Conformationally Constrained Lipid A Mimetics for Exploration of Structural Basis of TLR4/MD-2 Activation by Lipopolysaccharide

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SUPPORTING INFORMATION

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Supplementary Tables and Figures

Table 1S. Torsion angles about oxymethyl (-OCH_2-) and *O*-glycosidic linkages in MD-2-bound antagonistic and agonistic Lipid A ligands (measurements were performed in JMol, Protein Workshop and Mercury).

Ligand	Action on TLR4	PDB code	ω	ψ	ϕ	*O5'-C1'-C6-O5*
Eritoran-hMD-2/TLR4	antagonist	2Z65	- 82.4	- 169.8	- 75.2	42.7
Lipid IVa – hMD-2	antagonist	2E59	- 71.1	- 103.8	- 84.2	100.8
LipidIVa-mMD-2/TLR4	agonist	3VQ1	-27.0	-134.5	-103.4	79.5
RaLPS-hMD-2/TLR4	agonist	3FXI	- 54.8	- 147.6	- 72.2	86.3

Table 2S. Distances between the phosphates (1- and 4'- phosphates for Lipid A; 4- and 4'- phosphates for simulated **DA193**) and distances between the sites of attachments of functional groups in simulated **DA193 – hMD-2** and **DA193 – mMD-2** compared to h- and mMD2-bound lipid IVa (PDB code: 2E59 and 3VQ1, respectively) and hMD2-bound Eritoran (PDB code: 2Z65) (measurements were performed in JMol and PyMol).

Distances are given in Å **PDB code:**	**Da193-mMD-2**	**LipidIVa-mMD-2 3VQ1**	**DA193-hMD-2**	**Lipid IVa-hMD-2 2E59**	**Eritoran-hMD-2 2Z65**	**Functional group attached**
P4'-P1 (P4-P4' in **DA193**)	11.1	12.0	11.8	12.5	12.2	
C4'-C1 (C4-C4' in **DA193)**	6.7	7.7	7.0	8.2	8.3	$OP(O)(OH)_2$
C3'-C2 (C3-C3' in **DA193**)	6.4	7.4	6.2	7.3	7.9	Fatty acid
C2'-C3 (C2-C2' in **DA193**)	4.8	5.8	4.5	5.6	6.0	Fatty acid

Figure 1S

Conformationally constrained lipid IVa mimetics **1** (except for **DA187**) inhibit activation of hTLR4/MD-2 and mTLR4/MD-2 complexes by *E. coli* Lipid A in TLR4-transfected HEK293 cells independently of the mode of application of antagonists **1** and *E. coli* Lipid A to the cells.

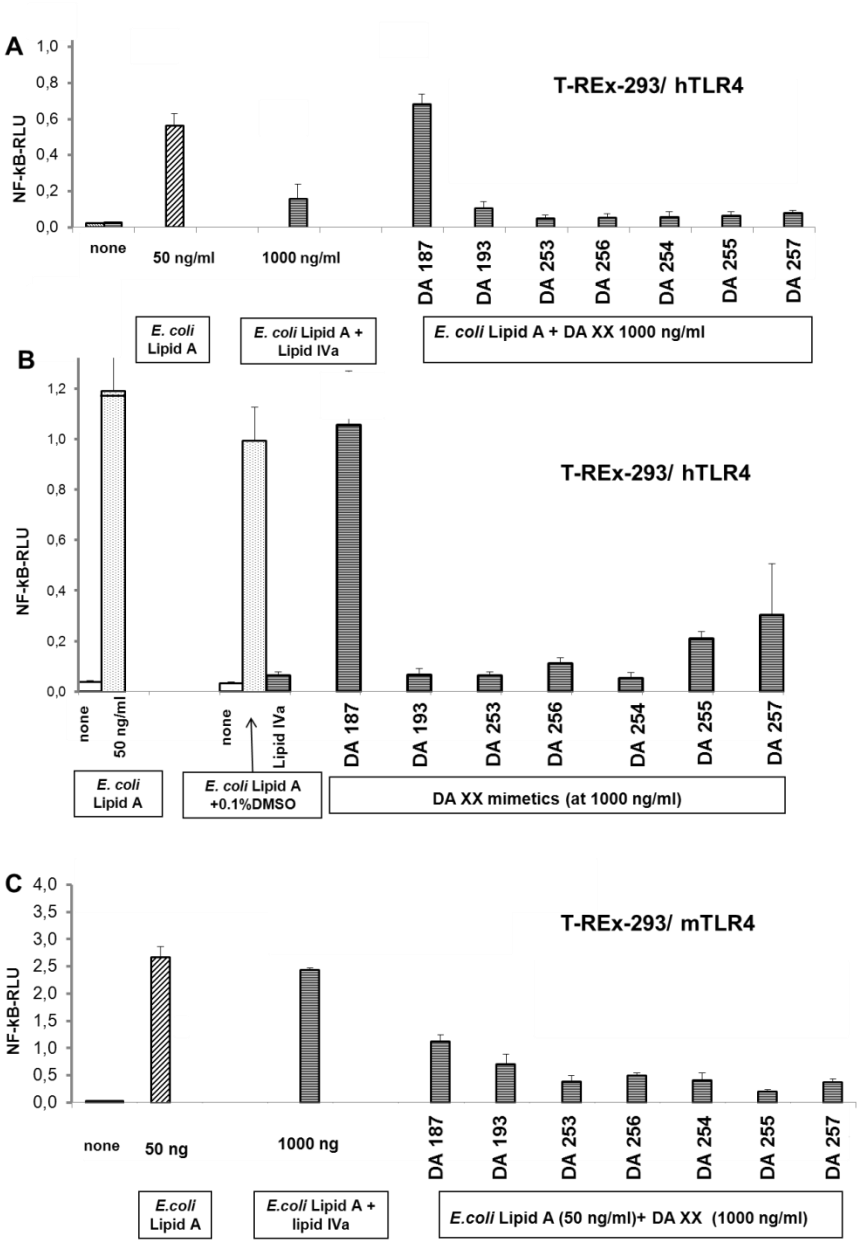

Figure 1S (A,B): Inhibition of hMD-2/TLR4 complex by mimetics **1** (compared to lipid IVa) in T-REx-293/hTLR4 cells transfected with hMD-2/fLuc/rLuc. **(A)** cells were pre-incubated with mimetics **1** or lipid IVa (1000 ng/ml) for 1h, then stimulated with *E. coli* Lipid A (50 ng/ml); **(B)** Cells were pre-activated with *E. coli* Lipid A (50 ng/ml) for 1 h, then mimetics **1** or lipid IVa were added

Figure 1S (C): Inhibition of mMD-2/TLR4 complex by mimetics **1** (compared to lipid IVa) in T-REx-293/mTLR4 cells transfected with mMD-2/fLuc/rLuc. Cells were pre-activated with *E. coli* Lipid A (50 ng/ml) for 1 h, then mimetics **1** or lipid IVa were added.

Figure 2S

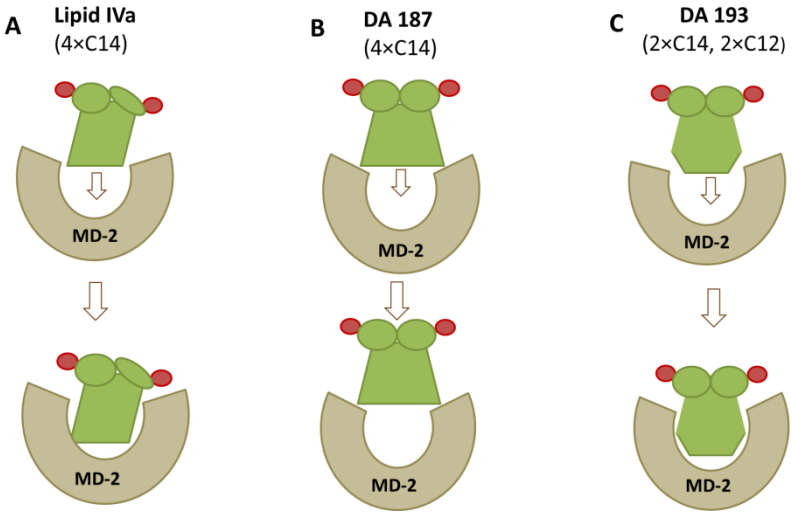

Figure 2S. The failure of DA187 to compete with *E. coli* Lipid A for the binding site on MD-2 can only be speculated by inability of **DA187** to enter the binding pocket of MD-2 (the entrance of the binding groove of MD-2 is rather narrow and "closed" in the absence of the ligand, but there is enough space inside the binding groove of MD-2 to accommodate all four C14 lipid chains of lipid IVa). The hydrophobic volume of the rigid lipid cluster in **DA187** which is imposed by a co-planar orientation of GlcN rings in (1↔1) diglucosamine scaffold could be too large to enter the binding groove of MD-2 (as shown in Figure 4S-**B**). In contrast to (1→6) connected lipid IVa, the reduced flexibility of the (1↔1)-glycosidic linkage would not allow the rearrangement of the diglucosamine backbone of **DA187** to a more compact conformation (as shown in Figure 4S-**A** for lipid IVa) wherein the cluster of four C-14 lipid chains would have lower hydrophobic volume to enter the binding pocket of MD-2. **DA193** differs from **DA187** in two shorter outer chains (C12) which is obviously enough to diminish the terminal hydrophobic volume of the ligand allowing **DA193** enter the binding groove of MD-2 (as shown in Figure 4S-**C**).

Figure 3S

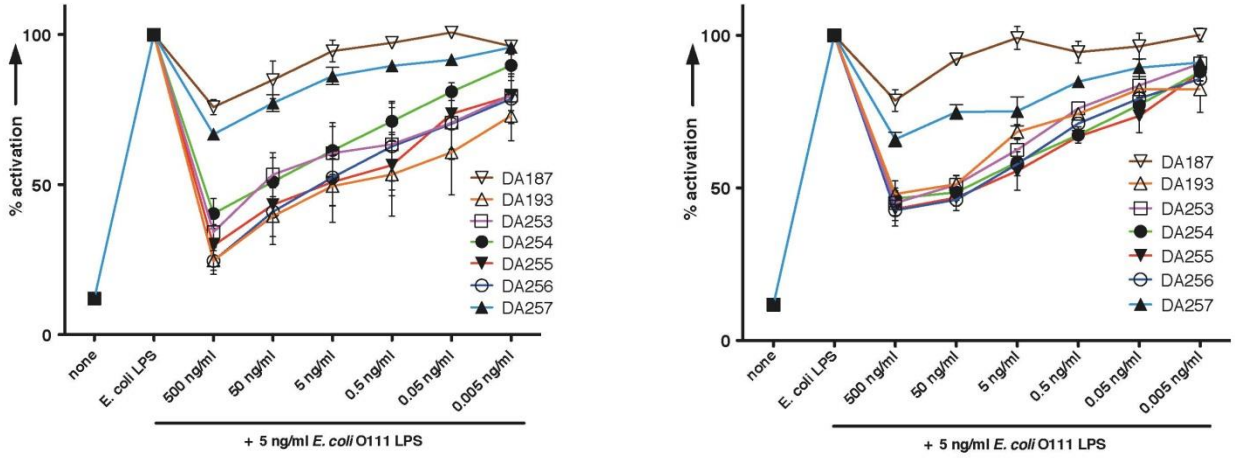

Figure 3S. Antagonistic activity of mimetics 1 on the action of *E. coli* O111 LPS in TLR4-transfected HEK293 cells (HEKBlue). **Left: mimetics 1 can compete with LPS for the binding site on hMD2.** HEKBlue human TLR4 cells were stimulated with 5 ng/ml *E. coli* O111 LPS, mimetics **1** (at the concentrations indicated in the graph) were applied simultaneously with *E. coli* LPS. TLR4-dependent NFκB activation was measured after 24h; **Right: mimetics 1 can displace LPS from the binding site on hMD-2.** HEKBlue human TLR4 cells were pre-stimulated with 5 ng/ml *E. coli O111* LPS for 1h, then mimetics **1** (at the concentrations indicated in the graph) were applied. TLR4-dependent NFκB activation was measured after 24h. Maximal activation (5 ng/ml *E. coli* O111 LPS) was set to 100% for each condition and experiment. Data were combined from n=3 independent experiments, error bars indicate standard error of the mean.

Figure 4S

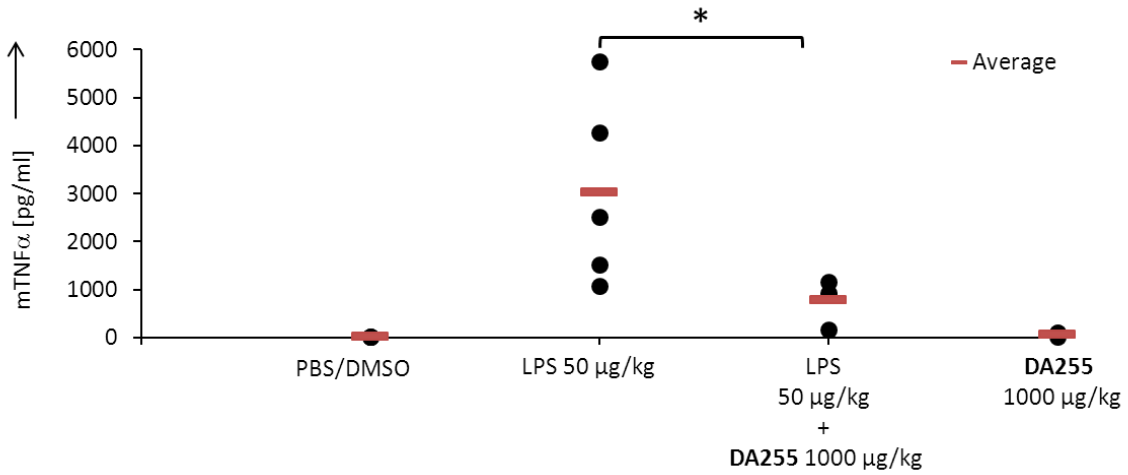

Figure 4S. Inhibition of LPS-induced expression of TNF-α in vivo by lipid IVa mimetic DA255.
DA255 does not activate murine TNF-α response (t-test: p=0,1 - DA255 1000 ug/kg vs. PBS/DMSO control) and efficiently inhibits LPS-induced immune response in mice at 1:20 ratio (50 ug/kg LPS + 1000 ug/kg **DA255**). Mice (C3H/HeN) were injected with the indicated doses of LPS, **DA255,** a mixture of both or the vehicle control. Blood was colected 1 h latter and TNF-α was determined in serum with ELISA. * p<0,04 (t-test). N=3-5 (N=3 (**DA255**), N=4 (vehicle, LPS+**DA255**), N=5 (LPS).

Table 3S

Torsional angles ϕ and ψ in the pseudo-trehalose-like diglucosamine scaffold of Lipid A mimetic DA 193.

	Environment	*ψ* *O5-C1-O-C1'* (°)	*ϕ* *O5'-C1'-O-C1* (°)
DA193	water	-71 ± 0	109 ± 1
DA193	octanol/water	-65 ± 1	99 ± 2
DA193	hMD2	-65 ± 1	93 ± 3
DA193	mMD2	-69 ± 1	78 ± 2

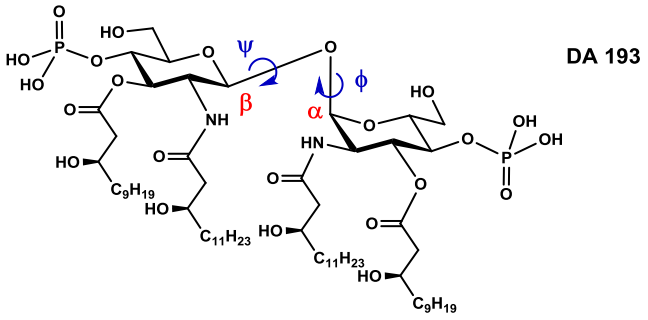

Figure 5S

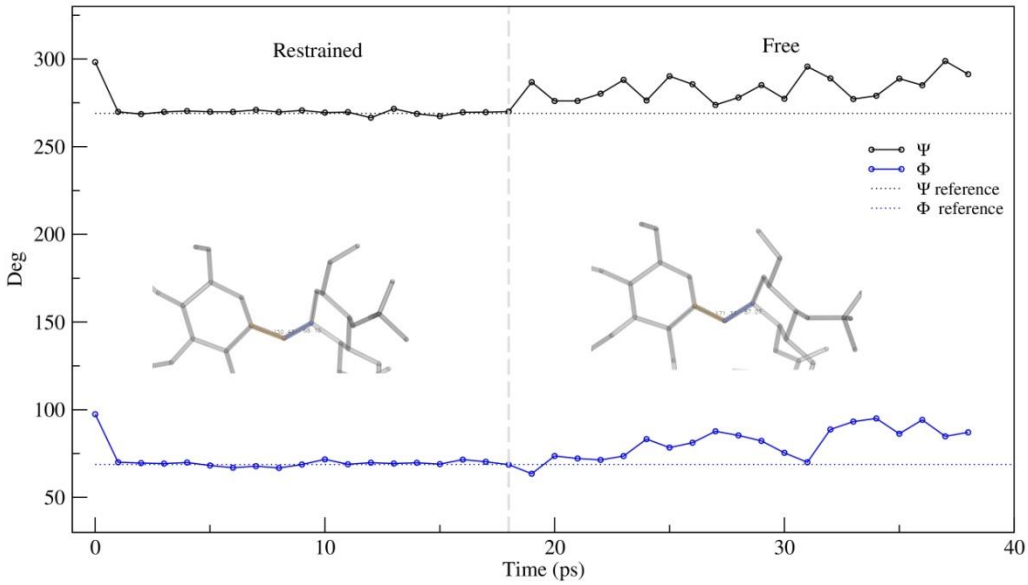

Figure 5S. Plots of ϕ and ψ dihedral angles in α,β trehalose-like backbone over time. In the first half of the simulation, the angles are restrained to the values of trehalose in the X-ray structure (70 and 270 (-90) degrees; (doi: 10.1107/S0108270196012693). As soon as the restraints are released, the dihedral angles move back to the values which are observed in the simulations of **DA193** within the binding pocket of MD-2 (~ 100 and ~300 degrees).

Figure 6S

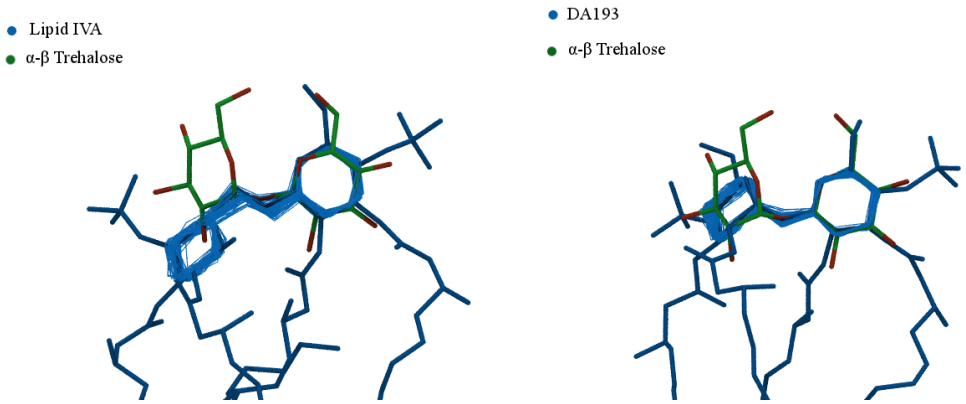

Figure 6S. Alignment of the disaccharide backbone of DA193 and β,α-trehalose (vs. lipid IVa - β,α-trehalose) at the octane-water interface (acyl chains of **DA193** are placed in the hydrophobic solvent simulating hydrophobic surrounding of the binding pocket of MD-2, carbohydrate backbone of pseudo-trehalose or bis-phosphorylated diglucosamine backbone of **DA193** are placed in water). The lipid tails display internal plasticity in a hydrophobic surrounding, whereas the sugar rings adopt their preferred conformations and are not particularly flexible anymore.

Figure 7S

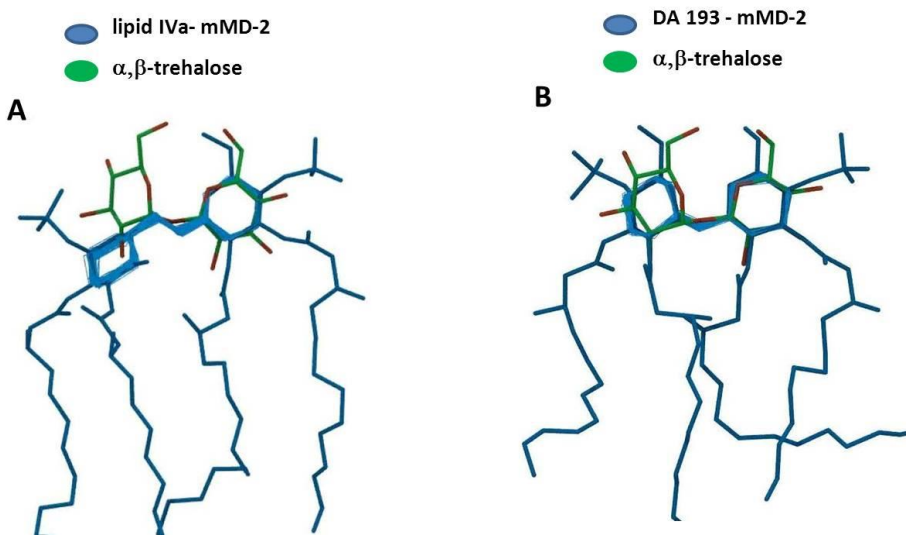

Figure 7S. Superimposition of the disaccharide backbone of lipid IVa – mMD-2 with β,α-trehalose and DA193 – mMD-2 with β,α-trehalose (both ligands are placed into the binding pocket of MD-2). "Tilted" orientation of the proximal GlcN ring of lipid IVa which is obviously important for the presentation of one acyl chain on the surface of MD-2 is achieved due to a greater flexibility of (1→6) linked diglucosamine backbone of lipid IVa. More rigid backbone of **DA193** (which is seen by superimposition with β,α-trehalose) does not allow the GlcN ring situated at the dimerization interface to flip into the "tilted" orientation as seen in Figure 7S-A. This apparently allows **DA193** to submerge deeper into the binding pocket of MD-2, which prevents the presentation of one lipid chain on the surface of mMD-2 and renders **DA193** to antagonist in mouse system.

Biological assay

Reagents

Human embryonic kidney (HEK) 293 cells were kindly provided by Dr. J. Chow (Eisai Research Institute, Andover, USA). Flp-In T-REx cells and the Flp-In system were purchased from Invitrogen (CA, USA). Expression plasmids with sequences of human TLR4 and MD-2 as well as the pELAM-1 firefly luciferase plasmid were a kind gift from Dr. C. Kirschning (Technical University of Munich, Germany). Expression plasmid for mouse MD-2 was a gift from Dr. Y. Nagai (University of Tokyo, Japan). Expression plasmid containing sequence of mouse TLR4 was purchased from InvivoGen (CA, USA) and the Renilla luciferase phRL-TK plasmid was purchased from Promega (WI, USA). HEKBlue hTLR4 (HEK293 stably expressing human TLR4, MD-2, CD14 and a secreted NFκB dependent reporter) were purchased from InvivoGen, growth conditions and endotoxicity assay for HEKBlue cells were set as recommended by InvivoGen. "ReadySetGo" ELISA kit was purchased from eBioScience. *E. coli* O111 LPS and *E.coli* 055:B5 LPS were purchased from Sigma-Aldrich, *E. coli* Lipid A and lipid IVa were purchased from the Peptide Institute (Osaka, Japan). The nucleotide sequence encoding human TLR4 was cloned into pUNO vector with C-terminal HA tag. Transfection reagent JetPEI was purchased from Polyplus-Transfection (France) and was used according to the manufacturer's instructions.

Molecular dynamics simulation

DA193 was modeled using a combination of the CHARMM36 all-atom carbohydrate force field [1-4] and CHARMM36 lipid parameter set, as previously done.[5] **DA193** was manually placed in the cavity of hMD2 and mMD2, using the coordinates of Lipid A and lipid IVa of the 3.1 and 2.84 Å resolution X-ray crystal structure of hMD2 (PDB 3FXI)[6] and mMD2 (PDB 2Z64)[7] obtained from the Research Collaboratory for Structural Bioinformatics Data Bank,[8] respectively, as templates. **DA 193** was solvated in aqueous surrounding and at a pre-equilibrated octanol/water interface. For this a periodic cell was constructed with dimensions of 5 x 5 x 5 nm^3, containing approximately 18,000 atoms. **Da 193** was manually placed in the binding pocket of h- or mMD-2 using the indicated crystal structures as templates in a pose found in PDB 2E59 (lipid Iva-hMD-2) for human and PDB 3Vq1 (lipid IVa-mMD-2) for murine systems wherein β–configured GlcN moieties of **DA 193** corresponding to distal GlcN rings in natural lipid A backbone were overlapped. The complexes were solvated in periodic simulation boxes of roughly 7.0 x 6.6 x 7.6 nm^3, containing around 32,000 atoms. All systems were electro-neutralized by addition of sodium ions, and built using the program VMDv1.91 (visual molecular dynamics)[9] and the program PackMol.[10] The simulations of **DA193** alone and in complex with h- and mMD-2 in aqueous solution or at an octanol/water interface were performed with the MD program NAMDv2.9[11] with the CHARMM27 and CHARMM36 parameter sets and the TIP3P water model for a total simulation time of 10 ns, for each simulated system.

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Chemical synthesis: Experimental procedure

General

Column chromatography was performed on silica gel 60 (0.040–0.063 mm, Merck), Reactions were monitored by TLC on (A): Silica gel 60 F254 HPTLC precoated glass plates with 2.5 cm concentration zone (Merck) or on (B): Silica gel 60 F254 precoated glass plates (Merck), spots were visualized by spraying with anisaldehyde–H_2SO_4; concentration of solutions was performed at reduced pressure at temperatures below 40°C. Dry solvents: acetonitrile, diisopropylethylamine, triethylamine, MeOH and DMF were purchased from Aldrich, dichloromethane were dried by refluxing with CaH_2 (5 g/l) for 16 h, then distilled and stored under argon. Toluene was distilled from phosphorus pentaoxide and redistilled from CaH_2. The liquids were stored over molecular sieves 0.4 nm, DMF and acetonitrile were stored over activated molecular sieves 0.3 nm. Triethylammonium bicarbonate (TEAB) (1 M) buffer was purchased from Fluka, BioBeads SX1 gel was purchased from BioRad. Optical rotations were measured with a Perkin–Elmer 243 B polarimeter. $[\alpha]_D^{20}$ -Values are given in units of 10^{-1} deg cm^3 g^{-1}. 1H NMR spectra were recorded at 297 K with a Bruker DPX instrument operating at 300, 400, or 600 MHz for 1H with $CDCl_3$ as the solvent and Me_4Si as the standard, unless stated otherwise. ^{13}C NMR spectra were measured at 75.47, 100.62, or 150.9 MHz and referenced to 1,4-dioxane (67.40 ppm). Homo- and heteronuclear 2D NMR spectroscopy was performed with Bruker standard software. ^{31}P NMR spectra were measured at 242.96 MHz and referenced externally to 85% aq H_3PO_4 (d 0.0). HPLC–HRMS analysis was carried out with H_2O/MeCN solutions (concentration 1 mg/L) with an HTC PAL system autosampler (CTC Analytics AG), an Agilent 1100/1200 HPLC with binary pumps, degasser, and column thermostat (Agilent Technologies, Waldbronn, Germany), and Agilent 6210 ESI-TOF mass spectrometer (Agilent Technologies, Palo Alto, U.S.). The mass spectrometer was previously tuned with Agilent tune mix and further reference masses were added to provide a mass accuracy below 2 ppm. Data analysis was performed with Mass Hunter software (Agilent Technologies). MALDI-TOF-MS was performed in the positive or negative modes using a Bruker Autoflex Speed TOF-TOF instrument with 6-aza-2-thiothymine (ATT) as matrix. Spectra were processed with the manufacturer's software (Bruker Flexanalysis 3.3.80) using the SNAP algorithm with a signal/noise threshold of 6 (unsmoothed).

Synthesis of (3)

Allyl 4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (3)

To a stirred solution of **2** (10.1 g, 21.0 mmol) in dry DMF (16 ml) imidazole (3.44g, 50.5mmol) and *tert*-butyldimetylsilyl chloride (6.50 g, 43.09 mmol) were added under atmosphere of Ar. The reaction mixture was stirred for 3 h, diluted with toluene (300ml) and washed with water (150ml), sat. aq. $NaHCO_3$ (150 ml) and brine (50 ml). The organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc, 9:1→3:2) to afford **3** (11.9 g, 95 %) as colourless syrup; R_f 0.38 (B, toluene/EtOAc 5:1), $[\alpha]_D^{20}$= +38.1 (*c* 1.2, $CHCl_3$);

^1H NMR (600MHz, $CDCl_3$): δ 7.49-7.46 (m, 2H, CH*Ph*), 7.37-7.33 (m, 3H, CH*Ph*), 5.91 (m, 1H, C*H*=CH_2), 5.51 (s, 1H, PhC*H*), 5.31 (dd, 1H, $^2J_{=CH2cis,\ =CH2trans}$= 1.4, $^3J_{CH=,\ =CH2cis}$= 17.2 Hz, =CH_{2cis}), 5.25 (dd, 1H, $^3J_{CH=,\ =CH2trans}$ 10.3 Hz, =CH_{2trans}), 5.14 (d, 1H, $^3J_{NH,\ 2}$= 9.8 Hz, NH), 4.89 (d, 1H, $^3J_{1,2}$= 3.7 Hz, H-1), 4.80 and 4.60 (2AB, 2H, $^2J_{AB}$= 11.9 Hz, CH_2CCl_3), 4.25 (dd, 1H, $^3J_{6a,5}$=4.80, $^2J_{6a,6b}$ =10.2 Hz, H-6a), 4.20 (m, 1H, OC*H*H, All.), 4.03 (m, 1H, OCH*H*, All.), 3.95 (ddd, 1H, $^3J_{1,2}$= 3.7, $^3J_{2,3}$= 9.7, $^3J_{2,NH}$=10.0 Hz, H-2), 3.89 (dd, 1H, $^3J_{3,4}$=8.8, $^3J_{2,3}$=9.7 Hz, H-3), 3.84 (ddd, 1H, $^3J_{5,6a}$= 4.8, $^3J_{4,5}$= 9.7, $^3J_{5,6b}$= 10.2 Hz, H-5), 3.74 (dd, 1H, $^3J_{5,6b}$=10.1, $^2J_{6a,6b}$=10.3 Hz, H-6b), 3.53 (dd, 1H, $^3J_{3,4}$=8.9, $^3J_{4,5}$= 9.4 Hz, H-4), 0.81 (s, 9H, tBu), 0.04 and -0,03 (2s, 6H, $SiMe_2$);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 154.21 (1C, NHCO), 137.17 (1C, C_q-Ph), 133.37 (1C, *C*H=CH_2), 129.02 + 128.11 + 126.27 (5C, Ph), 118.37 (1C, CH=*C*H_2), 101.95 (1C, Ph*C*H), 97.53 (1C, C-1), 82.48 (1C, C-4), 74.96 (1C, *C*H_2CCl_3), 70.79 (1C, C-3), 68.89 (1C, C-6), 68.62 (1C, OCH_2, All.), 62.97 (1C, C-5), 56.49 (1C, C-2), 25.68 (3C, C*C*H_3), 18.11 (1C, *C*CH_3), -4.11 and -5.00 (2C, SiMe2);
HRMS (ESI-TOF): calcd. for $C_{25}H_{37}Cl_3NO_7Si$ $[M+H]^+$ 596.1399; found 596.1405

Synthesis of (4)

4,6-*O*-Benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-D-glucopyranose (4).

A solution of {(1,5-Cyclooctadiene)bis(methyldiphenylphosphine)iridium(I)} hexafluorophosphate (0,108 g, 0.13 mmol) in dry THF (25 ml) in a three-neck flask was repeatedly (× 4) degassed and filled with argon. Subsequently, the flask was evacuated and filled with H_2 which was kept in the reaction mixture for 10 sec., the procedure was repeated 3 times until the solution of the catalyst changed the colour from pink to colourless. The flask was repeatedly degassed and filled with Ar (× 4). A solution of **3** (7.59 g, 12.71 mmol) in dry THF (25 ml) was added to the activated catalyst and the reaction mixture was stirred under Ar for 30 min, cooled to 0°C and a solution of I_2 (3.87 g, 15.26 mmol) in THF/H_2O (15 ml) was added dropwise. The mixture was stirred for 3h, diluted with EtOAc (200 ml) and washed with 5% aq. NaS_2O_3 (2×50 ml) (decolouration, but yellow colour remains), satd. aq. $NaHCO_3$ (30 ml) and brine (30 ml). The organic phase was dried with Na_2SO_4, filtered and concentrated. The residue was purified by MPLC on silica gel (gradient elution toluene→ toluene/EtOAc, 8:1) to give **4** (6.0 g, 85%); R_f 0.23 (A, hexane/EtOAc 3:1), $[\alpha]_D^{20}$= +3,9 (*c* 1.0, $CHCl_3$)
^{1}H NMR (600 MHz, $CDCl_3$) α-anomer: δ 7.49-7.45 (m, 2H, CH*Ph*), 7.38-7.33 (m, 3H, CH*Ph*), 5.52 (s, 1H, PhC*H*), 5.27 (t, 1H, $^3J_{1,2}$=$^3J_{1,OH}$= 3.5 Hz, H-1), 5.24 (d, 1H, $^3J_{2,NH}$=9.5 Hz, NH), 4.78 and 4.61 (2AB, 2H, J_{AB}=11.9 Hz, CH_2CCl_3), 4.25 (dd, 1H, $^3J_{5,6a}$ =4.9, $^2J_{6a,6b}$=10.3 Hz, H-6a), 4.05 (ddd, 1H, $^3J_{5,6a}$ =4.9, $^3J_{H\text{-}5,H\text{-}4}$ =10.0, $^2J_{5,6b}$ = 10.0 Hz, H-5), 3.96 (dd, 1H, $^3J_{3,4}$ = 8.70, $^3J_{2,3}$ = 9.8 Hz, H-3), 3.91 (ddd, 1H, $^3J_{1,2}$=3.4, $^3J_{NH,2}$= 9.4, $^3J_{2,3}$= 9.8 Hz, H-2), 3.74 (dd, 1H, $^2J_{6a,6b}$ =10.3, $^3J_{5,6b}$ =10.3 Hz, 1H, H-6b), 3.53 (dd, 1H, $^3J_{4,5}$ =9.2, $^3J_{3,4}$ = 9.2 Hz, H-4), 3.17 (d, 1H, *J*=2.8 Hz, OH), 0.82 (s, 9H, *t*Bu), 0.05 and -0.02 (2s, 6H, $SiMe_2$)
^{13}C NMR (151 MHz, $CDCl_3$): δ 154.30 (1C, NHCO), 137.15 (1C, C_q-Ph), 129.14 + 128.17 + 126.3 (5C, Ph), 101.95 (1C, Ph*C*H), 92.97 (1C, C-1), 82.49 (1C, C-4), 74.99 (1C, *C*H_2CCl_3), 70.35 (1C, C-3), 68.94 (1C, C-6), 62.97 (1C, C-5), 56.71 (1C, C-2), 25.66 (3C, C*C*H_3), 18.13 (1C, *C*CH_3), -4.12 and -5.01 (2C, SiMe2)
HRMS (ESI-TOF): calcd. for $C_{22}H_{33}Cl_3NO_7Si$ $[M+H]^+$ 556.1100; found 596.1094

Synthesis of (5)

4,6-*O*-Benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-(2,2,2-trichloro-ethoxycarbonylamino)-D-glucopyranose *N*-phenyltrifluoroacetimidate (5)

A solution of **4** (2.03 g, 3.64 mmol), imidoylchloride (1.13 ml, 5.46 mmol) and K_2CO_3 (0.76 g, 5.46 mmol) in acetone (20 ml) was stirred for 1h at rt. The reaction mixture was filtered over Celite®, washed with acetone (50 ml) and concentrated. The residue was taken up in EtOAc (150 ml), washed with satd. aq. $NaHCO_3$ (150ml) and brine (50ml). The organic phase was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (0.1% Et_3N in toluene) to afford **5** as a white solid (2.12 g, 80%); R_f 0.35 (A, hexane/EtOAc 8:1);
^{1}H NMR (600 MHz, d6-DMSO, ref. to DMSO 2.50ppm): δ 7.67-7.65 (m, 5H, NHβ, NPh), 7.62 (d, 1H, $^3J_{2\alpha,NH\alpha}$= 9.2 Hz, NHα), 7.34-7.35 (m, 14H, Ph, NPh), 7.24-7.21 (m, 2H, NPh), 5.63, 5.62 (2s, 2H, PhCHα, PhCHβ), 5.01 (t, 1H, $^3J_{1\alpha,2\alpha}$= 3.8 Hz, H-1α), 4.82 and 4.68 (2AB, 2H, J_{AB}=12.3 Hz, CH_2CCl_3), 4.77 and 4.65 (2AB, 2H, J_{AB}=12.4 Hz, CH_2CCl_3), 4.61 (d, 1H, $^3J_{1\beta,2\beta}$= 8.3 Hz, H-1β), 4.18 (dd, 1H, $^3J_{5\beta,6a\beta}$ =4.9, $^2J_{6a\beta,6b\beta}$=10.2 Hz, H-6aβ), 4.11 (dd, 1H, $^3J_{5\alpha,6a\alpha}$ =4.9, $^2J_{6a\alpha,6b\alpha}$=10.0 Hz, H-6aα), 3.93 (t, 1H, $^3J_{3\alpha,4\alpha}$ = $^3J_{2\alpha,3\alpha}$ = 9.5 Hz, H-3α), 3.87 (dt, 1H, $^3J_{5\alpha,6a\alpha}$ =$^3J_{5\alpha,6b\alpha}$ =4.8, $^3J_{4\alpha,5\alpha}$ =9.9 Hz, H-5α), 3.76 (t,

1H, $^3J_{3\beta,4\beta} = {}^3J_{2\beta,3\beta}$ = 9.2 Hz, H-3β), 3.74-3.71 (m, 2H, H-6bα, H-6bβ), 3.60 (dt, 1H, $^3J_{1\alpha,2\alpha}$=3.7, $^3J_{NH\alpha,2\alpha}$= $^3J_{2\alpha,3\alpha}$= 9.7 Hz, H-2α), 3.48 (t, 1H, $^3J_{4\alpha,5\alpha} = {}^3J_{3\alpha,4\alpha}$ = 9.2 Hz, H-4α), 3.46 (t, 1H, $^3J_{4\beta,5\beta} = {}^3J_{3\beta,4\beta}$ = 9.2 Hz, H-4β), 3.32-3.27 (m, 2H, H-2β, H-5β), 0.76 and 0.75 (2s, 18H, 2 tBu), 0.02, -0.01 and -0.08 (4s, 12H, $SiMe_2$);
^{13}C NMR (150.9 MHz, d6-DMSO, ref. DMSO = 39.52 ppm): δ 154.52, 154.33, 154.25 (4C, NHC(O), OC(NPh)), 137.66, 137.59, 136.25 (3C, C_q-Ph), 128.95, 128.87, 127.92, 126.16, 126.13, 125.62 (Ph), 100.86, 100.66 (2C, 2 Ph*C*H), 95.79 (1C, C-1β), 91.82 (1C, C-1α), 82.41 (1C, C-4α), 81.51 (1C, C-4β), 73.77, 73.64 (2C, 2 *C*H_2CCl_3), 70.25 (1C, C-3β), 69.55 (1C, C-3α), 68.18 (1C, C-6α), 67.81 (1C, C-6β), 65.50 (1C, C-5β), 61.74 (1C, C-5α), 59.98 (1C, C-2β), 57.26 (1C, C-2α), 25.76, 25.65 (6C, 2 tBu), 17.85, 17.81 (2C, *C*CH_3), -4.28, -4.35, -5.0 and -5.02 (4C, SiMe2)

Synthesis of (6)

4,6-*O*-Benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-(2,2,2-trichloroethoxy-carbonylamino)-α-D-glucopyranoside (6)

A solution of **4** (180 mg, 0.323 mmol) and **5** (353 mg, 0.485 mmol) in dry CH_2Cl_2 (10 ml) was stirred with powdered activated molecular sieves (4Å) under atmosphere of Ar for 30 min., the mixture was cooled to 0°C and trimethylsilyl trifluoromethanesulfonate (TMSOTf) (10% solution in CH_2Cl_2, 59 µl, 0.32 mmol) was added dropwise. The stirring was continued for 20 min. and the reaction was stopped by addition of Et_3N (0.4 mmol). The mixture was let to warm up to rt, the solids were removed by filtration through the pad of Celite®, the filtrate was diluted with CH_2Cl_2 (100 ml) and washed with satd. aq. $NaHCO_3$ (50 ml) and brine (30 ml), dried over Na_2SO_4 and concentrated. The residue was purified by MPLC on silica gel (gradient elution with toluene/EtOAc, 19:1→5:1) to give the disaccharide **6** as white solid (272 mg, 77%); R_f 0.44 (A, hexane, EtOAc 3:1); $[\alpha]_D^{20}$= 8.26 (*c* 1.2, $CHCl_3$);
^{1}H NMR (400 MHz, DMSO, 80°C, ref. to solvent signal 2.5ppm): δ 7.46-7.43 and 7.39-7.34 (m, 10H, 2x CH*Ph*), 5.63 and 5.62 (2s, 2H, 2x C*H*Ph), 5.09 (d, 1H, $^3J_{1',2'}$=3.6 Hz, H-1'), 4.91 and 4.63 (2AB, 2H, $^2J_{AB}$=12.2 Hz, CH_2CCl_3), 4.87 and 4.70 (2AB, 2H, $^2J_{AB}$=12.1 Hz, CH_2CCl_3), 4.81 (d, 1H, $^3J_{1,2}$=8.5 Hz, H-1), 4.22 (dd, 1H, $^3J_{H\text{-}6a,H\text{-}5}$=5.0, $^2J_{6a,6b}$ =10.2 Hz, H-6a), 4.10 (dd, 1H, $^3J_{H\text{-}6a',H\text{-}5'}$ =5.0, $^2J_{6a',6b'}$ =9.9 Hz, H-6a'), 4.07-3.90 (m, 3H, H-3, H-5', H-3'), 3.83-3.72 (m, 3H, H-6b, H-2', H-6b'), 3.58 (m, 2H, H-4, H-4'), 3.49 (dd, 1H, *J*=8.8, 17.9 Hz, H-2), 3.41 (ddd, 1H, $^3J_{H\text{-}6a,H\text{-}5}$=5.0 Hz, *J*= 9.8 Hz, *J*= 9.6 Hz, H-5), 0.82 and 0.81 (2s, 18H, 2 tBu), 0.04 and -0.02 (4s, 12H, 4 SiMe);
^{13}C NMR (100.6 MHz, DMSO, 80°C, ref. to solvent signal 39.25ppm) δ 137.03 (2C, C_q-Ph), 128.16 + 127.24 + 125.64 (10C, Ph), 100.62 and 100.46 (3C, 2 Ph*C*H, C-1'), 98.51 (invisible, via HSQC) (1C, C-1), 81.24 and 80.65 (2C, C-4 and C-4'), 73.90 and 73.80 (2C, 2 *C*H_2CCl_3), 71.51 (1C, C-3), 69.83 (1C, C-3'), 67.26 and 67.21 (2C, C-6 and C-6'), 65.42 (1C, C-5), 62.73 (1C, C-5'), 58.90 (1-C, C-2), 56.44 (1C, C-2'), 25.14 and 25.10 (2 tBu), -4.91 and -5.36 (Si*Me*$_2$);

Anal. calcd. for $C_{44}H_{62}Cl_6N_2O_{13}Si_2$: 48.22 % C, 5.7% H, 2.56 % N, found 48.19 % C, 5.62% H, 2.41% N; HRMS (ESI-TOF): calcd. for $C_{44}H_{62}Cl_6N_2NaO_{13}Si_2$ $[M+Na]^+$ 1115.1814; found 1115.1808

Synthesis of (7)

2-Amino-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranosyl-(1→1)-2-amino-4,6-*O*-benzylidene-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranoside (7)

A solution of the disaccharide **6** (0.93 g, 0.84 mmol) in glacial acetic acid (15 ml) was stirred with Zn powder (2.8 g, 42.3 mmol) for 2h under atmosphere of Ar. The solids were removed by filtration over a pad of Celite®, the filtrate was concentrated and repeatedly evaporated with toluene (3×30 ml). The residue was diluted with EtOAc (200 ml) and washed with satd. aq. $NaHCO_3$ (50 ml) and water (50 ml), dried and concentrated. The residue was purified by silica gel chromatography (hexane/EtOAc 2:1→ 0.5% Et_3N in EtOAc /MeOH 8:1) to afford **7** as colourless solid (0.51 g, 82%); R_f 0.4 (B, EtOAc); $[\alpha]_D^{20}$= 33.6 (*c* 0.9, $CHCl_3$);

^{1}H NMR (600 MHz, $CHCl_3$): δ 7.48-7.46 and 7.37-7.34 (m, 10H, 2x CH*Ph*), 5.48 (2s, 2H, 2x C*H*Ph), 5.17 (d, 1H, $^3J_{1',2'}$=3.8 Hz, H-1'), 4.53 (d, 1H, $^3J_{1,2}$=8.1 Hz, H-1), 4.26 (dd, 1H, $^3J_{5,6a}$=4.5, $^2J_{6a,6b}$ =10.5 Hz, H-6a), 4.18 (dd, 1H, $^3J_{5',6a'}$=5.0, $^2J_{6a',6b'}$ =10.2 Hz, H-6a'), 4.05 (dt, 1H, $^3J_{5',6a'}$ = 5.0, $^3J_{5',6b'}$ = $^3J_{4',5'}$ = 10.0 Hz, H-5'), 3.77 (t, 1H, $^3J_{6a,6b}$ = $^3J_{5,6b}$ = 10.0 Hz, H-6b), 3.74 (t, 1H, $^3J_{2',3'}$ = $^3J_{3',4'}$ = 9.1 Hz, H-3'), 3.69 (t, 1H, $^3J_{5',6b'}$ = $^3J_{6a',6b'}$ = 10.2 Hz, H-3), 3.67 (t, 1H, $^3J_{2,3}$ = $^3J_{3,4}$ = 8.8 Hz, H-3), 2.95 (dd, 1H, $^3J_{1,2}$ = 8.2, $^3J_{2,3}$ = 8.9 Hz, H-2), 2.81 (dd, 1H, $^3J_{1',2'}$ = 3.7, $^3J_{2',3'}$ = 9.2 Hz, H-2'), 0.86 (2s, 18H, 2tBu), 0.09 and 0.08 (2s, 6H, 2 SiMe), -0.01 (s, 6H, 2SiMe);

^{13}C NMR (150.9 MHz, $CHCl_3$): δ 137.38 and 137.21 (2C, C_q-Ph), 129.05, 128.99, 128.13, 126.34 (10C, Ph), 104.71 (1C, C-1) 102.05 and 102.04 (2C, 2 Ph*C*H), 101.93 (1C, C-1'), 82.16 (1C, C-4'), 81.50 (1C, C-4), 74.97 (1C, C-3), 74.40 (1C, C-3'), 68.90 (1C, C-6'), 68.81 (1C, C-6), 67.04 (1C, C-5), 63.57 (1C, C-5'), 59.38 (1C, C-2), 57.95 (1C, C-2'), 25.91 (2C, 2 tBu), -3.91, -4.64 and -4.78 (Si*Me*$_2$);

Anal. calcd. For $C_{38}H_{60}N_2O_9Si_2$: 61.26 % C, 8.12% H, 3.76% N, found: 61.29% C, 8.01% H, 3.56%; N HRMS (ESI-TOF): calcd. for $C_{38}H_{61}N_2O_9Si_2$ $[M+H]^+$ 745.391; found 745.3908.

Synthesis of (8-10)

3-*O*-Benzyl protected β-hydroxy fatty acids **8-10** were prepared according to the reported procedures.[1-3]

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(2) Bazin, H.G., Bess, L.S., Livesay, M.T., Ryter, K.T., Johnson, C.L., Arnold, J.S., and Johnson, D.A. (2006) New synthesis of glycolipid immunostimulants RC-529 and CRX-524. *Tetrahedron Letters 47,* 2087-2092.

(3) Fukase, K., Fukase, Y., Oikawa, M., Liu, W.C., Suda, Y., and Kusumoto, S. (1998) Divergent synthesis and biological activities of lipid A analogues of shorter acyl chains. *Tetrahedron 54,* 4033-4050.

Synthesis of (11)

4,6-*O*-Benzylidene-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranoside (11)

To a solution of **10** (162 mg, 0.483 mmol) and DIPEA (0.580 mmol, 96 µl) in DMF (1 ml) a solution of O-(7-azabenzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium hexafluorophosphate (HATU, 0.532 mmol, 202 mg) in DMF (1 ml) was added. The mixture was stirred under Ar for 30 min, then a solution of amine **7** (120 mg, 0.161 mmol) in 1 ml DMF was added. The stirring was continued for 5 h, the reaction mixture was diluted with EtOAc (100 ml), washed with satd. aq. $NaHCO_3$ (30 ml) and water (30 ml), dried over Na_2SO_4 and concentrated. The residue was purified by size exclusion chromatography (BioBeads SX1, 15×800 mm, elution with toluene/CH_2Cl_2 3:1, 0.5 ml/min) followed by silica gel chromatography (hexane/EtOAc; 6:1) to give **11** (186 mg, 82%) as colorless sirup; R_f 0.74 (A, hexane/EtOAc 2:1), $[\alpha]_D^{20}$= -30.2 (*c* 0.7, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$); δ 7.50-7.48 and 7.46-7.43 and 7.39-7.31 and 7.18-7.15 (m, 20H, Ph), 6.84 (d, 1H, $^3J_{2,NH}$ =8.7 Hz, NH), 6.55 (d, 1H, $^3J_{2',NH'}$ =9.8 Hz, NH'), 5.51 (s, 1H, PhC*H'*), 5.42 (s, 1H, PhC*H*), 4.80 (d, 1H, $^3J_{1',2'}$ =3.5 Hz, H-1'), 4.58 and 4.54 (2AB, 2H, J_{AB}=10.7 Hz, PhCH_2'), 4.44 (dt, 1H, $^3J_{2',3'}$= $^3J_{2',NH'}$= 9.8, $^3J_{1',2'}$ =3.5 Hz, H-2'), 4.33 and 3.66 (2AB, J_{AB}=11.0 Hz, 2H, CH_2Ph), 4.19 (dd, 1H, $^3J_{5,6a}$ =5.0, $^3J_{6a,6b}$ =10.4 Hz, H-6a), 4.08 (m, 3H, 5',6a', ^{Myr}βCH), 3.96 (d, 1H, $^3J_{1,2}$ =8.2 Hz, H-1), 3.94 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ =9.3 Hz, H-3'), 3.81 (dt, 1H, $^3J_{2,NH}$ =$^3J_{2,3}$ =8.9, $^3J_{1,2}$ =8.6 Hz, H-2), 3.71 (m, 2H, H-6b, H-6b'), 3.55 (m, 2H, H-4', ^{Myr}βCH'), 3.35 (t, 1H, $^3J_{3,4}$ =$^3J_{4,5}$ =9.1 Hz, H-4), 3.08 (dt, 1H, $^3J_{4,5}$ =$^3J_{H\text{-}5,H\text{-}5}$ =9.7, $^3J_{5,6a}$ =5.0 Hz, H-5), 3.02 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ =9.1 Hz, H-3), 2.53 (m, 2H, ^{Myr}αCHa, ^{Myr}αCHa'), 2.38 (dd, 1H, $^3J_{MyrαCHa',\ MyrβCH'}$ =3.0, $^2J_{MyrαCHa',\ MyrαCHb'}$ =15.1 Hz, ^{Myr}αCHb'), 2.22 (dd, 1H, $^3J_{MyrαCHa,\ MyrβC'}$ =2.2, $^2J_{MyrαCHa,\ MyrαCHb}$=15.9 Hz, ^{Myr}αCHb), 1.68-1.19 (m, 53H, $^{Myr}CH_2$), 0.89 (t, 6H, $^{Myr}CH_3$), 0.81 and 0.75 (2s, 9H, tBu), 0.01, -0.03, -0.16 and -0.18 (4s, 12H, SiMe);

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 173.09 and 171.28 (2C, FA-C=O), 139.70, 137.92, 137.28 and 137.11 (4C, Ph-C_q), 129.10, 128.95, 128.87, 128.42, 128.30, 128.20, 128.14, 128.09, 127.65, 126.32 and 126.28 (20C, Ph), 102.87 (1C, C-1), 101.90 (1C, Ph*C*H'), 101.79 (1C, Ph*C*H), 101.15 (1C, C-1'), 82.42 (1C, C-4'), 81.14 (1C, C-4), 77.84 (1C, ^{Myr}βC'), 76.25 (1C, ^{Myr}βC), 73.34 (1C, $^{Myr}CH_2$Ph'), 72.81 (1C, C-3), 71.07 (1C, C-3'), 70.96 (1C, $^{Myr}CH_2$Ph'), 68.69 (1C, C-6), 68.57 (1C, C-6'), 65.63 (1C, C-5), 63.53 (1C, C-5'), 56.84 (1C, C-2), 53.43 (1C, C-2'), 42.26 (FA-CO*C*H_2'), 40.84 (FA-CO*C*H_2), 35.05, 32.75, 31.92, 29.96, 29.86, 29.68, 29.36, 25.82, 22.88, 22.68, 18.04 and 17.94 ($^{Myr}CH_2$), 25.68 and 25.64 (6C, tBu), 14.09 (2C, $^{Myr}CH_3$), -4.08, -4.17, -4.74 and -4.95 (4C, SiMe);

HRMS (ESI-TOF): calcd. for $C_{80}H_{124}N_2NaO_{13}Si_2$ $[M+H]^+$ 1376.8642; found 1399.8536

Synthesis of (12)

4,6-*O*-Benzylidene-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranoside (12)

Compound **12** was prepared from **7** (300 mg, 0.403 mmol) in the way described for the synthesis of **11** using **9** (1.21 mmol, 336 mg), HATU (459 mg, 1.21 mmol) and DIPEA (220 µl, 1.33 mmol). Yield: 399 mg (75 %), R_f 0.74 (A, hexane/EtOAc 2:1), $[\alpha]_D^{20}$= -34.45 (*c* 0.9, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.48 and 7.45-7.43 and 7.39-7.32 and 7.17-7.16 (m, 20H, Ph), 6.83 (d, 1H, $^3J_{2,NH}$ =8.7 Hz, NH), 6.54 (d, 1H, $^3J_{2',NH'}$ =9.8 Hz, NH'), 5.50 (s, 1H, PhC*H'*), 5.41 (s,1H, PhC*H*), 4.79 (d, 1H, $^3J_{1',2'}$ =3.5 Hz, H-1'), 4.58 and 4.54 (2AB, 2H, J_{AB}=10.7 Hz, CH_2Ph'), 4.44 (dt, 1H, $^3J_{2',3'}$= $^3J_{2',NH'}$= 9.8, $^3J_{1',2'}$ =3.5 Hz, H-2'), 4.33 and 3.66 (2AB, 2H, J_{AB}=11.1 Hz, CH_2Ph), 4.19 (dd, 1H, $^3J_{5,6a}$ =5.1, $^3J_{6a,6b}$ =10.5 Hz, H-6a), 4.08 (m, 3H, H-5',H-6a', ^{Laur}βCH'), 3.96 (d, 1H, $^3J_{1,2}$ =8.2 Hz, H-1), 3.93 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ =9.4 Hz, H-3'), 3.81 (dt, 1H, $^3J_{2,NH}$ =$^3J_{2,3}$ =8.9, $^3J_{1,2}$ =8.6 Hz, H-2), 3.71 (t, 1H, $^3J_{5',6b'}$ =$^2J_{6a',6b'}$ =9.8 Hz H-6b'), 3.71 (t, 1H, $^3J_{5,6b}$ =$^2J_{6a,6b}$ =10.3 Hz, H-6b), 3.57 (t, 1H, $^3J_{4',5'}$ =$^3J_{3',4'}$ =9.3 Hz, H-4'), 3.53 (m, 1H, ^{Laur}βCH), 3.35 (t, 1H, $^3J_{3,4}$ =$^3J_{4,5}$ =9.1 Hz, H-4), 3.08 (dt, 1H, $^3J_{4,5}$ =$^3J_{5,6b}$ =9.7, $^3J_{5,6a}$ =5.1 Hz, H-5), 3.02 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ =9.2 Hz, H-3), 2.53 (m, 2H, ^{Laur}αCHa, ^{Laur}αCHa'), 2.38 (dd, $^3J_{\text{LaurαCHb', LaurβCH'}}$ =3.0, $^2J_{\text{LaurαCHa', LaurαCHb'}}$ =15.1 Hz, 1H, ^{Laur}αCHb'), 2.22 (dd, $^3J_{\text{LaurαCHb, LaurβCH}}$ =2.3, $^2J_{\text{LaurαCHa, LaurαCHb}}$ =16.0 Hz, 1H, ^{Laur}αCHb), 1.67-1.19 (m, 38H, $^{Laur}CH_2$), 0.90 (t, *J*=7.0 Hz, 3H, $^{Laur}CH_3$) 0.89 (t, 3H, *J*=7.0 Hz, $^{Laur}CH_3$), 0.80 and 0.74 (2s,9H, tBu), 0.01, -0.03, -0.16 and -0.18 (4s, 12H, SiMe);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 173.10 and 171.29 (2C, FA-C=O), 139.73, 137.95, 137.32 and 137.15 (4C, Ph-C_q), 129.12, 128.97, 128.89, 128.44, 128.35, 128.22, 128.17, 128.11, 128.07 127.67, 126.35 and 126.31 (20C, Ph), 102.89 (1C, C-1), 101.93 (1C, Ph*C*H'), 101.82 (1C, Ph*C*H), 101.18 (1C, C-1'), 82.46 (1C, C-4'), 81.17 (1C, C-4), 77.86 (1C, ^{Laur}βC'), 76.28 (1C, ^{Laur}βC), 73.35 (1C, $^{Laur}CH_2$Ph'), 72.84 (1C, C-3), 71.10 (1C, C-3'), 70.99 (1C, $^{Laur}CH_2$Ph), 68.72 (1C, C-6), 68.60 (1C, C-6'), 65.67 (1C, C-5), 63.56 (1C, C-5'), 56.87 (1C, C-2), 53.46 (1C, C-2'), 42.28 (^{Laur}αC'), 40.88 (^{Laur}αC), 35.08, 32.79, 31.94, 29.97, 29.87, 29.70, 29.64, 29.36, 25.84, 22.92, 22.70 ($^{Laur}CH_2$), 25.70 and 25.66 (6C, tBu), 14.11 (2C, $^{Laur}CH_3$), -4.05, -4.14 and -4.92 (4C, SiMe);

HRMS (ESI-TOF): calcd. for $C_{76}H_{118}N_2O_{13}Si_2$ $[M+2H]^{2+}$ 661.4086; found 661.4089.

Synthesis of (13)

4,6-*O*-Benzylidene-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-2-deoxy-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-*tert*-butyldimethylsilyl-2-deoxy-α-D-glucopyranoside (13)

Compound **13** was prepared from **7** (138 mg, 0.185 mmol) in the way described for the synthesis of **11** using **8** (833 mmol, 232 mg), HATU (324 mg, 0.852 mmol) and DIPEA (141 µl, 852 mmol). Yield: 163 mg (70 %), R_f 0.74 (A, hexane/EtOAc 2:1), $[\alpha]_D^{20}$= -33.4 (*c* 1, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51-7.49 and 7.46-7.44 and 7.40-7.33 and 7.18-7.17 (m, 20H, Ph), 6.84 (d, 1H, $^3J_{H,NH}$ =8.7 Hz, NH), 6.53 (d, 1H, $^3J_{2,NH'}$ =9.8 Hz, NH'), 5.51 (s, 1H, PhC*H*'), 5.42 (s,1H, PhC*H*), 4.80 (d, 1H, $^3J_{1',2'}$ =3.5 Hz, H-1'), 4.59 and 4.55 (2AB, 2H, J_{AB}=10.7 Hz, CH_2Ph'), 4.45 (dt, 1H, $^3J_{2',3'}$= $^3J_{2',NH'}$= 9.8, $^3J_{1',2'}$ =3.5 Hz, H-2'), 4.34 and 3.66 (2AB, 2H, J_{AB}=11.1 Hz, CH_2Ph), 4.20 (dd, 1H, $^3J_{5,6a}$ =5.0, $^3J_{6a,6b}$ =10.4 Hz, H-6a), 4.11 (m, 2H, H-6a', ^{Capr}βCH), 4.07 (dd, 1H, $^3J_{5',6a'}$ =5.0, $^3J_{4',5'}$ =9.9 Hz, H-5'), 3.97 (d, 1H, $^3J_{1,2}$ =8.2 Hz, H-1), 3.94 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ =9.4 Hz, H-3'), 3.81 (dt, 1H, $^3J_{2,NH}$ =$^3J_{2,3}$ =8.9, $^3J_{1,2}$ =8.6 Hz, H-2), 3.72 (t, 1H, $^3J_{5',6b'}$ =$^2J_{6a',6b'}$ =9.7 Hz, H-6b'), 3.71 (t, 1H, $^3J_{5,6b}$ =$^2J_{6a,6b}$ =10.3 Hz, H-6b), 3.58 (t, 1H, $^3J_{4',5'}$ =$^3J_{3',4'}$ =9.2 Hz, H-4'), 3.54 (m, 1H, ^{Capr}βCH), 3.35 (t, 1H, $^3J_{3,4}$ =$^3J_{4,5}$ =9.1 Hz, H-4), 3.09 (dt, 1H, $^3J_{4,5}$ =$^3J_{5,6b}$ =9.7, $^3J_{5,6a}$ =5.0 Hz, H-5), 3.03 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ =9.2 Hz, H-3), 2.53 (m, 2H, ^{Capr}αCHa, ^{Capr}αCHa'), 2.39 (dd, 1H, $J_{Capr\alpha CHa' Capr\beta CH'}$=3.0, $^2J_{Capr\alpha CHa', Capr\alpha CHb'}$=15.1 Hz, ^{Capr}αCHb'), 2.22 (dd, 1H, $^3J_{Capr\alpha CHa Capr\beta CH}$=2.2, $^2J_{Capr\alpha CHa, Capr\alpha CHb}$=15.9 Hz, ^{Capr}αCHb'), 1.67-1.19 (m, 38H, $^{Capr}CH_2$), 0.91 (t, *J*=7.1 Hz, 3H, $^{Capr}CH_3$) 0.90 (t, 3H, *J*=7.0 Hz, $^{Capr}CH_3$), 0.81 and 0.75 (2s,9H, tBu), 0.01, -0.02, -0.16 and -0.18 (4s, 12H, SiMe);

^{13}C NMR (75.47 MHz, $CDCl_3$): δ 173.08 and 171.26 (2C, FA-C=O), 139.69, 137.91, 137.28 and 137.11 (4C, Ph-C_q), 129.09, 128.94, 128.86, 128.41, 128.32, 128.19, 128.14, 128.08, 127.64, 126.31 and 126.27 (20C, Ph), 102.86 (1C, C-1), 101.89 (1C, Ph*C*H'), 101.78 (1C, Ph*C*H), 101.14 (1C, C-1'), 82.41 (1C, C-4'), 81.13 (1C, C-4), 77.84 (1C, ^{Capr}βC'), 76.24 (1C, ^{Capr}βC), 73.33 (1C, CH_2Ph), 72.80 (1C, C-3), 71.07 (1C, C-3'), 70.95 (1C, CH_2Ph), 68.68 (1C, C-6), 68.56 (1C, C-6'), 65.62 (1C, C-5), 63.52 (1C, C-5'), 56.83 (1C, C-2), 53.41 (1C, C-2'), 42.25 (^{Capr}αC'), 40.83 (^{Capr}αC), 35.04, 32.74, 31.85, 29.88, 29.79, 29.30, 29.24, 25.81, 22.86, 22.63 ($^{Capr}CH_2$), 25.67 and 25.63 (6C, tBu), 14.08 (2C, $^{Capr}CH_3$), -4.08, -4.18, -4.75 and -4.96 (4C, SiMe)

HRMS (ESI-TOF): calcd. for $C_{72}H_{110}N_2O_{13}Si_2$ $[M+2H]^{2+}$ 633.3773; found 633.3768

Synthesis of (14)

4,6-*O*-Benzylidene-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-α-D-glucopyranoside (14)

A solution of disaccharide **11** (623 mg, 0.452 mmol)) in dry THF (5 ml) and tetrabutylammonium fluoride (TBAF) (1M in THF) (4.52 mmol, 4.52 ml) was stirred under atmosphere of Ar for 5h. The reaction mixture was diluted with EtOAc (150 ml), washed with satd. aq. $NaHCO_3$ (50 ml) and water (50 ml), dried over Na_2SO_4 and concentrated. The residue was purified by precipitation (3×) with EtOH (25 ml) from CH_2Cl_2 (5 ml) as follows: the residue was dissolved in CH_2Cl_2 (5 mL), then EtOH (25 mL) was added. The volume was reduced to 10 mL by concentration, the suspension was diluted with EtOH (10 mL) and kept at 4°C for 1h, the precipitate was separated on the glass filter and washed with EtOH (10 mL). The solids were re-dissolved in CH_2Cl_2 (10 ml) and the solution was concentrated to dryness. The residue was additionally purified by flash chromatography on silica gel (toluene/ EtOAc, 1:1) to give **14** (503 mg, 96%) as white amorphous solid; R_f 0.5 (A, hexane/EtOAc, 1:1), $[\alpha]_D^{20}$= -9.0 (*c* 0.8, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.47 and 7.41-7.25 (m, 20H, Ph), 6.62 (d, 1H, $^3J_{2',NH'}$ =8.8 Hz, NH'), 6.36 (d, 1H, $^3J_{2,NH}$ =7.2 Hz, NH), 5.51 and 5.50 (2s, 2H, 2 PhC*H*), 4.77 (d, 1H, $^3J_{1',2'}$ =3.8 Hz, H-1'), 4.61 and 4.50 (2AB, J_{AB}=11.3 Hz, 2H, CH_2Ph'), 4.52 and 4.32 (2AB, J_{AB}=11.8 Hz, 2H, CH_2Ph), 4.20 (m, 2H, H-2', H-6a), 4.11 (dd, 1H, $J_{5',6a'}$ =4.8, $J_{6a',6b'}$ =9.9 Hz, H-6a'), 4.05 (m, 1H, ^{Myr}βCH'), 3.94 (td, 1H, $J_{4',5'}$= $J_{5',6b'}$ =9.9, $J_{5',6a'}$ =5.0 Hz, H-5'), 3.88 (d, 1H, $J_{1,2}$ =8.1 Hz, H-1), 3.85 (m, 1H, H-2), 3.74 (m, 1H, ^{Myr}βCH), 3.68 (m, 3H, H-3', H-6b, H-6b'), 3.51 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.4 Hz, H-4'), 3.45 (t, $J_{3,4}$ =

$J_{4,5}$ = 9.2 Hz, 1H, H-4), 3.21-3.10 (m, 3H, H-3, H-5, OH), 2.93 (br. s, 1H, OH'), 2.55-2.43 (m, 4H, $^{Myr}\alpha CH_2$, $^{Myr}\alpha CH_2$'), 1.80-1.21 (m, 40H, $^{Myr}CH_2$), 0.88 (t, 6H, $^{Myr}CH_3$);

^{13}C NMR (100.6MHz, $CDCl_3$): δ 173.67 and 173.10 (2C, 2 C=O), 138.96, 137.95, 137.14 and 136.97 (4C, Ph-C_q), 129.28, 129.16, 128.70, 128.63, 128.31, 128.27, 128.24, 128.08, 128.04, 127.78, 126.34 and 126.30 (20C, Ph), 102.3 (1C, C-1), 101.80 (2C, Ph*C*H, Ph*C*H'), 100.18 (1C, C-1'), 81.69 (1C, C-4'), 80.83 (1C, C-4), 78.26 (1C, $^{Myr}\beta C$'), 76.92 (1C, $^{Myr}\beta C$), 72.34 (1C, C-3), 72.29 (1C, *C*H_2Ph'), 71.20 (1C, CH_2Ph), 70.21 (1C, C-3'), 68.53 (1C, C-6 or C-6'), 68.47 (1C, C-6 or C-6'), 66.14 (1C, C-5), 63.04 (1C, C-5'), 56.46 (1C, C-2), 53.85 (1C, C-2'), 41.59 and 40.97 (2C, $^{Myr}\alpha C$ and $^{Myr}\alpha C$'), 34.34, 33.31, 31.92, 29.80, 29.66, 29.60, 29.36, 25.66, 25.24 and 22.69 (*C*H_2), 14.12 (2C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{68}H_{97}N_2O_{13}$ $[M+H]^+$ 1149.6985; found 1149.6984.

Synthesis of (15)

4,6-*O*-Benzylidene-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-2-deoxy-α-D-glucopyranoside (15)

Compound **15** was prepared from **12** (364 mg, 0.257 mmol) in the way described for the synthesis of **14** using a 1M solution of TBAF in THF (2.75 mmol, 2.75 ml). Yield: 279 mg (93 %), R_f 0.5 (A, hexane/EtOAc 1:1),
$[\alpha]_D^{20}$= -9.5 (*c* 1.2, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49-7.47 and 7.39-7.27 (m, 20H, Ph), 6.61 (d, 1H, $^3J_{2',NH'}$ =8.8 Hz, NH'), 6.36 (d, 1H, $^3J_{2,NH}$ =7.6 Hz, NH), 5.51 and 5.41 (2s, 2H, 2 PhC*H*), 4.79 (d, 1H, $^3J_{1',2'}$ =3.8 Hz, H-1'), 4.61 and 4.50 (2AB, 2H, J_{AB}=11.3 Hz, CH_2Ph'), 4.52 and 4.32 (2AB, 2H, J_{AB}=11.8 Hz, CH_2Ph), 4.21 (m, 2H, H-2', H-6a), 4.11 (dd, 1H, $J_{5',6a'}$ =5.1, $J_{6a',6b'}$ =10.2 Hz, H-6a'), 4.04 (m, 1H, $^{Laur}\beta CH$'), 3.94 (td, 1H, $J_{4',5'}$= $J_{5',6b'}$ =10.0, $J_{5',6a'}$ =5.07 Hz, H-5'), 3.91 (d, 1H, $J_{1,2}$ =8.3 Hz, H-1), 3.85 (td, 1H, $J_{1,2}$ = $J_{2,NH}$ =7.9, $J_{2,3}$ = 9.9 Hz, H-2), 3.74 (m, 1H, $^{Laur}\beta CH$), 3.69 (m, 3H, H-3', H-6b, H-6b'), 3.52 (t, 1H, $J_{3',4'}$ = $J_{4',5'}$ = 9.4 Hz, H-4'), 3.46 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.2 Hz, H-4), 3.20 (br. t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, H-3), 3.14 (m, 2H, H-5, OH), 2.92 (br. d, 1H, $J_{H\text{-}3',OH'}$ = 3.0 Hz, OH') 2.57-2.43 (m, 4H, $^{Laur}\alpha CH_2$, $^{Laur}\alpha CH_2$'), 1.77-1.23 (m, 32H, CH_2), 0.88 (t, 6H, CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 173.62 and 173.08 (2C, 2 C=O), 138.96, 137.94, 137.14 and 136.97 (4C, 4 Ph-C_q), 129.26, 129.13, 128.69, 128.61, 128.29, 128.25, 128.22, 128.05, 128.02, 127.77, 126.33 and 126.28 (20C, Ph), 102.30 (1C, C-1), 101.80 and 101.79 (2C, Ph*C*H, Ph*C*H'), 100.17 (1C, C-1'), 81.69 (1C, C-4'), 80.83 (1C, C-4), 78.21 (1C, $^{Laur}\beta C$'), 76.91 (1C, $^{Laur}\beta C$), 72.33 (1C, C-3), 72.27 (1C, *C*H_2Ph'), 71.21 (1C, CH_2Ph), 70.25 (1C, C-3'), 68.53 (1C, C-6'), 68.47 (1C, C-6), 66.14 (1C, C-5), 63.03 (1C, C-5'), 56.45 (1C, C-2), 53.84 (1C, C-2'), 41.57 and 40.96 (2C, $^{Laur}\alpha C$' and $^{Laur}\alpha C$), 34.32, 33.30, 31.89, 29.77, 29.69, 29.63, 29.58, 29.56, 29.31, 25.63, 25.23 and 22.66 (*C*H_2), 14.08 (2C, 2 *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{64}H_{89}N_2O_{13}$ $[M+H]^+$ 1093.6359; found 1093.6366.

Synthesis of (16)

4,6-*O*-Benzylidene-2-[(*R*)-3-(benzyloxy)decanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-2-[(*R*)-3-(benzyloxy)decanoylamino]-2-deoxy-α-D-glucopyranoside (16)

Compound **16** was prepared from **13** (300 mg, 0.237 mmol) in the way described for the synthesis of **14** using a 1M solution of TBAF in THF (2.37 mmol, 2.37 ml). Yield: 223 mg (91 %), R_f 0.45 (A, hexane/EtOAc 1:1),
$[\alpha]_D^{20}$= -10.4 (*c* 1.3, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.50-7.47 and 7.40-7.24 (m, 20H, Ph), 6.62 (d, 1H, $^3J_{2',NH'}$ =8.4 Hz, NH'), 6.36 (d, 1H, $^3J_{2,NH}$ =7.8 Hz, NH), 5.51 and 5.50 (2s, 2H, 2 PhC*H*), 4.79 (d, 1H, $^3J_{1',2'}$ =3.6 Hz, H-1'), 4.61 and 4.50 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph'), 4.51 and 4.32 (2AB, 2H, J_{AB}=12 Hz, CH_2Ph), 4.23-4.18 (m, 2H, H-2', H-6a), 4.11 (dd, 1H, $J_{5',6a'}$ =5.4, $J_{6a',6b'}$ =10.2 Hz, H-6a'), 4.04 (m, 1H, $^{Capr}\beta CH$'), 3.94 (td, 1H, $J_{4',5'}$= $J_{5',6b'}$ =10.2, $J_{5',6a'}$ =5.4 Hz, H-5'), 3.91 (d, 1H, $J_{1,2}$ =8.4 Hz, H-1), 3.85 (td, 1H, $J_{1,2}$ = $J_{2,NH}$ =7.9, $J_{2,3}$ = 9.9 Hz, H-2), 3.74 (m, 1H, $^{Capr}\beta CH$), 3.72-3.66 (m, 3H, H-3', H-6b, H-6b'), 3.52 (t,

1H, $J_{3',4'} = J_{4',5'}$ = 9.6 Hz, H-4'), 3.45 (t, 1H, $J_{3,4} = J_{4,5}$ = 9 Hz, H-4), 3.20 (br. t, 1H, $J_{2,3} = J_{3,4}$ = 9.3 Hz, H-3), 3.14 (m, 2H, H-5, OH), 2.95 (br. s, 1H, OH') 2.57-2.44 (m, 4H, $^{Capr}\alpha CH_2$, $^{Capr}\alpha CH_2'$), 1.77-1.23 (m, 24H, CH_2), 0.88 (2t, 6H, 2 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 173.61 and 173.08 (2C, 2 C=O), 138.96, 137.94, 137.14 and 136.97 (4C, Ph-C_q), 129.25, 129.12, 128.68, 128.60, 128.28, 128.24, 128.21, 128.03, 128.01, 127.98, 127.76, 126.32 and 126.28 (20C, Ph), 102.30 (1C, C-1), 101.78 (2C, Ph*C*H, Ph*C*H'), 100.15 (1C, C-1'), 81.68 (1C, C-4'), 80.81 (1C, C-4), 78.20 (1C, $^{Capr}\beta CH'$), 76.90 (1C, $^{Capr}\beta CH$), 72.31 (1C, C-3), 72.26 (1C, *C*H_2Ph'), 71.20 (1C, CH_2Ph), 70.26 (1C, C-3'), 68.52 and 68.46 (2C, C-6', C-6), 66.14 (1C, C-5), 63.02 (1C, C-5'), 56.45 (1C, C-2), 53.84 (1C, C-2'), 41.57 and 40.95 (2C, $^{Capr}\alpha C'$ and $^{Capr}\alpha C$), 34.32, 33.29, 31.80, 31.78, 29.71, 29.63, 29.27, 29.20, 25.62, 25.21, 22.62 and 22.61 (*C*H_2), 14.06 (2C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{60}H_{81}N_2O_{13}$ $[M+H]^+$ 1037.5733; found 1037.5734.

Synthesis of (17)

4,6-*O*-Benzylidene-3-[(*R*)-3-(benzyloxy)tetradecanoyl]-2-[(*R*)-3-*O*-(benzyloxy)tetradecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-3-[(*R*)-3-*O*-(benzyloxy)tetradecanoyl]-2-[(*R*)-3-*O*-(benzyloxy)-tetradecanoylamino]-2-deoxy-α-D-glucopyranoside (17)

To a stirred solution of diol **14** (50 mg, 0.04 mmol) in dry CH_2Cl_2 (1 ml), fatty acid **10** (0.13 mmol, 44 mg), diisopropylcarbodiimide (DIC) (0.9 mmol, 14 µl) and dimethylaminopyridine (DMAP) (cat.) were added under argon atmosphere. The reaction mixture was stirred under atmosphere of Ar for 6h, filtered over cotton, diluted with CH_2Cl_2 (50 ml) and washed with $NaHCO_3$ (2×10 ml) and water (20 ml). The organic phase was dried over cotton and concentrated. The residue was purified by precipitation (3×) with EtOH (10 ml) from CH_2Cl_2 (1.5 ml) as follows: the residue was dissolved in CH_2Cl_2 (1.5 mL), then EtOH (10 mL) was added. The volume was reduced to 5 ml by concentration, the suspension was diluted with EtOH (5 mL) and kept at 4°C for 1h; white fluffy precipitate was separated on the glass-filter and washed with EtOH (3 mL). The precipitate was re-dissolved in CH_2Cl_2 (10 mL) and the solution was concentrated to dryness. The residue was re-purified by HPLC (YMC-silica gel, 5µ, hexane/EtOAc; 2/1) to give **17** as white solid (62 mg, 80%); R_f 0.5 (hexane/EtOAc, 2:1); $[\alpha]_D^{20}$= -14.7 (*c* 1.0, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.19 (m, 30H, Ph), 6.48 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.39 (d, 1H, $^3J_{2,NH}$ =8.4 Hz, NH), 5.42 and 5.38 (2s, 2H, 2 PhC*H*), 5.38 (t, 1H, $^3J_{2',3'} = {}^3J_{3',4'}$ = 10.1 Hz, H-3'), 4.97 (t, 1H, $^3J_{2,3} = {}^3J_{3,4}$ 10.2 Hz, H-3), 4.68 (d, 1H, $^3J_{1',2'}$ =4 Hz, H-1'), 4.57 and 4.49 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.46 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.45 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.41 and 4.18 (2AB, 2H, J_{AB}=12 Hz, CH_2Ph) 4.46 (m, 1H, H-2'), 4.20 (dd, 1H, $J_{5,6a}$ =5.4, $J_{6a,6b}$ =10.2 Hz, H-6a), 4.15-4.10 (m, 2H, 5',6a'), 4.07 (m, 1H, H-2), 3.95 (m, 1H, $^{Myr}\beta CH$), 3.88 (d, $J_{1,2}$ =8.0 Hz, 1H, H-1), 3.81-3.73 (m, 2H, 2 $^{Myr}\beta CH$), 3.73-3.67 (m, 3H, H-4', H-6b, H-6b'), 3.57 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.6 Hz, H-4), 3.52 (m, 1H, $^{Myr}\beta CH$), 3.24 (dt, 1H, $J_{5,6a}$ =5.4, $J_{4,5} = J_{5,6b}$ = 9.6 Hz, H-5), 2.68-2.60 and 2.47-2.26 (m, 8H, $^{Myr}\alpha CH_2$), 1.66-1.10 (m, 80H, CH_2), 0.88 (t, 12H, CH_3),

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.38, 171.55, 171.38, 171.33 (4C, 4 C=O), 139.23, 138.63, 138.43, 138.17, 136.86, 136.67 (6C, Ph-C_q), 129.06, 128.96, 128.62, 128.38, 128.21, 128.15, 128.01, 127.93, 127.69, 127.66, 127.42, 127.28, 126.06 (30C, Ph), 102.53 (1C, C-1), 101.35 (2C, Ph*C*H, Ph*C*H'), 100.22 (1C, C-1'), 79.05 (1C, C-4'), 78.17 (1C, C-4), 77.15 (1C, $^{Myr}\beta C$), 75.73 (1C, $^{Myr}\beta C$), 75.49 (1C, $^{Myr}\beta C$), 75.37 (1C, $^{Myr}\beta C$), 72.08 (1C, *C*H_2Ph), 71.08 (2C, 2 *C*H_2Ph), 71.03 (1C, C-3), 70.58 (1C, *C*H_2Ph), 70.49 (1C, C-3'), 68.46 (2C, C-6', C-6), 66.28 (1C, C-5), 63.36 (1C, C-5'), 54.04 (1C, C-2), 51.32 (1C, C-2'), 41.49, 41.06, 39.80 and 39.74 (4C, 4 αC), 34.62, 34.46, 34.41, 33.37, 31.92, 31.84, 29.84, 29.70, 29.68, 29.65, 29.56, 29.37, 25.61, 25.16, 25.08, 25.01, 22.68, (*C*H_2), 14.11 (4C, *C*H_3)
HRMS (ESI-TOF): calcd. for $C_{110}H_{160}N_2NaO_{17}$ $[M+Na]^+$ 1804.1609; found 1804.1597

Synthesis of (18)

4,6-*O*-Benzylidene-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)-tetradecanoylamino]-2-deoxy-α-D-glucopyranoside (18)

Compound **18** was prepared from **14** (50 mg, 0.043 mmol) in the way described for the synthesis of **17** using fatty acid **9** (0.13 mmol, 40 mg), DIC (0.087 mmol, 14 µl) and DMAP. Yield: 65 mg (89 %), R_f 0.5 (hexane/EtOAc, 2:1); $[\alpha]_D^{20}$= -14.7 (*c* 0.9, $CHCl_3$)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41-7.19 (m, 30H, Ph), 6.45 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.39 (d, 1H, $^3J_{2,NH}$ =8.4 Hz, NH), 5.41 and 5.38 (2s, 2H, 2 PhC*H*), 5.38 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ 10.0 Hz, H-3'), 4.97 (t, $^3J_{2,3}$ =$^3J_{3,4}$ = 9.8 Hz, 1H, H-3), 4.67 (d, 1H, $^3J_{1',2'}$ =3.6 Hz, H-1'), 4.57 and 4.49 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.46 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.45 and 4.35 (2AB, J_{AB}=11.4 Hz, 2H, CH_2Ph), 4.41 and 4.18 (2AB, J_{AB}=12 Hz, 2H, CH_2Ph) 4.47 (m, 1H, H-2'), 4.20 (dd, 1H, $J_{5,6a}$ =5.4, $J_{6a,6b}$ =10.2 Hz, H-6a), 4.15-4.09 (m, 2H, 5',6a'), 4.06 (m, 1H, H-2), 3.95 (m, 1H, ^{Laur}βCH), 3.90 (d, 1H, $J_{1,2}$ =8.4 Hz, H-1), 3.81-3.73 (m, 2H, 2 ^{Myr}βCH) 3.73-3.66 (m, 3H, H-4', H-6b, H-6b'), 3.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.52 (m, 1H, ^{Laur}βCH), 3.23 (dt, 1H, $J_{5,6a}$ =5.4, $J_{4,5}$ = $J_{5,6b}$ = 9.6 Hz, H-5), 2.68-2.58 (m, 2H, ^{Myr}αCH_2), 2.47-2.26 (m, 6H, 2 ^{Laur}αCH_2, ^{Myr}αCH_2), 1.63-1.10 (m, 72H, CH_2), 0.88 (t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.35, 171.55, 171.37, 171.30 (4C, 4 C=O), 139.25, 138.66, 138.46, 138.19, 136.89, 136.70 (6C, Ph-C_q), 129.05, 128.95, 128.62, 128.48, 128.37, 128.21, 128.15, 128.00, 127.92, 127.68, 127.66, 127.42, 127.27, 126.07 (30C, Ph), 102.52 (1C, C-1), 101.37 (2C, Ph*C*H, Ph*C*H'), 100.22 (1C, C-1'), 79.07 (1C, C-4'), 78.20 (1C, C-4), 77.13 (1C, ^{Laur}βC), 75.76 (1C, ^{Laur}βC), 75.51 (1C, ^{Myr}βC), 75.39 (1C, ^{Myr}βC), 72.07 (1C, *C*H_2Ph), 71.09 (2C, 2 *C*H_2Ph), 71.05 (1C, C-3), 70.60 (1C, *C*H_2Ph), 70.53 (1C, C-3'), 68.48 (2C, C-6', C-6), 66.30 (1C, C-5), 63.38 (1C, C-5'), 54.08 (1C, C-2), 51.33 (1C, C-2'), 41.49, 41.09, 39.82 and 39.75 (4C, 4 αC), 34.64, 34.47, 34.43, 33.39, 31.91, 29.84, 29.70, 29.67, 29.56, 29.37, 29.33, 25.61, 25.15, 25.07, 25.02, 22.67 (*C*H_2), 14.10 (4C, 4 *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{106}H_{152}N_2NaO_{17}$ $[M+Na]^+$ 1748.0983; found 1748,0985.

Synthesis of (19)

4,6-*O*-Benzylidene-3-*O*-[(*R*)-3-*O*-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)tetra-decanoylamino]-2-deoxy-α-D-glucopyranoside (19)

Compound **19** was prepared from **14** (120 mg, 0.104 mmol) in the way described for the synthesis of **17** using fatty acid **8** (0.261 mmol, 73 mg), DIC (0.312 mmol, 49 µl) and DMAP. Yield: 111 mg (64 %), R_f 0.48 (hexane/EtOAc 2:1); $[\alpha]_D^{20}$= -12.53 (*c* 0.9, $CHCl_3$);

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.41-7.18 (m, 30H, Ph), 6.50 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.38 (d, 1H, $^3J_{2,NH}$ =8.7 Hz, NH), 5.42 and 5.38 (2s, 2H, 2 PhC*H*), 5.38 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ 10.2 Hz, H-3'), 4.97 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ = 9.6 Hz, H-3), 4.68 (d, 1H, $^3J_{1',2'}$ =3.6 Hz, H-1'), 4.58-4.33 (m, 5H, 4 CH_2Ph, H-2'), 4.23-4.16 (m, 2H, H-6a, C*H*aPh), 4.13-4.02 (m, 3H, H-5',H-6a', H-2), 3.95 (m, 1H, ^{Myr}βCH), 3.91 (d, 1H, $J_{1,2}$ =8.4 Hz, H-1), 3.80-3.74 (m, 2H, 2 ^{Capr}βCH) 3.73-3.67 (m, 3H, H-4', H-6b, H-6b'), 3.58 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.53 (m, 1H, ^{Myr}βCH), 3.24 (dt, 1H, $J_{5,6a}$ =5.4, $J_{4,5}$ = $J_{5,6b}$ = 9.6 Hz, H-5), 2.68-2.60 and 2.48-2.25 (m, 8H, 4 αCH_2), 1.65-1.05 (m, 64H, CH_2), 0.88 + 0.89 (2t, 12H, 4 CH_3);

^{13}C NMR (70.47 MHz, $CDCl_3$): δ 172.39, 171.59, 171.39, 171.36 (4C, 4 C=O), 139.26, 138.66, 138.47, 138.21, 136.90, 136.71 (6C, Ph-C_q), 129.07, 128.98, 128.64, 128.41, 128.23, 128.17, 128.04, 127.95, 127.71, 127.68, 127.43, 127.30, 126.09 (30C, Ph), 102.55 (1C, C-1), 101.39 (2C, Ph*C*H, Ph*C*H'), 100.25 (1C, C-1'), 79.09 (1C, C-4'), 78.21 (1C, C-4), 77.19 (1C, ^{Capr}βC), 75.77 (1C, ^{Capr}βC), 75.53 (1C, ^{Myr}βC), 75.41 (1C, ^{Myr}βC), 72.11 (1C, *C*H_2Ph), 71.11 (2C, 2 *C*H_2Ph), 70.62 (1C, *C*H_2Ph), 70.51 (1C, C-3'), 68.49 (2C, C-6', C-6), 66.31 (1C, C-5), 63.40 (1C, C-5'), 54.08 (1C, C-2), 51.38 (1C,

C-2'), 41.54, 41.11, 39.76 (4C, 4 αC), 34.64, 34.48, 33.41, 31.93, 31.83, 29.85, 29.78, 29.71, 29.68, 29.55, 29.52, 29.38, 29.29, 25.63, 25.16, 25.08, 22.69, 22.65 (*C*H_2), 14.10 (4C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{102}H_{144}N_2NaO_{17}$ $[M+Na]^+$ 1692.0348; found 1692.0356.

Synthesis of (20)

4,6-*O*-Benzylidene-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)dodecanoyl-amino]-2-deoxy-α-D-glucopyranoside (20)

Compound **20** was prepared from **15** (110 mg, 0.101 mmol) in the way described for the synthesis of **17** using fatty acid **9** (0.302 mmol, 92 mg), DIC (0.302 mmol, 47 µl) and DMAP. Yield: 132 mg (79 %), R_f 0.45 (hexane/EtOAc, 2:1); $[\alpha]_D^{20}$= -10.6 (*c* 0.9, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.20 (m, 30H, Ph), 6.47 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.39 (d, 1H, $^3J_{2,NH}$ =9 Hz, NH), 5.42 and 5.38 (2s, 2H, 2 PhC*H*), 5.38 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ 10.2 Hz, H-3'), 4.97 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ 10.2 Hz, H-3), 4.68 (d, 1H, $^3J_{1',2'}$ =3.6 Hz, H-1'), 4.56 and 4.49 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.46 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.45 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.41 and 4.18 (2AB, 2H, J_{AB}=12 Hz, CH_2Ph) 4.46-4.41 (m, 1H, H-2'), 4.20 (dd, 1H, $J_{5,6a}$ =5.4, $J_{6a,6b}$ =10.2 Hz, H-6a), 4.15-4.10 (m, 2H, H-5',H-6a'), 4.09-4.04 (m,1H, H-2), 3.95 (m, 1H, ^{Laur}βCH), 3.91 (d, $J_{1,2}$ =8.4 Hz, 1H, H-1), 3.80-3.74 (m, 2H, 2 ^{Laur}βCH) 3.73-3.67 (m, 3H, H-4', H-6b, H-6b'), 3.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.6 Hz, H-4), 3.53 (m, 1H, ^{Laur}βCH), 3.24 (dt, 1H, $J_{5,6a}$ =5.4, $J_{4,5}$ = $J_{5,6b}$ = 9.6 Hz, H-5), 2.66-2.61 and 2.46-2.27 (m, 8H, 4 ^{Laur}αCH_2), 1.66-1.10 (m, 64H, CH_2), 0.88 (t, 12H, 4 CH_3),

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.36, 171.56, 171.37, 171.32 (4C, FA-C=O), 139.26, 138.67, 138.47, 138.20, 136.90, 136.71 (6C, Ph-C_q), 129.05, 128.96, 128.63, 128.38, 128.22, 128.19, 128.16, 128.12, 128.02, 127.93, 127.91, 127.73, 127.69, 127.66, 127.42, 127.28, 126.08 (30C, Ph), 102.53 (1C, C-1), 101.40 and 101.37 (2C, Ph*C*H, Ph*C*H'), 100.23 (1C, C-1'), 79.08 (1C, C-4'), 78.20 (1C, C-4), 77.15 (1C, ^{Laur}βC), 75.76 (1C, ^{Laur}βC), 75.52 (1C, ^{Laur}βC), 75.40 (1C, ^{Laur}βC), 72.08 (1C, *C*H_2Ph), 71.10 (2C, 2 *C*H_2Ph), 71.07 (1C, C-3), 70.61 (1C, *C*H_2Ph), 70.53 (1C, C-3'), 68.53 and 68.48 (2C, C-6', C-6), 66.31 (1C, C-5), 63.39 (1C, C-5'), 54.08 (1C, C-2), 51.35 (1C, C-2'), 41.51, 41.10, 39.82 and 39.75 (4C, 4 ^{Laur}αCH_2), 34.64, 34.47, 34.43, 33.40, 31.90, 29.83, 29.76, 29.72, 29.68, 29.61, 29.58, 29.56, 39.35, 29.33, 25.60, 25.15, 25.08, 25.02, 22.67, (*C*H_2), 14.09 (2C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{102}H_{144}N_2NaO_{17}$ $[M+Na]^+$ 1692.0357; found 1692.0356.

Synthesis of (21)

4,6-*O*-Benzylidene-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-[(*R*)-3-(benzyloxy)dodecanoyl-amino]-2-deoxy-α-D-glucopyranoside (21)

Compound **21** was prepared from **15** (110 mg, 0.101 mmol) in the way described for the synthesis of **17** using fatty acid **8** (0.302 mmol, 84 mg), DIC (0.302 mmol, 47 µl) and DMAP. Yield: 126 mg (78 %), R_f 0.38 (hexane/EtOAc, 2:1); $[\alpha]_D^{20}$= -14.2 (*c* 1.1, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39-7.20 (m, 30H, Ph), 6.47 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.39 (d, 1H, $^3J_{2,NH}$ =9 Hz, NH), 5.42 and 5.38 (2s, 2H, 2 PhC*H*), 5.38 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ 10.1 Hz, H-3'), 4.97 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ 10.2 Hz, H-3), 4.68 (d, 1H, $^3J_{1',2'}$ =3.5 Hz, H-1'), 4.56 and 4.49 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.46 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.45 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.41 and 4.18 (2AB, 2H, J_{AB}=12 Hz, CH_2Ph) 4.46-4.41 (m, 1H, H-2'), 4.20 (dd, 1H, $J_{5,6a}$ =5.4, $J_{6a,6b}$ =10.2 Hz, H-6a), 4.15-4.10 (m, 2H,H-5',H-6a'), 4.09-4.04(m, 1H, H-2), 3.95 (m, 1H, ^{Laur}βCH), 3.91 (d, $J_{1,2}$ =8.3 Hz, 1H, H-1), 3.80-3.74 (m, 2H, 2 ^{Capr}βCH) 3.73-3.67 (m, 3H, H-4', H-6b, H-6b'), 3.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4), 3.53 (m, 1H, ^{Laur}βCH), 3.24 (dt, 1H, $J_{5,6a}$ =5.4, $J_{4,5}$ = $J_{5,6b}$ = 9.6 Hz, H-5), 2.66-2.61 (m, 2H, ^{Capr}αCH_2), 2.46-2.27 (m, 8H, ^{Capr}αCH_2, 2 ^{Laur}αCH_2), 1.66-1.10 (m, 56H, CH_2), 0.88 and 0.87 (2t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.38, 171.57, 171.39, 171.34 (4C, 4 C=O), 139.28, 138.69, 138.49, 138.22, 136.92, 136.73 (6C, Ph-C_q), 129.08, 128.98, 128.65, 128.40, 128.24, 128.19, 128.18, 128.15, 128.03, 127.95, 127.93, 127.77, 127.71, 127.68, 127.44, 127.30, 126.10 (30C, Ph), 102.55 (1C, C-1), 101.42 and 101.39 (2C, Ph*C*H, Ph*C*H'), 100.25 (1C, C-1'), 79.10 (1C, C-4'), 78.22 (1C, C-4), 77.17 (1C, ^{Capr}βC), 75.78 (1C, ^{Capr}βC), 75.54 (1C, ^{Laur}βC), 75.42 (1C, ^{Laur}βC), 72.10 (1C, *C*H_2Ph), 71.12 (2C, 2 *C*H_2Ph), 71.09 (1C, C-3), 70.63 (1C, *C*H_2Ph), 70.55 (1C, C-3'), 68.55 and 68.50 (2C, C-6', C-6), 66.32 (1C, C-5), 63.41 (1C, C-5'), 54.10 (1C, C-2), 51.37 (1C, C-2'), 41.53, 41.12, 39.84 and 39.77 (4C, 4 αC), 34.66, 34.49, 34.45, 33.42, 31.92, 31.84, 31.82, 29.85, 29.77, 29.73, 29.70, 29.66, 29.56, 29.53, 29.37, 29.30, 29.27, 25.62, 25.17, 25.09, 25.04, 22.69, 22.66, 22.64 (*C*H_2), 14.16 and 14.11 (4C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{98}H_{136}N_2NaO_{17}$ $[M+Na]^+$ 1635.9731; found 1635.9726.s

Synthesis of (22)

4,6-*O*-Benzylidene-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)-dodecanoyl]-2-deoxy-α-D-glucopyranoside (22)

Compound **22** was prepared from **16** (100 mg, 0.096 mmol) in the way described for the synthesis of **17** using fatty acid **9** (0.289 mmol, 89 mg), DIC (0.289 mmol, 45 µl) and DMAP. Yield: 126 mg (80 %), R_f 0.43 (hexane/EtOAc, 2:1); $[\alpha]_D^{20}$= -14.2 (*c* 1.0, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40-7.20 (m, 30H, Ph), 6.49 (d, 1H, $^3J_{2',NH'}$ =9.5 Hz, NH'), 6.39 (d, 1H, $^3J_{2,NH}$ =9.1 Hz, NH), 5.42 and 5.38 (2s, 2H, 2 PhC*H*), 5.38 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ 10.1 Hz, H-3'), 4.97 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ =10.2 Hz, H-3), 4.68 (d, 1H, $^3J_{1',2'}$ =3.6 Hz, H-1'), 4.56 and 4.49 (2AB, 2H, J_{AB}= 11.4 Hz, CH_2Ph), 4.46 and 4.35 (2AB, 2H, J_{AB}= 11.4 Hz, CH_2Ph), 4.45 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.41 and 4.18 (2AB, 2H, J_{AB}=12 Hz, CH_2Ph) 4.44 (m, 1H, H-2'), 4.20 (dd, 1H, $J_{5,6a}$ =5.6, $J_{6a,6b}$ =10.1 Hz, H-6a), 4.15-4.10 (m, 2H, H-5',H-6a'), 4.07 (m, 1H, H-2), 3.97 (m, 1H, ^{Capr}βCH), 3.91 (d, 1H, $J_{1,2}$ =8.3 Hz, H-1), 3.80-3.74 (m, 2H, 2 ^{Laur}βCH) 3.73-3.67 (m, 3H, H-4', H-6b, H-6b'), 3.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4), 3.53 (m, 1H, ^{Capr}βCH), 3.24 (dt, 1H, $J_{5,6a}$ =5.4, $J_{4,5}$ = $J_{5,6b}$ = 9.6 Hz, H-5), 2.66-2.61 (m, 2H, ^{Capr}αCH$_2$), 2.46-2.25 (m, 6H, 2 ^{Laur}αCH$_2$, ^{Capr}αCH$_2$), 1.66-1.12 (m, 61H, CH_2), 0.88 (t, 13H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.36, 171.55, 171.36, 171.32 (4C, FA-C=O), 139.25, 138.65, 138.45, 138.19, 136.89, 136.70 (6C, Ph-C_q), 129.05, 128.95, 128.62, 128.38, 128.21, 128.16, 128.15, 128.11, 128.01, 127.93, 127.90, 127.73, 127.68, 127.66, 127.42, 127.28, 126.07 (30C, Ph), 102.52 (1C, C-1), 101.39 and 101.36 (2C, Ph*C*H, Ph*C*H'), 100.22 (1C, C-1'), 79.07 (1C, C-4'), 78.20 (1C, C-4), 77.14 (1C, ^{Laur}βC), 75.75 (1C, ^{Laur}βC), 75.51 (1C, ^{Capr}βC), 75.39 (1C, ^{Capr}βC), 72.08 (1C, *C*H_2Ph), 71.09 (2C, 2 *C*H_2Ph), 71.06 (1C, C-3), 70.60 (1C, *C*H_2Ph), 70.51 (1C, C-3'), 68.52 and 68.47 (2C, C-6', C-6), 66.30 (1C, C-5), 63.38 (1C, C-5'), 54.07 (1C, C-2), 51.35 (1C, C-2'), 41.50, 41.08, 39.81 and 39.75 (4C, 4 αC), 34.63, 34.46, 34.41, 33.39, 31.89, 31.85, 29.76, 29.68, 29.62, 29.59, 29.58, 29.56, 29.55, 29.34, 29.31, 29.26, 25.58, 25.14, 25.06, 25.01, 22.66, 22.64, 22.61 (*C*H_2), 14.12 and 14.07 (4C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{98}H_{136}N_2NaO_{17}$ $[M+Na]^+$ 1635.9731; found 1635.9734.

Synthesis of (23)

4,6-*O*-Benzylidene-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-[(*R*)-3-(benzyloxy)decanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-4,6-*O*-benzylidene-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-[(*R*)-3-(benzyloxy)decanoylamino]-2-deoxy-α-D-glucopyranoside (23)

Compound **23** was prepared from **16** (100 mg, 0.096 mmol) in the way described for the synthesis of **17** using fatty acid **8** (0.289 mmol, 81 mg), DIC (0.289 mmol, 45 µl) and DMAP. Yield: 116 mg (77 %), R_f 0.44 (hexane/EtOAc, 2:1); $[\alpha]_D^{20}$= -13.9 (*c* 1.1, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$):δ 7.40-7.20 (m, 30H, Ph), 6.49 (d, 1H, $^{3}J_{2',NH'}$ =9.5 Hz, NH'), 6.39 (d, 1H, $^{3}J_{2,NH}$ =9.1 Hz, NH), 5.42 and 5.38 (2s, 2H, 2 PhC*H*), 5.38 (t, 1H, $^{3}J_{2',3'}$ =$^{3}J_{3',4'}$ 10.1 Hz, H-3'), 4.97 (t, 1H, $^{3}J_{2,3}$ =$^{3}J_{3,4}$ 10.2 Hz, H-3), 4.69 (d, 1H, $^{3}J_{1',2'}$ =3.6 Hz, H-1'), 4.56 and 4.49 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.46 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.45 and 4.35 (2AB, 2H, J_{AB}=11.4 Hz, CH_2Ph), 4.41 and 4.18 (2AB, 2H, J_{AB}=12 Hz, CH_2Ph), 4.46-4.44 (m, 1H, H-2'), 4.20 (dd, 1H, $J_{5,6a}$ =5.6, $J_{6a,6b}$ =10.1 Hz, H-6a), 4.15-4.10 (m, 2H, H-5',H-6a'), 4.09-4.04 (m, 1H, H-2), 3.95 (m, 1H, ^{Capr}βCH), 3.91 (d, 1H, $J_{1,2}$ =8.3 Hz, H-1), 3.80-3.74 (m, 2H, 2 ^{Capr}βCH) 3.73-3.67 (m, 3H, H-4', H-6b, H-6b'), 3.57 (t, 1H, $J_{3,4}$ = $J_{4,5}$ = 9.7 Hz, H-4), 3.53 (m, 1H, ^{Capr}βCH), 3.24 (dt, 1H, $J_{5,6a}$ =5.4, $J_{4,5}$ = $J_{5,6b}$ = 9.6 Hz, H-5), 2.67-2.61 and 2.46-2.25 (m, 8H, ^{Capr}αCH_2), 1.66-1.12 (m, 52H, CH_2), 0.88 and 0.87 (2t, 13H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.39, 171.58, 171.39, 171.35 (4C, 4 C=O), 139.28, 138.68, 138.48, 138.22, 136.92, 136.72 (6C, Ph-C_q), 129.08, 128.98, 128.65, 128.41, 128.24, 128.19, 128.18, 128.14, 128.04, 127.96, 127.93, 127.77, 127.71, 127.69, 127.44, 127.31, 126.10 (30C, Ph), 102.55 (1C, C-1), 101.42 and 101.39 (2C, Ph*C*H, Ph*C*H'), 100.25 (1C, C-1'), 79.10 (1C, C-4'), 78.22 (1C, C-4), 77.18 (1C, ^{Capr}βC), 75.78 (1C, ^{Capr}βC), 75.54 (1C, ^{Capr}βC), 75.42 (1C, ^{Capr}βC), 72.11 (1C, *C*H_2Ph), 71.12 (2C, 2 *C*H_2Ph), 71.09 (1C, C-3), 70.63 (1C, *C*H_2Ph), 70.55 (1C, C-3'), 68.55 and 68.50 (2C, C-6', C-6), 66.32 (1C, C-5), 63.41 (1C, C-5'), 54.10 (1C, C-2), 51.38 (1C, C-2'), 41.53, 41.12, 39.83 and 39.77 (4C, 4 ^{Capr}αC), 34.65, 34.48, 34.44, 33.42, 31.87, 31.83, 31.82, 29.79, 29.71, 29.56, 29.52, 29.36, 29.33, 29.29, 29.27, 25.60, 25.17, 25.09, 25.03, , 22.66, 22.63 (*C*H_2), 14.13 and 14.09 (4C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{94}H_{128}N_2NaO_{17}$ $[M+Na]^+$ 1579.9105; found 1579.9102.

Synthesis of (24)

6-*O*-Benzyl-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]3-*O*-[(*R*)-3-(benzyloxy)tetradecanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)tetradecanoyl]-2-deoxy-α-D-glucopyranoside (24)

A solution of the bis-benzylidene derivative **17** (100 mg, 0.056 mmol) in dry CH_2Cl_2 (5 ml) was stirred with activated powdered molecular sieves (4Å, 0.5 g) under atmosphere of Ar for 3h at rt. The mixture was cooled to -78°C and Et_3SiH (74µl, 0.46 mmol,) and TfOH (0.56 mmol, 50µl) were added successively under atmosphere of Ar. The reaction mixture was stirred at -78°C for 3h, then Et_3N (0.589 mmol, 82µl) and MeOH (0.5ml) were added, the mixture was stirred for 10 min. The mixture was let to warm up to rt, diluted with EtOAc (100 ml) and washed successively with satd. aq. $NaHCO_3$ (30 ml), water (30 ml) and brine (20 ml).The organic phase was dried and concentrated. The residue was purified by HPLC (YMC silica gel, 20x250mm, gradient elution with toluene/EtOAc, 9:1→3:1) which afforded **24** as colourless syrup (90 mg, 89%); R_f 0.42 (A, toluene/EtOAc, 2:1), $[\alpha]_D^{20}$= 6.5 (*c* 1.1, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34-7.21 (m, 30H, Ph), 6.43 (d, 1H, $^{3}J_{2',NH'}$ =9.6 Hz, NH'), 6.32 (d, 1H, $^{3}J_{2,NH}$ =7.8 Hz, NH), 5.11 (dd, 1H, $^{3}J_{2',3'}$ =10.2, $^{3}J_{3',4'}$ = 9 Hz, H-3'), 4.76 (d, 1H, $^{3}J_{1',2'}$ =4.2 Hz, H-1'), 4.74 (dd, 1H, $^{3}J_{2,3}$ =10.8, $^{3}J_{3,4}$ =9 Hz, H-3), 4.53-4.38 (m, 10H, 5 $PhCH_2$), 4.38-4.33 (m, 2H, H-2', PhCH_2a), 4.21 (d, 1H J_{AB} =11.4 Hz, PhCH_2b), 4.10 (m, 1H, H5'), 4.02 (d, 1H, $^{3}J_{1,2}$ = 8.4 Hz, H-1), 3.93-3.88 (m, 2H, H-2, ^{Myr}βCH), 3.86-3.81 (m, 2H, 2 ^{Myr}βCH), 3.72 (br. dt, 1H, $^{3}J_{3',4'}$=$^{3}J_{4',5'}$ = 9.6 Hz, $^{3}J_{H\text{-}4',OH'}$= 3 Hz, H-4'), 3.61-3.50 (m, 6H, H-4, H-6ab, H-6'ab, ^{Myr}βCH), 3.30 (app dt, 1H,$^{3}J_{4,5}$=$^{3}J_{5,6a}$ =9.6 Hz, $^{3}J_{5,6b}$ =4.8 Hz, H-5), 2.90 (br s, OH), 2.61 (m, 2H, αCH_2a, OH') 2.56 (dd, 1H, ^{Myr}αCH_2a), 2.44-2.31 (m, 5H, ^{Myr}αCH_2), 2.23 (dd, 1H, ^{Myr}αCH_2), 1.66-1.10 (m, 80H, CH_2), 0.88 (2t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.62, 172.32, 171.38 (4C, 4×C=O), 139.16, 138.37, 138.18, 138.13, 138.07, 137.76 (6C, Ph-C_q), 128.57, 128.46, 128.34, 127.94, 127.88, 127.81, 127.76, 127.69, 127.61, 127.52 (30C, Ph), 101.35 (1C, C-1), 99.32 (1C, C-1'), 75.88, 75.83 and 75.80 (3C, 3 ^{Myr}βC), 75.23 (C-3), 75.03 (C-3'), 74.05 (C-5), 73.55 and 73.46 (2C, CH_2Ph), 71.96 (CH_2Ph), 71.60 (C-5'), 71.18 and 71.03 (2C, CH_2Ph), 70.62 (CH_2Ph), 70.02 (1C, C-4), 69.98 (1C, C-6), 69.54 (C-4'), 69.07 (C-6'), 53.44 (C-2), 50.53 (C-2') 41.53, 41.14, 39.87 and 39.78 (4C, 4 ^{Myr}αC), 34.50, 34.27, 34.11, 33.51, 31.93, 31.86, 29.83, 29.77, 29.68, 29.63, 29.38, 29.36, 29.31, 25.62, 25.15, 22.69 (*C*H_2), 14.10 (4C, 4 *C*H_3);

HRMS (ESI-TOF): calcd. for $C_{110}H_{166}N_2O_{17}$ $[M+2H]^{2+}$ 893.6093; found 893.6074

Synthesis of (25)

6-*O*-Benzyl-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-α-D-glucopyranoside (25)

Compound **25** was prepared from **18** (140 mg, 0.081 mmol) in the way described for the synthesis of **24** using Et_3SiH (0.49 mmol, 79 µl), TfOH (0.649 mmol, 58 µl) and Et_3N (0.689 mmol, 96µl). Yield: 120 mg (86 %), R_f 0.42 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$= 5.0 (*c* 1.0, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 30H, Ph), 6.43 (d, 1H, $^3J_{2',NH'}$ =9.4 Hz, NH'), 6.33 (d, 1H, $^3J_{2,NH}$ =7.9 Hz, NH), 5.11 (dd, 1H, $^3J_{2',3'}$ =10.3, $^3J_{3',4'}$ = 9.1 Hz, H-3'), 4.76 (d, 1H, $^3J_{1',2'}$ =4.2 Hz, H-1'), 4.74 (dd, 1H, $^3J_{2,3}$ =10.7, $^3J_{3,4}$ = 9.2 Hz, H-3), 4.54-4.38 (m, 10H, 5 $PhCH_2$) 4.38-4.33 (m, 2H, H-2', $PhCH_2$a), 4.22 (d, 1H J_{AB} =11.4 Hz, $PhCH_2$b), 4.10 (m, 1H, H5'), 4.02 (d, 1H, $^3J_{1,2}$ = 8.5 Hz, H-1), 3.94-3.89 (m, 2H, H-2, ^{Myr}βCH), 3.86-3.81 (m, 2H, 2 ^{Laur}βCH), 3.73 (br. dt, 1H, $^3J_{3',4'}$=$^3J_{4',5'}$ =9.6 Hz, $^3J_{H\text{-}4',OH'}$= 3 Hz, H-4'), 3.61-3.50 (m, 6H, H-4, H-6ab, H-6'ab, ^{Myr}βCH), 3.30 (app dt, 1H, $^3J_{4,5}$=$^3J_{5,6a}$ =9.5 Hz, $^3J_{5,6b}$ =4.8 Hz, H-5), 2.91 (br s, 1H, OH), 2.64-2.53 (m, 3H, ^{Myr}αCH_2, OH'), 2.45-2.31 (m, 5H, ^{Myr}αCH_2, ^{Laur}αCH_2, ^{Laur}αCH_2a), 2.23 (dd, 1H, ^{Laur}αCH_2b), 1.65-1.10 (m, 72H, CH_2), 0.88 (t, 12H, 4 CH_3);

^{13}C NMR (75.47 MHz, $CDCl_3$): δ 172.61, 172.33, 172.30, 171.38 (4C, 4 C=O), 139.15, 138.34, 138.15, 138.12, 138.04, 137.74 (6C, Ph-C_q), 128.56, 128.44, 128.32, 127.92, 127.86, 127.80, 127.74, 127.68, 127.60, 127.51 (30C, Ph), 101.34 (1C, C-1), 99.32 (1C, C-1'), 75.87, 75.78 (3C, 3 βC) 75.20 (C-3), 75.01 (C-3'), 74.03 (C-5), 73.53 and 73.44 (2C, CH_2Ph), 71.94 (CH_2Ph), 71.58 (C-5'), 71.17 and 71.02 (2C, CH_2Ph), 70.59 (CH_2Ph), 69.99 (1C, C-4), 69.96 (1C, C-6), 69.50 (C-4'), 69.03 (C-6'), 53.41 (C-2), 50.51 (C-2') 41.52, 41.11, 39.85 and 39.76 (4C, αC), 34.48, 34.24, 34.09, 33.48, 31.91, 31.89, 29.81, 29.69, 29.61, 29.56, 29.36, 29.31, 25.61, 25.13, 22.67 (CH_2), 14.09 (4C, 4 CH_3);
HRMS (ESI-TOF): calcd. for $C_{106}H_{156}N_2O_{17}$ $[M+Na]^+$ 1752.1296; found 1752.1299.

Synthesis of (26)

6-*O*-Benzyl-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-2-deoxy-α-D-glucopyranoside (26)

Compound **26** was prepared from **19** (107 mg, 0.064 mmol) in the way described for the synthesis of **24** using Et_3SiH (0.255 mmol, 42 µl), TfOH (0.255 mmol, 23 µl) and Et_3N (0.383 mmol, 53µl). Yield: 86 mg (80 %), R_f 0.43 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$= 9.9 (*c* 1.1, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.21 (m, 30H, Ph), 6.44 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.32 (d, 1H, $^3J_{2,NH}$ =7.8 Hz, NH), 5.11 (dd, 1H, $^3J_{2',3'}$ =10.2, $^3J_{3',4'}$ = 9 Hz, H-3'), 4.76 (d, 1H, $^3J_{1',2'}$ =4.2 Hz, H-1'), 4.74 (dd, 1H, $^3J_{2,3}$ =10.8, $^3J_{3,4}$ = 9 Hz, H-3), 4.53-4.38 (m, 10H, 5 $PhCH_2$) 4.38-4.33 (m, 2H, H-2', PhCH_2a), 4.21 (d, 1H, J_{AB} =11.4 Hz, PhCH_2b), 4.10 (m, 1H, H5'), 4.02 (d, 1H, $^3J_{1,2}$ = 8.4 Hz, H-1), 3.93-3.88 (m, 2H, H-2, ^{Capr}βCH), 3.86-3.81 (m, 2H, 2 ^{Myr}βCH), 3.72 (br. dt, 1H, $^3J_{3',4'}$=$^3J_{4',5'}$ =9.6 Hz, $^3J_{H\text{-}4',OH'}$= 3 Hz, H-4'), 3.62-3.50 (m, 6H, H-4, H-6ab, H-6'ab, ^{Capr}βCH), 3.30 (app dt, 1H, $^3J_{4,5}$=$^3J_{5,6a}$ =9.6 Hz, $^3J_{5,6b}$ =4.8 Hz, H-5), 2.93 (d, 1H, $^3J_{4,OH}$= 3 Hz, OH), 2.65 (d, 1H, $^3J_{4',OH'}$= 3 Hz, OH'), 2.61 (dd, 1H, ^{Capr}αCH_2a) 2.56 (dd, 1H, ^{Capr}αCH_2a), 2.44-2.32 (m, 5H, ^{Capr}αCH_2b, ^{Myr}αCH_2, ^{Myr}αCH_2a), 2.23 (dd, 1H, ^{Myr}αCH_2b) , 1.63-1.22 (m, 64H, CH_2), 0.88 (2t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.62, 172.36, 172.31, 171.40 (4C, 4 C=O), 139.17, 138.36, 138.19, 138.14, 138.06, 137.77 (6C, Ph-C_q), 128.58, 128.47, 128.36, 128.35, 128.32, 127.95, 127.90, 127.89, 127.83, 127.77, 127.71, 127.63, 127.61, 127.55, 127.54 (30C, Ph), 101.36 (1C, C-1), 99.35 (1C, C-1'), 75.90, 75.83 and 75.82 (3C, βC) 75.24 (C-3), 75.02 (C-3'), 74.06 (H-5), 73.56 and 73.47 (2 C, CH_2Ph), 71.98 (CH_2Ph), 71.61 (H-5'), 71.21 and 71.06 (2C, CH_2Ph),

70.62 (CH_2Ph), 69.99 (2C, C-4, C-6), 69.52 (C-4'), 69.07 (C-6'), 53.44 (C-2), 50.55 (C-2') 41.55, 41.14, 39.87 and 39.78 (4C, 4 αC), 34.51, 34.25, 34.11, 33.51, 31.94, 31.83, 31.81, 29.84, 29.78, 29.74, 29.73, 29.71, 29.68, 29.62, 29.58, 29.38, 29.28, 29.25, 25.63, 25.16, 22.70, 22.66 (CH_2), 14.11 and 14.10 (4C, 4 CH_3);
HRMS (ESI-TOF): calcd. for $C_{102}H_{148}N_2NaO_{17}$ $[M+Na]^+$ 1696.067; found 1696.0669.

Synthesis of (27)

6-*O*-Benzyl-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)-dodecanoyl]-2-deoxy-α-D-glucopyranoside (27)

Compound **27** was prepared from **20** (168 mg, 0.101 mmol) in the way described for the synthesis of **24** using Et_3SiH (0.402 mmol, 65 µl), TfOH (0.604 mmol, 54 µl) and Et_3N (0.503 mmol, 70µl). Yield: 111 mg (65 %), R_f 0.36 (toluene/EtOA, 2:1); $[\alpha]_D^{20}$= 6.24 (*c* 1.0, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.21 (m, 30H, Ph), 6.43 (d, 1H, $^3J_{2',NH'}$ =9.4 Hz, NH'), 6.32 (d, 1H, $^3J_{2,NH}$ =7.7 Hz, NH), 5.12 (dd, 1H, $^3J_{2',3'}$ =10.3, $^3J_{3',4'}$ = 9.1 Hz, H-3'), 4.77 (d, 1H, $^3J_{1',2'}$ =4.2 Hz, H-1'), 4.76 (dd, 1H, $^3J_{2,3}$ =10.7, $^3J_{3,4}$ = 9.2 Hz, H-3), 4.53-4.38 (m, 10H, 5 $PhCH_2$) 4.38-4.33 (m, 2H, H-2', $PhCH_2$a), 4.22 (d, 1H J_{AB} =11.4 Hz, $PhCH_2$b), 4.10 (m, 1H, H5'), 4.02 (d, 1H, $^3J_{1,2}$ = 8.5 Hz, H-1), 3.95-3.90 (m, 2H, H-2, ^{Laur}βCH), 3.87-3.82 (m, 2H, 2 ^{Laur}βCH), 3.73 (br. dt, 1H, $^3J_{3',4'}$=$^3J_{4',5'}$ =9.5 Hz, $^3J_{H\text{-}4',OH'}$= 3 Hz, H-4'), 3.60-3.50 (m, 6H, H-4, H-6ab, H-6'ab, ^{Laur}βCH), 3.30 (app dt, 1H, $^3J_{4,5}$=$^3J_{5,6a}$ =9.4 Hz, $^3J_{5,6b}$ =4.8 Hz, H-5), 2.97 (br. d, 1H, OH), 2.70 (br. d, 1H, OH'), 2.63-2.54 (m, 2H, ^{Laur}αCH_2a), 2.44-2.32 (m, 5H, ^{Laur}αCH_2), 2.23 (dd, 1H, ^{Laur}αCH_2b) , 1.65-1.20 (m, 64H, CH_2), 0.88 (t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.62, 172.37, 172.31, 171.41 (4C, 4 C=O), 139.17, 138.34, 138.19, 138.15, 138.05, 137.78 (6C, Ph-C_q), 128.58, 128.47, 128.37, 128.35, 128.33, 127.96, 127.91, 127.90, 127.83, 127.77, 127.72 (30C, Ph), 101.36 (1C, C-1), 99.36 (1C, C-1'), 75.91, 75.83 (3C, 3 ^{Laur}βC) 75.25 (C-3), 74.99 (C-3'), 74.09 (C-5), 73.57 and 73.47 (2C, 2 CH_2Ph), 71.98 (CH_2Ph), 71.62 (C-5'), 71.23 and 71.08 (2C, CH_2Ph), 70.62 (CH_2Ph), 69.98 (2C, C-4, C-6), 69.50 (C-4'), 69.07 (C-6'), 53.44 (C-2), 50.58 (C-2') 41.56, 41.14, 39.87 and 39.78 (4C, 4 ^{Laur}αC), 34.50, 34.24, 34.10, 33.52, 31.92, 31.83, 29.77, 29.73, 29.69, 29.68, 29.63, 29.61, 29.58, 29.37, 29.34, 25.63, 25.16, 22.69 (CH_2), 14.14 and 14.11 (4C, 4 CH_3);
HRMS (ESI-TOF): calcd. for $C_{102}H_{148}N_2NaO_{17}$ $[M+Na]^+$ 1696.067; found 1696.0669.

Synthesis of (28)

6-*O*-Benzyl-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-α-D-glucopyranoside (28)

Compound **28** was prepared from **21** (111 mg, 0.069 mmol) in the way described for the synthesis of **24** using Et_3SiH (0.257 mmol, 44 µl), TfOH (0.413 mmol, 37 µl) and Et_3N (0.481 mmol, 67µl). Yield: 90 mg (80 %), R_f 0.29 (toluene/EtOAc, 3:1); $[\alpha]_D^{20}$= 7.9 (*c* 1.2, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.20 (m, 30H, Ph), 6.44 (d, 1H, $^3J_{2',NH'}$ =9.4 Hz, NH'), 6.32 (d, 1H, $^3J_{2,NH}$ =7.7 Hz, NH), 5.12 (dd, 1H, $^3J_{2',3'}$ =10.2, $^3J_{3',4'}$ = 9.2 Hz, H-3'), 4.77 (d, 1H, $^3J_{1',2'}$ =4.2 Hz, H-1'), 4.76 (dd, 1H, $^3J_{2,3}$ =10.7, $^3J_{3,4}$ = 9.2 Hz, H-3), 4.53-4.38 (m, 10H, 5 $PhCH_2$) 4.38-4.33 (m, 2H, H-2', $PhCH_2$a), 4.22 (d, 1H, J_{AB} =11.4 Hz, $PhCH_2$b), 4.10 (m, 1H, H5'), 4.02 (d, 1H, $^3J_{1,2}$ = 8.4 Hz, H-1), 3.93-3.88 (m, 2H, H-2, ^{Laur}βCH), 3.86-3.81 (m, 2H, 2 ^{Capr}βCH), 3.72 (br. dt, 1H, $^3J_{3',4'}$=$^3J_{4',5'}$ =9.5 Hz, $^3J_{H\text{-}4',OH'}$= 3 Hz, H-4'), 3.61-3.49 (m, 6H, H-4, H-6ab, H-6'ab, ^{Laur}βCH), 3.30 (app dt, 1H, $^3J_{4,5}$=$^3J_{5,6a}$ =9.3 Hz, $^3J_{5,6b}$ =4.7 Hz, H-5), 2.94 (br. d, 1H, OH), 2.67 (br. d, 1H, OH'), 2.67-2.54 (m, 2H, ^{Capr}αCH_2), 2.44-2.32 (m, 5H, ^{Capr}αCH_2, ^{Laur}αCH_2, ^{Laur}αCH_2a), 2.23 (dd, 1H, ^{Laur}αCH_2b), 1.65-1.20 (m, 56H, CH_2), 0.88 (t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.62, 172.36, 172.31, 171.40 (4C, FA-C=O), 139.18, 138.36, 138.19, 138.15, 138.06, 137.77 (6C, Ph-C_q), 128.59, 128.47, 128.37, 128.35, 128.33, 128.21, 127.95, 127.90, 127.83, 127.77, 127.71, 127.63, 127.61, 127.55, 127.54 (30C, Ph), 101.36 (1C, C-1), 99.35 (1C, C-1'), 75.90, 75.83, 75.82 (3C, 3 βC) 75.24 (C-3), 75.02 (C-3'), 74.06 (C-5), 73.57 and 73.47 (2C, FA-CH_2Ph), 71.97 (CH_2Ph), 71.61 (C-5'), 71.21 and 71.06 (2C, CH_2Ph), 70.62 (CH_2Ph), 70.01 (2C, C-4, C-6 or C-6'), 69.53 (C-4'), 69.07 (C-6 or C-6'), 53.44 (C-2), 50.55 (C-2') 41.55, 41.14, 39.87 and 39.78 (4C, α*C*H_2), 34.50, 34.26, 34.11, 33.51, 31.92, 31.83, 29.77, 29.73, 29.69, 29.65, 29.62, 29.58, 29.36, 29.27, 29.25, 25.62, 25.15, 22.69 (*C*H_2), 14.10 (4C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{98}H_{140}N_2NaO_{17}$ $[M+Na]^+$ 1640.0049; found 1640.0035.

Synthesis of (29)

6-*O*-Benzyl-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-deoxy-α-D-glucopyranoside (29)

Compound **29** was prepared from **22** (114 mg, 0.071 mmol) in the way described for the synthesis of **24** using Et_3SiH (0.283 mmol, 46 µl), TfOH (0.424 mmol, 38 µl) and Et_3N (0.494 mmol, 69µl). Yield: 95 mg (83 %), R_f 0.43 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$= 6.2 (*c* 1.1, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.21 (m, 30H, Ph), 6.45 (d, 1H, $^3J_{2',NH'}$ =9.3 Hz, NH'), 6.33 (d, 1H, $^3J_{H\text{-}2,NH}$ =7.6 Hz, NH), 5.12 (dd, 1H, $^3J_{2',3'}$ =10.2, $^3J_{3',4'}$ = 9.2 Hz, H-3'), 4.77 (d, 1H, $^3J_{1',2'}$ =4.2 Hz, H-1'), 4.75 (dd, 1H, $^3J_{2,3}$ =10.6, $^3J_{3,4}$ = 9.2 Hz, H-3), 4.54-4.39 (m, 10H, 5 $PhCH_2$) 4.38-4.34 (m, 2H, H-2', $PhCH_2$a), 4.22 (d, 1H, J_{AB} =11.4 Hz, $PhCH_2$b), 4.10 (m, 1H, H-5'), 4.02 (d, 1H, $^3J_{1,2}$ = 8.3 Hz, H-1), 3.93-3.89 (m, 2H, H-2, ^{Capr}βCH), 3.86-3.82 (m, 2H, 2 ^{Laur}βCH), 3.72 (br. dt, 1H, $^3J_{3',4'}$=$^3J_{4',5'}$ =9.4 Hz, $^3J_{4',OH'}$= 3.3 Hz, H-4'), 3.62-3.50 (m, 6H, H-4, H-6ab, H-6'ab, ^{Capr}βCH), 3.30 (app dt, 1H, $^3J_{4,5}$=$^3J_{5,6a}$ =9.2 Hz, $^3J_{5,6b}$ =4.6 Hz, H-5), 2.94 (br. d, 1H, OH), 2.66 (br. d, 1H, OH'), 2.63-2.54 (m, 2H, ^{Laur}αCH_2), 2.44-2.32 (m, 5H, ^{Laur}αCH_2, ^{Capr}αCH_2), 2.23 (dd, 1H, ^{Capr}αCH_2) , 1.65-1.19 (m, 56H, CH_2), 0.90-0.84 (m, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.62, 172.35, 172.31, 171.40 (4C, 4 C=O), 139.18, 138.36, 138.19, 138.15, 138.06, 137.78 (6C, Ph-C_q), 128.58, 128.47, 128.35, 128.33, 127.95, 127.90, 127.83, 127.77, 127.71, 127.63, 127.61, 127.54 (30C, Ph), 101.35 (1C, C-1), 99.33 (1C, C-1'), 75.90, 75.83 (3C, 3 βC) 75.25 (C-3), 75.01 (C-3'), 74.09 (C-5), 73.57 and 73.48 (2C, 2 CH_2Ph), 71.97 (CH_2Ph), 71.62 (C-5'), 71.21 and 71.07 (2C, CH_2Ph), 70.63 (CH_2Ph), 69.98 (2C, C-4, C-6), 69.52 (C-4'), 69.09 (C-6'), 53.45 (C-2), 50.57 (C-2') 41.55, 41.14, 39.87 and 39.78 (4C, CO*C*H_2), 34.50, 34.25, 34.10, 33.51, 31.90, 31.87, 29.77, 29.71, 29.67 29.63, 29.60, 29.58, 29.36, 29.32, 25.61, 25.15, 22.66 (*C*H_2), 14.09 (4C, *C*H_3);
HRMS (ESI-TOF): calcd. for $C_{98}H_{142}N_2O_{17}$ $[M+2H]^{2+}$ 809.5154; found 809,5132.

Synthesis of (30)

6-*O*-Benzyl-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-α-D-glucopyranoside (30)

Compound **30** was prepared from **23** (104 mg, 0.067 mmol) in the way described for the synthesis of **24** using Et_3SiH (0.267 mmol, 43 µl), TfOH (0.401 mmol, 36 µl) and Et_3N (0.467 mmol, 65µl). Yield: 73 mg (70 %), R_f 0.41 (toluene/EtOAc, 2:1); $[\alpha]_D^{20}$= 5.7 (*c* 1.0, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.17 (m, 30H, Ph), 6.45 (d, 1H, $^3J_{2',NH'}$ =9.4 Hz, NH'), 6.32 (d, 1H, $^3J_{2,NH}$ =7.7 Hz, NH), 5.12 (dd, 1H, $^3J_{2',3'}$ =10.2, $^3J_{3',4'}$ = 9.2 Hz, H-3'), 4.77 (d, 1H, $^3J_{1',2'}$ =4.2 Hz, H-1'), 4.75 (dd, 1H, $^3J_{2,3}$ =10.6, $^3J_{3,4}$ = 9.2 Hz, H-3), 4.53-4.38 (m, 10H, 5 $PhCH_2$) 4.38-4.33 (m, 2H, H-2', $PhCH_2$a), 4.22 (d, 1H, J_{AB} =11.4 Hz, $PhCH_2$b), 4.10 (m, 1H, H5'), 4.02 (d, 1H, $^3J_{1,2}$ = 8.3 Hz, H-1), 3.93-3.89 (m, 2H, H-2, ^{Capr}βCH), 3.86-3.82 (m, 2H, ^{Capr}βCH), 3.72 (br. dt, 1H, $^3J_{3',4'}$=$^3J_{4',5'}$ =9.4 Hz, $^3J_{4',OH'}$= 3.2 Hz, H-4'), 3.62-3.50 (m, 6H, H-4, H-6ab, H-6'ab, ^{Capr}βCH), 3.30 (app dt, 1H, $^3J_{4,5}$=$^3J_{5,6a}$

=9.2 Hz, $^{3}J_{5,6b}$ =4.6 Hz, H-5), 2.97 (br. d, 1H, OH), 2.70 (br. d, 1H, OH'), 2.63-2.54 (m, 2H, $^{Capr}\alpha CH_2$), 2.44-2.32 (m, 5H, $^{Capr}\alpha CH_2$), 2.23 (dd, 1H, $^{Capr}\alpha CH_2$b), 1.65-1.19 (m, 48H, CH_2), 0.89-0.85 (m, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$) δ 172.61, 172.36, 172.30, 171.40 (4C, 4 C=O), 139.17, 138.34, 138.19, 138.14, 138.05, 137.77 (6C, Ph-C_q), 128.58, 128.47, 128.37, 128.35, 128.33, 127.96, 127.90, 127.83, 127.77, 127.72, 127.63, 127.61, 127.56, 127.54 (30C, Ph), 101.36 (1C, C-1), 99.34 (1C, C-1'), 75.90, 75.83 (3C, 3 $^{Capr}\beta C$) 75.24 (C-3), 75.00 (C-3'), 74.08 (C-5), 73.57 and 73.47 (2C, 2 CH_2Ph), 71.98 (CH_2Ph), 71.61 (C-5'), 71.22 and 71.08 (2C, CH_2Ph), 70.62 (CH_2Ph), 69.99 (2C, C-4, C-6), 69.50 (C-4'), 69.08 (C-6'), 53.44 (C-2), 50.57 (C-2') 41.55, 41.14, 39.87 and 39.78 (4C, 4 αCH_2), 34.50, 34.24, 34.09, 33.51, 31.86, 31.82, 31.81 29.77, 29.71, 29.62, 29.58, 29.36, 29.32 29.27, 29.24, 25.61, 25.15, 22.66 (CH_2), 14.09 (4C, 4 CH_3);
HRMS (ESI-TOF): calcd. for $C_{94}H_{134}N_2O_{17}$ $[M+2H]^{2+}$ 781.4841; found 781.4823.

Synthesis of (31)

6-*O*-Benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)tetradecanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-[(R)-3-(benzyloxy)tetradecanoyl]-2-deoxy-α-D-glucopyranoside (31).

The tetraacylated diol **24** was dried by repeated coevaporation with dry toluene (3×10 ml). To a stirred solution of diol **24** (77 mg, 0.043 mmol) and di-*O*-benzyloxy-(*N,N*-diisopropylamino)phosphine (0.175 mmol, 59µl) in CH_2Cl_2 (3 ml) a 0.45M solution of 1*H*-tetrazole in acetonitrile (0.175 mmol, 389 µl) was added under atmosphere of Ar. The mixture was stirred for 1h, then cooled to -78°C and a solution of *m*-chloroperbenzoic acid (0.2 mmol, 35 mg) in CH_2Cl_2 (1 ml) was slowly added. The stirring was continued at -78°C for 30 min, then a solution of Et_3N (0.3 mmol) in CH_2Cl_2 (1ml) was added and the reaction mixture was allowed to warm to rt. The mixture was diluted with EtOAc (50ml) and washed with 0.1 M TEAB-buffer (2x20ml). The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by HPLC (YMC silica, 250x20), elution with toluene/EtOAc, 4:1→ 2:1), appropriate fractions were collected and passed through a gel bed of BioRad SX1 column (800x 5mm), elution with toluene/CH_2Cl_2, 3:1) to afford the diphosphate **31** (90 mg, 90%) as colorless syrup; R_f 0.39 (A, toluene/EtOAc, 3:2), $[\alpha]_D^{20}$=+9.5 (*c* 1.0, $CHCl_3$);
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.12 (m, 50H, 10Ph), 6.40 (d, 1H, $^{3}J_{2',NH'}$ =9.2 Hz, NH'), 6.28 (d, 1H, $^{3}J_{2,NH}$ =8.0 Hz, NH), 5.36 (dd, 1H, $^{3}J_{2',3'}$ =10.4, $^{3}J_{3',4'}$ = 9.2 Hz, H-3'), 4.91 (dd, 1H, $^{3}J_{2,3}$ =11,5, $^{3}J_{3,4}$ = 9.5 Hz H-3), 4.91-4.78 (m, 8H, 4CH_2, 4x $(BnO)_2P(O)$-), 4.72 (d, 1H, $^{3}J_{1',2'}$ =3.6 Hz, H-1'), 4.69 (dt, 1H, $^{3}J_{3',4'}$ =$^{3}J_{4',5'}$ =9.2, $^{3}J_{,4',P}$ = 9.8 Hz, H-4'), 4,40 (t, 1H, H-4), 4,38 (dd, 1H, H-2'), 4.52-4.13 (m, 12H, 6 CH_2Ph,), 4,20 (dt, 1H, H-5'), 3.94-3.86 (m, 3H, H-1, H-2, $\beta^{Myr}CHOBn$), 3.75-3.71 (m, 2H, 2 $\beta^{Laur}CHOBn$), 3.60-3.49 (m, 4H, H-6a, H-6'ab, $\beta^{Myr}CHOBn$), 3,47 (dd, 1H, $^{3}J_{5,6}$=5,0, $^{2}J_{6a,6b}$=11,1 Hz, H-6b) 3.29 (ddd, 1H, $^{3}J_{4,5}$=9,5, $^{3}J_{5,6a}$=1,7 Hz, H-5), 2.64-2.54 (m, 2H, $^{Myr}\alpha CH_2$ Myr), 2.43-2.10 (m, 6H, 3$^{Myr}\alpha CH_2$), 1,45-1,35 (m, 8H, 4$\gamma^{Myr}CH_2$), 1.32-1.17 (m, 80H, 36 CH_2), 0.88 (t, 12H, 4 CH_3);

^{13}C NMR (100.62 MHz, $CDCl_3$): δ 172.29, 171.63, 171.57, 171.38 (4C, 4x C=O), 139.27, 138.86, 138.73, 138.35, 138.23, 137.95 (6C, 6xPh-C_q), 135.67-135.58 (m, 4C, Ph, 2x$(BnO)_2P(O)$-), 128.55, 128.45, 128.38, 128.35, 128.19, 128.16, 128.11, 128.09, 128.02, 127.98, 127.95, 127.91, 127.72, 127.66, 127.58, 127.53, 127.38, 127.34, 127.20 (50C, 10xPh), 101.17 (1C, C-1), 99.16 (1C, C-1'), 77.14, 75.57, 75.21, 75.07 (4C, 4 $^{Myr,\ Laur}\beta CH$), 73.97 (d, 1C, $J_{C,P}$ = 5.0 Hz, C-5), 73.43, 73.35 (2C, $J_{4,P}$ = $J_{4',P}$ = 6.5 Hz, C-4, C-4'), 73.18 (2 CH_2Ph), 72.47 (C-3), 72.18 (CH_2Ph), 71.89 (C-3'), 70.97 (CH_2Ph), 70.77 (CH_2Ph), 70.58 (d, $J_{5',P}$ = 5.6 Hz, C-5'), 70.47 (CH_2Ph), 69.69-69.34 (m, 4 CH_2, 2x $(BnO)_2P(O)$-), 68.14 (C-6), 67.63 (C-6'), 53.85 (C-2), 51.10 (C-2'), 41.50, 41.12, 39.16 and 39.00 (4C, 4 $^{Myr}\alpha CH_2$), 34.46, 34.35, 34.52, 31.93, 29.88, 29.73, 29.70, 29.38, 25.58, 25.19, 25.15, 24.70, 22.68 (40 CH_2), 14.10 (4C, 4 CH_3);
^{31}P NMR ($CDCl_3$): δ -2.13, -2.26;
HRMS (ESI-TOF): calcd. for $C_{138}H_{192}N_2O_{23}P_2$ $[M+2H]^{2+}$ 1153.6695; found 1153.6677.

Synthesis of (32)

6-*O*-Benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-[(R)-3-(benzyloxy)dodecanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-[(*R)*-3-(benzyloxy)dodecanoyl]-2-deoxy-α-D-glucopyranoside (32).

Compound **32** was prepared from **25** (96 mg, 0.057 mmol) in the way described for the synthesis of **31** using 0.22 mmol, 73 µl of di-*O*-benzyloxy-(*N,N*-diisopropylamino)phosphine, a 0.45 M solution of 1*H*-tetrazole in acetonitrile (0.217 mmol, 483 µl) and *m*-chloroperbenzoic acid (0.24 mmol, 42 mg). Yield: 96 mg (74 %); R_f 0.40 (A, toluene/EtOAc, 3:2), $[\alpha]_D^{20}$=+8.5 (*c* 1.0, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.32-7.13 (m, 50H, 10 Ph), 6.34 (d, 1H, $^3J_{2',NH'}$ =9.5 Hz, NH'), 6.29 (d, 1H, $^3J_{2,NH}$ =7.8 Hz, NH), 5.36 (dd, 1H, $^3J_{2',3'}$ =10.5, $^3J_{3',4'}$ = 9.2 Hz, H-3'), 4,94-4.91 (m, 1H, H-3), 4.91-4.79 (m, 8H, 4CH_2, 4x $(BnO)_2P(O)$-), 4.72 (d, 1H, $^3J_{1',2'}$ =3.7 Hz, H-1'), 4.68 (dt , 1H, $^3J_{3',4'}$ =$^3J_{4',5'}$ = 9.3, $^3J_{4',P}$ = 9.6 Hz, H-4'), 4.51-4.22 (m, 13H, 5 CH_2Ph, CH_2aPh, H-2', H-4), 4.20 (dt, 1H, $^3J_{4',5'}$ =10.3, $^3J_{5',6a'}$=$^3J_{5',6b'}$= 2.6Hz, H-5'), 4.14 (AB, 1H, J_{AB}= 12 Hz, CH_2bPh), 3.93-3.88 (m, 3H, H-1, H-2, β^{Myr}C*H*OBn), 3.75-3.71 (m, 2H, 2 β^{Laur}C*H*OBn), 3.59-3.49 (m, 4H, H-6a, H-6'ab, β^{Myr}C*H*OBn), 3,47 (dd, 1H, 1H, $^3J_{5,6}$=5,0, $^2J_{6a,6b}$=10,8 Hz, H-6b) 3.29 (ddd, 1H,$^3J_{4,5}$ =9.8, $^3J_{5,6a}$= 1.8, $^3J_{5,6b}$= 4.9 Hz, H-5), 2.61 (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=16,5, $^3J_{\alpha H,\beta H}$=6,5 Hz, αCH_2-*Ha*), 2,56 (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=16,2, $^3J_{\alpha H,\beta H}$=6,5 Hz, αCH_2-*Ha),* 2.42-2.10 (m, 6H, 3^{Myr} αCH_2), 1.45-1.33 (m, 8H, 2$\gamma^{Myr}CH_2$, 2$\gamma^{Laur}CH_2$), 1,31-1,16 (m, 64H, 32 CH_2), 0.88 (2t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.27, 172.59, 172.58, 171.35 (4C, 4x C=O), 139.30, 138.91, 138.76, 138.38, 138.27, 137.98 (6C, 6xPh-C_q), 135.81-135.58 (m, 4C, Ph, 2x $(BnO)_2P(O)$-), 128.57, 128.55, 128.47, 128.46, 128.38, 128.37, 128.21, 128.18, 128.13, 128.08, 128.03, 127.98, 127.97, 127.92, 127.73, 127.67, 127.65, 127.59, 127.54, 127.39, 127.35, 127.20 (50C, 10xPh), 101.15 (1C, C-1), 99.13 (1C, C-1'), 77.10, 75.61, 75.23, 75.11 (4C, 2^{Myr}βCH, 2^{Laur}ßCH), 74.00 (d, $J_{C,P}$=5.4 Hz, C-5), 73.44, 73.38 (2C, $J_{4,P}$ = $J_{4',P}$ = 6.5 Hz, C-4, C-4'), 73.20, 73.17 (2 CH_2Ph), 72.49 (C-3), 72.17 (CH_2Ph), 71.96 (C-3'), 70.99 (CH_2Ph), 70.79 (CH_2Ph), 70.62 (d, $J_{C,P}$=5.5 Hz, C-5'), 70.49 (CH_2Ch), 69.69-69.35 (m, 4 C, 2x $(BnO)_2P(O)$), 68.16 (C-6), 67.69 (C-6'), 53.91 (C-2), 51.10 (C-2'), 41.50, 41.15, 39.18 and 39.03 (4C, 2$^{Myr}\alpha CH_2$, 2$^{Laur}\alpha CH_2$), 34.50, 34.38, 33.53, 31.94, 29.89, 29.81, 29.75, 29.74, 25.65, 29.63, 29.39, 25.60, 25.20, 25.17, 24.70, 22.70 (36 *C*H_2), 14.11 (4C,4 *C*H_3);

^{31}P NMR ($CDCl_3$): δ -2.11, -2.23;

HRMS (ESI-TOF): calcd. for $C_{134}H_{184}N_2O_{23}P_2$ $[M+2H]^{2+}$ 1126.6682; found 1125.6363.

Synthesis of (33)

6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)tetradecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-α-D-glucopyranoside (33).

Compound **33** was prepared from **26** (76 mg, 0.045 mmol) in the way described for the synthesis of **31** using 0.16 mmol, 53 µl of di-*O*-benzyloxy(*N,N*-diisopropylamino)phosphine, a 0.45 M solution of 1*H*-tetrazole in acetonitrile (0.16 mmol, 35 µl) and *m*-chloroperbenzoic acid (0.18 mmol, 32 mg). Yield: 91 mg (91 %); R_f 0.33 (A, toluene/EtOAc, 2:1), $[\alpha]_D^{20}$=+8.9 (*c* 1.0, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.13 (m, 50H, Ph), 6.38 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.28 (d, 1H, $^3J_{2,NH}$ =7.8 Hz, NH), 5.36 (dd, 1H, $^3J_{2',3'}$ =10.8, $^3J_{3',4'}$ = 9.0 Hz, H-3'), 4.91 (m, 1H, H-3), 4.91-4.79 (m, 8H, 4CH_2, 4x $(BnO)_2P(O)$-), 4.72 (d, 1H, $^3J_{1',2'}$ =3.6 Hz,, H-1'), 4.68 (dt , 1H, $^3J_{3',4'}$ =$^3J_{4',5'}$ = 9.4, $^3J_{4',p}$ = 9.9 Hz, H-4'), 4.52-4.22 (m, 13H, 5CH_2Ph, CH_2aPh, H-2', H-4), 4.20 (dt, 1H, $^3J_{4',5'}$ =9.6, $^3J_{5',6a'}$=$^3J_{5',6b'}$= 2.4Hz, H-5'), 4.15 (d, 1H, J_{AB}= 12 Hz, CH_2bPh), 3.93-3.87 (m, 3H, H-1, H-2, β^{Myr}C*H*OBn), 3.75-3.70 (m, 2H, 2 β^{Capr}C*H*OBn), 3.59-3.49 (m, 4H, H-6a, H-6'ab, β^{Myr}C*H*OBn), 3.48 (dd, 1H, $J_{6a,6b}$ =11.0, $^3J_{5,6b}$= 5.0 Hz, H-6b), 3,29 (ddd, 1H, $J_{4,5}$ =9.8, $^3J_{5,6a}$=2.0, $^3J_{5,6b}$= 4.9 Hz, H-5), 2.61(dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=16,4, $^3J_{\alpha H,\beta H}$=6,4 Hz, αCH_2-*Ha*), 2,57 (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=16,3, $^3J_{\alpha H,\beta H}$=6,5 Hz, αCH_2-*Ha),* 2,40 (dd, 1H,$^2J_{\alpha Ha,\alpha Hb}$=16,7, $^3J_{\alpha H,\beta H}$=6,0 Hz, αCH_2-*Hb*),

2.38-2.34 (m, 2H, αCHa, αCHb), 2.29 (dd, 1H, $^{2}J_{\alpha Ha,\alpha Hb}$=15,3, $^{3}J_{\alpha H,\beta H}$=8,0 Hz, αCH$_2$-*Ha),* 2.23 (dd, 1H, $^{2}J_{\alpha Ha,\alpha Hb}$=14,8, $^{3}J_{\alpha H,\beta H}$=3,6 Hz, αCH$_2$-*Hb)* 2.12 (dd, 1H, $^{2}J_{\alpha Ha,\alpha Hb}$=15,2, $^{3}J_{\alpha H,\beta H}$=3,7 Hz, αCH$_2$-*Hb)*, 1,45-1,41 (m, 8H, 2γ^{Myr}CH$_2$, 2γ^{Capr}CH$_2$)1.30-1.21 (m, 56H, 28 CH$_2$), 0.87 (dt 12H, 4 CH$_3$)

^{13}C NMR (150.9 MHz, CDCl$_3$): δ 172.27, 171.61, 171.58, 171.37 (4C, 4x C=O), 139.28, 138.88, 138.74, 138.37, 138.25, 137.96 (6C, 6xPh-C$_q$), 135.74, 135.70, 135.65, 135.60 (4C, Ph, 2x(BnO)$_2$P(O)-), 128.57, 125.55, 128.54, 128.47, 128.46, 128.39, 128.36, 128.20, 128.17, 128.12, 128.08, 128.02, 127.98, 127.95, 127.91, 127.73, 127.67, 127.58, 127.53, 127.39, 127.34, 127.20 (50C, 10xPh), 101.17 (1C, C-1), 99.15 (1C, C-1'), 77.13, 75.29, 75.22, 75.10 (4C, 2^{Myr}βCH, 2^{Capr}ßCH), 73.98 (d, $J_{5,P}$=5.4 Hz, C-5), 73.43 (d, $J_{4',P}$=6.5 Hz, C-4'), 73.36 (d, $J_{4,P}$=6.3 Hz, C-4), 73.19 (CH$_2$Ph), 73.17 (CH$_2$Ph), 72.49 (C-3), 72.18 (CH$_2$Ph), 71.92 (C-3'), 70.98 (CH$_2$Ph), 70.78 (CH$_2$Ph), 70.61 (d, $J_{C,P}$=5.4 Hz, C-5'), 70.48 (CH$_2$Ph), 69.69 (d, $J_{C,P}$=5.6 Hz, (BnO)P(O)-), 69.58 (d, $J_{C,P}$=5.2 Hz, (BnO)P(O)-), 69.55 (d, $J_{C,P}$=4.8 Hz, (BnO)P(O)-), 69.37 (d, $J_{C,P}$=5.5 Hz, (BnO)P(O)-), 68.15 (C-6), 67.66 (C-6'), 53.88 (C-2), 51.10 (C-2'), 41.50, 41.14, 39.16 and 39.02 (4C, 2^{Myr} α*C*H$_2$, 2^{Capr}αCH$_2$), 34.46, 34.36, 34.53, 31.93, 31.87, 31.85, 29.88, 29.74, 29.72, 29.69, 29.64, 29.38, 29.37, 29.33, 25.58, 25.18, 25.14, 24.69, 22.68 (32 *C*H$_2$), 14.10 (4C, 4 *C*H$_3$);

^{31}P NMR (CDCl$_3$): δ -2.09, -2.21
HRMS (ESI-TOF): calcd. for $C_{130}H_{176}N_2O_{23}P_2$ $[M+2H]^{2+}$ 1097.6069; found 1097.6068.

Synthesis of (34)

6-*O*-Benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-α-D-glucopyranoside (34).

Compound **34** was prepared from **27** (93 mg, 0.056 mmol) in the way described for the synthesis of **31** using 0.19 mmol, 65 µl of di-*O*-benzyloxy(*N,N*-diisopropylamino)phosphine, a 0.45 M solution of 1*H*-tetrazole in acetonitrile (0.19 mmol, 43 µl) and *m*-chloroperbenzoic acid (0.22 mmol, 39 mg). Yield: 81 mg (66 %); R_f 0.22 (A, toluene/EtOAc, 2:1), $[\alpha]_D^{20}$=+8.9 (*c* 0.9, $CHCl_3$);

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.33-7.13 (m, 50H, Ph), 6.37 (d, 1H, $^{3}J_{2',NH'}$ =9.4 Hz, NH'), 6.28 (d, 1H, $^{3}J_{2,NH}$ =8.1 Hz, NH), 5.37 (dd, $^{3}J_{2',3'}$ =10.4, $^{3}J_{3',4'}$ = 9.1 Hz, 1H, H-3'), 4.92 (m, 1H, H-3), 4.90-4.79 (m, 8H, 4x (BnO)$_2$P(O)-), 4.72 (d, 1H $^{3}J_{1',2'}$ =3.6 Hz, , H-1'), 4.69 (dt , 1H, $^{3}J_{3',4'}$ =$^{3}J_{4',5'}$ = 9.2, $^{3}J_{H\text{-}4',P}$ = 9.8 Hz, H-4'), 4.52-4.22 (m, 13H, 5 CH$_2$Ph, CH$_2$aPh, H-2', H-4), 4.20 (dt, 1H, $^{3}J_{4',5'}$ =10.0, $^{3}J_{5',6a'}$=$^{3}J_{5',6b'}$= 2.7 Hz, H-5'), 4.14 (AB, 1H, J_{AB}= 11.9 Hz, CH$_2$bPh), 3.93-3.88 (m, 3H, H-1, H-2, β^{Laur}C*H*OBn), 3.75-3.71 (m, 2H, 2 β^{Laur}C*H*OBn), 3.59-3.49 (m, 4H, H-6a, H-6'ab, β^{Laur}C*H*OBn), 3.47 (dd, 1H, $J_{6a,6b}$ =11.0, $^{3}J_{5,6b}$= 5.0 Hz, H-6b), 3,30 (ddd, 1H, $^{3}J_{4,5}$ =9.8, $^{3}J_{5,6a}$= 1.8, $^{3}J_{5,6b}$= 4.9 Hz, H-5), 2.61 (dd, 1H, $^{2}J_{\alpha Ha,\alpha Hb}$=16,5, $^{3}J_{\alpha H,\beta H}$=6,4 Hz, αCH$_2$-*Ha*), 2.57 (dd, 1H, $^{2}J_{\alpha Ha,\alpha Hb}$=16,3, $^{3}J_{\alpha H,\beta H}$=6,5 Hz, αCH$_2$-*Ha),* 2.42-2.34 (m, 2H, αCHa, αCHb), 2.30 (dd, 1H, (dd, 1H, $^{2}J_{\alpha Ha,\alpha Hb}$=15,3, $^{3}J_{\alpha H,\beta H}$=7,9 Hz, αCH$_2$-*Ha*), 2.24 (dd, 1H, (dd, 1H, $^{2}J_{\alpha Ha,\alpha Hb}$=15,0, $^{3}J_{\alpha H,\beta H}$=3,4 Hz, αCH$_2$-*Ha*), 2.12 (dd, 1H, , $^{2}J_{\alpha Ha,\alpha Hb}$=15,2, $^{3}J_{\alpha H,\beta H}$=3,8 Hz, αCH$_2$-*Hb*), 1,45-1,42 (m, 8H, 4γ^{Laur}CH$_2$), 1.33-1.16 (m, 56H, 28 CH$_2$), 0.88 (m, 12H, 4 CH$_3$);

^{13}C NMR (150.9 MHz, CDCl$_3$): δ 172.27, 171.61, 171.57, 171.36 (4C, 4x C=O), 139.28, 138.88, 138.74, 138.37, 138.25, 137.96 (6C, 6xPh-C$_q$), 135.79-135.55 (m, 4C, 2x(BnO)$_2$P(O)-), 128.56, 128.54, 128.53, 128.46, 128.45, 128.38, 128.36, 128.20, 128.16, 128.12, 128.08, 128.02, 127.98, 127.95, 127.91, 127.72, 127.66, 127.58, 127.53, 127.39, 127.34, 127.20 (50C, 10xPh), 101.15 (1C, C-1), 99.14 (1C, C-1'), 77.12, 75.59, 75.22, 75.09 (4C, 4 ^{Laur}βCH), 73.98 (d, $J_{C,P}$=5.4 Hz, C-5), 73.43 (d, $J_{4',P}$=6.2 Hz, C-4'), 73.37 (d, $J_{4,P}$=6.5 Hz, C-4), 73.19 (CH$_2$Ph), 73.16 (CH$_2$Ph), 72.47 (C-3), 72.17 (CH$_2$Ph), 71.92 (C-3'), 70.98 (CH$_2$Ph), 70.78 (CH$_2$Ph), 70.60 (d, $J_{C,P}$=5.4 Hz, C-5'), 70.48 (CH$_2$Ph), 69.66 (d, $J_{C,P}$=5.8 Hz, (BnO)P(O)-), 69.58 (d, $J_{C,P}$=5.0 Hz, (BnO)P(O)-), 69.55 (d, $J_{C,P}$=4.7 Hz, (BnO)P(O)-), 69.37 (d, $J_{C,P}$=5.4 Hz, (BnO)P(O)-), 68.15 (C-6), 67.66 (C-6'), 53.88 (C-2), 51.10 (C-2'), 41.50, 41.13, 39.17 and 39.02 (4C, ^{Laur}α*C*H$_2$), 34.48,

34.37, 33.53, 31.92, 29.87, 29.79, 29.75, 29.73, 29.70, 29.67, 29.64, 29.62, 29.37, 29.36, 25.57, 25.19, 25.15, 24.69, 22.68 (32 *C*H_2), 14.09 (4C, 4 *C*H_3);

^{31}P NMR ($CDCl_3$): δ -2.11, -2.23;
HRMS (ESI-TOF): calcd. for $C_{130}H_{176}N_2O_{23}P_2$ $[M+2H]^{2+}$ 1097.6069; found 1097.6075.

Synthesis of (35)

6-*O*-Benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)dodecanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-α-D-glucopyranoside (35).

Compound **35** was prepared from **28** (74 mg, 0.046 mmol) in the way described for the synthesis of **31** using 0.16 mmol, 54 µl of di-*O*-benzyloxy(*N,N*-diisopropylamino)phosphine, a 0.45 M solution of 1*H*-tetrazole in acetonitrile (0.16 mmol, 35 µl) and *m*-chloroperbenzoic acid (0.18 mmol, 32 mg). Yield: 88 mg (90 %); R_f 0.14 (A, toluene/EtOAc, 2:1), $[\alpha]_D^{20}$=+8.5 (*c* 1.1, $CHCl_3$);
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.13 (m, 50H, Ph), 6.35 (d, 1H, $^3J_{2',NH'}$ =9.5 Hz, NH'), 6.29 (d, 1H, $^3J_{2,NH}$ =7.9 Hz, NH), 5.36 (dd, 1H, $^3J_{2',3'}$ =10.6, $^3J_{3',4'}$ = 9.2 Hz, H-3'), 4.92 (m, 1H, H-3), 4.90-4.79 (m, 8H, 4x $(BnO)_2P(O)$-), 4.72 (d, 1H, $^3J_{1',2'}$ =3.7 Hz, H-1'), 4.68 (dt, 1H, $^3J_{3',4'}$ =$^3J_{4',5'}$ = 9.0, $^3J_{4',P}$ = 9.8 Hz, H-4'), 4.52-4.22 (m, 13H, 5 CH_2Ph, CH_2aPh, H-2', H-4),4.20 (dt, 1H, $^3J_{4',5'}$ =10.2, $^3J_{5',6a'}$=$^3J_{5',6b'}$= 3.1Hz, H-5'), 4.14 (AB, 1H, J_{AB}= 11.9 Hz, CH_2bPh), 3.92-3.87 (m, 3H, H-1, H-2, β^{Laur}C*H*OBn), 3.74-3.72 (m, 2H, 2 β^{Capr}C*H*OBn), 3.59-3.57 (m, 2H, H-6'ab), 3,54 (dd, 1H, H-6a), 3,51-3,49 (m, 1H, β^{Laur}C*H*OBn), 3.47 (dd, 1H, $J_{6a,6b}$ =11.1, $^3J_{5,6b}$= 5.0 Hz, H-6b), 3,29 (ddd, 1H, $^3J_{4,5}$ =9.7, $^3J_{5,6a}$= 1.9, $^3J_{5,6b}$= 4.8 Hz, H-5), 2.61 (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=16,5, $^3J_{\alpha H,\beta H}$=6,4 Hz, αCH$_2$-*Ha*), 2,57 (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=16,3, $^3J_{\alpha H,\beta H}$=6,5 Hz, αCH$_2$-*Ha*),2.40 (dd, 1H, ,$^2J_{\alpha Ha,\alpha Hb}$=16,7, $^3J_{\alpha H,\beta H}$=6,0 Hz, αCH$_2$-*Hb*), 2.38-2.35 (m, 2HαCHa, αCHb), 2.29 (dd, 1H, (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=15,3, $^3J_{\alpha H,\beta H}$=8,0 Hz, αCH$_2$-*Ha*), 2.24 (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=15,3, $^3J_{\alpha H,\beta H}$=8,0 Hz, αCH$_2$-*Hb)*), 2.12 (dd, 1H, $^2J_{\alpha Ha,\alpha Hb}$=15,2, $^3J_{\alpha H,\beta H}$=3,8 Hz, αCH$_2$-*Hb),*, 1,45-1,42 (m, 8H, 2γ^{Laur}CH$_2$, 2γ^{Capr}CH$_2$), 1.30-1.16 (m, 48H, 24 CH_2), 0.88 (dt, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.26, 171.60, 171.36 (4C, 4xC=O), 139.29, 138.90, 138.75, 138.38, 138.27, 137.98 (6C, 6xPh-C_q), 135.73-135.60 (m, 4C, Ph, 2x$(BnO)_2P(O)$-),), 128.57, 125.55, 128.47, 128.45, 128.38, 128.36, 128.20, 128.17, 128.12, 128.08, 128.03, 127.99, 127.98, 127.93, 127.89, 127.74, 127.69, 127.59, 127.40, 127.36, 127.21 (50C, 10xPh), 101.16 (1C, C-1), 99.14 (1C, C-1'), 77.13, 75.62, 75.24, 75.12 (4C, 2^{Laur}βCH, 2^{Capr}ßCH), 74.01 (d, 1C, $J_{5,P}$=5.7 Hz, C-5), 73.45 (d, $J_{4',P}$=6.7 Hz, C-4'), 73.39 (d, $J_{4,P}$=5.5 Hz, C-4), 73.21 (CH_2Ph), 73.17 (CH_2Ph), 72.50 (C-3), 72.18 (CH_2Ph), 71.97 (C-3'), 71.00 (CH_2Ph), 70.80 (CH_2Ph), 70.62 (d, $J_{C,P}$=4.6 Hz, C-5'), 70.50 (CH_2Ph), 69.67 (d, $J_{C,P}$=5.6 Hz, (BnO)P(O)-), 69.58 (d, $J_{C,P}$=5.2 Hz, (BnO)P(O)-), 69.55 (d, $J_{C,P}$=4.8 Hz, (BnO)P(O)-), 69.37 (d, $J_{C,P}$=5.5 Hz, (BnO)P(O)-), 68.17 (C-6), 67.70 (C-6'), 53.92 (C-2), 51.12 (C-2'), 41.51, 41.16, 39.18 and 39.04 (4C, 2^{Myr} α*C*H$_2$, 2^{Capr}αCH$_2$), 34.50, 34.39, 33.55, 31.94, 31.89, 31.87, 29.88, 29.80, 29.71, 29.68, 29.67, 29.39, 29.36, 29.34, 25.58, 25.20, 25.16, 24.70, 22.69 (28 *C*H_2), 14.10 (4C, 4 *C*H_3);

^{31}P NMR ($CDCl_3$): δ -2.08, -2.20;
HRMS (ESI-TOF): calcd. for $C_{126}H_{168}N_2O_{23}P_2$ $[M+2H]^{2+}$ 1069.5757; found 1069.5756.

Synthesis of (36)

6-*O*-Benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-O-[(*R*)-3-(benzyloxy)-dodecanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)-decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)dodecanoyl]-2-deoxy-α-D-glucopyranoside (36).

Compound **36** was prepared from **29** (85 mg, 0.053 mmol) in the way described for the synthesis of **31** using 0.18 mmol, 62 µl of di-*O*-benzyloxy(*N,N*-diisopropylamino)phosphine, a 0.45 M solution of 1*H*-tetrazole in acetonitrile

(0.18 mmol, 41 µl) and *m*-chloroperbenzoic acid (0.21 mmol, 37 mg). Yield: 85 mg (76 %); R_f 0.14 (A, toluene/EtOAc, 2:1), $[\alpha]_D^{20}$=+9.7 (*c* 1.0, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.13 (m, 50H, Ph), 6.36 (d, 1H, $^3J_{2',NH'}$ =9.6 Hz, NH'), 6.29 (d, 1H, $^3J_{2,NH}$ =7.8 Hz, NH), 5.36 (dd, 1H, $^3J_{2',3'}$ =10.4, $^3J_{3',4'}$ = 8.6 Hz, H-3'), 4.92 (m, 1H, H-3). 4.90-4.79 (m, 8H, 4x $(BnO)_2P(O)$-), 4.72 (d, 1H, $^3J_{1',2'}$ =3.6 Hz, H-1'), 4.68 (dt , 1H, $^3J_{3',4'}$ =$^3J_{4',5'}$ = 9.4, $^3J_{H4',P}$ = 9.8 Hz, H-4'), 4.51-4.22 (m, 13H, 5 CH_2Ph, CH_2aPh, , H-2', H-4), 4.20 (dt, 1H, $^3J_{4',5'}$ =9.9, $^3J_{5',6a'}$=$^3J_{5',6b'}$= 2.7 Hz, H-5'), 4.14 (AB, 1H, J_{AB}= 12 Hz, CH_2bPh), 3.93-3.87 (m, 3H, H-1, H-2, β^{Capr}C*H*OBn), 3.75-3.71 (m, 2H, 2 β^{Laur}C*H*OBn), 3.59-3.46 (m, 5H, H-6a, H-6'ab, β^{Capr}C*H*OBn), 3.48 (dd, 1H, $J_{6a,6b}$ =11.0, $^3J_{5,6b}$= 5.0 Hz, H-6b), 3,30 (ddd, 1H, $^3J_{4,5}$ =9.6, $^3J_{5,6a}$= 1.8, $^3J_{5,6b}$= 4.8 Hz, H-5), 2.61 (dd, 1H, $^2J_{αHa,αHb}$=16,5, $^3J_{αH,ßH}$=6,4 Hz, αCH$_2$-*Ha*), 2.57 (dd, 1H, $^2J_{αHa,αHb}$=16.3, $^3J_{αH,ßH}$=6.5 Hz, αCH$_2$-*Ha*), 2.40 (dd, 1H, $^2J_{αHa,αHb}$=16.7, $^3J_{αH,ßH}$=5.7 Hz, αCH$_2$-*Hb*), 2.38-2.34 (m, 2H, αCHa, αCHb), 2.29 (dd, 1H, $^2J_{αHa,αHb}$=15.3, $^3J_{αH,ßH}$=7,9 Hz, αCH$_2$-*Ha*), 2.24 (dd, 1H, $^2J_{αHa,αHb}$=14.9, $^3J_{αH,ßH}$=3,4 Hz, αCH$_2$-*Hb*), 2.12 (dd, 1H, $^2J_{αHa,αHb}$=15,2, $^3J_{αH,ßH}$=3,7 Hz, αCH$_2$-*Hb*), 1.46-1.42 (m, 8H, 2γ^{Laur}CH$_2$, 2γ^{Capr}CH$_2$), 1.30-1.21 (m, 48H, 24 CH_2), 0.88 (t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.26, 171.59, 171.57, 171.34 (4C, 4xC=O), 139.28, 138.90, 138.74, 138.37, 138.25, 137.97 (6C, 6xPh-C_q), 135.79-135.61 (m, 4C, 2x$(BnO)_2P(O)$-), 128.58, 125.56, 128.54, 128.47, 128.45, 128.36, 128.20, 128.17, 128.12, 128.06, 128.02, 127.97, 127.95, 127.91, 127.73, 127.67, 127.64, 127.58, 127.53, 127.38, 127.35, 127.19 (50C, Ph), 101.13 (1C, C-1), 99.11 (1C, C-1'), 77.09, 75.60, 75.22, 75.10 (4C, 2^{Laur}βCH, 2^{Capr}ßCH), 73.99 (d, $J_{5,P}$=5.5 Hz, C-5), 73.43 (d, $J_{4',P}$=6.5 Hz, C-4'), 73.39 (d, $J_{4,P}$=6.3 Hz, C-4), 73.19 (CH_2Ph), 73.17 (CH_2Ph), 72.47 (C-3), 72.16 (CH_2Ph), 71.94 (C-3'), 70.98 (CH_2Ph), 70.78 (CH_2Ph), 70.61 (d, $J_{C,P}$=5.4 Hz, C-5'), 70.49 (CH_2Ph), 69.67 (d, $J_{C,P}$=5.6 Hz, $(BnO)_2P(O)$-), 69.58 (d, $J_{C,P}$=5.2 Hz, $(BnO)_2P(O)$-), 69.55 (d, $J_{C,P}$=4.8 Hz, $(BnO)_2P(O)$-), 69.37 (d, $J_{C,P}$=5.5 Hz, $(BnO)_2P(O)$-), 68.15 (C-6), 67.68 (C-6'), 53.91 (C-2), 51.09 (C-2'), 41.49, 41.14, 39.17 and 39.02 (4C, 2^{Laur}αC, 2^{Capr}αC), 34.48, 34.38, 33.52, 31.92, 31.90, 31.88, 29.80, 29.75, 29.73, 29.69, 29.64, 29.61, 29.35, 29.33, 25.56, 25.19, 25.15, 24.68, 22.68, 22.66 (28 *C*H_2), 14.10 and 14.08 (4C, 4 *C*H_3);

^{31}P NMR ($CDCl_3$): δ -2.11, -2.22;

HRMS (ESI-TOF): calcd. for $C_{126}H_{168}N_2O_{23}P_2$ $[M+2H]^{2+}$ 1069.5757; found 1069.5755

Synthesis of (37)

6-*O*-Benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-β-D-glucopyranosyl-(1→1)-6-*O*-benzyl-4-*O*-[bis(benzyloxy)phosphoryl]-2-[(*R*)-3-(benzyloxy)decanoylamino]-3-*O*-[(*R*)-3-(benzyloxy)decanoyl]-2-deoxy-α-D-glucopyranoside (37).

Compound **37** was prepared from **30** (56 mg, 0.036 mmol) in the way described for the synthesis of **31** using 0.13 mmol, 42 µl of di-*O*-benzyloxy(*N,N*-diisopropylamino)phosphine, a 0.45 M solution of 1*H*-tetrazole in acetonitrile (0.13 mmol, 28 µl) and *m*-chloroperbenzoic acid (0.14 mmol, 25 mg). Yield: 65 mg (87 %); R_f 0.21 (A, toluene/EtOAc, 2:1), $[\alpha]_D^{20}$=+8.9 (*c* 0.9, $CHCl_3$);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33-7.13 (m, 50H, Ph), 6.37 (d, 1H, $^3J_{2',NH'}$ =9.4 Hz, NH'), 6.29 (d, 1H, $^3J_{2,NH}$ =7.8 Hz, NH), 5.37 (dd, 1H, $^3J_{2',3'}$ =10.5, $^3J_{3',4'}$ = 9.2 Hz, H-3'), 4.92 (m, 1H, H-3). 4.90-4.79 (m, 8H, 4x $(BnO)_2P(O)$-), 4.72 (d, 1H, $^3J_{1',2'}$ =3.7 Hz, H-1'), 4.68 (dt , $^3J_{3',4'}$ =$^3J_{4',5'}$ = 9.4, $^3J_{4',P}$ = 9.6 Hz, 1H, H-4'), 4.52-4.22 (m, 13H, 5 CH_2Ph, CH_2aPh, H-2', H-4), 4.20 (dt, 1H, $^3J_{4',5'}$ =10.0, $^3J_{5',6a'}$=$^3J_{5',6b'}$= 2.7 Hz, H-5'), 4.15 (AB, 1H, J_{AB}= 11.9 Hz, CH_2bPh), 3.93-3.88 (m, 3H, H-1, H-2, β^{Capr}C*H*OBn), 3.75-3.71 (m, 2H, 2 β^{Capr}C*H*OBn), 3.59-3.49 (m, 4H, H-6a, H-6'ab, β^{Capr}C*H*OBn), 3.48 (dd, 1H, $J_{6a,6b}$ =11.0, $^3J_{5,6b}$= 4.9 Hz, H-6b), 3.31-3.29 (ddd, 1H, $^3J_{4,5}$ =9.8, $^3J_{5,6a}$= 1.7, $^3J_{5,6b}$= 4.9 Hz, H-5), 2.61 (dd, 1H, $^2J_{αHa,αHb}$=16,5, $^3J_{αH,ßH}$=6,4 Hz, αCH$_2$-*Ha*), 2.57 (dd, 1H, $^2J_{αHa,αHb}$=16,3, $^3J_{αH,ßH}$=6,5 Hz, αCH$_2$-*Ha*), 2.40 (dd, 1H, $^2J_{αHa,αHb}$=16,6, $^3J_{αH,ßH}$=5,8 Hz, αCH$_2$-), 2.38-2.34 (m, 2H, αCHa, αCHb), 2.29 (dd, 1H, $^2J_{αHa,αHb}$=15.3, $^3J_{αH,ßH}$=7.9 Hz, αCH$_2$-*Ha*), 2.24 (dd, 1H, $^2J_{αHa,αHb}$=14.9, $^3J_{αH,ßH}$=3.4 Hz, αCH$_2$-*Hb*), 2.12 (dd, 1H, , $^2J_{αHa,αHb}$=15.2, $^3J_{αH,ßH}$=3.7 Hz, αCH$_2$-*Hb*), 1.45-1.42 (m, 8H, 4γ^{Capr}CH$_2$), 1.30-1.16 (m, 40H, 20 CH_2), 0.87 (m, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 172.26, 171.60, 171.57, 171.35 (4C, 4x C=O), 139.28, 138.88, 138.74, 138.37, 138.25, 137.96 (6C, 6xPh-C_q), 135.79-135.55 (m, 4C, 2x$(BnO)_2P(O)$-), 128.58, 128.56, 128.54, 128.46, 128.45, 128.38, 128.35, 128.19, 128.16, 128.12, 128.07, 128.02, 127.97, 127.95, 127.90, 127.72, 127.66, 127.58, 127.52, 127.38, 127.35, 127.19 (50C, 10xPh), 101.14 (1C, C-1), 99.12 (1C, C-1'), 77.11, 75.60, 75.21, 75.10 (4C, 4 ^{Capryl}βCH), 73.98 (d, $J_{5,P}$=5.3 Hz, C-5), 73.43 (d, $J_{4',P}$=6.6 Hz, C-4'), 73.37 (d, $J_{4,P}$=6.7 Hz, C-4), 73.19 (CH_2Ph), 73.16 (CH_2Ph), 72.48 (C-3), 72.16 (CH_2Ph), 71.93 (C-3'), 70.97 (CH_2Ph), 70.77 (CH_2Ph), 70.60 (d, $J_{C,P}$=5.8 Hz, C-5'), 70.49 (CH_2Ph), 69.66 (d, $J_{C,P}$=5.6 Hz, (BnO)P(O)-), 69.58 (d, $J_{C,P}$=4.9 Hz, (BnO)P(O)-), 69.55 (d, $J_{C,P}$=4.9 Hz, (BnO)P(O)-), 69.37 (d, $J_{C,P}$=5.5 Hz, (BnO)P(O)-), 68.14 (C-6), 67.67 (C-6'), 53.89 (C-2), 51.09 (C-2'), 41.49, 41.13, 39.16 and 39.01 (4C, αCH_2), 34.47, 34.36, 33.52, 31.87, 31.84, 29.79, 29.71, 29.68, 29.64, 29.67, 29.64, 29.36, 29.31, 25.55, 25.17, 25.14, 24.67, 22.66 (28 CH2), 14.08 (4C, FA-CH_3);

^{31}P NMR ($CDCl_3$): δ -2.11, -2.23;
HRMS (ESI-TOF): calcd. for $C_{122}H_{160}N_2O_{23}P_2$ $[M+2H]^{2+}$ 1041.5443; found 1041.5431.

Synthesis of (DA 187)

2-Deoxy-2-[(*R*)-3-hydroxytetradecanoylamino]-3-*O*-[(*R*)-3-hydroxytetradecanoyl]-β-D-glucopyranosyl-(1→1)-2-deoxy-2-[(*R*)-3-hydroxytetradecanoylamino]-3-*O*-[(*R)*-3-hydroxytetradecanoyl]-α-D-glucopyranoside 4,4'-bisphosphate (DA 187)

Perbenzylated diphosphate **31** (21 mg, 0.01 mmol) was dissolved in toluene/MeOH (3:1,5ml) and the solution was hydrogenated in the presence of Pd black (200 mg) at rt and atmospheric pressure for 6h (The reaction mixture was sonicated every 30 min). The reaction mixture was diluted with toluene/MeOH (3:1, 10 ml) and sonicated. The catalyst was removed by filtration over 0.45µ Phenex-RC (regenerated cellulose) syringe filter (15 mm). The filtrate was concentrated, the residue was purified by gel filtration chromatography on BioBeads SX1 column (10×900mm, $CHCl_3$/MeOH 3:1, flow rate 0.5 ml/min) to provide **DA 187** (13 mg, 98%) as a solid. R_f 0.37 (A, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), 0.49 (B, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), 0.6 (B, $CHCl_3$/MeOH/H_2O, 100:75:15); $[\alpha]_D^{20}$= +13.4 (*c* 0.5, $CHCl_3$/MeOH 3:1);
^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD, 4:1): δ 5,26 (dd, 1H, $^3J_{2',3'}$= 8,9, $^3J_{3',4'}$=10.7 Hz, H-3'), 5.17 (dd, 1H, $^3J_{2,3}$=9.0, $^3J_{3,4}$=10.5 Hz, H-3), 5.07 (d, 1H, $^3J_{1',2'}$=3.7 Hz, H-1'), 4.70 (d, 1H, $^3J_{1,2}$=8.6 Hz, H-1), 4.29 (t, 1H, H-4'), 4.26 (t, 1H, H-4), 4.25-4.21 (m, 1H, H-2'), 4.11 (t, 1H, H2), 4.11-4.07 (m, 1H, H-5'), 4.05-3.98 (m, 4H, 2ß^{Myr}C*H*OH, 2ß'^{Myr}C*H*OH), 3.87-3.78 (m, 4H, H-6ab, H-6'ab), 3.51 (ddd, 1H, H-5', $^3J_{4,5}$=9,8, $^3J_{5,6a}$=1,8, $^3J_{5,6b}$=2,8 Hz, H-5), 2.55-2.20 (m, 8H, 2α^{Myr}CH_2, 2α'^{Myr}CH_2), 1.48-1.43 (t, 8H, 4γ^{Myr}CH_2, 4γ'^{Myr}CH_2), 1.35-1.28 (m, 72H,36 CH_2), 0.88 (t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$/CD_3OD, 4:1): δ 173.15, 173.11, 172.32, 171.55 (4C, 4 C=O), 100.87 (C-1'), 98.39 (C-1), 75.32 (C-5), 73.44 (C-3), 71.98, 71.68 (C-4, C-4'), 71.45 (C-5'), 71.12 (C-3'), 68.48, 68.41, 67.85, 67.82 (4C, 4ß^{Myr}*C*H), 60.28, 60.14 (C-6, C-6'), 53.23 (C-2), 51.57 (C-2'), 43.30, 42.75, 41.60, 41.57 (4C, 4γ^{Myr}CH_2) 37.42, 37.37, 36.53, 36.47, 31.41, 29.25-28.84, 25.24, 24.98, 24.91, 23.07, 22.13 (36 CH_2), 13.32 (4C, 4 CH_3);

^{31}P ($CDCl_3$/CD_3OD, 4:1): δ 3.65 (*J*=9,7 Hz), 3.39 (*J*=9,7 Hz);
MALDI-TOF-MS m/z 1403.868 $[M-H]^-$, calc. for $C_{68}H_{130}N_2O_{23}P_2$ 1403.847 $[M-H]^-$

Synthesis of (DA 193)

2-Deoxy-2-[(*R*)-3-hydroxytetradecanoylamino]-3-*O*-[(*R)*-3-hydroxydodecanoyl]-β-D-glucopyranosyl-(1→1)-2-deoxy-2-[(*R*)-3-hydroxytetradecanoylamino]-3-*O*-[(*R*)-3-hydroxydodecanoyl]-α-D-glucopyranoside 4,4'-bisphosphate (DA 193)

Compound **DA 193** was prepared from **32** (47 mg, 0.024 mmol) in the way described for the synthesis of **DA 187**. Yield 28 mg (98%), R_f 0.38 (A, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), 0.6 (B, $CHCl_3$/MeOH/H_2O, 100:75:15); $[\alpha]_D^{20}$= +13.8 (*c* 0.7, $CHCl_3$/MeOH, 3:1);

^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD, 4:1): δ 5.13 (t, 1H, $^3J_{2',3'}$= 9.9 Hz, H-3'), 5.01 (t, 1H, $^3J_{2,3}$=9.3 Hz, H-3), 4.97 (d, 1H, $^3J_{1',2'}$=3.0 Hz, H-1'), 4.55 (d, 1H, $^3J_{1,2}$=9.0 Hz, H-1), 4.20-4.10 (m, 3H, H-2', H-4, H-4'), 4.01 (t, 1H, H-2), 3.99-3.90 (m, 4H, 2ß^{Myr}C*H*OH, 2ß^{Laur}C*H*OH), 3.89-3.81 (m, 3H, H-6ab, H-5'), 3.61 (dd, 2H, H-6'ab), 3.30-3.28 (m, 1H, H-5), 2.40-2.09 (m, 8H, 2α$^{Myr}CH_2$, 2α$^{Laur}CH_2$), 1.23 (t, 8H, 2γ$^{Myr}CH_2$, 2γ$^{Laur}CH_2$), 1.20-1.17 (m, 64H, 32 CH_2), 0.80 (t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$/CD_3OD, 4:1): δ 173.11, 172.88, 172.74, 171.99 (4C, 4 C=O), 101.16 (C-1'), 98.72 (C-1'), 75.73 (C-5), 74.12 (C-3'), 72.04 (C-3), 71.86 (C-5'), 70.31, 70.11 (C-4, C-4'), 68.60-68.33 (4C, 2ß^{Myr}CH, 2ß^{Laur}*C*H), 60.33, 59.89 (2C, C-6,6'), 53.35 (C-2), 51,77 (C-2'), 43.44, 42.88, 41.79, 41.71 (4C, 2α$^{Myr}CH_2$, 2α$^{Laur}CH_2$), 37.49, 36.97 (4C, 2γ$^{Myr}CH_2$, 2γ$^{Laur}CH_2$), 31.57, 31.54, 31.57, 31.54, 30.02-28.97, 25.15, 25.09, 25.06, 22.51, 22.30 (32 CH_2), 8,01 (4C, 4 CH_3);

^{31}P ($CDCl_3$/CD_3OD, 4:1): δ 4.43, 4.37;
MALDI-TOF-MS: m/z 1347.799 $[M-H]^-$, calc. for $C_{64}H_{122}N_2O_{23}P_2$ 1347.784 $[M-H]^-$

Synthesis of (DA 253)

2-Deoxy-2-[(*R*)-3-hydroxytetradecanoylamino]-3-*O*-[(*R*)-3-hydroxydecanoyl]-β-D-glucopyranosyl-(1→1)-2-deoxy-2-[(*R*)-3-hydroxytetradecanoylamino]-3-*O*-[(*R*)-3-hydroxydecanoyl]-α-D-glucopyranoside 4,4'-bisphosphate (DA 253)

Compound **DA 253** was prepared from **33** (30 mg, 0.014 mmol) in the way described for the synthesis of **DA 187**. Yield 16 mg (92%), R_f 0.34 (A, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), 0.6 (B, $CHCl_3$/MeOH/H_2O, 100:75:15); $[\alpha]_D^{20}$= +17.5 (*c* 0.4, $CHCl_3$/MeOH, 3:1);

^{1}H NMR (600 MHz, $CDCl_3$/CD_3OD, 4:1): δ 5.25 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ = 9.8 Hz, H-3'), 5,16 (t, 1H, $^3J_{2,3}$=$^3J_{3,4}$=9.8 Hz, H-3), 5,07 (d, 1H, $^3J_{1',2'}$=3.6 Hz, H-1'), 4,70 (d, 1H, $^3J_{1,2}$=8.6 Hz, H-1), 4,29 (t, 1H, H-4'), 4,26 (t, 1H, H-4), 4,24-4,21 (m, 1H, H-2'), 4,12-4,06 (m, 2H, H2, H-5'), 4,05-3,98 (m, 4H, ß^{Myr}C*H*OH, ß'^{Myr}C*H*OH, ß^{Capr}C*H*OH, ß'^{Capr}C*H*OH), 3,86-3,80 (m, 4H, H-6ab, H-6'ab), 3,50 (m, 1H, H-5), 2,54-2,19 (m, 8H, α$^{Myr}CH_2$, α'$^{Myr}CH_2$, α$^{Capr}CH_2$, α'$^{Capr}CH_2$), 1,44 (broad, 8H, 2γ$^{Myr}CH_2$, 2γ'$^{Myr}CH_2$, 2γ$^{Capr}CH_2$, 2γ'$^{Capr}CH_2$), 1,35-1,26 (m, 56H, 28 CH_2), 0,89 (t, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$/CD_3OD, 4:1): δ 173,26, 173,17, 172,50 (4C, 4 C=O), 100,94 (C-1'), 98,42 (C-1), 75,21 (C-5), 73,60 (C-3), 71,51, 71,50 (C-4, C-4'), 71,28 (C-3'), 71,27 (C-5'), 68,60, 68,55, 68,04, 67,03 (4C, 2ß^{Myr}*C*H, 2ß^{Capr}*C*H), 60,23, 60,22 (C-6, C-6'), 53,29 (C-2), 51,67 (C-2'), 43,39, 42,90, 37,52, 37,47 (4C, 2γ$^{Myr}CH_2$, 2γ$^{Capr}CH_2$), 36,64, 36,59, 31,53, 31,44, 31,43, 29,35-28,87, 25,14, 25,09, 25,07, 22,26, 22,23 (28 CH_2), 13,50 (4C, 4 CH_3);

^{31}P NMR ($CDCl_3$/CD_3OD, 4:1): δ 3,59, 3,35;
MALDI-TOF-MS: m/z 1291.841 $[M-H]^-$, calc. for $C_{60}H_{114}N_2O_{23}P_2$ 1291.721 $[M-H]^-$

Synthesis of (DA 256)

2-Deoxy-2-[(*R*)-3-hydroxydodecanoylamino]-3-*O*-[(*R*)-3-hydroxydodecanoyl]-β-D-glucopyranosyl-(1→1)-2-deoxy-2-[(*R*)-3-hydroxydodecanoylamino]-3-*O*-[(*R*)-3-hydroxydodecanoyl]-α-D-glucopyranoside 4,4'-bisphosphate (DA 256)

Compound **DA 256** was prepared from **34** (30 mg, 0.014 mmol) in the way described for the synthesis of **DA 187**. Yield 15 mg (85%), R_f 0.30 (A, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), 0.45 (B, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15); $[\alpha]_D^{20}$= 14.8 (*c* 0.5, $CHCl_3$/MeOH, 3:1);

^{1}H NMR (600 MHz, $CDCl_3$/2-Propanole-d_8/CD_3OD 4:1:0.5, 40°C): δ 5.23 (t, 1H, $^3J_{2',3'}$= $^3J_{3',4'}$=10.0 Hz, H-3'), 5.12 (t, 1H, $^3J_{2,3}$= $^3J_{3,4}$=10.1 Hz, H-3), 5.06 (d, 1H, $^3J_{1',2'}$=4.0 Hz, H-1'), 4.67 (d, 1H, $^3J_{1,2}$=8.5 Hz, H-1), 4.27 (t, 2H, H-4, H-4'), 4.21 (dd, 1H, $^3J_{3',4'}$=7.5 Hz, H-2'), 4.10 (t, 1H, $^3J_{3,4}$=9.5 Hz, H-2), 4.06-3.99 (m, 5H, 4ß^{Laur}C*H*OH, H-5') 3.93-3.88 (m, 2H, H-6a, H-6a'), 3.76-3.71 (m, 2H, H-6b, H-6'b), 3.46-3.42 (m, 1H, H-5), 3.20 (broad, 8H, 4 N-CH_2), 2.47-2.25 (m, 8H, 4α$^{Laur}CH_2$), 1.42-1.27(broad, 20H, 4 N-CH_2-C*H*$_3$, 4γ$^{Laur}CH_2$), 1.15-1.13 (m, 56H, 28 CH_2), 0.88 (t, 12H, 4 CH_3);

^{1}H NMR (600 MHz, DMSO-d_6, ref. to solvent signal 2.50 ppm): δ 7.82 (d, 1H, , $^3J_{2,NH}$ = 9.1 Hz, NH), 6.93 (d, 1H, , $^3J_{2',NH'}$ = 9.4 Hz, NH'), 5.10 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ = 10.1 Hz, H-3), 5.05 (t, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ = 10.2 Hz, H-3'), 4.88 (d, 1H, $^3J_{1',2'}$ =3.5 Hz, H-1'), 4.69 (d, 1H, $^3J_{1,2}$ =8.5 Hz, H-1), 4.11-3.99 (m, 3H, H-2', H-4, H-4'), 3.94 (m, 1H, H-5'), 3.81-3.72 (m, 5H, H-2, 4ß^{Laur}C*H*OH), 3.63-3.55 (m, 4H, H-6ab, H-6'ab), 3.38 (m, 1H, H-5), 2.37-1.96 (m, 8H, 4α$^{Laur}CH_2$), 1.38-1.16 (m, 64H, 32 CH_2), 0.85 (m, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$/2-Propanole-d_8/CD_3OD 4:1:0.5): δ 173.23, 172.98, 172.87, 172.16 (4C, 4 C=O), 101.28 (C-1), 98.75 (C-1'), 75.74 (C-5), 74.22 (C-3), 71.99, 71.89 (C-3', C-5'), 70.78, 70.53 (C-4, C-4'), 68.75, 68.49 (4C, 4ß^{Laur}*C*H), 60.54, 60.12 (C-6, C-6'), 53.47 (C-2), 51.96 (C-2'), 45.78 (4C, 4 N-CH_2), 43.60, 43.08, 41.88 (4C, 4γ$^{Laur}CH_2$) 37.67, 37.15, 36.53, 31.65, 29.50-29.08, 25.31, 22.45 (28 CH_2), 13.77 (4C, 4 CH_3), 8.16 (4C, 4 N-CH_2-*C*H_3);

^{13}C NMR (150.9 MHz, DMSO-d_6, ref. to solvent signal 39.52 ppm): δ 171.63, 171.39, 170.95, 170.65 (4C, 4 C=O), 99.91 (1C, C-1), 98.52 (1C, C-1'), 75.71 (1C, C-5), 72.91 (1C, C-3), 72.03 (1C, C-5'), 71.47 (m, 2C, C-4, C-4'), 70.78 (1C, C-3'), 67.20, , 66.84, 66.82 (4C, 4 β^{Laur}CHOH), 60.24 and 59.66 (2C, C-6, C-6'), 53.52 (C-2), 50.61 (C-2'), 43.80, 43.05, 42.76, 42.66 (4C, 4α$^{Laur}CH_2$), 37.09, 36.81, 36.75 (4$_C$, 4γ$^{Laur}CH_2$), 31.34, 29.34, 29.28, 29.25, 29.20, 29.13, 29.11, 28.79, 28.77, 25.32, 25.24, 22.10 (CH_2) 13.90 and 13.88 (4C, *C*H_3);

^{31}P NMR (DMSO-d_6): δ -0.37, -0.52;

MALDI-TOF-MS m/z 1291.830 $[M-H]^-$, calc. for $C_{60}H_{114}N_2O_{23}P_2$ 1291.721 $[M-H]^-$

Synthesis of (DA 254)

2-Deoxy-2-[(*R*)-3-hydroxydodecanoylamino]-3-*O*-[(*R*)-3-hydroxydecanoyl]-β-D-glucopyranosyl-(1→1)-2-deoxy-2-[(*R*)-3-hydroxydodecanoylamino]-3-*O*-[(*R*)-3-hydroxydecanoyl]-α-D-glucopyranoside 4,4'-bisphosphate (DA 254)

Compound **DA 254** was prepared from **35** (32 mg, 0.015 mmol) in the way described for the synthesis of **DA 187**. Yield 17 mg (93%), R_f 0.32 (A, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), 0.45 (B, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15); $[\alpha]_D^{20}$= +10.9 (*c* 0.4, $CHCl_3$/MeOH, 3:1);

^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD, 4:1, triethylammonium salt): δ 5.22 (dd, 1H, $^3J_{2',3'}$= 9.3, $^3J_{3',4'}$=10.2 Hz, H-3'), 5.09 (dd, 1H, $^3J_{2,3}$=9.6, $^3J_{3,4}$=9.7 Hz, H-3), 5.06 (d, 1H, $^3J_{1',2'}$=3.7 Hz, H-1'), 4.63 (d, 1H, $^3J_{1,2}$=8.5 Hz, H-1), 4.28-4.19 (m, 3H, H-4, H-4', H-2'), 4.14-3.92 (m, 8H, H2, H-5', H-6ab, 2ß^{Laur}C*H*OH, 2ß^{Capr}C*H*OH), 3.74-3.64 (m, 2H, H-6'ab), 3.42 (broad, 1H, H-5), 3.09 (q, 8H, 4 N-CH_2), 2.50-2.15 (m, 8H, 2α$^{Laur}CH_2$, 2α$^{Capr}CH_2$), 1.44-1.42 (broad, 20H, 4 N-CH_2-C*H*$_3$, 2γ$^{Capr}CH_2$, 2γ$^{Laur}CH_2$), 1.35-1.27 (m, 48H, 24 CH_2), 0.88 (t, 12H, 4 CH_3);

^{1}H NMR (600 MHz, DMSO-d_6, ref. to solvent signal 2.50 ppm): δ 7.83 (d, 1H, , $^3J_{2,NH}$ = 9.1 Hz, NH), 6.92 (d, 1H, $^3J_{2',NH'}$ = 9.4 Hz, NH'), 5.10 (t, 1H, $^3J_{2,3}$ =$^3J_{3,4}$ = 10.1 Hz, H-3), 5.05 (t 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ = 9.7 Hz, H-3'), 4.88 (d, 1H, $^3J_{1',2'}$ =3.5 Hz, H-1'), 4.68 (d, 1H, $^3J_{1,2}$ =8.6 Hz, H-1), 4.11-4.00 (m, 3H, H-2', H-4, H-4'), 3.94 (m, 1H, H-5'), 3.80-3.74 (m, 5H, H-2,

2ß^{Laur}C*H*OH, 2ß^{Capr}C*H*OH), 3.65-3.54 (m, 4H, H-6ab, H-6'ab), 3.37 (m, 1H, H-5), 2.39-2.09 (m, 8H, 2α^{Laur}CH_2, 2α^{Capr}CH_2), 1.35-1.16 (m, 56H, 28 CH_2), 0.85, 0.85 (2xt, 12H, 4 CH_3);

^{13}C NMR (150.9 MHz, $CDCl_3$/CD_3OD, 4:1): δ 173.43, 173.26, 172.71, 172.06 (4C, 4 C=O), 101.03 (C-1), 98.60 (C-1'), 75.28 (C-5), 73.79 (C-3), 72.37, 72.01 (2C, C-4, C-4'), 71.56 (C-5', C-3'), 68.71, 68.38, (4C, 2ß^{Laur}*C*H, 2ß^{Capr}*C*H), 60.61 (C-6, C-6'), 53.46 (C-2), 51.82 (C-2'), 43.59, 43.07, 41.86 (4C, 2α^{Laur}CH_2, 2α^{Capr}CH_2), 37.68, 37.54, 36.81 (4C, 2γ^{Laur}CH_2, 2γ^{Capr}CH_2), 31.74, 31.56, 29.53-29.10, 25.43, 25.32, 22.48, 22.45 (24 CH_2), 13.81 (4C, 4 CH_3);
^{13}C NMR (150.9 MHz, DMSO-d_6, ref. to solvent signal 39.52 ppm): δ 171.64, 171.36, 170.96, 170.69 (4C, 4 C=O), 99.88 (1C, C-1), 98.49 (1C, C-1'), 75.76 (1C, C-5), 72.97 (1C, C-3), 72.08 (1C, C-5'), 71.27 (m, 2C, C-4, C-4'), 70.86 (1C, C-3'), 67.21, 67.17, 66.84, 66.81 (4C, 2ß^{Laur}*C*HOH, 2ß^{Capr}*C*HOH), 60.21 and 59.62 (2C, C-6, C-6'), 53.54 (C-2), 50.63 (C-2'), 43.84, 43.03, 42.78, 42.68 (4C, 4 α*C*$H_2$2α^{Laur}CH_2, 2α^{Capr}CH_2), 37.03, 36.87, 36.80, 36.76 (4C, 2γ^{Laur}CH_2, 2γ^{Capr}CH_2), 31.36, 31.32, 29.30, 29.25, 29.21, 29.14, 29.10, 28.92, 28.87, 28.77, 28.76, 25.29, 25.21, 22.12, 22.09 (24 CH_2) 13.91 and 13.89 (4C, 4 *C*H_3);

^{31}P NMR (DMSO-d_6): δ -0.44, -0.60;
MALDI-TOF-MS m/z 1235.747 $[M-H]^-$, calc. for $C_{56}H_{106}N_2O_{23}P_2$ 1235.659 $[M-H]^-$

Synthesis of (DA 255)

2-Deoxy-2-[(*R*)-3-hydroxydecanoylamino]-3-*O*-[(*R*)-3-hydroxydodecanoyl]-β-D-glucopyranosyl-(1→1)-2-deoxy-2-[(*R*)-3-hydroxydecanoylamino]-3-*O*-[(*R*)-3-hydroxydodecanoyl]-α-D-glucopyranoside 4,4'-bisphosphate (DA 255)

Compound **DA 255** was prepared from **36** (28 mg, 0.013 mmol) in the way described for the synthesis of **DA 187**. Yield 15 mg (95%), R_f 0.27 (A, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), 0.65 (B, $CHCl_3$/MeOH/H_2O, 100:75:15); $[\alpha]_D^{20}$= 19.9 (*c* 0.5, $CHCl_3$/MeOH, 3:1);
^{1}H NMR (300 MHz, $CDCl_3$/CD_3OD, 4:1, triethylammonium salt): δ 5.22 (dd, 1H, $^3J_{2',3'}$= 9.2, $^3J_{3',4'}$=10.5 Hz, H-3'), 5.10 (t, 1H, $^3J_{2,3}$=9.5, $^3J_{3,4}$=9.5 Hz, H-3), 5.06 (d, 1H, $^3J_{1',2'}$=3.6 Hz, H-1'), 4.63 (d, 1H, $J_{1,2}$=8.5 Hz, H-1), 4.28-4.19 (m, 3H, H-4, H-4', H-2'), 4.13-3.94 (m, 8H, H2, H-5', H-6ab, 2ß^{Laur}*C*HOH, 2ß^{Capr}C*H*OH), 3.74-3.69 (m, 2H, H-6'ab), 3.41 (broad, 1H, H-5), 3.09 (q, 8H, 4 N-CH_2), 2.51-2.15 (m, 8H, 2α^{Laur}CH_2, 2α^{Capr}CH_2), 1.43-1.35 (broad, 20H, 4 N-CH_2-C*H*$_3$, 2γ^{Capr}CH_2, 2γ^{Laur}CH_2), 1.23-1.27 (m, 48H, 24 CH_2), 0.88 (t, 12H, 4x -CH_3);
^{1}H NMR (600 MHz, DMSO-d_6, ref. to solvent signal 2.50 ppm): δ 7.83 (d, 1H, , $^3J_{2,NH}$ = 8.2 Hz, NH), 6.93 (d, 1H, , $^3J_{2',NH'}$ = 9.2 Hz, NH'), 5.11 (**t,** 1H, $^3J_{2,3}$ =$^3J_{3,4}$ = 9.8 Hz, H-3), 5.07 (**t**, 1H, $^3J_{2',3'}$ =$^3J_{3',4'}$ = 10.0 Hz, H-3'), 4.90 (d, 1H, $^3J_{1',2'}$ =3.4 Hz, H-1'), 4.70 (d, 1H, $^3J_{1,2}$ =8.3 Hz, H-1), 4.13-3.99 (m, 3H, H-2', H-4, H-4'), 3.94 (m, 1H, H-5'), 3.82-3.76 (m, 5H, H-2, 2ß^{Laur}C*H*OH, 2ß^{Capr}C*H*OH), 3.68-3.53 (m, 4H, H-6ab, H-6'ab), 3.36 (m, 1H, H-5), 2.37-2.11 (m, 8H, 2α^{Laur}CH_2, 2α^{Capr}CH_2), 1.35-1.16 (m, 56H, 28 CH_2), 0.85 (t, 12H, ^3J =8.8 Hz, 4 CH_3);
^{13}C NMR (150.9 MHz, $CDCl_3$/CD_3OD, 4:1): δ 173.42, 173.24, 172.74, 172.04 (4C, 4 C=O), 101.05 (C-1), 98.54 (C-1'), 75.28 (C-5), 73.77 (C-3), 72.30, 71,96 (2C, C-4, C-4'), 71.55 (2C, C-3', C-5'), 68.73, 68.36 (4C, 2ß^{Laur}*C*H, 2ß^{Capr}*C*H), 60.54 (2C, C-6, C-6'), 53.40 (C-2), 51.82 (C-2'), 43.56, 43.06, 41.83 (4C, 2α^{Laur}CH_2, 2α^{Capr}CH_2) 37.67, 37.15, 36.53, (4C, 2γ^{Laur}CH_2, 2γ^{Capr}CH_2), 31.69, 31.66, 29.40-29.13, 25.35, 25.30, 22.45 (24 CH_2), 13.77 (4C, 4 CH_3);
^{13}C NMR (150.9 MHz, DMSO-d_6, ref. to solvent signal 39.52 ppm): δ 171.61, 171.35, 170.97, 170.7 (4C, 4 C=O), 99.87 (1C, C-1), 98.49 (1C, C-1'), 75.80 (1C, C-5), 72.98 (1C, C-3), 72.10 (1C, C-5'), 71.32-71.11 (m, 2C, C-4, C-4'), 70.86 (1C, C-3'), 67.22, 67.18, 66.83, 66.81 (4C, 2ß^{Laur}CHOH, 2ß^{Capr}CHOH), 60.19 and 59.60 (2C, C-6, C-6'), 53.54 (C-2), 50.63 (C-2'), 43.84, 43.05, 42.79, 42.69 (4C, 2α^{Laur}CH_2, 2α^{Capr}CH_2), 37.03, 36.87, 36.77 (2γ^{Laur}CH_2, 2γ^{Capr}CH_2), 31.36, 31.33, 29.27, 29.25, 29.22, 29.18, 29.09, 29.08, 28.89 28.86, 28.76, 25.29, 25.23, 25.20, 22.11, 22.09 (24 CH_2) 13.90 and 13.89 (4C, *C*H_3);

^{31}P NMR (DMSO-d_6): δ -0.38, -0.53
MALDI-TOF-MS m/z 1235.779 $[M-H]^-$, calc. for $C_{56}H_{106}N_2O_{23}P_2$ 1235.659 $[M-H]^-$

Synthesis of (DA 257)

2-Deoxy-2-[(*R*)-3-hydroxydecanoylamino]-3-*O*-[(*R*)-3-hydroxycanoyl]-β-D-glucopyranosyl-(1→1)-2-deoxy-2-[(*R*)-3-hydroxydecanoylamino]-3-*O*-[(*R*)-3-hydroxydecanoyl]-α-D-glucopyranoside 4,4'-bisphosphate (DA 257)

Compound **DA 257** was prepared from **37** (30 mg, 0.014 mmol) in the way described for the synthesis of **DA 187**. Yield 13 mg (87%), R_f 0.43 (A, $CHCl_3$/MeOH/10% aq. NH_4OH, 100:75:15), $[\alpha]_D^{20}$= +15.8 (*c* 0.3, $CHCl_3$/MeOH, 3:1);
^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$, 4:1): δ 5.26 (dd, 1H, $^3J_{2',3'}$= 9.1, $^3J_{3',4'}$=9.2 Hz, H-3'), 5.17 (dd, 1H, $^3J_{2,3}$=9.5, $^3J_{3,4}$=9.6 Hz, H-3), 5.08 (d, 1H, $^3J_{1',2'}$=3.7 Hz, H-1'), 4.71 (d, 1H, $^3J_{1,2}$=8.6 Hz, H-1), 4.28-4.21 (m, 3H, H-2', H-4, H-4'), 4.13-4.06 (m, 2H, H2, H-5'), 4.05-3.98 (m, 4H, 4ß^{Capr}C*H*OH), 3.83 (broad, 4H, H-6ab, H-6'ab), 3.51-3.49 (m, 1H, H-5), 2.54-2.19 (m, 8H, 4α$^{Capr}CH_2$), 1.48-1.43 (m, 8H, 4γ$^{Capr}CH_2$), 1.31-1.26 (m, 40H, 20 CH_2), 0.91-0.88 (m, 12H, 4 CH_3);

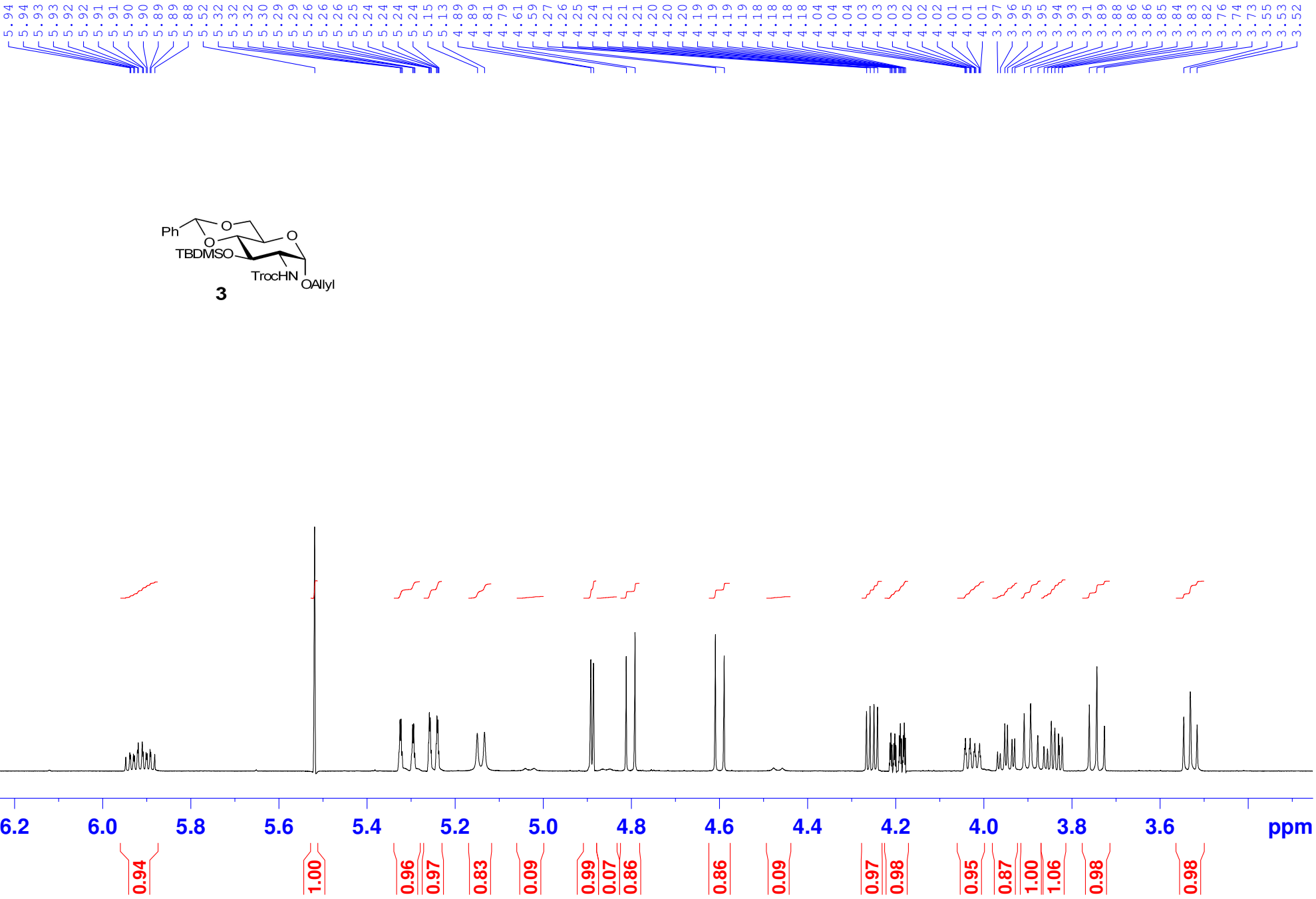
^{13}C NMR (150.9 MHz, $CDCl_3/CD_3OD$, 4:1): δ 173.57, 173.49, 172.81, 172.05 (4C, 4 C=O), 101.00 (C-1), 98.35 (C-1'), 75.30 (C-5), 73.51 (C-3), 71.86 (C-3'), 71.81, 71.55 (C-4, C-4'), 71.35 (C-5'), 68.49, 68.43, 67.89 (4C, 4ß^{Capr}*C*H), 60.51 (2C, C-6, C-6'), 53.22 (C-2), 51.58 (C-2'), 43,41, 42,00, 41.97 (4C, 4α$^{Capr}CH_2$), 36.57, 36.52 (4C, 4γ$^{Capr}CH_2$), 31.34, 29.08-28.83, 25.01, 22.14, (20 CH_2), 13.10 (4C, 4CH_3);

^{31}P ($CDCl_3/CD_3OD$): δ -0.21, -0.32
MALDI-TOF-MS m/z 1179.668 [M-H], calc. for $C_{52}H_{98}N_2O_{23}P_2$ 1179.596 [M-H]

^{1}H and ^{13}C NMR Spectra

For the series **DA 193**

^{1}H and ^{13}C NMR Spectra of all final compounds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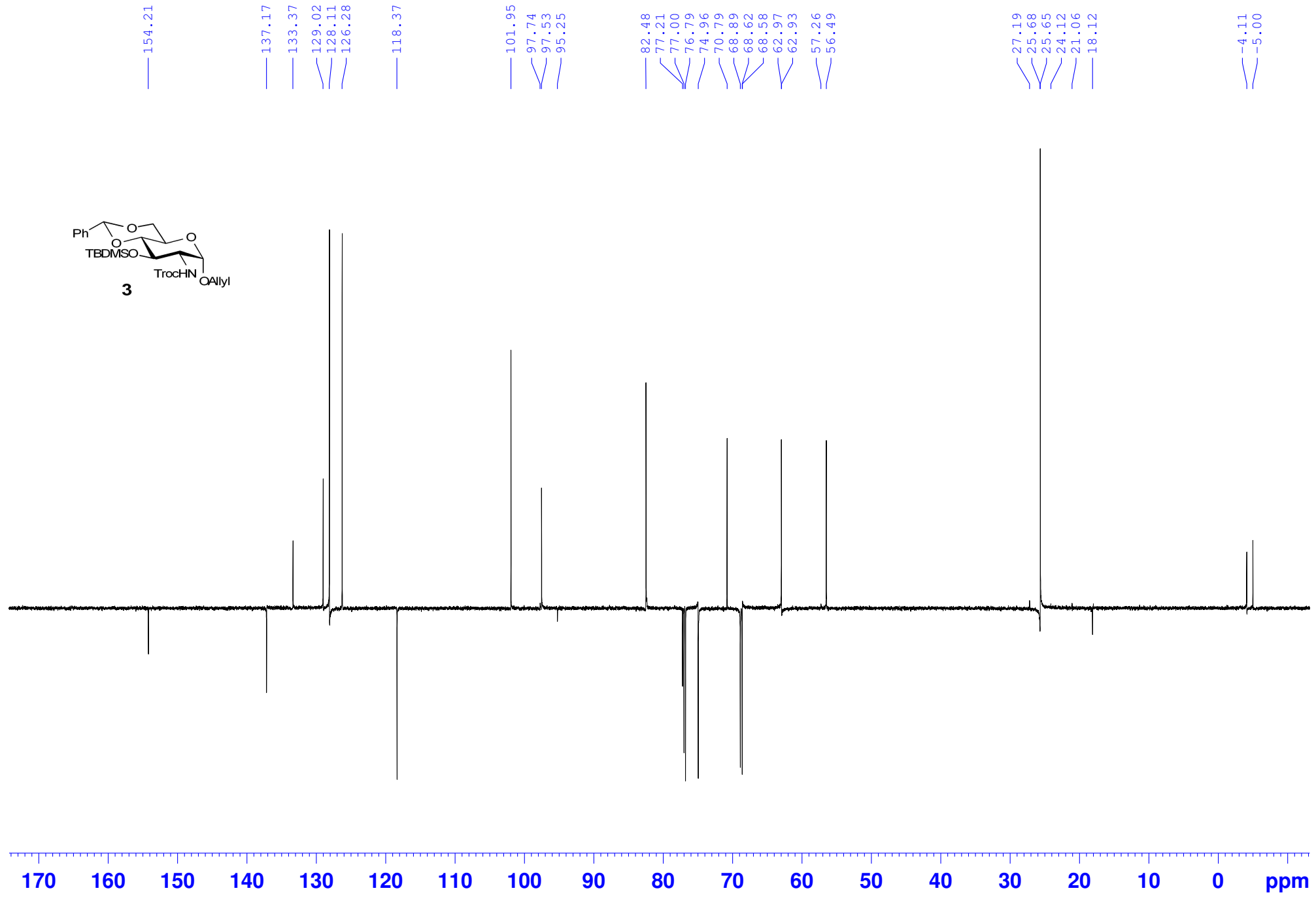
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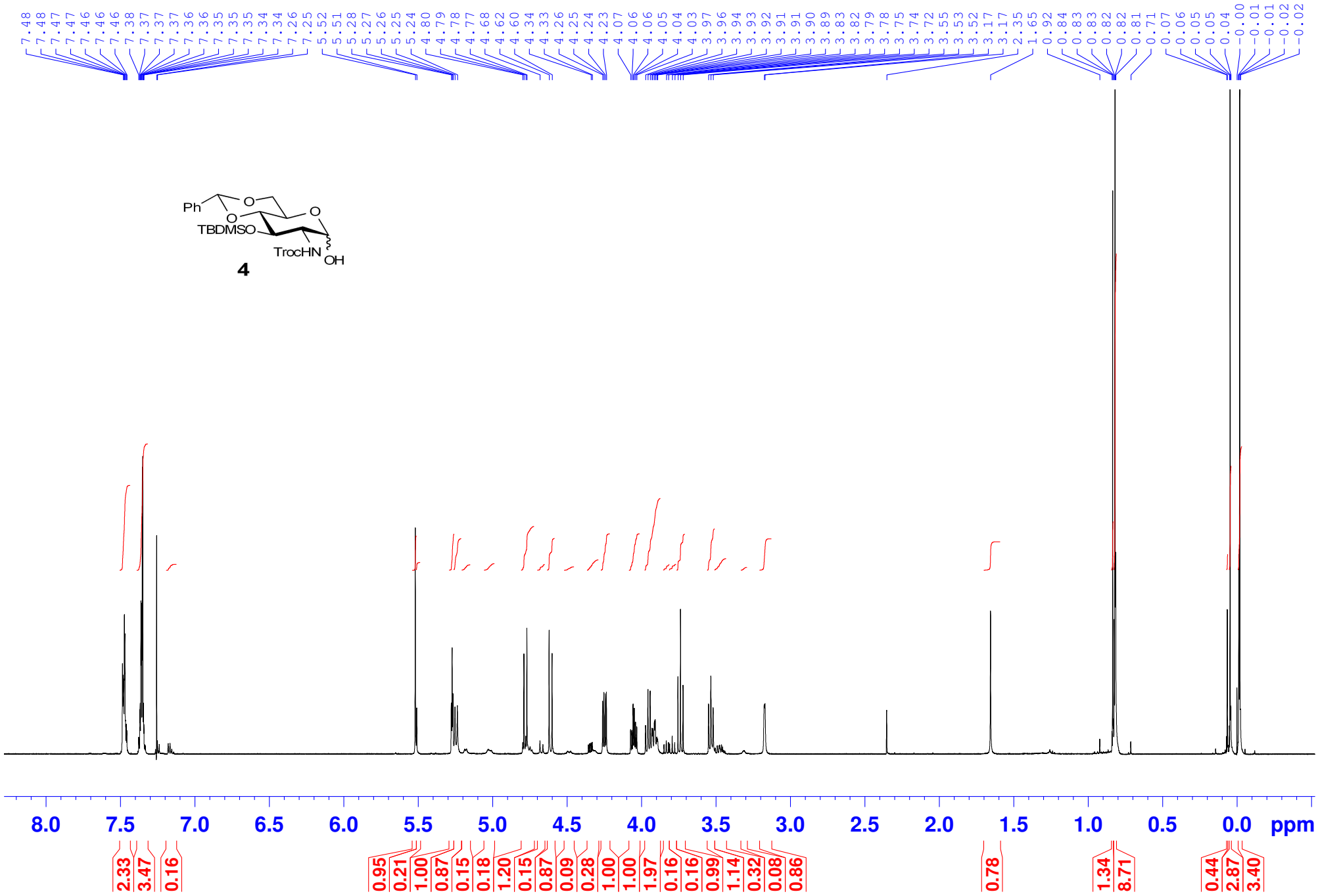
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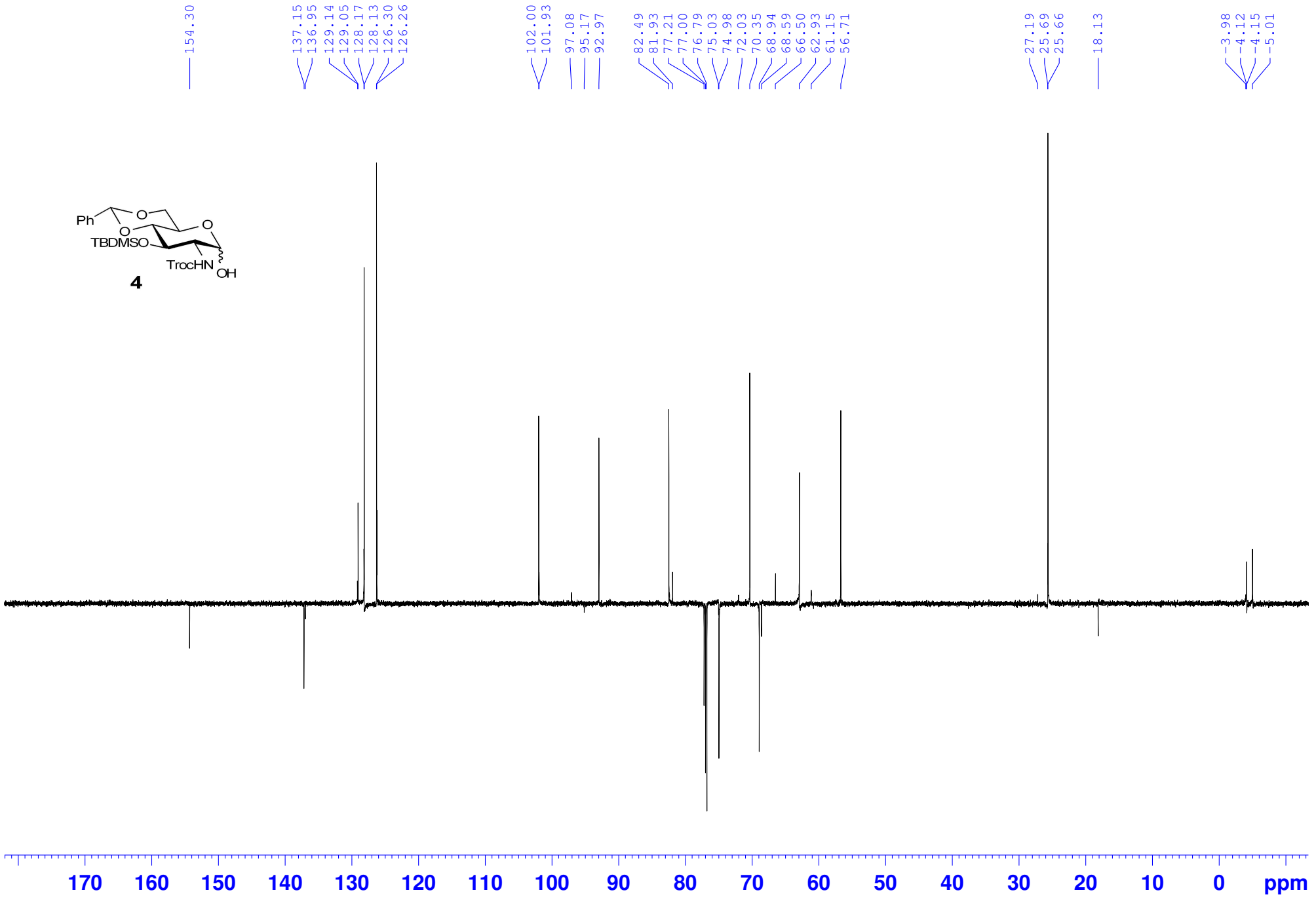
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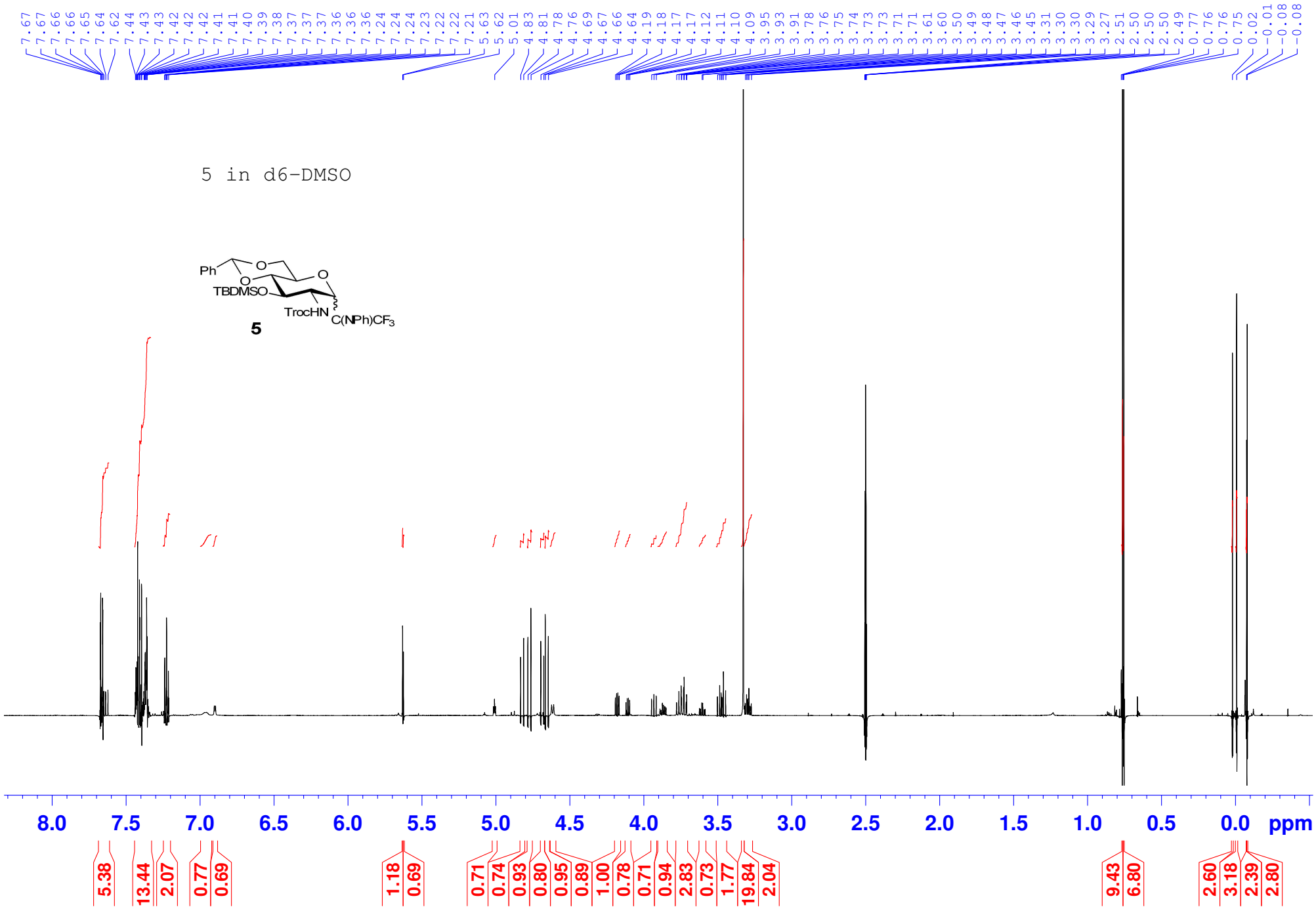
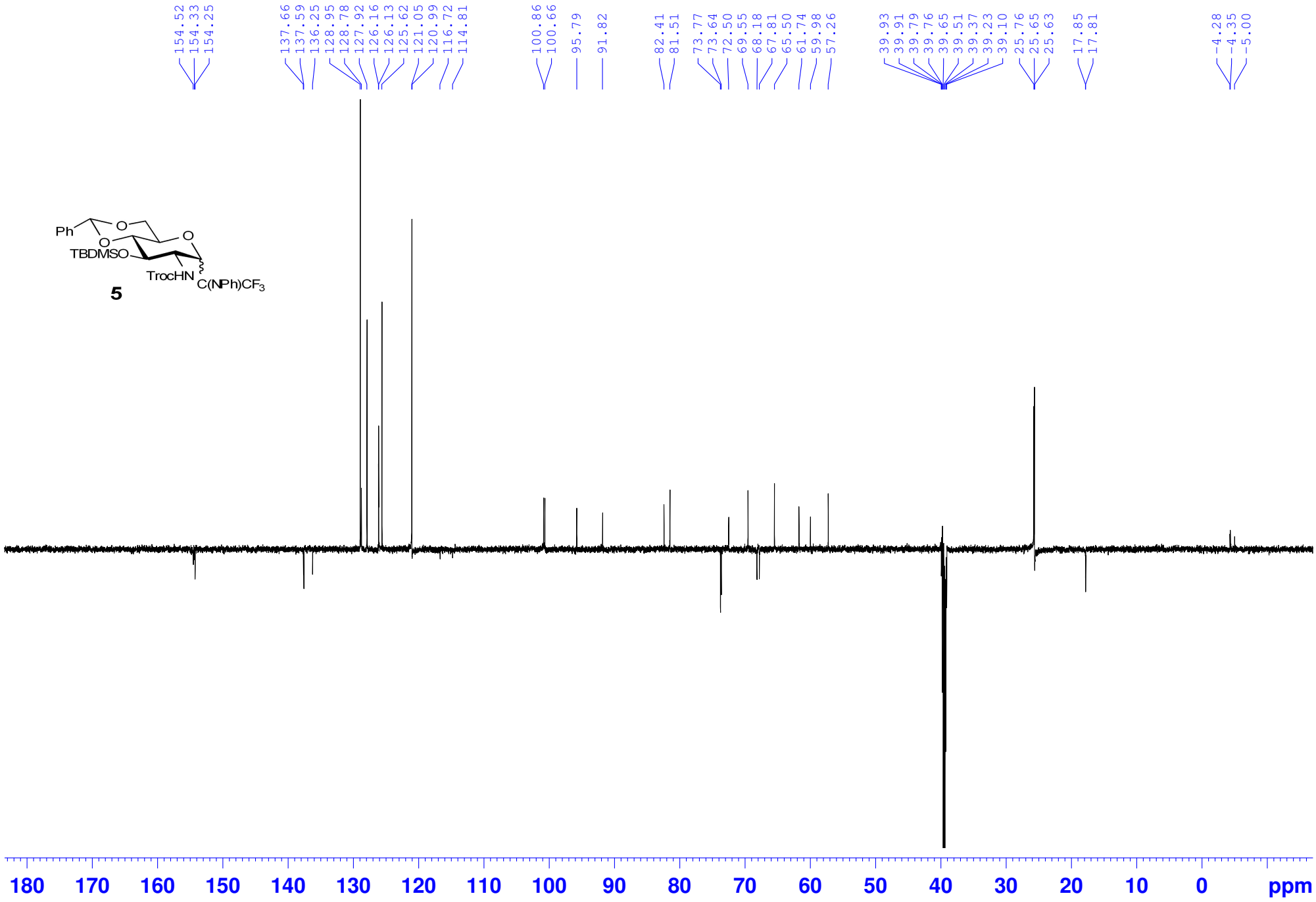
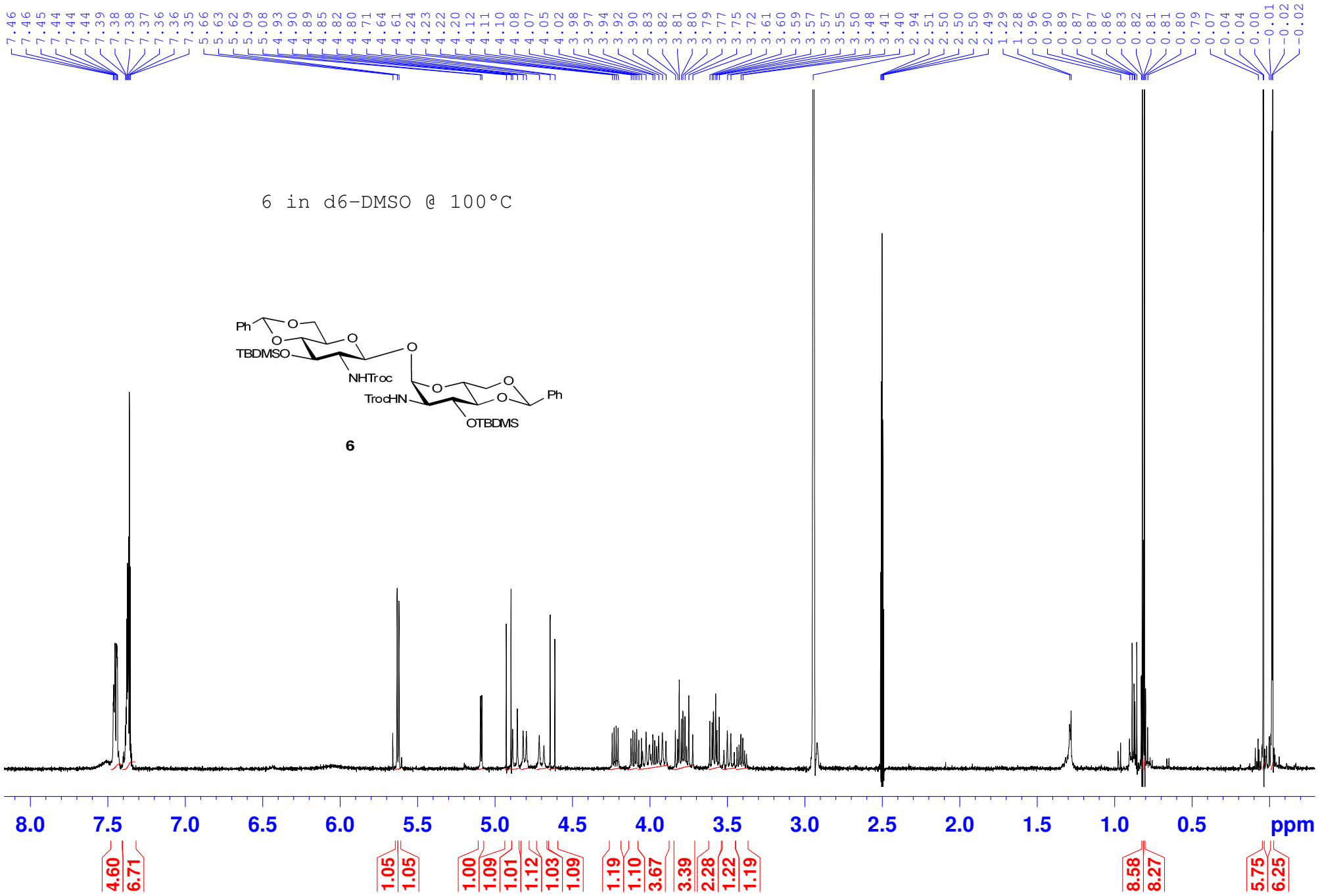
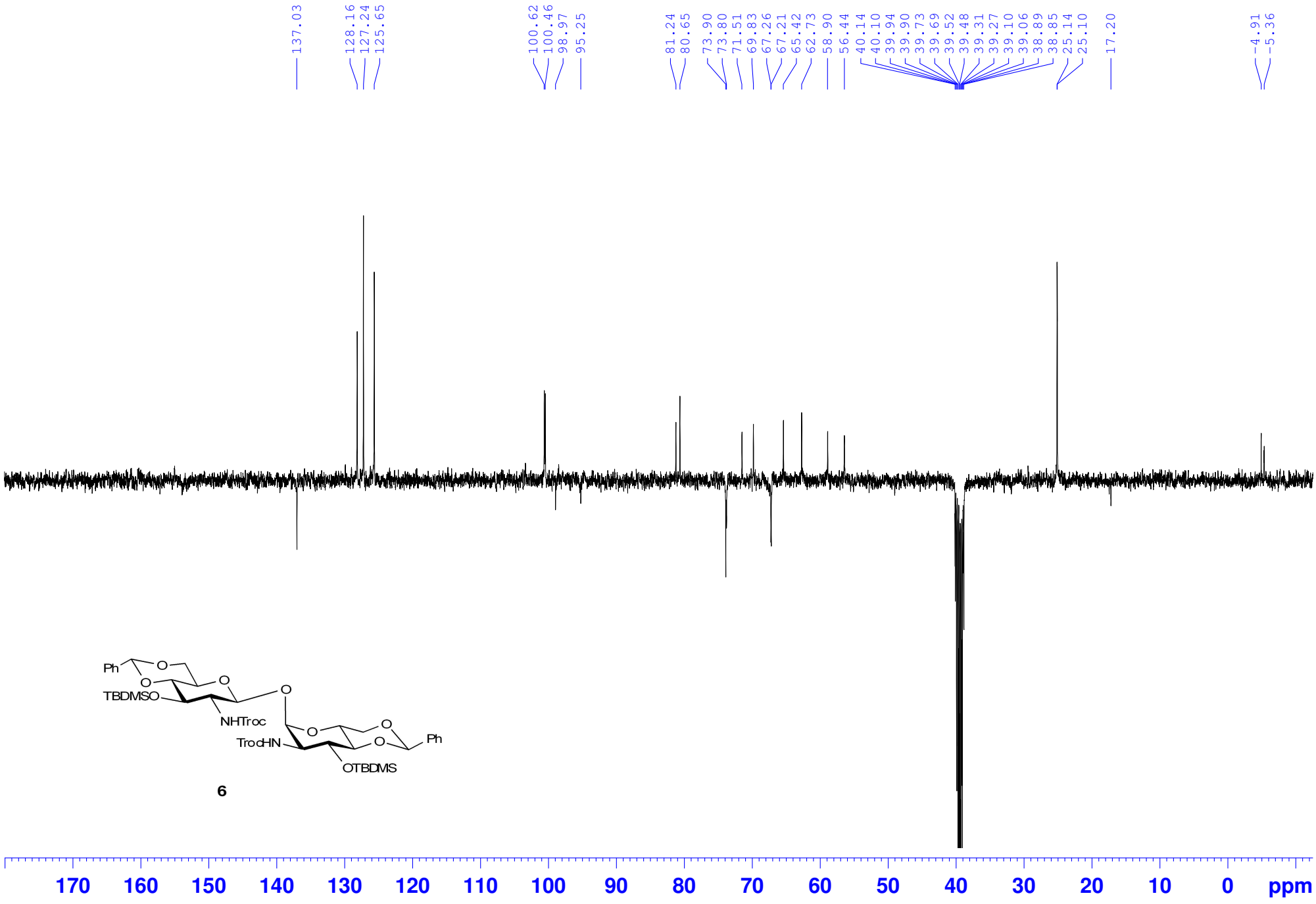
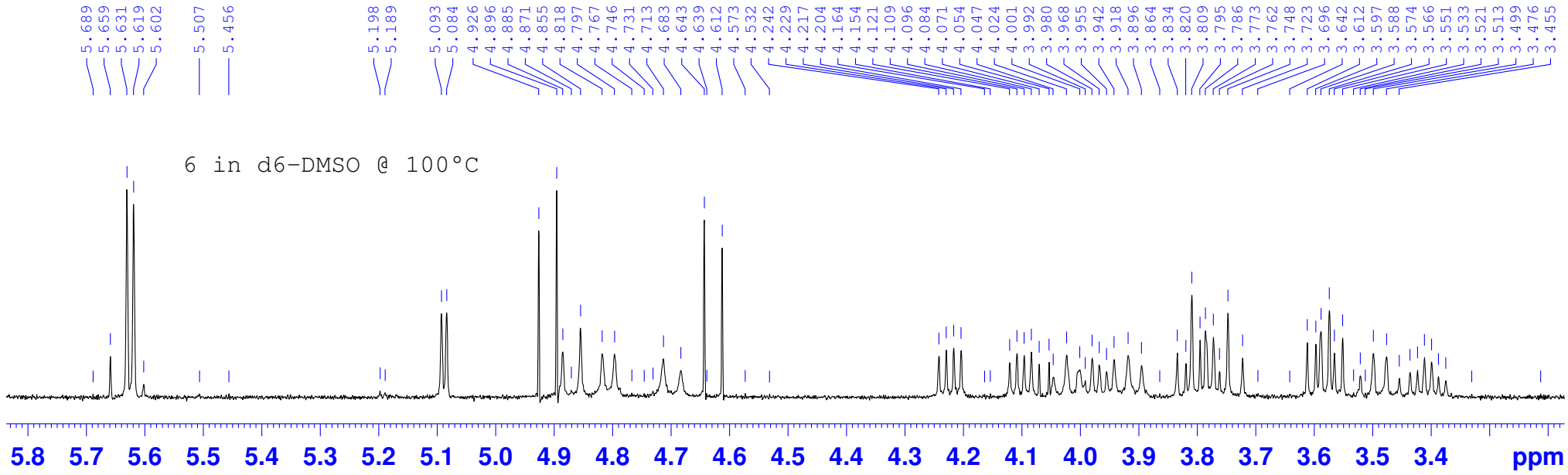
0
ppm

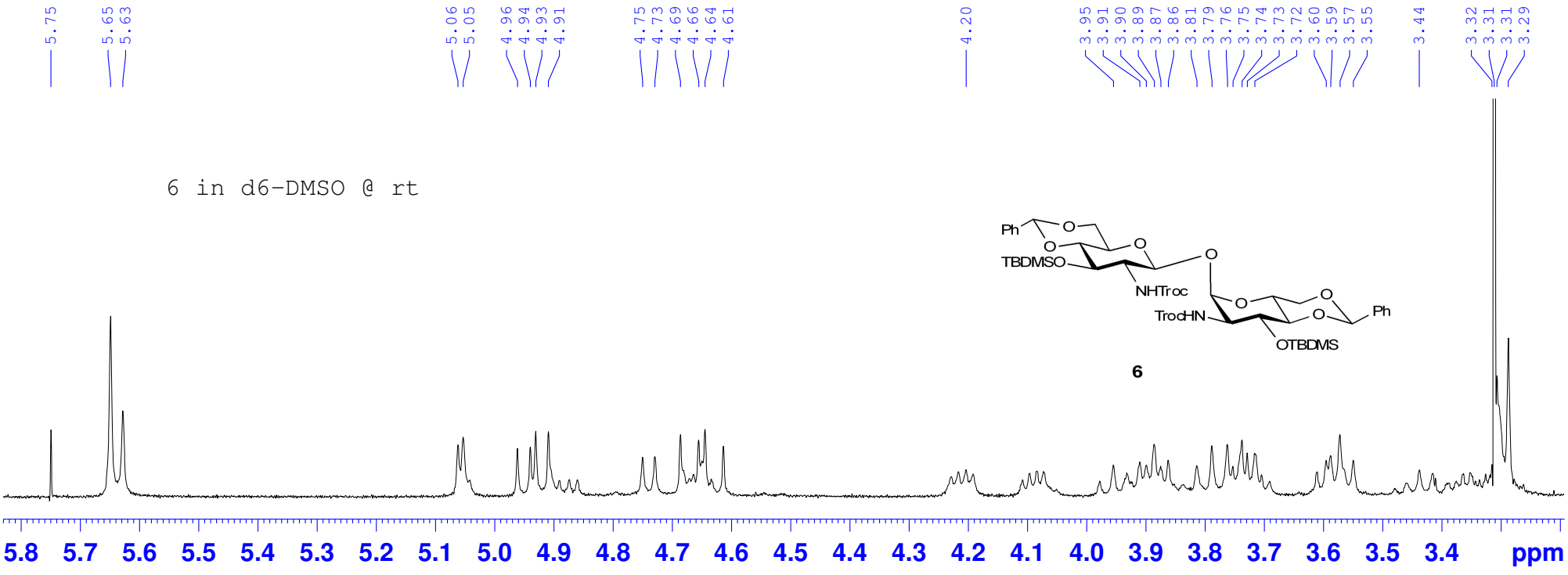

7.67 7.67 7.66 7.66 7.65 7.64 7.62 7.44 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.39 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.24 7.24 7.24 7.23 7.22 7.22 7.21 5.63 5.62 5.01 4.83 4.81 4.78 4.76 4.69 4.67 4.66 4.64 4.19 4.18 4.17 4.17 4.12 4.11 4.10 4.09 3.95 3.93 3.91 3.78 3.76 3.75 3.74 3.73 3.73 3.71 3.71 3.61 3.60 3.50 3.49 3.48 3.47 3.46 3.45 3.31 3.30 3.30 3.29 3.27 2.51 2.50 2.50 2.50 2.49 0.77 0.76 0.76 0.75 0.02 -0.01 -0.08 -0.08
5 in d6-DMSO
Ph
O
O
O
TBDMSO
TrocHN
C(NPh)CF3
5
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
5.38 13.44 2.07 0.77 0.69 1.18 0.69 0.71 0.74 0.93 0.80 0.95 0.89 1.00 0.78 0.71 0.94 2.83 0.73 1.77 19.84 2.04 9.43 6.80 2.60 3.18 2.39 2.80

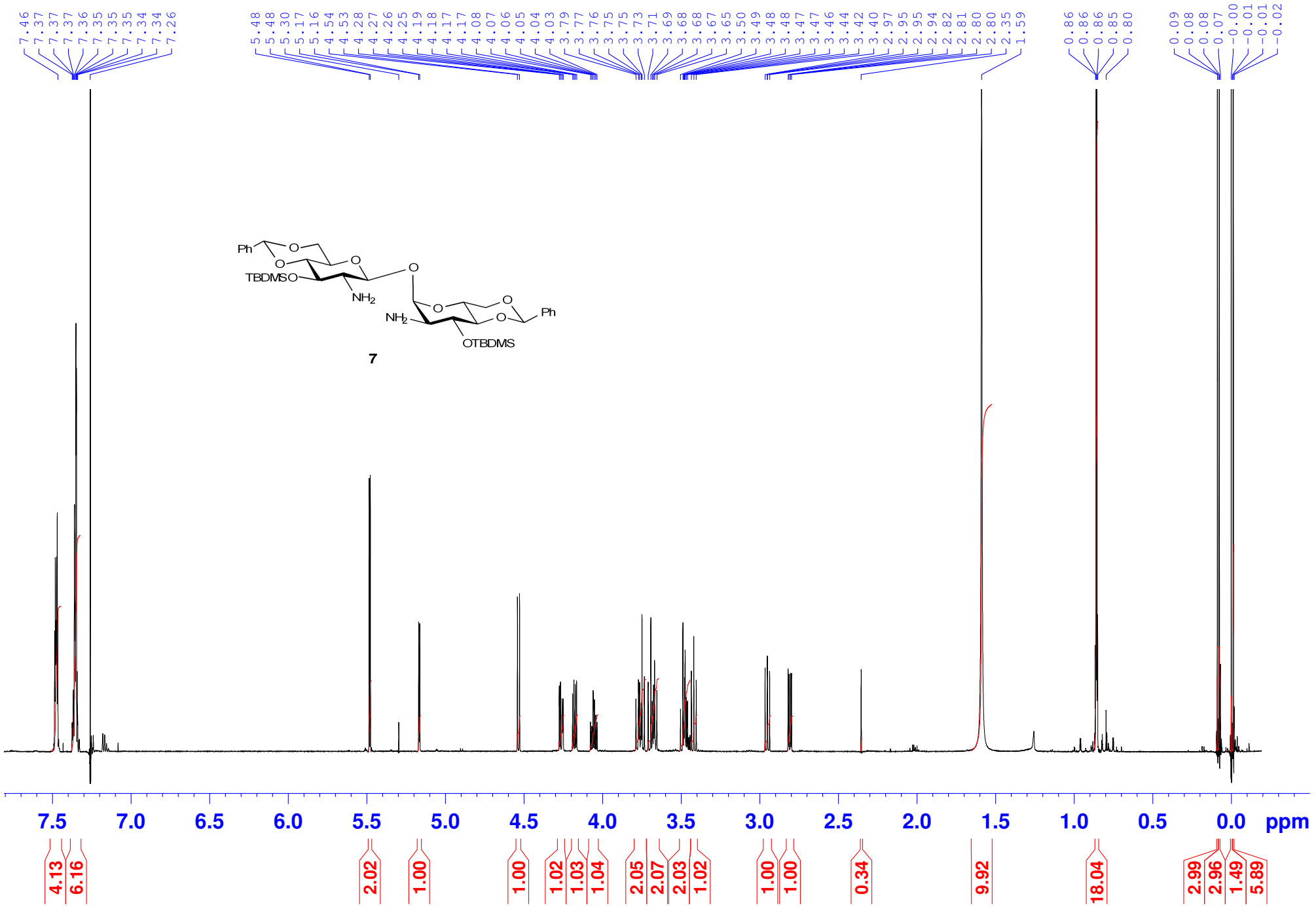

154.52
154.33
154.25
137.66
137.59
136.25
128.95
128.78
127.92
126.16
126.13
125.62
121.05
120.99
116.72
114.81
100.86
100.66
95.79
91.82
82.41
81.51
73.77
73.64
72.50
69.55
68.18
67.81
65.50
61.74
59.98
57.26
39.93
39.91
39.79
39.76
39.65
39.51
39.37
39.23
39.10
25.76
25.65
25.63
17.85
17.81
-4.28
-4.35
-5.00
Ph
O
O
O
TBDMSO
TrocHN
C(NPh)CF3
5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

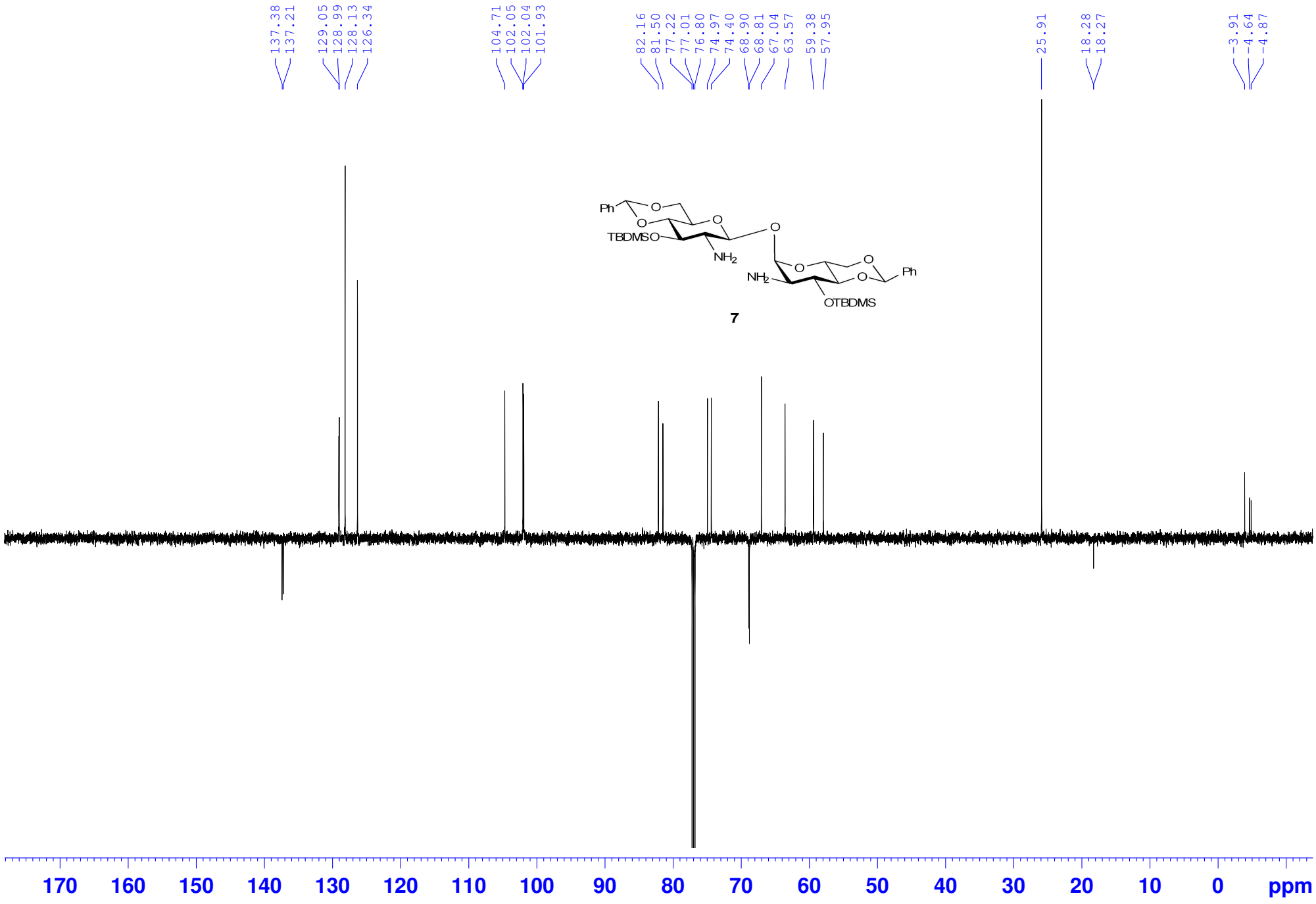

7.46 7.46 7.45 7.44 7.44 7.44 7.39 7.38 7.38 7.37 7.36 7.35
5.66 5.63 5.62 5.09 5.08 4.93 4.90 4.89 4.85 4.82 4.80 4.71 4.64 4.61 4.24 4.23 4.22 4.20 4.12 4.11 4.10 4.08 4.07 4.05 4.02 3.98 3.97 3.94 3.92 3.90 3.83 3.82 3.81 3.80 3.79 3.77 3.75 3.72 3.61 3.60 3.59 3.57 3.57 3.55 3.50 3.48 3.41 3.40 2.94 2.51 2.50 2.50 2.50 2.49 1.29 1.28 0.96 0.90 0.89 0.87 0.87 0.86 0.83 0.82 0.81 0.81 0.80 0.79 0.07 0.04 0.04 0.00 -0.01 -0.02
6 in d6-DMSO @ 100°C
Ph
TBDMSO
NHTroc
TrocHN
OTBDMS
Ph
6
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.60 6.71
1.05 1.05
1.00 1.09 1.01 1.12 1.03 1.09
1.19 1.10 3.67 3.39 2.28 1.22 1.19
8.58 8.27
5.75 6.25

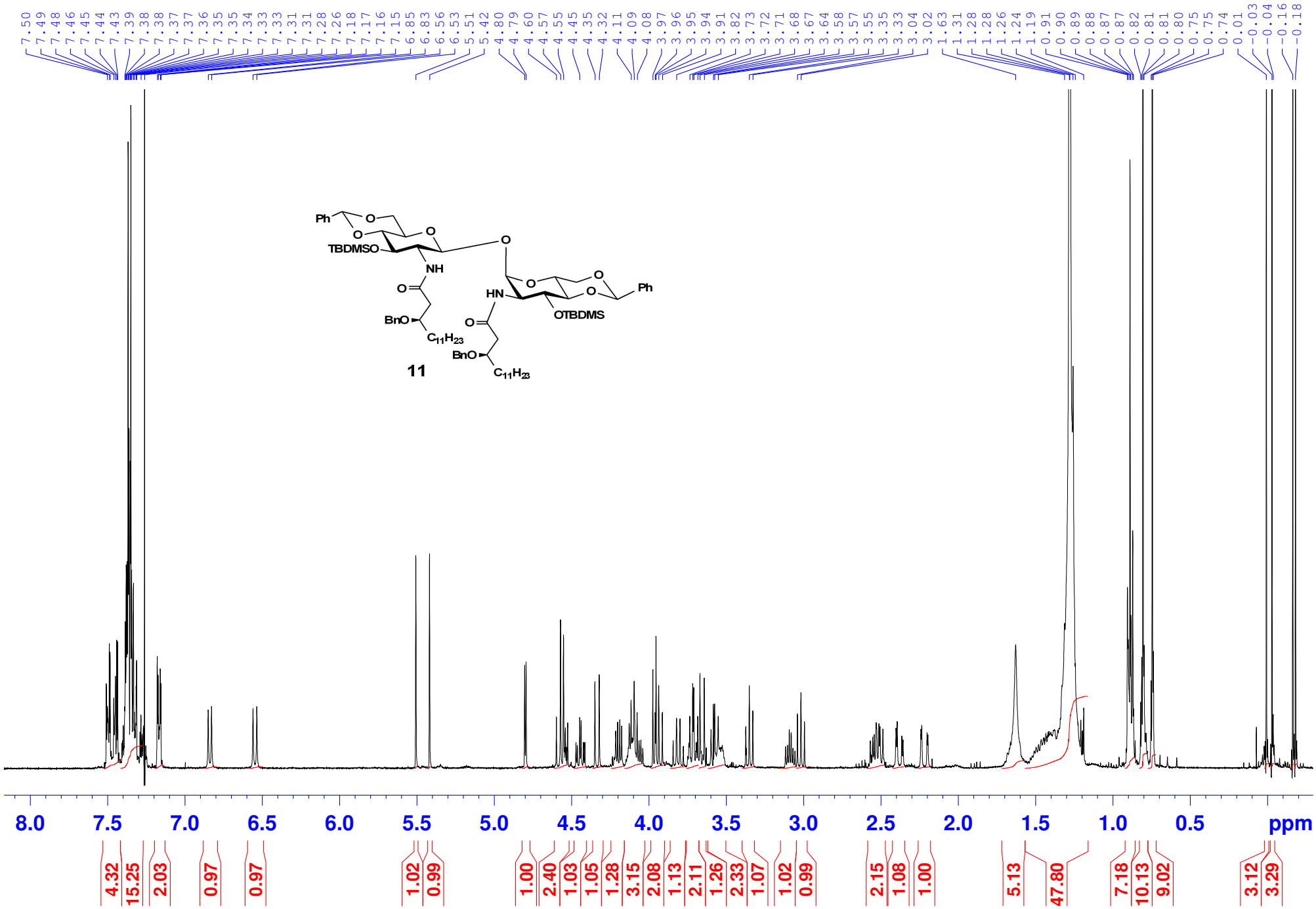

137.03
128.16
127.24
125.65
100.62
100.46
98.97
95.25
81.24
80.65
73.90
73.80
71.51
69.83
67.26
67.21
65.42
62.73
58.90
56.44
40.14
40.10
39.94
39.90
39.73
39.69
39.52
39.48
39.31
39.27
39.10
39.06
38.89
38.85
25.14
25.10
17.20
-4.91
-5.36
Ph
TBDMSO
NHTroc
TrocHN
OTBDMS
Ph
6
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

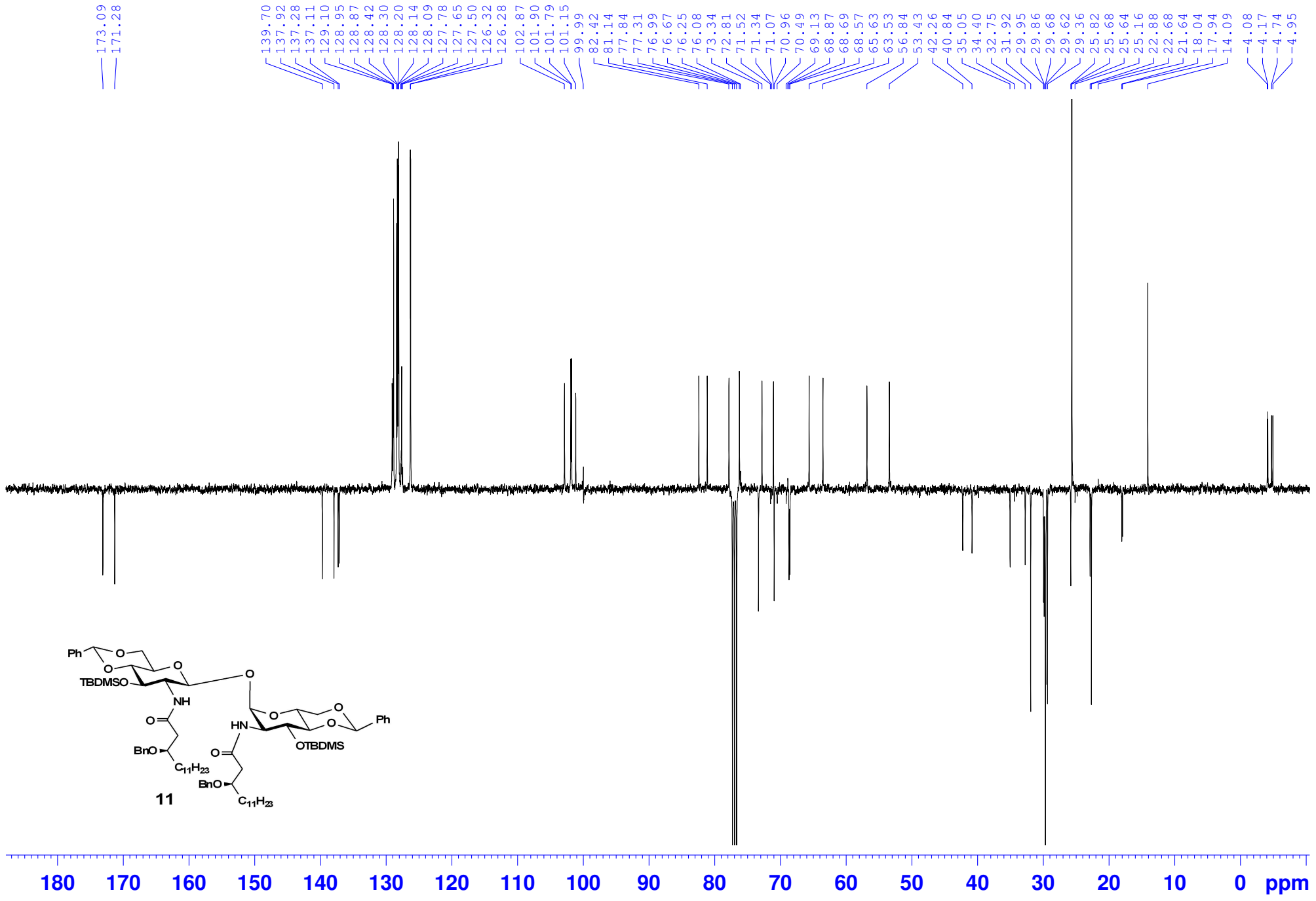

5.689
5.659
5.631
5.619
5.602
5.507
5.456
5.198
5.189
5.093
5.084
4.926
4.896
4.885
4.871
4.855
4.818
4.797
4.767
4.746
4.731
4.713
4.683
4.643
4.639
4.612
4.573
4.532
4.242
4.229
4.217
4.204
4.164
4.154
4.121
4.109
4.096
4.084
4.071
4.054
4.047
4.024
4.001
3.992
3.980
3.968
3.955
3.942
3.918
3.896
3.864
3.834
3.820
3.809
3.795
3.786
3.773
3.762
3.748
3.723
3.696
3.642
3.612
3.597
3.588
3.574
3.566
3.551
3.533
3.521
3.513
3.499
3.476
3.455
6 in d6-DMSO @ 100°C
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 ppm


5.75
5.65
5.63
5.06
5.05
4.96
4.94
4.93
4.91
4.75
4.73
4.69
4.66
4.64
4.61
4.20
3.95
3.91
3.90
3.89
3.87
3.86
3.81
3.79
3.76
3.75
3.74
3.73
3.72
3.60
3.59
3.57
3.55
3.44
3.32
3.31
3.31
3.29
6 in d6-DMSO @ rt
Ph
O
O
O
TBDMSO
O
NHTroc
O
O
TrocHN
O
Ph
OTBDMS
6
5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5 3.4 ppm


7.46 7.37 7.37 7.37 7.36 7.35 7.35 7.35 7.34 7.34 7.26
5.48 5.48 5.30 5.17 5.16 4.54 4.53 4.28 4.27 4.26 4.25 4.19 4.18 4.17 4.17 4.08 4.07 4.06 4.05 4.04 4.03 3.79 3.77 3.76 3.75 3.75 3.73 3.71 3.69 3.68 3.68 3.67 3.65 3.50 3.49 3.48 3.48 3.47 3.47 3.46 3.44 3.42 3.40 2.97 2.95 2.95 2.94 2.82 2.81 2.80 2.80 2.35 1.59
0.86 0.86 0.86 0.85 0.80
0.09 0.08 0.08 0.07 -0.00 -0.01 -0.01 -0.02
Ph
TBDMSO
NH2
NH2
OTBDMS
Ph
7
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
4.13 6.16 2.02 1.00 1.00 1.02 1.03 1.04 2.05 2.07 2.03 1.02 1.00 1.00 0.34 9.92 18.04 2.99 2.96 1.49 5.89


137.38
137.21
129.05
128.99
128.13
126.34
104.71
102.05
102.04
101.93
82.16
81.50
77.22
77.01
76.80
74.97
74.40
68.90
68.81
67.04
63.57
59.38
57.95
25.91
18.28
18.27
-3.91
-4.64
-4.87
Ph
TBDMSO
NH2
NH2
Ph
OTBDMS
7
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.50 7.49 7.48 7.46 7.45 7.44 7.43 7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.33 7.31 7.31 7.28 7.26 7.18 7.17 7.16 7.15 6.85 6.83 6.56 6.53 5.51 5.42 4.80 4.79 4.60 4.57 4.55 4.45 4.35 4.32 4.11 4.09 4.08 3.97 3.96 3.95 3.94 3.91 3.82 3.73 3.72 3.71 3.68 3.67 3.64 3.58 3.57 3.55 3.35 3.33 3.04 3.02 1.63 1.31 1.28 1.28 1.26 1.24 1.19 0.91 0.90 0.89 0.88 0.87 0.87 0.82 0.81 0.81 0.80 0.75 0.74 0.01 -0.03 -0.04 -0.16 -0.18
Ph
TBDMSO
NH
HN
OTBDMS
BnO
$C_{11}H_{23}$
11
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.32 15.25 2.03 0.97 0.97 1.02 0.99 1.00 2.40 1.03 1.05 1.28 3.15 2.08 1.13 2.11 1.26 2.33 1.07 1.02 0.99 2.15 1.08 1.00 5.13 47.80 7.18 10.13 9.02 3.12 3.29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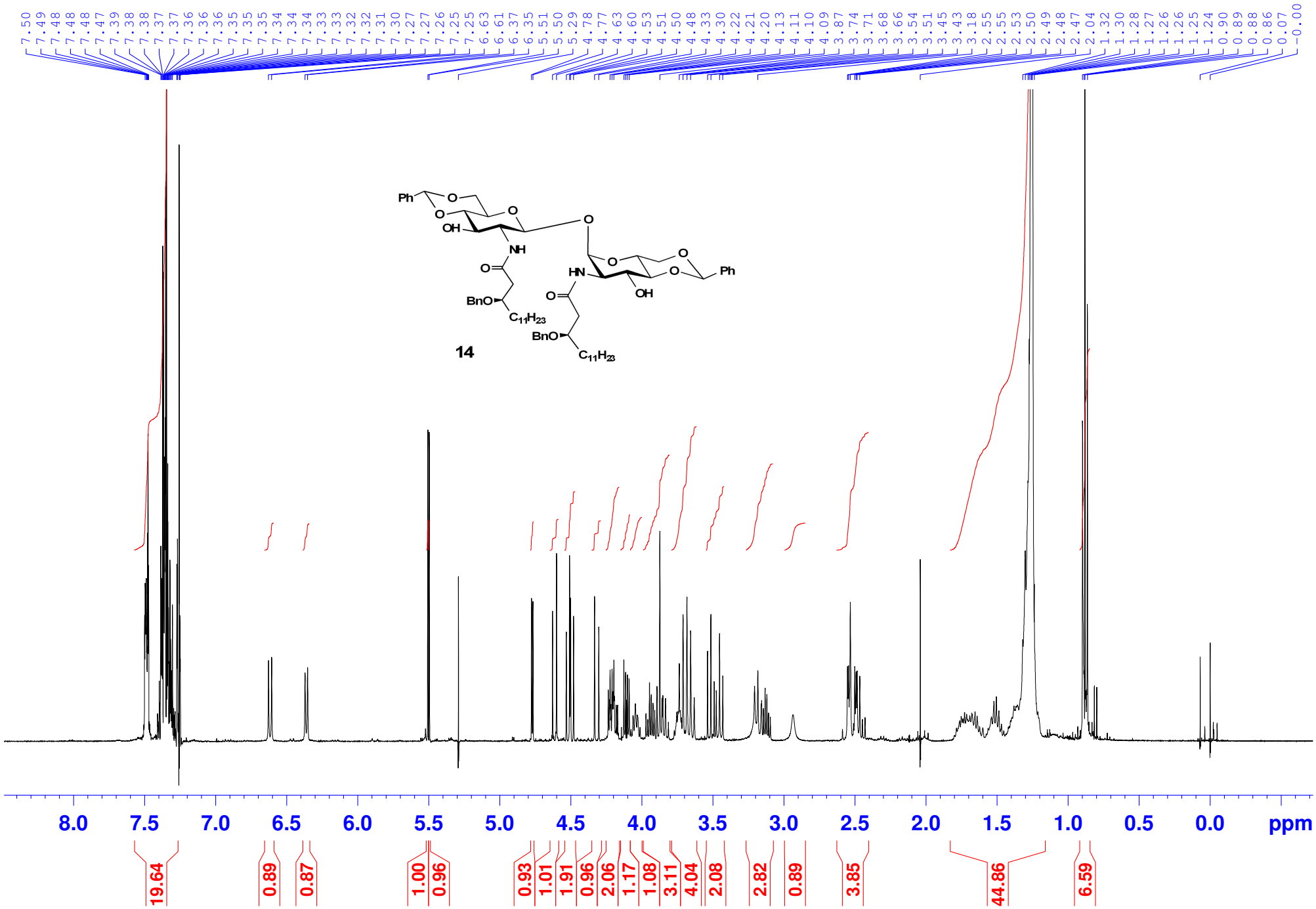
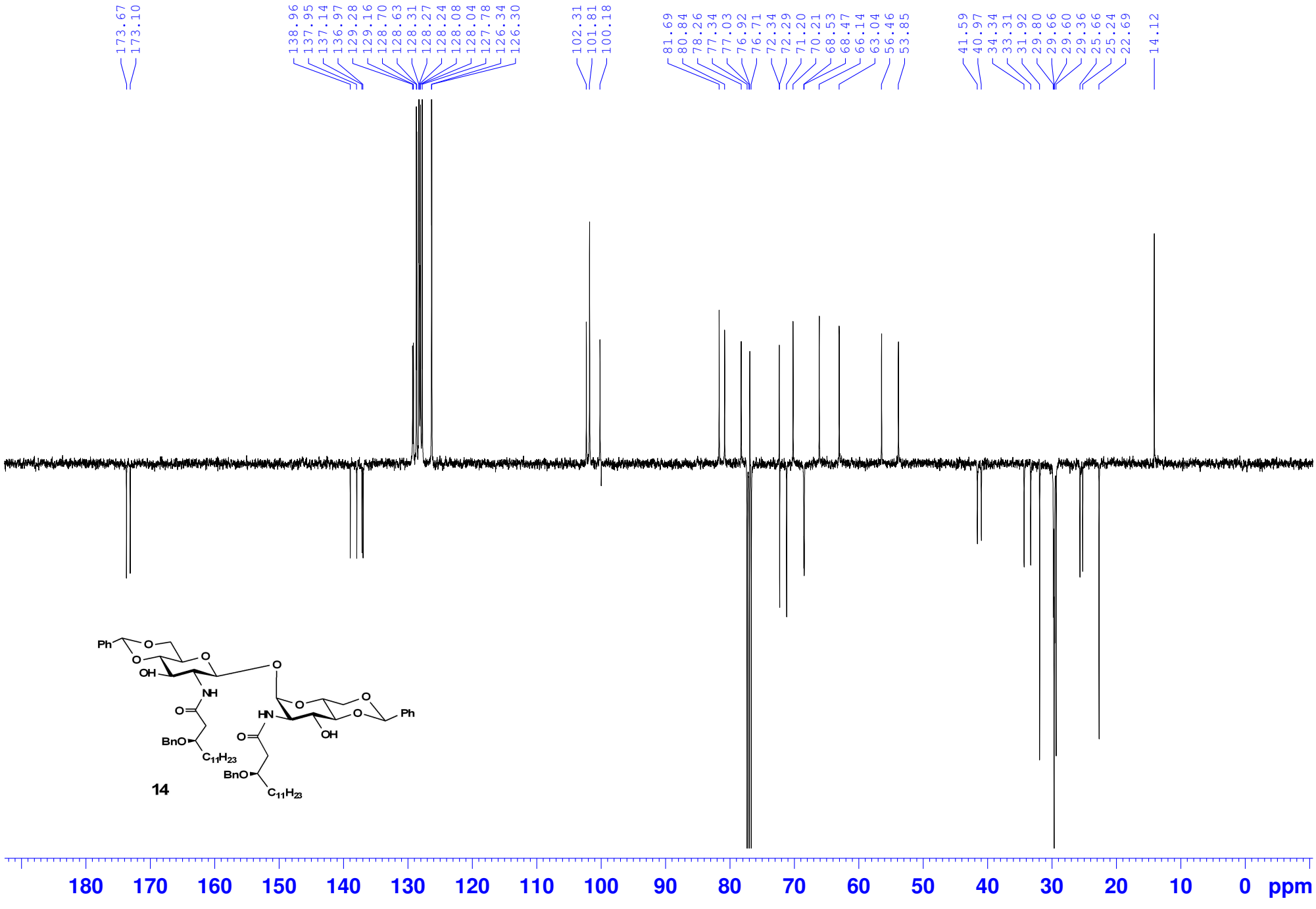
171.28
139.70
137.92
137.28
137.11
129.10
128.95
128.87
128.42
128.30
128.20
128.14
128.09
127.78
127.65
127.50
126.32
126.28
102.87
101.90
101.79
101.15
99.99
82.42
81.14
77.84
77.31
76.99
76.67
76.25
76.08
73.34
72.81
71.52
71.34
71.07
70.96
70.49
69.13
68.87
68.69
68.57
65.63
63.53
56.84
53.43
42.26
40.84
35.05
34.40
32.75
31.92
29.95
29.86
29.68
29.62
29.36
25.82
25.68
25.64
25.16
22.88
22.68
21.64
18.04
17.94
14.09
-4.08
-4.17
-4.74
-4.95
Ph
O
O
O
TBDMSO
NH
O
BnO
C11H23
O
HN
O
BnO
C11H23
O
O
O
Ph
OTBDMS
11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.50 7.49 7.48 7.48 7.48 7.47 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.27 7.27 7.26 7.25 7.25 6.63 6.61 6.37 6.35 5.51 5.50 5.29 4.78 4.77 4.63 4.60 4.53 4.51 4.50 4.48 4.33 4.30 4.22 4.21 4.20 4.13 4.11 4.10 4.09 3.87 3.74 3.71 3.68 3.66 3.54 3.51 3.45 3.43 3.18 2.55 2.55 2.53 2.50 2.49 2.48 2.47 2.04 1.32 1.30 1.28 1.27 1.26 1.26 1.25 1.24 0.90 0.89 0.88 0.86 0.07 -0.00
Ph
O
O
O
OH
NH
O
BnO
C11H23
O
BnO
C11H23
O
HN
OH
O
O
O
Ph
14
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
19.64
0.89
0.87
1.00
0.96
0.93
1.01
1.91
0.96
2.06
1.17
1.08
3.11
4.04
2.08
2.82
0.89
3.85
44.86
6.59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173.10
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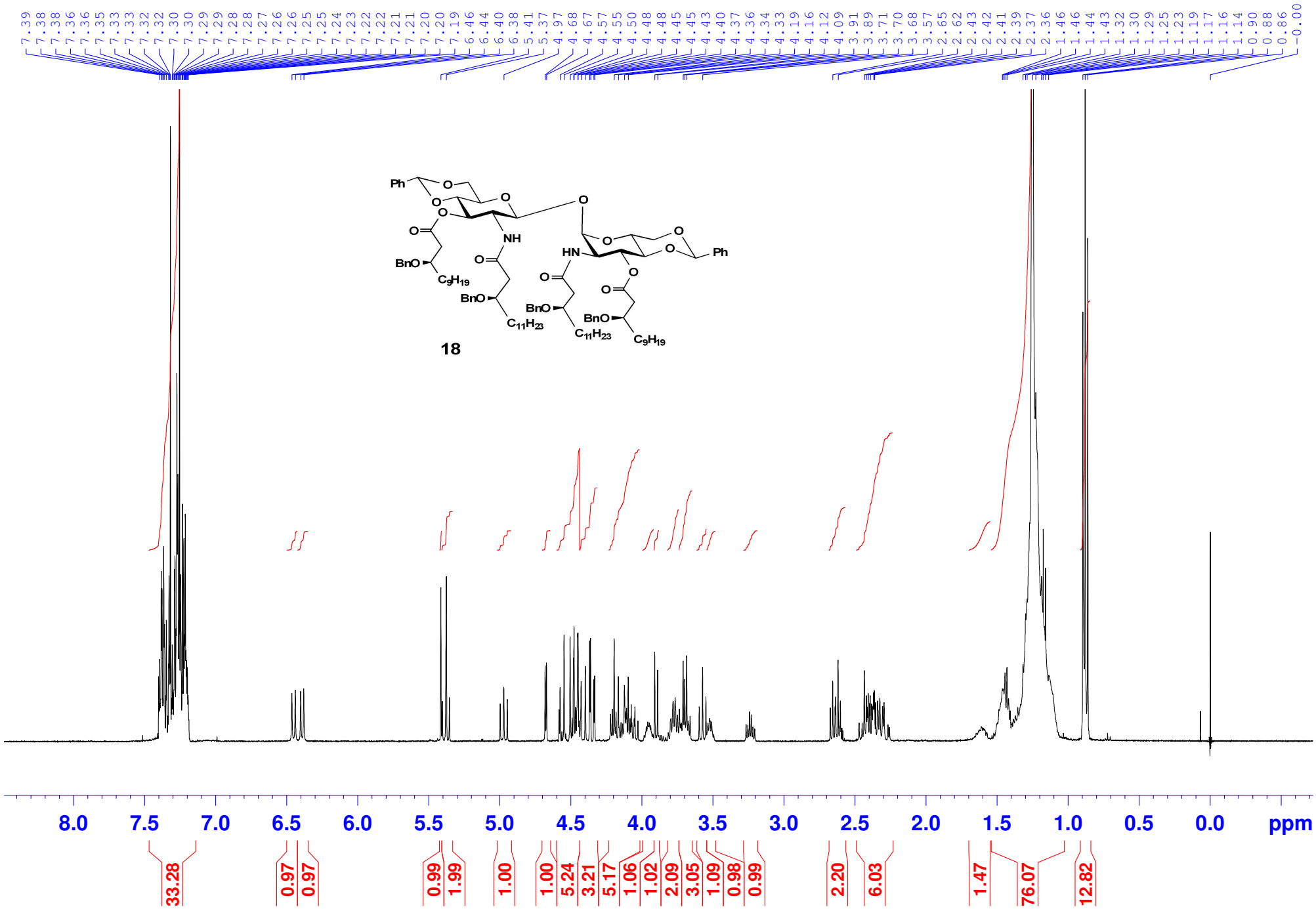
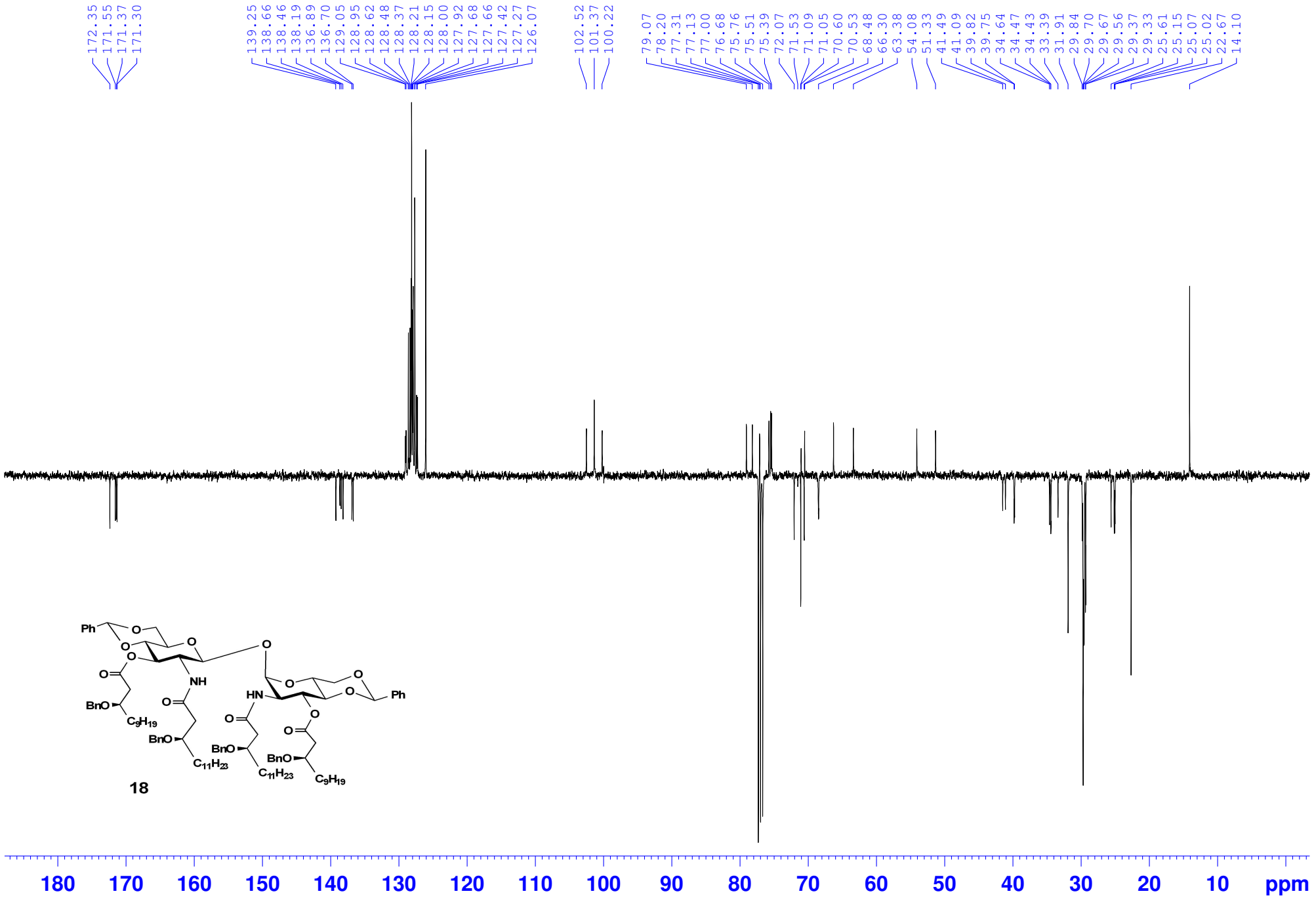
137.95
137.14
136.97
129.28
129.16
128.70
128.63
128.31
128.27
128.24
128.08
128.04
127.78
126.34
126.30
102.31
101.81
100.18
81.69
80.84
78.26
77.34
77.03
76.92
76.71
72.34
72.29
71.20
70.21
68.53
68.47
66.14
63.04
56.46
53.85
41.59
40.97
34.34
33.31
31.92
29.80
29.66
29.60
29.36
25.66
25.24
22.69
14.12
Ph
O
O
O
OH
NH
O
BnO
C11H23
BnO
C11H23
O
HN
O
O
O
O
OH
Ph
14
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.39 7.38 7.38 7.36 7.36 7.35 7.33 7.33 7.32 7.32 7.30 7.30 7.29 7.29 7.28 7.28 7.27 7.26 7.26 7.25 7.25 7.24 7.23 7.22 7.22 7.21 7.21 7.20 7.20 7.19 6.46 6.44 6.40 6.38 5.41 5.37 4.97 4.68 4.67 4.57 4.55 4.50 4.48 4.48 4.45 4.45 4.43 4.40 4.37 4.36 4.34 4.33 4.19 4.16 4.12 4.09 3.91 3.89 3.71 3.70 3.68 3.57 2.65 2.62 2.43 2.42 2.41 2.39 2.37 2.36 1.46 1.44 1.43 1.32 1.30 1.29 1.25 1.23 1.19 1.17 1.16 1.14 0.90 0.88 0.86 -0.00
Ph
O
NH
HN
BnO
C_9H_{19}
$C_{11}H_{23}$
18
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
33.28 0.97 0.97 0.99 1.99 1.00 1.00 5.24 3.21 5.17 1.06 1.02 2.09 3.05 1.09 0.98 0.99 2.20 6.03 1.47 76.07 12.82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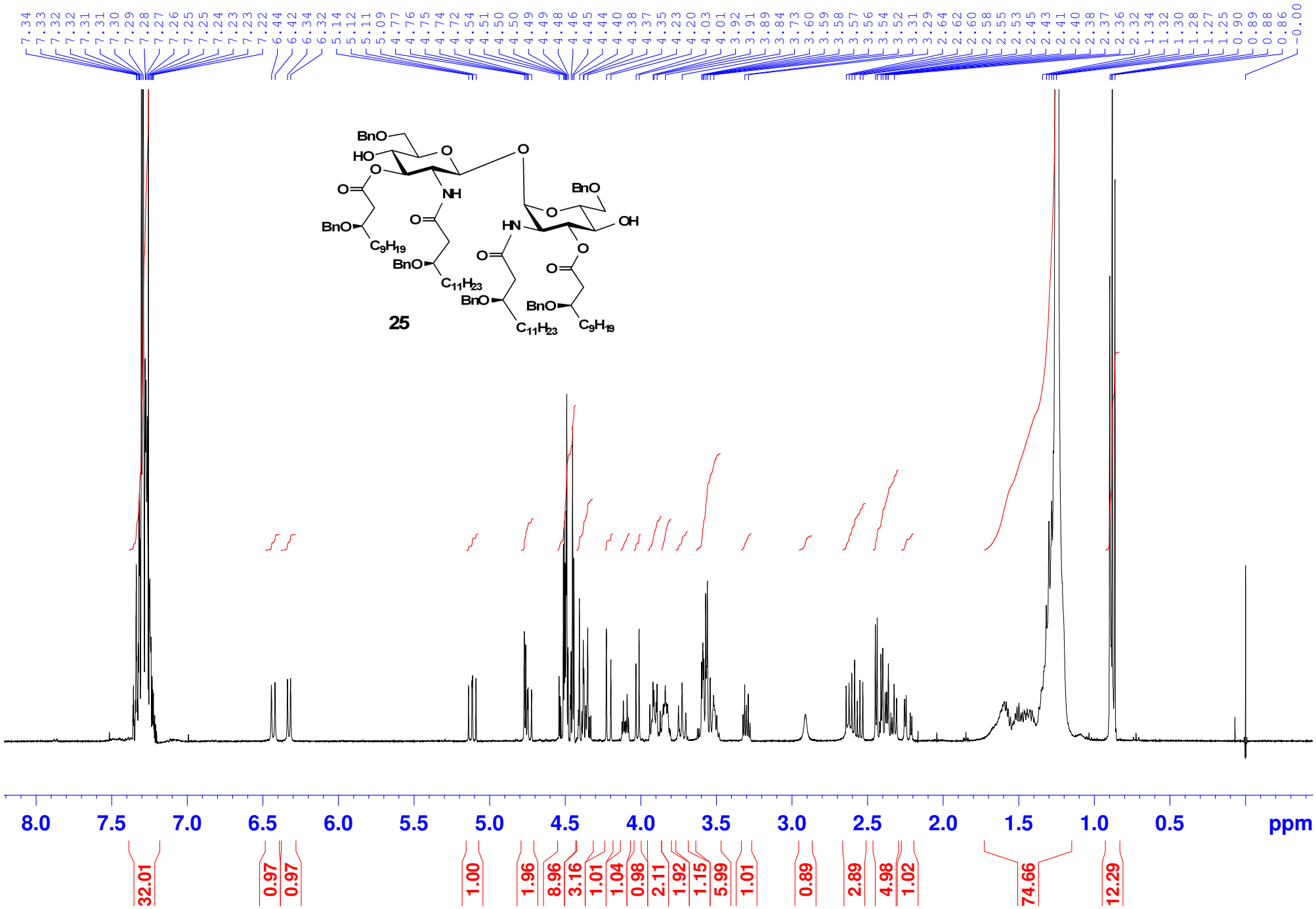
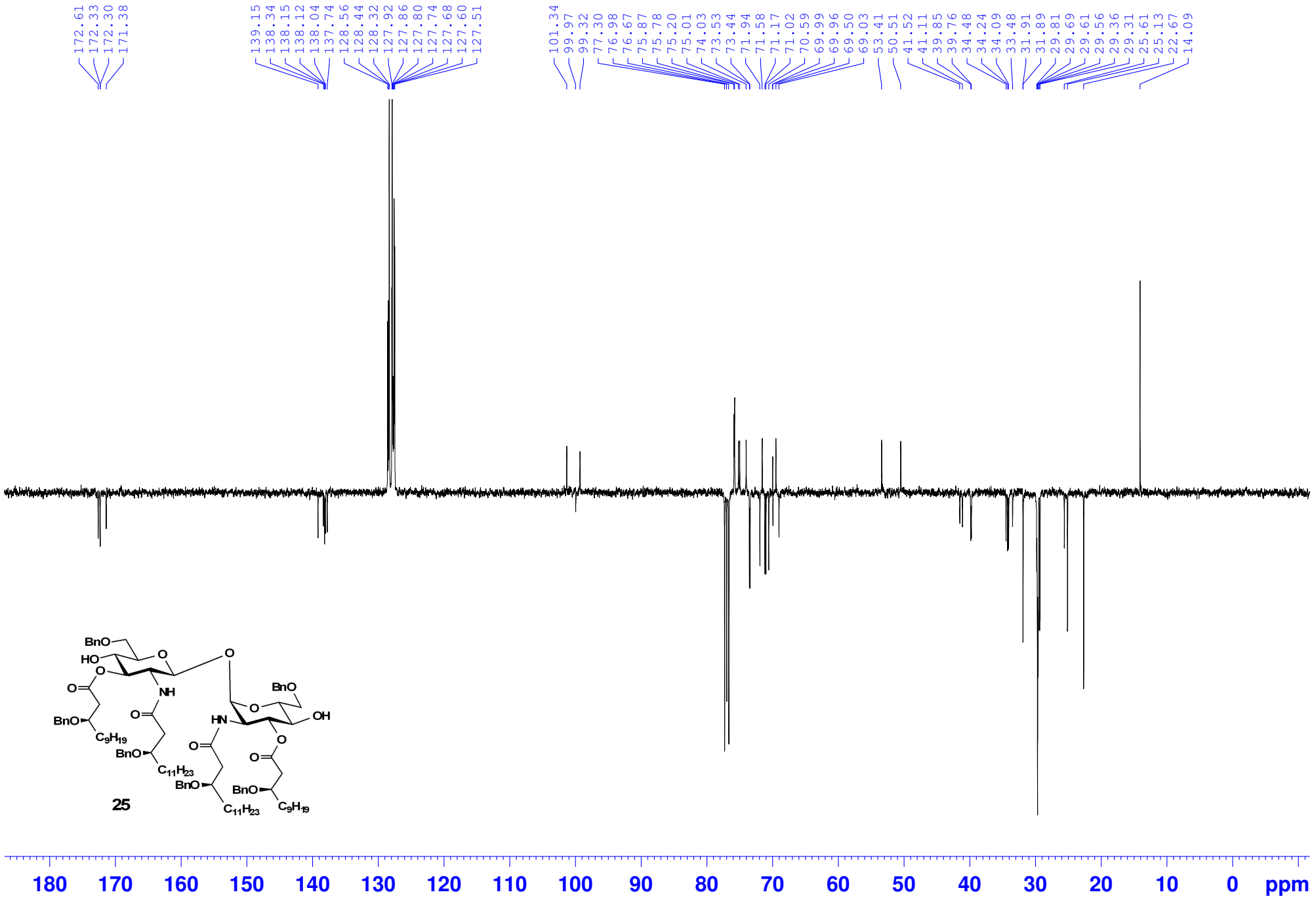
171.37
171.30
139.25
138.66
138.46
138.19
136.89
136.70
129.05
128.95
128.62
128.48
128.37
128.21
128.15
128.00
127.92
127.68
127.66
127.42
127.27
126.07
102.52
101.37
100.22
79.07
78.20
77.31
77.13
77.00
76.68
75.76
75.51
75.39
72.07
71.53
71.09
71.05
70.60
70.53
68.48
66.30
63.38
54.08
51.33
41.49
41.09
39.82
39.75
34.64
34.47
34.43
33.39
31.91
29.84
29.70
29.67
29.56
29.37
29.33
25.61
25.15
25.07
25.02
22.67
14.10
Ph
O
NH
HN
BnO
C_9H_{19}
$C_{11}H_{23}$
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

18


7.34 7.33 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.27 7.26 7.25 7.25 7.24 7.23 7.23 7.22 6.44 6.42 6.34 6.32 5.14 5.12 5.11 5.09 4.77 4.76 4.75 4.74 4.72 4.54 4.51 4.50 4.50 4.49 4.49 4.48 4.46 4.45 4.44 4.40 4.38 4.37 4.35 4.23 4.20 4.03 4.01 3.92 3.91 3.89 3.84 3.73 3.60 3.59 3.58 3.57 3.56 3.54 3.52 3.31 3.29 2.64 2.62 2.60 2.58 2.55 2.53 2.45 2.43 2.41 2.40 2.38 2.37 2.36 2.32 1.34 1.32 1.30 1.28 1.27 1.25 0.90 0.89 0.88 0.86 -0.00
BnO
HO
O
NH
O
BnO
C9H19
BnO
C11H23
BnO
C11H23
HN
BnO
OH
O
O
BnO
C9H19
25
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
32.01 0.97 0.97 1.00 1.96 8.96 3.16 1.01 1.04 0.98 2.11 1.92 1.15 5.99 1.01 0.89 2.89 4.98 1.02 74.66 12.29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172.33
172.30
171.38
139.15
138.34
138.15
138.12
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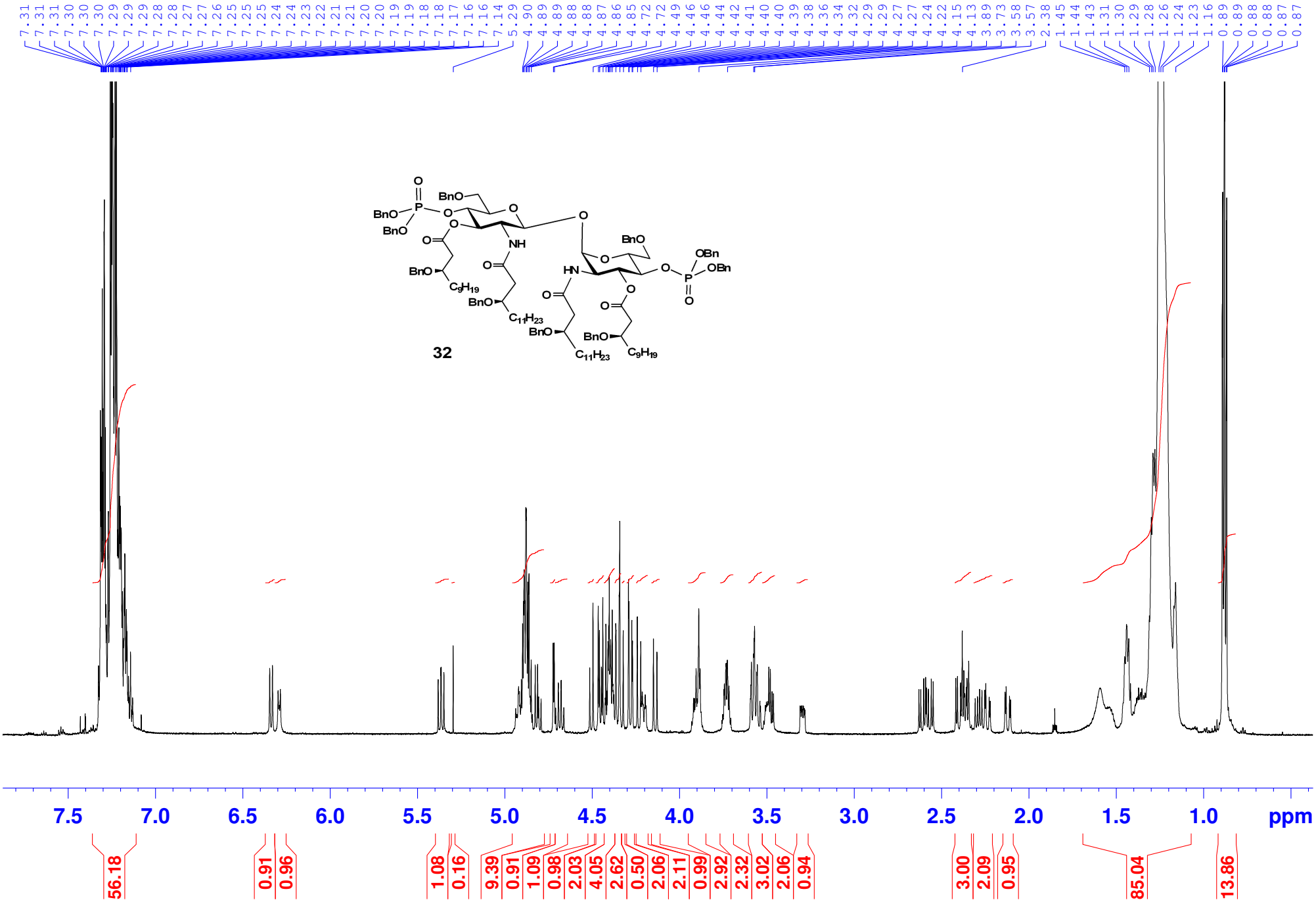
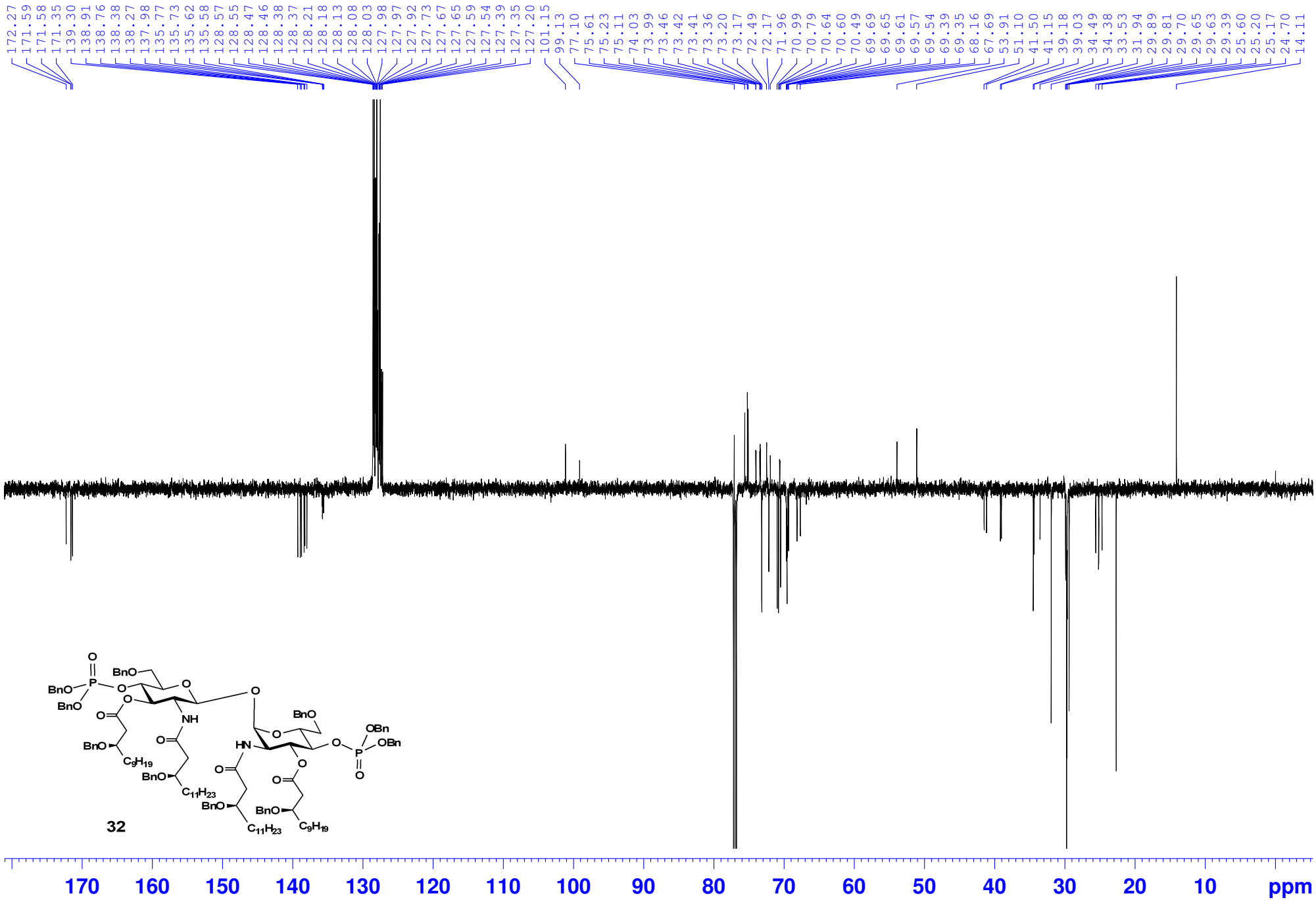
137.74
128.56
128.44
128.32
127.92
127.86
127.80
127.74
127.68
127.60
127.51
101.34
99.97
99.32
77.30
76.98
76.67
75.87
75.78
75.20
75.01
74.03
73.53
73.44
71.94
71.58
71.17
71.02
70.59
69.99
69.96
69.50
69.03
53.41
50.51
41.52
41.11
39.85
39.76
34.48
34.24
34.09
33.48
31.91
31.89
29.81
29.69
29.61
29.56
29.36
29.31
25.61
25.13
22.67
14.09
BnO
HO
O
NH
HN
OH
C_9H_{19}
$C_{11}H_{23}$
25
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.24 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.16 7.16 7.14 5.29 4.90 4.89 4.89 4.88 4.88 4.87 4.86 4.85 4.72 4.72 4.49 4.46 4.46 4.44 4.42 4.41 4.40 4.40 4.39 4.38 4.36 4.34 4.32 4.29 4.29 4.27 4.24 4.22 4.15 4.13 3.89 3.73 3.58 3.57 2.38 1.45 1.44 1.43 1.31 1.30 1.29 1.28 1.26 1.24 1.23 1.16 0.89 0.89 0.88 0.88 0.87 0.87
32
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 ppm
56.18 0.91 0.96 1.08 0.16 9.39 0.91 1.09 0.98 2.03 4.05 2.62 0.50 2.06 2.11 0.99 2.92 2.32 3.02 2.06 0.94 3.00 2.09 0.95 85.04 13.86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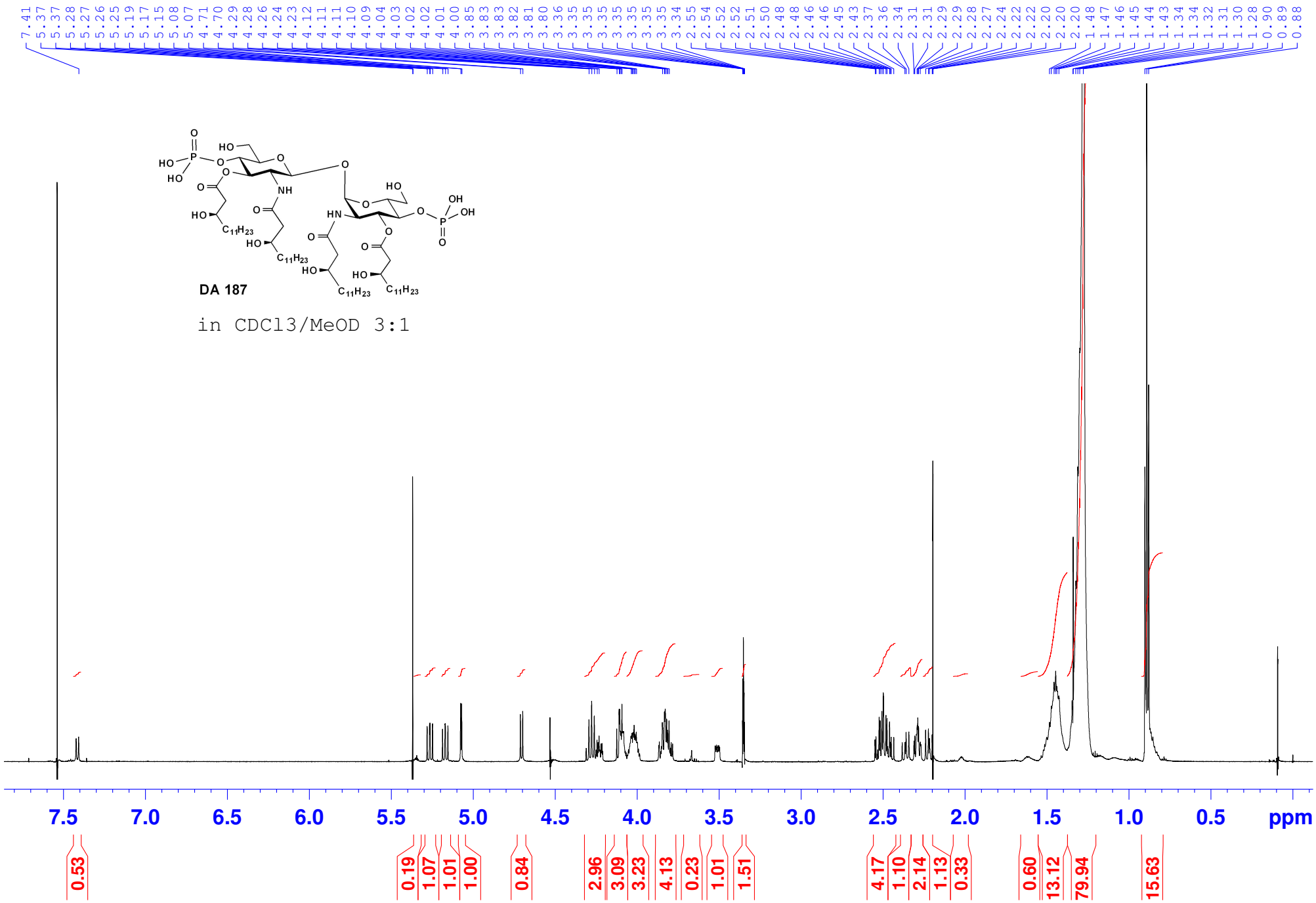
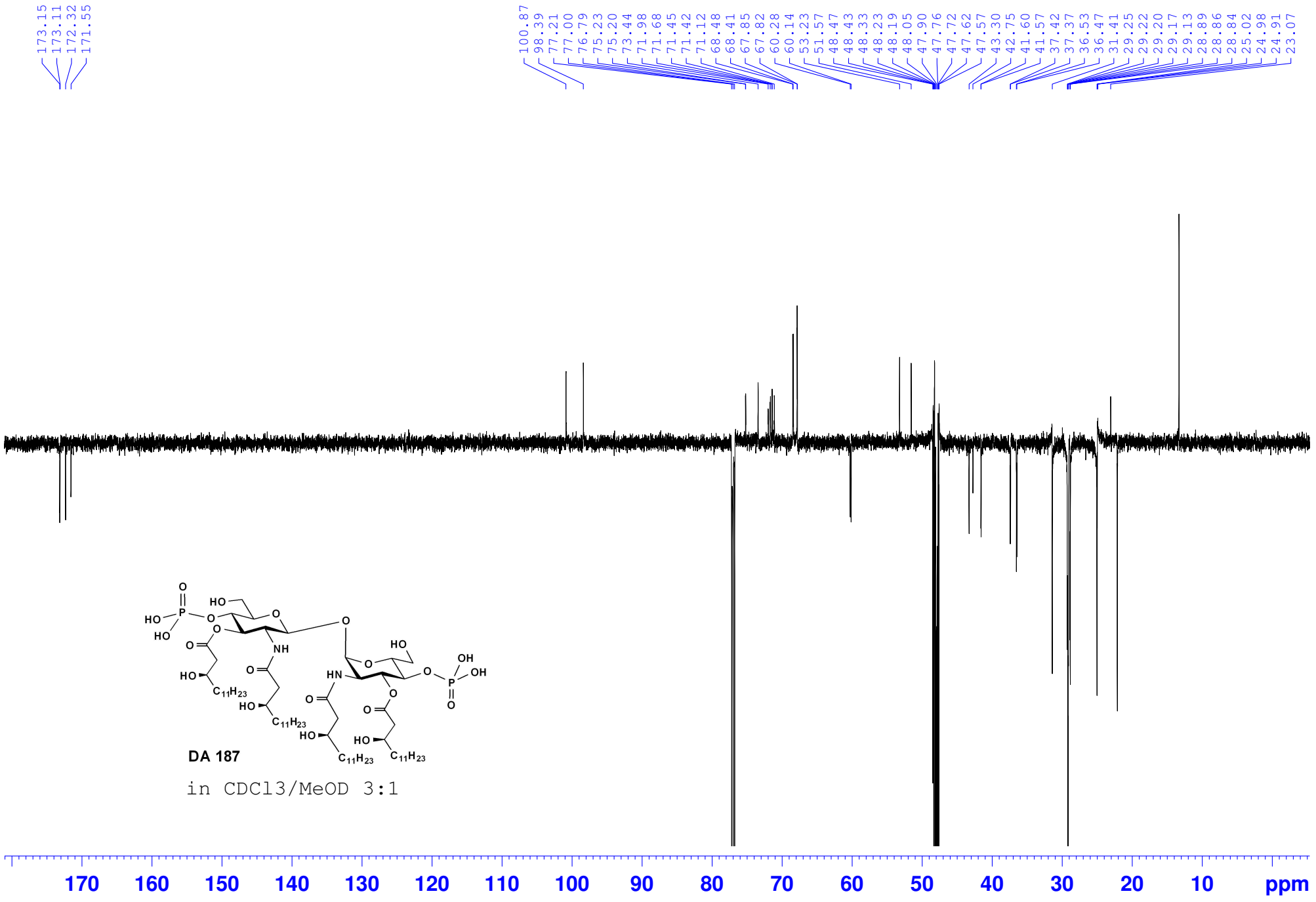
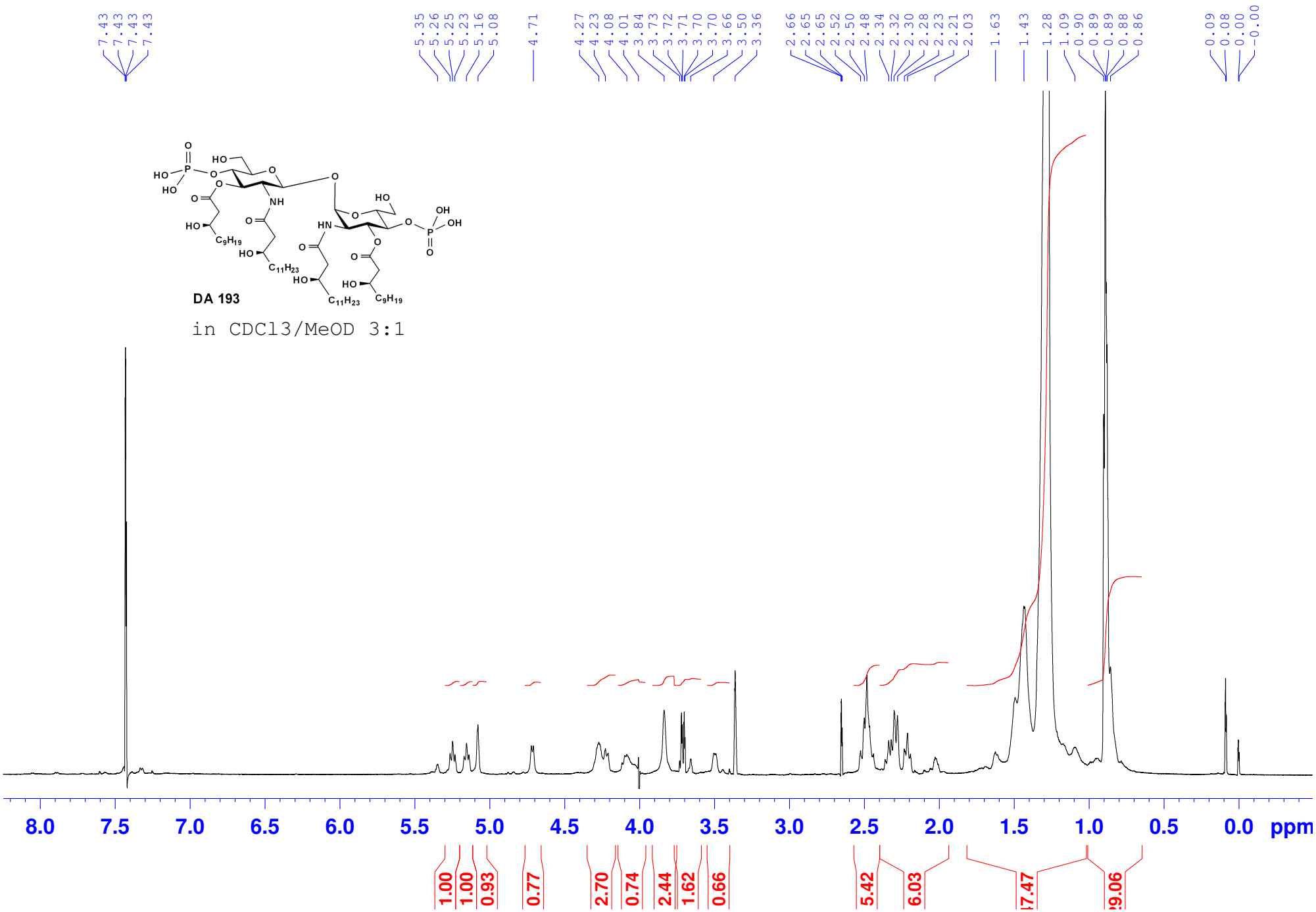
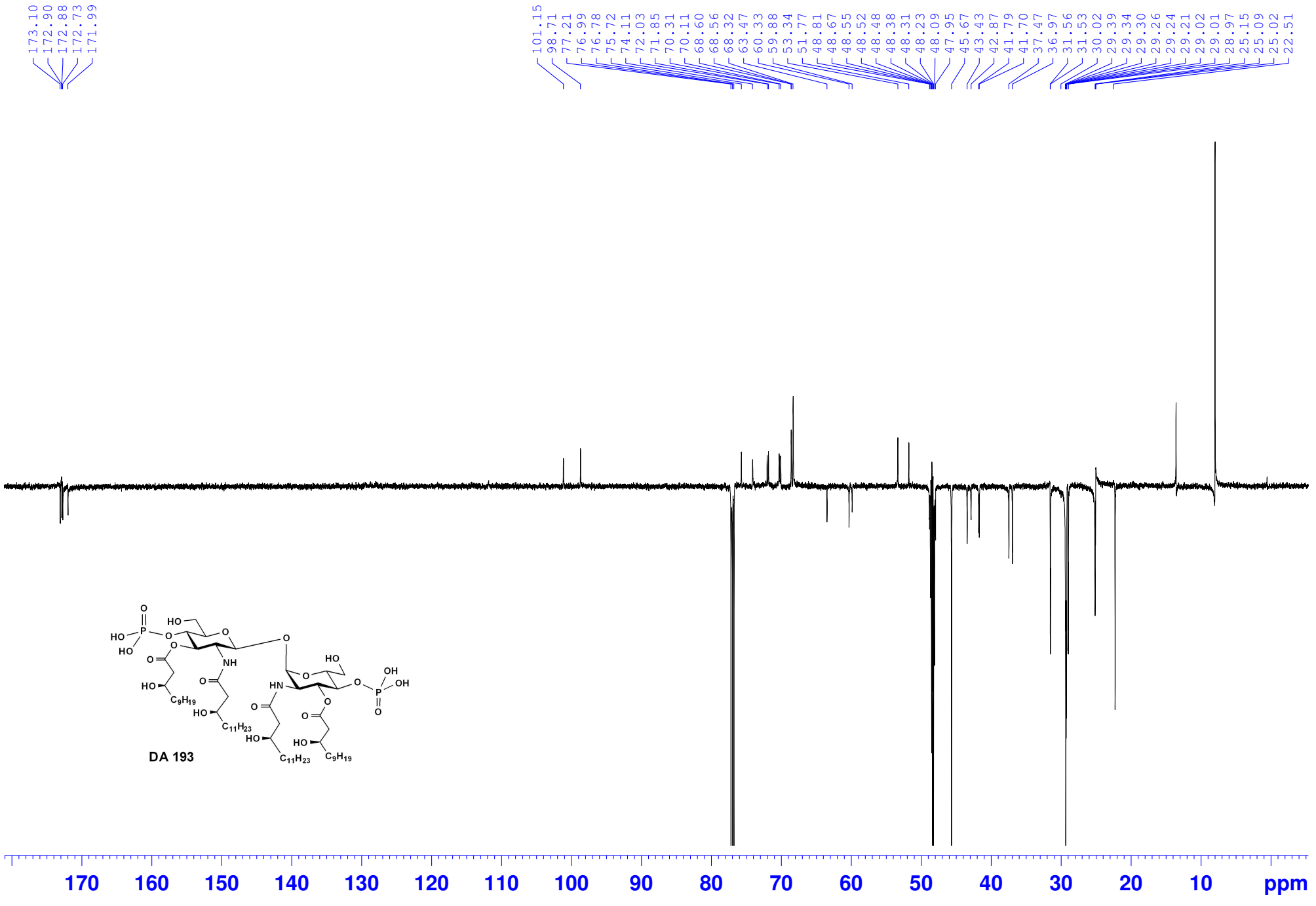
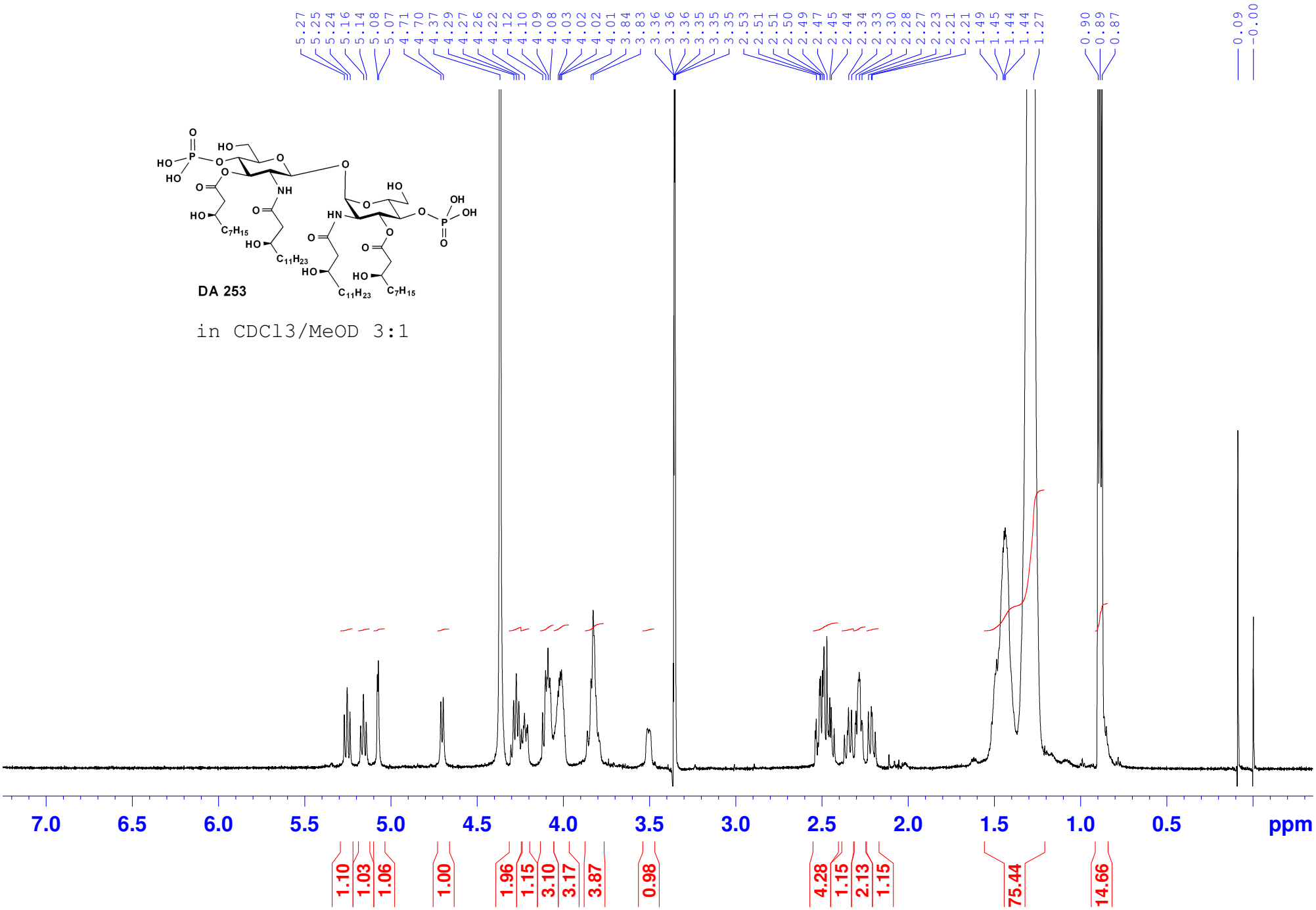
171.58
171.35
139.30
138.91
138.76
138.38
138.27
137.98
135.77
135.73
135.62
135.58
128.57
128.55
128.47
128.46
128.38
128.37
128.21
128.18
128.13
128.08
128.03
127.98
127.97
127.92
127.73
127.67
127.65
127.59
127.54
127.39
127.35
127.20
101.15
99.13
77.10
75.61
75.23
75.11
74.03
73.99
73.46
73.42
73.41
73.36
73.20
73.17
72.49
72.17
71.96
70.99
70.79
70.64
70.60
70.49
69.69
69.65
69.61
69.57
69.54
69.39
69.35
68.16
67.69
53.91
51.10
41.50
41.15
39.18
39.03
34.49
34.38
33.53
31.94
29.89
29.81
29.70
29.65
29.63
29.39
25.60
25.20
25.17
24.70
14.11
BnO
BnO
BnO
O
P
O
O
O
O
NH
O
BnO
C9H19
BnO
C11H23
BnO
C11H23
O
HN
BnO
O
O
O
P
OBn
OBn
O
BnO
C9H19
32
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

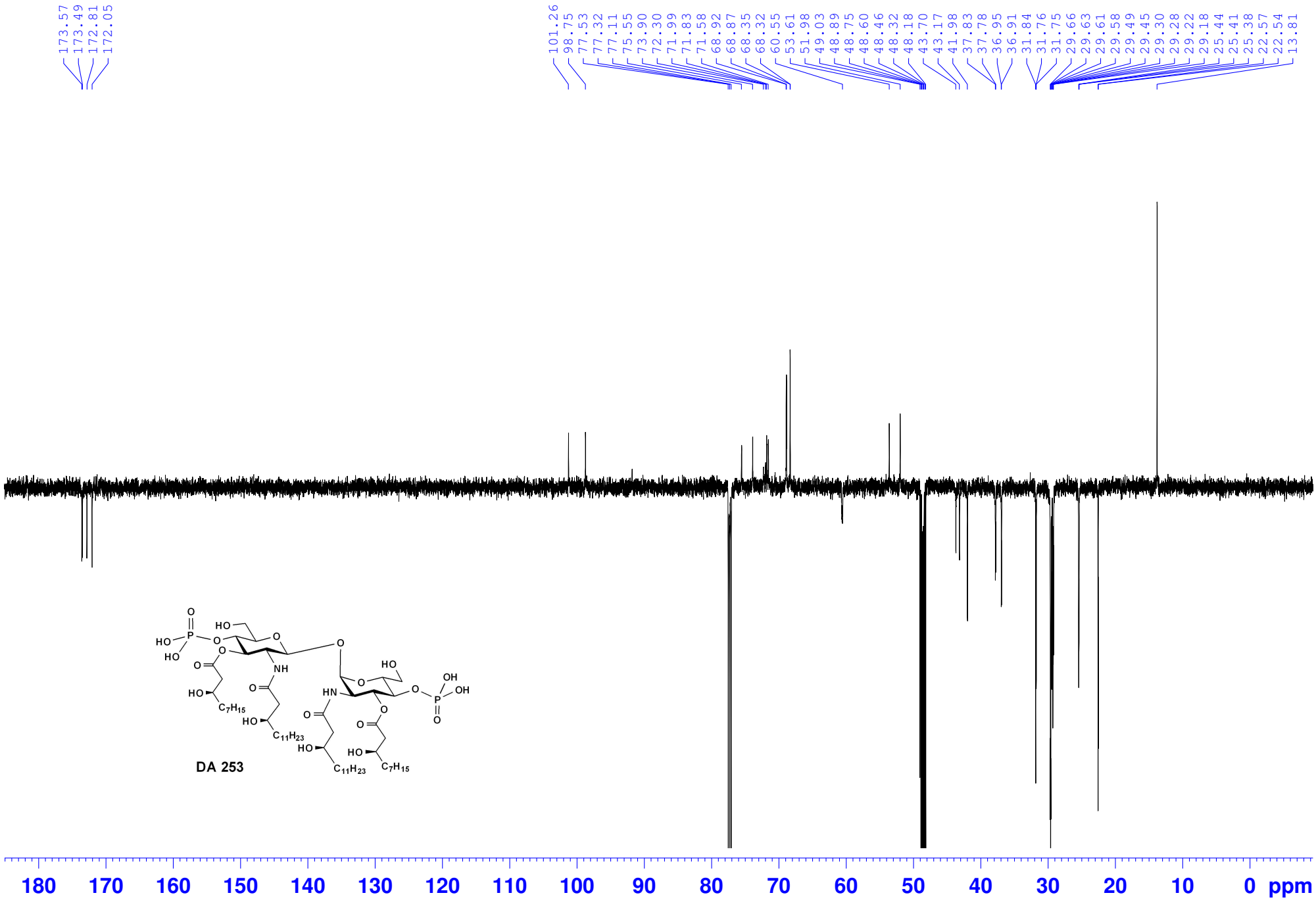

DA 187
in CDCl3/MeOD 3:1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.53
0.19
1.07
1.01
1.00
0.84
2.96
3.09
3.23
4.13
0.23
1.01
1.51
4.17
1.10
2.14
1.13
0.33
0.60
13.12
79.94
15.63

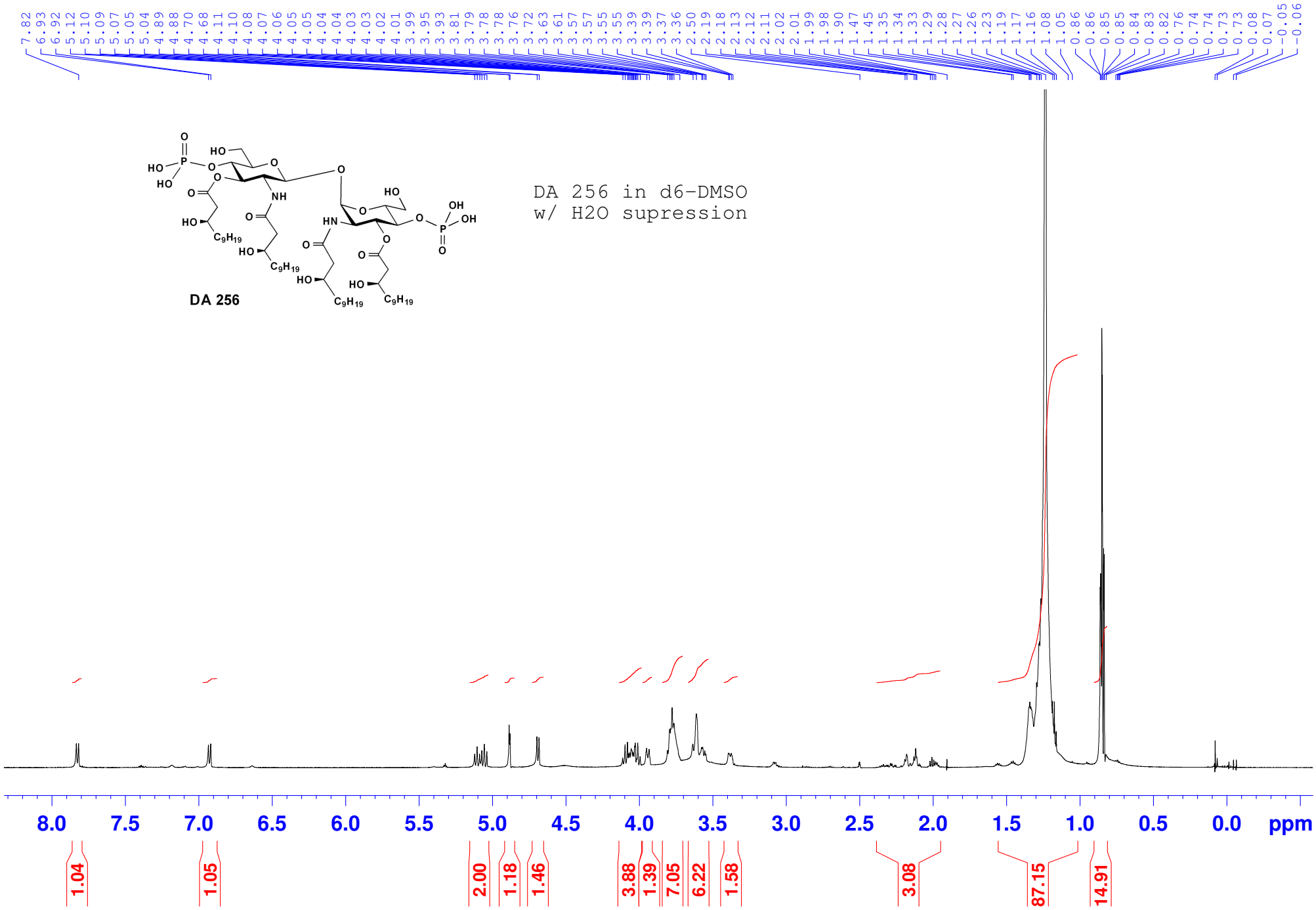

173.15
173.11
172.32
171.55
100.87
98.39
77.21
77.00
76.79
75.23
75.20
73.44
71.98
71.68
71.45
71.42
71.12
68.48
68.41
67.85
67.82
60.28
60.14
53.23
51.57
48.47
48.43
48.33
48.23
48.19
48.05
47.90
47.76
47.72
47.62
47.57
43.30
42.75
41.60
41.57
37.42
37.37
36.53
36.47
31.41
29.25
29.22
29.20
29.17
29.13
28.89
28.86
28.84
25.02
24.98
24.91
23.07
DA 187
in CDCl3/MeOD 3:1
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

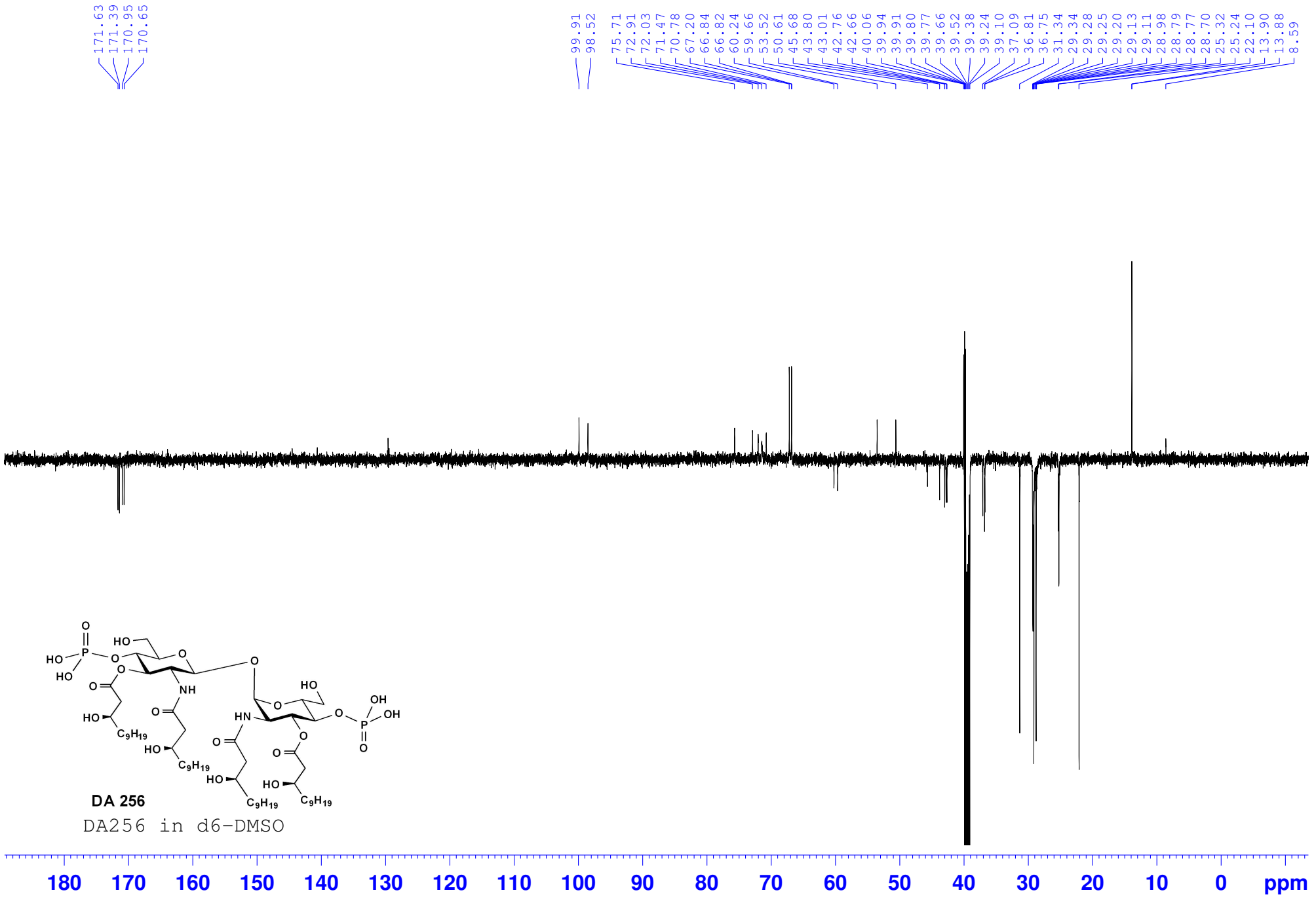

7.43
7.43
7.43
7.43
5.35
5.26
5.25
5.23
5.16
5.08
4.71
4.27
4.23
4.08
4.01
3.84
3.73
3.72
3.71
3.70
3.70
3.66
3.50
3.36
2.66
2.65
2.65
2.52
2.50
2.48
2.34
2.32
2.30
2.28
2.23
2.21
2.03
1.63
1.43
1.28
1.09
0.90
0.89
0.89
0.88
0.86
0.09
0.08
0.00
-0.00
DA 193
in CDCl3/MeOD 3:1
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
1.00
0.93
0.77
2.70
0.74
2.44
1.62
0.66
5.42
6.03
17.47
29.06

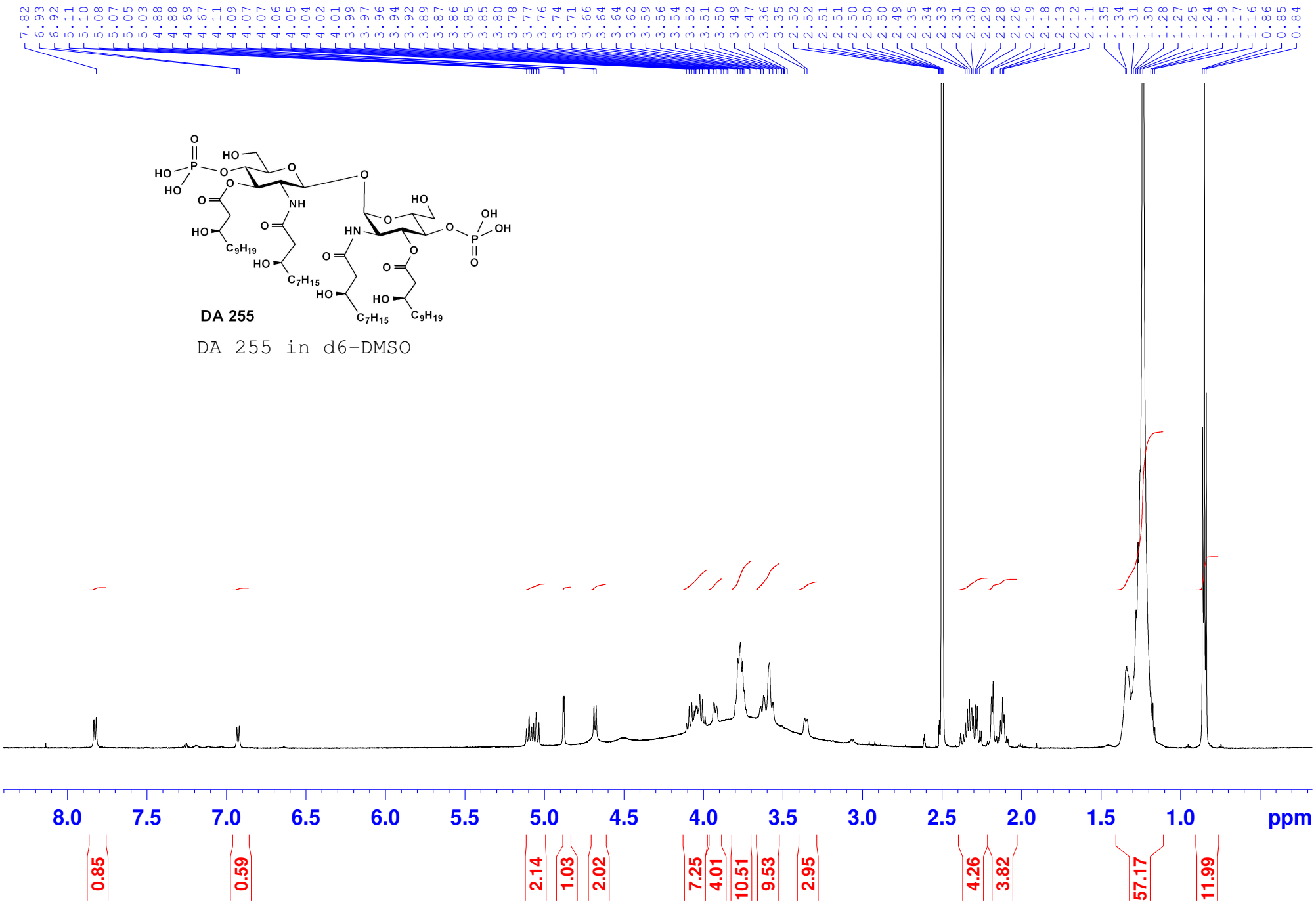

173.10
172.90
172.88
172.73
171.99
101.15
98.71
77.21
76.99
76.78
75.72
74.11
72.03
71.85
70.31
70.11
68.60
68.56
68.32
63.47
60.33
59.88
53.34
51.77
48.81
48.67
48.55
48.52
48.48
48.38
48.31
48.23
48.09
47.95
45.67
43.43
42.87
41.79
41.70
37.47
36.97
31.56
31.53
30.02
29.39
29.34
29.30
29.26
29.24
29.21
29.02
29.01
28.97
25.15
25.09
25.02
22.51
DA 193
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

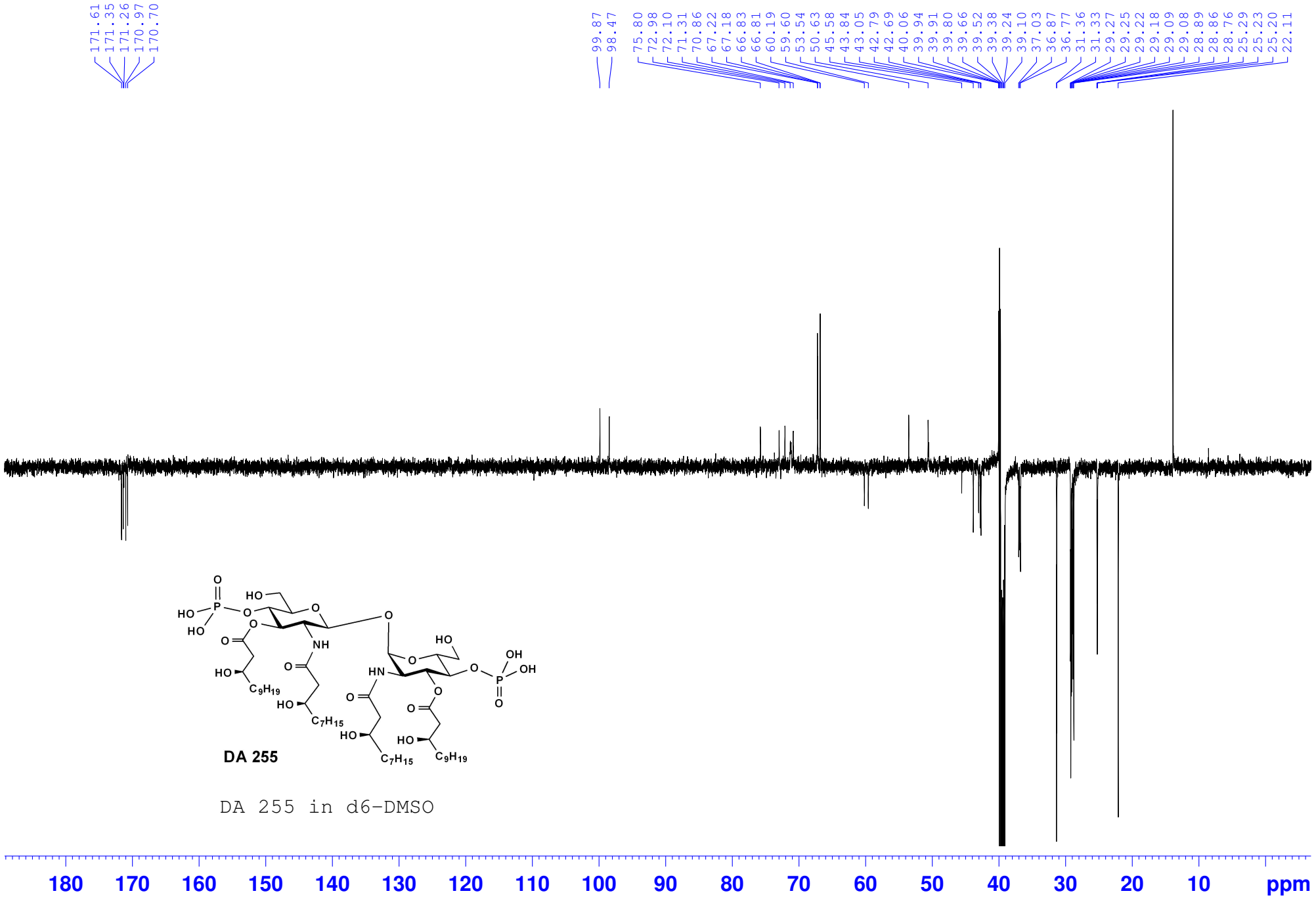

DA 253
in CDCl3/MeOD 3:1
5.27 5.25 5.24 5.16 5.14 5.08 5.07 4.71 4.70 4.37 4.29 4.27 4.26 4.22 4.12 4.10 4.09 4.08 4.03 4.02 4.02 4.01 3.84 3.83 3.36 3.36 3.35 3.35 3.35 2.53 2.51 2.51 2.50 2.49 2.47 2.45 2.44 2.34 2.33 2.30 2.28 2.27 2.23 2.21 2.21 1.49 1.45 1.44 1.44 1.27 0.90 0.89 0.87 0.09 -0.00
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 ppm
1.10 1.03 1.06 1.00 1.96 1.15 3.10 3.17 3.87 0.98 4.28 1.15 2.13 1.15 75.44 14.66

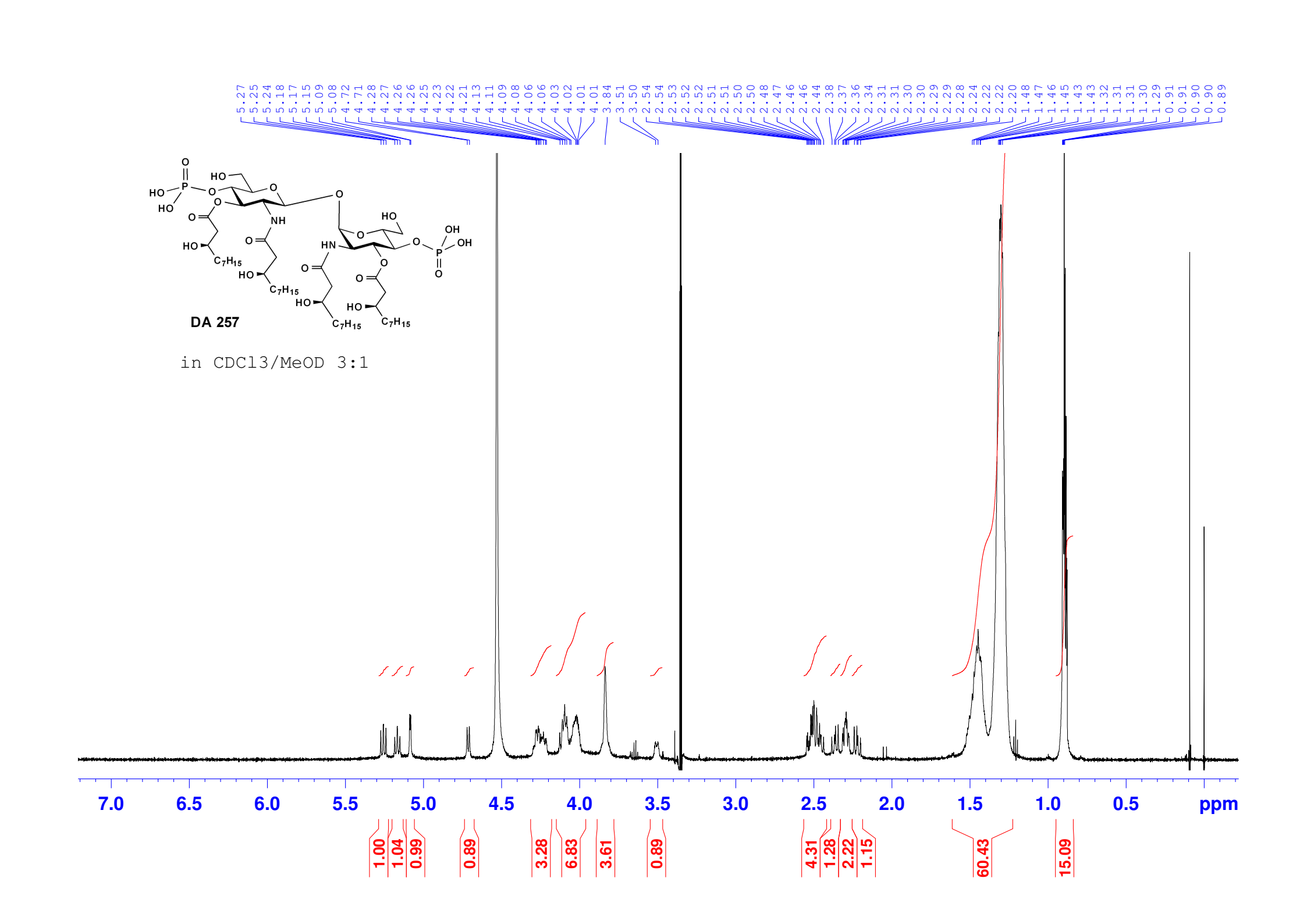

173.57
173.49
172.81
172.05
101.26
98.75
77.53
77.32
77.11
75.55
73.90
72.30
71.99
71.83
71.58
68.92
68.87
68.35
68.32
60.55
53.61
51.98
49.03
48.89
48.75
48.60
48.46
48.32
48.18
43.70
43.17
41.98
37.83
37.78
36.95
36.91
31.84
31.76
31.75
29.66
29.63
29.61
29.58
29.49
29.45
29.30
29.28
29.22
29.18
25.44
25.41
25.38
22.57
22.54
13.81
DA 253
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

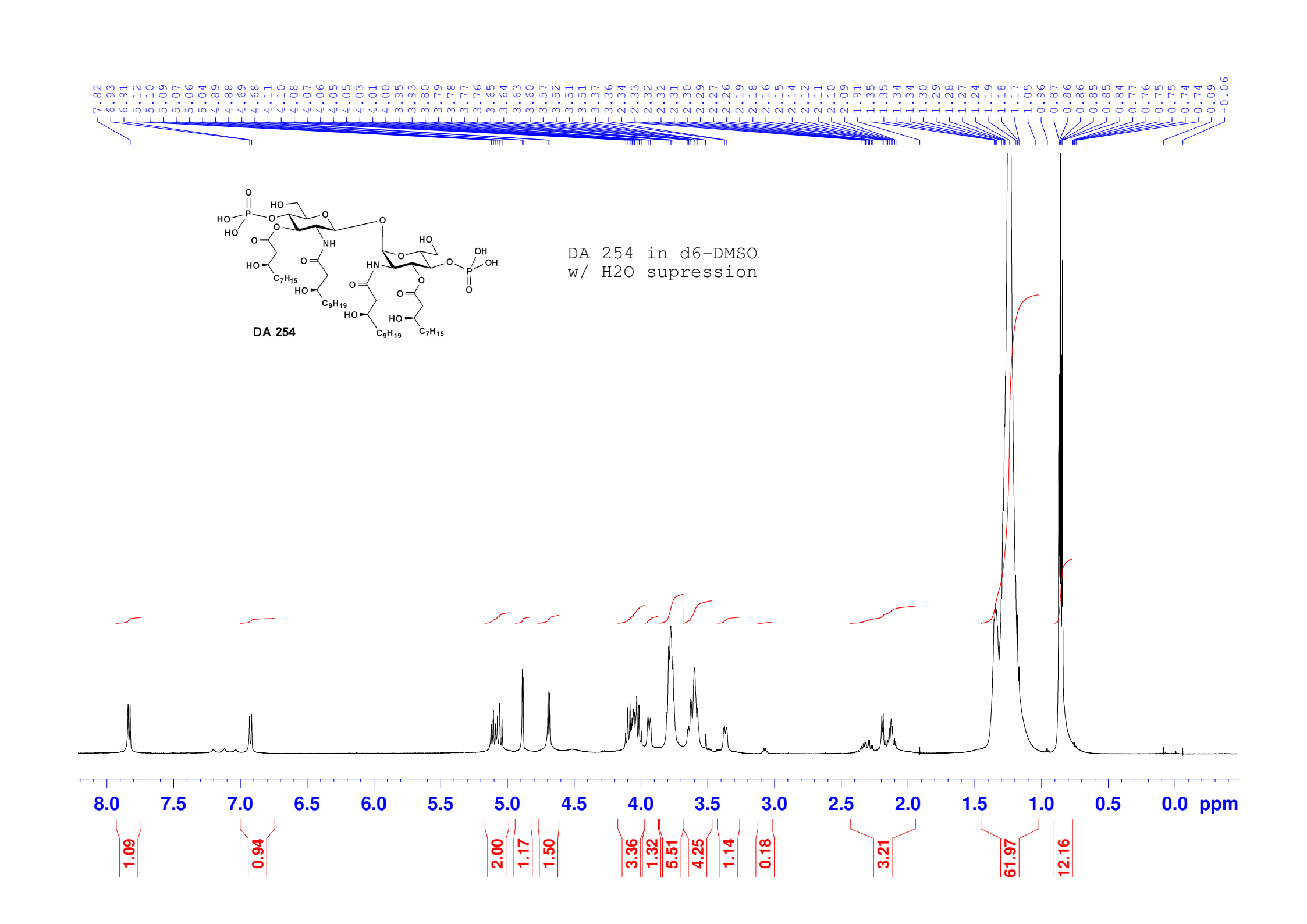

DA 256 in d6-DMSO
w/ H2O supression
DA 256
ppm
1.04
1.05
2.00
1.18
1.46
3.88
1.39
7.05
6.22
1.58
3.08
87.15
14.91

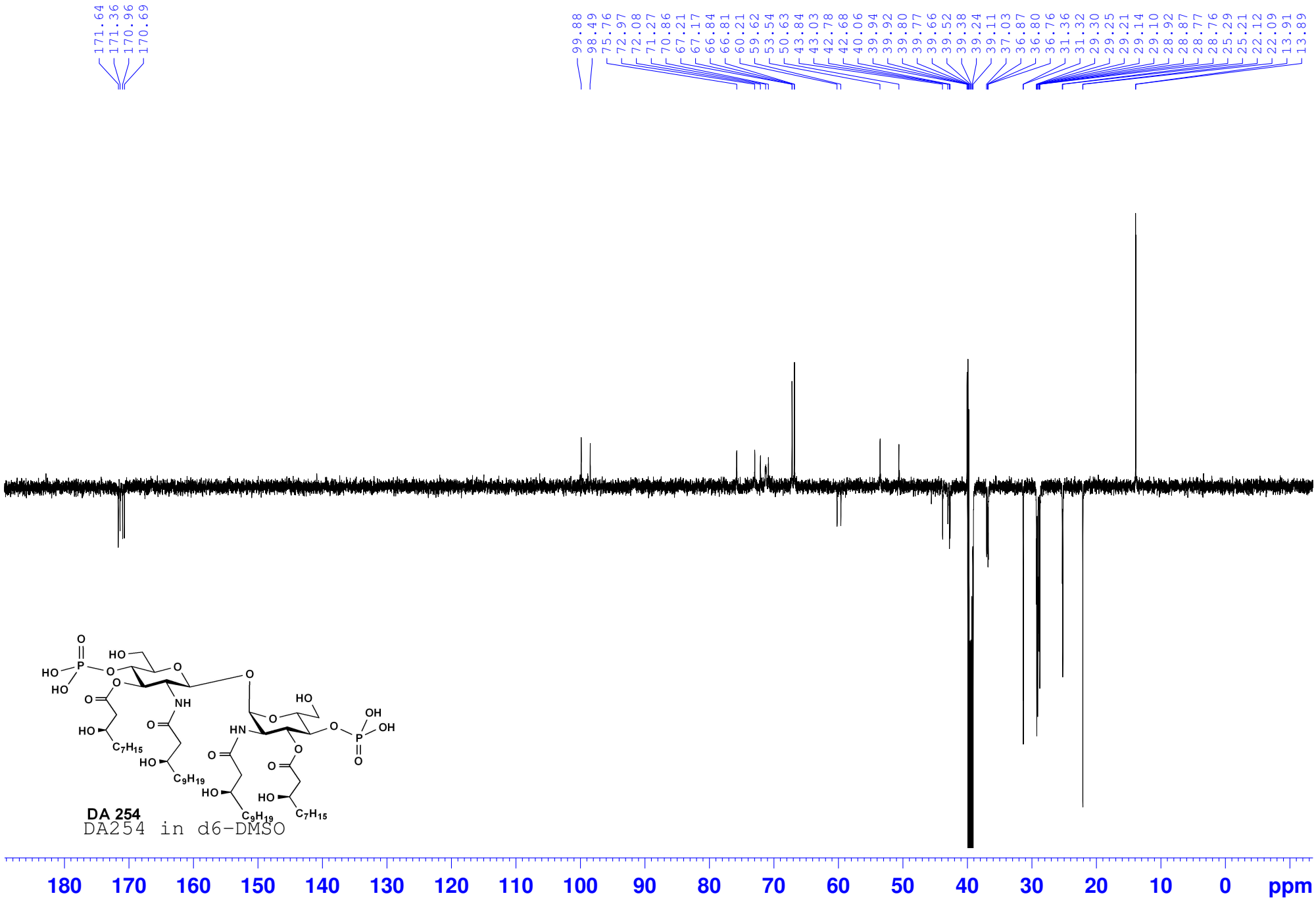

171.63
171.39
170.95
170.65
99.91
98.52
75.71
72.91
72.03
71.47
70.78
67.20
66.84
66.82
60.24
59.66
53.52
50.61
45.68
43.80
43.01
42.76
42.66
40.06
39.94
39.91
39.80
39.77
39.66
39.52
39.38
39.24
39.10
37.09
36.81
36.75
31.34
29.34
29.28
29.25
29.20
29.13
29.11
28.98
28.79
28.77
28.70
25.32
25.24
22.10
13.90
13.88
8.59
DA 256
DA256 in d6-DMSO
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.82 6.93 6.92 5.11 5.10 5.08 5.07 5.05 5.03 4.88 4.88 4.69 4.67 4.11 4.09 4.07 4.07 4.06 4.05 4.04 4.02 4.01 3.99 3.97 3.96 3.94 3.92 3.89 3.87 3.86 3.85 3.85 3.80 3.78 3.77 3.76 3.74 3.71 3.66 3.64 3.64 3.62 3.59 3.56 3.54 3.52 3.51 3.50 3.49 3.47 3.36 3.35 2.52 2.52 2.51 2.51 2.50 2.50 2.50 2.50 2.49 2.35 2.34 2.33 2.31 2.30 2.29 2.28 2.26 2.19 2.18 2.13 2.12 2.11 1.35 1.34 1.31 1.30 1.28 1.27 1.25 1.24 1.19 1.17 1.16 0.86 0.85 0.84
DA 255
DA 255 in d6-DMSO
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.85 0.59 2.14 1.03 2.02 7.25 4.01 10.51 9.53 2.95 4.26 3.82 57.17 11.99


171.61
171.35
171.26
170.97
170.70
99.87
98.47
75.80
72.98
72.10
71.31
70.86
67.22
67.18
66.83
66.81
60.19
59.60
53.54
50.63
45.58
43.84
43.05
42.79
42.69
40.06
39.94
39.91
39.80
39.66
39.52
39.38
39.24
39.10
37.03
36.87
36.77
31.36
31.33
29.27
29.25
29.22
29.18
29.09
29.08
28.89
28.86
28.76
25.29
25.23
25.20
22.11
DA 255
DA 255 in d6-DMSO
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


DA 257
in CDCl3/MeOD 3:1
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
ppm
1.00
1.04
0.99
0.89
3.28
6.83
3.61
0.89
4.31
1.28
2.22
1.15
60.43
15.09


DA 254 in d6-DMSO
w/ H2O supression
DA 254
7.82 6.93 6.91 5.12 5.10 5.09 5.07 5.06 5.04 4.89 4.88 4.69 4.68 4.11 4.10 4.08 4.07 4.06 4.05 4.05 4.03 4.01 4.00 3.95 3.93 3.80 3.79 3.78 3.77 3.76 3.65 3.64 3.63 3.60 3.57 3.52 3.51 3.51 3.37 3.36 2.34 2.33 2.32 2.32 2.31 2.30 2.29 2.27 2.26 2.19 2.18 2.16 2.15 2.14 2.12 2.11 2.10 2.09 1.91 1.35 1.34 1.34 1.30 1.29 1.28 1.27 1.24 1.19 1.18 1.17 1.05 0.96 0.87 0.86 0.86 0.85 0.85 0.84 0.77 0.76 0.75 0.75 0.74 0.74 0.09 -0.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.09 0.94 2.00 1.17 1.50 3.36 1.32 5.51 4.25 1.14 0.18 3.21 61.97 12.16


171.64
171.36
170.96
170.69
99.88
98.49
75.76
72.97
72.08
71.27
70.86
67.21
67.17
66.84
66.81
60.21
59.62
53.54
50.63
43.84
43.03
42.78
42.68
40.06
39.94
39.92
39.80
39.77
39.66
39.52
39.38
39.24
39.11
37.03
36.87
36.80
36.76
31.36
31.32
29.30
29.25
29.21
29.14
29.10
28.92
28.87
28.77
28.76
25.29
25.21
22.12
22.09
13.91
13.89
DA 254
DA254 in d6-DMSO
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm