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

Concise Synthesis of Single Components of Partially Sulfated Oligomannans

Kwok-Kong Tony Mong,[*a] *Kai-Sheng Shiau,*[a] *Yu Hsien Lin,*[a] *Kuang-Chun Cheng,*[a] *and Chun-Hung Lin*[b]

[a]*Applied Chemistry Department, National Chiao Tung University of Taiwan, 1001, University Road, Hsinchu, Taiwan, Republic of China.*

E-mail: tmong@mail.ncut.edu.tw; Fax: +886-3-5723764

[b]*Institute of Biological Chemistry, Academia Sinica, Room 802, 128, Academia Road Sec. 2, Nankang, Taipei 115, Taiwan, Republic of China.*

Supporting information

General Procedures:

Reagent-grade chemical reagents were purchased from vendors and used without further purification. All reactions were executed with flame-dried vessels under a positive pressure of nitrogen. Acetonitrile, dichloromethane, and tetrahydrofuran were dried through solvent purification system AWS-1000. Chemical reactions were monitored by thin-layer chromatography (TLC) on silica gel 60 F-254 plate. Compounds trapped in TLC plate were visualized by UV absorption and/or by staining with acidic ceric ammonium molybdate or *p*-anilaldehyde. Silica gels (Si-60, 0.063-0.200 mm) used in purification were attained from Merck. Co. NMR spectra were recorded on 500MHz (^{1}H NMR) and 125MHz (^{13}C NMR) or 400MHz (^{1}H NMR) and 100MHz (^{13}C NMR) in $CDCl_3$. Chemical shifts were reported in ppm referred to TMS

(0.00 ppm for ^{1}H) and the central line of $CDCl_3$ (77.5ppm for ^{13}C) as internal standards. Coupling constants were reported in Hz derived from ^{1}H NMR.

NIS and TMSOTf (or NIS and TfOH) promoted glycosylation Protocol: Thiomannosyl donor (1.1~1.3 equiv.), thiomannosyl acceptor (1.0 equiv.), and flame-dried MS (4Å) (10 wt% to solvent volume) were added to dry CH_2Cl_2 (final concentration of acceptor = *ca* 50 mM) and the mixture was stirred at RT for 15 to 30 min. The reaction mixture was then cooled to –20 ˚C, followed by addition of *N*-Iodosuccinimide (NIS, 1.1~1.3 equiv) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) [or trimethylsilyl trifluoromethanesulfonic acid (TfOH)] (0.1~0.3 equiv). The progress of the reaction was monitored by TLC examination. When the mannosyl acceptor was consumed, the reaction was quenched by addition of triethylamine, followed by $Na_2S_2O_3$ and satd. $NaHCO_3$. The crude mixture was filtered over celite and concentrated for flash column chromatography.

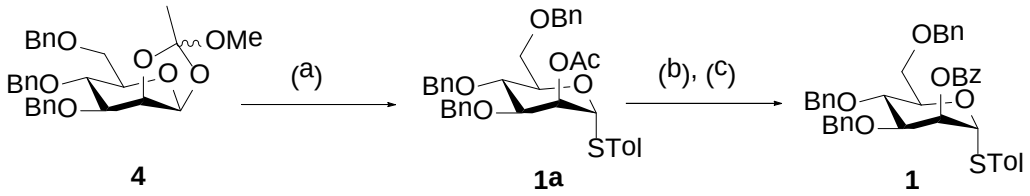
DMF-Modulated glycosylation Protocol: Thiomannosyl donor (1.1~1.3 equiv.), activated MS (4Å), and DMF (1.2~1.5 equiv.) were added to dried CH_2Cl_2 (final concentration of acceptor = *ca* 50 mM) and the mixture was stirred at RT for 15 to 30 min. The reaction mixture was then cooled to –20 ˚C, followed by addition of NIS (1.2~1.5 equiv.) and TMSOTf or TfOH (1.5~1.8 equiv.). After the activation of the donor (evidenced by TLC), the thiomannosyl acceptor (1.0 equiv.) was added. The reaction temperature was increased to effect the glycosylation. When the acceptor was nearly (or completely) consumed, the reaction was quenched by triethylamine, followed by $Na_2S_2O_{3(s)}$ and satd. $NaHCO_3$. The crude product mixture was filtered over celite and concentrated for purification with flash column chromatography.[S1]

Me_2S_2-Tf_2O promoted glycosylation protocol: Thiomannosyl donor (1.1~1.3 equiv.), thiomannosyl acceptor (1.0 equiv.), and flame-dried MS (4Å) (10 wt% to solvent volume) were added to dry CH_2Cl_2 (final concentration of acceptor = *ca* 50 mM). The reaction mixture was stirred at RT for 15 min. and at –20 or –10 ˚C for 15 min, followed

by addition of Me_2S_2-Tf_2O complex (1.3~1.5 equiv) and di-*t*-butylmethyl pyridine (DTBMP, 1.5 equiv). Progress of the reaction was monitored by TLC. When the glycosyl acceptor was consumed, the reaction was quenched by addition of triethylamine. The crude reaction mixture was filtered over celite to remove MS and concentrated for purification with flash column chromatography.

Preparation of Me_2S_2-Tf_2O reagent: a 1.0 M reagent was made by mixing triflic anhydride (Tf_2O) (0.168 mL, 1.0 mmol) with dimethylsulfide (Me_2S_2) (0.10 mL, 1.1 mmol) in dry CH_2Cl_2 (0.75 mL) at 0 ^oC. The resulting mixture was stirred for 30 min before use.[S2]

Thiomannoside 1[S1]



4 **1a** **1**

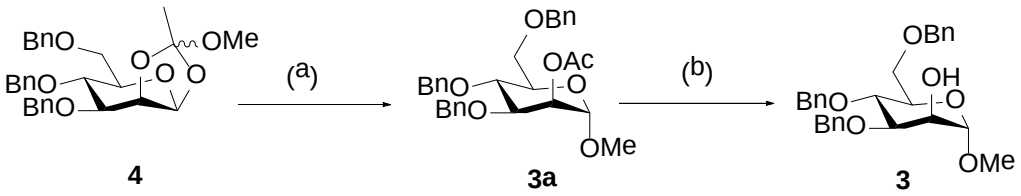
Step (a): To a stirred suspension of known ortho-ester **4** (20.0 g, 39.22 mmol) in anhydrous CH_2Cl_2 was added thiocresol (7.40 g, 59.28 mmol) and $BF_3{\cdot}OEt_2$ (7.5 mL, 59.22 mmol) in ice bath. The mixture was vigorously stirred from 0 ˚C to RT for 18h, the reaction was then quenched with addition of H_2O. The crude mixture was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and the filtrate was concentrated for purification with flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:6) to afford thiomannoside **1a** (20.17 g, 86%).

Step (b): To a stirred suspension of thiomannoside **1a** (20.17 g, 33.71 mmol) in methanol was added a piece of Na metal. After vigorously stirring at RT for 3h, the reaction was quenched with addition of H_2O. The crude was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated for purification with flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:3).

Step (c): The crude product from procedure (b) was stirred in CH_2Cl_2 at RT. BzCl

(12.5 mL, 46.88 mmol), triethylamine (8.9 mL, 46.88 mmol), and 4-dimethylaminopyridine (DMAP) (795 mg, 0.15 mmol) were added. After vigorously stirring for 3 h, the reaction was quenched with H_2O. The crude was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated for purification with flash chromatography (EtOAc/Hexanes/CH_2Cl_2 5:1:1) to afford thiomannoside **1** (15.8 g, 72% over two steps).[S1]

Methyl mannoside 3[S3]

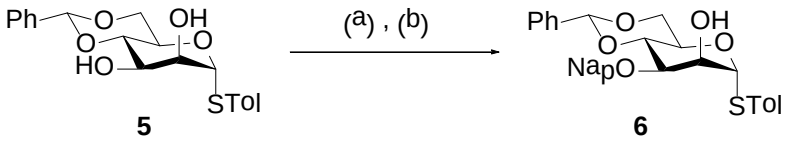


(a) MeOH, $BF_3{\cdot}OEt_2$, CH_2Cl_2, 0°C to RT, 4h, 60% (b) Na, MeOH, 76%

Procedure (a): To a stirred suspension of known ester **4** (10.0 g, 19.61 mmol) in CH_2Cl_2 was added MeOH (3.5 mL, 91.50 mmol) and $BF_3{\cdot}OEt_2$ (3.8 mL, 29.70 mmol) in ice bath. The mixture was vigorously stirred from 0 ˚C to RT for 4 h and was quenched with addition of H_2O. The crude was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated for purification with flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:4) to afford the reducing end mannoside **3a** (5.9 g, 60%).

Procedure (b): To a stirred suspension of reducing end mannoside **3a** (5.9 g, 12.0 mmol) in methanol without further distillation was added a piece of sodium solid at RT. After vigorously stirred for 4 h, the reaction was quenched with addition of H_2O. The crude was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and then concentrated for purification with flash chromatography (EtOAc/hexanes/CH_2Cl_2 3:1:1) to afford the reducing end mannoside **3** (4.2 g, 76%).

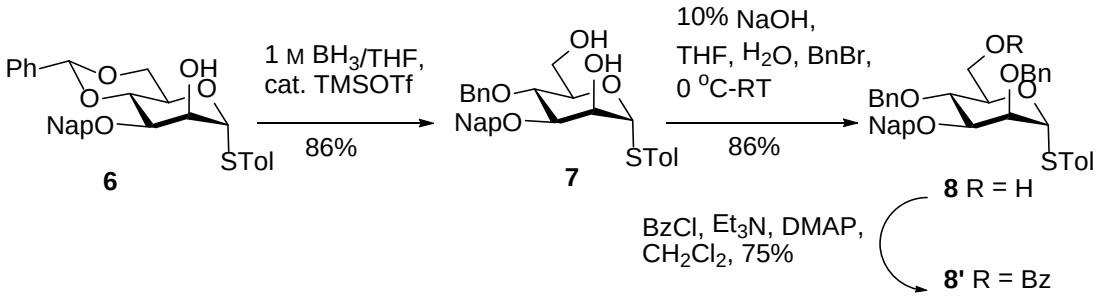
Thiomannoside 6



(a) Bu_2SnO, Toluene, reflux, 3h ; (b) 2-NapBr, CsF, 70 ^oC, 15 h, 71% (2 steps)

To a stirred suspension of known thiomannoside **5** (10.7 g, 28.56 mmol) in toluene (100 mL) was added di-butyltin oxide (10.8 g, 42.9 mmol). The mixture was heated under reflux for 3 h, and then cooled down to RT. To the stannylene acetal generated in previous step was added naphthylmethylene bromide (NapBr, 9.5 g, 42.9 mmol) and cesium fluoride (CsF, 6.5 g, 42.9 mmol). The mixture was stirred at 70 $^{\circ}C$ for 6-15 h, and then cooled down to RT. The reaction mixture was filtered over celite, and the filtrate was concentrated for purification with flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:5) to afford thiomannoside **6**. For thiomannoside **6**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:5); $[\alpha]_D^{23}$ +176.6 (*c* 2.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.84-7.81 (m, 3H, ArH), 7.76-7.73 (m, 1H, ArH), 7.54-7.46 (m, 5H, ArH), 7.41-7.38 (m, 3H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.10 (d, *J* = 8.0 Hz, 2H, ArH), 5.64 (s, 1H, benzylidene-H), 5.51 (s, 1H, H-1), 5.01 (d, *J* = 12.0 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.35-4.31 (m, 2H), 4.23-4.18 (m, 2H), 4.02 (dd, *J* = 9.6, 3.4 Hz, 1H), 3.85 (t, *J* = 10.3 Hz, 1H), 2.89 (s, 1H, OH), 2.32 (s, 3H, CH_3): ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.0, 137.5, 135.1, 133.2, 133.1, 132.4, 129.9, 129.3, 129.0, 128.33, 128.26, 128.0, 127.7, 126.7, 126.2, 126.14, 126.10, 125.6, 101.7, 88.1 (C-1), 79.0, 75.7, 73.1, 71.3, 68.6, 64.5, 21.1. HRMS (ESI) *m/z* calcd for $C_{31}H_{30}NaO_5S$ $[M + Na]^+$: 537.1706, found: 537. 1706.

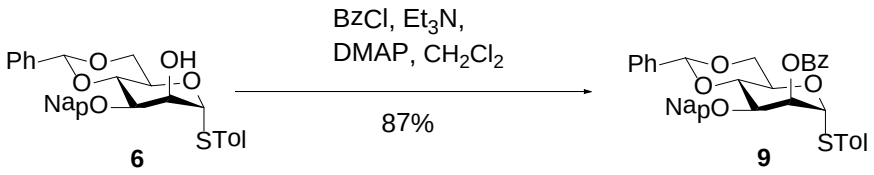
Thiomannosides 7, 8, and 8′.



To thiomannoside **6** (10.24 g, 19.9 mmol) was added 1.0 M BH_3·THF (60 mL, 60 mmol) at 0˚C. Then TMSOTf (180 μL) was added under nitrogen and the mixture was stirred from 0˚C to RT. After stirring at RT for 2 h, the borane reagent was quenched with the addition of MeOH at 0˚C and the solvent was reduced by rotary evaporator. The residue was concentrated for chromatography purification (EtOAc/Hexanes 1:4 to 1:1) to obtain the diol intermediate **7** (8.8 g, 17.1 mmol).

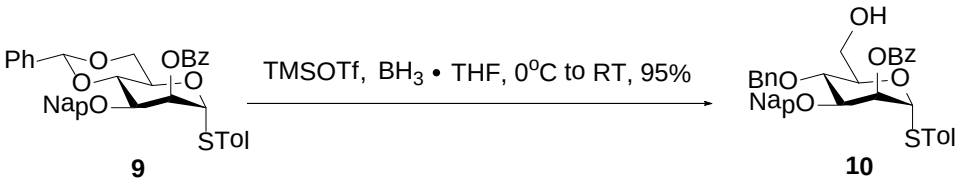
The diol **7** (9.4 g, 17.1 mmol), BnBr (2.2 mL, 18.3 mmol) and TBAB (5.9 g, 18.3 mmol) were treated with 10% NaOH in THF (13 mL) at RT. The reaction mixture was vigorously stirred at RT. After stirring at RT for 1.5 h, the solvent was reduced by rotary evaporator and the residue was dissolved in EtOAc, which was washed with dilute HCl, brine, and dried ($MgSO_4$). After filtration and concentration, the crude mixture was subjected to chromatography purification (EtOAc:CH_2Cl_2:Hexanes 1: 1:5) to obtain the product **8** (8.9 g, 14.7 mmol) The alkylation product 8 (from previous step) in CH2Cl2 was treated with BzCl (2.6 mL, 22.0 mmol), Et3N (4 mL, 29.4 mmol), and DMAP (180 mg, 1.47 mmol). Upon completion of benzoylation, satd. NaHCO3 was added to the mixture and the benzoylation product was extracted with EtOAc. The EtOAc solution was wshed with diluted HCl solution, H2O, brine, dried (over NgSO4), filtered, and concentrated for chromatography purification to afford **8′** in 75% yield. For **8′**, ^{1}H NMR (500 MHz, $CDCl_3$): δ8.00 (dd, *J* = 1.0, 8.0 Hz, 2H, Ar*H*), 7.84-7.80 (m, 3H, Ar*H*), 7.76 (dd, J = 3.5, 6.0 Hz, 1H, Ar*H*), 7.54-7.50 (m, 1H, Ar*H*), 7.49-7.45 (m, 3H, Ar*H*), 7.38-7.36 (m, 3H, Ar*H*), 7.34-7.32 (m, 2H, Ar*H*), 7.30-7.25 (m, 8H, Ar*H*), 7.24-7.21 (m, 1H, Ar*H*), 6.98 (d, *J* = 8.0 Hz, 2H, Ar*H*), 5.55 (d, *J* = 1.5 Hz, 1H), 5.00 (d, *J* = 11.0 Hz, 1H), 4.80 (s, 2H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.5 Hz, 2H), 4.58 (d, *J* = 3.5 Hz, 2H), 4.49-4.46 (m, 1H), 4.15 (t, *J* = 9.5 Hz, 1H), 4.07 (dd, *J* = 1.5, 2.5 Hz, 1H), 4.01 (dd, *J* = 3.0, 9.5 Hz, 1H), 2.27 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): d 166.87 (C=O), 138.5, 138.3, 138.2, 135.9, 133.8, 133.5, 133.3, 132.5, 130.6, 130.5, 130.3, 130.2, 128.89, 128.86, 128.7, 128.2, 127.1, 126.6, 126.4, 126.3, 86.3, 80.7, 76.7, 75.8, 75.1, 72.7, 72.4, 71.5, 64.4, 21.6 (*C*H_3). HRMS (ESI) *m*/*z* calcd for $C_{45}H_{42}NaO_6S^+$ [M + Na]$^+$: 733.2594, found: 733.2606.

Thiomannoside 9



To a well-stirred suspension thiomannoside **6** (6.3 g, 12.25 mmol) in anhydrous CH_2Cl_2 was added triethylamine (3.4 mL, 24.4 mmol), benzoyl chloride (2.2 mL, 18.4 mmol) and 4-dimethylaminopyridine (DMAP) (147 mg, 1.25 mmol). After vigorously stirred at RT for 3 h, the reaction was quenched with addition of H_2O. The crude mixture was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, and concentrated for purification with flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:7) to give thiomannoside **9** (5.4 g, 76%). For **9**, R_f 0.25 (EtOAc/CH_2Cl_2/Hexanes 1:1:7); $[\alpha]_D^{23}$ +60 (*c* 0.46, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07-8.14 (m, 2H), 7.70-7.82 (m, 3H), 7.52-7.62 (m, 4H), 7.32-7.47 (m, 10H), 7.06-7.11 (m, 2H), 5.90 (d, *J* = 2.7Hz, 1H, H-2), 5.71 (s, 1H, benzylidene-H), 5.55 (s, 1H, H-1), 4.93 (d, *J* = 12.8 Hz, 1H, Naphthylmethylene-*H*), 4.87 (d, *J* = 12.8 Hz, 1H, Naphthylmethylene-*H*), 4.45 (dt, *J* = 3.9, 4.7 Hz, 1H), 4.24-4.33 (m, 2H), 4.19 (dd, *J* = 3.2, 9.9 Hz, 1H), 3.92 (t, *J* = 10.2 Hz, 1H), 2.32 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1 (C=O), 138.8, 137.9, 135.7, 133.8, 133.7, 133.4, 133.2, 130.5, 130.4, 130.1, 129.6, 129.5, 128.9, 128.7, 128.5, 128.4, 128.1, 126.8, 126.7, 126.4, 126.2, 126.0, 103.3, 88.0 (C-1), 79.3, 74.7, 72.4, 72.2 (C-2), 69.0, 65.6, 21.6; HRMS (MALDI) *m*/*z* calcd for $C_{38}H_{34}NaO_6S$ $[M + Na]^+$: 641.2076 , found: 641.2105.

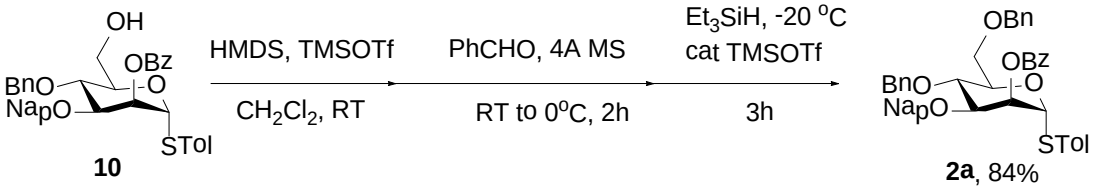
Thiomannoside 10



To a stirred suspension thiomannoside **9** (7.1 g, 12.15 mmol) in anhydrous THF was added 1.0 M Borane-THF complex (36.6 mL, 36.6 mmol), and TMSOTf (0.5 mL,

3.00 mmol). After vigorously stirred for 1h, the reaction was slowly quenched with MeOH under ice bath. The crude mixture was then concentrated for purification with flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:4) to afford thiomannoside **10** (6.8 g, 95%). For thiomannoside **10**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:4); $[\alpha]_D^{23}$ +43.3 (*c* 2.40, $CHCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.07 (m, 2H, ArH), 7.80-7.73 (m, 3H, ArH), 7.61-7.67 (m, 1H, ArH), 7.58 (tt, *J* = 7.2, 1.2 Hz, 1H, ArH), 7.39-7.50 (m, 5H, ArH), 7.27-7.37 (m, 7H, ArH), 7.05-7.15 (d, *J* = 8.0 Hz, 2H, ArH), 5.90 (dd, *J* = 1.8, 2.9 Hz, 1H, H-2), 5.52 (d, *J* = 1.5 Hz, 1H, H-1), 5.27 (s, signal arising from contamination of CH_2Cl_2), 4.97 (d, *J* = 13.7 Hz, 1H), 4.95 (d, *J* = 14.5 Hz, 1H), 4.77 (d, *J* = 14.5 Hz, 1H), 4.70 (d, *J* = 13.7 Hz, 1H), 4.26 (dt, *J* = 3.4, 9.6 Hz, 1H) 4.15 (dd, *J* = 3.0, 9.3 Hz, 1H), 4.07 (t, *J* = 9.5 Hz, 1H), 3.76-3.92 (m, 2H, OH), 2.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1 (C=O), 138.8, 138.6, 135.6, 133.84 133.7, 133.5, 133.3, 130.44, 130.36, 130.2, 129.9, 129.0, 128.9, 128.63, 128.59, 128.4, 128.3, 128.1, 127.4, 126.5, 126.5, 87.2 (C-1), 78.9, 75.8, 74.6, 73.4, 72.2, 71.2, 62.5, 21.6. HRMS (ESI) *m*/*z* calcd for $C_{38}H_{36}NaO_6S$ $[M + Na]^+$: 643.2131, found: 643.2125.

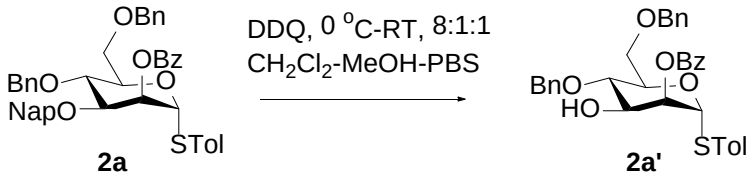
Thiomannoside 2a



TMSOTf (229 μL, 1.27 mmol) was added to a solution of thiomannoside **10** (1.57 g, 2.53 mmol) and HMDS (369 μL, 1.77 mmol) in CH_2Cl_2. After stirring for 1 h, a stream of N_2 was purged over the reaction to get rid of the ammonia byproduct generated in the silylation. Then, activated MS (500 mg) and benzaldehyde (772 μL, 7.59 mmol) were added, and the mixture was stirred at 0℃ for 1 h. Subsequently, the the reaction temperature was brought to –20 ˚C, and triethylsilane (TES) (1.2 mL, 7.59 mmol) and TMSOTf (2.29 μL, 1.27 mmol) were added. After stirring at –20 ˚C for 3 h, the desired product **2a** was formed. The crude mixture was neutralized with Et_3N and

then concentrated for purification with flash chromatography (Elution: EtOAc/CH_2Cl_2/Hexane 1:1:8) to afford thiomannoside **2a** (1.5 g, 84%). For thiomannoside **2a**, R_f 0.3 (EtOAc/CH_2Cl_2/Hexanes 1:1:8); $[\alpha]_D^{23}$ +39.0 (*c* 2.67, $CHCl_3$); ^{1}H NMR (400 MHz , $CDCl_3$): δ 8.07 (d, *J* = 7.2 Hz, 2H, ArH), 7.80-7.70 (m, 3H, ArH), 7.67-7.61 (m, 1H, ArH), 7.58-7.47 (m, 1H, ArH), 7.46-7.40 (m, 3H), 7.38-7.23 (m, 12H, ArH), 7.17-7.24 (m, 2H, ArH), 7.05 (d, *J* = 8.0 Hz, 1H, ArH), 5.92 (t, *J* = 2.1Hz, 1H, H-2), 5.59 (d, *J* = 1.5 Hz, 1H, H-1), 4.92 (d, *J* = 10.2 Hz, 1H), 4.86 (m, 2H), 4.60 (m, 1H), 4.58 (d, *J* = 10.4 Hz), 4.41 (dd, *J* = 2.5, 9.3 Hz, 1H), 4.16 (m, 2H), 3.95 (dd, *J* = 4.2, 10.9 Hz, 1H), 3.79 (dd, *J* = 1.6, 10.8 Hz, 1H), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1 (C=O), 138.9, 138.8, 138.4, 135.6, 133.72, 133.67, 133.5, 132.9, 130.4, 130.3, 128.9, 128.82, 128.78, 128.6, 128.4, 128.14, 128.10, 128.0, 127.9, 127.4, 126.6, 126.4, 126.3, 87.2 (C-1), 79.1, 75.8, 75.0, 73.9, 73.1, 72.2, 71.1, 69.6, 21.6. **HRMS** (ESI) *m*/*z* calcd for $C_{45}H_{42}NaO_6S$ $[M + Na]^+$: 733.2594 found: 733.2601.

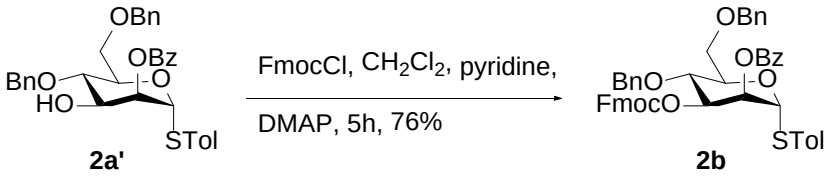
Thiomannoside 2a′



To a stirred suspension thiomannoside **2a** (3.04g, 4.28 mmol) in 8:1:1 CH_2Cl_2-MeOH-PBS (20 mL) solvent mixture was added DDQ (1.46 g, 6.42 mmol). After vigorously stirred from 0˚C to RT for 3 h, the reaction was quenched with addition of satd. $NaHCO_3$ and $Na_2S_2O_3$. The crude was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, concentrated, followed by purification with flash chromatography (Elution: EtOAc/CH_2Cl_2/Hexanes 1:1:7) to afford thiomannoside **2a′** (1.9 g, 75%). For thiomannoside **2a′**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:7); $[\alpha]_D^{23}$ +103.5 (*c* 2.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 6.4, 1.2 Hz, 2H, ArH), 7.51 (t, *J* = 7.2, 1.2 Hz, 1H, ArH), 7.22-

7.38 (m, 14H, ArH), 7.03 (d, *J* = 8.0 Hz, 2H, ArH), 5.61 (dd, *J* = 3.2, 2 Hz, 1H, H-2), 5.57 (d, *J* = 1.6 Hz, 1H, H-1), 4.83 (d, *J* = 11.2 Hz, 1H), 4.67 (dd, *J* = 13.4, 12.0 Hz, 2H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.38 (ddd, *J* = 9.6, 4.0, 1.6 Hz, 1H), 4.21 (ddd, *J* = 9.2, 4.8, 3.2 Hz, 1H) 4.06 (t, *J* = 9.2 Hz, 1H) 3.94 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.78 (dd, *J* = 11.2, 1.6 Hz, 1H) 2.62 (d, *J* = 4.8 Hz, 1H) 2.26 (s, 3H, C*H*$_3$) 2.24 (d, *J* = 5.2 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4 (C=O), 138.7 138.5, 138.2, 133.7, 132.7, 132.6, 130.27, 130.25, 130.17, 130.0, 128.9, 128.8, 128.7, 128.4, 128.3, 128.1, 127.94, 127.87, 86.80 (C-1), 77.8, 77.2, 76.2, 75.9, 74.9, 73.8, 72.7, 71.5, 69.4, 21.5 (*C*H_3). HRMS (ESI) *m*/*z* calcd for $C_{34}H_{34}NaO_6S$ $[M + Na]^+$: 593.1968, found: 593.1969.

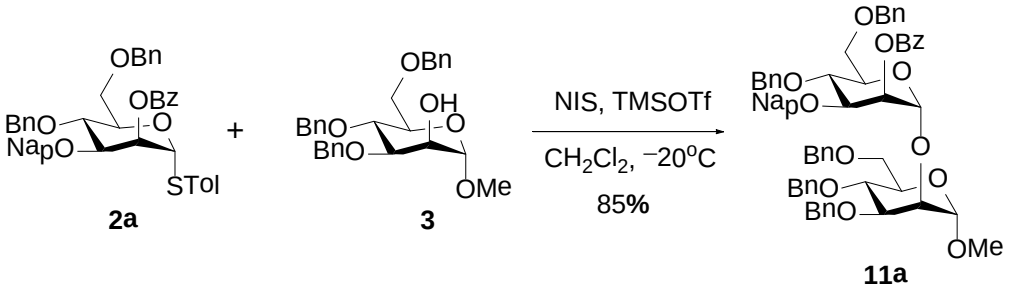
Thiomannoside 2b



To a stirred suspension thiomannoside **2a′** (393 mg, 0.69 mmol) in anhydrous solvent system (CH_2Cl_2/Pyridine = 1/1) was added FmocCl (536 mg, 2.07 mmol) and 4-Dimethylaminopyridine (DMAP) (17 mg, 0.14 mmol). After vigorously stirred for 5 h, the reaction was quenched with addition of H_2O. The crude was washed with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, concentrated, followed by purification with flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:7) to afford thiomannoside **2b** (388 mg, 76%). For thiomannoside **2b**, R_f 0.2 (EtOAc/DCM/Hexanes 1:1:7 v/v) $[\alpha]_D^{23}$ +48.6 (*c* 2.46, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (dd, *J* = 8.0, 1.2 Hz, 2H, ArH), 7.80 (d, *J* = 7.2 Hz, 1H, ArH), 7.73 (d, *J* = 5.6 Hz, 2H, ArH), 7.51-7.65 (m, 4H, ArH), 7.41-7.21 (m, 15H, ArH), 7.15 (dt, *J* = 7.2, 0.8 Hz, 1H, ArH), 7.07 (d, *J* = 8.0 Hz, 2H, ArH), 5.91 (dd, *J* = 1.3, 3.1 Hz, 1H, H-2), 5.59 (d, *J* = 1.7 Hz, 1H, H-1), 5.31 (dd, *J* = 3.1, 9.7 Hz, 1H, H-3), 5.28 (s, 1H), 4.73 (d, *J* = 11.8 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0. Hz, 1H), 4.42-4.57 (m, 3H), 4.22-4.35 (m, 2H), 3.98 (dd, *J* = 3.8, 11.0 Hz, 1H), 3.78 (dd, *J* = 1.6, 11.0 Hz,

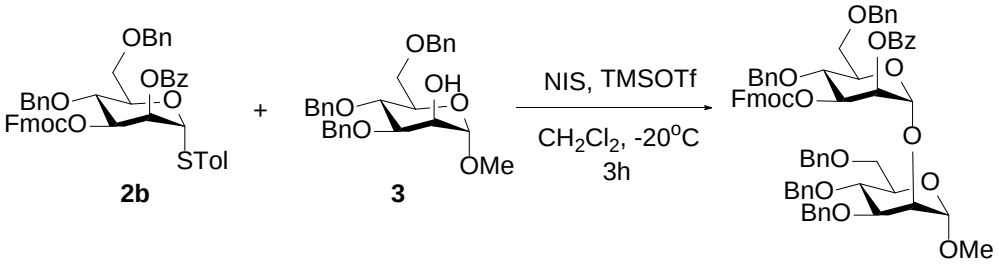
1H), 2.29 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9 (C=O), 154.7 (carbamate C=O), 144.1, 143.8, 143.6, 141.8, 141.7, 138.7, 138.6, 138.3, 133.9, 133.0, 130.5, 130.4, 120.0, 129.0, 128.8, 128.3, 128.1, 127.7, 125.8, 125.7, 125.6, 120.6, 120.5, 86.7 (C-1), 75.7, 74.0, 73.5, 73.0, 72.1, 70.8, 70.4, 69.2, 47.3, 47.2, 21.6. HRMS (ESI) *m*/*z* calcd for $C_{49}H_{44}NaO_8S$ $[M + Na]^+$: 815.2656 found: 815.2649.

Nap protected Man-α-(1→2)-Man disaccharide 11a



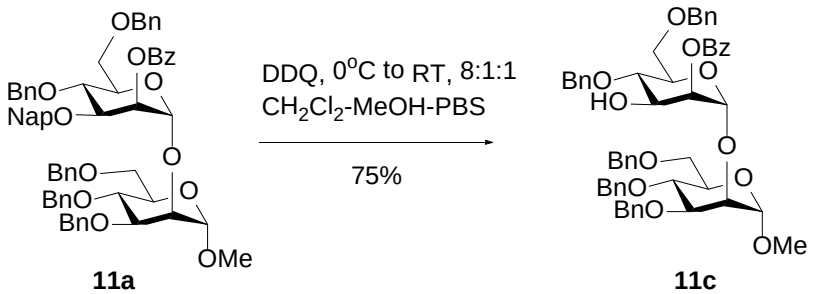
Preparation of **11a** is referred to the NIS/TMSOTf promoted glycosylation protocol. The amounts of reagents used are given as follows: thiomannoside **2a** (860 mg, 1.21 mmol), reducing end acceptor **3** (511 mg, 1.10 mmol), NIS (300 mg, 1.32 mmol), TMSOTf (43 μL, 0.33 mmol), and 4Å molecular sieves (250 mg). For disaccharide **11a**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:7 v/v); $[\alpha]_D^{23}$ −0.48 (*c* 1.67, $CHCl_3$); ^{1}H NMR (500 MHz , $CDCl_3$): δ 8.11 (t, *J* = 7.5 Hz, 2H, ArH), 7.90 (t, *J* = 7.0 Hz, 3H, ArH), 7.60 (dd, *J* = 6.5, 2.5 Hz, 1H, ArH), 7.53 (t, *J* = 7.5 Hz, 1H, ArH), 7.12-7.42 (m, 30H, ArH), 5.86 (d, *J* = 1.9 Hz, 1H, H-2′), 5.23 (s, 1H, H-1′), 4.82 (m, 2H including H-1), 4.59-4.74 (m, 5H), 4.45-4.57 (m, 4H), 4.18 (d, *J* = 5.8 Hz, 1H, H-3′), 4.01-4.11 (m, 3H), 3.86-3.94 (m, 2H), 3.77-3.83 (m, 2H), 3.66-3.75 (m, 3H), 3.26 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9 (C=O), 138.94, 138.86, 138.81, 138.7, 138.6, 136.0, 133.6, 133.5, 133.3, 130.5, 130.4, 128.8, 128.70, 128.68, 128.4, 128.31, 128.27, 128.20, 128.0, 127.92, 127.88, 127.80, 127.2, 126.5, 126.2, 126.1, 100.1 (C-1′), 100.0 (C-1), 80.2, 78.6, 75.7, 75.5, 75.4, 75.0, 74.9, 73.8, 73.7, 72.6, 72.5, 72.1, 69.7, 69.6, 55.1. HRMS (ESI) *m*/*z* calcd for $C_{66}H_{66}NaO_{12}$ $[M + Na]^+$: 1073.4446, found: 1073.4481.

Fmoc protected Man-α-(1→2)-Man disaccharide 11b



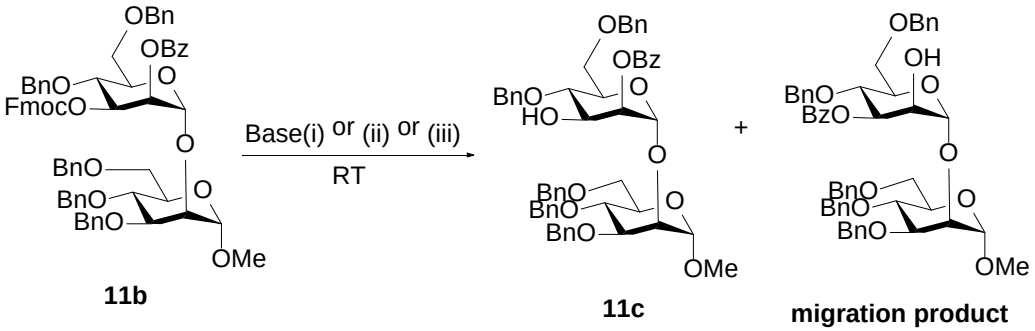
Preparation of **11b** is referred to the NIS and TMSOTf promoted glycosylation. The exact amounts of reagents used are given as follows: thiomannosyl donor **2b** (511 mg, 0.65 mmol), reducing end acceptor **3** (251 mg, 0.54 mmol), NIS (159 mg, 0.70 mmol), TMSOTf (39 μL, 0.22 mmol), and activated 4Å MS (200 mg). For disaccharide **11b**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:6 v/v) $[\alpha]_D^{23}$ +4.50 (*c* 1.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04-8.13 (m, 2H, ArH), 7.66-7.76 (m, 2H, ArH), 7.50-7.62 (m, 3H, ArH), 7.12-7.44 (m,30H, ArH), 7.04-7.10 (m, 1H, ArH), 5.91 (d, *J* = 9.4 Hz, 1H, H-2′), 5.45 (t, *J* = 8.5 Hz, 1H, H-3′), 5.20 (d, *J* = 5.6, 1H, H-1′), 4.78-4.90 (m, 3H), 4.66-4.76 (m, 2H), 4.46-4.64 (m, 7H), 4.12-4.33 (m, 4H), 4.02(d, *J* = 8.2 Hz, 1H), 3.91 (d, *J* = 5.9Hz, 3H), 3.68-3.84 (m, 4H), 3.30 (d, *J* = 7.0Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7 (C=O of Bz), 154.5 (C=O of Fmoc), 144.2, 143.6, 141.7, 141.6, 138.94, 138.85, 138.74, 138.70, 138.4, 133.7, 130.5, 130.1, 128.9, 128.8, 128.74, 128.69, 128.5, 128.21, 128.16, 128.1, 128.00, 127.98, 127.92, 127.86, 127.7, 127.6, 127.5, 125.9, 125.6, 120.4, 120.3, 100.1 (C-1′), 99.9 (C-1), 80.3, 77.0, 76.2 (C-3′), 75.6, 75.4, 75.3, 73.9, 73.7, 73.4, 72.8, 72.3, 70.6, 70.5 (C-2’), 69.8, 69.3, 55.1, 47.1. **HRMS** (ESI) *m*/*z* calcd for $C_{70}H_{68}NaO_{14}$ $[M + Na]^+$: 1155.4510, found: 1155.4501.

Man-α-(1→2)-Man disaccharide 11c from 11a



Deprotecetion of **11a** employed the same procedure as for DDQ deprotection of **2a** described before. The crude reaction mixture was purified by flash chromatography (EtOAc/CH_2Cl_2/Hexanes 1:1:5) to afford **11c**. For disaccharide **11c**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:5); $[\alpha]_D^{23}$ +18.0 (*c* 2.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.0 Hz, 2H, ArH), 7.51 (t, *J* = 7.5 Hz, 1H, ArH), 7.15-7.40 (m, 26H, ArH), 7.09-7.15 (m, 1H, ArH), 5.56 (s, 1H, H-2′), 5.18 (s, 1H, H-1′), 4.86 (d, *J* = 10.0 Hz, 2H), 4.79 (d, *J* = 11.0 Hz, 1H), 4.47-4.75 (m, 8H), 4.33 (bs, 1H, H-3′), 3.83-4.10 (m, 6H), 3.66-3.82 (m. 4H), 3.25 (s, 3H, CH_3), 2.28 (bs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3 (C=O), 138.8, 138.6, 133.5, 130.2, 130.1, 128.7, 128.63, 128.60, 128.5, 128.3, 128.1, 127.9, 127.76, 127.72, 100.0 (C-1), 99.8 (C-1′), 80.0, 76.0, 75.7, 75.4, 75.1, 75.0, 73.7, 73.6 (C-2′), 73.2, 72.5, 72.1, 72.0, 70.8 (C-3′), 69.5, 69.5, 55.0. HRMS (ESI) *m*/*z* calcd for $C_{55}H_{58}NaO_{12}$ $[M + Na]^+$: 933.3820 found: 933.3822.

Man-α-(1→2)-Man disaccharide 11c from 11b



11b **11c** **migration product**

To a stirred suspension of oligomannan dimer **11b** (124 mg, 0.11 mmol) in CH_2Cl_2, an organic base was added including piperidine (22 μL, 0.22 mmol), DBU (28 μL, 0.22 mmol) or 50% morpholine (760 μL morpholine and 760 μL CH_2Cl_2 mixture, 0.22 mmol). After vigorously stirring for 3h, the reaction was quenched with addition of H_2O. The crude was washed with H_2O, diluted HCl (0.05 N), and brine. The organic layer was dried over $MgSO_4$, concentrated, followed by chromatography purification (EtOAc/CH_2Cl_2/Hexanes 1:1:5) to afford disaccharides **11c** along with a migratory byproduct. The yields derived from the use of different bases were given in Table S1. For migration byproduct, R_f 0.1 (EtOAc/CH_2Cl_2/Hexanes 1:1:5 v/v); $[\alpha]_D^{23}$

+18.75 (*c* 2.67, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04-8.10 (m, 2H, ArH), 7.53-7.59 (m, 1H, ArH), 7.40-7.48 (m, 2H, ArH), 7.12-7.38 (m, 24H, ArH), 7.04-7.10 (m, 2H, ArH), 5.58 (m, 1H, H-3′), 5.08 (s, 1H, H-1′), 4.82 (d, *J* = 9.9 Hz, 2H), 4.56-4.71 (m, 6H), 4.45-4.55(m, 3H), 4.34 (s, 1H, H-2′), 4.05-4.13 (m, 2H), 4.02 (s, 1H), 3.81-3.92 (m, 2H), 3.66- 3.79 (m, 5H), 3.26 (s, 3H, CH_3), 2.30 (bs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9 (C=O), 139.0, 138.9, 138.8, 138.5, 138.2, 133.6, 130.5, 130.4, 130.2, 128.9, 128.9, 128.80, 128.75, 128.71, 128.5, 128.4, 128.3, 128.1, 128.04, 127.99, 127.8, 102.3 (C-1′), 100.2 (C-1), 80.4, 76.2, 75.6, 75.4, 75.0, 74.9 (C-3′), 73.9, 73.8, 73.7, 72.9, 72.3, 72.0, 70.0 (C-2’), 69.9, 69.3, 55.1.

Table S1. Fmoc deprotection for disaccharide**11b**

Entry	Base	Time (h)	*T* (°C)	Product [a]	
				11c (%)	Migration product (%)
1	piperidine	3	25	35	36
2	piperidine	3	0	33	37
3	DBU	1	25	35	32
4	morpholine	3	25	70	10

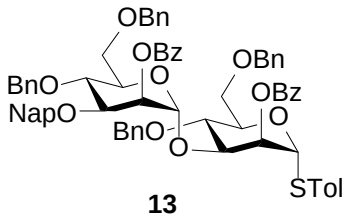
[a] 1.0 Equiv of **11b** and 1.5 equiv of base were used in al entries.

Man-α-(1→3)-Man disaccharide 12

Preparation of **12** is referred to the DMF-modulated glycosylation procedure. The amounts of reagents used are given as follows: thiomannoside donor **1** (370 mg, 0.56 mmol), thiomannoside acceptor **2a** (245 mg, 0.43 mmol), NIS (136 mg, 0.6 mmol), TfOH (58 μL, 0.65 mmol), DMF (43 μL, 0.56 mmol), and 4Å MS (450 mg). For disaccharide **12**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:9); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.04 (d, *J* = 10.8 Hz, 4H, ArH), 7.54 (m, 2H), 7.36-7.03 (m, 33H), 5.74 (d, *J* = 2.4 Hz, 1H), 5.65 (d, *J* = 2.4 Hz, 1H), 5.60 (s, 1H), 5.37 (s, 1H), 4.86-4.67 (m, 4H), 4.64-4.58 (m, 2H), 4.54-4.46 (m, 3H), 4.41-4.33 (m, 3H), 4.29-4.22 (m, 1 H), 4.17-4.09 (m, 1H),

4.01-3.92 (m, 3H), 3.77-3.67 (m, 3H), 2.27 (s, 3H, OC*H*$_3$); **^{13}C NMR (100 MHz, CDCl$_3$)**: δ 166.1 (C=O), 165.9 (C=O), 139.0, 138.7, 138.3, 138.2, 133.7, 133.6, 130.4, 130.24, 130.18, 129.0, 128.9, 128.8, 128.7, 128.62, 128.58, 128.48, 128.3, 128.2, 128.0, 127.9, 127.8, 100.2 (C-1′), 86.7 (C-1), 78.4, 78.2, 75.9, 75.3, 75.1, 74.4, 74.3, 73.8, 73.1, 73.0, 72.1, 69.6, 69.3, 69.0, 21.5 (*C*H$_3$). HRMS (ESI) *m*/*z* calcd for $C_{68}H_{66}NaO_{12}S$ $[M + Na]^+$: 1130.4201, found: 1129.4214.

Man-α-(1→3)-Man disaccharide 13

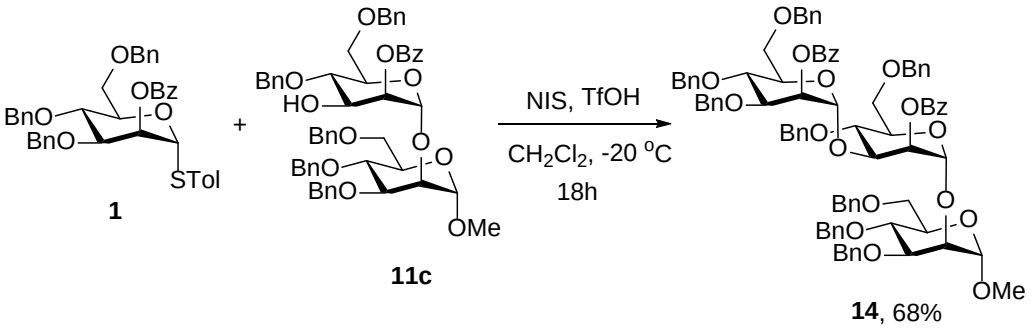


13

Preparation of disaccharide **13** is referred to the DMF-modulated glycosylation procedure. The exact amounts of reagents are given as follows: thiomannosyl donor **2** (376 mg, 0.53 mmol), thiomannosyl acceptor **2′** (251 mg, 0.44 mmol), NIS (129 mg, 0.57 mmol), TfOH (58 μL, 0.66 mmol), DMF (44 μL, 0.57 mmol), and 4Å MS (400 mg). The isolation yield of **13** was 75%. For disaccharide **13**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:7); $[\alpha]_D^{23}$ +8.9 (*c* 1.80, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97-8.11 (m, 4H, ArH), 7.69 (d, *J* = 7.5 Hz, 1H, ArH), 7.61-7.58 (m, 2H, ArH), 7.56-7.48 (m, 3H, ArH), 7.44-7.25 (m, 23H, ArH), 7.23-7.16 (m, 4H, ArH), 7.12-7.01 (m, 4H, ArH), 5.74 (s,1H, H-2), 5.70 (s, 1H, H-2′), 5.59 (d, *J* = 2.4 Hz, 1H, H-1), 5.36 (d, *J* = 1.8 Hz, 1H, H-1′), 4.83 (dd, *J* = 3.6, 11.2 Hz, 1H), 4.80-4.73 (m, 3H), 4.68 (dd, *J* = 3.0, 11.8 Hz, 1H), 4.56-4.44 (m, 5H), 4.31-4.39 (m, 2H), 4.22 (dt, *J* = 5.8, 9.5, Hz, 1H), 4.16 (dt, *J* = 5.8, 9.5, Hz, 1H), 4.05 (dt, *J* = 2.1, 9.5 Hz, 1H, H-3′), 3.96-3.87 (m, 2H), 3.77-3.66 (m, 3H), 2.28 (s, 3H, C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.1 (C=O), 166.0 (C=O), 139.0, 138.8, 138.3, 138.2, 135.9, 133.7, 133.6, 133.3, 132.8, 130.4, 130.3, 130.2, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.03, 127.98, 127.8, 126.9, 126.34, 126.29, 126.1, 100.3 (C-1′), 86.7 (C-1), 78.6 (C-3′), 78.4 (C-3), 75.9, 75.3, 75.2, 74.40, 74.35, 73.9 (C-2′), 73.2, 73.1, 72.1, 69.7 (C-2), 69.3, 69.0, 21.5 (*C*H$_3$).

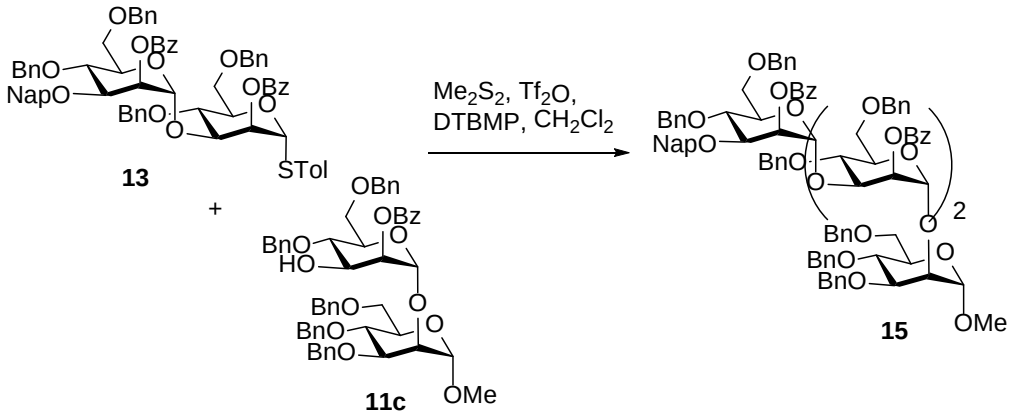
HRMS (ESI) *m*/*z* calcd for $C_{72}H_{68}NaO_{12}S$ [M + Na]$^+$: 1179.4324, found: 1179.4327.

Oligomannan trimer 14



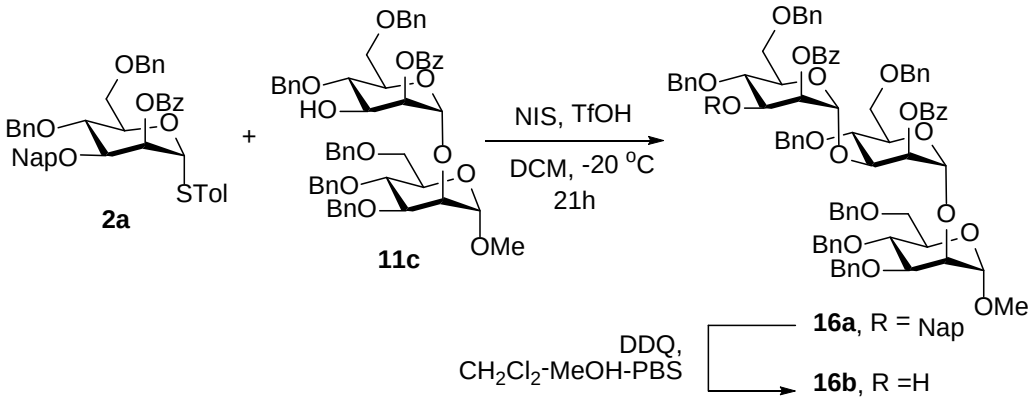
Procedure for preparation of oligomannan trimer **14** is referred to the NIS and TfOH promoted glycosylation method. The exact amounts of reagents used are given as follows: thiomannosyl donor **1** (335 mg, 0.51 mmol), disaccharide acceptor **11c** (395 mg, 0.42 mmol), NIS (69 mg, 0.55 mmol), TfOH (11 μL, 0.13 mmol), and 4Å MS (350 mg). For oligomannan trimer **14** (68%), R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:5); $[\alpha]_D^{23}$ –12.0 (*c* 1.33, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (m, 4H, ArH), 7.70 (d, *J* = 3.0 Hz, 1H, ArH), 7.60-7.50 (m, 4H, ArH), 7.29-7.04 (m, 41H, ArH), 5.73 (s, 1H, H-2″), 5.67 (s, 1H, H-2′), 5.32 (s, 1H, H-1″), 5.23 (s, 1H, H-1′), 4.75-4.86 (m, 4H including H-1), 4.45-4.71 (m, 11H), 4.41 (dd, *J* = 2.9, 9.2 Hz, 1H), 4.36 (d, *J* = 11.3 Hz, 1H), 4.30 (d, *J* = 11.9 Hz, 1H), 4.11-4.19 (m, 2H), 3.82-4.07 (m, 6H), 3.67-3.78 (m, 5H), 3.61 (dd, J = 11.1, 30.1 Hz, 2H), 3.25 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.0 (C=O), 165.9 (C=O), 139.2, 139.1, 138.92, 138.89, 138.87, 138.80, 138.5, 138.4, 133.6, 133.5, 130.43, 130.39, 130.3, 129.0, 128.89, 128.85, 128.82, 128.80, 128.72, 128.66, 128.63, 128.57, 128.50, 128.42, 128.39, 128.2, 128.10, 128.04, 128.00, 127.90, 127.83, 127.79, 127.75, 127.71, 100.1 (C-1″), 100.0 (C-1), 99.8 (C-1′), 79.8, 78.5 (C-3″), 78.2 (C-3′), 76.6, 75.7, 75.6, 75.24, 75.19, 75.10, 74.3, 73.9, 73.73, 73.67, 73.0, 72.7, 72.5 (C-2′), 72.3, 72.07, 71.97, 69.8, 69.7, 69.5 (C-2″), 68.9, 55.2 (O*C*H$_3$). HRMS (ESI) *m*/*z* calcd for $C_{89}H_{90}NaO_{18}$ [M + Na]$^+$: 1469.6019, found: 1469.6038. Partial assignment of NMR signals is based on 2D COSY, HSQC, and HMBC experiments.

Oligomannan tetramer 15



Procedure for preparation of oligomannan tetramer **15** is referred to the Me_2S_2-Tf_2O promoted glycosylation. The exact amounts of reagents are given as follows: Man-α-(1→3)-Man disaccharide donor **13** (128 mg, 0.11 mmol), disaccharide acceptor **11c** (77 mg, 0.09 mmol), Me_2S_2-Tf_2O (128 μL 1.0 M stock solution, 0.13 mmol), and DTBMP (25 mg, 0.09 mmol). The tetramer **15** was obtained as a white glassy solid (141 mg, 85%) after column chromatography purification. For **15**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:6); $[\alpha]_D^{23}$ – 33.6 (*c* 2.80, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94-8.09 (m, 6H, ArH), 7.65-7.72 (m, 1H, ArH), 7.43-7.62 (m, 6H, ArH), 7.00-7.42 (m, 54H, ArH), 5.61 (s, 3H, unresolved H-2′, H-2″, and H-2‴), 5.34 (s, 1H, H-1‴), 5.21 (s, 1H, H-2″), 5.14 (s, 1H, H-1′), 4.96 (d, *J* = 13.0 Hz, 1H), 4.84-4.81 (m, 2H included H-1), 4.75 (d, *J* = 15.5 Hz, 1H), 4.69-4.37 (m, 14H), 4.29-4.09 (m, 6H), 4.06-3.93 (m, 4H), 3.88-3.67 (m, 9H), 3.62-3.50 (m, 3H), 3.37 (d, *J* = 10.9 Hz, 1H), 3.26-3.24 (m, 4H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 166.1 (C=O), 165.9 (C=O), 165.7 (C=O), 139.1, 139.0, 138.9, 138.8, 138.6, 138.4, 136.0, 133.6, 133.4, 133.3, 130.4, 130.3, 130.2, 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.00, 127.97, 127.91, 127.81, 127.77, 127.70, 126.9, 126.3, 126.2, 126.1, 100.2 (C-1′), 100.0 (C-1), 99.7 (unresolved C-1‴ and C-1″), 80.1, 79.8, 78.5, 78.3, 78.0, 76.6, 76.1, 75.6, 75.2, 75.2, 75.1, 74.6, 74.2, 73.8, 73.74, 73.65, 73.0, 72.9, 72.7, 72.4, 72.3, 72.1, 72.0, 69.8, 69.5, 68.8, 55.2 (O*C*H$_3$). **HRMS** (ESI) *m*/*z* calcd for $C_{120}H_{118}NaO_{24}$ $[M + Na]^+$: 1965.8057, found: 1965.7913. Partial assignment of NMR signals is based on 2D COSY, HSQC, and reference to the signal assignment of trimer **14**.

Oligomannan trimers 16a and 16b

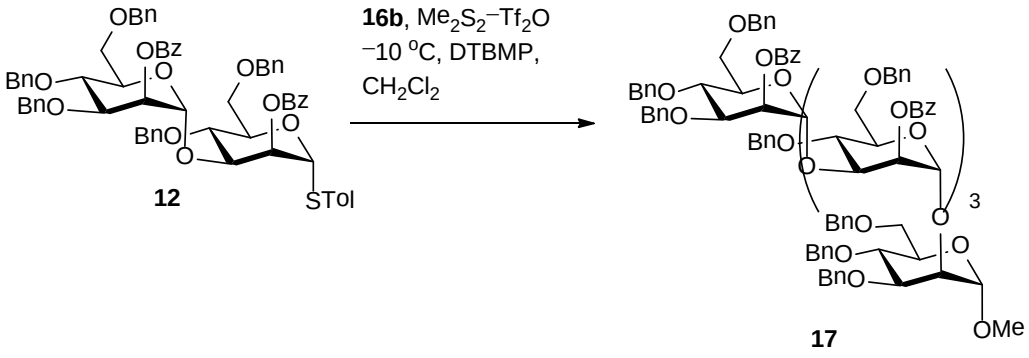


Procedure for preparation of oligomannan trimer **16a** is referred the NIS and TfOH glycosylation protocol. The exact amounts of reagents used are given as follows: thiomannosyl donor **2a** (835 mg, 1.2 mmol), disaccharide acceptor **11c** (730 mg, 0.8 mmol), NIS (290 mg, 1.3 mmol), TfOH (21.0 μL, 0.24 mmol), and 4Å MS (1.5 g). For oligomannan trimer **16a**, R_f 0.2 (EtOAc/CH_2Cl_2/Hexanes 1:1:8 v/v); $[\alpha]_D^{23}$ –20.0 (*c* 0.80, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (bs, 4H, ArH), 7.70 (d, *J* = 2.0 Hz, 1H, ArH), 7.62-7.60 (m, 2H, ArH), 7.54-7.50 (m, 3H, ArH), 7.38-7.04 (m, 42H, ArH), 5.72 (s, 1H, H-2″), 5.67 (s, 1H, H-2′), 5.31 (s, 1H, H-1″), 5.23 (s, 1H, H- 1′), 4.86-4.77 (m ,5H), 4.70-4.49 (m, 11H), 4.41 (broad m, 1H, H-3′), 4.33-4.31 (m, 1H), 4.22-4.20 (m, 1H), 4.12-4.07 (m, 3H), 3.96-3.59 (m, 11H), 3.23 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.5 (C=O), 165.4 (C=O), 138.7, 138.5, 138.4, 138.2, 137.8, 135.5, 133.11, 133.09, 133.00, 132.8, 129.9, 129.82, 129.76, 128.43, 128.31, 128.29, 128.2, 128.14, 128.13, 128.1, 128.0, 127.9, 127.83, 127.81, 127.79, 127.72, 127.51, 127.49, 127.42, 127.29, 127.27, 127.25, 127.20, 126.4, 125.9, 125.7, 125.6, 99.6 (C-1″), 99.5 (C-1), 99.2 (C-1′), 79.2, 78.0 (C-3″), 77.7 (C-3′), 76.0, 75.2, 75.1, 74.74, 74.67, 74.58, 73.8, 73.4, 73.22, 73.16, 73.0, 72.5, 72.2 (C-2′), 71.9, 71.8 (C-2″), 71.6, 71.5, 69.3, 69.1 69.0, 54.7 (O*C*H$_3$). HRMS (ESI) *m*/*z* calcd for $C_{93}H_{92}NaO_{18}S$ $[M + Na]^+$: 1519.6165, found: 1519.6176. Partial assignment of NMR signals is based on 2D COSY, HSQC, and HMBC spectroscopy.

Procedure for preparation of **16b** is the same as the DDQ deprotection procedure

for **11a**. For oligomannan trimer **16b**, R_f 0.25 (EtOAc/CH_2Cl_2/Hexanes 1:1:5 v/v); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, J = 3.5 Hz, 2H, ArH), 7.98 (d, J = 3.5 Hz, 2H, ArH), 7.59 (t, J = 6.0 Hz, 1H, ArH), 7.54 (t, J = 6.0 Hz, 1H, ArH), 7.41-7.08 (m, 39H, ArH), 5.61 (s, 1H, H-2′), 5.42 (s, 1H, H-2″), 5.27 (s, 1H, H-1″), 5.20 (s, 1H, H-1′), 4.87-4.83 (m, 3H including H-1 at 4.83), 4.78-4.68 (m, 3H), 4.66-4.62 (m, 3H), 4.60-4.49 (m, 6H), 4.40 (dd, J = 7.5, 2.0 Hz, 1H, H-3′), 4.32 (d, J = 10.0 Hz, 1H), 4.17-4.12 (m, 2H, included H-4′ and H-3″), 4.06 (t, J = 8.0 Hz, 2H), 3.96 (bs, 1H, H-2), 3.90 (dd, J = 7.5, 2.5 Hz, 2H), 3.85 (dd, J = 9.0, 3.0 Hz, 1H), 3.79 (t, J = 8.0 Hz, 1H), 3.74-3.64 (m, 6H), 3.26 (s, 3H, OCH_3), 2.06 (s, 1H, OH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.8 (C=O), 165.6 (C=O), 138.44, 138.42, 138.41, 138.38, 138.37, 138.30, 137.9, 129.89, 129.85, 129.81, 129.7, 128.5, 128.4, 128.3, 128.25, 128.23, 128.20, 128.18, 128.0, 127.79, 127.73, 127.66, 127.60, 127.52, 127.49, 127.40, 127.2, 99.6 (C-1), 99.44 (C-1″), 99.40 (C-1′), 79.3, 77.2 (C-3′ overlapped with solvent $CDCl_3$, indicated by HSQC and HMBC), 76.3 (C-2), 75.2, 75.1, 75.0, 74.84, 74.82 (C-4′), 74.0, 73.38, 73.36, 73.2, 72.6 (C-2″), 72.34 (C-2′), 72.25, 72.00, 71.98, 71.0, 70.0 (C-3″), 69.4, 69.1, 68.5, 54.7 (OCH_3). HRMS (ESI) m/z calcd. for C_{82} H_{85} O_{18} $[M + H]^+$: 1357.5730, found: 1357.5753. Partial assignment of NMR signals is based on 2D COSY, HSQC, and HMBC spectroscopy.

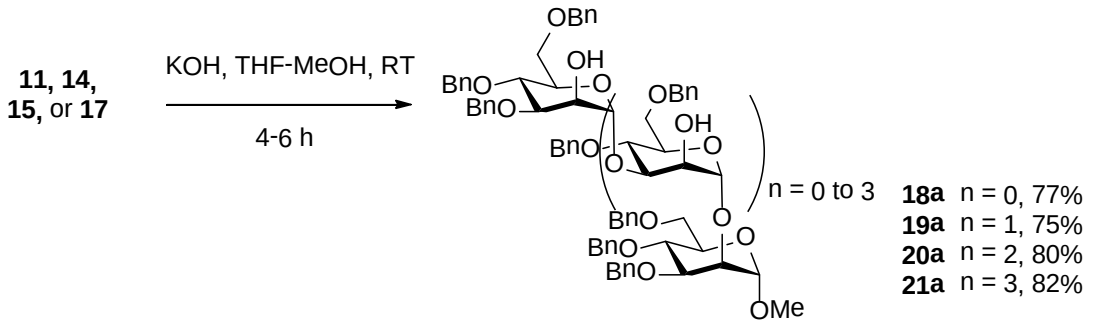
Oligomannan pentamer 17



Procedure for preparation of oligomannan pentamer **17** is referred to the Me_2S_2–Tf_2O promoted glycosylation. The exact amounts of reagents are given as

follows: thiodisaccharide donor **12** (277 mg, 0.25 mmol), trisaccharide acceptor **16b** (250 mg, 0.18 mmol), Me_2S_2–Tf_2O (400 μL 1.0 M stock solution, 0.40 mmol), DTBMP (55 mg, 0.27 mmol), and 4Å MS (300 mg). The crude glycosylation yield of **17** was 243 mg, 57%. HRMS (MALDI) *m*/*z* calcd for $C_{143}H_{142}NaO_{30}$ $[M + Na]^+$: 2361.9478, found: 2361.9534. Noted due to the presence of some inseparable contaminants, NMR spectroscopic data were obtained after deprotection of the Bz functions (refer to partial deprotected pentamer **21a**).

Oligomannan dimer 18a, trimer 19a, tetramer 20a, and pentamer 21a



To a stirred suspension of oligomannans **11**, **14**, **15** or **17** (1.0 equiv) in 3:1 THF/MeOH was added potassium hydroxide (3-5 equiv). The mixture was vigorously stirred at RT for couple of hours, and was diluted with CH_2Cl_2 followed by washing with H_2O, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$, filtered, concentrated for chromatography purification (EtOAc/CH_2Cl_2/Hexanes 1:1:4 for **18a** and **19a**, EtOAc/Hexanes 1:4 for **20a**, and EtOAc/CH_2Cl_2/Hexanes 1:1:3 for **21a**) to target oligomannans **18–21a** (77% for **18a**, 75% for **19b**, 80% for **20a** and 82% for **21a**).

For oligomannan dimer **18a**, R_f 0.1 (EtOAc/CH_2Cl_2/Hexanes 1:1:4); $[\alpha]_D^{23}$ +26.4 (*c* 3.33, $CHCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69-7.80 (m, 4H, ArH), 7.12-7.40 (m, 28H, ArH), 5.15 (s, 1H, H-1′), 4.72-4.90 (m, 4H, including H-1), 4.60-4.71 (m, 5H), 4.42-4.57 (m, 4H), 4.18 (s, 1H, H-2′), 3.83-4.07 (m, 5H), 3.65-3.81 (m, 6H), 3.23 (s, 3H, (OC*H*$_3$), 2.54 (bs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 138.9, 138.8, 138.7, 138.6, 135.9, 133.6, 133.4, 128.91, 128.85, 128.72, 128.71, 128.6, 128.5, 128.32, 128.29, 128.25, 128.21, 128.1, 128.00, 127.98, 127.96, 127.83, 127.78, 127.0, 126.6,

126.4, 126.2, 101.6 (C-1′), 100.2 (C-1), 80.6, 80.4, 80.1, 75.4, 75.2, 74.9, 73.8, 73.7, 72.62, 72.60, 72.3, 72.1, 72.0, 69.7, 69.6, 69.0, 55.1 (O*C*H$_3$). HRMS (ESI) *m*/*z* calcd for $C_{59}H_{62}NaO_{11}$ $[M + Na]^+$: 969.4184, found: 969.4176.

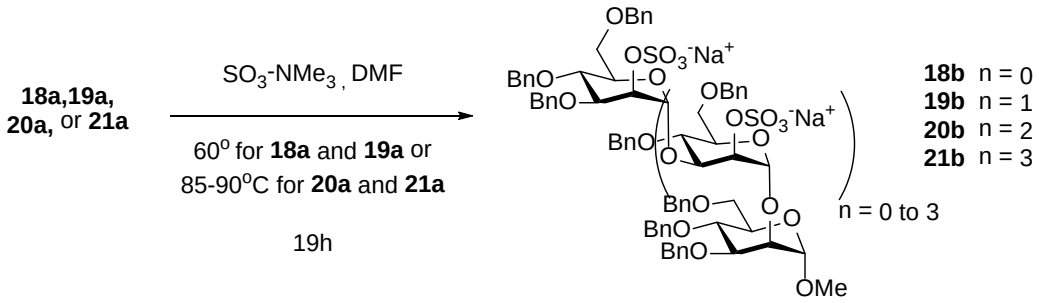
For oligomannan trimer **19a**, R_f 0.1 (EtOAc/CH_2Cl_2/Hexanes 1:1:6); $[\alpha]_D^{23}$ +43.8 (*c* 0.86, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21-7.35 (m, 32H), 7.12-7.20 (m, 8H), 5.03 (d, *J* = 1.2 Hz, 1H, H-1″), 4.97 (d, *J* = 1.4 Hz, 1H, H-1′), 4.86 (d, *J* = 10.8 Hz, 1H), 4.80 (m, 2H, included H-1), 4.59-4.70 (m, 5H), 4.49-4.58 (m, 5H), 4.44-4.48 (m, 3H), 4.38-4.42 (m, 2H), 4.34 (s, 1H, H-2′), 4.27 (t, *J* = 8.7 Hz, 1H, H-3′ based on COSY), 4.02 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.99 (t, *J* = 2.5 Hz, 1H, H-2 based on HSQC and HMBC), 3.96 (t, *J* = 2.5 Hz, 1H, H-2″), 3.95-3.92 (m, 1H), 3.88 (dd, *J* = 3.0, 9.5 Hz, 1H), 3.77-3.84 (m, 4H), 3.66-3.76 (m, 6H), 3.59 (t, *J* = 9.1 Hz, 1H), 3.46 (t, *J* = 9.4 Hz, 1H), 3.21 (s, 3H, OC*H*$_3$), 2.40 (bs, 1H, OH), 1.82 (bs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$); δ 139.1, 139.0, 138.94, 138.85, 138.8, 138.3, 138.1, 137.6, 130.0, 128.9, 128.80, 128.76, 128.73, 128.70, 128.5, 128.43, 128.36, 128.35, 128.33, 128.27, 128.25, 128.21, 128.1, 128.02, 127.97, 127.92, 127.90, 127.8, 102.6 (C-1′ based on HSQC and HMBC), 100.3 (C-1), 100.2 (C-1″), 83.0, 80.5, 80.1, 75.52, 75.47, 75.4, 75.3, 75.13, 75.10, 74.3, 73.9, 73.8, 73.7, 72.5, 72.4, 72.1, 71.9 (C-3′), 69.84, 69.79, 69.6, 69.4 (C-2′), 69.3 (C-2″), 55.1 (O*C*H$_3$). HRMS (ESI) *m*/*z* calcd for $C_{75}H_{82}NaO_{16}$ $[M + Na]^+$: 1261.5495, found: 1261.5501.

For oligomannan tetramer **20a**, R_f 0.18 (EtOAc/Hexanes 1:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (t, *J* = 10 Hz, 2H, ArH), 7.67 (s, 1H, ArH), 7.61 (d, *J* = 7.5 Hz, 1H, ArH), 7.43-7.34 (m, 5H, ArH), 7.31-7.15 (m, 39H, ArH), 7.11-7.09 (m, 2H, ArH), 4.94 (d, *J* = 1.5 Hz, 1H), 4.93 (s, 1H), 4.87-4.83 (m, 3H), 4.74-4.71 (m, 3H), 4.67 (s, 1H, H-1 based on HSQC), 4.66-4.59 (m, 4H), 4.55 (s, 1H), 4.53-4.51 (m, 2H), 4.50-4.46 (m, 3H), 4.44-4.40 (m, 5H), 4.29-4.22 (m, 4H), 4.18 (bs, 1H, H-2 based on HSQC and COSY), 3.99-3.94 (m, 4H), 3.90-3.88 (m, 2H), 3.84-3.76 (m, 5H), 3.77-3.69 (m, 5H), 3.66 (d, *J* = 10 Hz, 1H), 3.62 (d, *J* = 10 Hz, 1H), 3.54 (t, *J* = 9.0 Hz, 1H), 3.47 (t, *J* = 9.0 Hz, 1H), 3.41 (t, *J* = 9.0 Hz, 1H), 3.21 (s, 3H, OC*H*$_3$), 2.47 (bs, 1H, OH), 1.79 (m, 2H. OH × 2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.41, 139.39, 139.38, 138.35,

138.30, 137.9, 137.8, 137.2, 137.0, 134.9, 133.1, 133.0, 128.6, 128.39, 128.38, 128.35, 128.31, 128.22, 128.20, 128.1, 127.90, 127.86, 127.83, 127.78, 127.75, 127.70, 127.61, 127.58, 127.56, 127.49, 127.46, 127.43, 126.3, 126.0, 125.6, 100.6 (C-1 based on HSQC), 100.2, 99.7, 82.8, 82.1, 80.0, 79.6, 75.2, 75.02, 75.00, 74.91, 74.8, 74.6, 73.88, 73.81, 73.7, 73.4, 73.3, 73.2, 72.1, 72.0, 71.6, 71.5, 71.4, 69.5, 69.4, 69.37, 69.29, 69.04, 68.9, 54.6 (O*C*H_3). The tetramer **20a** obtained was converted to **20b** and HRMS analysis was not performed for this intermediate.

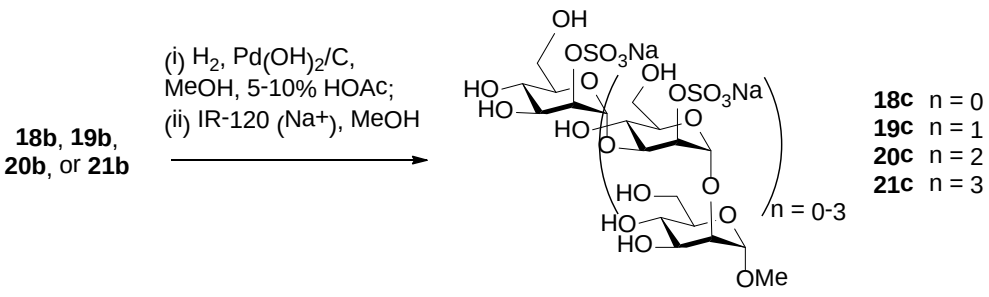
For oligomannan pentamer **21a**, R_f 0.1 (EtOAc/CH_2Cl_2/Hexanes 1:1:3); $[\alpha]_D^{23}$ +18.9 (*c* 1.33, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35-7.14 (m, 60H, ArH), 4.95 (d, *J* =1.2 Hz, 1H, anomeric H based on HSQC), 4.94 (d, *J* =1.2 Hz, 1H, anomeric H based on HSQC), 4.86 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* =1.2 Hz, 1H, anomeric H based on HSQC), 4.79 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 1.8 Hz, 1H), 4.715-4.713 (m, 2H, including an anomeric H), 4.68 (bs, 1H, H-1 based on HSQC and COSY), 4.66 (d, *J* = 2.4 Hz, 1H), 4.64-4.58 (m, 5H), 4.563-4.553 (m, 3H), 4.52 (dd, *J* = 11.0, 1.8 Hz, 2H), 4.49 (d, *J* = 1.8 Hz, 1H), 4.46-4.37 (m, 11H), 4.30 (bs, 1H), 4.26-4.20 5H), 4.15 (bs, 1H, H-2 based on COSY), 3.99-3.96 (m 6H), 3.92 (dd, *J* = 9.0, 3.0 Hz, 2H), 3.88 (dd, *J* = 9.0, 3.0 Hz, 2H), 3.82-3.78 (m, 4H), 3.74-3.68 (m, 9H), 3.62-3.56 (m, 4H), 3.45 (dd, *J* = 8.4, 1.8 Hz, 2H), 3.41 (dd, *J* = 9.6, 1.2 Hz, 2H), 3.21 (s, 3H, OC*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$): δ 138.5, 138.44, 138.40, 138.35, 138.0, 137.9, 137.8, 137.5, 137.3, 137.2, 137.0, 128.56, 128.55, 128.50, 128.44, 128.42, 128.39, 128.37, 128.36, 128.27, 128.24, 128.20, 128.10, 128.06, 128.00, 127.97, 127.96, 127.87, 127.80, 127.79, 127.75, 127.69, 127.62, 127.60, 127.52, 127.50, 127.45, 127.37, 102.4 (anomeric C based on HSQC), 101.4 (anomeric C based on HSQC), 100.9 (C-1 based on HSQC and COSY), 100.3 (anomeric C based on HSQC), 99.8 (anomeric C based on HSQC), 82.9, 82.6, 82.1, 80.0, 79.7, 75.3, 75.2, 75.07, 75.03, 74.99, 74.90, 74.5, 74.07, 74.06, 73.9, 79.7, 73.54, 73.46, 73.3, 73.2, 72.03, 72.00, 71.64, 71.58, 71.55, 69.7, 69.61, 69.58, 69.50 (C-2 based on HSQC and COSY), 69.43, 69.40, 69.3, 69.0, 68.9, 54.6 (O*C*H_3). HRMS (ESI) *m*/*z* calcd for C_{115} H_{127} O_{26} $[M + H]^+$: 1924.8644, found: 1924.8679.

Oligomannans 18b-20b



To a stirred suspension of oligomannan **18a**, **19a**, **20a**, or **21a** (1.0 equiv.) in anhydrous DMF was added SO_3–trimethylamine (TMA) complex (*ca.* 1.5–2.0 equiv. per OH), and the mixture was stirred vigorously at 60℃ (for **18a** and **19a**) or 85–90℃ (for **20a** and **21a**) for 5–10 h, the reaction was diluted CH_2Cl_2 and washed with brine (× 4) to remove DMF. The organic phase was treated with IR-120 (Na+ form) for 4 h and filtered, then concentrated for flash column chromatography (CH_2Cl_2/MeOH 1:9 for **18b** and **19b**; EtOAc/CH_2Cl_2/MeOH 2.5:1.5:0.3 for **20b** and **21b**) to produce the oligomannans **18–21b** (74% for **18b**, 87% for **19b**, 80% for **20b**, and 78% for **21b**). The identities of the **18b** and **21b** intermediates were confirmed by HRMS. For oligomannan dimer **18b**, HRMS (ESI) *m*/*z* calcd for $C_{59}H_{61}Na_2O_{14}S$ $[M + Na]^+$: 1071.3578, found: 1071.3572. For oligomannan trimer **19b**, **HRMS** (ESI) *m*/*z* calcd for $C_{75}H_{80}Na_3O_{22}S_2$ $[M + Na]^+$: 1465.4270, found: 1465.4280. The oligomannan tetramer **20b** and pentamer **21b** obtained were subjected to hydrogenolysis without characterization.

Fully deprotected oligomannans 18c, **19c, 20c, and 21c**



To a solution of oligomannan **18b**, **19b**, **20b** or **21b** in MeOH with *ca.* 5-10% acetic acid was added $Pd(OH)_2/C$ (50-100 mol% with respect to oligomannan). The reaction mixture was degased with N_2 for 10 min and the reaction mixture was then stirred at RT under H_2 (1 atm) for 10 h. The crude mixture was filtered over celite to obtain the filtrate, which was treated with IR-120 (Na^+) for 4 h and concentrated for purification with FPLC on Superdex 30 prep grade gel from TOSOH (size range:100-7000 Da) (Elution: 1:1 MeOH/H_2O) to afford the deprotected oligomannans **18c–21c** (83% for **18c**, 78% for **19c**, 70% for **20c**, and 80% for **21c**).

For oligomannan dimer **18c**, R_f 0.3 (EtOAc/MeOH/H_2O 4:2:1 v/v); $[\alpha]_D^{23}$ +33.8 (*c* 0.53, CH_3OH): ^1H NMR (500 MHz, D_2O): δ 5.35 (d, *J* = 1.4 Hz, 1H, H-1′), 5.02 (d, *J* = 1.2 Hz, 1H, H-1), 4.70 (m, 1H, H-2′), 4.01 (d, *J* = 3.1 Hz, 1H, H-2), 3.99 (d, *J* = 3.1 Hz, 1H, H-3′), 3.86-3.95 (m, 3H), 3.75-3.84 (m, 3H), 3.71 (t, *J* = 11.3 Hz, 1H), 3.61-3.67 (m, 2H), 3.43 (s, 3H, CH_3); ^{13}C NMR (125 MHz, D_2O): δ 99.7 (C-1′), 99.2 (C-1), 78.8 (C-2), 76.7 (C-2′), 73.2, 72.5, 70.0, 68.8 (C-3′), 66.9, 66.7, 60.90, 60.86, 54.8. **HRMS** (ESI) *m*/*z* calcd for $C_{13}H_{23}Na_2O_{14}S$ $[M + Na]^+$: 481.0598, found: 481.0599. Partial assignment of NMR signals is based on 2D COSY, HSQC, and HMBC spectroscopy.

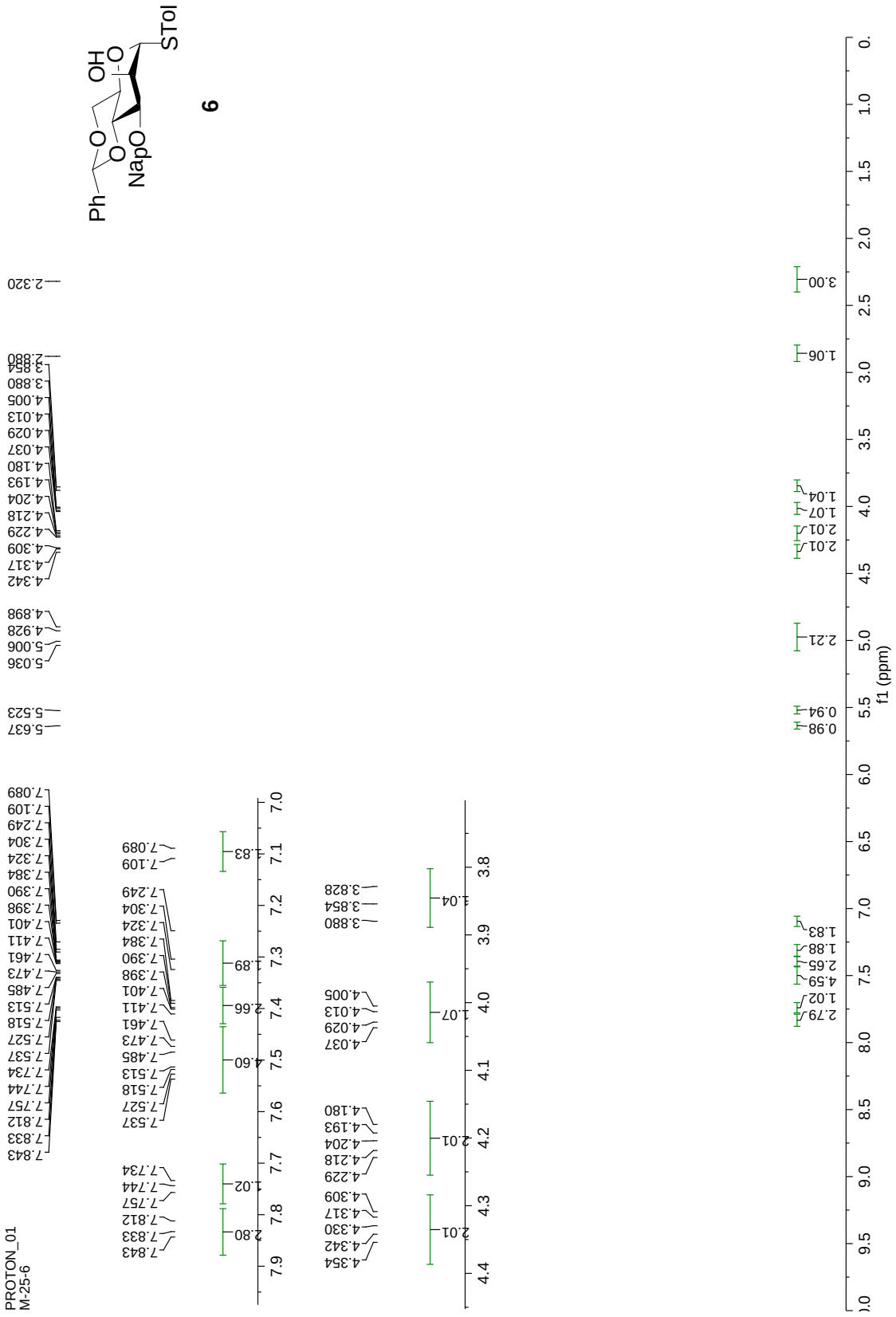
For oligomannan trimer **19c**, R_f 0.3 (EtOAc/MeOH/H_2O 4:2:1 v/v); $[\alpha]_D^{23}$ +39.5 (*c* 2.93, CH_3OH); ^1H NMR (500 MHz, D_2O): δ 5.53 (s, 1H, H-1″), 5.39 (s, 1H, H-1′), 5.01 (s, 1H, H-1), 4.79 (m, 1H, H-2′, overlapped with residual signal from *d*-solvent), 4.70 (s, 1H, H-2″), 4.18 (d, *J* = 9.3 Hz, 1H, H-3′), 4.06 (d, *J* = 9.3 Hz, 1H, H-3″), 4.04 (s, 1H, H-2), 3.87-4.01 (m, 5H), 3.75-3.86 (m, 5H), 3.58-3.74 (m, 3H), 3.44 (s, 3H, CH_3); **^{13}C NMR** (125 MHz, D_2O): δ 99.6 (C-1″), 99.5 (C-1′), 99.2 (C-1), 78.5 (C-2), 76.9 (C-2″), 76.4 (C-2′), 74.8 (C-3′), 73.3, 73.1, 72.6, 70.1, 68.8 (C-3″), 66.9, 66.7, 66.4, 60.9, 60.74, 60.67, 54.8 (*C*H_3). HRMS (ESI) *m*/*z* calcd for $C_{19}H_{32}Na_3O_{22}S_2$ $[M + Na]^+$: 745.0517, found: 745.0514. Partial assignment of NMR signals is based on 2D COSY, HSQC, and HMBC spectroscopy.

For oligomannan tetramer **20c**, R_f 0.15 (EtOAc/CH_2Cl_2/MeOH/H_2O 1:1:1:0.2); $[\alpha]_D^{23}$ +45.0 (*c* 0.82, H_2O); ^{1}H NMR (500 MHz, D_2O): δ 5.412 (d, *J* = 1.5 Hz, 1H, H-1‴), 5.408 (d, *J* = 2.5 Hz, 1H, H-1″), 5.29 (s, 1H, H-1′), 4.91 (s, 1H, H-1), 4.68 (1H, H-2′ overlapped with residual signal from D_2O), 4.65 (dd, *J* = 3.5, 1.5 Hz, 1H, H-2″), 4.58 (dd, *J* = 3.5, 1.5 Hz, 1H, H-2‴), 4.14 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3″), 4.04 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3′), 3.95 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3‴), 3.91 (dd, *J* = 2.0, 4.0 Hz, 1H, H-2), 3.89-3.86 (m, 1H), 3.84-3.66 (m, 13H), 3.62 (d, *J* = 10.0 Hz, 1H), 3.57 (d, *J* = 10.0 Hz, 1H), 3.54 (dd, *J* = 2.0, 7.0 Hz, 1H), 3.33 (s, 3H, OC*H*$_3$); ^{13}C NMR (125 MHz, D_2O): δ 99.51 (C-1‴), 99.49 (C-1″), 99.4 (C-1′), 99.1 (C-1), 78.54 (H-2), 76.8 (C-2‴), 76.5 (C-2″), 76.2 (C-2′), 75.7 (C-3′), 74.9 (C-3″), 73.3, 73.0, 72.5, 70.0, 68.7, 66.8, 66.6, 66.3, 66.1, 54.7 (O*C*H$_3$). HRMS (ESI) *m*/*z* calcd for $C_{25}H_{41}Na_4O_{30}S_3$ [M + Na]$^+$: 1009.0430; found 1009.0367. Partial assignment of NMR signals is based on 2D COSY, HSQC, and reference to the peak assignment of **18c** and **19c**.

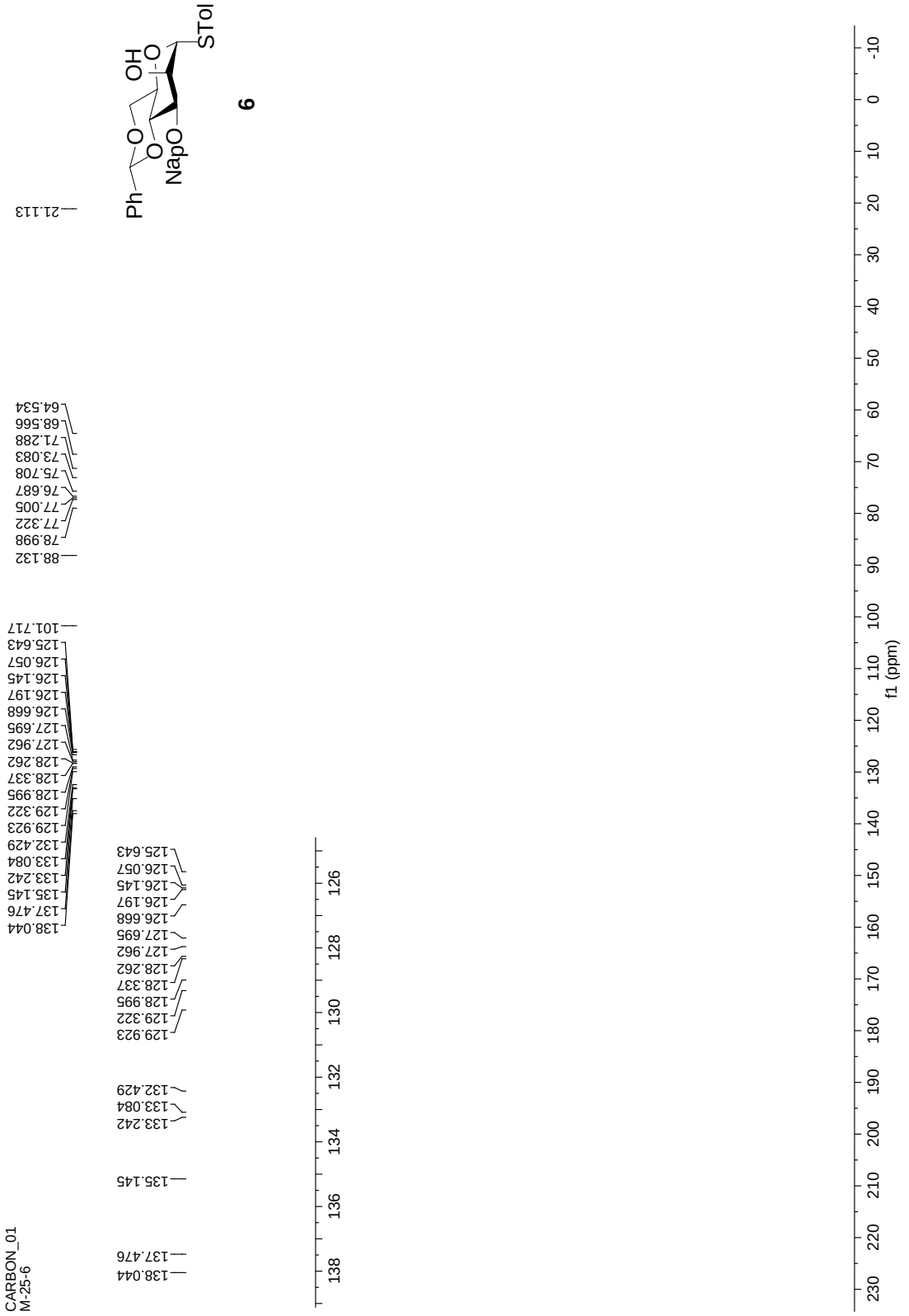
For oligomannan pentamer **21c**, R_f 0.10 (EtOAc/CH_2Cl_2/MeOH/H_2O 1:1:1:0.2); $[\alpha]_D^{23}$ +64.0 (*c* 0.25, H_2O); ^{1}H NMR (500 MHz, D_2O): δ 5.42-5.41 (bs, 3H including H-1″, H-1‴, and H-1⁗), 5.29 (d, *J* = 1.5 Hz, 1H, H-1′), 4.91 (s, 1H, H-1), 4.66 (m, 1H, H-2′, overlapped with residual signal from D_2O but indicated in HSQC and COSY spectroscopies), 4.66-4.65 (m, 2H, H-2″, H-2‴ partial overlapped with residual signal from D_2O), 4.58 (dd, *J* = 1.5, 3.5 Hz, H-2′), 4.13 (dd, *J* = 3.5, 10.0 Hz, 2H, H-3″ and H-3‴), 4.04 (dd, *J* = 3.5, 10.0 Hz, 1H, H-3′), 3.95 (dd, *J* = 3.5, 10.0 Hz, 1H, H-3⁗), 3.93-3.87 (m, 4H including H-2), 3.85-3.81 (m, 5H), 3.77 (dd, *J* = 3.5, 10.0 Hz, 1H), 3.74-3.66 (m, 10H), 3.64-3.56 (m, 2H), 3.55-3.53 (m, 1H), 3.32 (s, 3H, OC*H*$_3$); **^{13}C NMR** (125 MHz, D_2O): δ 99.52 (C-1⁗), 99.47 (C × 2 including C-1″, and C-1‴), 99.4 (C-1′), 99.1 (C-1), 78.6 (C-2), 76.9 (C-2′), 76.5 and 76.4 (C-2″ and C-2‴), 76.2 (C-2′), 75.8 (C-3′), 75.4 and 74.8 (C-3″ and C-3‴), 73.3, 73.03, 73.01, 72.99, 72.5, 70.0, 68.7 (C-3⁗), 66.8, 66.6, 66.4, 66.3, 66.2, 66.1, 60.9, 60.6, 60.5, 54.7 (*C*H$_3$). **HRMS** (ESI TOF) *m*/*z* calcd for $C_{31}H_{50}Na_5O_{38}S_4$ [M + Na]$^+$: 1273.0346, found: 1273.0361. Partial assignment of NMR signals is based on 2D COSY, HSQC, and reference to the peak

assignment of **18c**–**20c**.

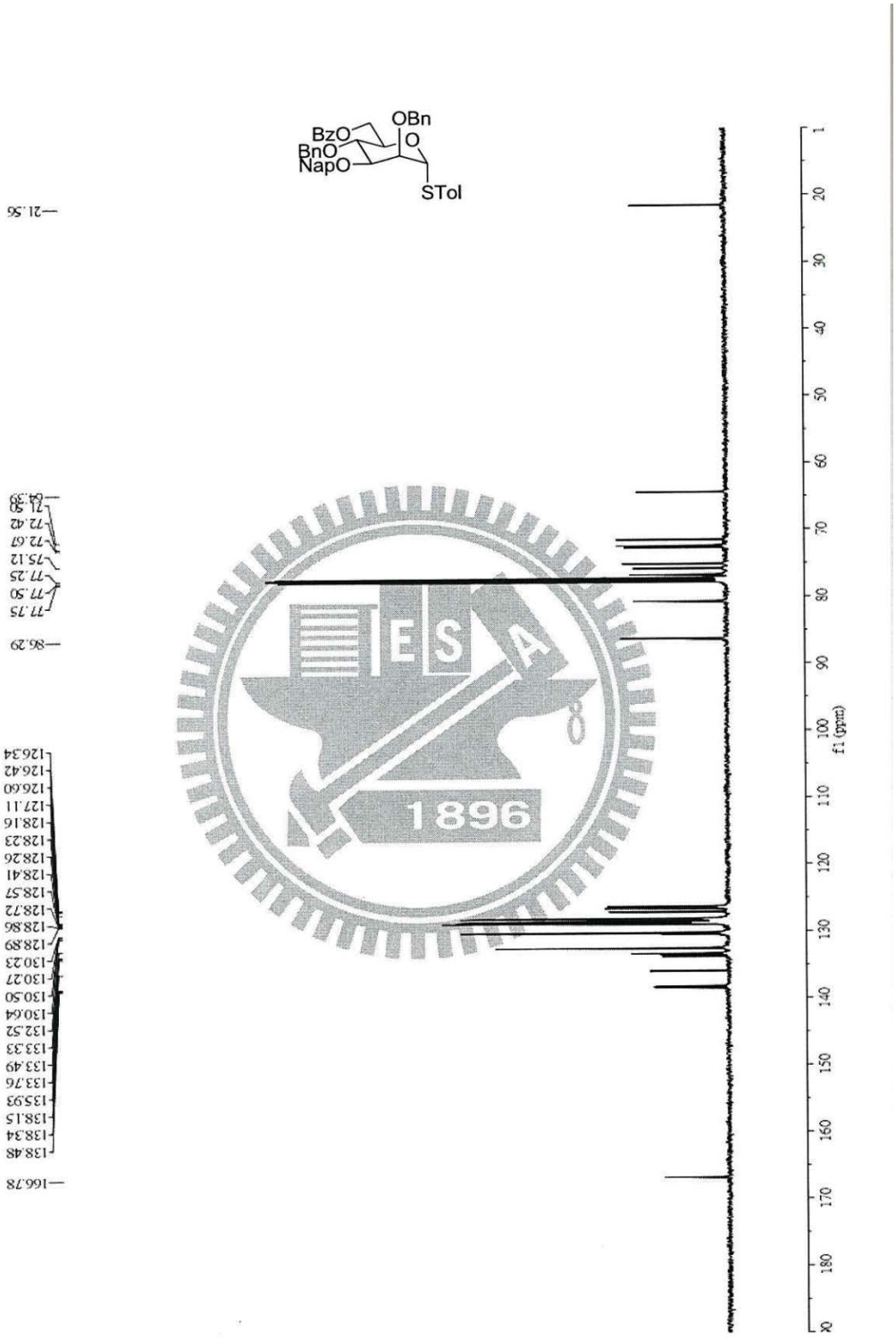
^{1}H NMR spectrum of building block **6**



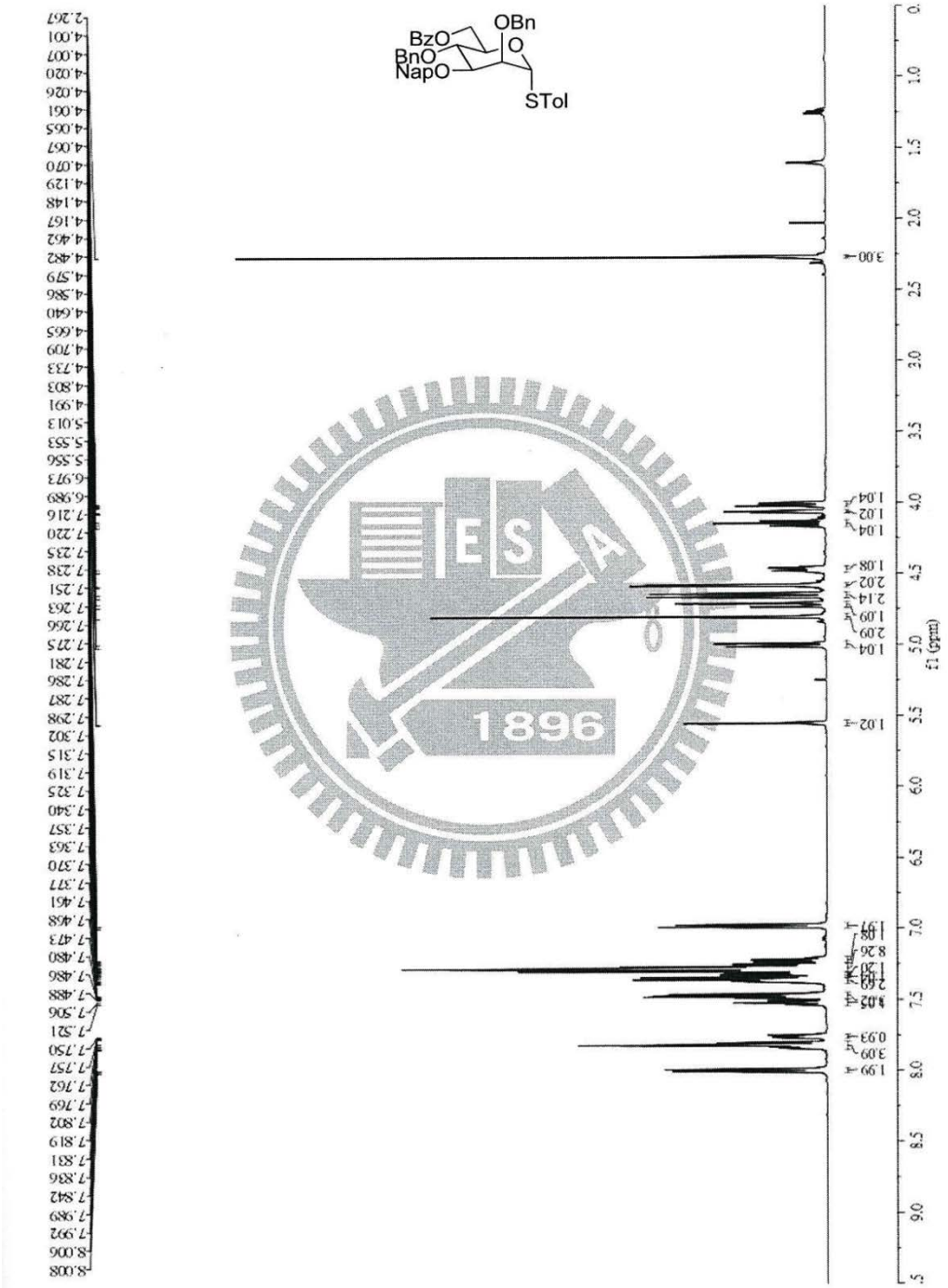
^{13}C NMR spectrum of building block **6**



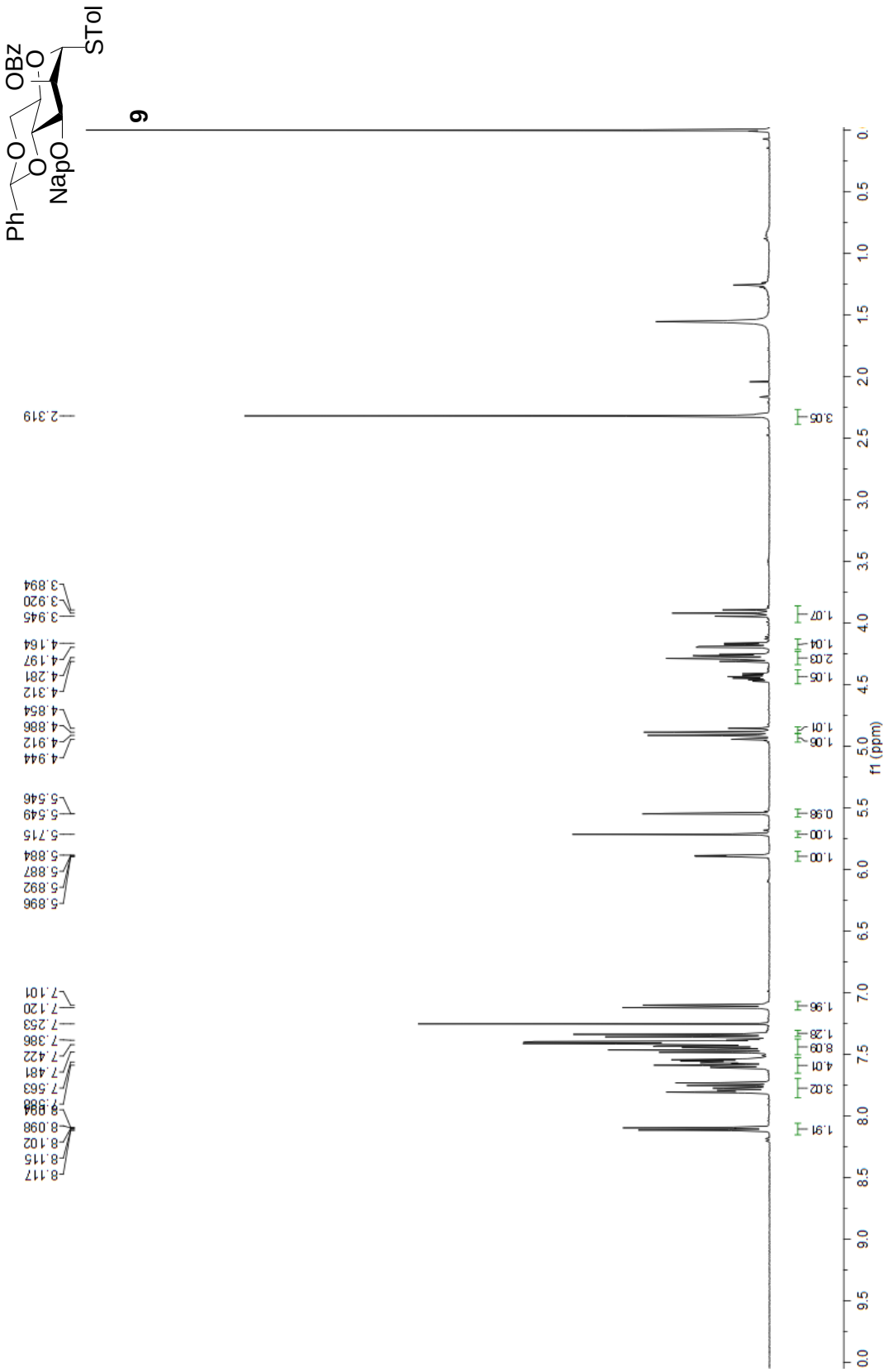
^{1}H NMR spectrum of building block **8′**



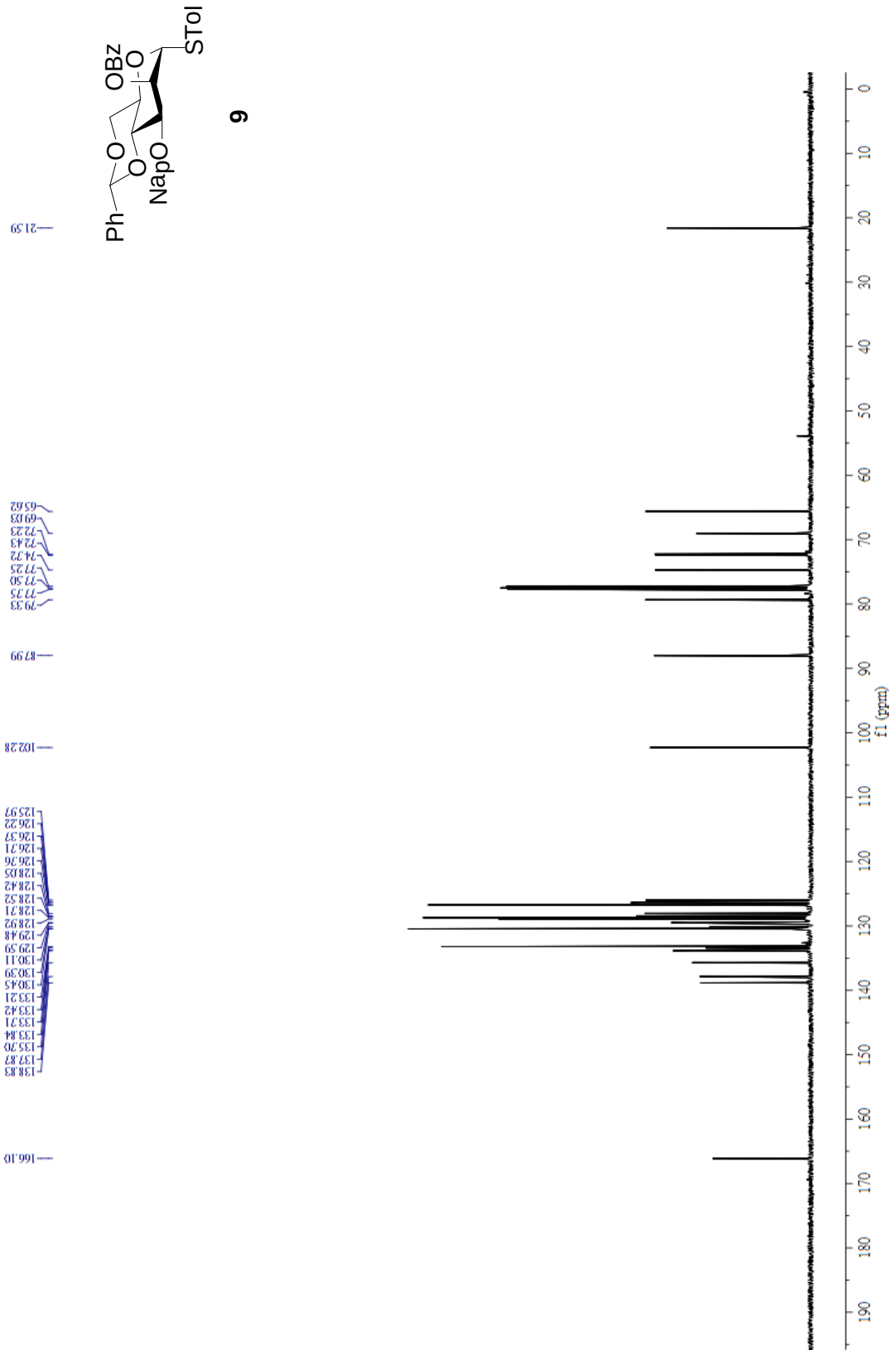
^{13}C NMR spectrum of building block **8′**



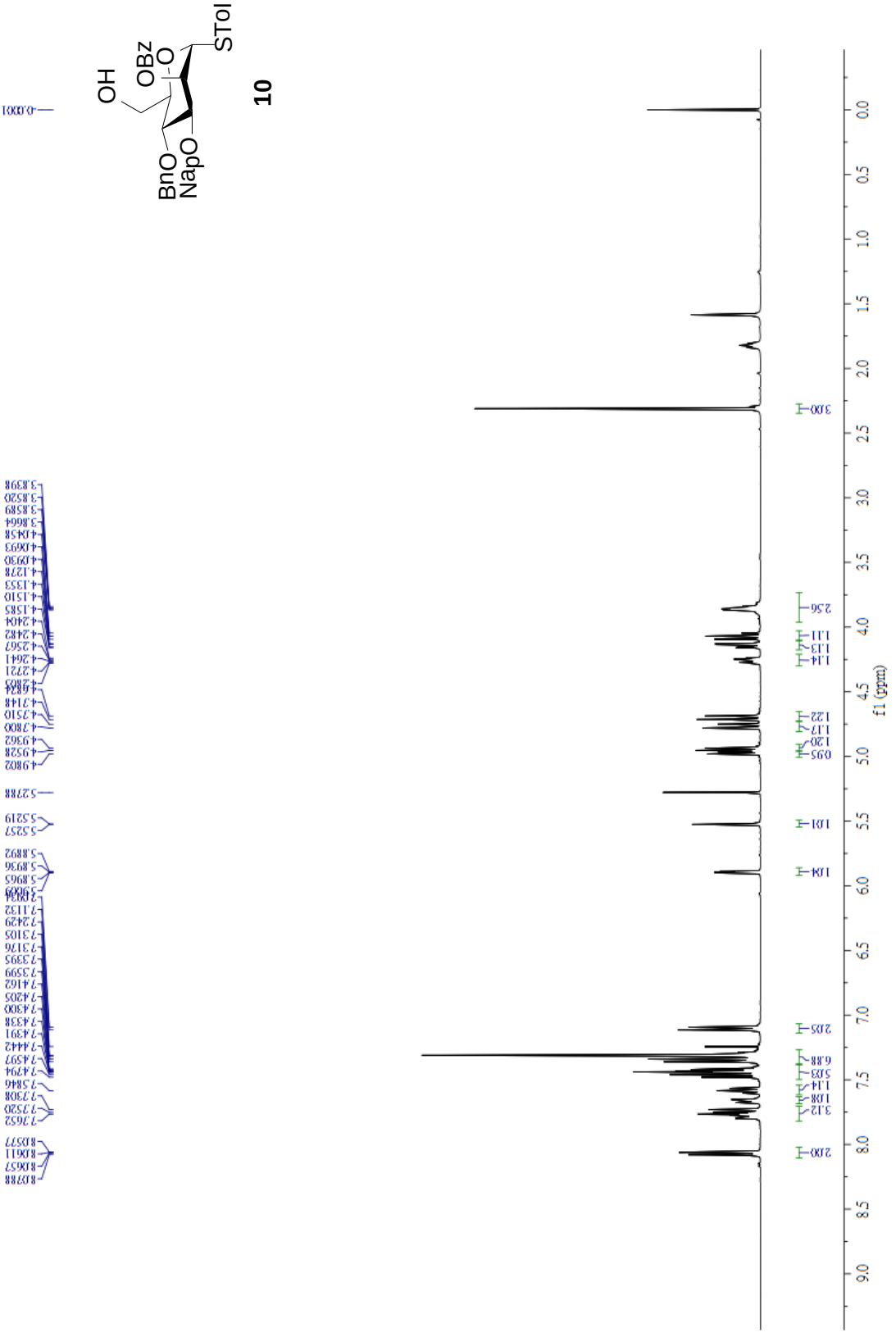
^{1}H NMR spectrum of building block **9**



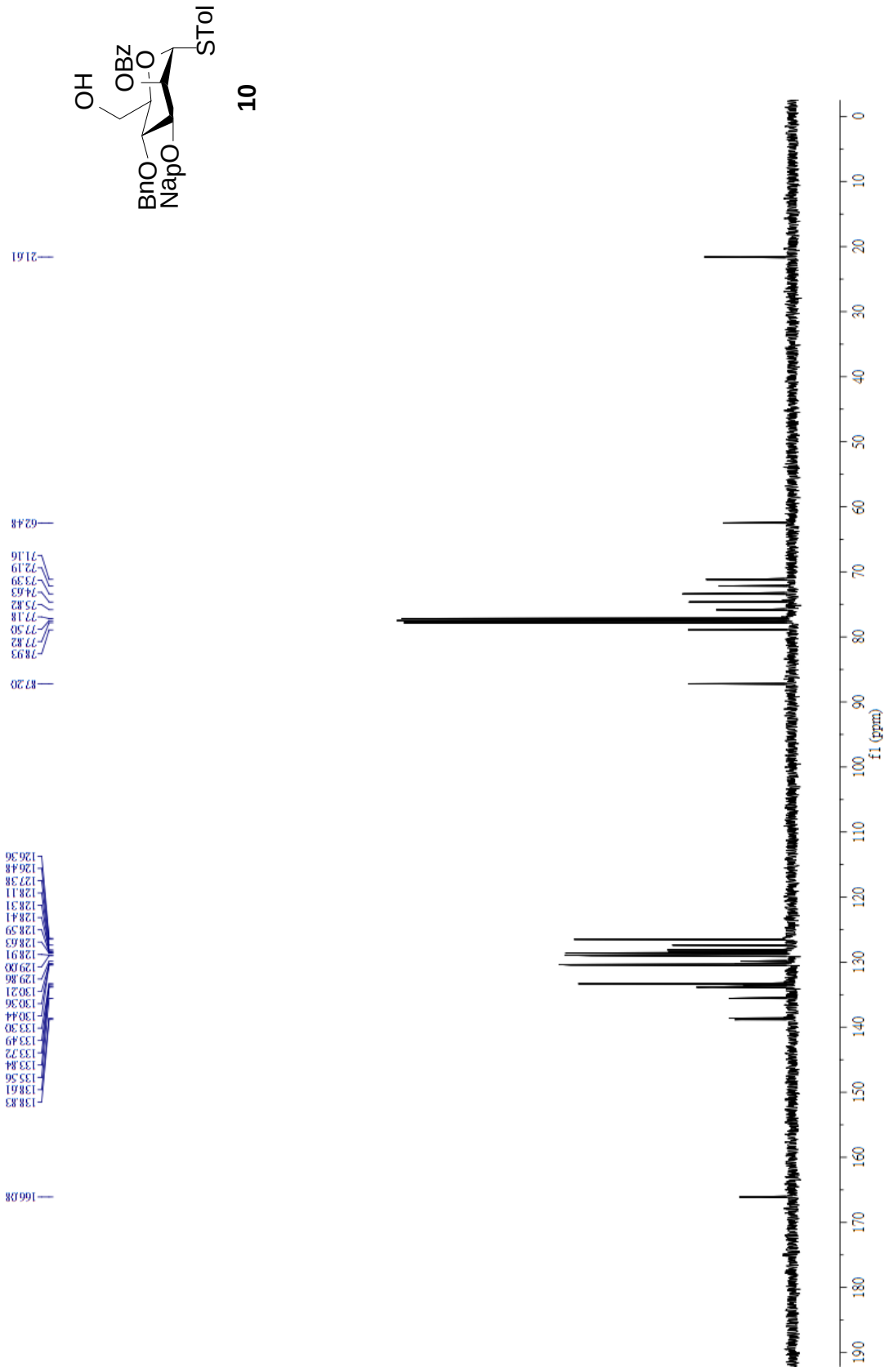
^{13}C NMR spectrum of building block **9**



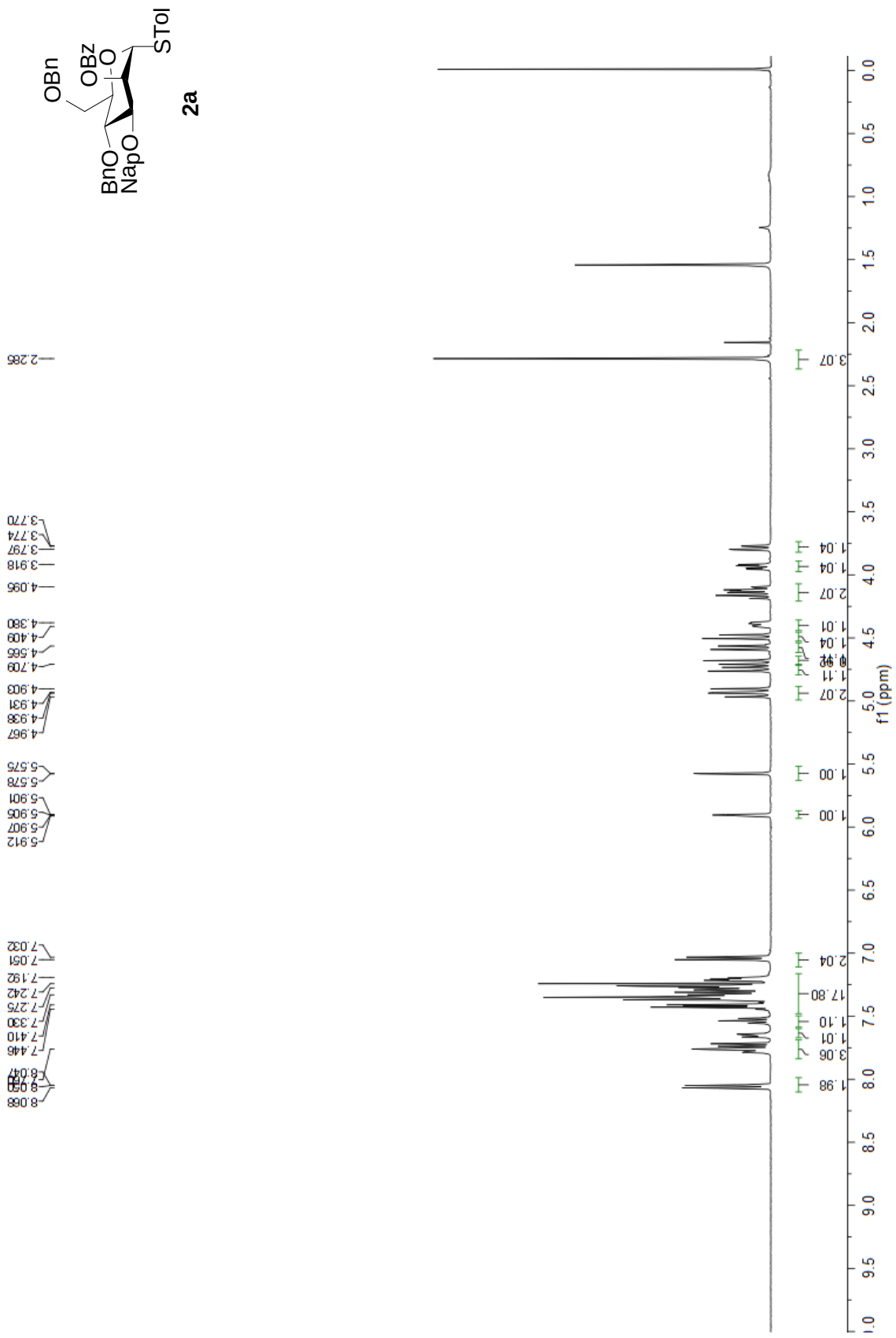
^{1}H NMR spectrum of **10**



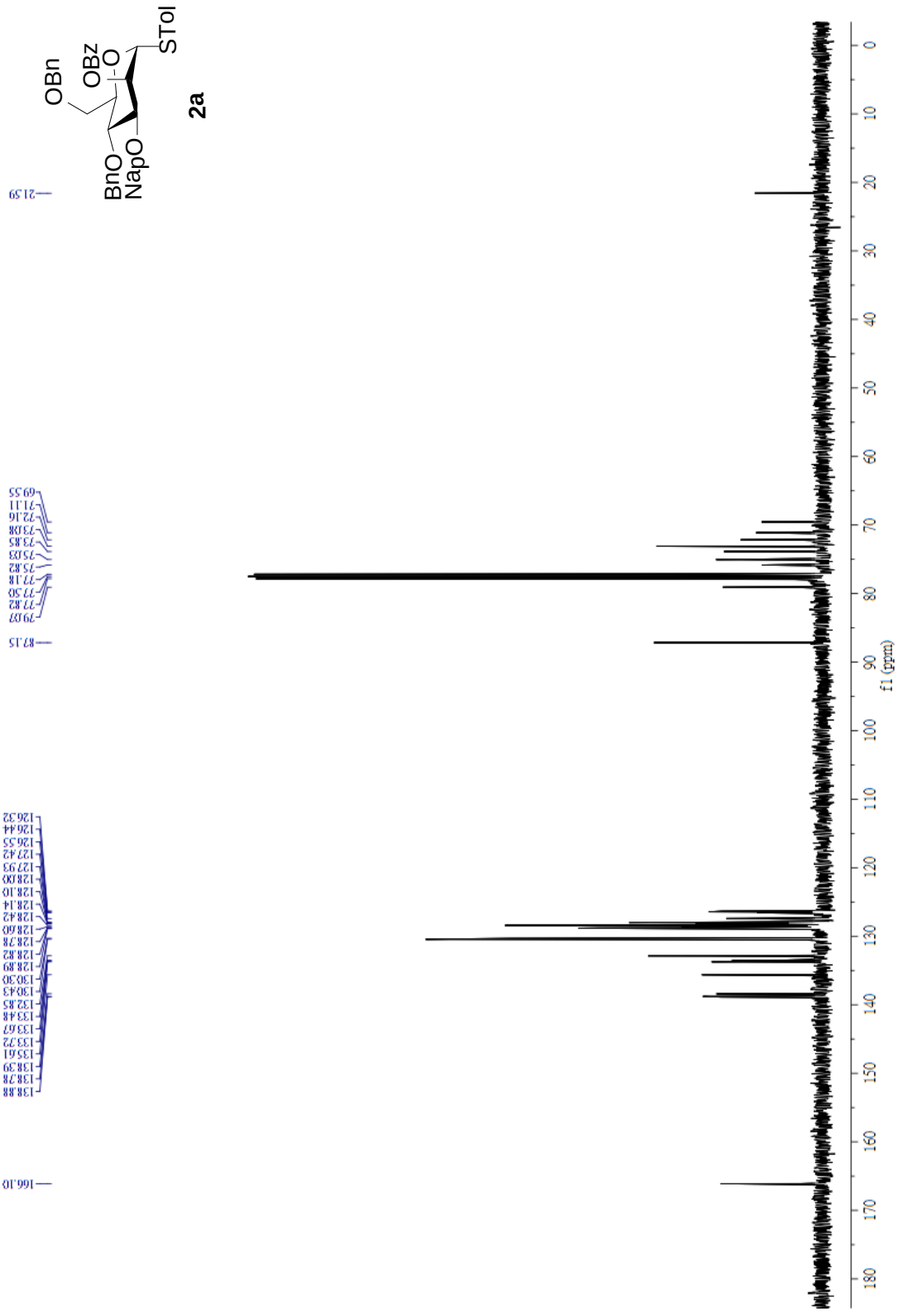
^{13}C NMR spectrum of **10**



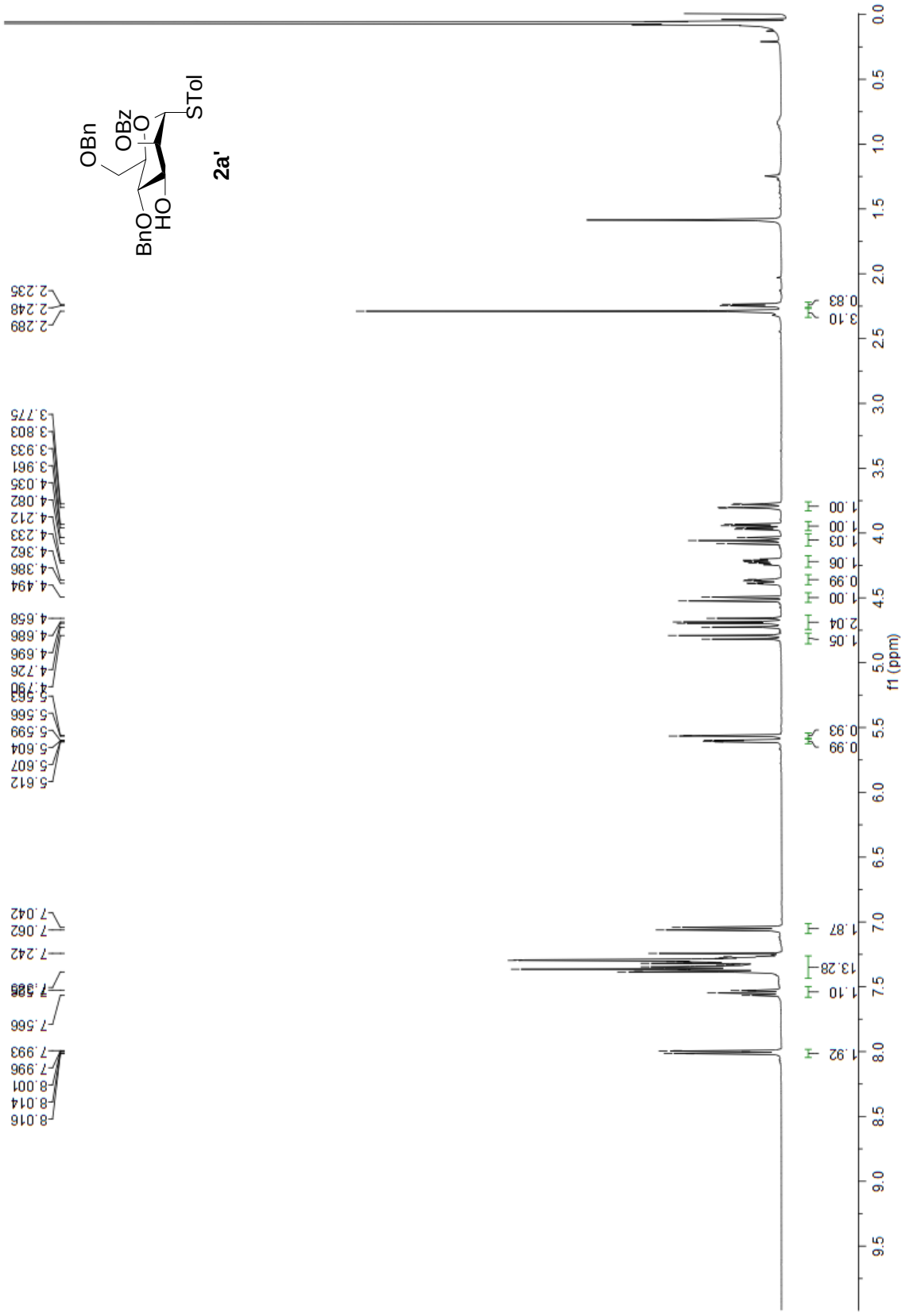
^{1}H NMR spectrum of **2a**



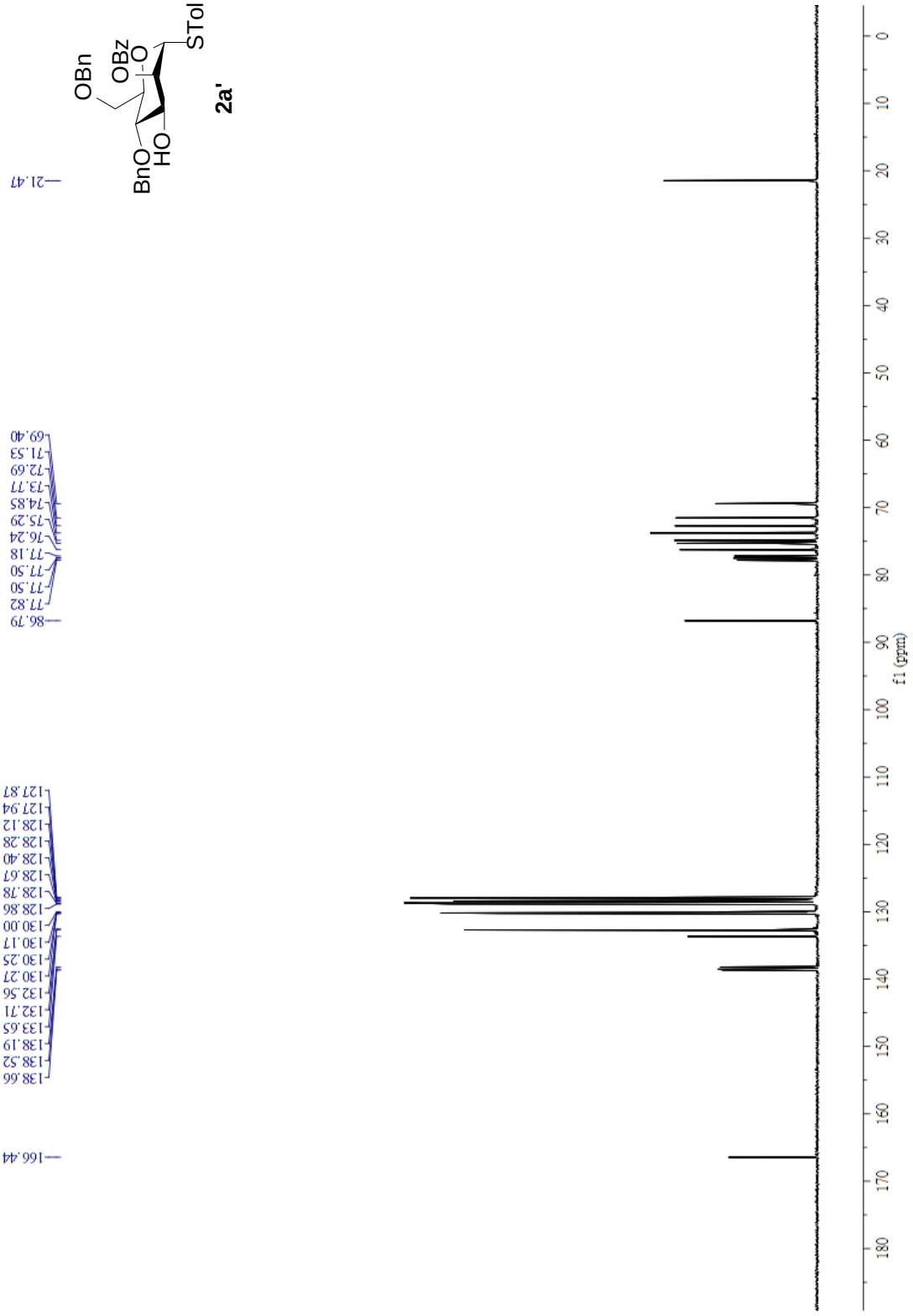
^{13}C NMR spectrum of **2a**



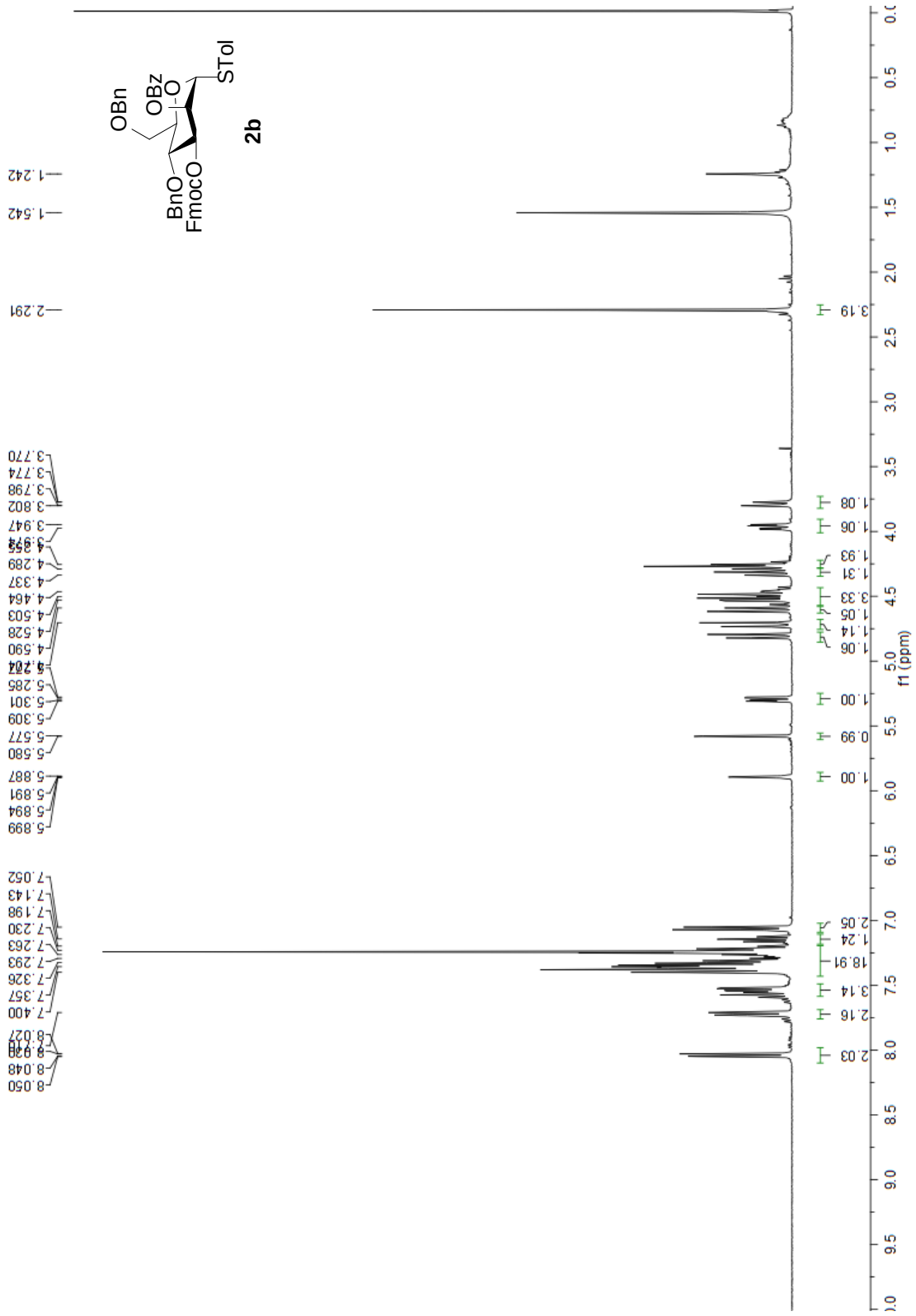
^{1}H NMR spectrum of **2a′**



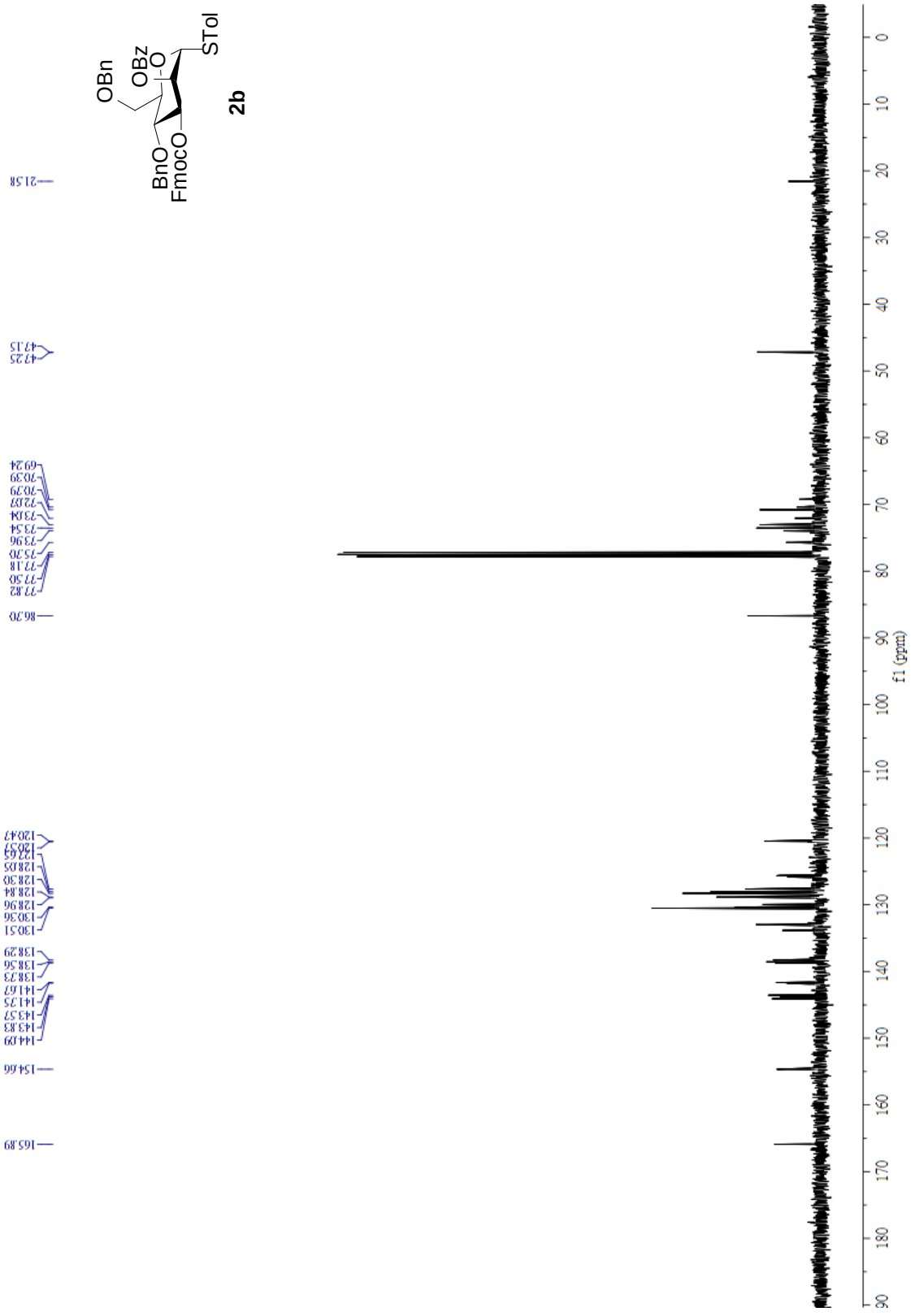
^{13}C NMR spectrum of **2a′**



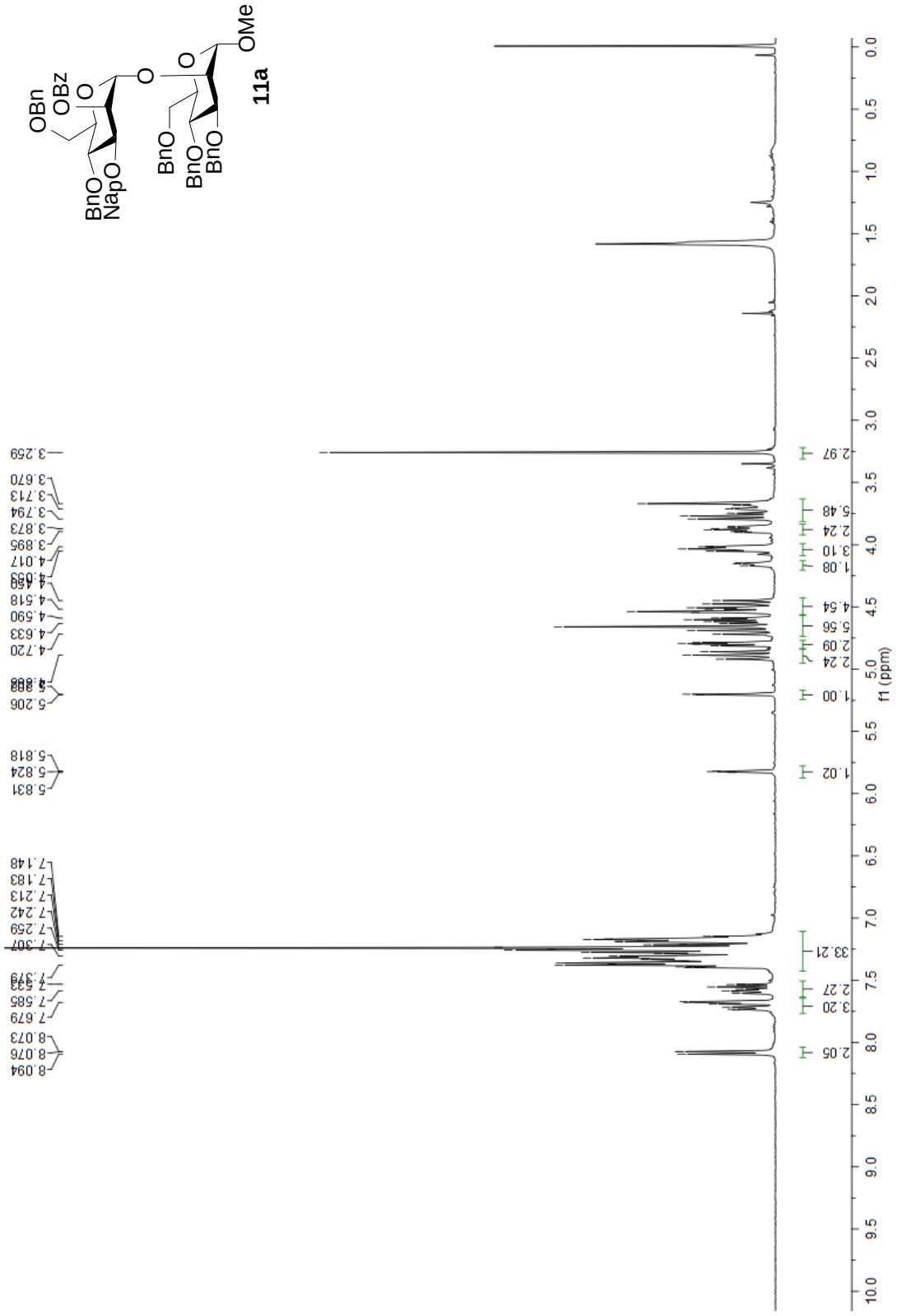
^{1}H NMR spectrum of **2b**



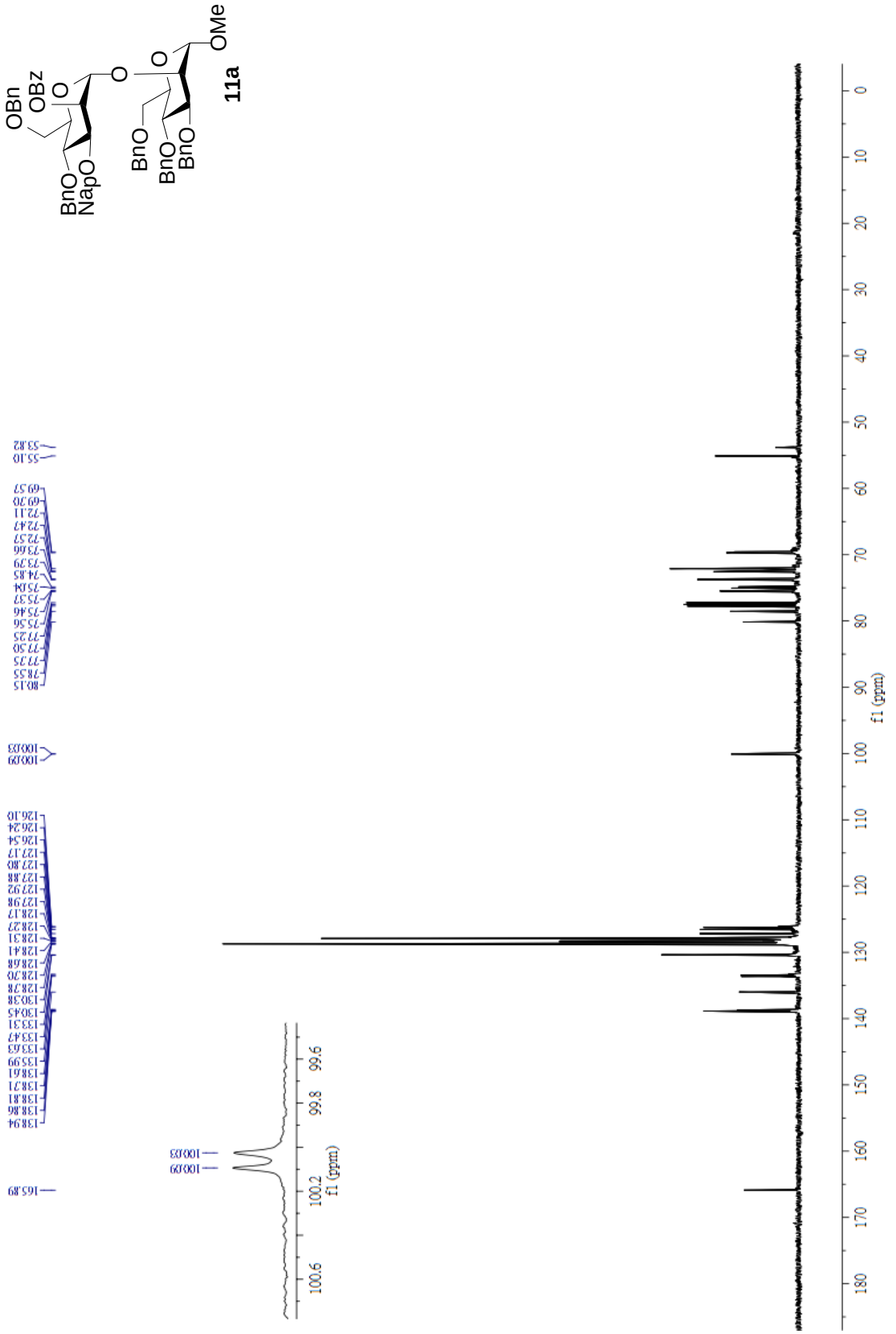
^{13}C NMR spectrum of **2b**



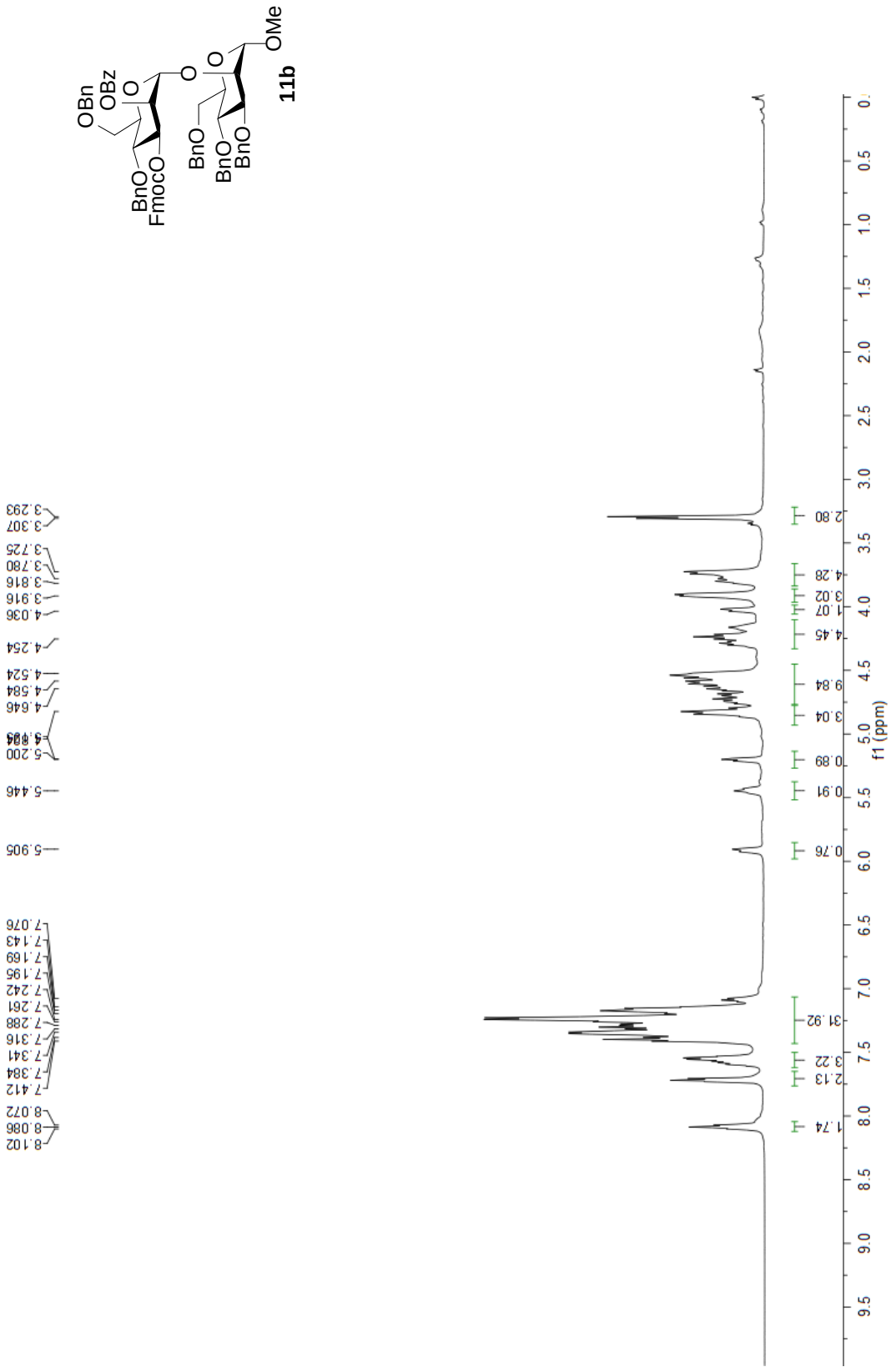
^{1}H NMR spectrum of **11a**



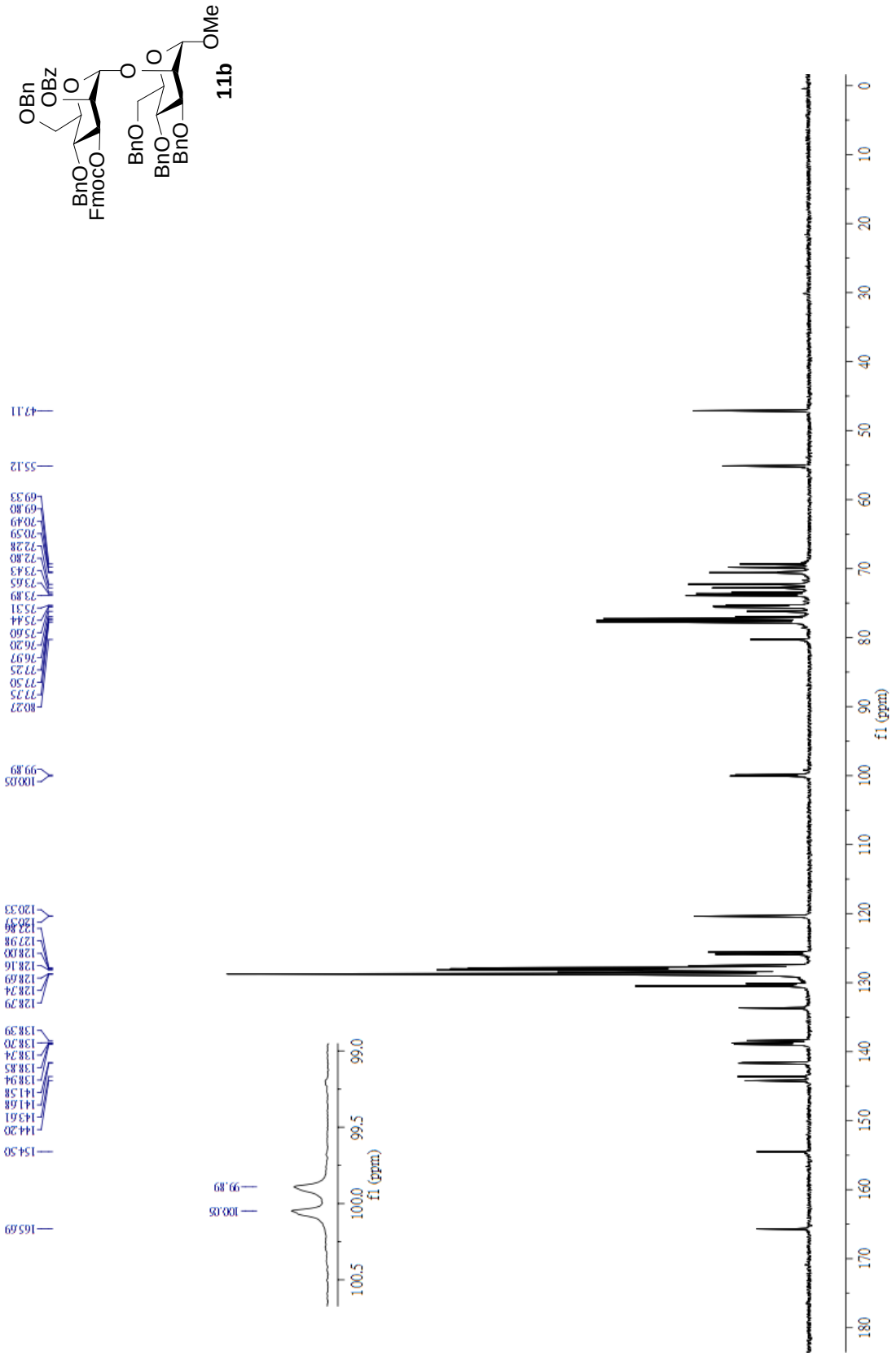
^{13}C NMR spectrum of **11a**



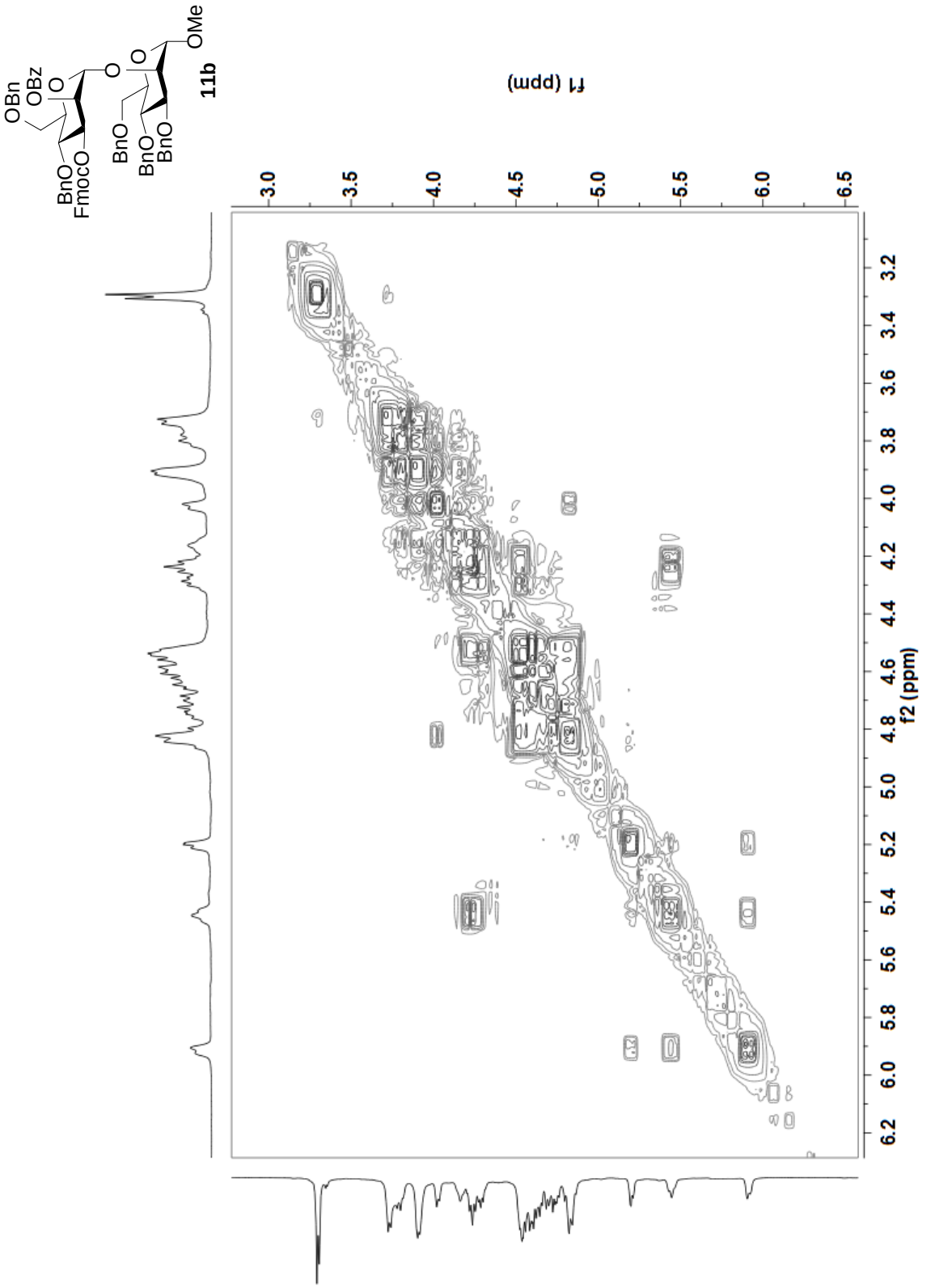
^{1}H NMR spectrum of **11b**



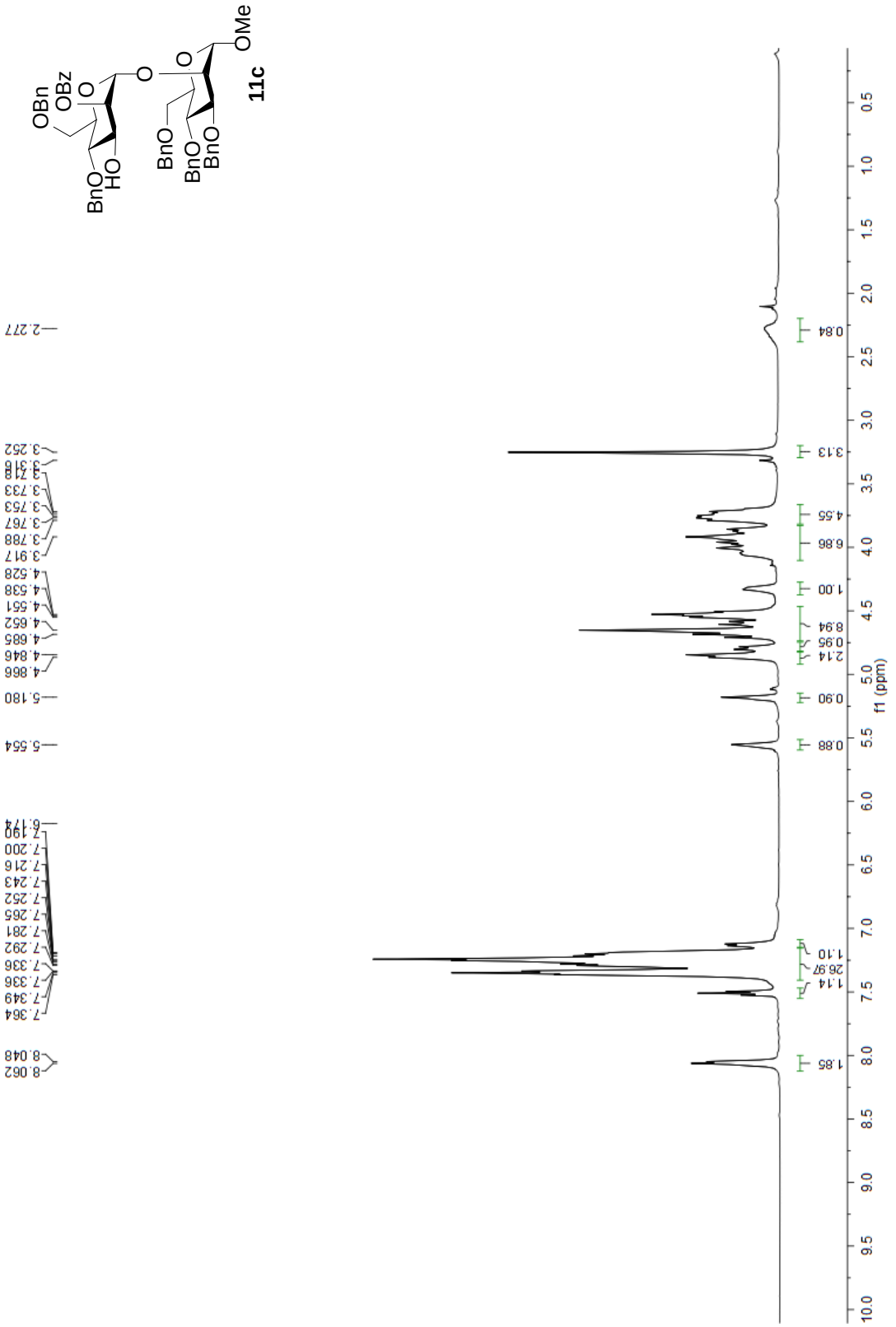
^{13}C NMR spectrum of **11b**



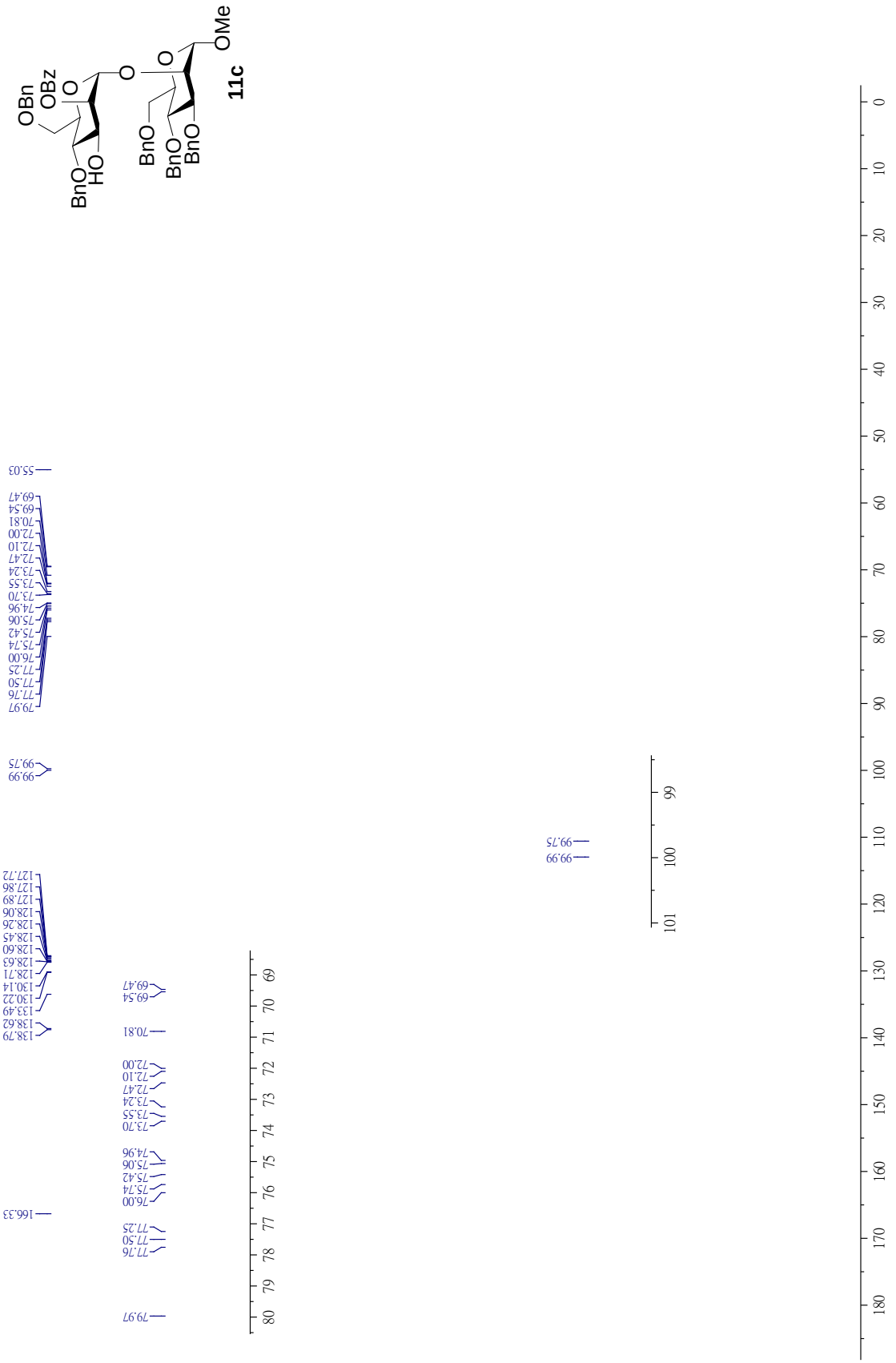
COSY spectrum of **11b**



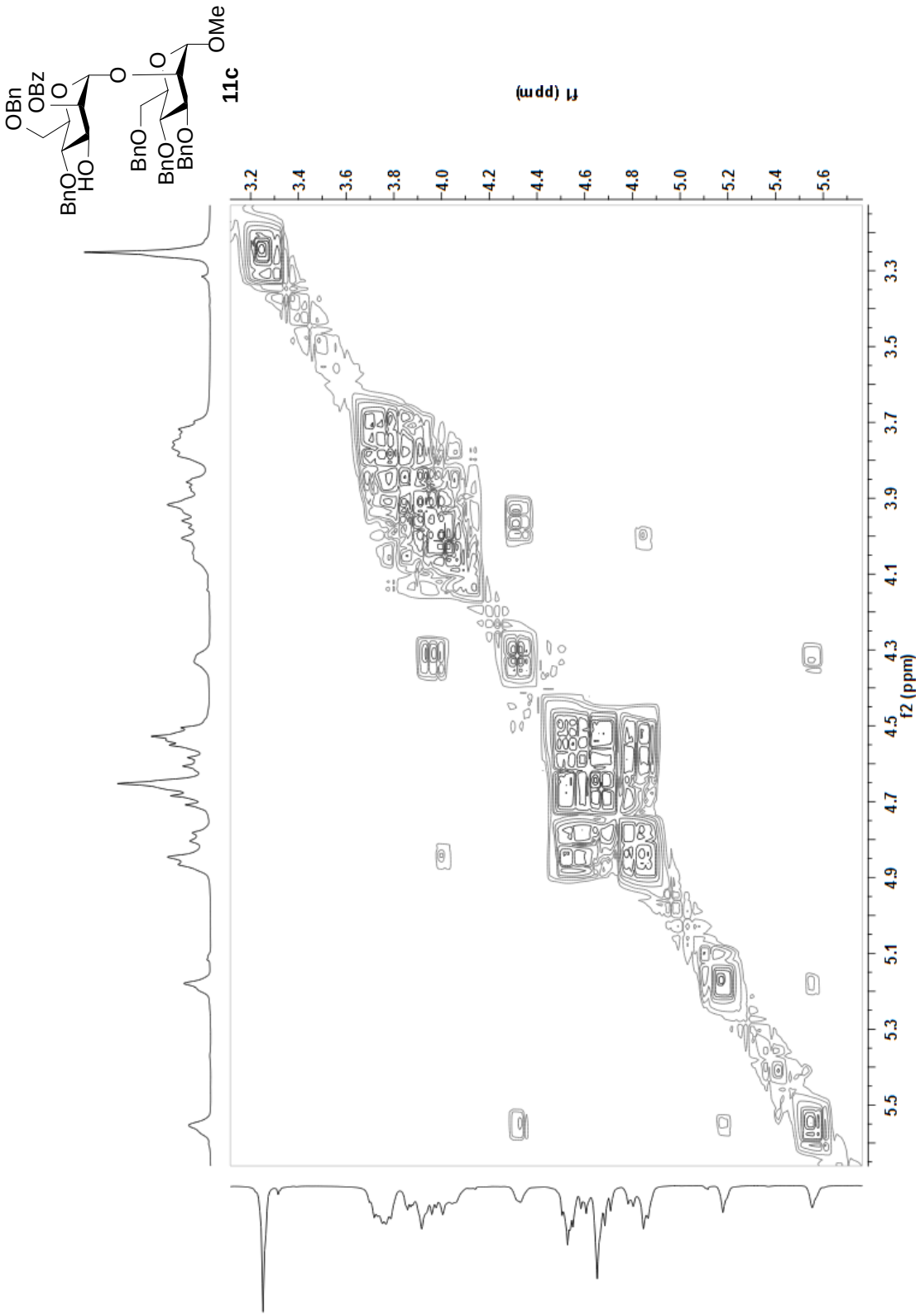
^{1}H NMR spectrum of **11c**



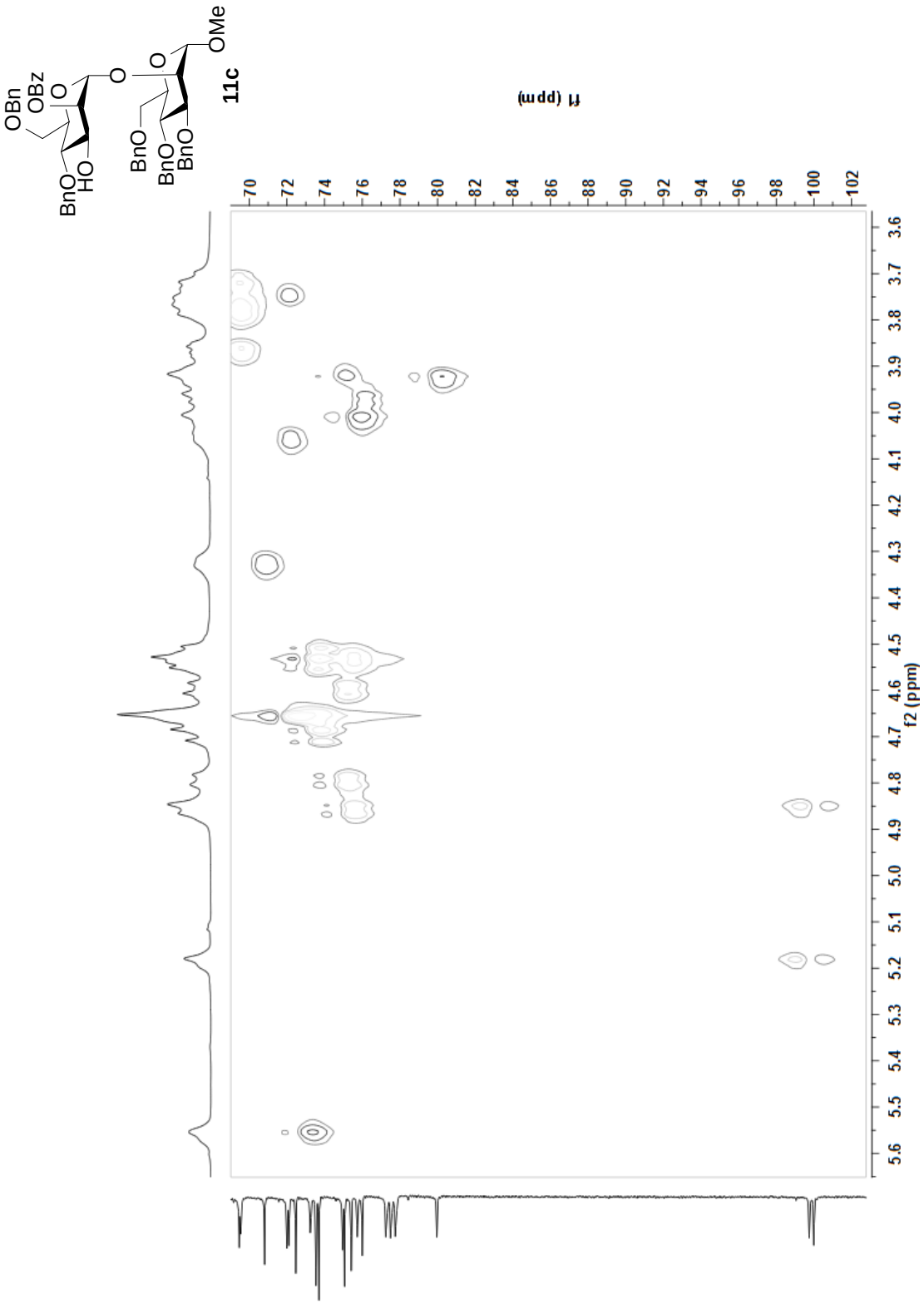
^{13}C NMR spectrum of **11c**



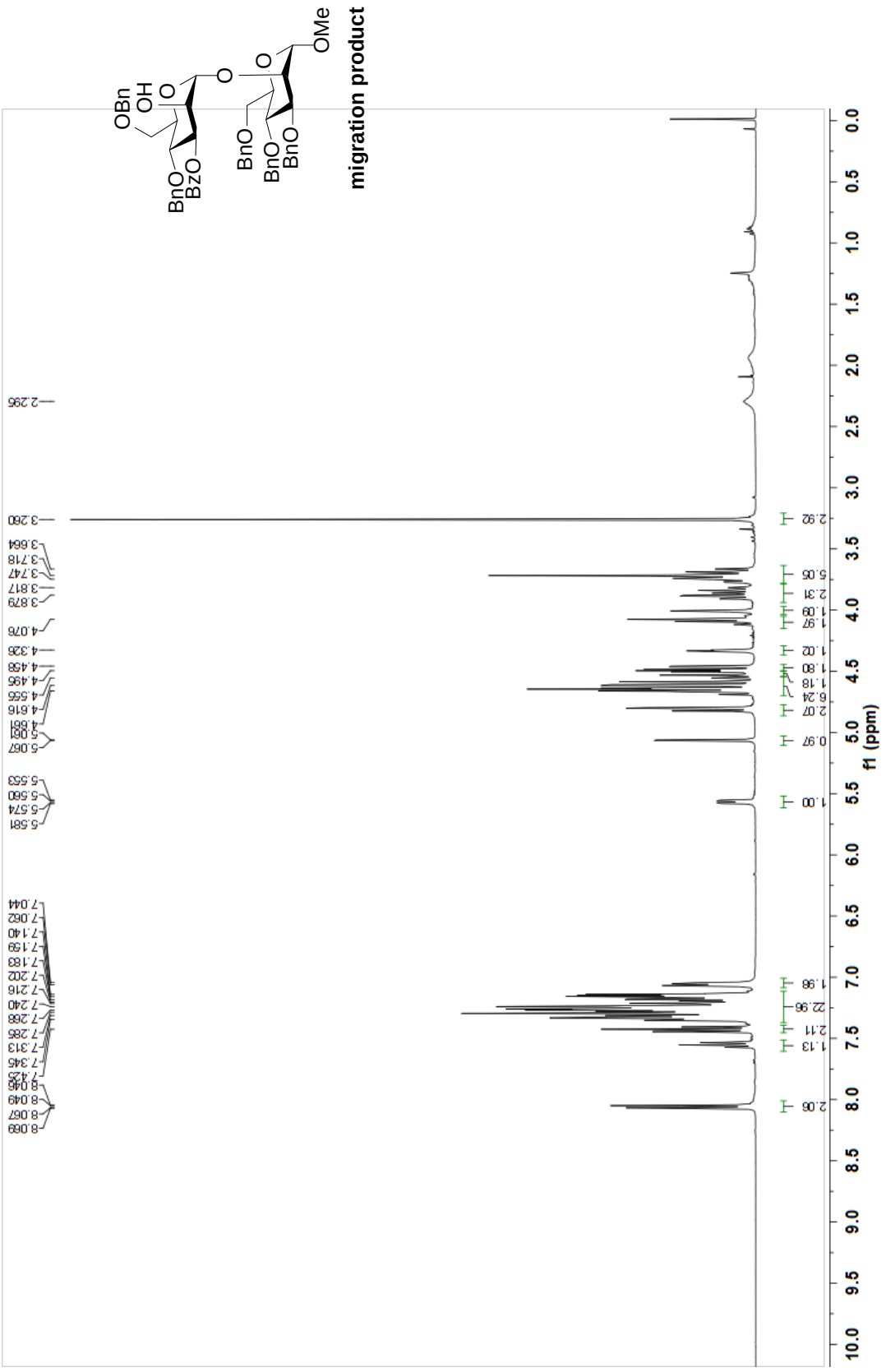
COSY spectrum of **11c**



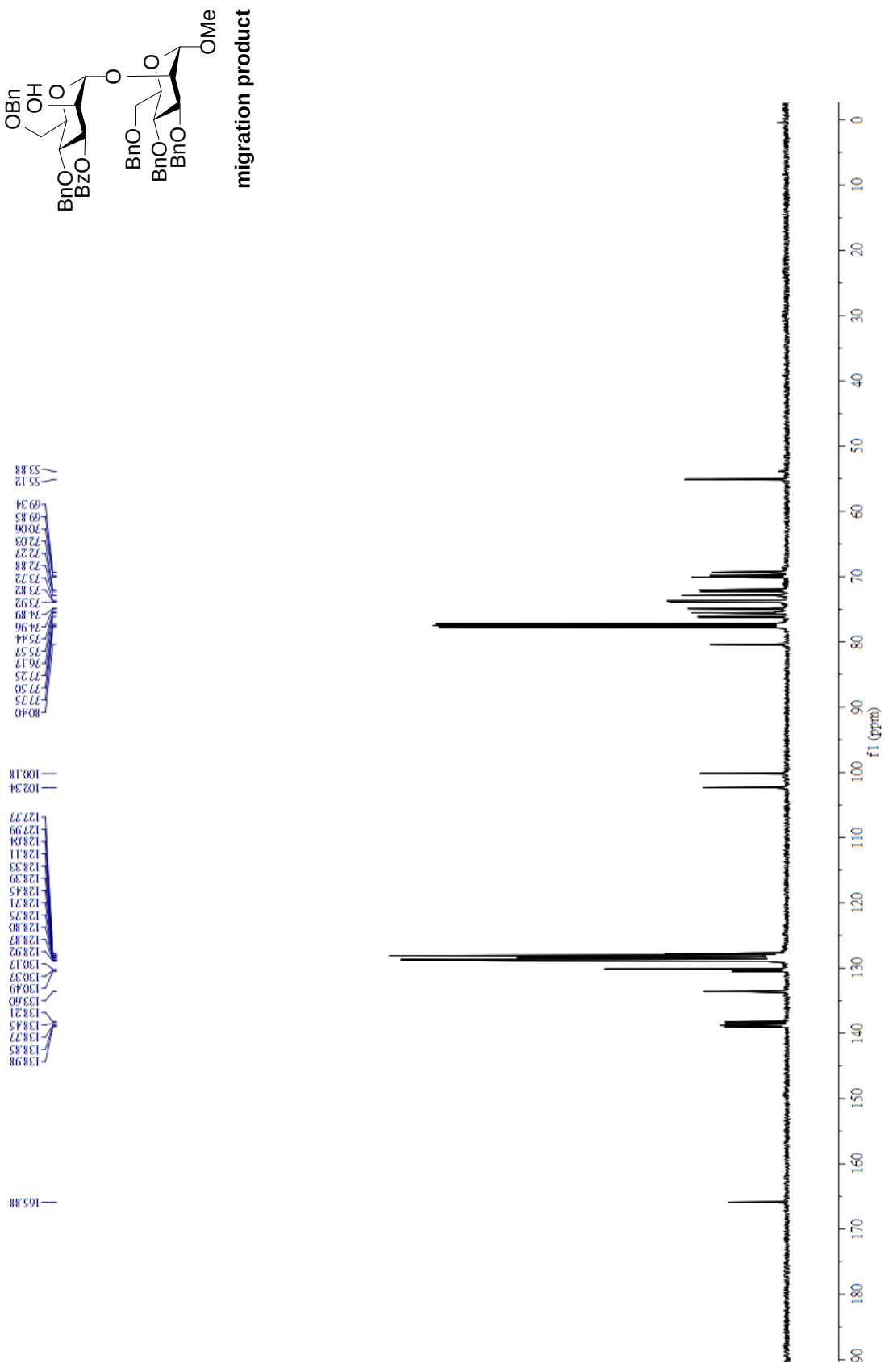
HSQC spectrum of **11c**



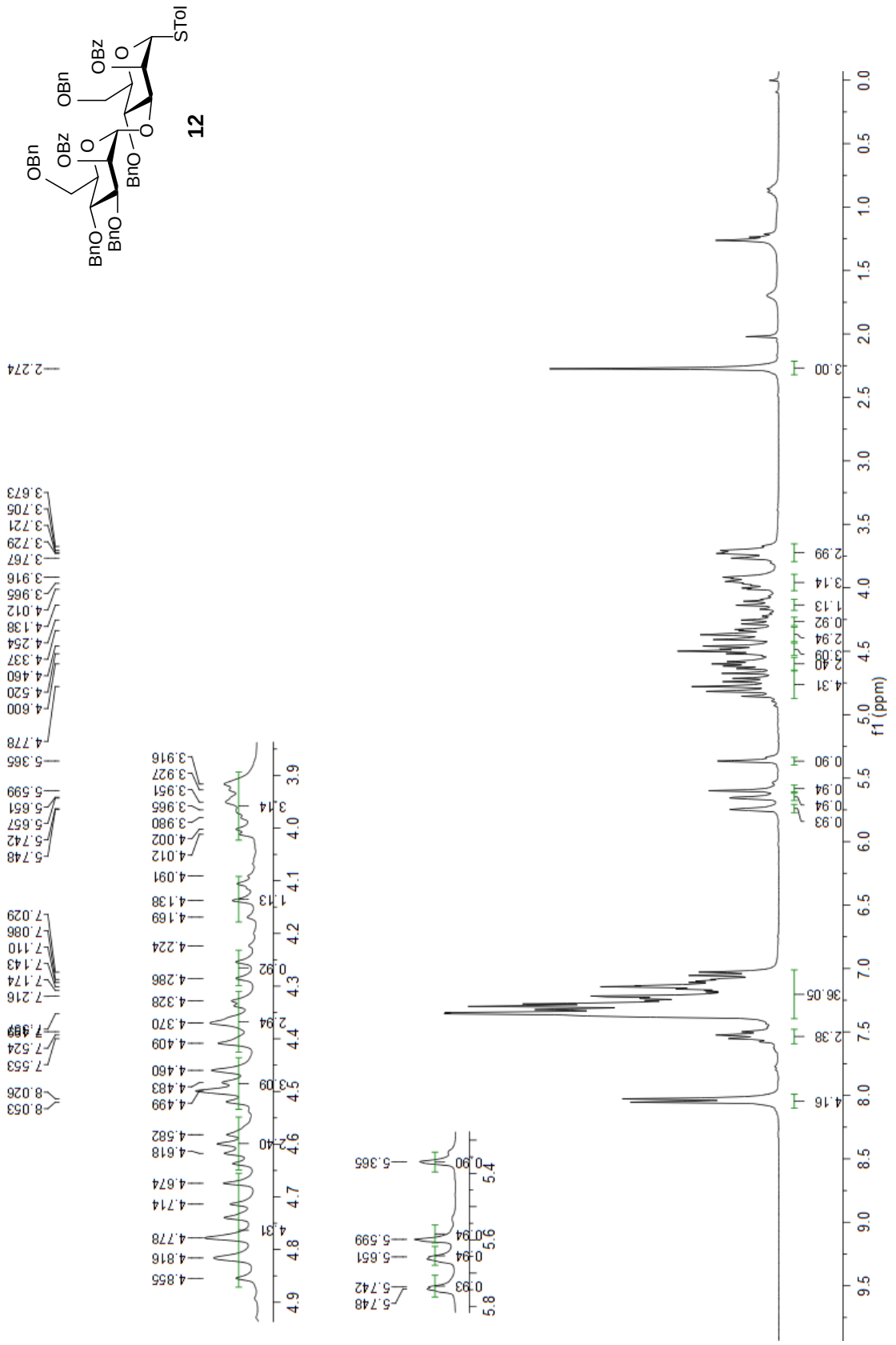
^{1}H NMR spectrum of migration product



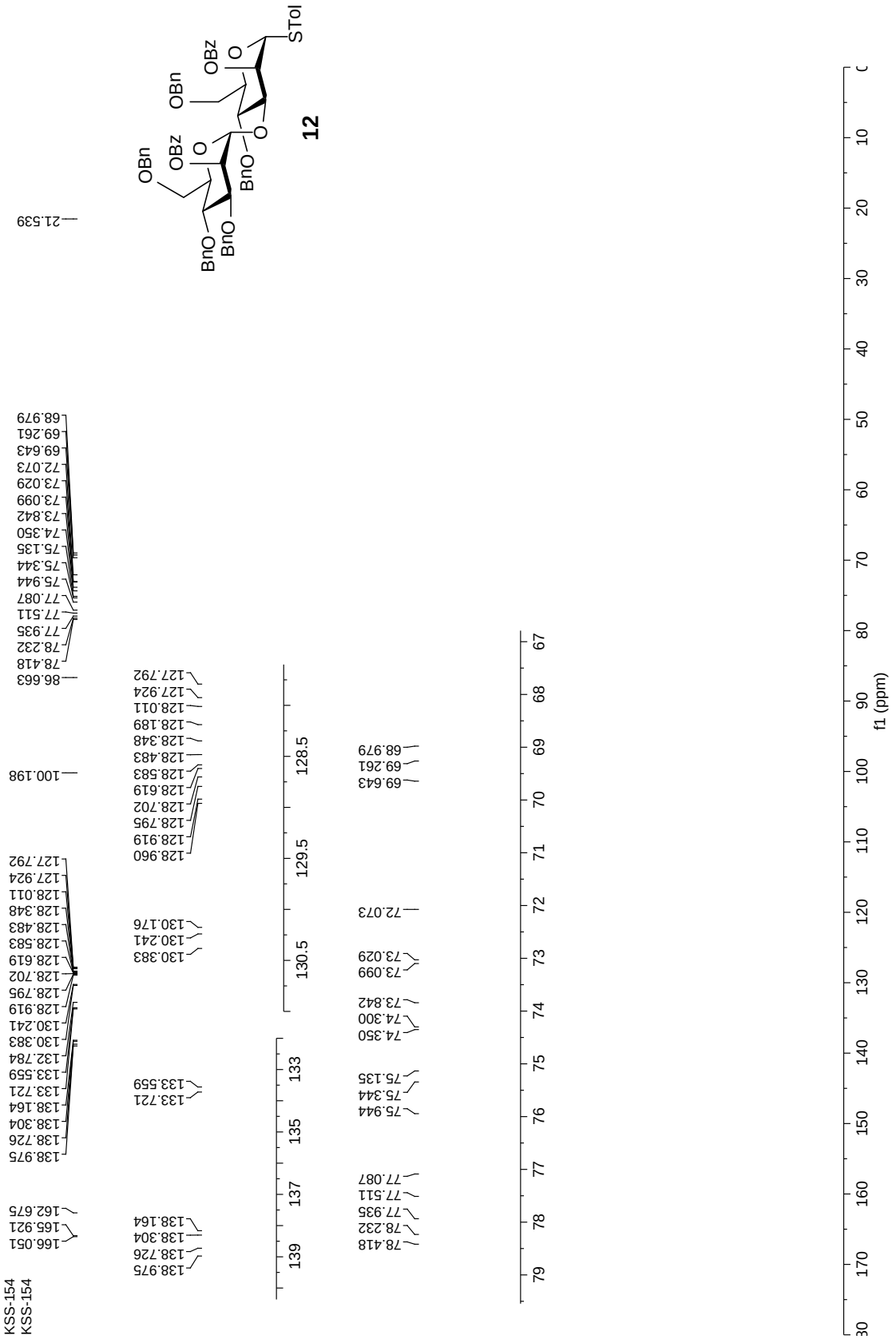
^{13}C NMR spectrum of migration product



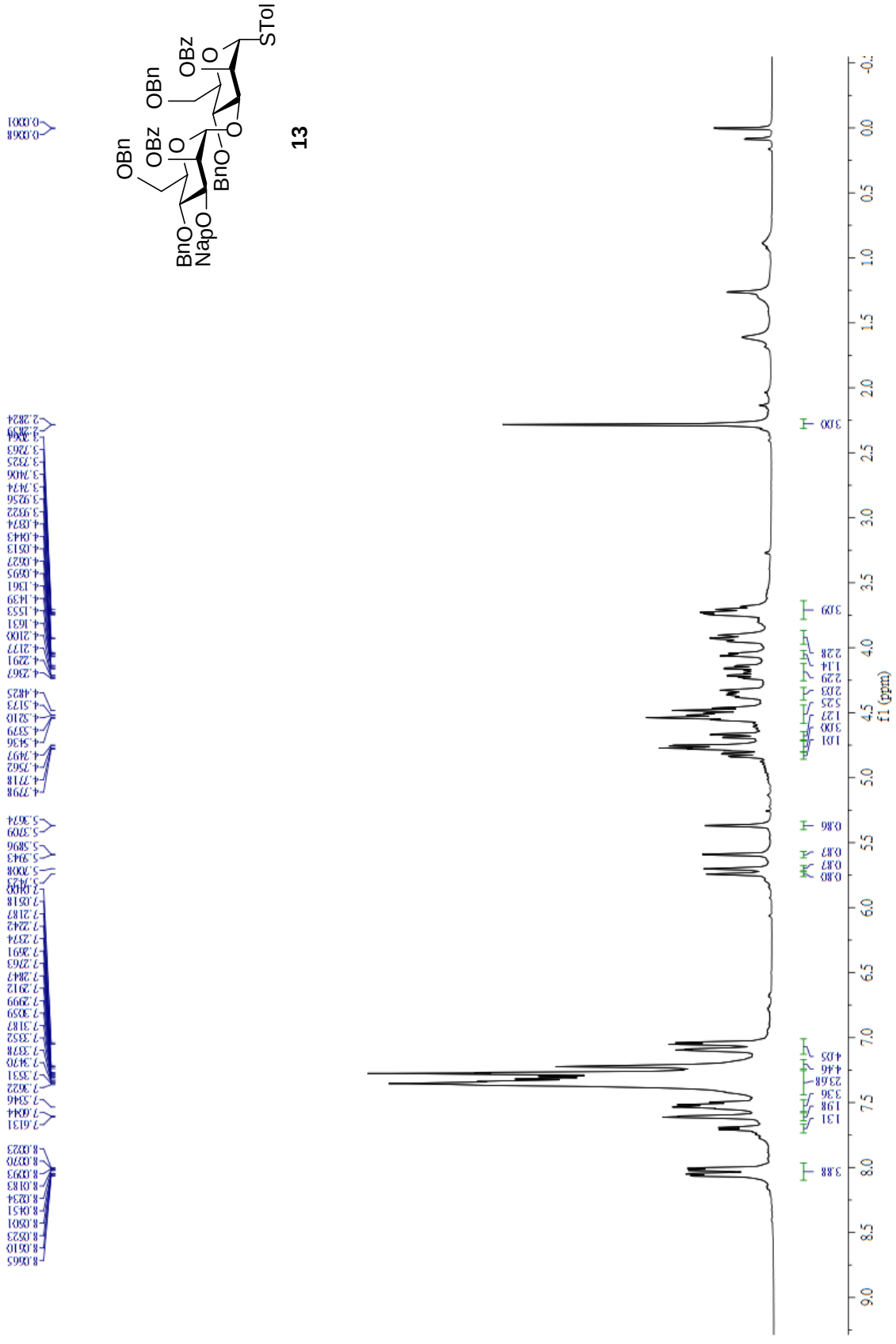
^{1}H NMR spectrum of **12**



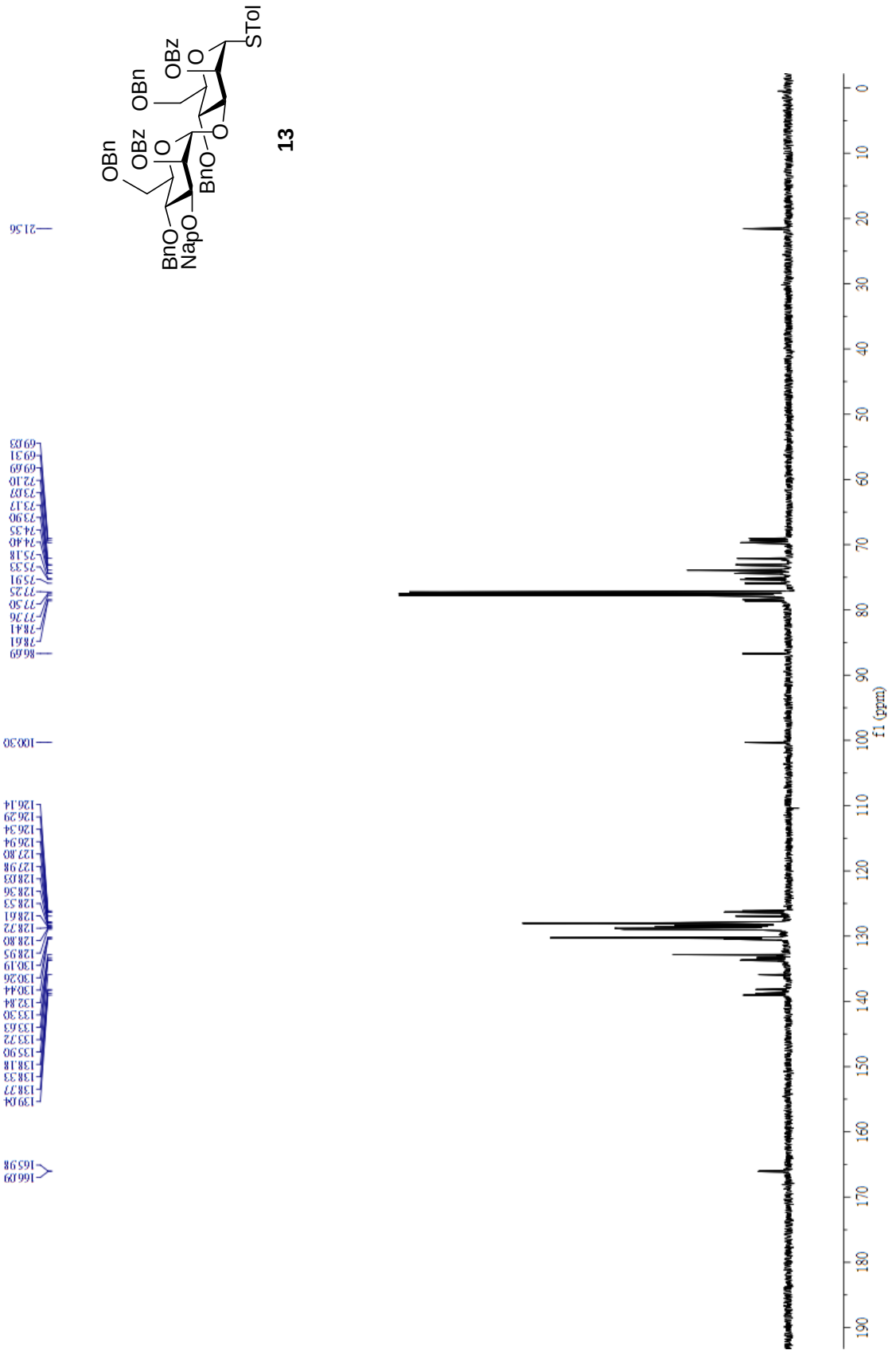
^{13}C NMR spectrum of **12**



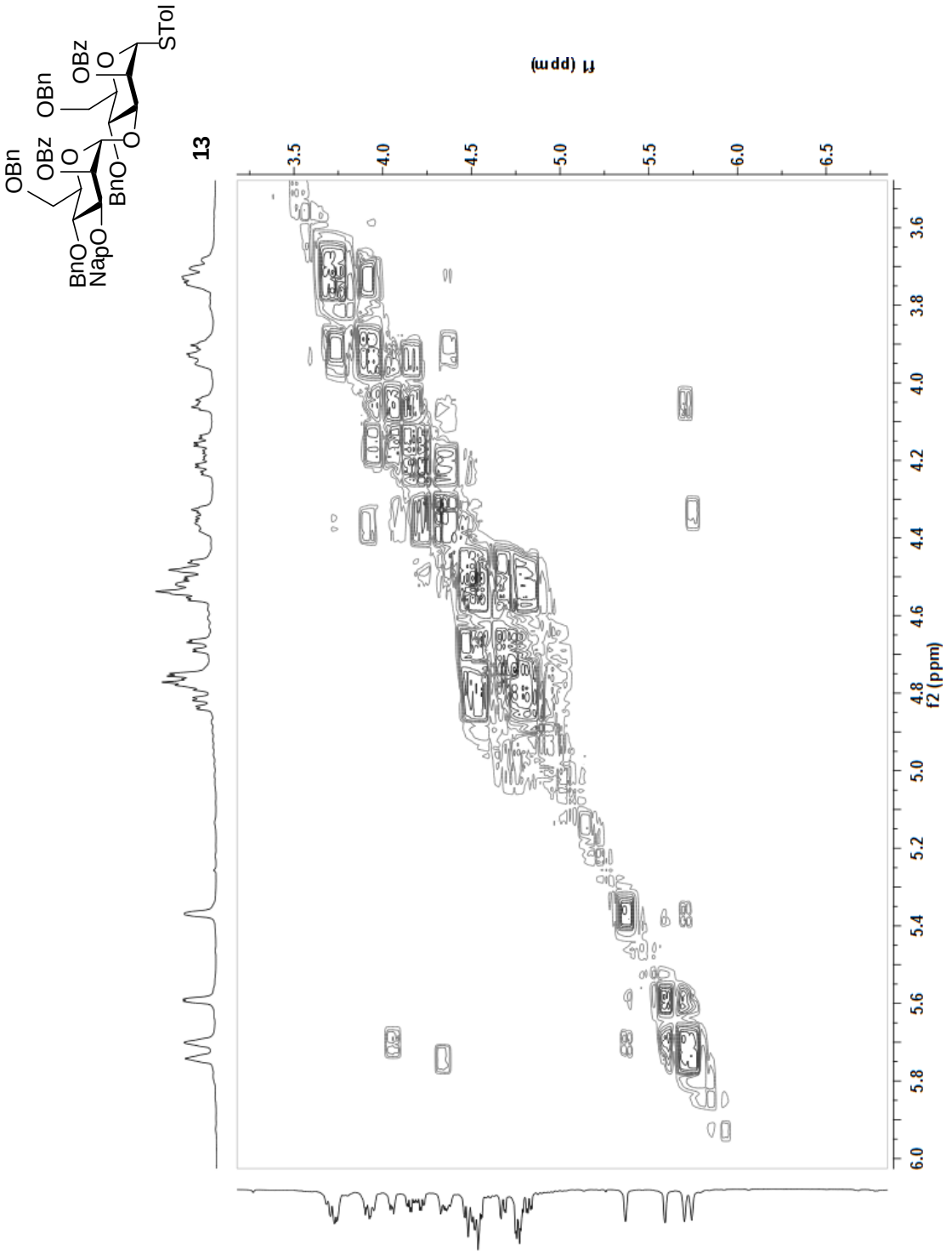
^{1}H NMR spectrum of **13**



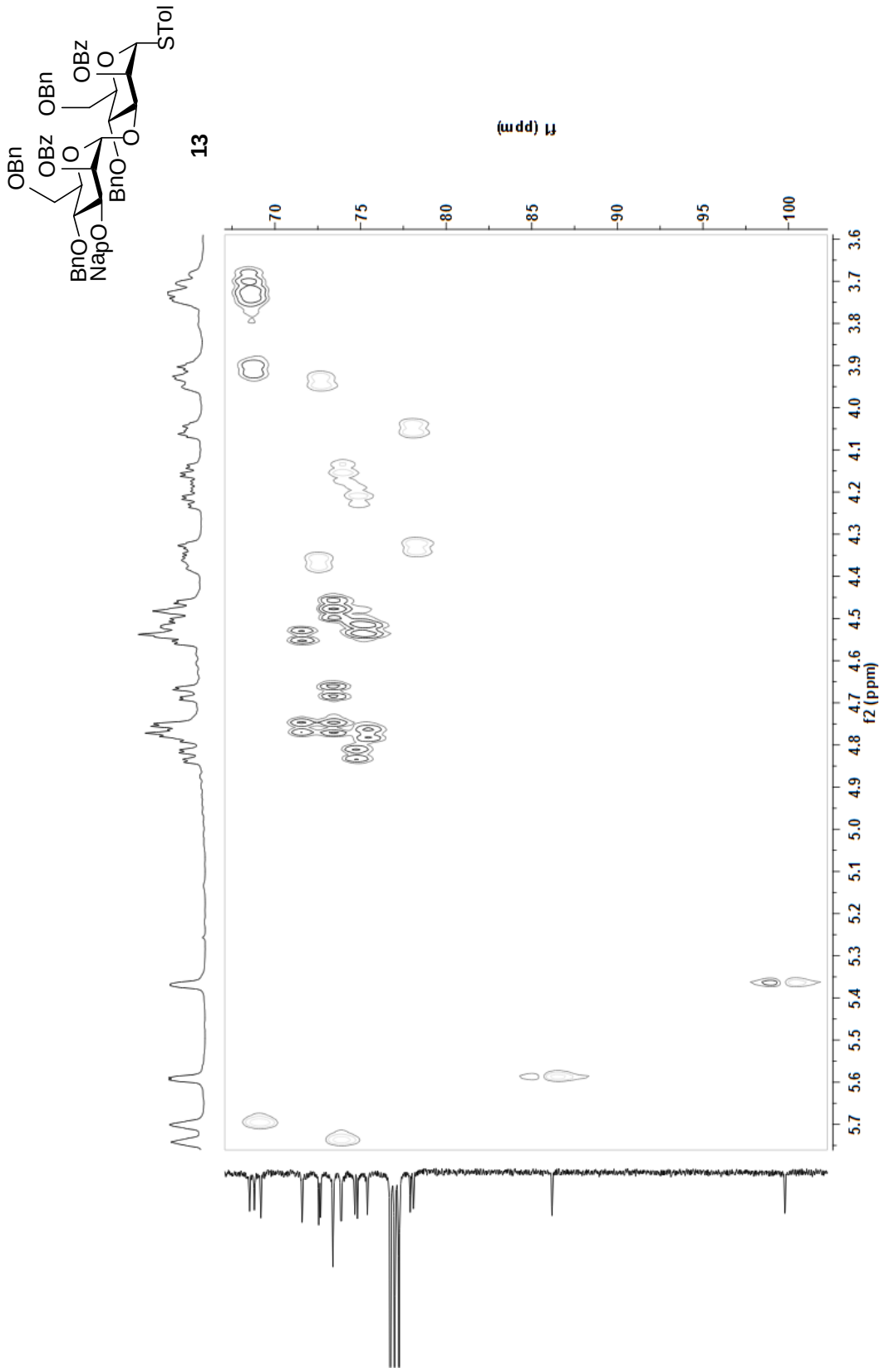
^{13}C NMR spectrum of **13**



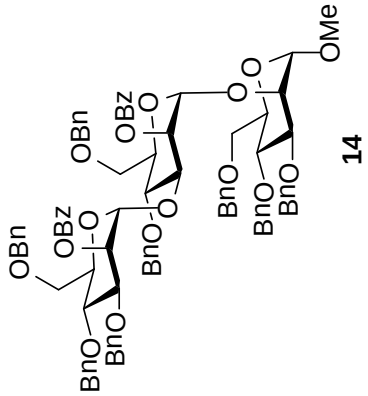
COSY spectrum of **13**



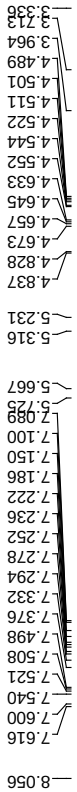
HSQC spectrum of **13**

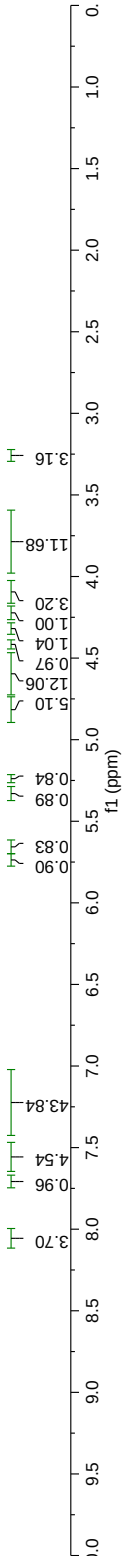


^{1}H NMR spectrum of **14**

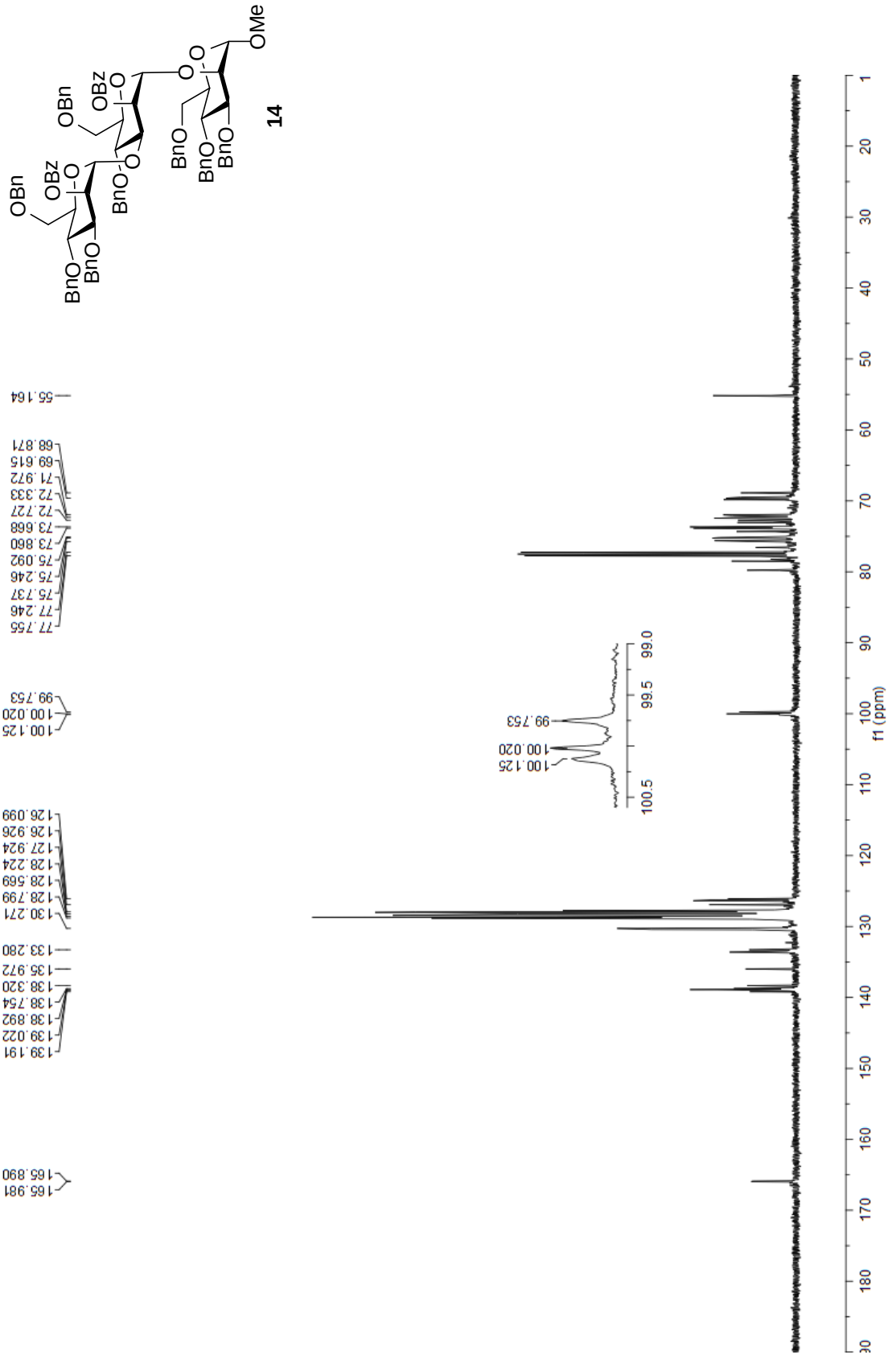


14



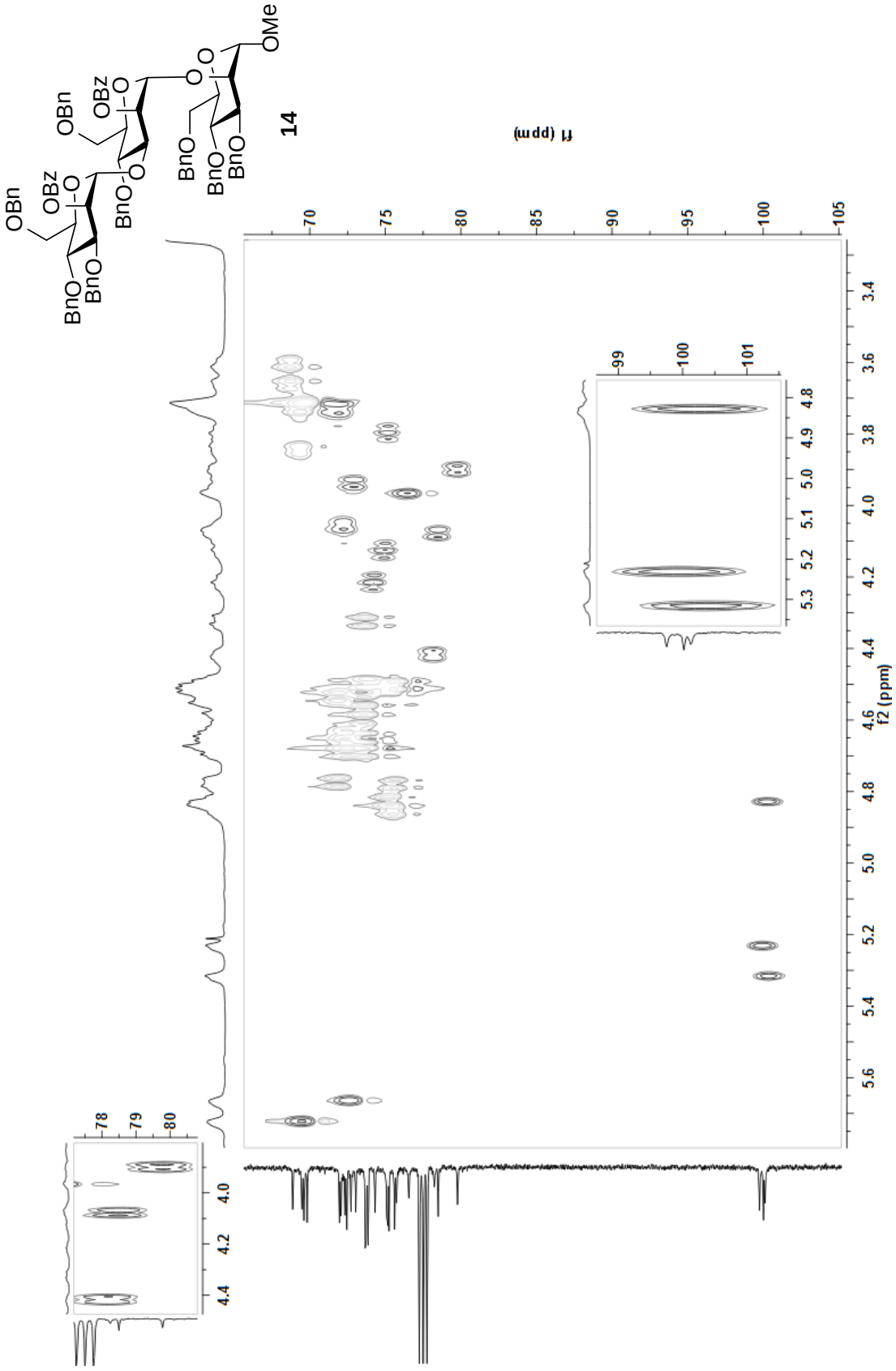


^{13}C NMR spectrum of **14**

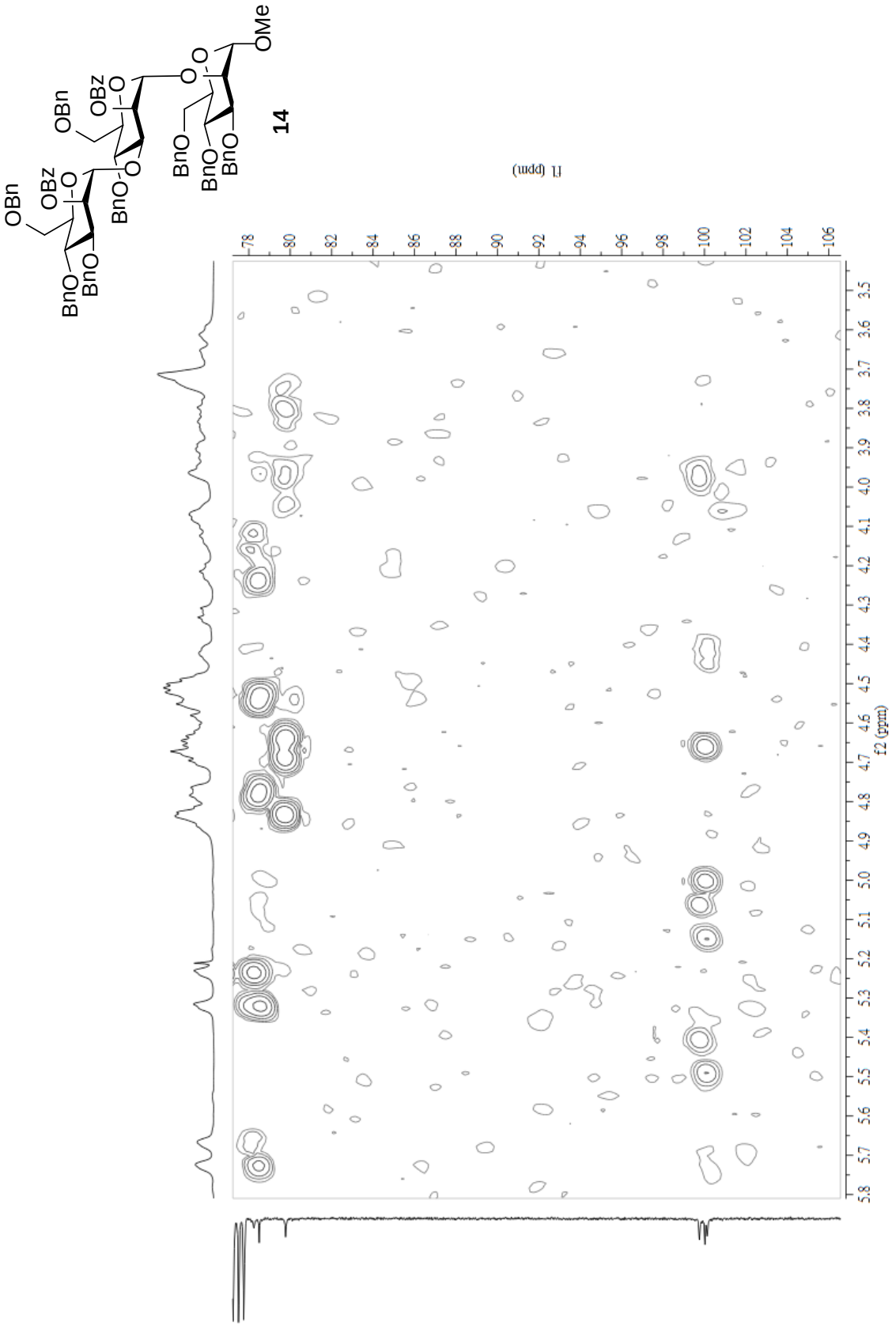


COSY spectrum of **14**

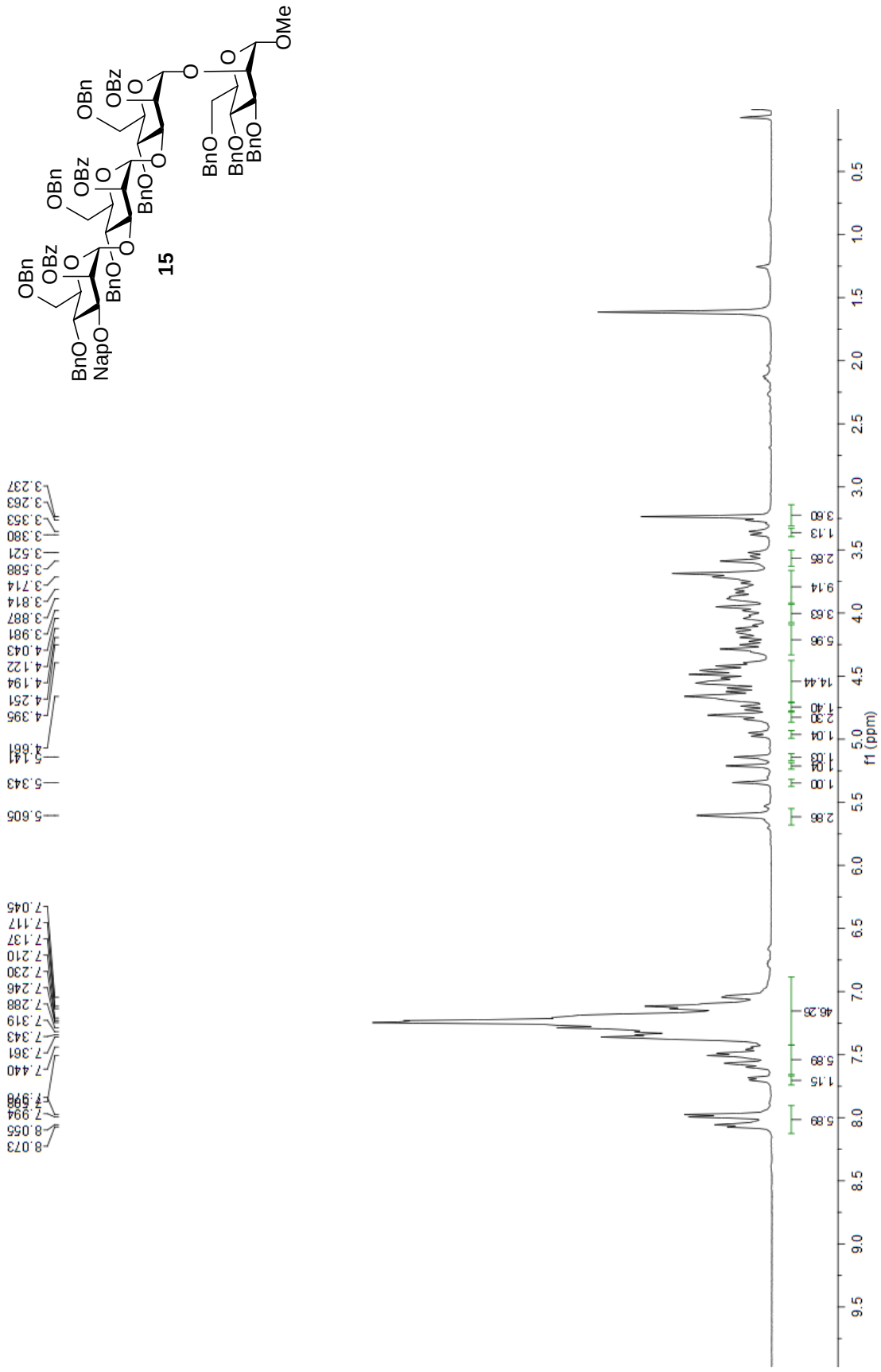
HSQC spectrum of **14**



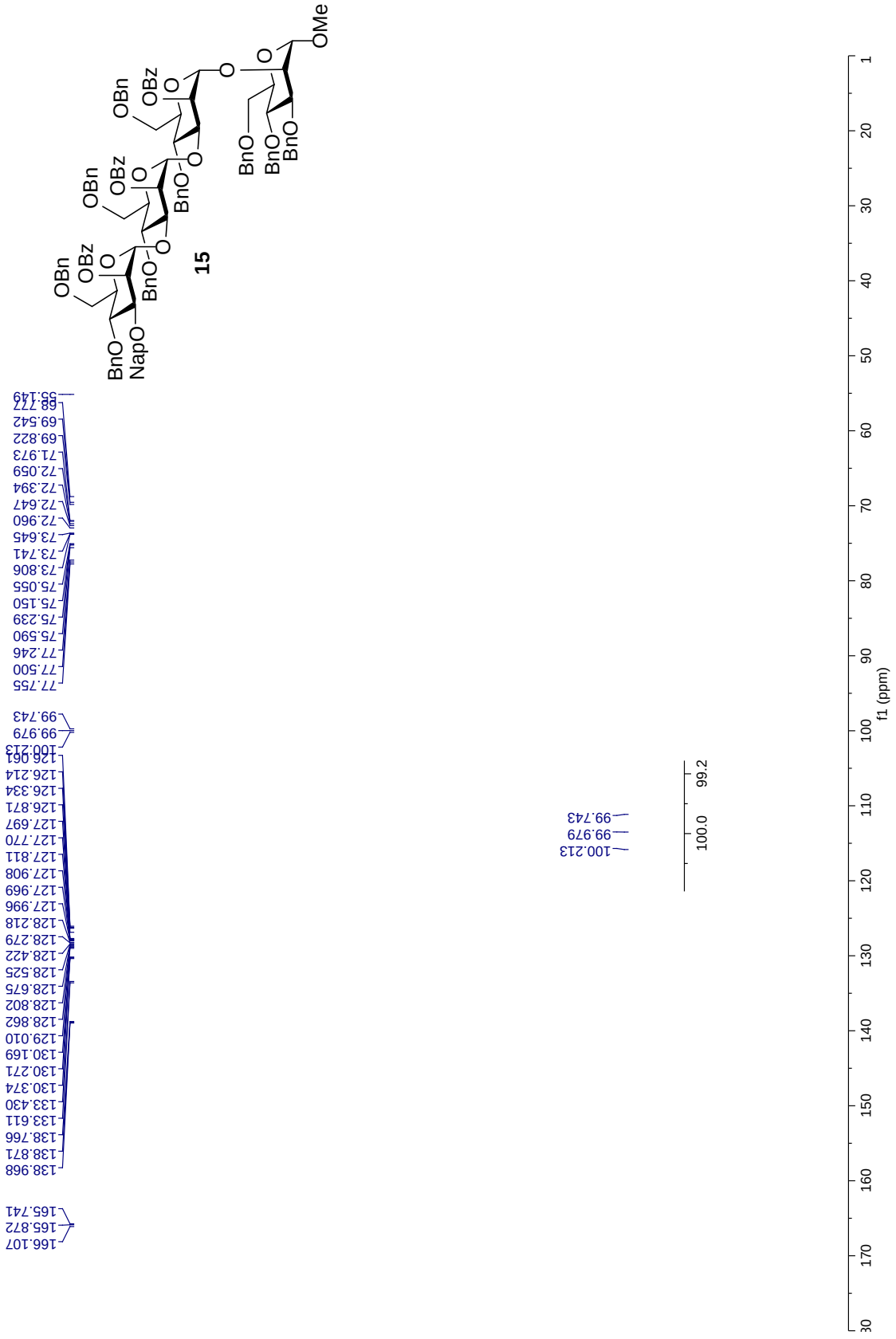
HMBC spectrum of **14**



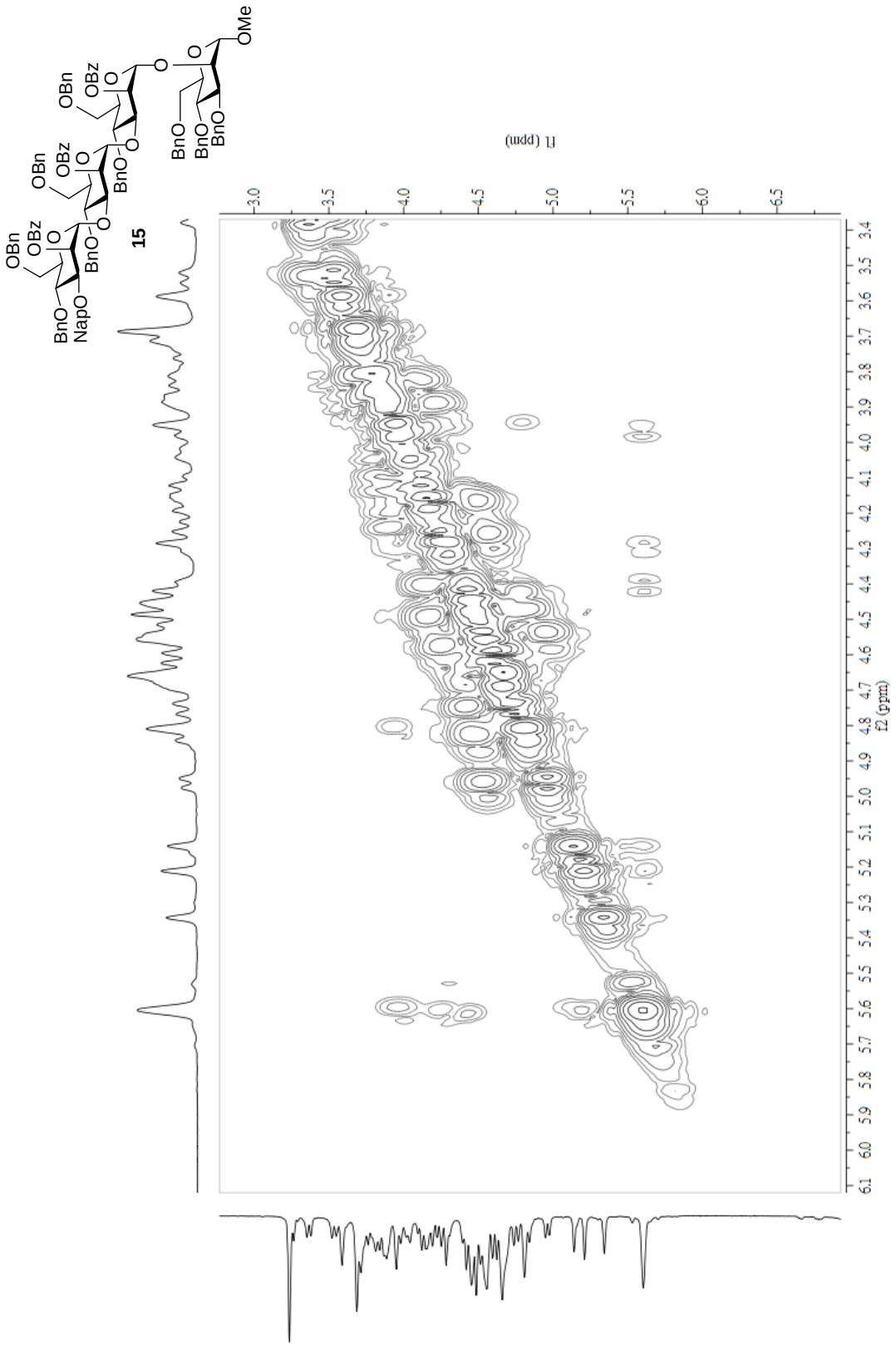
^{1}H NMR spectrum of **15**



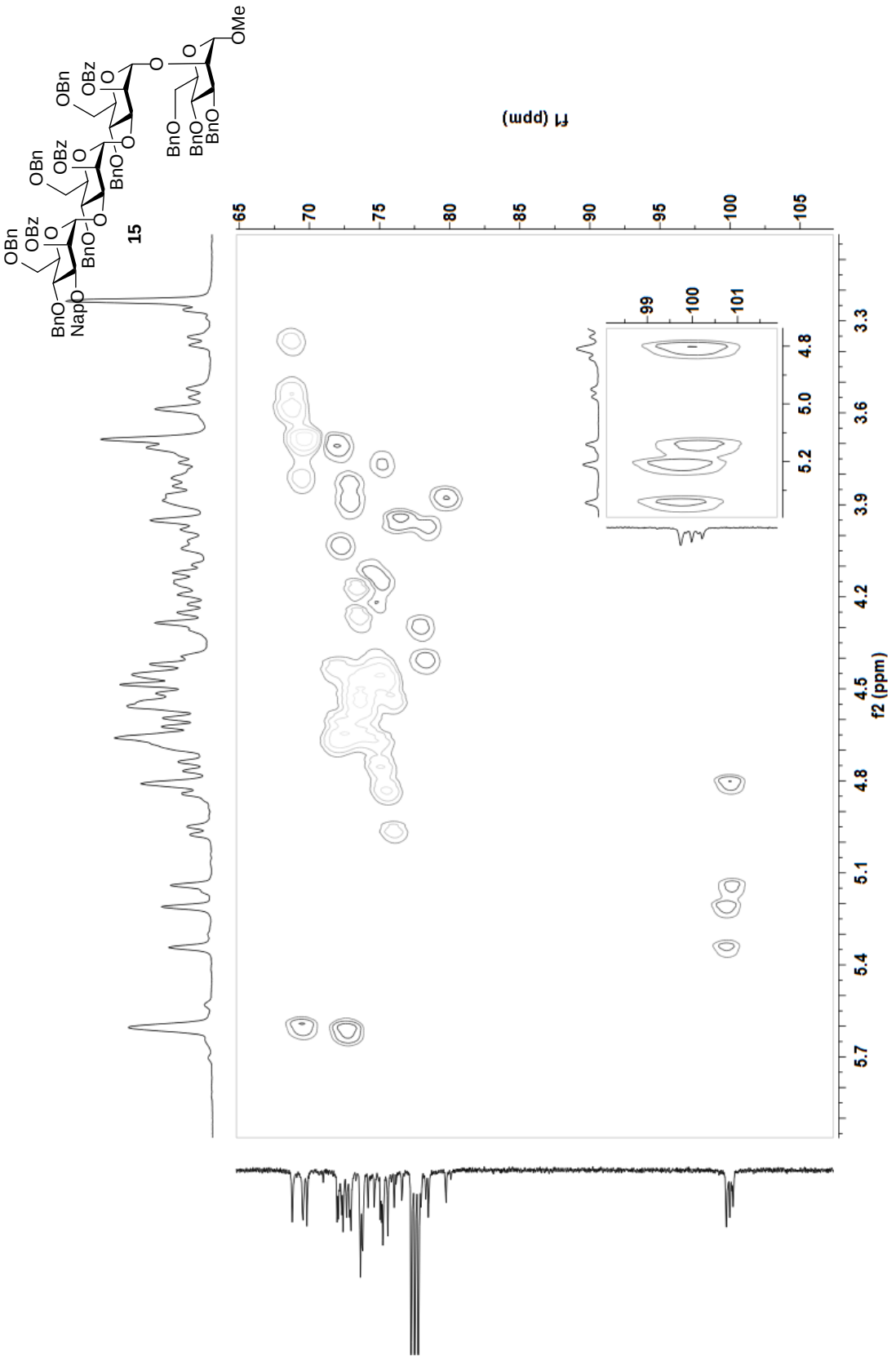
^{13}C NMR spectrum of **15**



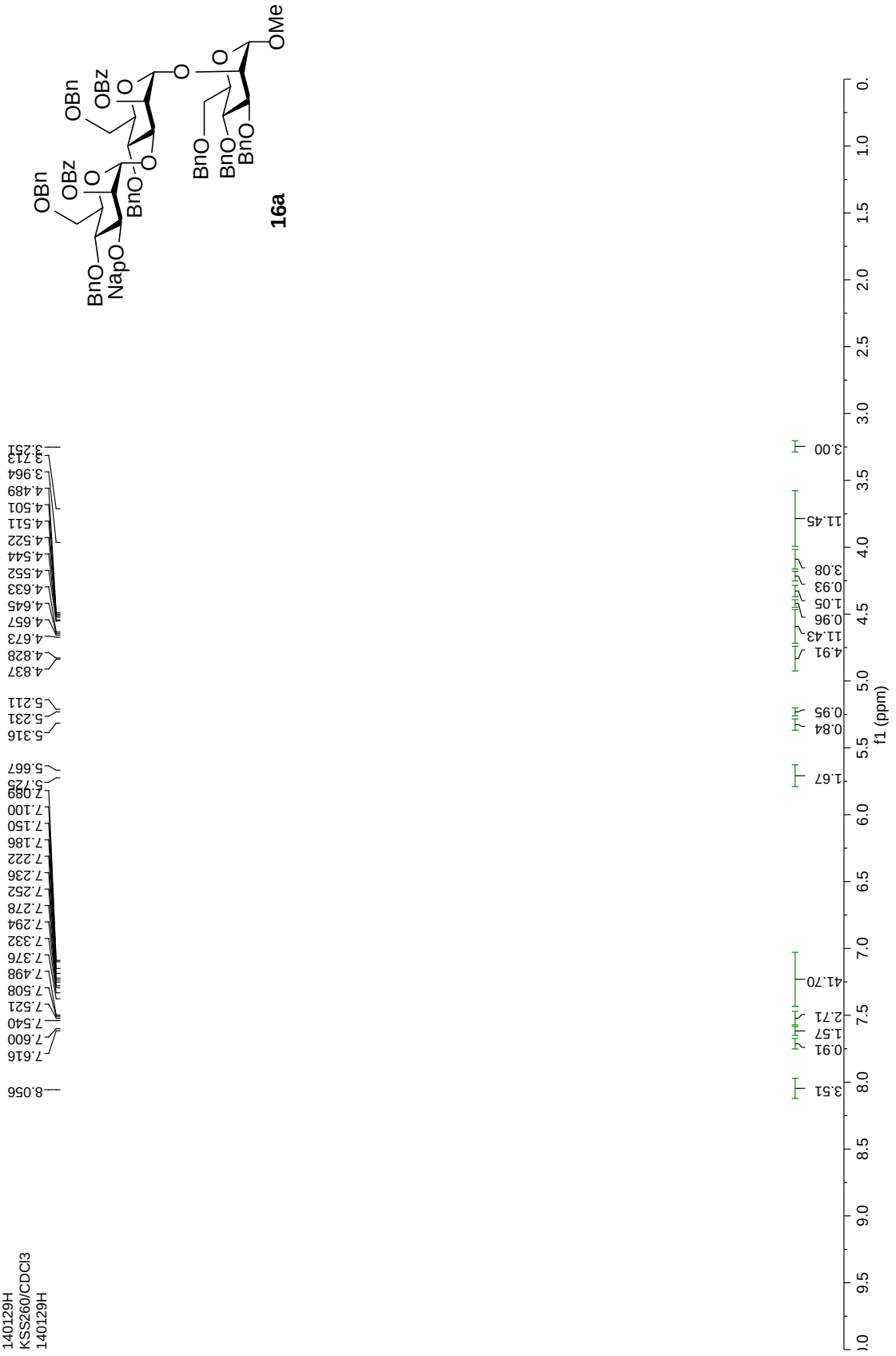
2D COSY of tetramer **15**



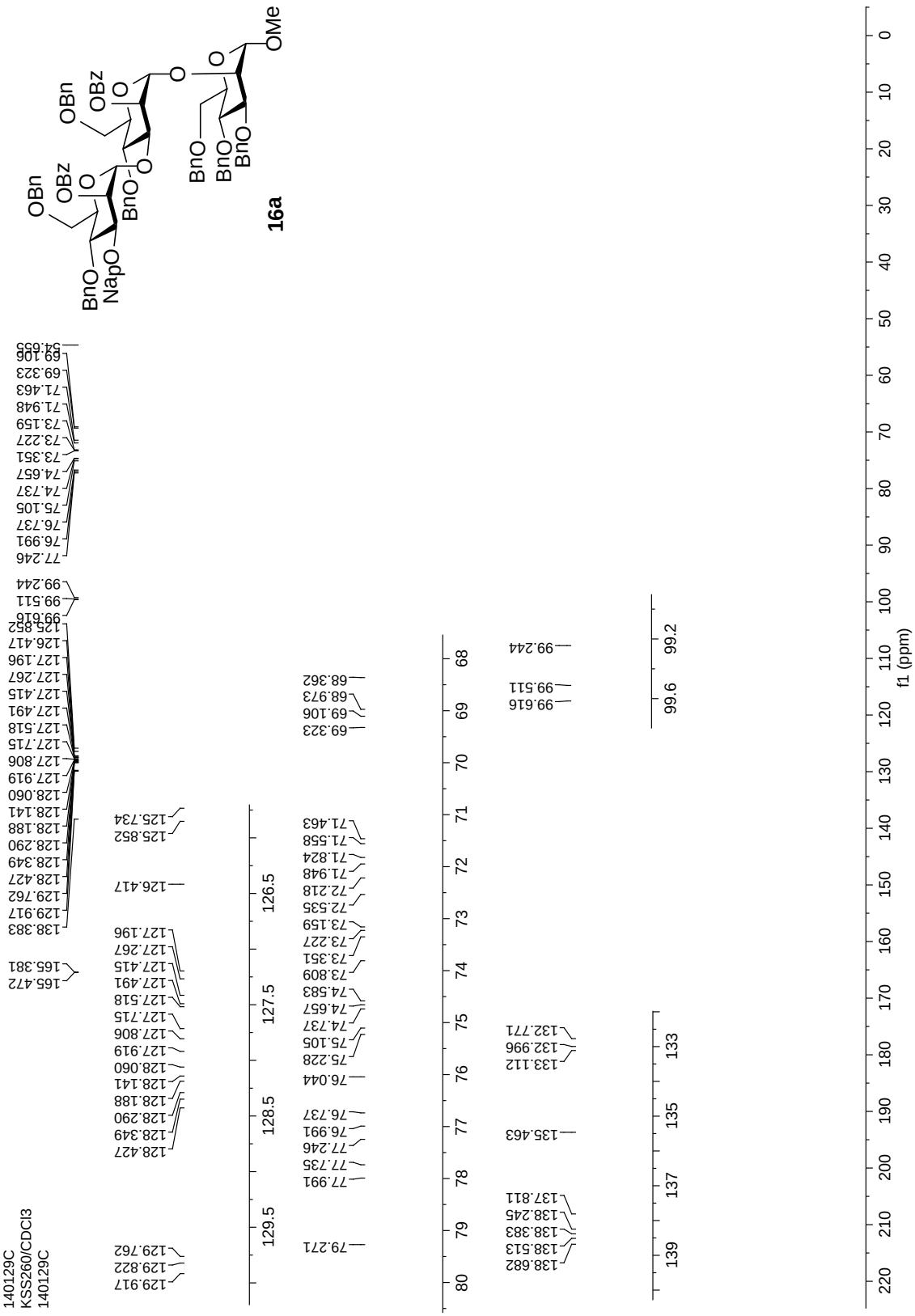
2D HSQC of tetramer **15**



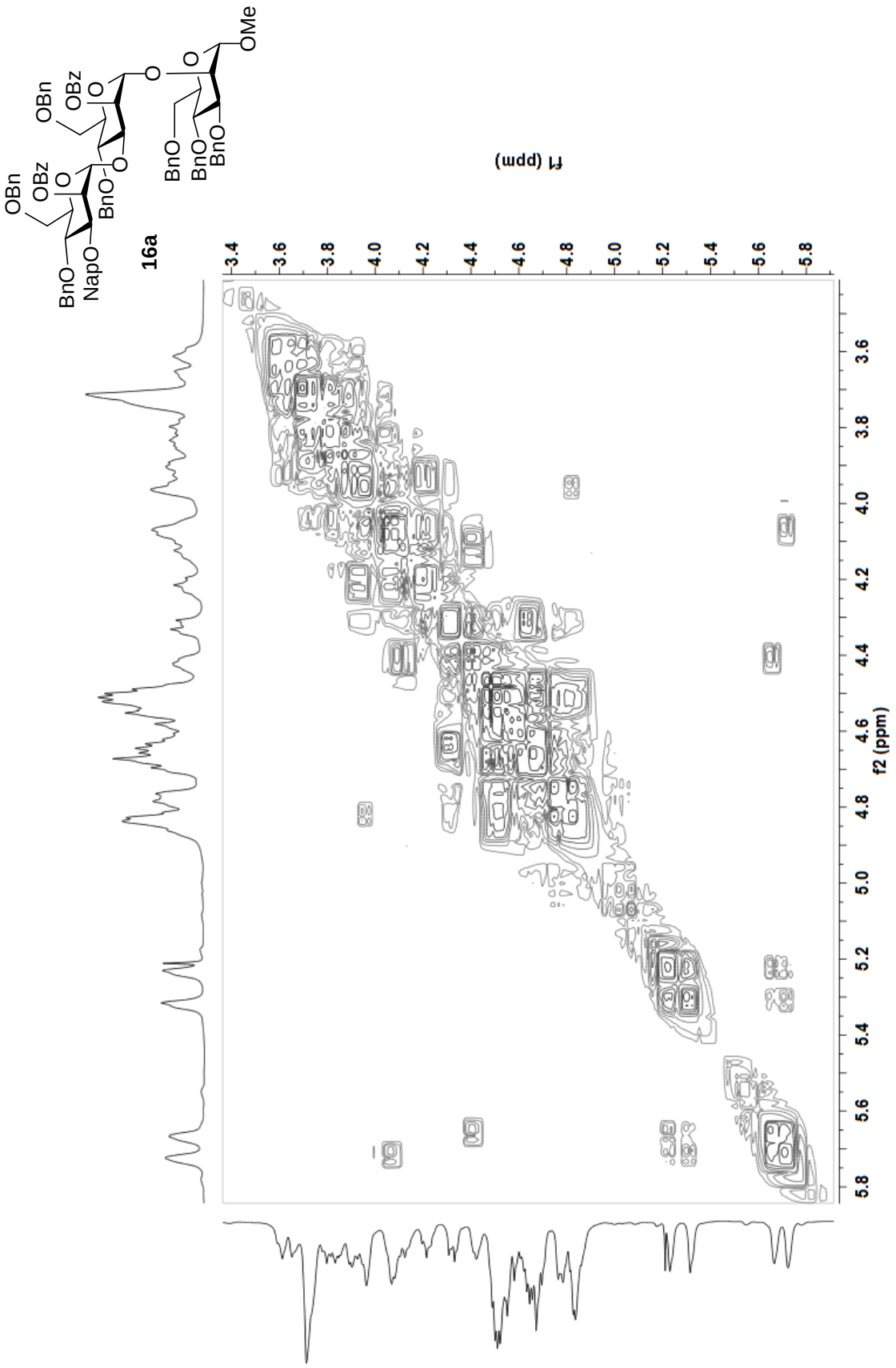
^{1}H NMR of trisaccharide acceptor **16a**



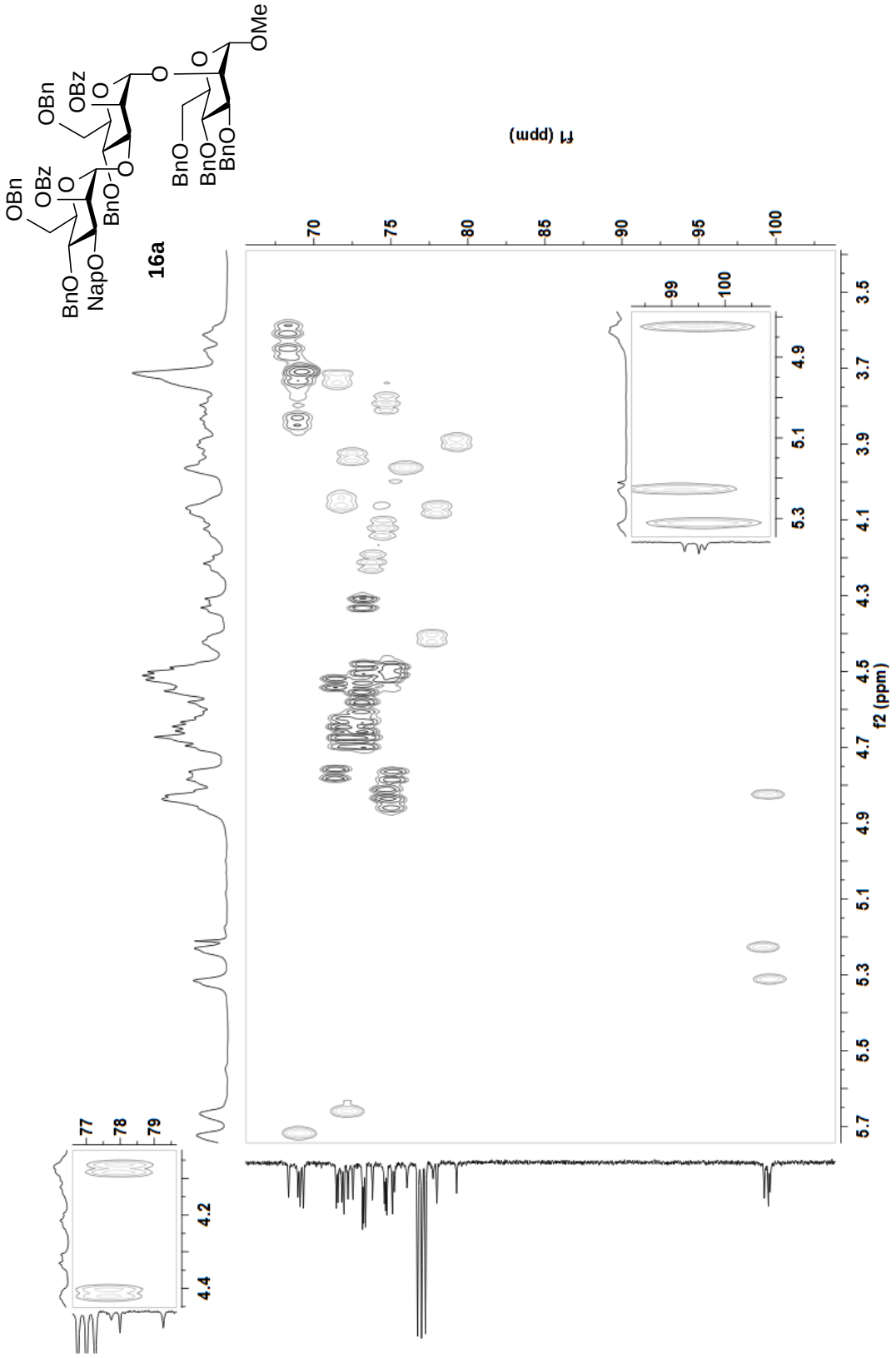
^{13}C NMR of trisaccharide acceptor **16a**



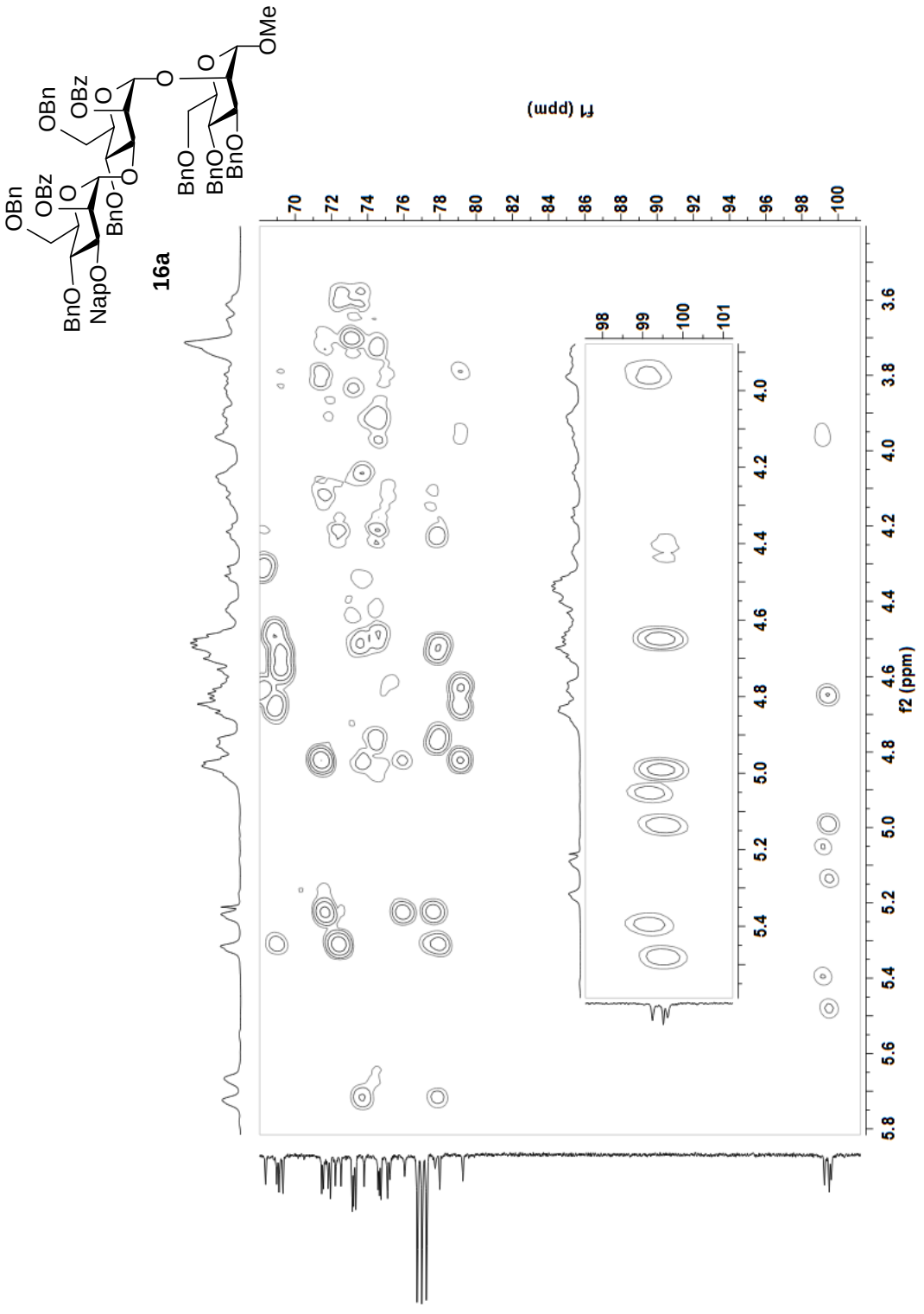
2D COSY of trisaccharide acceptor **16a**



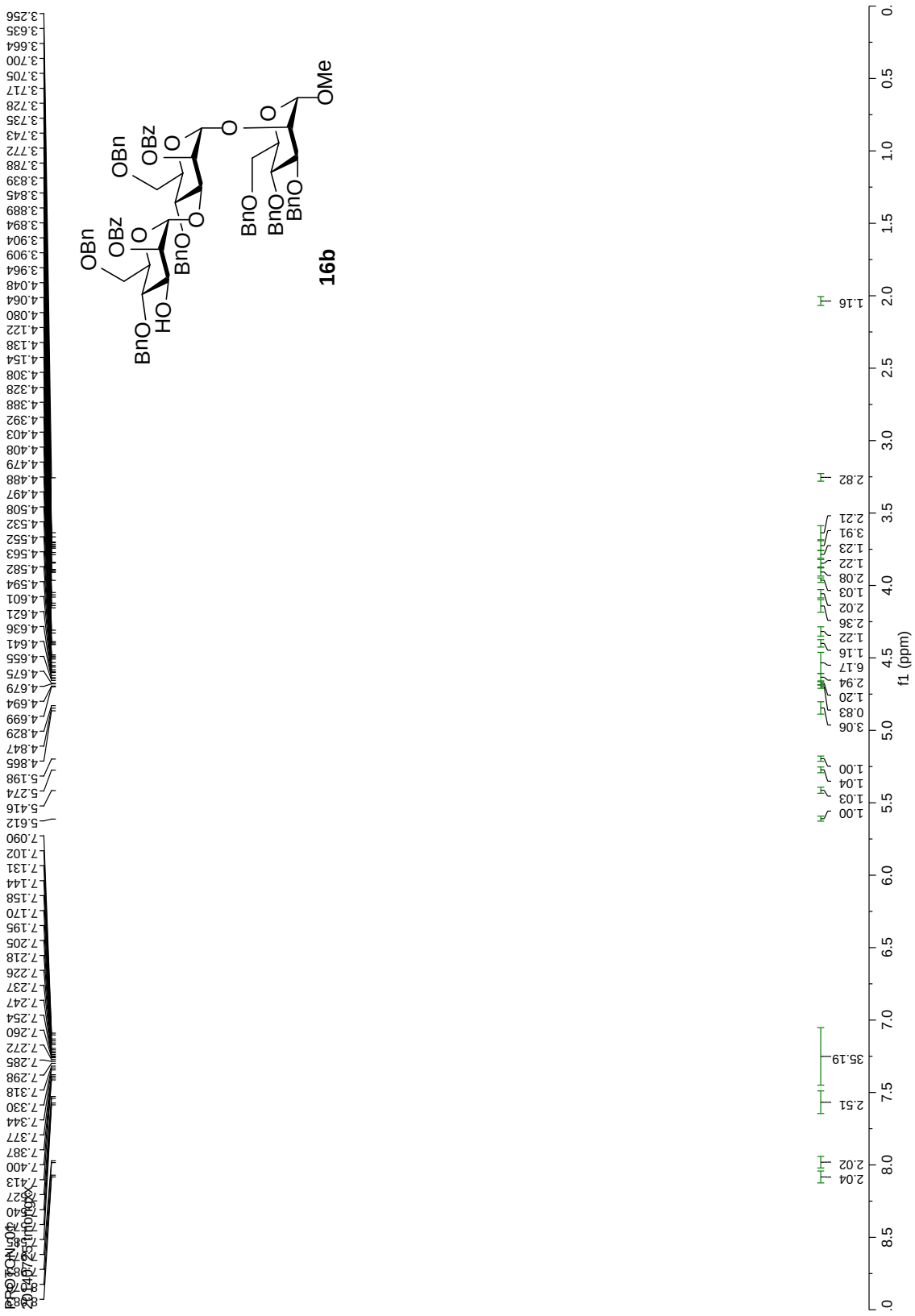
2D HSQC of trisaccharide acceptor **16a**



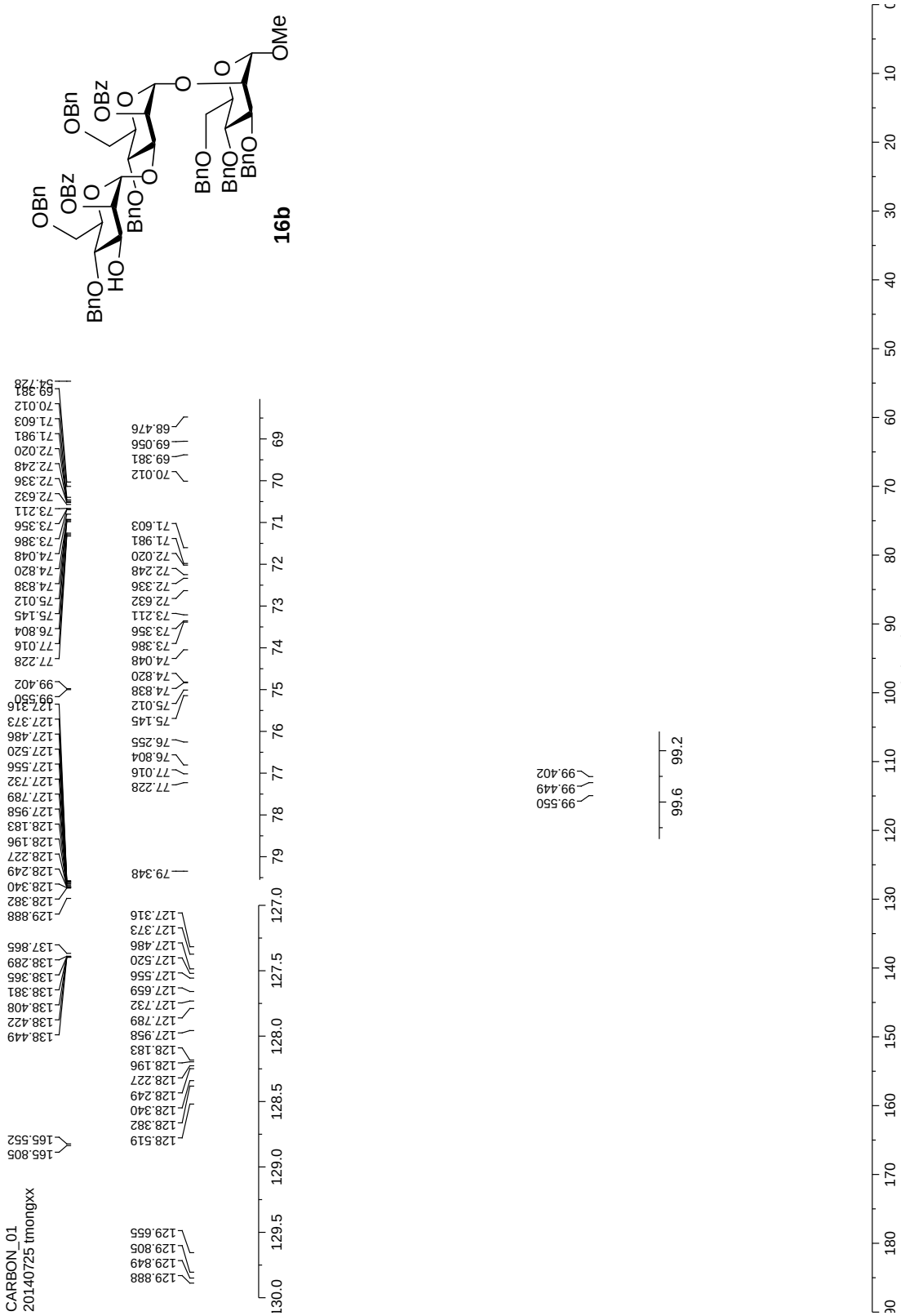
2D HMBC of trisaccharide acceptor **16a**



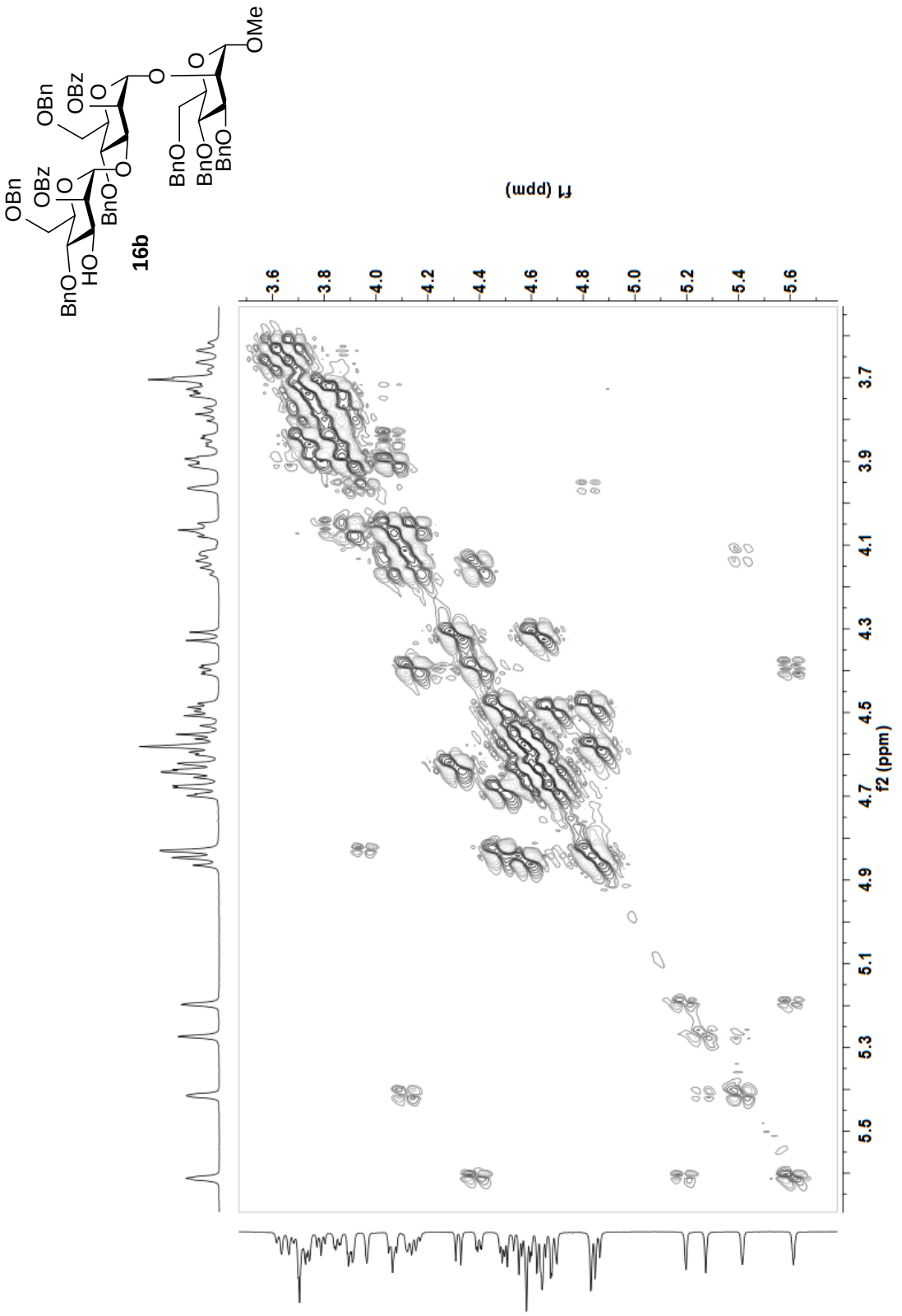
^{1}H NMR of trisaccharide acceptor **16b**



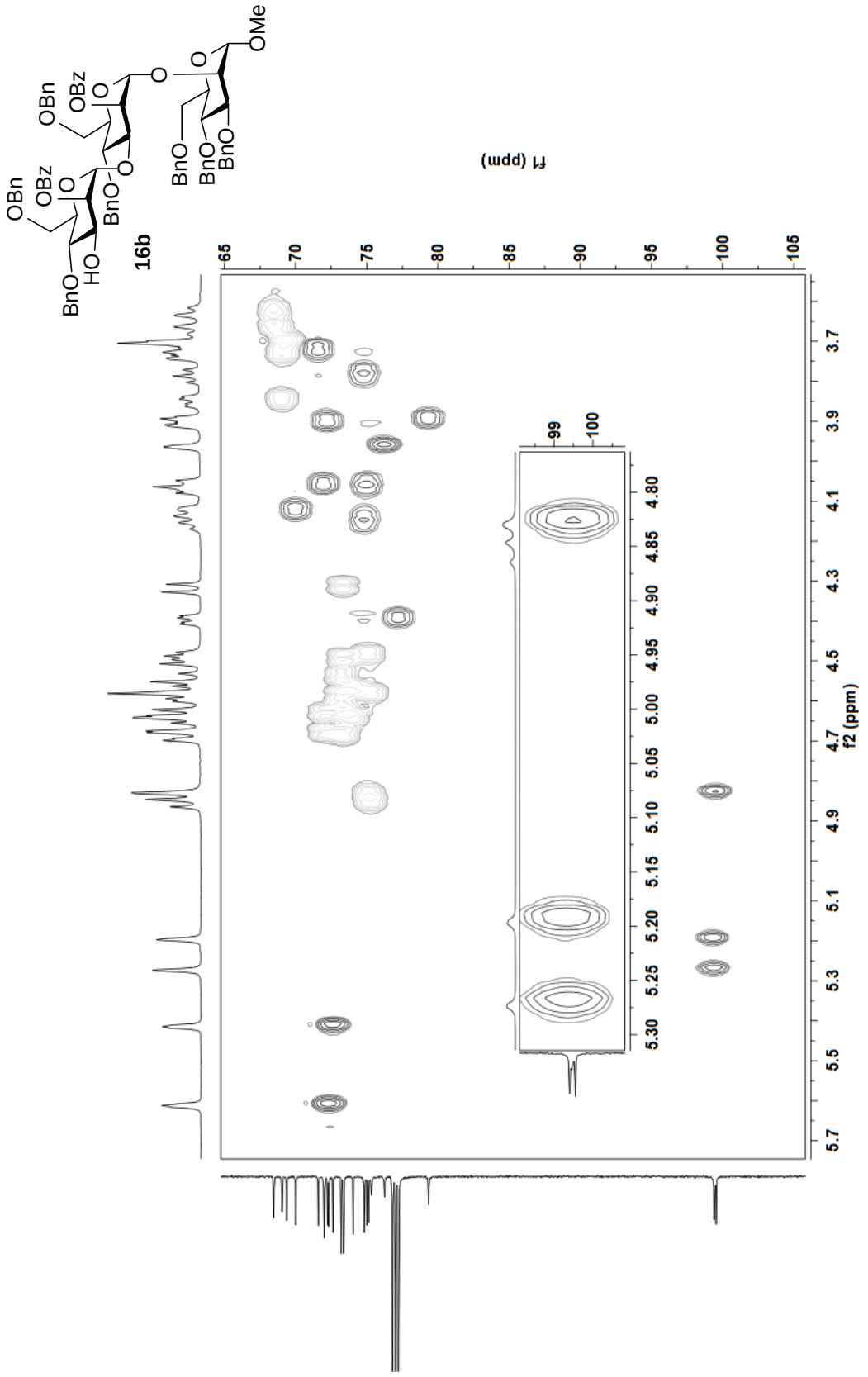
^{13}C NMR of trisaccharide acceptor **16b**



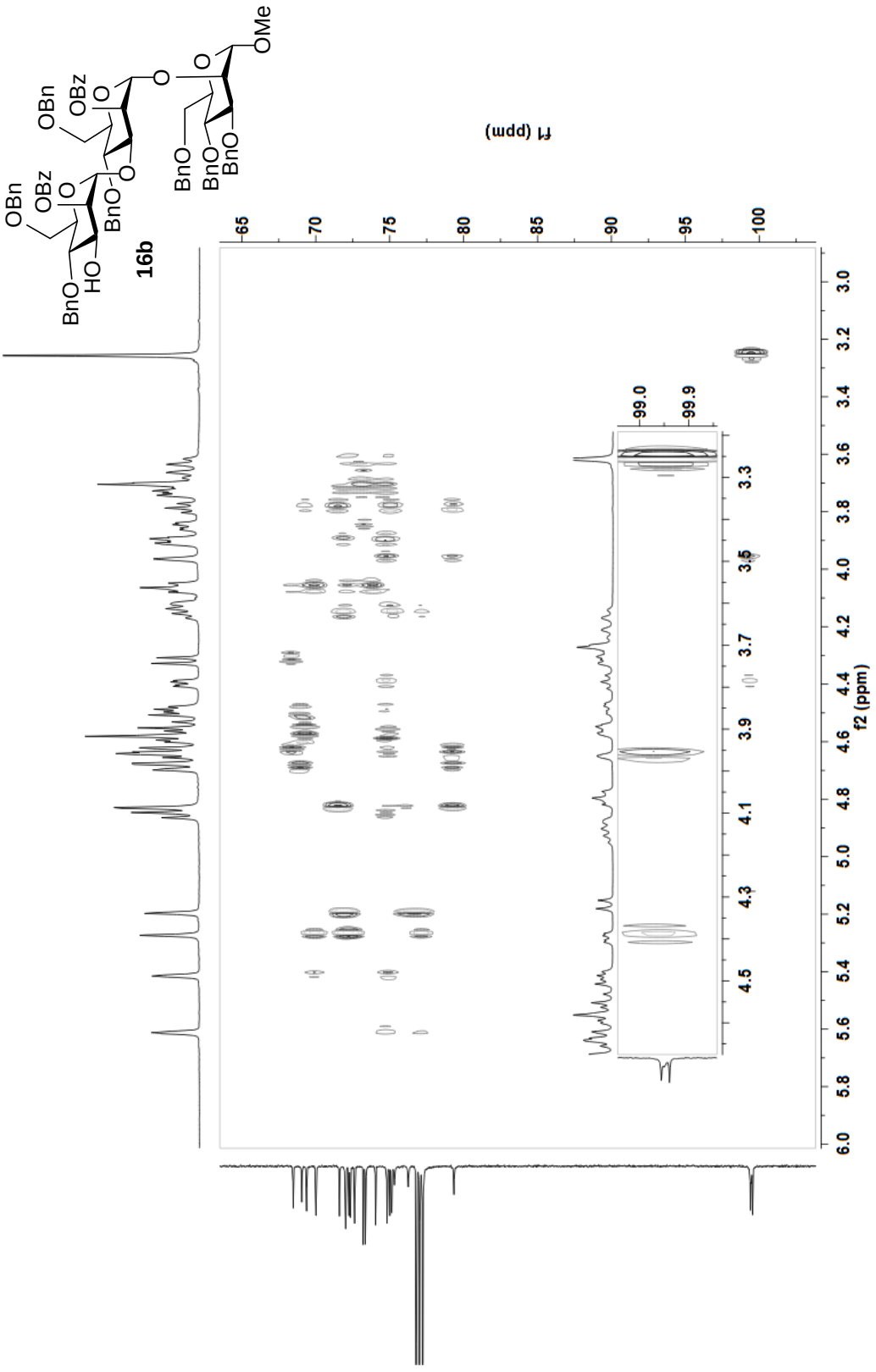
2D COSY of trisaccharide acceptor **16b**



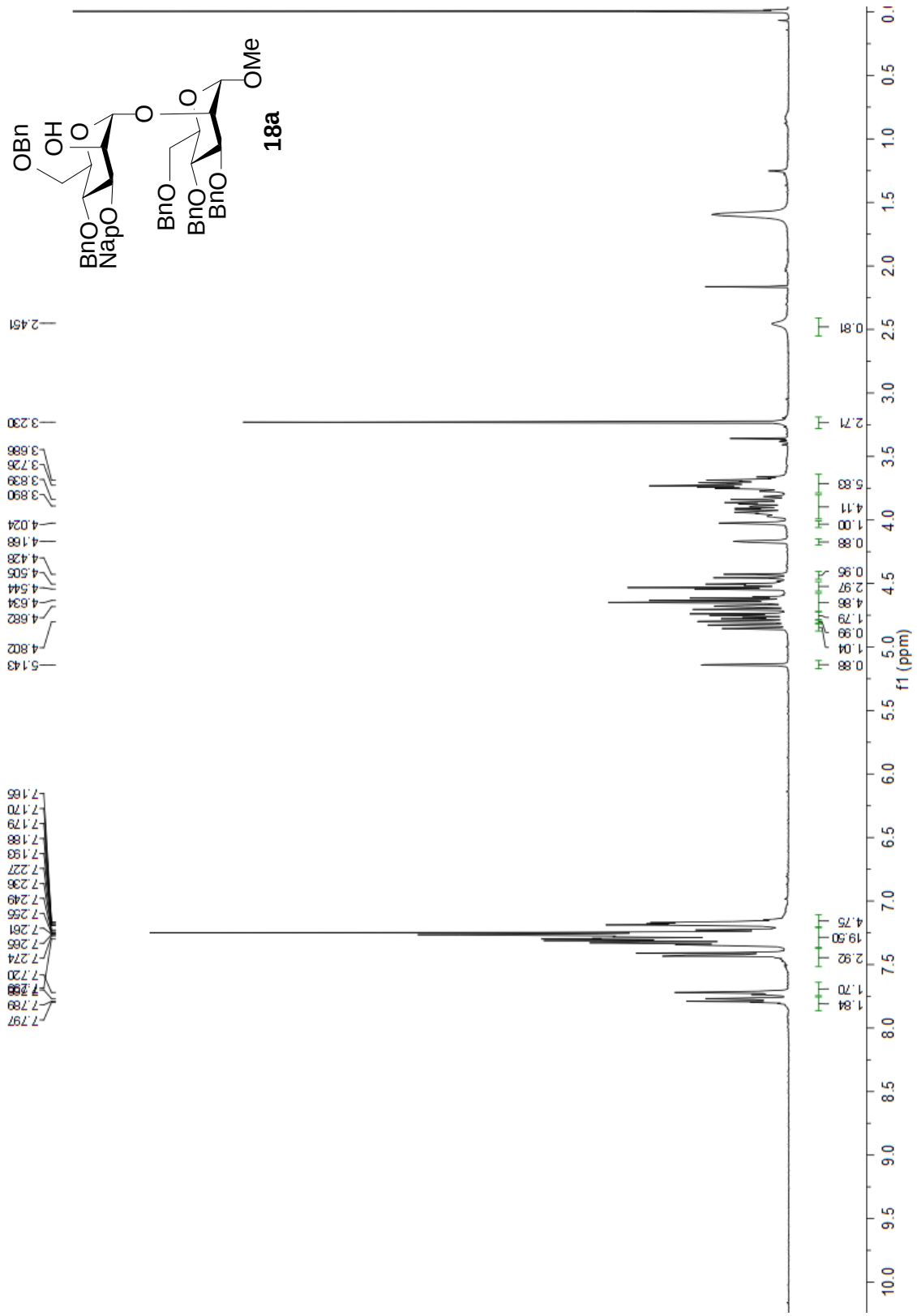
2D HSQC of trisaccharide acceptor **16b**



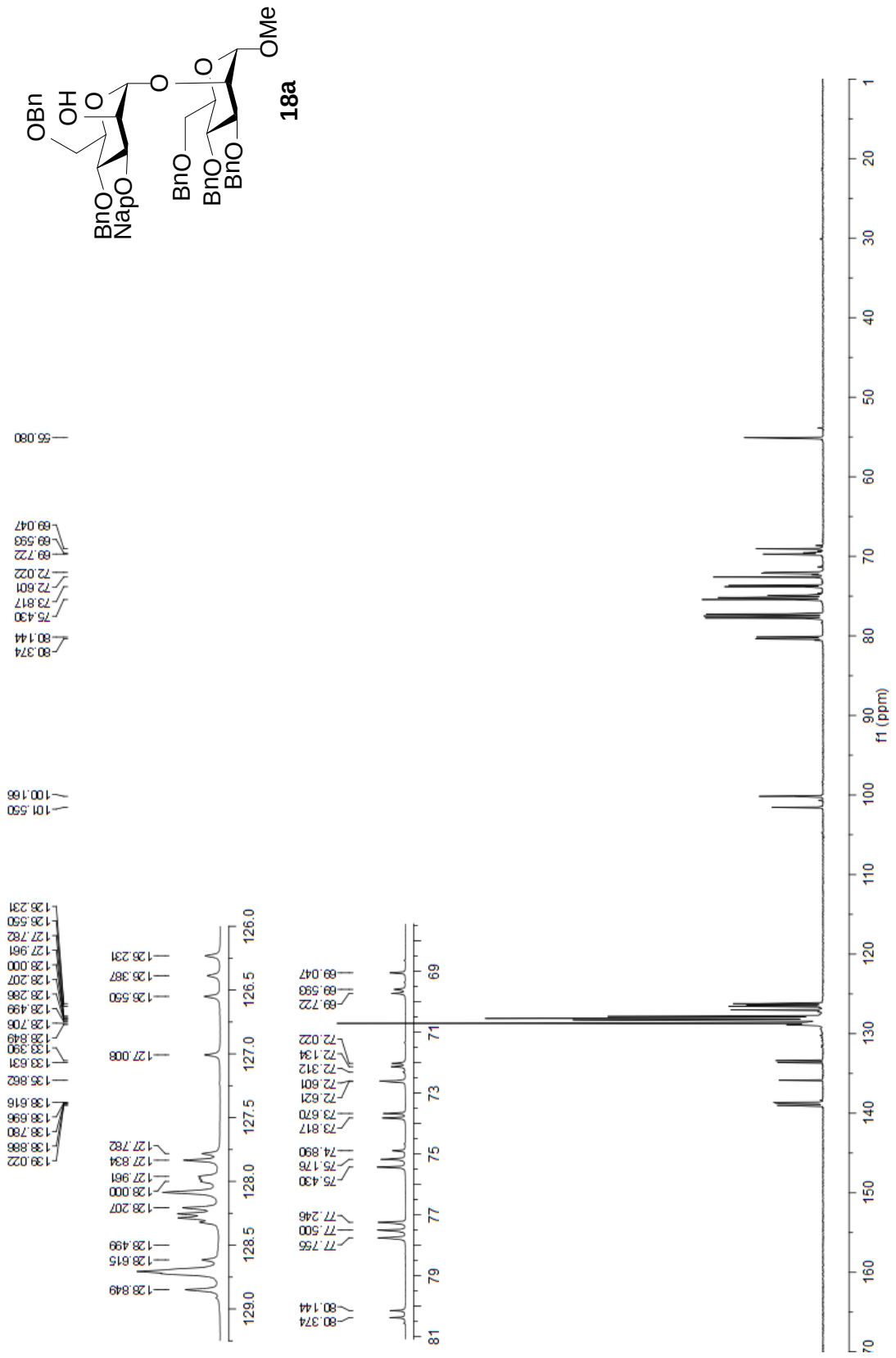
2D HMBC of trisaccharide acceptor **16b**



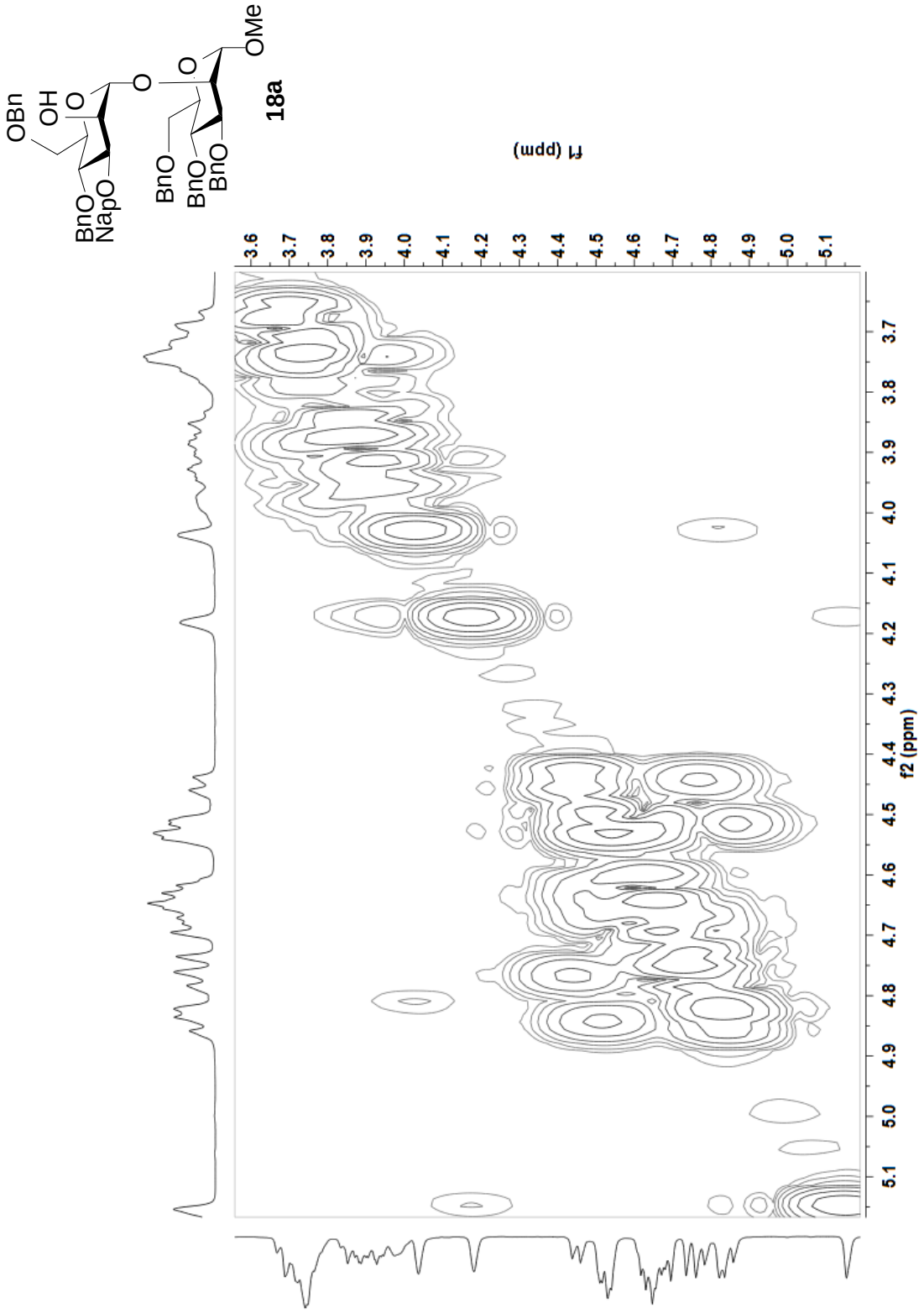
^{1}H NMR spectrum of **18a**



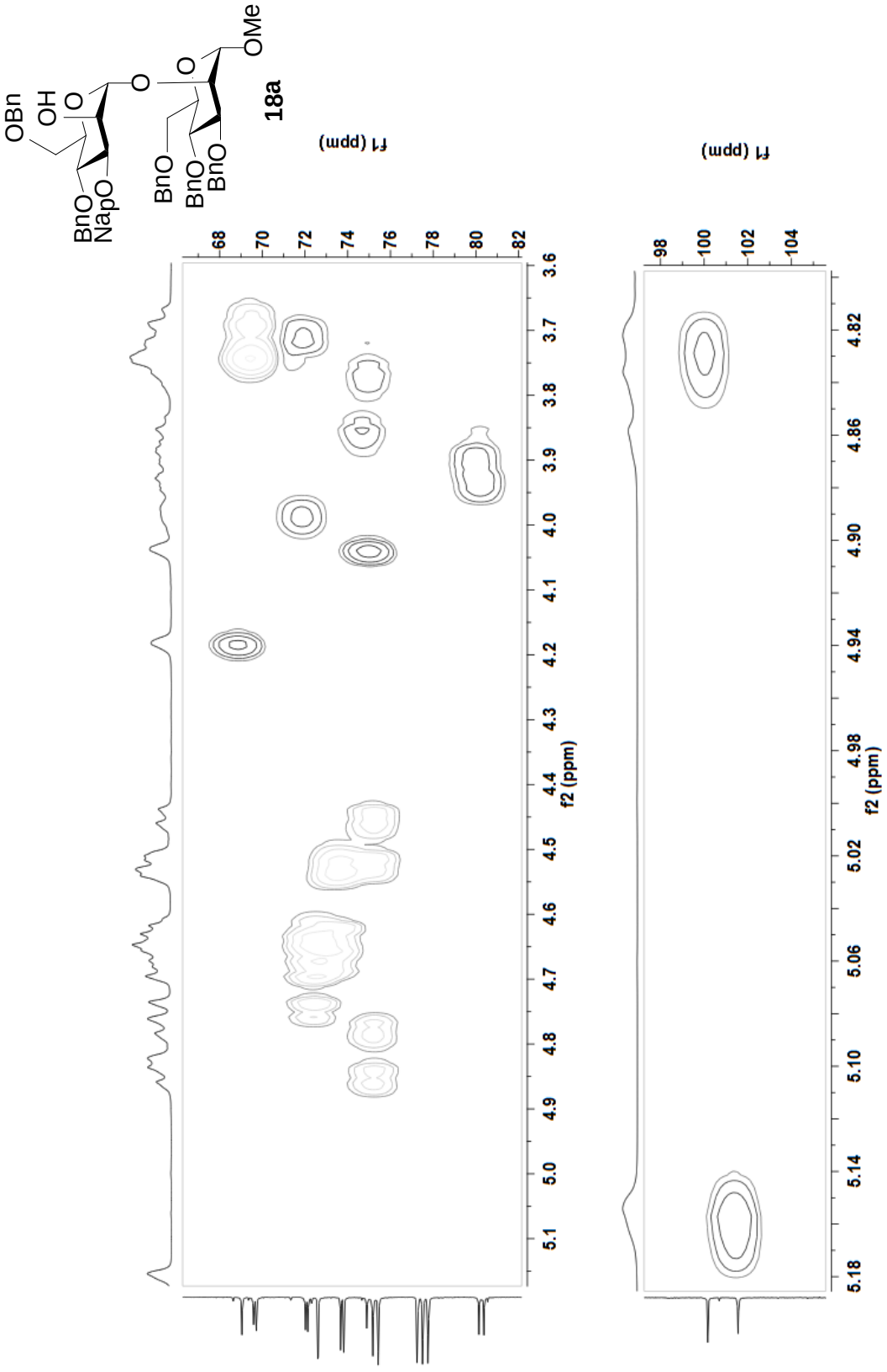
^{13}C NMR spectrum of **18a**



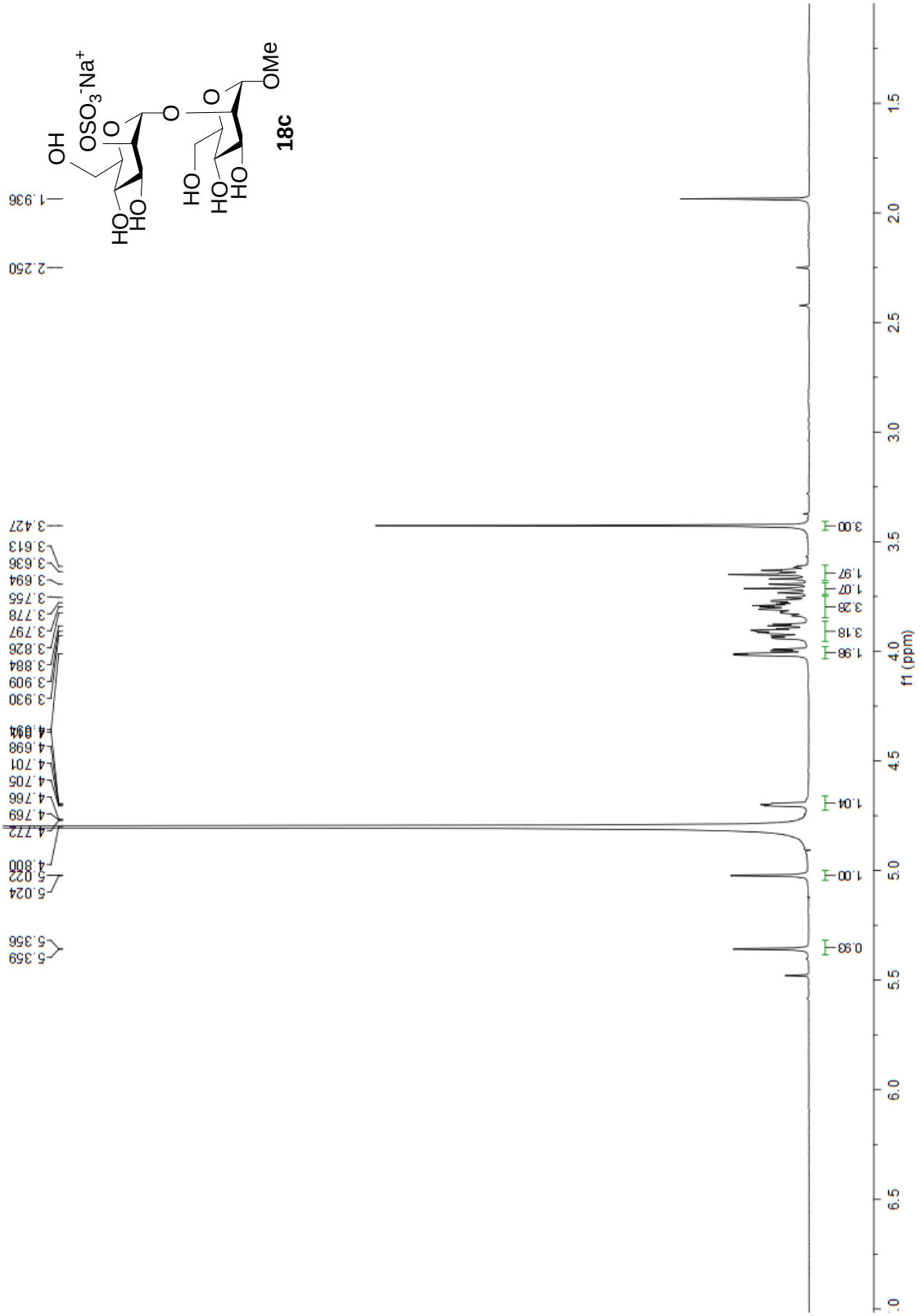
COSY spectrum of **18a**



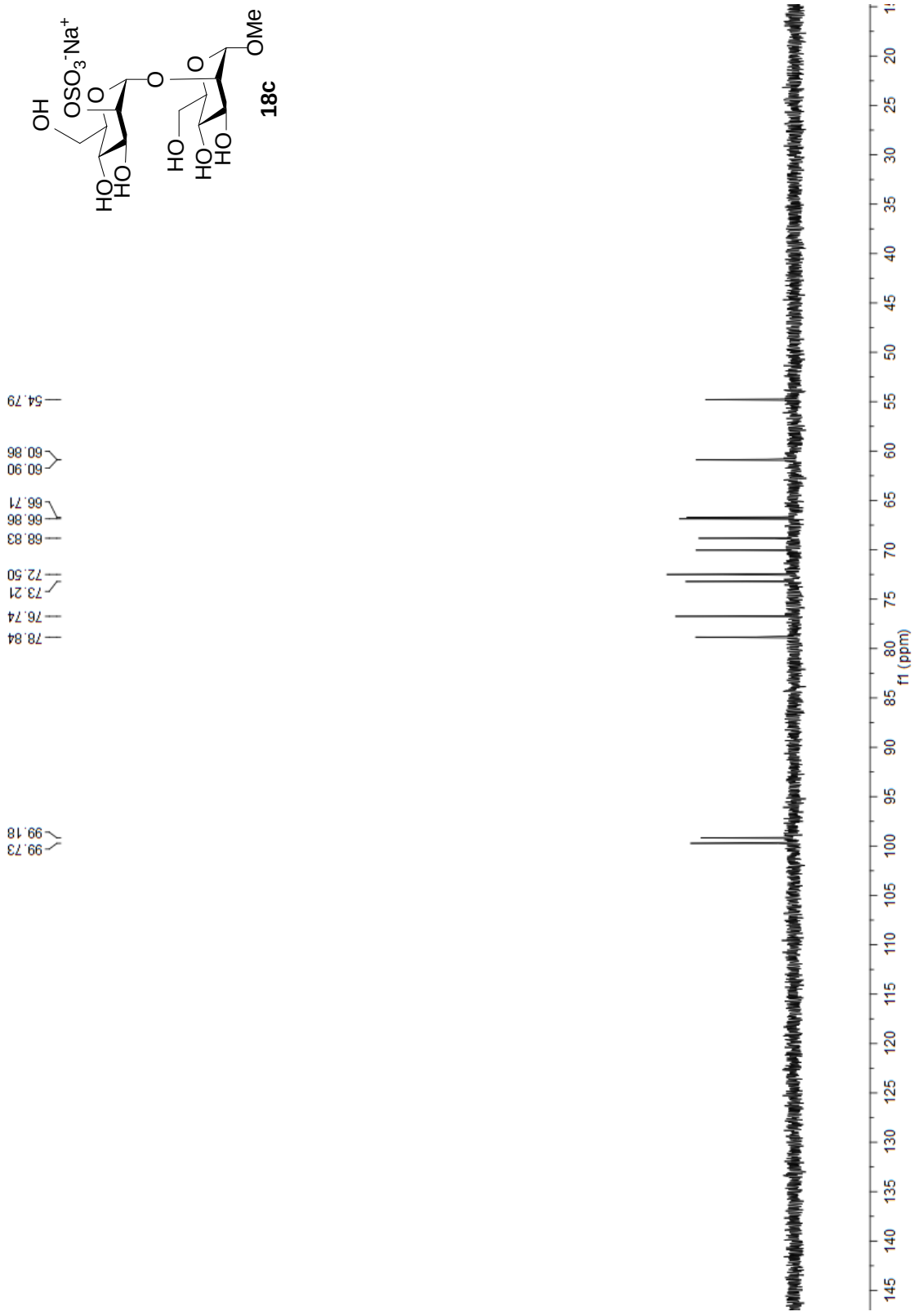
HSQC spectrum of **18a**



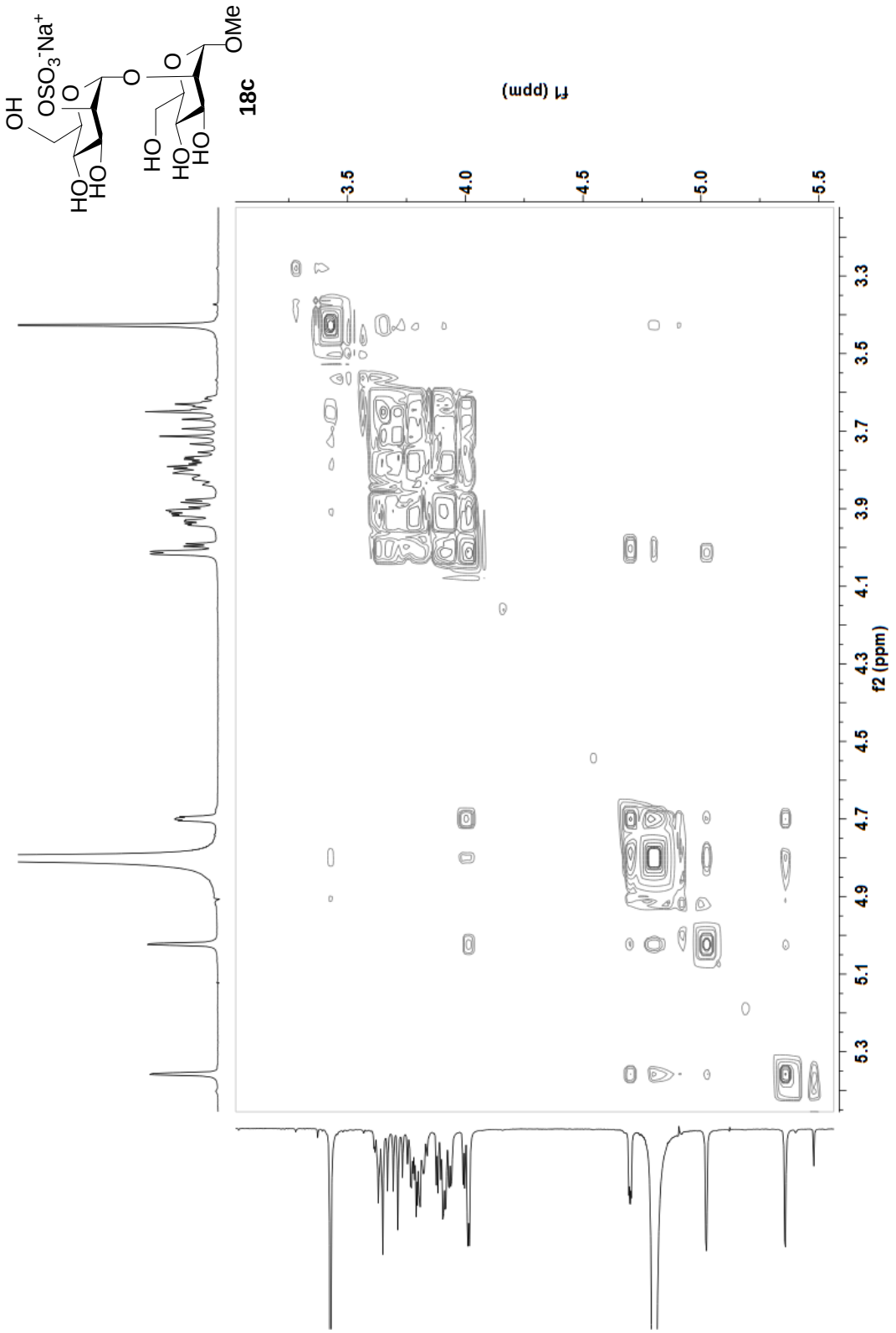
^{1}H NMR spectrum of **18c**



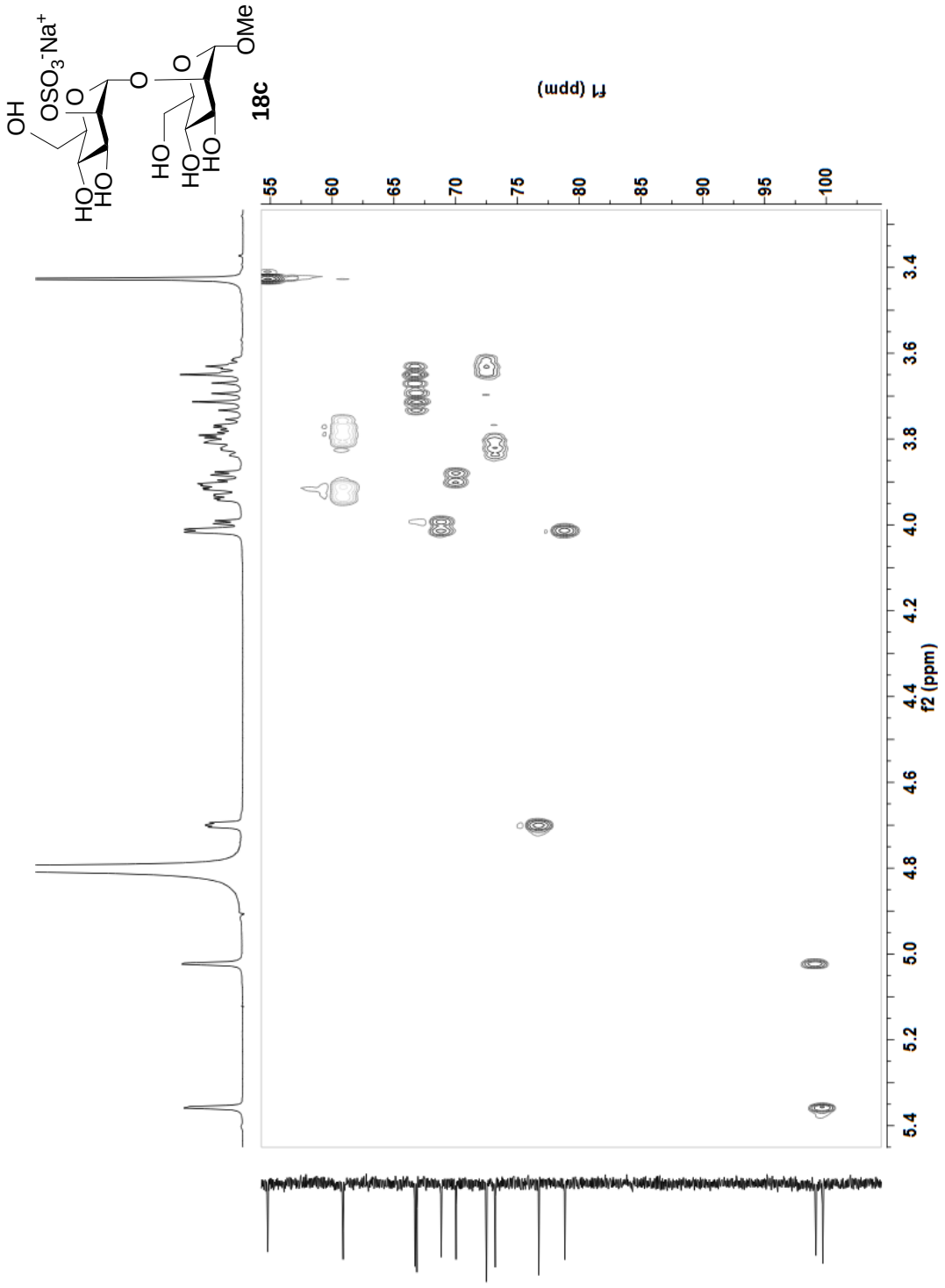
^{13}C NMR spectrum of **18c**



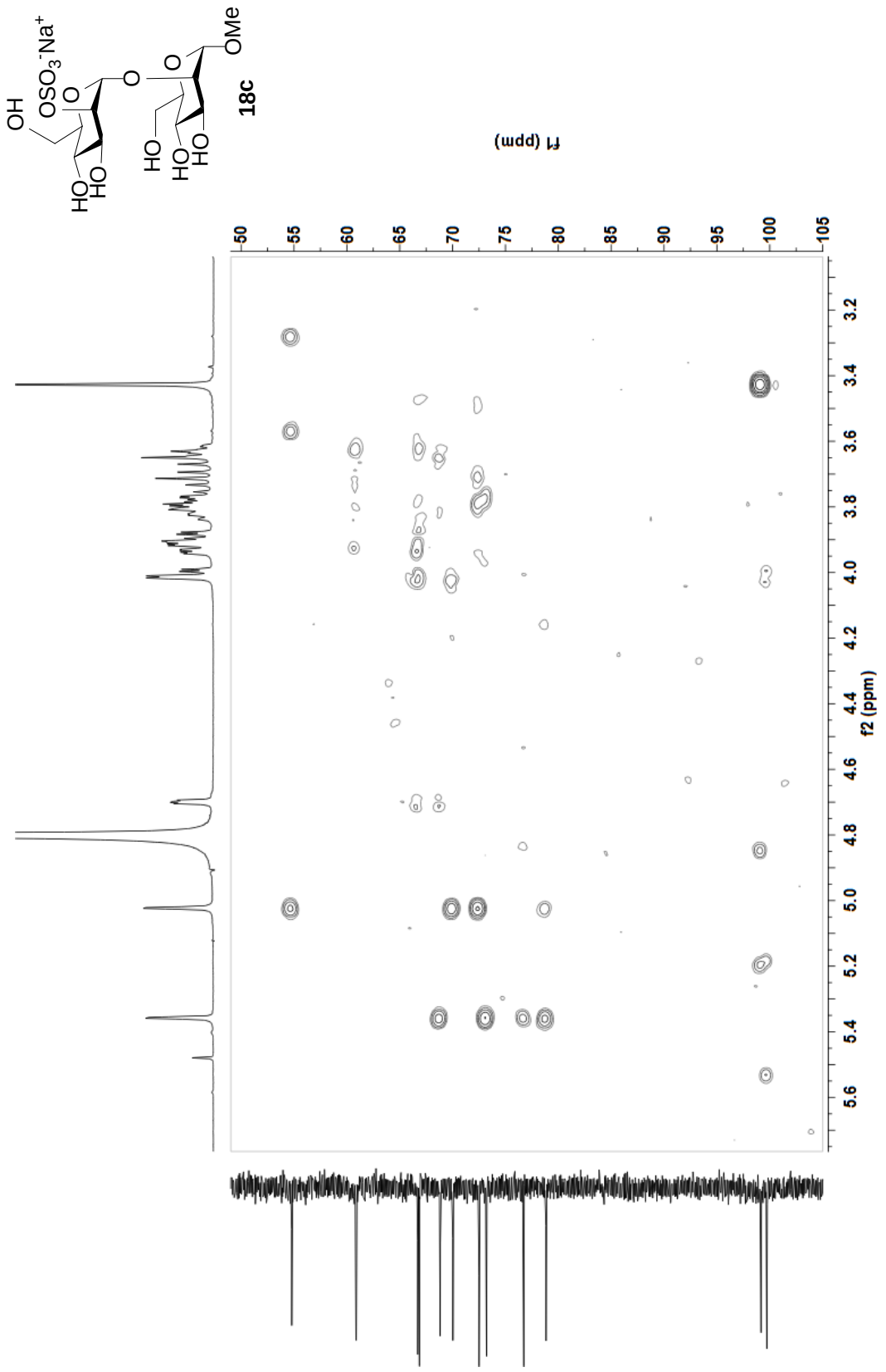
COSY NMR spectrum of **18c**



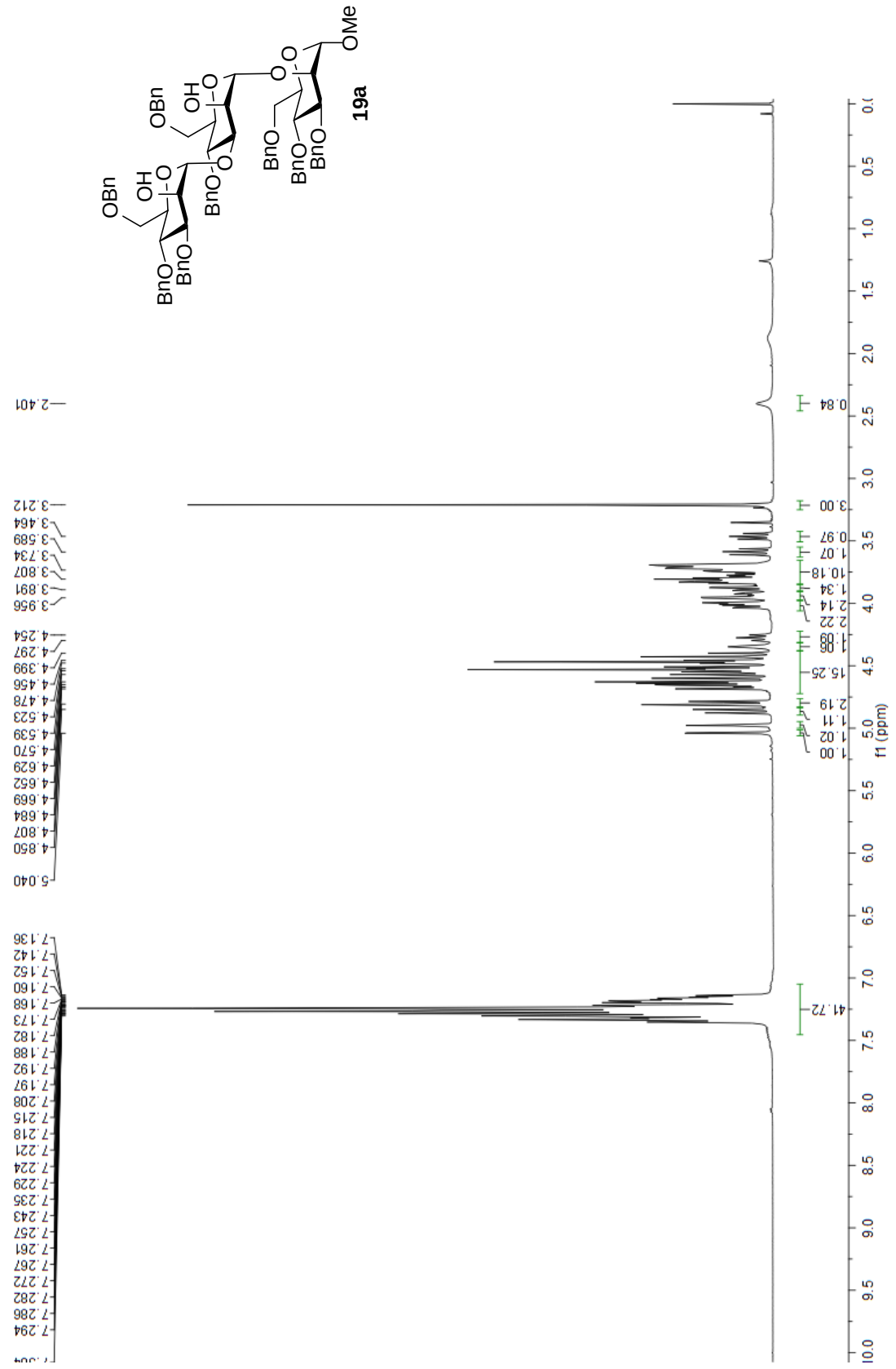
HSQC spectrum of **18c**



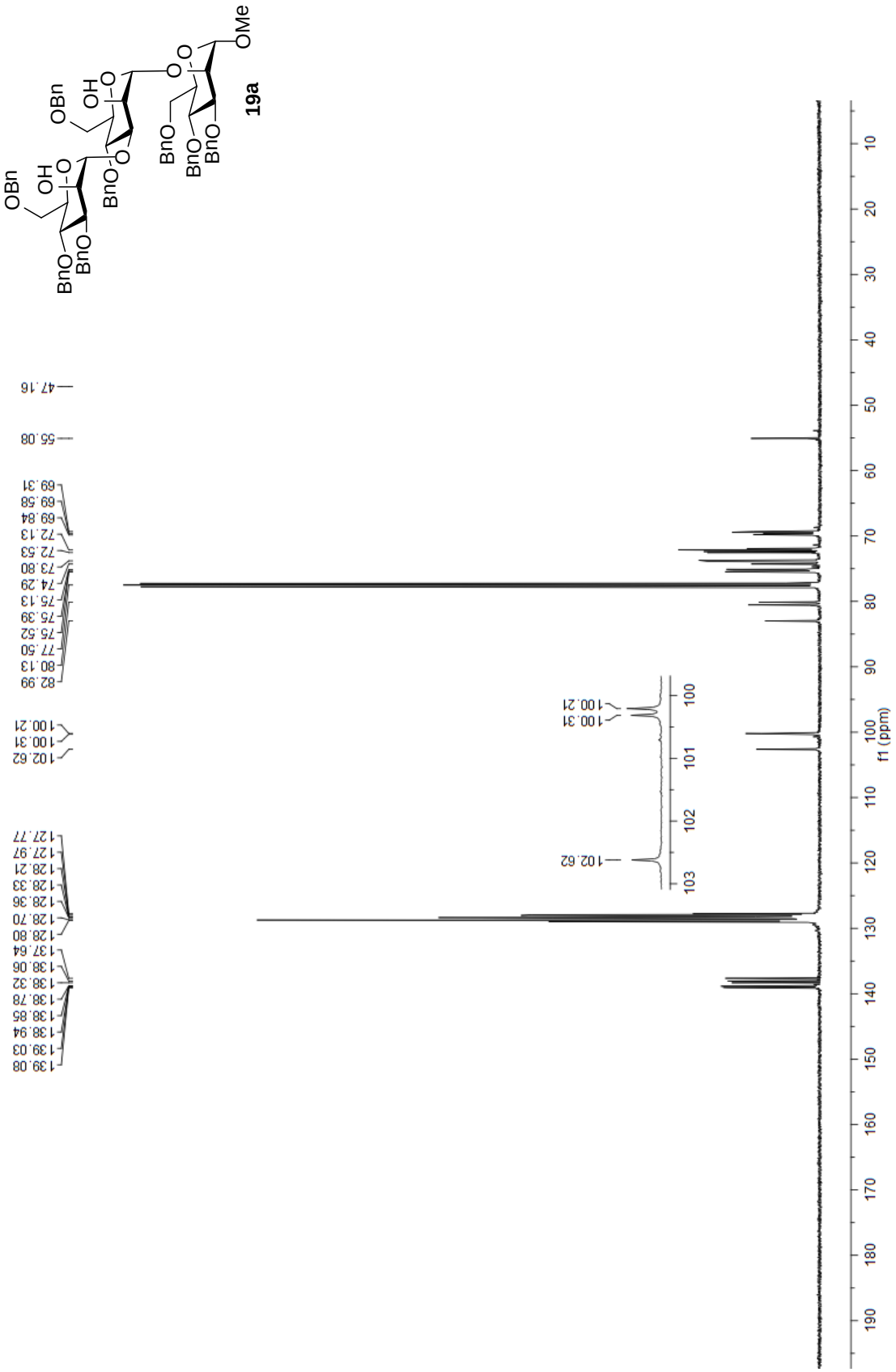
2D HMBC of oligomannan dimer **18c**



^{1}H NMR spectrum of **19a**

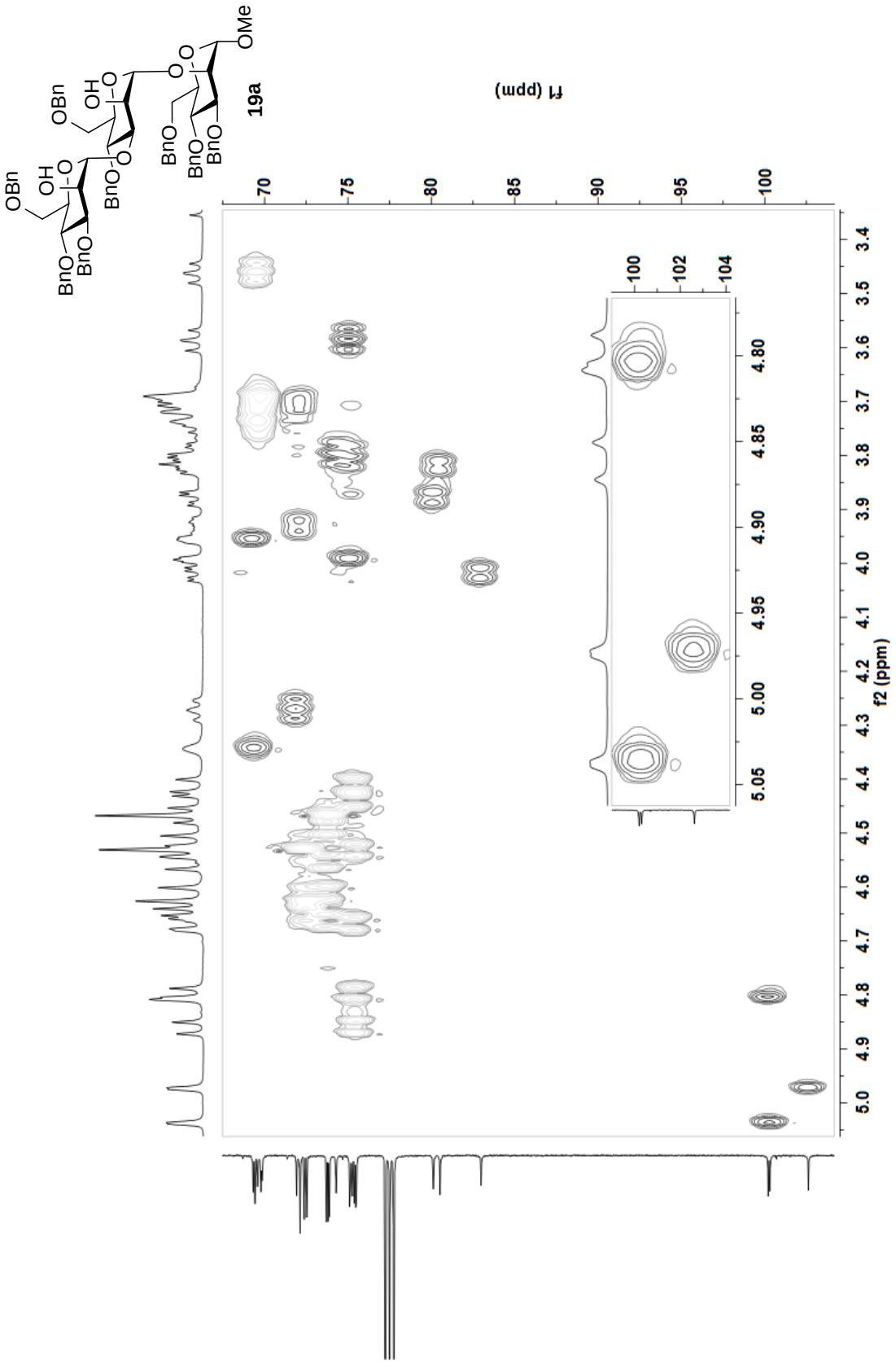


^{13}C NMR spectrum of **19a**

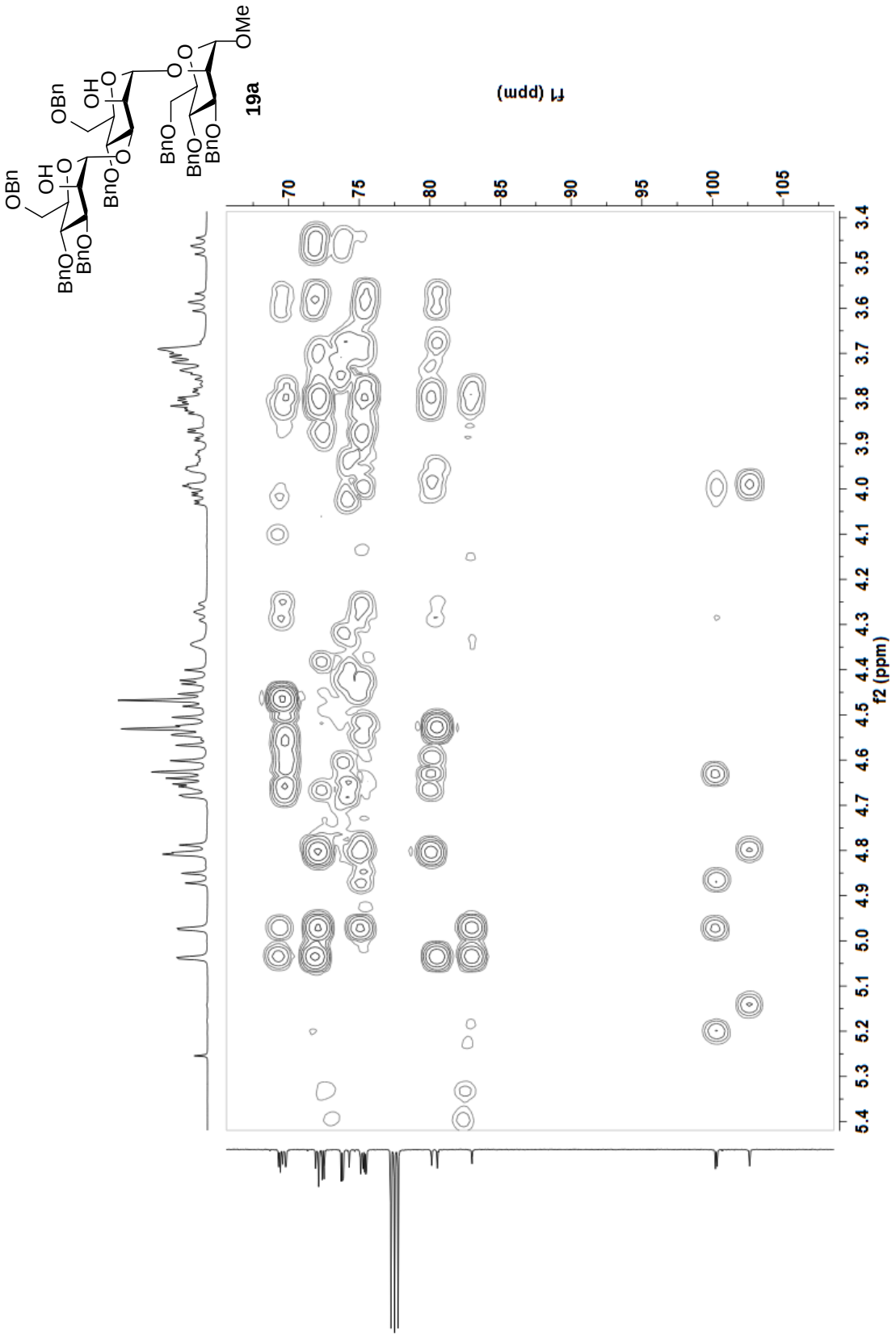


COSY spectrum of **19a**

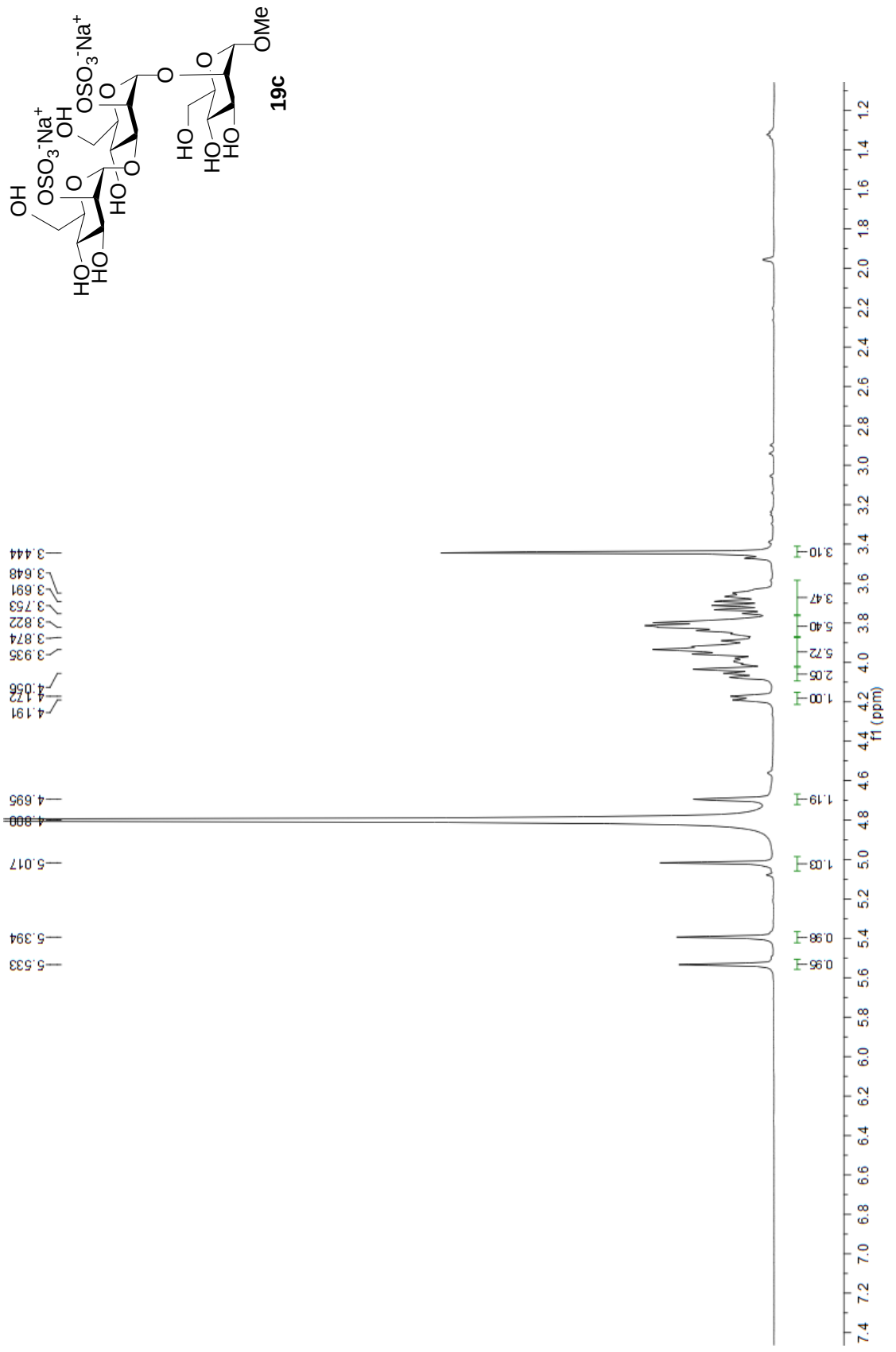
HSQC spectrum of **19a**



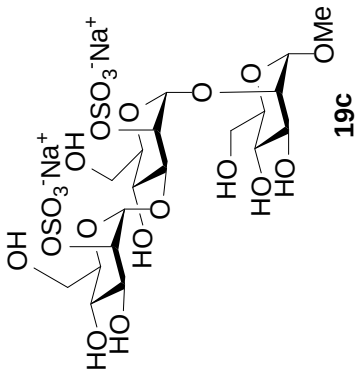
HMBC spectrum of **19a**

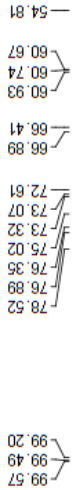


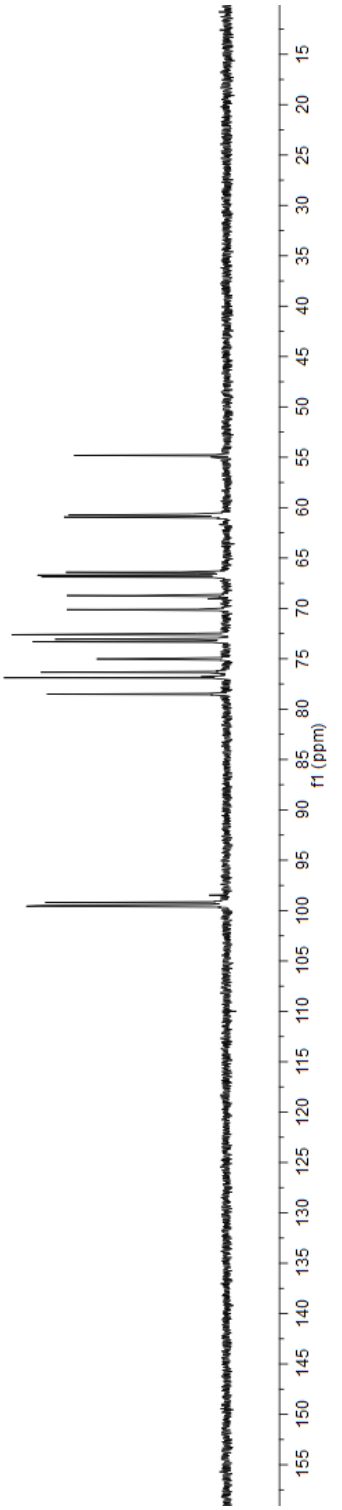
^{1}H NMR spectrum of **19c**



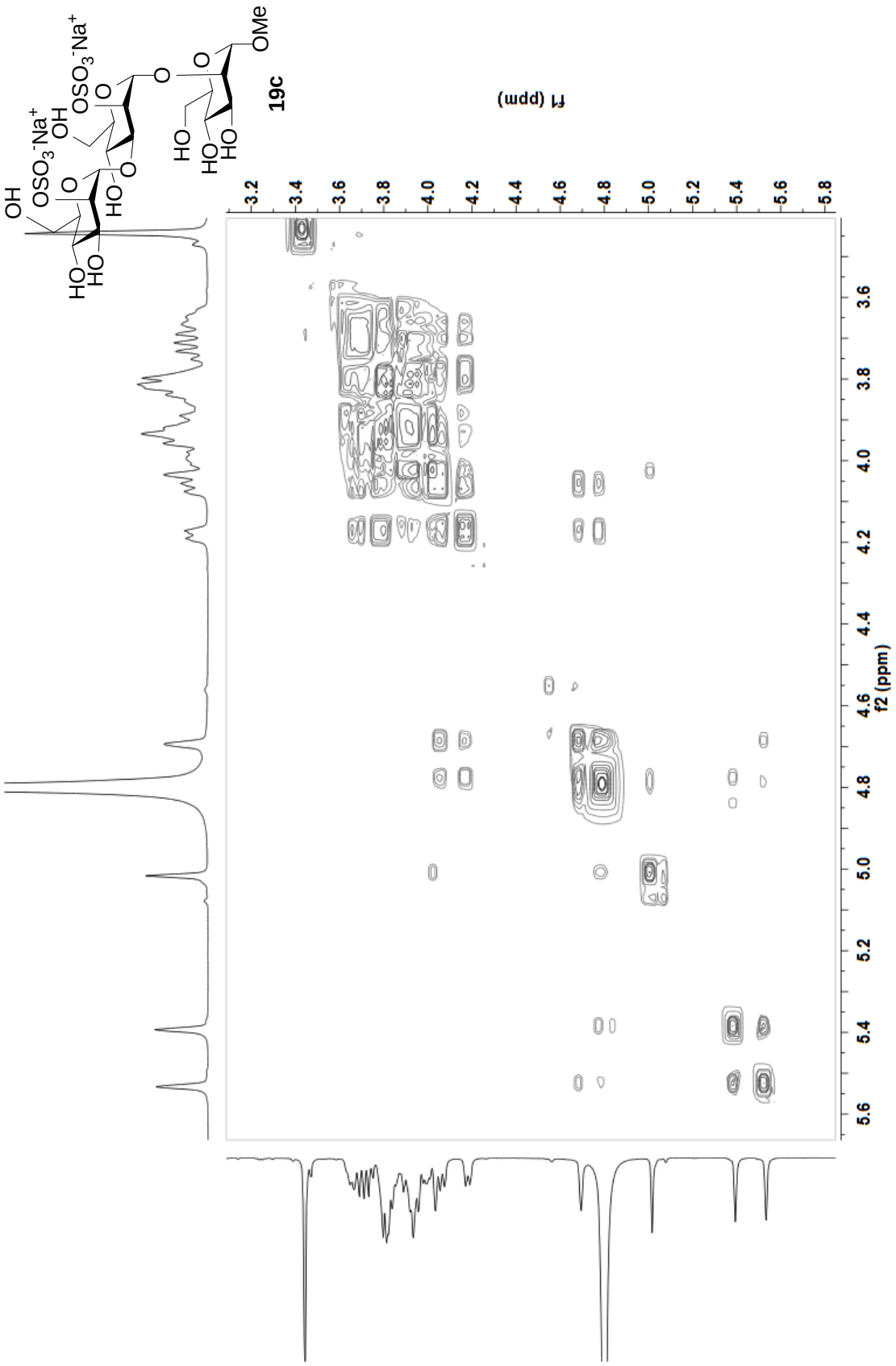
^{13}C NMR spectrum of **19c**



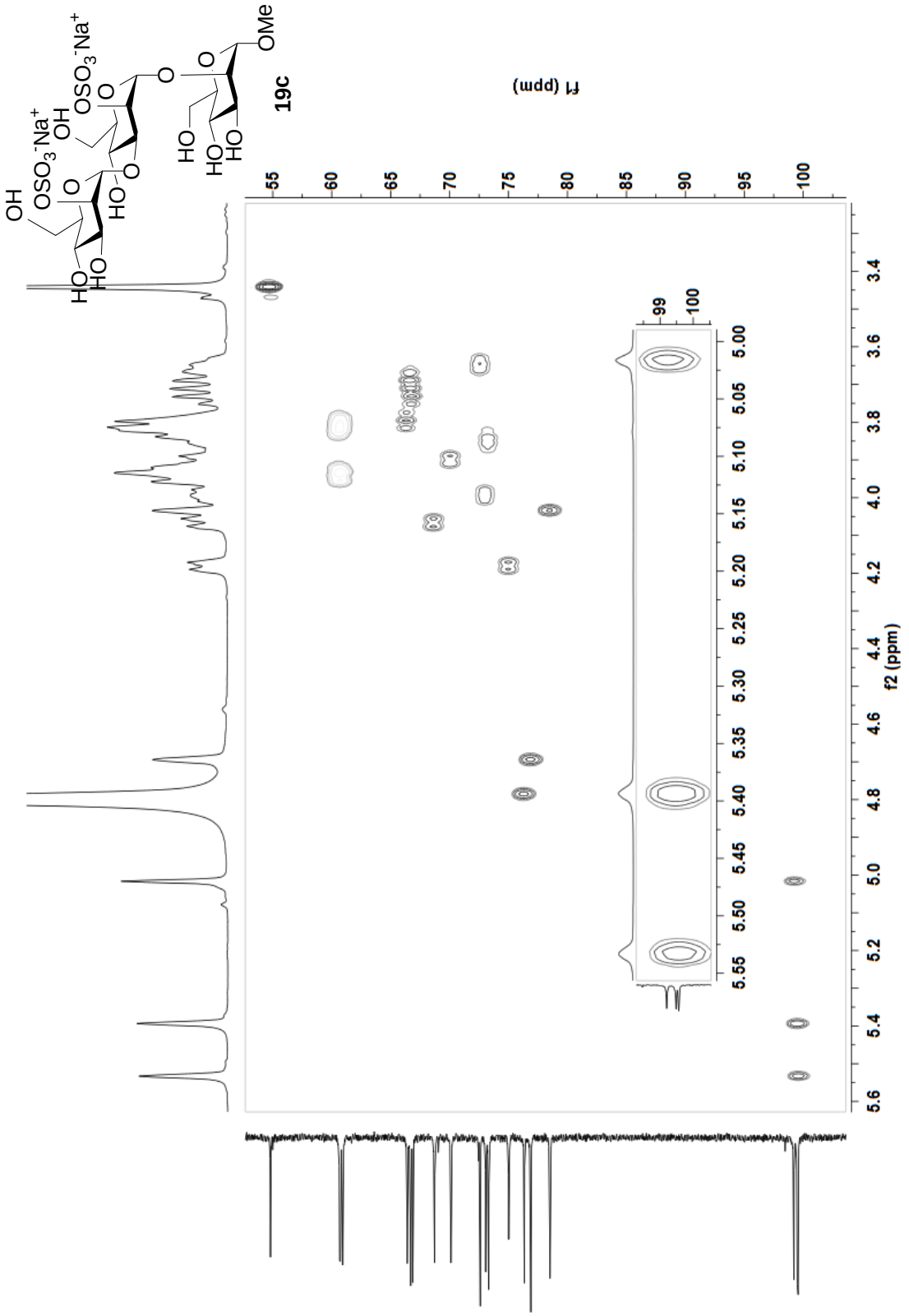




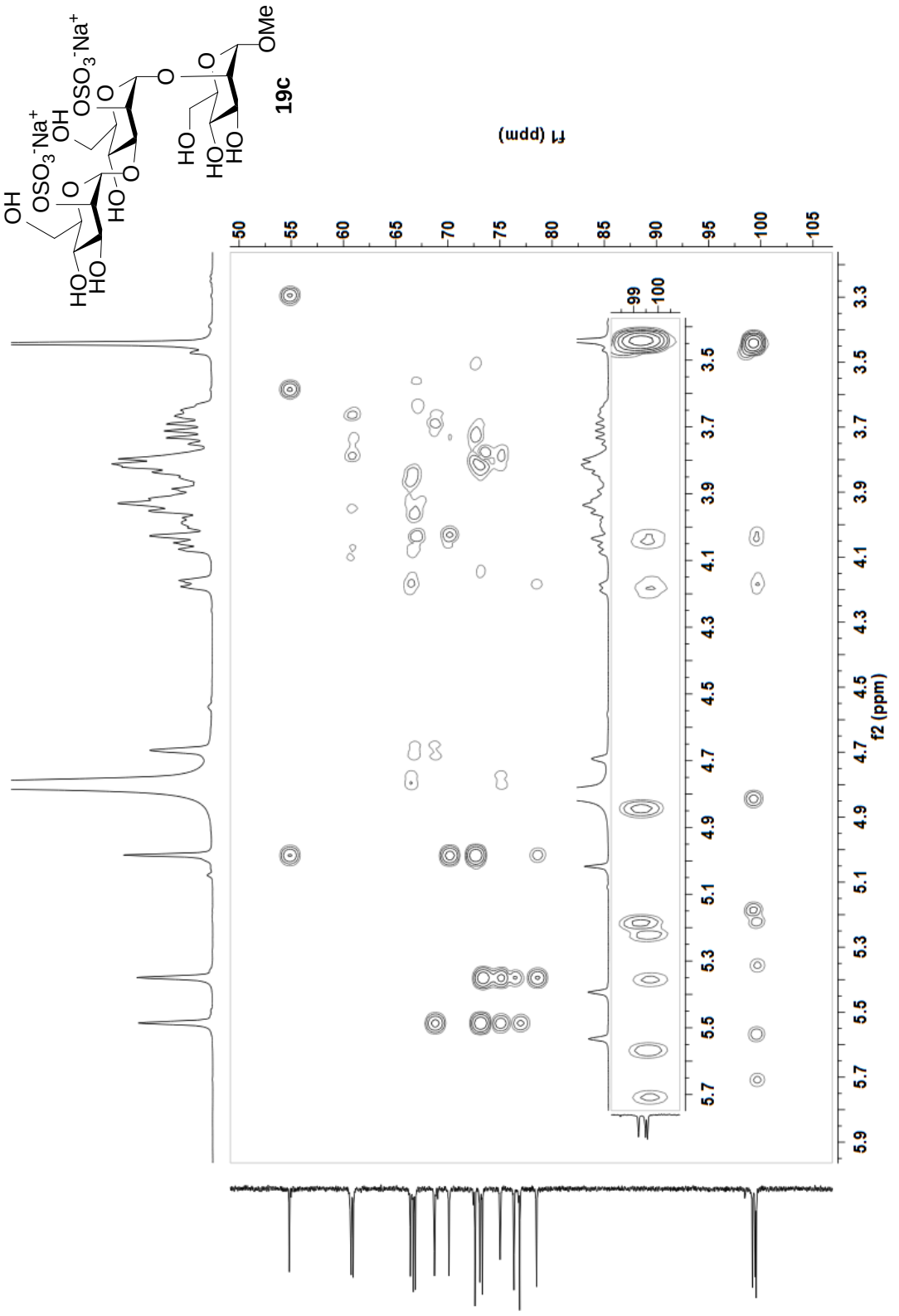
COSY NMR spectrum of **19c**



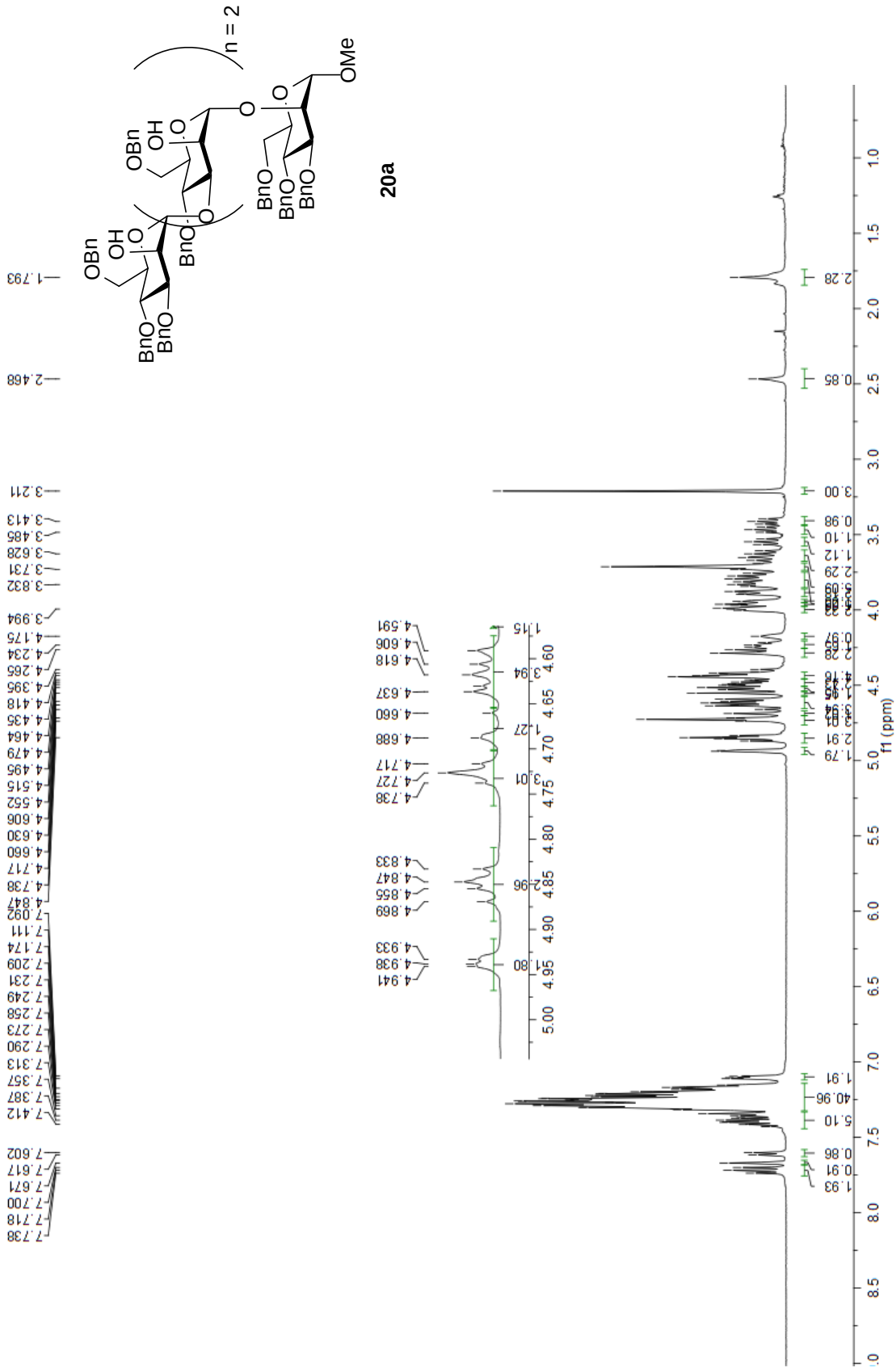
HSQC NMR spectrum of **19c**



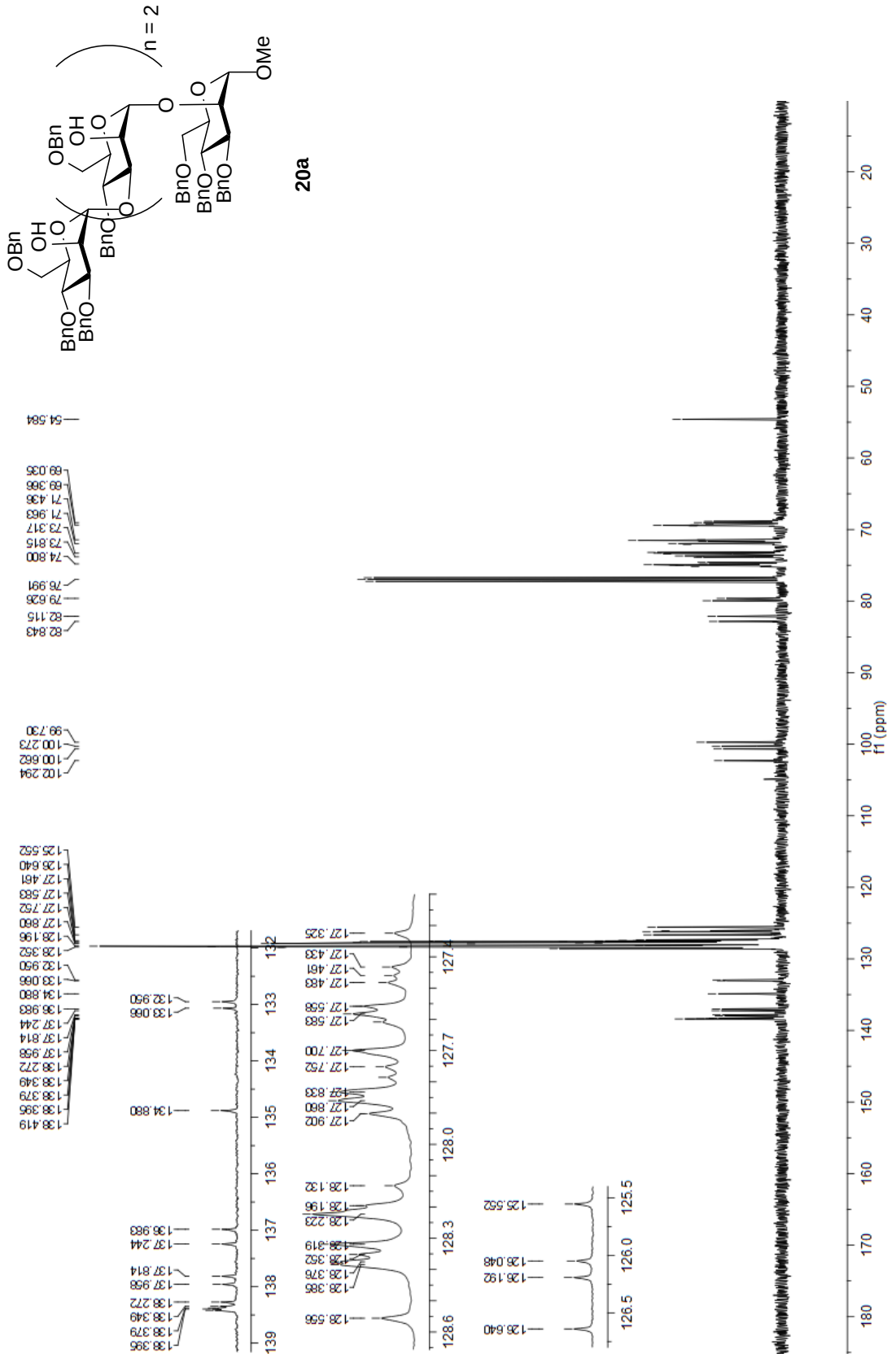
HMBC NMR spectrum of **19c**



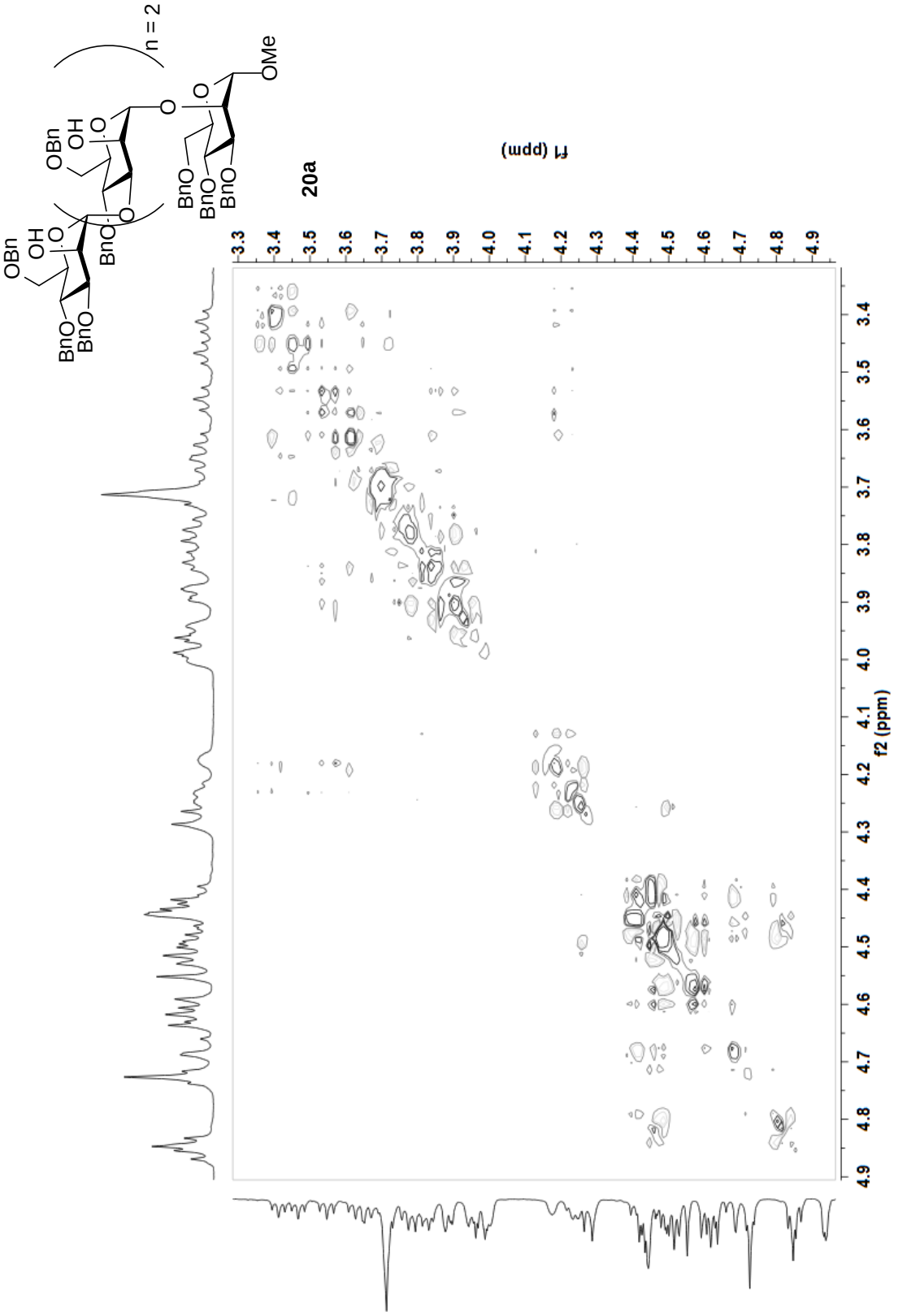
^{1}H NMR of oligomannan tetramer **20a**



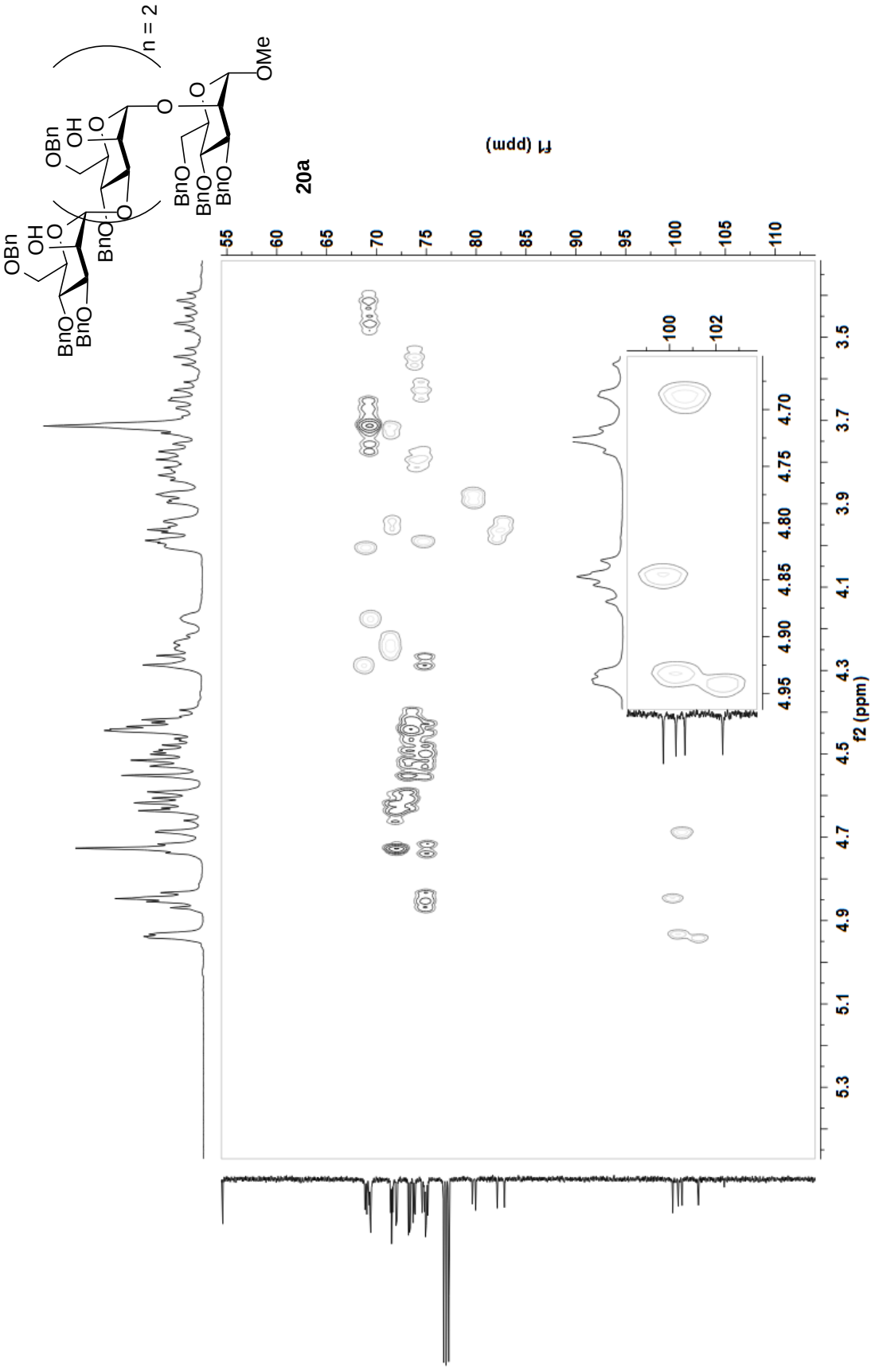
^{13}C NMR of oligomannan tetramer **20a**



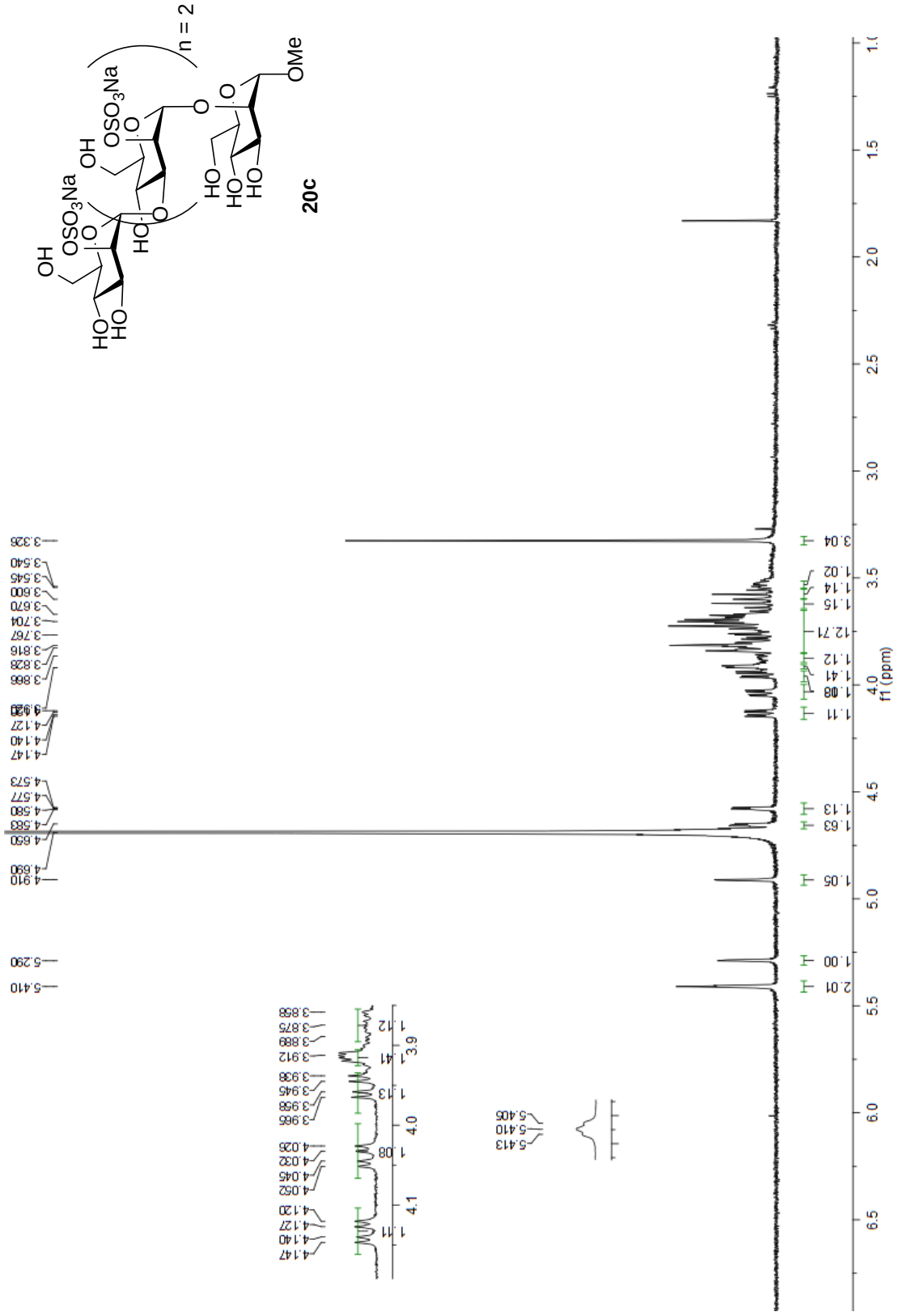
2D COSY of oligomannan tetramer **20a**



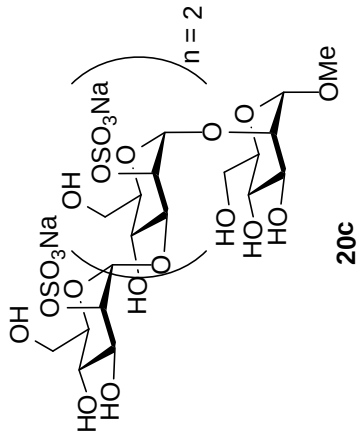
HSQC of oligomannan tetramer **20a**



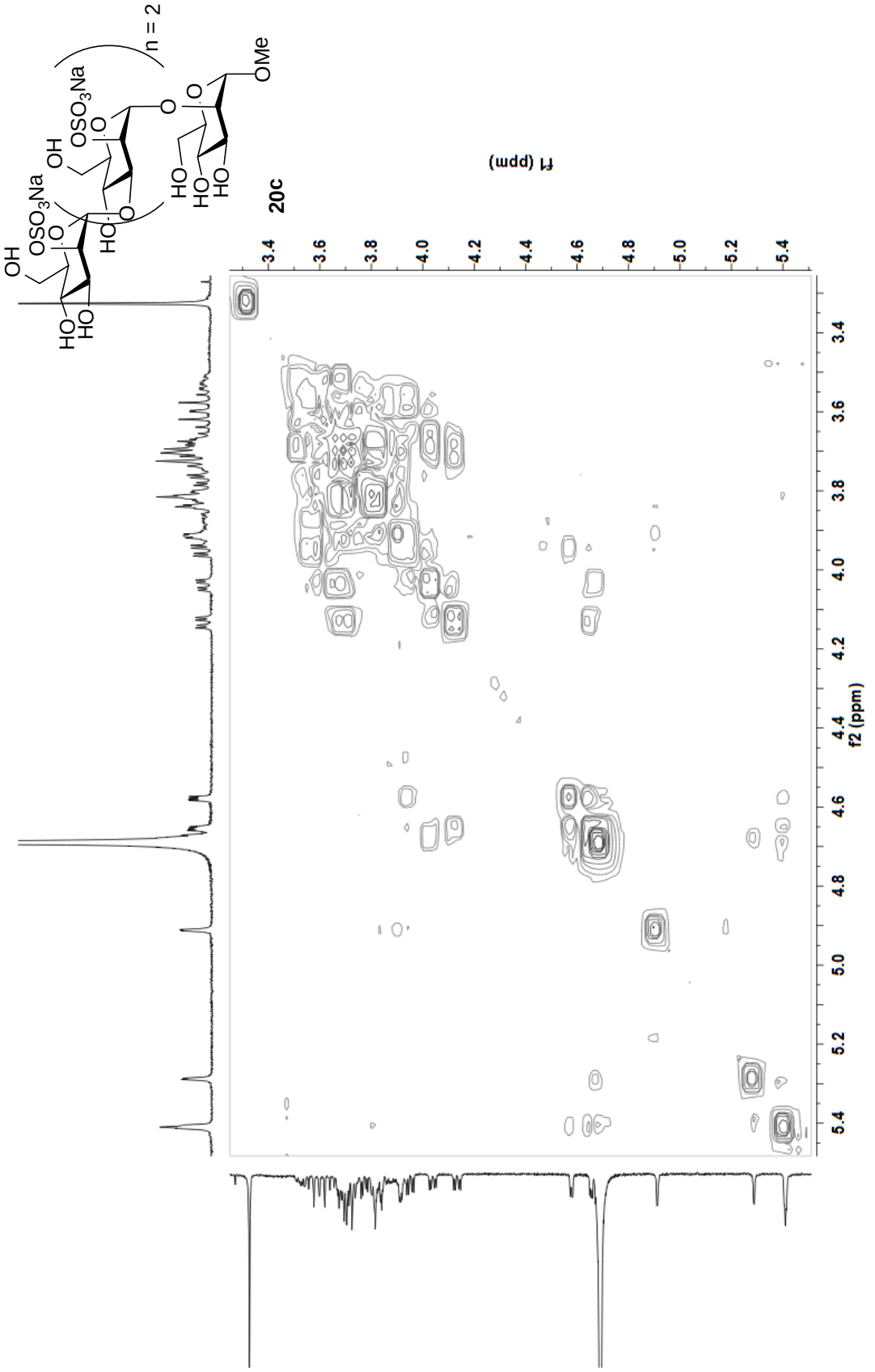
^{1}H NMR of oligomannan tetramer **20c**



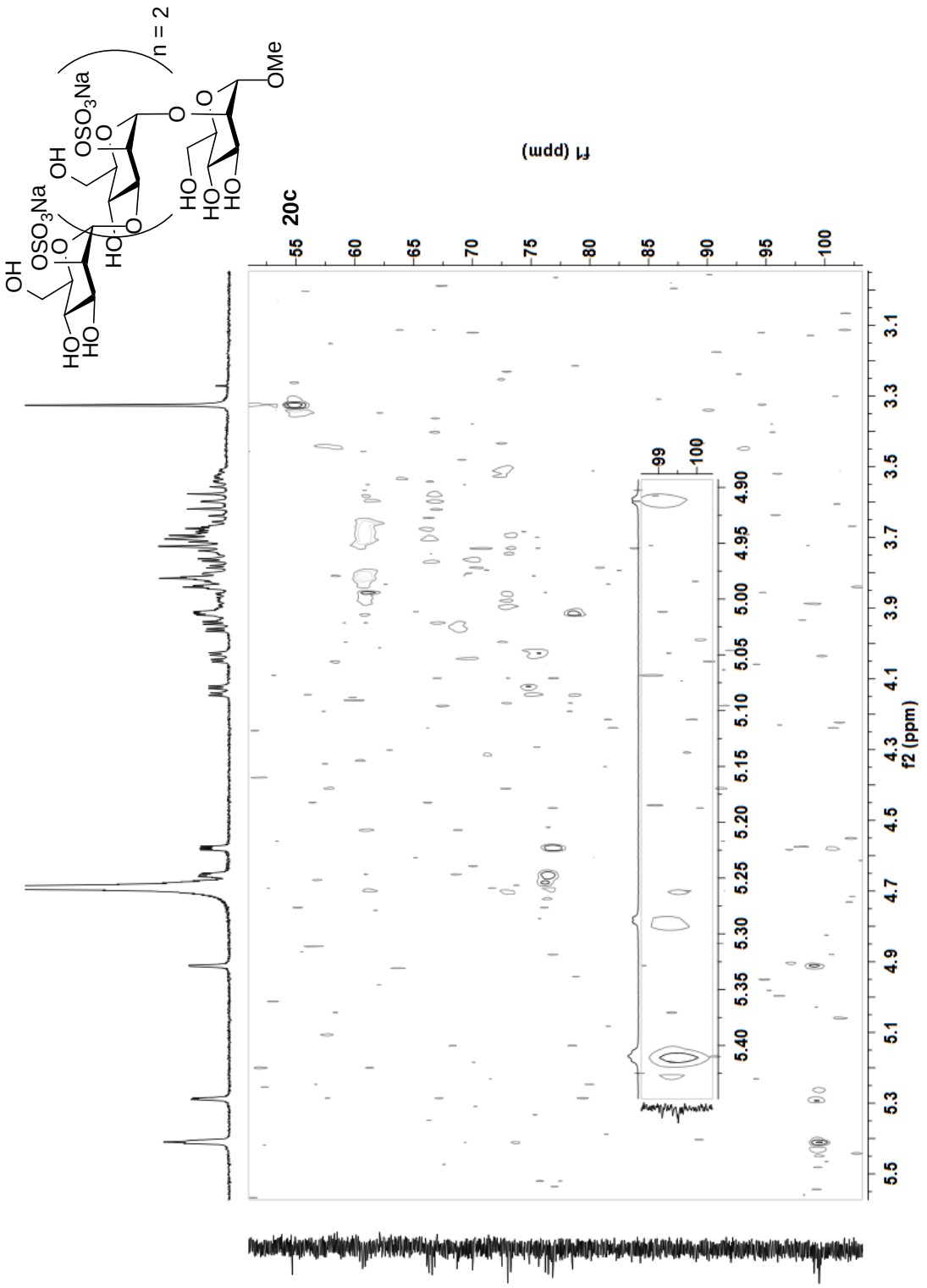
^{13}C NMR of oligomannan tetramer **20c**



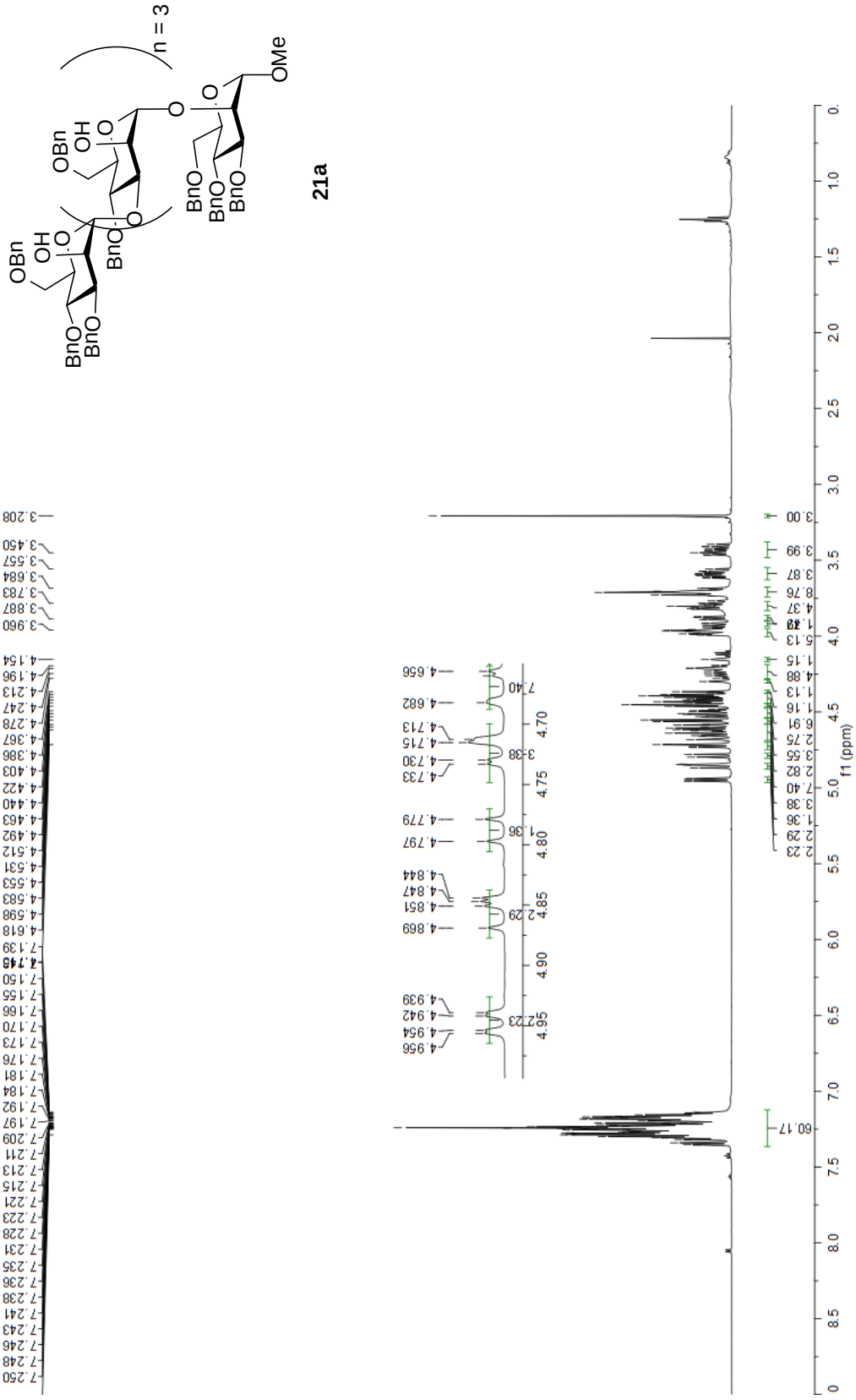
2D COSY of oligomannan tetramer **20c**



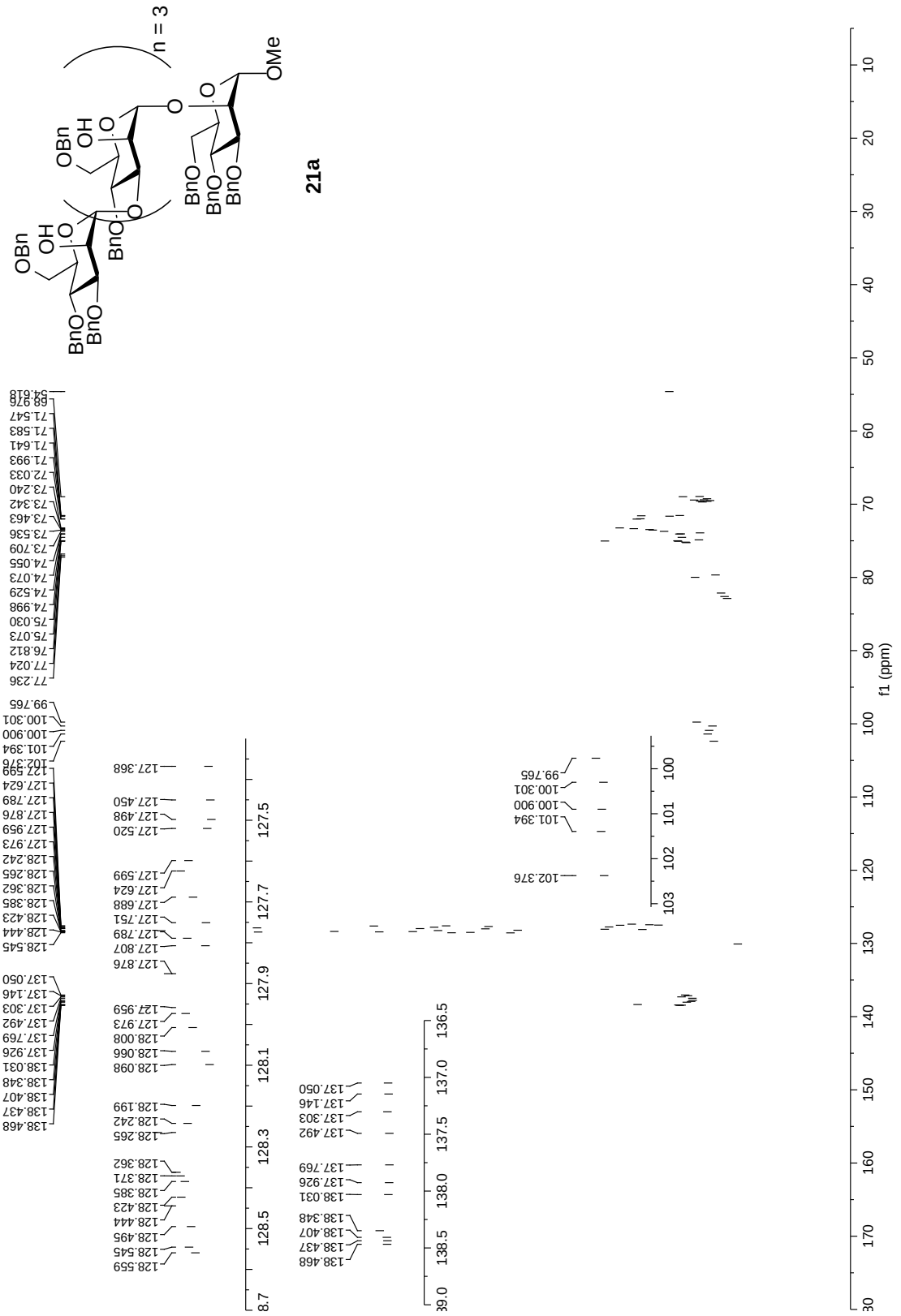
2D HSQC of oligomannan tetramer **20c**



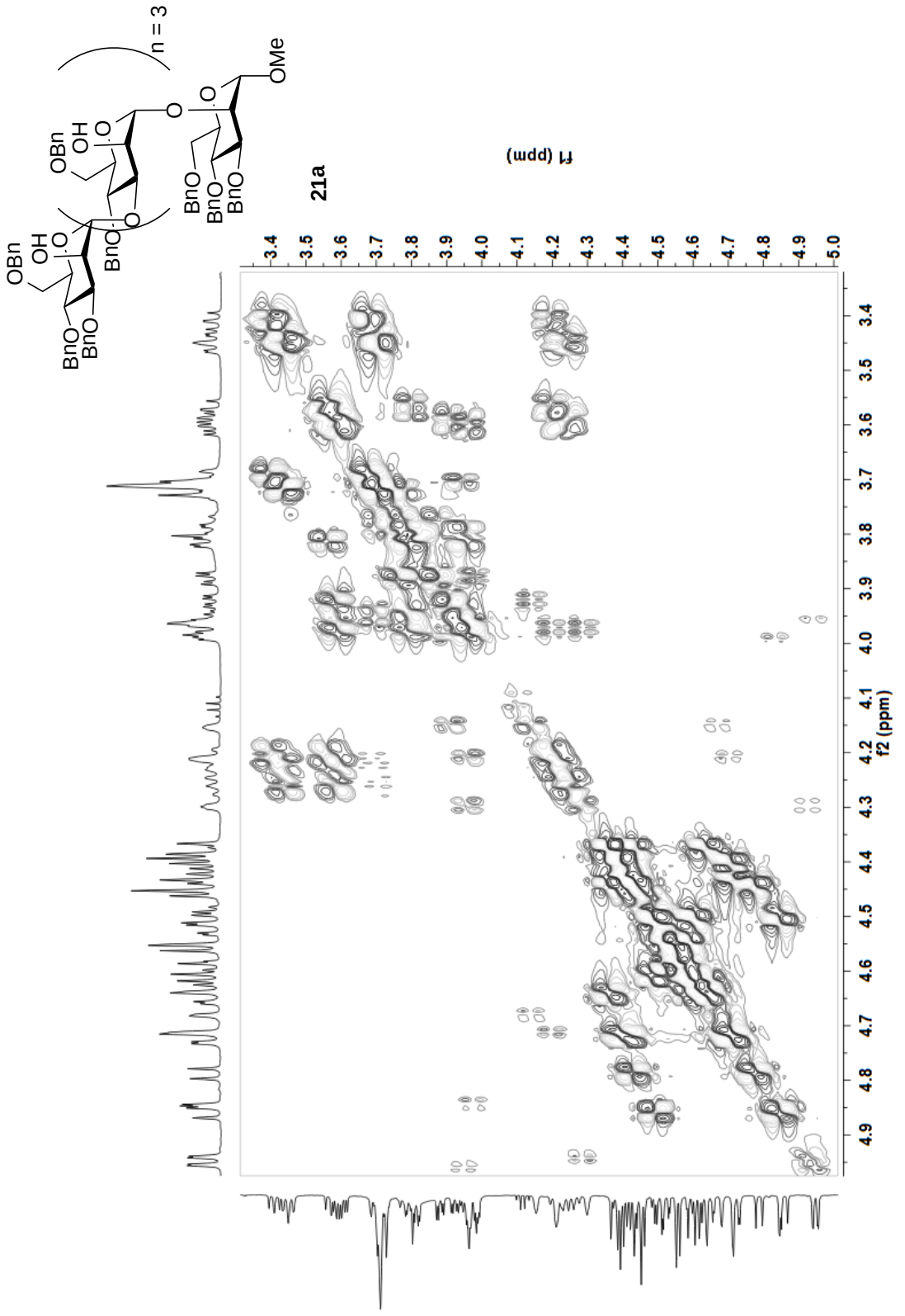
^{1}H NMR of oligomannan pentamer **21a**



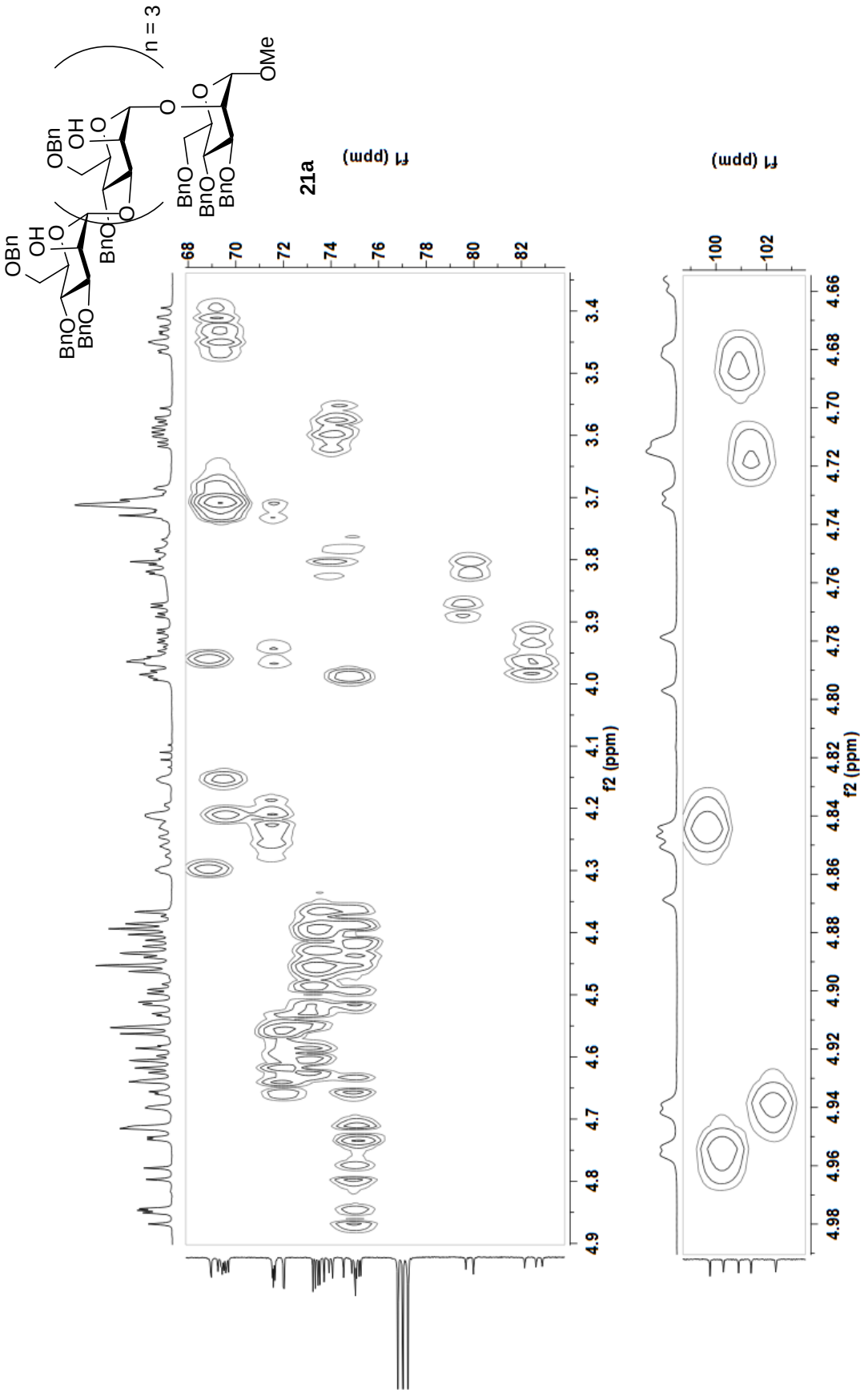
^{13}C NMR of oligomannan pentamer **21a**



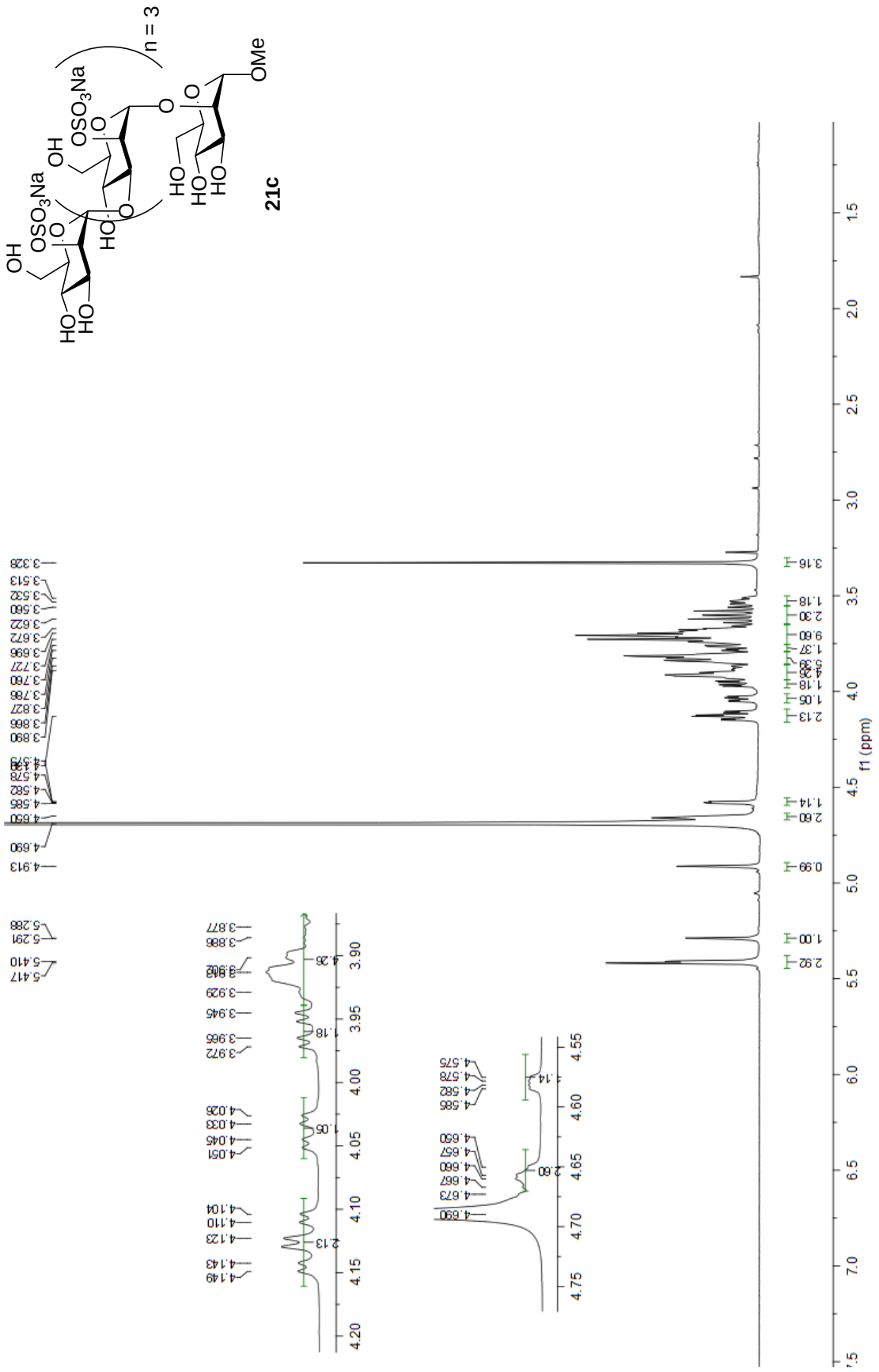
2D COSY of oligomannan pentamer **21a**



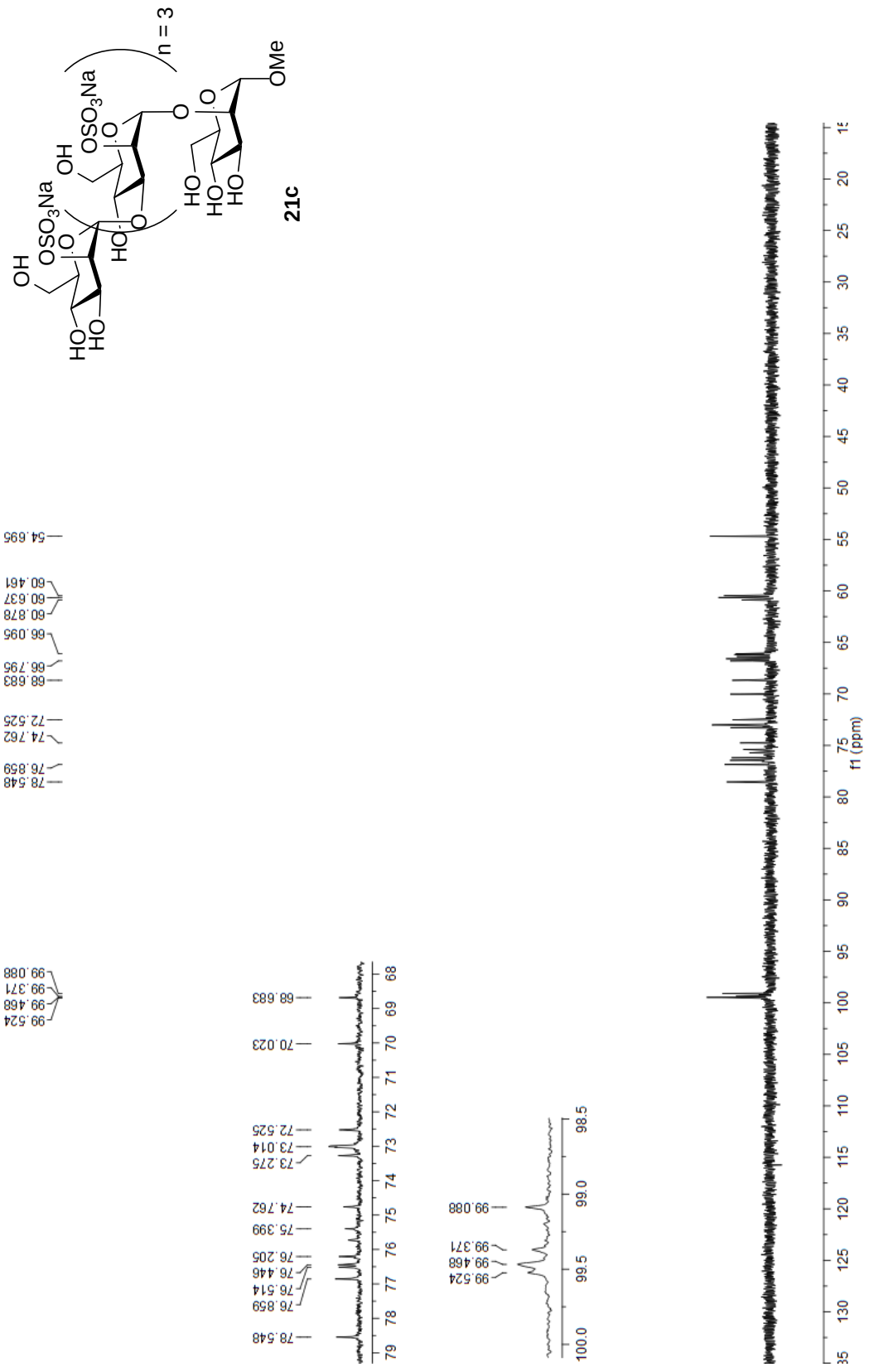
2D HSQC of oligomannan pentamer **21a**



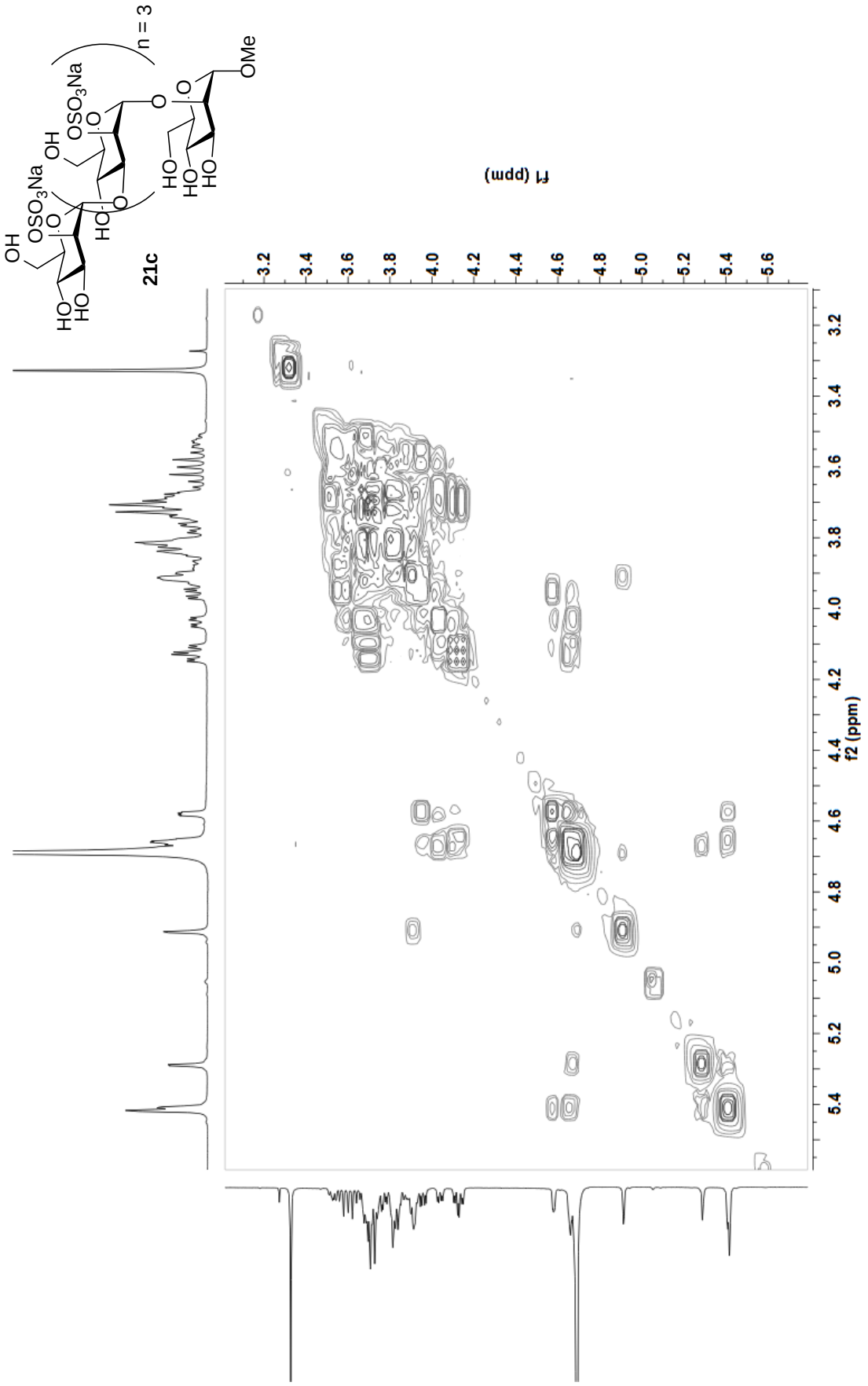
^{1}H NMR of oligomannan pentamer **21c**



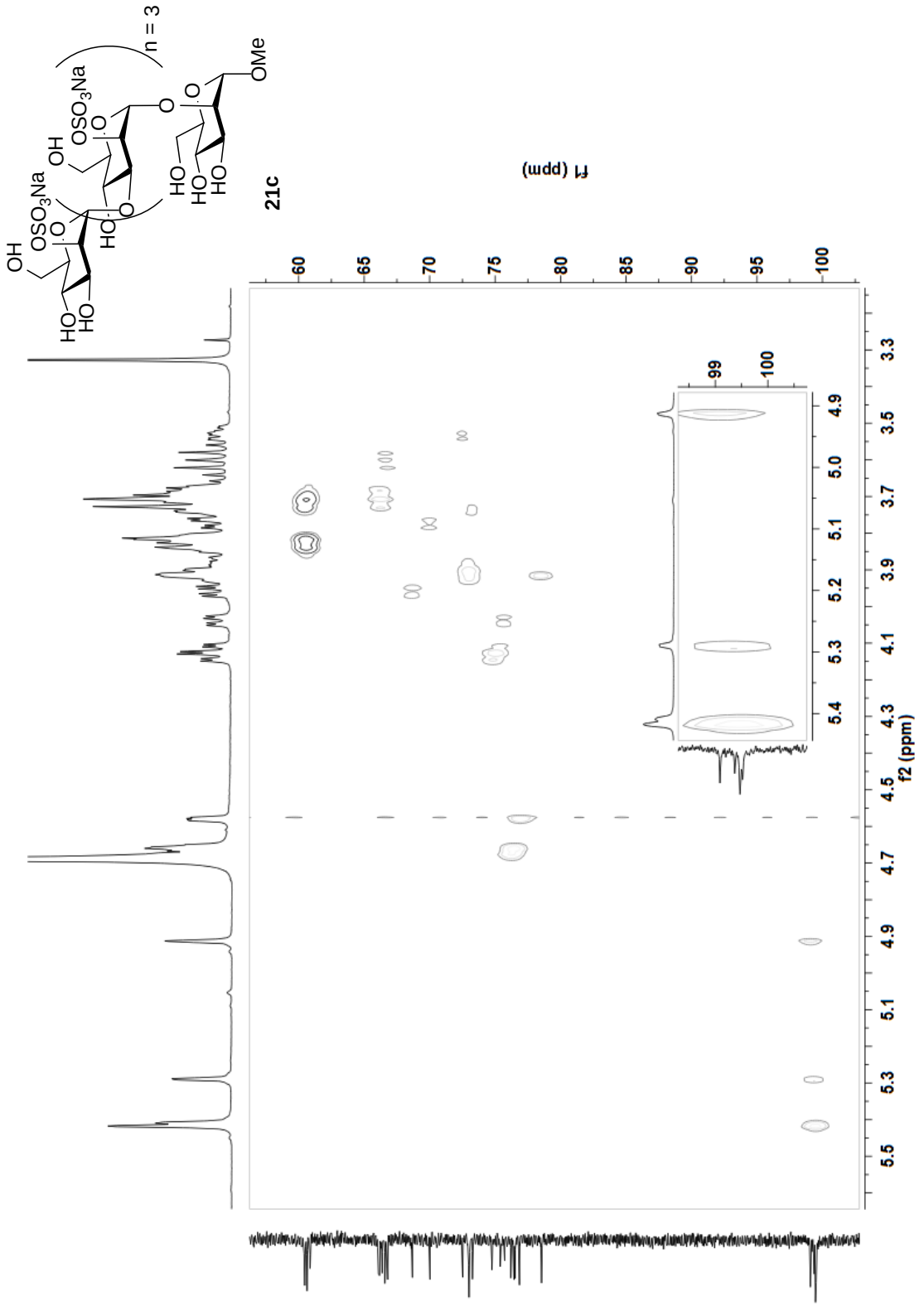
^{13}C NMR of oligomannan pentamer **21c**



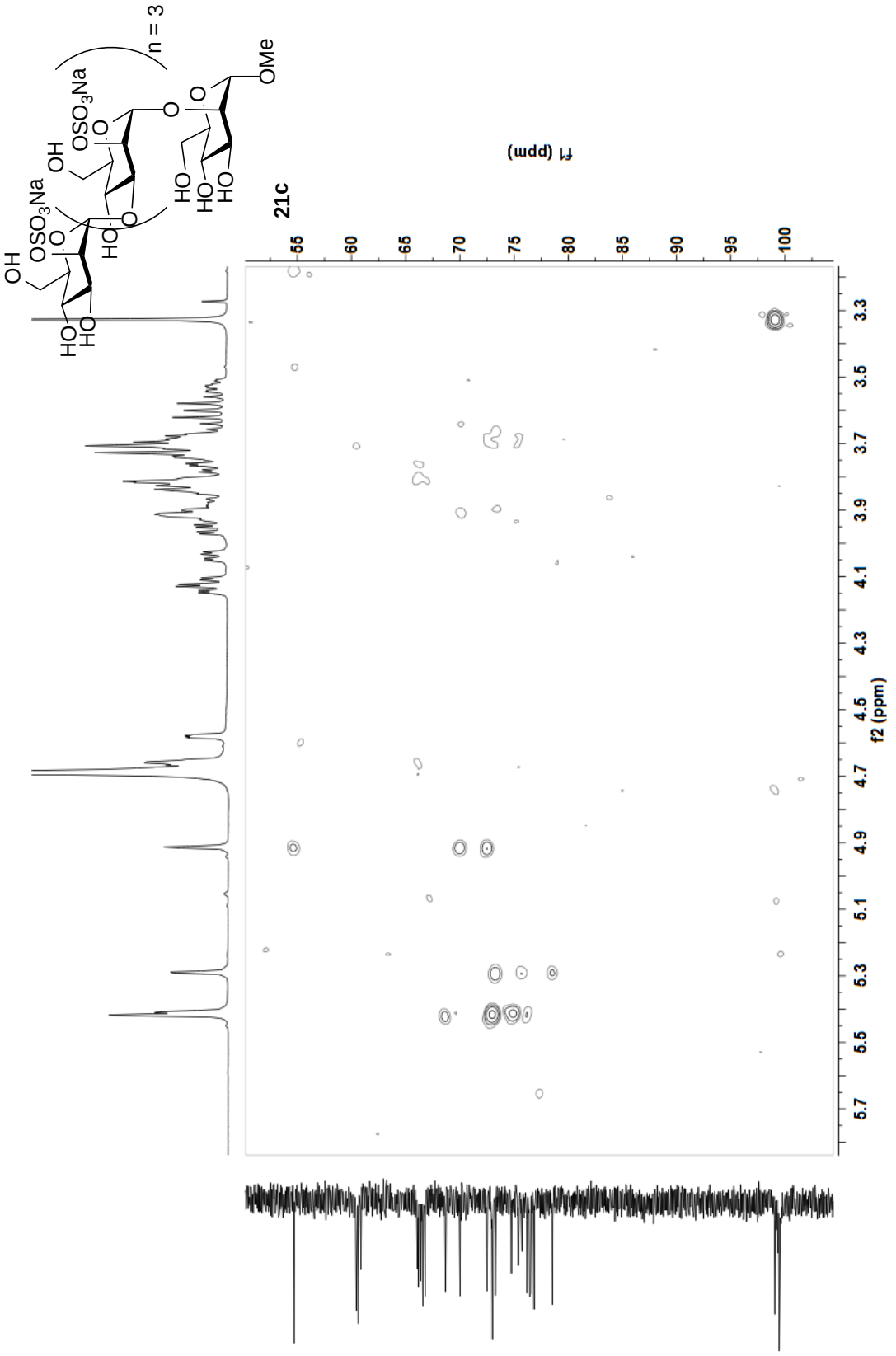
2D COSY of oligomannan pentamer **21c**



2D HSQC of oligomannan pentamer **21c**



2D HMBC of oligomannan pentamer **21c**



Reference

S1. Y-H Lin, B. Ghosh, K.K. T. Mong, *Chem. Commun.*, **2012**, *48*, 10910–10912.

S2. J. Tatai, P. Fugedi, *Org. Lett*., **2007**, *9*, 4647-4650.

S3. J. B J. Beignet, J. Tiernan, H.W Chang, B. M. Kariuki, L.R. Cox, *J. Org. Chem*. **2004**, *69*, 6341-6356.