Supporting Information for

Enhanced Epimerization of Glycosylated Amino Acids During Solid Phase Glycopeptide Synthesis

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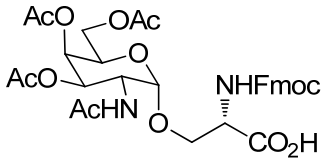
General methods

Unless otherwise stated, reagents were purchased from commercial suppliers and used without purification. 2-Chlorotrityl chloride resin, Fmoc-Ser(Trt)-OH, Fmoc-D-Ser(Trt)-OH, Fmoc-OSu were purchased from AnaSpec, Inc. (San Jose, CA). Fmoc-6-aminohexanoic acid (Fmoc-Hex-OH), Fmoc-Gly-OH, and Fmoc-Pro-OPfp were purchased from Novabiochem (Darmstadt, Germany). 2-(7-Aza-1H-benzotriazol-1-yl)-*N,N,N',N'*-tetramethyl uronium hexafluorophosphate (HATU), 1-hydroxy-7-azabenzotriazole (HOAt), 2-(1H-benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HBTU), *N*-hydroxybenzotriazole (HOBt), *N,N*′-Dicyclohexylcarbodiimide (DCC), benzotriazol-1-yl-oxy-tris-pyrrolidino-phosphonium hexafluorophosphate (PyBOP), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), *N,N*-diisopropylethylamine (DIEA), *N*-methylmorpholine (NMM), 2,4,6-trimethylpyridine (TMP) were purchased from Sigma (St. Louis, MO). All RP-HPLC purifications were carried using a preparative C-18 reversed phase column (VYDAC® 218 TP Protein & Peptide C18 22 mm × 250 mm) on a Waters PropLC 4000 system (HPLC) with a waters 2996 photodiode array detector at room temperature. All ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz or 500 MHz Varian spectrometer. The mass spectra were recorded on Shimadzu Axima-CFR MALDI-TOF or on Agilent LC/MSD SL mass spectrometers. Analysis of yields and epimerization were recorded on an Agilent 1200 Series HPLC using Waters XTerra® RP 18 (5μm 4.6 mm × 250 mm) reversed phase column.

Preparation of Fmoc-protected glyco-amino acids

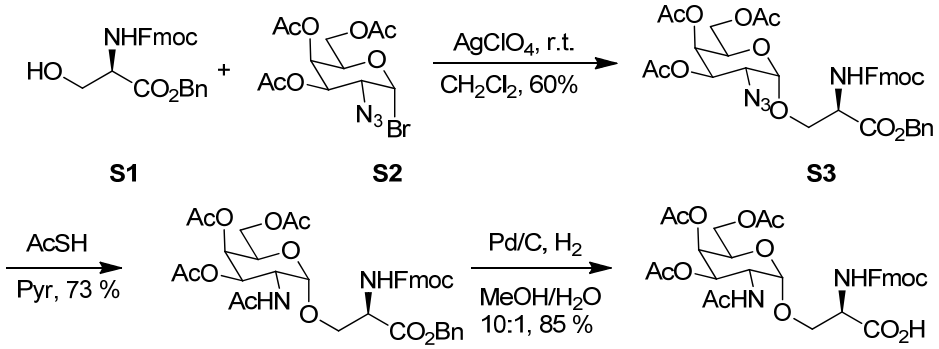
Fmoc-Ser(Ac$_3$GalNAcα)-OH (7)



7

N-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-tri-*O*-α-D-galactopyranosyl)-L-serine (**7**) was prepared according to the previously reported method.[1] ^{1}H-NMR (400 MHz, *N,N*-dimethylformamide-d$_7$) δ 7.93 (d, *J* = 7.5 Hz, 2H, H-Fmoc), 7.88 (d, *J* = 8.8 Hz, 1H, NH-S), 7.83 (d, *J* = 8.7 Hz, 1H, NH-GalNAc), 7.74 (dd, *J* = 7.3, 2.3 Hz, 2H, H-Fmoc), 7.44 (t, *J* = 7.5 Hz, 2H, H-Fmoc), 7.34 (t, *J* = 7.5 Hz, 2H, H-Fmoc), 5.41 (d, *J* = 2.3 Hz, 1H, H4'), 5.17 (dd, *J* = 11.7, 3.2 Hz, 1H, H3'), 5.01 (d, *J* = 3.5 Hz, 1H, H1'), 4.47-4.50 (m, 1H, S$^{\alpha}$), 4.33-4.40 (m, 4H, H2' {4.38}, H5' {4.33}, CH$_2$-Fmoc {4.33}), 4.29 (m, 1H, H-Fmoc), 4.08-4.16 (m, 2H, H6'), 3.97-4.04 (m, 2H, S$^{\beta}$), 2.14 (s, 3H, CH$_3$-Ac), 1.99 (s, 3H, CH$_3$-Ac), 1.93 (s, 3H, CH$_3$-Ac), 1.89 (s, 3H, CH$_3$-Ac); ^{13}C-NMR (100 MHz, *N,N*-dimethylformamide-d$_7$) δ 176.1, 174.6, 174.4, 174.2, 160.9, 148.6, 145.5, 132.1, 131.5, 129.7, 124.5, 102.9, 72.8, 72.4, 71.8, 71.2, 70.8, 66.2, 59.0, 51.8, 51.4, 26.5, 24.3, 24.25, 24.2. HRMS calcd for $C_{32}H_{36}N_2O_{13}$ $[M + Na]^+$ 679.2110, measured 679.2115.

Fmoc-D-Ser(Ac$_3$GalNAcα)-OH (8)



S1 **S2** **S3** **S4** **8**

The unnatural glyco-amino acid, Fmoc-D-Ser(Ac$_3$GalNAc*α*)-OH **8**, was synthesized with similar procedures reported for **7**. Briefly, the bromide donor **S2** (2.64 g, 6.70 mmol), *N*-Fmoc-D-serine

benzyl ester **S1** (2.33 g, 5.58 mmol), and 2 g 4 Å molecular sieve were added to a flask under argon. The mixture was dissolved in 20 mL CH_2Cl_2, then silver perchlorate (2.31 g, 11.2 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. The mixture was filtered, concentrated, and the residue was purified by flash chromatography on silica gel (120g) with EtOAc/Hexane (1/3) to give compound **S3** (2.44 g, 60 %, α:β=5:1) as a white solid. Reductive acetylation using thiolacetic acid/pyridine (2/1, v/v, 3 mL) produced the fully protected Fmoc-D-Ser(Ac_3GalNAc*α*)-OBn **S4** in a 73% yield. Hydrogenation of **S4** with10% Pd/C in MeOH/H_2O/Formic acid (10/1/1, v/v/v, 12 mL) followed by RP- HPLC purification using a 0-48% acetonitrile/H_2O (0.1% TFA) gradient over 45 min to provide compound **8** in 71% yield as white solid.

***N*-(9H-fluoren-9-ylmethoxycarbonyl)-D-serine benzyl ester (S1)**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.26-7.39 (m, 7H), 5.69 (d, *J* = 7.0 Hz, 1H), 5.20 (Br, 2H), 4.35-4.47 (m, 3H), 4.18 (t, *J* = 6.7 Hz, 1H), 3.99 (d, *J* = 8.5 Hz, 1H), 3.91 (d, *J* = 10.3 Hz, 1H); ^{13}C-NMR(100 MHz, $CDCl_3$) δ 170.1, 155.5, 143.6, 141.3, 141.2, 135.0, 128.6, 128.5, 128.2, 127.7, 127.1, 127.0, 125.0, 120.0, 119.9, 67.5, 67.2, 63.3, 56.1, 47.1. ESI MS calcd for $C_{25}H_{23}NO_5$ $[M + Na]^+$ 440.16, measured 440.1.

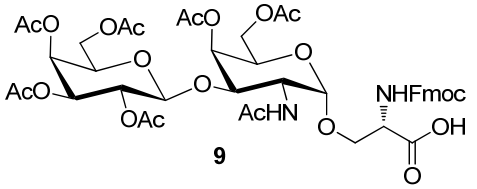
***N*-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-azido-2-deoxy-3,4,6-tri-*O*-α-D-galactopyranosyl)-D-serine benzyl ester (S3)**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H). 7.57 (d, *J* = 7.4 Hz, 2H), 7.26-7.39 (m, 9H), 5.84 (d, *J* = 8.4 Hz, 1H), 5.35 (d, *J* = 12.0 Hz, 1H), 5.19 (d, *J* = 3.0 Hz, 1H), 5.10 (d, *J* = 11.9 Hz, 1H), 4.91 (d, *J* = 3.5 Hz, 1H), 4.61-4.64 (m, 1 H), 4.33-4.42 (m, 2H), 4.17-4.22 (m, 2H), 3.79-3.90 (m, 2H), 3.69 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.63 (t, *J* = 6.1 Hz, 1H), 3.55 (dd, *J* = 11.2, 3.6 Hz, 1H), 2.09 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.2, 169.2, 155.9, 143.6, 141.3, 135.1, 128.7, 125.1, 119.9, 169.5, 169.9, 98.7, 67.5, 67.0, 61.9, 54.1, 47.1, 20.61, 20.6, 20.5. MALDI MS calcd for $C_{37}H_{38}N_4O_{12}$ $[M + Na]^+$ 753.2378, measured 753.2382.

***N*-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-tri-*O*-α-D-galactopyranosyl)-D-serine benzyl ester (S4)**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.25-7.38 (m, 9H), 6.02 (d, *J* = 9.3 Hz, 1H), 5.77 (d, *J* = 8.0

Hz, 1H), 5.29 (d, *J* = 11.9 Hz, 1H), 5.10-5.14 (m, 2 H), 4.81-4.88 (m, 2H), 4.58-4.61 (m, 1H), 4.50-4.52 (m, 1H), 4.43 (d, *J* = 6.5 Hz, 2H), 4.18 (t, *J* = 6.6 Hz, 1H), 3.97 (dd, *J* = 10.3, 4.2 Hz, 1H), 3.90 (d, *J* = 6.3 Hz, 2H), 3.71-3.74 (m, 2H), 2.10 (s, 3H), 1.95 (s, 3H), 1.94 (s, 3H), 1.88 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.7, 170.32, 170.3, 170.2, 169.7, 156.0, 143.6, 141.3, 134.8, 128.9, 128.8, 128.7, 127.7, 127.1, 124.8, 120.0, 98.5, 68.7, 68.1, 67.9, 67.2, 67.1, 66.9, 62.1, 54.4, 47.5, 47.0, 23.0, 20.7, 20.66, 20.6. MALDI MS calcd for $C_{39}H_{42}N_2O_{13}$ $[M + Na]^+$ 769.2579, measured 769.2585.

***N*-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-tri-*O*-α-D-galactopyranosyl)-D-serine (8)**. ^{1}H-NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.94 (d, *J* = 7.6 Hz, 2H, H-Fmoc), 7.45 (d, *J* = 7.5 Hz, 2H, H-Fmoc), 7.75-7.79 (m, 2H, H-Fmoc), 7.34 (t, *J* = 7.4 Hz, 2H, H-Fmoc), 5.37 (d, *J* = 3.1 Hz, 1H, H4'), 5.05 (dd, *J* = 11.6, 3.2 Hz, 1H, H3'), 4.99 (d, *J* = 3.5 Hz, 1H , H1'), 4.57-4.61 (m, 1H, S^{α}), 4.48-4.54 (m, 1H, H2'), 4.40 (dd, *J* = 9.9, 7.0 Hz, 1H, H6a'), 4.19-4.34 (m, 5H, H6' {4.32}, S^{β}{4.26}, CH_2-Fmoc {4.20}), 4.01-4.07 (m, 1H, CH-Fmoc), 3.74 (dd, *J* = 9.5, 3.3 Hz, 1H, H5'), 2.15 (s, 3H, CH_3-Ac), 2.02 (s, 3H, CH_3-Ac), 1.95 (s, 3H, CH_3-Ac), 1.93 (s, 3H, CH_3-Ac). ^{13}C-NMR (100 MHz, *N,N*-dimethylformamide-d_7) δ 176.0, 174.6, 174.4, 174.36, 174.1, 160.9, 148.7, 148.5, 145.5, 145.52, 132.1, 131.5, 131.4, 124.5, 124.4, 102.2, 72.7, 72.6, 71.8, 71.4, 70.8, 66.1, 58.4, 51.4, 26.5, 24.3, 24.2. HRMS calcd for $C_{32}H_{36}N_2O_{13}$ $[M + Na]^+$ 679.2115, found 679.2116.

Fmoc-Ser(Ac$_4$Galβ1,3Ac$_2$GalNAcα)-OH (9)



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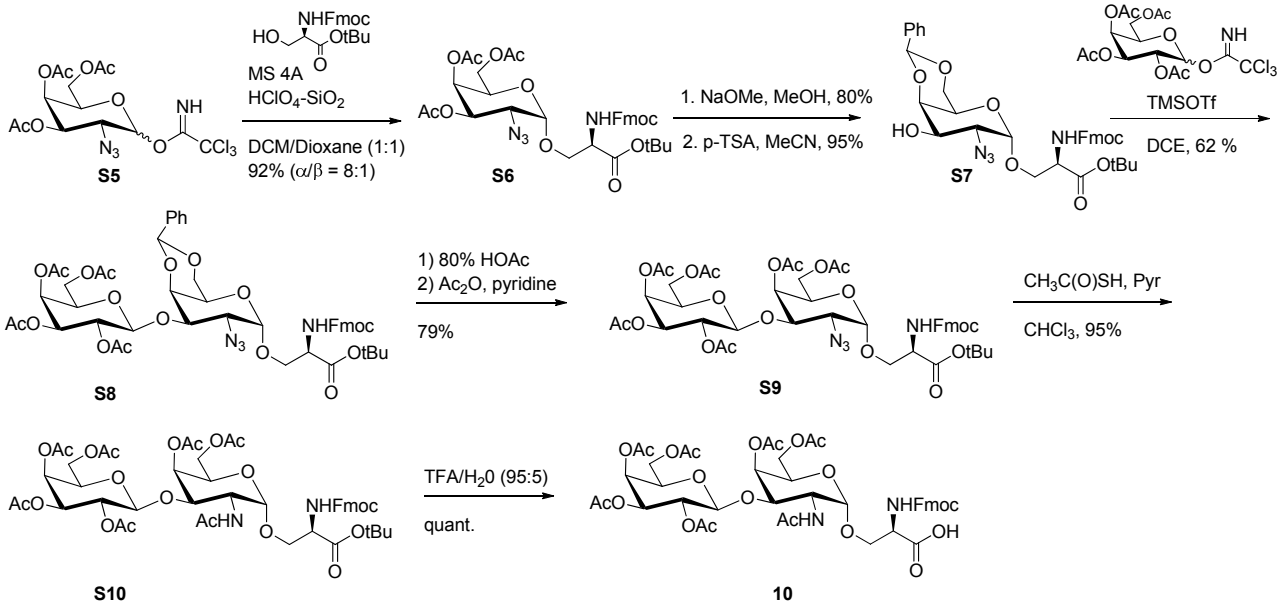
N-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-[*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1,3)-2-acetamido-4,6-di-*O*-acetoxy-2-deoxy-α-D-galactopyranosyl]-L-serine (**9**) was prepared according to a reported method**.**[1] ^{1}H NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.66-7.79 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.34-7.38 (m, 2H), 5.45 (d, *J* = 3.2 Hz, 1H), 5.38 (d, *J* = 3.6 Hz, 1H), 5.11– 5.13 (m, 1H), 5.01-5.03 (m, 2H), 4.89 (d, *J* = 3.6 Hz, 1H), 3.95–4.49 (m, 15H), 2.14 (s, 3H), 2.10 (s, 3H), 2.08 (s, 3H), 2.02-2.03 (m, 6H), 1.95 (s,

6H); ^{13}C NMR (100 MHz, *N,N*-dimethylformamide-d_7) δ 171.9, 170.3, 170.31, 170.1, 168.8, 169.7, 169.5, 156.7, 144.4, 144.3, 127.9, 127.3, 125.5, 125.47, 120.3, 101.1, 98.9, 73.5, 70.9, 70.4, 70.1, 68.9, 67.5, 66.7, 63.0, 61.1, 54.9, 49.0, 47.3, 22.6, 20.2, 20.15, 20.1, 20.0, 19.9. HRMS calcd for $C_{44}H_{52}N_2O_{21}$ $[M + H]^+$ 945.3141, measured 945.3136.

Fmoc-D-Ser(Ac$_4$Galβ1,3Ac$_2$GalNAcα)-OH (10)



S6: Trichloroacetimidate donor **S5** (3.50 g, 7.36 mmol) and D-serine *tert*-butyl ester (2.17 g, 5.66 mmol) were dissolved in anhydrous CH_2Cl_2 / 1,4-dioxane (1:1, 70 mL) at room temperature. Activated molecular sieves (4Å, 3.50 g) were added and the mixture was stirred for 0.5 h at room temperature. The reaction mixture was cooled to 0°C and $HClO_4$-SiO_2 (0.4 mmol/g, 1.32 g) was added in one portion with rapid stirring. The reaction was stirred for 1 h at 0°C and then neutralized by addition of a diluted DIEA solution (92 μL, 0.53 mmol in 10 mL of CH_2Cl_2). The solids were filtered off and the solvent was removed under reduced pressure. The crude residue was purified by silica-gel flash chromatography (EtOAc in hexanes 20 – 45 %) to yield the alpha-glycosylated serine **S6** (4.20 g, 82 %), together with the beta product (512 mg, 10 %) as colorless foams. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.40 – 7.25 (m, 4H), 5.74 (d, *J* = 8.7 Hz, 1H), 5.40 (d, *J* = 3.0 Hz, 1H), 5.26 (dd, *J* = 11.1, 3.0 Hz, 1H), 4.98 (d, *J* = 3.3 Hz, 1H), 4.47 (ddd, *J* = 8.7, 2.9, 2.9 Hz, 1H), 4.37 (d, *J* = 7.2 Hz, 2H), 4.24 – 4.02 (m, 5H), 3.68 (dd, *J* = 9.8, 2.9 Hz, 1H), 3.58 (dd, *J* = 11.1, 3.4 Hz, 1H), 2.12 (s,

3H), 2.04 (s, 3H), 2.02 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.0, 169.66, 168.2, 155.8, 143.9, 143.7, 141.3, 141.26, 127.7, 127.0, 125.1, 119.9, 98.7, 83.2, 69.0, 67.7, 67.4, 67.1, 61.6, 57.4, 54.5, 47.1, 27.9, 20.6, 20.57. ESI-MS calcd for $C_{34}H_{40}N_4O_{20}$ $[M + Na]^+$ 719.2, measured: 719.1.

S7: Deacetylation of **S6** using Zemplén conditions (sodium methoxide in methanol) produced the triol product as a colorless foam in 80 % yield. Triol product (1.00 g, 1.75 mmol) and α,α-dimethoxytoluene (0.502 mL, 3.51 mmol) were dissolved in anhydrous MeCN (20 mL) and a catalytic amount of *p*-toluenesulfonic acid (*p*-TSA, 80 mg, 0.421 mmol) was added in one portion. The reaction was stirred for 1 h at room temperature and then neutralized by slow addition of a diluted diisopropylethylamine solution (DIEA, 74 μL, 0.421 mmol in 10 mL of MeCN). The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (EtOAc in hexanes, 20 – 45 %) to yield the benzylidene protected product **S7** (1.10 g, 95 %) as a colorless foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.6 Hz, 2H), 7.59 (dd, J = 7.2, 2.3 Hz, 2H), 7.47 – 7.44 (m, 2H), 7.40–7.35 (m, 5H), 7.31–7.26 (m, 2H), 5.77 (d, J = 9.0 Hz, 1H), 5.55 (s, 1H), 4.99 (d, J = 3.3 Hz, 1H), 4.46 (ddd, J = 8.8, 2.6, 2.6 Hz, 1H), 4.40–4.32 (m, 2H), 4.30–4.18 (m, 4H), 4.08 (bd, J = 10.5 Hz, 1H), 4.05 (dd, J = 12.6, 1.6 Hz, 1H), 3.70 (s, 1H), 3.66 (dd, J = 9.7, 2.8 Hz, 1H), 3.53 (dd, J = 10.5, 3.3 Hz, 1H), 2.40 (bs, 1H), 1.45 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 155.9, 143.9, 143.7, 141.3, 141.25, 137.1, 129.4, 128.3, 127.7, 127.0, 126.2, 125.2, 119.9, 101.3, 99.5, 82.7, 75.3, 69.2, 69.0, 67.2, 63.1, 60.7, 54.6, 47.1, 28.0. ESI-MS calcd for $C_{35}H_{38}N_4O_9$ $[M + Na]^+$ 681.2, measured: 681.1.

S8: A mixture of **S7** (1.10 g, 1.67 mmol) and galactose donor (1.32 g, 2.67 mmol) were coevaporated with anhydrous toluene (2 ×5.0 mL) and then dissolved in anhydrous dichloroethane (DCE, 20.0 mL). The reaction mixture was cooled to 10°C and TMSOTf (48 μL, 0.267 mmol) was added. After stirring for 45 min at 10°C TLC analysis (EtOAc / hexanes (4:6)) showed complete consumption of starting material and the reaction was neutralized by slow addition of diluted DIEA (47 μL, 0.267 mmol in 10 mL of CH_2Cl_2). The solvent was evaporated off and the crude was purified by flash chromatography on silica gel (EtOAc in hexanes, 30–50%) to yield the beta glycosylated product **S8** (1.05 g, 62%) as a colorless foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 2H), 7.59 (dd, J = 7.2, 2.1 Hz, 2H), 7.50 (dd, J = 7.7, 1.8 Hz,

2H), 7.40–7.25 (m, 7H), 5.74 (d, J = 8.6 Hz, 1H), 5.51 (s, 1H), 5.38 (d, J = 2.6 Hz, 1H), 5.26 (dd, J = 10.0, 8.1 Hz, 1H), 5.03–4.98 (m, 2H), 4.70 (d, J = 7.8 Hz, 1H), 4.50–4.45 (m, 1H), 4.42–4.35 (m, 2H), 4.32 (d, J = 2.6 Hz, 1H), 4.26–4.20 (m, 2H), 4.16 (dd, J = 9.7, 2.4 Hz, 1H), 4.13–4.08 (m, 2H), 3.98–4.02 (m, 2H), 3.87 (dd, J = 6.6, 6.6 Hz, 1H), 3.78 (dd, J = 10.8, 3.3 Hz, 1H), 3.68 (dd, J = 9.7, 2.6 Hz, 1H), 3.63 (s, 1H), 2.14 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.17, 170.1, 169.4, 168.8, 155.9, 143.8, 143.7, 141.3, 141.27, 137.5, 128.9, 128.1, 127.7, 127.0, 126.1, 125.1, 120.0, 102.6, 100.6, 99.4, 82.6, 76.7, 75.7, 70.9, 70.86, 69.0, 68.6, 67.2, 66.8, 63.4, 61.2, 58.7, 54.6, 47.1, 28.0, 20.7, 20.5. HRMS calcd for $C_{49}H_{56}N_4O_{18}$ $[M + Na]^+$ 1011.3487, measured 1011.3496.

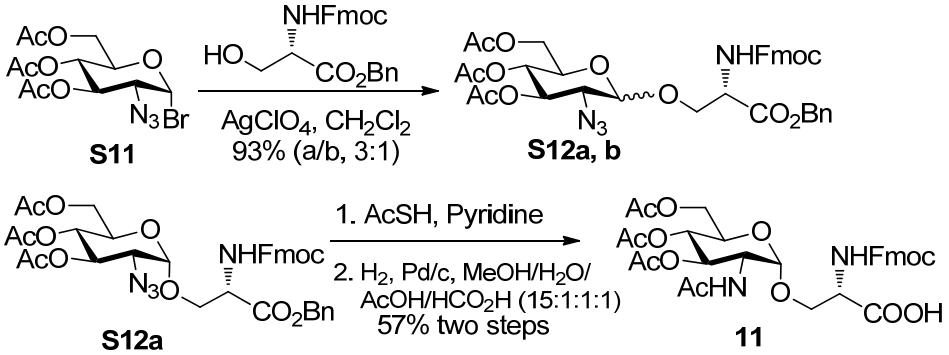
S9: Benzylidene protected disaccharide **S8** (1.00 g, 1.01 mmol) was dissolved in 80% aqueous acetic acid solution (15 mL) and stirred at 80°C for 2h. After cooling to room temperature, the solvent was evaporated off and the residue was evaporated with toluene (3 × 10 mL). The residue was dissolved in a mixture of anhydrous pyridine (5.0 mL) and acetic anhydride (5.0 mL). The reaction was stirred overnight at room temperature. The solvent was evaporated off and the residue was dissolved in CH_2Cl_2 (100 mL). The organic phase was extracted with water (50 mL) and 1 M hydrochloric acid (50 mL). The combined aqueous washings were back-extracted with CH_2Cl_2 (50 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated. The crude was purified by flash chromatography on silica gel (EtOAc in hexanes, 20 – 45 %) to yield the peracetylated disaccharide **S9** (786 mg, 79%) as a colorless foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 2H), 7.58 (dd, J = 7.3, 3.0 Hz, 2H), 7.38 (vt, J = 7.5 Hz, 2H), 7.29 (tt, J = 7.5, 1.0 Hz, 2H), 5.74 (d, J = 8.7 Hz, 1H), 5.40 (d, J = 3.1 Hz, 1H), 5.34 (d, J = 3.2 Hz, 1H), 5.14 (dd, J = 10.5, 7.8 Hz, 1H), 4.96 (dd, J = 10.5, 3.2 Hz, 1H), 4.93 (d, J = 3.3 Hz, 1H), 4.61 (d, J = 7.8 Hz, 1H), 4.45–4.50 (m, 1H), 4.41 (dd, J = 10.6, 7.7 Hz, 1H), 4.36 (dd, J = 10.6, 7.3 Hz, 1H), 4.21 (dd, J = 7.2, 7.2 Hz, 1H), 4.00–4.13 (m, 5H), 3.94–4.00 (m, 2H), 3.85 (dd, J = 6.7, 6.7 Hz, 1H), 3.66 (dd, J = 9.8, 2.9 Hz, 1H), 3.60 (dd, J = 10.7, 3.5 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.95 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.29, 170.2, 170.0, 169.6, 169.5, 168.46, 155.8, 143.8, 143.7, 141.3, 141.3, 127.7, 127.0, 125.1, 120.0, 101.4, 98.5, 82.8, 74.3, 70.8, 70.7, 69.1, 68.8, 68.7, 67.8, 67.1, 66.7, 62.5, 60.9, 59.5, 54.7, 47.1, 28.0, 20.7, 20.66, 20.6, 20.5. ESI-MS calcd for $C_{46}H_{56}N_4O_{20}$[M + Na]$^+$ 1007.3, measured: 1007.1.

S10: To a solution of compound **S9** (780 mg, 0.792 mmol) in chloroform (7.0 mL) were added pyridine (7.0 mL) and thioacetic acid (7.0 mL). The reaction was stirred overnight at room temperature. The solvent was evaporated off and the residue was dissolved in EtOAc (100 mL). The organic phase was extracted sequentially with 1 M aqueous HCl (50 mL), saturated aqueous $NaHCO_3$ (50 mL) and water (50 mL). The individual aqueous washings were back-extracted with EtOAc (25 mL, respectively). The combined organic extracts were dried with $MgSO_4$ and concentrated. The crude was purified by flash chromatography on silica gel (EtOAc in hexanes 70 – 90 %) to yield the acetyl amine **S10** (753 mg, 95%) as a hygroscopic solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.57 (dd, *J* = 9.2, 8.2 Hz, 2H), 7.39 (dt, *J* = 7.5, 3.5 Hz, 2H); 7.31 (dt, *J* = 7.4, 1.2 Hz, 2H), 6.31 (d, *J* = 8.8 Hz, 1H), 5.64 (d, *J* = 8.0 Hz, 1H), 5.24 (d, *J* = 2.7 Hz, 1H), 5.22 (d, *J* = 2.8 Hz, 1H), 4.99 (dd, *J* = 10.2, 8.0 Hz, 1H), 4.87 (d, *J* = 3.0 Hz, 1H), 4.72 (dd, *J* = 10.5, 3.2 Hz, 1H), 4.50 – 4.35 (m, 4H), 4.21 (dd, *J* = 6.9, 6.9 Hz, 1H), 4.20 (d, *J* = 7.8 Hz, 1H), 4.11 (dd, *J* = 10.9, 4.3 Hz, 1H), 4.03 – 3.90 (m, 4H), 3.84 (dd, *J* = 10.3, 6.1 Hz, 1H), 3.71 (dd, *J* = 10.3, 2.5 Hz, 1H), 3.63 (dd, *J* = 11.0, 3.0 Hz, 1H), 3.61 – 3.57 (m, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.91 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 170.28, 170.1, 170.12, 170.0, 169.5, 168.8, 156.1, 143.6, 141.3, 141.26, 127.9, 127.2, 127.15, 124.9, 124.8, 120.2, 100.7, 98.9, 83.4, 73.6, 70.7, 70.5, 69.5, 68.5, 68.4, 67.7, 67.2, 66.6, 62.8, 60.7, 54.8, 48.6, 47.1, 27.9, 23.1, 20.7, 20.69, 20.6, 20.5. HRMS calcd for $C_{48}H_{60}N_2O_{21}$ $[M + H]^+$ 1001.3767, measured 1001.3771.

***N*-(Fluoren-9-ylmethoxycarbonyl)-*O*-[*O*-(2',3',4',6'-tetra-*O*-acetyl-β-D-galactopyranosyl)-(1,3)-2-acetamido-4,6-di-*O*-acetoxy-2-deoxy-α-D-galactopyranosyl]-D-serine(10),** Compound **S10** (750 mg, 0.749 mmol) was dissolved in a TFA-water mixture (95:5, 10 mL) and stirred at room temperature for 1 h. TLC-analysis of the reaction (EtOAc/hexanes 3:1) showed complete consumption of the starting material. The solvent was evaporated off and the residue was coevaporated with toluene (3 × 10 mL). The residue was dissolved in a water-acetonitrile mixture (1:1, 10 mL) and lyophilized to yield the carboxylic acid **10** (708 mg, quant.) as a colorless powder. The acid was purified with RP-HPLC as the same method for purifying **9.** ^{1}H NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.98 (d, *J* = 9.7 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 2H), 7.77 (t, *J* = 7.6 Hz, 2H), 7.53-7.45 (m, 3H), 7.34-7.38 (m, 2H), 5.41 (d, *J* = 3.2 Hz, 1H),

5.38 (d, *J* = 3.6 Hz, 1H), 5.12 (dd, *J* = 10.4, 3.6 Hz, 1H), 5.02 (dd, *J* = 10.3, 7.8 Hz, 1H), 4.93 (d, *J* = 7.9 Hz, 1H), 4.88 (d, *J* = 3.7 Hz, 1H), 4.58 – 4.48 (m, 2H), 4.45-4.35 (m, 2H), 4.32-4.21 (m, 2H), 4.20 – 4.04 (m, 7H), 3.91 (dd, *J* = 11.3, 7.4 Hz, 1H), 3.75 (dd, *J* = 9.8, 3.9 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.04 (s, 6H), 1.98 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, *N,N*-dimethylformamide-d_7) δ 171.8, 170.34, 170.31, 170.2, 170.1, 169.8, 169.4, 156.7, 144.5, 141.3, 127.9, 127.3, 125.5, 120.3, 101.1, 98.3, 73.9, 70.8, 70.5, 70.0, 68.9, 68.0, 66.6, 62.9, 61.2, 54.2, 48.7, 47.3, 22.6, 20.2, 20.15, 19.95, 19.9. HRMS calcd for $C_{44}H_{52}N_2O_{21}$ $[M + H]^+$ 945.3141, measured 945.3147.

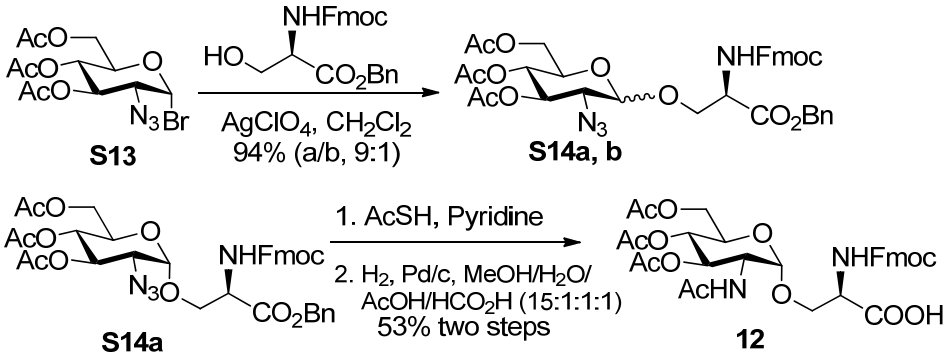
Fmoc-Ser(Ac$_3$GlcNAcα)-OH (11)



N-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-tri-*O*-α-D-gluctopyranosyl)-L-serine **11** was synthesized following a reported method.[1] Peracetylated 2-azido-2-deoxy-D-Glucopyranosyl bromide (**S11**)[2] (0.85 g, 2.04 mmol), Fmoc-L-serine benzyl ester (1.12 g, 2.84 mmol), and 4 Å molecular sieves were placed in a flask under argon. Anhydrous DCM (30 mL) was added, and the reaction mixture was stirred at room temperature for 20 min. $AgClO_4$ (0.85 g, 4.10 mmol) was added to the reaction mixture was allowed to stir at room temperature for 3h, and monitored by TLC Hex/EtOAc (2:1). The reaction mixture was diluted with DCM, filtered over celite, and concentrated. The residue was filtered through a silica gel column with Hex/EtOAc (3:1) to give compounds **S12a** and **S12b** (α/β, 3:1) in 93% yield. Compound **S12a** (1.08 g, 1.48 mmol) was dissolved in pyridine (4mL) followed by addition of thioacetic acid (8mL). The reaction mixture was stirred at room temperature overnight and monitored by TLC Hex/EtOAc (1:2). The reaction mixture was diluted with DCM, filtered, concentrated, and filtered through a silica gel column to provide Fmoc-L-Ser(GlcNAcα)OBn (1.07 g, 97%). Fmoc-L-Ser(GlcNAcα)OBn (0.62 g, 0.83 mmol) was dissolved in MeOH (15 mL). Water (1 mL), acetic acid (1mL), and formic acid (1mL) were added, followed by addition of Pd/C 10%

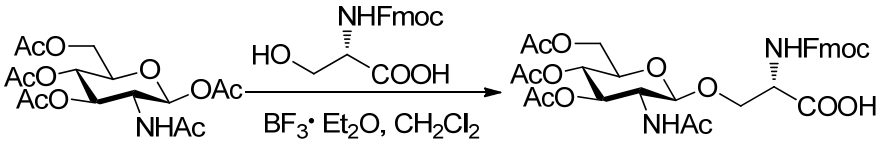
(0.15g). The reaction mixture was purged with H_2 and stirred under H_2 for 2h at room temperature. The reaction mixture was filtered over celite, concentrated, and purified by RP-HPLC followed by silica gel column to provide compound **11** as a white solid (0.40g, 73%). ^{1}H NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.96-7.93 (m, 3H), 7.75 (d, *J* = 7.4Hz, 2H), 7.70 (d, *J* = 9.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 5.27 (t, *J* = 9.5 Hz, 1H), 5.01 (t, *J* = 9.7 Hz, 1H), 4.95 (d, *J* = 3.6 Hz, 1H), 4.53-4.49 (m, 1H), 4.37–4.06 (m, 9H), 2.06 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100MHz, *N,N*-dimethylformamide-d_7) δ 172.0, 170.4, 170.2, 170.1, 156.8, 144.40, 144.36, 141.35, 141.32, 127.9, 127.3, 125.6, 125.5, 120.3, 98.6, 71.0, 69.2, 68.6, 68.1, 66.7, 62.1, 54.9, 51.6, 47.3, 22.2, 20.1. HRMS calcd for $C_{32}H_{36}N_2O_{13}$[M + Na]$^+$ 679.2115, measured 679.2104.

Fmoc-D-Ser(Ac$_3$GlcNAcα)-OH (12)



N-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-tri-*O*-α-D-gluctopyranosyl)-D-serine **12** was synthesized in a similar method described for preparing **11** starting from peracetylated 2-azido-2-deoxy-D-Glucopyranosyl bromide (**S13**)[1] and Fmoc-D-serine benzyl ester (**S1**). ^{1}H NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 8.00-7.90 (m, 4H), 7.80-7.75 (m, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.34 (td, *J* = 1.0, 7.5 Hz, 2H), 5.17 (t, *J* = 9.5 Hz, 1H), 5.00 (t, *J* = 9.7 Hz, 1H), 4.94 (d, *J* = 3.6 Hz, 1H), 4.65-4.61(m, 1H), 4.39–4.02 (m, 8H), 3.74 (dd, *J* = 3.1, 9.6 Hz, 1H), 2.07 (s, 3H), 1.99 (s, 3H), 1.96 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100MHz, *N,N*-dimethylformamide-d_7) δ 171.7, 170.4, 170.3, 169.9, 169.6, 156.8, 144.5, 144.3, 141.3, 127.9, 127.30, 127.29, 125.6, 125.5, 120.3, 97.8, 71.2, 68.9, 68.7, 68.2, 66.7, 62.0, 54.2, 51.4, 47.3, 22.2, 20.1, 20.0. HRMS calcd for $C_{32}H_{36}N_2O_{13}$ [M + Na]$^+$ 679.2115, measured 679.2115.

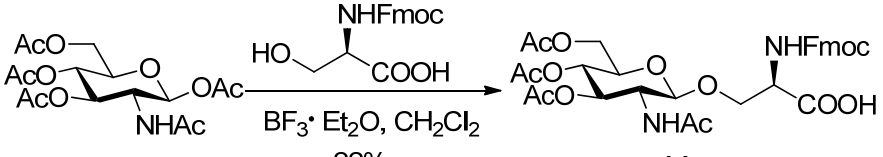
Fmoc-Ser(Ac$_3$GlcNAcβ)-OH (13)



S15 47% **13**

N-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-tri-*O*-β-D-gluctopyranosyl)-L-serine **13** was synthesized according to reported method[3]. PeracetylatedGlcNAc **S15** (1.08 g, 2.77 mmol) with 4 Å molecular sieves were placed in a flask under argon, and anhydrous DCM (15 mL) was added. The reaction mixture was cooled to 0 ºC and $BF_3{\cdot}Et_2O$ (1.00 mL, 8.10 mmol) was added dropwise and stirred at room temperature overnight. The reaction mixture was cooled to 0 ^oC and Et_3N (0.40 mL, 1 equiv.) was added and stirred for 10 min. A solution of Fmoc-serine (1.20g, 3.67 mmol) in DCM/MeCN (1:2) was added, and the reaction was allowed to stir at room temperature for 4 days and monitored by TLC $CDCl_3$/MeOH/AcOH (10:1:0.2). The reaction mixture with neutralized with Et_3N, diluted with DCM, filtered over celite, and concentrated. The residue was first filtered through a silica gel column with $CHCl_3$/MeOH (40:1-10:1), then purified by RP-HPLC, and filtered through silica gel column DCM/MeOH (30:1-10:1) to provide compound **13** as a white solid (0.86g, 47%). ^{1}H NMR (400 MHz, *N,N*-dimethylformamide-d$_7$) δ 8.00 (d, *J* = 8.8Hz, 1H, NH-GalNAc), 7.93 (d, *J* = 7.6 Hz, 2H, H-Fmoc), 7.80–7.77 (m, 2H, H-Fmoc), 7.46–7.33 (m, 4H, H-Fmoc), 7.28 (d, *J* = 8.4Hz, 1H, NH-S), 5.28 (t, *J* = 9.2 Hz, 1H, H4'), 4.99-4.93 (m, 2H, H3' {4.97}, H1' {4.94}), 4.46–4.42 (m, 1H, S$^{\alpha}$), 4.35–4.17 (m, 5H, H2' {4.35}, CH_2-Fmoc{4.33}, H6a' {4.19}, S$^{\beta}$a {4.18}), 4.11 (dd, *J* = 2.4, 12.4 Hz, 1H, H6b'), 3.97–3.85 (m, 3H, S$^{\beta}$b {3.95}, H-Fmoc {3.87}, H5'), 2.04 (s, 3H, CH_3-Ac), 2.02 (s, 3H, CH_3-Ac), 1.97 (s, 3H, CH_3-Ac), 1.85 (s, 3H, CH_3-Ac); ^{13}C NMR (100MHz, *N,N*-dimethylformamide-d$_7$) δ 171.5, 170.4, 170.01, 169.7, 156.5, 144.40, 144.35, 141.33, 141.31, 127.9, 127.3, 125.63, 125.60, 120.3, 101.2, 73.0, 71.7, 69.2, 66.7, 62.3, 54.7, 54.0, 47.2, 22.5, 20.13, 20.08. HRMS calcd for $C_{32}H_{36}N_2O_{13}$ $[M + Na]^+$ 679.2115, measured 679.2091.

Fmoc-D-Ser(Ac$_3$GlcNAcβ)-OH (14)

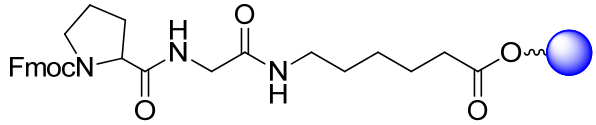


S15 22% **14**

The synthesis of *N*-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-tri-*O*-β-D-gluctopyranosyl)-D-serine (**14**) was carried out according to reported method[3] in similar procedure described for compound **13** to provide compound **14** as a white solid (0.350g, 22%). ^{1}H NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.93 (d, *J* = 7.3 Hz, 3H, H-Fmoc), 7.79 (d, *J* = 7.4 Hz, 2H, H-Fmoc), 7.46–7.34 (m, 5H, H-Fmoc), 5.27 (t, *J* = 9.8 Hz, 1H, H4'), 4.96(t, *J* = 9.6 Hz, 1H, H3'), 4.86 (d, *J* = 8.4 Hz, 1H, H1'), 4.45–4.25 (m, 5H, S^{α} {4.43}, CH_2-Fmoc {4.32}, H2' {4.32}, H6a' {4.25}), 4.14–3.86 (m, 5H, H6b' {4.12}, S^{β} {4.12}, {4.03}, H-Fmoc {3.91}, H5' {3.88}), 2.14–1.96 (m, 9H, CH_3-Ac), 1.83 (s, 3H, CH_3-Ac); ^{13}C NMR (100MHz, *N,N*-dimethylformamide-d_7) δ 171.5, 170.4, 170.01, 169.95, 169.7, 156.5, 144.43, 144.41, 141.34, 141.31, 127.9, 127.3, 125.63, 125.60, 120.2, 101.7, 73.1, 71.6, 69.9, 69.3, 66.6, 62.4, 54.9, 54.0, 47.2, 22.5, 20.13, 20.10, 20.07. HRMS calcd for $C_{32}H_{36}N_2O_{13}$ $[M + Na]^+$ 679.2115, measured 679.2092.

Preparation of peptide and glycopeptide standards

Fmoc-Pro-Gly-Hex-resin (S16)



S16

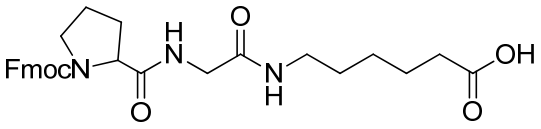
The solid-phase synthesis of Fmoc-Pro-Gly-Hex **S16** was carried out using 2-Chlorotrityl chloride resin (1.0g, 1.55 mmol/g) manually functionalized with Fmoc-6-aminohexanoic acid (0.17 g, 0.48 mmol) and DIEA (0.34 mL, 1.92 mmol) in DCM (8.0 mL), followed by capping the resin with DCM/MeOH/DIEA (17:2:1, v/v/v, 3×5 mL) for 20 min. The resin was washed with DMF (2×5 mL), DCM (3×5 mL) and dried overnight under vacuum. The loading density of the Fmoc-6-aminohexanoic acid was calculated using Fmoc test by measuring piperidine-dibenzylfulvene adduct absorption at 290 nm with the following equation:

$$Loading\ Density\ \left(\frac{mmol}{g}\right) = \frac{A \times V\ (\mu L)}{5800 \times m\ (mg)}$$

where A is the absorption at 290 nm, V is the volume of 20% piperidine-DMF solution, and m is the weight of the loaded resin. [4]

Fmoc groups on resin were removed with 20% piperidine in DMF (2×5 mL) for 15 min and then washed with DCM (3×5 mL) and DMF (2×5 mL). The first amino acid Fmoc-Gly-OH was preactivated with HBTU (0.67 g, 1.8 mmol), HOBt (0.28 g, 1.8 mmol), and DIEA (0.31 mL, 1.8 mmol) in DMF (8.0 mL) for 30 min, then coupled to the resin (1.0 g, 0.36 mmol) at room temperature for 1.5 h. The unreacted amino groups on the resin were capped with 10% acetic anhydride/10% pyridine in THF (2×5 mL) for 20 min. The resin was then deprotected with 20% piperidine, washed and then coupled with Fmoc-Pro-OPfp (0.89 g, 1.77 mmol) and DIEA (0.31 mL, 1.77 mmol) in DMF (8.0 mL) at room temperature for 2.0 h, followed by capping the resin with 10% acetic anhydride/10% pyridine in THF. The resin was washed with DMF (2×5 mL), DCM (3×5 mL) and dried under vacuum overnight.

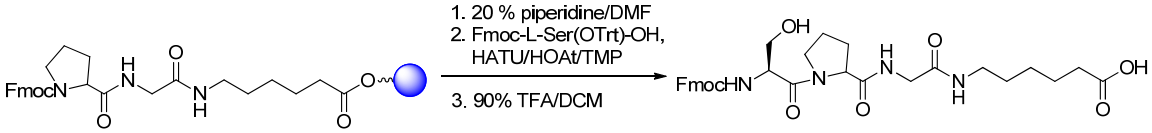
Fmoc-Pro-Gly-Hex-OH (6)



6

The Fmoc-Pro-Gly-Hex resin was treated with TFA/DCM (9/1, v/v, 2 mL) at room temperature and the crude product was purified by RP-HPLC. The flow rate is 10 mL/min and elute was monitored at 290 nm. Buffer A was MilliQ water containing 0.1% TFA, and buffer B was acetonitrile containing 0.1% TFA. For other peptides and glycopeptides, the percentage of B was increased after 1 min according to a linear gradient of 1%-35% in 18 min, kept at 35% for 4 min, increased from 35% to 48% in 56 min, increase to 100% B in 5 min, kept at 100 for 4 min, and then dropped back to 1% over 4 min and kept at 1% for 3 min (95 min total time). The trace amount of TFA was removed from the glycopeptides by a silica flash chromatography using a mixture of MeOH and DCM (10/90, v/v) to give **6** as a white foam. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.81 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 6.9 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.28-7.35 (m, 2H), 4.37-4.50 (m, 2H), 4.11-4.31 (m, 2H), 3.69-3.91 (m, 2H), 3.41-3.62 (m, 2H), 3.08-3.19 (m, 2H), 2.14-2.28 (m, 3H), 1.84-2.11 (m, 3H), 1.38-1.59 (m, 4H), 1.23-1.33 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 178.2, 176.4, 172.3, 158.0, 146.1, 143.5, 129.7, 129.1, 121.8, 69.7, 63.2, 44.5, 41.2, 35.6, 32.0, 30.7, 28.3, 26.5. HRMS calcd for $C_{28}H_{33}N_3O_6$ $[M + Na]^+$ 530.2265, measured 530.2250.

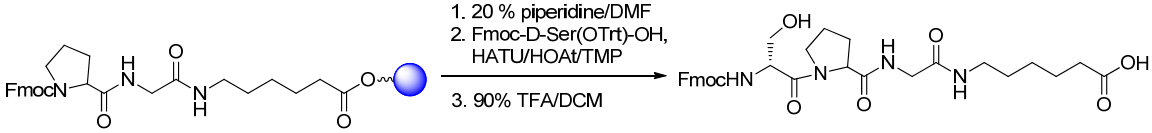
Fmoc-Ser-Pro-Gly-Hex-OH (1a)



S16 **1a**

Compound **1a** was synthesized starting from **S16**. Prior to coupling the resin (100 mg) was swollen in DCM for 0.5 h, followed by removal of the Fmoc-group with 20% piperidine in DMF (2× 2.0 mL) for 15 min, and then washed with DCM (3× 2.0 mL) and DMF (2× 2.0 mL). The appropriate amount of Fmoc-serine (2 eq), HATU (2 eq), HOAt (2 eq), and TMP (2eq) in DMF were mixed and immediately added to the resin. The reaction was allowed to mix at room temperature for 2 h, followed by washing and capping the unreacted amino groups with FmocOSu (10 eq) and DIEA (10 eq) in DMF at room temperature for 2 h. The resin was washed with DMF (2×5 mL), DCM (3×5 mL), and the peptide was cleaved off with a mixture TFA/DCM (90:10) (1.5 mL) at room temperature for 1.5 h. The crude product was purified by RP-HPLC using the same method for purifying **6**. The trace amount of TFA was removed from the glycopeptides by a silica flash chromatography using a mixture of methanol and dichloromethane to give as white foam. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.79 (d, J = 7.5 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 4.57 (t, J = 6.6 Hz, 1H), 4.32-4.46 (m, 3H), 4.21 (t, J = 6.7 Hz, 1H), 3.70-3.87 (m, 6H), 3.15-3.25 (m, 2H), 2.19-2.30 (m, 3H), 1.93-2.11 (m, 3H), 1.50-1.66 (m, 4H), 1.31-1.41 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 176.1, 173.4, 171.1, 169.9, 156.9, 143.7, 141.1, 127.3, 124.7, 119.5, 66.5, 54.5, 42.1, 38.8, 33.3, 28.9, 28.5, 25.9, 24.5, 24.2. HRMS calcd for $C_{31}H_{38}N_4O_8$ $[M + Na]^+$ 617.2582, measured 617.2553.

Fmoc-D-Ser-Pro-Gly-Hex-OH (1b)

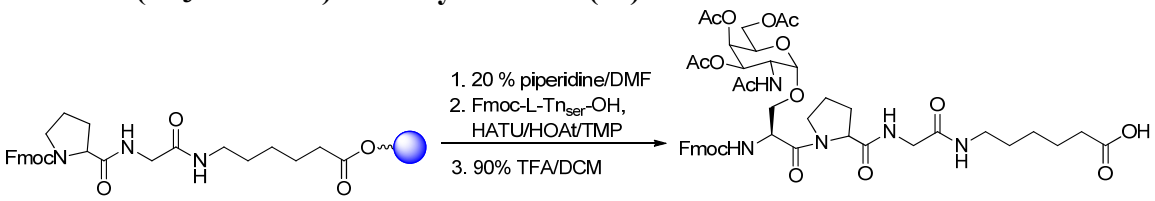


S16 **1b**

Compound **1b** was synthesized and purified according to the general procedure described for **1a**. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.79 (d, J = 7.5 Hz, 2H), 7.64 (dd, J = 7.5, 2.6 Hz, 2H), 7.38 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.4 Hz, 2H), 4.47 (t, J = 6.7 Hz, 1H), 4.36-4.44 (m, 1H), 4.29 (dd, J = 10.5, 6.4 Hz, 1H), 3.66-3.93 (m, 6H), 2.96-3.19 (m, 2H), 2.22-2.28 (m, 3H), 1.93-2.09 (m, 3H),

1.43-1.59 (m, 4H), 1.24-1.36 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 176.1, 173.3, 171.5, 169.9, 157.2, 143.7, 143.6, 141.2, 127.4, 126.7, 119.5, 66.6, 54.9, 42.1, 38.8, 33.4, 28.9, 28.3, 25.9, 24.3, 24.2. HRMS calcd for $C_{31}H_{38}N_4O_8$ $[M + H]^+$ 595.2766, measured 595.2754.

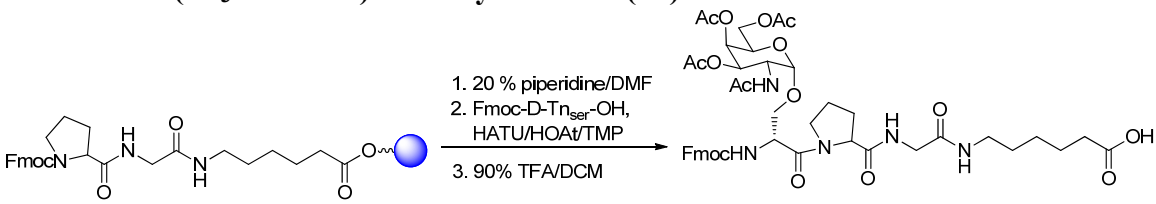
Fmoc-Ser(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH (2a)



S16 **2a**

Fmoc-Ser(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH (**2a**) was synthesized and purified according to the general procedure described for **6**. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.80 (d, J = 7.5 Hz, 2H), 7.65 (t, J = 6.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.31 (t, J = 7.0 Hz, 2H), 5.40 (d, J = 2.2 Hz, 1H), 5.17 (dd, J = 11.5, 3.0 Hz, 1H), 4.93 (d, J = 3.4 Hz, 1H), 4.72 (t, J = 5.5 Hz, 1H), 4.40-4.51 (m, 3H), 4.37 (dd, J = 12.4, 5.8 Hz, 1H), 4.21-4.26 (m, 2H), 4.09 (dd, J = 11.0, 6.4 Hz, 1H), 3.88-4.04 (m, 3H), 3.78-3.87 (m, 1H), 3.63-3.78 (m, 3H), 3.02-3.30 (m, 2H), 2.27 (t, J = 7.4 Hz, 2H), 2.19-2.24 (m, 1H), 2.12 (m, 4H), 1.88-2.05 (m, 11H), 1.47-1.68 (m, 4H), 1.30-1.43 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 177.5, 173.7, 172.2, 172.1, 171.9, 171.5, 158.3, 145.2, 142.7, 128.9, 128.2, 126.2, 121.1, 99.8, 69.8, 68.9, 68.6, 68.2, 68.0, 62.9, 62.3, 54.2, 43.7, 40.4, 34.8, 30.5, 30.1, 27.5, 25.8, 22.8, 20.7, 20.6. HRMS calcd for $C_{45}H_{57}N_5O_{16}$ $[M + Na]^+$ 946.3700, measured 946.369.

Fmoc-D- Ser(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH (2b)

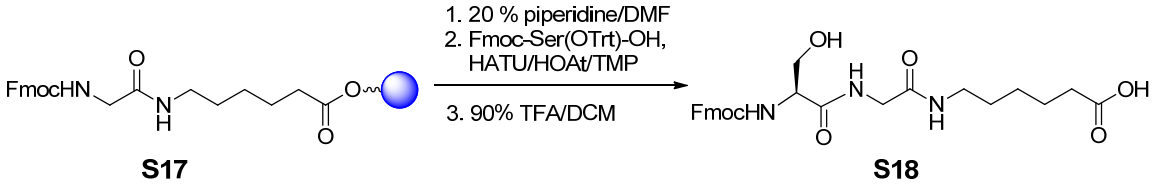


S16 **2b**

Compound **2b** was synthesized and purified according to the general procedure described for **6**. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.79 (d, J = 7.5 Hz, 2H), 7.66 (dd, J = 14.9, 7.2 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.30-7.33 (m, 2H), 5.34-5.38 (m, 1H), 5.06-5.10 (m, 1H), 4.92-4.95 (m, 1H), 4.61-4.65 (m, 2H), 4.31-4.51 (m, 3H), 4.15-4.24 (m, 2H), 4.01-4.12 (m, 2H), 3.77-3.82 (m, 4H), 3.55-3.61 (m, 2H), 3.06-3.20 (m, 2H), 2.24-2.29 (m, 3H), 2.12-2.13 (m, 3H), 1.92-1.98 (m, 12H),

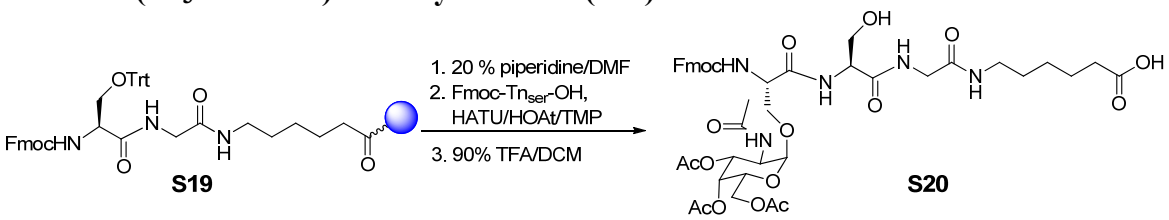
1.47-1.62 (m, 4H), 1.28-1.40 (m, 2H). HRMS calcd for $C_{45}H_{57}N_5O_{16}$ $[M + Na]^+$ 946.3700, measured 946.3700.

Fmoc-Ser-Gly-Hex-OH (S18)



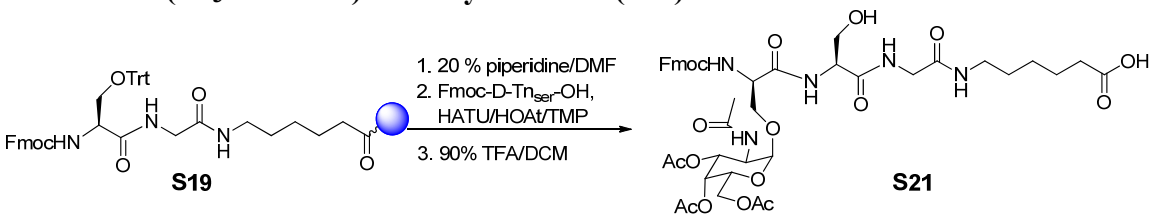
Compound **S18** was synthesized from **S17** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 20%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.83 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 6.9 Hz, 2H), 7.42 (t, J = 7.2 Hz, 2H), 7.37-7.33 (m, 2H), 4.49-4.39 (m, 2H), 4.27 (t, J = 6.9 Hz, 1H), 4.17 (t, J = 5.3 Hz, 1H), 3.88-3.79 (m, 4H), 3.20-3.17 (m, 2H), 2.26 (t, J = 7.3 Hz, 2H), 1.63-1.48 (m, 4H), 1.39-1.31 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 174.6, 172.3, 159.6, 146.1, 143.5, 129.7, 129.1, 127.1, 121.8, 69.0, 63.8, 59.7, 44.5, 41.1, 30.7, 28.3, 26.8. HRMS calcd for $C_{26}H_{31}N_3O_7$ $[M + Na]^+$ 520.2060, measured 520.2046.

Fmoc-Ser(Ac$_3$GalNAcα)-Ser-Gly-Hex-OH (S20)



Compound **S20** was synthesized from **S19** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 20%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.83 (d, J = 7.5 Hz, 2H), 7.71 (t, J = 7.7 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.36-7.34 (m, 2H), 5.41 (d, J = 3.0 Hz, 1H), 5.18 (dd, J =11.5, 3.5 Hz, 1H), 4.49-4.44 (m, 5H), 4.27 (t, J = 6.5 Hz, 1H), 4.10-4.06 (m, 3H), 3.96-3.85 (m, 6H), 2.27 (t, J = 7.4 Hz, 2H), 2.16 (s, 3H), 1.98 (br, 9 H), 1.67-1.50 (m, 4H), 1.40-1.32 (m, 2H), ^{13}C-NMR (100 MHz, CD_3OD) δ 171.21, 170.8, 170.7, 170.6, 170.4, 169.9, 161.94, 161.6, 157.1, 143.8, 143.7, 141.2, 141.17, 127.4, 126.8, 124.7, 119.5, 118.1, 115.2, 98.4, 68.2, 67.83, 67.24, 66.72, 61.45, 61.35, 55.58, 54.81, 42.14, 38.84, 28.47, 25.99, 24.42, 21.30, 19.21, 19.13, 19.07. HRMS calcd for $C_{43}H_{55}N_5O_{17}$ $[M + Na]^+$ 936.345, measured 936.352.

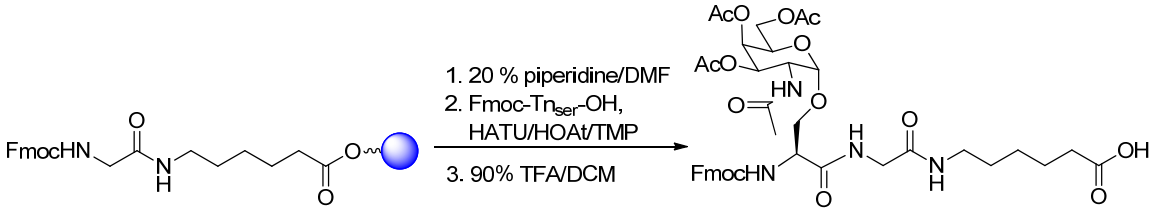
Fmoc-D-Ser(Ac$_3$GalNAcα)-Ser-Gly-Hex-OH (S21)



S19 S21

Compound **S21** was synthesized from **S19** according to the general procedure described for **5.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 20%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.70 (t, *J* = 6.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.37-7.33 (m, 2H), 5.40 (d, *J* = 2.9 Hz, 1H), 5.13 (dd, *J* = 11.5, 3.2 Hz, 1H), 4.59-4.45 (m, 5H), 4.28 (t, *J* = 6.2 Hz, 1H), 4.20-3.83 (m, 8H), 3.72-3.69 (m, 1H), 3.24-3.11 (m, 2H), 2.28 (t, *J* = 7.4 Hz, 2H), 2.16 (s, 3H), 2.02 (s, 3 H), 1.97 (s, 3 H), 1.95 (s, 3 H), 1.65-1.48 (m, 4H), 1.39-1.33 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 173.1, 172.9, 172.7, 172.2, 146.0, 143.52, 143.51, 129.7, 129.1, 129.07, 126.9, 121.9, 99.8, 70.5, 69.6, 69.0, 63.8, 63.6, 58.1, 57.0, 44.5, 41.1, 30.8, 28.3, 26.7, 23.6, 21.5, 21.4. HRMS calcd for $C_{43}H_{55}N_5O_{17}$ $[M + Na]^+$ 936.349, measured 936.353.

Fmoc-Ser(Ac$_3$GalNAcα)Gly-Hex-OH (S22)

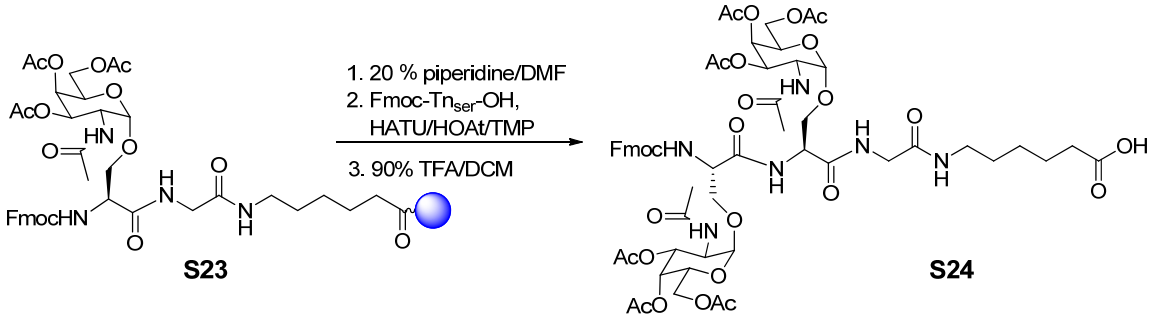


S17 S22

Compound **S22** was synthesized from **S17** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 20%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J* = 6.8 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39-7.36 (m, 2H), 5.42 (dd, *J* = 3.1, 1.1 Hz, 1H), 5.19 (dd, *J* = 11.6, 3.2 Hz, 1H), 4.94 (t, *J* = 3.6 Hz, 1H), 4.57-4.46 (m, 3H), 4.42 (t, *J* = 5.0 Hz, 1H), 4.30-4.24 (m, 2H), 4.09-4.03 (m, 2H), 3.99-3.80 (m, 4H), 3.22-3.18 (m, 2 H), 2.28 (t, *J* = 7.4 Hz, 2H), 2.17, (s, 3H), 1.99 (s, 3H), 1.96 (s, 6H), 1.65-1.50 (m, 4H), 1.41-1.32 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 174.5, 173.4, 173.35, 173.0, 172.96, 172.7, 171.9, 146.1, 146.0, 129.7, 129.1, 127.0, 121.9, 100.6, 70.6, 69.9, 69.5, 69.1, 69.0, 63.8, 57.4, 44.2,

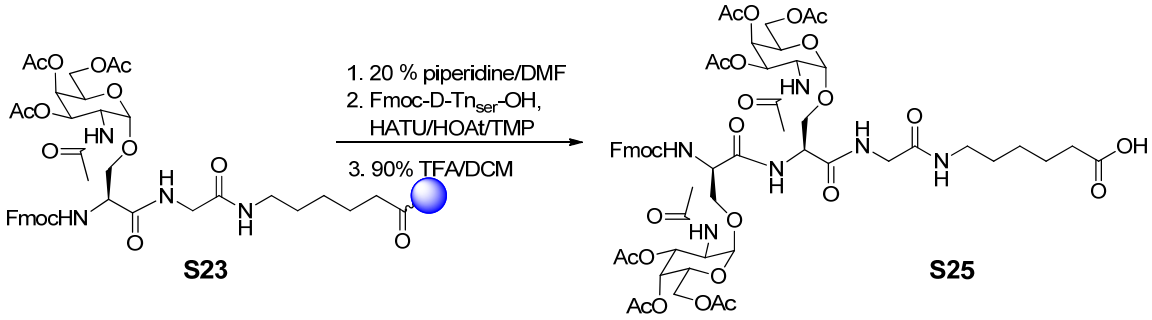
41.2, 30.9, 28.4, 26.8, 23.6, 21.5, 21.4, 21.38. HRMS calcd for $C_{40}H_{50}N_4O_{15}$ $[M + Na]^+$ 849.317, measured 849.314.

Fmoc-Ser(Ac$_3$GalNAcα)-Ser(Ac$_3$GalNAcα)-Gly-Hex-OH (S24)



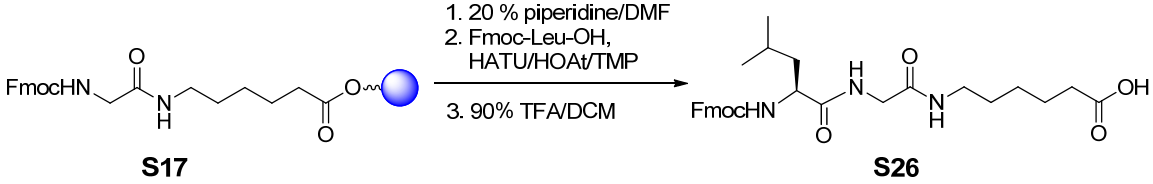
Compound **S24** was synthesized from **S24** according to the general procedure described for **5.** The crude product was purified by flash chromatography with MeOH/CH_2Cl_2 (5% then 20%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.80 (d, *J* = 7.3 Hz, 2H), 7.69-7.66 (m, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.34-7.31 (m, 2H), 5.40-5.37 (m, 2H), 5.19-5.13 (m, 2H), 4.95-4.93 (m, 2H), 4.69 (t, *J* = 5.1 Hz, 1H) 4.78-4.43 (m, 5H), 4.28-4.21 (m, 3H), 4.11-3.93 (m, 6H), 3.87-3.79 (m, 4 H), 3.25-3.11 (m, 2 H), 2.28 (t, *J* = 7.4 Hz, 2H), 2.13, (s, 3H), 2.11 (s, 3H), 1.95 (s, 15H), 1.88 (s, 3H), 1.65-1.57 (m, 2H), 1.55-1.48 (m, 2H), 1.40-1.33 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 178.4, 174.5, 174.45, 173.1, 173.0, 172.4, 171.6, 159.3, 146.2, 146.0, 143.5, 129.7, 129.1, 129.08, 127.1, 127.0, 121.9, 100.8, 100.5, 70.6, 70.5, 70.2, 69.8, 69.6, 69.5, 69.0, 69.01, 68.98, 63.8, 63.7, 57.0, 55.5, 44.2, 41.2, 35.8, 30.9, 28.3, 26.6, 23.7, 23.6, 21.6, 21.51, 21.50, 21.40, 21.38. HRMS calcd for $C_{57}H_{74}N_6O_{25}$ $[M + Na]^+$ 1265.460, measured 1265.464.

Fmoc-D-Ser(Ac$_3$GalNAcα)-Ser(Ac$_3$GalNAcα)-Gly-Hex-OH (S25)



Compound **S25** was was synthesized from **S23** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 20%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.75-7.72 (m, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.38-7.34 (m, 2H), 5.46 (br, 1H), 5.39 (d, *J* = 3.1 Hz, 1H), 5.20 (dd, *J* = 11.5, 3.3 Hz, 1H), 5.10 (dd, *J* = 11.4, 3.2 Hz, 1H) 4.96-4.94 (m, 2H), 4.73 (t, *J* = 4.4 Hz, 1H), 4.65-4.61 (m, 1H), 4.52-4.48 (m, 4H), 4.31 (t, *J* = 6.4 Hz, 2H), 4.17-3.90 (m, 10 H), 3.78-3.75 (m, 1 H), 3.26-3.13 (m, 2 H), 2.30 (t, *J* = 7.4 Hz, 2H), 2.16, (s, 3H), 2.15 (s, 3H), 1.99 (s, 3H), 2.02-1.96 (m, 18H), 1.68-1.50 (m, 4H), 1.39-1.32 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 174.5, 174.4, 173.1, 172.9, 172.8, 172.7, 172.6, 172.5, 171.7, 146.2, 146.1, 143.5, 129.7, 129.14, 129.10, 127.0, 126.99, 121.9, 100.4, 99.7, 70.54, 70.50, 69.6, 69.14, 69.11, 69.06, 63.9, 63.8, 57.4, 55.3, 44.2, 41.2, 36.0, 30.9, 28.4, 26.7, 23.6, 21.6, 21.53, 21.52, 21.4. HRMS calcd for $C_{57}H_{74}N_6O_{25}$ $[M + Na]^+$ 1265.460, measured 1265.460.

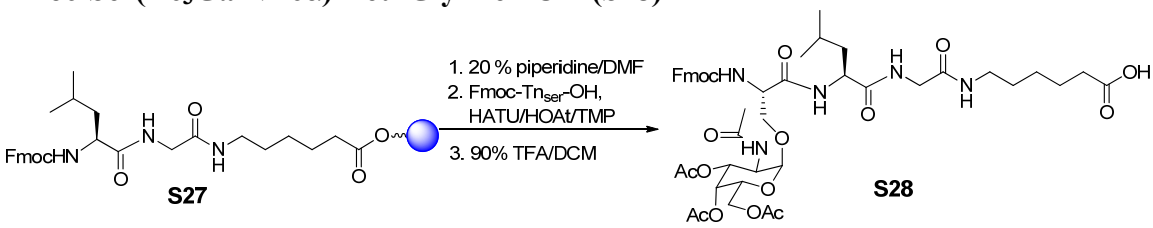
Fmoc-Leu-Gly-Hex-OH (S26)



S17 **S26**

Compound **S26** was synthesized from **S17** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 15%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.35-7.31 (m, 2H), 4.50-4.46 (m, 2H), 4.25 (t, *J* = 6.8 Hz, 1H), 4.10-4.06 (m, 1H), 3.94 (d, *J* = 16.8 Hz, 1H), 3.73 (t, *J* = 16.8 Hz, 1H), 3.21-3.06 (m, 2H), 2.23 (t, *J* = 7.4 Hz, 2H), 1.73-1.46 (m, 7H), 1.34-1.27 (m, 2H), 0.98 (dd, *J* = 13.7, 6.4 Hz, 6H); ^{13}C-NMR (100 MHz, CD_3OD) δ 178.4, 176.9, 172.2, 159.7, 146.0, 143.5, 129.7, 129.1, 129.0, 127.1, 127.0, 121.8, 68.8, 56.3, 44.4, 42.2, 41.3, 41.1, 35.7, 30.8, 28.3, 26.7, 26.6, 24.2, 22.9, 19.1. HRMS calcd for $C_{29}H_{37}N_3O_6$ $[M + H]^+$ 524.2761, measured 524.2731.

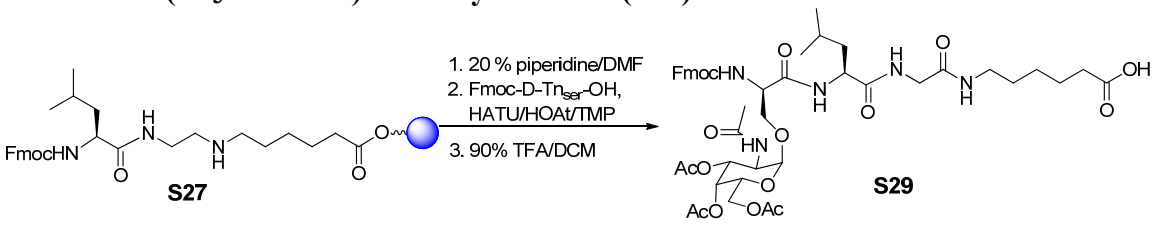
Fmoc-Ser(Ac$_3$GalNAcα)-Leu-Gly-Hex-OH (S28)



S27 **S28**

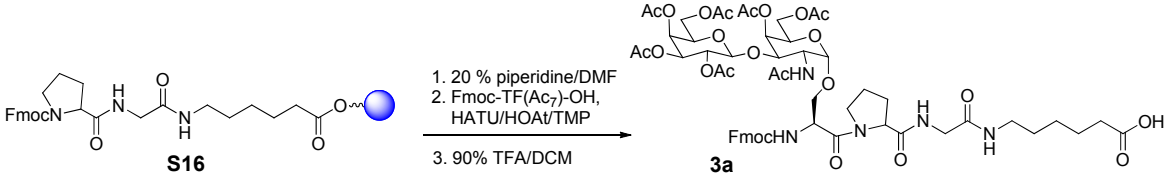
Compound **S28** was was synthesized from **S27** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 15%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.25-7.21 (m, 2H), 5.29 (d, *J* = 3.0 Hz, 1H), 5.05 (dd, *J* = 11.5, 3.0 Hz, 1H), 4.83 (d, *J* = 3.2 Hz, 1H), 4.37-4.32 (m, 4H), 4.25 (dd, *J* = 8.8, 5.9 Hz, 1H), 4.14 (d, *J* = 6.6 Hz, 2H), 4.02-3.89 (m, 2H), 3.84-3.80 (m, 2H), 3.72-3.63 (m, 2H), 3.17-3.04 (m, 2H), 2.18 (t, *J* = 7.4 Hz, 2H), 2.04 (s, 3H), 1.86 (s, 3 H), 1.85 (s, 3 H), 1.84 (s, 3 H), 1.57-1.40 (m, 7H), 1.29-1.19 (m, 2H), 0.85 (dd, *J* = 11.3, 5.9 Hz, 6H); ^{13}C-NMR (100 MHz, CD_3OD) δ 176.1, 173.4, 172.1, 170.8, 170.4, 169.8, 156.9, 143.8, 143.7, 141.2, 127.4, 126.8, 124.7, 119.5, 98.5, 68.3, 68.0, 67.2, 66.7, 66.66, 61.4, 54.6, 52.3, 42.0, 40.1, 38.9, 33.4, 28.6, 26.0, 24.4, 24.3, 19.2, 19.1, 19.07, . HRMS calcd for $C_{46}H_{61}N_5O_{16}$ $[M + Na]^+$ 962.401, measured 962.408.

Fmoc-D-Ser(Ac$_3$GalNAcα)-Leu-Gly-Hex-OH (S29)



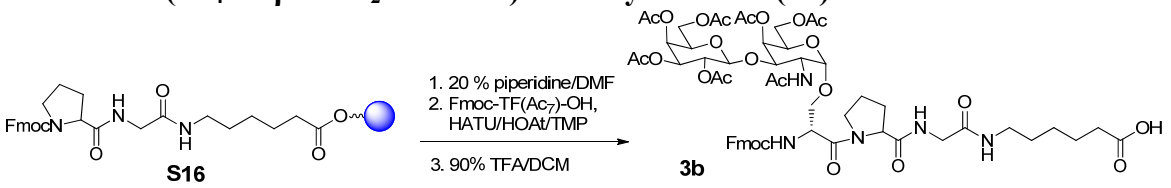
Compound **S29** was was synthesized from **S27** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 15%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.61-7.56 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.25-7.21 (m, 2H), 5.27 (d, *J* = 3.1 Hz, 1H), 4.99 (dd, *J* = 11.5, 3.2 Hz, 1H), 4.46-4.35 (m, 5H), 4.15 (t, *J* = 6.1 Hz, 1H), 4.05-4.00 (m, 2H), 3.93-3.85 (m, 2H), 3.78-3.67 (m, 2H), 3.60 (dd, *J* = 10.0, 3.2 Hz, 2H), 3.14-2.99 (m, 2 H), 2.16 (t, *J* = 7.4 Hz, 1H), 2.04 (s, 3H), 1.88 (s, 3 H), 1.85 (s, 3 H), 1.81 (s, 3 H), 1.58-1.51 (m, 5H), 1.42-1.36 (m, 2H), 1.26-1.19 (m, 2H), 0.85 (dd, *J* = 8.2, 5.6 Hz, 1H); ^{13}C-NMR (100 MHz, CD_3OD) δ 178.4, 175.8, 174.4, 173.2, 173.0, 172.9, 172.7, 172.1, 159.4, 146.1, 146.05, 143.6, 143.5, 129.7, 129.1, 129.1, 126.9, 126.8, 121.9, 99.9, 70.5, 70.0, 69.5, 69.0, 68.9, 63.7, 57.0, 54.6, 44.4, 42.4, 41.1, 35.7, 30.8, 28.3, 26.9, 26.6, 24.3, 23.6, 22.8, 21.5, 21.4. HRMS calcd for $C_{46}H_{61}N_5O_{16}$ $[M + Na]^+$ 962.401, measured 962.408.

Fmoc-Ser(Ac$_4$Galβ1-3Ac$_2$GalNAcα)-Pro-Gly-Hex-OH (3a)



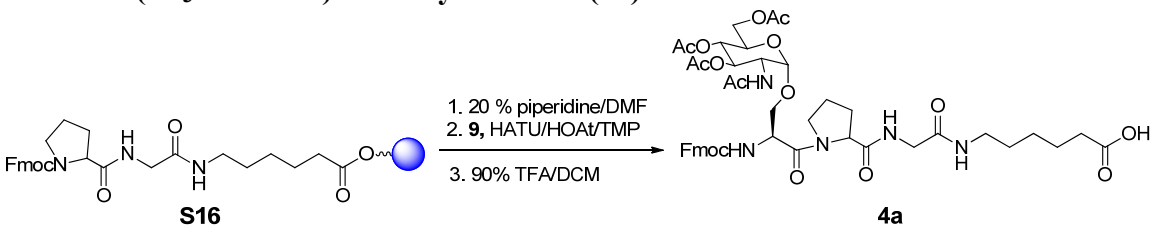
Compound **3a** was synthesized from **S16** according to the general procedure described for **6.** The crude product was purified by flash chromatography MeOH/CH_2Cl_2 (5% then 15%). The product was lyophilized to give a white solid. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 2H), 5.29 (br, 1H), 5.25 (d, *J* = 3.3 Hz, 1H), 5.03-4.99 (m, 1H), 4.89 (dd, *J* = 10.2, 8.04 Hz, 1H), 4.65-4.60 (m, 1H), 4.52 (d, *J* = 7.7 Hz, 1H), 4.39-3.50 (m, 18H), 3.31-3.24 (m, 2H), 3.03-2.91 (m, 2H), 2.17 (t, *J* = 7.4 Hz, 3H), 2.02 (s, 3H), 2.01 (s, 3 H), 1.93-1.89 (m, 13H), 1.83 (s, 3H), 1.57-1.46 (m, 4H), 1.34-1.26 (m, 2H); ^{13}C-NMR (100 MHz, CD_3OD) δ 178.3, 175.9, 173.9, 173.2, 172.9, 172.9, 172.8, 172.3, 172.28, 171.9, 171.2, 159.0, 146.0, 146.0, 143.5, 129.8, 129.1, 127.0, 126.9, 121.9, 103.6, 100.3, 76.7, 73.2, 72.4, 72.1, 71.1, 69.9, 69.5, 69.1, 68.9, 64.9, 63.2, 54.8, 50.9, 49.3, 44.7, 41.4, 35.7, 31.3, 31.0, 28.4, 27.2, 26.6, 24.0, 21.9, 21.7, 21.6, 21.61, 21.3. HRMS calcd for $C_{57}H_{73}N_5O_{24}$ $[M + Na]^+$ 1234.454, measured 1234.457.

Fmoc-D-Ser(Ac$_4$Galβ1-3Ac$_2$GalNAcα)-Pro-Gly-Hex-OH (3b)



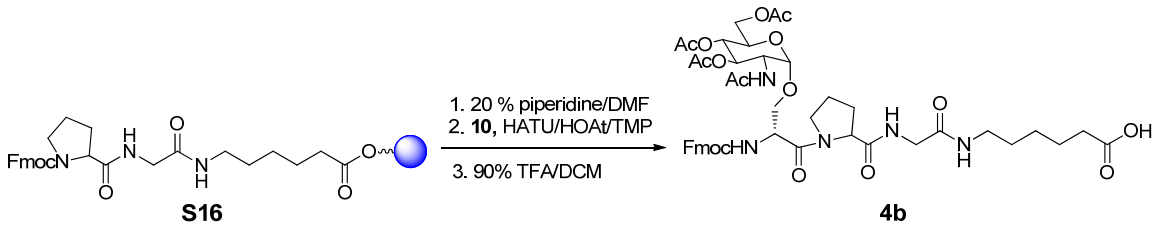
Compound **3b** was synthesized and purified according to the general procedure described for **6**. ^{1}H-NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.96-7.94 (m, 2H), 7.82-7.74 (m, 2H), 7.48-7.44 (m, 2H), 7.39-7.34 (m, 2H), 5.44-5.36 (m, 2H), 5.22-4.73 (m, 5H), 4.64-3.61 (m, 19H), 3.28-3.03 (m, 2H), 2.29-2.24 (m, 3H), 2.13-1.95 (m, 23H), 1.58-1.51 (m, 4H), 1.38-1.30 (m, 2H). HRMS calcd for $C_{57}H_{73}N_5O_{24}$ $[M + Na]^+$ 1234.454, measured 1234.458.

Fmoc-Ser(Ac$_3$GlcNAcα)-Pro-Gly-Hex-OH (4a)



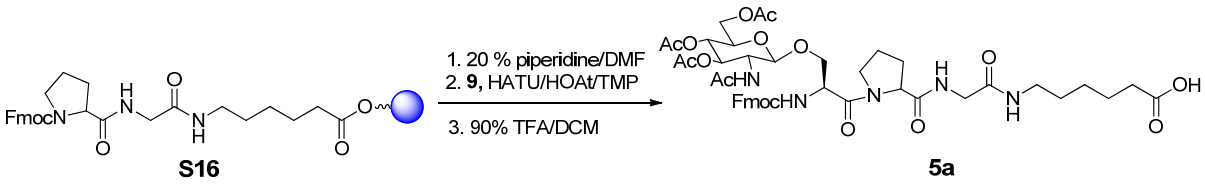
Glycopeptide **4a** was synthesized and purified according to the general procedure described for **6**. ^{1}H NMR (400 MHz, CD_3OD) δ 7.81 (d, *J* = 7.5Hz, 2H), 7.7.66 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 5.21(t, *J* = 9.9 Hz, 1H), 5.00 (t, *J* = 10.0 Hz, 1H), 4.90-3.68 (m, 16H), 3.27-3.13(m, 2H), 2.29-1.92 (m, 17H), 1.66-1.35 (m, 6H); ^{13}C NMR (100MHz, CD_3OD) δ 176.0, 172.1, 170.9, 170.4, 170.1, 169.8, 168.9, 156.8, 143.8, 143.7, 141.2, 127.4, 126.8, 124.6, 119.5, 98.0, 71.0, 68.7, 67.8, 67.2, 66.5, 61.8, 60.8, 52.8, 51.4, 42.2, 38.9, 33.3, 28.9, 28.6, 26.0, 24.8, 24.3, 21.2, 19.20, 19.16. HRMS calcd for $C_{45}H_{57}N_5O_{16}[M + Na]^+$ 946.370, measured 946.363.

Fmoc-D-Ser(Ac$_3$GlcNAcα)-Pro-Gly-Hex-OH (4b)



Compound **4b** was synthesized and purified according to the general procedure described for **6**. ^{1}H NMR (400 MHz, CD_3OD) δ 7.80 (d, *J* = 7.5Hz, 2H), 7.70-7.64 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 2H), 5.20(t, *J* = 10.1 Hz, 1H), 5.00 (t, *J* = 9.8 Hz, 1H), 4.75-3.54 (m, 16H), 3.25-3.08(m, 2H), 2.28-1.82 (m, 17H), 1.63-1.29 (m, 6H); ^{13}C NMR (100MHz, CD_3OD) δ 176.0, 173.3, 171.93, 171.92, 170.9, 170.5, 169.9, 169.7, 169.1, 157.2, 143.9, 143.6, 141.3, 127.42, 127.40, 126.8, 124.74, 124.69, 119.5, 97.2, 70.8, 68.6, 67.8, 67.1, 66.8, 66.4, 61.8, 61.3, 52.6, 51.4, 42.7, 42.2, 38.9, 33.3, 28.9, 28.7, 28.4, 26.0, 24.7, 24.2, 19.2., 19.1, 19.0. HRMS calcd for $C_{45}H_{57}N_5O_{16}[M + Na]^+$ 946.370, measured 946.364.

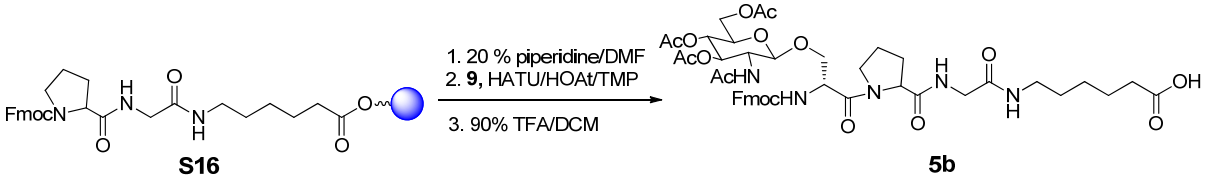
Fmoc-Ser(Ac$_3$GlcNAcβ)-Pro-Gly-Hex-OH (5a)



S16 5a

Compound **5a** was synthesized and purified according to the general procedure described for **6**. ^{1}H NMR (400 MHz, CD_3OD) δ 7.80 (d, *J* = 7.5Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 5.20 (t, *J* = 9.8 Hz, 1H), 4.98 (t, *J* = 9.8 Hz, 1H), 4.69-4.10 (m, 8H), 3.95-3.13 (m, 10H), 2.31-1.86(m, 17H), 1.64-1.34 (m, 6H); ^{13}C NMR (100MHz, CD_3OD) δ 176.0, 173.3, 172.0, 170.9, 170.4, 170.2, 169.9, 169.8, 156.8, 143.7, 141.2, 127.4, 126.8, 124.7, 119.5, 100.5, 72.7, 71.7, 68.6, 68.2, 66.5, 61.8, 61.0, 53.8, 52.7, 42.1, 38.9, 33.3, 29.0, 28.5, 26.0, 24.7, 24.3, 21.5, 19.2, 19.11, 19.09. HRMS calcd for $C_{45}H_{57}N_5O_{16}[M + Na]^+$ 946.370, measured 946.367.

Fmoc-D-Ser(Ac$_3$GlcNAcβ)-Pro-Gly-Hex-OH (5b)



S16 5b

Compound **5b** was synthesized and purified according to the general procedure described for **6**. ^{1}H NMR (400 MHz, CD_3OD) δ 7.79 (d, *J* = 7.5Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.41-7.29 (m, 4H), 5.17 (t, *J* = 9.3 Hz, 1H), 4.98 (t, *J* = 9.8 Hz, 1H), 4.64-3.68 (m, 16H), 3.19-2.98 (m, 2H), 2.27-1.88 (m, 17H), 1.60-1.30 (m, 6H); ^{13}C NMR (100MHz, CD_3OD) δ 176.0, 173.2, 172.0, 170.9, 170.7, 170.4, 169.9, 169.8, 157.0, 143.7, 143.6, 141.25, 141.20, 127.4, 126.8, 124.7, 124.6, 119.5, 119.6, 100.9, 72.6, 71.6, 68.5, 66.5, 61.6, 61.3, 53.7, 53.0, 42.1, 38.8, 33.4, 29.0, 28.4, 25.9, 24.4, 24.2, 21.4, 19.3, 19.11, 19.07. HRMS calcd for $C_{45}H_{57}N_5O_{16}[M + Na]^+$ 946.370, measured 946.364.

HPLC analysis of products in coupling reactions

HPLC trace of Fmoc-Ser-Pro-Gly-Hex-OH

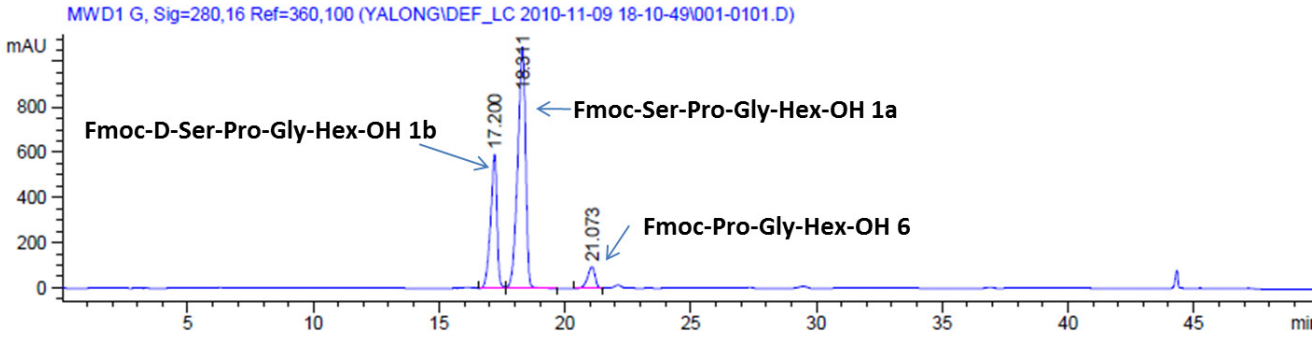


Figure S1. HPLC trace of Fmoc-Ser-Pro-Gly-Hex-OH **1a**, its racemized D isomer **1b** and the unreacted starting peptide **6**. Analyses were performed with Waters XTerra® RP 18 (4.6 mm × 250 mm) reverse phase column. UV absorption was measured at 280 nm and the flow rate was 1 mL/min. The percentage of B was increased according to a linear gradient of 1%-35% in 9 min, kept at 35% for 3 min, and then increased from 35% to 48% in 27 min.

HPLC trace of Fmoc-Ser(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH

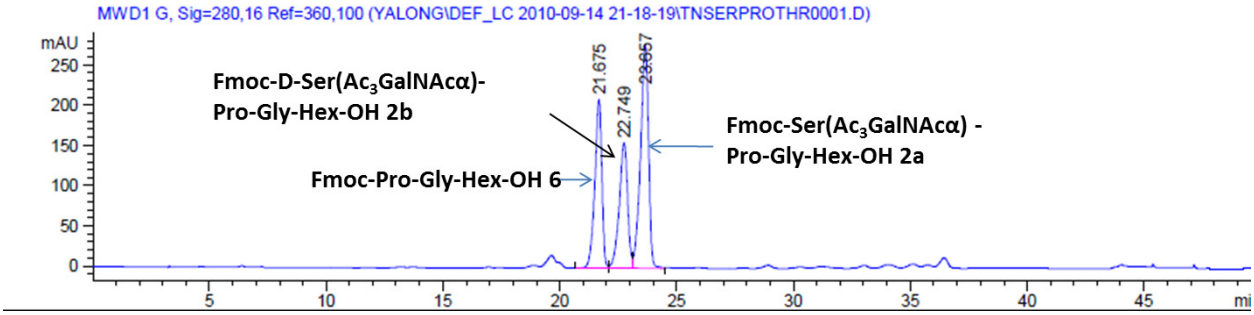


Figure S2. HPLC trace of Fmoc-Ser(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH **2a**, its epimerization D isomer **2b** and the unreacted starting peptide **6**. Analyses were performed with the same conditions as those for obtaining Figure S1.

HPLC trace of Fmoc-Ser(Ac_3GalNAcα)-Ser-Gly-Hex-OH

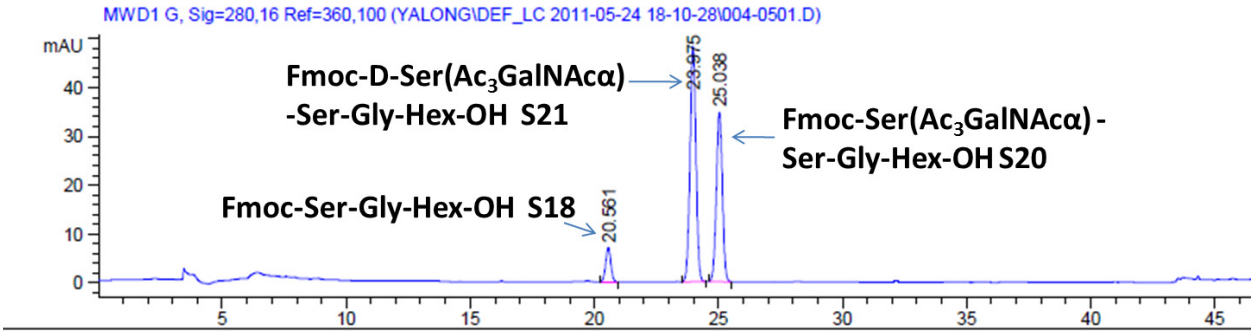


Figure S3. HPLC trace of Fmoc-Ser(Ac_3GalNAcα)-Ser-Gly-Hex-OH **S20**, its epimerization D isomer **S21** and the unreacted starting peptide **S18**. Analyses were performed with the same conditions as those for obtaining Figure S1.

HPLC trace of Fmoc-Ser(Ac_3GalNAcα)-Ser(Ac_3GalNAcα)-Gly-Hex-OH

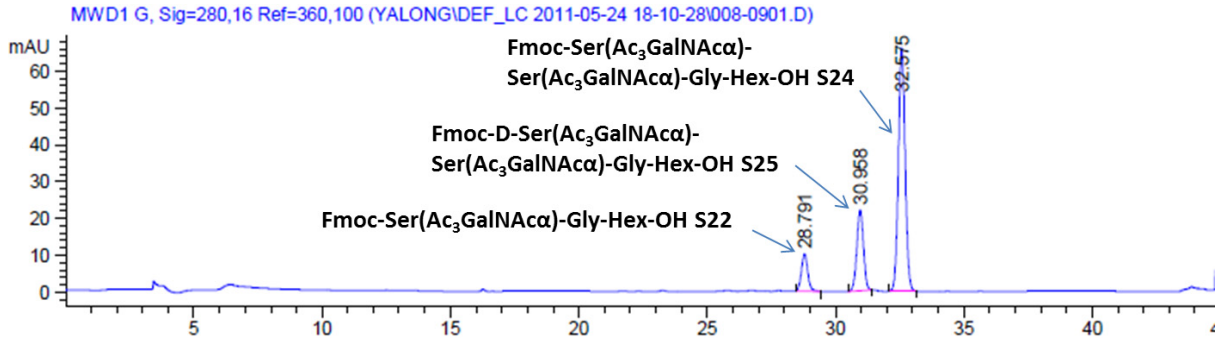


Figure S4. HPLC trace of Fmoc-Ser(Ac_3GalNAcα)-Ser(Ac_3GalNAcα)-Gly-Hex-OH **S24**, its epimerization D isomer **S25** and the unreacted starting glycopeptide **S22**. Analyses were performed with the same conditions as those for obtaining Figure S1.

HPLC trace of Fmoc-Ser(Ac$_3$GalNAcα)-Leu-Gly-Hex-OH

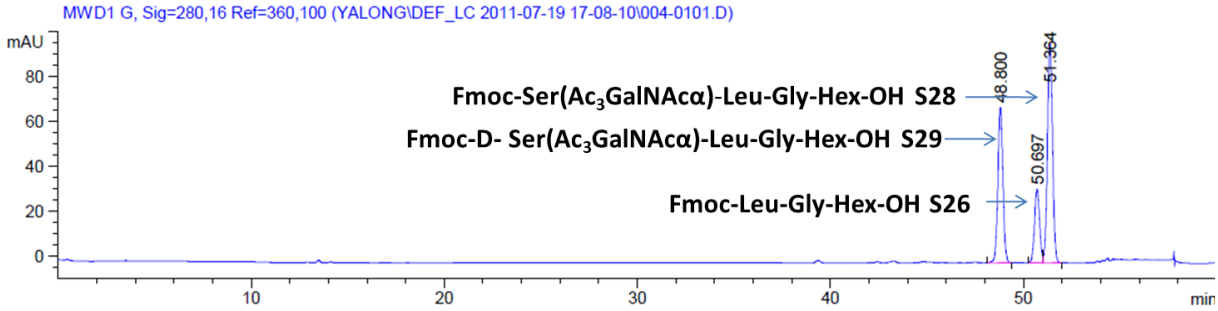


Figure S5. HPLC trace of Fmoc-Ser(Ac$_3$GalNAcα)-Leu-Gly-Hex-OH **S28**, its epimerization D isomer **S29** and the unreacted starting peptide **S26**. Analyses were performed with Waters XTerra® RP 18 (4.6 mm × 250 mm) reverse phase column. UV absorption was measured at 280 nm and the flow rate was 1 mL/min. The percentage of B was increased according to a linear gradient of 1%-25% in 9 min, kept at 25% for 1 min, increased from 25% to 29% in 8 min, kept at 29% for 1.5 min, increased from 29% to 32% for 3.5 min, and then increased from 32% to 45% in 16 min.

HPLC trace of Fmoc-Ser(Ac_4Galβ1-3Ac2GalNAcα)-Pro-Gly-Hex-OH

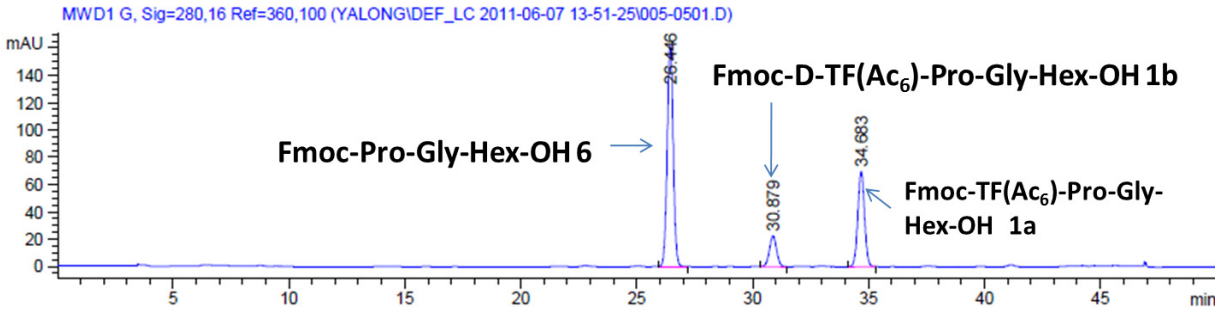


Figure S6. HPLC trace of Fmoc-Ser(Ac_4Galβ1-3Ac_2GalNAcα)(TF(Ac_6))-Pro-Gly-Hex-OH **3a**, its epimerization D isomer **3b** and the unreacted starting peptide **6**. Analyses Waters XTerra® RP 18 (4.6 mm × 250 mm) reverse phase column. UV absorption was measured at 280 nm and the flow rate was 1 mL/min. The percentage of B was increased according to a linear gradient of 1%-35% in 7 min, kept at 35% for 3 min, increased from 35% to 48% in 27 min.

HPLC trace of Fmoc-Ser(Ac$_3$GlcNAcα)-Pro-Gly-Hex-OH

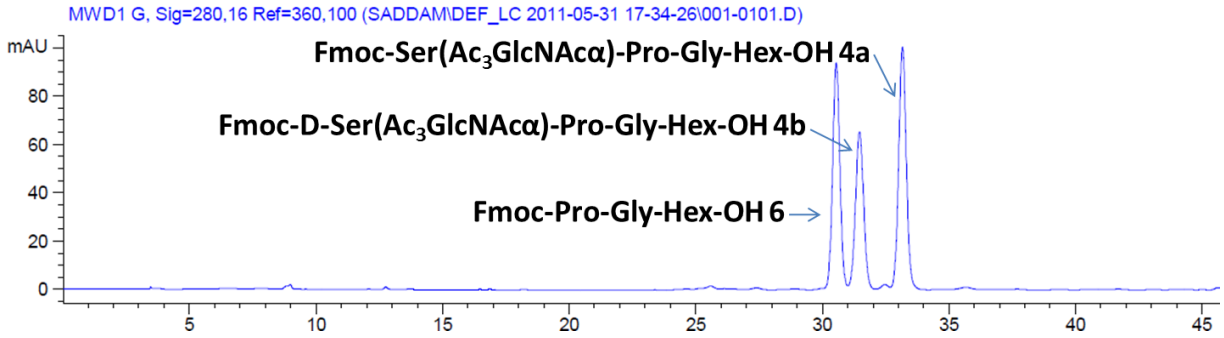


Figure S7. HPLC trace of Fmoc-Ser(Ac$_3$GlcNAcα)-Pro-Gly-Hex-OH **4a**, its epimerization D isomer **4b** and the unreacted starting peptide **6**. Analyses were performed with Waters XTerra® RP 18 (4.6 mm × 250 mm) reverse phase column. UV absorption was measured at 280 nm and the flow rate was 1 mL/min. The percentage of B was increased according to a linear gradient of 1%-35% in 9 min, kept at 35% for 3 min, increased from 35% to 48% in 27 min.

HPLC trace of Fmoc-Ser(Ac_3GlcNAcβ)-Pro-Gly-Hex-OH

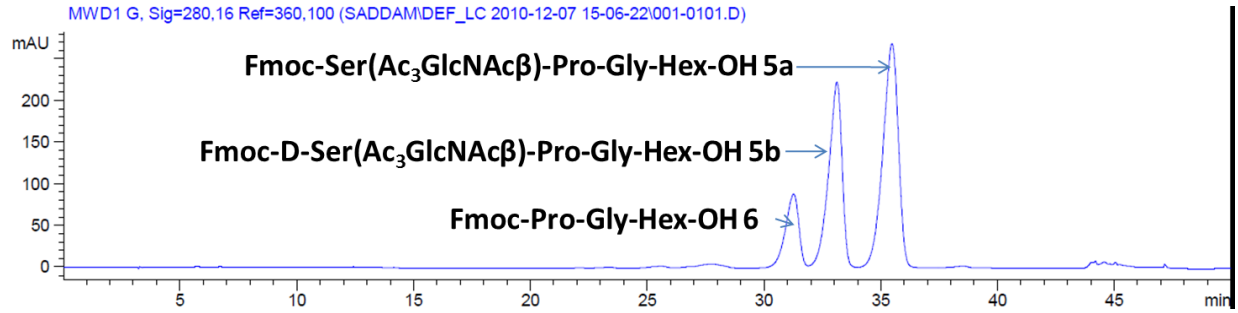


Figure S8. HPLC trace of Fmoc-Ser(Ac_3GlcNAcβ)-Pro-Gly-Hex-OH **5a,** its epimerization D isomer **5b** and the unreacted starting peptide **6**. Analyses were performed with Waters XTerra® RP 18 (4.6 mm × 250 mm) reverse phase column. UV absorption was measured at 280 nm and the flow rate was 1 mL/min. The percentage of B was increased according to a linear gradient of 1%-31% in 7 min, kept at 31% for 5 min, increased from 38% to 48% in 27 min

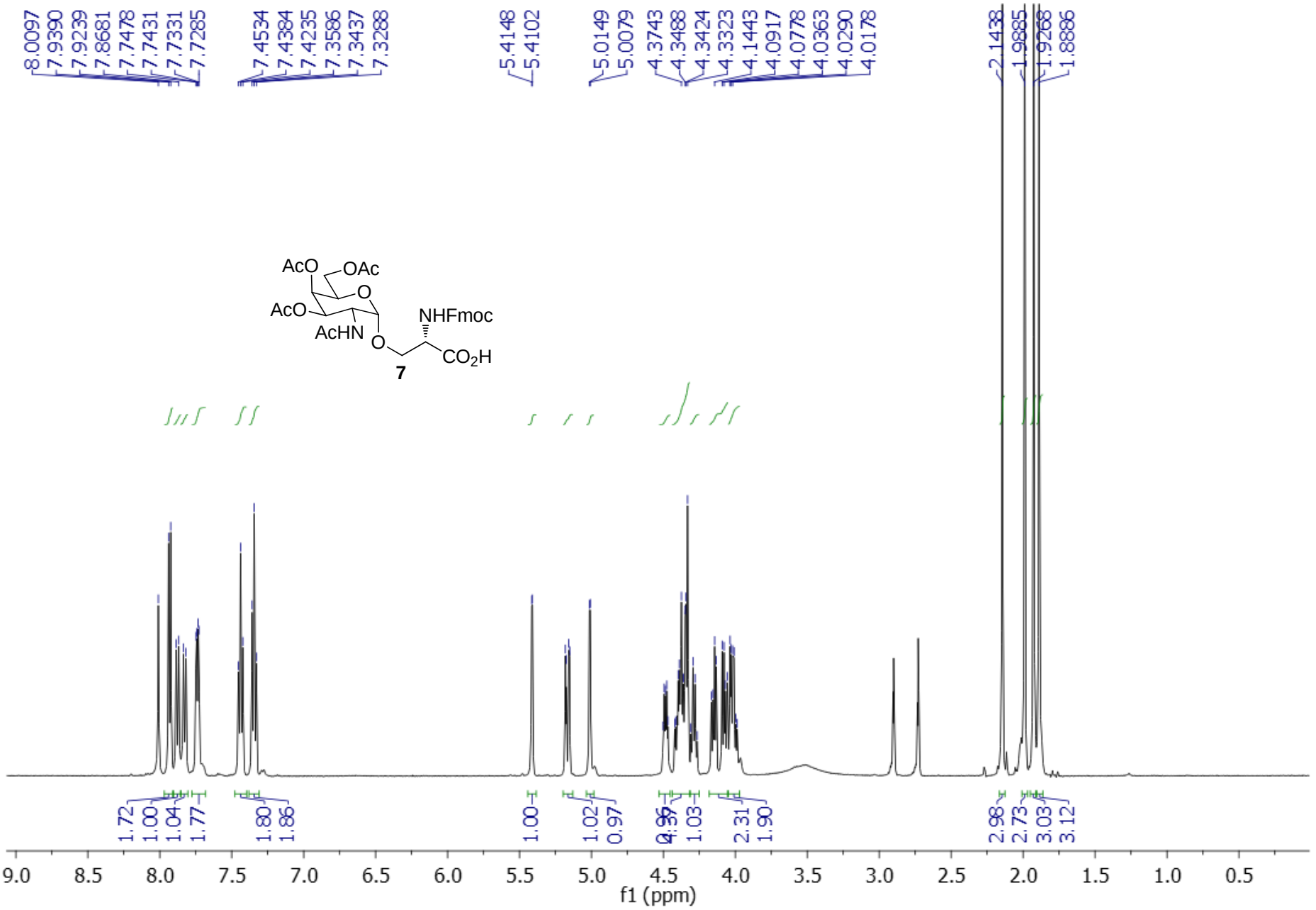
References

(1) Kuduk, S. D.; Schwarz, J. B.; Chen, X.-T.; Glunz, P. W.; Sames, D.; Ragupathi, G.; Livingston, P. O.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 12474.

(2) Montero, J. L.; Winum, J. Y.; Leydet, A.; Kamal, M.; Pavia, A. A.; Roque, J. P. *Carbohydrate Research* **1997**, *297*, 175.

(3) Arsequell, G.; Krippner, L.; Dwek, R. A.; Wong, S. Y. C. *Journal of the Chemical Society-Chemical Communications* **1994**, 2383.

(4) Kay, C.; Lorthioir, O. E.; Parr, N. J.; Congreve, M.; McKeown, S. C.; Scicinski, J. J.; Ley, S. V. *Biotechnol Bioeng* **2000**, *71*, 110.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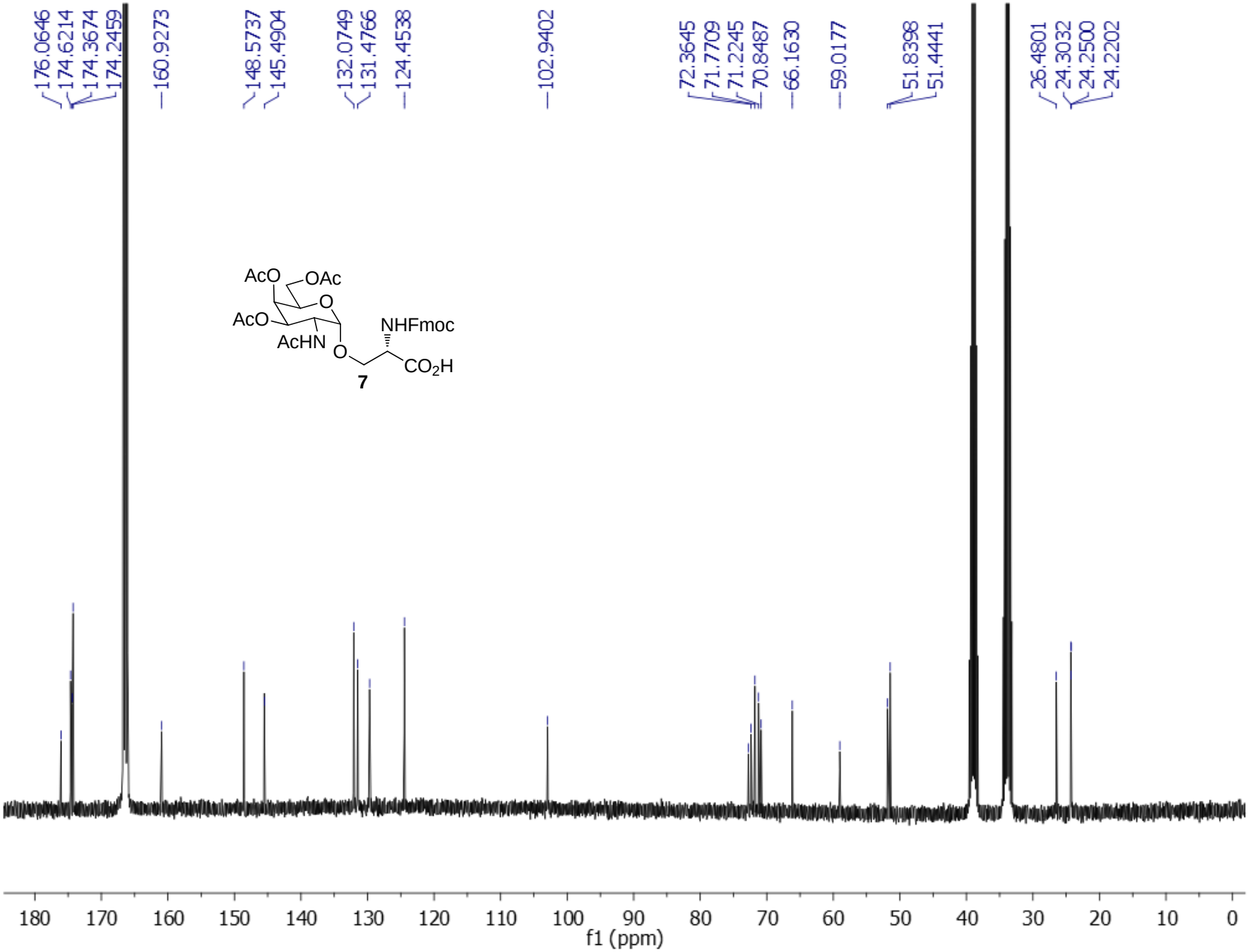
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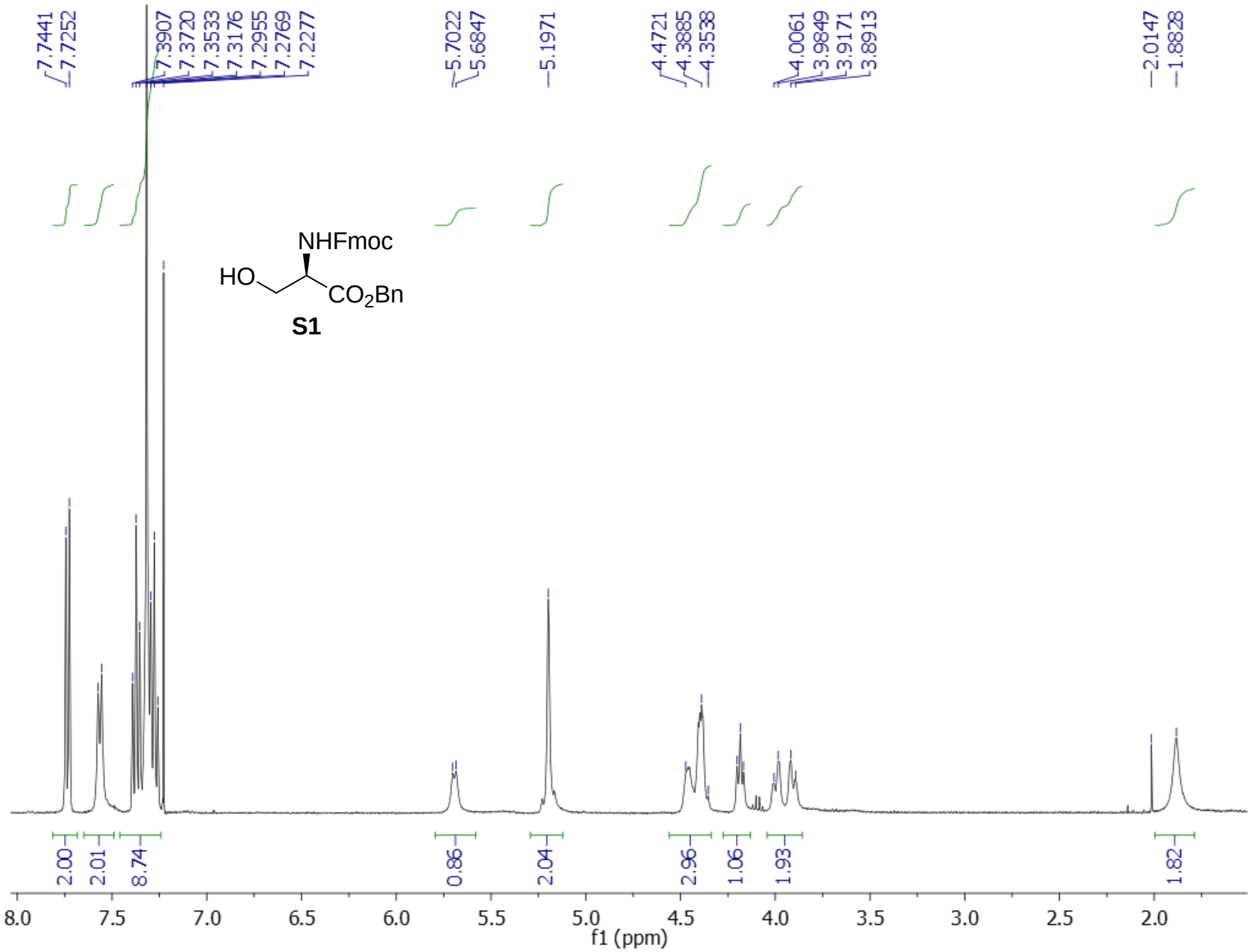
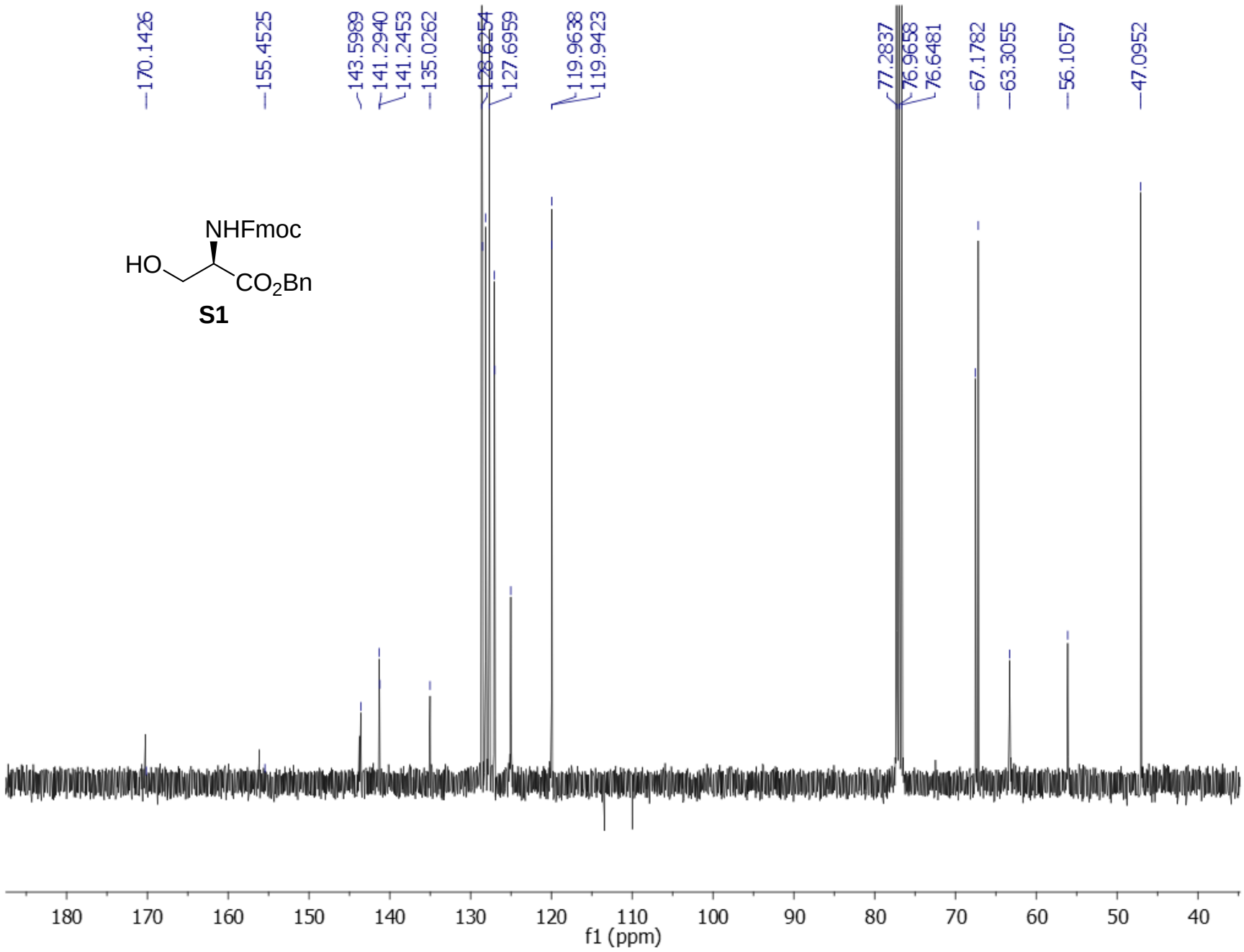
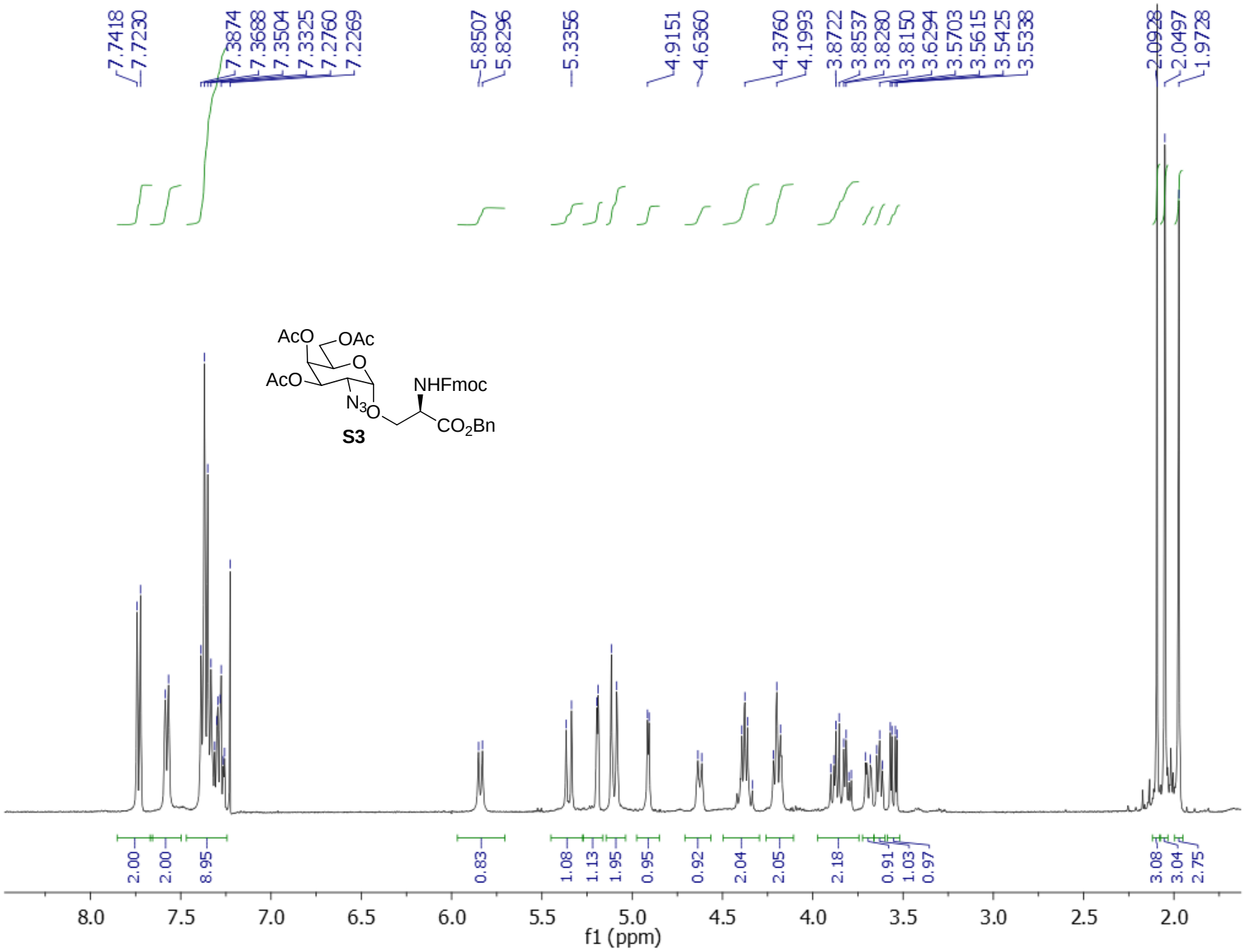
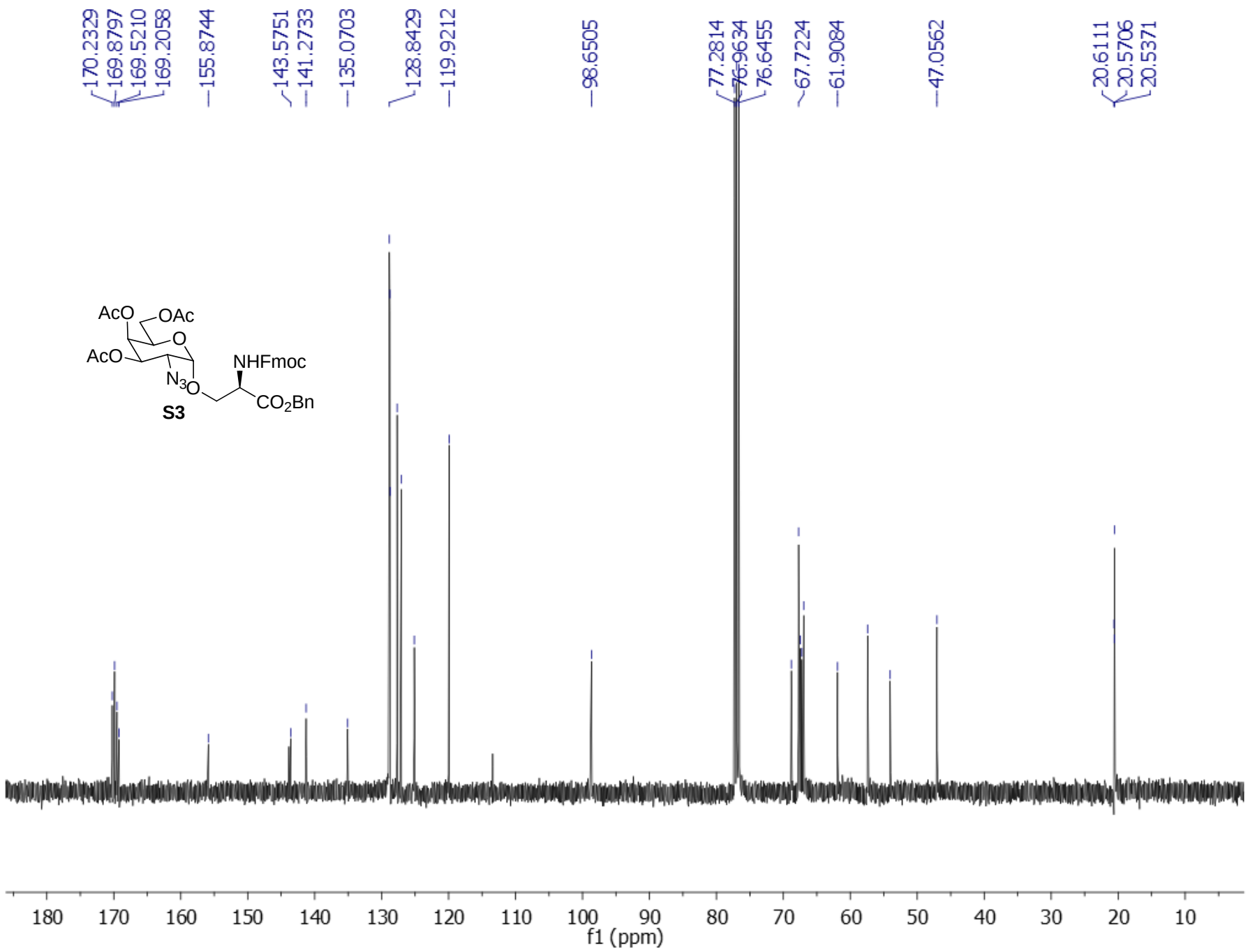
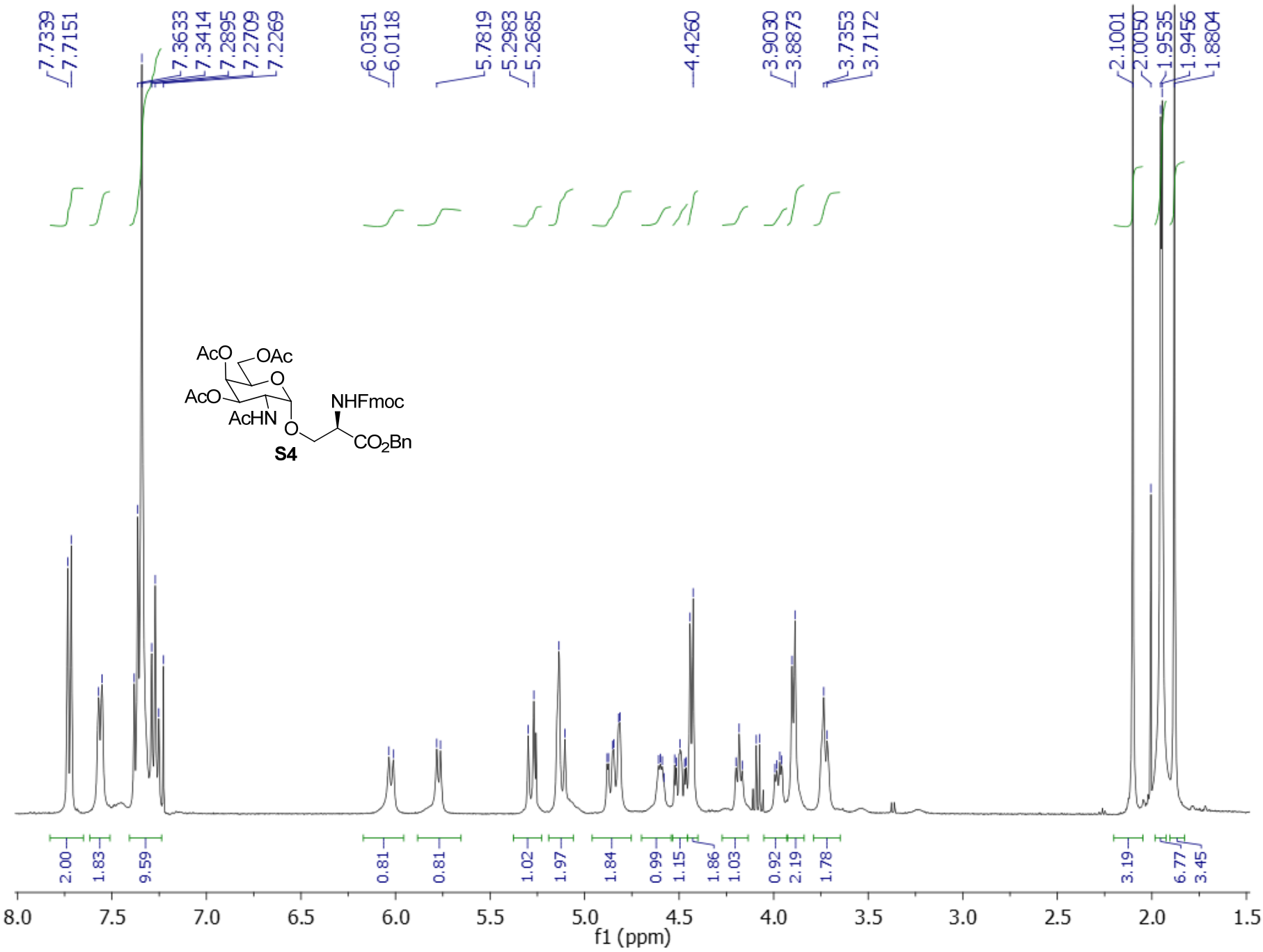
145.4904
132.0749
131.4766
124.4538
102.9402
72.3645
71.7709
71.2245
70.8487
66.1630
59.0177
51.8398
51.4441
26.4801
24.3032
24.2500
24.2202
AcO
OAc
O
AcO
AcHN
O
NHFmoc
CO2H
7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

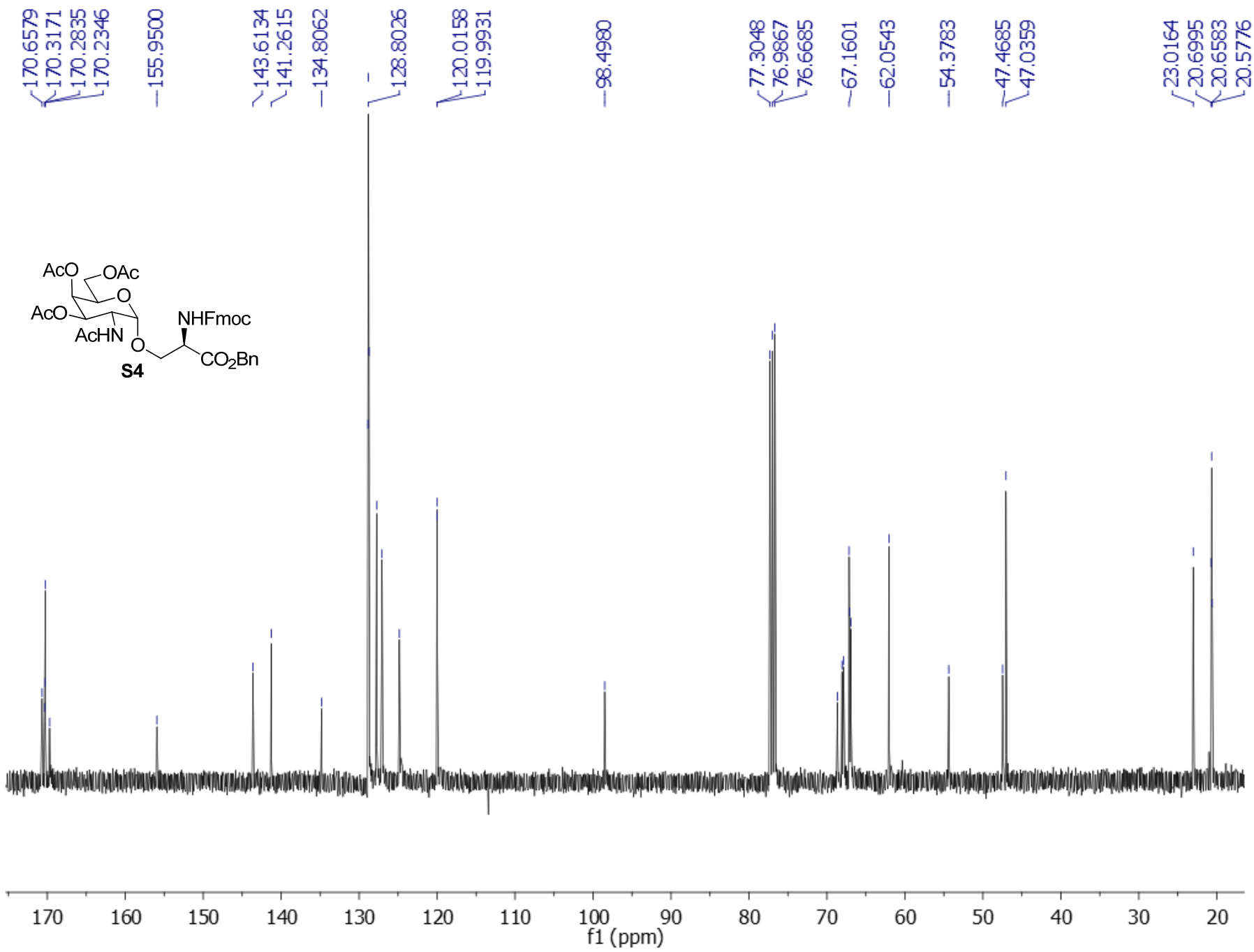

7.7441
7.7252
7.3907
7.3720
7.3533
7.3176
7.2955
7.2769
7.2277
5.7022
5.6847
5.1971
4.4721
4.3885
4.3538
4.0061
3.9849
3.9171
3.8913
2.0147
1.8828
NHFmoc
HO
CO2Bn
S1
2.00
2.01
8.74
0.86
2.04
2.96
1.06
1.93
1.82
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)

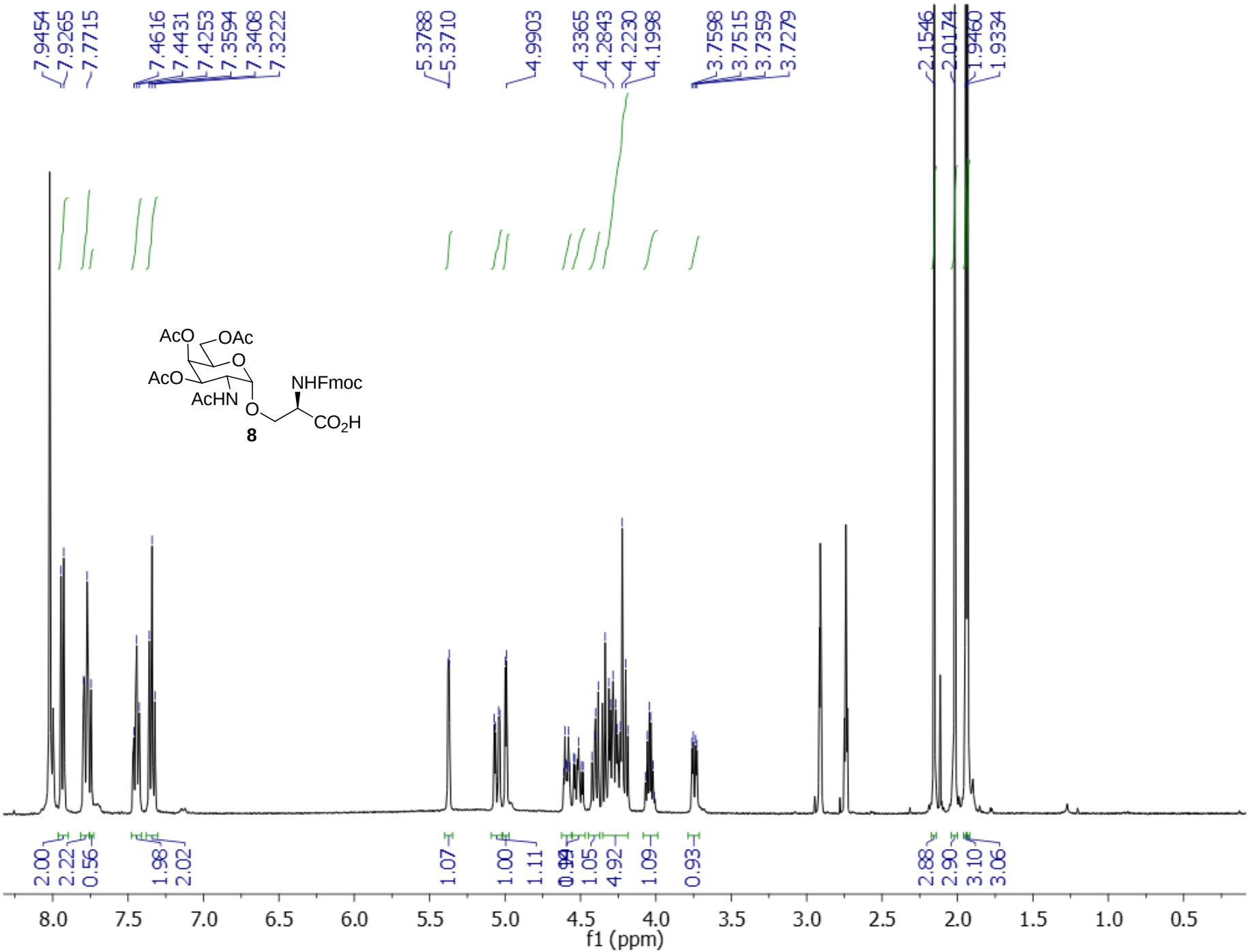

170.1426
155.4525
143.5989
141.2940
141.2453
135.0262
128.6254
127.6959
119.9638
119.9423
77.2837
76.9658
76.6481
67.1782
63.3055
56.1057
47.0952
NHFmoc
HO
CO2Bn
S1
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

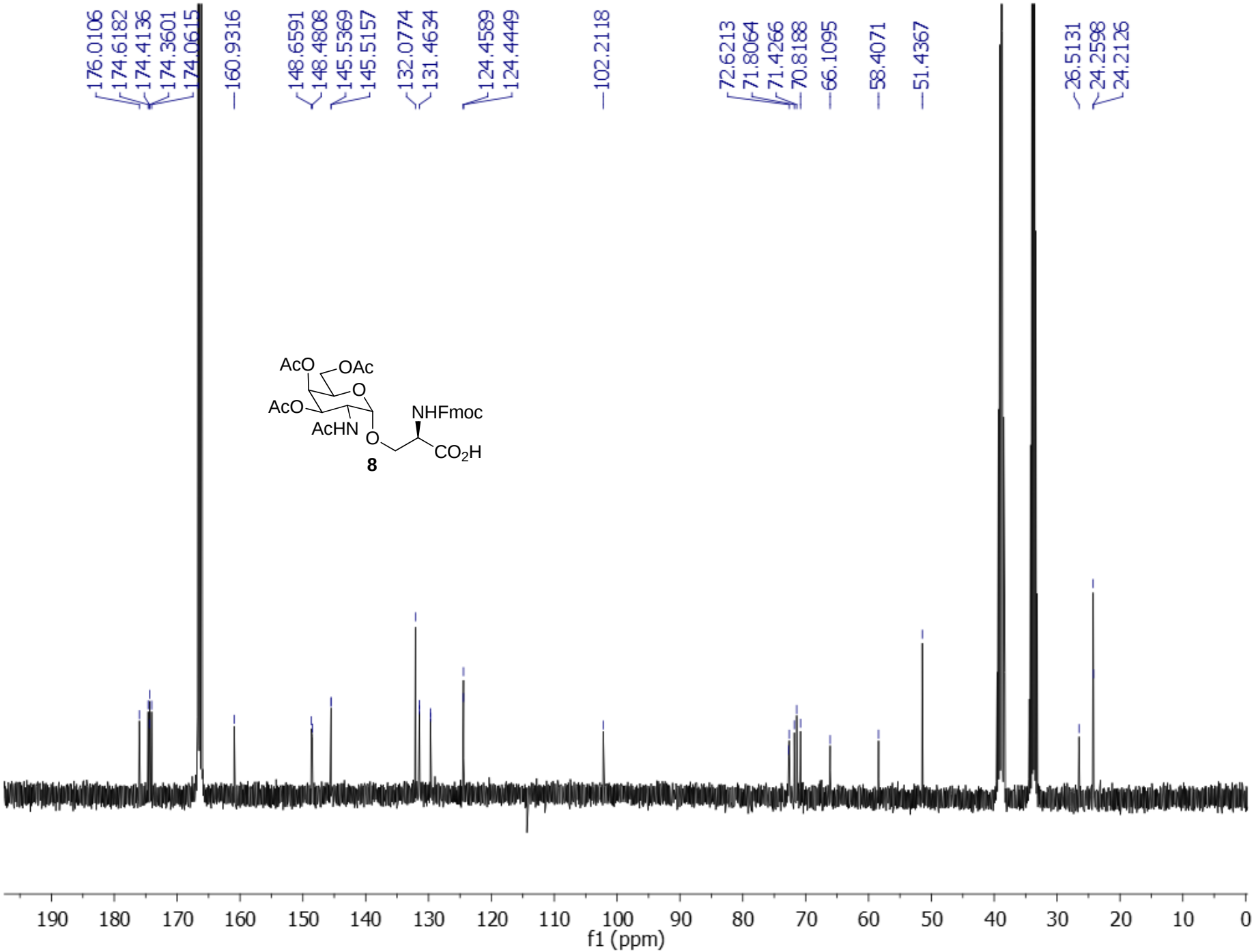

7.7418
7.7230
7.3874
7.3688
7.3504
7.3325
7.2760
7.2269
5.8507
5.8296
5.3356
4.9151
4.6360
4.3760
4.1993
3.8722
3.8537
3.8280
3.8150
3.6294
3.5703
3.5615
3.5425
3.5338
2.0928
2.0497
1.9728
AcO
OAc
O
AcO
N3
O
NHFmoc
CO2Bn
S3
2.00
2.00
8.95
0.83
1.08
1.13
1.95
0.95
0.92
2.04
2.05
2.18
0.91
1.03
0.97
3.08
3.04
2.75
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
f1 (ppm)

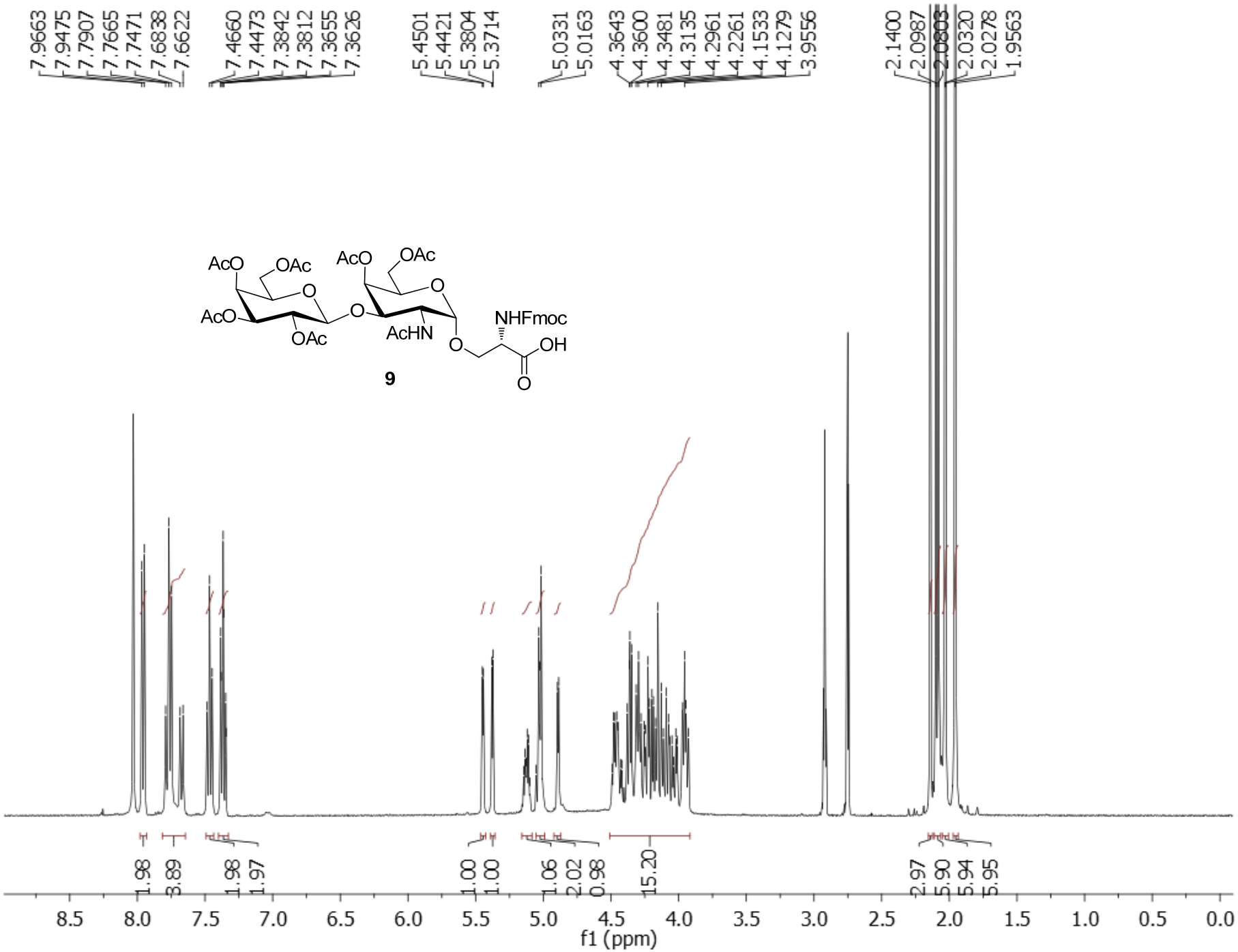

170.2329
169.8797
169.5210
169.2058
155.8744
143.5751
141.2733
135.0703
128.8429
119.9212
98.6505
77.2814
76.9634
76.6455
67.7224
61.9084
47.0562
20.6111
20.5706
20.5371
AcO
OAc
O
AcO
NHFmoc
N3
O
CO2Bn
S3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

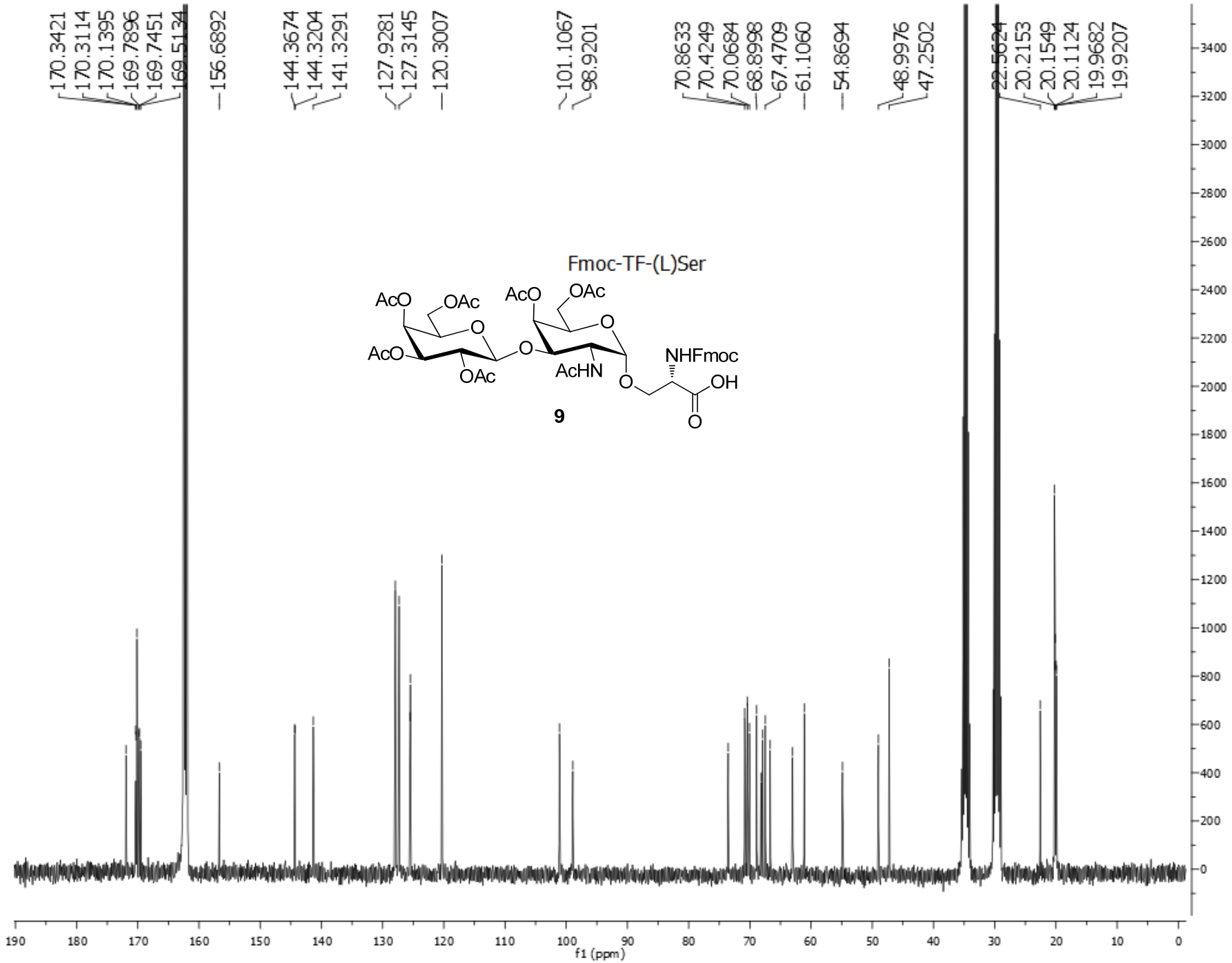

7.7339
7.7151
7.3633
7.3414
7.2895
7.2709
7.2269
6.0351
6.0118
5.7819
5.2983
5.2685
4.4260
3.9030
3.8873
3.7353
3.7172
2.1001
2.0050
1.9535
1.9456
1.8804
AcO
OAc
O
AcO
AcHN
O
NHFmoc
CO2Bn
S4
2.00
1.83
9.59
0.81
0.81
1.02
1.97
1.84
0.99
1.15
1.86
1.03
0.92
2.19
1.78
3.19
6.77
3.45
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

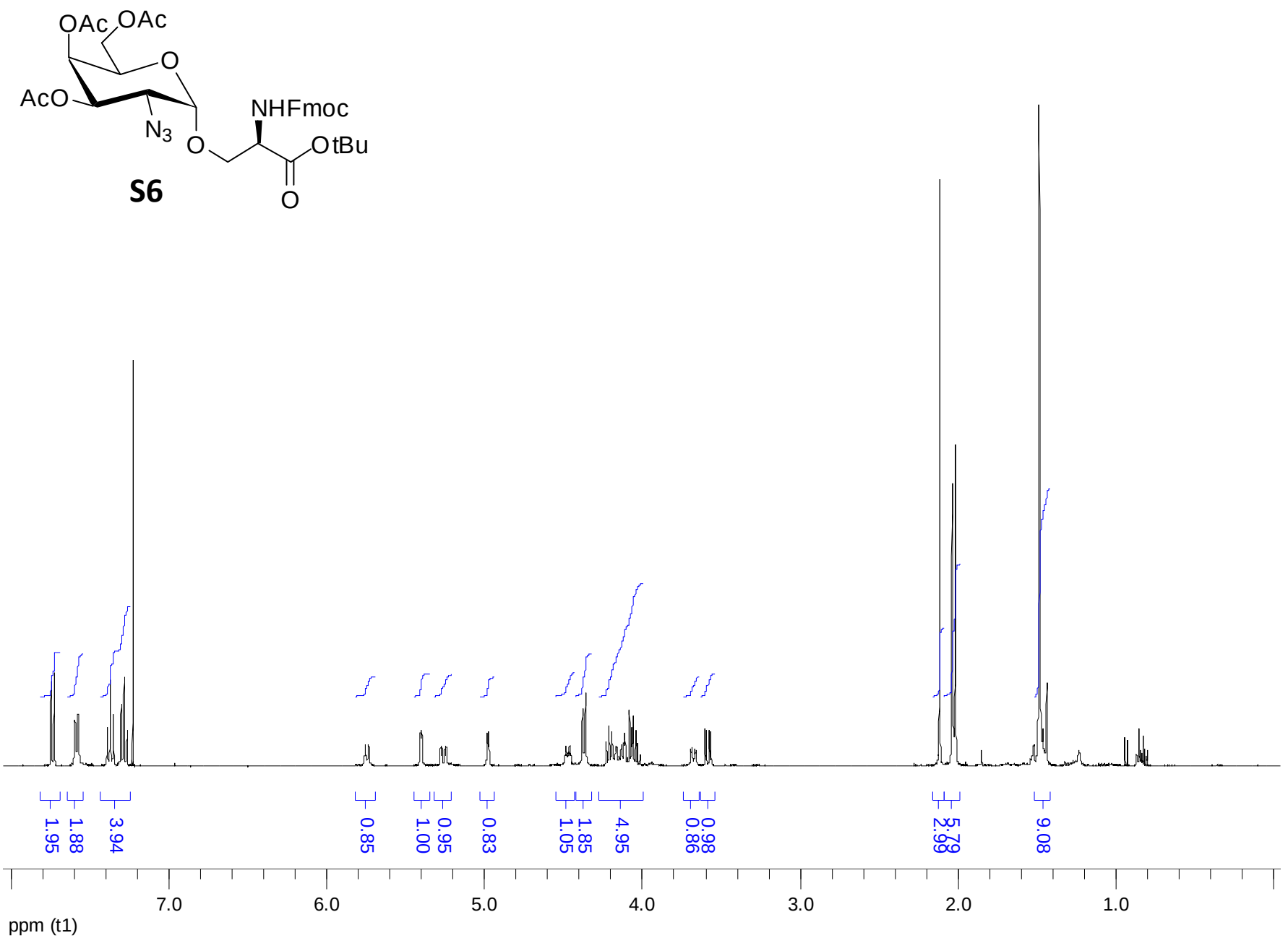

170.6579
170.3171
170.2835
170.2346
155.9500
143.6134
141.2615
134.8062
128.8026
120.0158
119.9931
98.4980
77.3048
76.9867
76.6685
67.1601
62.0543
54.3783
47.4685
47.0359
23.0164
20.6995
20.6583
20.5776
AcO
OAc
O
AcO
AcHN
O
NHFmoc
CO2Bn
S4
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


7.9454
7.9265
7.7715
7.4616
7.4431
7.4253
7.3594
7.3408
7.3222
5.3788
5.3710
4.9903
4.3365
4.2843
4.2230
4.1998
3.7598
3.7515
3.7359
3.7279
2.1546
2.0174
1.9460
1.9334
AcO
OAc
O
AcO
NHFmoc
AcHN
O
CO2H
8
2.00
2.22
0.56
1.98
2.02
1.07
1.00
1.11
1.05
4.92
1.09
0.93
2.88
2.90
3.10
3.06
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
f1 (ppm)


176.0106
174.6182
174.4136
174.3601
174.0615
160.9316
148.6591
148.4808
145.5369
145.5157
132.0774
131.4634
124.4589
124.4449
102.2118
72.6213
71.8064
71.4266
70.8188
66.1095
58.4071
51.4367
26.5131
24.2598
24.2126
AcO
OAc
O
AcO
AcHN
O
NHFmoc
CO2H
8
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.9663
7.9475
7.7907
7.7665
7.7471
7.6838
7.6622
7.4660
7.4473
7.3842
7.3812
7.3655
7.3626
5.4501
5.4421
5.3804
5.3714
5.0331
5.0163
4.3643
4.3600
4.3481
4.3135
4.2961
4.2261
4.1533
4.1279
3.9556
2.1400
2.0987
2.0803
2.0320
2.0278
1.9563
AcO
OAc
AcO
OAc
AcO
OAc
AcHN
NHFmoc
OH
9
1.98
3.89
1.98
1.97
1.00
1.00
1.06
2.02
0.98
15.20
2.97
5.90
5.94
5.95
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
f1 (ppm)


170.3421
170.3114
170.1395
169.7896
169.7451
169.5134
156.6892
144.3674
144.3204
141.3291
127.9281
127.3145
120.3007
101.1067
98.9201
70.8633
70.4249
70.0684
68.8998
67.4709
61.1060
54.8694
48.9976
47.2502
22.5624
20.2153
20.1549
20.1124
19.9682
19.9207
Fmoc-TF-(L)Ser
AcO
OAc
AcO
OAc
O
O
AcO
OAc
O
AcHN
NHFmoc
O
OH
O
9
f1 (ppm)


OAc
OAc
O
AcO
N3
O
NHFmoc
OtBu
O
S6
1.95
1.88
3.94
0.85
1.00
0.95
0.83
1.05
1.85
4.95
0.86
0.98
2.99
5.79
9.08
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

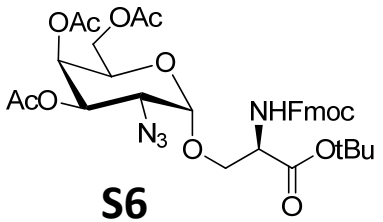
WGA100frak36C

Sample Name:
WGA100frak36C
Data Collected on:
jette2.ncifcrf.gov-inova400
Archive directory:
/home/ORL152/vnmrsys/data
Sample directory:
WGA100frak36C_20100201_01
FidFile: WGA100Frak36C_CARBON_C13_001

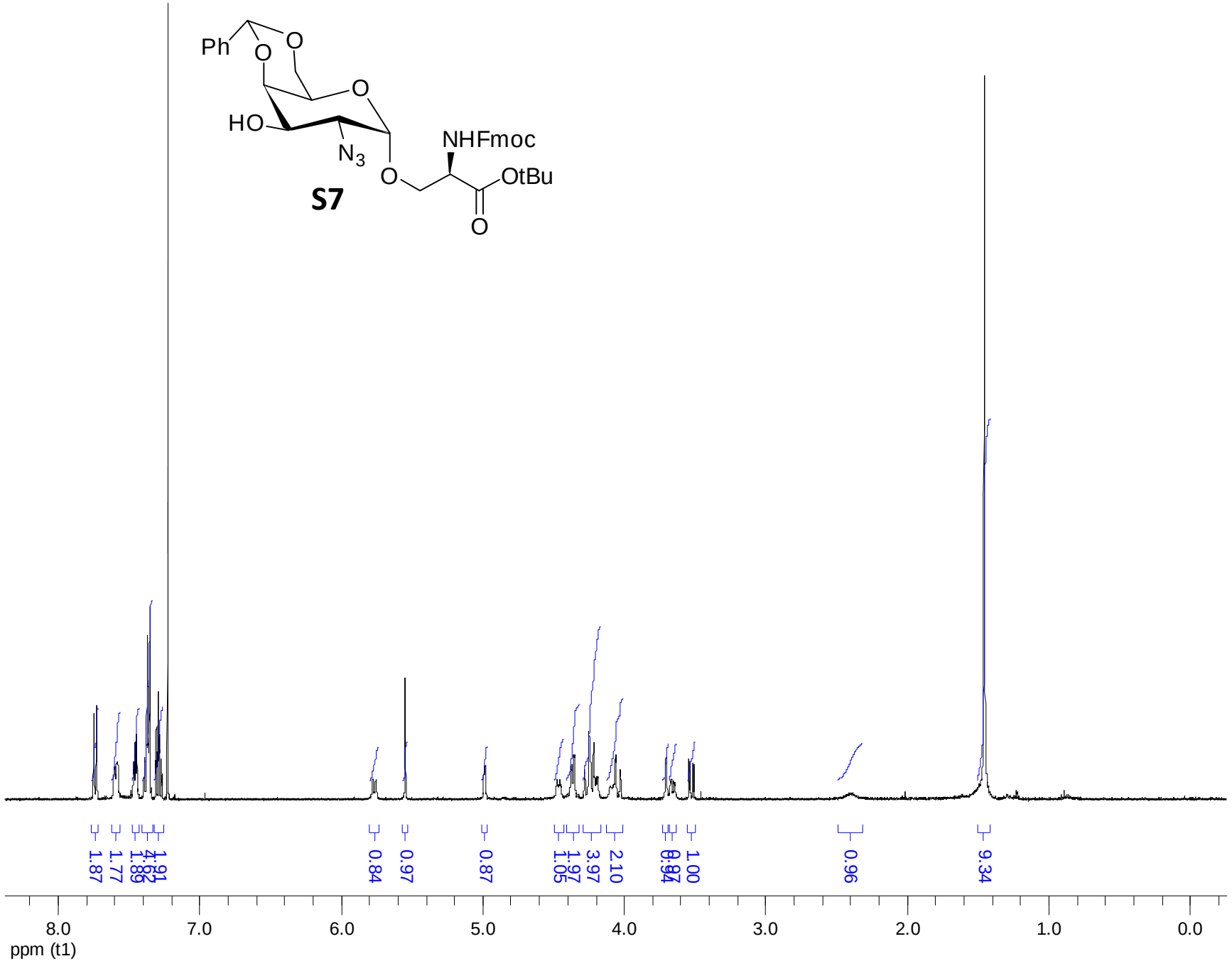
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 1 2010

Operator: ORL152

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
23000 repetitions
OBSERVE C13, 100.5142667 MHz
DECOUPLE H1, 399.7402438 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 14 hr, 46 min



S6


Ph
O
O
O
HO
N3
O
NHFmoc
OtBu
O
S7
1.87
1.77
1.89
1.91
0.84
0.97
0.87
1.05
1.97
3.97
2.10
0.94
0.97
1.00
0.96
9.34
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

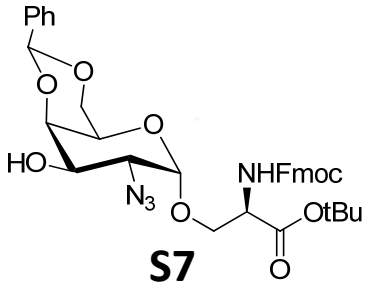
152F038C

Sample Name:
152F038C
Data Collected on:
jette2.ncifcrf.gov-inova400
Archive directory:
/home/ORL152/vnmrsys/data
Sample directory:
152F038C_20100325_01
FidFile: 152F038C_CARBON_C13_001

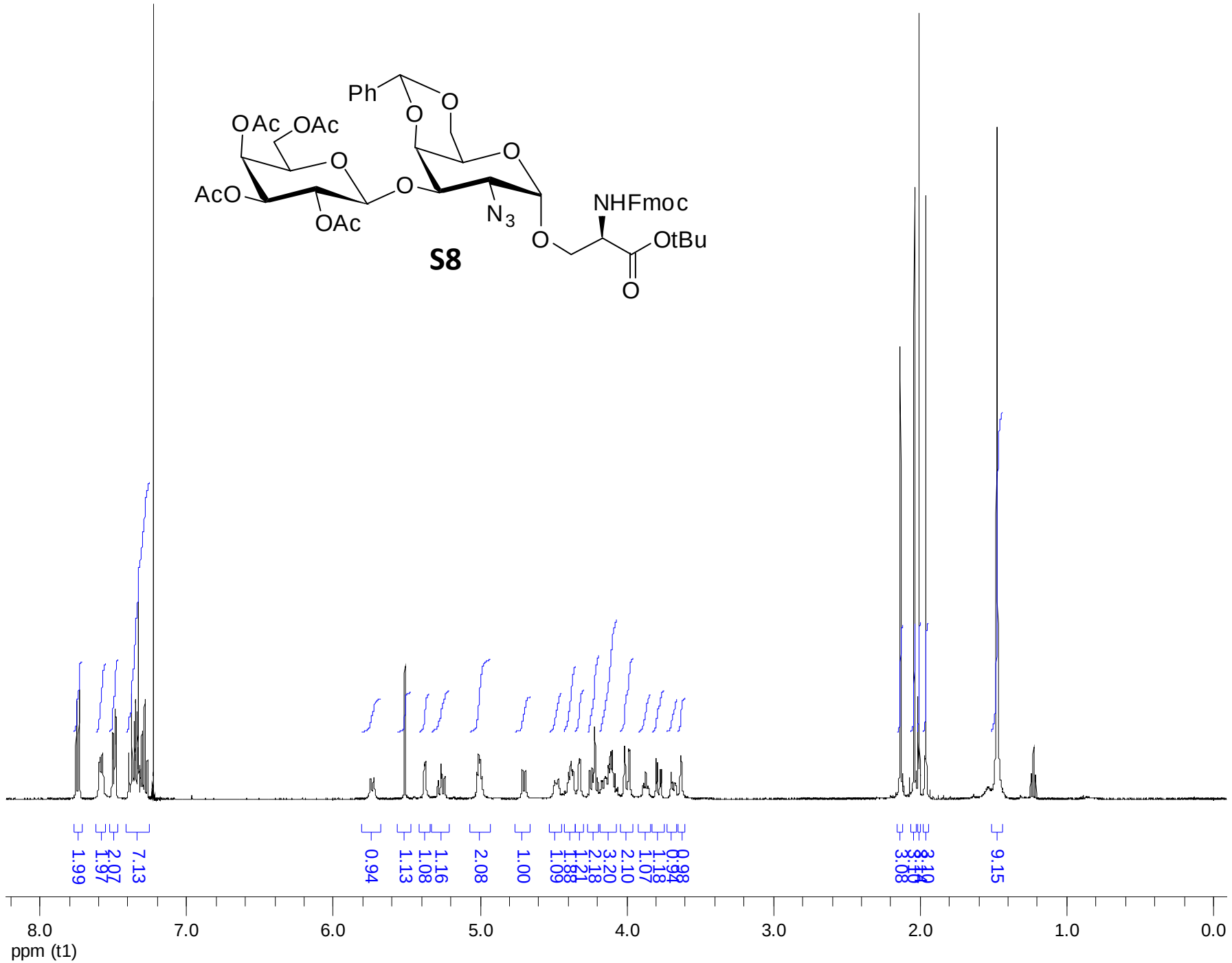
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 25 2010

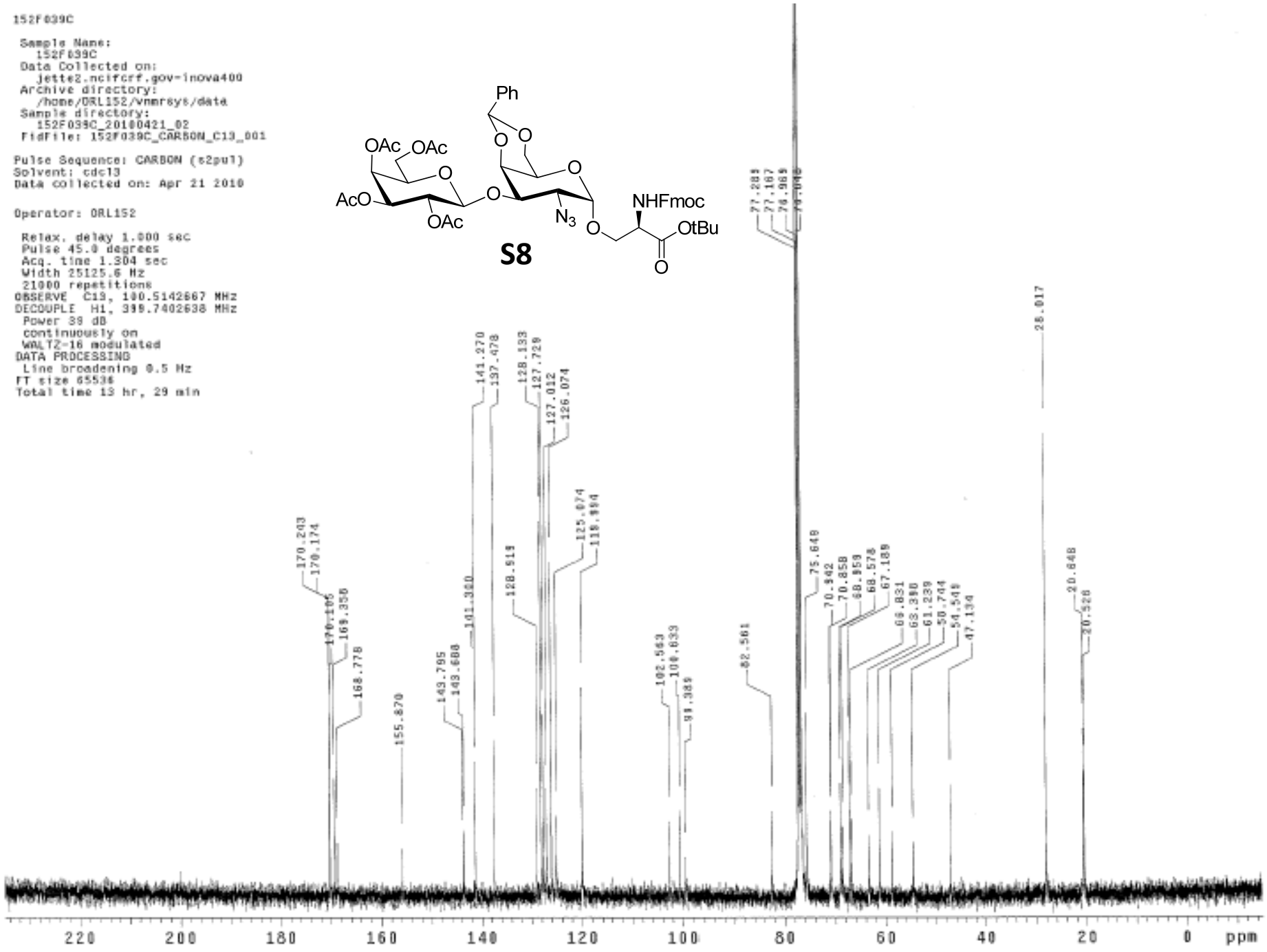
Operator: ORL152

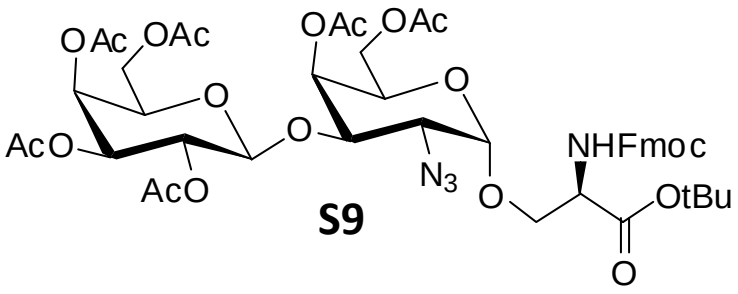
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
20000 repetitions
OBSERVE C13, 100.5142667 MHz
DECOUPLE H1, 399.7402630 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 12 hr, 51 min



S7

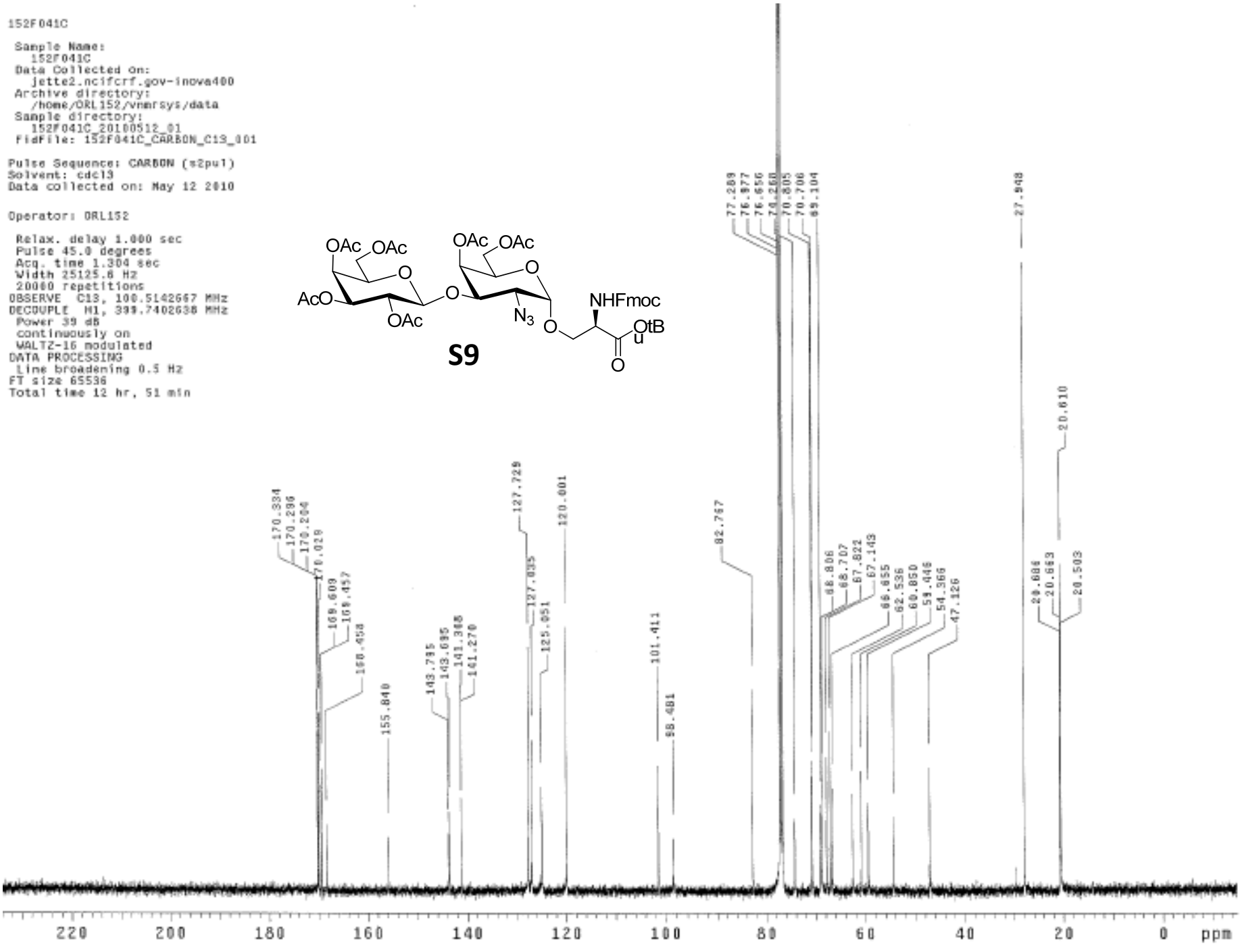

Ph
O
O
OAc
OAc
O
O
AcO
O
N3
NHFmoc
O
OtBu
OAc
O
S8
1.99
2.07
7.13
0.94
1.13
1.08
1.16
2.08
1.00
1.09
2.18
3.20
2.10
1.07
1.18
3.08
9.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

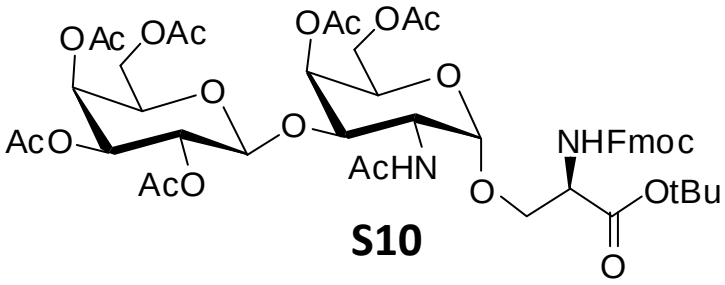

152F039C
Sample Name:
152F039C
Data Collected on:
jette2.ncifcrf.gov-inova400
Archive directory:
/home/ORL152/vnmrsys/data
Sample directory:
152F039C_20100421_02
FidFile: 152F039C_CARBON_C13_001
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 21 2010
Operator: ORL152
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
21000 repetitions
OBSERVE C13, 100.5142867 MHz
DECOUPLE H1, 399.7402638 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 13 hr, 29 min
Ph
OAc
OAc
AcO
OAc
N3
NHFmoc
OtBu
S8
170.243
170.174
169.356
168.778
155.870
143.795
143.688
141.270
131.380
128.513
197.478
128.133
127.729
127.012
126.074
125.074
118.994
102.563
100.639
91.385
82.561
77.288
77.167
76.965
75.648
70.842
70.858
68.859
68.578
67.189
66.831
63.380
61.239
50.704
54.548
47.134
28.017
20.648
20.526
220
200
180
160
140
120
100
80
60
40
20
0
ppm


OAc
OAc
O
AcO
AcO
O
OAc
OAc
O
N3
O
NHFmoc
OtBu
O

S9

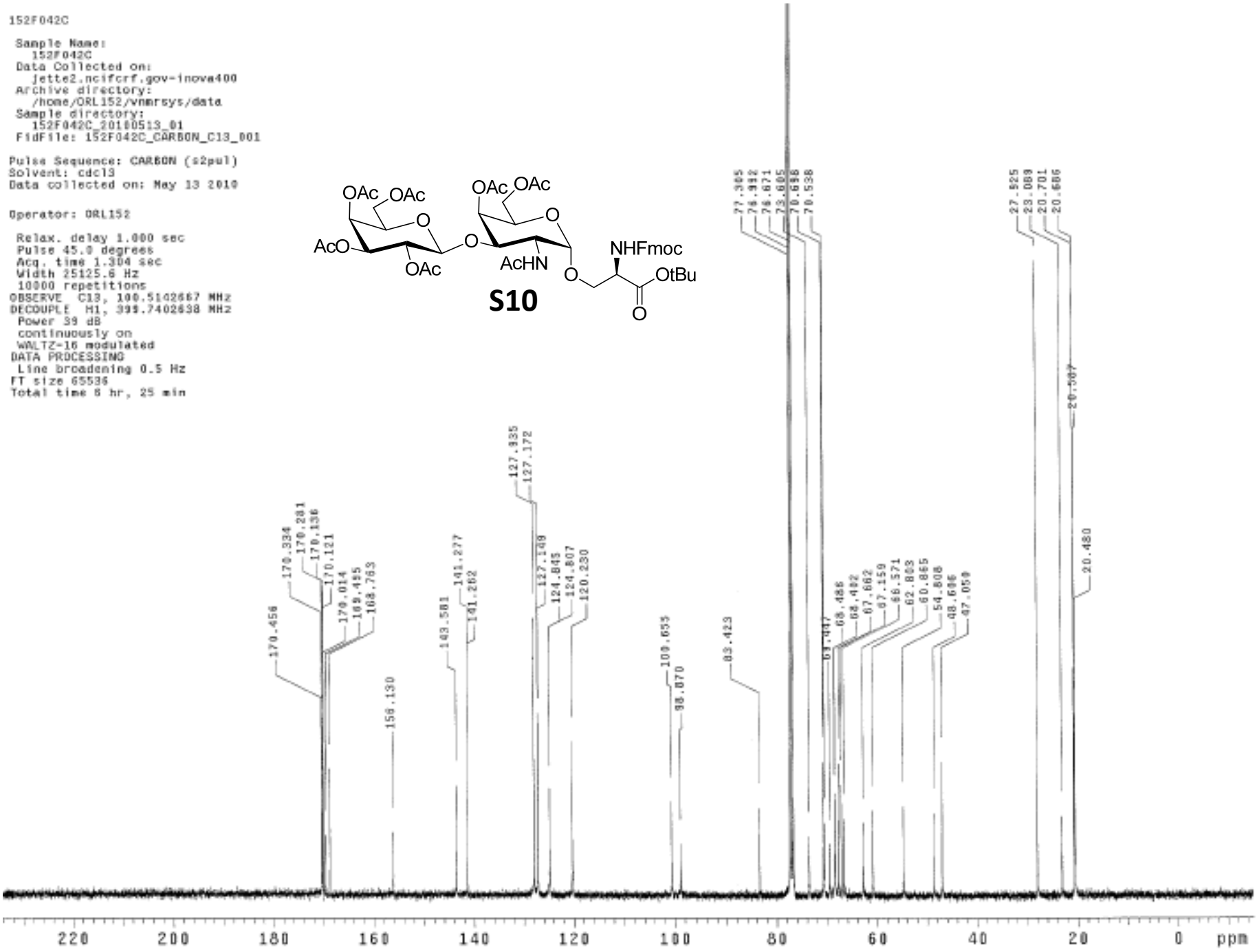
2.19
2.06
2.24
2.18
0.89
1.17
1.12
1.00
2.10
0.99
1.06
2.12
1.14
5.30
2.16
1.08
0.92
1.11
6.20
8.98
3.24
9.25
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

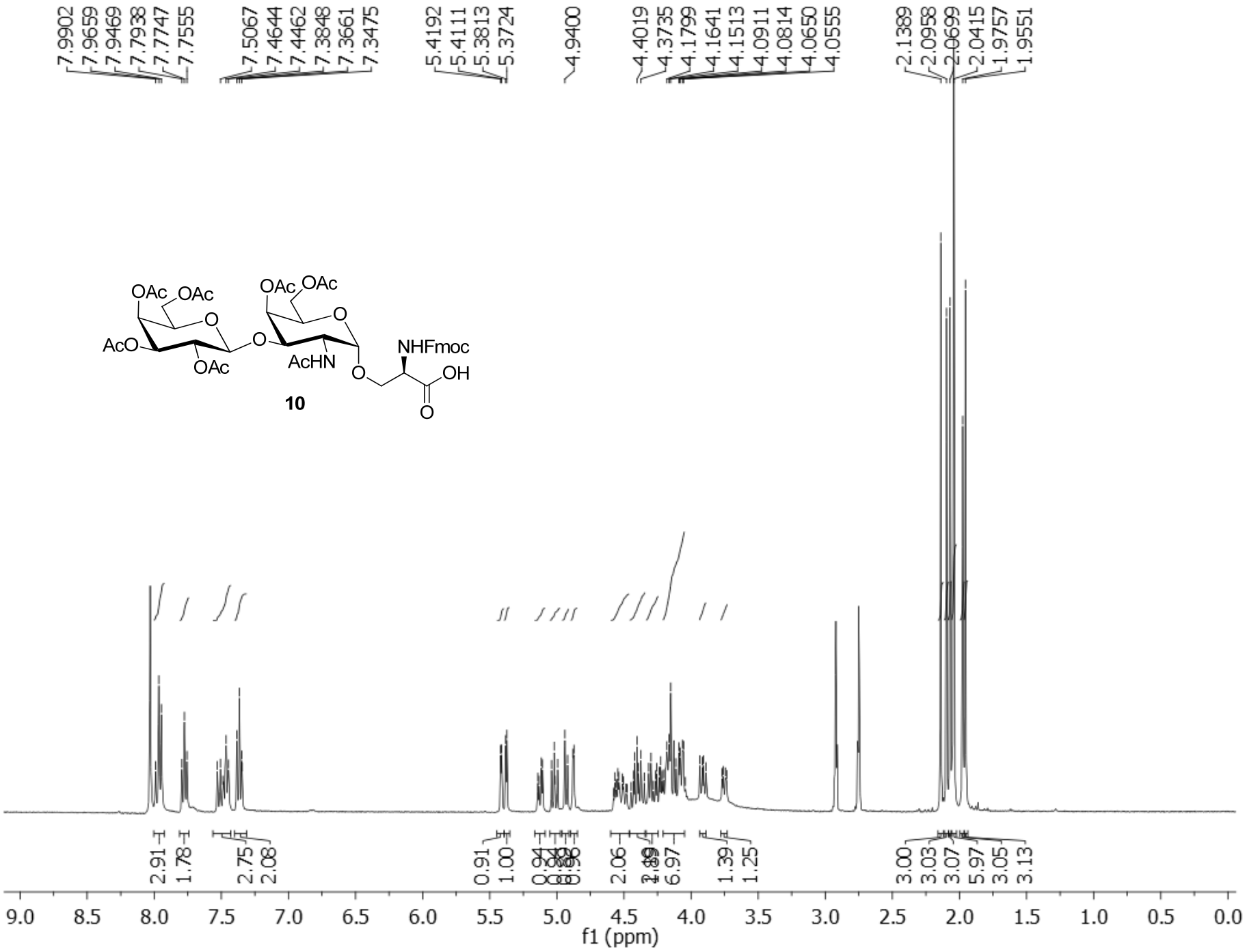

152F041C
Sample Name:
152F041C
Data Collected on:
jette2.ncifcrf.gov-inova400
Archive directory:
/home/ORL152/vnmrsys/data
Sample directory:
152F041C_20100512_01
FidFile: 152F041C_CARBON_C13_001
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 12 2010
Operator: ORL152
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
20000 repetitions
OBSERVE C13, 100.5142667 MHz
DECOUPLE H1, 399.7402638 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 12 hr, 51 min
OAc
OAc
AcO
OAc
O
O
OAc
OAc
O
N3
O
NHFmoc
OtBu
O
S9
170.334
170.296
170.264
170.029
169.609
169.457
168.458
155.840
143.735
143.695
141.388
141.270
127.729
127.035
125.951
120.601
101.411
98.481
82.767
77.289
76.977
76.656
74.260
70.805
70.706
69.104
68.806
68.707
67.822
67.143
66.655
62.536
60.850
59.448
54.366
47.126
27.948
20.686
20.663
20.610
20.503
220
200
180
160
140
120
100
80
60
40
20
0
ppm

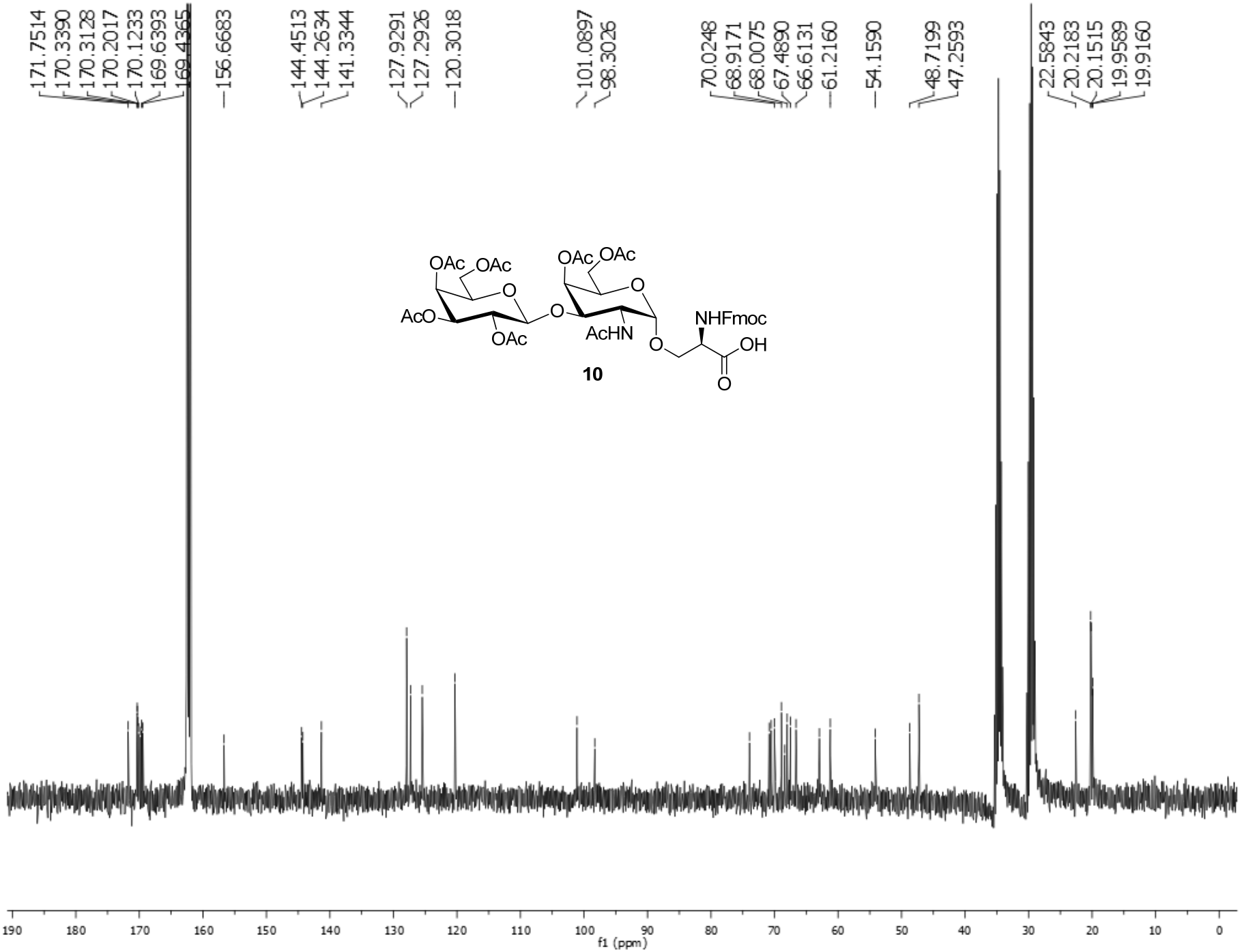

OAc
OAc
O
AcO
AcO
O
OAc
OAc
O
AcHN
O
NHFmoc
OtBu
O

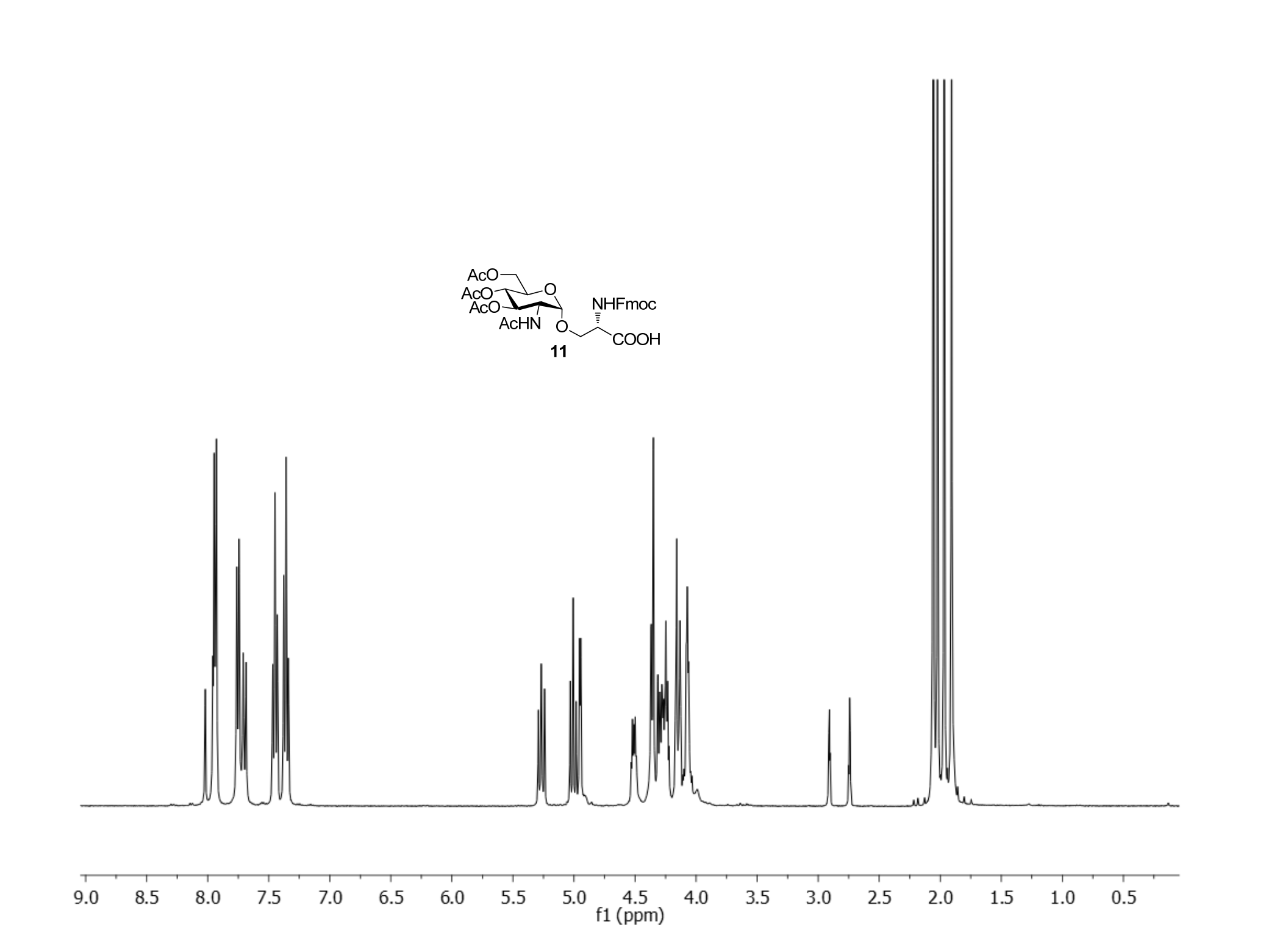
S10

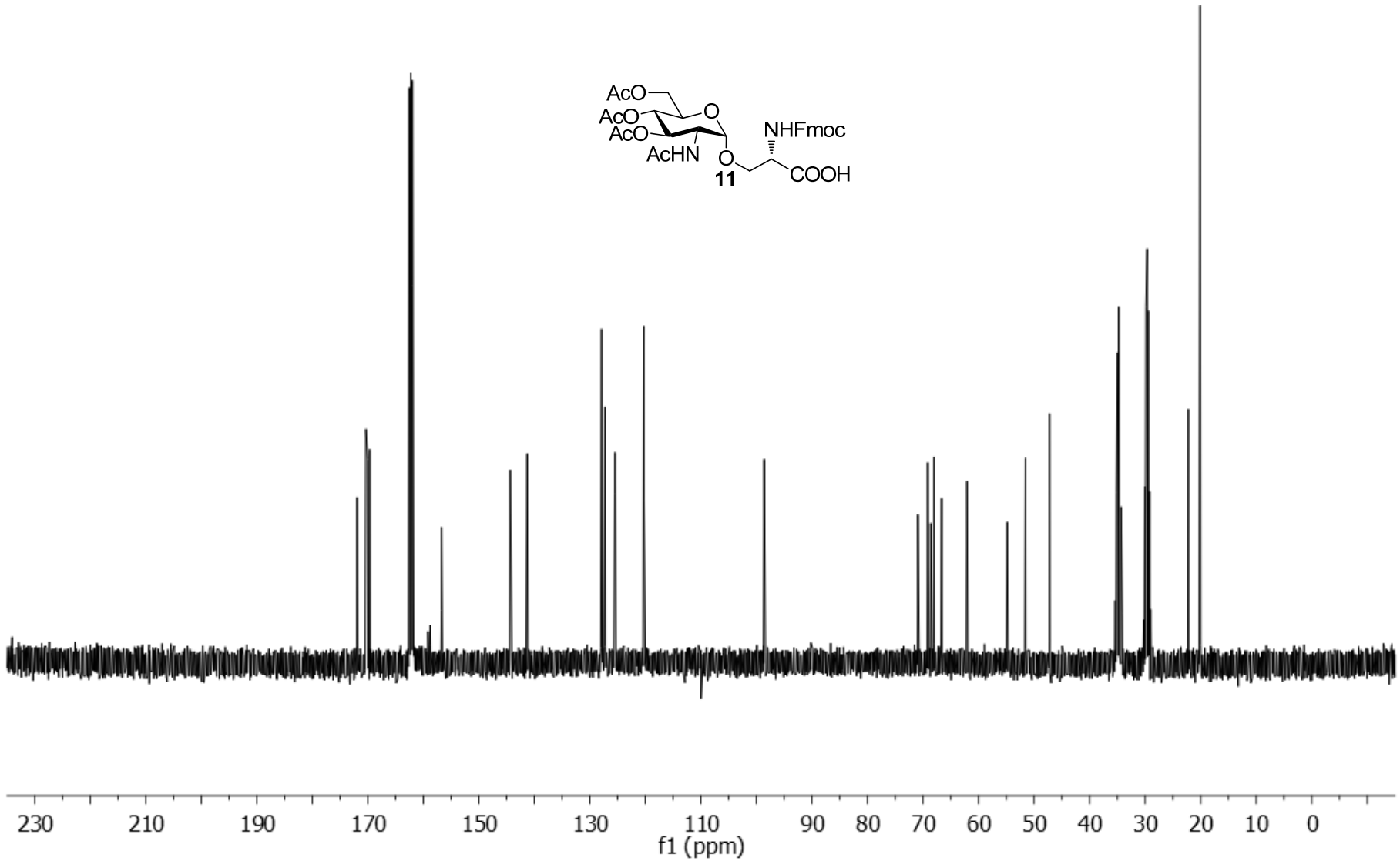
2.03
2.18
2.22
0.82
0.85
2.21
1.02
0.99
1.00
4.28
2.22
1.19
4.25
1.05
1.02
2.10
6.40
9.86
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

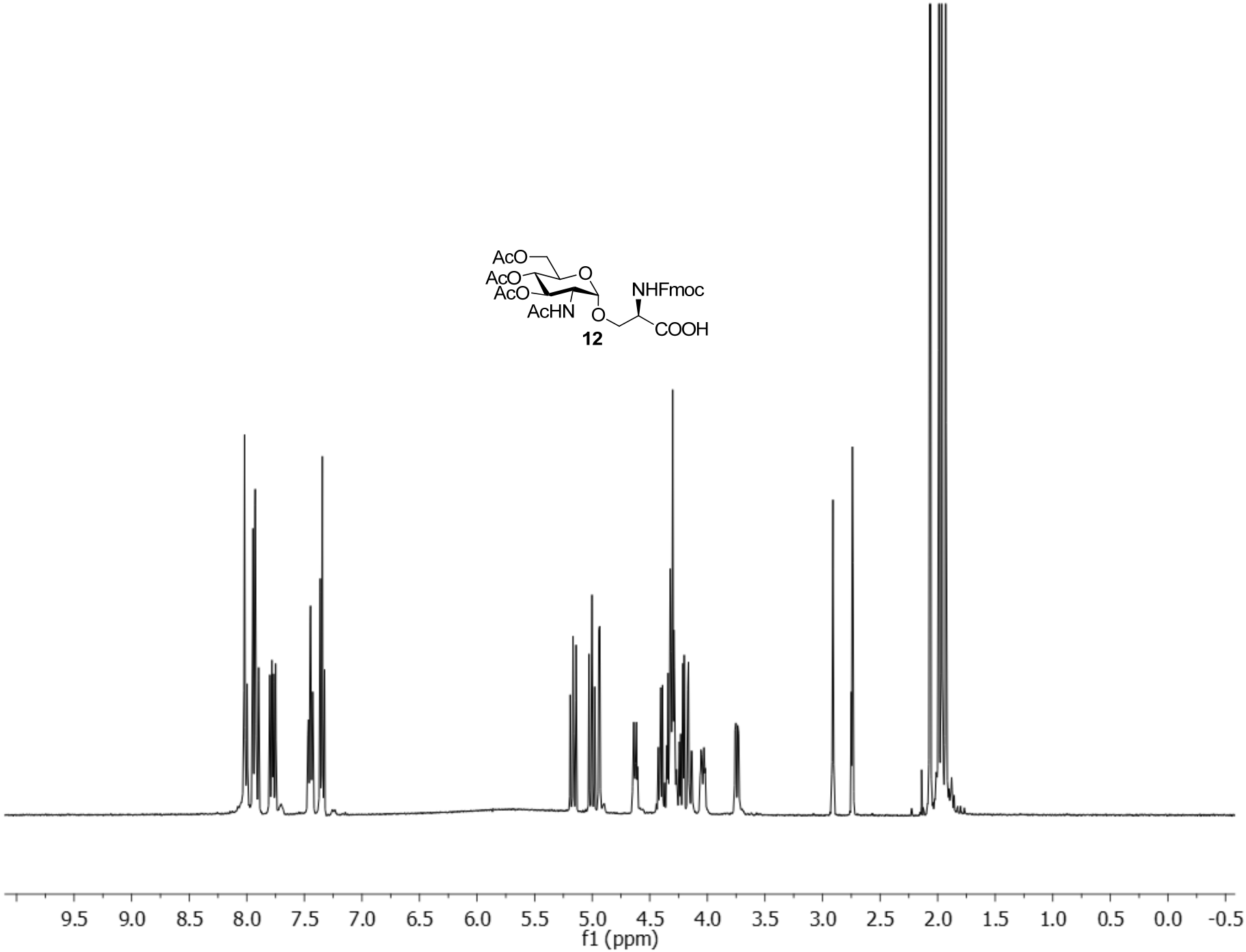

152F042C
Sample Name:
152F042C
Data Collected on:
jette2.ncifcrf.gov-inova400
Archive directory:
/home/ORL152/vnmrsys/data
Sample directory:
152F042C_20100513_01
FidFile: 152F042C_CARBON_C13_001
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 13 2010
Operator: ORL152
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.304 sec
Width 25125.6 Hz
10000 repetitions
OBSERVE C13, 100.5102667 MHz
DECOUPLE H1, 399.7402638 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 8 hr, 25 min
OAc
OAc
OAc
OAc
O
O
O
AcO
OAc
AcHN
NHFmoc
O
OtBu
O
S10
170.456
170.334
170.281
170.136
170.121
170.014
169.455
168.763
158.130
143.581
141.277
141.262
127.335
127.172
127.149
124.845
124.807
120.230
109.653
98.870
83.423
77.365
76.942
76.671
73.685
70.688
70.538
68.486
68.492
67.662
67.159
66.571
62.803
60.865
54.808
48.696
47.059
27.525
23.089
20.701
20.686
20.507
20.480
220
200
180
160
140
120
100
80
60
40
20
0
ppm

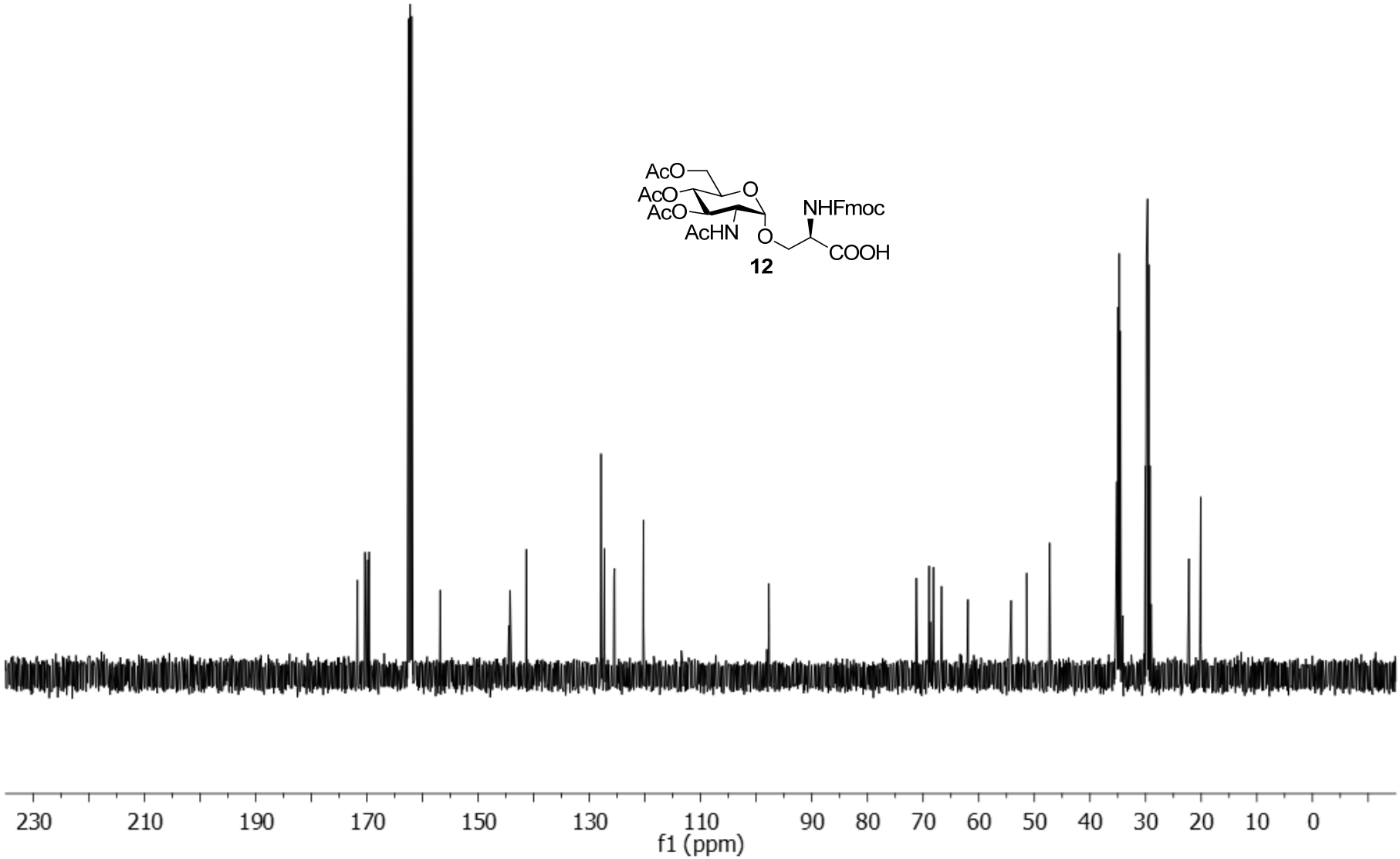

7.9902
7.9659
7.9469
7.7938
7.7747
7.7555
7.5067
7.4644
7.4462
7.3848
7.3661
7.3475
5.4192
5.4111
5.3813
5.3724
4.9400
4.4019
4.3735
4.1799
4.1641
4.1513
4.0911
4.0814
4.0650
4.0555
2.1389
2.0958
2.0699
2.0415
1.9757
1.9551
OAc
OAc
O
AcO
OAc
O
OAc
OAc
O
AcHN
O
NHFmoc
OH
O
10
2.91
1.78
2.75
2.08
0.91
1.00
0.94
2.06
6.97
1.39
1.25
3.00
3.03
3.07
5.97
3.05
3.13
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
f1 (ppm)

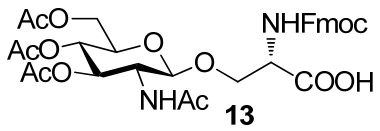

171.7514
170.3390
170.3128
170.2017
170.1233
169.6393
169.4365
156.6683
144.4513
144.2634
141.3344
127.9291
127.2926
120.3018
101.0897
98.3026
70.0248
68.9171
68.0075
67.4890
66.6131
61.2160
54.1590
48.7199
47.2593
22.5843
20.2183
20.1515
19.9589
19.9160
OAc
OAc
O
AcO
OAc
O
OAc
OAc
O
AcHN
O
NHFmoc
OH
O
10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


AcO
AcO
AcO
AcHN
O
O
NHFmoc
COOH
11
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
f1 (ppm)


AcO
AcO
AcO
AcHN
O
O
NHFmoc
COOH
11
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

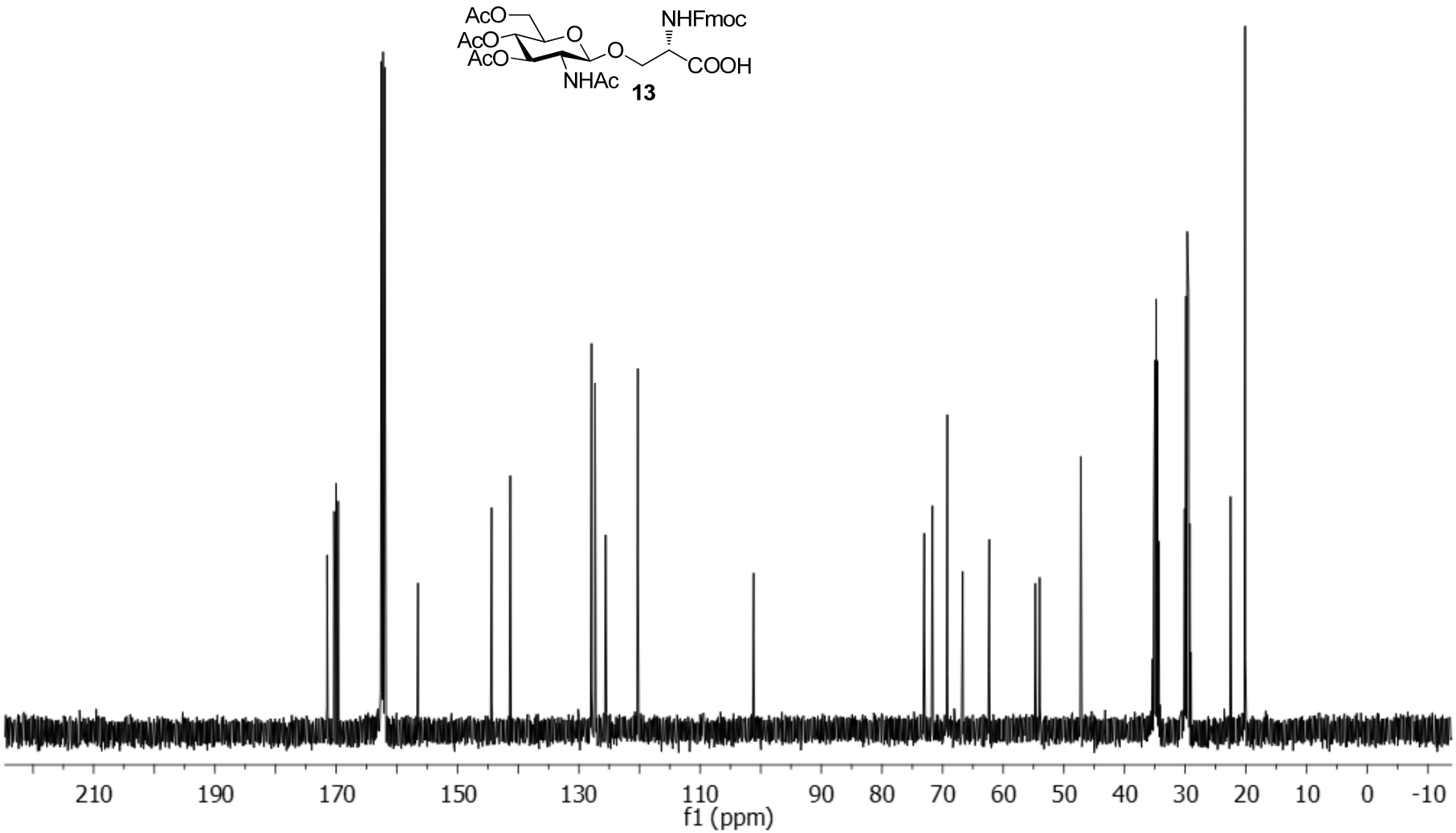

AcO
AcO
AcO
AcHN
O
O
NHFmoc
COOH
12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

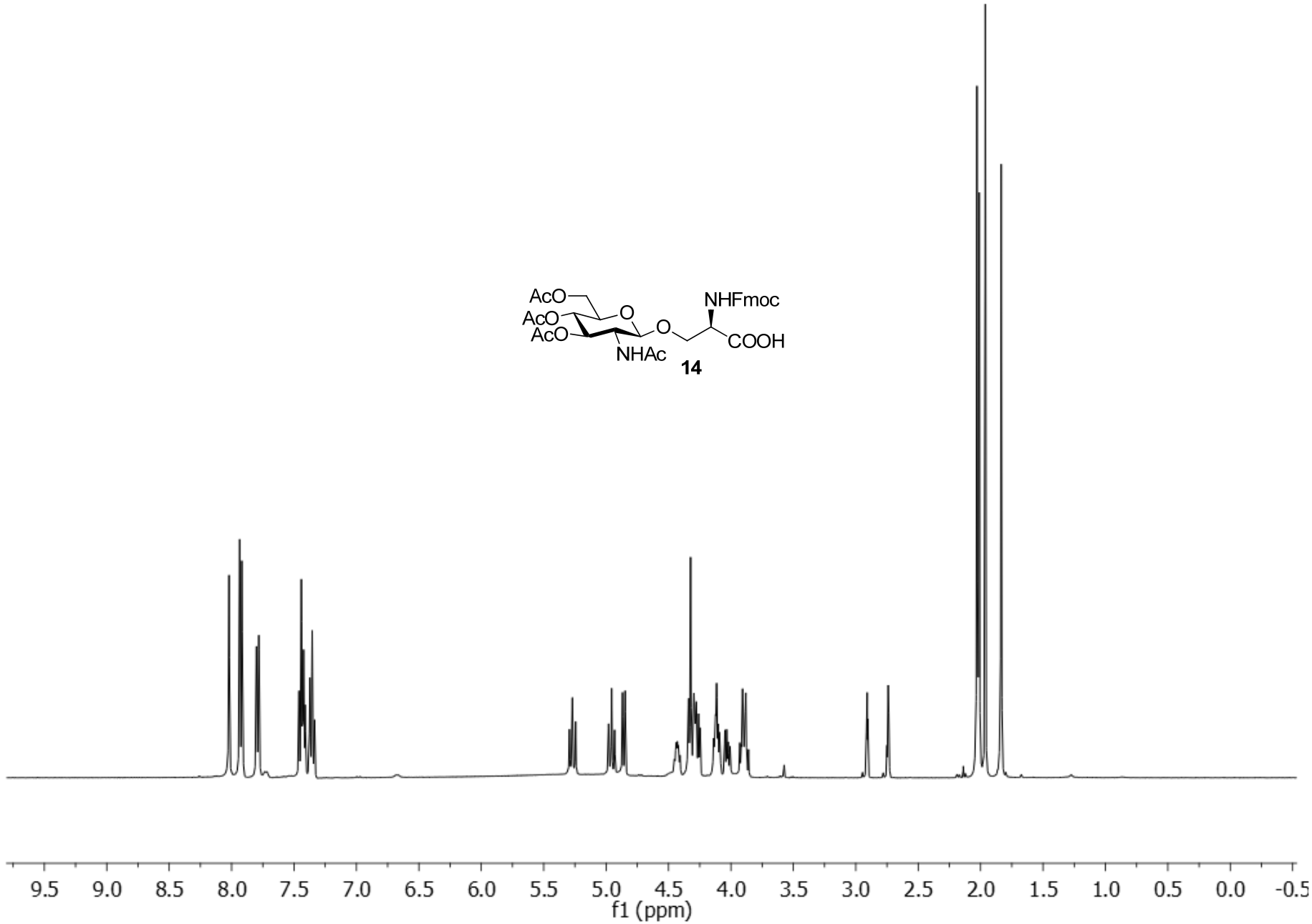

AcO
AcO
AcO
AcHN
O
O
NHFmoc
COOH
12
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

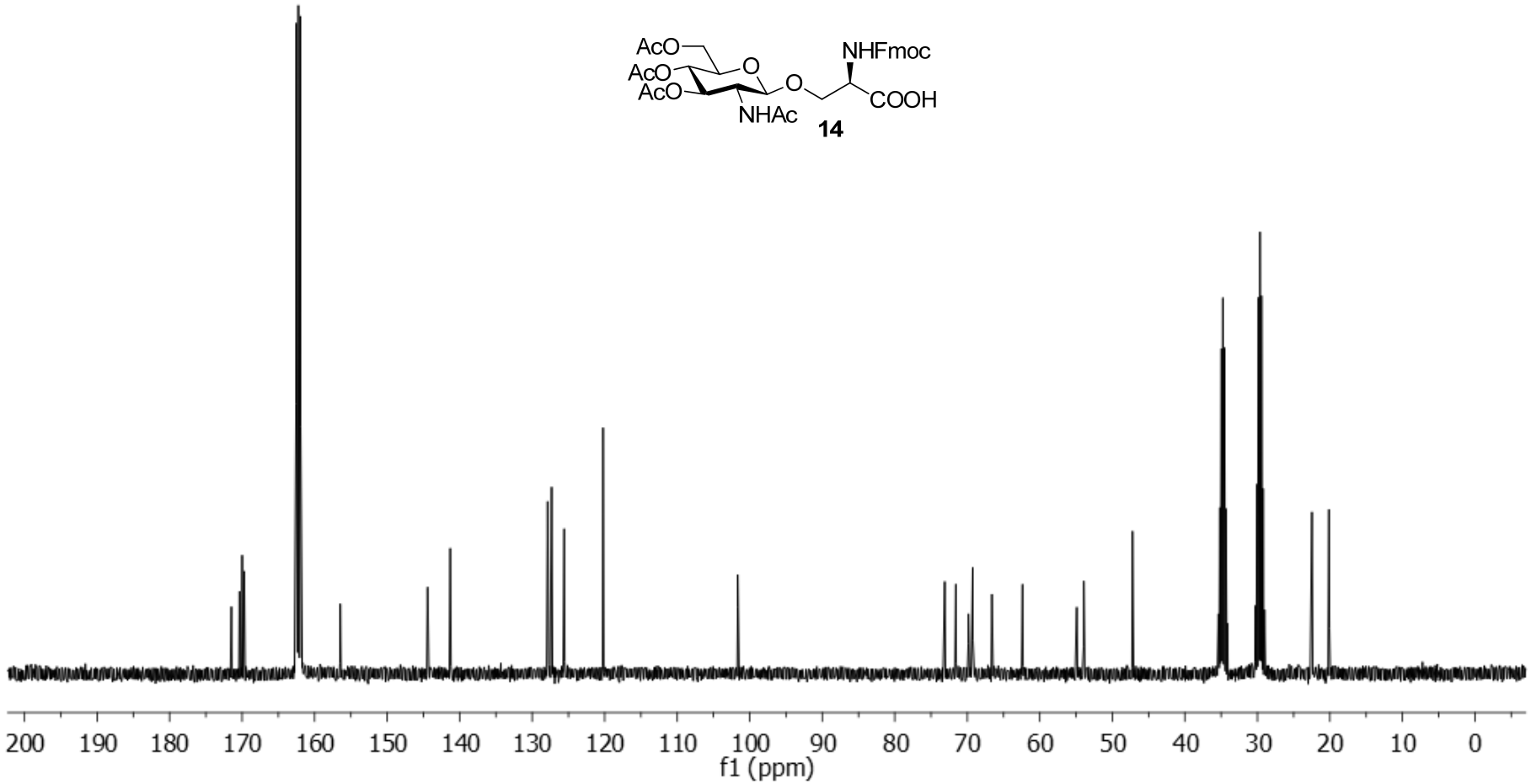

AcO
AcO
AcO
O
NHAc
O
NHFmoc
COOH

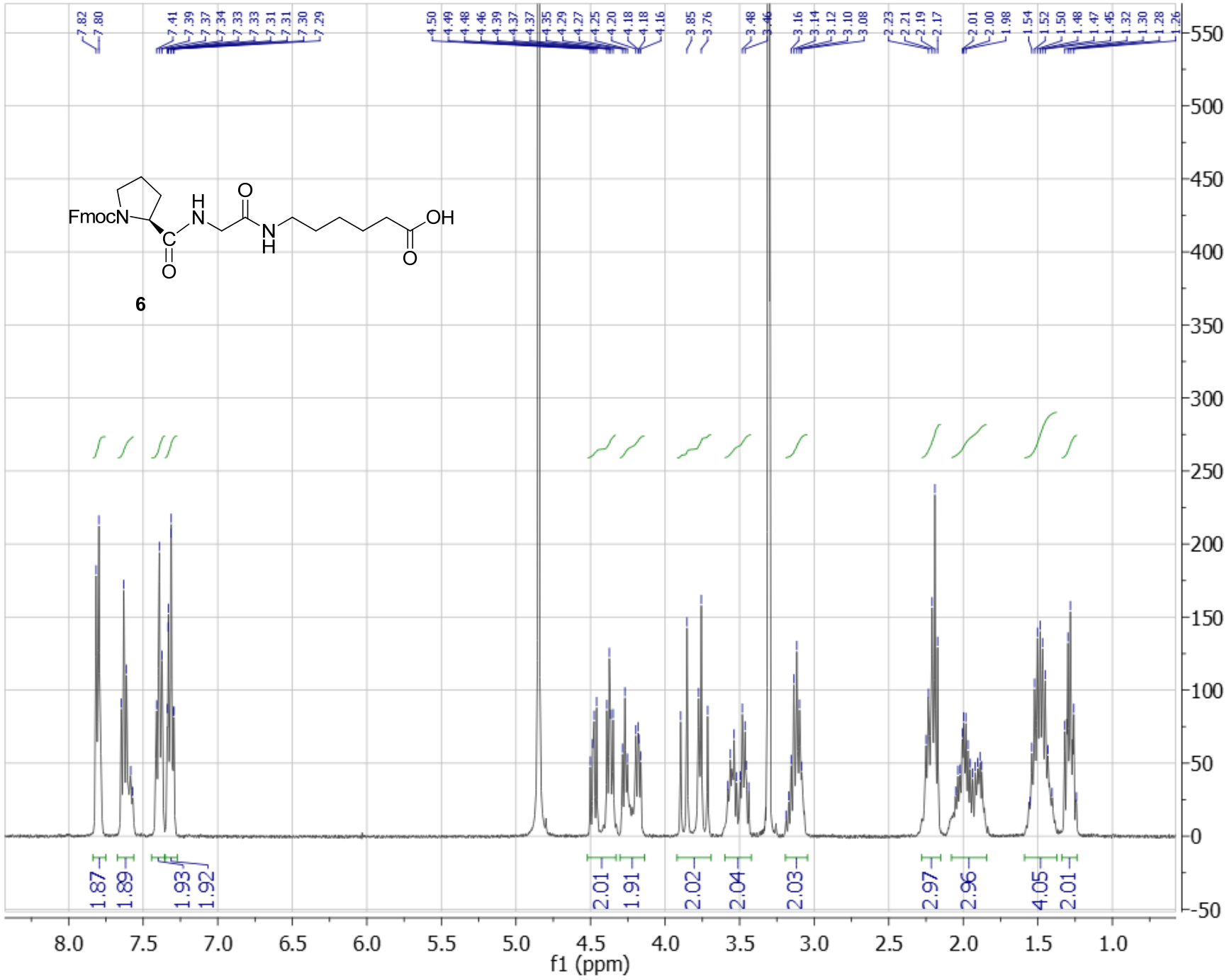
13

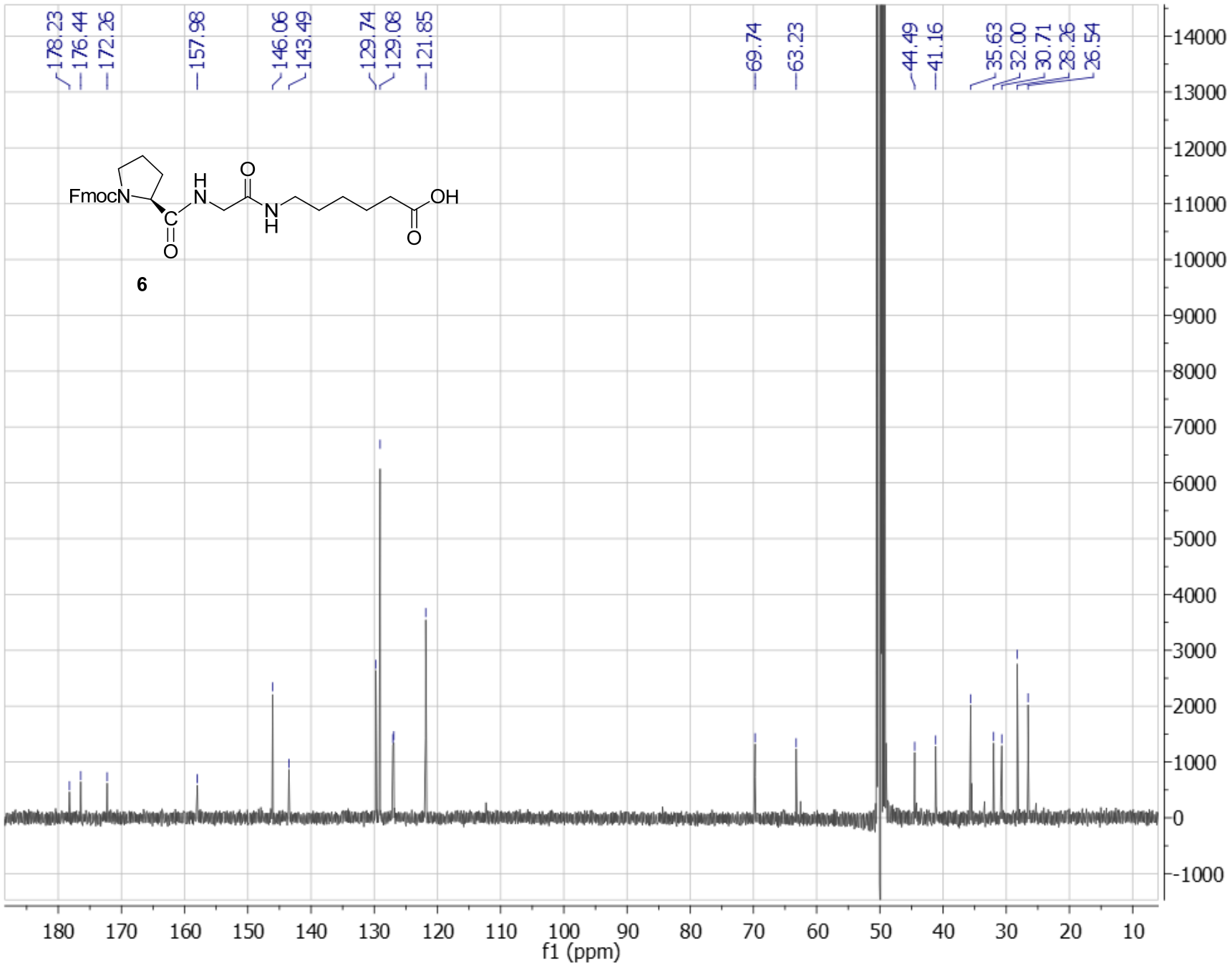
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

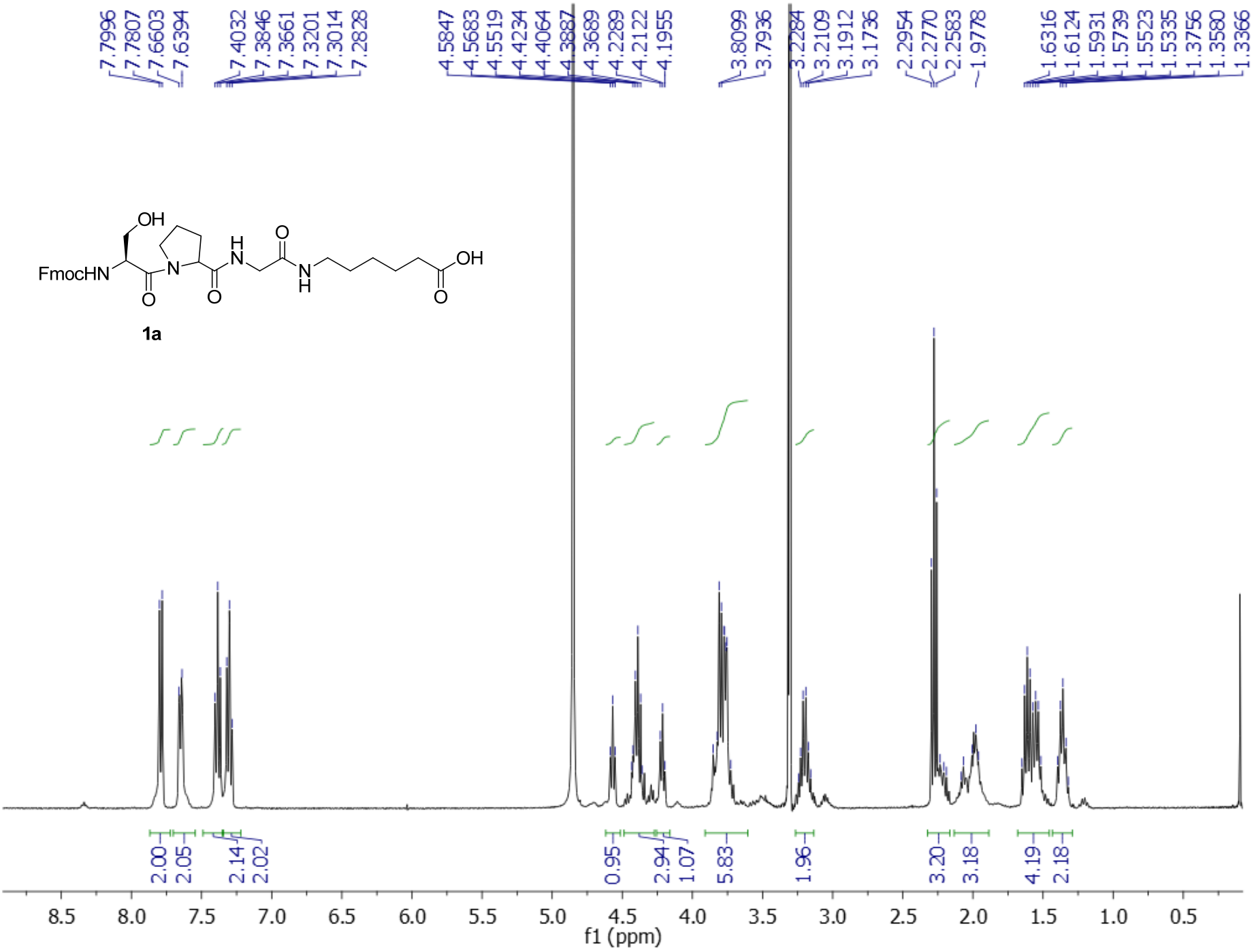

AcO
AcO
AcO
O
NHAc
O
NHFmoc
COOH
13
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

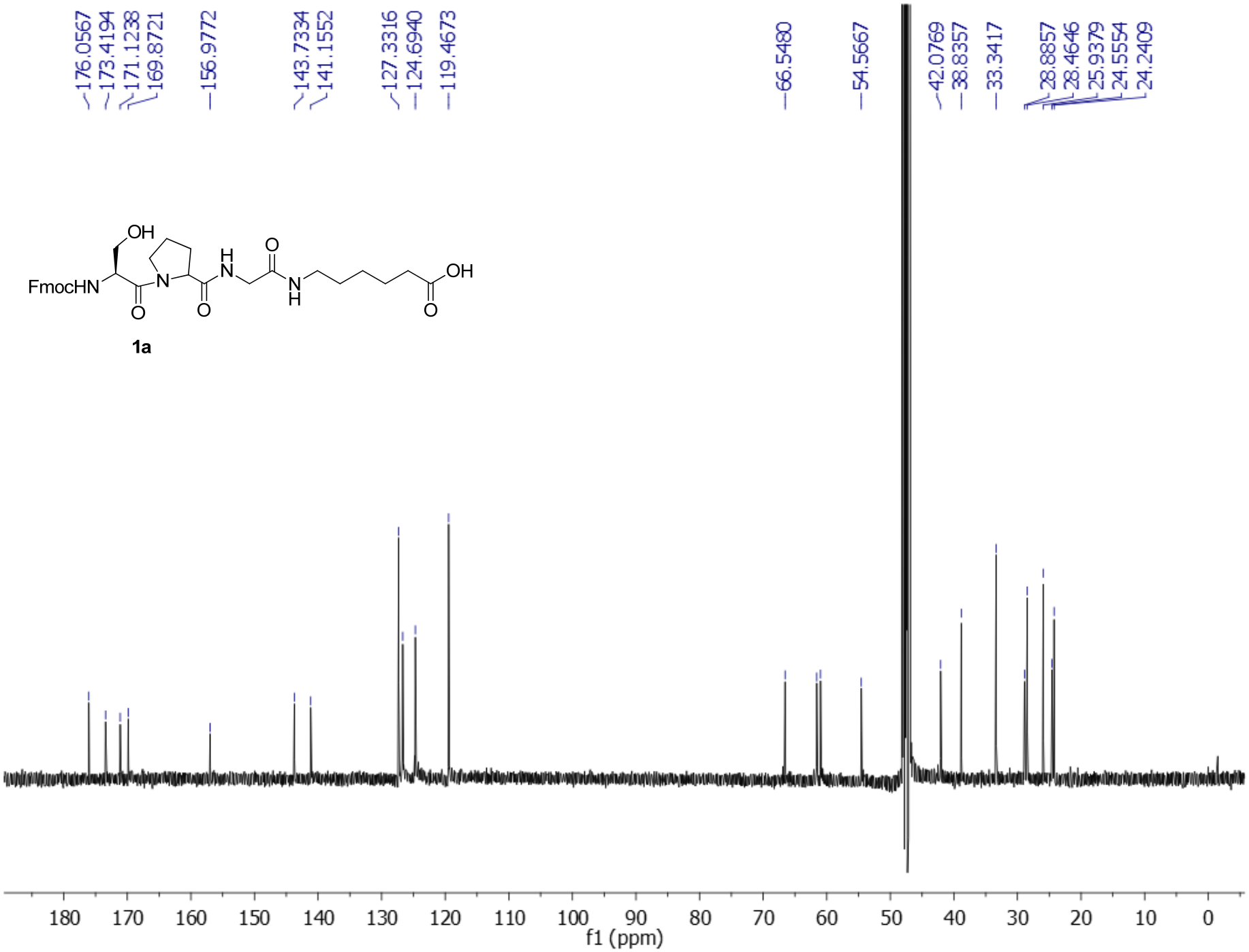

AcO
AcO
AcO
O
O
NHAc
NHFmoc
COOH
14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


AcO
AcO
AcO
O
O
NHAc
NHFmoc
COOH
14
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.82
7.80
7.41
7.39
7.37
7.34
7.33
7.33
7.31
7.31
7.30
7.29
4.50
4.49
4.48
4.46
4.39
4.37
4.37
4.35
4.29
4.27
4.25
4.20
4.18
4.18
4.16
3.85
3.76
3.48
3.46
3.16
3.14
3.12
3.10
3.08
2.23
2.21
2.19
2.17
2.01
2.00
1.98
1.54
1.52
1.50
1.48
1.47
1.45
1.32
1.30
1.28
1.26
FmocN
H
N
O
C
O
N
H
O
OH
6
1.87
1.89
1.93
1.92
2.01
1.91
2.02
2.04
2.03
2.97
2.96
4.05
2.01
f1 (ppm)


178.23
176.44
172.26
157.98
146.06
143.49
129.74
129.08
121.85
69.74
63.23
44.49
41.16
35.63
32.00
30.71
28.26
26.54
FmocN
H
N
O
C
O
N
H
OH
O
6
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.7996
7.7807
7.6603
7.6394
7.4032
7.3846
7.3661
7.3201
7.3014
7.2828
4.5847
4.5683
4.5519
4.4234
4.4064
4.3887
4.3689
4.2289
4.2122
4.1955
3.8099
3.7936
3.2284
3.2109
3.1912
3.1736
2.2954
2.2770
2.2583
1.9778
1.6316
1.6124
1.5931
1.5739
1.5523
1.5335
1.3756
1.3580
1.3366
OH
FmocHN
N
O
H
N
O
N
H
O
OH
O
1a
2.00
2.05
2.14
2.02
0.95
2.94
1.07
5.83
1.96
3.20
3.18
4.19
2.18
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
f1 (ppm)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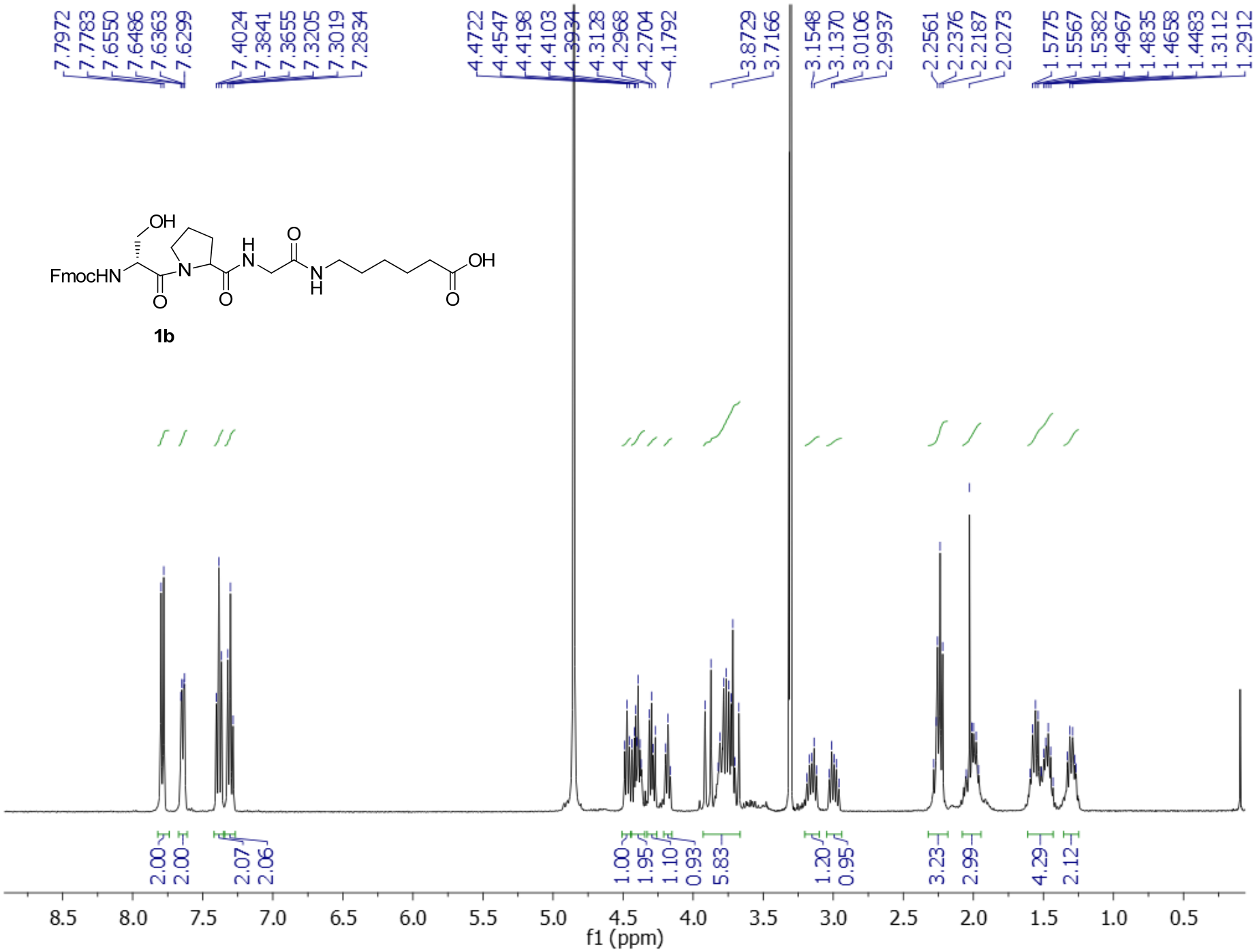
173.4194
171.1238
169.8721
156.9772
143.7334
141.1552
127.3316
124.6940
119.4673
66.5480
54.5667
42.0769
38.8357
33.3417
28.8857
28.4646
25.9379
24.5554
24.2409
OH
FmocHN
N
H
N
O
O
O
N
H
OH
O
O
1a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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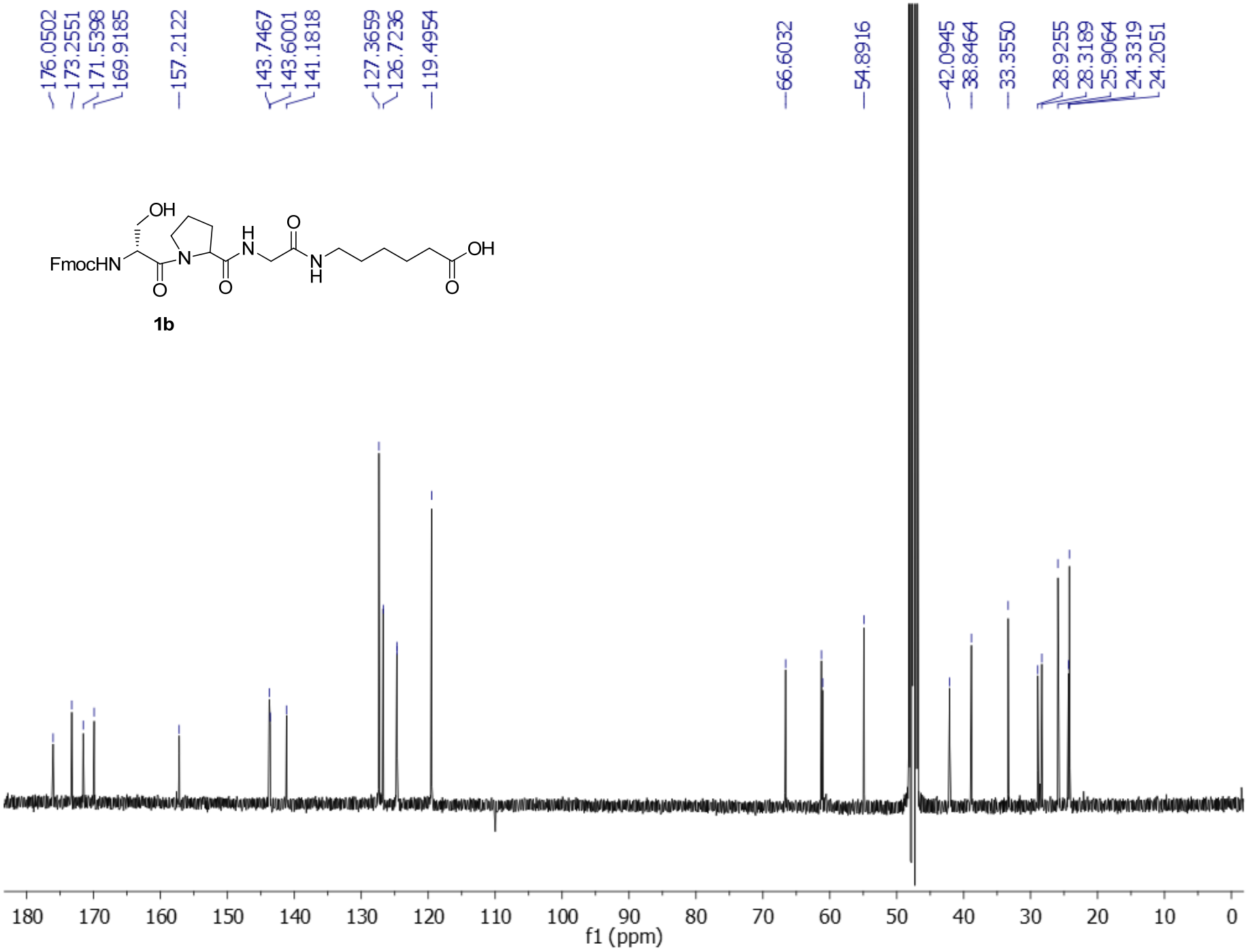
7.7783
7.6550
7.6486
7.6363
7.6299
7.4024
7.3841
7.3655
7.3205
7.3019
7.2834
4.4722
4.4547
4.4198
4.4103
4.3934
4.3128
4.2968
4.2704
4.1792
3.8729
3.7166
3.1548
3.1370
3.0106
2.9937
2.2561
2.2376
2.2187
2.0273
1.5775
1.5567
1.5382
1.4967
1.4835
1.4658
1.4483
1.3112
1.2912
OH
FmocHN
N
O
H
N
O
O
N
H
OH
O
1b
2.00
2.00
2.07
2.06
1.00
1.95
1.10
0.93
5.83
1.20
0.95
3.23
2.99
4.29
2.12
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
f1 (ppm)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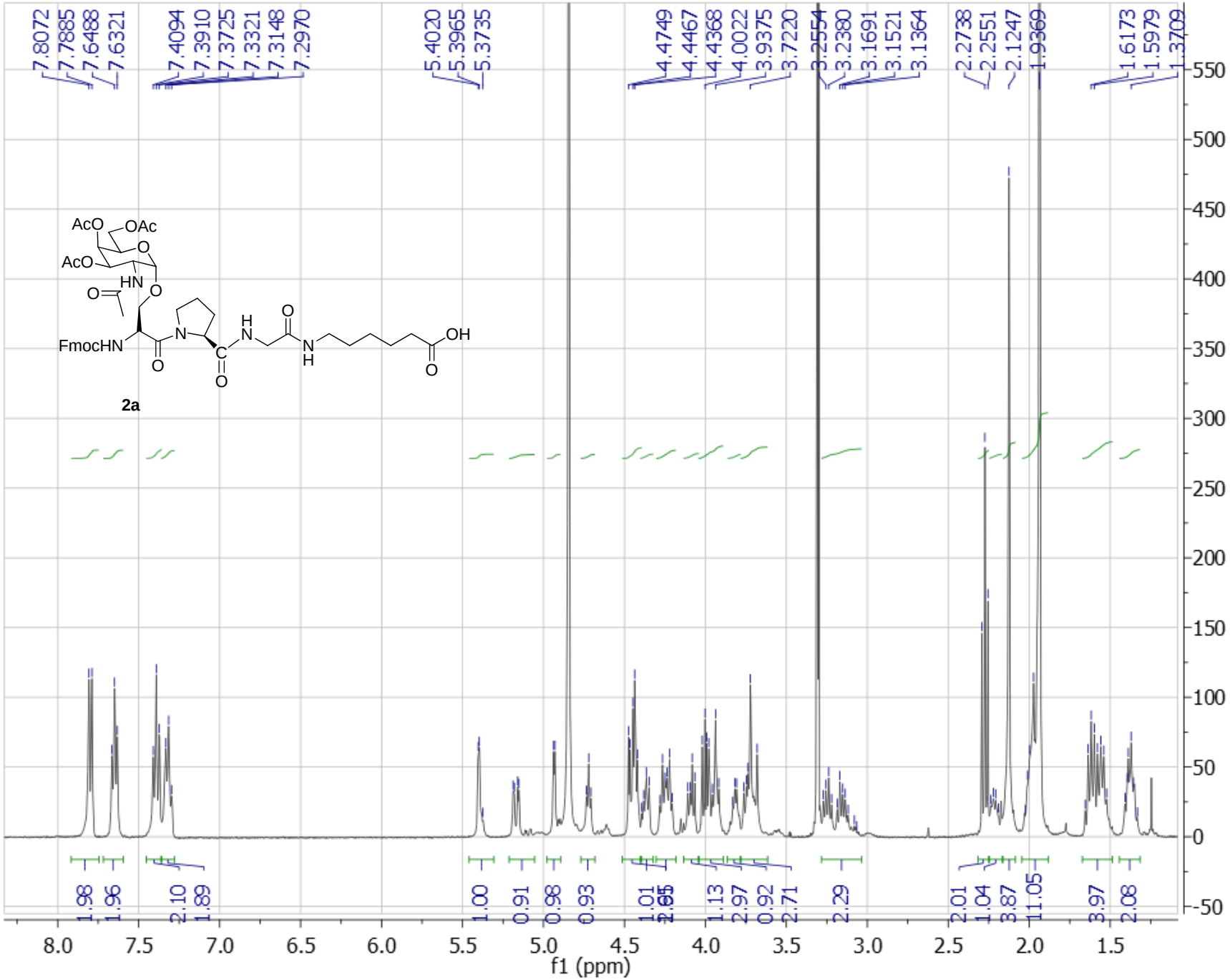
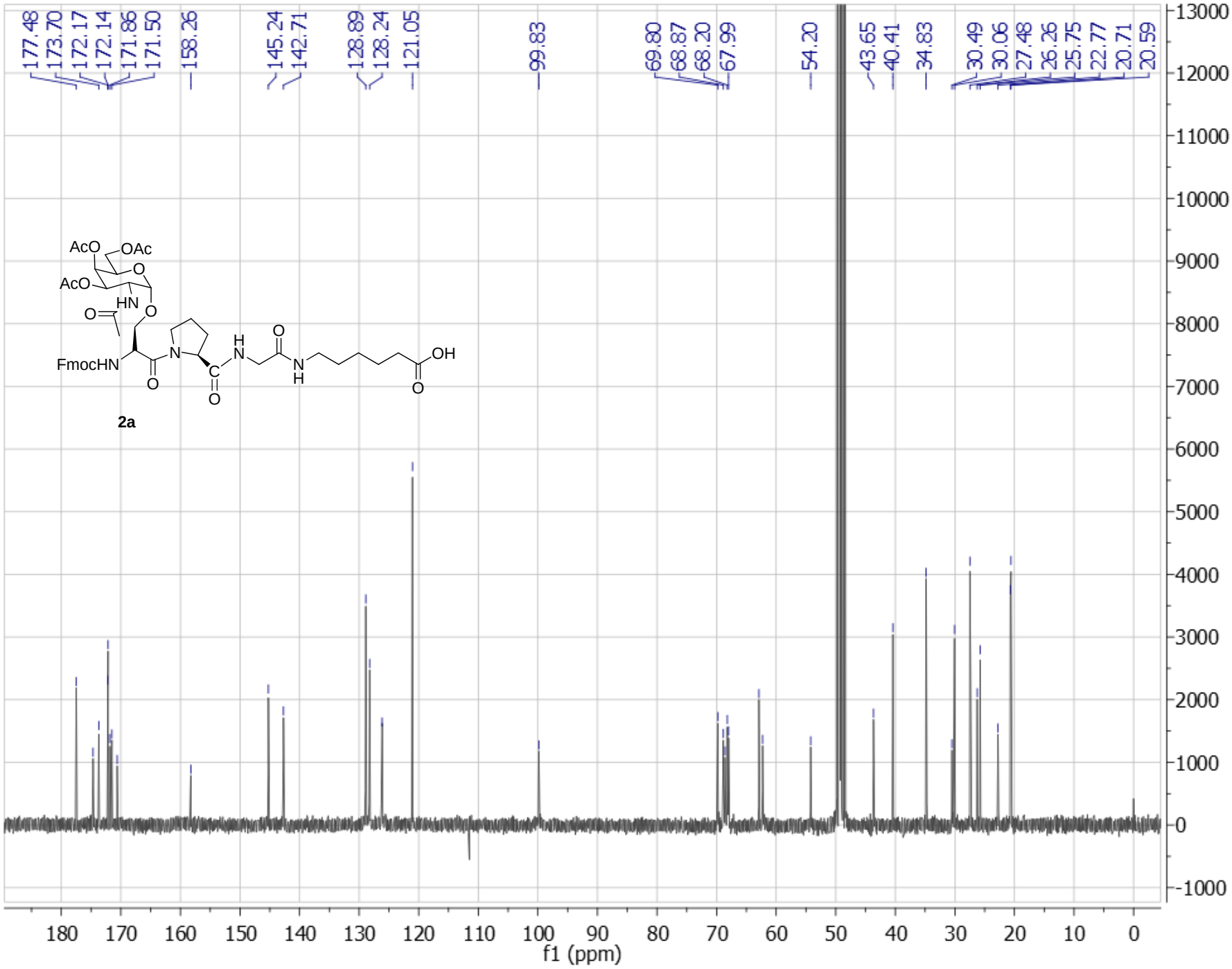
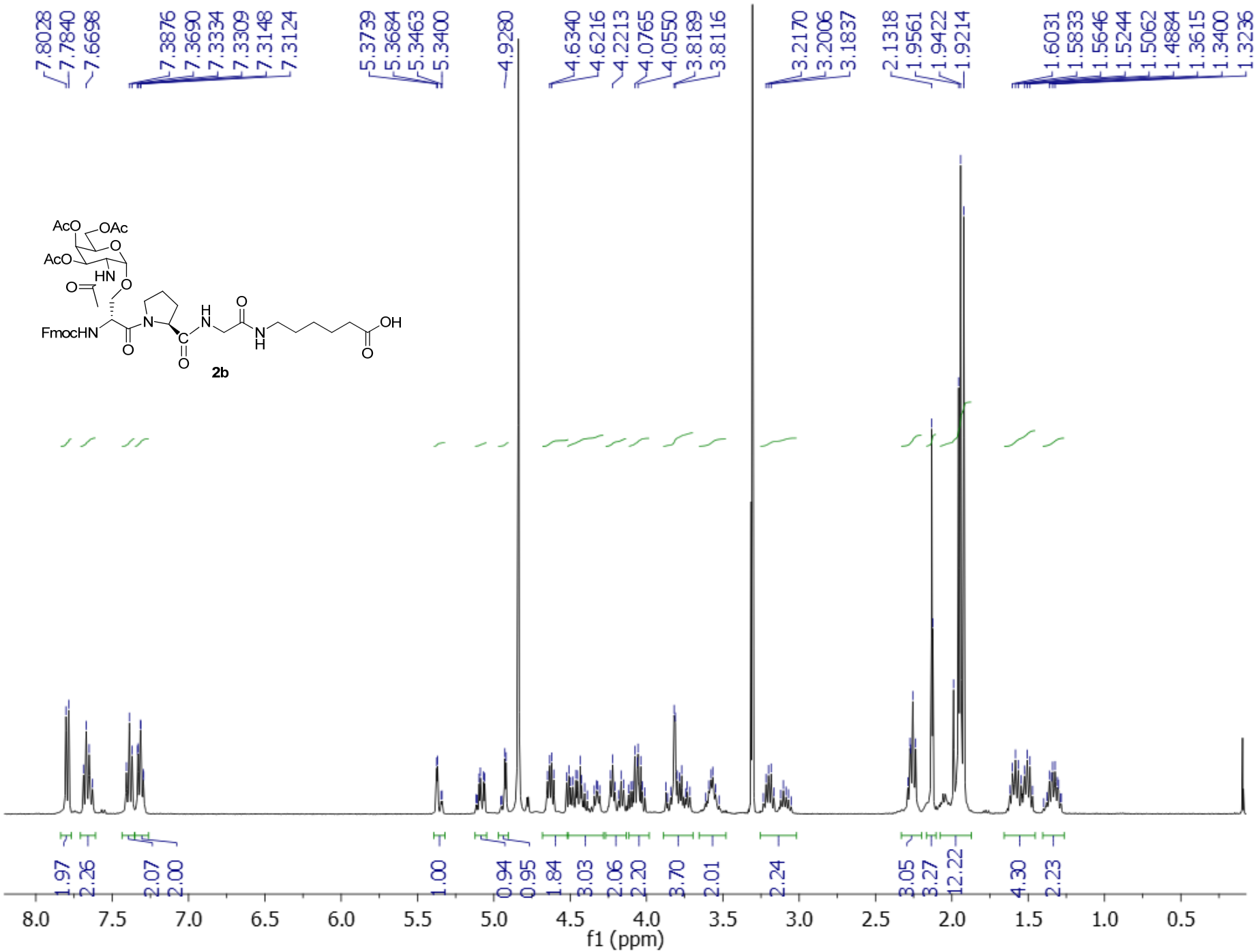
173.2551
171.5398
169.9185
157.2122
143.7467
143.6001
141.1818
127.3659
126.7236
119.4954
66.6032
54.8916
42.0945
38.8464
33.3550
28.9255
28.3189
25.9064
24.3319
24.2051
OH
FmocHN
N
O
H
N
O
O
N
H
OH
O
1b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.8072
7.7885
7.6488
7.6321
7.4094
7.3910
7.3725
7.3321
7.3148
7.2970
5.4020
5.3965
5.3735
4.4749
4.4467
4.4368
4.0022
3.9375
3.7220
3.2554
3.2380
3.1691
3.1521
3.1364
2.2738
2.2551
2.1247
1.9369
1.6173
1.5979
1.3709
AcO
OAc
AcO
O
HN
O
O
FmocHN
N
O
C
O
H
N
O
N
H
OH
O
2a
1.98
1.96
2.10
1.89
1.00
0.91
0.98
0.93
1.01
1.13
2.97
0.92
2.71
2.29
2.01
1.04
3.87
11.05
3.97
2.08
f1 (ppm)


177.48
173.70
172.17
172.14
171.86
171.50
158.26
145.24
142.71
128.89
128.24
121.05
99.83
69.80
68.87
68.20
67.99
54.20
43.65
40.41
34.83
30.49
30.06
27.48
26.26
25.75
22.77
20.71
20.59
AcO
OAc
AcO
O
HN
O
O
FmocHN
N
O
C
O
H
N
O
N
H
OH
O
2a
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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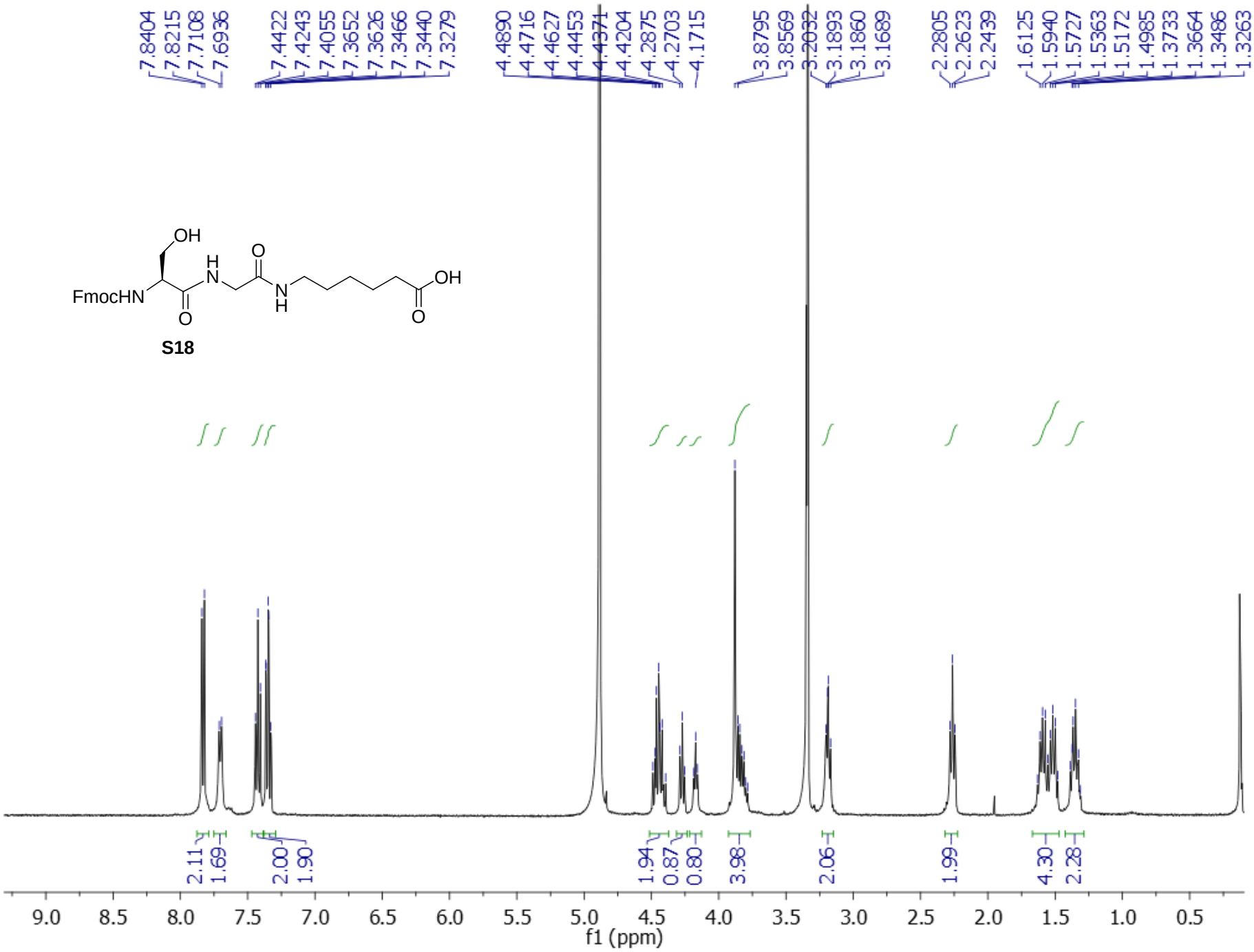
7.7840
7.6698
7.3876
7.3690
7.3334
7.3309
7.3148
7.3124
5.3739
5.3684
5.3463
5.3400
4.9280
4.6340
4.6216
4.2213
4.0765
4.0550
3.8189
3.8116
3.2170
3.2006
3.1837
2.1318
1.9561
1.9422
1.9214
1.6031
1.5833
1.5646
1.5244
1.5062
1.4884
1.3615
1.3400
1.3236
AcO
OAc
AcO
HN
O
FmocHN
N
H
N
OH
2b
1.97
2.26
2.07
2.00
1.00
0.94
0.95
1.84
3.03
2.06
2.20
3.70
2.01
2.24
3.05
3.27
12.22
4.30
2.23
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
f1 (ppm)


7.8404
7.8215
7.7108
7.6936
7.4422
7.4243
7.4055
7.3652
7.3626
7.3466
7.3440
7.3279
4.4890
4.4716
4.4627
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4.2703
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3.1860
3.1689
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2.2439
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1.5172
1.4985
1.3733
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1.3486
1.3263
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FmocHN
H
N
O
N
H
OH
O
O
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1.99
4.30
2.28
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8.0
7.5
7.0
6.5
6.0
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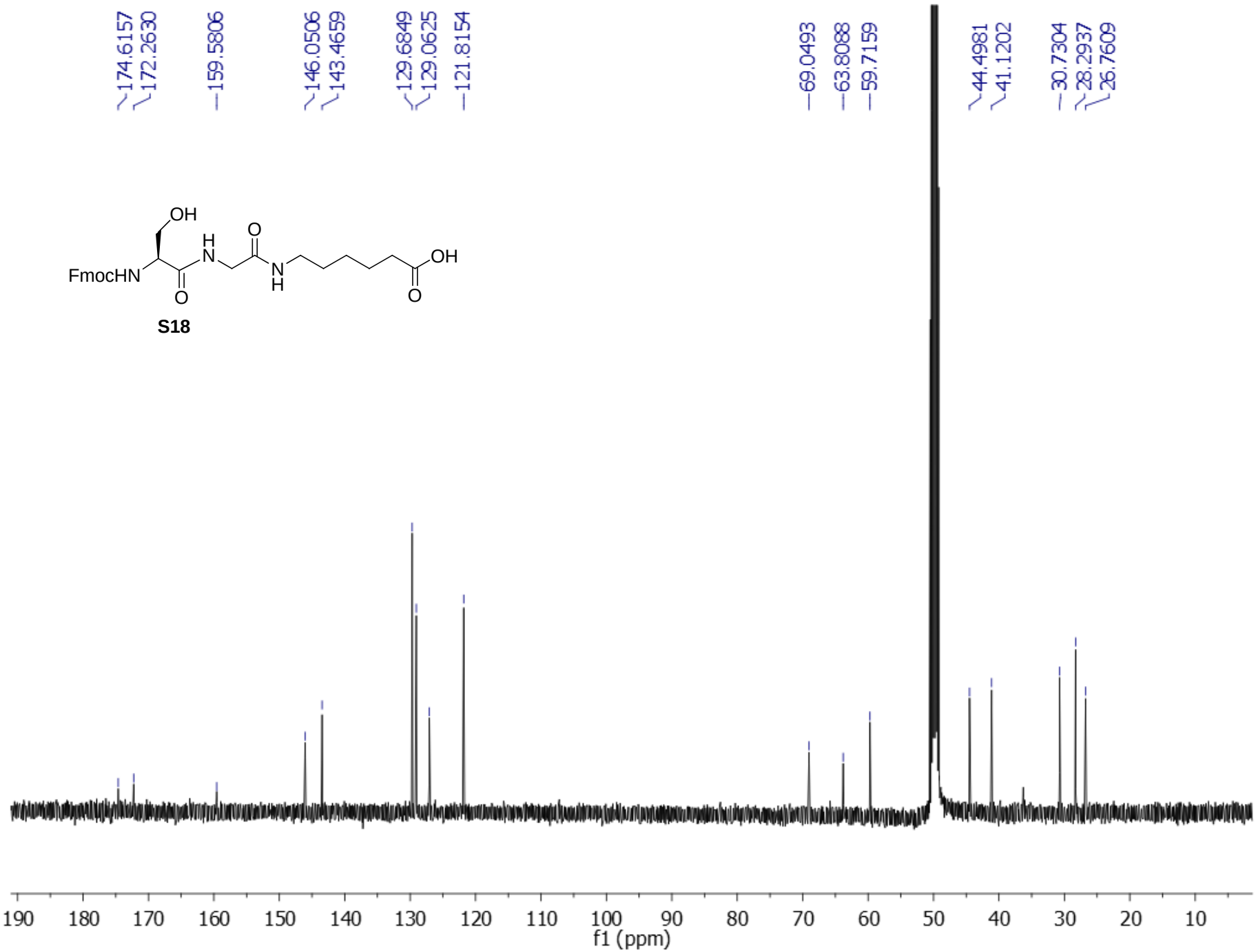
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41.1202
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28.2937
26.7609
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FmocHN
H
N
O
N
H
OH
O
O
S18
190
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100
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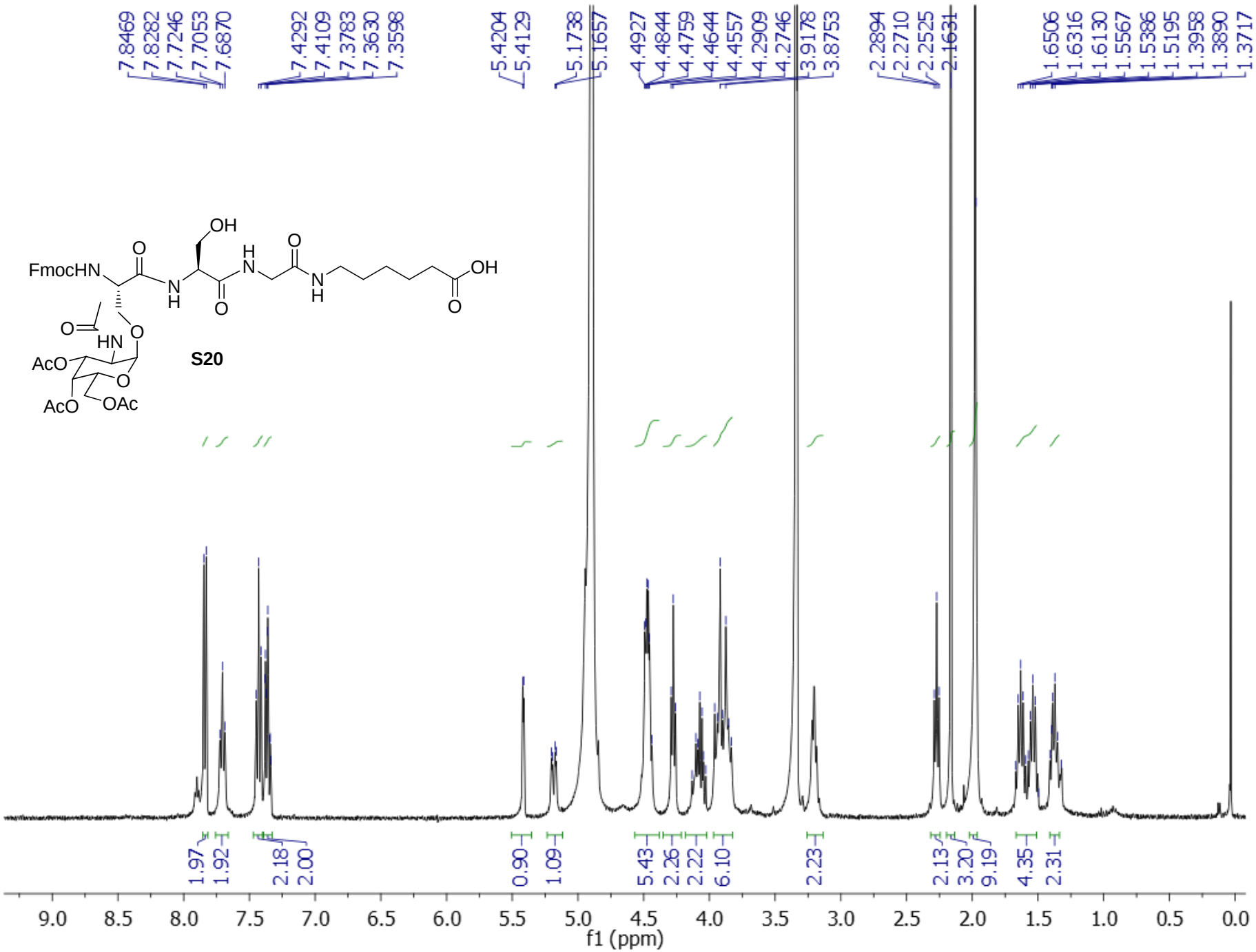
f1 (ppm)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5.1657
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4.4759
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4.4557
4.2909
4.2746
3.9178
3.8753
2.2894
2.2710
2.2525
2.1631
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1.6130
1.5567
1.5386
1.5195
1.3958
1.3890
1.3717
FmocHN
OH
HN
AcO
AcO
OAc
S20
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1.09
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2.26
2.22
6.10
2.23
2.13
3.20
9.19
4.35
2.31
9.0
8.5
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7.0
6.5
6.0
5.5
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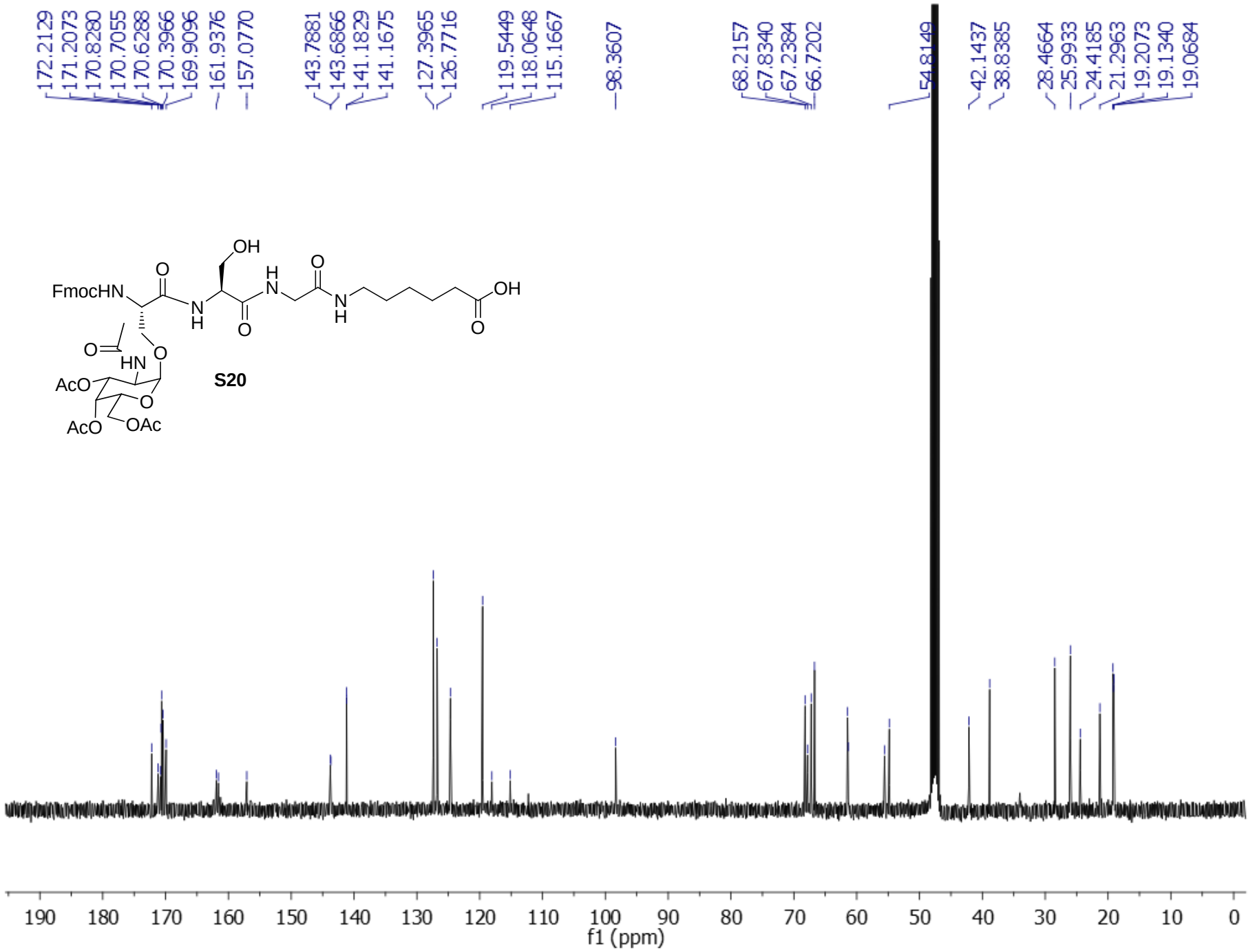
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24.4185
21.2963
19.2073
19.1340
19.0684
FmocHN
OH
O
N
H
HN
AcO
AcO
OAc
S20
190
180
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110
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90
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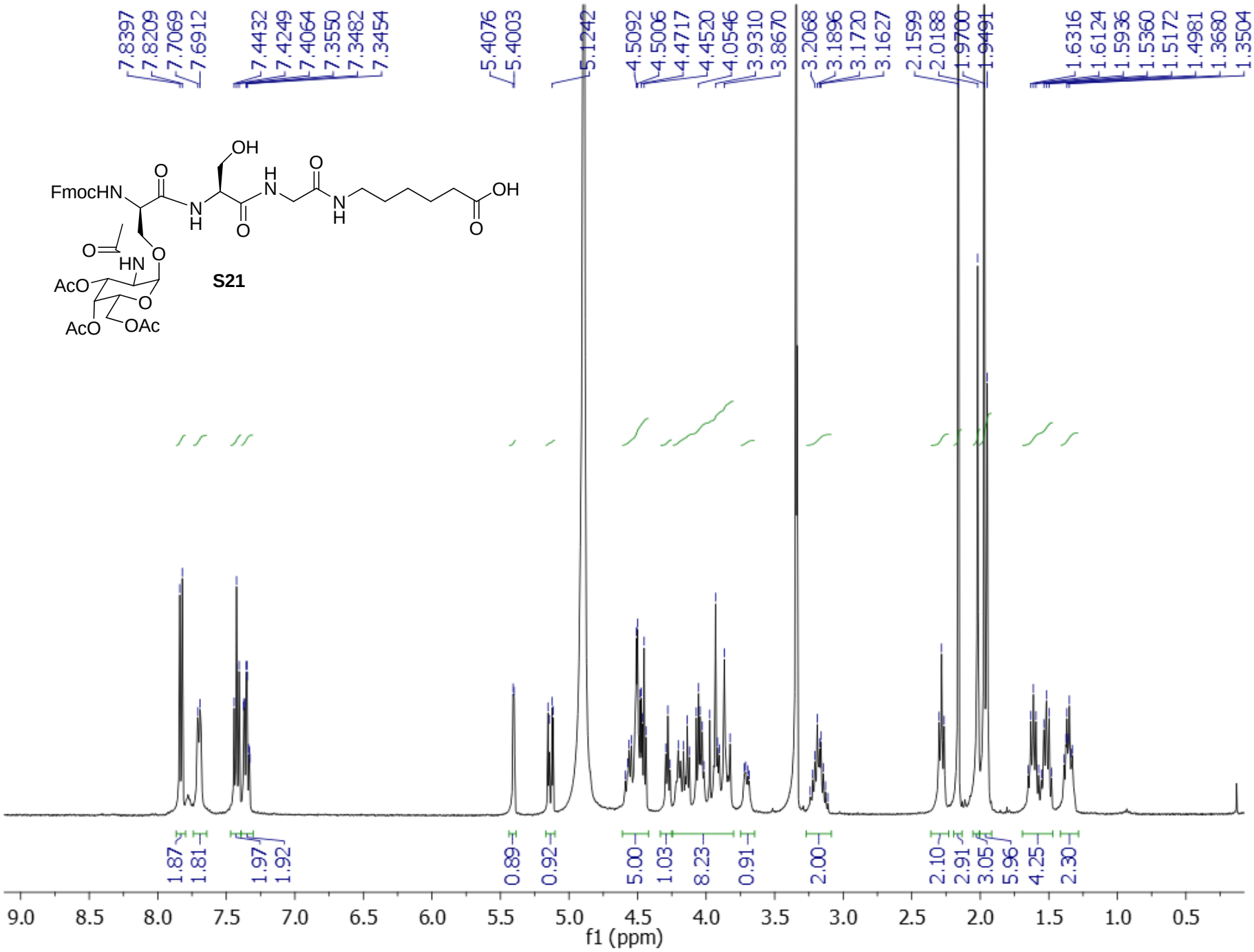
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7.4064
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5.4076
5.4003
5.1242
4.5092
4.5006
4.4717
4.4520
4.0546
3.9310
3.8670
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3.1896
3.1720
3.1627
2.1599
2.0188
1.9700
1.9491
1.6316
1.6124
1.5936
1.5360
1.5172
1.4981
1.3680
1.3504
FmocHN
OH
O
N
H
O
HN
O
AcO
AcO
OAc
S21
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1.81
1.97
1.92
0.89
0.92
5.00
1.03
8.23
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2.00
2.10
2.91
3.05
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4.25
2.30
9.0
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8.0
7.5
7.0
6.5
6.0
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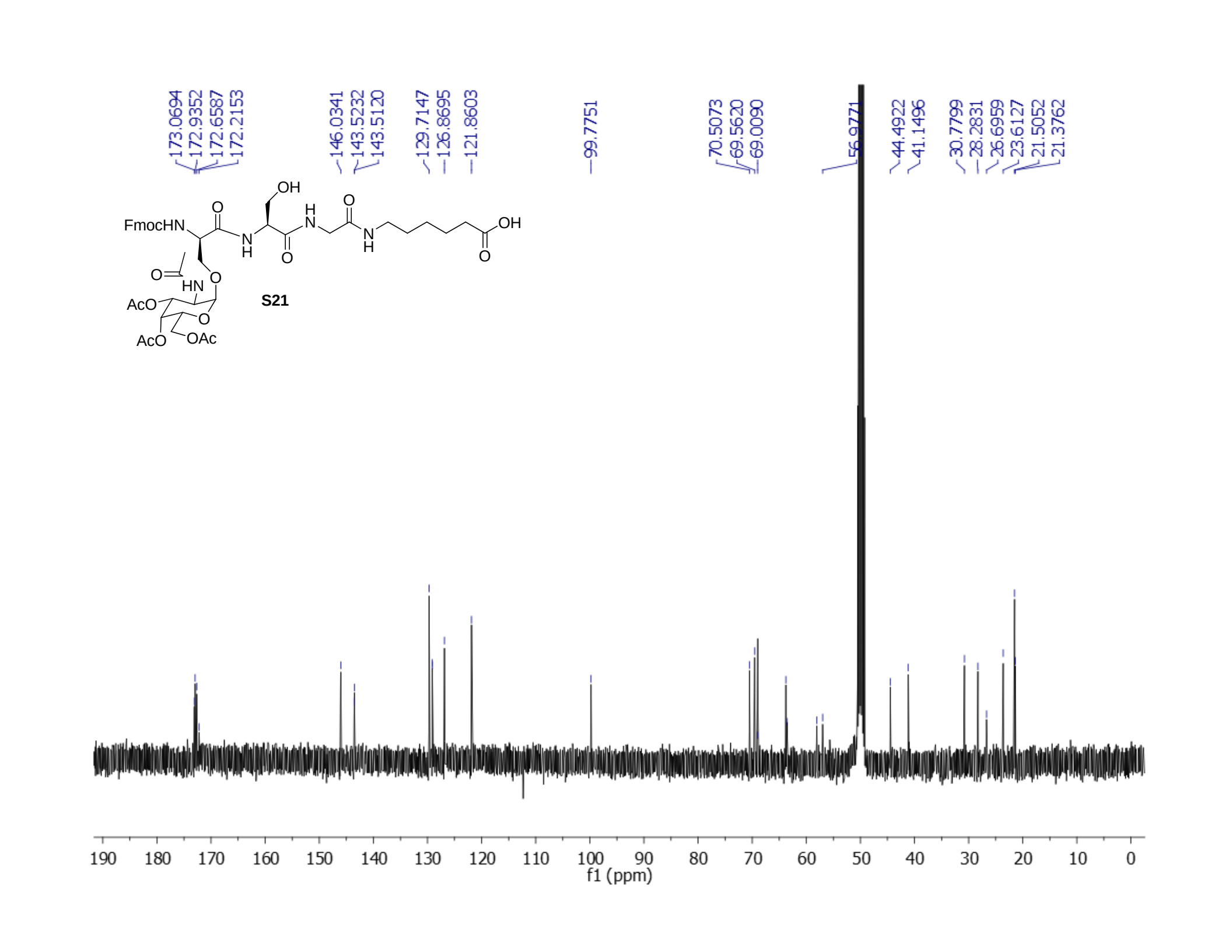
f1 (ppm)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69.5620
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56.9771
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41.1496
30.7799
28.2831
26.6959
23.6127
21.5052
21.3762
FmocHN
OH
O
N
H
O
H
N
O
N
H
OH
O
O
HN
O
AcO
O
AcO
OAc
S21
190
180
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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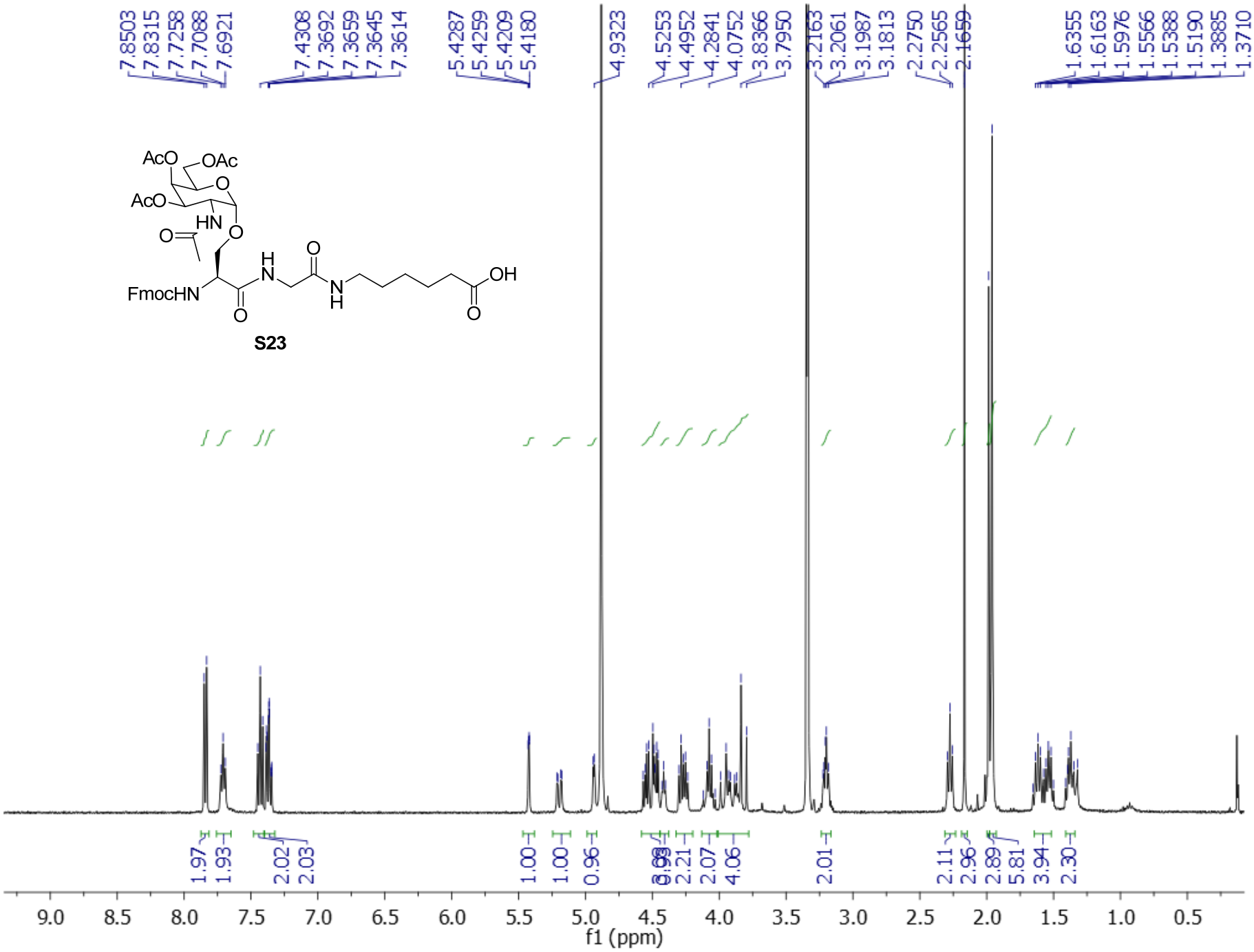
f1 (ppm)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5.4259
5.4209
5.4180
4.9323
4.5253
4.4952
4.2841
4.0752
3.8366
3.7950
3.2163
3.2061
3.1987
3.1813
2.2750
2.2565
2.1659
1.6355
1.6163
1.5976
1.5566
1.5388
1.5190
1.3885
1.3710
AcO
OAc
AcO
HN
O
O
FmocHN
H
N
O
N
H
O
OH
O
S23
1.97
1.93
2.02
2.03
1.00
1.00
0.96
2.21
2.07
4.06
2.01
2.11
2.96
2.89
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3.94
2.30
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8.0
7.5
7.0
6.5
6.0
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3.0
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2.0
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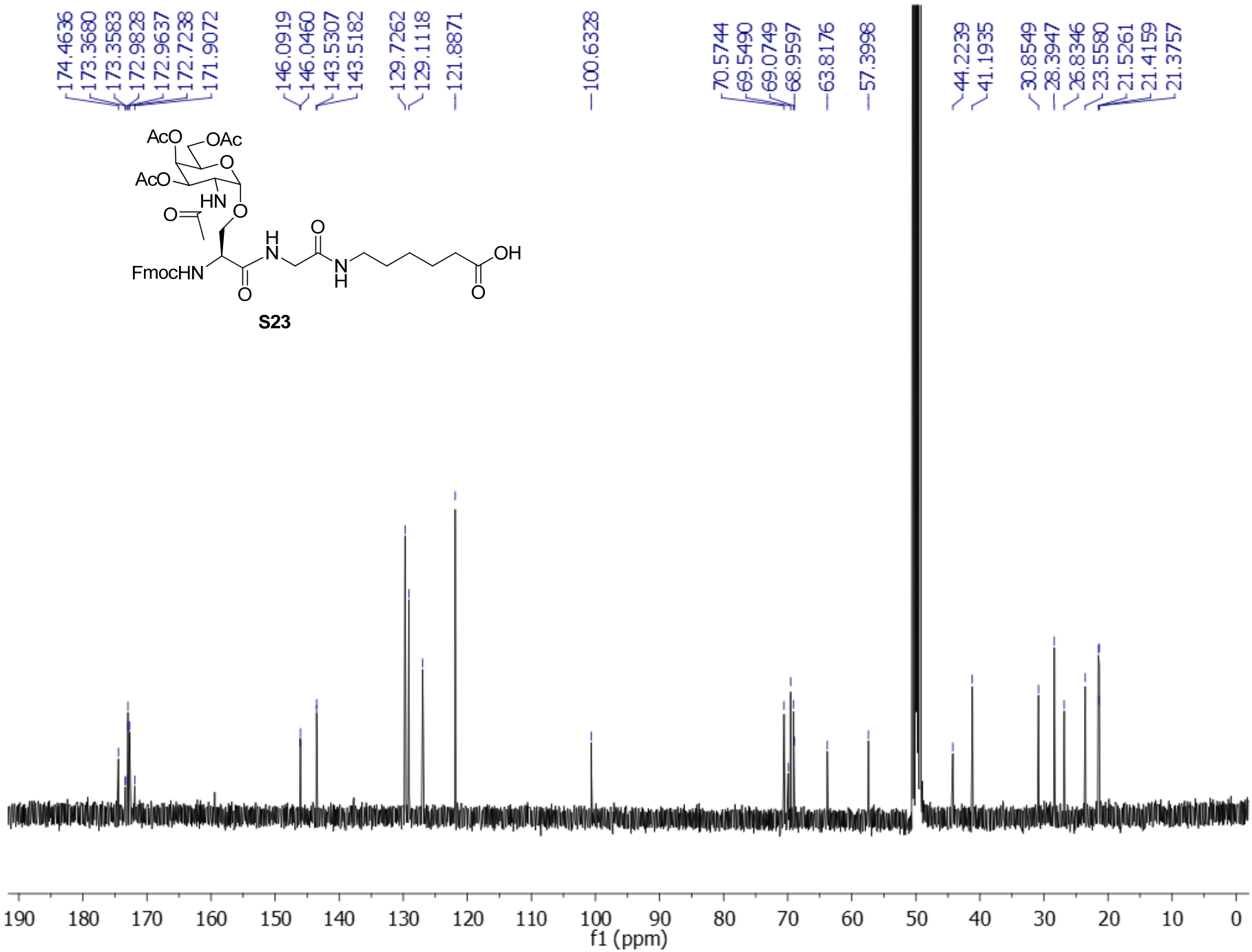
1.0
0.5
f1 (ppm)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63.8176
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44.2239
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30.8549
28.3947
26.8346
23.5580
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21.3757
AcO
OAc
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AcO
HN
O
O
H
N
O
N
H
OH
FmocHN
O
O
190
180
170
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140
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120
110
100
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80
70
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40
30
20
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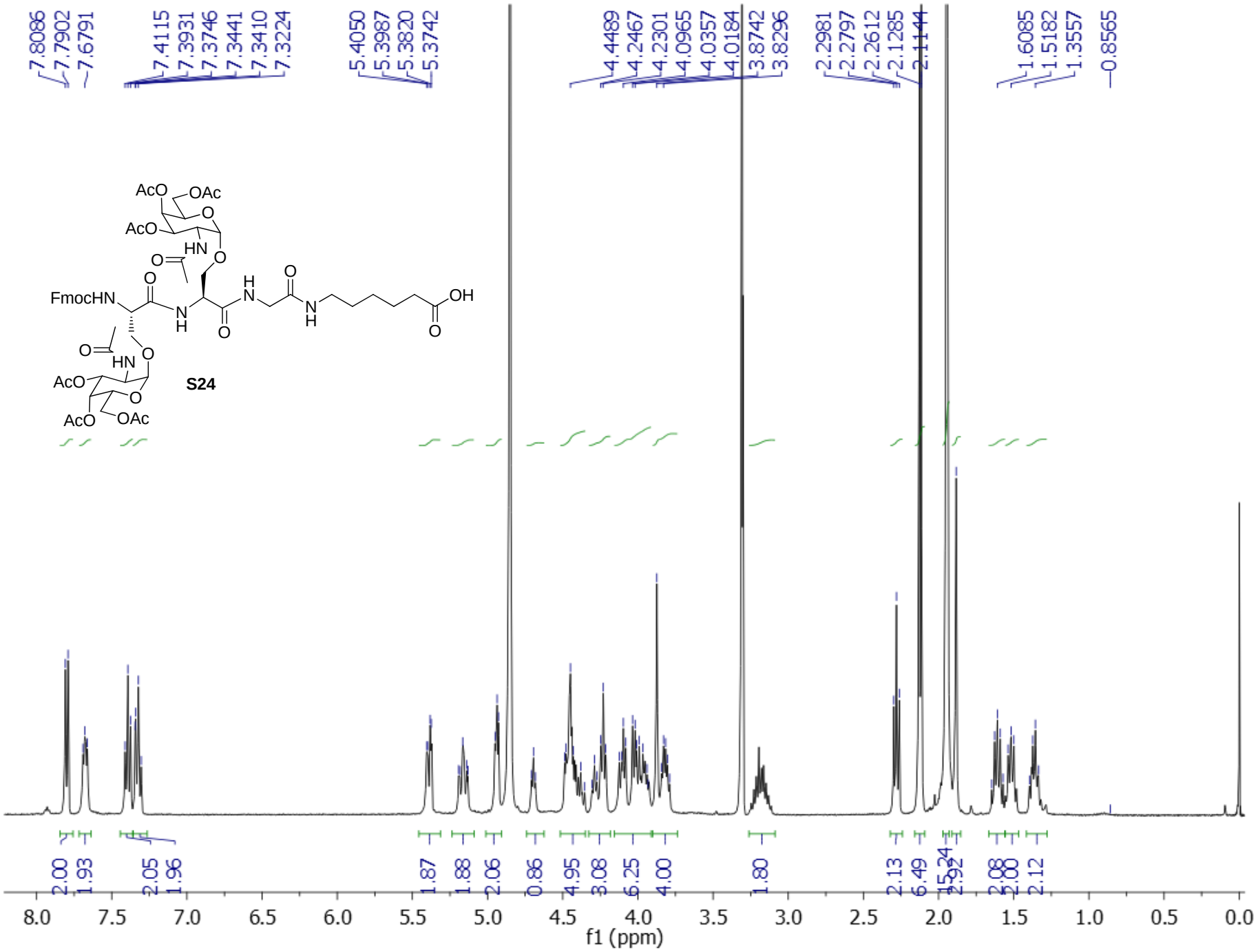
f1 (ppm)

S23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5.3987
5.3820
5.3742
4.4489
4.2467
4.2301
4.0965
4.0357
4.0184
3.8742
3.8296
2.2981
2.2797
2.2612
2.1285
2.1144
1.6085
1.5182
1.3557
0.8565
AcO
OAc
AcO
HN
O
FmocHN
O
N
H
O
H
N
O
N
H
OH
O
O
HN
O
AcO
O
AcO
OAc
S24
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1.93
2.05
1.96
1.87
1.88
2.06
0.86
4.95
3.08
6.25
4.00
1.80
2.13
6.49
15.24
2.92
2.08
2.00
2.12
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
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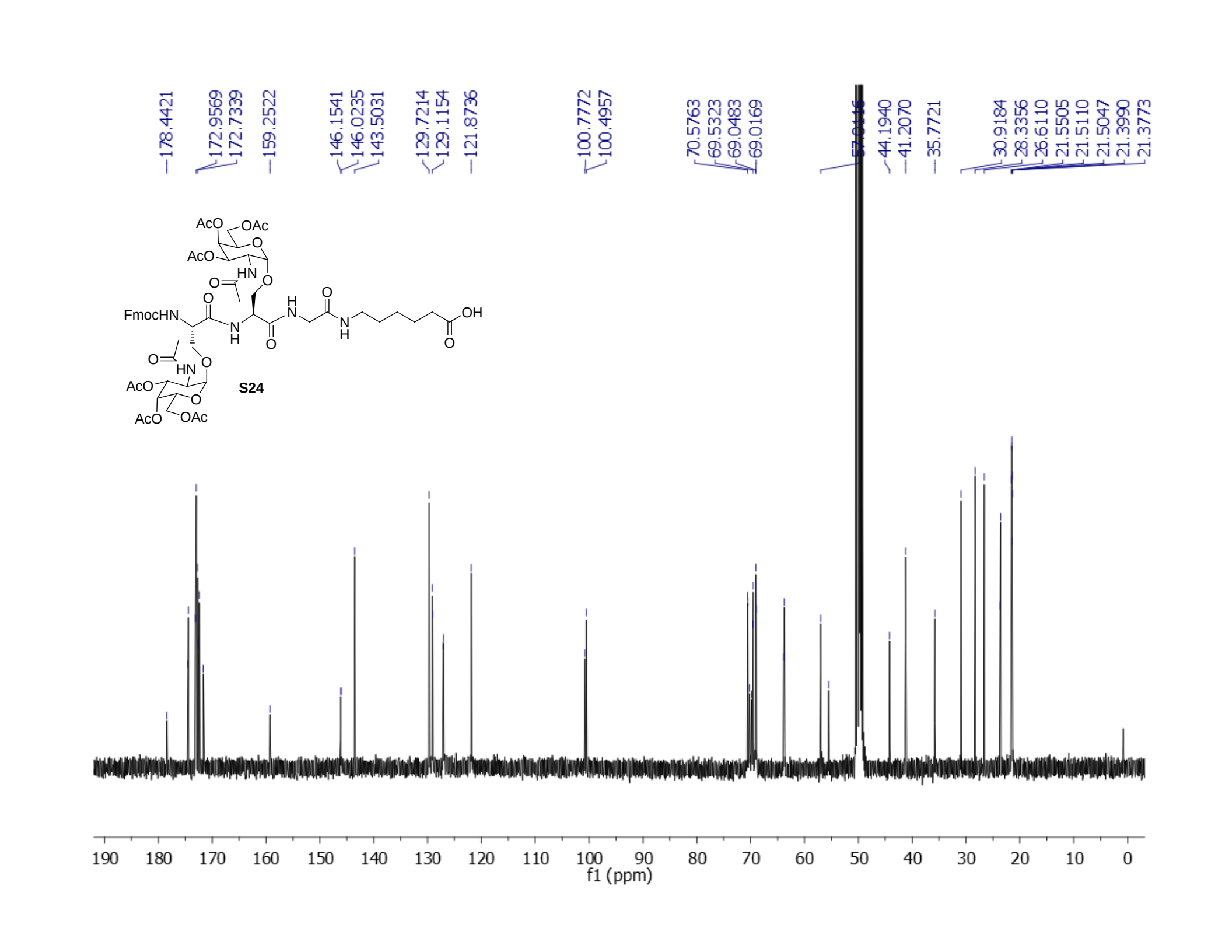
0.0
f1 (ppm)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100.4957
70.5763
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69.0169
57.0116
44.1940
41.2070
35.7721
30.9184
28.3356
26.6110
21.5505
21.5110
21.5047
21.3990
21.3773
AcO
OAc
AcO
HN
O
FmocHN
N
H
H
N
O
N
H
OH
HN
AcO
AcO
OAc
S24
190
180
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120
110
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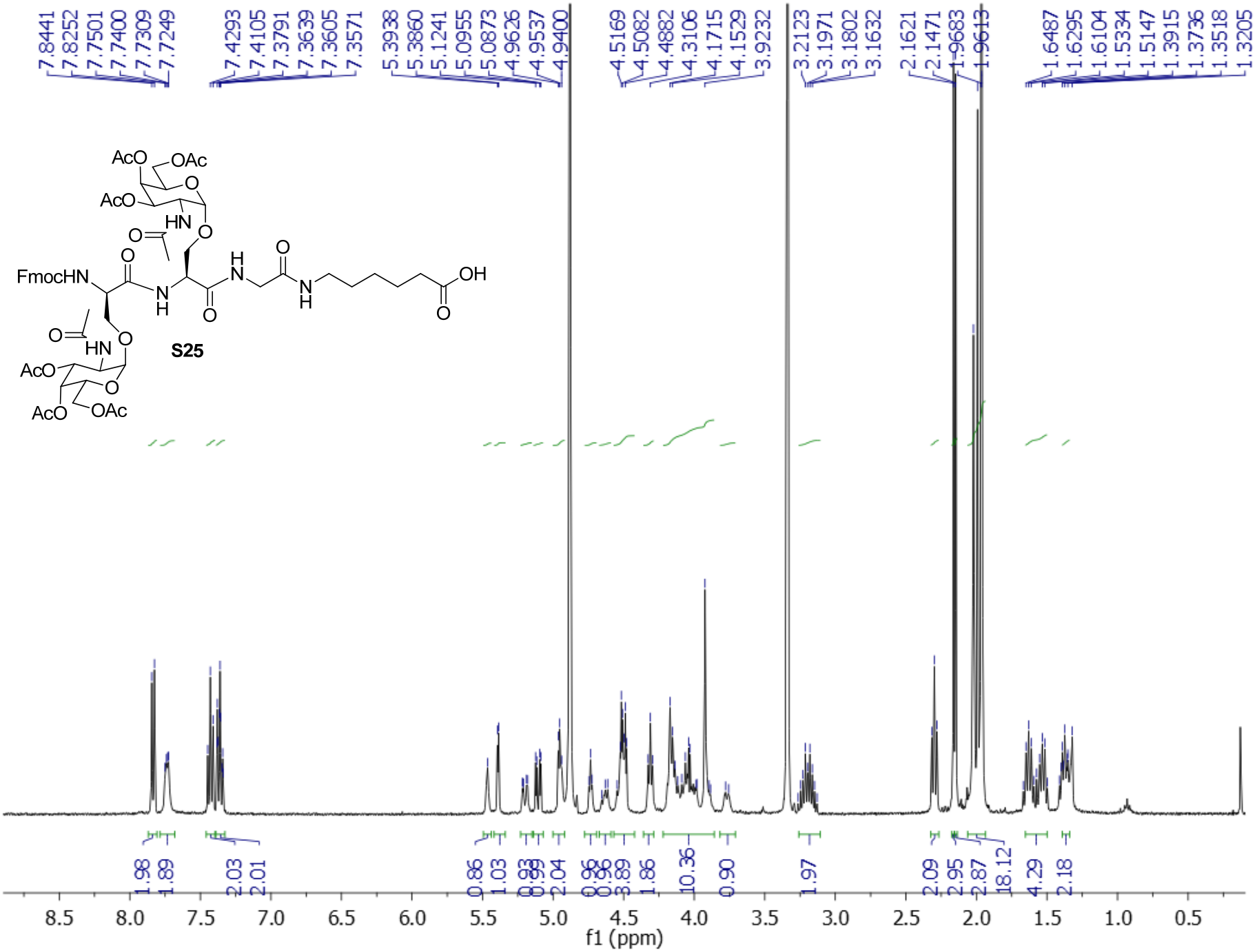
f1 (ppm)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5.3938
5.3860
5.1241
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2.1621
2.1471
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1.6104
1.5334
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1.3915
1.3736
1.3518
1.3205
AcO
OAc
AcO
HN
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FmocHN
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H
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H
N
O
N
H
OH
O
O
HN
O
AcO
O
AcO
OAc
S25
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1.03
0.93
2.04
0.96
3.89
1.86
10.36
0.90
1.97
2.09
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4.29
2.18
8.5
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7.5
7.0
6.5
6.0
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1.5
1.0
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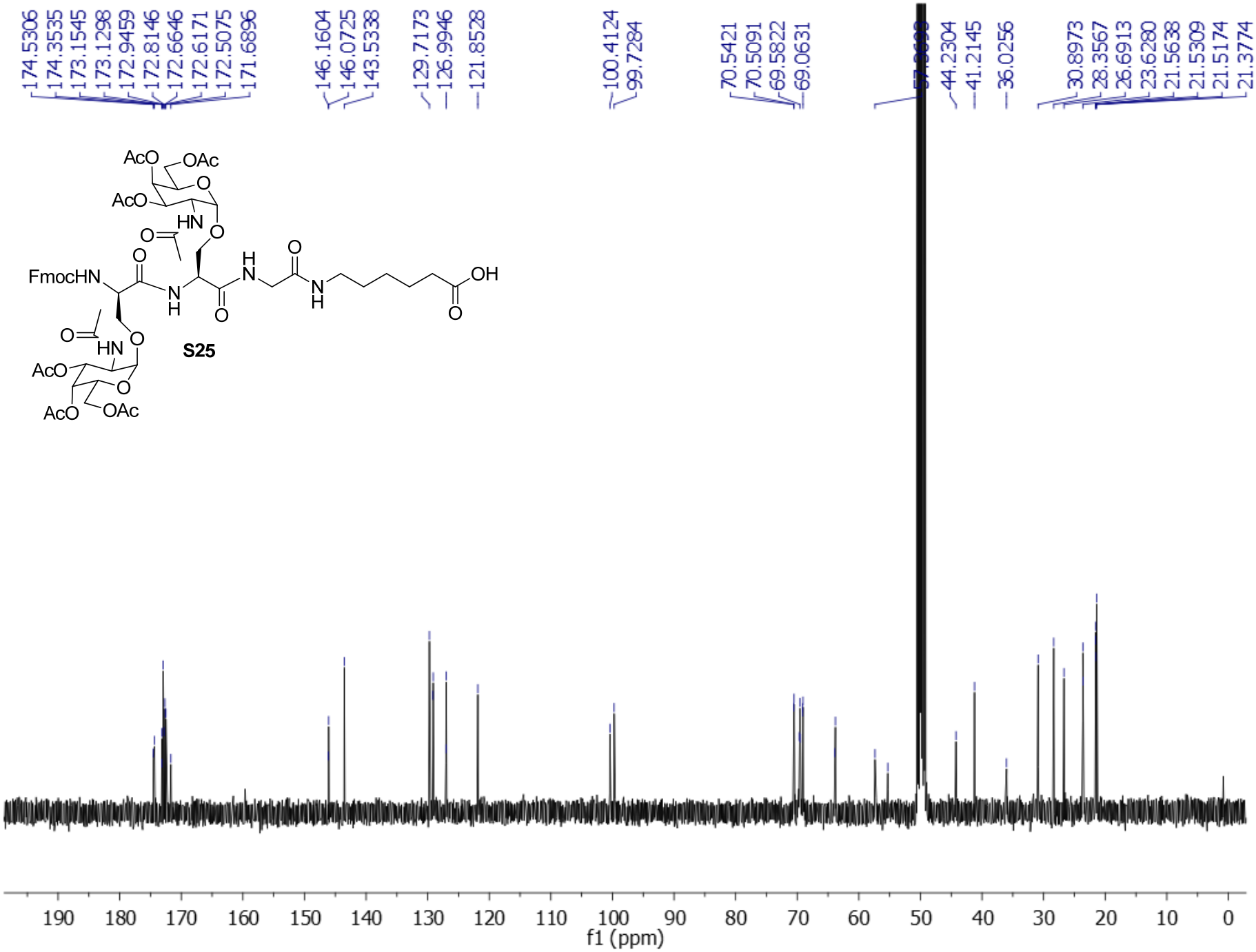
f1 (ppm)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OAc
AcO
HN
O
O
FmocHN
N
H
O
H
N
O
N
H
OH
O
O
HN
O
AcO
O
AcO
OAc
S25
190
180
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130
120
110
100
90
80
70
60
50
40
30
20
10
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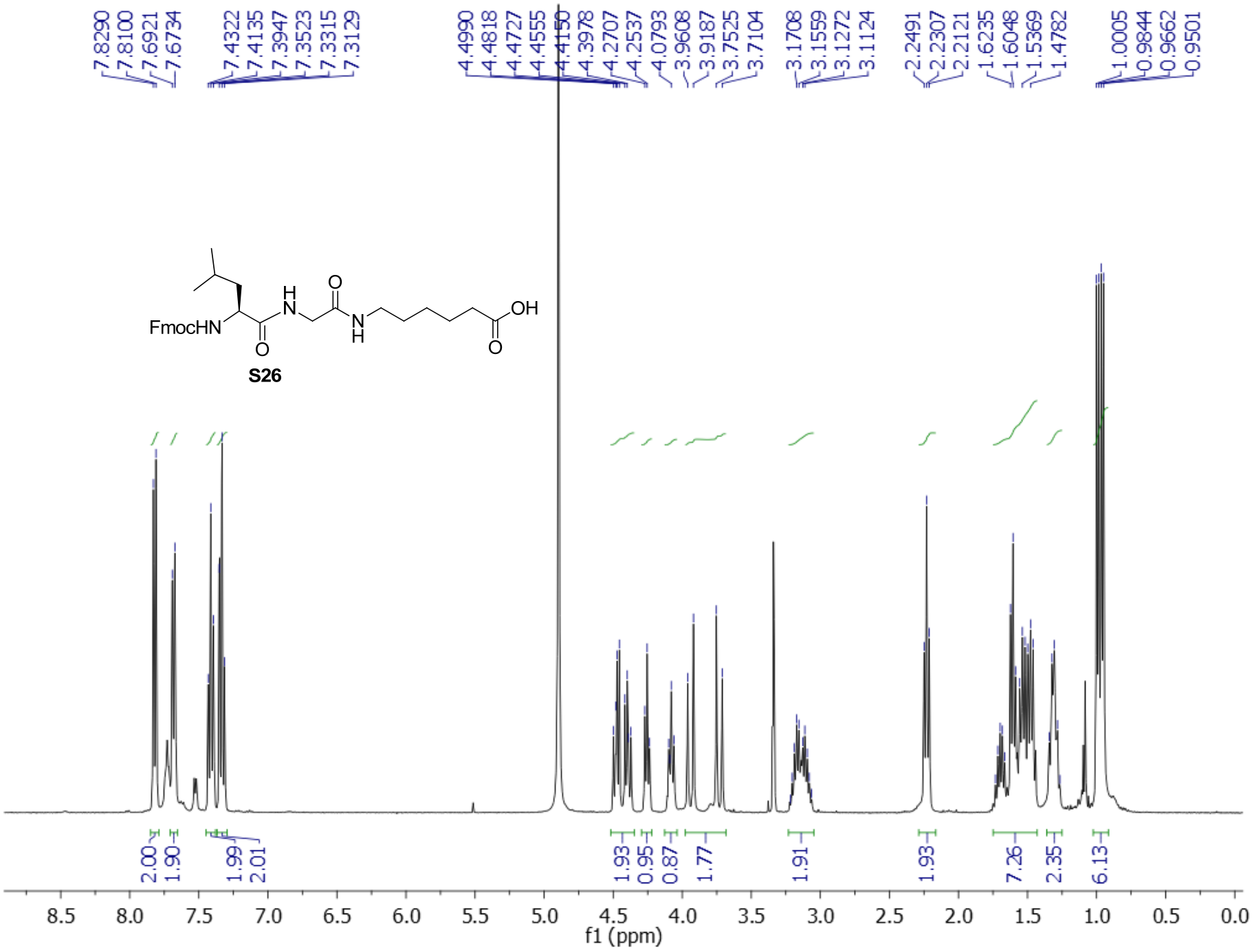
f1 (ppm)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3.9187
3.7525
3.7104
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3.1559
3.1272
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2.2491
2.2307
2.2121
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1.0005
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N
H
O
OH
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1.99
2.01
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0.95
0.87
1.77
1.91
1.93
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2.35
6.13
8.5
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7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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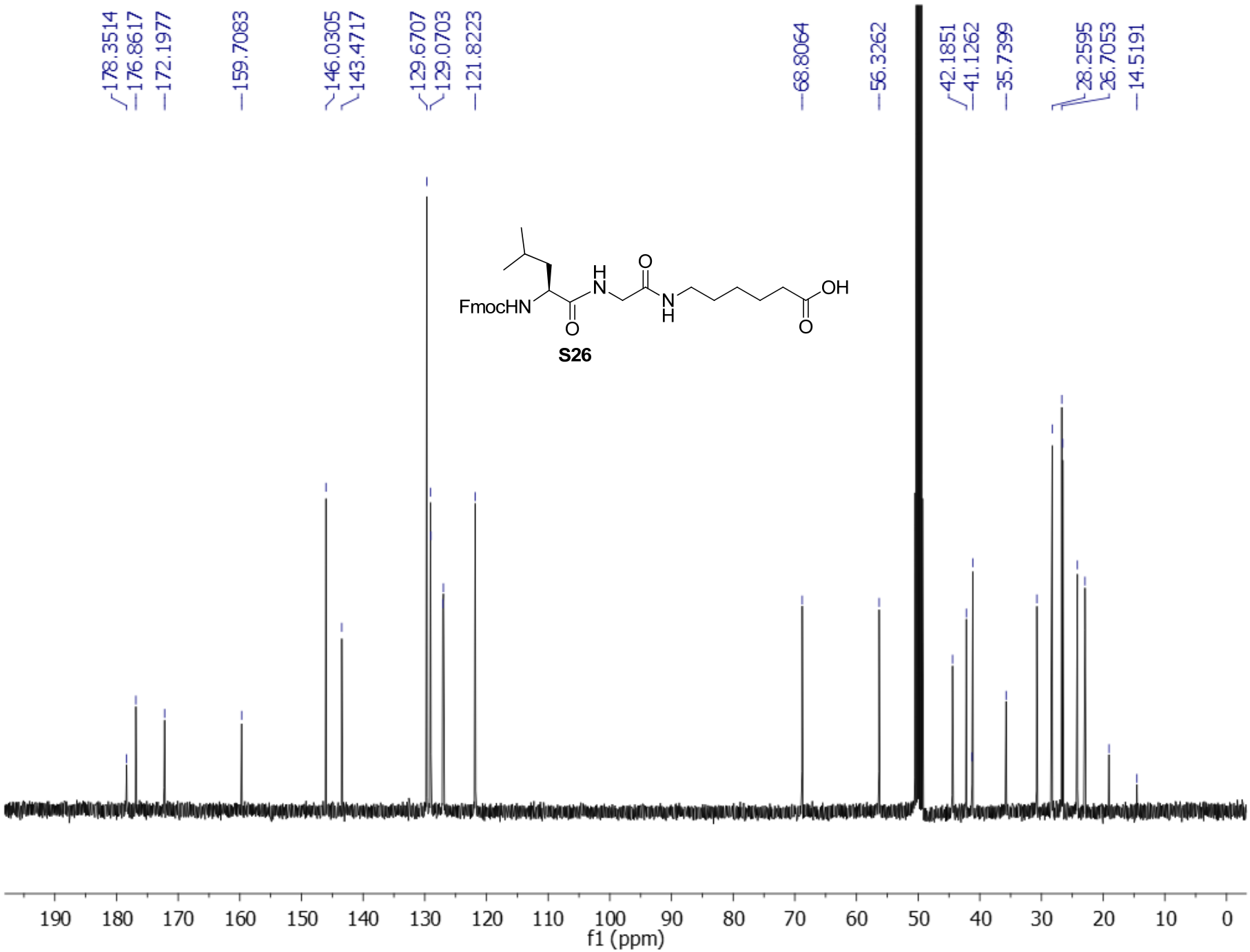
0.0
f1 (ppm)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FmocHN
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N
O
N
H
O
OH
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S26
190
180
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110
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90
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40
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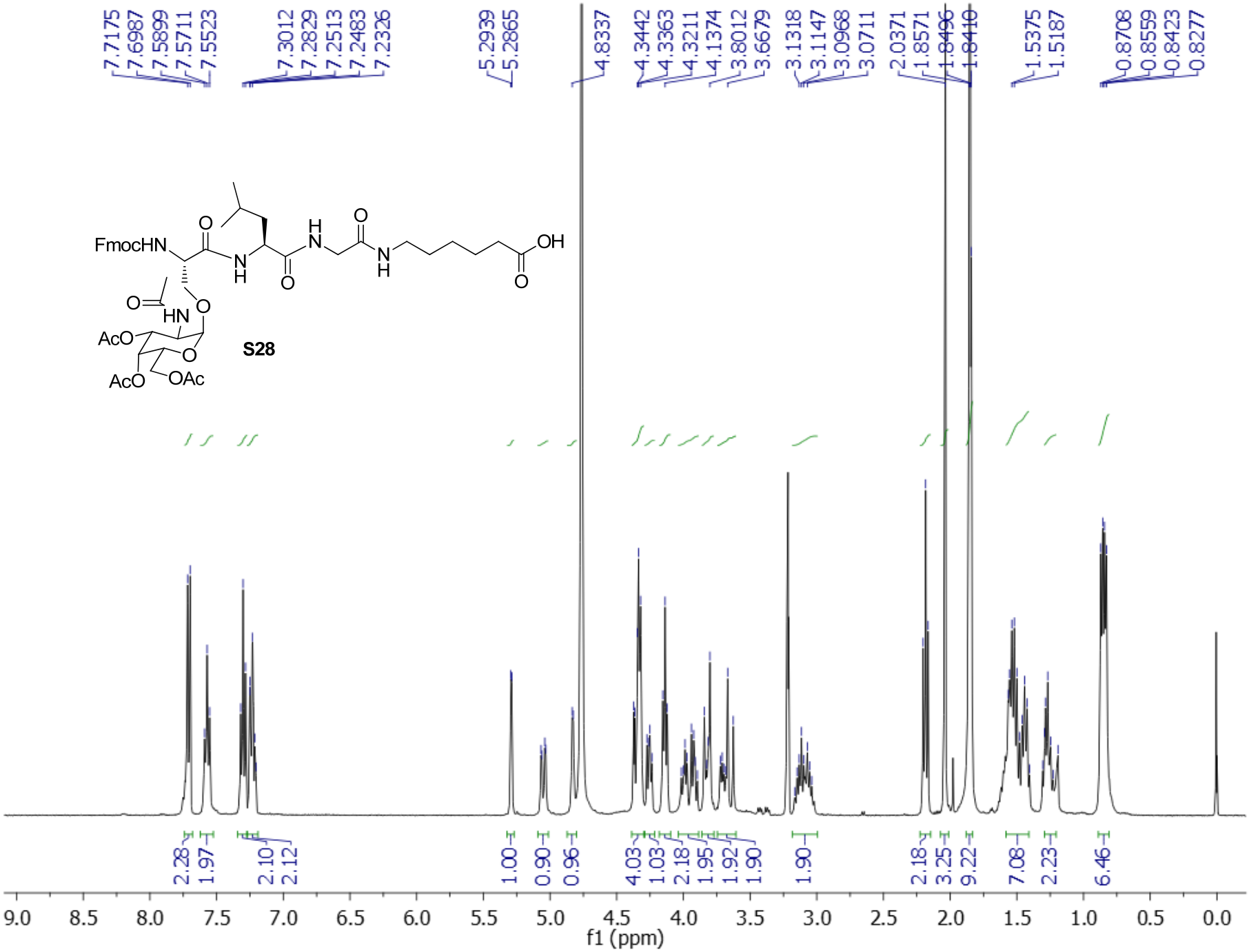
f1 (ppm)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4.3442
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4.1374
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3.1147
3.0968
3.0711
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1.8496
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N
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N
H
OH
O
O
HN
O
AcO
O
AcO
OAc
S28
2.28
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2.10
2.12
1.00
0.90
0.96
4.03
1.03
2.18
1.95
1.92
1.90
1.90
2.18
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7.08
2.23
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8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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1.0
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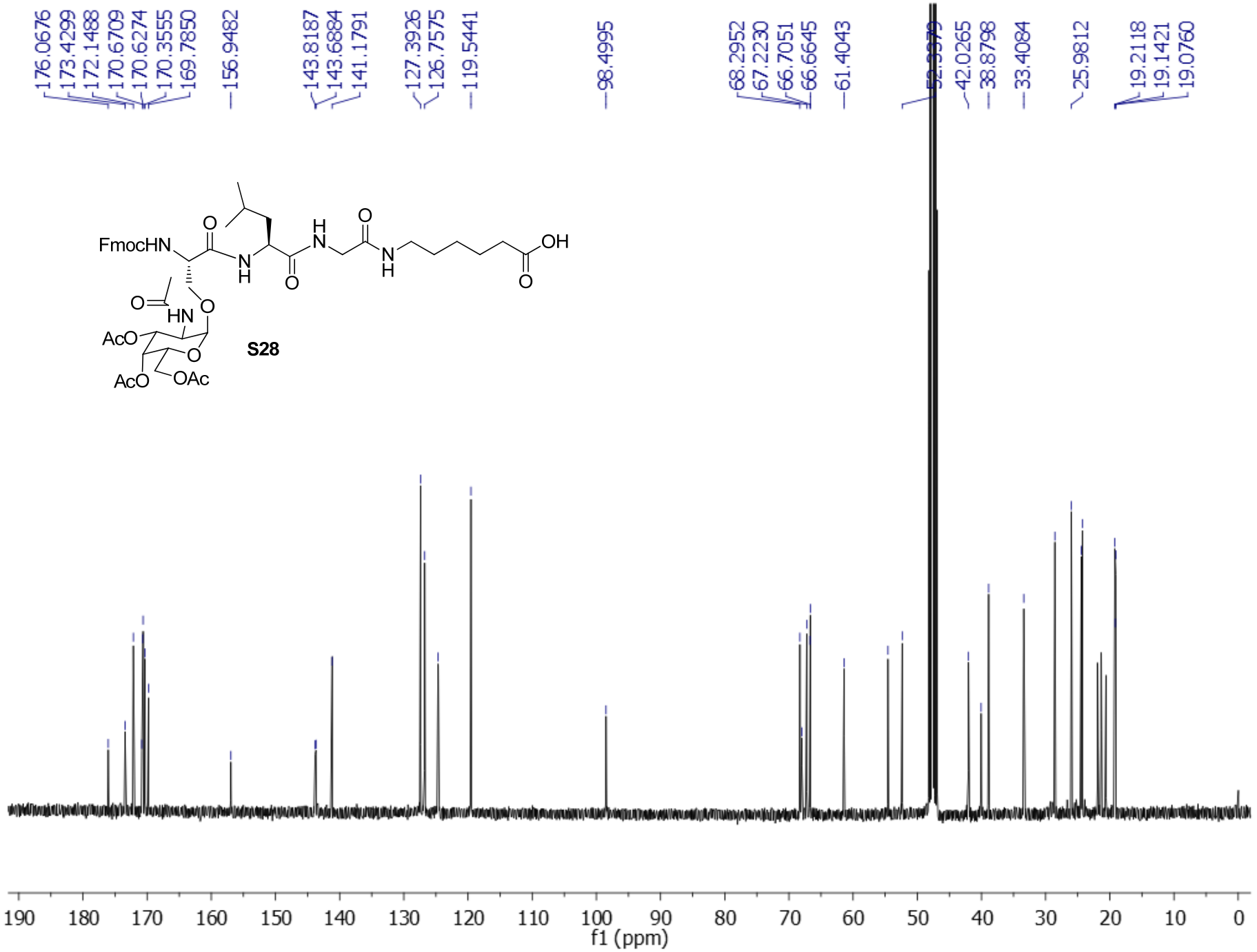
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127.3926
126.7575
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67.2230
66.7051
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61.4043
52.9379
42.0265
38.8798
33.4084
25.9812
19.2118
19.1421
19.0760
FmocHN
O
H
N
O
N
H
O
OH
O
HN
O
AcO
O
AcO
OAc
S28
190
180
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110
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90
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50
40
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20
10
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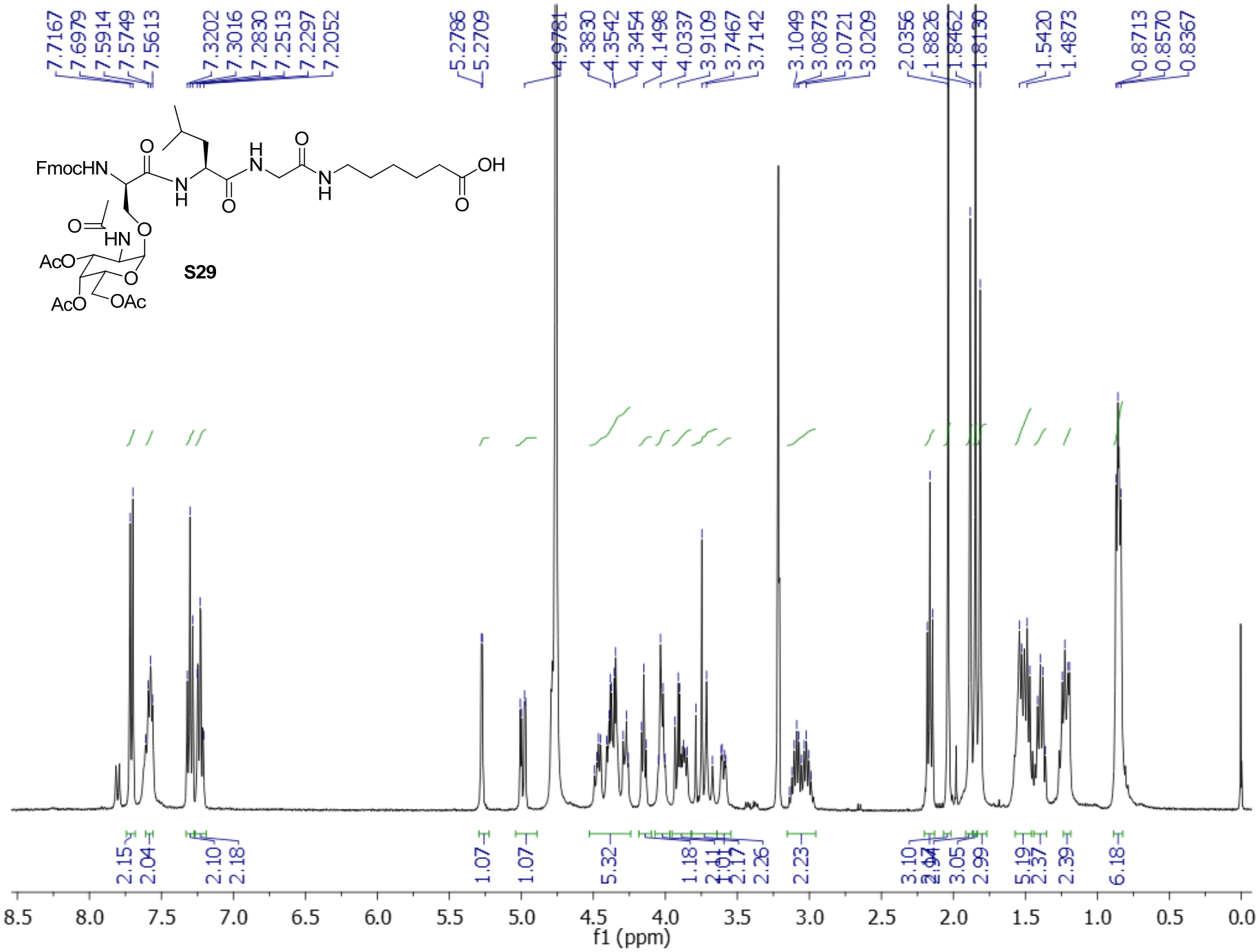
f1 (ppm)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3.7142
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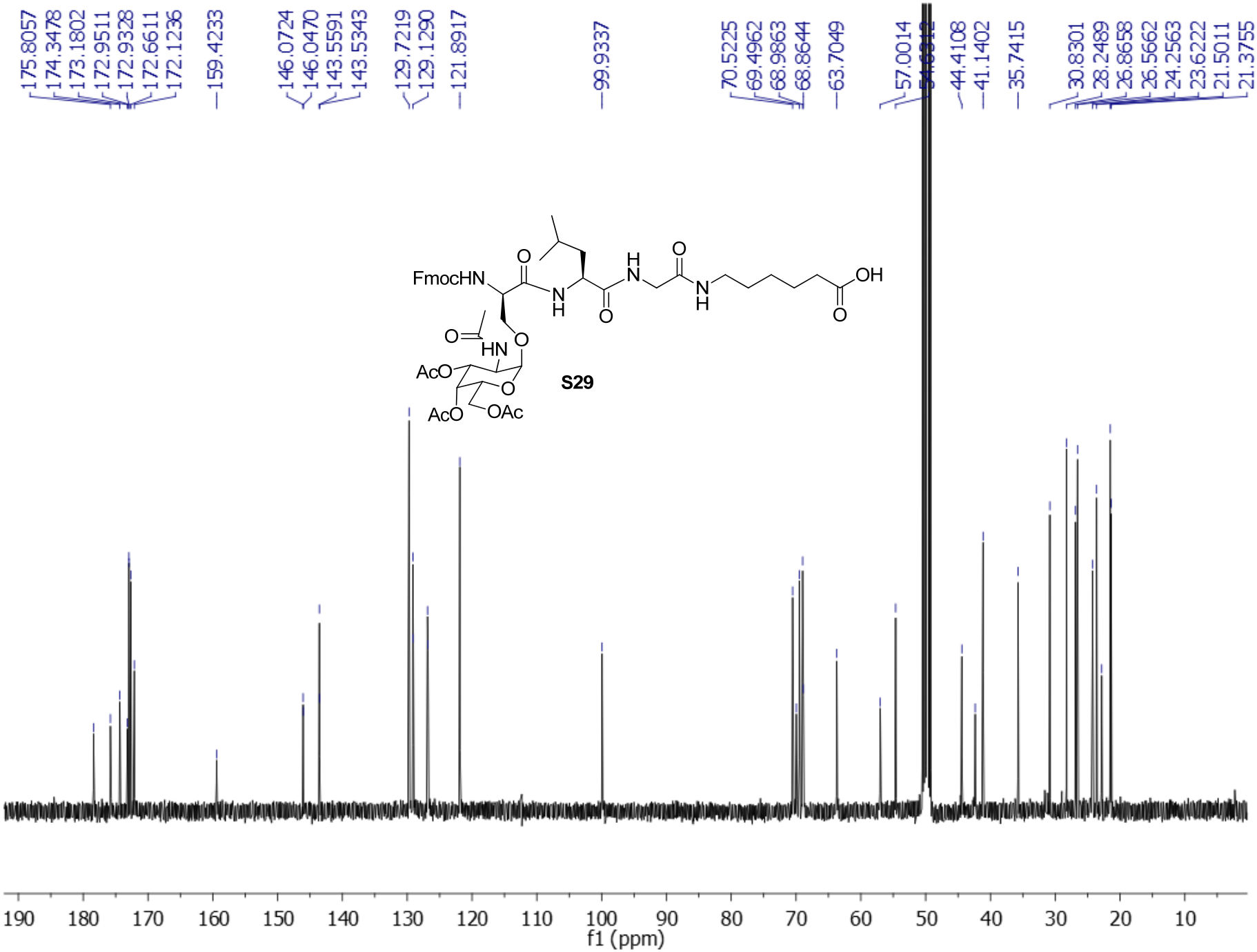
0.8570
0.8367
FmocHN
OH
AcO
AcO
OAc
HN
S29
2.15
2.04
2.10
2.18
1.07
1.07
5.32
1.18
2.11
2.01
2.17
2.26
2.23
3.10
3.05
2.99
5.19
2.37
2.39
6.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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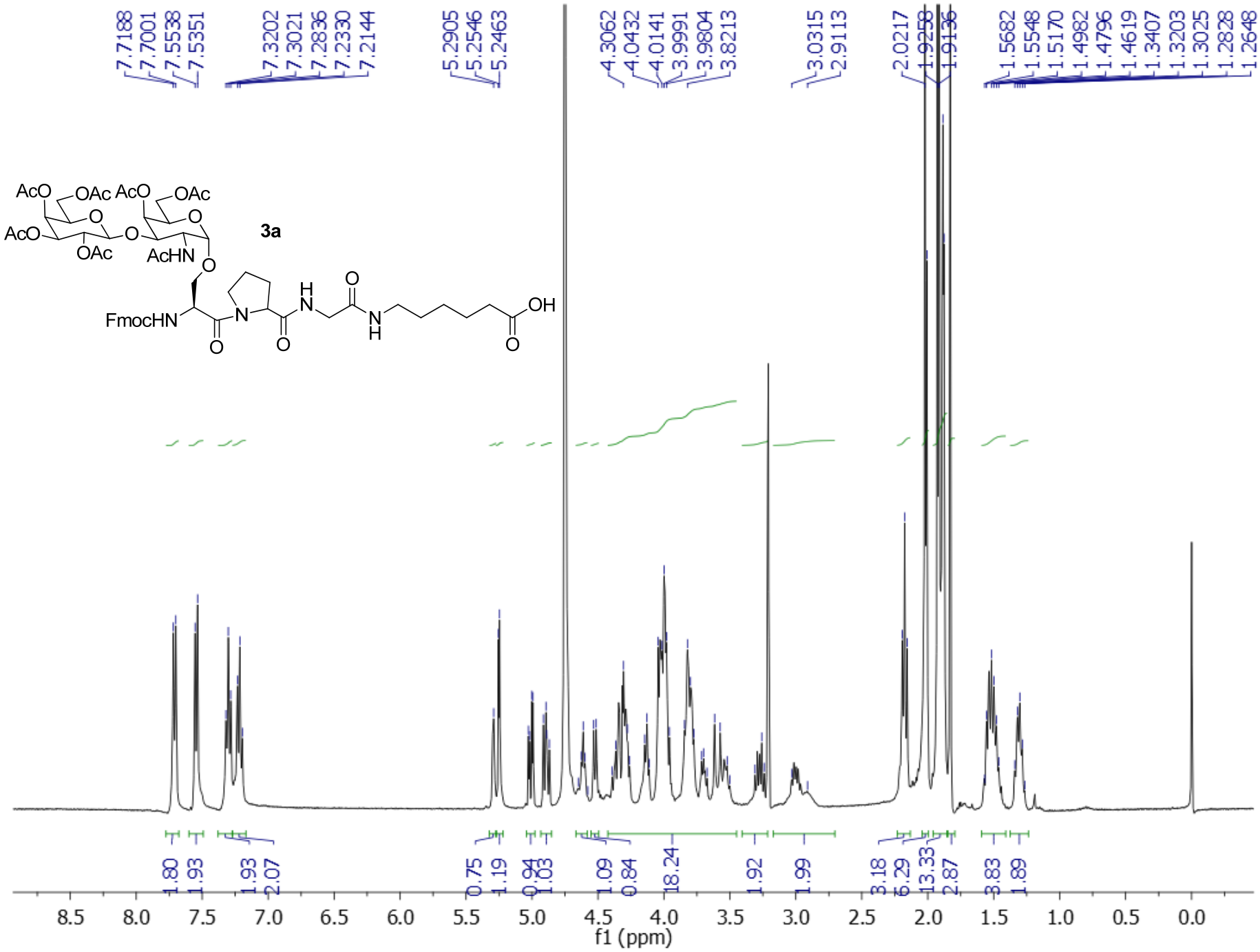
174.3478
173.1802
172.9511
172.9328
172.6611
172.1236
159.4233
146.0724
146.0470
143.5591
143.5343
129.7219
129.1290
121.8917
99.9337
70.5225
69.4962
68.9863
68.8644
63.7049
57.0014
54.6812
44.4108
41.1402
35.7415
30.8301
28.2489
26.8658
26.5662
24.2563
23.6222
21.5011
21.3755
FmocHN
O
N
H
O
H
N
O
N
H
OH
O
O
HN
O
AcO
O
AcO
OAc
S29
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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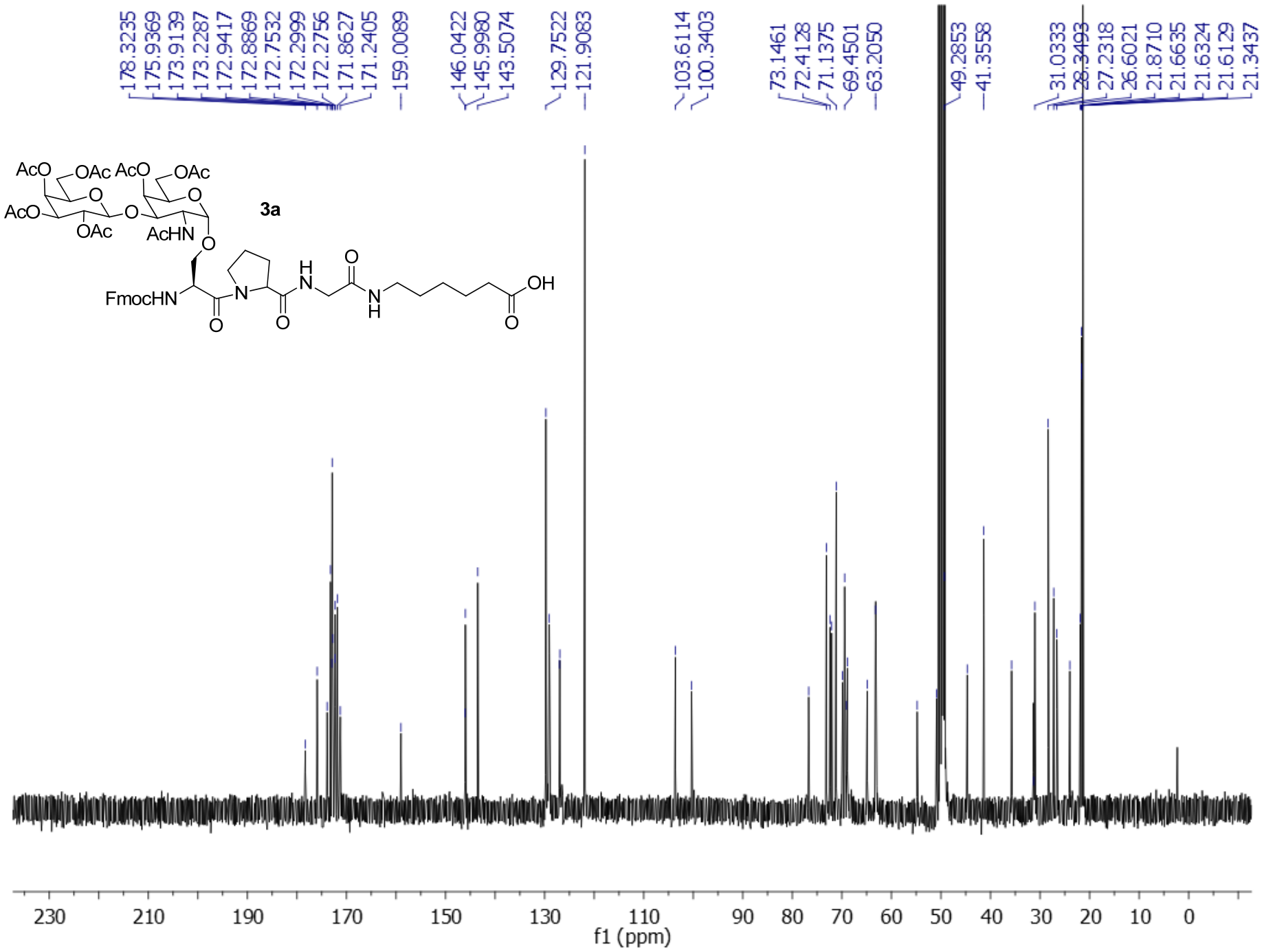
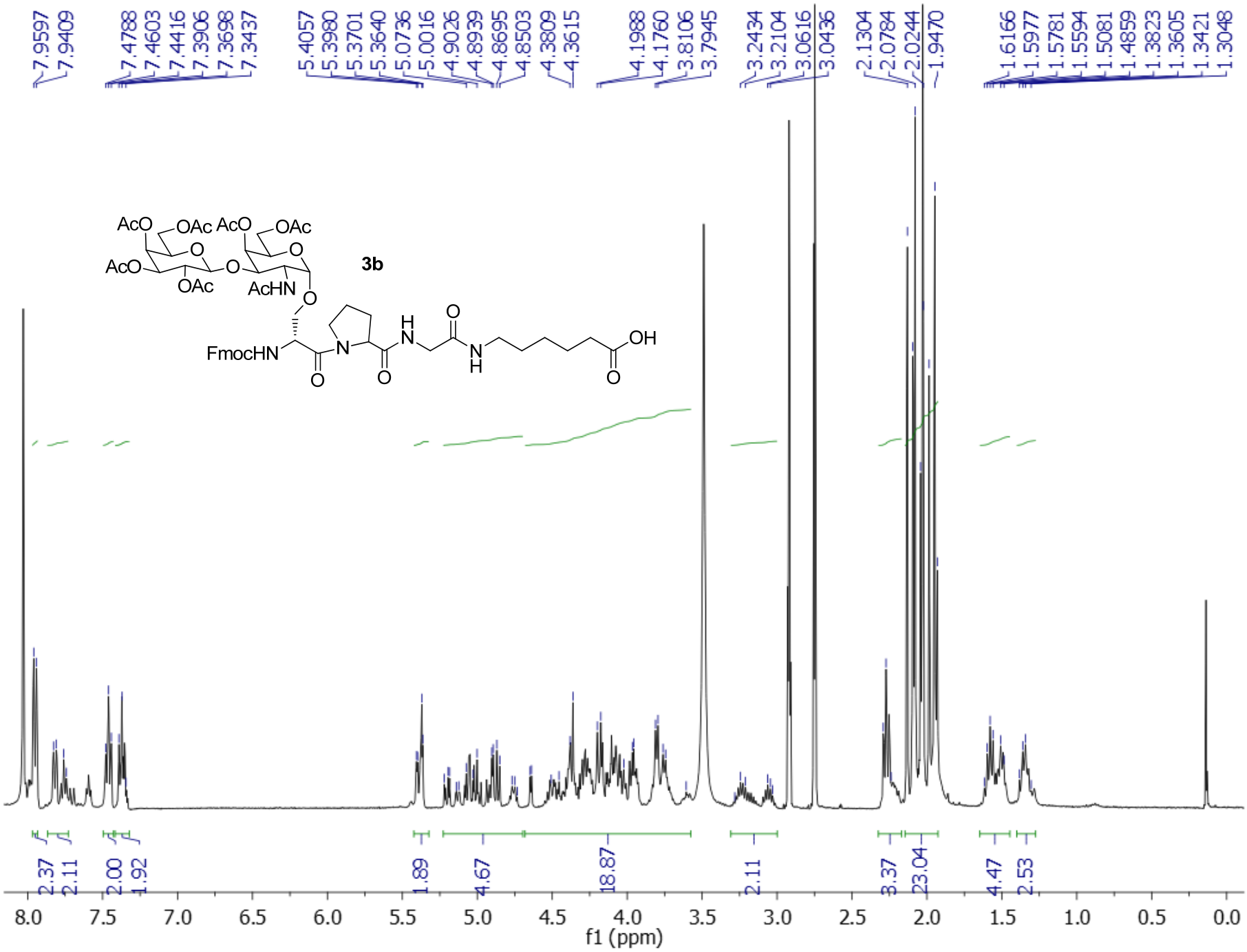
7.7001
7.5538
7.5351
7.3202
7.3021
7.2836
7.2330
7.2144
5.2905
5.2546
5.2463
4.3062
4.0432
4.0141
3.9991
3.9804
3.8213
3.0315
2.9113
2.0217
1.9258
1.9136
1.5682
1.5548
1.5170
1.4982
1.4796
1.4619
1.3407
1.3203
1.3025
1.2828
1.2648
AcO
OAc
AcO
OAc
AcO
O
O
OAc
AcHN
O
3a
FmocHN
N
O
O
H
N
O
O
N
H
OH
O
1.80
1.93
1.93
2.07
0.75
1.19
0.94
1.03
1.09
0.84
18.24
1.92
1.99
3.18
6.29
13.33
2.87
3.83
1.89
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
f1 (ppm)


178.3235
175.9369
173.9139
173.2287
172.9417
172.8869
172.7532
172.2999
172.2756
171.8627
171.2405
159.0089
146.0422
145.9980
143.5074
129.7522
121.9083
103.6114
100.3403
73.1461
72.4128
71.1375
69.4501
63.2050
49.2853
41.3558
31.0333
28.3493
27.2318
26.6021
21.8710
21.6635
21.6324
21.6129
21.3437
AcO
OAc
AcO
OAc
AcO
OAc
AcHN
FmocHN
OH
3a
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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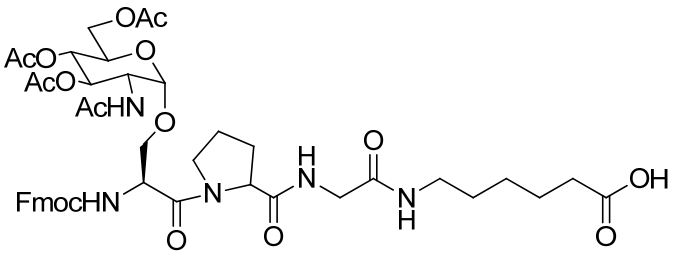
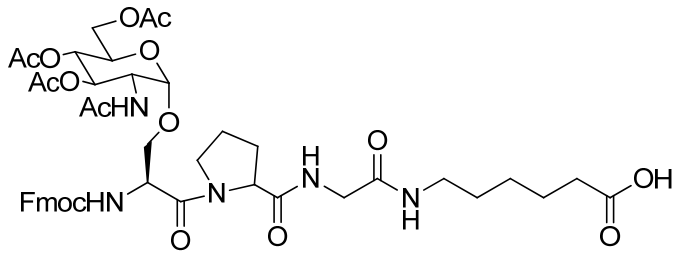
7.9409
7.4788
7.4603
7.4416
7.3906
7.3698
7.3437
5.4057
5.3980
5.3701
5.3640
5.0736
5.0016
4.9026
4.8939
4.8695
4.8503
4.3809
4.3615
4.1988
4.1760
3.8106
3.7945
3.2434
3.2104
3.0616
3.0436
2.1304
2.0784
2.0244
1.9470
1.6166
1.5977
1.5781
1.5594
1.5081
1.4859
1.3823
1.3605
1.3421
1.3048
AcO
OAc
AcO
OAc
AcO
OAc
AcHN
FmocHN
3b
OH
2.37
2.11
2.00
1.92
1.89
4.67
18.87
2.11
3.37
23.04
4.47
2.53
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
f1 (ppm)


OAc
AcO
AcO
AcHN
O
FmocHN
N
H
N
O
N
H
OH
O
O
O
O

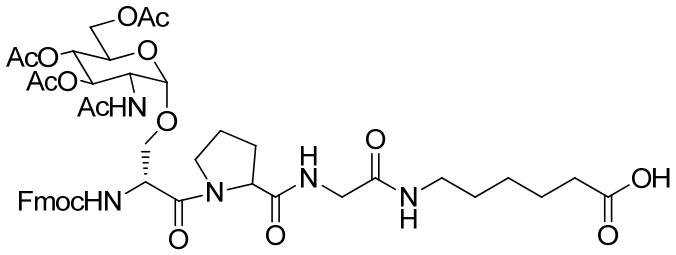
4a

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
f1 (ppm)


OAc
AcO
AcO
AcHN
O
FmocHN
N
H
N
O
N
H
OH
O
O
O
O

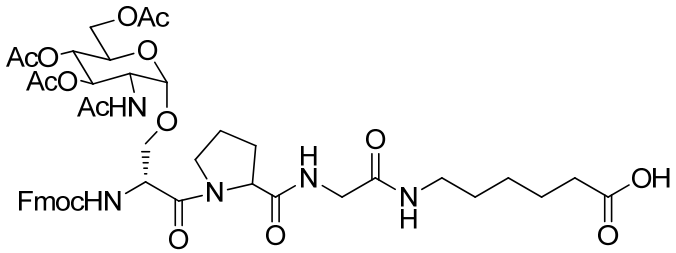
4a

230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
AcO
AcO
AcHN
O
FmocHN
N
H
N
O
H
N
O
OH
O
O
O

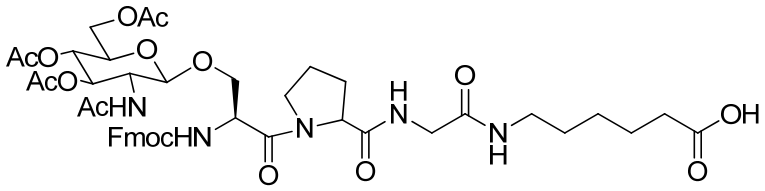
4b

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
f1 (ppm)


OAc
AcO
AcO
AcHN
O
FmocHN
N
H
N
O
H
N
O
OH
O
O
O

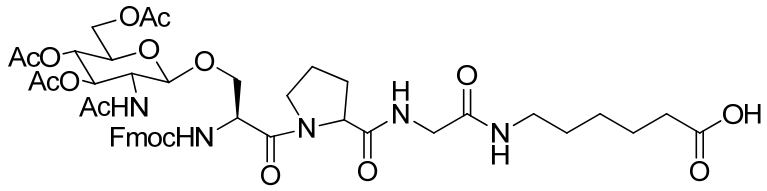
4b

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


OAc
AcO
AcO
AcHN
FmocHN
O
N
H
N
O
N
H
OH
O
O
O

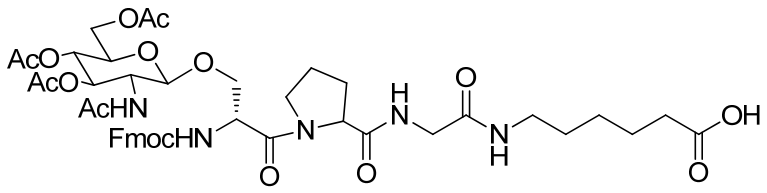
5a

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


OAc
AcO
AcO
AcHN
FmocHN
O
N
H
N
O
N
H
OH
O
O
O

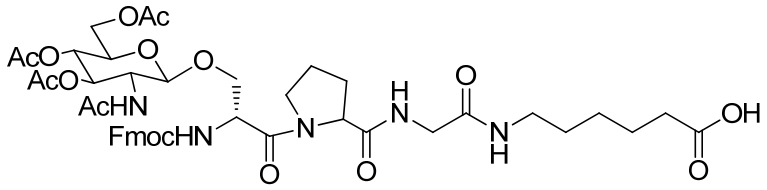
5a

230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
AcO
AcO
AcHN
FmocHN
O
O
O
N
O
H
N
O
N
H
OH
O

5b

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
f1 (ppm)


OAc
AcO
AcO
AcHN
FmocHN
O
O
O
N
O
H
N
O
N
H
OH
O

5b

230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)