Supporting Information

Simple glucosyl glycosides are potent human Mincle agonists

Chriselle D. Braganza,[a] Thomas Teunissen,[a] Kristel Kodar,[a] Sarah Andreassend,[a] Ayesha Khan,[a] Mattie S. M. Timmer,[a*] Bridget L. Stocker[a*]

[a]School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington, New Zealand

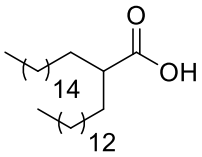
*Email: bridget.stocker@vuw.ac.nz, mattie.timmer@vuw.ac.nz

Table of Contents

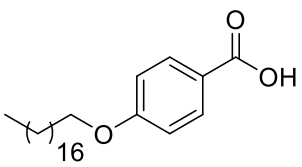
Chemistry Experimental

General experimental: Unless otherwise stated, all reactions were performed under an atmosphere of argon. Reactions were monitored by TLC analysis on Macherey-Nagel silica gel coated plastic sheets (0.20 mm with fluorescent indicator UV_{254}) via detection by UV absorption (254 nm) where relevant and dipping in 10% H_2SO_4 in EtOH followed by charring, dipping in an aqueous solution of $KMnO_4$ (0.05 M), K_2CO_3 (0.4 M), and NaOH (0.06%) or dipping in ceric ammonium molybdate solution. Column chromatography was performed using Pure Science silica gel (40–63 μm) and Agilent Bondesil C18 (40 μm). All solvents were removed by evaporation under reduced pressure. High resolution mass spectra (HRMS) were recorded on an Agilent 6530 Q-TOF mass spectrometer utilising a JetStream™ electro-spray ionisation (ESI) source in positive or negative mode. Optical rotations were recorded on an Autopol II (Rudolph Research Analytical) at 589 nm (sodium D line). Infrared (IR) spectra were recorded as thin films using either a Bruker Platinum-ATR spectrometer. Nuclear magnetic resonance spectra were obtained at 20 °C in $CDCl_3$ or C_5D_5N using a Varian INOVA

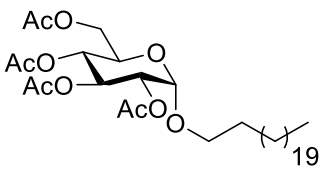
operating at 500 MHz. Chemical shifts are given in ppm (δ) relative to the solvent residual peak. NMR peak assignments were made using COSY, HSQC, and HMBC 2D experiments.



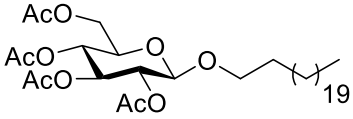
2-Tetradecyloctadecanoic acid (20). Diisopropylamine (1.3 mL, 9.4 mmol) and 2M butyllithium in cyclohexane (8.6 mL, 17.2 mmol) were added to freshly distilled THF (5 mL) at -78 °C under an argon atmosphere and the resulting mixture was stirred for 15 min to prepare LDA. In a separate flask, palmitic acid (2.0 g, 7.8 mmol) and NaH (322 mg of 60% dispersion in mineral oil, 9.4 mmol) were stirred together in freshly distilled THF (20 mL) at 0 °C for 10 min, after which time the freshly prepared LDA was added to the suspension and the resulting mixture was brought to r.t. After stirring for 30 min, 1-bromotetradecane (2.9 mL, 9.4 mmol) was added and the reaction stirred for 3 hours at 45 °C. The reaction mixture was quenched with 1M HCl and extracted three times with 50 mL diethyl ether. The product was purified using silica gel flash column chromatography (100:0 → 9:1, hexane:EtOAc) to afford **20** (914 mg, 1.9 mmol, 20%) as an amorphous white solid. Recorded data matched that in literature.[1] IR (film) 2954, 2915, 2849, 1706, 1466, 719 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.38-2.30 (m, 1H, H-1), 1.67-1.56 (m, 2H, H-2a, H-2′a), 1.52-1.40 (m, 2H, H-2b, H-2′b), 1.36-1.17 (m, 52H, CH_2-lipid), 0.88 (t, J = 6.8 Hz, 6H, CH_3-lipid); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.6 (C-1), 45.6 (C-2), 32.3, 32.1, 29.9, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 27.5, 22.9 (C-CH_2-lipid), 14.3 (C-CH_3-lipid); HRMS (ESI) *m/z* calcd for $[C_{32}H_{63}O_2]^-$ 479.4834, obsd 479.4856.



4-(Octadecyloxy)benzoic acid (23). The lipid was synthesised using the procedure reported by Foster *et al.*[2] from commercially available 4-hydroxy methyl benzoate. All characterisation data matched that reported in literature.[2] IR (film) 2915, 2848, 1710, 1358, 1220, 529 cm^{-1}; ^1H NMR (600 MHz, C_5D_5N) δ 8.50 (d, $J_{2,3}$ = 8.6 Hz, 2H, H-2), 7.17 (d, $J_{3,2}$ = 8.5 Hz, 2H, H-3), 4.00 (t, $J_{6,7}$ = 6.5 Hz, 2H, CH_2-6), 1.77 (p, $J_{7,6}$ = 6.7 Hz, 2H, CH_2-7), 1.49-1.39 (m, 2H, CH_2-8), 1.37-1.09 (m, 28H, CH_2-9-CH_2-22), 0.88 (t, $J_{23,22}$ = 6.9 Hz, 3H, CH_3-23); ^{13}C NMR (150 MHz, C_5D_5N) δ 169.2 (C-5), 163.5 (C-4), 132.7 (C-2), 125.1 (C-1), 115.0 (C-3), 68.8 (C-6), 32.5, 30.4, 30.3, 30.3, 30.3, 30.2, 30.2, 30.0, 30.0, 23.3 (C-9-C-22), 29.8 (C-7), 26.6 (C-8), 14.6 (C-23); HRMS *m/z* calcd for $[C_{25}H_{41}O_3]^-$ 389.3061, obsd 389.3068.



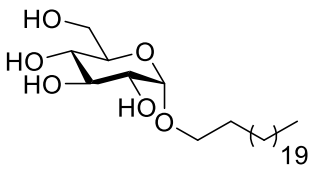
Docosyl (2,3,4,6-tetra-*O*-acetyl)-α-D-glucopyranoside (32). Peracetylated D-glucose (500 mg, 1.28 mmol) and 1-docosanol (627 mg, 1.92 mmol) were co-evaporated three times with anhydrous toluene (40 mL) to remove any traces of water, leaving toluene (20 mL) on the final co-evaporation. Activated 4 Å molecular sieves were then added to the mixture, which was cooled to 0 °C under argon, and $BF_3.Et_2O$ (316 μL, 2.56 mmol) was added slowly. The mixture was then heated to reflux for 4 hours, after which time all starting material was consumed. The reaction was quenched with sat. $NaHCO_3$ (aq.) and extracted with CH_2Cl_2 (3 x 20 mL). The organic phase was washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. The resulting oil was purified by silica gel flash column chromatography (20:1 → 1:1 hexane : EtOAc) to give the desired α-glycoside (722 mg, 1.10 mmol, 86%). IR (film) 2915, 2849, 1742, 1227, 1033 cm^{-1}; $[\alpha]_D^{25}$ = + 59.4 (*c* = 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.47 (dd, $J_{3',2'}$ = 10.2, $J_{3',4'}$ = 9.4 Hz, 1H, H-3′), 5.05 (d, $J_{1',2'}$ = 3.6 Hz, 1H, H-1′), 5.04 (t, $J_{4',3'} = J_{4',5'}$ = 9.9 Hz, 1H, H-4′), 4.84 (dd, $J_{2',3'}$ = 10.2, $J_{2',1'}$ = 3.7 Hz, 1H, H-2′), 4.25 (dd, $J_{6'a,6'b}$ = 12.3, $J_{6'a,5'}$ = 4.5 Hz, 1H, H-6′a), 4.08 (dd, $J_{6'b,6'a}$ = 12.3, $J_{6'b,5'}$ = 2.3 Hz, 1H, H-6′b), 4.01 (ddd, $J_{5',4'}$ = 10.3, $J_{5',6'a}$ = 4.5, $J_{5',6'b}$ = 2.3 Hz, 1H, H-5′), 3.66 (dt, $J_{1a,1b}$ = 9.8, $J_{1a,2}$ = 6.6 Hz, 1H, H-1a), 3.41 (dt, $J_{1b,1a}$ = 9.9, $J_{1b,2}$ = 6.7 Hz, 1H, H-1b), 2.08 (s, 3H, CH_3-Ac), 2.05 (s, 3H, CH_3-Ac), 2.02 (s, 3H, CH_3-Ac), 2.00 (s, 3H, CH_3-Ac), 1.65 – 1.53 (m, 2H), 1.42-1.14 (m, 38H, H-3-H-21), 0.87 (t, $J_{22,21}$ = 6.9 Hz, 3H, CH_3-22); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8 (C-Ac), 170.3 (C-Ac), 170.3 (C-Ac), 169.8 (C-Ac), 95.7 (C-1′), 71.1 (C-2′), 70.4 (C-3′), 68.9 (C-1), 68.7 (C-4′), 67.2 (C-5′), 62.0 (C-6′), 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.5, 29.5, 29.4, 26.2, 22.8, 20.9, 20.9, 20.8, 20.8 (C-2-C-21), 14.3 (C-22); HRMS *m/z* calcd for $[C_{36}H_{68}NO_{10}]^+$ 674.4838, obsd 674.4877.



Docosyl (2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranoside (33). Peracetylated D-glucose (300 mg, 0.77 mmol) and 1-docosanol (377 mg, 1.15 mmol) were co-evaporated three times with anhydrous toluene (40 mL) to remove any traces of water, leaving toluene (20 mL) on the final co-evaporation. Activated 4 Å molecular sieves were then added to the mixture, which was cooled to 0 °C under argon, and $BF_3.Et_2O$ (190 μL, 1.54 mmol) was added slowly. The mixture was brought to room temperature and then stirred for 16 hours, after which time all starting material was consumed. The reaction was quenched with sat. $NaHCO_3$ (aq.) and extracted with CH_2Cl_2 (3 x 20 mL). The organic phase was washed with brine, dried with $MgSO_4$ and

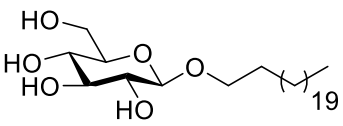
concentrated *in vacuo*. The resulting oil was purified by silica gel flash column chromatography (20:1 → 1:1 hexane : EtOAc) to give the desired β-product (395 mg, 0.60 mmol, 78%). IR (film) 2917, 2849, 1745, 1230, 1042 cm^{-1}; $[\alpha]_D^{25}$ = - 27.4 (*c* = 0.1, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 5.20 (t, $J_{3',2'} = J_{3',4'}$ = 9.5 Hz, 1H, H-3′), 5.09 (t, $J_{4',3'} = J_{4',5'}$ = 9.7 Hz, 1H, H-4′), 4.98 (dd, $J_{2',3'}$ = 9.7, $J_{2',1'}$ = 8.0 Hz, 1H, H-2′), 4.49 (d, $J_{1',2'}$ = 8.0 Hz, 1H, H-1′), 4.26 (dd, $J_{6'a,6'b}$ = 12.3, $J_{6'a,5'}$ = 4.7 Hz, 1H, H-6′a), 4.13 (dd, $J_{6'b,6'a}$ = 12.3, $J_{6'b,5'}$ = 2.5 Hz, 1H, H-6′b), 3.87 (dt, $J_{1a,1b}$ = 9.6, $J_{1a,2}$ = 6.3 Hz, 1H, H-1a), 3.68 (ddd, $J_{5',4'}$ = 10.0, $J_{5',6'a}$ = 4.7, $J_{5',6'b}$ = 2.5 Hz, 1H, H-5′), 3.46 (dt, $J_{1b,1a}$ = 9.6, $J_{1b,2}$ = 6.8 Hz, 1H, H-1b), 2.09 (s, 3H, CH_3-Ac), 2.01 (s, 3H, CH_3-Ac), 2.02 (s, 3H, CH_3-Ac), 2.00 (s, 3H, CH_3-Ac), 1.70-1.45 (m, 2H, CH_2-2), 1.39-1.16 (m, 38H, H-3-H-21), 0.88 (t, $J_{22,21}$ = 6.9 Hz, 3H, CH_3-22); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.9 (C-Ac), 170.5 (C-Ac), 169.6 (C-Ac), 169.4 (C-Ac), 101.0 (C-1′), 73.0 (C-3′), 71.9 (C-5′), 71.5 (C-2′), 70.4 (C-1), 68.6 (C-4′), 62.1 (C-6′), 32.1, 29.9, 29.8, 29.8, 29.8, 29.8, 29.5, 29.5, 29.5, 26.0, 22.8, 20.9, 20.8, 20.8, 20.8 (C-2-C-21), 14.3 (C-22); HRMS *m/z* calcd for $[C_{36}H_{68}NO_{10}]^+$ 674.4838, obsd 674.4870.

General procedure for deacetylation: The peracetylated compound was dissolved in MeOH (50 mL/mmol) before NaOMe (0.1 equiv.) was added to the solution. The reaction mixture was allowed to stir overnight at r.t., after which time complete conversion of starting material was observed. The solution was neutralised using Dowex H^+ (~ pH 7), followed by filtration of the beads and concentration of the filtrate *in vacuo*. The residue was purified by silica gel flash column chromatography (100:0 EtOAc : MeOH → 10:1 EtOAc: MeOH) to afford the pure product.



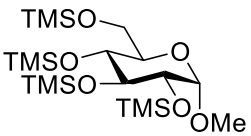
Docosyl α-D-glucopyranoside (11). The general procedure for deacetylation was carried out on **32** (178 mg, 0.30 mmol) to yield **11** (141 mg, 0.29 mmol, 96%) as an amorphous solid. IR (film) 3408, 2915, 2848, 1420, 1091 cm^{-1}; $[\alpha]_D^{25}$ = + 57.8 (*c* = 0.1, C_5D_5N); ^1H NMR (500 MHz, C_5D_5N) δ 5.35 (d, $J_{1',2'}$ = 3.6 Hz, 1H, H-1′), 4.65 (t, $J_{3',2'} = J_{3',4'}$ = 9.1 Hz, 1H, H-3′), 4.58 (dd, $J_{6'a,6'b}$ = 11.2, $J_{6'a,5'}$ = 2.0 Hz, 1H, H-6′a), 4.48-4.35 (m, 2H, H-5′, H-6′b), 4.25 (t, $J_{4',3'} = J_{4',5'}$ = 9.0 Hz, 1H, H-4′), 4.19 (dd, $J_{2',3'}$ = 9.6, $J_{2',1'}$ = 3.6 Hz, 1H, H-2′), 4.11-3.86 (m, 1H, H-1a), 3.62-3.52 (m, 1H, H-1b), 1.73-1.56 (m, 2H, CH_2-2), 1.50-1.07 (m, 38H, H-3-H-21), 0.88 (t, $J_{22,21}$ = 6.7 Hz, 3H, CH_3-22); ^{13}C NMR (125 MHz, C_5D_5N) δ 100.8 (C-1′), 76.0 (C-3′), 74.7 (C-5′), 74.4 (C-2′), 72.8 (C-4′), 68.5 (C-1), 63.4 (C-6′), 32.5, 30.4, 30.4, 30.4, 30.3,

30.3, 30.3, 30.2, 30.0, 27.0, 23.3 (C-2-C-21), 14.6 (C-22); HRMS *m/z* calcd for $[C_{28}H_{60}NO_6]^+$ 506.4415, obsd 506.4407.



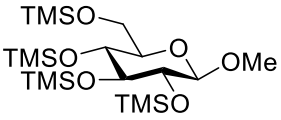
Docosyl β-D-glucopyranoside (12). The general procedure for deacetylation was carried out on **33** (267 mg, 0.41 mmol) to yield **12** (187 mg, 0.38 mmol, 94%) as an amorphous solid. IR (film) 3379, 2915, 2849, 1466, 1078 cm^{-1}; $[\alpha]_D^{26}$ = - 3.6 (*c* = 0.5, C_5D_5N); ^1H NMR (500 MHz, C_5D_5N) δ 4.89 (d, $J_{1',2'}$ = 7.7 Hz, 1H, H-1′), 4.61 (d, $J_{6'a,6'b}$ = 11.7 Hz, 1H, H-6′a), 4.44 (dd, $J_{6'b,6'a}$ = 11.8, $J_{6'b,5'}$ = 5.3 Hz, 1H, H-6′b), 4.34-4.25 (m, 2H, H-3′, H-4′), 4.14 (q, $J_{1a,1b}$ = $J_{1a,2}$ = 7.3 Hz, 1H, H-1a), 4.12-4.05 (m, 1H, H-2′), 4.00-3.96 (m, 1H, H-5′), 3.70 (q, $J_{1b,1a}$ = $J_{1b,2}$ = 7.0 Hz, 1H, H-1b), 1.70 (p, $J_{2,1}$ = $J_{2,3}$ = 7.0 Hz, 2H, CH_2-2), 1.48-1.12 (m, 38H, H-3-H-21), 0.88 (t, $J_{22,21}$ = 6.7 Hz, 3H, CH_3-22); ^{13}C NMR (125 MHz, C_5D_5N) δ 106.1 (C-1′), 80.0 (C-3′), 79.9 (C-5′), 76.6 (C-2′), 73.0 (C-4′), 71.2 (C-1), 64.2 (C-6′), 33.4, 31.6, 31.3, 31.3, 31.3, 31.2, 31.1, 30.9, 27.8, 24.2 (C-2-C-21), 15.6 (C-22); HRMS *m/z* calcd for $[C_{28}H_{60}NO_6]^+$ 506.4415, obsd 506.4437.

General procedure for TMS protection: The sugar was co-evaporated three times with pyridine (5 mL/mmol) and then dissolved in freshly distilled pyridine (20 mL/mmol). TMSCl (6 equiv.) was added dropwise to the solution at r.t. and the mixture then stirred for 4 hours. The reaction was then quenched with the addition of ice and the product extracted with hexane (2 x 20 mL). The combined organic extracts were then washed with $NaHCO_3$, brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (100:0 → 4:5, hexane : toluene) to afford the pure product.

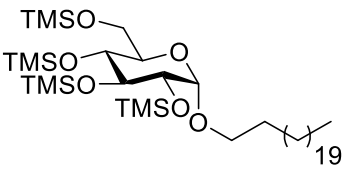


Methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside. The general procedure for TMS protection was carried out on methyl α-D-glucopyranoside (500 mg, 2.57 mmol) to yield methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside (1057 mg, 2.19 mmol, 85%) as a colourless oil. IR (film) 2955, 1247, 1048, 833, 707 cm^{-1}; $[\alpha]_D^{22}$ = + 72.0 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.59 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.79-3.69 (m, 2H, H-4, H-6a), 3.65 (dd, $J_{6b,6a}$ = 11.3, $J_{6b,5}$ = 5.2 Hz, 1H, H-6b), 3.56-3.36 (m, 3H, H-2, H-3, H-5), 3.32 (s, 3H, CH_3-Me), 0.14 (s, 3H, CH_3-TMS), 0.13 (s, 3H, CH_3-TMS), 0.13 (s, 3H, CH_3-TMS), 0.10 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 99.8 (C-1), 75.4 (C-4), 74.1 (C-2), 72.3 (C-3), 72.1 (C-5), 62.3 (C-6),

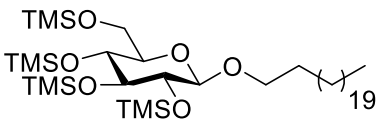
54.6 (C-Me), 1.5 (C-TMS), 1.0 (C-TMS), 0.7 (C-TMS), -0.1 (C-TMS); HRMS *m/z* calcd for $[C_{19}H_{46}NaO_6Si_4]^+$ 505.2264, obsd 505.2282.



Methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside. The general procedure for TMS protection was carried out on methyl β-D-glucopyranoside (500 mg, 2.57 mmol) to yield methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside (1105 mg, 2.29 mmol, 89%) as a colourless oil. IR (film) 2954, 1248, 1048, 838, 708 cm^{-1}; $[\alpha]_D^{24}$ = - 3.8 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.05 (d, $J_{1,2}$ = 7.5 Hz, 1H, H-1), 3.80 (dd, $J_{6a,6b}$ = 11.4, $J_{6a,5}$ = 2.0 Hz, 1H, H-6a), 3.68 (dd, $J_{6b,6a}$ = 11.4, $J_{6b,5}$ = 5.0 Hz, 1H, H-6b), 3.52-3.35 (m, 5H, H-3, H-5, CH_3-Me), 3.31-3.22 (m, 1H, H-2), 3.20-3.10 (m, 1H, H-4), 0.15 (s, 3H, CH_3-TMS), 0.14 (s, 3H, CH_3-TMS), 0.13 (s, 3H, CH_3-TMS), 0.10 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.2 (C-1), 79.0 (C-3), 76.5 (C-4), 76.4 (C-2), 71.7 (C-5), 62.3 (C-6), 56.4 (C-OMe), 1.5 (C-TMS), 1.3 (C-TMS), 1.0 (C-TMS), -0.1 (C-TMS); HRMS *m/z* calcd for $[C_{19}H_{50}NO_6Si_4]^+$ 500.2710, obsd 500.2761.



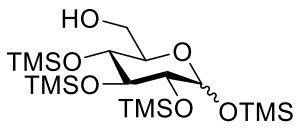
Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside. The general procedure for TMS protection was carried out on **11** (100 mg, 0.20 mmol) to yield docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside (132 mg, 0.17 mmol, 83%) as a colourless oil. IR (film) 2922, 2853, 1248, 1071, 836, 682 cm^{-1}; $[\alpha]_D^{25}$ = + 48.0 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.70 (d, $J_{1',2'}$ = 3.6 Hz, 1H, H-1′), 3.82-3.72 (m, 2H, H-3′, H-6′a), 3.69-3.57 (m, 2H, H-1a, H-6′b), 3.59-3.52 (m, 1H, H-5′), 3.50-3.26 (m, 3H, H-1b, H-2′, H-4′), 1.67-1.49 (m, 2H, CH_2-2), 1.49-1.31 (m, 38H, H-3-H-21), 0.88 (t, $J_{22,21}$ = 6.8 Hz, 3H, CH_3-22), 0.16 (s, 3H, CH_3-TMS), 0.14 (s, 3H, CH_3-TMS), 0.13 (s, 3H, CH_3-TMS), 0.11 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 98.8 (C-1′), 75.4 (C-3′), 74.1, 72.5 (C-2′, C-5′), 72.3 (C-4′), 68.0 (C-1), 62.5 (C-6′), 32.1, 29.9, 29.8, 29.8, 29.6, 29.5, 29.5, 26.3, 22.8 (C-2-C-21), 14.3 (C-22), 1.5 (C-TMS), 1.1 (C-TMS), 0.8 (C-TMS), -0.1 (C-TMS); HRMS *m/z* calcd for $[C_{40}H_{92}NO_6Si_4]^+$ 794.5996, obsd 794.5989.



Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside. The general procedure for TMS protection was carried out on **12** (100 mg, 0.20 mmol) to yield docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside (135 mg, 0.17 mmol, 87%) as a colourless oil. IR (film) 2922, 2852, 1247, 1078, 838, 683 cm^{-1}; $[\alpha]_D^{22}$ = -5.2 (*c* = 1.0, $CHCl_3$);

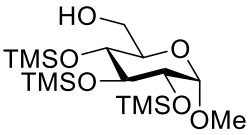
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.15 (d, $J_{1',2'}$ = 7.5 Hz, 1H, H-1′), 3.88-3.73 (m, 2H, H-1a, H-6′a), 3.68 (dd, $J_{6'b,6'a}$ = 11.4, $J_{6'b,5'}$ = 5.2 Hz, 1H, H-6′b), 3.50-3.37 (m, 3H, H-1b, H-3′ H-4′), 3.33-3.25 (m, 1H, H-2′), 3.21-3.11 (m, 1H, H-5′), 1.70-1.53 (m, 2H, CH_2-2), 1.49-1.09 (m, 38H, H-3-H-21), 0.88 (t, $J_{22,21}$ = 6.9 Hz, 3H, CH_3-22), 0.16 (s, 3H, CH_3-TMS), 0.15 (s, 3H, CH_3-TMS), 0.14 (s, 3H, CH_3-TMS), 0.11 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 103.0 (C-1′), 78.8 (C-3′), 76.6 (C-5′), 76.3 (C-2′), 71.8 (C-4′), 69.5 (C-1), 62.5 (C-6′), 32.1, 29.9, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 26.3, 22.9 (C-2-C-21), 14.3 (C-22), 1.5 (C-TMS), 1.4 (C-TMS), 1.0 (C-TMS), 0.0 (C-TMS); HRMS *m/z* calcd for $[C_{40}H_{92}NO_6Si_4]^+$ 794.5996, obsd 794.5990.

General procedure for removal of TMS group at the 6-position: Ammonium acetate (2 equiv.) was added to a solution of per-*O*-TMS protected sugar (1 equiv.) in 1:1 CH_2Cl_2:MeOH (50 mL/mmol) and the resulting mixture was stirred for 16 hours at r.t. The solvent was evaporated *in vacuo*, the residue was suspended in CH_2Cl_2 (50 mL) and the organic phase was washed with water (3 x 50 mL), brine, dried with $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel flash column chromatography (100:0 → 4:5, hexane:toluene) to afford the product.

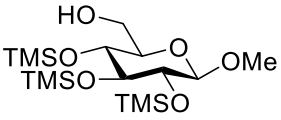


2,3,4-Tris-*O*-trimethylsilyl-α-D-glucose (27). The general procedure for removal of TMS group at the 6-position was carried out on 2,3,4,6-tetra-*O*-trimethylsilyl glucose (200 mg, 0.37 mmol) to yield **27** (125 mg, 0.27 mmol, 72%) as a colourless oil. IR (film) 2957, 1248, 1075, 834 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.00 (d, $J_{1,2}$ = 2.9 Hz, 1H, H-1α), 4.51 (d, $J_{1,2}$ = 7.9 Hz, 1H, H-1β), 3.86-3.56 (m, 7H, H-3α, H-5α, H-5β, CH_2-6α, CH_2-6β), 3.45 (t, $J_{4,3}$ = $J_{4,5}$ = 9.2 Hz, 1H, H-4α), 3.42-3.37 (m, 1H, H-3β), 3.31-3.26 (m, 1H, H-4β), 3.34 (dd, $J_{2,3}$ = 9.0, $J_{2,1}$ = 2.0 Hz, 1H, H-2α), 3.25-3.20 (m, 1H, H-2β), 1.91-1.68 (m, 2H, OHα/β), 0.36-0.01 (m, 72H, CH_3-TMSα/β); ^{13}C NMR (125 MHz, $CDCl_3$) δ 98.1 (C-1β), 94.1 (C-1α), 77.5 (C-3β), 76.9 (C-2β), 76.3 (C-4β), 74.2 (C-2α), 73.7 (C-3α), 72.1 (C-5β), 72.0 (C-5α), 71.9 (C-4α), 62.0 (C-6α, C-6β), 1.4 (C-CH_3-TMSα/β), 1.0 (C-CH_3-TMSα/β), 0.5 (C-CH_3-TMSα/β), 0.3 (C-CH_3-TMSα/β); HRMS *m/z* calcd for $[C_{18}H_{44}NaO_6Si_4]^+$ 491.2107, obsd 491.2927.

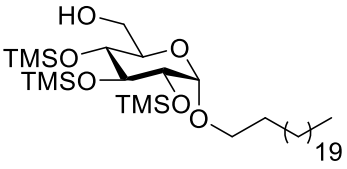
Methyl (2,3,4-tris-*O*-trimethylsilyl)-α-D-glucopyranoside (28). The general procedure for removal of TMS group at the 6-position was carried out on methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside (150 mg, 0.31 mmol) to yield **28** (88 mg, 0.21 mmol, 69%)



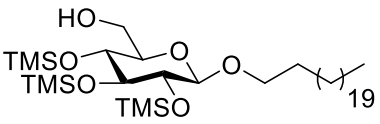
as a colourless oil. IR (film) 2954, 1249, 1077, 840 cm^{-1}; $[\alpha]_D^{25}$ = + 67.8 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.61 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1), 3.82-3.76 (m, 2H, H-4, H-6a), 3.74-3.63 (m, 1H, H-6b), 3.61-3.53 (m, 1H, H-5), 3.51-3.43 (m, 2H, H-2, H-3), 3.35 (s, 3H, CH_3-Me), 1.78 (t, $J_{OH,6}$ = 6.2 Hz, 1H, OH), 0.18 (s, 3H, CH_3-TMS), 0.16 (s, 3H, CH_3-TMS), 0.15 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 100.1 (C-1), 75.0 (C-4), 74.0 (C-2), 72.1 (C-3), 71.7 (C-5), 62.1 (C-6), 55.0 (C-Me), 1.5, 1.0, 0.6; HRMS *m/z* calcd for $[C_{16}H_{38}NaO_6Si_3]^+$ 433.1868, obsd 433.1886.



Methyl (2,3,4-tris-*O*-trimethylsilyl)-β-D-glucopyranoside (29). The general procedure for removal of TMS group at the 6-position was carried out on methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside (150 mg, 0.31 mmol) to yield **29** (82 mg, 0.20 mmol, 63%) as a colourless oil. IR (film) 2956, 1249, 1078, 841 cm^{-1}; $[\alpha]_D^{25}$ = - 5.2 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.13 (d, $J_{1,2}$ = 7.6 Hz, 1H, H-1), 3.87-3.77 (m, 1H, H-6a), 3.67 (dd, $J_{6b,6a}$ = 11.8, $J_{6b,5}$ = 5.3 Hz, 1H, H-6b), 3.49 (s, 3H, CH_3-Me), 3.48-3.40 (m, 2H, H-3, H-5), 3.32 – 3.19 (m, 2H, H-2, H-4), 1.93 (m, 1H, OH), 0.17 (s, 3H, CH_3-TMS), 0.16 (s, 3H, CH_3-TMS), 0.14 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.6 (C-1), 78.4 (C-3), 76.1 (C-2), 76.1 (C-4), 71.7 (C-5), 62.3 (C-6), 57.1 (C-OMe), 1.5 (C-TMS), 1.2 (C-TMS), 1.0 (C-TMS); HRMS *m/z* calcd for $[C_{16}H_{38}NaO_6Si_3]^+$ 433.1868, obsd 433.1882.

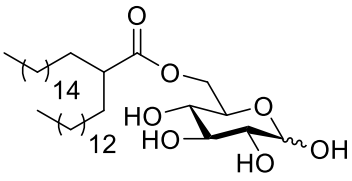


Docosyl (2,3,4-tris-*O*-trimethylsilyl)-α-D-glucopyranoside (34). The general procedure for removal of TMS group at the 6-position was carried out on docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside (132 mg, 0.17 mmol) to yield **34** (88 mg, 0.12 mmol, 73%) as a colourless oil. IR (film) 2922, 2853, 1249, 1077, 841 cm^{-1}; $[\alpha]_D^{26}$ = + 45.6 (*c* = 0.5, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.69 (d, $J_{1',2'}$ = 3.5 Hz, 1H, H-1′), 3.81-3.73 (m, 2H, H-3′, H-6′a), 3.72-3.55 (m, 3H, H-1a, H-4′, H-6′b), 3.49-3.41 (m, 2H, H-2′, H-5′), 3.42-3.33 (m, 1H, H-1b), 1.77 (t, $J_{OH,6}$ = 6.3 Hz, 1H, OH), 1.68-1.58 (m, 2H, CH_2-2), 1.44-1.12 (m, 38H, H-3-H-21), 0.88 (t, $J_{22,21}$ = 6.8 Hz, 3H, CH_3-22), 0.18 (s, 3H, CH_3-TMS), 0.15 (s, 3H, CH_3-TMS), 0.14 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 99.1 (C-1′), 74.9 (C-3′), 74.0, 72.1 (C-2′, C-5′), 71.8 (C-4′), 68.3 (C-1), 62.1 (C-6′), 32.1, 29.9, 29.8, 29.8, 29.8, 29.6, 29.5, 29.5, 26.3, 22.8 (C-2-C-21), 14.3 (C-22), 1.4 (C-TMS), 1.1 (C-TMS), 0.7 (C-TMS); HRMS *m/z* calcd for $[C_{37}H_{80}NaO_6Si_3]^+$ 727.5155, obsd 727.5158.



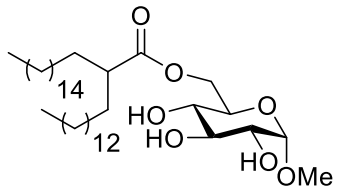
Docosyl (2,3,4-tris-*O*-trimethylsilyl)-β-D-glucopyranoside (35). The general procedure for removal of TMS group at the 6-position was carried out on docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside (135 mg, 0.17 mmol) to yield **35** (80 mg, 0.11 mmol, 67%) as a colourless oil. IR (film) 2922, 2852, 1248, 1079, 841 cm^{-1}; $[\alpha]_D^{26}$ = - 10.0 (*c* = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 4.22 (d, $J_{1',2}$ = 7.6 Hz, 1H, H-1′), 3.88-3.75 (m, 2H, H-1a, H-6′a), 3.70-3.59 (m, 1H, H-6′b), 3.52-3.39 (m, 3H, H-1b, H-3′ H-4′), 3.33-3.21 (m, 2H, H-2′, H-5′), 1.96 (t, $J_{OH,6}$ = 6.2 Hz, 1H, OH), 1.70-1.44 (m, 2H, CH_2-2), 1.45-1.09 (m, 38H, H-3-H-21), 0.88 (t, $J_{22,21}$ = 6.8 Hz, 3H, CH_3-22), 0.17 (s, 3H, CH_3-TMS), 0.16 (s, 3H, CH_3-TMS), 0.15 (s, 3H, CH_3-TMS); ^{13}C NMR (125 MHz, $CDCl_3$) δ 103.5 (C-1′), 78.2 (C-3′), 76.1, 75.9 (C-2′, C-5′), 71.8 (C-4′), 70.2 (C-1), 62.5 (C-6′), 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 26.2, 22.8 (C-2-C-21), 14.3 (C-22), 1.5 (C-TMS), 1.3 (C-TMS), 1.0 (C-TMS); HRMS *m/z* calcd for $[C_{37}H_{80}NaO_6Si_3]^+$ 727.5155, obsd 727.5174.

Branched glycolipids - General procedure for esterification and TMS removal: The sugar or glycoside with the 6-position deprotected (1 equiv.) and **20** (5 equiv.) were co-evaporated together three times with dry toluene (2 mL), then suspended in freshly distilled CH_2Cl_2 (20 mL/mmol). To the reaction mixture, EDCI (3 equiv.) and DMAP (1 equiv.) were added and the resulting suspension was heated to 30 °C under an argon atmosphere until TLC analysis (PE/EtOAc, 20:1, v/v) showed complete conversion of the starting material to a higher running product. The reaction was cooled to r.t. and diluted with CH_2Cl_2 (5 mL). The organic layer was then washed with water, brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The resulting residue was dissolved in 1:1 CH_2Cl_2:MeOH (50 mL/mmol), Dowex H^+ (10% by weight) was added, and the reaction was stirred at room temperature until TLC analysis showed complete consumption of the starting material. The mixture was filtered and concentrated *in vacuo*. The residue was subjected to silica gel flash column chromatography (1:1 → 100:0 hexane:EtOAc and 100:0 → 5:1 EtOAc:MeOH) to give the pure glycolipid.

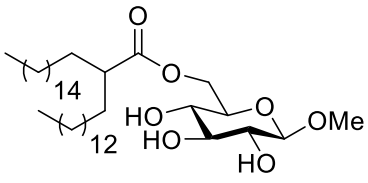


6-*O*-(2-tetradecyloctadecanoyl)-D-glucose (GlcC14C18, 3). The general procedure for the synthesis of branched glycolipids was carried out on **27** (50 mg, 0.11 mmol) to yield **3** (43 mg, 0.07 mmol, 62%) as a colourless film. IR (film) 3391, 2920, 2851, 1713, 1464, 1055 cm^{-1}; ^1H NMR (500 MHz, C_5D_5N) δ 9.07-8.96 (m, 1H, 1β-OH), 8.67 (d,

$J_{OH,1\alpha}$ = 4.0 Hz, 1H, 1α-OH), 7.40-7.25 (m, 4H, 2β-OH, 3β-OH, 4α-OH, 4β-OH), 7.19-7.08 (m, 1H, 3α-OH), 6.60-6.45 (m, 1H, 2α-OH), 5.89 (t, $J_{1,2}$ = 3.8 Hz, 1H, H-1α), 5.35-5.29 (m, 1H, H-1β), 5.22 (m, 2H, H-6aα, H-6aβ), 4.95-4.79 (m, 3H, H-5α, H-6bα, H-6bβ), 4.75 (t, $J_{3,2}$ = $J_{3,4}$ = 9.1 Hz, 1H, H-3α), 4.32-4.01 (m, 6H, H-2α, H-2β, H-3β, H-4α, H-4β, H-5β), 2.70-2.51 (m, 1H, H-2′), 1.91-1.73 (m, 2H, CH_2-lipid), 1.68-1.05 (m, 54H, CH_2-lipid), 0.88 (t, J = 6.8 Hz, 6H, CH_3-lipid); ^{13}C NMR (125 MHz, C_5D_5N) δ 176.9 (C-1′), 99.4 (C-1β), 94.6 (C-1α), 79.0 (C-3β), 77.2 (C-2β), 75.9 (C-4β), 75.7 (C-3α), 74.8 (C-2α), 72.6 (C-4α), 72.2 (C-5β), 71.4 (C-5α), 65.2, 65.1 (C-6α, C-β), 46.6, 46.5 (C-2′α, C-2′β), 33.3, 33.2, 33.2, 32.5, 30.4, 30.4, 30.4, 30.3, 30.3, 30.3, 30.3, 30.2, 30.2, 30.0, 28.2, 28.2, 28.1, 23.3 (C-CH_2-lipid), 14.7 (C-CH_3-lipid); HRMS *m/z* calcd for $[C_{38}H_{78}NO_7]^+$ 660.5773, obsd 660.5793.

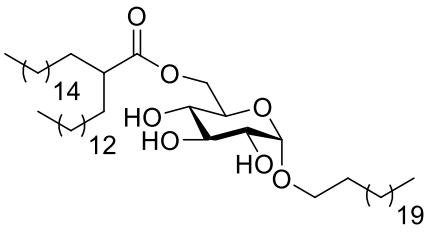


Methyl 6-*O*-(2-tetradecyloctadecanoyl)-α-D-glucoside (C14C18GlcαOMe, 7). The general procedure for the synthesis of branched glycolipids was carried out on **28** (70 mg, 0.17 mmol) to yield **7** (87 mg, 0.13 mmol, 78%) as a colourless film. IR (film) 3384, 2920, 2851, 1735, 1463, 1053 cm^{-1}; $[\alpha]_D^{26}$ = + 32.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (m, 1H, H-1), 4.56-4.44 (m, 1H, H-6a), 4.31-4.22 (m, 1H, H-6b), 3.80-3.65 (m, 2H, H-3, H-5), 3.50 (dd, $J_{2,3}$ = 9.5, $J_{2,1}$ = 3.9 Hz, 1H, H-2), 3.43 (s, 3H, CH_3-Me), 3.31 (t, $J_{4,3}$ = $J_{4,5}$ = 9.5 Hz, 1H, H-4), 2.44-2.34 (m, 1H, H-2′), 1.66-1.53 (m, 2H, CH_2-lipid), 1.52-1.40 (m, 2H, CH_2-lipid), 1.36-1.14 (m, 52H, CH_2-lipid), 0.87 (t, J = 6.9 Hz, 6H, CH_3-lipid); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6 (C-1′), 99.4 (C-1), 74.4 (C-3), 72.4 (C-2), 70.2 (C-4), 70.1 (C-5), 63.0 (C-6), 55.6 (C-Me), 45.8 (C-2′), 32.5, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.7, 29.7, 29.5, 27.6, 27.6, 22.8 (C-CH_2-lipid), 14.3 (C-CH_3-lipid); HRMS *m/z* calcd for $[C_{39}H_{80}NO_7]^+$ 674.5929, obsd 674.5956.

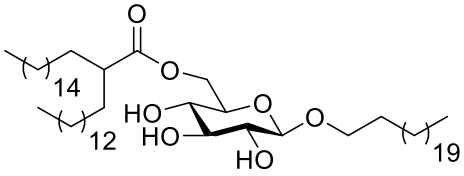


Methyl 6-*O*-(2-tetradecyloctadecanoyl)-β-D-glucoside (C14C18GlcβOMe, 8). The general procedure for the synthesis of branched glycolipids was carried out on **29** (50 mg, 0.12 mmol) to yield **8** (65 mg, 0.10 mmol, 81%) as a colourless film. IR (film) 3406, 2920, 2851, 1735, 1464, 1049 cm^{-1}; $[\alpha]_D^{26}$ = - 22.6 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.49-4.39 (m, 1H, H-6a), 4.28-4.20 (m, 1H, H-6b), 4.18 (d, $J_{1,2}$ = 7.7 Hz, 1H, H-1), 3.58-3.44 (m, 2H, H-3, H-5), 3.50 (s, 3H, CH_3-Me), 3.41-3.24 (m, 2H, H-2, H-4), 2.41-2.30 (m, 1H, H-2′), 1.66-1.50 (m, 2H, CH_2-lipid), 1.50-1.38 (m, 2H, CH_2-lipid), 1.38-1.08 (m, 52H, CH_2-lipid), 0.86 (t, J = 6.9 Hz, 6H, CH_3-lipid); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.1 (C-1′), 103.5 (C-1), 76.3 (C-3), 74.1 (C-5), 73.5 (C-2), 70.7 (C-4), 63.6 (C-6), 57.1 (C-Me),

45.7 (C-2′), 32.3, 32.3, 32.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 27.5, 27.5, 22.8 (C-CH_2-lipid), 14.3 (C-CH_3-lipid); HRMS *m/z* calcd for $[C_{39}H_{80}NO_7]^+$ 674.5929, obsd 674.5957.

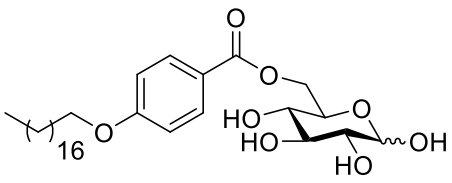


Docosyl 6-*O*-(2-tetradecyloctadecanoyl)-α-D-glucoside (C14C18GlcαOC22, 9). The general procedure for the synthesis of branched glycolipids was carried out on **34** (20 mg, 0.03 mmol) to yield **9** (20 mg, 0.02 mmol, 73%) as a colourless film. IR (film) 3389, 2916, 2849, 1734, 1467, 1053, 720 cm^{-1}; $[\alpha]_D^{25}$ = + 21.0 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.86 (d, $J_{1',2}$ = 3.9 Hz, 1H, H-1′), 4.54 (dd, $J_{6'a,6'b}$ = 12.3, $J_{6'a,5'}$ = 4.3 Hz, 1H, H-6′a), 4.22 (dd, $J_{6'b,6'a}$ = 12.3, $J_{6'b,5}$ = 2.2 Hz, 1H, H-6′b), 3.79-3.64 (m, 3H, H-1a, H-3′, H-5′), 3.53-3.40 (m, 2H, H-1b, H-2′), 3.32 (t, $J_{4',3'}$ = $J_{4',5'}$ = 9.0 Hz, 1H, H-4′), 2.44-2.36 (m, 1H, H-2″), 1.67-1.55 (m, 4H, CH_2-2, CH_2-lipid), 1.51-1.40 (m, 2H, CH_2-lipid), 1.39-1.17 (m, 90H, CH_2-lipid), 0.88 (t, *J* = 7.0 Hz, 9H, CH_3-lipid); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.7 (C-1″), 98.2 (C-1′), 74.7 (C-3′), 72.5 (C-2′), 70.2 (C-4′), 70.1 (C-5′), 68.7 (C-1), 62.9 (C-6′), 45.9 (C-2″), 32.5, 32.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.5, 27.6, 27.6, 26.3, 22.8 (C-CH_2-lipid), 14.3 (C-CH_3-lipid); HRMS *m/z* calcd for $[C_{60}H_{122}NO_7]^+$ 968.9216, obsd 968.9249.

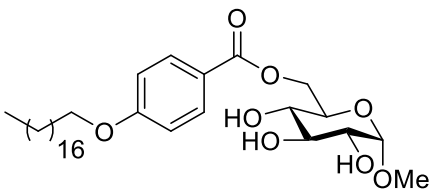


Docosyl 6-*O*-(2-tetradecyloctadecanoyl)-β-D-glucoside (C14C18GlcβOC22, 10). The general procedure for the synthesis of branched glycolipids was carried out on **35** (20 mg, 0.03 mmol) to yield **10** (19 mg, 0.02 mmol, 69%) as a colourless film. IR (film) 3370, 2916, 2849, 1734, 1467, 1057, 720 cm^{-1}; $[\alpha]_D^{25}$ = - 9.2 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.46 (dd, $J_{6'a,6'b}$ = 12.2, $J_{6'a,5'}$ = 4.8 Hz, 1H, H-6′a), 4.33 (dd, $J_{6'b,6'a}$ = 12.1, $J_{6'b,5'}$ = 2.2 Hz, 1H, H-6′b), 4.26 (d, $J_{1',2}$ = 7.7 Hz, 1H, H-1′), 3.88 (dt, $J_{1a,1b}$ = 9.3, $J_{1a,2}$ = 6.9 Hz, 1H, H-1a), 3.57 (t, $J_{3',2'}$ = $J_{3',4'}$ = 9.1 Hz, 1H, H-3′), 3.53-3.42 (m, 2H, H-1b, H-5′), 3.41-3.30 (m, 2H, H-2′, H-4′), 3.15-3.08 (m, 1H, 2′-OH), 2.97-2.88 (m, 1H, 3′-OH), 2.58-2.50 (m, 1H, 4′-OH), 2.39 (m, 1H, H-2″), 1.72-1.53 (m, 4H, CH_2-2, CH_2-lipid), 1.51-1.40 (m, 2H, CH_2-lipid), 1.3-1.05 (m, 90H, CH_2-lipid), 0.88 (t, *J* = 6.8 Hz, 9H, CH_3-lipid); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6 (C-1″), 102.7 (C-1′), 76.0 (C-3′), 74.2 (C-5′), 73.9 (C-4′), 70.3 (C-1, C-2′), 63.1 (C-6′), 45.8 (C-2″), 32.5, 32.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 27.6, 27.6, 26.1, 22.8 (C-CH_2-lipid), 14.3 (C-CH_3-lipid); HRMS *m/z* calcd for $[C_{60}H_{122}NO_7]^+$ 968.9216, obsd 968.9203.

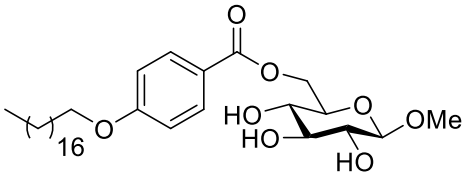
Aromatic glycolipids - General procedure for esterification and TMS removal: The sugar or glycoside with the 6-position deprotected (1 equiv.) and **23** (5 equiv.) were co-evaporated together three times with dry toluene (10 mL), leaving 5 mL on the third evaporation. To the reaction mixture, EDCI (3 equiv.) and DMAP (1 equiv.) were added and the resulting suspension was heated to 70 °C under an argon atmosphere until TLC analysis (PE/EtOAc, 20:1, v/v) showed complete conversion of the starting material to a higher running product. The reaction was cooled to r.t. and diluted with CH_2Cl_2 (5 mL). The organic layer was then washed with water, brine, dried with anhydrous $MgSO_4$, and concentrated *in vacuo*. The resulting residue was dissolved in 1:1 CH_2Cl_2:MeOH (50 mL/mmol), Dowex H^+ (10% by weight) was added, and the reaction was stirred at room temperature until TLC analysis showed complete consumption of the starting material. The mixture was filtered and concentrated *in vacuo*. The residue was subjected to silica gel flash column chromatography (1:1 → 100:0 hexane:EtOAc and 100:0 → 5:1 EtOAc:MeOH) to give the pure glycolipid.



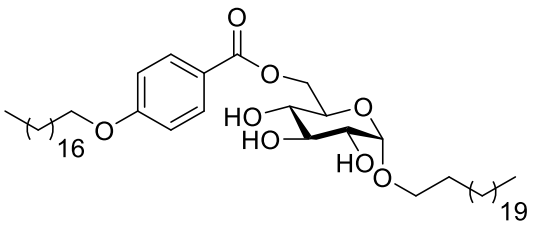
6-*O*-(4-octadecyloxybenzoyl)-α-D-glucose (GlcBzC18, 13). The general procedure for the synthesis of aromatic glycolipids was carried out on **27** (50 mg, 0.11 mmol) to yield **13** (37 mg, 0.07 mmol, 61%) as a colourless film. IR (film) 3431, 2914, 2848, 1709, 1601, 1251, 1052, 768 cm^{-1}; ^1H NMR (500 MHz, C_5D_5N) δ 8.23 (d, $J_{3',4'}$ = 8.7 Hz, 2H, H-3′), 7.01 (d, $J_{4',3'}$ = 8.7 Hz, 2H, H-4′), 5.93 (d, $J_{1,2}$ = 3.6 Hz, 1H, H-1α), 5.40 (d, $J_{1,2}$ = 7.1 Hz, 1H, H-1β), 5.33-5.26 (m, 2H, H-6aα, H-6aβ), 5.13-4.95 (m, 3H, H-5α, H-6bα, H-6bβ), 4.83 (t, $J_{3,2} = J_{3,4}$ = 9.1 Hz, 1H, H-3α), 4.32-4.23 (m, 5H, H-2α, H-3β, H-4α, H-4β, H-5β), 4.22-4.17 (m, 1H, H-2β), 3.96 (t, $J_{6',7'}$ = 6.6 Hz, 2H, CH_2-6′), 1.83-1.66 (m, 2H, CH_2-7′), 1.48-1.36 (m, 2H, CH_2-8′), 1.35-1.15 (m, 28H, CH_2-9′-CH_2-22′), 0.88 (t, $J_{23',22'}$ = 6.9 Hz, 3H, CH_3-23′); ^{13}C NMR (125 MHz, C_5D_5N) δ 166.9 (C-1′), 163.7 (C-5′), 132.4 (C-3′), 122.9 (C-2′), 114.9 (C-4′), 99.0 (C-1β), 94.7 (C-1α), 75.8 (C-3β), 75.7 (C-2β), 74.8 (C-3α, C-4β), 74.2 (C-2α), 72.8 (C-4α), 71.4 (C-5β), 70.8 (C-5α), 68.8 (C-6′), 66.0 (C-6), 32.5, 30.4, 30.3, 30.3, 30.3, 30.2, 30.2, 30.0, 30.0, 29.7, 26.6, 23.3 (C-9′-C-22′), 29.2 (C-7′), 26.1 (C-8′), 14.6 (C-23′); HRMS *m/z* calcd for $[C_{31}H_{52}NaO_8]^+$ 575.3554, obsd 575.3580.



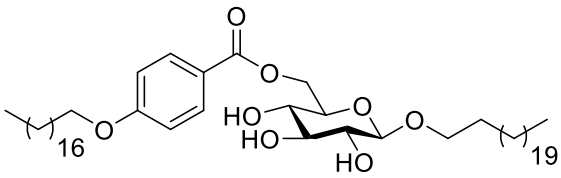
Methyl 6-*O*-(4-octadecyloxybenzoyl)-α-D-glucoside (BzC18GlcαOMe, 14). The general procedure for the synthesis of aromatic glycolipids was carried out on **28** (50 mg, 0.12 mmol) to yield **14** (39 mg, 0.07 mmol, 58%) as a colourless film. IR (film) 3464, 2914, 2848, 1709, 1606, 1251, 1052, 767 cm^{-1}; $[\alpha]_D^{25}$ = + 61.0 (*c* = 0.1, C_5D_5N); ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, $J_{3',4'}$ = 8.9 Hz, 2H, H-3′), 6.86 (d, $J_{4',3'}$ = 8.9 Hz, 2H, H-4′), 4.75 (d, $J_{1,2}$ = 3.7 Hz, 1H, H-1), 4.71-4.63 (m, 1H, 3-OH), 4.58 (dd, $J_{6a,6b}$ = 12.1, $J_{6a,5}$ = 5.3 Hz, 1H, H-6a), 4.51 (dd, $J_{6b,6a}$ = 12.2, $J_{6b,5}$ = 2.1 Hz, 1H, H-6b), 4.48-4.40 (m, 1H, 4-OH), 3.95 (t, $J_{6',7'}$ = 6.6 Hz, 2H, CH_2-6′), 3.89-3.76 (m, 2H, H-3, H-5), 3.75-3.69 (m, 1H, 2-OH), 3.61-3.50 (m, 1H, H-2), 3.47-3.40 (m, 1H, H-4), 3.39 (s, 3H, CH_3-Me), 1.76 (p, $J_{7',6'}$ = $J_{7',8'}$ = 6.7 Hz, 2H, CH_2-7′), 1.48-1.38 (m, 2H, CH_2-8′) 1.37-1.13 (m, 28H, CH_2-9′-CH_2-22′), 0.87 (t, $J_{23',22'}$ = 6.9 Hz, 3H, CH_3-23′); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0 (C-1′), 163.4 (C-5′), 132.0 (C-3′), 121.8 (C-2′), 114.3 (C-4′), 99.5 (C-1), 74.3 (C-3), 72.2 (C-2), 70.4 (C-4), 70.1 (C-5), 68.4 (C-6′), 63.8 (C-6), 55.4 (C-Me), 32.1, 29.8, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.3, 26.1, 22.8 (C-9′-C-22′), 29.2 (C-7′), 25.7 (C-8′), 14.3 (C-23′); HRMS *m/z* calcd for $[C_{32}H_{55}O_8]^+$ 567.3891, obsd 567.3868.



Methyl 6-*O*-(4-octadecyloxybenzoyl)-β-D-glucoside (BzC18GlcβOMe, 15). The general procedure for the synthesis of aromatic glycolipids was carried out on **29** (50 mg, 0.12 mmol) to yield **15** (38 mg, 0.07 mmol, 56%) as a colourless film. IR (film) 3465, 2914, 1716, 1608, 1054, 769 cm^{-1}; $[\alpha]_D^{26}$ = + 6.6 (*c* = 0.1, C_5D_5N); ^1H NMR (600 MHz, C_5D_5N) δ 8.25 (d, $J_{3',4'}$ = 8.8 Hz, 2H, H-3′), 7.62, (d, $J_{4\text{-OH},H\text{-}4}$ = 4.9 Hz, 1H, 4-OH), 7.50-7.45 (m, 2H, 2-OH, 3-OH), 7.03 (d, $J_{4',3'}$ = 8.9 Hz, 2H, H-4′), 5.23 (dd, $J_{6a,6b}$ = 11.6, $J_{6a,5}$ = 2.0 Hz, 1H, H-6a), 5.06 (dd, $J_{6b,6a}$ = 11.7, $J_{6b,5}$ = 5.7 Hz, 1H, H-6b), 4.76 (d, $J_{1,2}$ = 7.8 Hz, 1H, H-1), 4.32-4.27 (m, 1H, H-3), 4.24 (td, $J_{4,3}$ = 9.1, $J_{4,5}$ = 4.6 Hz, 1H, H-4), 4.18 – 4.05 (m, 2H, H-2, H-5), 3.96 (t, $J_{6',7'}$ = 6.5 Hz, 2H, CH_2-6′), 3.64 (s, 3H, CH_3-Me), 1.74 (dt, $J_{7',8'}$ = 14.4, $J_{7',6'}$ = 6.7 Hz, 2H, CH_2-7′), 1.47-1.37 (m, 2H, CH_2-8′), 1.36-1.16 (m, 28H, CH_2-9′-CH_2-22′), 0.88 (t, $J_{23',22'}$ = 6.9 Hz, 2H, CH_3-23′); ^{13}C NMR (150 MHz, C_5D_5N) δ 166.8 (C-1′), 163.8 (C-5′), 125.2 (C-2′), 132.4 (C-3′), 115.0 (C-4′), 106.1 (C-1), 78.8 (C-3), 75.7 (C-5), 75.4 (C-2), 71.9 (C-4), 68.8 (C-6′), 65.3 (C-6), 57.1 (C-Me), 32.5, 30.4, 30.3, 30.3, 30.3, 30.2, 30.2, 30.0, 30.0, 29.7, 26.6, 23.3 (C-9′-C-22′), 30.6 (C-7′), 27.5 (C-8′), 14.6 (C-23′); HRMS *m/z* calcd for $[C_{32}H_{55}O_8]^+$ 567.3891, obsd 567.3868.



Docosyl 6-*O*-(4-octadecyloxybenzoyl)-α-D-glucoside (BzC18GlcαOC22, 16). The general procedure for the synthesis of aromatic glycolipids was carried out on **34** (20 mg, 0.03 mmol) to yield **16** (14 mg, 0.02 mmol, 54%) as a colourless film. IR (film) 3354, 2914, 2849, 1705, 1468, 1255 cm^{-1}; $[\alpha]_D^{25}$ = + 16.2 (*c* = 0.1, C_5D_5N); ^1H NMR (500 MHz, C_5D_5N) δ 8.32 (d, $J_{3'',4''}$ = 8.4 Hz, 2H, H-3″), 7.54 (d, $J_{4'\text{-OH,H-}4'}$ = 6.6 Hz, 1H, 4′-OH), 7.29 (d, $J_{3'\text{-OH,H-}3'}$ = 4.7 Hz, 1H, 3′-OH), 7.11 (d, $J_{4'',3''}$ = 8.4 Hz, 2H, H-4″), 6.75 (d, $J_{2'\text{-OH,H-}2'}$ = 6.1 Hz, 1H, 2′-OH), 5.46-5.29 (m, 2H, H-1′, H-6′a), 4.75-4.55 (m, 2H, H-3′, H-5′), 4.29-4.11 (m, 2H, H-2′, H-4′), 4.09-3.12 (m, 3H, H-1a, CH_2-6″), 3.65-3.58 (m, 1H, H-1b), 1.90-1.55 (m, 4H, CH_2-2, CH_2-7″), 1.59-1.05 (m, 68H, CH_2-lipid), 0.88 (t, *J* = 6.8 Hz, 6H, CH_3-22, CH_3-23″); ^{13}C NMR (150 MHz, C_5D_5N) δ 166.8 (C-1″), 163.8 (C-5″), 132.4 (C-3″), 122.9 (C-2″), 115.0 (C-4″), 100.8 (C-1′), 75.9 (C-3′), 74.2 (C-2′), 72.6 (C-4′), 71.8 (C-5′), 68.9 (C-6″), 68.7 (C-1), 65.7 (C-6′), 32.5, 30.4, 30.4, 30.4, 30.4, 30.4, 30.4, 30.4, 30.3, 30.3, 30.3, 30.3, 30.2, 30.1, 30.0, 30.0, 30.0, 29.8, 27.0, 26.6, 23.3 (C-CH_2-lipid), 14.7 (C-CH_3-22, CH_3-23″); HRMS *m/z* calcd for $[C_{53}H_{97}O_8]^+$ 861.7178, obsd 861.7184.



Docosyl 6-*O*-(4-octadecyloxybenzoyl)-β-D-glucoside (BzC18GlcβOC22, 17). The general procedure for the synthesis of aromatic glycolipids was carried out on **35** (30 mg, 0.04 mmol) to yield **17** (21 mg, 0.02 mmol, 57%) as a colourless film. IR (film) 3353, 2914, 2849, 1704, 1468, 1050, 716 cm^{-1}; $[\alpha]_D^{26}$ = + 5.2 (*c* = 0.1, C_5D_5N); ^1H NMR (500 MHz, C_5D_5N) δ 8.27 (d, $J_{3'',4''}$ = 8.4 Hz, 2H, H-3″), 7.05 (d, $J_{4'',3''}$ = 8.2 Hz, 2H, H-4″), 5.25 (d, $J_{6'a,6'b}$ = 11.6 Hz, 1H, H-6′a), 5.07 (dd, $J_{6'b,6'a}$ = 12.0, $J_{6'b,5'}$ = 5.7 Hz, 1H, H-6′b), 4.89 (d, $J_{1',2'}$ = 7.7 Hz, 1H, H-1′), 4.31 (t, $J_{3',2'} = J_{3',4'}$ = 8.7 Hz, 1H, H-3′), 4.24 (t, $J_{4',3'} = J_{4',5'}$ = 9.1 Hz, 1H, H-4′), 4.21-4.09 (m, 3H, H-1a, H-2′, H-5′), 3.98 (t, $J_{6'',7''}$ = 6.5 Hz, 2H, CH_2-6″), 3.80-3.71 (m, 1H, H-1b), 1.73 (m, 4H, CH_2-2, CH_2-7″), 1.52-1.13 (m, 68H, CH_2-lipid), 0.89 (t, *J* = 6.6 Hz, 6H, CH_3-22, CH_3-23″); ^{13}C NMR (150 MHz, C_5D_5N) δ 166.8 (C-1″), 163.8 (C-5″), 132.4 (C-3″), 123.4 (C-2″), 115.0 (C-4″), 105.2 (C-1′), 78.8 (C-3′), 75.7 (C-5′), 75.6 (C-2′), 72.0 (C-4′), 70.4 (C-1), 68.8 (C-6″), 65.4 (C-6′), 32.5, 30.7, 30.4, 30.4, 30.4, 30.3, 30.3, 30.3, 30.3, 30.3, 30.2, 30.1, 30.0, 30.0, 29.7, 26.8, 26.6, 23.3 (C-CH_2-lipid), 14.7 (C-CH_3-22, CH_3-23″); HRMS *m/z* calcd for $[C_{53}H_{96}NaO_8]^+$ 883.6997, obsd 883.6993.

Biology Experimental

Endotoxin Testing. All synthesized glycolipids were confirmed to be endotoxin free at a sensitivity of ≤0.1 EU/mL by using the Pierce Limulus amebocyte lysate (LAL) chromogenic endotoxin quantitation kit (Thermo Scientific).

Preparation of Ligand-Coated Plates. TDB and other synthesized ligands were dissolved in $CHCl_3$/MeOH (2:1, 1 mM), diluted in isopropanol (0.05 mM) and added to 96-well plates (20 μL/well). The solvents were evaporated open to air in a sterile environment, and the coated plates were used immediately.

2B4-NFAT-GFP Reporter Cells. 2B4-NFAT-GFP reporter cells expressing mMincle + FcRγ, hMincle + FcRγ, hMincle$^{EPN-QPD}$ + FcRγ or FcRγ only were used as previously described.[3-4] Here, 100 uL of NFAT-GFP 2B4 reporter cells were incubated with ligand-coated plates (0.1 or 1 nmol/well) at $1x10^6$ cells/mL for 18 h. The reporter cells were harvested, stained with DAPI, and analyzed for NFAT-GFP expression using flow cytometry (FACS Calibur).

Mice. C57BL/6 wild-type and Mincle$^{-/-}$ mice were bred and housed in a conventional animal facility at the Malaghan Institute of Medical Research, New Zealand. All mice used for experiments were aged between 8 and 12 weeks, and experimental procedures were approved by the Victoria University Animal Ethics Committee in accordance with their guidelines for the care of animals (protocol nr 22371).

Murine Bone-Marrow Derived Macrophages. For the preparation of murine bone marrow-derived macrophages (BMDMs), bone marrow cells were collected from the tibias and femurs of C57BL/6 mice and cultured (250,000 cells/mL) in complete RPMI media [RPMI-1640 (Gibco) with 10% heat inactivated fetal bovine serum (Gibco), 100 unit/mL penicillin−streptomycin (Gibco), and 2 mM Glutamax (Gibco)] supplemented with 50 ng/mL GM-CSF (clone X63/GM-CSF murine cells). Cells were incubated at 37 °C (5% CO_2) for 8 days, whereby cells were fed by replacing half the media on days 3 and 6. On day 8, all media was removed and the cells were washed with Dulbecco's phosphate buffered saline (DPBS, Gibco) to remove any loosely adherent cells. The BMDMs were harvested with StemPro Accutase (1 mL/well, 15 min at room temperature, Gibco) and seeded onto a pre-coated 96-well plate. The supernatant was collected after 24 h and analyzed for cytokine/chemokine production.

Human Monocytes. The use of human leukocytes from healthy donors was approved by New Zealand Northern A Health and Disability Ethics Committee (approval number 15/NTA/178). Human monocytes were negatively selected using RosetteSep™ Human Monocyte Enrichment Cocktail (STEMCELL Technologies) from whole blood according to the manufacturer's protocol. The purity of monocytes was assessed using flow cytometry, and in all instances, the percentage or purity was in the range quoted by the manufacturer. Cell concentration was adjusted to $1x10^6$ cells/mL in complete RPMI media and 100 uL of cells were added per well into ligand-coated plates (0.1 or 1 nmol/well) and incubated at 37 °C, 5% CO_2. The supernatant was collected after 24 h and analyzed for cytokine/chemokine production.

Cytokine Analysis. Murine IL-6, human IL-1β, human IL-8, human TNF (BD Biosciences), and murine IL-1β, murine MIP-2, human, IL-6, human MIP-2 (R&D) levels were determined via sandwich ELISA according to the manufacturer's instructions.

Statistics. The unpaired t-test was used for all statistical analyses (GraphPad Prism 8).

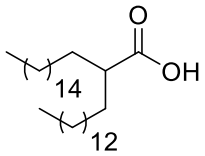
References

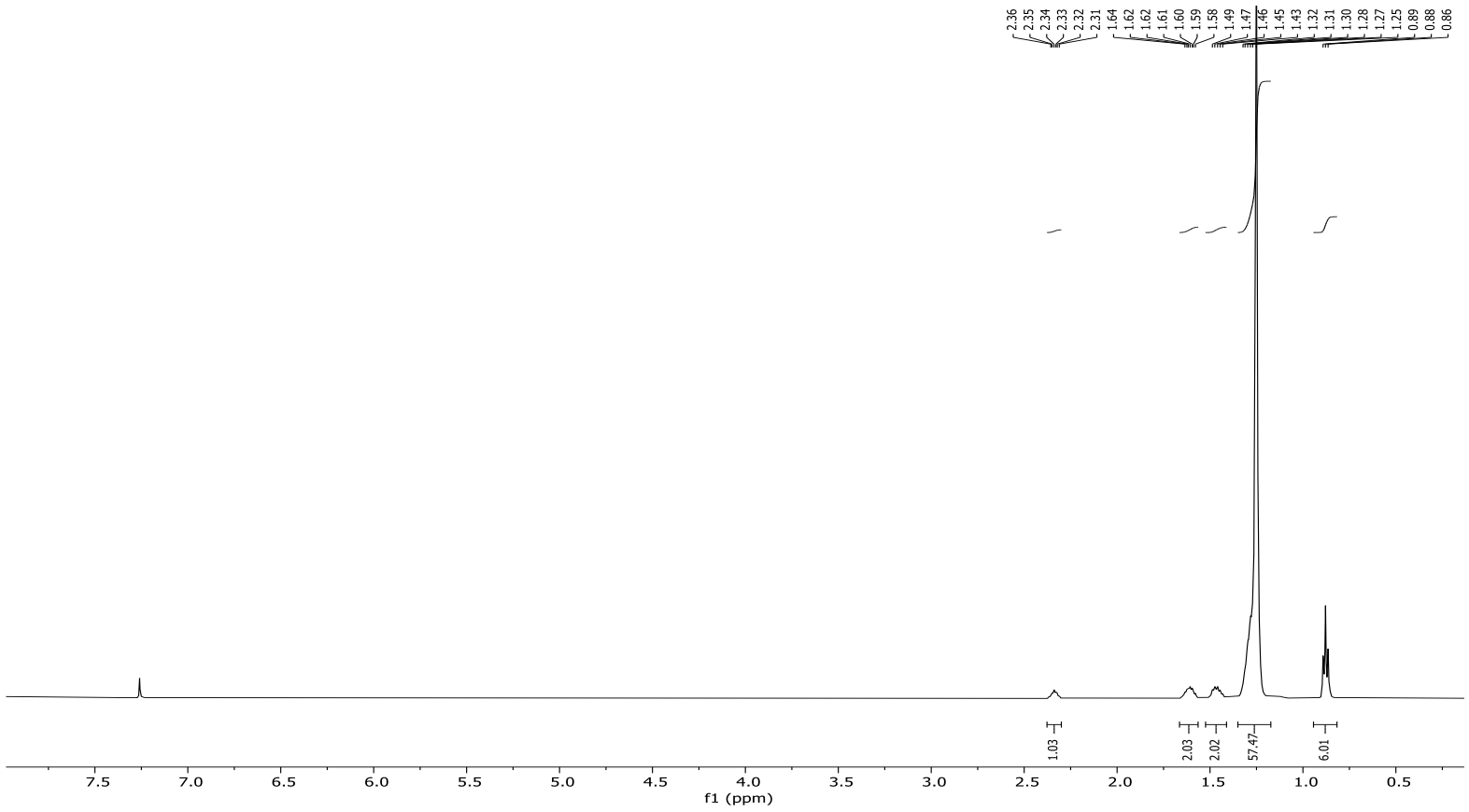
1. Yamamoto, H.; Oda, M.; Nakano, M.; Watanabe, N.; Yabiku, K.; Shibutani, M.; Inoue, M.; Imagawa, H.; Nagahama, M.; Himeno, S.; Setsu, K.; Sakurai, J.; Nishizawa, M., Development of Vizantin, a Safe Immunostimulant, Based on the Structure–Activity Relationship of Trehalose-6,6′-dicorynomycolate. *Journal of Medicinal Chemistry* **2013,** *56* (1), 381-385.
2. Foster, A. J.; Nagata, M.; Lu, X.; Lynch, A. T.; Omahdi, Z.; Ishikawa, E.; Yamasaki, S.; Timmer, M. S. M.; Stocker, B. L., Lipidated Brartemicin Analogues Are Potent Th1-Stimulating Vaccine Adjuvants. *J Med Chem* **2018,** *61* (3), 1045-1060.
3. Yamasaki, S.; Ishikawa, E.; Sakuma, M.; Hara, H.; Ogata, K.; Saito, T., Mincle is an ITAM-coupled activating receptor that senses damaged cells. *Nature immunology* **2008,** *9* (10), 1179-88.
4. Ishikawa, E.; Ishikawa, T.; Morita, Y. S.; Toyonaga, K.; Yamada, H.; Takeuchi, O.; Kinoshita, T.; Akira, S.; Yoshikai, Y.; Yamasaki, S., Direct recognition of the mycobacterial glycolipid, trehalose dimycolate, by C-type lectin Mincle. *The Journal of experimental medicine* **2009,** *206* (13), 2879-88.

NMR Spectra

2-Tetradecyloctadecanoic acid (**20**)

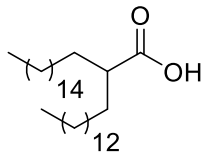
^{1}H NMR ($CDCl_3$, 500 MHz)

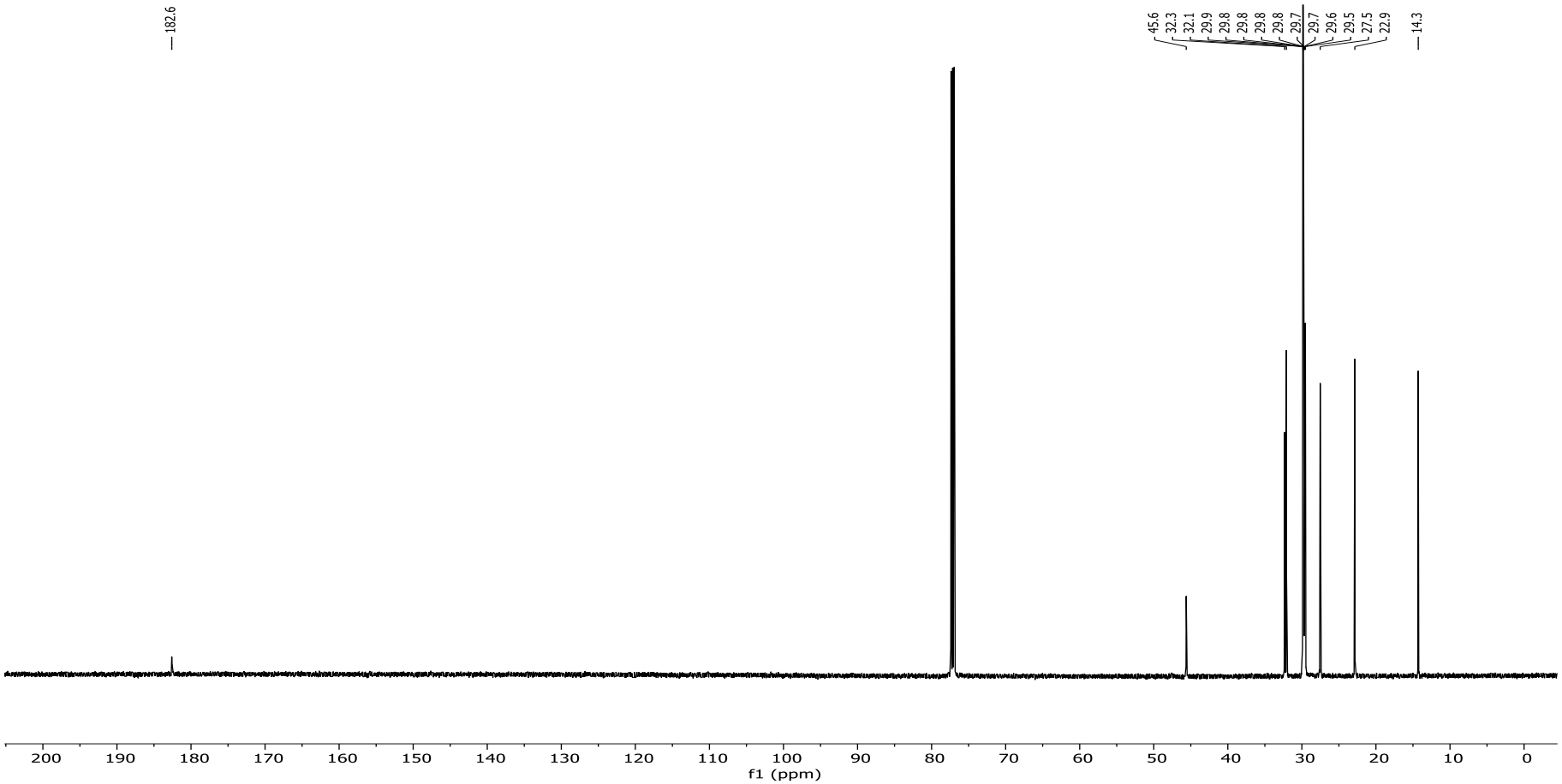




2-Tetradecyloctadecanoic acid (**20**)

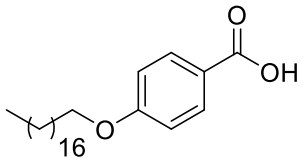
^{13}C NMR ($CDCl_3$, 125 MHz)

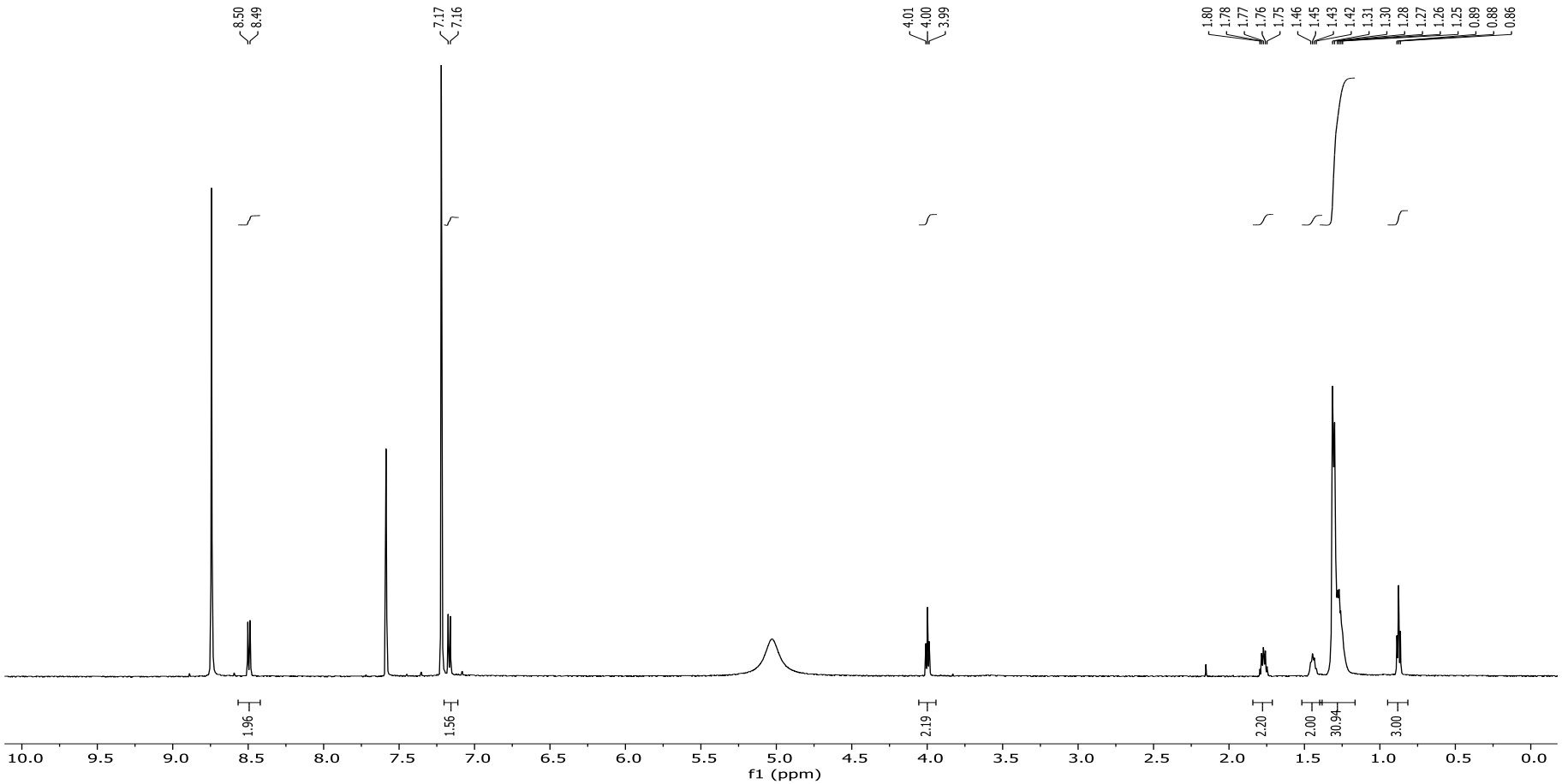




4-(Octadecyloxy)benzoic acid (**23**)

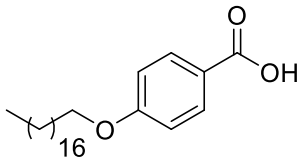
^{1}H NMR (C_5D_5N, 500 MHz)

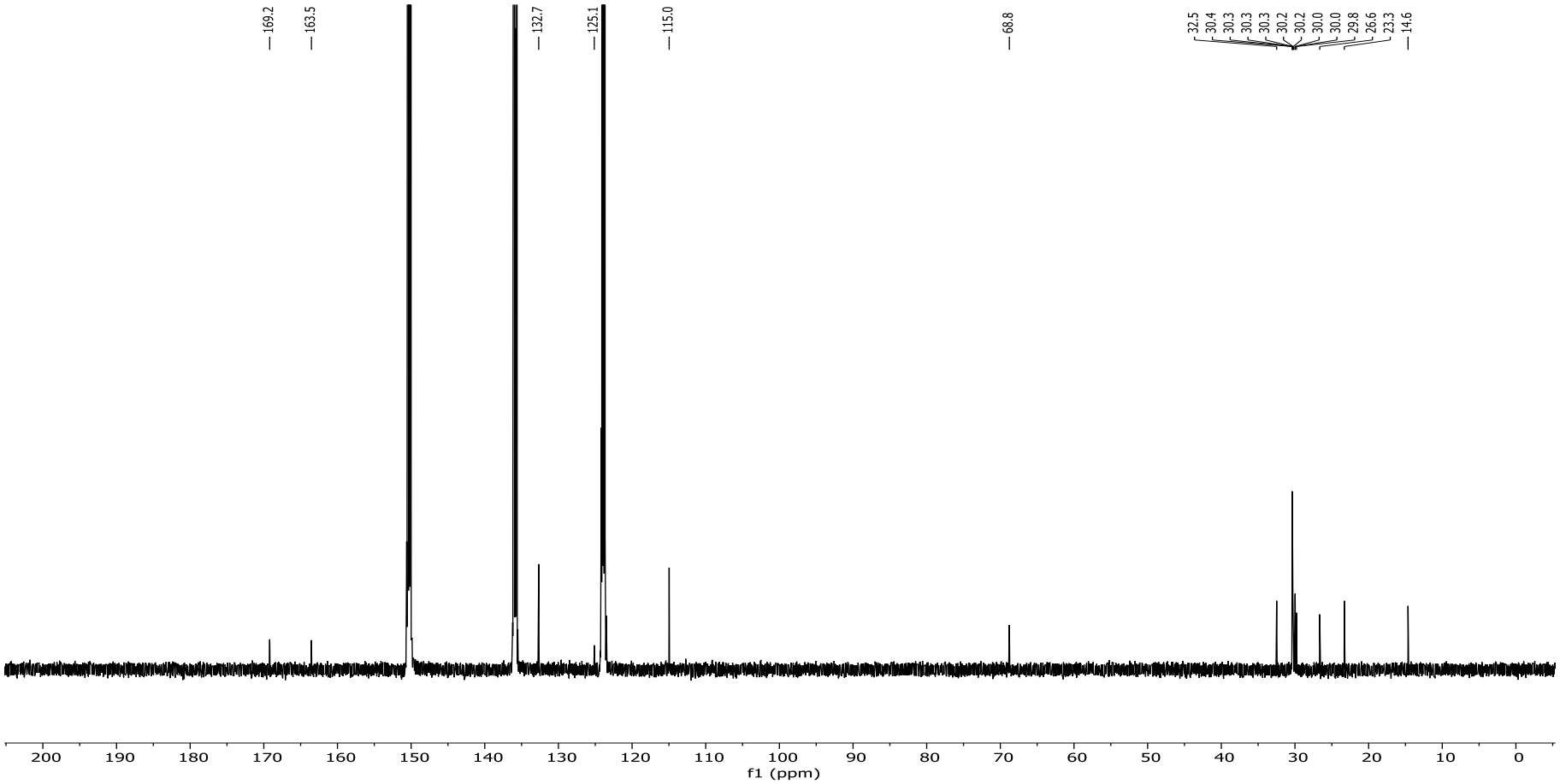




4-(Octadecyloxy)benzoic acid (**23**)

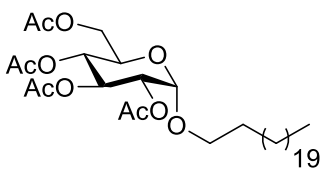
^{13}C NMR (C_5D_5N, 150 MHz)

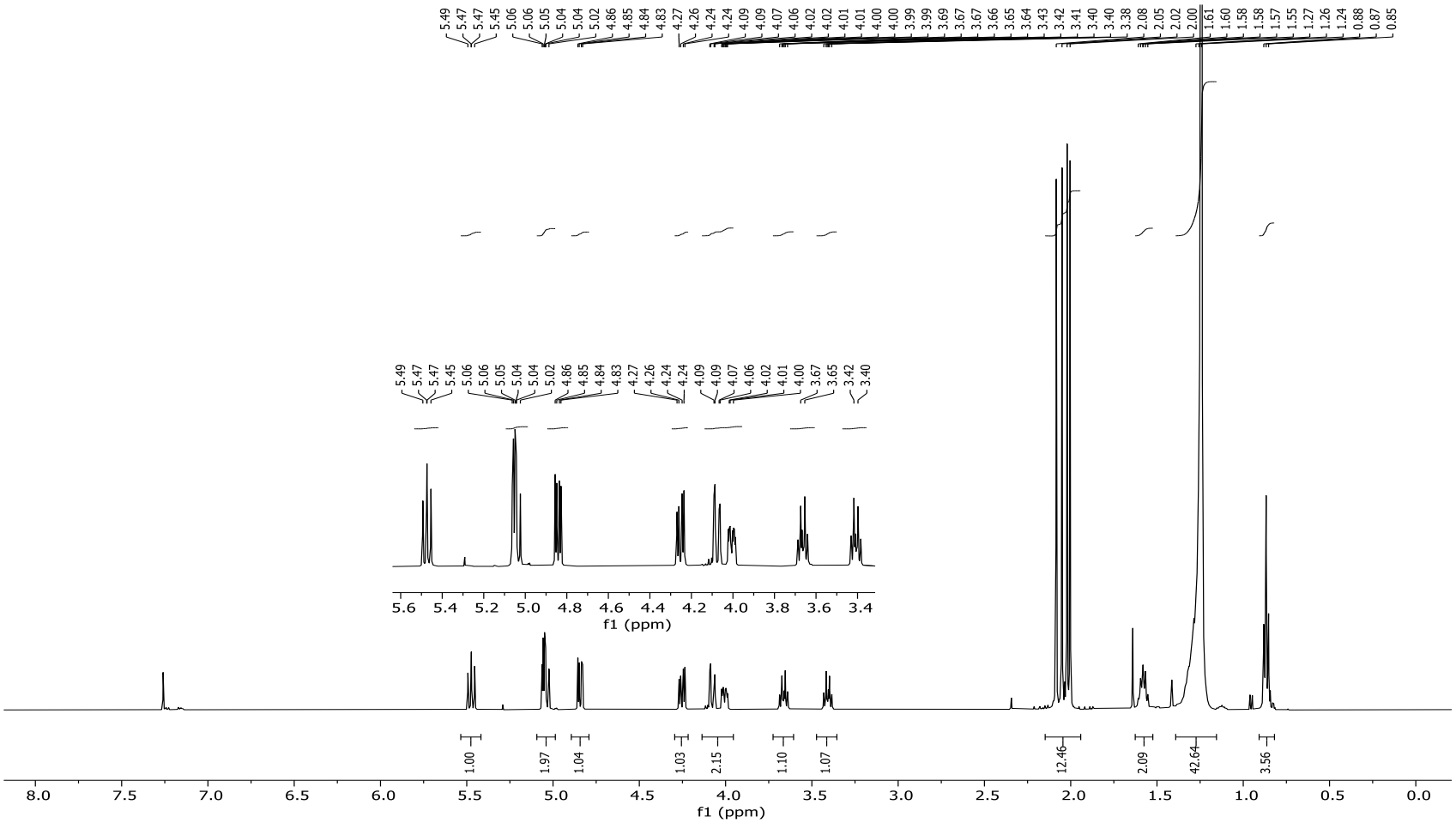




Docosyl (2,3,4,6-tetra-*O*-acetyl)-α-D-glucopyranoside (**32**)

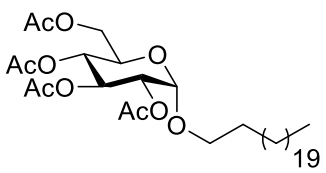
^{1}H NMR ($CDCl_3$, 500 MHz)

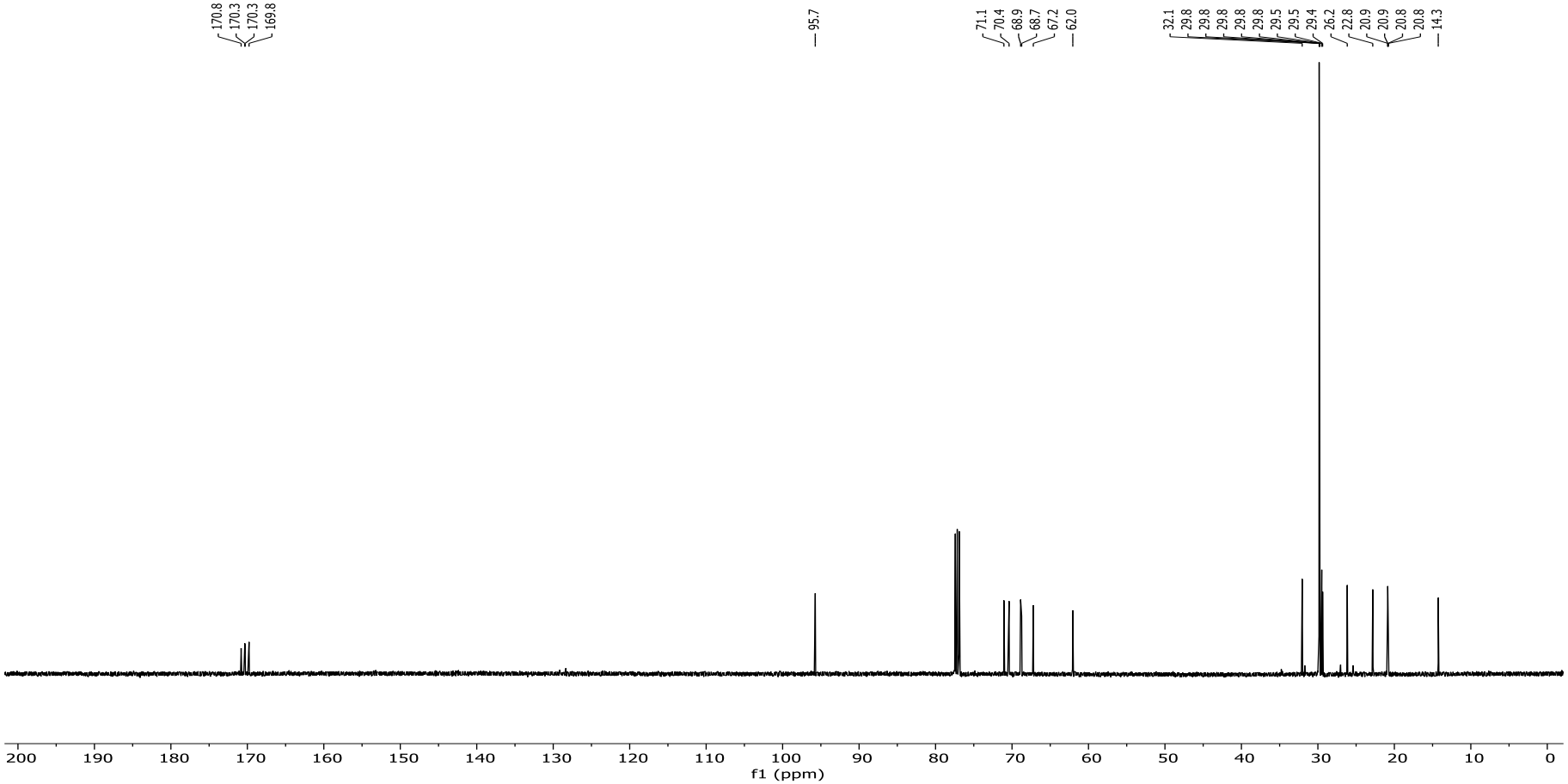




Docosyl (2,3,4,6-tetra-*O*-acetyl)-α-D-glucopyranoside (**32**)

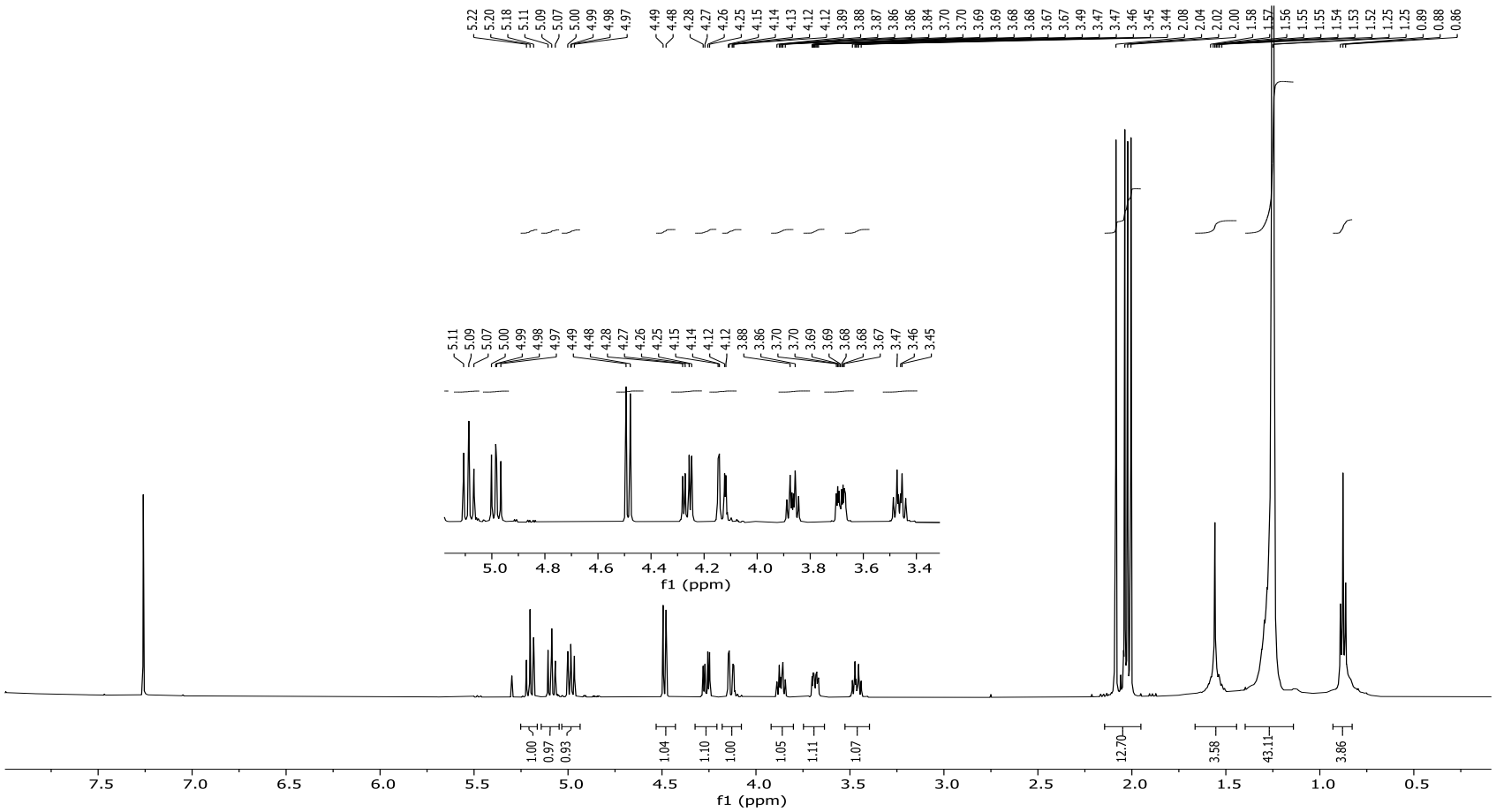
^{13}C NMR ($CDCl_3$, 125 MHz)





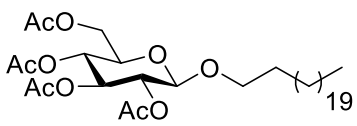
Docosyl (2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranoside (**33**)

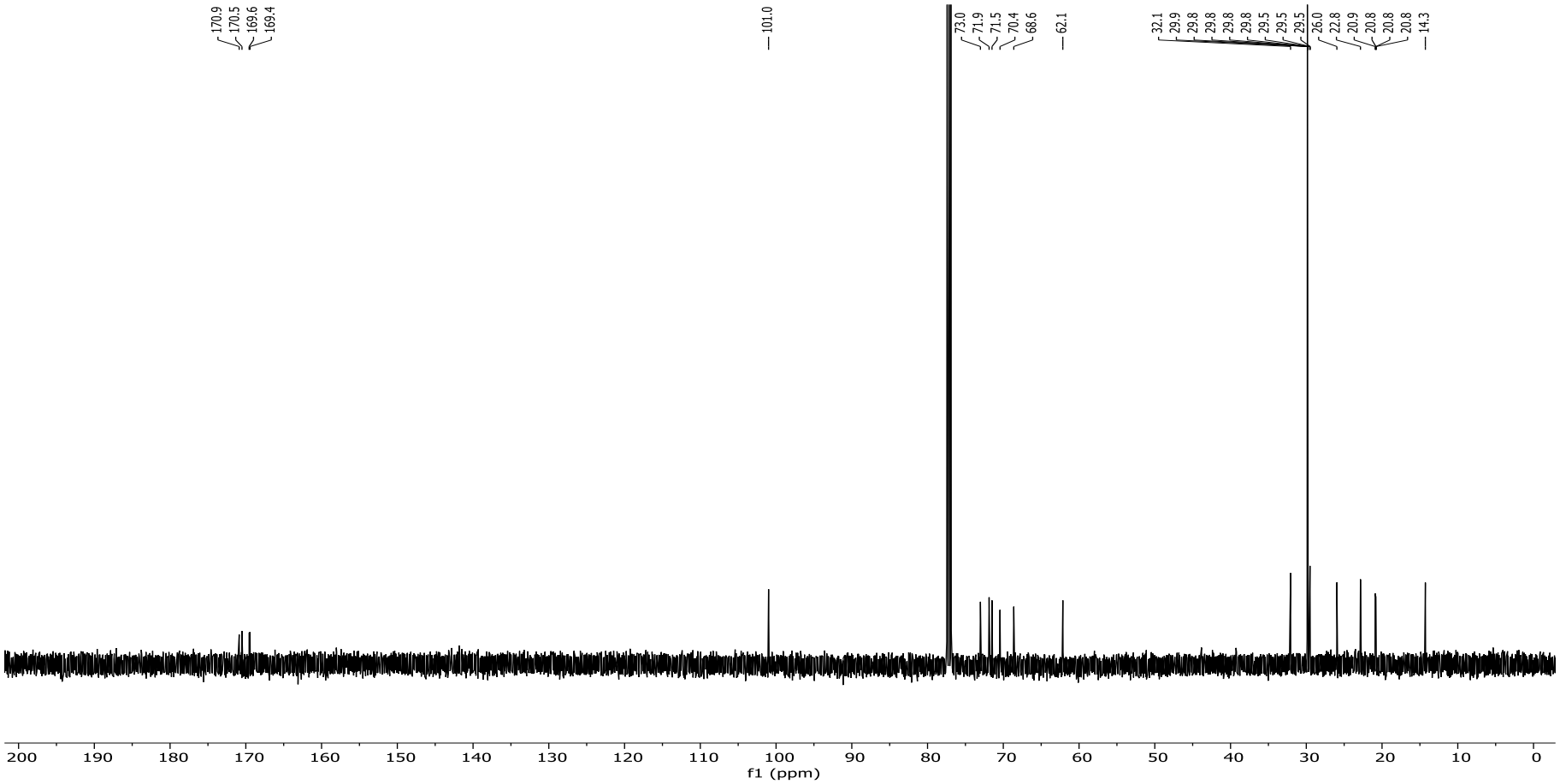
^{1}H NMR ($CDCl_3$, 500 MHz)



Docosyl (2,3,4,6-tetra-*O*-acetyl)-β-D-glucopyranoside (**33**)

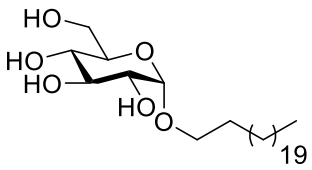
^{13}C NMR ($CDCl_3$, 125 MHz)

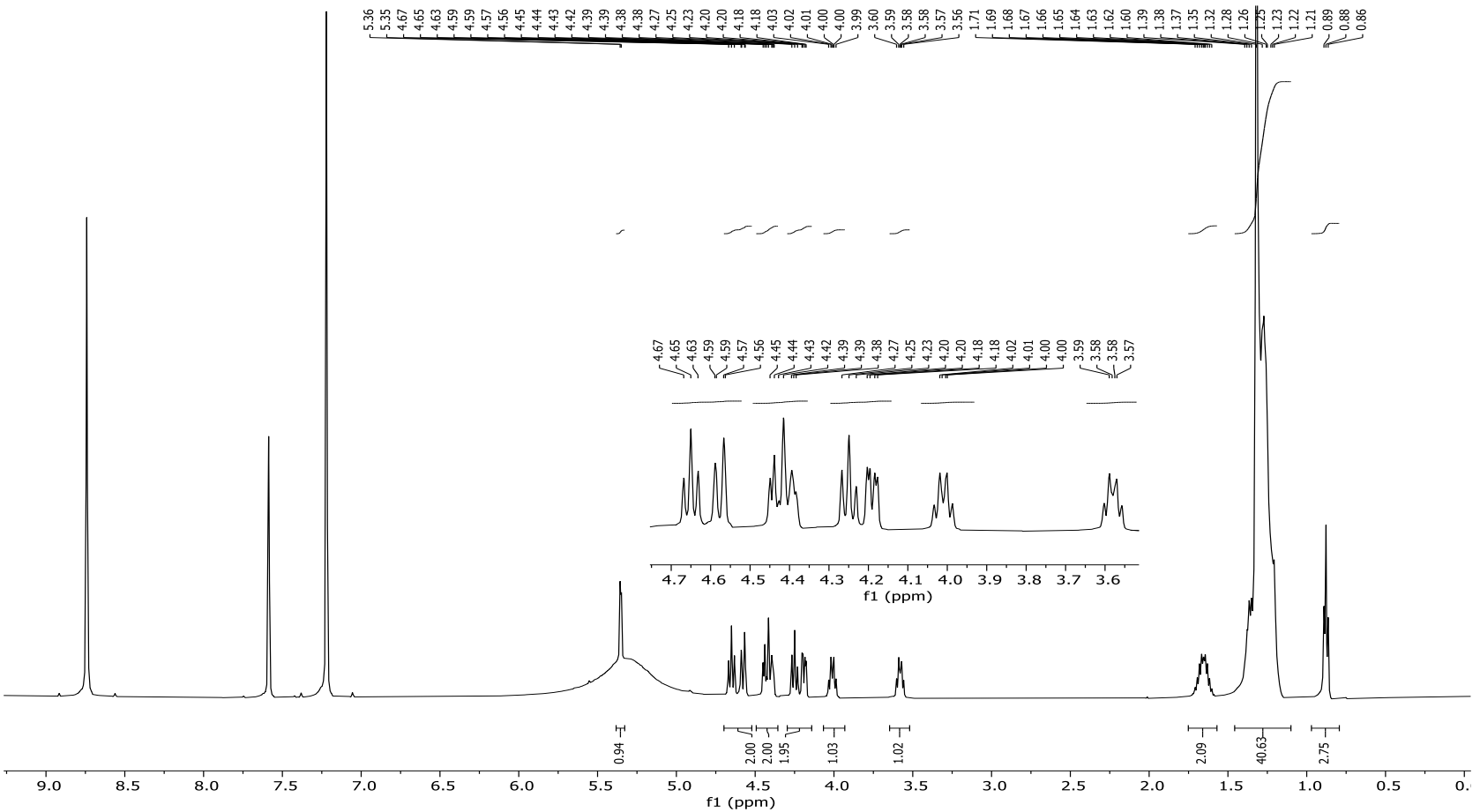




Docosyl α-D-glucopyranoside (**11**)

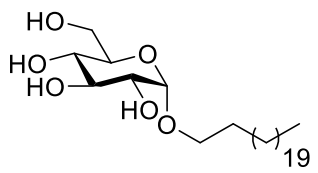
^{1}H NMR (C_5D_5N, 500 MHz)

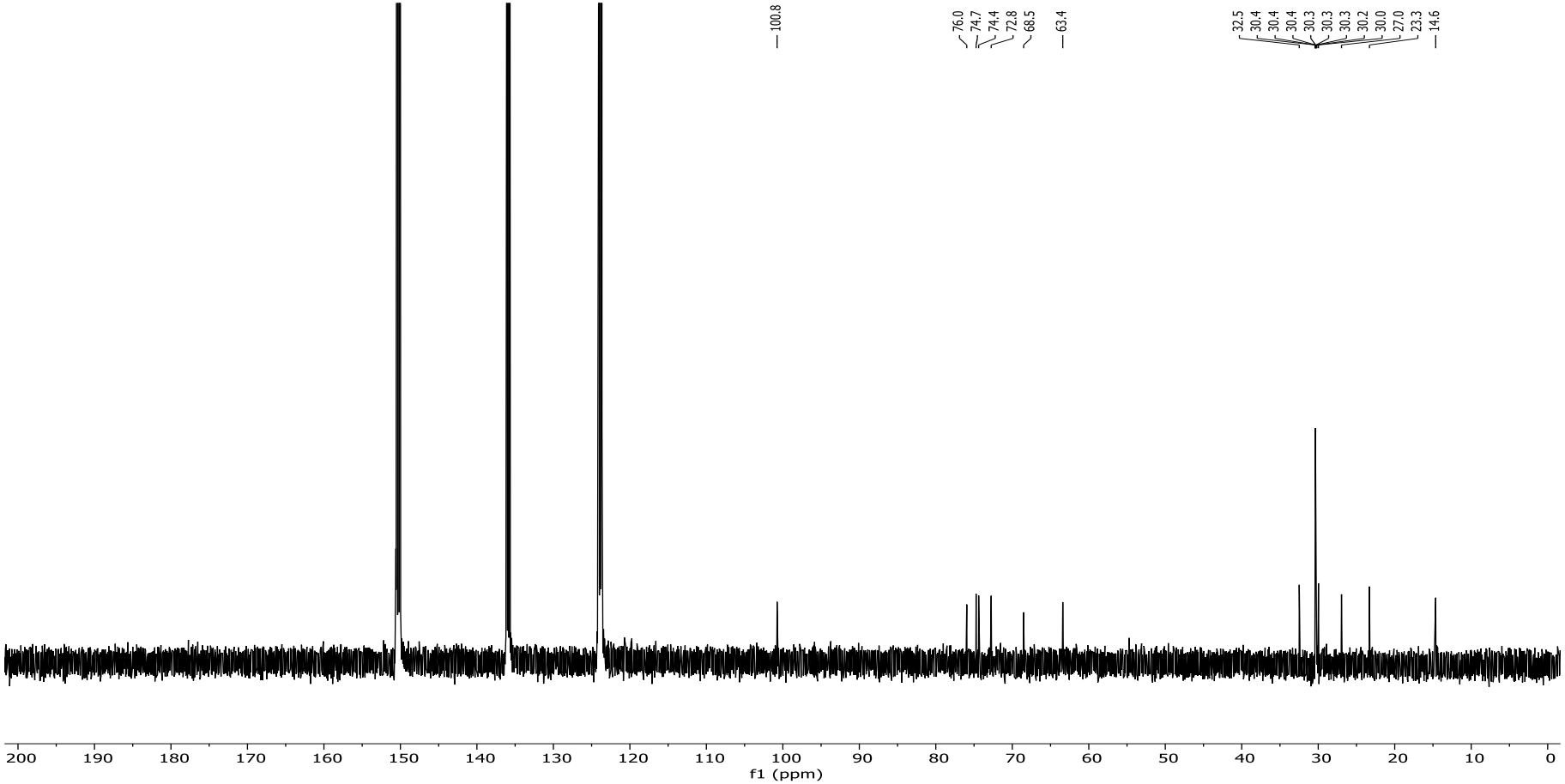




Docosyl α-D-glucopyranoside (**11**)

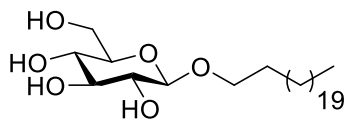
^{13}C NMR (C_5D_5N, 150 MHz)

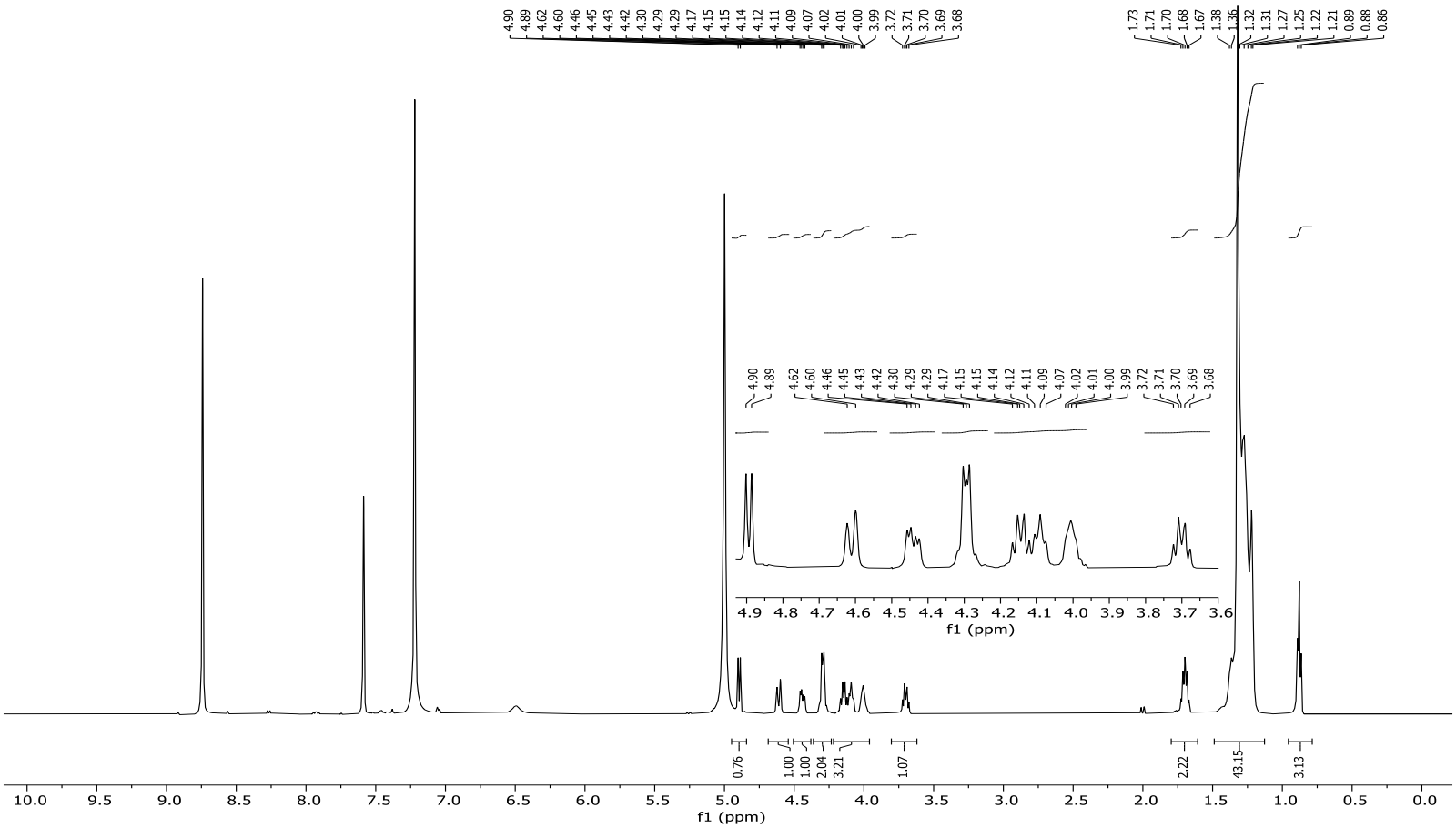




Docosyl β-D-glucopyranoside (**12**)

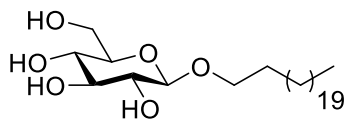
^{1}H NMR (C_5D_5N, 500 MHz)

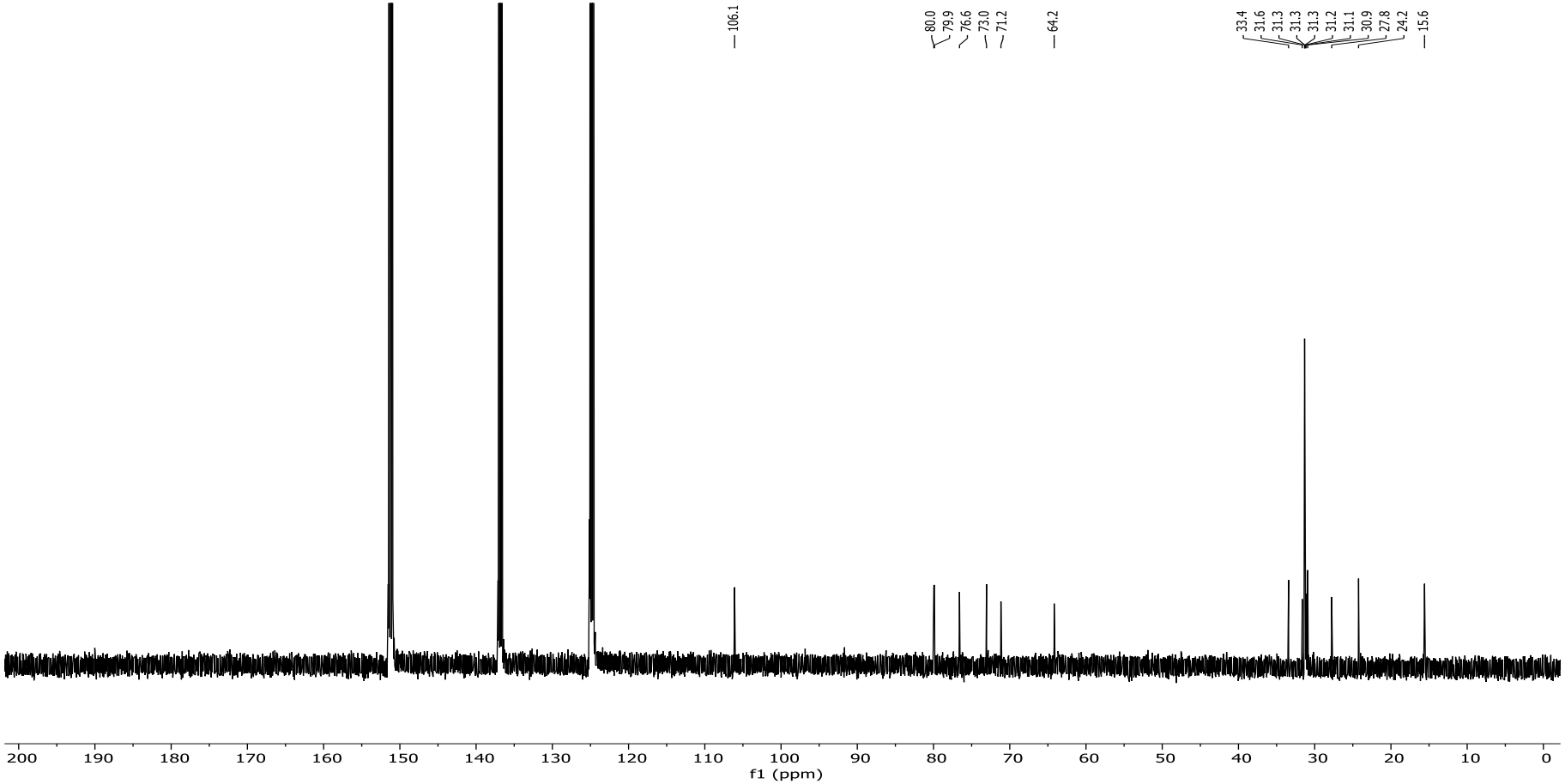




Docosyl β-D-glucopyranoside (**12**)

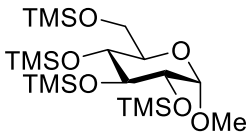
^{13}C NMR (C_5D_5N, 150 MHz)

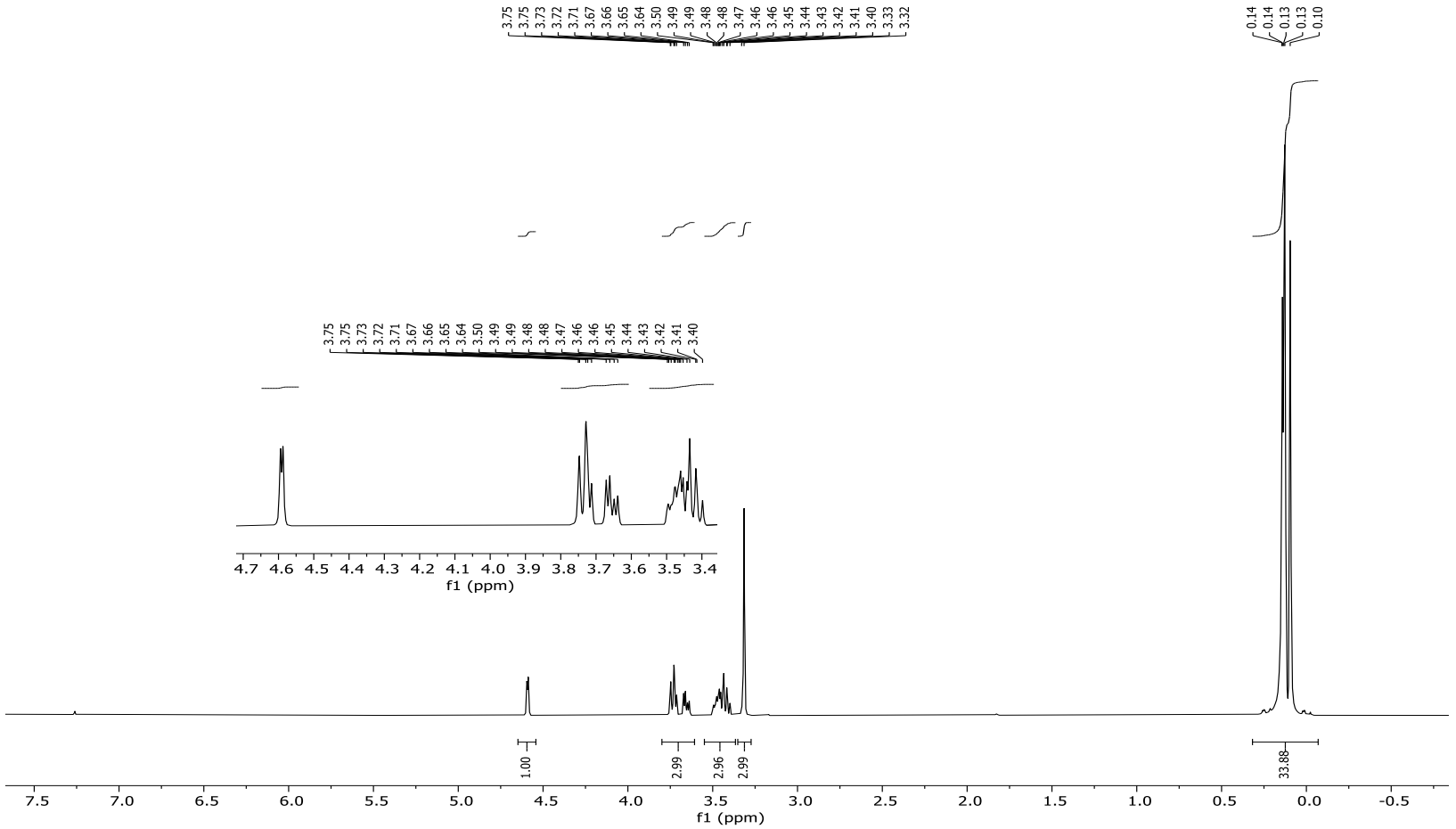




Methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside

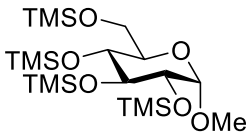
^{1}H NMR ($CDCl_3$, 500 MHz)

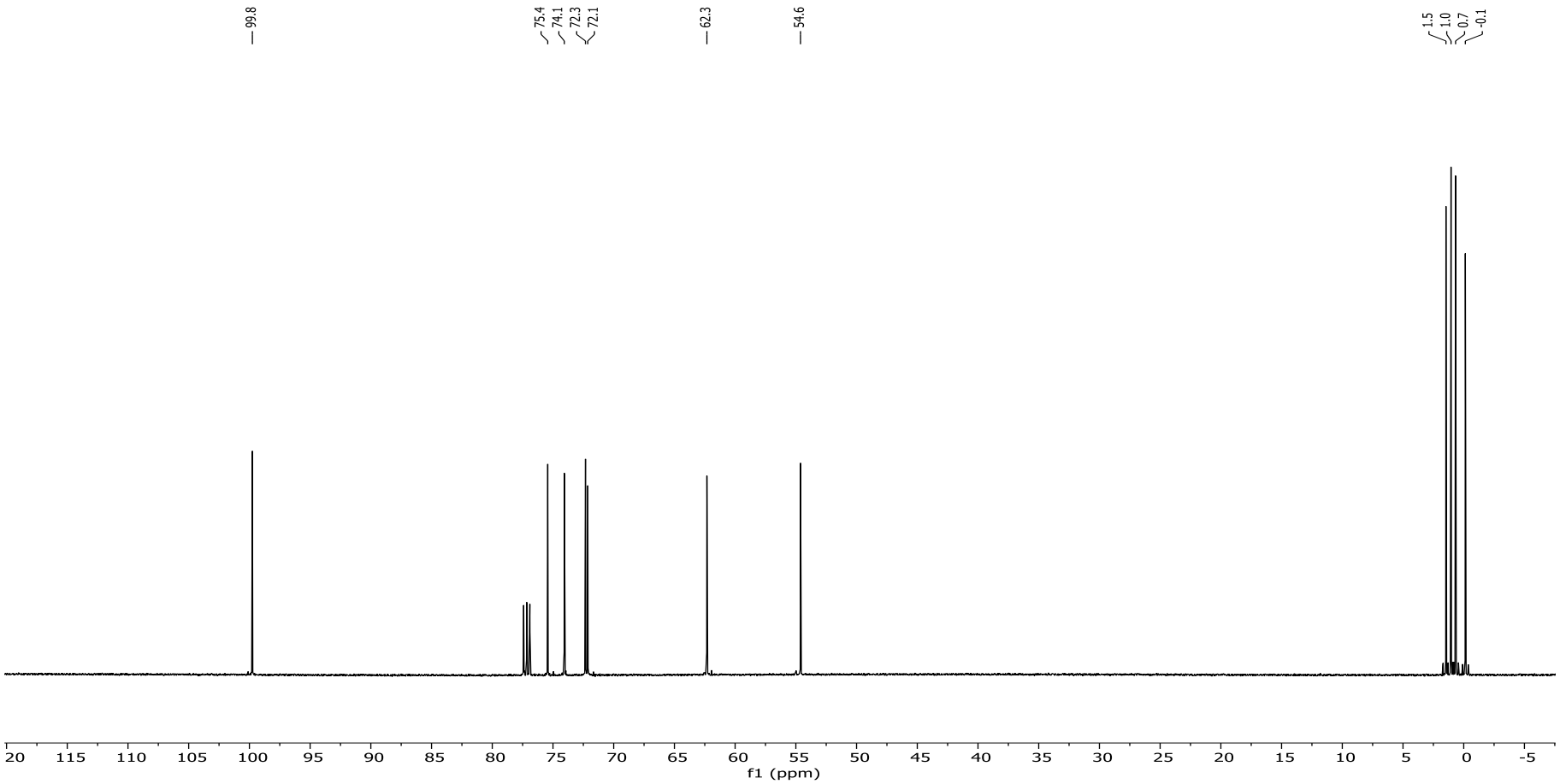




Methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside

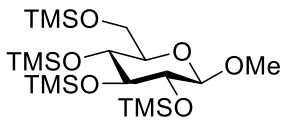
^{13}C NMR ($CDCl_3$, 125 MHz)

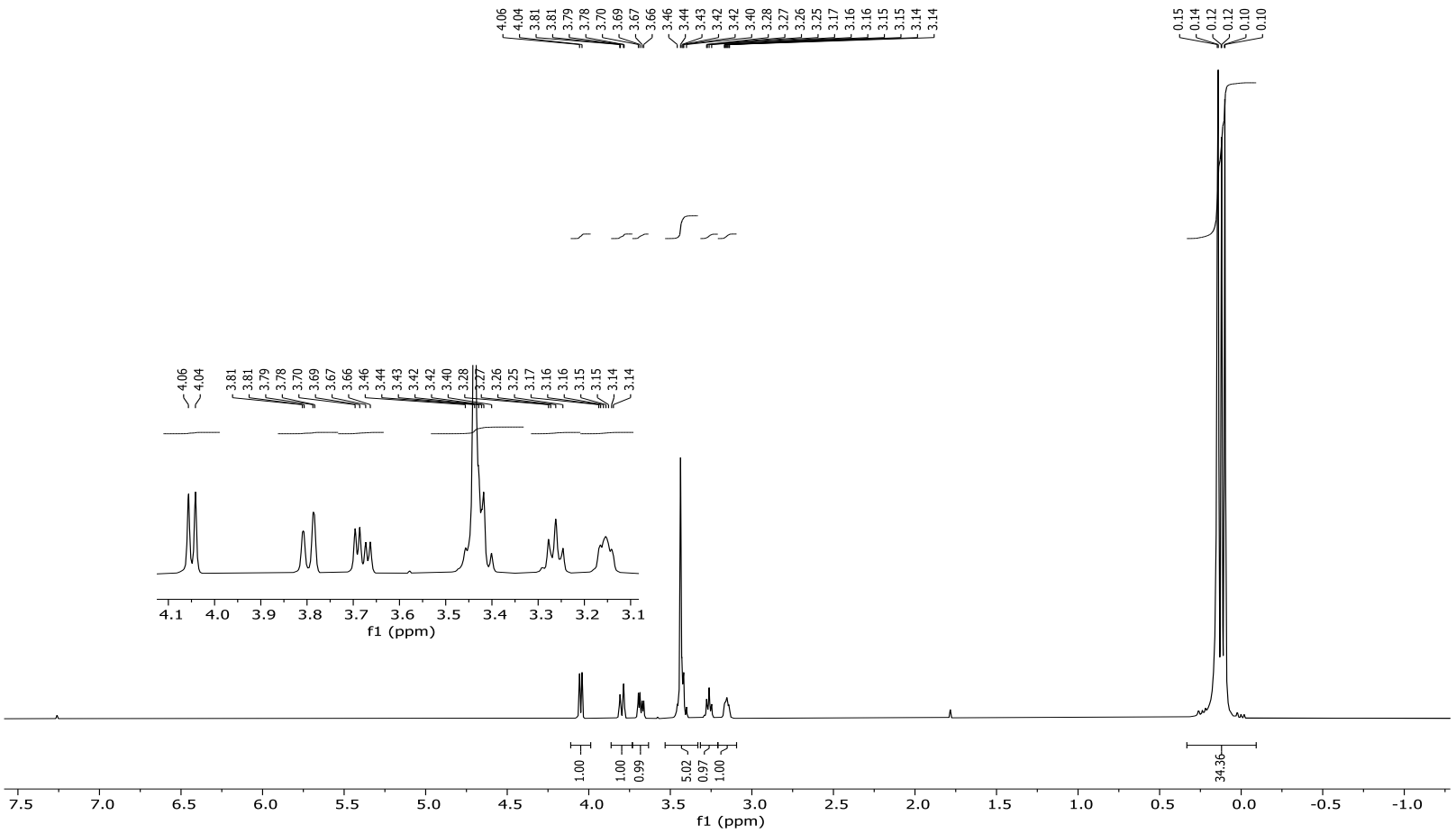




Methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside

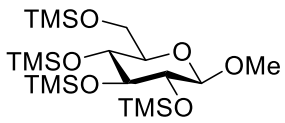
^{1}H NMR ($CDCl_3$, 500 MHz)

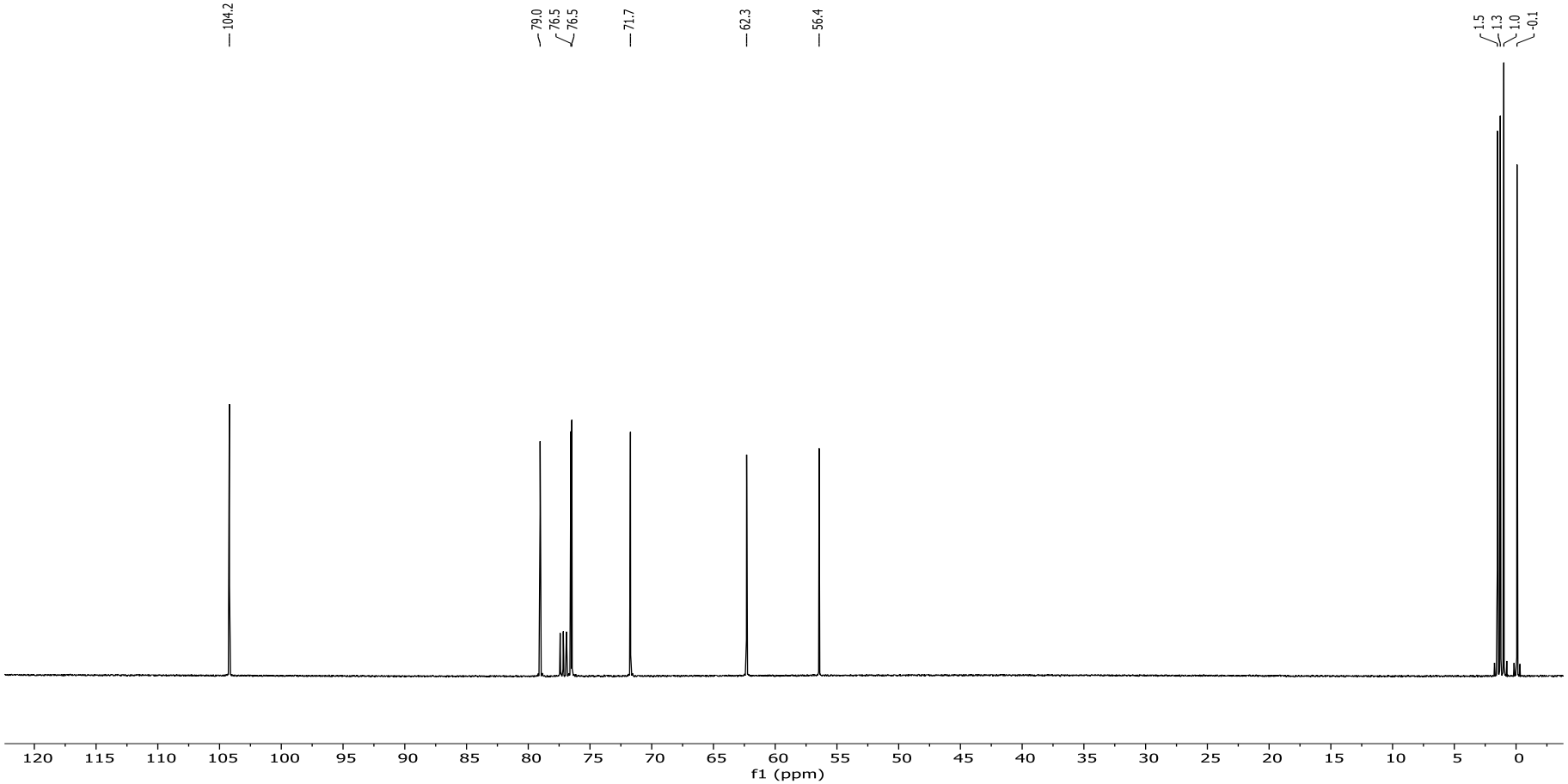




Methyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside

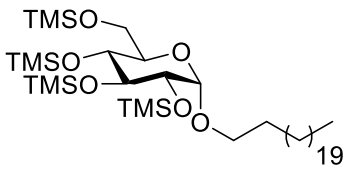
^{13}C NMR ($CDCl_3$, 125 MHz)

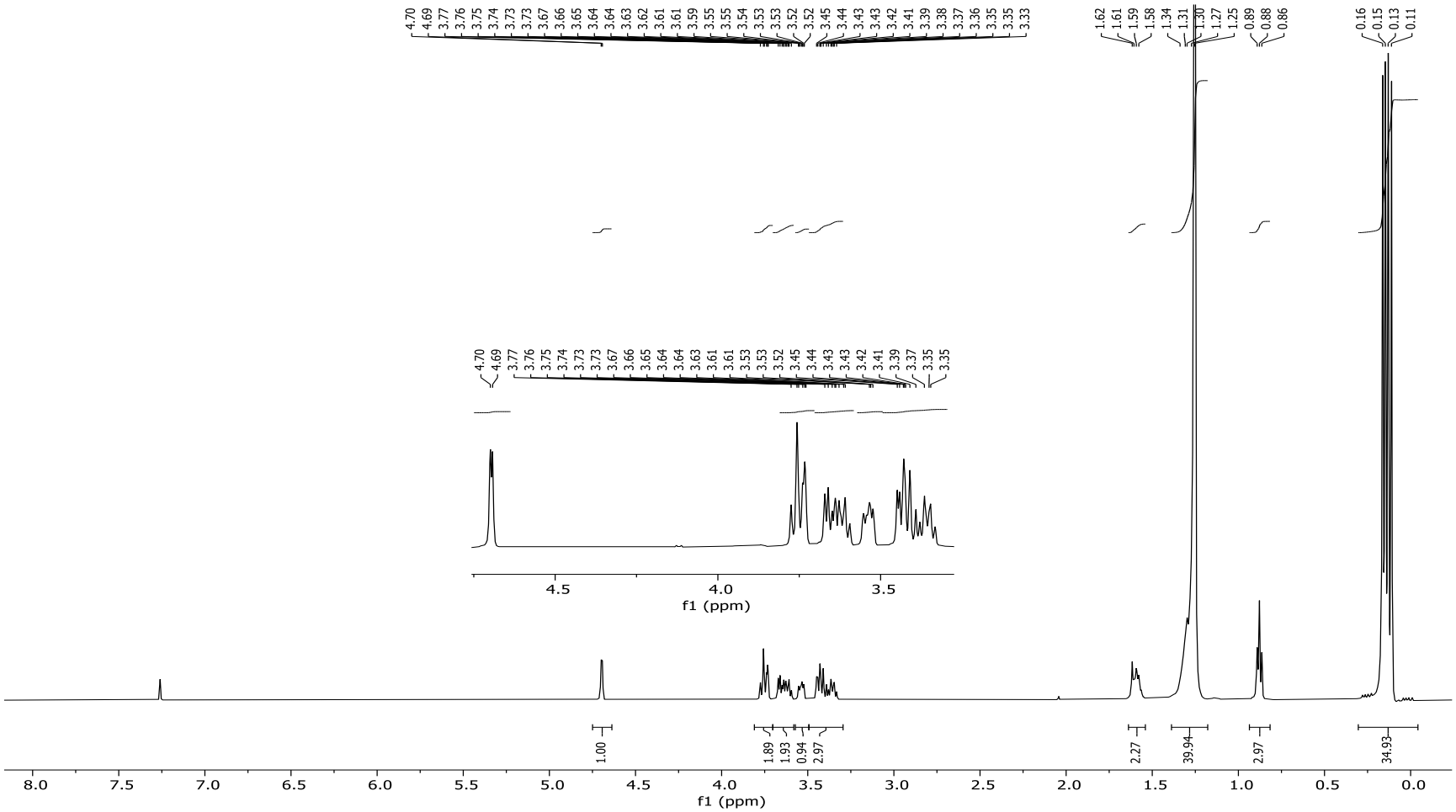




Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside

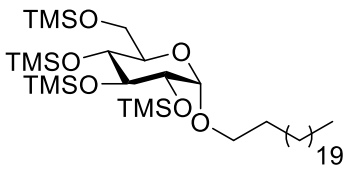
^{1}H NMR ($CDCl_3$, 500 MHz)

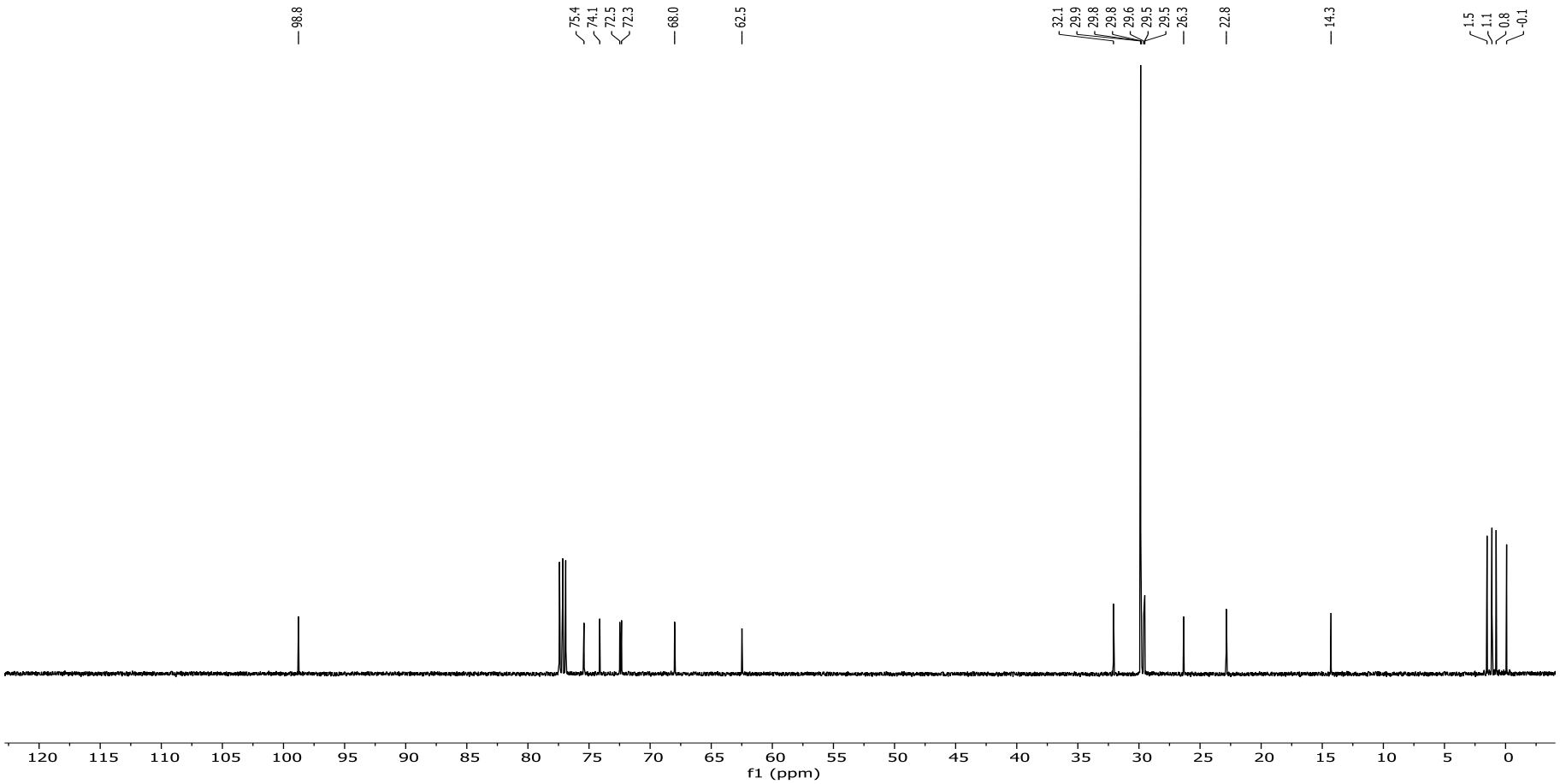




Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside

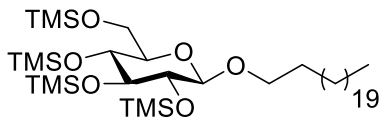
^{13}C NMR ($CDCl_3$, 125 MHz)

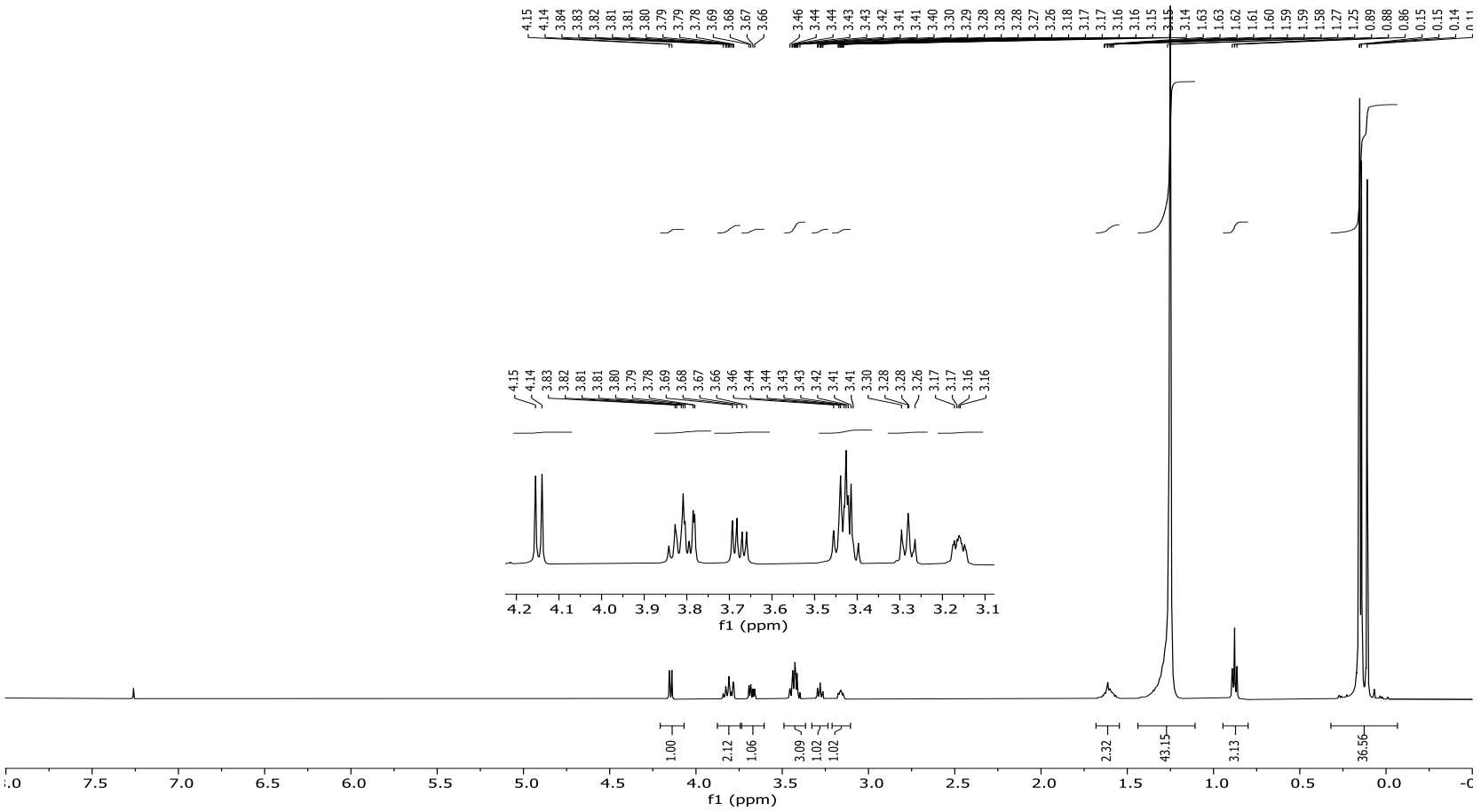




Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside

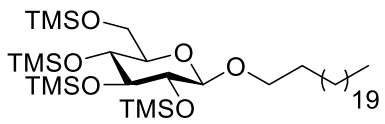
^{1}H NMR ($CDCl_3$, 500 MHz)

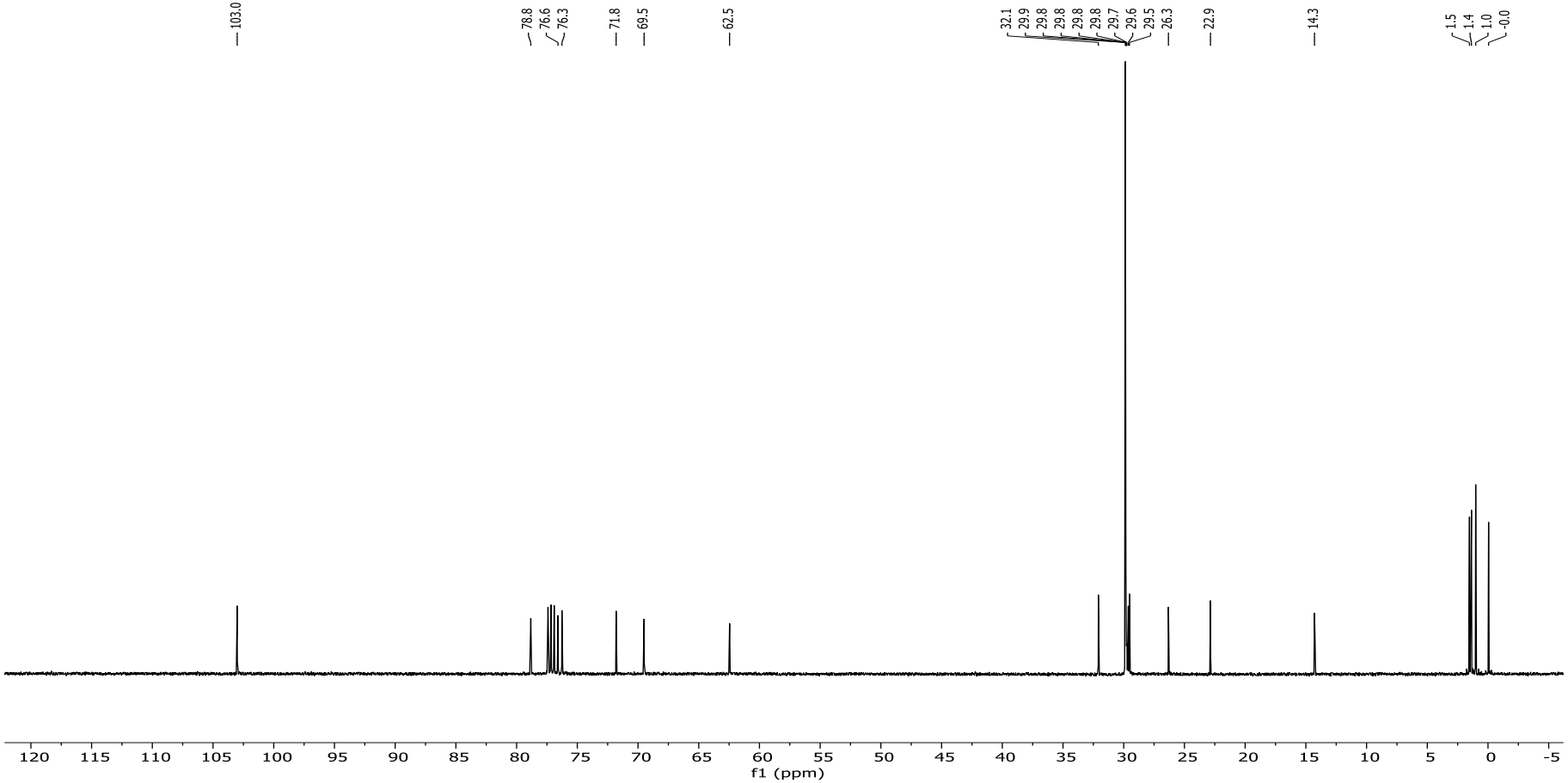




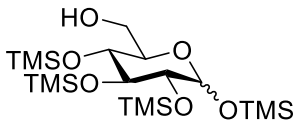
Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-β-D-glucopyranoside

^{13}C NMR ($CDCl_3$, 125 MHz)

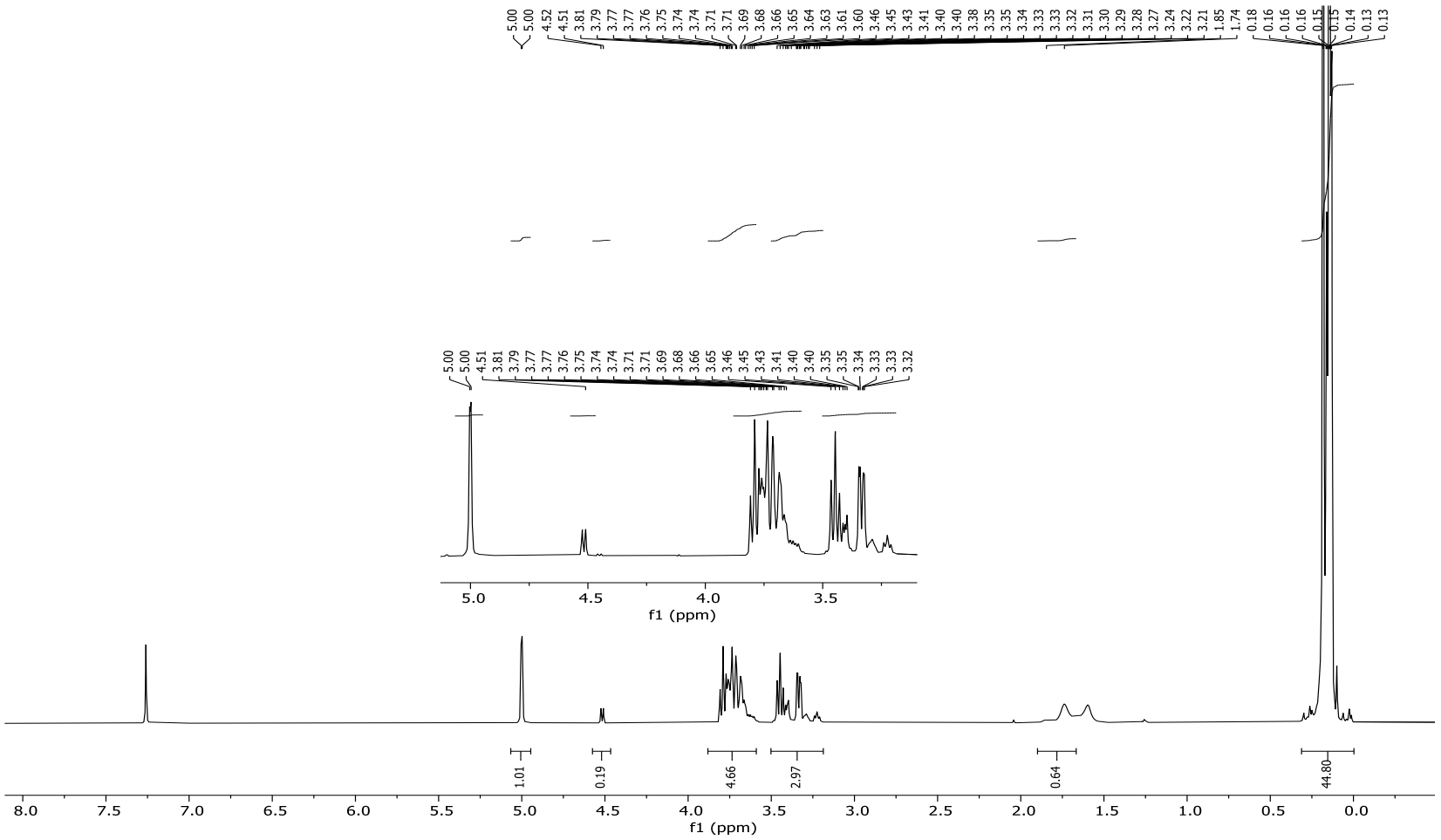




2,3,4-Tris-*O*-trimethylsilyl-α-D-glucose (**27**)

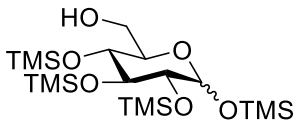


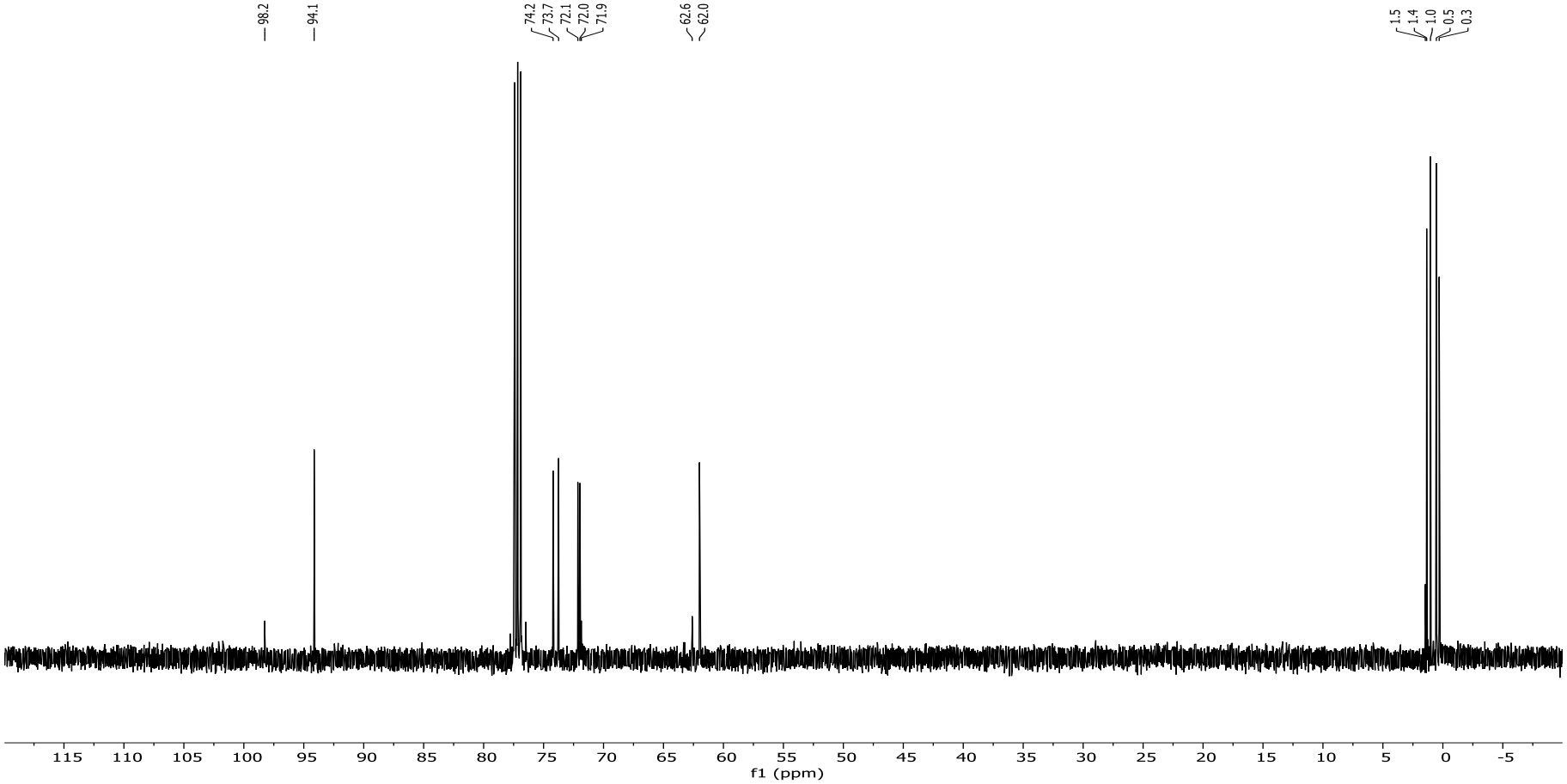
^{1}H NMR ($CDCl_3$, 500 MHz)



2,3,4-Tris-*O*-trimethylsilyl-α-D-glucose (**27**)

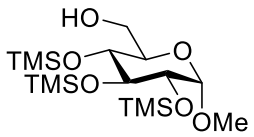
^{13}C NMR ($CDCl_3$, 125 MHz)

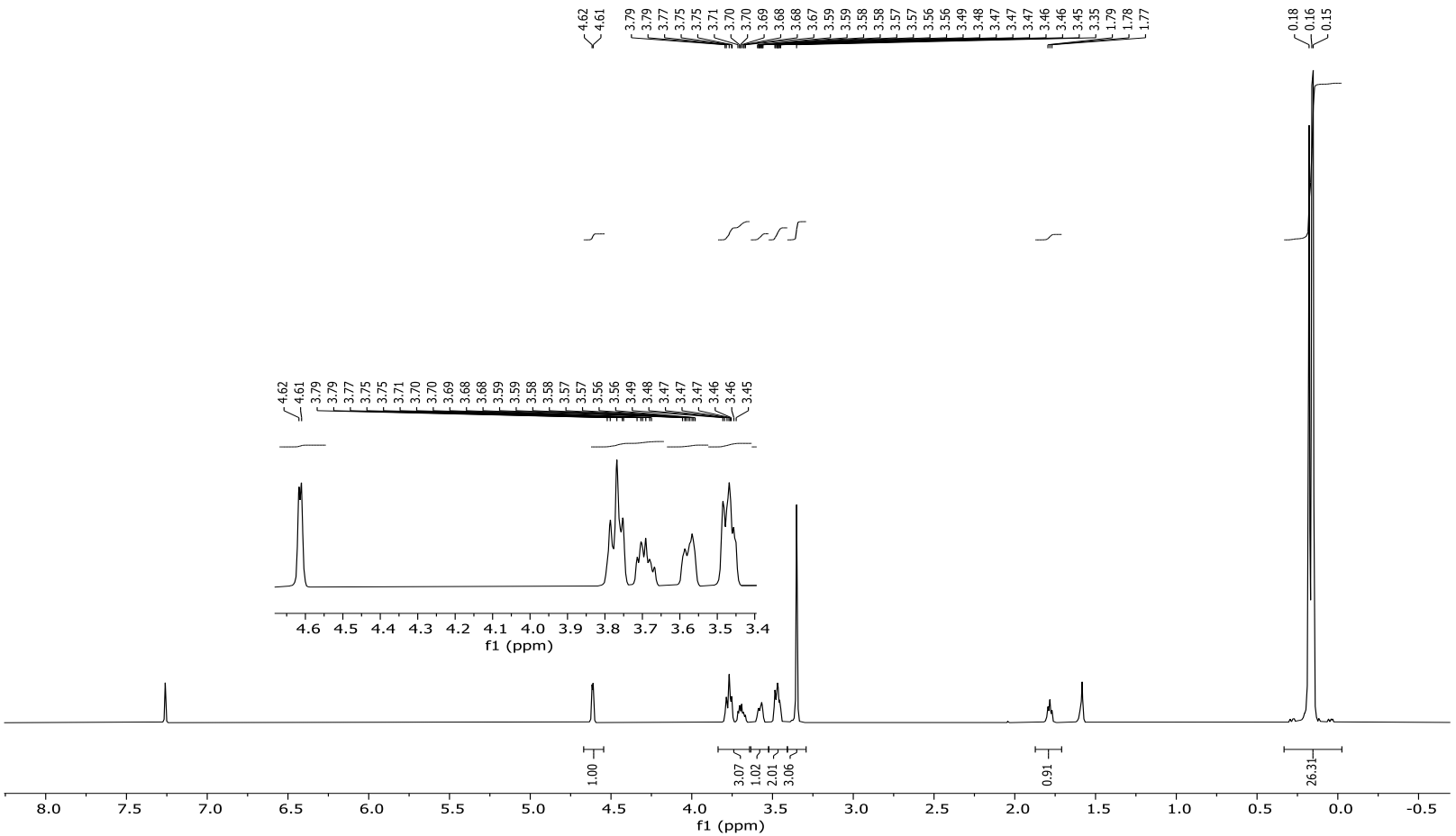




Methyl (2,3,4-tris-*O*-trimethylsilyl)-α-D-glucopyranoside (**28**)

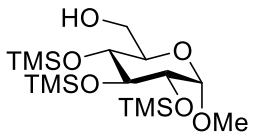
^{1}H NMR ($CDCl_3$, 500 MHz)

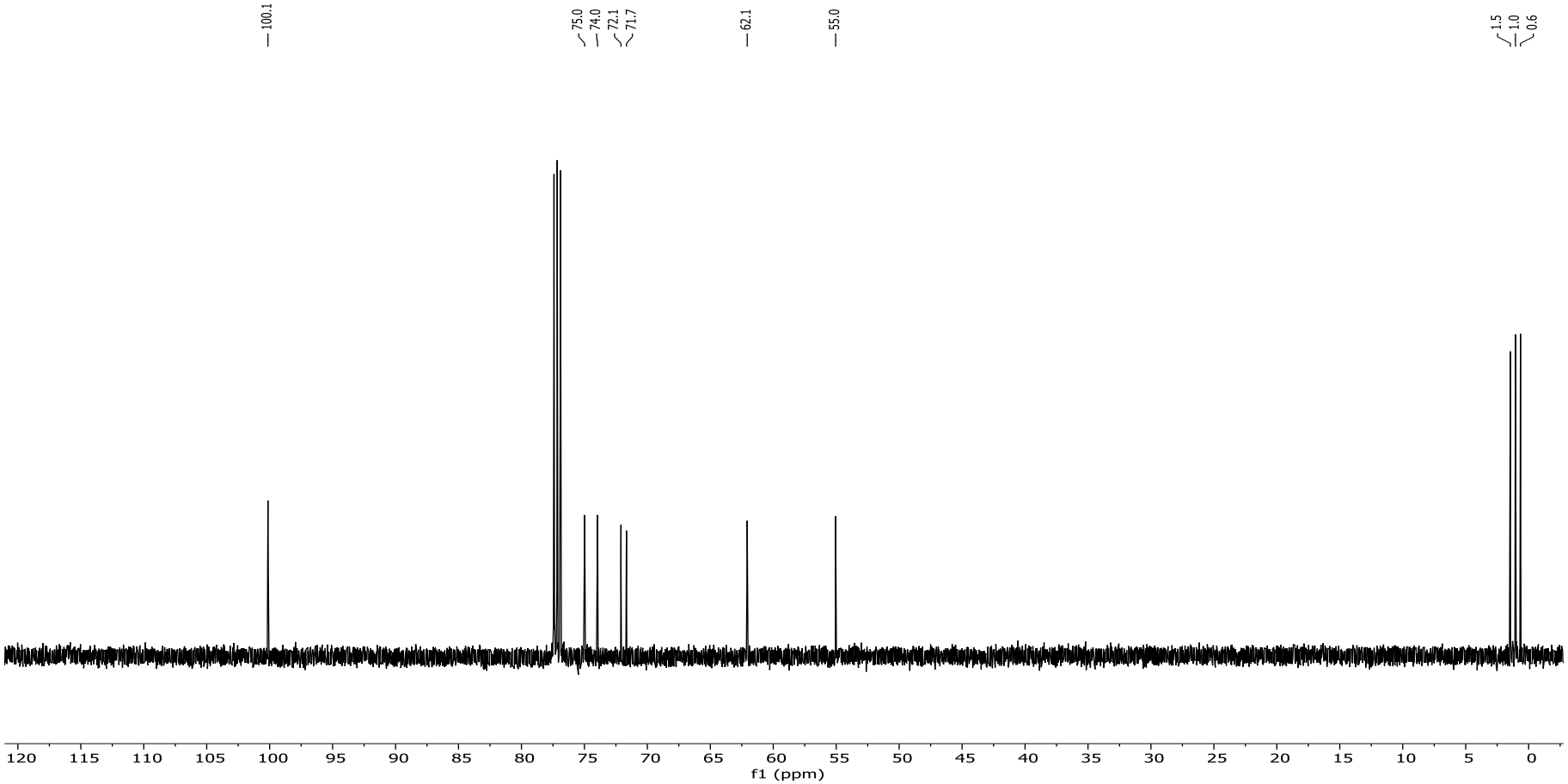




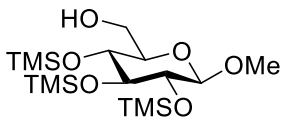
Methyl (2,3,4-tris-*O*-trimethylsilyl)-α-D-glucopyranoside (**28**)

^{13}C NMR ($CDCl_3$, 125 MHz)

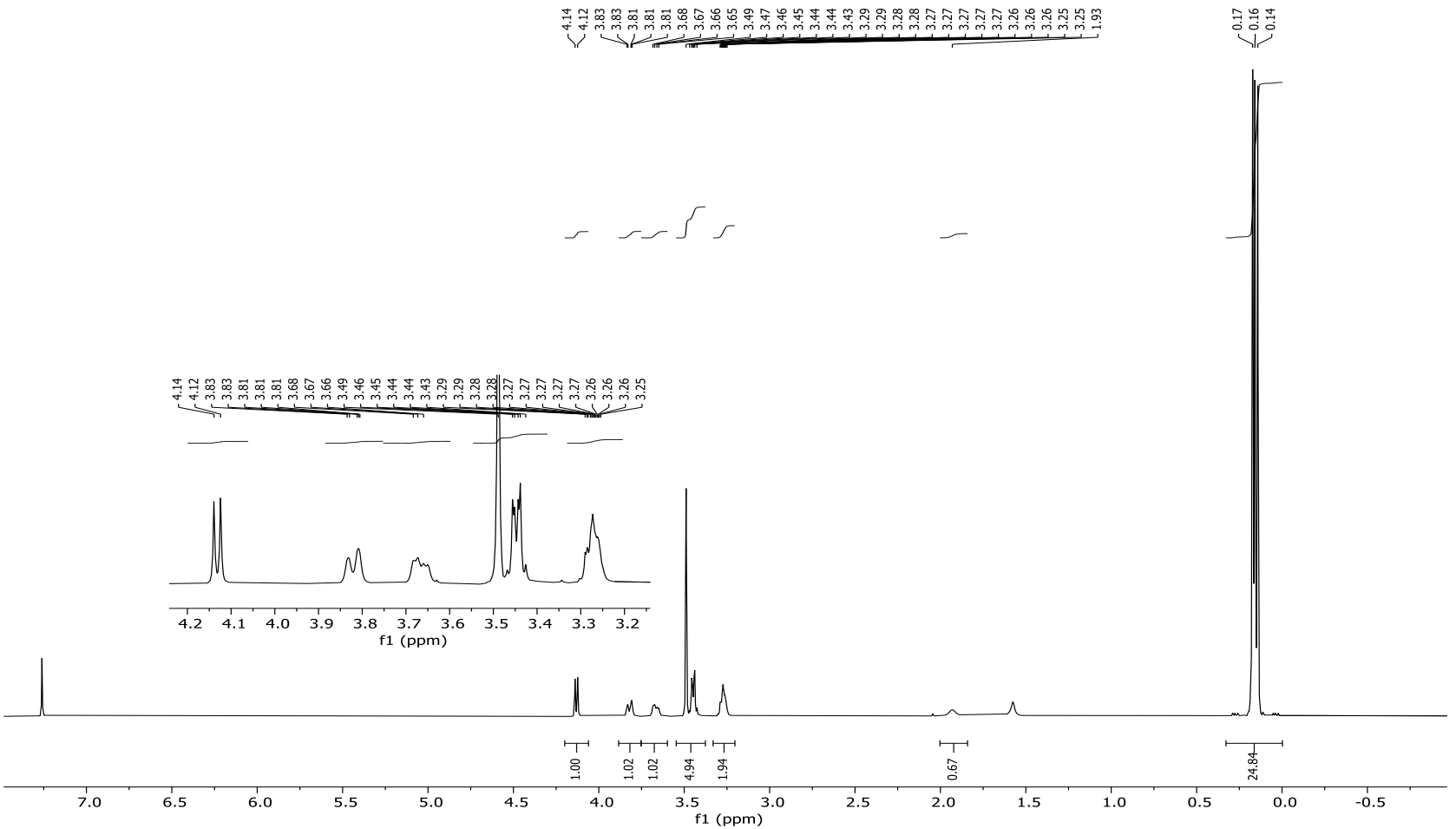




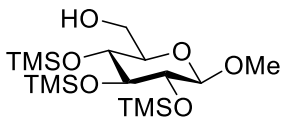
Methyl (2,3,4-tris-*O*-trimethylsilyl)-β-D-glucopyranoside (**29**)



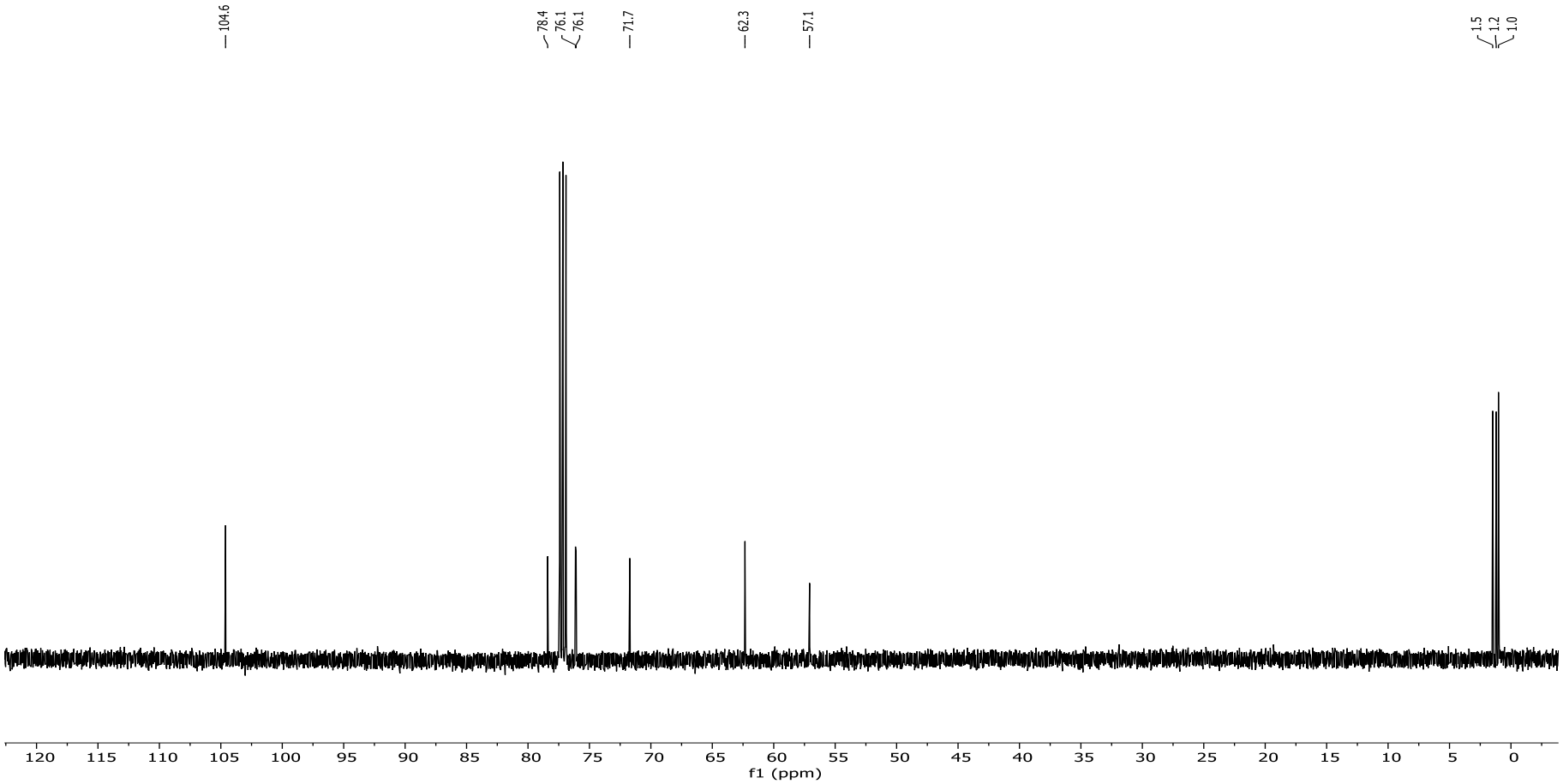
^{1}H NMR ($CDCl_3$, 500 MHz)



Methyl (2,3,4-tris-*O*-trimethylsilyl)-β-D-glucopyranoside (**29**)

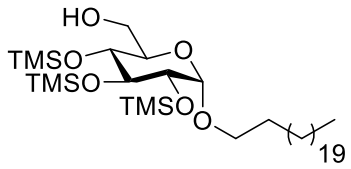


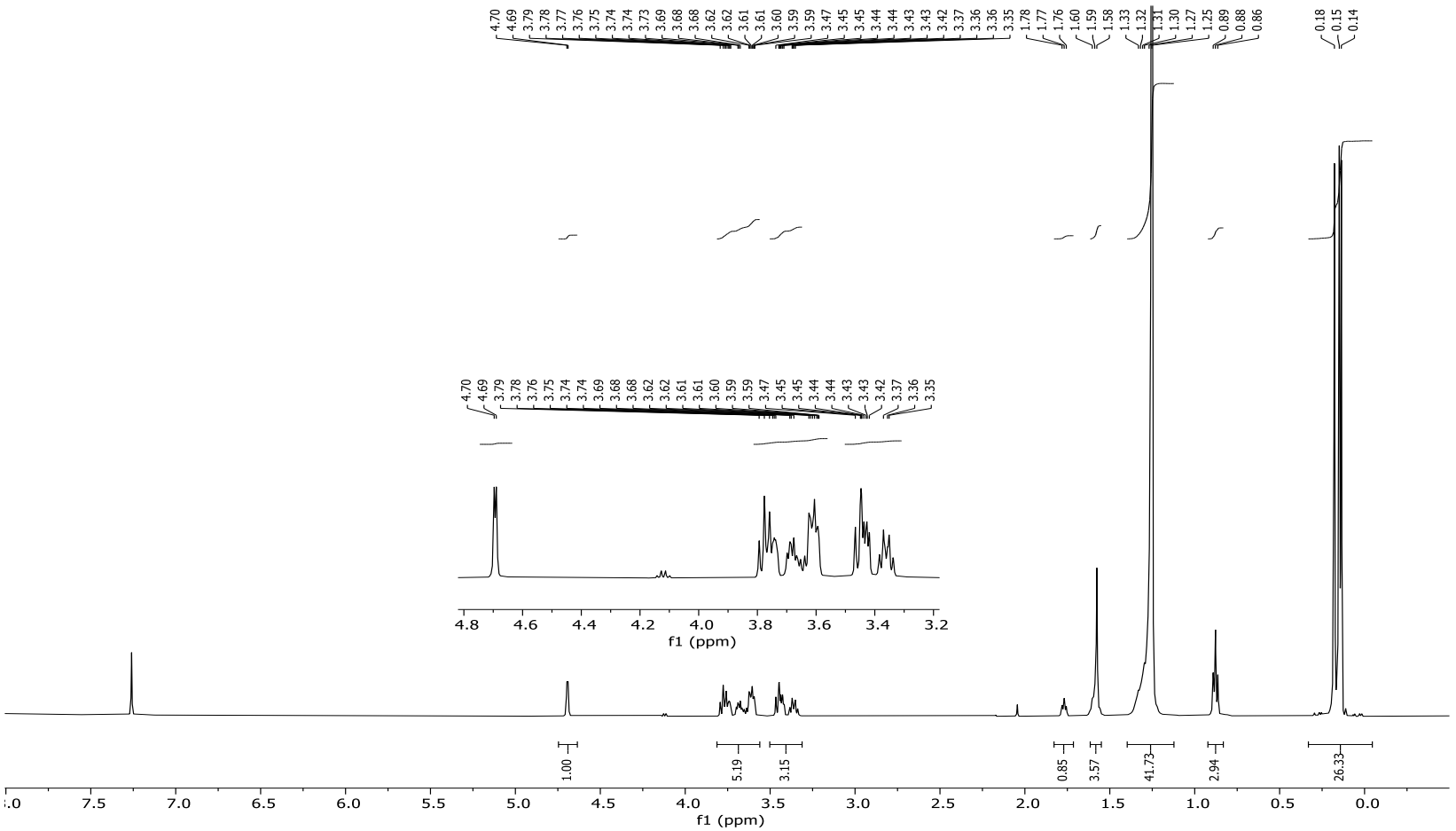
^{13}C NMR ($CDCl_3$, 125 MHz)



Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside (**34**)

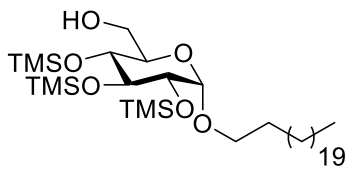
^{1}H NMR ($CDCl_3$, 500 MHz)

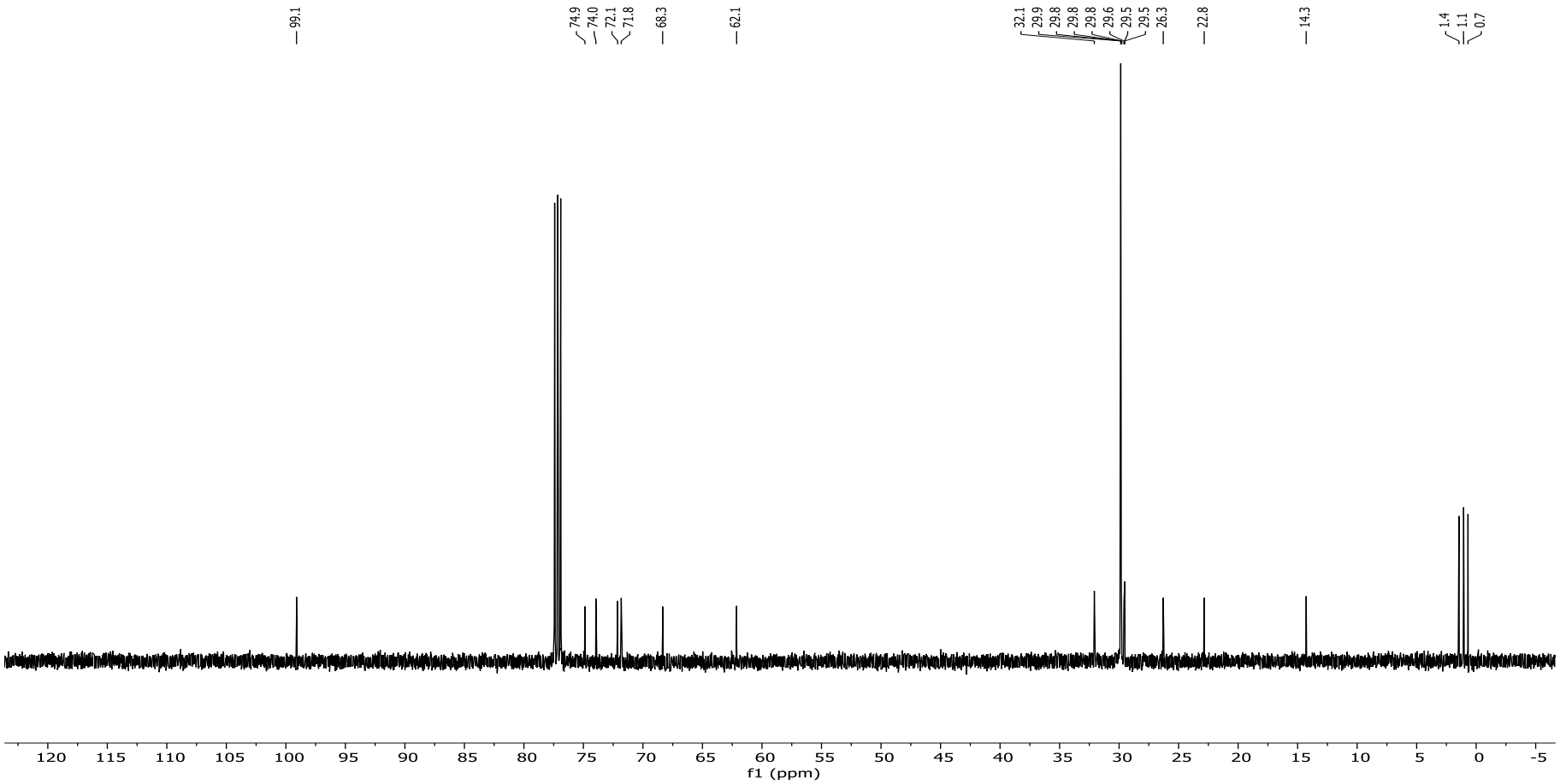




Docosyl (2,3,4,6-tetra-*O*-trimethylsilyl)-α-D-glucopyranoside (**34**)

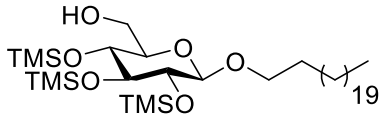
^{13}C NMR ($CDCl_3$, 125 MHz)

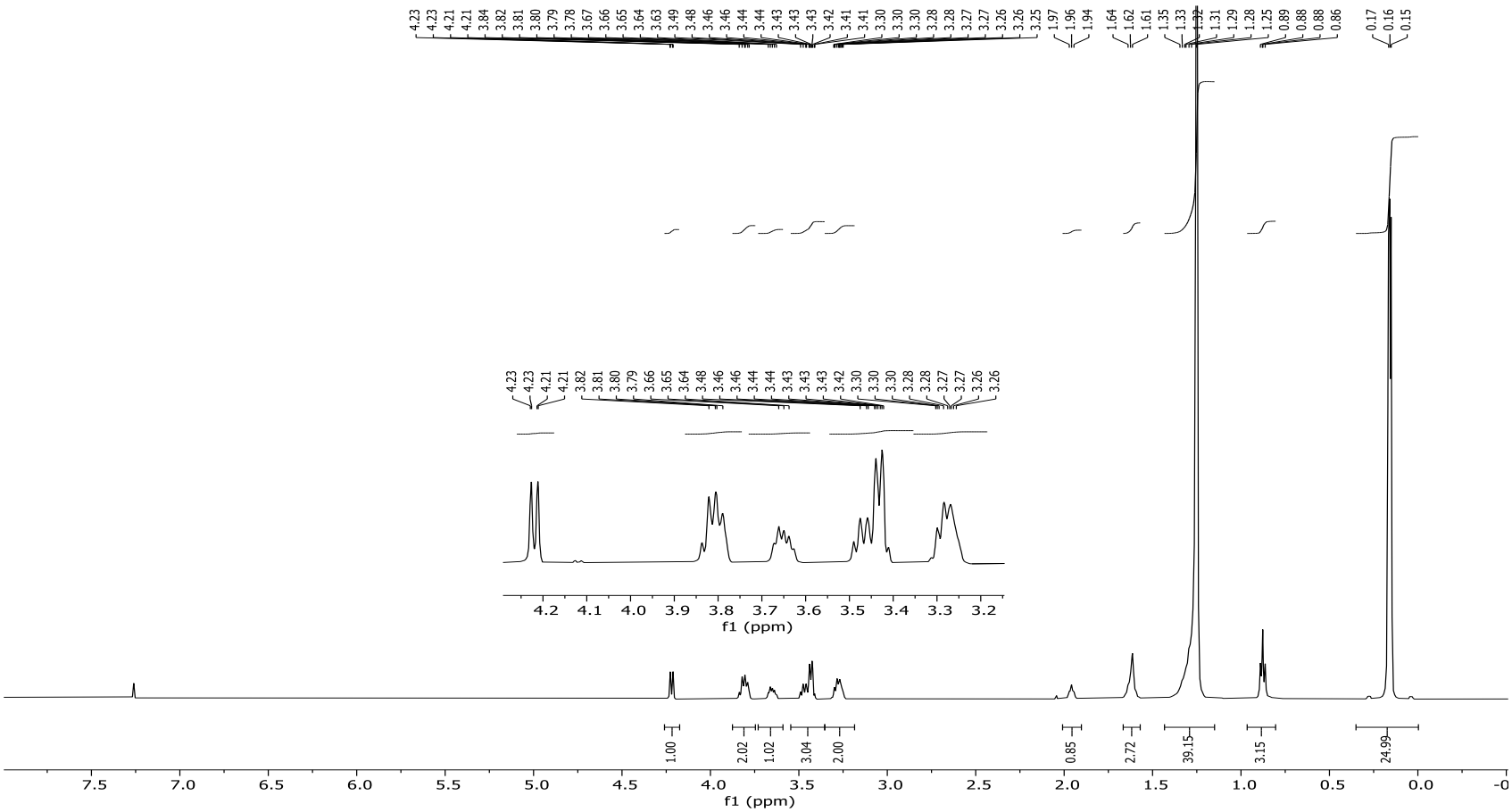




Docosyl (2,3,4-tris-*O*-trimethylsilyl)-β-D-glucopyranoside (**35**)

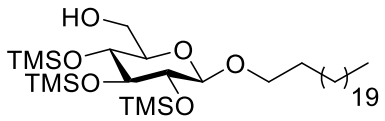
^{1}H NMR ($CDCl_3$, 500 MHz)

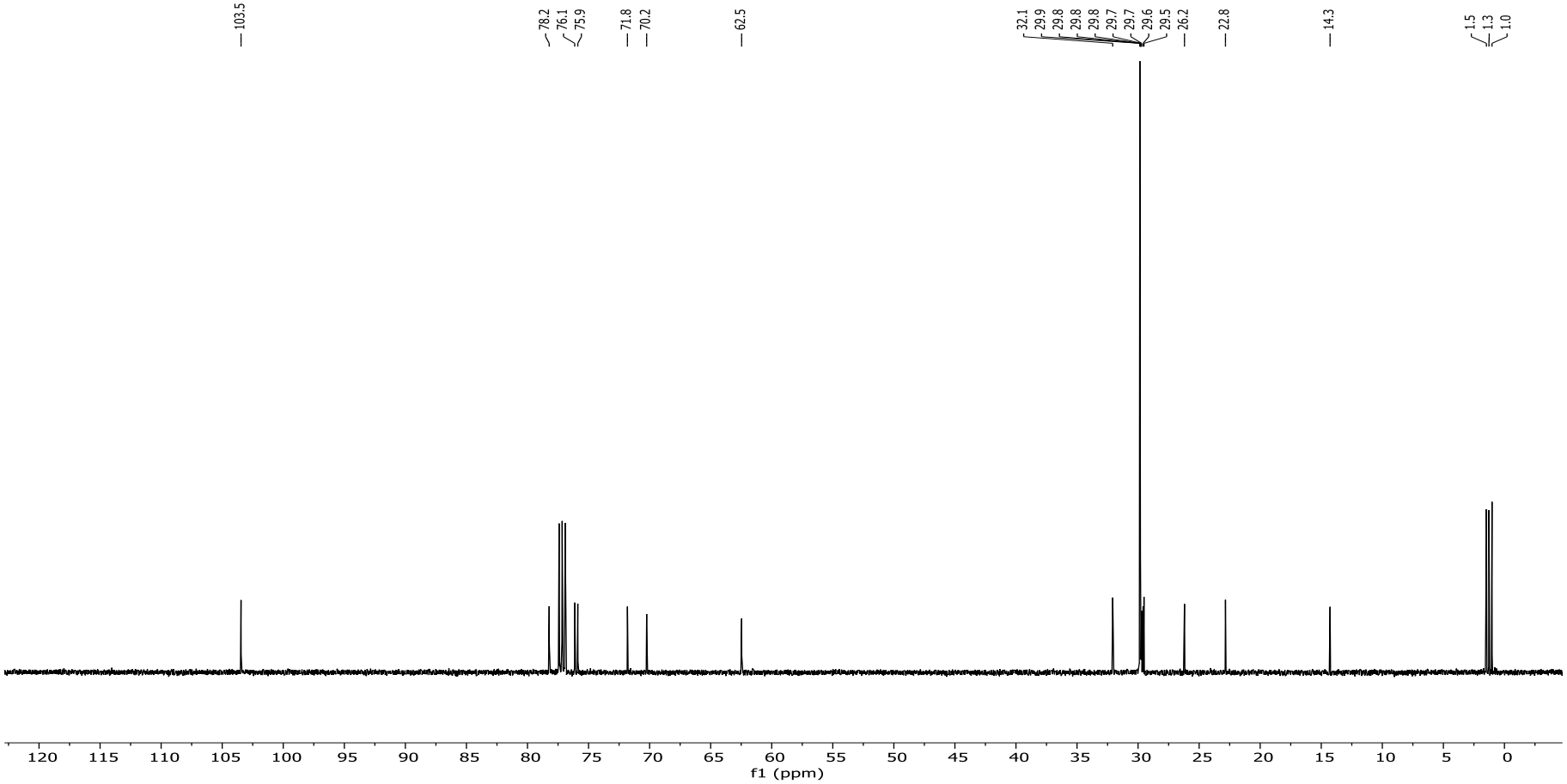




Docosyl (2,3,4-tris-*O*-trimethylsilyl)-β-D-glucopyranoside (**35**)

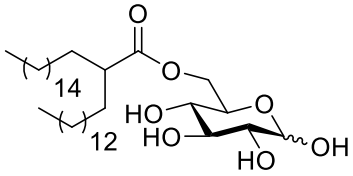
^{13}C NMR ($CDCl_3$, 125 MHz)

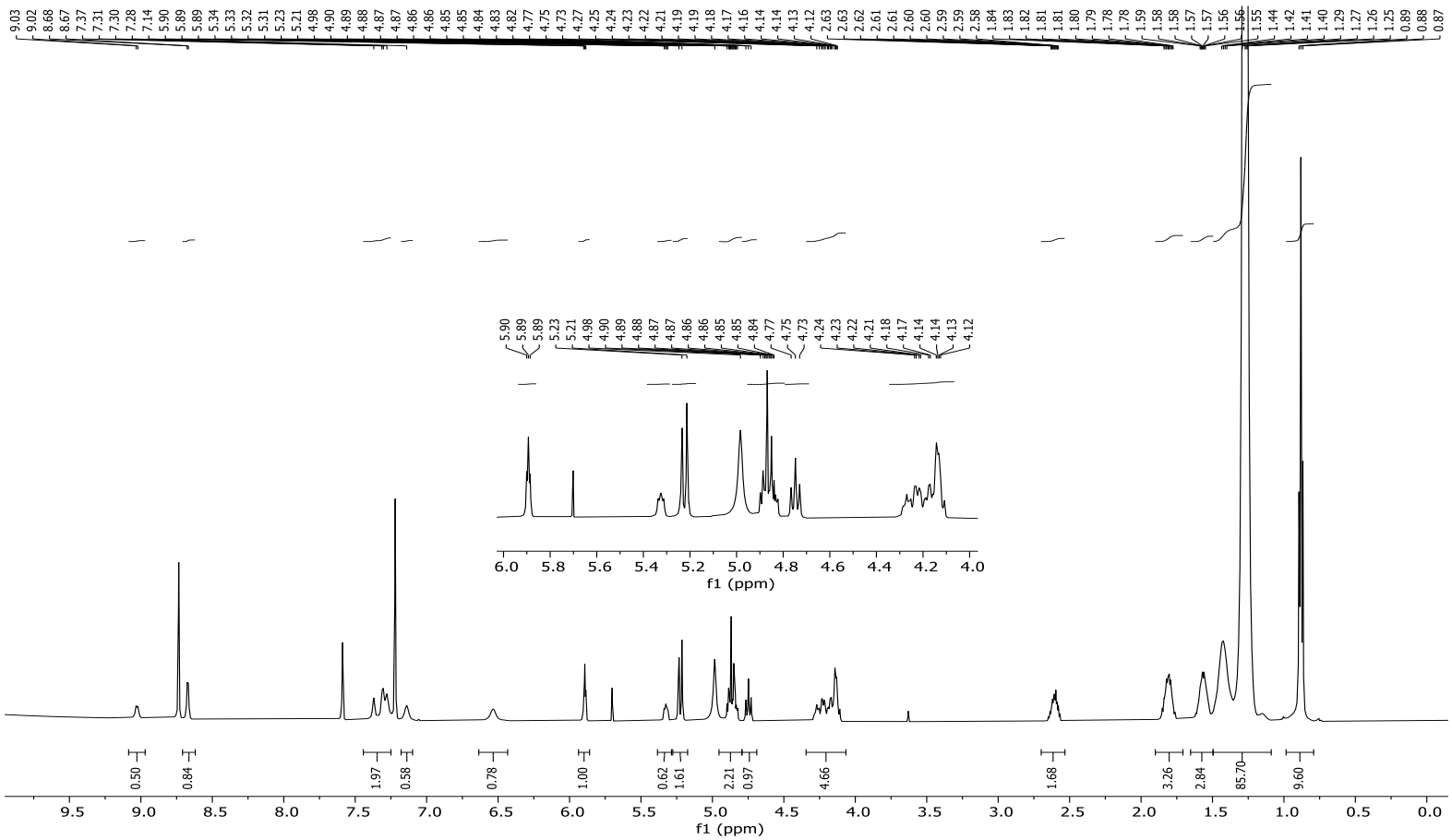




6-*O*-(2-tetradecyloctadecanoyl)-D-glucose (GlcC14C18, **3**)

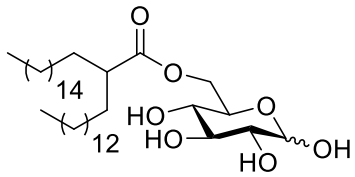
^{1}H NMR (C_5D_5N, 500 MHz)

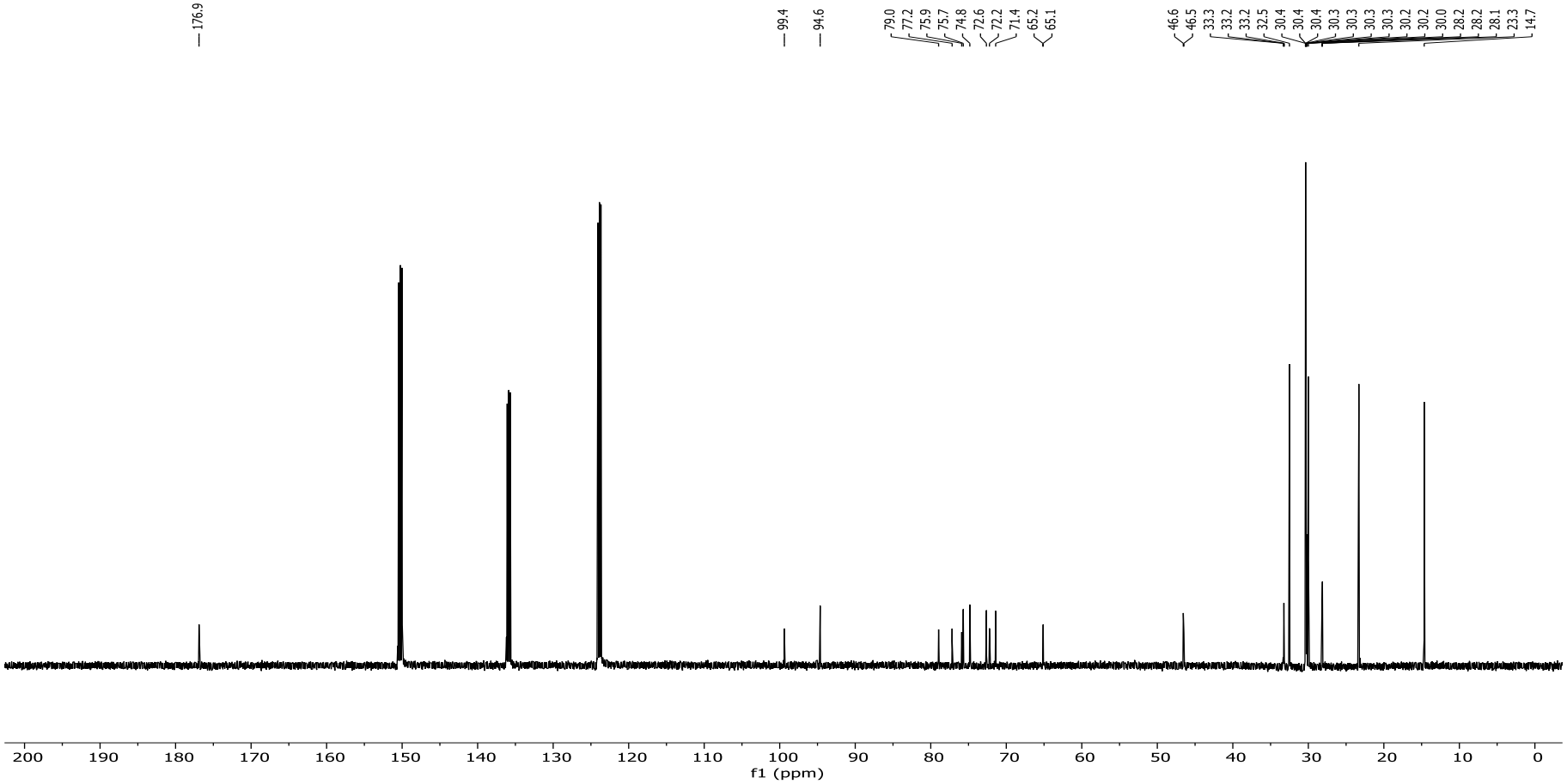




6-*O*-(2-tetradecyloctadecanoyl)-D-glucose (GlcC14C18, **3**)

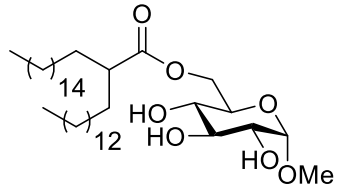
^{13}C NMR (C_5D_5N, 125 MHz)

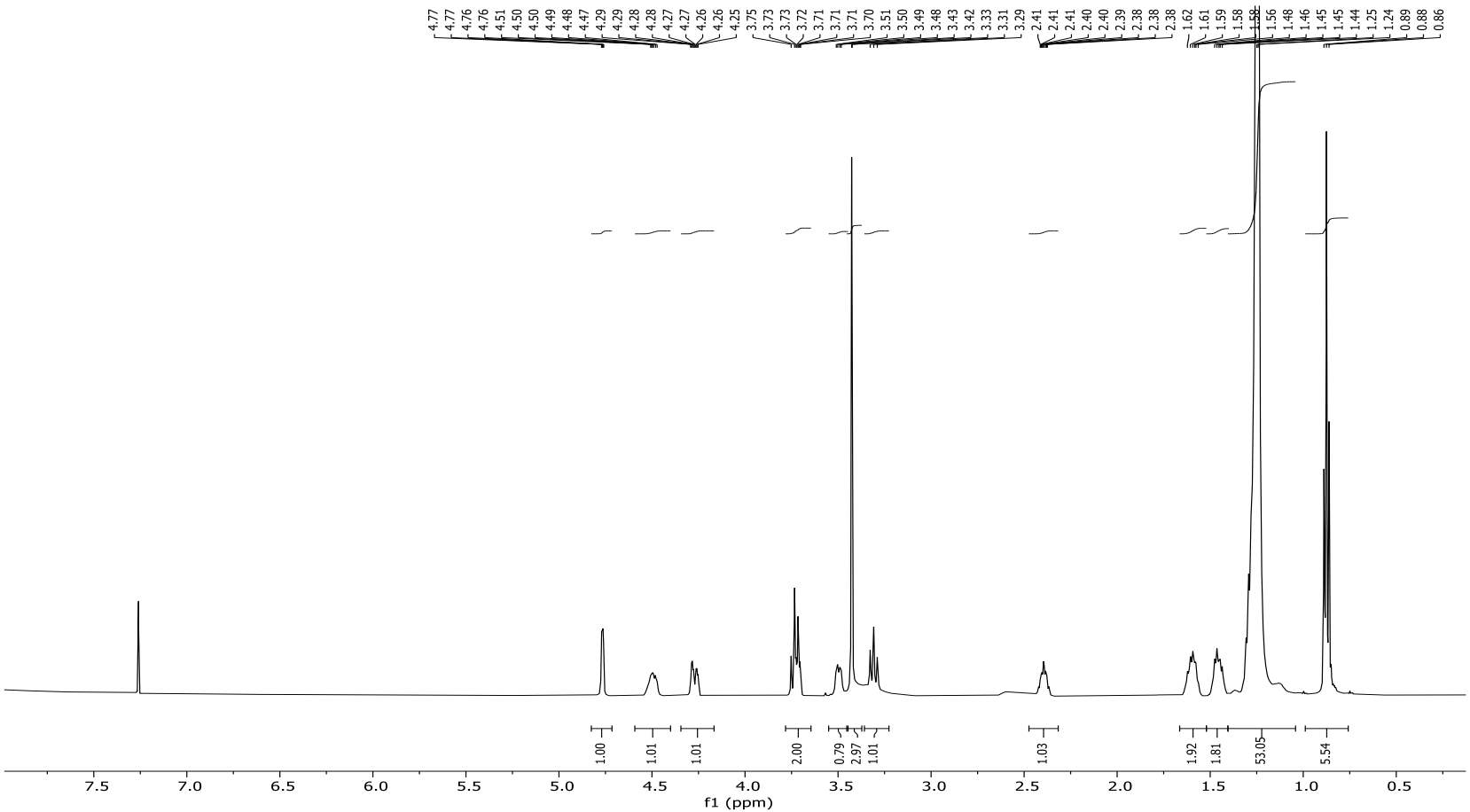




Methyl 6-*O*-(2-tetradecyloctadecanoyl)-α-D-glucoside (C14C18GlcαOMe, **7**)

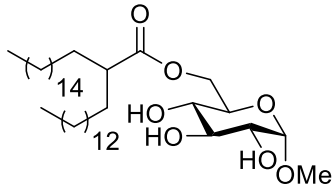
^{1}H NMR ($CDCl_3$, 500 MHz)

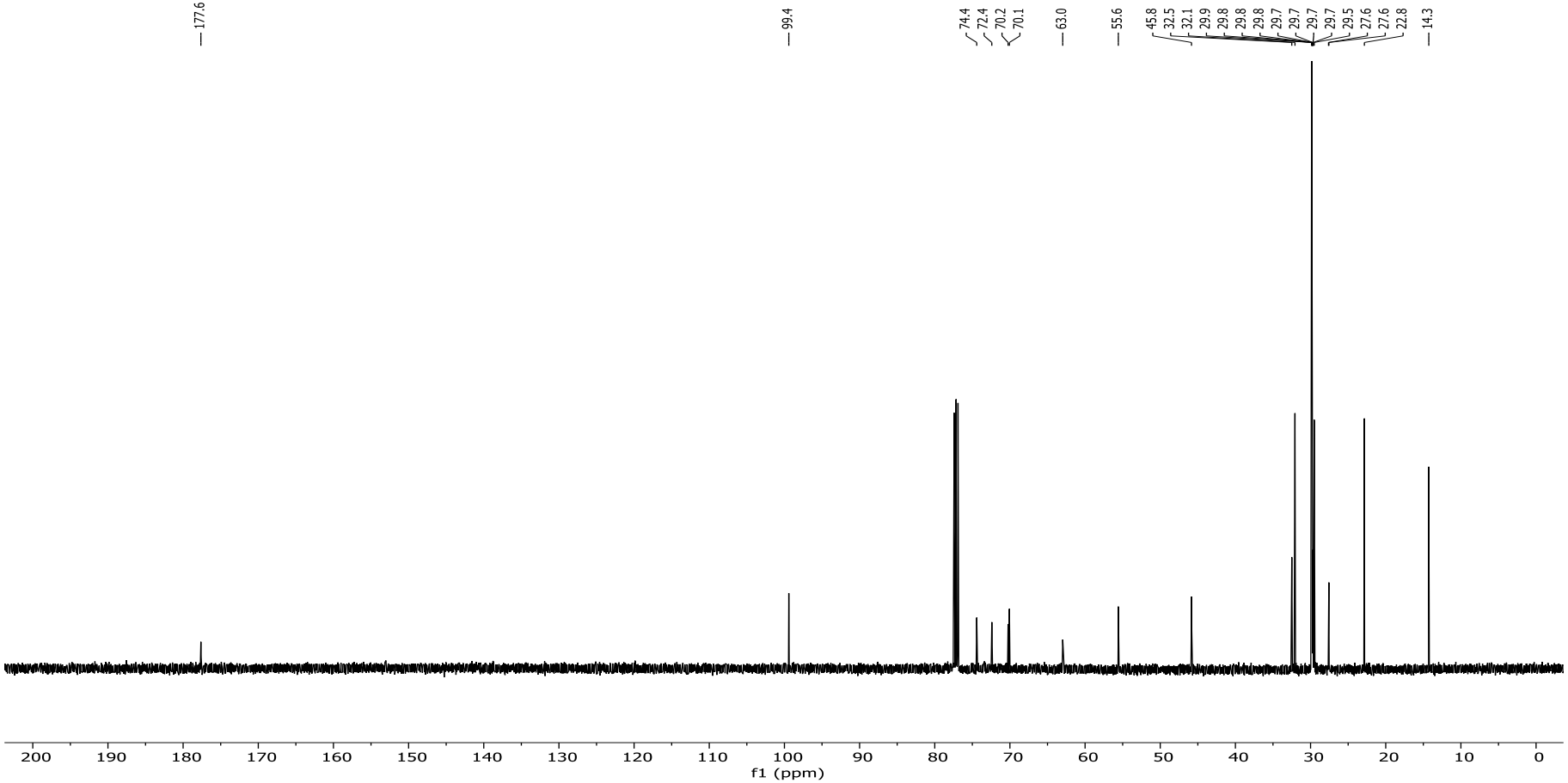




Methyl 6-*O*-(2-tetradecyloctadecanoyl)-α-D-glucoside (C14C18GlcαOMe, **7**)

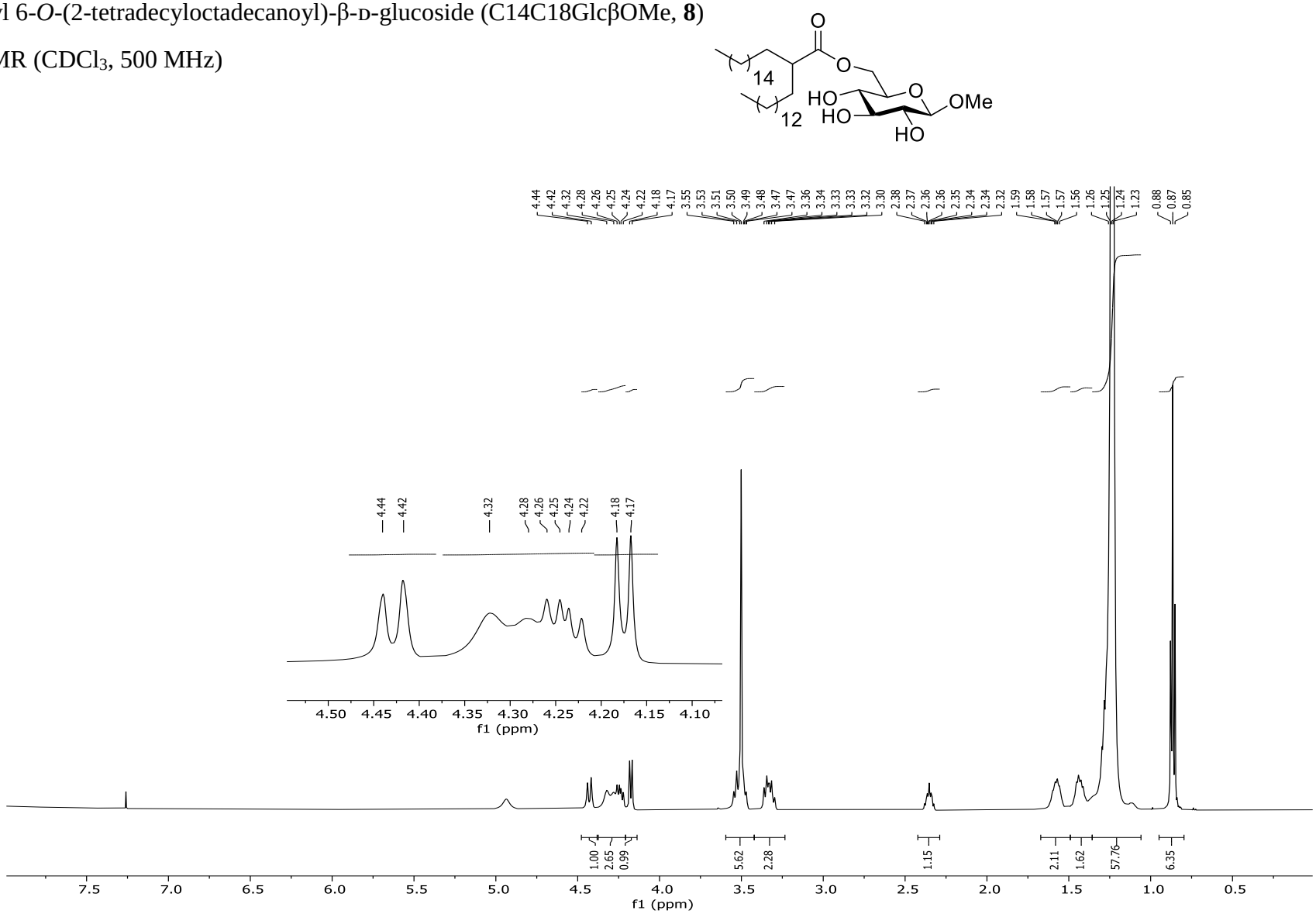
^{13}C NMR ($CDCl_3$, 125 MHz)





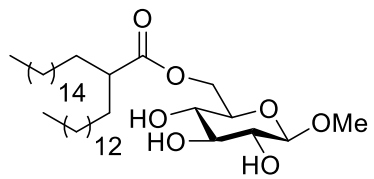
Methyl 6-*O*-(2-tetradecyloctadecanoyl)-β-D-glucoside (C14C18GlcβOMe, **8**)

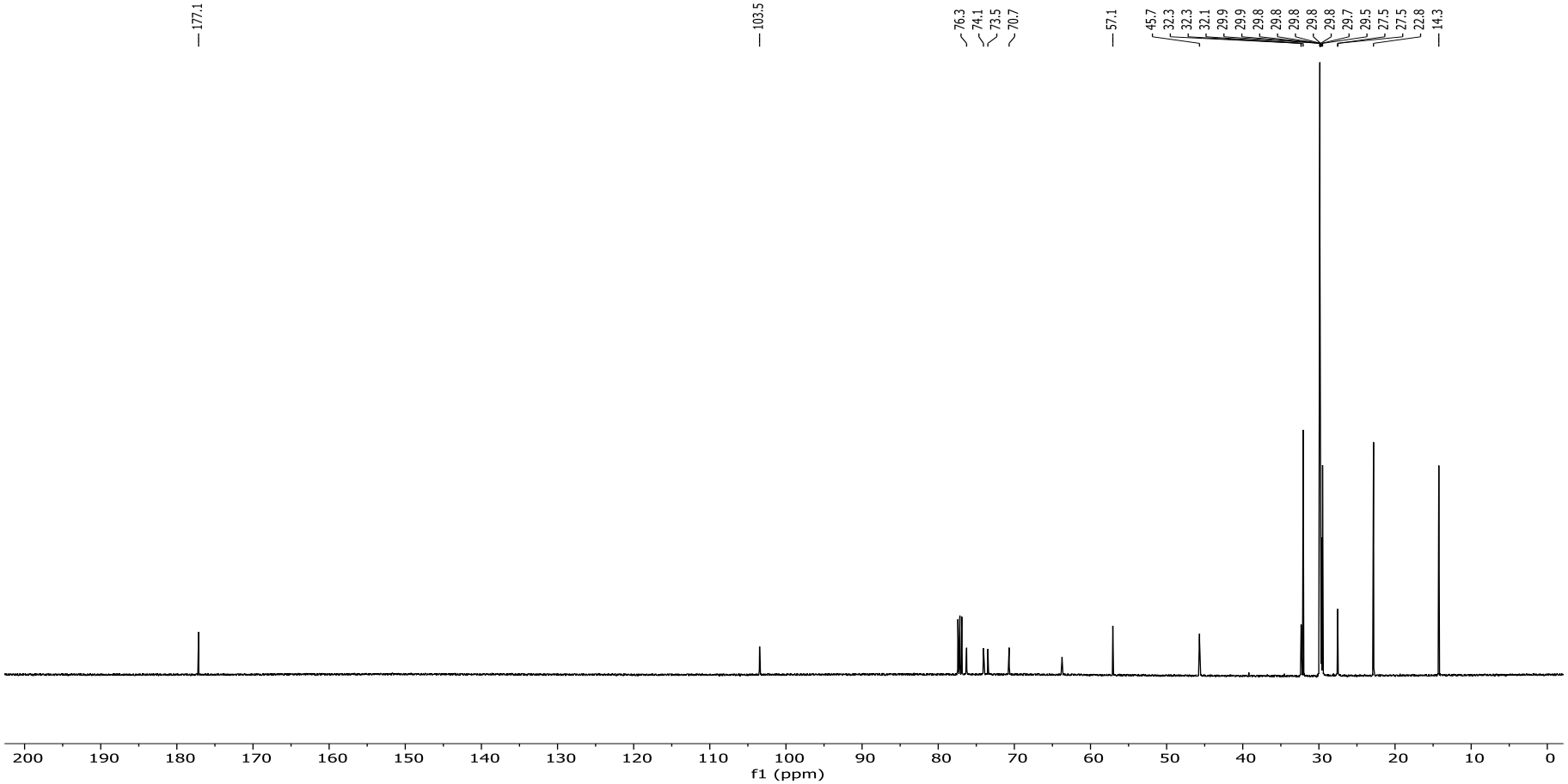
^{1}H NMR ($CDCl_3$, 500 MHz)



Methyl 6-*O*-(2-tetradecyloctadecanoyl)-β-D-glucoside (C14C18GlcβOMe, **8**)

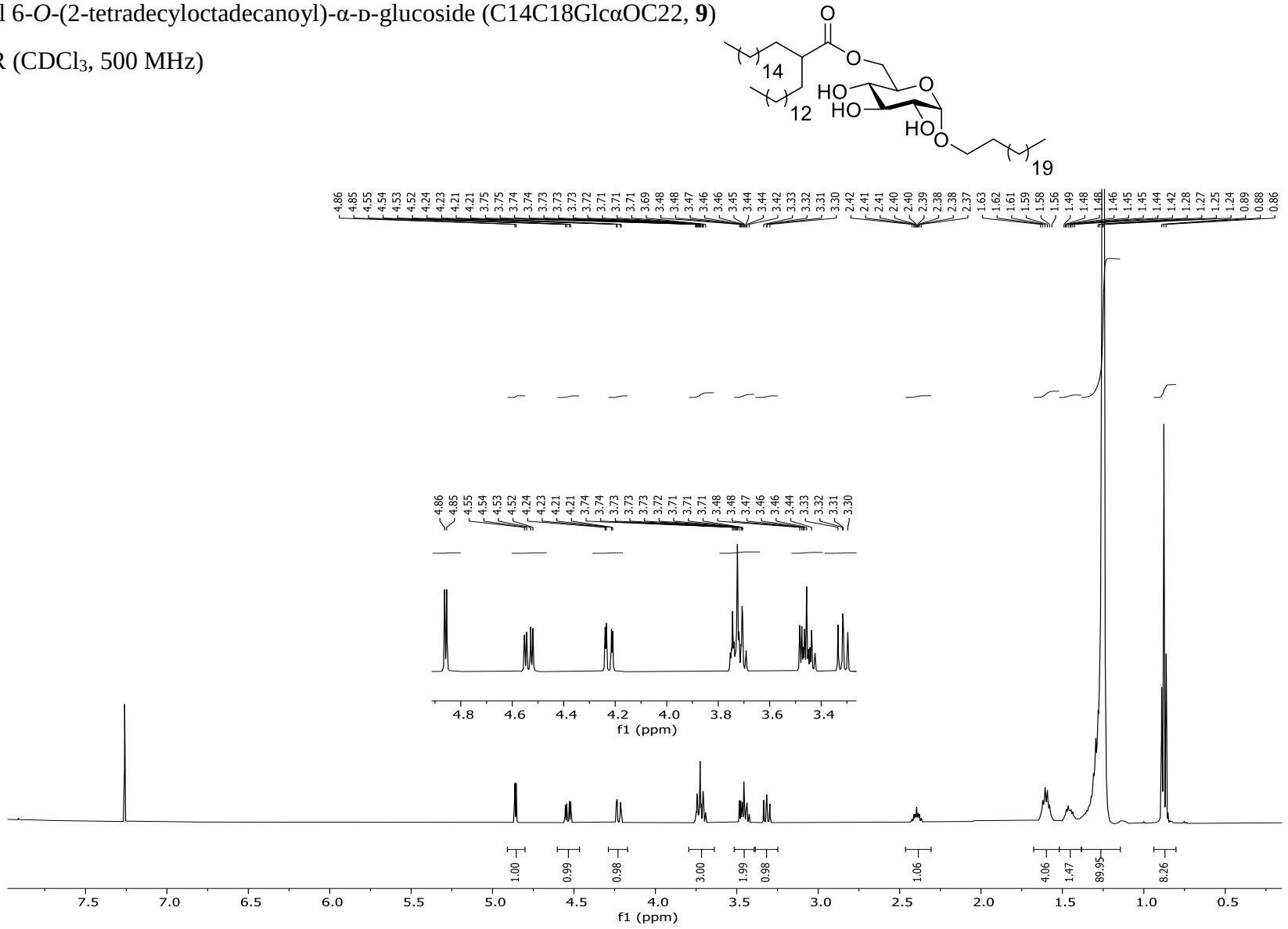
^{13}C NMR ($CDCl_3$, 125 MHz)





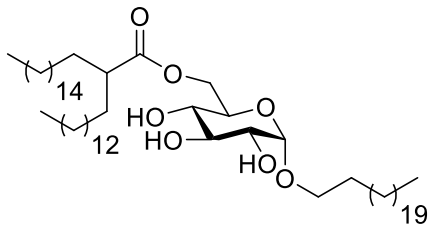
Docosyl 6-*O*-(2-tetradecyloctadecanoyl)-α-D-glucoside (C14C18GlcαOC22, **9**)

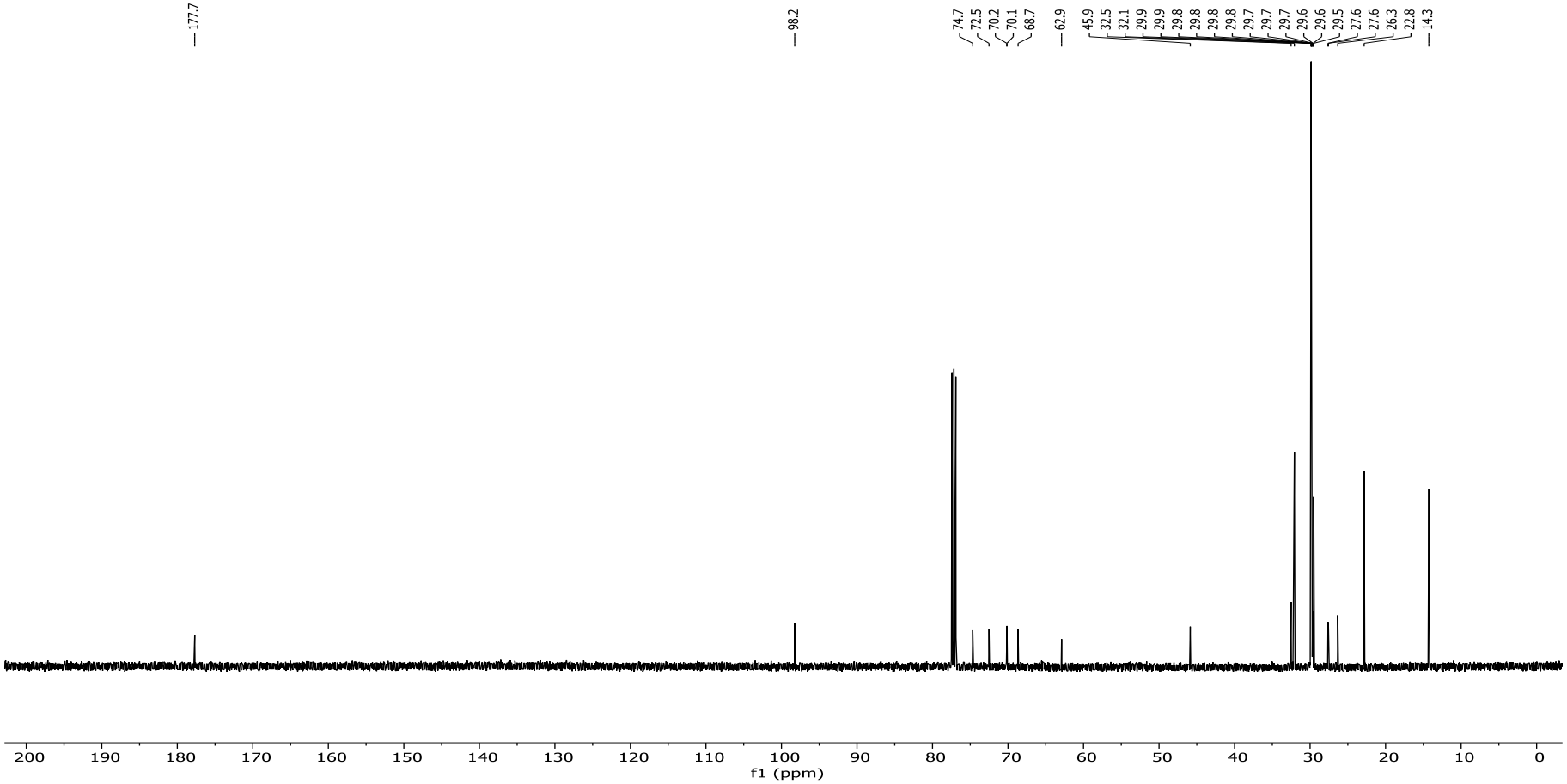
^{1}H NMR ($CDCl_3$, 500 MHz)



Docosyl 6-*O*-(2-tetradecyloctadecanoyl)-α-D-glucoside (C14C18GlcαOC22, **9**)

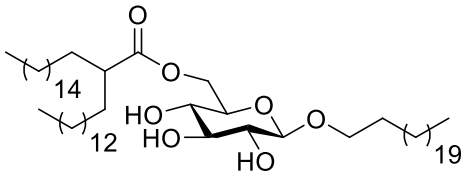
^{13}C NMR ($CDCl_3$, 125 MHz)

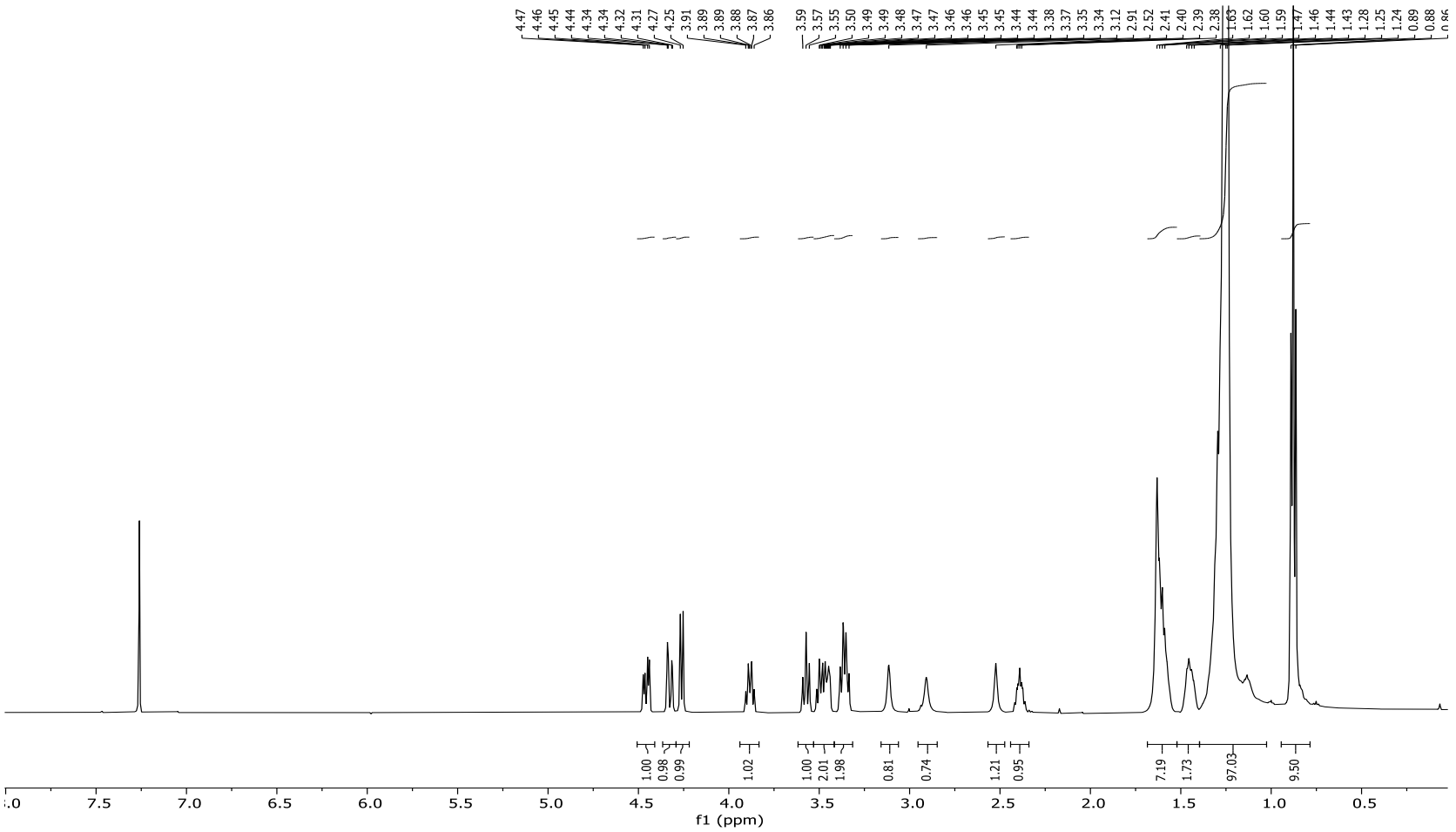




Docosyl 6-*O*-(2-tetradecyloctadecanoyl)-β-D-glucoside (C14C18GlcβOC22, **10**)

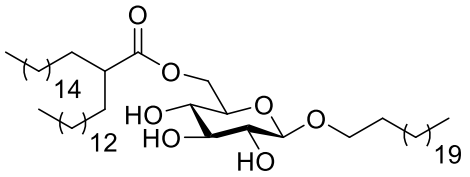
^{1}H NMR ($CDCl_3$, 500 MHz)

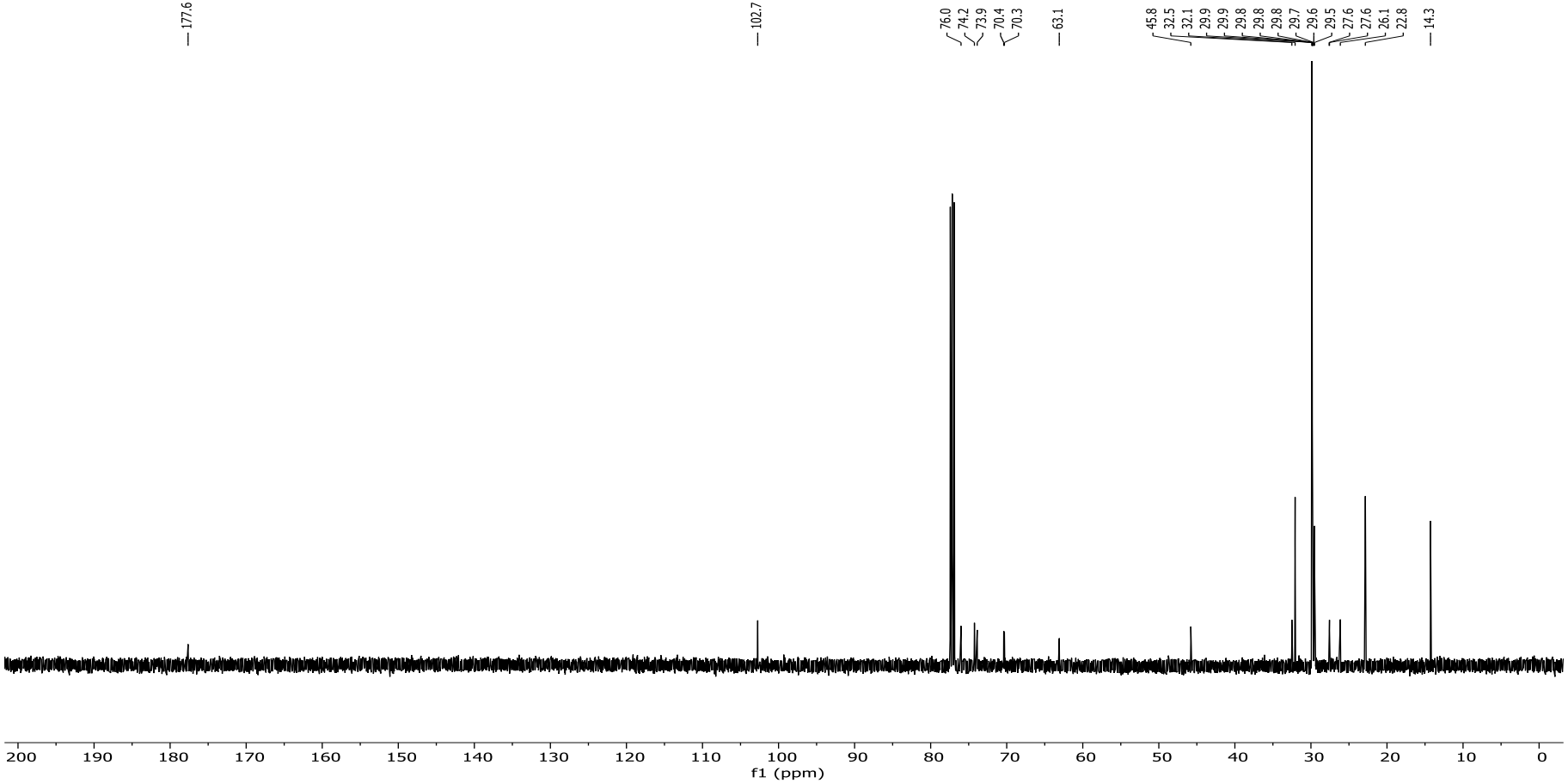




Docosyl 6-*O*-(2-tetradecyloctadecanoyl)-β-D-glucoside (C14C18GlcβOC22, **10**)

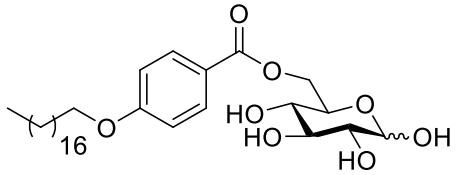
^{13}C NMR ($CDCl_3$, 125 MHz)

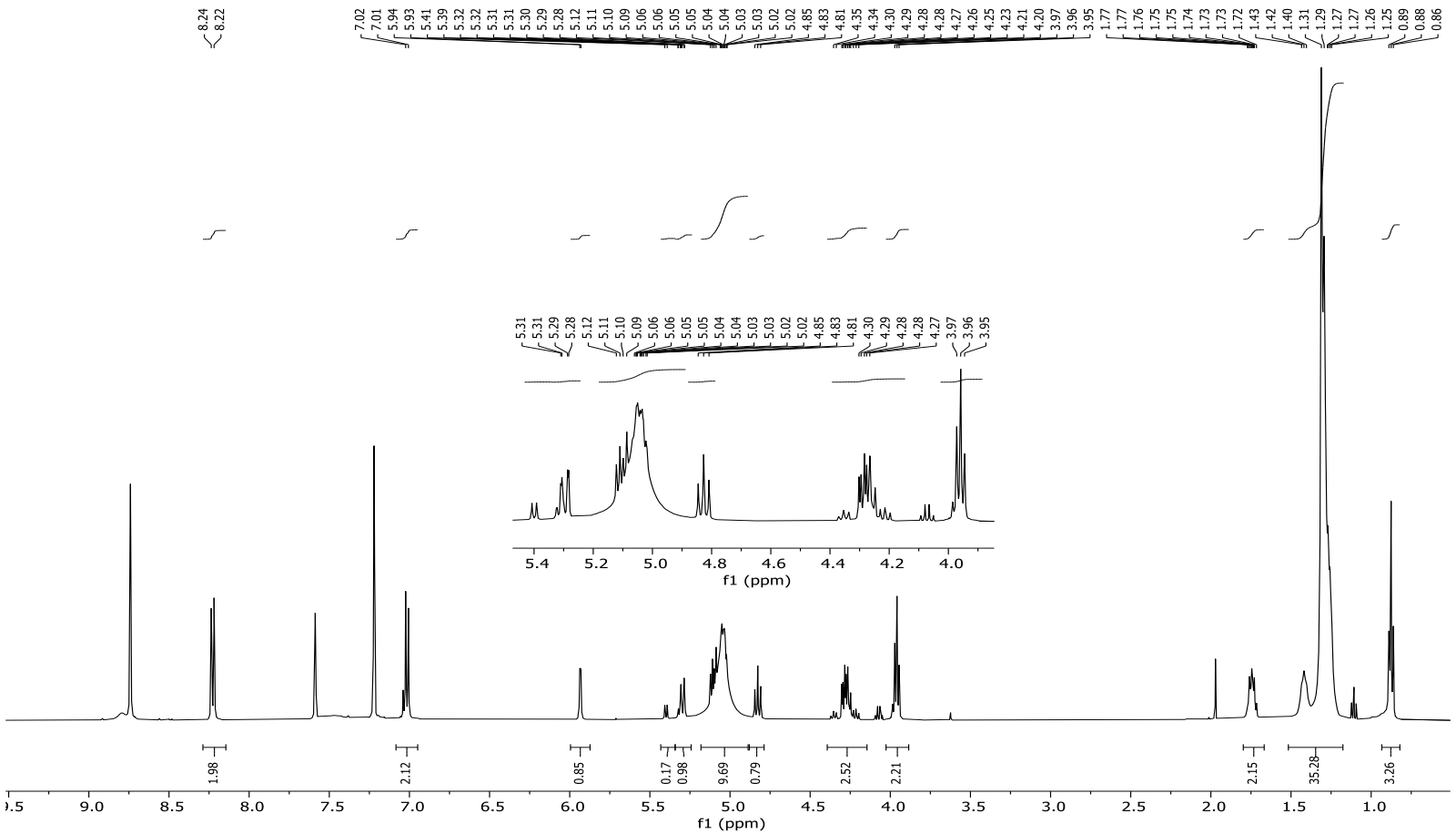




6-*O*-(4-octadecyloxybenzoyl)-α-D-glucose (GlcBzC18, **13**)

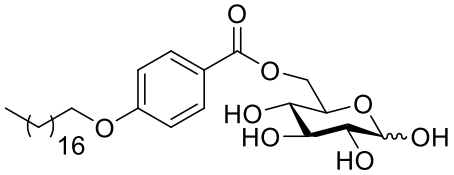
^{1}H NMR (C_5D_5N, 500 MHz)

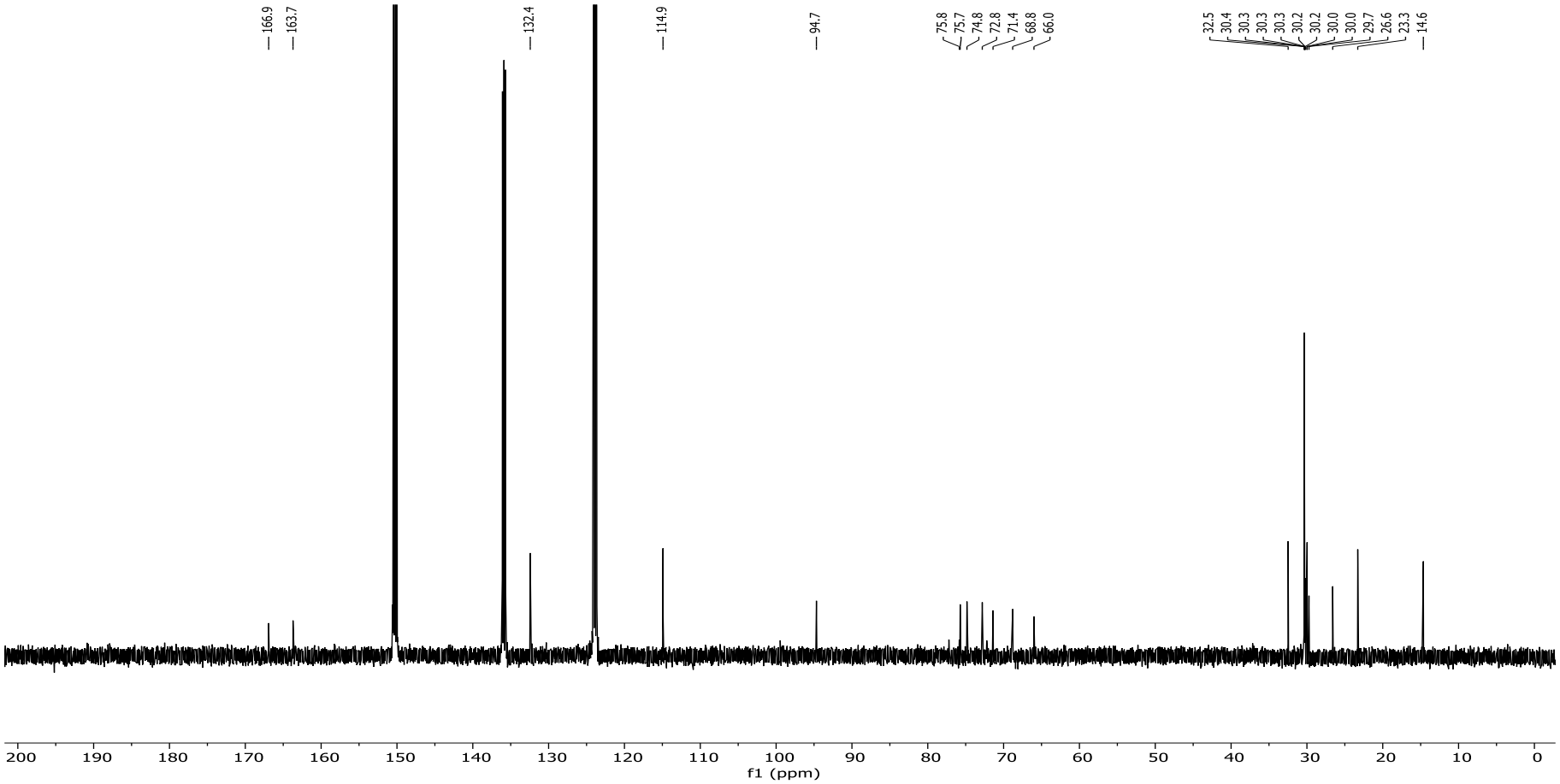




6-*O*-(4-octadecyloxybenzoyl)-α-D-glucose (GlcBzC18, **13**)

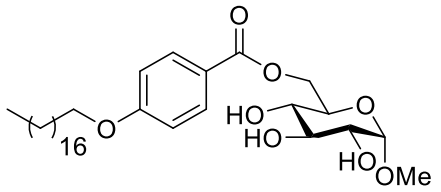
^{13}C NMR (C_5D_5N, 125 MHz)

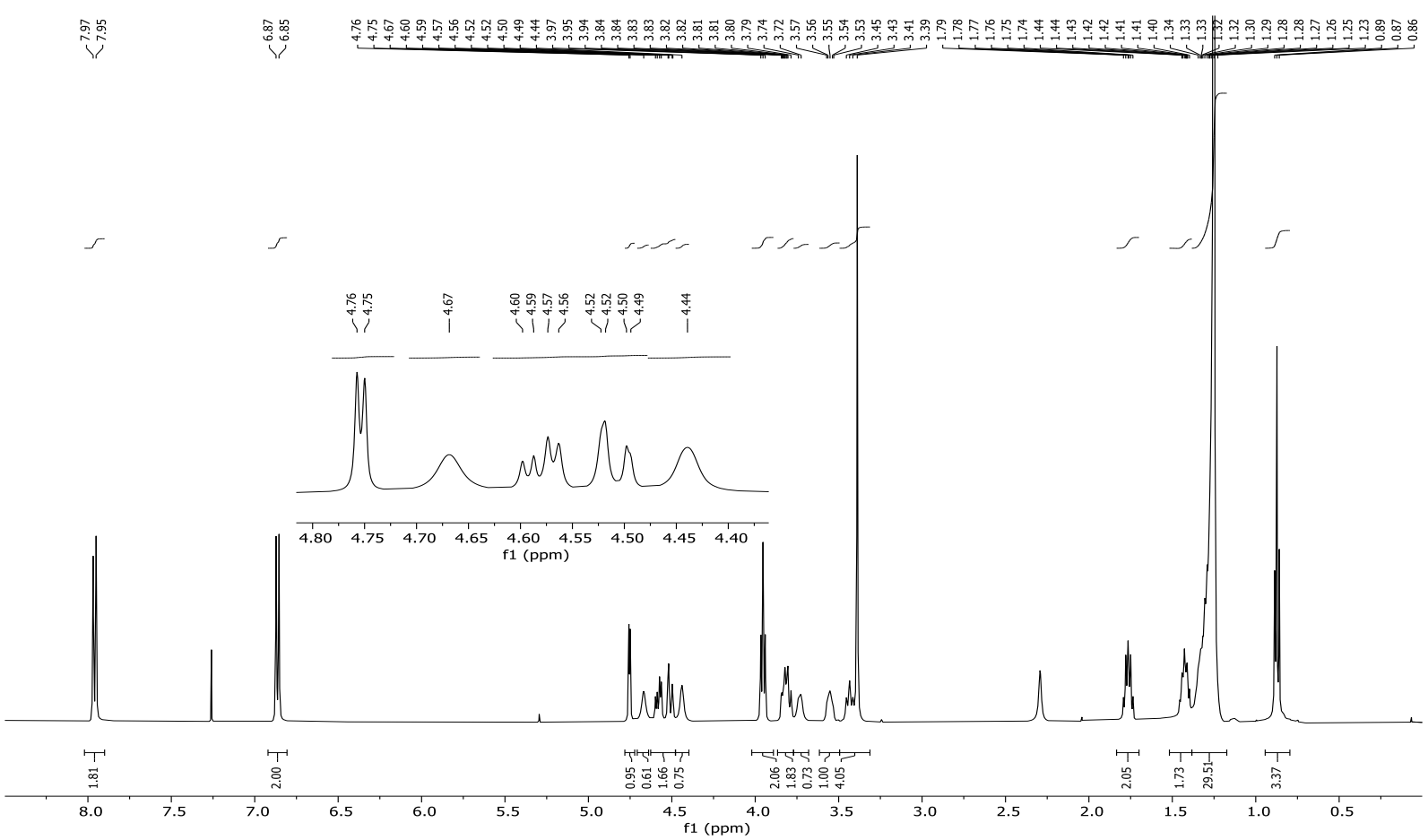




Methyl 6-*O*-(4-octadecyloxybenzoyl)-α-D-glucoside (BzC18GlcαOMe, **14**)

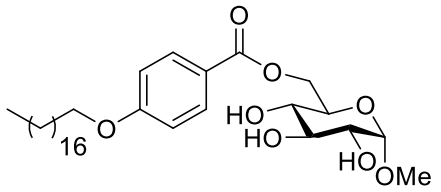
^{1}H NMR ($CDCl_3$, 500 MHz)

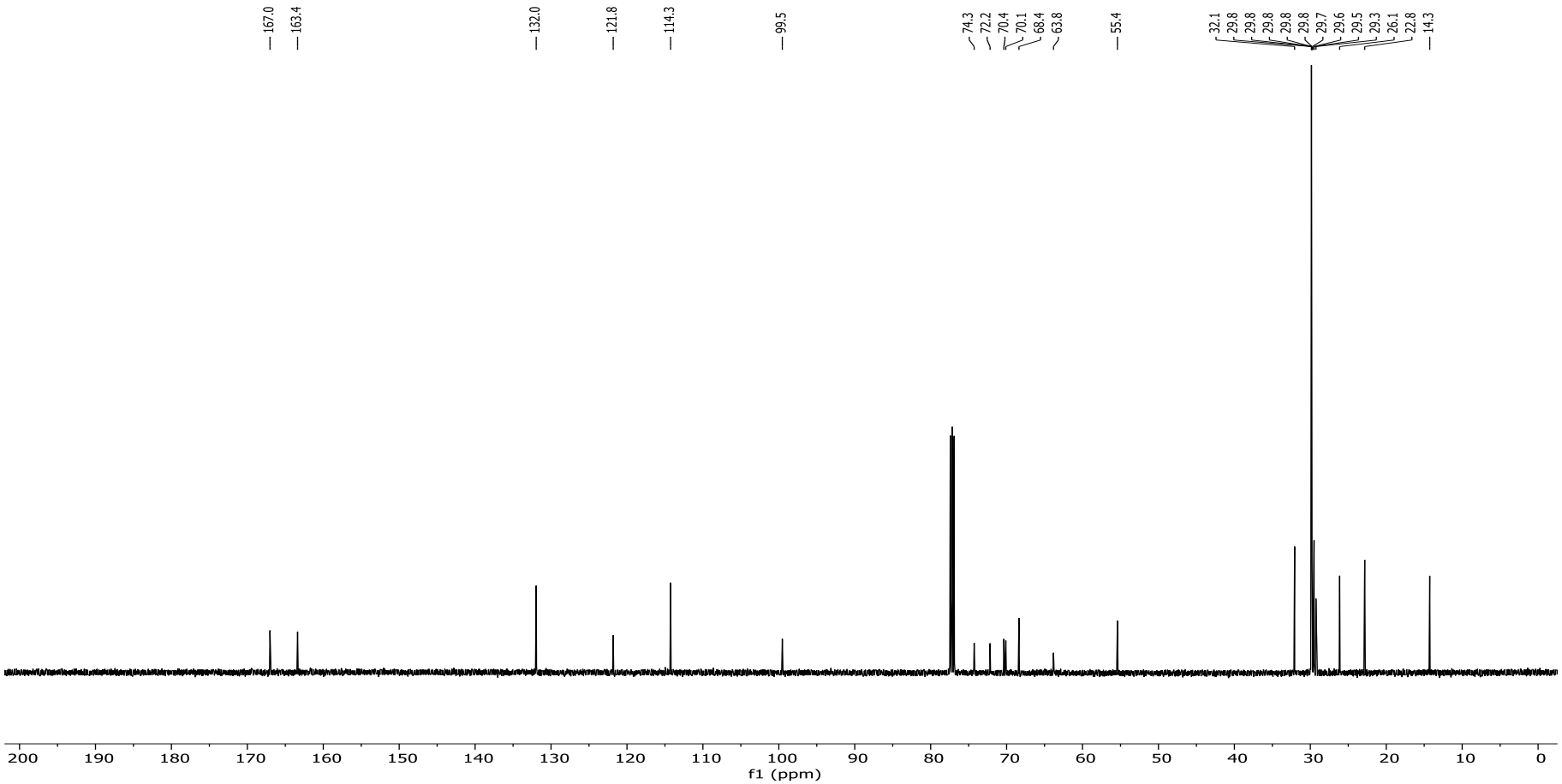




Methyl 6-*O*-(4-octadecyloxybenzoyl)-α-D-glucoside (BzC18GlcαOMe, **14**)

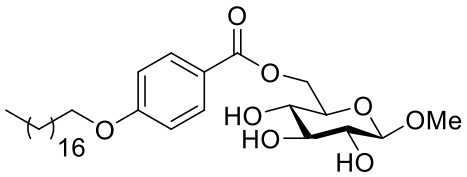
^{13}C NMR ($CDCl_3$, 125 MHz)

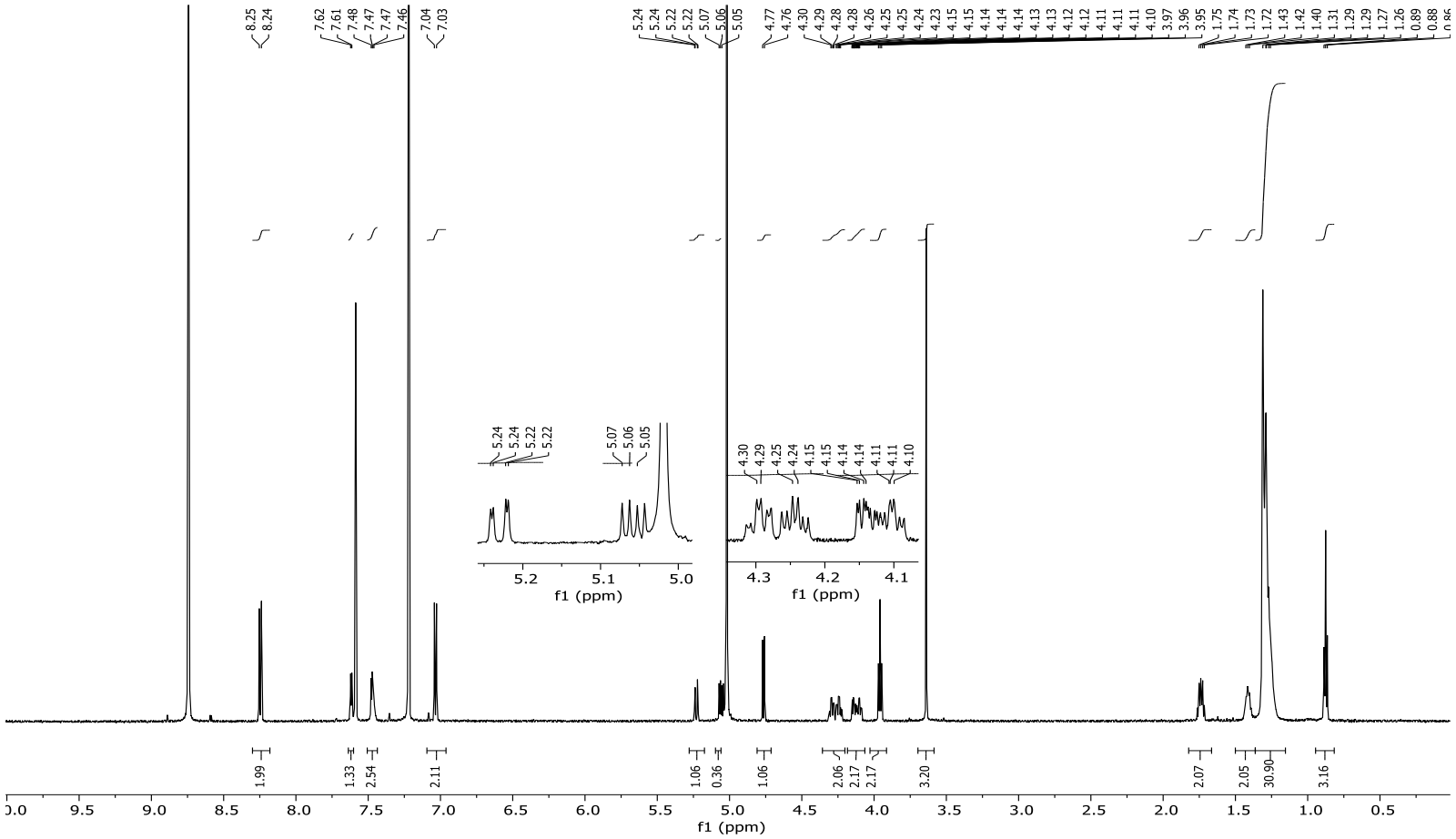




Methyl 6-*O*-(4-octadecyloxybenzoyl)-β-D-glucoside (BzC18GlcβOMe, **15**)

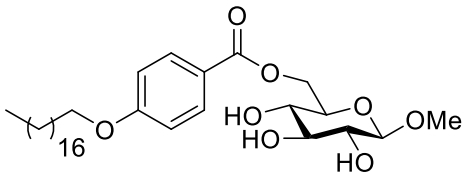
^{1}H NMR (C_5D_5N, 500 MHz)

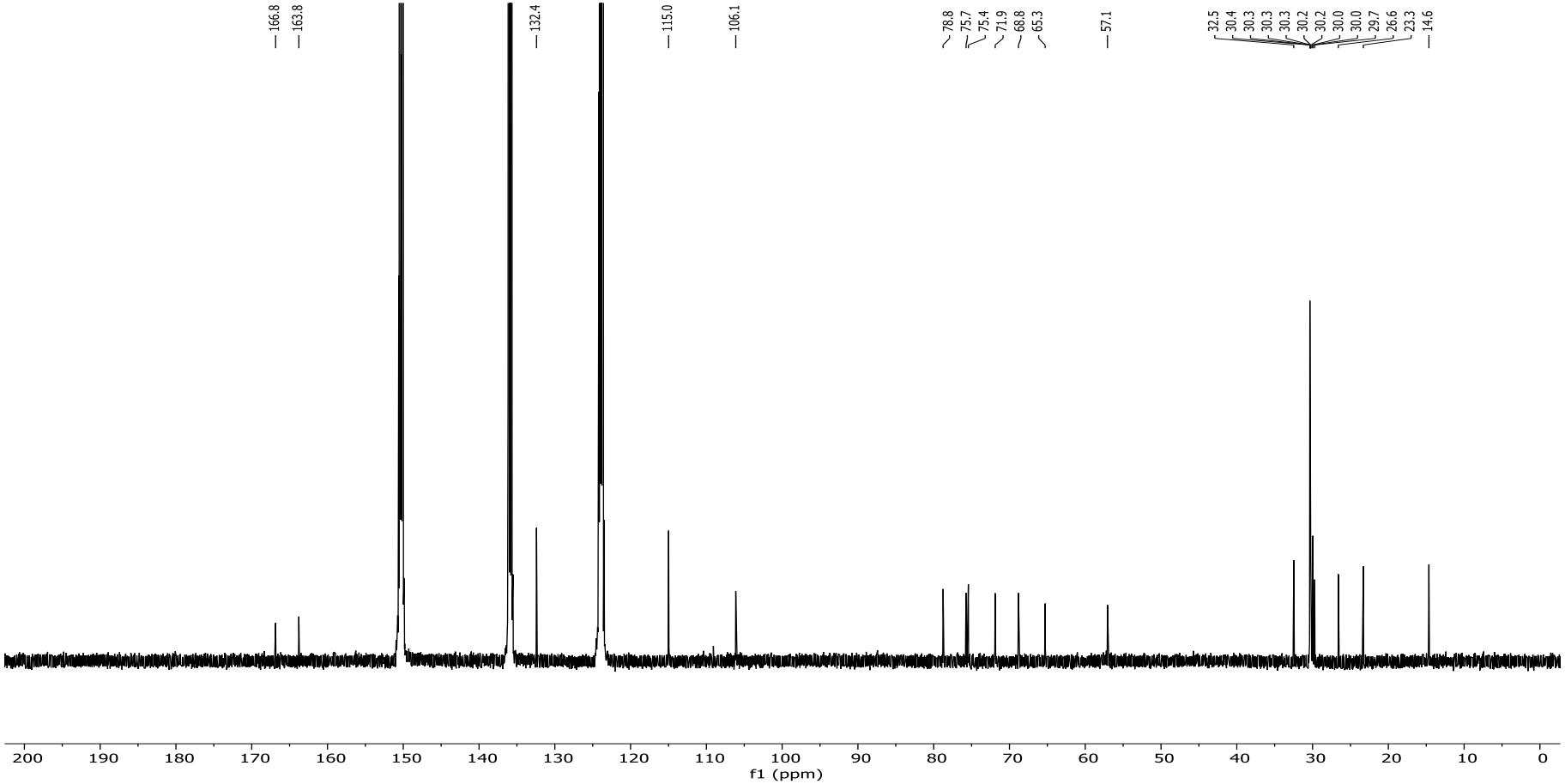




Methyl 6-*O*-(4-octadecyloxybenzoyl)-β-D-glucoside (BzC18GlcβOMe, **15**)

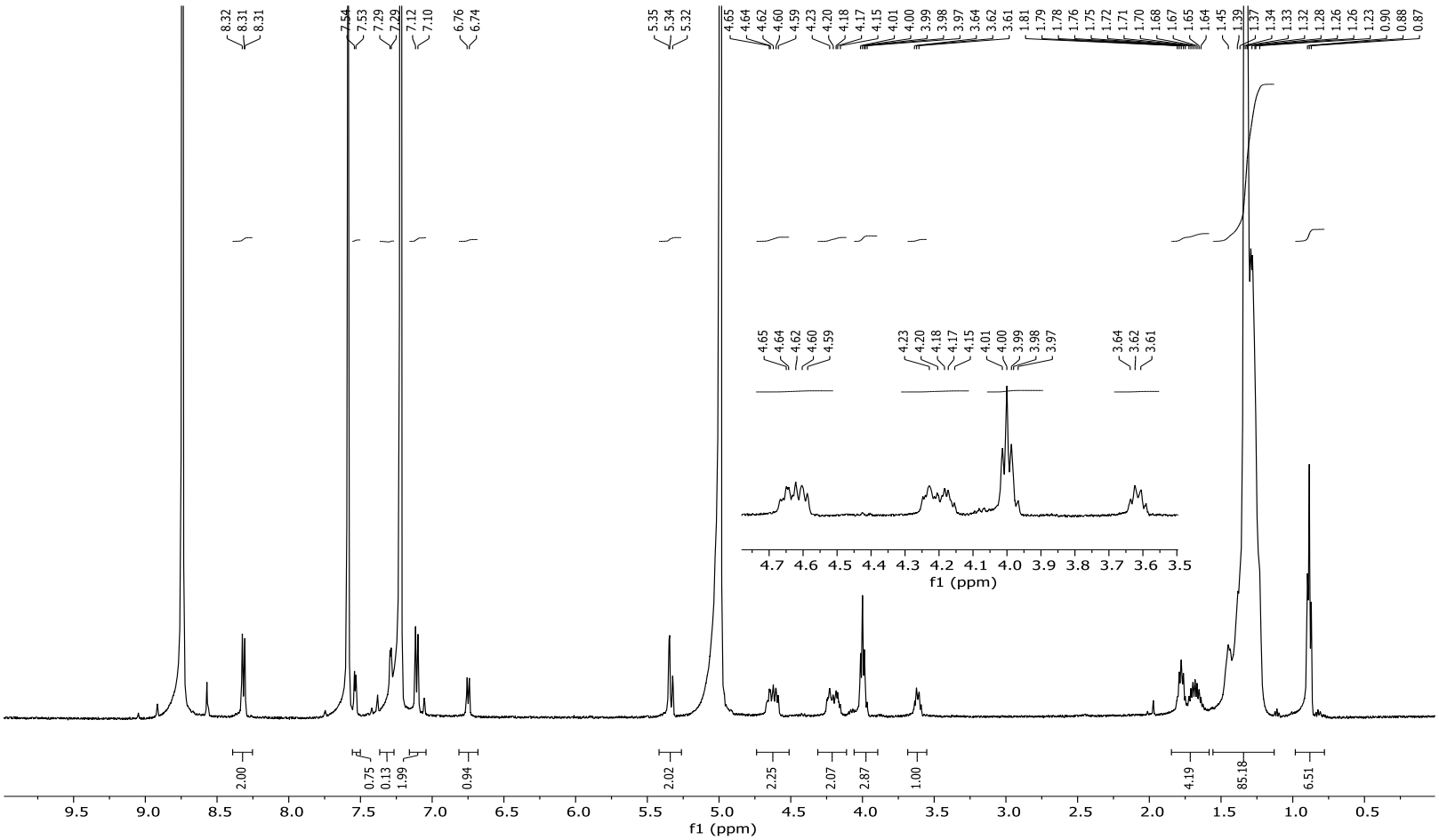
^{13}C NMR (C_5D_5N, 125 MHz)





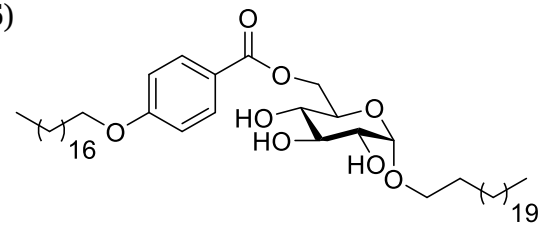
Docosyl 6-*O*-(4-octadecyloxybenzoyl)-α-D-glucoside (BzC18GlcαOC22, **16**)

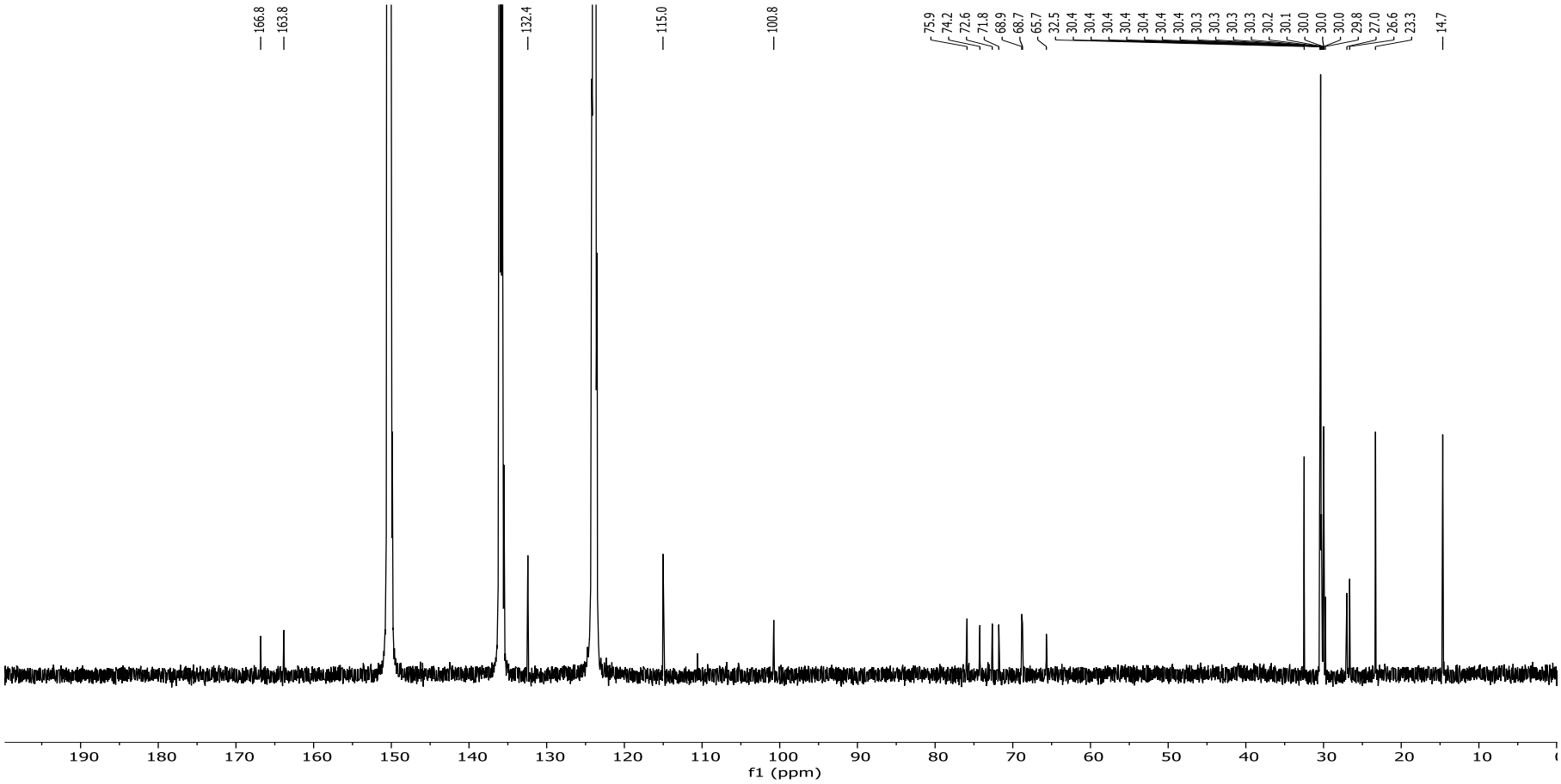
^{1}H NMR (C_5D_5N, 500 MHz)



Docosyl 6-*O*-(4-octadecyloxybenzoyl)-α-D-glucoside (BzC18GlcαOC22, **16**)

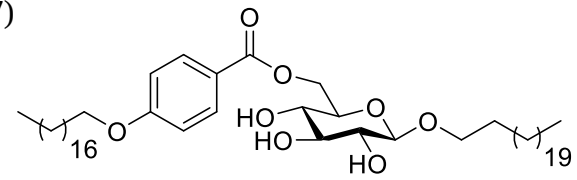
^{13}C NMR (C_5D_5N, 125 MHz)

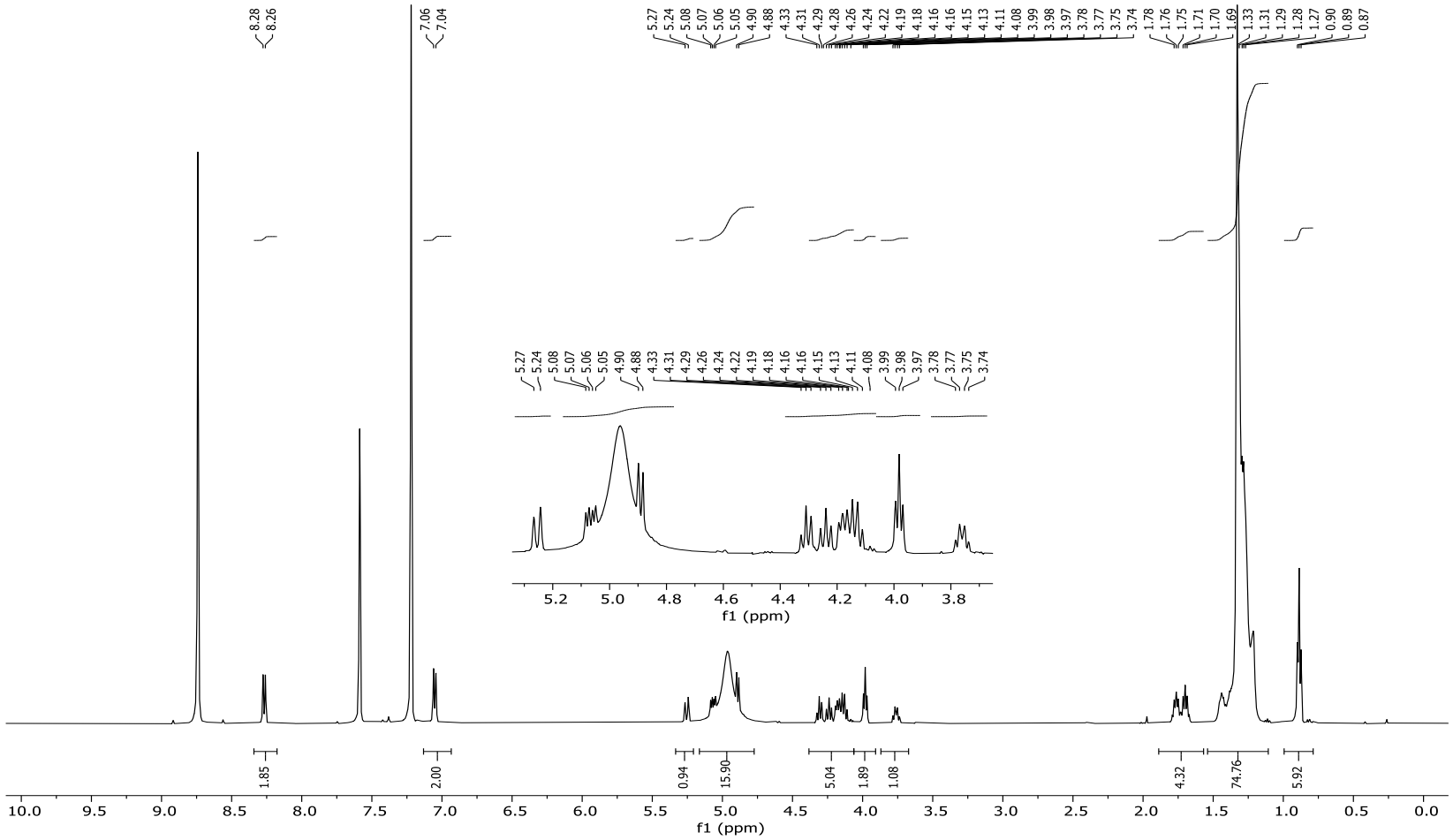




Docosyl 6-*O*-(4-octadecyloxybenzoyl)-β-D-glucoside (BzC18GlcβOC22, **17**)

^{1}H NMR (C_5D_5N, 500 MHz)





Docosyl 6-*O*-(4-octadecyloxybenzoyl)-β-D-glucoside (BzC18GlcβOC22, **17**)

^{13}C NMR (C_5D_5N, 125 MHz)