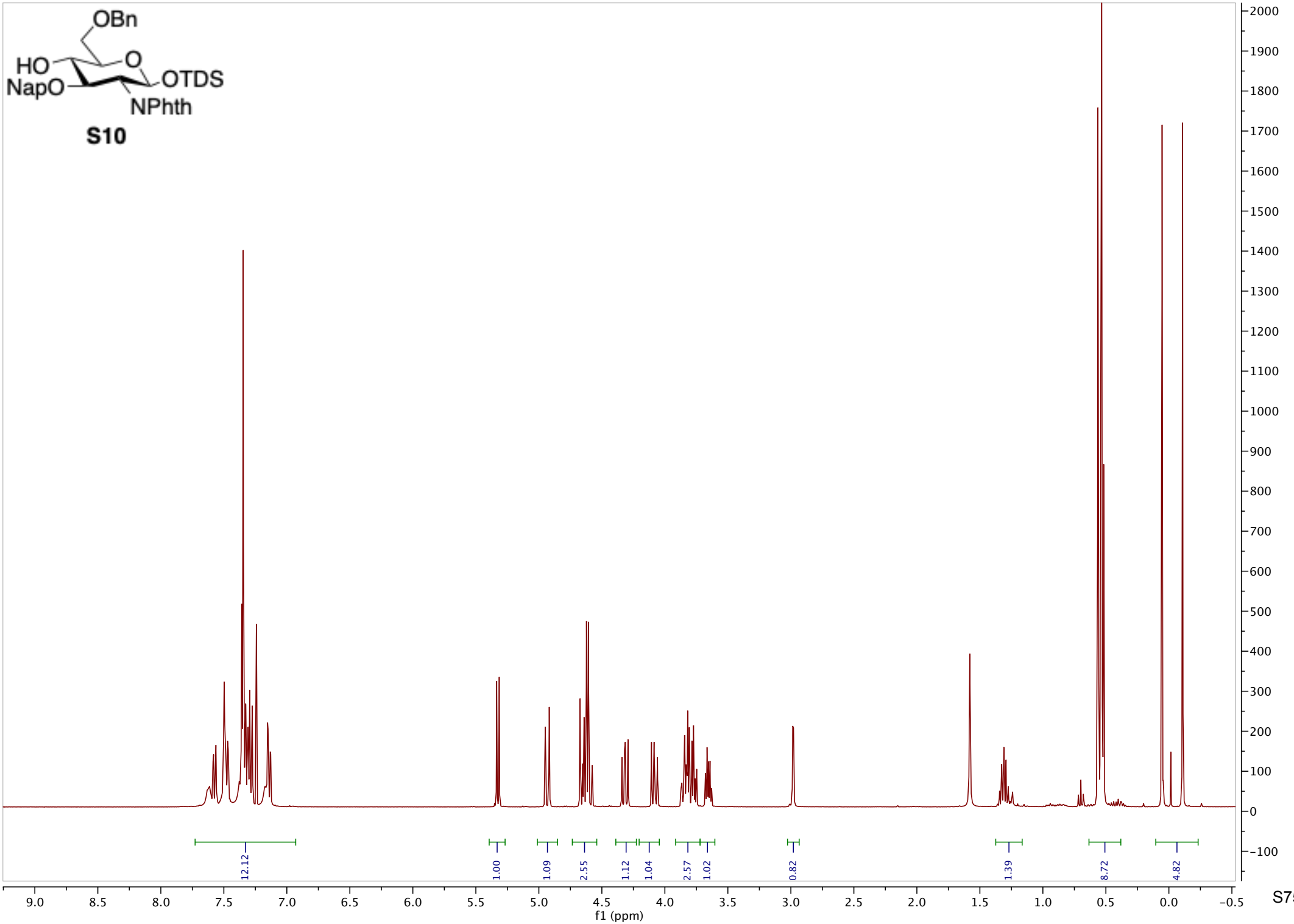


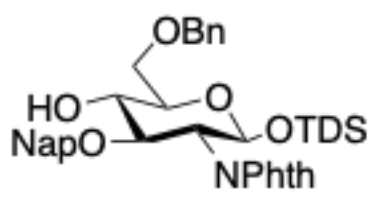
S9


Ph
O
O
O
HO
OTDS
NPhth

S9

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)

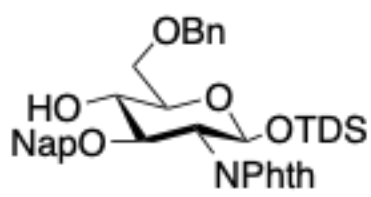

OBn
HO
O
NapO
OTDS
NPhth
S10
12.12
1.00
1.09
2.55
1.12
1.04
2.57
1.02
0.82
1.39
8.72
4.82
f1 (ppm)



S10

f2 (ppm)

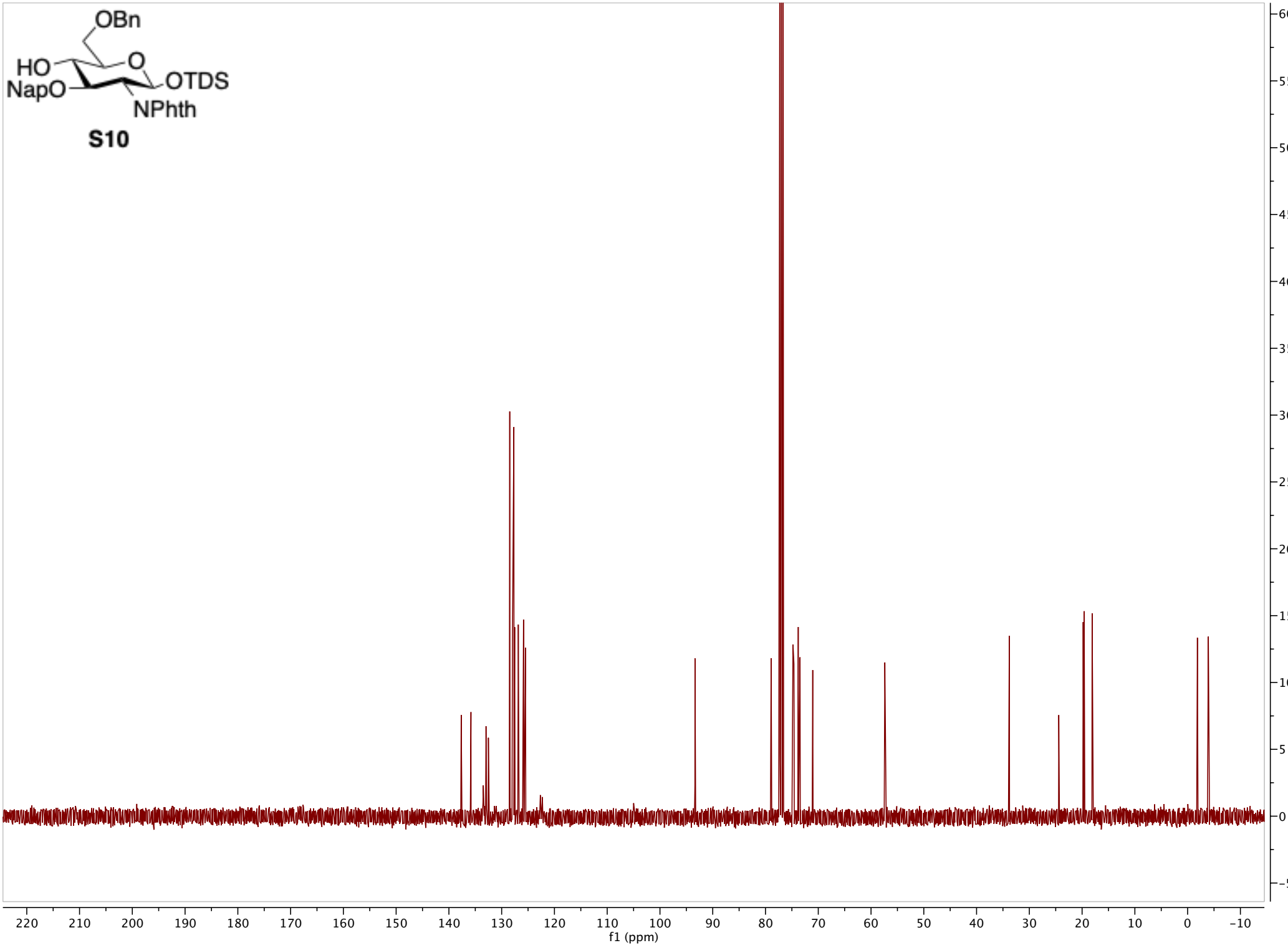
f1 (ppm)

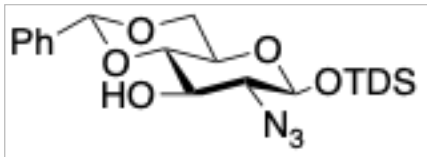


S10

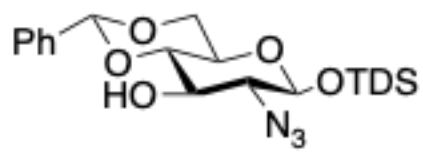
f2 (ppm)

f1 (ppm)

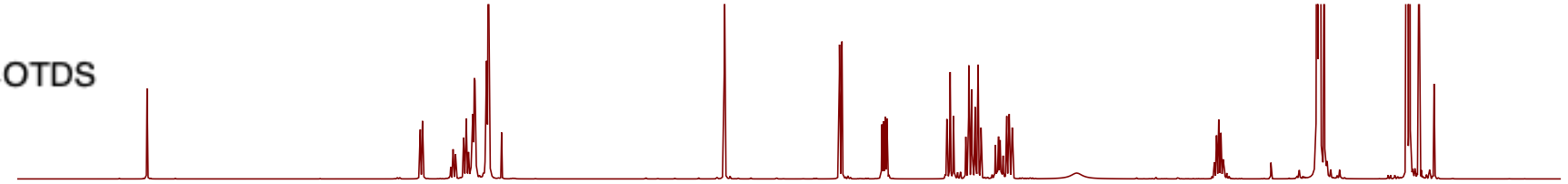

OBn
HO
O
NapO
OTDS
NPhth
S10
f1 (ppm)

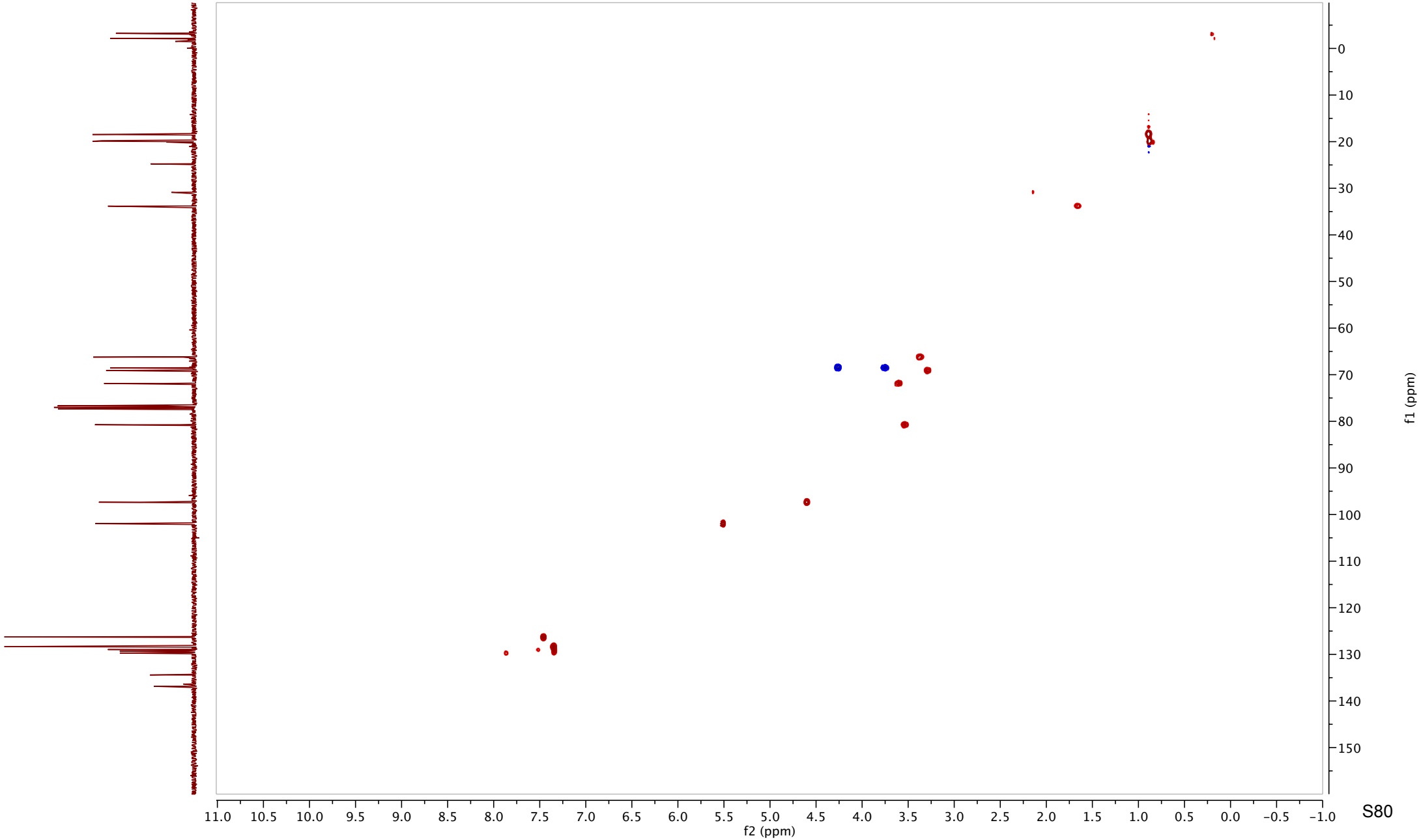


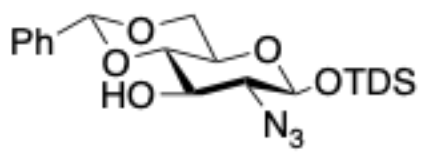
S12


Ph
O
O
O
HO
OTDS
N3

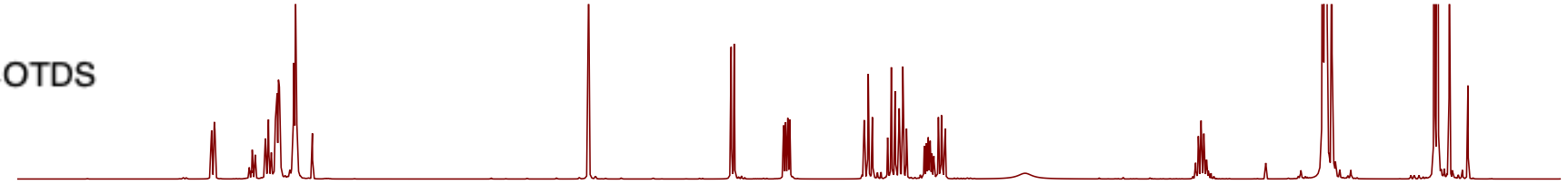
S12

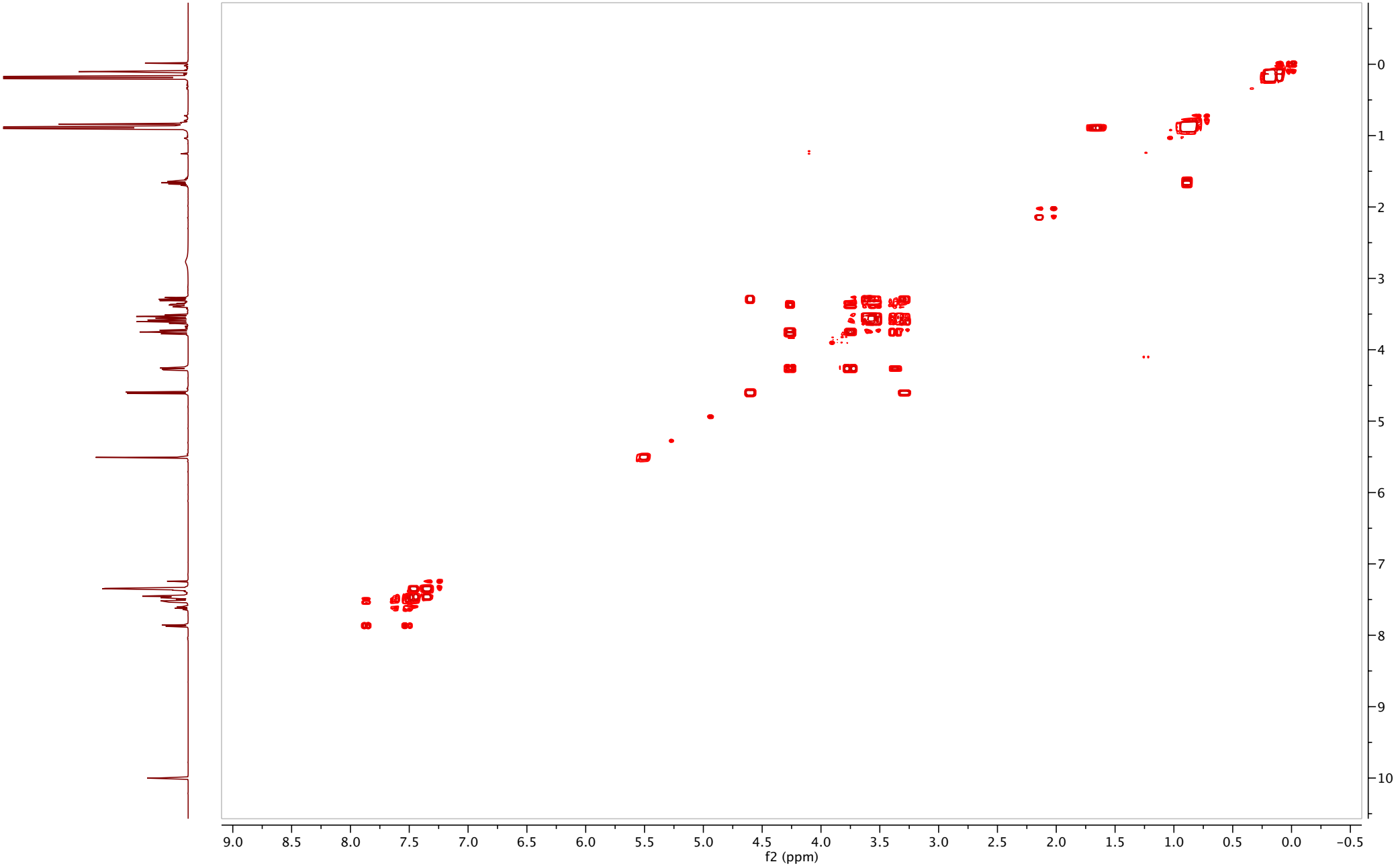


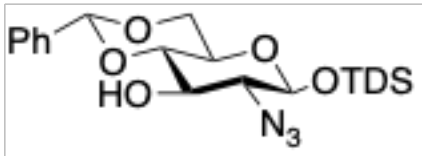

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)


Ph
O
O
O
HO
OTDS
N3

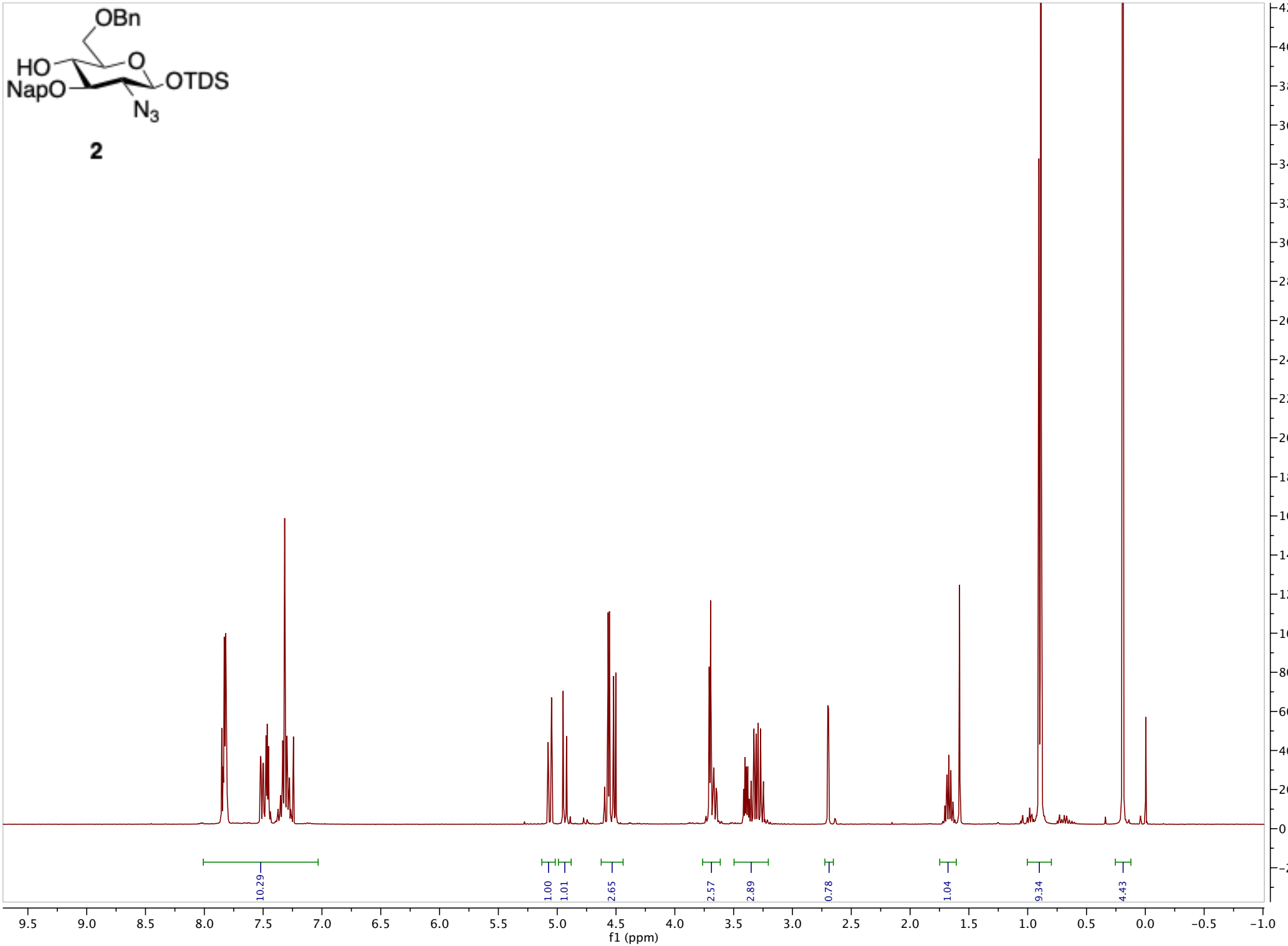
S12

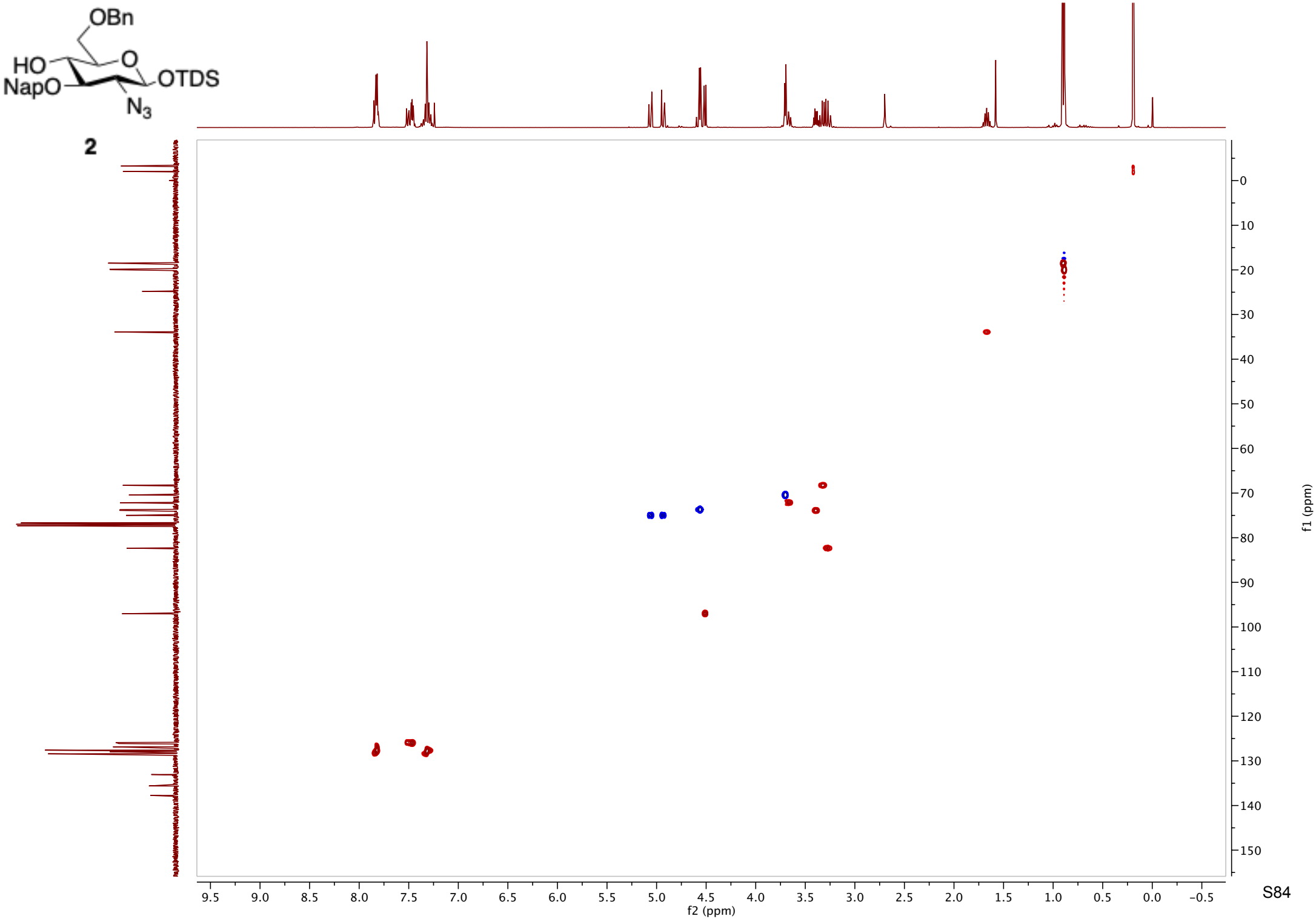


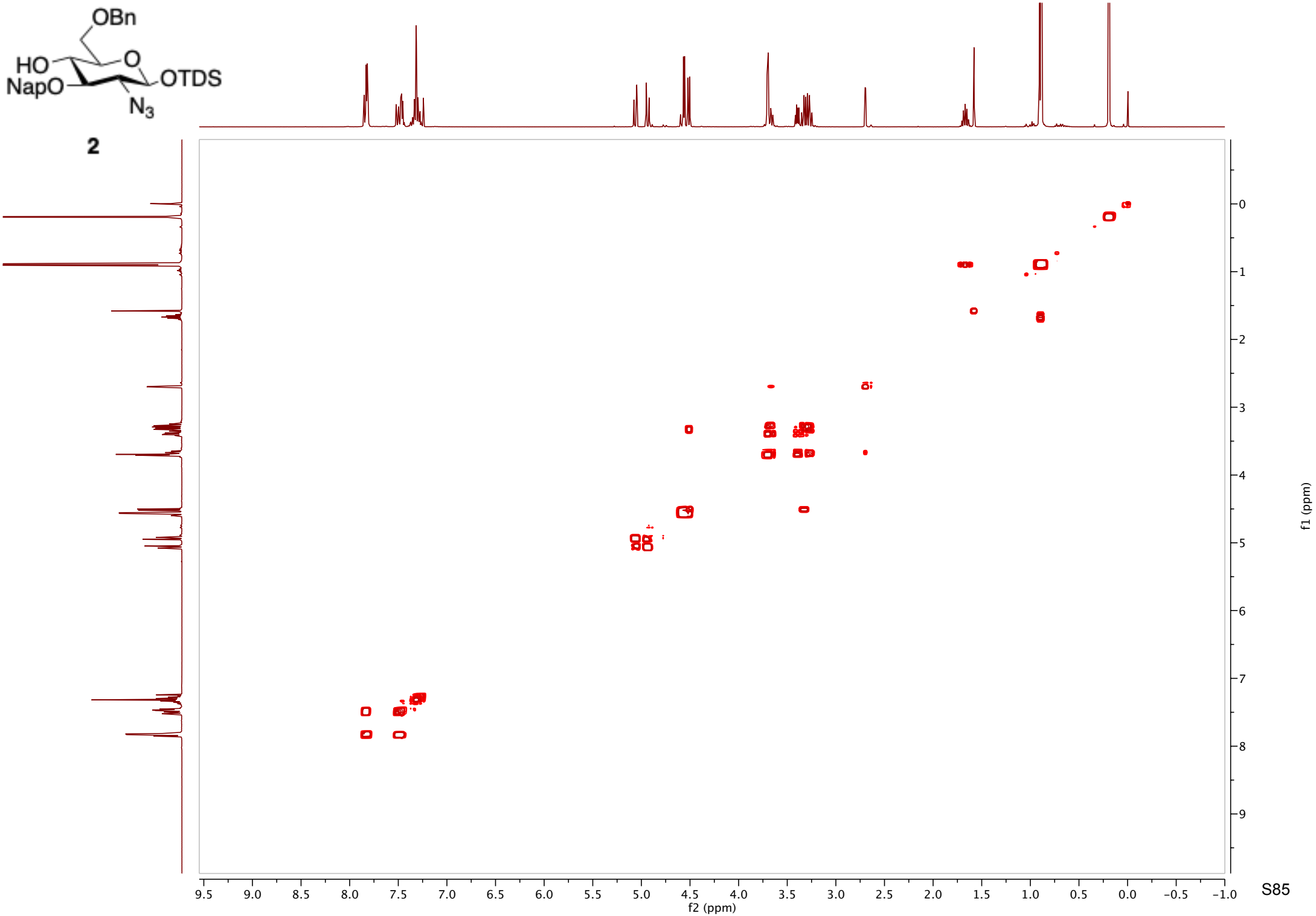

f1 (ppm)
0
1
2
3
4
5
6
7
8
9
10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)

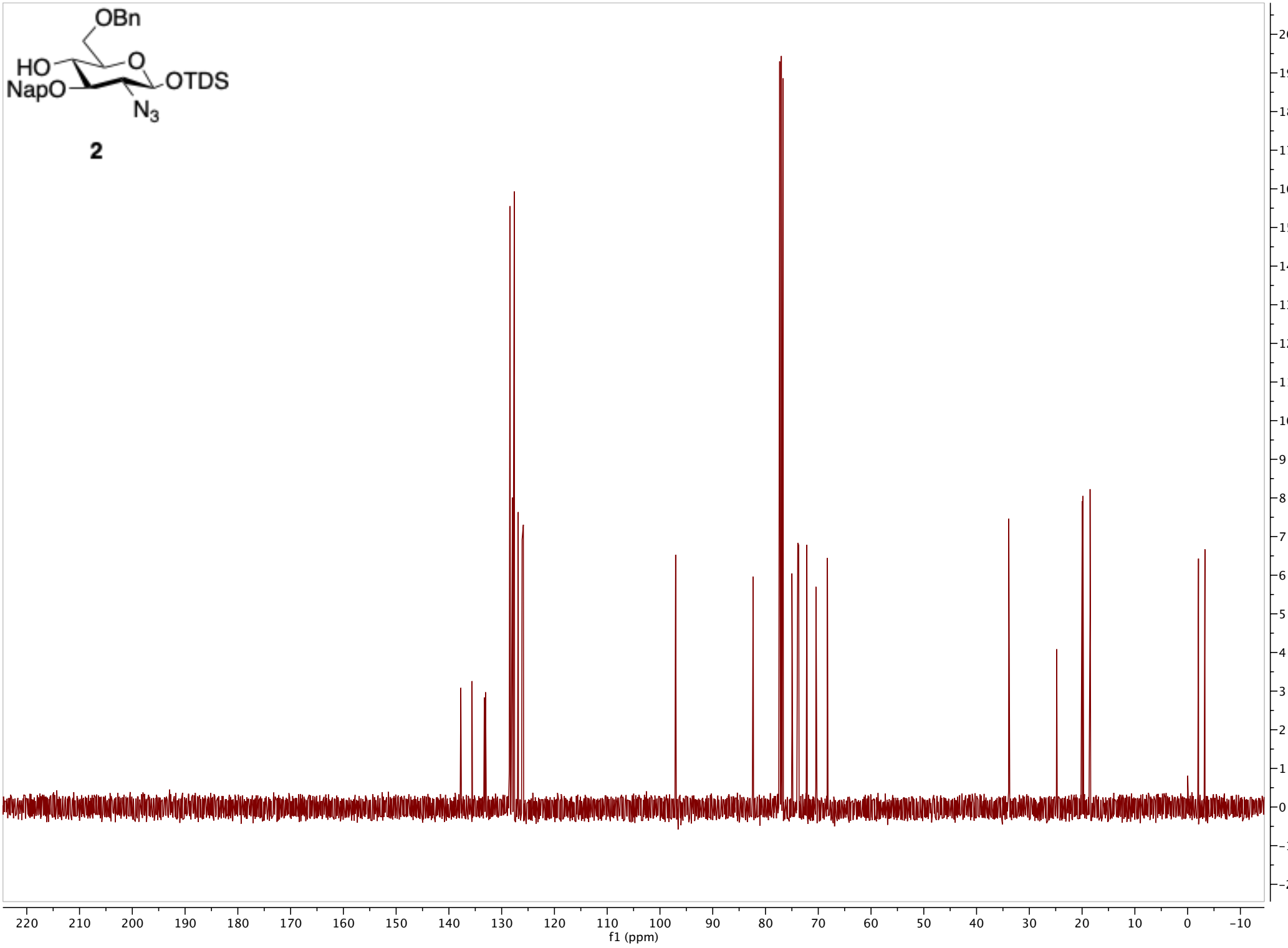


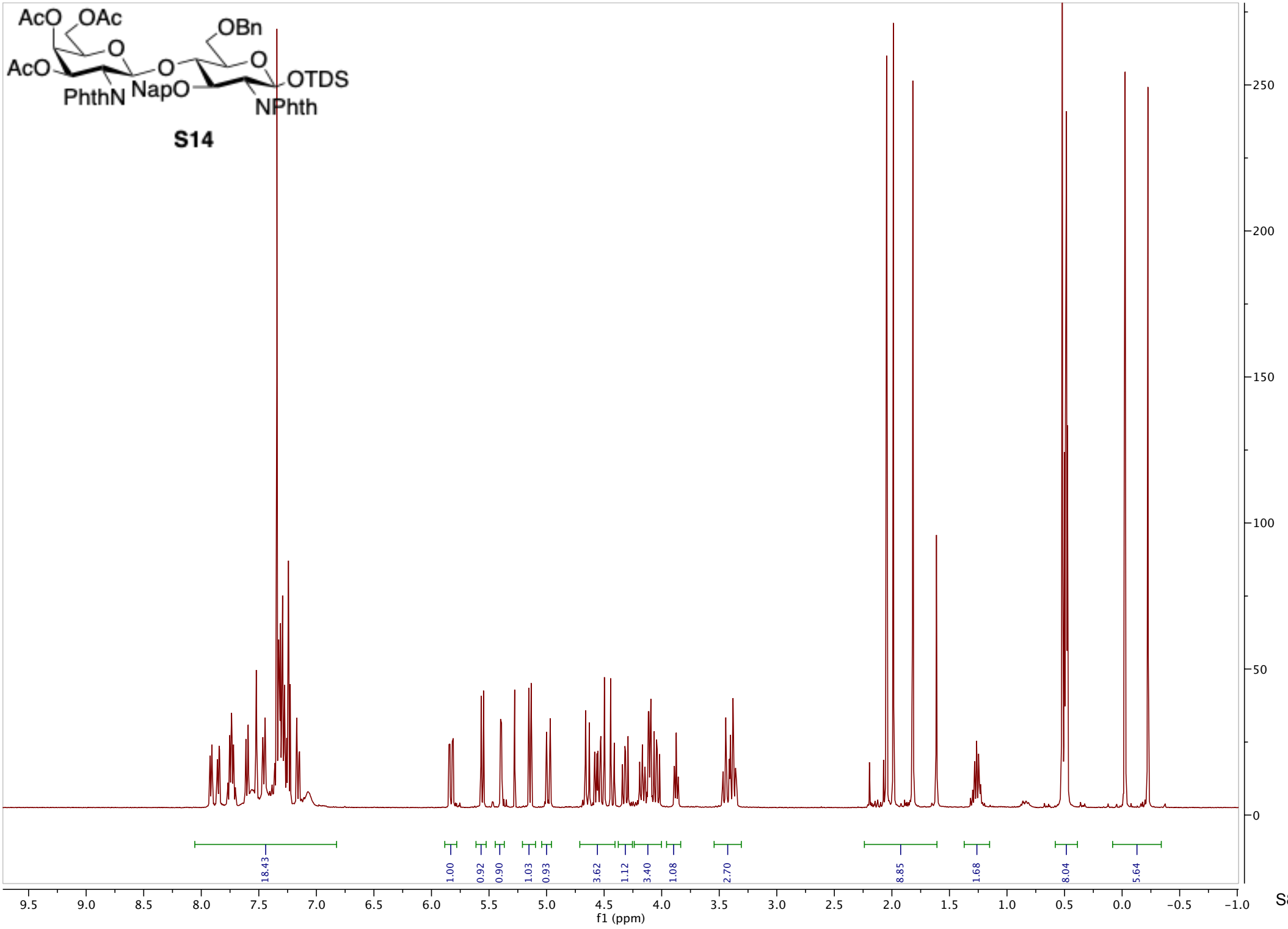
S12

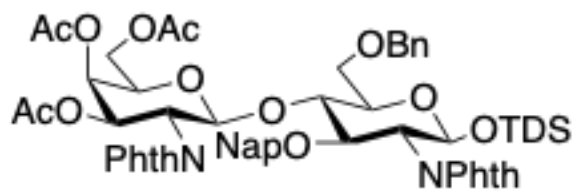

OBn
HO
O
NapO
OTDS
N3
2
10.29
1.00
1.01
2.65
2.57
2.89
0.78
1.04
9.34
4.43
f1 (ppm)


OBn
HO
O
NapO
OTDS
N_3
2
f2 (ppm)
f1 (ppm)

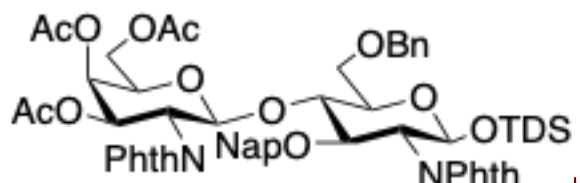

OBn
HO
O
NapO
OTDS
N_3
2
f2 (ppm)
f1 (ppm)


OBn
HO
O
NapO
OTDS
N_3
2
f1 (ppm)


AcO
OAc
O
AcO
O
OBn
O
OTDS
PhthN
NapO
NPhth
S14
250
200
150
100
50
0
18.43
1.00
0.92
0.90
1.03
0.93
3.62
1.12
3.40
1.08
2.70
8.85
1.68
8.04
5.64
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
AcO
O
O
OBn
O
OTDS
PhthN
NapO
NPhth

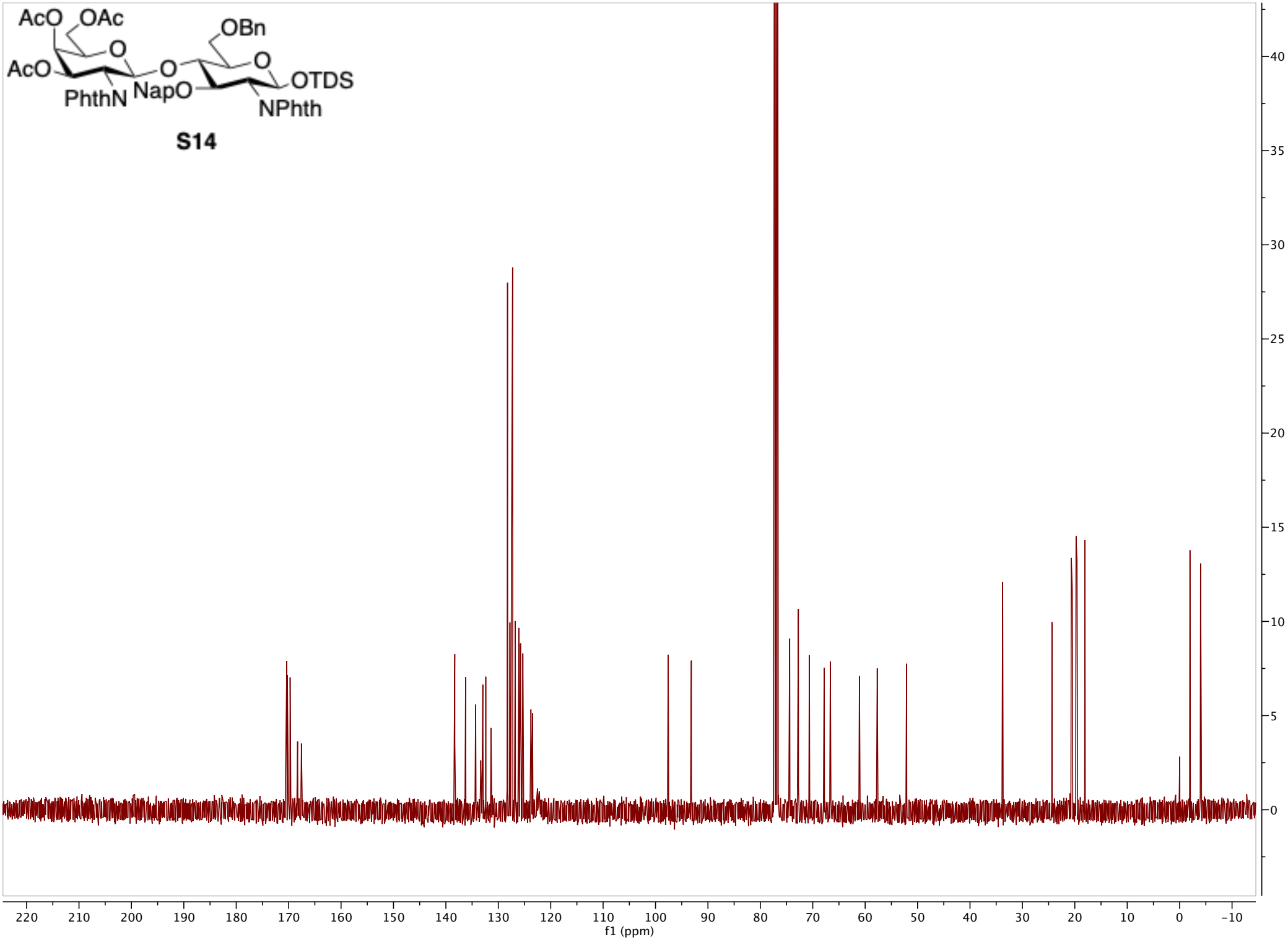
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

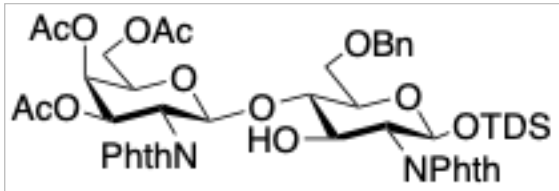


S14

f2 (ppm)

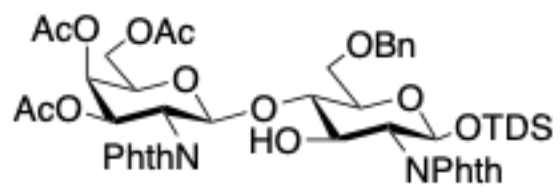
f1 (ppm)


AcO
OAc
O
AcO
O
OBn
O
OTDS
PhthN
NapO
NPhth
S14
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)


AcO
OAc
O
AcO
PhthN
O
HO
OBn
O
OTDS
NPhth

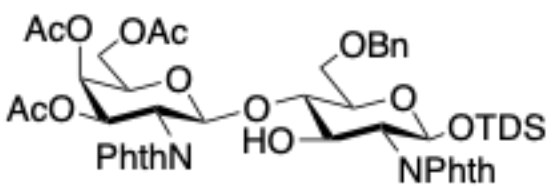
S15

8.23
4.77
1.00
1.88
1.00
0.90
1.08
6.06
0.99
1.02
1.87
3.10
5.54
0.94
11.54
6.64
f1 (ppm)



f2 (ppm)

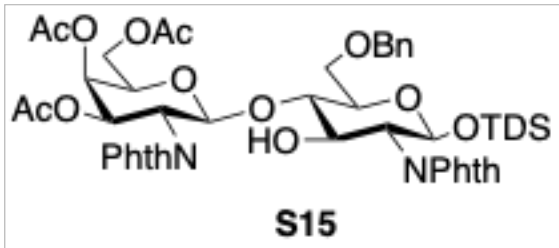
f1 (ppm)



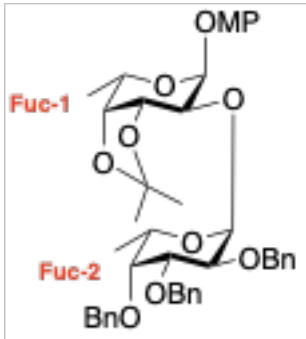
S15

f2 (ppm)

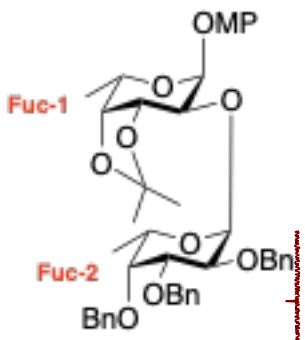
f1 (ppm)



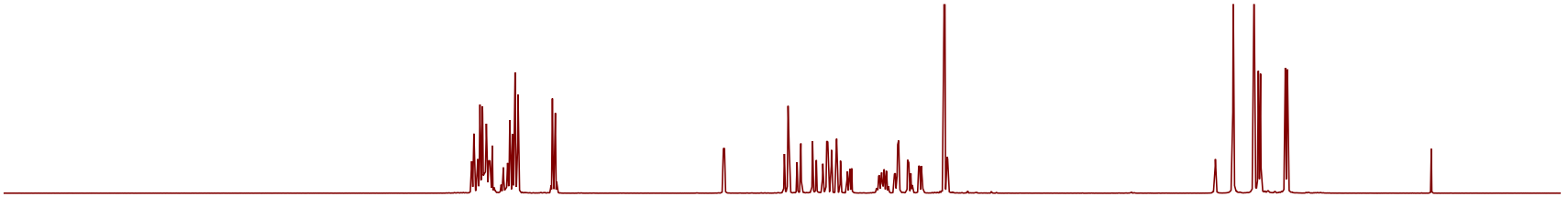
S15

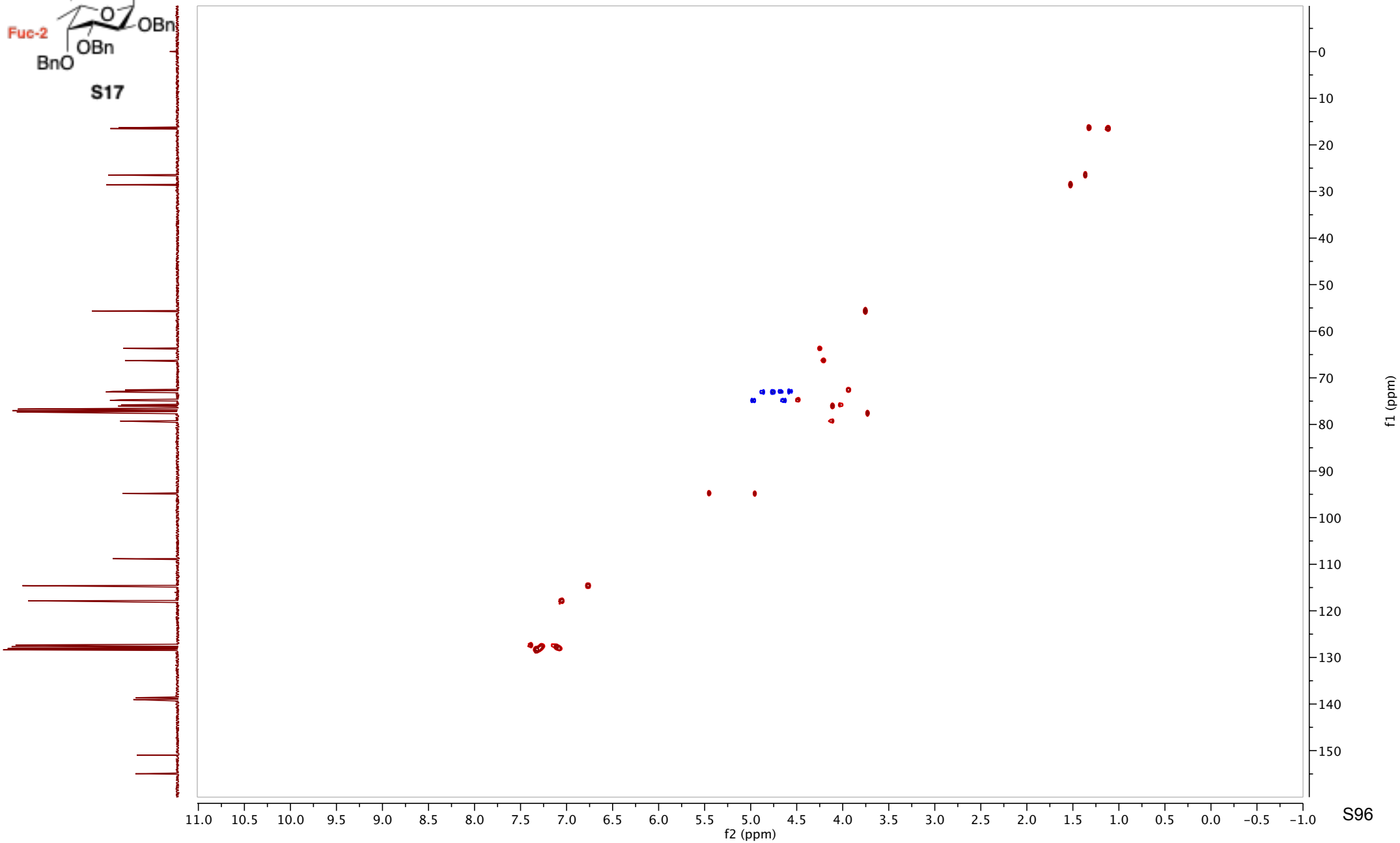


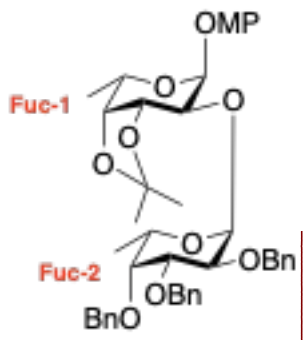
S17


OMP
Fuc-1
O
O
O
O
Fuc-2
OBn
OBn
BnO

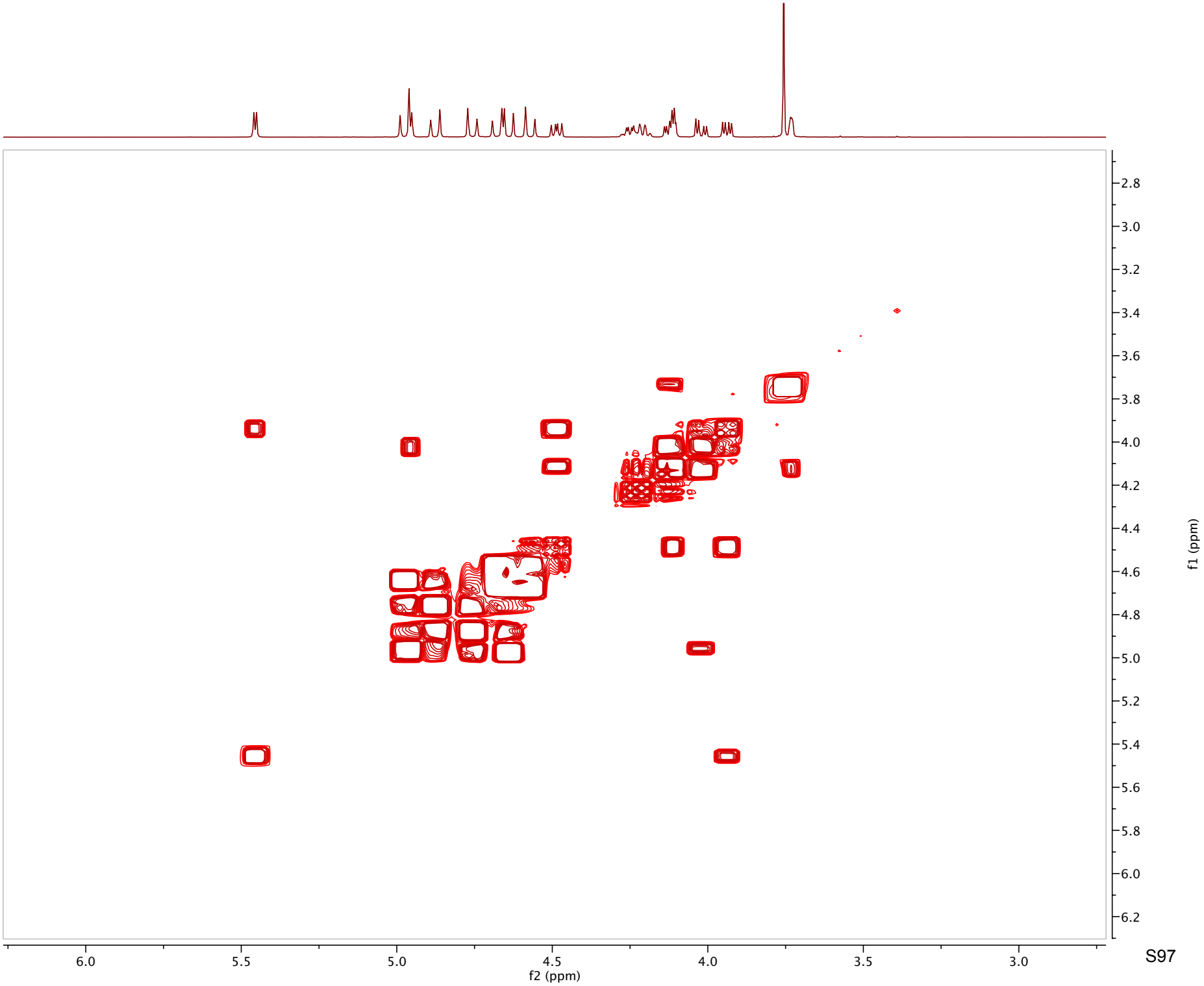
S17

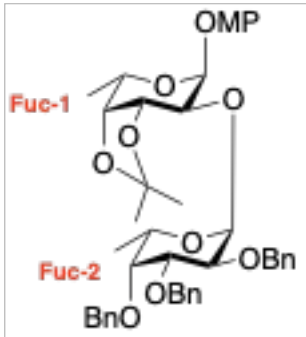



0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)

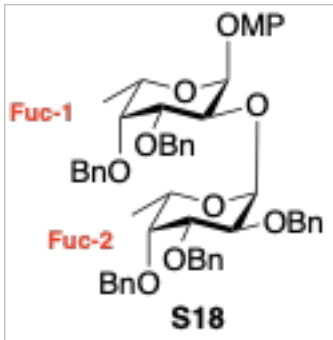

OMP
Fuc-1
O
O
O
O
Fuc-2
OBn
OBn
BnO

S17

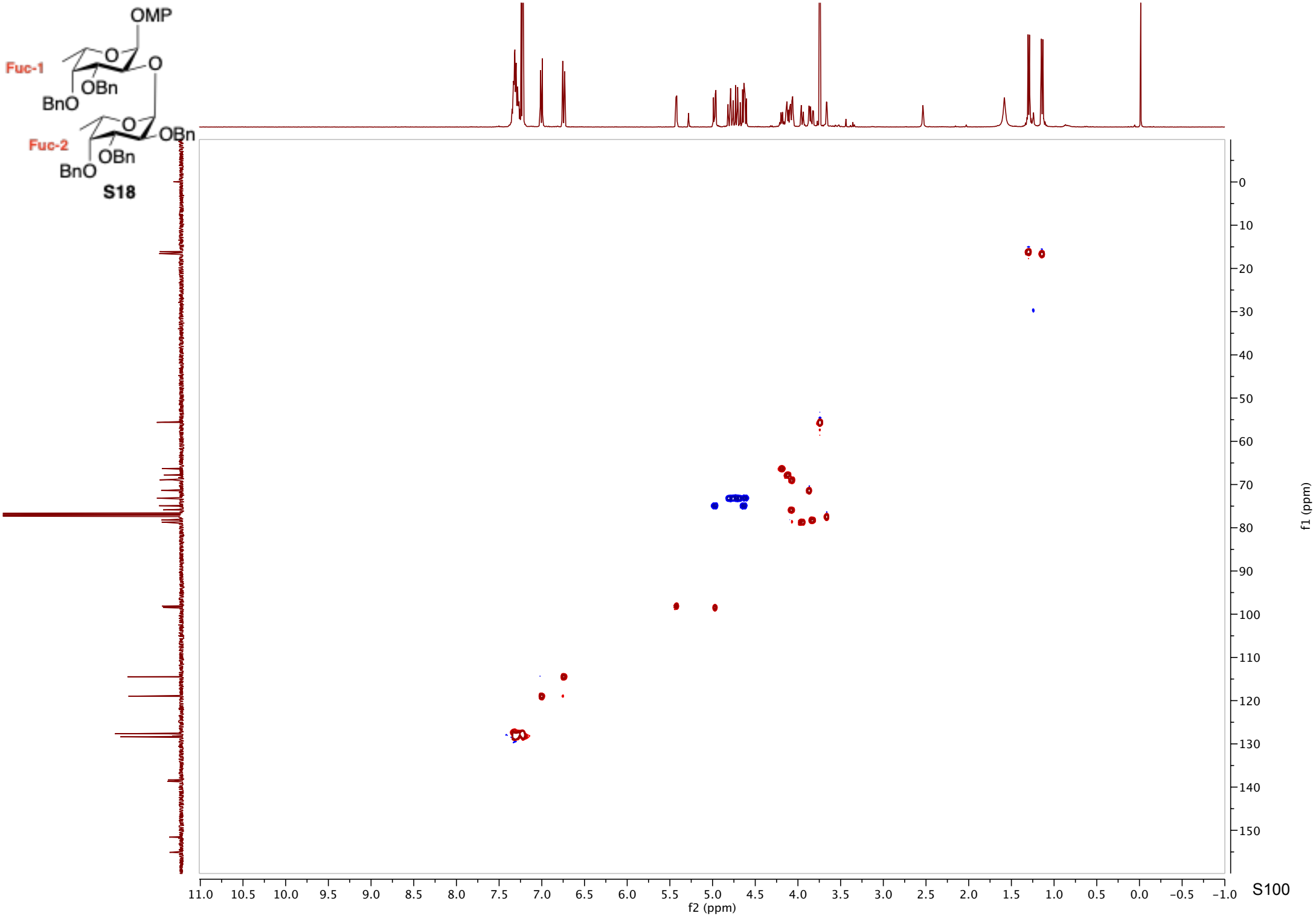

2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
5.6
5.8
6.0
6.2
f1 (ppm)
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)

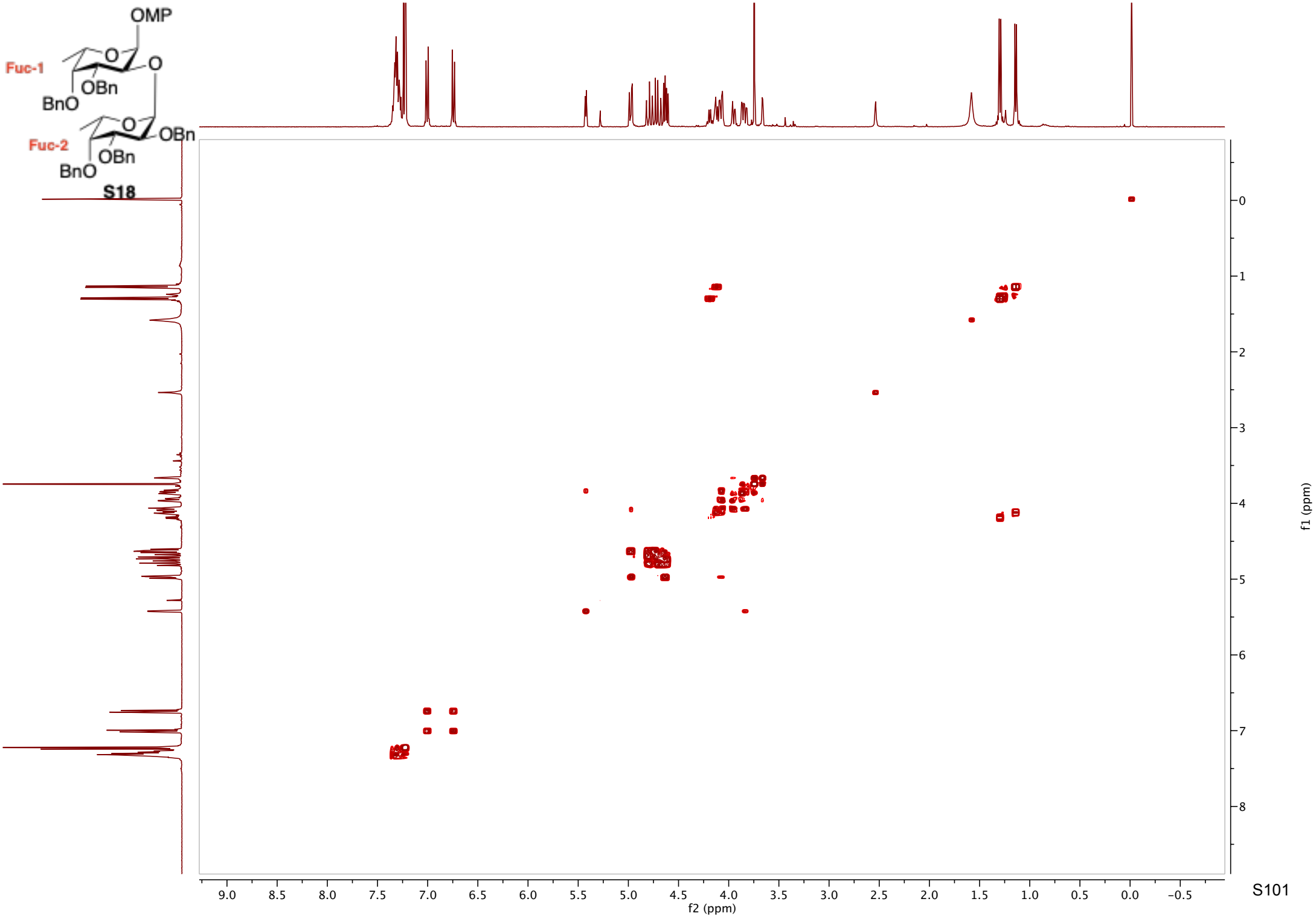


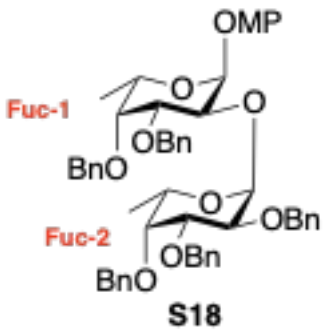
S17



S18

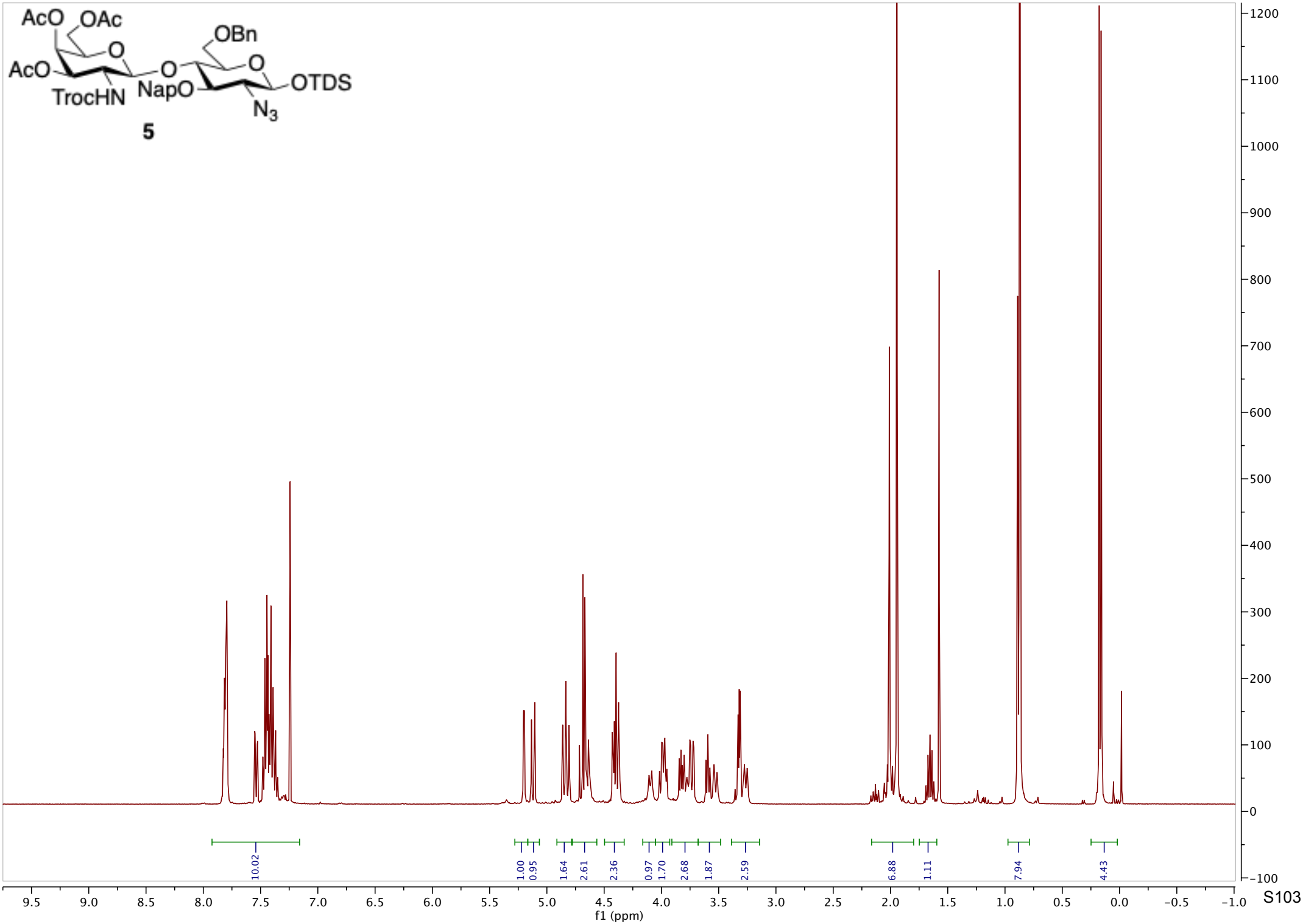

OMP
Fuc-1
O
O
OBn
BnO
O
OBn
Fuc-2
OBn
BnO
S18
f2 (ppm)
f1 (ppm)

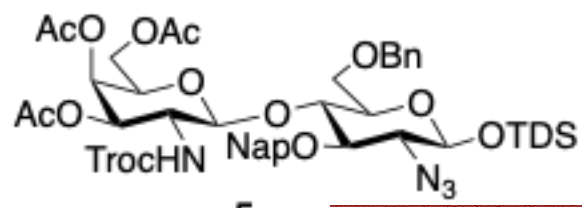

OMP
Fuc-1
O
O
OBn
BnO
O
OBn
Fuc-2
OBn
BnO
S18
f2 (ppm)
f1 (ppm)



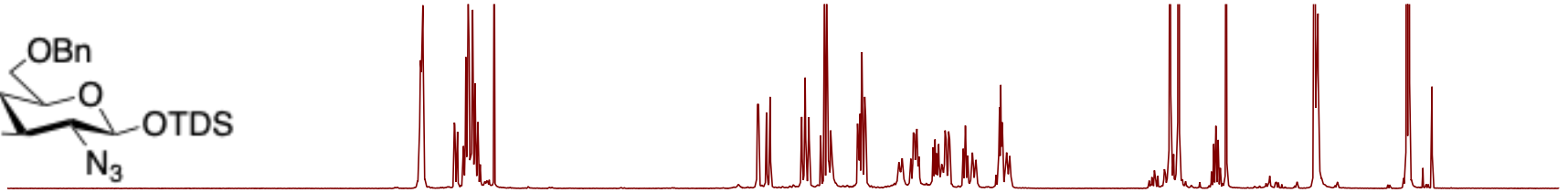
S18

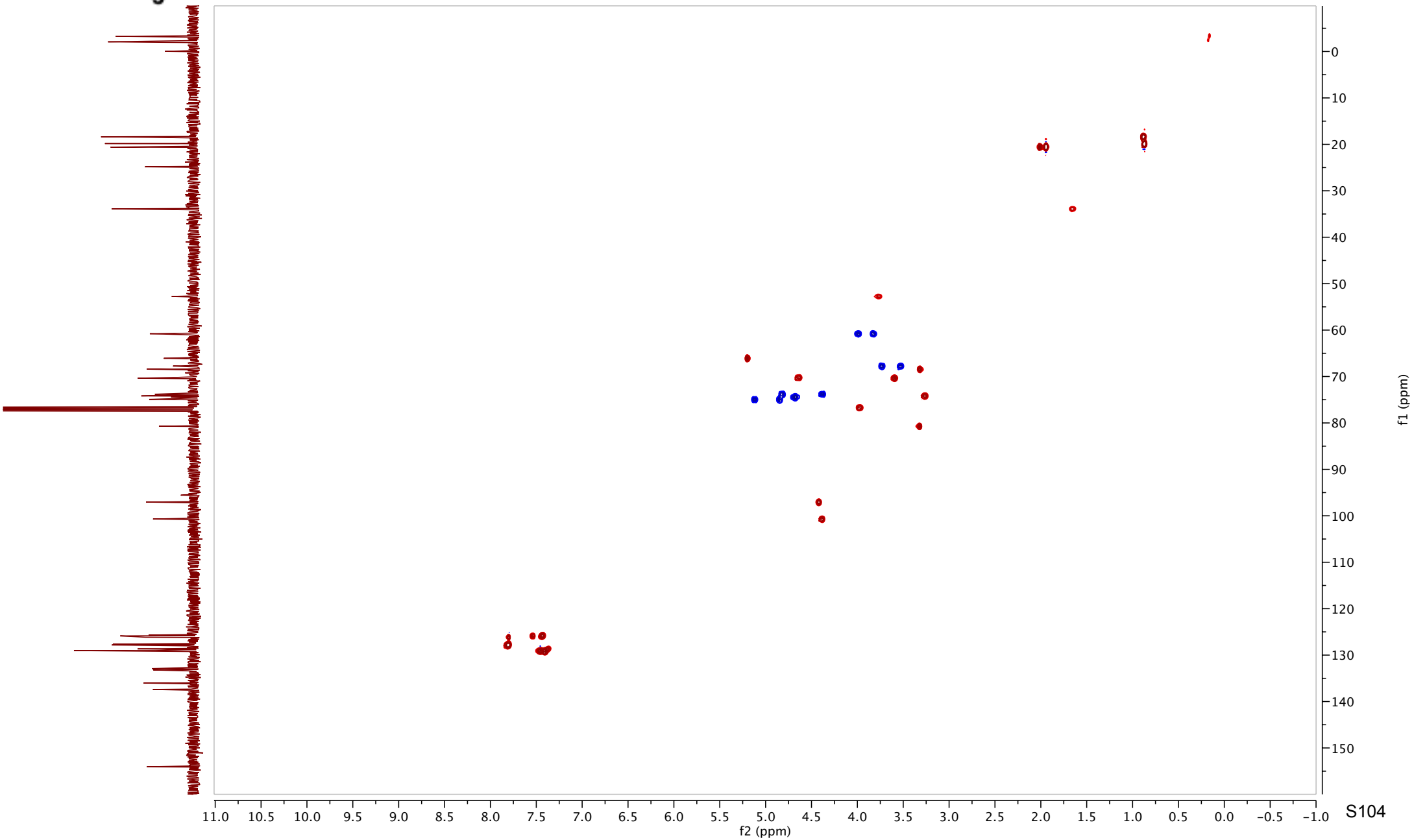
f1 (ppm)

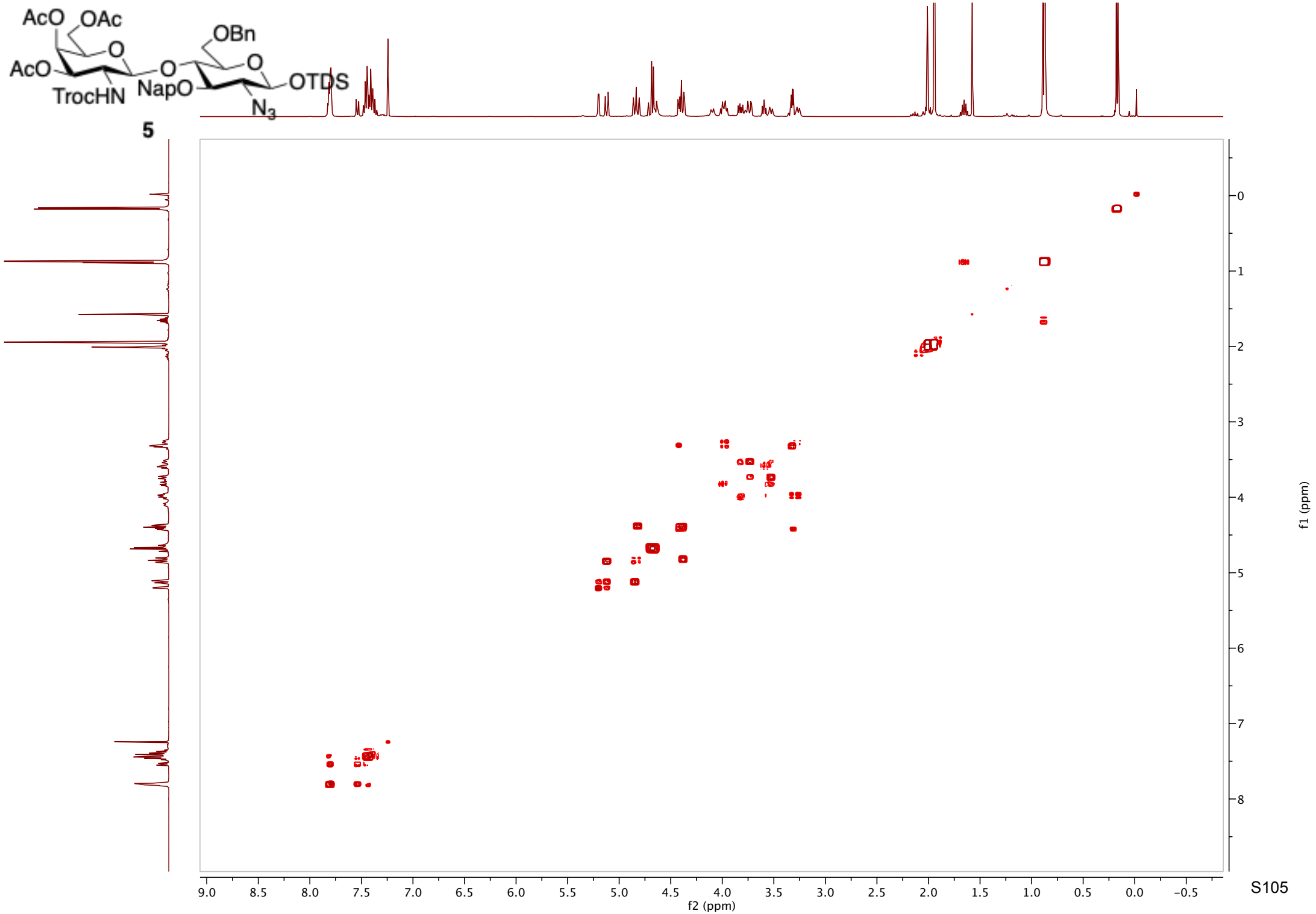

AcO
OAc
O
AcO
O
OBn
O
TrocHN
NapO
OTDS
N_3
5
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
10.02
1.00
0.95
1.64
2.61
2.36
0.97
1.70
2.68
1.87
2.59
6.88
1.11
7.94
4.43
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f1 (ppm)

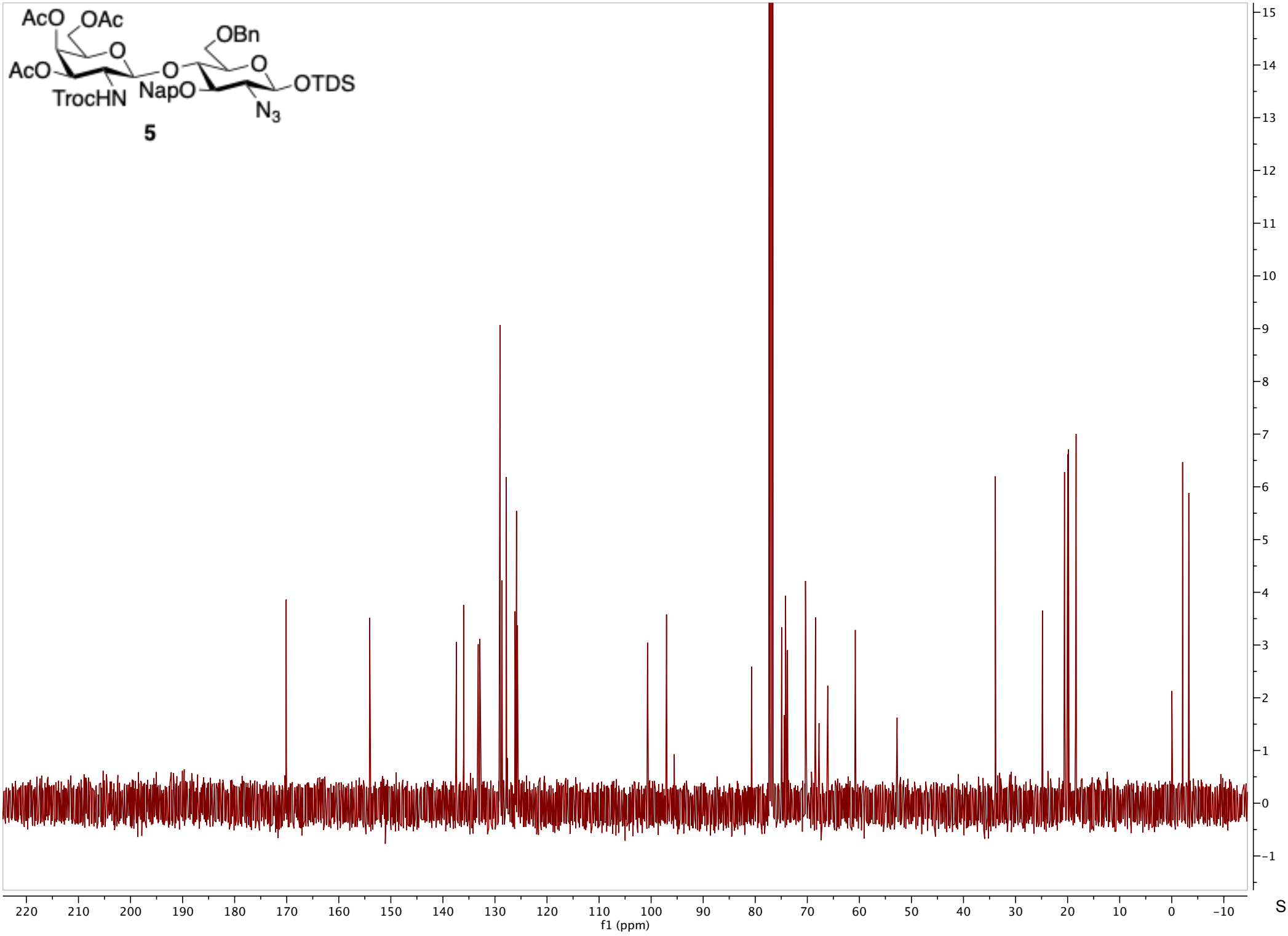

AcO
OAc
O
AcO
O
OBn
O
OTDS
TrocHN
NapO
N3

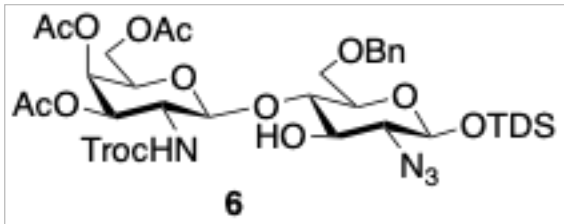
5



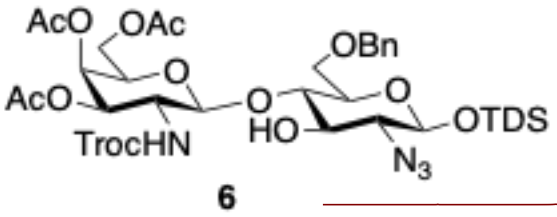

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)


AcO
OAc
AcO
O
TrocHN
O
NapO
OBn
O
OTDS
N3
5
f2 (ppm)
f1 (ppm)

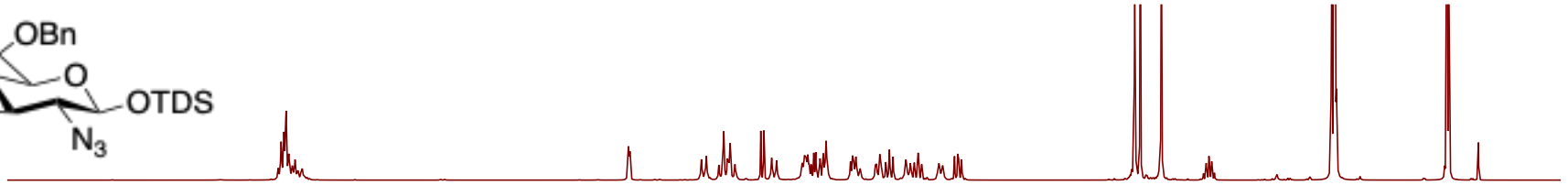

AcO
OAc
O
AcO
TrocHN
O
NapO
OBn
O
OTDS
N3
5
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

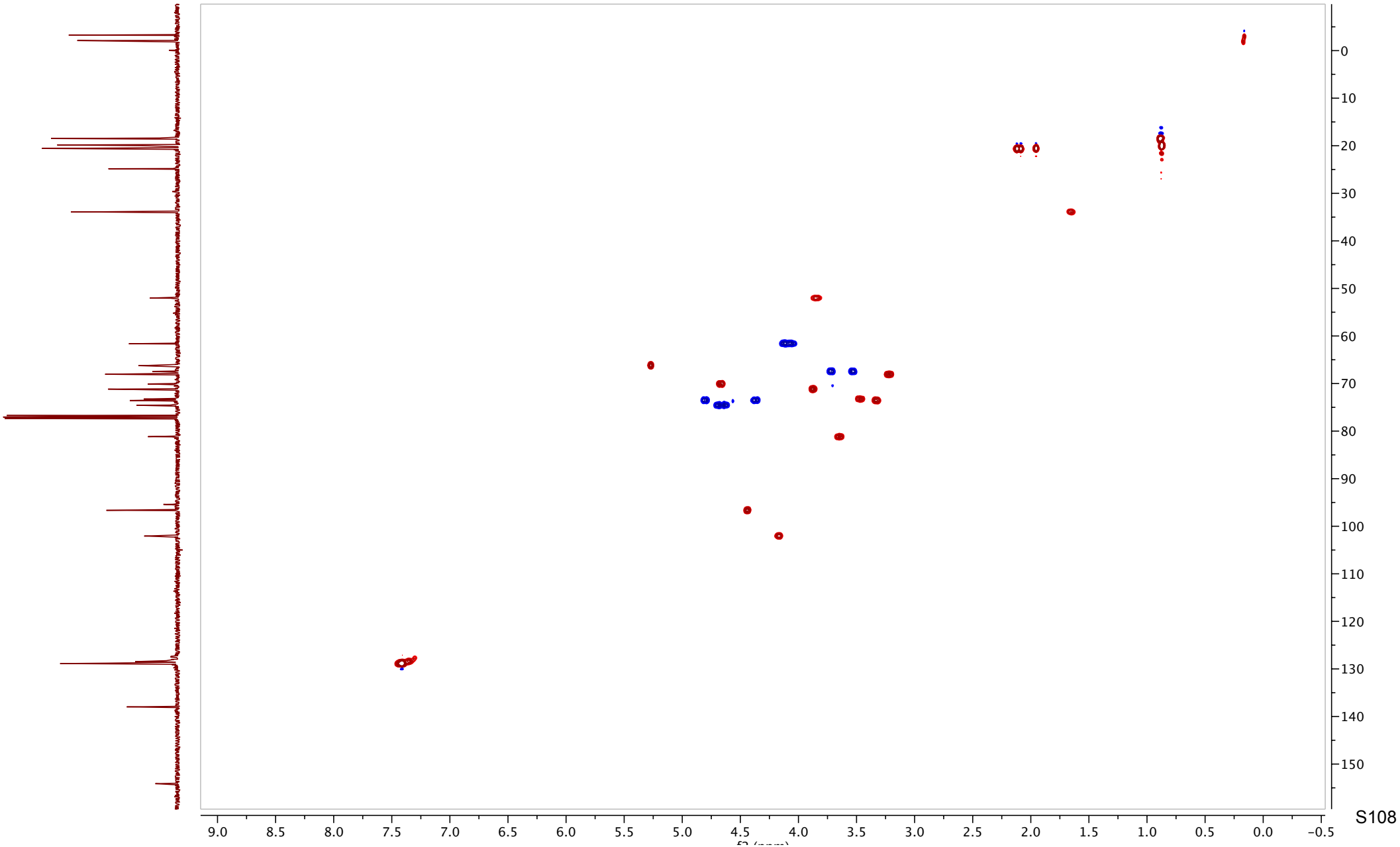


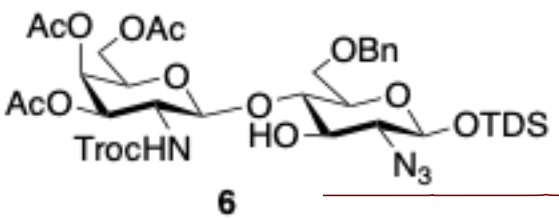
6


AcO
OAc
AcO
O
TrocHN
O
HO
OBn
O
OTDS
N3

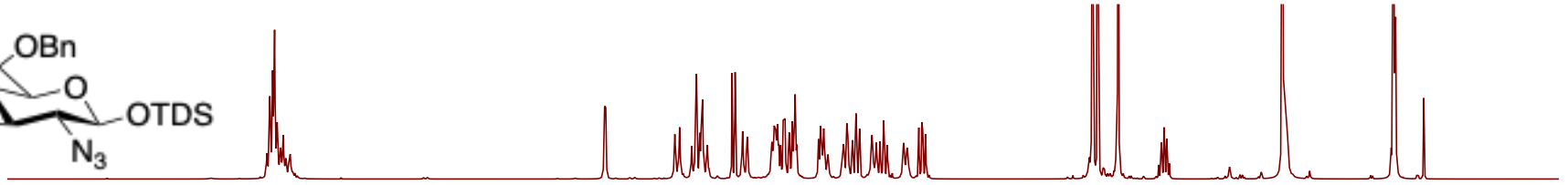
6

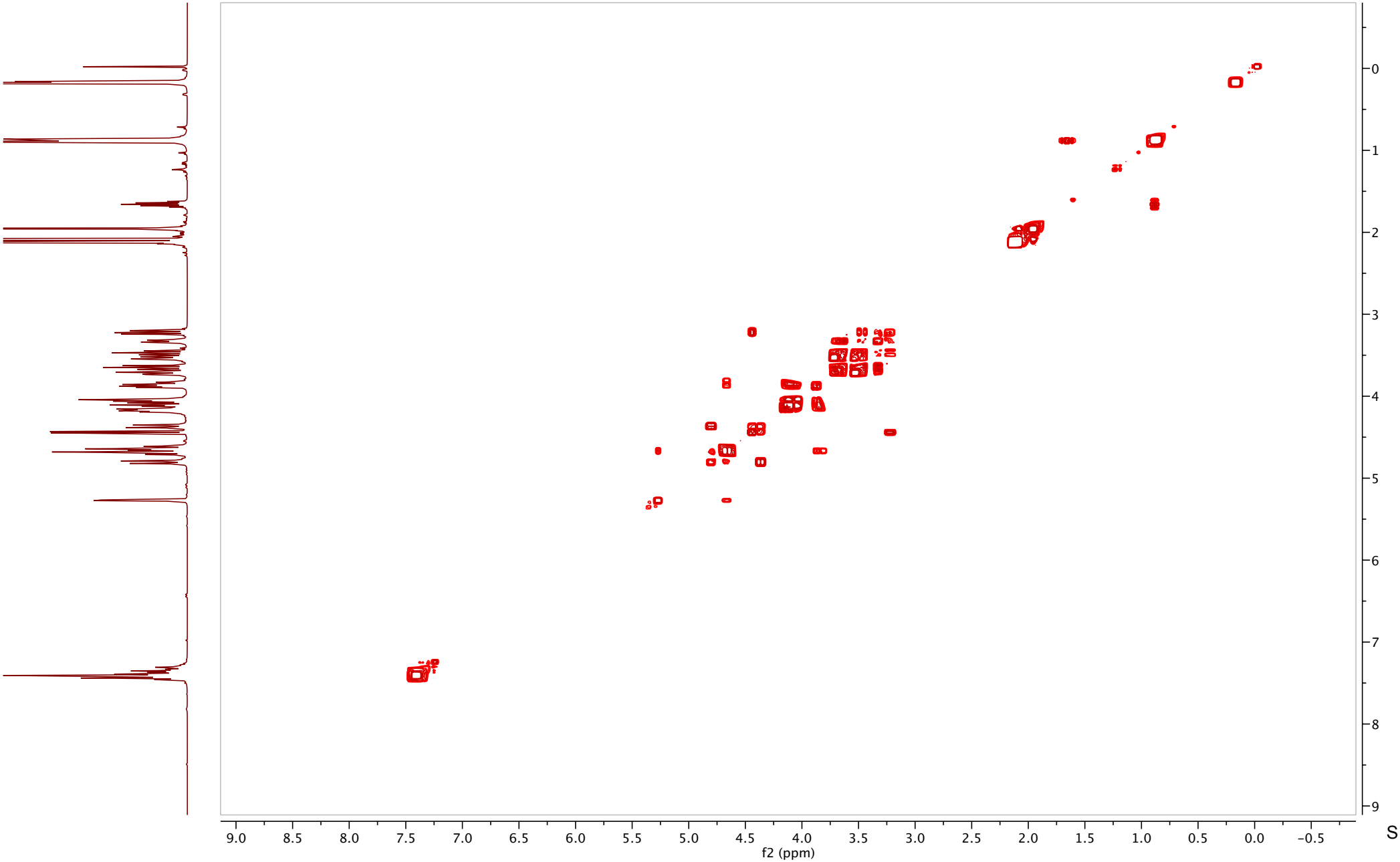


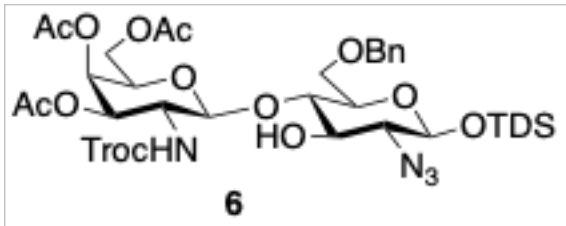

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5


AcO
OAc
O
AcO
TrocHN
O
HO
OBn
O
OTDS
N3

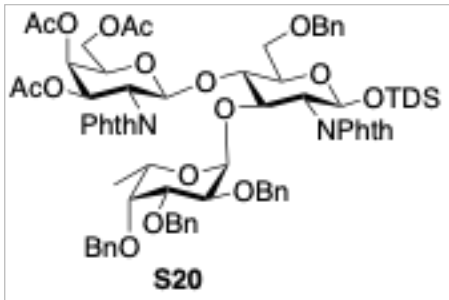
6




0
1
2
3
4
5
6
7
8
9
f1 (ppm)
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)

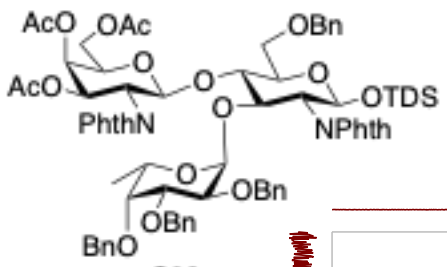


6


AcO
OAc
OBn
AcO
O
O
O
OTDS
PhthN
NPhth
O
O
OBn
OBn
BnO

S20

32.08
1.08
1.00
1.05
0.87
0.93
1.21
5.43
1.43
2.07
3.29
1.34
2.12
2.23
1.08
1.82
1.05
9.02
5.32
11.22
6.81
f1 (ppm)

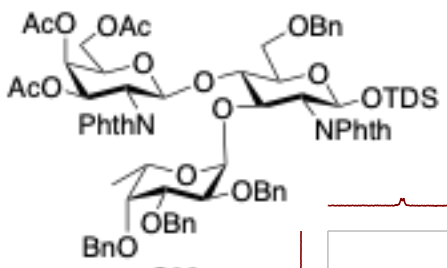


S20

f2 (ppm)

f1 (ppm)

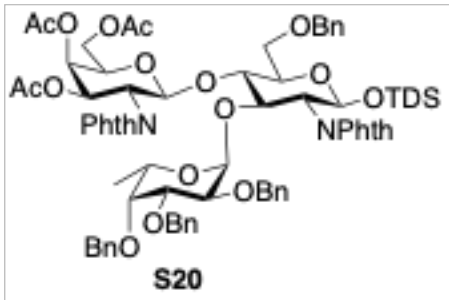
S112



S20

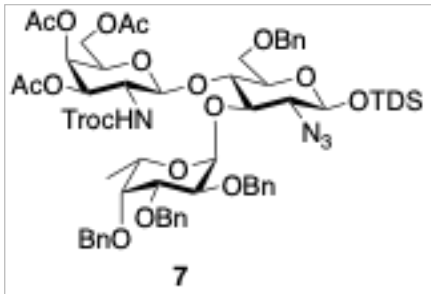
f2 (ppm)

f1 (ppm)

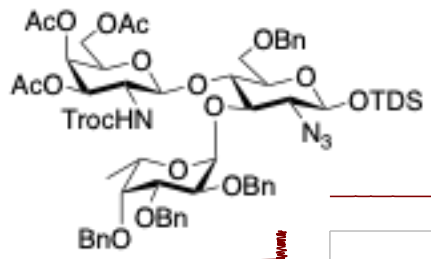

AcO
OAc
OBn
AcO
O
O
O
O
OTDS
PhthN
NPhth
O
OBn
OBn
BnO

S20

18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
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)

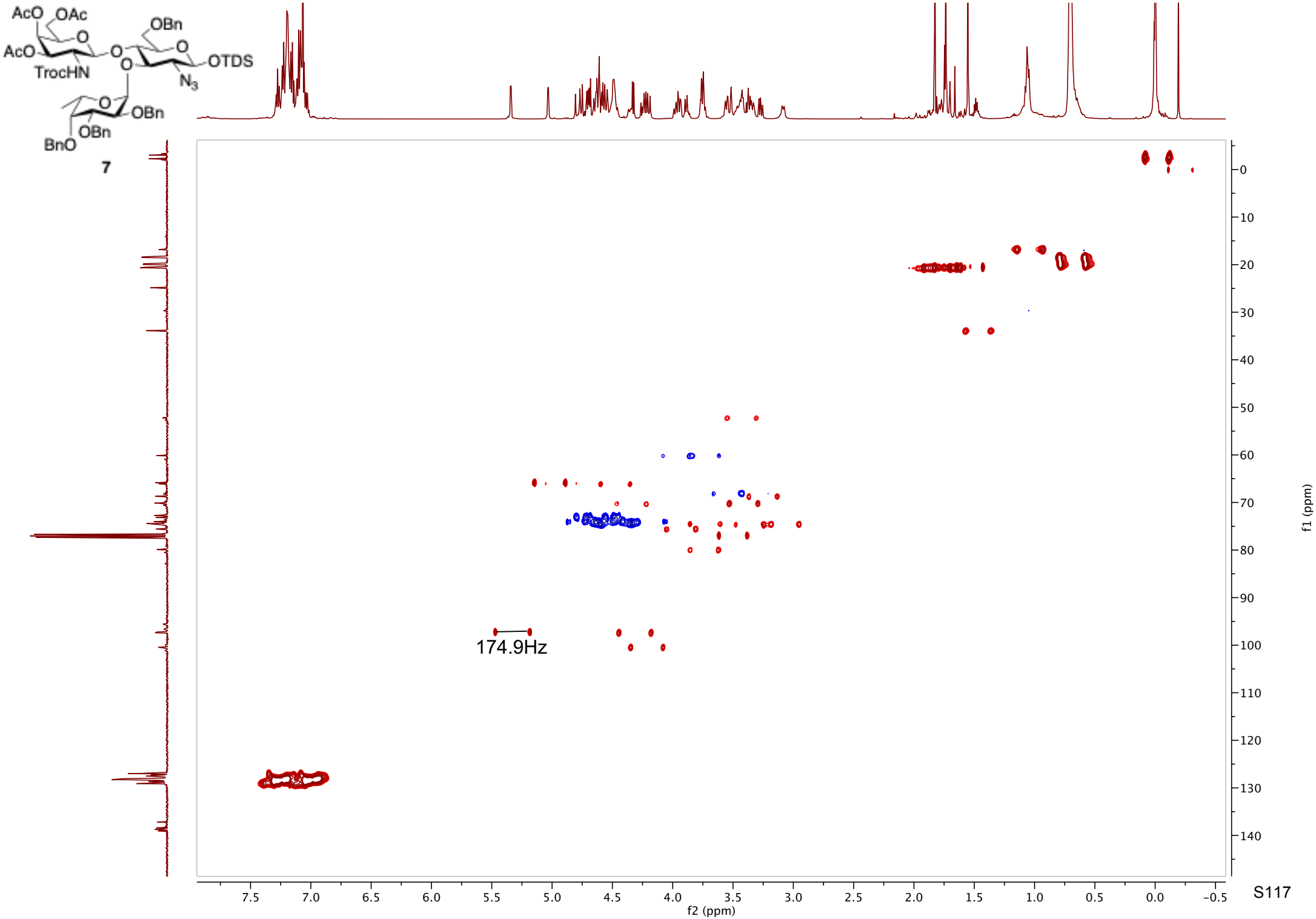


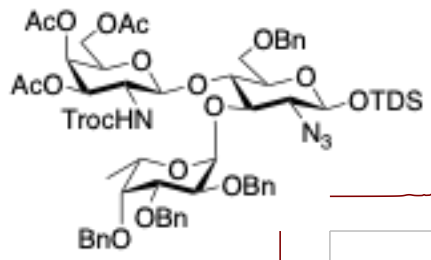
7



f2 (ppm)

f1 (ppm)

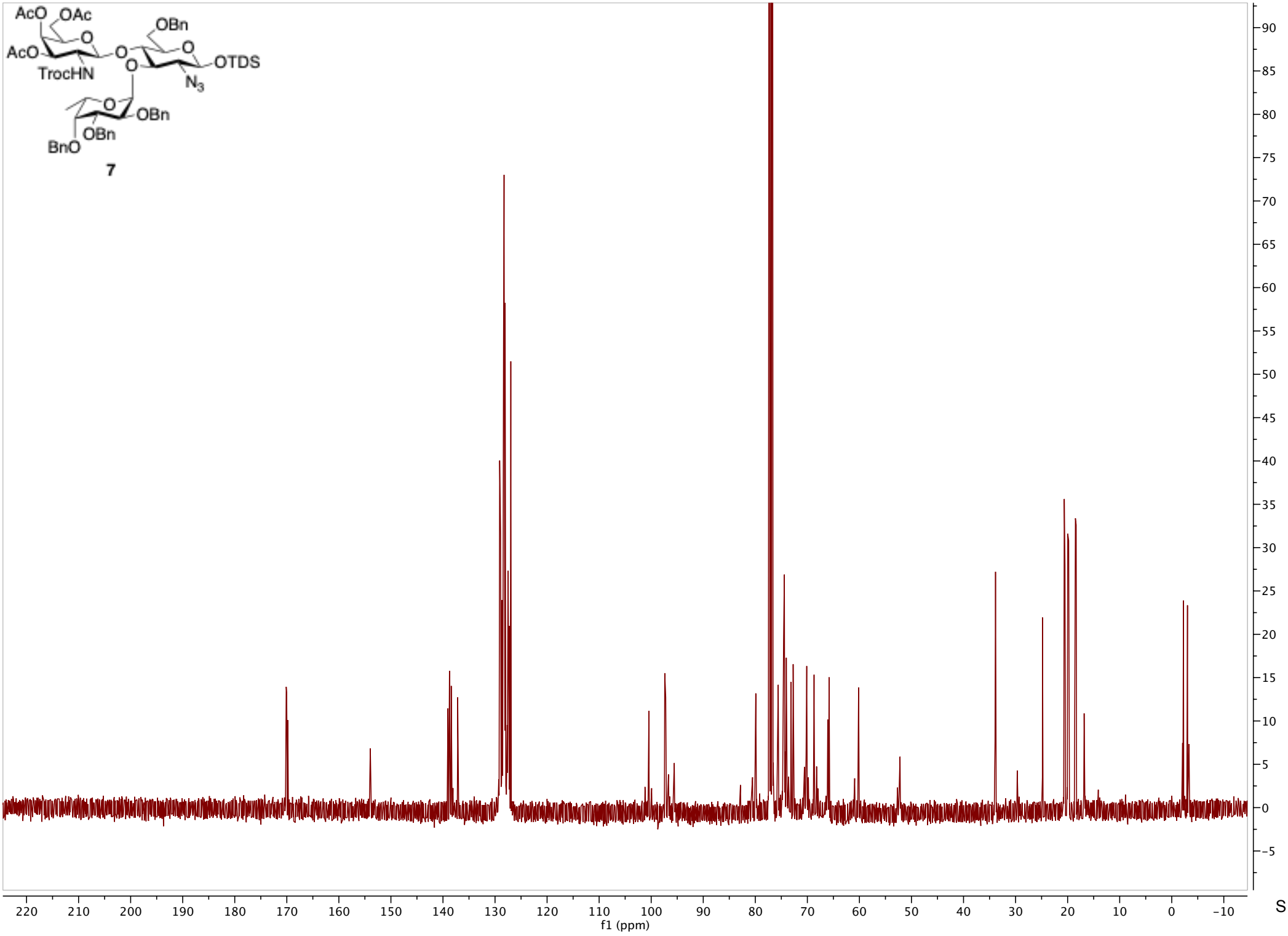

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OBn
OBn
BnO
7
174.9Hz
f2 (ppm)
f1 (ppm)

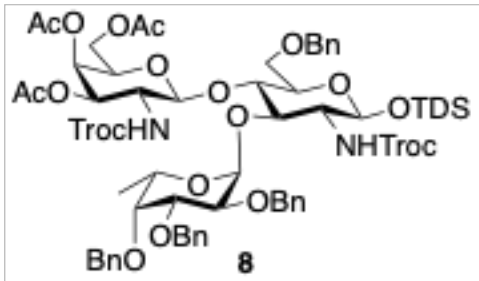


7

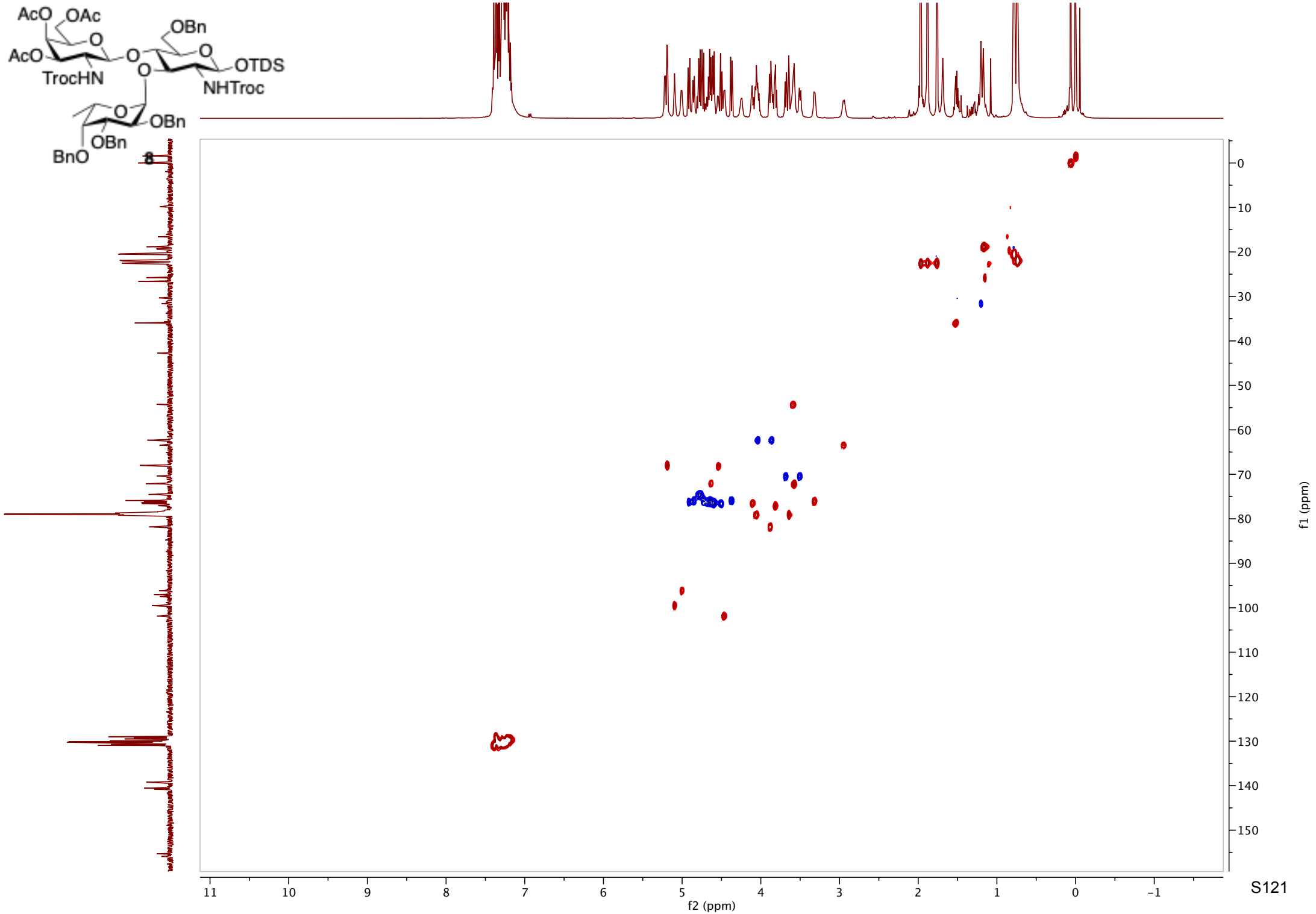
f2 (ppm)

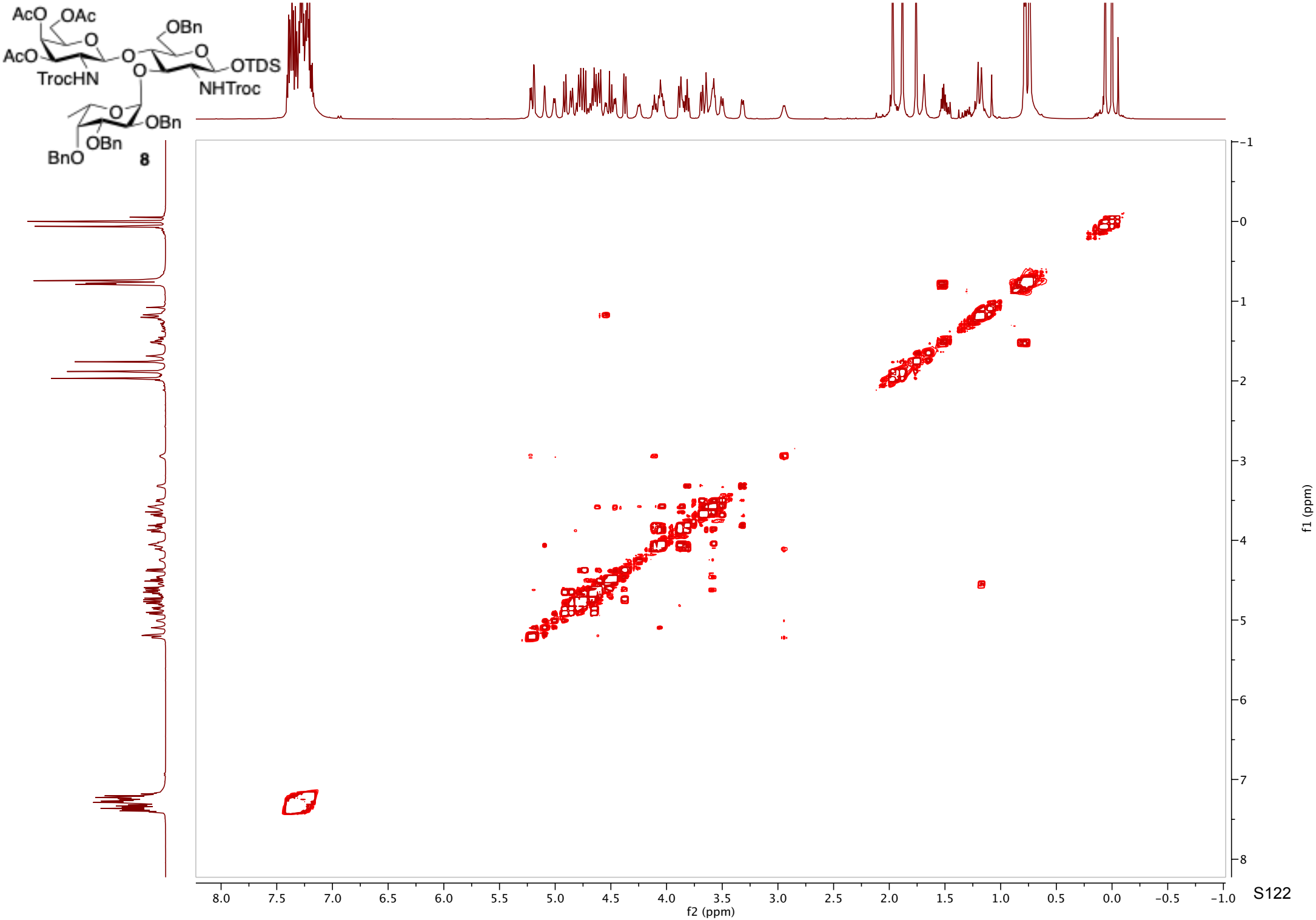
f1 (ppm)

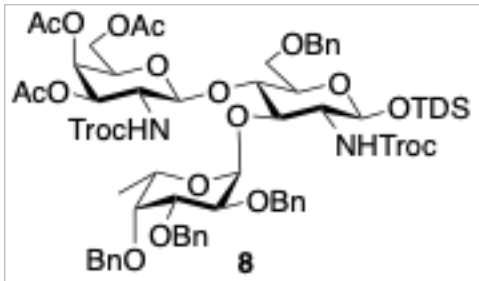

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OBn
OBn
BnO
7
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
−5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


AcO
OAc
AcO
TrocHN
OBn
OTDS
NHTroc
OBn
OBn
BnO
8

1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
24.05
2.31
1.10
1.01
5.78
4.44
2.64
1.08
0.94
3.52
3.27
2.20
2.63
1.31
1.01
1.00
3.29
3.61
2.89
1.40
2.99
13.04
5.91
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)

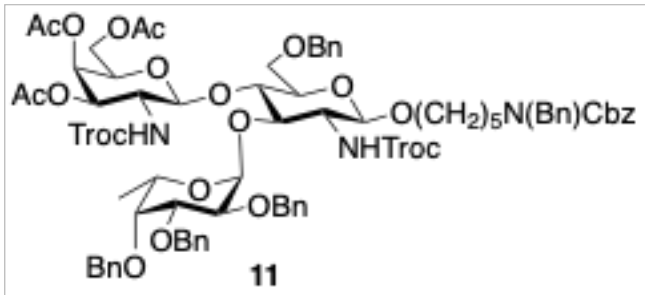

AcO
OAc
AcO
O
TrocHN
O
O
OBn
O
OTDS
NHTroc
O
OBn
OBn
BnO
8
f2 (ppm)
f1 (ppm)

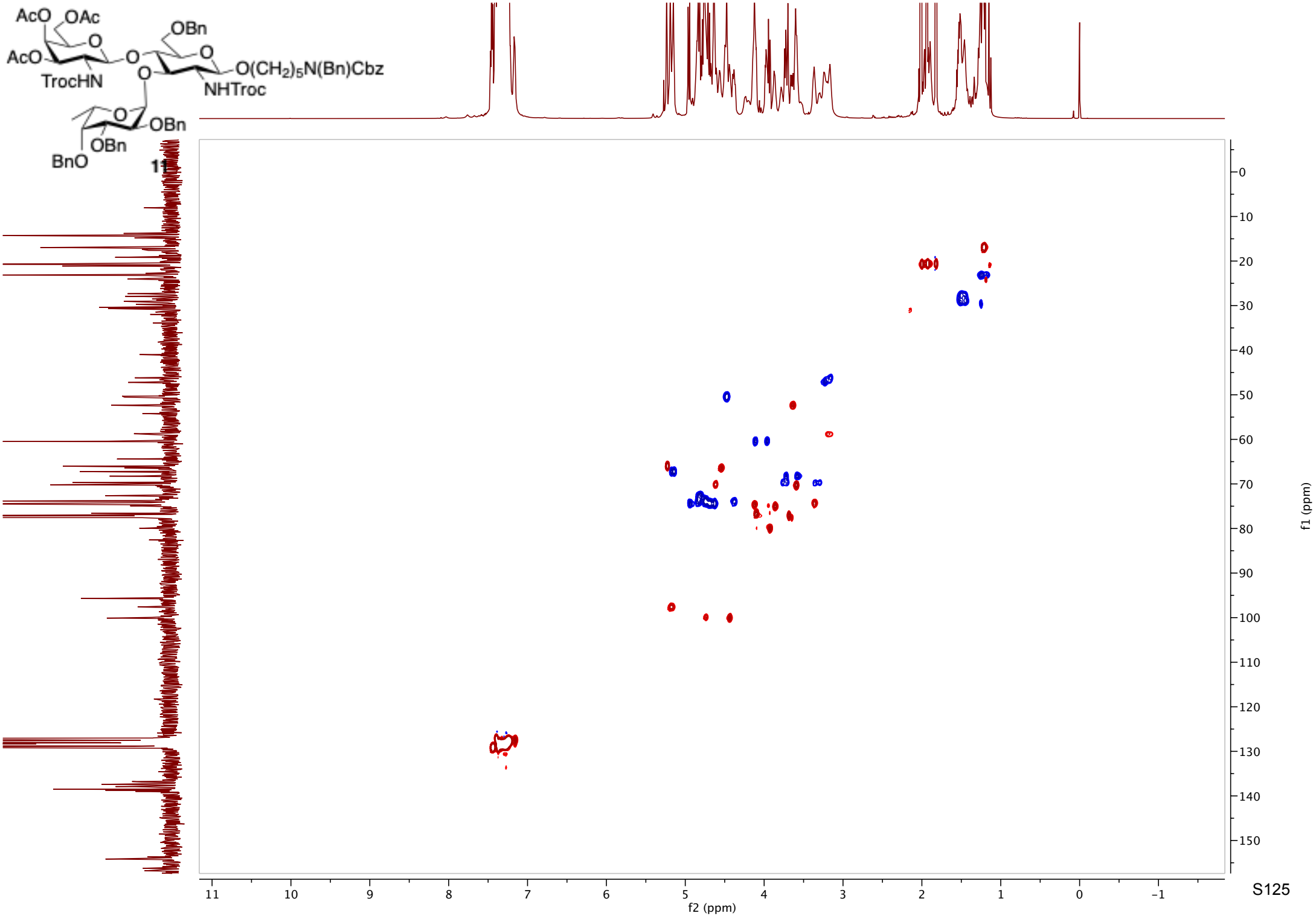

AcO
OAc
AcO
TrocHN
OBn
OTDS
NHTroc
OBn
OBn
BnO
8
f2 (ppm)
f1 (ppm)

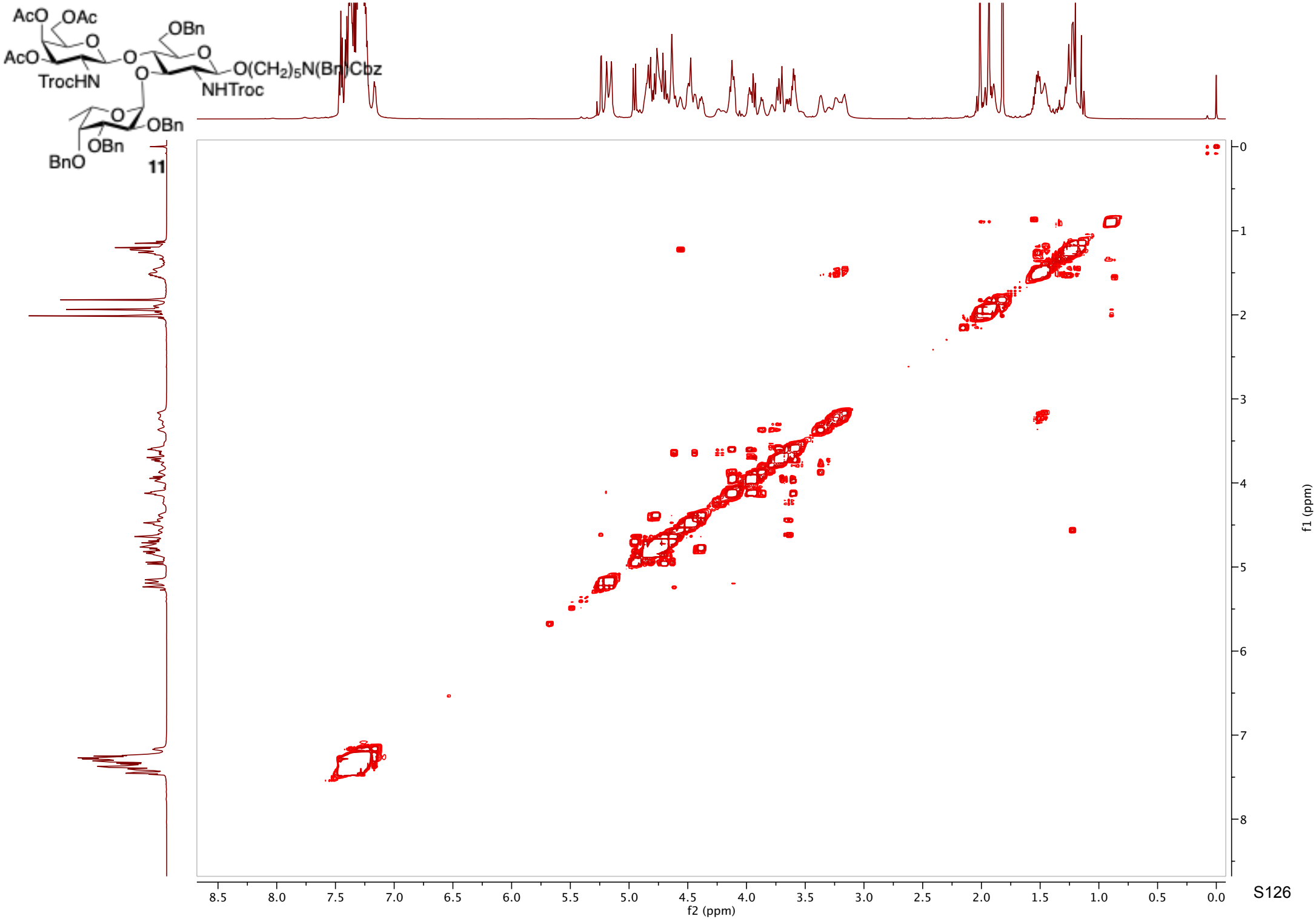


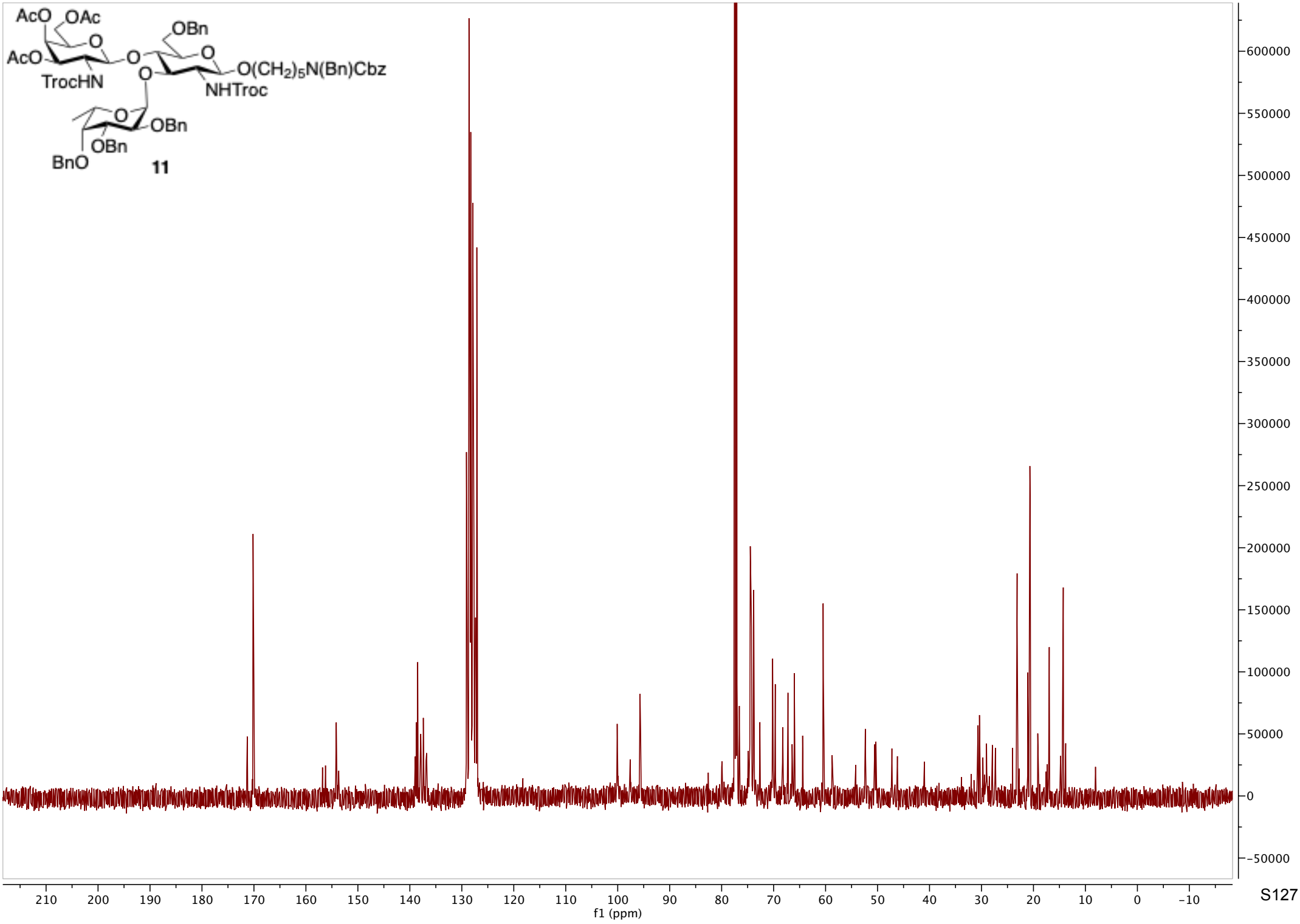
8

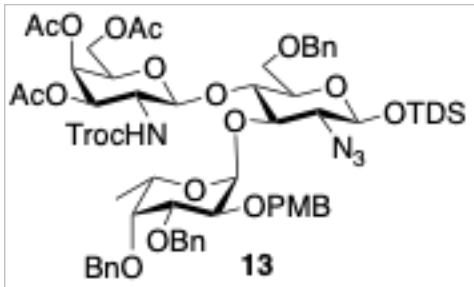
f1 (ppm)


AcO
OAc
AcO
TrocHN
OBn
O(CH2)5N(Bn)Cbz
NHTroc
OBn
OBn
BnO
11


AcO
OAc
AcO
O
TrocHN
O
OBn
O
O(CH2)5N(Bn)Cbz
NHTroc
O
OBn
OBn
BnO
11
f2 (ppm)
f1 (ppm)

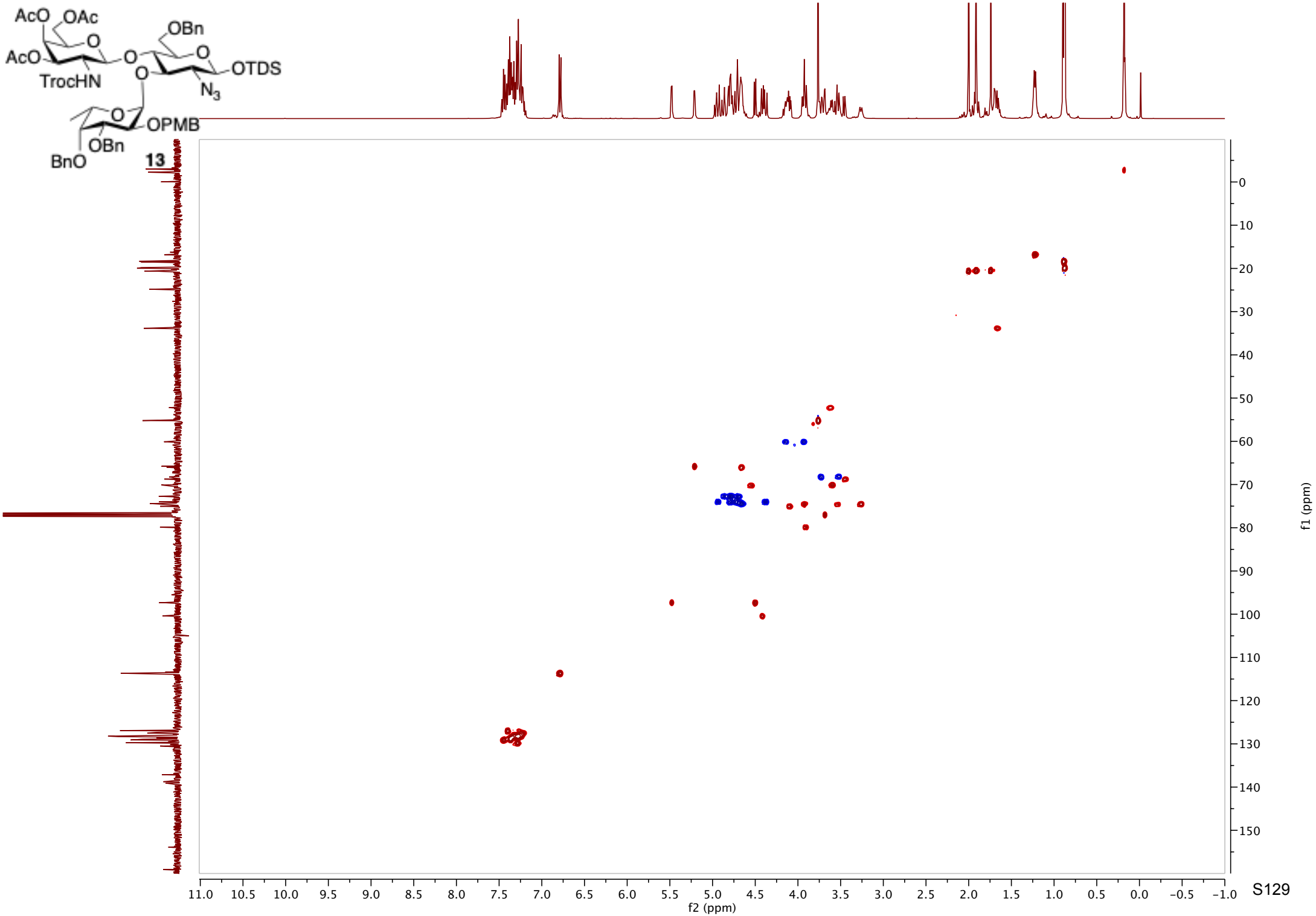

AcO
OAc
AcO
O
TrocHN
O
OBn
O
O(CH2)5N(Bn)Cbz
NHTroc
O
OBn
OBn
BnO
11
f2 (ppm)
f1 (ppm)

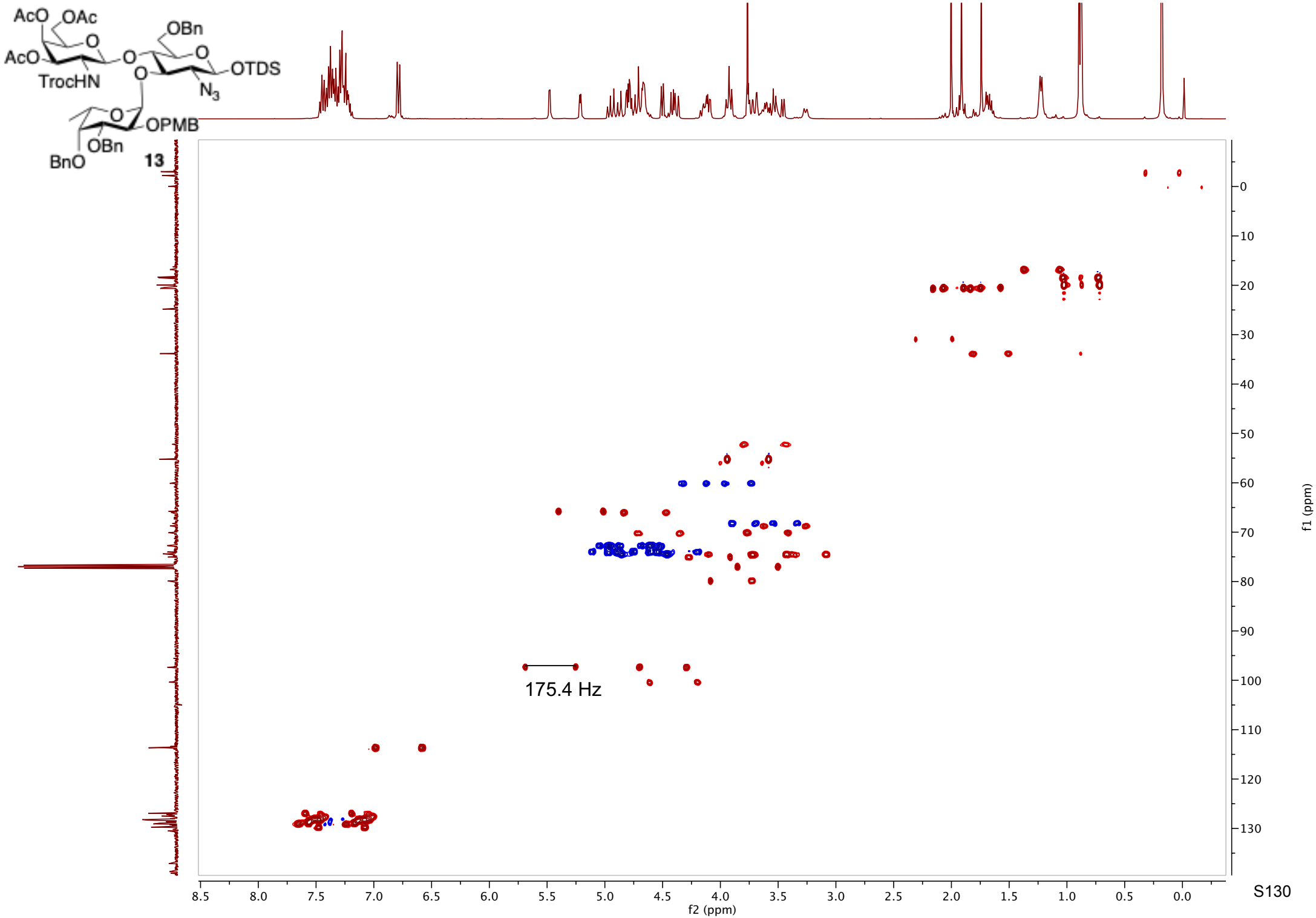

AcO
OAc
AcO
TrocHN
OBn
O(CH2)5N(Bn)Cbz
NHTroc
OBn
OBn
BnO
11
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

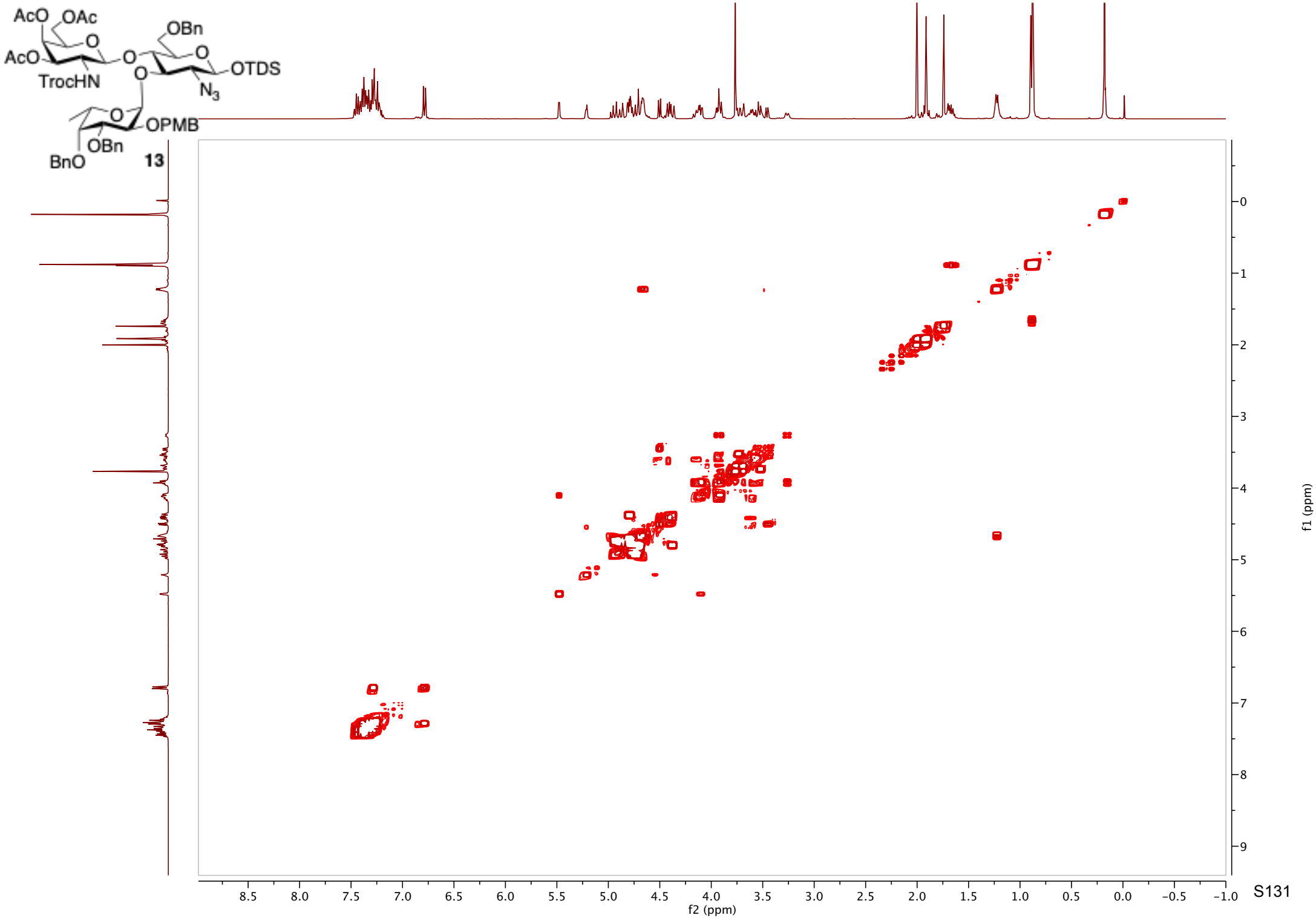

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OPMB
OBn
BnO

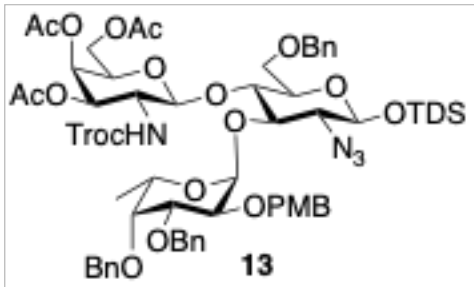
13

18.45
2.19
1.00
1.04
2.43
3.18
5.47
1.11
2.33
2.85
3.33
5.68
4.09
0.87
1.01
2.98
3.52
3.04
1.66
3.07
14.88
7.18
f1 (ppm)


AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OPMB
OBn
BnO
13
f2 (ppm)
f1 (ppm)

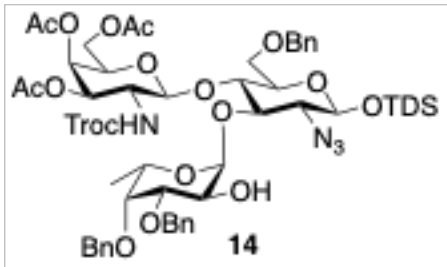

AcO
OAc
AcO
O
TrocHN
O
O
OBn
O
OTDS
N3
O
OPMB
OBn
BnO
13
175.4 Hz
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
f1 (ppm)


AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OPMB
OBn
BnO
13
f2 (ppm)
f1 (ppm)

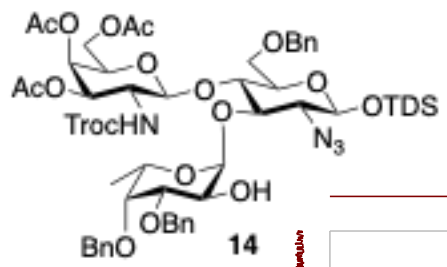

AcO
OAc
AcO
O
TrocHN
O
O
OBn
O
OTDS
N3
O
OPMB
OBn
BnO

13

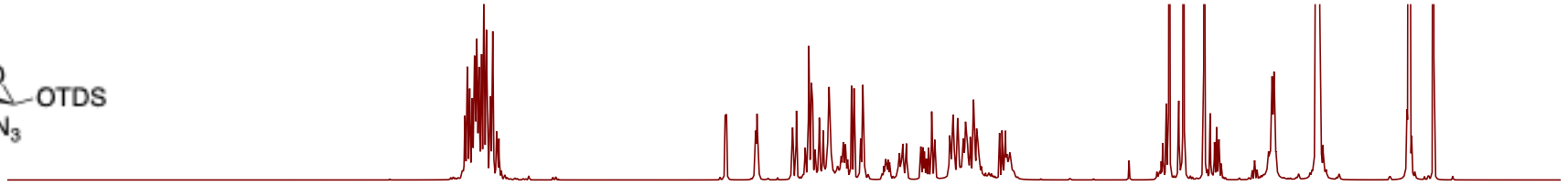
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)
19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2

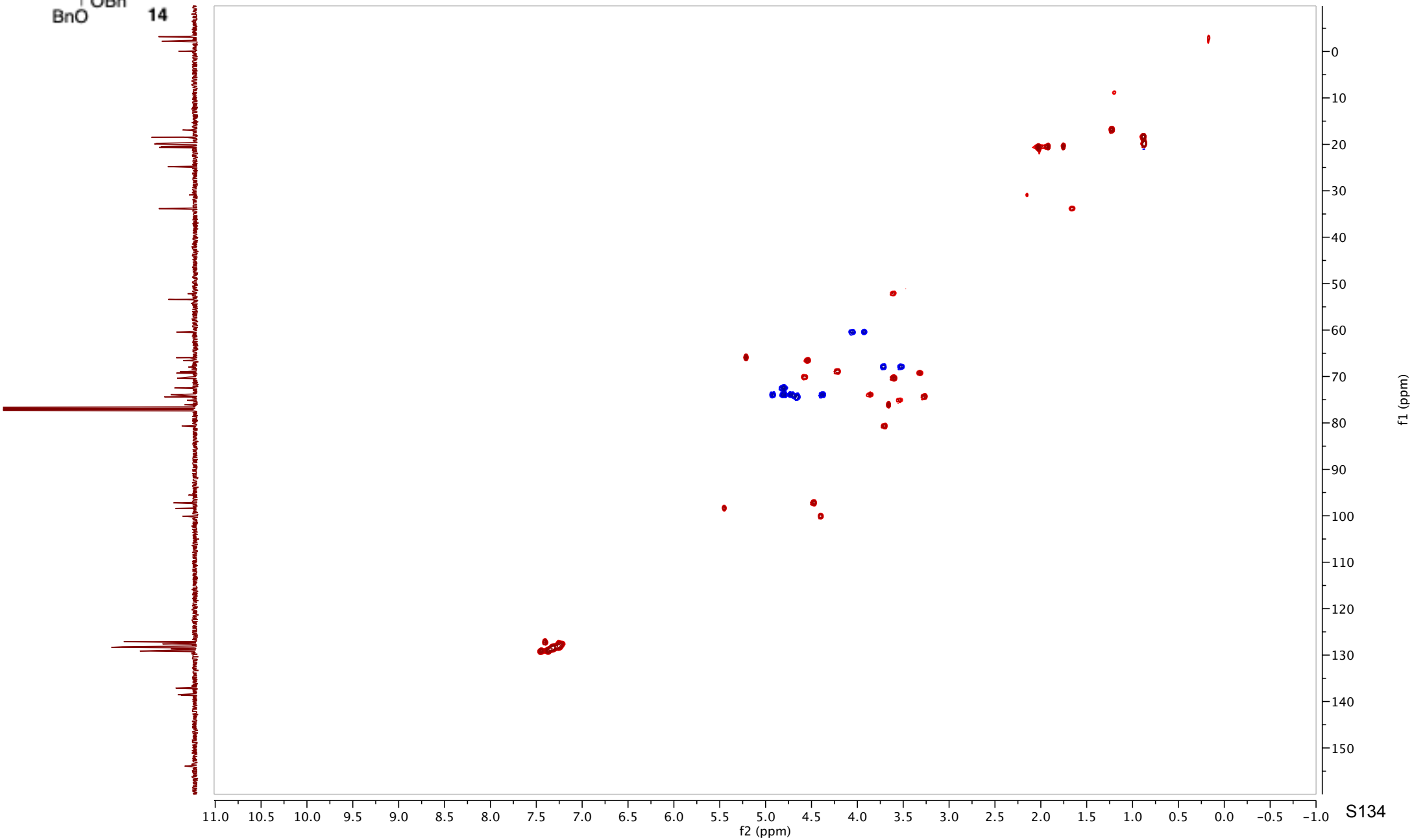

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OH
OBn
BnO
14

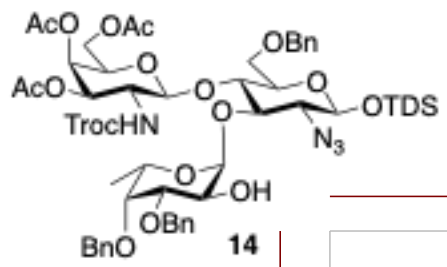
14.17
0.73
1.00
1.03
5.14
1.63
1.12
1.44
0.78
1.38
1.88
1.66
2.91
2.37
2.20
3.18
2.97
2.32
1.04
2.92
12.11
6.81
f1 (ppm)

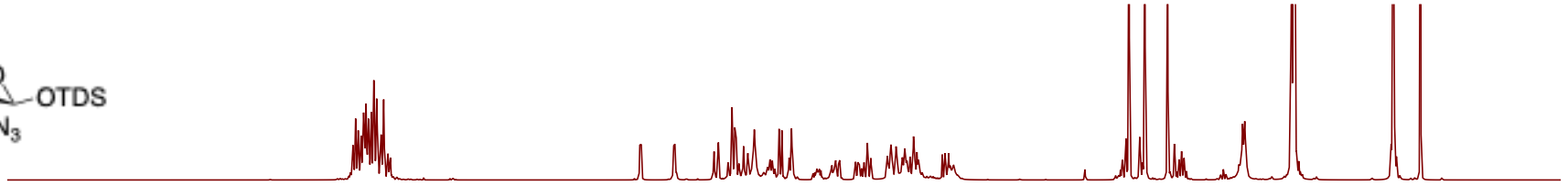

AcO
OAc
AcO
TrocHN
O
OBn
OTDS
N_3
OH
OBn
BnO

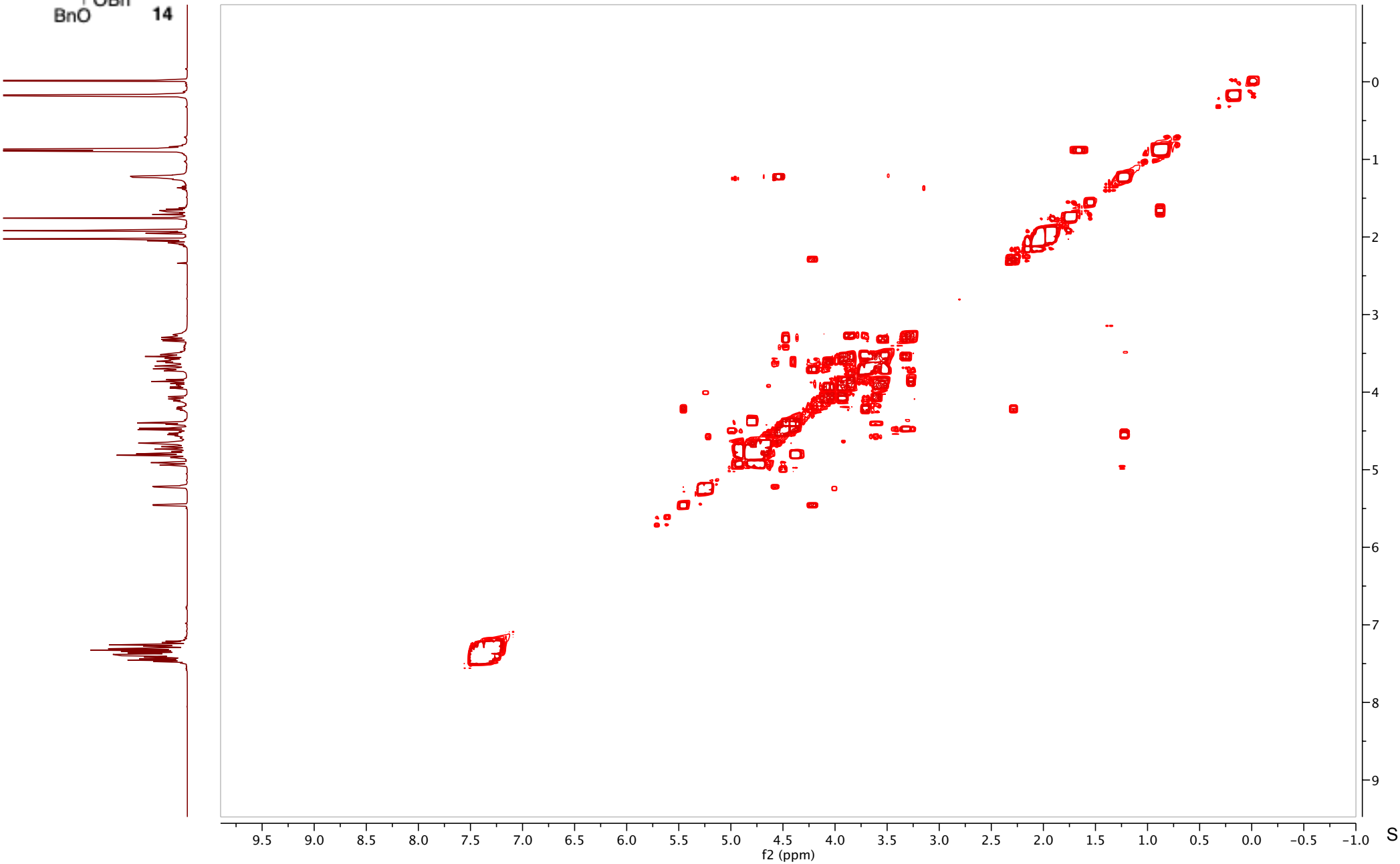
14

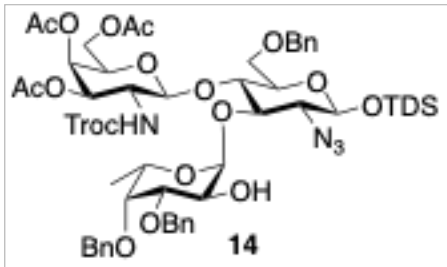



f1 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)

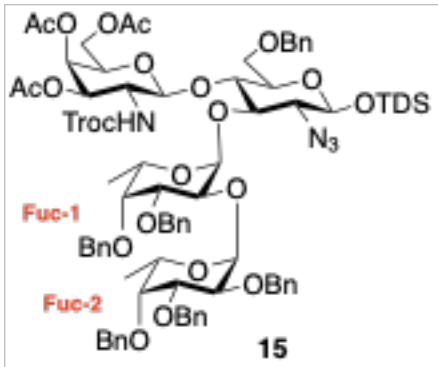

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OH
OBn
BnO
14



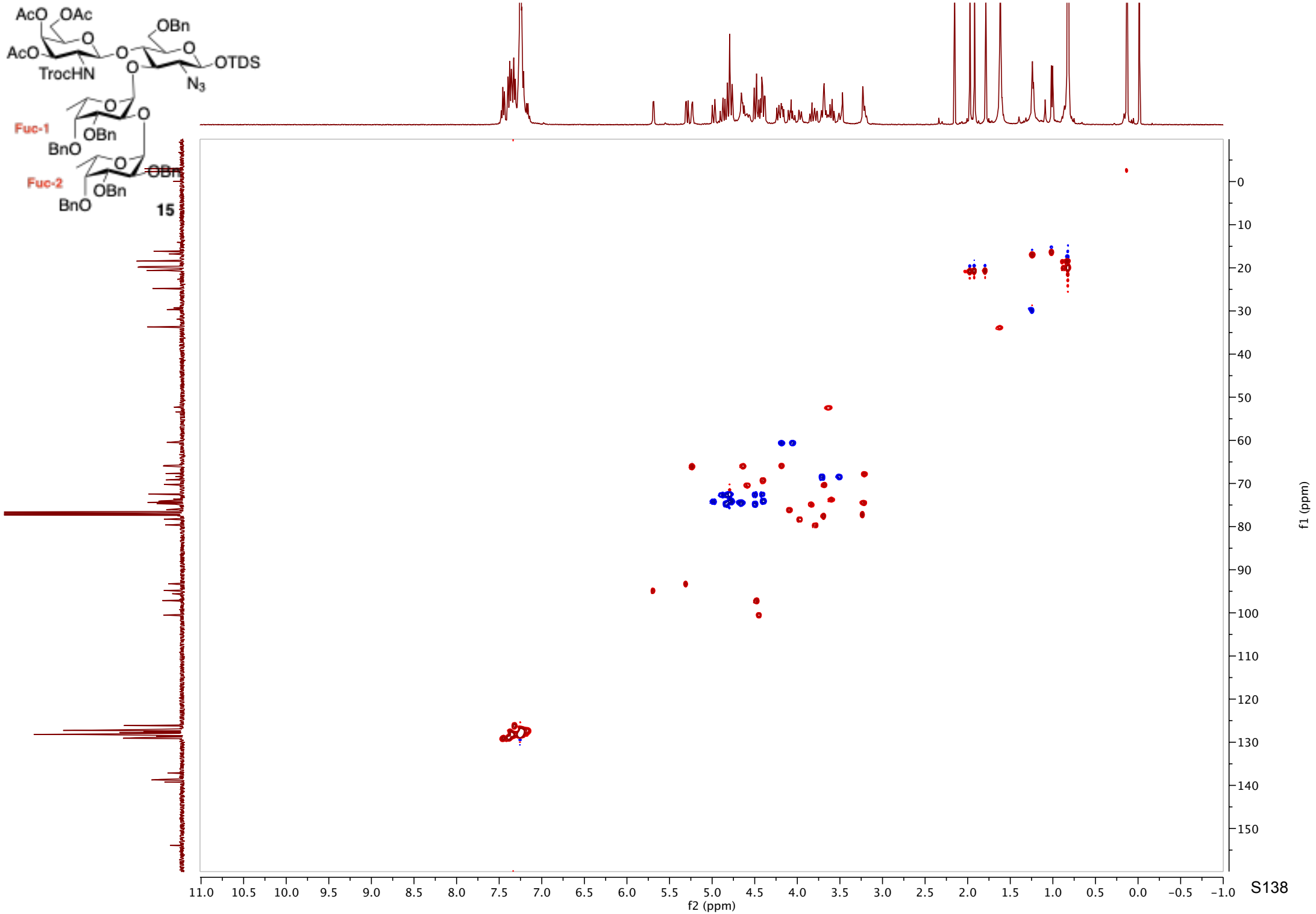

f1 (ppm)
0
1
2
3
4
5
6
7
8
9
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)

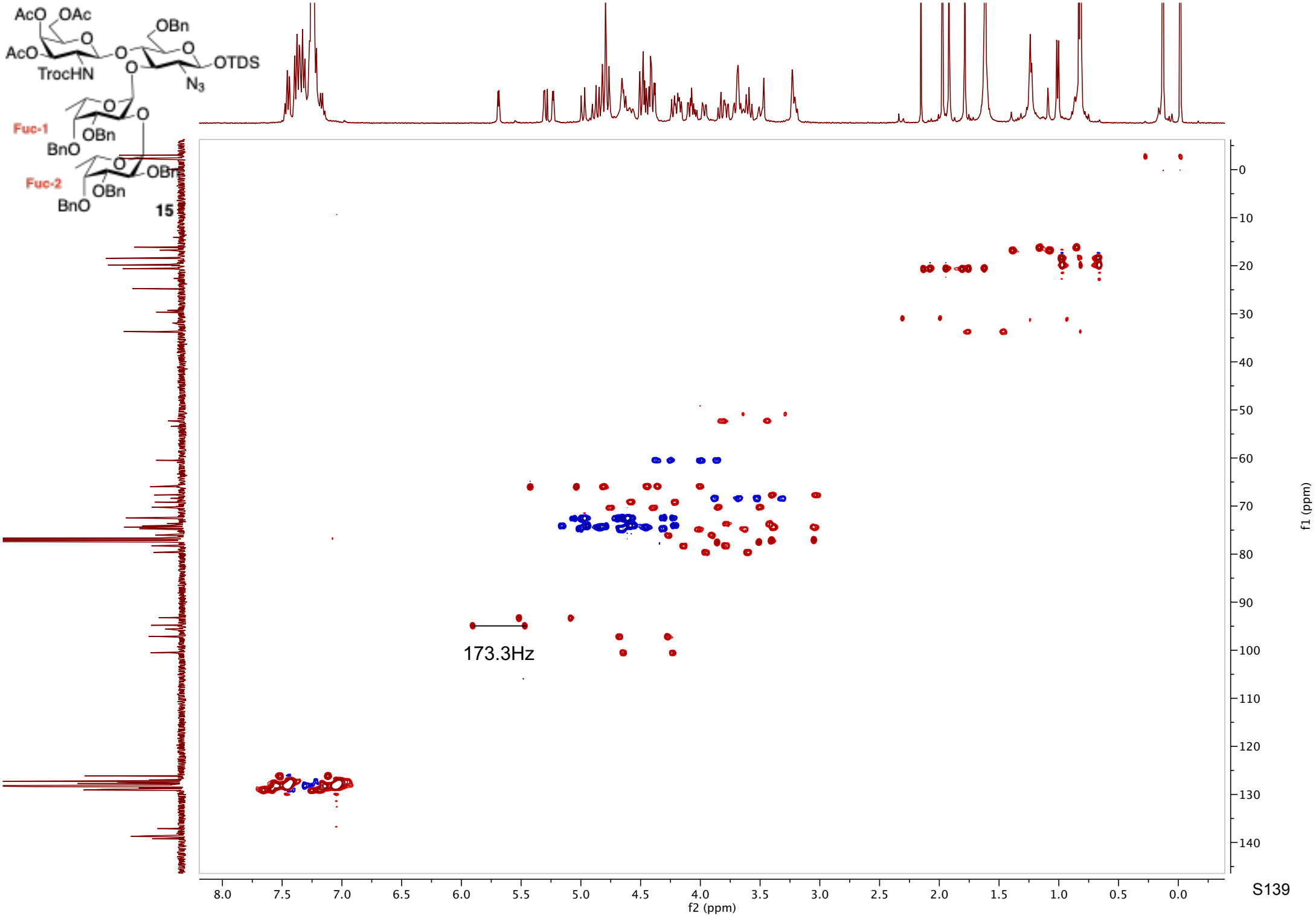

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
OH
OBn
BnO
14

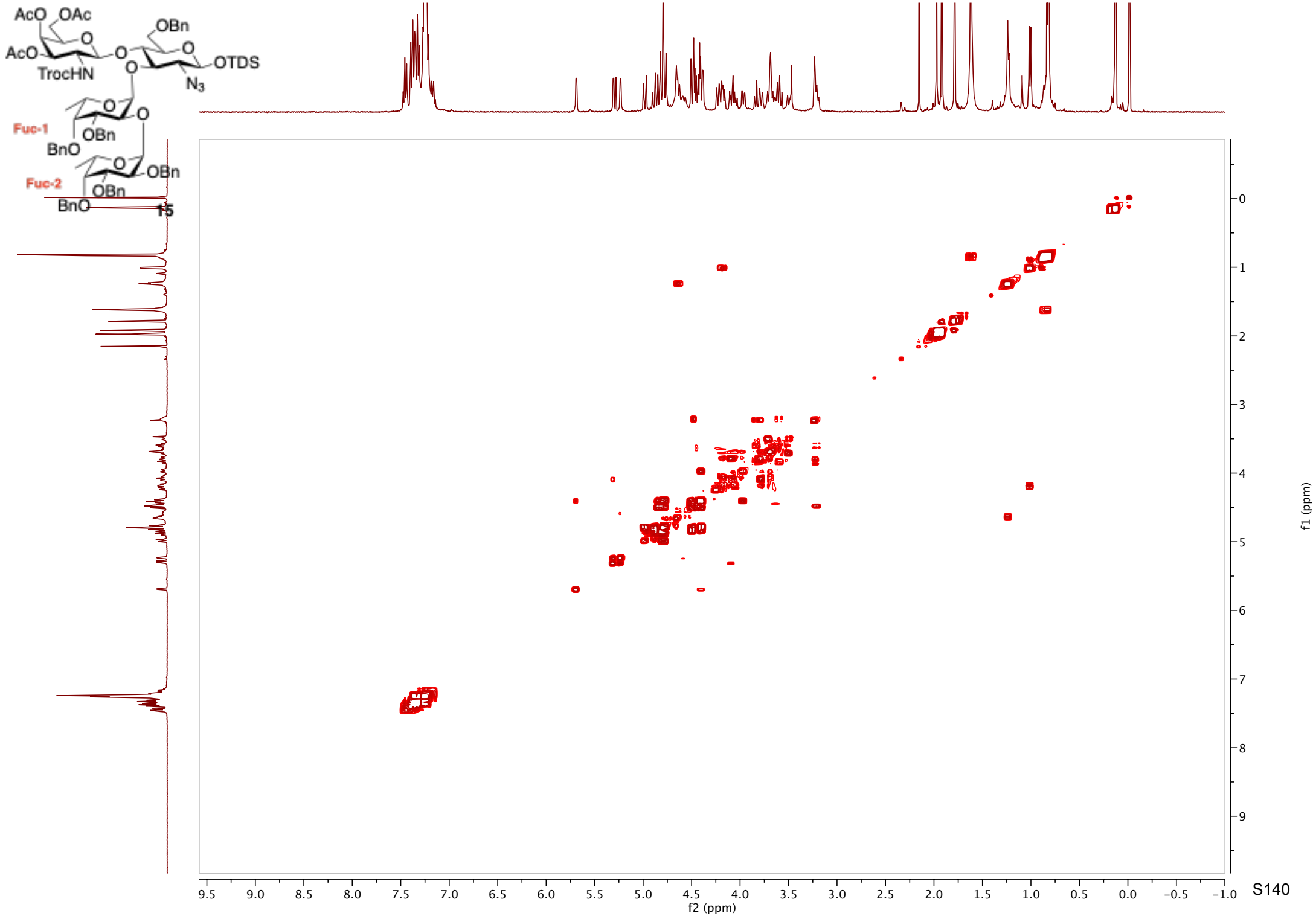
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
−2
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

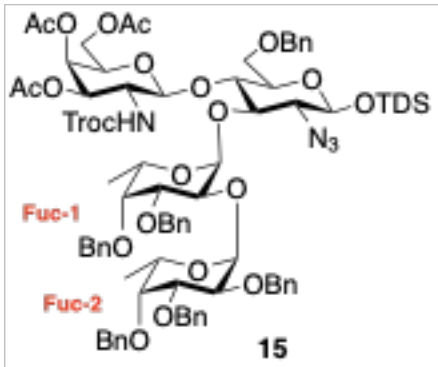

AcO
OAc
OBn
AcO
O
O
O
OTDS
TrocHN
N3
Fuc-1
OBn
BnO
OBn
Fuc-2
OBn
BnO
15

29.53
0.91
0.92
1.00
8.33
4.01
3.58
2.98
2.69
2.18
1.27
2.41
3.19
1.93
1.38
2.81
8.59
3.38
2.99
11.50
4.36
2.84
f1 (ppm)


AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
Fuc-1
BnO
OBn
Fuc-2
BnO
OBn
15
f2 (ppm)
f1 (ppm)

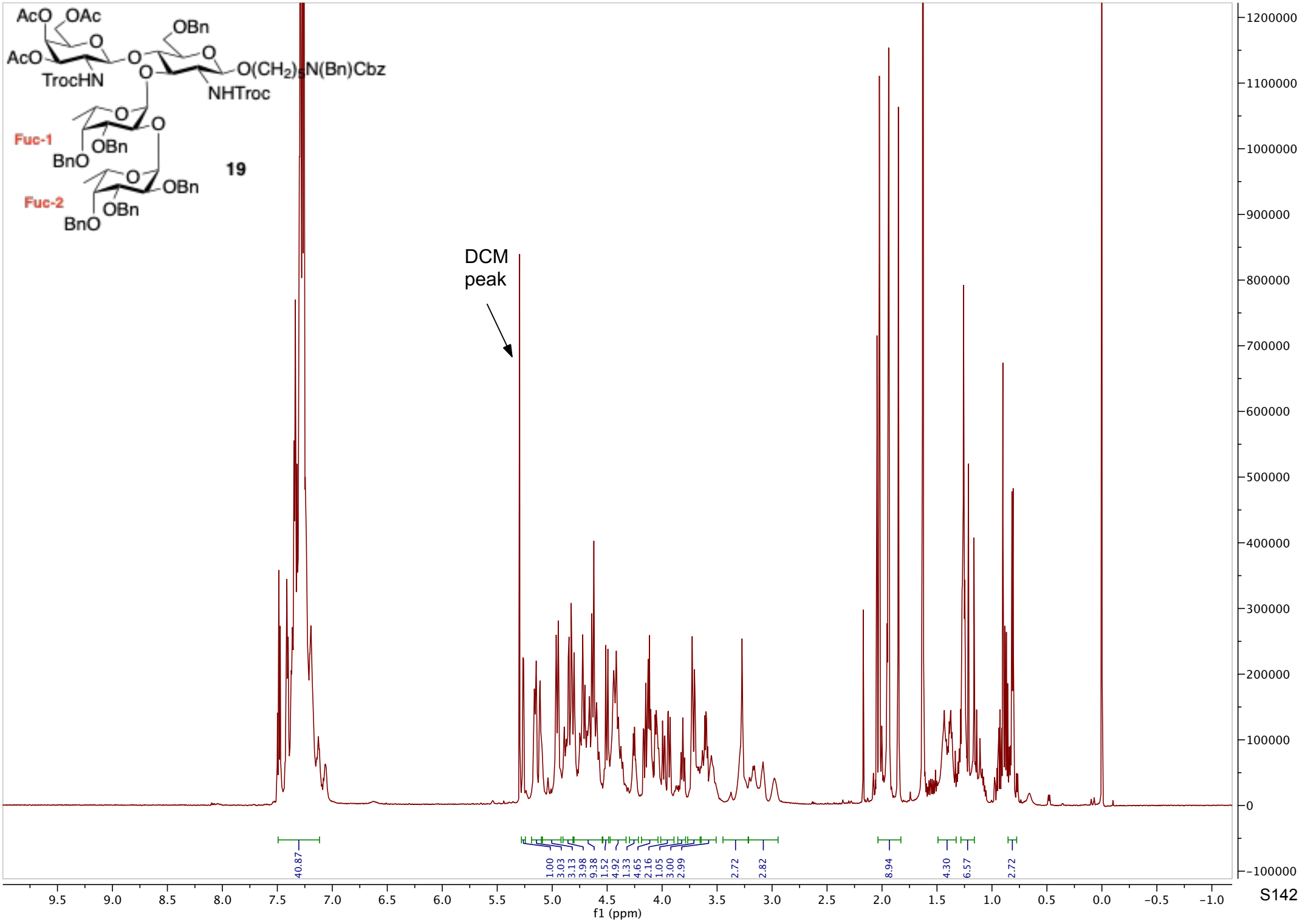

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
Fuc-1
BnO
OBn
Fuc-2
BnO
OBn
15
173.3Hz
f2 (ppm)
f1 (ppm)

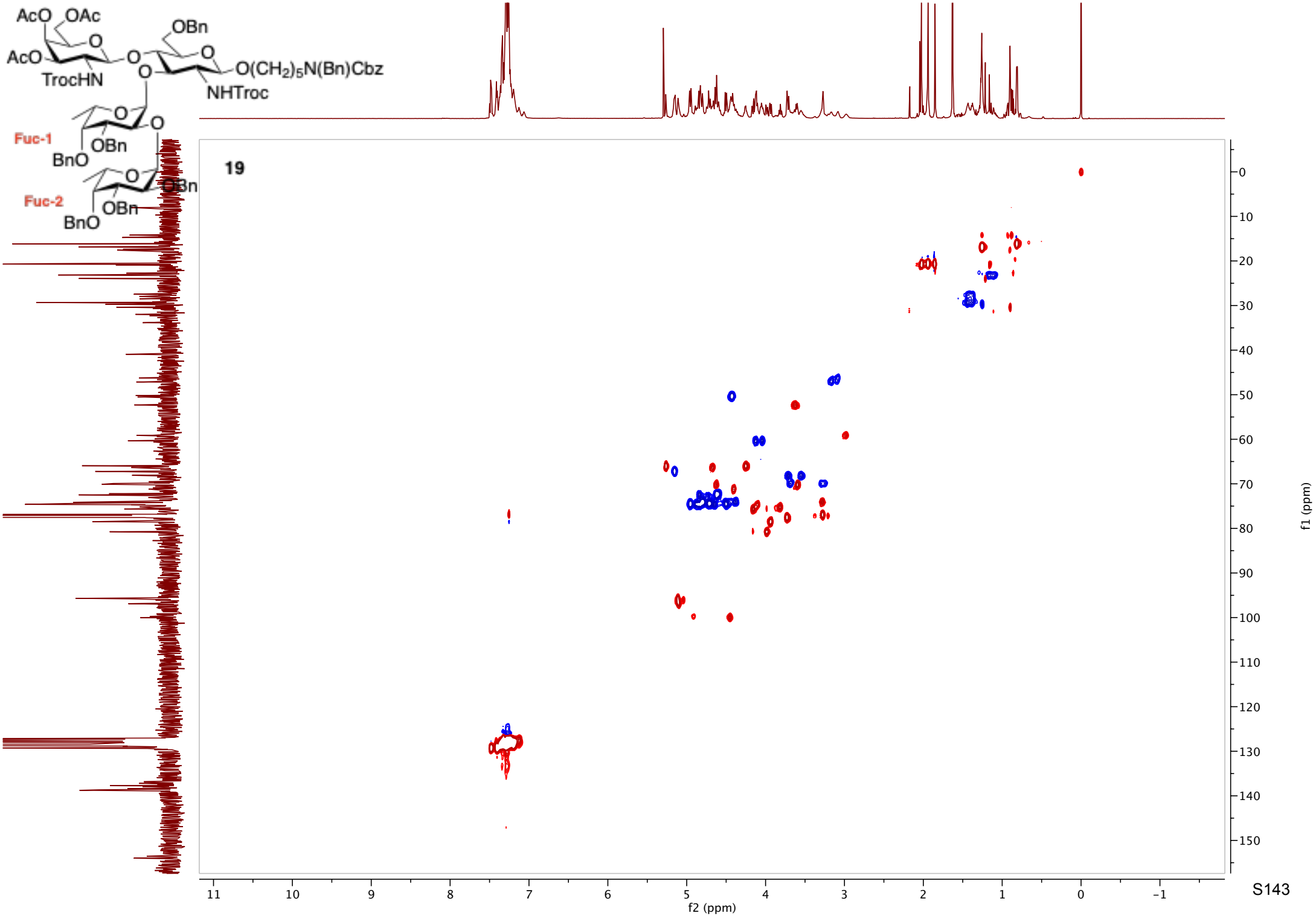

AcO
OAc
AcO
TrocHN
OBn
OTDS
N_3
Fuc-1
BnO
OBn
Fuc-2
BnO
OBn
OBn
f5
f2 (ppm)
f1 (ppm)

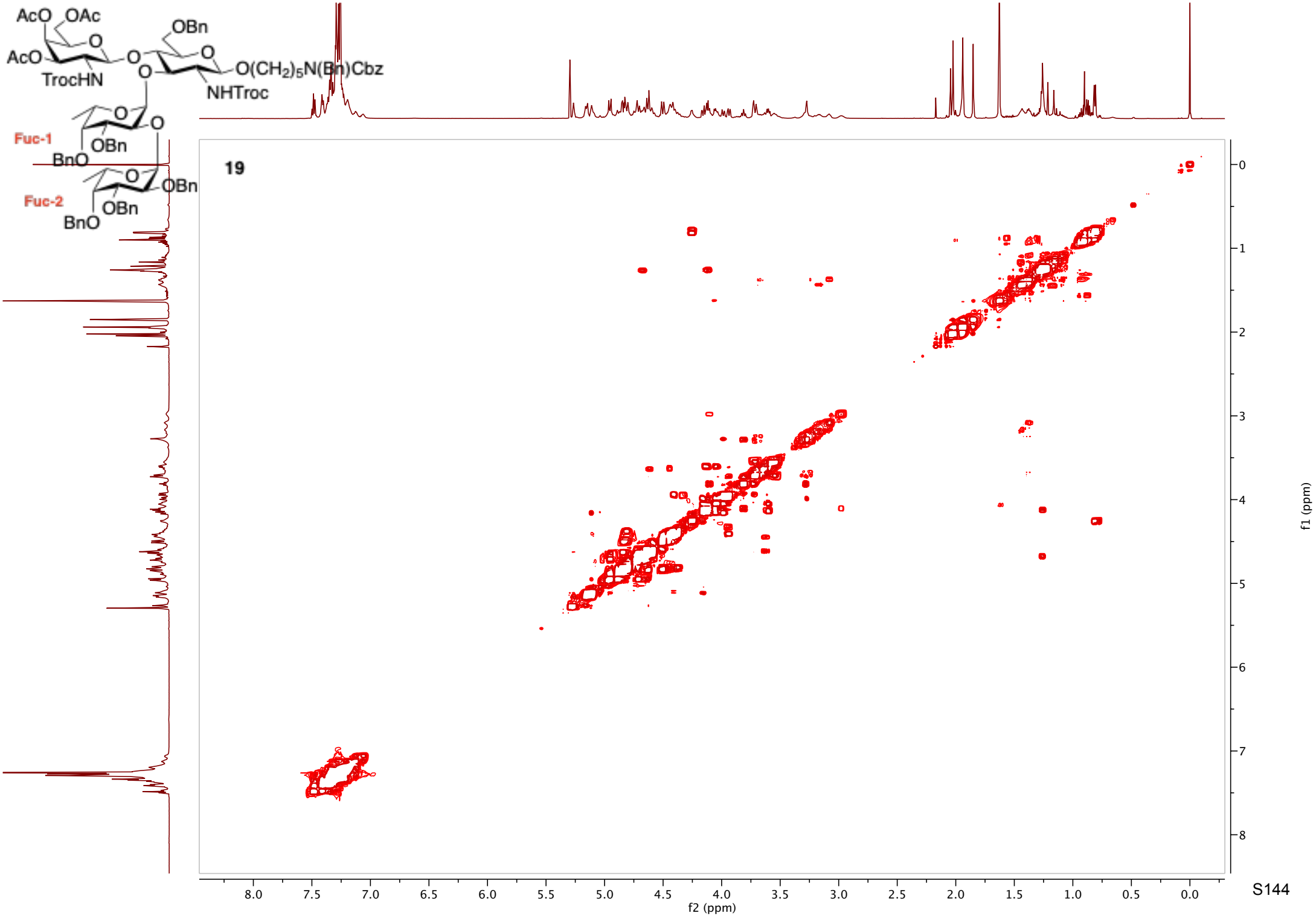

AcO
OAc
OBn
AcO
O
O
O
OTDS
TrocHN
N3
Fuc-1
OBn
BnO
Fuc-2
OBn
OBn
BnO

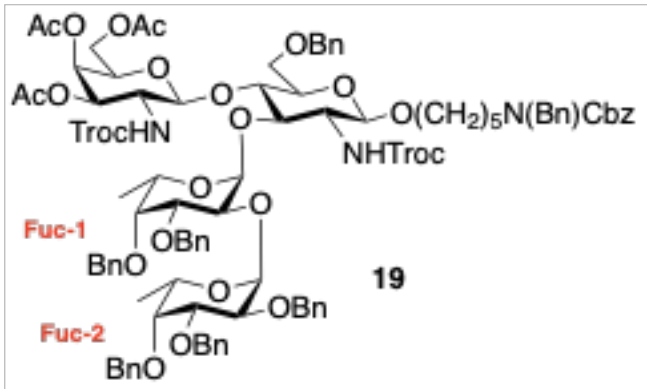
15

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)

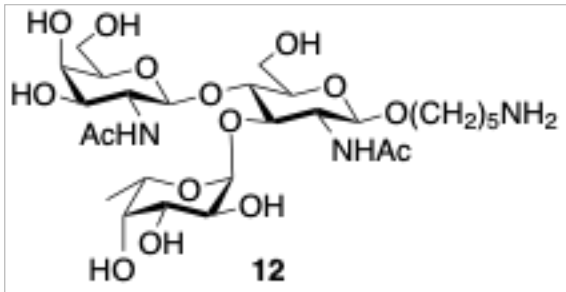

AcO
OAc
OBn
AcO
O
O
O
O(CH2)5N(Bn)Cbz
TrocHN
NHTroc
Fuc-1
OBn
BnO
19
Fuc-2
OBn
OBn
BnO
DCM
peak
40.87
1.00
3.03
3.13
3.98
9.38
1.52
4.92
1.33
4.65
2.16
1.05
3.00
2.99
2.72
2.82
8.94
4.30
6.57
2.72
f1 (ppm)


AcO
OAc
AcO
TrocHN
O
OBn
O(CH2)5N(Bn)Cbz
NHTroc
Fuc-1
BnO
OBn
Fuc-2
BnO
OBn
OBn
19
f2 (ppm)
f1 (ppm)


AcO
OAc
AcO
TrocHN
O
OBn
O
O(CH2)5N(Bn)Cbz
NHTroc
Fuc-1
BnO
OBn
Fuc-2
BnO
OBn
OBn
19
f2 (ppm)
f1 (ppm)

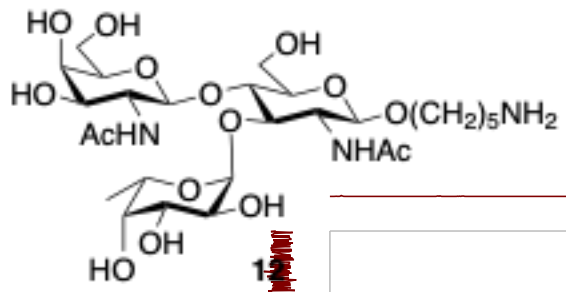

AcO
OAc
OBn
AcO
O
O
O
O(CH2)5N(Bn)Cbz
TrocHN
NHTroc
Fuc-1
OBn
BnO
19
OBn
Fuc-2
OBn
BnO

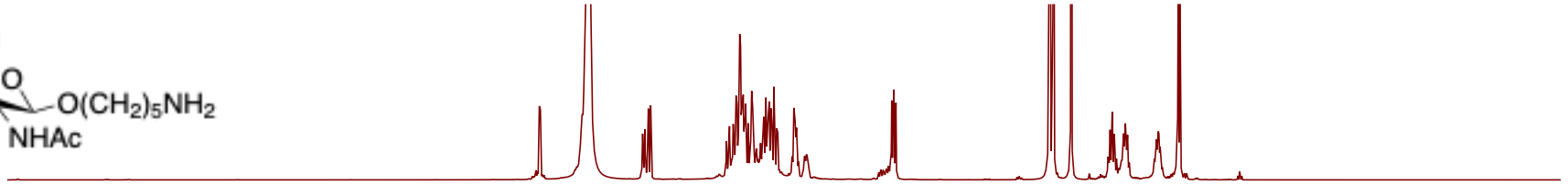
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
−50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

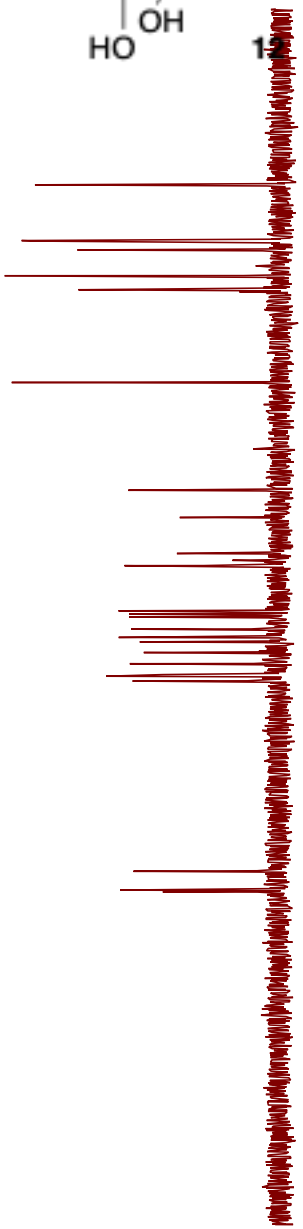

HO
OH
O
HO
O
OH
O
O
O(CH2)5NH2
AcHN
NHAc
O
OH
OH
HO

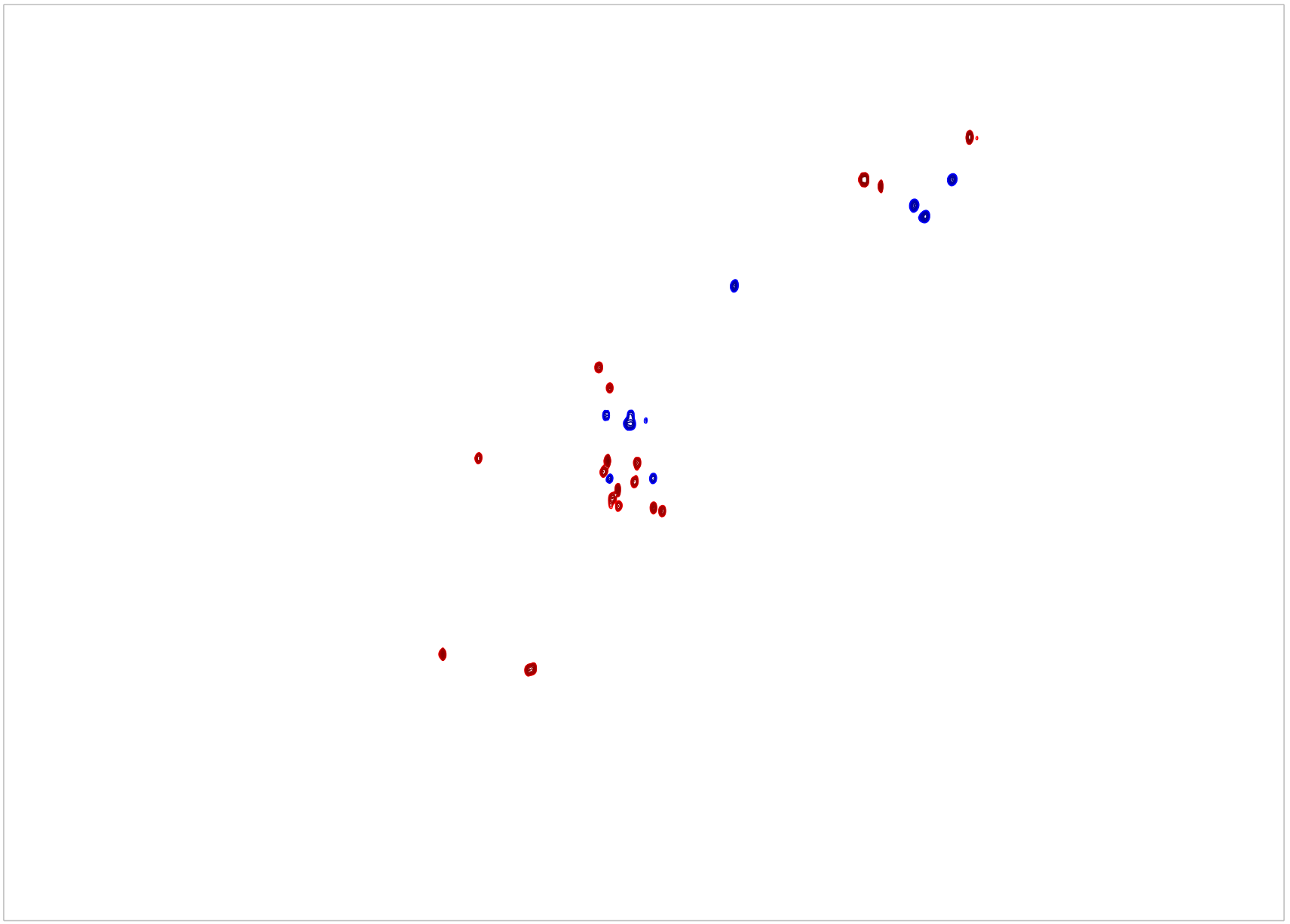
12

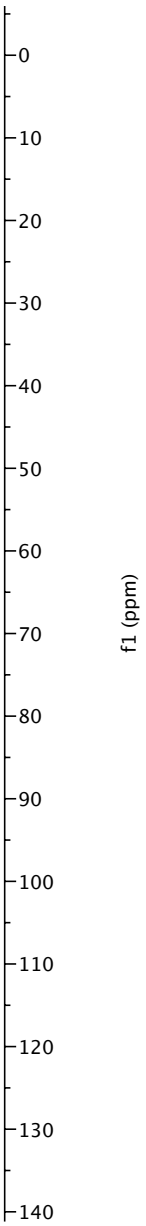
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
−500000
1.00
0.81
0.84
9.83
5.33
2.11
1.00
2.39
6.19
1.86
2.08
2.11
2.92
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

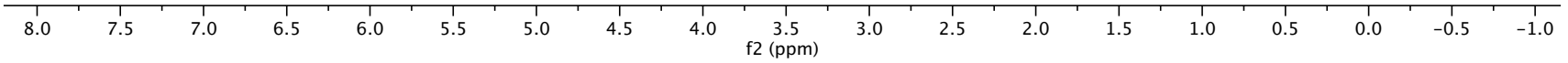

HO
OH
O
HO
O
OH
O
O
O(CH2)5NH2
AcHN
NHAc
O
OH
OH
HO
12

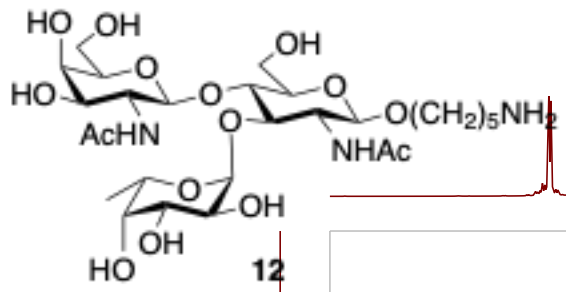


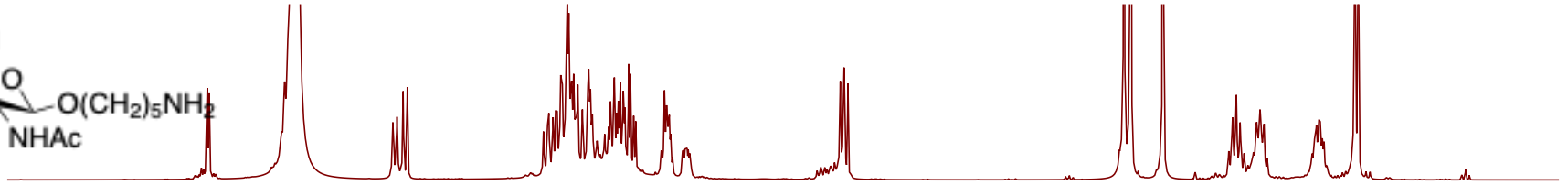


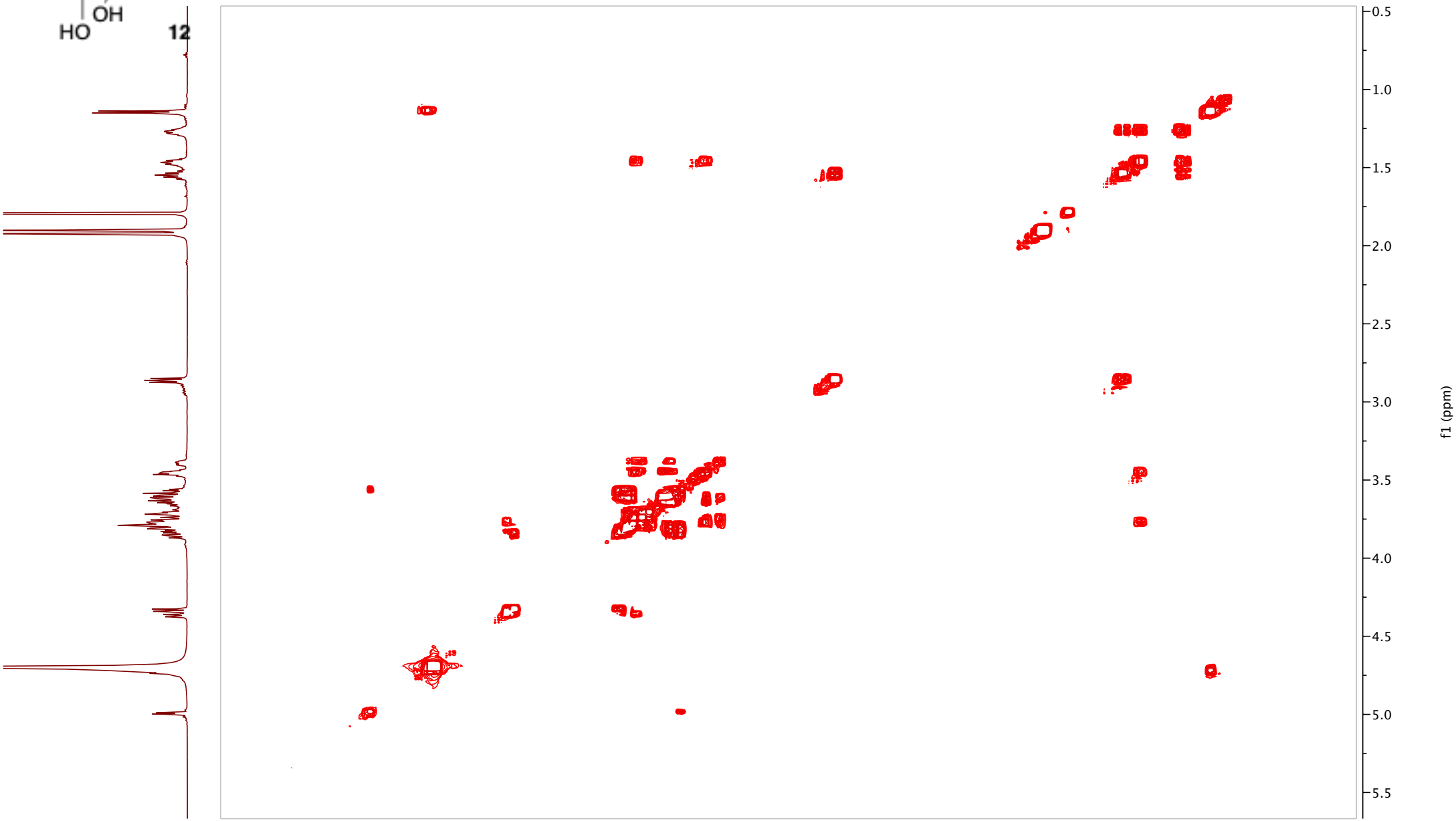


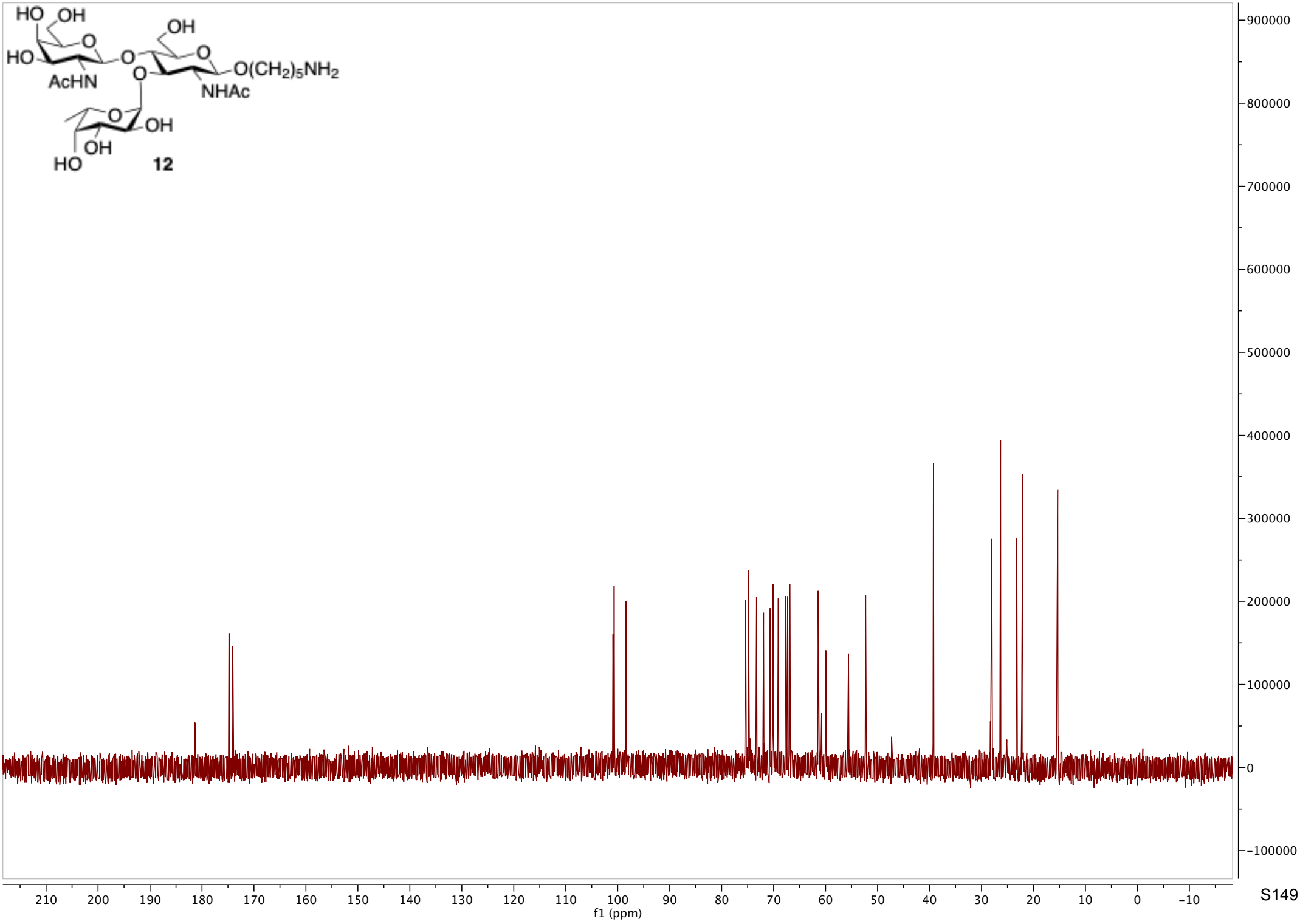

0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
f1 (ppm)

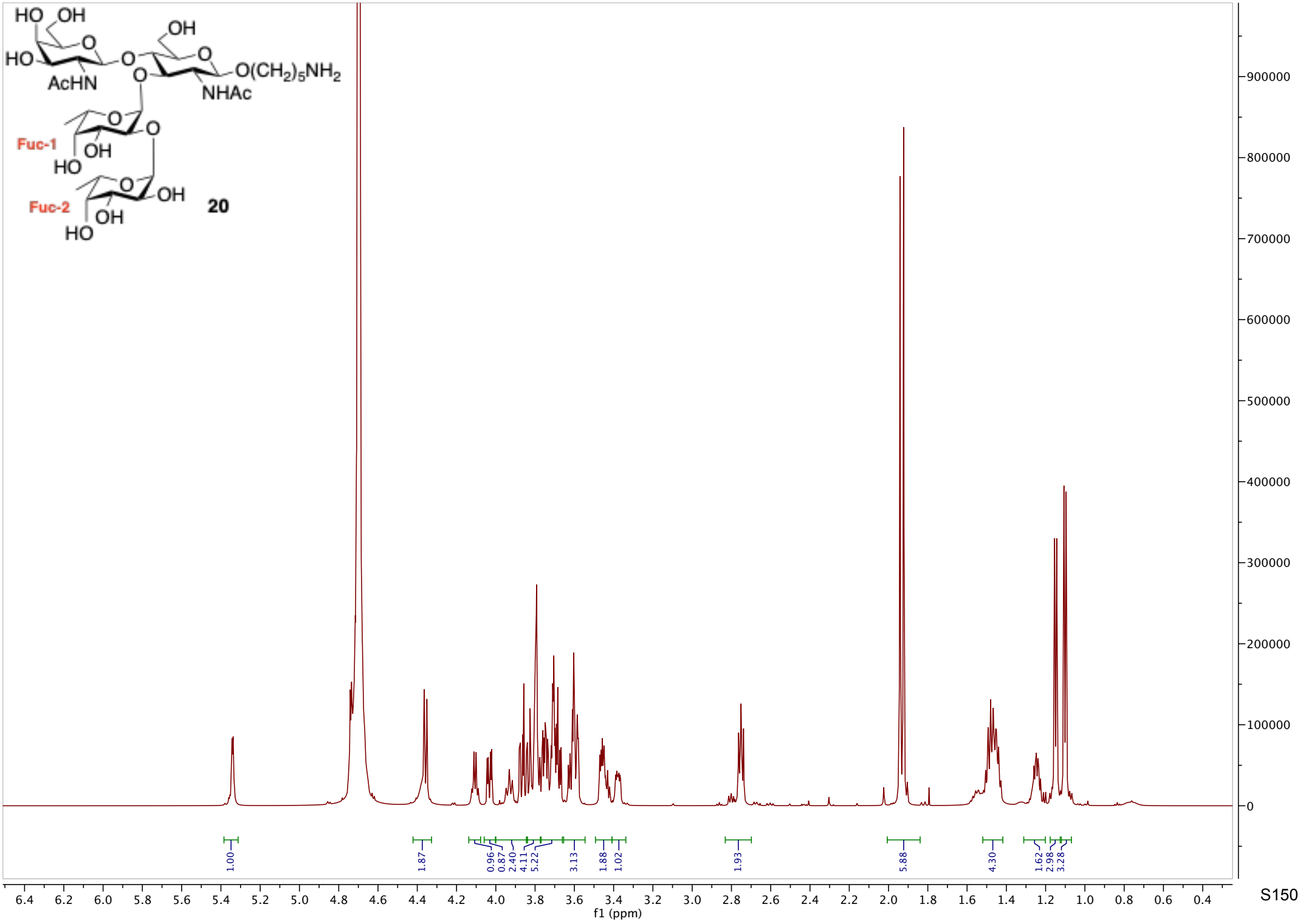

8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
f2 (ppm)

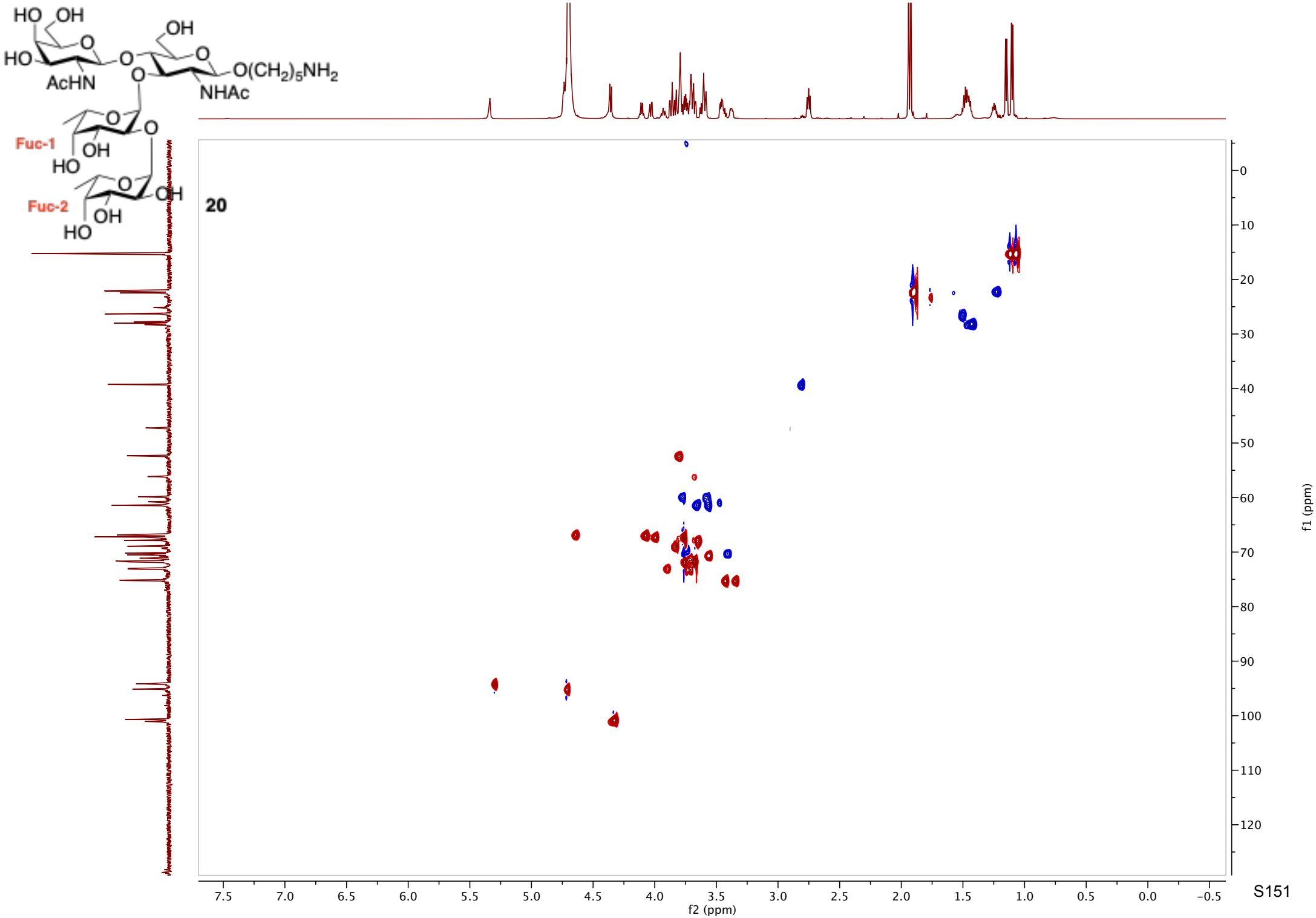

HO
OH
O
HO
O
OH
O
O
AcHN
O
O(CH2)5NH2
NHAc
O
OH
OH
HO
12

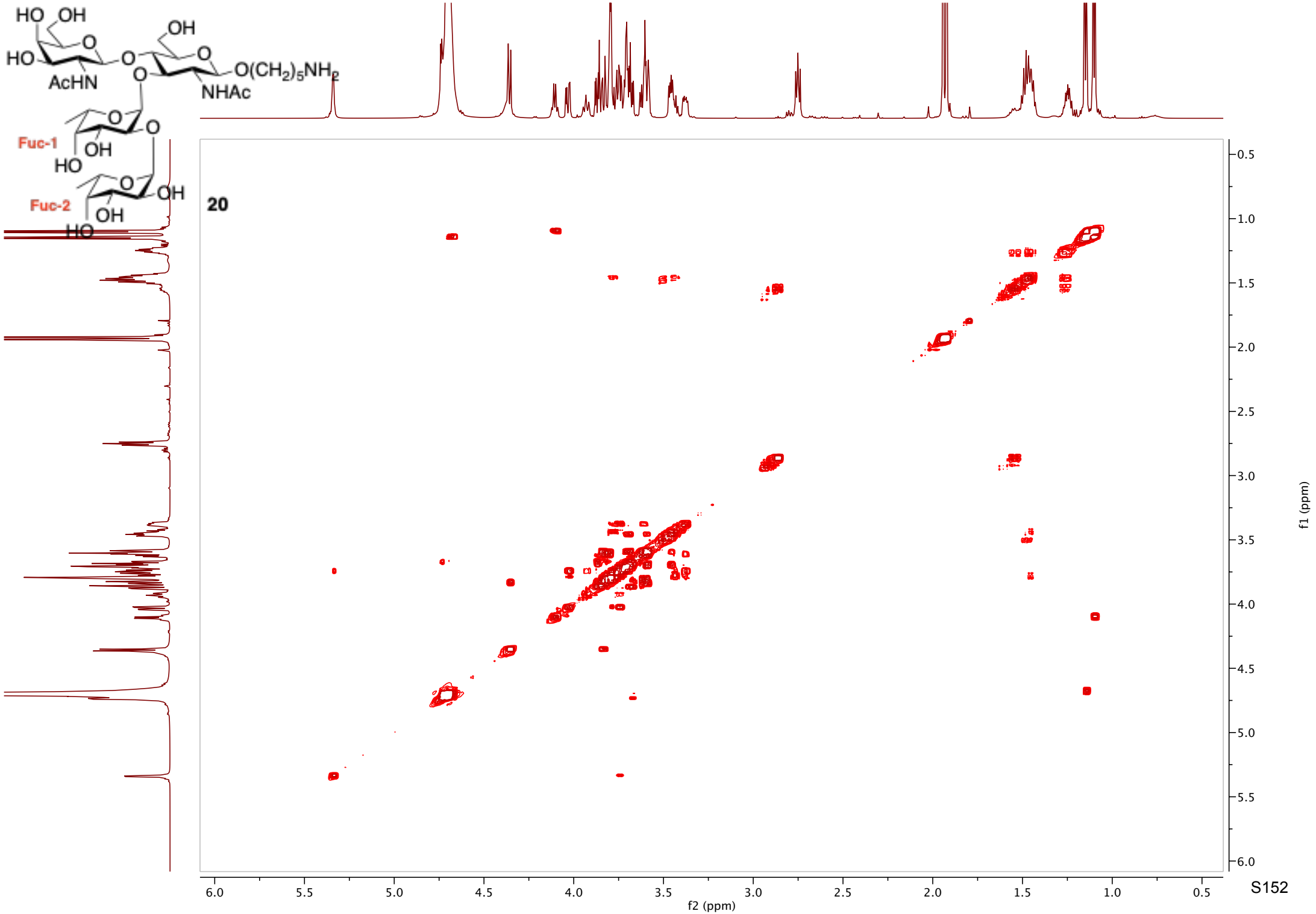


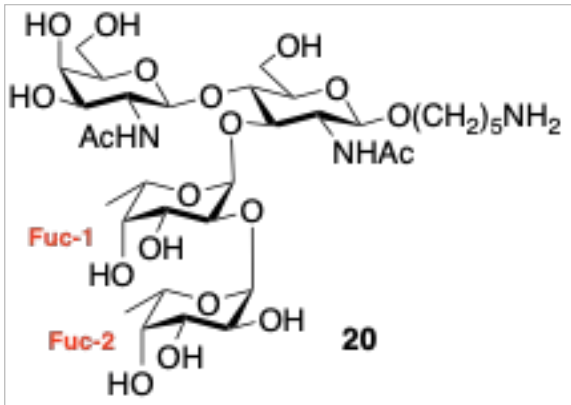

0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
f1 (ppm)
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
f2 (ppm)


HO
OH
O
HO
AcHN
O
O
OH
O
O(CH2)5NH2
NHAc
O
OH
OH
HO
12
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)


HO
OH
O
HO
AcHN
O
O
OH
O
O
O(CH2)5NH2
NHAc
Fuc-1
HO
OH
O
Fuc-2
HO
OH
O
OH
20
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
1.00
1.87
0.96
0.87
2.40
4.11
5.22
3.13
1.88
1.02
1.93
5.88
4.30
1.62
2.98
3.28
6.4
6.2
6.0
5.8
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
0.4
f1 (ppm)


HO
OH
O
HO
AcHN
O
O
OH
O
O
O(CH2)5NH2
NHAc
Fuc-1
HO
OH
O
O
Fuc-2
HO
OH
OH
20
f2 (ppm)
f1 (ppm)
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
0
10
20
30
40
50
60
70
80
90
100
110
120


HO
OH
O
HO
AcHN
OH
O
O
O
O(CH2)5NH2
NHAc
Fuc-1
HO
OH
Fuc-2
HO
OH
20
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
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
f2 (ppm)


HO
OH
O
HO
AcHN
O
OH
O
O
O(CH2)5NH2
NHAc
O
O
Fuc-1
OH
HO
O
O
Fuc-2
OH
OH
HO

20

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)