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Supplementary Information For
Direct O-Glycosidation of Resin Bound Thioglycosides.

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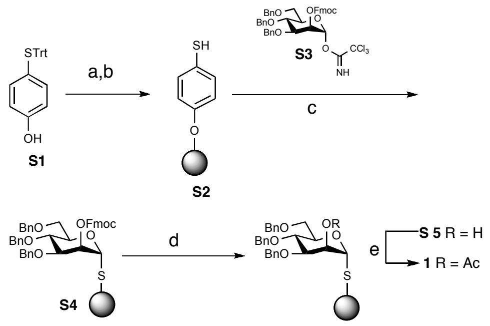
General Experimental Details.

All reactions were performed under and Argon atmosphere unless otherwise stated. Powdered molecular sieves were flame dried *in* vacuo immediately prior to reactions. Flash column chromatography was performed on Whatman silica gel, 230-400 Mesh. Analytical and preparative thin layer chromatography was carried out on EMD silica gel 60 F254 plates. Products were visualized using UV or by staining with 5% aqueous sulfuric acid or ceric ammonium molybdate. NMR spectra were recorded on a Bruker Advance III NMR spectrometer at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR. Chemical shifts were reported in ppm relative to TMS (for ^{1}H-NMR) or $CDCl_3$ (for ^{13}C-NMR). Coupling constants were reported in Hz. Mass spectra were recorded using a Finnigan LTQ ESI-MS with an additional APCI source. UV/Vis spectra were measured using a Cary 100Bio UV/Vis spectrometer. High-resolution mass spectra (HRMS) were obtained at the MIT Department of Chemistry Instrumentation Facility using a peak-matching protocol to determine the mass and error range of the molecular ion. Optical rotations were measured on a Rudolph Research Analysis AUTOPUL IV polarimiter @ 589 nm in a 5 cm cell at 24°C inside the chamber.

Materials.

Prior to running reactions, all reagents were dried by azeotropic removal of water using toluene and a rotary evaporator. Methanol, dichloromethane, and toluene were dried on an Innovative Technologies PureSolv 400 solvent purifier. All other solvents were purchased from Sigma-Aldrich at the highest quality possible and used as received. NMR solvents were obtained from Cambridge Isotope Labs (Andover, MA). All chemicals were purchased at the highest possible purity from Sigma-Aldrich and used as received.

Synthesis of Donor 1:



Scheme S1 *Reagents and conditions:* (a) NaH (60%), JandaJel-Cl, DMF; (b) THF, Et_3SiH (15 equiv.), CH_2Cl_2 (69%, 2 steps); (c) **3**, TMSOTf, CH_2Cl_2 (3 cycles); (d) 20% piperidine/DMF (99%, 2 steps); (e) Ac_2O, pyridine (99%).

Sulfhydryl Resin S2:

A flame dried flask containing JandaJel (0.12 mmol/g, 3.5 mmol) was charged with 50 mL DMF. After 5 min the reaction was treated with **1** (3.87 g, 10.5 mmol) followed by NaH (0.25g, 10.5 mmol). The resulting suspension was stirred for 19 h, then filtered, washed sequentially with DMF

(3X), CH_2Cl_2 (3X), MeOH (3X), and CH_2Cl_2 (3X) and dried under high vacuum for several hours before taking forward.

A portion of this material (1.75 mmol, based on initial loading of JandaJel) was suspended in 50 ml CH_2Cl_2 and treated with TFA (1.0 ml, 13.06 mmol) and triethylsilane (2.8 ml, 17.50 mmol). After 1 hour the reagents were removed by filtration, and the resin was washed with CH_2Cl_2 (3X). The process was repeated one more time to afford resin **4**, which was dried under high vacuumed overnight. Sulfhydryl loading was measured by concentrating the combined washes from both runs, and measuring the amount of triphenylmethanol formed in the reaction (296 mg, 1.23 mmol, 69%).

Mannose Resin S5:

Resin **2** (1.21 mmol) was suspended in CH_2Cl_2 (30 ml) and treated with **3**[1] (2.97 g, 3.6 mmol). The reaction was cooled to -40^{o}C and treated with TMSOTf (.55 ml, 3.10 mmol). After 2 h, the reaction mixture was filtered away and the resin was washed sequentially with CH_2Cl_2 (3 X 10 ml), MeOH (10 ml), CH_2Cl_2 (10 ml), MeOH (10 ml), and CH_2Cl_2 (10 ml). The resin was then dried under high vacuum for 4 h. This process was repeated two more times to afford **S4**.

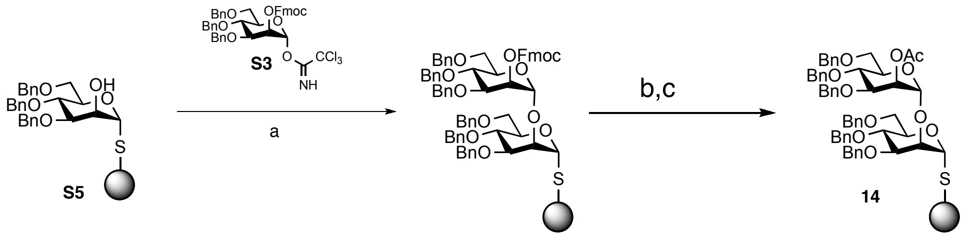
Resin **S4** was suspended in 50 ml of a mixture of DMF and piperidine (4:1). After 20 min, the solvent was removed by filtration, and the resin was washed sequentially with CH_2Cl_2, 1:1 CH_2Cl_2 : MeOH, and CH_2Cl_2. The resin was dried under high vacuum prior to the next step.

The free glycan loading on **S5** was calculated based on the absorbance of the dibenzofulvene-piperidine adduct at 301 nm[2] to be 1.20 mmol (99%).

Acetylated Resin 1:

Resin **S5** (1.20 mmol) was dissolved in pyridine (30 ml) and treated with acetic anhydride (1 ml, 10.56 mmol). After 1 h the resin was collected by filtration and washed sequentially with THF (10 ml), 1:1 THF:AcOH (10 ml), THF (10 ml), CH_2Cl_2 (10 ml), MeOH (10 ml), and CH_2Cl_2 (10 ml). The resin was then dried under high vacuum overnight.

Synthesis of Donor 14:



Scheme S2 *Reagents and conditions:* (a) **3**, TMSOTf, CH_2Cl_2 (3 cycles); (b) 20% piperidine/DMF (99%, 2 steps); (c) Ac_2O, pyridine (99%).

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[1] S. Jonke, K.-G. Liu, R. R. Schmidt, *Chem. Eur. J.* 2006, **12**, 1274-1290.
[2] W. S. Newcomb, T. L. Deegan, W. Miller, J. A. Porco Jr., Biotechnol. Bioeng. 1998, 61, 55-60.

Resin **S5** (0.84 mmol) was suspended in CH_2Cl_2, treated with **S3** (2.08 g, 2.53 mmol), cooled to -40 ^{o}C, and treated with TMSOTf (0.38 ml, 2.11 mmol). After 2 h, the resin was isolated by filtration, washed sequentially with CH_2Cl_2 (3 X 10 ml), MeOH (10 ml), CH_2Cl_2 (10 ml), MeOH (10 ml), and CH_2Cl_2 (10 ml), and dried under high vacuum overnight.

The resin was suspended in 4:1 DMF: piperidine (100 ml). After 20 min, the solvent was removed by filtration, and the resin was washed sequentially with CH_2Cl_2, 1:1 CH_2Cl_2 : MeOH, and CH_2Cl_2. The resin was dried under high vacuum prior to the next step.

The free glycan loading on **14** was calculated based on the absorbance of the dibenzofulvene-piperidine adduct at 301 nm to be 0.62 mmol (74%).

The resin was dissolved in pyridine (80 ml) and treated with acetic anhydride (10 ml, 105 mmol). After 1 h the resin was collected by filtration and washed sequentially with THF (10 ml), 1:1 THF: AcOH (10 ml), THF (10 ml), CH_2Cl_2 (10 ml), MeOH (10 ml), and CH_2Cl_2 (10 ml). The resin was then dried under high vacuum overnight.

General Procedure for BSP/Tf_2O-mediated transfer of sugar from resin to aglycone:

The glycosylated resin (0.10 mmol of sugar) and AW300MS were suspended in CH_2Cl_2, and treated with a solution of tri-tert-butylpyrimidine (0.20 mmol) in CH_2Cl_2 (1 ml) and a solution of benzenesulfinyl piperidine (0.11 mmol) in CH_2Cl_2 (1 ml). After stirring at room temperature for 5 min the reaction was cooled to – 60 ^{o}C and stirred for an additional 30 min. The reaction was then treated with Tf_2O (0.12 mmol), stirred for 5 min, and treated with a solution of acceptor (0.15 mmol) in CH_2Cl_2 (1 ml). The solution was maintained at -60 ^{o}C for an additional 2 h, then allowed to slowly to warm to room temperature overnight. The reaction was then neutralized with a few drops of Et_3N, and filtered and concentrated *in vacuo*. The crude mixture was purified by either flash column chromatography (ethyl acetate/hexanes) or preparative thin layer chromatography to afford the desired product.

Cholestryl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (3): $[\alpha]_D$ = +0.03 (c = 0.25, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 - 7.24 (m, 13H), 7.18 - 7.13 (m, 2H), 5.33 (t, *J* = 1.9 Hz, 1H), 5.28 (d, *J* = 5.1 Hz, 1H), 5.00 (d, *J* = 1.5 Hz, 1H), 4.86 (d, *J* = 10.6 Hz, 1H), 4.72 (d, *J* = 10.8 Hz, 1H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.2 Hz, 1H), 4.49 (d, *J* = 12.5 Hz, 1H), 4.47 (d, *J* = 11.1 Hz, 1H), 4.02-4.00 (m, 1H), 3.92 - 3.88 (m, 2H), 3.84 - 3.80 (m, 1H), 3.71 (d, *J* = 10.6 Hz, 1H), 3.53 – 3.45 (m, 1H), 2.33 - 2.27 (m, 2H), 2.15 (s, 3H), 2.01 (d, *J* = 12.4 Hz, 1H), 1.94 (d, *J* = 17.2 Hz, 1H), 1.90 - 1.79 (m, 3H), 1.53 - 1.41 (m, 6H), 1.38 - 1.31 (m, 3H), 1.27 – 1.24 (m, 1H), 1.18 - 1.02 (m, 7H), 1.01 – 0.89 (m, 10H), 0.87 (dd, *J* = 6.5, 1.8 Hz, 6H), 0.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.61, 140.57, 138.42, 138.29, 138.10, 128.28, 128.33, 128.28, 128.04, 127.96, 127.79, 127.68, 127.64, 127.53, 121.93, 95.84, 78.36, 75.24, 74.54, 73.40, 71.78, 71.36, 69.36, 68.99, 56.78, 56.17, 50.10, 42.34, 39.86, 39.78, 39.53, 36.98, 36.68, 36.20, 35.79, 31.94, 31.89, 29.70, 28.23, 28.02, 27.70, 24.30, 23.83, 22.81, 22.56, 21.17, 21.05, 19.33, 18.72, 11.86; LRMS (ESI) m/z: calcd for $C_{56}H_{76}O_7Na$ (m+23) 883.23, found 883.64; HRMS (ESI) m/z: calcd for $C_{56}H_{76}O_7Na$ (m+23) 883.5483, found 883.5465.

***O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)- stearyl glycyrrhetinate (9):** $[\alpha]_D$ = +0.31 (c = 0.40, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.25 (m, 13H), 7.19 – 7.14 (m, 2H), 5.64 (s, 1H), 5.27 (s, 1H), 5.10 (s, 1H), 4.86 (d, *J* = 10.7 Hz, 1H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.68 (d, *J* = 12.1

Hz, 1H), 4.55 (d, *J* = 11.2 Hz, 1H), 4.50 (d, *J* = 12.6 Hz, 1H), 4.48 (d, *J* = 10.9 Hz, 1H), 4.09 (m, 2H), 3.98 – 3.86 (m, 3H), 3.80 (d, *J* = 10.0 Hz, 1H), 3.68 (d, *J* = 10.6 Hz, 1H), 3.24 (dd, *J* = 11.6, 4.0 Hz, 1H), 2.82(d, *J* = 13.6 Hz, 1H), 2.31 (s, 1H), 2.15 (s, 3H), 2.11 (dd, *J* = 10.5, 3.3 Hz, 1H), 2.08 – 1.96 (m, 2H), 1.92 (d, *J* = 13.4 Hz, 1H), 1.82 (dt, *J* = 10.0, 3.3 Hz, 1H), 1.76 – 1.68 (m, 1H), 1.68 – 1.57 (m, 4H), 1.42 – 1.21 (m, 40H), 1.18 – 1.10 (m, 10H), 1.01 (d, *J* = 11.7 Hz, 1H), 0.96 (s, 3H), 0.93 – 0.85 (m, 4H), 0.79 (d, *J* = 14.5 Hz, 6H), 0.68 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.99, 176.47, 170.51, 138.49, 138.45, 137.92, 128.58, 128.37, 128.30, 128.25, 128.01, 127.74, 127.67, 127.62, 127.47, 94.44, 83.02, 78.09, 75.19, 74.44, 73.37, 72.14, 71.79, 69.91, 69.09, 64.57, 61.79, 55.26, 48.34, 45.42, 43.99, 43.24, 41.13, 38.68, 38.64, 37.80, 37.02, 32.81, 31.92, 31.84, 31.19, 30.88, 29.70, 29.67, 29.66, 29.64, 29.56, 29.52, 29.35, 29.18, 28.74, 28.56, 28.42, 26.51, 26.48, 25.98, 23.40, 22.68, 21.96, 21.15, 18.74, 17.47, 16.48, 16.37, 14.10; LRMS (ESI) (m/z): calcd for $C_{77}H_{112}O_{10}Na$ (m + 23) 1220.71, found 1220.07; HRMS (ESI) (m/z): calcd for $C_{77}H_{112}O_{10}Na$ (m + 23) 1219.8153, found 1219.8132.

_O_-(2-_O_-acetyl-3,4,6-tri-_O_-benzyl-α-D-mannopyranosyl)-_N_-[(9H-fluoren-9-ylmethoxy)carbonyl]-L-serine allyl ester (10): $[\alpha]_D$ = +0.01 (c = 0.23, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.5 Hz, 2H), 7.60 – 7.56 (m, 2H), 7.40 – 7.21 (m, 17H), 7.17 – 7.12 (m, 2H), 5.96 – 5.86 (m, 1H), 5.81 (d, *J* = 8.5 Hz, 1H), 5.34 (d, *J* = 17.1 Hz, 1H), 5.30 (s, 1H), 5.26 (d, *J* = 10.3 Hz, 1H), 4.87 – 4.80 (m, 2H), 4.71 – 4.62 (m, 4H), 4.60 – 4.56 (m, 1H), 4.54 (d, *J* = 4.5 Hz, 1H), 4.49 (d, *J* = 8.1 Hz, 1H), 4.46 (d, *J* = 6.8 Hz, 1H), 4.39 (dd, *J* = 10.5, 3.3 Hz, 1H), 3.97-3.94 (m, 1H), 4.21 (t, *J* = 7.2 Hz, 1H), 4.05 – 4.00 (m, 1H), 3.99 – 3.93 (m, 1H), 3.93 – 3.84 (m, 2H), 3.79 (d, *J* = 8.0 Hz, 1H), 3.76 (d, *J* = 4.0 Hz, 1H), 3.69 (d, *J* = 9.3 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.55, 169.72, 156.16, 144.05, 141.50, 138.49, 138.32, 138.03, 131.64, 128.66, 128.54, 128.33, 128.18, 128.15, 128.00, 127.93, 127.82, 127.35, 125.40, 120.18, 119.48, 114.93, 99.09, 78.10, 75.49, 74.34, 73.69, 72.29, 72.16, 69.48, 68.94, 68.80, 67.59, 66.65, 54.68, 47.32, 21.27; LRMS (ESI) (m/z): calcd for $C_{50}H_{51}NO_{11}Na$ (m + 23) 864.35, found 864.41; HRMS (ESI) (m/z): calcd for $C_{50}H_{51}NO_{11}Na$ (m + 23) 864.3354, found 864.3341.

_O_-(2-_O_-acetyl-3,4,6-tri-_O_-benzyl-α-D-mannopyranosyl)-_N_-(tert-butoxycarbonyl)-L-serine benzyl ester (11): $[\alpha]_D$ = +0.01 (c = 0.30, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 - 7.25 (m, 18H), 7.16 - 7.12 (m, 2H), 5.41 (d, *J* = 8.6 Hz, 1H), 5.25-5.22 (m, 2H), 5.15 (d, *J* = 12.3 Hz, 1H), 4.82 (d, *J* = 10.6 Hz, 1H), 4.75 (s, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.64 (d, *J* = 11.1 Hz, 1H), 4.58 - 4.49 (m, 1H), 4.48 (d, *J* = 5.1 Hz, 1H), 4.46-4.43 (m, 2H), 3.96 - 3.81 (m, 3H), 3.82 (dd, *J* = 9.3, 3.1 Hz, 1H), 3.80 - 3.74 (m, 1H), 3.72-3.70 (m, 1H), 3.66 (d, *J* = 10.6 Hz, 1H), 2.14 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.49, 170.28, 155.57, 138.56, 138.38, 138.07, 135.53, 128.88, 128.70, 128.64, 128.55, 128.53, 127.37, 128.13, 128.04, 127.84, 114.93, 98.85, 78.12, 77.11, 75.43, 74.22, 73.72, 72.14, 69.21, 68.78, 68.74, 67.64, 56.21, 54.22, 29.82, 28.53, 21.29; LRMS (m/z): calcd for $C_{44}H_{51}NO_{11}Na$ (m + 23) 792.88, found 792.44; HRMS (ESI) (m/z): calcd for $C_{44}H_{51}NO_{11}Na$ (m + 23) 792.3354, found 792.3370.

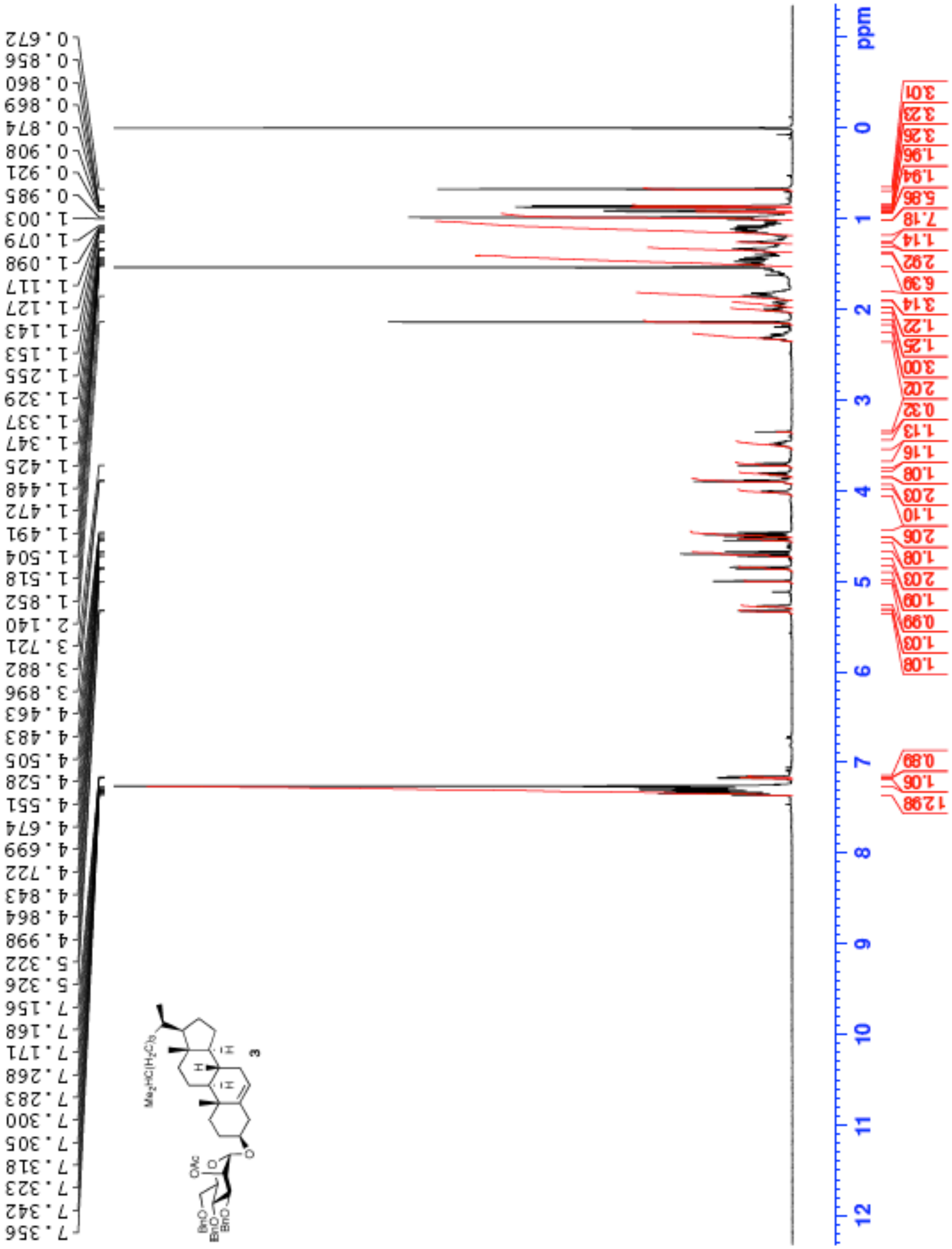
Phenyl 2-_O_-acetyl-3,4,6-tri-_O_-benzyl-α-D-mannopyranoside (12): $[\alpha]_D$ = -0.06 (c = 0.08, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 - 7.24 (m, 15H), 7.19 - 7.13 (m, 2H), 7.08 - 7.01 (m, 3H), 5.59 (s, 1H), 5.55 (d, *J* = 1.9 Hz, 1H), 4.89 (d, *J* = 10.6 Hz, 1H), 4.78 (d, *J* = 11.1 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 11.2 Hz, 1H), 4.50 (d, *J* = 10.7 Hz, 1H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.21 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.02 (t, *J* = 9.7 Hz, 1H), 3.92-3.91 (m, 1H), 3.81 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.65 (dd, *J* = 9.5, 1.1 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.41, 156.00, 138.41, 138.23, 138.00, 129.53, 128.44, 128.32, 128.28, 128.10, 127.84, 127.81, 127.78, 127.78, 127.64, 127.57, 127.55, 127.53, 96.11, 78.02, 75.23, 74.14, 73.37, 72.03, 68.66, 21.08. LRMS (ESI) (m/z): calcd for $C_{35}H_{36}O_7Na$ (m + 23) 591.66, found 591.38; HRMS (ESI) (m/z): calcd for $C_{35}H_{36}O_7Na$ (m + 23) 591.2353, found 591.2346.

Cedryl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (13): $[\alpha]_D$ = +0.04 (c = 0.10, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): δ 7.35 - 7.26 (m, 13H), 7.18-7.16 (m, 2H), 5.24 (s, 1H), 5.19 (s, 1H), 4.85 (d, *J* = 10.6 Hz, 1H), 4.69 (d, *J* = 9.0 Hz, 1H), 4.68 (d, *J* = 8.2 Hz, 1H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.48 (s, 1H), 4.5 (d, *J* = 3.7 Hz, 1H), 4.01-3.90 (m, 3H), 3.80 (dd, *J* = 10.6, 3.7 Hz, 1H), 3.64 (d, *J* = 10.6 Hz, 1H), 2.15 (s, 3H), 190-1.84 (m, 2H), 1.76-1.74 (m, 2H), 1.66-1.61 (m, 3H), 1.52-1.49 (m, 1H), 1.40-1.33 (m, 4H), 1.31 (s, 3H), 1.29-1.25 (m, 1H), 1.22 (s, 3H), 0.98 (s, 3H), 0.82 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.77, 138.50, 138.36, 138.02, 128.35, 128.28, 128.21, 128.06, 127.93, 127.71, 127.69, 127.57, 127.45, 92.16, 82.08, 77.18, 75.14, 74.67, 73.36, 71.63, 71.34, 70.28, 69.05, 57.39, 56.65, 53.84, 43.34, 41.37, 41.28, 36.96, 36.69, 31.04, 29.01, 27.85, 25.24, 25.07, 21.19, 15.54; LRMS (ESI) m/z: calcd for $C_{44}H_{56}O_7Na$ (m+23) 719.91, found 719.49; HRMS (ESI) m/z: calcd for $C_{44}H_{56}O_7Na$ (m+23) 719.3918, found 719.3936.

Cholesteryl 2-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (15): $[\alpha]_D$ = -0.02 (c = 0.25, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.27 7.14 (m, 30H), 5.62 (s, 1H), 5.30 (t, *J* = 2.5 Hz, 1H), 5.22 (s, 1H), 4.86 (d, *J* = 6.4 Hz, 1H), 4.84 (d, *J* = 6.8 Hz, 1H), 4.73-4,64 (m, 5 H), 4.62 (d, *J* = 5.1 Hz, 1H), 4.58(d, *J* = 8.9 Hz, 1H), 4.55(d, J = 12.0 Hz, 1H), 4.4.51-4.46 (m, 4H), 4.43 (d, J = 10.8 Hz, 1H), 4.16 (d, *J* = 2.3 Hz, 1H), 4.12 (dd, *J* = 9.3, 3.3 Hz, 1H), 3.93 (m, 1H), 3.84 – 3.75 (m, 3H), 3.72 (d, *J* = 5.6 Hz, 1H), 3.70 – 3.66 (m, 1H), 3.58 – 3.51 (m, 2H), 3.42 – 3.34 (m, 2H), 2.29 – 2.24 (m, 1H), 2.23 – 2.13 (m, 2H), 2.09 (s, 3H), 2.05 – 1.97 (m, 2H), 1.86 – 1.80 (m, 1H), 1.78 (d, *J* = 13.6 Hz, 1H), 1.62 (s, 1H), 1.60 – 1.55 (m, 1H), 1.53 – 1.44 (m, 5H), 1.43 (d, *J* = 4.4 Hz, 1H), 1.40 – 1.27 (m, 5H), 1.26 (s, 2H), 1.17 – 1.08 (m, 4H), 1.01 (dt, *J* = 3.1, 2.8 Hz, 3H), 0.95 (s, 2H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.69 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.44, 140.81, 139.37, 138.72, 138.64, 138.56, 138.20, 135.69, 128.60, 128.55, 128.53, 128.47, 128.44, 128.40, 128.34, 128.31, 128.01, 127.91, 127.71, 127.96, 127.68, 127.66, 127.53, 127.39, 127.35, 122.12, 98.79, 97.90, 82.91, 78.60, 78.38, 75.95, 75.34, 74.99, 74.79, 74.62, 73.73, 73.58, 72.93, 72.17, 72.01, 71.24, 69.73, 69.25, 69.15, 57.02, 56.41, 50.42, 42.58, 40.04, 39.77, 39.02, 37.41, 36.97, 36.44, 36.03, 32.19, 32.15, 29.81, 28.47, 28.25, 24.54, 24.07, 23.04, 22.79, 21.42, 21.29, 19.54, 18.96, 12.11. LRMS (ESI) m/z: calcd for $C_{83}H_{104}O_{12}Na$ (m+23) 1315.03, found 1315.76; HRMS (ESI) m/z: calcd for $C_{83}H_{104}O_{12}Na$ (m+23) 1315.7420, found 1315.7404.

***O*-[2-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)- 3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl]-*N*-[(9H-fluoren-9-ylmethoxy)carbonyl]-L-serine allyl ester (16):** $[\alpha]_D$ = -0.01 (c = 0.50, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.60 Hz, 2H), 7.61 – 7.55 (m, 2H), 7.37 – 7.27 (m, 20H), 7.25 – 7.17 (m, 11H), 7.17 – 7.13 (m, 3H), 5.90 – 5.80 (m, 2H), 5.51 (s, 1H), 5.31 – 5.25 (m, 1H), 5.19 (d, *J* = 10.5 Hz, 1H), 5.01 (s, 1H), 4.88 (s, 1H), 4.84 (s 1H), 4.83 (s, 1H), 4.67 (d, *J* = 4.3 Hz, 1H), 4.66 – 4.59 (m, 5H), 4.56 (d, *J* = 8.5 Hz, 1H), 4.51 (d, *J* = 9.3 Hz, 1H), 4.49 – 4.43 (m, 3H), 4.40 (d, *J* = 10.9 Hz, 1H), 4.37 – 4.26 (m, 3H), 4.20 (t, *J* = 7.2 Hz, 1H), 3.97 – 3.90 (m, 2H), 3.89 (s, 1H), 3.86 – 3.77 (m, 5H), 3.76 – 3.72 (m, 2H), 3.72 – 3.67 (m, 2H), 3.35 (s, 1H), 2.11 (s, 3H), ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.32, 169.80, 156.19, 144.09, 144.02, 141.49, 138.62, 138.58, 138.53, 138.46, 138.34, 138.20, 131.76, 128.66, 128.56, 128.51, 128.36, 128.30, 128.15, 128.13, 128.08, 127.93, 127.91, 127.88, 127.87, 127.84, 127.80, 127.73, 127.63, 127.34, 125.42, 120.15, 119.07, 114.93, 100.03, 99.90, 79.41, 78.31, 75.45, 75.36, 75.33, 74.61, 73.69, 73.52, 72.66, 72.46, 72.15, 69.41, 69.36, 69.32, 68.97, 67.53, 66.36, 54.70, 47.32, 31.29, 29.92, 21.32; LRMS (ESI) m/z: calcd for $C_{77}H_{79}NO_{16}Na$ (m+23) 1296.00, found 1296.55; HRMS (ESI) m/z: calcd for $C_{77}H_{79}NO_{16}Na$ (m+23) 1296.5291, found 1296.5264.

Phenyl 2-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-Mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (17): $[\alpha]_D$ = +0.01 (c = 0.17, CH_2Cl_2); ^1H ^1H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.30 (m, 4H), 7.31 – 7.19 (m, 25H), 7.17 – 7.11 (m, 3H), 7.03 (d, *J* = 8.25 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 5.68 (s, 1H), 5.58 (s, 1H), 5.12 (s, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.7 Hz, 1H), 4.77 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.67 (d, *J* = 10.9 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.59 (d, J = 12.7 Hz, 2H), 4.47-4.43 (m, 3H), 4.41 (d, *J* = 10.9 Hz, 1H), 4.18 (s, 1H), 4.15 (dd, *J* = 9.4, 2.8 Hz, 1H), 4.03 – 3.96 (m, 3H), 3.88 – 3.835 (m, 1H), 3.82 (d, *J* = 9.7 Hz, 1H), 3.80 - 3.75 (m, 1H), 3.74-3.71 (m, 1H), 3.70 – 3.63 (m, 3H), 2.12 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 170.34, 156.29, 138.69, 138.63, 138.61, 138.54, 138.35, 138.25, 129.68, 128.66, 128.56, 128.52, 128.50, 128.47, 128.38, 128.07, 127.95, 127.89, 127.85, 127.79, 127.76, 127.72, 127.59, 122.49, 116.76, 99.90, 97.12, 79.65, 78.41, 75.41, 75.33, 74.95, 74.68, 74.63, 73.56, 73.45, 72.69, 72.55, 72.28, 72.22, 69.28, 69.19, 68.98, 21.34. LRMS (ESI) m/z: calcd for $C_{62}H_{64}O_{12}Na$ (m+23) 1024.15, found 1123.49; HRMS (ESI) m/z: calcd for $C_{62}H_{64}O_{12}Na$ (m+23) 1023.4295, found 1023.4298.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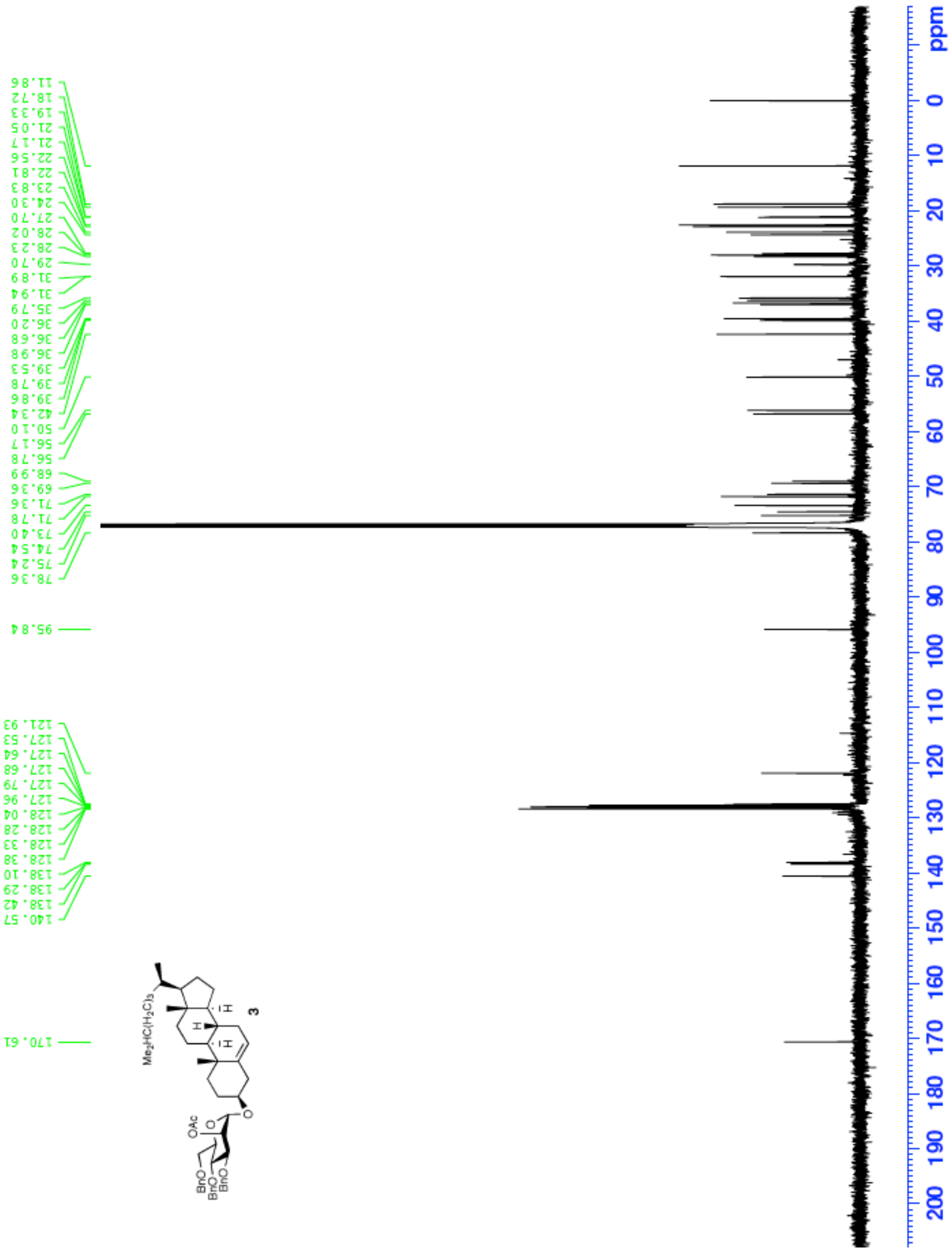
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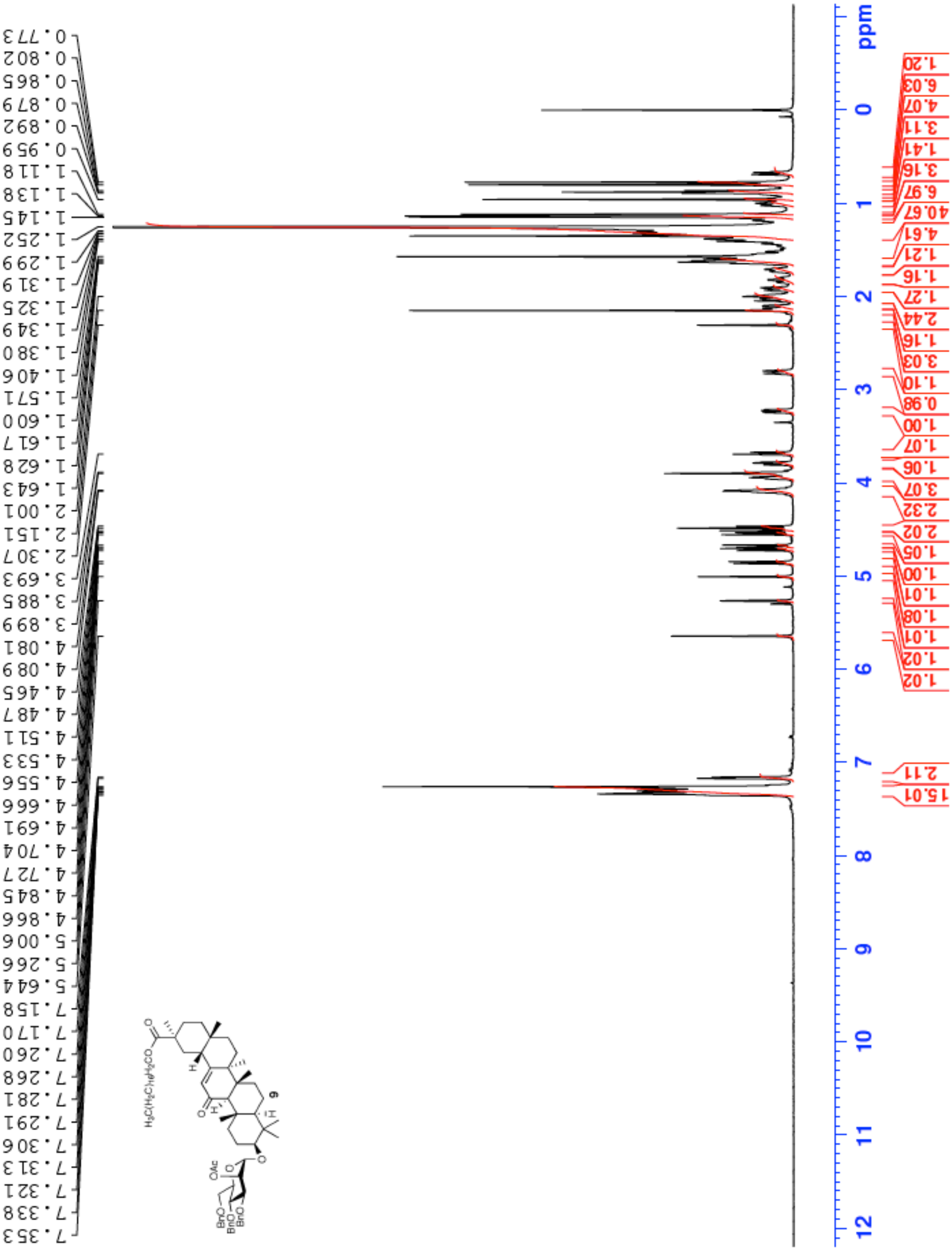
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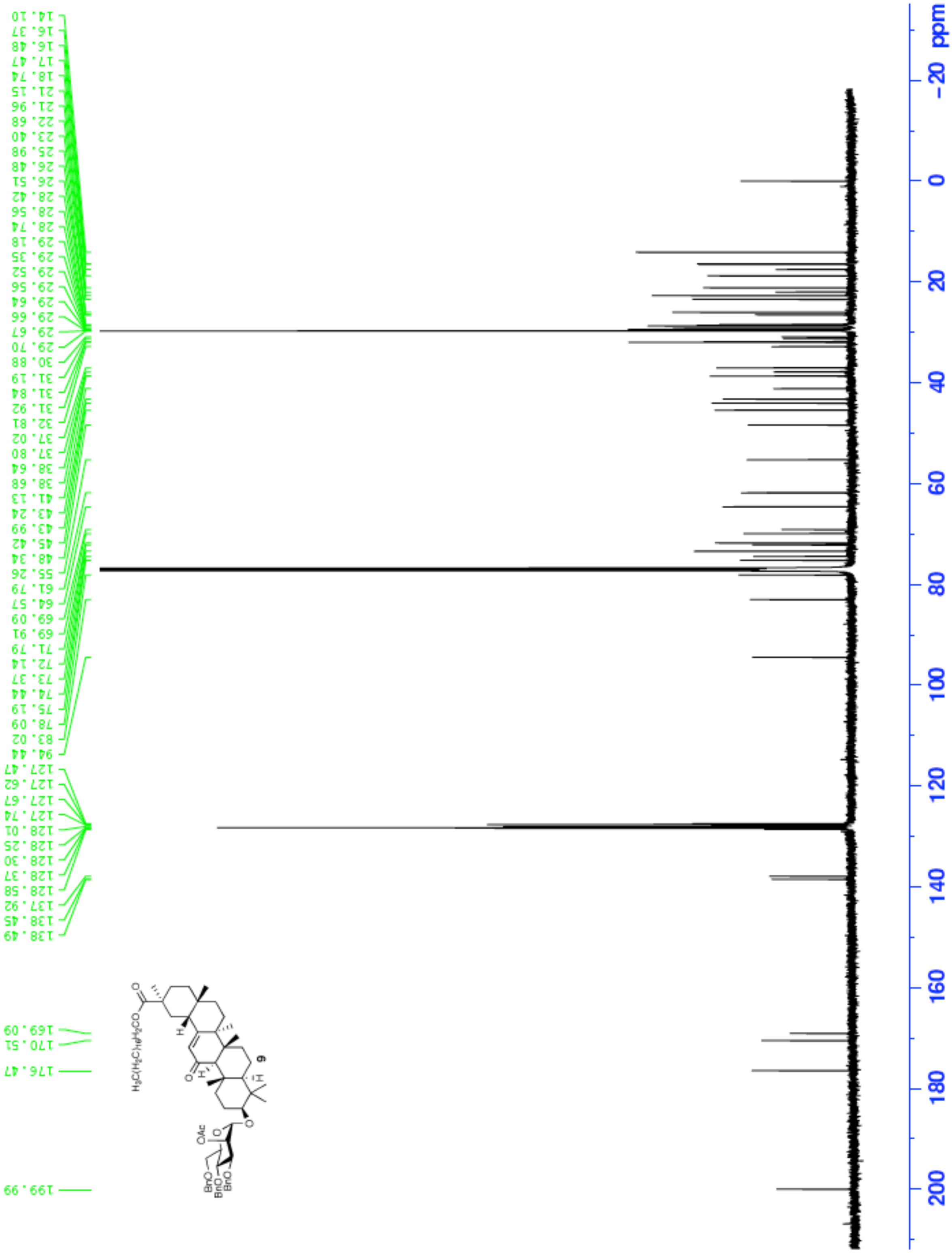
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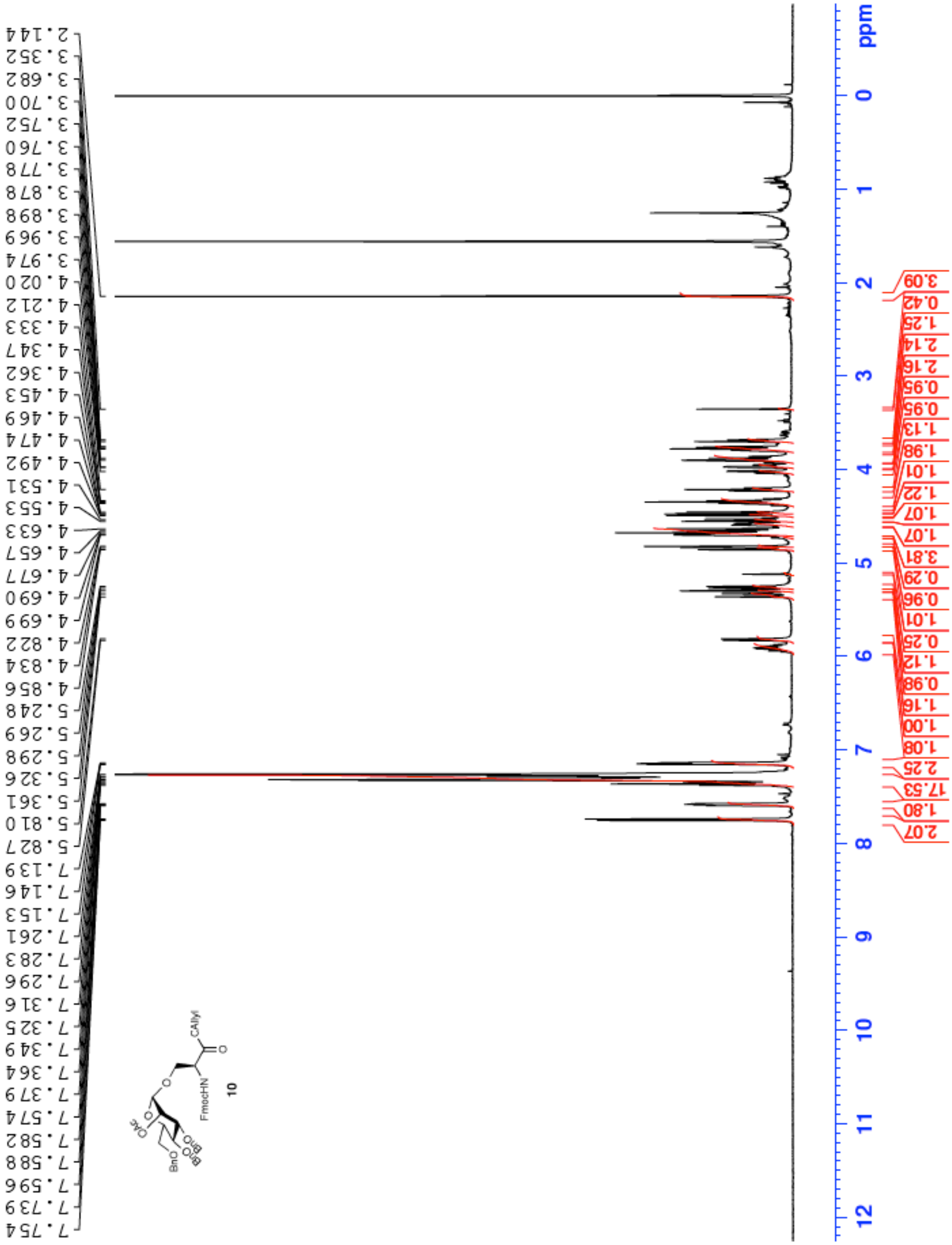
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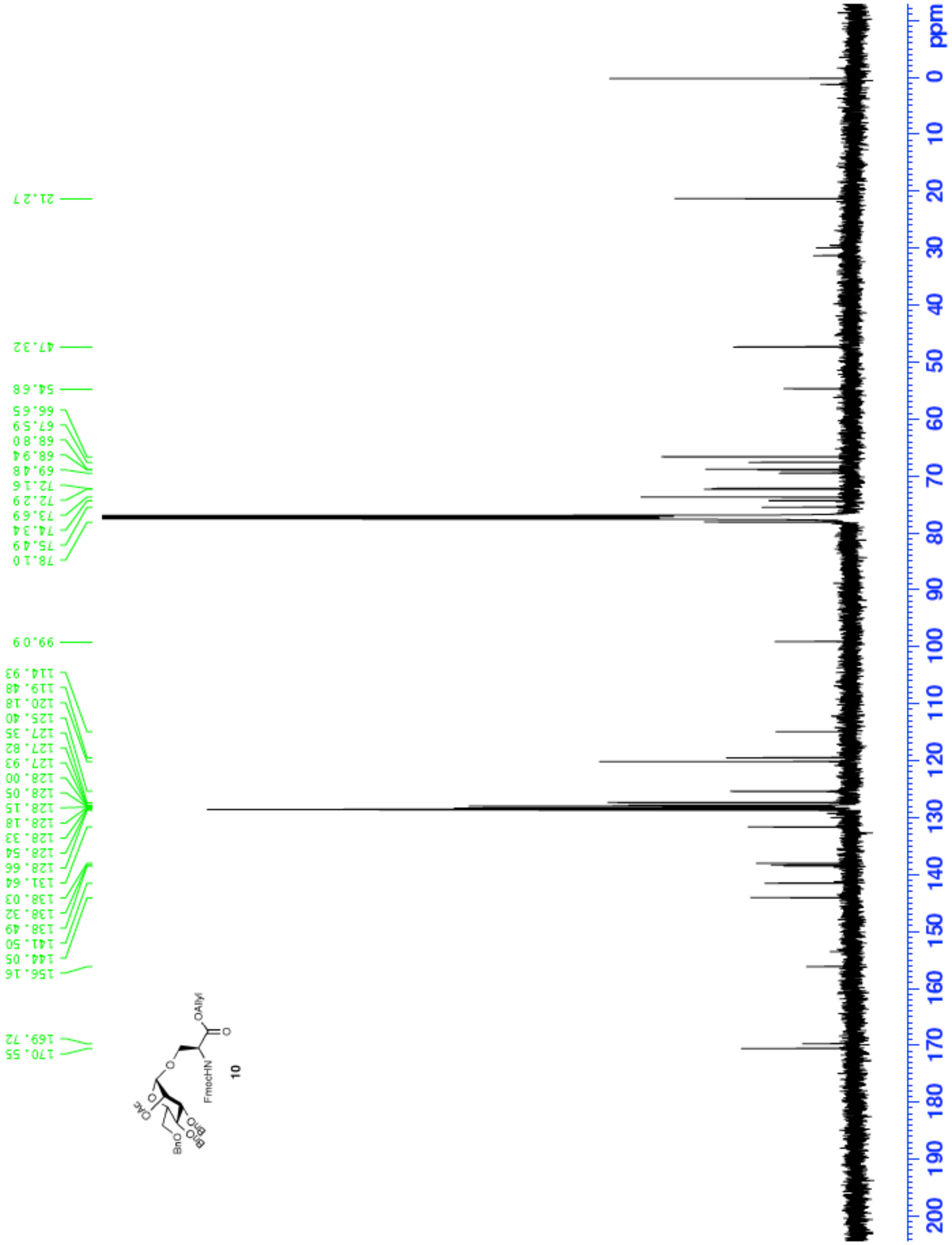
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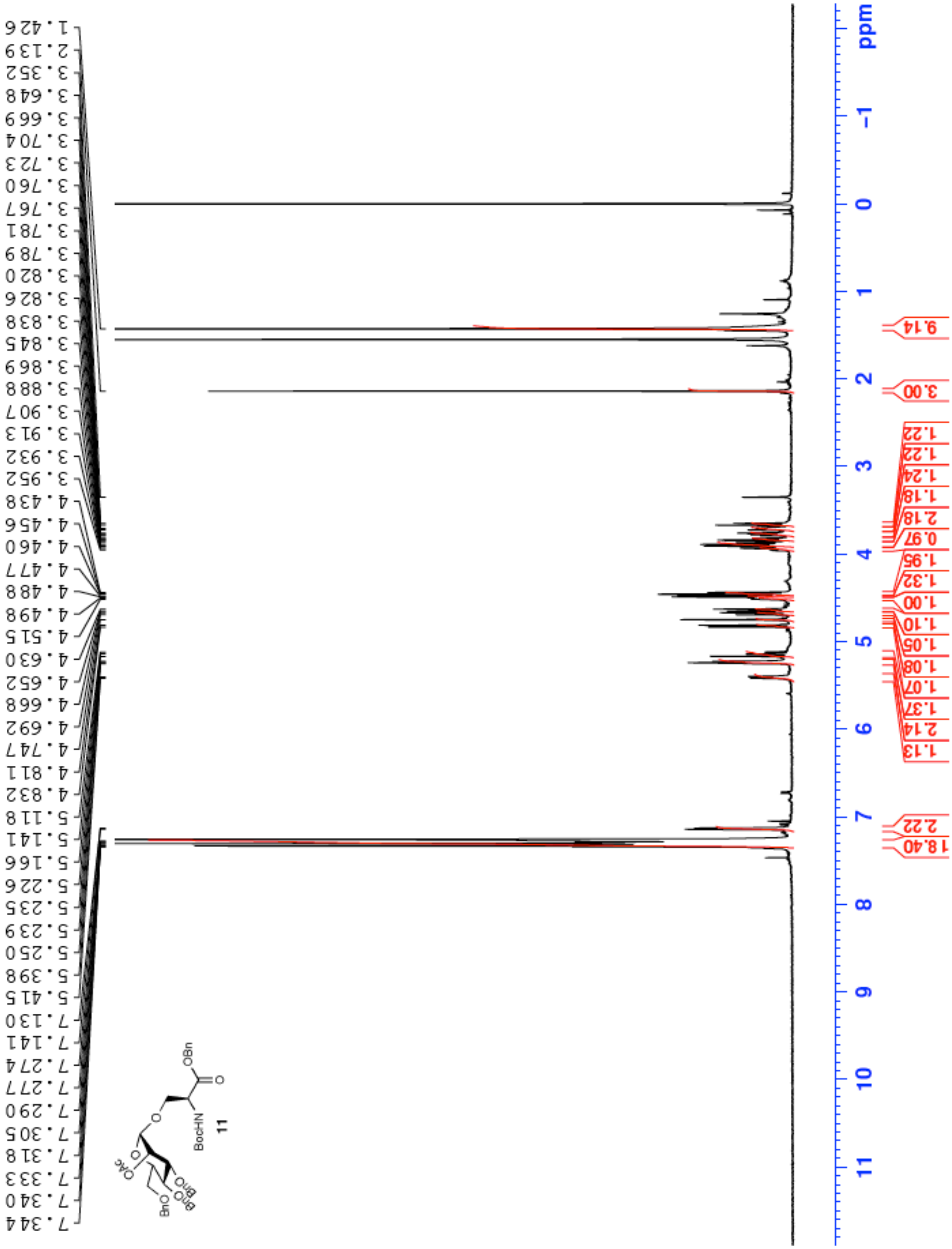
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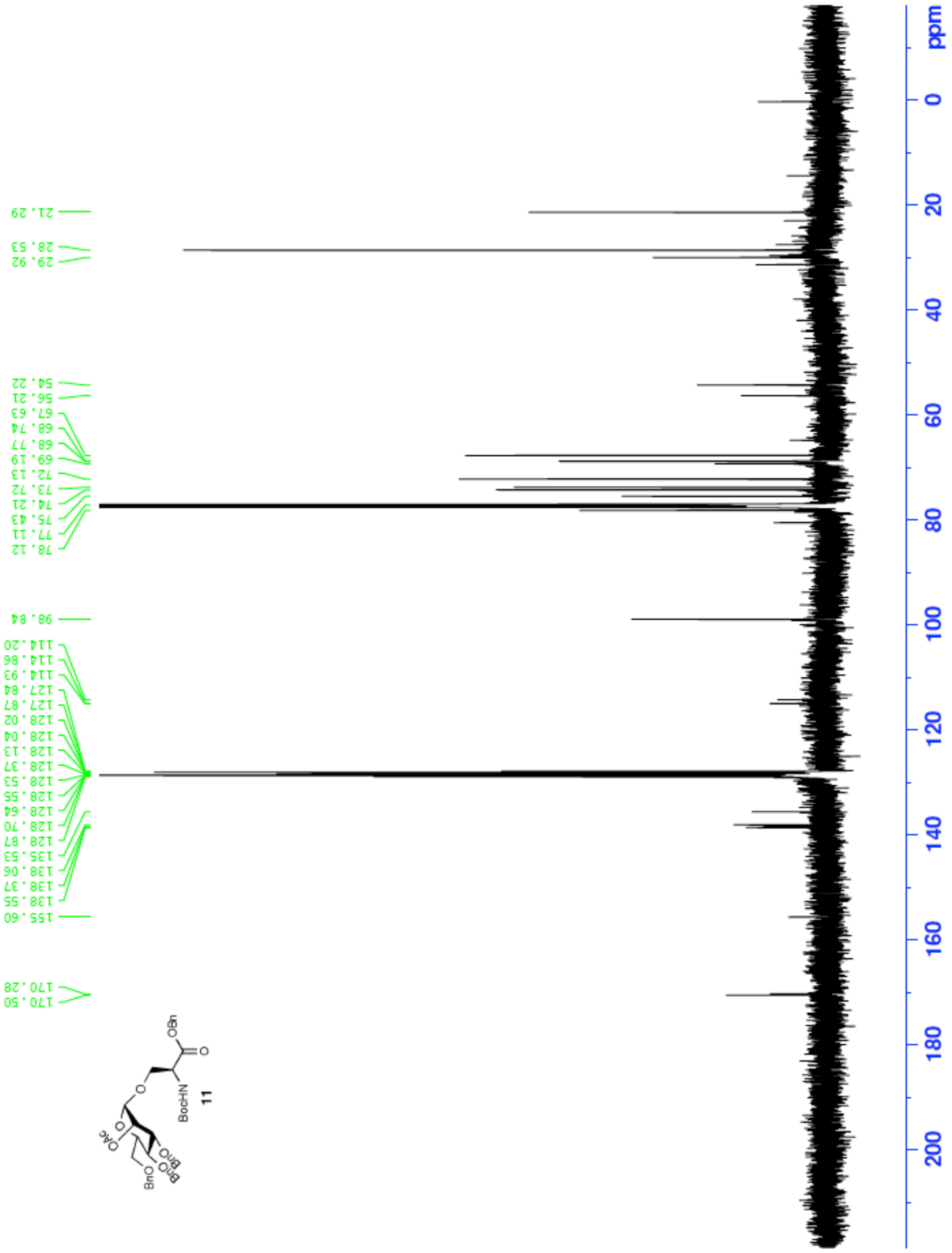
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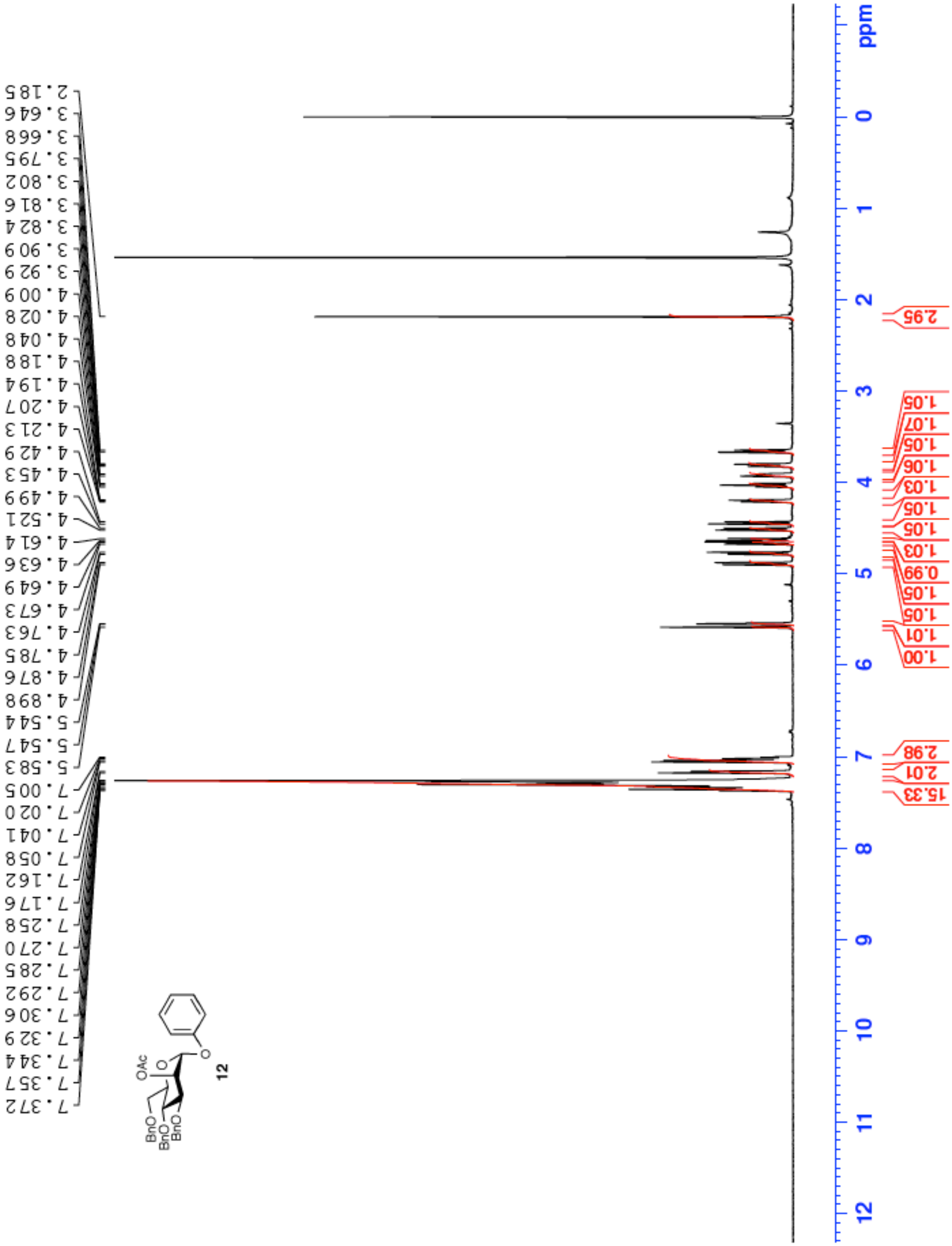
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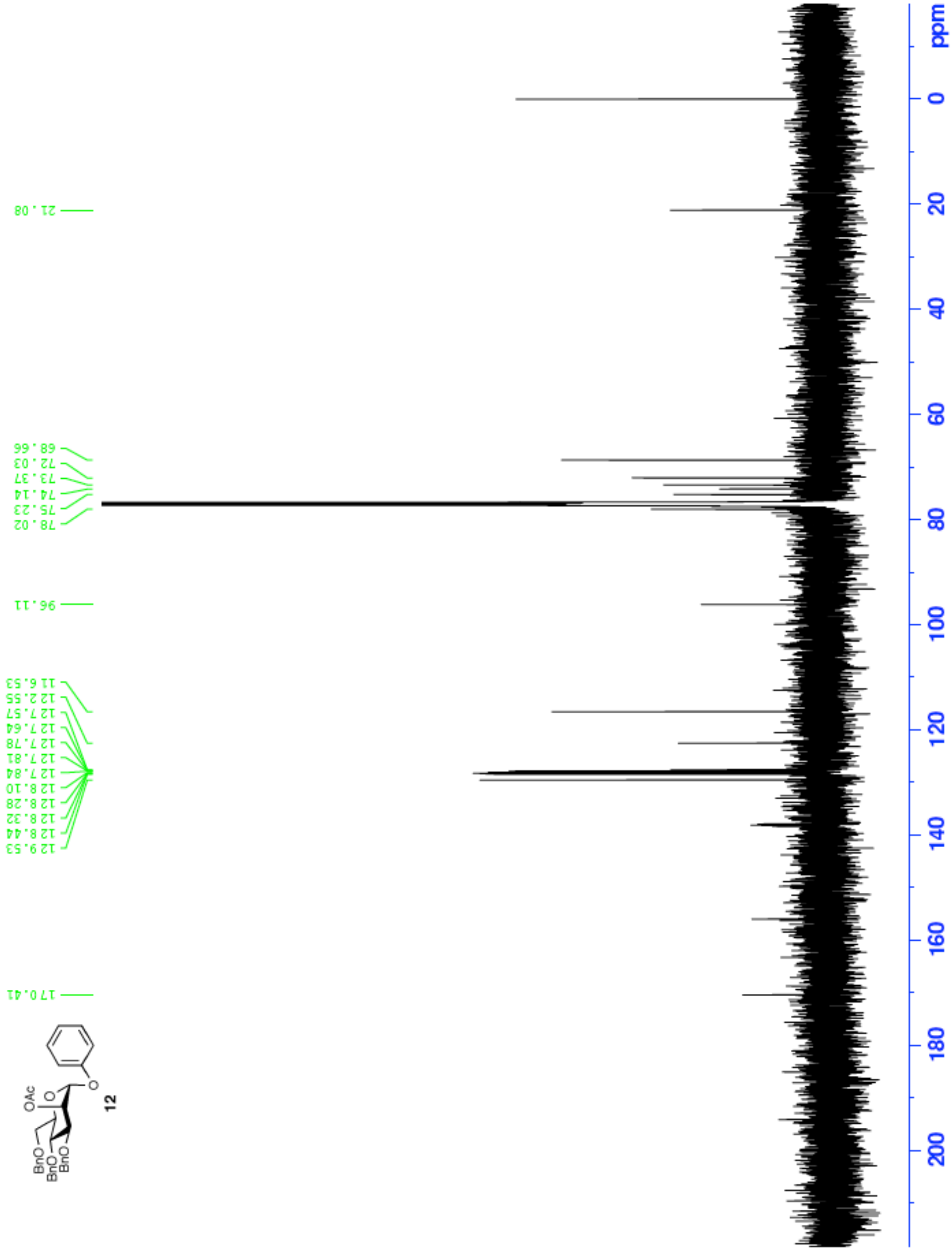
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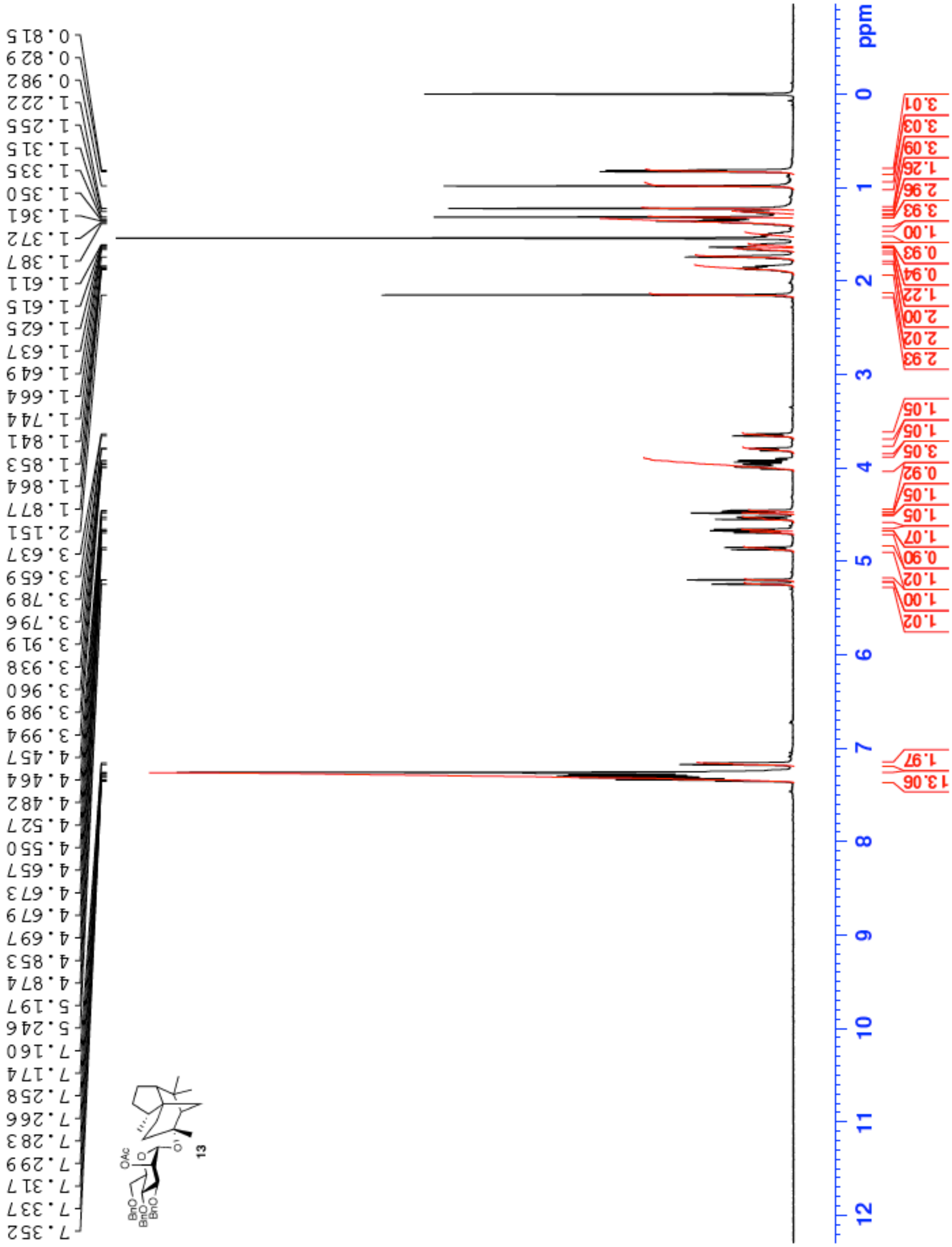
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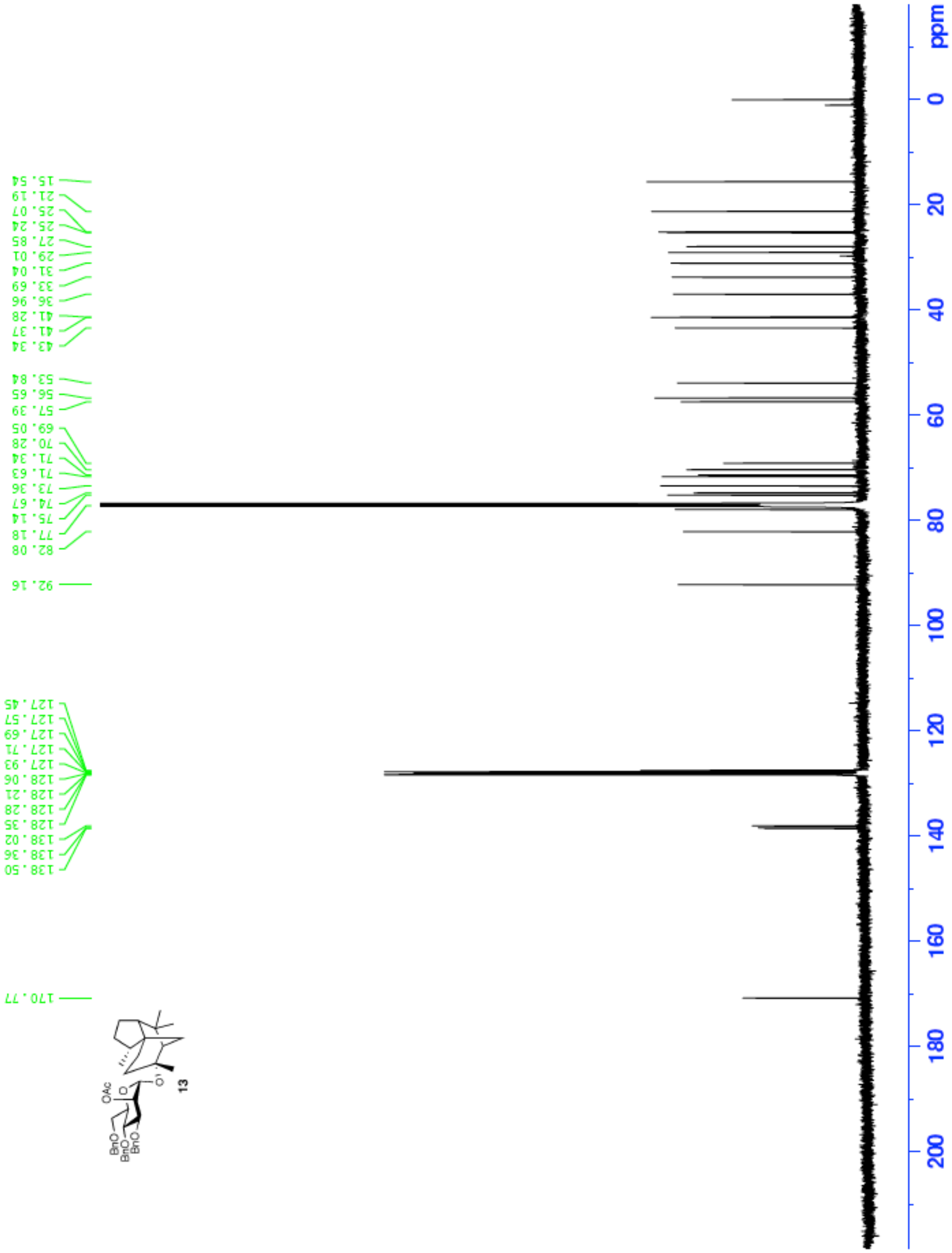
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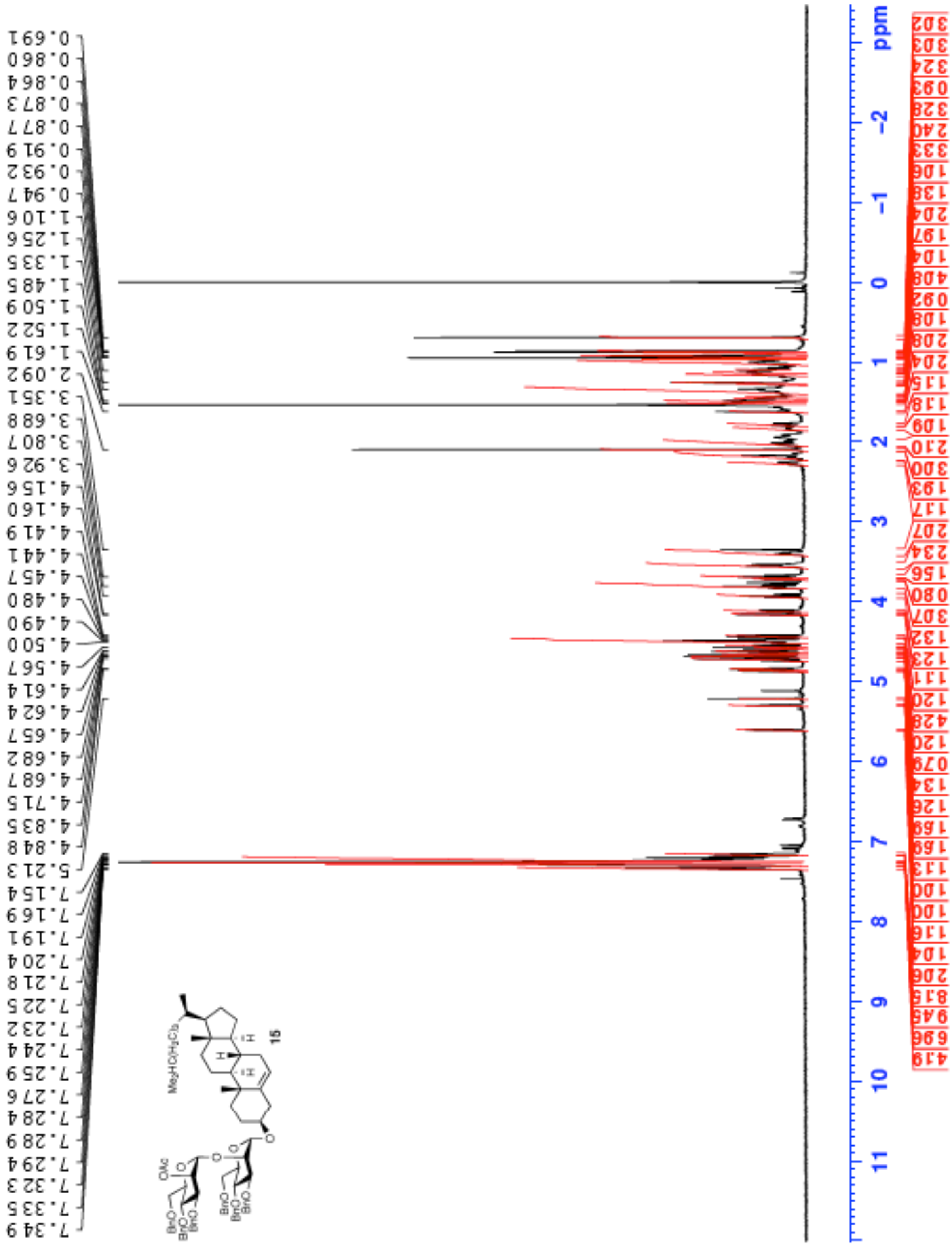
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4.457
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4.490
4.500
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9
10
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3.03
3.24
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1.00
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1.04
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6.96
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BnO
BnO
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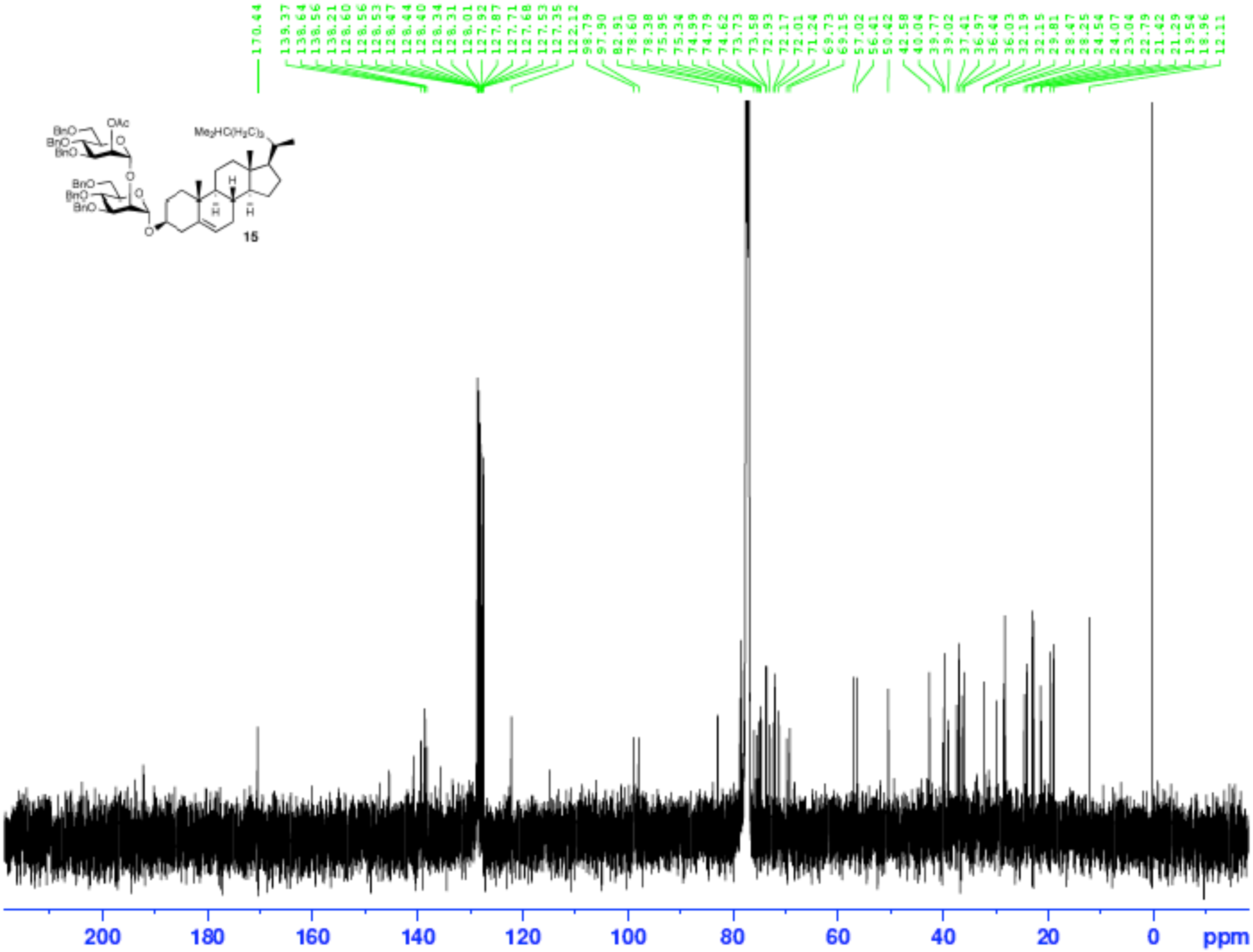
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78.38
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74.79
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73.73
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72.01
71.24
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69.15
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39.77
39.02
37.41
36.97
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28.25
24.54
24.07
23.04
22.79
21.42
21.29
19.54
18.96
12.11
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BnO
BnO
OAc
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O
BnO
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BnO
O
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H
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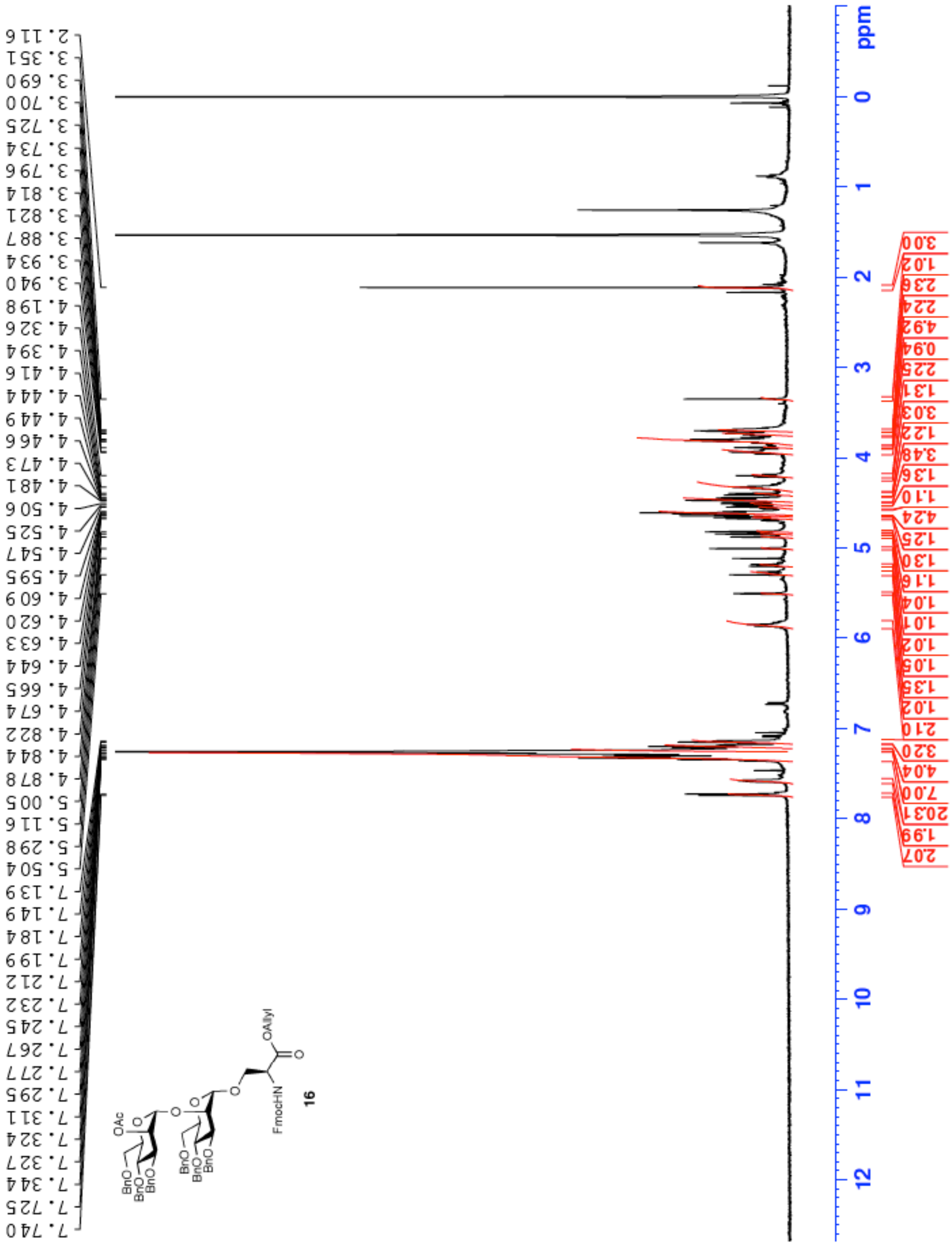
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4.24
1.25
1.30
1.16
1.04
1.01
1.02
1.05
1.35
1.02
2.10
3.20
4.04
7.00
20.31
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2.07
OAc
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BnO
BnO
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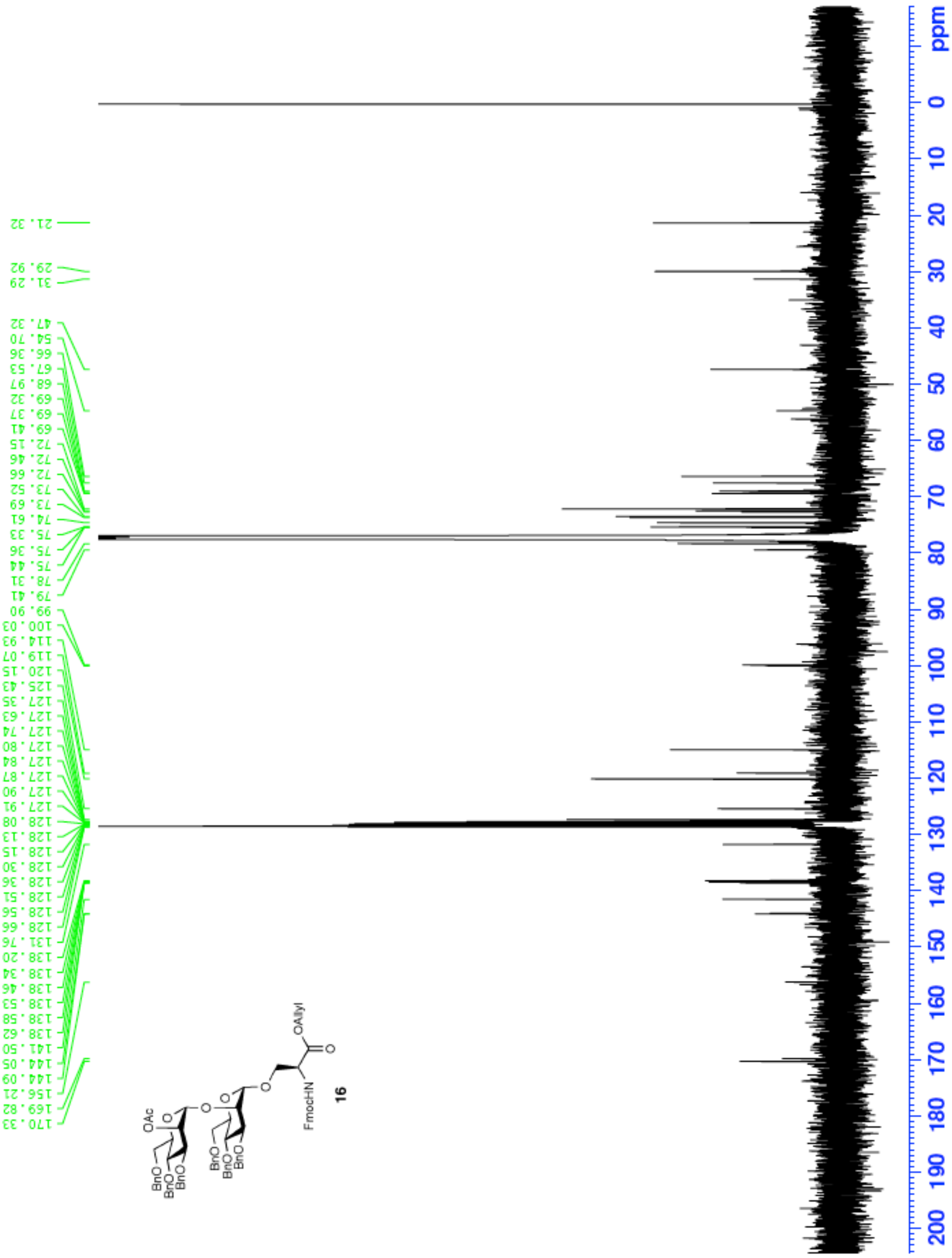
FmocHN
O
OAllyl
16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138.62
141.50
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156.21
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170.33
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BnO
BnO
OAc
O
O
BnO
BnO
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O
O
FmocHN
OAllyl
O
16
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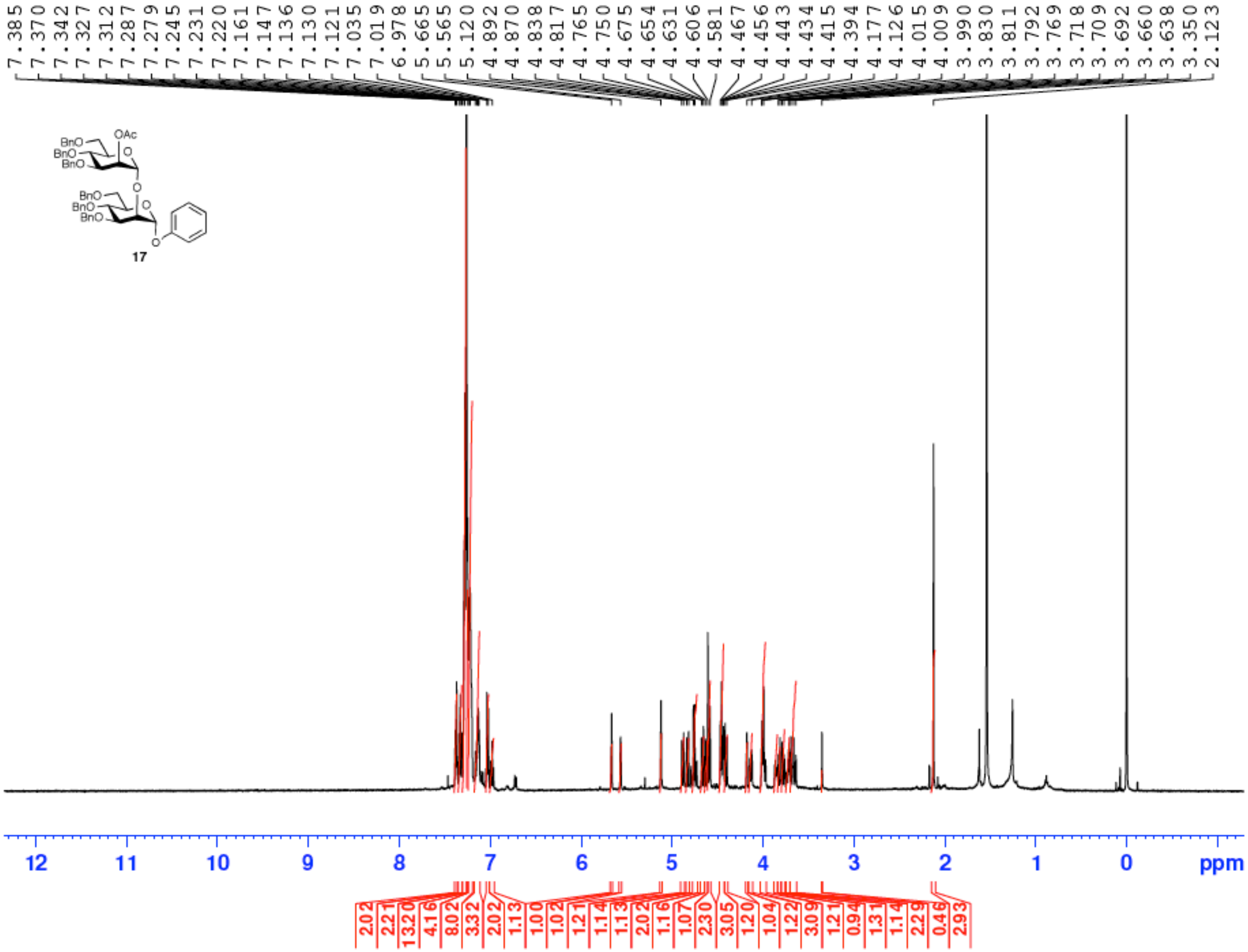
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4.654
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3.638
3.350
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BnO
BnO
OAc
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BnO
BnO
BnO
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8
7
6
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4
3
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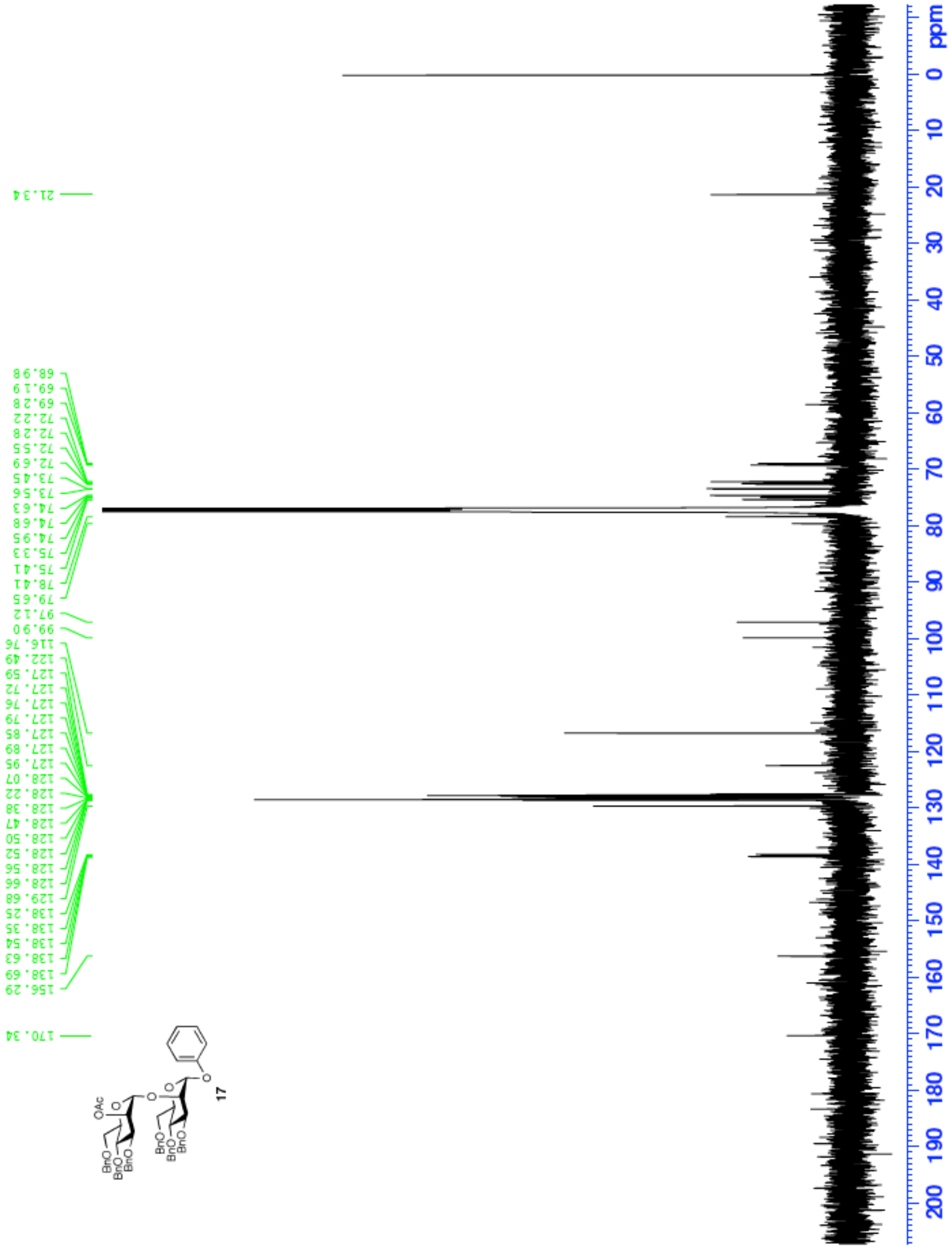
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OAc
BnO
BnO
BnO
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BnO
BnO
BnO
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ppm
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50
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90
100
110
120
130
140
150
160
170
180
190
200

17