Supporting Information

Stereoselective Chemical Synthesis of α(2,8) octasialosides, the minimum structure of polysialic acids

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NMR spectra were recorded on a JEOL Model ECP-400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) or Bruker AVANCE III HD (400 MHz for ^{1}H, 100 MHz for ^{13}C) instrument in the indicated solvent. Chemical shifts are reported in units of parts per million (ppm) relative to the signal for internal tetramethylsilane (0 ppm for ^{1}H) for solutions in $CDCl_3$. ^{1}H NMR spectral data are reported as follows: $CDCl_3$ (7.26 ppm) or CD_3CN-d_3 (1.94 ppm) or D_2O (internal aceton : 2.22 ppm). ^{13}C NMR spectral data are reported as follows: $CDCl_3$ (77.0 ppm), or CD_3CN-d_3 (118.3 ppm) or D_2O (internal aceton : 30.9 ppm). Multiplicities are reported by using the following abbreviations: s, singlet; br-s, broaded-singlet; d, doublet; br-d, broaded-doublet; dd, doublet of doublets; br-dd, broaded-doublet of doublets; t, triplet; dq, doublet of quartets; q, quartet, m, multiplet; and, *J*, coupling constants in Hertz.

IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrophotometer or JASCO FT/IR-4200 spectrophotometer. Only the strongest and/or structurally important absorption is reported as the IR data in cm^{-1}.

Optical rotations were measured on a JASCO model P-1020 polarimeter.

All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light, visualized by *p*-anisaldehyde solution, ceric sulfate or ethanolic phosphomolybdic acid.

Column chromatography separations were performed using silica gel (Merck silica gel 60, 0.063 – 0.200 mm). NH column chromatography separations were performed using silica gel (Fuji Silysia CHROMATOREX NH-DM1020). Flash column chromatography separations were performed using silica gel (KANTO, silica gel 60 N, spherical, neutral, 40-100μm).

High performance liquid chromatography (HPLC) for qualitative and quantitative analysis were performed on a Gilson 506C system using a SHODEX ODS column (4.6 × 250 mm).

ESI-TOF Mass spectra were measured with AppliedBioSystems Mariner TK-3500 Biospectrometry Workstation mass spectrometers and Waters LCT Premier™ XE. HRMS(ESI-TOF) were calibrated with angiotensin I (SIGMA), bradykinin (SIGMA), and neurotensin (SIGMA) as an internal standard.

Gel permeation chromatography (GPC) for quantitative analysis were performed on a Japan Analytical Industry Model LC 605 (recycling preparative HPLC), with a Japan Analytical Industry Model RI-5 refractive index detector and a Japan Analytical Industry Model 301 ultra violet detector with polystylene gel column (JAIGEL1H, 20 mm x 600 mm) using chloroform as a solvent (3.50 mL/min).

Microwave-assisted syntheses were performed on CEM Discover® SP with 10 mL and 35 mL sealed reaction vessels.

Dry CH_2Cl_2, Et_2O, MeCN, PhMe and THF were purified by GlassCountour. Dry EtCN was distilled from calcium hydride. Dry DMF was distilled from CaH_2. *N*-iodosuccinimide was purified by recrystallization from dioxane-CCl_4 at 0 °C. *N*-bromosuccinimide was purified by recrystallization from water at 0 °C.

Methyl (phenyl 5-amino-9-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-β-D-*galacto*-2-nonulopyranosid)onate (12)

To a solution of methyl (phenyl 5-amino-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-β-D-*galacto*-2-nonulopyranosid)onate (**11**) (52.1 mg, 0.130 mmol) in CH_2Cl_2 (1.30 mL, 10.0 mL/mmol) was added imidazole (17.7 mg, 0.261 mmol) and TBSCl (29.6 mg, 0.196 mmol) at 0 ºC to room temperature. After being stirred at the same temperature for 1 h, the reaction mixture was poured into ethyl acetate and saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. NH_4Cl and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 97:3 chloroform-methanol to give **12** (63.9 mg, 0.124 mmol, 95%).

$[\alpha]_D^{14}$ -181 (c 1.97, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.32 (m, 5H, aromatic), 6.12 (s, 1H, NH), 4.70 (ddd, 1H, H-4, $J_{3ax.,4}$, $J_{4,5}$ = 11.2 Hz, $J_{3eq.,4}$ = 3.6 Hz), 4.44 (dd, 1H, H-6, $J_{5,6}$ = 10.0 Hz, $J_{6,7}$ = 6.4 Hz), 3.86 (dd, 1H, H-8, $J_{7,8}$ = 4.0 Hz, J = 10.0 Hz), 3.77 (dd, H-7, $J_{6,7}$ = 10.0 Hz, $J_{7,8}$ = 5.6 Hz), 3.67-3.64 (m, 4H, H-9a, OMe), 3.56-3.55 (m, 1H, H-9b), 3.09 (d, 1H, OH, J = 4.8 Hz), 2.96 (d, 1H, OH, J = 4.0 Hz), 2.92 (dd, 1H, H-3eq, $J_{3eq.,4}$ = 4.0 Hz J_{gem} = 12.8 Hz), 2.36 (t, 1H, H-3ax, $J_{3ax.,4}$, $J_{3eq.,3ax.}$ = 12.8 Hz), 0.92 (s, 9H, Si-^{t}Bu), 0.13 (s, 3H, Si-Me-a), 0.11 (s, 3H, Si-Me-b); **^{13}C NMR** (100MHz, $CDCl_3$) δ 178.2, 168.8, 168.3, 159.9, 159.8, 136.7, 136.4, 130.6, 130.1, 129.1, 129.09, 129.05, 129.0, 128.4, 128.3, 88.8, 87.6, 79.9, 78.2, 77.5, 77.4, 77.2, 76.8, 73.0, 72.7, 70.5, 70.0, 65.0, 64.0, 58.9, 57.7, 53.3, 52.9 37.0, 29.7, 25.9, 18.4, 18.3, -5.31, -5.36; **IR** (KBr) 3437, 3387, 2949, 2933, 2886, 2859, 1765, 1256, 1066, 1016, 834 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{23}H_{35}NO_8SSi$ $[M+H]^+$ 514.1932, found 514.1931.

Methyl (phenyl 5-amino-8,9-di-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-β-D-*galacto*-2-nonulopyranosid)onate (13)

To a solution of **12** (112 mg, 0.217 mmol) in Pyridine (1.80 mL, 8.50 mL/mmol) was added TBSOTf (80.0 μL, 0.347 mmol) at 0 ºC. After being stirred and warmed up to room temperature for 22 h, the reaction mixture was poured into ethyl acetate and saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. NH_4Cl and brine, dried over $MgSO_4$, filtered, and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 90:10 chloroform-methanol to give **13** (128 mg, 0.204 mmol, 94%).

$[\alpha]_D^{16}$ -88.8 (c 1.27, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.30 (m, 5H, aromatic), 5.08 (s, 1H, NH), 4.67 (dt, 1H, H-4, $J_{3ax.,4}$, $J_{4,5}$ = 3.9 Hz, $J_{3eq.,4}$ = 12.7 Hz), 4.56 (dd, 1H, H-6, $J_{5,6}$ = 9.8 Hz, $J_{6,7}$ = 3.9 Hz), 3.87 (dd, 1H, H-7, $J_{6,7}$ = 3.9 Hz, $J_{7,8}$ = 10.2 Hz), 3.79-3.74 (m, 3H, H-8, H-9a, H-9b), 3.59 (s, 3H, OMe), 3.52 (t, 1H, H-5, $J_{4,5}$, $J_{5,6}$ = 10.8 Hz), 2.85 (dd, 1H, H-3eq., $J_{3eq.,4}$ = 3.9 Hz J_{gem} = 13.2 Hz), 2.33 (t, 1H, H-3ax., $J_{3ax.,4}$, $J_{3eq.,3ax.}$ = 12.7 Hz), 0.98 (s, 9H, Si-^{t}Bu-a), 0.92 (s, 9H, Si-^{t}Bu-b), 0.16 (s, 3H, Si-Me-a), 0.14 (s, 3H, Si-Me-b), 0.096 (s, 3H, Si-Me-c), 0.085 (s, 3H, Si-Me-d); **^{13}C NMR** (100MHz, $CDCl_3$) δ 168.3, 159.2, 136.6, 136.0, 130.0, 129.6, 129.2, 129.0, 89.0, 77.6, 77.5, 77.4, 77.2, 76.8, 74.7, 74.0, 73.5, 66.0,

59.2, 52.9, 36.9, 30.8, 26.5, 26.1, 26.0, 19.0, 18.6, 18.3, -3.90, -4.23, -4.27, -5.28, -5.35; **IR** (KBr) 3321, 2953, 2931, 2889, 2857, 1767, 1255, 834, 777 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{29}H_{49}NO_8SSi_2$ $[M+H]^+$ 628.2795, found 628.2796.

Methyl (phenyl 5-amino-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-β-D-*galacto*-2-nonulopyranosid)onate (14)

To a solution of **13** (93.6 mg, 0.149 mmol) in CH_2Cl_2 (3.00 mL, 20.0 mL/mmol) was added $BF_3 \cdot OEt_2$ (20.5 μL, 0.164 mmol) at -78 ºC. After being stirred and warmed up to -35 ºC for 4 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 99:1 chloroform-methanol to give **14** (65.0 mg, 0.126 mmol, 85%).

$[\alpha]_D^{29}$ -27.0 (c 0.192, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.33 (m, 5H, aromatic), 5.79 (s, 1H, NH), 4.71 (dt, 1H, H-4, $J_{3ax.,4}$, $J_{4,5}$ = 2.9 Hz, $J_{3eq.,4}$ = 11.2 Hz), 4.44 (dd, 1H, H-6, $J_{5\text{-}6}$ = 9.8 Hz, $J_{6,7}$ = 2.4 Hz), 3.82-3.80 (m, 2H, H-7, H-9a), 3.68-3.62 (m, 6H, H-5, H-8, H-9b, OMe), 3.52 (brs, 1H, OH) 2.87 (dd, 1H, H-3eq., $J_{3eq.,4}$ = 3.9 Hz J_{gem} = 13.7 Hz), 2.77 (brs, 1H, OH) 2.33 (t, 1H, H-3ax., $J_{3ax.,4}$, $J_{3eq.,3ax.}$ = 13.2 Hz), 0.92 (s, 9H, Si-^{t}Bu), 0.14 (s, 3H, Si-Me-a), 0.13 (s, 3H, Si-Me-b); **^{13}C NMR** (100MHz, $CDCl_3$) δ 168.8, 160.1, 134.0, 130.1, 129.5, 129.3, 88.8, 75.2, 73.0, 72.7, 64.5, 58.6, 53.1, 36.7, 26.1, 18.3, -4.02, -4.22; **IR** (KBr) 3349, 3330, 2952, 2930, 2856, 1760, 1258, 1015 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{23}H_{36}NO_8SSi$ $[M+H]^+$ 514.1931, found 514.1931.

Methyl (phenyl 5-amino-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-β-D-*galacto*-2-nonulopyranosid)onate (15)

To a solution of **14** (94.1 mg, 0.183 mmol) in CH_2Cl_2 (7.34 mL, 40.0 mL/mmol) were added DMAP (47.0 mg, 0.385 mmol) and *N*,*N*'-Disuccinimidyl carbonate (49.3 mg, 0.193 mmol) at 0 ºC. After being stirred at room temperature for 4 h, the reaction mixture was poured into ethyl acetate and saturated aq. H_2O. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. NH_4Cl and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 99:1 chloroform-methanol to give **15** (98.1 mg, 0.182 mmol, quant.).

$[\alpha]_D^{17}$ -227 (c 2.15, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.26 (m, 5H, aromatic), 5.55 (s, 1H, NH), 4.81 (dt, 1H, H-4, $J_{3ax.,4}$, $J_{4,5}$ = 11.7 Hz, $J_{3eq.,4}$ = 2.9 Hz),4.39-4.36 (m, 2H, H-9a, H-7), 4.29 (dd, 1H, H-6, $J_{5\text{-}6}$ = 9.8 Hz, $J_{6,7}$ = 2.0 Hz), 3.82 (dt, 1H, H-9b, $J_{9a,9b}$, $J_{7,9b}$ = 2.9 Hz, $J_{8,9b}$ = 12.2 Hz), 3.77 (s, 3H, OMe), 3.68 (dt, 1H, H-5, $J_{6,5}$ = 11.2, $J_{5,4}$ = 11.2 Hz), 3.57 (dt, 1H, H-8, $J_{8,9a}$, $J_{8,9b}$, $J_{7\text{-}8}$ = 2.0,) 2.82 (dd, 1H, H-3eq., $J_{3eq.,4}$ = 3.9 Hz J_{gem} = 13.2 Hz), 2.36 (t, 1H, H-3ax., $J_{3ax.,4}$, $J_{3eq.,3ax.}$ = 13.2 Hz), 0.88 (s, 9H, Si-^{t}Bu), 0.100 (s, 3H, Si-Me-a), 0.09 (s, 3H, Si-Me-b); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.2, 159.3, 147.6, 136.0, 130.4, 129.4, 129.0, 87.8, 82.5, 74.2, 71.4, 63.2, 57.4, 53.3, 36.4, 25.7, 18.0, -4.41, -4.54; **IR** (KBr) 2953, 2931, 2898, 2857, 1776, 1757, 1257, 1110 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{24}H_{33}NO_9SSi$ $[M+H]^+$ 540.1724,

found 540.1724.

Methyl (phenyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-β-D-*galacto*-2-nonulopyranosid)onate (7)

To a solution of **15** (21.3 mg, 0.0395 mmol) in CH_2Cl_2 (1.19 mL, 30.0 mL/mmol) was added DIPEA (21.0 μL, 0.119 mmol) at 0 ºC. After being stirred and warmed up to room temperature for 0.5 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 99:1 chloroform-methanol to give **7** (21.6 mg, 0.0371 mmol, 94%).

$[\alpha]_D^{29}$ -8.93 (c 0.106, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42-7.23 (m, 5H, aromatic), 5.47 (d, 1H, H-7, $J_{7,9'}$ = 0.96 Hz), 4.81 (dt, 1H, H-4, $J_{3ax.,4}$, $J_{4,5}$ = 12.7 Hz, $J_{3eq.,4}$ = 3.4 Hz), 4.59 (d, 1H, H-6, $J_{5,6}$ = 9.8 Hz), 4.33 (dd, 1H, H-9a, $J_{8,9a}$ = 2.9 Hz, $J_{9a,9b}$ = 11.2 Hz), 4.02 (dd, 1H, H-5, $J_{4,5}$ = 10.8 Hz, $J_{5,6}$ = 10.8 Hz), 3.84 (ddd, 1H, H-9b, $J_{7,9b}$ = 0.96 Hz, $J_{8,9b}$ = 3.4 Hz, $J_{9a,9b}$ = 11.2 Hz), 3.77-3.72 (m, 4H, H-8, OMe), 2.78 (dd, 1H. H-3eq., $J_{3eq,4}$ = 3.9, J_{gem} = 13.2 Hz), 2.54 (s, 3H, NAc), 2.29 (dd, 1H, H-3ax., $J_{3ax,4}$ = 13.2 Hz, J_{gem} =13.2 Hz), 0.91 (s, 9H, Si-^{t}Bu), 0.14 (s, 3H, Si-Me-a), 0.11 (s, 3H, Si-Me-b); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.6, 167.9, 153.4, 148.3, 136.2, 130.6, 129.5, 128.7, 87.3, 83.3, 75.3, 74.6, 71.3, 63.6, 59.3, 53.3, 35.0, 25.7, 25.0, 18.1, -4.45; **IR** (KBr) 2930, 2857, 1796, 1746, 1260, 1173, 1104(cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{26}H_{36}NO_{10}SSi$ $[M+H]^+$ 582.1819, found 582.1829.

Methyl (octyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (16)

A mixture of **8** (1.05 g, 1.80 mmol), octhanol (0.568 mL, 3.60 mmol) and pulverized activated MS-3A (3.60 g, 2.00 g/mmol) in dry CH_2Cl_2 (36.0 mL, 20.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 ºC. *N*-iodosuccinimide (810 mg, 3.60 mmol) and trifluoromethanesulfonic acid (0.160 mL, 1.80 mmol) were added to reaction mixture at -78 ºC. After being stirred and warmed up to -45 ºC for 5 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 97:3 toluene-acetone to give **16** (1.03 g, 1.71 mmol, 95%, α only).

$[\alpha]_D^{26}$ +1.30 (c 0.191, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.30 (d, 1H, H-7, J = 5.6 Hz), 4.40-4.32 (m, 3H, H-6, H-8, H-9a), 4.12-4.00 (m, 3H, H-4, H-5, H-9b), 3.83 (s, 3H, OMe), 3.64 (dt, 1H, OCH-a, J = 6.4 Hz, J_{gem} = 8.8 Hz), 3.32 (dt, 1H, OCH-b, J = 6.7 Hz, J_{gem} = 8.8 Hz), 2.87 (dd, 1H, 3-$H_{eq.}$, $J_{3eq.,4}$ = 3.4 Hz, J_{gem} = 12.2 Hz), 2.20 (t, 1H, 3-$H_{ax.}$, $J_{3ax.,4}$, $J_{3eq.,3ax.}$ = 12.8 Hz), 1.55 (m, 2H, octhanol-$OCCH_2$), 1.30 (m, 10H, octhanol-$OCCCH_2CH_2CH_2CH_2CH_2$), 0.90-0.86 (m, 12H, Si-^{t}Bu, octhanol-$OCCCCCCCCCH_3$), 0.15 (s, 3H, Si-Me-a), 0.13

(s, 3H, Si-Me-b); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 168.9, 153.8, 149.3, 99.7, 83.3, 75.8, 75.0, 69.9, 65.5, 62.9, 59.0, 53.2, 35.8, 32.0, 29.6, 29.4, 29.3, 26.0, 25.8, 25.0, 22.8, 18.0, 14.2, -4.50, -4.69; **IR** (KBr) 2930, 2857, 1798, 1748, 1304, 1173, 1104 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{28}H_{48}NO_{11}Si$ $[M+H]^+$ 602.3007, found 602.2997.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (8)

To a solution of **16** (551 mg, 0.920 mmol, 1.00 eq.) in tetrahydrofuran (46.0 mL, 50.0 mL/mmol) was added HF·Py (9.20 mL, 8.00 mL/mmol) at 0 ºC. After being stirred and warmed up to room temperature for 4.5 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 97:3 chloroformate-methanol to give **8** (427 mg, 0.877 mmol, 96%).

$[\alpha]_D^{28}$ -2.89 (c 0.210, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.10 (dd, 1H, H-7, $J_{6,7}$ = 1.6 Hz, $J_{7,8}$ = 7.5 Hz), 4.52-4.48 (m, 2H, H-8, H-9a), 4.28 (dd, 1H, H-6, $J_{6,7}$ = 1.6 Hz, $J_{5,6}$ = 9.2 Hz), 4.21 (t, 1H, H-9b, J = 8.4 Hz × 2), 4.05 (t, 1H, H-5, $J_{4,5}$, $J_{5,6}$ = 9.2 Hz), 3.92 (dt, 1H, H-4, $J_{3eq.,4}$ = 3.6 Hz, $J_{3ax.,4}$, $J_{4,5}$ = 13.2 Hz), 3.87 (s, 3H, OMe), 3.69 (dt, 1H, OCH-a, J = 6.4 Hz, J_{gem} = 8.8 Hz), 3.35 (d, 1H, OH, J = 4.5 Hz), 3.29 (dt, 1H, OCH-b, J = 6.7 Hz, J_{gem} = 8.8 Hz), 2.97 (dd, 1H, H-3eq., $J_{3eq.,4}$ = 3.6 Hz, J_{gem} = 12.2 Hz), 2.51 (s, 3H, Ac), 2.19 (dd, 1H, H-3ax., J_{gem} = 12.4 Hz, $J_{3ax.,4}$ = 13.2 Hz), 1.54 (m, 2H, octhanol-$OCCH_2$), 1.30 (m, 10H, octhanol-$OCCCH_2CH_2CH_2CH_2CH_2$), 0.88 (m, 3H, octhanol-$OCCCCCCCCCH_3$); **^{13}C NMR** (100MHz, $CDCl_3$) δ 172.3, 169.2, 153.7, 148.9, 99.6, 81.2, 75.6, 74.3, 70.2, 65.5, 61.2, 58.5, 53.6, 35.9, 31.9, 29.5, 29.4, 29.3, 26.0, 24.9, 22.7, 14.2; **IR** (KBr) 3423, 2927, 2856, 1798, 1745, 1293, 1223, 1174, 1145, 1095, 1047 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{22}H_{34}NO_{11}$ $[M+H]^+$ 488.2132, found 488.2132.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-v-2-nonulopyranosid)onate (18)

A mixture of **8** (672 mg, 1.38 mmol), **7** (1.20 g, 2.07 mmol) and pulverized activated MS-3A (2.72 g, 2.00 g/mmol) in dry CH_2Cl_2 (27.6 mL, 20.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 ºC. *N*-iodosuccinimide (932 mg, 4.14 mmol) and trifluoromethanesulfonic acid (123 μL, 1.38 mmol) were added to reaction mixture at -78 ºC. After being stirred and warmed up to -65 ºC for 13 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 90:10 toluene-acetone to **18** (1.12 g, 1.17 mmol, 86%, α only).

$[\alpha]_D^{27}$ -4.05 (c 0.194, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.49 (d, 1H, *J* = 1.2 Hz), 5.20 (d, 1H, *J* = 6.0 Hz), 4.67-4.64 (m, 2H), 4.40-4.33 (m, 2H), 4.28-4.24 (m, 3H), 5.15-3.97 (m, 5H), 3.87 (s, 3H), 3.85 (s, 3H), 3.61 (dt, 1H, *J* = 6.4 Hz, *J* = 8.8 Hz), 3.31 (dt, 1H, *J* = 6.6 Hz, *J* = 8.7 Hz), 2.97 (dd, 1H, *J* = 3.4 Hz, *J* = 11.8 Hz), 2.92 (dd, 1H, *J* = 3.6 Hz, *J* = 12.1 Hz), 2.54 (s, 3H), 2.50 (s, 3H), 2.31 (t, 1H, *J* = 12.2 Hz×2), 2.14 (t, 1H, *J* = 12.3 Hz × 2), 1.59-1.54 (m, 2H), 1.24-1.21 (m, 10H), 0.92-0.86 (m, 12H), 0.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 171.9, 168.2, 167.6, 153.60, 153.58, 149.2, 148.6, 99.8, 99.4, 82.6, 81.9, 76.24, 76.15, 74.8, 74.7, 70.4, 69.9, 66.3, 65.5, 62.5, 59.0, 58.6, 53.8, 53.4, 35.7, 34.7, 31.9, 29.5, 29.3, 29.2, 25.9, 25.7, 25.0, 24.9, 22.7, 17.9, 14.2, -4.43, -4.74; **IR** (KBr) 2954, 2931, 2857, 1799, 1748, 1290, 1174(cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{42}H_{62}N_2O_{21}SiNa$ $[M+Na]^+$ 981.3532, found 981.3512.

Methyl (octyl 5-amino-9-*O*-benzyl-5-*N*,4-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (19)

A mixture of **7** (28.2 mg, 0.0554 mmol), **17** (48.0 mg, 0.0831 mmol) and pulverized activated MS-3A (111 mg, 2.00 g/mmol) in dry CH_2Cl_2 (1.11 mL, 20.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. *N*-iodosuccinimide (37.4 mg, 0.166 mmol) and trifluoromethanesulfonic acid (4.90 μL, 0.0554 mmol) were added to reaction mixture at -78 °C. After being stirred and warmed up to -55 °C for 4 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 90:10 toluene-acetone to give **19** (28.3 mg, 0.0288 mmol, 52%, α only).

$[\alpha]_D^{17}$ -15.1 (c 1.43, $CHCl_3$);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.27 (m, 5H), 5.42 (s, 1H), 5.26 (d, 1H, *J* = 5.6 Hz), 4.38-4.35 (m, 1H), 4.31-4.23 (m, 3H), 4.10-4.01 (m, 5H), 3.91-3.78 (m, 12H), 3.62 (dt, 1H, *J* = 6.4 Hz, *J* = 8.8 Hz), 3.52 (t, 1H, *J* = 10.8 Hz), 3.20 (dt, 1H, *J* = 6.8 Hz, *J* = 9.2 Hz), 2.94-2.87 (m, 3H), 2.53 (s, 3H), 2.33 (dd, 1H, *J* = 12.4, *J* = 12.4 Hz), 2.04 (dd, 1H, J = 12.0 Hz), 1.52-1.48 (m, 2H), 1.31-1.25 (m, 10H), 0.89-0.86 (m, 12H), 0.14 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 168.8 ($^3J_{C1,H\text{-}3ax}$ = 5.0 Hz), 168.0 ($^3J_{C1,H\text{-}3ax}$ = 5.0 Hz), 159.7, 153.7, 149.4, 137.7, 128.6, 128.0, 100.5, 100.3, 80.0, 77.4, 77.3, 76.3, 76.0, 75.9, 74.9, 73.7, 71.9, 70.6, 69.6, 65.4, 62.4, 58.6, 58.2, 53.7, 53.0, 37.5, 35.4, 31.9, 29.7, 29.5, 29.3, 26.1, 25.7, 25.1, 22.8, 17.9, 14.2, -4.37, -4.73; **HRMS** (ESI-TOF) Calcd for $C_{46}H_{68}N_2O_{19}Si$ $[M+H]^+$ 981.4246, found 981.4246.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (20)

To a solution of **18** (1.10 g, 1.15 mmol) in tetrahydrofuran (57.5 mL, 50.0 mL/mmol) was added HF·Py (9.20

mL, 8.00 mL/mmol) at 0 °C. After being stirred and warmed up to room temperature for 2.5 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 99:1 chloroformate-methanol to give **20** (958 mg, 1.13 mmol, 99%).

$[\alpha]_D^{25}$ -19.7 (c 0.285, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.61 (s, 1H), 4.93-4.91 (m, 1H), 4.79 (dd, 1H, *J* = 1.6 Hz, *J* = 9.2 Hz), 4.45-4.21 (m, 9H), 4.12 (t, 1H, *J* = 10.0 Hz), 4.00-3.79 (m, 9H), 3.60 (dt, 1H, *J* = 6.4 Hz, *J* = 8.7 Hz), 3.36 (dt, 1H, *J* = 6.6 Hz, *J* = 8.7 Hz), 3.23 (d, 1H, *J* = 5.4 Hz), 2.98 (dd, 1H, *J* = 3.7 Hz, *J* = 11.9 Hz), 2.90 (dd, 1H, *J* = 3.9 Hz, *J* = 12.0 Hz), 2.53-2.51 (m, 7H), 2.07 (dd, 1H, *J* =13.2 Hz), 1.55-1.53 (m, 2H), 1.40-1.22 (m, 10H), 0.90-0.86 (m, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 168.0, 167.7, 153.7, 153.5, 149.5, 148.3, 100.2, 99.8, 83.5, 80.1, 75.7, 75.6, 74.9, 74.3, 70.3, 69.4, 66.9, 65.4, 59.9, 59.1, 57.7, 54.3, 53.7, 35.6, 33.2, 31.9, 29.6, 29.4, 29.3, 26.0, 24.9, 22.8, 14.2; **IR** (KBr) 3457, 2954, 2928, 2856, 1797, 1744, 1292, 1227, 1174, 1144, 1096, 1045 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{36}H_{48}N_2O_{21}Na$ $[M+Na]^+$ 867.2689, found 867.2647.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (21)

A mixture of **7** (1.52 g, 2.70 mmol), **20** (913 mg, 1.08 mmol) and pulverized activated MS-3A (2.16 g, 2.00 g/mmol) in dry CH_2Cl_2 (21.6 mL, 20.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. *N*-iodosuccinimide (1.20 g, 5.40 mmol) and trifluoromethanesulfonic acid (96.0 μL, 1.08mmol) were added to reaction mixture at -78 °C. After being stirred at the same temperature for 5 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 95:5 toluene-acetone to give **21** (1.20 g, 0.912 mmol, 84%, α only).

$[\alpha]_D^{23}$ -11.9 (c 0.324, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.46 (d, 1H, *J* = 1.3 Hz), 5.40 (d, 1H, *J* = 2.2 Hz), 5.14 (d, 1H, *J* = 5.3 Hz), 4.73 (d, 1H, *J* = 1.6 Hz), 4.62-4.59 (m, 3H), 4.33-4.25 (m, 7H), 4.13-3.39 (m, 7H), 3.89 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 3.61 (dt, 1H, *J* = 6.5 Hz, *J* = 8.7 Hz), 3.31 (dt, 1H, *J* = 6.6 Hz, *J* = 8.6 Hz), 3.02 (dd, 1H, *J* = 3.6 Hz, *J* = 11.9 Hz), 2.94 (dd, 2H, *J* = 4.0 Hz, *J* = 12.4 Hz), 2.54 (s, 3H), 2.53 (s, 3H), 2.50 (s, 3H), 2.44 (t, 1H, *J* = 12.1 Hz ×2), 2.31 (t, 1H, *J* = 12.7 Hz×2), 2.14 (t, 1H, *J* = 12.2 Hz×2), 1.53-1.50 (m, 2H), 1.30-1.27 (m, 10H), 0.90-0.86 (m, 12H), 0.14 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 172.4, 172.1, 168.2, 167.5, 167.2, 153.7, 153.6, 153.5, 149.0, 148.5, 100.1, 99.9, 99.4, 82.3, 82.0, 81.3, 77.5, 77.2, 76.8, 76.1, 75.9, 74.8, 76.2, 76.1, 76.0, 74.8, 74.4, 70.3, 70.2, 69.6, 66.1, 65.8, 65.5, 62.2, 59.0, 58,7, 58.5, 54.2, 54.0, 53.7,

35.6, 34.3, 33.9, 31.9, 29.6, 29.4, 29.2, 25.9, 25.7, 25.0, 22.7, 17.9, 14.2, -4.38, -4.72; **IR** (KBr) 2955, 2931, 2857, 1799, 1752, 1291, 1174, 1131, 1101, 1042 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{56}H_{81}N_4O_{31}Si$ $[M+NH_4]^+$ 1333.4702, found 1333.4654.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (22)

To a solution of **21** (1.17 g, 0.889 mmol) in tetrahydrofuran (44.0 mL, 50.0 mL/mmol) was added HF•Py (7.10 mL, 8.00 mL/mmol) at 0 ºC. After being stirred and warmed up to room temperature for 3 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 97:3 chloroformate-methanol to give **22** (977 mg, 0.813 mmol, 91%).

$[\alpha]_D^{26}$ -11.5 (c 0.286, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.63 (d, 1H, *J* = 1.6 Hz), 5.47 (d, 1H, *J* = 1.3 Hz), 4.99-4.94 (m, 1H), 4.75 (d, 1H, *J* = 1.2 Hz), 4.72 (d, 1H, *J* = 6.4 Hz), 4.62 (dd, 1H, *J* = 2.8 Hz, *J* = 11.6 Hz), 4.45-4.40 (m, 1H), 4.35-3.60 (m, 23H), 3.62-3.58 (m, 1H), 3.33-3.26 (m, 2H), 3.07 (dd, 1H, *J* = 2.4 Hz, *J* =11.8 Hz), 2.93 (dt, 2H, *J* = 3.4 Hz×2, *J* = 12.2 Hz), 2.78 (t, 1H, *J* = 12.5 Hz×2), 2.54 (s, 3H), 2.52 (s, 3H), 2.51 (s, 3H), 2.21-2.14 (m, 2H), 1.55 (m, 2H), 1.30-1.27 (m, 10H), 0.88 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 172.4, 172.1,168.5, 168.0, 167.6, 153.9, 153.42, 153.36, 149.8, 148.5, 148.3, 100.5, 99.9, 98.9, 83.1, 81.8, 79.9, 77.4, 76.7, 76.4, 75.6, 74.8, 74.3, 70.9, 70.5, 67.7, 66.6, 65.9, 65.6, 59.9, 59.0, 58.9, 57.8, 54.4, 54.3, 53.7, 35.7, 35.0, 33.1, 31.9, 29.6, 29.4, 29.3, 26.0, 25.1, 24.8, 22.7, 14.2; **IR** (KBr) 3477, 2955, 2929, 2857, 1799, 1746, 1376, 1291, 1227, 1174, 1144, 1097, 1043 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{50}H_{64}N_3O_{31}$ $[M+H]^+$ 1202.3524, found 1202.3524.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (23)

A mixture of **22** (977 mg, 0.813 mmol), **7** (1.40 g, 2.44 mmol) and pulverized activated MS-3A (1.60 g, 2.00 g/mmol) in dry CH_2Cl_2 (16.0 mL, 20.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 ºC. *N*-iodosuccinimide (1.10 g, 4.88 mmol) and trifluoromethanesulfonic acid (72.0 μL, 0.813 mmol) were added to reaction mixture at -78 ºC. After being stirred at the same temperature for 4 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and

saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 95:5 toluene-acetone to give **23** (1.32 g, 0.789 mmol, 97%, α only).

$[\alpha]_D^{26}$ -9.02 (c 0.201, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.45 (dd, 2H, *J* = 12.4 Hz, *J* = 2.8 Hz), 5.30 (s, 1H), 5.20 (d, 1H, *J* = 4.8 Hz), 4.78-4.74 (m, 2H), 4.66-4.63 (m, 2H), 4.51 (dd, 1H, *J* = 3.2 Hz, *J* = 5.7 Hz), 4.43-4.19 (m, 10H), 4.15-3.96 (m, 11H), 3.91 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.61 (dt, 1H, *J* = 6.4 Hz, *J* = 8.8 Hz), 3.28 (dt, 1H, *J* = 6.7 Hz, *J* = 8.6 Hz), 3.07 (dd, 1H, *J* = 4.0 Hz, *J* = 12 Hz), 2.99-2.92 (m, 3H), 2.54-2.51 (m, 13H), 2.32-2.23 (m, 2H), 2.14 (t, 1H, *J* = 12.8 Hz×2), 1.56-1.52 (m, 2H), 1.30-1.27 (m, 10H), 0.90-0.86 (m, 12H), 0.14 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.6, 172.54, 172.50, 172.1, 168.3 ($^3J_{C1,H\text{-}3ax}$ = 6.9 Hz), 167.7 ($^3J_{C1,H\text{-}3ax}$ = 4.6 Hz), 167.1 ($^3J_{C1,H\text{-}3ax}$ = 6.1 Hz), 167.0 ($^3J_{C1,H\text{-}3ax}$ = 6.1 Hz), 153.65, 153.56, 153.48, 149.2, 148.8, 148.3, 148.0, 100.1, 99.9, 99.8, 99.1, 82.6, 81.7, 81.6, 80.8, 77.4, 76.5, 76.3, 76.1, 74.7, 74.5, 74.3, 70.6, 70.0, 68.9, 66.2, 66.0, 65.6, 65.3, 62.4, 58.9, 58.7, 58.5, 54.3, 54.2, 54.0, 35.7, 34.1, 33.3, 31.8, 29.5, 29.3, 29.2, 25.9, 25.6, 24.9, 24.8, 22.7, 17.9, 14.2, -4.47, -4.75; **IR** (KBr) 2955, 2931, 2858, 1799, 1750, 1291, 1228, 1174, 1132, 1101, 1041 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{70}H_{96}N_5O_{41}Si$ $[M+NH_4]^+$ 1690.5358, found 1690.5350.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (24)

To a solution of **23** (945 mg, 0.565 mmol) in tetrahydrofuran (28.0 mL, 50.0 mL/mmol) was added HF•Py (4.50 mL, 8.00 mL/mmol) at 0 ºC. After being stirred and warmed up to room temperature for 4 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 97:3 chloroformate-methanol to give **24** (804 mg, 0.516 mmol, 91%).

$[\alpha]_D^{29}$ -27.0 (c 0.192, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.54 (d, 1H, *J* = 1.6 Hz), 5.44 (d, 1H, *J* = 1.2 Hz), 5.36 (d, 1H, *J* = 2.4 Hz), 4.81 (d, 1H, *J* = 8.0 Hz), 4.78-4.79 (m, 1H), 4.71 (d, 1H, *J* = 1.6 Hz), 4.67-4.62 (m, 2H), 4.56 (dd, 1H, *J* = 11.5 Hz, *J* = 4.4 Hz), 4.38-4.11 (m, 16H), 4.01-3.87 (m, 16H), 3.60 (dt, 1H, *J* = 6.4 Hz, *J* = 8.7 Hz), 3.41 (d, 1H, *J* = 4.9 Hz), 3.30 (dt, 1H, *J* = 6.6 Hz, *J* = 8.7 Hz), 3.03-2.93 (m, 4H), 2.56-2.52 (m, 13H), 2.37-2.32 (m, 2H), 2.13 (t, 1H, *J* = 12.8 Hz×2), 1.60-1.56 (m, 2H), 1.30-1.24 (m, 10H), 0.90-0.86 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.74, 172.67, 172.5, 172.3, 168.3, 167.6, 167.5, 167.4, 153.7, 153.6, 153.5, 153.3, 149.5, 148.53, 148.45, 148.4, 100.3, 100.0, 99.9, 99.6, 82.7, 81.7, 81.1, 80.2, 77.4, 76.7, 76.1, 75.4, 74.8, 74.5, 70.4, 70.0, 68.4, 66.34, 66.28, 65.8, 65.6, 60.0, 59.0, 58.7, 58.6, 57.8, 54.4, 53.7, 35.7, 34.1, 33.5, 31.9, 29.6, 29.4, 29.3, 26.0, 25.03, 24.97, 24.9, 22.8, 14.2 ; **IR** (KBr) 3505, 2955, 2930, 2856, 1798, 1748, 1291, 1227, 1174, 1144, 1098, 1041

(cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{64}H_{82}N_5O_{41}$ $[M+NH_4]^+$ 1576.4476, found 1576.4485.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-tert-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (25)

A mixture of **24** (329 mg, 0.211 mmol, 1.00 eq.), **7** (404 mg, 0.696 mmol) and pulverized activated MS-3A (633 mg, 3.00 g/mmol) in dry CH_2Cl_2 (6.30 mL, 30.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. *N*-iodosuccinimide (380 mg, 1.69 mmol) and trifluoromethanesulfonic acid (19.0 μL, 0.210 mmol) were added to reaction mixture at -78 °C. After being stirred and warmed up to -60 °C for 4 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 95:5 toluene-acetone to give **25** (355 mg, 0.175 mmol, 83%, α only).

$[\alpha]_D^{29}$ -27.0 (c 0.192, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.42-5.41 (m, 2H), 5.37 (d, 1H, *J* = 2.4 Hz), 5.32 (s, 1H), 5.18 (d, 1H, *J* = 5.3 Hz), 4.76-4.73 (m, 2H), 4.62-4.45 (m, 6H), 4.34-3.97 (m, 22H), 3.913 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.61 (dt, 1H, *J* = 6.4 Hz, *J* = 8.6 Hz), 3.29 (dt, 1H, *J* = 6.7 Hz, *J* = 8.8 Hz), 3.08-2.92 (m, 5H), 2.54-2.45 (m, 16H), 2.37-2.24 (m, 3H), 2.12 (t, 1H, *J* = 12.8 Hz×2), 1.55-1.50 (m, 2H), 1.28-1.26 (m, 10H), 0.91-0.86 (m, 12H), 0.14 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.71, 172.66, 172.60, 172.55, 172.2, 168.3, 167.6, 167.2, 167.1, 167.0, 153.60, 153.55 153.50, 149.2, 148.7, 148.4, 148.3, 148.2, 138.0, 129.2, 128.4, 125.4, 100.0, 99.92, 99.90, 99.3, 82.6, 81.7, 81.4, 81.1, 77.4, 76.7, 76.4, 76.3, 76.2, 74.8, 74.6, 74.5, 74.4, 70.5, 70.3, 70.2, 70.0, 69.3, 66.1, 65.7, 65.6, 65.4, 62.4, 59.0, 58.7, 58.63, 58.59, 58.5, 54.4, 54.3, 54.0, 53.7, 35.7, 34.6, 34.1, 33.7, 33.6, 31.9, 29.6, 29.4, 29.3, 26.0, 25.7, 25.02, 24.98, 24.93, 24.89, 22.8, 21.6, 17.9, 14.2, -4.39, -4.70 ; **IR** (KBr) 3013, 2956, 2931, 2857, 1799, 1751, 1291, 1228, 1174, 1133, 1101, 1040 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{84}H_{111}N_6O_{51}Si$ $[M+NH_4]^+$ 2047.6023, found 2047.6046.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α -D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-

nonulopyranosid)onate (26)

To a solution of **25** (720 mg 0.350 mmol) in tetrahydrofuran (18.0 mL, 50.0 mL/mmol) was added HF•Py (2.80 mL, 8.00 mL/mmol) at 0 ºC. After being stirred and warmed up to room temperature for 5 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 99:1 chloroformate-methanol to give **26** (640 mg, 0.334 mmol, 94%).

$[\alpha]_D^{22}$ -14.3 (c 0.319, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.57 (d, 1H, *J* = 1.8 Hz), 5.42 (dd, 2H, *J* = 2.4 Hz, *J* = 6.8 Hz), 5.28 (s, 1H), 4.84-4.79 (m, 2H), 4.74-4.71 (m, 2H), 4.64-4.59 (m, 2H), 4.54-4.50 (m, 2H), 4.40-3.87 (m, 38H), 3.61 (dt, 1H, *J* = 6.4 Hz, *J* = 8.6 Hz), 3.36 (d, 1H, *J* = 5.0 Hz), 3.28 (dt, 1H, *J* = 6.8 Hz, *J* = 8.7 Hz), 3.08-2.93 (m, 5H), 2.55-2.51 (m, 16H), 2.31-2.08 (m, 4H), 1.55-1.50 (m, 2H), 1.30-1.21 (m, 10H), 0.88 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 172.73, 172.70, 172.34, 172.30, 168.3, 167.6, 167.54, 167.48, 167.1, 153.7, 153.62, 153.58, 153.5, 153.2, 149.7, 148.8, 148.54, 148.45, 147.9, 100.16, 100.15, 100.14, 99.9, 99.5, 99.4, 82.78, 82.76, 81.8, 81.52, 81.54, 80.5, 80.3, 77.4, 76.7, 76.6, 76.3, 75.4, 74.8, 74.7, 74.5, 74.38, 74.37, 74.32, 74.28, 71.1, 70.6, 70.2, 69.3, 69.2, 68.0, 66.3, 66.1, 65.6, 65.3, 60.1, 59.0, 58.8, 58.70, 58.68, 58.6, 58.4, 57.8, 54.5, 54.42, 54.40, 54.36, 53.8, 35.8, 34.58, 34.57, 34.50, 34.45, 33.58, 33.55, 33.4, 33.3, 31.9, 29.6, 29.4, 29.3, 26.0, 25.0, 24.9, 24.8, 22.8, 14.2 ; **IR** (KBr) 3527, 3013, 2956, 2931, 2856, 1799, 1750, 1291, 1228, 1174, 1142, 1098, 1040 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{78}H_{94}N_5O_{51}$ $[M+CH_3OH+NH_4]^+$ 1965.5397, found 1965.5443.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (27)

A mixture of **26** (289 mg, 0.150 mmol), **7** (349 mg, 0.600 mmol) and pulverized activated MS-3A (450 mg, 3.00 g/mmol) in dry CH_2Cl_2 (4.50 mL, 30.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 ºC. *N*-iodosuccinimide (338 mg, 1.50 mmol) and trifluoromethanesulfonic acid (13.0 μL, 0.150 mmol) was added to reaction mixture at -78 ºC. After being stirred and warmed up to -60 ºC for 5 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 80:20 toluene-acetone to give **27** (309 mg, 0.130 mmol, 86%, α only).

$[\alpha]_D^{23}$ -11.7 (c 0.243, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.42 (s, 2H), 5.38-5.36 (m, 2H), 5.28 (s, 1H), 5.17 (d, 1H, 5.8 Hz), 4.76-4.73 (m, 2H), 4.65-4.47 (m, 8H), 4.37-3.87 (m, 45H), 3.62 (dt, 1H, *J* = 6.4 Hz, *J* = 8.8 Hz), 3.28 (dt, 1H, *J* = 6.8 Hz, *J* = 8.4 Hz), 3.09-2.92 (m, 6H), 2.54-2.47 (m, 19H), 2.40-2.23 (m, 4H), 2.12 (t, 1H, *J* = 12.4 Hz ×2), 1.55-1.52 (m, 2H), 1.30-1.27 (m, 10H), 0.90-0.86 (m, 12H), 0.15 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 172.7, 172.6, 172.5, 172.2, 168.3, 167., 167.18, 167.15, 167.1, 153.6, 153.5, 153.4, 149.2, 148.7, 148.4, 148.3, 148.0, 100.1, 99.9, 99.8, 99.7, 99.2, 82.5, 81.7, 81.4, 81.0, 80.8, 77.4, 76.7, 76.5, 76.3, 76.1, 74.7, 74.6, 74.4, 74.3, 70.6, 70.2, 70.1, 69.9, 69.1, 66.2, 66.0, 65.6, 65.4, 62.3, 59.0, 58.6, 58.5, 54.5, 54.4, 54.3, 54.0, 53.7, 35.7, 34.7, 33.9, 33.7, 31.9, 29.6, 29.4, 29.2, 25.9, 25.7, 25.0, 24.9, 22.7, 17.9, 14.2, -4.42, -4.72 ; **IR** (KBr) 3017, 2956, 2930, 2857, 1798, 1750, 1291, 1228, 1173, 1132, 1100, 1039 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{98}H_{125}N_6O_{62}Si$ $[M+H_2O+H]^+$ 2405.6541, found 2405.6582.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (28)

To a solution of **27** (395 mg 0.165 mmol) in tetrahydrofuran (8.30 mL, 50.0 mL/mmol) was added HF•Py (1.32 mL, 8.00 mL/mmol) at 0 ºC. After being stirred and warmed up to room temperature for 5 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 98:2 chloroformate-methanol to give **28** (304 mg, 0.134 mmol, 87%).

$[\alpha]_D^{25}$ -10.2 (c 0.170, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.58 (d, 1H, *J* = 1.7 Hz), 5.43-5.42 (m, 2H), 5.35 (s, 1H), 5.29 (s, 1H), 4.86-4.73 (m, 4H), 4.63-3.87 (m, 52H), 3.60 (dt, 1H, *J* = 6.4 Hz, *J* = 8.8 Hz), 3.31-3.25 (m, 2H), 3.09-2.92 (m, 6H), 2.61-2.51 (m, 19H), 2.38-2.07 (m, 5H), 1.58-1.50 (m, 2H), 1.30-1.21 (m, 10H), 0.88 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 172.8, 172.7, 172.3, 172.2, 168.4, 167.7, 167.60, 167.56, 167.06, 167.05, 153.7, 153.61, 153.55, 153.3, 153.2, 149.7, 148.9, 148.5, 148.4, 148.14, 148.12, 100.19, 100.16, 99.9, 99.4, 99.2, 82.9, 81.8, 81.5, 81.0, 80.7, 80.1, 77.4, 76.5, 76.3, 75.5, 74.8, 74.6, 74.5, 74.4, 74.3, 70.9, 70.8, 70.7, 70.3, 69.0, 67.9, 66.3, 66.2, 66.0, 65.8, 65.6, 65.2, 60.0, 59.0, 58.8, 58.6, 57.8, 54.51, 54.46, 54.4, 53.8, 35.8, 34.8, 34.4, 33.6, 33.5, 33.4, 31.9, 29.6, 29.4, 29.3, 26.6, 26.0, 25.03, 25.00, 24.95, 24.88, 24.85, 24.8, 22.8, 14.2; **IR** (KBr) 3526, 3013, 2957, 2930, 2856, 1799, 1750, 1291, 1228, 1174, 1134, 1098, 1040 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{93}H_{116}N_7O_{62}$ $[M+CH_3OH+NH_4]^+$ 2322.6145, found 2322.6139.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-

acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (29)

A mixture of **28** (304 mg, 0.134 mmol), **7** (467 mg, 0.803 mmol) and pulverized activated MS-3A (402 mg, 3.00 g/mmol) in dry CH_2Cl_2 (5.30 mL, 40.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. *N*-iodosuccinimide (402 mg, 1.07 mmol, 8.00 eq.) and trifluoromethanesulfonic acid (12.0 μL, 0.134 mmol) were added to reaction mixture at -78 °C. After being stirred and warmed up to -60 °C for 5 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 75:25 toluene-acetone to give **29** (368 mg, 0.134 mmol, quant., α only).

$[\alpha]_D^{29}$ -27.0 (c 0.192, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.42 (s, 2H), 5,38 (s, 1H), 5.35 (s, 2H), 5.28 (s, 1H), 5.18 (d, 1H, *J* = 5.6 Hz), 4.77-4.74 (m, 2H), 4.66-4.45 (m, 10H), 4.34-3.84 (m, 51H), 3.62 (dt, 1H, *J* = 7.6 Hz, *J* = 8.8 Hz), 3.28 (dt, 1H, *J* = 6.8 Hz, *J* = 8.4 Hz), 3.09-2.89 (m, 7H), 2.54-2.51 (m, 21H), 2.42-2.21 (m, 5H), 2.15-2.02 (m, 2H), 1.55-1.51 (m, 2H), 1.30-1.27 (m, 10H), 0.91-0.86 (m, 12H), 0.14 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.82, 172.75, 172.63, 172.59, 172.1, 168.4, 167.7, 167.3, 167.2, 167.13, 167.08, 167.0, 153.6, 153.54, 153.52, 153.48, 153.45, 153.4, 149.2, 148.8, 148.5, 148.4, 148.29, 148.25, 148.1, 100.1, 99.92, 99.89, 99.8, 99.7, 99.2, 82.6, 81.8, 81.5, 81.2, 81.0, 80.9, 77.4, 76.6., 76.5, 76.4, 76.3, 76.2, 74.8, 74.6, 74.4, 70.6, 70.4, 70.3, 70.1, 69.6, 69.1, 66.3, 66.1, 65.8, 65.7, 65.6, 65.5, 65.4, 62.4, 59.0, 58.8, 58.7, 58.5, 54.50, 54.45, 54.4, 54.1, 53.8, 35.8, 34.8, 34.1, 34.0, 33.6, 33.5, 31.9, 29.6, 29.4, 29.3, 26.0, 25.8, 25.7, 25.02, 24.95, 24.9, 22.8, 18.0, 17.9, 14.2, -4.37, -4.68 ; **IR** (KBr) 3023, 2956, 2857, 1799, 1749, 1291, 1228, 1174, 1134, 1100, 1039 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{112}H_{138}N_7O_{71}Si$ $[M+H]^+$ 2744.7173, found 2744.7172.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methy 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-

nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (30)

To a solution of **29** (221 mg 0.0810 mmol) in tetrahydrofuran (4.00 mL, 50.0 mL/mmol) was added HF•Py (0.810 mL, 10.0 mL/mmol) at 0 °C. After being stirred and warmed up to room temperature for 4.0 h, the reaction mixture was poured into ethyl acetate and saturated aq. $NaHCO_3$. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and evaporated in *vacuo*. The residue was purified by column chromatography on silica gel with 97:3 chloroformate-methanol to give **30** (228 mg, 0.0865 mmol, quant.).

$[\alpha]_D^{29}$ -27.0 (c 0.192, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.57 (d, 1H, J = 2.0 Hz), 5.41 (s, 2H), 5.37 (s, 1H), 5.35 (s, 1H), 5.29 (s, 1H), 4.85-4.72 (m, 4H), 4.62-4.50 (m, 8H), 4.38-3.81 (m, 54H), 3.60 (dt, 1H, J = 6.4 Hz , J = 8.8 Hz), 3.28 (dt, 1H, J = 6.4 Hz, J = 9.2 Hz), 3.08-2.92 (m, 7H), 2.57-2.45 (m, 21H), 2.41-2.21 (m, 5H), 2.18-2.08 (m, 2H), 1.54-1.52 (m, 2H), 1.32-1.27 (m, 10H), 0.88 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 172.80, 172.75, 172.68, 172.65, 172.3, 172.2, 168.3, 167.6, 167.5, 167.2, 167.1, 153.7, 153.60, 153.57, 153.42, 153.36, 153.2, 149.7, 148.7, 148.5, 148.4, 148.3, 148.2, 148.1, 100.2, 100.0, 99.92, 99.87, 99.5, 99.3, 83.0, 81.8, 81.4, 81.1, 81.0, 80.9, 80.8, 80.1, 77.4, 76.3, 75.5, 74.8, 74.58, 74.55, 74.42, 74.38, 70.72, 70.69, 70.61, 70.58, 70.3, 70.0, 69.9, 69.3, 67.98, 67.95, 66.3, 66.19, 66.17, 66.1, 65.8, 65.7, 65.6, 65.3, 60.0, 59.02, 59.01, 58.8, 58.7, 58.6, 57.8, 54.54, 54.50, 54.46, 54.4, 53.8, 35.79, 35.77, 35.72, 35.69, 34.7, 34.3, 33.7, 33.63, 33.61, 33.4, 33.3, 31.9, 29.6, 29.4, 29.3, 26.0, 25.8, 25.04, 25.01, 24.93, 24.89, 24.85, 24.8, 22.8, 14.2; **IR** (KBr) 3564, 3013, 2956, 2930, 2856, 1798, 1749, 1291, 1229, 1173, 1133, 1098, 1040 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{107}H_{130}N_7O_{73}$ $[M+CH_3OH+H_3O]^+$ 2680.6711, found 2680.6675.

Methyl (octyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-8-*O*-(methyl 5-acetoamido-8-*O*-*tert*-butyldimethylsilyl-5-*N*,4-*O*-carbonyl-7-*O*,9-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (31)

A mixture of **30** (226 mg, 0.0860 mmol, **7** (300 mg, 0.516 mmol) and pulverized activated MS-3A (258 mg, 3.00 g/mmol) in dry CH_2Cl_2 (3.44 mL, 40.0 mL/mmol) and dry CH_3CN (0.860 mL, 10.0 mL/mmol) was stirred at room temperature for 1 h under argon to remove a trace amount of water. Then the reaction mixture was cooled to -78 °C. *N*-iodosuccinimide (155 mg, 0.688 mmol) and trifluoromethanesulfonic acid (7.70 μL, 0.0860 mmol) were added to reaction mixture at -78 °C. After being stirred and warmed up to -65 °C for 5 h, the reaction mixture was neutralized with triethylamine and filtered through a pad of Celite. The filtrate

mixture was poured into a mixture of saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ with cooling. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with saturated aq. $NaHCO_3$ and saturated aq. $Na_2S_2O_3$ and brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel with 80:20 toluene-acetone to give **31** (202 mg, 0.0651 mmol, 76%, α only).

$[\alpha]_D^{30}$ -9.66 (c 0.196, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.41-5.28 (m, 6H), 5.18 (s, 1H), 4.73-4.47 (m, 14H), 4.33-3.84 (m, 59H), 3.60 (dt, 1H, J = 6.4 Hz, J = 8.4 Hz), 3.28 (dt, 1H, J = 6.8 Hz, J = 8.4 Hz), 3.09-2.93 (m, 8H), 2.53-2.50 (m, 24H), 2.40-2.23 (m, 6H), 2.15-2.09 (m, 2H), 1.55-1.51 (m, 2H), 1.30-1.27 (m, 10H,), 0.90-0.86 (m, 12H), 0.14 (s, 3H), 0.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.8, 172.6, 172.2, 168.3, 167.6, 167.2, 167.0, 153.6, 153.5, 149.2, 148.7, 148.3, 148.0, 100.1, 99.9, 99.82, 99.75, 99.3, 82.5, 81.7, 81.3, 80.9, 77.4, 76.7, 76.4, 76.1, 74.7, 74.6, 74.5, 74.3, 70.6, 70.1, 69.2, 66.1, 66.0, 65.6, 62.4, 58.9, 58.6, 54.5, 54.0, 53.8, 35.7, 34.7, 34.1, 31.9, 29.6, 29.4, 29.2, 25.9, 25.6, 24.9, 24.8, 22.7, 17.9, 14.2, -4.44, -4.73 ; **IR** (KBr) 2956, 2856, 1799, 1749, 1292, 1230, 1174, 1133, 1100, 1039 (cm^{-1}). **HRMS** (ESI-TOF) Calcd for $C_{96}H_{155}N_8O_{65}$ $[M+H]^{2+}$ 2459.9070, found 2459.9069.

Octyl 5-acetoamido-8-(5-acetoamido-8-(5-acetoamide-8-(5-acetoamide-8-(5-acetoamide-8-(5-acetoamide-8-(5-acetomide-8-(5-acetomide-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoslonic acid)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopranosylonic acid)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoslonic acid) -3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoslonic acid)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoslonic acid) -3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoslonic acid)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoslonic acid)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranoslonic acid (6)

To a solution of **31** (10.2 mg, 3.29 μmol) in CH_3CN (0.494 mL) was added ethanethiol (12.3 μL, 165 μmol) and K_2CO_3 (1.36 mg, 9.87 μmol) at room temperature. After being stirred at the same temperature for 1 day, the reaction mixture was poured into ethyl acetate and saturated aq. NH_4Cl. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was dissolved in tetrahydrofuran (0.987 mL) and H_2O (0.494 mL) was added dimethyldioxirane (1.88 mL, 132 μmol) at room temperature. After being stirred at the same temperature for 6 h, the reaction mixture was evaporated *in vacuo*. The residue was dissolved to tetrahydrofuran (0.329 mL) was added tetra-n-butylammonium fluoride (33 μL, 165 μmol) at room temperature. After being stirred at the same temperature for 6 h then a H_2O (2.00 mL) solution of $LiOH \cdot H_2O$ (1.38 mg, 0.0329 mmol) was added to the reaction mixture. After being stirred for 1 day, the residue was purified by size exclusion column chromatography on Sephadex LH-20 eluted with water to give **6** (5.0 mg, 2.02 μmol, 62%).

$[\alpha]_D^{18}$ +4.74 (c 0.210, H_2O); **^{1}H NMR** (400 MHz, D_2O) δ 4.11-4.00 (m, 14H), 3.83-3.30 (m, 46H), 2.67-2.53 (m, 8H), 1.98-1.93 (m, 24H), 1.67-1.62 (m, 7H), 1.51-1.45 (m, 3H), 1.17 (bs, 10H), 0.76-0.74 (m, 3H); **^{13}C NMR** (100 MHz, D_2O) δ 175.0, 174.9, 173.5504 ($^3J_{C1,H-3ax}$ = 5.8 Hz), 173.4872 ($^3J_{C1,H-3ax}$ = 5.5 Hz), 173.2216 ($^3J_{C1,H-3ax}$ = 5.2 Hz), 173.1341 ($^3J_{C1,H-3ax}$ = 4.3 Hz), 101.2, 101.1, 101.0, 100.3, 78.0, 77.8, 73.8, 73.5, 73.2, 72.6, 71.7, 69.3, 69.1,

68.4, 68.2, 65.2, 62.6, 61.5, 61.2, 52.4, 51.7, 40.5, 39.8, 31.1, 28.9, 28.5, 28.3, 25.2, 22.5, 22.3, 22.04, 22.00, 13.4; **IR** (KBr) 3400, 2938, 1620, 1563, 1440, 1402, 1074, 1038 (cm^{-1}); **HRMS** (ESI-TOF) Calcd for $C_{96}H_{155}N_8O_{65}$ $[M+H]^+$ 2459.9070, found 2459.9069.

Com file

N-Ac-carbony-acc.mae

N-Ac-carbony-acc-out.maegz

MMOD	0	1	0	0	0.0000	0.0000	0.0000	0.0000
FFLD	16	1	0	0	1.0000	0.0000	0.0000	0.0000
SOLV	3	5	0	0	0.0000	0.0000	0.0000	0.0000
EXNB	0	0	0	0	0.0000	0.0000	0.0000	0.0000
BDCO	0	0	0	0	89.4427	99999.0000	0.0000	0.0000
READ	0	0	0	0	0.0000	0.0000	0.0000	0.0000
CRMS	0	0	0	0	0.0000	0.5000	0.0000	0.0000
LMCS	2000	0	0	0	0.0000	0.0000	3.0000	6.0000
NANT	0	0	0	0	0.0000	0.0000	0.0000	0.0000
MCNV	1	5	0	0	0.0000	0.0000	0.0000	0.0000
MCSS	2	0	0	0	21.0000	0.0000	0.0000	0.0000
MCOP	1	0	0	0	0.5000	0.0000	0.0000	0.0000
DEMX	0	833	0	0	21.0000	42.0000	0.0000	0.0000
COMP	1	2	3	4	0.0000	0.0000	0.0000	0.0000
COMP	5	11	12	13	0.0000	0.0000	0.0000	0.0000
COMP	14	15	16	17	0.0000	0.0000	0.0000	0.0000
COMP	18	19	23	24	0.0000	0.0000	0.0000	0.0000
COMP	28	30	32	35	0.0000	0.0000	0.0000	0.0000
COMP	36	37	38	39	0.0000	0.0000	0.0000	0.0000
COMP	43	44	45	46	0.0000	0.0000	0.0000	0.0000
MSYM	0	0	0	0	0.0000	0.0000	0.0000	0.0000
CHIG	1	3	4	5	0.0000	0.0000	0.0000	0.0000
CHIG	28	30	0	0	0.0000	0.0000	0.0000	0.0000
AUOP	0	0	0	0	100.0000	0.0000	0.0000	0.0000
TORS	1	11	0	0	0.0000	180.0000	0.0000	0.0000
TORS	1	12	0	0	0.0000	180.0000	0.0000	0.0000
TORS	1	14	0	0	0.0000	180.0000	0.0000	0.0000
TORS	2	3	0	0	0.0000	180.0000	0.0000	0.0000
TORS	3	4	0	0	0.0000	180.0000	0.0000	0.0000
TORS	4	5	0	0	0.0000	180.0000	0.0000	0.0000
TORS	4	13	0	0	0.0000	180.0000	0.0000	0.0000
TORS	5	11	0	0	0.0000	180.0000	0.0000	0.0000
TORS	5	28	0	0	0.0000	180.0000	0.0000	0.0000
TORS	13	16	0	0	0.0000	180.0000	0.0000	0.0000
TORS	13	37	0	0	0.0000	180.0000	0.0000	0.0000
TORS	16	18	0	0	0.0000	180.0000	0.0000	0.0000

TORS	28	44	0	0	0.0000	180.0000	0.0000	0.0000
TORS	30	32	0	0	0.0000	180.0000	0.0000	0.0000
TORS	30	36	0	0	0.0000	180.0000	0.0000	0.0000
TORS	32	35	0	0	0.0000	180.0000	0.0000	0.0000
TORS	35	45	0	0	0.0000	180.0000	0.0000	0.0000
TORS	44	45	0	0	0.0000	180.0000	0.0000	0.0000
TORC	24	23	14	15	0.0000	90.0000	0.0000	0.0000
RCA4	4	3	18	16	0.5000	2.5000	0.0000	0.0000
RCA4	11	1	2	3	0.5000	2.5000	0.0000	0.0000
RCA4	44	28	30	32	0.5000	2.5000	0.0000	0.0000
CONV	2	0	0	0	0.0500	0.0000	0.0000	0.0000
MINI	1	0	2500	0	0.0000	0.0000	0.0000	0.0000

Final report:

32 unique conformations found

32 minimized with good convergence

Found 2 confs within 1.00 kcal/mol (4.18 kJ/mol) of glob. min.

Found 8 confs within 2.00 kcal/mol (8.37 kJ/mol) of glob. min.

Found 12 confs within 3.00 kcal/mol (12.55 kJ/mol) of glob. min.

Found 32 confs within 5.00 kcal/mol (20.92 kJ/mol) of glob. min.

Global minimum E = -53.78 found 54 times.

Total number of structures processed = 2000

Conformations with poor convergence marked with a *

Conformation	1 (	-53.77902	kJ/mol) was found	54 times
Conformation	2 (	-49.77315	kJ/mol) was found	94 times
Conformation	3 (	-48.17202	kJ/mol) was found	38 times
Conformation	4 (	-47.30288	kJ/mol) was found	55 times
Conformation	5 (	-46.94449	kJ/mol) was found	89 times
Conformation	6 (	-46.94240	kJ/mol) was found	48 times
Conformation	7 (	-45.49200	kJ/mol) was found	23 times
Conformation	8 (	-45.41121	kJ/mol) was found	36 times
Conformation	9 (	-44.73383	kJ/mol) was found	20 times
Conformation	10 (	-43.05256	kJ/mol) was found	14 times
Conformation	11 (	-42.27179	kJ/mol) was found	13 times
Conformation	12 (	-42.19503	kJ/mol) was found	16 times
Conformation	13 (	-40.33296	kJ/mol) was found	8 times
Conformation	14 (	-40.26244	kJ/mol) was found	18 times
Conformation	15 (	-39.54509	kJ/mol) was found	11 times
Conformation	16 (	-39.37304	kJ/mol) was found	15 times

Conformation	17 (	-39.05172	kJ/mol) was found	19 times
Conformation	18 (	-38.94464	kJ/mol) was found	36 times
Conformation	19 (	-37.47754	kJ/mol) was found	2 times
Conformation	20 (	-37.36001	kJ/mol) was found	14 times
Conformation	21 (	-37.25628	kJ/mol) was found	6 times
Conformation	22 (	-37.08435	kJ/mol) was found	16 times
Conformation	23 (	-36.41439	kJ/mol) was found	2 times
Conformation	24 (	-36.29348	kJ/mol) was found	25 times
Conformation	25 (	-35.92690	kJ/mol) was found	7 times
Conformation	26 (	-35.73057	kJ/mol) was found	20 times
Conformation	27 (	-35.42857	kJ/mol) was found	6 times
Conformation	28 (	-34.75748	kJ/mol) was found	20 times
Conformation	29 (	-34.47337	kJ/mol) was found	12 times
Conformation	30 (	-34.38362	kJ/mol) was found	10 times
Conformation	31 (	-33.60769	kJ/mol) was found	13 times
Conformation	32 (	-33.34118	kJ/mol) was found	23 times

Global minium

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9 41 4.844409 -13.034352 14.068579 1 21 0.09922 0.09922 " " " 1 FFFFFF H9 0 9

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13 25 4.379741 -14.679700 12.876542 1 38 -0.08137 -0.08137 " " c1" 7 2F2FFF N13 0 13

14 2 3.158676 -15.140691 17.580839 1 2 0.50316 0.50316 " " c1" 6 A0A0A0 C14 0 14

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17 15 6.275758 -15.688084 11.913997 1 75 -0.47545 -0.47545 " " c3" 8 FF5757 O17 0 17

18 16 6.136696 -15.138720 14.125523 1 75 -0.32410 -0.32410 " " c1" 8 FF5757 O18 0 18

19 3 3.593868 -12.385403 18.886780 1 2 0.15268 0.15268 " " c1" 6 A0A0A0 C19 3 19

20 41 4.081915 -11.926810 19.746662 1 21 0.04261 0.04261 " " n2" 1 FFFFFF H20 0 20

21 41 2.753200 -12.970366 19.261108 1 21 0.04261 0.04261 " " " 1 FFFFFF H21 0 21

22 41 3.208049 -11.577389 18.264082 1 21 0.04261 0.04261 " " " 1 FFFFFF H22 0 22

23 16 3.895948 -16.152943 18.086245 1 75 -0.27560 -0.27560 " " c1" 8 FF5757 O23 0 23

24 3 3.256570 -17.309084 18.609274 1 2 0.09077 0.09077 " " c1" 6 A0A0A0 C24 3 24

25 41 2.603149 -17.053164 19.445091 1 21 0.05110 0.05110 " " n2" 1 FFFFFF H25 0 25

26 41 4.004170 -18.015478 18.970642 1 21 0.05110 0.05110 " " " 1 FFFFFF H26 0 26

27 41 2.659766 -17.810383 17.845427 1 21 0.05110 0.05110 " " " 1 FFFFFF H27 0 27

28 3 2.080550 -12.472985 14.247098 1 2 0.10317 0.10317 " " c1" 6 A0A0A0 C28 1 28

29 41 1.903443 -12.758588 13.212569 1 21 0.09533 0.09533 " " " 1 FFFFFF H29 0 29

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31 41 0.264552 -13.308169 15.120224 1 21 0.09055 0.09055 " " " 1 FFFFFF H31 0 31

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34 41 1.279771 -12.109942 16.952835 1 21 0.07527 0.07527 " " " 1 FFFFFF H34 0 34

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36 16 -0.243354 -11.718606 13.995258 1 75 -0.62930 -0.62930 " " c1" 8 FF5757 O36 1 36

37 2 3.356814 -15.006002 12.044450 1 2 0.41492 0.41492 " " c1" 6 A0A0A0 C37 0 37

38 15 2.180287 -14.909256 12.388782 1 75 -0.50996 -0.50996 " " c3" 8 FF5757 O38 0 38

39 3 3.630350 -15.520701 10.625316 1 2 -0.09199 -0.09199 " " " c1" 6 A0A0A0 C39 3 39

40 41 3.929121 -16.568590 10.650806 1 21 0.07286 0.07286 " " " n2" 1 FFFFFF H40 0 40

41 41 2.733100 -15.438590 10.011765 1 21 0.07286 0.07286 " " " " 1 FFFFFF H41 0 41

42 41 4.418171 -14.943113 10.141395 1 21 0.07286 0.07286 " " " " 1 FFFFFF H42 0 42

43 42 0.056775 -10.826004 13.790678 1 21 0.42786 0.42786 " " " " 1 FFFFFF H43 0 43

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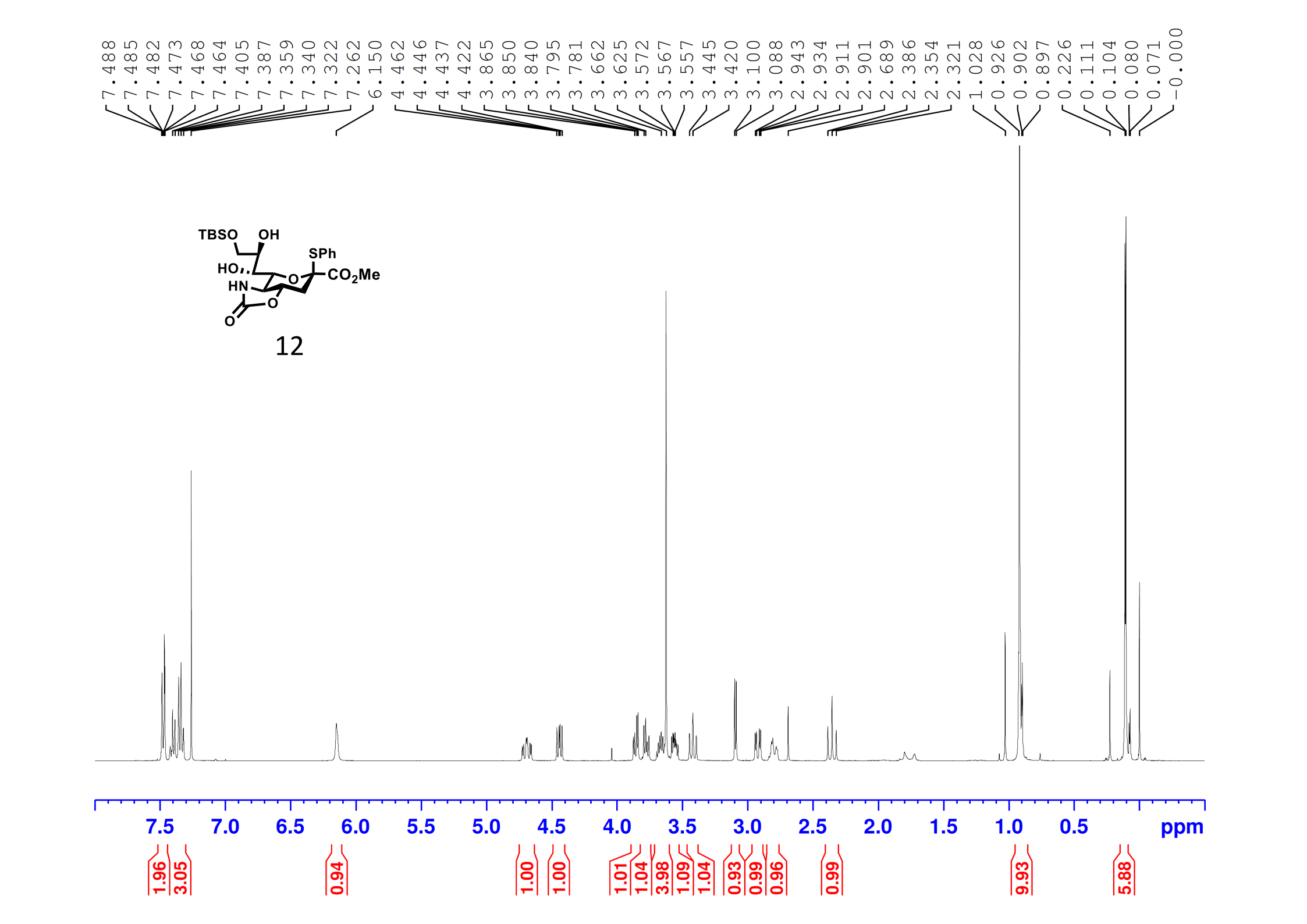
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SPh
HO
HN
O
CO2Me
O
O
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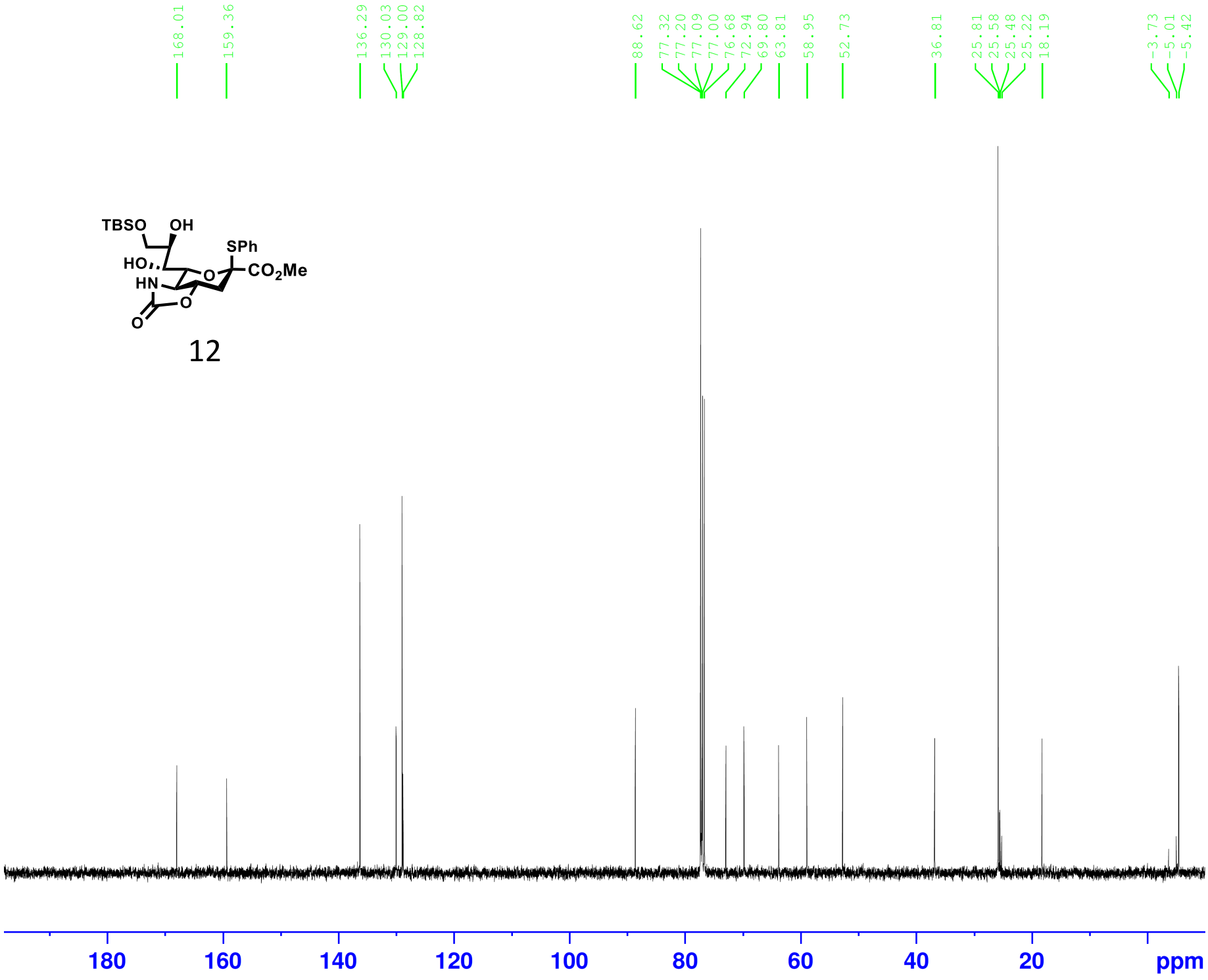
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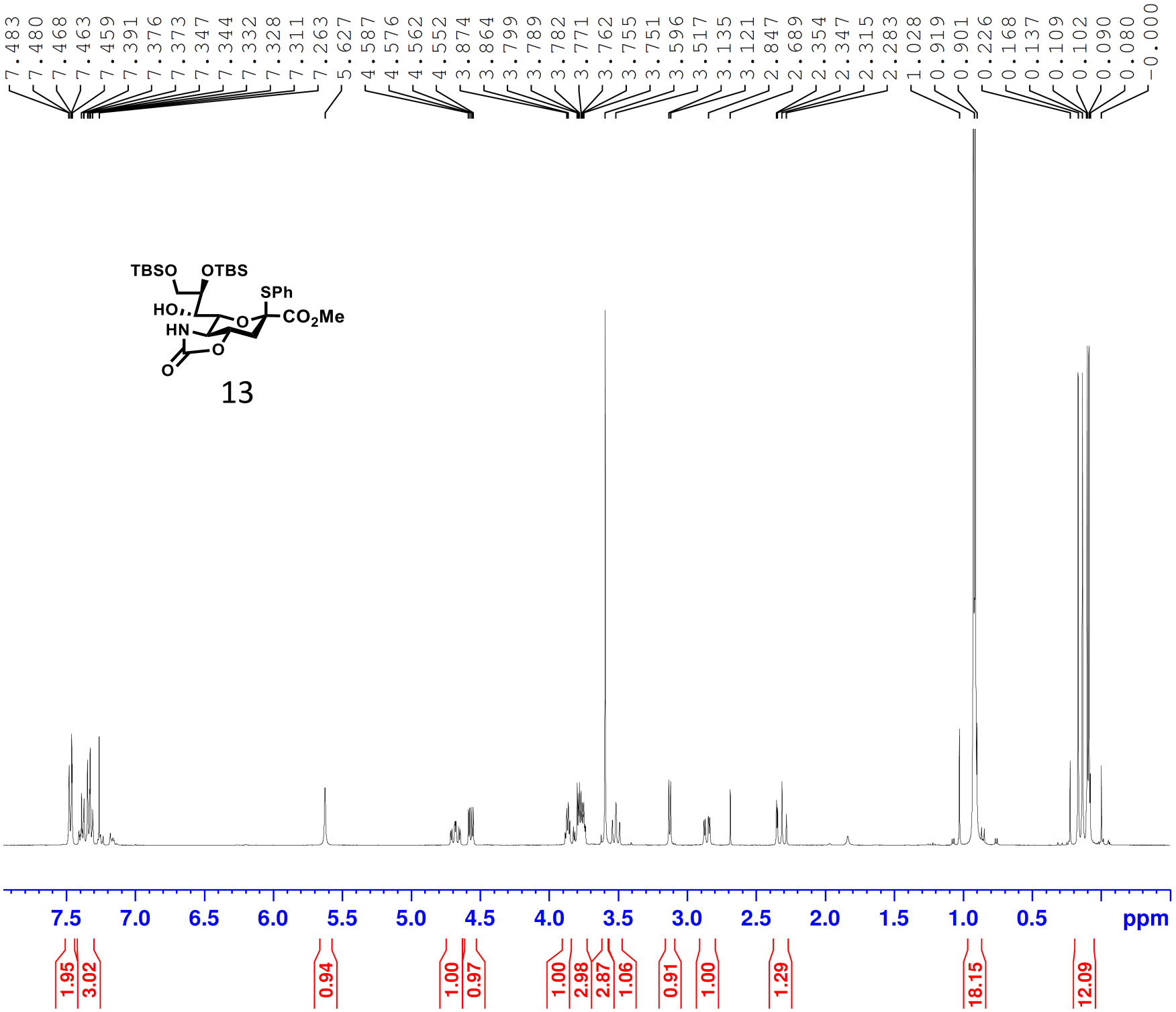
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0.080
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TBSO
OTBS
SPh
HO
HN
O
CO2Me
O
O
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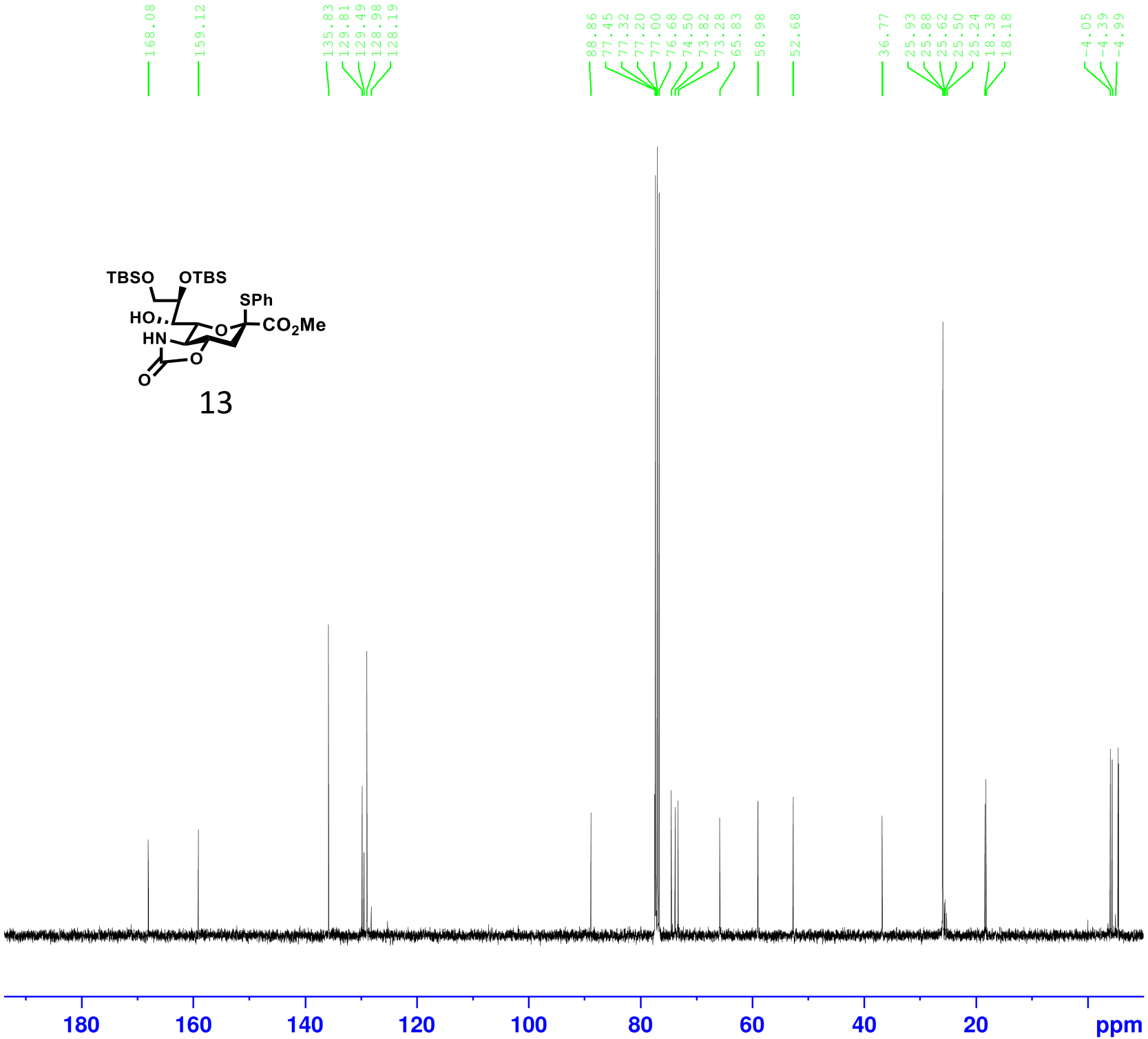
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CO2Me
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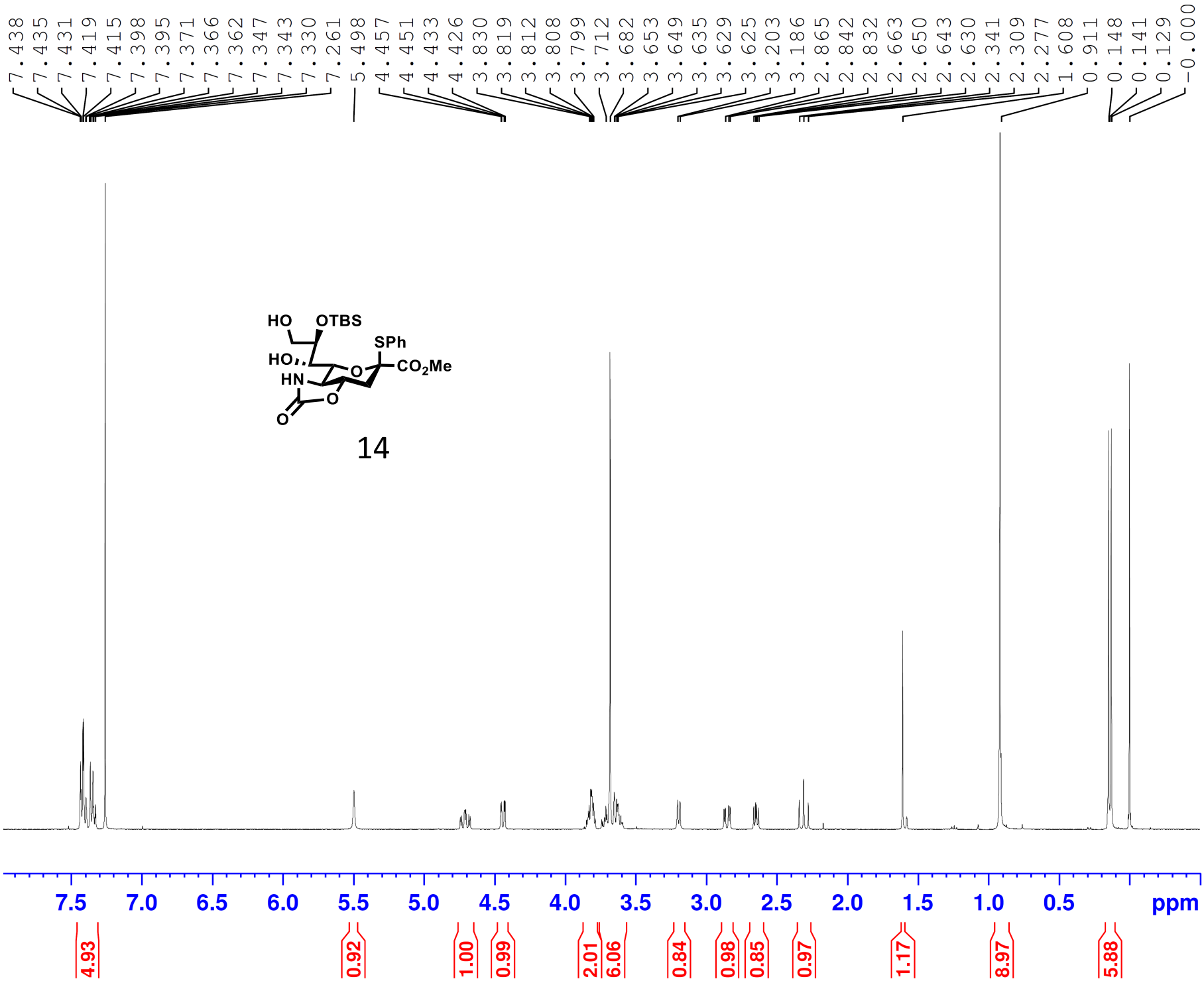
ppm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2.643
2.630
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0.141
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OTBS
SPh
HO
HN
O
CO2Me
O
O
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4.0
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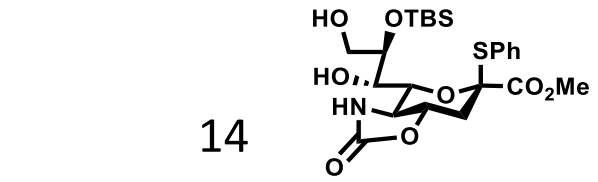
HO
OTBS
SPh
HO
HN
O
CO2Me
O
O

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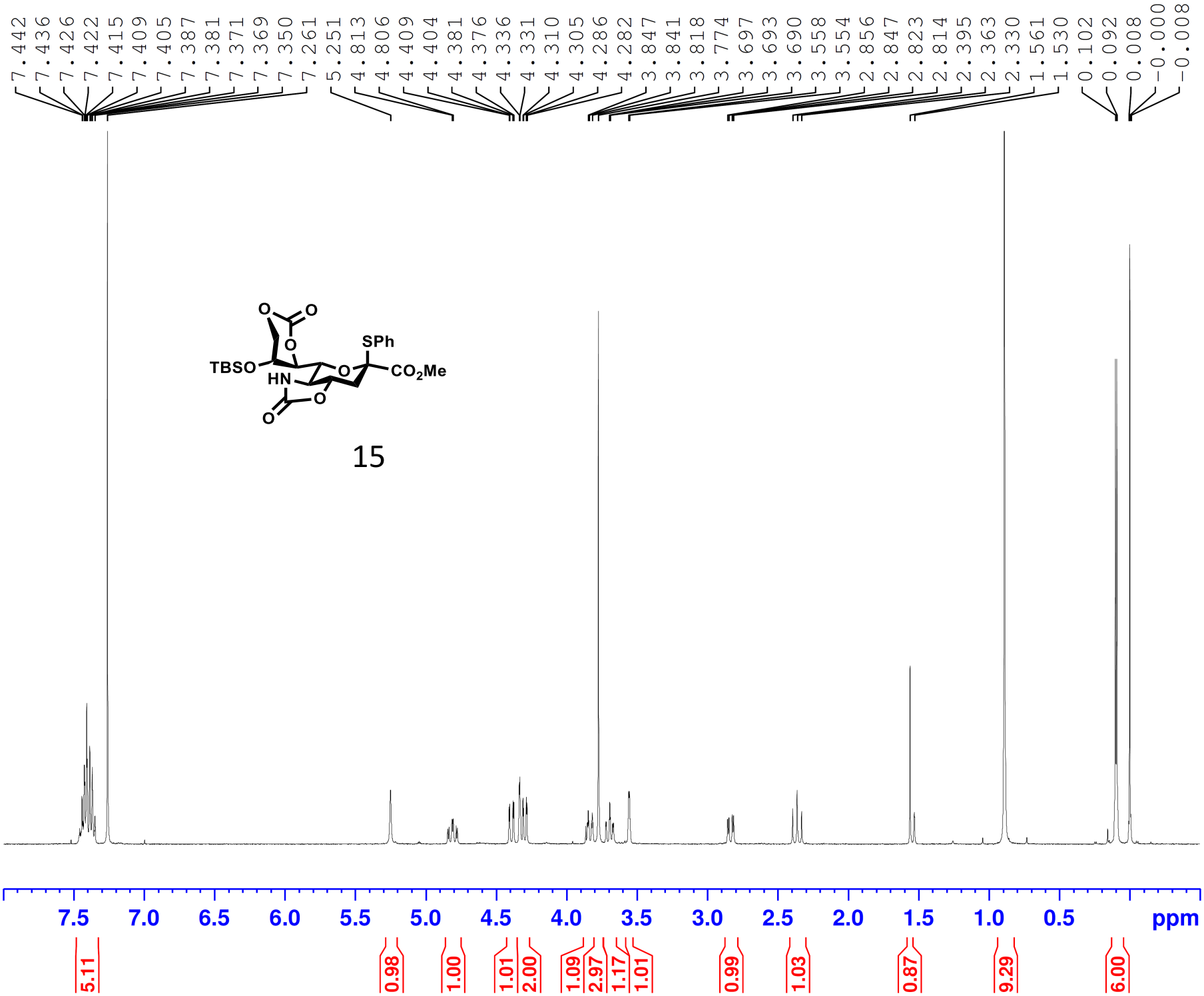
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HN
SPh
CO2Me
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4.0
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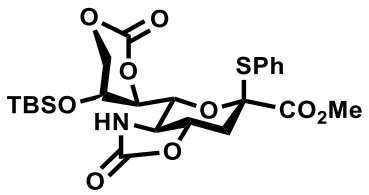
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O
O
SPh
TBSO
HN
O
CO2Me
O
O

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130.0
120.0
110.0
100.0
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70.0
60.0
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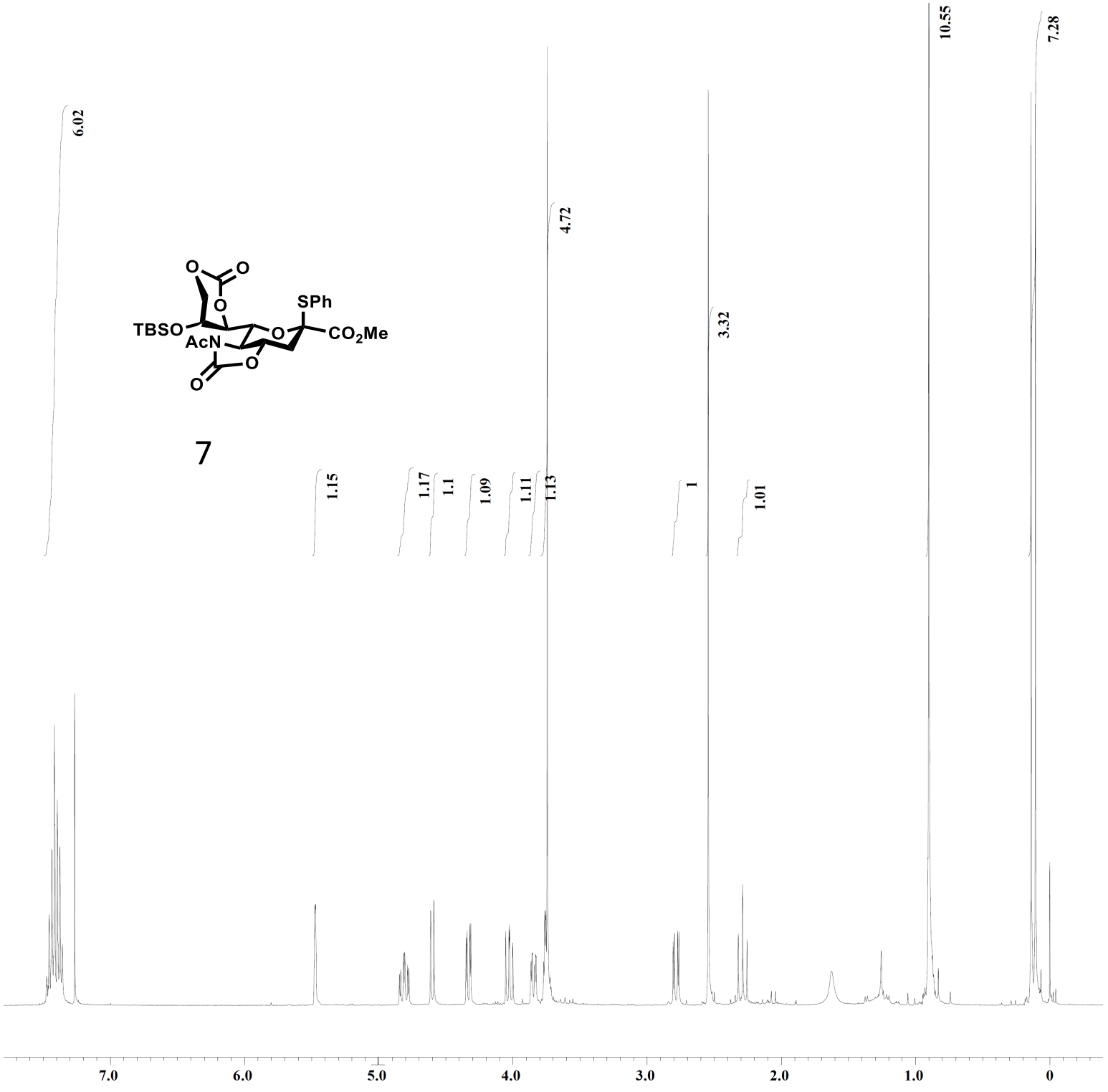
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1
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SPh
CO2Me
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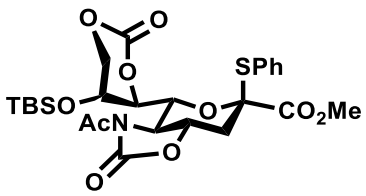
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SPh
TBSO
AcN
O
CO2Me
O
O

7

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140.0
130.0
120.0
110.0
100.0
90.0
80.0
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60.0
50.0
40.0
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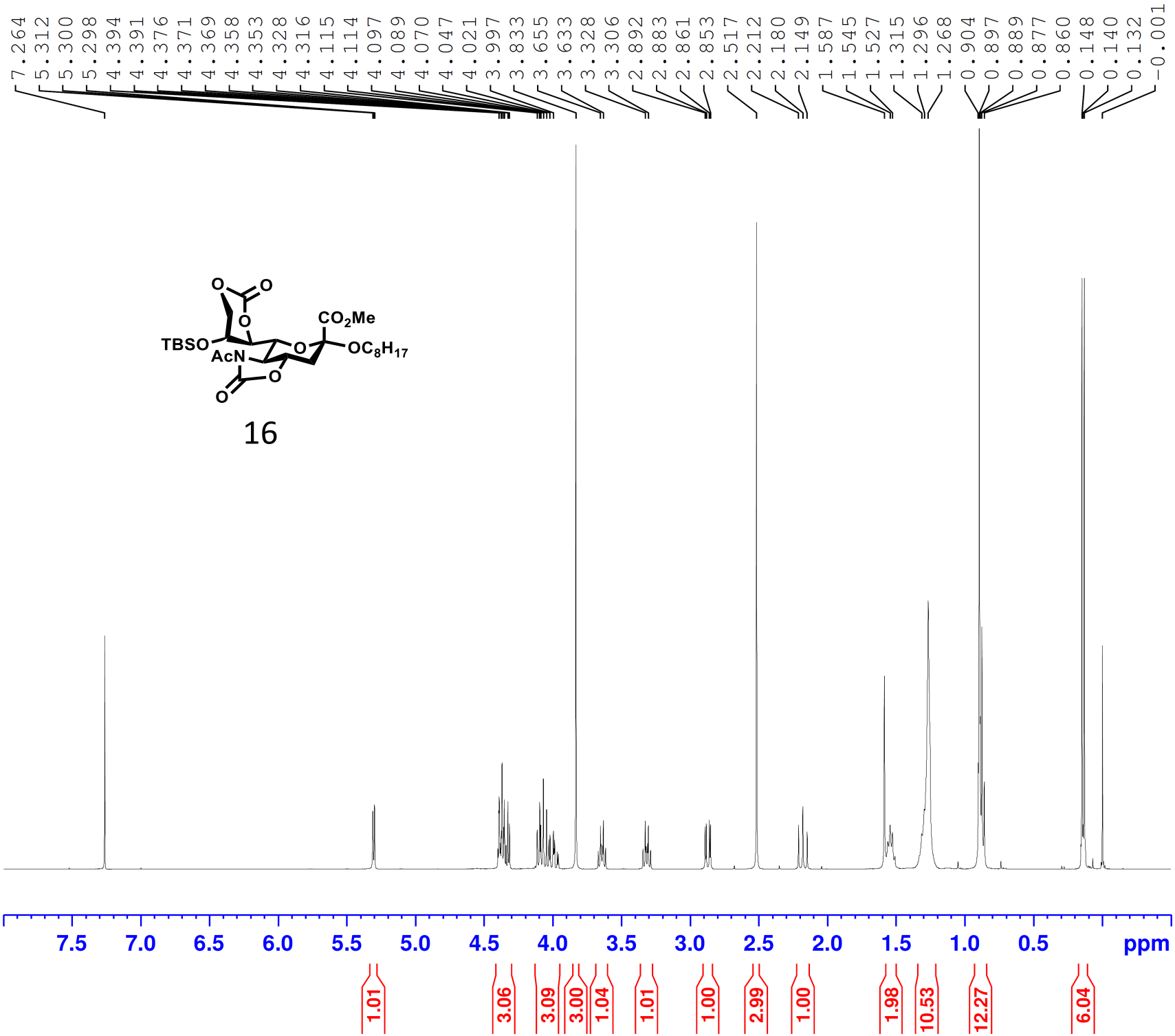
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CO2Me
OC8H17
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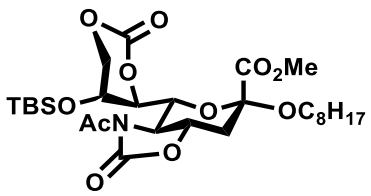
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CO2Me
TBSO
AcN
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O

16

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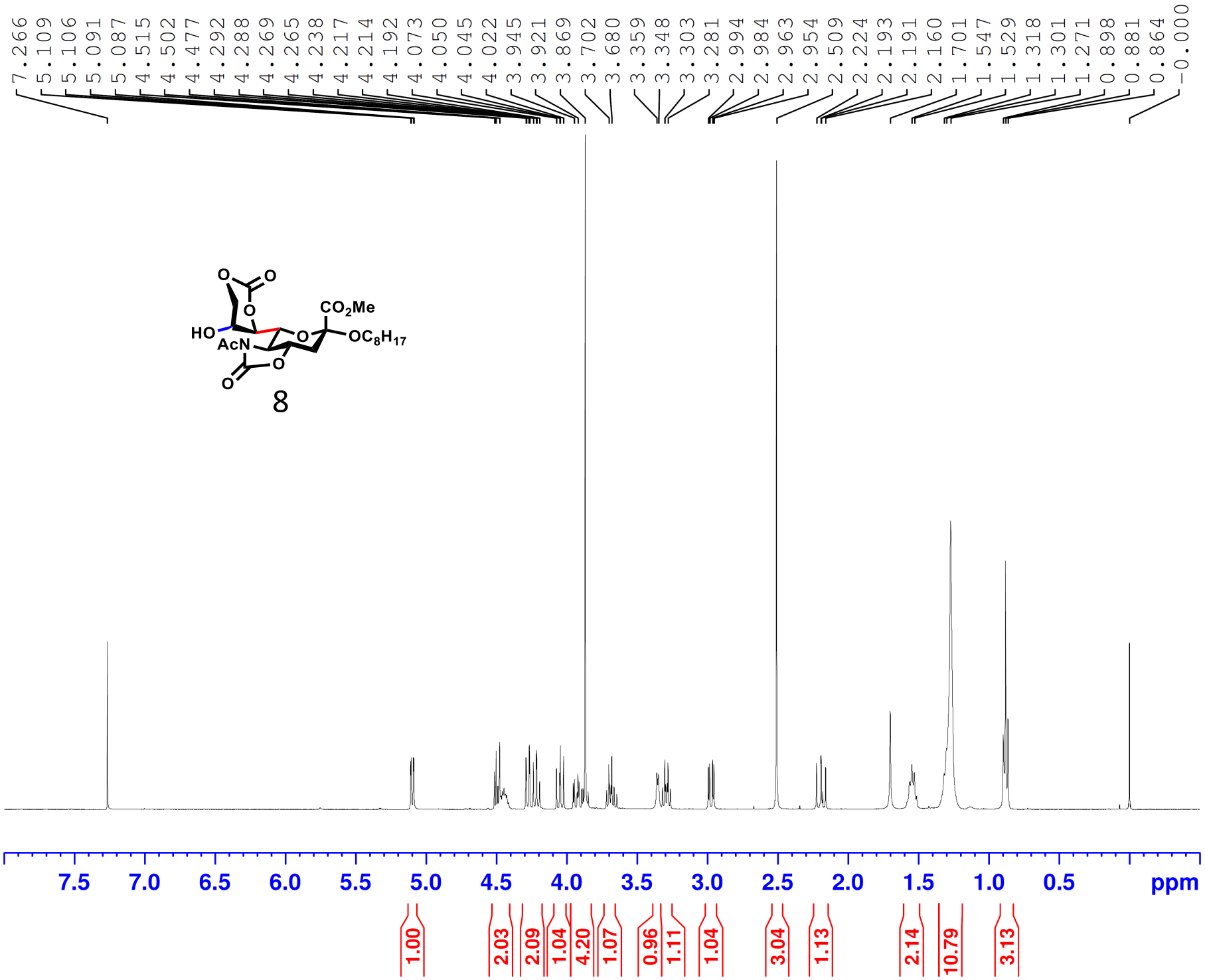
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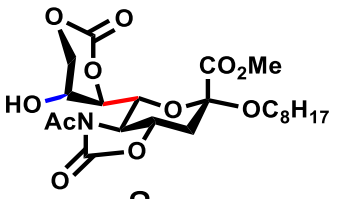
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8

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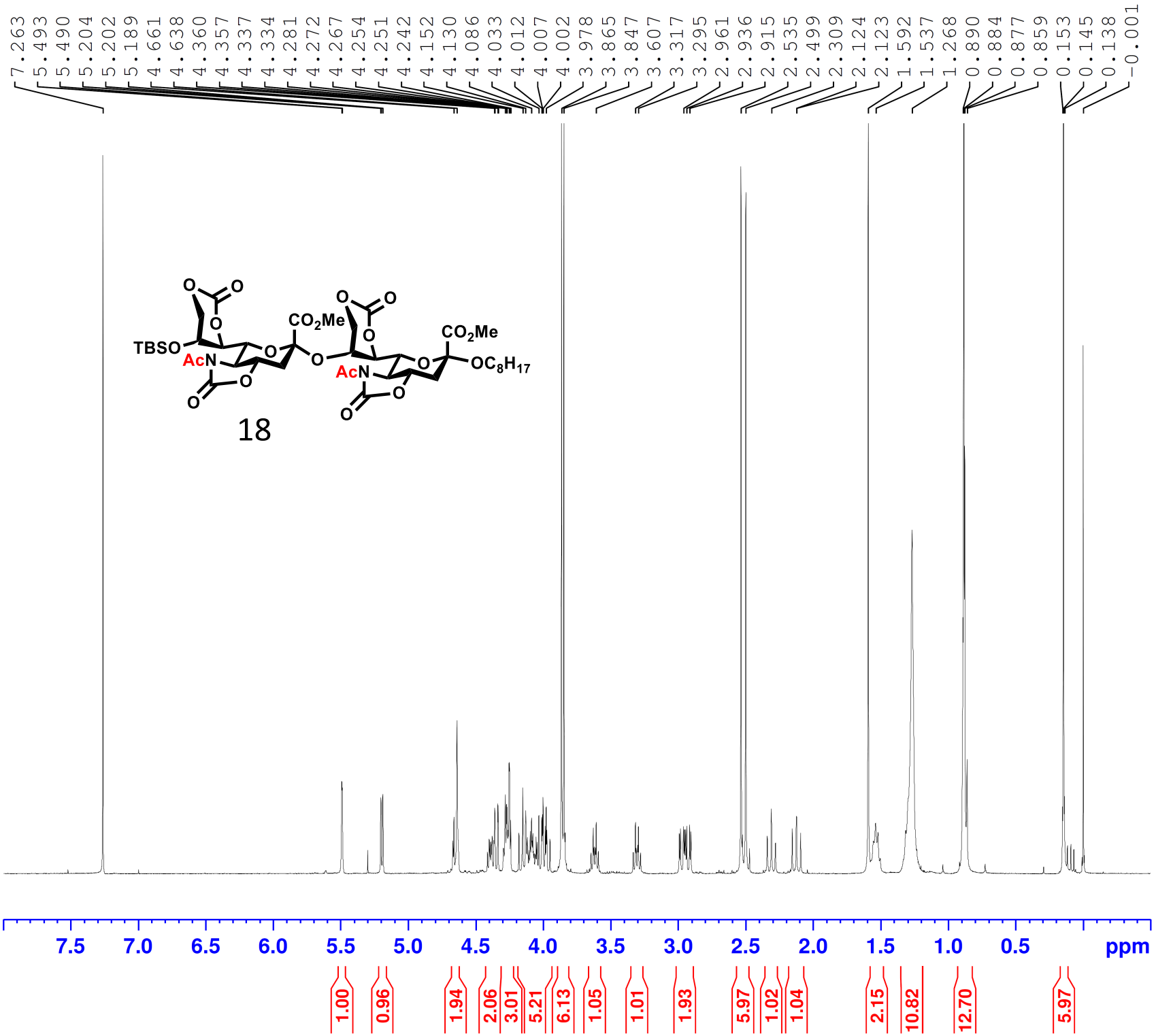
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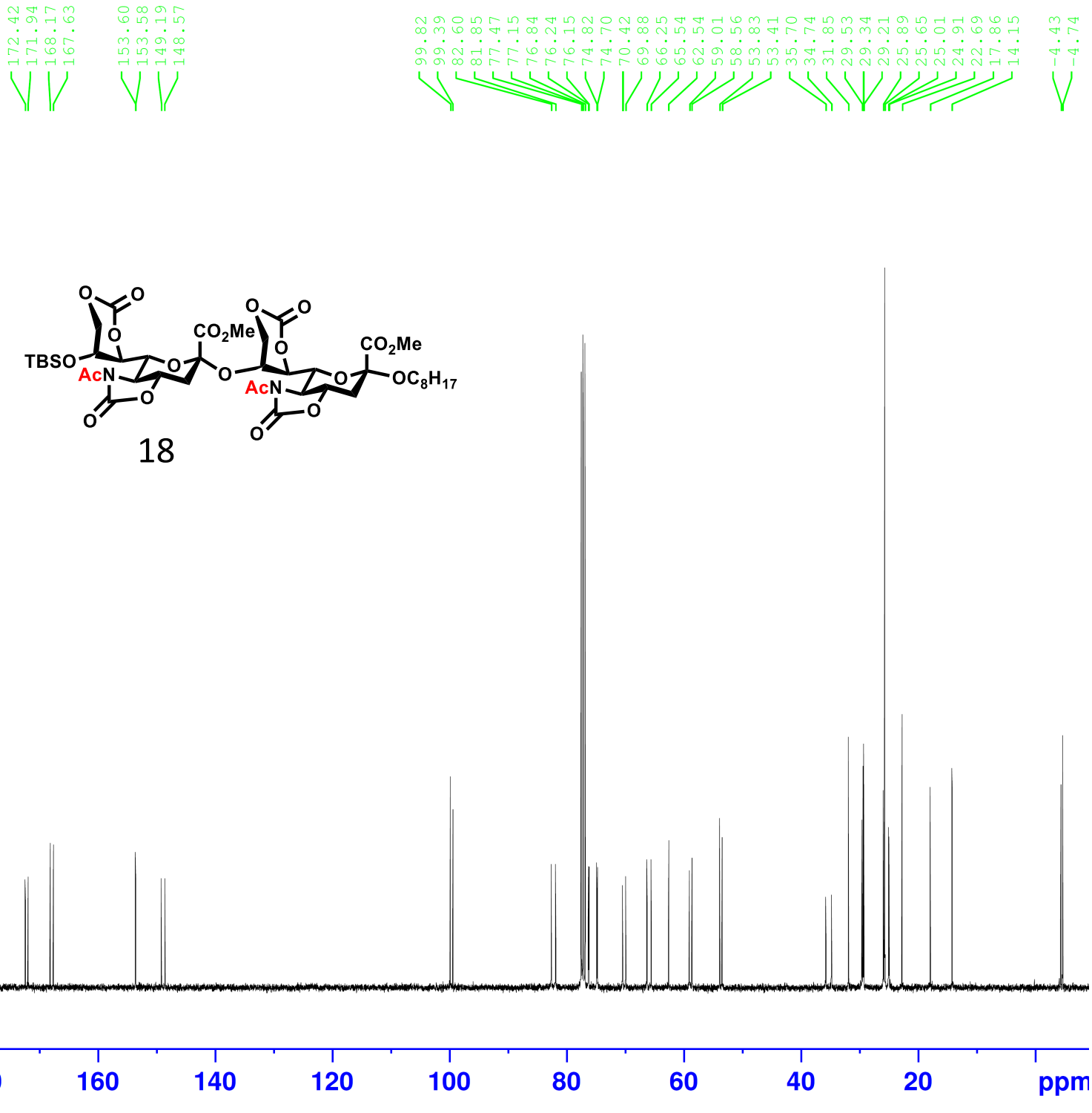
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TBSO
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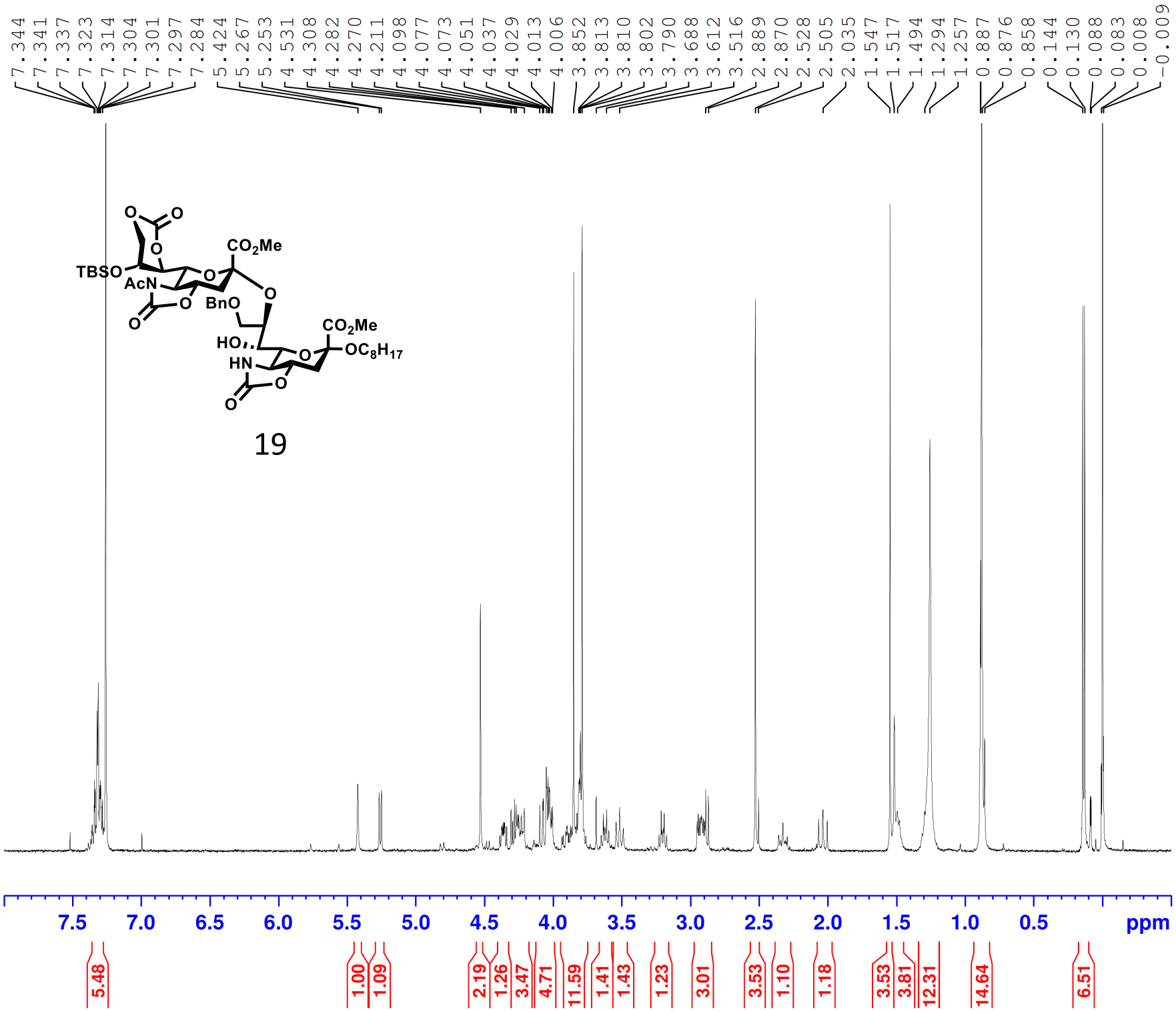
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CO2Me
OC8H17
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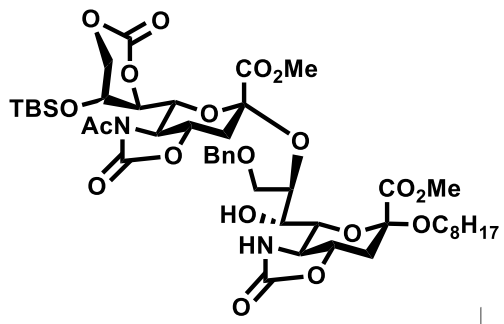
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BnO
HO
HN
CO2Me
CO2Me
OC8H17

19

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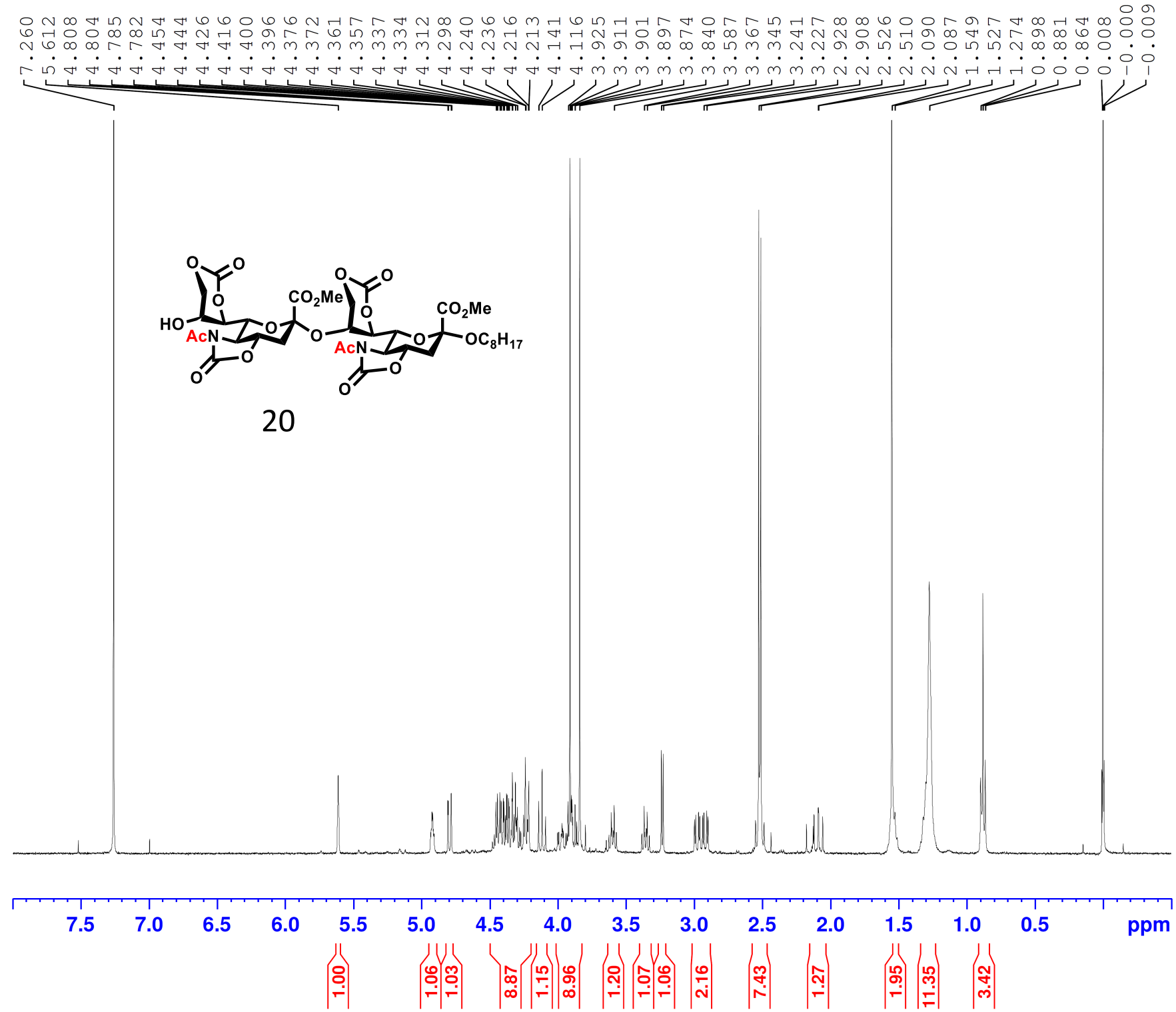
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2.928
2.908
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-0.009
HO
AcN
CO2Me
O
AcN
CO2Me
OC8H17
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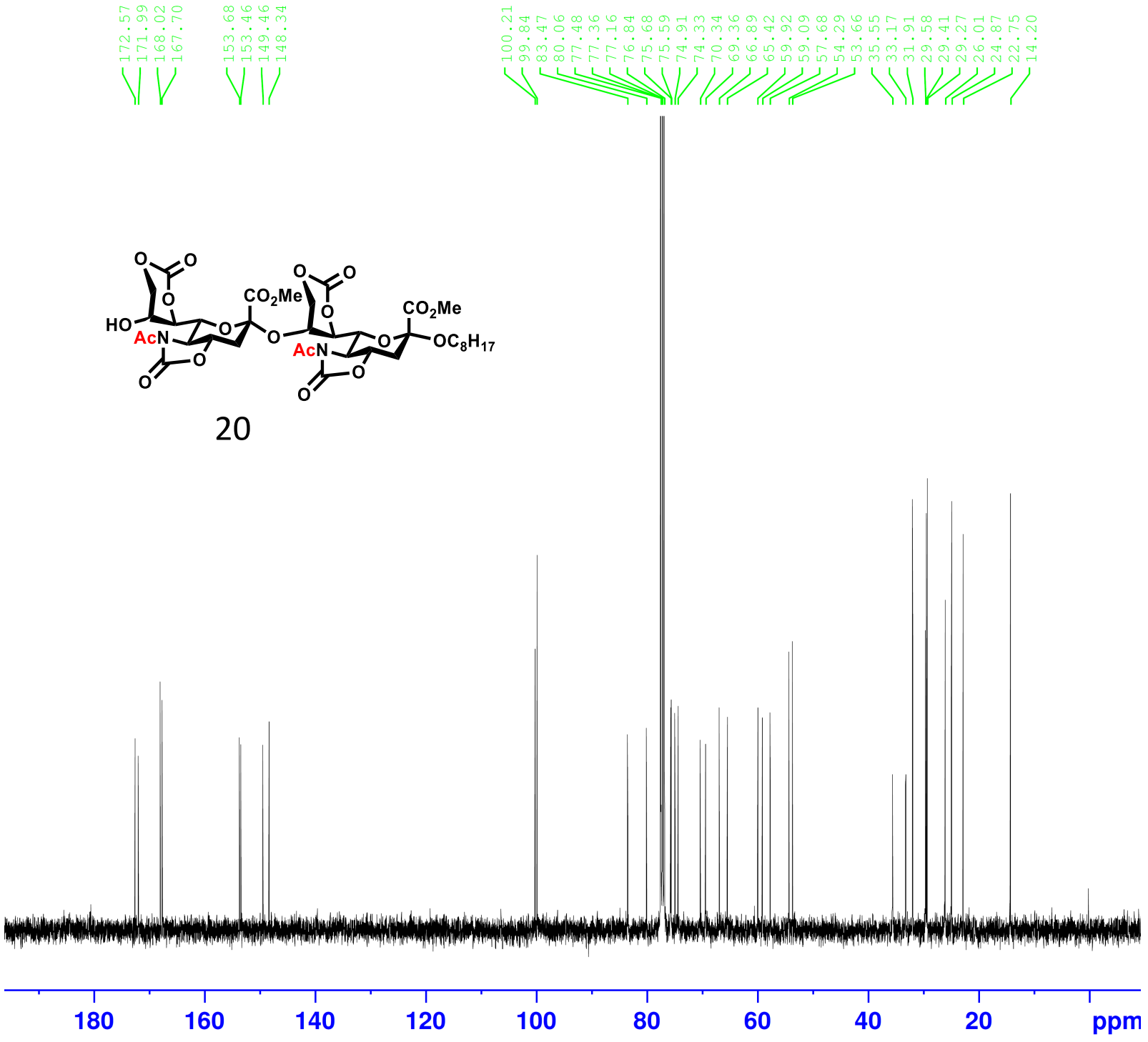
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14.20
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CO2Me
O
AcN
CO2Me
OC8H17
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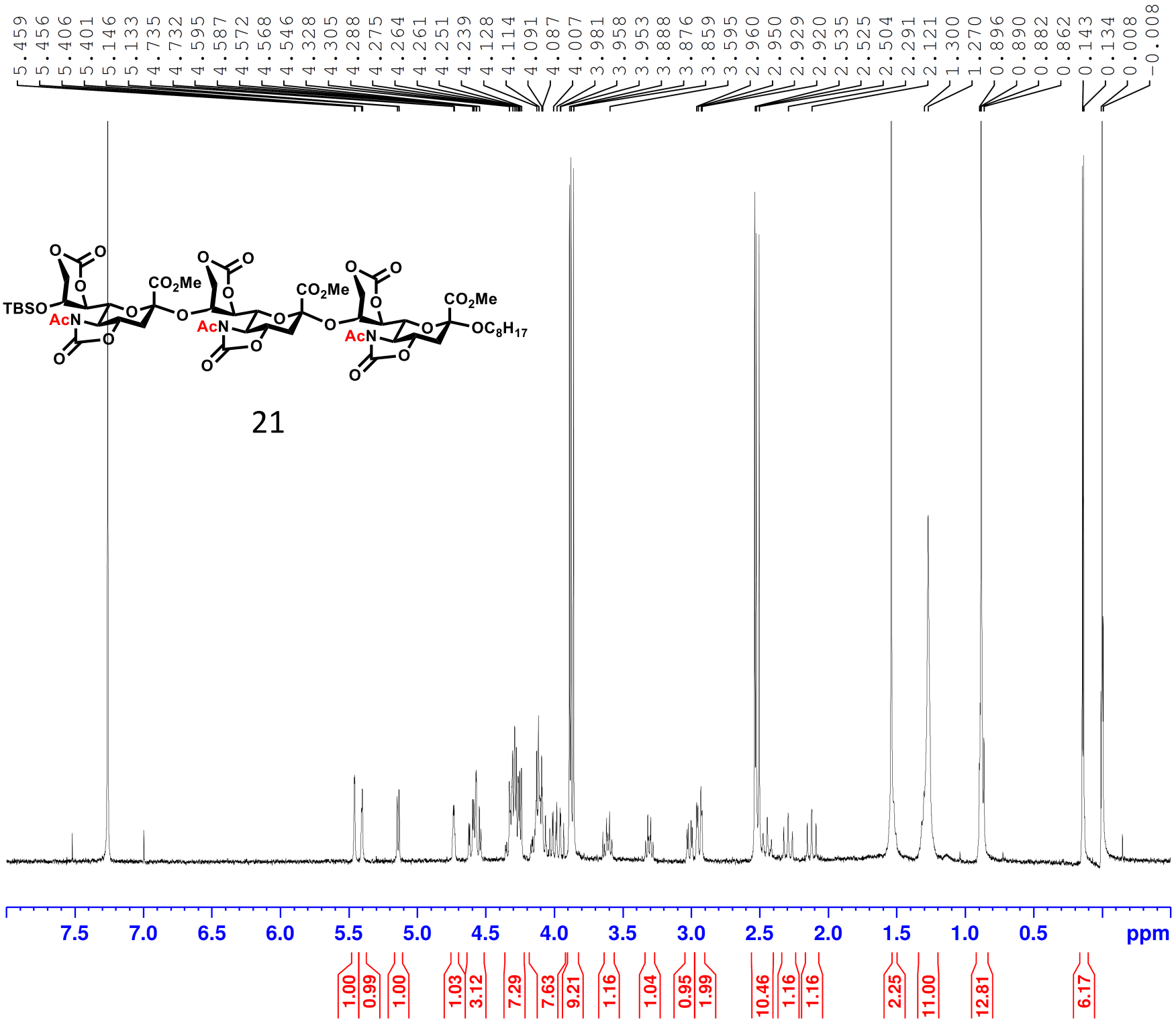
120
100
80
60
40
20
ppm

20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4.251
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4.007
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3.888
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TBSO
AcN
CO2Me
OC8H17
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0.5
ppm
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1.16
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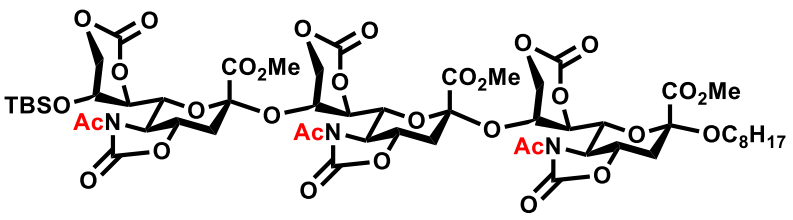
6.17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AcN
AcN
AcN
CO2Me
CO2Me
CO2Me
OC8H17

21

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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
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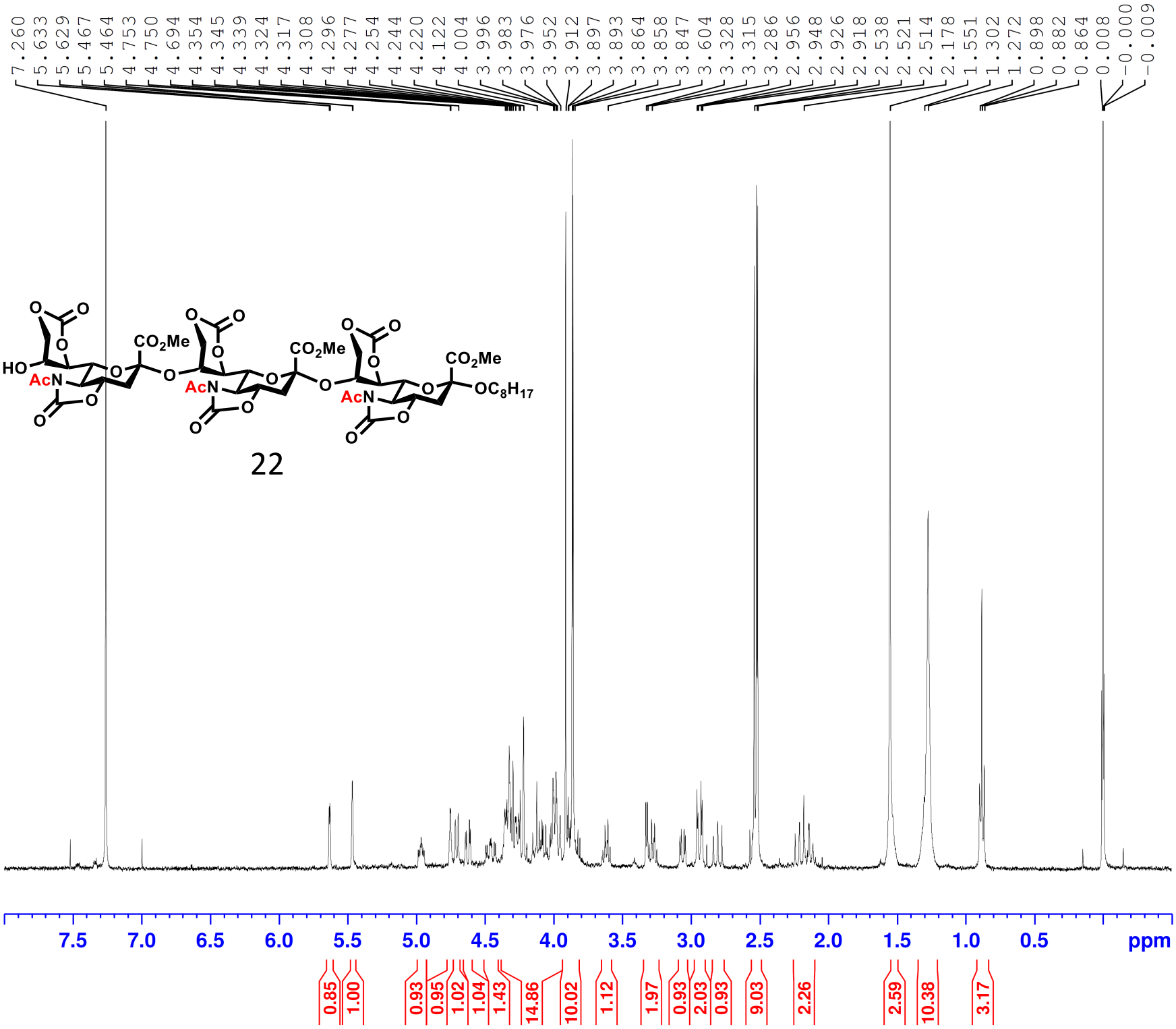
−4.7197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4.308
4.296
4.277
4.254
4.244
4.220
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3.976
3.952
3.912
3.897
3.893
3.864
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3.847
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3.328
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3.286
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2.926
2.918
2.538
2.521
2.514
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1.302
1.272
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0.882
0.864
0.008
-0.000
-0.009
HO
AcN
CO2Me
OC8H17
22
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6.5
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4.0
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1.5
1.0
0.5
ppm
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0.95
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1.04
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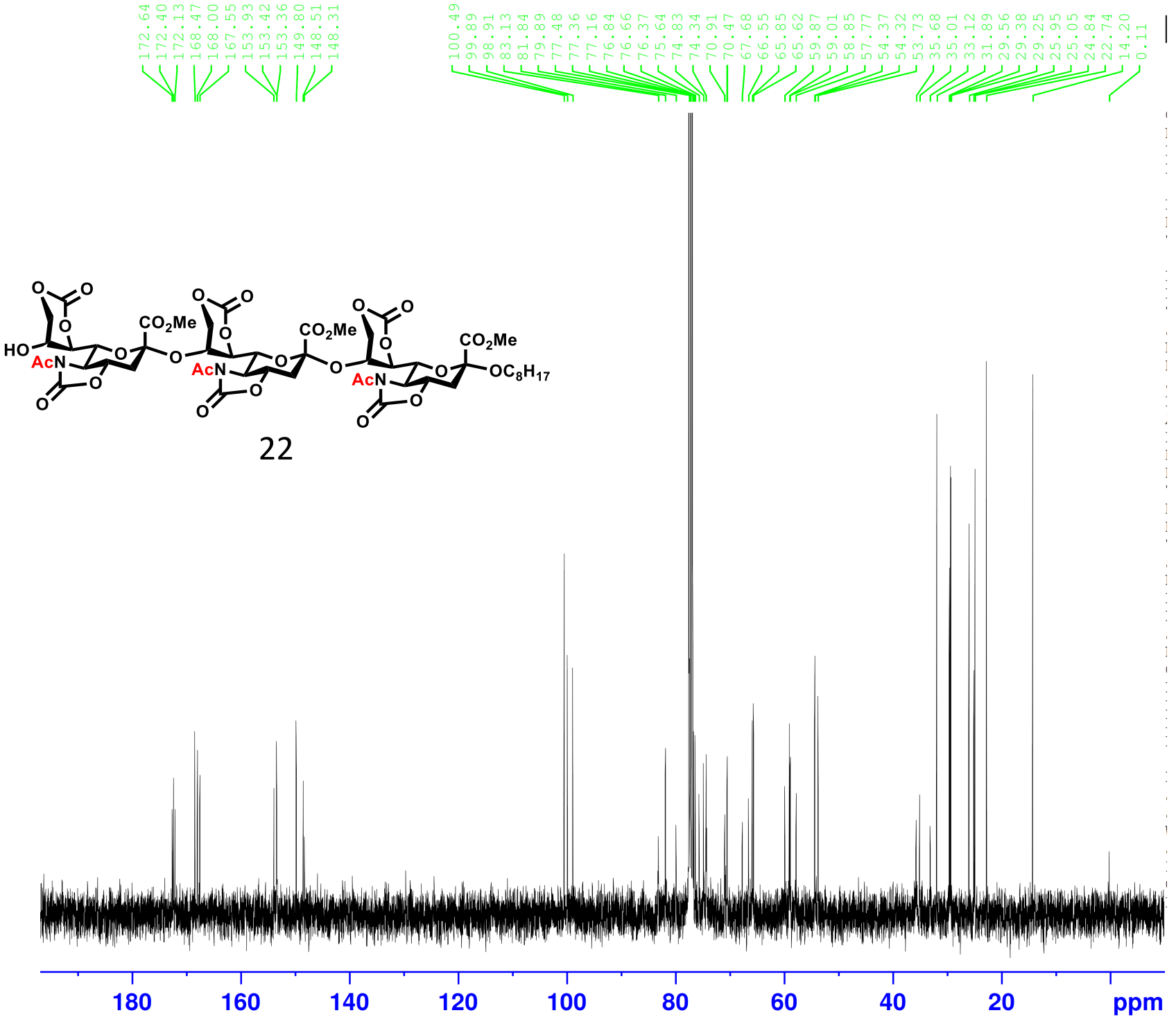
3.17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77.48
77.36
77.16
76.84
76.66
76.37
75.64
74.83
74.34
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70.47
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29.38
29.25
25.95
25.05
24.84
22.74
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AcN
CO2Me
OC8H17
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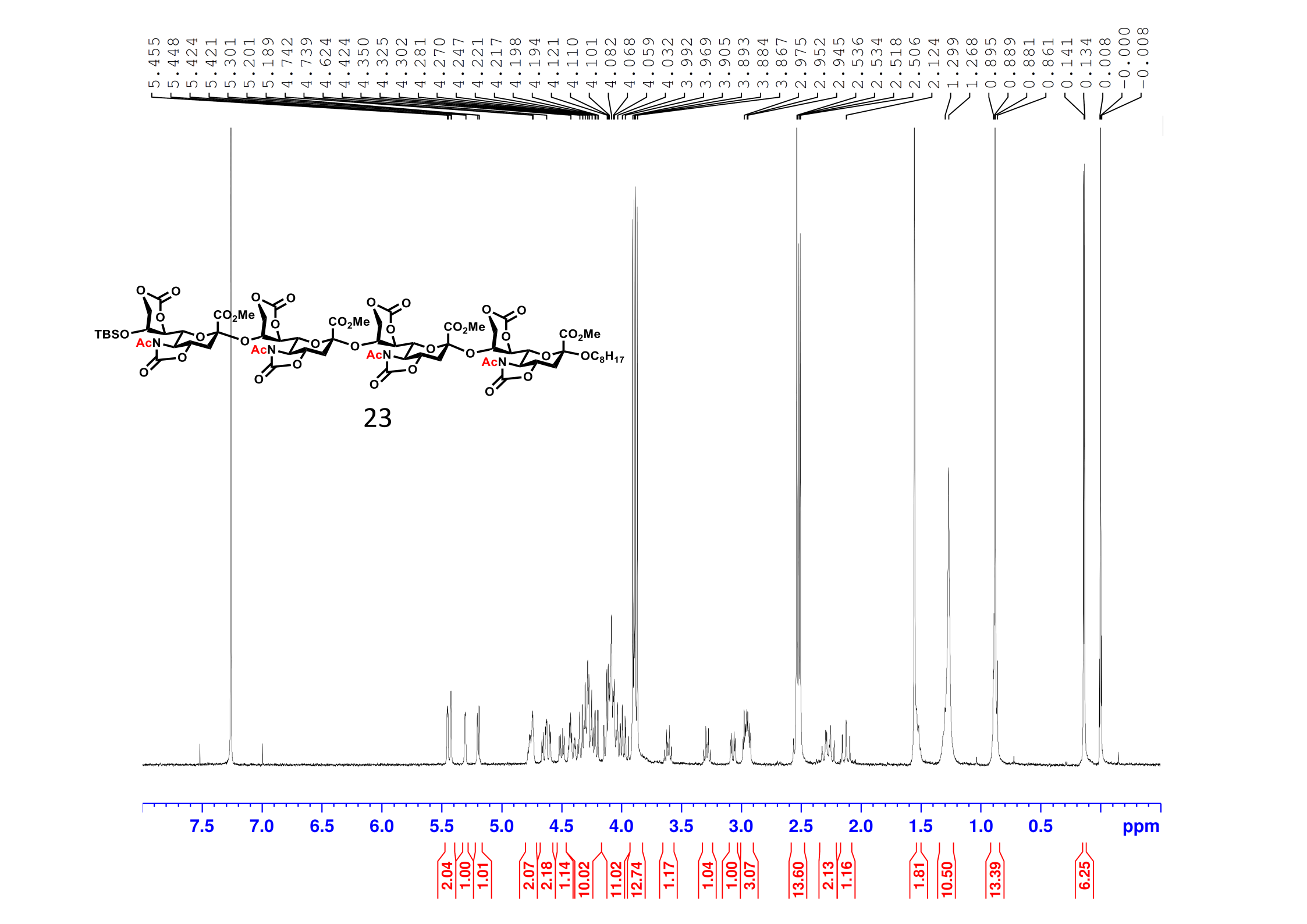
140
120
100
80
60
40
20
ppm

22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3.867
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2.952
2.945
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2.534
2.518
2.506
2.124
1.299
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0.889
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0.861
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TBSO
AcN
CO2Me
OC8H17
23
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6.5
6.0
5.5
5.0
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4.0
3.5
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1.0
0.5
ppm
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1.00
1.01
2.07
2.18
1.14
10.02
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1.00
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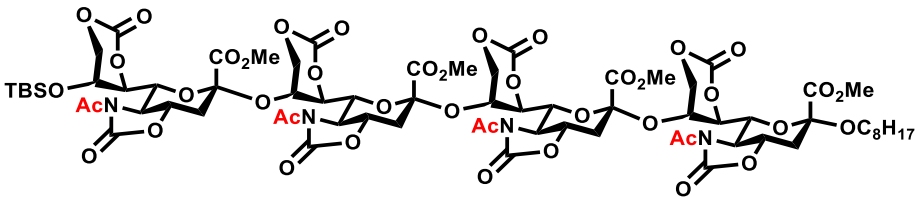
6.25


TBSO
AcN
CO2Me
OC8H17

23

#
.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 −10.
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172.5411
168.3210
167.6635
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153.4817
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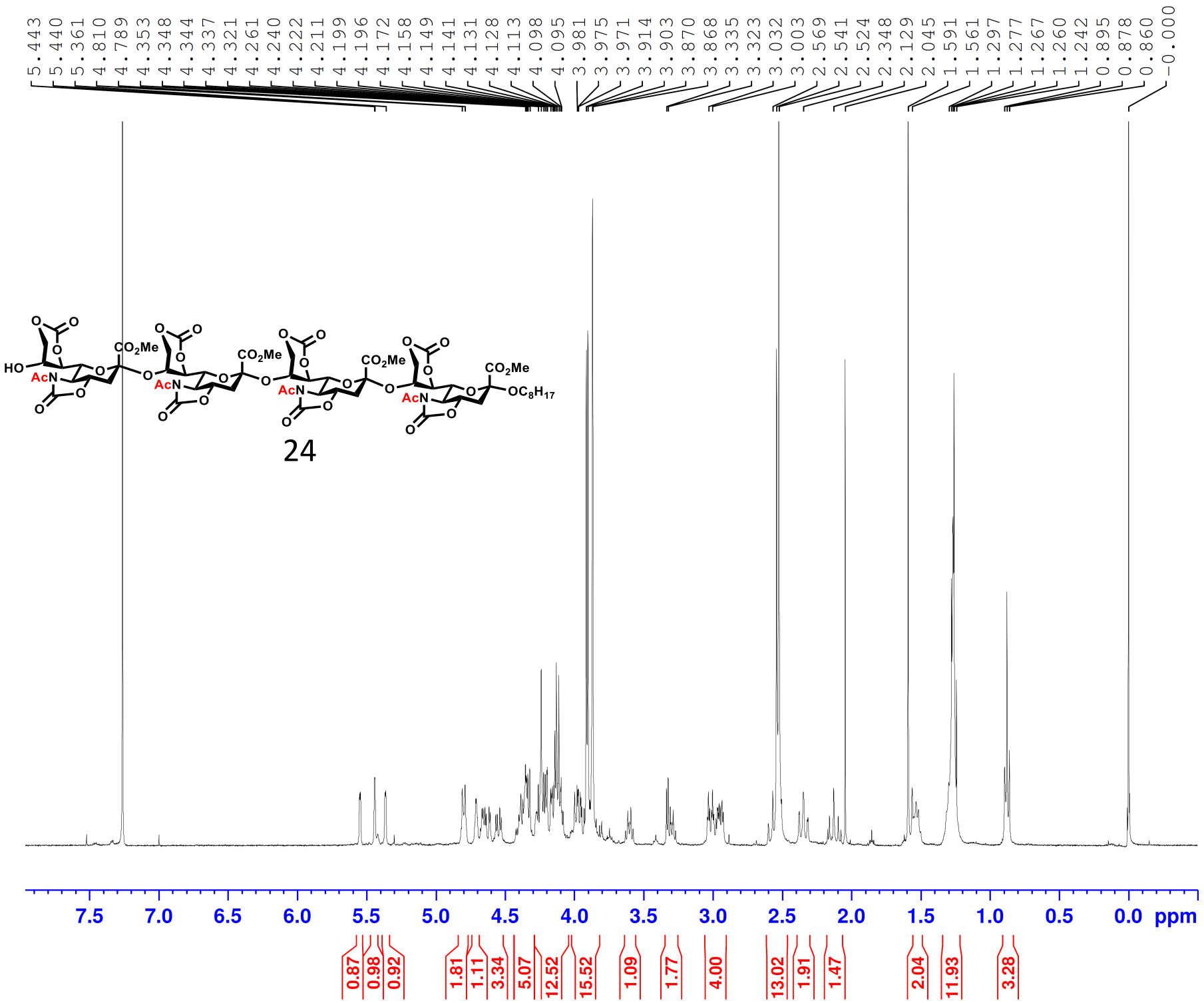
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-0.000
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AcN
CO2Me
OC8H17
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6.5
6.0
5.5
5.0
4.5
4.0
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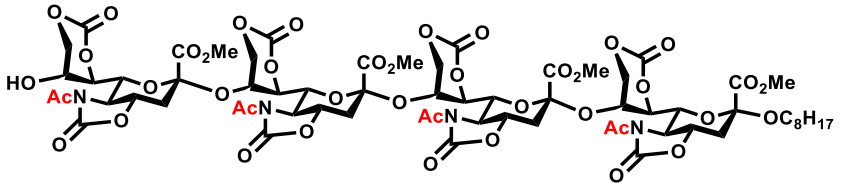
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AcN
AcN
AcN
CO2Me
CO2Me
CO2Me
CO2Me
OC8H17

24

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60.02
59.02
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29.40
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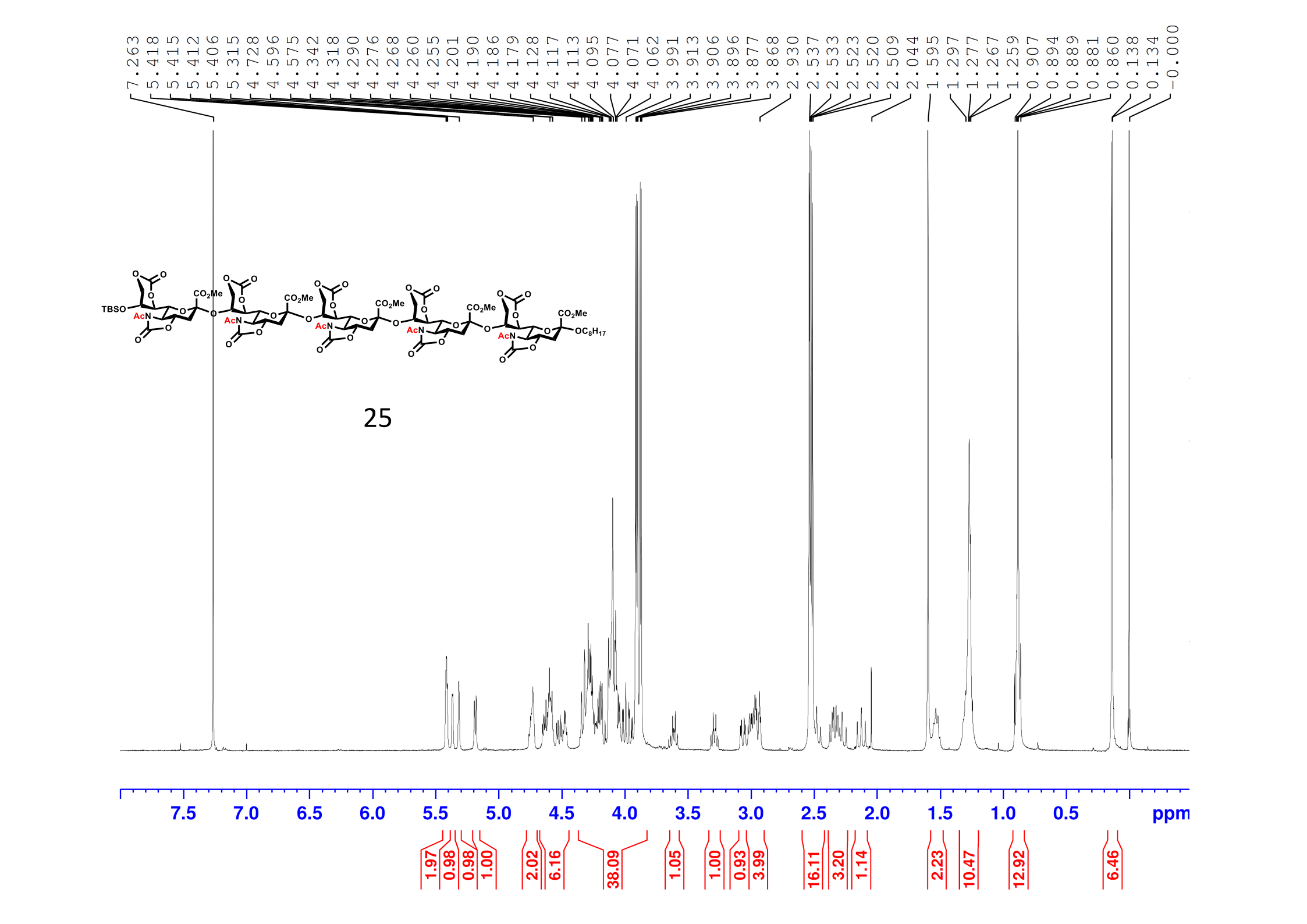
40
20
ppm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TBSO
AcN
CO2Me
OC8H17
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6.0
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4.0
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ppm
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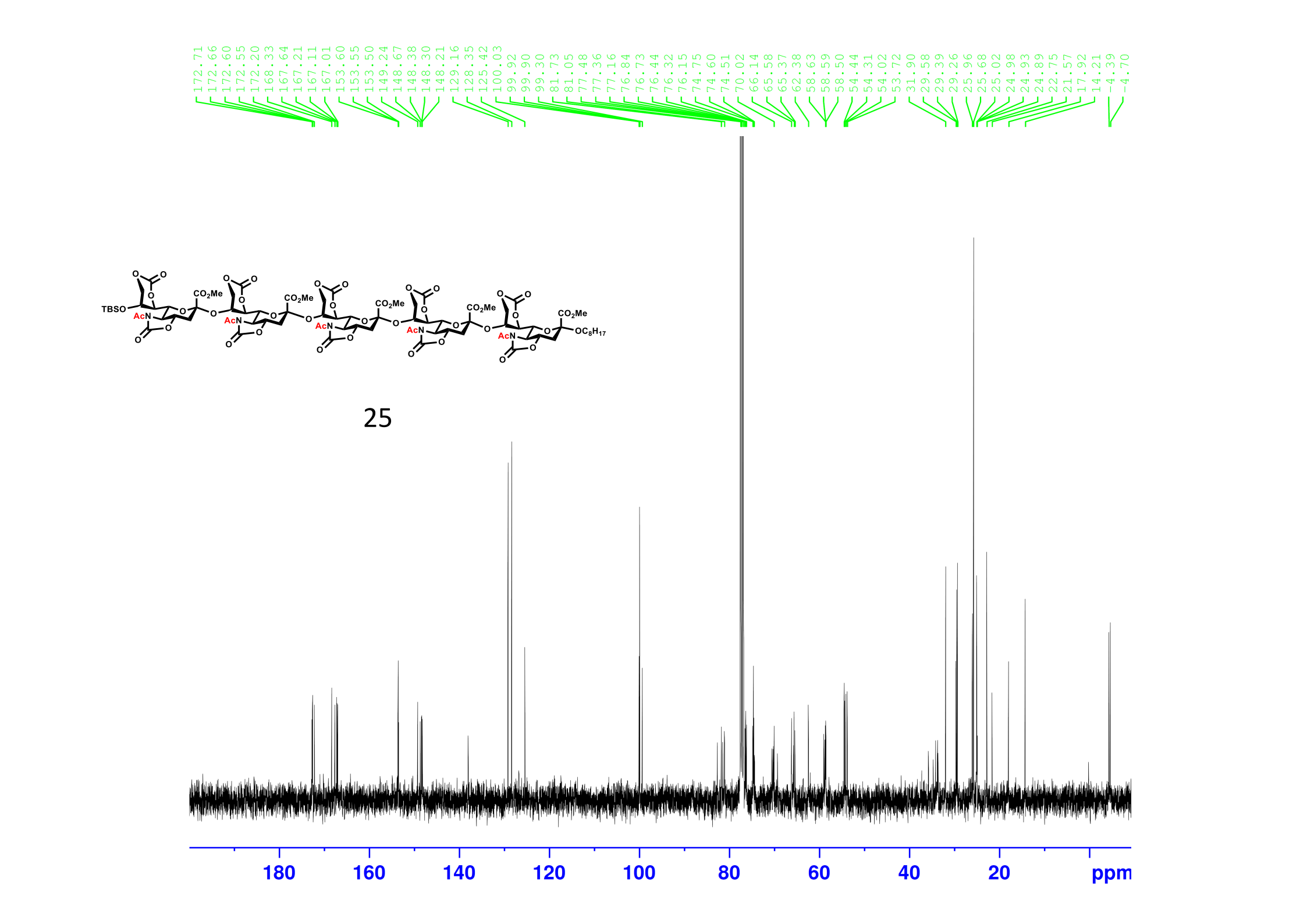
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AcN
CO2Me
OC8H17
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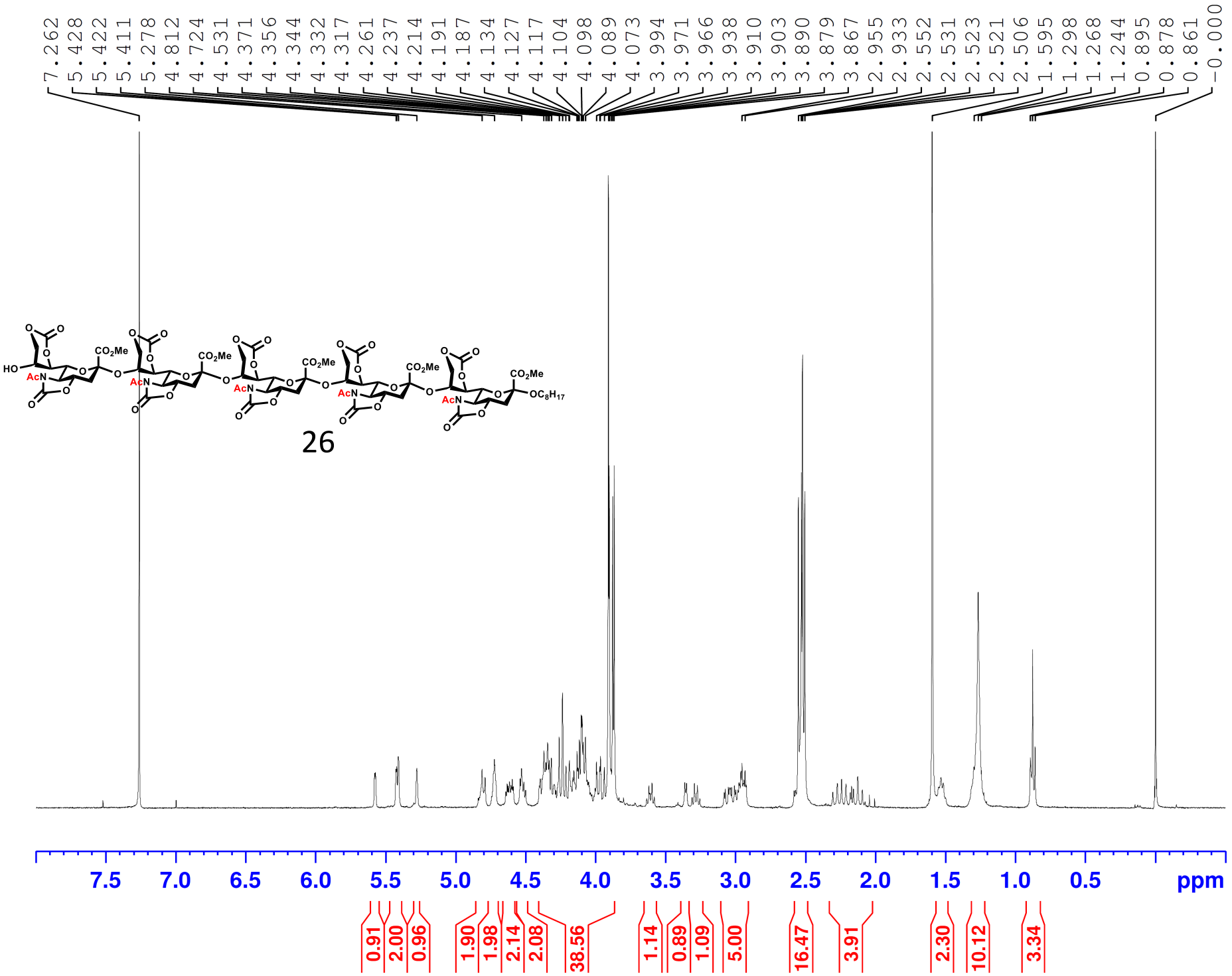
20
ppm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AcN
CO2Me
OC8H17
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ppm
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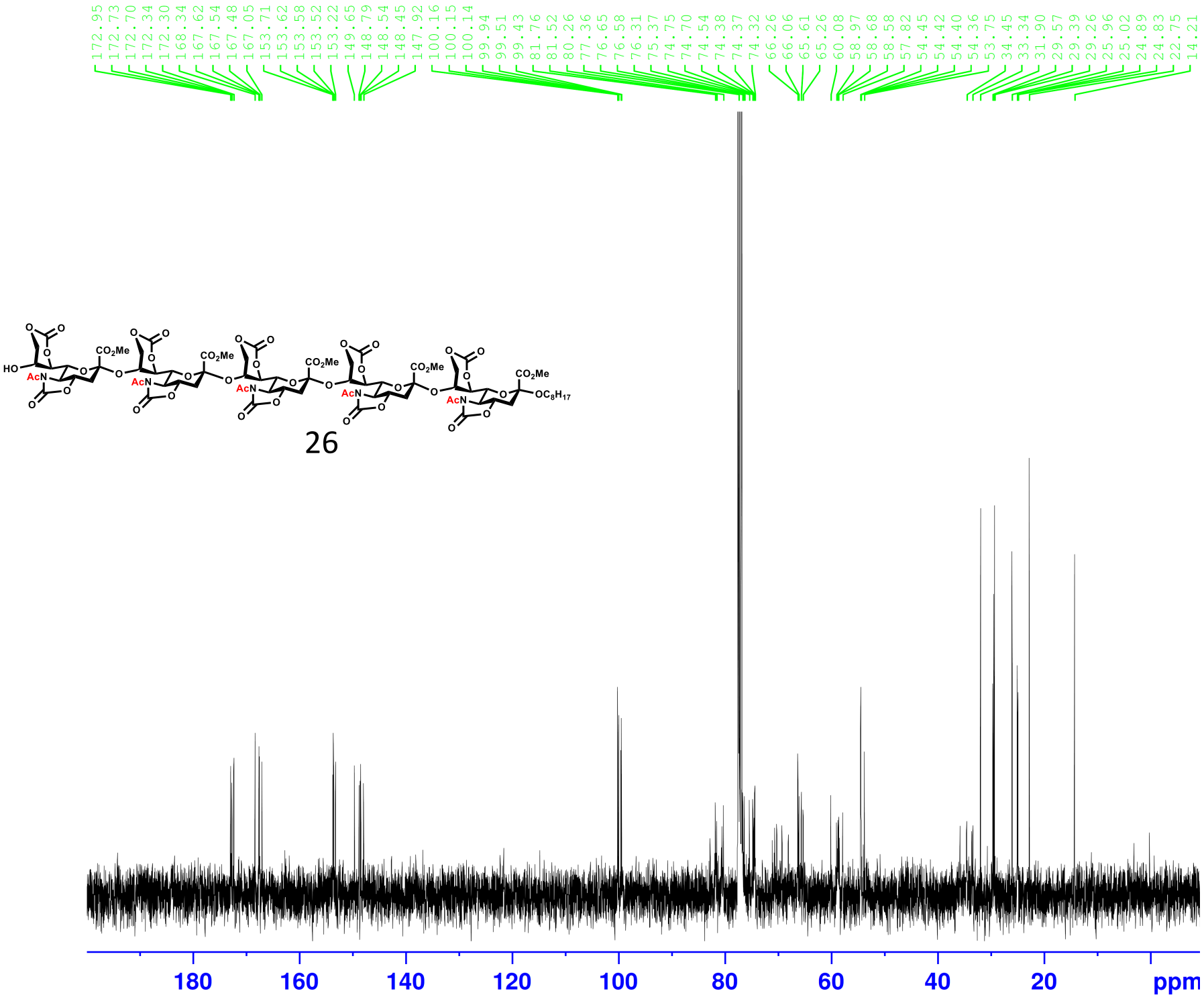
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AcN
CO2Me
OC8H17
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140
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60
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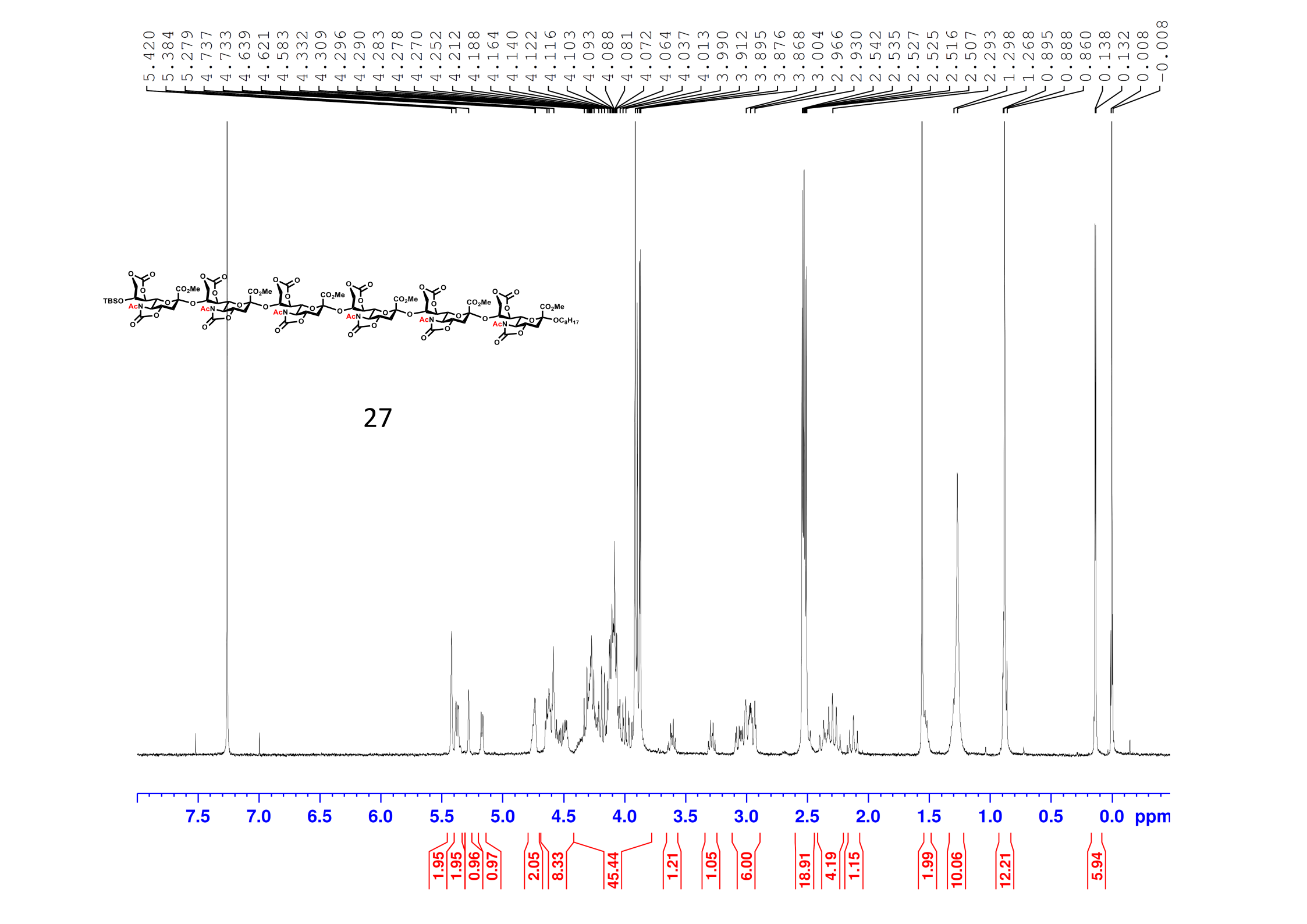
20
ppm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2.527
2.525
2.516
2.507
2.293
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1.268
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0.860
0.138
0.132
0.008
-0.008
TBSO
AcN
CO2Me
OC8H17
27
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6.5
6.0
5.5
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4.0
3.5
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1.5
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0.0
ppm
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1.95
0.96
0.97
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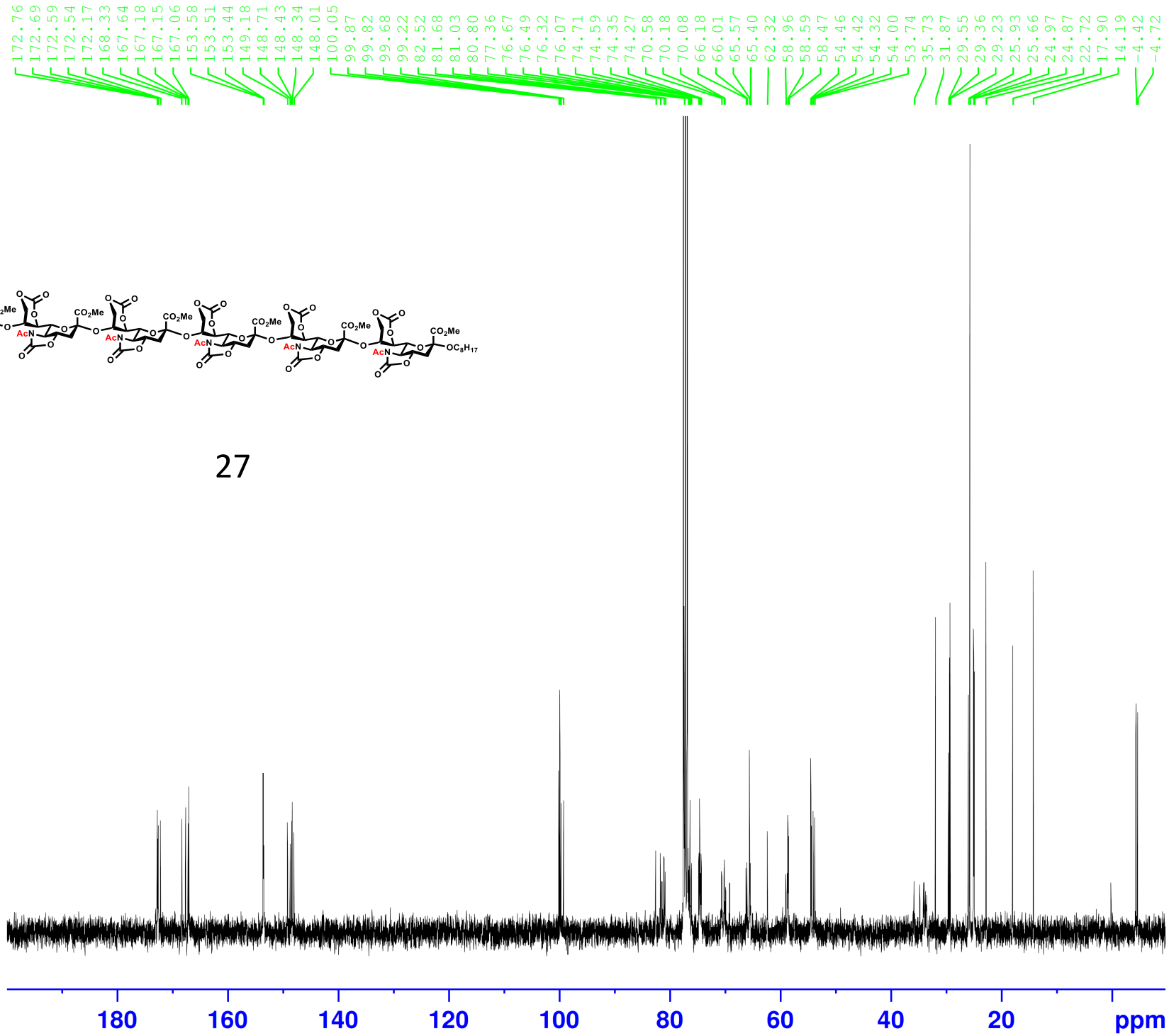
5.94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148.71
148.43
148.34
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99.87
99.82
99.68
99.22
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81.03
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70.18
70.08
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66.01
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65.40
62.32
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54.00
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29.55
29.36
29.23
25.93
25.66
24.97
24.87
22.72
17.90
14.19
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AcN
CO2Me
OC8H17
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120
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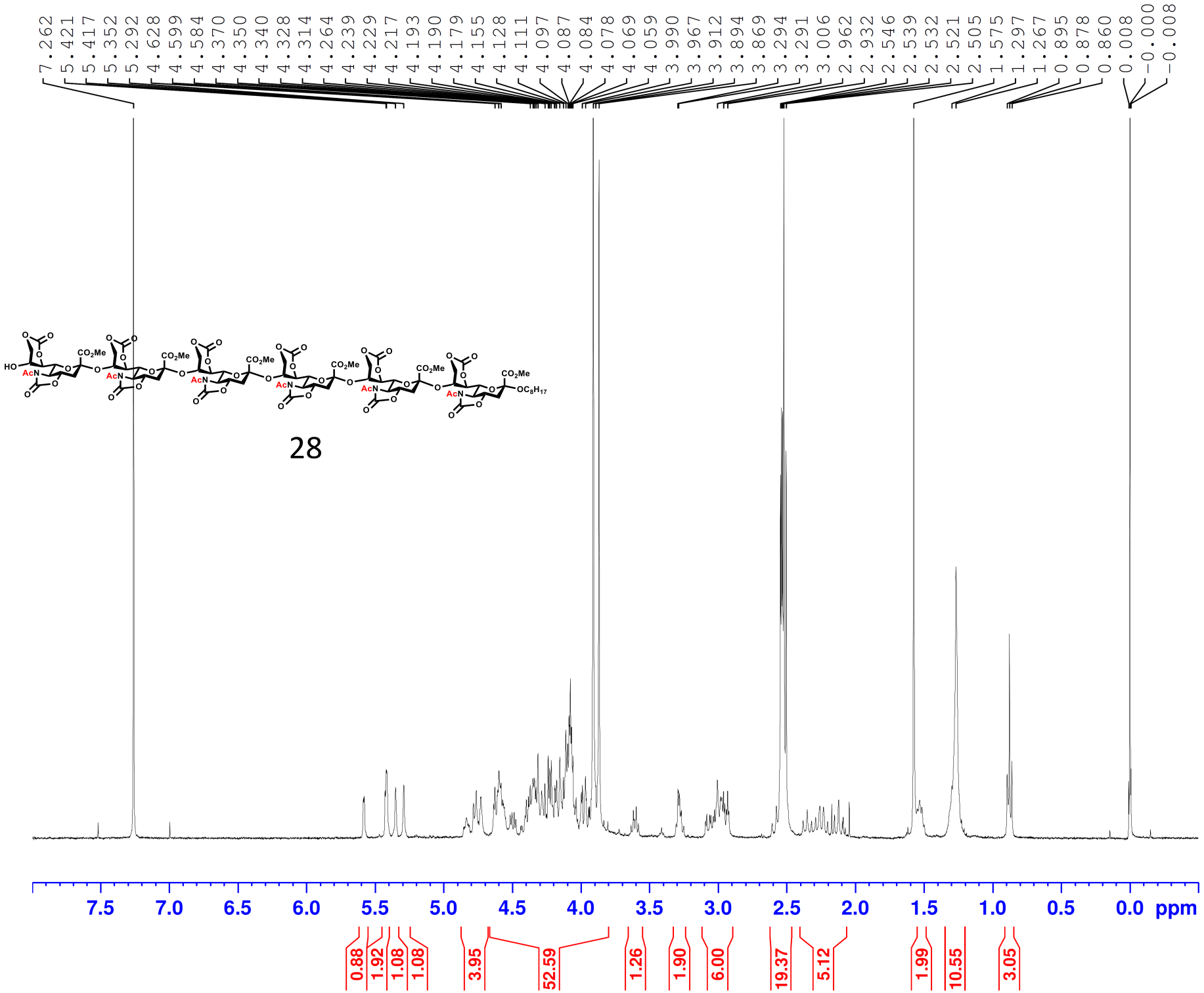
60
40
20
ppm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4.239
4.229
4.217
4.193
4.190
4.179
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4.111
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4.087
4.084
4.078
4.069
4.059
3.990
3.967
3.912
3.894
3.869
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3.291
3.006
2.962
2.932
2.546
2.539
2.532
2.521
2.505
1.575
1.297
1.267
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0.878
0.860
0.008
-0.000
-0.008
28
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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ppm
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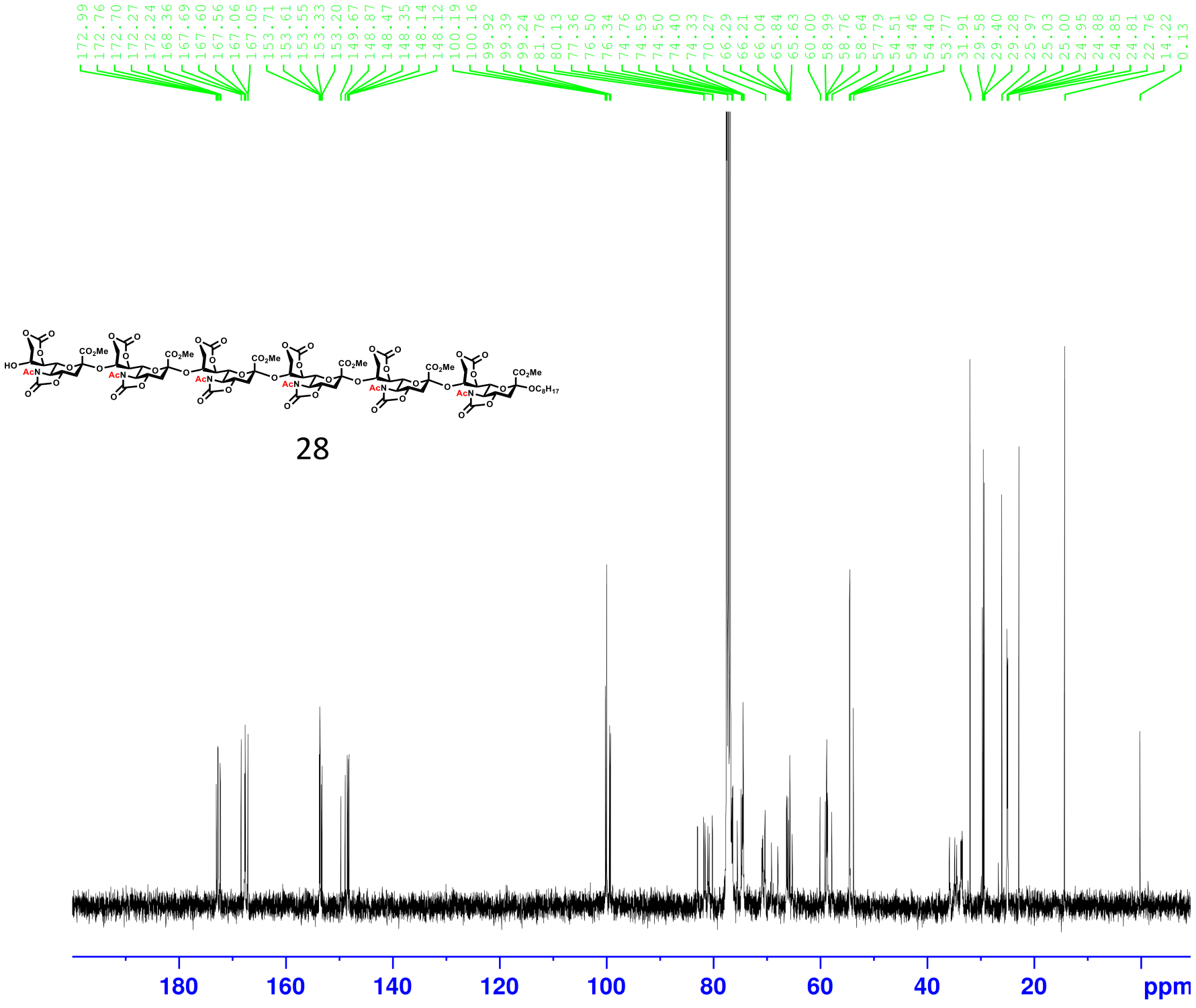
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153.55
153.33
153.20
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148.47
148.35
148.14
148.12
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100.16
99.92
99.39
99.24
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80.13
77.36
76.50
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74.76
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74.50
74.40
74.33
70.27
66.29
66.21
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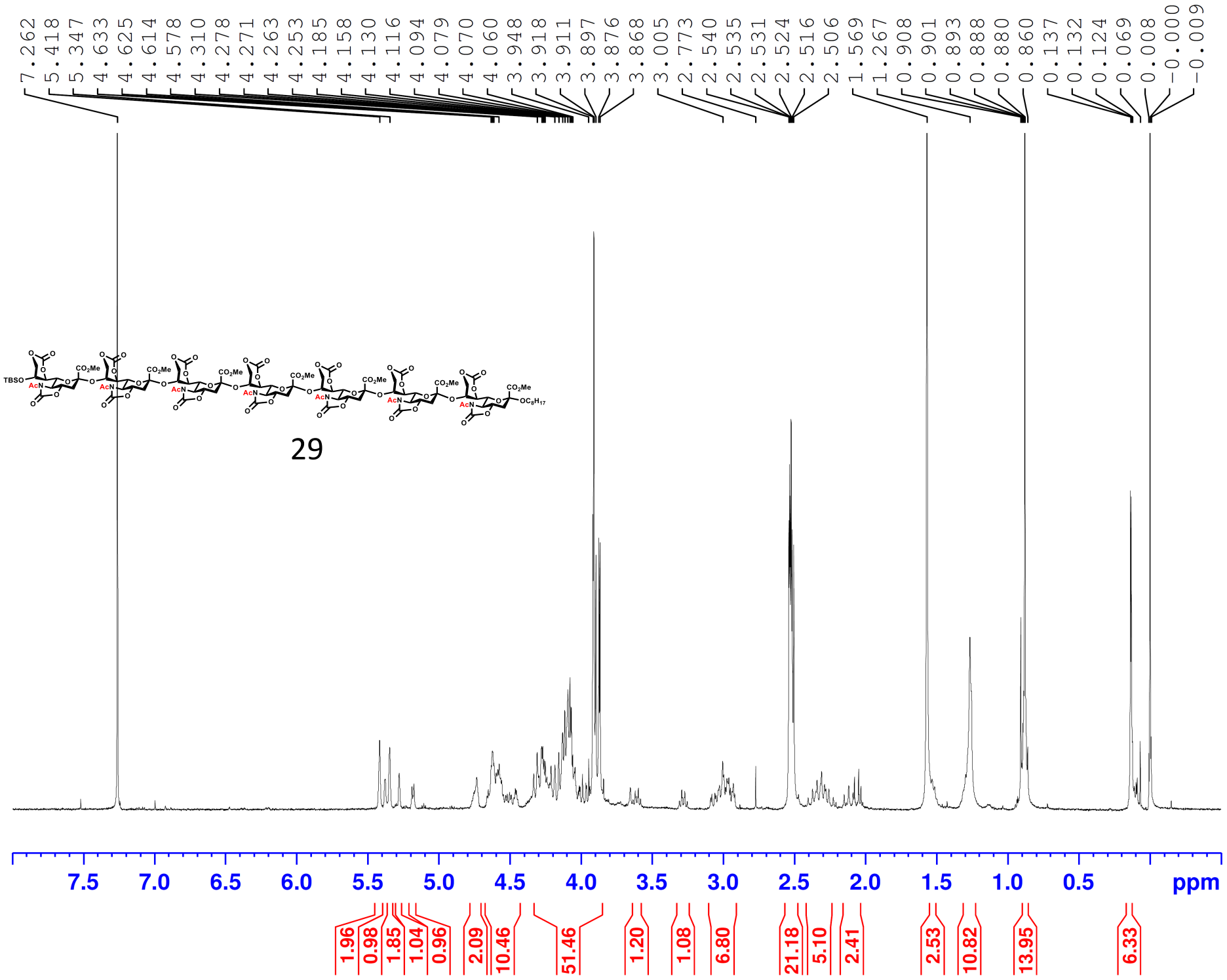
29.58
29.40
29.28
25.97
25.03
25.00
24.95
24.88
24.85
24.81
22.76
14.22
0.13
HO
AcN
CO2Me
OC8H17
28
180
160
140
120
100
80
60
40
20
ppm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4.158
4.130
4.116
4.094
4.079
4.070
4.060
3.948
3.918
3.911
3.897
3.876
3.868
3.005
2.773
2.540
2.535
2.531
2.524
2.516
2.506
1.569
1.267
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0.901
0.893
0.888
0.880
0.860
0.137
0.132
0.124
0.069
0.008
-0.000
-0.009
TBSO
AcN
CO2Me
OC8H17
29
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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
ppm
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0.98
1.85
1.04
0.96
2.09
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1.20
1.08
6.80
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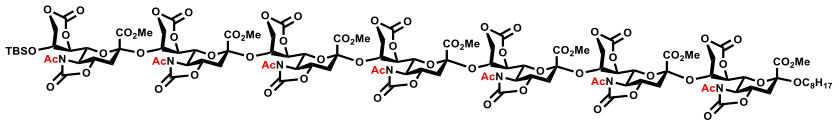
2.41
2.53
10.82
13.95
6.33


TBSO
AcN
CO2Me
OC8H17

29

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167.25
167.18
167.13
167.08
167.03
153.58
153.54
153.52
153.48
153.45
153.37
149.24
148.77
148.54
148.44
148.29
148.25
148.05
100.08
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99.89
99.76
99.62
99.23
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76.59
76.52
76.37
76.28
76.16
74.60
74.39
70.05
65.75
65.61
62.36
58.65
58.54
54.50
54.45
54.35
54.06
53.75
31.92
29.60
29.42
29.28
25.98
25.75
25.69
25.02
24.95
24.90
22.77
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-4.68
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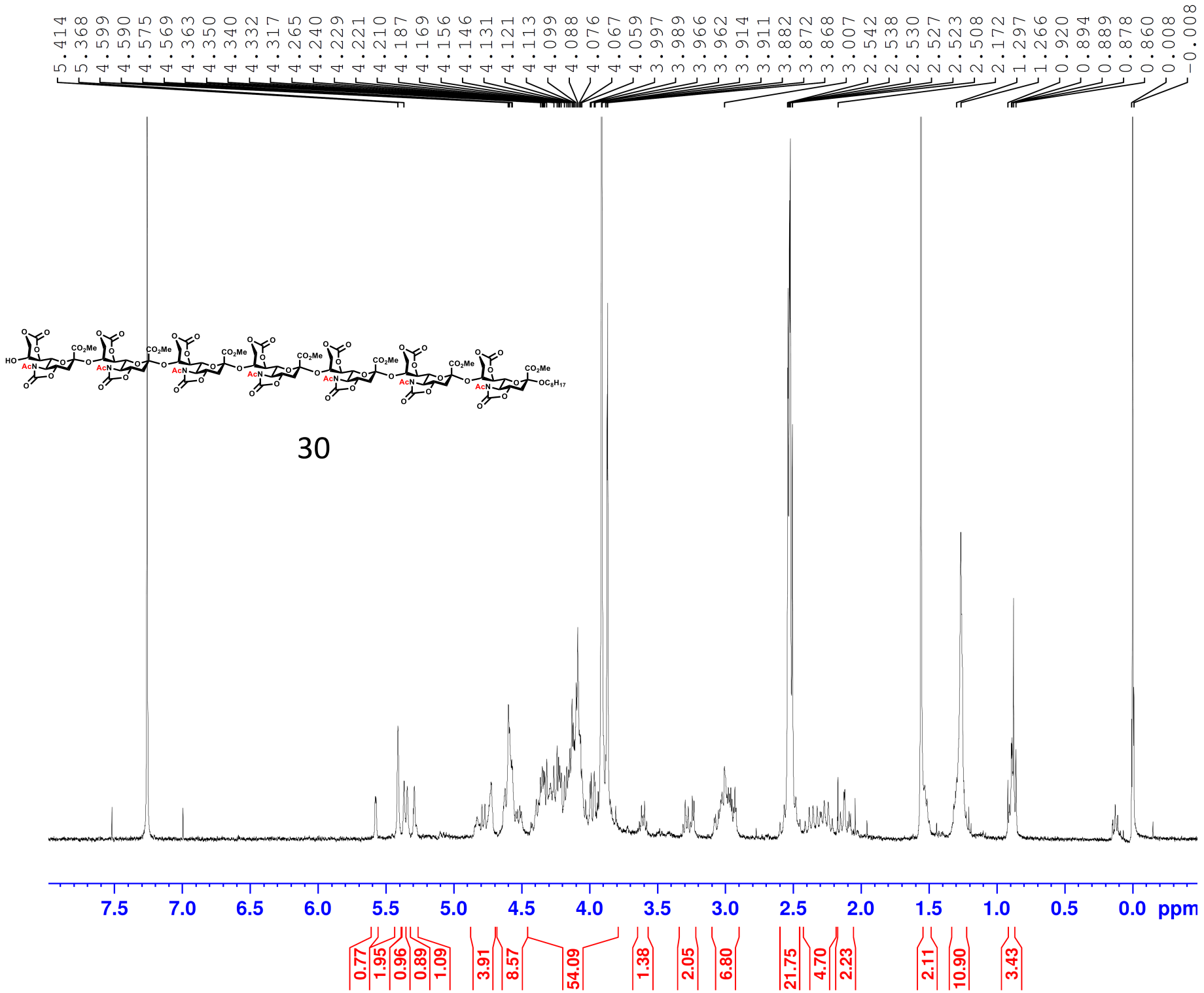
160
140
120
100
80
60
40
20
ppm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4.229
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4.210
4.187
4.169
4.156
4.146
4.131
4.121
4.113
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4.088
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4.067
4.059
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3.966
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3.914
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3.868
3.007
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2.538
2.530
2.527
2.523
2.508
2.172
1.297
1.266
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0.894
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0.878
0.860
0.008
-0.008
30
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
ppm
0.77
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0.96
0.89
1.09
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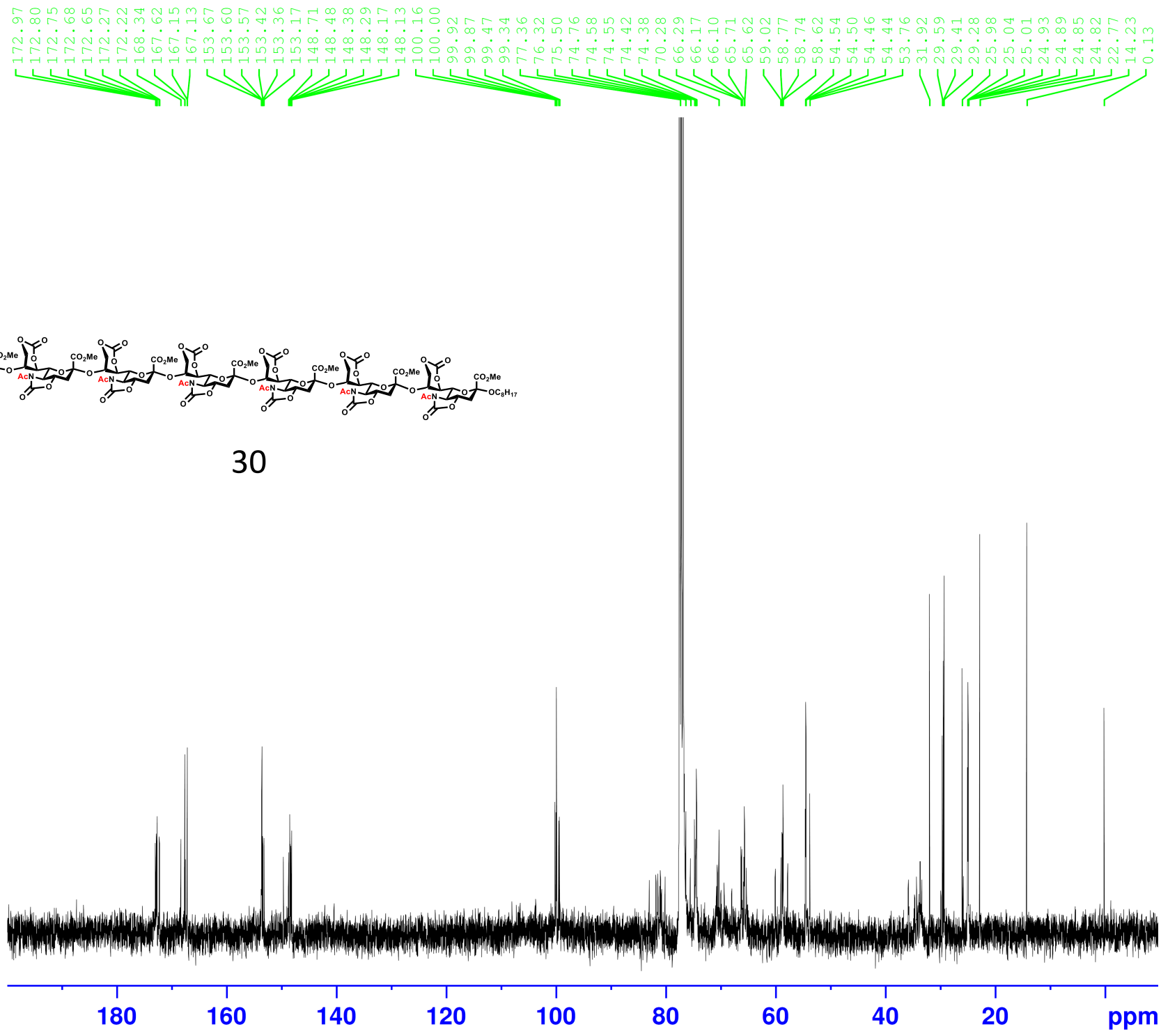
2.11
10.90
3.43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167.13
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153.60
153.57
153.42
153.36
153.17
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148.48
148.38
148.29
148.17
148.13
100.16
100.00
99.92
99.87
99.47
99.34
77.36
76.32
75.50
74.76
74.58
74.55
74.42
74.38
70.28
66.29
66.17
66.10
65.71
65.62
59.02
58.77
58.74
58.62
54.54
54.50
54.46
54.44
53.76
31.92
29.59
29.41
29.28
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25.04
25.01
24.93
24.89
24.85
24.82
22.77
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HO
AcN
CO2Me
OC8H17
30
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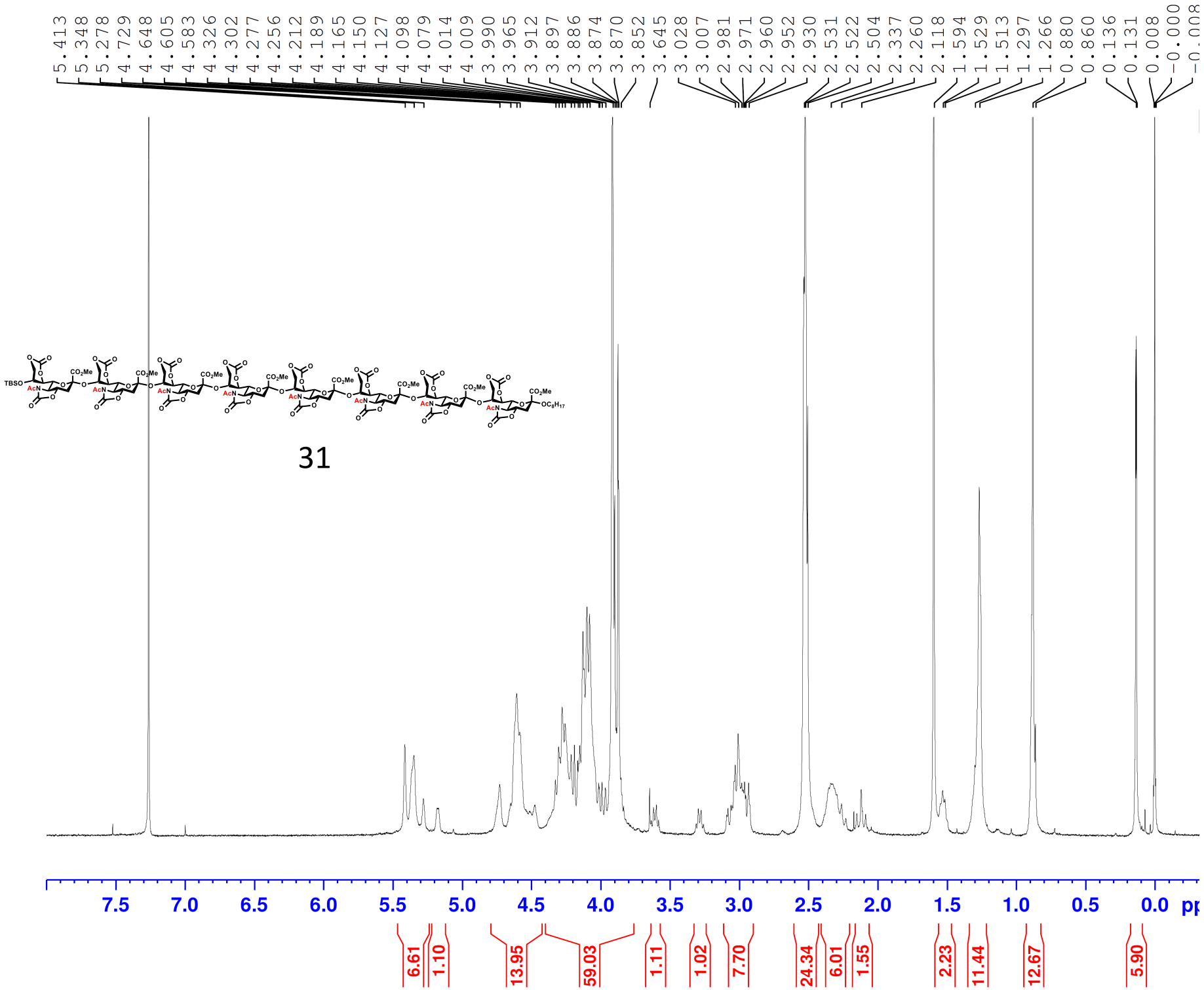
160
140
120
100
80
60
40
20
ppm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4.165
4.150
4.127
4.098
4.079
4.014
4.009
3.990
3.965
3.912
3.897
3.886
3.874
3.870
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3.028
3.007
2.981
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2.952
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2.531
2.522
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2.337
2.260
2.118
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1.529
1.513
1.297
1.266
0.880
0.860
0.136
0.131
0.008
-0.000
TBSO
AcN
CO2Me
OC8H17
31
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
ppm
6.61
1.10
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1.11
1.02
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24.34
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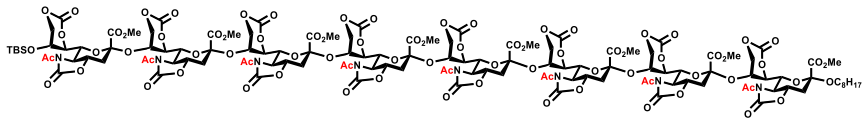
1.55
2.23
11.44
12.67
5.90



31

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172.58
172.18
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167.61
167.18
167.03
153.62
153.50
149.18
148.67
148.33
148.03
100.07
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99.82
99.75
99.26
82.53
81.66
81.28
80.93
77.36
76.66
76.41
76.13
74.68
74.57
74.48
74.32
70.62
70.05
69.18
66.13
65.99
65.56
62.37
58.94
58.58
54.47
54.00
53.75
35.74
34.74
34.10
31.86
29.55
29.36
29.23
25.92
25.64
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24.81
22.71
17.89
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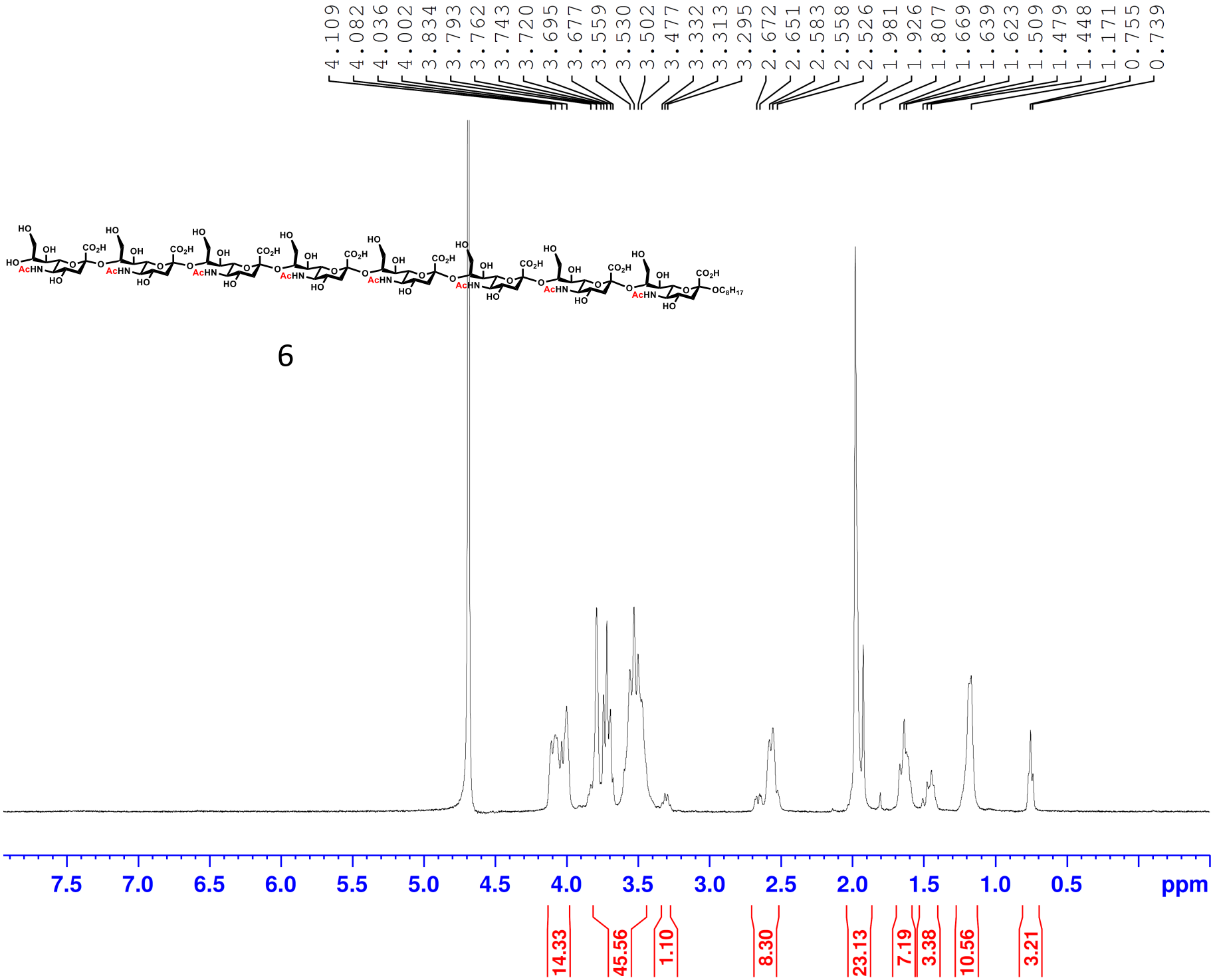
140
120
100
80
60
40
20
ppm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3.502
3.477
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3.313
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2.651
2.583
2.558
2.526
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1.926
1.807
1.669
1.639
1.623
1.509
1.479
1.448
1.171
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0.739
6
7.5
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6.5
6.0
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
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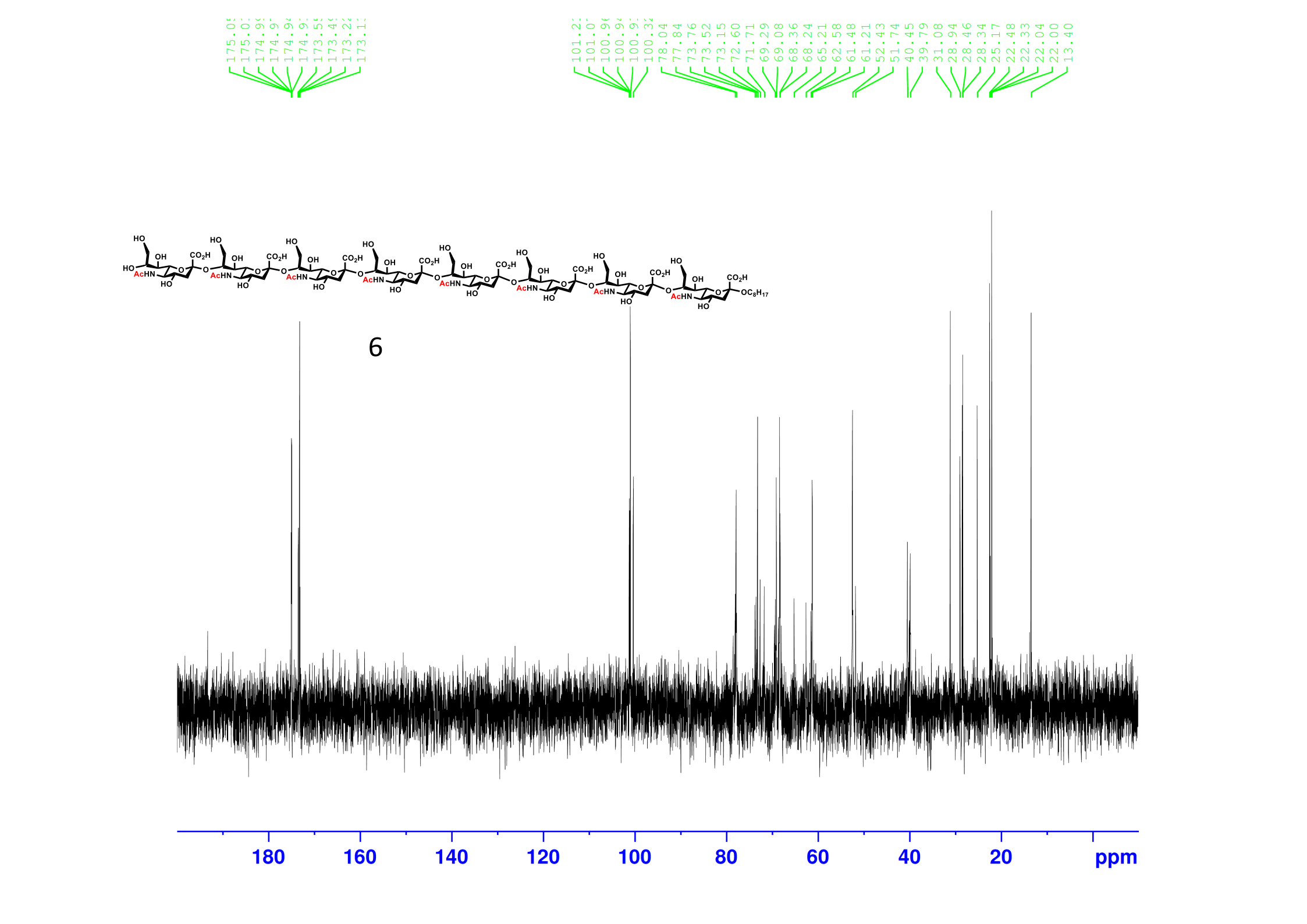
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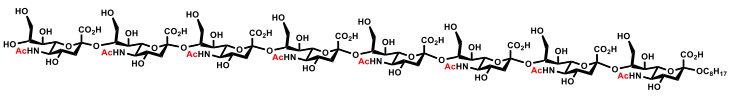
174.93
173.55
173.49
173.22
173.13
101.21
101.07
100.96
100.94
100.93
100.32
78.04
77.84
73.76
73.52
73.15
72.60
71.71
69.29
69.08
68.36
68.24
65.21
62.58
61.48
61.21
52.43
51.74
40.45
39.79
31.08
28.94
28.46
28.34
25.17
22.48
22.33
22.04
22.00
13.40
6
180
160
140
120
100
80
60
40
20
ppm



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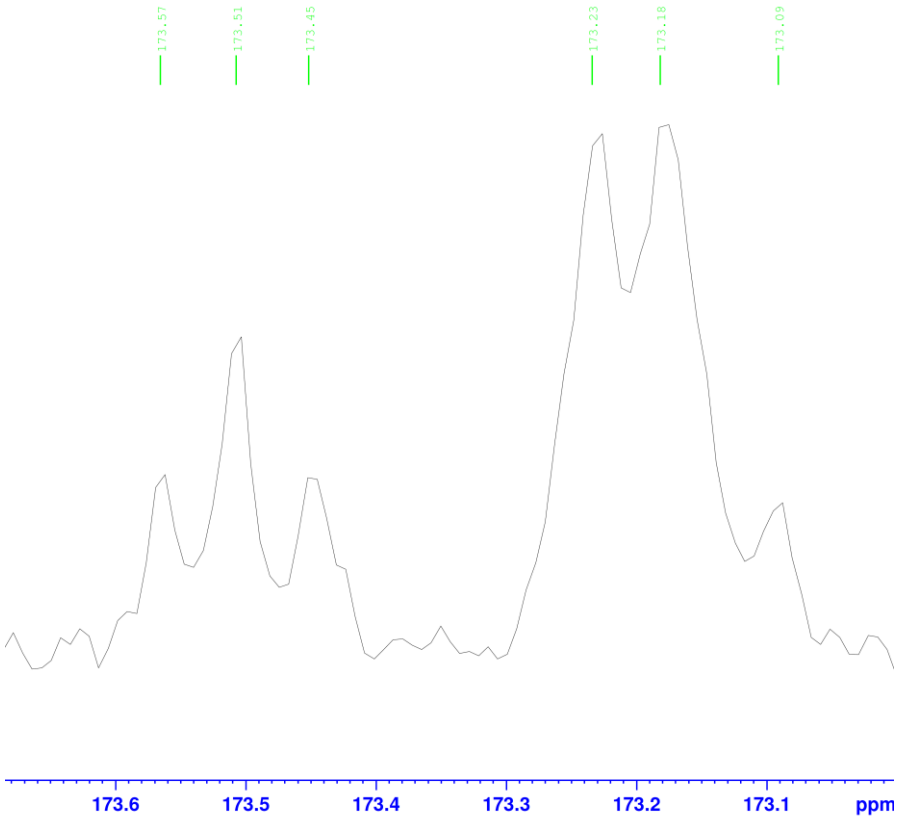
173.4
173.3
173.2
173.1
ppm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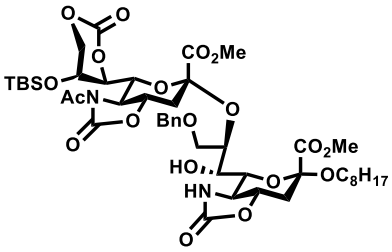
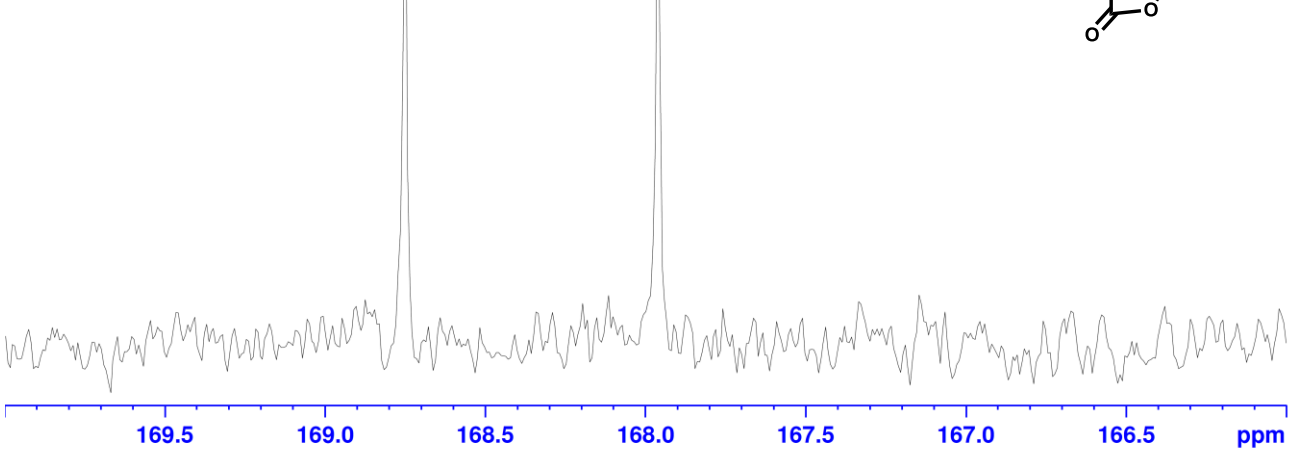
173.45
173.23
173.18
173.09
173.6
173.5
173.4
173.3
173.2
173.1
ppm

^{13}C {^{1}H}

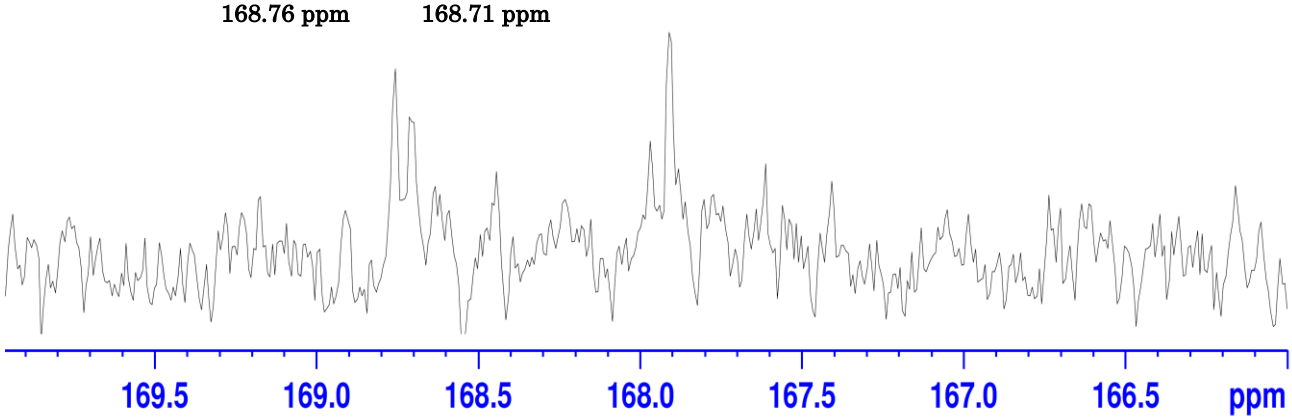
168.75 ppm 167.96 ppm





LSPD

168.76 ppm 168.71 ppm



LSPD

167.97 ppm 167.92 ppm