Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Synthesis and Evaluation of Monophosphoryl Lipid A Derivatives as Fully Synthetic Self-Adjuvanting Glycoconjugate Cancer Vaccine Carriers

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Table of Contents:

Experimental

General Methods. Starting materials and solvents were obtained from commercial sources and used without further purification unless otherwise noted. Anhydrous solvents were obtained either commercially or from a solvent purification system. Molecular sieves 4Å were activated at 180 ^{o}C under high vacuum for 3-4 h immediately before use. Thin-layer chromatography (TLC) was performed on silica gel 60 Å plates and analyzed with a UV lamp and by charring with phosphomolybdic acid or 5% H_2SO_4 in EtOH. ^{1}H NMR spectra were recorded at 400 or 500 MHz with chemical shifts reported in ppm (δ) relative to that of tetramethylsilane (δ 0.00) or $CHCl_3$ (δ 7.26), and ^{13}C NMR spectra were recorded at 100 or 125 MHz. Mass spectra were recorded with a MALDI TOF MS instrument.

2-Azidoethyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranosyl-(1→6)-3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranoside (11).[32] After a mixture of glycosyl donor **12** (2.89 g, 5.29 mmol), acceptor **13** (1.8 g, 3.53 mmol) and molecular sieves 4Å (5.00 g) in dry dichloromethane (DCM, 50 mL) was stirred under an Argon atmosphere at room temperature (rt) for 3h and then cooled to -50 ^{o}C, AgOTf (300 mg) and NIS (1.85 g, 8.23 mmol) were sequentially added. The mixture was stirred at -50 ^{o}C for another hour and then stirred at rt for 24h. The mixture was quenched with aqueous (aq.) $NaHCO_3$, diluted with DCM, and filtered off to remove molecular sieves. The organic solution was washed with aq. $Na_2S_2O_3$, dried over Na_2SO_4, concentrated under vacuum, and the residue was finally purified by silica gel column chromatography using 10% ethyl acetate in toluene as the eluent to afford **11** (2.00 g, 78%) as a white solid. Its spectroscopic data were identical to that reported in the literature.[32]

2-Azidoethyl 2-amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl-(1→6)-2-amino-4-*O*-benzyl-2-deoxy-β-D-glucopyranoside (14).[32] After **11** (2.6 g, mmol, 2.80 mmol) and hydrazine monohydrate (20 mL) was refluxed in absolute EtOH (100 mL) for 5h, the solvent was removed under vacuum. The product was purified by silica gel column chromatography with 2% MeOH in DCM as the eluent to give **14** (1.1 g, 67%) as a white solid, the spectroscopic data of which were the same as that reported in the literature.[32]

2-Azidoethyl 4,6-*O*-benzylidene-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecanamido]-β-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecanamido]-β-D-glucopyranoside (16):[32] After a solution of **15** (1.74 mg, 4.08 mmol) and EDC·HCl (2.61 mg, 13.61 mmol) in anhydrous DCM (30 mL) was stirred at rt for 1 h, it was cooled to 0 ^{o}C, and then a solution of **14** (800 mg, 1.36 mmol) in DMF (5 mL) was added. The mixture was stirred at rt overnight and diluted with DCM, washed with brine, dried over Na_2SO_4 and condensed under reduced pressure. The product was recrystallized from MeOH to get **16** (1.8 g, 94%) as a white solid, which had the same spectroscopic data as that reported in the literature.[32]

2-Azidoethyl 4,6-*O*-benzylidene-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecanamido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyl-oxy)tetradecanoyl]-β-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)-tetradecanamido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetrade-canoyl]/[(R)-3-(dodecyl-oxy)tetradecanoyl]-β-D-glucopyranoside (21/22/23/24): After a solution of EDC·HCl (0.14-1.16 g, 0.72-6.05 mmol) and **17-20** (0.29-2.42 mmol) in anhydrous DCM (20 mL) was stirred at rt for 1h, a solution of **28** (0.10-0.85 g, 0.071-0.605 mmol) and *N*,*N*-dimethylaminopyridine (369 mg, 3.03 mmol) in DCM (20 mL) was added. The mixture was stirred at rt for 18h and then diluted with DCM, washed with brine, dried over Na_2SO_4 and finally condensed under reduced pressure. The residue was purified by flash column chromatography using 8% acetone in DCM as the eluent to afford **21-24**. Compound **21** (900 mg from 0.605 mmol of **28**, 84%) was obtained as a white solid which had the same spectroscopic data as that reported in the literature.[32] Compound **22** (270 mg from 0.178 mmol of **28**, 77%) as a white solid: $[\alpha]^{24}_{D}$ = -12.0 (*c* 1.1, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.37 (m, 2 H), 7.31-7.23 (m, 16 H), 7.20-7.17 (m, 2 H), 5.93 (d, J = 8.9 Hz, 1 H, NH), 5.87 (d, J = 8.9 Hz, 1 H, NH'), 5.45 (s, 1 H, PhC<u>H</u>), 5.35 (t, J = 10.1 Hz, 1 H, H-3'), 5.23 (t, J = 9.3 Hz, 1 H, H-3), 5.12-5.06 (m, 1 H, lipid-H), 5.05-4.99 (m, 1 H, lipid-H), 4.82 (d, J = 8.1 Hz, 1 H, H-1'), 4.66 (d, J = 8.1 Hz, 1 H, H-1), 4.56 (d, J = 11.3 Hz, 1 H, PhC$\underline{H}_2$), 4.52-4.45 (m, 4 H, 2×PhC$\underline{H}_2$), 4.39 (d, J = 11.3 Hz, 1 H, PhC$\underline{H}_2$), 4.32 (dd, J = 4.8, 10.5 Hz, 1 H, H-6'), 4.02(dd, J = 1.0, 10.5 Hz, 1 H, H-6), 3.95 (ddd, J = 4.0, 4.8, 10.5 Hz, 1 H, OC$\underline{H}_2$CH$_2$N$_3$), 3.90-3.77 (m, 4 H, H-2,2', 2×BnOC<u>H</u>), 3.76-3.63 (m, 4 H, H-6,6', H-4' OC$\underline{H}_2$CH$_2$N$_3$), 3.61-3.43 (m, 4 H, H-5, H-5', H-4, OCH$_2$C$\underline{H}_2$N$_3$), 3.34 (ddd, J = 3.2, 4.0, 13.0 Hz, 1 H OCH$_2$C$\underline{H}_2$N$_3$), 2.65 (dd, J = 6.5, 15.4 Hz, 1 H, COC$\underline{H}_2$), 2.56 (dd, J = 7.3, 16.2 Hz, 1 H, COC$\underline{H}_2$), 2.51-2.45 (m, 2 H, COC$\underline{H}_2$), 2.40-2.23 (m, 7 H, COC$\underline{H}_2$), 2.18 (dd, J = 6.5, 15.4 Hz, 1 H, COC$\underline{H}_2$), 1.70-1.43 (m, 8 H, lipid-H), 1.25 (br, 104 H, 52×CH_2), 0.88 (t, J = 6.5 Hz, 18 H, 6×CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 173.8, 171.8, 171.5, 167.0, 169.8, 138.7, 138.6, 137.8, 137.1, 129.2, 128.7, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 126.3, 101.6, 100.5, 79.0, 76.1, 75.8, 75.7, 75.2, 74.9, 74.5, 71.6, 71.5, 71.3, 71.1, 68.8, 68.0, 67.4, 66.5, 55.2, 54.2, 50.9, 42.0, 41.7, 39.7, 32.2, 29.9, 29.9, 29.7, 29.7, 29.6, 29.5, 25.5, 25.8, 25.3, 25.3, 22.9, 14.3. MALDI-TOF MS (*m*/*z*): calcd for $C_{118}H_{189}N_5O_{19}$, 1980.4; found, 2003.7 $[M + Na]^+$. Compound **23** (95 mg from 0.071 mmol of **28**, 66%) as a white solid: $[\alpha]^{24}_D$ = -12.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40-7.38 (m, 2 H), 7.28-7.25 (m, 16 H), 7.20-7.18 (m, 2 H), 5.96 (d, J = 8.9 Hz, 1 H, NH'), 5.90 (d, J = 8.9 Hz, 1 H, NH), 5.42 (s, 1 H, PhC<u>H</u>), 5.36 (t, J = 9.7 Hz, 1 H, H-3'), 5.24 (t, J = 9.3 Hz, 1 H, H-3), 5.13-5.06 (m, 1 H, lipid-H), 5.06-4.99 (m, 1 H, lipid-H), 4.82 (d, J = 8.1 Hz, 1 H, H-1'), 4.67 (d, J = 8.1 Hz, 1 H, H-1), 4.58 (d, J = 11 Hz, 1 H, PhC<u>H</u>$_2$), 4.52-4.45 (m, 4 H, 2×PhC<u>H</u>$_2$), 4.40 (d, J = 12.1 Hz, 1 H, PhC<u>H</u>$_2$), 4.30 (dd, J = 4.8, 10.5 Hz, 1 H, H-6'), 4.01(dd, J = 1.0, 10.4 Hz, 1 H, H-6), 3.94 (dt, J = 4.8, 10.5 Hz, 1 H, OC<u>H</u>$_2$CH$_2$N$_3$), 3.91-3.77 (m, 4 H, H-2,2', 2×BnOC<u>H</u>), 3.74-3.63 (m, 4 H, H-6,6', H-4' OC<u>H</u>$_2$CH$_2$N$_3$), 3.61-3.43 (m, 4 H, H-5, H-5', H-4, OCH$_2$C<u>H</u>$_2$N$_3$), 3.33 (dt, J = 4.0, 13.0 Hz, 1 H OCH$_2$C<u>H</u>$_2$N$_3$), 2.69-2.46 (m, 4 H, COC<u>H</u>$_2$), 2.40-2.16 (m, 8 H, COC<u>H</u>$_2$), 1.65-1.42 (m, 8 H, lipid-H), 1.26 (br, 108 H, 54×CH_2), 0.88 (t, J = 6.5 Hz, 18 H, 6×CH_3). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 174.0, 173.9, 171.8, 171.5, 170.0, 169.8, 138.7, 138.7, 137.7, 137.1, 129.3, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 126.3, 101.7, 101.6, 100.5, 79.0, 76.1, 75.9, 75.7, 75.2, 74.9, 74.5, 71.6, 71.4, 71.1, 68.8, 68.1, 67.4, 66.6, 55.3, 54.2, 50.9, 42.0, 41.7, 39.8, 34.8, 34.7, 34.6, 34.6, 34.4, 34.4, 32.2, 29.9, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 25.5, 25.4, 25.3, 25.3, 22.9, 14.4. MALDI-TOF MS (*m*/*z*): calcd for $C_{122}H_{197}N_5O_{19}$, 2036.4; found, 2059.5 $[M + Na]^+$. Compound **24** (200 mg from 0.178 mmol of **28**, 52%) as a white solid: $[\alpha]^{24}_D$ = -15.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41-7.40 (m, 2 H), 7.31-7.24 (m, 8 H), 6.00 (d, J = 8.9 Hz, 1 H, NH), 5.97 (d, J = 8.9 Hz, 1 H, NH), 5.47 (s, 1 H, PhC<u>H</u>), 5.30 (t, J = 9.7 Hz, 1 H, H-3'), 5.20 (t, J = 9.5 Hz, 1 H, H-3), 5.13-5.07 (m, 1 H, lipid-H), 5.05-4.98 (m, 1 H, lipid-H), 4.76 (d, J = 8.1 Hz, 1 H, H-1'), 4.67-4.64 (m, 2 H, H-1, PhC<u>H</u>$_2$), 4.51 (d, J = 11.1 Hz, 1 H, PhC<u>H</u>$_2$), 4.30 (dd, J = 4.8, 10.5 Hz, 1 H, H-6'), 4.02 (dd, J = 1.0, 10.4 Hz, 1 H, H-6), 3.95-3.77 (m, 3 H,), 3.77-3.57 (m, 7 H), 3.53-3.22 (m, 8 H), 2.60-2.24 (m, 12 H, COC<u>H</u>$_2$), 1.65-1.42 (m, 12 H, lipid-H), 1.26 (br, 144 H, 72×CH_2), 0.88 (t, J = 6.5 Hz, 24 H, 8×CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.0, 173.8, 171.9, 171.8, 169.9, 169.8, 137.8, 137.1, 129.3, 128.7, 128.4, 128.1, 128.0, 126.4, 101.9, 101.6, 100.5, 79.0, 76.1, 76.0, 75.3, 74.9, 74.4, 71.5, 71.2, 71.1, 69.8, 69.6, 68.8, 68.2, 67.3, 66.7, 55.1, 54.1, 50.9, 42.1, 41.8, 39.9, 39.8, 34.8, 34.8, 34.7, 34.6, 34.4, 32.2, 30.3, 30.2, 30.0, 29.9, 29.9, 29.8, 29.7, 29.6, 29.5, 26.4, 25.5, 25.3, 25.2, 22.9, 14.3 ppm. MALDI-TOF MS (*m*/*z*): calcd for $C_{132}H_{233}N_5O_{19}$, 2192.7; found 2215.1 $[M + Na]^+$

2-Azidoethyl 6-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecanamido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradeca-noyl]-β-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)-tetradecan-amido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyl-oxy)tetradecanoyl]-β-D-glucopyranoside (25/26/27/28): To a stirred mixture of **21-24** (44-678 μmol), sodium cyanoborohydride (41.5-639 mg, 0.66-10.17 mmol) and molecular sieves 4Å (0.32-5 g) in THF was added HCl in dry ether (1 M, 2.60-40 mL) slowly at 0 ^{o}C until pH reached 2-3. Three hours later, the reaction was quenched with aq. $NaHCO_3$, and the solid materials were filtered off and washed with DCM. The combined organic solution was dried and concentrated, and the residue was purified by column chromatography using 10% acetone in DCM as the eluent to obtain **25-28**. Compound **25** (800 mg from 678 μmol of **21**, 67%) was obtained as a white solid that had the same spectroscopic data as that reported in the literature.[32] Compound **26** (155 mg from 131 μmol of **22**, 61%) as a white solid: $[\alpha]^{24}_{D}$ = -7.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.34-7.16 (m, 20 H), 5.91 (d, J = 8.1 Hz, 1 H, NH), 5.86 (d, J = 7.3 Hz, 1 H, NH), 5.22 (t, J = 9.3 Hz, 1 H, H-3), 5.10-5.02 (m, 3 H, H-3', 2×lipid-H), 4.63 (d, J = 8.1 Hz, 2 H, H-1, H-1'), 4.59-4.44 (m, 8 H, PhC<u>H</u>$_2$), 4.01 (dd, J = 1.0, 9.5 Hz, 1 H, H-6), 3.94-3.75 (m, 5 H, OC<u>H</u>$_2$CH$_2$N$_3$, 2×lipid-H, H-2, H-2'), 3.70-3.48 (m, 8 H, H-5, H-5', H-6, H-6', H-4, OC<u>H</u>$_2$CH$_2$N$_3$, H-4', H-6'), 3.43 (ddd, J = 3.2, 7.3, 12.9 Hz, 1 H, OCH$_2$C<u>H</u>$_2$N$_3$), 3.31 (ddd, J = 3.2, 4.8, 12.9 Hz, 1 H, OCH$_2$C<u>H</u>$_2$N$_3$), 3.07 (b, 1 H, O<u>H</u>), 2.63 (dd, J = 7.3, 14.4 Hz, 1 H, COC<u>H</u>$_2$), 2.57-2.43 (m, 3 H, COC<u>H</u>$_2$), 2.39-2.16 (m, 8 H, COC<u>H</u>$_2$), 1.68-1.46 (m, 8 H, lipid-H), 1.25 (b, 100 H, 50×CH$_2$), 0.88 (t, J = 6.8 Hz, 18 H, 6×CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 173.9, 172.6, 171.8, 170.1, 167.0, 138.7, 138.3, 138.0, 137.8, 128.7, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0 , 127.9, 127.9, 127.8, 101.3, 100.6, 76.1, 76.1, 75.8, 75.7, 75.1, 74.9, 74.5, 74.5, 73.8, 71.5, 71.3, 71.8, 71.1, 70.5, 70.3, 67.9, 67.5, 54.3, 54.2, 50.9, 42.0, 41.8, 39.8, 39.8, 34.8, 34.5, 34.3, 34.8, 32.2, 30.0, 29.9, 29.91, 29.8, 29.81 , 29.7, 29.71, 29.6, 29.6, 29.5, 25.51, 25.4, 25.3, 22.9, 14.4. MALDI-TOF MS (*m*/*z*): calcd for $C_{118}H_{191}N_5O_{19}$, 1982.4; found 2005.8 $[M + Na]^+$. Compound **27** (61 mg from 44 μmol of **23**, 75%) as a white solid: $[\alpha]^{24}_{D}$ = -8.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.16 (m, 20 H), 5.86 (d, J = 8.9 Hz, 1 H, NH), 5.80 (d, J = 8.1 Hz, 1 H, NH), 5.20 (t, J = 9.0 Hz, 1 H, H-3), 5.10-5.00 (m, 3 H, H-3', 2×lipid-H), 4.67 (d, J = 8.1 Hz, 1 H, H-1'), 4.62 (d, J = 8.1 Hz, 1 H, H-1), 4.59-4.43 (m, 8 H, PhC<u>H</u>$_2$), 4.01 (dd, J = 1.0, 10.5 Hz, 1 H, H-6), 3.93-3.76 (m, 5 H, OC<u>H</u>$_2$CH$_2$N$_3$, 2×lipid-H, H-2, H-2'), 3.71-3.56 (m, 6 H, H-5, H-5', H-6, H-6', H-4, $OC\underline{H}_2CH_2N_3$), 3.53-3.49 (m, 2 H, H-4', H-6'), 3.42 (ddd, J = 3.2, 7.3, 13.5 Hz, 1 H, $OC\underline{H}_2C\underline{H}_2N_3$), 3.30 (ddd, J = 3.2, 4.8, 13.5 Hz, 1 H, $OC\underline{H}_2C\underline{H}_2N_3$), 2.98 (b, 1 H, O$\underline{H}$), 2.62 (dd, J = 8.1, 15.4 Hz, 1 H, $COC\underline{H}_2$), 2.57-2.42 (m, 3 H, $COC\underline{H}_2$), 2.39-2.16 (m, 8 H, $COC\underline{H}_2$), 1.62-1.45 (m, 8 H, lipid-H), 1.25 (b, 108 H, 54×CH_2), 0.88 (t, J = 6.5 Hz, 18 H, 6×CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 173.9, 172.5, 171.8, 169.9, 169.8, 138.7, 138.3, 138.0, 137.7, 128.7, 128.6, 128.6, 128.5, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 101.2, 100.6, 76.1, 75.8, 75.7, 75.1, 74.9, 74.5, 73.8, 71.5, 71.3, 71.1, 71.1, 70.6, 70.3, 67.5, 50.9, 42.0, 41.7, 39.8, 39.7, 34.7, 34.5, 34.4, 34.3, 34.3, 32.2, 29.9, 29.8, 29.7, 29.7, 29.5, 25.5, 25.4, 25.3, 22.9, 14.4. MALDI-TOF MS (*m*/*z*): calcd for $C_{122}H_{199}N_5O_{19}$, 2038.4; found 2061.7 $[M + Na]^+$. Compound **28:** (75 mg from 50 μmol of **24**, 62%) as a white solid: $[\alpha]^{24}_D$ = -7.3 (*c* 0.80, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33-7.23 (m, 10 H), 5.89 (d, J = 8.9 Hz, 1 H, NH), 5.85 (d, J = 7.3 Hz, 1 H, NH), 5.17 (t, J = 9.3 Hz, 1 H, H-3), 5.12-4.97 (m, 3 H, H-3', 2×lipid-H), 4.64-4.50 (m, 6 H, $PhC\underline{H}_2$, H-1, H-1'), 4.01 (dd, J = 1.0, 9.5 Hz, 1 H, H-6), 3.94-3.83 (m, 3 H, $OC\underline{H}_2CH_2N_3$, H-2, H-2'), 3.78-3.57 (m, 9 H, H-4', H-6, $OC\underline{H}_2CH_2N_3$, 6×lipid-H), 3.53-3.27 (m, , 7 H, H-4, H-5, 2×H-6, 2×$OCH_2C\underline{H}_2N_3$), 3.14 (d, J = 2.4 Hz, 1 H, 4'-OH), 2.59-2.22 (m, 12 H, $COC\underline{H}_2$), 1.65-1.42 (m, 12 H, lipid-H), 1.26 (br, 144 H, 72×CH_2), 0.88 (t, J = 6.5 Hz, 24 H, 8×CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 173.8, 172.6, 171.9, 169.9, 169.7, 138.1, 137.8, 128.7, 128.6, 128.1, 127.9, 127.9, 101.5, 100.6, 76.5, 76.1, 76.0, 75.9, 75.2, 75.0, 74.7, 74.4, 73.8, 71.2, 71.1, 70.5, 70.2, 69.8, 69.7, 67.4, 54.1, 54.0, 50.9, 42.1, 41.8, 39.8, 34.7, 34.5, 34.3, 32.2, 30.3, 30.1, 30.0, 29.93, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 26.4, 26.3, 25.5, 25.3, 22.9, 14.4. [MALDI-TOF MS (*m*/*z*): calcd for $C_{132}H_{235}N_5O_{19}$, 2194.7; found 2217.3 $[M + Na]^+$.

2-Azidoethyl 6-*O*-benzyl-4-*O*-(di-*O*-benzylphosphoryl)-2-deoxy-2-[(R)-3-(dodecanoyloxy)-tetradecanamido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradecanoyl]-β-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)-tetradecan-amido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradecanoyl]-β-D-glucopyranoside (7/8/9/10): After a solution of **25-28** (30-262 μmol), dibenzyl diisopropylphosphoramidite (**29**, 31.15-272 mg, 90.11-787 μmol) and 1*H*-tetrazole in CH_3CN (0.45 M, 0.35-3.0 mL) was stirred at rt for 2h, *t*-BuOOH in decane (5.5 M, 0.05-0.40 mL, 0.24-2.10 mmol) was added at 0 ^{o}C, and the stirring continued at rt for 4 h. The solvent was removed under reduced pressure, and the crude product was subjected to silica gel column chromatography to obtain **7-10** as colorless and very viscous syrup. Compound **7** (350 mg from 262 μmol of **25**, 66%) had the same spectroscopic data as that reported in the literature.[32] Compound **8** (70 mg from 55 μmol of **26**, 57%): $[\alpha]^{24}_{D}$ = -7.8 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.16 (m, 30 H), 5.86 (d, J = 8.9 Hz, 1 H, NH), 5.68 (d, J = 8.1 Hz, 1 H, NH), 5.47 (t, J = 9.7 Hz, 1 H, H-3'), 5.19 (t, J = 9.3, Hz, 1 H, H-3), 5.10-5.00 (m, 3 H, H-1', 2×lipid-H), 4.92-4.83 (m, 4 H, 2×$PhCH_2$), 4.59 (d, J = 8.9 Hz, 1 H, H-1), 4.53-4.37 (m, 9 H, 4×$PhC\underline{H}_2$, H-4'), 3.99 (dd, J = 1.0, 10.5 Hz, 1 H, H-6), 3.95-3.62 (m, 9 H, 2×$OC\underline{H}_2CH_2N_3$, 2×lipid-H, H-5', H-2, 2×H-6', H-6), 3.58-3.37 (m, 4 H, H-5, H-2', H-4, $OC\underline{H}_2CH_2N_3$), 3.28 (dt, J = 4.0, 13.1 Hz, 1 H, $OC\underline{H}_2C\underline{H}_2N_3$), 2.58-2.19 (m, 11 H, $COC\underline{H}_2$), 2.03 (dd, J = 5.5, 15.0 Hz, 1 H, $COC\underline{H}_2$), 1.60-1.45 (m, 8 H, lipid-H), 1.25 (b, 100 H, 50×CH_2), 0.88 (t, J = 4.5 Hz, 18 H, 6×CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 173.6, 171.5, 170.9, 169.7, 169.7, 138.5, 138.2, 137.4, 135.6, 135.5, 129.4, 128.52, 128.5, 128.4, 128.4, 128.3, 128.3, 128.0, 127.9, 127.9, 127.7, 127.6, 127.5, 127.0, 100.4, 100.0, 76.0, 75.6, 75.4, 74.9, 74.3, 74.1, 73.3, 72.3, 71.3, 70.9, 70.5, 69.6, 69.5, 69.5, 69.4, 68.7, 68.1, 67.4, 55.8, 54.0, 50.6, 41.7, 41.1, 39.5, 38.6, 34.5, 34.3, 34.2, 34.2, 34.0, 31.9, 29.7, 29.6, 29.54, 29.5, 29.41, 29.0, 29.3, 29.2, 25.4, 25.3, 25.2, 25.0, 22.7, 14.1. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.04. MALDI-TOF MS (*m*/*z*): calcd for $C_{132}H_{204}N_5O_{22}P$, 2242.4; found 2267.3 $[M + Na]^+$. Compound **9** (42 mg from 30 μmol of **27**, 61%): $[\alpha]^{24}_{D}$ = -9.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.17 (m, 30 H), 5.63 (d, J = 8.1 Hz, 1 H, NH'), 5.47 (d, J = 8.9 Hz, 1 H, NH), 5.47 (dd, J = 8.9, 10.5 Hz, 1 H, H-3'), 5.18 (dd, J = 8.9, 10.5 Hz, 1 H, H-3), 5.10-4.98 (m, 3 H, H-1', 2×lipid-H), 4.91-4.82 (m, 4 H, 2×$PhCH_2$), 4.59 (d, J = 8.1 Hz, 1 H, H-1), 4.59-4.43 (m, 9 H, 4×$PhC\underline{H}_2$, H-4'), 3.99 (dd, J = 1.0, 10.5 Hz, 1 H, H-6), 3.95-3.62 (m, 9 H, 2×$OC\underline{H}_2CH_2N_3$, 2×lipid-H, H-5', H-2, 2×H-6', H-6), 3.58-3.35 (m, 4 H, H-5, H-2', H-4, $OC\underline{H}_2CH_2N_3$), 3.27 (dt, J = 4.0, 13.0 Hz, 1 H, $OC\underline{H}_2C\underline{H}_2N_3$), 2.58-2.18 (m, 11 H, $COC\underline{H}_2$), 2.01 (dd, J = 5.5, 15.0 Hz, 1 H, $COC\underline{H}_2$), 1.60-1.42 (m, 8 H, lipid-H), 1.25 (b, 108 H, 54×CH_2), 0.88 (t, J = 4.5 Hz, 18 H, 6×CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 173.6, 171.5, 170.9, 169.7, 169.7, 138.5, 138.2, 137.4, 135.6, 135.5, 128.7, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 100.4, 99.9, 76.0, 75.6, 75.4, 74.9, 74.3, 74.1, 73.3, 72.2, 71.3, 70.9, 70.8, 70.5, 69.6, 69.5, 69.5, 7.4, 68.7, 68.1, 67.4, 65.0, 55.8, 54.0, 50.7, 5.2, 45.2, 41.7, 41.1, 39.5, 38.63, 34.5, 34.2, 34.1, 34.0, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.4, 25.3, 25.2, 25.0, 23.0, 22.7, 14.1. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.03. MALDI-TOF MS (*m*/*z*): calcd for $C_{136}H_{212}N_5O_{22}P$, 2298.5; found, 2321.3 $[M + Na]^+$. Compound **10** **(**60 mg from 33 μmol of **28**, 73%): $[\alpha]^{24}_{D}$ = -4.6 (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ

7.34-7.21 (m, 20 H), 5.97 (d, J = 8.1 Hz, 1 H, NH), 5.88 (d, J = 8.9 Hz, 1 H, NH), 5.39 (t, J = 9.7 Hz, 1 H, H-3'), 5.16 (t, J = 9.7 Hz, 1 H, H-3), 5.12-5.03 (m, 2 H, 2×lipid-H), 4.97 (d, J = 8.9 Hz, 1 H, H-1'), 4.91-4.86 (m, 4 H, PhC$\underline{H}_2$), 4.62 (d, J = 11.4 Hz, 1 H, PhC$\underline{H}_2$), 4.58 (d, J = 8.1 Hz, 1 H, H-1), 4.52-4.30 (m, 4 H, PhC$\underline{H}_2$, H-4'), 4.01 (dd, J = 1.0, 10.5 Hz, 1 H, H-6), 3.95-3.86 (m, 2 H, H-2, OC$\underline{H}_2$CH$_2$N$_3$), 3.79-3.47 (m, 10 H), 3.45-3.47 (m, 5 H), 3.18 (dt, J = 6.5, 8.9 Hz, 1 H), 2.49-2.22 (m, 12 H, COC$\underline{H}_2$), 1.65-1.42 (m, 12 H, lipid-H), 1.26 (br, 144 H, 72×CH$_2$), 0.88 (t, J = 6.5 Hz, 24 H, 8×CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$): δ 174.0, 173.8, 171.9, 171.6, 169.9, 169.8, 138.4, 137.7, 135.8, 135.8, 128.8, 128.7, 128.7, 128.6, 128.2, 128.2, 128.1, 127.8, 127.7, 100.64, 100.6, 76.2, 75.9, 75.8, 75.3, 75.1, 74.5, 74.3, 73.5, 72.6, 71.1, 71.0, 70.1, 69.8, 69.7, 69.7, 69.3, 68.9, 67.5, 55.7, 54.1, 53.7, 50.9, 42.0, 41.7, 39.8, 38.9, 34.7, 34.73, 34.6, 34.5, 32.2, 30.3, 30.1, 30.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5, 26.4, 26.4, 25.7, 25.5, 25.2, 22.9, 14.4. ^{31}P NMR (CDCl$_3$, 161 MHz): δ -1.24. MALDI-TOF MS (*m/z*): calcd for $C_{146}H_{248}N_5O_{22}P$, 2454.8; found 2477.9 [M + Na]$^+$.

2-(3-Carboxypropanamido)ethyl 6-*O*-benzyl-4-*O*-(di-*O*-benzylphosphoryl)-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecanamido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradecanoyl]-β-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)-tetradecan-amido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/ [(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradecanoyl]-β-D-glucopyranoside (34/35/36/37): To a vigorously stirred mixture of **7-10** (18-153 μmol) and activated zinc dust (58.70-499 mg, 0.90-7.63 mmol) in DCM (1.20-10 mL) was added acetic acid (0.02-0.1 mL), and the mixture was stirred at rt overnight. The insoluble materials were removed via filtration and washed with DCM. The filtrates were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained amine was used for the next step without further purification. Therefore, after the crude products were dissolved in DMF ad DCM (1:3), succinic anhydride (7.17-61 mg, 71.76-610 μmol), DIPEA (23.18-197 mg, 0.18-1.53 mmol) and DMAP (1.18-10 mg) were added. The solution was stirred at rt overnight. After the solvent was removed under reduced pressure, the products were purified by flash column chromatography to afford **34-37**. Compound **34** (210 mg from 153 μmol of **7**, 65%) was obtained as a white solid which had the same spectroscopic data as that reported in the literature.[32] Compound **35** (40 mg from 31 μmol of **8**, 59%) as a white solid: $[\alpha]^{24}_D$ = -11.1 (*c* 1.0, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.30-7.26 (m, 30 H), 6.82 (t, J = 4.9 Hz, 1 H, NH), 6.10 (d, J = 7.9 Hz, 1 H, NH), 6.07

(d, J = 8.8 Hz, 1 H, NH), 5.51 (t, J = 9.5 Hz, 1 H, H-3'), 5.15 (t, J = 9.5 Hz, 1 H, H-3), 5.05-5.01 (m, 3 H, 2×lipid-H, H-1'), 4.87-4.84 (m, 4 H, 2×PhC$\underline{H}_2$), 4.53-4.36 (m, 10 H, 4×PhC$\underline{H}_2$, H-4',H-1), 3.98 (dd, J = 1, 11.6 Hz, 1 H, H-6), 3.93 (dd, J = 8.9, 10.0 Hz, 1 H, H-2), 3.83-3.62 (m, 8 H, H-6, 2×H-6', H-5', 2×lipid-H, 2×OC$\underline{H}_2$CH_2N_3), 3.57-3.45 (m, 4 H, H-4, H-5, H-2', OCH_2C$\underline{H}_2$$N_3$), 3.28-3.23 (m, 1 H, OCH_2C$\underline{H}_2$$N_3$), 2.80-2.72 (m, 1 H, COC$\underline{H}_2$), 2.64-2.37 (m, 9 H, COC$\underline{H}_2$), 2.32-2.22 (m, 5 H, COC$\underline{H}_2$), 2.11 (dd, J = 5.5, 15.0 Hz, 1 H, COC$\underline{H}_2$), 1.58-1.47 (m, 8 H), 1.25 (b, 100 H, 50×CH_2), 0.90-0.88 (m, 18 H, 3×C$\underline{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.9, 173.6, 172.6, 172.1, 171.3, 170.1, 170.0, 138.5, 138.4, 138.1, 137.4, 135.5, 135.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 100.9, 99.9, 76.2, 75.5, 75.3, 75.2, 74.6, 74.5, 74.4, 73.8, 73.7, 73.3, 72.3, 71.3, 71.2, 70.9, 70.8, 69.8, 69.6, 69.5, 68.7, 68.4, 67.9, 55.4, 54.1, 41.7, 41.1, 40.1, 39.5, 38.7, 34.5, 34.3, 34.1, 34.0, 31.9, 30.7, 29.8, 29.7, 29.5, 29.42, 29.4, 29. 3, 29.2, 25.3, 25.29, 25.2, 25.1, 25.0, 22.7, 14.1. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.24. MALDI-TOF MS (*m*/*z*): calcd for $C_{136}H_{210}N_3O_{25}P$, 2316.5; found 2339.1 [M + Na]$^+$. Compound **36 (**19 mg from 18 μmol of **9**, 52%) as a white solid: $[\alpha]^{24}_D$ = -11.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.35-7.18 (m, 30 H), 6.78 (t, J = 4.9 Hz, 1 H, NH), 6.09 (d, J = 7.9 Hz, 1 H, NH'), 6.04 (d, J = 8.8 Hz, 1 H, NH), 5.53 (t, J = 9.1 Hz, 1 H, H-3'), 5.17 (t, J = 9.1 Hz, 1 H, H-3), 5.08-5.03 (m, 3 H, 2×lipid-H, H-1'), 4.91-4.83 (m, 4 H, 2×PhC$\underline{H}_2$), 4.54-4.42 (m, 9 H, 4×PhC$\underline{H}_2$, H-4'), 4.38 (d, J = 10.0 Hz, 1 H, H-1), 3.98 (dd, J = 1, 11.6 Hz, 1 H, H-6), 3.93 (dd, J = 8.9, 10.0 Hz, 1 H, H-2), 3.84-3.64 (m, 8 H, H-6, 2×H-6', H-5', 2×lipid-H, 2×OC$\underline{H}_2$CH_2N_3) 3.58-3.47 (m, 4 H, H-4, H-5, H-2', OCH_2C$\underline{H}_2$$N_3$), 3.28-3.25 (m, 1 H, OCH_2C$\underline{H}_2$$N_3$), 2.80-2.57 (m, 1 H, COC$\underline{H}_2$), 2.64-2.37 (m, 9 H, COC$\underline{H}_2$), 2.33-2.25 (m, 5 H, COC$\underline{H}_2$), 2.11 (dd, J = 5.5, 15.0 Hz, 1 H, COC$\underline{H}_2$), 1.58-1.47 (m, 8 H), 1.25 (b, 108 H, 54×CH_2), 0.90-0.88 (m, 18 H, 3×C$\underline{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.0, 173.9, 173.6, 172.6, 172.1, 171.3, 170.1, 170.0, 138.5, 138.1, 137.4, 135.5, 128.5, 128.5, 128.4, 128.4, 128.3, 128.0, 128.0, 127.7, 127.6, 127.6, 127.5, 100.9, 99.9, 76.2, 75.5, 75.3, 75.2, 74.6, 74.4, 73.9, 73.8, 73.3, 72.4, 71.2, 70.9, 70.8, 69.7, 69.6, 69.6, 69.5, 68.7, 68.5, 67.9, 55.6, 54.1, 41.7, 41.1, 40.1, 39.6, 38.7, 34.5, 34.3, 34.1, 34.0, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.4, 25.3, 25.2, 25.2, 25.0, 22.7, 14.1. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.24. MALDI-TOF MS (*m*/*z*): calcd for $C_{140}H_{218}N_3O_{25}P$, 2372.5; found, 2394.3 [M+Na]$^+$. Compound **37 (**50 mg from 24 μmol of **10**, 79%) as a white solid: $[\alpha]^{24}_D$ = -6.5 (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31-7.21 (m, 20 H), 6.95 (d, J = 4.8 Hz, 1 H, NH). 6.38 (d, J = 8.1 Hz, 1 H, NH), 6.03 (d, J = 8.9 Hz, 1 H, NH), 5.5.47 (t, J = 9.7 Hz, 1 H, H-3’), 5.13 (t, J = 10.5 Hz, 1 H, H-3), 5.12-5.03 (m, 2 H, 2×lipid-H), 4.97 (d, J = 8.1 Hz, 1 H, H-1’), 4.93-4.84 (m, 4 H, PhC<u>H</u>$_2$), 4.61 (d, J = 11.1 Hz, 1 H, PhC<u>H</u>$_2$), 4.52-4.44 (m, 4 H, H-4, 3×PhC<u>H</u>$_2$) 4.41 (d, J = 8.1 Hz, 1 H, H-1), 3.99 (dd, J = 1.0, 10.5 Hz, 1 H, H-6), 3.92 (dt, J = 8.1, 10.5 Hz, 1 H, H-2), 3.79-3.45 (m, 12 H), 3.40-3.17 (m, 5 H), 2.80-2.73 (m, 1 H), 2.61-2.24 (m, 15 H, COC<u>H</u>$_2$), 1.65-1.42 (m, 12 H, lipid-H), 1.26 (br, 144 H, 72×CH_2), 0.88 (t, J = 6.5 Hz, 24 H, 8×CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.1, 173.9, 173.6, 172.5, 172.3, 171.6, 170.0, 169.9, 138.1, 137.4, 135.5, 135.5, 128.6, 128.5, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.6, 127.5, 100.9, 100.3, 77.2, 76.3, 75.6, 75.5, 75.2, 74.6, 74.4, 73.9, 73.3, 72.5, 71.2, 71.0, 69.7, 69.6, 69.6, 69.5, 68.8, 68.7, 68.0, 55.4, 54.0, 41.7, 41.3, 40.0, 39.7, 38.9, 34.5, 34.3, 34.2, 34.1, 31.9, 30.0, 30.0, 29.8, 29.7, 29.73, 29.71, 29.70, 29.67, 29.65, 29.60, 29.57, 29.5, 29.54, 29.51, 29.49, 29.40, 29.38, 29.3, 29.2, 26.2, 26.1, 25.4, 25.3, 25.3, 25.0, 22.7, 14.1. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.30. MALDI-TOF MS (*m*/*z*): calcd for $C_{150}H_{254}N_3O_{25}P$, 2528.8; found, 2551.5 $[M+Na]^+$.

2-{4-[2-(3,5-Dideoxy-5-phenylacetamido-D-*glycero*-α-D-*galacto*-non-2-ulopyranosylonic acid]-(2→6)-*O*-2-acetamido-2-deoxy-*β*-D-galactopyranosyloxy)ethylamino]-4-oxobutanamido} ethyl 6-*O*-benzyl-4-*O*-(di-*O*-benzylphosphoryl)-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecan-amido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradecanoyl]-β-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecan-amido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradecanoyl]-β-D-glucopyranoside (43/44/45/46): To a stirred solution of **34-37** (3.9-8.0 μmol) and *p*-nitrophenol (2.71-5.56 mg, 19.5-40.0 μmol) in DCM was added EDC:HCl (3.76-7.71 mg, 19.5-40.0 μmol) at 0 ^oC. The mixture was stirred at rt for another 5h. Then, the solvent was removed under reduced pressure, and the products were purified by silica gel column chromatography using 5% acetone in DCM as the eluent to get activated esters **45-48**, which was only briefly characterized by ^{1}H and ^{31}P NMR spectroscopy and the used directly in the next step due to their relatively high reactivity. Compound **38** (10 mg from 5.7 μmol of **34**, 83%) was obtained as a white solid which had the same ^{1}H and ^{31}P NMR spectroscopic data as that reported in the literature.[32] Compound **39** (12 mg from 6.5 μmol of **35**, 76%) as a pale yellow solid: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.20 (d, J = 9.7 Hz, 2 H), 7.30-6.89 (m, 32 H), 7.85 (t, J = 4.8 Hz, 1 H, NH), 5.88 (d, J = 8.9 Hz, 1 H, NH), 5.86 (d, J = 8.1 Hz, 1 H, NH’), 5.44 (dd, J = 8.9, 10.4 Hz, 1 H, H-3’), 5.07-4.95 (m, 3 H, 2×lipid-H, H-3), 4.94 (d, J = 8.1

Hz, 1 H, H-1’), 4.88-4.84 (m, 4 H, 2×PhC$\underline{H}_2$), 4.52-4.35 (m, 10 H, 4×PhC$\underline{H}_2$, H-1’, H-4’), 3.96 (dd, J = 1.0, 10.0 Hz, 1 H, H-6), 3.88-3.71 (m, 6 H, H-2’, H-6, H-6’, OC$\underline{H}_2$CH$_2$NH, 2×lipid-H), 3.69-3.61 (m, 4 H, H-5, H-5’, H-6’, OC$\underline{H}_2$CH$_2$NH), 3.36-3.44 (m, 2 H, H-2, H-4), 3.36-3.41 (m, 2 H, OCH$_2\underline{CH}_2$NH), 2.90 (t, J = 6.5 Hz, 2 H, COC$\underline{H}_2$), 2.62 (t, J = 6.5 Hz, 2 H, COC$\underline{H}_2$), 2.55-2.39 (m, 6 H, COC$\underline{H}_2$), 2.35-2.17 (m, 5 H, COC$\underline{H}_2$), 2.03 (dd, J = 4.8, 15.4 Hz, 1 H, COC$\underline{H}_2$), 1.55-1.39 (m, 8 H), 1.25 (b, 100 H, 50×CH$_2$), 0.89-0.85 (m, 18 H, 6×CH$_3$). ^{31}P NMR (CDCl$_3$, 161 MHz): δ -1.82. Compound **40** (12 mg from 8.0 μmol of **36**, 62%) as a pale yellow solid: ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.19 (d, J = 8.9 Hz, 2 H), 7.31-7.14 (m, 32 H), 7.05 (t, J = 4.8 Hz, 1 H, NH), 6.08 (d, J = 8.1 Hz, 1 H, NH’), 6.01 (d, J = 8.1 Hz, 1 H, NH), 5.45 (t, J = 8.1 Hz, 1 H, H-3’), 5.08-4.99 (m, 3 H, 2×lipid-H, H-3), 4.94 (d, J = 8.1 Hz, 1 H, H-1’), 4.90-4.81 (m, 4 H, 2×PhC$\underline{H}_2$), 4.54-4.36 (m, 10 H, 4×PhC$\underline{H}_2$, H-1’, H-4’), 3.96 (dd, J = 1.0, 10.0 Hz, 1 H, H-6), 3.87-3.69 (m, 6 H, H-2’, H-6, H-6’, OC$\underline{H}_2$CH$_2$NH, 2×lipid-H), 3.69-3.61 (m, 4 H, H-5, H-5’, H-6’, OC$\underline{H}_2$CH$_2$NH), 3.44 (m, 2 H, H-2, H-4), 3.36-3.41 (m, 2 H, OCH$_2\underline{CH}_2$NH), 2.91 (t, J = 6.5 Hz, 2 H, COC$\underline{H}_2$), 2.63 (t, J = 6.5 Hz, 2 H, COC$\underline{H}_2$), 2.52-2.30 (m, 6 H, COC$\underline{H}_2$), 2.30-2.20 (m, 5 H, COC$\underline{H}_2$), 2.03 (dd, J = 4.8, 15.4 Hz, 1 H, COC$\underline{H}_2$), 1.55-1.39 (m, 8 H), 1.25 (b, 108 H, 54×CH$_2$), 0.89-0.85 (m, 18 H, 6×CH$_3$). ^{31}P NMR (CDCl$_3$, 161 MHz): δ -0.98. Compound **41** (9 mg from 3.9 μmol of **37**, 87%) as a pale yellow solid: ^{1}H NMR (CDCl3, 400 MHz): δ 8.20 (d, J = 9.7 Hz, 2 H), 7.31-7.21 (m, 22 H), 6.90 (t, J = 5.6 Hz, 1 H, NH), 6.23 (d, J = 8.1 Hz, 1 H, NH), 5.94 (d, J = 8.9 Hz, 1 H, NH), 5.38 (t, J = 9.7 Hz, 1 H, H-3’), 5.12-5.00 (m, 3 H, 2×lipid-H, H-3), 4.91-4.86 (m, 5 H, H-1 2×PhC$\underline{H}_2$), 4.60 (d, J = 11.5 Hz, 1 H, PhC$\underline{H}_2$), 4.50-4.38 (m, 5 H, PhC$\underline{H}_2$, H-4’, H-1), 3.98 (dd, J = 1.0, 10.0 Hz, 1 H, H-6), 3.85 (dt, J = 8.5, 9.7 Hz, 1 H, H-2), 3.77-3.35 (m, 2 H), 3.68-3.57 (m, 5 H), 3.54-3.30 (m, 9 H), 3.21-3.15 (m, 1 H, OCH$_2\underline{CH}_2$NH), 2.90 (t, J = 6.5 Hz, 2 H, COC$\underline{H}_2$), 2.62 (t, J = 6.5 Hz, 2 H, COC$\underline{H}_2$), 2.47-2.20 (m, 12 H, COC$\underline{H}_2$), 1.57-1.39 (m, 12 H), 1.25 (b, 144 H, 72×CH$_2$), 0.89 (m, 24 H, 8×CH$_3$). ^{31}P NMR (CDCl$_3$, 161 MHz): δ -1.05.

To a stirred solution of **38-41** (3.4-4.9 μmol) and **42** (3.21-4.63 mg, 5.09-7.34 μmol) in DMF (0.76-1.10 mL) was added *N*-methylmorpholine (NMM, 4.30-4.95 mg, 33.92-48.89 μmol) at 0 ^{o}C, and the mixture was stirred at rt overnight. The solvent was removed under reduced pressure, and the residues were purified on preparative silica gel TLC plates with DCM and MeOH (3:1) as the eluent to afford **43-46**. Compound **43** (7 mg from 4.5 μmol of **38**, 58%) as a white solid: $[\alpha]^{24}_D$ = -11.4 (*c* 0.35, CHCl$_3$). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.10-6.99 (m, 25 H), 5.13 (t, *J* =

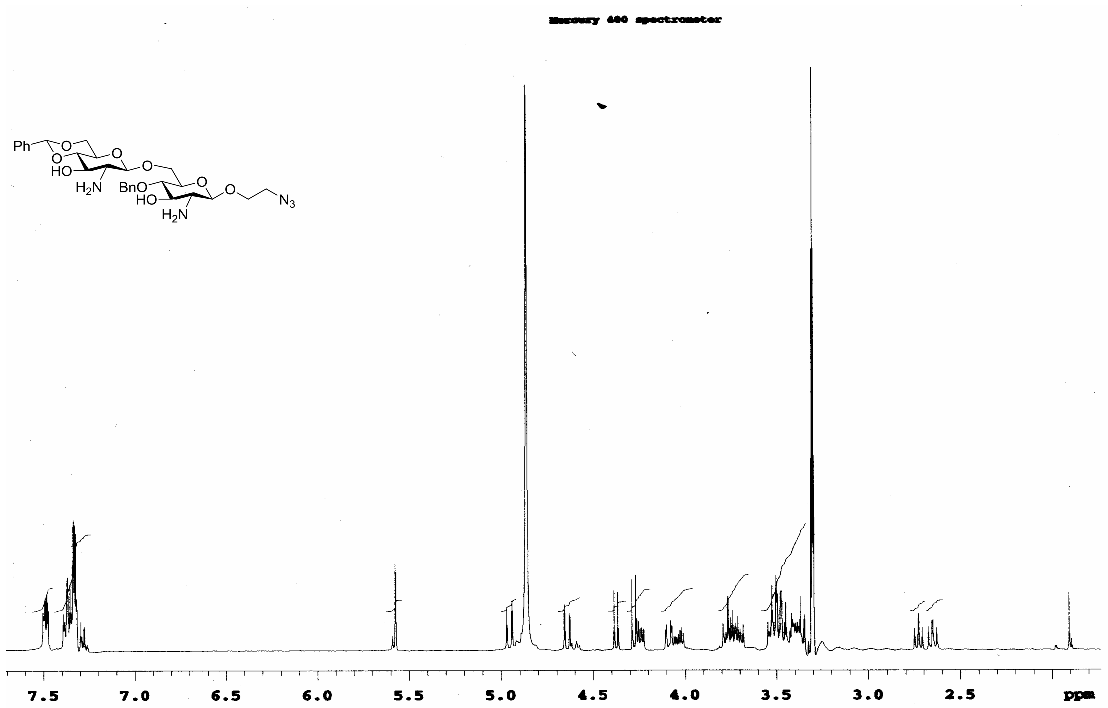
10.0 Hz, 1 H, H-3'), 4.90-4.82 (m, 3 H), 4.63-4.66 (m, 4 H, H-1, 2×PhC<u>H</u>$_2$), 4.52 (d, J = 8.9 Hz, 1H), 4.33-4.06 (m, 6 H, H-4' H-1', PhC<u>H</u>$_2$), 3.87-3.75 (m, 2 H) 3.69-3.06 (m, 29 H), 2.56-2.53 (m, 1 H), 2.27-2.15 (m, 6 H), 2.07-1.86 (m, 12 H), 1.77 (s, 3 H), 1.40-1.19 (m, 5 H), 1.02 (br, 108 H), 0.64 (t, J = 6.1 Hz, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$) : δ 174.8, 173.7(2C), 173.4, 173.3(2C), 173.1, 173.0, 137.6, 137.3, 135.0, 134.7, 128.7, 128.4, 128.3, 128.2, 128.1, 127.7, 127.4, 127.3, 126.7, 101.4, 100.8, 100.5, 100.2, 76.1, 74.2, 74.1, 73.8, 73.6, 73.6, 73.1, 73.0, 72.9, 72.1, 72.0, 71.3, 71.1, 70.8, 70.5, 69.6, 69.6, 69.5, 69.5, 69.1, 68.2, 68.0, 67.9, 67.7, 67.5, 67.3, 63.6, 61.8, 53.5, 53.2, 52.6, 52.6, 49.2, 42.5, 40.7, 40.6, 39.2, 39.1, 34.2, 33.9, 33.6, 31.6, 30.7, 29.4, 29.2, 29.1, 28.9, 25.1, 24.8, 24.5, 24.3, 22.4, 13.6. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.83. MALDI-TOF MS (*m*/*z*): calcd for $C_{149}H_{237}N_6O_{36}P$, 2717.6; found, 2715.1 $[M-H]^-$.
Compound **44** (10 mg from 4.9 μmol of **39**, 70%) as a white solid: $[\alpha]^{24}_D$ = -6.9 (*c* 0.50, MeOH:$CHCl_3$ = 2:3). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.10-6.99 (m, 35 H), 5.25 (t, *J* = 10.0 Hz, 1 H, H-3'), 4.96-4.81 (m, 3 H), 4.65-4.61 (m, 5 H, H-1, 2×PhC<u>H</u>$_2$), 4.18-4.06 (m, 10 H, H-1', 4×PhC<u>H</u>$_2$), 4.81-3.09 (m, 33 H), 2.58 (dd, J = 4.0, 12.0 Hz, 1 H, sTn H-3_e), 2.20-2.38 (m, 10 H), 2.06-2.08 (m, 7 H), 1.82-1.87 (m, 1 H), 1.78 (s, 3 H), 1.45-1.20 (m, 9 H), 1.03 (br, 100 H), 0.67-0.65 (m, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.8, 173.7, 173.7, 172.9, 171.4, 170.9, 170.7, 170.4, 138.1, 137.6, 137.2, 135.0, 134.8, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 126.7, 101.4, 100.8, 100.5, 99.9, 75.8, 75.2, 75.1, 74.7, 74.2, 74.2, 74.1, 73.8, 73.6, 73.5, 73.1, 72.9, 72.9, 72.0, 71.3, 71.1, 71.04, 70.8, 70.7, 70.2, 69.7, 69.6, 69.5, 69.4, 69.1, 68.1, 68.0, 67.9, 67.5, 67.3, 63.6, 61.7, 54.9, 53.7, 52.6, 48.9, 48.7, 48.5, 48.4, 48.2, 48.0, 47.9, 42.5, 40.8, 40.7, 40., 39.3, 39.1, 38.4, 34.2, 34.0, 33.9, 33.8, 31.6, 30.7, 29.5, 29.4, 29.3, 29.2, 29.2, 29.1, 29.0, 28.9, 25.0, 24.9, 24.8, 22.4, 13.6. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.70. MALDI-TOF MS (*m*/*z*): calcd for $C_{163}H_{249}N_6O_{38}P$, 2929.7; found, 2928.3 $[M-H]^-$.
Compound **45** (6 mg from 4.8 μmol of **40**, 61%) as a white solid: $[\alpha]^{24}_D$ = -8.2 (*c* 0.45, MeOH:$CHCl_3$ = 2:3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.21-7.10 (m, 35 H), 5.43 (t, *J* = 10.0 Hz, 1 H, H-3'), 5.08-4.97 (m, 3 H), 4.85 (d, J = 8.1 Hz, 1 H, H-1), 4.78-4.74 (m, 4 H, 2×PhC<u>H</u>$_2$), 4.45-4.35 (m, 8 H, H-4' PhC<u>H</u>$_2$), 4.26 (d, J = 11.3 Hz, 1 H, PhC<u>H</u>$_2$), 4.22(d, J = 8.1 Hz, 1 H, H-1') 3.96-3.22 (m, 33 H), 2.58 (b, J = 10.5 Hz, 1 H), 2.49-2.31 (m, 10 H), 2.21-2.17 (m, 7 H), 2.01 - 1.99 (m, 1 H), 1.91 (s, 3 H), 1.55-1.30 (m, 9 H), 1.03 (br, 108 H), 0.67-0.65 (m, 18 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 173.7, 173.7, 172.9, 171.4, 170.9, 170.7, 170.4, 138.2, 137.7, 137.2, 135.1, 134.8, 128.8, 128.5, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.8, 127.7, 127.6,

127.5, 127.4, 127.3, 126.8, 101.4, 100.9, 100.5, 99.9, 75.8, 75.2, 75.2, 74.7, 74.1, 73.9, 73.6, 73.1, 72.9, 72.0, 71.4 71.1, 70.8, 70.3, 69.7, 69.7, 69.5, 69.2, 68.2, 68.1, 67.9, 67.6, 67.3, 63.7, 61.8, 53.2, 52.7, 52.6, 49.3, 49.0, 48.8, 48.6, 48.5, 48.3, 48.1, 48.0, 42.6, 40.9, 40.7, 40.5, 39.3, 39.1, 38.5, 34.3, 34.0, 33.9, 33.8, 31.7, 30.7, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.0, 28.9, 25.1, 24.9, 24.8, 22.5, 22.4, 13.7. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.44. MALDI-TOF MS (*m*/*z*): calcd for $C_{167}H_{257}N_6O_{38}P$, 2985.8; found, 2984.6 $[M-H]^-$. Compound **46** (6 mg from 3.4 μmol of **41**, 59%) as a white solid: $[\alpha]^{24}_{D}$ = -5.6 (*c* 0.3, MeOH:$CHCl_3$ = 2:3). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.14-7.05 (m, 25 H), 5.31 (t, *J* = 10.0 Hz, 1 H, H-3’), 4.99-4.91 (m, 3 H), 4.74-4.68 (m, 5 H, H-1, 2×PhC<u>H</u>$_2$), 4.43 (d, J = 11.0 Hz, 1H), 4.35-4.12 (m, 5H, H-4’ PhC<u>H</u>$_2$), 3.88 (bd, J = 10.5 Hz, 1 H) 3.75-3.12 (m, 35 H), 3.03-2.98 (m, 1 H), 2.60 (m, 1 H), 2.37-2.03 (m, 18 H), 1.82 (s, 3 H), 1.41-1.22 (m, 13 H), 1.08 (br, 144 H), 0.73 (t, J = 6.4 Hz, 24 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 174.8, 173.7, 173.7, 172.9, 171.5, 171.2, 170.7, 170.4, 137.7, 137.3, 135.1, 135.1, 134.7, 128.8, 128.5, 128.4, 128.2, 128.1, 127.8, 127.7, 127.7, 127.4, 126.8, 101.3, 100.8, 100.5, 100.0, 75.8, 75.4, 75.3, 74.6, 74.3, 74.2, 74.0, 73.9, 73.6, 73.5, 73.1, 72.9, 72.0, 71.4, 71.1, 70.9, 70.4, 69.7, 69.5, 69.5, 69.3, 68.8, 68.2, 68.2, 68.1, 68.0, 67.9, 67.6, 67.3, 67.1, 54.9, 53.7, 52.7, 52.6, 49.0, 48.8, 48.6, 48.5, 48.3, 48.1, 48.0, 42.6, 40.9, 40.7, 40.6, 39.4, 39.2, 39.1, 38.6, 34.3, 34.1, 33.8, 31.7, 30.7, 29.8, 29.7, 29.6, 29.5, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 25.9, 25.9, 25.2, 25.1, 25.0, 24.8, 22.4, 13.7. ^{31}P NMR ($CDCl_3$, 161 MHz): δ -1.72. MALDI-TOF MS (*m*/*z*): calcd for $C_{177}H_{293}N_6O_{38}P$, 3142.09; found, 3140.75 $[M-H]^-$

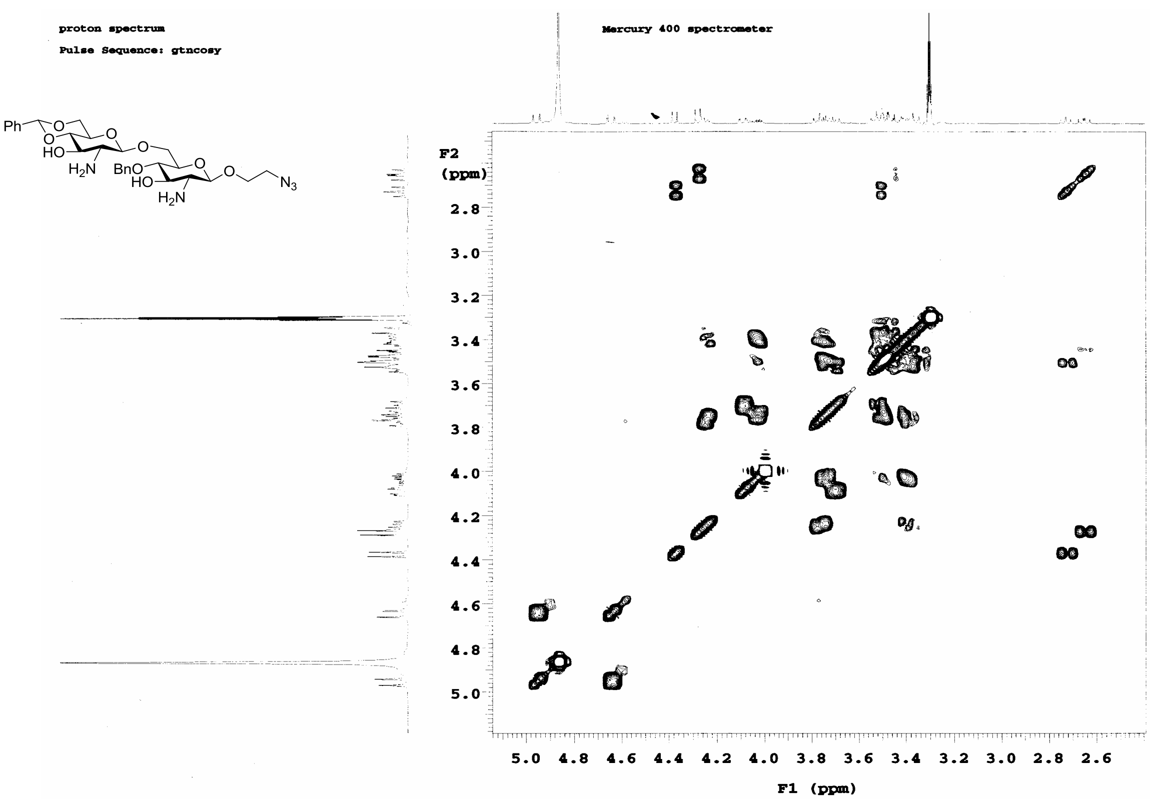
2-{4-[2-(3,5-Dideoxy-5-phenylacetamido-D-*glycero*-α-D-*galacto*-non-2-ulopyranosylonic acid]-(2→6)-*O*-2-acetamido-2-deoxy-*β*-D-galactopyranosyloxy)ethylamino]-4-oxobutanamido} ethyl 2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecanamido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)-dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dodecyloxy)tetradecanoyl]-4-*O*-phosphoryl-β-D-glucopyranosyl-(1→6)-4-*O*-benzyl-2-deoxy-2-[(R)-3-(dodecanoyloxy)tetradecanamido]-3-*O*-dodecanoyl/[(R)-3-(benzyloxy)dodecanoyl]/[(R)-3-(benzyloxy)tetradecanoyl]/[(R)-3-(dode-cyloxy)tetradecanoyl]-β-D-glucopyranoside (3/4/5/6): After a mixture of **43-46** (2.58 μmol) and Pd/C (10%, 5 mg) in DCM and MeOH (1:1) was stirred vigorously at rt under a H_2 atmosphere for 24h, the solid materials were removed by filtration through a syringe filter (0.2 μm). The filtrate was concentrated under reduced pressure to afford **3-6**. Compound **3** (5.2 mg, 85%) as an off-white solid. ^{1}H NMR ($CDCl_3$ and CD_3OD 1:1, 500 MHz): δ 7.20-7.10 (m, 5 H, Ph), 5.08 (t, *J* = 9.0 Hz, 1 H, H-3’), 5.00-4.90 (m, 2 H, 2×lipid H-3), 4.80 (t, *J* = 8.5 Hz, 1 H, H-3), 4.35 (bd, 1

H, H-1), 4.25 (bd, 1 H, H-1'), 4.20 (bd, 1 H, H-1''), 2.60 (m, 1 H, sialyl H-3e), 2.40-2.30 (m, 6 H, lipid), 2.20-2.05 (m, 12 H, lipid), 1.87 (s, 3 H, Ac), 1.40-1.19 (m, 12 H, lipid), 1.02 (br, lipid), 0.65 (t, *J* = 6.5 Hz, 18 H, lipid). ^{31}P NMR ($CDCl_3$ and CD_3OD 1:1, 161 MHz): δ 1.28. MALDI-TOF MS (*m*/*z*): calcd for $C_{121}H_{213}N_6O_{36}P$, 2357.4; found, 2356.2 $[M-H]^-$. Compound **4** (5.4 mg, 87%)**:** ^{1}H NMR ($CDCl_3$ and CD_3OD 1:1, 500 MHz): δ 7.20-7.10 (m, 5 H, Ph), 5.25 (t, *J* = 9.5 Hz, 1 H, H-3'), 5.15-5.05 (m, 2 H, 2×lipid H-3), 4.97 (t, *J* = 9.0 Hz, 1 H, H-3), 4.65 (d, 1 H, H-1), 4.48 (d, 1 H, *J* = 8.0 Hz, H-1'), 4.40 (d, 1 H, *J* = 7.5 Hz, H-1''), 4.25 (m, 1 H, H-4'), 2.70 (m, 1 H, sialyl H-3e), 2.55-2.25 (m, 12 H, lipid), 1.98 (s, 3 H, Ac), 1.60-1.50 (m, 8 H, lipid), 1.45-1.40 (m, 4 H, lipid), 1.40-1.12 (m, lipid), 0.65 (t, *J* = 6.5 Hz, 18 H, lipid). ^{31}P NMR ($CDCl_3$ and CD_3OD 1:1, 161 MHz): δ 0.55. MALDI-TOF MS (*m*/*z*): calcd for $C_{121}H_{213}N_6O_{38}P$, 2389.4; found, 2410.2 $[M+Na-2H]^-$. Compound **5** (5.2 mg, 83%): ^{1}H NMR ($CDCl_3$ and CD_3OD 1:1, 500 MHz): δ 7.20-7.10 (m, 5 H, Ph), 5.26 (t, *J* = 9.5 Hz, 1 H, H-3'), 5.18-5.10 (m, 2 H, 2×lipid H-3), 4.96 (t, *J* = 9.0 Hz, 1 H, H-3), 4.67 (d, 1 H, *J* = 7.8 Hz, H-1), 4.49 (d, 1 H, *J* = 8.0 Hz, H-1'), 4.35 (d, 1 H, *J* = 8.0 Hz, H-1''), 4.25 (m, 1 H, H-4'), 2.71 (m, 1 H, sialyl H-3e), 2.55-2.25 (m, 12 H, lipid), 1.99 (s, 3 H, Ac), 1.60-1.50 (m, 8 H, lipid), 1.45-1.40 (m, 4 H, lipid), 1.40-1.12 (m, lipid), 0.65 (t, *J* = 6.5 Hz, 18 H, lipid). ^{31}P NMR ($CDCl_3$ and CD_3OD 1:1, 161 MHz): δ -0.50. MALDI-TOF MS (*m*/*z*): calcd for $C_{125}H_{221}N_6O_{38}P$, 2445.5; found, 2467.7 $[M+Na-2H]^-$. Compound **6** (6.1 mg, 85%): ^{1}H NMR ($CDCl_3$ and CD_3OD 1:1, 500 MHz): δ 7.20-7.10 (m, 5 H, Ph), 5.23 (t, *J* = 9.0 Hz, 1 H, H-3'), 5.18-5.10 (m, 2 H, 2×lipid H-3), 4.97 (t, *J* = 9.0 Hz, 1 H, H-3), 4.62 (d, 1 H, H-1), 4.47 (d, 1 H, *J* = 8.0 Hz, H-1'), 4.33 (d, 1 H, *J* = 7.5 Hz, H-1''), 4.26 (m, 1 H, H-4'), 2.70 (m, 1 H, sialyl H-3e), 2.55-2.25 (m, 12 H, lipid), 1.99 (s, 3 H, Ac), 1.60-1.40 (m, 16 H, lipid), 1.40-1.12 (m, lipid), 0.65 (t, *J* = 6.5 Hz, 24 H, lipid). ^{31}P NMR ($CDCl_3$ and CD_3OD 1:1, 161 MHz): δ 1.01. MALDI-TOF MS (*m*/*z*): calcd for $C_{149}H_{269}N_6O_{38}P$, 2781.9; found, 2802.4 $[M+Na-2H]^-$.

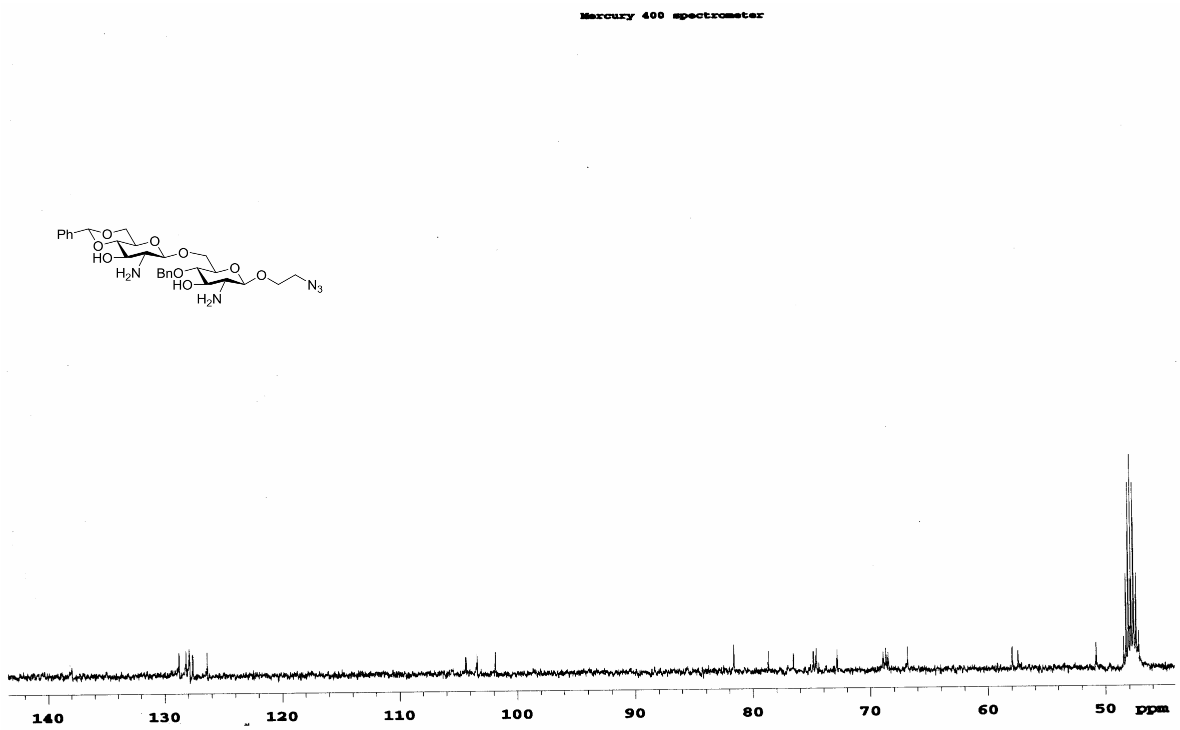
Reference 32. Q. Wang and Z. Guo, *Chem. Commun.*, 2009, 5536-5537.



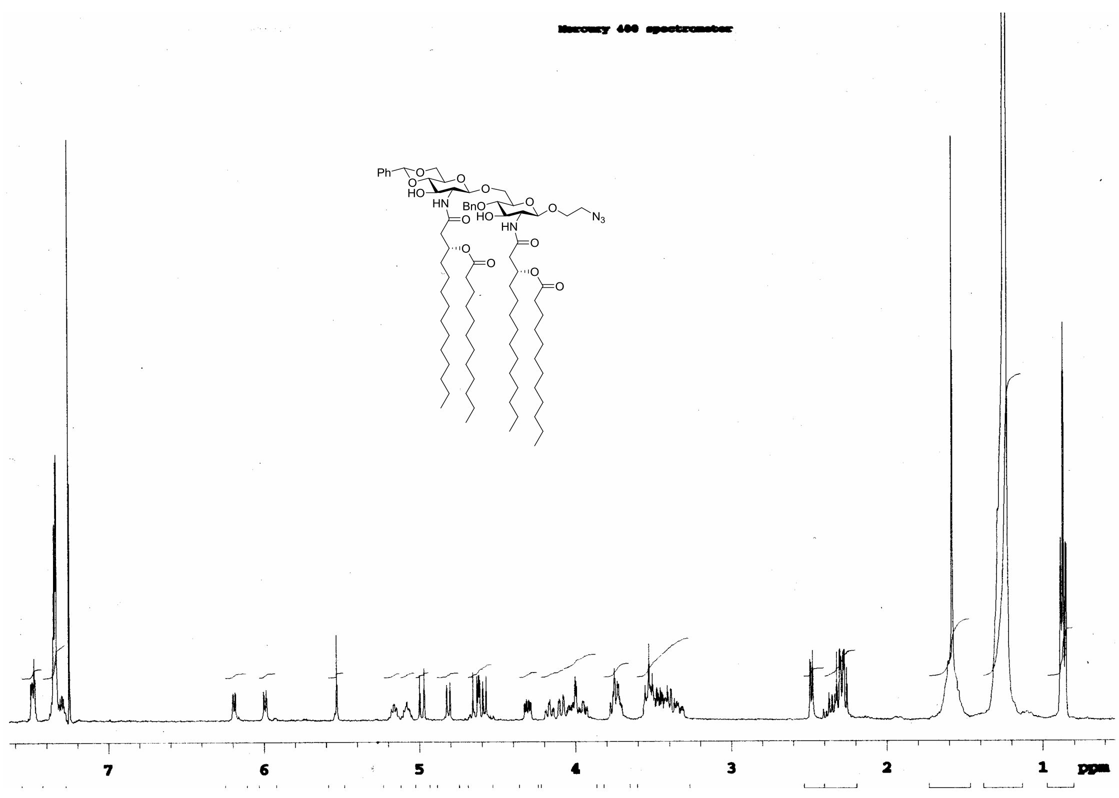
[1]H NMR spectrum of **14** ($CDCl_3$, 400 MHz) [Ref. 32]



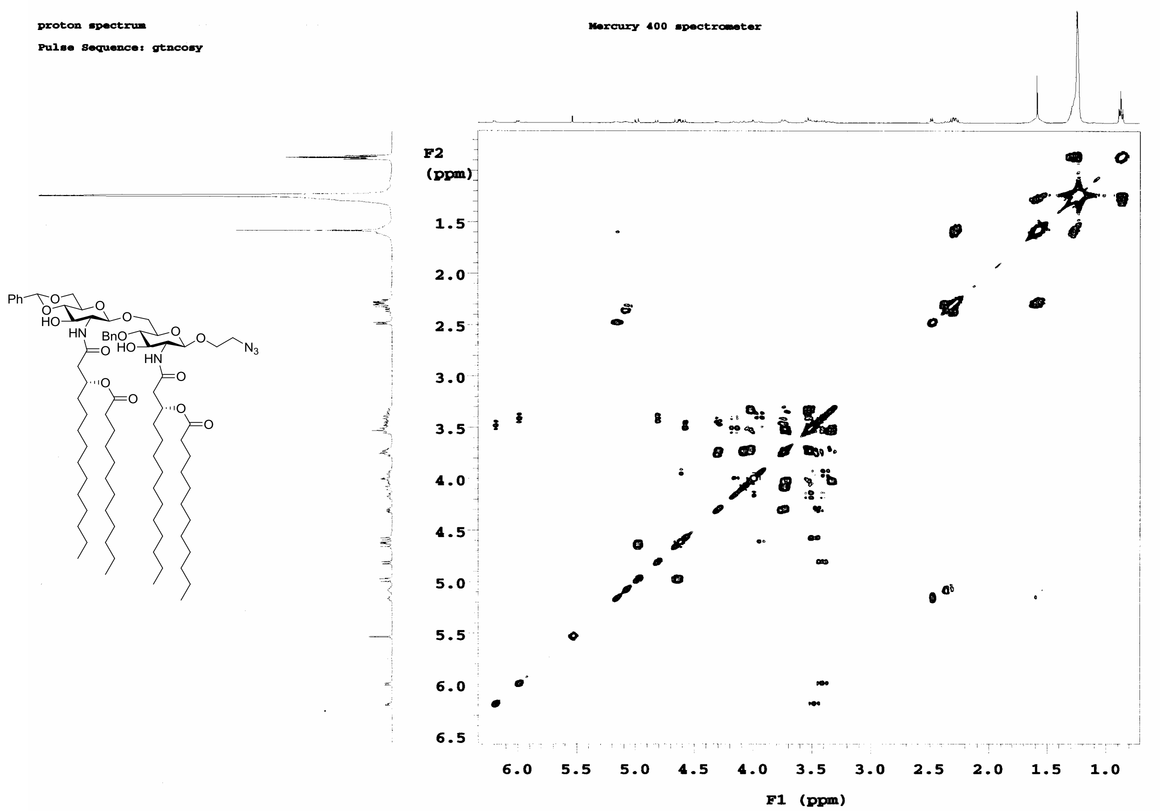
[1]H-[1]H COSY NMR spectrum of **14** ($CDCl_3$, 400 MHz) [Ref. 32]



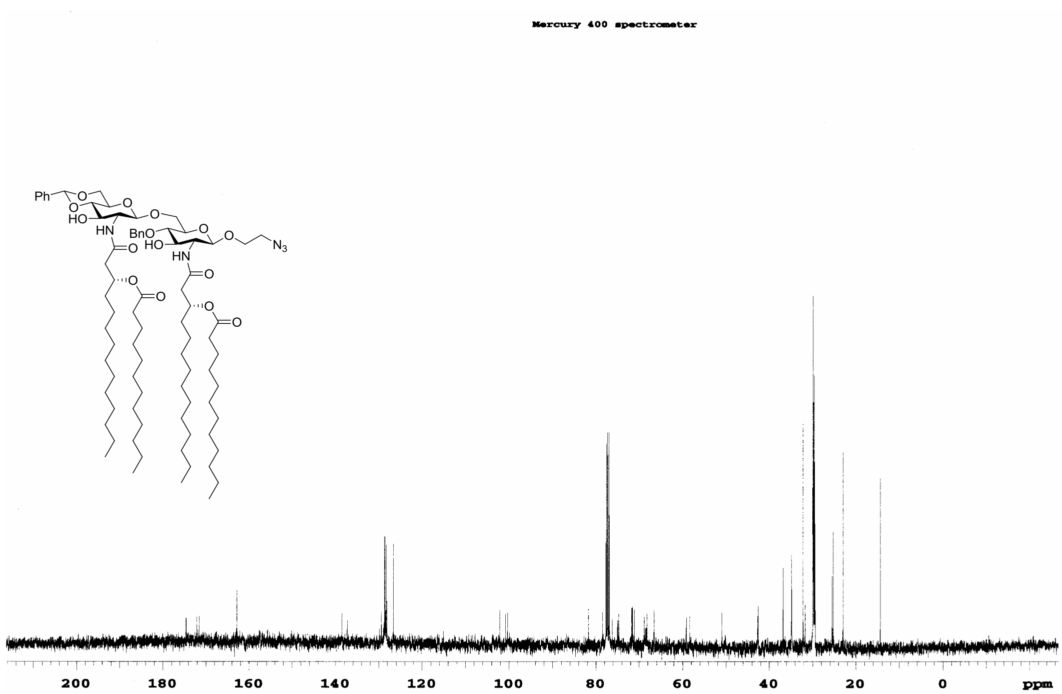
^{13}C NMR spectrum of **14** ($CDCl_3$, 100 MHz) [Ref. 32]



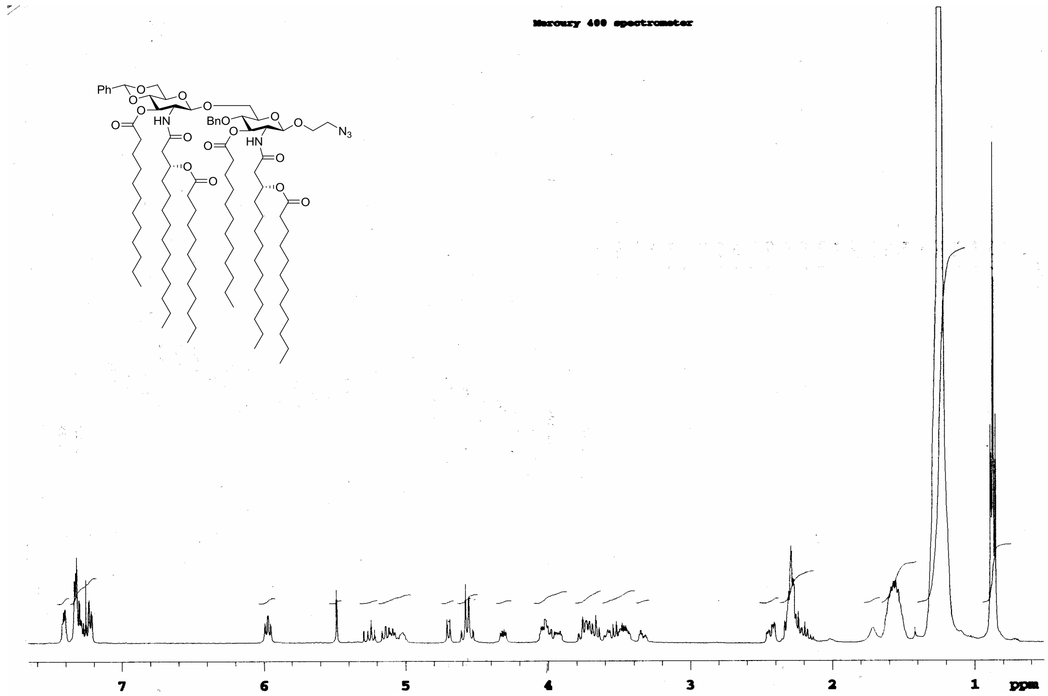
^{1}H NMR spectrum of **16** ($CDCl_3$, 400 MHz) [Ref. 32]



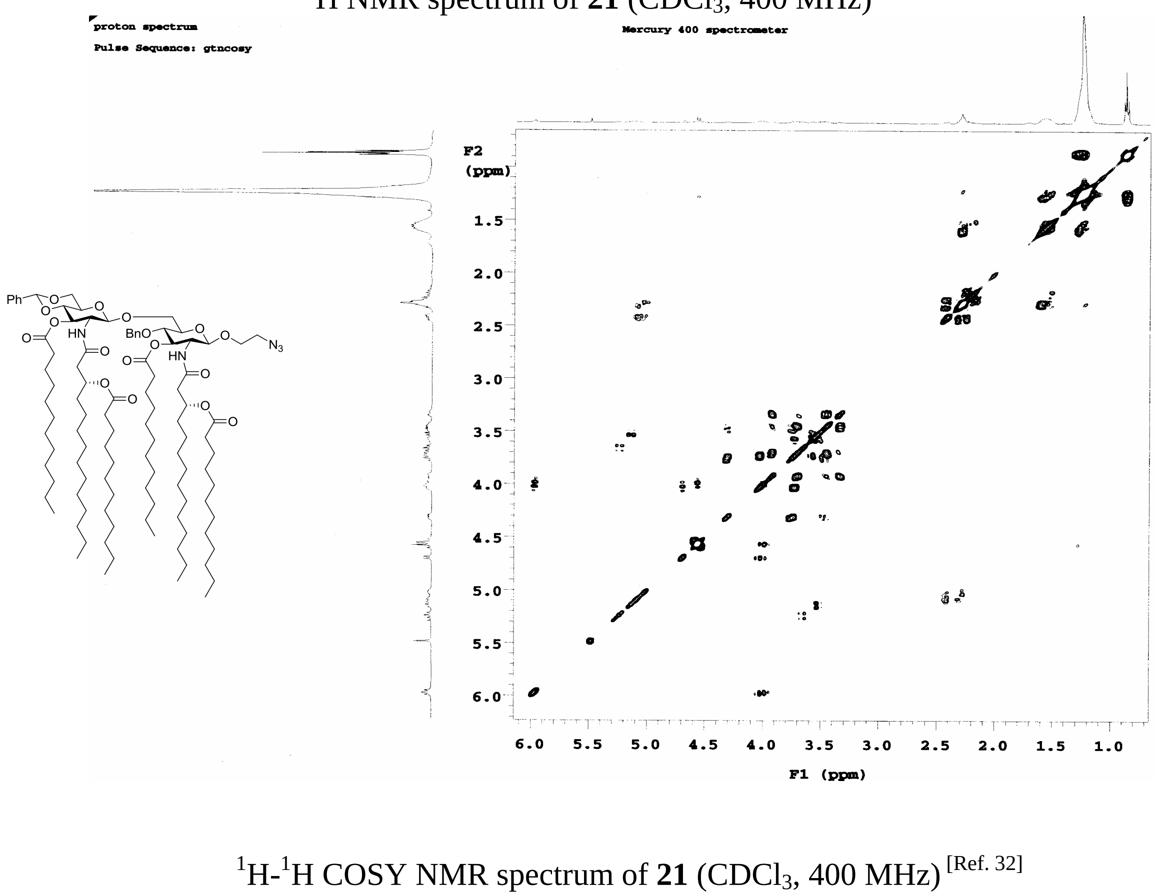
^{1}H-^{1}H COSY NMR spectrum of **16** ($CDCl_3$, 400 MHz) [Ref. 32]



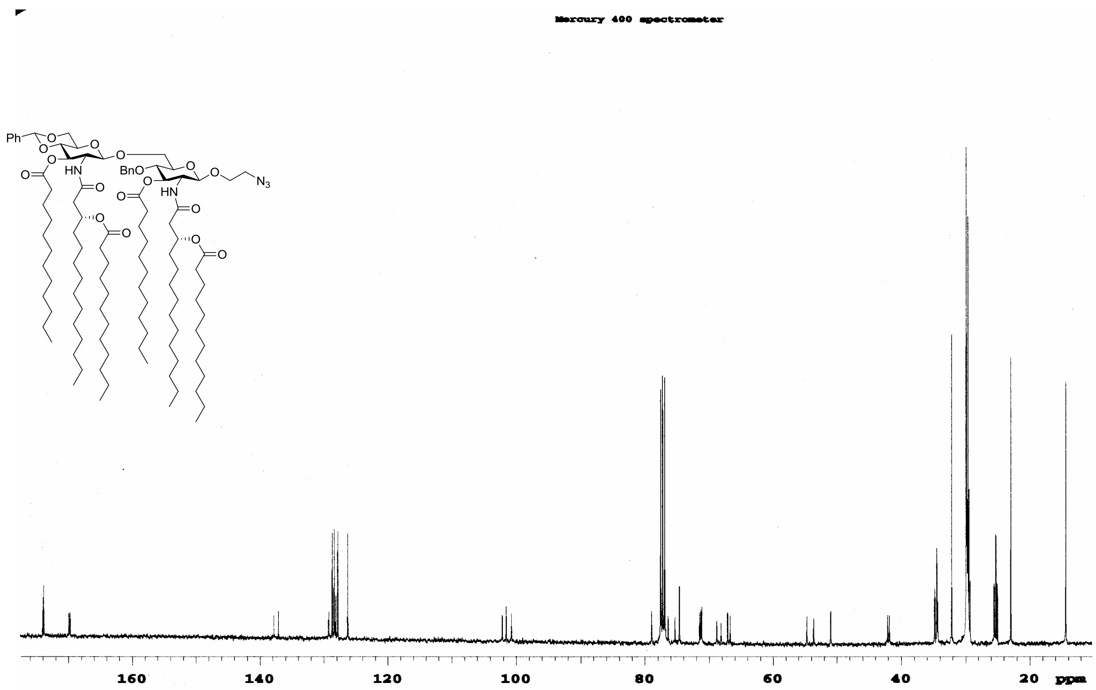
^{13}C NMR spectrum of **16** ($CDCl_3$, 100 MHz) [Ref. 32]



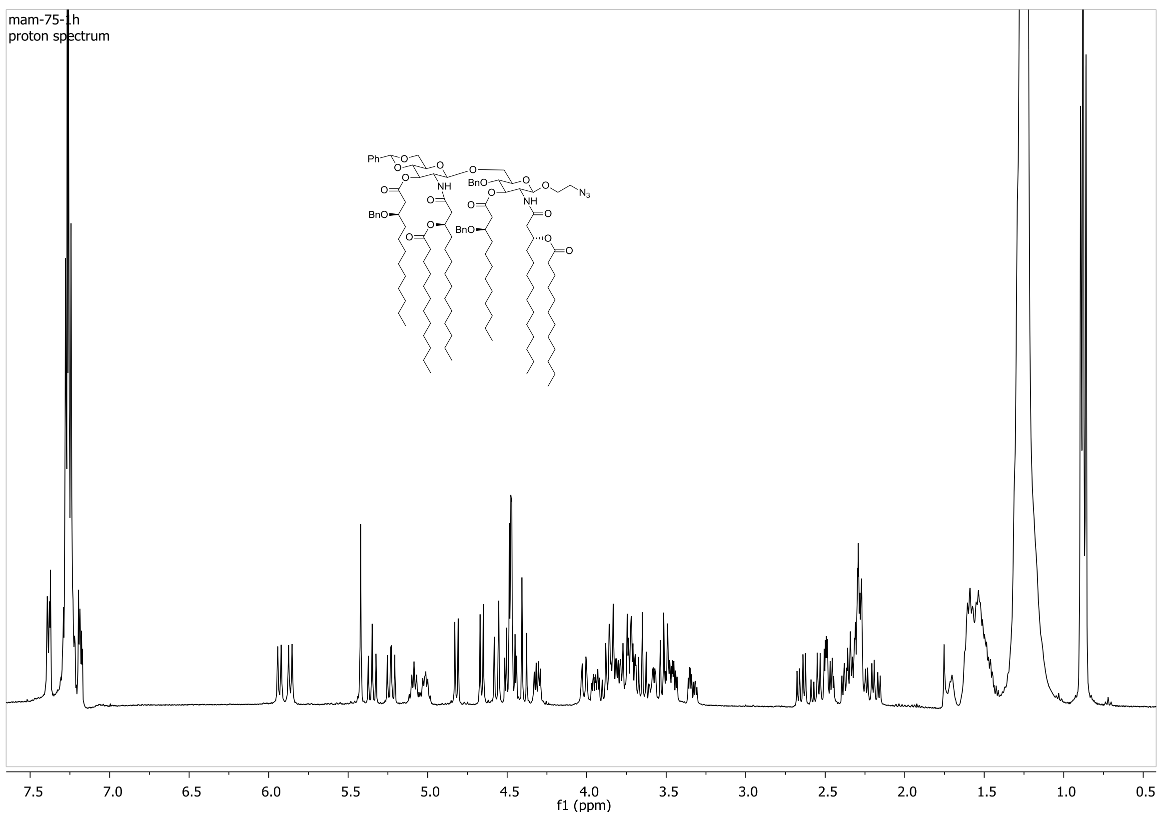
^{1}H NMR spectrum of **21** ($CDCl_3$, 400 MHz) [Ref. 32]



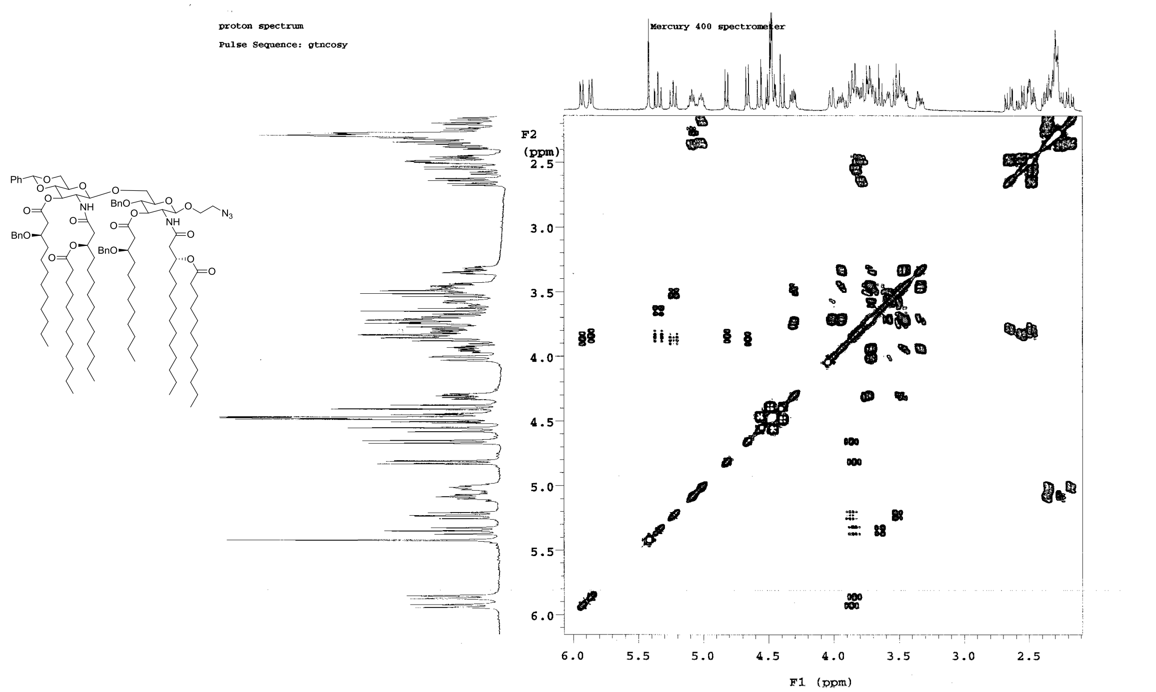
^{1}H-^{1}H COSY NMR spectrum of **21** ($CDCl_3$, 400 MHz) [Ref. 32]



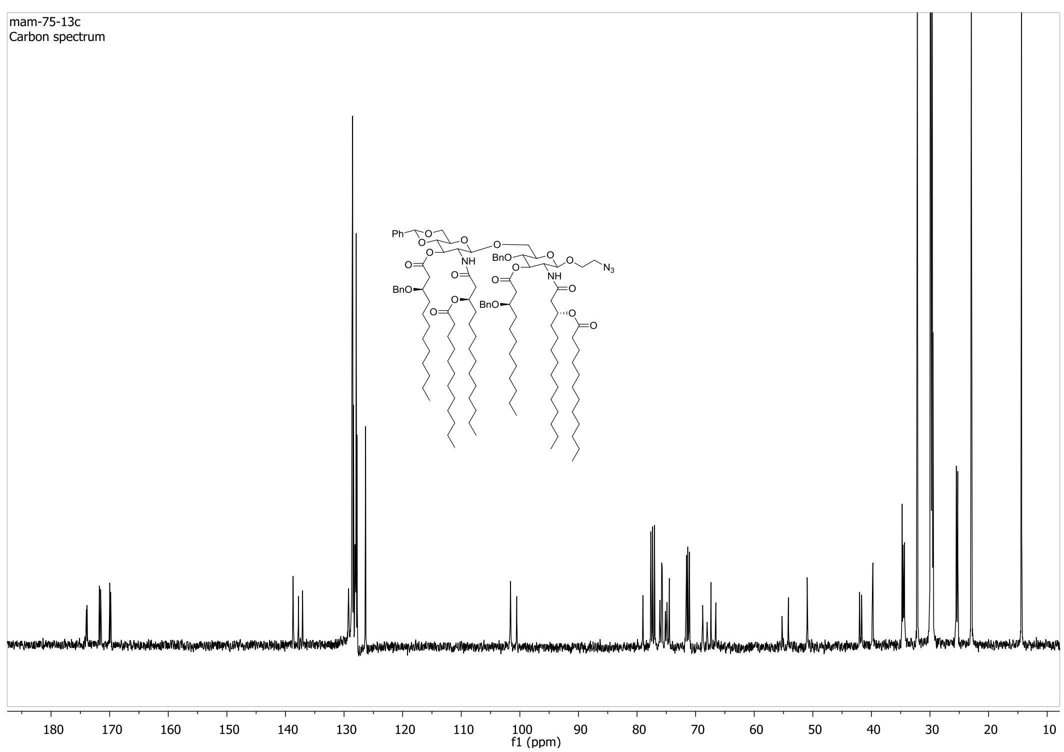
^{13}C NMR spectrum of **21** ($CDCl_3$, 100 MHz) [Ref. 32]



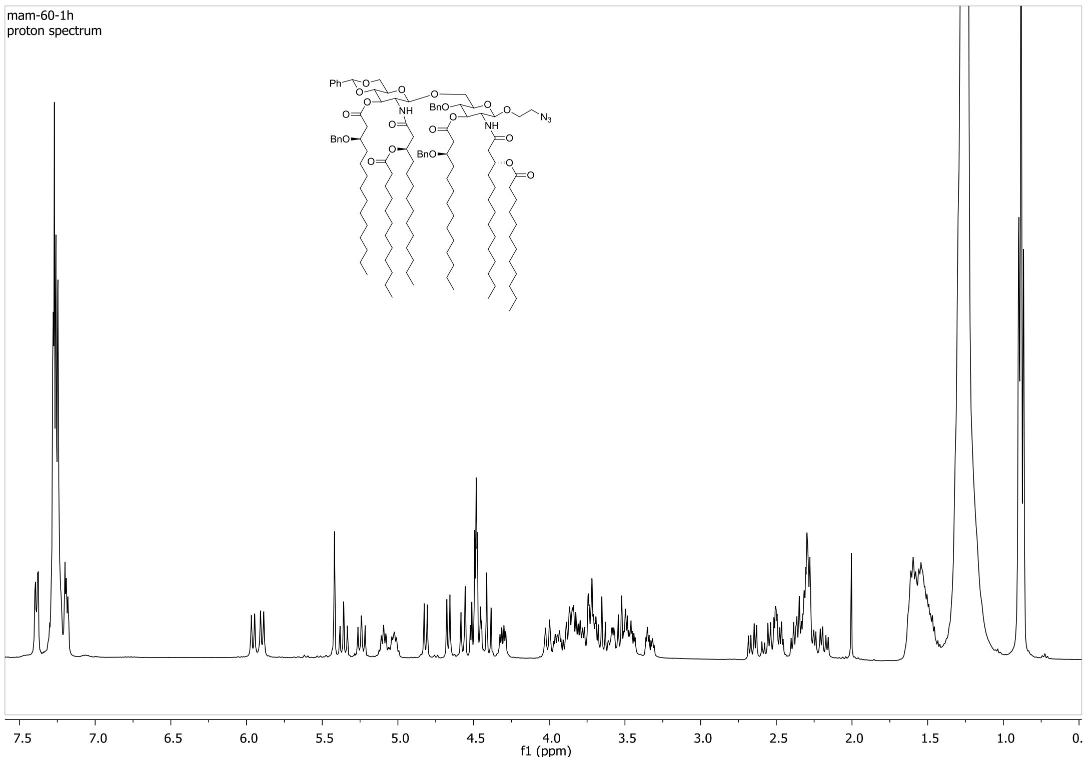
^{1}H NMR spectrum of **22** ($CDCl_3$, 400 MHz)



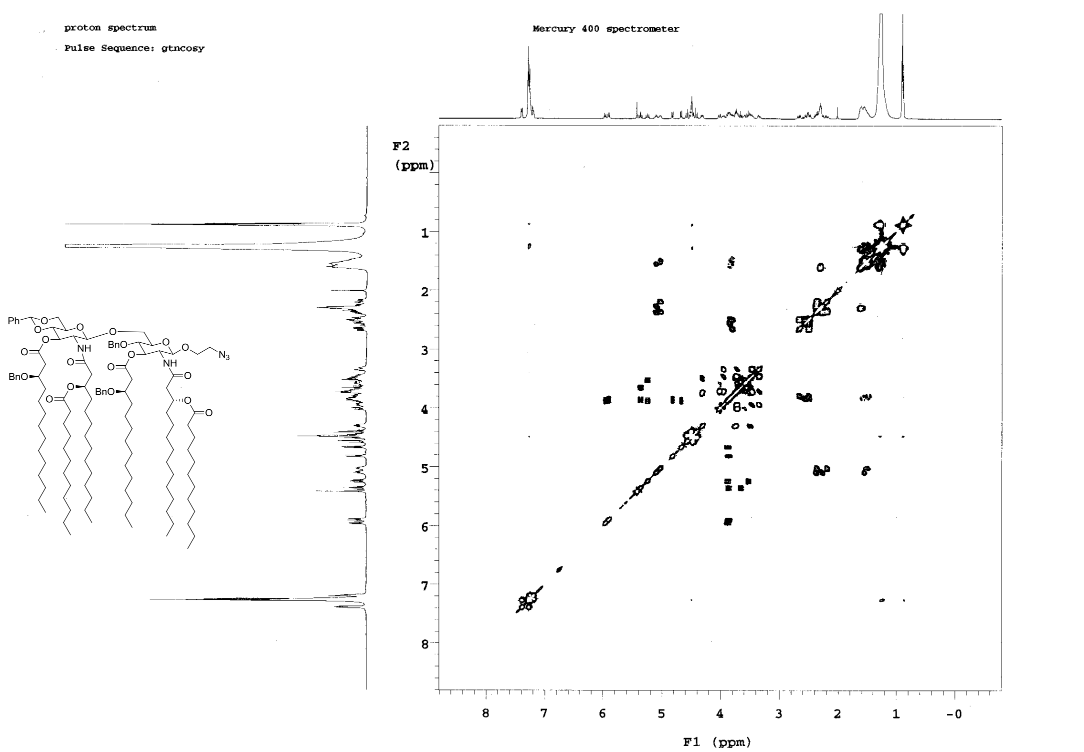
^{1}H-^{1}H COSY NMR spectrum of **22** ($CDCl_3$, 400 MHz)



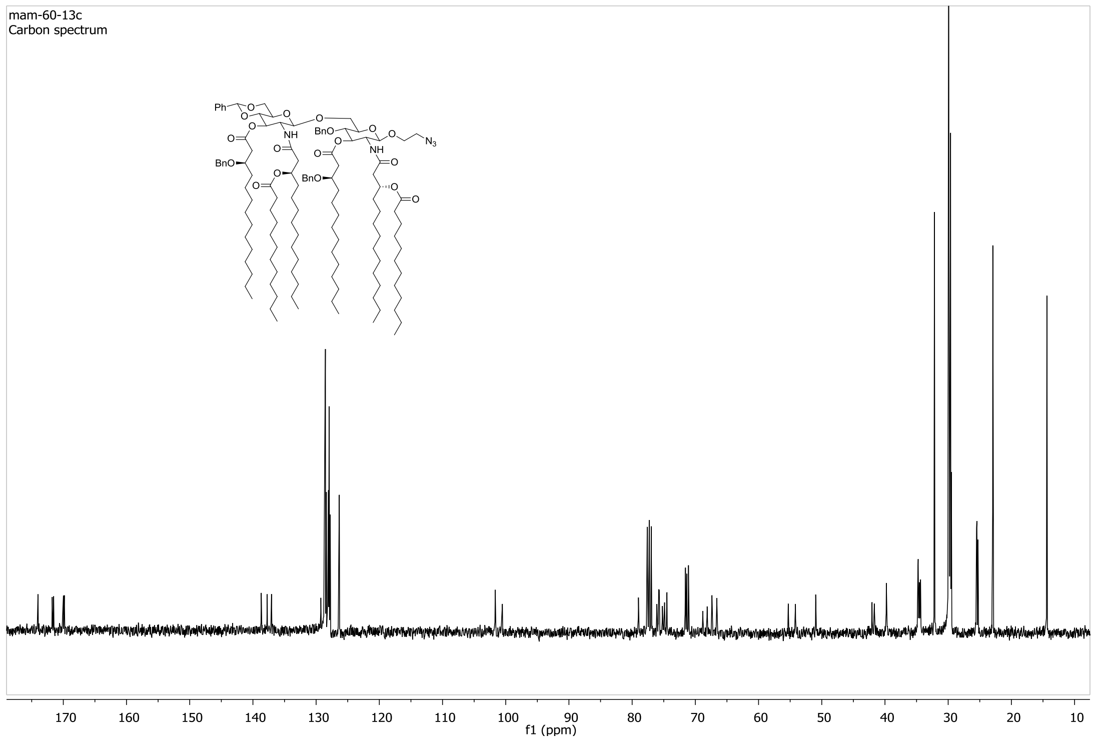
^{13}C NMR spectrum of **22** ($CDCl_3$, 100 MHz)



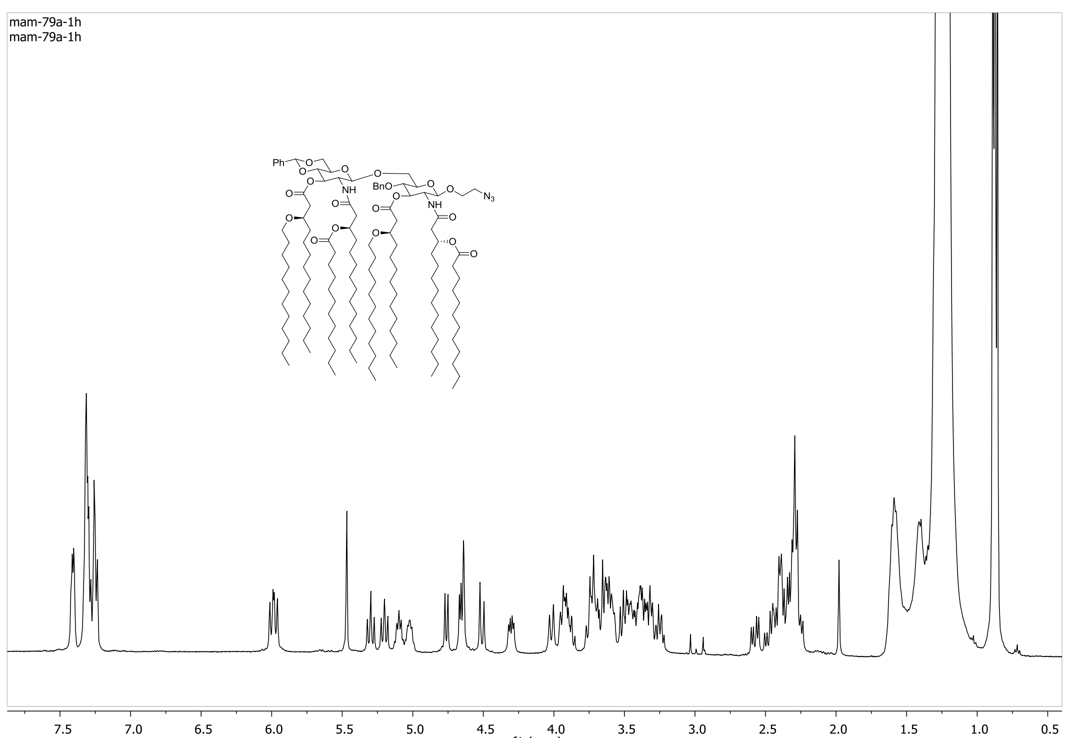
^{1}H NMR spectrum of **23** ($CDCl_3$, 400 MHz)



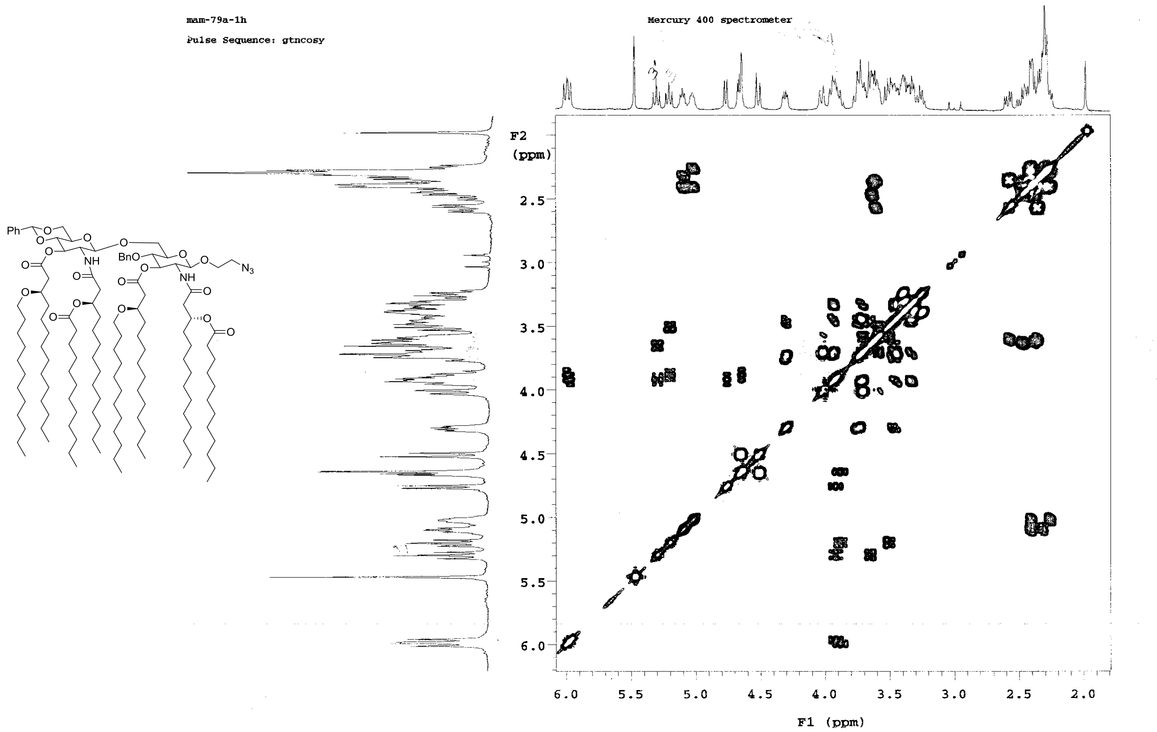
^{1}H-^{1}H COSY NMR spectrum of **23** ($CDCl_3$, 400 MHz)



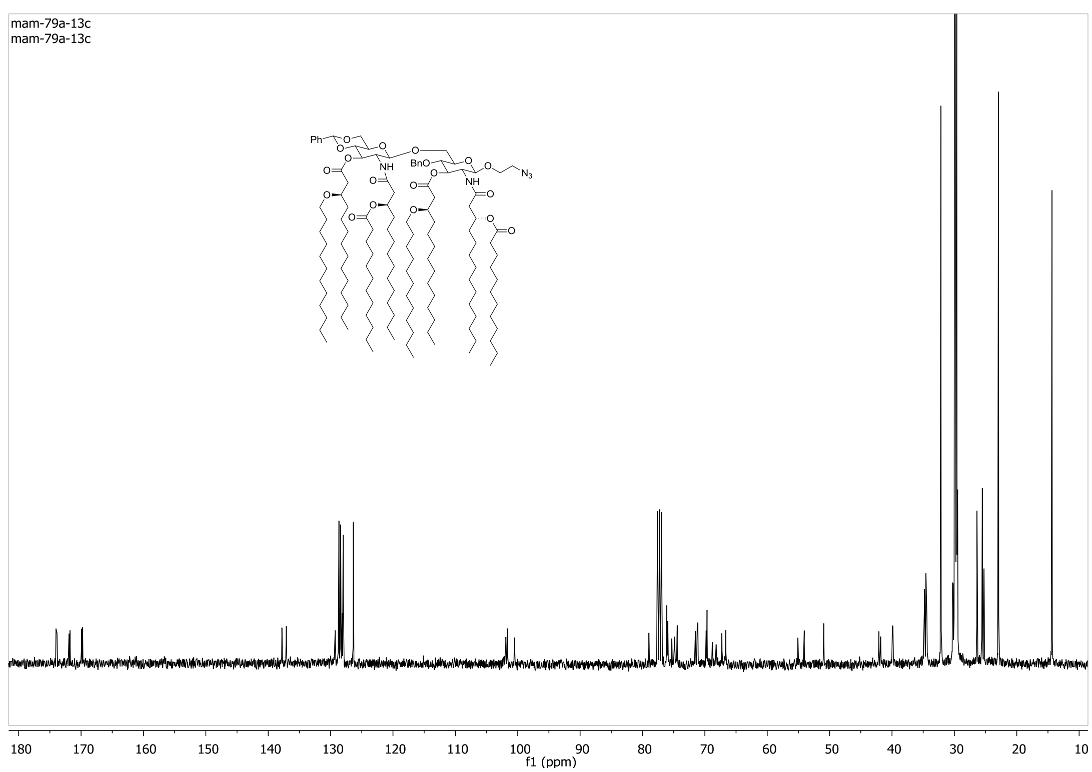
^{13}C NMR spectrum of **23** ($CDCl_3$, 100 MHz)



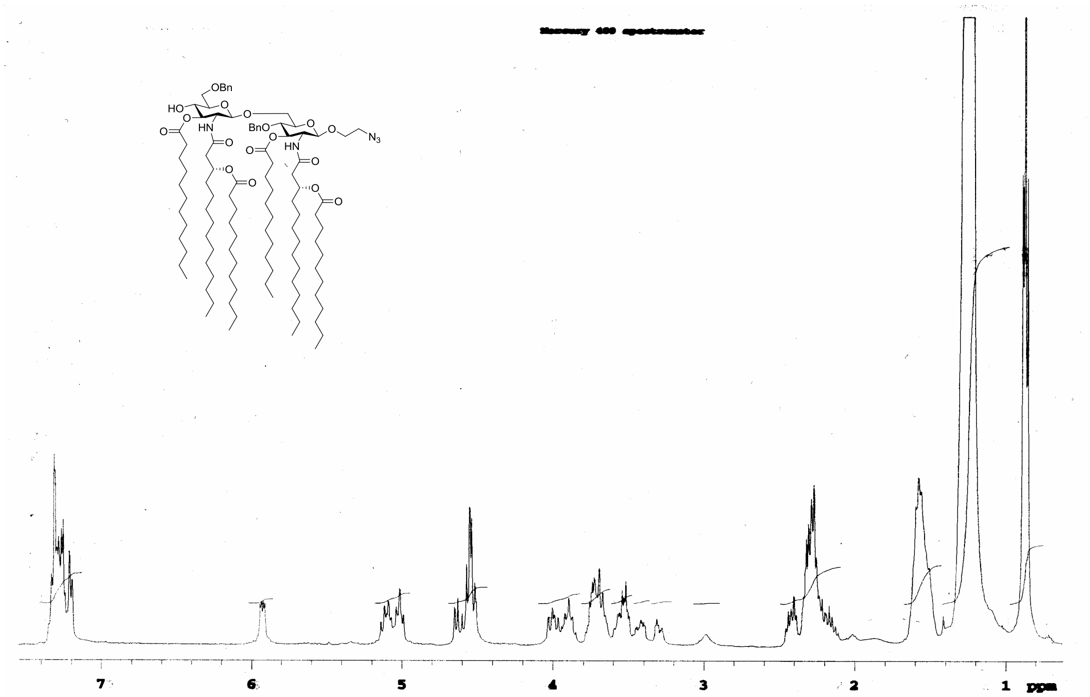
^{1}H NMR spectrum of **24** ($CDCl_3$, 400 MHz)



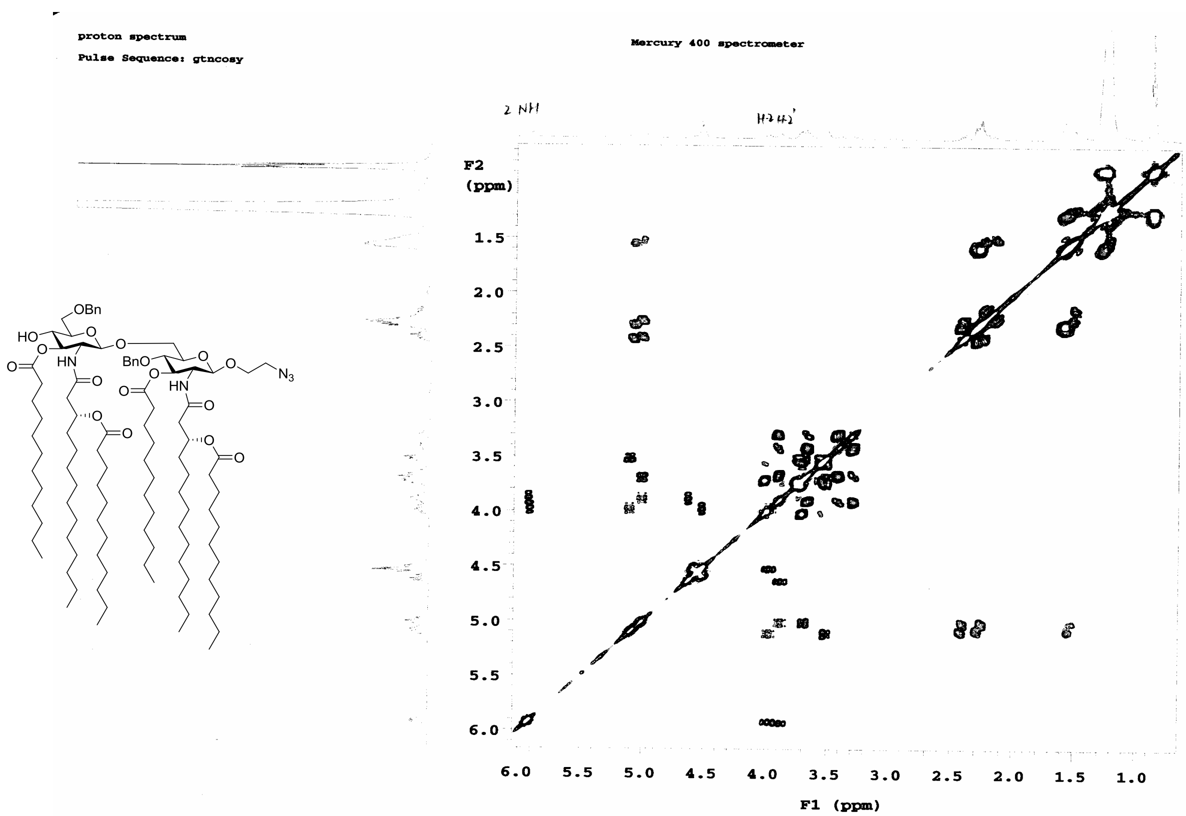
^{1}H-^{1}H COSY NMR spectrum of **24** ($CDCl_3$, 400 MHz)



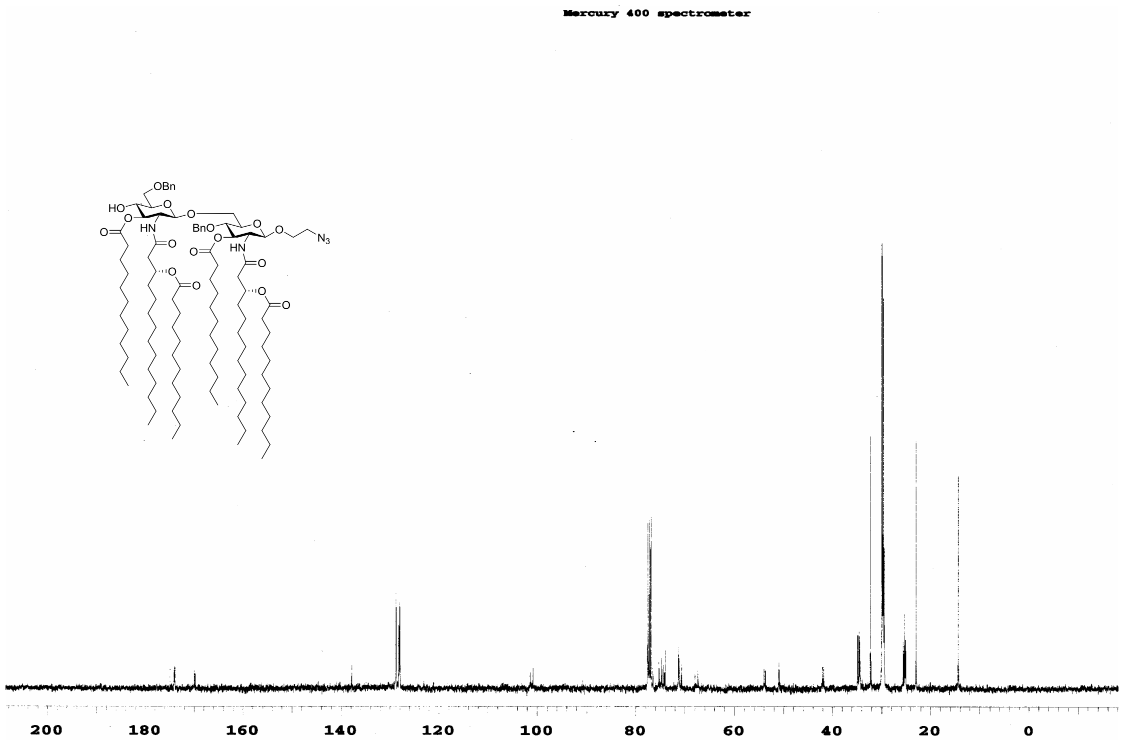
^{13}C NMR spectrum of **24** ($CDCl_3$, 100 MHz)



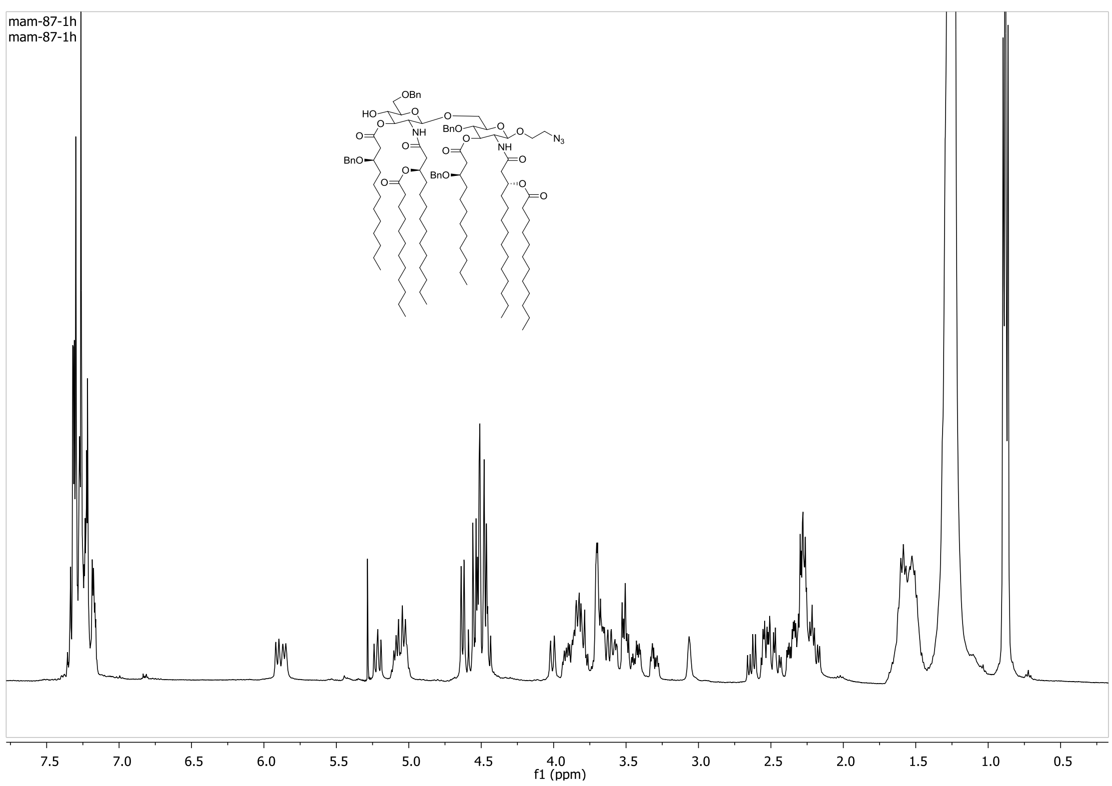
^{1}H NMR spectrum of **25** ($CDCl_3$, 400 MHz) [Ref. 32]



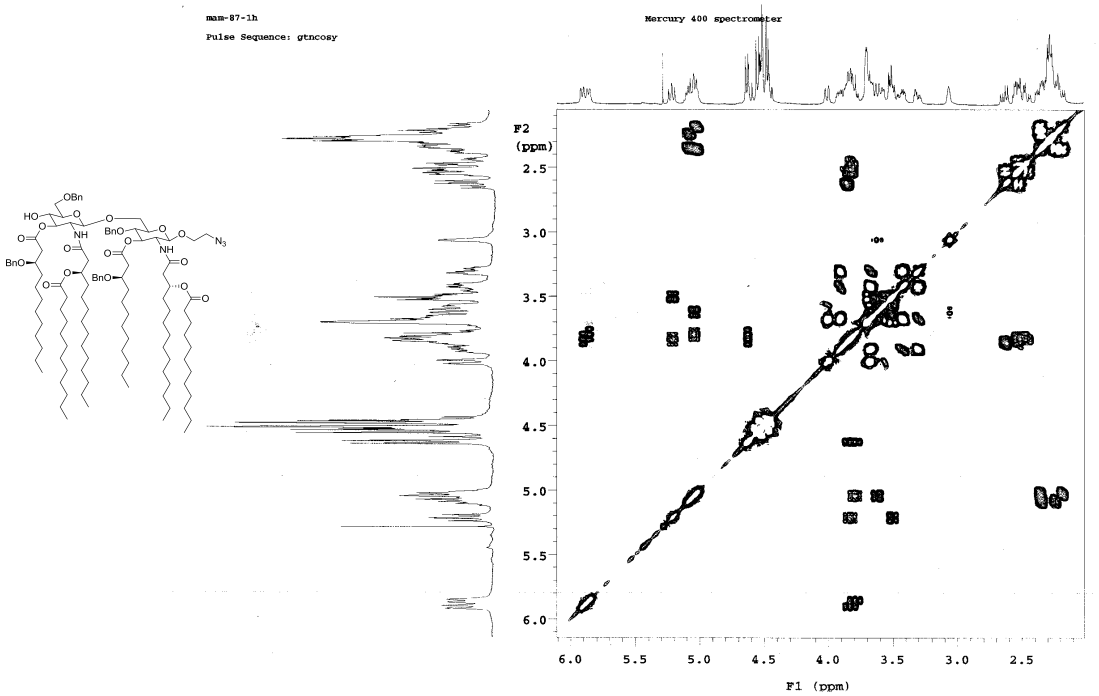
^{1}H-^{1}H COSY NMR spectrum of **25** ($CDCl_3$, 400 MHz) [Ref. 32]



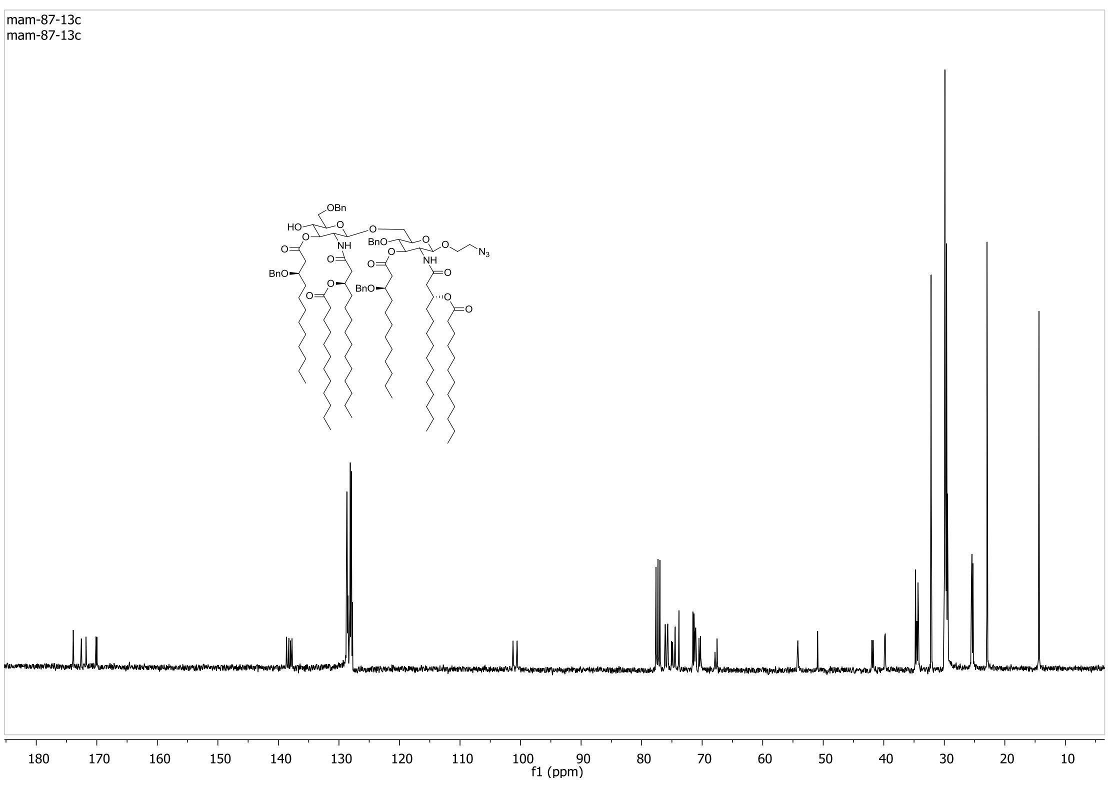
^{13}C NMR spectrum of **25** ($CDCl_3$, 100 MHz) [Ref. 32]



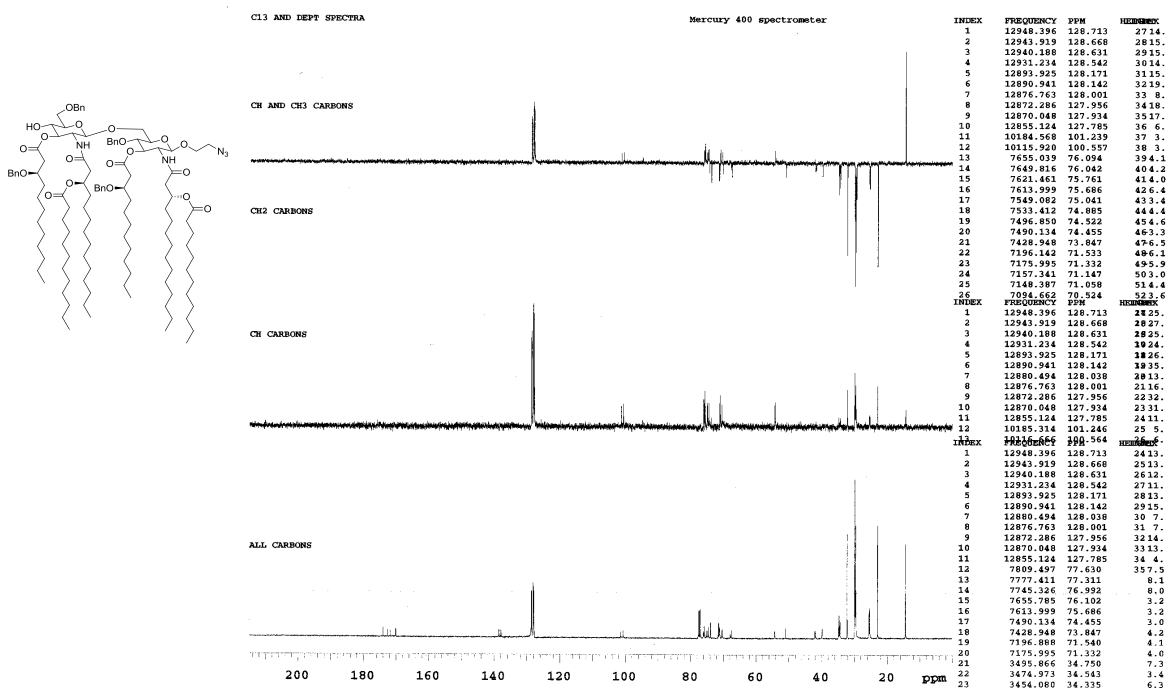
^{1}H NMR spectrum of **26** ($CDCl_3$, 400 MHz)



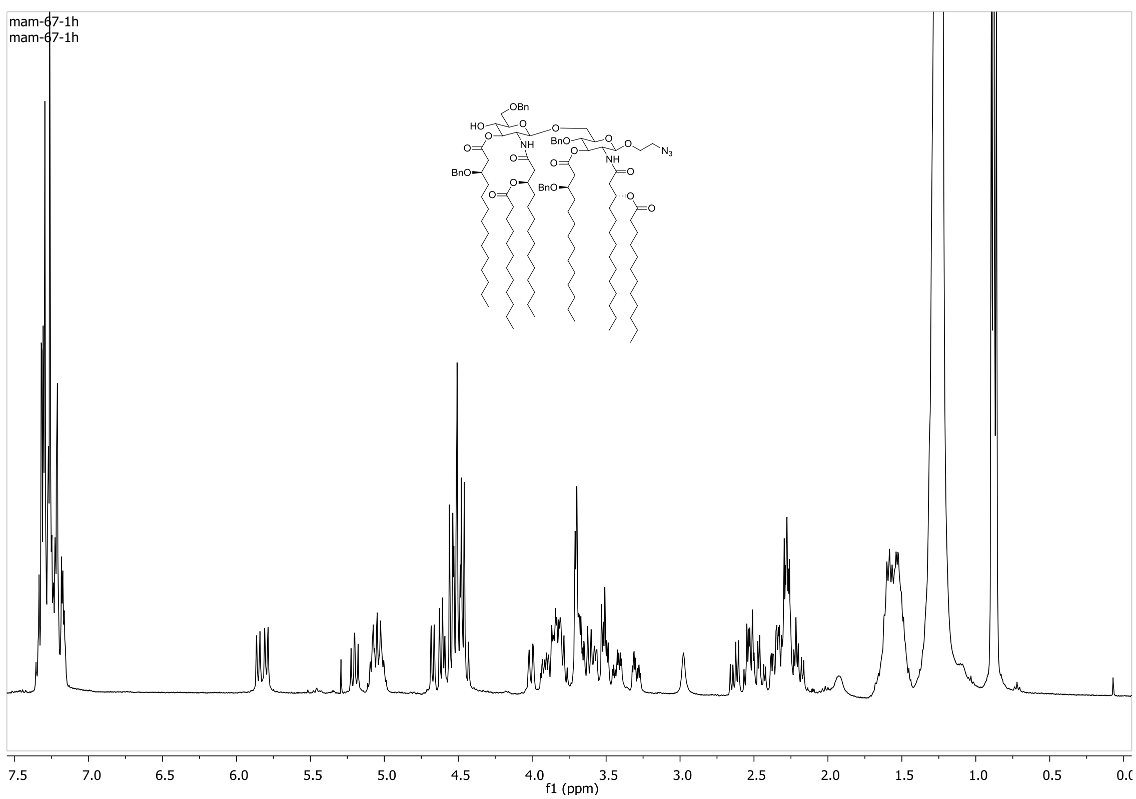
^{1}H-^{1}H COSY NMR spectrum of **26** ($CDCl_3$, 400 MHz)



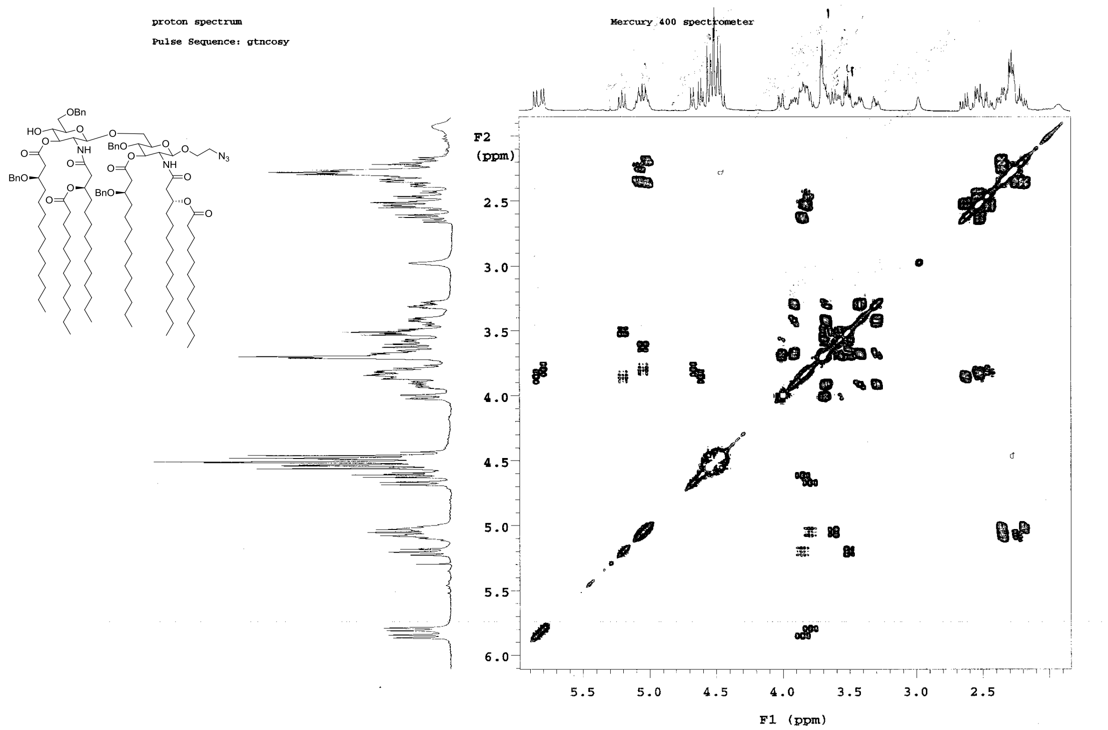
^{13}C NMR spectrum of **26** ($CDCl_3$, 100 MHz)



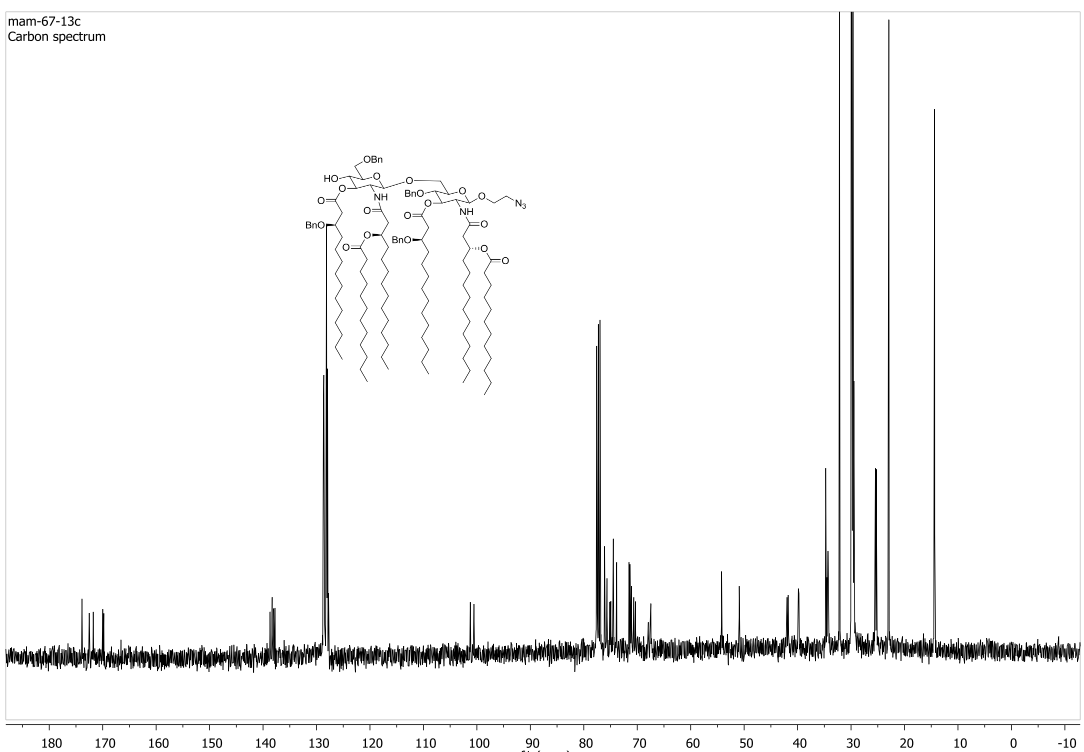
^{13}C DEPT NMR spectrum of **26** ($CDCl_3$, 100 MHz)



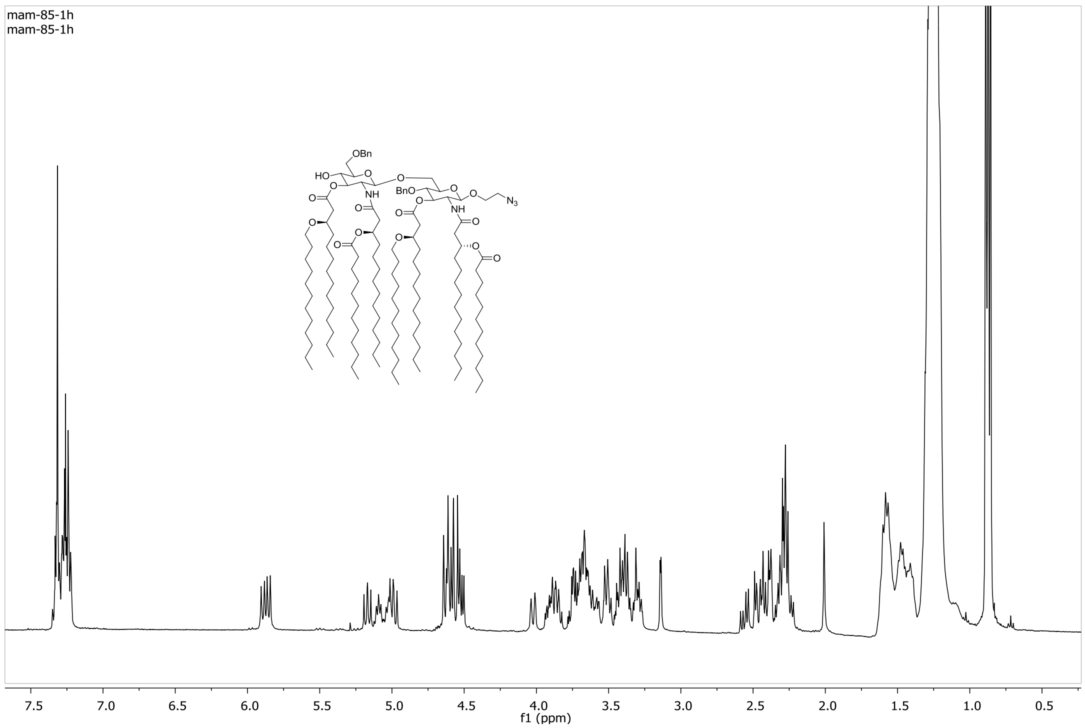
^{1}H NMR spectrum of **27** ($CDCl_3$, 400 MHz)



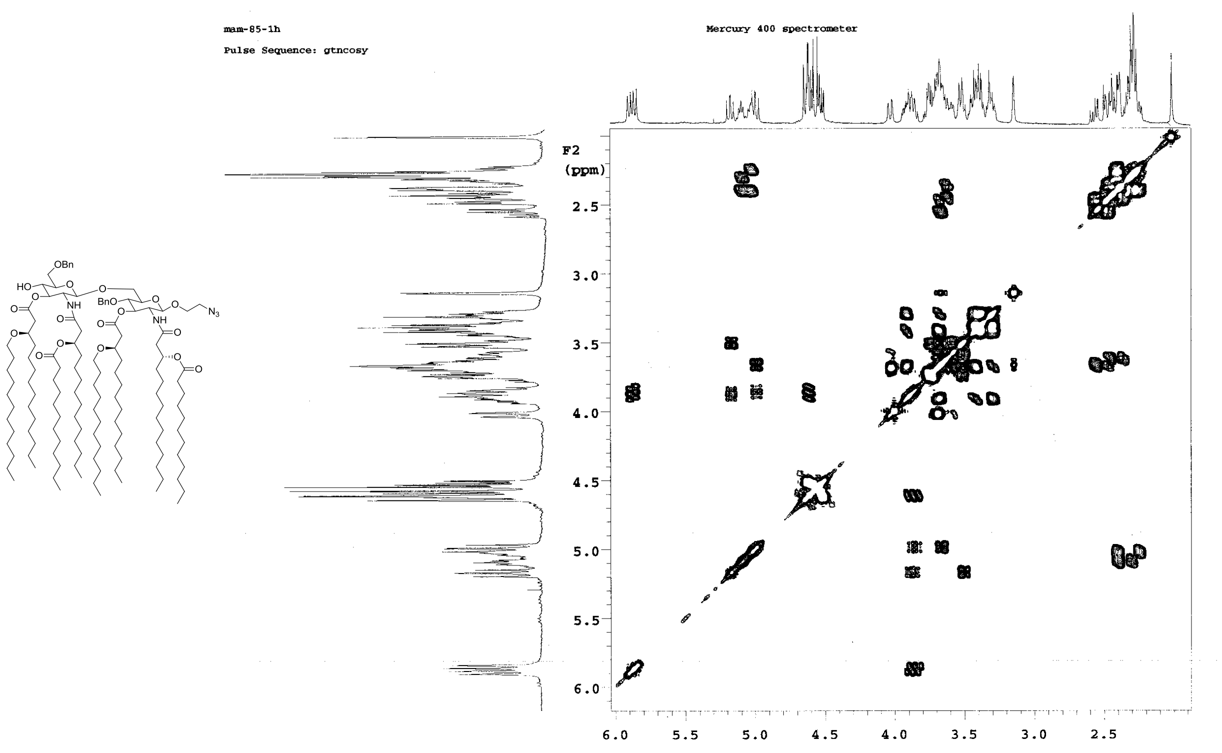
^{1}H-^{1}H COSY NMR spectrum of **27** ($CDCl_3$, 400 MHz)



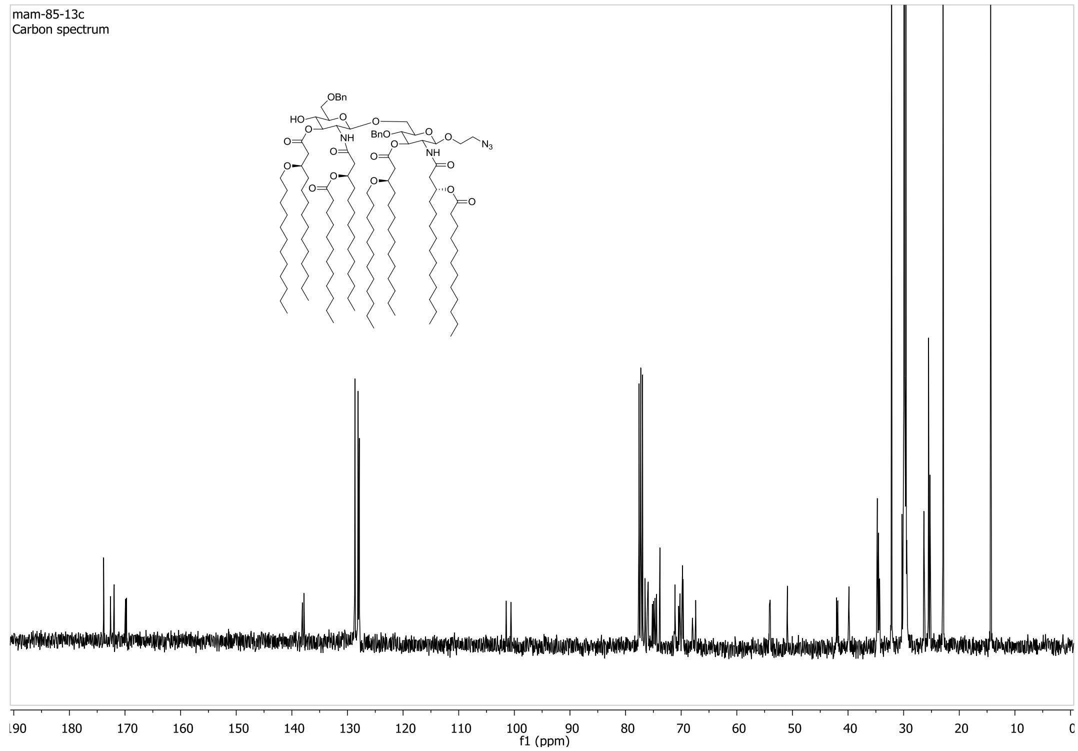
^{13}C NMR spectrum of **27** ($CDCl_3$, 100 MHz)



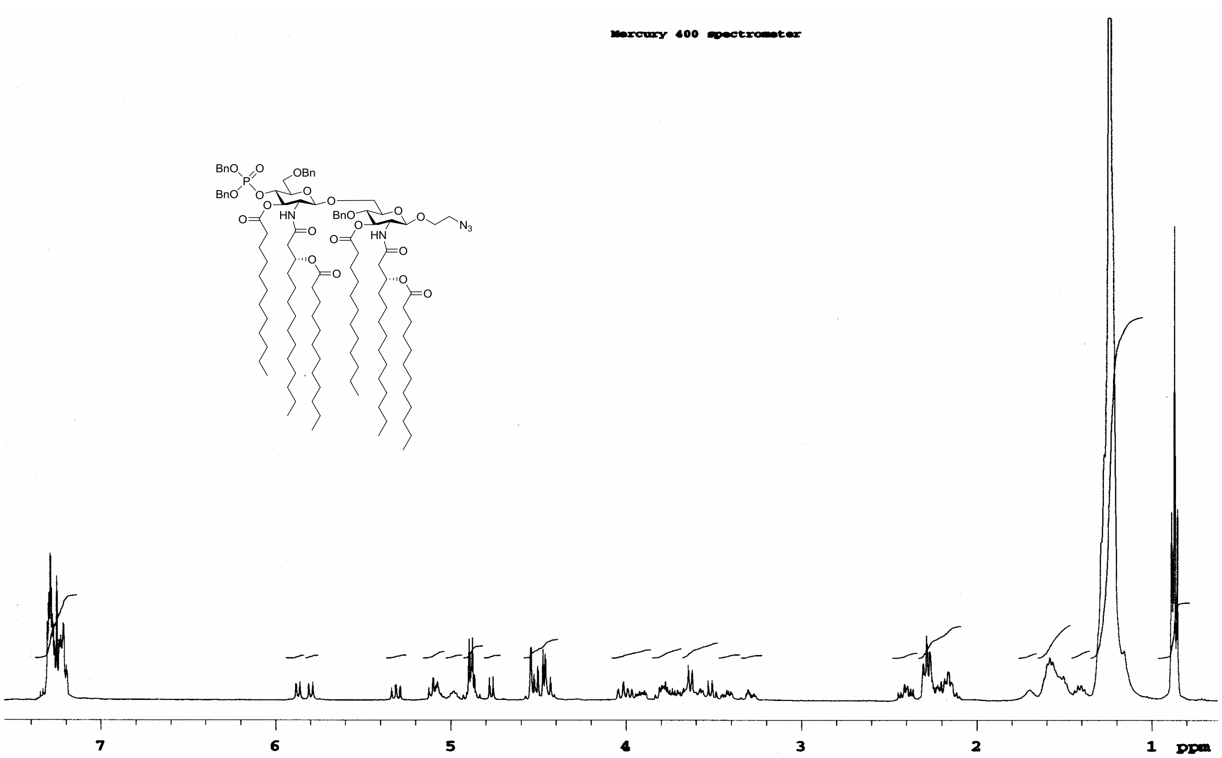
^{1}H NMR spectrum of **28** ($CDCl_3$, 400 MHz)



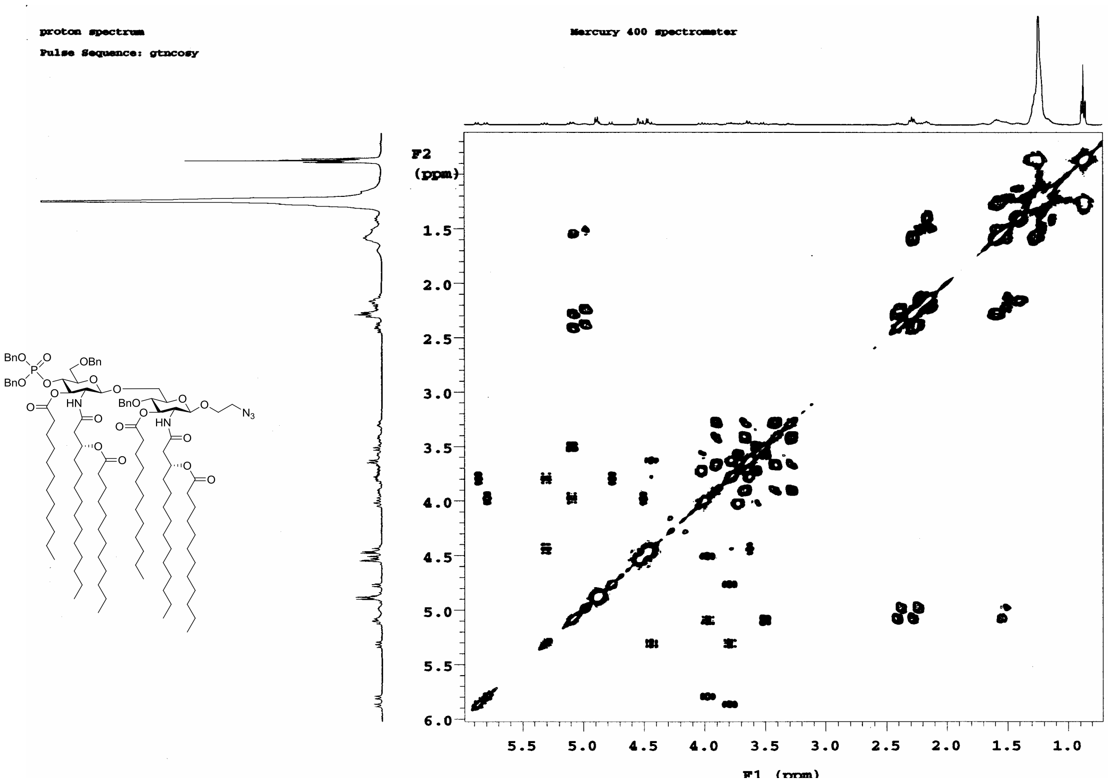
^{1}H-^{1}H COSY NMR spectrum of **28** ($CDCl_3$, 400 MHz)



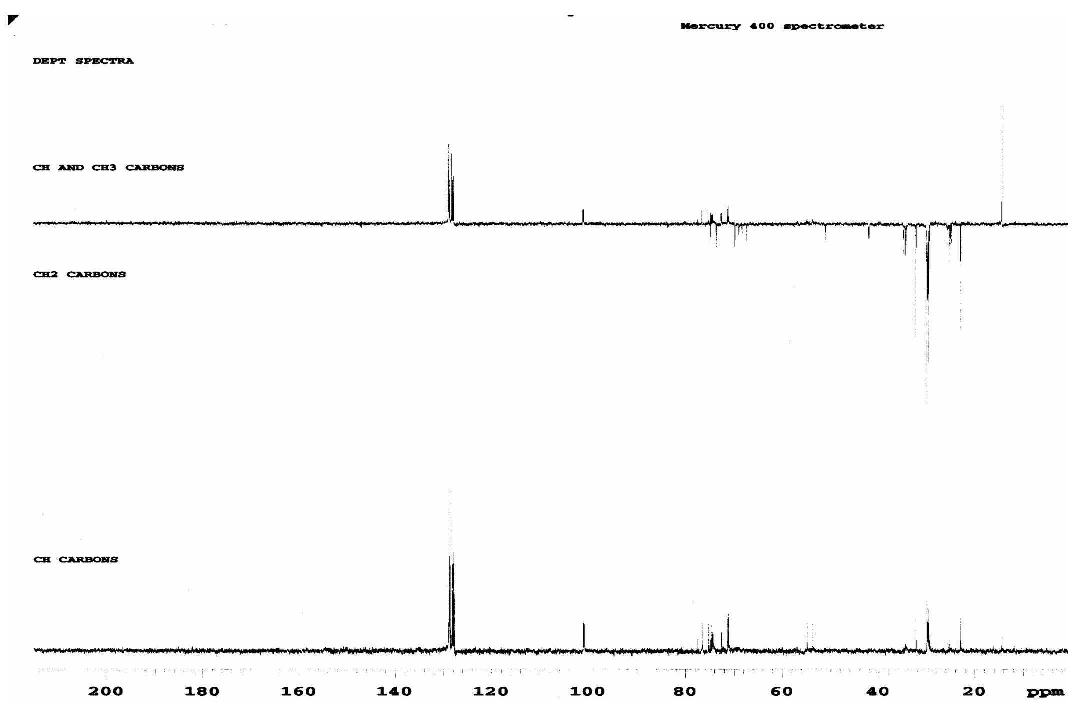
^{13}C NMR spectrum of **28** ($CDCl_3$, 100 MHz)



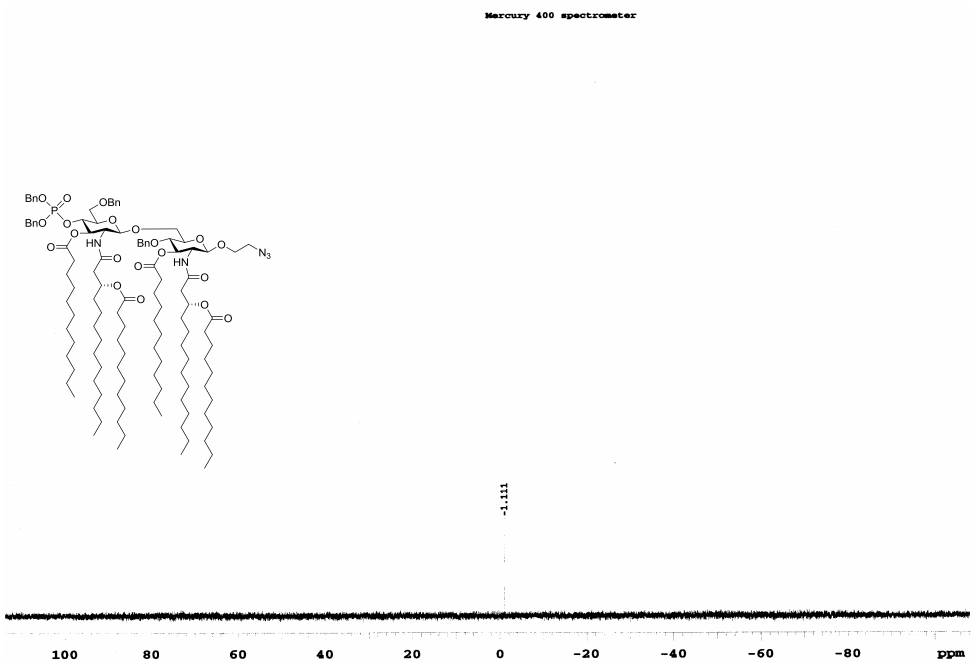
^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz) [Ref. 32]



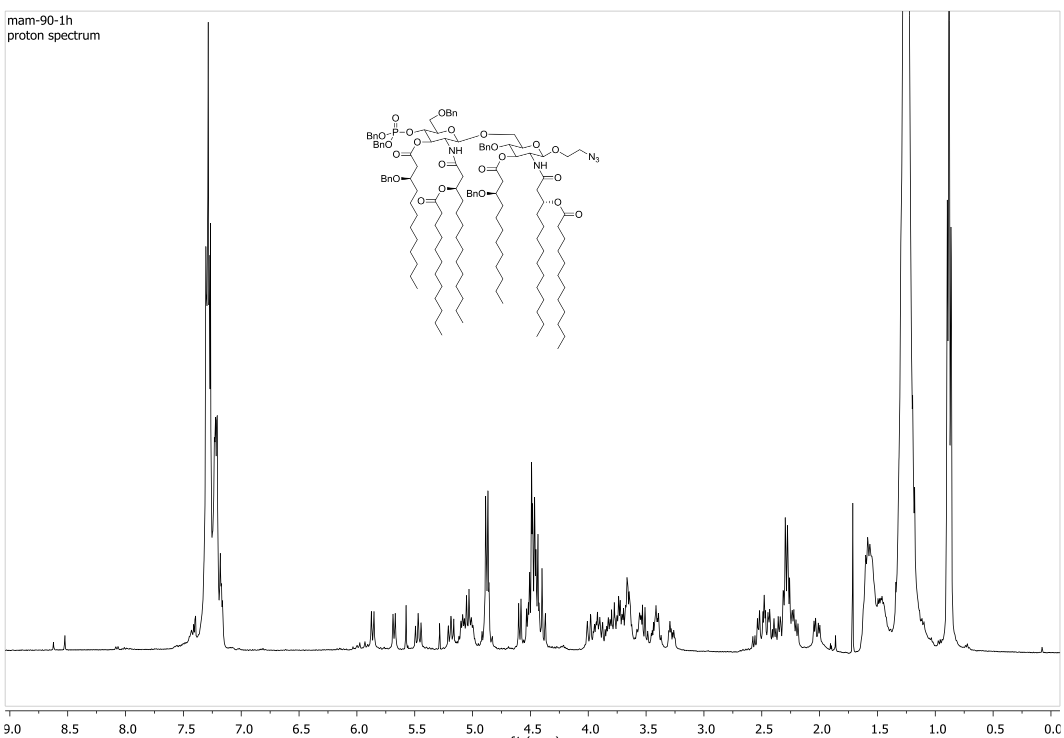
^{1}H-^{1}H COSY NMR spectrum of **7** ($CDCl_3$, 400 MHz) [Ref. 32]



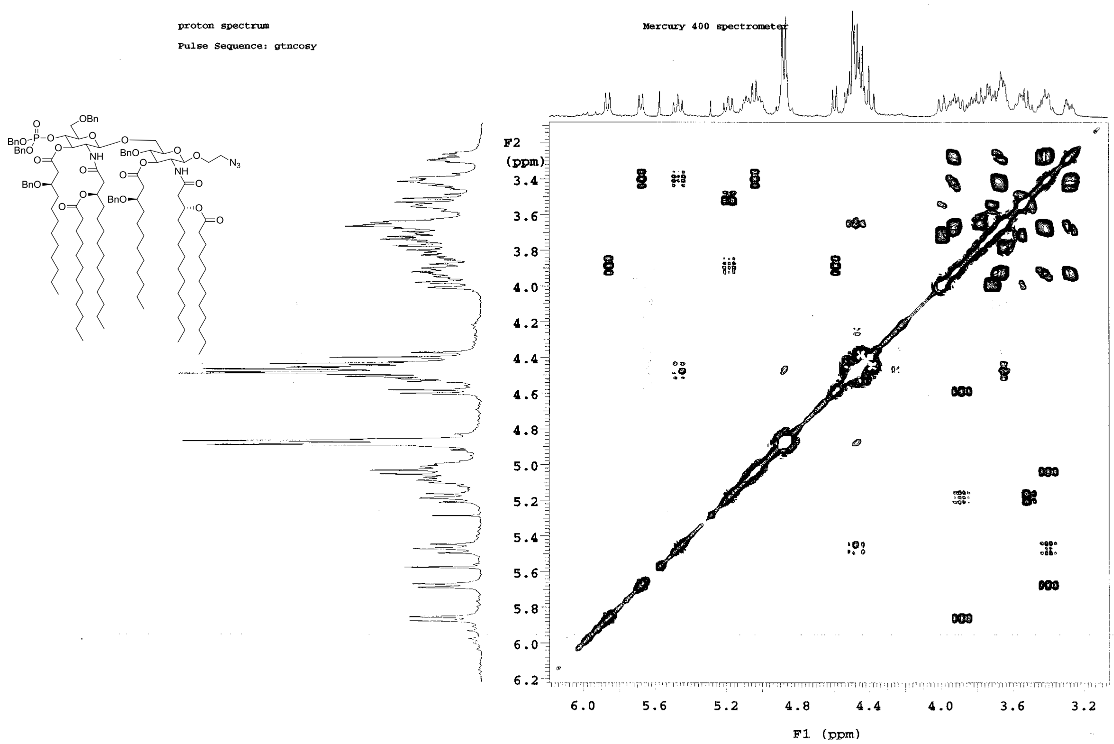
^{13}C NMR (including DEPT-135) spectrum of **7** ($CDCl_3$, 100 MHz) [Ref. 32]



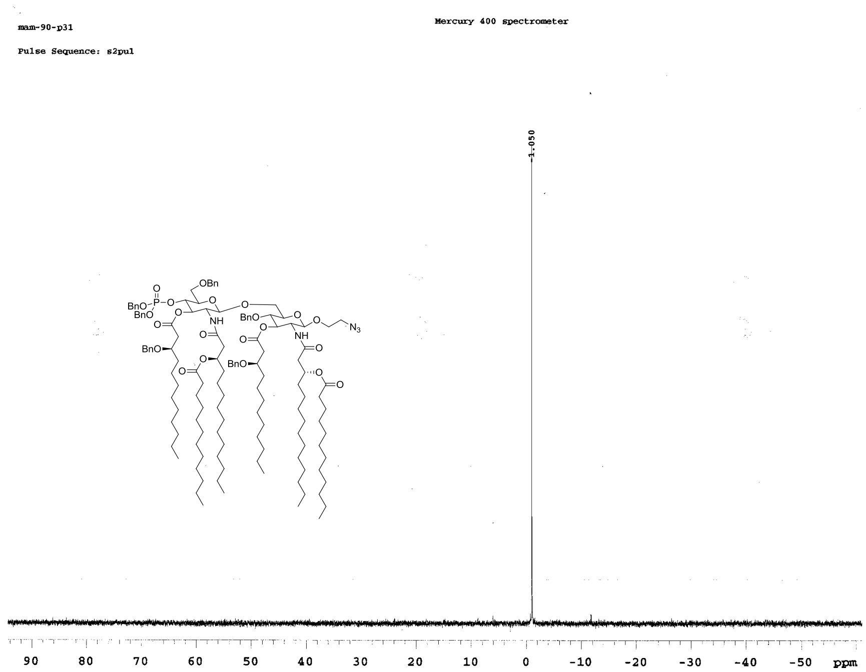
^{31}P NMR spectrum of **7** ($CDCl_3$, 161 MHz) [Ref. 32]



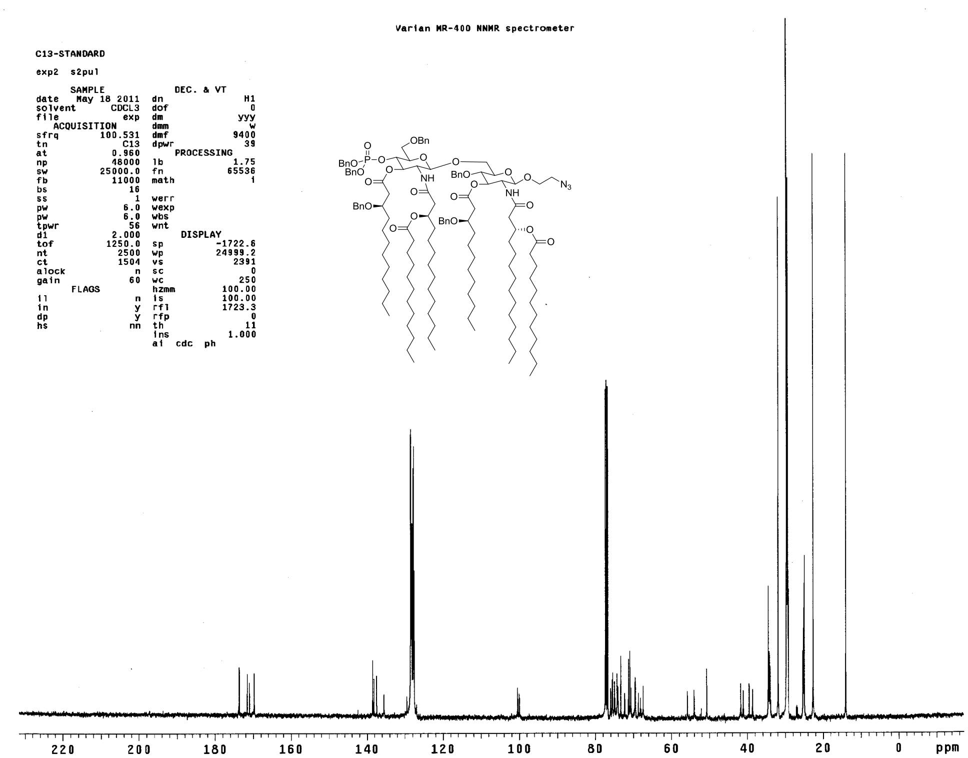
^{1}H NMR spectrum of **8** ($CDCl_3$, 400 MHz)



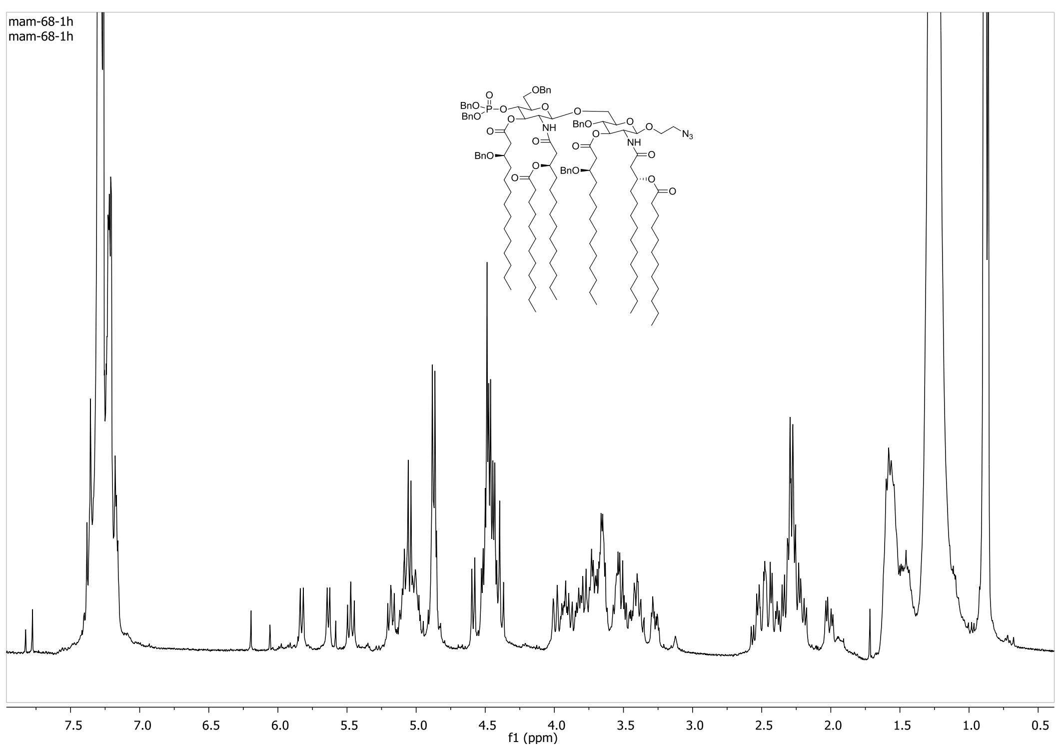
^{1}H-^{1}H COSY NMR spectrum of **8** ($CDCl_3$, 400 MHz)



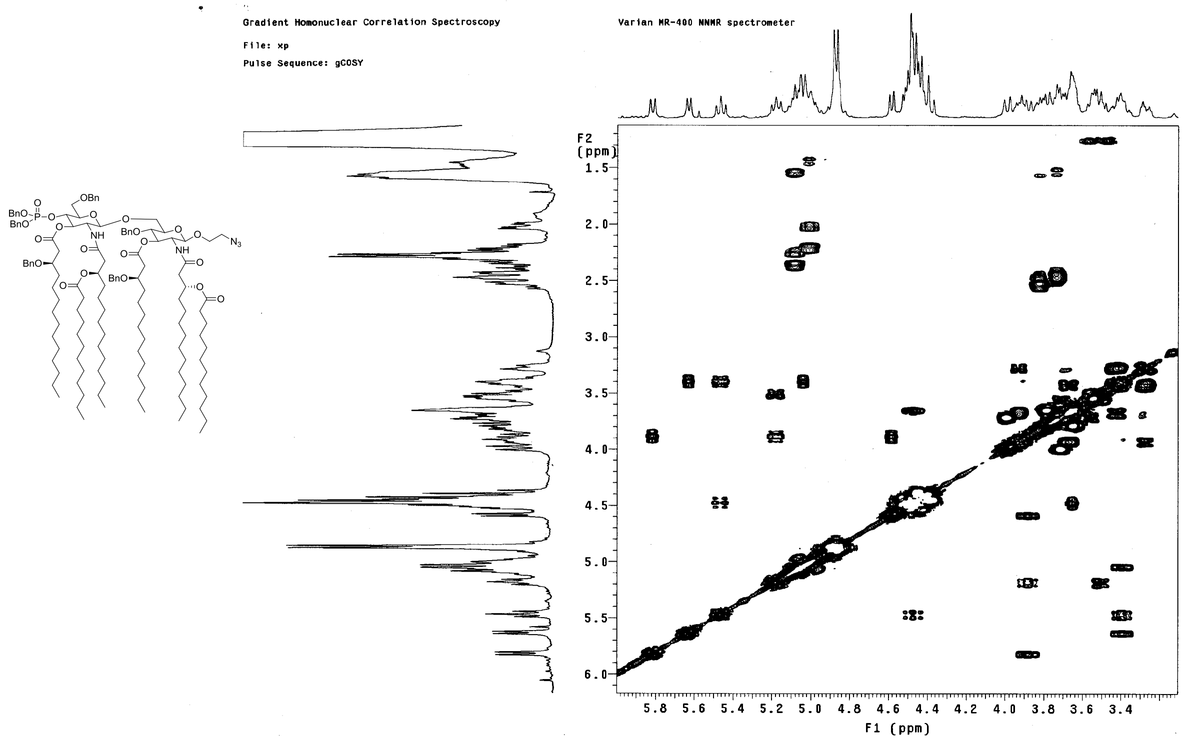
^{31}P NMR spectrum of **8** ($CDCl_3$, 161 MHz)



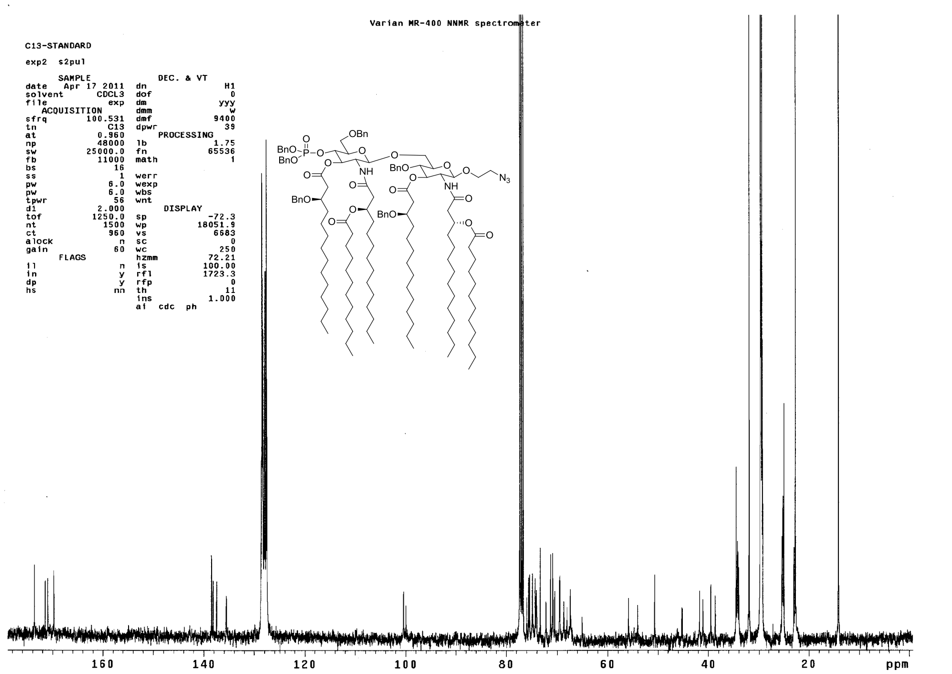
^{13}C NMR spectrum of **8** ($CDCl_3$, 100 MHz)



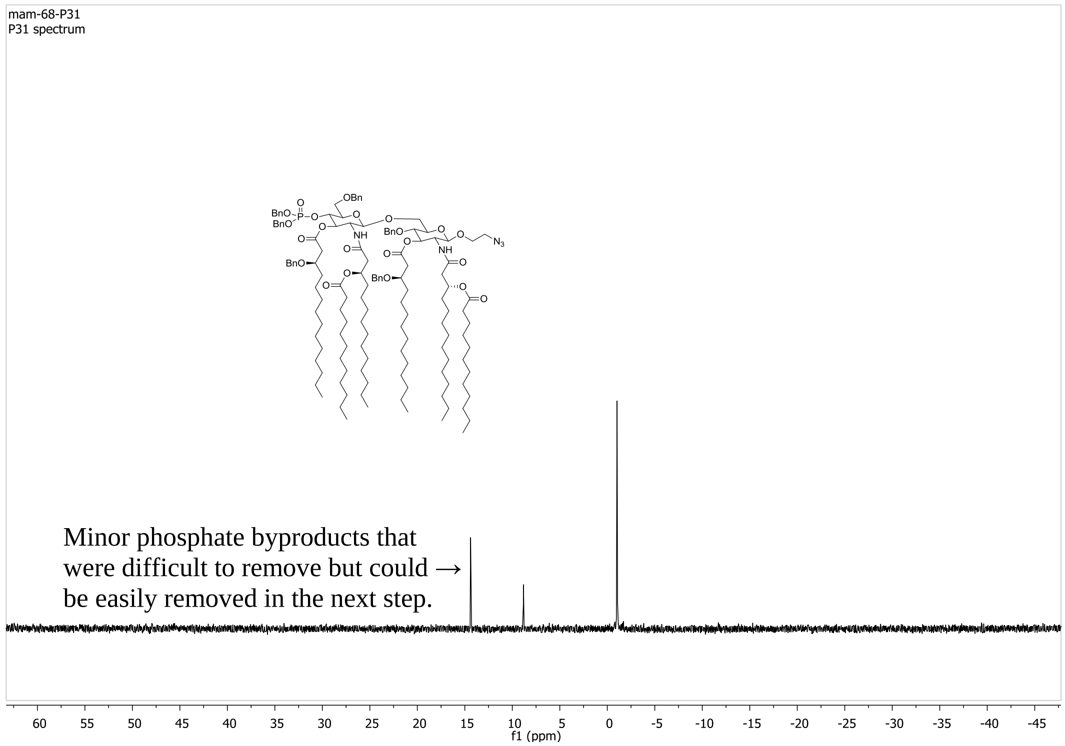
^{1}H NMR spectrum of **9** ($CDCl_3$, 400 MHz)



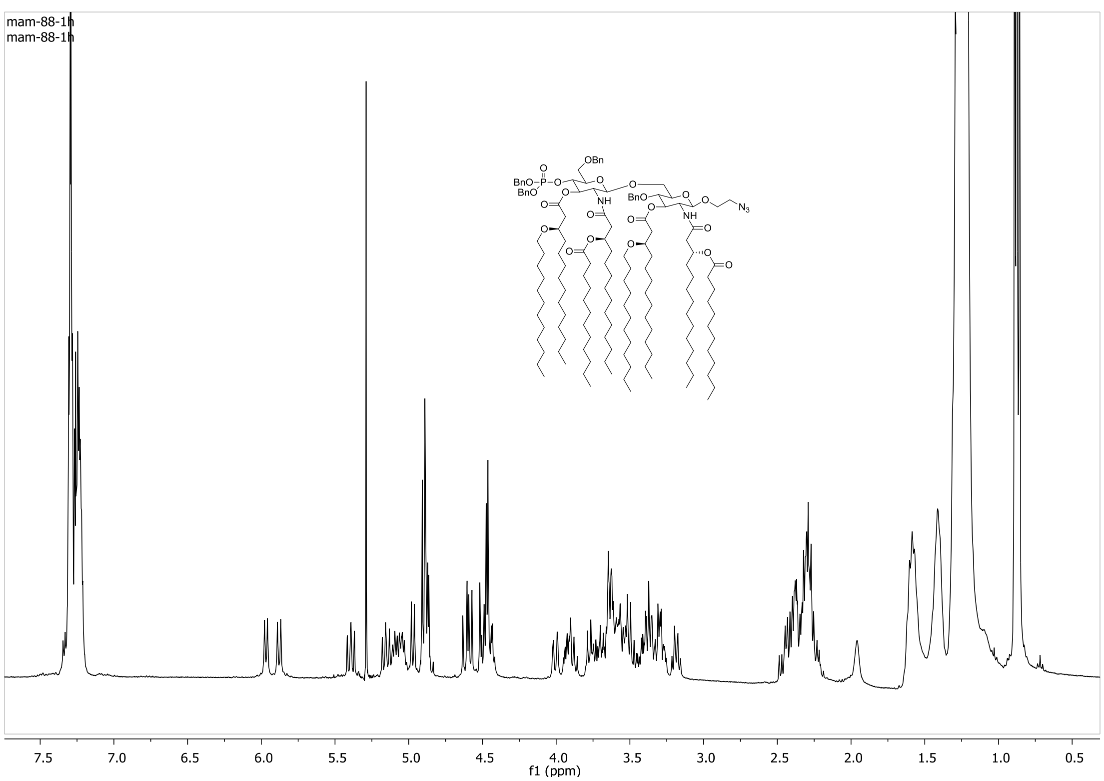
^{1}H-^{1}H COSY NMR spectrum of **9** ($CDCl_3$, 400 MHz)



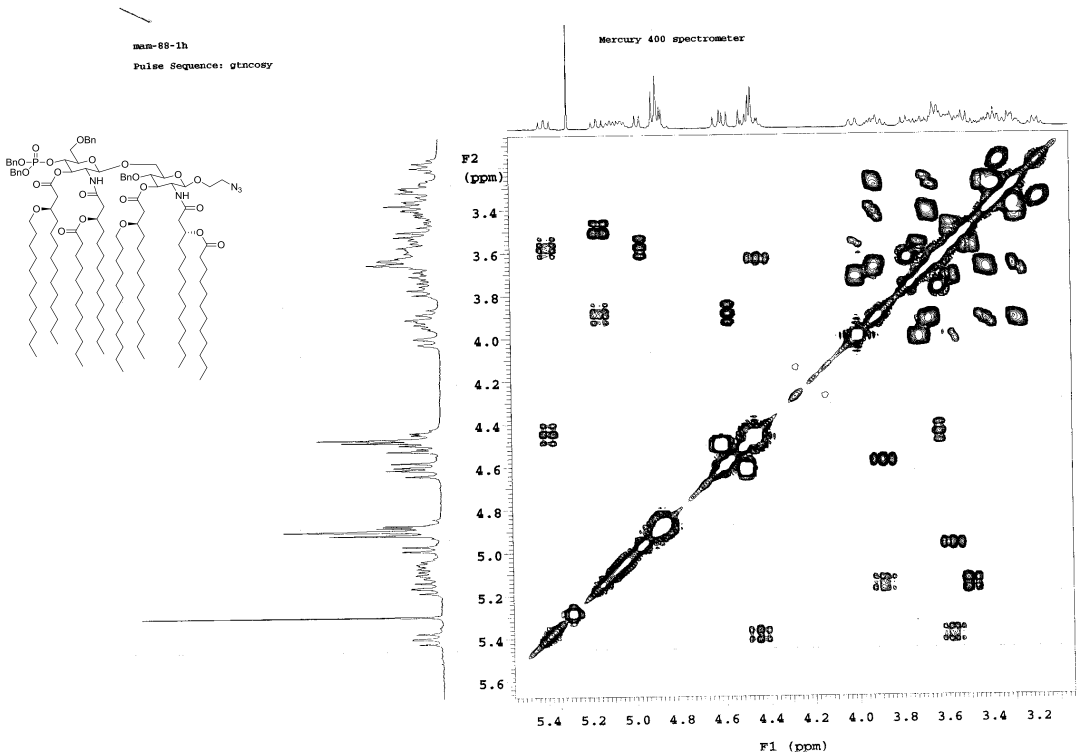
^{13}C NMR spectrum of **9** ($CDCl_3$, 100 MHz)



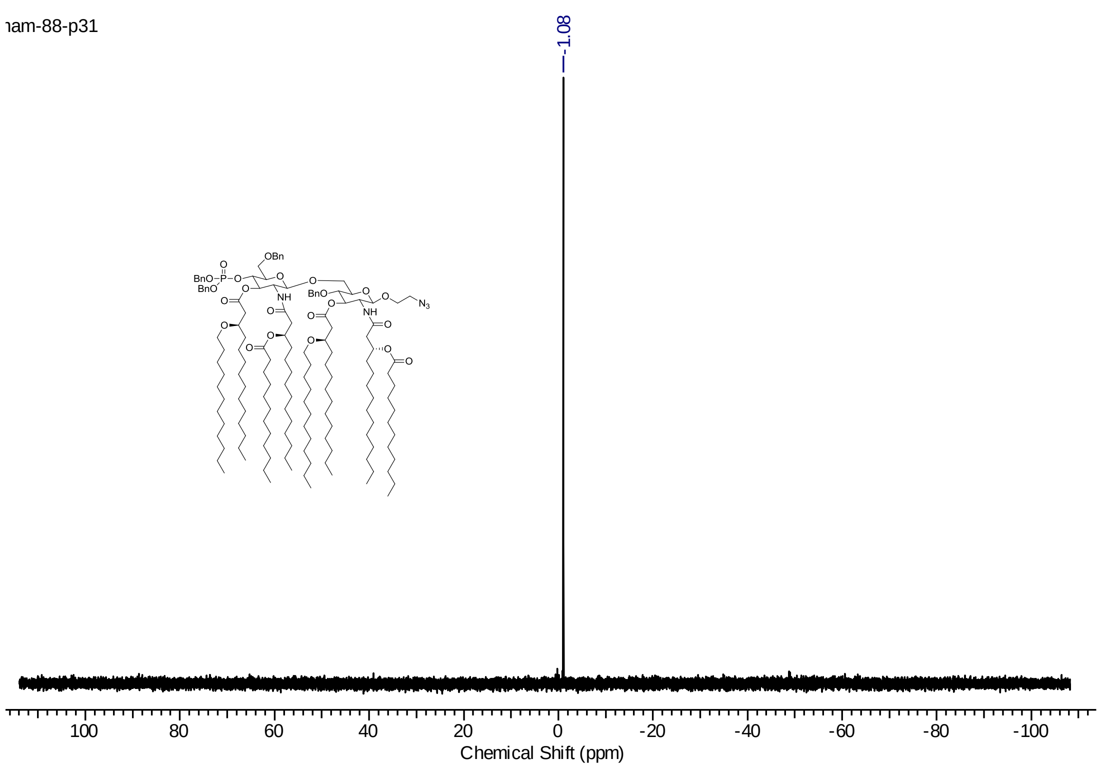
^{31}P NMR spectrum of **9** ($CDCl_3$, 161 MHz)



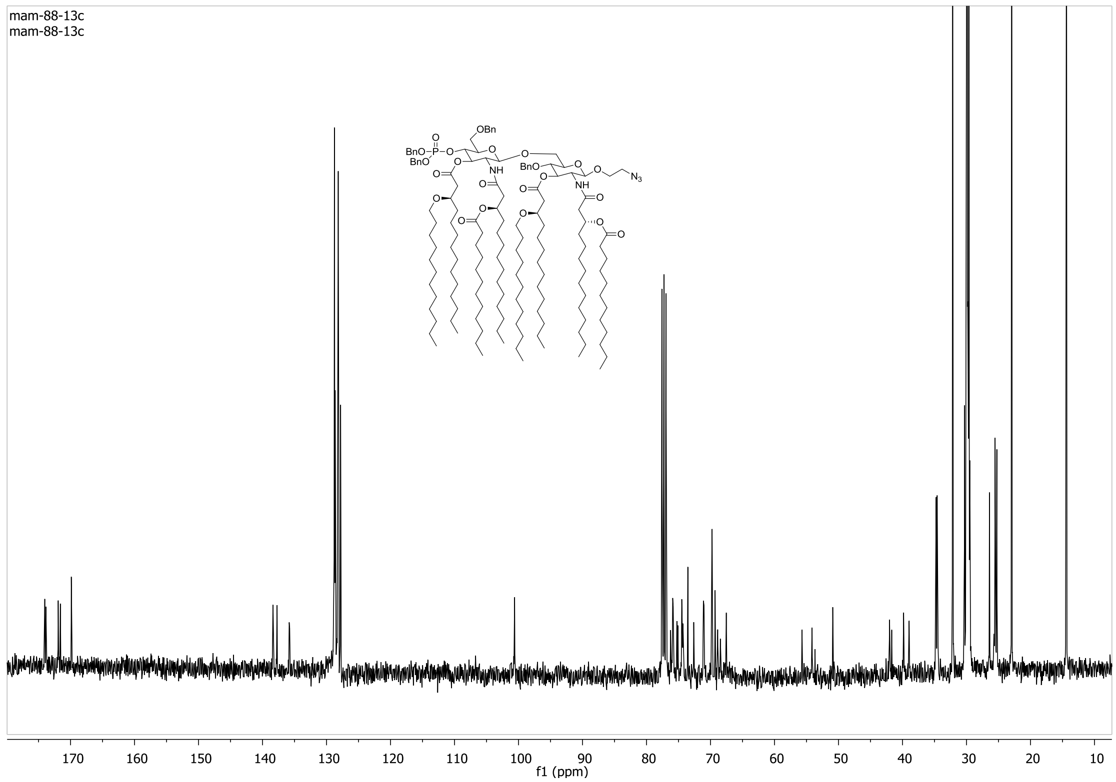
^{1}H NMR spectrum of **10** ($CDCl_3$, 400 MHz)



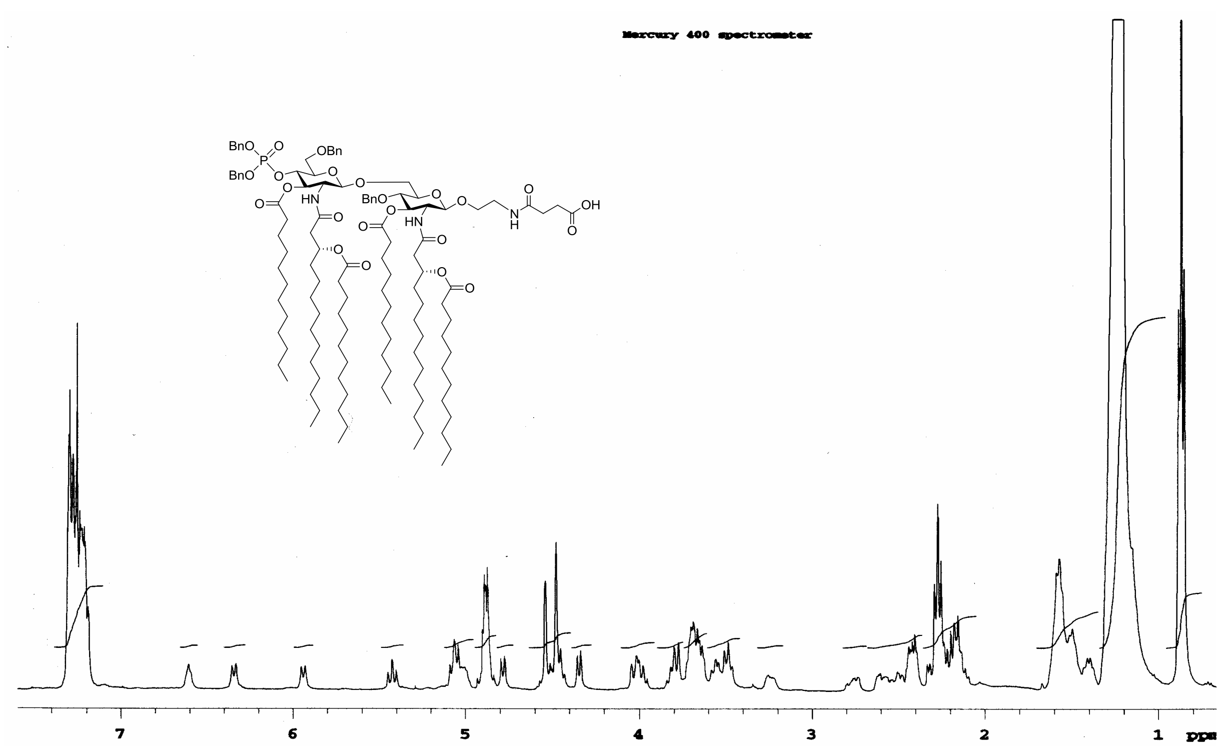
^{1}H-^{1}H COSY NMR spectrum of **10** ($CDCl_3$, 400 MHz)



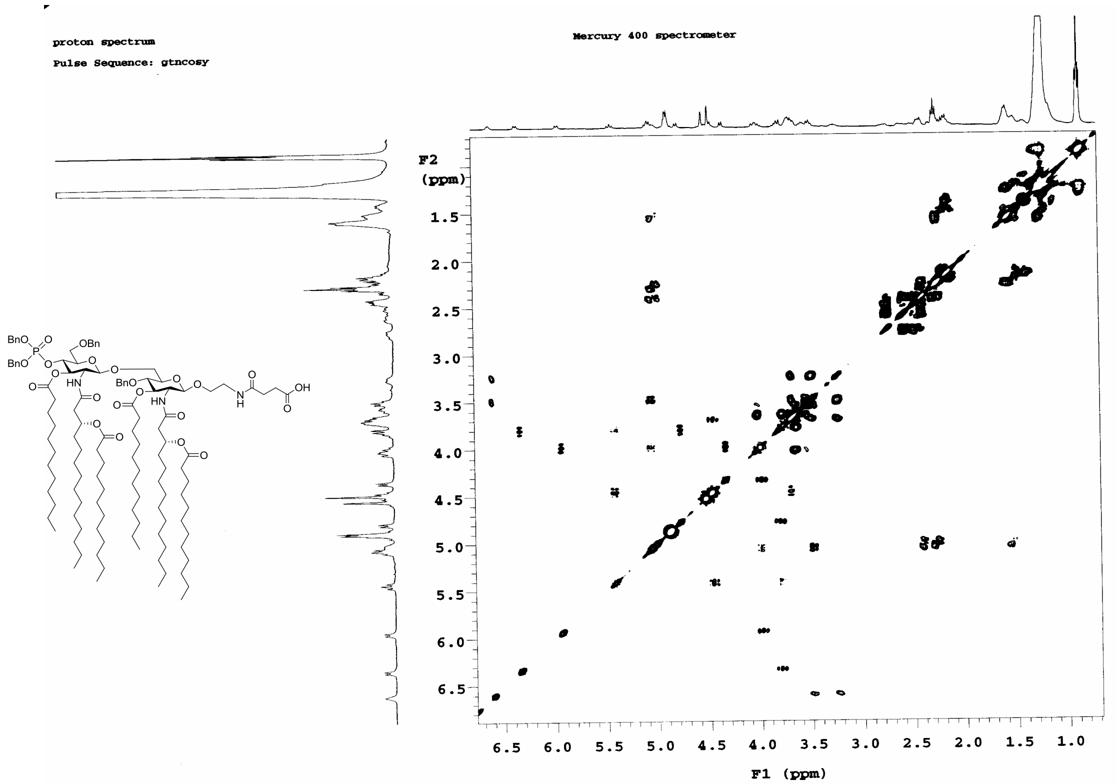
^{31}P NMR spectrum of **10** ($CDCl_3$, 161 MHz)



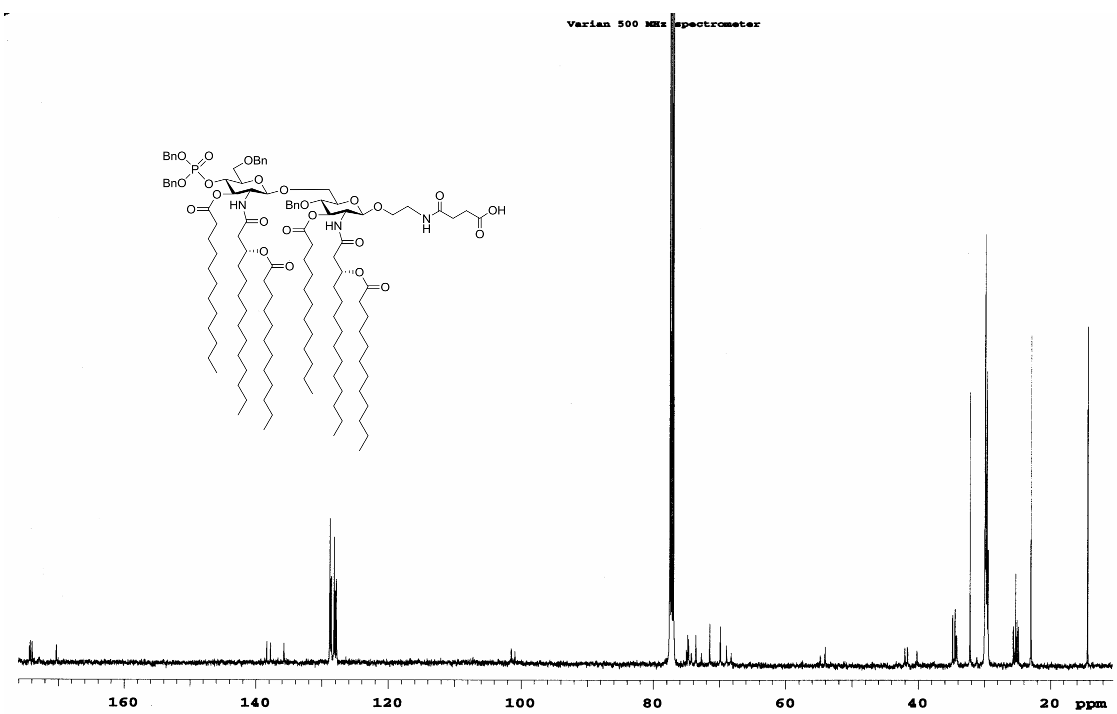
^{13}C NMR spectrum of **10** ($CDCl_3$, 100 MHz)



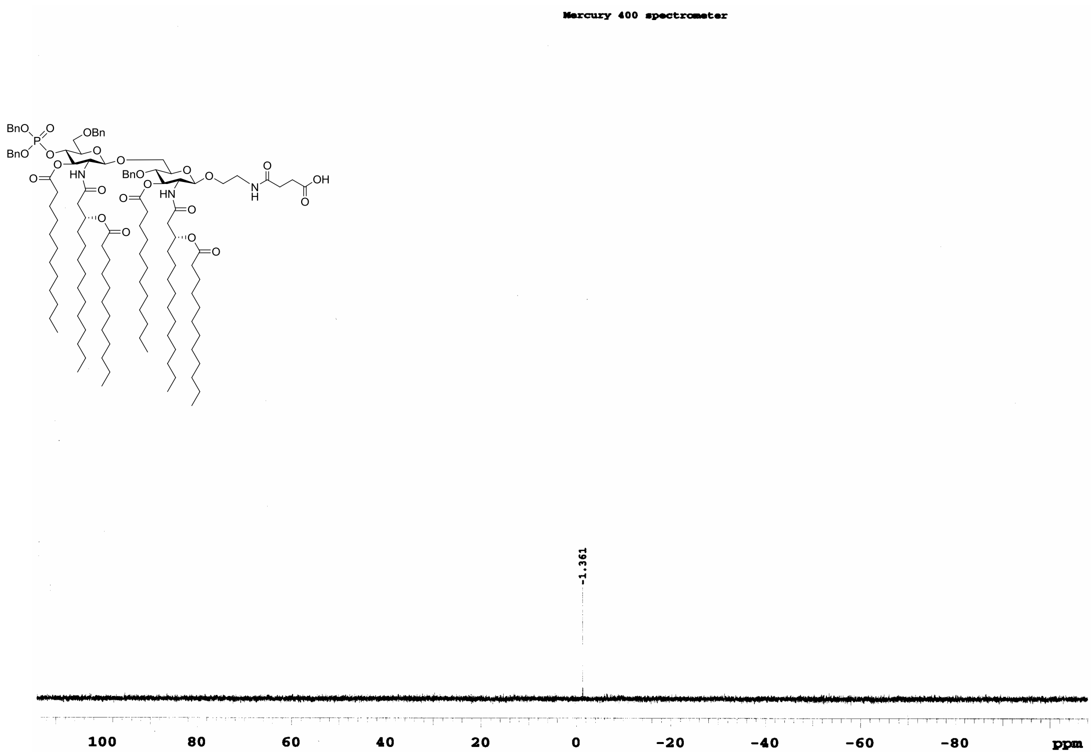
^{1}H NMR spectrum of **34** ($CDCl_3$, 400 MHz) [Ref. 32]



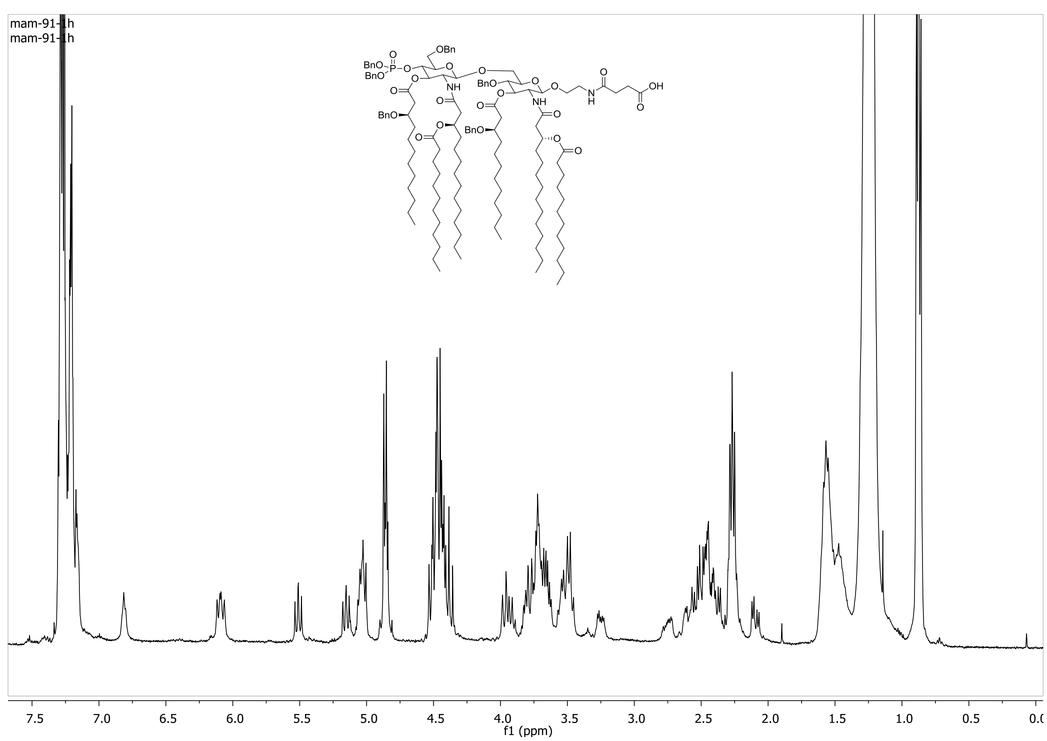
^{1}H-^{1}H COSY NMR spectrum of **34** ($CDCl_3$, 400 MHz) [Ref. 32]



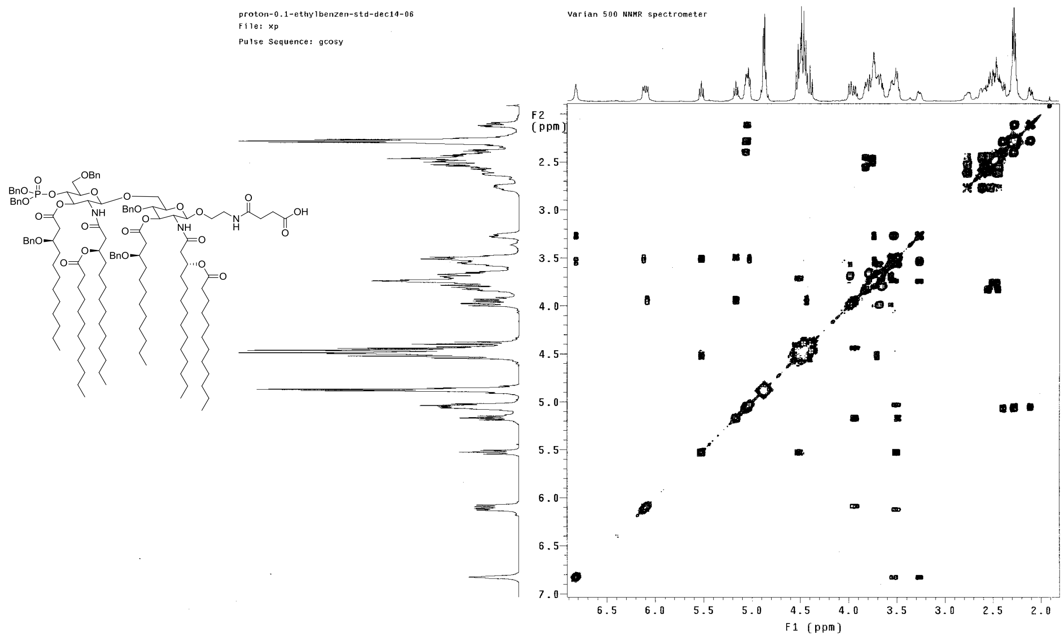
^{13}C NMR spectrum of **34** ($CDCl_3$, 100 MHz) [Ref. 32]



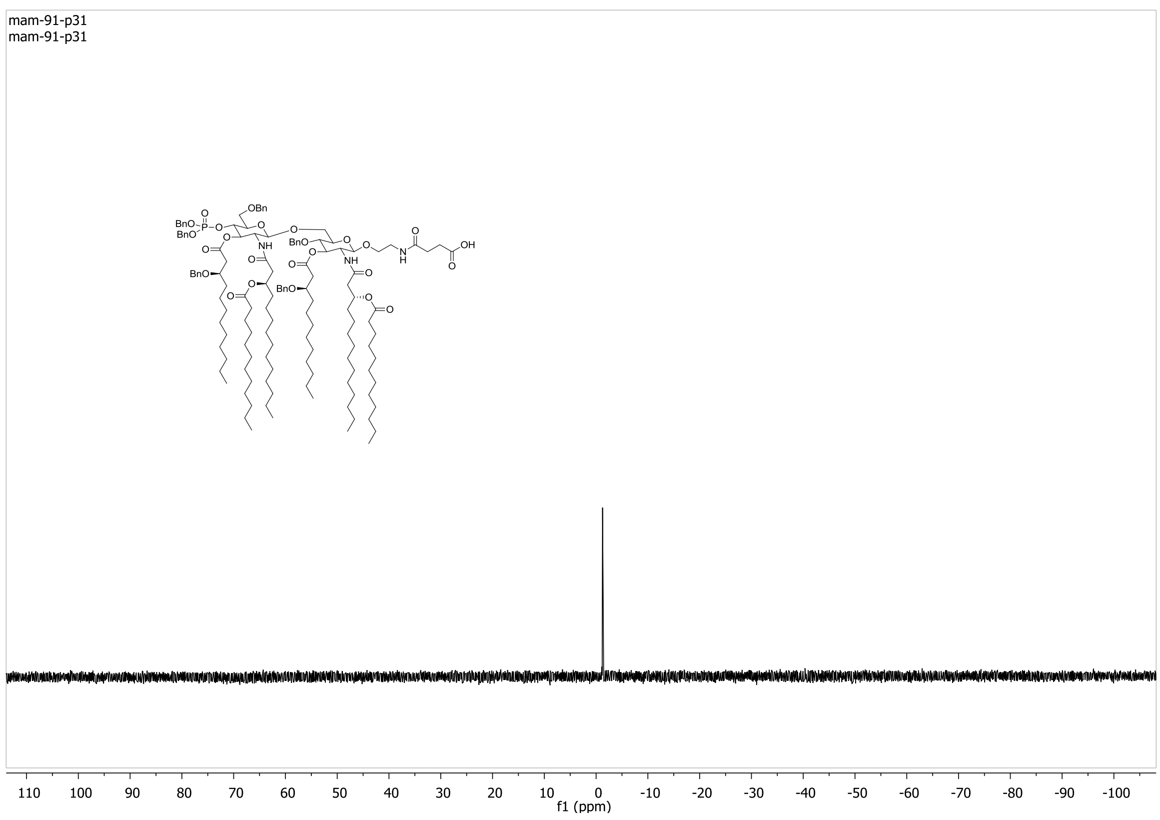
^{31}P NMR spectrum of **34** (CDCl$_3$, 161 MHz) [Ref. 32]



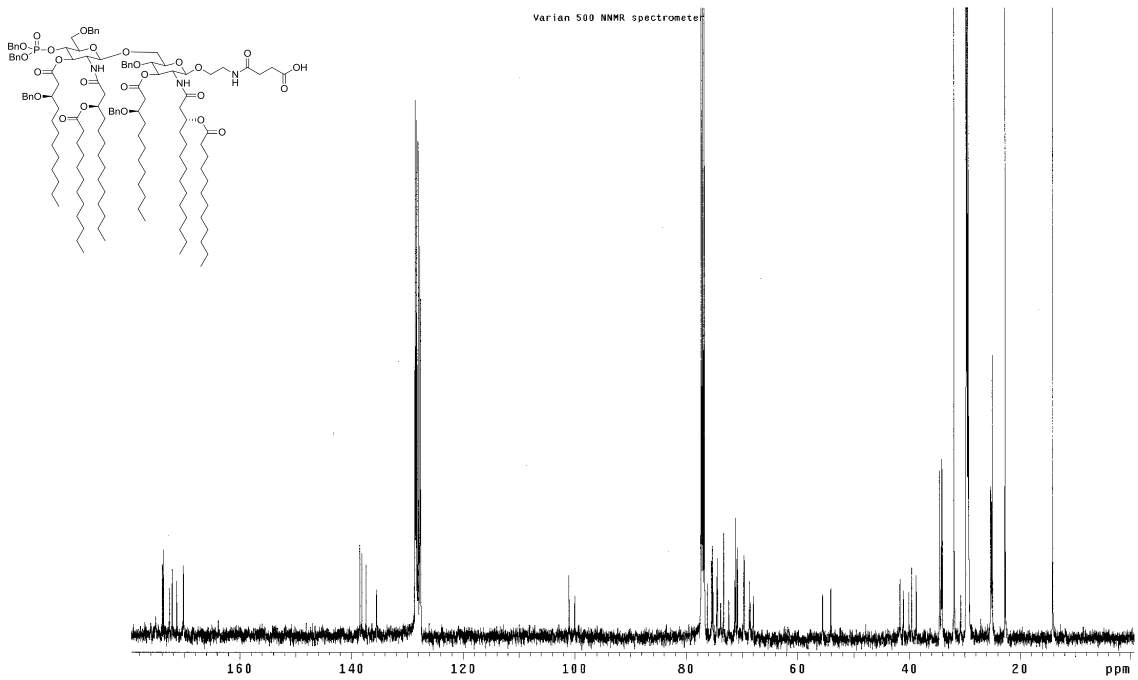
^{1}H NMR spectrum of **35** (CDCl$_3$, 400 MHz)



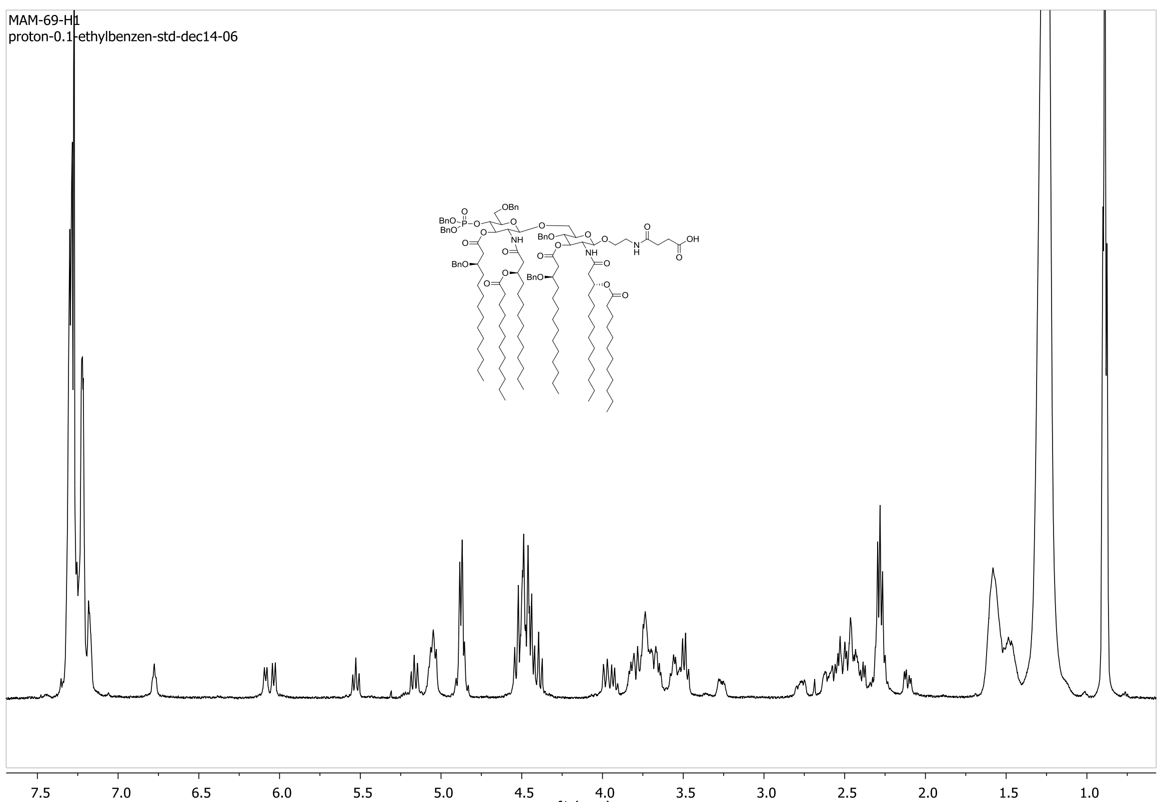
^{1}H-^{1}H COSY NMR spectrum of **35** ($CDCl_3$, 400 MHz)



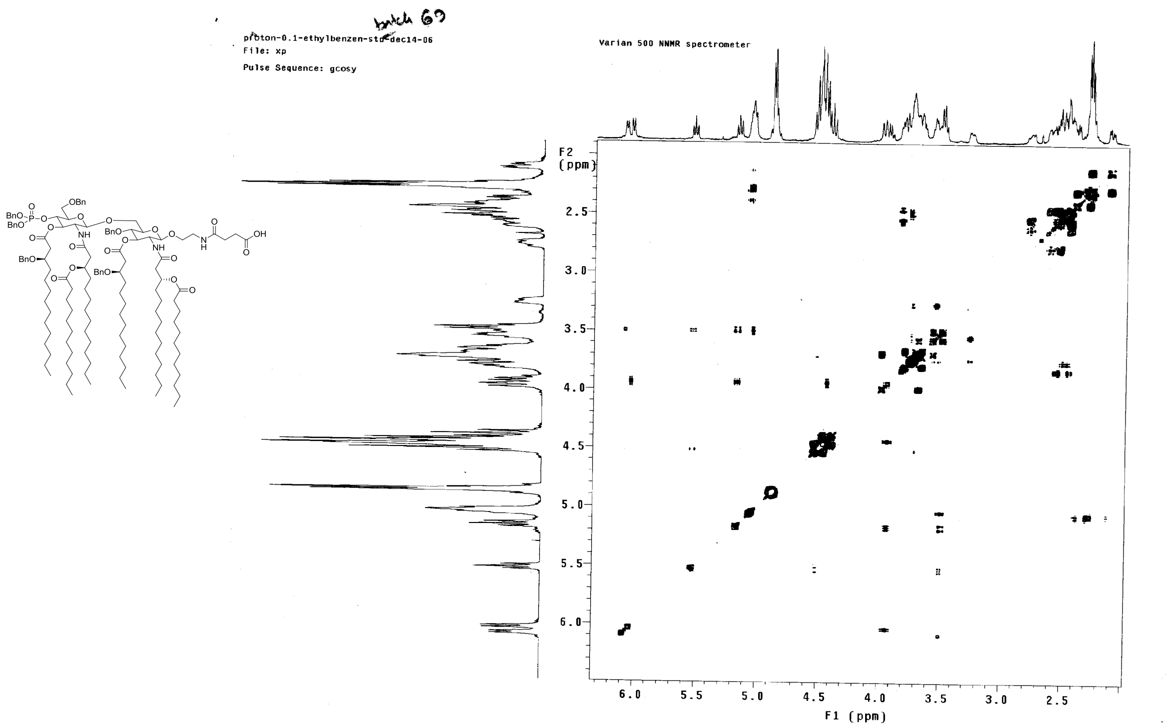
^{31}P NMR spectrum of **35** ($CDCl_3$, 161 MHz)



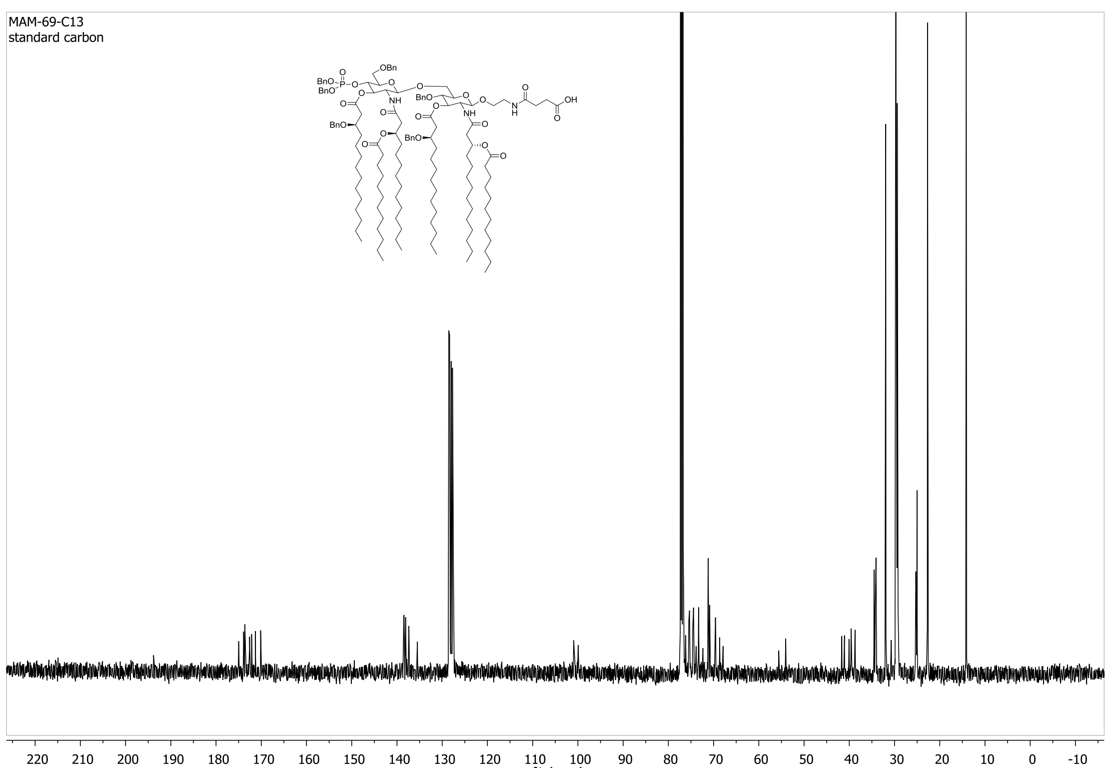
^{13}C NMR spectrum of **35** ($CDCl_3$, 100 MHz)



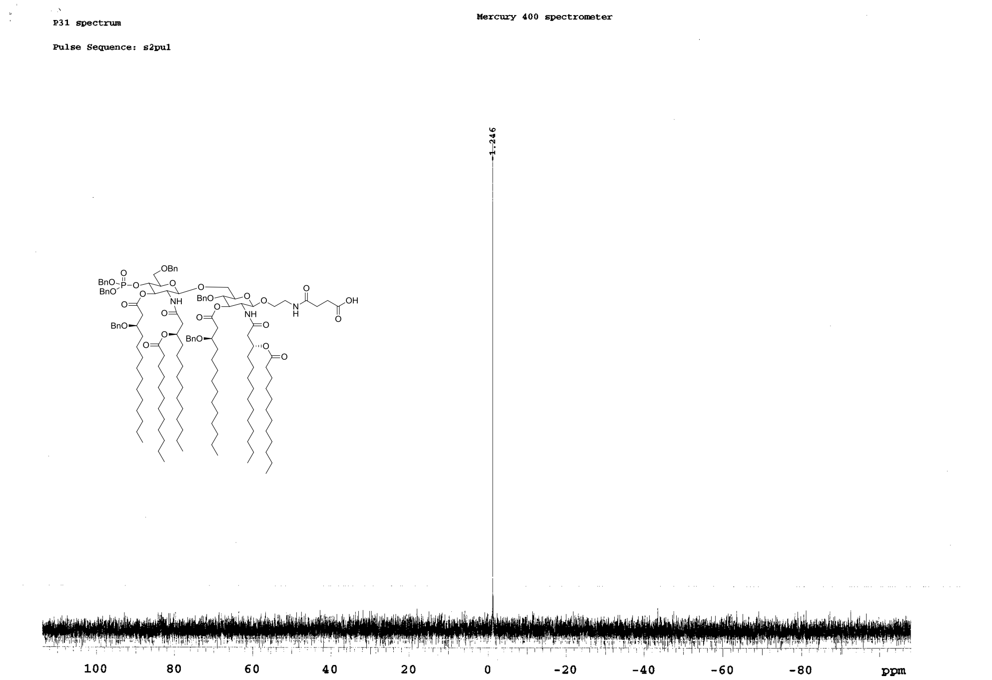
^{1}H NMR spectrum of **36** ($CDCl_3$, 400 MHz)



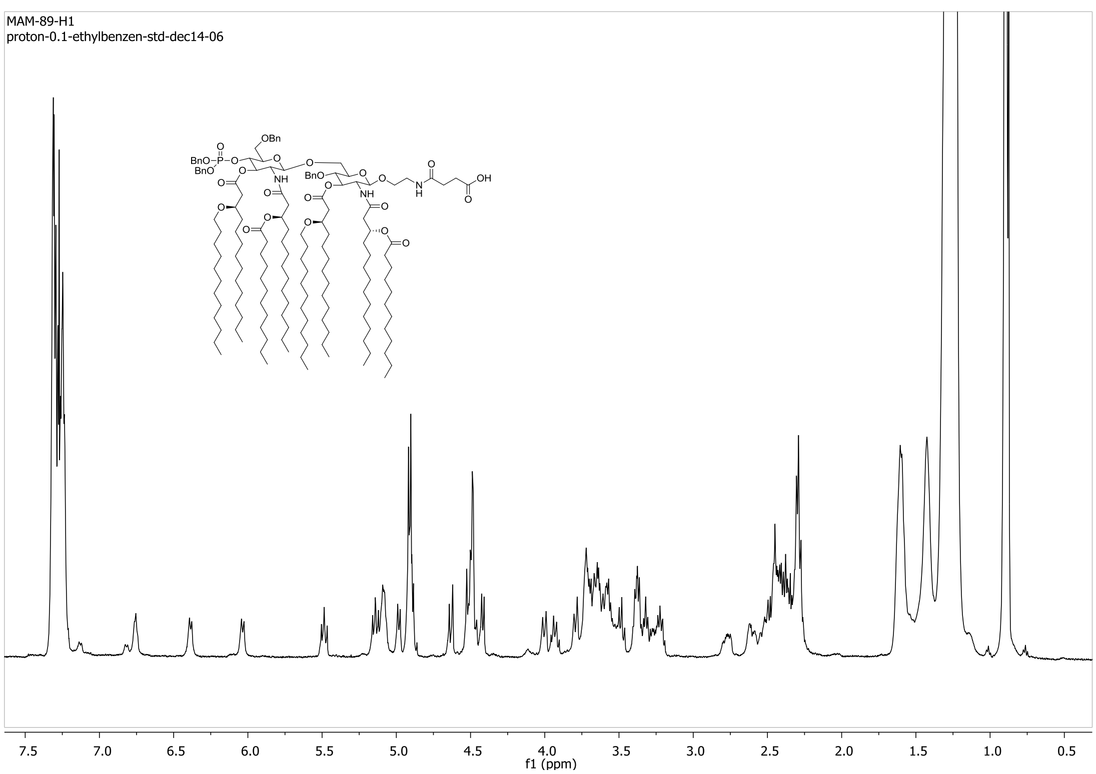
^{1}H-^{1}H COSY NMR spectrum of **36** ($CDCl_3$, 400 MHz)



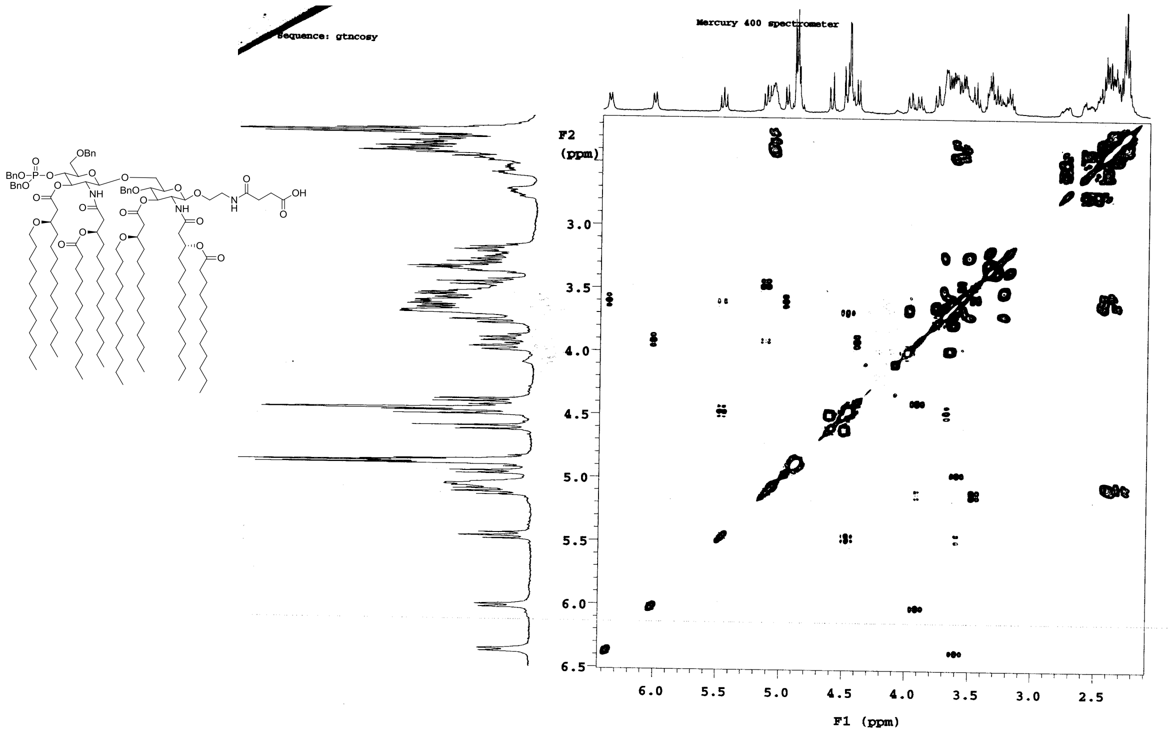
^{13}C NMR spectrum of **36** ($CDCl_3$, 100 MHz)



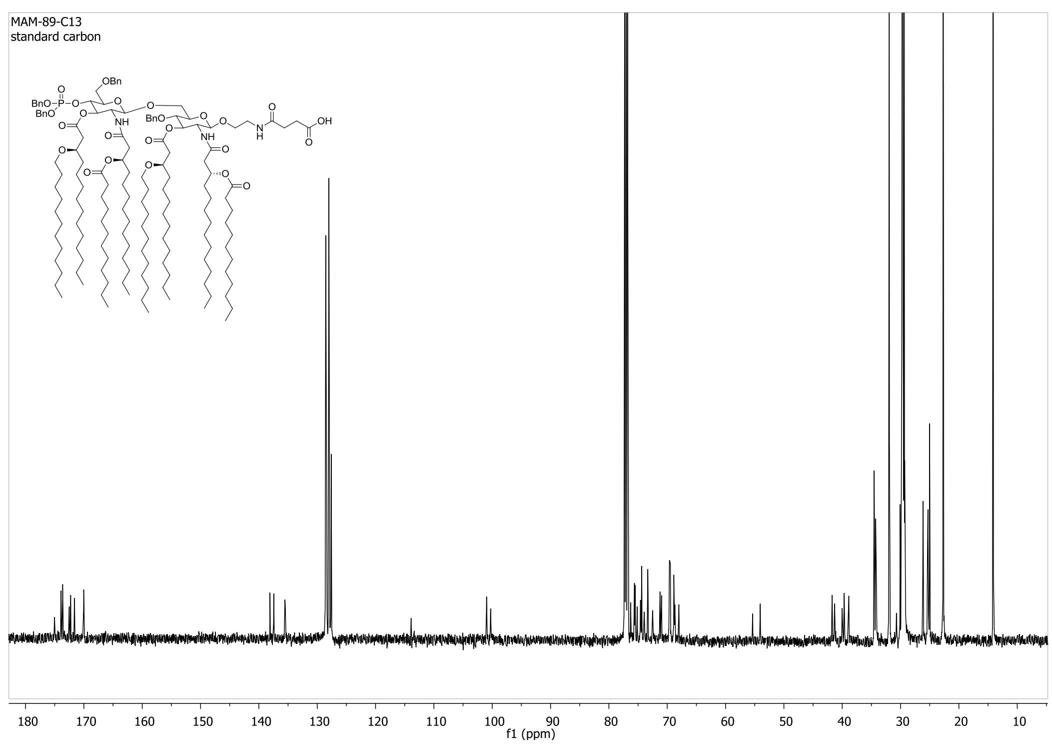
^{31}P NMR spectrum of **36** ($CDCl_3$, 161 MHz)



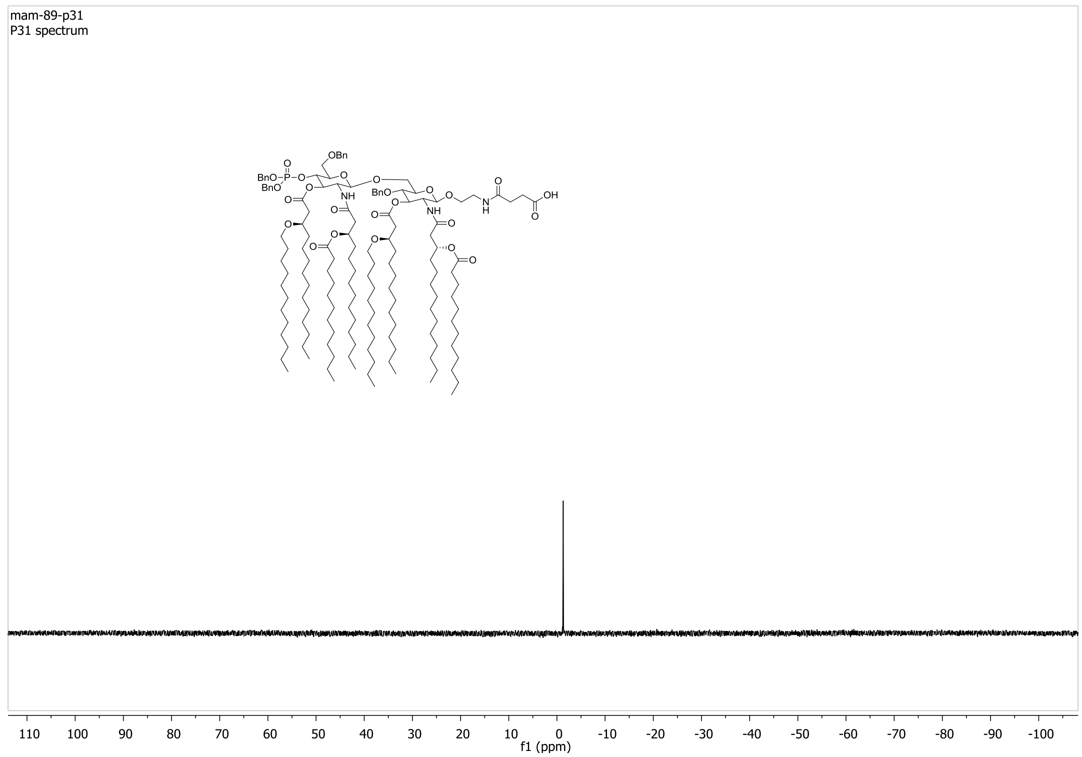
^{1}H NMR spectrum of **37** ($CDCl_3$, 400 MHz)



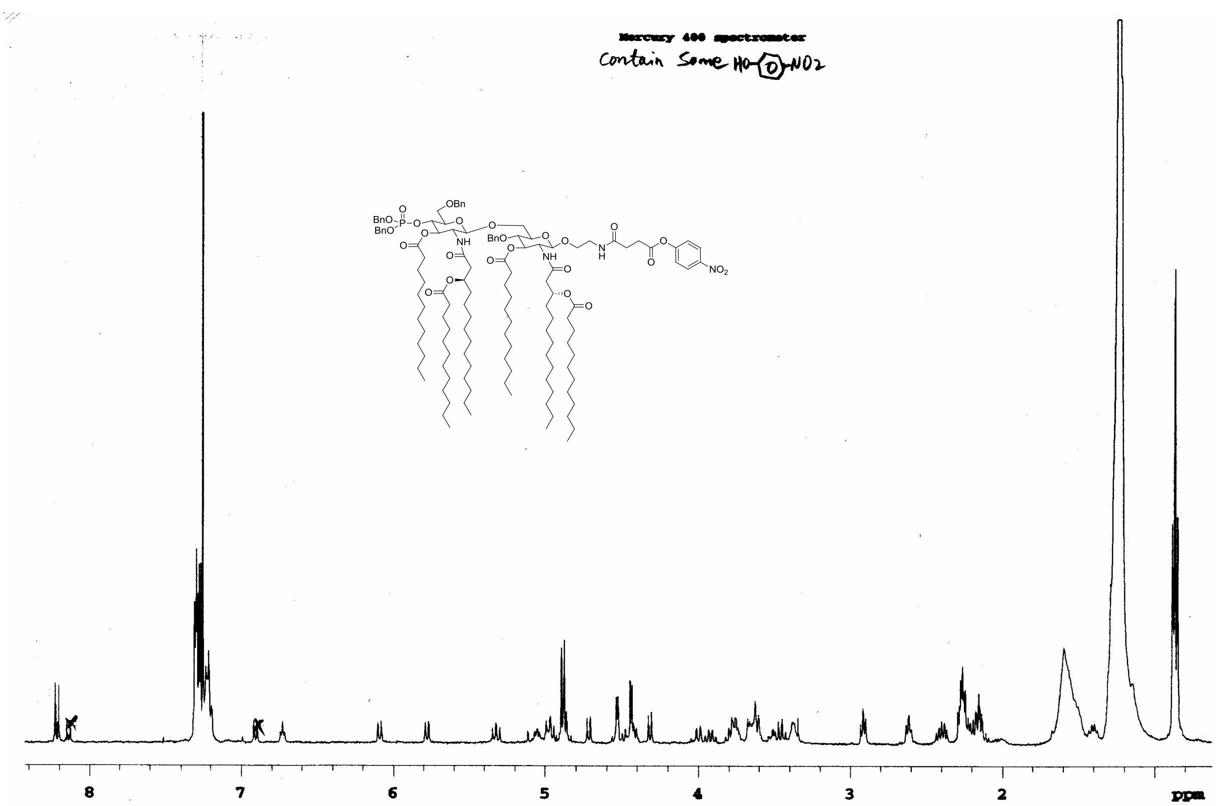
^{1}H-^{1}H COSY NMR spectrum of **37** ($CDCl_3$, 400 MHz)



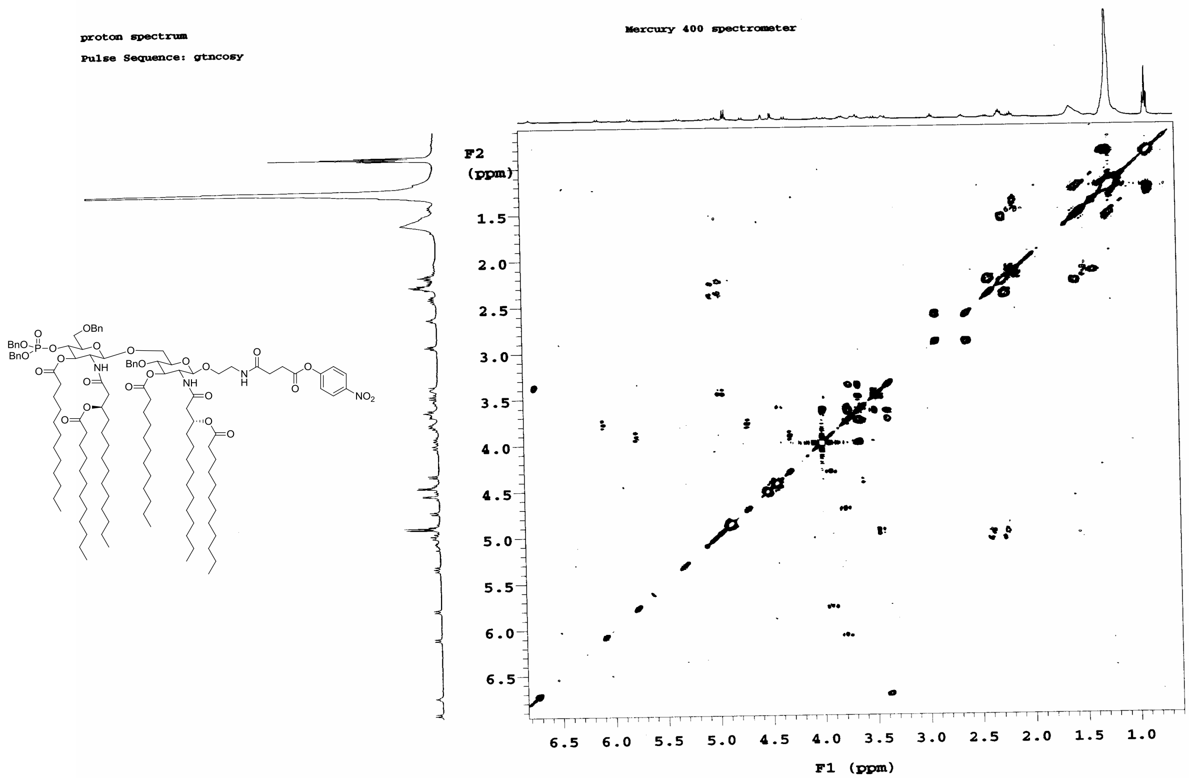
^{13}C NMR spectrum of **37** ($CDCl_3$, 100 MHz)



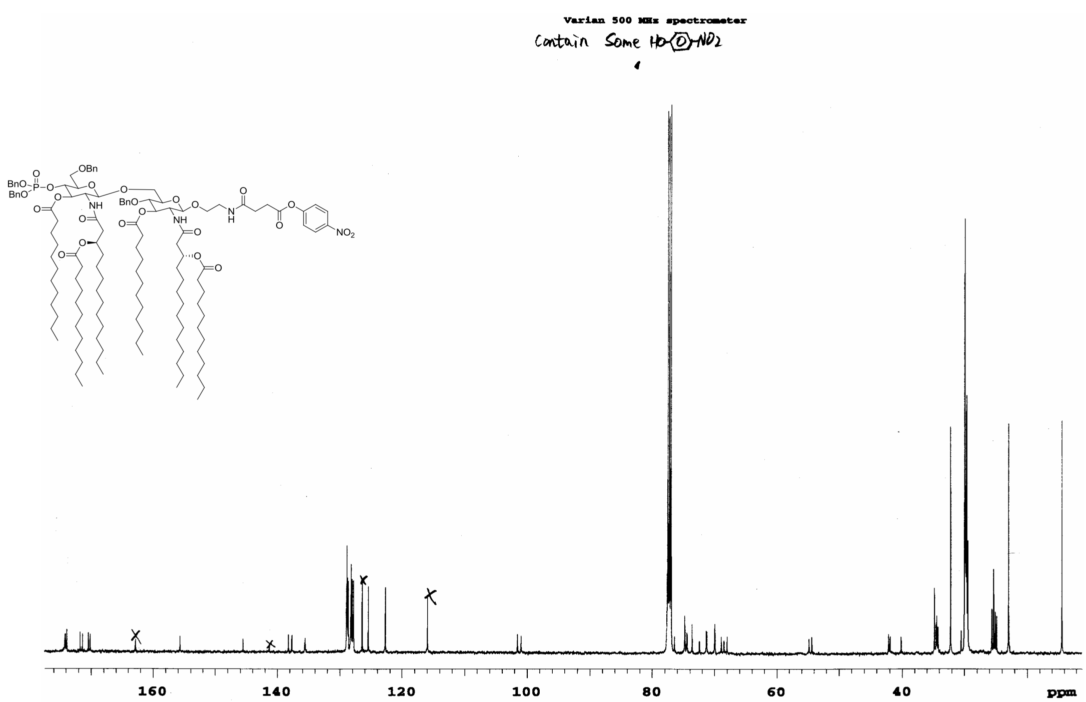
^{31}P NMR spectrum of **37** ($CDCl_3$, 161 MHz)



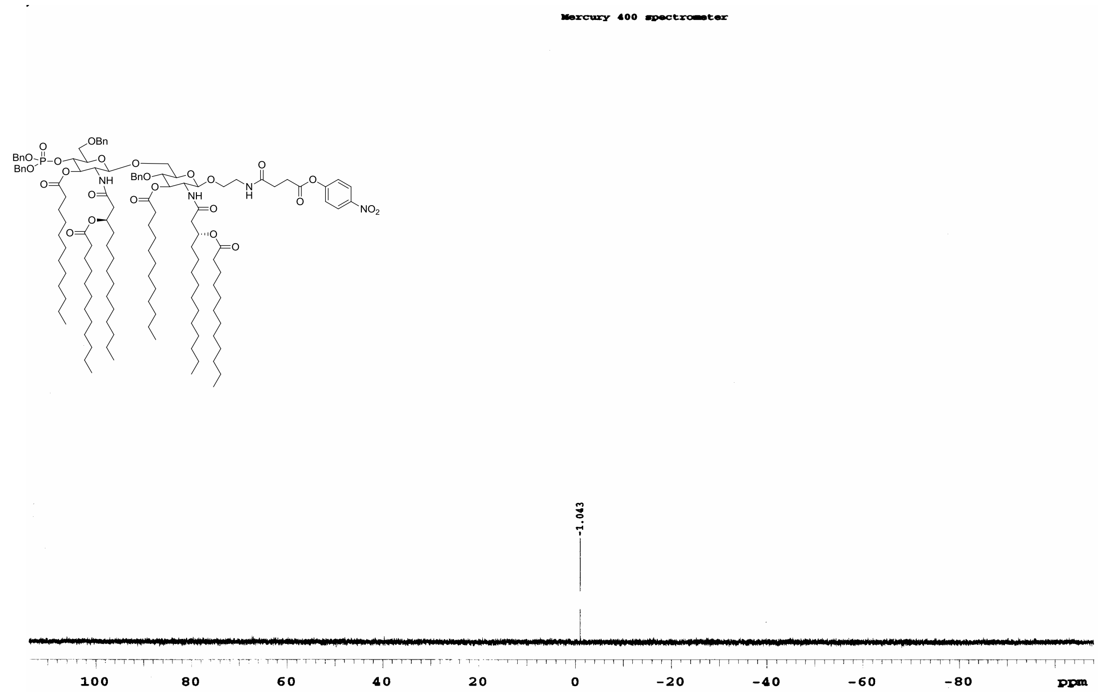
^{1}H NMR spectrum of **38** ($CDCl_3$, 400 MHz) [Ref. 32]



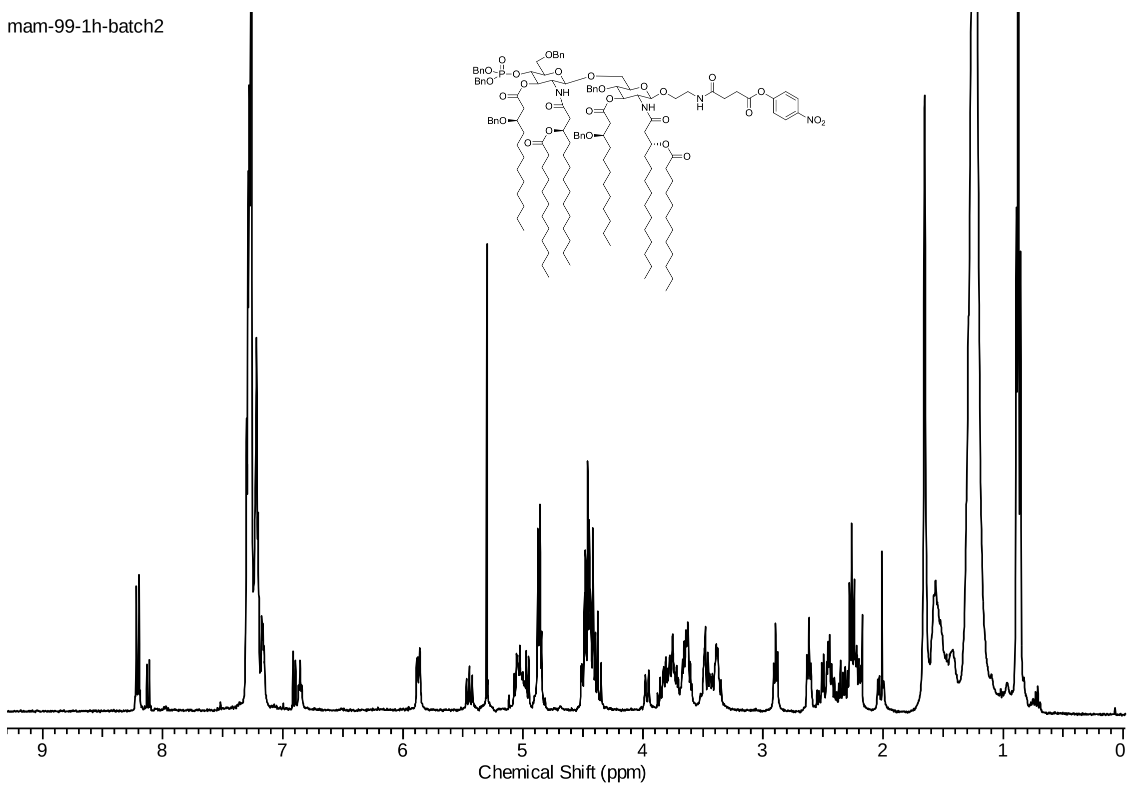
^1H-^1H COSY NMR spectrum of **38** ($CDCl_3$, 400 MHz) [Ref. 32]



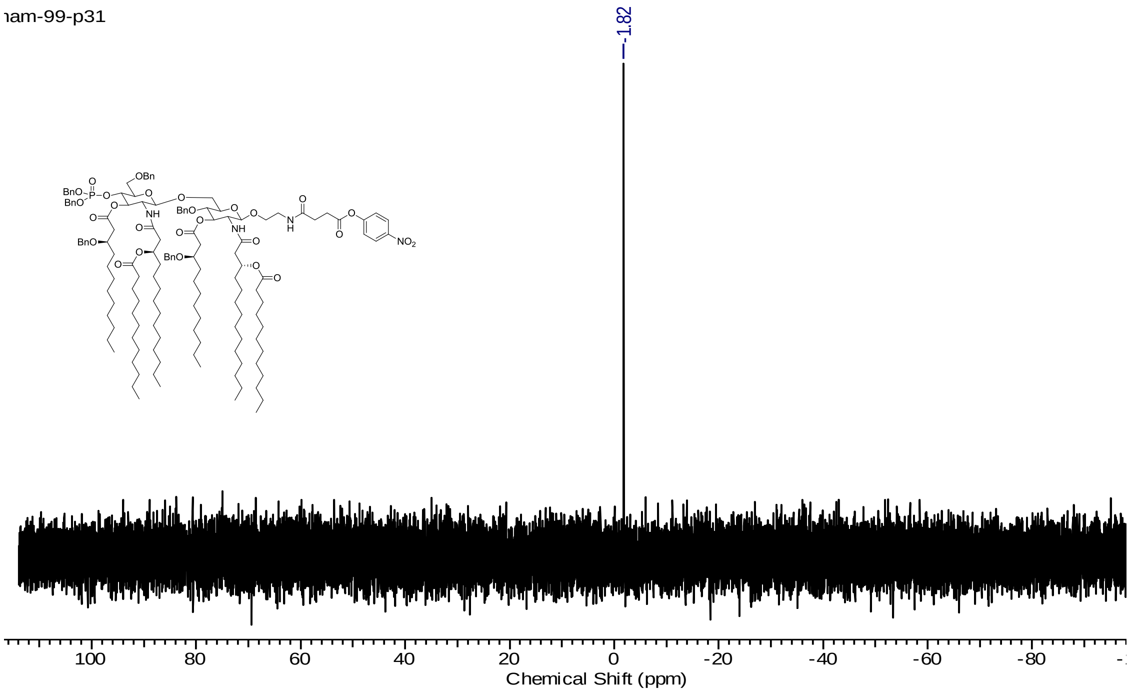
^{13}C NMR spectrum of **38** ($CDCl_3$, 125 MHz) [Ref. 32]



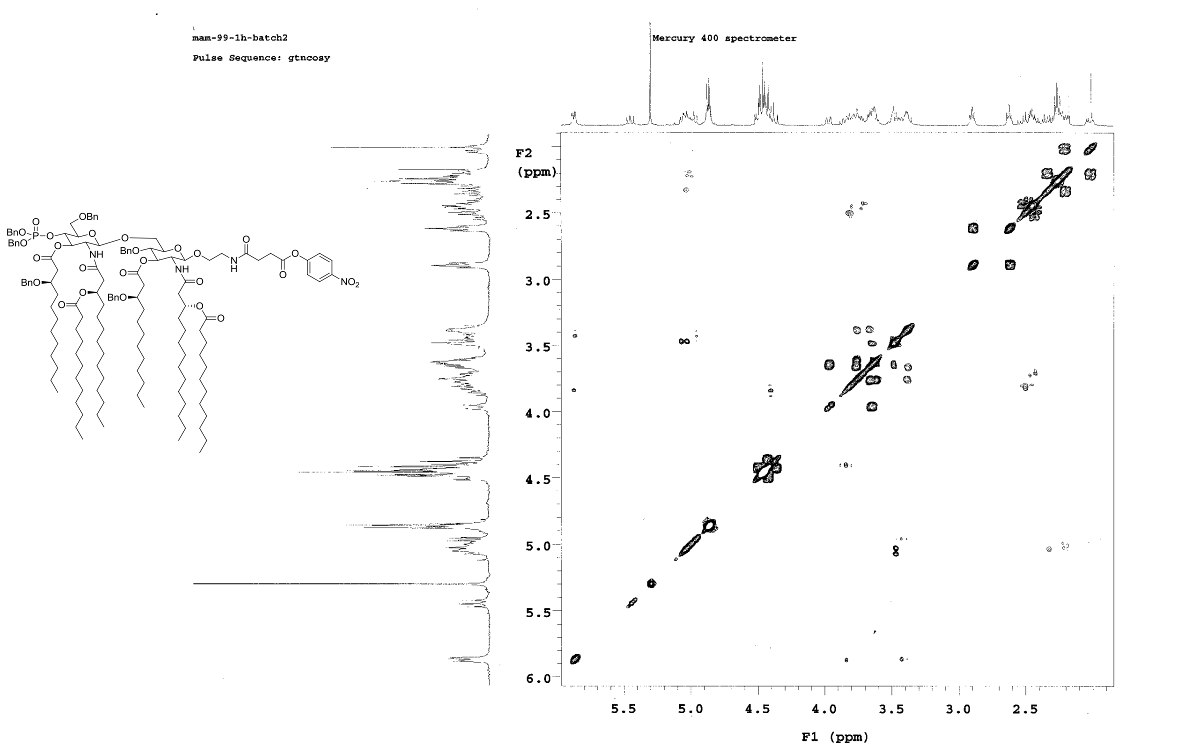
^{31}P NMR spectrum of **38** ($CDCl_3$, 161 MHz) [Ref. 32]



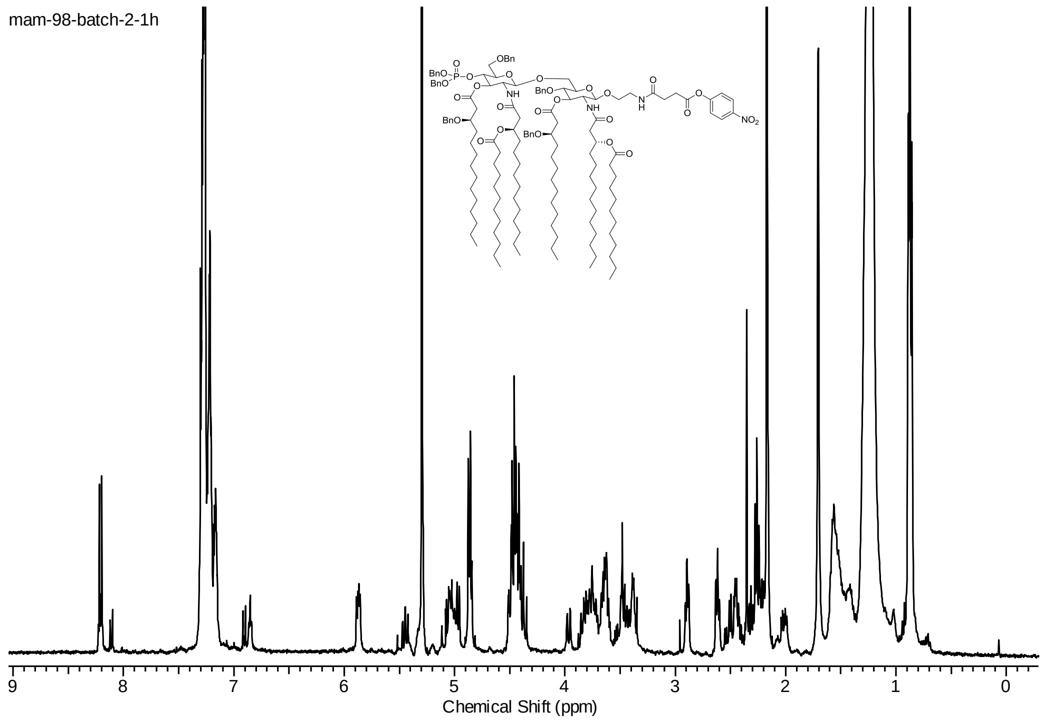
^{1}H NMR spectrum of **39** ($CDCl_3$, 400 MHz)



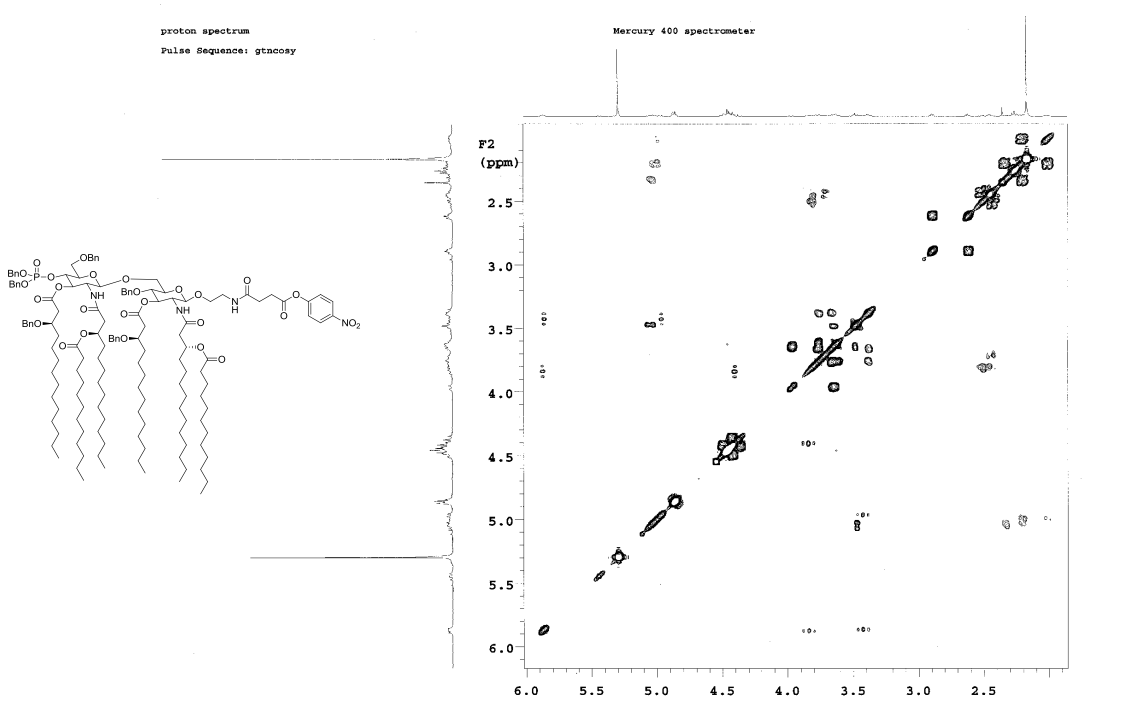
^{31}P NMR spectrum of **39** ($CDCl_3$, 161 MHz)



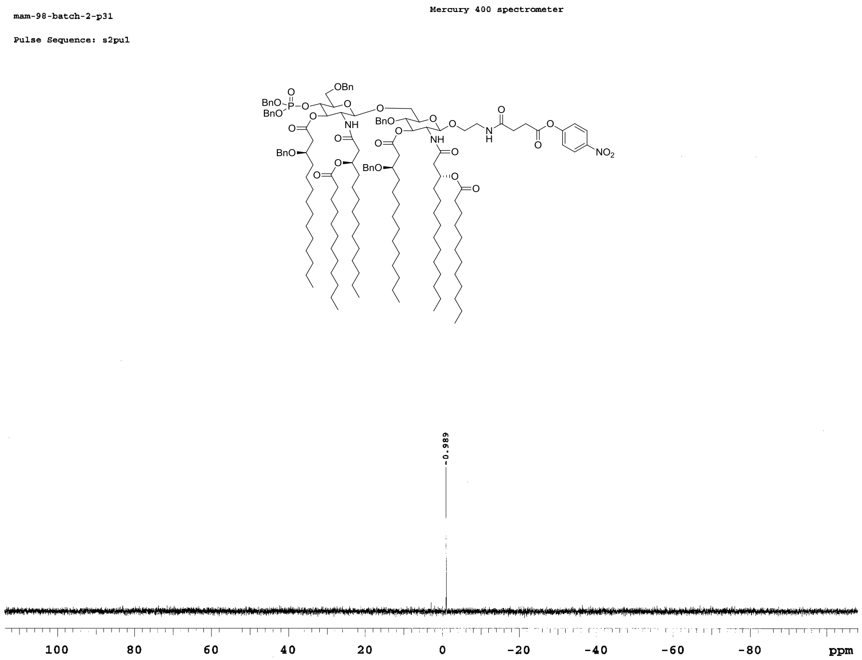
^{1}H-^{1}H COSY NMR spectrum of **39** ($CDCl_3$, 400 MHz)



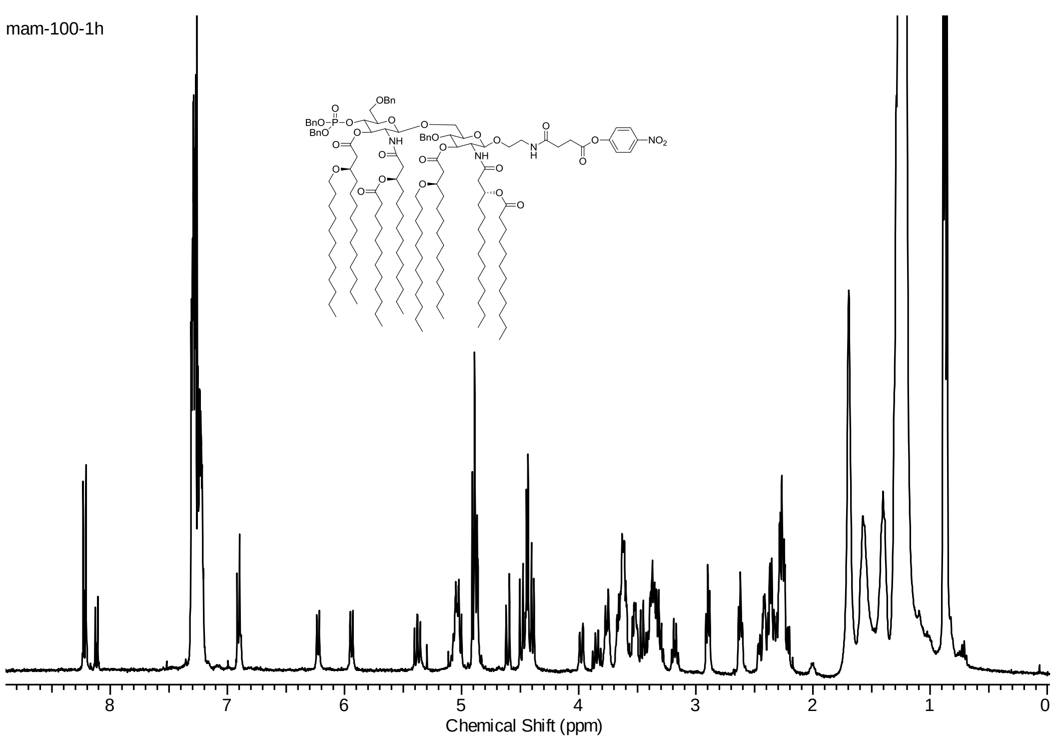
^{1}H NMR spectrum of **40** ($CDCl_3$, 400 MHz)



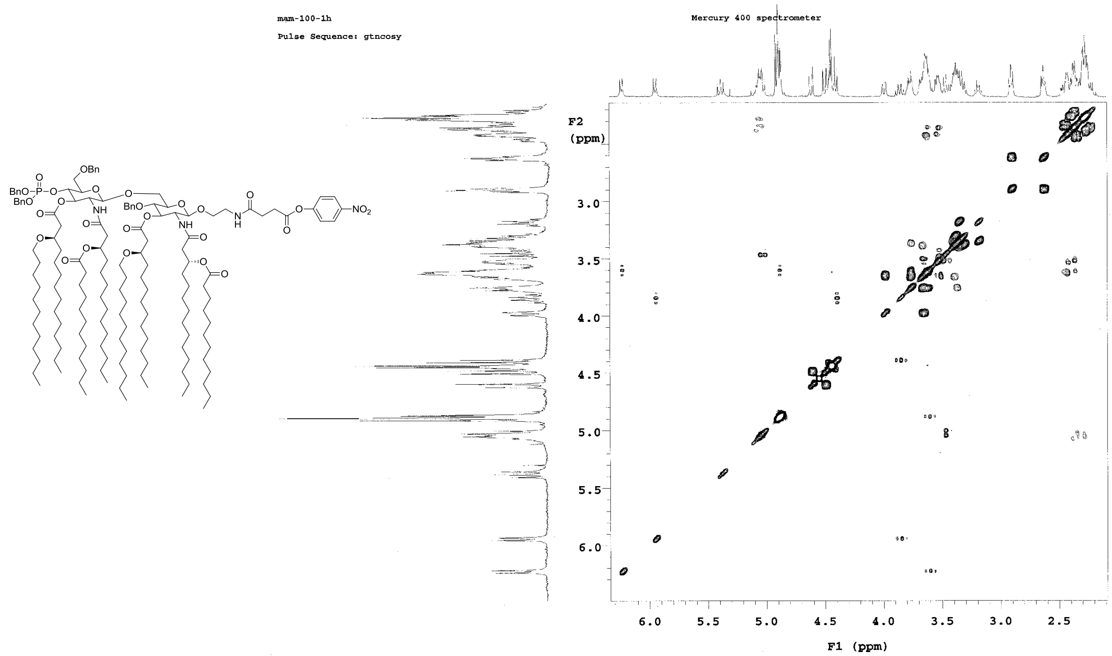
^{1}H-^{1}H COSY NMR spectrum of **40** ($CDCl_3$, 400 MHz)



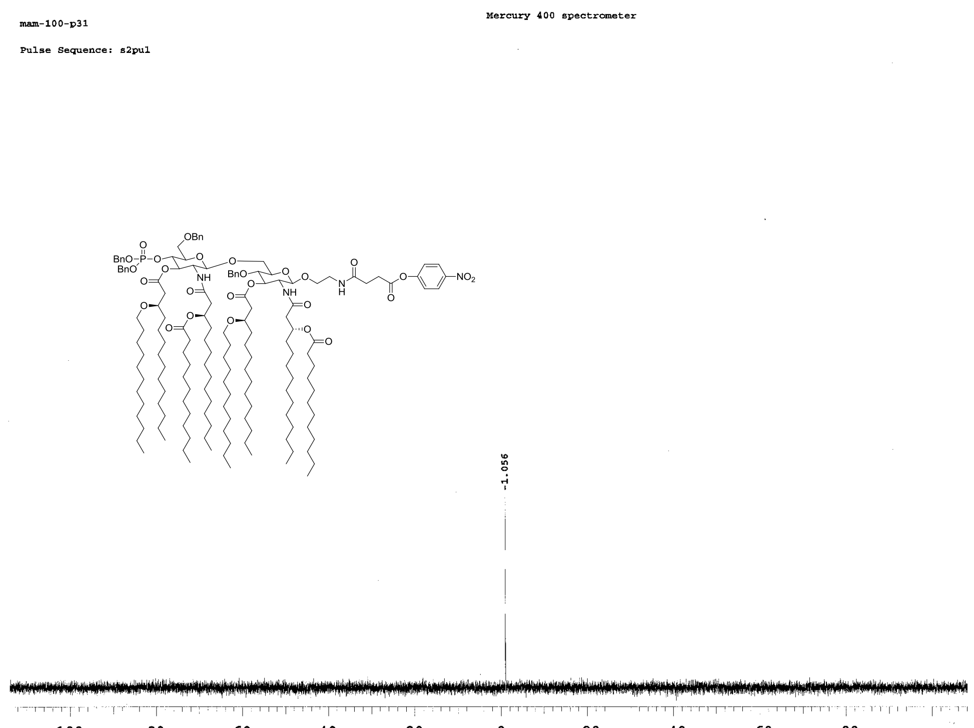
^{31}P NMR spectrum of **40** ($CDCl_3$, 161 MHz)



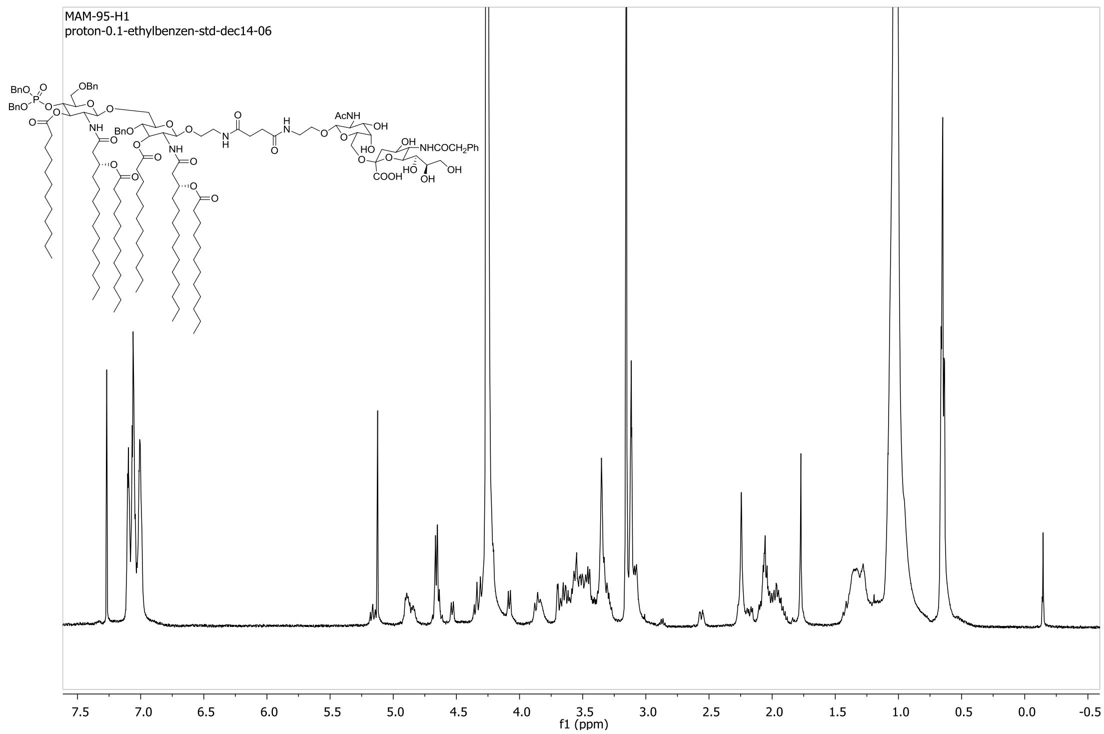
^{1}H NMR spectrum of **41** ($CDCl_3$, 400 MHz)



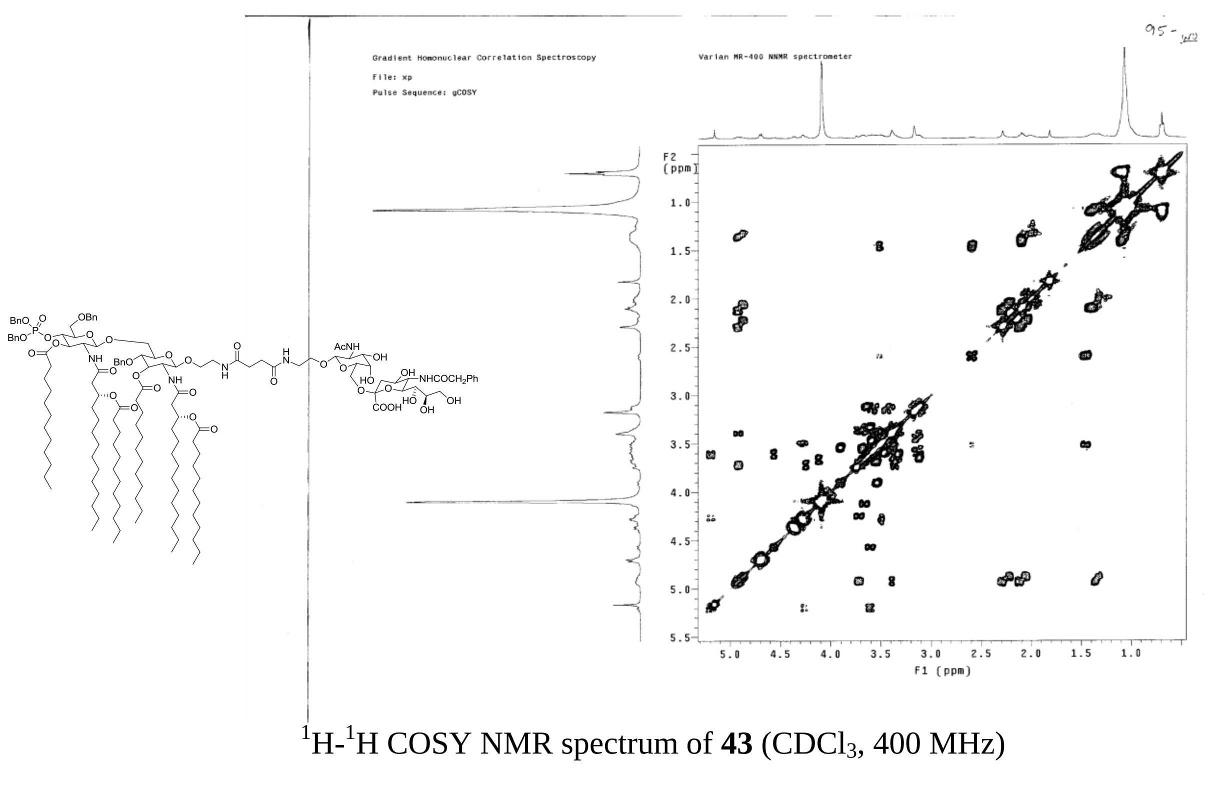
^{1}H-^{1}H COSY NMR spectrum of **41** ($CDCl_3$, 400 MHz)



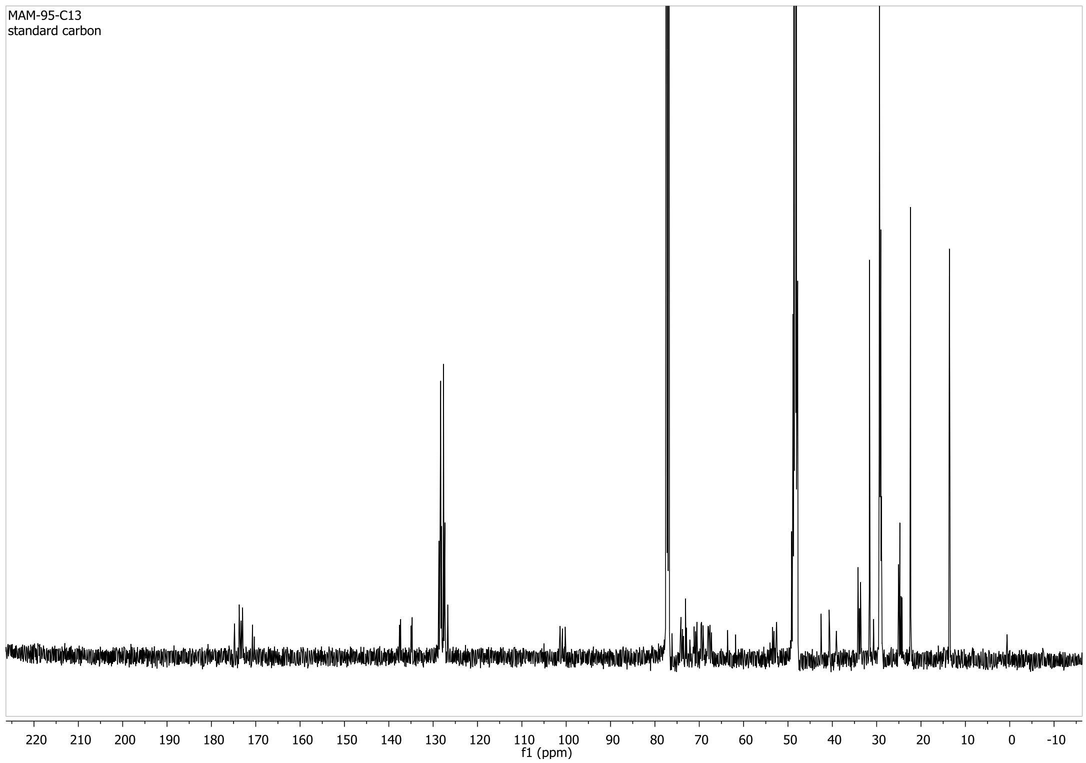
^{31}P NMR spectrum of **41** ($CDCl_3$, 161 MHz)



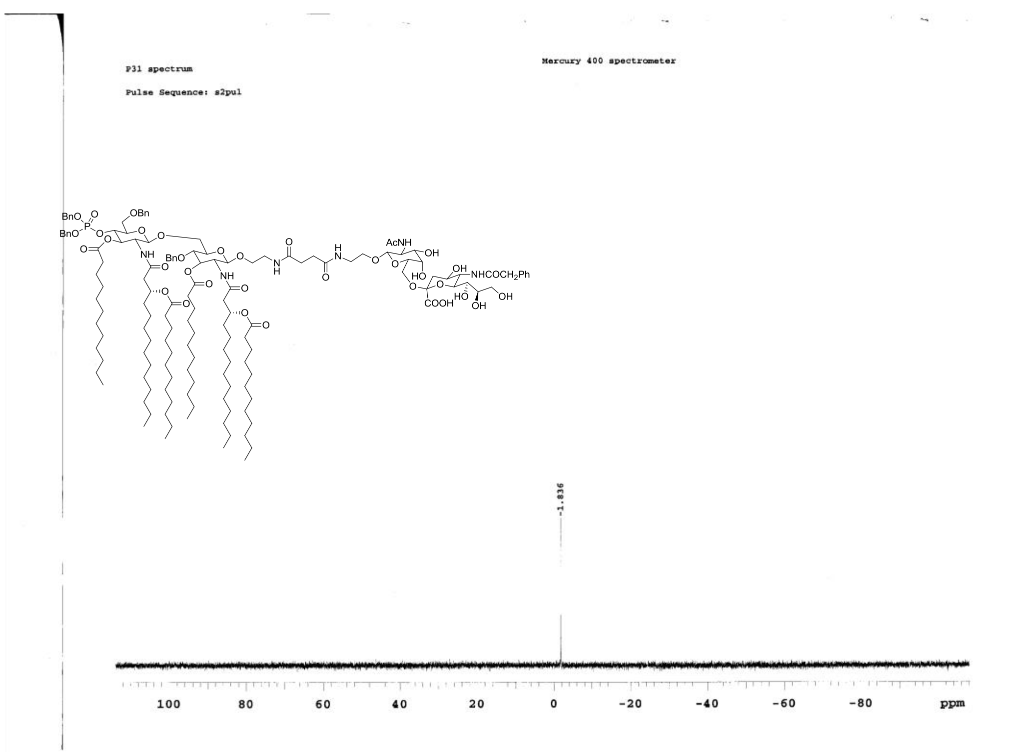
[1]H NMR spectrum of **43** ($CDCl_3$, 400 MHz)



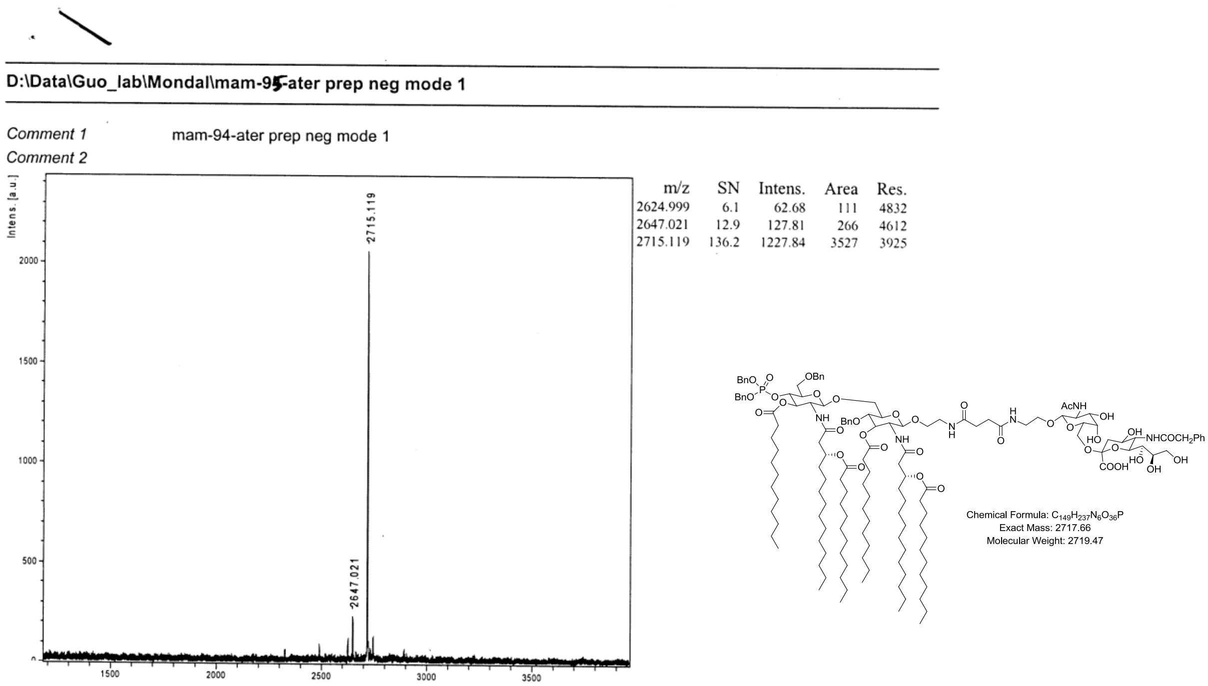
[1]H-[1]H COSY NMR spectrum of **43** ($CDCl_3$, 400 MHz)



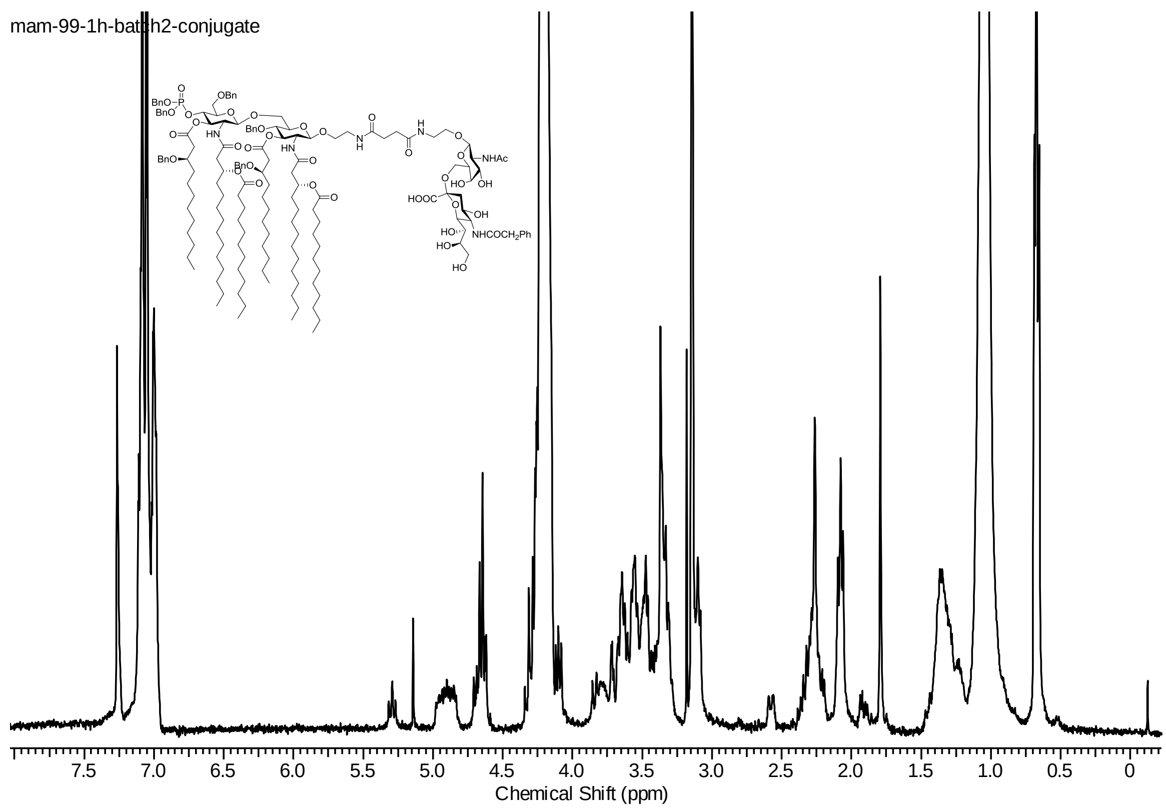
[13]C NMR spectrum of **43** ($CDCl_3$, 100 MHz)



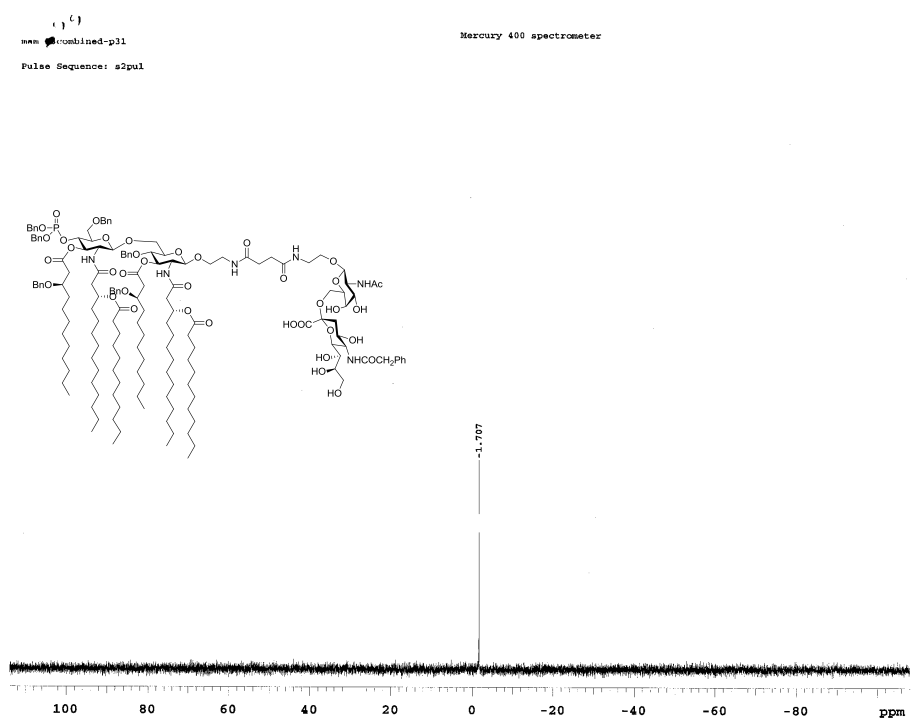
[31]P NMR spectrum of **43** ($CDCl_3$, 161 MHz)



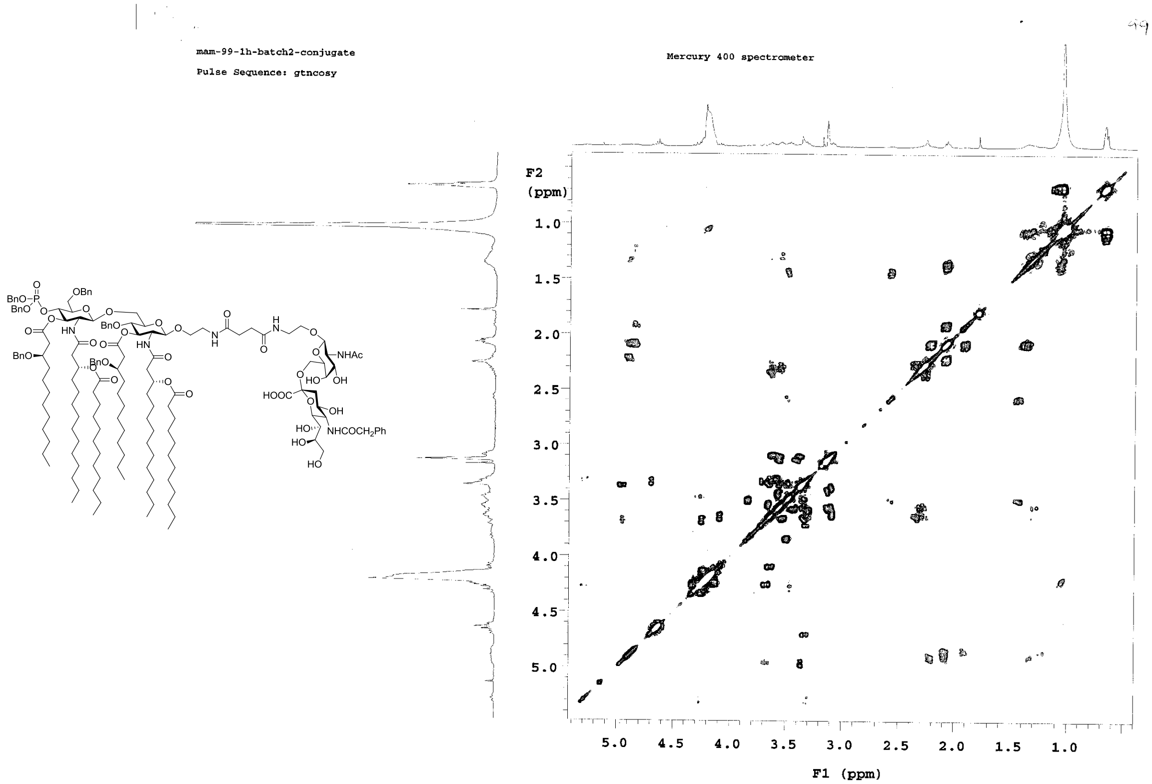
MALDI-TOF MS spectrum of **43** (negative mode)



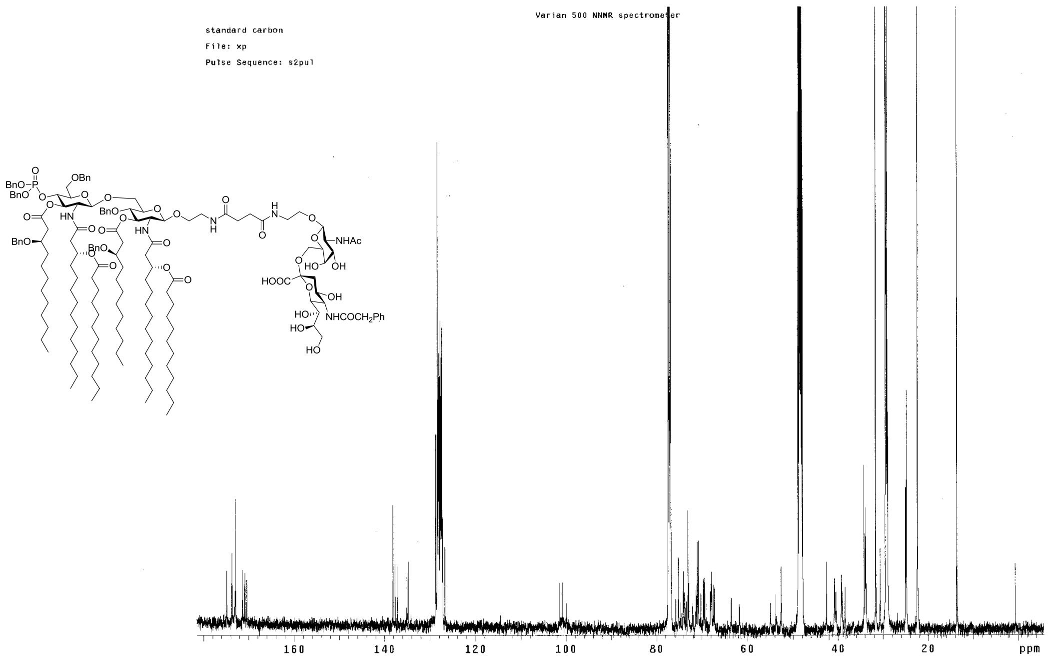
^{1}H NMR spectrum of **44** ($CDCl_3$, 500 MHz)



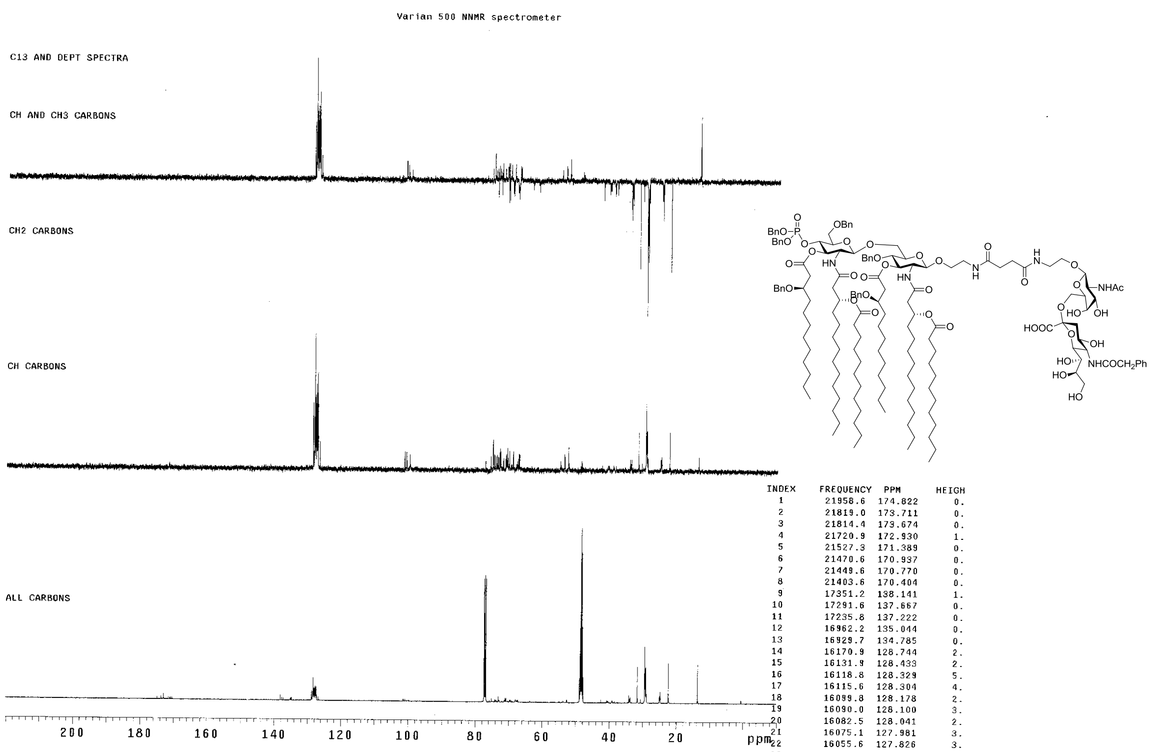
^{31}P NMR spectrum of **44** ($CDCl_3$, 161 MHz)



^{1}H-^{1}H COSY NMR spectrum of **44** ($CDCl_3$, 400 MHz)

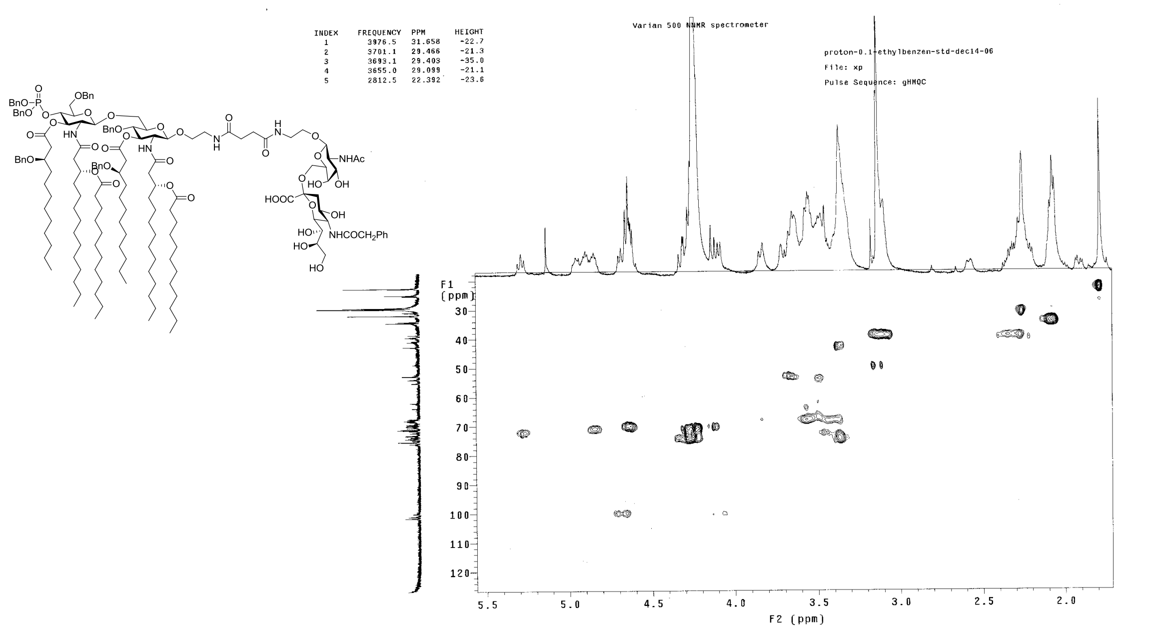


^{13}C NMR spectrum of **44** ($CDCl_3$, 100 MHz)



INDEX	FREQUENCY	PPM	HEIGH
1	21958.6	174.822	0.
2	21819.0	173.711	0.
3	21814.4	173.674	0.
4	21720.9	172.930	1.
5	21527.3	171.389	0.
6	21470.6	170.937	0.
7	21449.6	170.770	0.
8	21403.6	170.404	0.
9	17351.2	138.141	1.
10	17291.6	137.667	0.
11	17235.8	137.222	0.
12	16962.2	135.044	0.
13	16929.7	134.785	0.
14	16170.9	128.744	2.
15	16131.9	128.433	2.
16	16118.8	128.329	5.
17	16115.6	128.304	4.
18	16099.8	128.178	2.
19	16090.0	128.100	3.
20	16082.5	128.041	2.
21	16075.1	127.981	3.
22	16055.6	127.826	3.
23	16043.5	127.729	3.
24	16024.9	127.581	2.
[illegible]	[illegible]	[illegible]	[illegible]

^{13}C DEPT spectrum of **44** ($CDCl_3$, 100 MHz)

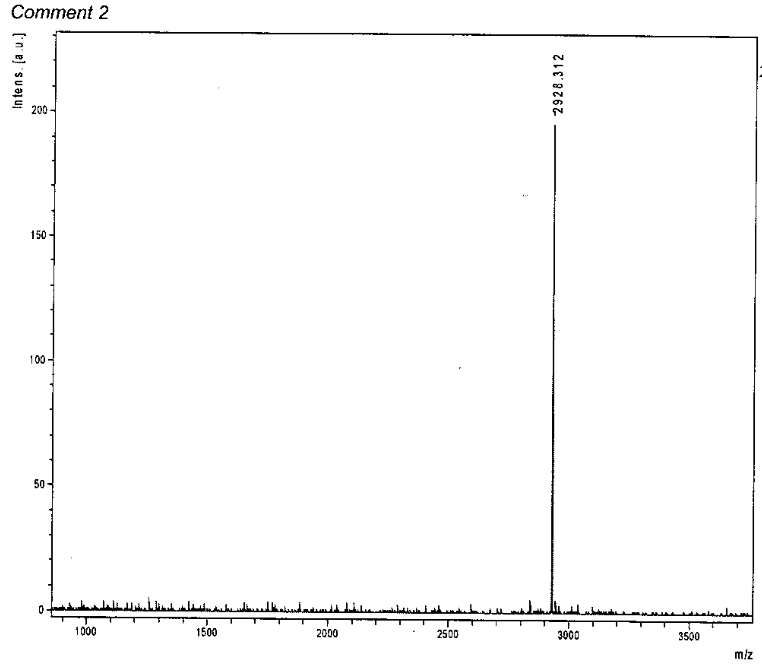


^1H-^{13}C HMQC NMR spectrum of **44** ($CDCl_3$, 400/100 MHz)

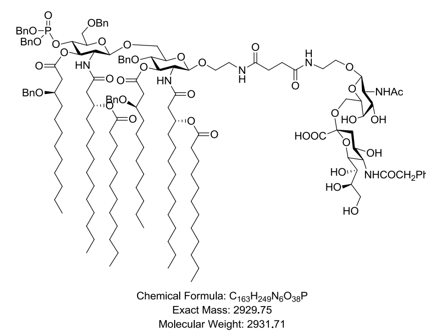
D:\Data\Guo_lab\Mondal\mam-99-conjugate-batch2

Comment 1 mam-99-conjugate-batch2

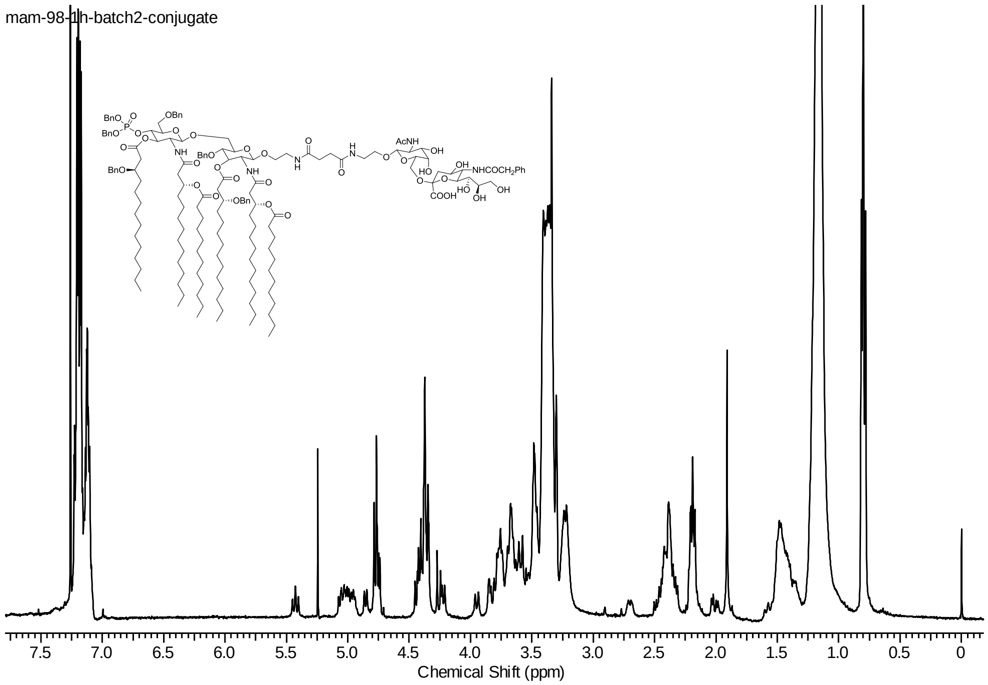
Comment 2



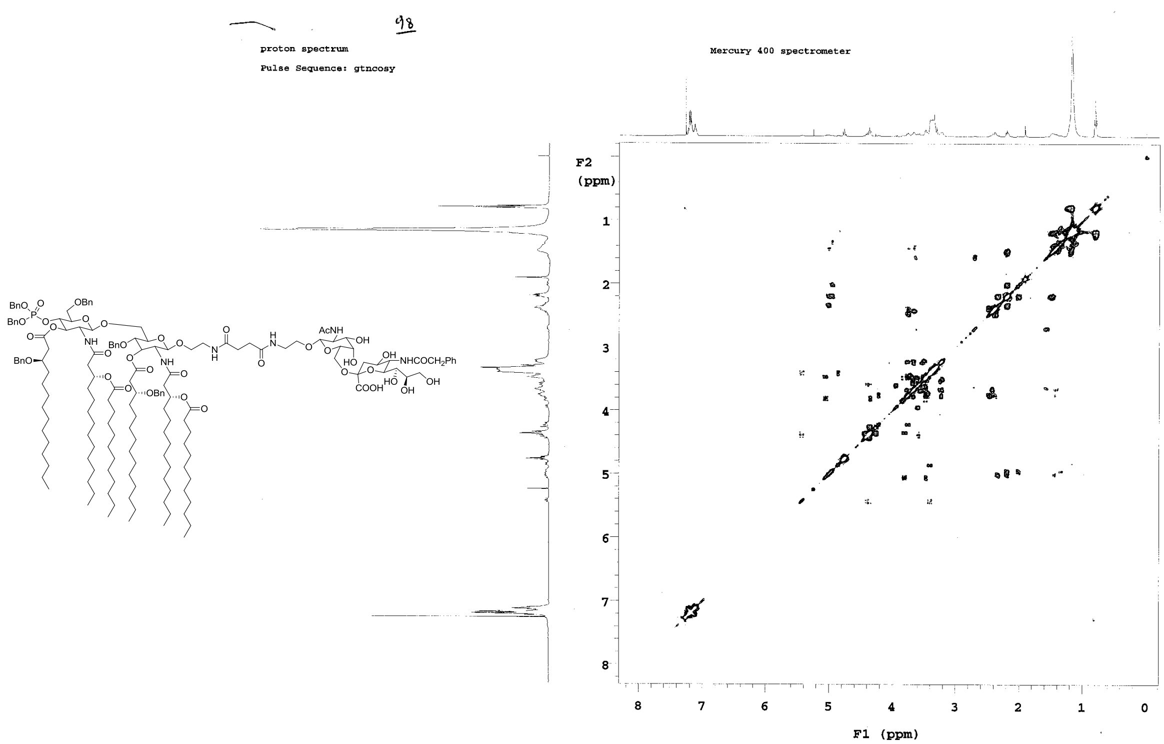
m/z	SN	Intens.	Area	Res.
2928.312	471.3	184.00	110	5065



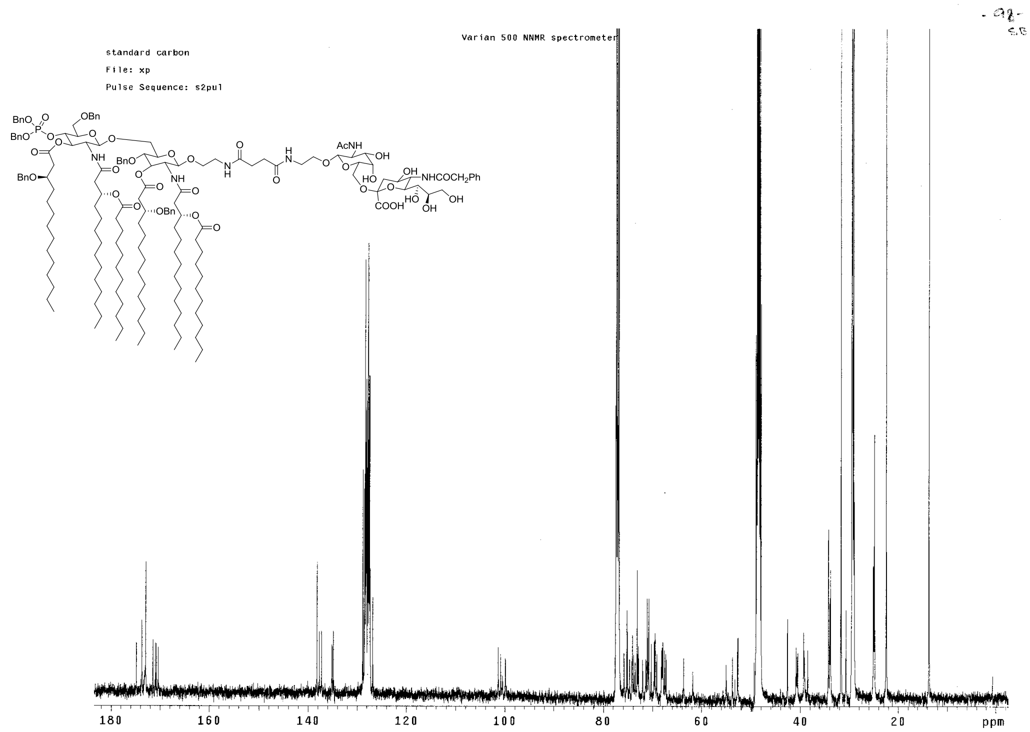
MALDI-TOF MS spectrum of **44** (negative mode)



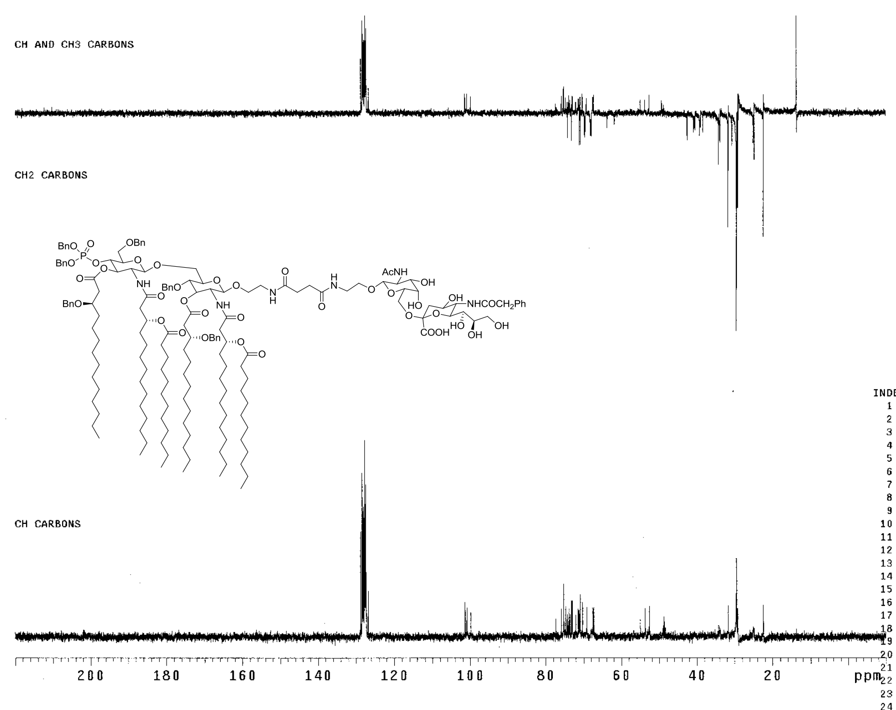
^{1}H NMR spectrum of **45** ($CDCl_3$, 400 MHz)



^{1}H-^{1}H COSY NMR spectrum of **45** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **45** ($CDCl_3$, 100 MHz)



INDEX	FREQUENCY	PPM	HEIGH
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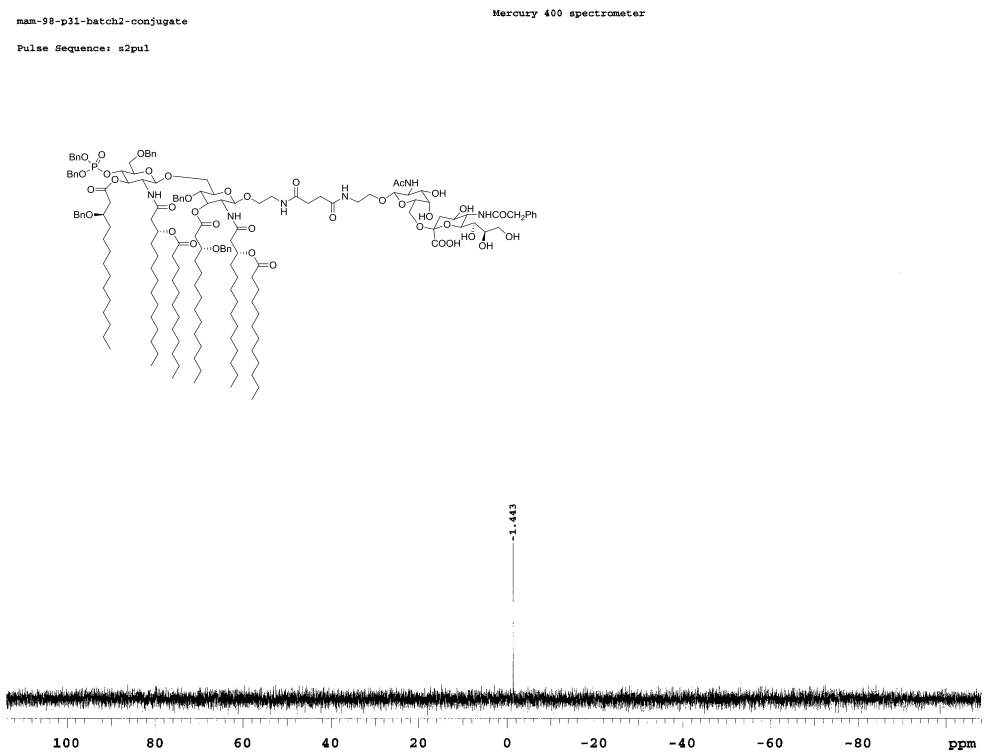
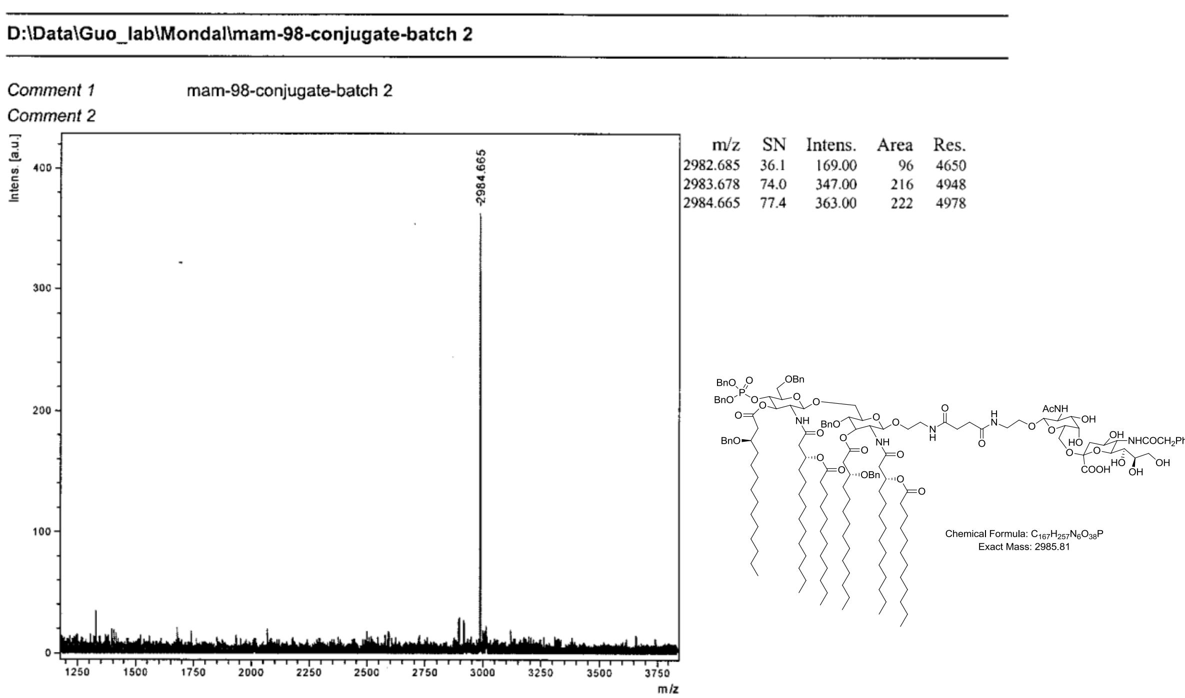
2	16136.5	128.470	18.
3	16123.9	128.370	37.
4	16120.7	128.344	31.
5	16105.3	128.222	25.
6	16096.0	128.148	28.
7	16088.6	128.089	26.
8	16081.1	128.029	29.
9	16060.2	127.863	26.
10	16048.1	127.767	45.
11	16029.5	127.618	27.
12	16019.3	127.537	30.
13	16005.8	127.429	34.
14	15990.4	127.307	14.
15	15924.8	126.785	10.
16	12734.0	101.381	7.
17	12667.9	100.855	6.
18	12542.8	99.859	5.
19	9713.9	77.337	4.
20	9523.6	75.822	6.
21	9451.9	75.251	9.
22	9444.0	75.188	11.
23	9384.5	74.714	6.
24	9322.6	74.222	4.
[illegible]	[illegible]	[illegible]	[illegible]

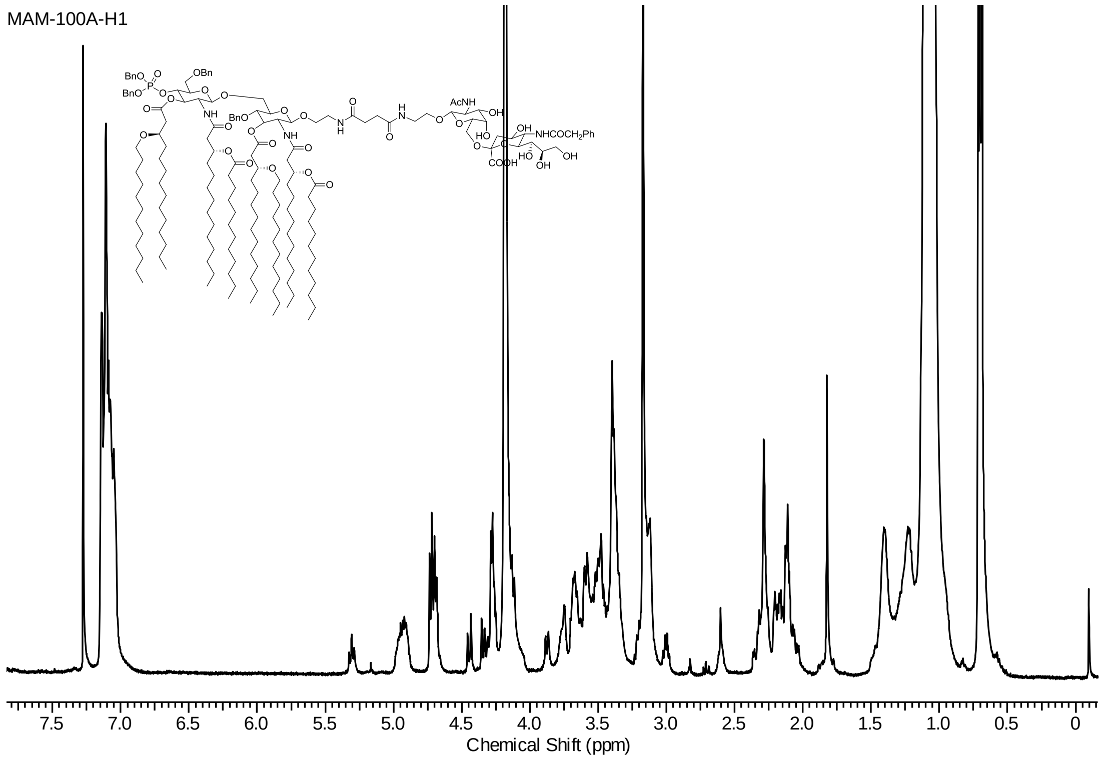
^{13}C DEPT NMR spectrum of **45** ($CDCl_3$, 100 MHz)



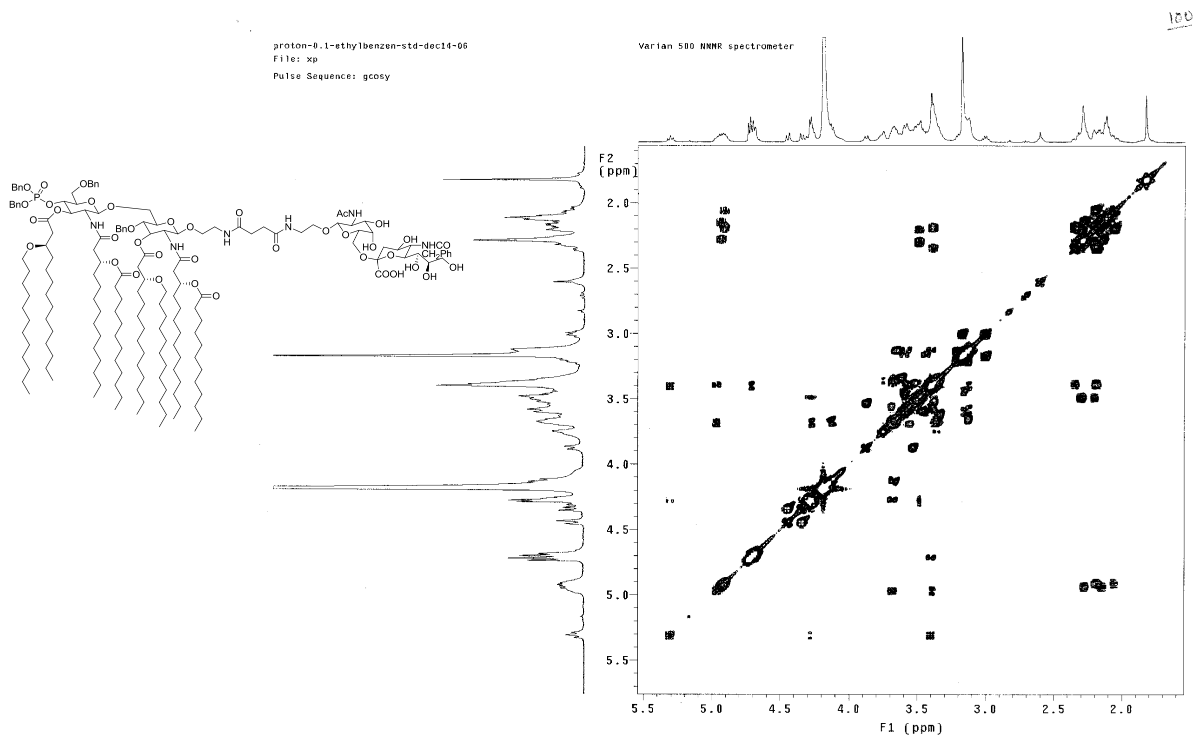
^{31}P NMR spectrum of **45** ($CDCl_3$, 161 MHz)



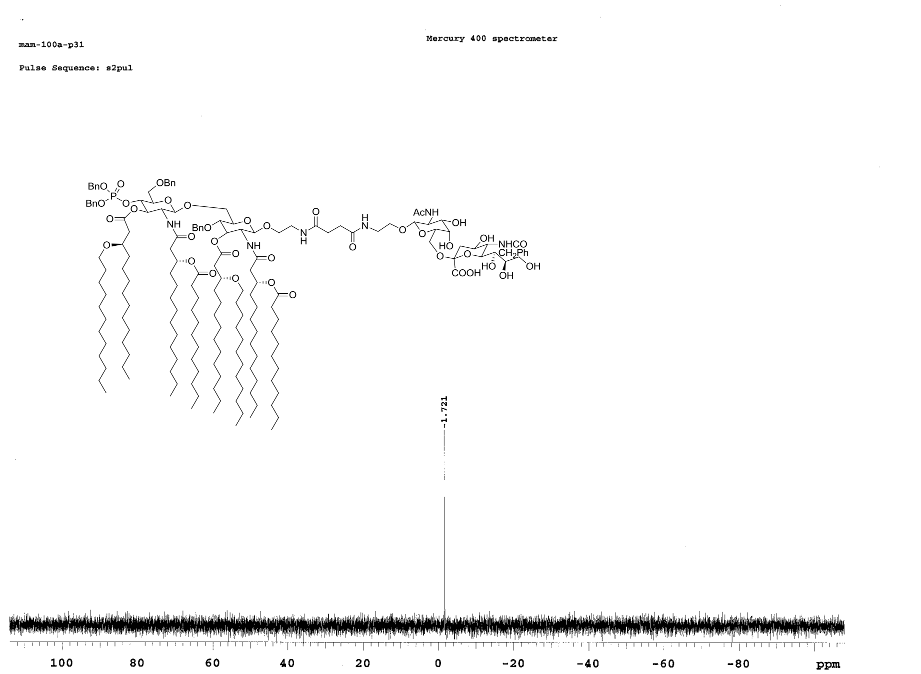
MALDI-TOF MS spectrum of **45** (negative mode)



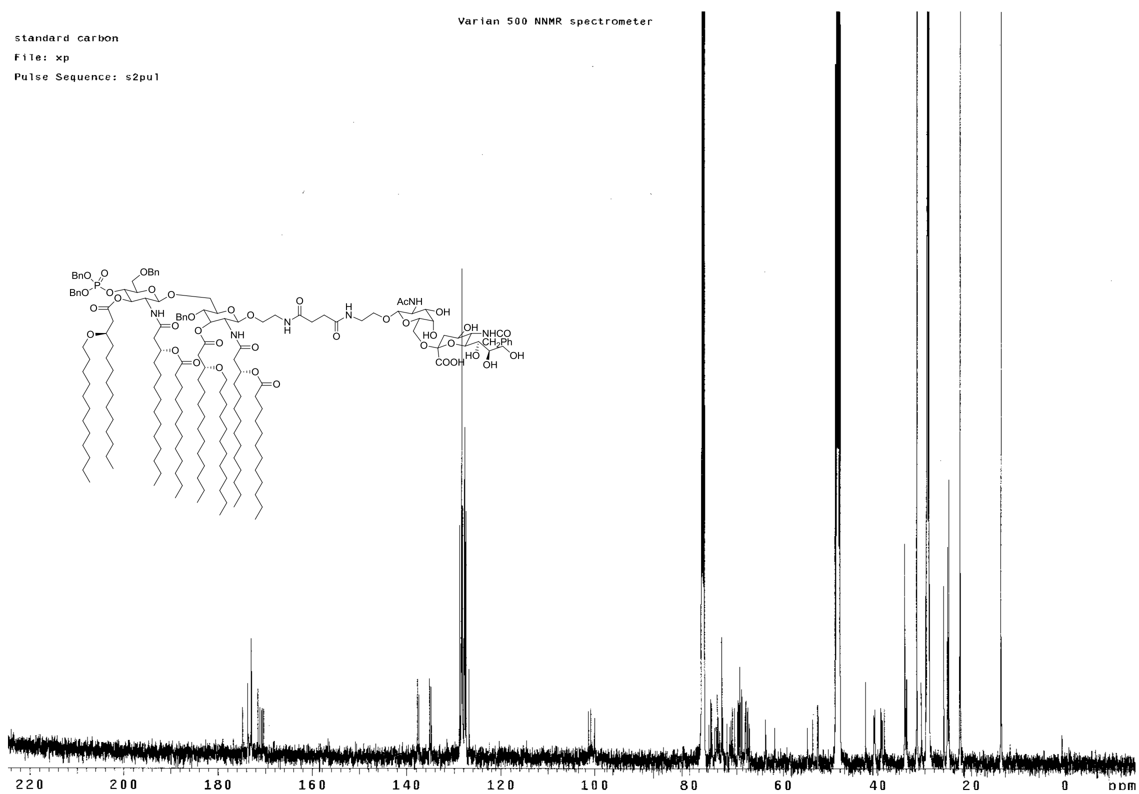
^{1}H NMR spectrum of **46** ($CDCl_3$, 500 MHz)



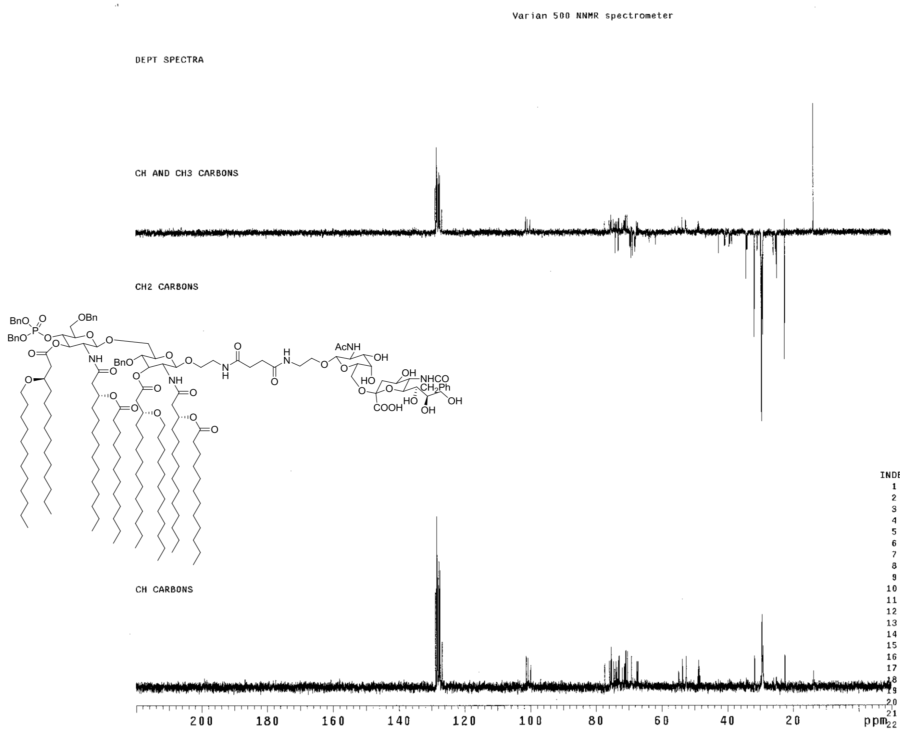
^{1}H-^{1}H COSY NMR spectrum of **46** ($CDCl_3$, 500 MHz)



^{31}P NMR spectrum of **46** ($CDCl_3$, 161 MHz)



^{13}C NMR spectrum of **46** ($CDCl_3$, 100 MHz)



INDEX	FREQUENCY	PPM	HEIGH
1	16175.6	128.781	24.
2	16138.4	128.485	25.
3	16123.5	128.367	45.
4	16104.9	128.218	28.
5	16095.6	128.144	28.
6	16055.6	127.826	26.
7	16046.3	127.752	33.
8	16037.0	127.678	27.
9	16004.9	127.422	30.
10	15926.7	126.800	11.
11	12731.7	101.363	8.
12	12665.6	100.837	7.
13	12560.0	99.996	5.
14	9713.4	77.333	6.
15	9528.2	75.859	6.
16	9475.7	75.440	10.
17	9453.8	75.266	10.
18	9372.9	74.622	6.
19	9277.5	73.862	6.
20	9186.3	73.137	6.
21	9158.4	72.914	8.
22	8937.9	71.159	6.
23	8901.1	70.866	9.
24	8843.0	70.403	9.
[illegible]	[illegible]	[illegible]	[illegible]

^{13}C DEPT spectrum of **46** ($CDCl_3$, 100 MHz)

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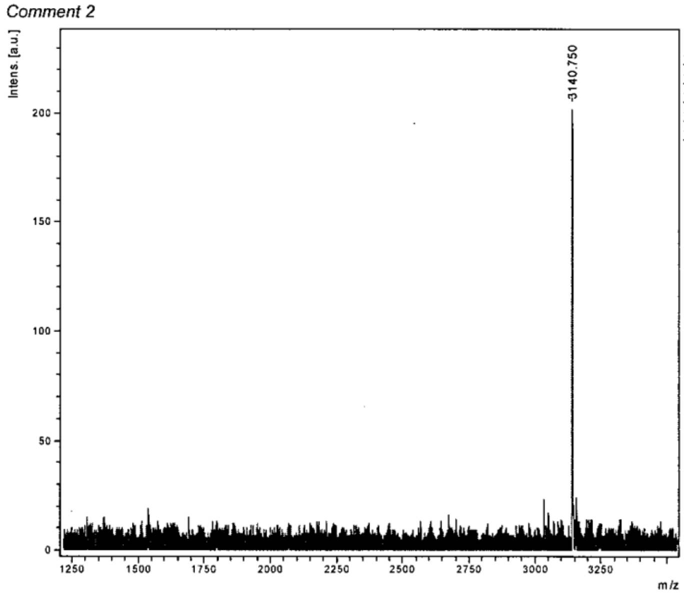
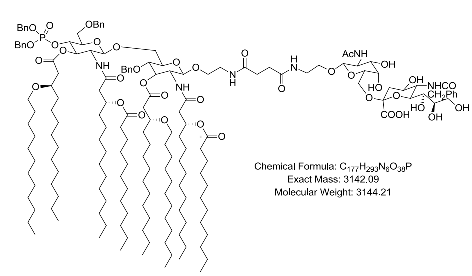
Comment 1 mam-100-conjugate2

Comment 2

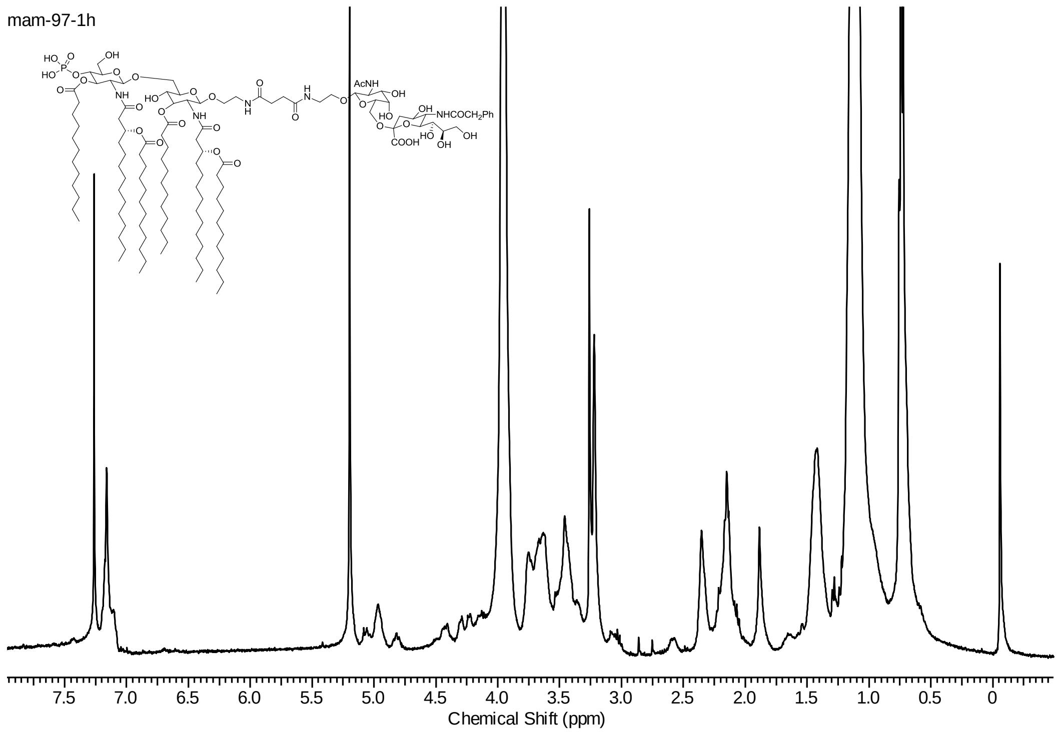


m/z	SN	Intens.	Area	Res.
3138.872	17.2	78.00	45	4901
3139.808	38.1	173.00	128	4382
3140.750	44.5	202.00	157	1214
3141.698	34.6	157.00	126	2844
3142.643	24.9	113.00	76	4267

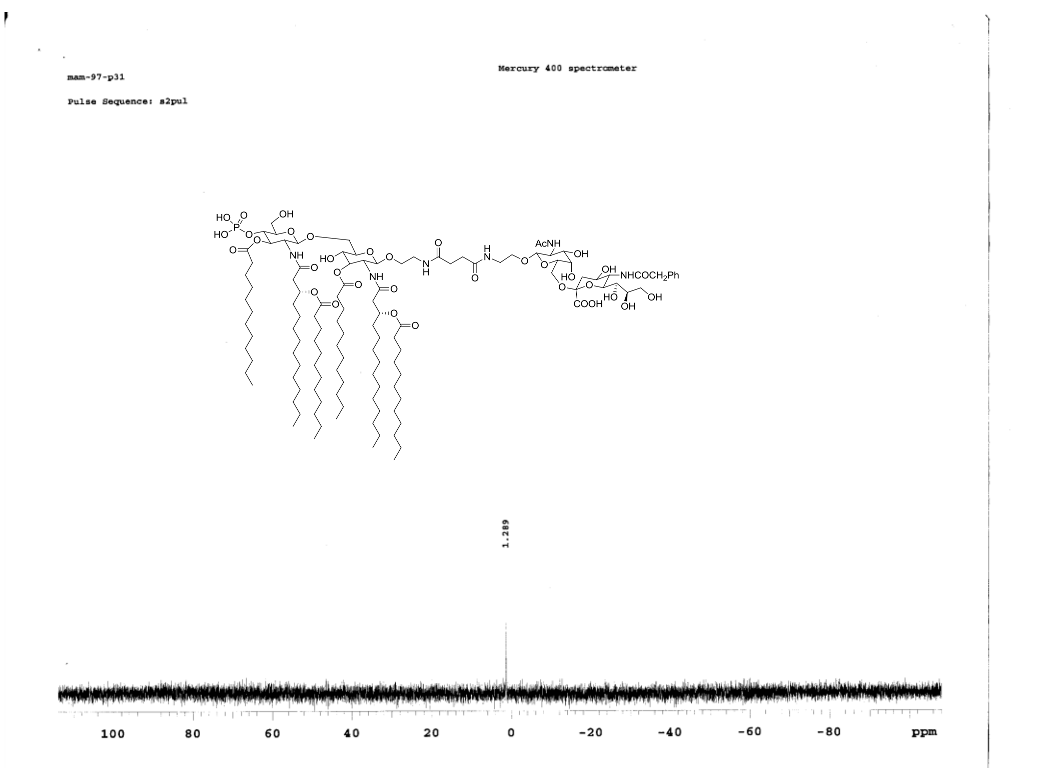


Chemical Formula: $C_{177}H_{293}N_6O_{38}P$
Exact Mass: 3142.09
Molecular Weight: 3144.21

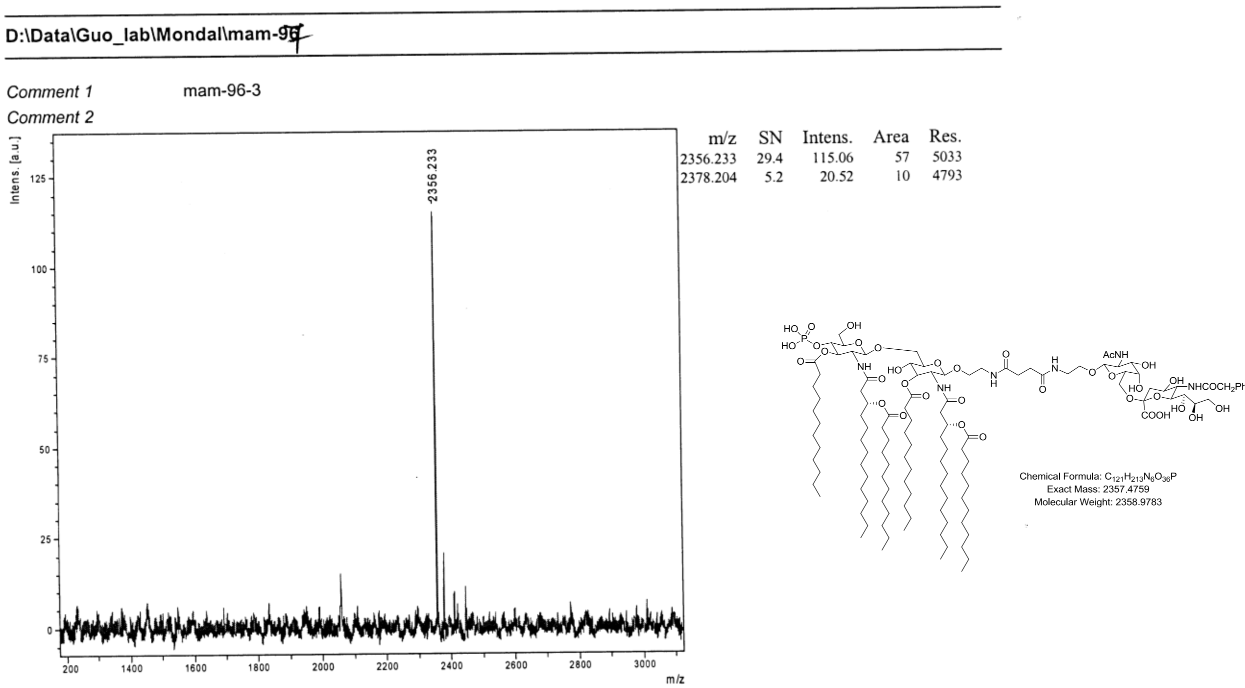
MALDI-TOF MS spectrum of **46** (negative mode)



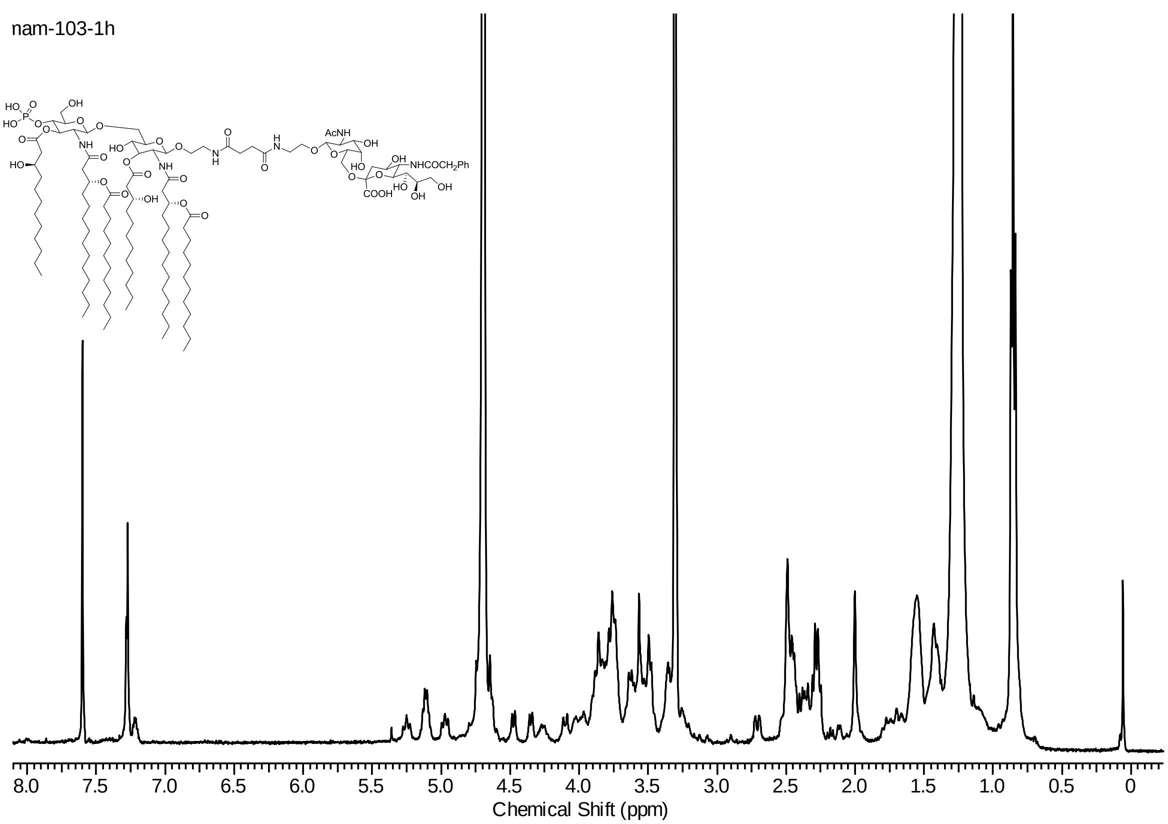
^{1}H NMR spectrum of **3** ($CDCl_3$ and CD_3OD 1:1, 500 MHz)



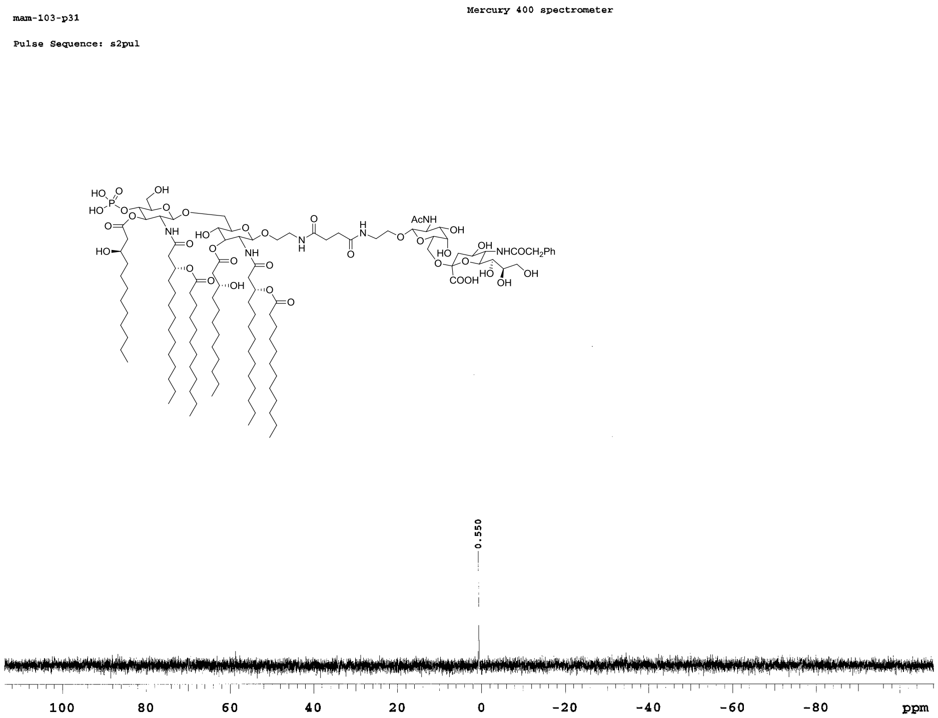
^{31}P NMR spectrum of **3** ($CDCl_3$ and CD_3OD 1:1, 161 MHz)



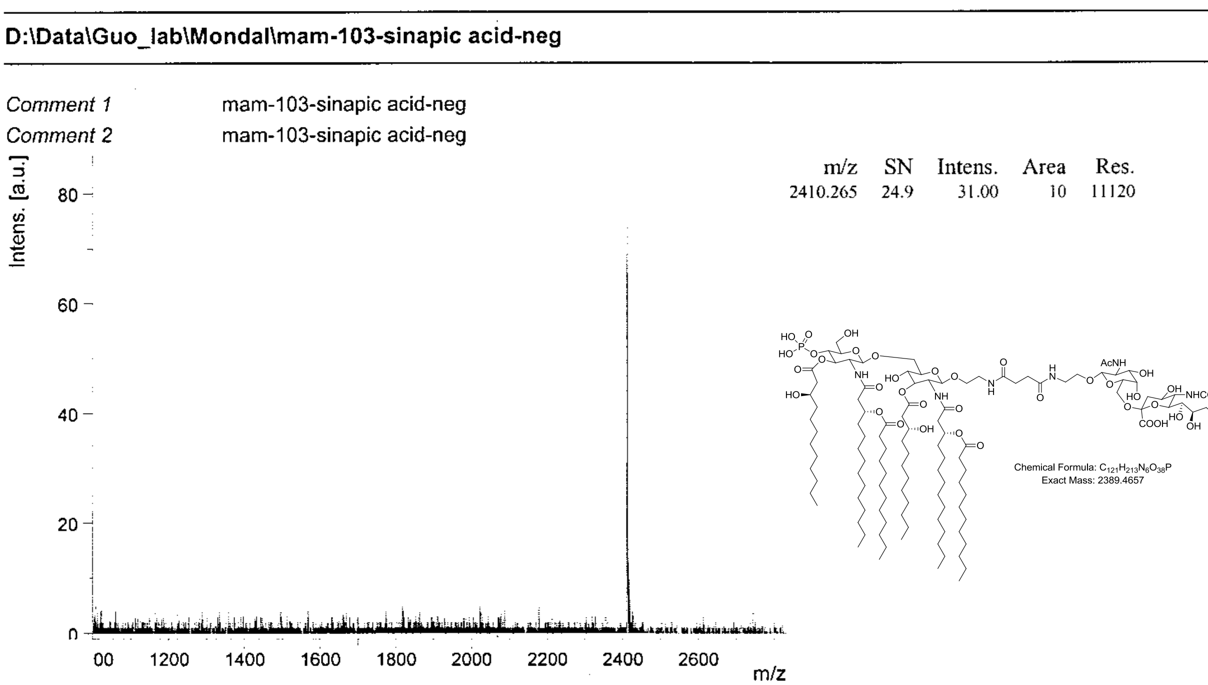
MALDI-TOF MS spectrum of **3** (negative mode)



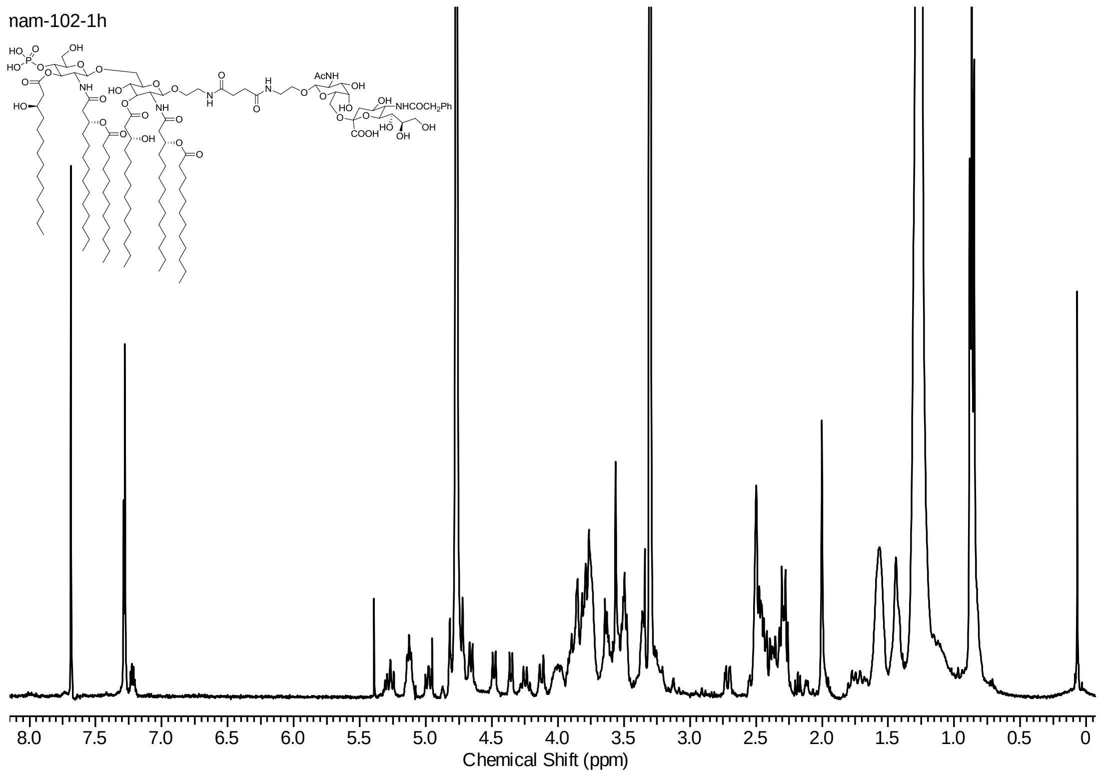
^{1}H NMR spectrum of **4** ($CDCl_3$ and CD_3OD 1:1, 500 MHz)



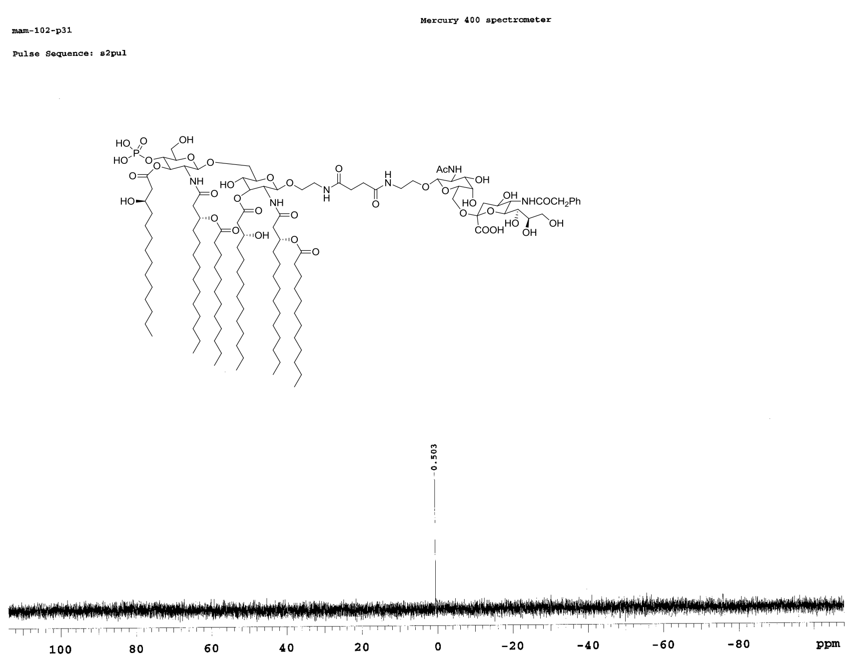
^{31}P NMR spectrum of **4** ($CDCl_3$ and CD_3OD 1:1, 161 MHz)



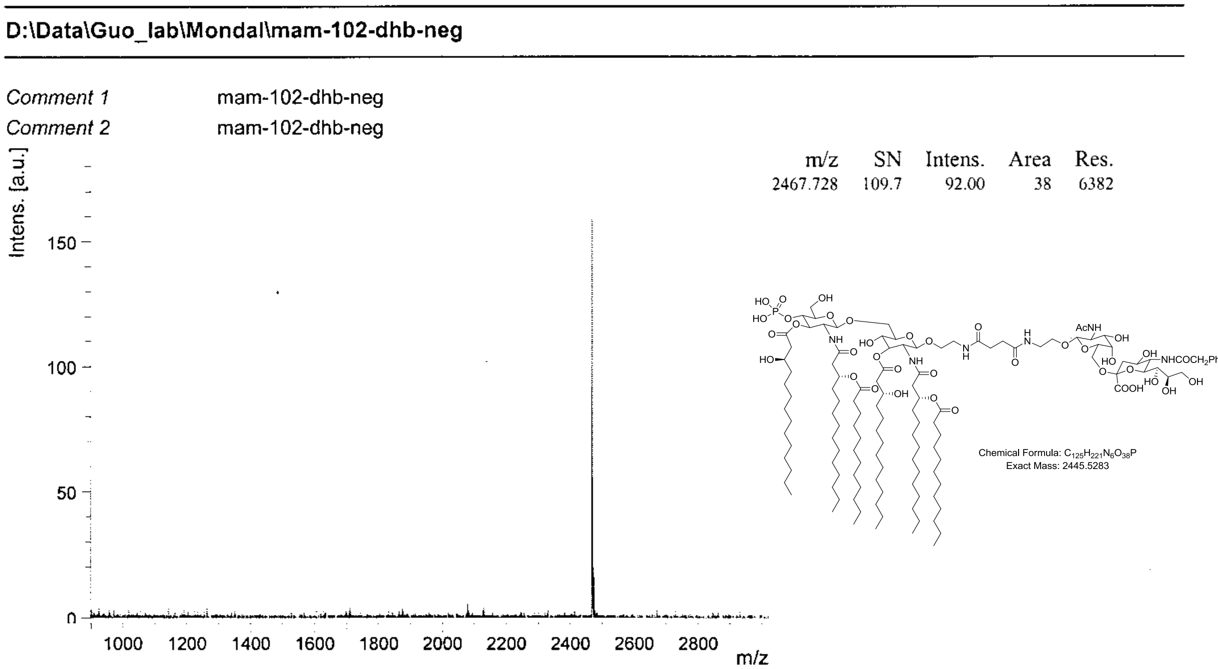
MALDI-TOF MS spectrum of **4** (negative mode)



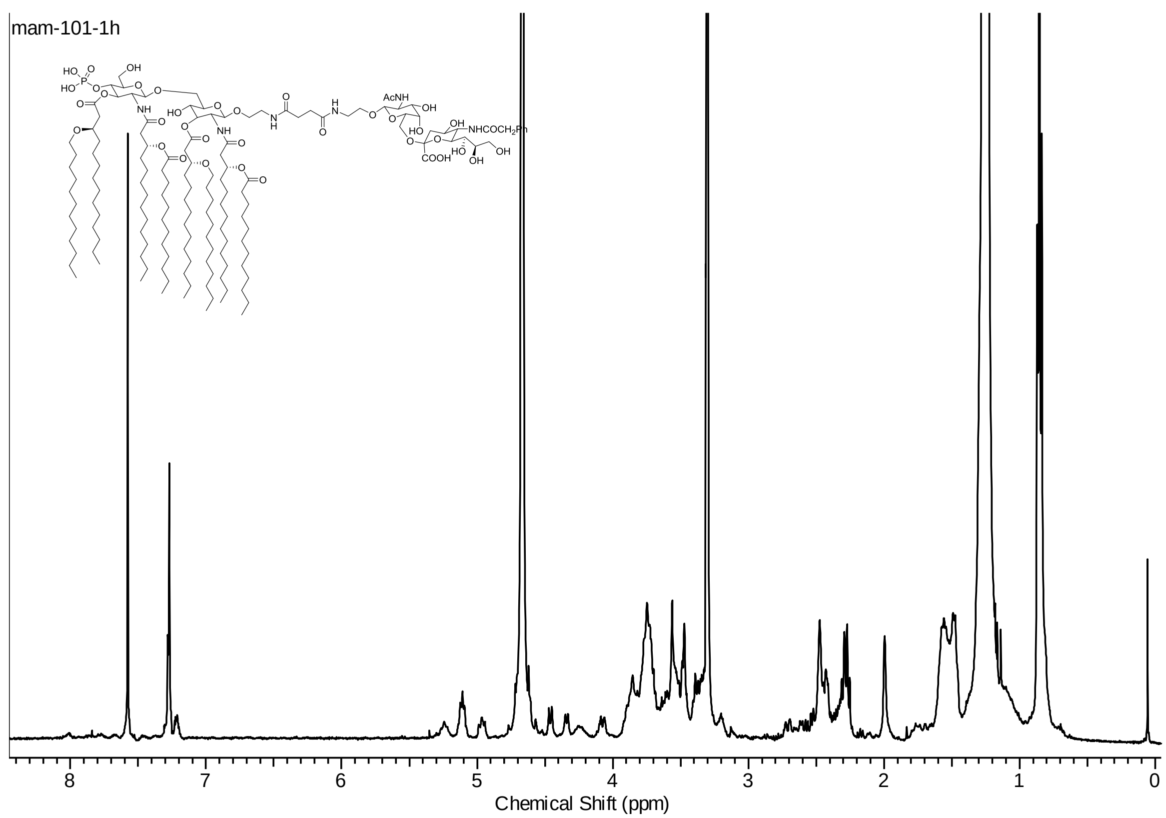
[1]H NMR spectrum of **5** ($CDCl_3$ and CD_3OD 1:1, 500 MHz)



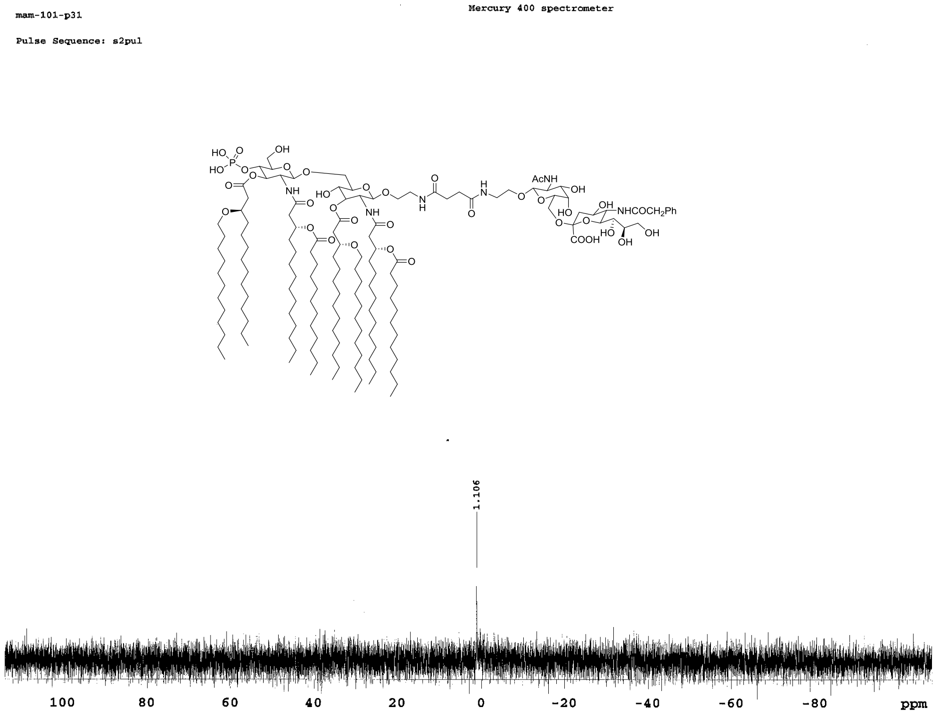
[31]P NMR spectrum of **5** ($CDCl_3$ and CD_3OD 1:1, 161 MHz)



MALDI-TOF MS spectrum of **5** (negative mode)



[1]H NMR spectrum of **6** ($CDCl_3$ and CD_3OD 1:1, 500 MHz)



^{31}P NMR spectrum of **6** ($CDCl_3$ and CD_3OD 1:1, 161 MHz)

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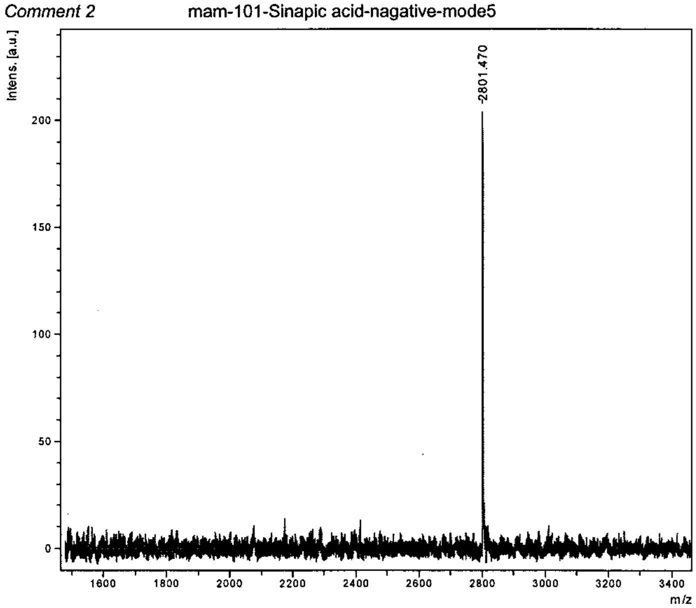
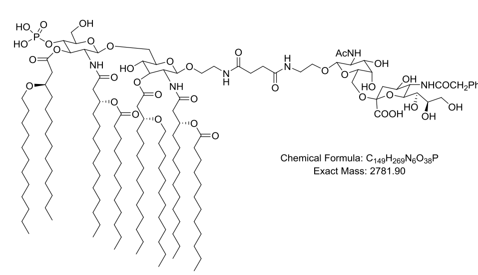
Comment 1 mam-101-Sinapic acid-nagative-mode5
Comment 2 mam-101-Sinapic acid-nagative-mode5



m/z	SN	Intens.	Area	Res.
2800.477	18.9	112.47	64	5304
2801.470	34.3	204.09	116	5277
2802.469	28.5	169.88	106	4924
2803.456	19.0	112.96	63	5112



MALDI-TOF MS spectrum of **6** (negative mode)