Supporting Information for

Divergent Behavior of Glycosylated Threonine and Serine Derivatives in Solid Phase Peptide Synthesis

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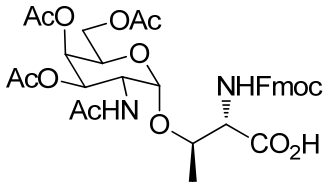
General methods

Unless otherwise stated, reagents were purchased from commercial suppliers and used without purification. 2-Chlorotrityl chloride resin, Fmoc-Thr(Trt)-OH, Fmoc-D-Thr(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 aminium hexafluorophosphate (HATU), 1-Hydroxy-7-azabenzotriazole (HOAt), 2-(1H-benzotriazol-1-yl)-*N,N,N',N'*-tetramethylaminium hexafluorophosphate (HBTU), *N*-Hydroxybenzotriazole (HOBt), *N,N'*-Dicyclohexylcarbodiimide (DCC), benzotriazol-1-yloxy)tripyrrolidinophosphonium hexafluorophosphate (BOP), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP), *N,N*-diisopropylethylamine (DIEA), *N*-methylmorpholine (NMM), and 2,4,6-trimethylpyridine (TMP) were 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. Analyses of yields, epimerization and β-elimination were recorded on an Agilent 1200 Series HPLC using Waters XTerra® RP 18 (5μm 4.6 mm× 250mm). 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.

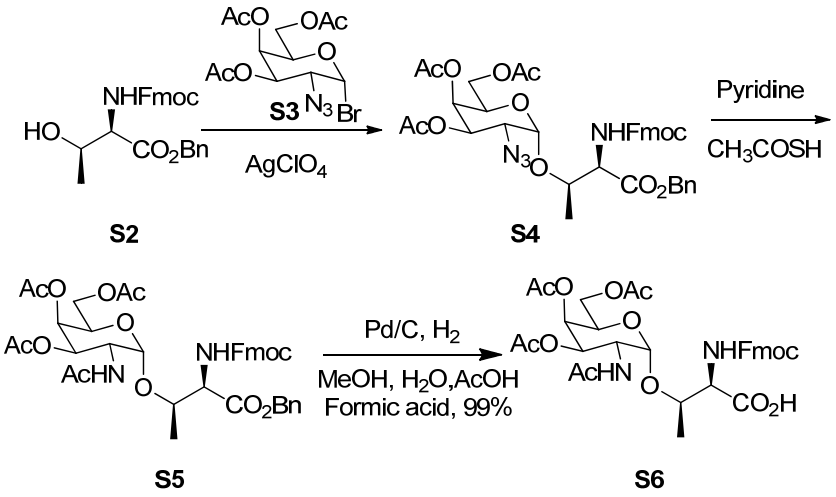
Preparation of Fmoc-protected glyco-amino acids

Fmoc-Thr(Ac$_3$GalNAcα)-OH (S1)



***N*-(9H-fluoren-9ylmethoxycarbonyl)-(2-acetyl-2-deoxy-3,4,6-triacetyl-*O*-α-D-galactopyranosyl)-L-threonine acid (S1)**. Compound **S1** was prepare according to a previously reported method.[1] ^{1}H-NMR (400 MHz, *N,N*-dimethylformamide-d$_7$) δ 7.96 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 9.9 Hz, 1H), 7.76 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 9.4 Hz, 1H), 7.46 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 5.44 (d, J = 2.4 Hz, 1H), 5.16 (dd, J = 11.6, 3.2 Hz, 1H), 5.03 (d, J = 3.7 Hz, 1H), 4.53 (dd, J = 6.4, 1.5 Hz, 1H), 4.46 – 4.30 (m, 6H), 4.16 (d, J = 6.8 Hz, 2H), 2.17 (s, 3H), 2.06 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H), 1.37 (d, J = 6.4 Hz, 3H). ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 172.3, 170.4, 170.3, 170.2, 170.0, 162.4, 157.4, 144.4, 144.3, 141.34, 141.3, 127.9, 127.3, 127.25, 125.52, 125.50, 120.30, 120.29, 99.5, 75.9, 68.3, 67.7, 67.1, 66.7, 62.4, 59.0, 47.3, 22.5, 20.1, 20.08, 20.0, 18.7. HRMS calcd for $C_{33}H_{38}N_2O_{13}Na$ $[M + Na]^+$ 693.2272, found 693.2225.

Fmoc-D-Thr(Ac$_3$GalNAcα)-OH (S6)



The unnatural glyco-amino acid, Fmoc-D-Thr(Ac$_3$GalNAc*α*)-OH **S6**, was synthesized using similar procedures reported for **S1**. Briefly, *N*-Fmoc-D-threonine benzyl ester **S2** (0.85 g, 0.1.97 mmol), the bromide donor **S3** (0.93 g, 2.36 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 (0.81 g, 3.94 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 with silica gel (80g) by EtOAc/Hexane (1:3) to give compound **S4** (0.93 g, 64 %) as a white solid. Reductive acetylation using thiolacetic acid produced the fully protected Fmoc-D-Thr(Ac$_3$GalNAc*α*)-OBn **S5** (0.60 g) in a 63% yield. Hydrogenation of **S5** with10% Pd/C in MeOH/H_2O/Formic acid (10/1/1, 6 mL) followed by RP- HPLC purification using a 0-48% acetonitrile/H_2O (0.1% TFA) gradient over 45 minutes to provide compound **S6** (0.38 g) in 72% yield as a white solid.

***N*-(9H-fluoren-9ylmethoxycarbonyl)-D-threonine benzyl ester (S2)**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* =7.4 Hz, 2H), 7.29-7.42 (m, 9H), 5.71 (d, *J* = 8.9 Hz, 1H), 5.22 (dd, *J* = 17.1, 12.3 Hz, 2H), 4.38-4.46 (m, 3H), 4.23 (t, *J* = 7.0 Hz, 1H), 2.16 (br,

1H), 1.24 (d, *J* = 6.0 Hz, 3H). ^{13}C-NMR(100 MHz, $CDCl_3$) δ 171.0, 156.7, 143.6, 141.3, 141.2, 135.2, 128.5, 127.6, 125.1, 120.0, 119.9, 68.0, 67.4, 67.2, 59.2, 47.1, 19.9, HRMS calcd fro $C_{26}H_{25}NO_5$ $[M + H]^+$ 432.2, found432.1

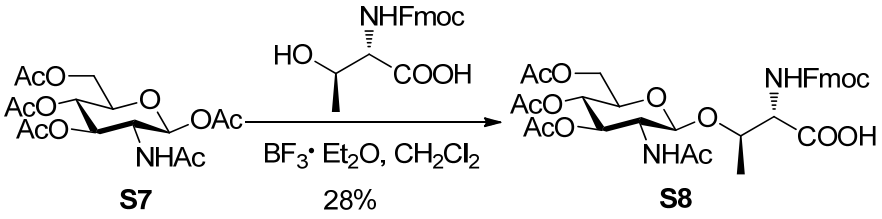
***N*-(9H-fluoren-9ylmethoxycarbonyl)-(2-azido-2-deoxy-3,4,6-tri-*O*-α-D-galactopyranosyl)-D-threonine benzyl ester (S4)**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.29-7.42 (m, 9H), 5.61 (d, *J* = 9.7 Hz, 1H), 5.23-5.26 (m, 3H), 5.19 (dd, *J* = 11.2, 3.2 Hz, 1H), 5.11 (d, *J* = 3.6 Hz, 1H), 4.59 (dd, *J* = 9.7, 2.3 Hz, 1H), 4.47 (dd, *J* = 6.4, 2.3 Hz, 1H), 4.41 (dd, *J* = 7.5, 1.5 Hz, 2H), 4.23 (t, *J* = 7.1 Hz, 1H), 3.85-3.91 (m, 3H), 3.55 (dd, *J* = 11.2, 3.6 Hz, 1H), 2.13 (s, 3H), 2.09 (s, 3H), 1.99 (s, 3H), 1.30 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.3, 169.93, 169.9, 169.6, 156.6, 143.6, 414.3, 141.2, 134.9, 128.7, 125.1, 119.9, 95.2, 73.1, 67.3, 61.7, 58.4, 57.2, 47.1, 20.6, 20.5, 15.2. HRMS calcd for $C_{38}H_{40}N_4O_{12}Na$ $[M + Na]^+$ 744.2540, found744.2548.

***N*-(9H-fluoren-9ylmethoxycarbonyl)-(2-acetyl-2-deoxy-3,4,6-triacetyl-*O*-α-D-galactopyranosyl)-D-threonine benzyl ester (S5)**. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.28-7.41 (m, 9H), 5.75 (t, *J* = 9.8 Hz, 2H), 5.24-5.16 (m, 3H), 4.98-4.93 (m, 2H), 4.56-4.44 (m, 3H), 4.30 (dd, *J* = 6.2, 3.1 Hz, 1H), 4.23 (d, *J* = 6.6 Hz, 1H), 3.93-3.88 (m, 3H), 2.13 (s, 3H), 2.01 (s, 3H), 1.94 (s, 6H), 1.31 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 170.9, 170.3, 170.2, 170.0, 156.5, 143.7, 143.5, 141.3, 134.8, 128.7, 128.5, 127.7, 127.0, 124.9, 124.8, 120.0, 119.97, 94.9, 72.9, 68.0, 67.7, 67.1, 67.07, 67.0, 61.8, 58.5, 47.7, 47.2, 23.1, 20.73, 20.7, 20.5, 15.5. ESI MS calcd for $C_{40}H_{44}N_2O_{13}Na$ $[M + Na]^+$ 783.2741, found 783.2795.

***N*-(9H-fluoren-9ylmethoxycarbonyl)-(2-acetyl-2-deoxy-3,4,6- triacetyl-*O*-α-D-galactopyranosyl)-D-threonine acid (S6)**. ^{1}H-NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ

7.98 – 7.92 (m, 3H), 7.77 (dd, J = 21.1, 7.5 Hz, 2H), 7.63 (d, J = 9.8 Hz, 1H), 7.46 (td, J = 7.4, 4.4 Hz, 2H), 7.40 – 7.30 (m, 2H), 5.37 (d, J = 2.4 Hz, 1H), 5.11 – 5.03 (m, 2H), 4.56 – 4.37 (m, 6H), 4.24 (m, 3H), 3.99 (dd, J = 10.8, 6.3 Hz, 1H), 2.15 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.24 (d, J = 6.2 Hz, 3H). ^{13}C-NMR (100 MHz, *N,N*-dimethylformamide-d_7) δ 172.5, 170.6, 170.4, 170.3, 169.9, 157.4, 144.7, 144.3, 141.5, 128.1, 127.4, 125.7, 125.6, 120.4, 94.2, 71.7, 68.6, 67.6, 67.2, 66.7, 61.8, 59.1, 47.5, 47.3, 22.5, 20.3, 20.2, 14.8. HRMS calcd for $C_{33}H_{38}N_2O_{13}Na$ $[M + Na]^+$ 693.2272, found 693.2282.

Fmoc-Thr(Ac$_3$GlcNAcβ)-OH (S8)

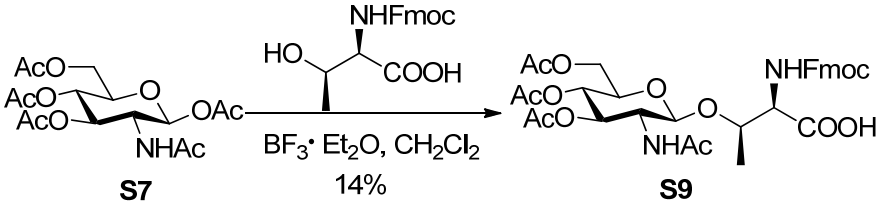


S7 **S8**

N-(9H-fluoren-9-ylmethoxycarbonyl)-O-(2-acetyl-2-deoxy-3,4,6-triacetyl-*O*-β-D-gluctopyranosyl)-L-threonine **S8** was synthesized according to a reported method[2]. Peracetylated GlcNAc **S7**(1.2 g, 3.08 mmol) and 4 Å molecular sieves were placed in a flask under argon, and anhydrous CH_2Cl_2 (15 mL) was added. The reaction mixture was cooled to 0 ºC, $BF_3{\cdot}Et_2O$ (1.17 mL, 9.25 mmol) was added dropwise, and the reaction was stirred at room temperature overnight. The reaction mixture was cooled to 0 ^oC, Et_3N (0.43 mL, 1 equiv.) was added, and the reaction was stirred for 10 min. A solution of Fmoc-Thr(Trt)-OH (1.28, 3.76 mmol) in CH_2CL_2/MeCN (1:2) was added, and the reaction was allowed to stir at room temperature for 4d and monitored by TLC $CDCl_3$/MeOH/AcOH (10:1:0.2). The reaction mixture with neutralized with Et_3N, diluted with CH_2Cl_2, 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 CH_2Cl_2/MeOH (20:1-5:1) to provide compound **S8** as a white solid (0.28 g, 28%). ^{1}H-NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.47-7.43 (m, 2H), 7.40 – 7.34 (m, 2H), 6.65 (d, *J* = 8.9 Hz, 1H), 5.31 (t, *J* = 10.0 Hz, 1H), 4.96 (dd, *J* = 18.8, 9.2 Hz, 2H), 4.48-4.42 (m, 1H), 4.36-4.25 (m, 5H), 4.12 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.93-3.88 (m, 1H), 3.83 (dd, *J* = 19.2, 8.8 Hz, 1H), 2.03 (s,

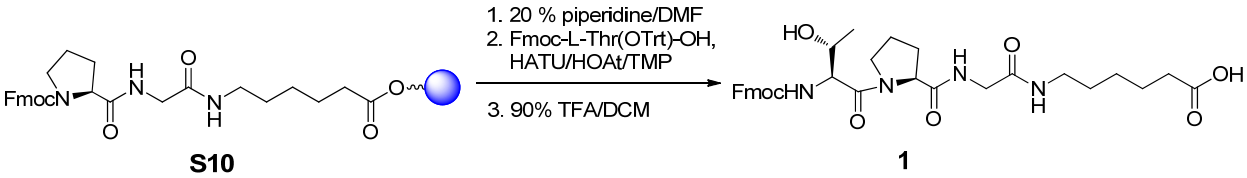
3H), 2.027 (s, 3H), 1.99 (s, 3H), 1.90 (s, 3H), 1.28 (d, J = 6.3 Hz, 3H). ^{13}C-NMR (100 MHz, *N,N*-dimethylformamide-d_7) δ 171.9, 170.5, 170.2, 170.15, 169.8, 157.0, 144.5, 144.4, 141.5, 128.0, 127.5, 125.8, 125.8, 120.4, 120.38, 99.6, 75.3, 73.0, 71.6, 69.6, 67.0, 62.6, 59.2, 54.5, 47.4, 22.7, 20.3, 20.25, 20.2, 17.1. HRMS calcd for $C_{33}H_{38}N_2O_{13}Na$ $[M + Na]^+$ 693.2272, found 693.2266.

Fmoc-D-Thr(Ac$_3$GlcNAcβ)-OH (S9)



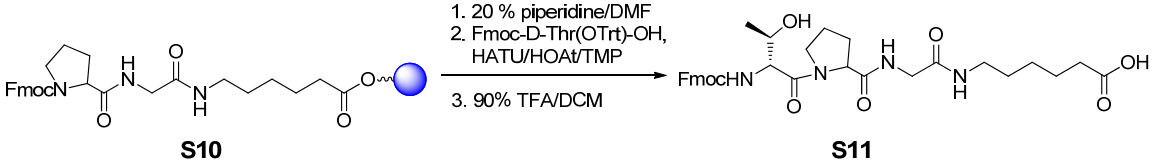
The synthesis of *N*-(9H-fluoren-9-ylmethoxycarbonyl)-*O*-(2-acetyl-2-deoxy-3,4,6-triacetyl-*O*-β-D- gluctopyranosyl)-D-threonine (**S9**) was carried out using a similar procedure as described for compound **S8** to provide compound **S9** as a white solid (0.14 g, 14%). ^{1}H NMR (400 MHz, *N,N*-dimethylformamide-d_7) δ 7.94 (d, J = 7.5 Hz, 2H), 7.85 (d, J = 7.4 Hz, 2H), 7.80 (d, J = 8.9 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.40 – 7.32 (m, 2H), 6.97 (d, J = 9.2 Hz, 1H), 5.32 (dd, J = 10.4, 9.5 Hz, 1H), 4.93 (dd, J = 18.3, 9.0 Hz, 2H), 4.44 – 4.25 (m, 6H), 4.14 (dd, J = 12.1, 2.4 Hz, 1H), 3.95 – 3.79 (m, 2H), 2.06 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.88 (s, 3H), 1.34 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100MHz, *N,N*-dimethylformamide-d_7) δ 171.9, 170.5, 170.4, 170.1, 169.9, 162.7, 162.4, 162.1, 157.2, 144.5, 144.47, 141.4, 141.43, 128.0, 127.5, 127.4, 125.9, 120.4, 102.1, 77.2, 73.0, 71.5, 69.6, 66.9, 62.5, 59.1, 54.5, 47.3, 22.8, 20.3, 20.2, 18.9. HRMS calcd for $C_{33}H_{38}N_2O_{13}Na$ $[M + Na]^+$ 693.2272, found 693.2254.

Fmoc-Thr-Pro-Gly-Hex-OH (1)



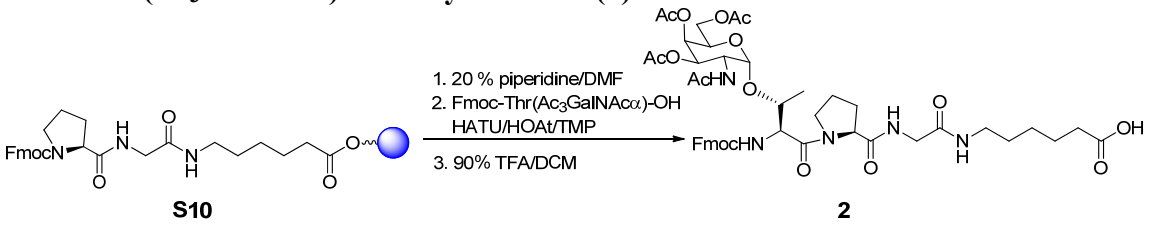
Compound **1** was synthesized starting from **S10**. Prior to coupling, the resin (60 mg, 17.8 µmol) was swollen in CH_2Cl_2 for 0.5 h, followed by removal of the Fmoc-group with 20% piperidine in DMF (2× 2.0 mL) for 15 min, and then washed with CH_2Cl_2 (3× 2.0 mL) and DMF (2× 2.0 mL). The appropriate amount of Fmoc-Thr(Trt)-OH (2 eq, 35.6 µmol), HATU (2 eq, 35.6 µmol), HOAt (2 eq, 35.6 µmol), and TMP (2eq, 35.6 µmol) in DMF(0.5 mL) 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 Ac_2O (10%)/pyridine (10%) in THF (2×1 mL) at room temperature for 15 min. The resin was washed with DMF (2×5 mL), CH_2Cl_2 (3×5 mL), and the peptide was cleaved off with a mixture TFA/ CH_2Cl_2 (90:10) (1.0 mL) at room temperature for 1.5 h. The crude product was purified by silica gel flash chromatography using a mixture of MeOH and CH_2Cl_2 (1:20)to give **1** as white foam. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 4.49 – 4.36 (m, 3H), 4.26 (t, *J* = 6.5 Hz, 1H), 4.11 (dd, *J* = 10.0, 4.1 Hz, 1H), 4.00 – 3.82 (m, 2H), 3.79 – 3.67 (m, 1H), 3.30-3.16 (m, 2H), 2.29 (dd, *J* = 14.7, 7.3 Hz, 2H), 2.17 – 1.96 (m, 3H), 1.67-1.54 (m, 5H), 1.45 – 1.30 (m, 4H), 1.24 (d, *J* = 6.4 Hz, 3H). 13C-NMR (100 MHz, CD_3OD) δ 173.5, 170.8, 169.9, 157.2, 143.8, 141.2, 127.4, 126.7, 124.7, 119.5, 67.0, 66.5, 61.0, 58.2, 42.1, 38.9, 38.8, 28.9, 28.6, 28.4, 26.1, 26.0, 24.8, 24.5, 24.3, 21.1, 18.4. HRMS calcd for $C_{32}H_{40}N_4O_8$ $[M + Na]^+$ 631.2744, measured 631.2732.

Fmoc-D-Thr-Pro-Gly-Hex-OH (S11)



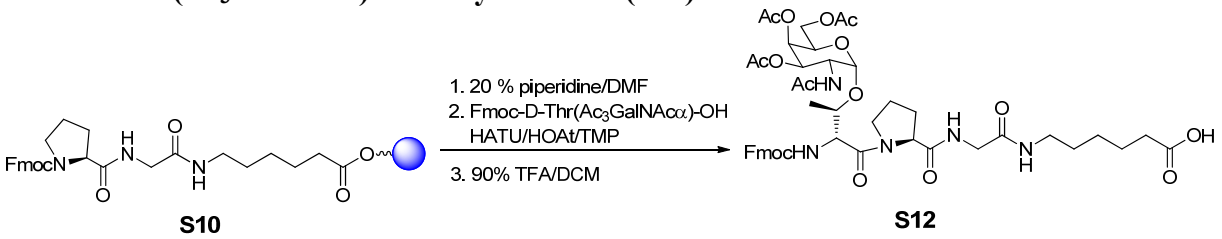
Compound **S11** was synthesized and purified according to the general procedure described for **1**. ^{1}H-NMR (400 MHz, CD_3OD) δ7.83 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 4.49 – 4.36 (m, 3H), 4.26 (t, *J* = 6.5 Hz, 1H), 4.14-4.07 (m, 1H), 4.00 – 3.82 (m, 2H), 3.79 – 3.67 (m, 1H), 3.30-3.16 (m, 2H), 2.29 (dd, *J* = 14.7, 7.3 Hz, 2H), 2.17 – 1.96 (m, 3H), 1.69-1.52 (m, 5H), 1.45 – 1.30 (m, 4H), 1.24 (d, *J* = 6.4 Hz, 3H). ^{13}C-NMR (100 MHz, CD_3OD) δ 173.5, 170.8, 169.9, 157.2, 143.8, 141.2, 127.4, 126.7, 124.7, 119.5, 67.0, 66.5, 61.0, 58.2, 42.1, 38.9, 38.8, 28.9, 28.6, 28.4, 26.1, 26.0, 24.8, 24.5, 24.3, 21.1, 18.4. HRMS calcd for $C_{32}H_{40}N_4O_8$ $[M + Na]^+$ 631.2744, measured 631.2737.

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



Fmoc-Thr(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH **2** was synthesized and purified according to the general procedure described for **1**. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.90 – 7.80 (m, 3H), 7.71 (d, J = 7.2 Hz, 2H), 7.56 (d, J = 9.2 Hz, 1H), 7.43 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 5.43 (d, J = 2.4 Hz, 1H), 5.16 (d, J = 3.5 Hz, 1H), 5.10 (dd, J = 11.4, 3.0 Hz, 1H), 4.56 (dd, J = 6.1, 2.8 Hz, 2H), 4.49 – 4.05 (m, 9H), 3.81 (d, J = 3.5 Hz, 2H), 3.69 (t, J = 5.2 Hz, 2H), 3.21 (m, 3H), 2.31 (t, J = 7.3 Hz, 3H), 2.17 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H), 1.94 (d, J = 7.5 Hz, 3H), 1.66 (m, 2H), 1.55 (m, 2H), 1.43 – 1.35 (m, 2H), 1.32 (d, J = 5.2 Hz, 3H), 0.92 (m, 2H). ^{13}C-NMR (100 MHz, CD_3OD) 175.7, 174.6, 173.0, 172.9, 172.1, 172.0, 159.7, 146.1, 146.05, 143.6, 143.58, 129.7, 129.1, 129.0, 127.0, 126.9, 121.9, 121.9, 101.7, 78.2, 71.2, 69.8, 69.1, 68.5, 64.2, 62.7, 59.7, 44.4, 41.2, 36.0, 31.3, 31.0, 30.9, 28.4, 28.35, 26.9, 26.7, 23.9, 23.4, 21.6, 21.5, 21.4, 20.3. HRMS calcd for $C_{46}H_{59}N_5O_{16}$ $[M + Na]^+$ 960.3854, measured 960.3845.

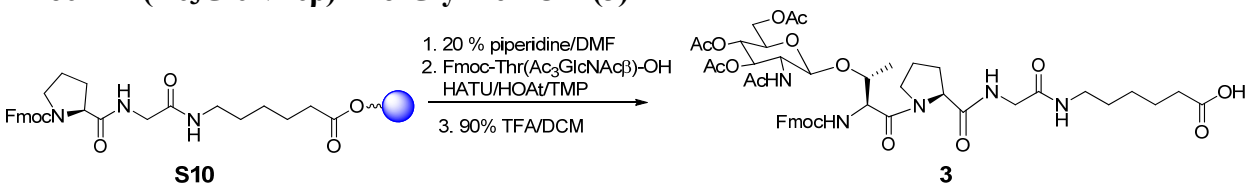
Fmoc-D-Thr(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH (S12)



Compound **S12** was synthesized and purified according to the general procedure described for **1**. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.72 (dd, *J* = 6.8, 2.7 Hz, 2H), 7.42 (m, 2H), 7.35 (m, 2H), 7.29 (d, *J* = 8.6 Hz, 1H), 5.41 (d, *J* = 2.8 Hz, 1H), 5.09 (dd, *J* = 11.6, 3.1 Hz, 1H), 5.04 (d, *J* = 3.6 Hz, 1H), 4.72 (dd, *J* = 10.8, 5.8 Hz, 1H), 4.55-4.50 (m, 2H), 4.37 (dd, *J* = 8.4, 4.7 Hz, 1H), 4.27 (t, *J* = 5.9 Hz, 1H), 4.21-4.00 (m, 4H), 3.88 – 3.81 (m, 1H), 3.80 – 3.63 (m, 2H), 3.31 – 3.03 (m, 1H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.18 – 2.09 (m, 4H), 2.07 – 1.92 (m, 10H), 1.69 – 1.49 (m, 4H), 1.44 – 1.28 (m, 6H), 1.21 (d, *J* = 6.1 Hz, 3H), 0.94-0.88 (m, 1h). ^{13}C-NMR (100 MHz, CD_3OD) δ 175.6, 174.3, 173.0, 172.9, 172.7, 172.2, 171.8, 159.8, 146.1, 146.0, 143.6,

143.55, 129.73, 129.71, 129.1, 129.07, 127.0, 126.9, 121.9, 96.2, 73.1, 70.4, 69.3, 68.8, 68.7, 63.4, 63.3, 59.7, 44.5, 41.2, 35.7, 31.64, 31.63, 31.56, 31.5, 31.2, 31.19, 30.7, 28.2, 26.9, 26.5, 23.5, 21.5, 21.47, 21.4, 16.7. HRMS calcd for $C_{46}H_{59}N_5O_{16}$ $[M + Na]^+$ 960.3854, measured 960.3843.

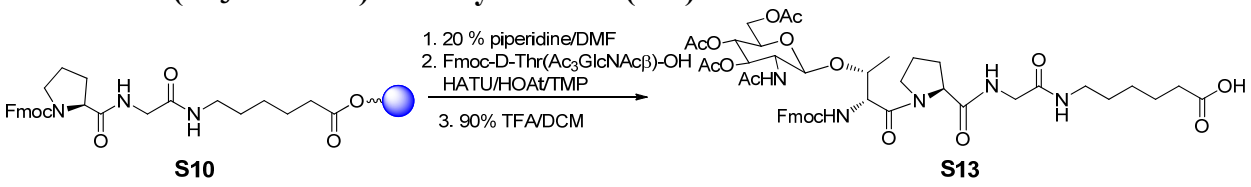
Fmoc-Thr(Ac$_3$GlcNAcβ)-Pro-Gly-Hex-OH (3)



S10 **3**

Fmoc-Thr(Ac$_3$GlcNAcβ)-Pro-Gly-Hex-OH **3** was synthesized and purified according to the general procedure described for **1**. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.71 (d, *J* = 7.1 Hz, 3H), 7.55 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.27 – 7.18 (m, 2H), 5.19 – 5.10 (m, 1H), 4.91 – 4.82 (m, 1H), 4.62 (d, *J* = 8.5 Hz, 1H), 4.38 – 4.22 (m, 3H), 4.16-4.11 (m, 2H), 4.03 – 3.64 (m, 7H), 3.50 (dd, *J* = 16.4, 7.4 Hz, 1H), 3.15 – 3.04 (m, 2H), 2.18 (t, *J* = 7.4 Hz, 3H), 1.92 – 1.81 (m, 13H), 1.56 – 1.41 (m, 5H), 1.26 (dt, *J* = 14.5, 7.4 Hz, 4H), 1.12 (d, *J* = 6.3 Hz, 3H). ^{13}C-NMR (100 MHz, CD_3OD) δ 173.2, 172.2, 170.8, 170.3, 170.0, 169.8, 162.0, 161.6, 156.9, 143.7, 143.66, 141.2, 141.18, 127.4, 126.8, 124.7, 124.6, 119.6, 118.1, 115.2, 99.6, 75.9, 72.4, 71.6, 68.7, 66.4, 61.8, 61.3, 57.8, 54.1, 42.1, 38.9, 29.0, 28.6, 28.5, 26.1, 26.0, 24.8, 24.4, 24.38, 21.4, 19.3, 19.1, 19.09, 15.6. HRMS calcd for $C_{46}H_{59}N_5O_{16}$ $[M + Na]^+$ 960.3854, measured 960.3839.

Fmoc-D-Thr(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH (S13)

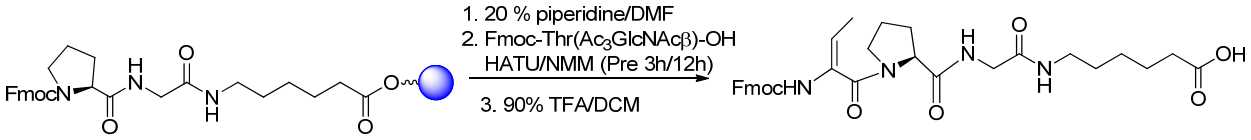


S10 **S13**

Compound **S13** was synthesized and purified according to the general procedure described for **1**. ^{1}H-NMR (400 MHz, CD_3OD) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.56 (dd, *J* = 7.2, 4.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (t, *J* = 7.1 Hz, 2H), 5.15 – 5.06 (m, 1H), 4.85 (t, *J* = 9.7 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 1H), 4.41 – 4.27 (m, 3H), 4.19 – 3.92 (m, 4H), 3.79 – 3.59 (m, 5H), 3.06 (dd, *J* = 13.8, 7.0 Hz, 1H), 2.97 – 2.86 (m, 1H), 2.21 – 2.10 (m, 3H), 1.95 – 1.71 (m, 14H), 1.56 – 1.32 (m, 5H), 1.24 – 1.15 (m, 6H). ^{13}C-NMR (100 MHz, CD_3OD) δ 173.2, 172.3, 170.8, 170.4, 169.9, 169.9, 169.8, 157.1, 143.7, 143.5, 141.2, 141.18, 127.4, 126.8, 126.78, 124.7, 124.6, 119.6, 101.2, 77.0,

72.6, 71.4, 68.7, 66.6, 61.8, 61.3, 57.6, 54.2, 42.1, 38.8, 28.9, 28.6, 28.4, 25.9, 24.3, 21.7, 19.2, 19.1, 17.3. HRMS calcd for $C_{46}H_{59}N_5O_{16}$ $[M + Na]^+$ 960.3854, measured 960.3838.

Fmoc-Dehydroaminobutyrate-Pro-Gly-Hex-OH (S14)



S10 **S14**

Compound **S14** was synthesized starting from **S10**. Prior to coupling, the resin (60 mg, 17.8 μmol) was swollen in CH_2Cl_2 for 0.5 h, treated with 20% piperidine in DMF (2× 2.0 mL) for 15 min to remove the Fmoc-group, and then washed with CH_2Cl_2 (3× 2.0 mL) and DMF (2× 2.0 mL). The appropriate amounts of Fmoc-Thr(Ac_3GlcNAcβ)-OH (2 eq, 35.6 μmol), HATU (2 eq, 35.6 μmol), and NMM (8 eq, 142.4 μmol) were preincubated at room temperature in DMF (0.5 mL) for 3 h, and then the mixture was immediately added to the resin. The reaction was allowed to mix at room temperature for 12 h, followed by washing and capping the unreacted amino groups with Ac_2O (10%)/pyridine (10%) in THF (2×1 mL) at room temperature for 15 min. The resin was washed with DMF (2×5 mL), CH_2Cl_2 (3×5 mL), and the peptide was cleaved off with a mixture TFA/ CH_2Cl_2 (90:10) (1.0 mL) at room temperature for 1.5 h. The crude product was purified by RP-HPLC using MeCN/water and silica flash chromatography using MeOH/ CH_2Cl_2 (1:20) to give **1** as white foam. ^{1}H-NMR (400 MHz, CD_3OD) δ7.83 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.3 Hz, 2H), 7.43 (t, J = 7.3 Hz, 2H), 7.40 – 7.32 (m, 2H), 5.70 (q, J = 6.8 Hz, 1H), 4.76 (dd, J = 10.9, 5.8 Hz, 1H), 4.49 (dd, J = 10.9, 5.9 Hz, 1H), 4.41 – 4.33 (m, 1H), 4.26 (t, J = 5.6 Hz, 1H), 3.89 (dd, J = 110.2, 17.0 Hz, 2H), 3.57 – 3.46 (m, 1H), 3.27 – 3.09 (m, 3H), 2.40 – 2.18 (m, 3H), 2.07 – 1.83 (m, 3H), 1.74 (d, J = 7.1 Hz, 3H), 1.63 – 1.45 (m, 4H), 1.39 – 1.28 (m, 4H), 0.93 (t, J = 6.7 Hz, 1H). ^{13}C-NMR (100 MHz, CD_3OD) δ 175.5, 172.3, 170.2, 157.8, 146.0, 145.8, 143.7, 143.6, 133.0, 129.8, 129.7, 129.1, 127.0, 126.9, 122.8, 122.7, 121.9, 121.8, 68.5, 63.6, 51.4, 44.3, 41.1, 31.4, 30.6, 28.3, 26.9, 26.8, 12.9. HRMS calcd for $C_{32}H_{38}N_4O_7$ $[M + Na]^+$ 613.2638, measured 613.2624.

HPLC analyses of products in coupling reactions

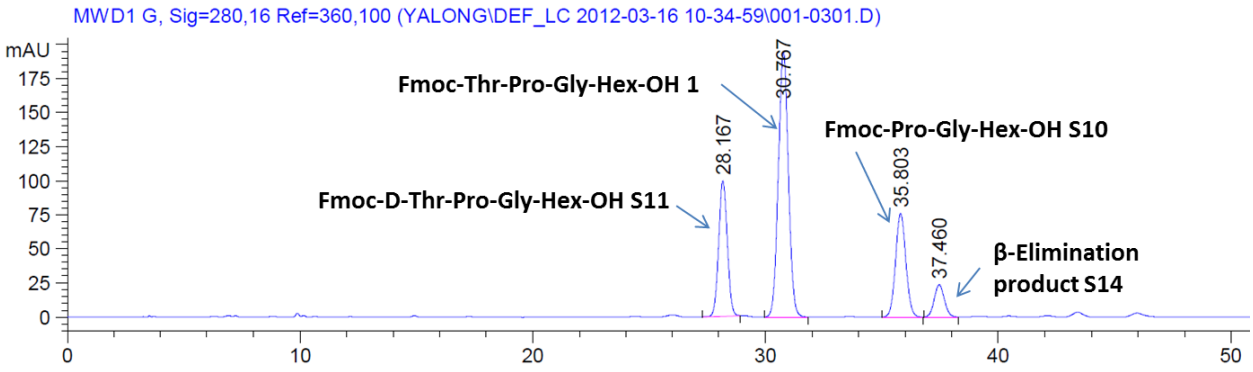


Figure S1. HPLC trace of Fmoc-Thr-Pro-Gly-Hex-OH.
Analyses of Fmoc-Thr-Pro-Gly-Hex-OH **1**, its racemized D isomer **S11**, β-elimination product **S14** and the unreacted starting peptide Fmoc-Pro-Gly-Hex-OH **S10** were performed with Waters XTerra® RP 18 (4.6 mm × 250 mm) reverse phase column. UV absorption was measured at 280 nm and the flow rate was 1 mL/min with water (0.1 % TFA, solvent A) and acetonitrile (0.1% TFA, solvent B). 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. All data have an error of less than 0.3% based on repeat HPLC assays using the same standard glycopeptide sample from our previous studies. The yield, epimerization, and β-elimination were calculated from the peak area of corresponding peptides or glycopeptides that are absorbed at 280 nm by Fmoc groups.

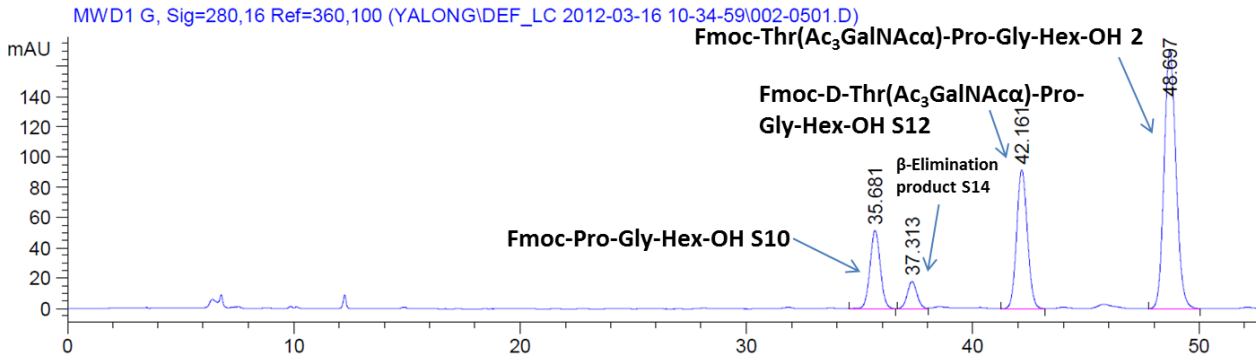


Figure S2. HPLC trace of Fmoc-Thr(Ac_3GalNAcα)-Pro-Gly-Hex-OH.
Analyses of Fmoc-Thr(Ac_3GalNAcα)-Pro-Gly-Hex-OH **2**, its racemized D isomer **S12**, β-elimination product **S14** and the unreacted starting peptide Fmoc-Pro-Gly-Hex-OH **S10** were performed with the same conditions as those described in Figure S1.

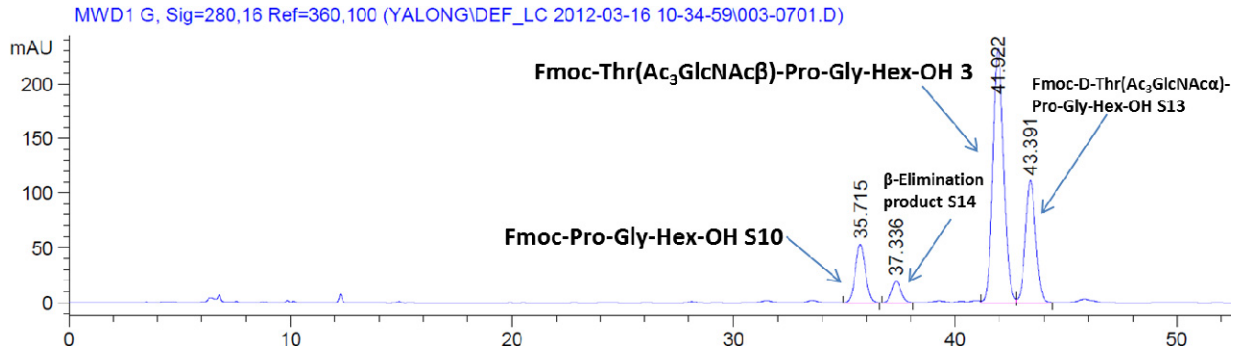


Figure S3. HPLC trace of Fmoc-Thr(Ac_3GlcNAcβ)-Pro-Gly-Hex-OH.
Analyses of Fmoc-Thr(Ac_3GlcNAcβ)-Pro-Gly-Hex-OH **3,** its racemized D isomer **S13**, β-elimination product **S14** and the unreacted starting peptide Fmoc-Pro-Gly-Hex-OH **S10** were performed with the same conditions as those described in Figure S1.

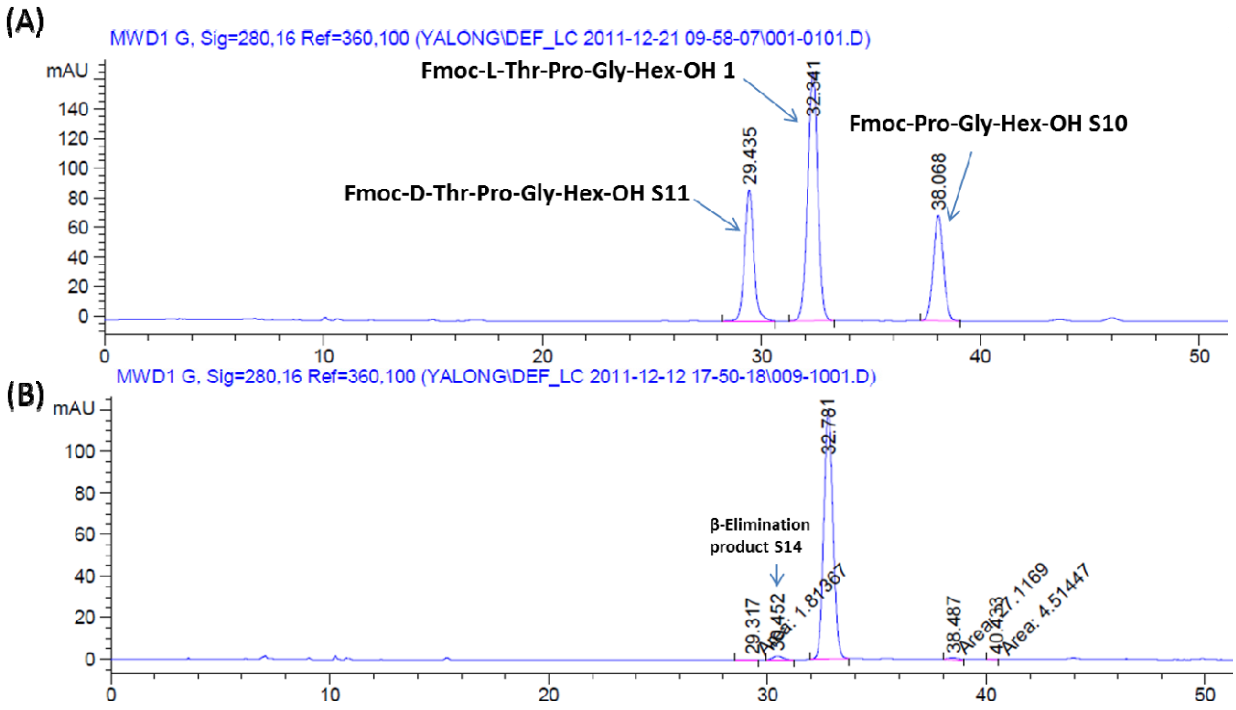


Figure S4. Measurement of the yield, epimerization and β-elimination of condition 7 for Fmoc-Thr(Trt)-OH via a HPLC assay.

(A) HPLC trace of three standard peptides mixtures, Fmoc-Pro-Gly-Hex-OH **S10**, Fmoc-Thr-Pro-Gly-Hex-OH **1**, and its racemized D isomer **S11**; (B) HPLC trace of the products from coupling Fmoc-Thr(Trt)-OH to ProGlyHex resin using condition 7. Analyses were performed with the same conditions as those for obtaining Figure S1. The β-Elimination product standard, which was only obtained with small amount and not stable in solution, was not added to the standard peptide mixtures for routine analysis. Three standard peptides mixtures, **S10**, **1** , and **S11**, were analyzed each time and compared with the HPLC trace in Figure S1 to determine the retention time of the β-elimination product for each HPLC assay.

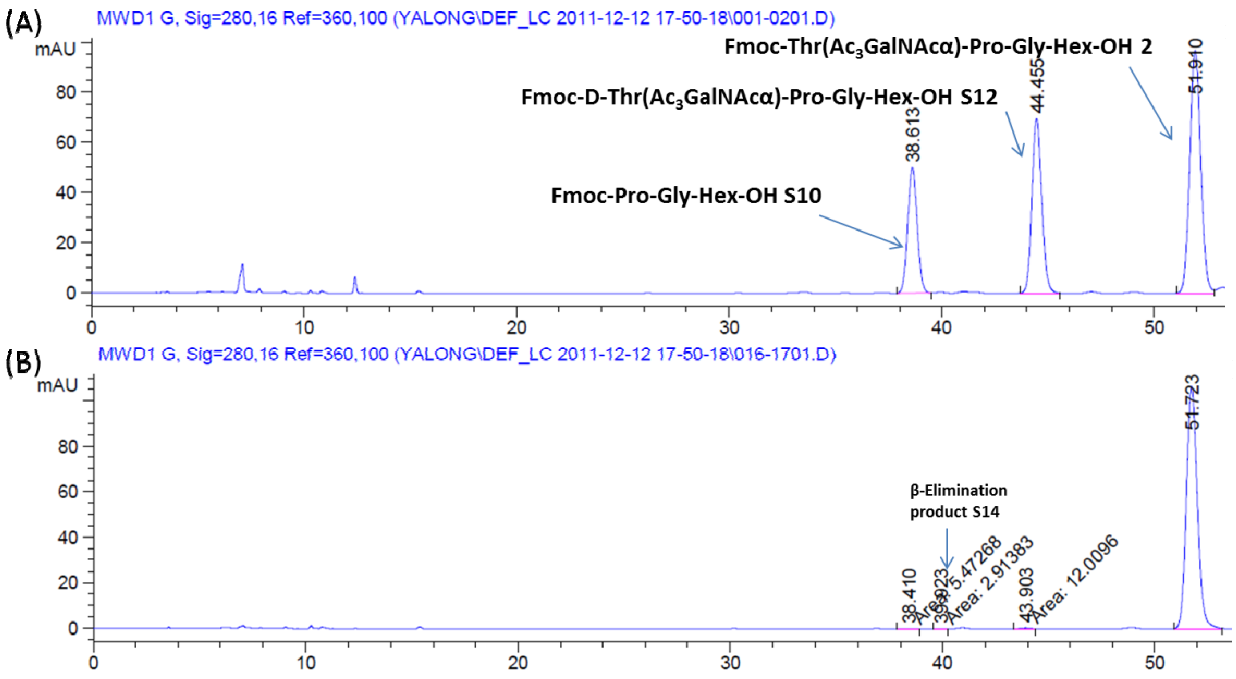


Figure S5. Measurement of the yield, epimerization and β-elimination of condition 7 for Fmoc-Thr(Ac$_3$GalNAcα)-OH via a HPLC assay.
(A) HPLC trace of three standard peptides mixtures, Fmoc-Pro-Gly-Hex-OH **S10**, Fmoc-Thr(Ac$_3$GalNAcα)-Pro-Gly-Hex-OH **2**, and its racemized D isomer **S12**; (B) HPLC trace of the products from coupling Fmoc-Thr(Ac$_3$GalNAcα)-OH to ProGlyHex resin using condition 7. Analyses were performed with the same conditions as those described in Figure S1. The retention time of the β-elimination product for each HPLC assay was derived from Figure S2 using the similar method as that in Figure S4.

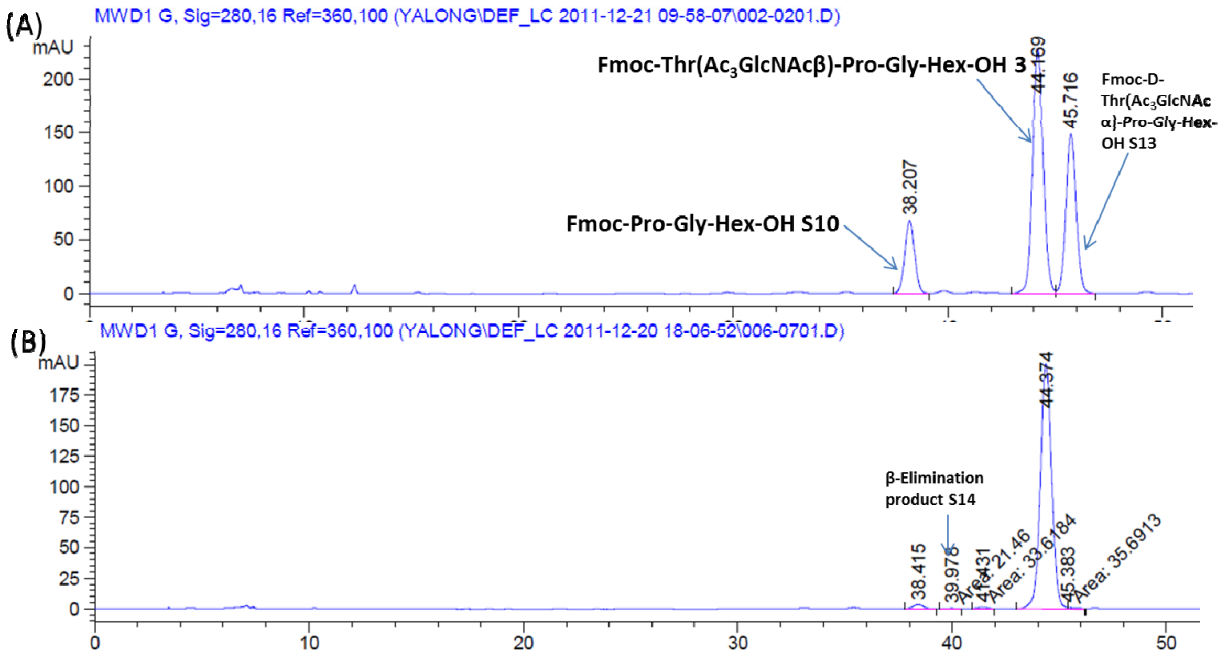


Figure S6. Measurement of the yield, epimerization and β-elimination of condition 7 for Fmoc-Thr(Ac_3GlcNAcβ)-OH via a HPLC assay.
(A) HPLC trace of three standard peptides mixtures, Fmoc-Pro-Gly-Hex-OH **S10**, Fmoc-Thr(Ac_3GlcNAcβ)-Pro-Gly-Hex-OH **3**, and its racemized D isomer **S13**; (B) HPLC trace of the products from coupling Fmoc- Thr(Ac_3GlcNAcβ)-OH to ProGlyHex resin using condition 7. Analyses were performed with the same conditions as those described in Figure S1. The retention time of the β-elimination product for each HPLC assay was derived from Figure S3 using the similar method as that in Figure S4.

Table S1. Summary of yields, epimerization and β-eliminaion for D-amino acids coupling to ProGlyHex with condition 2

		Fmoc-D-Thr(R)-OH, where R =		
Coupling Conditions [a]		**Trt**	**Ac_3GalNAcα**	**Ac_3GlcNAcβ**
AAs: 4.4 eq	Yields (%)[b]	40.3	97.0	7.6
HATU/HOAt: 4.4/0 eq	Epimerization (%)[b]	4.13	0.18	24.4
NMM: 8.8 eq in NMP	β-Elimination (%)[b]	16.6	2.3	92.4
3/12 h				

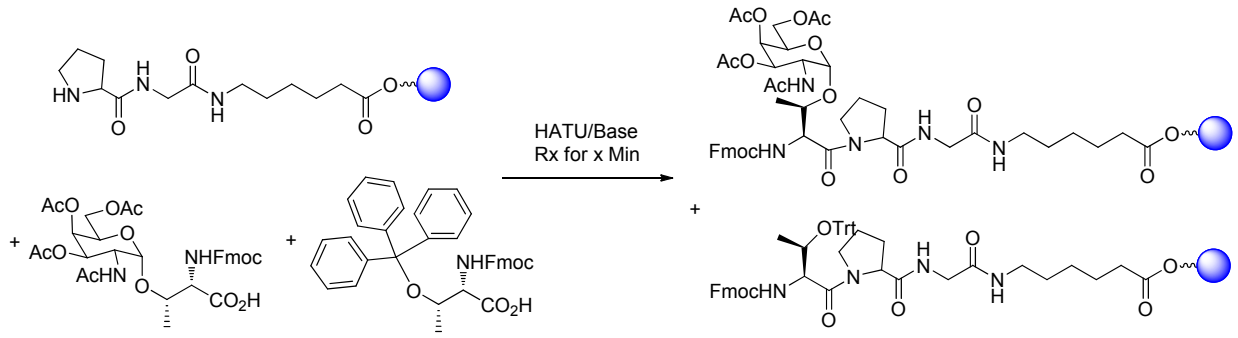
[a]Glyco-amino acids were coupled to Pro-Gly-Hex resin (10 mg, 2.97 μmol) in 0.15 mL NMP. Preincubation time and coupling times are listed as x/y h format. (e.g. 3/12 h = 3 h pre-incubation followed by 12 h reaction time). [b]All yield and epimerization data have an error of less than 0.3%. The yield refers to the percentage of D+L products relative to the total peptide (D+L products, β-elimination product, and truncated peptide). Epimerization referes to the ratio of D glycopetide to the combined amount of D+L glycopeptide products.

Table S2. Epimerization and β-elimination as a function of the concentration of TMP

Coupling Conditions [a]		Fmoc-Thr(R)-OH, where R =		
AA/HATU /TMP (1:1:x), x=		**Trt**	**$Ac_3GalNAc\alpha$**	**$Ac_3GlcNAc\beta$**
1 eq	Yields (%)[b]	74.2	86.6	93.2
	Epimerization (%)[b]	<0.2%	0.6	0.3
	β-Elimination (%)[b]	0.2	<0.2%	0.4
2 eq	Yields (%)[b]	82.6	91.2	99.0
	Epimerization (%)[b]	<0.2%	0.5	0.4
	β-Elimination (%)[b]	0.2	<0.2%	0.8
4 eq	Yields (%)[b]	88.8	98.5	97.9
	Epimerization (%)[b]	<0.2%	0.5	0.3
	β-Elimination (%)[b]	<0.2%	0.2	1.6
8 eq	Yields (%)[b]	99.7	95.6	95.2
	Epimerization (%)[b]	0.2	0.5	0.5
	β-Elimination (%)[b]	<0.2%	0.2	4.2
12 eq	Yields (%)[b]	99.6	97.5	93.6
	Epimerization (%)[b]	0.2	0.5	0.6
	β-Elimination (%)[b]	0.2	<0.2%	6.1
16 eq	Yields (%)[b]	99.7	93.2	92.1
	Epimerization (%)[b]	<0.2%	0.5	0.5
	β-Elimination (%)[b]	0.2	0.2	7.5
20 eq	Yields (%)[b]	94.2	94.8	90.6
	Epimerization (%)[b]	<0.2%	0.6	0.2
	β-Elimination (%)[b]	<0.2%	0.2	9.0

[a]Glyco-amino acids were coupled to Pro-Gly-Hex resin (10 mg, 2.96 μmol) using the condition: AA/HATU/TMP=1:1:x in 0.15 mL DMF with 3 h pre-incubation followed by 2 h reaction time. [b]All data have an error of less than 0.3%. The yield refers to the percentage of D+L products relative to the total peptide (D+L products, β-elimination product, and truncated peptide). Epimerization referes to the ratio of D glycopetide to the combined amount of D+L glycopeptide products.

Table S3. Raw data for Table 2 (relative reaction rates)



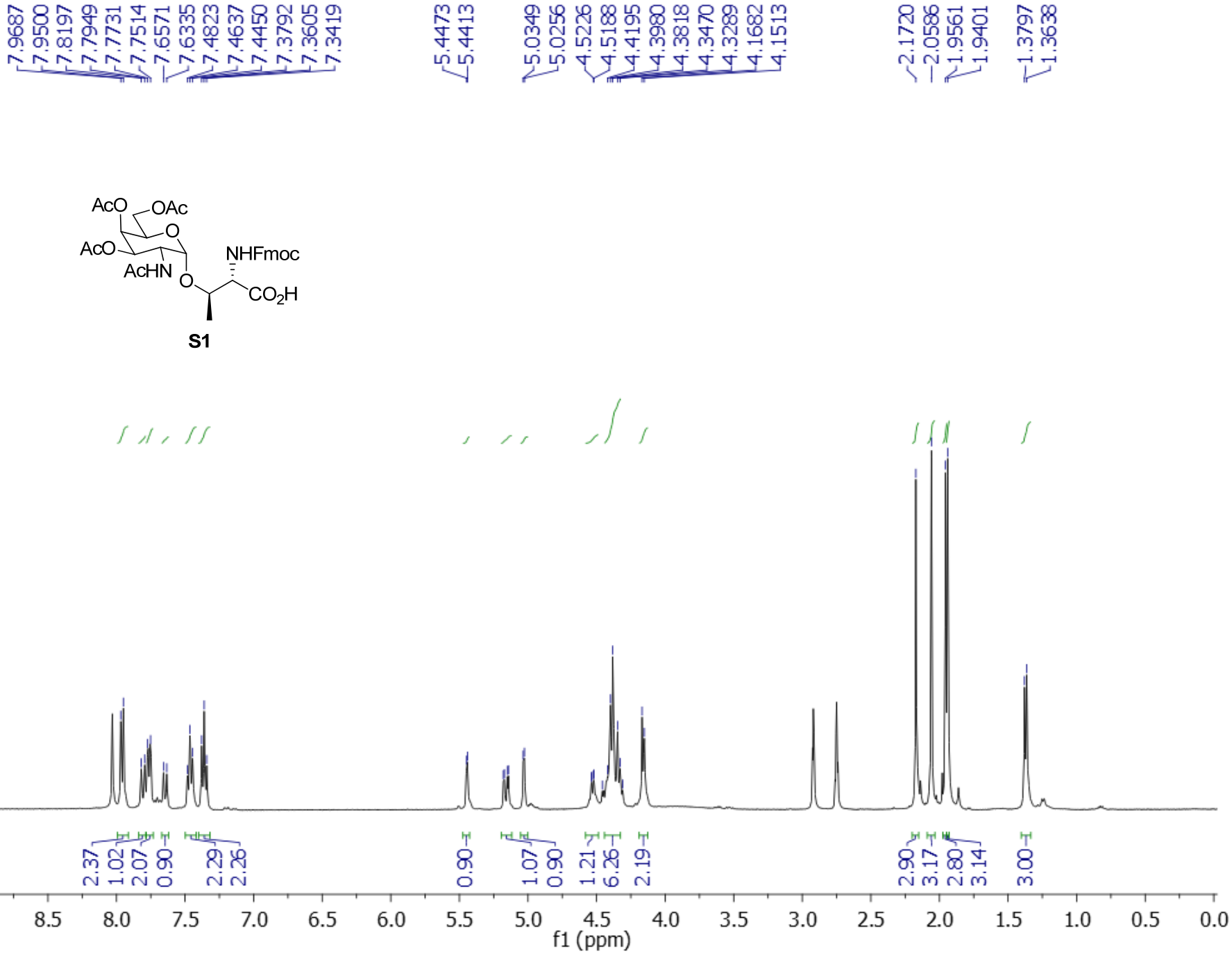
Entry	Rx time (min)/Vol (mL)	Activation reagent (eq)	GAAs(eq) Fmoc-AAs-OH	Fmoc-Thr(OTrt)-OH (eq)	Base (eq)	A(Truncated)	A(Thr)	A(Other)	GAA/Thr ratio
						23.97min[a]	**21.26 min[a]**	**28.49 min [Thr(GalNAcα)][a]**	
Tr1a	5/1.5	HATU/HOAt (4.0/4.0)	**Thr(GalNAcα) (2.0)**	**2.0**	**TMP (4.0)**	3531.1	512.8	373.7	**0.73**
Tr1b	5/1.5	HATU/HOAt (4.0/4.0)	**Thr(GalNAcα) (2.0)**	**2.0**	**TMP (4.0)**	3562.1	478	325.3	**0.68**
Tr1c	5/1.5	HATU/HOAt (4.0/4.0)	**Thr(GalNAcα) (2.0)**	**2.0**	**TMP (4.0)**	2749	411.4	283.1	**0.69**
						23.97min[a]	**21.26 min[a]**	**25.18 min [D-Thr(GalNAcα)][a]**	
Tr2a	5/1.5	HATU/HOAt (4.0/4.0)	**D- Thr(GalNAcα) (2.0)**	**2.0**	**TMP (4.0)**	2856.4	409.5	376.8	**0.92**
Tr2b	5/1.5	HATU/HOAt (4.0/4.0)	**D- Thr(GalNAcα) (2.0)**	**2.0**	**TMP (4.0)**	3023.3	441.2	391.6	**0.89**
Tr2c	5/1.5	HATU/HOAt (4.0/4.0)	**D- Thr(GalNAcα) (2.0)**	**2.0**	**TMP (4.0)**	2935.1	382	344	**0.90**
						23.97min[a]	**21.26 min[a]**	**20.25 min (Ser) [a]**	
Tr3a	5/1.5	HATU/HOAt (4.0/4.0)	**Ser(OTrt) (2.0)**	**2.0**	**TMP (4.0)**	2467.6	327.6	1133.1	**3.46**
Tr3b	5/1.5	HATU/HOAt (4.0/4.0)	**Ser(OTrt) (2.0)**	**2.0**	**TMP (4.0)**	4031	539.6	1481.7	**2.75**
Tr3c	5/1.5	HATU/HOAt (4.0/4.0)	**Ser(OTrt) (2.0)**	**2.0**	**TMP (4.0)**	2637.9	341.6	1288.2	**3.77**
						38.78 min[b]	**32.91 min[b]**	**44.71 min [Thr(GlcNAcβ)][b]**	
Tr4a	5/1.5	HATU/HOAt (4.0/4.0)	**Thr(GlcNAcβ) (2.0)**	**2.0**	**TMP (4.0)**	881	372.8	950.3	**2.55**
Tr4b	5/1.5	HATU/HOAt (4.0/4.0)	**Thr(GlcNAcβ) (2.0)**	**2.0**	**TMP (4.0)**	815.6	400	1070.2	**2.68**
Tr4c	5/1.5	HATU/HOAt (4.0/4.0)	**Thr(GlcNAcβ) (2.0)**	**2.0**	**TMP (4.0)**	840.5	356.8	939.7	**2.63**
						38.78 min[b]	**32.91 min[b]**	**46.15 min [D-Thr(GlcNAcβ)] [b]**	
Tr5a	5/1.5	HATU/ HOAt (4.0/4.0)	**D-Thr(GlcNAcβ) (2.0)**	**2.0**	**TMP (4.0)**	848.8	510.7	533.8	**1.05**
Tr5b	5/1.5	HATU/ HOAt (4.0/4.0)	**D-Thr(GlcNAcβ) (2.0)**	**2.0**	**TMP (4.0)**	962.5	533.9	541.4	**1.01**
Tr5c	5/1.5	HATU/ HOAt (4.0/4.0)	**D-Thr(GlcNAcβ) (2.0)**	**2.0**	**TMP (4.0)**	846.8	446.9	434.7	**0.97**

Product ratios were evaluated with Waters XTerra® RP 18 (4.6 mm × 250 mm) reverse phase column using 2 different HPLC methods. UV absorption was measured at 280 nm and the flow rate was 1 mL/min with water (0.1 % TFA, solvent A) and acetonitrile (0.1% TFA, solvent B). a) the percentage of solvent 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; b) the percentage of solvent B was increased according to a linear gradient of 1%-28% in 8 min, kept at 28% for 3 min, increased from 28% to 36% in 39 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) Arsequell, G.; Krippner, L.; Dwek, R. A.; Wong, S. Y. C. *Journal of the Chemical Society-Chemical Communications* **1994**, 2383.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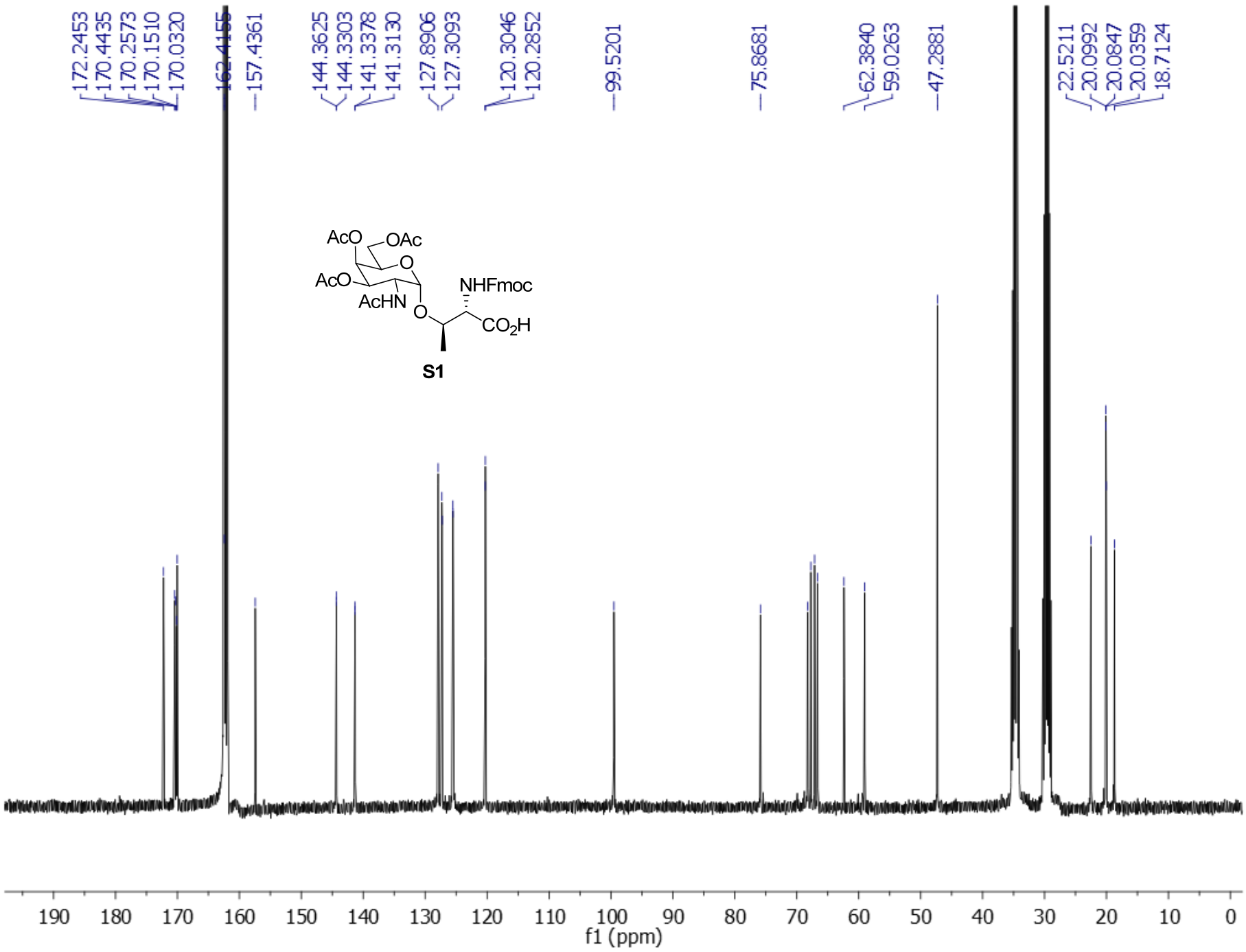
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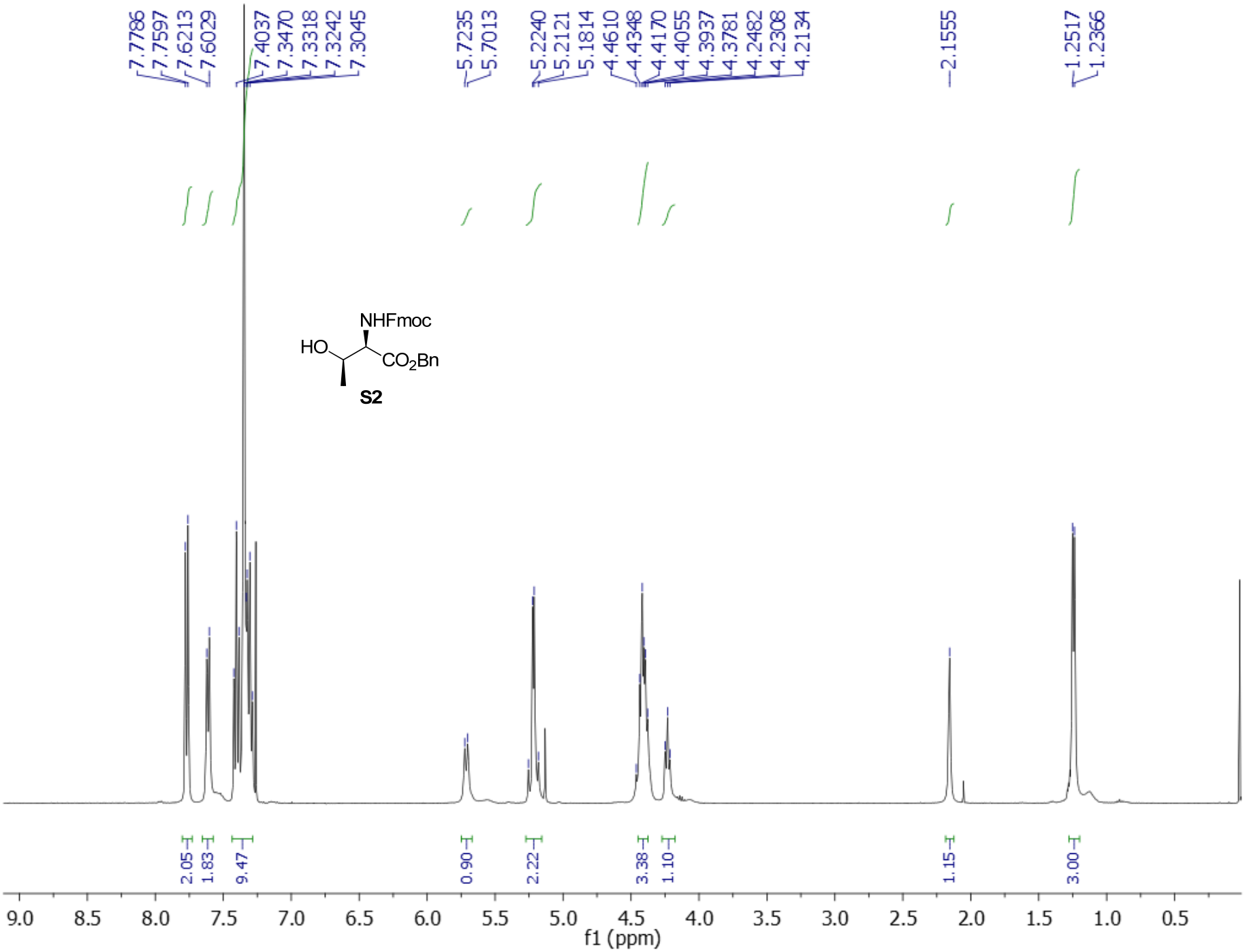
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1.2366
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HO
CO2Bn
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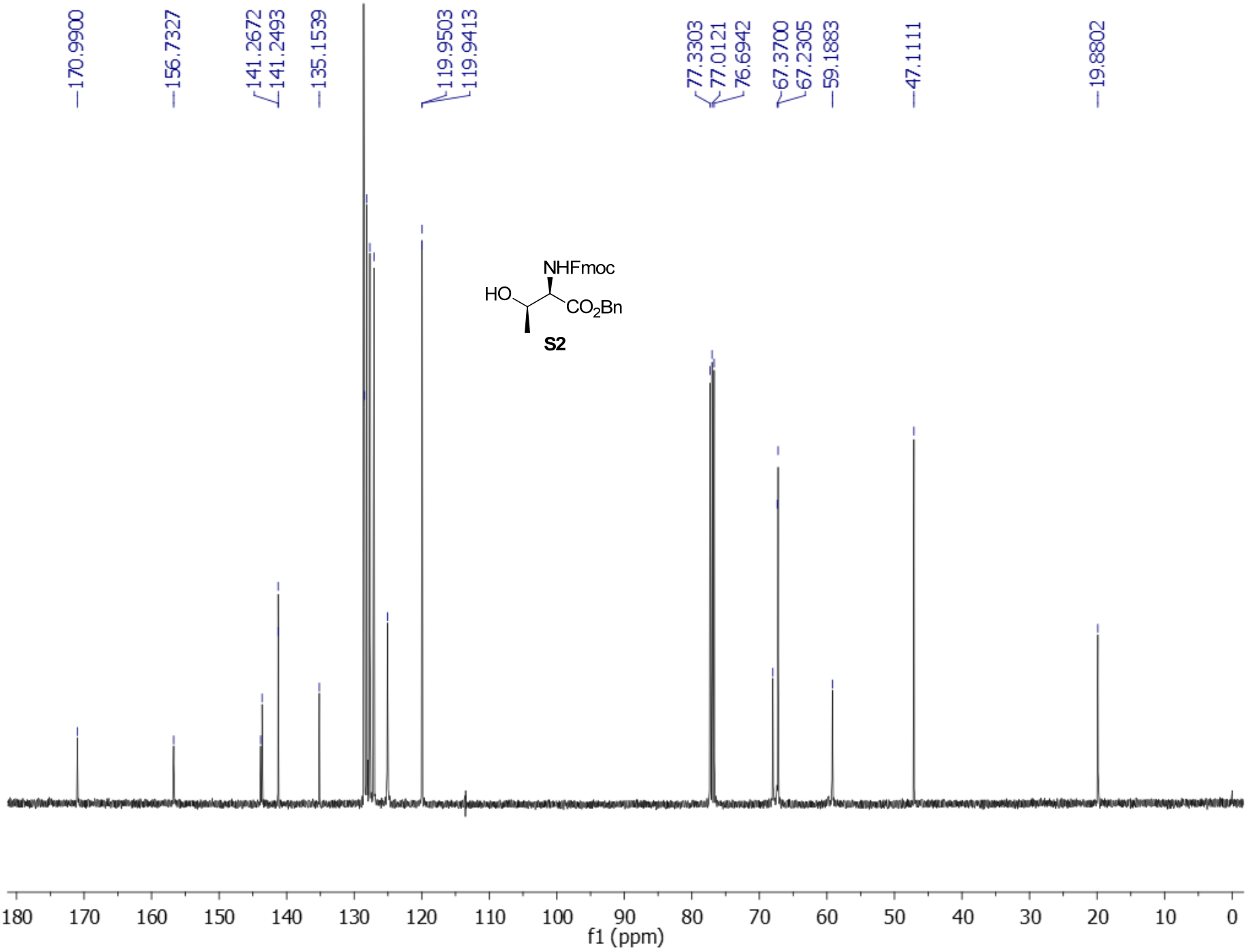
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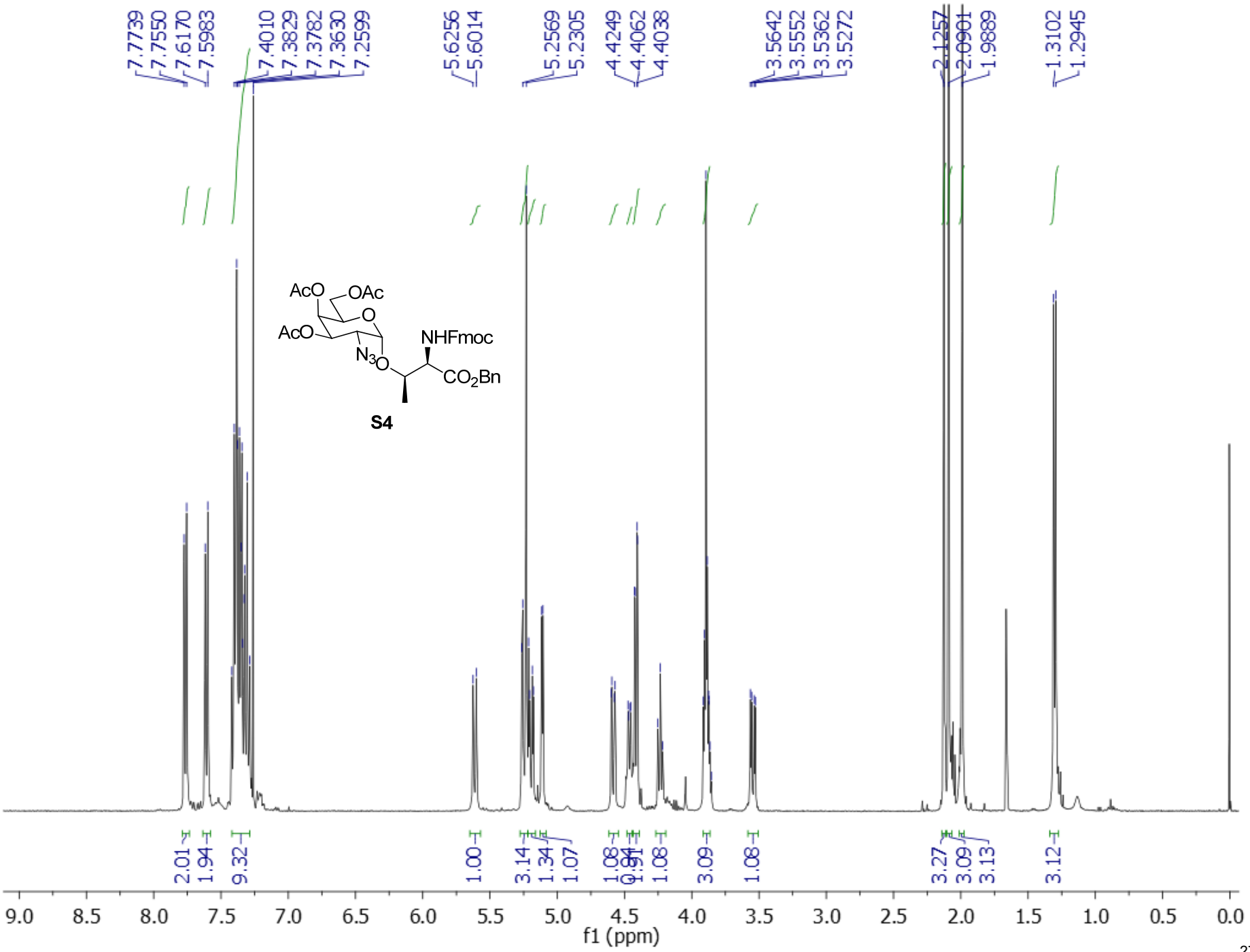
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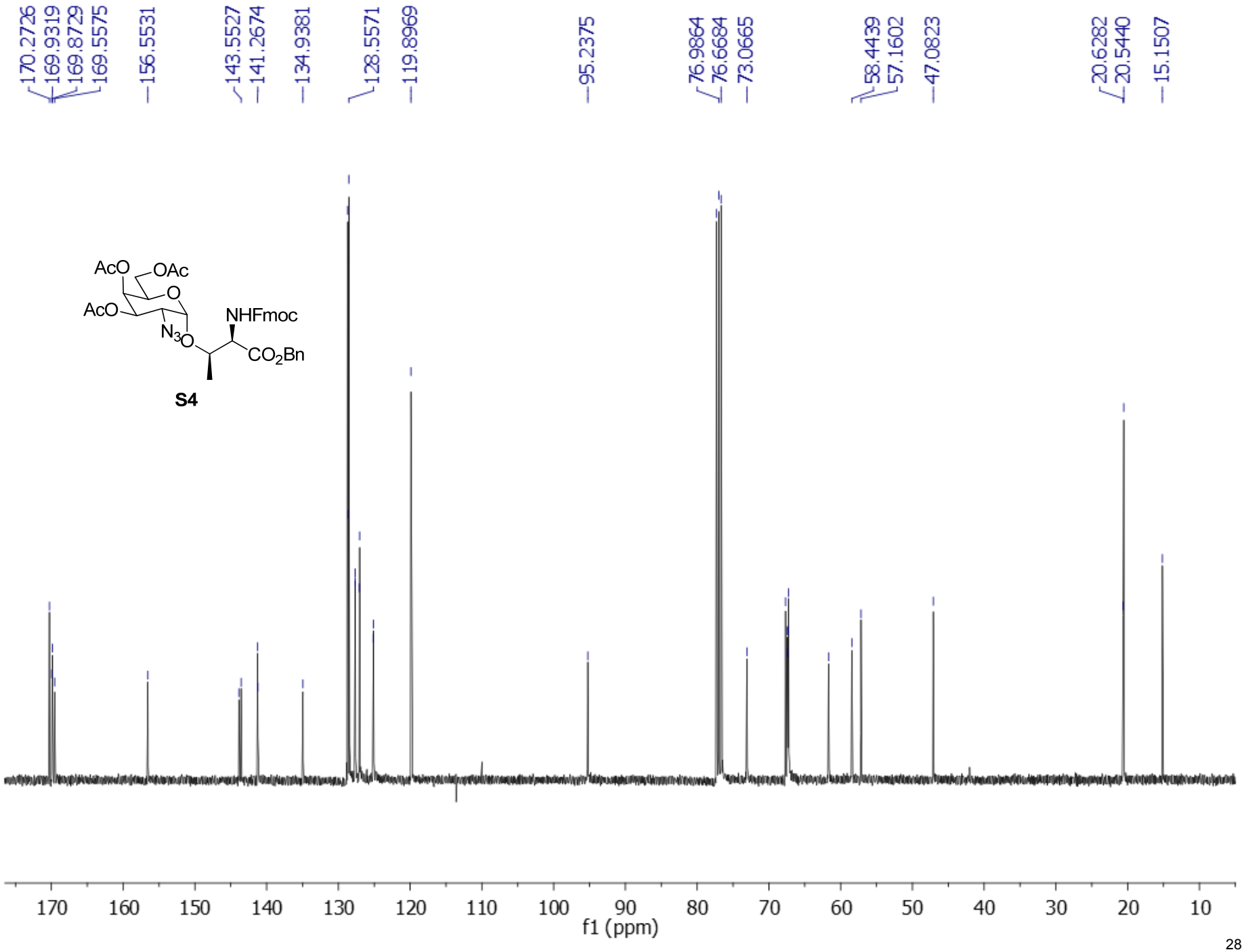
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CO2Bn
S4
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100
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80
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60
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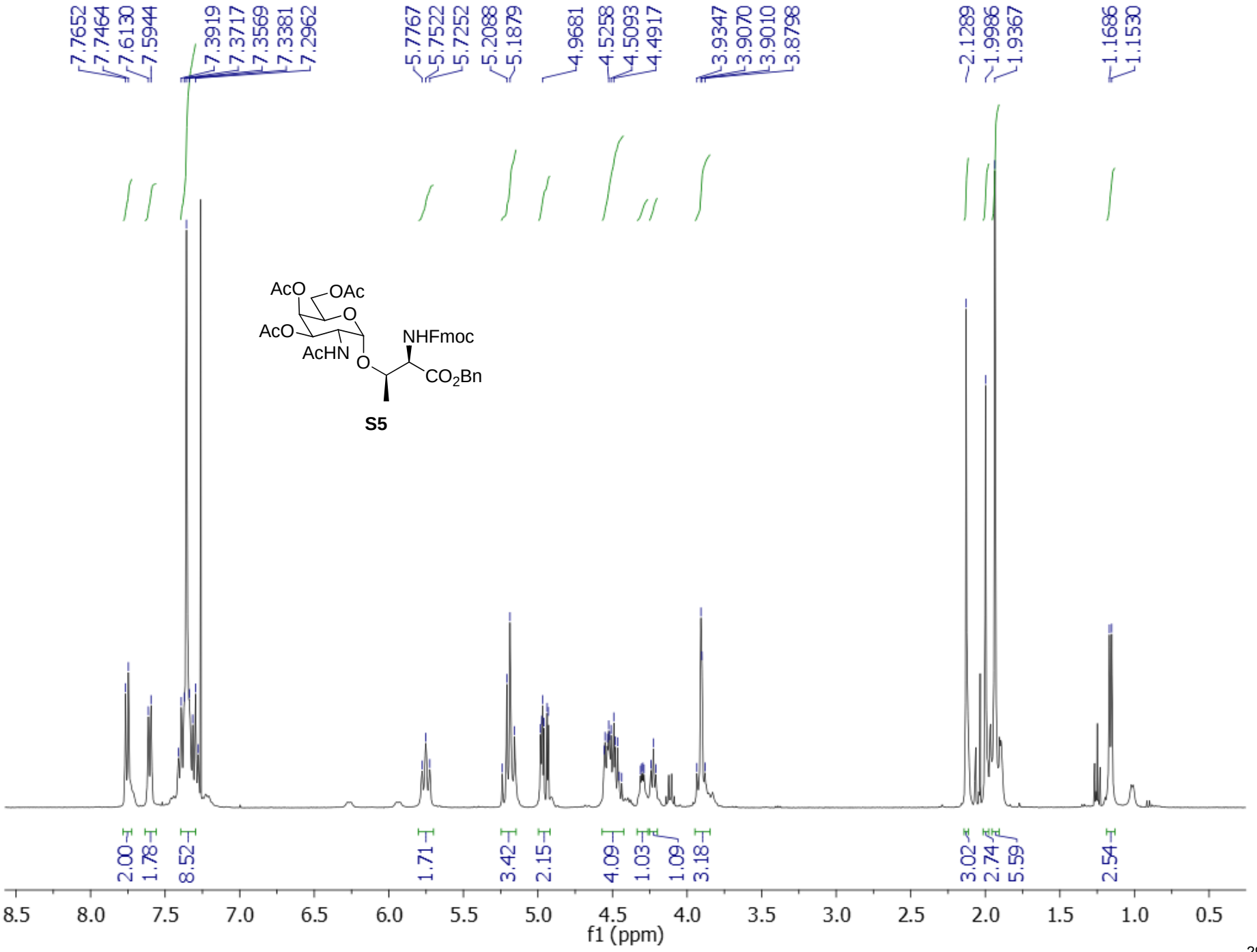
f1 (ppm)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CO2Bn
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3.02
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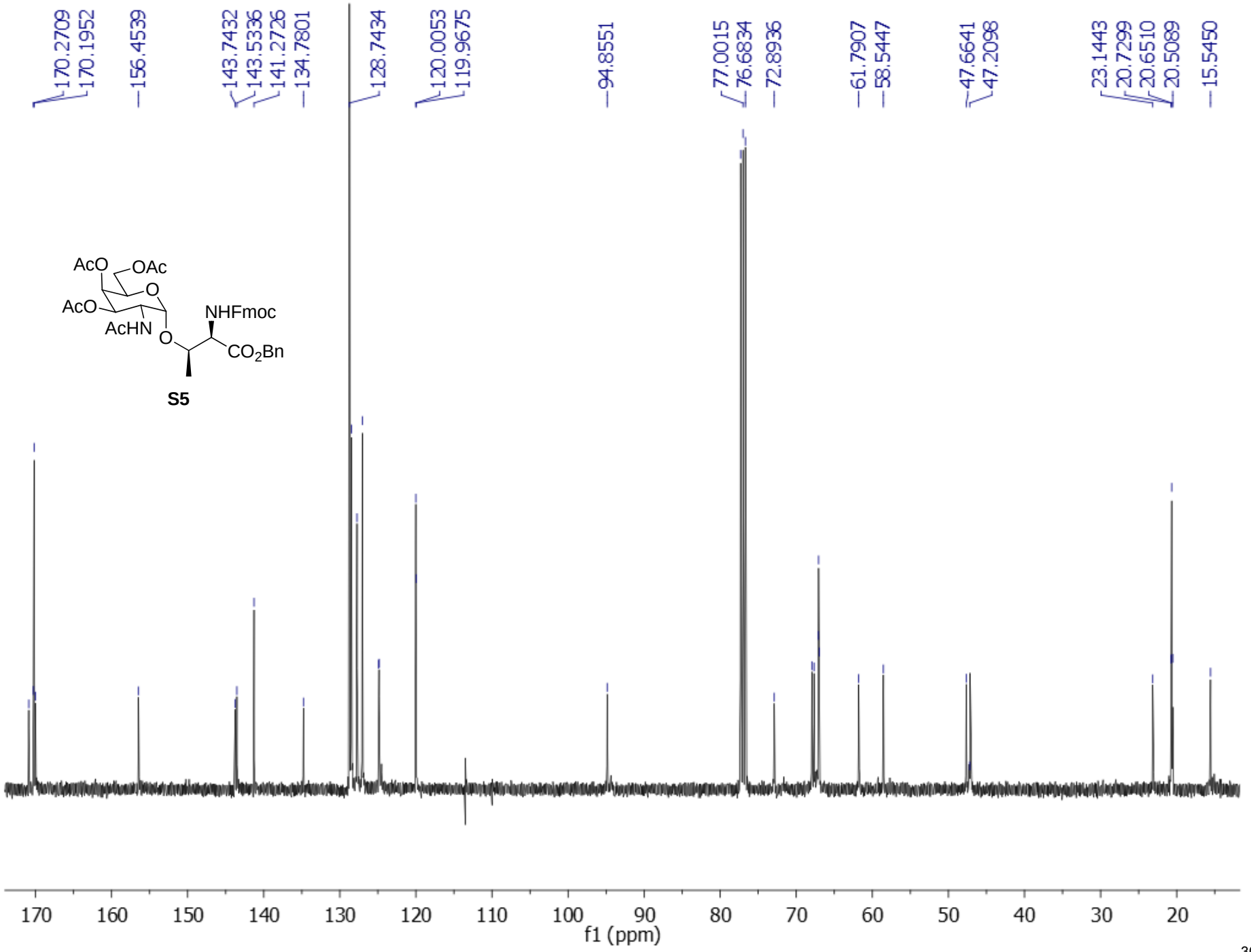
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NHFmoc
CO2Bn
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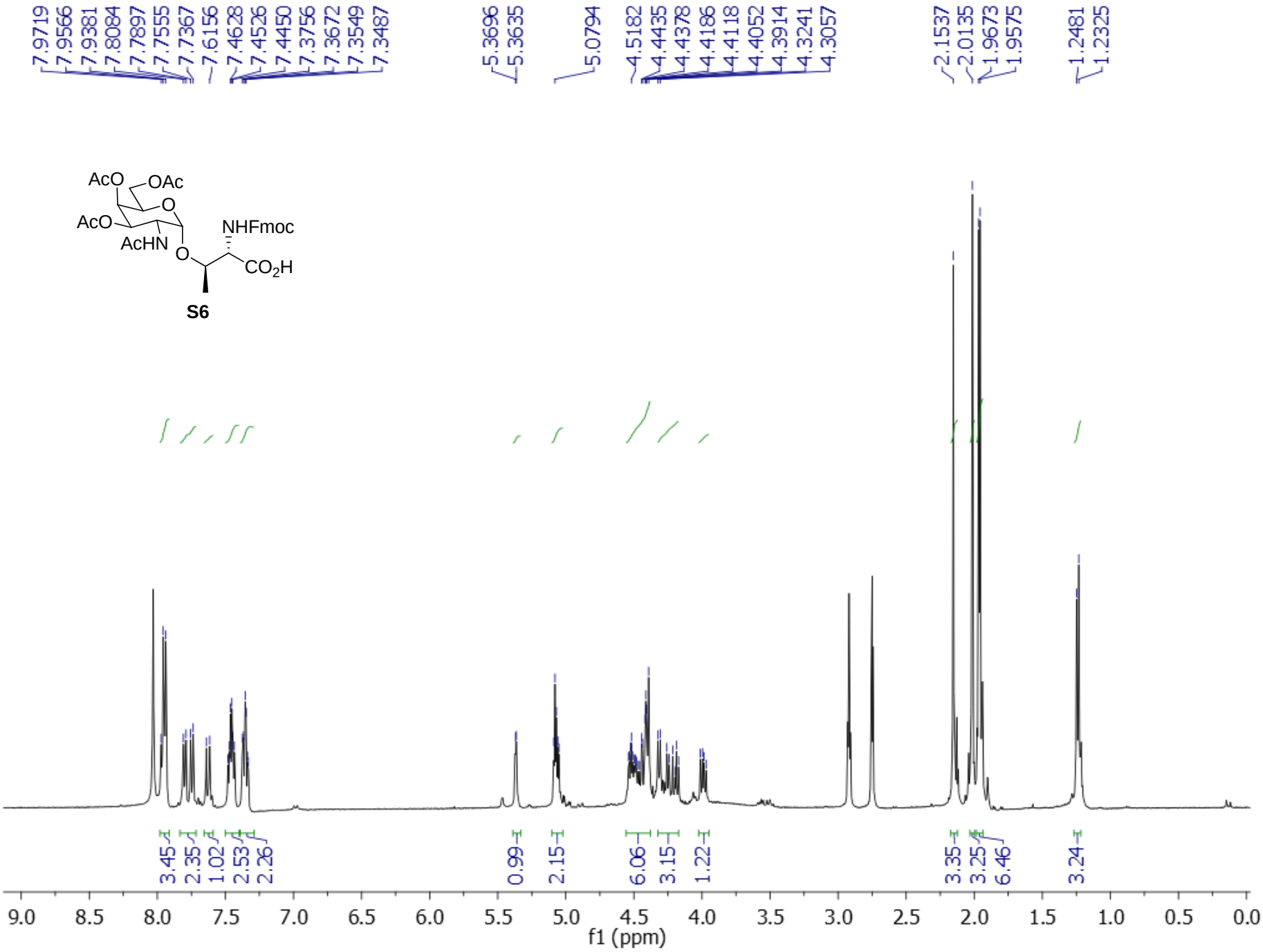
f1 (ppm)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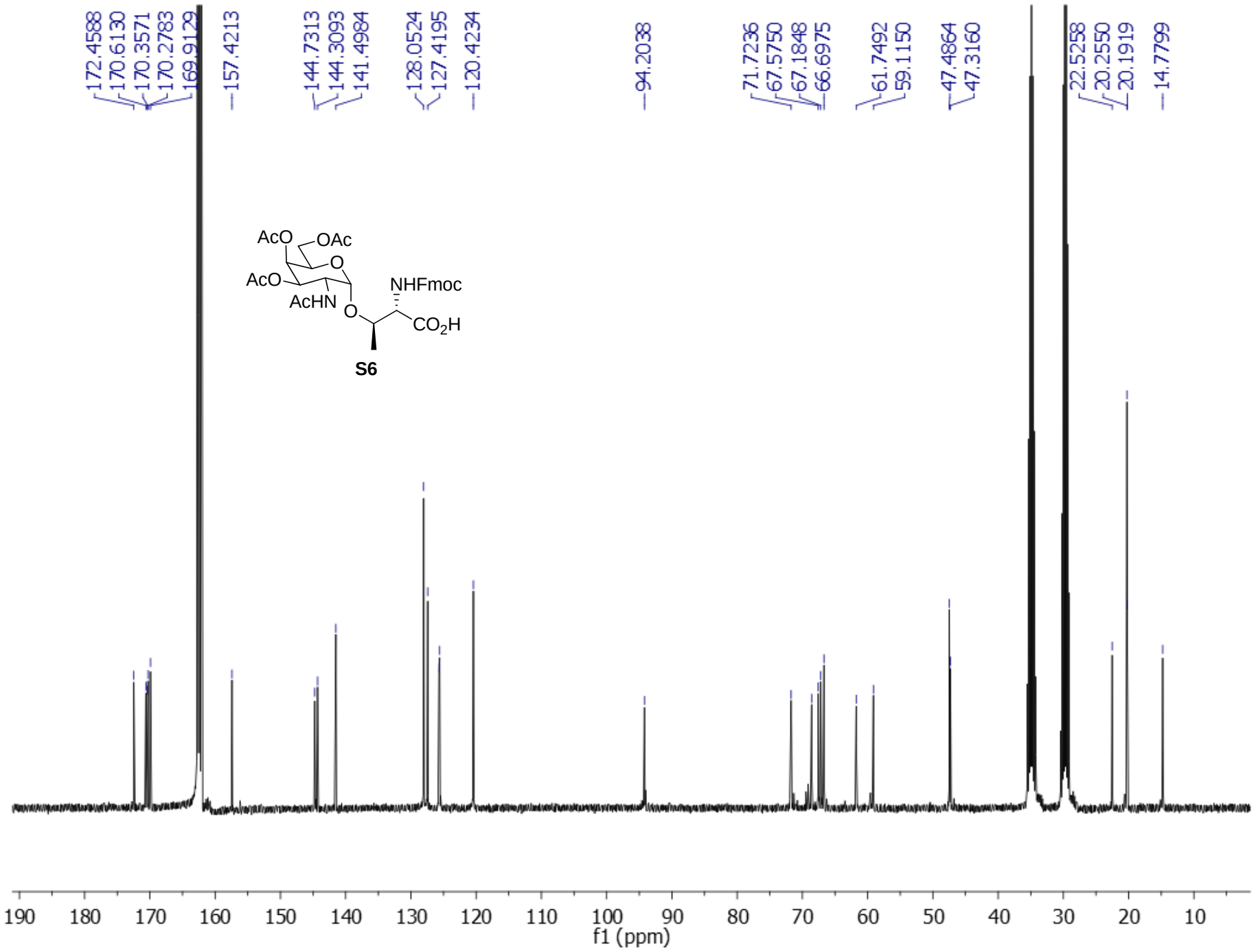
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CO2H
S6
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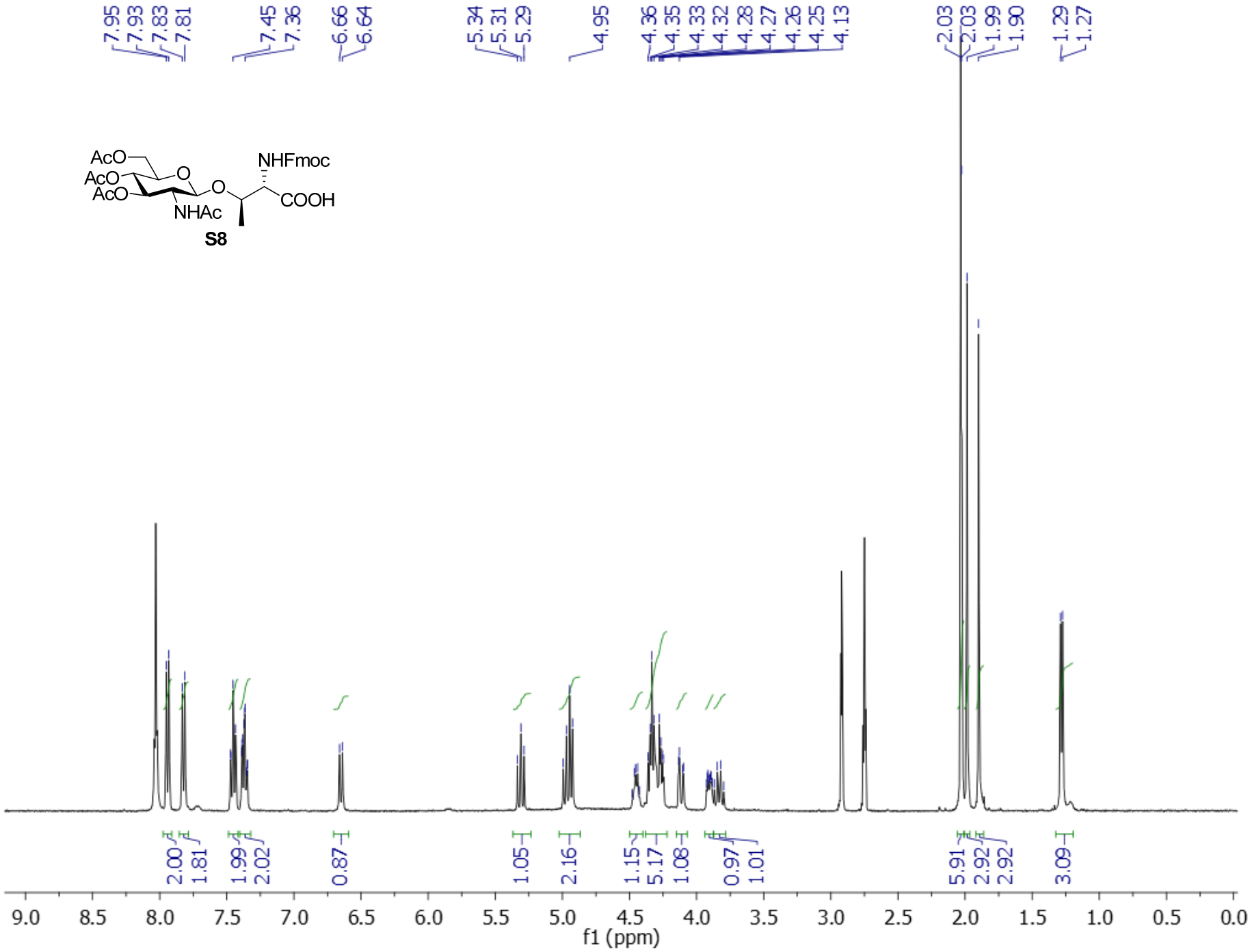
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4.25
4.13
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2.03
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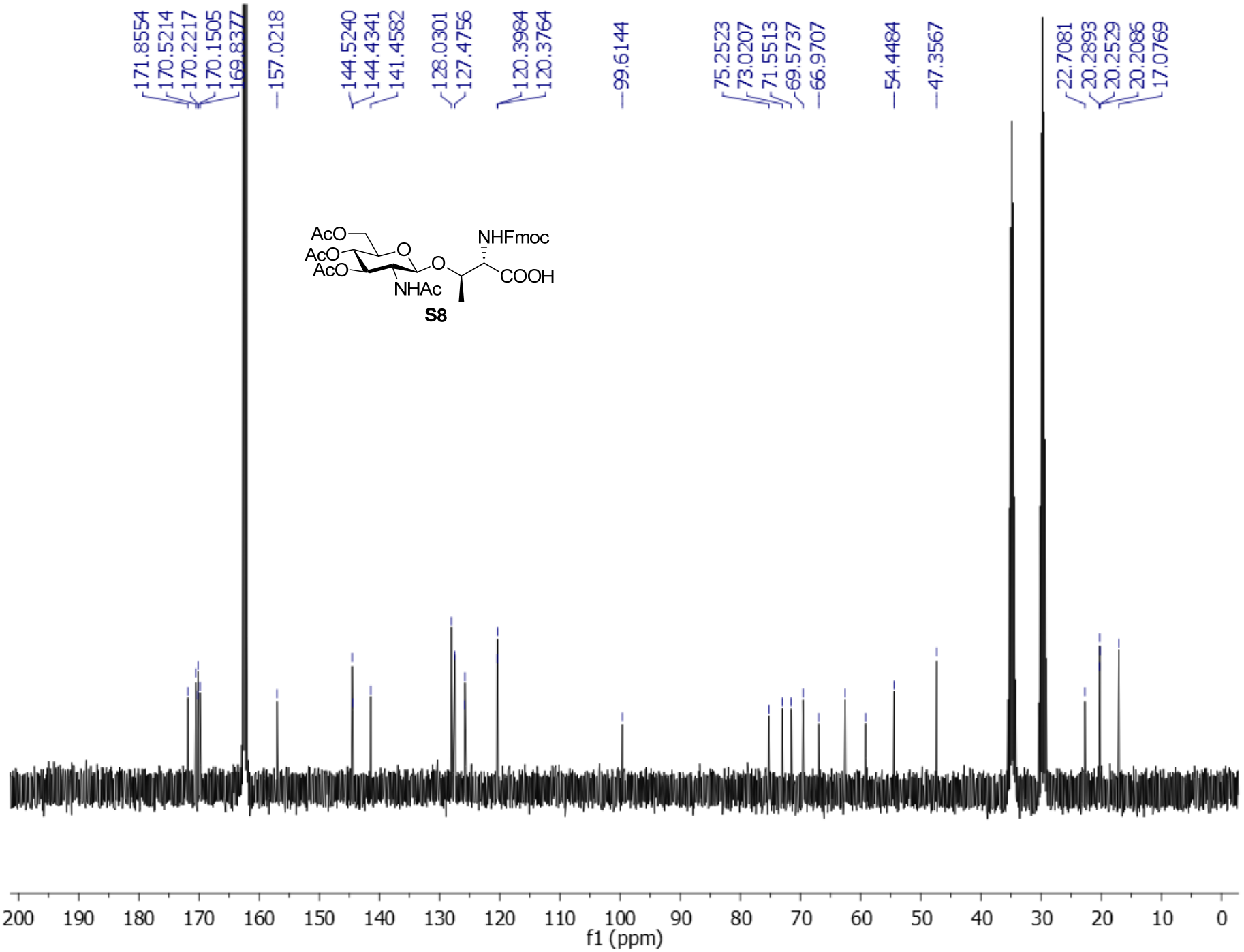
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COOH
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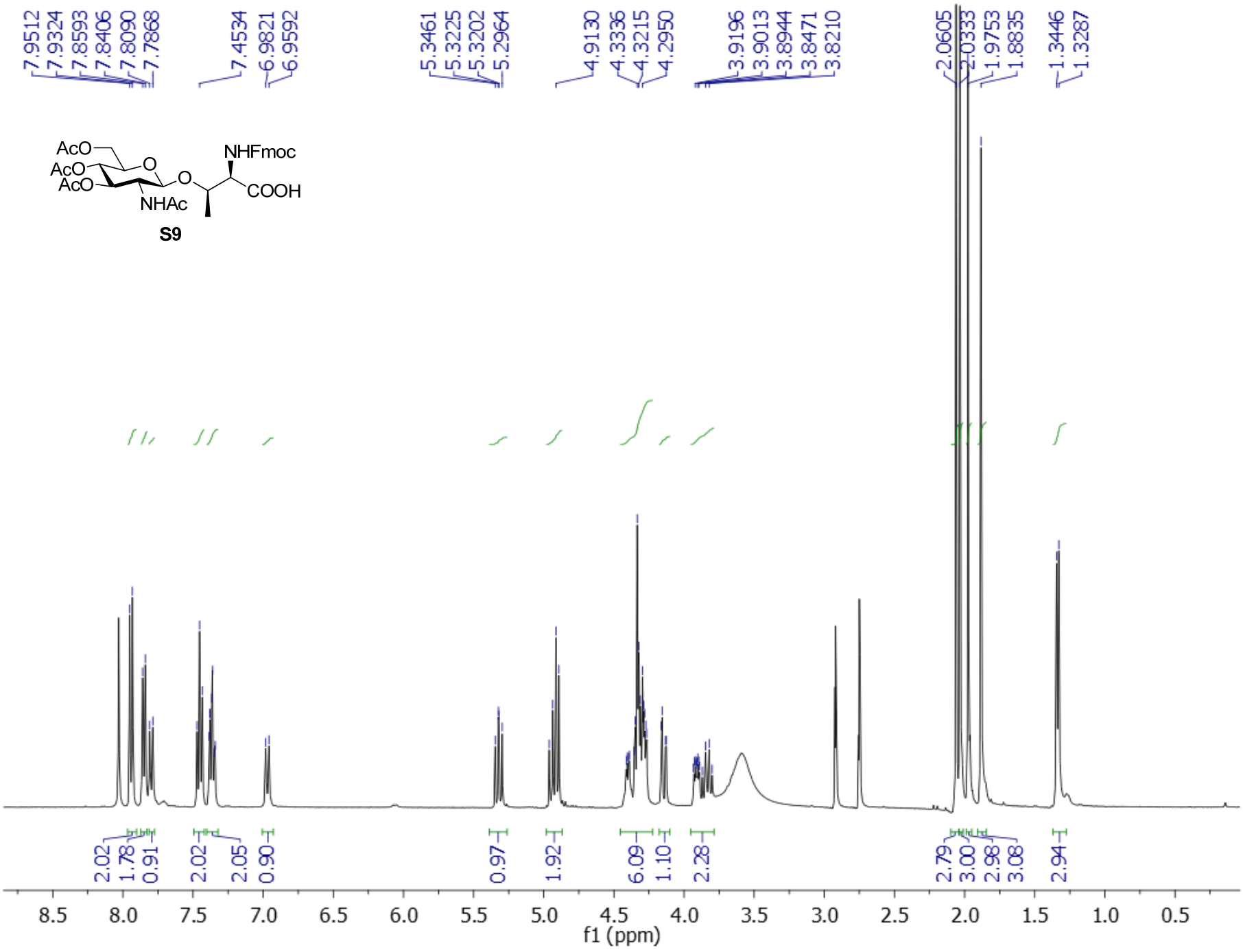
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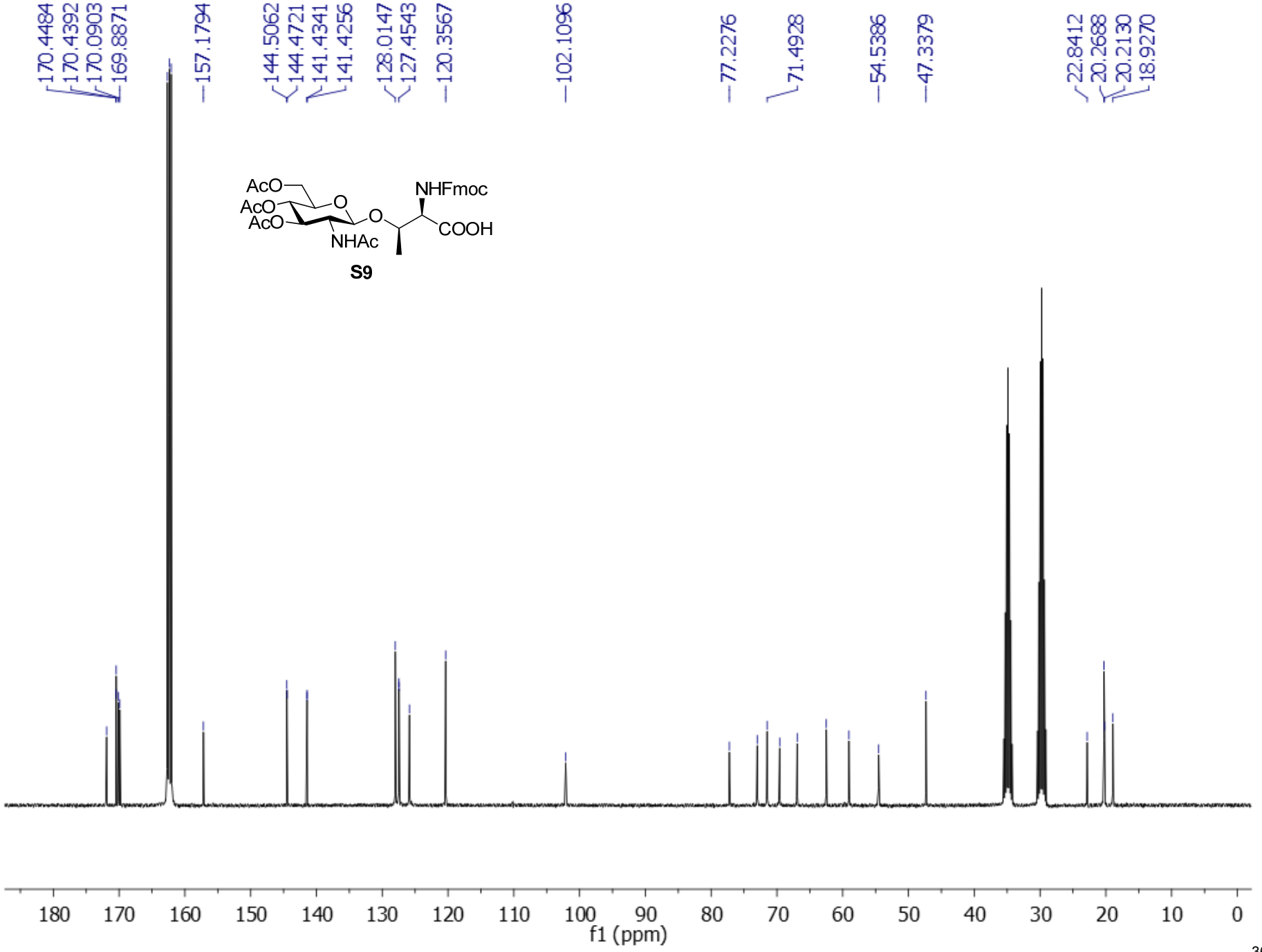
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COOH
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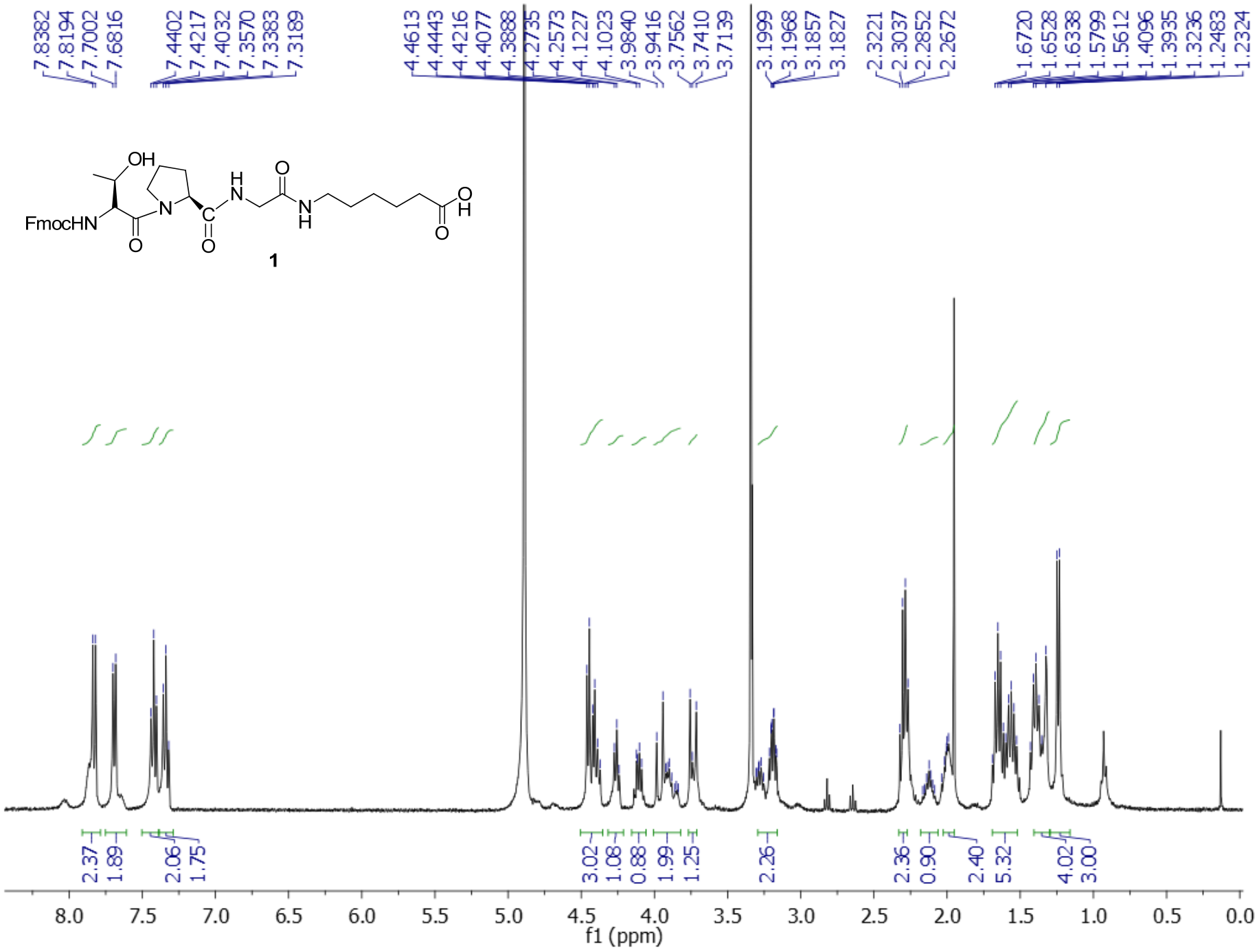
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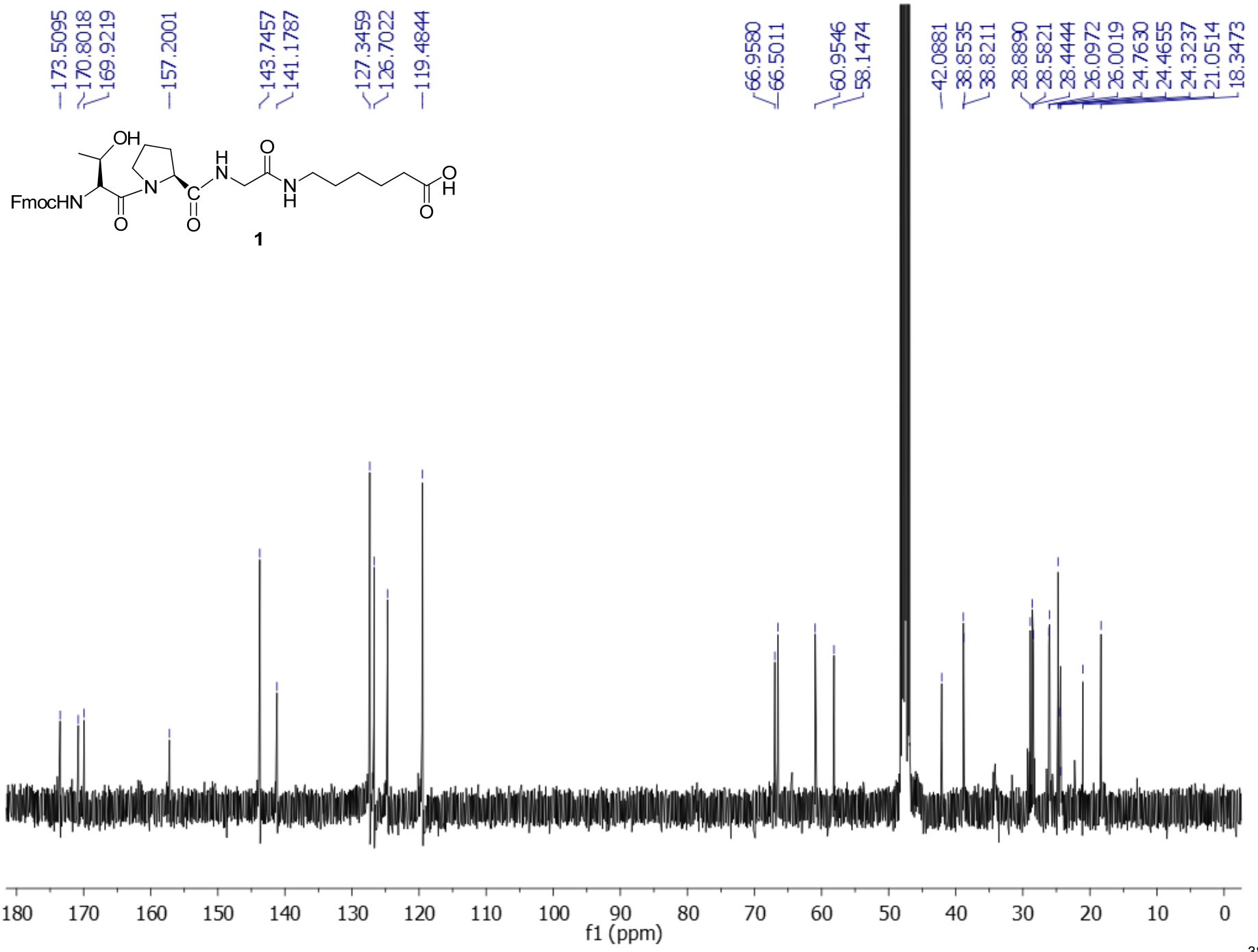
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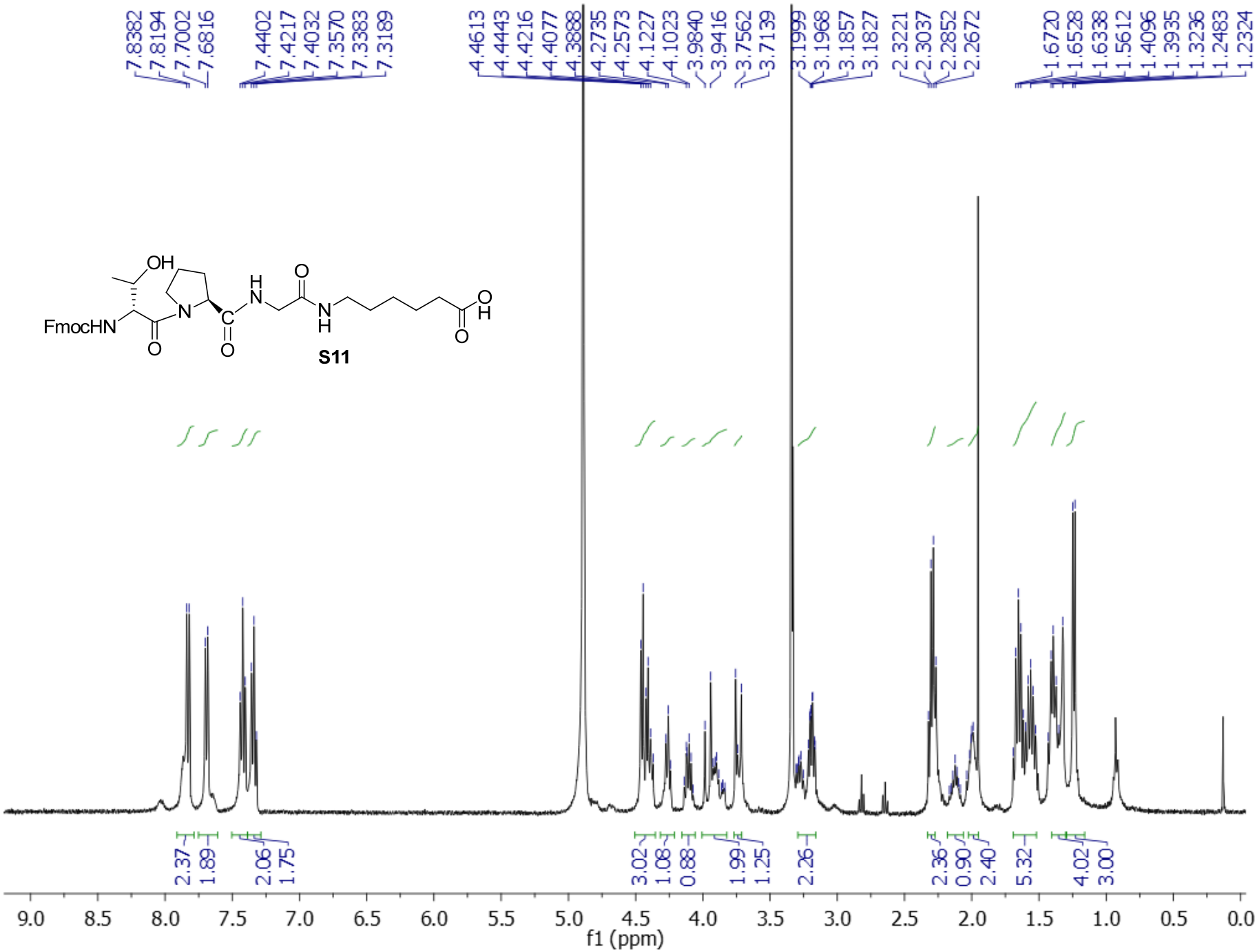
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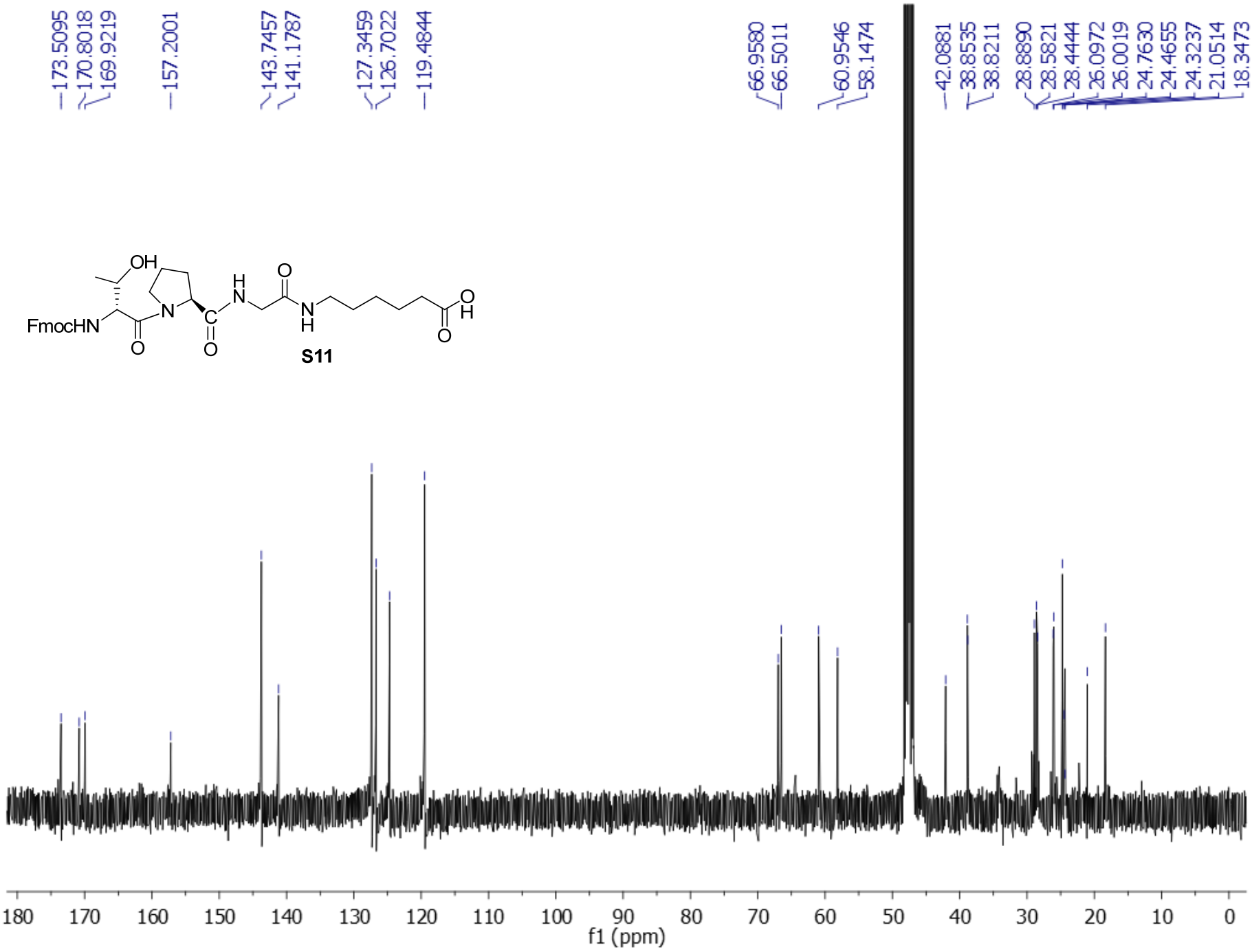
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S11
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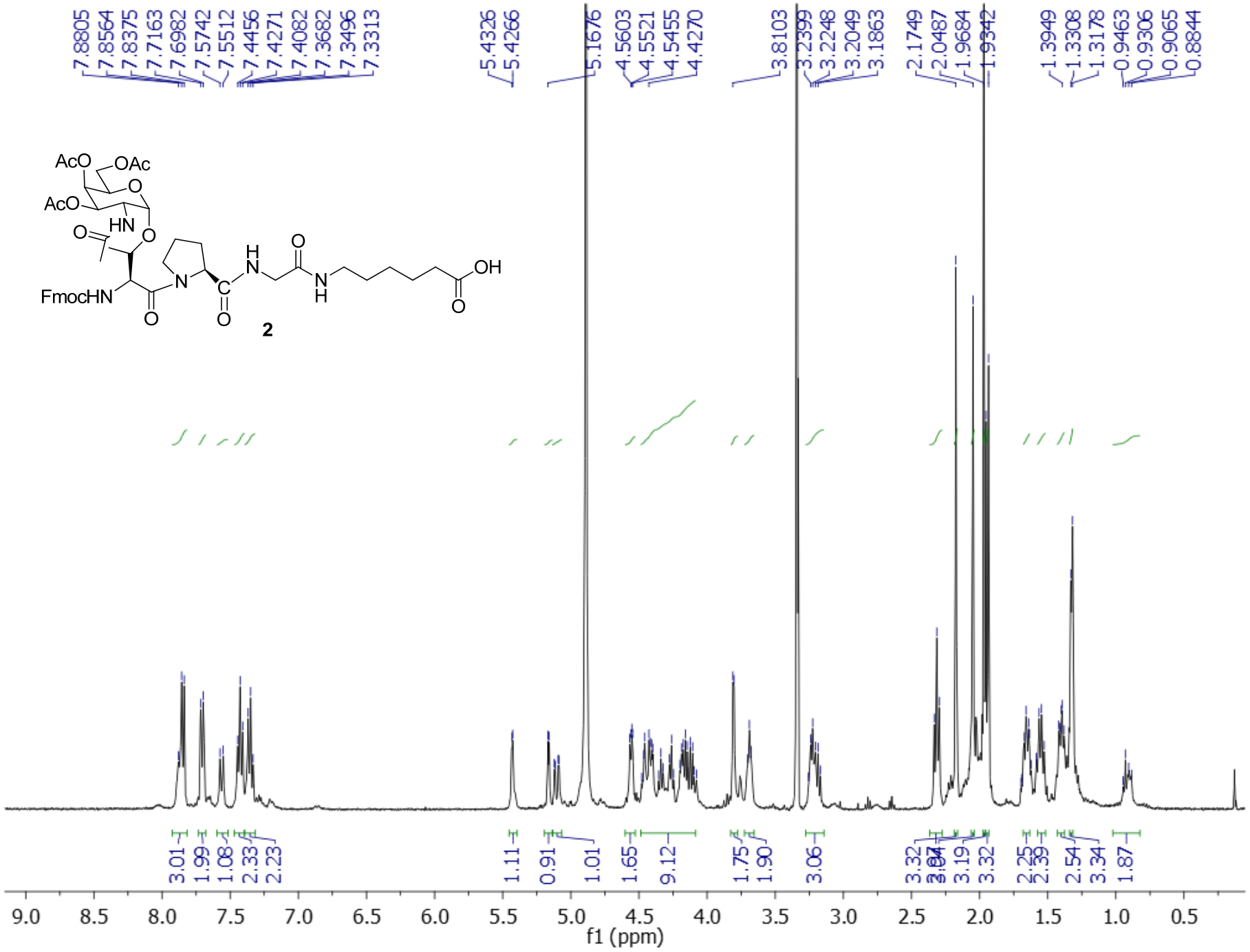
f1 (ppm)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7.3496
7.3313
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5.4266
5.1676
4.5603
4.5521
4.5455
4.4270
3.8103
3.2399
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3.1863
2.1749
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0.9306
0.9065
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OAc
AcO
O
HN
O
O
FmocHN
O
N
C
O
H
N
O
H
N
OH
O
2
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1.99
1.08
2.33
2.23
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0.91
1.01
1.65
9.12
1.75
1.90
3.06
3.32
3.19
3.32
2.25
2.39
2.54
3.34
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8.0
7.5
7.0
6.5
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3.0
2.5
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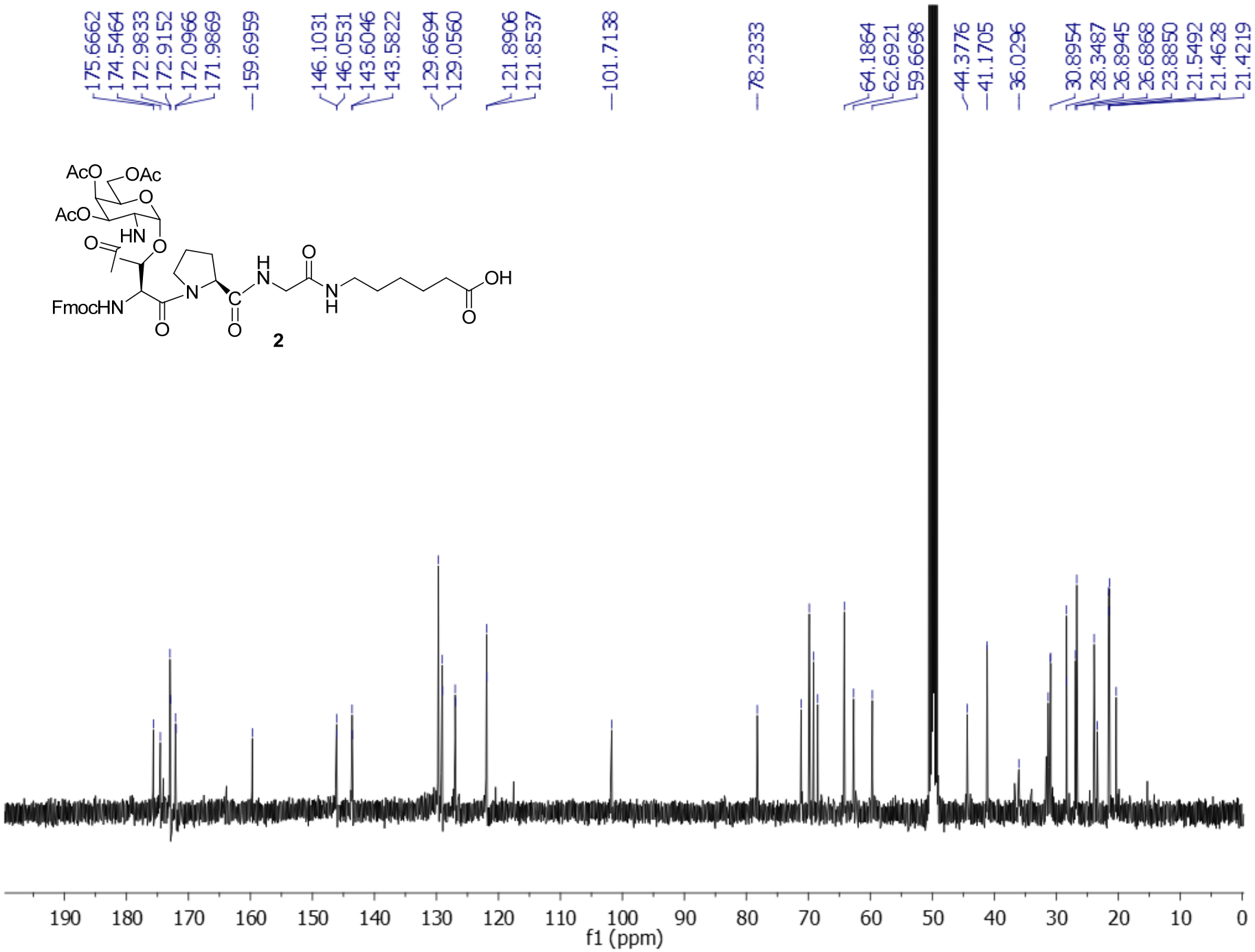
1.5
1.0
0.5
f1 (ppm)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129.0560
121.8906
121.8537
101.7138
78.2333
64.1864
62.6921
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44.3776
41.1705
36.0296
30.8954
28.3487
26.8945
26.6868
23.8850
21.5492
21.4628
21.4219
AcO
OAc
AcO
O
HN
O
O
FmocHN
O
N
H
N
C
O
O
H
N
O
N
H
OH
O
2
190
180
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120
110
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90
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30
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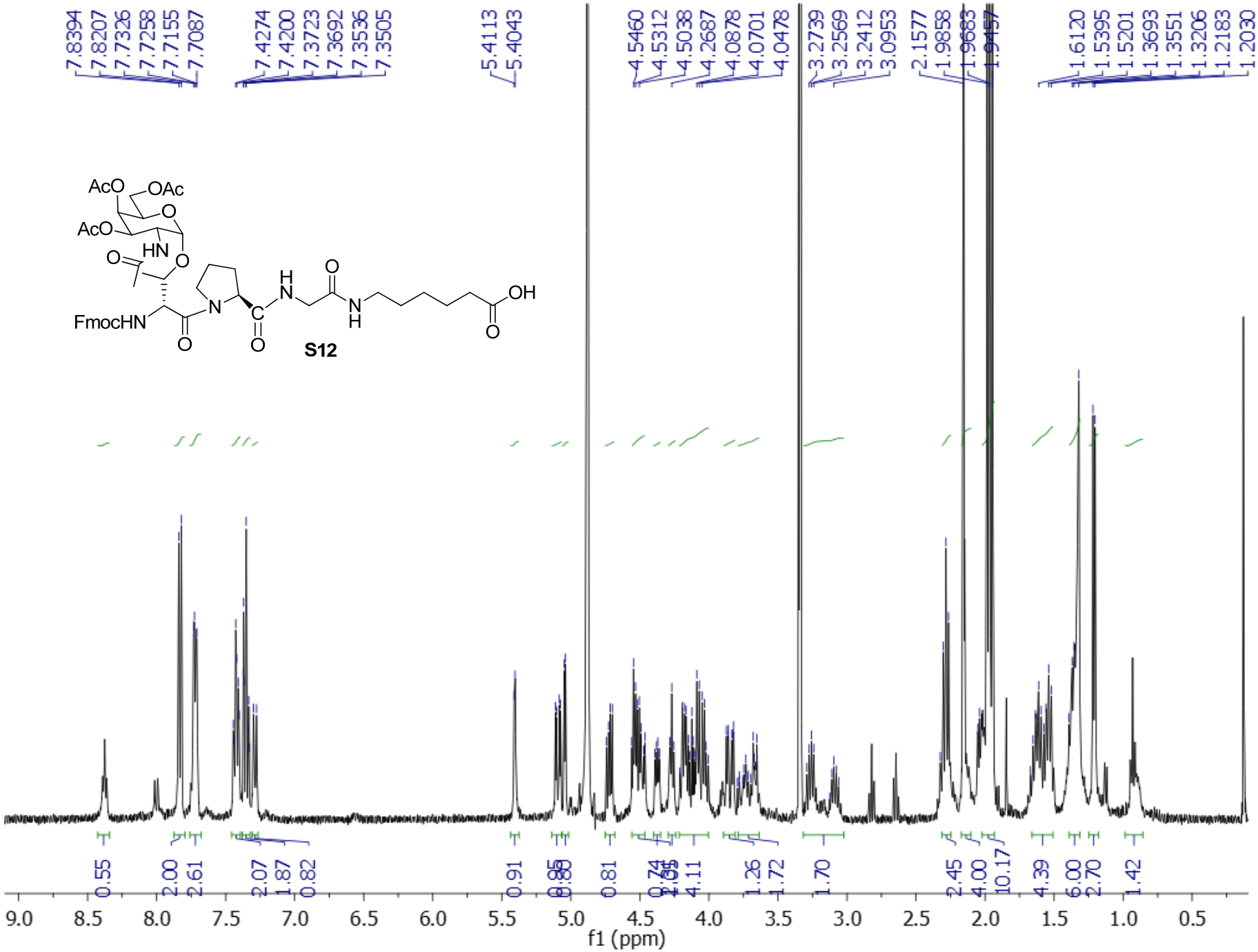
f1 (ppm)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7.4200
7.3723
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7.3536
7.3505
5.4113
5.4043
4.5460
4.5312
4.5038
4.2687
4.0878
4.0701
4.0478
3.2739
3.2569
3.2412
3.0953
2.1577
1.9858
1.9683
1.9457
1.6120
1.5395
1.5201
1.3693
1.3551
1.3206
1.2183
1.2030
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OAc
AcO
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C
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N
O
N
H
O
OH
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S12
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1.87
0.82
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4.11
1.26
1.72
1.70
2.45
4.00
10.17
4.39
6.00
2.70
1.42
9.0
8.5
8.0
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7.0
6.5
6.0
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3.0
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2.0
1.5
1.0
0.5
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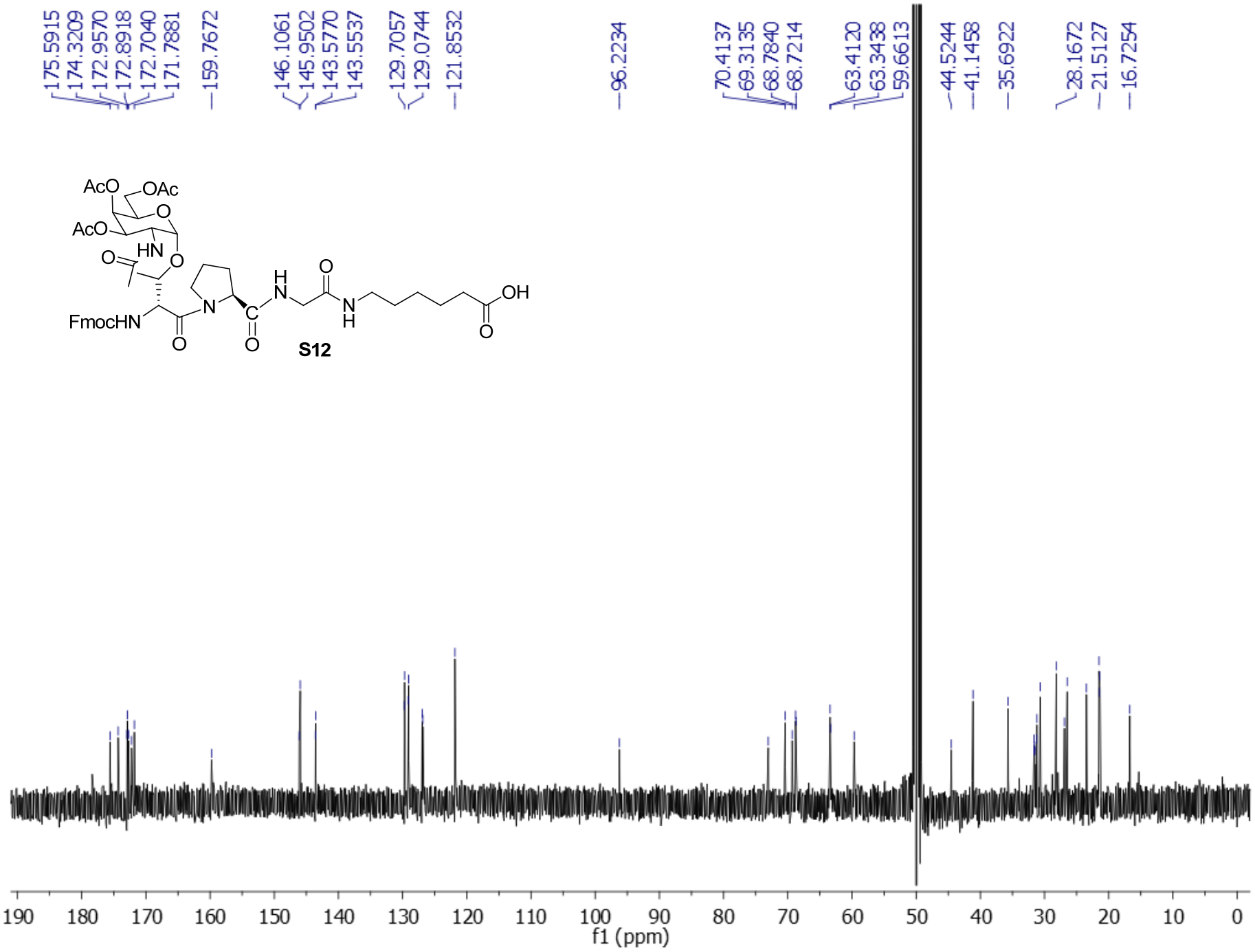
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129.0744
121.8532
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70.4137
69.3135
68.7840
68.7214
63.4120
63.3438
59.6613
44.5244
41.1458
35.6922
28.1672
21.5127
16.7254
AcO
OAc
AcO
HN
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O
FmocHN
O
N
C
O
H
N
O
N
H
OH
O
S12
190
180
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130
120
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100
90
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40
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10
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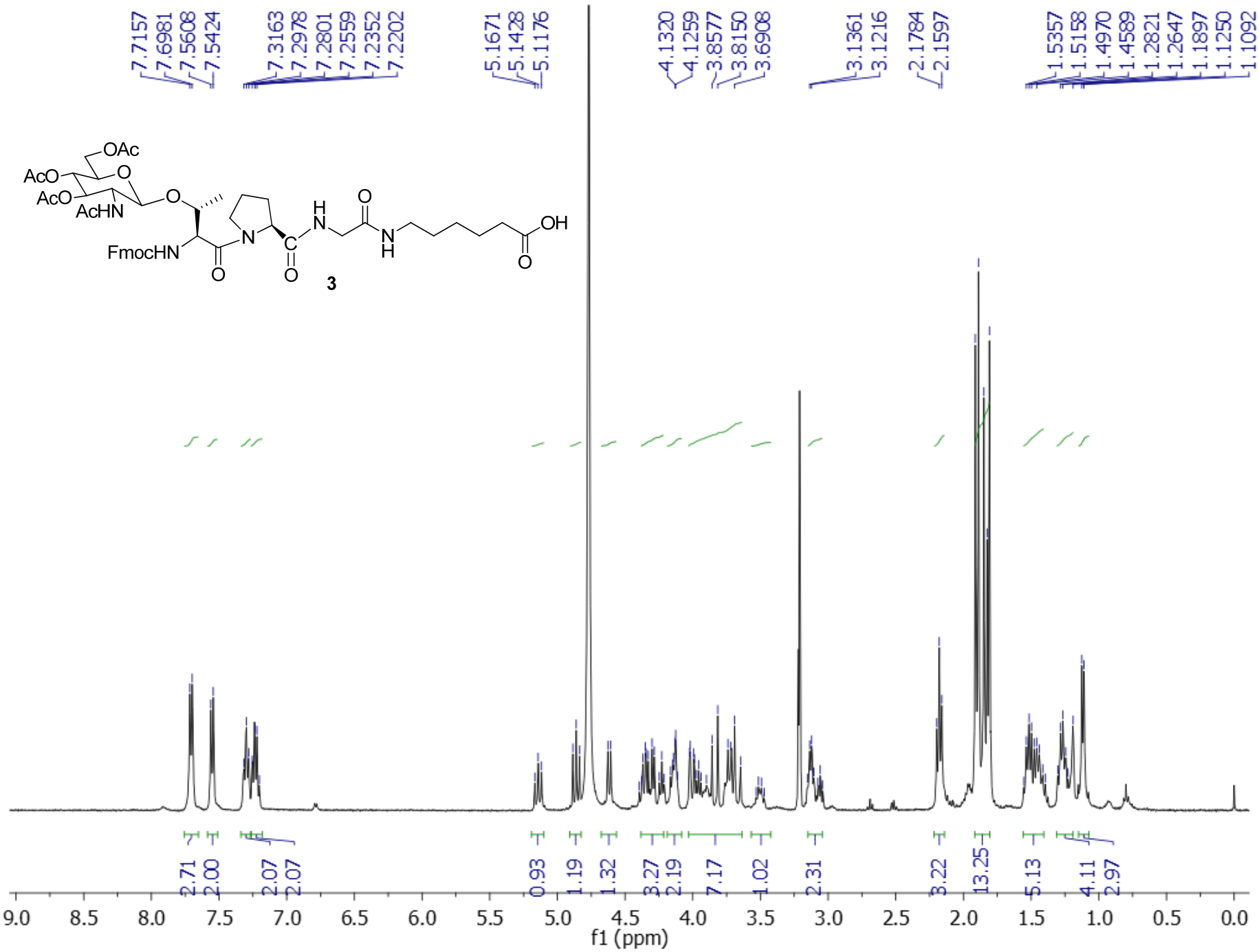
f1 (ppm)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7.2801
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7.2352
7.2202
5.1671
5.1428
5.1176
4.1320
4.1259
3.8577
3.8150
3.6908
3.1361
3.1216
2.1784
2.1597
1.5357
1.5158
1.4970
1.4589
1.2821
1.2647
1.1897
1.1250
1.1092
OAc
AcO
AcO
AcHN
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O
FmocHN
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C
H
N
O
O
O
N
H
OH
O
3
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2.00
2.07
2.07
0.93
1.19
1.32
3.27
2.19
7.17
1.02
2.31
3.22
13.25
5.13
4.11
2.97
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
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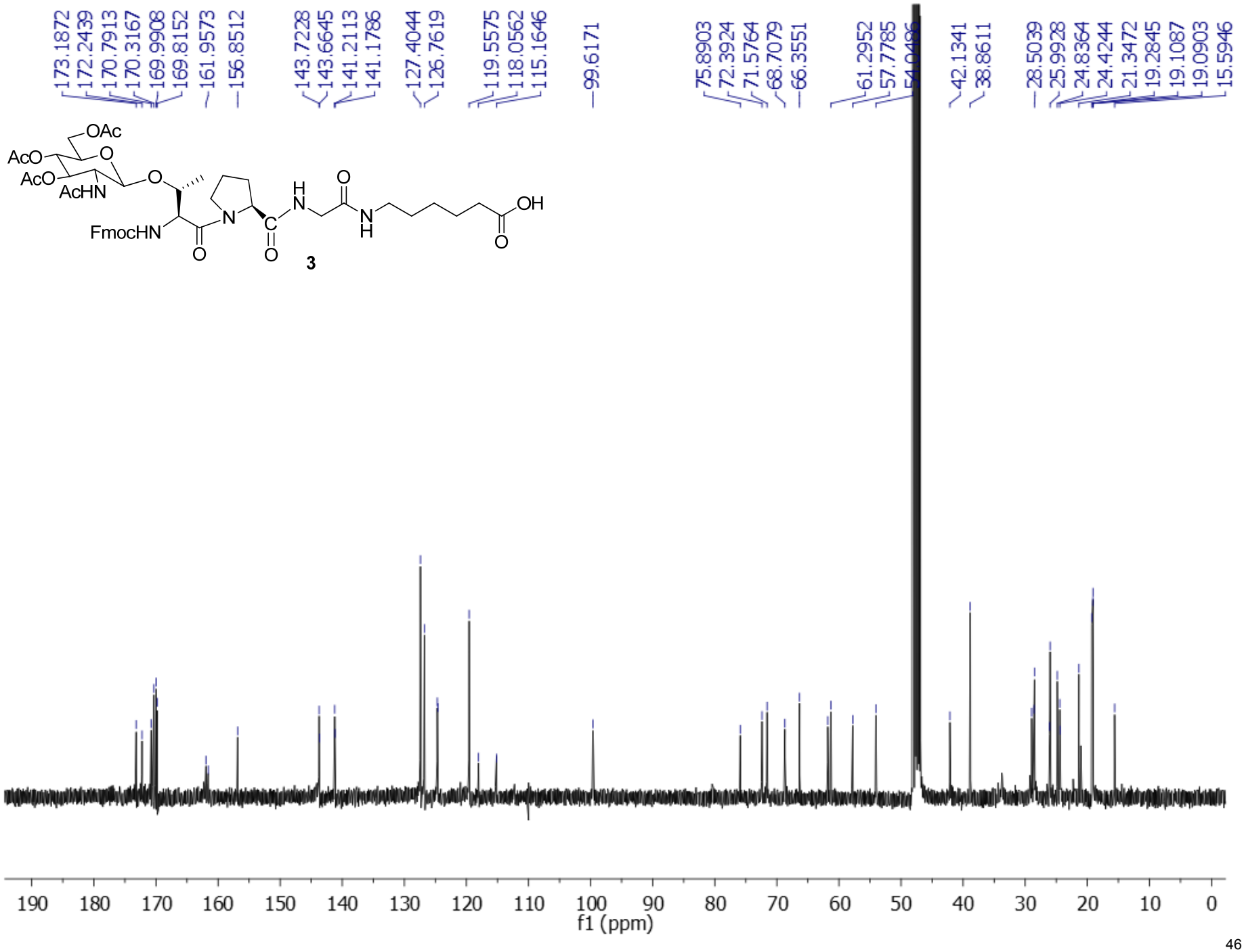
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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141.1786
127.4044
126.7619
119.5575
118.0562
115.1646
99.6171
75.8903
72.3924
71.5764
68.7079
66.3551
61.2952
57.7785
42.1341
38.8611
28.5039
25.9928
24.8364
24.4244
21.3472
19.2845
19.1087
19.0903
15.5946
OAc
AcO
AcO
AcHN
O
O
FmocHN
N
H
N
C
O
O
H
N
O
OH
O
3
190
180
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120
110
100
90
80
70
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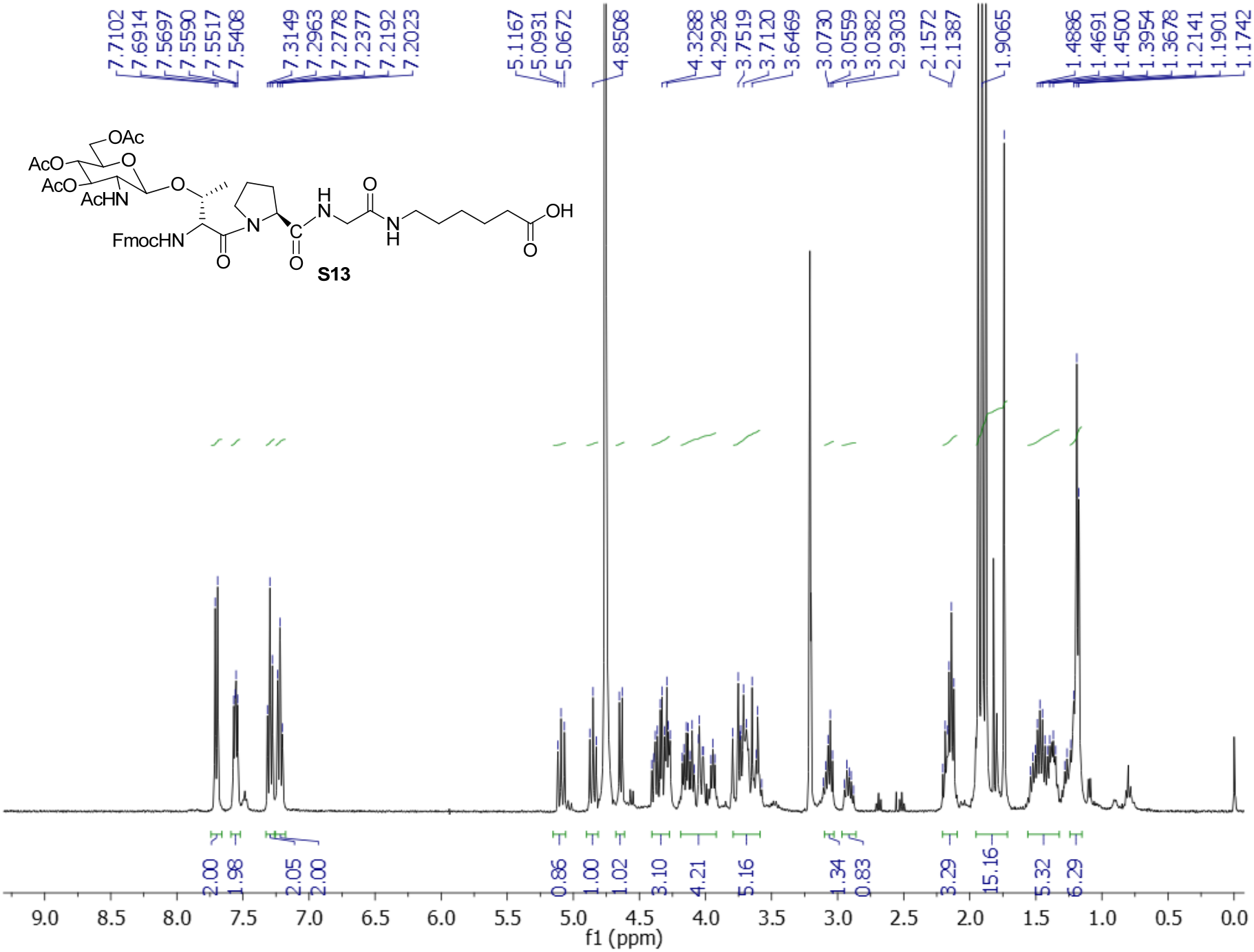
50
40
30
20
10
0
f1 (ppm)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7.2192
7.2023
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5.0931
5.0672
4.8508
4.3288
4.2926
3.7519
3.7120
3.6469
3.0730
3.0559
3.0382
2.9303
2.1572
2.1387
1.9065
1.4886
1.4691
1.4500
1.3954
1.3678
1.2141
1.1901
1.1742
OAc
AcO
AcO
AcHN
O
O
O
FmocHN
N
H
N
C
O
O
H
N
O
N
H
OH
O
S13
2.00
1.98
2.05
2.00
0.86
1.00
1.02
3.10
4.21
5.16
1.34
0.83
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15.16
5.32
6.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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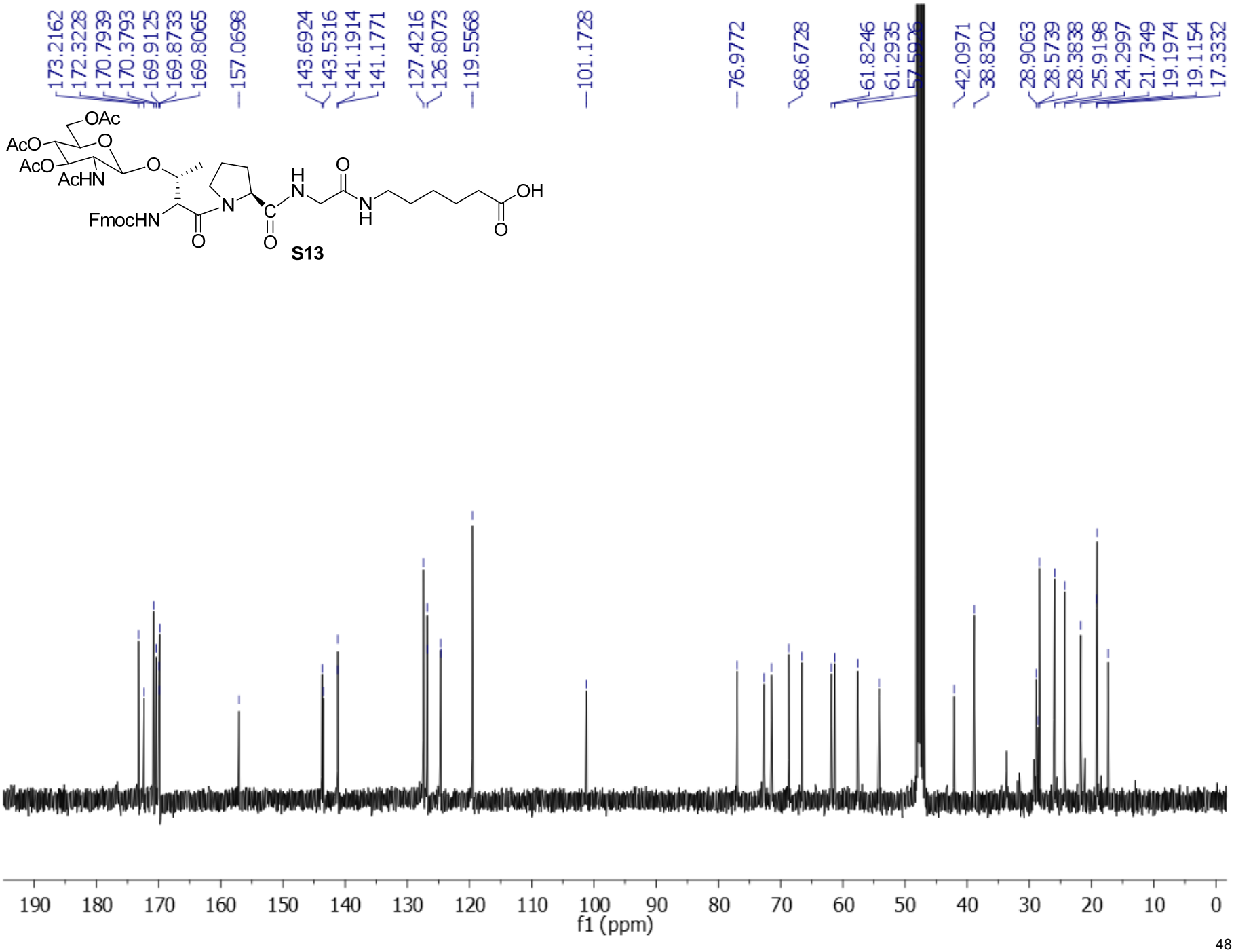
0.0
f1 (ppm)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141.1771
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28.5739
28.3838
25.9198
24.2997
21.7349
19.1974
19.1154
17.3332
OAc
AcO
AcO
AcHN
O
O
O
FmocHN
N
H
N
C
O
O
H
N
O
N
H
OH
O
S13
190
180
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140
130
120
110
100
90
80
70
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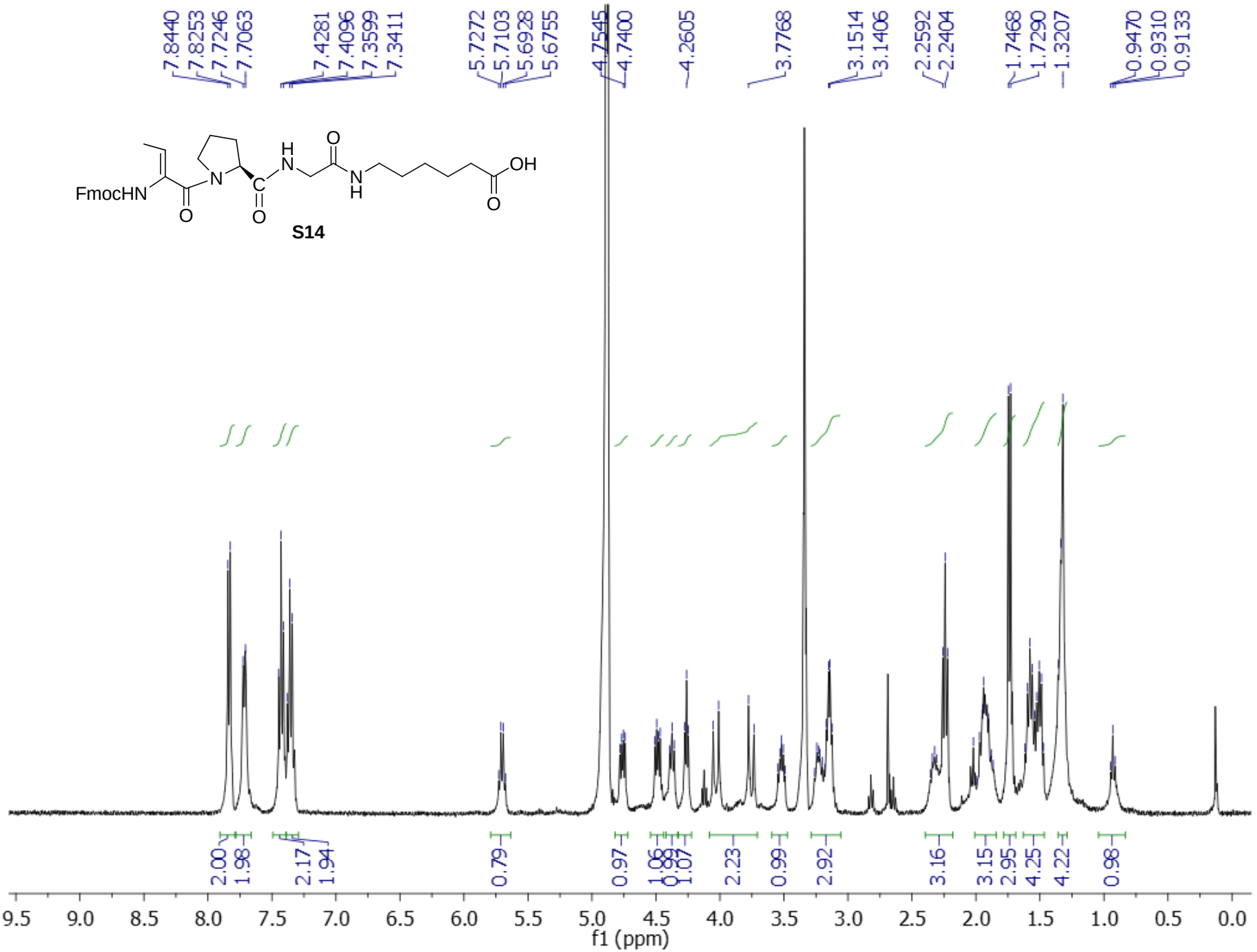
50
40
30
20
10
0
f1 (ppm)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5.7272
5.7103
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5.6755
4.7545
4.7400
4.2605
3.7768
3.1514
3.1406
2.2592
2.2404
1.7468
1.7290
1.3207
0.9470
0.9310
0.9133
FmocHN
O
N
C
O
H
N
O
N
H
OH
O
S14
2.00
1.98
2.17
1.94
0.79
0.97
1.06
0.88
1.07
2.23
0.99
2.92
3.16
3.15
2.95
4.25
4.22
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
0.5
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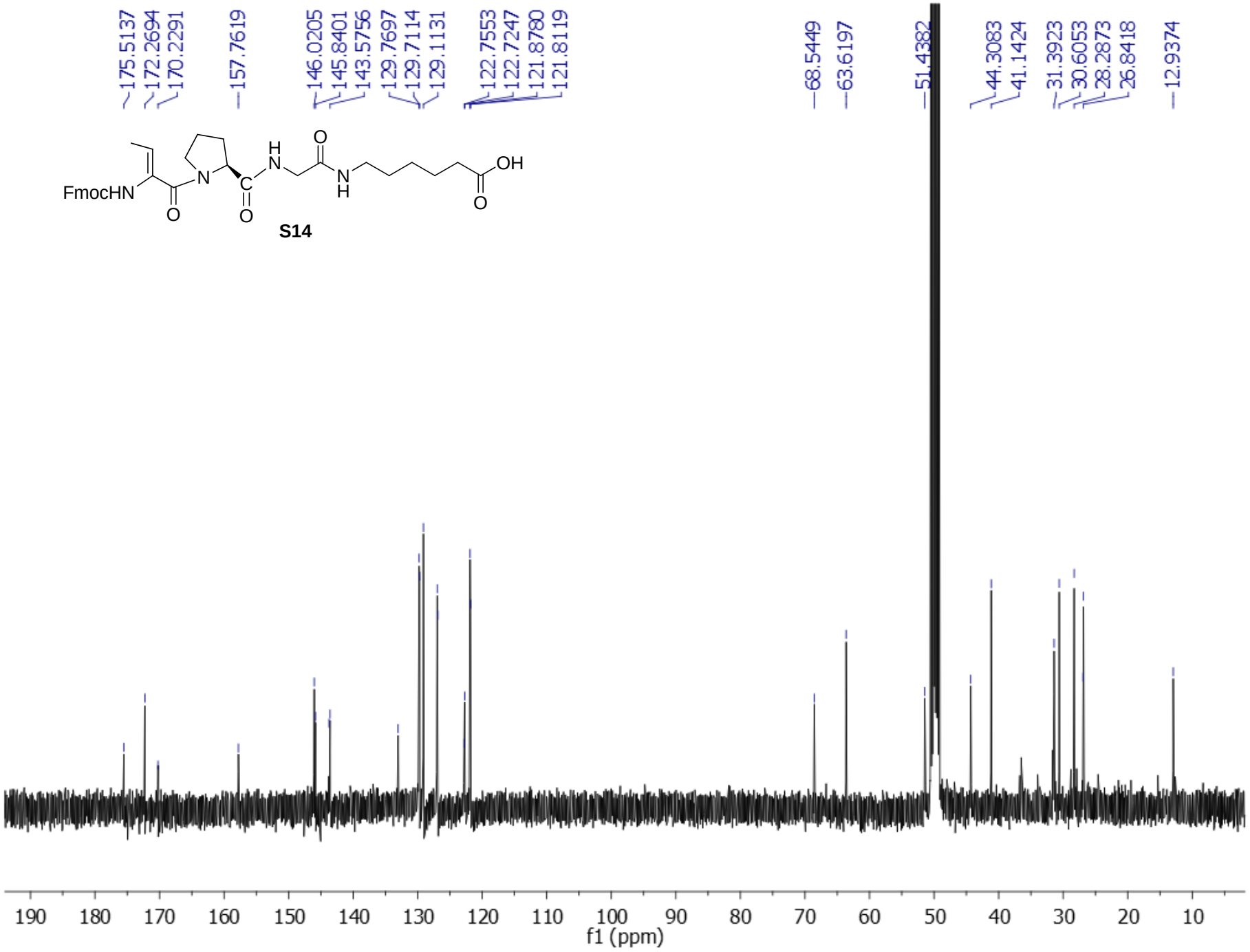
f1 (ppm)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122.7247
121.8780
121.8119
68.5449
63.6197
51.4382
44.3083
41.1424
31.3923
30.6053
28.2873
26.8418
12.9374
FmocHN
O
N
C
O
H
N
O
N
H
OH
O
S14
190
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)