Molecular recognition of Brucella A and M antigens dissected by synthetic oligosaccharide glycoconjugates leads to a disaccharide diagnostic for brucellosis

N. Vijaya Ganesh[1], Joanna M. Sadowska[1], Susmita Sarkar[1], Laurence Howells[2], John McGiven[2] and David R. Bundle*[1]

1 Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

[2]FAO/WHO Collaborating Centre for Brucellosis, OIE Brucellosis Reference Centre, Department of Bacteriology, Animal Health and Veterinary Laboratories Agency, Woodham Lane, Addlestone, Surrey, United Kingdom, KT15 3NB.

Email: dave.bundle@ualberta.ca

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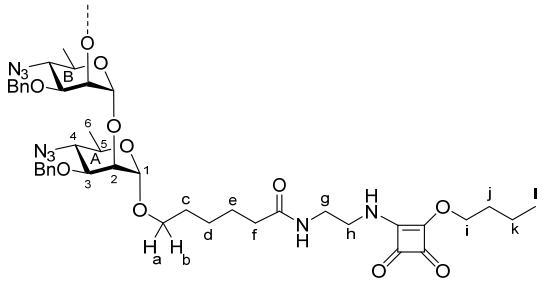
I. GENERAL INFORMATION

Materials and Methods

Analytical TLC was performed on Silica Gel 60-F_{254} (Merck, Darmstadt) with detection by quenching of fluorescence and/or by charring with 10% sulfuric acid in ethanol. All commercial reagents were used as supplied. Column chromatography was performed on Silica Gel 230-400 mesh, 60 Å (Silicycle, Ontario) with HPLC quality solvents. Bovine Serum Albumin (purchased from Sigma Aldrich) and Tetanus toxoid (purchased from STATENS SERUM INSTITUT, Denmark) was used. Molecular sieves (3 Å or 4 Å), were crushed and stored in an oven at 150 °C after activation at 500 °C for 48 h and dried under vacuum before use. Organic solutions were dried with anhydrous $MgSO_4$ prior to concentration under vacuum at <40 ^oC (bath). All final compounds were purified by reverse phase chromatography performed on a Waters 600 HPLC system, using a Beckmann semi-preparative C-18 column (10 x 250 mm, 5 μ) with a combination of acetonitrile and water as eluents. Products were detected with a Waters 2487 UV detector. Optical rotations were measured with a Perkin-Elmer 241 polarimeter for samples in a 10 cm cell at 22 ± 2 ^oC. $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. ^1H NMR spectra were recorded on 500, 600 or 700 MHz spectrometers. First order proton chemical shifts δ_H are referenced to either residual $CHCl_3$ (δ_H 7.26, $CDCl_3$) or CD_2HOD (δ_H 3.30, CD_3OD), or external acetone (δ_H 2.225, D_2O). The assignment of resonances for all compounds was made by two-dimensional homonuclear and for a limited subset also by heteronuclear chemical shift correlation experiments. Specifically for mono- to trisaccharides: peak assignments were based on 2D-^1H-^1H-gCOSY experiments. Peak assignments for tetra- to hexasaccharides were based on 2D-^1H-^1H-gCOSY, selective 1D-^1H-CSSF-TOCSY (Chemical Shift Selective Filter - TOCSY) experiments and selective 1D-ROESY experiments. Mass analysis was performed by positive-mode electrospray ionization on a hybrid sector-TOF mass spectrometer and for protein glycoconjugates by MALDI mass analysis, employing sinapinic acid as matrix.

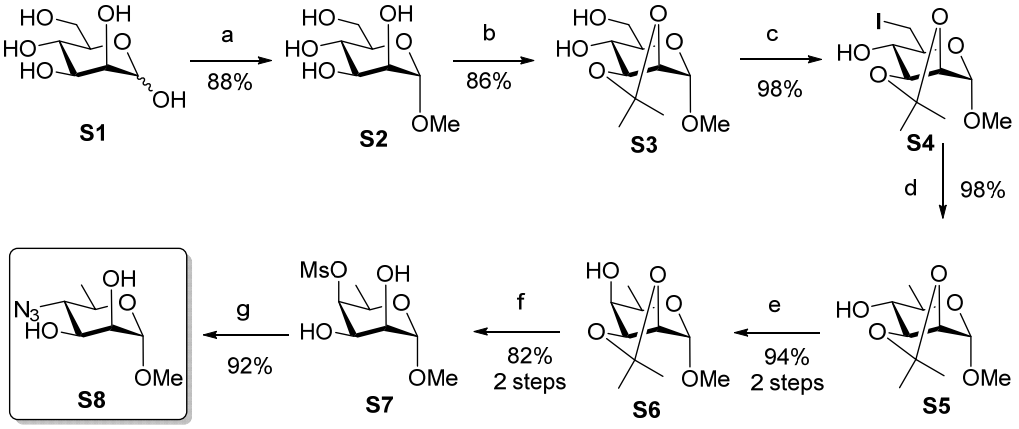
The numbering used for resonance assignments was as follows:



II. SYNTHESIS OF RHAMNOSIDE BUILDING BLOCK

Synthesis of Methyl 4-azido-4,6-dideoxy-α-D-mannopyranoside (S8)

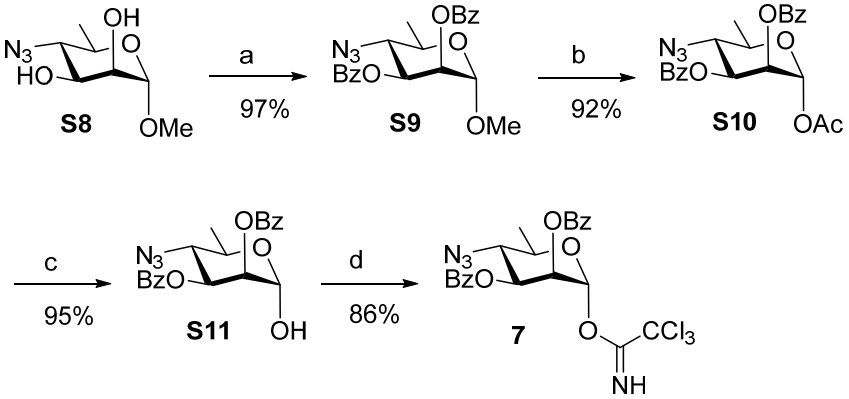
The key precursor **S8** was prepared according to scheme 1S and analytical data for the title compound was essentially the same as previously described.[1]



Scheme 1S. Conditions: a) AcCl, MeOH, 70 ^{o}C, 6h; b) DMP, PTSA, rt, H_2O, 4h; c) PPh_3, Imid, I_2, PhMe, 10 min; d) Pd/C, H_2, rt, EtOH/Et_3N,16h; e) i) OxCl, DMSO, DIPEA, CH_2Cl_2, -78 ^{o}C-rt, 16h; ii) $NaBH_4$, EtOH, rt, 2h; f) i) MsCl, Py, 0 ^{o}C-rt, 2h; ii) TFA/H_2O (9:1), CH_2Cl_2, rt, 10 min. g) NaN_3, 15-crown-5, DMF, 100 ^{o}C, 6h.

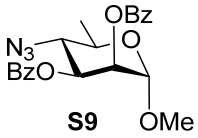
III. SYNTHESIS OF GLYCOSYL DONORS

A. Synthesis of trichloroacetimidate glycosyl donor 7



Scheme 2S: Conditions: a) BzCl, Py, rt, 10 h; b) Ac_2O, AcOH, H_2SO_4, rt, 6 h; c) NH_2NH_2.AcOH, DMF, 60 ^{o}C, 0.5 h; d) CCl_3CN, DBU, CH_2Cl_2, rt, 10 min.

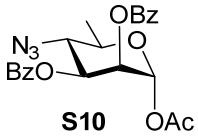
Methyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranoside (S9)[2].



S9

Benzoyl chloride (2.0 mL, 17.2 mmol) was added dropwise to a stirred solution of Methyl 4-azido-4,6-dideoxy-α-D-mannopyranoside **S8** (1.59 g, 7.82 mmol) in pyridine (5 mL) containing DMAP (0.191 g, 1.56 mmol) at 0 ^{o}C. The resulting mixture was stirred under argon for 10 h at 21 ^{o}C. After that, CH_3OH (2 mL) was added to the reaction mixture, stirred for 10 min, then diluted with CH_2Cl_2 (~100 mL) and washed with aq. HCl (1M, 2 x 50 mL), water (100 mL), sat.aq. $NaHCO_3$ (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (3.12 g, 97%) as a white foam. Analytical data for **S9**: R_f = 0.40 (ethyl acetate/hexane, 1/9, v/v); $[\alpha]_D^{21}$ = -130.8 (c = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21-7.31 (m, 10H, H-Ar), 5.60 (dd, 1H, $J_{2,3}$ =1.8 Hz, H-2), 5.59 (dd, 1H, $J_{3,4}$ = 3.6 Hz, H-3), 4.85 (d, 1H, $J_{1,2}$ = 1.2 Hz, H-1), 3.83 (dq, 1H, $J_{4,5}$ = 10.2 Hz, $J_{5,6}$ = 6.0 Hz, H-5), 3.76 (dd, 1H, $J_{4,5}$ = 10.2 Hz, H-4), 3.45 (s, 3H, -OCH_3), 1.48 ppm (d, 3H, $J_{5,6}$ = 6.0 Hz, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.4, 165.3, 133.8, 133.5, 133.3, 130.2, 129.8, 129.8, 129.5, 129.3, 128.6, 128.5, 128.4, 98.6, 71.1, 69.8, 66.9, 63.5, 55.4, 18.6 ppm; HRMS (ESI): *m/z* calcd for $C_{21}H_{21}N_3O_6Na$ $[M+Na]^+$: 434.1323, found: 434.1317.

1-*O*-Acetyl-4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranose (S10).

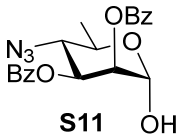


S10

A solution of **S9** (3.10 g, 7.54 mmol) in acetic anhydride/acetic acid/sulfuric acid (50:20:0.5, 70 mL) was stirred at 21 ^{o}C for 6 h, and then poured into ice-cold 1M K_2CO_3 solution (100 mL). The mixture was then diluted with CH_2Cl_2 (~200 mL) and washed with water (2 x 100 mL), sat. aq. $NaHCO_3$ (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (3.04 g, 92%) as a white foam. Analytical data for **S10**: R_f = 0.30 (ethyl acetate/hexane, 1/9, v/v); $[\alpha]_D^{21}$ = -119.8 (c = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ

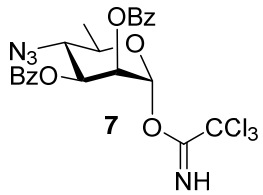
7.35-8.09 (m, 10H, H-Ar), 6.25 (d, J = 1.5 Hz, 1H, H-1), 5.65 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-2), 5.61 (dd, $J_{3,4}$ = 10.1 Hz, 1H, H-3), 3.91 (dq, J = 10.2, 6.2 Hz, 1H, H-5), 3.85 (dd, $J_{4,5}$ = 10.1 Hz, 1H, H-4), 2.24 (s, 3H, -OC-CH_3), 1.51 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.4, 165.4, 165.1, 133.7, 133.5, 129.9, 129.8, 129.1, 129.0, 128.6, 128.5, 90.7, 70.9, 69.4, 68.6, 63.0, 21.0, 18.7 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}N_3O_7Na$ $[M+Na]^+$: 462.1272, found: 462.1265.

4-Azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α/β-D-mannopyranose (S11).



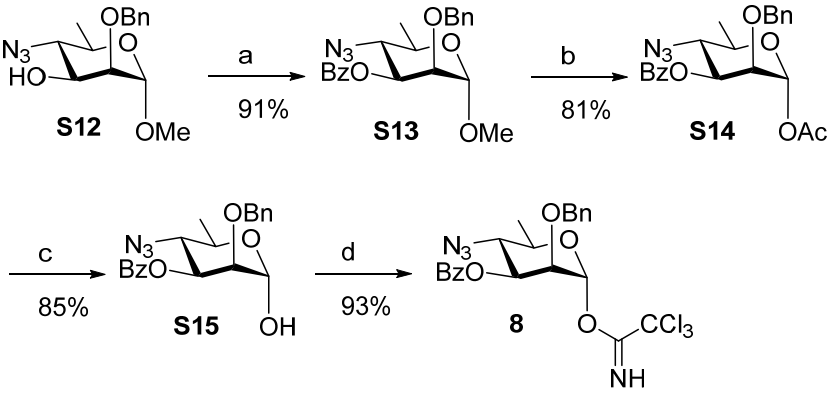
To a stirred solution of **S10** (0.224 g, 0.510 mmol) in DMF (1 mL) was added hydrazine acetate (0.056 g, 0.612 mmol) under argon atmosphere and stirred at 60 °C for 30 min. Then the mixture was cooled to 21 °C, diluted with ethyl acetate (50 mL), washed with water (2 x 50 mL) and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (0.191 g, 95%) as a white foam. Analytical data for **S11**: R_f = 0.30 (ethyl acetate/hexane, 1/4, v/v); ^{1}H NMR (500 MHz, $CDCl_3$): α:β ratio = 7:1; δ 7.11-8.06 (m, 20H, H-Ar), 5.78 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2$_\beta$), 5.66 (dd, $J_{3,4}$ = 10 Hz, 1H, H-3$_\alpha$), 5.63 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2$_\alpha$), 5.36 (dd, $J_{1,2}$ = 1.6 Hz, 1H, H-1$_\alpha$), 5.30 (dd, $J_{3,4}$ = 10.3 Hz, 1H, H-3$_\beta$), 5.07 (dd, $J_{1,2}$ = 1.5 Hz, 1H, H-1$_\beta$), 4.04-4.13 (m, 1H, H-5$_\alpha$), 3.75 (dd, $J_{4,5}$ = 10.1 Hz, 1H, H-4$_\alpha$), 3.70(dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4$_\beta$), 3.64 (d, $J_{1,\text{-OH}}$ = 9.3 Hz, 1H, OH$_\beta$), 3.53 (m, 1H, H-5$_\beta$), 3.14 (d, $J_{1,\text{-OH}}$ = 3.8 Hz, 1H, OH$_\alpha$), 1.52 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6$_\beta$), 1.45 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6$_\alpha$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.1, 165.5, 165.4, 133.8, 133.5, 133.4, 130.0, 129.8 (x2), 129.4, 129.2, 129.0 (x2), 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 92.9, 92.1, 73.3, 71.4, 70.9, 70.8, 70.2, 67.1, 63.6, 62.8, 18.7, 18.6 ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{19}N_3O_6Na$ $[M+Na]^+$: 420.1166, found: 420.1163.

4-Azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl trichloroacetimidate (7).



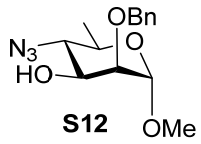
To a stirred solution of **S11** (2.0 g, 5.03 mmol) in CH_2Cl_2 (20 mL) containing CCl_3CN (10.1 mL, 100 mmol), DBU (0.150 mL, 1.00 mmol) was added at 21 ^oC under argon atmosphere. After 10 min, solvents were evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (2.335 g, 86 %) as off-white foam. Analytical data for **7**: R_f = 0.60 (ethyl acetate/hexane, 1/4, v/v); $[\alpha]_D^{21}$ = -101.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.79 (s, 1H, N-*H*), 7.33-8.09 (m, 10H, H-Ar), 6.43 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1), 5.85 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-2), 5.68 (dd, $J_{3,4}$ = 10.5 Hz, 1H, H-3), 4.07 (dq, J = 10.2, 6.2 Hz, 1H, H-5), 3.88 (dd, $J_{4,5}$ = 10.2 Hz, 1H, H-4), 1.53 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.3, 165.1, 160.0, 133.7, 133.5, 129.9, 129.8, 129.1, 129.0, 128.7, 128.5, 94.7, 90.7, 70.9, 69.9, 68.1, 62.9, 18.7 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{19}Cl_3N_4O_6Na$ $[M+Na]^+$: 563.0262, found: 563.0251.

B. Synthesis of trichloroacetimidate glycosyl donor 8



Scheme 3S: Conditions: a) BzCl, Py, rt, 3 h; b) Ac_2O, AcOH, H_2SO_4, rt, 3 h; c) NH_2NH_2.AcOH, DMF, 60 ^oC, 0.5 h; d) CCl_3CN, DBU, CH_2Cl_2, rt, 10 min.

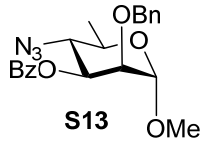
Methyl 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (S12).



S12

Analytical data for the title compound was essentially the same as previously described.[3]

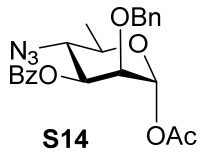
Methyl 4-azido-3-*O*-benzoyl-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (S13).



S13

Benzoyl chloride (0.872 mL, 7.5 mmol) was added dropwise to a stirred solution of **S12** (2.0 g, 6.82 mmol) in pyridine (10 mL) containing DMAP (0.166 g, 1.36 mmol) at 0 ^{o}C. The resulting mixture was stirred under argon for 3 h at 21 ^{o}C. After that, CH_3OH (2 mL) was added to the reaction mixture, stirred for 10 min, then diluted with CH_2Cl_2 (~80 mL) and washed with aq. HCl (1M, 2 x 50 mL), water (100 mL), sat. aq. $NaHCO_3$ (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (2.47 g, 91%) as oil. Analytical data for **S13**: R_f = 0.50 (ethyl acetate/hexane, 1/9, v/v); $[\alpha]_D^{21}$ = -18.8 (c = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13-8.10 (m, 10H, H-Ar), 5.32 (dd, $J_{3,4}$ = 10.4 Hz, 1H, H-3), 4.71 (d, $J_{1,2}$ = 1.4 Hz, 1H, H-1), 4.60 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 3.99 (dd, $J_{2,3}$ = 3.1 Hz, 1H, H-2), 3.81 (dd, $J_{4,5}$ = 10.2 Hz, 1H, H-4), 3.67 (dq, J = 10.2, 6.2 Hz, 1H, H-5), 3.37 (s, 3H, -OCH_3), 1.42 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 137.5, 133.3, 129.9, 129.5, 128.5, 128.3, 127.8 (x2), 98.9, 74.8, 73.3, 73.2, 67.0, 63.2, 55.0, 18.5 ppm; HRMS (ESI): *m/z* calcd for $C_{21}H_{23}N_3O_5Na$ $[M+Na]^+$: 420.1530, found: 420.1521.

1-*O*-Acetyl-4-azido-3-*O*-benzoyl-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranose (S14).

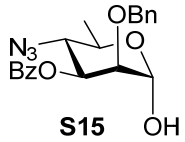


S14

A solution of **S13** (1.40 g, 3.52 mmol) in acetic anhydride/acetic acid/sulfuric acid (50:20:0.5, 35 mL) was stirred at 21 ^{o}C for 3 h, and then poured into ice-cold 1M K_2CO_3 solution (100 mL). The mixture was then diluted with CH_2Cl_2 (~100 mL) and washed with

water (2 x 80 mL), sat. aq. $NaHCO_3$ (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (1.22 g, 81%) as a white foam. Analytical data for **S14**: R_f = 0.30 (ethyl acetate/hexane, 1/9, v/v); $[\alpha]_D^{21}$ = -9.9 (c = 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.10-8.08 (m, 10H, H-Ar), 6.17 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1), 5.29 (dd, $J_{3,4}$ = 10.5 Hz, 1H, H-3), 4.62 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.00 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-2), 3.91 (dd, $J_{4,5}$ = 10.5 Hz, 1H, H-4), 3.78 (dq, J = 10.0, 6.1 Hz, 1H, H-5), 2.15 (s, 3H, -OC-CH_3), 1.42 ppm (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 169.0, 165.6, 136.9, 133.5, 129.9, 129.2, 128.5, 128.4, 128.0, 127.9, 91.1, 73.5, 73.0, 72.7, 69.6, 62.6, 21.0, 18.5 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}N_3O_6Na$ $[M+Na]^+$: 448.1479, found: 448.1471.

4-Azido-3-*O*-benzoyl-2-*O*-benzyl-4,6-dideoxy-α/β-D-mannopyranose (S15).

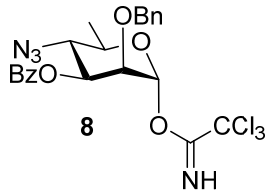


S15

To a stirred solution of **S14** (1.190 g, 2.79 mmol) in DMF (10 mL) was added hydrazine acetate (0.310 g, 3.35 mmol) under argon atmosphere and stirred at 60 °C for 30 min. Then the mixture was cooled to 21 °C, diluted with ethyl acetate (100 mL), washed with water (2 x 80 mL) and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (0. 912 g, 85%) as a white foam. Analytical data for **S15**: R_f = 0.30 (ethyl acetate/hexane, 1/4, v/v); ^{1}H NMR (500 MHz, $CDCl_3$): α:β ratio = 5:1; δ 7.16-8.14 (m, 20H, H-Ar), 5.43 (dd, $J_{3,4}$ = 10.4 Hz, 1H, H-3$_\alpha$), 5.27 (dd, $J_{1,2}$ = 1.8 Hz, $J_{1,\text{-OH}}$ = 3.3 Hz, 1H, H-1$_\alpha$), 5.13 (dd, $J_{3,4}$ = 10.5 Hz, 1H, H-3$_\beta$), 4.72 (dd, J^2 = 11.6 Hz, 2H, CH_2Ph$_\beta$), 4.82 (dd, $J_{1,2}$ = 1.5 Hz, $J_{1,\text{-OH}}$ = 11.6 Hz, 1H, H-1$_\beta$), 4.63 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph$_\alpha$), 4.14 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2$_\beta$), 4.06 (dd, $J_{2,3}$ = 3.1 Hz, 1H, H-2$_\alpha$), 3.97 (dq, J = 10.0, 6.1 Hz, 1H, H-5$_\alpha$), 3.83 (dd, $J_{4,5}$ = 10.5 Hz, 1H, H-4$_\alpha$), 3.77 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4$_\beta$), 3.58 (d, $J_{1,\text{-OH}}$ =11.6 Hz, 1H, -OH$_\beta$), 3.40 (dq, J = 10.0, 6.2 Hz, 1H, H-5$_\beta$), 2.83 (d, $J_{1,\text{-OH}}$ = 3.5 Hz, 1H, -OH$_\alpha$), 1.46 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6$_\beta$), 1.42 ppm (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6$_\alpha$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6 (x2), 137.4, 137.1, 133.8, 133.4, 129.9, 129.5, 128.9, 128.7, 128.5, 128.3 (x2), 128.2, 127.9, 127.8, 93.2, 92.7, 76.3,

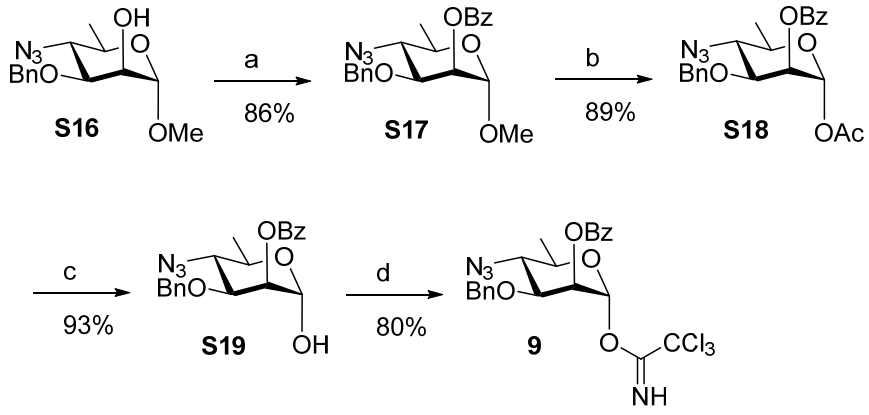
75.8, 75.7, 75.0, 73.3, 72.9, 70.9, 67.2, 63.2, 62.6, 18.6, 18.5 ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}N_3O_5Na$ $[M+Na]^+$: 406.1373, found: 406.1366.

4-Azido-3-*O*-benzoyl-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl trichloroacetimidate (8).



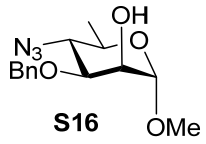
To a stirred solution of **S15** (0.890 g, 2.32 mmol) in CH_2Cl_2 (15 mL) containing CCl_3CN (4.65 mL, 46.4 mmol), DBU (70 µL, 0.464 mmol) was added at 21 °C under argon atmosphere. After 10 min, solvents were evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (1.136 g, 93 %) as off-white foam. Analytical data for **8**: R_f = 0.80 (ethyl acetate/toluene, 1/9, v/v); $[\alpha]_D^{21}$ = -7.3 (c = 1.5, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (s, 1H, -C=N*H*), 7.12-8.10 (m, 10H, H-Ar), 6.36 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1), 5.39 (dd, $J_{3,4}$ = 7.2 Hz, 1H, H-3), 4.67 (dd, J^2 = 12.0 Hz, 2H, C*H*$_2$Ph), 4.26 (dd, $J_{2,3}$ = 3.1 Hz, 1H, H-2), 3.91-3.99 (m, 2H, H-4, H-5), 1.48 ppm (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.5, 160.4, 137.0, 133.5, 129.9, 129.2, 128.5, 128.4, 128.0 (x2), 127.9, 95.3, 90.8, 73.2, 73.0, 72.8, 70.1, 62.5, 18.6 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}Cl_3N_4O_5Na$ $[M+Na]^+$: 549.0470, found: 549.0465.

C. Synthesis of trichloroacetimidate glycosyl donor 9



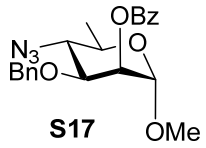
Scheme 4S: Conditions: a) BzCl, Py, rt, 3 h; b) Ac_2O, AcOH, H_2SO_4, rt, 3 h; c) NH_2NH_2.AcOH, DMF, 60 °C, 0.5 h; d) CCl_3CN, DBU, CH_2Cl_2, rt, 10 min.

Methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (S16).



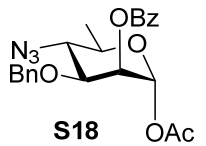
Analytical data for the title compound was essentially the same as previously described.[1a]

Methyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (S17).



Benzoyl chloride (0.872 mL, 7.5 mmol) was added dropwise to a stirred solution of **S16** (2.0 g, 6.82 mmol) in pyridine (10 mL) containing DMAP (0.166 g, 1.36 mmol) at 0 ^{o}C. The resulting mixture was stirred under argon for 3 h at 21 ^{o}C. After that, CH_3OH (2 mL) was added to the reaction mixture, stirred for 10 min, then diluted with CH_2Cl_2 (~80 mL) and washed with aq. HCl (1M, 2 x 50 mL), water (100 mL), sat. aq. $NaHCO_3$ (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (2.32 g, 86%) as a white foam. Analytical data for **S17**: R_f = 0.50 (ethyl acetate/hexane, 1/9, v/v); $[\alpha]_D^{21}$ = -27.9 (c = 1.7, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21-8.10 (m, 10H, H-Ar), 5.55 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 4.77 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1), 4.66 (dd, J^2 = 11.5 Hz, 2H, CH_2Ph), 3.91 (dd, $J_{3,4}$ = 9.7 Hz, 1H, H-3), 3.55-3.64 (m, 1H, H-5), 3.51 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4), 3.37 (s, 3H, -OCH_3), 1.38 ppm (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.6, 137.3, 133.3, 129.9, 129.7, 128.4, 128.3, 128.1, 127.8, 98.8, 76.1, 71.4, 67.8, 66.8, 64.3, 55.1, 18.7 ppm; HRMS (ESI): *m/z* calcd for $C_{21}H_{23}N_3O_5Na$ $[M+Na]^+$: 420.1530, found: 420.1528.

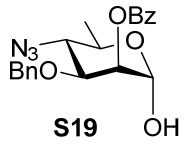
1-*O*-Acetyl-4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α/β-D-mannopyranose (S18).



A solution of **S17** (2.06 g, 5.19 mmol) in acetic anhydride/acetic acid/sulfuric acid (50:20:0.5, 35 mL) was stirred at 21 ^{o}C for 3 h, and then poured into ice-cold 1M K_2CO_3

solution (100 mL). The mixture was then diluted with CH_2Cl_2 (~100 mL) and washed with water (2 x 80 mL), sat. aq. $NaHCO_3$ (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (1.95 g, 89%) as a white foam. α:β ratio = 9:1 (isolated yield); Analytical data for **S18**: α:β ratio = 9:1 (isolated yield); α-anomer: R_f = 0.45 (ethyl acetate/hexane, 1.5/8.5, v/v); $[\alpha]_D^{21}$ = +1.8 (c = 1.9, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-8.09 (m, 10H, H-Ar), 6.16 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1), 5.56 55 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2), 4.70 (dd, J^2 = 11.5 Hz, 2H, CH_2Ph), 3.91 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3), 3.64-3.73 (m, 1H, H-5), 3.58 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4), 2.13 (s, 3H, -OC-CH_3), 1.40 ppm (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3, 165.3, 136.9, 133.5, 129.9, 129.3, 128.5, 128.4, 128.2, 128.0, 91.1, 75.8, 71.6, 69.3, 66.7, 63.8, 20.9, 18.7 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}N_3O_6Na$ $[M+Na]^+$: 448.1479, found: 448.1475; β-anomer: R_f = 0.40 (ethyl acetate/hexane, 1.5/8.5, v/v); $[\alpha]_D^{21}$ = -50.2 (c = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-8.13 (m, 10H, H-Ar), 5.82 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-2), 5.77 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1),4.66 (dd, J^2 = 11.4 Hz, 2H, CH_2Ph), 3.68 (dd, $J_{3,4}$ = 9.7 Hz, 1H, H-3), 3.53 (dd, $J_{4,5}$ = 9.8 Hz, 1H, H-4), 3.34-3.44 (m, 1H, H-5), 2.03 (s, 3H, -OC-CH_3),), 1.46 ppm (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.8, 165.8, 136.6, 133.4, 130.0, 129.5, 128.5 (x2), 128.3, 128.1, 91.2, 78.1, 72.1, 71.4, 66.8, 63.6, 20.8, 18.6 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{23}N_3O_6Na$ $[M+Na]^+$: 448.1479, found: 448.1474.

4-Azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α/β-D-mannopyranose (S19).

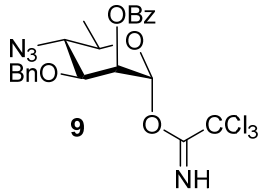


S19

To a stirred solution of **S18** (2.20 g, 5.17 mmol) in DMF (7 mL) was added hydrazine acetate (0.572 g, 6.20 mmol) under argon atmosphere and stirred at 60 °C for 30 min. Then the mixture was cooled to 21 °C, diluted with ethyl acetate (100 mL), washed with water (2 x 80 mL) and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (1.83 g, 93%) as a white foam. Analytical data for **S19**: R_f = 0.30 (ethyl acetate/hexane, 1/4, v/v); ^{1}H NMR (500 MHz, $CDCl_3$): α:β ratio = 5:1; δ 7.25-8.15 (m, 20H, H-Ar), 5.74 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-

2$_\beta$), 5.60 (dd, $J_{2,3}$ = 3.1 Hz, 1H, H-2$_\alpha$), 5.32 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1$_\alpha$), 4.89 (s, 1H, H-1$_\beta$), 4.73 (dd, J^2 = 11.4 Hz, 2H, CH_2Ph$_\beta$), 4.70 (dd, J^2 = 11.4 Hz, 2H, CH_2Ph$_\alpha$), 4.02 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3$_\alpha$), 3.84-3.94 (m, 1H, H-5$_\alpha$), 3.64 (dd, $J_{3,4}$ = 9.7 Hz, 1H, H-3$_\beta$), 3.56 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4$_\alpha$), 3.48 (dd, $J_{4,5}$ = 9.8 Hz, 1H, H-4$_\beta$), 3.33 (m, 1H, H-5$_\beta$), 3.05 (br. s., 2H, -OH$_\alpha$, -OH$_\beta$), 1.47 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6$_\beta$), 1.40 ppm (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6$_\alpha$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3, 165.7, 137.2, 136.8, 133.6, 133.3, 130.0, 129.9, 129.6, 129.2, 128.5, 128.4 (x2), 128.3, 128.2, 128.0, 127.8, 93.2, 92.5, 78.5, 75.6, 71.5 (x2), 71.3, 69.2, 68.2, 67.1, 64.3, 63.7, 18.7 (x2) ppm; HRMS (ESI): *m/z* calcd for $C_{20}H_{21}N_3O_5Na$ $[M+Na]^+$: 406.1373, found: 406.1374.

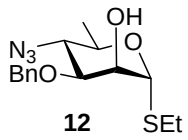
4-Azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl trichloroacetimidate (9).



To a stirred solution of **S19** (1.820 g, 4.75 mmol) in CH_2Cl_2 (20 mL) containing CCl_3CN (9.50 mL, 95.0 mmol), DBU (140 μL, 0.95 mmol) was added at 21 ^oC under argon atmosphere. After 10 min, solvents were evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (ethyl acetate – hexane gradient elution) to afford the title compound (2.0 g, 80%) as off-white foam. Analytical data for **9**: R_f = 0.60 (ethyl acetate/hexane, 1/4, v/v); $[\alpha]_D^{21}$ = -10.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1H, -C=N*H*), 7.28-8.12 (m, 10H, H-Ar), 6.31 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1), 5.67 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-2), 4.70 (dd, J^2 = 11.4 Hz, 2H, CH_2Ph), 3.98 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3), 3.73-3.84 (m, 1H, H-5), 3.57-3.66 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4), 1.38-1.44 ppm (d, $J_{5,6}$ = 6.5 Hz, 3H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.3, 159.8, 136.7, 133.5, 129.9, 129.3, 128.6 (x3), 128.5 (x2), 128.4, 128.1, 95.0, 90.7, 75.2, 71.6, 69.9, 66.4, 63.7, 18.7 ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{21}Cl_3N_4O_5Na$ $[M+Na]^+$: 549.0470, found: 549.0475.

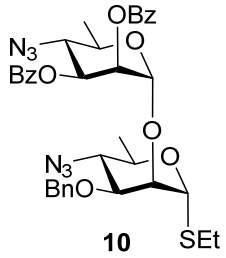
D. Synthesis of thiglycoside donors 10 & 11

Ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-α-D-mannopyranoside (12).



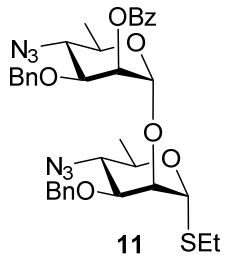
Analytical data for the title compound was essentially the same as previously described.[4]

Ethyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-α-D-mannopyranoside (10).



A mixture of glycosyl donor **7** (1.010 g, 1.87 mmol), glycosyl acceptor **12** (0.550 g, 1.70 mmol), and freshly activated molecular sieves (3 Å, 2.0 g) in CH_2Cl_2 (30 mL) was stirred under argon for 5 h at 21 ^oC. TMSOTf (67 µL, 0.374 mmol) was added and the resulting mixture was stirred for additional 1 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate (~100 mL) was washed with sat. aq. $NaHCO_3$ (50 mL), water (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (1.073 g, 90%) as a white foam. Analytical data for **10**: R_f = 0.70 (ethyl acetate/toluene, 1/9, v/v); $[\alpha]_D^{21}$ = -18.4 (c = 1.1, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.12-8.03 (m, 15H, H-Ar), 5.70 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2^B), 5.62 (dd, $J_{3,4}$ = 10.3 Hz, 1H, H-3^B), 5.24 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^A), 4.98 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^B), 4.67 (dd, J^2 = 12.0 Hz, 2H, C*H*$_2$Ph), 3.93-3.97 (m, 2H, H-2^A, H-5^B), 3.83-3.87 (m, 1H, H-5^A), 3.73 (dd, $J_{4,5}$ = 10.5 Hz, 1H, H-4^B), 3.70 (dd, $J_{3,4}$ = 9.8 Hz, 1H, H-3^A), 3.60 (dd, $J_{4,5}$ = 10.5 Hz, 1H, H-4^A), 2.54-2.67 (m, 2H, S-C*H*$_2$-), 1.44 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^B), 1.37 (d, $J_{5,6}$ = 6.1 Hz, 3H, H-6^A), 1.29 ppm (t, J = 7.4 Hz, 3H, S-CH$_2$-C*H*$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.2, 164.9, 137.4, 133.4, 133.3, 129.8 (x2), 129.5, 129.3, 128.5 (x2), 128.4, 128.1, 127.9, 99.4, 83.3, 78.4, 76.5, 72.4, 70.8, 69.5, 67.8, 67.6, 64.2, 63.5, 25.6, 18.6, 18.4, 14.9 ppm; HRMS (ESI): *m/z* calcd for $C_{35}H_{38}N_6O_8SNa$ $[M+Na]^+$: 725.2364, found: 725.2350.

Ethyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-α-D-mannopyranoside (11).

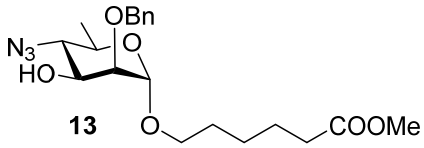


11

A mixture of glycosyl donor **9** (1.980 g, 3.76 mmol), glycosyl acceptor **12** (1.106 g, 3.42 mmol), and freshly activated molecular sieves (3 Å, 4.0 g) in CH_2Cl_2 (30 mL) was stirred under argon for 5 h at 21 ^oC. TMSOTf (0.136 mL, 0.753 mmol) was added and the resulting mixture was stirred for additional 1 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 30 mL). The combined filtrate (~120 mL) was washed with sat. aq. $NaHCO_3$ (50 mL), water (50 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (2.010 g, 85%) as a white foam. Analytical data for **11**: R_f = 0.50 (ethyl acetate/hexane, 1/9, v/v); $[\alpha]_D^{21}$ = +50.0 (c = 1.4, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.21-8.11 (m, 15H, H-Ar), 5.63 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^B), 5.22 (d, $J_{1,2}$ = 1.0 Hz, 1H, H-1^A), 4.95 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1^B), 4.72 (dd, J^2 = 11.4 Hz, 2H, CH_2Ph), 4.67 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 3.91-3.97 (m, 2H, H-2^A, H-3^B), 3.81-3.90 (dq, 1H, $J_{4,5}$ = 9.5 Hz, $J_{5,6}$ = 6.0 Hz, H-5^A), 3.72-3.78 (dq, 1H, $J_{4,5}$ = 10.0 Hz, $J_{5,6}$ = 6.0 Hz, H-5^B), 3.70 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^A), 3.54 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^B), 3.39 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^A), 2.50 - 2.69 (m, 2H, S-CH_2-), 1.37 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^B), 1.33 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^A), 1.28 ppm (t, J = 7.3 Hz, 3H, S-CH_2-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ 165.3, 137.3, 137.1, 133.3, 129.9, 129.7, 128.6, 128.5, 128.4 (x2), 128.2, 128.1, 127.9, 99.6, 83.3, 78.1, 76.6, 75.3, 72.3, 71.4, 67.7, 67.6, 64.4, 64.1, 25.6, 18.7, 18.5, 14.9 ppm; HRMS (ESI): *m/z* calcd for $C_{35}H_{40}N_6O_7SNa$ $[M+Na]^+$: 711.2571, found: 711.2570.

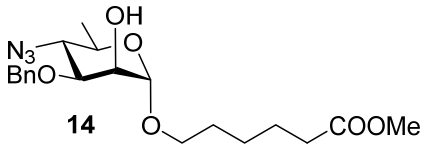
IV. SYNTHESIS OF OLIGOSACCHARIDES 1-6

5'-Methoxycarbonylpentyl 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (13).



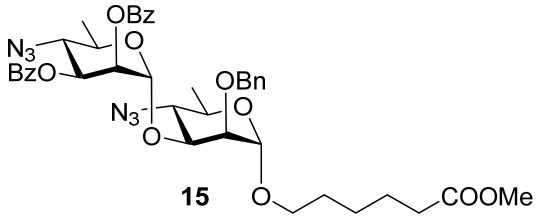
Analytical data for the title compound was essentially the same as previously described.[3b]

5'-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (14).



Analytical data for the title compound was essentially the same as previously described.[5]

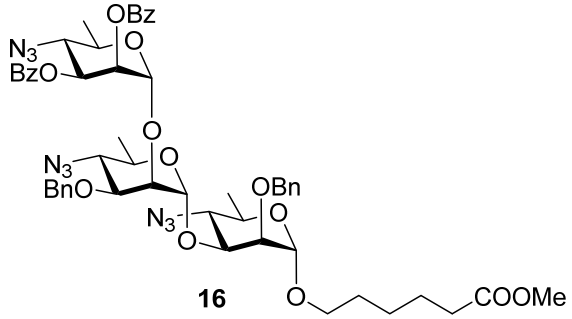
5'-Methoxycarbonylpentyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (15).



A mixture of glycosyl donor **7** (0.292 g, 0.540 mmol), glycosyl acceptor **13** (0.200 g, 0.491 mmol) and freshly activated molecular sieves (3 Å, 0.6 g) in CH_2Cl_2 (8 mL) was stirred under argon for 5 h at 21 ^oC. TMSOTf (20 μL, 0.108 mmol) was added and the resulting mixture was stirred for additional 1 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate (80 mL) was washed with sat. aq. $NaHCO_3$ (40 mL), water (30 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.374 g, 97%) as a white foam. Analytical data for **15**: R_f = 0.40 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = -41.2 (c = 1.6, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29-8.06 (m, 15H, H-Ar), 5.72 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2^B), 5.66 (dd, $J_{3,4}$ = 10.3 Hz, 1H, H-3^B), 5.29 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^B), 4.82 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^A), 4.73 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 3.95 (dd, $J_{3,4}$ = 10.1 Hz, 1H, H-3^A), 3.88 (dq, J = 10.0, 6.1 Hz, 1H, H-5^B),

3.76 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^{B}), 3.72 (dd, $J_{2,3}$ = 3.1 Hz, 1H, H-2^{A}), 3.68 (dd, $J_{4,5}$ = 10.2 Hz, 1H, H-4^{A}), 3.66 (s, 3H, -OCH_3), 3.63 (dt, J = 9.6, 6.7 Hz, 1H, -O-CH_{2a}-), 3.52 (dq, J = 10.2, 6.2 Hz, 1H, H-5^{A}), 3.36 (dt, J = 9.6, 6.5 Hz, 1H, -O-CH_{2b}-), 2.31 (t, J = 7.8 Hz, 2H, -CH_{2f}-), 1.61-1.66 (m, 2H, -CH_{2e}-), 1.52 - 1.59 (m, 2H, -CH_{2c}-), 1.37 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^{B}), 1.36 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^{A}), 1.32-1.36 ppm (m, 2H, -CH_{2d}-); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.2, 165.1, 137.6, 133.5, 133.3, 129.8, 129.4, 129.3, 128.6, 128.5, 128.4, 127.9, 127.6, 99.2, 97.0, 78.6, 72.5, 70.7, 70.0, 67.7, 67.6 (x2), 64.7, 63.4, 51.5, 33.9, 29.0, 25.7, 24.6, 18.6, 18.5 ppm; HRMS (ESI): *m/z* calcd for $C_{40}H_{46}N_6O_{11}Na$ $[M+Na]^+$: 809.3117, found: 809.3107.

5'-Methoxycarbonylpentyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (16).



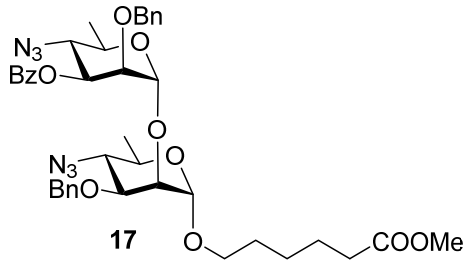
MeOTf-promoted glycosylation. A mixture of glycosyl donor **10** (0.151 g, 0.216 mmol), glycosyl acceptor **13** (0.080 g, 0.196 mmol) and freshly activated molecular sieves (3 Å, 0.5 g) in CH_2Cl_2 (4 mL) was stirred under argon for 5 h at 21 ^{o}C. MeOTf (133 μL, 1.17 mmol) was added and continued stirring for additional 48 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate (70 mL) was washed with sat. aq. $NaHCO_3$ (40 mL), water (30 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.182 g, 89%) as a white foam. Analytical data for **16**: R_f = 0.40 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = -27.7 (c = 2.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.06-8.01 (m, 20H, H-Ar), 5.71 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2^{C}), 5.58 (dd, $J_{3,4}$ = 10.4 Hz, 1H, H-3^{C}), 5.07 (s, 2H, H-1^{B}, H-1^{C}), 4.78 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^{A}), 4.65 (dd, J^2 = 12.0 Hz, 4H, CH_2Ph), 4.17 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^{B}), 3.86-3.92 (m, 2H, H-3^{A}, H-5^{C}), 3.77 - 3.81 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3^{B}), 3.72 (dd, $J_{4,5}$ = 10.1 Hz, 1H, H-4^{C}), 3.68 (s, 3H, -

OCH_3), 3.66 (dd, $J_{2,3}$ = 2.8 Hz, 1H, H-2^A), 3.55 - 3.64 (m, 4H, H-4^A, H-4^B, H-5^B, -O-CH_{2a}-), 3.46-3.54 (dq, J = 10.5, 6.0 Hz, 1H, H-5^A), 3.36 (dt, J = 9.7, 6.5 Hz, 1H, -O-CH_{2b}-), 2.33 (t, J = 7.5 Hz, 2H, -CH_{2f}-), 1.65 (quin, J = 7.6 Hz, 2H, -CH_{2e}-), 1.57 (quin, J = 7.1 Hz, 2H, -CH_{2c}-), 1.46 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^C). 1.35-1.39 (m, 2H, -CH_{2d}-), 1.34 (d, $J_{5,6}$ = 6.5 Hz, 3H, H-6^B), 1.32 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^A); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.2, 164.9, 137.6, 137.4, 133.4, 133.2, 129.8, 129.7, 129.5, 129.3, 128.5 (x2), 128.4, 128.2, 127.9, 127.8, 127.7, 127.6, 101.0, 99.2, 97.0, 78.2, 77.8, 73.4, 72.6, 72.1, 70.9, 69.3, 68.2, 67.7, 67.3, 64.9, 63.7, 63.4, 51.5, 33.9, 29.0, 25.7, 24.6, 18.6 (x2), 18.5 ppm; HRMS (ESI): *m/z* calcd for $C_{53}H_{61}N_9O_{14}Na$ $[M+Na]^+$: 1070.4230, found: 1070.4209.

NIS/AgOTf-promoted glycosylation. A mixture the glycosyl donor **10** (0.184 g, 0.262 mmol), glycosyl acceptor **13** (0.097 g, 0.238 mmol), and freshly activated molecular sieves (3Å, 500 mg) in CH_2Cl_2 (4 mL) was stirred under argon for 3 h. NIS (0.118 g, 0.524 mmol), followed by AgOTf (0.030 g, 0.119 mmol), was added and the reaction mixture was stirred for 1 h at 21 ^{o}C. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate was washed with 20% aq. $Na_2S_2O_3$ (30 mL) and water (3 x 20 mL), the organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo.* The residue was purified by column chromatography on silica gel (ethyl acetate - toluene gradient elution) to afford the title compound **16** (0.180 g, 82%) as a white foam and the corresponding β-anomer (0.030 g, 12%). Analytical data for **16β**: R_f = 0.30 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = -24.1 (c = 1.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.10-8.00 (m, 20H, H-Ar), 5.79 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2^C), 5.68 (dd, $J_{3,4}$ = 10.2 Hz, 1H, H-3^C), 5.22 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^C), 4.78 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^A), 4.67 (dd, J^2 = 12.0 Hz, 4H, CH_2Ph), 4.40 (dq, J = 10.2, 6.0 Hz, 1H, H-5^C), 4.21 (s, 1H, H-1^B), 3.97-4.00 (m, 2H, H-2^B, H-3^A), 3.71 (dd, $J_{4,5}$ = 10.2 Hz, 1H, H-4^C), 3.67 (s, 3H, -OCH_3), 3.59-3.63 (m, 2H, H-2^A, H-5^A), 3.58 (dd, $J_{4,5}$ = 9.8 Hz, 1H, H-4^B), 3.52 (dt, J = 10.6, 6.6 Hz, 1H, -O-CH_{2a}-), 3.37 (dd, $J_{4,5}$ = 9.6 Hz, 1H, H-4^A), 3.36 (dt, J = 9.6, 6.5 Hz, 1H, -O-CH_{2b}-), 3.25 (dd, $J_{4,5}$ = 9.8 Hz, 1H, H-3^B), 3.08 (dq, J = 9.8, 6.1 Hz, 1H, H-5^B), 2.31 (t, J = 7.7 Hz, 2H, -CH_{2f}-), 1.64 (quin, J = 7.6 Hz, 2H, -CH_{2e}-), 1.53-1.58 (m, 2H, -CH_{2c}-), 1.44 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^C), 1.42 (d, $J_{5,6}$ = 6.3 Hz, 3H, H-6^B), 1.35 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^A), 1.30-1.35 ppm (m, 2H, -CH_{2d}-); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.2, 164.9, 137.7, 137.1, 133.2, 133.0, 129.8, 129.7 (x2), 129.6, 128.5, 128.4 (x2), 128.3 (x2), 128.0, 127.9, 127.7, 98.5, 97.3, 96.4, 80.7, 75.5, 73.0, 72.7, 72.4, 72.3, 71.4, 71.2, 69.6, 67.5, 67.2, 67.1, 63.9, 63.6, 62.9, 51.5,

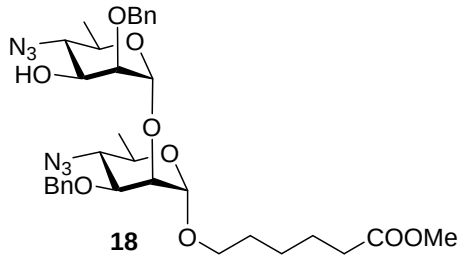
33.9, 29.0, 25.7, 24.7, 18.6, 18.4 (x2) ppm; HRMS (ESI): *m/z* calcd for $C_{53}H_{61}N_9O_{14}Na$ $[M+Na]^+$: 1070.4230, found: 1070.4233.

5'-Methoxycarbonylpentyl 4-azido-3-*O*-benzoyl-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (17).



A mixture of glycosyl donor **8** (0.168 g, 0.318 mmol), glycosyl acceptor **14** (0.118 g, 0.289 mmol) and freshly activated molecular sieves (3 Å, 0.350 g) in PhMe (3 mL) was stirred under argon for 2 h at 21 ^oC. Then it was heated to 95 ^oC and TMSOTf (12 μL, 0.064 mmol) was added, stirred for additional 1 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 30 mL). The combined filtrate (100 mL) was washed with sat. aq. $NaHCO_3$ (50 mL), water (30 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.203 g, 91%) as a white foam. Analytical data for **17**: R_f = 0.40 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = -4.4 (c = 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.00-8.06 (m, 15H, H-Ar), 5.30 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^B), 5.07 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1^B), 4.70 (dd, J^2 = 11.0 Hz, 2H, CH_2Ph), 4.70 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^A), 4.22 (dd, J^2 = 12.1 Hz, 2H, CH_2Ph), 3.98-4.03 (m, 2H, H-2^A, H-2^B), 3.70-3.82 (m, 3H, H-3^A, H-5^A, H-4^B), 3.69 (s, 3H, -OCH_3), 3.63 (dt, J = 9.7, 6.7 Hz, 1H, -O-CH_{2a}-), 3.45-3.55 (m, 2H, H-4^A, H-5^B), 3.39 (dt, J = 9.7, 6.4 Hz, 1H, -O-CH_{2b}-), 2.34 (t, J = 7.5 Hz, 2H, -CH_{2f}-), 1.67 (quin, J = 7.6 Hz, 2H, -CH_{2e}-), 1.56-1.63 (m, 2H, -CH_{2c}-), 1.39 (d, J = 5.9 Hz, 3H, H-6^A), 1.36-1.42 (m, 2H, -CH_{2d}-), 1.34 ppm (d, J = 5.7 Hz, 3H, H-6^B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.4, 137.4, 137.3, 133.2, 129.8, 129.5, 128.5, 128.4, 128.2, 128.1, 127.8, 127.6, 99.1, 98.8, 78.6, 74.4, 73.3, 72.8, 72.6, 72.5, 67.6, 67.4, 67.3, 64.3, 63.1, 51.5, 33.9, 29.1, 25.7, 24.7, 18.5 (x2) ppm; HRMS (ESI): *m/z* calcd for $C_{40}H_{48}N_6O_{10}Na$ $[M+Na]^+$: 795.3324, found: 795.3314.

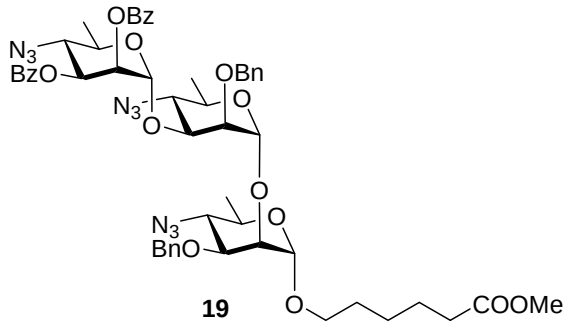
5'-Methoxycarbonylpentyl 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (18).



18

Sodium methoxide (~0.5 mL, 0.5 M solution) was added to a solution of **17** (0.910 g, 1.178 mmol) in CH_3OH (20 mL) until pH ~9 and the resulting mixture was stirred under argon for 4 h at 21 ^oC. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.755 g, 96%) as oil. Analytical data for **18**: R_f = 0.50 (ethyl acetate/toluene, 1/9, v/v); $[\alpha]_D^{21}$ = +43.2 (c = 1.2, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.11-7.41 (m, 10H, H-Ar), 5.11(d, $J_{1,2}$ = 1.3 Hz, 1H, H-1^B), 4.66 (dd, J^2 = 11.0 Hz, 2H, CH_2Ph), 4.65 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^A), 4.18 (dd, J^2 = 11.7 Hz, 2H, CH_2Ph), 3.99 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2^A), 3.83 (dd, $J_{3,4}$ = 10.5 Hz, 1H, H-3^B), 3.76 (dd, $J_{3,4}$ = 9.8 Hz, 1H, H-3^A), 3.68 (s, 3H, -OCH_3), 3.67 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-2^B), 3.61 (dq, J = 9.7, 6.7 Hz, 1H, H-5^A), 3.56 (dq, J = 10.1, 6.2 Hz, 1H, H-5^B), 3.47 (dt, J = 10.0, 6.1 Hz, 1H, -O-CH_{2a}-), 3.37 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^A), 3.36 (dt, J = 9.6, 6.5 Hz, 1H, -O-CH_{2b}-), 3.23 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^B), 2.33 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 2.29 (d, $J_{3,\text{-OH}}$ = 10.4 Hz, 1H, -OH^B), 1.62-1.69 (m, 2H, -CH_{2e}-), 1.55-1.62 (m, 2H, -CH_{2c}-), 1.33-1.41 (m, 2H, -CH_{2d}-), 1.30 (d, $J_{5,6}$ = 6.5 Hz, 3H, H-6^A), 1.29 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 137.3, 137.1, 128.6, 128.5, 128.2, 128.1, 128.0, 98.8, 97.9, 78.5, 76.5, 72.9, 72.6, 72.1, 69.8, 67.5, 67.2, 67.1, 66.4, 64.6, 51.5, 33.9, 29.0, 25.7, 24.7, 18.5, 18.4 ppm; HRMS (ESI): *m/z* calcd for $C_{33}H_{44}N_6O_9Na$ $[M+Na]^+$: 691.3062, found: 691.3054.

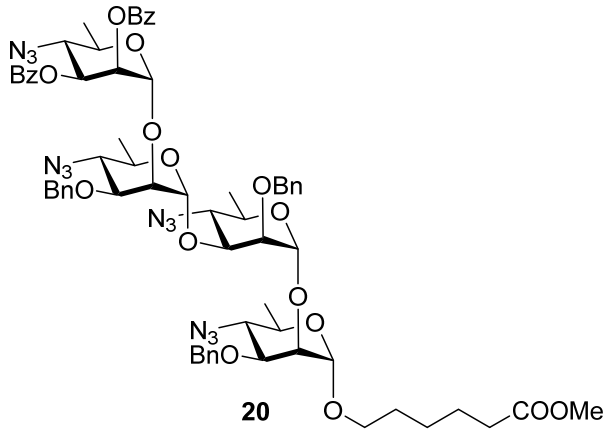
5'-Methoxycarbonylpentyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (19).



19

A mixture of glycosyl donor **7** (0.124 g, 0.230 mmol), glycosyl acceptor **18** (0.140 g, 0.210 mmol) and freshly activated molecular sieves (3 Å, 0.5 g) in CH_2Cl_2 (4 mL) was stirred under argon for 5 h at 21 ^oC. TMSOTf (8 μL, 0.046 mmol) was added and the resulting mixture was stirred for additional 1 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate (80 mL) was washed with sat. aq. $NaHCO_3$ (50 mL), water (30 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.210 g, 96%) as a white foam. Analytical data for **19**: R_f = 0.40 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = -29.0 (c = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22-8.07 (m, 20H, H-Ar), 5.70 (dd, $J_{2,3}$ = 3.4 Hz, 1H, H-2^C), 5.59 (dd, $J_{3,4}$ = 9.8 Hz, 1H, H-3^C), 5.26 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^C), 5.10 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^B), 4.67 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^A), 4.65 (dd, J^2 = 11.0 Hz, 2H, CH_2Ph), 4.35 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 3.98 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2^A), 3.96 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^B), 3.76 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3^A), 3.73 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^C), 3.69-3.72 (m, 2H, H-2^B, H-5^C), 3.68 (s, 3H, -OCH_3), 3.67 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^B), 3.57-3.64 (m, 2H, H-5^A, H-5^B), 3.47 (dt, J = 10.0, 6.1 Hz, 1H, -O-CH_{2a}-), 3.31-3.40 (m, 2H, H-4^A, -O-CH_{2b}-), 2.33 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 1.63-1.69 (m, 2H, -CH_{2e}-), 1.55-1.61 (m, 2H, -CH_{2c}-), 1.34-1.40 (m, 2H, -CH_{2d}-), 1.35 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^C), 1.29 (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^A), 1.28 ppm (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^B); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.2, 165.0, 137.4, 137.3, 133.4, 133.2, 129.8 (x2), 129.4, 129.3, 128.6, 128.5 (x2), 128.3, 128.2, 128.1, 127.8, 127.6, 99.1, 98.8, 98.4, 78.4, 77.6, 76.1, 73.4, 72.4, 71.8, 70.7, 69.8, 68.2, 67.7, 67.5, 67.1, 64.7, 64.5, 63.3, 51.5, 33.9, 29.0, 25.7, 24.7, 18.6 (x2), 18.5 ppm; HRMS (ESI): *m/z* calcd for $C_{53}H_{61}N_9O_{14}Na$ $[M+Na]^+$: 1070.4230, found: 1070.4249.

5'-Methoxycarbonylpentyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (20).

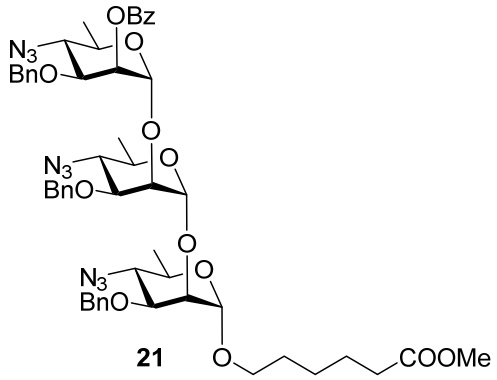


20

A mixture of glycosyl donor **10** (0.208 g, 0.296 mmol), glycosyl acceptor **18** (0.180 g, 0.269 mmol) and freshly activated molecular sieves (3 Å, 0.5 g) in CH_2Cl_2 (4 mL) was stirred under argon for 4 h at 21 ^oC. MeOTf (213 μL, 1.88 mmol) was added and continued stirring for additional 48 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate (70 mL) was washed with sat. aq. $NaHCO_3$ (40 mL), water (30 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.321 g, 91%) as a white foam. Analytical data for **20**: R_f = 0.30 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = -17.9 (c = 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ 7.05-8.00 (m, 25H, H-Ar), 5.71 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2^D), 5.58 (dd, $J_{3,4}$ = 10.3 Hz, 1H, H-3^D), 5.09 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^B), 5.07 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^C), 5.04 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^D), 4.69 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.68 (s, 1H, H-1^A), 4.60 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.22 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.11 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^C), 3.99 (dd, $J_{2,3}$ = 2.9 Hz, 1H, H-2^A), 3.88-3.94 (m, 2H, H-3^B, H-5^D), 3.76 (dd, $J_{3,4}$ = 9.8 Hz, 1H, H-3^A), 3.70-3.74 (m, 2H, H-3^C, H-4^D), 3.69 (s, 3H, -OCH_3), 3.66 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2^B), 3.63 (dt, J = 9.6, 6.7 Hz, 1H, -O-CH_{2a}-), 3.54-3.60 (m, 3H, H-4^B, H-4^C, H-5^B), 3.42-3.52 (m, 2H, H-5^A, H-5^C), 3.33-3.41 (m, 2H, H-4^A, -O-CH_{2b}-), 2.34 (t, J = 7.5 Hz, 2H, -CH_{2f}-), 1.67 (quin, J = 7.6 Hz, 2H, -CH_{2e}-), 1.55-1.62 (m, 2H, -CH_{2c}-), 1.46 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^D), 1.35-1.41 (m, 2H, -CH_{2d}-), 1.31-1.35 (m, 6H, H-6^A, H-6^B), 1.26 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^C);

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.2, 164.8, 137.5, 137.4, 137.3, 133.3, 133.2, 129.8, 129.7, 129.5, 129.3, 128.5 (x2), 128.4, 128.3, 128.2, 128.0, 127.8 (x2), 127.7, 127.6, 100.8, 99.2, 98.8, 98.3, 78.4, 77.9, 77.4, 76.4, 73.7, 73.2, 72.5, 72.1, 71.9, 70.9, 69.3, 68.1, 67.9, 67.7, 67.5, 67.2, 64.6, 63.6, 63.4, 51.5, 33.9, 29.1, 25.7, 24.7, 18.6 (x2), 18.5 ppm; HRMS (ESI): *m/z* calcd for $C_{66}H_{76}N_{12}O_{17}Na$ $[M+Na]^+$: 1331.5344, found: 1331.5341.

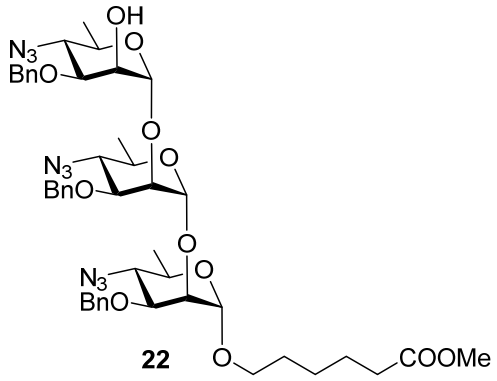
5'-Methoxycarbonylpentyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (21).



A mixture of glycosyl donor **11** (0.743 g, 1.08 mmol), glycosyl acceptor **14** (0.400 g, 0.982 mmol) and freshly activated molecular sieves (3 Å, 1.5 g) in CH_2Cl_2 (10 mL) was stirred under argon for 4 h at 21 °C. MeOTf (0.890 mL, 7.86 mmol) was added and continued stirring for additional 48 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 30 mL). The combined filtrate (100 mL) was washed with sat. aq. $NaHCO_3$ (40 mL), water (30 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.865 g, 85%) as oil. Analytical data for **21**: R_f = 0.50 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = +36.7 (c = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15-8.11 (m, 20H, H-Ar), 5.61 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2^C), 4.99 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^B), 4.90 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^C), 4.72 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.64 (s, 1H, H-1^A), 4.57-4.74 (m, 4H, 2 x CH_2Ph), 3.87-3.90 (m, 2H, H-2^B, H-3^C), 3.83 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^A), 3.75 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^B), 3.71 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3^A), 3.70 (s, 3H, -OCH_3), 3.52-3.64 (m, 3H, H-5^B, H-5^C, -O-CH_{2a}-), 3.48 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^C), 3.41-3.46 (m, 1H, H-5^A), 3.37 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^B), 3.33-3.38 (m, 1H, -O-CH_{2b}-), 3.23 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^A), 2.34 (t, J = 7.5 Hz, 2H, -CH_{2f}-), 1.63-1.70 (m, 2H, -CH_{2e}-),

1.54-1.61 (m, 2H, -CH_{2c}-), 1.32-1.40 (m, 2H, -CH_{2d}-), 1.30 (d, $J_{5,6}$ = 6.0 Hz, 6H, H-6^{B}, H-6^{C}), 1.25 ppm (d, $J_{5,6}$ = 6.0 Hz, 3H, H-6^{A}); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.3, 137.4, 137.3, 137.2, 133.3, 129.9, 129.8, 128.5 (x3), 128.4, 128.3, 128.1, 128.0 (x2), 127.9, 100.4, 99.2, 98.7, 77.6, 76.7, 75.4, 74.2, 74.1, 72.2, 72.1, 71.4, 67.7 (x2), 67.5, 67.1, 64.4, 64.1 (x2), 51.5, 33.9, 29.1, 25.7, 24.7, 18.7, 18.6 ppm; HRMS (ESI): *m/z* calcd for $C_{53}H_{63}N_9O_{13}Na$ $[M+Na]^+$: 1056.4438, found: 1056.4436.

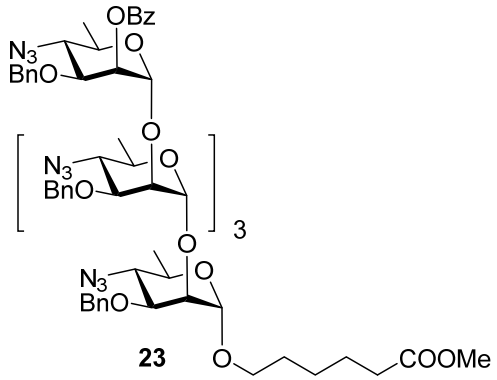
5'-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (22).



Sodium methoxide (0.7 mL, 0.5 M solution) was added to a solution of **21** (0.855 g, 0.827 mmol) in CH_3OH (10 mL) until pH ~9 and the resulting mixture was stirred under argon for 4 h at 21 ^{o}C. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.720 g, 94%) as oil. Analytical data for **22**: R_f = 0.30 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = +94.4 (c = 1.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.45 (m, 15H, H-Ar), 4.95 (br. s., 2H, H-1^{B}, H-1^{C}), 4.63 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^{A}), 4.58-4.73 (m, 6H, 3 x CH_2Ph), 4.01 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2^{C}), 3.95 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^{B}), 3.82 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^{A}), 3.71-3.76 (m, 6H, H-3^{A} H-3^{B} H-3^{C}), 3.70 (s, 3H, -OCH_3), 3.50-3.63 (m, 3H, H-5^{B}, H-5^{C}, -O-CH_{2a}-), 3.39-3.47 (m, 1H, H-5^{A}), 3.42 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^{C}), 3.31-3.39 (m, 2H, H-4^{B}, -O-CH_{2b}-), 3.23 (dd, $J_{4,5}$ = 9.9 Hz, 1H, H-4^{A}), 2.34 (t, J = 7.5 Hz, 2H, -CH_{2f}-), 2.30 (br. s., 1H, -OH^{C}), 1.63-1.70 (m, 2H, -CH_{2e}-), 1.52-1.60 (m, 2H, -CH_{2c}-), 1.32-1.41 (m, 2H, -CH_{2d}-), 1.28-1.31 (m, 6H, H-6^{B}, H-6^{C}), 1.21 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^{A}); ^{13}C NMR (126 MHz,

$CDCl_3$): δ 174.0, 137.4, 137.3, 137.1, 128.6 (x2), 128.3 (x2), 128.2 (x3), 128.1, 100.5 (x2), 98.7, 77.6, 77.5, 76.9, 74.0, 73.3, 72.2, 72.1 (x2), 67.7, 67.5, 67.3, 67.2, 67.1, 64.4, 64.2, 63.8, 51.5, 33.9, 29.0, 25.7, 24.7, 18.6 (x2), 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{46}H_{59}N_9O_{12}Na$ $[M+Na]^+$: 952.4175, found: 952.4176.

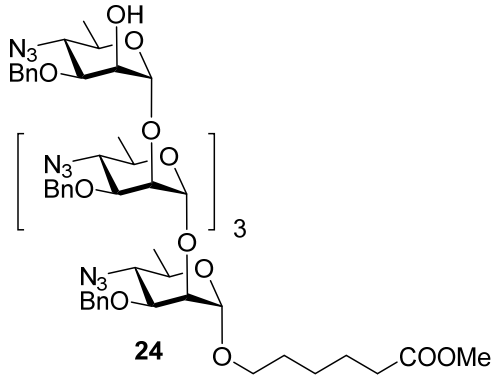
5'-Methoxycarbonylpentyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (23).



A mixture of glycosyl donor **11** (0.262 g, 0.381 mmol), glycosyl acceptor **22** (0.322 g, 0.346 mmol) and freshly activated molecular sieves (3 Å, 0.5 g) in CH_2Cl_2 (8 mL) was stirred under argon for 4 h at 21 ^oC. MeOTf (320 μL, 2.77 mmol) was added and continued stirring for additional 48 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate (70 mL) was washed with sat. aq. $NaHCO_3$ (40 mL), water (30 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.461 g, 86%) as a white foam. Analytical data for **23**: R_f = 0.30 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = +52.7 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.16-8.09 (m, 30H, H-Ar), 5.60 (dd, $J_{2,3}$ = 3.1 Hz, 1H, H-2^E), 4.98 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^D), 4.92 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^E), 4.88 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^C), 4.86 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^B), 4.57-4.79 (m, 11H, H-1^A, 5 x CH_2Ph), 3.87-3.91 (m, 2H, H-2^D, H-3^E), 3.85 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^C), 3.81 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^B), 3.77 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^A), 3.72 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^D), 3.63-3.70 (m, 6H, H-3^A, H-3^B, H-3^C, -OCH_3), 3.54-3.63 (m, 2H, H-5^E, -O-CH_{2a}-), 3.45-3.52 (m, 3H, H-5^B, H-5^D, H-4^E), 3.38-3.43 (m, 2H, H-5^A,

H-5^{C}), 3.35 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^{D}), 3.30-3.34 (m, 1H, -O-CH_{2b}-), 3.16-3.24 (m, 3H, H-4^{A}, H-4^{B}, H-4^{C}), 2.32 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 1.61-1.67 (m, 2H, -CH_{2e}-), 1.50-1.59 (m, 2H, -CH_{2c}-), 1.29-1.37 (m, 2H, -CH_{2d}-), 1.23-1.29 (m, 9H, H-6^{B}, H-6^{C} H-6^{D}), 1.19 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^{E}), 1.15 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^{A}); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 165.3, 137.4, 137.3, 137.1 (x2), 133.3, 129.9, 129.8, 128.7, 128.6 (x3), 128.5 (x2), 128.4 (x2), 128.3 (x3), 128.2 (x2), 128.1 (x3), 127.9 (x2), 100.4, 100.2, 100.1, 99.2, 98.6, 77.4, 76.6, 75.3, 74.1, 74.0, 73.6, 72.2 (x2), 72.1 (x2), 71.3, 67.8 (x2), 67.7 (x2), 67.5, 67.1, 64.4, 64.3, 64.2, 64.1 (x2), 51.5, 33.9, 29.0, 25.7, 24.7, 18.6, 18.5 (x2) ppm; HRMS (ESI): *m/z* calcd for $C_{79}H_{93}N_{15}O_{19}Na$ $[M+Na]^+$: 1578.6664, found: 1578.6667.

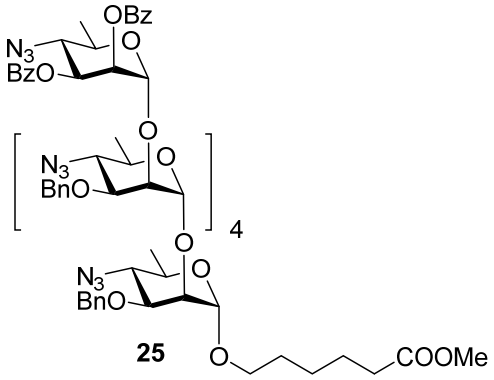
5'-Methoxycarbonylpentyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (24).



Sodium methoxide (0.8 mL, 0.5 M solution) was added to a solution of **23** (0.450 g, 0.289 mmol) in CH_3OH (10 mL) until pH ~9 and the resulting mixture was stirred under argon for 4 h at 21 ^{o}C. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.395 g, 94%) as oil. Analytical data for **24**: R_f = 0.40 (ethyl acetate/toluene, 1/9, v/v); $[\alpha]_D^{21}$ = +81.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28-7.41 (m, 25H, H-Ar), 4.97 (d, $J_{1,2}$ = 1.1 Hz, 1H, H-1^{E}), 4.96 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^{D}), 4.87 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1^{C}), 4.85 (d, $J_{1,2}$ = 1.3 Hz, 1H, H-1^{B}), 4.58-4.76 (m, 11H, H-1^{A}, 5 x CH_2Ph), 4.00 (dd, $J_{2,3}$ = 3.5 Hz, 1H, H-2^{E}), 3.93 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^{D}), 3.83 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^{C}), 3.80 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^{B}), 3.76 (dd, $J_{2,3}$ = 2.0 Hz, 1H, H-2^{A}), 3.63-3.73 (m, 8H, H-3^{A}, H-3^{B}, H-3^{C}, H-3^{D}, H-3^{E}, -

OCH_3), 3.51-3.59 (m, 2H, H-5^D, -O-CH_{2a}-), 3.37-3.51 (m, 5H, H-5^A, H-5^B, H-5^C, H-5^E, H-4^E), 3.29-3.34 (m, 2H, H-4^D, -O-CH_{2b}-), 3.16-3.24 (m, 3H, H-4^A, H-4^B, H-4^C), 2.32 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 2.28 (d, $J_{2,\text{-OH}}$ = 1.8 Hz, 1H,-OH^E), 1.60-1.67 (m, 2H, -CH_{2e}-), 1.51-1.58 (m, 2H, -CH_{2c}-), 1.30-1.38 (m, 2H, -CH_{2d}-), 1.14-1.26 ppm (m, 15H, H-6^A, H-6^B, H-6^C, H-6^D, H-6^E); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 137.3 (x2), 137.2, 137.1 (x2), 128.6 (x4), 128.4 (x2), 128.3 (x3), 128.2 (x2), 128.1 (x2), 100.5, 100.4, 100.2 (x2), 98.6, 77.7, 77.4, 76.6, 76.5, 74.0, 73.6, 73.5, 73.3, 72.2 (x2), 72.1 (x2), 67.8, 67.7, 67.5, 67.3, 67.1 (x2), 64.4, 64.2, 63.8, 51.5, 33.9, 29.0, 25.7, 24.7, 18.6 (x2), 18.5 (x2), 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{72}H_{89}N_{15}O_{18}Na$ $[M+Na]^+$: 1474.6402, found: 1474.6406.

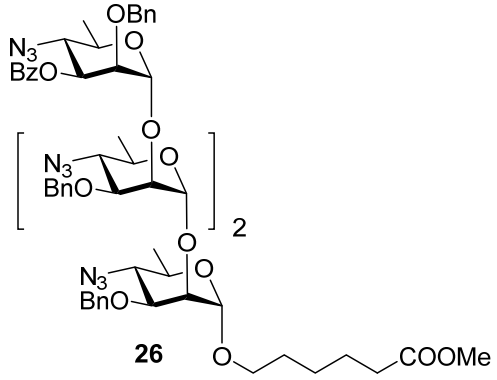
5'-Methoxycarbonylpentyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (25).



A mixture of glycosyl donor **7** (0.158 g, 0.292 mmol), glycosyl acceptor **24** (0.386 g, 0.266 mmol) and freshly activated molecular sieves (3 Å, 0.5 g) in CH_2Cl_2 (5 mL) was stirred under argon for 5 h at 21 ^oC. TMSOTf (11 μL, 0.058 mmol) was added and the resulting mixture was stirred for additional 1 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 20 mL). The combined filtrate (80 mL) was washed with sat. aq. $NaHCO_3$ (50 mL), water (30 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.487 g, 90%) as a white foam. Analytical data for **25**: R_f = 0.70 (ethyl acetate/toluene, 1/9, v/v); $[\alpha]_D^{21}$ = +31.7 (c = 1.4, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ

7.13-8.03 (m, 35H, H-Ar), 5.70 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2^F), 5.59 (dd, $J_{3,4}$ = 10.2 Hz, 1H, H-3^F), 5.02-5.03 (m, 2H, H-1^E, H-1^F), 4.90 (dd, $J_{1,2}$ = 1.8 Hz, 1H, H-1^D), 4.88 (dd, $J_{1,2}$ = 1.8 Hz, 1H, H-1^C), 4.86 (dd, $J_{1,2}$ = 1.8 Hz, 1H, H-1^B), 4.61-4.76 (m, 10H, 5 x CH_2Ph), 4.60 (dd, $J_{1,2}$ = 1.8 Hz, 1H, H-1^A), 3.94 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^E), 3.91 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^D), 3.83 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^C), 3.81 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^B), 3.77-3.80 (m, 1H, H-5^F), 3.77 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^A), 3.74 (dd, $J_{3,4}$ = 10.2 Hz, 1H, H-3^E), 3.65-3.71 (m, 8H, H-3^A, H-3^B, H-3^C, H-3^D, H-4^F, -OCH_3), 3.55-3.59 (m, 2H, H-4^E, -O-CH_{2a}-), 3.38- 3.53 (m, 5H, H-5^A, H-5^B, H-5^C, H-5^D, H-5^E), 3.32 (dt, J = 9.6, 6.4 Hz, 1H, -O-CH_{2b}-), 3.16-3.27 (m, 4H, H-4^A, H-4^B, H-4^C, H-4^D), 2.32 (t, J = 7.8 Hz, 2H, -CH_{2f}-), 1.62-1.67 (m, 2H, -CH_{2e}-), 1.52-1.58 (m, 2H, -CH_{2c}-), 1.32-1.36 (m, 2H, -CH_{2d}-), 1.14-1.31 ppm (m, 18H, H-6^A, H-6^B, H-6^C, H-6^D, H-6^E, H-6^F); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.2, 164.9, 137.4, 137.3, 137.1 (x3), 133.4, 133.2, 129.8, 129.7, 129.5, 129.3, 129.0, 128.7, 128.6 (x3), 128.5 (x2), 128.4 (x3), 128.3 (x2), 128.2, 128.1 (x2), 127.9 (x3), 100.4, 100.3, 100.1, 100.0, 98.9, 98.6, 77.4, 77.1, 76.6, 76.5, 74.0, 73.8, 73.6, 73.5, 73.0, 72.3 (x2), 72.2 (x2), 72.1, 70.9, 69.4, 68.1, 67.9, 67.8 (x2), 67.6, 67.5, 67.1, 64.4, 64.3, 64.2 (x2), 63.9, 63.4, 51.5, 33.9, 29.0, 25.7, 24.7, 18.6 (x2), 18.5 (x2), 18.4 ppm; HRMS (ESI): *m/z* calcd for $C_{92}H_{106}N_{18}O_{23}Na$ $[M+Na]^+$: 1853.7570, found: 1853.7550.

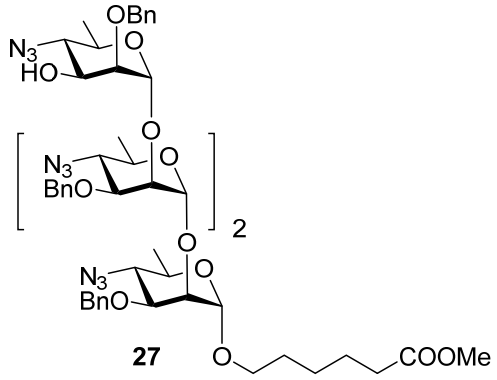
5'-Methoxycarbonylpentyl 4-azido-3-*O*-benzoyl-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (26).



A mixture of glycosyl donor **8** (0.228 g, 0.433 mmol), glycosyl acceptor **22** (0.366 g, 0.394 mmol) and freshly activated molecular sieves (3 Å, 0.500 g) in PhMe (10 mL) was stirred under argon for 2 h at 21 ^oC. Then it was heated to 95 ^oC and TMSOTf (16 µL, 0.087 mmol) was added, stirred for additional 1 h. After that, Et_3N (1 mL) was added, the solid was

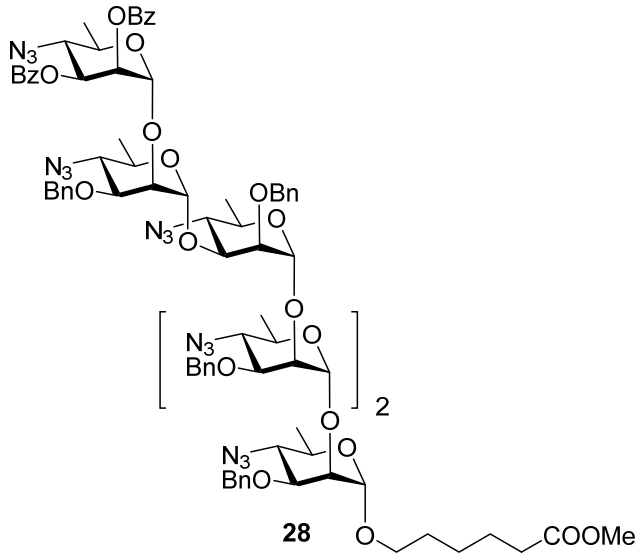
filtered off and the residue was rinsed with CH_2Cl_2 (3 x 30 mL). The combined filtrate (100 mL) was washed with sat. aq. $NaHCO_3$ (50 mL), water (30 mL), and brine (30 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.444 g, 87%) as a white foam. Analytical data for **26**: R_f = 0.50 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = +42.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.03-8.05 (m, 25H, H-Ar), 5.29 (dd, $J_{3,4}$ = 10.3 Hz, 1H, H-3^D), 5.07 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^D), 4.96 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^C), 4.91 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^B), 4.60-4.73 (m, 7H, H-1^A, 3 x C*H*$_2$Ph), 4.21 (dd, J^2 = 12.0 Hz, 2H, C*H*$_2$Ph), 4.05 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^C), 4.00 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2^D), 3.90 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^B), 3.80 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^A), 3.76 (dd, $J_{4,5}$ = 10.2 Hz, 1H, H-4^D), 3.68-3.73 (m, 6H, H-3^A, H-3^B H-3^C, -OC*H*$_3$), 3.56-3.63 (m, 2H, H-5^D, -O-C*H*$_{2a}$-), 3.39-3.54 (m, 4H, H-4^C, H-5^A, H-5^B, H-5^C), 3.31-3.35 (m, 2H, H-4^B, -O-C*H*$_{2b}$-), 3.21 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^A), 2.32 (t, J = 7.5 Hz, 2H, -C*H*$_{2f}$-), 1.62-1.67 (m, 2H, -C*H*$_{2e}$-), 1.53-1.58 (m, 2H, -C*H*$_{2c}$-), 1.31-1.36 (m, 2H, -C*H*$_{2d}$-), 1.22-1.29 ppm (m, 12H, H-6^A, H-6^B, H-6^C, H-6^D); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.4, 137.4, 137.3 (x2), 137.1, 133.3, 129.8, 129.5, 128.7, 128.6 (x2), 128.4, 128.3 (x2), 128.2 (x2), 128.1, 127.8, 127.6, 100.6, 100.1, 98.8, 98.6, 77.9, 77.4, 76.9, 74.4, 74.2, 72.9, 72.8, 72.7, 72.6, 72.5, 72.3, 72.2, 68.1, 67.8, 67.7, 67.5, 67.1, 64.4, 64.2, 64.1, 63.1, 51.5, 33.9, 29.0, 25.7, 24.6, 18.6 (x2), 18.4, 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{66}H_{78}N_{12}O_{16}Na$ $[M+Na]^+$: 1317.5551, found: 1317.5549.

5'-Methoxycarbonylpentyl 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (27).



Sodium methoxide (0.8 mL, 0.5 M solution) was added to a solution of **26** (0.434 g, 0.335 mmol) in CH_3OH (10 mL) until pH ~9 and the resulting mixture was stirred under argon for 4 h at 21 ^oC. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin; the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.356 g, 89%) as a white foam. Analytical data for **27**: R_f = 0.50 (ethyl acetate/toluene, 1/9, v/v); $[\alpha]_D^{21}$ = +65.6 (c = 1.3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13-7.42 (m, 20H, H-Ar), 5.10 (d, $J_{1,2}$ = 0.9 Hz, 1H, H-1^D), 4.93 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1^C), 4.90 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^B), 4.59-4.75 (m, 7H, H-1^A, 3 x CH_2Ph), 4.23 (dd, J^2 = 11.5 Hz, 2H, CH_2Ph), 4.04 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^C), 3.88 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^B), 3.83 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3^D), 3.79 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^A), 3.72 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^D), 3.65-3.70 (m, 6H, H-3^A, H-3^B, H-3^C, -OCH_3), 3.49-3.61 (m, 2H, H-5^C, -O-CH_{2a}-), 3.43 (m, 3H, H-5^A, H-5^B, H-5^D), 3.35-3.39 (m, 1H, H-4^C), 3.29-3.35 (m, 2H, H-4^D, -O-CH_{2b}-), 3.22 (m, 2H, H-4^A, H-4^B), 2.32 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 2.31 (br. s, 1H, -OH^D), 1.61-1.68 (m, 2H, -CH_{2e}-), 1.51-1.58 (m, 2H, -CH_{2c}-), 1.30-1.38 (m, 2H, -CH_{2d}-), 1.19-1.29 ppm (m, 12H, H-6^A, H-6^B, H-6^C, H-6^D); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 137.3 (x2), 137.2, 137.1, 128.7, 128.6 (x2), 128.4, 128.3 (x2), 128.2, 128.1 (x2), 100.5, 100.2, 98.6, 97.8, 77.8, 77.5, 76.9, 76.5, 74.1, 73.1, 72.7, 72.5, 72.3, 72.2, 70.0, 67.9, 67.8, 67.5, 67.3, 67.1, 66.5, 64.5, 64.4, 64.3, 51.5, 33.9, 29.1, 25.7, 24.7, 18.7, 18.6, 18.4, 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{59}H_{74}N_{12}O_{15}Na$ $[M+Na]^+$: 1213.5289, found: 1213.5284.

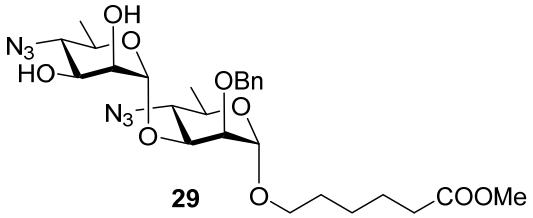
5'-Methoxycarbonylpentyl 4-azido-2,3-di-*O*-benzoyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (28).



A mixture of glycosyl donor **10** (0.220 g, 0.313 mmol), glycosyl acceptor **27** (0.339 g, 0.285 mmol) and freshly activated molecular sieves (3 Å, 0.5 g) in CH_2Cl_2 (10 mL) was stirred under argon for 4 h at 21 ^oC. MeOTf (260 µL, 2.28 mmol) was added and continued stirring for additional 48 h. After that, Et_3N (1 mL) was added, the solid was filtered off and the residue was rinsed with CH_2Cl_2 (3 x 30 mL). The combined filtrate (100 mL) was washed with sat. aq. $NaHCO_3$ (40 mL), water (40 mL), and brine (20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.479 g, 92%) as a white foam. Analytical data for **28**: R_f = 0.60 (ethyl acetate/toluene, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = +15.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.06-8.00 (m, 35H, H-Ar), 5.71 (dd, $J_{2,3}$ = 3.3 Hz, 1H, H-2^F), 5.58 (dd, $J_{3,4}$ = 10.3 Hz, 1H, H-3^F), 5.09 (d, $J_{1,2}$ = 1.2 Hz, 1H, H-1^E), 5.05-5.07 (m, 2H, H-1^D, H-1^F), 4.95 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^C), 4.90 (d, $J_{1,2}$ = 1.7 Hz, 1H, H-1^B), 4.58-4.71 (m, 9H, H-1^A, 4 x CH_2Ph), 4.25 (dd, J^2 = 11.4 Hz, 2H, CH_2Ph), 4.12 (dd, $J_{2,3}$ = 2.1 Hz, 1H, H-2^E), 4.02 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^C), 3.86-3.93 (m, 3H, H-2^B, H-3^D, H-5^F), 3.79 (dd, $J_{2,3}$ = 2.4 Hz, 1H, H-2^A), 3.68-3.74 (m, 8H, H-3^A, H-3^B, H-3^C, H-3^E, H-4^F, -OCH_3), 3.65 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2^D), 3.54-3.59 (m, 3H, H-4^D, H-4^E, -O-CH_{2a}-), 3.39-3.53 (m, 5H, H-5^A, H-5^B, H-5^C, H-5^D, H-5^E), 3.29-3.36 (m,

3H, H-4^{B}, H-4^{C}, -O-CH_{2b}-), 3.21 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^{A}), 2.32 (t, J = 7.5 Hz, 2H, -CH_{2f}-), 1.61-1.66 (m, 2H, -CH_{2e}-), 1.53-1.57 (m, 2H, -CH_{2c}-), 1.44 (d, J = 6.1 Hz, 3H, H-6^{F}), 1.31-1.38 (m, 2H, -CH_{2d}-), 1.20-1.29 ppm (m, 15H, H-6^{A}, H-6^{B}, H-6^{C}, H-6^{D}, H-6^{E}); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 165.2, 164.9, 137.5, 137.4, 137.3, 137.2, 137.1, 133.4, 133.3, 129.8 (x2), 129.5, 129.4, 129.0, 128.7, 128.6 (x2), 128.5 (x3), 128.4 (x2), 128.3 (x2), 128.2 (x2), 128.1, 127.9, 127.8, 127.7, 127.6, 100.9, 100.5, 100.2, 99.2, 98.6, 98.2, 77.9, 77.7, 77.5, 76.9, 76.4, 74.1, 73.6, 73.1, 72.9, 72.5, 72.4, 72.2 (x2), 72.0, 71.0, 69.4, 68.2, 68.1, 67.9, 67.8, 67.7, 67.5, 67.1, 64.7, 64.5, 64.4, 64.3, 63.6, 63.5, 51.5, 33.9, 29.1, 25.7, 24.7, 18.6 (x3), 18.5 (x2), 18.4 ppm; HRMS (ESI): *m/z* calcd for $C_{92}H_{110}N_{19}O_{23}$ $[M+NH_4]^+$: 1848.8016, found: 1848.8005.

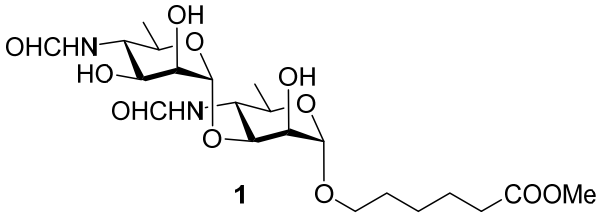
5'-Methoxycarbonylpentyl 4-azido-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (29).



Sodium methoxide (0.2 mL, 0.5 M solution) was added to a solution of **15** (0.350 g, 0.445 mmol) in CH_3OH (5 mL) until pH ~9 and the resulting mixture was stirred under argon for 4 h at 21 ^{o}C. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.221 g, 86%) as a white foam. Analytical data for **29**: R_f = 0.50 (CH_3OH/CH_2Cl_2, 0.5/9.5, v/v); $[\alpha]_D^{21}$ = +73.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.41 (m, 5H, H-Ar), 5.07 (s, 1H, H-1^{B}), 4.78 (s, 1H, H-1^{A}), 4.63 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.05 (br. s., 1H, H-2^{B}), 3.83-3.92 (m, 2H, H-3^{A}, H-3^{B}), 3.63-3.71 (m, 5H, H-2^{A}, H-5^{B}, -OCH_3), 3.59-3.62 (m, 1H, -O-CH_{2a}-), 3.56 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^{A}), 3.48 (dq, J = 12.0, 6.4 Hz, 1H, H-5^{A}), 3.33-3.39 (m, 1H, -O-CH_{2b}-), 3.31 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^{B}), 2.64 (br. s., 2H, 2 x -OH^{B}), 2.31 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 1.64 (quin, J = 7.6 Hz, 2H, -CH_{2e}-), 1.56 (quin, J = 7.0 Hz, 2H, -CH_{2c}-), 1.31-1.38 (m, 2H, -CH_{2d}-), 1.32 (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^{A}), 1.27 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^{B}); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.1, 137.6, 128.5, 127.9, 127.6, 101.5, 96.9, 78.3, 76.9,

72.4, 70.3, 70.2, 67.7, 67.5, 67.3, 65.7, 64.7, 51.5, 33.9, 29.0, 25.7, 24.6, 18.5, 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{26}H_{38}N_6O_9Na$ $[M+Na]^+$: 601.2592, found: 601.2581.

5'-Methoxycarbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (1).



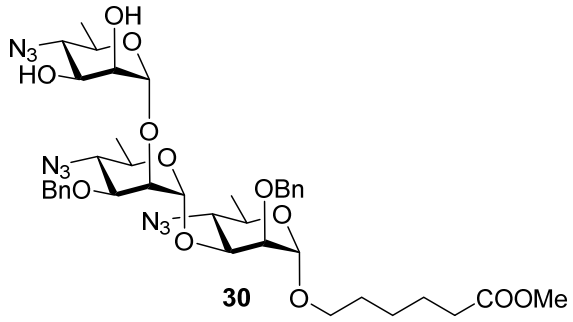
To a stirred solution of **29** (0.150 g, 0.259 mmol), in pyridine (5 mL) and water (2 mL) mixture, H_2S was bubbled for 0.5 h at 40 °C, and continued stirring for 16 h. After that, argon was bubbled for 10 min, solvents were removed *in vacuo*, and the residue was co-evaporated with toluene (3 x 10 mL) and dried. The high resolution mass spectrometry analysis showed completion of reaction to corresponding amine compound **29a** and no products arising from incomplete reduction. HRMS (ESI): *m/z* calcd for $C_{26}H_{43}N_2O_9$ $[M+H]^+$: 527.2963; found: 527.2964. This crude material was directly used for formylation.

Compound **29a** in CH_3OH (5 mL) at -20 °C was added a freshly prepared formic anhydride[6] (5 mL, ethereal solution) and stirred for 3 h, then slowly allowed to warm to 21 °C. After that, solvents were evaporated and the residue was passed through column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford disaccharide **29b**. HRMS (ESI): *m/z* calcd for $C_{28}H_{42}N_2NaO_{11}$ $[M+Na]^+$: 605.2681; found: 605.2675.

Compound **29b** was dissolved in CH_3OH/H_2O (2:1, 6 mL), $Pd(OH)_2$ on carbon (20%, 0.050 g) was added. Then it was stirred under a pressure of hydrogen gas at 21 °C for 16 h. After filtration through celite pad and washed with CH_3OH (3 x 10 mL), and solvents were removed *in vacuo*. The residue was purified by column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford the title compound (0.075 g, 59%, over 3 steps) as a white foam. Analytical data for **1**: R_f = 0.20 (CH_3OH/CH_2Cl_2, 1.5/8.5, v/v); ^{1}H NMR (700 MHz, D_2O): δ 8.21 ((d, *J* = 15.4 Hz) and 8.03 (d, *J* = 13.3 Hz), 2H, NC*H*O), 4.81-4.95 (m, 2H, 2 x H-1), 3.85-4.04 (m, 8H, 2 x H-2, 2 x H-3, 2 x H-4, 2 x H-5), 3.69-3.74 (m, 1H, -O-CH_{2a}-), 3.70 (s, 3H, -OCH_3), 3.33-3.58 (m, 1H, -O-CH_{2b}-), 2.42 (t, $J_{f,e}$ = 7.4 Hz, 2H, -CH_{2f}-), 1.58-1.69 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.34-1.45 (m, 2H, -CH_{2d}-), 1.20-1.30 ppm (m, 6H, 2 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.5, 168.9, 168.8, 165.8, 165.7, 103.3, 103.2, 100.6, 100.5, 77.8 (x2), 70.2, 70.0, 69.9 (x2), 69.0, 68.9 (x2), 68.8 (x2), 68.6, 68.4,

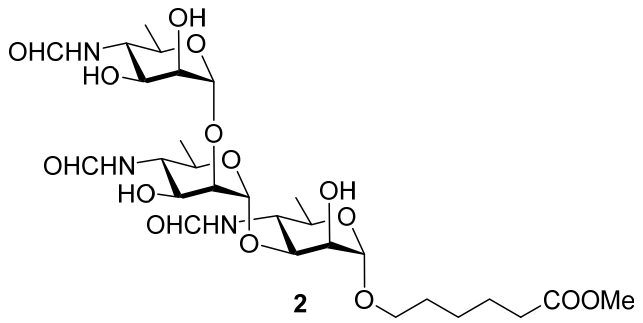
68.2, 67.8, 57.6, 56.5, 53.1, 52.7, 52.6, 51.6, 34.6, 29.1, 25.9, 25.0, 17.8, 17.7, 17.6 ppm; HRMS (ESI): *m/z* calcd for $C_{21}H_{36}N_2O_{11}Na$ $[M+Na]^+$: 515.2211, found: 515.2210.

5'-Methoxycarbonylpentyl 4-azido-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (30).



Sodium methoxide (0.2 mL, 0.5 M solution) was added to a solution of **16** (0.352 g, 0.336 mmol) in CH_3OH (5 mL) until pH ~9 and the resulting mixture was stirred under argon for 4 h at 21 ^oC. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.256 g, 91%) as off-white foam. Analytical data for **30**: R_f = 0.30 (ethyl acetate/toluene, 1/4, v/v); $[\alpha]_D^{21}$ = +72.4 (c = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.27-7.39 (m, 10H, H-Ar), 5.02 (s, 1H, H-1^B), 4.93 (s, 1H, H-1^C), 4.77 (s, 1H, H-1^A), 4.65 (dd, J^2 = 11.0 Hz, 2H, CH_2Ph), 4.58 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.11 (br. s., 1H, H-2^B), 3.94 (br. s., 1H, H-2^C), 3.81-3.87 (m, 2H, H-3^A, H-3^C), 3.78 (dd, $J_{3,4}$ = 10.1 Hz, 1H, H-3^B), 3.67 (s, 3H, -OCH_3), 3.53-3.66 (m, 5H, H-2^A H-4^A H-5^B H-5^C, -O-CH_{2a}-), 3.44-3.53 (m, 1H, H-5^A), 3.40 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^B), 3.32-3.37 (m, 1H, -O-CH_{2b}-), 3.34 (dd, $J_{4,5}$ = 9.9 Hz, 1H, H-4^C), 2.56 (d, $J_{2,\text{-OH}}$ = 6.2 Hz, 1H, -OH^C), 2.31 (t, J = 7.4 Hz, 3H, -CH_{2f}-, 3-OH^C), 1.63 (quin, J = 7.4 Hz, 2H, -CH_{2e}-), 1.56 (quin, J = 7.1 Hz, 2H, -CH_{2c}-), 1.28-1.39 (m, 8H, H-6^A, H-6^B, -CH_{2d}-), 1.24 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^C); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 137.6, 137.4, 128.6, 128.5, 128.1, 127.9, 127.5, 101.0 (x2), 97.0, 78.3, 77.8, 73.1, 72.5, 72.1, 70.2, 69.9, 67.9, 67.6, 67.4, 67.3, 65.8, 64.8, 64.0, 51.5, 33.9, 29.0, 25.6, 24.6, 18.6, 18.5, 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{39}H_{53}N_9O_{12}Na$ $[M+Na]^+$: 862.3706, found: 862.3691.

5'-Methoxycarbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (2).



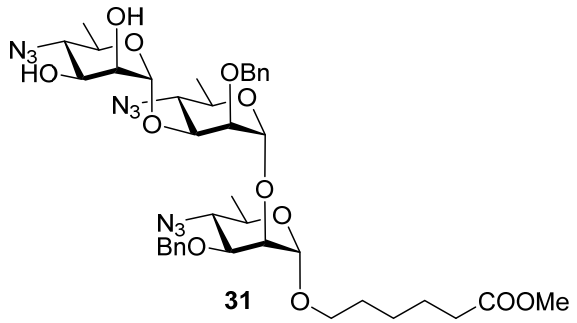
To a stirred solution of **30** (0.114 g, 0.136 mmol), in pyridine (5 mL) and water (2 mL) mixture, H_2S was bubbled for 0.5 h at 40 °C, and continued stirring for 16 h. After that, argon was bubbled for 10 min, solvents were removed *in vacuo*, and the residue was co-evaporated with toluene (3 x 10 mL) and dried. The high resolution mass spectrometry analysis showed completion of reaction to corresponding amine compound **30a** and no products arising from incomplete reduction. HRMS (ESI): *m*/*z* calcd for $C_{39}H_{60}N_3O_{12}$ [*M*+H]+: 762.4172; found: 762.4171. This crude material was directly used for formylation.

Compound **30a** in CH_3OH (5 mL) at -20 °C was added a freshly prepared formic anhydride (5 mL, ethereal solution) and stirred for 3 h, then slowly allowed to warm to 21 °C. After that, solvents were evaporated and the residue was passed through column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford disaccharide **30b**. HRMS (ESI): *m*/*z* calcd for $C_{42}H_{59}N_3O_{15}Na$ $[M+Na]^+$: 868.3838; found: 868.3827.

Compound **30b** was dissolved in CH_3OH/H_2O (2:1, 5 mL), $Pd(OH)_2$ on carbon (20%, 0.040 g) was added. Then it was stirred under a pressure of hydrogen gas at 21 °C for 16 h. After filtration through celite pad and washed with CH_3OH (3 x 10 mL), and solvents were removed *in vacuo*. The residue was purified by column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford the title compound (0.046 g, 51%, over 3 steps) as a white foam. Analytical data for **2**: R_f = 0.40 (CH_3OH/CH_2Cl_2, 3/7, v/v); ^{1}H NMR (700 MHz, D_2O): δ 8.20-8.24 (*Z*) and 8.02-8.06 (*E*) (m, 3H, NC*H*O), 4.82-5.08 (m, 3H, 3 x H-1), 3.84-4.14 (m, 12H, 3 x H-2, 3 x H-3, 3 x H-4, 3 x H-5), 3.69-3.75 (m, 1H, -O-CH_{2a}-), 3.70 (s, 3H, -OCH_3), 3.36-3.57 (m, 1H, -O-CH_{2b}-), 2.42 (t, $J_{f,e}$ = 7.4 Hz, 2H, -CH_{2f}-), 1.60-1.68 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.36-1.44 (m, 2H, -CH_{2d}-), 1.21-1.32 ppm (m, 9H, 3 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.5, 168.8, 168.7, 165.8 (x2), 165.6 (x2), 103.4, 103.3, 102.9, 101.8, 101.7, 100.6, 100.5, 79.0 (x2), 78.9, 78.2, 78.0, 77.7 (x3), 70.0, 69.9, 69.8, 69.4,

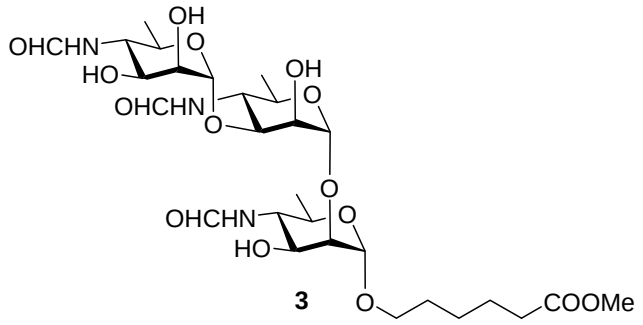
69.2, 69.0, 68.9 (x2), 68.8 (x2), 68.7, 68.6 (x2), 68.5 (x2), 68.3 (x2), 67.9, 67.7, 57.8, 57.7, 56.4, 53.1, 52.8, 52.7, 51.9, 34.6, 29.1, 25.9, 25.0, 18.1, 17.9 (x3), 17.8, 17.7 ppm; HRMS (ESI): *m/z* calcd for $C_{28}H_{47}N_3O_{15}Na$ $[M+Na]^+$: 688.2899, found: 688.2895.

5'-Methoxycarbonylpentyl 4-azido-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (31).



Sodium methoxide (0.5 mL, 0.5 M solution) was added to a solution of **19** (0.458 g, 0.437 mmol) in CH_3OH (10 mL) until pH ~9 and the resulting mixture was stirred under argon for 4 h at 21 ^oC. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.341 g, 93%) as oil. Analytical data for **31**: R_f = 0.30 (ethyl acetate/toluene, 1/4, v/v); $[\alpha]_D^{21}$ = +58.9 (c = 1.3, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.12-7.39 (m, 10H, H-Ar), 5.08 (d, $J_{1,2}$ = 1.8 Hz, 1H, H-1^B), 5.05 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^C), 4.66 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^A), 4.65 (dd, J^2 = 11.0 Hz, 2H, CH_2Ph), 4.21 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.00 (br. s., 1H, H-2^C), 3.97 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^A), 3.90 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3^B), 3.77-3.81 (m, 1H, H-3^C), 3.75 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^A), 3.68 (s, 3H, -OCH_3), 3.65 (dd, $J_{2,3}$ = 3.1 Hz, 1H, H-2^B), 3.59-3.61 (m, 1H, -O-CH_{2a}-), 3.52-3.58 (m, 2H, H-4^B, H-5^B), 3.45-3.50 (m, 2H, H-5^A, H-5^C), 3.34-3.40 (m, 1H, -O-CH_{2b}-), 3.33 (dd, $J_{4,5}$ = 9.5 Hz, 1H, H-4^A), 3.28 (dd, $J_{4,5}$ = 11.0 Hz, 1H, H-4^C), 2.61 (br. s., 2H, 2 x -OH^C), 2.33 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 1.62-1.73 (m, 2H, -CH_{2e}-), 1.54-1.61 (m, 2H, -CH_{2c}-), 1.33-1.42 (m, 2H, -CH_{2d}-), 1.28-1.32 (m, 6H, H-6^A, H-6^B), 1.19 ppm (d, $J_{5,6}$ = 6.2 Hz, 3H, H-6^C); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.1, 137.3 (x2), 128.5, 128.4, 128.2, 128.1, 127.8, 127.6, 101.5, 98.8, 98.1, 78.4, 77.5, 76.4, 73.2, 72.6, 71.7, 70.1, 70.0, 67.9, 67.5, 67.4, 67.2, 65.5, 64.7, 64.4, 51.5, 33.9, 29.0, 25.7, 24.6, 18.6, 18.5, 18.2 ppm; HRMS (ESI): *m/z* calcd for $C_{39}H_{53}N_9O_{12}Na$ $[M+Na]^+$: 862.3706, found: 862.3700.

5'-Methoxycarbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (3).



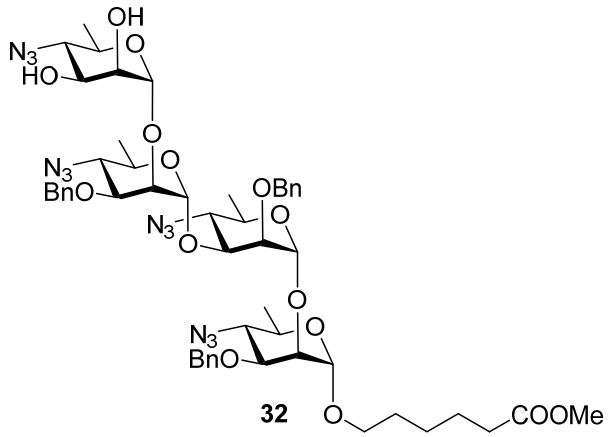
To a stirred solution of **31** (0.157 g, 0.187 mmol), in pyridine (5 mL) and water (2 mL) mixture, H_2S was bubbled for 0.5 h at 40 ^oC, and continued stirring for 16 h. After that, argon was bubbled for 10 min, solvents were removed *in vacuo*, and the residue was co-evaporated with toluene (3 x 10 mL) and dried. The high resolution mass spectrometry analysis showed completion of reaction to corresponding amine compound **31a** and no products arising from incomplete reduction. HRMS (ESI): *m*/*z* calcd for $C_{39}H_{60}N_3O_{12}$ [*M*+H]+: 762.4172; found: 762.4182. This crude material was directly used for formylation.

Compound **31a** in CH_3OH (5 mL) at -20 ^oC was added a freshly prepared formic anhydride (5 mL, ethereal solution) and stirred for 3 h, then slowly allowed to warm to 21 ^oC. After that, solvents were evaporated and the residue was passed through column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford disaccharide **31b**. HRMS (ESI): *m*/*z* calcd for $C_{42}H_{59}N_3O_{15}Na$ $[M+Na]^+$: 868.3838; found: 868.3834.

Compound **31b** was dissolved in CH_3OH/H_2O (2:1, 5 mL), $Pd(OH)_2$ on carbon (20%, 0.050 g) was added. Then it was stirred under a pressure of hydrogen gas at 21 ^oC for 16 h. After filtration through celite pad and washed with CH_3OH (3 x 10 mL), and solvents were removed *in vacuo*. The residue was purified by column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford the title compound (0.053 g, 43%, over 3 steps) as a white foam. Analytical data for **3**: R_f = 0.50 (CH_3OH/CH_2Cl_2, 3/7, v/v); ^1H NMR (700 MHz, D_2O): δ 8.20-8.24 (*Z*) and 8.02-8.06 (*E*) (m, 3H, NC*H*O), 4.92-5.04 (m, 3H, 3 x H-1), 3.80-4.23 (m, 12H, 3 x H-2, 3 x H-3, 3 x H-4, 3 x H-5), 3.69-3.74 (m, 1H, -O-CH_{2a}-), 3.70 (s, 3H, -OCH_3), 3.35-3.58 (m, 1H, -O-CH_{2b}-), 2.42 (t, $J_{f,e}$ = 7.4 Hz, 2H, -CH_{2f}-), 1.58-1.67 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.35-1.44 (m, 2H, -CH_{2d}-), 1.22-1.31 ppm (m, 9H, 3 x H-6); ^{13}C NMR (176 MHz, D_2O): δ 178.3, 168.7, 168.6, 168.5, 165.6 (x2), 165.5, 103.1, 102.9

(x2), 102.8, 102.7 (x2), 99.0 (x3), 78.6 (x2), 78.5, 77.3, 77.2, 77.1, 70.1, 70.0, 69.8, 69.5, 69.4, 68.9, 68.8 (x2), 68.7 (x2), 68.6 (x2), 68.5 (x2), 68.4 (x2), 68.3, 68.2, 67.8, 57.7, 57.4, 56.3, 52.9, 52.8, 52.4, 51.3, 34.4, 28.9, 25.7, 24.8, 17.6 (x2), 17.5, 17.4 ppm; HRMS (ESI): *m/z* calcd for $C_{28}H_{47}N_3O_{15}Na$ $[M+Na]^+$: 688.2899, found: 688.2893.

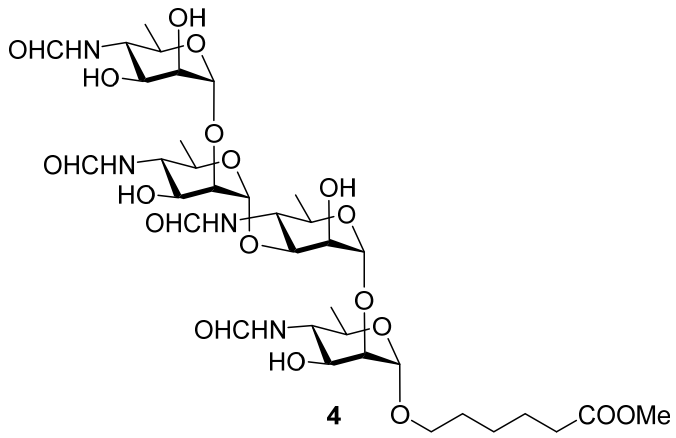
5'-Methoxycarbonylpentyl 4-azido-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (32).



Sodium methoxide (0.5 mL, 0.5 M solution) was added to a solution of **20** (0.391 g, 0.299 mmol) in CH_3OH /THF mixture (4:1, 15 mL) until pH ~9 and the resulting mixture was stirred under argon for 5 h at 21 ^oC. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.311 g, 95%) as oil. Analytical data for **32**: R_f = 0.40 (ethyl acetate/toluene, 1/4, v/v); $[\alpha]_D^{21}$ = +51.2 (c = 1.0, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ 7.10-7.39 (m, 15H, H-Ar), 5.07 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^B), 5.02 (d, $J_{1,2}$ = 1.6 Hz, 1H, H-1^C), 4.91 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^D), 4.67 (dd, J^2 = 11.0 Hz, 2H, CH_2Ph), 4.66 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^A), 4.60 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.20 (dd, J^2 = 12.0 Hz, 2H, CH_2Ph), 4.08 (dd, $J_{2,3}$ = 3.0 Hz, 1H, H-2^C), 3.96 (dd, $J_{2,3}$ = 2.8 Hz, 1H, H-2^A), 3.93 (m, 1H, H-2^D), 3.82-3.88 (m, 2H, H-3^B H-3^D), 3.75 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^A), 3.70 (dd, $J_{3,4}$ = 10.0 Hz, 1H, H-3^C), 3.68 (s, 3H, -OCH_3), 3.64-3.67 (m, 1H, H-5^D), 3.58-3.64 (m, 2H, H-2^B, -O-CH_{2a}-), 3.52-3.58 (m, 2H, H-4^B, H-5^B), 3.44-3.51 (m, 1H, H-5^A), 3.39-3.43 (m, 1H, H-5^C), 3.34-3.39 (m, 2H, H-4^C, -O-CH_{2b}-), 3.32 (dd, $J_{4,5}$ = 10.5 Hz, 1H, H-4^A), 3.29 (dd, $J_{4,5}$ = 10.0 Hz, 1H, H-4^D), 2.42 (d, $J_{3,\text{-OH}}$ = 7.3 Hz, 1H, -OH^D), 2.33 (t, J = 7.5 Hz, 2H, -CH_{2f}-), 2.12 (d, $J_{2,\text{-OH}}$ = 4.0 Hz, 1H, -OH^D), 1.66 (quin, J

= 7.6 Hz, 2H, -CH_{2e}-), 1.53-1.61 (m, 2H, -CH_{2c}-), 1.35-1.42 (m, 2H, -CH_{2d}-), 1.26-1.35 (m, 9H, H-6^{A}, H-6^{B} H-6^{C}), 1.17 ppm (d, $J_{5,6}$ = 5.9 Hz, 3H, H-6^{D}); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 137.5, 137.4, 137.3, 128.5, 128.4, 128.2, 128.0 (x2), 127.8, 127.5, 101.0, 100.8, 98.8, 98.2, 78.4, 77.9, 77.5, 76.4, 73.2, 72.5, 72.1, 71.8, 70.0, 69.7, 67.9 (x2), 67.5 (x2), 67.1, 65.8 (x2), 64.7, 64.6, 63.9, 51.5, 33.9, 29.0, 25.7, 24.7, 18.6 (x2), 18.5, 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{52}H_{68}N_{12}O_{15}Na$ $[M+Na]^+$: 1123.4806, found: 1123.4812.

5'-Methoxycarbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (4).



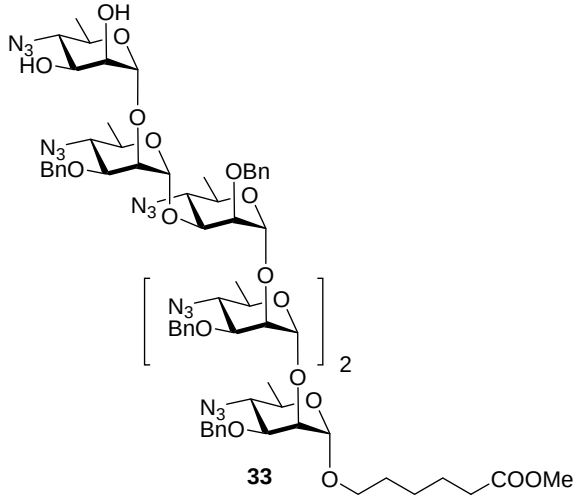
To a stirred solution of **32** (0.146 g, 0.132 mmol), in pyridine (5 mL) and water (2 mL) mixture, H_2S was bubbled for 0.5 h at 40 ^{o}C, and continued stirring for 16 h. After that, argon was bubbled for 10 min, solvents were removed *in vacuo*, and the residue was co-evaporated with toluene (3 x 10 mL) and dried. The high resolution mass spectrometry analysis showed completion of reaction to corresponding amine compound **32a** and no products arising from incomplete reduction. HRMS (ESI): *m/z* calcd for $C_{52}H_{77}N_4O_{15}$ [*M*+H]+: 997.5380; found: 997.5366. This crude material was directly used for formylation.

Compound **32a** in CH_3OH (5 mL) at -20 ^{o}C was added a freshly prepared formic anhydride (5 mL, ethereal solution) and stirred for 3 h, then slowly allowed to warm to 21 ^{o}C. After that, solvents were evaporated and the residue was passed through column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford disaccharide **32b**. HRMS (ESI): *m/z* calcd for $C_{56}H_{76}N_4O_{19}Na$ $[M+Na]^+$: 1131.4996; found: 1131.4992.

Compound **32b** was dissolved in CH_3OH/H_2O (2:1, 5 mL), $Pd(OH)_2$ on carbon (20%, 0.050 g) was added. Then it was stirred under a pressure of hydrogen gas at 21 ^{o}C for 16 h. After filtration through celite pad and washed with CH_3OH (3 x 10 mL), and solvents were

removed *in vacuo*. The residue was purified by column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford the title compound (0.068 g, 61%, over 3 steps) as a white foam. Analytical data for **4**: R_f = 0.30 (CH_3OH/CH_2Cl_2, 3/7, v/v); ^{1}H NMR (500 MHz, D_2O): δ 8.26-8.33 (*Z*) and 8.06-8.14 (*E*) (m, 4H, NC*H*O), 4.98-5.20 (m, 4H, 4 x H-1), 3.85-4.28 (m, 16H, 4 x H-2, 4 x H-3, 4 x H-4, 4 x H-5), 3.74-3.82 (m, 4H, -O-CH_{2a}-, -OCH_3), 3.44-3.66 (m, 1H, -O-CH_{2b}-), 2.49 (t, $J_{f,e}$ = 7.4 Hz, 2H, -CH_{2f}-), 1.65-1.75 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.42-1.51 (m, 2H, -CH_{2d}-), 1.28-1.39 ppm (m, 12H, 4 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.5, 168.8, 168.7, 168.6, 165.8, 165.6, 103.3, 103.2, 102.9, 102.8, 102.7, 101.9, 101.6, 99.3, 99.2, 79.3, 78.9, 78.7, 78.5, 78.4, 78.1, 77.3, 69.9 (x2), 69.8, 69.7, 69.4, 69.3, 69.0, 68.9, 68.8 (x2), 68.7, 68.6, 68.5, 68.4, 68.3, 68.0, 58.0, 57.7, 56.5, 53.1, 52.9, 52.8, 52.7, 51.8, 34.6, 29.1, 25.9, 25.0, 18.1 (x2), 18.0 (x2), 17.9 (x2), 17.8 (x2), 17.7 (x2) ppm; HRMS (ESI): *m/z* calcd for $C_{35}H_{58}N_4O_{19}Na$ $[M+Na]^+$: 861.3587, found: 861.3580.

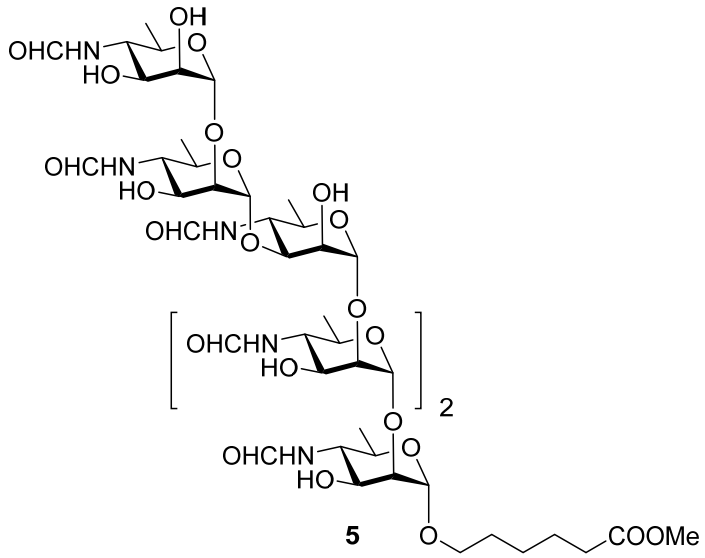
5'-Methoxycarbonylpentyl 4-azido-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→3) 4-azido-2-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (33).



Sodium methoxide (0.8 mL, 0.5 M solution) was added to a solution of **28** (0.413 g, 0.225 mmol) in CH_3OH (12 mL) until pH ~9 and the resulting mixture was stirred under argon for 6 h at 21 °C. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl

acetate – toluene gradient elution) to afford the title compound (0.334 g, 91%) as a white foam. Analytical data for **33**: R_f = 0.40 (ethyl acetate/toluene, 1/9, v/v); $[\alpha]_D^{21}$ = +61.0 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14-7.38 (m, 25H, H-Ar), 5.03-5.05 (br. s., 2H, H-1^D, H-1^E), 4.94 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^C), 4.91 (d, $J_{1,2}$ = 1.2 Hz, 1H, H-1^B), 4.90 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^F), 4.57-4.70 (m, 9H, H-1^A, 4 x CH_2Ph), 4.23 (dd, J^2 = 11.5 Hz, 2H, CH_2Ph), 4.10 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^E), 4.01 (dd, $J_{2,3}$ = 2.0 Hz, 1H, H-2^C), 3.95 (br. s., 1H, H-3^F), 3.82-3.88 (m, 3H, H-2^B, H-3^D, H-2^F), 3.79 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^A), 3.65-3.73 (m, 8H, H-3^A, H-3^B, H-3^C, H-3^E, H-4^F, -OCH_3), 3.63 (dd, $J_{2,3}$ = 2.3 Hz, 1H, H-2^D), 3.48-3.60 (m, 3H, H-4^E, H-5^F, -O-CH_{2a}-), 3.37-3.49 (m, 5H, H-5^A, H-5^B, H-5^C, H-5^D, H-5^E), 3.27-3.35 (m, 4H, H-4^B, H-4^C, H-4^D, -O-CH_{2b}-), 3.20 (dd, $J_{4,5}$ = 9.9 Hz, 1H, H-4^A), 2.38 (d, $J_{2,\text{-OH}}$ = 6.8 Hz, 1H, -OH^F), 2.34 (t, J = 7.4 Hz, 2H, -CH_{2f}-), 2.05 (d, $J_{3,\text{-OH}}$ = 3.5 Hz, 1H, -OH^F), 1.61-1.67 (m, 2H, -CH_{2e}-), 1.51-1.58 (m, 2H, -CH_{2c}-), 1.15-1.35 ppm (m, 20H, -CH_{2d}-, H-6^A, H-6^B, H-6^C, H-6^D, H-6^E, H-6^F); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 137.5, 137.4, 137.3, 137.2, 137.1, 128.7, 128.6 (x3), 128.4 (x2), 128.3 (x2), 128.2 (x2), 128.1 (x2), 128.0 (x2), 127.9, 127.5, 101.0, 100.9, 100.4, 100.2, 98.6, 98.1, 78.0, 77.6, 77.5 (x2), 76.9, 76.4, 74.0, 73.3, 73.1, 72.9, 72.5, 72.4, 72.2, 72.1, 71.9, 70.2, 69.9, 68.1, 67.9 (x2), 67.8, 67.5 (x2), 67.1, 65.8, 64.6, 64.5, 64.4, 64.3, 64.0, 51.5, 33.9, 29.1, 25.7, 24.7, 18.6 (x3), 18.5, 18.4, 18.3 ppm; HRMS (ESI): *m/z* calcd for $C_{78}H_{98}N_{18}O_{21}Na$ $[M+Na]^+$: 1645.7046, found: 1645.7035.

5'-Methoxycarbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (5).



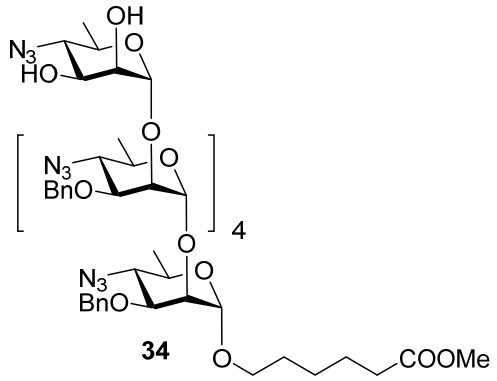
To a stirred solution of **33** (0.150 g, 0.092 mmol), in pyridine (5 mL) and water (2 mL) mixture, H_2S was bubbled for 0.5 h at 40 ^oC, and stirring was continued for 16 h. Then argon was bubbled through the solution for 10 min, solvents were removed *in vacuo*, and the residue was co-evaporated with toluene (3 x 10 mL) and dried. The high resolution mass spectrometry analysis showed completion of reaction to corresponding amine compound **33a** and no products arising from incomplete reduction. HRMS (ESI): *m*/*z* calcd for $C_{78}H_{111}N_6O_{21}$ [*M*+H]+: 1467.7797; found: 1467.7781. This crude material was directly used for formylation.

Compound **33a** in CH_3OH (5 mL) at -20 ^oC was added a freshly prepared formic anhydride (5 mL, ethereal solution) and stirred for 3 h, then slowly allowed to warm to 21 ^oC. Then solvents were evaporated and the residue was passed through column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford disaccharide **33b**. HRMS (ESI): *m*/*z* calcd for $C_{84}H_{110}N_6O_{27}Na$ $[M+Na]^+$: 1657.7311; found: 1657.7314.

Compound **33b** was dissolved in CH_3OH/H_2O (2:1, 5 mL), $Pd(OH)_2$ on carbon (20%, 0.050 g) was added. Then it was stirred under a pressure of hydrogen gas at 21 ^oC for 16 h. After filtration through celite pad and washed with CH_3OH (3 x 10 mL), and solvents were removed *in vacuo*. The residue was purified by column chromatography on silica gel

(methanol – dichloromethane gradient elution) to afford the title compound (0.066 g, 60%, over 3 steps) as a white foam. Analytical data for **5**: R*f* = 0.30 (CH_3OH/CH_2Cl_2, 1/1, v/v); ^1H NMR (700 MHz, D_2O): δ 8.20-8.25 (*Z*) and 8.02-8.06 (*E*) (m, 6H, NC*H*O), 4.89-5.23 (m, 6H, 6 x H-1), 3.79-4.22 (m, 23H, 6 x H-2, 6 x H-3, 6 x H-4, 5 x H-5), 3.70-3.74 (m, 4H, -O-CH_{2a}-, -OCH_3), 3.47-3.57 (m, 1H, -O-CH_{2b}-), 3.38-3.46 (m, 1H, H-5), 2.42 (t, $J_{f,e}$ = 7.7 Hz, 2H, -CH_{2f}-), 1.58-1.66 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.36-1.44 (m, 2H, -CH_{2d}-), 1.19-1.31 ppm (m, 18H, 6 x H-6); ^{13}C NMR (176 MHz, D_2O): δ 178.4, 168.6, 165.7 (x2), 165.4 (x2), 103.1, 102.4, 101.5 (x2), 101.3, 99.1 (x2), 78.8, 78.4, 78.2, 78.0, 77.9, 77.6, 77.2, 69.7 (x2), 69.6 (x2), 69.5, 69.1, 69.0, 68.8, 68.7 (x2), 68.6, 68.5, 68.4 (x2), 68.3, 68.2, 67.9, 57.8, 57.7, 57.6, 52.9, 52.8, 52.7, 52.6, 52.5, 51.7, 34.4, 28.9, 25.7, 24.8, 18.0, 17.9, 17.8 (x2), 17.7 (x2), 17.6 (x3), 17.5 ppm; HRMS (ESI): *m/z* calcd for $C_{49}H_{80}N_6O_{27}Na$ $[M+Na]^+$: 1207.4964, found: 1207.4963.

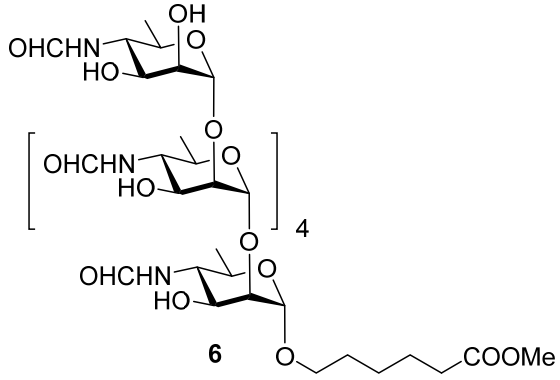
5'-Methoxycarbonylpentyl 4-azido-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl (1→2) 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (34).



Sodium methoxide (0.8 mL, 0.5 M solution) was added to a solution of **25** (0.483 g, 0.264 mmol) in CH_3OH (12 mL) until pH ~9 and the resulting mixture was stirred under argon for 6 h at 21 °C. After that, the reaction mixture was neutralized with Amberlite IR 120 (H^+) ion exchange resin, the resin was filtered off and rinsed successively with CH_3OH. The combined filtrate was concentrated *in vacuo* and purified by column chromatography on silica gel (ethyl acetate – toluene gradient elution) to afford the title compound (0.375 g, 87%) as oil. Analytical data for **34**: R_f = 0.30 (ethyl acetate/toluene, 1.5/8.5, v/v); $[\alpha]_D^{21}$ = +101.4 (c = 1.1,

$CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.40 (m, 25H, H-Ar), 4.98 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^F), 4.90 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^E), 4.89 (d, $J_{1,2}$ = 1.5 Hz, 1H, H-1^D), 4.86 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^C), 4.85 (d, $J_{1,2}$ = 2.0 Hz, 1H, H-1^B), 4.67 (dd, J^2 = 11.5 Hz, 2H, CH_2Ph), 4.56-4.75 (m, 9H, H-1^A, 4 x CH_2Ph), 3.93-3.97 (m, 2H, H-2^E, H-2^F), 3.83-3.89 (m, 2H, H-2^D, H-3^F), 3.82 (dd, $J_{2,3}$ = 2.0 Hz, 1H, H-2^C), 3.79 (dd, $J_{2,3}$ = 3.2 Hz, 1H, H-2^B), 3.76 (dd, $J_{2,3}$ = 2.5 Hz, 1H, H-2^A), 3.73 (dd, $J_{3,4}$ = 9.9 Hz, 1H, H-3^E), 3.63-3.70 (m, 7H, H-3^A, H-3^B, H-3^C, H-3^D, -OCH_3), 3.52-3.60 (m, 2H, H-5^E, -O-CH_{2a}-), 3.35-3.50 (m, 6H, H-4^F, H-5^A, H-5^B, H-5^C, H-5^D, H-5^F), 3.32 (dt, J = 9.7, 6.4 Hz, 1H, -O-CH_{2b}-), 3.23-3.29 (m, 2H, H-4^D, H-4^E), 3.15-3.22 (m, 3H, H-4^A, H-4^B, H-4^C), 2.41 (d, $J_{2,\text{-OH}}$ = 7.3 Hz, 1H, -OH^F), 2.32 (t, J = 7.8 Hz, 2H, -CH_{2f}-), 2.08 (d, $J_{3,\text{-OH}}$ = 4.3 Hz, 1H, -OH^F), 1.60-1.67 (m, 2H, -CH_{2e}-), 1.51-1.56 (m, 2H, -CH_{2c}-), 1.29-1.38 (m, 2H, -CH_{2d}-), 1.13-1.26 ppm (m, 18H, H-6^A, H-6^B, H-6^C, H-6^D, H-6^E, H-6^F); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.0, 137.4 (x2), 137.2 (x3), 128.7 (x2), 128.6 (x2), 128.4 (x2), 128.3 (x4), 128.1 (x2), 100.7, 100.4, 100.2 (x2), 100.1, 98.6, 77.5, 76.9, 76.6 (x2), 74.1, 73.6, 73.5, 73.3, 73.2, 72.3 (x2), 72.2 (x2), 70.2, 70.0, 67.9, 67.8 (x2), 67.5, 67.4, 67.1, 65.8, 64.4, 64.3, 64.2, 51.5, 33.9, 29.1, 25.7, 24.7, 18.6 (x2), 18.5 (x3), 18.2 ppm; HRMS (ESI): *m/z* calcd for $C_{78}H_{98}N_{18}O_{21}Na$ $[M+Na]^+$: 1645.7046, found: 1645.7043.

5'-Methoxycarbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (6).



To a stirred solution of **34** (0.130 g, 0.080 mmol), in pyridine (5 mL) and water (2 mL) mixture, H_2S was bubbled for 0.5 h at 40 °C, and continued stirring for 16 h. After that, argon was bubbled for 10 min, solvents were removed *in vacuo*, and the residue was co-evaporated with toluene (3 x 10 mL) and dried. The high resolution mass spectrometry analysis showed

completion of reaction to corresponding amine compound **34a** and no products arising from incomplete reduction. HRMS (ESI): *m*/*z* calcd for $C_{78}H_{111}N_6O_{21}$ [*M*+H]+: 1467.7797; found: 1467.7795. This crude material was directly used for formylation.

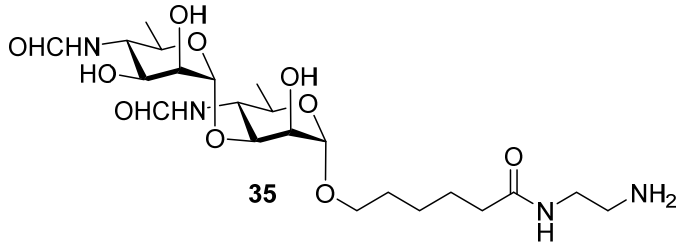
Compound **34a** in CH_3OH (5 mL) at -20 ^oC was added a freshly prepared formic anhydride (5 mL, ethereal solution) and stirred for 3 h, then slowly allowed to warm to 21 ^oC. After that, solvents were evaporated and the residue was passed through column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford disaccharide **34b**. HRMS (ESI): *m*/*z* calcd for $C_{84}H_{111}N_6O_{27}Na$ $[M+H]^+$: 1635.7492; found: 1635.7485.

Compound **34b** was dissolved in CH_3OH/H_2O (2:1, 5 mL), $Pd(OH)_2$ on carbon (20%, 0.050 g) was added. Then it was stirred under a pressure of hydrogen gas at 21 ^oC for 16 h. After filtration through celite pad and washed with CH_3OH (3 x 10 mL), and solvents were removed *in vacuo*. The residue was purified by column chromatography on silica gel (methanol – dichloromethane gradient elution) to afford the title compound (0.052 g, 55%, over 3 steps) as a white foam. Analytical data for **6**: R_f = 0.20 (CH_3OH/CH_2Cl_2, 2/3, v/v); ^1H NMR (500 MHz, D_2O): δ 8.17-8.19 (*Z*) and 7.99-8.02 (*E*) (m, 6H, NC*H*O), 4.84-5.20 (m, 6H, 6 x H-1), 3.76-4.17 (m, 24H, 6 x H-2, 6 x H-3, 6 x H-4, 6 x H-5), 3.66-3.72 (m, 4H, -O-CH_{2a}-, -OCH_3), 3.35-3.56 (m, 1H, -O-CH_{2b}-), 2.39 (t, $J_{f,e}$ = 7.4 Hz, 2H, -CH_{2f}-), 1.55-1.65 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.32-1.41 (m, 2H, -CH_{2d}-), 1.16-1.27 ppm (m, 18H, 6 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.5, 168.8, 165.9, 103.0, 102.9, 101.6, 101.5 (x2), 99.2, 78.6, 78.3, 78.1 (x2), 78.0 (x2), 77.9, 69.9 (x2), 69.2 (x2), 69.0, 68.9 (x2), 68.8, 68.7, 68.6 (x2), 68.5 (x3), 57.9, 57.7, 53.1, 53.0, 52.9, 52.8 (x2), 52.7, 49.9, 34.6, 29.0, 25.8, 24.9, 17.9 (x2), 17.8, 17.7 (x2), 17.6 (x2) ppm; HRMS (ESI): *m*/*z* calcd for $C_{49}H_{80}N_6O_{27}Na$ $[M+Na]^+$: 1207.4964, found: 1207.4941.

V. PREPARATION OF GLYCOCONJUGATES

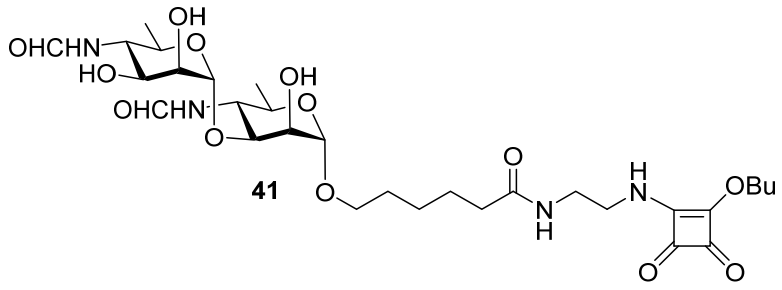
A. Synthesis of squarate derived oligosaccharides 41-46

(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (35).



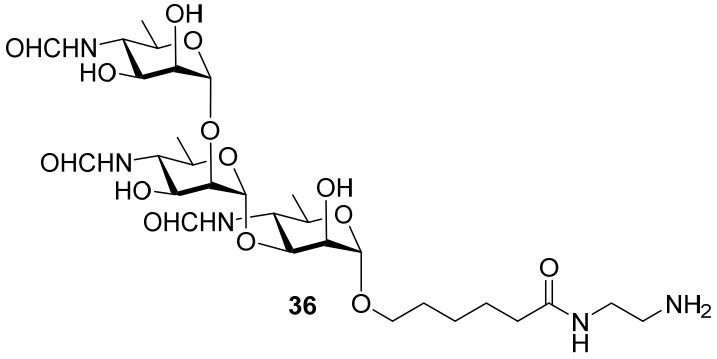
A solution of **1** (0.009g, 0.018 mmol) in freshly distilled 1,2-diaminoethane (0.5 mL) was stirred at 65 °C for 48 h. After that, excess reagent was removed *in vacuo*, and the residue was co-evaporated with CH_3OH (3 x 10 mL) and dried. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.0075 g, 79%) as a white foam. Analytical data for **35**: R_f = 0.15 (CH_3OH/CH_2Cl_2, 1/1, v/v); ^{1}H NMR (700 MHz, D_2O): δ 8.19-8.22 (*Z*) and 8.01-8.02 (*E*) (m, 2H, NC*H*O), 4.80-4.95 (m, 2H, 2 x H-1), 3.80-4.04 (m, 8H, 2 x H-2, 2 x H-3, 2 x H-4, 2 x H-5), 3.67-3.74 (m, 1H, -O-CH_{2a}-), 3.42-3.56 (m, 1H, -O-CH_{2b}-), 3.12-3.32 (m, 2H, -CH_{2g}-), 2.71-2.83 (m, 2H, -CH_{2h}-), 2.28 (t, $J_{f,e}$ = 7.5 Hz, 2H, -CH_{2f}-), 1.58-1.69 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.34-1.44 (m, 2H, -CH_{2d}-), 1.19-1.30 ppm (m, 6H, 2 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.4, 168.9, 168.8, 165.8, 165.7, 103.6, 103.3 (x2), 100.6, 100.5, 77.8, 77.4, 71.1, 70.4, 70.2, 70.0, 69.8, 69.0, 68.9, 68.8 (x3), 68.6, 68.4, 68.2, 67.8, 57.6, 56.5, 54.5, 52.6, 51.8, 51.6, 41.7, 41.4, 40.9, 40.7, 36.7, 29.2, 26.0, 25.9, 17.9, 17.8, 17.7 (x2) ppm; HRMS (ESI): *m/z* calcd for $C_{22}H_{40}N_4O_{10}Na$ $[M+Na]^+$: 543.2637, found: 543.2642.

1-[(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranoside]-2-butoxycyclobutene-3,4-dione (41).



To a stirred solution of **35** (0.0075 g, 0.014 mmol) in water (0.5 mL) and EtOH (0.4 mL), a solution of 3,4-dibutoxy-3-cyclobutene-1,2-dione (20% in ethanol, 70 µL) was added and pH was adjusted to 8 by careful addition of aq.$NaHCO_3$ (1%) solution. After 0.5 h, TLC showed the reaction was complete; the reaction mixture was neutralized using CH_3COOH (10%) and concentrated *in vacuo*. The residue purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.0089 g, 92%) as a white foam. Analytical data for **41**: R_f = 0.20 (CH_3OH/CH_2Cl_2, 1.5/8.5, v/v); ^{1}H NMR (500 MHz, D_2O): δ 8.26-8.30 (*Z*) and 8.09-8.12 (*E*) (m, 2H, NC*H*O), 4.83-5.03 (m, 2H, 2 x H-1), 4.74-4.81 (m, 2H, -CH_{2i}-), 3.88-4.10 (m, 8H, 2 x H-2, 2 x H-3, 2 x H-4, 2 x H-5), 3.66-3.82 (m, 3H, -O-CH_{2a}-, -CH_{2g}-), 3.52-3.61 (m, 1H, -O-CH_{2b}-), 3.40-3.52 (m, 2H, -CH_{2h}-), 2.26-2.34 (m, 2H, -CH_{2f}-), 1.82-1.91 (m, 2H, -CH_{2j}-), 1.58-1.70 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.47-1.56 (m, 2H, -CH_{2k}-), 1.38-1.44 (m, 2H, -CH_{2d}-), 1.26-1.37 (m, 6H, 2 x H-6), 0.99-1.05 ppm (m, 3H, -CH_{3l}); ^{13}C NMR (126 MHz, D_2O): δ 189.8, 189.6, 184.3 (x2), 178.5, 178.1, 178.0, 177.9, 174.8, 174.7, 168.9, 168.8, 165.8, 165.7, 103.3, 103.2, 100.5 (x2), 77.8, 75.4, 75.3, 70.2, 70.0, 69.9, 69.0, 68.9 (x2), 68.8, 68.7, 68.6, 68.4, 68.2, 67.7, 57.6, 56.5, 52.7, 52.6, 51.7, 45.2, 45.0, 40.3, 40.2, 36.7, 32.4, 31.2, 29.3 (x2), 26.2, 26.1, 25.9 (x2), 19.1, 19.0, 17.8 (x2), 17.7, 13.9 ppm; HRMS (ESI): *m/z* calcd for $C_{30}H_{48}N_4O_{13}Na$ $[M+Na]^+$: 695.3110, found: 695.3113.

(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (36).

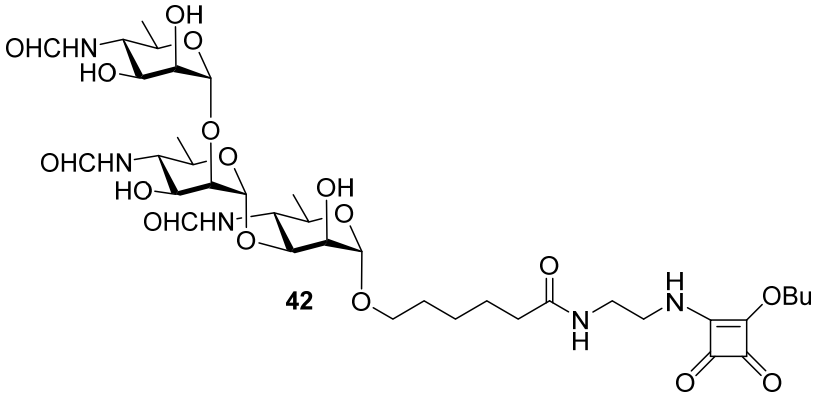


36

A solution of **2** (0.012g, 0.018 mmol) in freshly distilled 1,2-diaminoethane (0.5 mL) was stirred at 65 °C for 48 h. After that, excess reagent was removed *in vacuo*, and the residue was co-evaporated with CH_3OH (3 x 10 mL) and dried. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title

compound (0.0112 g, 90%) as a white foam. Analytical data for **36**: R_f = 0.10 (CH_3OH/CH_2Cl_2, 1/1, v/v); ^{1}H NMR (500 MHz, D_2O): δ 8.26-8.31 (*Z*) and 8.08-8.13 (*E*) (m, 3H, NC*H*O), 4.88-5.16 (m, 3H, 3 x H-1), 3.88-4.20 (m, 12H, 3 x H-2, 3 x H-3, 3 x H-4, 3 x H-5), 3.75-3.82 (m, 1H, -O-CH_{2a}-), 3.44-3.64 (m, 1H, -O-CH_{2b}-), 3.18-3.39 (m, 2H, -CH_{2g}-), 2.86-3.08 (m, 2H, -CH_{2h}-), 2.30-2.37 (m, 2H, -CH_{2f}-), 1.64-1.74 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.40-1.48 (m, 2H, -CH_{2d}-), 1.20-1.37 (m, 9H, 3 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.4, 178.2, 168.8 (x2), 165.9, 165.8, 165.6 (x3), 103.3 (x2), 101.7 (x2), 100.5 (x2), 79.0, 77.7, 70.0, 69.9, 69.2, 69.0, 68.9, 68.8, 68.6, 68.4, 68.0, 67.7, 57.8, 57.7, 52.8, 52.7, 51.9, 41.5 (x2), 41.5, 41.4, 40.9, 40.6 (x2), 36.6, 29.2, 26.0 (x2), 25.9, 25.8, 18.1, 18.0, 17.9 (x3), 17.7 ppm; HRMS (ESI): *m/z* calcd for $C_{29}H_{51}N_5O_{14}Na$ $[M+Na]^+$: 716.3325, found: 716.3311.

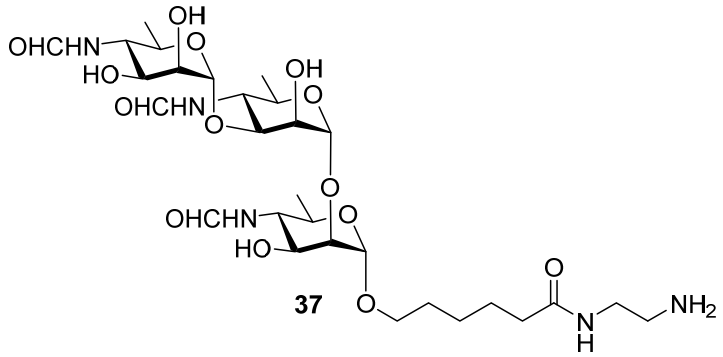
1-[(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranoside]-2-butoxycyclobutene-3,4-dione (42).



To a stirred solution of **36** (0.0075 g, 0.011 mmol) in water (0.5 mL) and EtOH (0.4 mL), a solution of 3,4-dibutoxy-3-cyclobutene-1,2-dione (20% in ethanol, 50 μL) was added and pH was adjusted to 8 by careful addition of aq.$NaHCO_3$ (1%) solution. After 0.5 h, TLC showed the reaction was complete; the reaction mixture was neutralized using CH_3COOH (10%) and concentrated *in vacuo*. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.0065 g, 71%) as a white foam. Analytical data for **42**: R_f = 0.20 (CH_3OH/CH_2Cl_2, 1/4, v/v); ^{1}H NMR (500 MHz, D_2O): δ 8.27-8.31 (*Z*) and 8.08-8.13 (*E*) (m, 3H, NC*H*O), 4.86-5.15 (m, 3H, 3 x H-1), 4.74-4.81 (m, 2H, -CH_{2i}-), 3.90-4.20 (m, 12H, 3 x H-2, 3 x H-3, 3 x H-4, 3 x H-5), 3.66-3.82 (m, 3H, -O-CH_{2a}-, -CH_{2g}-), 3.52-3.61 (m, 1H, -O-CH_{2b}-), 3.43-3.51 (m, 2H, -CH_{2h}-), 2.25-2.33 (m, 2H, -CH_{2f}-), 1.82-1.91 (m, 2H, -CH_{2j}-), 1.57-1.70 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.46-1.56

(m, 2H, -CH_{2k}-), 1.37-1.44 (m, 2H, -CH_{2d}-), 1.26-1.36 (m, 9H, 3 x H-6), 0.98-1.05 ppm (m, 3H, -CH_{3l}); ^{13}C NMR (126 MHz, D_2O): δ 189.8, 189.6, 184.3 (x2), 178.5, 178.1, 178.0, 177.9, 174.8, 174.7, 168.8, 168.7, 165.8 (x2), 165.6, 103.4, 103.3, 102.9, 101.8, 101.7, 100.6, 100.5, 79.0, 78.9, 78.8, 78.2, 78.0, 77.7 (x2), 75.4, 75.3, 70.0, 69.9, 69.3, 69.2, 69.0, 68.9, 68.9, 68.8, 68.6, 68.5 (x2), 68.4, 68.3, 67.9, 67.7, 57.8, 57.7, 56.5, 52.8, 52.8, 52.7, 51.9, 45.2, 45.0, 40.3, 40.2, 36.7, 32.4, 29.3 (x2), 26.2, 26.1, 25.9 (x2), 19.1, 19.0, 18.1, 18.0, 17.9 (x3), 17.7, 13.9 ppm; HRMS (ESI): *m/z* calcd for $C_{37}H_{59}N_5O_{17}Na$ $[M+Na]^+$: 868.3798, found: 868.3800.

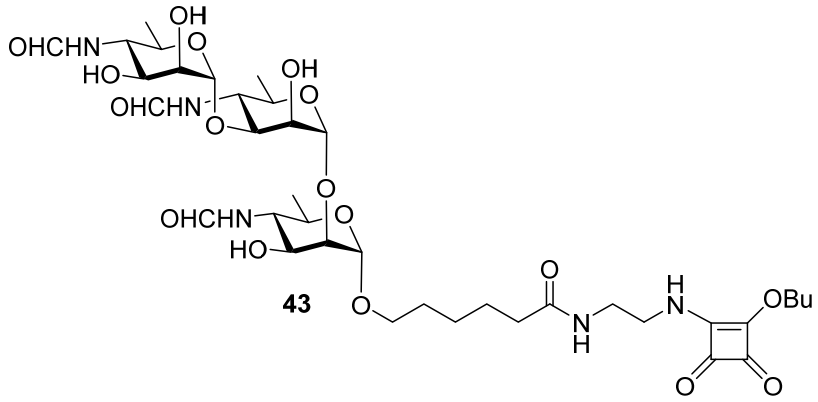
(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (37).



A solution of **3** (0.010g, 0.015 mmol) in freshly distilled 1,2-diaminoethane (0.5 mL) was stirred at 65 °C for 48 h. After that, excess reagent was removed *in vacuo*, and the residue was co-evaporated with CH_3OH (3 x 10 mL) and dried. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.0084 g, 81%) as a white foam. Analytical data for **37**: R_f = 0.10 (CH_3OH/CH_2Cl_2, 1/1, v/v); ^{1}H NMR (500 MHz, D_2O): δ 8.26-8.31 (*Z*) and 8.09-8.13 (*E*) (m, 3H, NC*H*O), 4.98 - 5.11 (m, 3H, 3 x H-1), 3.83-4.29 (m, 12H, 3 x H-2, 3 x H-3, 3 x H-4, 3 x H-5), 3.74-3.82 (m, 1H, -O-CH_{2a}-), 3.50-3.65 (m, 1H, -O-CH_{2b}-), 3.18-3.47 (m, 2H, -CH_{2g}-), 3.02 (t, $J_{h,g}$ = 5.8 Hz, 2H, -CH_{2h}-), 2.31-2.39 (m, 2H, -CH_{2f}-), 1.64-1.75 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.40-1.50 (m, 2H, -CH_{2d}-), 1.26-1.38 ppm (m, 9H, 3 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.6, 178.1, 168.9, 168.8, 168.7, 165.8, 165.7, 165.6, 161.6, 103.3, 103.1 (x2), 103.1, 102.9, 99.2 (x2), 78.8 (x3), 77.8, 77.5, 77.4, 77.3, 77.1, 71.0, 70.8, 70.4, 70.2, 70.0, 69.8, 69.7, 69.6, 69.1, 69.0, 68.9 (x2), 68.8 (x2), 68.7 (x2), 68.6, 68.5 (x2), 68.0, 57.9, 57.6, 56.5, 54.5, 53.0, 52.7, 52.6, 51.6, 51.5, 41.4, 40.9, 40.4, 40.0, 36.7, 36.6, 29.1, 26.0, 25.9,

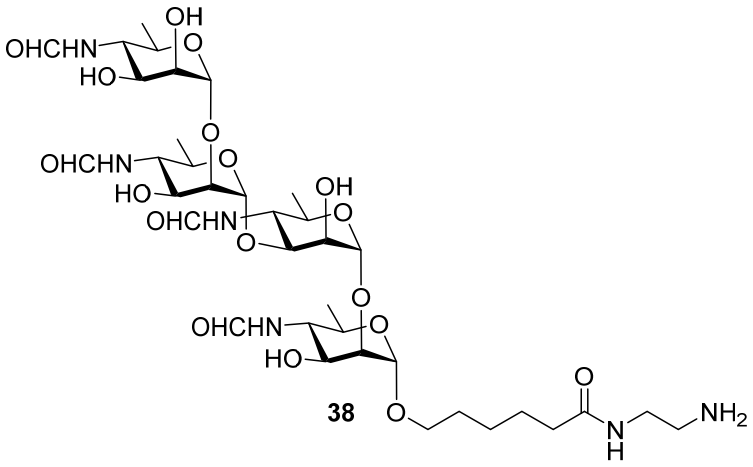
25.8, 18.0, 17.8, 17.7, 17.6 ppm; HRMS (ESI): *m/z* calcd for $C_{29}H_{51}N_5O_{14}Na$ $[M+Na]^+$: 716.3325, found: 716.3322.

1-[(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside]-2-butoxycyclobutene-3,4-dione (43).



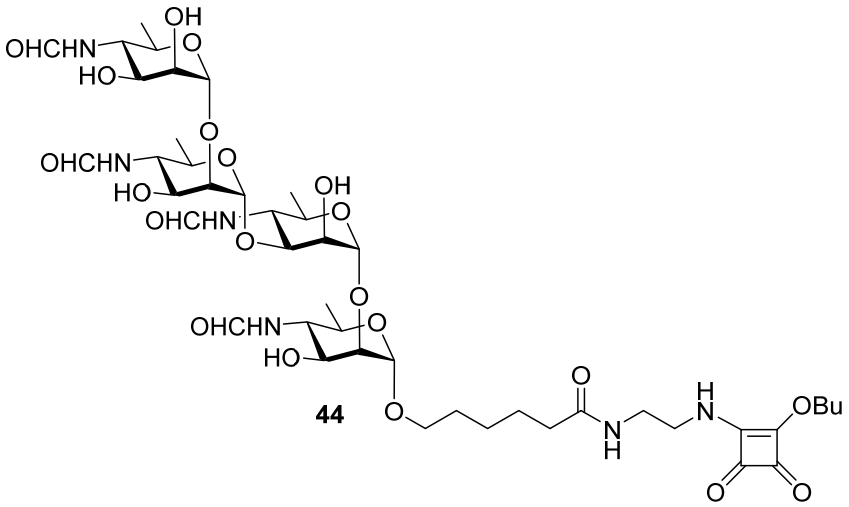
To a stirred solution of **37** (0.0074 g, 0.0106 mmol) in water (0.5 mL) and EtOH (0.4 mL), a solution of 3,4-dibutoxy-3-cyclobutene-1,2-dione (20% in ethanol, 50 μL) was added and pH was adjusted to 8 by careful addition of aq.$NaHCO_3$ (1%) solution. After 0.5 h, TLC showed the reaction was complete; the reaction mixture was neutralized using CH_3COOH (10%) and concentrated *in vacuo*. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.0072 g, 80%) as a white foam. Analytical data for **43**: R_f = 0.20 (CH_3OH/CH_2Cl_2, 1/4, v/v); ^{1}H NMR (500 MHz, D_2O): δ 8.16-8.21 (*Z*) and 7.99-8.03 (*E*) (m, 3H, NC*H*O), 4.87-5.01 (m, 3H, 3 x H-1), 4.64-4.73 (m, 2H, -CH_{2i}-), 3.75-4.18 (m, 12H, 3 x H-2, 3 x H-3, 3 x H-4, 3 x H-5), 3.55-3.71 (m, 3H, -O-CH_{2a}-, -CH_{2g}-), 3.44-3.51 (m, 1H, -O-CH_{2b}-), 3.31-3.42 (m, 2H, -CH_{2h}-), 2.16-2.24 (m, 2H, -CH_{2f}-), 1.72-1.81 (m, 2H, -CH_{2j}-), 1.47-1.61 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.36-1.46 (m, 2H, -CH_{2k}-), 1.27-1.34 (m, 2H, -CH_{2d}-), 1.18-1.27 (m, 9H, 3 x H-6), 0.86-0.95 ppm (m, 3H, -CH_{3l}); ^{13}C NMR (126 MHz, D_2O): δ 189.8, 189.6, 184.2, 178.5, 178.0, 177.9 (x2), 174.8, 174.7, 168.8, 168.7, 166.6, 165.8, 165.7, 103.1, 102.8, 99.1 (x2), 78.7, 77.4 (x2), 75.4, 75.3, 70.2, 69.7, 69.6, 69.1, 69.0, 68.9, 68.7 (x3), 68.5, 68.4, 53.0, 52.6, 51.5, 45.1, 44.9, 40.3, 40.1, 36.7, 32.4, 29.2, 26.1, 26.0, 25.9 (x2), 19.0 (x2), 17.8 (x3), 17.6, 13.9 ppm; HRMS (ESI): *m/z* calcd for $C_{37}H_{59}N_5O_{17}Na$ $[M+Na]^+$: 868.3798, found: 868.3791.

(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (38).



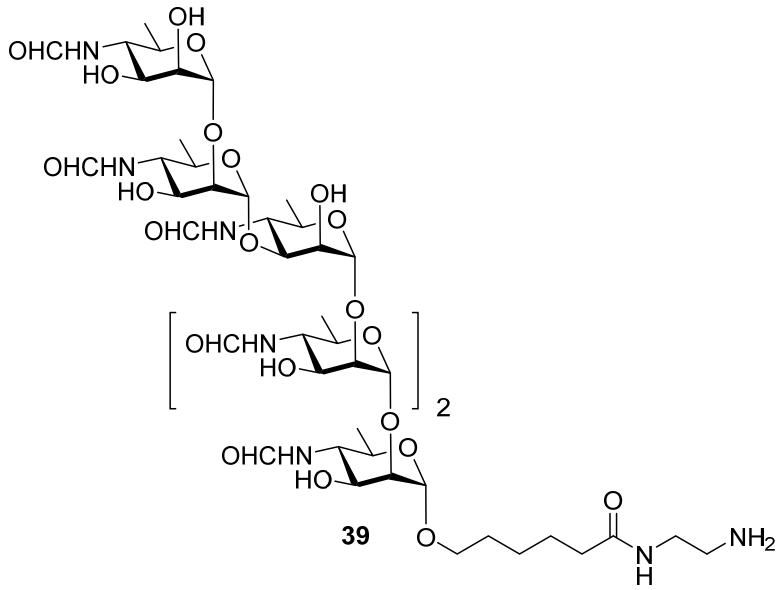
A solution of **4** (0.0134 g, 0.016 mmol) in freshly distilled 1,2-diaminoethane (0.5 mL) was stirred at 65 °C for 48 h. After that, excess reagent was removed *in vacuo*, and the residue was co-evaporated with CH_3OH (3 x 10 mL) and dried. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.0113 g, 82%) as a white foam. Analytical data for **38**: R_f = 0.10 (CH_3OH/CH_2Cl_2, 1/1, v/v); ^{1}H NMR (500 MHz, D_2O): δ 8.16-8.23 (*Z*) and 7.98-8.05 (*E*) (m, 4H, NC*H*O), 4.84-5.10 (m, 4H, 4 x H-1), 3.60-4.18 (m, 17H, 4 x H-2, 4 x H-3, 4 x H-4, 4 x H-5, -O-CH_{2a}-), 3.46-3.56 (m, 1H, -O-CH_{2b}-), 3.10-3.28 (m, 2H, -CH_{2g}-), 2.72-2.81 (m, 2H, -CH_{2h}-), 2.22-2.28 (m, 2H, -CH_{2f}-), 1.54-1.64 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.30-1.41 (m, 2H, -CH_{2d}-), 1.18-1.30 ppm (m, 12H, 4 x H-6); ^{13}C NMR (125 MHz, D_2O): δ 178.3, 178.2, 168.7, 165.7, 165.5, 103.5, 103.2 (x2), 102.7, 102.6, 102.0, 99.4, 99.1, 79.0, 78.5, 78.4, 77.6, 77.2, 71.2, 71.0, 70.9, 70.8, 70.7, 70.3, 70.0, 69.8, 69.7, 69.6, 69.1, 68.8, 68.6, 68.5, 68.2, 54.8, 54.6, 54.4, 52.9, 52.7, 52.0, 51.7 (x2), 41.5, 41.4, 41.2, 40.5, 36.5, 29.0, 25.9, 25.8 (x2), 25.7, 17.9 (x2), 17.7 (x2) ppm; HRMS (ESI): *m/z* calcd for $C_{36}H_{62}N_6O_{18}Na$ $[M+Na]^+$: 889.4013, found: 889.4020.

1-[(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside]-2-butoxycyclobutene-3,4-dione (44).



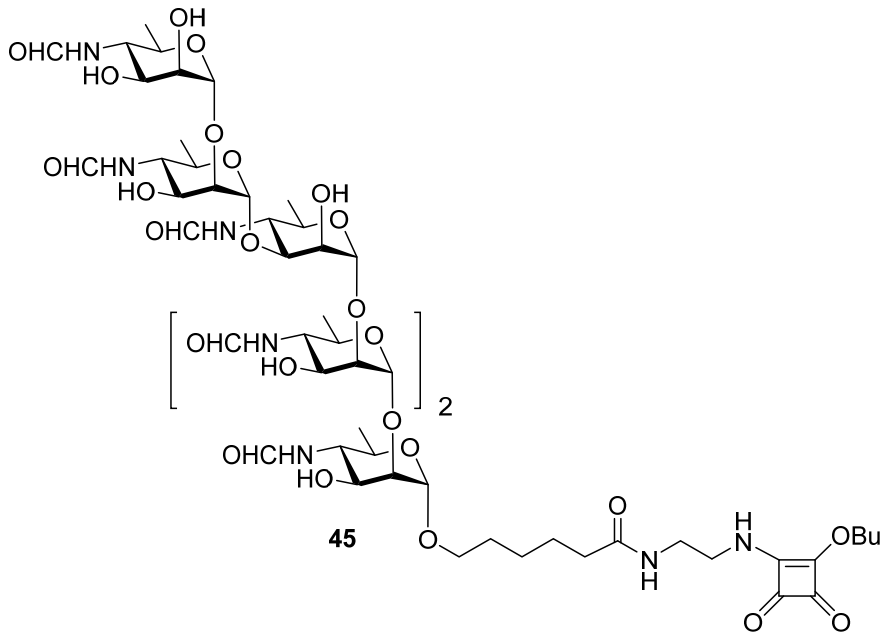
To a stirred solution of **38** (0.013 g, 0.015 mmol) in water (0.5 mL) and EtOH (0.4 mL), a solution of 3,4-dibutoxy-3-cyclobutene-1,2-dione (20% in ethanol, 70 μL) was added and pH was adjusted to 8 by careful addition of aq.$NaHCO_3$ (1%) solution. After 0.5 h, TLC showed the reaction was complete; the reaction mixture was neutralized using CH_3COOH (10%) and concentrated *in vacuo*. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.0109 g, 72%) as a white foam. Analytical data for **44**: R_f = 0.20 (CH_3OH/CH_2Cl_2, 1/4, v/v); ^{1}H NMR (600 MHz, D_2O): δ 8.18-8.24 (*Z*) and 7.98-8.06 (*E*) (m, 4H, NC*H*O), 4.90-5.10 (m, 4H, 4 x H-1), 4.65-4.73 (m, 2H, -CH_{2i}-), 3.76-4.20 (m, 16H, 4 x H-2, 4 x H-3, 4 x H-4, 4 x H-5), 3.57-3.73 (m, 3H, -O-CH_{2a}-, -CH_{2g}-), 3.45-3.52 (m, 1H, -O-CH_{2b}-), 3.36-3.43 (m, 2H, -CH_{2h}-), 2.18-2.25 (m, 2H, -CH_{2f}-), 1.74-1.82 (m, 2H, -CH_{2j}-), 1.49 -1.63 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.38-1.48 (m, 2H, -CH_{2k}-), 1.20-1.35 (m, 14H, -CH_{2d}-, 4 x H-6), 0.87-0.96 ppm (m, 3H, -CH_{3l}); ^{13}C NMR (126 MHz, D_2O): δ 189.8, 189.6, 184.3 (x2), 178.5, 178.2, 178.1, 178.0, 177.9, 174.8, 174.7, 168.8, 168.7, 168.6, 165.8, 165.6, 103.3 (x2), 103.2, 102.8 (x2), 102.7, 101.7 (x2), 101.6 (x2), 99.2, 78.9 (x2), 78.4, 78.1, 77.3, 75.4, 75.3, 69.9 (x2), 69.8 (x2), 69.7, 69.3, 69.0 (x2), 68.9, 68.8 (x4), 68.6 (x2), 68.5, 68.4 (x2), 68.0, 62.5, 52.9, 52.8 (x2), 52.7, 51.8, 45.2, 45.0, 44.2, 40.6, 40.3, 40.2, 36.7, 34.4, 32.4, 29.2, 26.2, 26.1, 26.0 (x2), 25.9 (x2), 25.8, 19.3, 19.1, 19.0, 18.1, 18.0 (x2), 17.9, 17.8 (x2), 17.7 (x2), 14.0, 13.9 ppm; HRMS (ESI): *m/z* calcd for $C_{44}H_{70}N_6O_{21}Na$ $[M+Na]^+$: 1041.4486, found: 1041.4484.

(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (39).



A solution of **5** (0.041 g, 0.035 mmol) in freshly distilled 1,2-diaminoethane (0.5 mL) was stirred at 21 °C for 48 h. Then excess reagent was removed *in vacuo*, and the residue was co-evaporated with CH_3OH (3 x 10 mL) and dried. The residue was purified by reversed phase HPLC on a C18 column with a gradient of water-acetonitrile and lyophilized, to give the title compound (0.039 g, 93%) as a white foam. Analytical data for **39**: R_f = 0.20 (CH_3OH); ^{1}H NMR (500 MHz, D_2O): δ 8.15-8.20 (*Z*) and 7.95-8.02 (*E*) (m, 6H, NC*H*O), 4.82-5.18 (m, 6H, 6 x H-1), 3.73-4.17 (m, 23H, 6 x H-2, 6 x H-3, 6 x H-4, 5 x H-5), 3.63-3.69 (m, 1H, -O-CH_{2a}-), 3.47-3.53 (m, 1H, -O-CH_{2b}-), 3.31-3.46 (m, 1H, H-5), 3.08-3.25 (m, 2H, -CH_{2g}-), 2.72-2.77 (m, 2H, -CH_{2h}-), 2.20-2.25 (m, 2H, -CH_{2f}-), 1.53-1.63 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.28-1.38 (m, 2H, -CH_{2d}-), 1.13-1.28 ppm (m, 18H, 6 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.4, 178.1, 168.8 (x2), 165.9, 165.6, 103.3 (x2), 102.6, 101.9, 101.8, 101.6, 101.5, 99.3, 99.2, 78.9, 78.6, 78.5, 78.1, 77.8, 77.4, 71.0, 69.9 (x2), 69.7 (x2), 69.6, 69.4, 69.2, 69.0, 69.0, 68.9, 68.8, 68.6 (x2), 68.5 (x2), 68.4, 68.0, 57.9 (x2), 57.8, 57.7, 56.4, 53.0, 52.8 (x2), 52.7, 51.8, 41.4, 41.1, 40.6, 36.6, 29.1, 26.0, 25.9 (x2), 18.1 (x3), 18.0, 17.9, 17.8, 17.7, 17.6 ppm; HRMS (ESI): *m/z* calcd for $C_{50}H_{85}N_8O_{26}$ $[M+H]^+$: 1213.5570, found: 1213.5564.

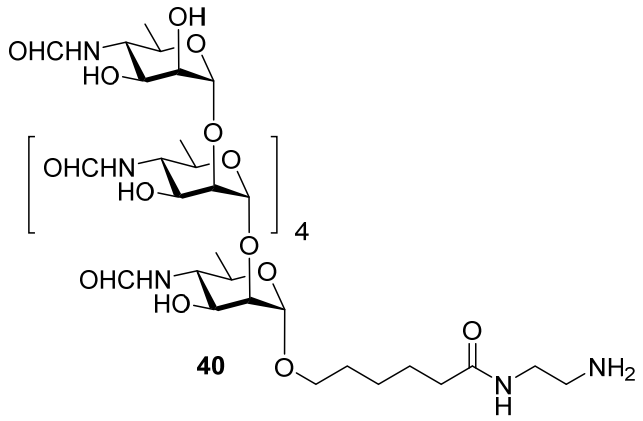
1-[(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→3) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside]-2-butoxycyclobutene-3,4-dione (45).



To a stirred solution of **39** (0.014 g, 0.011 mmol) in water (0.8 mL) and EtOH (0.6 mL), a solution of 3,4-dibutoxy-3-cyclobutene-1,2-dione (20% in ethanol, 55 μL) was added and the pH was adjusted to 8 by careful addition of aq.$NaHCO_3$ (1%) solution. After 0.5 h, TLC showed the reaction was complete; the reaction mixture was neutralized using CH_3COOH (10%) and concentrated *in vacuo*. The residue was purified by reversed phase HPLC on a C18 column with a gradient of water-acetonitrile and lyophilized, to give the title compound (0.012 g, 76%) as a white foam. Analytical data for **45**: R*f* = 0.40 (CH_3OH/CH_2Cl_2, 1/1, v/v); ^{1}H NMR (700 MHz, D_2O): δ 8.14-8.20 (*Z*) and 7.96-8.02 (*E*) (m, 6H, NC*H*O), 4.83-5.18 (m, 6H, 6 x H-1), 4.62-4.69 (m, 2H, -CH_{2i}-), 3.72-4.17 (m, 24H, 6 x H-2, 6 x H-3, 6 x H-4, 6 x H-5), 3.66-3.69 (m, 1H, -CH_{2g}-), 3.60-3.65 (m, 1H, -O-CH_{2a}-), 3.55-3.58 (m, 1H, -CH_{2g}-), 3.42-3.48 (m, 1H, -O-CH_{2b}-), 3.32-3.41 (m, 2H, -CH_{2h}-), 2.14-2.21 (m, 2H, -CH_{2f}-), 1.71-1.79 (m, 2H, -CH_{2j}-), 1.46-1.60 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.36-1.44 (m, 2H, -CH_{2k}-), 1.15-1.30 (m, 20H, -CH_{2d}-, 6 x H-6), 0.88-0.93 ppm (m, 3H, -CH_{3l}); ^{13}C NMR (126 MHz, D_2O): δ 189.8, 189.7, 184.3, 178.5, 178.1, 177.9 (x2), 174.8, 174.7, 168.8, 165.9, 165.6, 103.3, 102.6, 101.6, 101.5, 99.2, 78.9, 78.5, 78.2, 77.8, 77.3, 75.4, 75.3, 70.8, 69.9, 69.7, 69.2, 69.0, 68.8,

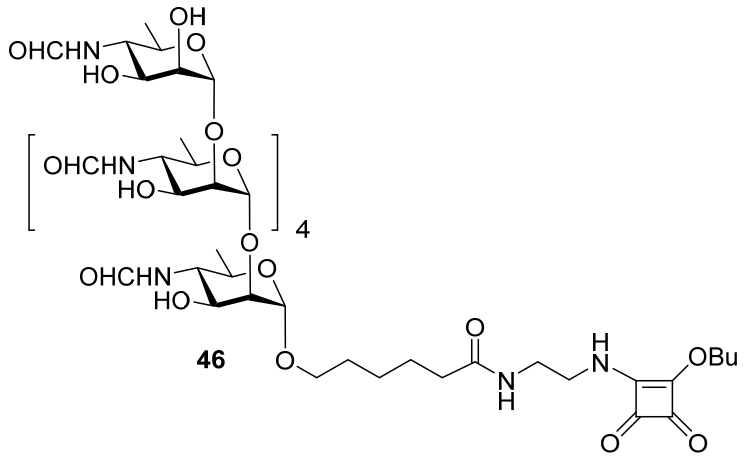
68.7, 68.6, 68.5, 68.4, 57.9, 57.7, 53.0, 52.8, 52.7, 51.8, 45.2, 45.0, 40.3, 40.2, 36.7, 32.4, 29.2, 26.1, 26.0, 25.9 (x2), 19.1, 19.0, 18.1, 18.0, 17.9 (x2), 17.8, 17.7, 13.9 ppm; HRMS (ESI): *m/z* calcd for $C_{58}H_{92}N_8O_{29}Na$ $[M+Na]^+$: 1387.5862, found: 1387.5864.

(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside (40).



A solution of **6** (0.034 g, 0.029 mmol) in freshly distilled 1,2-diaminoethane (0.5 mL) was stirred at 21 °C for 48 h. After that, excess reagent was removed *in vacuo*, and the residue was co-evaporated with CH_3OH (3 x 10 mL) and dried. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.034 g, 97%) as a white foam. Analytical data for **40**: R_f = 0.20 (CH_3OH); ^{1}H NMR (500 MHz, D_2O): δ 8.16-8.19 (*Z*) and 7.98-8.02 (*E*) (m, 6H, NC*H*O), 4.81-5.19 (m, 6H, 6 x H-1), 3.64-4.18 (m, 25H, 6 x H-2, 6 x H-3, 6 x H-4, 6 x H-5, -O-CH_{2a}-), 3.32-3.55 (m, 1H, -O-CH_{2b}-), 3.08-3.27 (m, 2H, -CH_{2g}-), 2.70-2.79 (m, 2H, -CH_{2h}-), 2.22-2.27 (m, 2H, -CH_{2f}-), 1.55-1.65 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.28-1.40 (m, 2H, -CH_{2d}-), 1.14-1.26 ppm (m, 18H, 6 x H-6); ^{13}C NMR (126 MHz, D_2O): δ 178.3, 178.1, 168.8, 168.7, 165.8, 103.4, 103.0 (x2), 102.9, 102.0, 101.7, 101.6, 101.5, 99.5, 99.3, 99.2, 78.7, 78.6, 78.3, 78.2, 78.1(x2), 78.0, 77.7, 71.3, 71.2, 71.0, 70.9, 70.4, 70.2, 69.9, 69.2, 69.0, 68.9 (x2), 68.8, 68.7, 68.7, 68.6 (x2), 68.5 (x3), 68.0, 57.9, 57.8, 57.7, 54.8, 54.8, 54.5, 53.0, 52.8, 52.6, 41.8, 41.4, 40.9, 40.7, 36.7, 29.1, 26.0, 25.9 (x2), 18.0, 17.9 (x2), 17.8, 17.7, 17.6 ppm; HRMS (ESI): *m/z* calcd for $C_{50}H_{84}N_8O_{26}Na$ $[M+Na]^+$: 1235.5389, found: 1235.5384.

1-[(2'-Aminoethylamido)carbonylpentyl 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranosyl (1→2) 4,6-dideoxy-4-formamido-α-D-mannopyranoside]-2-butoxycyclobutene-3,4-dione (46).



To a stirred solution of **40** (0.0142 g, 0.012 mmol) in water (0.5 mL) and EtOH (0.4 mL), a solution of 3,4-dibutoxy-3-cyclobutene-1,2-dione (20% in ethanol, 55 μL) was added and pH was adjusted to 8 by careful addition of aq.$NaHCO_3$ (1%) solution. After 0.5 h, TLC showed the reaction was complete; the reaction mixture was neutralized using CH_3COOH (10%) and concentrated *in vacuo*. The residue was purified by reversed phase HPLC on C18 column in gradient water-acetonitrile and lyophilized, to give the title compound (0.014 g, 88%) as a white foam. Analytical data for **46**: R_f = 0.40 (CH_3OH/CH_2Cl_2, 1/1, v/v); ^{1}H NMR (700 MHz, D_2O): δ 8.14-8.19 (*Z*) and 7.97-8.01 (*E*) (m, 6H, NC*H*O), 4.82-5.18 (m, 6H, 6 x H-1), 4.62-4.70 (m, 2H, -CH_{2i}-), 3.72-4.15 (m, 24H, 6 x H-2, 6 x H-3, 6 x H-4, 6 x H-5), 3.66-3.69 (m, 1H, -CH_{2g}-), 3.60-3.65 (m, 1H, -O-CH_{2a}-), 3.55-3.58 (m, 1H, -CH_{2g}-), 3.42-3.48 (m, 1H, -O-CH_{2b}-), 3.31-3.41 (m, 2H, -CH_{2h}-), 2.14-2.21 (m, 2H, -CH_{2f}-), 1.71-1.79 (m, 2H, -CH_{2j}-), 1.46-1.59 (m, 4H, -CH_{2e}-, -CH_{2c}-), 1.35-1.44 (m, 2H, -CH_{2k}-), 1.14-1.31 (m, 20H, -CH_{2d}-, 6 x H-6), 0.87-0.93 ppm (m, 3H, -CH_{3l}); ^{13}C NMR (126 MHz, D_2O): δ 189.8, 189.6, 184.3, 178.5, 178.1, 177.9 (x2), 174.8, 174.7, 168.8, 165.9, 102.9, 101.5 (x3), 99.2 (x2), 78.5, 78.1(x2), 78.0, 75.4, 75.3, 71.4, 69.9, 69.2, 69.0, 68.9, 68.7, 68.6, 68.0, 57.8 (x2), 53.0, 52.9 (x2), 52.7, 45.2, 45.0, 40.3, 40.2, 36.7, 32.4, 32.3, 32.2, 29.2, 26.1(x2), 25.9 (x2), 19.1, 19.0, 17.9 (x2), 17.8 (x2), 17.7, 13.9, 13.8 ppm; HRMS (ESI): *m/z* calcd for $C_{58}H_{92}N_8O_{29}Na$ $[M+Na]^+$: 1387.5862, found: 1387.5856.

B. Protein conjugation

*Preparation of BSA conjugate **47**.* BSA (30 mg, 0.451 μmol) and disaccharide squarate **41** (4.5 mg, 6.77 μmol) were dissolved in 0.5 M borate buffer pH 9 (600 μL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was diluted with Mili-Q water, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL), lyophilized and the BSA-conjugate **47** was obtained as a white foam (30.4 mg, 89%). The MALDI-TOF mass spectrometry analysis indicated the conjugate **47** had an average of 15.2 disaccharides per BSA.

*Preparation of BSA conjugate **48**.* BSA (30 mg, 0.451 μmol) and trisaccharide squarate **42** (5.7 mg, 6.74 μmol) were dissolved in 0.5 M borate buffer pH 9 (700 μL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was diluted with Mili-Q water, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL), lyophilized and the BSA-conjugate **48** was obtained as a white foam (32.3 mg, 91%). The MALDI-TOF mass spectrometry analysis indicated the conjugate **48** had an average of 15.9 trisaccharides per BSA.

*Preparation of BSA conjugate **49**.* BSA (32.5 mg, 0.489 μmol) and trisaccharide squarate **43** (6.2 mg, 7.34 μmol) were dissolved in 0.5 M borate buffer pH 9 (700 μL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was diluted with Mili-Q water, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL), lyophilized and the BSA-conjugate **49** was obtained as a white foam (33.5 mg, 87%). The MALDI-TOF mass spectrometry analysis indicated the conjugate **49** had an average of 15.7 trisaccharides per BSA.

*Preparation of BSA conjugate **50**.* BSA (11 mg, 0.165 μmol) and tetrasaccharide squarate **44** (2.5 mg, 2.45 μmol) were dissolved in 0.5 M borate buffer pH 9 (400 μL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was diluted with Mili-Q water, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL), lyophilized and the BSA-conjugate **50** was obtained as a white foam (12 mg, 92%). The MALDI-TOF mass spectrometry analysis indicated the conjugate **50** had an average of 13.4 tetrasaccharides per BSA.

*Preparation of BSA conjugate **51**.* BSA (5 mg, 0.0752 μmol) and hexasaccharide squarate **45** (1.5 mg, 1.099 μmol) were dissolved in 0.5 M borate buffer pH 9 (400 μL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was diluted with Mili-Q water, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL), lyophilized and the BSA-conjugate **51** was obtained as a white foam (6 mg, 97%). The MALDI-TOF mass spectrometry analysis indicated the conjugate **51** had an average of 11.8 hexasaccharides per BSA.

*Preparation of BSA conjugate **52**.* BSA (5 mg, 0.0752 μmol) and hexasaccharide squarate **46** (1.5 mg, 1.099 μmol) were dissolved in 0.5 M borate buffer pH 9 (400 μL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was diluted with Mili-Q water, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL), lyophilized and the BSA-conjugate **52** was obtained as a white foam (5.5 mg, 87%). The MALDI-TOF mass spectrometry analysis indicated the conjugate **52** had an average of 13.8 hexasaccharides per BSA.

*Preparation of tetanus toxoid conjugate **53**:* Hexasaccharide squarate **45** (0.55 mg, 0.403 μmol) was added to the solution of tetanus toxoid (2 mg, 0.0133 μmol) in 0.5 M borate buffer pH 9 (1 mL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was washed with PBS buffer, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL) and the resulting tetanus toxoid-conjugate **53** was stored in PBS buffer. The MALDI-TOF mass spectrometry analysis indicated the conjugate **53** had an average of 15.1 hexasaccharides per tetanus toxoid.

*Preparation of tetanus toxoid conjugate **54**:* Hexasaccharide squarate **46** (0.55 mg, 0.403 μmol) was added to the solution of tetanus toxoid (2 mg, 0.0133 μmol) in 0.5 M borate buffer pH 9 (1 mL) and stirred slowly at 21 ^{o}C for 3 days. Then the reaction mixture was washed with PBS buffer, filtered through milipore filtration tube (10,000 MWCO, 4 x 10 mL) and the resulting tetanus toxoid-conjugate **54** was stored in PBS buffer. The MALDI-TOF mass spectrometry analysis indicated the conjugate **54** had an average of 14.6 hexasaccharides per tetanus toxoid.

ELISA titrations for conjugates 47-52 with Mouse mAbs

Figure S1 Plates coated with **47**

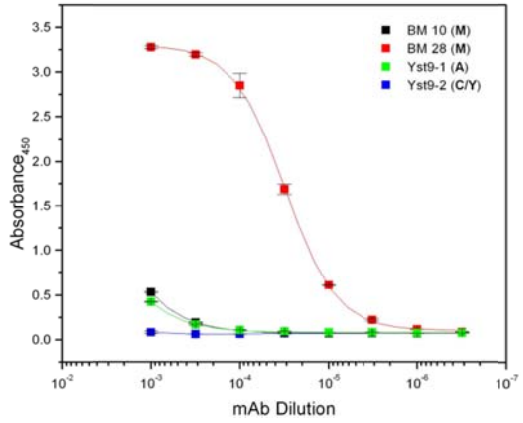


Figure S2 Plates coated with **48**

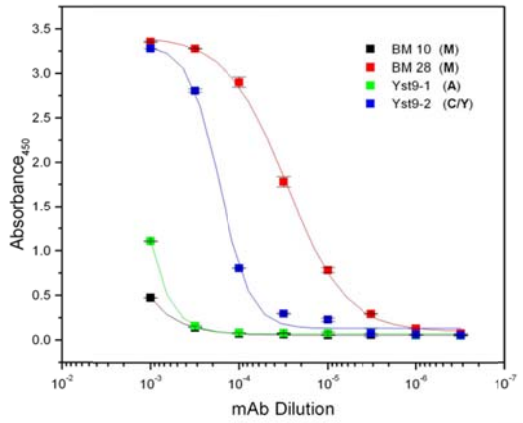


Figure S3 Plates coated with **49**

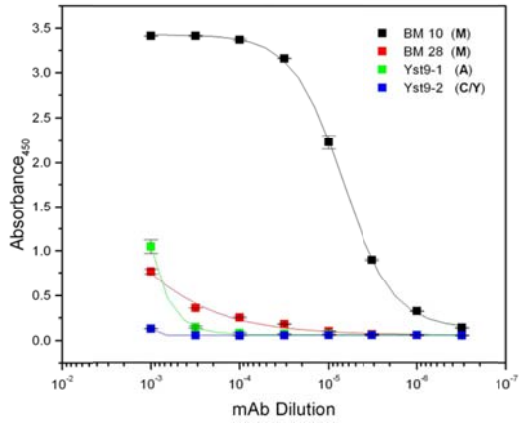


Figure S4 Plates coated with **50**

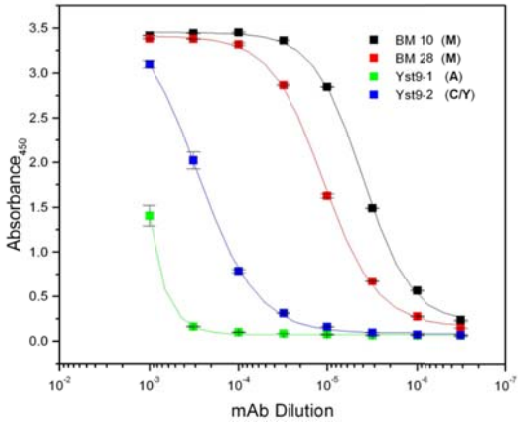


Figure S5 Plates coated with **51**

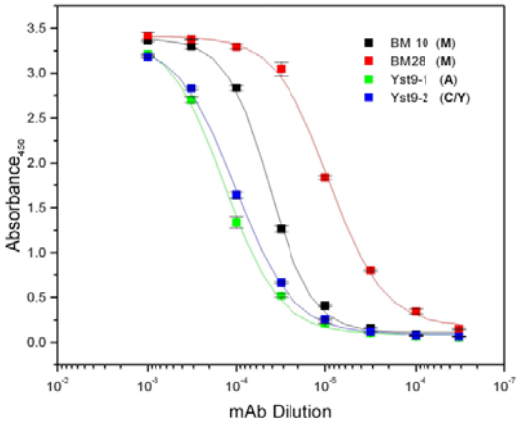


Figure S1 Plates coated with **52**

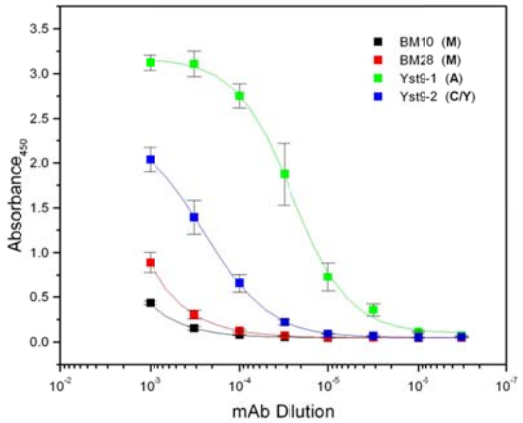


Figure S7 ELISA for Disaccharide conjugate 47 with OIE standard bovine sera

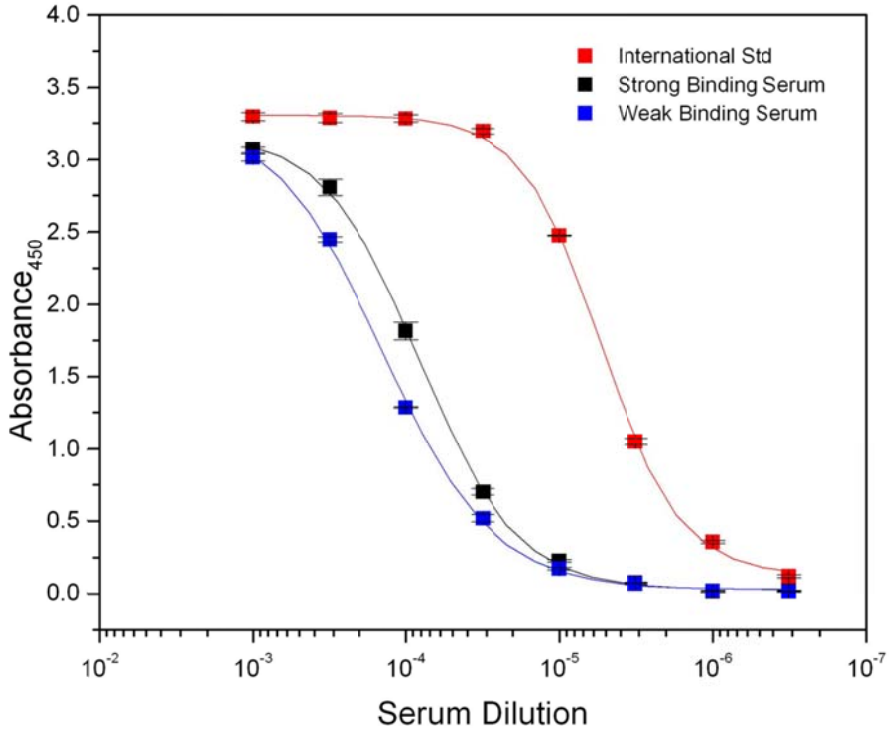


Figure S8 ELISA for tetrasaccharide conjugate 50 with OIE standard bovine sera

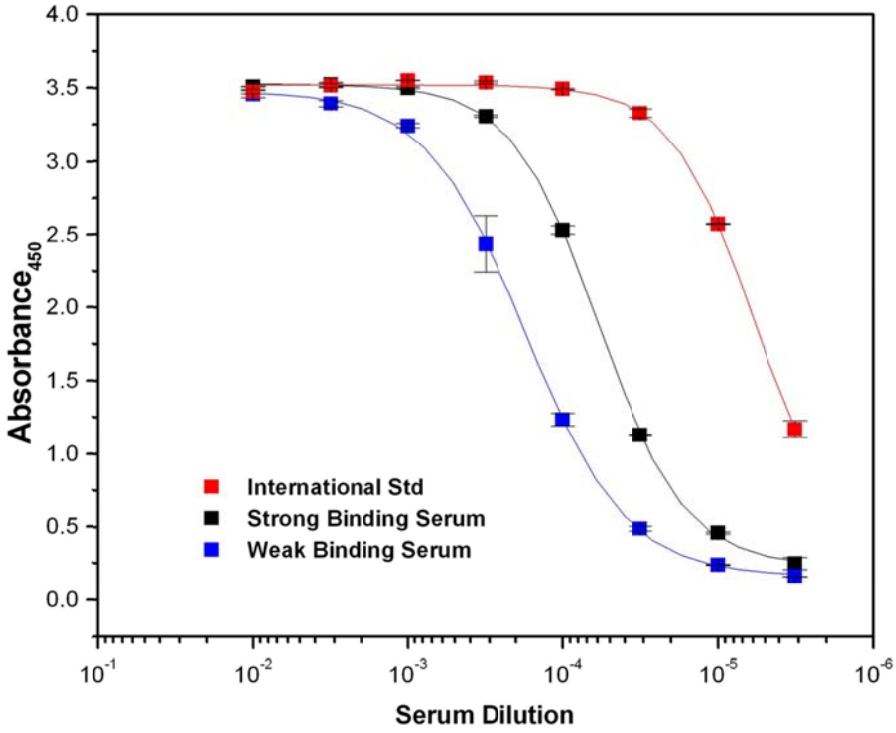


Figure S9 ELISA for hexasaccharide conjugate 52 with OIE standard bovine sera

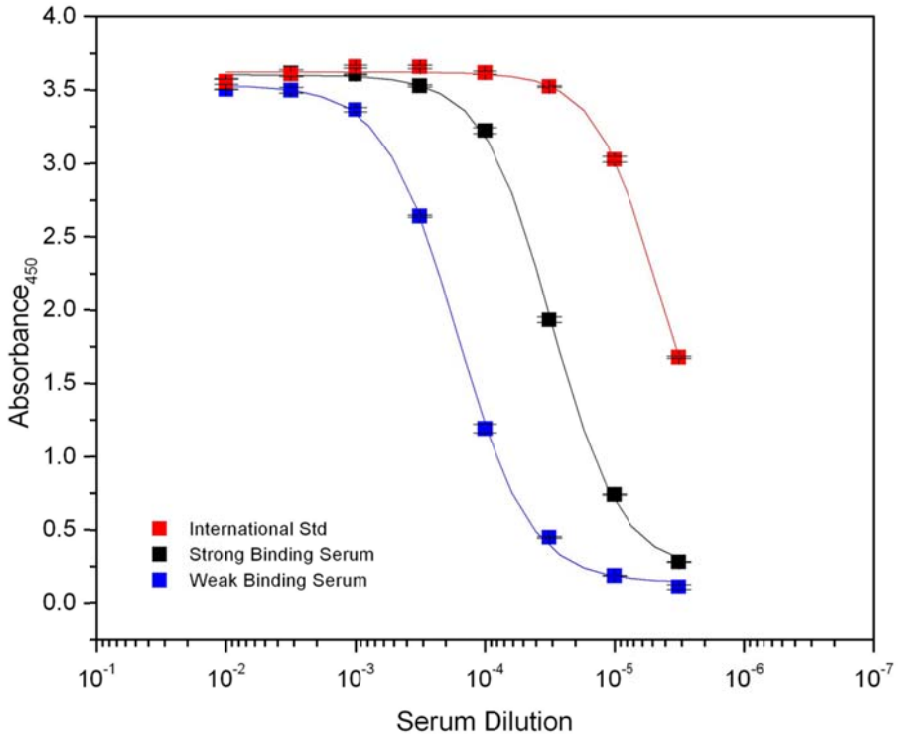
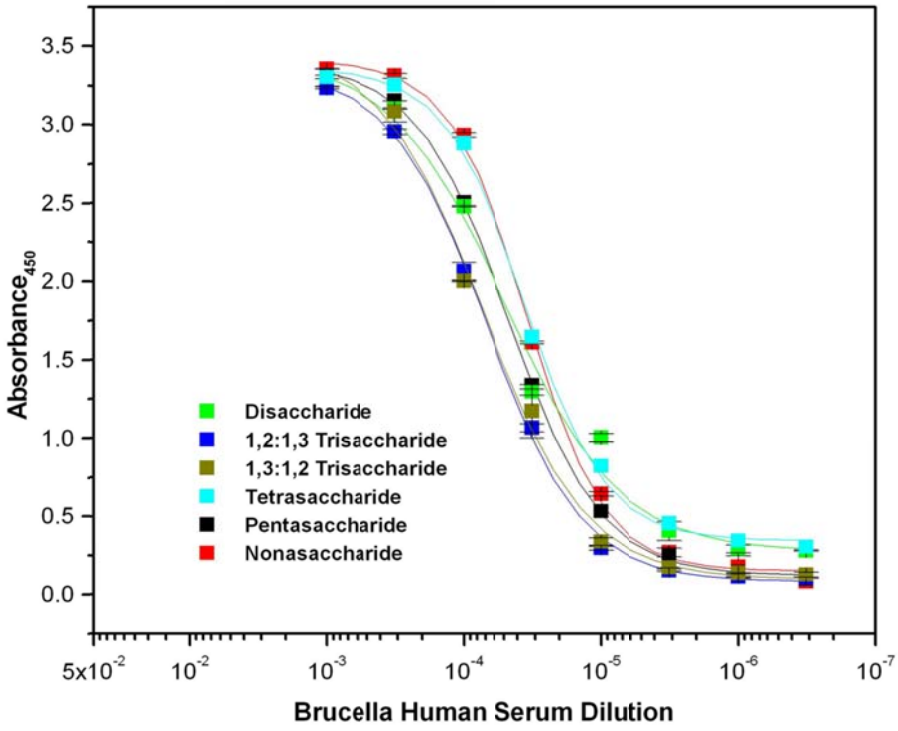


Figure S10 ELISA for human sera with conjugates 47-50 and penta and nonasaccharides previously reported[7]



Immune response for CD1 mice immunized with tetanus toxoid conjugated to hexsaccharide 6

Figure S11 Response titered on plates coated with conjugate 52

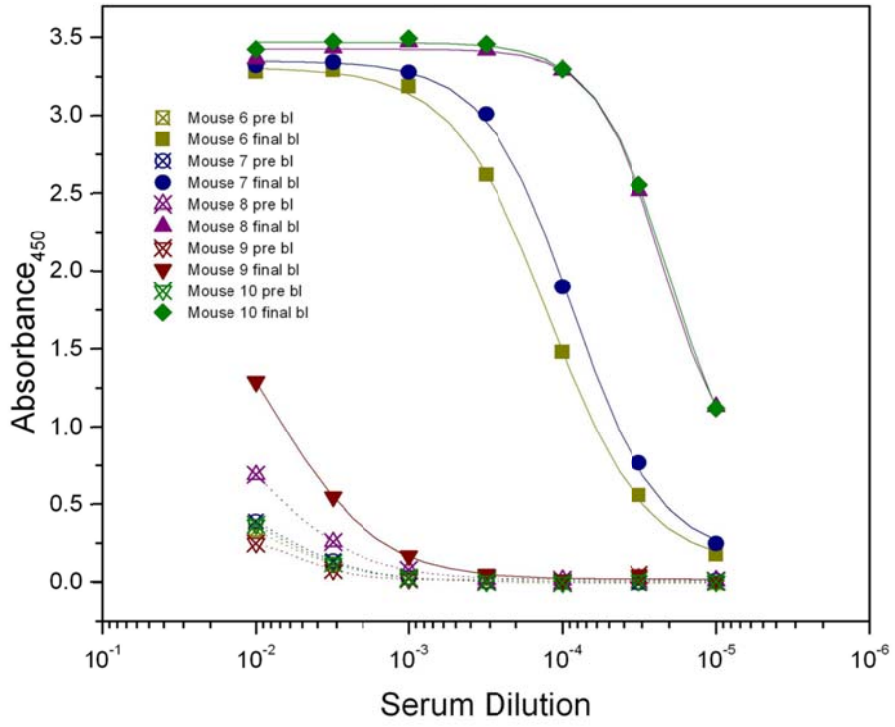


Figure S12 Response titered on plates coated with *B. abortus* LPS

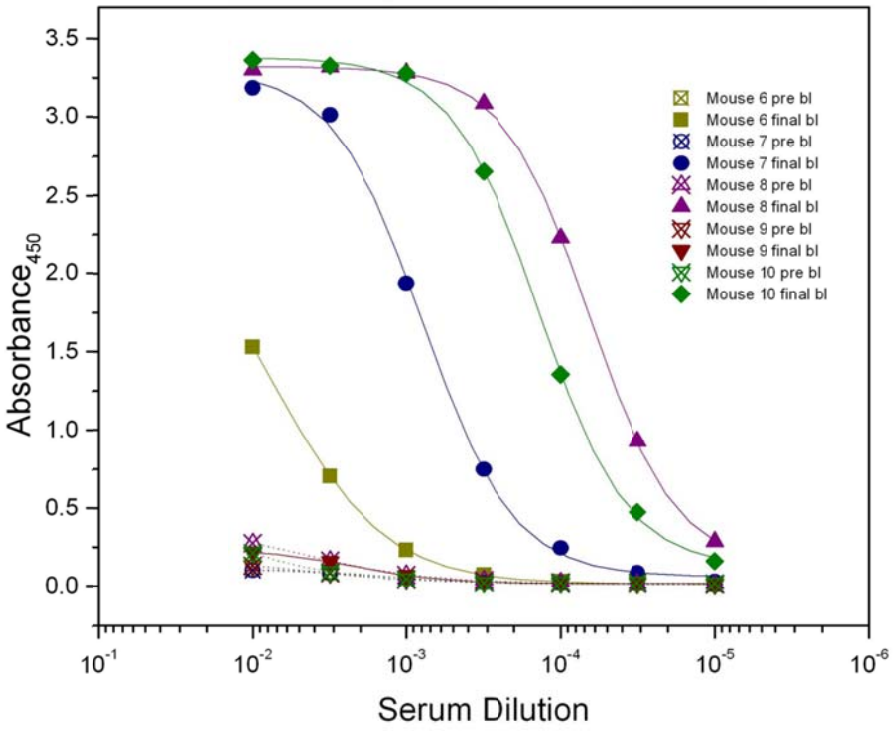
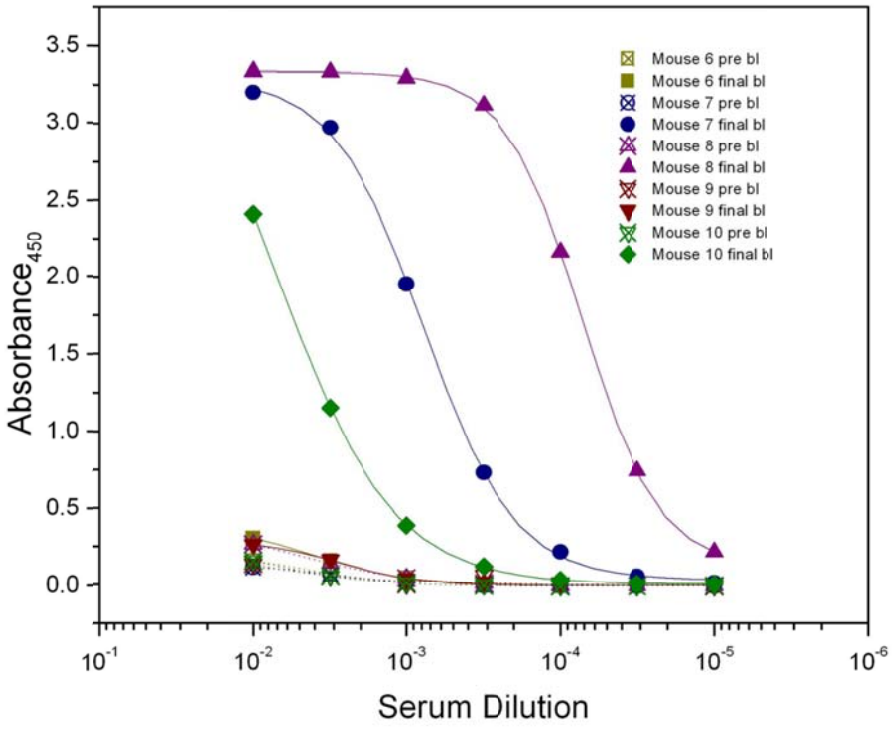


Figure S13 Response titered on plates coated with *B. melitensis* LPS



VI. REFERENCES

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[4] a) Peters, T.; Bundle, D. R. *Can. J. Chem.* **1989**, *67*, 491-496; b) Peters, T.; Bundle, D. R. *J. Chem. Soc. Chem. Commun*. **1987**, 1648-1650.

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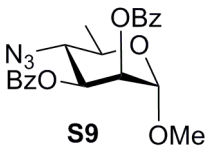
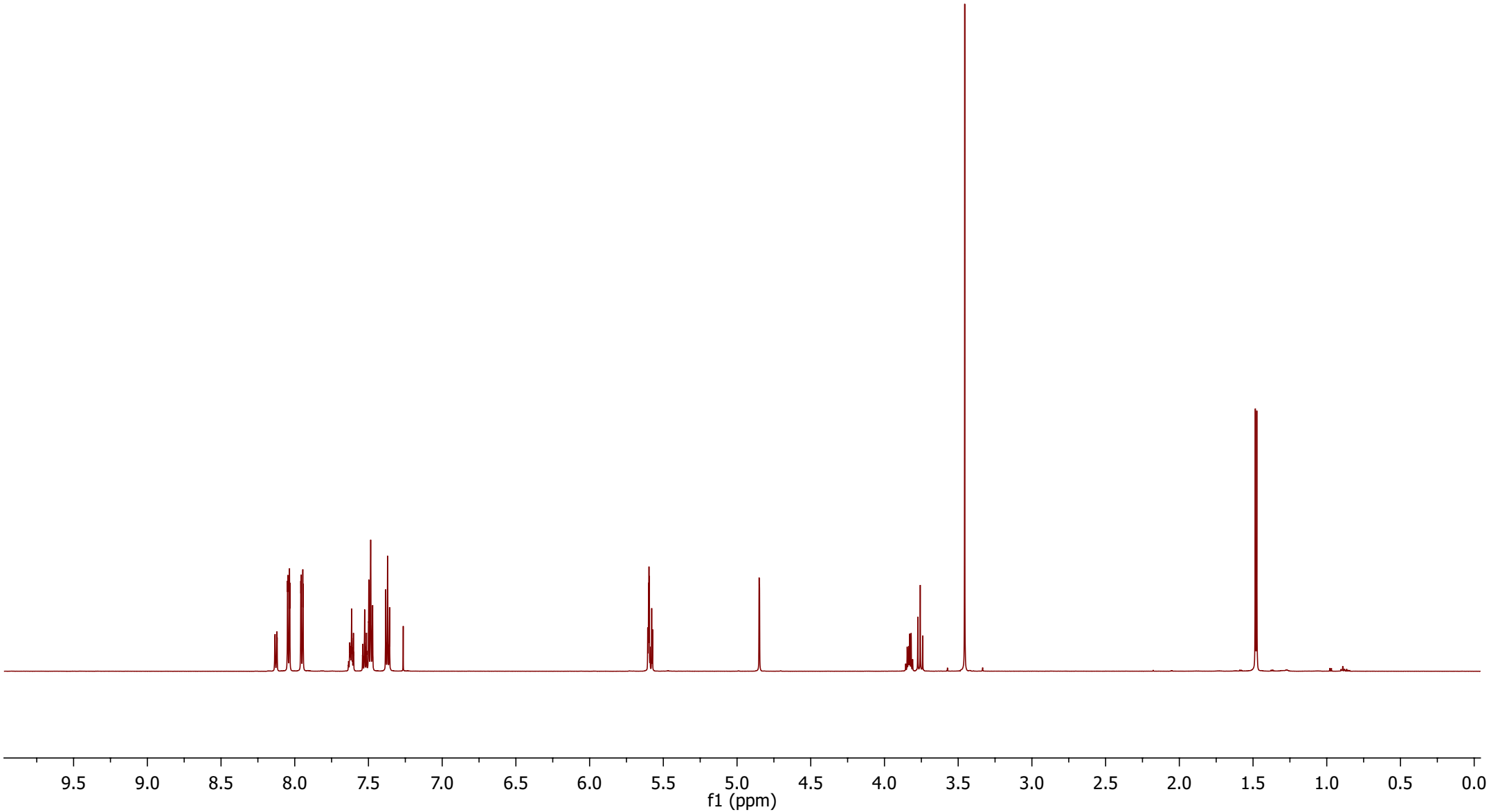
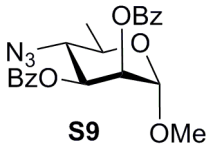


S9

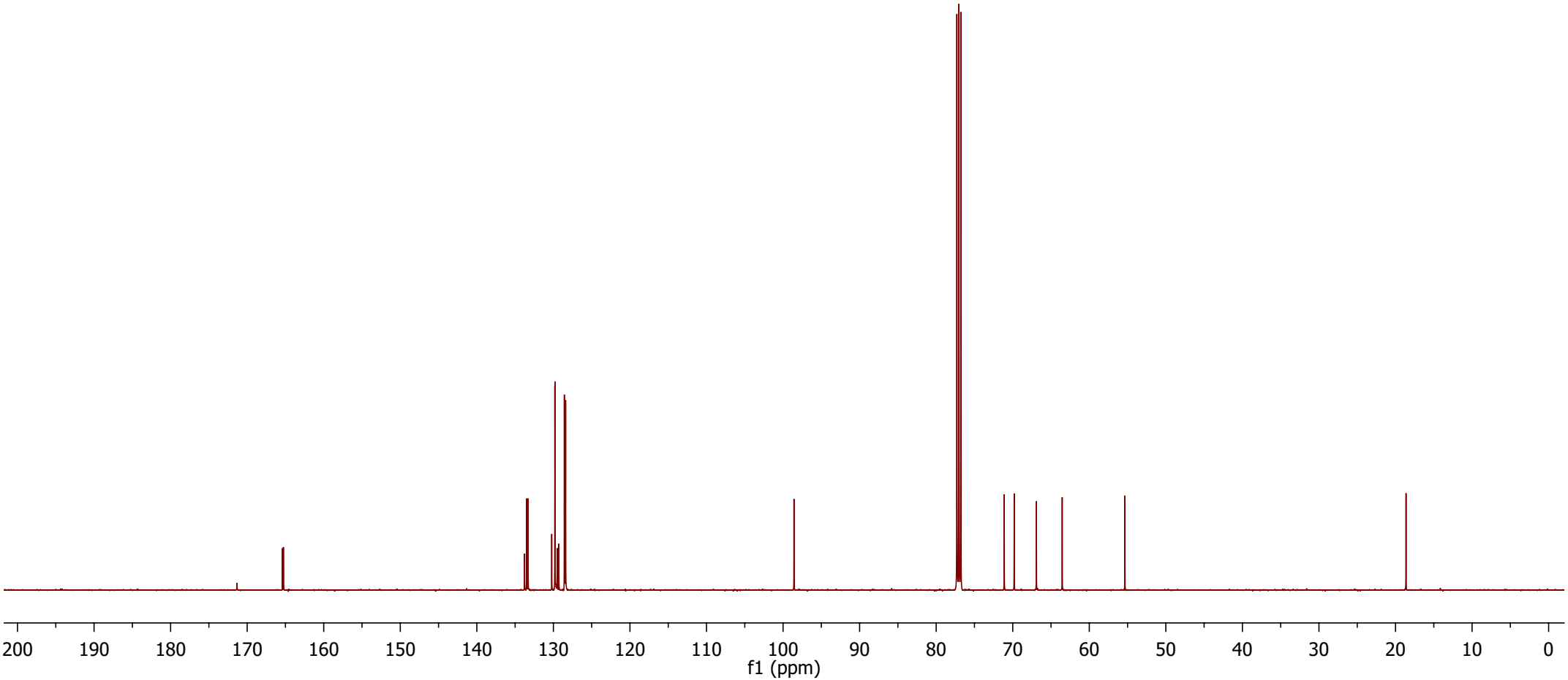
600 MHz, $CDCl_3$

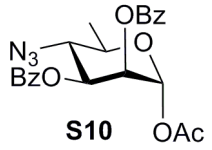




S9

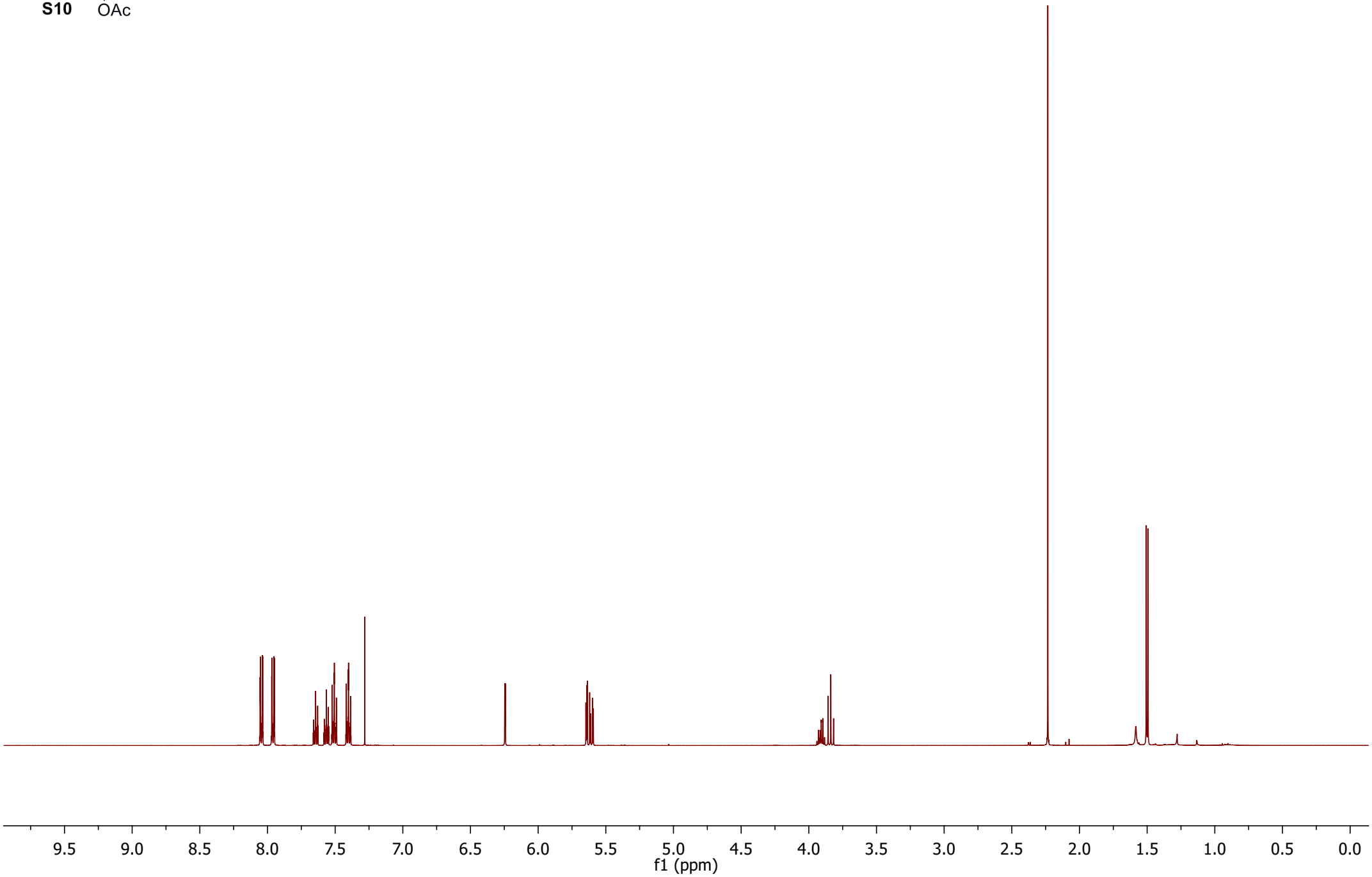
126 MHz, $CDCl_3$

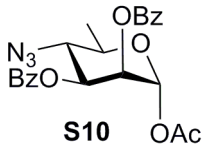




S10

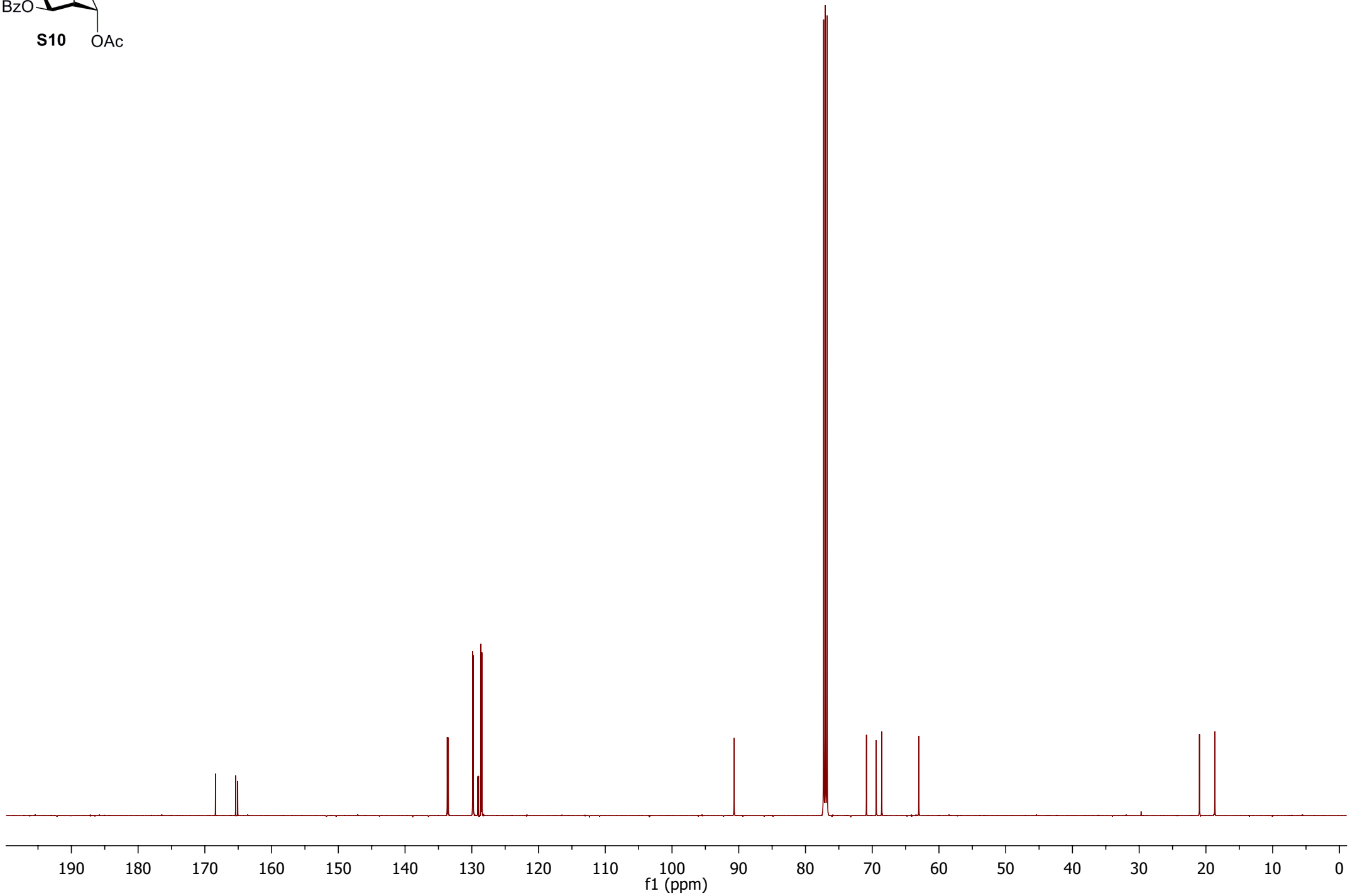
500 MHz, $CDCl_3$

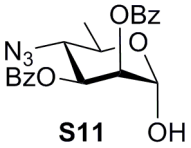




S10

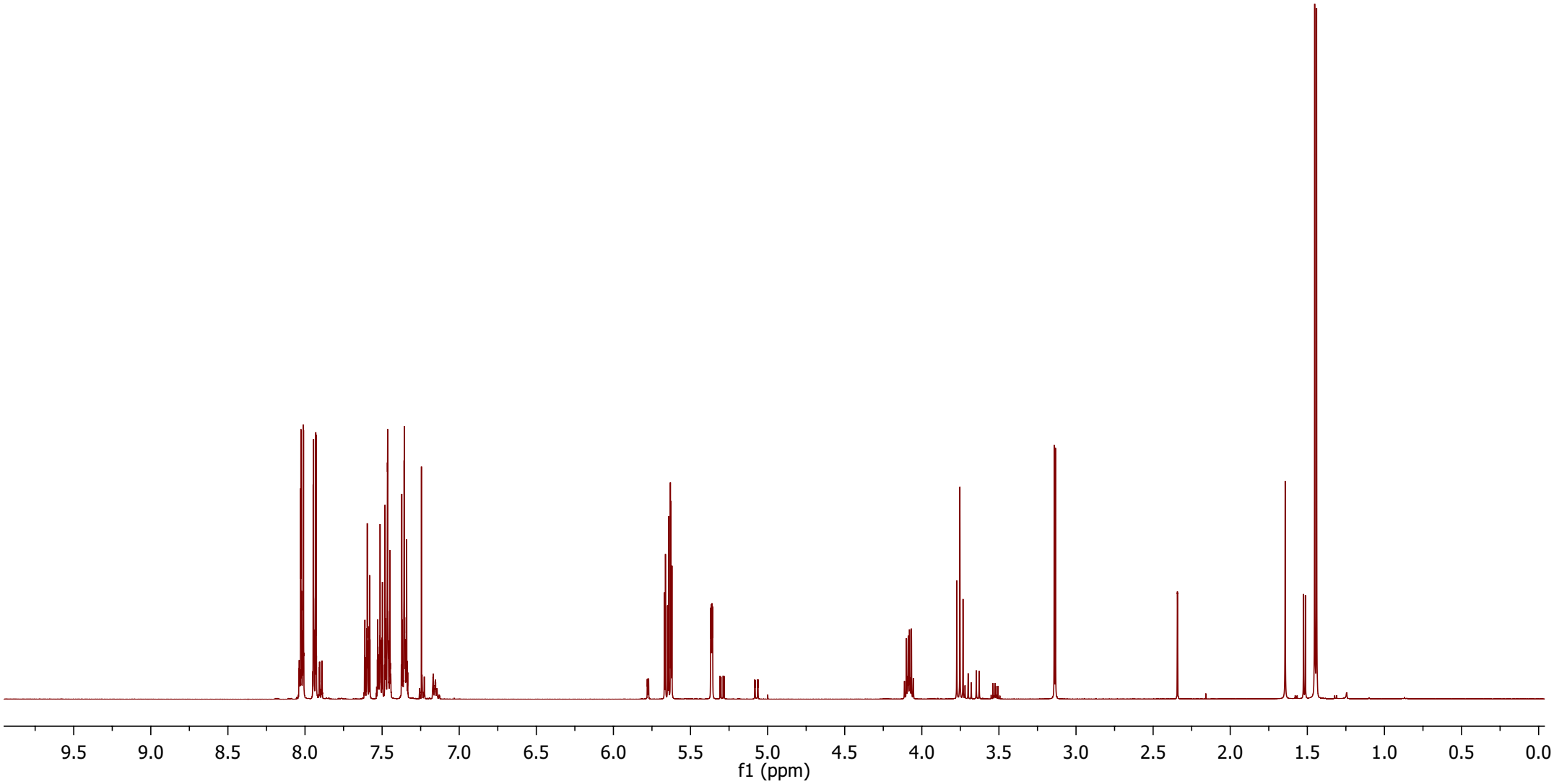
126 MHz, $CDCl_3$

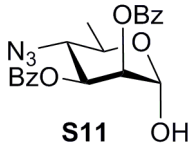




S11

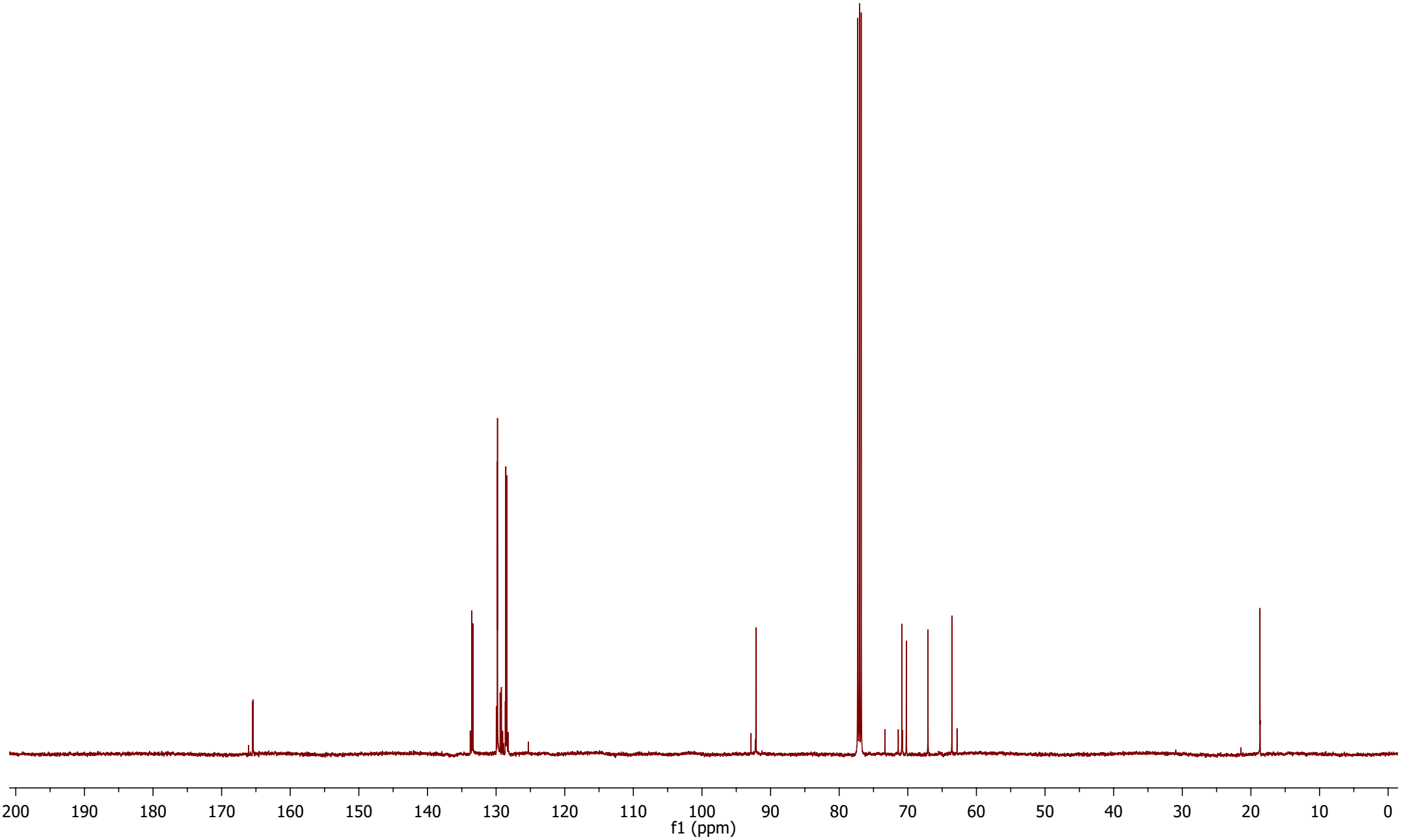
500 MHz, $CDCl_3$

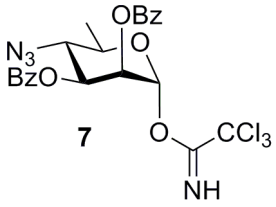




S11

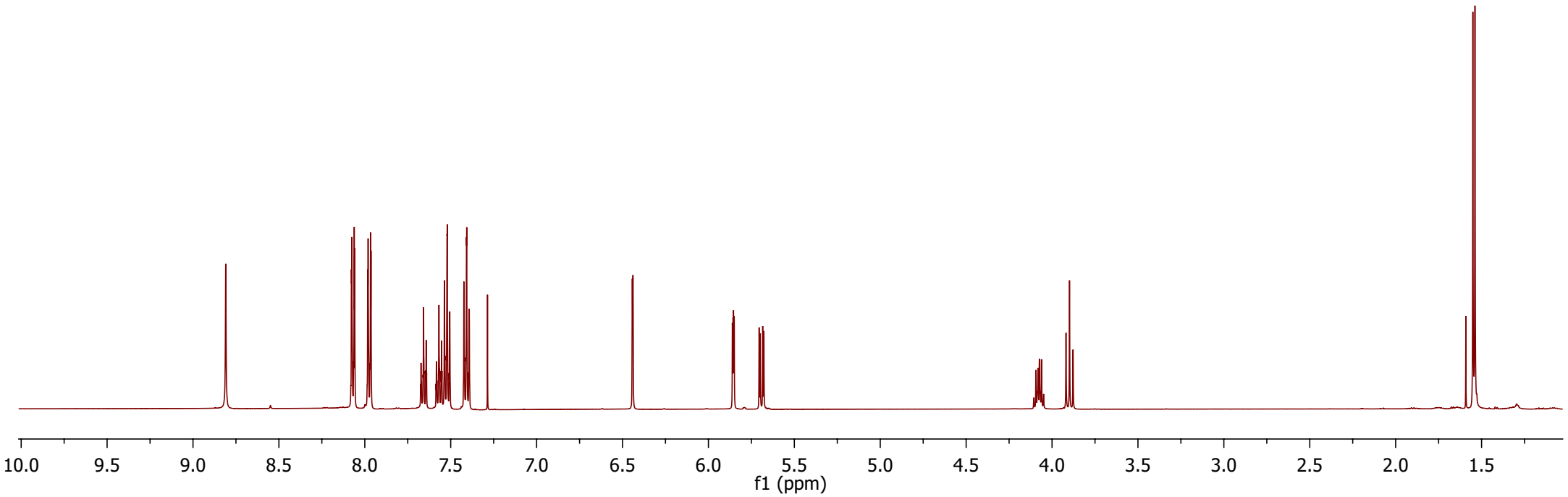
126 MHz, $CDCl_3$

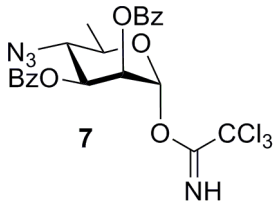




7

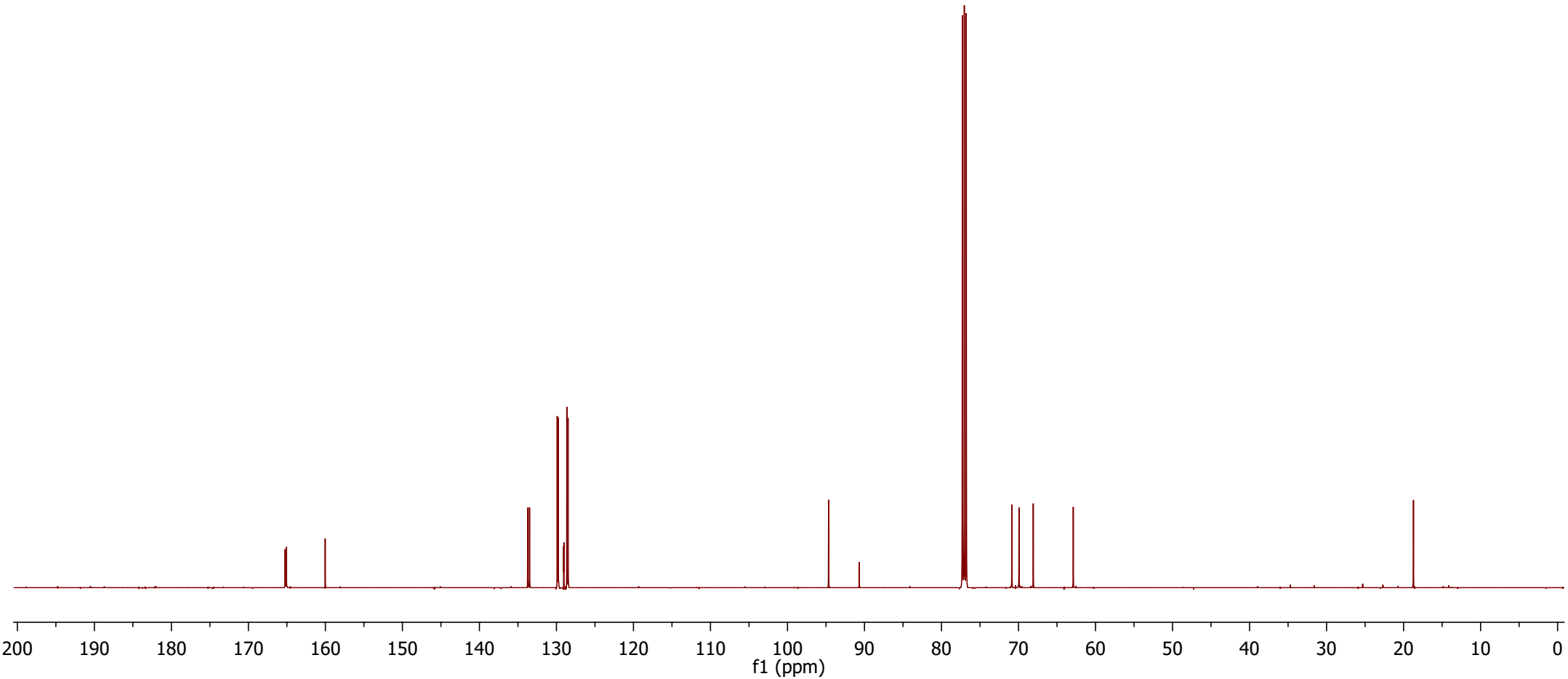
500 MHz, $CDCl_3$

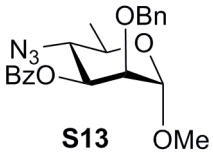




7

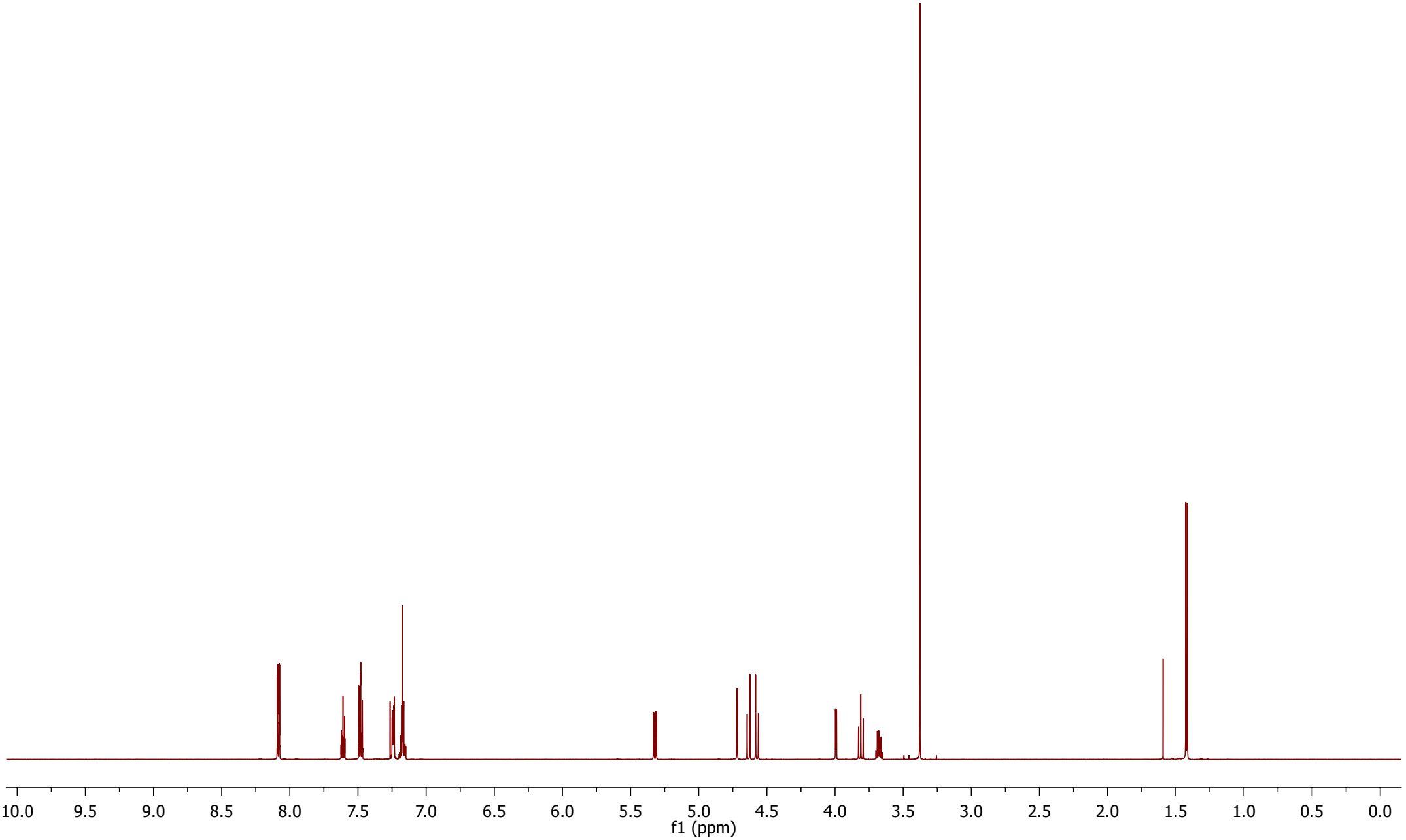
126 MHz, $CDCl_3$

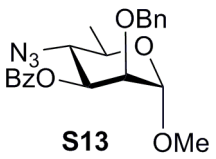




S13

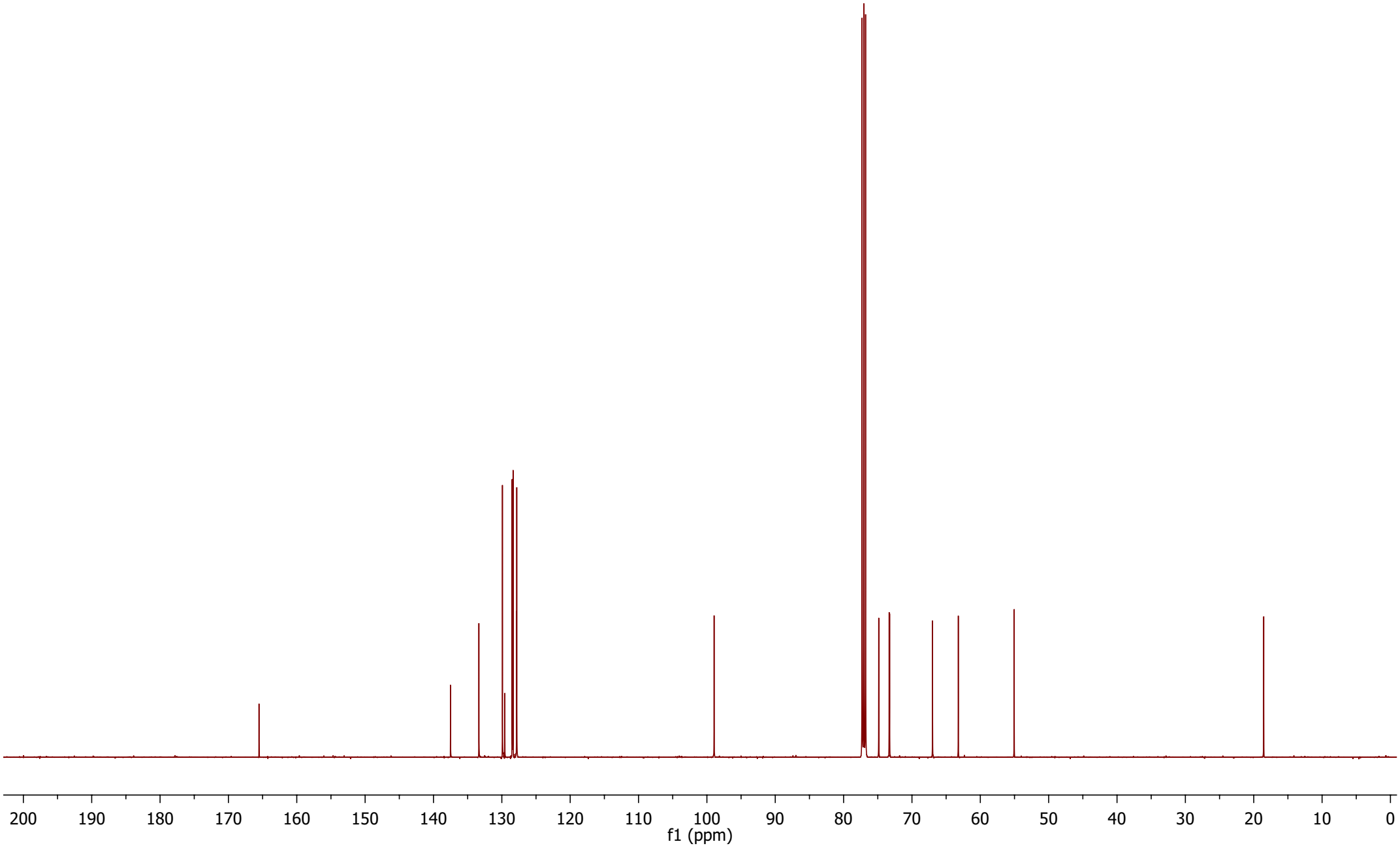
600 MHz, $CDCl_3$





S13

126 MHz, $CDCl_3$



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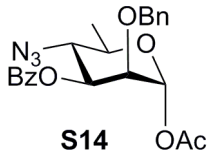
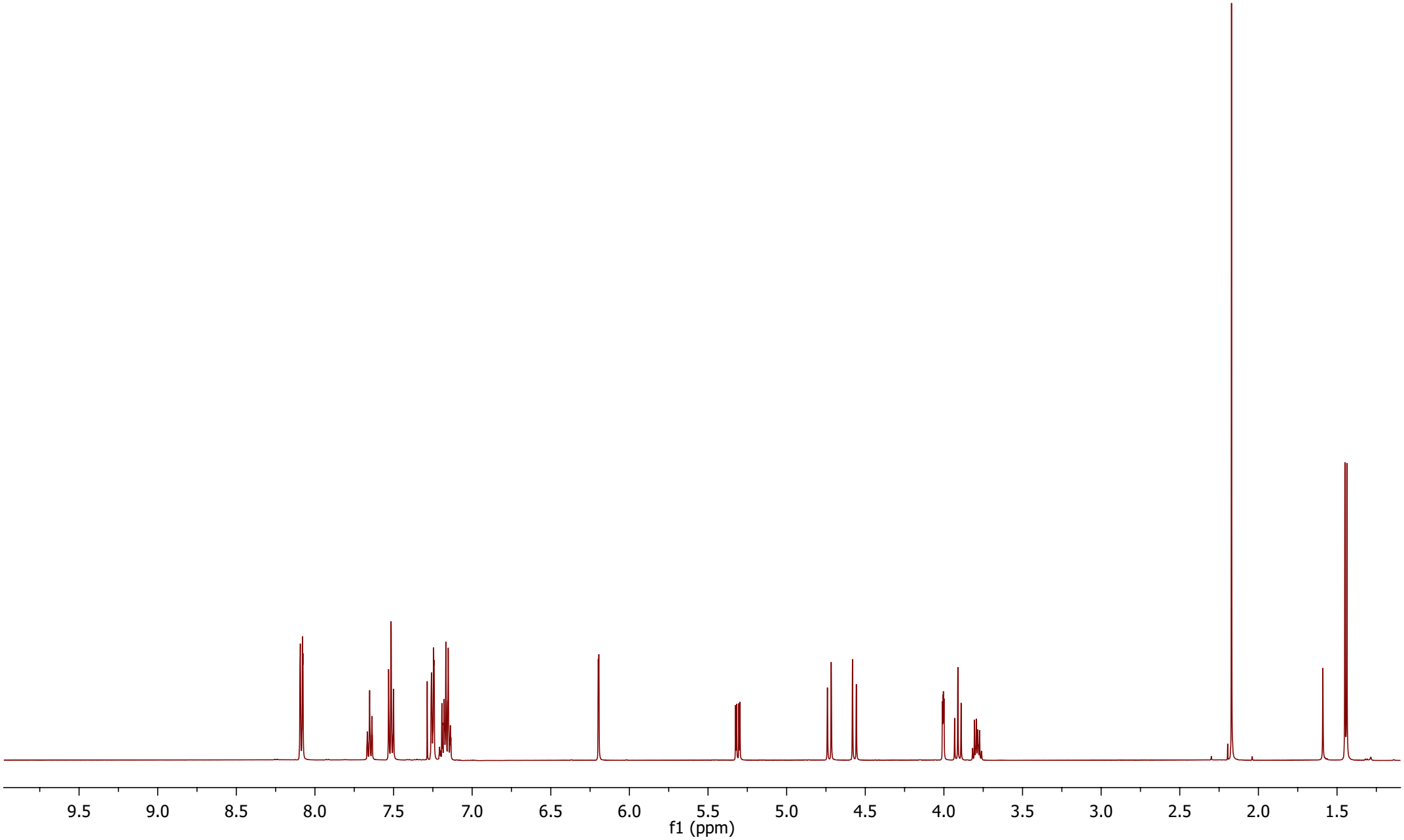
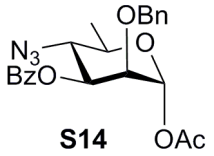


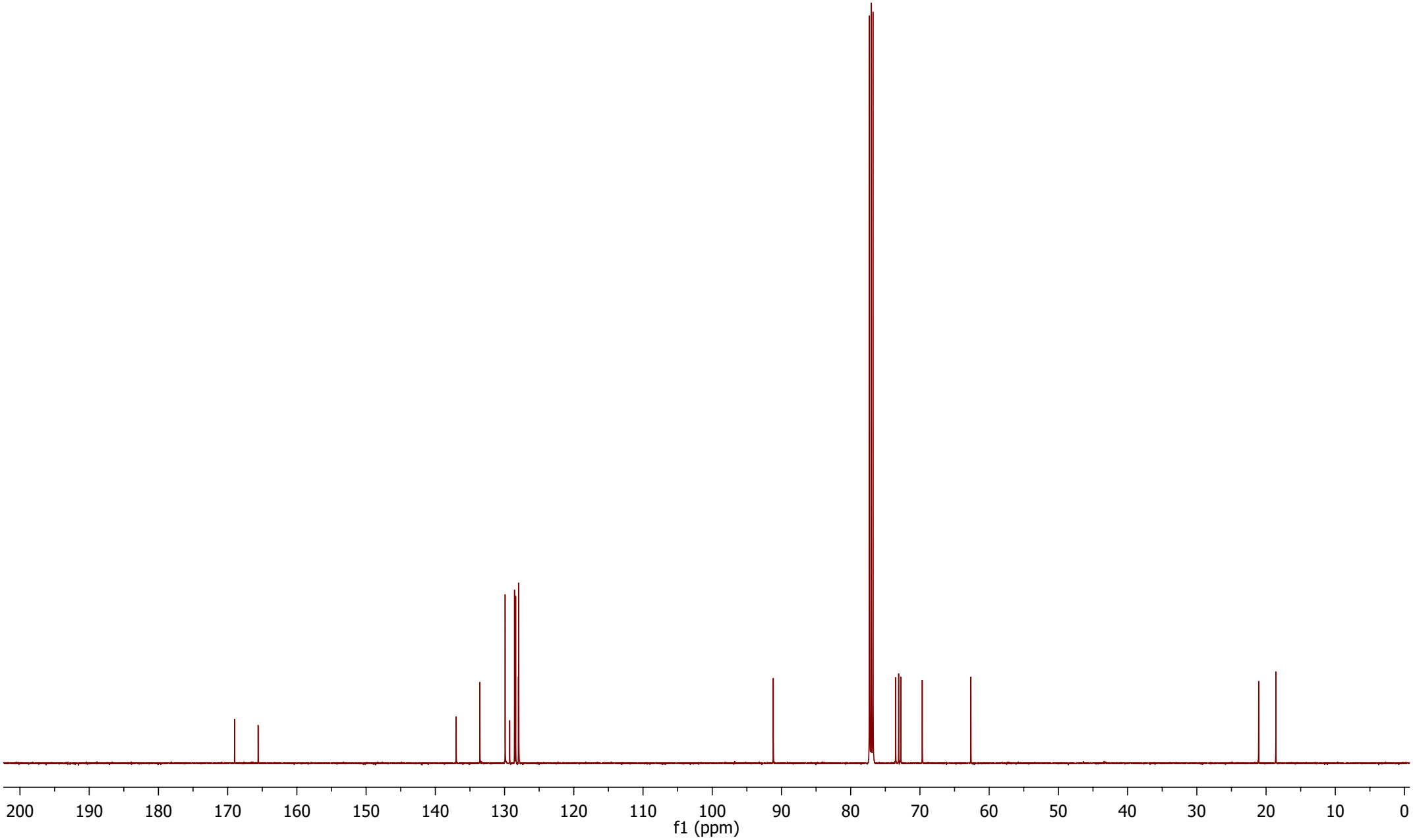
S14

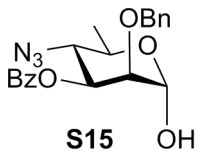




S14

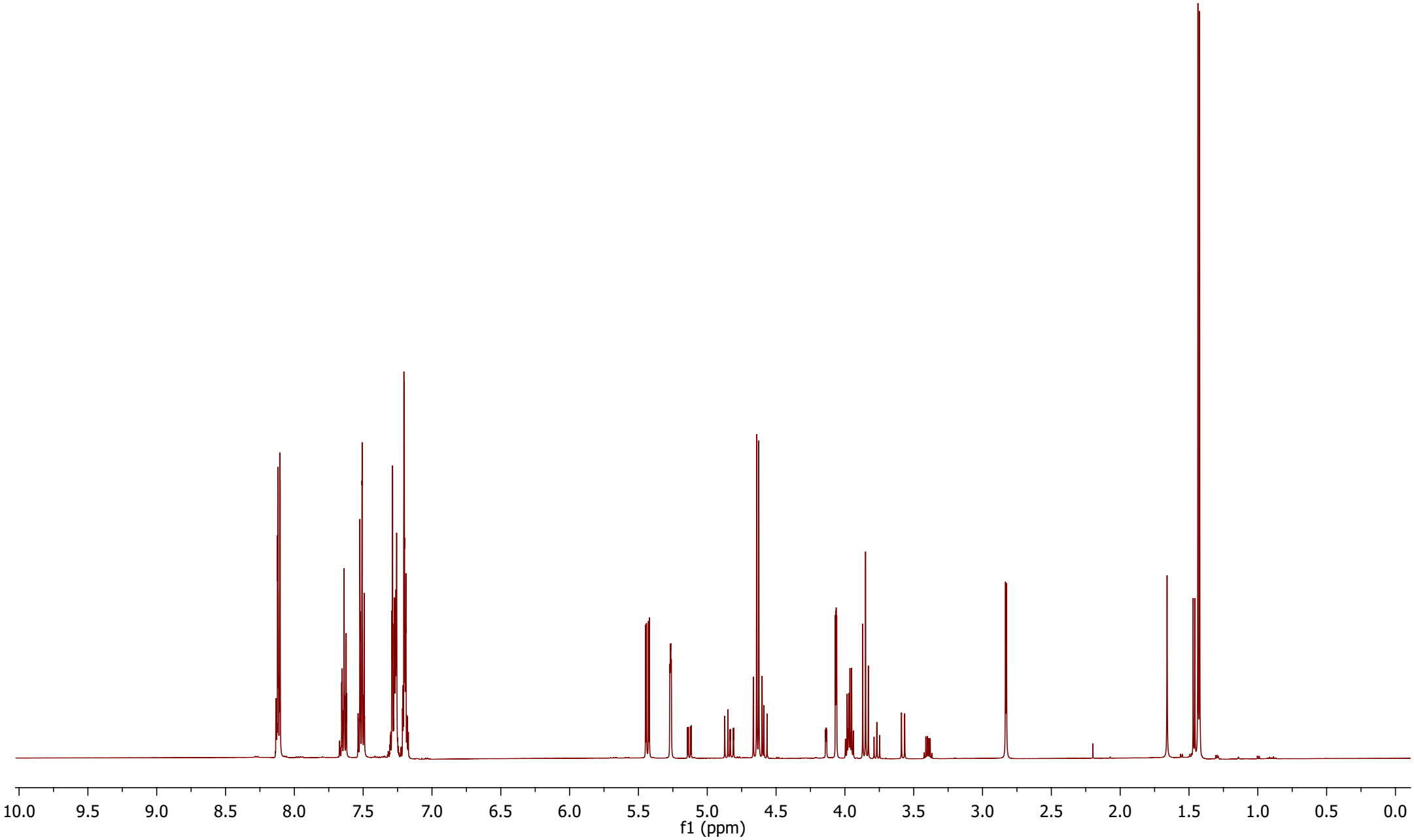
126 MHz, $CDCl_3$





S15

500 MHz, $CDCl_3$



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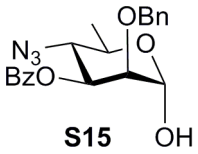
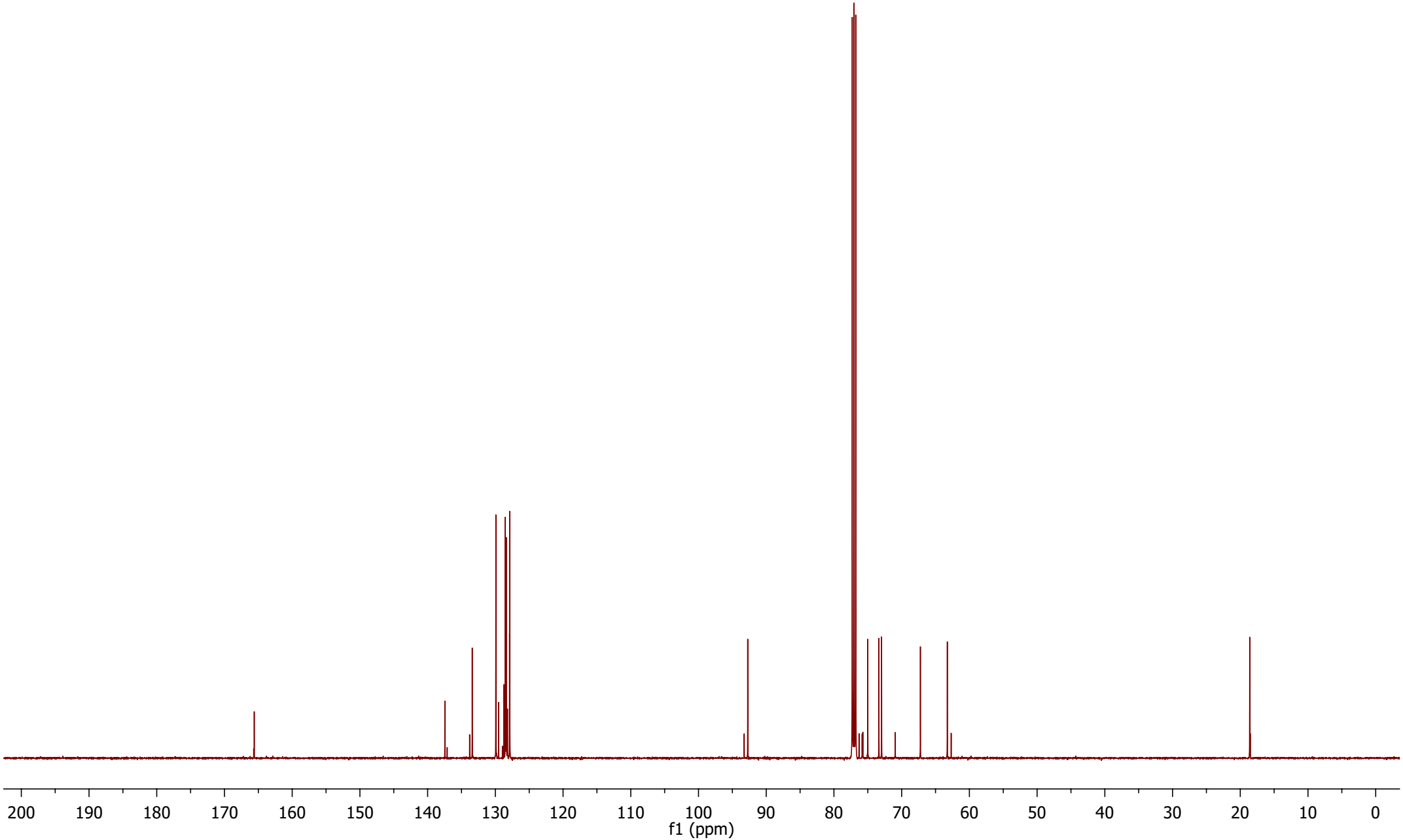
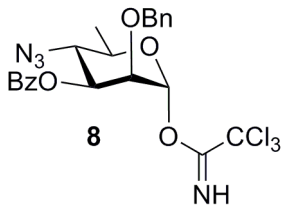


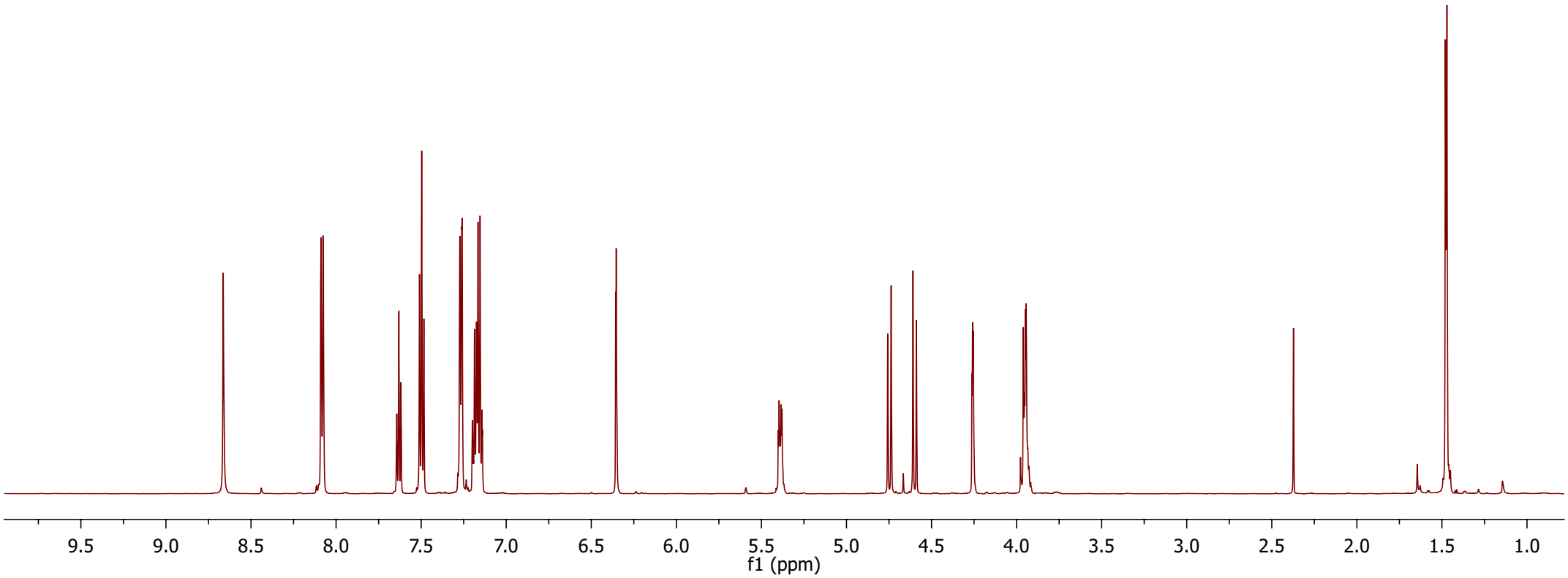
S15





8

600 MHz, $CDCl_3$



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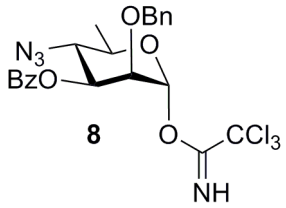
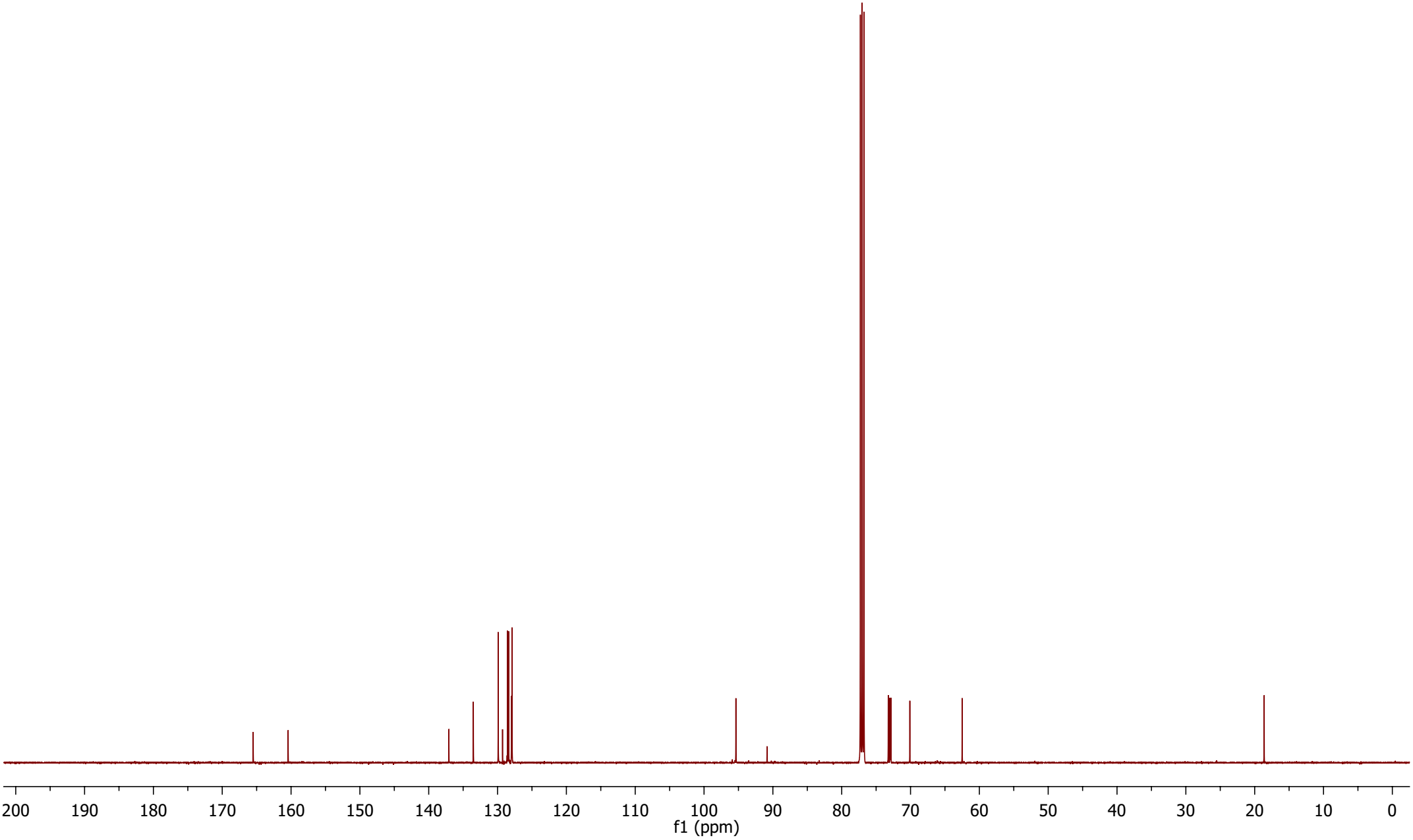
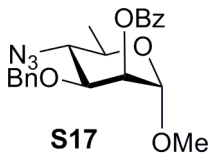


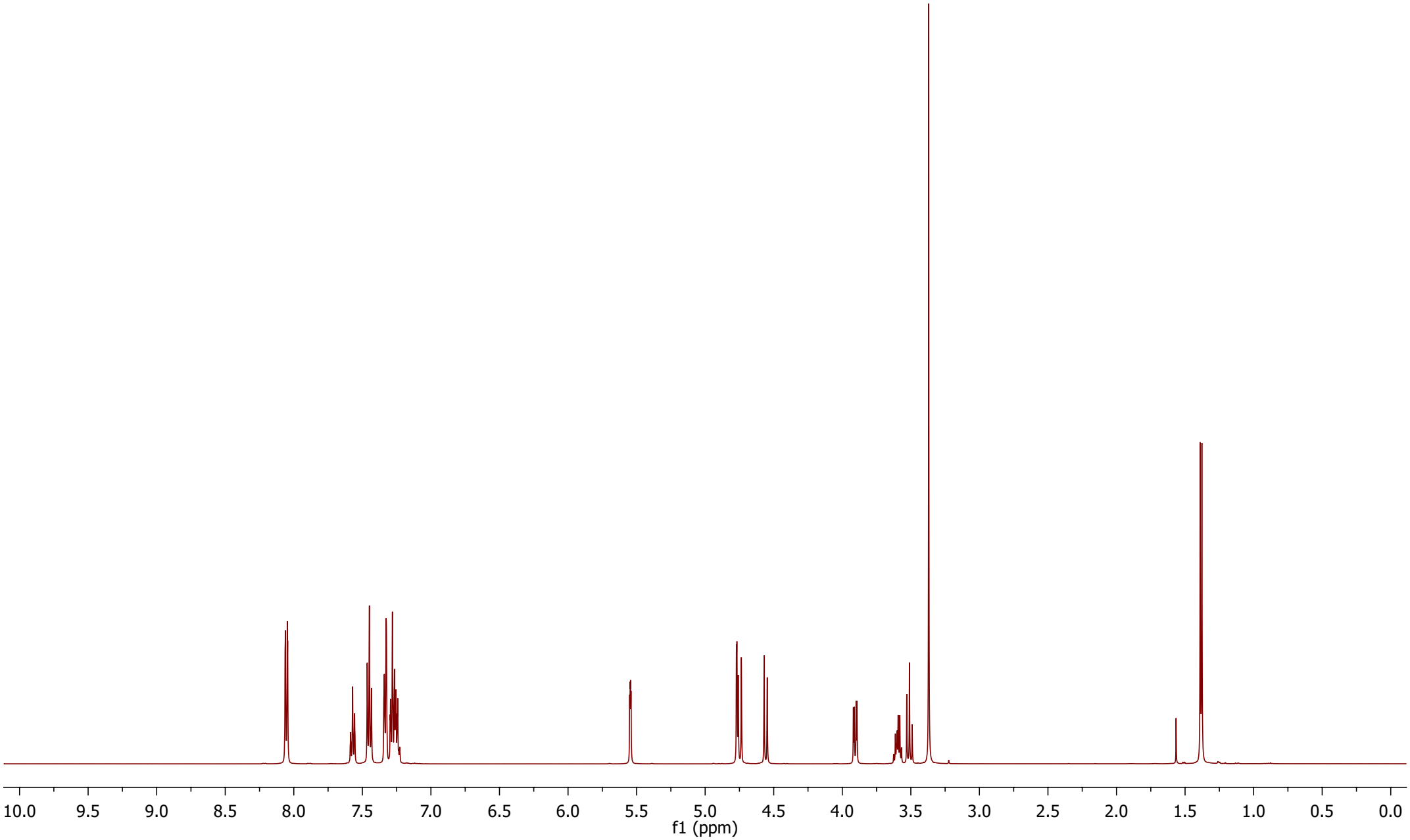
8

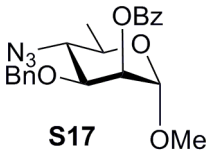




S17

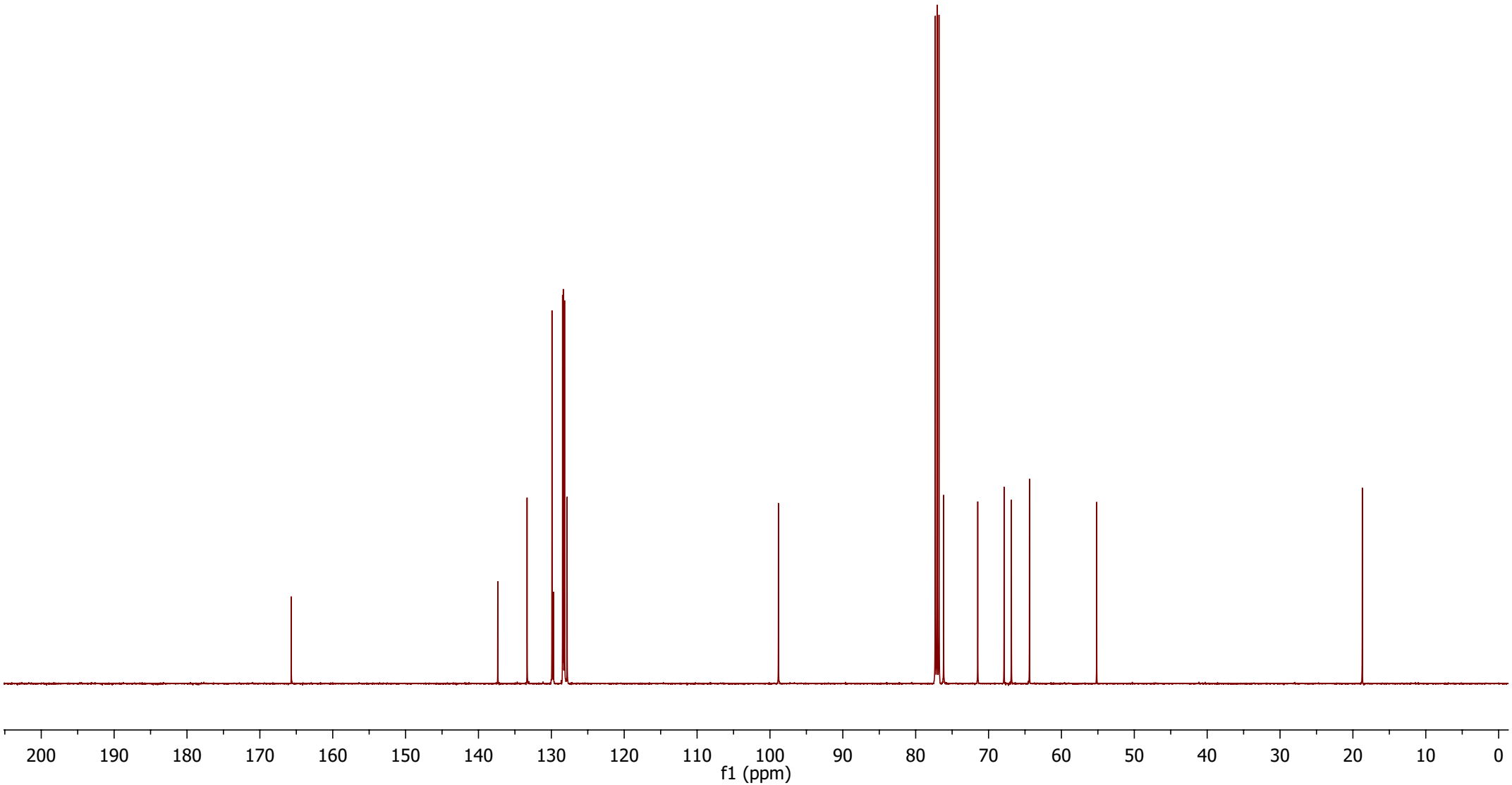
500 MHz, $CDCl_3$

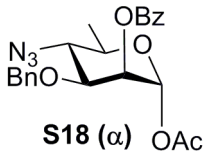




S17

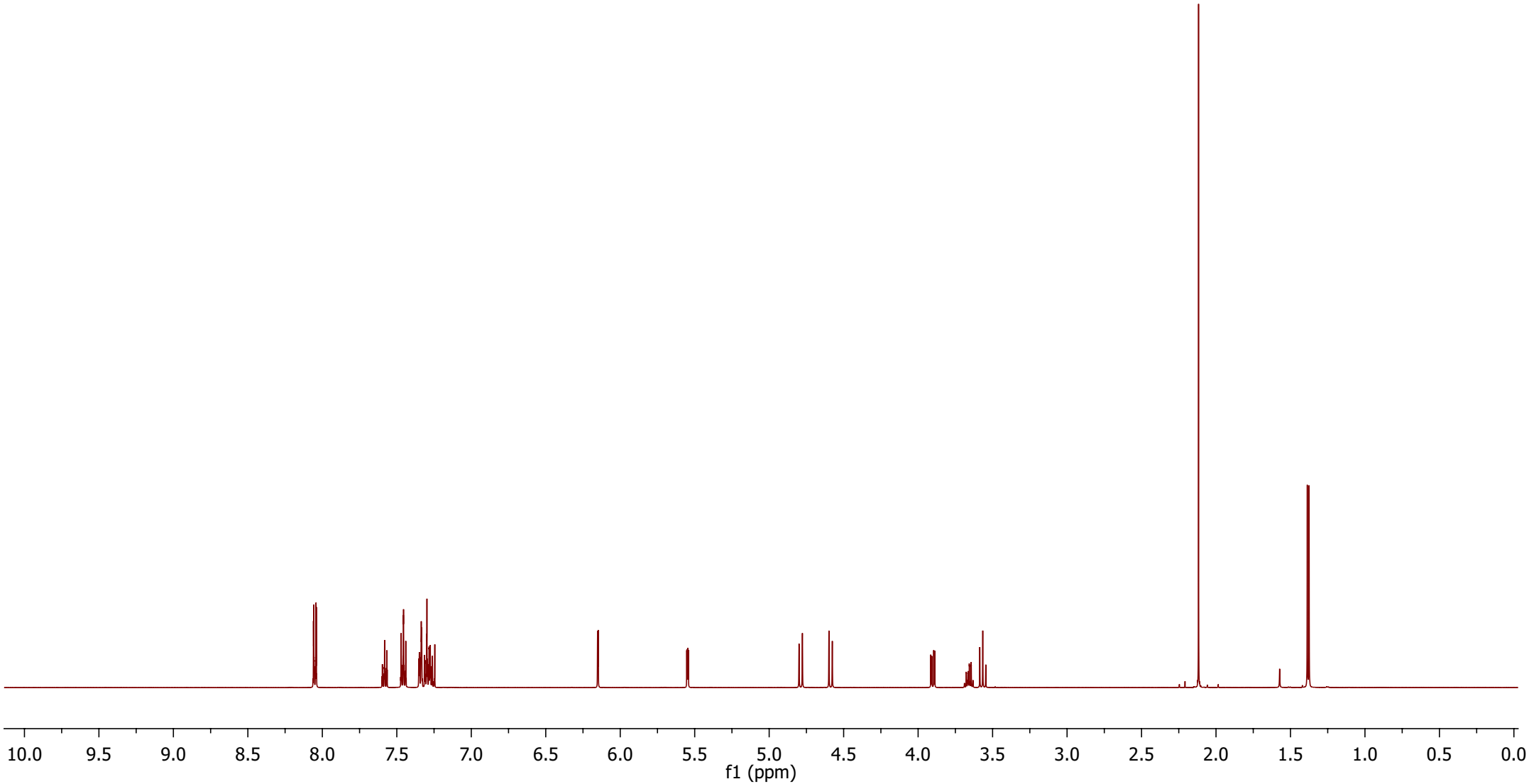
126 MHz, $CDCl_3$

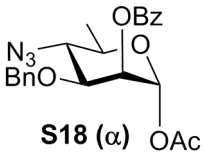




S18 (α)

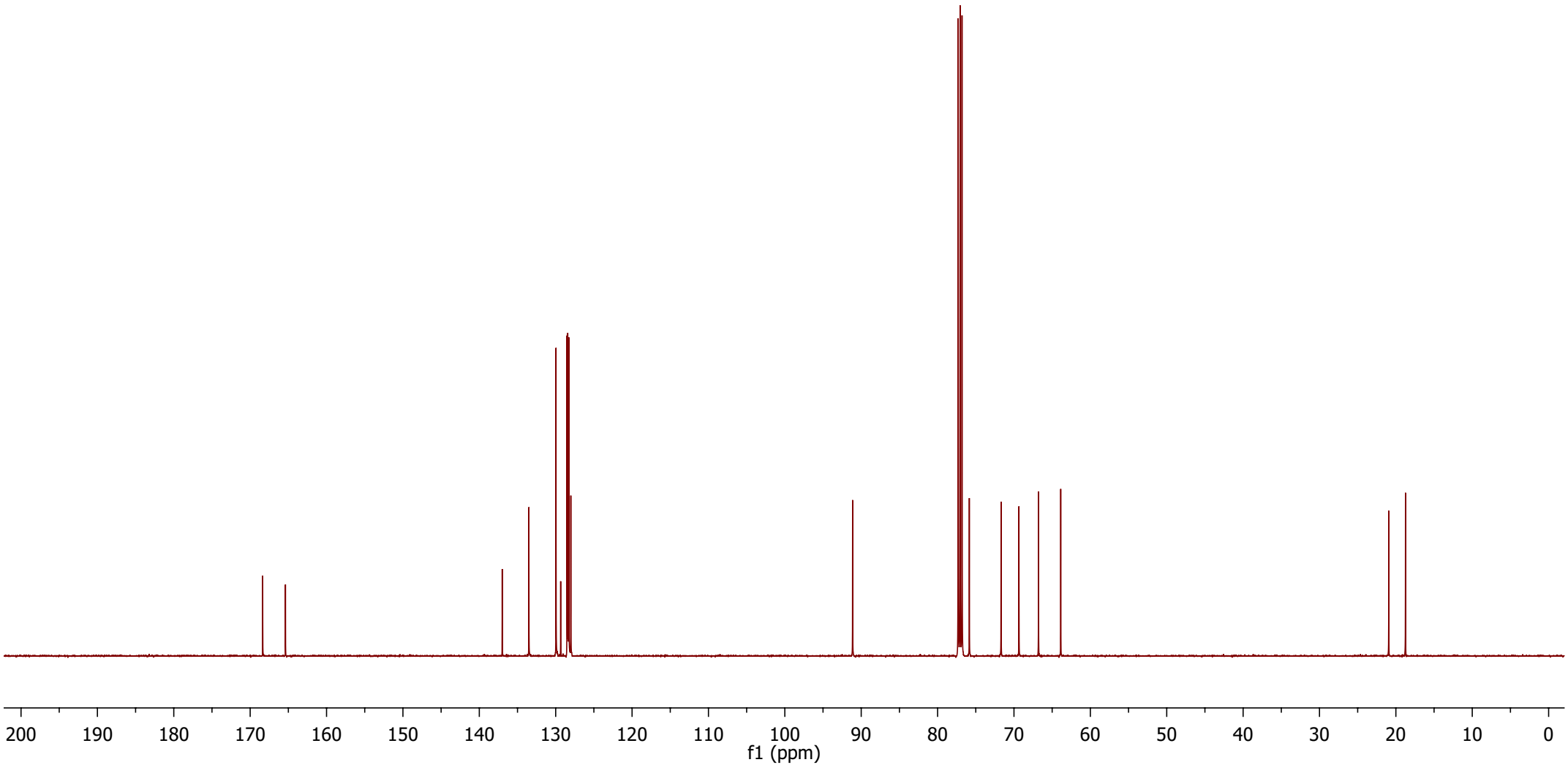
500 MHz, $CDCl_3$

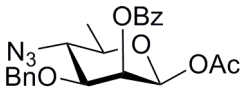




S18 (α)

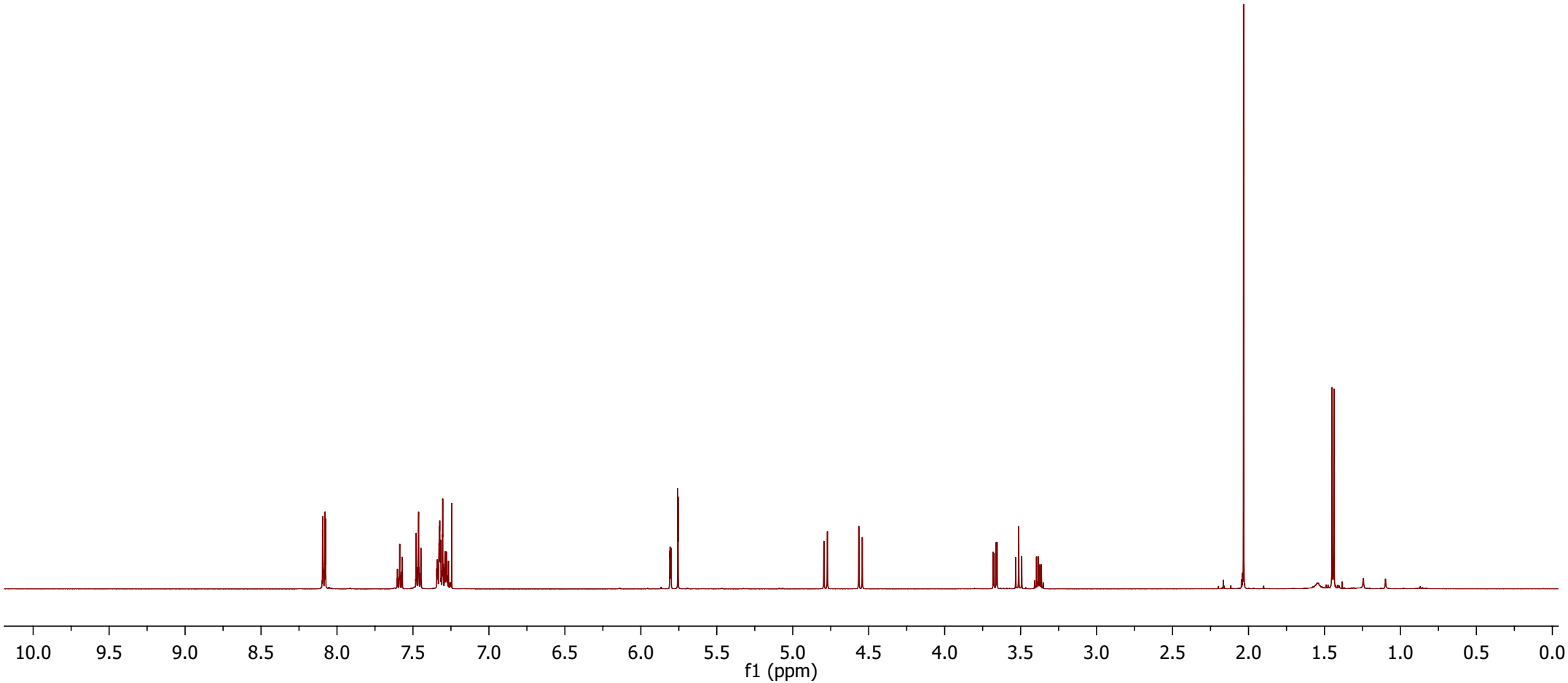
126 MHz, $CDCl_3$

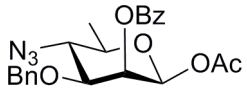




S18 (β)

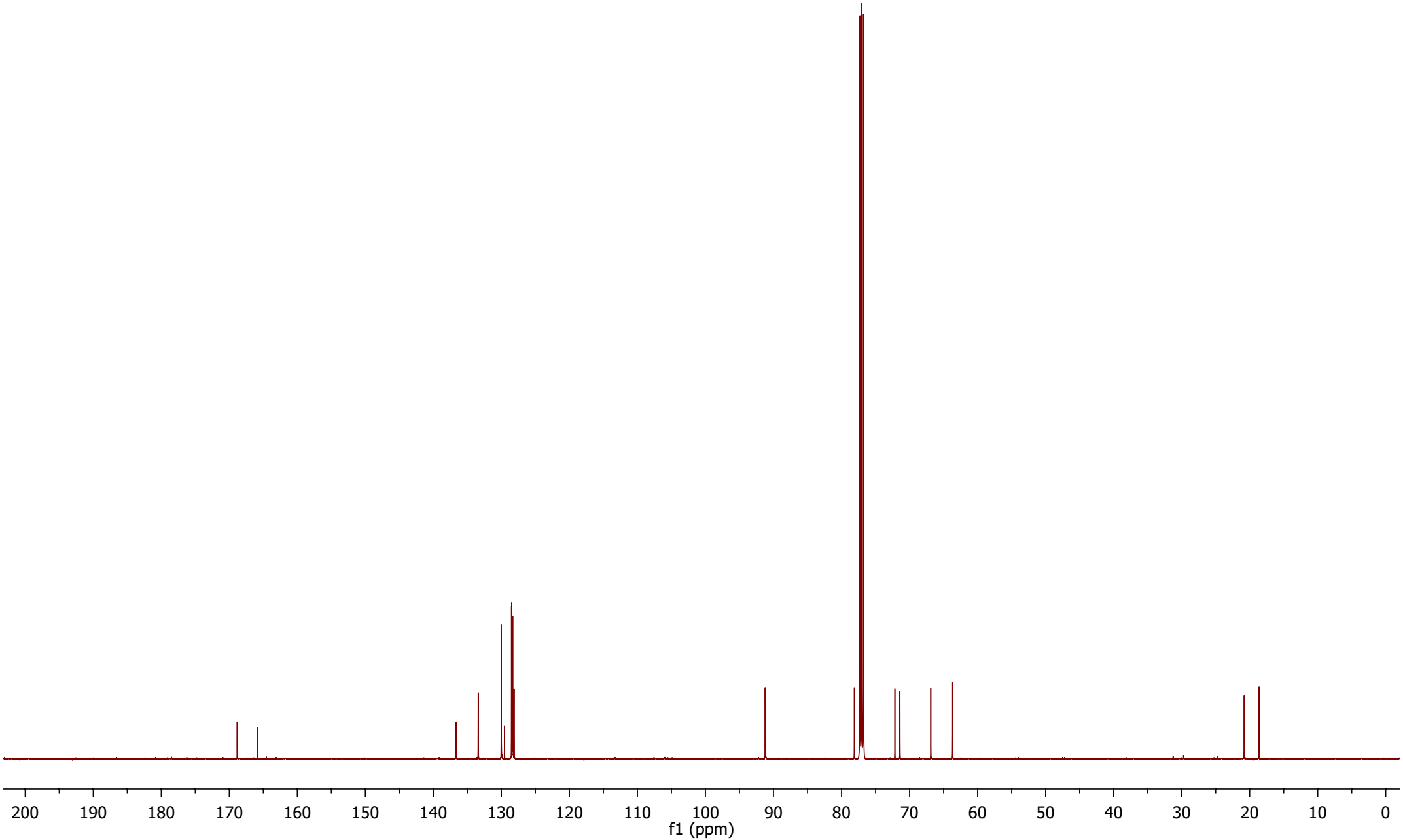
500 MHz, $CDCl_3$

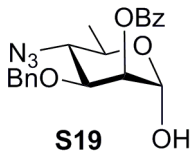




S18 (β)

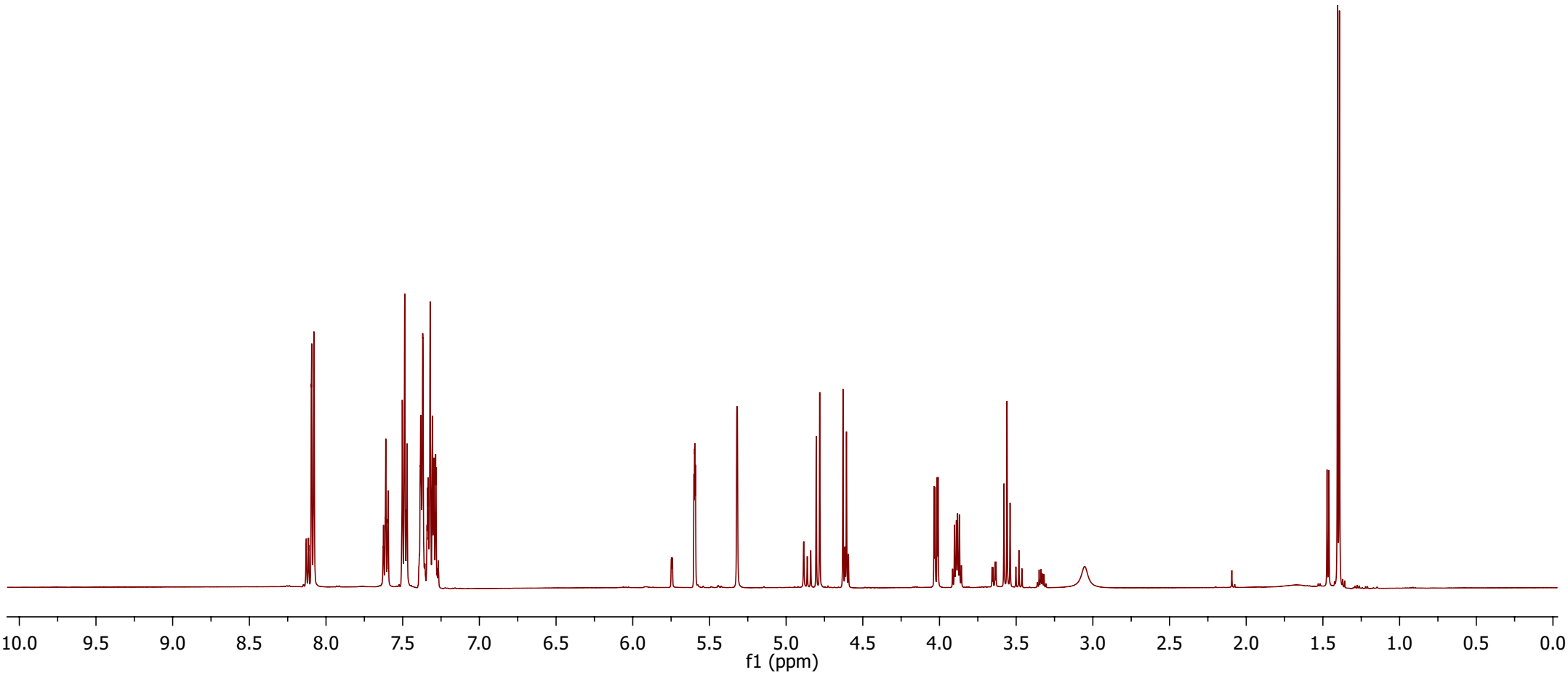
126 MHz, $CDCl_3$

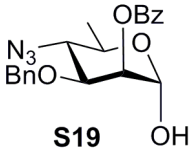




S19

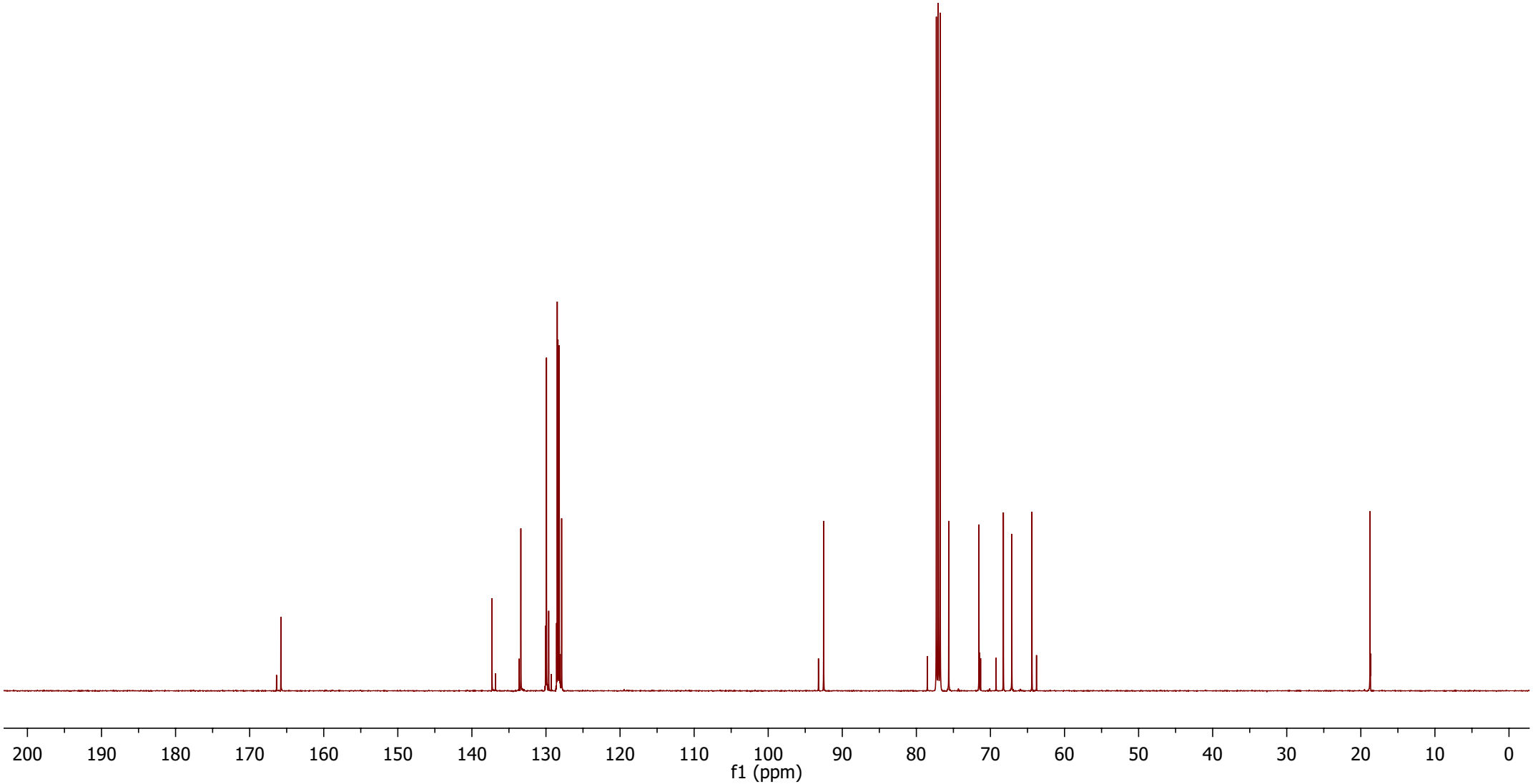
500 MHz, $CDCl_3$

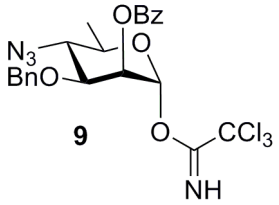




S19

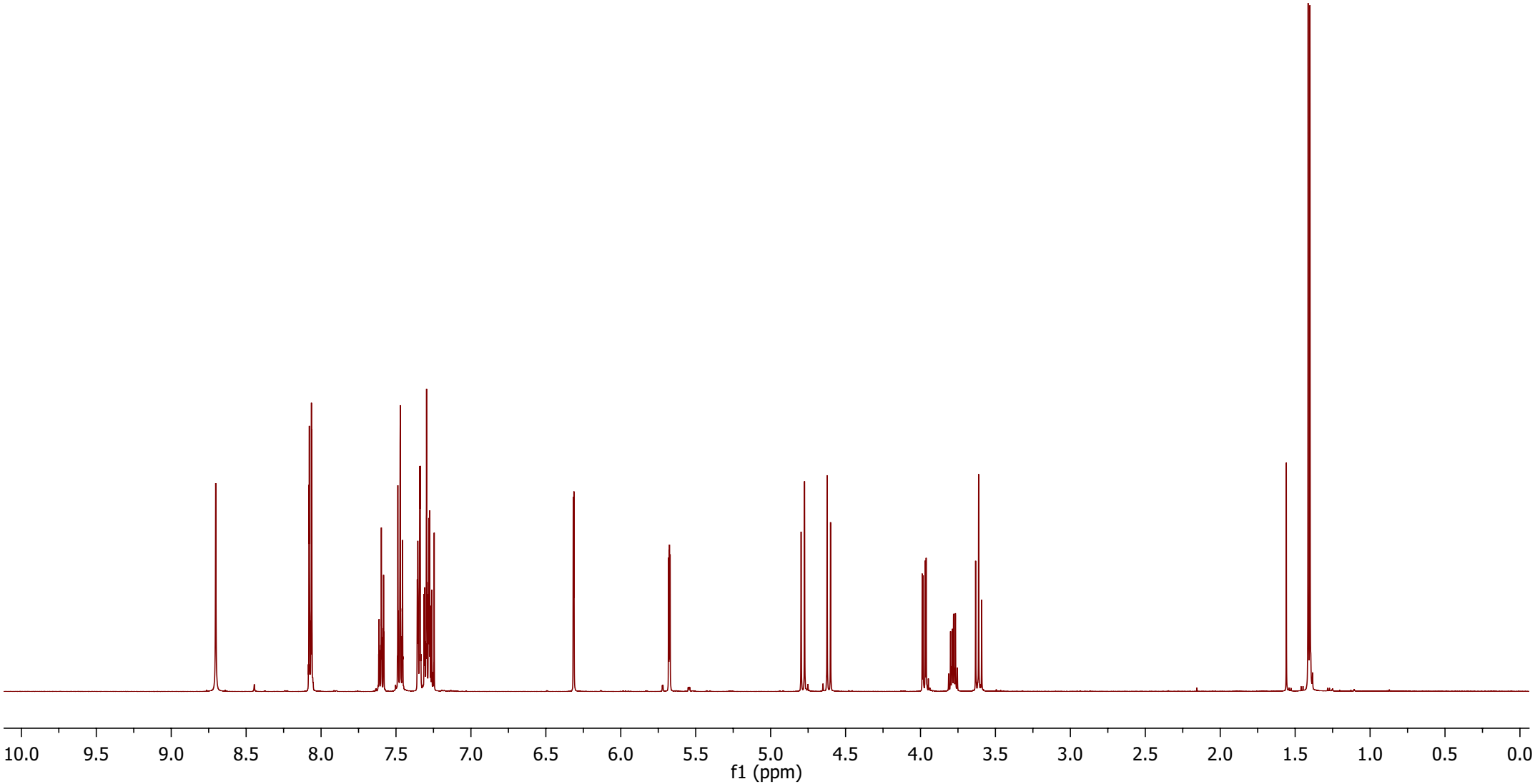
126 MHz, $CDCl_3$



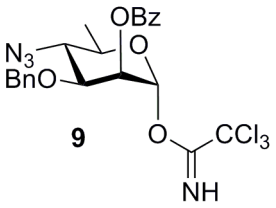


9

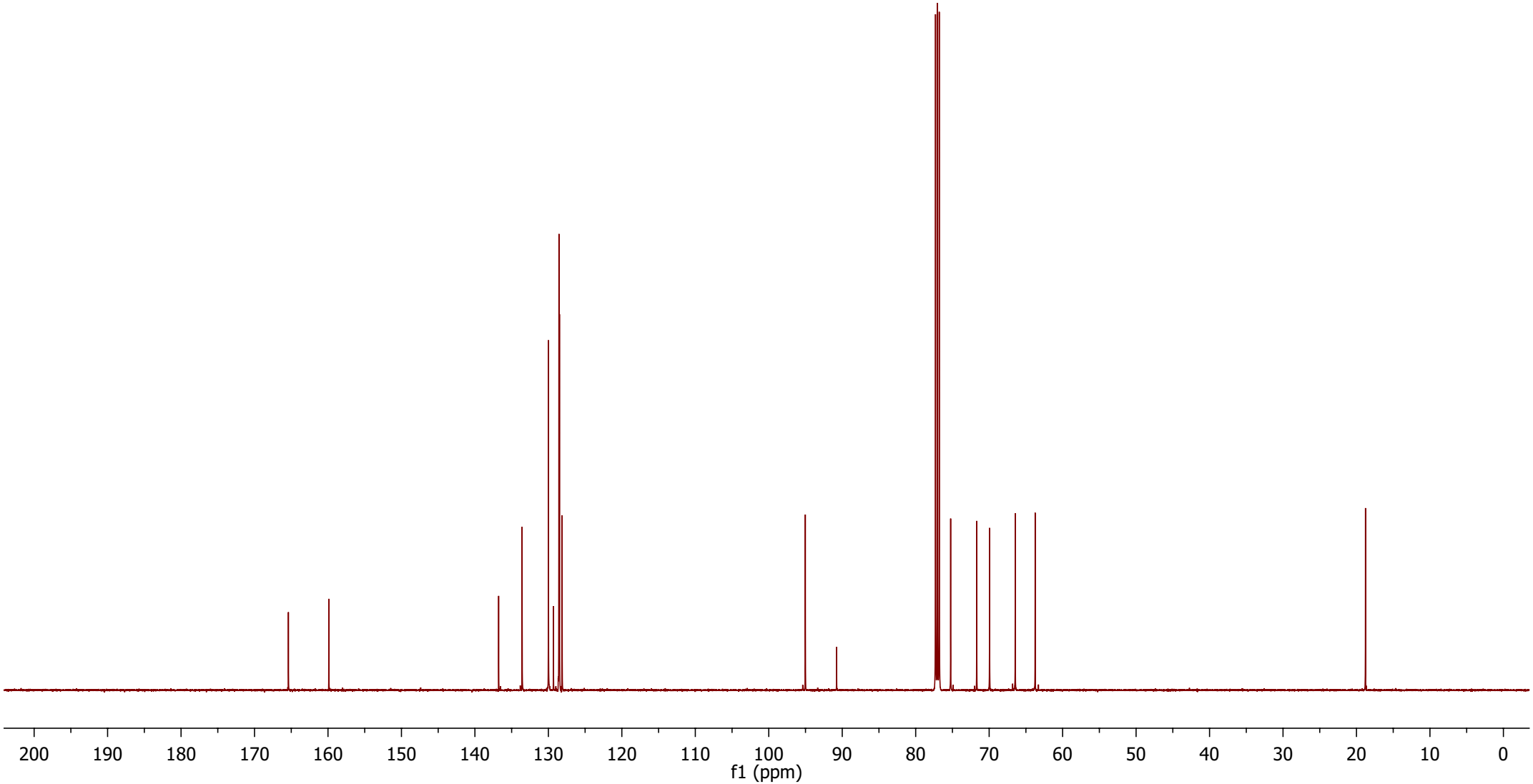
500 MHz, $CDCl_3$



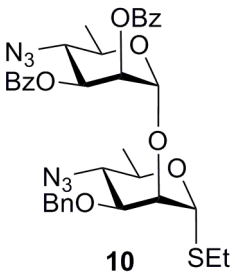
126 MHz, $CDCl_3$



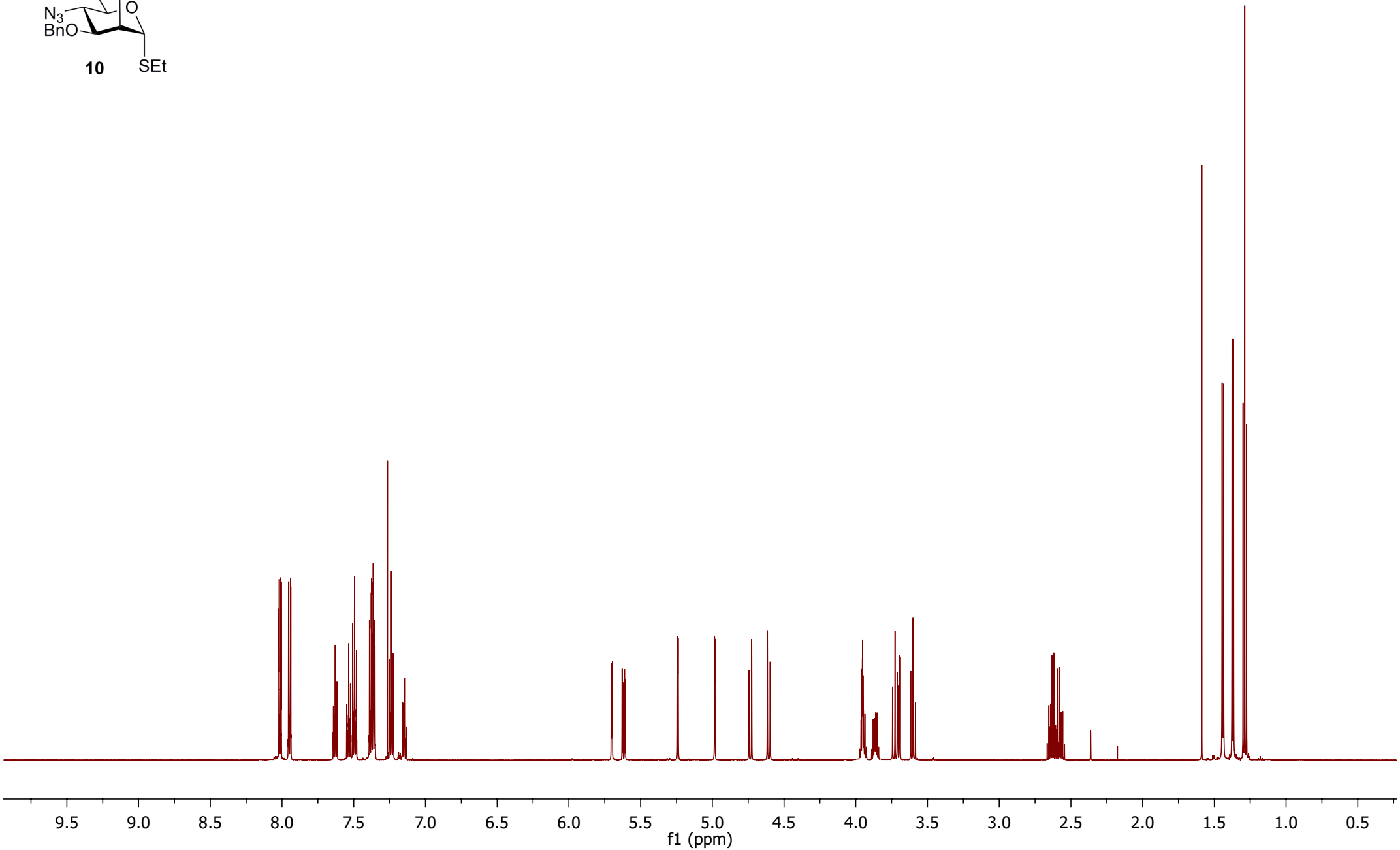
9



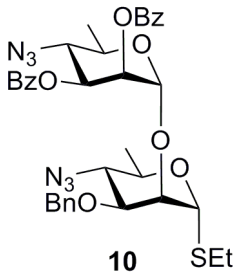
600 MHz, $CDCl_3$



10

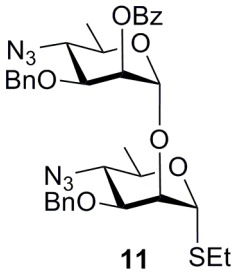


126 MHz, $CDCl_3$

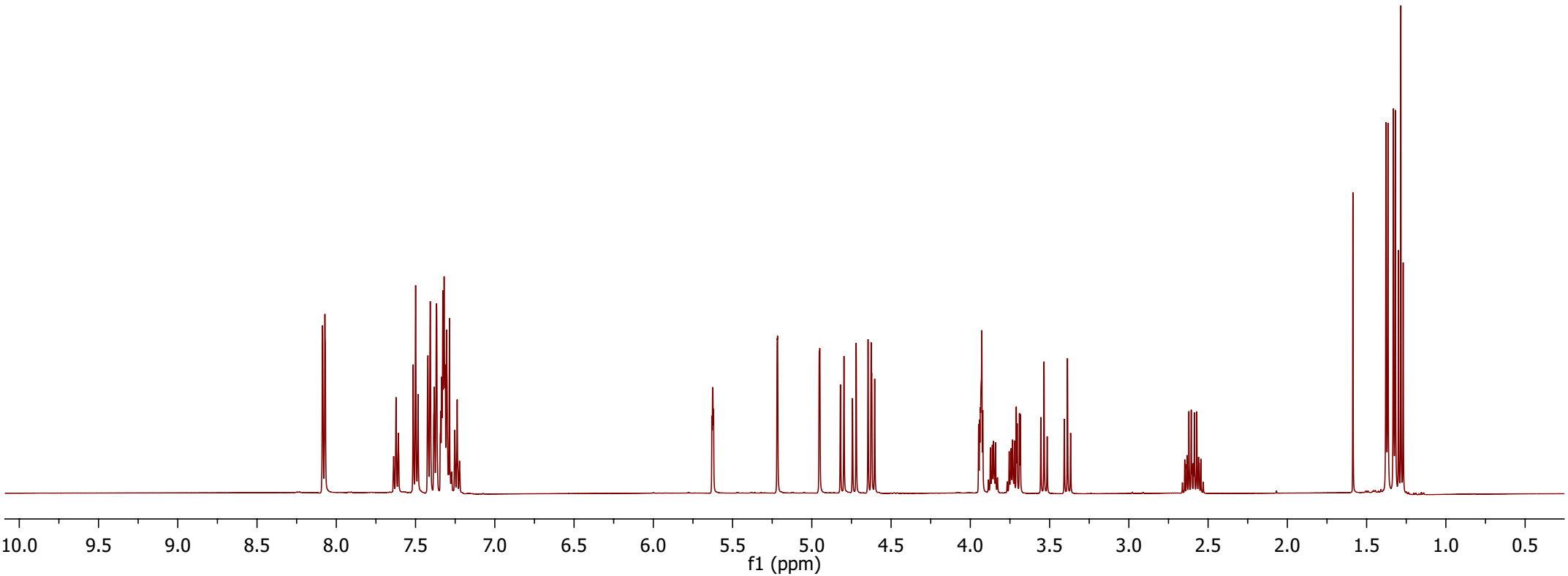


10

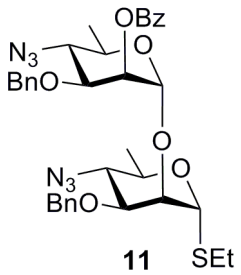
500 MHz, $CDCl_3$



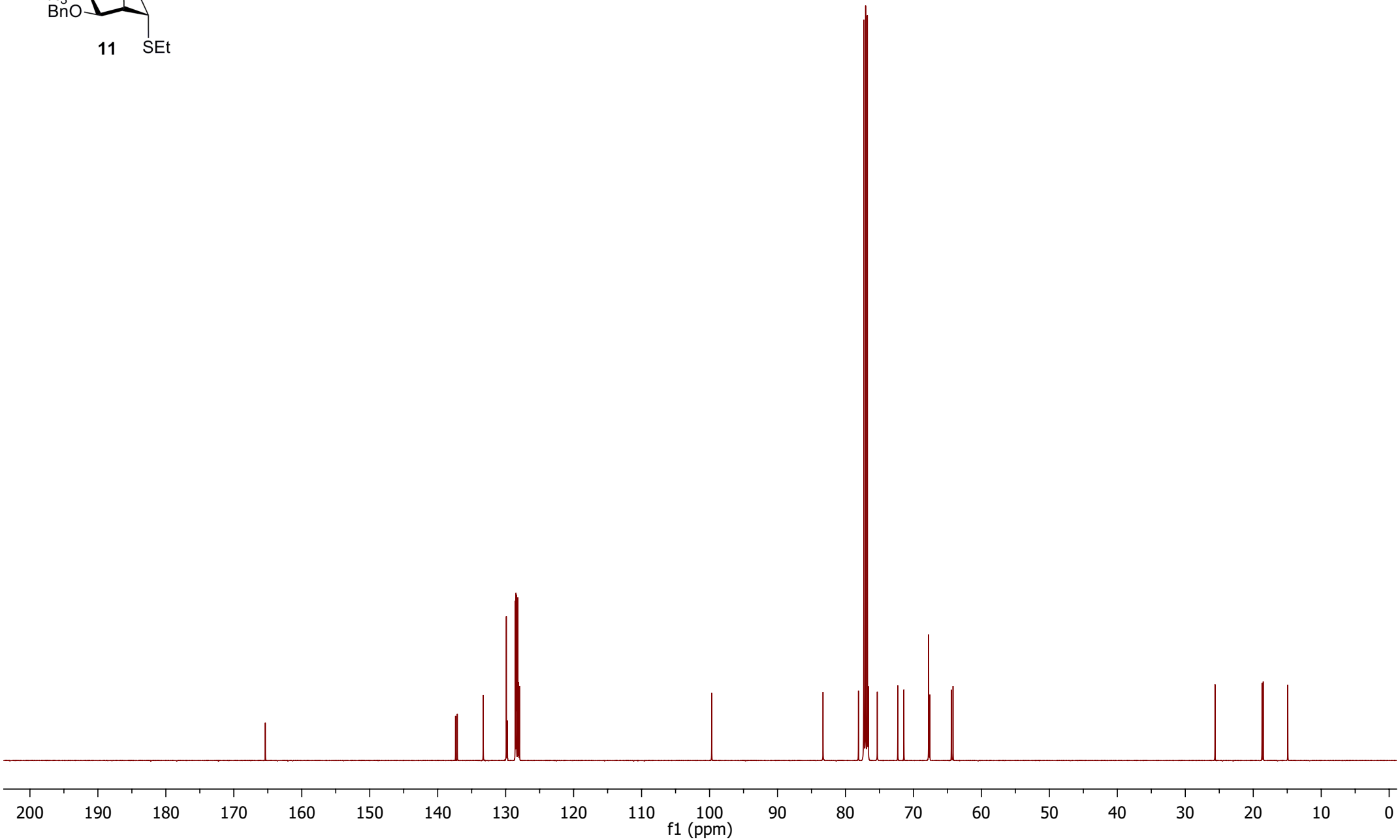
11



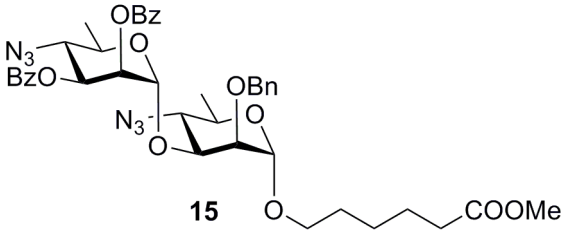
126 MHz, $CDCl_3$

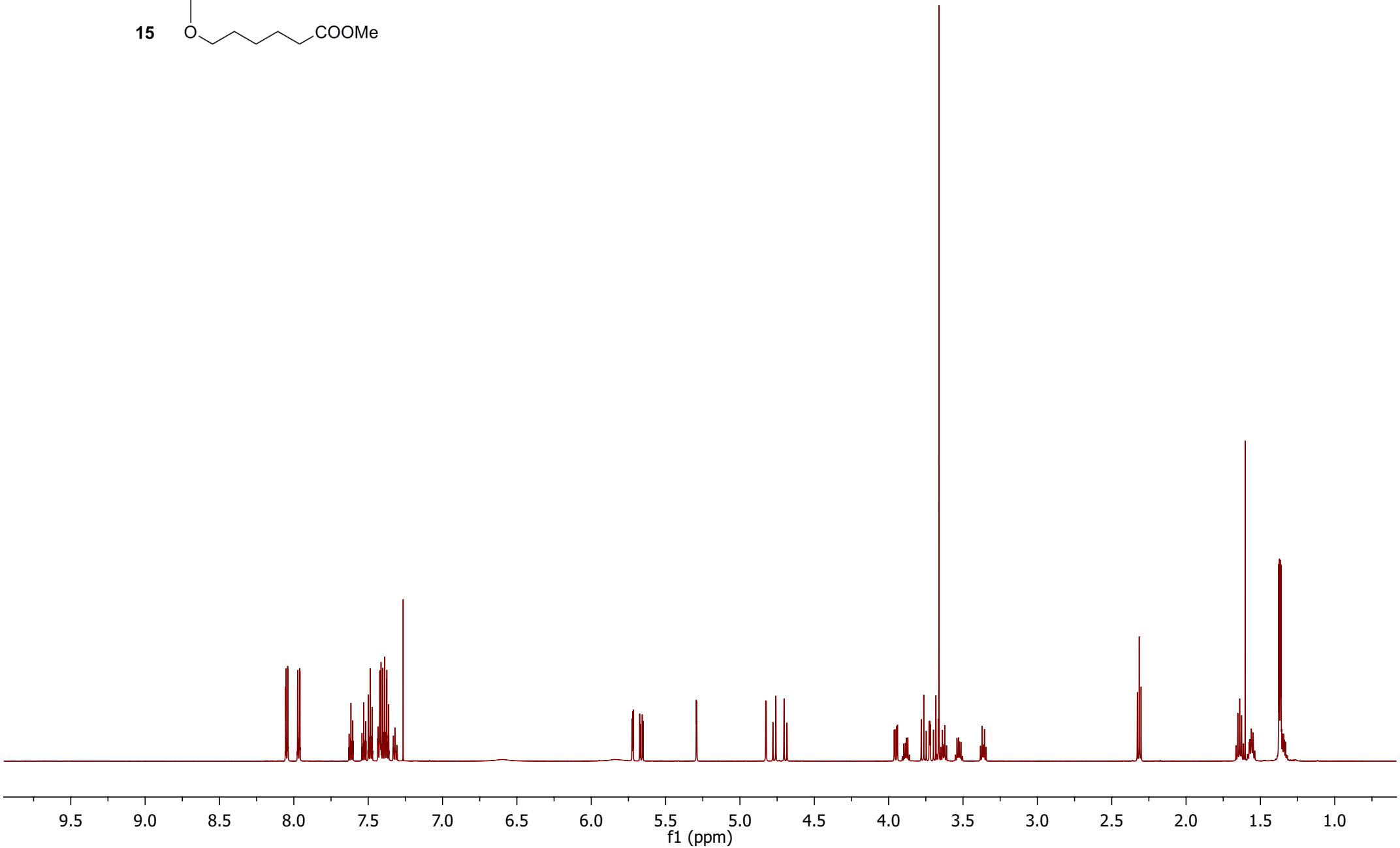


11

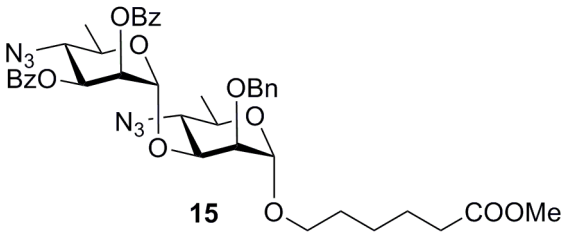


600 MHz, $CDCl_3$

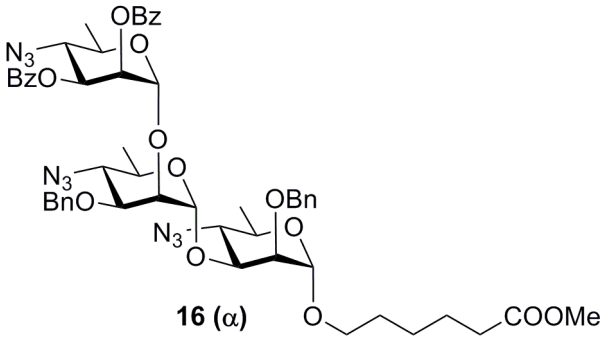




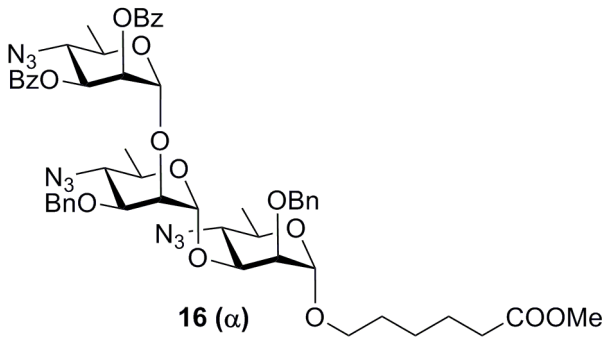
126 MHz, $CDCl_3$



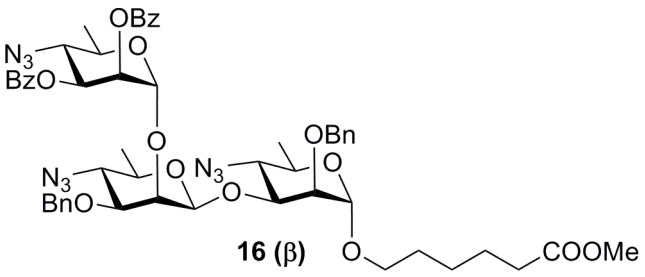
600 MHz, $CDCl_3$



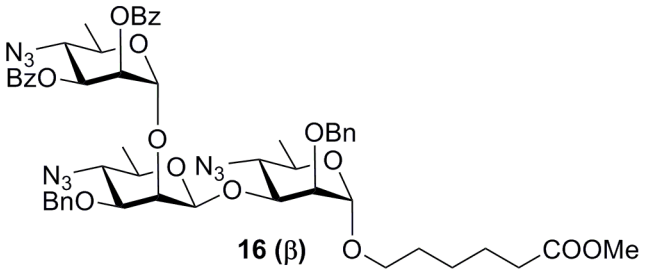
126 MHz, $CDCl_3$



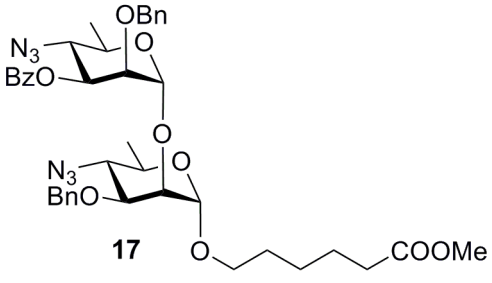
600 MHz, $CDCl_3$



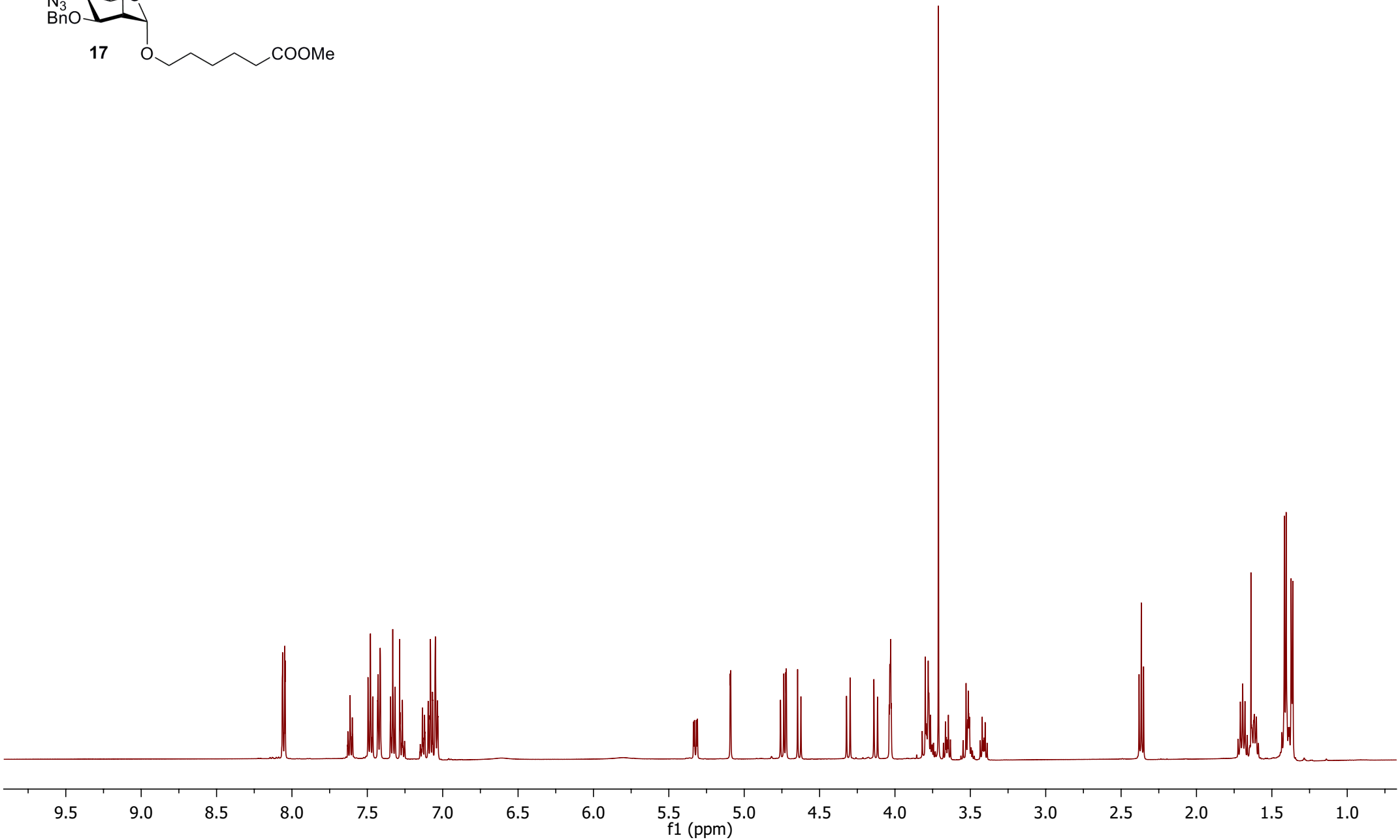
126 MHz, $CDCl_3$



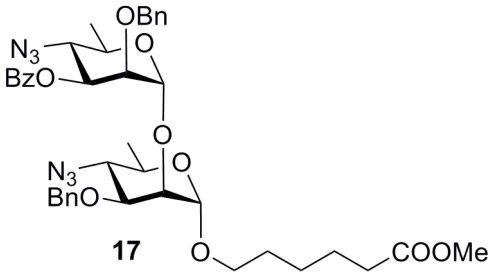
500 MHz, $CDCl_3$



17

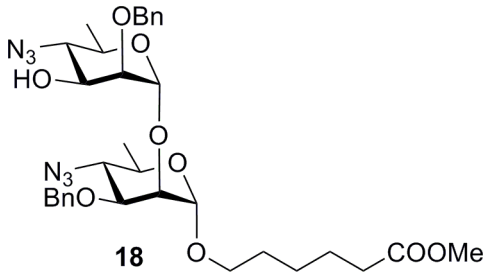


126 MHz, $CDCl_3$

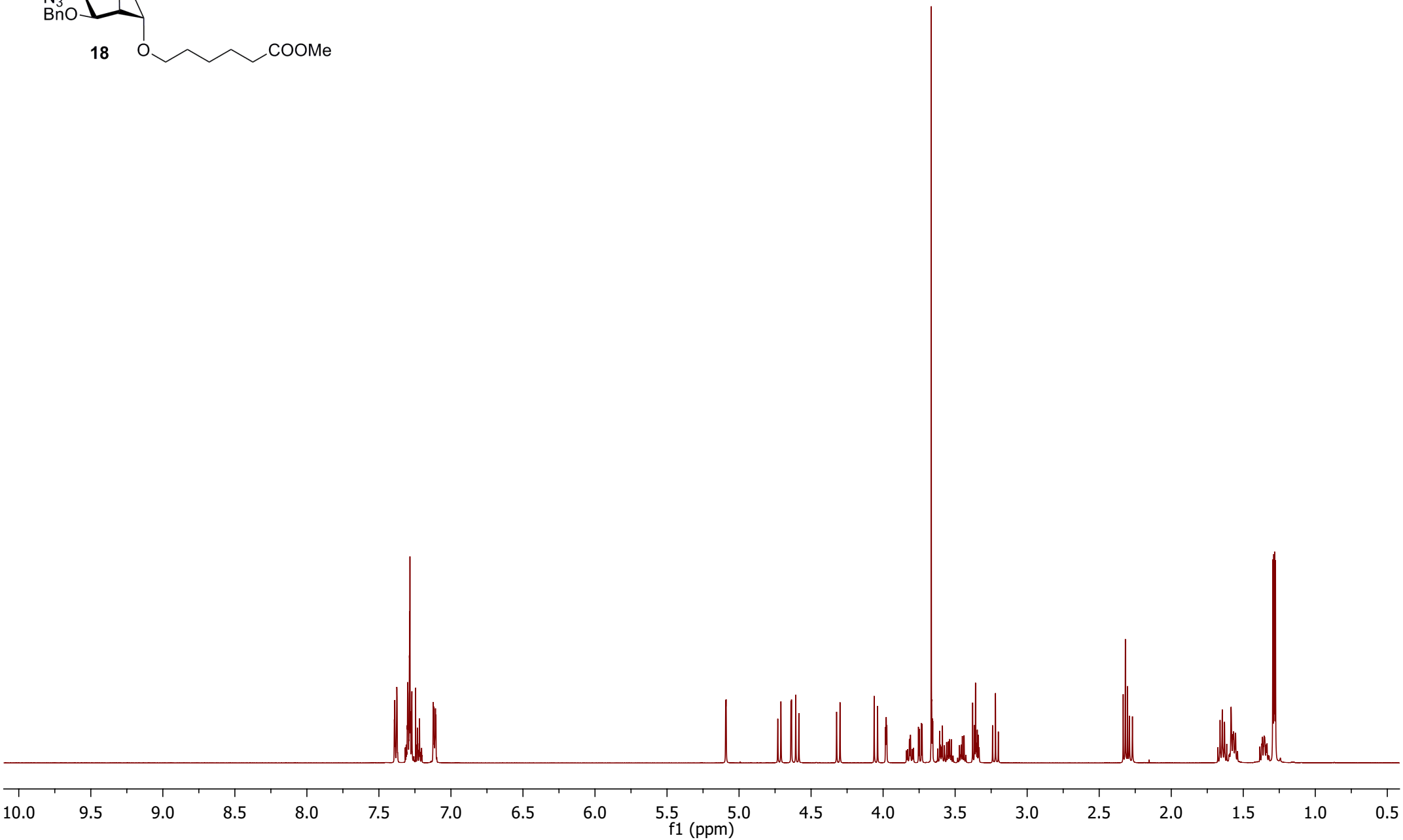


17

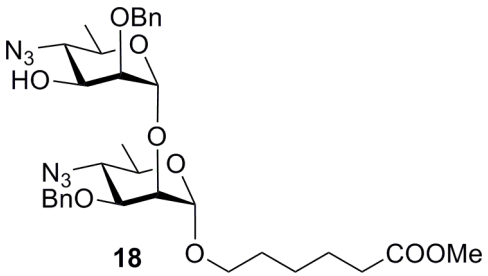
500 MHz, $CDCl_3$

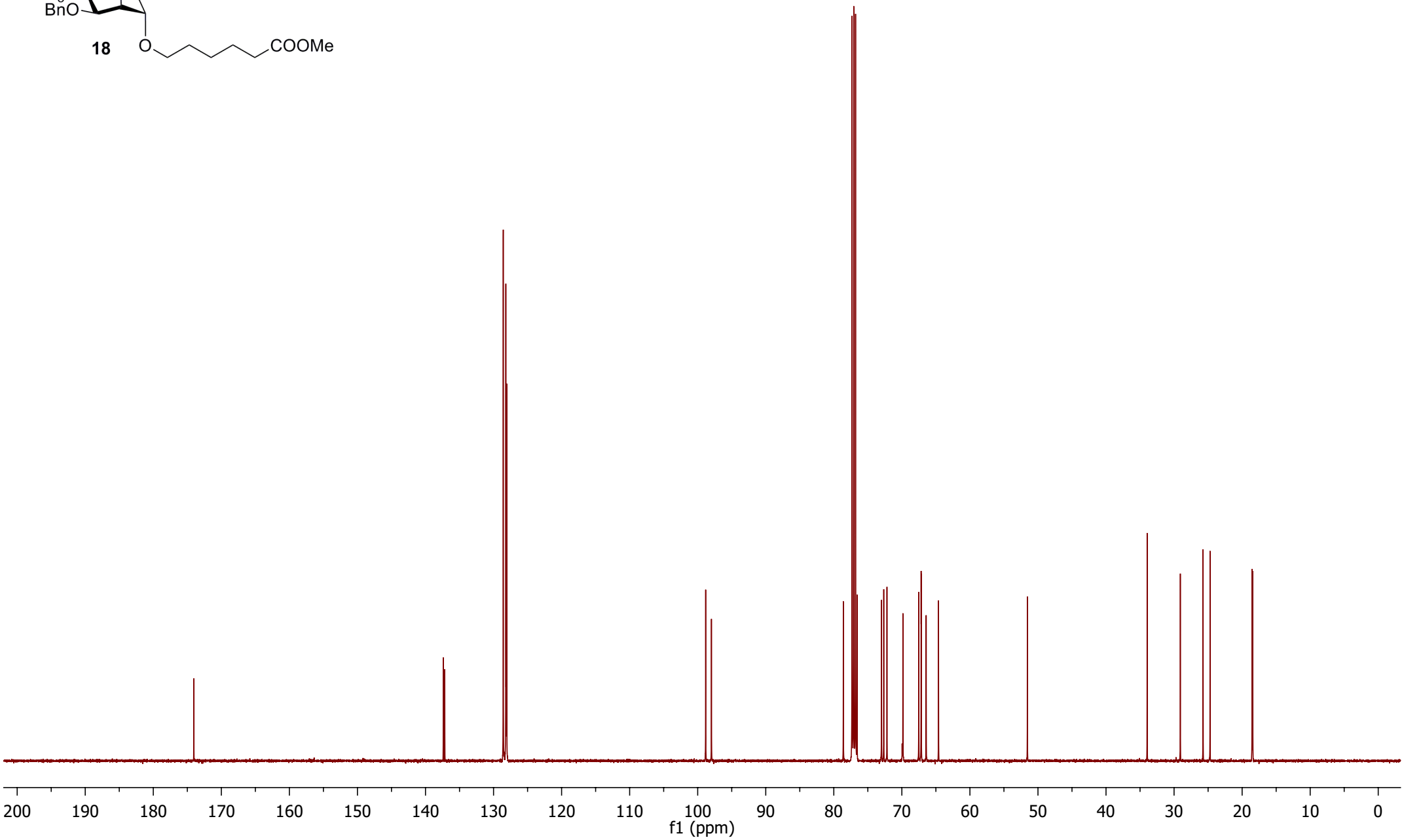


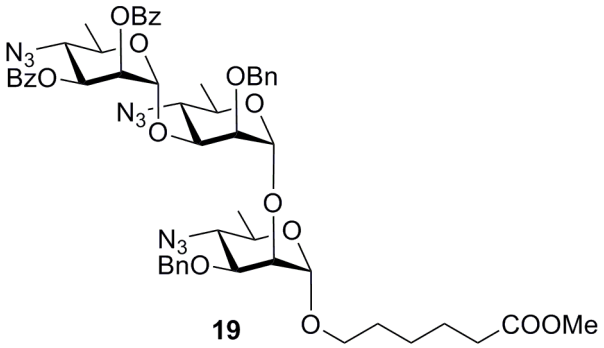
18



126 MHz, $CDCl_3$



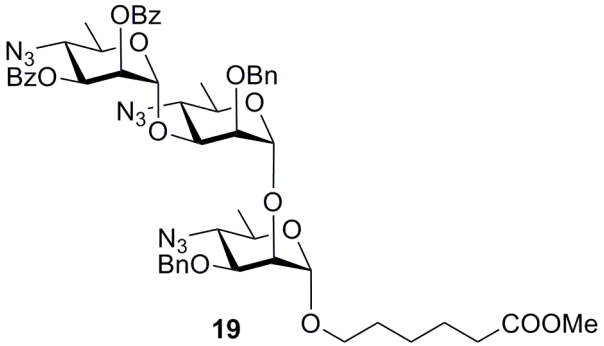




19

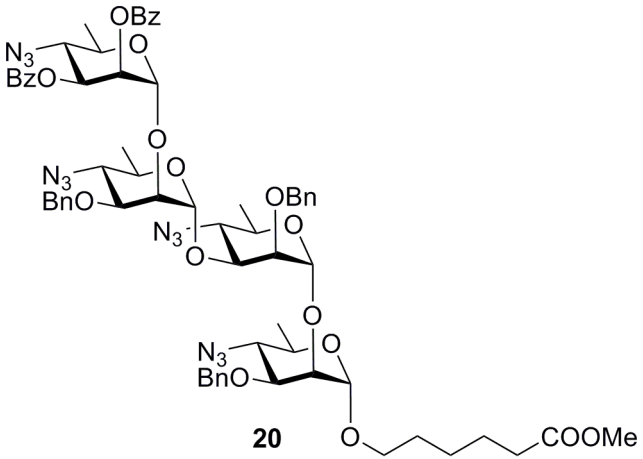
500 MHz, $CDCl_3$

126 MHz, $CDCl_3$



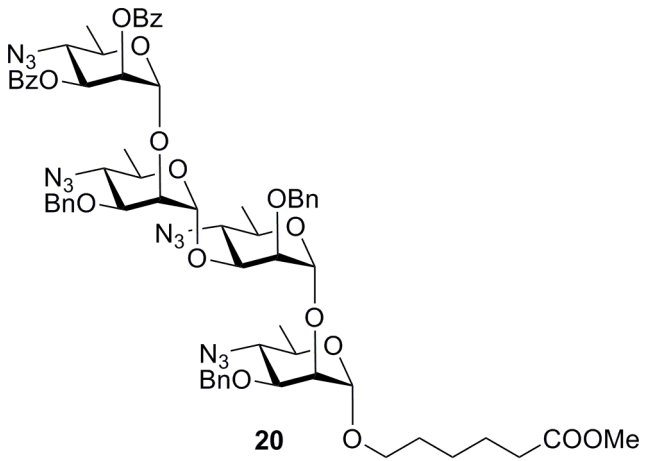
19

600 MHz, $CDCl_3$



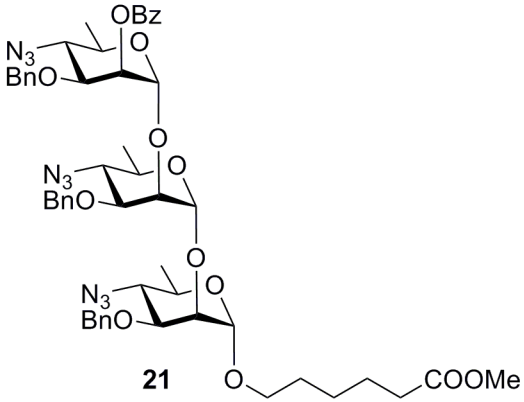
20

126 MHz, $CDCl_3$

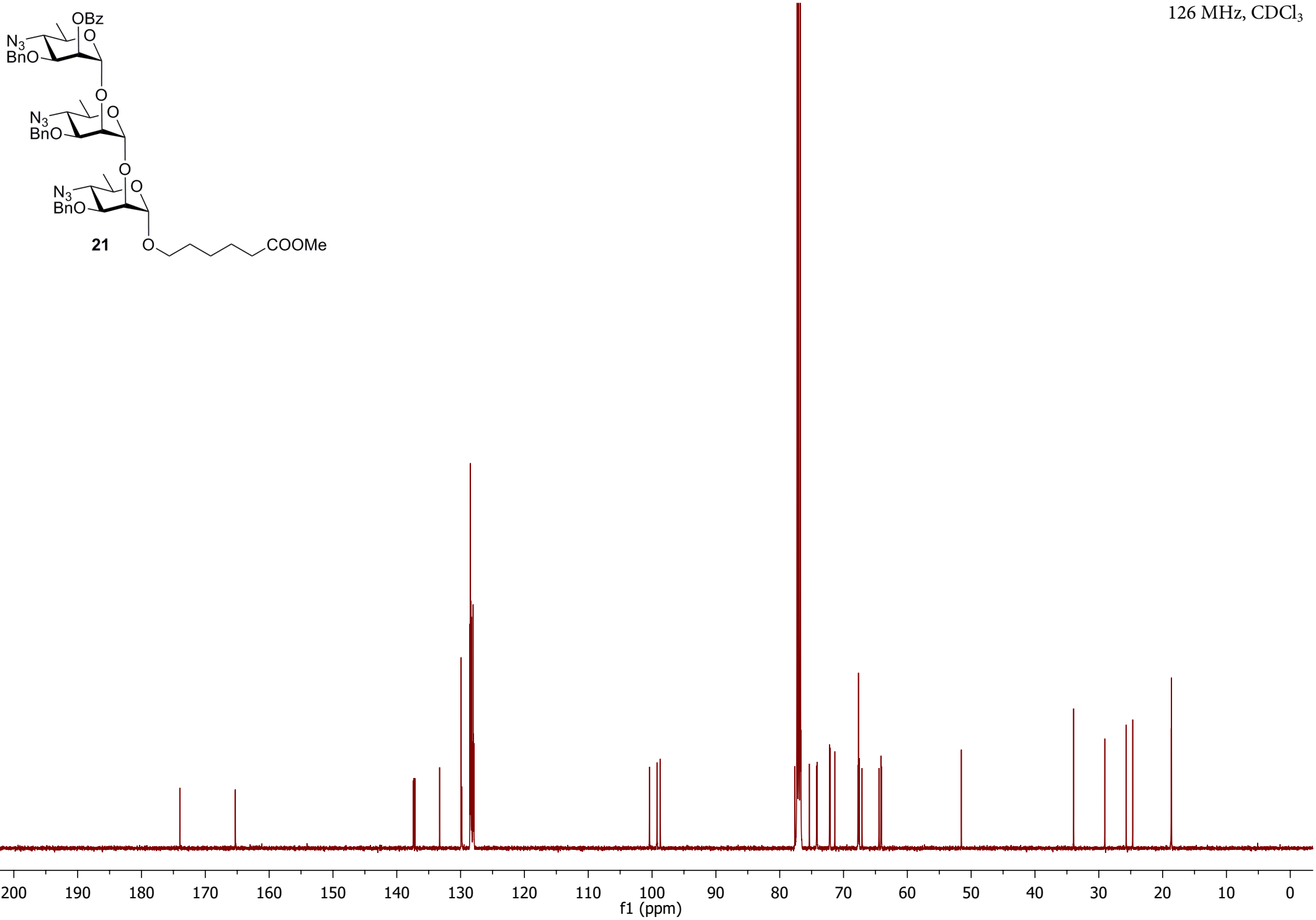


20

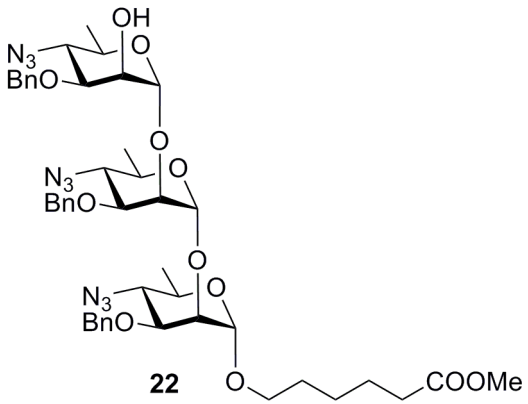
500 MHz, $CDCl_3$



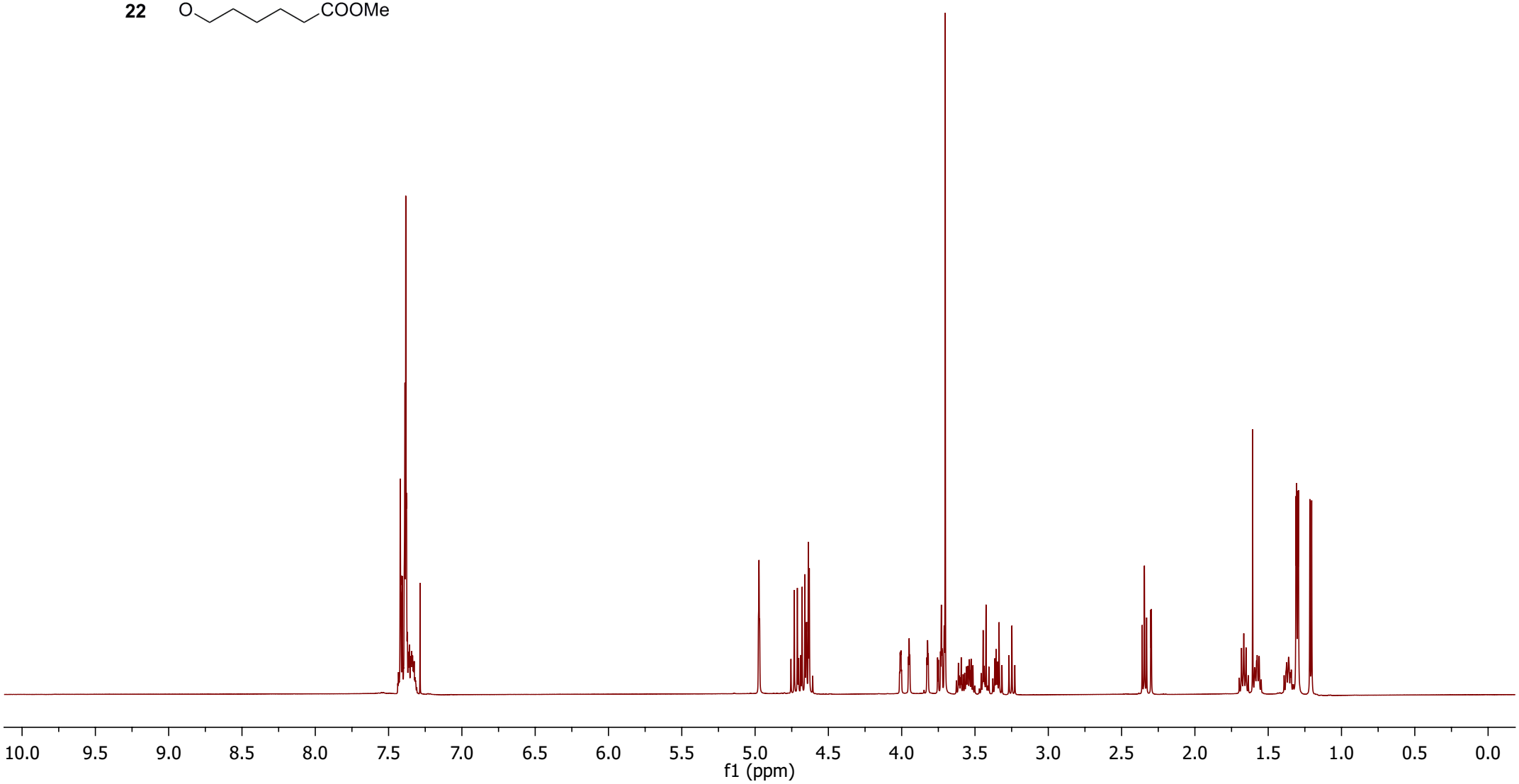
21


126 MHz, CDCl3
OBz
O
N3
BnO
O
O
N3
BnO
O
O
N3
BnO
21
O
COOMe
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

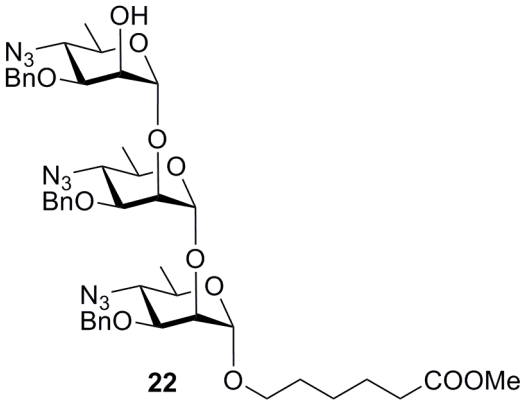
500 MHz, $CDCl_3$



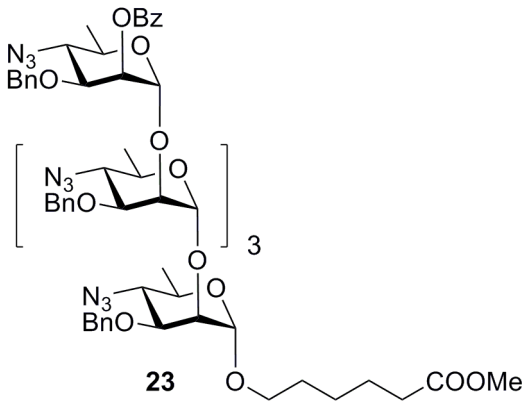
22



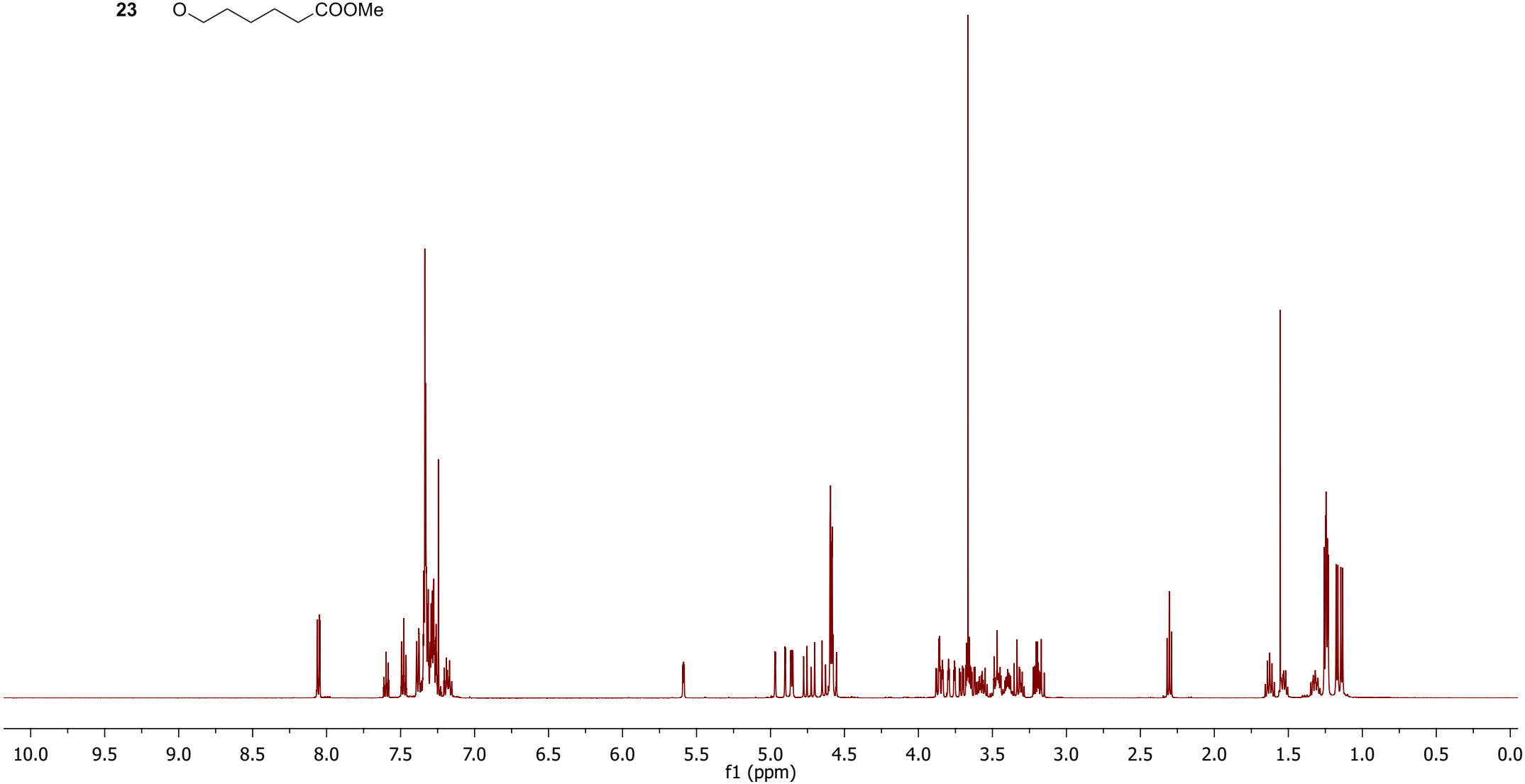
126 MHz, CDCl3

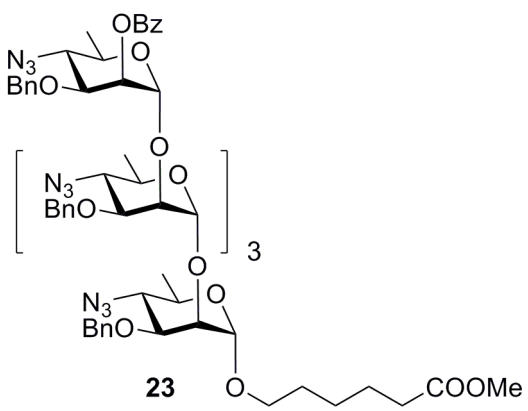


22



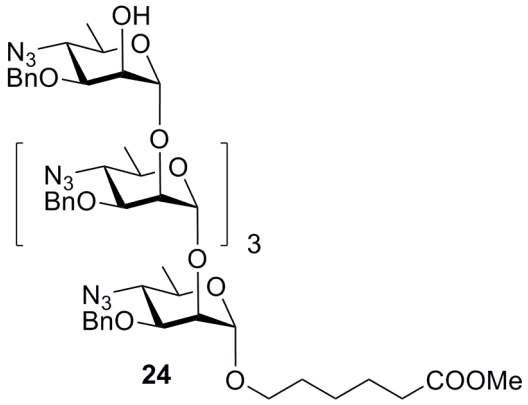
500 MHz, $CDCl_3$

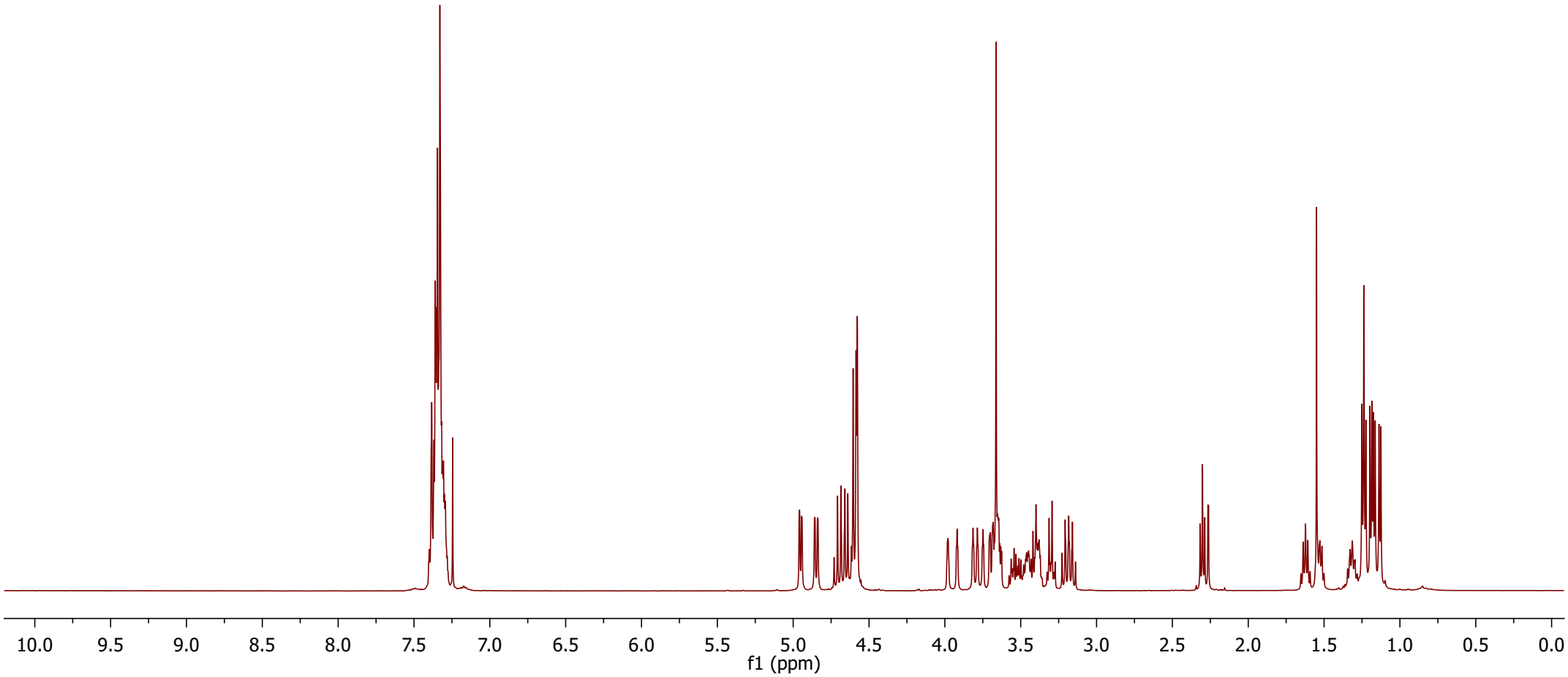




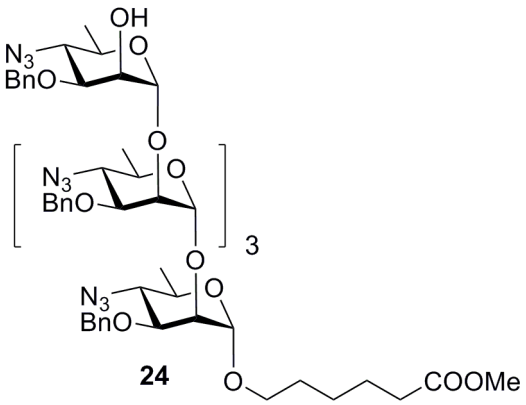
126 MHz, $CDCl_3$

500 MHz, $CDCl_3$

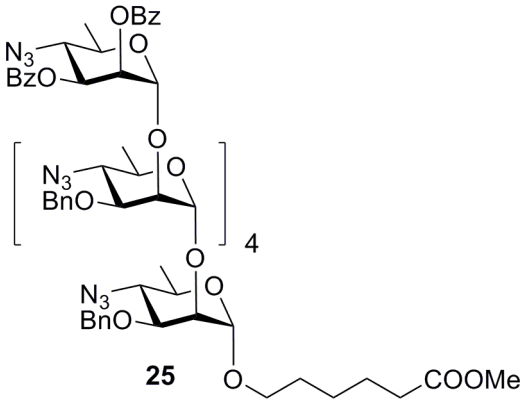


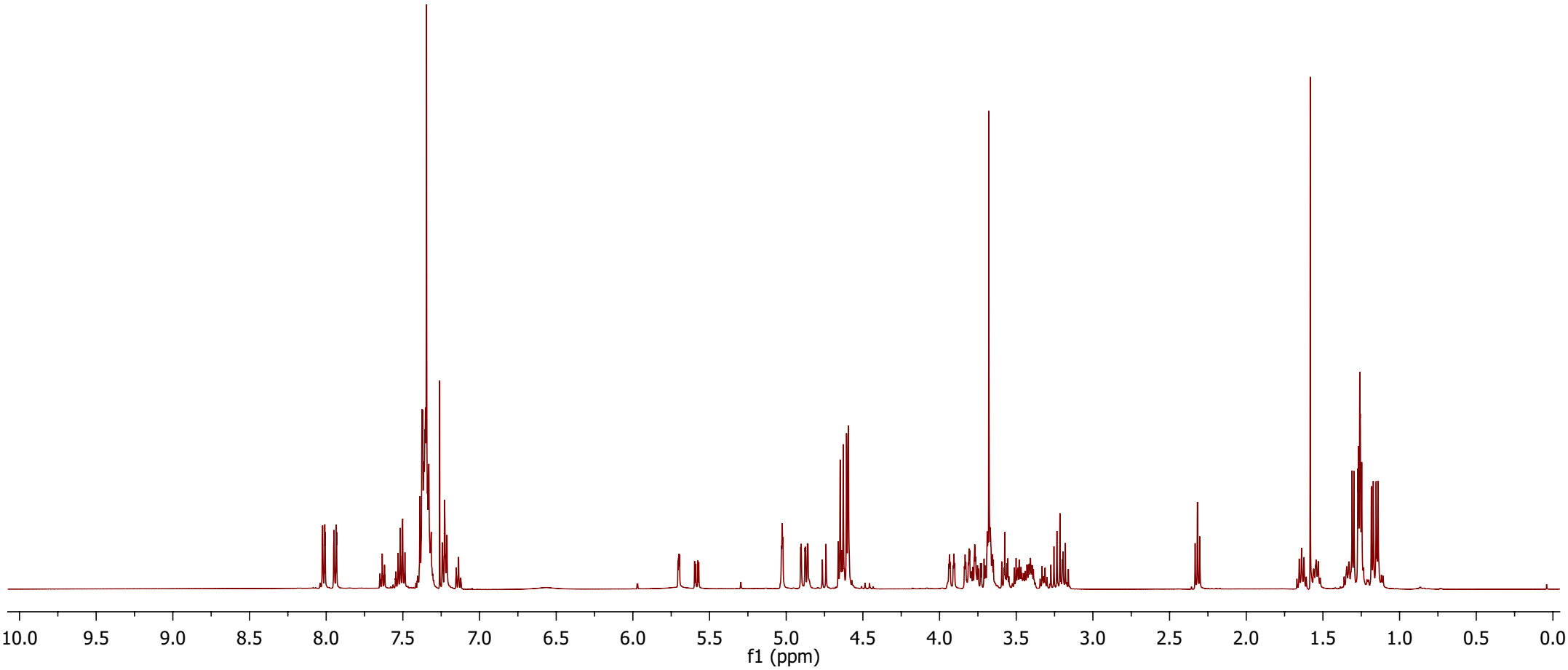


126 MHz, $CDCl_3$

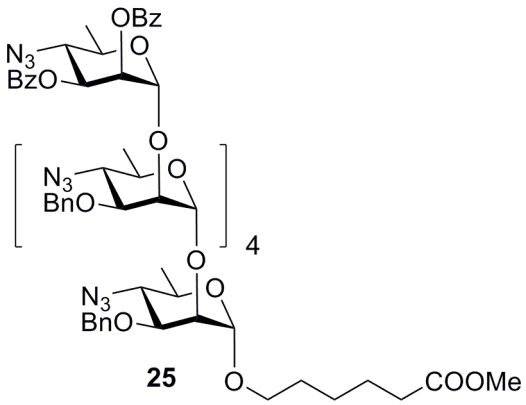


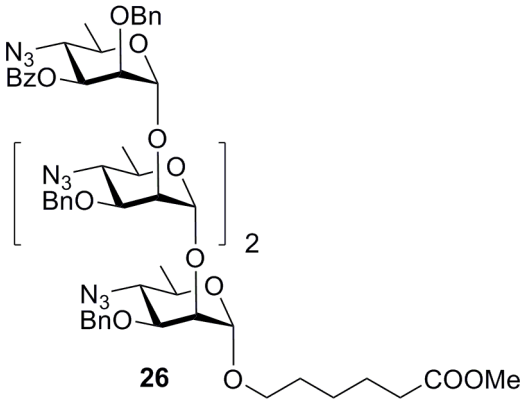
500 MHz, $CDCl_3$





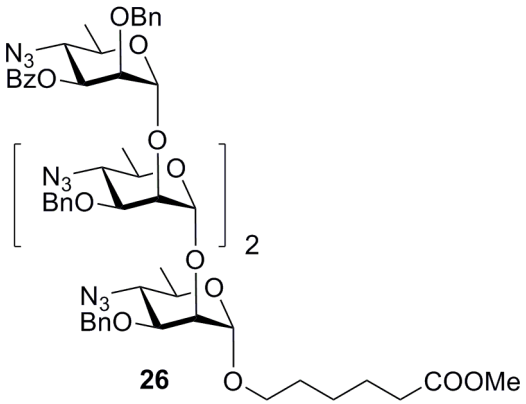
126 MHz, CDCl3



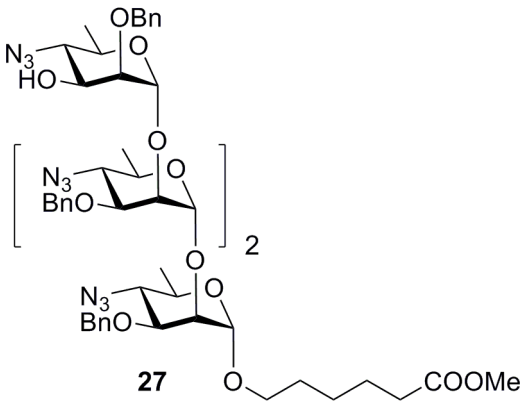


500 MHz, $CDCl_3$

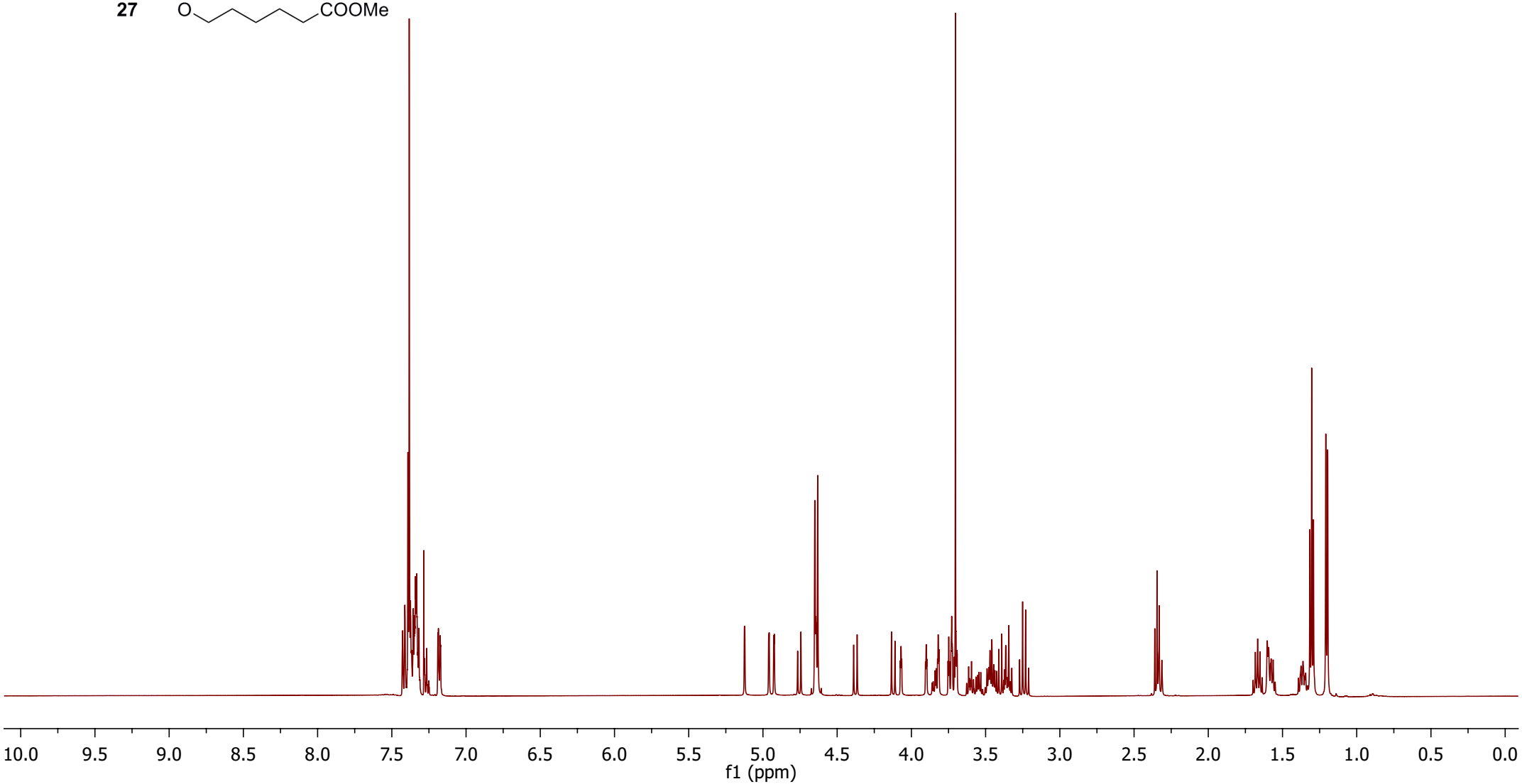
126 MHz, $CDCl_3$

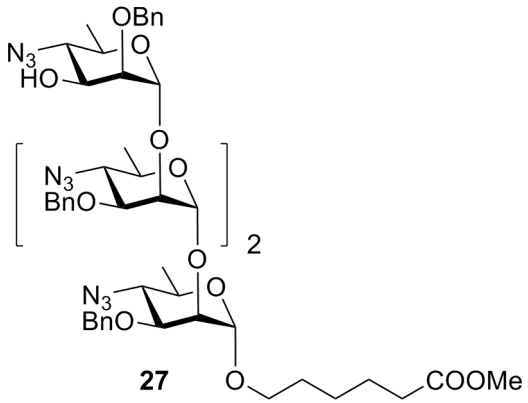


500 MHz, $CDCl_3$

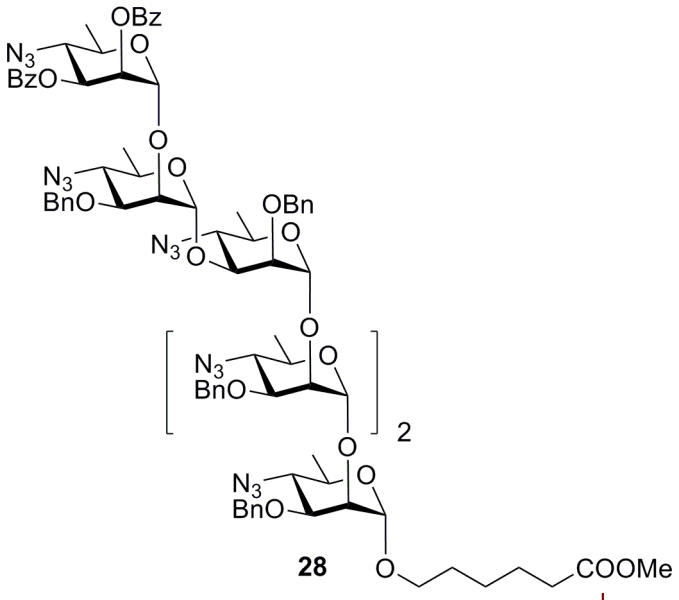


27

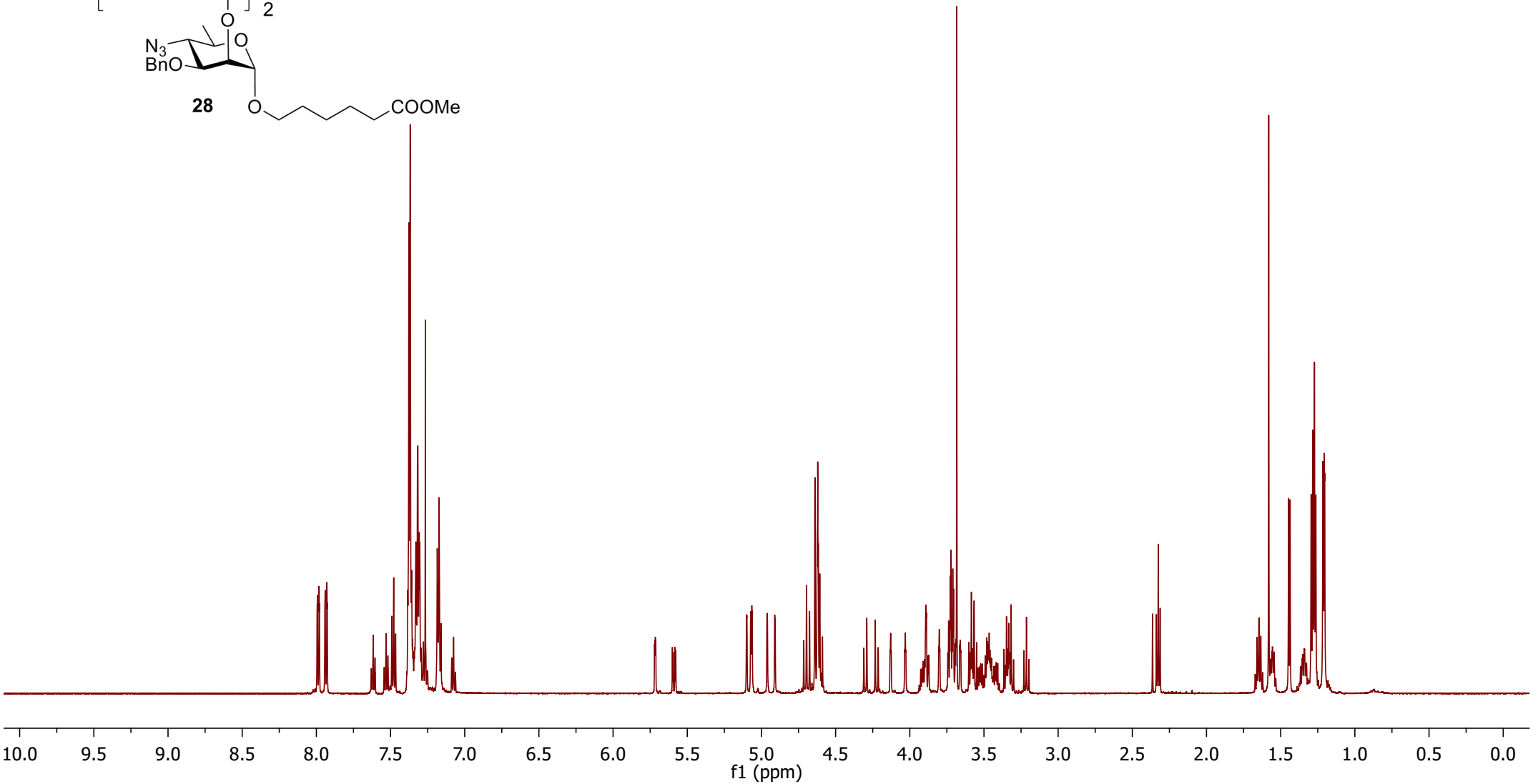


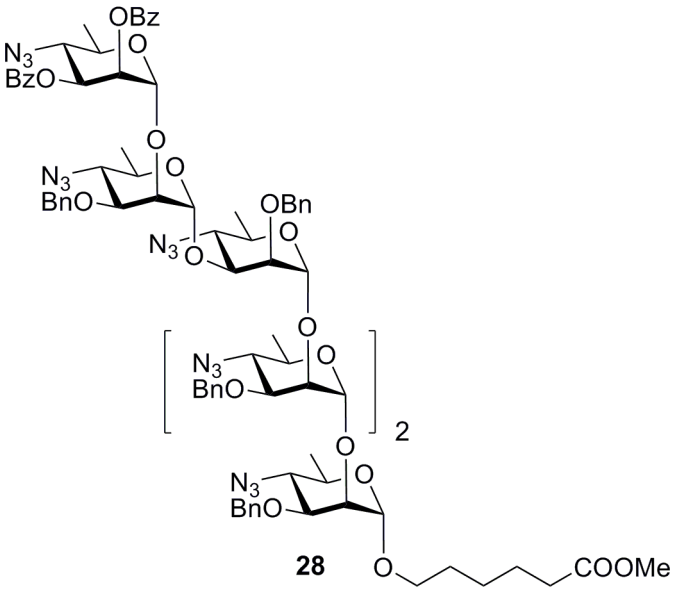


126 MHz, $CDCl_3$

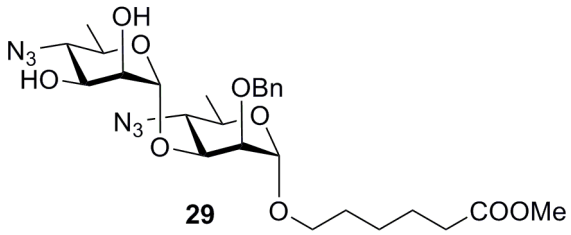


600 MHz, $CDCl_3$

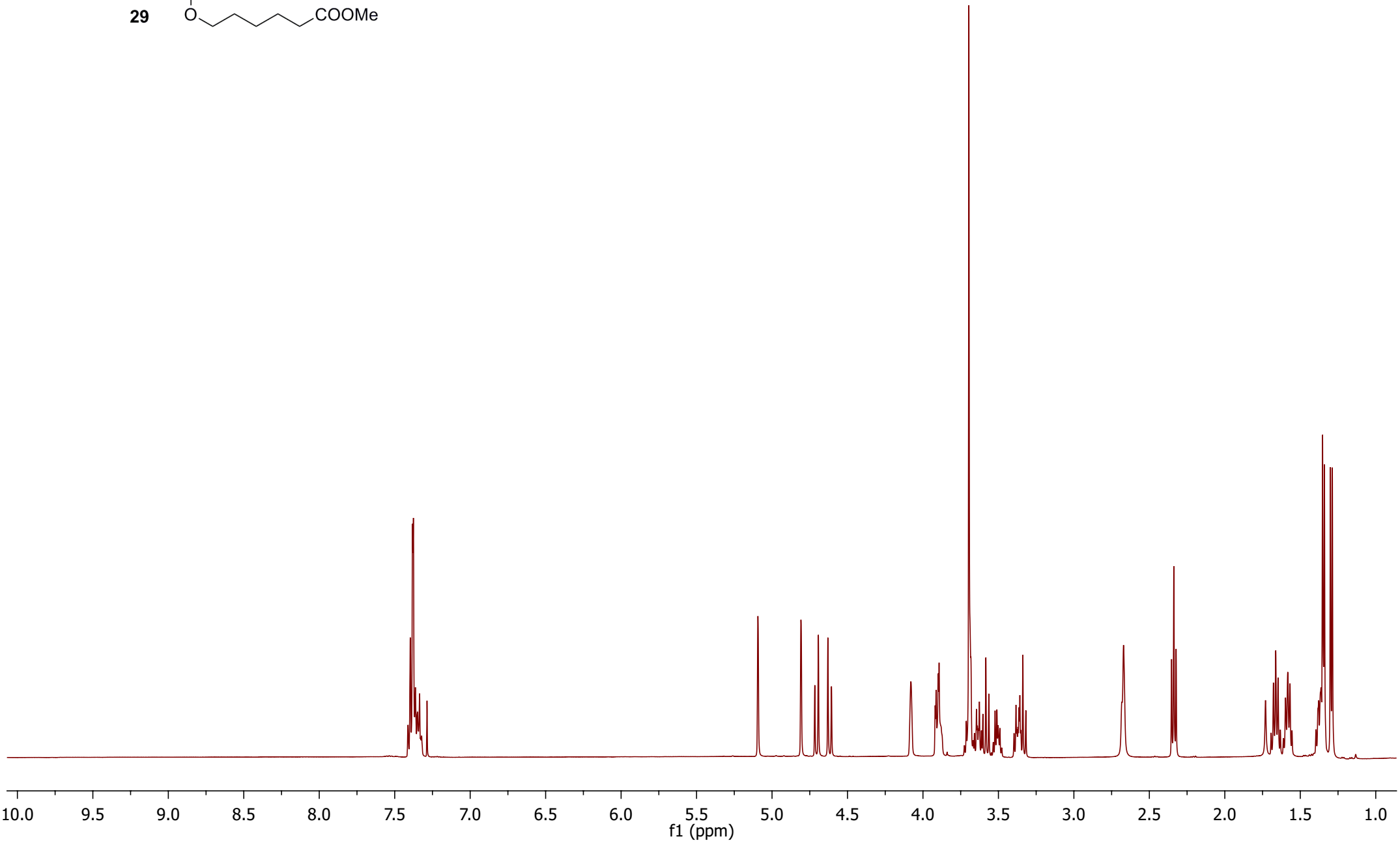




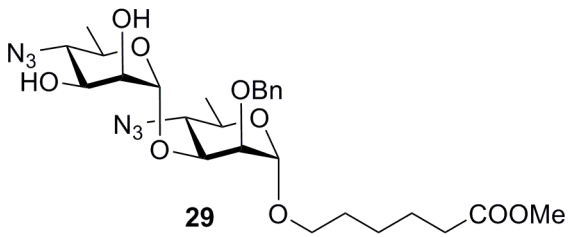
126 MHz, $CDCl_3$



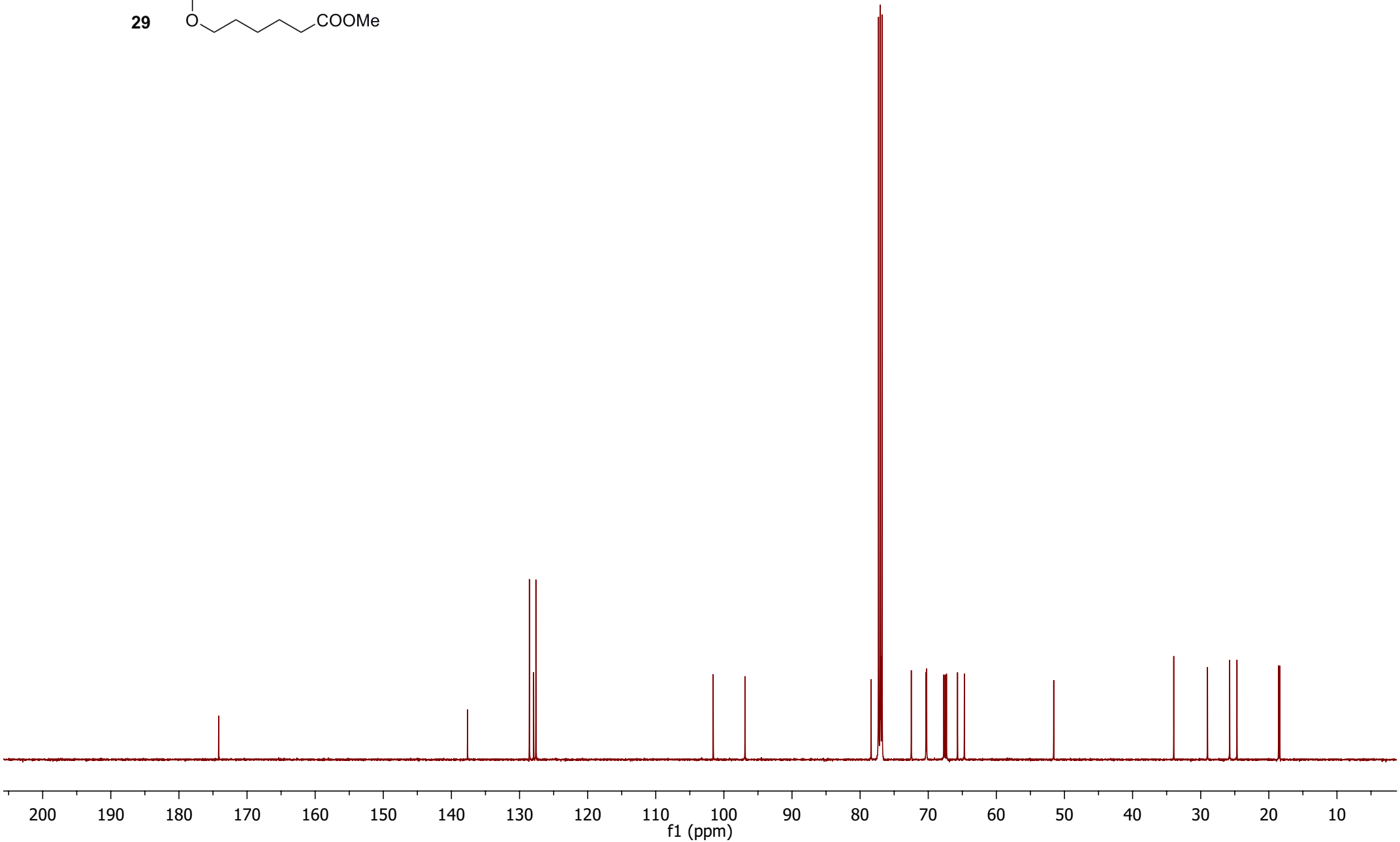
500 MHz, $CDCl_3$

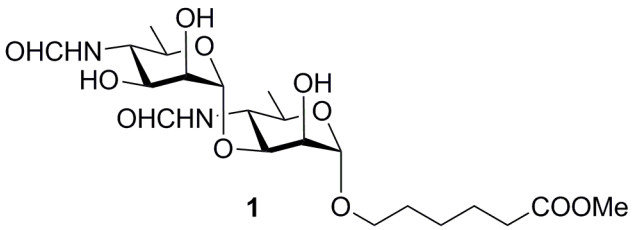


126 MHz, $CDCl_3$

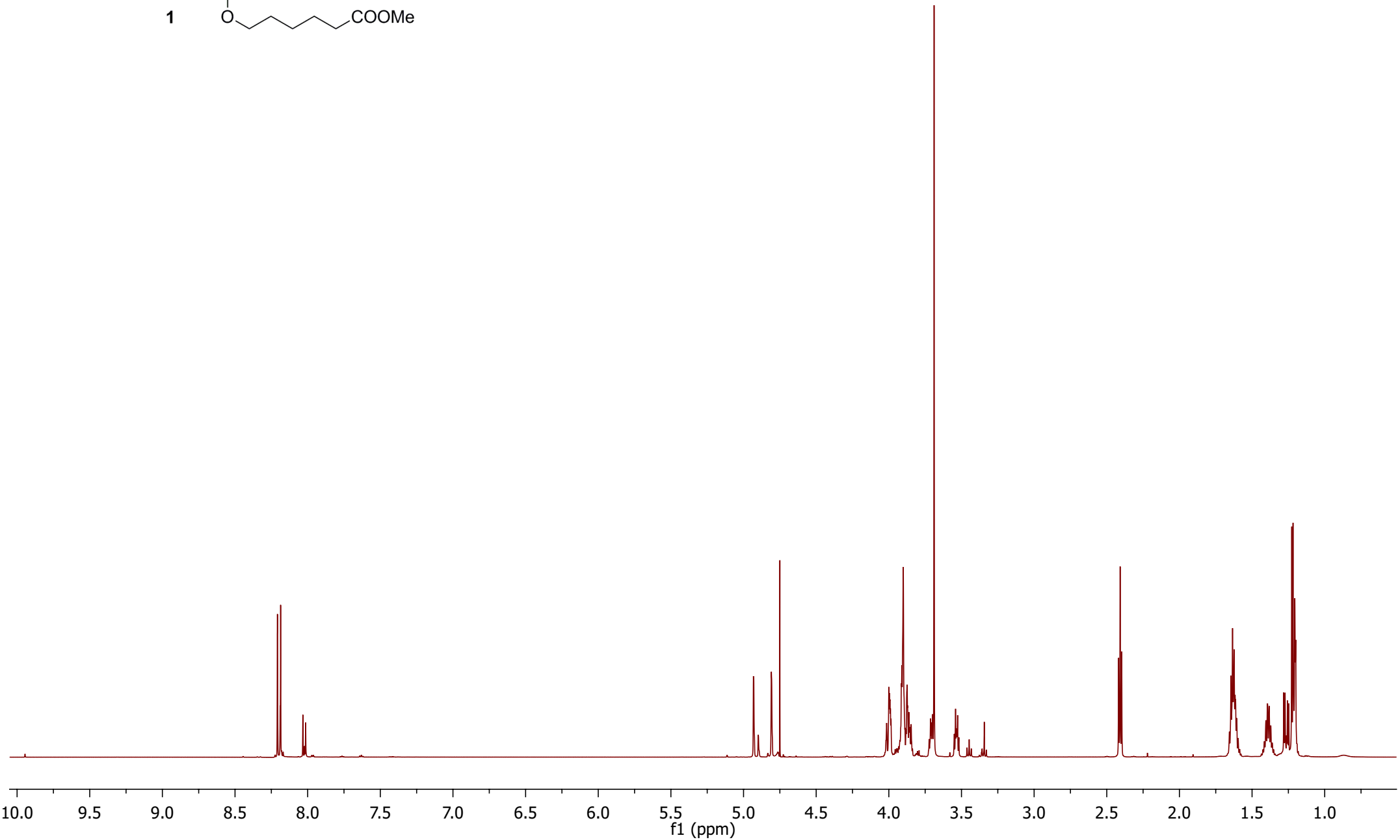


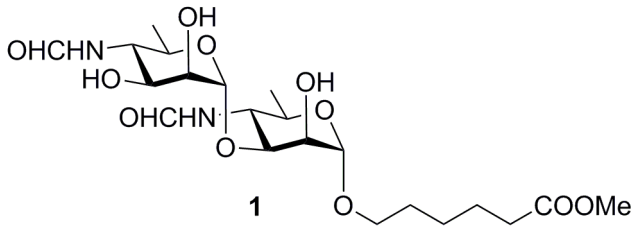
29



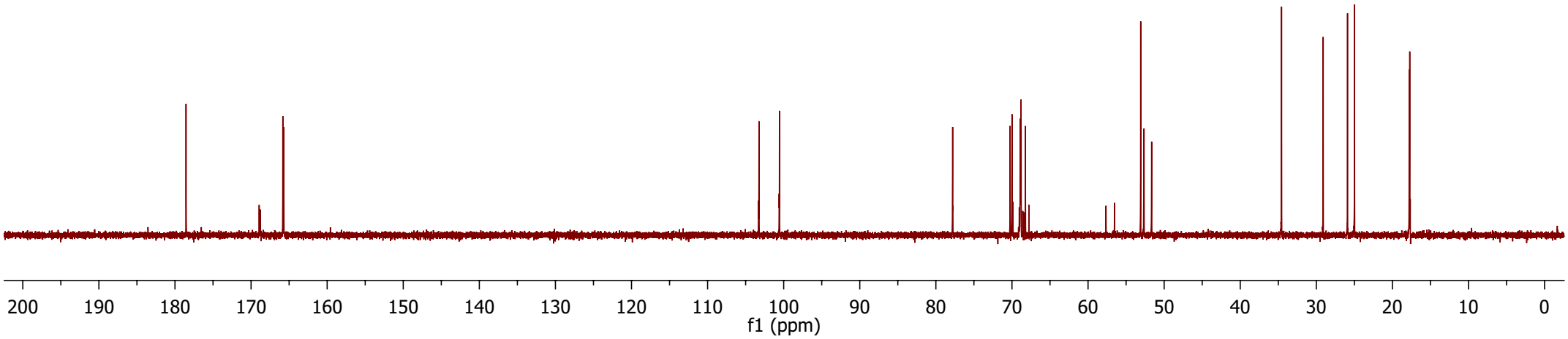

OH
OHCHN
O
HO
OH
OHCHN
O
O
1
O
COOMe

700 MHz, D_2O

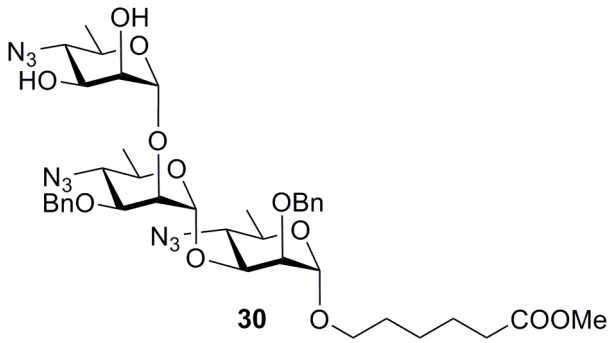

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

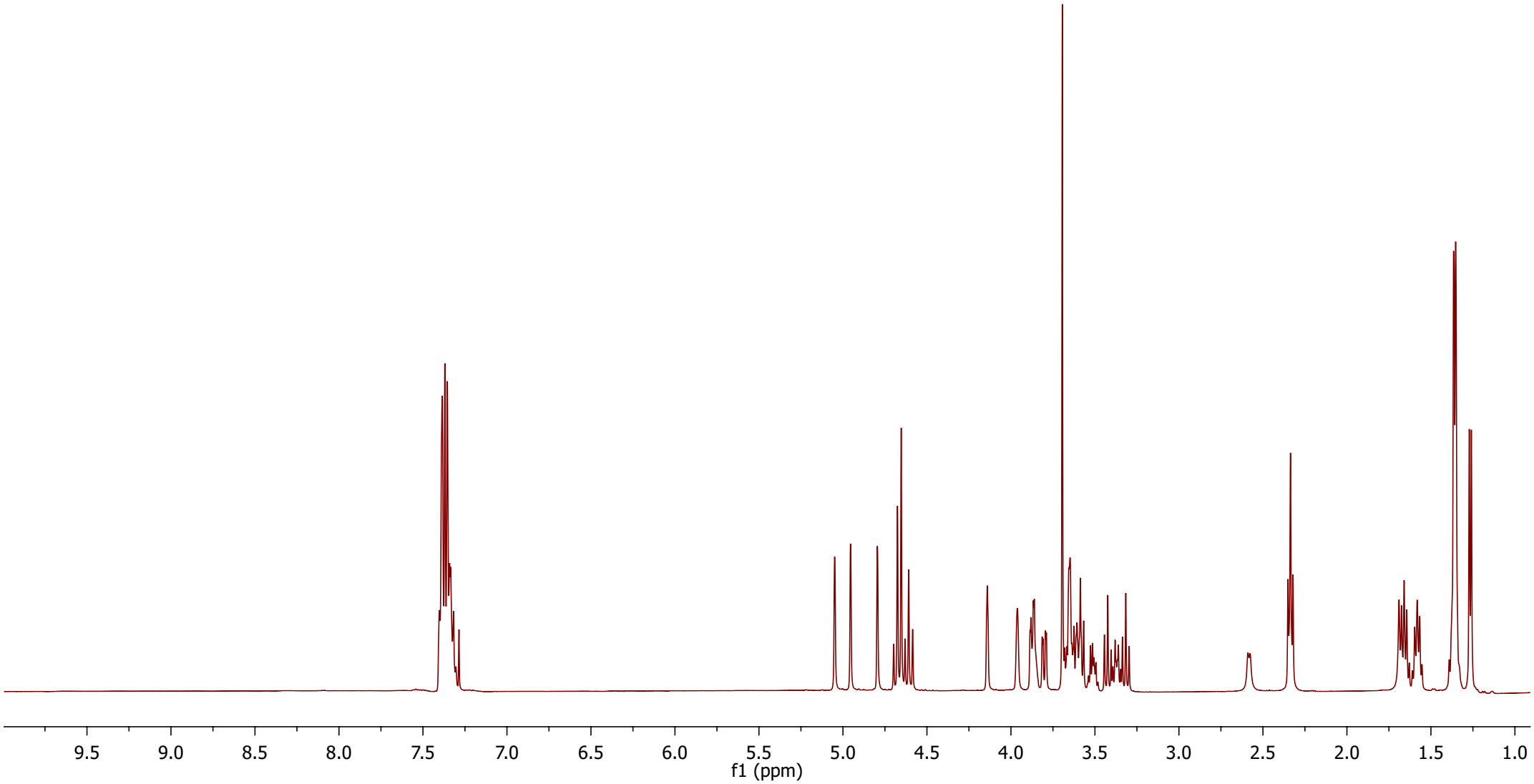

OH
OHCHN
O
HO
OH
OHCHN
O
O
1
O
COOMe

126 MHz, D_2O

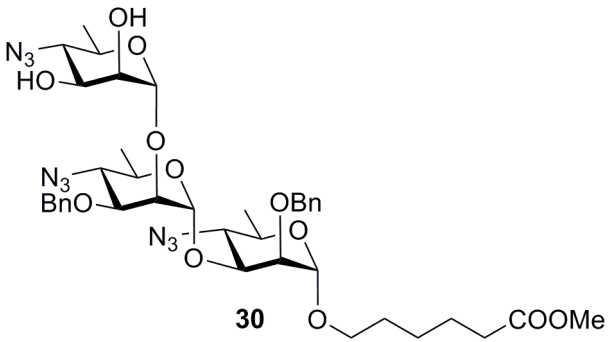

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

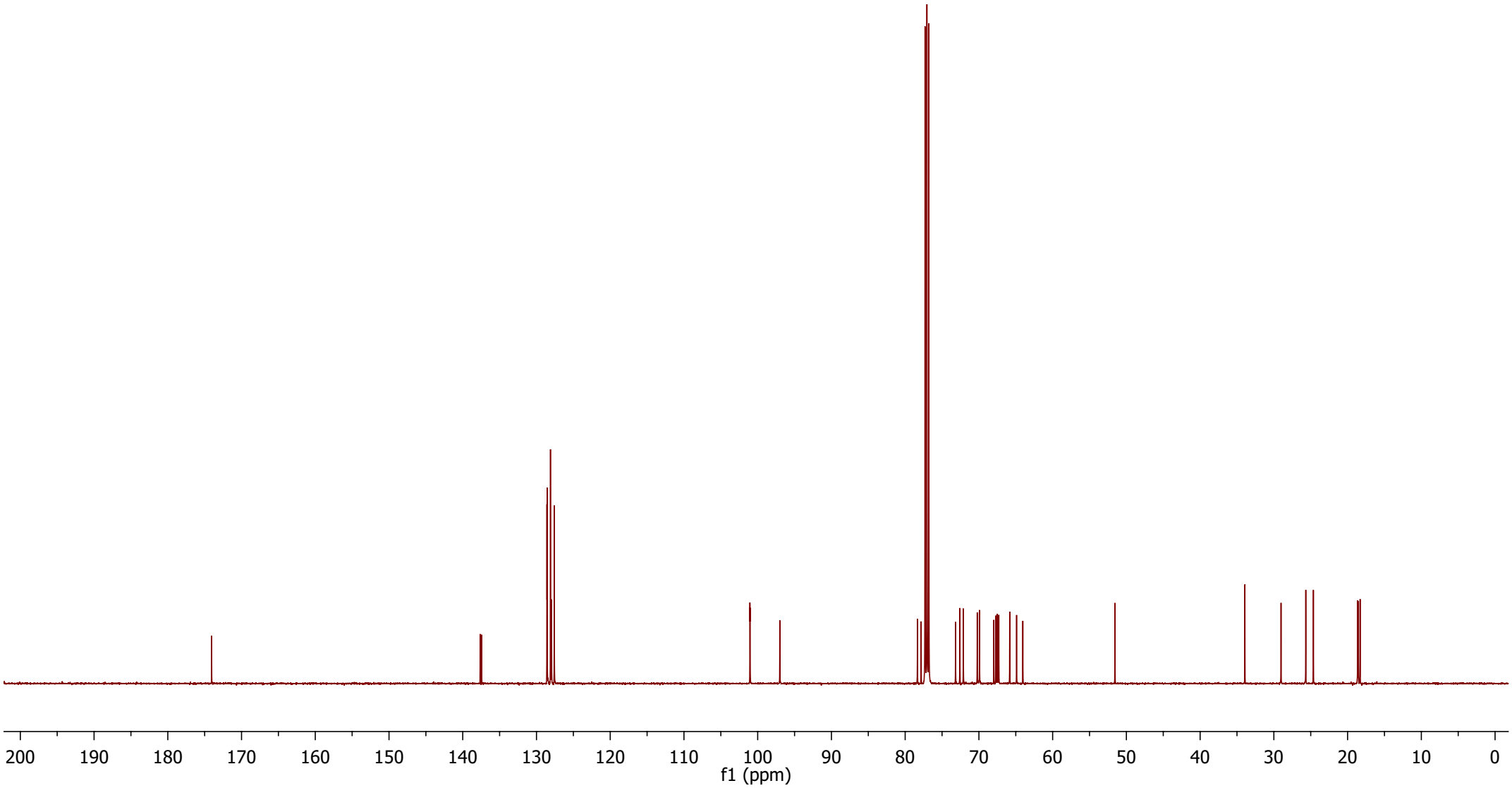
500 MHz, $CDCl_3$



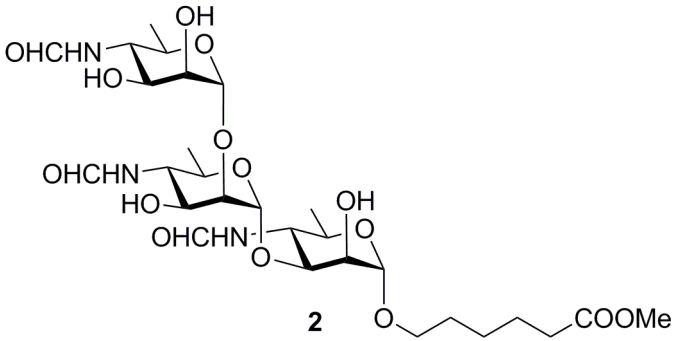


126 MHz, $CDCl_3$

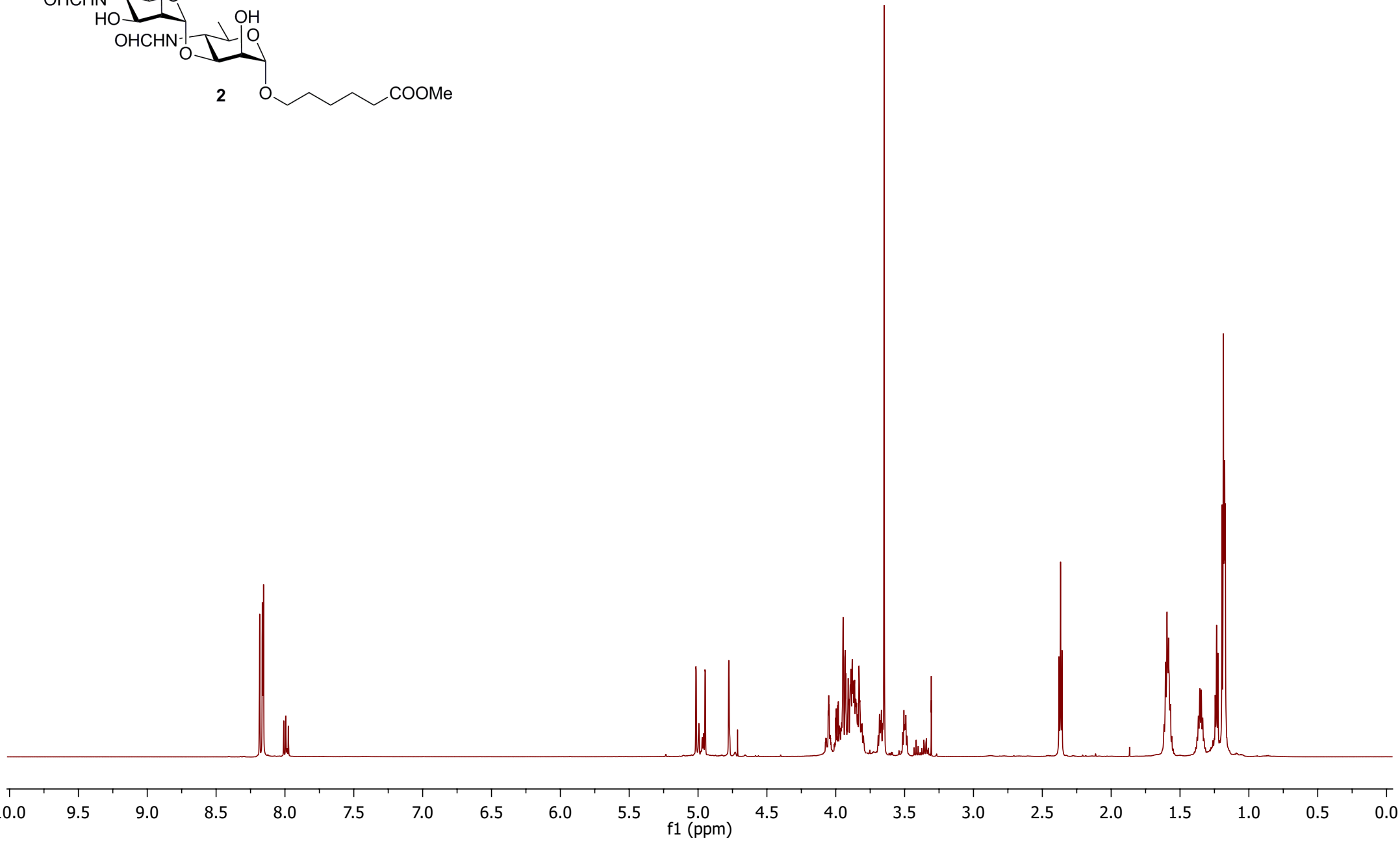




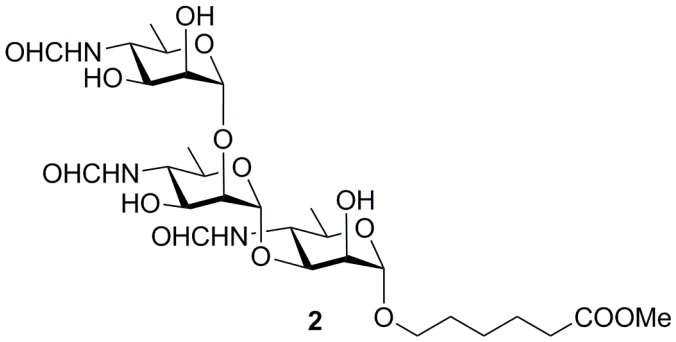
700 MHz, D_2O


OH
OHCHN
O
HO
O
OHCHN
O
HO
OH
OHCHN
O
O
O
COOMe

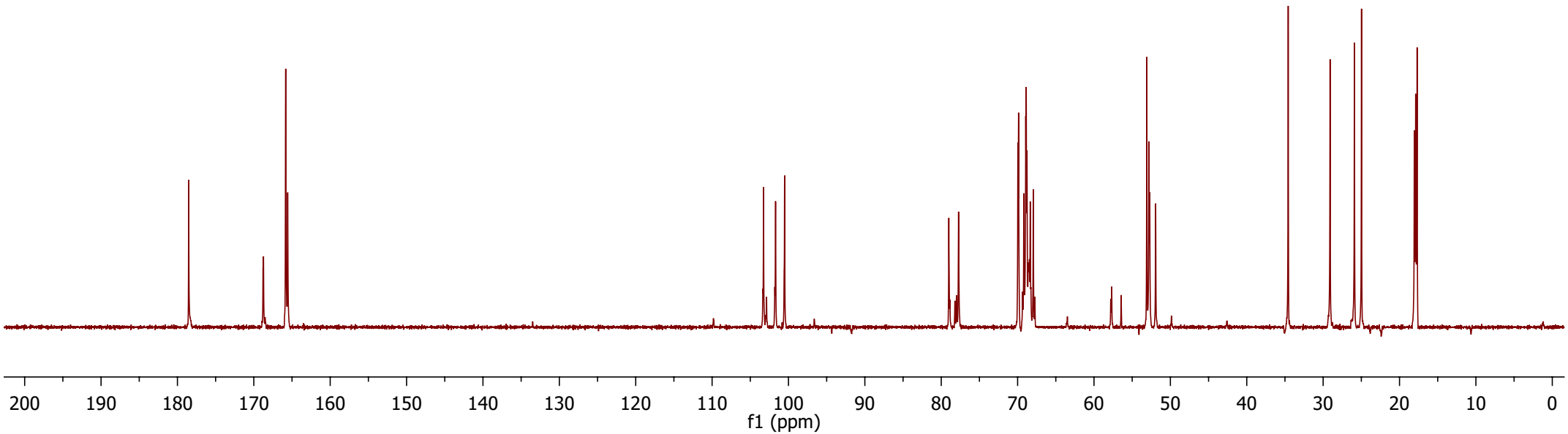
2


10.0
9.5
9.0
8.5
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
f1 (ppm)

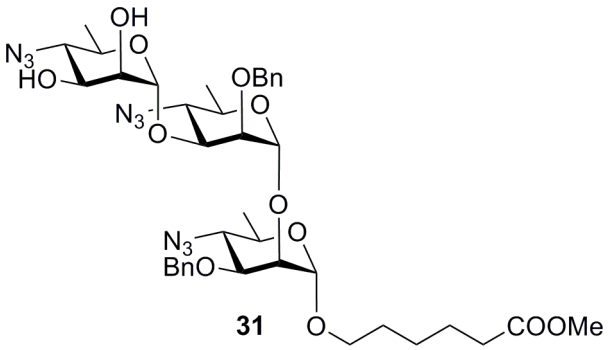
126 MHz, D_2O

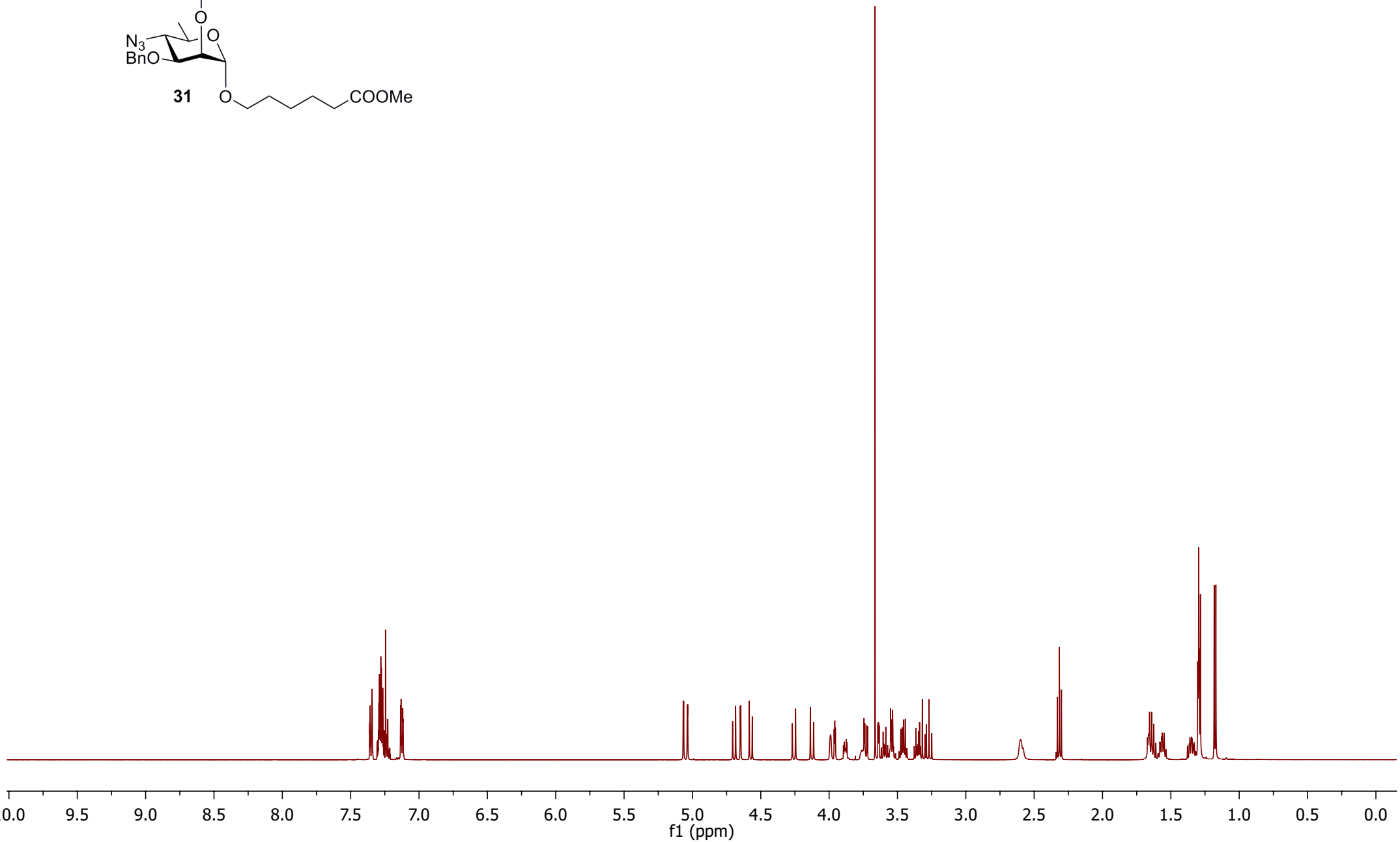

OH
OHCHN
O
HO
O
OHCHN
O
HO
OH
OHCHN
O
O
O
COOMe

2

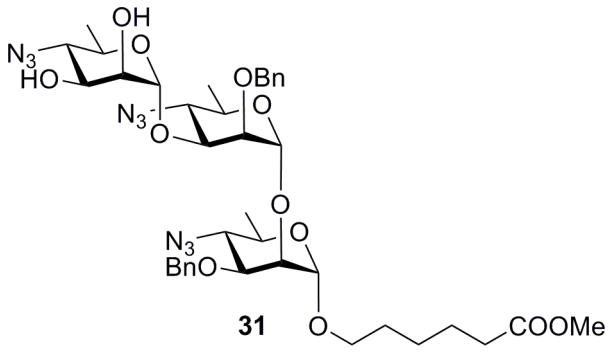

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

500 MHz, $CDCl_3$

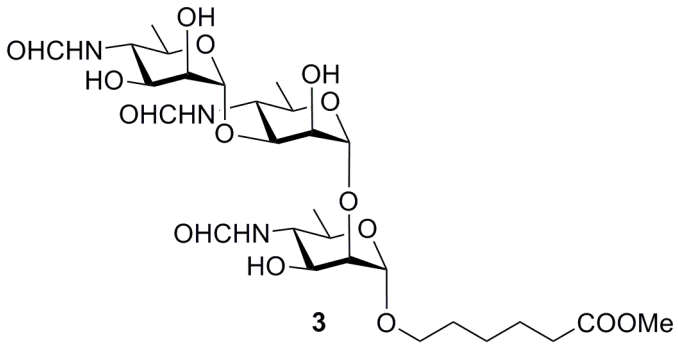




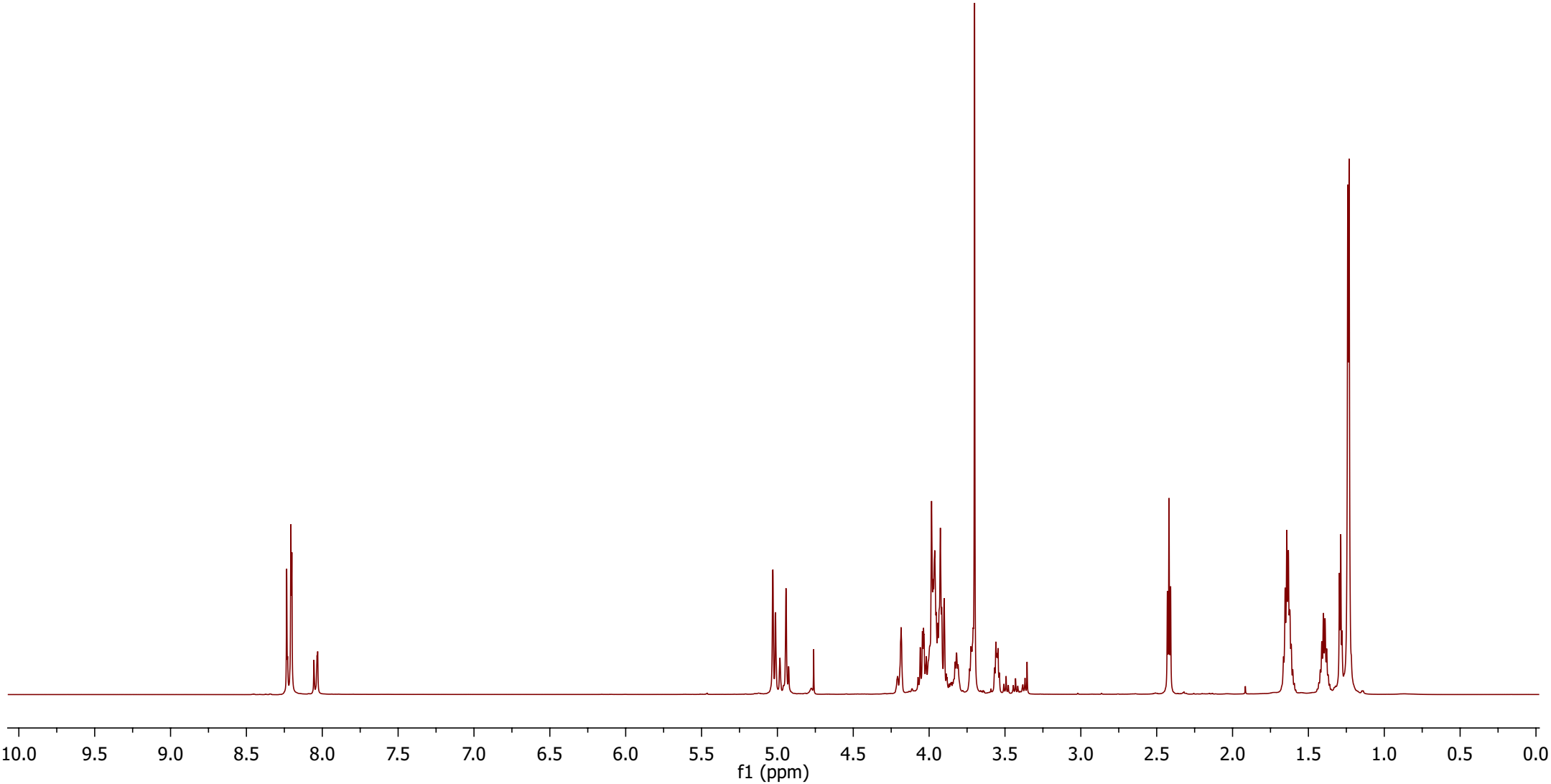
126 MHz, $CDCl_3$

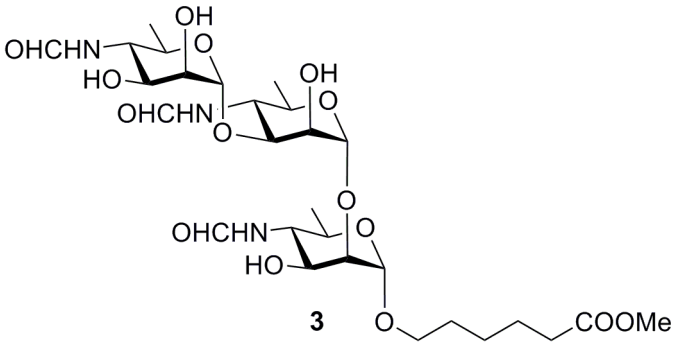


31

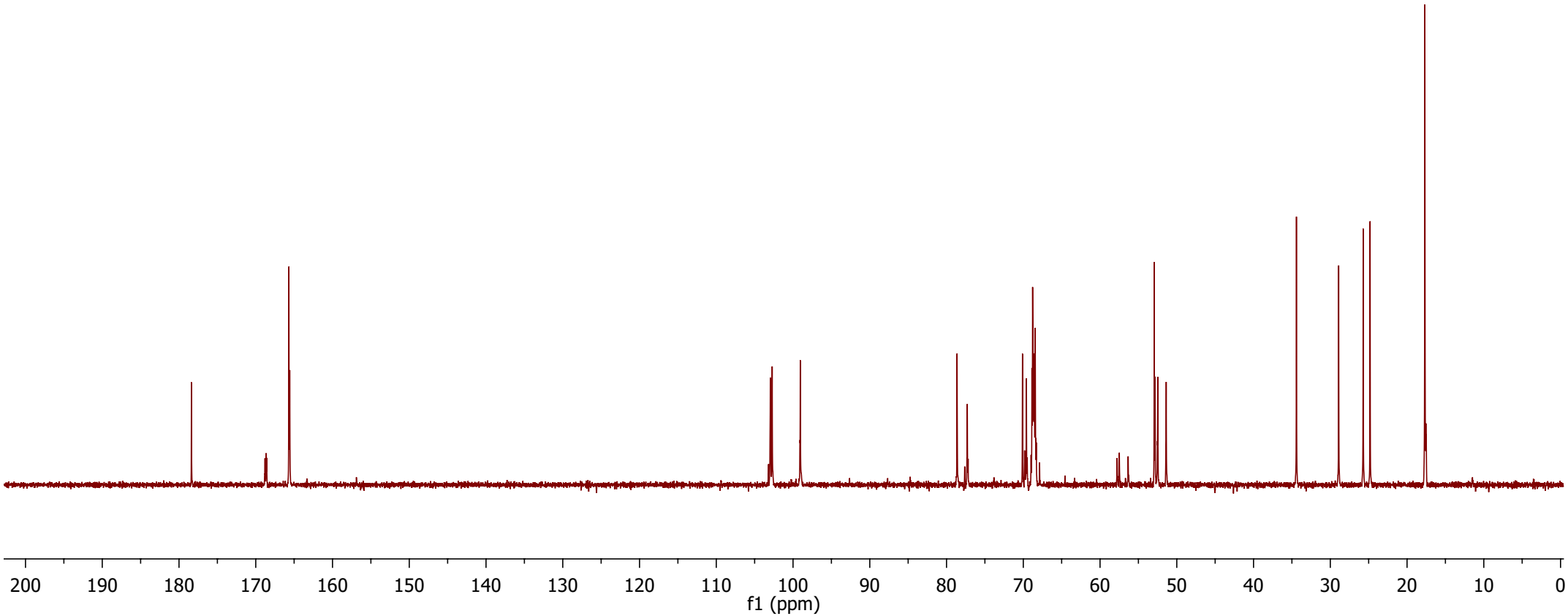

OH
OHCHN
O
HO
OH
OHCHN
O
O
O
OHCHN
O
HO
O
3
COOMe

700 MHz, D_2O

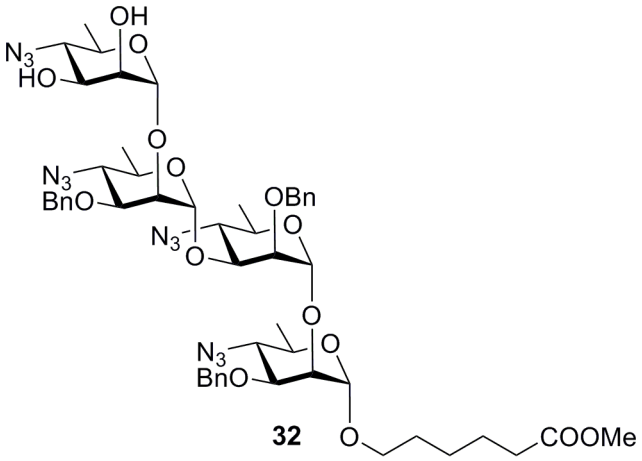

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OH
OHCHN
O
HO
OH
OHCHN
O
O
O
OHCHN
O
HO
3
O
COOMe

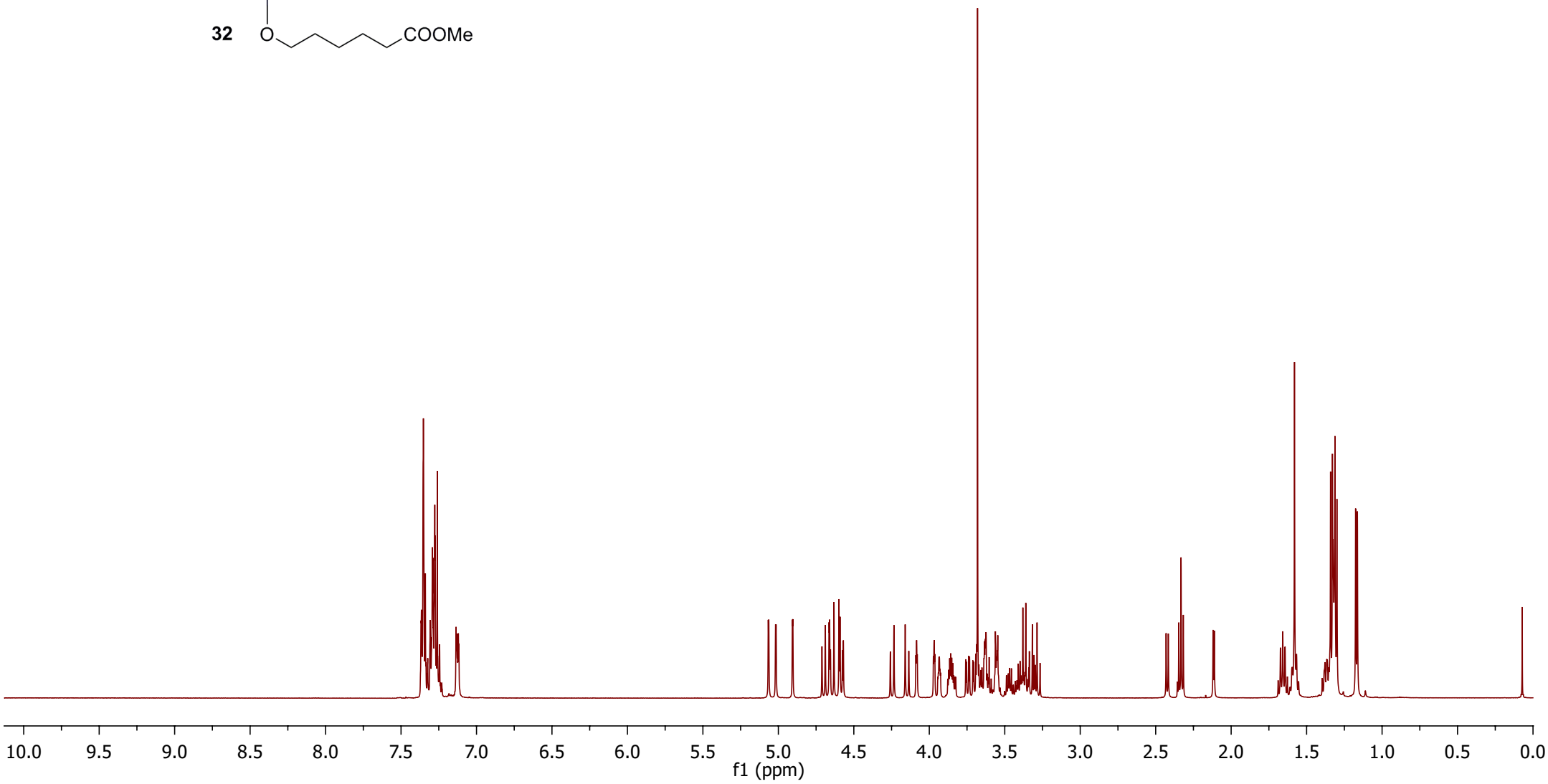
176 MHz, D_2O

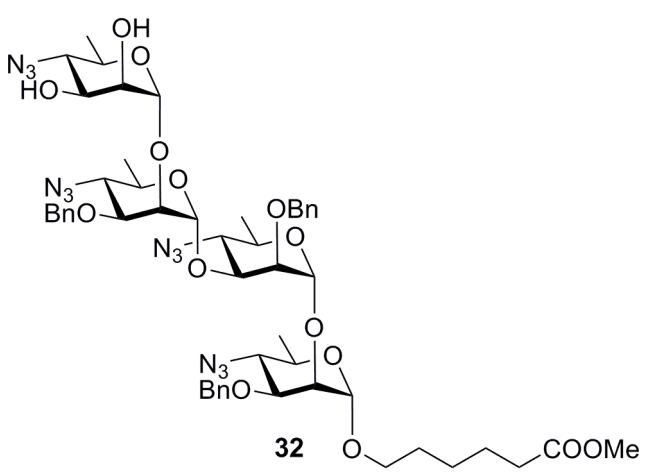

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

500 MHz, CDCl3



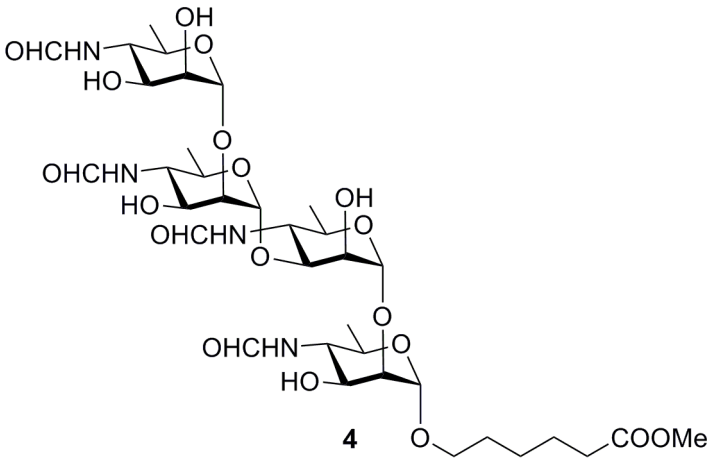
32



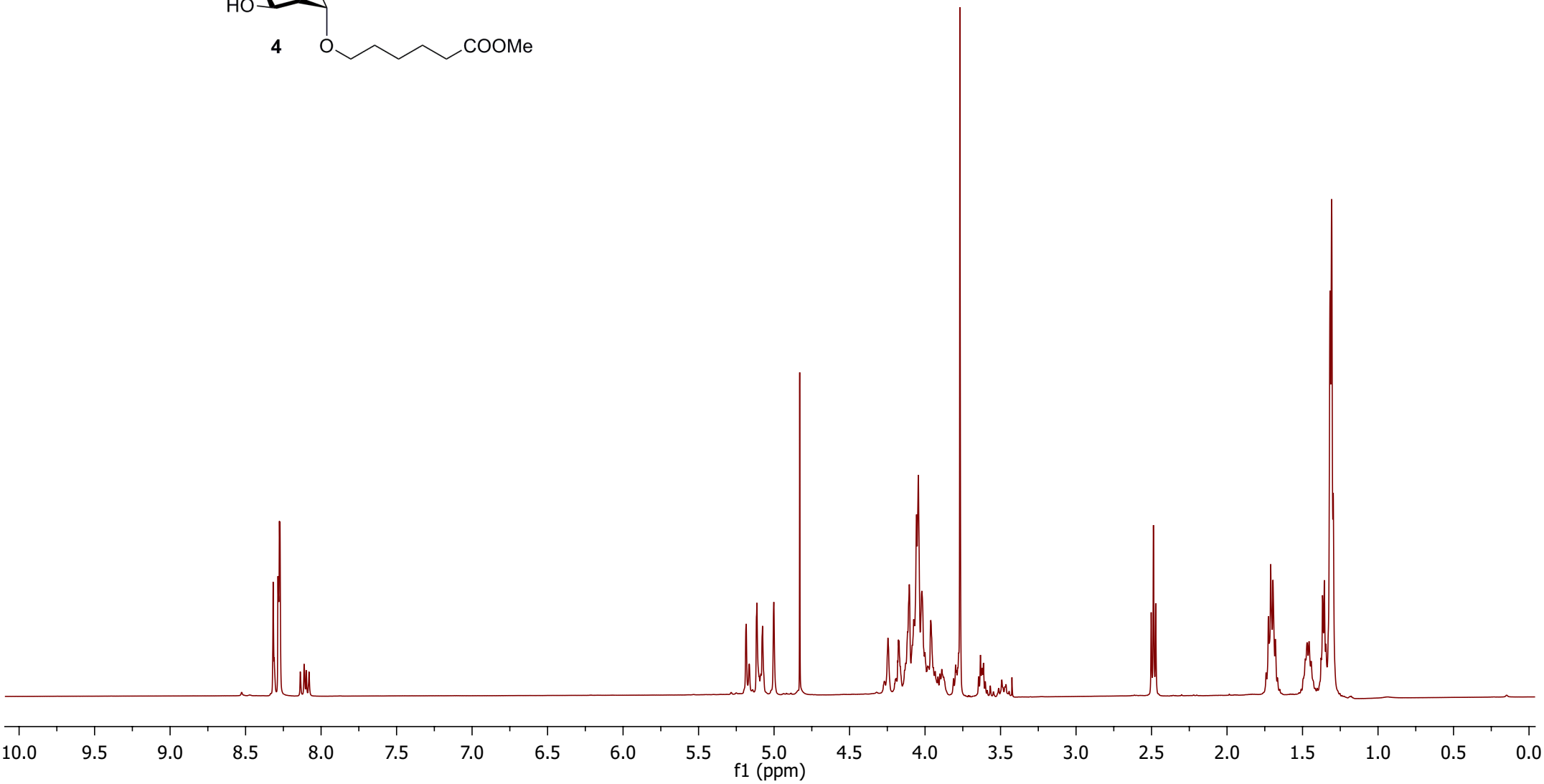


126 MHz, $CDCl_3$

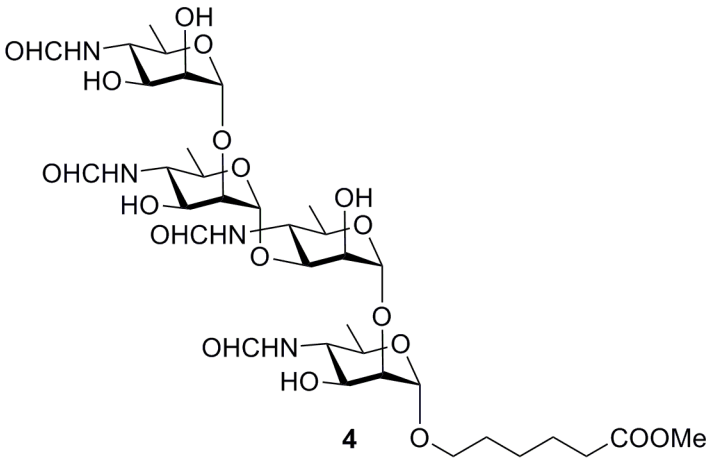
500 MHz, D_2O


OH
OHCHN
O
HO
O
OHCHN
O
HO
OH
OHCHN
O
O
O
OHCHN
O
HO
O
COOMe

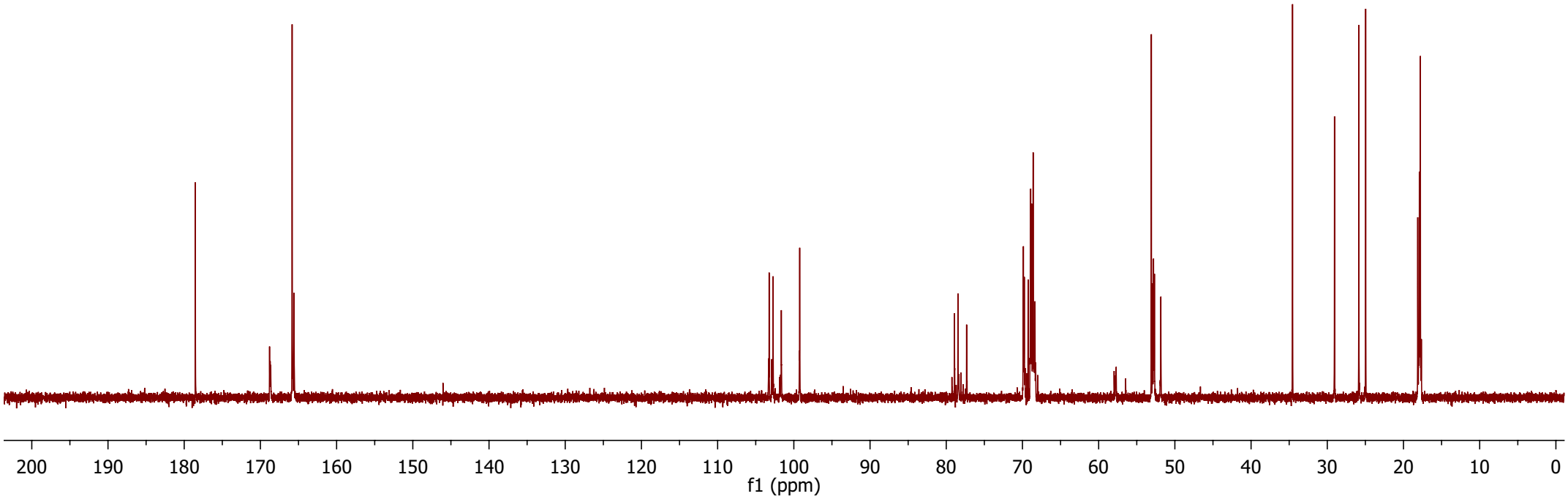
4


10.0
9.5
9.0
8.5
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
f1 (ppm)

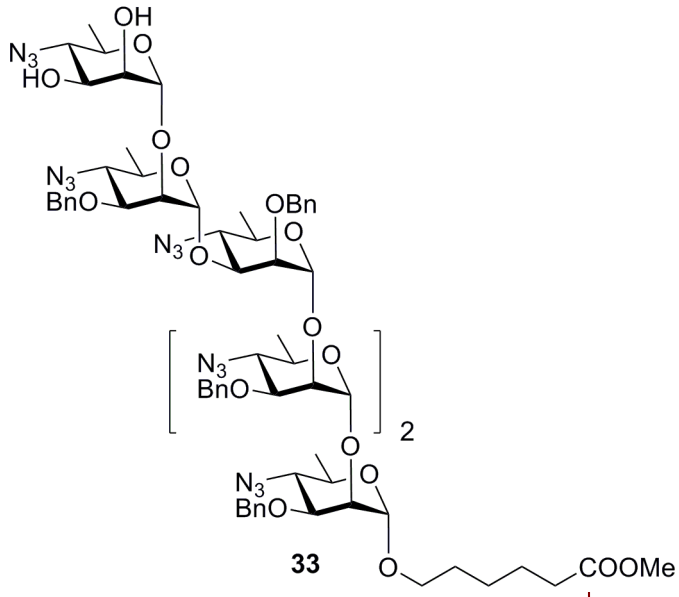
126 MHz, D_2O


OH
OHCHN
O
HO
O
OHCHN
O
HO
OH
OHCHN
O
O
O
OHCHN
O
HO
O
COOMe

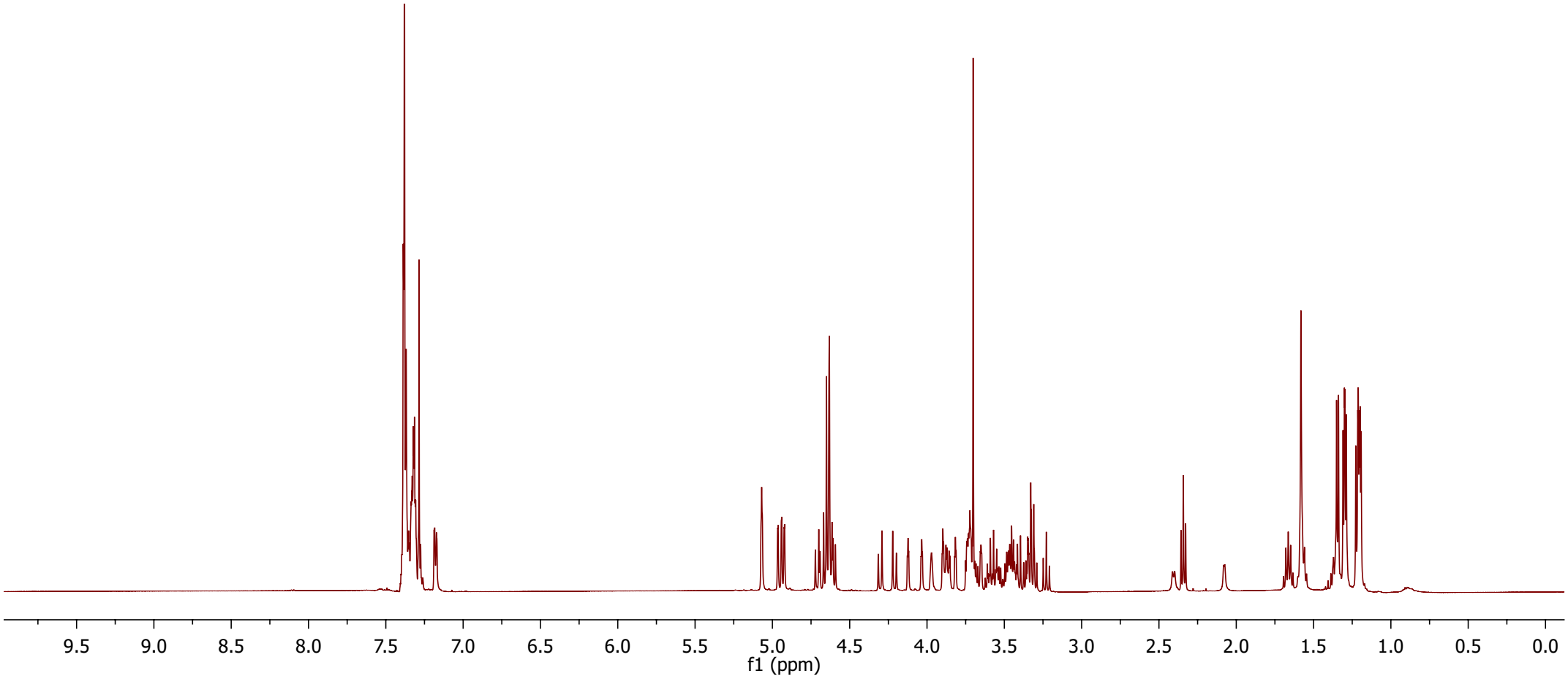
4

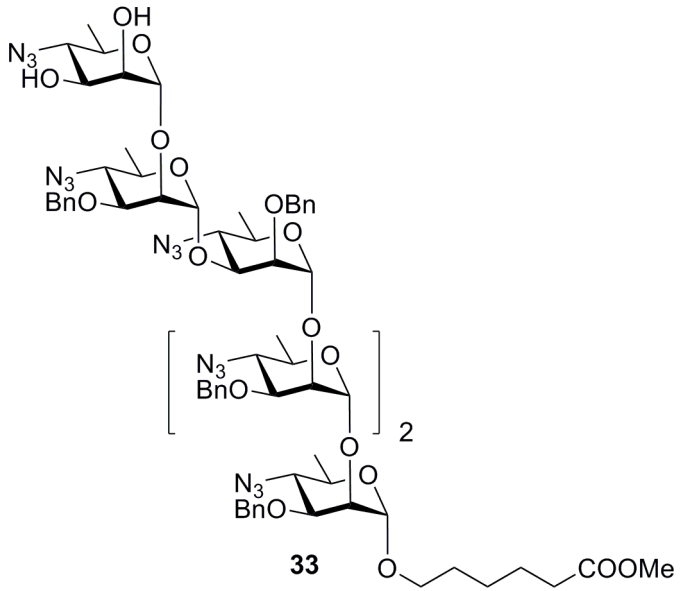

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

500 MHz, $CDCl_3$



33

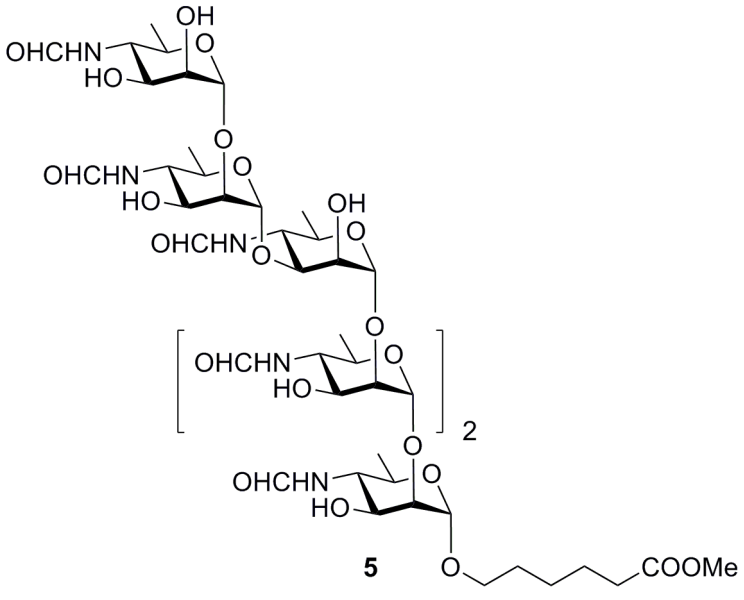




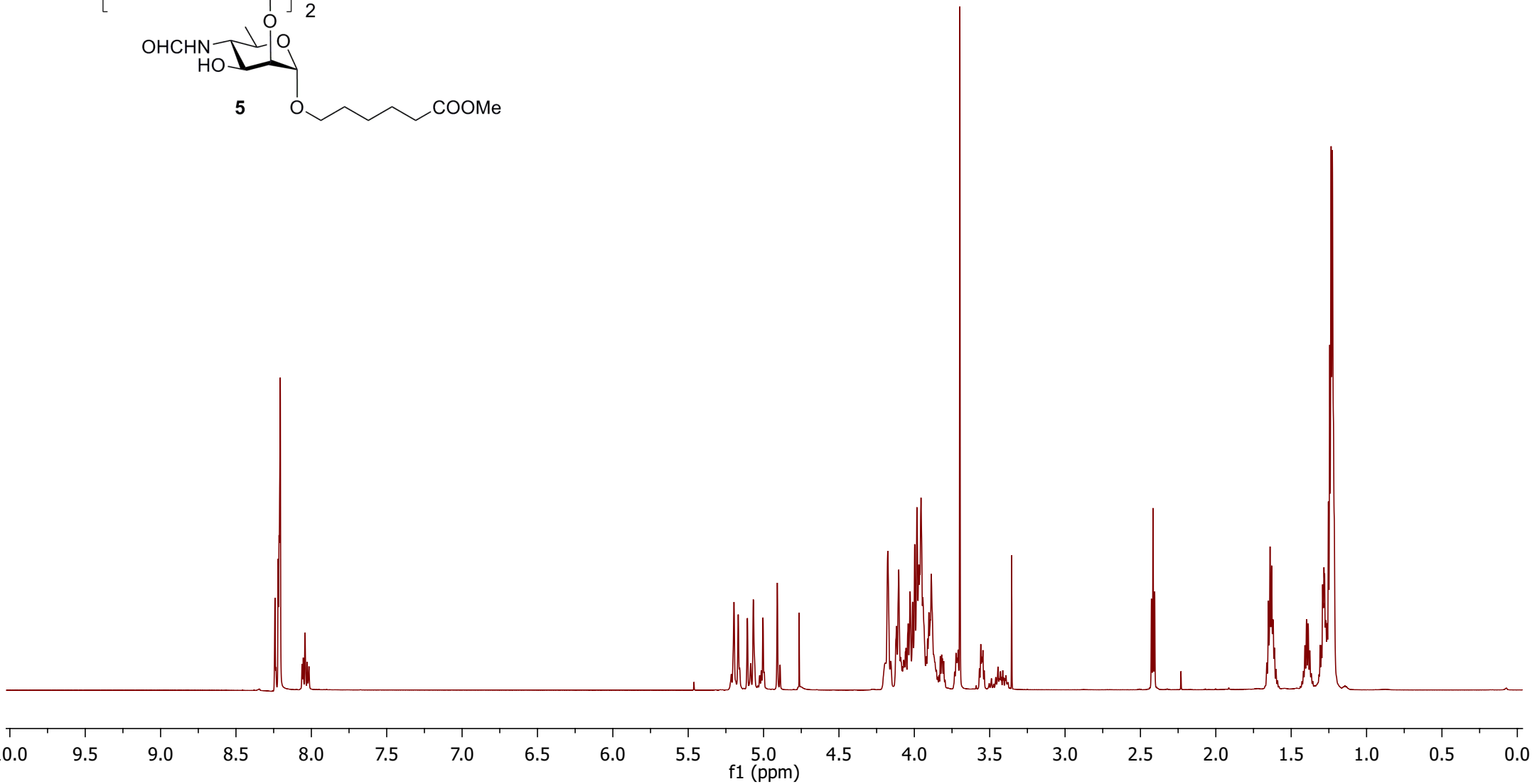
33

126 MHz, $CDCl_3$

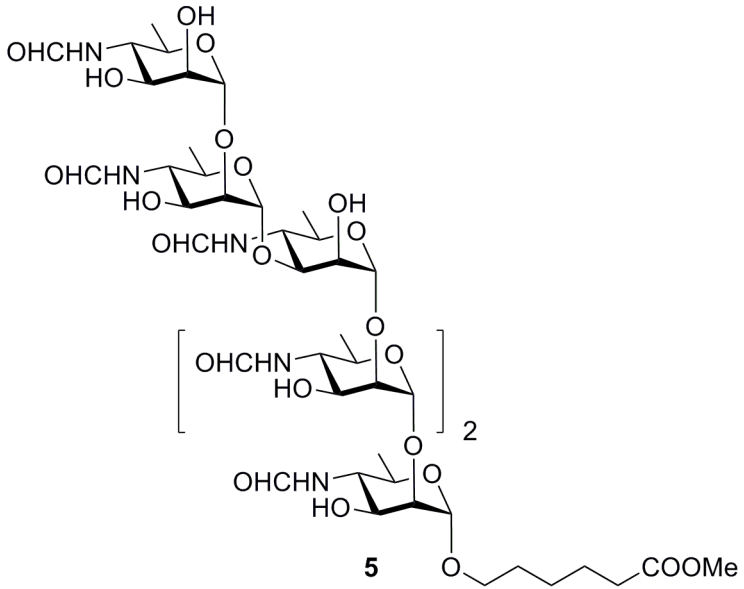
700 MHz, D_2O


OH
OHCHN
HO
O
OHCHN
HO
O
OH
OHCHN
O
O
O
OHCHN
HO
O
2
O
OHCHN
HO
O
O
COOMe

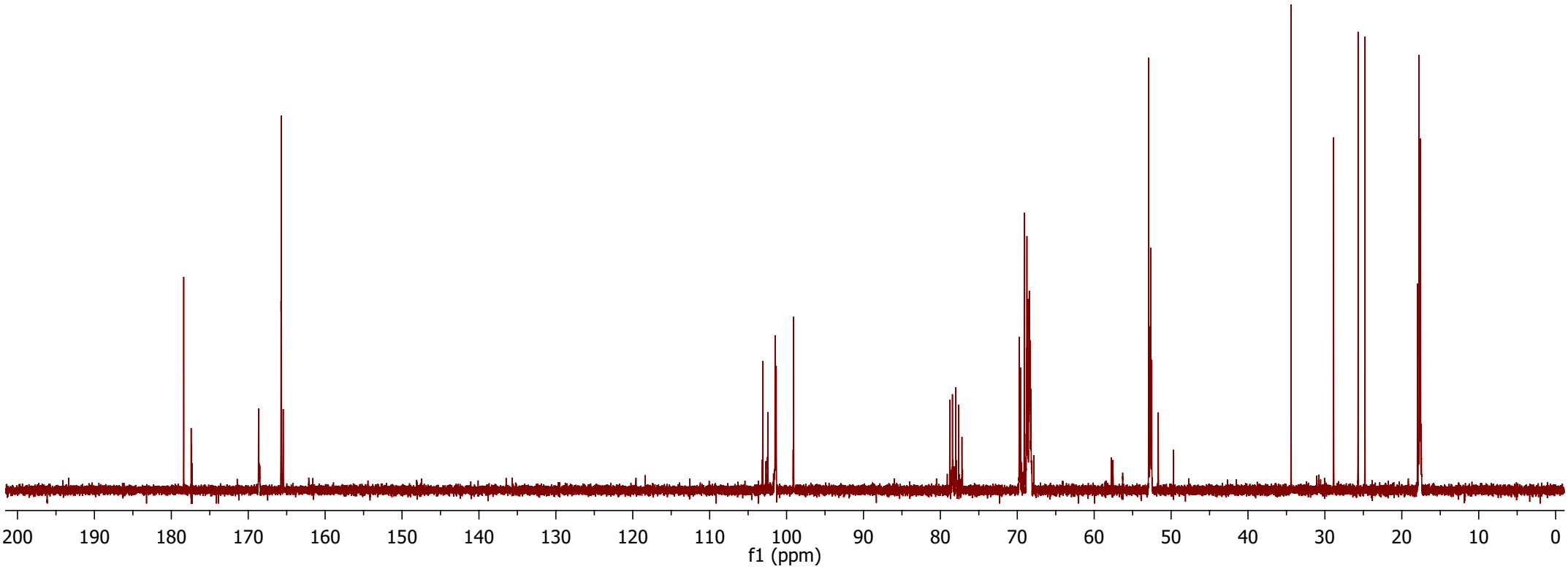
5

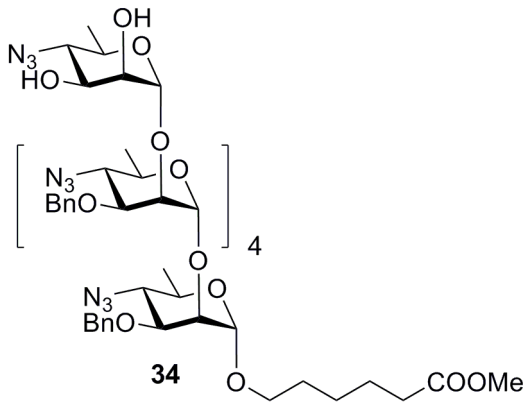

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

176 MHz, D_2O

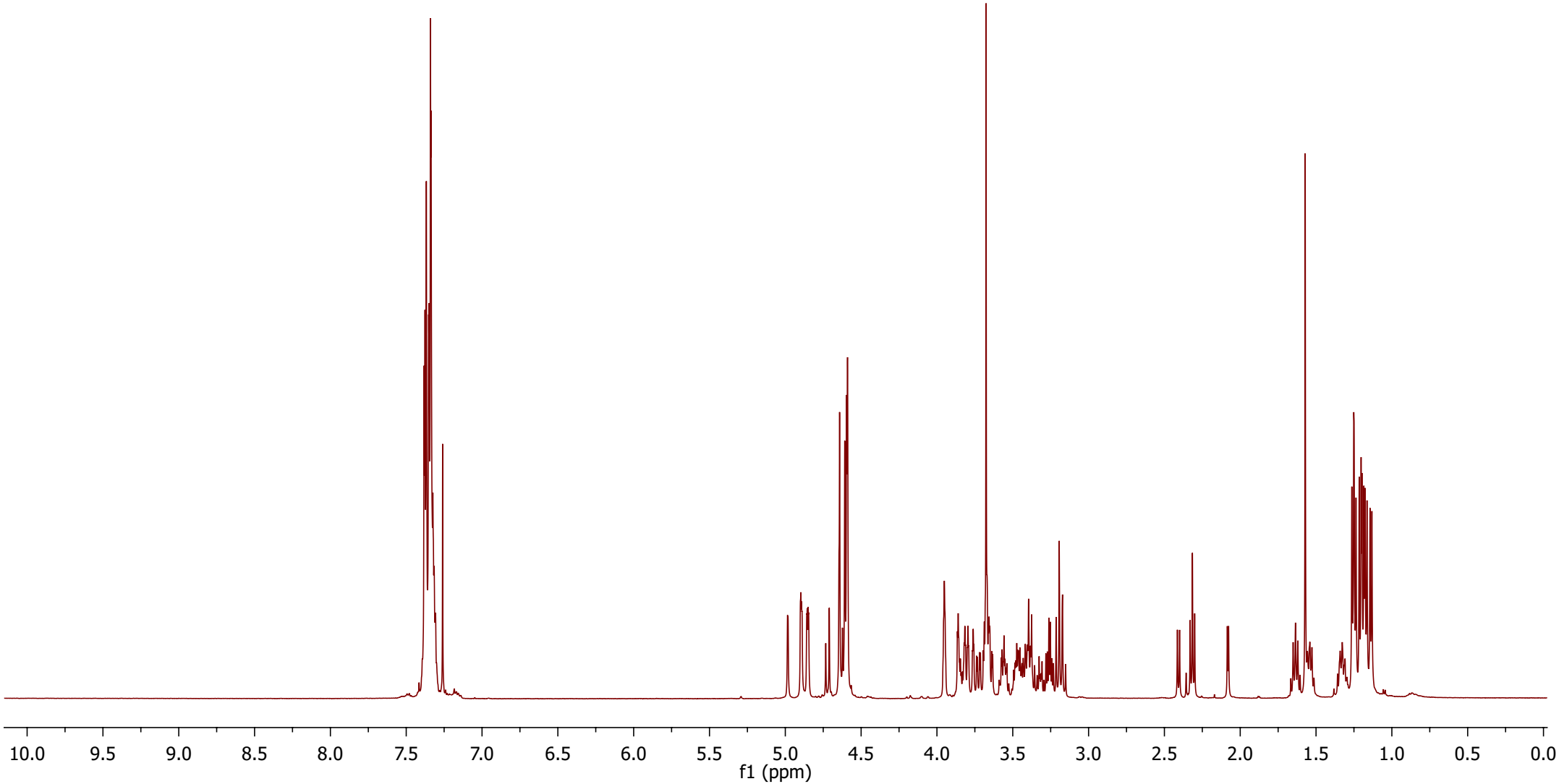

OH
OHCHN
HO
O
OHCHN
HO
O
OH
OHCHN
O
O
O
OHCHN
HO
O
2
O
OHCHN
HO
O
O
COOMe

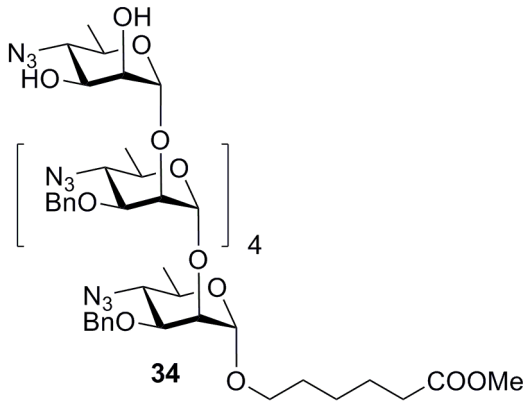
5


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

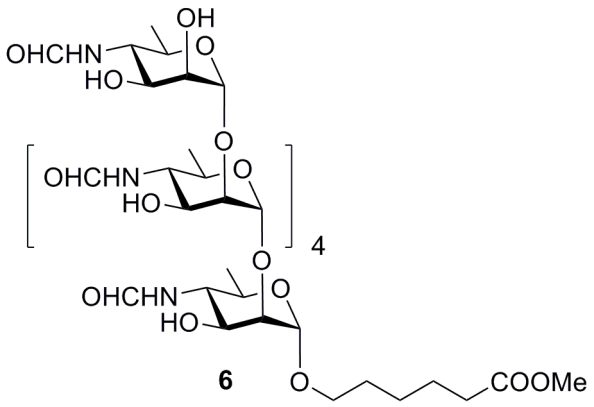


500 MHz, $CDCl_3$

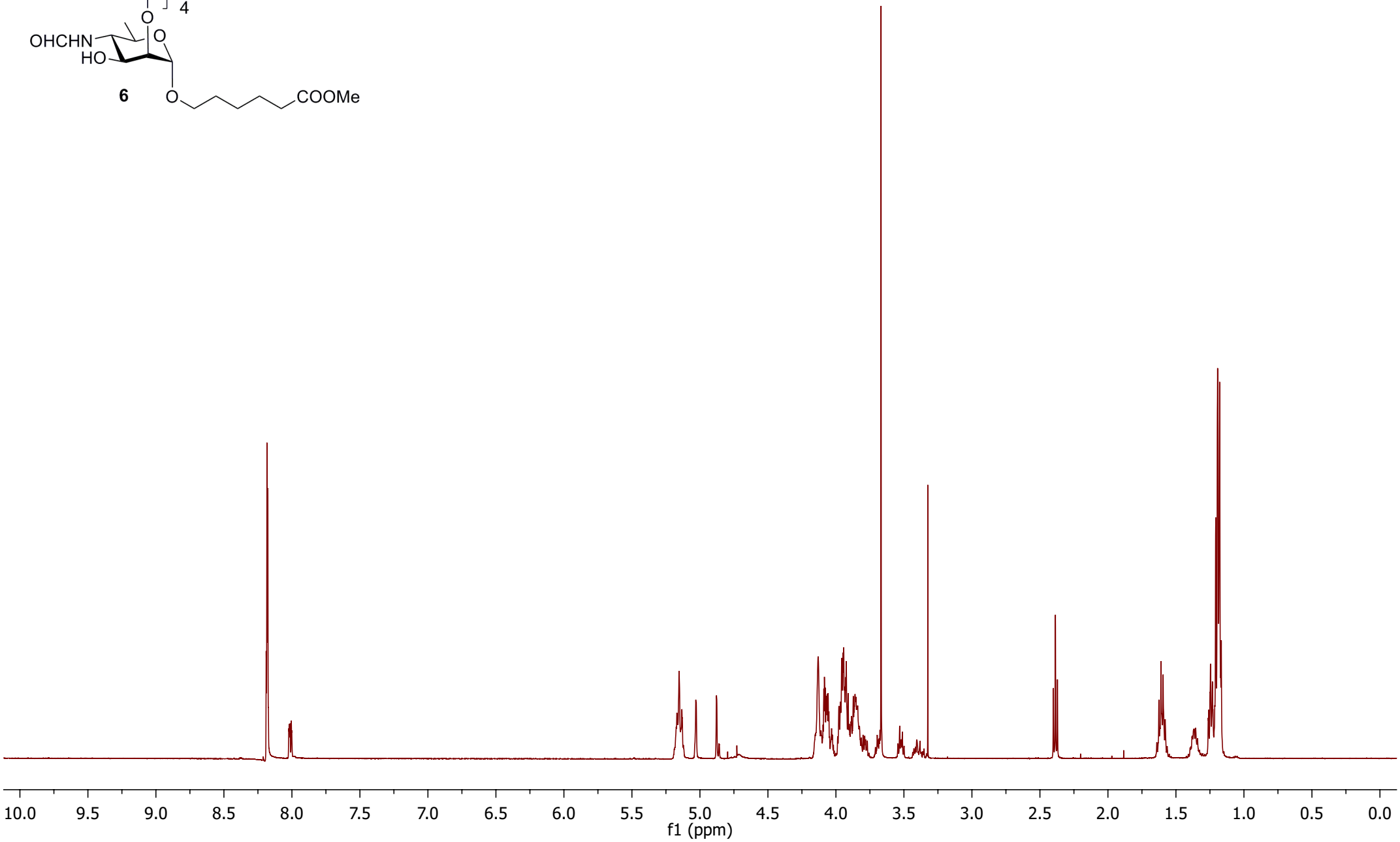


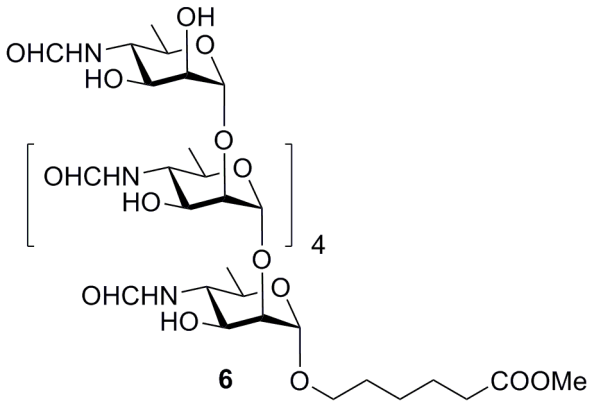


126 MHz, $CDCl_3$

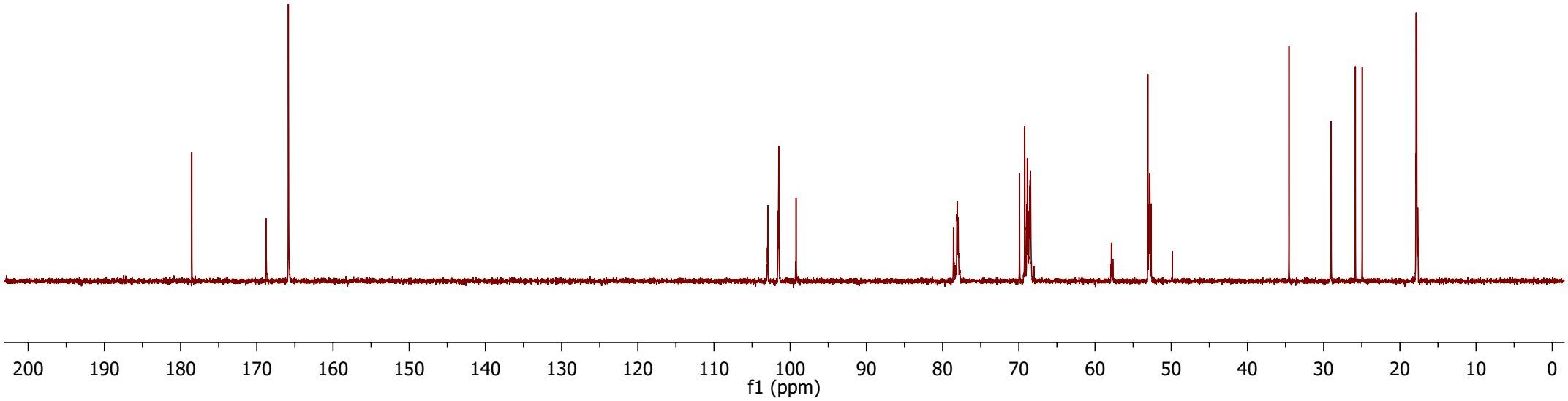

OH
OHCHN
HO
O
4
6
COOMe

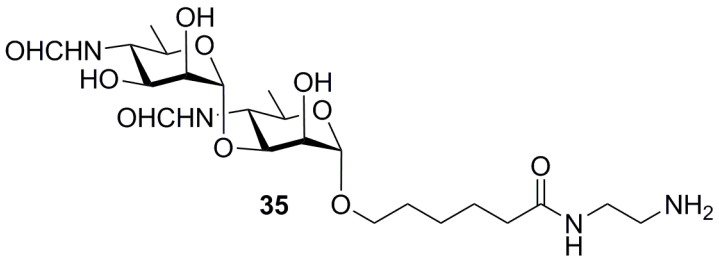
500 MHz, D_2O


10.0
9.5
9.0
8.5
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
f1 (ppm)

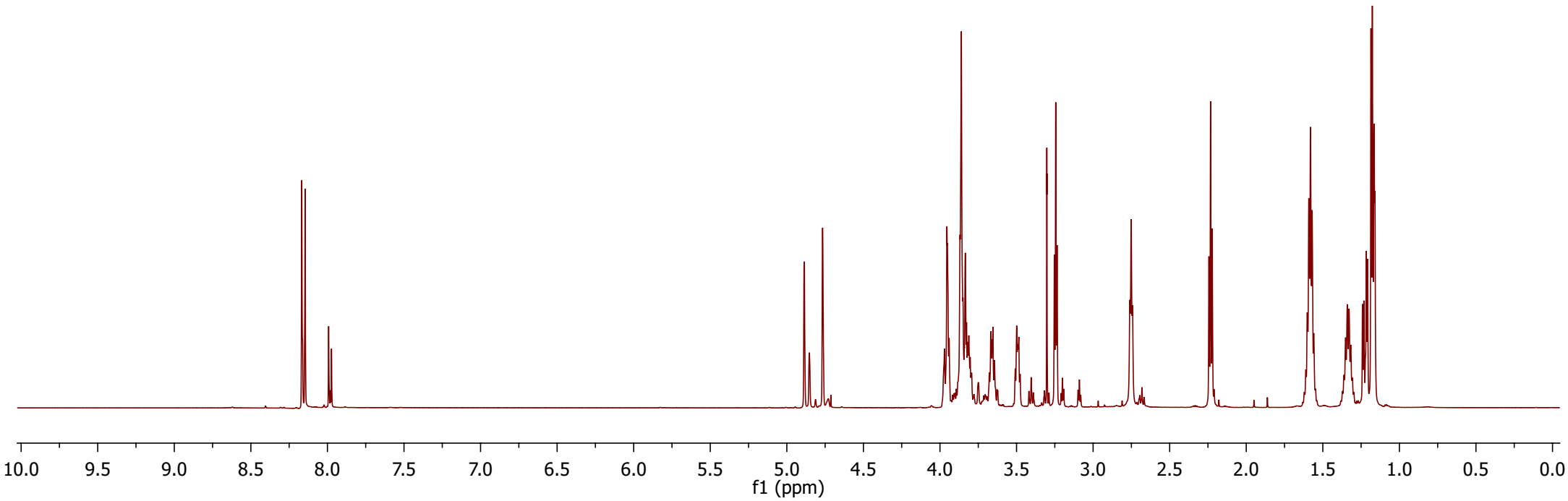

OH
OHCHN
HO
O
4
6
COOMe

126 MHz, D_2O

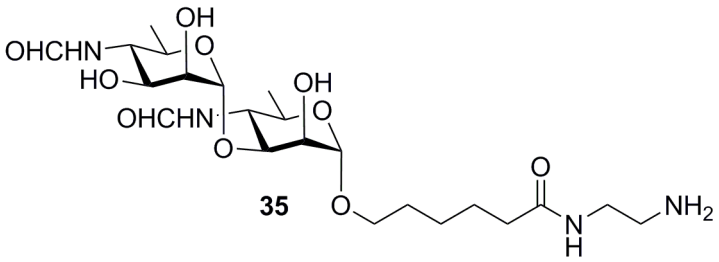

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
OHCHN
O
HO
OH
OHCHN
O
O
O
35
O
N
H
NH2

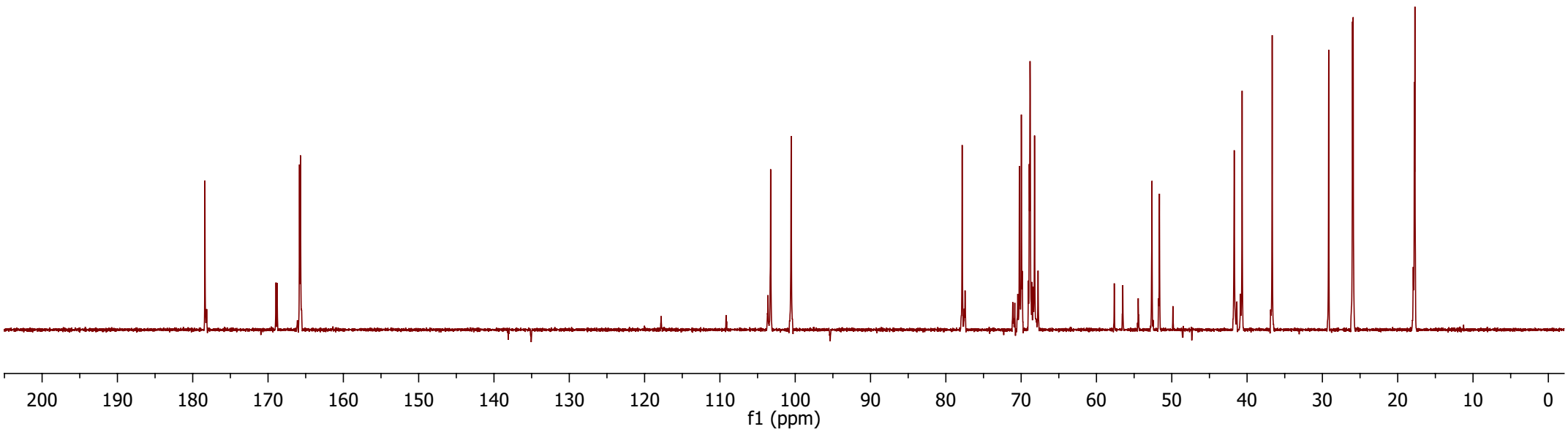
700 MHz, D_2O


10.0
9.5
9.0
8.5
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
f1 (ppm)

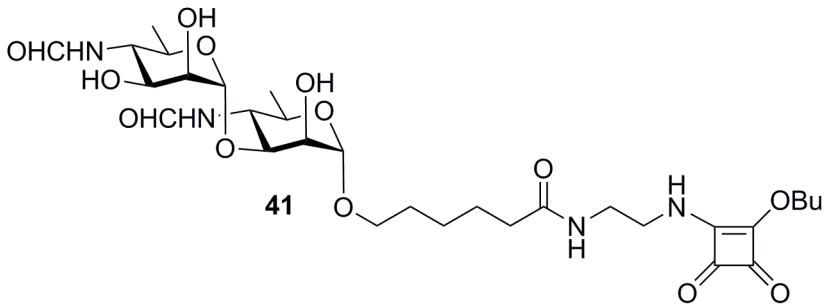
126 MHz, D_2O

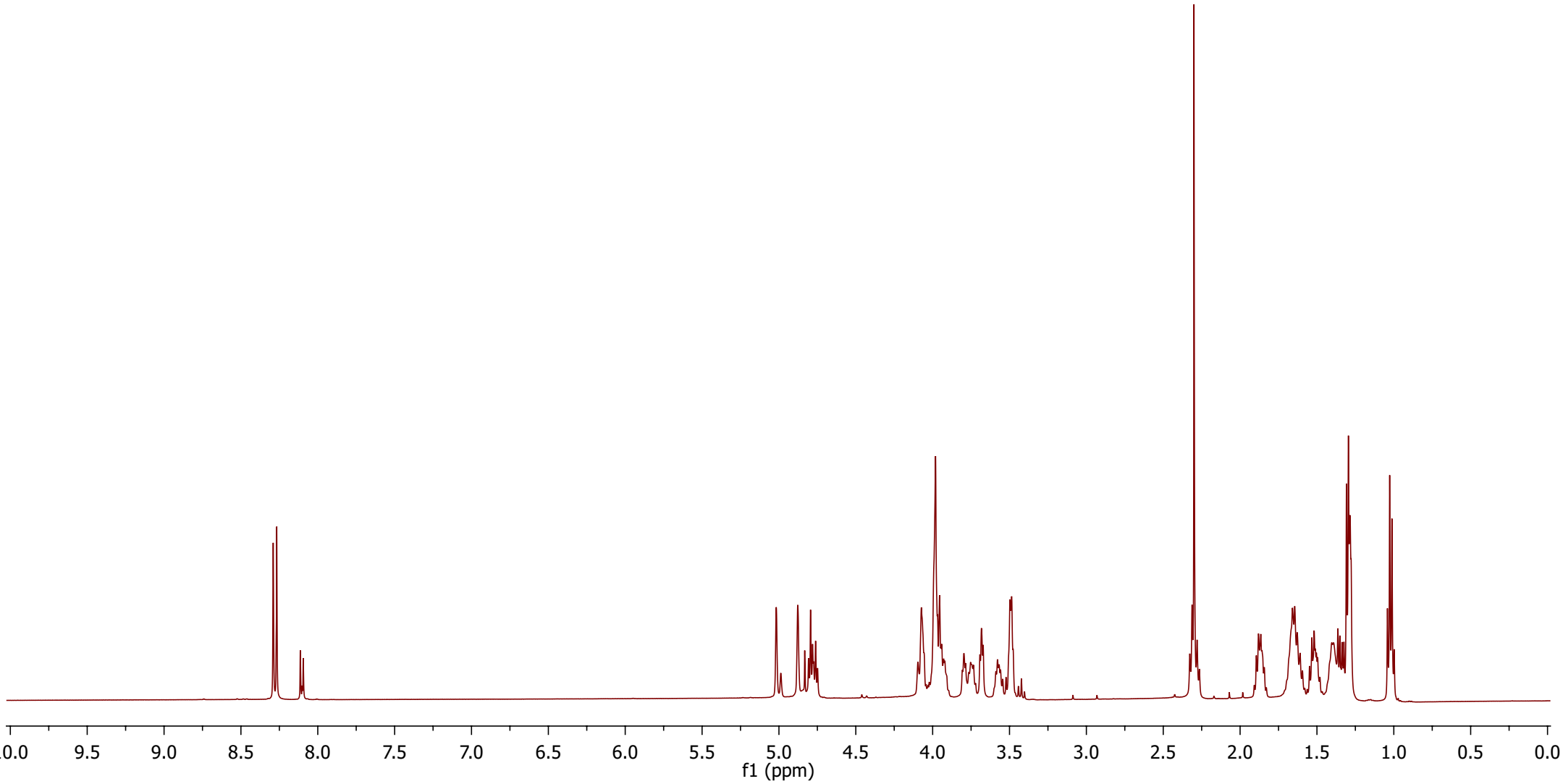


35

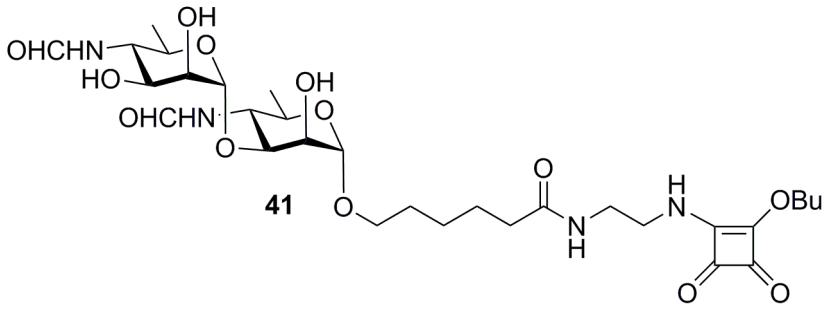


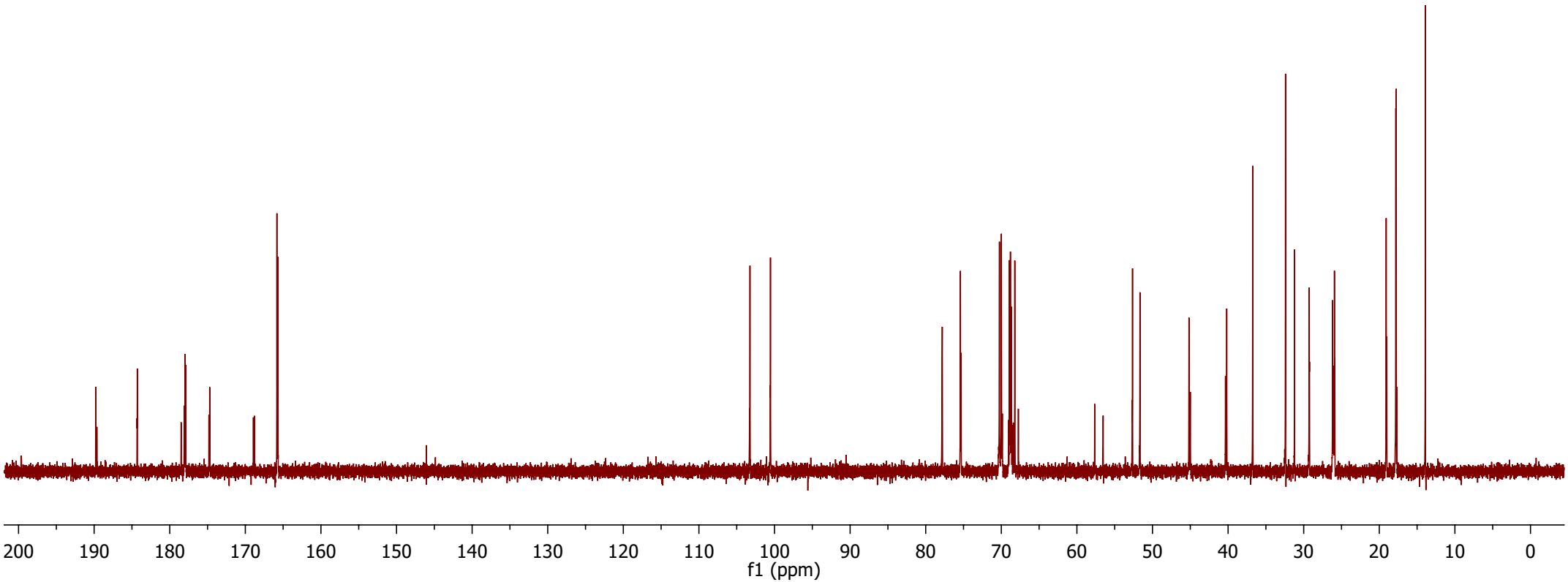
500 MHz, D_2O


OH
OHCHN
HO
OH
OHCHN
O
O
O
41
O
O
N
H
H
N
OBu
O
O

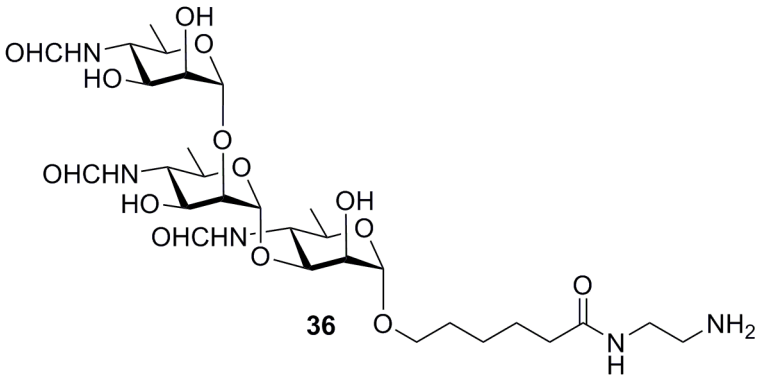

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

126 MHz, D_2O

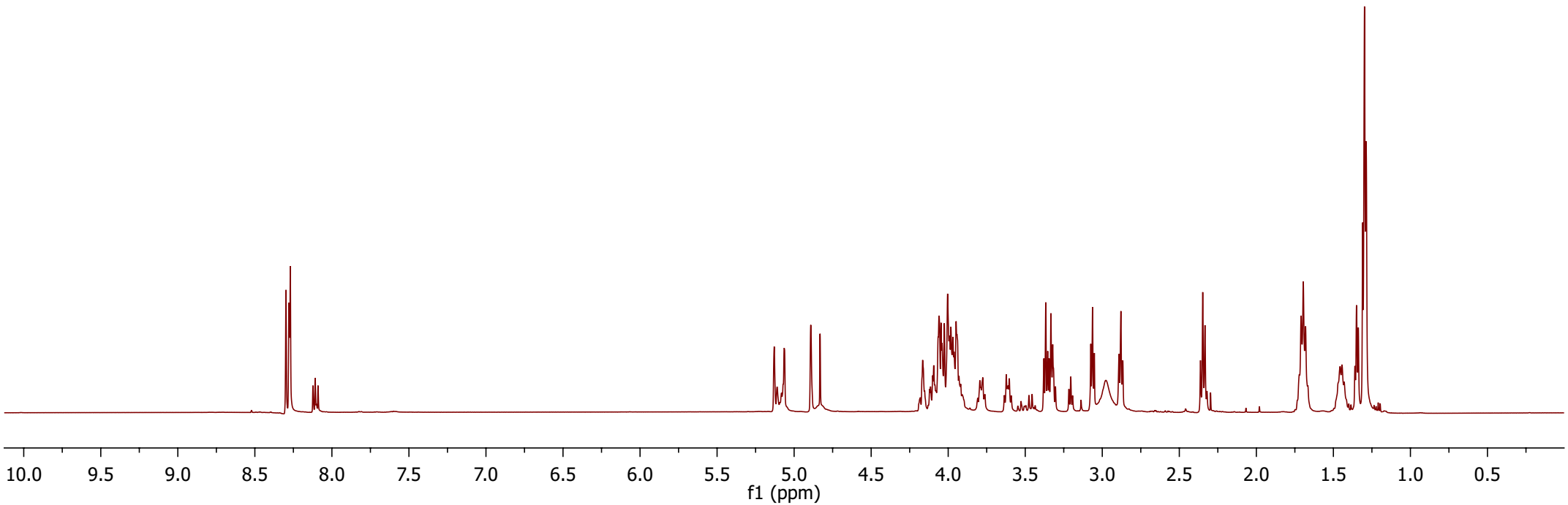

OH
OHCHN
HO
OH
OHCHN
O
O
O
O
41
O
N
H
H
N
OBu
O
O


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

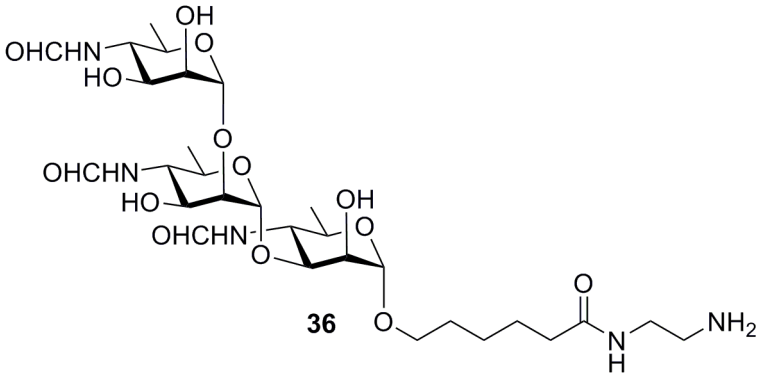
500 MHz, D_2O



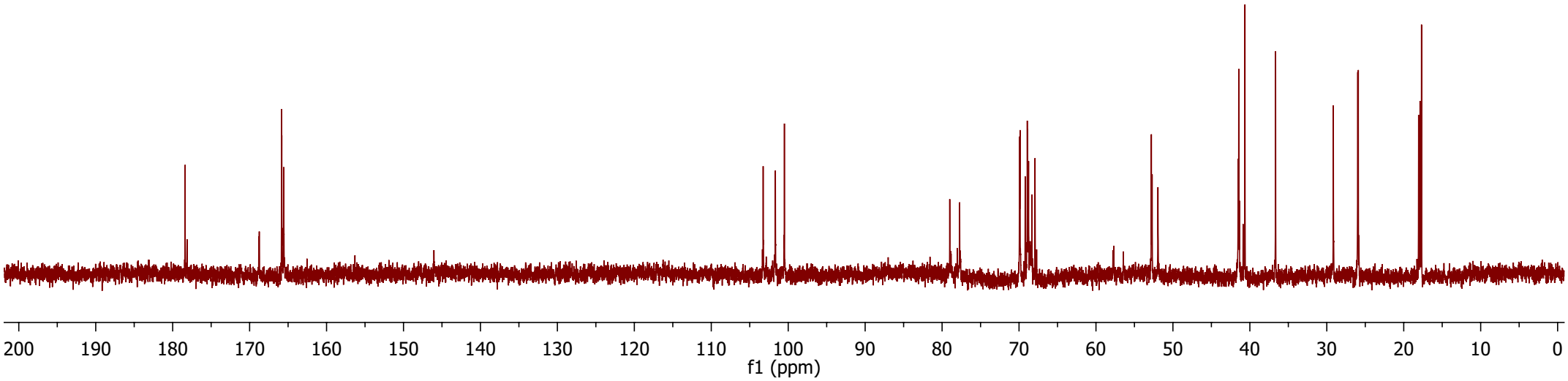
36



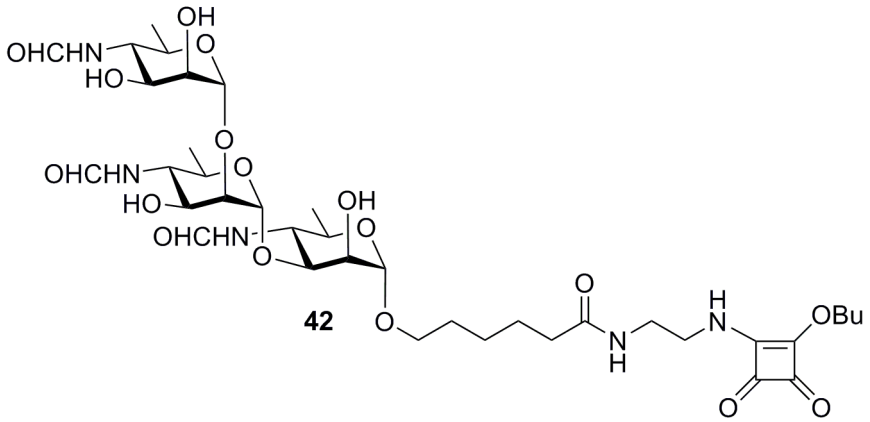
126 MHz, D_2O

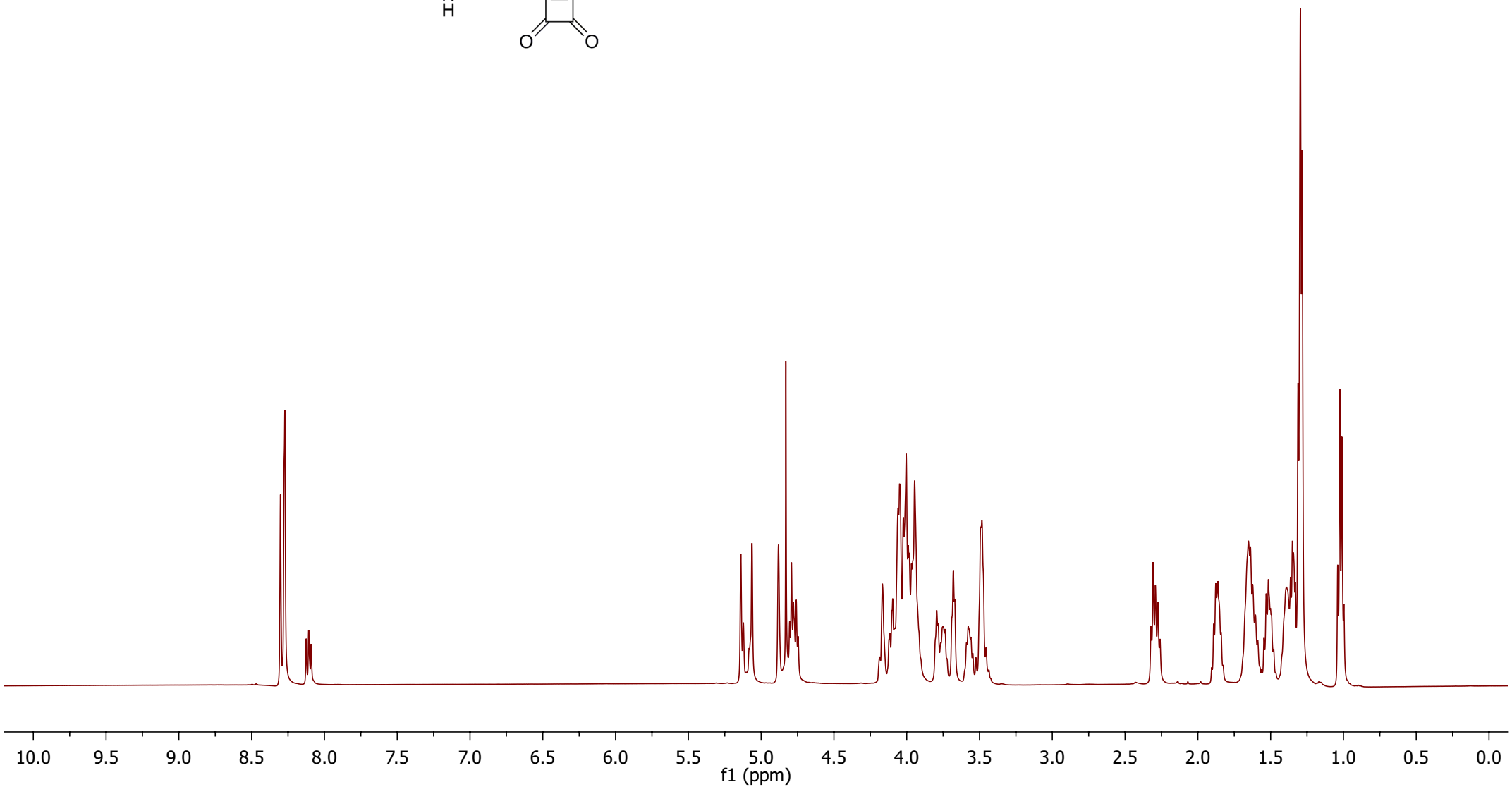


36

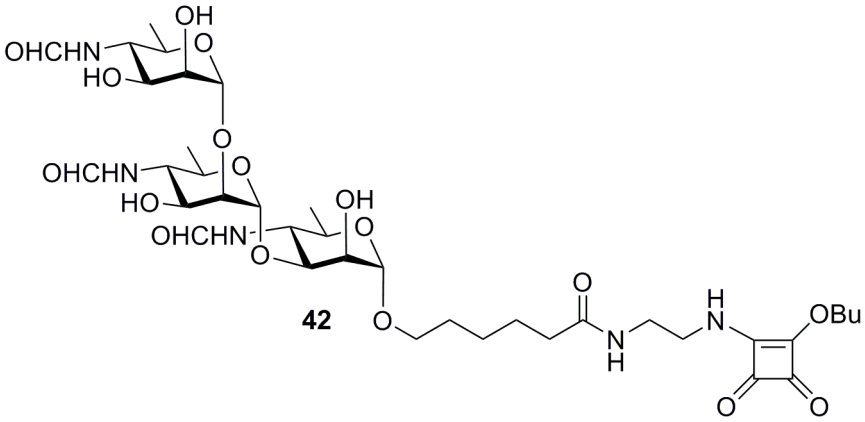


500 MHz, D_2O

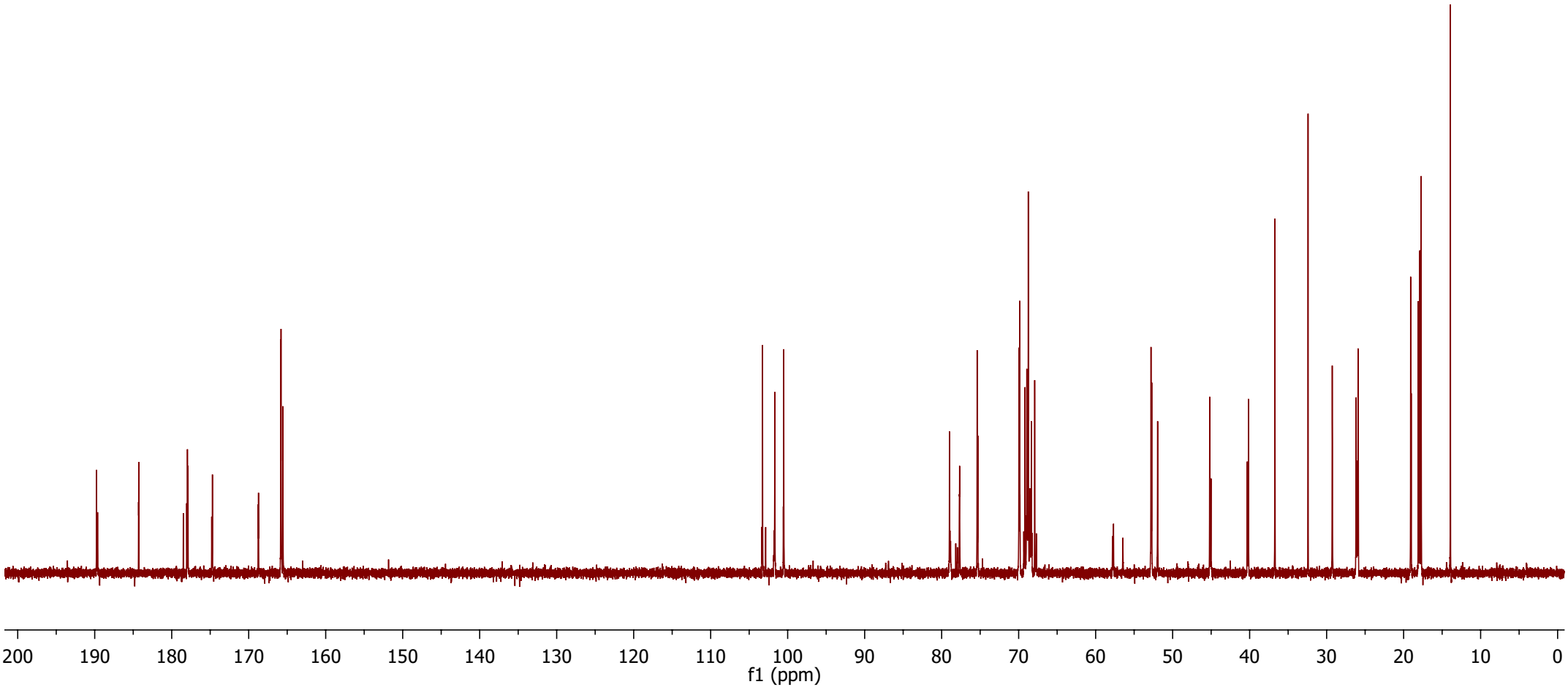

OH
OHCHN
HO
O
OHCHN
HO
OHCHN
OH
O
O
O
O
42
O
N
H
H
N
OBu
O
O


10.0
9.5
9.0
8.5
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
f1 (ppm)

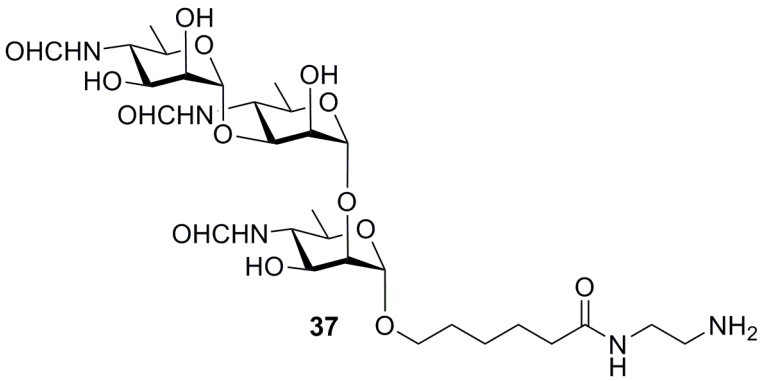
126 MHz, D_2O



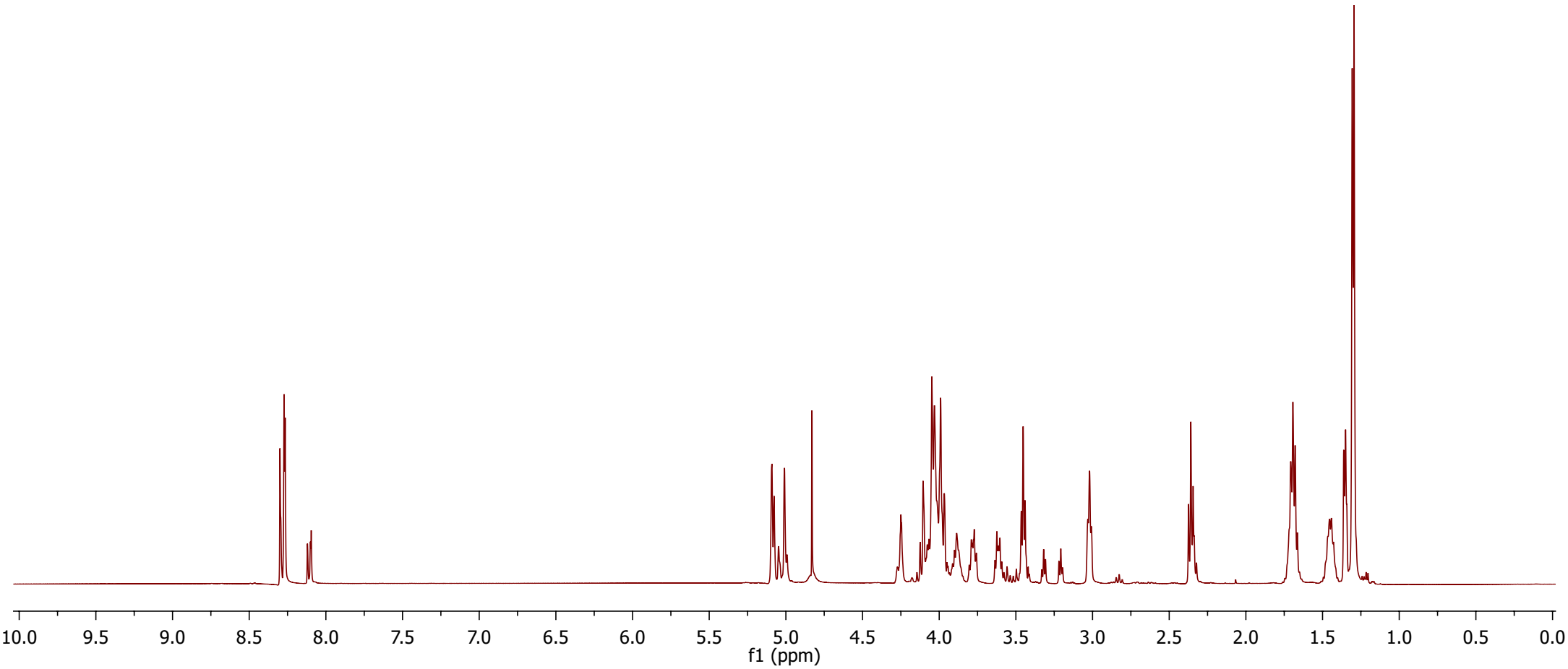
42



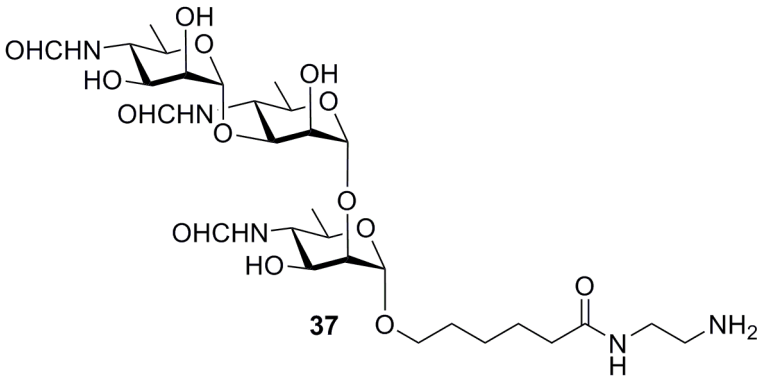
500 MHz, D_2O

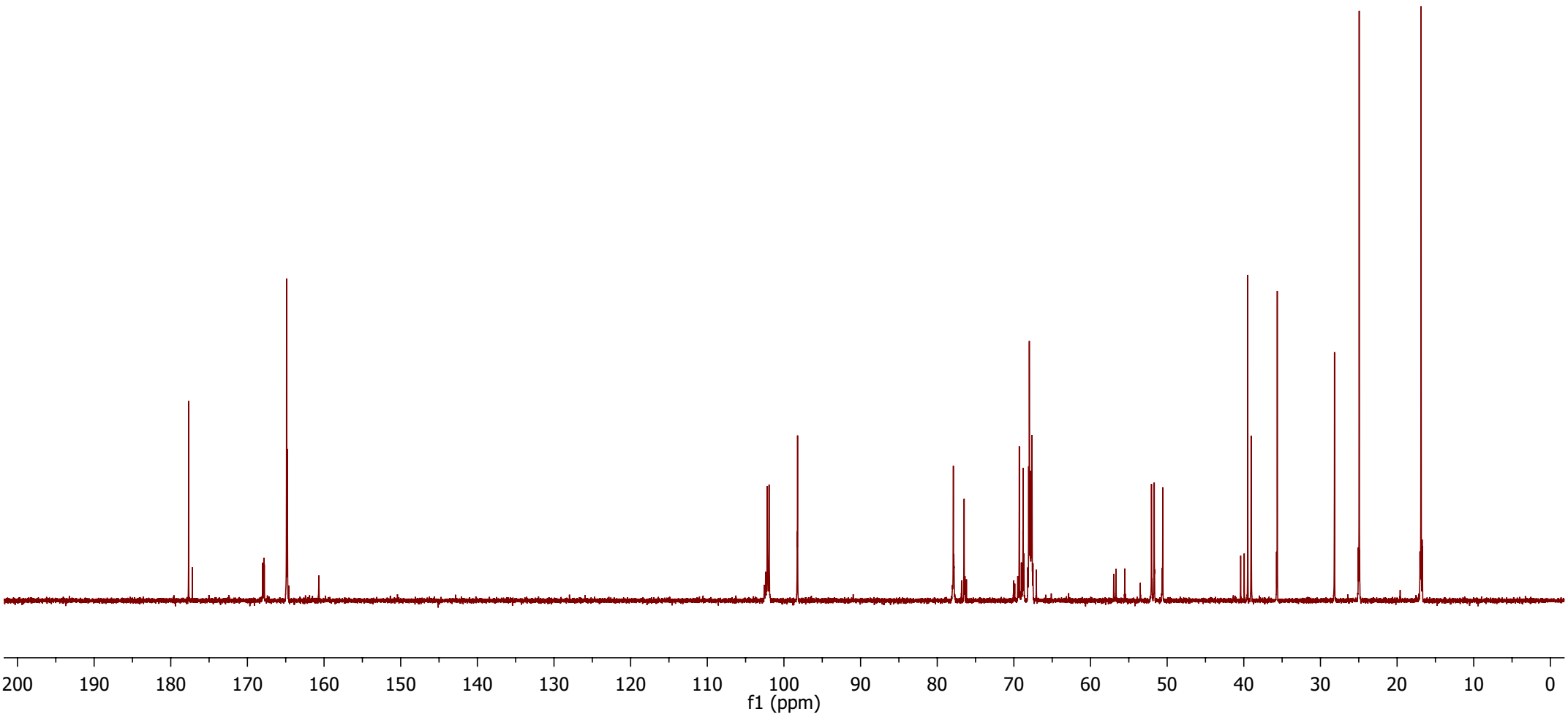


37

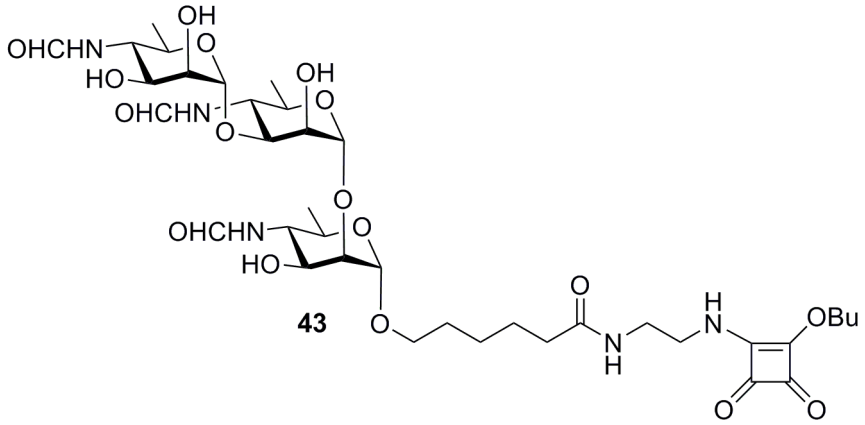


126 MHz, D_2O

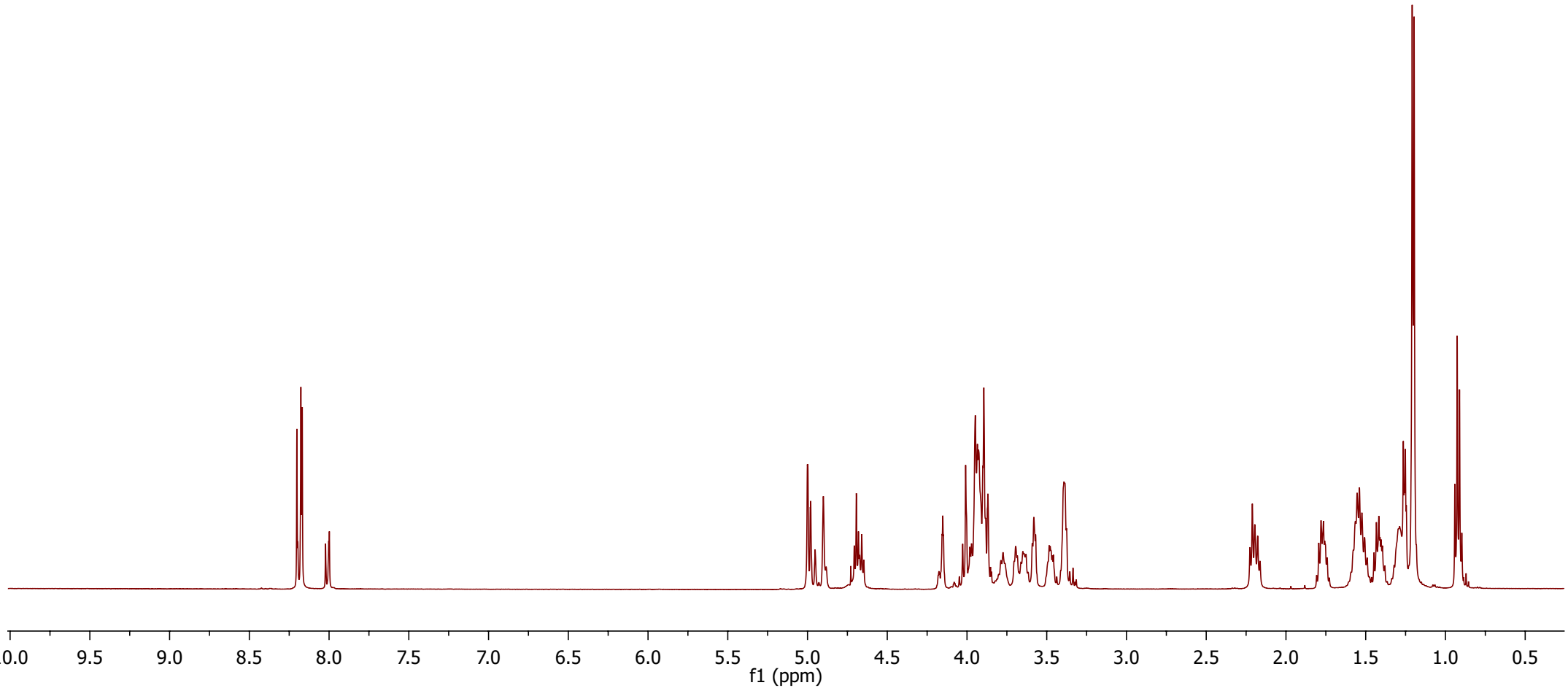

OH
OHCHN
HO
OH
OHCHN
O
O
O
O
OHCHN
HO
O
O
37
O
N
H
NH2


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

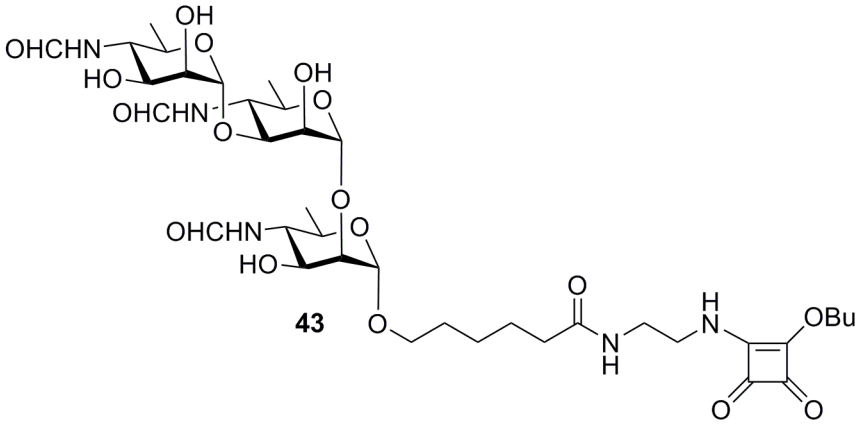
500 MHz, D_2O

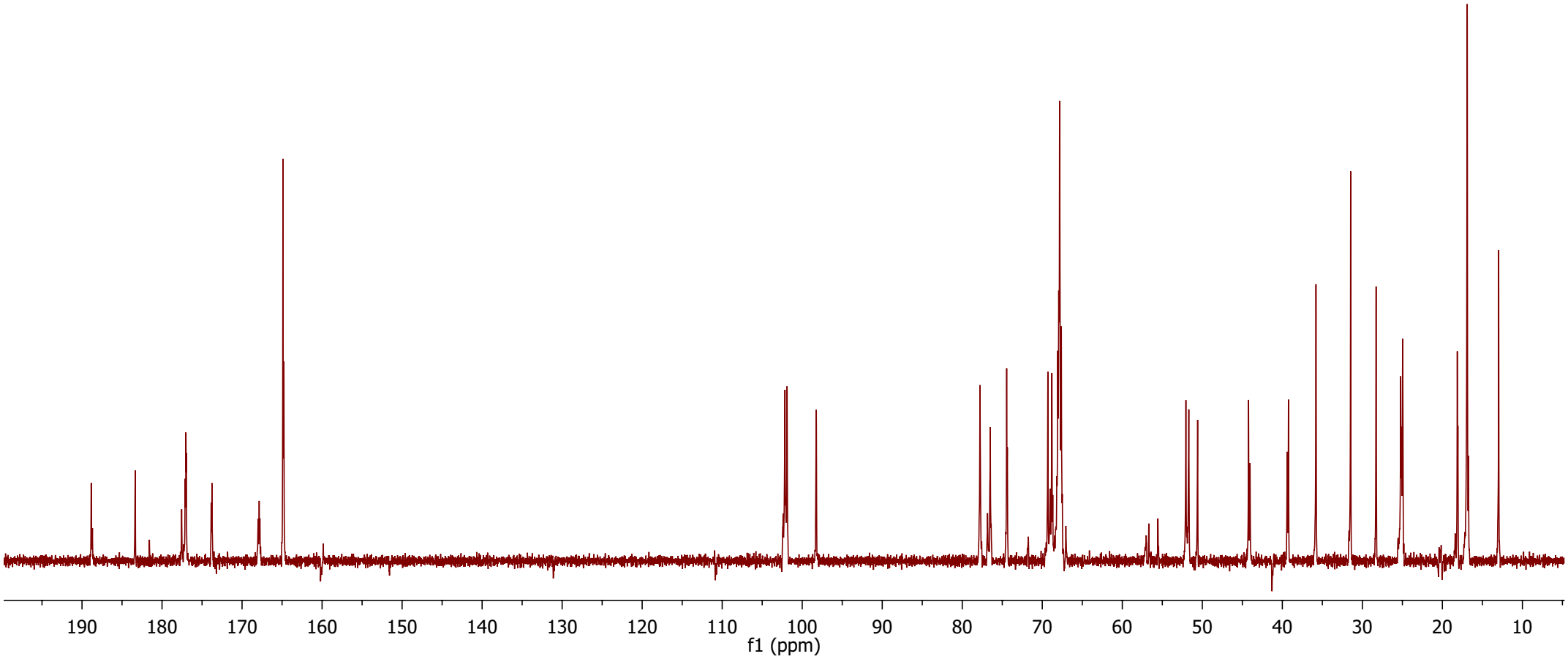


43

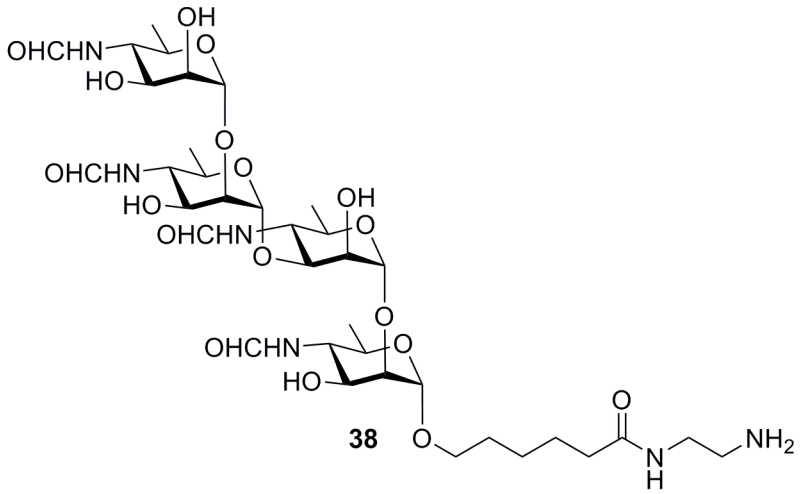


126 MHz, D_2O

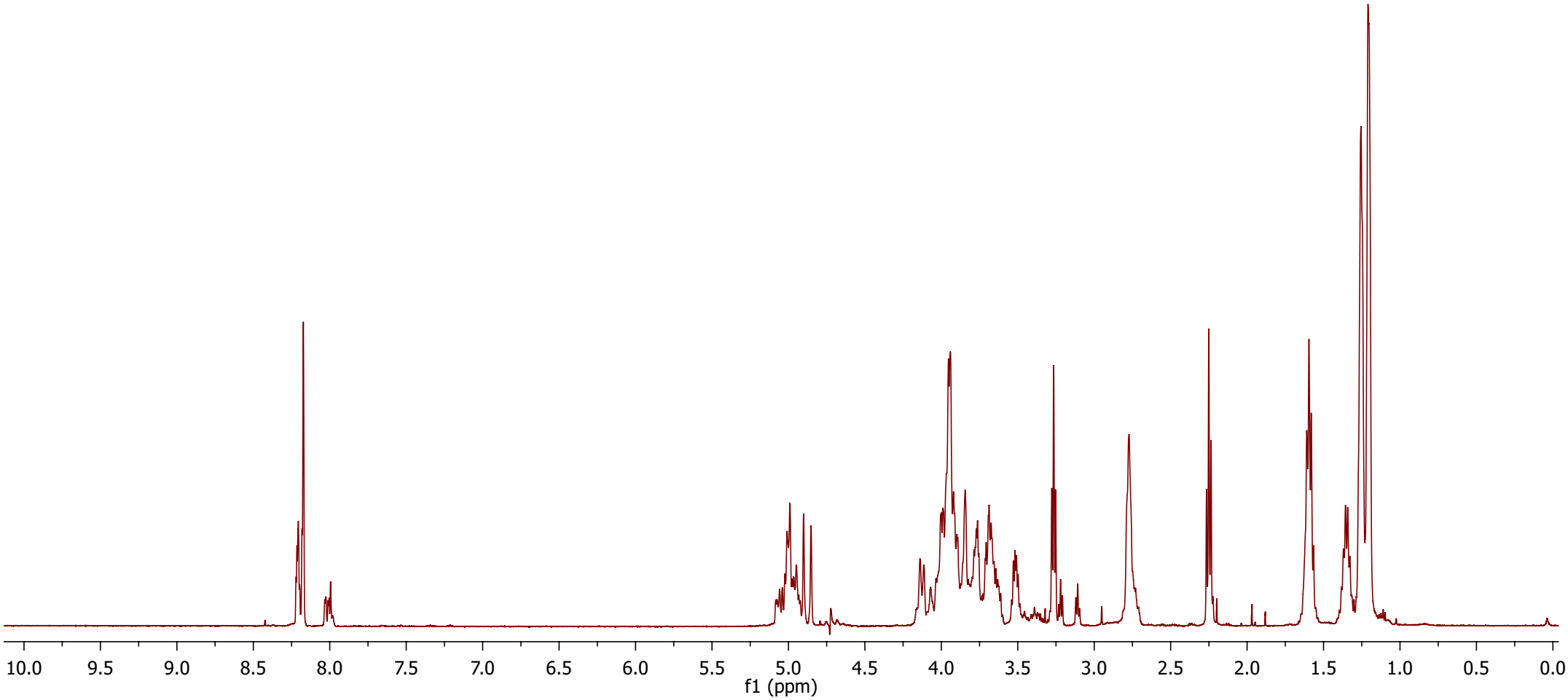

OH
OHCHN
O
HO
OH
OHCHN
O
O
OHCHN
O
HO
O
43
O
N
H
H
N
OBu
O
O


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

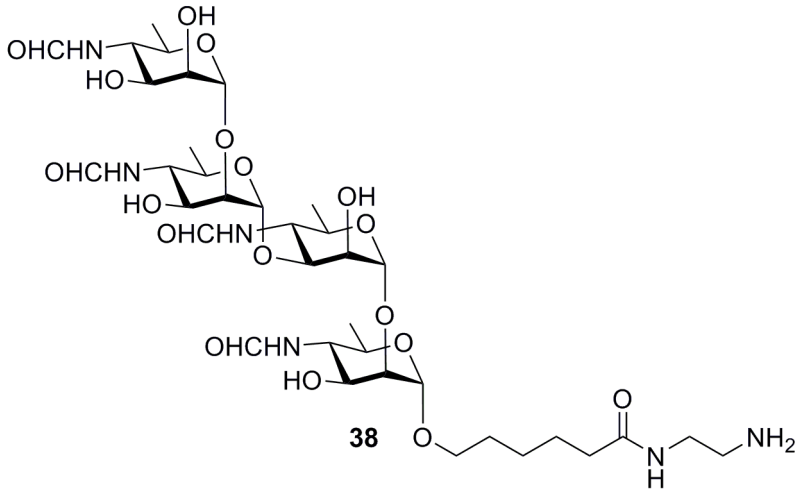
500 MHz, D_2O



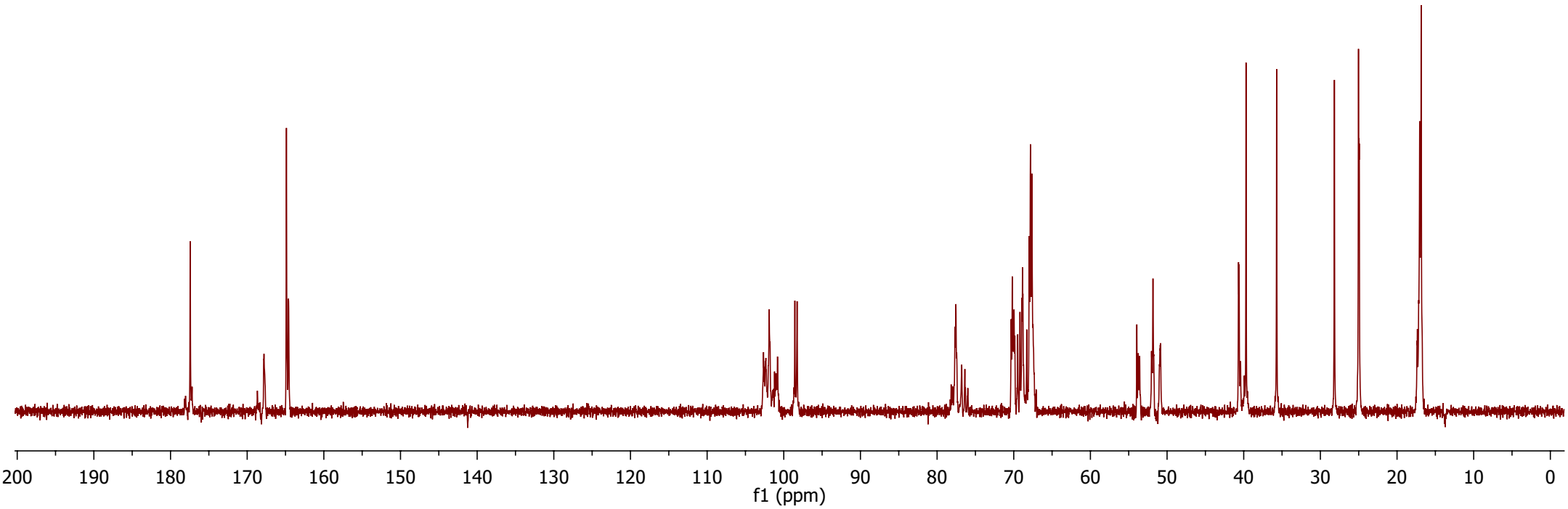
38



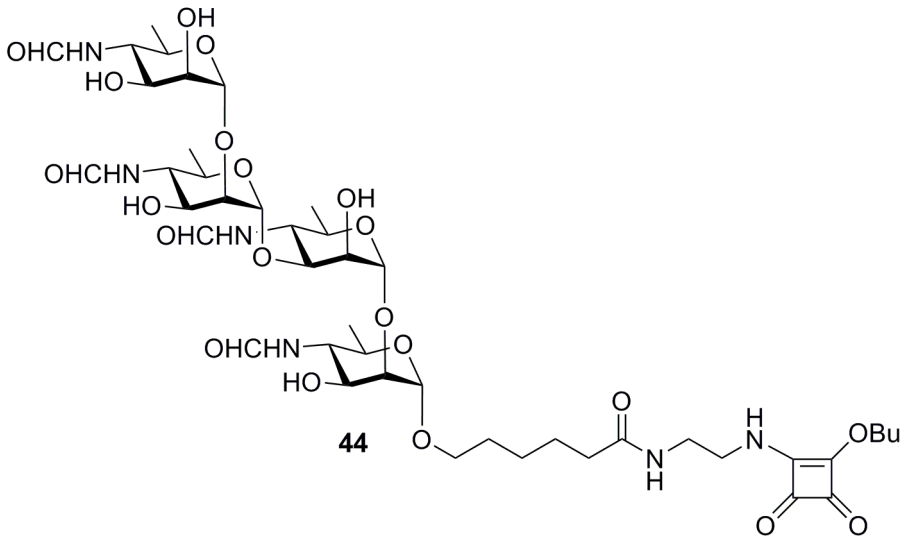
126 MHz, D_2O



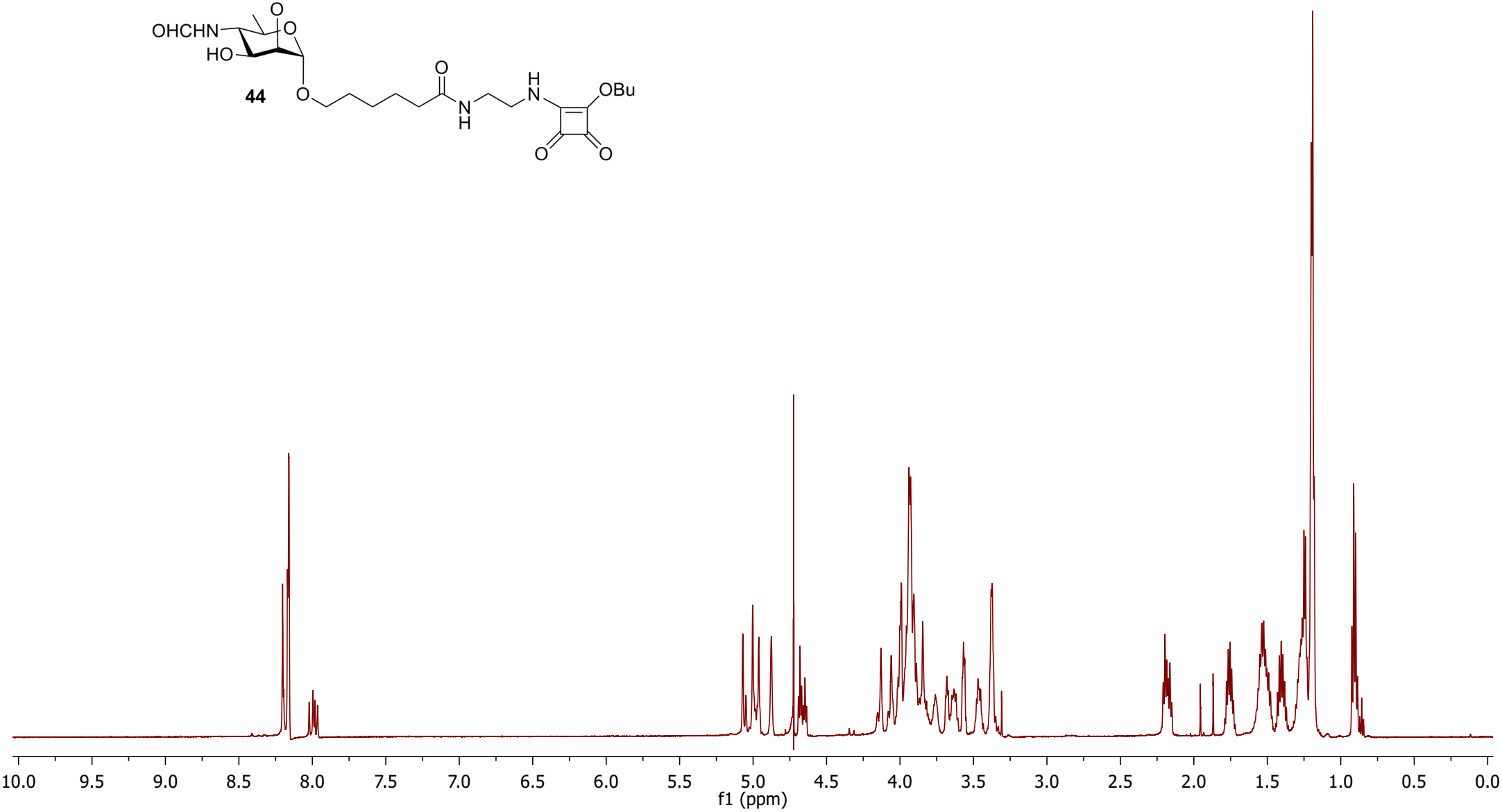
38



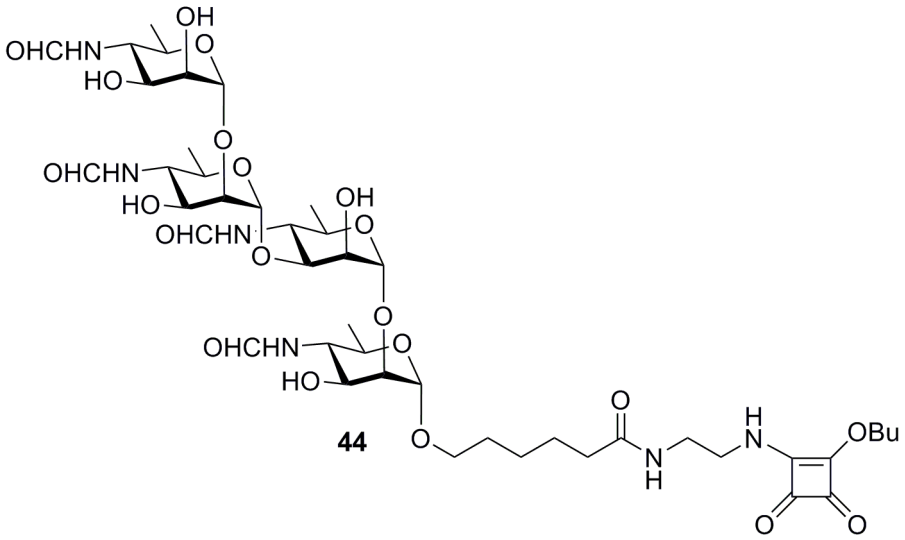
600 MHz, D_2O



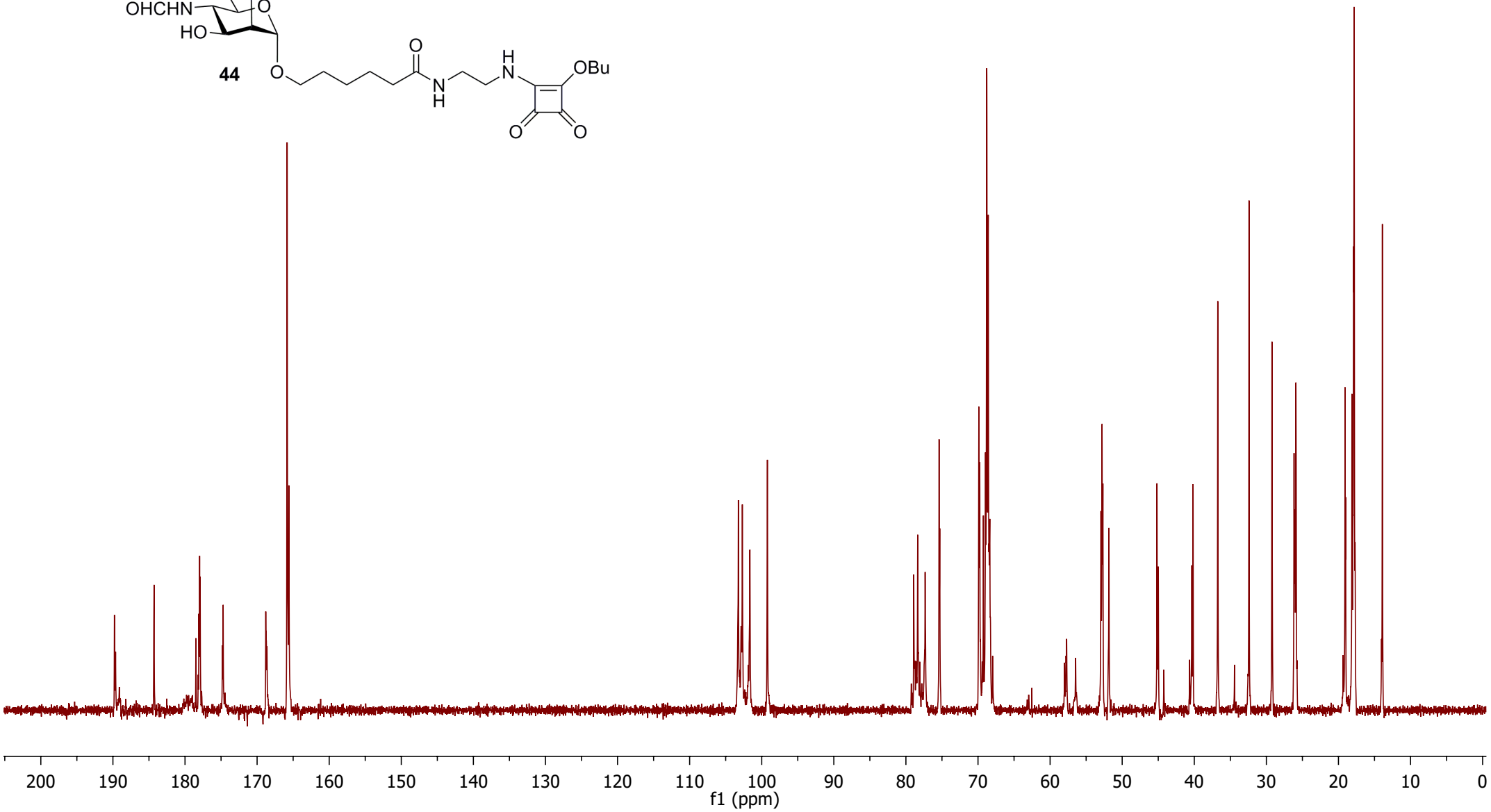
44



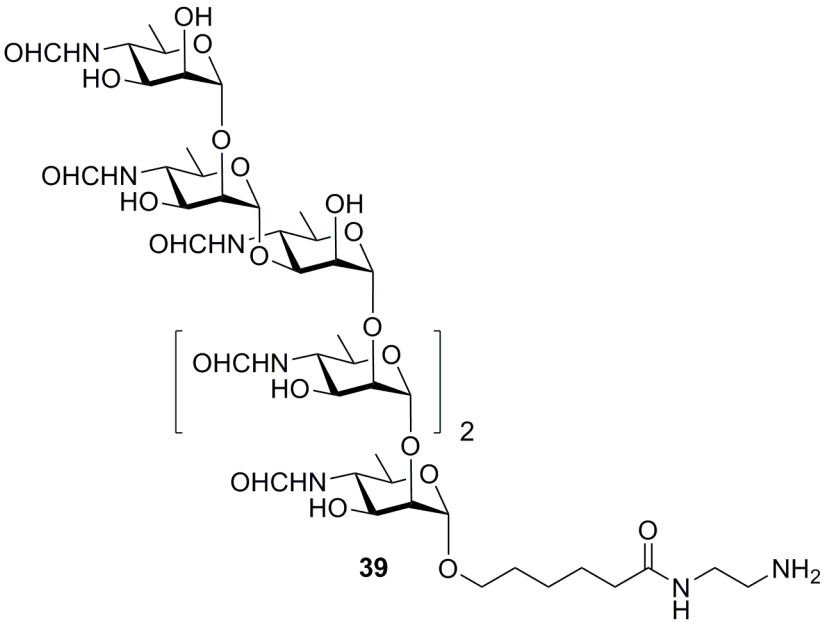
126 MHz, D_2O



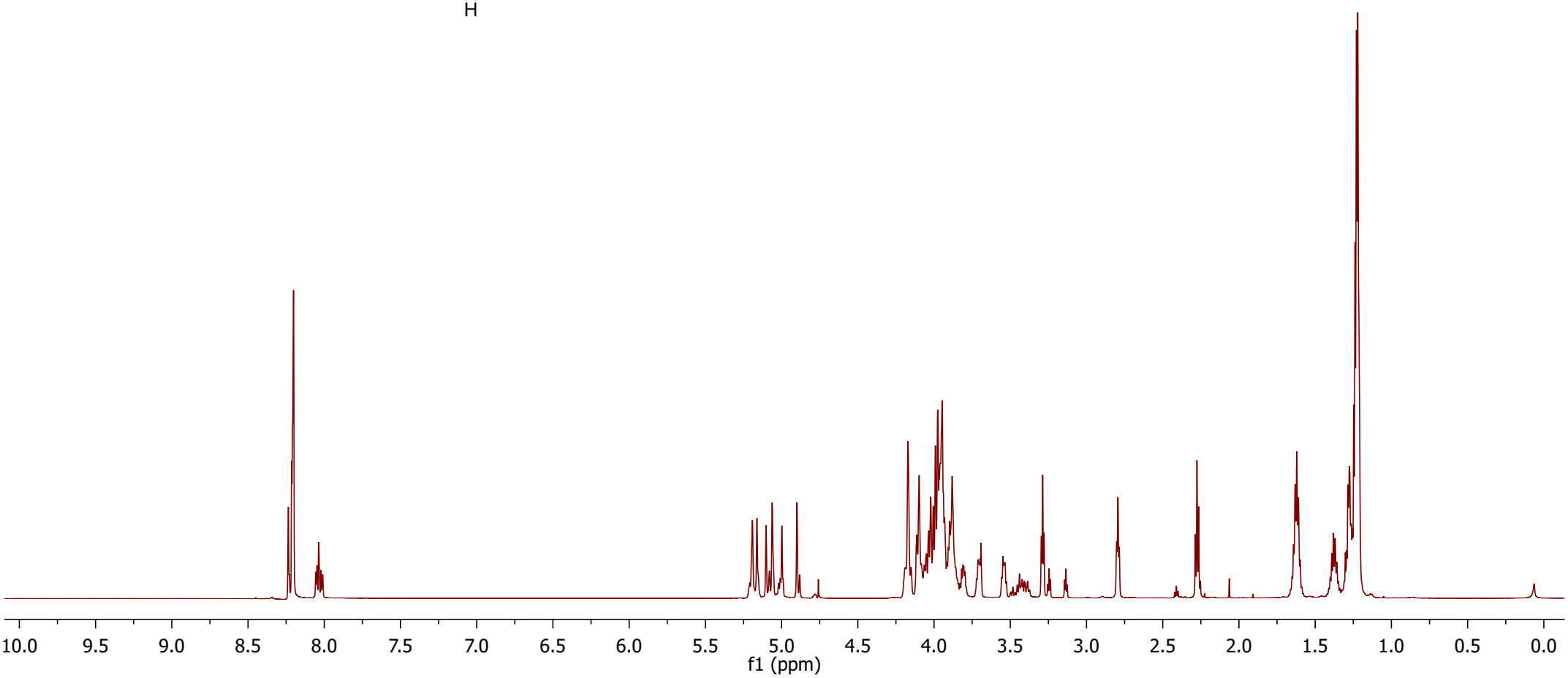
44



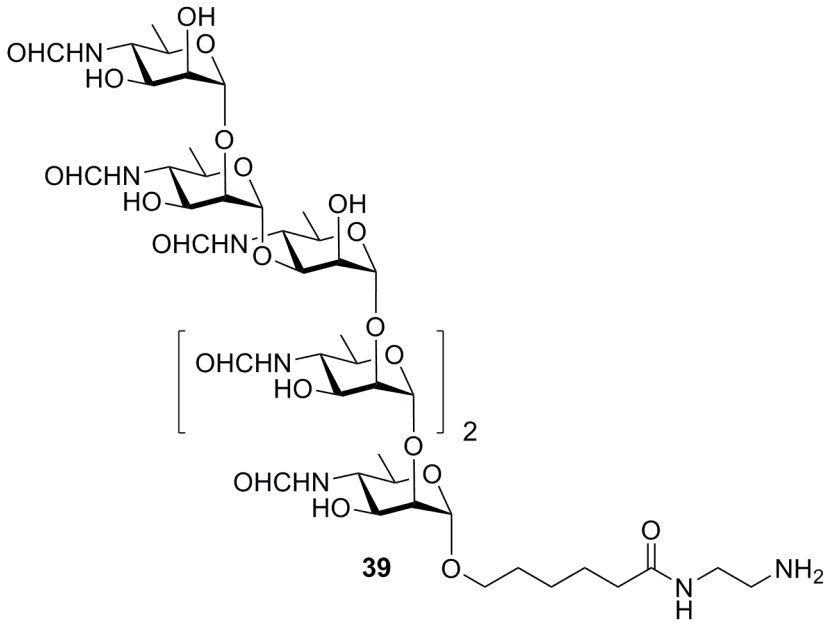
600 MHz, D_2O



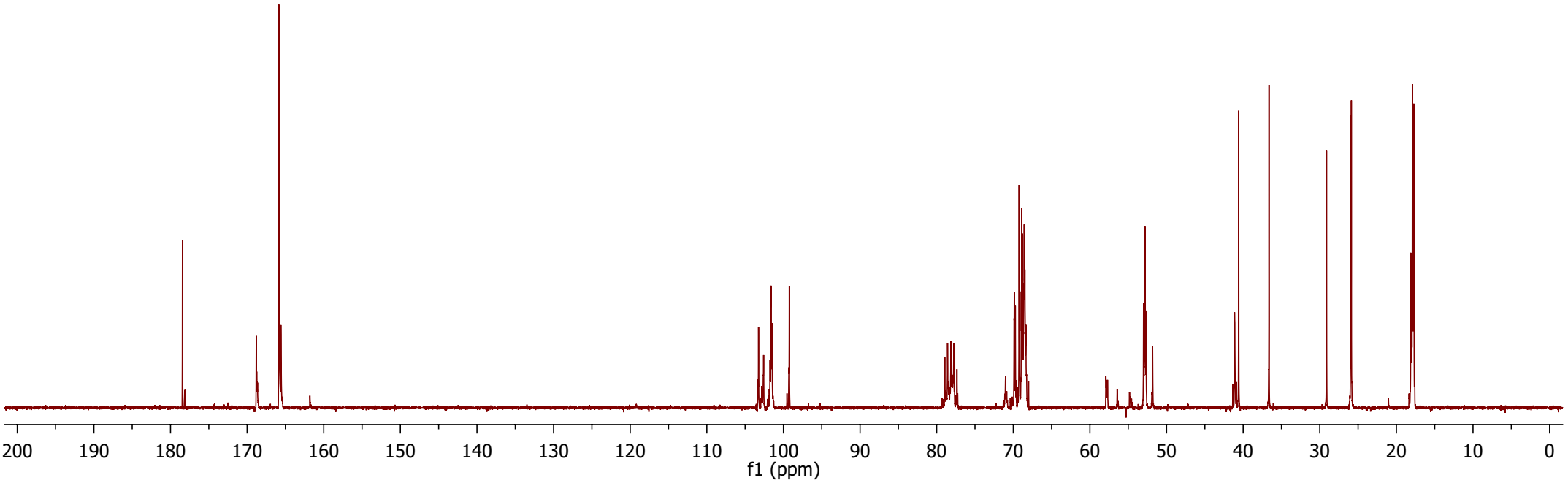
39



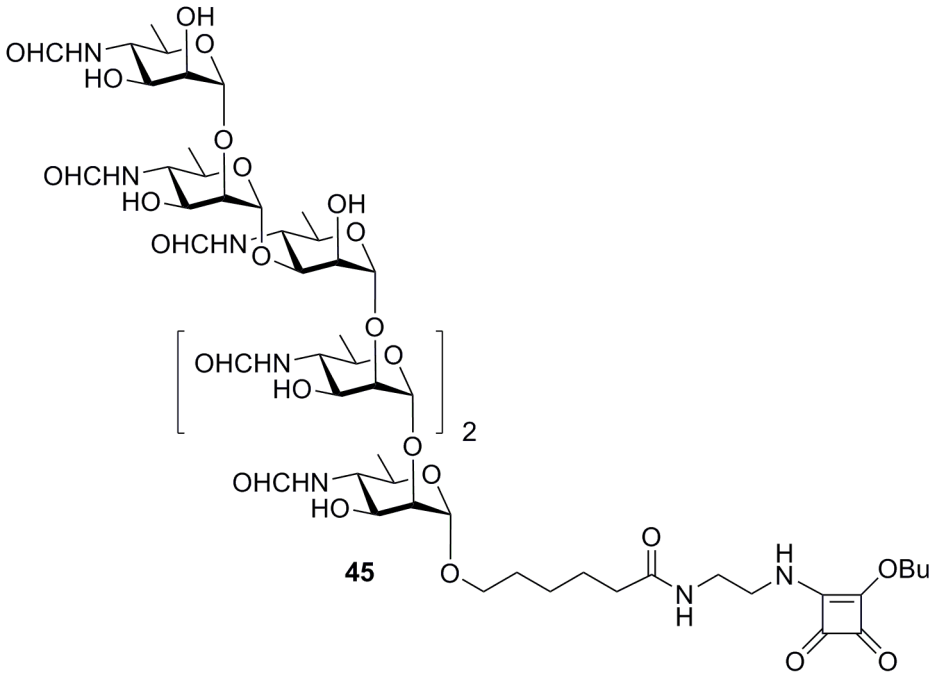
126 MHz, D_2O

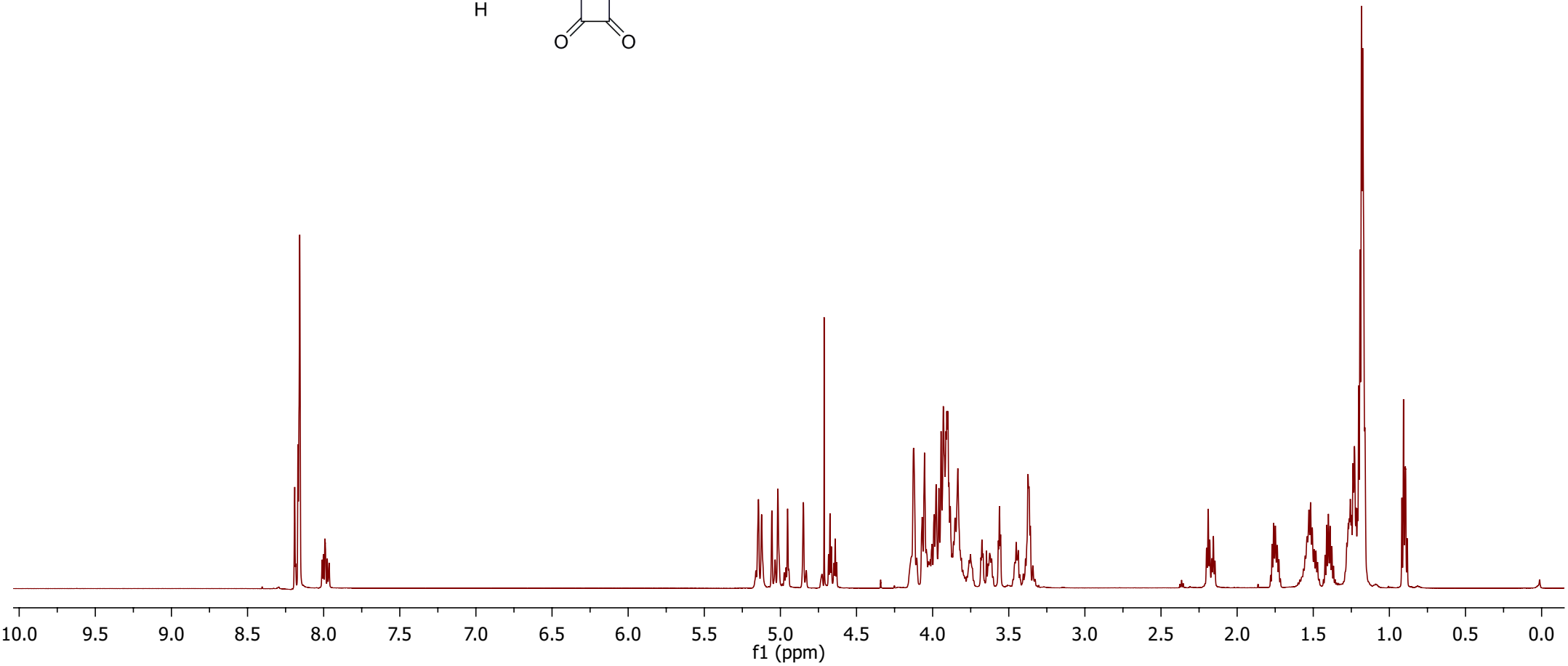


39

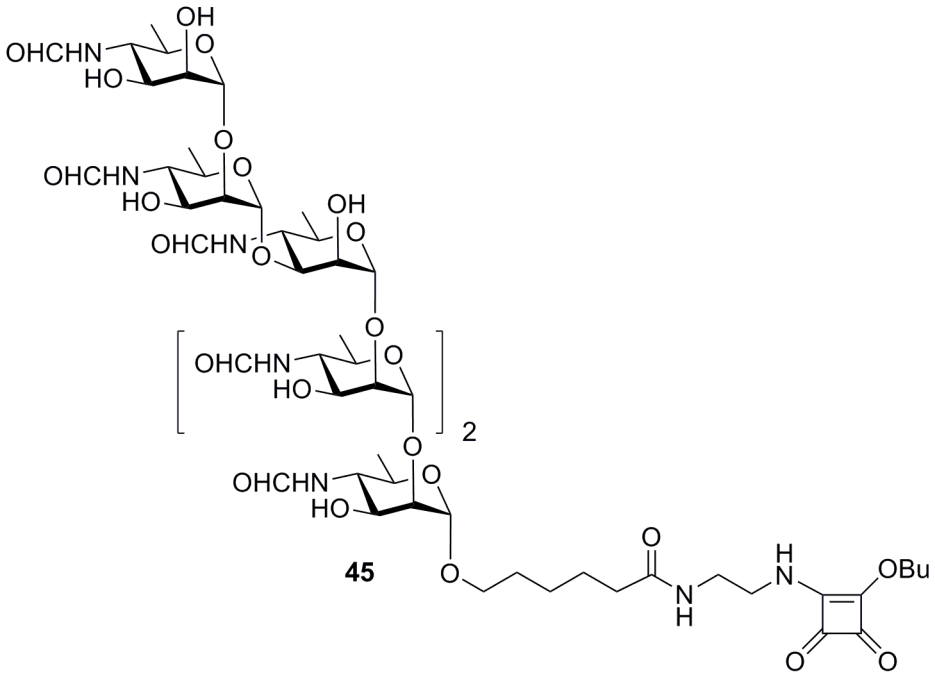


700 MHz, D_2O

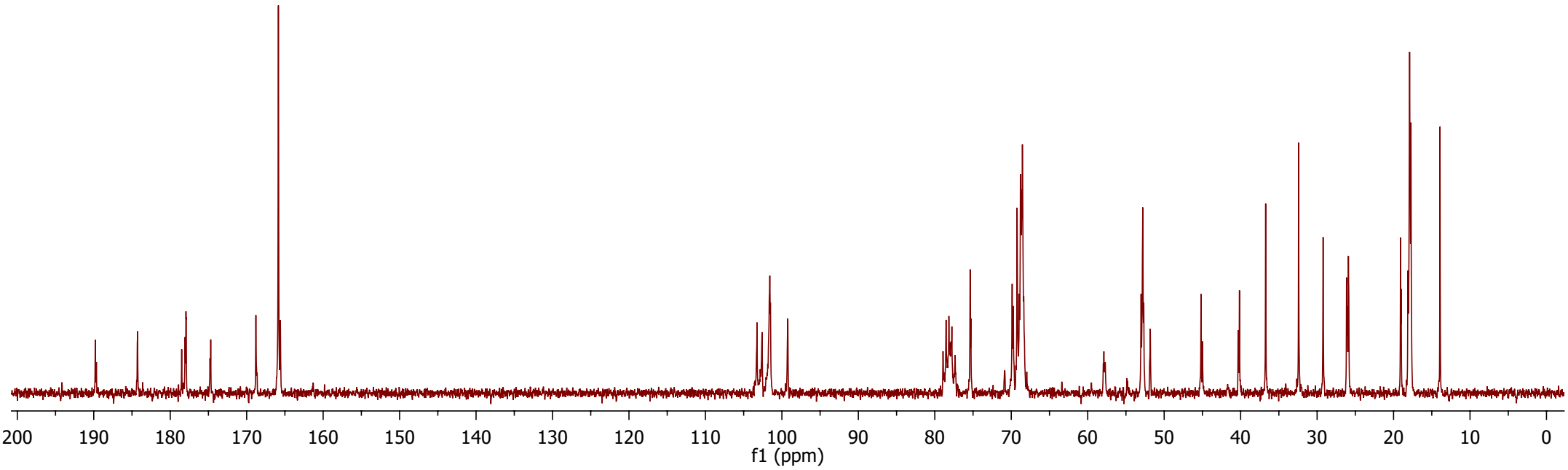

OH
OHCHN
HO
O
OH
2
45
OBu

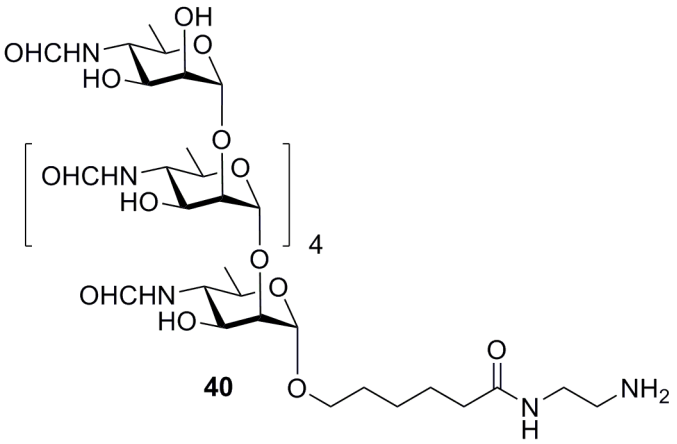

10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

126 MHz, D_2O



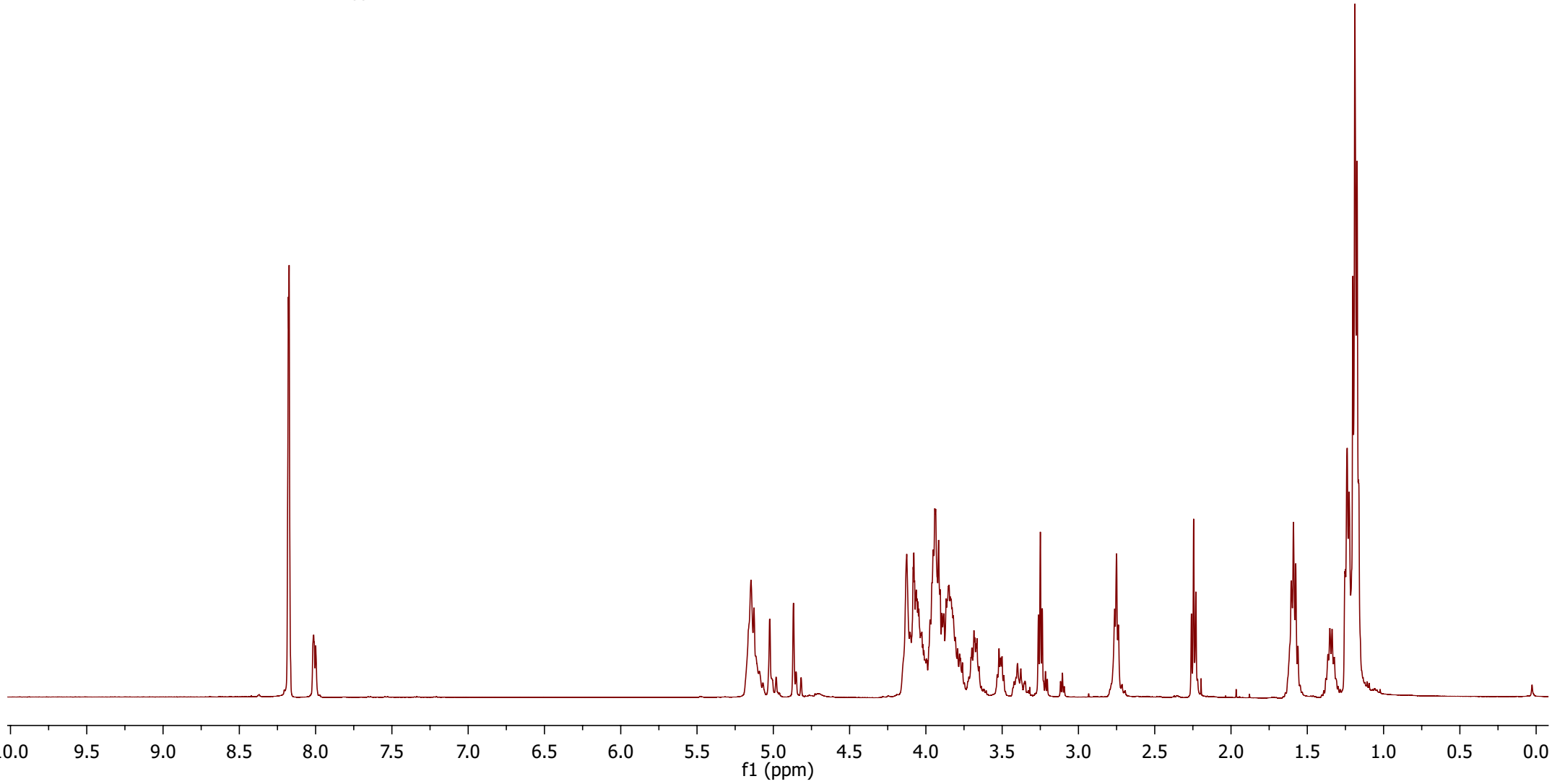
45

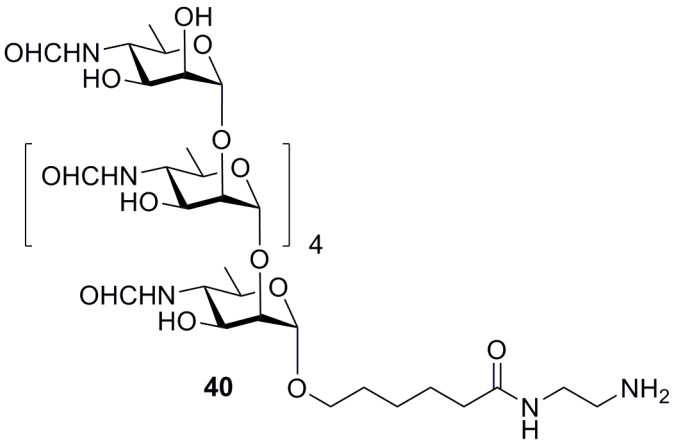




40

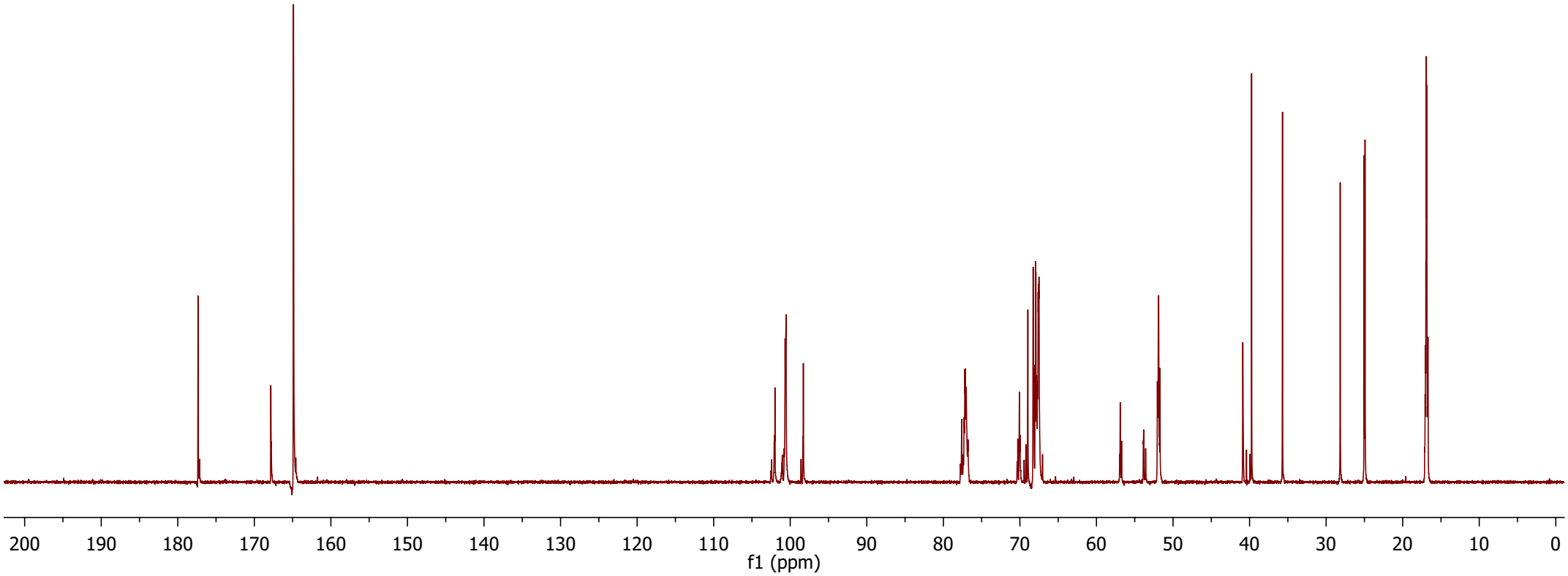
500 MHz, D_2O

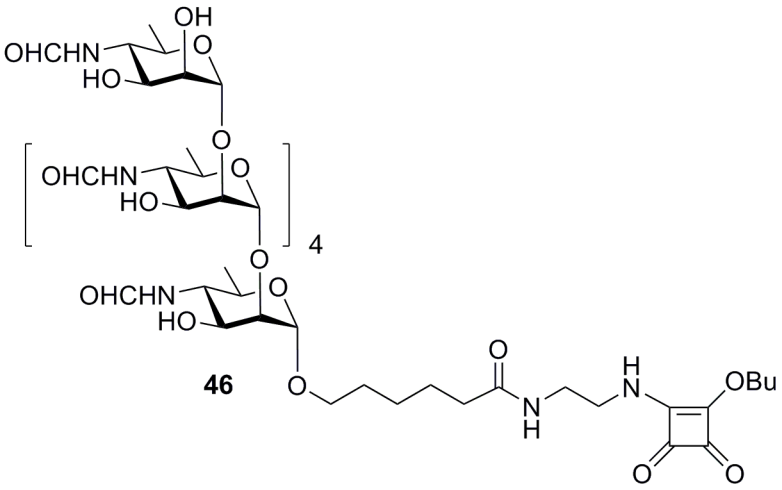




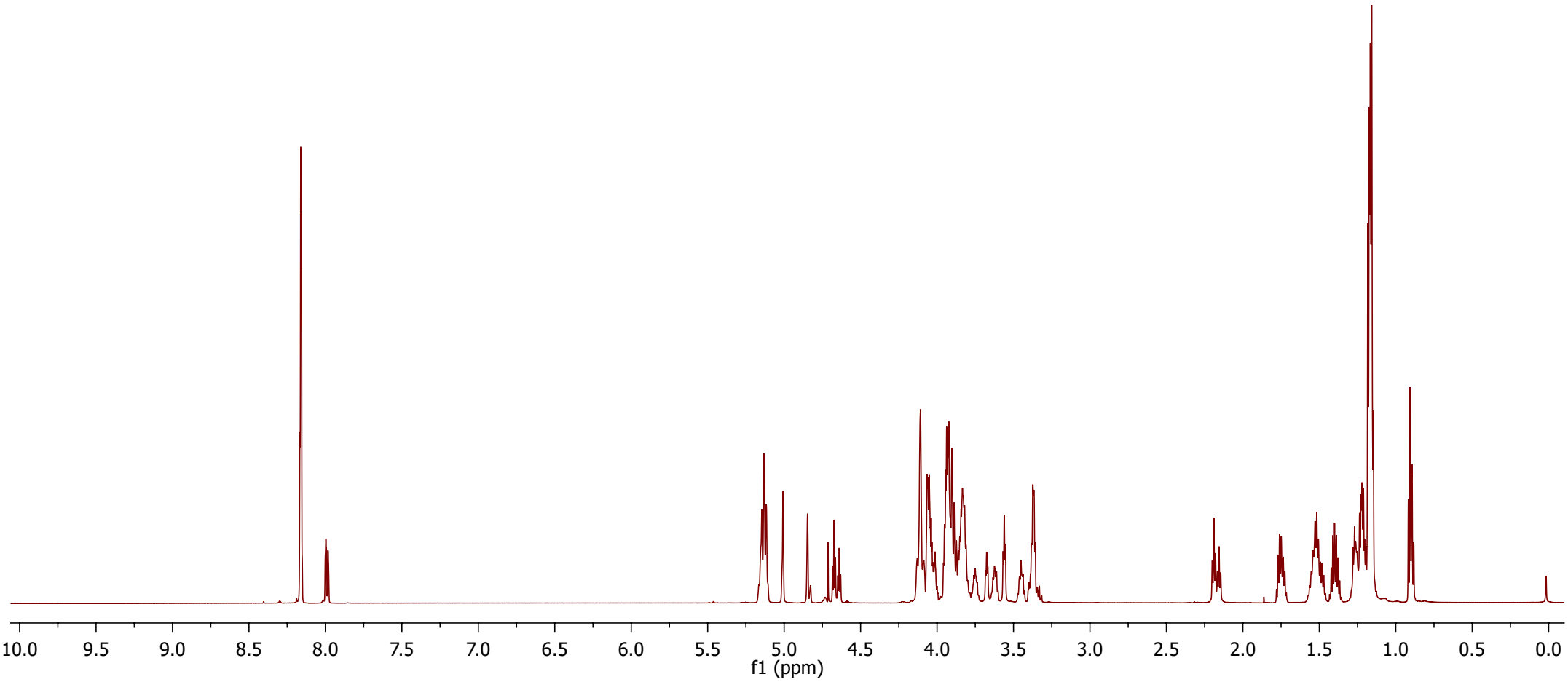
40

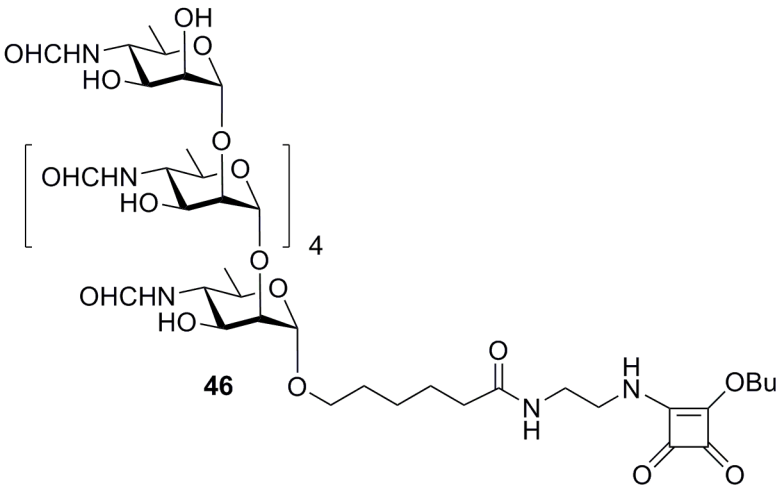
126 MHz, D_2O



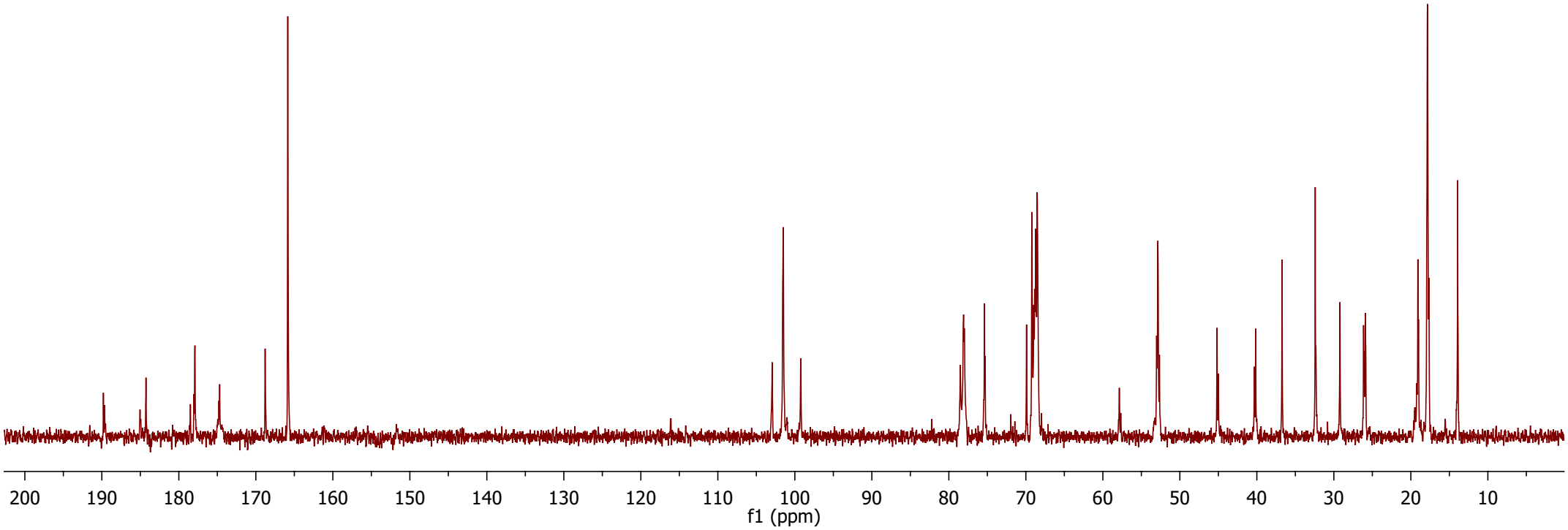

OH
OHCHN
HO
O
4
OBu
46

700 MHz, D_2O


10.0
9.5
9.0
8.5
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
f1 (ppm)


OH
OHCHN
HO
O
4
OBu
H
N
46

126 MHz, D_2O


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)