Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (47) 159

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-3-deoxy-D-*glycero*-*α*-D-*manno*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (48) 162

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5-*O*-isopropylidene-7-*O*-*t*butyldimethylsilyl-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (S15) 165

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-4,5-*O*-isopropylidene-3-*O*-phenoxythiocarbonyl)-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (S16) 168

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-tbutyldimethylsilyl-3-deoxy-4,5-*O*-isopropylidene-α-D-*lyxo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (49) 171

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (S17) 174

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-carbomethoxy-3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (50) 177

^{1}H NMR (400 MHz, $CDCl_3$) of trisaccharide (51) 180

^{1}H NMR (400 MHz, $CDCl_3$) of tetrasaccharide (52) 183

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4-*O*-benzyl-3-deoxy-7,8-*O*-isopropylidene-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (53) 186

^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[benzyl (4-*O*-benzyl-3-deoxy-7,8-*O*-isopropylidene-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (53 ´) 189

^{1}H NMR (400 MHz, $CDCl_3$) of tetrasaccharide (S18) 191

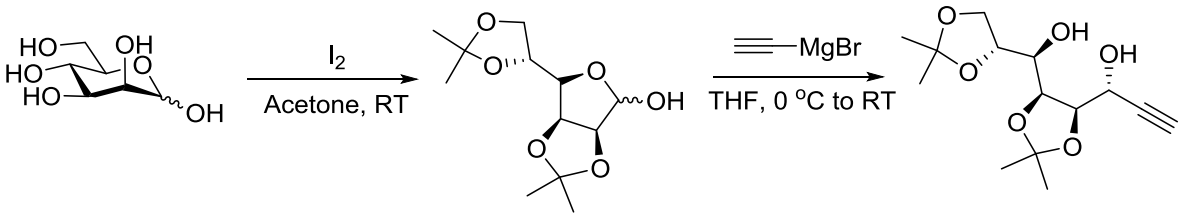
^{1}H NMR (400 MHz, $CDCl_3$) of tetrasaccharide (54) 193

General Information

Reagent-grade chemicals were purchased from commercial vendors and used without purification. Dichloromethane (DCM) was dried by Asianwong solvent system (AWS-1000). Progress of reactions was monitored by thin layer chromatography on silica gel 60 F-254 plate and visualized under UV illumination and/or by staining with acidic ceric ammonium molybdate or p-anisaldehyde. Silica gel (Geduran Si-60, 0.063-0.200 mm) for chromatography was obtained from Merck. NMR spectra were recorded 300 MHz in Brüker console and 400, 500, 600 MHz Varian console as specified. Coupling constants in Hz was calculated from chemical shifts of ^{1}H NMR spectra. Chemical shifts were reported in part per million (ppm) relative to the signal (0.00 ppm for ^{1}H-NMR spectra) and (77.00 ppm for ^{13}C-NMR spectra) for internal tetramethylsilane solutions in $CDCl_3$. NMR multiplicities are reported using the following abbreviations. (s: singlet, d: doublet, t: triplet, m: multiplet, br: broad, J: coupling constants in Hz.). Galatosyl acceptors **13** and chlorohexanol **21** are commercially available and acceptors **14**,[S1] **20**,[S2] **22**,[S1] **23**,[S3] **24**,[S4] **25**,[S5] **27**,[S6] **28**,[S7] and **31**[S8] were prepared according to the literature procedures.

Experimental Section

1,2-Dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*manno*-1-yno-octitol (S1)

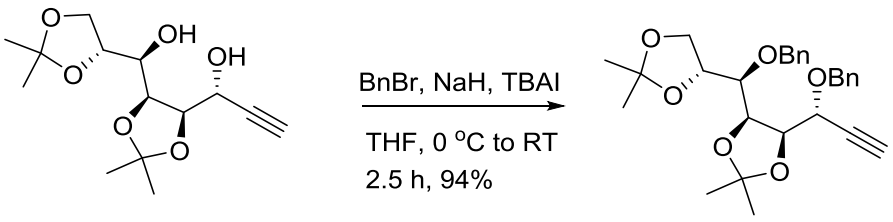


To a well-stirred suspension of D-mannose (50 g, 0.28 mol) in anhydrous acetone (2.5 L) was added iodine (13.96 g, 55.51 mmol) at RT. After vigorously stirred for 12 h, the reaction was quenched with addition of satd. $NaHCO_3$ and $Na_2S_2O_3$. The solvent was removed under reduced pressure. The residue, after dissolving in EtOAc (200 mL), was washed with satd. $NaHCO_3$ (2 ×

20 mL), H_2O, and brine (20 mL). The organic layer was dried over $MgSO_4$, concentrated, dried under *vacuo* to furnish D-*manno*furanose **1** as a yellow solid (65.0 g, 90%) without further purification.[S9]

Ethynyl magnesium bromide solution (384 mL, 192.0 mmol, 0.5 M in THF) was added to the D-*manno*furanose **1** (20 g, 77.0 mmol) at 0 °C. After stirred for 1 h, the solution was gradually warmed to RT and stirred for extra 5 h. The reaction was quenched by careful addition of satd. NH_4Cl (10 mL) at 0 °C, and all the solvent was removed under reduced pressure. The residue, after dissolving in EtOAc (250 mL), was washed satd. NH_4Cl (20 mL) twice, H_2O (30 mL), and brine (20 mL). The organic layer, dried over $MgSO_4$, was concentrated for flash chromatography purification over silica gel (Elution: Hexanes/EtOAc 4/1 to 1.5/1) to give octyne diol **S1** (20 g, 91%).[S10] For **S1**, R_f = 0.19 (hexanes/EtOAc = 1/1); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 4.71 (m, 1H), 4.46 (d, *J* = 6.0 Hz, 1H), 4.39 (d, *J* = 7.0 Hz, 1H), 4.22 (dd, *J* = 7.0, 5.5 Hz, 1H,), 4.08-3.97 (m, 4H), 3.36 (d, *J* = 5.0 Hz, 1H), 2.50 (d, *J* = 2.0 Hz, 1H, acetylene-*H*), 1.47 (s, 3H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.29 (s, 3H, C*H*$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 109.3 (*C*$(CH_3)_2$), 108.7 (*C*$(CH_3)_2$), 81.9, 78.4, 75.9, 75.5, 74.5, 68.9, 66.8, 60.7, 26.7 (*C*H_3), 26.4 (*C*H_3), 25.2 (*C*H_3), 24.8 (*C*H_3).

3,6-Di-*O*-benzyl-1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-1-yno-octitol (2)

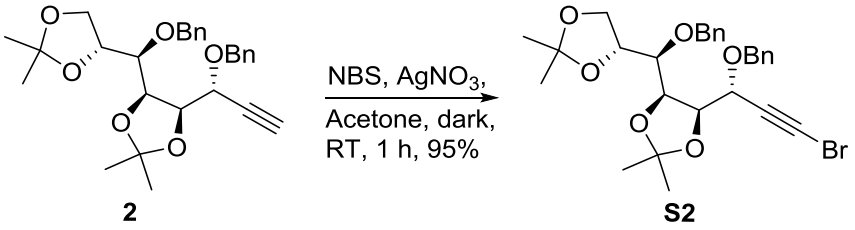


S1 **2**

To a stirred solution of diol **S1** (20.0 g, 70.89 mol) and tetrabutylammonium bromide (2.29 g, 7.09 mol) in anhydrous THF (236 mL) at 0 °C was portion-wisely added NaH (7.09 g, 177.23 mmol, 60% dispersion in mineral oil). After stirring for 0.5 h, the suspension was treated with BnBr (18.5 mL, 155.96 mmol). The reaction mixture was stirred from 0 °C to RT for 2 h. Then the reaction was quenched by addition of satd. NH_4Cl at 0 °C, and the solvent was removed under

reduced pressure. The residue, which dissolved in EtOAc (300 mL), was washed satd. NH_4Cl (20 mL) twice, H_2O (30 mL), brine (10 mL), dried over ($MgSO_4$), and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 15/1 to 8/1) to afford fully protected octyne **2** (31.0 g, 94%) as a light yellow, viscous oil. For **3**, R_f = 0.16 (Hexanes/EtOAc = 8/1); $[\alpha]_D^{30}$ = – 26.6 (*c* 0.7, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.39-7.22 (m, 10H, Ar*H*), 4.79 (d, *J* = 11.5 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.39 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.31 (dd, *J* = 8.0, 6.5 Hz, 1H), 4.21-4.16 (m, 2H), 4.00 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.93 (m, 1H), 3.86 (t, *J* = 4.0 Hz, 1H), 2.59 (d, *J* = 2.0 Hz, 1H, acetylene-*H*), 1.51 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.32 (s, 3H, C*H*$_3$), 1.28 (s, 3H, C*H*$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 138.6, 136.8, 128.7, 128.5, 128.2, 128.0, 127.3, 127.2, 109.4 (*C*$(CH_3)_2$), 108.3 (*C*$(CH_3)_2$), 80.7, 78.2, 77.8, 77.7, 76.4, 75.7, 73.1, 70.3, 67.6, 65.8, 26.5 (*C*H_3), 26.2 (*C*H_3), 25.6 (*C*H_3), 24.9 (*C*H_3); **HRMS** (ESI): *m*/*z* calcd. for $C_{28}H_{34}NaO_6^+$ [M + Na]$^+$: 489.2248, found: 489.2261.

3,6-Di-*O*-benzyl-1-bromo-1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-1-yno-octitol (S2)

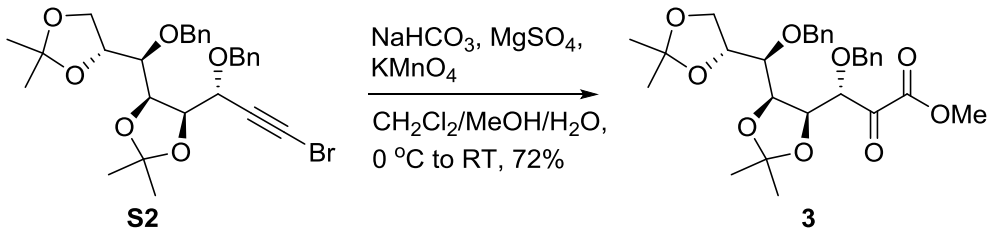


2 **S2**

To a solution of aforementioned octyne **2** (31.0 g, 66.44 mmol) in anhydrous acetone (110 mL) was added *N*-bromosuccinimide (14.2 g, 79.73 mmol) and $AgNO_3$ (1.13g, 6.64 mmol) in the dark at RT. The solution was stirred in the dark for 1 h, and the resulting suspension was filtered through celite. The filtrate was concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc = 15/1 to 8/1) to give the desired bromooctyne **S2** as a yellow crystallized solid (34.43 g, 95%), For **S2**, R_f 0.23 (hexanes/EtOAc 8/1); $[\alpha]_D^{34}$ = –32.4 (*c* 0.75, $CHCl_3$); **^{1}H**

NMR (500 MHz, $CDCl_3$): δ 7.37-7.23 (m, 10H, Ar*H*), 4.78 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.44 (t, *J* = 11.5 Hz, 2H), 4.40 (d, *J* = 7.0 Hz, 1H), 4.30 (t, *J* = 6.5 Hz, 1H), 4.21 (t, *J* = 6.0 Hz, 1H), 4.12 (m, 1H), 4.00 (dd, *J* = 8.0, 6.5 Hz, 1H), 3.87-3.81 (m, 2H), 1.53 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.25 (s, 3H, C*H*$_3$), 1.24 (s, 3H, C*H*$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 138.5, 136.9, 128.5, 128.4, 128.2, 128.0, 127.4, 127.4, 109.3 (*C*$(CH_3)_2$), 108.5 (*C*$(CH_3)_2$), 78.5, 78.0, 77.5, 77.4, 76.6, 73.4, 70.4, 68.9, 66.2, 47.4, 26.5 (*C*H_3), 26.1 (*C*H_3), 25.5 (*C*H_3), 24.8 (*C*H_3); **HRMS** (ESI): *m/z* calcd. for $C_{28}H_{33}BrNaO_6^+$ $[M + Na]^+$: 567.1353, found: 567.1368.

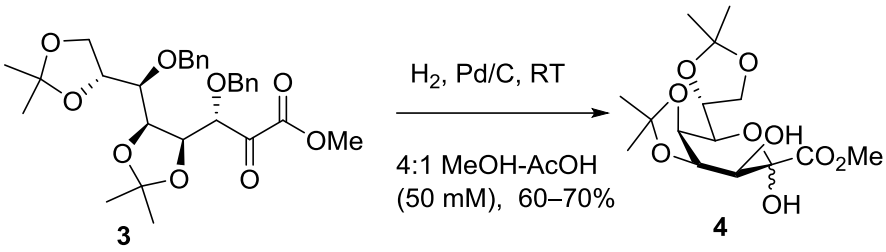
Methyl 3,6-Di-*O*-benzyl-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-2-octulosonate (3)



To a solution of the alkyne bromide **S2** (12.0 g, 22 mmol) in DCM (88 mL) was added the solution of $NaHCO_3$ (924 mg, 11 mmol) and $MgSO_4$ (5.30 g, 44 mmol) in H_2O (88 mL), followed by the addition of MeOH (264 mL) with vigorous stirring till a homogeneous solution was obtained. After cooling the solution to 0 °C, $KMnO_4$ (10.43 g, 66 mmol) was portion-wisely added. After stirring at 0 °C for 1.5 h, the solution was gradually warmed to RT and stirred for additional few hours. The reaction was filtered through Celite, and the solvent was removed under reduced pressure. The residue, diluted with EtOAc (300 mL), was washed with H_2O (300 mL), brine (300 mL). After separation, the aqueous layer was washed with Et_2O (50 mL) three times. The organic phase was dried over $MgSO_4$, concentrated for flash chromatography purification (Elution: hexanes/EtOAc 10/1 to 6/1) to furnish the desired α-keto acid ester **3** (8.24 g, 72%) as a yellow viscous oil. For **3**, R_f = 0.16 (hexanes/EtOAc = 6/1); $[\alpha]_D^{22}$ = +20.0 (*c* 0.5, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.36-7.26 (m, 8H, Ar*H*), 4.81 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 9.6 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 4.38 (dd, *J* = 9.6,

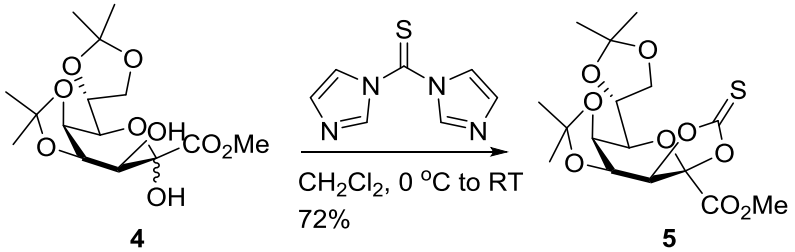
6.0 Hz, 1H), 4.32 (td, *J* = 7.2, 3.0 Hz, 1H), 4.27 (d, *J* = 11.4 Hz, 1H), 4.18 (t, *J* = 5.4 Hz, 1H), 4.04 (t, *J* = 7.8 Hz, 1H), 3.98 (dd, *J* = 7.8, 6.6 Hz, 1H), 3.85 (dd, *J* = 4.2, 3.6 Hz, 1H), 3.74 (s, 3H, OC*H*$_3$), 1.42 (s, 3H, C*H*$_3$), 1.41 (s, 3H, C*H*$_3$), 1.29 (s, 3H, C*H*$_3$), 1.27 (s, 3H, C*H*$_3$); **^{13}C NMR** (150 MHz, $CDCl_3$): δ = 194.0 (*C*2), 161.8 (*C*1), 138.4, 135.9, 128.8, 128.4, 128.3, 128.1, 127.5, 127.3, 109.7 (*C*$(CH_3)_2$), 108.2 (*C*$(CH_3)_2$), 78.5, 78.1, 77.2, 76.6, 75.3, 73.0, 72.3, 64.9, 52.6 (O*C*H$_3$), 26.3 (*C*H$_3$), 26.2 (*C*H$_3$), 25.2 (*C*H$_3$), 24.9 (*C*H$_3$); **HRMS** (ESI): *m/z* calcd. for $C_{29}H_{36}NaO_9^+$ $[M + Na]^+$: 551.2252, found: 551.2311.

Methyl 4,5:7,8-Di-*O*-isopropylidene-*α*-D-*manno*-D-*talo*-2-octulopyranosonate (4)



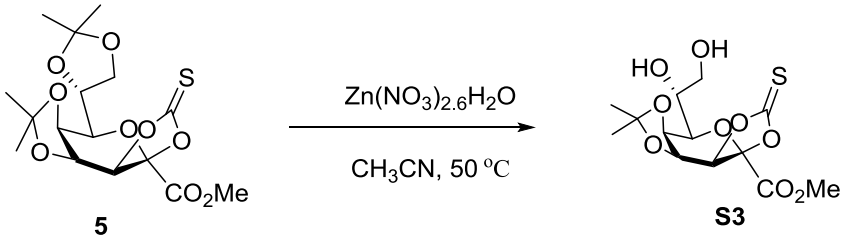
To a solution of α-ketoester **3** (3.8 g, 7.10 mmol) in 4:1 MeOH-AcOH (final [**3**] = 50 mM) was added Pd/C (0.78 g, 20 wt%) portion-wisely under N_2. The reaction mixture was degassed and saturated with H_2 (balloon) and stirred ON at RT. The mixture was filtered through Celite, and the filtrate was concentrated for flash chromatography purification (Elution: hexanes/EtOAc 2/1 to 2/3) to afford known methyl (2-octulopyranosyl)onate **4** as a *α*/*β* mixture (1.60 g, 65%).[S11] After crude purification, compound **4** was taken for the thiocarbonylation.

Methyl [4,5:7,8-Di-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (5)



To a solution of oct-2-ulopyranosyl-onate **4** (4.23 g, 12.14 mmol) in DCM (120 mL) was added 1, 1′-thiocarbonyldiimidazole (3.0 g, 15.12 mmol, 90% in purity) at 0 °C. After stirred at 0 °C for 20 min, the solution was gradually warmed to RT and stirred for extra 4 h. The reaction mixture was diluted with EtOAc (100 mL), washed with cold HCl (1 M) twice, satd. $NaHCO_3$ (10 mL), H_2O (10 mL), brine (20 mL), dried over $MgSO_4$ and concentrated for flash chromatography (Elution: Hexanes/EtOAc = 6/1 to 2/1) to give (2-octulopyranosonyl)onate thionocarbonate **5** as a foamy colorless solid, (3.18 g, 72%). For **5**, R_f 0.14 (hexanes/EtOAc/DCM 2/1/1); $[\alpha]_D^{22}$ +92.0 (c 0.5, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.05 (dd, *J* = 4.8, 2.4 Hz, 1H, H-3), 4.81 (dd, *J* = 7.8, 4.8 Hz, 1H, H-4), 4.47 (dd, *J* = 7.2, 1.8 Hz, 1H, H-5), 4.31 (m, 1H, H-7), 4.19 (dd, *J* = 9.0, 3.6 Hz, 1H, *H*-8a), 4.07 (m, 1H, *H*-8b), 3.88 (s, 3H, OCH_3), 3.42 (dd, *J* = 8.4, 1.8 Hz, 1H, *H*-6), 1.47 (s, 3H, CH_3), 1.36 (s, 6H, CH_3), 1.32 (s, 3H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 187.6 (*C*=S), 165.6 (*C*=O), 111.4, 109.7, 103.3, 77.4 (*C*-3), 74.9 (*C*-6), 72.8 (*C*-7), 70.5 (*C*-5), 69.7 (*C*-4), 66.3 (*C*-8), 54.0 (O*C*H_3), 26.9 (*C*H_3), 25.7 (*C*H_3), 25.1 (*C*H_3), 24.8 (*C*H_3); **HRMS** (ESI): *m/z* calcd. for $C_{16}H_{22}NaO_9S^+$ $[M + Na]^+$: 413.0877, found: 413.0848.

Methyl [4,5-*O*-Isopropylidene-2,3-*O*-thionocarbonyl-α-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (S3)

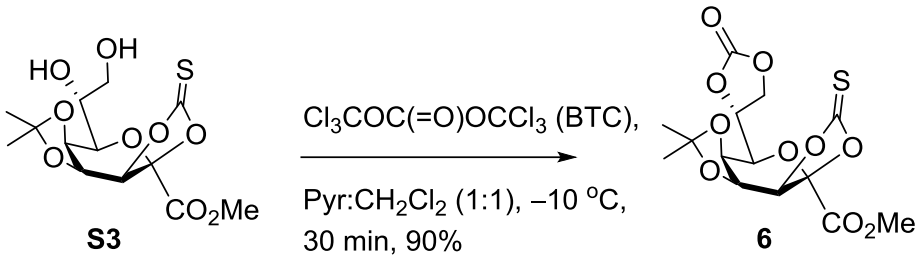


5 **S3**

To a solution of oct-2-ulopyranosyl thionocabonate **5** (3.0 g, 8.56 mmol) in Acetonitrile (83.9 mL, 0.035 M) was added Zinc nitrate hexahydrate (8.06 g, 27.08 mmol) and the reaction mixture was stirred for 4 h at 50 °C. The reaction mixture was brought to RT and neutralized with Et_3N and was filtered through a firmly packed celite bed, washed the celite bed with DCM. The filtrate was pooled and concentrated. The concentrated residue was suspended in DCM (contained some

Zn salt) and filtered through the celite bed (for the removal of the salts), washed the celite bed with DCM. The filtrate obtained was concentrated for flash chromatography purification (Elution: 10% MeOH/EtOAc) to afford expected diol **S3** as a colorless viscous liquid (2.4 g, 92%). For **S3**, R_f 0.3 (EtOAc); $[\alpha]_D^{22}$ +30.0 (*c* 0.9, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.99 (d, *J* = 4.4 Hz, 1H, C3-*H*), 4.83 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.57 (dd, *J* = 7.6, 2.0 Hz, 1H), 4.01-3.96 (m, 2H), 3.92 (s, 3H, OC*H*$_3$), 3.79 (dd, *J* = 13.2, 4.0 Hz, 1H), 3.57 (dd, *J* = 8.8, 2.0 Hz, 1H), 1.50 (s, 3H, C*H*$_3$), 1.39 (s, 3H, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.6 (*C*=S), 166.6 (*C*=O), 111.6 (*C*$(CH_3)_2$), 103.3 (*C*2), 77.6, 73.3, 70.6, 70.1, 69.3, 62.6, 54.5 (O*C*H$_3$), 25.9 (*C*H$_3$), 25.4 (*C*H$_3$); **HRMS** (ESI): *m/z* calcd. for $C_{13}H_{18}NaO_9S^+$ $[M + Na]^+$: 373.0564, found: 373.0575.

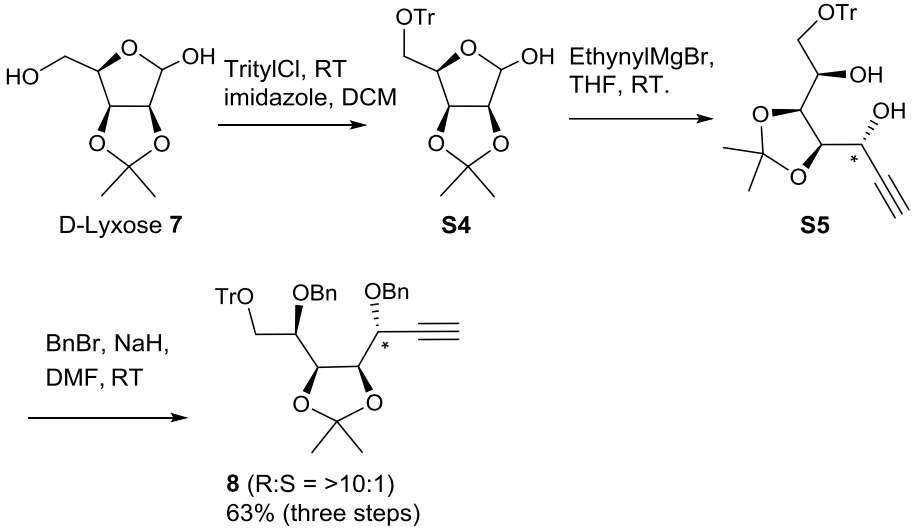
Methyl [7,8-*O*-Carbonyl-4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-α-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (6)



To a solution of oct-2-ulopyranosylonate **S3** (1.0 g, 2.85 mmol) in pyridine and DCM (10 mL) was added $Cl_3COC(=O)OCCl_3$ (2.537 g, 8.5 mmol) portionwise at –78 °C. After stirring at –78 °C 90 min, the reaction mixture was brought to 0 °C and stirred for couple of hours before quenching the reaction with satd. NH_4Cl (5.0 mL) and the product was extracted with DCM. The combined DCM extractions were washed with $CuSO_4$ solution (3 × 5 mL), water (5 mL), brine (5 mL), dried over Na_2SO_4, and concentrated for column chromatography on silica gel to give (Elution: 30% EtOAc in Hexanes) pure **6** (800 mg, 90%) as a light yellow syrup. For **6**, R_f 0.4 (50% EtOAc in petroleum ether); $[\alpha]_D^{19}$ +28.5 (*c* 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.06 (d, *J* = 4.4 Hz, 1H), 4.95 (dt, *J* = 8.4, 6.0 Hz, 1H), 4.86 (dd, *J* = 7.6, 4.4 Hz, 1H), 4.79 (dd, *J* = 9.2, 6.0 Hz, 1H), 4.56 (dd, *J* = 8.8, 8.0 Hz, 1H), 4.47 (dd, *J* = 7.6, 2.0 Hz, 1H), 3.95-3.91 (m, 4H), 1.51 (s, 3H, C*H*$_3$),

1.38 (s, 3H, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 187.0 (O*C*(=S)O), 165.4 (*C*=O), 154.2 (O*C*(=O)O), 111.9 (*C*(CH_3)$_2$), 102.9 (*C*(CH_3)$_2$), 77.3, 73.5, 73.3, 69.9, 69.8, 66.1, 54.4 (O*C*H$_3$), 25.6 (*C*H$_3$), 24.8 (*C*H$_3$); **HRMS** (ESI): *m/z* calcd. for $C_{14}H_{16}NaO_{10}S^+$ [M + Na]$^+$: 399.0356, found: 399.0361.

3,6-Di-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-1-yno-heptitol (8)

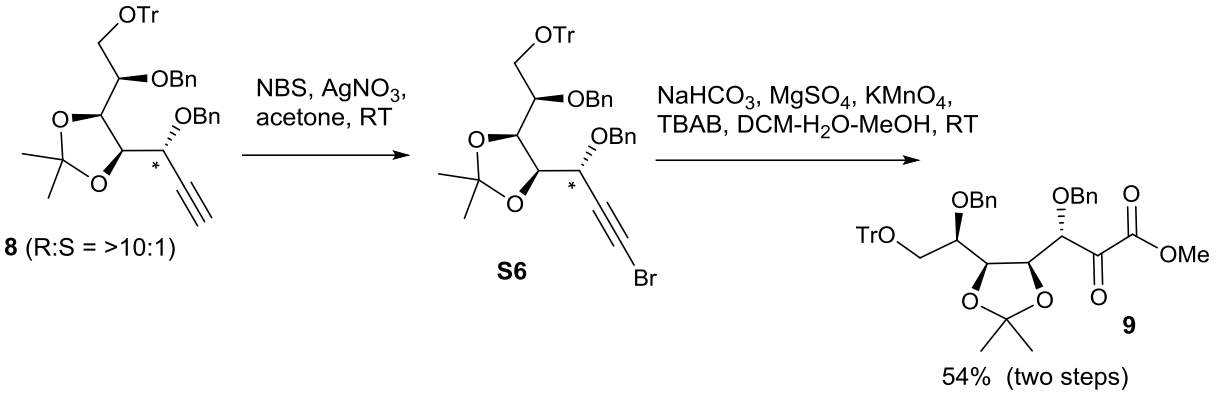


To a stirred solution of **7**[S12] (13 g, 66.6 mmol) and DMAP (2.44 g, 20 mmol) in pyridine (133 mL) was added chlorotriphenylmethane (24.14 g, 86.6 mmol) at RT. The reaction mixture was stirred for 5.5 h at 80 °C and concentrated under reduced pressure. The resulting residue was dissolved in EtOAc and then successively washed with 1 N cold $HCl_{(aq)}$, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc = 4:1) to give known lyxose intermediate **S4** (23.6 g, 82%).[S13] Data for **S4**: R_f = 0.27 (hexanes/EtOAc, 3:1); HRMS (ESI) *m/z* calcd. for $C_{27}H_{28}NaO_5^+$ [M + Na]$^+$: 455.1829, found: 455.1833.

Ethynyl magnesium bromide solution (328 mL, 163.9 mmol, 0.5M in THF) was added tritylated furanose **S4** (23.62 g, 54.6 mmol) at 0 °C. After stirred for 1 h, the solution was gradually warmed to 40 °C and stirred for overnight. The reaction was quenched by careful addition of satd. NH_4Cl at 0 °C, and all the solvent was removed under reduced pressure. The residue, after

dissolving in EtOAc, was washed satd. NH_4Cl twice, and brine. The organic layer, dried over $MgSO_4$, was concentrated under reduced pressure. Crude diol product **S5** was directly used for next step without further purification. To a solution of diol **S5** in DMF (182 mL) at 0 °C was portion-wisely added NaH (6.55 g, 163.9 mmol, 60 % dispersion in mineral oil). After stirring for 0.5 h, the suspension was treated with BnBr (14.3 mL, 120.1 mmol). The reaction mixture was stirred from 0 °C to RT for 2 h. Then the reaction was quenched by addition of satd. NH_4Cl at 0 °C, and the solvent was removed under reduced pressure. The residue, after dissolving in EtOAc, was washed satd. NH_4Cl twice, and brine, dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc, 15:1 to 9:1) to give dibenzylated alkyne **8** (25.47 g, 73 %) as a light yellow oily substance. Data for **8**: R_f = 0.43 (hexanes/EtOAc, 5:1); $[\alpha]_D^{24}$ = –24.3 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.5 Hz, 6H, ArH), 7.32-7.19 (m, 19H, ArH), 4.66 (d, *J* = 11.4 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.36 (t, *J* = 5.4 Hz, 1H), 4.31-4.23 (m, 3H), 4.11 dd, *J* = 8.3, 5.7 Hz, 1H), 3.72 (q, *J* = 5.0 Hz, 1H), 3.32-3.25 (m, 2H), 2.53 (t, *J* = 1.0 Hz, 1H), 1.45 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.12, 138.91, 136.96, 128.89, 128.73, 128.55, 128.33, 128.09, 127.89, 127.63, 127.40, 127.09, 109.23, 87.00, 80.86, 77.78, 77.62, 76.39, 75.53, 72.13, 70.42, 67.94, 64.11, 27.20, 25.79; HRMS (ESI) *m/z* calcd. for $C_{43}H_{42}NaO_5^+$ $[M + Na]^+$: 661.2928, found: 661.2924.

Preparation of 3,6-di-*O*-benzyl-1-bromo-1,2-dideoxy-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-1-yno-heptitol (S6) and methyl 3,6-Di-*O*-benzyl-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-hept-2-ulosonate (9)

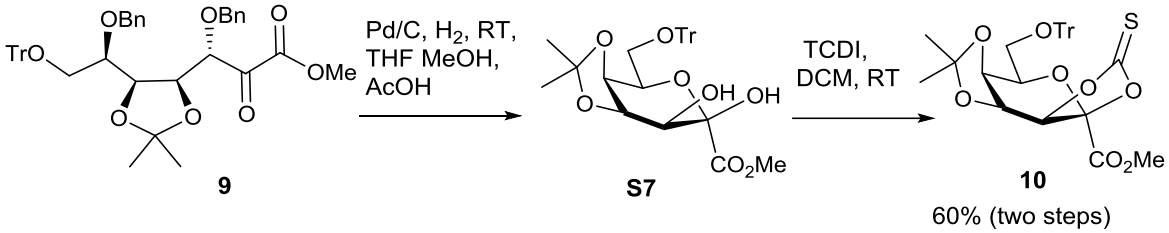


To a solution of aforementioned alkyne **8** (25.47 g, 39.9 mmol) in anhydrous ACN (80 mL) was added *N*-bromosuccinimide (10.65 g, 59.8 mmol) and $AgNO_3$ (0.67 g, 4.0 mmol) in the dark at RT. The reaction mixture was stirred in the dark for 2 h, and the resulting suspension was filtered through celite. The filtrate was diluted with EtOAc and washed satd. $Na_2S_2O_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc, 15:1 to 9:1) to give the desired bromo-alkyne **S6** (27.2 g, 95%). Data for **S6**: R_f = 0.42 (hexanes/EtOAc, 5:1); $[\alpha]_D^{28}$ = –20.0 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 7.8 Hz, 6H, ArH), 7.29-7.16 (m, 19H, ArH), 4.63 (d, *J* = 12.1 Hz, 1H), 4.56 (d, *J* = 12.1 Hz, 1H), 4.35 (dd, *J* = 13.2, 8.6 Hz, 2H), 4.24 (d, *J* = 9.6 Hz, 1H), 4.13-4.07 (m, 1H), 3.72 (dd, *J* = 10.0, 4.9 Hz, 1H), 3.28 (t, *J* = 4.9 Hz, 2H), 1.45 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.97, 138.76, 136.82, 128.77, 128.54, 128.46, 128.26, 128.01, 127.83, 127.58, 127.36, 127.03, 109.14, 86.95, 77.73, 77.60, 77.40, 77.36, 76.25, 72.13, 70.56, 69.06, 64.04, 47.22, 27.11, 25.70; **HRMS** (ESI): *m/z* calcd. for $C_{43}H_{41}BrNaO_5^+$ [M + Na]$^+$: 739.2030, found: 739.2028.

To a solution of bromoheptyne **S6** (10.5 g, 14.6 mmol) in DCM (90 mL) was added TBAB (1.4 g, 4.4 mmol), $NaHCO_3$ (0.61 g, 7.3 mmol), $MgSO_4$ (3.5 g, 29.3 mmol), H_2O (90 mL), and

MeOH (270 mL) with vigorous stirring to give a homogeneous solution at 0 °C. Then $KMnO_4$ (6.9 g, 43.9 mmol) was portion-wisely added. The reaction mixture was stirred at 0 °C for overnight, and the resulting suspension was filtered over celite. Then the filtrate was concentrated under reduced pressure. The residue, diluted with EtOAc, was washed with H_2O. The aqueous phase was washed with EtOAc (×2) and the organic phase was pooled together, then washed with brine, dried over $MgSO_4$, concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc, 9:1 to 4:1) to give desired α-keto acid ester **9** (5.95 g, 58%) as a white glassy material. Data for **9**: R_f = 0.3 (hexanes/EtOAc, 5:1); $[\alpha]_D^{24}$ = +8.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* =7.8 Hz, 6H), 7.36-7.28 (m, 8H), 7.24-7.2 (m, 9H), 7.12-7.10 (m, 2H), 4.65 (dd, *J* = 16.9, 10.6 Hz, 2H), 4.46 (dd, *J* = 11.3, 5.3 Hz, 2H), 4.29-4.23 (m, 2H), 4.05 (d, *J* = 11.2 Hz, 1H), 3.76 (s, 1H), 3.65 (q, *J* = 5.1 Hz, 1H), 3.32 (ddd, *J* = 14.3, 9.8, 4.9 Hz, 2H), 1.37 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.32, 162.07, 144.01, 138.63, 136.23, 128.94, 128.81, 128.76, 128.70, 128.62, 128.59, 128.51, 128.34, 128.08, 128.05, 128.01, 127.96, 127.86, 127.81, 127.51, 127.05, 109.63, 86.92, 78.88, 77.83, 76.69, 75.57, 72.28, 71.98, 63.66, 52.69, 26.80, 25.45; **HRMS** (ESI): *m/z* calcd. for $C_{44}H_{44}NaO_8^+$ $[M + Na]^+$: 723.2928, found: 723.2942.

Preparation of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-7-*O*-trityl-D-*talo*-2-hept-2-ulopyranosonyl]onate (10)

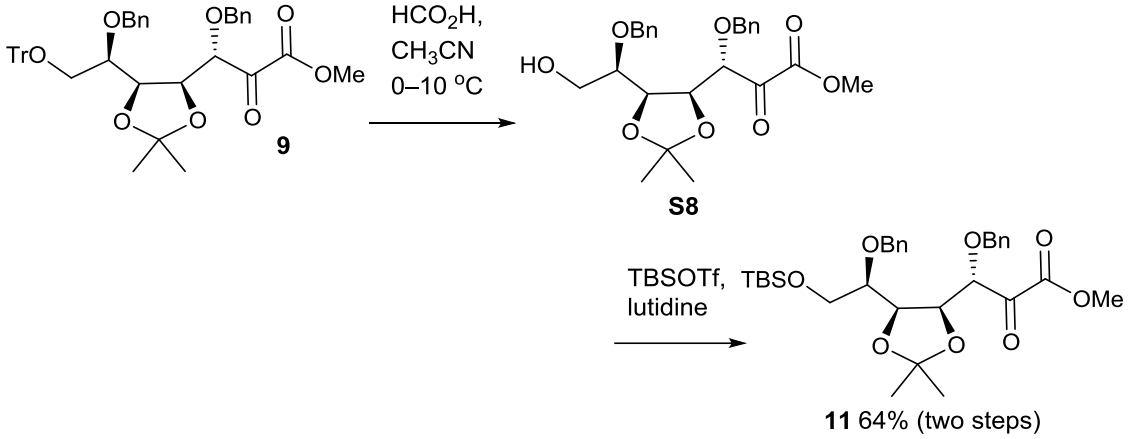


To a solution of α-keto acid ester **9** (0.8 g, 1.14 mmol) in THF (28.5 mL), MeOH (9.5 mL) and AcOH (1.9 mL) was added Pd/C (0.16 g, 10%) under N_2. The reaction mixture was degassed and saturated with H_2 (1 atm) and stirred for 3 h. The mixture was filtered through Celite, and the

filtrate was diluted with EtOAc and washed with satd. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc, 2:1) to give pyranose **S7** (0.44 g, 74%). Acquired data for **S7**: R_f = 0.3 (hexanes/EtOAc, 1:1); **HRMS** (ESI): *m/z* calcd. for $C_{30}H_{32}NaO_8^+$ $[M + Na]^+$: 543.1989, found: 543.1993.

To a solution of **S7** (0.44 g, 0.85 mmol) in DCM (16.9 mL) was added thiocarbonyl diimidazole (0.45 g, 2.54 mmol) at RT. After stirred for 3 h, the reaction solution was washed with cold HCl, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc, 3:1) to give cyclic thionocarbonate **10** (0.37 g, 78%) as a light yellowish oily substance. Data for **10**: R_f = 0.35 (hexanes/EtOAc, 2:1); $[\alpha]_D^{24}$ = +25.7 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, , *J* = 8.1 Hz, 6H), 7.30 (t, *J* = 7.5 Hz, 6H), 7.26-7.21 (m, 3H), 5.09 (d, *J* = 4.3 Hz, 1H), 4.76-4.72 (m, 1H), 4.27 (d, *J* = 7.4 Hz, 1H), 3.91 (s, 3H), 3.66-3.62 (m, 1H), 3.59-3.54 (m, 1H), 3.29 (dd, *J* = 10.1, 4.2 Hz, 1H), 1.40 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.94, 165.98, 143.71, 128.78, 127.96, 127.26, 111.81, 103.96, 87.07, 77.24, 74.74, 71.30, 70.24, 62.06, 54.10, 25.93, 25.66; **HRMS** (ESI): *m/z* calcd. for $C_{31}H_{30}NaO_8S^+$ $[M + Na]^+$: 585.1554, found: 585.1549.

Preparation of methyl 3,6-di-*O*-benzyl-4,5-*O*-isopropylidene-7-*O*-*t*butyldimethylsilyl-D-*talo*-hept-2-ulosonate (11)

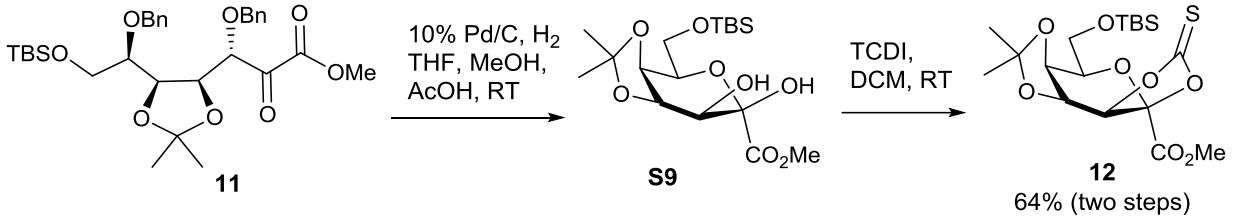


To a solution of α-keto acid ester **9** (4 g, 5.7 mmol) in CH_3CN (30 mL), and formic acid (10 mL, 95%) was added at 0 °C. After stirred at for 0.5 h, the solution was gradually warmed to 10 °C and stirred for 2.5 h. The reaction was quenched by addition of satd. $NaHCO_3$ at 0 °C. The mixture was diluted with EtOAc and washed with satd. $NaHCO_3$ (× 2), and brine. The organic phase was dried (over $MgSO_4$) and concentrated under reduced pressure for column chromatography purification (Elution: hexanes/EtOAc, 3:1) to give **S8** (1.86 g, 71%) as a foamy white solid. For **S8**: R_f = 0.18 (hexanes/EtOAc, 2:1); **HRMS** (ESI): *m/z* calcd. for $C_{25}H_{30}NaO_8^+$ $[M + Na]^+$: 481.1833, found: 481.1840.

To a solution of **S8** (1.86 g, 4.1 mmol) in DCM (13.5 mL) was added lutidine (0.95 mL, 8.1 mmol), and TBSOTf (1.4 mL, 6.1 mmol) at RT. After stirred for 1 h, the reaction was quenched with H_2O. The mixture was diluted with DCM and washed with H_2O and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc, 9:1) to give silyl ether **11** (2.11 g, 91%) as a colorless glassy solid. Data for **11**: R_f = 0.38 (hexanes/EtOAc, 5:1); $[\alpha]_D^{24}$ = +16.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93-7.22 (m, 10H), 4.82 (d, *J* = 8.3 Hz, 1H), 4.70 (d, *J* =12.0 Hz, 1H), 4.51 (d, *J* =12.0 Hz, 1H), 4.39 (d, *J* = 8.1 Hz, 3H), 4.19 (d, *J* = 11.2 Hz, 1H), 3.83-3.74 (m,

5H), 3.62-3.67 (m, 1H), 1.42 (s, 3H), 1.29 (s, 3H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.57, 162.12, 138.86, 136.35, 128.81, 128.60, 128.45, 128.35, 127.56, 127.47, 109.61, 78.93, 77.05, 76.93, 76.85, 72.37, 71.95, 63.05, 52.79, 26.78, 26.01, 25.38, 18.37, –5.29, –5.32; **HRMS** (ESI): *m/z* calcd. for $C_{31}H_{44}NaO_8Si^+$ $[M + Na]^+$: : 595.2698, found: 595.2711.

Preparation of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-7-*O*-*t*butyldimethylsilyl-D-*talo*-2-hept-2-ulopyranosonyl]onate (12)



To a solution of silyl ether **11** (2.11 g, 3.7 mmol) in THF (100 mL), MeOH (25 mL) and acetic acid (6.25 mL) was added Pd/C (0.42 g, 10%) under N_2. The reaction mixture was degassed and saturated with H_2 (1 atm) and stirred for 3 h. The mixture was filtered through Celite, and the filtrate was diluted with EtOAc and washed with satd. $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc, 3:1) to give pyranose **S9** (1.13 g, 78%). Data for: R_f = 0.18 (hexanes/EtOAc, 2:1); **HRMS** (ESI): *m/z* calcd. for $C_{17}H_{32}NaO_8Si^+$ $[M + Na]^+$: : 415.1759, found: 415.1762.

To a solution of **11a** (1.13 g, 2.9 mmol) in DCM (57 mL) was added TCDI (1.54 g, 8.7 mmol) at RT. After stirred for 4 h, the reaction solution was washed with cold HCl, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc, 3:1) to give thionocarbonate donor **12** (1 g, 80%) as a colorless oily substance. Data for **12**: R_f = 0.25 (hexanes/EtOAc, 2:1); $[\alpha]_D^{24}$ = +40.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.08 (d, *J* = 4.5 Hz, 1H), 4.78 (dd, *J* = 7.4, 4.5 Hz, 1H), 4.38 (dd, *J* = 7.4, 1.9 Hz, 1H), 3.88 (s, 3H), 3.84 (dd,

J = 6.2, 4.5 Hz, 2H), 3.70 (td, *J* = 6.2, 2.0 Hz, 1H), 1.50 (s, 3H), 1.36 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.96, 165.92, 111.62, 103.82, 77.40, 75.40, 70.57, 70.01, 61.24, 54.07, 25.95, 25.87, 25.53, 18.36, -5.29, -5.44; **HRMS** (ESI): *m/z* calcd. for $C_{18}H_{30}NaO_8SSi^+$ $[M + Na]^+$: 457.1323, found: 457.1325.

Preparation of Me_2S_2-Tf_2O promoting agent

A 1.0 M solution of the above reagent was prepared by mixing trifluoromethanesulfonic anhydride (0.168 mL, 1 mmol) to a solution of dimethyl disulfide (0.10 mL, 1.1 mmol) in dry DCM (0.75 mL) at 0 °C. The resulting mixture was stirred 0 °C for 30 min before use.[S14]

General glycosylation method for 2,3-*O*-thionocarbonate donors:

To a stirred solution of donor (1.0 equiv) and acceptor (1.2 equiv) in dry DCM (0.05 M) were added DTBMP (1.0 equiv) activated 4Å powdered molecular sieves (10 mol%) and then cooled it to –60 to –70 °C. Then 1 M solution (1.0 equiv) of promoter was added to it at same temperature. The reaction mixture was stirred for 30 min-few hours depend upon the acceptors and after that the reaction mixture was quenched by the addition of excess triethylamine, diluted with DCM, filtered through celite. The organic layer was concentrated at 40 °C for column chromatography.

General deprotection procedure for methylperoxycarbonyl group

To a solution of methylperoxycarbonyl protected glycoside (1 equiv.) in THF (0.1–0.5 M) was added H_2O (5 equiv.), Et_3N (5 equiv.), and DMAP (2 equiv.). The solution was stirred at RT for 3-6 h then worked up or concentrated for flash chromatography purification.

General procedure for introduction of phenoxythiocarbonyl group

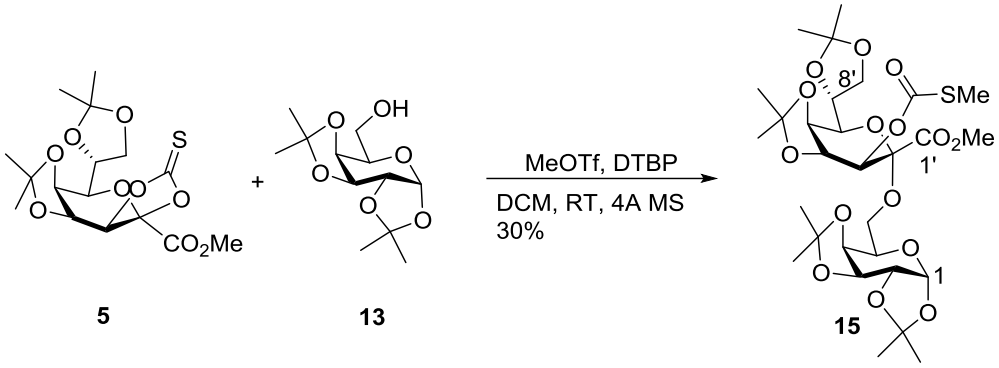
To a solution of hydroxyl substrate (1 equiv.) in CH_3CN (0.1–0.05 M), DBU (2–4 equiv.), DMAP (2 equiv.), and phenyl chlorothionoformate (2.5 equiv.) were added at 0 °C. The mixture was stirred at RT for ca. 3–5 h, then diluted with EtOAc, which was washed with 0.5-1 N HCl,

satd. $NaHCO_3$, brine, dried (over $MgSO_4$), filtered, and concentrated for column chromatography purification.

General deoxygenation procedure

To a solution of *O*-phenoxythiocarbonyl protected substrate (1 equiv.) in toluene (0.5 M), tributyl or triphenyl tin hydride (Bu_3SnH or Ph_3SnH) (1.5–2.0 equiv.) and AIBN (0.5 equiv.) were added. The mixture was subjected to 'freeze-vacuum-thaw' degassing cycle thrice and was stirred at 80–100 °C for *ca.* 2–4 h, then diluted with EtOAc, which was washed with H_2O, brine, dried (over $MgSO_4$), filtered, and concentrated for column chromatography purification.

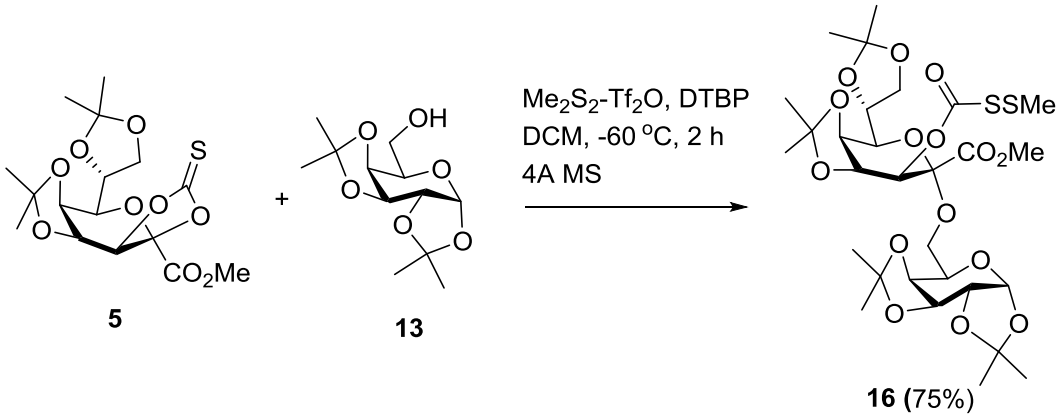
1,2:3,4-Di-*O*-isopropylidene-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(methyl-thiocarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glactopyranoside (15) (Table 1, entry 2)



To a stirred suspension of oct-2-ulopyranosyl thionocarbonate **5** (0.231 mmol, 90 mg), the commercially available galactosyl acceptor **13** (50 mg, 0.193 mmol), DTBP (0.386 mmol, 79 mg), and activated molecular sieve (4 Å) in anhydrous DCM (4 mL) was added MeOTf (27 μL, 0.25 mmol) at RT. After 12 h, the reaction was quenched with addition of Et_3N (2 drops), and the mixture was filtered and concentrated for flash chromatography purification (Elution: Hexanes/EtOAc 6/1 to 2/1) to afford the α-glycosylation product **15** as a colorless foamy solid (38 mg, 30%). For **15**, R_f 0.23 (hexanes/EtOAc/DCM = 2/1/1); $[\alpha]_D^{34}$ + 24.6 (*c* 0.30, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.50 (d, J = 5.0 Hz, 1H), 5.35 (d, J = 5.5 Hz, 1H), 4.59 (dd, J = 8.0, 2.5 Hz,

1H), 4.50 (dd, *J* = 10.5, 6.0 Hz, 1H), 4.48 (m, 1H), 4.33 (dd, *J* = 6.0, 3.0 Hz, 1H, H-2), 4.30 (dd, *J* = 5.0, 3.0 Hz, 1H), 4.20 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.17 -4.12 (m, 3H), 3.94 (dt, *J* = 8.0, 2.0 Hz, 1H), 3.78 (s, 3H, OC*H*$_3$), 3.71 (dd, *J* = 10.0, 8.5 Hz, 1H), 3.46 (dd, *J* = 10.5, 2.5 Hz, 1H), 2.33 (s, 3H, SC*H*$_3$), 1.54 (s, 3H, C*H*$_3$), 1.52 (s, 3H, C*H*$_3$), 1.44 (s, 3H, C*H*$_3$), 1.43 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 171.4 (O*C*(=O)SMe), 166.8 (C-1′), 110.6, 110.1, 109.8, 109.2, 99.2 (C-2′), 96.7 (C-1, $^2J_{C\text{-}H}$ = 180 Hz), 74.4, 71.8, 71.2, 70.8, 70.5, 70.4, 69.7, 67.7, 67.6, 63.8, 53.2 (O*C*H$_3$), 27.2 (*C*H$_3$), 26.5 (*C*H$_3$), 26.4 (*C*H$_3$), 26.3 (*C*H$_3$), 26.0 (*C*H$_3$), 25.5 (*C*H$_3$), 25.0 (*C*H$_3$), 14.1 (S*C*H$_3$); HRMS (ESI): *m/z* calcd. for $C_{29}H_{44}NaO_{15}S^+$ $[M + Na]^+$: 687.2293, found: 687.2310.

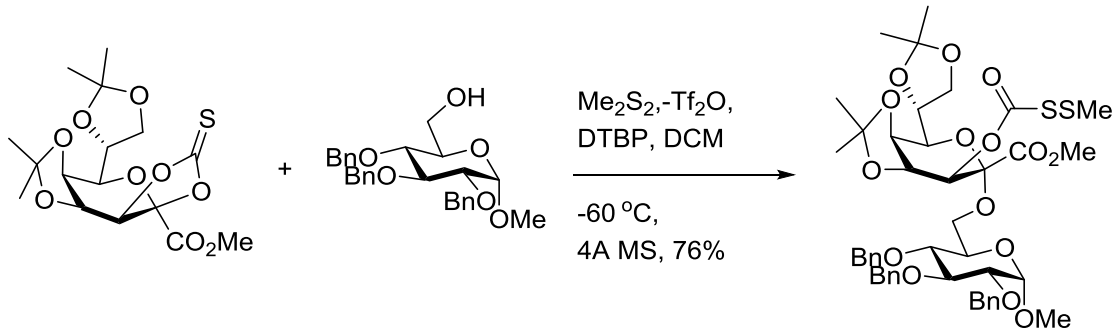
1,2:3,4-Di-*O*-isopropylidene-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-galactopyranoside (16) (Table 1, Entry 8)



Glycosylation of galactosyl acceptor **13** with donor **5** followed the general glycosylation procedure. Disaccharide **16** was obtained in 75% yield as a white foamy solid by flash chromatography purification (Elution: hexanes/EtOAc 6/1 to 3.5/1). For **16**, R_f = 0.28 (hexanes/EtOAc/DCM = 2/1/1); $[\alpha]_D^{30}$ – 34.7 (*c* 1.63, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.50 (d, *J* = 5.0 Hz, 1H, H-1), 5.37 (d, *J* = 5.0 Hz, 1H, H-3′), 4.59 (dd, *J* = 8.0, 2.5 Hz, 1H, H-5′), 4.53 (t, *J* = 6.0 Hz, 1H, H-4′), 4.48 (dq, *J* = 5.0, 6.0 Hz, 1H), 4.33 (dd, *J* = 6.5, 3.0 Hz, 1H, H-3), 4.30 (dd, *J* = 4.5, 2.5 Hz, H-2), 4.22 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.19-4.15 (m, 2H), 4.133 (d, *J* = 1.5

Hz, 1H, H-4), 3.94 (dt, *J* = 8.0, 2.0 Hz, 1H, H-5), 3.77 (s, 3H, OC*H*$_3$), 3.71 (dd, *J* = 10.0, 1.5 Hz, 1H, H-6a), 3.46 (dd, *J* = 10.5, 3.0 Hz, 1H, H-6b), 2.47 (s, 3H, SSC*H*$_3$), 1.54 (s, 3H, C*H*$_3$), 1.50 (s, 3H, C*H*$_3$), 1.44 (s, 3H, C*H*$_3$), 1.43 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): *δ* 168.8 (O*C*(=O)SSMe), 166.1 (*C*(=O)OMe), 110.1 (*C*(CH$_3$)$_2$), 109.6 (*C*(CH$_3$)$_2$), 109.3 (*C*(CH$_3$)$_2$), 108.7 (*C*(CH$_3$)$_2$), 98.5 (C-2′), 96.2 (C-1), 73.8, 71.3 (× 2 including C-3′), 70.7 (C-5′), 70.3 (C-2), 70.0 (C-4′), 69.9 (C-3), 67.2 (C-5), 67.0 (C-4), 63.4 (C-6), 52.8 (O*C*H$_3$), 26.7 (*C*H$_3$), 26.1 (*C*H$_3$), 25.9 (*C*H$_3$), 25.7 (*C*H$_3$), 25.4 (*C*H$_3$), 24.9 (*C*H$_3$), 24.5 (*C*H$_3$), 22.9 (SS*C*H$_3$); **HRMS** (ESI): *m/z* calcd. for $C_{29}H_{44}NaO_{15}S_2^+$ [M + Na]$^+$: 719.2014, found: 719.2043.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (17) (Table 1, Entry 10)

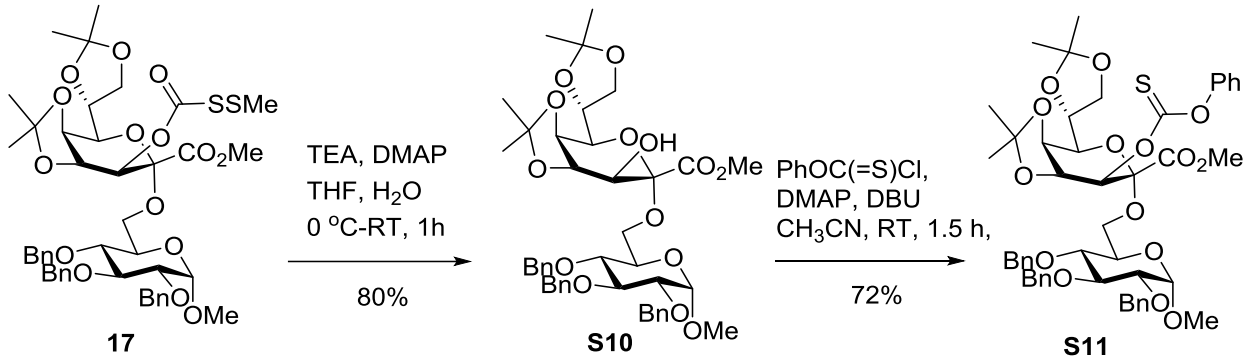


5 **14** **17**

Glycosylation of known acceptor **14**[S1] (209 mg, 0.451 mmol) with donor **5** (160 mg, 0.410 mmol) followed the general glycosylation procedure. Disaccharide **17** (281 mg, 76%) was obtained as a light yellow gummy liquid after column chromatography purification (Elution: 3:1:1 hexanes/EtOAc/DCM). For **17**, R_f 0.5 (3:1:1 hexanes/ EtOAc/DCM), $[\alpha]_D^{19}$ + 40.0 (*c* 1.15, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* 7.37–7.19 (m, 15H, Ar*H*), 5.35 (d, *J* = 5.2 Hz, 1H, H-3′), 4.98 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 12.4 Hz, 1H), 4.63 (d, *J* = 12.4 Hz, 1H), 4.50-4.39 (m, 5H including H-1 from HMQC), 4.21 (dd, *J* = 6.4, 2.8 Hz,

1H, H-6′), 4.09 (dd, *J* = 5.6, 3.2 Hz, 1H, H-7′), 3.96 (t, *J* = 9.2 Hz, 1H, H-5), 3.94 (dd, *J* = 8.0, 3.2 Hz, 1H, H-5′), 3.76 (dq, *J* = 1.6, 8.0 Hz, 1H, H-3), 3.63 (s, 3H, OC*H*$_3$), 3.59 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.49-3.45 (m, 2H including H-2), 3.34 (m, 4H from COSY), 3.22 (dd, *J* = 10.4, 8.8 Hz, 1H, H-4), 2.45 (s, 3H, SSC*H*$_3$), 1.48 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$); **^{13}C NMR** (100 MHz, CDCl$_3$): δ 168.8 (*C*(=O)SSMe), 165.6 (C-1′, *C*(=O)OMe), 138.6, 138.0, 137.9, 128.4, 128.4, 128.4, 128.1, 127.9, 127.8, 127.8, 127.8, 127.6, 110.2, 109.3, 98.6 (C-2′), 97.6 (C-1), 82.0 (C-5), 79.8 (C-2), 78.2 (C-4), 75.7, 74.8, 73.9 (C-4′), 73.4, 71.0 (C-3′), 70.1, 69.9 (C-6′), 69.3 (C-3), 69.2 (C-5′), 66.6, 63.9, 54.8, 52.6, 26.7 (*C*H$_3$), 25.9 (*C*H$_3$), 25.6 (*C*H$_3$), 25.3 (*C*H$_3$), 22.9 (SS*C*H$_3$); **HRMS** (ESI): *m*/*z* calcd. for $C_{45}H_{56}NaO_{15}S_2^+$ $[M + Na]^+$: 923.2953, found: 923.2959.

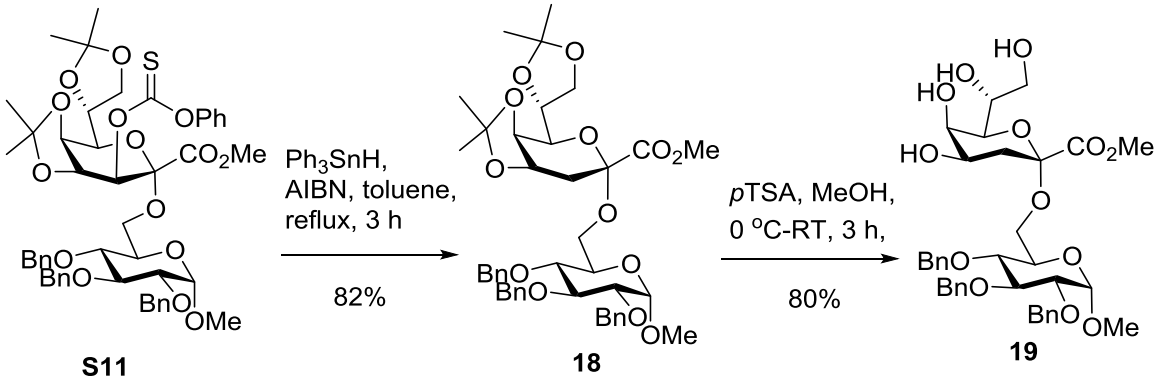
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (S10) and methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-phenoxythiocarbonyl-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (S11)



The methylperoxycarbonyl group of disaccharide **17** (1.05 g, 1.2 mmol) was cleaved according to general deprotection procedure. After chromatography purification (Elution: hexanes/EtOAc 4/1 to 1.5/1), known disaccharide **S10** (0.76 g, 80%) was obtained as a yellow viscous oil.[S11] To a solution of **S10** (100 mg, 0.125 mmol), DBU (74 µL, 0.5 mmol), DMAP (61 mg, 0.5 mmol) in anhydrous DCM (4 mL, 0.03 M) was added phenyl chlorothionoformate (43 µL, 0.314 mmol) at 0 °C. After stirred at 0°C for 30 min, the reaction mixture was gradually warmed to RT and stirred for extra 1 h. The reaction solution, diluted with EtOAc, was washed with cold

HCl (1.0 M) (× 2), satd. $NaHCO_3$ (5 mL), H_2O (5 mL), brine (5 mL), dried over $MgSO_4$, and concentrated for flash chromatography purification (Elution: Hexanes/EtOAc 4/1.5) to give a colorless oily liquid, **S11** (84 mg, 72%). For **S11**, R_f 0.3 (Hexanes/EtOAc 4/1.5); $[\alpha]_D^{22}$ + 31.4 (*c* 1.40, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43–7.21 (m, 18H), 7.04–6.99 (m, 2H), 5.87 (d, *J* = 5.2 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.4 Hz, 1H), 4.56 (dd, *J* = 6.4, 4.8 Hz, 1H), 4.54–4.48 (m, 2H), 4.29 (dd, *J* = 6.4, 2.8 Hz, 1H), 4.12 (m, 2H), 4.01 (dd, *J* = 8.0, 2.8 Hz, 1H), 3.99 (d, *J* = 9.2 Hz, 1H), 3.82 (dq, *J* = 2.0, 8.0 Hz, 1H), 3.68 (s, 3H), 3.66 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.498 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.497 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.35 (s, 3H), 3.25 (dd, *J* = 10.4, 8.8 Hz, 1H), 1.61 (s, 3H), 1.39 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 194.8 (*C*=S), 165.7 (*C*-1'), 153.5, 138.6, 138.0, 137.9, 129.5, 128.4, 128.4, 128.4, 128.1, 127.9, 127.8, 127.8, 127.7, 127.62, 126.6, 121.7, 110.4, 109.3, 98.6 (C-2′), 97.6 (C-1), 82.0, 79.9, 78.4, 75.8, 75.7, 74.8, 73.9, 73.4, 70.3, 70.2, 69.4, 69.3, 66.7, 63.9, 54.8, 52.5, 26.8, 25.6, 25.5, 25.4. **HRMS** (ESI): *m/z* calcd. for $C_{50}H_{58}O_{15}S^+$ $[M + Na]^+$ 953.3389, found 953.3314.

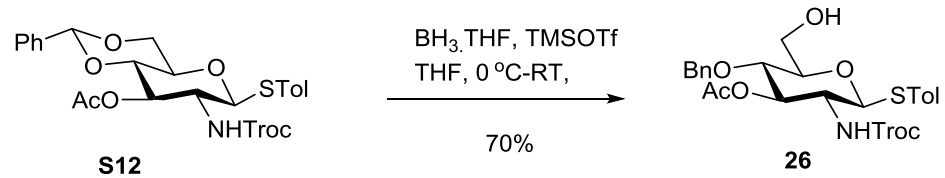
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (18) and methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (19)



A solution of disaccharide **S11** (60 mg, 0.064 mmol) in deoxygenated toluene was subjected to the general deoxygenation procedure to give known disaccharide **18** as a colorless oily liquid

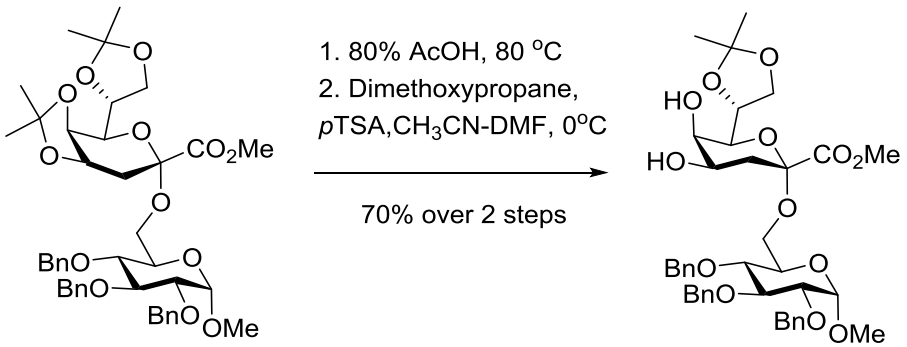
(41 mg, 82%).[S11] To a solution of disaccharide **18** (26 mg, 0.033 mmol) in dry MeOH (2 mL), was added *p*TSA (19 mg, 0.100 mmol) and the resulting mixture was stirred from 0 °C to RT for 3 h. The reaction was monitored by TLC and after complete consumption of **18**, the solution was neutralized with Et_3N and the solvent was removed for flash column chromatography purification (Elution: 10% MeOH in DCM) to give a disaccharide **19** (18 mg, 80%) as a colorless syrupy liquid. For disaccharide **19**, R_f 0.1 (EtOAc); $[\alpha]_D^{19}$ +80.0 (*c* 0.4, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.31–7.22 (m, 13H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.92 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 10.8 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 3.0 Hz, 1H, H-1), 4.46 (d, *J* = 11.4 Hz, 1H), 3.92 (t, *J* = 9.6 Hz, 2H including H-3 supported by COSY), 3.88 (dd, *J* = 4.8, 10.8 Hz, 2H including H-4′ supported by COSY), 3.74 (t, *J* = 9.0 Hz, 1H, H-5), 3.67–3.62 (m, 4H), 3.58 (dd, *J* = 5.4, 11.4 Hz, 1H), 3.52 (d, *J* = 10.2 Hz, 1H), 3.46 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.37 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.31 (s, 3H, OC*H*$_3$), 3.21 (t, *J* = 9.6 Hz, 1H, H-4), 2.57 (bs, 4H, OH × 4), 2.08 (dd, *J* = 12.8, 4.8 Hz, 1H, H-3′eq), 1.80 (t, *J* = 12.0 Hz, 1H, H-3′ax); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.9 (*C*-1'), 138.6, 138.0, 137.9, 128.4, 128.4, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 98.6 (C-2′), 97.6 (C-1), 81.9 (C-3), 80.0 (C-2), 78.2 (C-4), 77.3, 75.7, 74.7, 73.3, 71.5, 70.1, 69.6, 66.8, 66.0, 63.5, 63.5, 55.0, 52.7, 34.7 (C-3′); **HRMS** (ESI): *m/z* calcd. for $C_{37}H_{46}O_{13}Na^+$ $[M + Na]^+$ 721.2831, found 721.2736. Data for corresponding β isomer of **19** was given by ref S7.

Preparation of *p*-tolyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-(trichloroethoxycarbonyl)-*β*-D-thioglucopyranoside acceptor (26)



To a stirred solution of known thioglycoside **S12**[S14] (1.06 g, 1.80 mmol) in THF (120 mL, 0.015 mmol) wad added BH_3.THF (1 M) (9.04 mL, 9.04 mmol) at 0 °C. After 10 min TMSOTf (97 µL, 0.542 mmol) was added to the reaction mixture drop wise and allowed to stir at RT for 3 h. After completion of reaction, it was quenched with dry methanol (2 mL), and then diluted with Et_2O (100 mL), was washed with H_2O (30 mL) twice. After separation, the aqueous layer was washed with Et_2O (50 mL) three times. The combined organic layer was then washed with brine (30 mL), dried over $MgSO_4$, concentrated for flash chromatography purification (Elution: hexanes/DCM/EtOAc = 6/5/2) to furnish the desired product **26** (765 mg, 70%) as a yellow viscous oil. Analytical data for **26**, R_f = 0.3 (hexanes/EtOAc = 6/1); $[\alpha]_D^{22}$ = –11.4 (*c* 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39–7.21 (m, 8H, Ar*H*), 7.11 (d, *J* = 8.4 Hz, 2H, Ar*H*), 5.29 (d, *J* = 9.6 Hz, 1H), 5.15 (t, *J* = 9.6 Hz, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.66-4.56 (m, 3H), 3.87 (m, 1H), 3.77–3.62 (m, 3H), 3.41 (m, 1H), 2.33 (s, 3H, C*H*$_3$), 1.94 (s, 3H, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.8 (*C*=O), 154.2, 138.5, 137.5, 133.1, 129.8, 128.5, 128.5, 128.1, 127.9, 127.9, 87.4, 79.3, 75.7, 75.4, 74.8, 74.5, 61.7, 55.4 , 21.1 (*C*H$_3$), 20.8 (*C*H$_3$). **HRMS** (ESI) *m*/*z* calcd. for $C_{25}H_{28}Cl_3NaNO_7S^+$ $[M + Na]^+$: 614.0544, found: 614.0567.

Preparation of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (29)

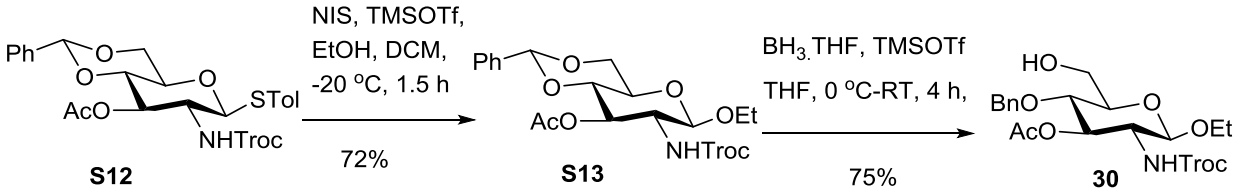


18 **29**

Disaccharide **18** (1.10 g, 1.42 mmol) was dissolved in 80% acetic acid (28 mL) and stirred at 80 °C until the completion of reaction. The solvent was reduced under reduced pressure and the

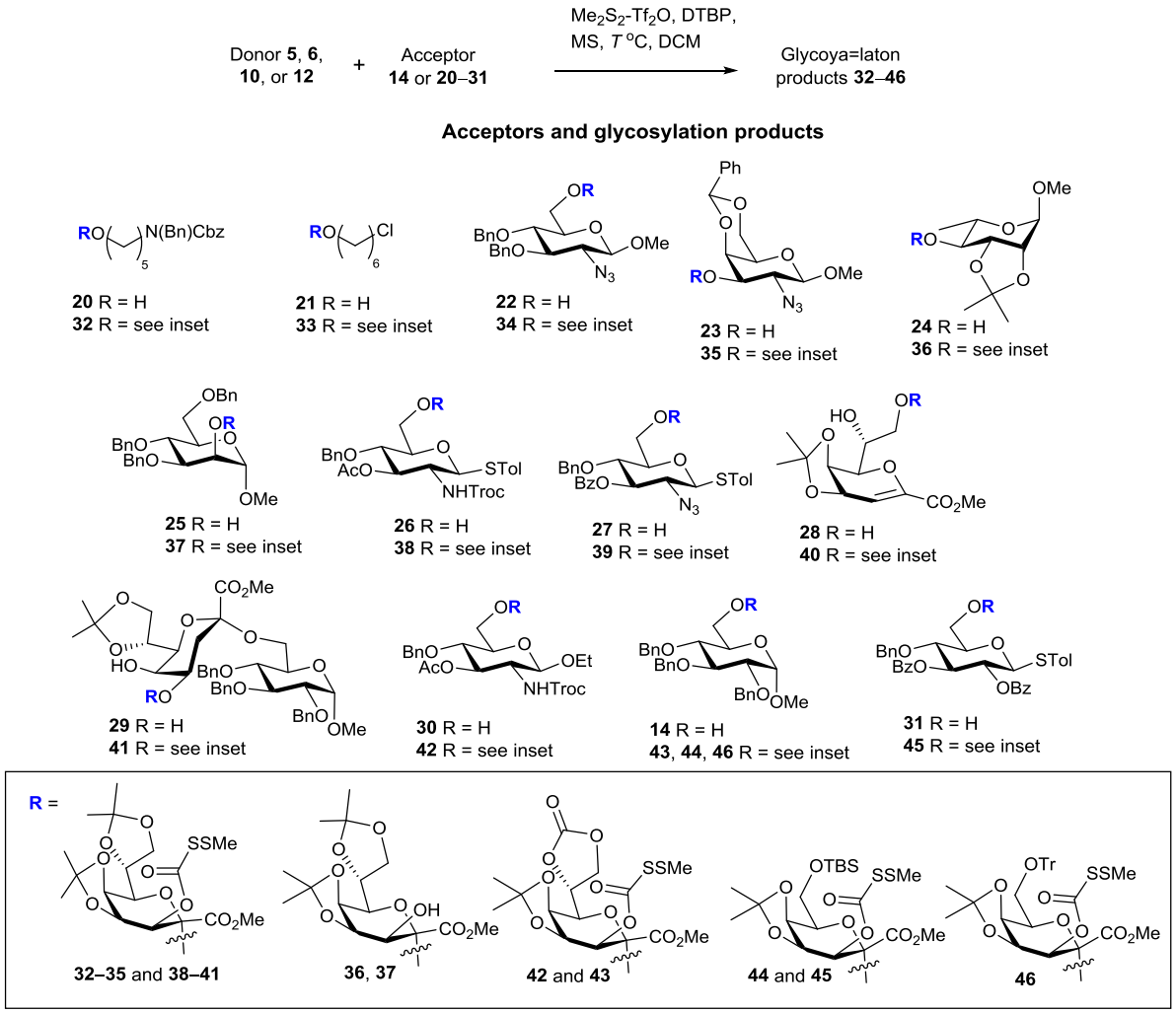
crude residue was purified by flash chromatography over silica gel (Elution: hexanes/EtOAc 1/2, followed by EtOAc/MeOH = 100/3) to afford the deprotected intermediate. To a stirred solution of the crude intermediate (687 mg, 0.98 mmol) and TsOH·H_2O (19 mg, 0.1 mmol) in a mixture of CH_3CN (18 mL) and DMF (2 mL) was added a solution of 2,2-dimethoxypropane (145 uL, 1.18 mmol) in CH_3CN (2 mL) at 0 °C. After addition of the reagents, the reaction mixture was stirred for 20 min at 0 °C and neutralized by Et_3N. The solution was concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 1/1 to 1/3) to afford disaccharide **29** (733 mg, 70% over two steps) as a colorless viscous liquid. For **29**, R_f 0.3 (hexanes/EtOAc 1/2); $[\alpha]_D^{34}$ + 45.0 (*c* 0.75, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39–7.19 (m, 15H), 4.97 (d, *J* = 11.0 Hz, 1H), 4.86 (d, *J* = 11.5 Hz, 1H), 4.78 (d, *J* = 10.5 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 3.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.34–4.30 (m, 1H), 4.08 (dd, *J* = 8.5, 6.5 Hz, 1H), 4.00-3.96 (m, 3H), 3.87 (dd, *J* = 9.0, 5.0 Hz, 1H), 3.80 (dq, *J* = 1.5, 8.5 Hz, 1H), 3.76 (d, *J* = 8.0 Hz, 2H), 3.71 (dd, *J* = 10.5, 1.5 Hz, 1H), 3.69 (s, 3H, C(O)OC*H*$_3$), 3.49 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.40 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.35 (s, 3H, OC*H*$_3$), 3.23 (dd, *J* = 10.0, 9.0 Hz, 1H), 2.15 (dd, *J* = 12.5, 6.0 Hz, 1H, *H*-3'), 1.85 (dd, *J* = 12.5, 10.5 Hz, 1H, *H*-3'), 1.35 (s, 3H, C*H*$_3$), 1.29 (s, 3H, C*H*$_3$).**^{13}C NMR** (125 MHz, $CDCl_3$): δ 168.2 (*C*-1'), 138.6, 138.1, 137.9, 128.4, 128.4, 128.5, 128.0, 127.9, 127.7, 127.7, 127.6, 109.4, 98.6 (*C*-2'), 97.6 (*C*-1), 82.0, 80.0, 78.6, 75.7, 74.8, 73.5, 73.4, 72.7, 69.5, 67.3, 66.7, 65.8, 63.6, 54.8 (OCH_3), 52.5 (C(O)OCH_3), 34.9 (*C*-3'), 26.7 (CH_3), 25.3 (CH_3); **HRMS** (ESI): *m/z* calcd. for $C_{40}H_{50}NaO_{13}^+$ [M + Na]$^+$ 761.3144, found 761.3149.

Preparation of ethyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-*N*-(trichloroethoxycarbonyl)-*β*-D-glucopyranoside (30)



A mixture of thioglycoside donor **S12**[S15] (1.0 g, 1.697 mmol), EtOH (0.497 mL, 8.45 mmol), and activated MS (AW300, 6.0 g) were suspended in DCM (34 mL). The resulting mixture was stirred at room temperature for 10 min and at −20 °C for an additional 20 min under N_2, and followed by the addition of NIS (764 mg, 3.39 mmol) and TMSOTf (0.459 mL, 2.54 mmol). Glycosylation coupling was monitored by TLC with either EtOAc/hexane as the developing solvent. Upon completion of glycosylation, a small volume of saturated $NaHCO_3$ and small lumps of $Na_2S_2O_3$(s) were added to the mixture, followed by vigorous stirring until the deep-red color of the reaction mixture turned to pale yellow. The resulting mixture was dried (over $MgSO_4$), filtered, and concentrated for flash chromatography purification over silica gel (Elution: hexanes/EtOAc 7.5/2.5) to furnish the glycosylation product **S13** (624 mg, 72%) which was taken to the next step. **S13** was converted to acceptor **30** in 75% yield as a colorless glassy solid in accordance with the same procedure as used for **26**. Analytical data for **30**, R_f = 0.3 (hexanes/EtOAc/DCM = 6/3/1); $[\alpha]_D^{22}$ = –16.6 (*c* 1.20, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36–7.22 (m, 5H, Ar*H*), 5.25 (d, *J* = 9.6 Hz, 1H), 5.19 (t, J = 9.4 Hz, 1H), 4.72 (dd, *J* = 16.8, 11.2 Hz, 2H), 4.63 (dd, *J* = 15.2, 11.2 Hz, 2H), 4.47 (d, *J* = 8.0 Hz, 1H), 3.93–3.84 (m, 2H), 3.79-3.60 (m, 3H), 3.54 (m, 1H), 3.42 (ddd, *J* = 9.6, 3.6, 2.8 Hz, 1H), 2.04 (brs, 1H), 1.96 (s, 3H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.9, 154.4, 137.6, 128.5, 128.0, 127.9, 101.2, 95.6, 75.6, 75.2, 74.8, 74.4, 74.3, 65.7, 61.5, 56.4, 20.8, 15.5. **HRMS** (ESI) *m*/*z* calcd. for $C_{20}H_{26}Cl_3NaNO_8^+$ $[M + Na]^+$: 536.0616, found: 536.0626.

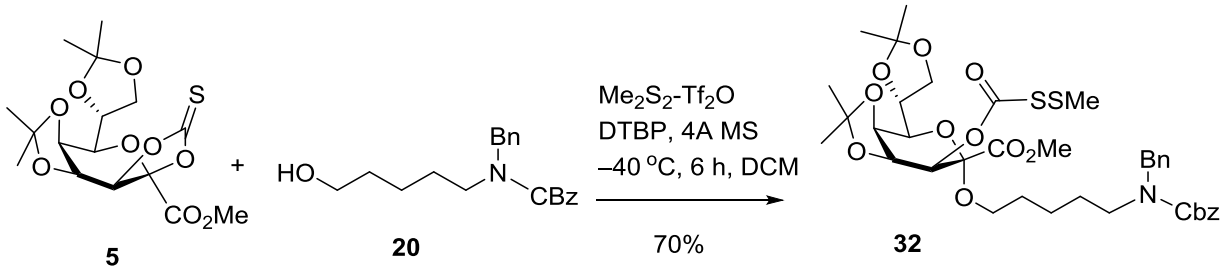
Table S1. Experimental details for glycosylation of acceptors **14**, **20**–**31** with thionocarbonate donors **5**, **6**, **10**, and **12**



Entry	Donor (mg, mmol)	Acceptor (mg, mmol)	1.0 M Me_2S_2-Tf_2O (µL)	*T* °C, h	Product, mg, (%)[a]
1	**5**, 67 (0.171)	**20**, 67 (0.206)	170	-40, 6 h	**32**, 91 mg (70%)
2	**5**, 60 (0.154)	**21**, 41 (0.31)	230	-40, 10 h	**33**, 67 mg (77%)
3	**5**, 91 (0.232)	**22**, 101 (0.255)	240	-60, 2 h	**34**, 157 mg (81%)
4	**5**, 60 (0.153)	**23**, 56 (0.184)	150	-60, 1 h	**35**, 74 mg (65%)
5	**5** (77, 0.197)	**24**, 43 (0.197)	200	-60, 1 h	**36**, 75 mg (70%)[b]
6	**5**, 60 (0.153)	**25**, 85 (0.184)	160	-60, 3 h	**37**, 48 mg (40%)[b]
7	**5**, 75 (0.192)	**26**, 136 (0.273)	210	-70, 2 h	**38,** 102 mg (65%)
8	**5**, 85 (0.217)	**27**, 121 (0.239)	190	-60, 10 h	**39**, 108 mg (60%)
9	**5**, 68 (0.174)	**28**, 50 (0.192)	190	-60, 1 h	**40**, 69 mg (56%)
10	**5**, 53 (0.135)	**29**, 110 (0.149)	140	-60, 8 h	**41**, 95 mg (60%)
11	**6**, 23 (0.061)	**30**, 27 (0.067)	80	-60, 2 h	**42**, 35 mg (62%)
12	**6**, 20 (0.053)	**14**, 27 (0.058)	60	-60, 1 h	**43**, 28 mg (60%)
13	**12**, 500 (1.15)	**14**, 640 (1.38)	1200	-45, 3 h	**44**, 850 mg (78%)
14	**12**, 400 (0.92)	**31**, 650 (1.1)	940	-45, 18 h	**45**, 650 mg (67%)
15	**10**, 1000 (1.77)	**14**, 990 (2.13)	1800	-45, 4 h	**46**, 1420 mg (75%)

[a] isolated yield. [b] Methythiperoxycarbonyl group of the crude product was cleaved to give the deprotected product for NMR characterization (the yield given is based on two steps).

Methyl *N*-Benzyl-*N*-benzyloxycarbonyl-5-aminopentyl-(4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate (32)

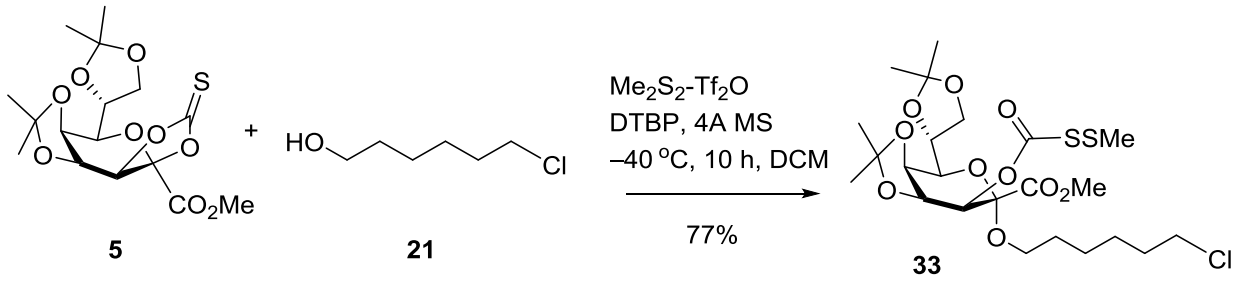


5 + **20** → **32**

Aglycone acceptor **20**[S2] (67 mg, 0.206 mmol) was glycosylated with (2-octulopyranosonyl)onate thionocarbonate **5** (67 mg, 0.171 mmol) using general glycosylation procedure (Table S1, entry 1). 2-Octulopyranosonyl-onate glycoside **32** (94 mg, 70%) was

obtained as a light yellow gummy liquid after column chromatography purification (Elution: 4:2:1 hexanes:DCM:EtOAc). For **32**, R_f = 0.30 (4:2:1 hexanes:DCM:EtOAc), $[\alpha]_D^{19}$ = +27.5 (*c* 1.6, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.42-7.10 (m, 10H), 5.36 (d, *J* = 4.8 Hz, 1H), 5.17 (d, *J* = 12.4 Hz, 2H), 4.55-4.44 (m, 4H), 4.27 (brs, 1H), 4.12 (d, *J* = 5.2 Hz, 2H), 3.80 (m, 1H), 3.74 (s, 1H, OC*H*$_3$), 3.47 (brs, 1H), 3.30-3.10 (m, 3H), 2.45 (s, 3H, SSC*H*$_3$), 1.75 (brs, 1H), 2.84-1.50 (m, 3H), 1.50-1.47 (m, 5H), 1.43 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 1.25 (s, 3H, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): *δ* = 168.8 (*C*(=O)SSMe), 166.2 (C-1), 156.2 (carbamate *C*=O), 137.8, 136.7, 128.5, 128.4, 127.9, 127.8, 127.3, 127.2, 110.2, 109.3, 98.8 (C-2), 74.2, 71.2, 70.1, 69.8, 69.1, 67.2, 66.4, 64.0, 52.6, 50.5, 50.2, 46.9, 46.0, 28.9, 26.9, 25.9, 25.5, 25.3, 23.3, 22.9; **HRMS** (ESI) *m*/*z* calcd. for $C_{37}H_{49}NNaO_{12}S_2^+$ $[M + Na]^+$: 786.2588, found: 786.2573.

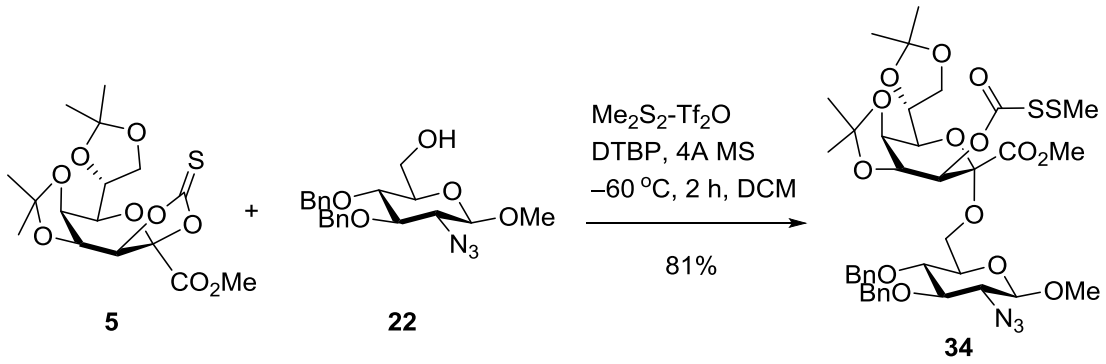
Methyl 6-chlorohexyl-(4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate (33)



Acceptor **21** (41 mg, 0.31 mmol) was glycosylated with (2-octulopyranosonyl)onate thionocarbonate **5** (60 mg, 0.154 mmol) using the general glycosylation procedure (Table S1, entry 2). 2-Octulopyranosonylonate glycoside **33** (68 mg, 77%) was obtained as a viscous colorless liquid after chromatography purification (Elution: hexanes/EtOAc = 5:1). For **33**, R_f = 0.30 (hexanes/EtOAc = 5:1), $[\alpha]_D^{19}$ = +30.6 (*c* 2.6, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): *δ* = 5.38 (d, *J* = 5.2 Hz 1H), 4.57 – 4.53 (m, 2H), 4.31 (dd, *J* = 5.8, 2.8 Hz, 1H), 4.14 (d, *J* = 5.2 Hz, 2H), 3.83 (dd, *J* = 7.0, 2.3 Hz, 1H), 3.77 (s, 3H), 3.53 (t, *J* = 6.4 Hz, 3H), 3.25 (dd, *J* = 15.3, 6.4 Hz, 1H), 2.47 (s, 3H), 1.80 – 1.73 (m, 3H), 1.59 – 1.54 (m, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.42 – 1.41 (m, 2H), 1.39 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* = 168.7 (C(=O)SSMe), 166.1

(carbamate C=O), 110.2, 109.3, 98.9 , 77.3 , 77.0 , 76.7, 74.1, 69.1, 66.4, 63.9, 52.6, 44.9, 32.4, 25.9, 25.3, 22.9; **HRMS** (ESI) *m*/*z* calcd. for $C_{23}H_{37}ClNaO_{10}S^+$ $[M + Na]^+$: 595.1414, found: 595.1424.

Methyl 2-Azido-3,4-di-*O*-benzyl-2-deoxy-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-glucopyranoside (34)

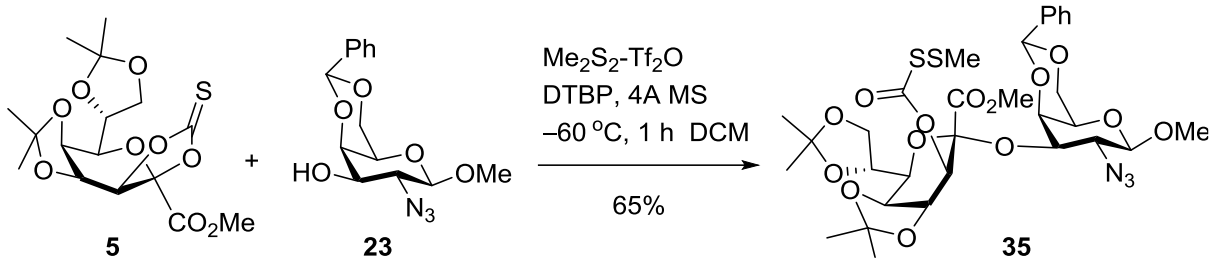


5 **22** **34**

Known 2-azido-glucosamine acceptor **22**[S1] (101 mg, 0.255 mmol) was coupled with oct-2-ulopyranosonyl thionocarbonate **5** (91 mg, 0.232 mmol) using general glycosylation procedure (Table S1, entry 3). Disaccharide **34** (157 mg, 81%) was obtained as a colorless foamy substance after chromatography purification (Elution: hexanes/EtOAc 9:1 to 6:1). For **34**, R_f 0.26 (hexanes/EtOAc/DCM = 3/1/1); $[\alpha]_D^{34}$ +23.7 (*c* 1.84, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.38–7.27 (m, 8H, Ar*H*), 7.22 (d, *J* = 7.2 Hz, 2 H, Ar*H*), 5.37 (d, *J* = 5.4 Hz, 1H, *H*-3′), 4.90 (d, *J* = 10.8 Hz, 1H, H-8a′), 4.83 (d, *J* = 10.8 Hz, 1H, H-6′), 4.78 (d, *J* = 10.8 Hz, 1H, H-8b′), 4.51 (d, *J* = 10.8 Hz, 1H, H-5′), 4.47 (q, *J* = 6.0 Hz, 1H, H-3), 4.42 (t, *J* = 6.0 Hz, 1H, H-4′), 4.21 (dd, *J* = 6.0, 3.0 Hz, 1H, H-2), 4.13 (d, *J* = 8.4 Hz, 2H, including H-1), 4.07 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.89 (dd, *J* = 7.8, 3.0 Hz, 1H, H-4), 3.68 (s, 3H, OCH_3), 3.65 (d, *J* = 10.8 Hz, 1H), 3.54 (dd, *J* = 11.4, 7.2 Hz, 1H), 3.51 (s, 3H, OCH_3), 3.45–3.40 (m, 2H), 3.38-3.31 (m, 2H), 2.46 (s, 3H, SSCH_3), 1.48 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.33 (s, 3H, CH_3). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 168.8 (*C*(=O)SSMe), 165.5 (*C*(=O)OMe), 137.7, 137.5, 128.5, 128.5, 128.0, 127.9,

127.9, 127.8, 110.3, 109.5, 102.7 (C-1, $^2J_{C\text{-}H}$ = 159 Hz), 98.6 (C-2′), 83.1, 78.0, 75.5, 75.0, 73.9, 73.7, 70.7, 69.9, 69.8, 69.5, 66.6, 66.2, 63.3, 56.9 (O*C*H$_3$), 52.6 (O*C*H$_3$), 26.7(*C*H$_3$), 25.9(*C*H$_3$), 25.6(*C*H$_3$), 25.3 (*C*H$_3$), 22.9 (SS*C*H$_3$); **HRMS** (ESI): *m/z* calcd. for $C_{38}H_{49}N_3NaO_{14}S_2^+$ $[M + Na]^+$ 858.2548, found 858.2577.

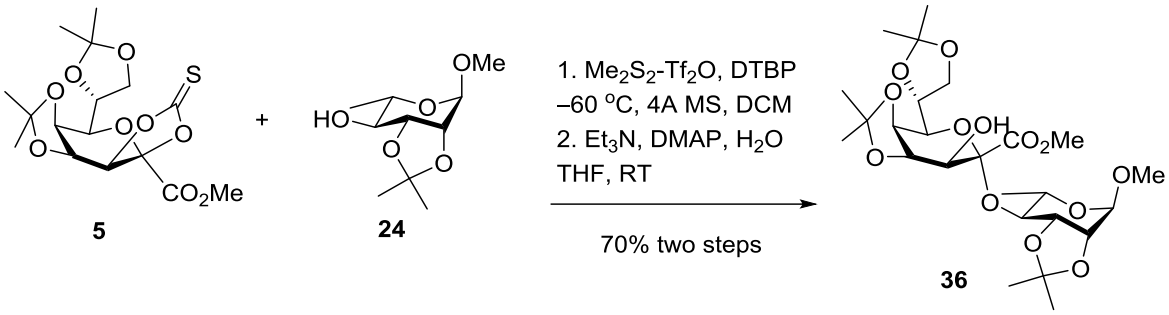
Methyl 2-Azido-2-deoxy-4,6-*O*-benzylidene-3-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-galactopyranoside (35)



Known 2-azido-2-deoxygalactosyl acceptor **23**[S3] (56 mg, 0.184 mmol) was glycosylated with oct-2-ulopyranosonyl thionocarbonate **5** (60 mg, 0.153 mmol) using the general glycosylation procedure (Table S1, entry 4). Disaccharide **35** (74 mg, 65%) was obtained as a light yellow oily liquid after chromatography purification (Elution: 40% EtOAc in hexanes). For **35**, R_f = 0.3 (40% EtOAc/hexanes), $[\alpha]_D^{23}$ = + 65.36 (*c* 2.05, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.54-7.47 (m, 2H), 7.41-7.32 (m, 3H), 5.53 (d, *J* = 4.8 Hz, 1H, H-3′), 5.39 (s, 1H, PhC*H*), 4.61 (dd, *J* = 6.4, 5.2 Hz, 1H, H-4′), 4.52 (dt, *J* = 4.4, 6.4 Hz, 1H, H-6′), 4.48 (dd, *J* = 6.8, 2.8 Hz, 1H), 4.35 (dd, *J* = 6.4, 2.8 Hz, 1H, H-5′), 4.31 (dd, *J* = 12.4, 1.6 Hz, 1H, H-3), 4.29 (dd, *J* = 9.2, 4.4 Hz, 1H, H-7a′), 4.21 (d, *J* = 7.6 Hz, 1H, H-1), 4.14 (dd, *J* = 9.2, 6.0 Hz, 1H, H-7b′), 4.00 (dd, *J* = 12.4, 1.6 Hz, 1H), 3.97 (d, *J* = 3.2 Hz, 1H), 3.79 (dd, *J* = 10.4, 7.6 Hz, 1H, H-2), 3.73 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.63 (s, 3H), 3.57 (s, 3H), 3.31 (brs, 1H), 2.42 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H), 1.36 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.7 (*C*(=O)SSMe), 167.2 (C-1′), 137.2, 129.0, 128.2, 126.0, 110.3, 109.4, 103.2 (C-1), 100.8 (Ph*C*H), 96.5 (C-2′), 74.5 (C-6′), 71.9, 71.8, 71.0 (C-6′), 69.75 (C-4′), 69.71 (C-5′), 69.3, 69.0, 66.12, 66.09 (C-7′), 61.1 (C-2), 57.0, 52.7, 26.8, 25.8,

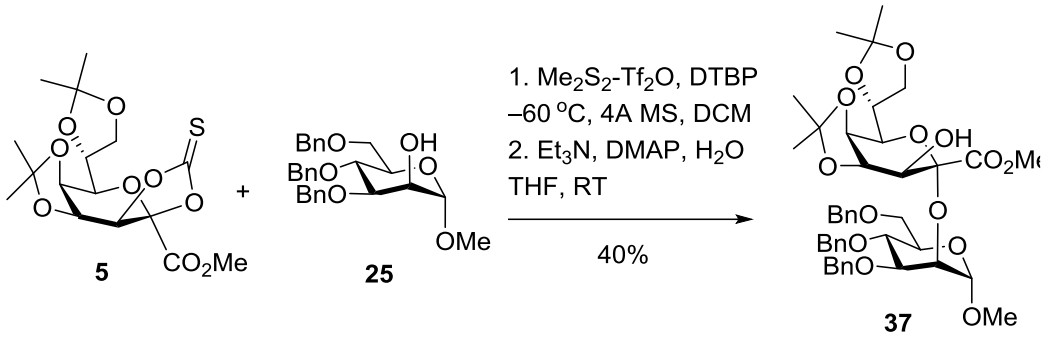
25.7, 25.2, 22.9; **HRMS** (ESI) *m*/*z* calcd. for $C_{31}H_{41}N_3NaO_{14}S_3^+$ [M + Na]$^+$: 766.1922, found: 766.1927.

Methyl 2,3-*O*-Isopropylidene-4-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-rhamnopyranoside (36)



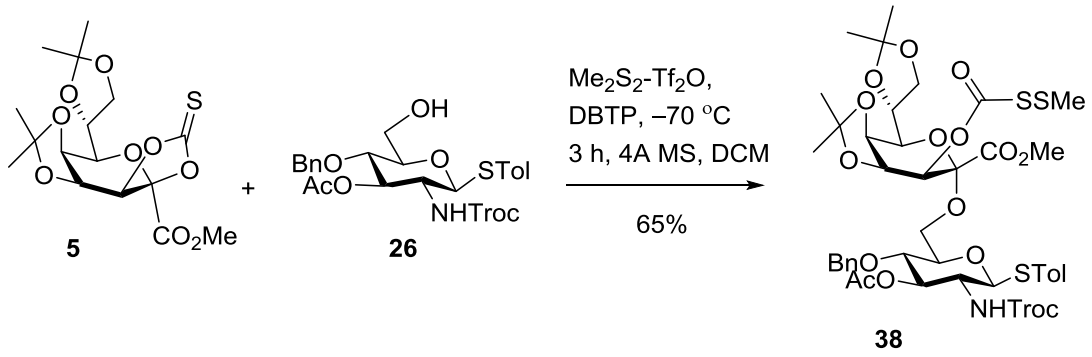
L-Rhamnose acceptor **24**[S4] (43 mg, 0.197 mmol) was coupled with oct-2-ulopyranosonyl thionocarbonate **5** (77 mg, 0.197 mmol) using the general glycosylation procedure (Table S1, entry 5). The crude product was subjected to the general deprotection procedure for the methylperoxycarbonyl protecting group. Disaccharide **36** (75 mg, 70%) was obtained as a light yellow gummy liquid after chromatography purification (Elution: hexanes/DCM/EtOAc 6:5:2). For **36**, R_f 0.2 (6:5:2 Hexanes/DCM/EtOAc), $[\alpha]_D^{19}$ + 28.5 (*c* 0.35, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.80 (s, 1H), 4.50 (dd, *J* = 7.2, 3.2 Hz, 1H), 4.42 (m, 3H), 4.16 (t, *J* = 6.0 Hz, 1H), 4.11-4.07 (m, 3H), 3.89 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.78 (s, 3H, OC*H*$_3$), 3.72 (d, *J* = 9.2 Hz, 1H), 3.63 (m, 1H), 3.37-3.31 (m, 4H), 1.47 (s, 6H, 2 x C*H*$_3$), 1.41 (s, 3H, C*H*$_3$), 1.36 (s, 6H, 2 x C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.25 (d, *J* = 6.4 Hz, 3H, rhaC*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.4 (C-1′), 109.7, 109.2, 109.1, 98.9 (C-2′), 98.0 (C-1′), 78.5, 76.8, 75.5, 73.9, 73.1, 72.4, 71.2, 70.2, 66.7, 64.2, 54.8 (O*C*H$_3$), 52.4 (CO_2*C*H$_3$), 27.8 (*C*H$_3$), 27.1 (*C*H$_3$), 26.0 (*C*H$_3$), 25.4 (*C*H$_3$), 25.0 (*C*H$_3$), 24.8 (*C*H$_3$), 17.8 (*C*H$_3$). HRMS (ESI) *m*/*z* calcd. for $C_{25}H_{40}NaO_{13}^+$ [M + Na]$^+$: 571.2361, found: 571.2365.

Methyl 3,4,6-Tri-*O*-benzyl-2-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-α-D-mannopyranoside (37)



Known mannoside acceptor **25**[S5] (85 mg, 0.184 mmol) was coupled with 2-octulopyranosonyl)onate thionocarbonate **5** (60 mg, 0.153 mmol) using general glycosylation procedure to give a disaccharide product, which was subjected to deprotection of *S*-methylperoxycarbonyl group to give disaccharide **37** as a yellow oily liquid (48 mg, 40% over two steps) after chromatography purification (Elution: 5:4:1 hexanes/DCM/EtOAc) (Table S1, entry 6). For **37**, R_f = 0.1 (5:4:1 hexanes/DCM/EtOAc), $[\alpha]_D^{22}$ = +40.0 (*c* = 0.65, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40-7.22 (m, 13H), 7.16-7.11 (m, 2H), 4.93 (d, *J* = 2.0 Hz, 1H, H-1), 4.80 (d, *J* = 10.8 Hz, 1H), 4.68 (d, *J* = 11.6 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.54 (d, *J* = 11.2 Hz, 1H), 4.51-4.44 (m, 3H), 4.34 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.21 (dd, *J* = 6.8, 2.4 Hz, 1H), 4.17-4.14 (m, 2H), 4.12 (d, *J* = 6.0 Hz, 1H), 4.10-4.07 (m, 2H), 4.05 (t, *J* = 2.8 Hz, 1H, H-2), 3.94 (d, *J* = 9.6 Hz, 1H), 3.88 (dd, *J* = 9.2, 2.8 Hz, 1H), 3.78 (dd, *J* = 10.8, 4.4 Hz, 1H), 3.72-3.66 (m, 2H), 3.64 (s, 3H), 3.57 (d, *J* = 8.8 Hz, 1H), 3.34 (s, 3H), 1.45 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.8 (*C*(=O)SSMe), 138.4, 138.4, 138.3, 128.3, 128.3, 128.3, 127.9, 127.6, 127.5, 127.5, 127.4, 109.7, 109.0, 99.6 (C-2′), 99.2 (C-1), 78.2, 74.9, 74.5, 74.4, 73.2, 72.8, 72.4, 72.0, 71.8, 71.6, 70.1, 69.5, 69.1, 66.1, 54.8, 52.5, 26.5, 25.8, 25.2, 25.1; HRMS (ESI) *m*/*z* calcd. for $C_{43}H_{54}NaO_{14}^+$ $[M + Na]^+$: 817.3406, found: 817.3383.

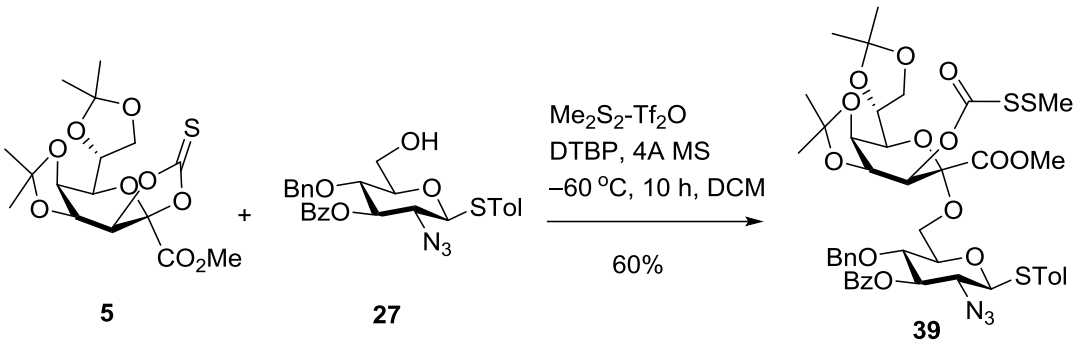
***p*-Tolyl 3-*O*-Acetyl-4-*O*-benzyl-2-deoxy-2-*N*-trichloroethoxycarbonyl-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl) onate]-*β*-D-thioglucopyranoside (38)**



N-Troc protected acceptor **26** (136 mg, 0.273 mmol) was coupled with 2-octulopyranosoyl thionocarbonate **5** (75 mg, 0.192 mmol) using the general glycosylation procedure (Table S1, entry 7). Disaccharide **38** (128 mg, 65%) was obtained as a colorless glassy solid after chromatography purification (Elution: hexanes/DCM/EtOAc 5:3:2). For **38**, R_f = 0.40 (hexanes:DCM:EtOAc = 5:3:2), $[\alpha]_D^{19}$ = +36.19 (*c* 1.05, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.37-7.26 (m, 5H, Ar*H*), 7.23-7.19 (m, 2H, Ar*H*), 7.15-7.10 (m, 2H, Ar*H*), 5.37 (d, *J* = 5.6 Hz, 1H, H-3′), 5.28 (b, 1H, NH), 5.17 (dd, *J* = 10.4, 9.2 Hz, 1H, H-3), 4.81 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 11.2 Hz, 1H, H-1), 4.69 (d, *J* = 12.4 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.49 (d, *J* = 11.2 Hz, 1H), 4.43 (dd, *J* = 12.4, 5.6 Hz, 1H, H-7′), 4.36 (t, *J* = 6.0 Hz, 1H, H-4′), 4.12 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.07 (dd, *J* = 8.8, 5.2 Hz, 1H), 4.04 (dd, *J* = 6.0, 3.2 Hz, 1H, H-5′), 3.92 (dd, *J* = 7.2, 3.2 Hz, 1H, H-6′), 3.75 (dd, *J* = 10.0 Hz, 1H, H-2), 3.68 (s, 3H, COOCH_3), 3.61-3.52 (m, 3H), 3.47 (dd, *J* = 9.2 Hz, 1H), H-4 2.46 (s, 3H, SSCH_3), 2.31 (s, 3H, STolCH_3), 1.98 (s, 3H, COCH_3), 1.46 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.28 (s, 3H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.7 (*C*=O), 168.8 (*C*=O), 165.6 (*C*=O), 154.2 (carbamate *C*=O), 137.7, 137.1, 130.6, 130.0, 129.7, 128.6, 128.2, 127.7, 110.1 (*C*$(CH_3)_2$), 109.4 (*C*$(CH_3)_2$), 98.7 (C-2′), 95.4 (*C*Cl_3), 87.3 (C-1), 76.7, 76.4 (C-4), 75.7 (C-3), 74.7, 74.5, 74.1 (C-7′), 70.6 (C-3′), 69.8, 69.6 (C-5′), 69.2 (C-6’), 66.5, 63.6, 55.3 (C-

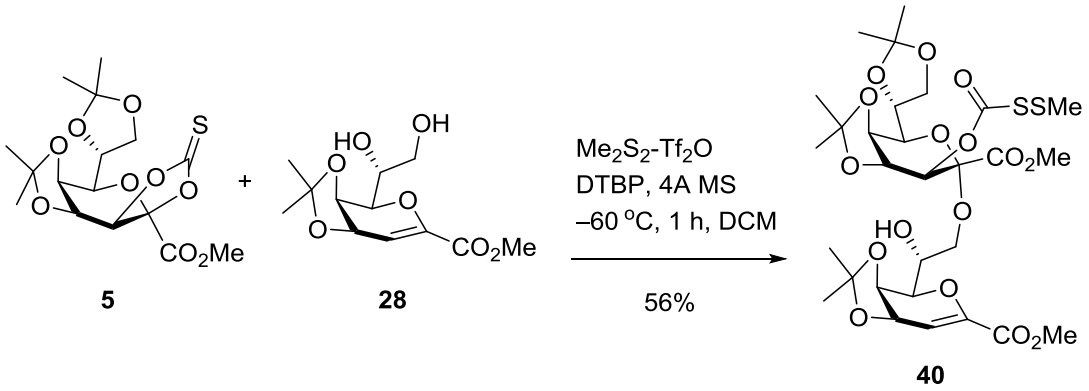
2), 52.8, 26.9, 25.9, 25.7, 25.3, 22.9 (SS*C*H$_3$), 21.1, 20.8 (CO*C*H$_3$); **HRMS** (ESI) *m*/*z* calcd. for $C_{42}H_{52}Cl_3NNaO_{16}S_3$ $[M + Na]^+$: 1050.1406, found: 1050.1416.

***p*-Tolyl 2-Azido-3-benzoyl-4-*O*-benzyl-2-deoxy-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-thioglucopyranoside (39)**



Known 2-azido-thioglucoaminyl acceptor **27**[S6] (121 mg, 0.24 mmol) was coupled with oct-2-ulopyranosonyl thionocarboncate donor **5** (85 mg, 0.22 mmol) using general glycosylation procedure (Table S1, entry 8). The disaccharide **39** (127 mg, 60%) was obtained as a viscous oily liquid after chromatography purification (Elution: 4:1:1 hexanes:DCM:EtOAc). For **39**, R_f = 0.40 (20% EtOAc in hexanes), $[\alpha]_D^{23}$ = +40.0 (*c* 0.3, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.09-8.05 (m, 2H), 7.60 (m, 1H), 7.51-7.39 (m, 4H), 7.21-7.16 (m, 5H), 7.08-7.04 (m, 2H), 5.42 (t, *J* = 9.2 Hz, 1H, H-3), 5.41 (d, *J* = 5.6 Hz, 1H, H-3′), 4.61 (d, *J* = 10.4 Hz, 1H, H-1, HSQC), 4.52 (d, *J* = 10.8 Hz, 1H), 4.46 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.41 (t, *J* = 6.0 Hz, 1H, H-4′, COSY), 4.39 (d, *J* = 10.8 Hz, 1H), 4.17-4.08 (m, 3H), 3.96 (s, 3H), 3.63-3.58 (m, 3H), 3.52 (t, *J* = 9.6 Hz, 1H, H-4), 3.48 (t, *J* = 10.0 Hz, 1H, H-2), 2.46 (s, 3H), 2.36 (s, 3H), 1.48 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.8 (C(=O)SSMe), 165.5, 165.3, 138.4, 136.7, 133.6, 132.1, 129.9, 129.8, 129.2, 128.6, 128.5, 128.4, 128.1, 127.9, 110.1, 109.4, 98.7 (C-2′, HSQC), 86.5 (C-1, HSQC), 77.7, 76.5 (C-3), 76.2, 74.7 (C-7′), 74.2, 70.6 (C-3′), 69.8, 69.6, 69.3, 66.5, 63.6, 63.5, 52.8, 26.8, 25.9, 25.7, 25.3, 22.9, 21.2; **HRMS** (ESI) *m*/*z* calcd. for $C_{44}H_{51}N_3NaO_{14}S_3^+$ $[M + Na]^+$: 964.2425, found: 964.2422.

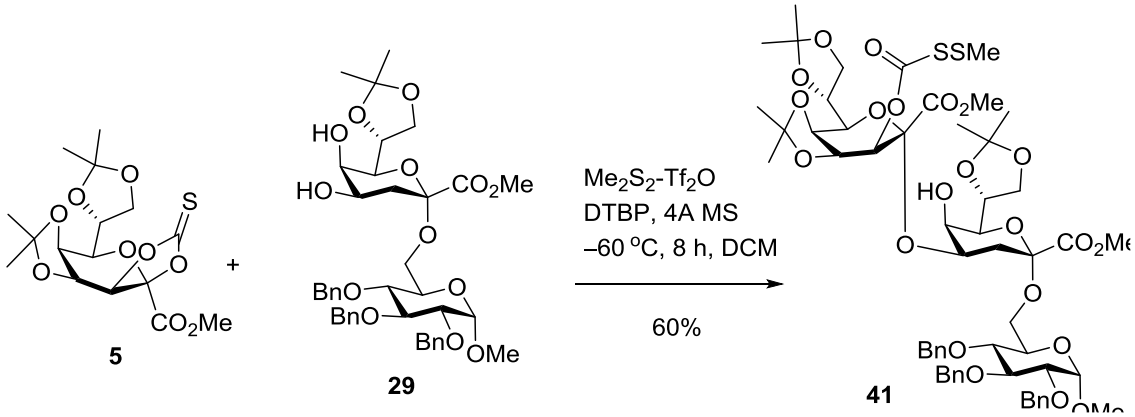
Methyl {2,6-Anhydro-3-deoxy-4,5-*O*-isopropylidene-8-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosyl)-onate]-D-*manno*-2-octulopyranosonyl}onate (40)



5 **28** **40**

Known Kdo glycal acceptor **28**[S7] (50 mg, 0.192 mmol) with oct-2-ulopyranosonyl thionocarbonate **5** (68 mg, 0.174 mmol) using general glycosylation procedure (Table S1, entry 9). Disaccharide **40** (69 mg, 56%) was obtained as a yellowish gummy liquid by column chromatography (Elution: hexanes/EtOAc 2:1 to 1:1.5). For **40**, R_f = 0.14 (hexanes/EtOAc = 1/1); $[\alpha]_D^{19}$= +43.75 (*c* 1.6, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ = 5.98 (d, *J* = 2.4 Hz, H-3), 5.33 (d, *J* = 4.2 Hz, 1H, H-3′), 4.80 (dd, *J* = 6.0, 3.6 Hz, 1H, H-4′), 4.58-4.54 (m, 2H), 4.45 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.38 (dd, *J* = 7.2, 2.4 Hz, 1H, H-5′), 4.16-4.09 (m, 3H), 3.98-3.95 (m, 2H), 3.93 (dd, *J* = 10.2, 4.8 Hz, 1H, H-4), 3.81 (s, 3H, OC*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 3.61 (dd, *J* = 10.2, 3.0 Hz, 1H), 2.49 (s, 3H, SSC*H*$_3$), 1.52 (s, 3H, C*H*$_3$), 1.44, (s, 3H, C*H*3), 1.38 (s, 9H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$). **^{13}C NMR** (150 MHz, $CDCl_3$) δ = 170.1 (*C*(=O)SSMe), 166.9 (C-1), 162.5 (C-1′), 145.3 (C-2), 111.6, 109.8, 109.4 (C-3, HMQC, DEPT), 109.3, 100.2 (C-2′), 77.9, 75.0, 74.3 (C-3′), 73.6, 72.5 (C-5′), 71.6 (C-4′), 70.6, 68.2, 67.2, 66.0, 62.0 (C-4), 53.6 (O*C*H$_3$), 52.7 (O*C*H$_3$), 27.3 (*C*H$_3$), 26.8 (*C*H$_3$), 26.0 (*C*H$_3$), 25.8 (*C*H$_3$), 25.5 (*C*H$_3$), 23.4 (SS*C*H$_3$); **HRMS** (ESI): *m/z* calcd. for $C_{29}H_{42}N_3NaO_{16}S_2^+$ $[M + Na]^+$ 733.1812, found 733.1827.

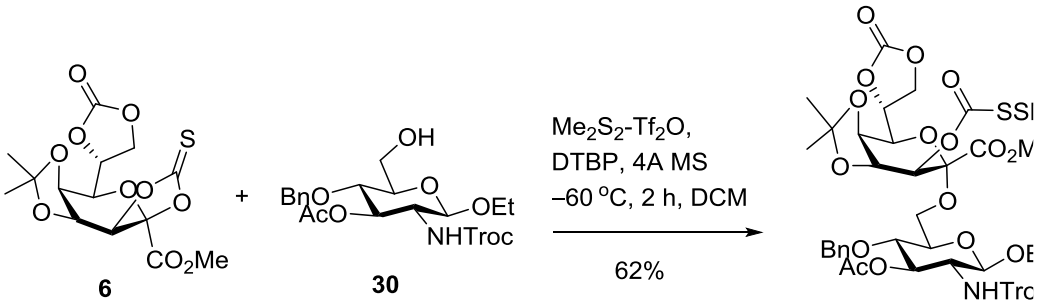
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (7,8-*O*-isopropylidene-3-deoxy-α-D-*manno*-2-octulopyranosyl)onate]-4-*O*-{4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methyldisulfanyl-carbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (41)



Disaccharide acceptor **29** (110 mg, 0.149 mmol) was coupled with 2-octulopyranosonyl thionocarbonate **5** (53 mg, 0.135 mmol) using general glycosylation procedure (Table S1, entry 10). Trisaccharide **41** (95 mg, 60%) was obtained as a white amorphous substance after chromatography purification (Elution: hexanes/EtOAc = 1:1). For **41**, R_f = 0.30 (EtOAc/hexanes = 7:3), $[\alpha]_D^{19}$ = +42.3 (*c* 0.85, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.20 (m, 15H), 5.34 (d, *J* = 4.4 Hz, 1H, H-3″), 4.96 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.54-4.50 (m, 2H), 4.48 (d, *J* = 10.8 Hz, 1H), 4.39 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.35-4.30 (m, 2H), 4.12-4.02 (m, 4H), 3.97 (m, 1H), 3.93-3.87 (m, 2H), 3.81-3.62 (m, 11H), 3.48 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40 (dd, *J* = 10.4, 8.8 Hz, 1H), 3.34 (s, 3H), 3.19 (dd, *J* = 10.0, 8.8 Hz, 1H), 2.48 (s, 3H), 2.27 (brs, 1H), 2.25 (dd, *J* = 12.5, 5.2 Hz, 1H, , H-3eq′), 2.09 (t, *J* = 12.5 Hz, 1H, H-3ax′), 1.47 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.33 (s, 6H), 1.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.4 (*C*(=O)SSMe), 167.7 (*C*(=O)OMe, C-1′), 166.2 (*C*(=O)OMe, C-1″ from HMBC), 138.6, 138.1, 137.9, 128.4, 128.4, 128.4, 128.0, 127.8, 127.8, 127.7, 127.6, 110.8, 109.2, 108.9, 98.8 (C-2″), 98.4 (C-2′), 97.6 (C-1), 81.9, 80.1, 78.6, 75.6, 74.9, 74.2, 73.3, 73.3, 73.0 (C-3″), 72.2, 71.2, 70.6, 70.1, 69.9, 69.6, 67.1,

66.1, 64.7, 63.5, 55.0, 52.6, 52.4, 33.0 (C-3′), 26.8, 26.6, 25.6, 25.5, 25.4, 25.1, 22.9. **HRMS** (ESI) *m*/*z* calcd. for $C_{57}H_{74}NaO_{22}S_2^+$ $[M + Na]^+$: 1197.4005, found: 1197.4047.

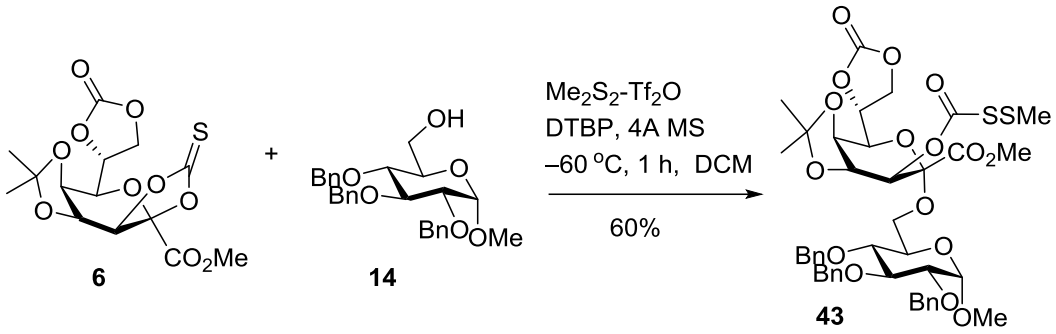
Ethyl {3-*O*-Acetyl-4-*O*-benzyl-2-*N*-(trichloroethoxycarbonyl)-2-deoxy-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)-onate]-*β*-D-glucopyranoside (42)



N-Troc protected glucosaminyl acceptor **30** (27 mg, 0.067 mmol) was glycosylated with (2-octulopyranosyl)onate **6** (23 mg, 0.061 mmol) using general glycosylation procedure as described above (Table S1, entry 11). Disaccharide **42** (35 mg, 62%) was obtained as a colorless sticky liquid after chromatography purification (Elution: 4:3:2 hexanes/EtOAc/DCM). For **42**, R_f = 0.25 (hexanes/EtOAc = 3/2); $[\alpha]_D^{19}$ = +20.0 (*c* 0.9, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.38-7.28 (m, 3H, Ar*H*), 7.25-7.21 (m, 2H, Ar*H*), 5.43 (d, *J* = 5.5 Hz, 1H, H-3′), 5.18 (t, *J* = 10.0 Hz, 1H, H-3), 5.10 (d, *J* = 9.0 Hz, 1H, NH), 4.97 (ddd, *J* = 8.5, 7.0, 3.0 Hz, 1H), 4.78 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 11.5 Hz, 1H), 4.54-4.49 (m, 2H), 4.47 (t, *J* = 6.0 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H, H-1), 4.35 (t, *J* = 3.0 Hz, 1H, H-6′), 4.09 (dd, *J* = 6.0, 4.0 Hz, 1H, H-5′), 3.81 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.70 (dd, *J* = 11.0, 2.0 Hz, 1H), 3.68 (s, 3H), 3.61 (dd, *J* = 11.0, 7.0 Hz, 2H), 3.55 (m, 2H), 3.50 (dd, *J* = 17.0, 8.5 Hz, 1H), 2.47 (s, 3H), 2.01 (s, 3H), 1.44 (s, 3H), 1.27 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ =168.5 (*C*(=O)SSMe), 164.9 (C-1′), 154.6 (carbamate *C*=O), 137.3, 128.6, 128.1, 127.6, 110.5, 101.0 (C-1), 98.5 (C-2′), 75.2, 74.7, 74.5, 74.3 (C-3), 73.5, 69.9 (C-3′ and C-4′), 69.0 (C-5′), 68.3

(C-6′), 65.7, 65.5 (C-4), 64.1 (C-2), 56.2, 52.8, 25.7, 25.1, 23.0, 20.8, 15.1. **HRMS** (ESI) *m*/*z* calcd. for $C_{35}H_{44}Cl_3NaNO_{18}S_2^+$ $[M + Na]^+$: 960.0928, found: 960.0972.

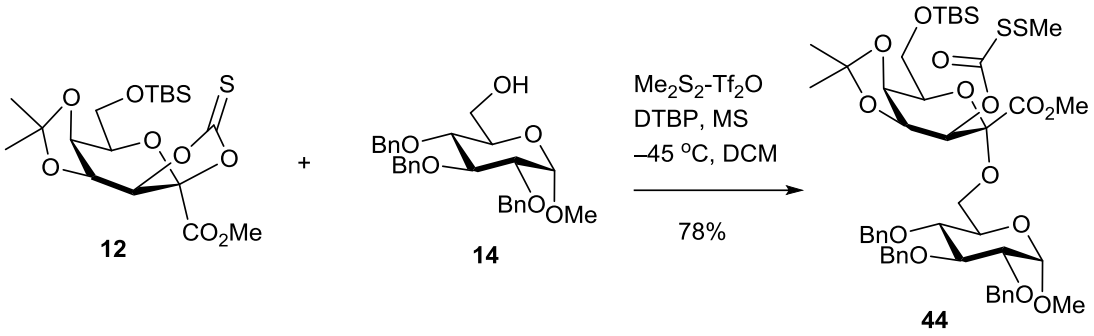
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)-onate]-*α*-D-glucopyranoside (43)



Glucoside acceptor **14** (27 mg, 0.058 mmol) was coupled with (2-octulopyranosonyl)onate thionocarbonate **6** (20 mg, 0.053 mmol) according to the general glycosylation procedure (Table S1, entry 12). Disaccharide **43** (28 mg, 60%) was obtained as a white amorphous substance after chromatography purification (Elution: 3:2 hexanes/EtOAc). For **43**, R_f = 0.3 (hexanes/EtOAc = 3/2); $[\alpha]_D^{19}$ = +93.0 (*c* 0.15, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.39-7.23 (m, 13H, Ar*H*), 7.22-7.21 (m, 2H, Ar*H*), 5.41 (d, *J* = 5.2 Hz, 1H, H-3′), 4.98 (d, *J* = 10.8 Hz, 1H), 4.94-4.87 (m, 2H), 4.79 (m, 1H), 4.76 (d, *J* = 3.2 Hz, 1H), 4.71 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 3.6 Hz, 1H, C1-*H*), 4.49 (dd, *J* = 8.4, 6.8 Hz, 1H), 4.46-4.43 (m, 2H), 4.35 (t, *J* = 4.0 Hz, 1H), 4.10 (dd, *J* = 6.4, 4.0 Hz, 1H), 3.97 (t, *J* = 9.2 Hz, 1H), 3.77 (m, 1H), 3.63 (s, 3H, COOCH_3), 3.59 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.50 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.33 (s, 3H, OCH_3), 3.25 (dd, *J* = 10.0, 8.8 Hz, 1H), 2.45 (s, 3H, SSCH_3), 1.43 (s, 3H, CH_3), 1.28 (s, 3H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.4 (*C*(=O)SSMe), 165.1 (*C*(=O)OMe, C-1′), 154.7 (carbonate *C*=O), 138.5, 137.9, 128.5, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.6, 127.6, 110.4 (*C*$(CH_3)_2$), 98.5 (C-2′), 97.8 (C-1), 81.9, 79.8, 78.0, 77.2, 75.7, 74.9, 74.8, 73.4, 69.9, 69.9, 69.3, 68.9, 67.9,

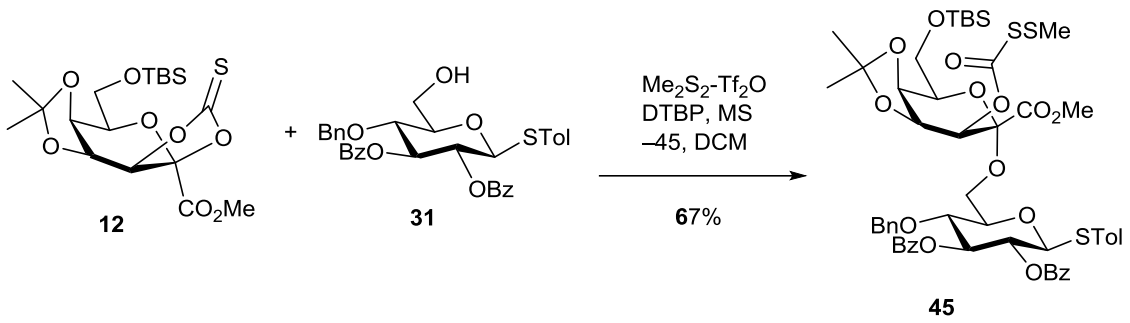
65.9, 64.5, 54.9 (O*C*H$_3$), 52.8 (COO*C*H$_3$), 25.8 (*C*H$_3$), 25.2 (*C*H$_3$), 22.9 (SS*C*H$_3$); **HRMS** (ESI) *m*/*z* calcd. for $C_{43}H_{50}NaO_{16}S_2^+$ $[M + Na]^+$: 909.2432, found: 909.2455.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-7-*O*-*t*butyldimethylsilyl-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (44)



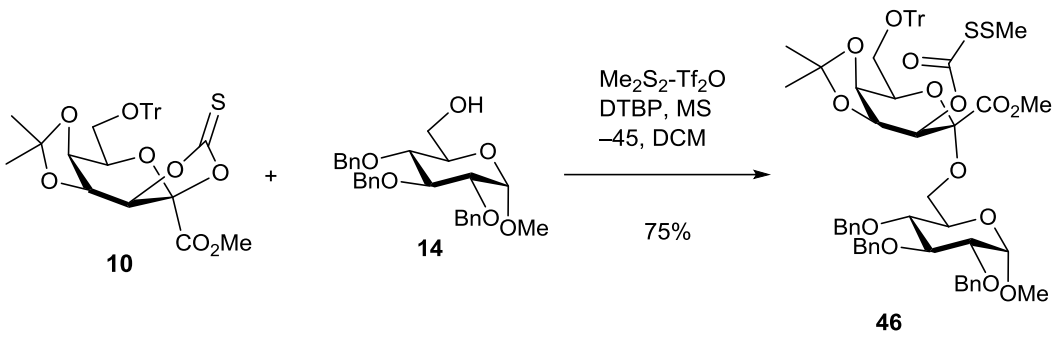
Thionocarbonate donor **12** (0.5 g, 1.15 mmol) was coupled with glucoside acceptor **14** (0.64 g, 1.38 mmol)[S1] using the general glycosylation procedure (Table S1, entry 13). Disaccharide **44** (0.85 g, 78%) was obtained as a colorless glassy solid by column chromatography (Elution hexanes/EtOAc, 5:1). Data for **44**: R_f = 0.42 (hexanes/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.21 (m, 15H, Ar*H*), 5.37 (d, *J* = 5.5 Hz, 1H), 4.98 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 11.1 Hz, 1H), 4.79 (d, *J* = 11.7 Hz, 2H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.51 (d, *J* = 3.5 Hz, 1H), 4.47 (d, *J* = 11.1 Hz, 1H), 4.41 (t, *J* = 5.8 Hz, 1H), 4.16 (dd, *J* = 6.0, 2.9 Hz, 1H), 4.08 (td, *J* = 6.5, 2.9 Hz, 1H), 3.97 (dd, *J* = 10.3, 7.8 Hz, 2H), 3.89 (dd, *J* = 10.0, 6.2 Hz, 1H), 3.79-3.72 (m, 1H), 3.61 (s, 3H), 3.58 (d, *J* = 4.5 Hz, 2H), 3.47 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.35 (s, 3H), 3.24 (t, *J* = 9.4 Hz, 1H), 2.45 (s, 3H), 1.46 (s, 3H), 1.30 (s, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.94, 166.07, 138.67, 138.17, 138.09, 128.62, 128.57, 128.24, 128.12, 128.11, 127.94, 127.86, 127.82, 110.02, 98.93, 97.84, 82.18, 79.89, 78.40, 75.91, 75.07, 73.51, 70.99, 70.04, 69.69, 69.64, 69.56, 63.93, 62.00, 55.06, 52.66, 26.24, 25.94, 25.44, 23.09, 18.35, –5.21, –5.39. **HRMS** (ESI) *m*/*z* calcd. for $C_{47}H_{64}NaO_{14}S_2Si^+$ $[M + Na]^+$: 967.3399, found: 967.3367.

***p*-Tolyl 4-*O*-benzyl-2,3-di-*O*-benzoyl-6-*O*-[methyl (4,5-*O*-isopropylidene-3-*O*-(methyldithioperoxy)carbonyl-7-*O*-*t*butyldimethylsilyl-*α*-D-*talo*-2-heptulopyranosyl)onate]-thio-*α*-D-glucopyranoside (45)**



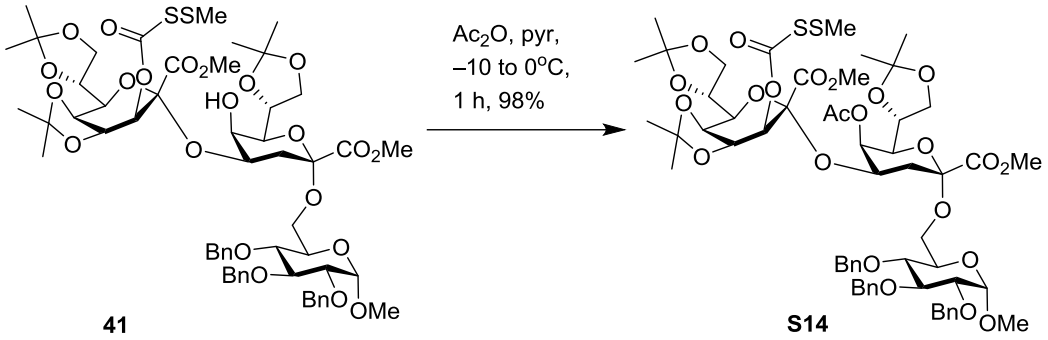
Thionocarbonate **12** (0.4 g, 0.92 mmol) was coupled with thioglucoside acceptor **31** (0.65 g, 1.1 mmol) based on the general glycosylation procedure (Table S1, entry 14). Disaccharide **45** (0.65 g, 67%) was obtained as a colorless gummy substance after column chromatography purification (Elution: hexanes/EtOAc, 5:1. Data for **45**: R_f = 0.5 (hexanes/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.88 (m, 4H), 7.49 (t, J = 7.3Hz, 2H), 7.36 (t, J = 7.6 Hz, 4H), 7.29 (d, J = 7.6 Hz, 2H), 7.25 (d, J = 1.4 Hz, 1H), 7.22-7.19 (m, 2H), 7.11 (dd, J = 16.7, 9.0 Hz, 4Hz), 5.75 (t, J = 9.2 Hz, 1H), 5.44 (d, J = 5.5 Hz, 1H), 5.35 (t, J = 9.7 Hz, 1H), 4.95 (d, J = 10.0 Hz, 1H), 4.57 (d, J = 11.0 Hz, 1H), 4.42 (dd, J = 11.8, 6.5 Hz, 2H), 4.15-4.13 (m, 1H), 3.98(dt, J = 22.4,8.0 Hz, 3H), 3.76 (t, J = 6.6 Hz, 2H), 3.71 (s, 3H), 3.69-3.64 (m, 2H), 2.47 (d, J = 1.2 Hz, 3H), 2.31 (s, 3H), 1.48 (s, 3H), 1.27 (s, 3H), 0.91 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.98, 165.97, 165.63, 165.39, 137.87, 136.92, 133.39, 133.33, 131.25, 129.93, 129.77, 129.28, 129.25, 128.52, 128.42, 128.16, 128.01, 109.84, 98.88, 86.08, 77.91, 77.36, 76.72, 76.43, 74.92, 70.77, 70.71, 69.80, 69.68, 69.45, 63.69, 61.95, 52.85, 26.22, 25.97, 25.35, 23.05, 21.18, 18.34, -5.13, -5.43; **HRMS** (ESI) m/z calcd. for $C_{53}H_{64}NaO_{15}S_3Si^+$ $[M + Na]^+$: 1087.3069, found: 1087.3081.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4,5-*O*-isopropylidene-3-*O*-(methyldithioperoxy)-carbonyl-7-*O*-trityl-*α*-D-*talo*-2-heptulopyranosyl)onate]-*α*-D-glucopyranoside (46)



Thionocarbonate donor **10** (1 g, 1.77 mmol) was coupled with methyl glucoside acceptor **14** (0.99 g, 2.13 mmol)[S1] according to the general glycosylation procedure (Table S1, entry 15). Disaccharide **46** (1.42 g, 75%) was obtained as a colorless oily substance after column chromatography purification (Elution: hexanes/EtOAc, 5:1) to give **46**. Data for **46**: R_f = 0.4 (hexanes/EtOAc, 2:1); $[\alpha]_D^{25}$ = +13.5 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 6H, ArH), 7.35-7.17 (m, 24H, ArH), 5.37 (d, *J* = 4.9 Hz, 1H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J* = 13.4 Hz, 2H), 4.79 (d, *J* = 3.9 Hz, 1H), 4.65 (d, *J* = 12.1 Hz, 1H), 4.55 (d, *J* = 3.0 Hz, 1H), 4.43 (dd, *J* = 11.5, 6.4 Hz, 2H), 4.24 (s, 1H), 4.14 (dd, *J* = 5.7, 2.1 Hz, 1H), 3.99 (t, *J* = 9.1 Hz, 1H), 3.82-3.77 (m, 1H), 3.62-3.57 (m, 2H), 3.62 (s, 3H), 3.58 (d, *J* = 7.5 Hz, 1H), 3.50 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.42 (dd, *J* = 9.3, 5.2 Hz, 1H), 3.37 (s, 3H), 3.26 (t, *J* = 9.4 Hz, 1H), 2.41 (s, 3H), 1.41 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.87, 166.02, 144.04, 138.73, 138.06, 137.98, 128.92, 128.54, 128.49, 128.16, 128.02, 127.98, 127.83, 127.77, 127.09, 110.20, 98.91, 97.76, 86.82, 82.11, 79.93, 78.55, 75.80, 75.09, 73.39, 70.98, 70.34, 70.18, 69.56, 68.76, 63.95, 63.01, 55.03, 52.62, 26.14, 25.43, 23.01; **HRMS** (ESI) *m*/*z* calcd. for $C_{60}H_{64}NaO_{14}S_2^+$ [M + Na]$^+$: 1095.3630, found: 1095.3633.

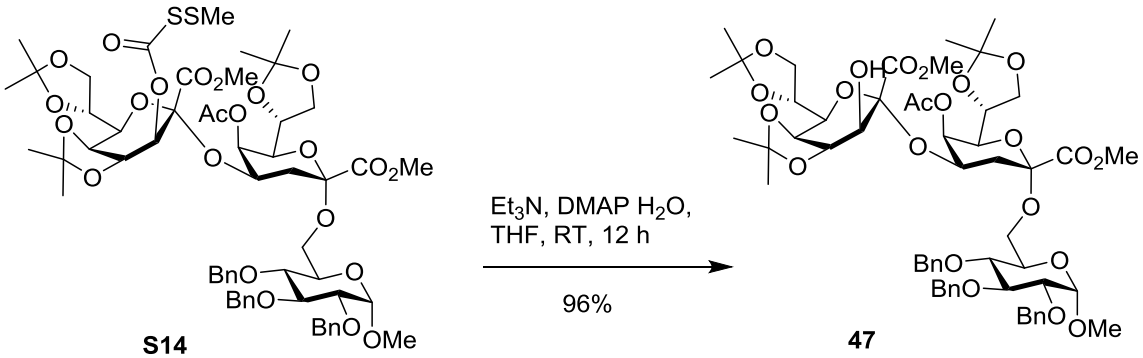
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}-onate-*α*-D-glucopyranoside (S14)



Trsiaccharide **39** (66 mg, 0.056 mmol) in DCM (2.0 mL) was treated with dry pyridine (4.6 μL, 0.056 mmol) at −10 °C. After for *ca* 5 min., acetic anhydride (6.0 μL, 0.067 mmol) and followed by 0.1 equiv of DMAP were added and the mixture stirred at 0 °C for 1 h. The acetylated product was then extracted with EtOAc, which was washed with satd. NH_4Cl, water, brine, dried (Na_2SO_4), and concentrated in *vacuo* to give acetylated trsiaccharide **S14** as colorless oily substance after chromatography purification (Elution: hexanes/EtOAc 2:1). For **S14**, R_f = 0.40 (hexanes/EtOAc 4/2), $[\alpha]_D^{23}$ = +45.7 (*c* 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.39-7.18 (m, 15H), 5.32 (d, *J* = 2.4 Hz, 1H, H-5′), 5.28 (d, *J* = 4.4 Hz, 1H, H-3″), 4.97 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 11.2 Hz, 1H), 4.78 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 9.2 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 3.6 Hz, 1H), 4.48 (d, *J* = 11.2 Hz, 1H), 4.45 (dd, *J* = 7.2, 1.8 Hz, 1H), 4.40 (dd, *J* = 11.6, 6.6 Hz, 1H), 4.26 (dd, *J* = 6.8, 3.2 Hz, 1H), 4.22 (m, 1H), 4.14 (dd, *J* = 9.2, 5.2 Hz, 1H), 4.09 (dd, *J* = 9.2, 6.4 Hz, 1H), 4.01 (m, 1H), 3.97 (t, *J* = 6.0 Hz, 1H), 3.96-3.92 (m, 2H), 3.91-3.85 (m, 2H), 3.78 (m, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.67 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.48 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.40-3.35 (m, 4H), 3.17 (dd, *J* = 14.0, 8.8 Hz, 1H), 2.49 (s, 3H), 2.35 (dd, *J* = 12.5, 4.8 Hz, 1H, H-3a′), 2.08 (s, 3H, CH_3CO), 2.03 (t, *J* = 12.5 Hz, 1H, H-3b′), 1.46 (s, 3H), 1.42 (s, 3H), 1.36 (s, 3H), 1.31 (s, 3H), 1.27 (s, 3H), 2.13 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ =169.1

(*C*=O), 168.8 (*C*(=O)SSMe), 167.5 (*C*=O), 165.6 (*C*=O), 138.6, 138.1, 137.9, 128.4, 128.4, 128.4, 128.0, 127.8, 127.8, 127.6, 110.5, 109.2, 109.1, 98.8, 98.2, 97.5 (C-1), 81.9, 80.1, 78.7, 75.7, 74.9, 74.3, 73.3, 73.1, 71.8, 71.7, 70.7, 70.5, 69.6, 69.4, 68.9, 66.6, 66.4, 65.9, 63.5, 60.4, 55.2, 52.5, 52.4, 33.8, 29.7, 26.7, 26.6, 25.7, 25.6, 25.4, 25.1, 22.9, 21.0, 20.8, 14.2; **HRMS** (ESI) *m*/*z* calcd for $C_{59}H_{76}NaO_{23}S_2^+$ $[M + Na]^+$: 1239.4111, found: 1239.4143.

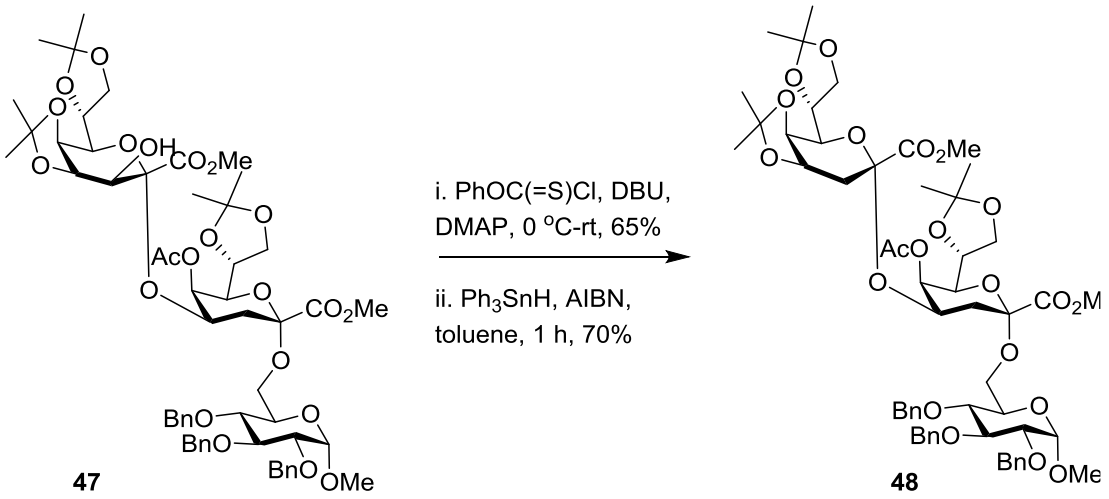
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (47)



To a solution of **S14** (30 mg, 0.024 mmol) in a solution of THF and H_2O (3 mL) mixture were treated Et_3N and DMAP in accordance with the general deprotection procedure. After complete cleavage, the reaction mixture was concentrated for flash chromatography purification (Elution: hexanes/EtOAc 1/1 to 1/2) to furnish **47** (24 mg, 96%) as a yellow viscous oil. For **47**, R_f 0.30 (hexanes/EtOAc/DCM = 1/2/1); $[\alpha]_D^{19}$ = –54.28 (*c* 0.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.36-7.21 (m, 15H, Ar*H*), 5.36 (d, *J* = 2.8 Hz, 1H, H5′), 4.97 (d, *J* = 10.8 Hz, 1H), 4.85 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 6.0 Hz, 1H), 4.76 (d, *J* = 7.6 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 3.6 Hz, 1H, H-1, HSQC), 4.48 (d, *J* = 7.6 Hz, 1H), 4.46 (dd, *J* = 7.6, 2.8 Hz, 1H), 4.33-4.24 (m, 3H), 4.11-4.02 (m, 3H), 4.00 (dd, *J* = 6.8, 2.8 Hz, 1H), 3.97 (m, 1H), 3.91-3.86 (m, 3H), 3.78 (m, 1H), 3.74 (s, 3H, COOC*H*$_3$), 3.72 (dd, *J* = 7.2, 2.4 Hz, 1H), 3.70 (s, 3H, OC*H*$_3$), 3.67 (dd, *J* = 10.0,1.6 Hz, 1H), 3.63 (d, *J* = 10.8 Hz, 1H), 3.48 (dd, *J* = 9.6, 4.0 Hz, 1H), 3.40-3.34 (m, 4H), 3.17

(dd, *J* = 10.0, 8.8 Hz, 1H), 2.23 (dd, *J* = 12.8, 4.8 Hz, 1H, *H*-3′eq), 2.11 (s, 3H, COC*H*$_3$), 2.01 (t, *J* = 12.4 Hz, 1H, *H*-3′axial), 1.43 (s, 3H, C*H*$_3$), 1.42 (s, 3H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$), 1.33 (s, 3H, C*H*$_3$), 1.28 (s, 3H, C*H*$_3$), 1.24 (s, 3H, C*H*$_3$); **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 170.2 (*C*=O), 167.6 (*C*=O), 167.4 (*C*=O), 138.6, 138.1, 137.9, 128.4, 128.4, 128.4, 128.0, 127.8, 127.8, 127.8, 127.6, 110.3, 109.2, 109.1, 98.9, 98.2, 97.5 (C-1), 81.9, 80.1, 78.7, 75.7, 74.9, 73.9, 73.3, 73.1, 72.9, 72.7, 71.6, 70.9, 70.1, 69.3, 68.5, 67.1 (C-5′), 66.8, 66.3, 63.5, 55.1, 52.4, 52.4, 34.4 (*C*2), 26.7, 25.4, 25.4, 24.9, 24.7, 20.9 (COCH_3); **HRMS** (ESI) *m*/*z* calcd. for $C_{57}H_{74}NaO_{22}^+$ $[M + Na]^+$: 1133.4564, found: 1133.4596.

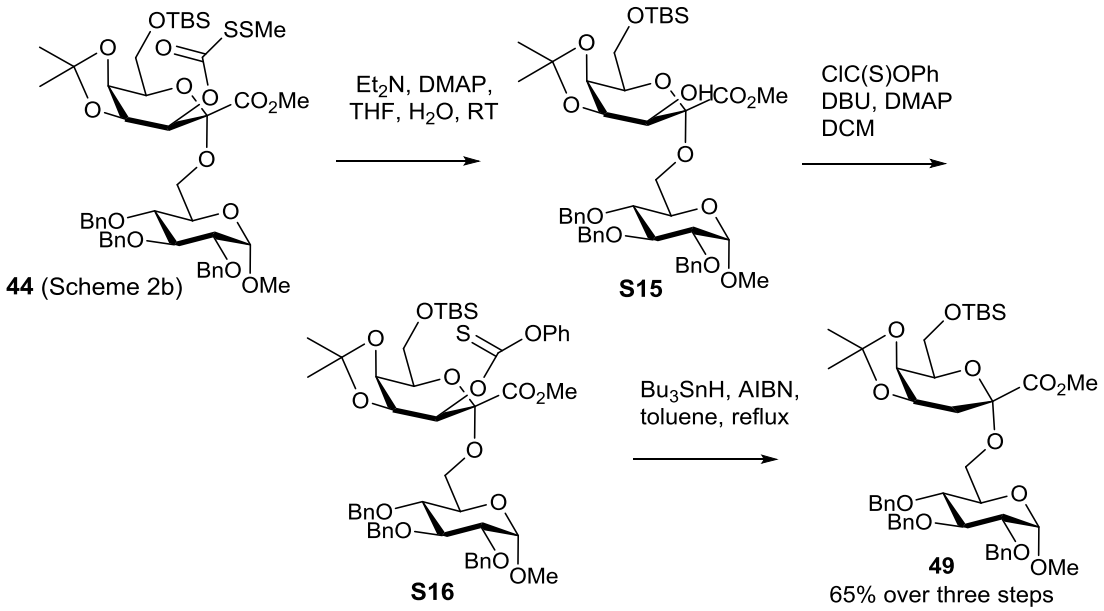
Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-3-deoxy-D-*glycero*-α-D-*manno*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (48)



Trisaccharide **47** was converted to a xanthate derivative in 65% yield following the general procedure for introduction of phenoxythiocarbonyl group and the phenoxythiocarbonyl protected intermediate obtained was taken to the deoxygenation followed the general deoxygenation procedure to give Kdo-*α*-(2→4)-Kdo-*α*-(2→6)-Glc trisaccharide **48** as a white foamy solid. For **48**, R_f = 0.4 (2/3 = hexanes/EtOAc); $[\alpha]_D^{19}$ = +60.0 (*c* 0.1, $CHCl_3$); **^{1}HNMR** (400 MHz, $CDCl_3$): δ = 7.38-7.22 (m, 15 H, Ar*H*), 5.11 (d, *J* = 2.4 Hz, 1H, H-5′), 4.98 (d, *J* = 11.2 Hz, 1H), 4.85 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 10.8 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H),

4.62 (d, *J* = 3.6 Hz, 1H, H-1), 4.53-4.44 (m, 3H including H-4′ and H-4″), 4.30-4.23 (m, 2H including H-5′ and H-5″), 4.10 (dd, *J* = 9.2, 6.0 Hz, 1H), 4.05 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.02-3.95 (m, 2H), 3.94 (d, *J* = 5.6 Hz, 1H), 3.92-3.87 (m, 2H), 3.81 (m, 1H), 3.73 (s, 3H, COOC*H*$_3$), 3.70 (s, 3H, COOC*H*$_3$), 3.53-3.48 (m, 2H), 3.45 (s, 3H), 3.39 (t, *J* = 10.0 Hz, 1H), 3.18 (dd, *J* = 10.0, 9.2 Hz, 1H), 2.93 (dd, *J* = 15.6, 3.6 Hz, 1H, *H*-3e″), 2.13-2.06 (m, 4H, including C*H*$_3$C=O and H-3a′), 2.02 (m, 1H, H-3b′), 1.69 (dd, *J* = 15.6, 2.4 Hz, 1H, *H*-3a″), 1.42 (s, 3H, C*H*$_3$), 1.35 (s, 3H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 1.29 (s, 3H, C*H*$_3$), 1.27 (s, 3H, C*H*$_3$), 1.24 (s, 3H, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.5 (*C*=O), 168.0 (*C*=O), 167.7 (*C*=O), 138.7, 138.1, 137.9, 128.4, 128.3, 128.0, 127.8, 127.8, 127.8, 127.5, 109.5, 109.2, 109.1, 98.2 (C-1′), 97.4 (C-1), 96.5 (C-2″), 82.1, 80.1, 78.9, 77.19, 75.7, 75.0, 73.8, 73.2, 73.2, 72.4, 71.6, 69.9, 69.3, 66.8, 66.7 (C-5′), 66.6, 65.9, 63.4, 55.4 (O*C*H$_3$), 52.4 (COO*C*H$_3$), 52.2 (COO*C*H$_3$), 34.5 (C-3′), 31.7 (C-3″), 27.1, 26.7, 25.5, 25.3, 25.2, 24.9, 20.9 (CO*C*H$_3$); **HRMS** (ESI) *m*/*z* calcd. for $C_{57}H_{74}NaO_{21}^+$ [M + Na]$^+$: 1117.4615, found: 1117.4663.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-3-deoxy-4,5-*O*-isopropylidene-l-*α*-D-*lyxo*-2-heptulopyranosyl)onate]-*α*-D-glucopyranoside (49)



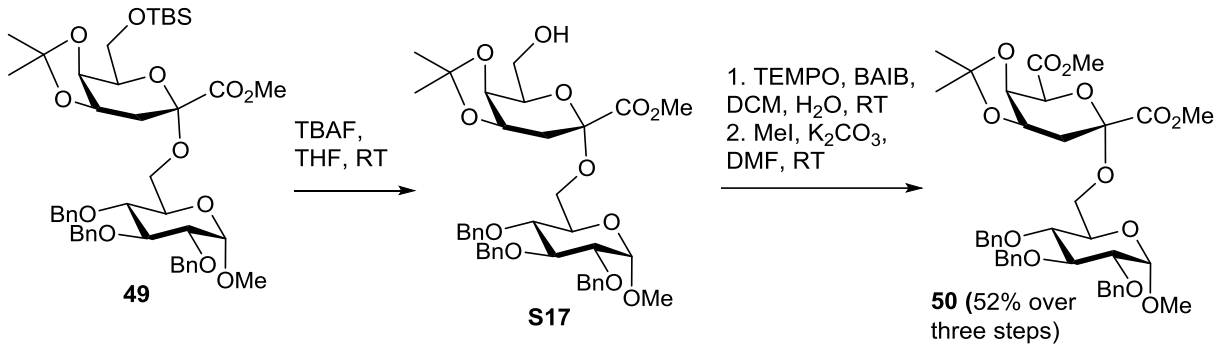
To a solution of **44** (0.85 g, 0.9 mmol) in THF (9 mL), H_2O (81 μL, 4.5 mmol), TEA (0.62 mL, 4.5 mmol) and DMAP (0.44 g, 3.6 mmol) were added. The solution was stirred at RT for 2.5 h and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc = 4:1) to give **S15** (0.62 g, 82%). Data for **S15**: R_f = 0.32 (hexanes/EtOAc, 2:1); $[\alpha]_D^{27}$ = +26.1 (*c* 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.22 (m, 15H, Ar*H*), 4.98 (d, *J* = 10.7 Hz, 1H), 4.88 (d, *J* = 11.1 Hz, 1H), 4.79 (d, *J* = 11.7 Hz, 2H), 4.65 (d, *J* = 12.2 Hz, 1H), 4.54 (d, *J* = 2.8 Hz, 1H), 4.49 (d, *J* = 11.1 Hz, 1H), 4.33 (t, *J* = 4.8 Hz, 1H), 4.19 (d, *J* = 5.8 Hz, 1H), 4.06 (d, *J* = 5.9 Hz, 1H), 4.01-3.84 (m, 5H), 3.82-3.75 (m, 2H), 3.68 (s, 3H), 3.65-3.54 (m, 3H), 3.49 (dd, *J* = 9.1, 2.9 Hz, 1H), 3.35 (s, 3H), 3.26 (t, *J* = 9.5 Hz, 1H), 2.59 (d, *J* = 9.2 Hz, 1H), 1.52 (s, 3H), 1.34 (s, 3H), 0.87 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.70, 138.67, 138.18, 138.13, 128.61, 128.56, 128.22, 128.14, 128.10, 127.91, 127.82, 127.78, 109.52, 100.28, 97.84, 82.20, 79.89, 78.44, 75.93, 75.02, 73.48, 72.06, 70.94, 69.62, 68.19, 63.95, 61.90, 55.05, 52.61, 25.93, 25.66, 25.57, –5.24, –5.41; **HRMS** (ESI) *m*/*z* calcd. for $C_{45}H_{62}NaO_{13}Si^+$ $[M + Na]^+$: 861.3852, found: 861.3883.

To a solution of **S15** (0.42 g, 0.5 mmol), DBU (0.3 mL, 2.0 mmol), DMAP (0.24 mg, 2.0 mmol) in anhydrous CH_3CN (10 mL) was added *O*-phenyl chlorothionoformate (0.17 mL, 1.3 mmol) at 0 °C. After stirred at 0 °C for 0.5 h, the reaction mixture was gradually warmed to RT and stirred for extra 2 h. The reaction solution, diluted with EtOAc, and washed with cold HCl (1 M) twice, satd. $NaHCO_3$, and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexanes/EtOAc, 6:1) to give **S16** (0.43 g, 88%). Data for **S16**: R_f = 0.6 (hexanes/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.22 (m, 18H, Ar*H*), 7.04-7.00 (m, 2H), 5.88 (d, *J* = 5.3 Hz, 1H), 4.99 (d, *J* = 10.8 Hz, 1H), 4.88 (d, *J* = 11.1 Hz, 1H), 4.82-4.77 (m, 2H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.57-4.52 (m, 2H), 4.49 (d, *J* = 11.2 Hz, 1H), 4.24 (dd, *J* = 6.0, 2.9 Hz, 1H), 4.15 (td, *J* = 6.6, 2.9 Hz, 1H), 4.06-3.90 (m, 3H), 3.82 (ddd, *J* = 9.7, 4.6, 2.1 Hz, 1H), 3.66 (s, 3H), 3.63 (d, *J* = 6.8 Hz,

2H), 3.49 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.36 (s, 3H), 3.28-3.23 (m, 1H), 1.60 (s, 3H), 1.35 (s, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.09, 166.12, 153.63, 138.67, 138.18, 138.13, 129.60, 128.61, 128.56, 128.23, 128.14, 128.09, 127.91, 127.82, 126.68, 121.89, 110.19, 99.00, 97.82, 82.19, 79.92, 78.55, 75.94, 75.84, 75.06, 73.49, 70.30, 69.96, 69.84, 69.62, 63.98, 62.02, 55.07, 55.54, 25.96, 25.91, 25.64, 25.58, 18.36, –5.21, –5.37; **HRMS** (ESI) *m*/*z* calcd. for $C_{52}H_{66}NaO_{14}SSi^+$ $[M + Na]^+$: 997.3835, found: 997.3895.

To a solution of **S16** (0.43 g, 4.4 mmol), Bu_3SnH (0.24 mL, 8.8 mmol) in toluene (8.8 mL) was added AIBN (36 mg, 2.2 mmol). The reaction mixture, subjected to "Freeze-Pump-Thaw" cycle three times, was stirred at 80 °C for 2 h. Then the mixture was diluted with EtOAc and washed with H_2O and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc = 6:1) to give **49** (0.33 g, 92%) as a light yellow glassy solid. Data for **49**: R_f = 0.47 (hexanes/EtOAc, 2:1); $[\alpha]_D^{27}$ = +18.6 (*c* 1.4, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.27 (m, 15H, Ar*H*), 4.97 (d, *J* = 10.8 Hz, 1H), 4.86 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 2H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.57 (t, *J* = 6.8 Hz, 2H), 4.48-4.42 (m, 1H), 4.17 (dd, *J* = 7.2, 1.6 Hz, 1H), 3.98 (t, *J* = 9.2 Hz, 1H), 3.90-3.71 (m, 6H), 3.68 (s, 3H), 3.57-3.53 (m, 1H), 3.51 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.40 (d, *J* = 9.4 Hz, 1H), 3.36 (s, 3H), 2.62 (dd, *J* = 15.0, 5.0 Hz, 1H), 1.96 (dd, *J* = 15.0, 3.6 Hz, 1H), 1.40 (s, 3H), 1.28 (s, 3H), 0.86 (s, 9H), 0.03 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.11, 138.81, 138.30, 138.27, 128.57, 128.51, 128.22, 128.12, 128.03, 127.79, 127.74, 109.18, 97.91, 82.23, 79.84, 78.34, 75.91, 74.99, 73.41, 71.46, 71.22, 70.13, 69.72, 62.65, 61.73, 55.11, 52.46, 33.53, 26.20, 25.96, 25.29, 18.40, –5.26, –5.45; **HRMS** (ESI) *m*/*z* calcd. for $C_{45}H_{62}NaO_{12}Si^+$ $[M + Na]^+$: 845.3903, found: 845.3937.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (7-carbomethoxy-3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (50)

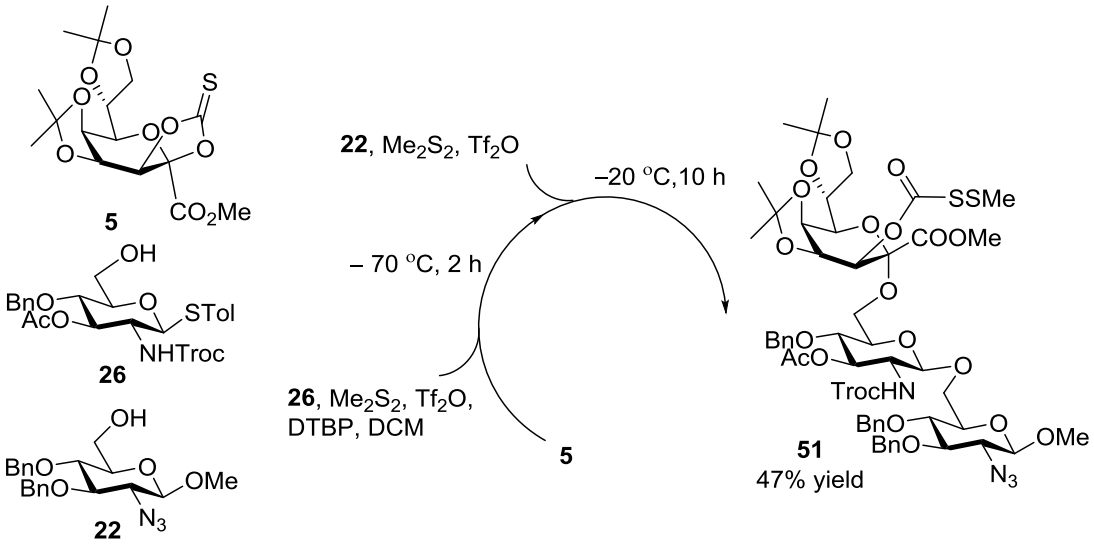


To a solution of **49** (0.52 mg, 0.63 mmol) in THF (2.1 mL), TBAF (3.2 mL, 3.2 mmol, 1M in THF) was added. The reaction mixture was stirred at RT for 2 h. The reaction was quenched with water and diluted with DCM and washed with H_2O and brine. The organic layer was dried over $MgSO_4$ and concentrated for column chromatography (Elution: hexanes/EtOAc, 2:1) to give **S17** (0.34 g, 76%). Data for **S17**: R_f = 0.15 (hexanes/EtOAc, 1:1); $[\alpha]_D^{28}$ = +33.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 15H, Ar*H*), 4.96 (d, *J* = 10.8 Hz, 1H), 4.87 (d, *J* = 11.2 Hz, 1H), 4.78 (d, *J* = 6.8 Hz, 1H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 3.6 Hz, 1H), 4.55 (d, *J* = 11.2 Hz, 1H), 4.49-4.44 (m, 1H), 4.14-4.09 (m, 2H), 3.98 (t, *J* = 9.2 Hz, 1H), 3.85 (dd, *J* = 10.9, 6.6 Hz, 1H), 3.76 (dt, *J* = 5.8, 3.9 Hz, 3H), 3.70 (s, 3H), 3.56-3.50 (m, 2H), 3.37 (s, 3H), 3.34 (d, *J* = 9.1 Hz, 1H), 2.69 (dd, *J* = 15.2, 4.7 Hz, 1H), 2.04 (s, 1H, O*H*), 1.91 (dd, *J* = 15.2, 3.3 Hz, 1H), 1.40 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.07, 138.71, 138.25, 138.14, 128.54, 128.50, 128.48, 128.14, 128.06, 127.98, 127.80, 127.70, 109.74, 97.73, 97.69, 82.11, 79.97, 78.06, 75.82, 74.72, 73.34, 72.68, 71.62, 70.37, 69.69, 62.80, 62.15, 55.13, 52.55, 33.18, 25.97, 25.22; **HRMS** (ESI) *m*/*z* calcd. for $C_{39}H_{48}NaO_{12}^+$ $[M + Na]^+$: 731.3038, found: 731.3068.

To a solution of **S17** (0.17 g, 0.24 mmol) in DCM (1.6 mL) and H_2O (0.8 mL), TEMPO (22 mg, 0.14 mmol) and BAIB (0.46 g, 1.4 mmol) were added. The reaction mixture was stirred at RT for 2 h. The mixture was diluted with DCM and washed with H_2O, and brine. The organic layer

was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was directly used for alkylation with no further purification. To a solution of the crude acid in DMF (2.4 mL), MeI (45 µL, 0.72 mmol) and K_2CO_3 (0.17 g, 1.2 mmol) were added. The reaction mixture was stirred at RT for 1.5 h. The reaction was quenched with satd. NaS_2O_3. The mixture was diluted with EtOAc and washed with water and brine. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (Elution: hexanes/EtOAc = 3:2) to give compound **50** (0.12 g, 68%) as a yellow gummy substance. Data for **50**: R_f = 0.2 (35% EtOAc in petroleum ether); $[\alpha]_D^{29}$ = + 34.2 (*c* 0.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.19 (m, 15H, Ar*H*), 4.95 (d, *J* = 10.8 Hz, 1H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.76 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 3.6 Hz, 1H, H-1), 4.52-4.43 (m, 3H, including H-4′ and H-5′), 4.40 (d, *J* = 2.0 Hz, 1H), 3.96 (t, *J* = 10.2 Hz, 1H, H-3), 3.82 (dd, *J* = 10.0, 6.0 Hz, 1H, H-6a), 3.77-3.71 (m, 4H including CO_2CH_3 × 1), 3.64 (s, 3H, CO_2CH_3), 3.59 (dd, *J* = 10.0, 2.0 Hz, 1H, H-6b), 3.49 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.37 (dd, *J* = 9.6, 8.8 Hz, 1H, H-4), 3.35 (s, 3H, OCH_3), 2.71 (dd, *J* = 15.2, 4.8 Hz, 1H, H-3′eq), 1.91 (dd, *J* = 15.2, 3.2 Hz, 1H, H-3′ax), 1.41 (s, 3H, CH_3), 1.28 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 (*C*=O), 167.9 (*C*=O), 138.6, 138.1, 138.0, 128.4, 128.4, 128.37, 128.1, 127.9, 127.9, 127.6, 127.6, 110.2 ($C(CH_3)_2$), 98.2 (C-2′), 97.8 (C-1), 81.9 (C-3), 79.7 (C-2), 77.9 (C-4), 75.7, 74.7, 73.3, 73.2 (C-5′), 70.7 (C-6′), 70.0 (C-4′), 69.4, 63.0 (C-6), 55.0 (OCH_3), 52.6 (CO_2CH_3), 52.3 (CO_2CH_3), 33.5 (C-3′), 25.9, 25.5; **HRMS** (ESI) *m*/*z* calcd. for $C_{40}H_{50}NaO_{13}^+$ [M + Na]$^+$: 759.2987, found: 759.2959.

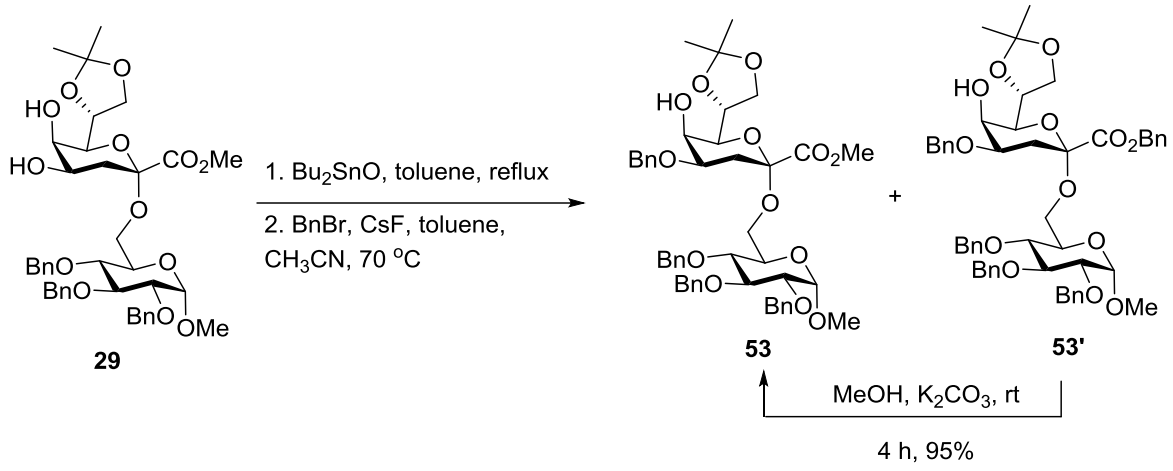
Methyl 2-Azido-3,4-di-*O*-benzyl-2-deoxy-6-*O*-{3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-trichloroethoxycarbonylamino-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(S-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]}-β-D-glucopyranoside (51)



The donor **5** (60 mg, 0.153 mmol), acceptor **26** (90 mg, 0.153 mmol), DTBP (38 mg, 0.184 mmol), 4Å MS (600 mg) were taken in DCM (3 mL, 0.05 M) and stirred for 30 min at room temperature and addition 20 min at –70 °C. Previously prepared $Me_2S_2.OTf_2$ (1 M, 142 µL) was added to the reaction mixture at same temperature. Reaction mixture was kept at –70 °C for 2 h. After completion of donor **5** it was allowed to reach –20 °C and then acceptor **22** (94 mg, 0.236 mmol) followed by $Me_2S_2.OTf_2$ (122 µL) were added. The reaction mixture was continuing to stirring at –20 °C for 10 h. After the disappearance of intermediate, the reaction mixture was quenched with Et_3N, filter over a celite pad, concentrated under reduce pressure purification by flash column chromatography (Elution: hexanes/DCM/EtOAc = 4:1:1) to furnish tisaccharide **51** (94 mg, 47%) as a colorless amorphous solid. Analytical data for **51**, R_f = 0.25 (hexanes:DCM:EtOAc = 4:1:1), $[\alpha]_D^{19}$ = +19.2 (*c* 1.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.40-7.19 (m, 15H, Ar*H*), 5.39 (d, *J* = 6.4 Hz, 1H, H-3″), 5.04 (dd, *J* = 10.4, 9.2 Hz, 1H, H-3′), 4.93 (d, *J* = 9.2 Hz, 1H), 4.88 (d, *J* = 10.8 Hz, 1H), 4.81 (d, *J* = 11.2 Hz, 1H), 4.75 (d, *J* = 10.8 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* =

11.6 Hz, 1H), 4.48-4.44 (m, 1H, H-7″), 4.37 (dd, *J* = 6.4, 5.2 Hz, 1H, H-4″), 4.23 (d, *J* = 8.0 Hz, 1H, H-1′), 4.19 (dd, *J* = 10.4, 3.2 Hz, 1H, H-5″), 4.15 (d, *J* = 8.0 Hz, 1H, H-1), 4.12 (quint, J = 4.0 Hz, 2H, H-8″), 4.05 (d, *J* = 10.8 Hz, 1H), 3.81 (dd, *J* = 7.2, 2.8 Hz, 1H, H-6″), 3.73 (m, 1H), 3.68 (s, 3H, COOCH_3), 3.64-3.55 (m, 3H, H-2′ and H-4′), 3.54 (s, 3H, OCH_3), 3.45-3.38 (m, 4H), 3.33 (dd, *J* = 17.2, 10.0 Hz, 1H, H-2), 2.46 (s, 3H, SSCH_3), 1.97 (s, 3H, COCH_3), 1.47 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.31 (s, 3H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.7 (*C*=O), 168.8 (*C*=O), 165.5 (*C*=O), 154.1 (carbamate *C*=O), 137.9, 137.7, 137.4, 128.6, 128.4, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 110.3 (*C*$(CH_3)_2$), 109.4 (*C*$(CH_3)_2$), 102.8 ($J_{C\text{-}H}$ = 160 Hz, C-1), 101.2 ($J_{C\text{-}H}$ = 164 Hz, C-1′), 98.8 (C-2″), 95.3 (*C*Cl_3), 83.2, 77.2, 76.2 (C-4′), 75.5, 74.7, 74.6, 74.4, 74.0, 73.9 (C-7″), 70.8 (C-3″), 70.1 (C-4″), 69.8 (C-5″), 69.6 (C-6″), 67.9, 66.5 (C-8″), 66.1 (C-2), 63.0, 57.1, 56.1 (C-2′), 52.7, 26.9, 25.8, 25.6, 25.3, 22.9 (SS*C*H_3), 20.8 (CO*C*H_3); **HRMS** (ESI) *m*/*z* calcd. for $C_{56}H_{69}Cl_3N_4NaO_{21}S_2^+$ $[M + Na]^+$: 1325.2854, found: 1325.2871.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4-*O*-benzyl-7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (53) and methyl 2,3,4-tri-*O*-benzyl-6-*O*-[benzyl (4-*O*-benzyl-7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate] *α*-D-glucopyranoside (53′)



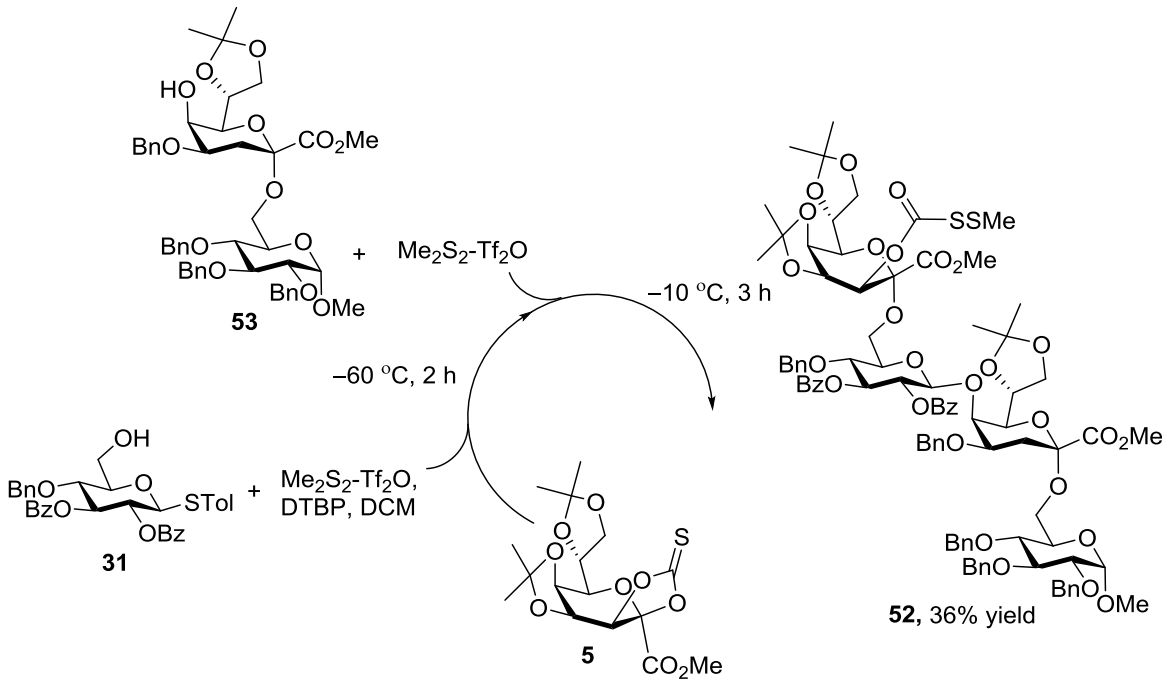
A mixture of diol **29** (247 mg, 0.334 mmol) and di-butyltin oxide (125 mg, 0.502 mmol) in dry toluene (10 mL) was refluxed for 1 h with dean stark apparatus. After that, *ca.* 50% (by vol)

of the solvent was removed and the remaining solution was cooled to RT. Then dry CH_3CN (5 mL), BnBr (60 µL, 0.502 mmol), and CsF (76 mg, 0.502 mmol) were added to the mixture, which was stirred at 70 °C for 3 h. After completion of the reaction, the reaction mixture was cooled to RT and filtered over Celite to remove the salts. The filtrate was concentrated for column chromatography purification (Elution: 1:2 EtOAc:hexanes) to afford **53** (180 mg of methyl ester 65%) together with **53′** (45 mg of benzyl ester, 15%) as a colorless syrupy. For compound **53**, R_f = 0.3 (40% EtOAc in petroleum ether); $[\alpha]_D^{19}$ +49.4 (*c* 1.7, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42-7.18 (m, 20H), 4.97 (d, *J* = 10.8 Hz, 1H), 4.83 (d, *J* = 11.2 Hz, 1H), 4.78 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.57 (s, 2H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 4.40 (dt, *J* = 8.0, 6.0 Hz, 1H), 4.10 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.06 (brs, 1H), 3.95 (t, *J* = 10.2 Hz, 1H), 3.89 (dd, *J* = 8.8, 5.6 Hz, 1H), 3.80 (m, 1H), 3.77-3.71 (m, 2H), 3.71-3.67 (m, 4H), 3.48 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.42 (dd, *J* = 10.4 , 8.0 Hz, 1H), 3.21 (dd, *J* = 10.0, 8.8 Hz, 1H), 3.18 (s, 3H), 2.27 (brs, 1H), 2.20 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.00 (t, *J* = 12.0 Hz, 1H), 1.36 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 168.1 (C-1′), 138.6, 138.2, 137.9, 137.5, 128.5, 128.4, 128.4, 128.0, 127.90, 127.8, 127.7, 127.7, 127.6, 127.5, 109.1, 98.6 (C-2′), 97.5 (C-1), 82.1, 79.9, 78.5, 75.7, 74.8, 73.3, 73.3, 72.6, 72.1, 69.8, 69.5, 67.3, 64.2, 63.3, 54.6, 52.4, 31.9, 26.6, 25.4; **HRMS** (ESI): *m/z* calcd. for $C_{47}H_{56}NaO_{13}^+$ $[M + Na]^+$ 851.3574, found 851.3574.

For compound **53′**, R_f 0.4 (40% EtOAc in petroleum ether); $[\alpha]_D^{19}$ +41.48 (*c* 1.35, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38-7.23 (m, 23H), 7.21-7.15 (m, 2H), 5.17 (d, *J* = 12.4 Hz, 1H), 5.07 (d, *J* = 12.4 Hz, 1H), 4.95 (d, *J* = 10.8 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 4.76 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.56 (dd, *J* = 16.0, 12.0 Hz, 1H), 4.49 (d, *J* = 3.2 Hz, 1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.39 (dd, *J* = 7.6, 5.6 Hz, 1H), 4.11 (dd, *J* = 9.6, 6.4 Hz, 1H), 4.06 (brs, 1H), 3.93 (dd, *J* = 17.6, 8.8 Hz, 1H), 3.92 (d, *J* = 8.8 Hz, 1H), 3.83-3.65 (m, 4H), 3.51-3.44 (m, 2H), 3.22 (dd, *J* = 9.6, 8.8 Hz, 1H), 3.16 (s, 3H), 2.22 (dd, *J* = 12.8,

5.2 Hz, 1H), 2.00 (t, J = 12.4 Hz, 1H), 1.37 (s, 3H), 1.27 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.3 (C-1′), 138.6, 138.1, 138.0, 137.5, 135.2, 128.6, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 109.1, 98.5 (C-2′), 97.5 (C-1′), 82.0, 79.9, 78.5, 75.7, 74.8, 73.4, 73.3, 72.7, 72.2, 69.9, 69.5, 67.2, 67.2, 64.2, 63.4, 54.7, 31.8, 26.6, 25.4; **HRMS** (ESI): *m/z* calcd. for $C_{53}H_{60}NaO_{13}^+$ $[M + Na]^+$ 927.3926, found 927.3867.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-{[methyl (4-*O*-benzyl-7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-5-*O*-(2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-glucopyranosyl)-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]}-*α*-D-glucopyranoside (52)

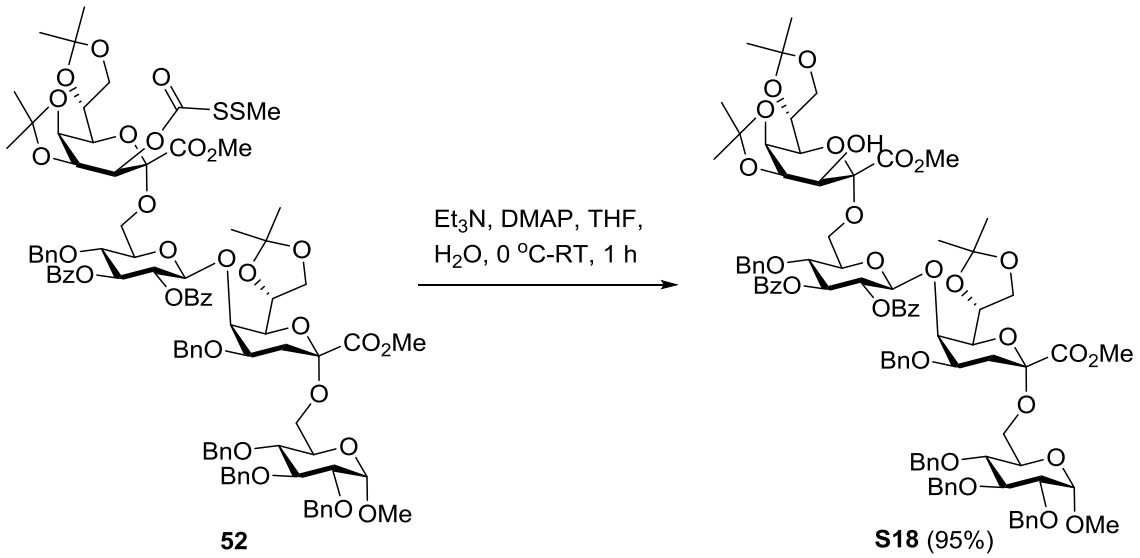


(2-Octulosopyranosonyl)onate donor **5** (72 mg, 0.185 mmol), thioglucoside acceptor **31** (107 mg, 0.183 mmol), DTBP (41 mg, 0.185 mmol), 4Å MS (600 mg) were taken in DCM (3.3 mL, 0.05 M), the mixture was stirred at RT for 30 min then at – 60 °C for 20 min. Freshly prepared Me_2S_2-Tf_2O (1.0 M, 185 µL) was added to the reaction mixture at – 60 °C. The reaction mixture was stirred at – 60 °C under N_2 for 3 h. After complete consumption of donor **5**, the reaction temperature was raised to – 10 °C followed by sequential addition of acceptor **53** (170 mg, 0.205 mmol) and $Me_2S_2.OTf_2$ (132 µL) promoter. The reaction mixture was stirred at –10 °C for 3 h.

After complete consumption of the disaccharide intermediate, the reaction mixture was quenched with Et_3N, filter over a celite pad, and concentrated under reduced pressure for purification with flash column chromatography (Elution: Elution: hexanes/EtOAc = 7:3) to furnish trisaccharide **52** (114 mg, 36%) as a light yellow glassy substance. Analytical data for **52**, $R_f = 0.45$ (hexanes/EtOAc = 7:3), $[\alpha]_D^{19} = +60.8$ (*c* 1.25, $CHCl_3$); **^{1}HNMR** (400 MHz, $CDCl_3$): δ = 7.99-7.94 (m, 2H, Ar*H*), 7.89-7.85 (m, 2H, Ar*H*), 7.53-7.48 (m, 1H, Ar*H*), 7.42-7.35 (m, 3H, Ar*H*), 7.34-7.24 (m, 16H, Ar*H*), 7.24-7.09 (m, 11H, Ar*H*), 5.70 (t, *J* = 9.6 Hz, 1H, H-3″), 5.44 (d, *J* = 5.2 Hz, 1H, H-3‴), 5.28 (dd, *J* = 8.0, 9.6 Hz, 1H, H-2″), 5.01 (d, *J* = 8.0 Hz, 1H, H-1″), 4.94 (d, *J* = 10.8 Hz, 1H), 4.77 (d, *J* = 8.8 Hz, 1H), 4.754 (t, *J* = 12.0 Hz, 2H), 4,747 (d, *J* = 10.8 Hz, 1H), 4.64 (d, *J* = 12.4 Hz, 1H), 4.60 (d, *J* = 11.6 Hz, 1H), 4.52-4.46 (m, 3H, including H-1 and H-7‴), 4.393 (d, *J* = 10.8 Hz, 1H), 4.387 (t, *J* = 6.0 Hz, 1H, H-4‴), 4.32 (dd, *J* = 12.4, 6.4 Hz, 1H, H-5'), 4.20 (dd, *J* = 6.4, 2.8 Hz, 1H, H-5‴), 4.17-4.08 (m, 5H, including H-8‴), 4.01-3.95 (m, 2H), 3.91 (t, *J* = 9.2 Hz, 1H, H-3), 3.84 (dd, *J* = 6.4, 2.8 Hz, 1H, H-6‴), 3.80 (t, *J* = 9.2 Hz, 1H, H-4″), 3.78-3.74 (m, 2H), 3.73 (s, 3H, COOCH_3), 3.69-3.63 (m, 4H, including H-5, H-5″, and H-4′), 3.80 (dd, *J* = 10.4, 1.2 Hz), 3.49 (s, 3H, COOCH_3), 3.45 (dd, *J* = 9.6, 3.6 Hz, 1H, H-2), 3.40 (dd, *J* = 10.4, 7.6 Hz, 1H, H-5′), 3.18 (dd, *J* = 10.0, 8.8 Hz, 1H, H-4), 3.10 (s, 3H, OCH_3), 2.47 (s, 3H, SSCH_3), 1.92 (dd, *J* = 12.4, 4.4 Hz, 1H, *H*-3′e), 1.74 (t, *J* = 12.4 Hz, 1H, *H*-3′a), 1.49 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.23 (s, 3H, CH_3); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.8 (*C*(=O)SSMe), 167.8 (*C*=O), 165.6 (*C*=O), 165.2 (*C*=O), 138.7, 138.1, 137.9, 137.8, 137.2, 133.2, 132.7, 129.8, 129.7, 129.7, 129.4, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.2, 110.3, 109.3, 108.4, 101.4 (C-1″), 99.1 (C-2‴), 98.5 (C-2′), 97.4 (C-1), 82.1 (C-3), 79.9 (C-2), 78.5 (C-4), 77.2 (C-4″) 75.6, 75.2 (C-3″), 74.8 (C-4‴), 74.6, 74.5 (C-5′), 74.2, 73.9, 73.7, 73.2, 72.9, 72.9, 72.1 (C-2″), 70.7 (C-3‴), 70.0, 69.7 (C-5‴), 69.6 (C-6‴), 69.4, 69.4, 66.3, 66.2, 63.9, 63.1 (C-5′), 54.6, 53.0, 52.1, 31.8 (C-3′), 26.8, 26.3, 25.9, 25.9, 25.6,

25.3, 22.9 (SS*C*H$_3$); **HRMS** (ESI) *m*/*z* calcd. for $C_{91}H_{104}NaO_{26}S_2^+$ [M + Na]$^+$: 1747.5997, found: 1747.5912.

Methyl {2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4-*O*-benzyl-7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-5-*O*-(2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-glucopyranosyl)-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)]onate}-α-D-glucopyranoside (S18)

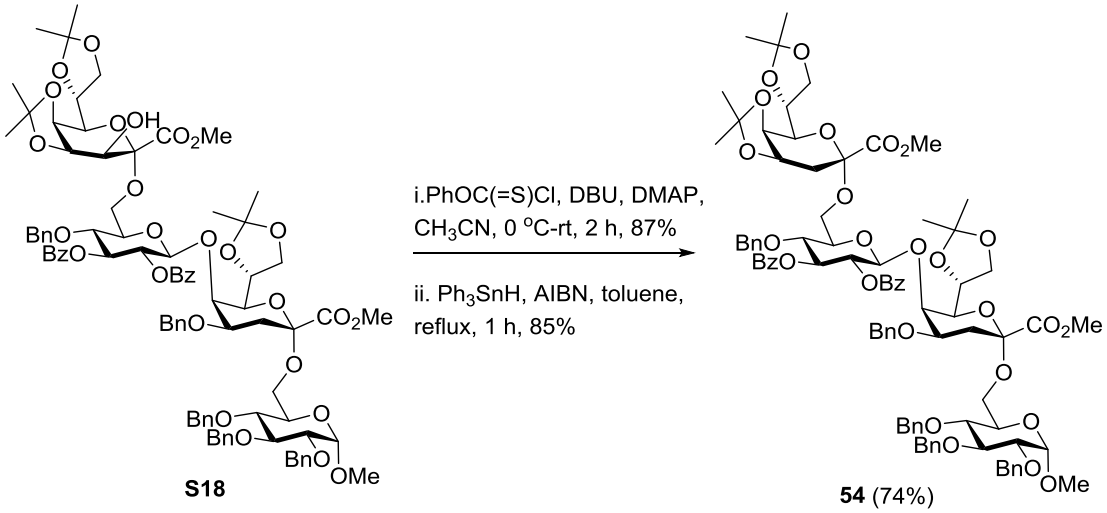


52 **S18** (95%)

A solution of Ko-*α*-(2→6)-Glc-*β*-(1→5)-Kdo-*α*-(2→6)-Glc tetrasaccharide **52** (75 mg, 0.043 mmol) in THF (3 mL) was taken to the general deprotection procedure for methylperoxycarbonyl group. After completion of the reaction (TLC examination), the reaction mixture was concentrated for flash chromatography purification (Elution: hexanes/EtOAc = 3:2) to furnish **S18** (66 mg, 95%) as a white foamy solid. For **S18**, R_f = 0.25 (hexanes/EtOAc = 3:2); $[\alpha]_D^{19}$ = +57.7 (*c* 0.9, $CHCl_3$); **^{1}HNMR** (400 MHz, $CDCl_3$): δ = 7.94-7.82 (m, 4H, Ar*H*), 7.48 (m, 1H, Ar*H*), 7.44-7.07 (m, 30H, Ar*H*), 5.67 (t, *J* = 9.6 Hz, 1H), 5.30 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.11 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.79-4.71 (m, 3H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.60 (d, *J* = 11.2 Hz, 1H), 4.54 (d, *J* = 11.2 Hz, 1H), 4.50 (d, *J* = 3.6 Hz, 1H), 4.46 (dd, *J* = 7.2, 4.0 Hz, 1H), 4.40 (t, *J* = 6.0 Hz, 1H), 4.38 (d, *J* = 4.8 Hz, 1H), 4.34 (dd, *J* =12. 4, 6.4 Hz, 1H), 4.30 (dd, *J* = 10.8, 2.4 Hz, 1H), 4.24 (s, 2H), 4.21 (dd, *J* = 8.8, 6.4 Hz, 1H), 4.11-4.05 (m, 3H), 4.04-3.97 (m, 2H), 3.91 (t, *J* = 9.2 Hz, 1H),

3.88-3.81 (m, 2H), 3.78 (dd, *J* = 6.4, 2.4 Hz, 1H), 3.74 (s, 3H), 3.72-3.66 (m, 4H), 3.65-3.56 (m, 3H), 3.48-3.41 (m, 5H), 3.23-3.17 (m, 1H), 3.12 (s, 3H, OC*H*$_3$), 1.94 (dd, *J* = 12.4, 4.4 Hz, 1H, *H*-3′e), 1.73 (t, *J* = 12.4 Hz, 1H, *H*-3′a), 1.51 (s, 3H, C*H*$_3$), 1.37 (s, 3H, C*H*$_3$), 1.36 (s, 6H, 2 x C*H*$_3$), 1.34 (s, 3H, C*H*$_3$), 1.26 (s, 3H, C*H*$_3$); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.9 (*C*=O), 167.6 (*C*=O), 165.6 (*C*=O), 165.1 (*C*=O), 138.7, 138.1, 138.0, 137.8, 137.2, 133.1, 132.7, 129.7, 129.7, 129.4, 128.4, 128.4, 128.3, 128.3, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.1, 110.2, 109.1, 108.4, 100.6 ($J_{C\text{-}H}$ = 168 Hz), 100.1, 98.5, 97.5 ($J_{C\text{-}H}$ = 164 Hz), 82.1, 79.8, 78.4, 75.6, 75.0, 74.8, 74.5, 74.2, 73.8, 73.2, 72.9, 72.8, 72.3, 72.1, 71.9, 70.0, 69.6, 69.5, 69.4, 66.4, 66.0, 63.2, 62.9, 54.6, 52.6, 52.0, 31.8 (C3′), 26.7 (*C*H$_3$), 26.2 (*C*H$_3$), 26.0 (*C*H$_3$), 25.4 (*C*H$_3$), 25.2 (*C*H$_3$), 25.0 (*C*H$_3$); **HRMS** (ESI) *m*/*z* calcd. for $C_{89}H_{102}NaO_{28}^+$ [M + Na]$^+$: 1641.6450, found: 1641.6339.

Methyl 2,3,4-Tri-*O*-benzyl-6-*O*-[methyl (4-*O*-benzyl-7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-5-*O*-(2,3-di-*O*-benzoyl-4-*O*-benzyl-*β*-D-glucopyranosyl)-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-α-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (54)



The Ko-*α*-(2→6)-Glc-*β*-(1→5)-Kdo-*α*-(2→6)-Glc terasaccharide **S18** (47 mg, 0.029 mmol) was converted to phenoxythiocarbonate derivative in 87% yield following the general procedure for introduction of phenoxythiocarbonyl group then followed by the general deoxygenation

procedure to obtain Kdo-α-(2→6)-Glc-β-(1→5)-Kdo-α-(2→6)-Glc terasaccharide **54** (35 mg, 74% over two steps) as a white foamy solid after workup and chromatography purification (Elution: hexanes/EtOAc 3:2). For **54**, R_f = 0.35 (hexanes/EtOAc = 3:2); $[\alpha]_D^{19}$ = + 64.0 (*c* 0.25, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.93-7.84 (m, 4H, Ar*H*), 7.52-7.45 (m, 1H, Ar*H*), 7.43-7.10 (m, 30H, Ar*H*), 5.64 (t, *J* = 9.2 Hz, 1H), 5.28 (dd, *J* = 9.6, 8.0 Hz, 1H), 5.08 (d, *J* = 7.6 Hz, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.75 (dd, *J* = 11.2, 8.0 Hz, 1H), 4.74 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 4.52-4.47 (m, 2H), 4.41-4.35 (m, 2H), 4.30 (dd, *J* = 11.2, 6.4 Hz, 1H), 4.26 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.24 (s, 2H), 4.16 (dd, *J* = 8.8, 6.8 Hz, 1H), 4.13 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.07-4.00 (m, 3H), 3.91 (t, *J* = 9.2 Hz, 1H), 3.87 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.79 (t, *J* = 9.2 Hz, 1H), 3.72-3.66 (m, 6H), 3.65-3.56 (m, 4H), 3.49-3.43 (m, 5H), 3.21 (dd, *J* = 9.6, 9.2 Hz, 1H), 3.13 (s, 3H, OC*H*$_3$), 2.89 (dd, *J* = 15.6, 4.0 Hz, 1H, *H*-3‴e), 1.93 (dd, *J* = 12.4, 4.4 Hz, 1H, *H*-3′e), 1.86 (dd, *J* = 15.6, 2.8 Hz, 1H, *H*-3‴a), 1.72 (t, *J* = 12.4 Hz, 1H, *H*-3′a), 1.40 (s, 3H, C*H*$_3$), 1.38 (s, 3H, C*H*$_3$), 1.35 (s, 6H, C*H*$_3$), 1.31 (s, 3H, C*H*$_3$), 1.25 (s, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6 (*C*=O), 167.9 (*C*=O), 165.6 (*C*=O), 165.1 (*C*=O), 138.7, 138.2, 138.0, 137.8, 137.3, 133.1, 132.7, 129.7, 129.7, 129.5, 128.5, 128.4, 128.5, 128.3, 128.3, 128.3, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.2, 109.5, 109.1, 108.2, 100.6, 98.5, 97.7, 97.5, 82.1, 79.8, 78.4, 75.7, 75.2, 75.0, 74.8, 74.6, 74.2, 73.9, 73.3, 73.2, 72.9, 72.4, 72.1, 72.0, 71.7, 70.0, 69.6, 69.4, 66.8, 65.8, 63.0, 62.9, 54.6, 52.5, 52.1, 32.6 (*C*-3‴), 31.8 (*C*-3′), 26.9 (*C*H$_3$), 26.2 (*C*H$_3$), 26.1 (*C*H$_3$), 25.4 (*C*H$_3$), 25.4 (*C*H$_3$), 24.8; **HRMS** (ESI) *m*/*z* calcd. for $C_{89}H_{102}NaO_{27}^+$ $[M + Na]^+$: 1625.6501, found: 1625.6444.

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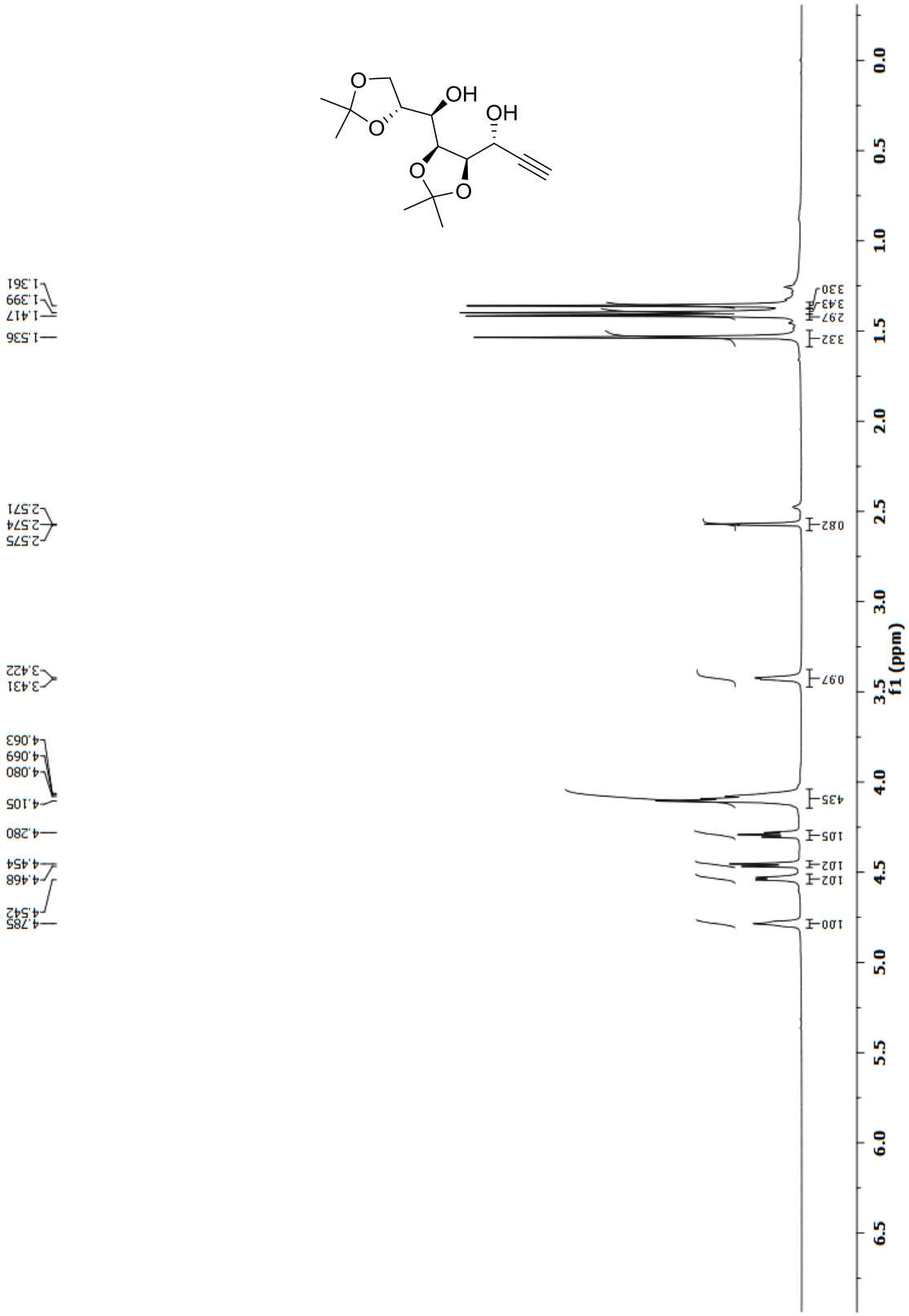
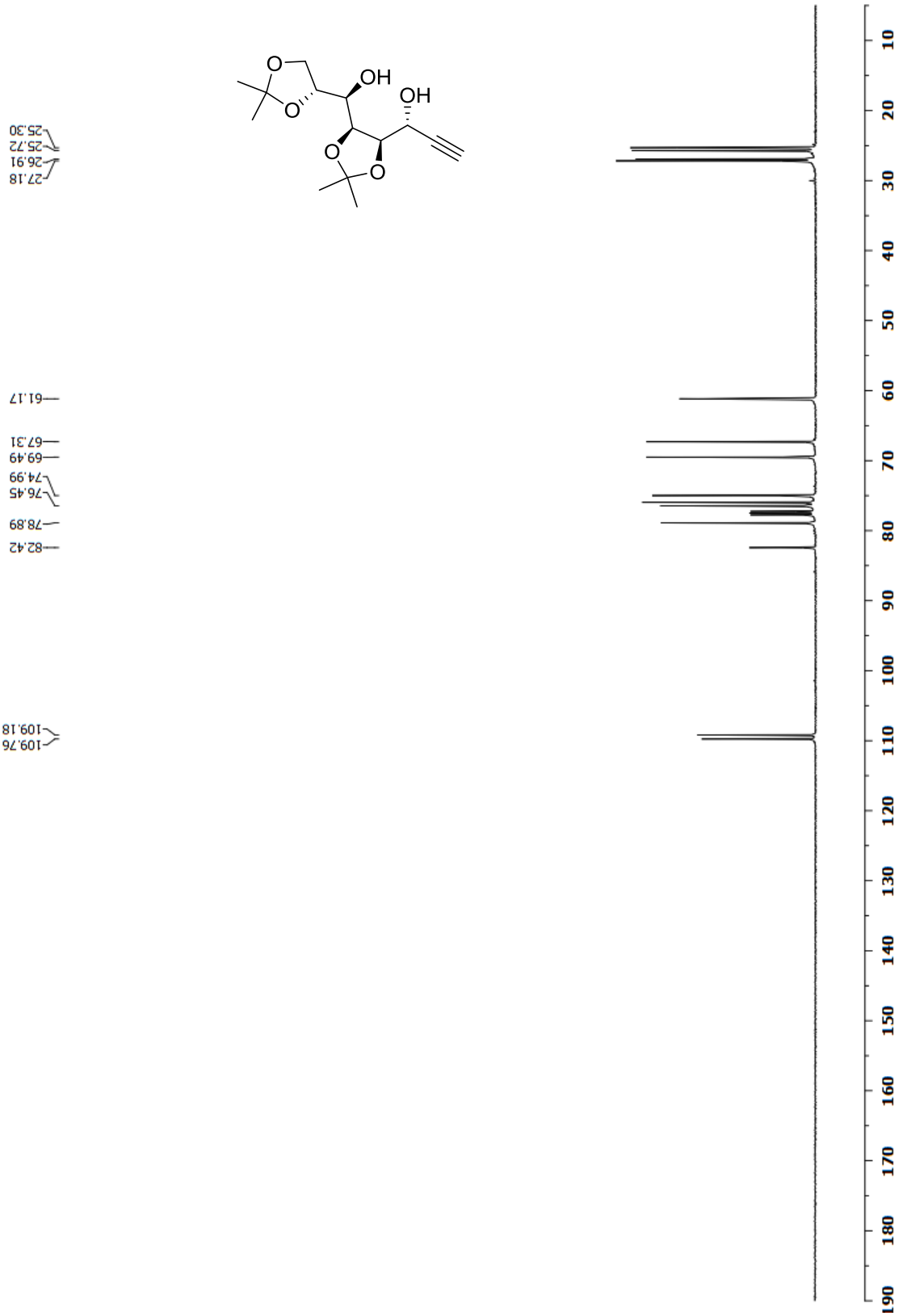
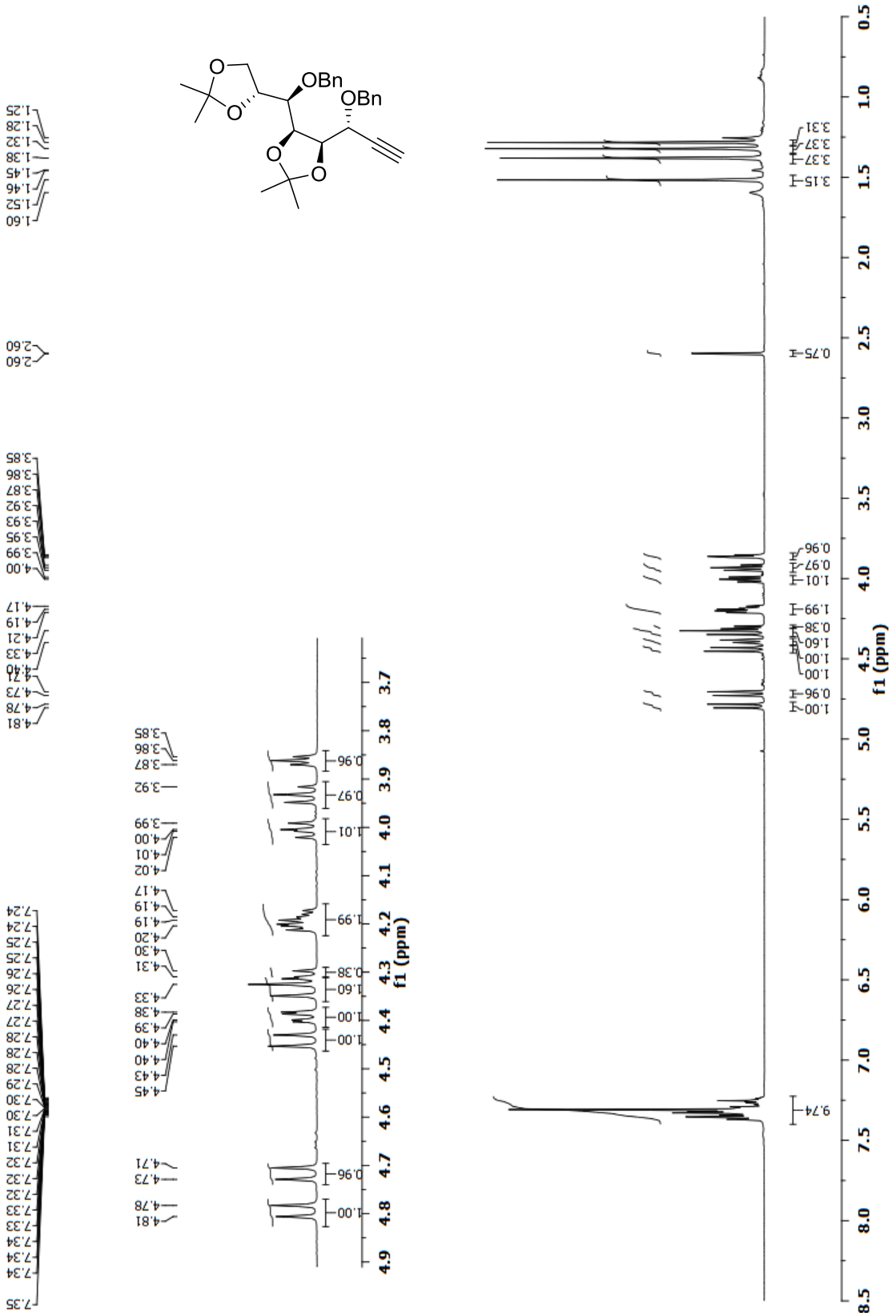
^{1}H NMR (500 MHz, $CDCl_3$) of 1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*manno*-1-yno-octitol (**S1**)



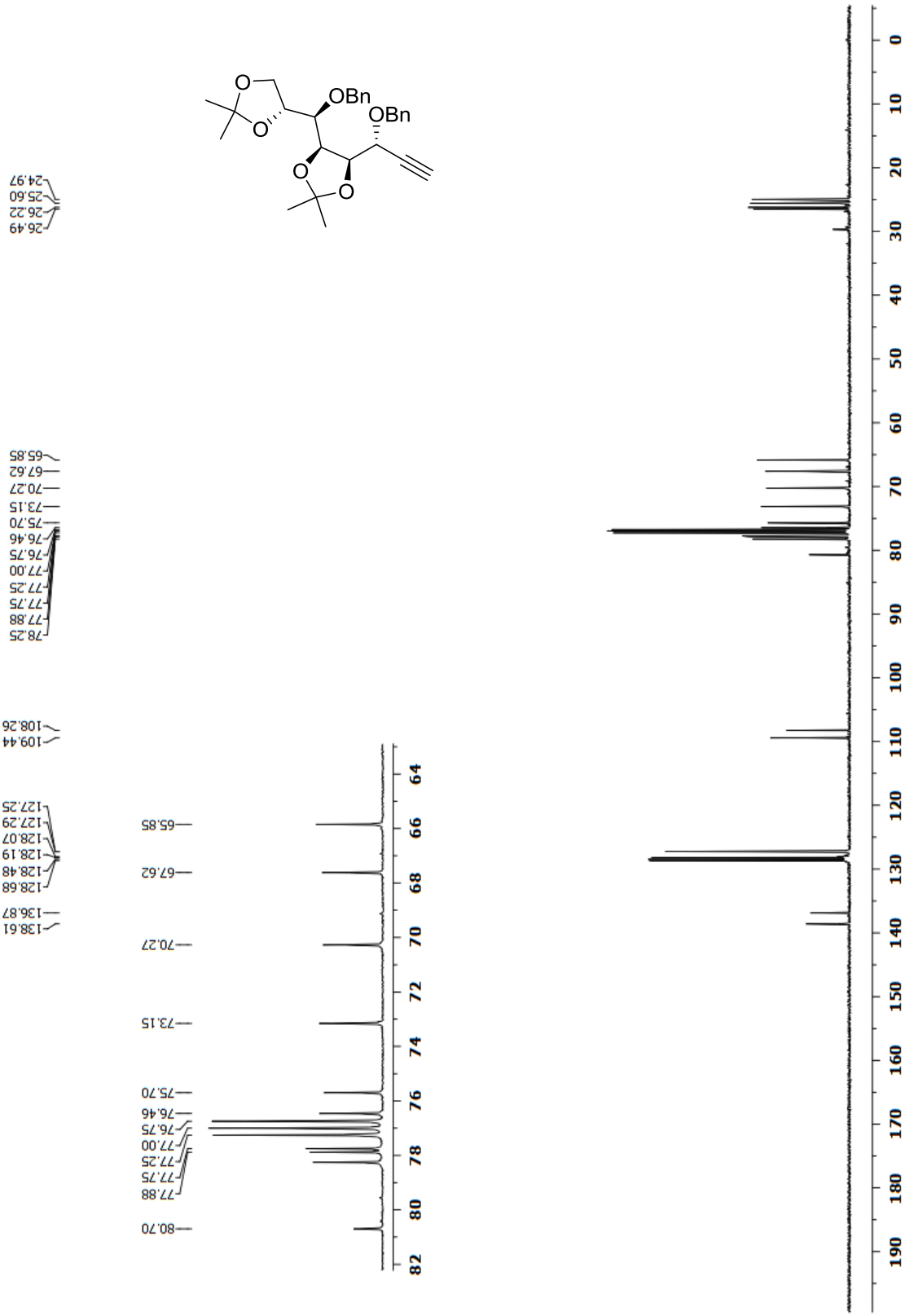
^{13}C NMR (125 MHz, $CDCl_3$) of 1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*manno*-1-yno-octitol (**S1**)



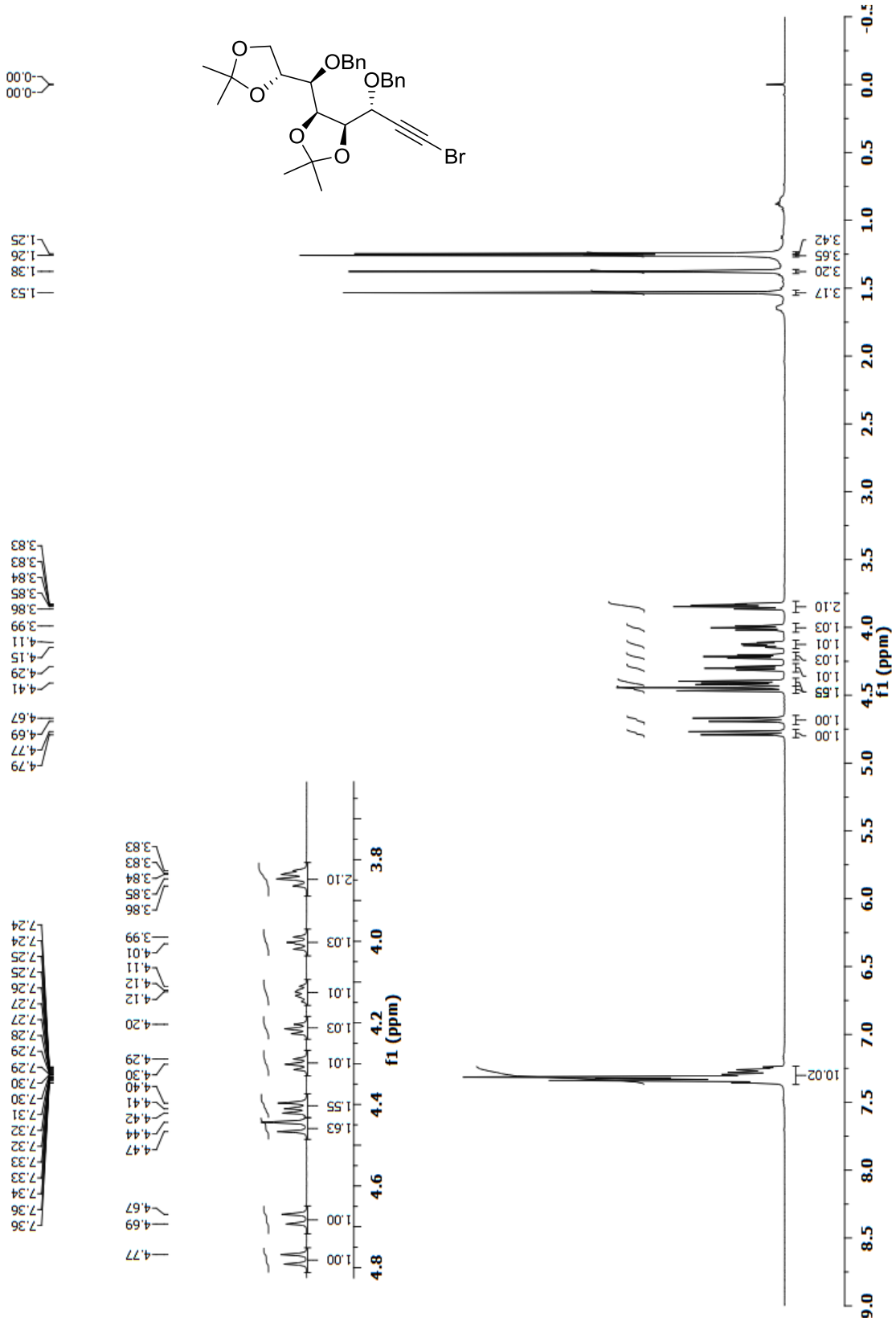
^{1}H NMR (500 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*manno*-1-yno-octitol **(2)**



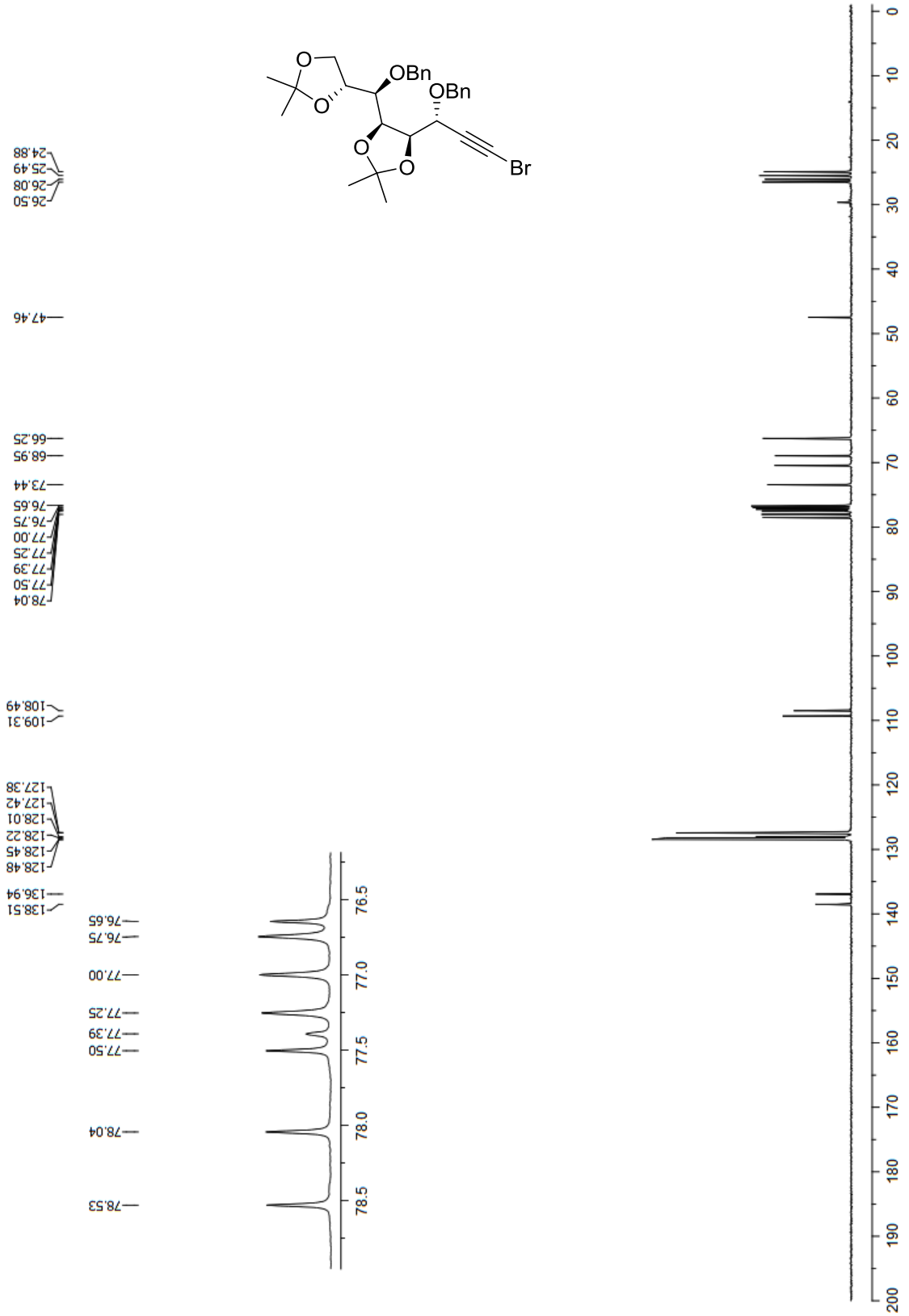
^{13}C NMR (125 MHz, $CDCl_3$) of **3,6-di-*O*-benzyl**-1,2-**d**ideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*manno*-1-yno-octitol **(2)**



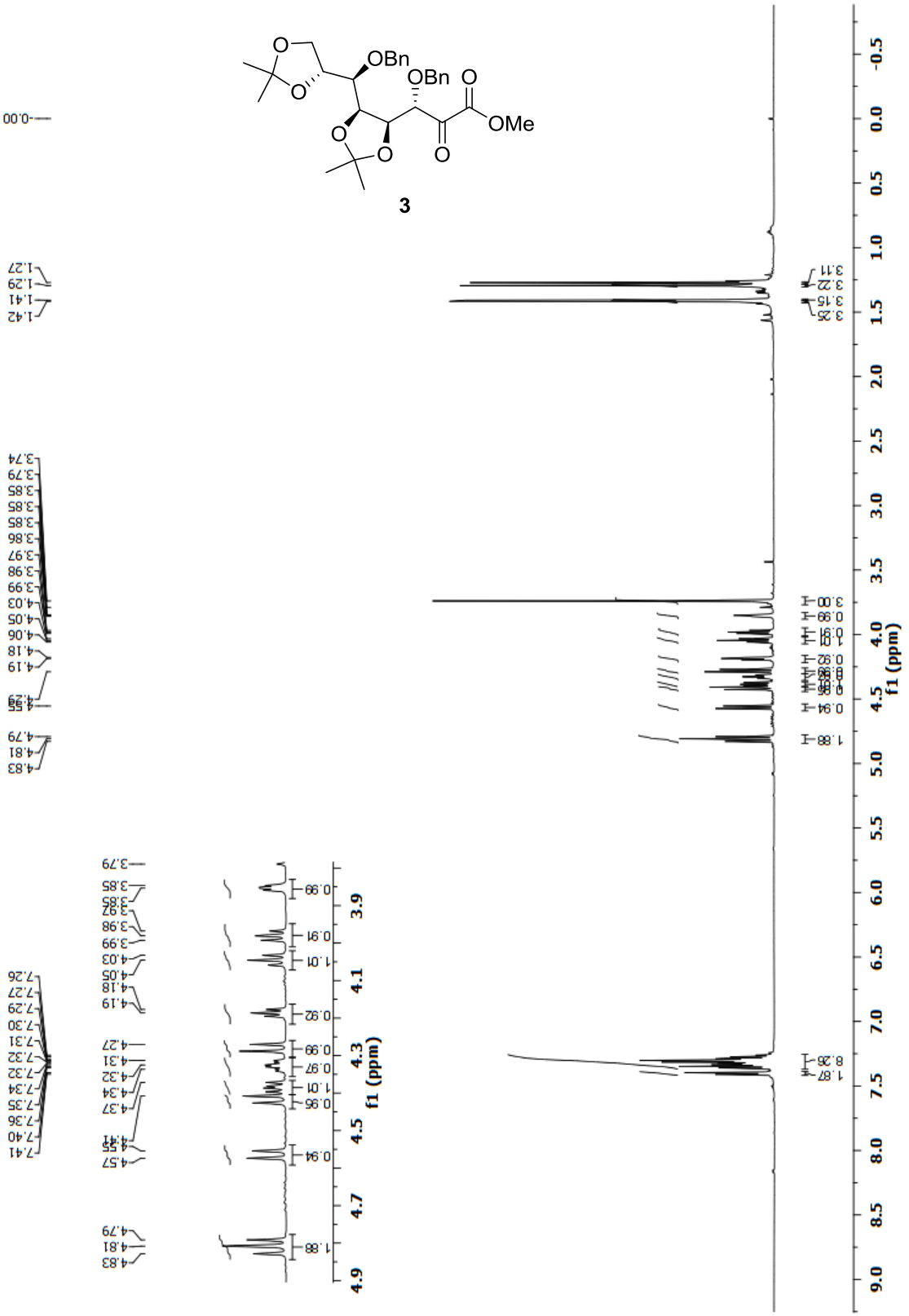
^{1}H NMR (500 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-1-bromo-1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*manno*-1-yno-octitol (**S2**)



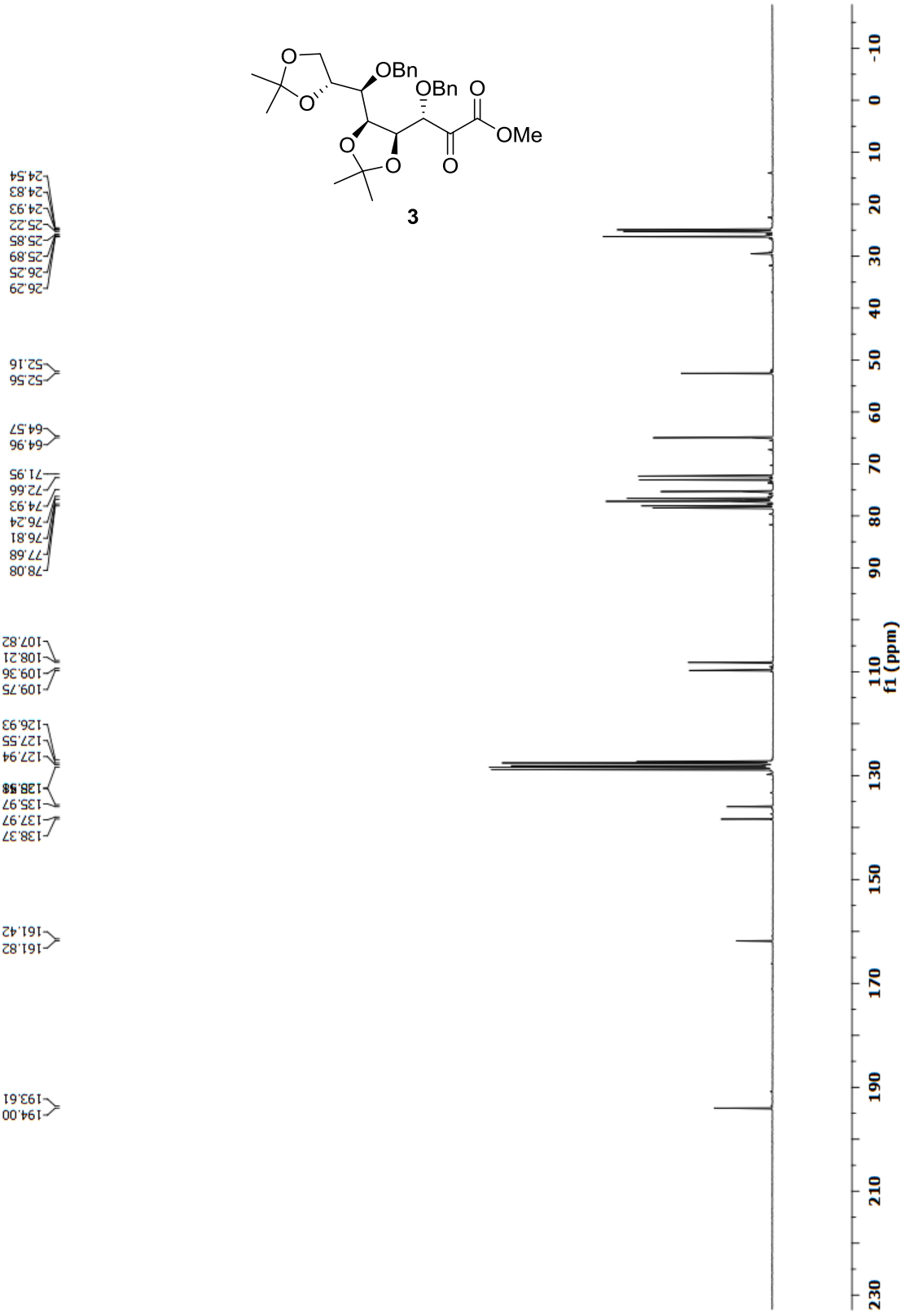
^{13}C NMR (125 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-1-bromo-1,2-dideoxy-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*manno*-1-yno-octitol (**S2**)



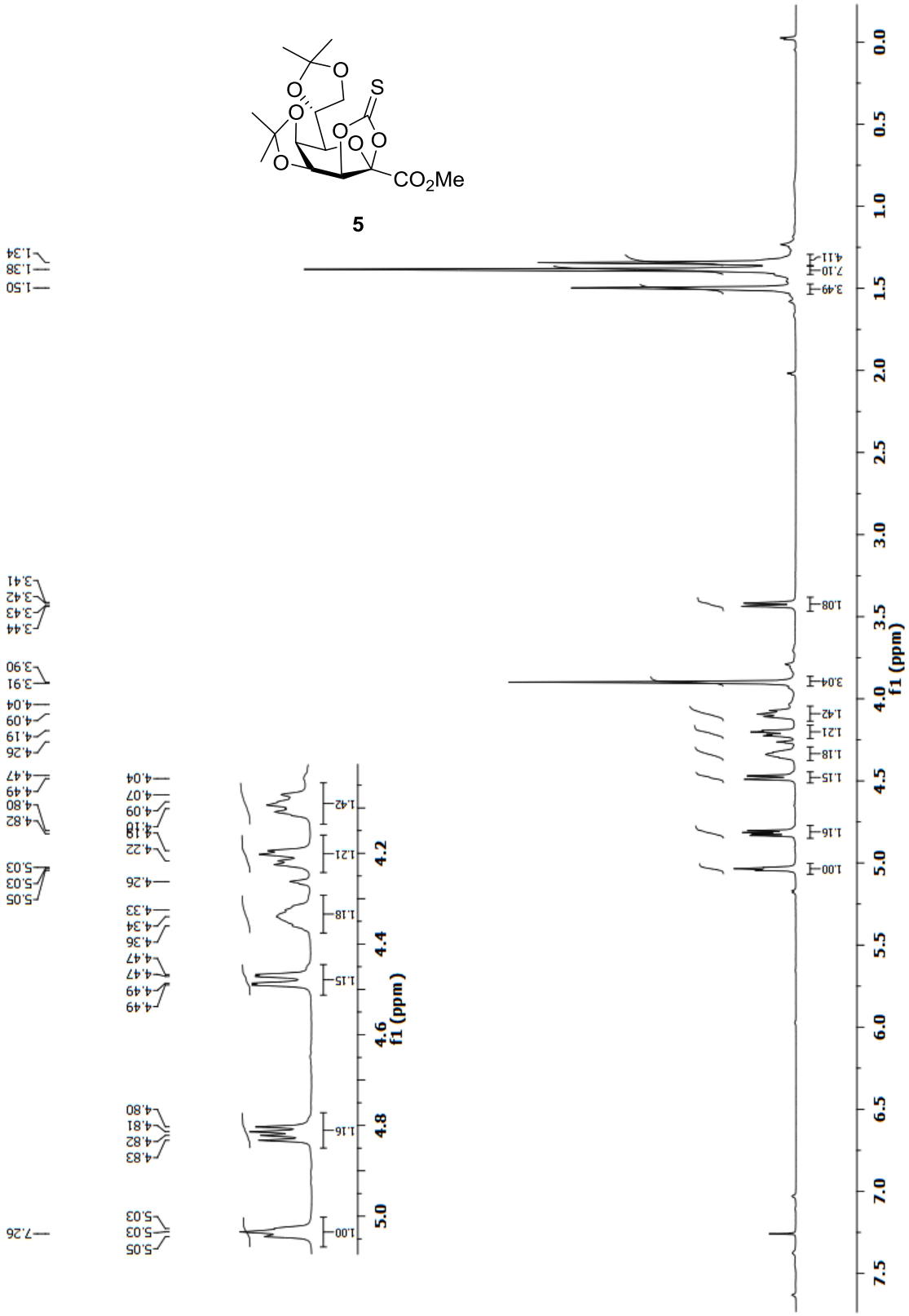
^{1}H NMR (600 MHz, $CDCl_3$) of methyl 3,6-di-*O*-benzyl-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-octulosonate (**3**)



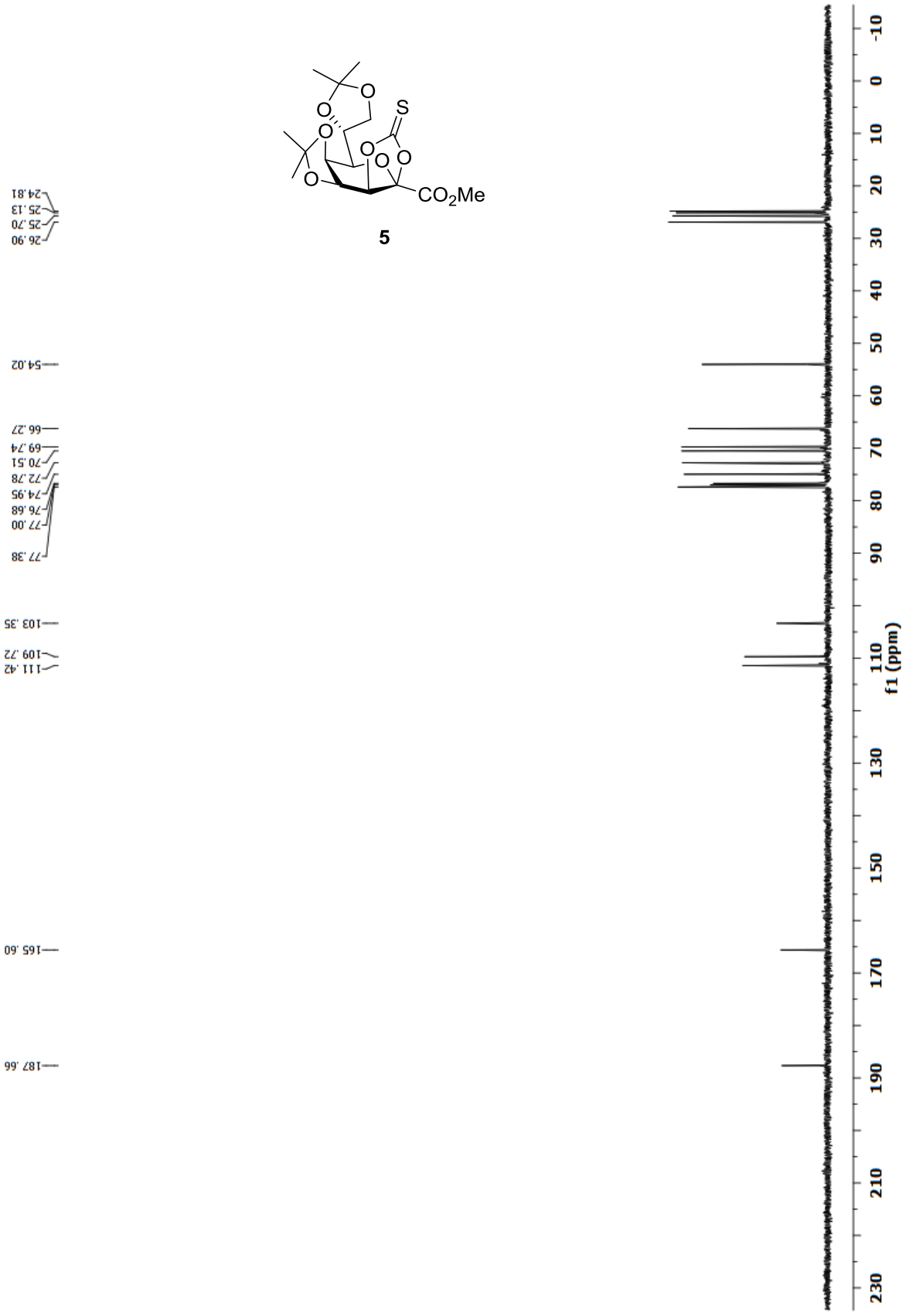
^{13}C NMR (150 MHz, $CDCl_3$) of methyl 3,6-di-*O*-benzyl-4,5:7,8-di-*O*-isopropylidene-D-*glycero*-D-*talo*-octulosonate (**3**)



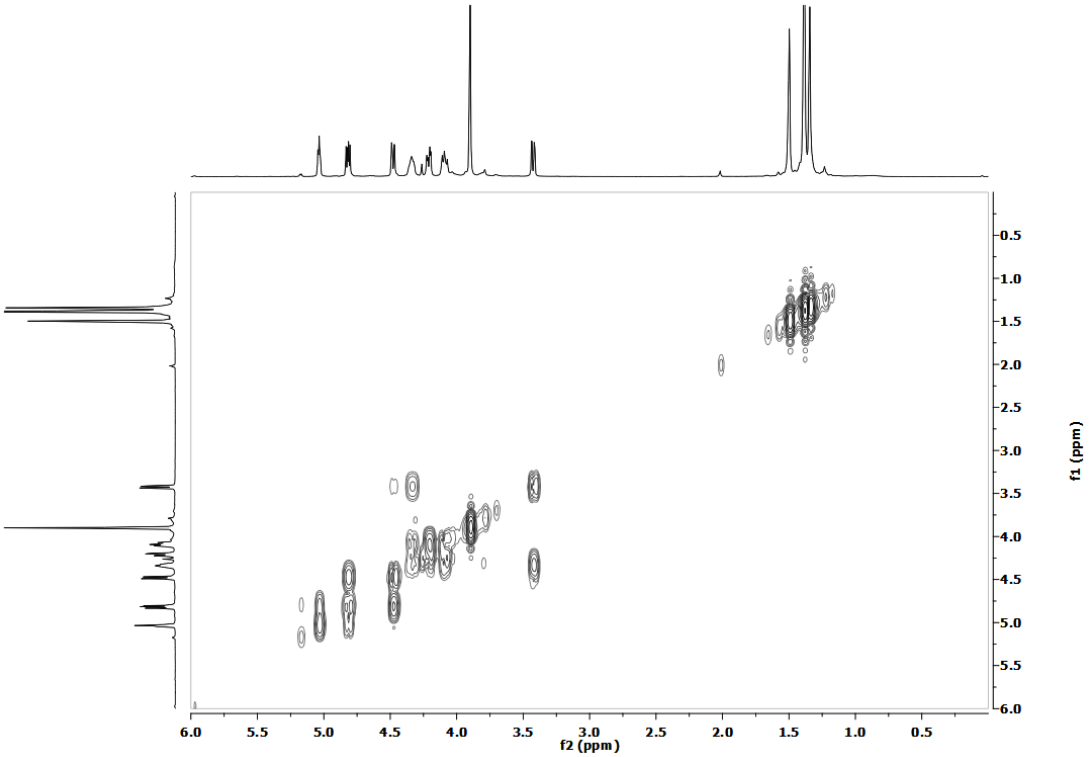
^{1}H NMR (400 MHz, $CDCl_3$) of methyl [4,5:7,8-di-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**5**)



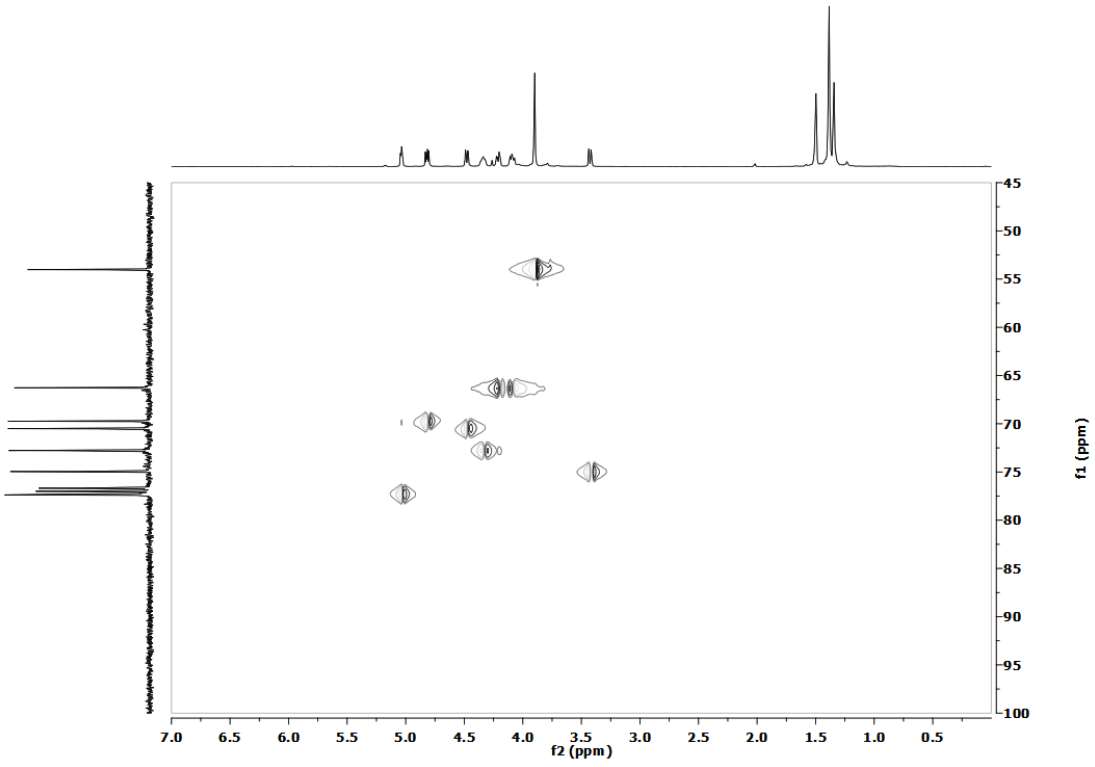
^{13}C NMR (100 MHz, $CDCl_3$) of methyl [4,5:7,8-di-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**5**)



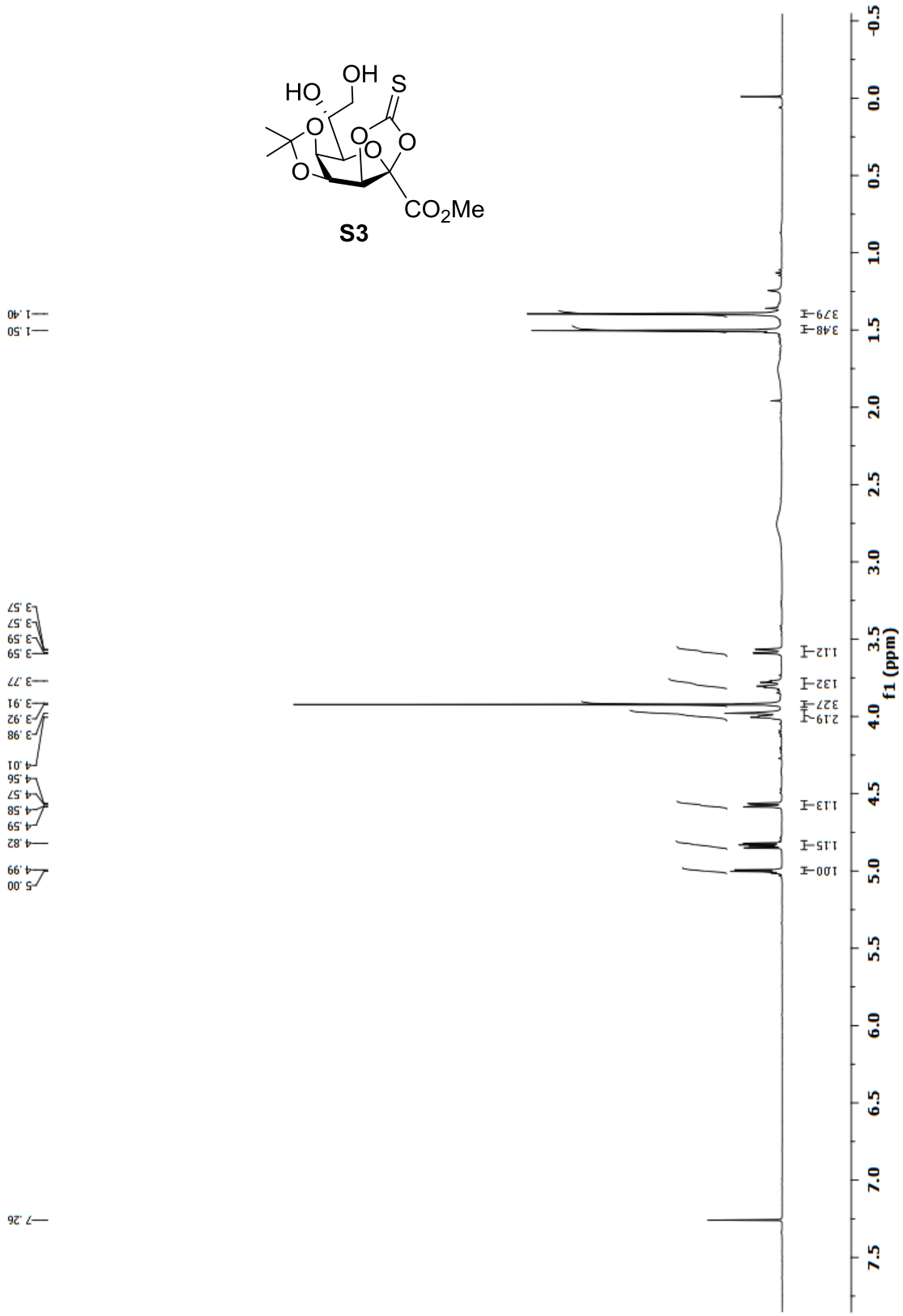
^{1}H-^{1}H GCOSY NMR (400 MHz, $CDCl_3$) of methyl [4,5:7,8-di-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**5**)



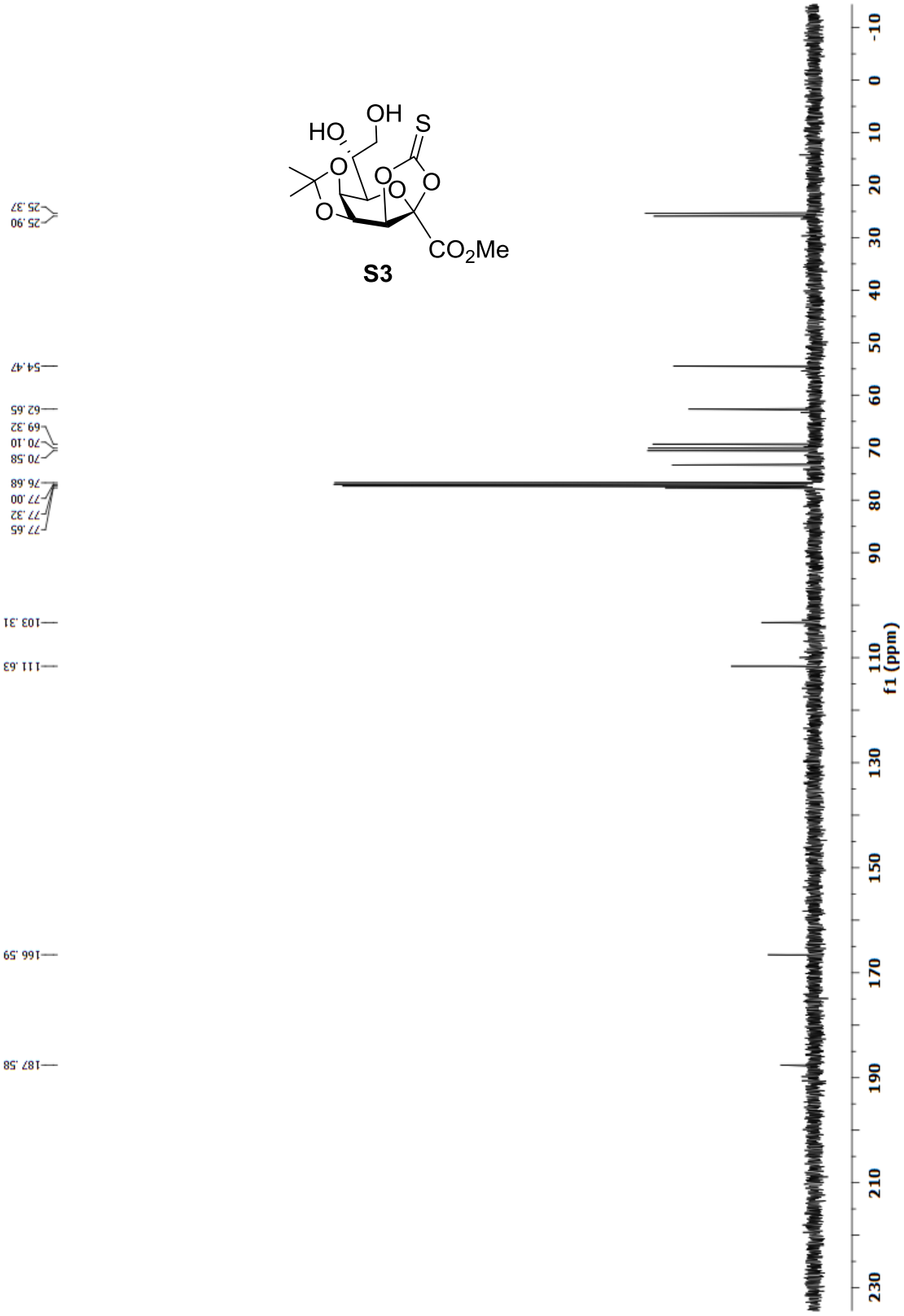
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of methyl [4,5:7,8-di-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**5**)



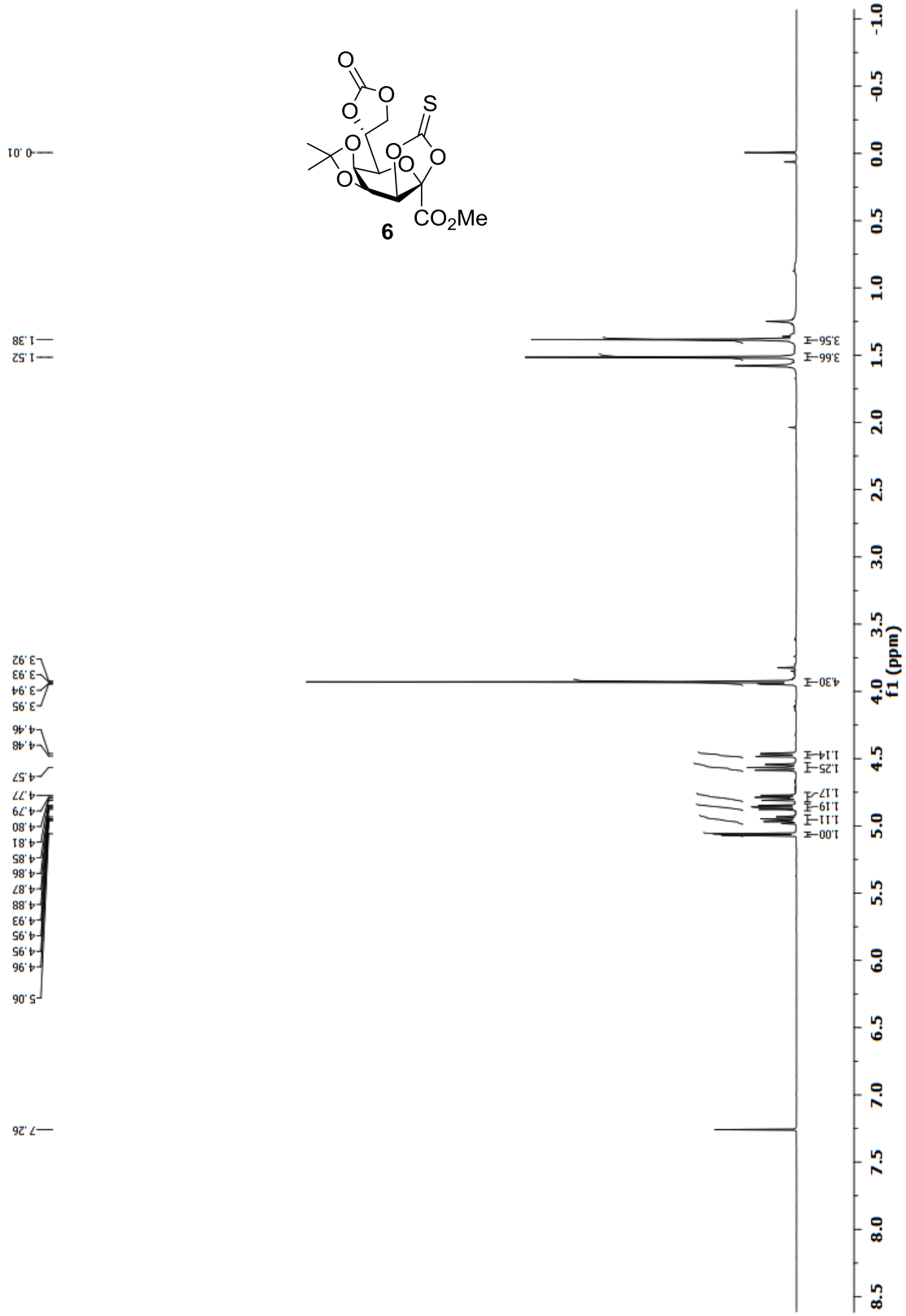
^{1}H NMR (400 MHz, $CDCl_3$) of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**S3**)



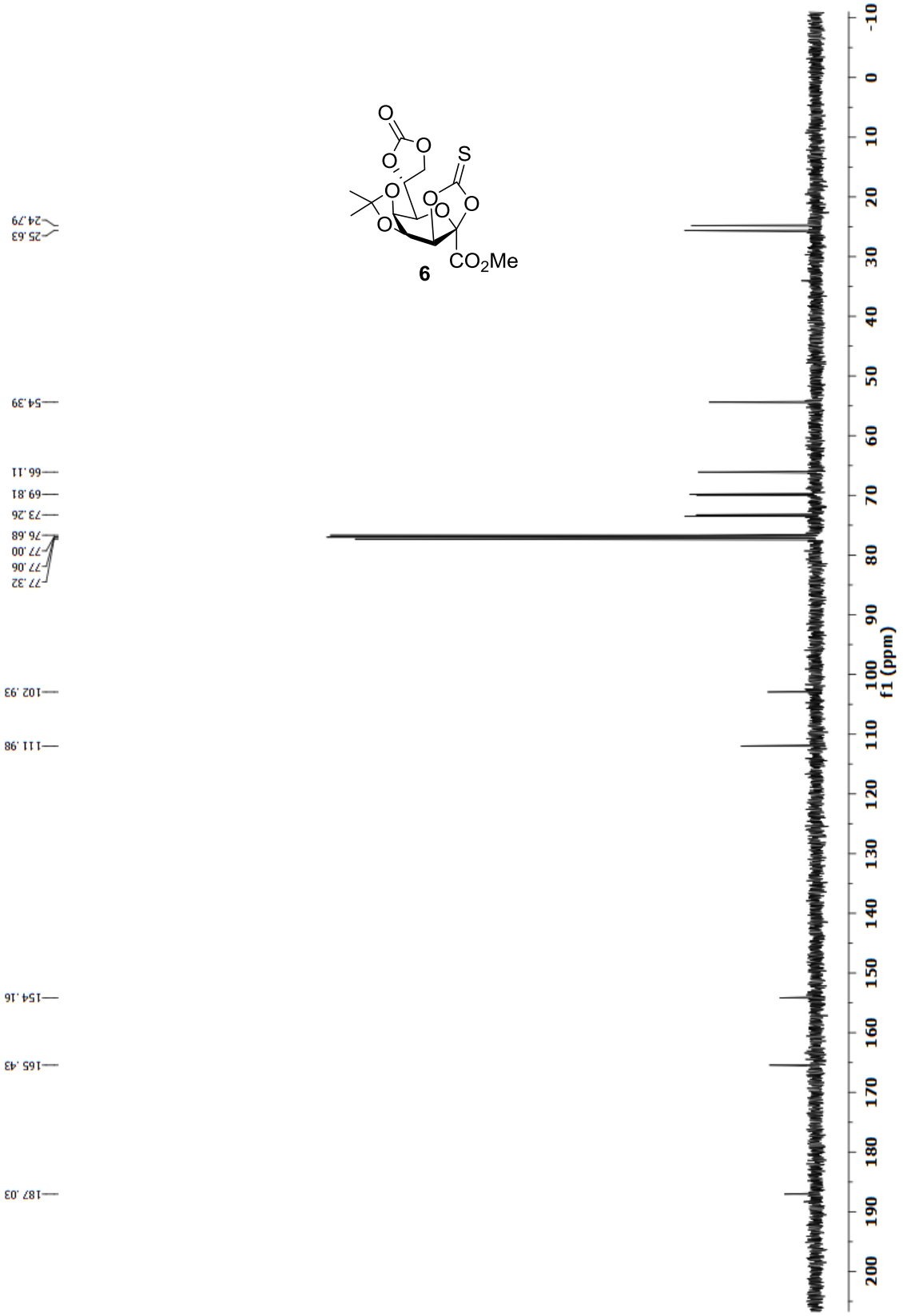
^{13}C NMR (100 MHz, $CDCl_3$) of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**S3**)



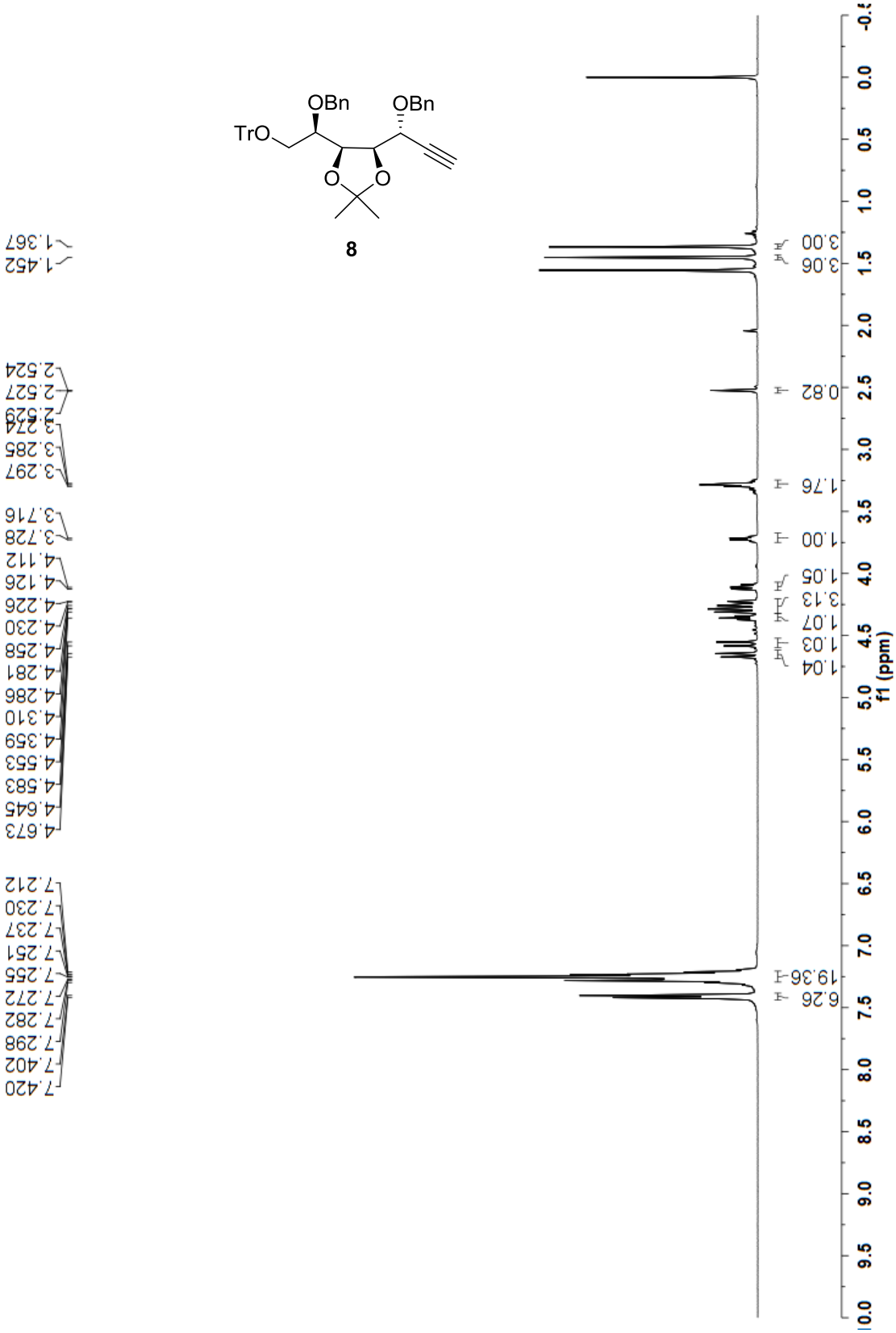
^{1}H NMR (400 MHz, $CDCl_3$) of methyl [7,8-*O*-carbonyl-4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**6**)



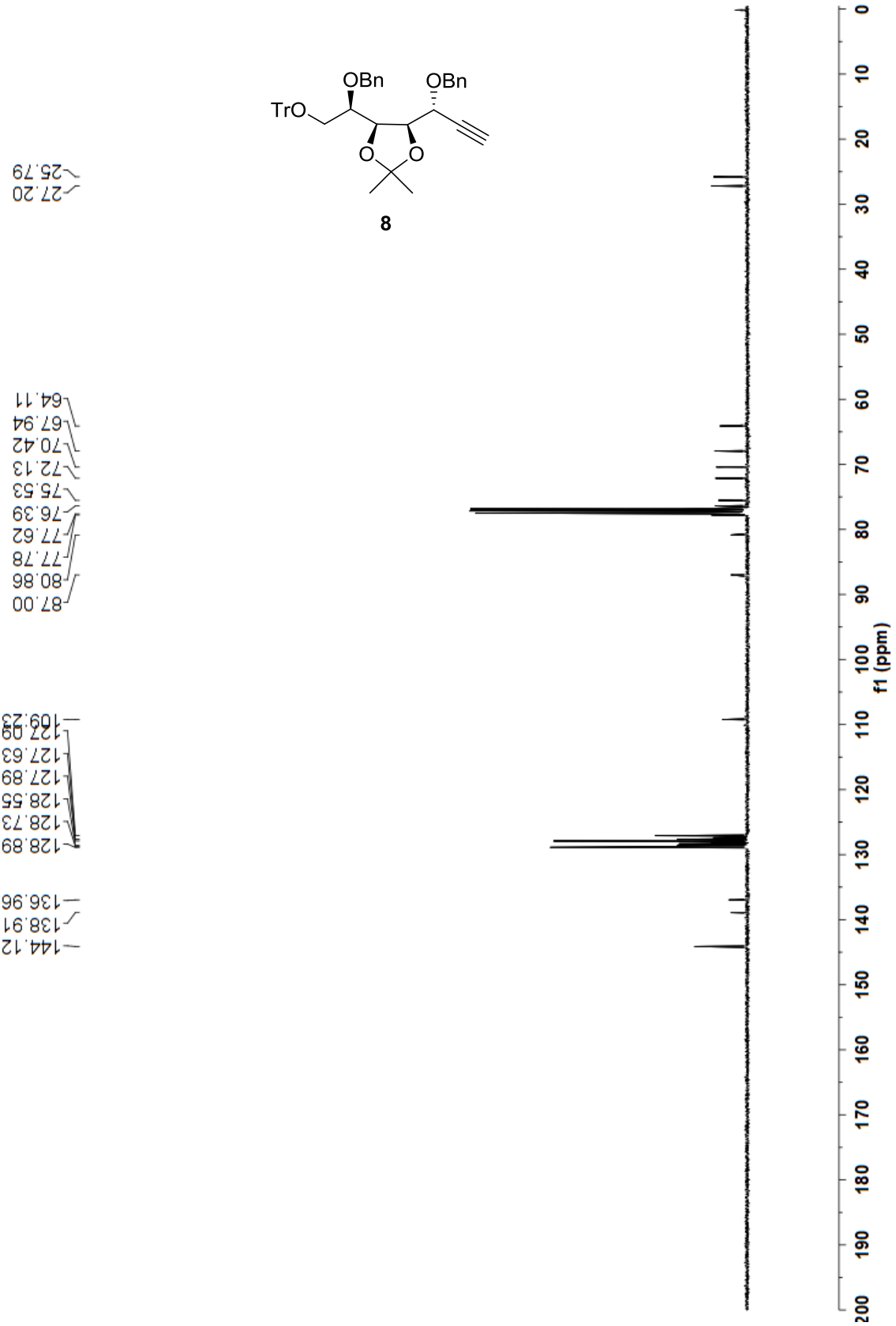
^{13}C NMR (100 MHz, $CDCl_3$) of methyl [7,8-*O*-carbonyl-4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-*α*-D-*manno*-D-*talo*-2-octulopyranosonyl]onate (**6**)



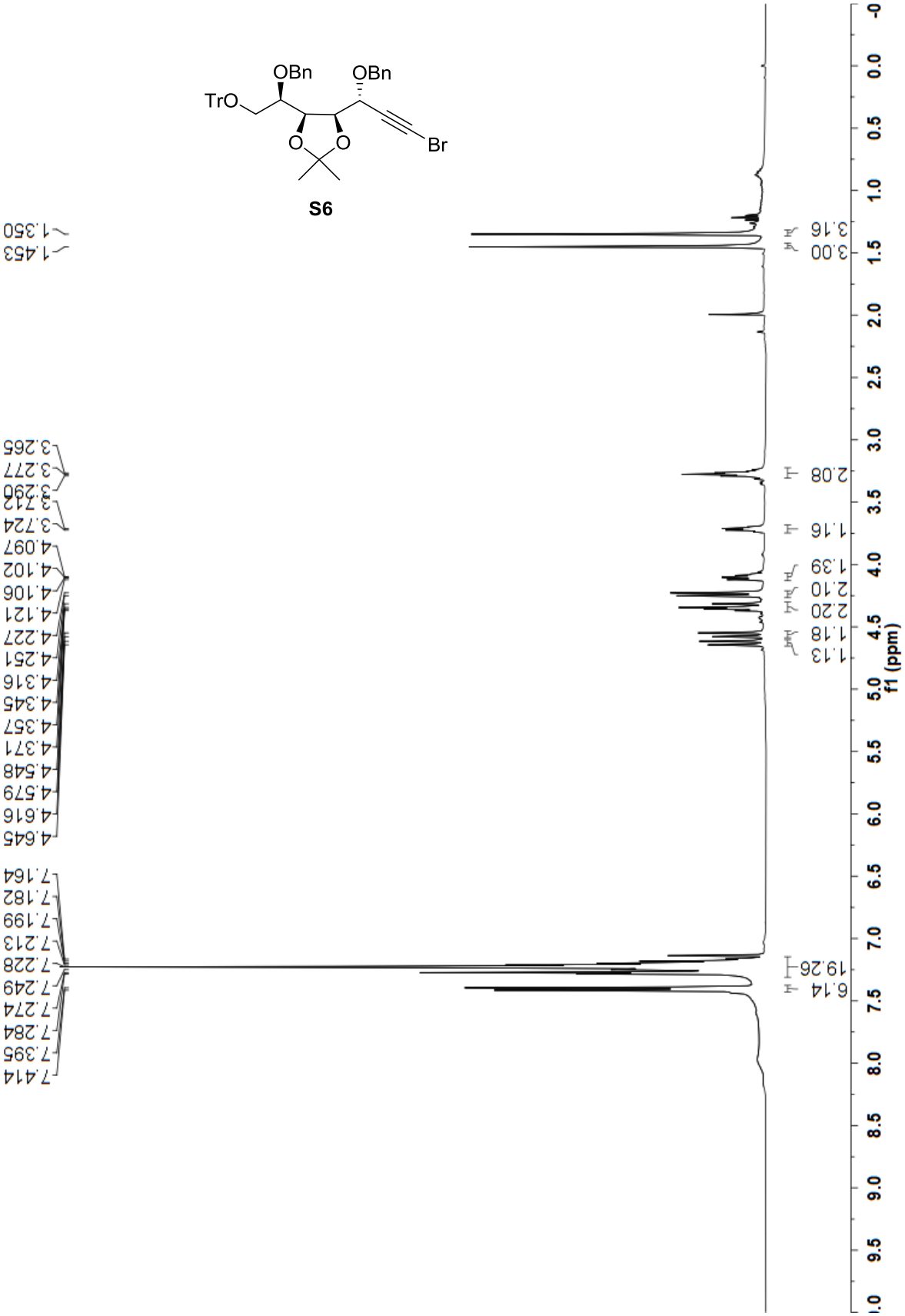
^{1}H NMR (400 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-1-yno-heptitol (**8**)



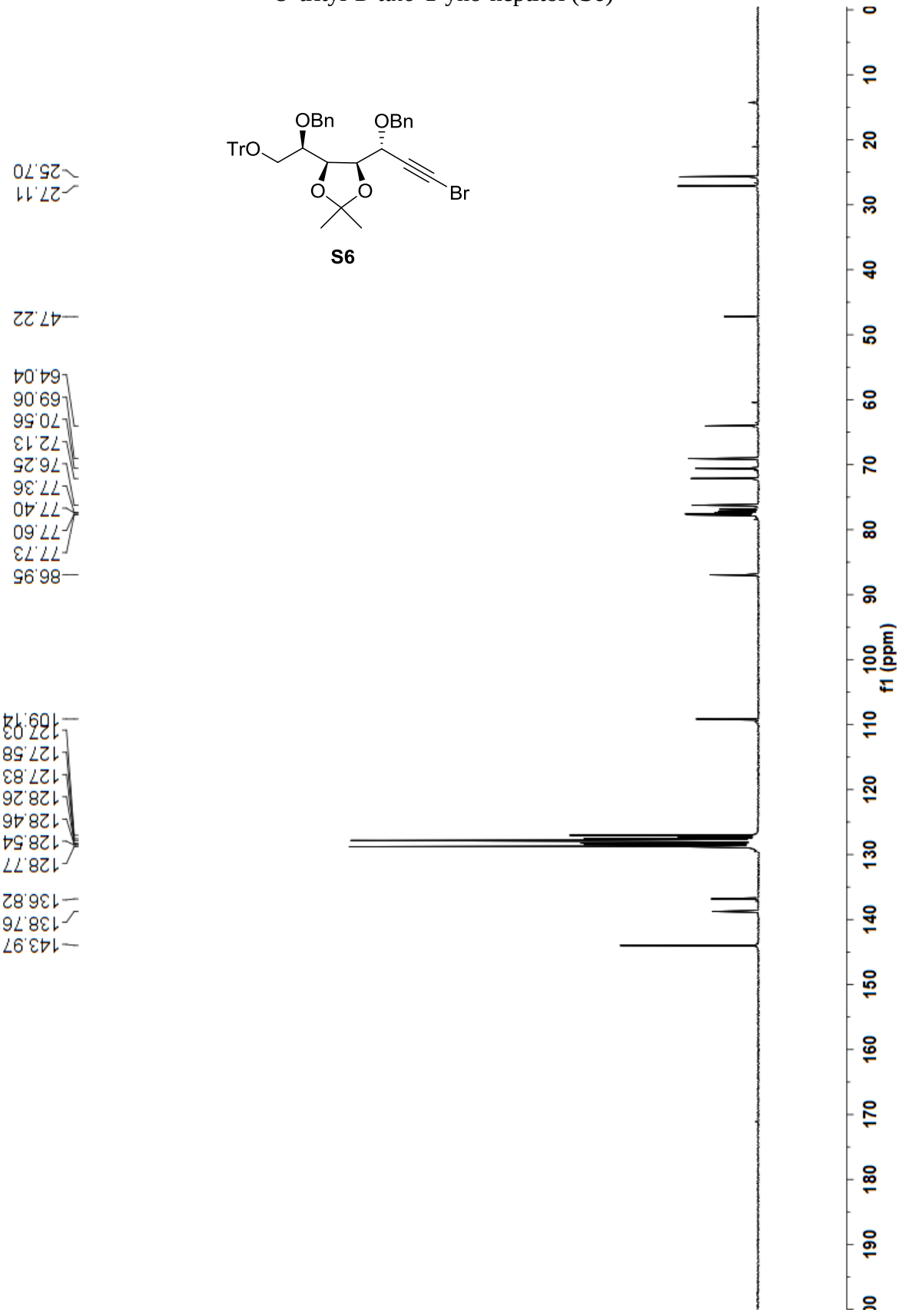
^{13}C NMR (100 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-1,2-dideoxy-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-1-yno-heptitol (**8**)



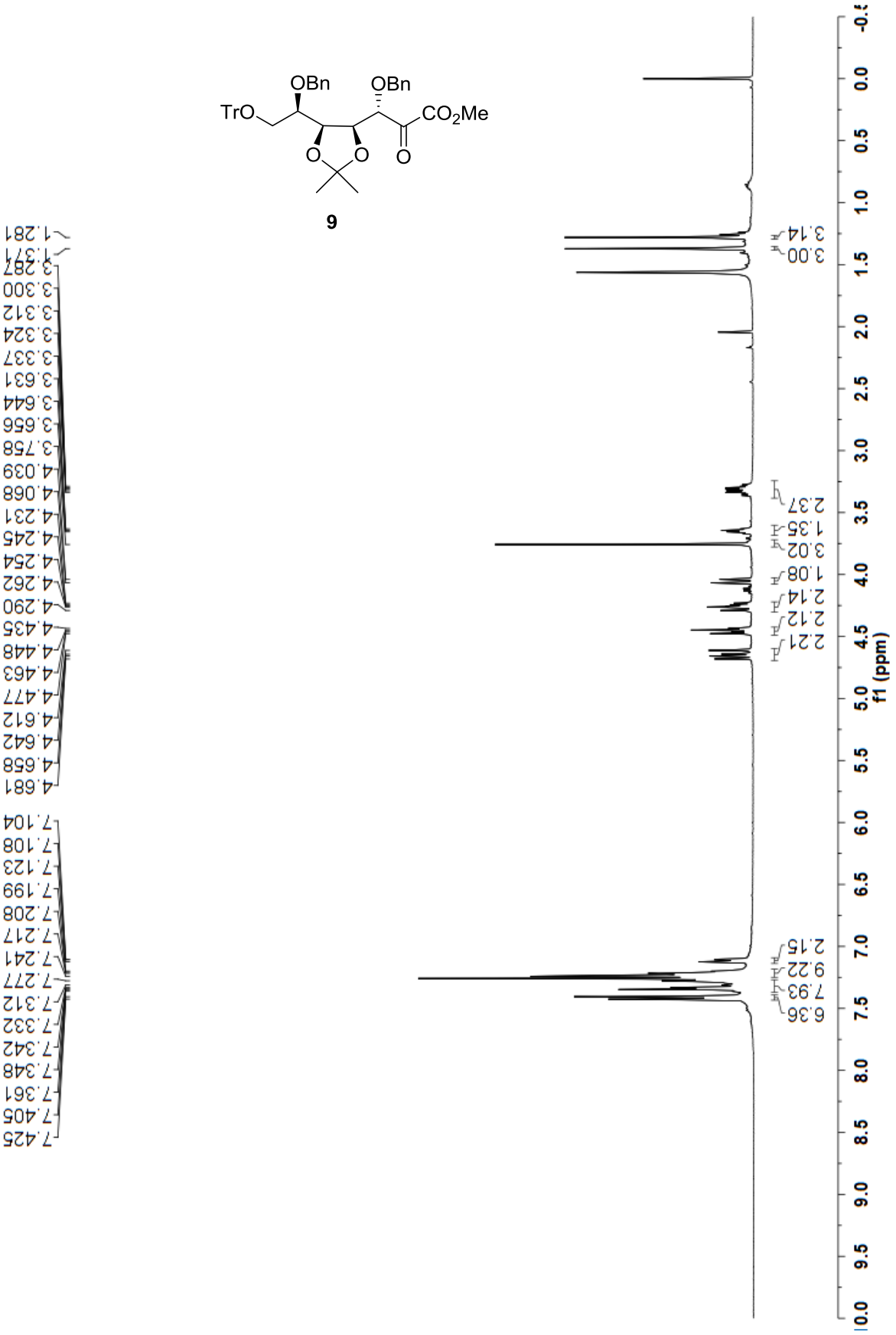
^{1}H NMR (400 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-1-bromo-1,2-dideoxy-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-1-yno-heptitol (**S6**)



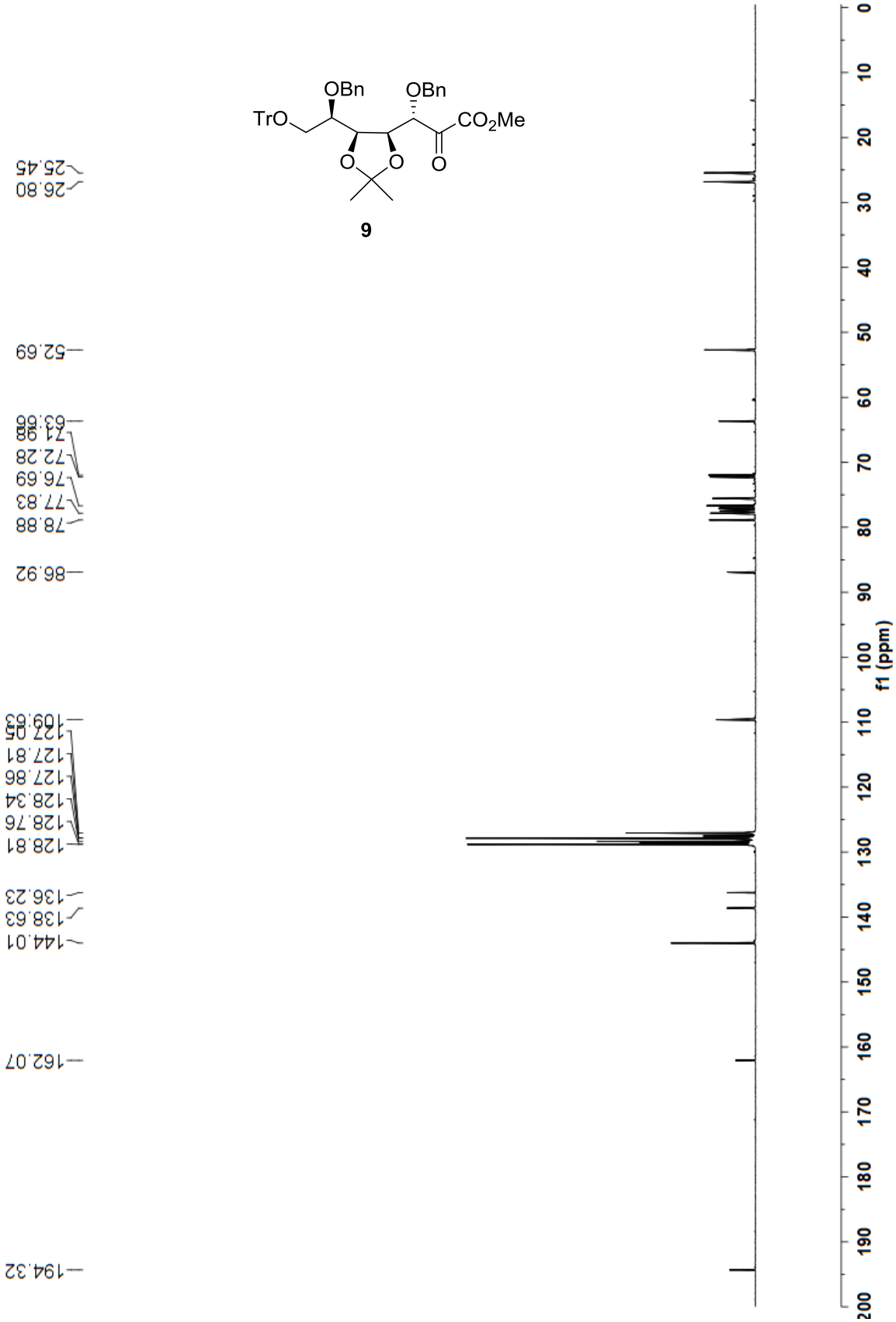
^{13}C NMR (100 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-1-bromo-1,2-dideoxy-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-1-yno-heptitol (**S6**)



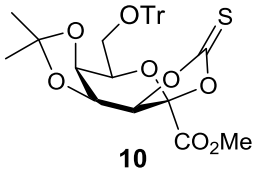
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 3,6-di-*O*-benzyl-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-hept-2-ulosonate (**9**)



^{13}C NMR (100 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-4,5-*O*-isopropylidene-7-*O*-trityl-D-*talo*-hept-2-ulosonate (**9**)

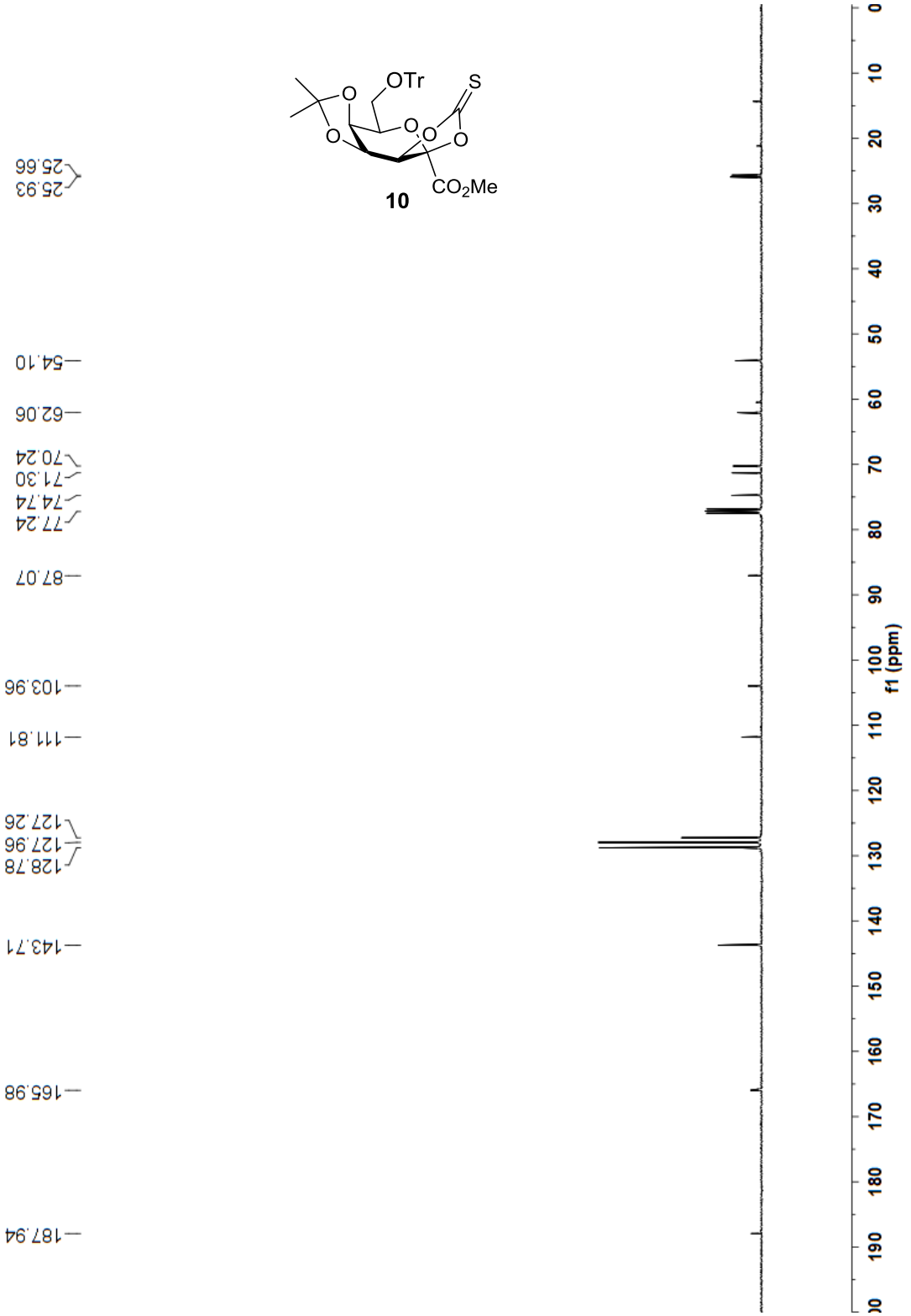


^{1}H NMR (400 MHz, $CDCl_3$) of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-7-*O*-trityl-D-*talo*-2-hept-2-ulopyranosonyl]onate (**10**)

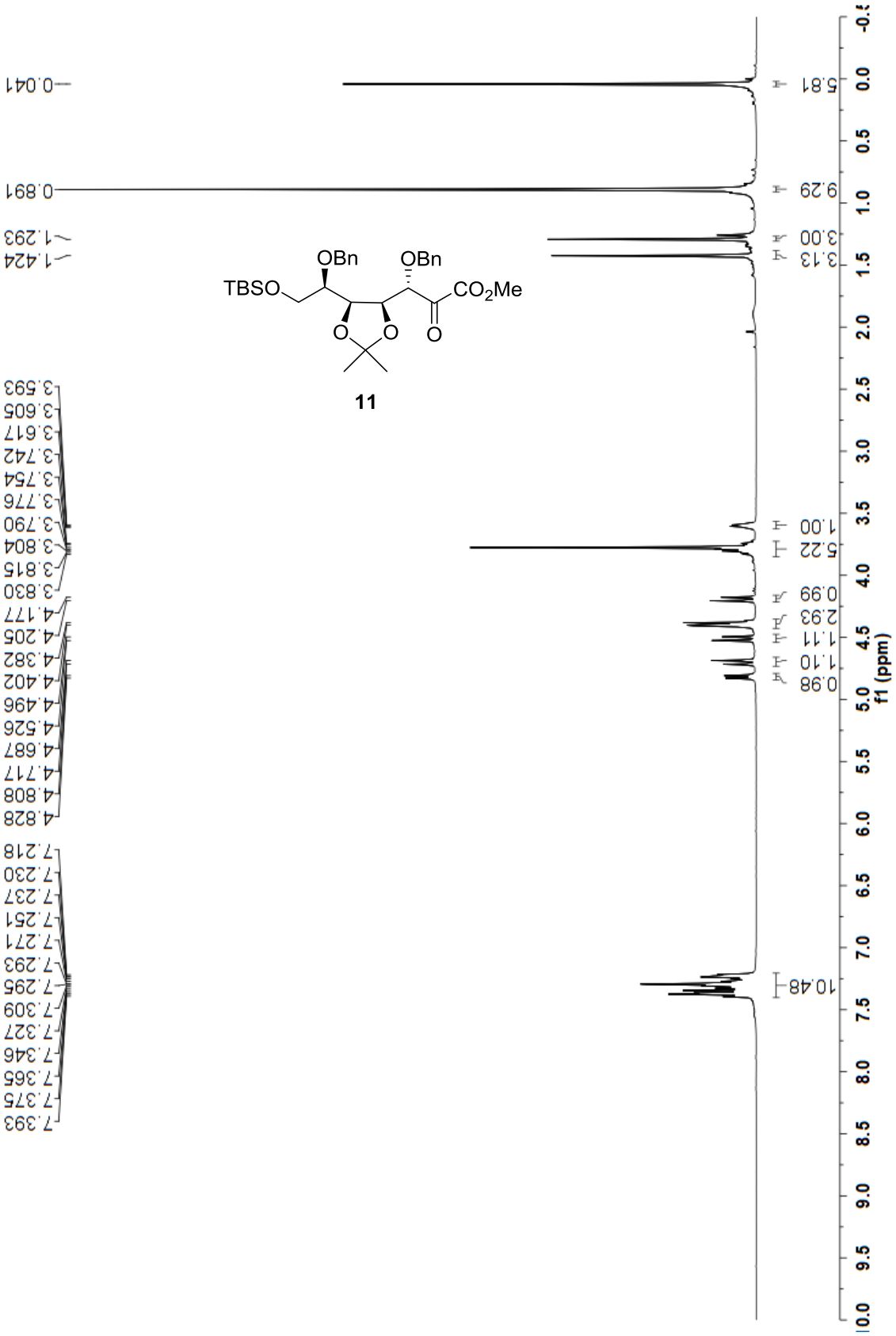


10

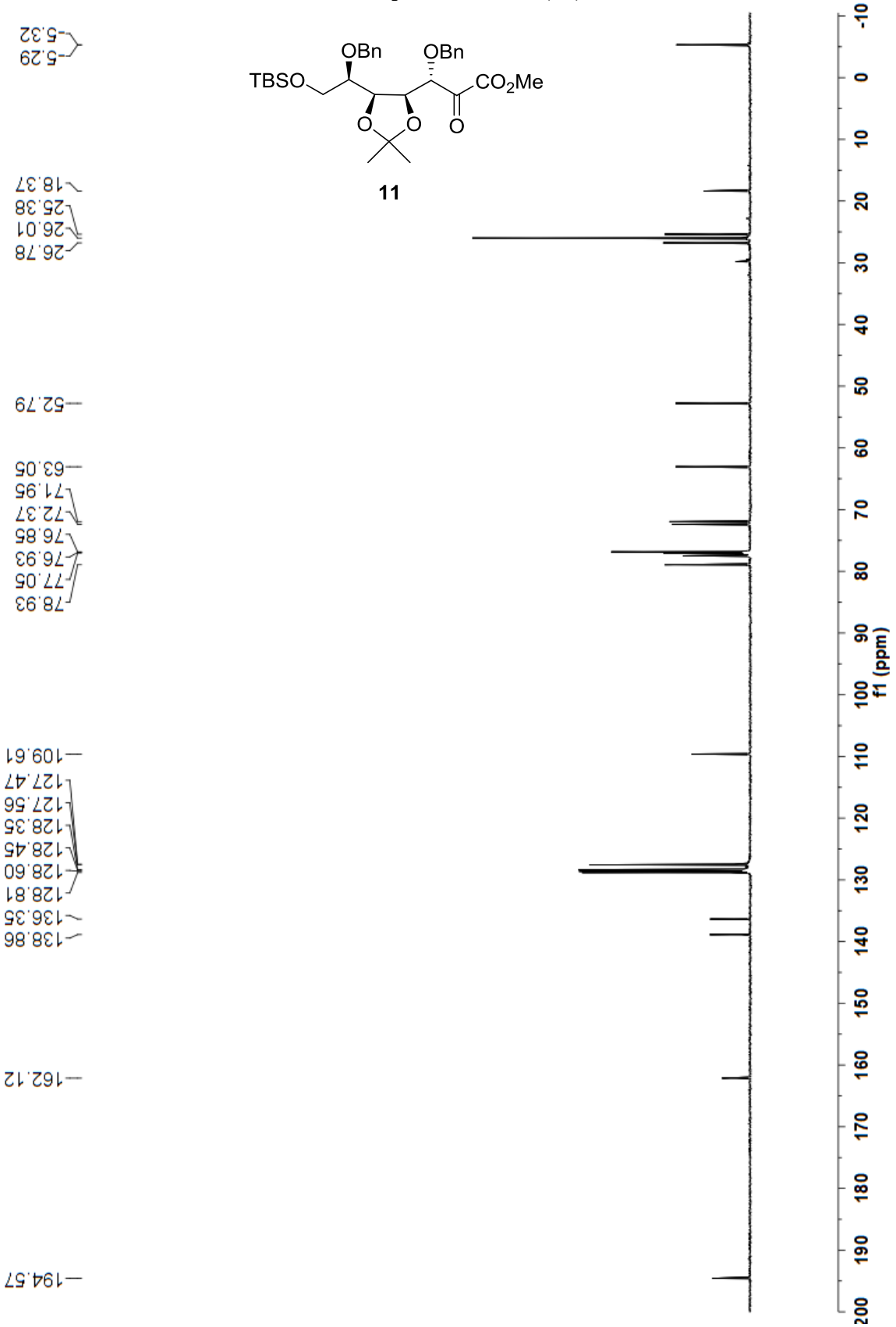
^{13}C NMR (100 MHz, $CDCl_3$) of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-7-*O*-trityl-D-*talo*-2-hept-2-ulopyranosonyl]onate (**10**)



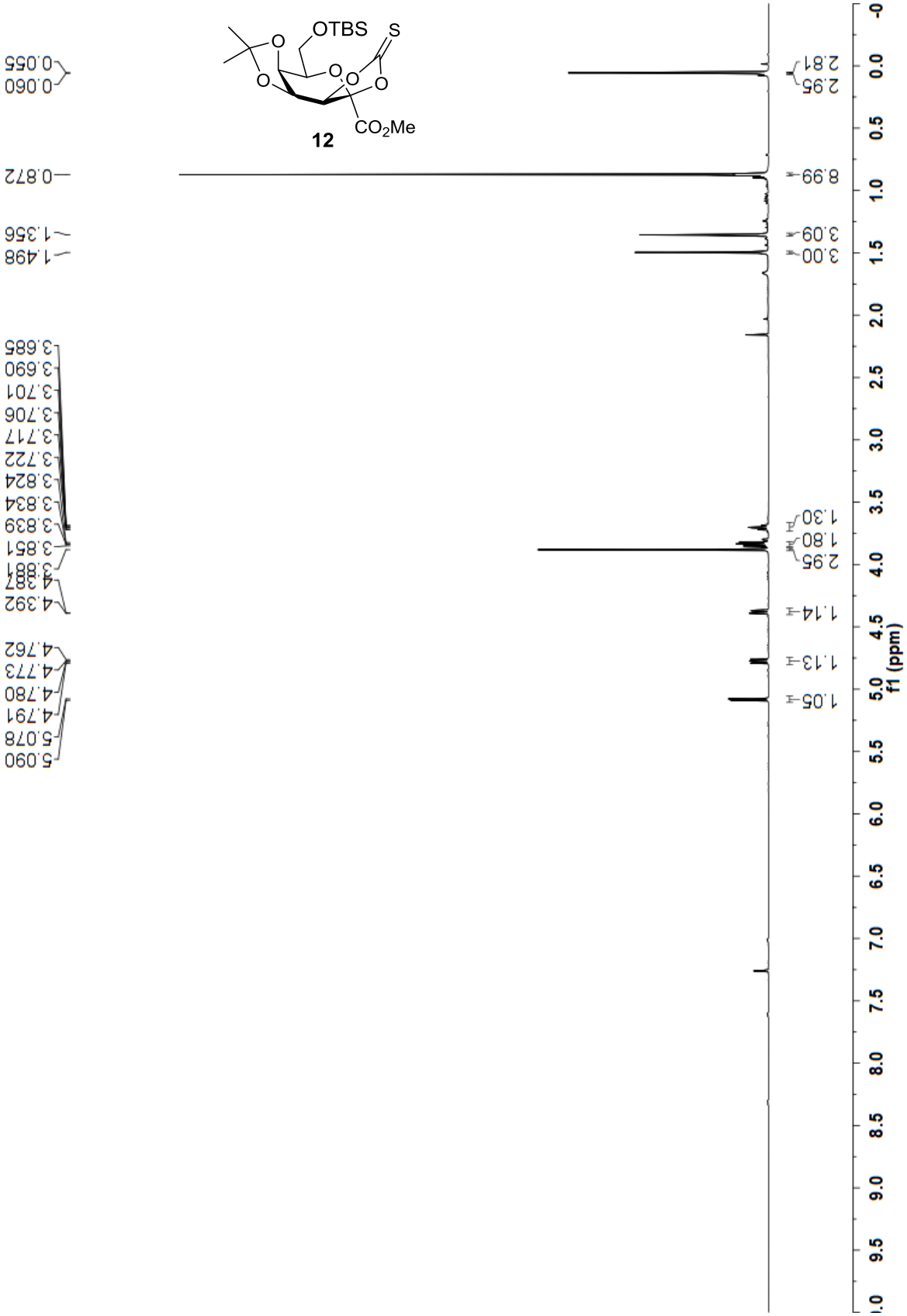
^{1}H NMR (400 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-4,5-*O*-isopropylidene-7-*O*-*t*butyldimethylsilyl-D-*talo*-hept-2-ulosonate (**11**)



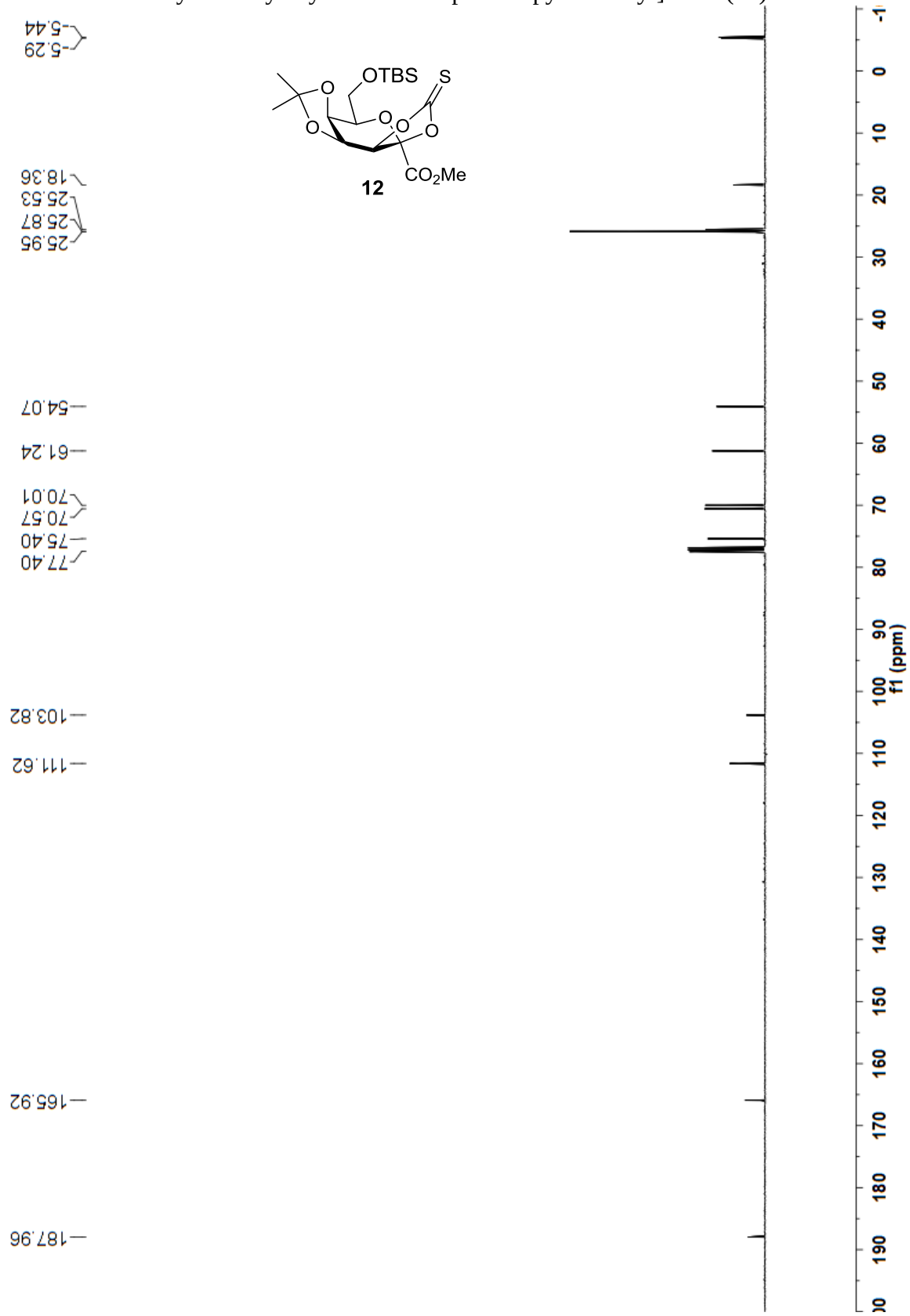
^{13}C NMR (100 MHz, $CDCl_3$) of 3,6-di-*O*-benzyl-4,5-*O*-isopropylidene-7-*O*-*t*butyldimethylsilyl-D-*talo*-hept-2-ulosonate (**11**)



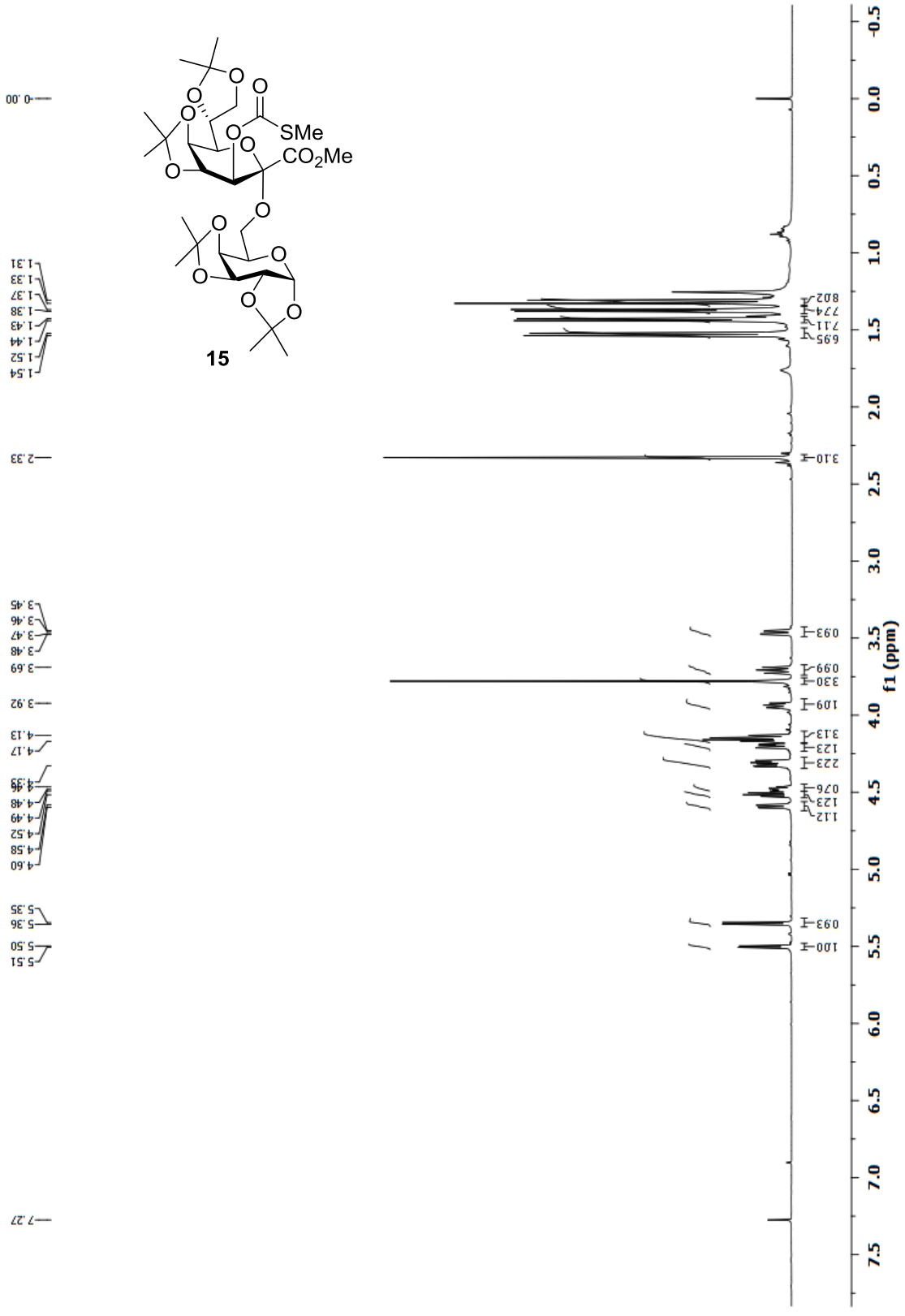
^{1}H NMR (400 MHz, $CDCl_3$) of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-7-*O*-*t*butyldimethylsilyl-D-*talo*-2-hept-2-ulopyranosonyl]onate (**12**)



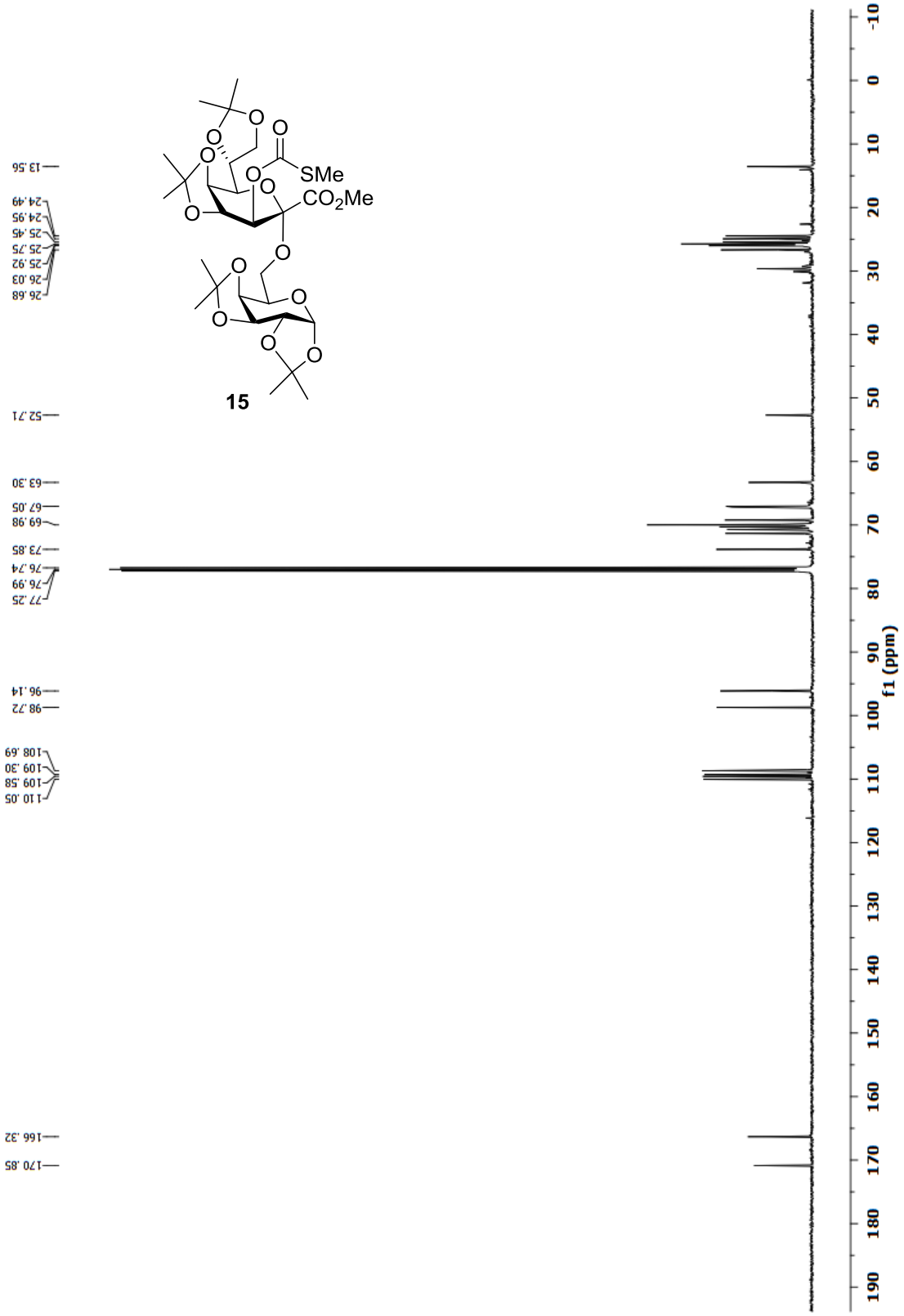
^{13}C NMR (100 MHz, $CDCl_3$) of methyl [4,5-*O*-isopropylidene-2,3-*O*-thionocarbonyl-7-*O*-*t*butyldimethylsilyl-D-*talo*-2-hept-2-ulopyranosonyl]onate (**12**)



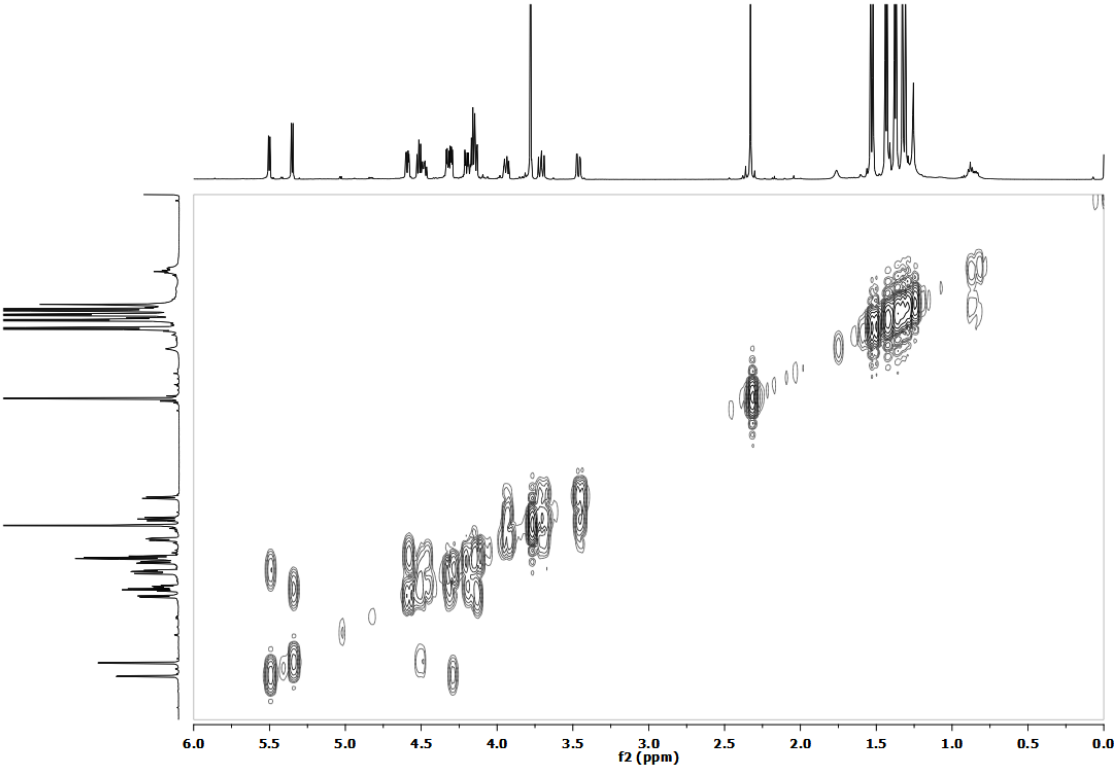
^{1}H NMR (500 MHz, $CDCl_3$) of 1,2:3,4-di-*O*-isopropylidene-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(methylthiocarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-galactopyranoside (**15**)



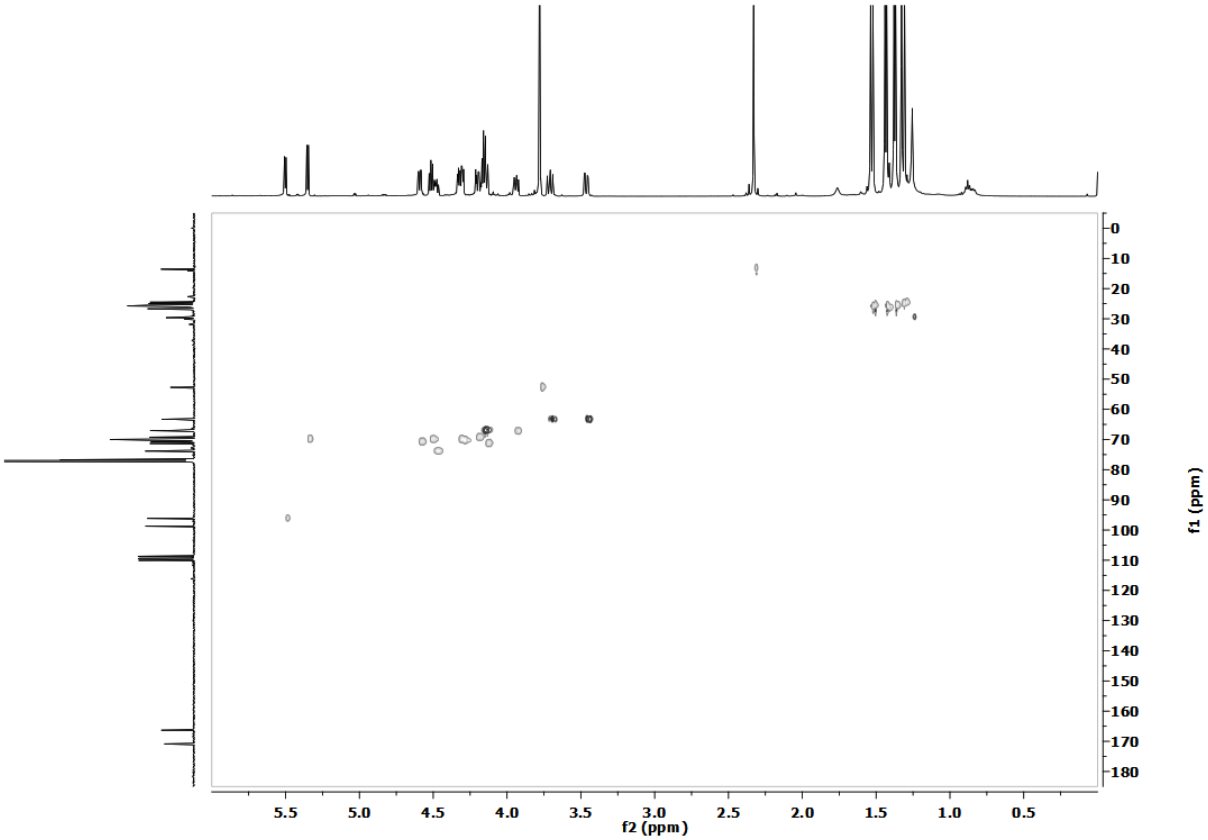
^{13}C NMR (125 MHz, $CDCl_3$) of 1,2:3,4-di-*O*-isopropylidene-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(methylthiocarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-galactopyranoside **(15)**



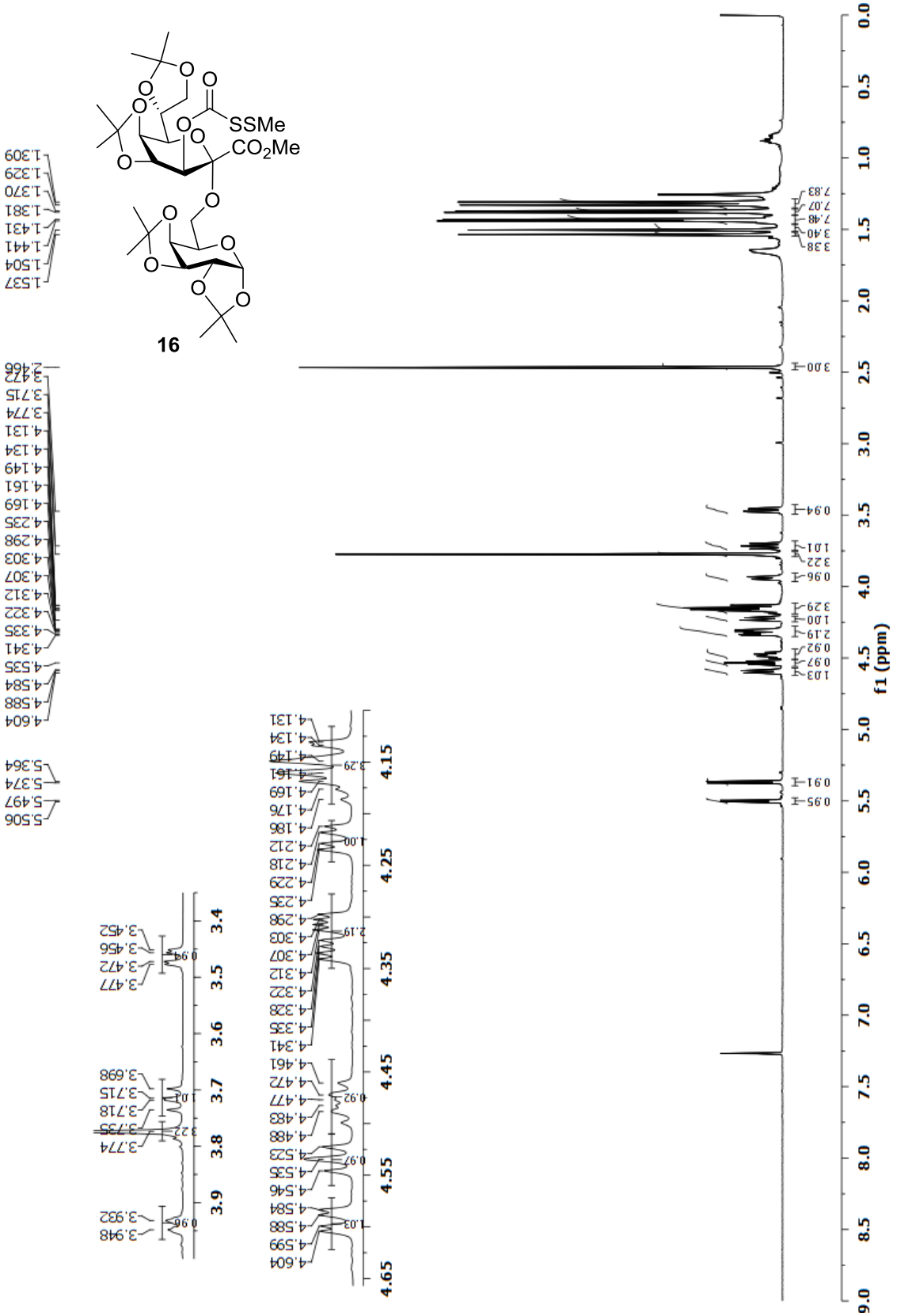
^{1}H-^{1}H GCOSY NMR (500 MHz, $CDCl_3$) of disaccharide (**15**)



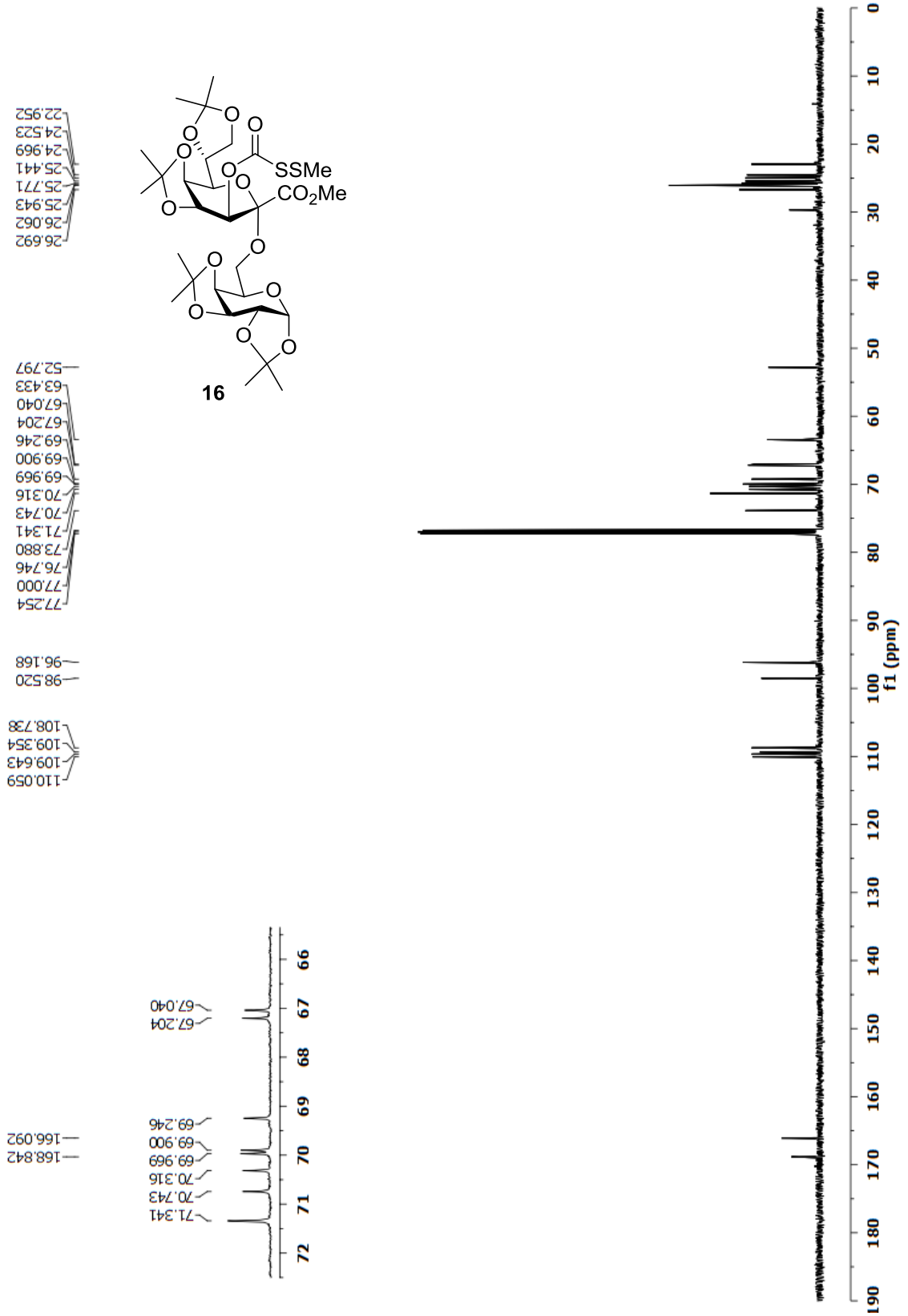
^{1}H-^{13}C HSQC NMR (125 MHz, $CDCl_3$) of disaccharide (**15**)



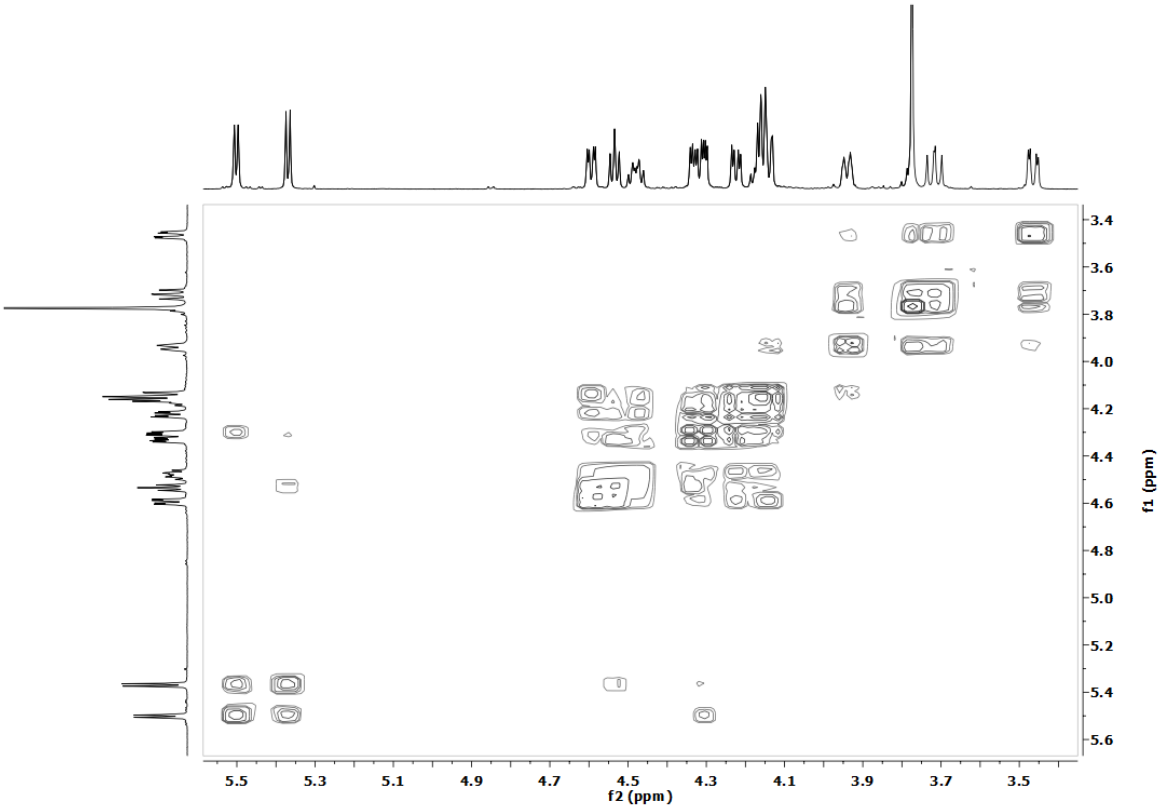
^{1}H NMR (500 MHz, $CDCl_3$) of 1,2:3,4-di-*O*-isopropylidene-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-galactopyranoside (**16**)



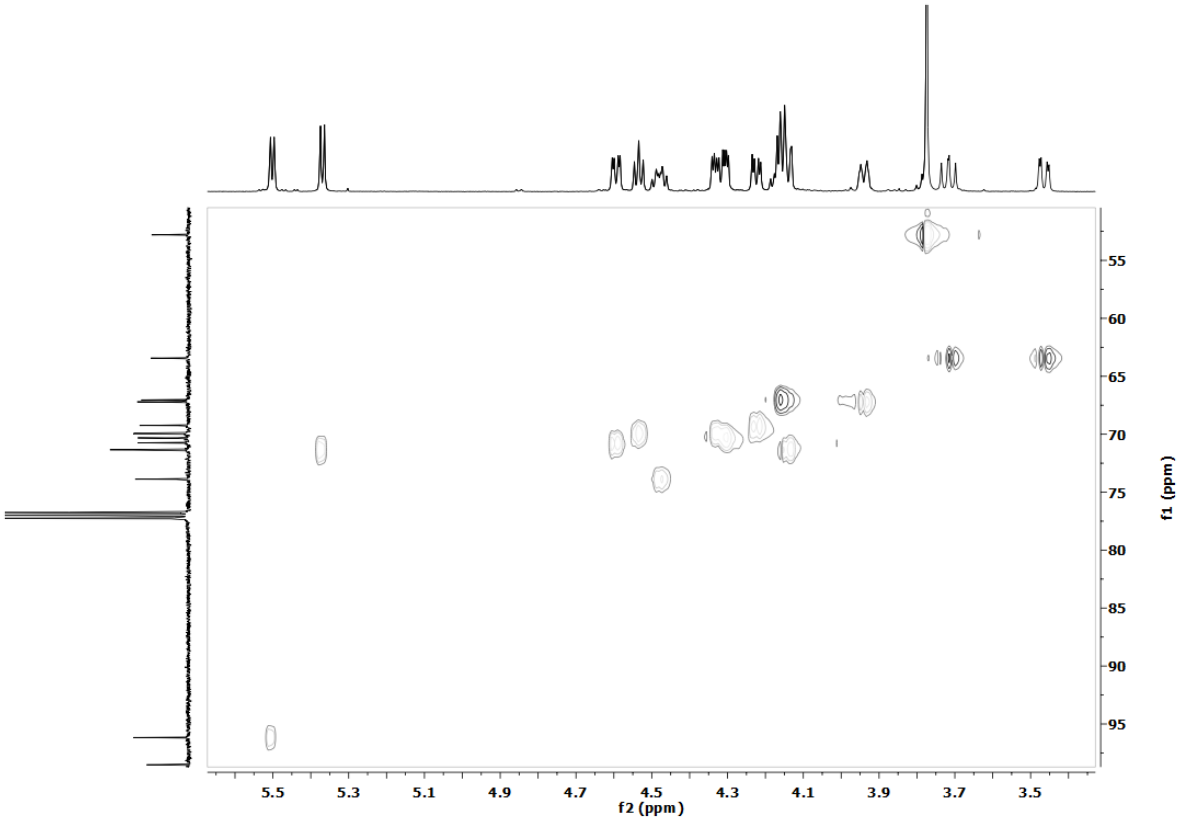
^{13}C NMR (125 MHz, $CDCl_3$) of 1,2:3,4-di-*O*-isopropylidene-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-galactopyranoside (**16**)



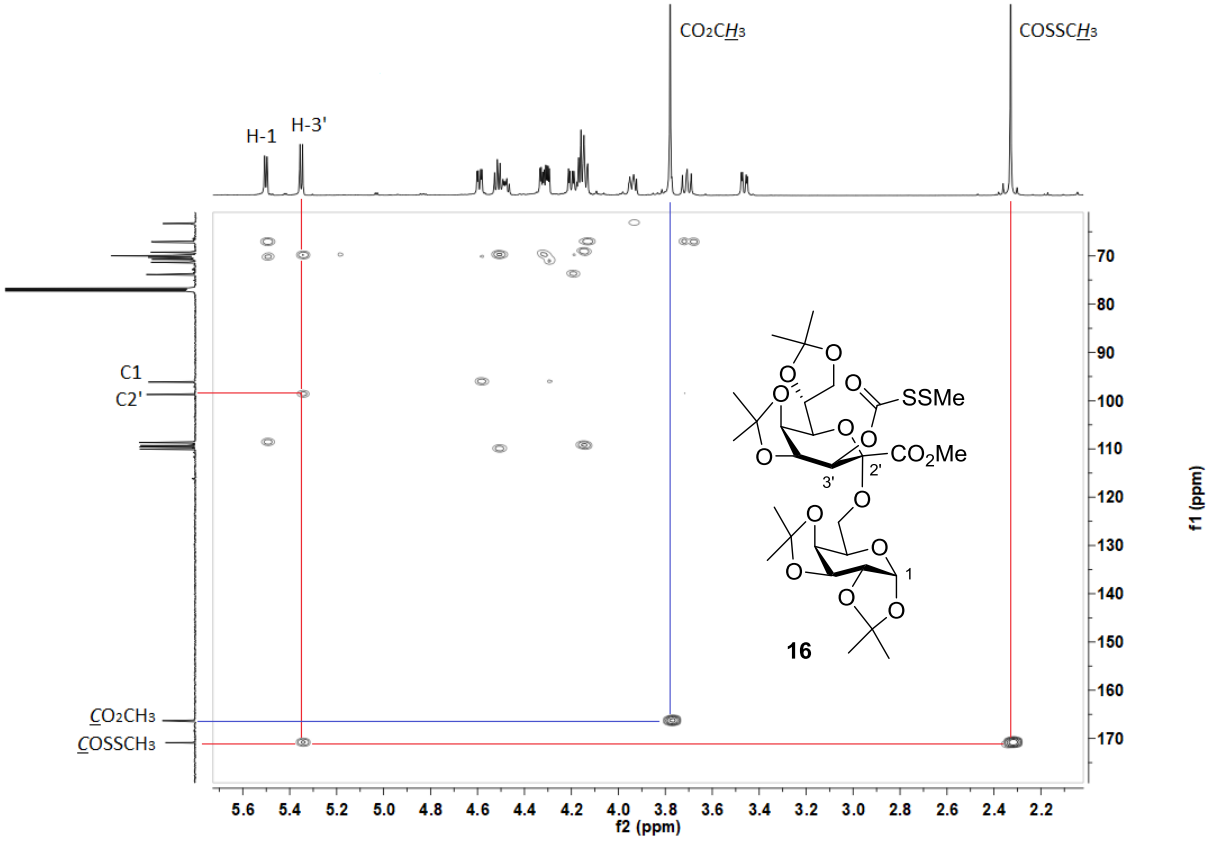
^{1}H-^{1}H GCOSY NMR (500 MHz, $CDCl_3$) of disaccharide (**16**)



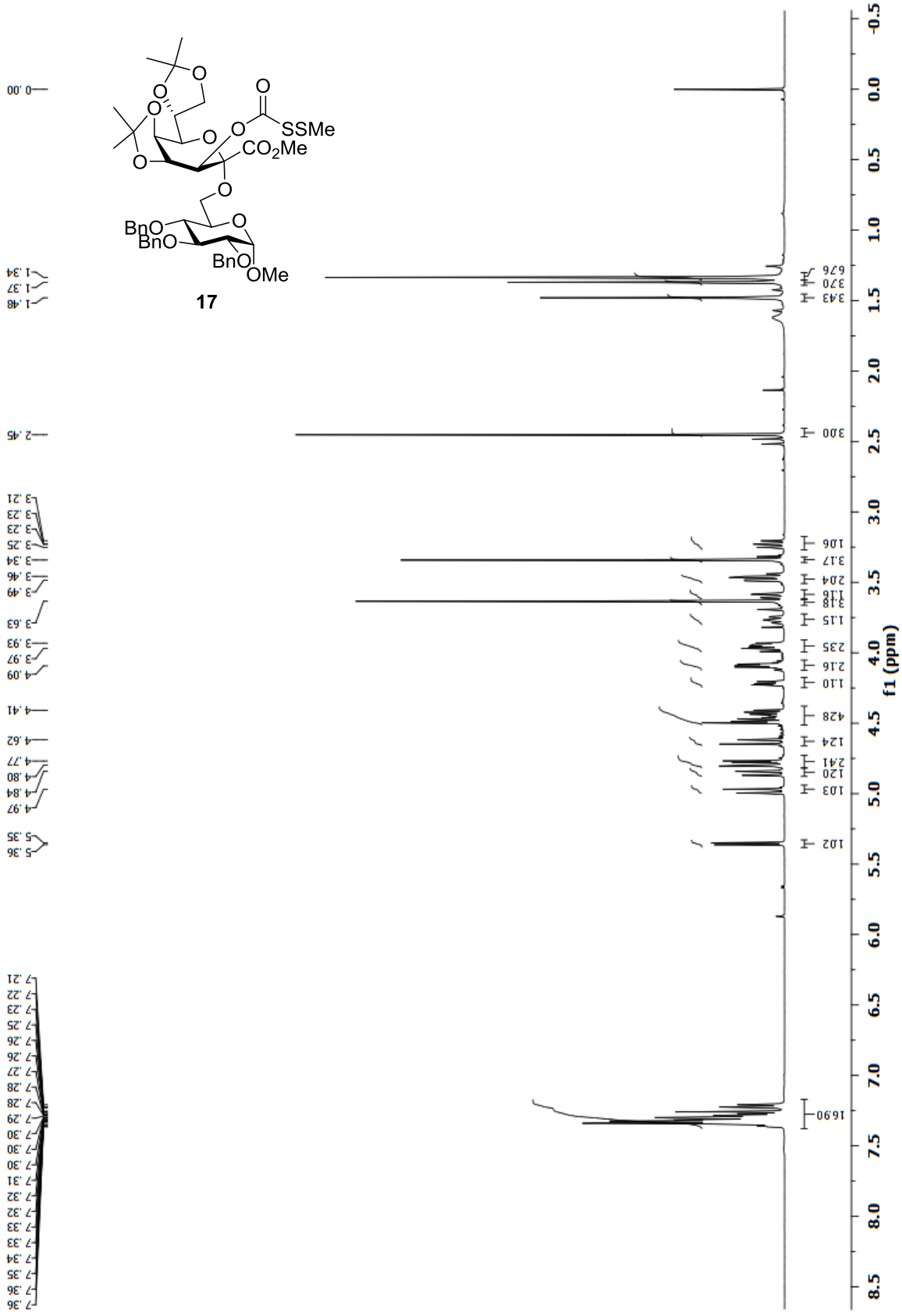
^{1}H-^{13}C HSQC NMR (125 MHz, $CDCl_3$) of disaccharide **16**



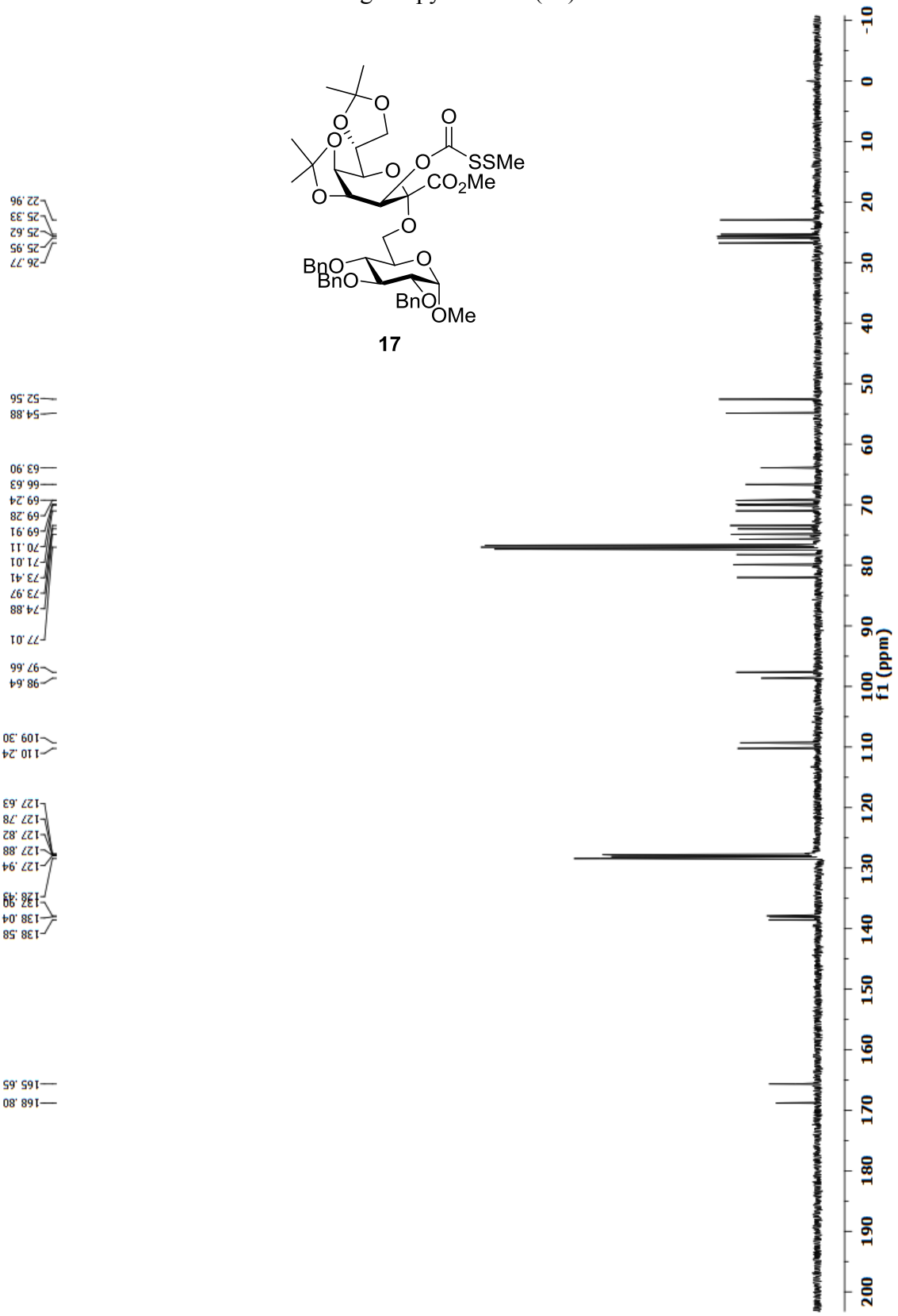
^{1}H-^{13}C HMBC NMR (125 MHz, $CDCl_3$) of disaccharide (**16**)



^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**17**)

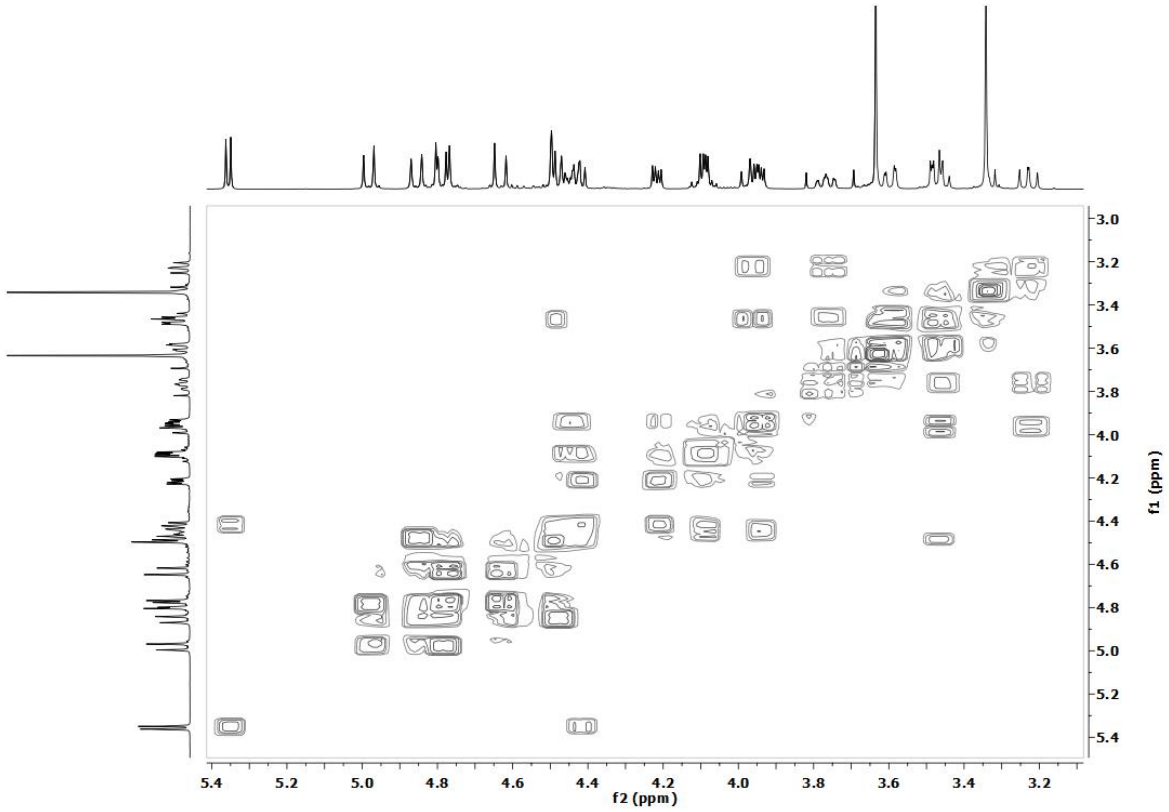


^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-**t**ri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**17**)

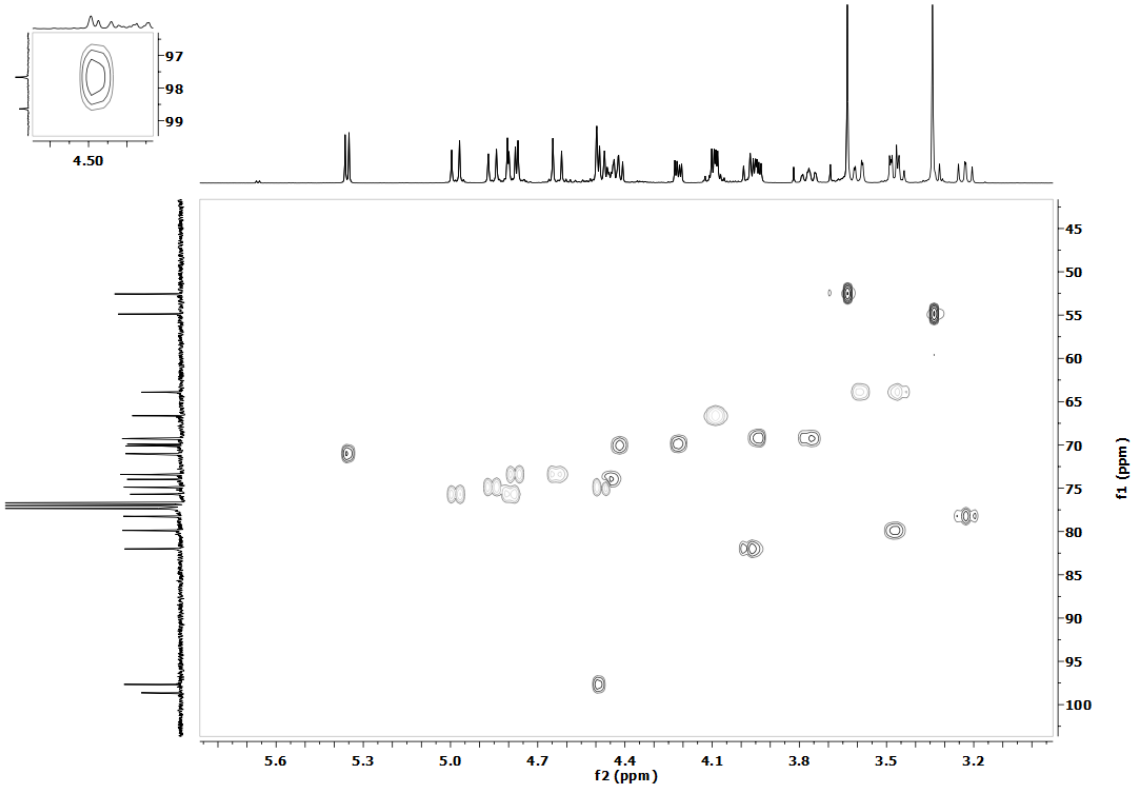


17

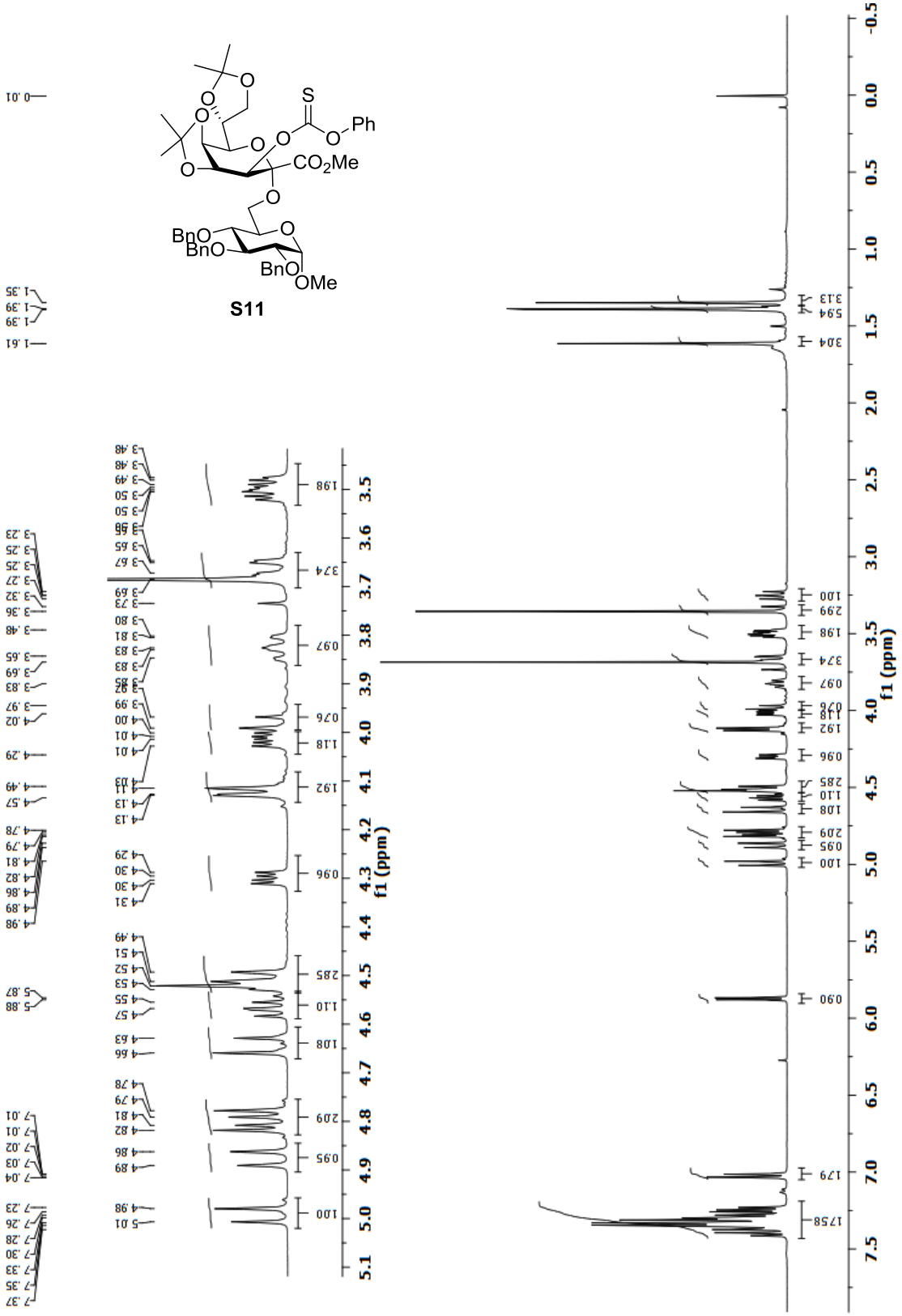
^{1}H-^{1}H GCOSY NMR (400 MHz, $CDCl_3$) of disaccharide **17**



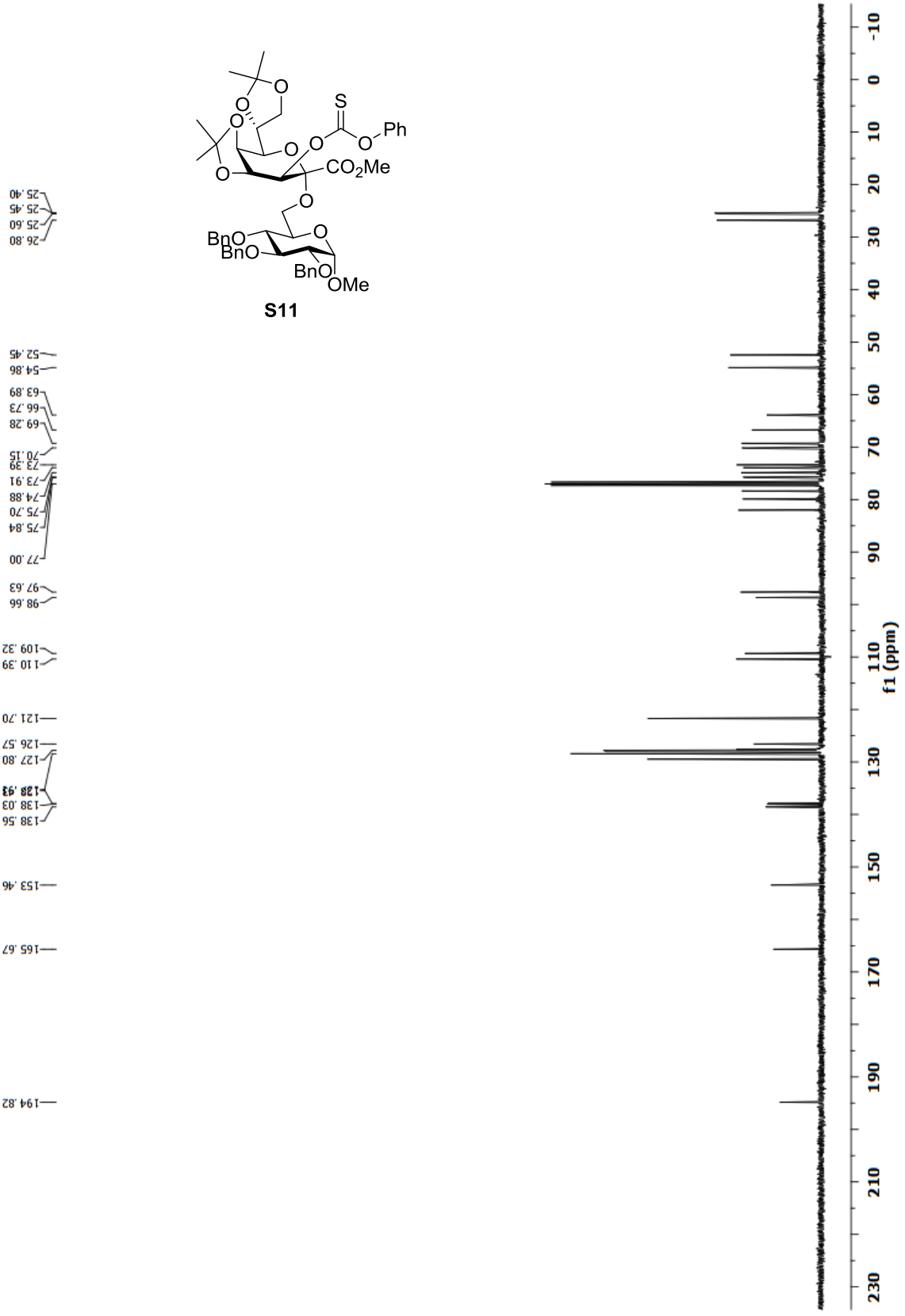
^{1}H-^{13}C HMQC NMR (100 MHz, $CDCl_3$) of disaccharide **17**



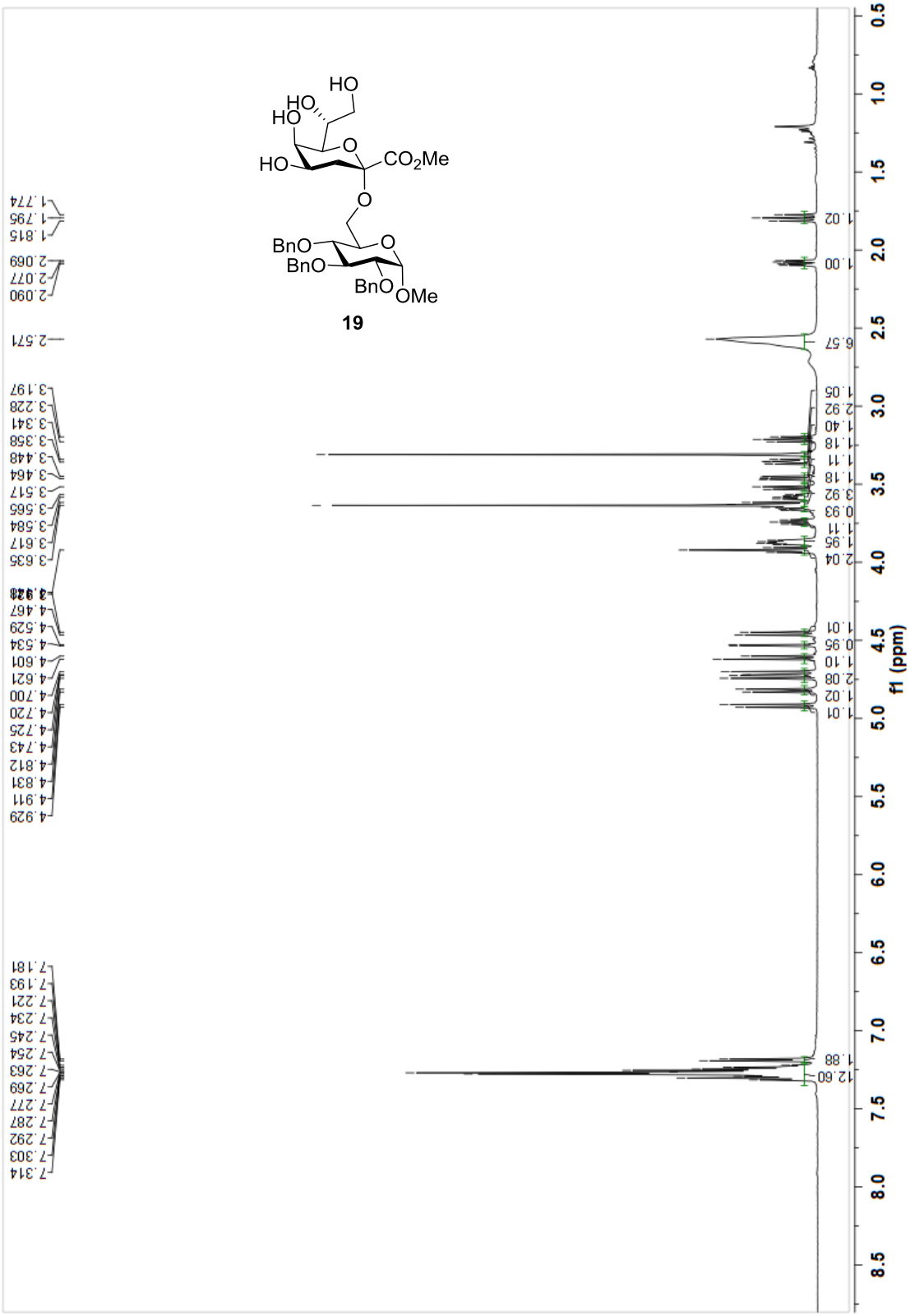
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-phenoxylthiocarbonyl-D-glycero-*α*-D-talo-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**S11**)



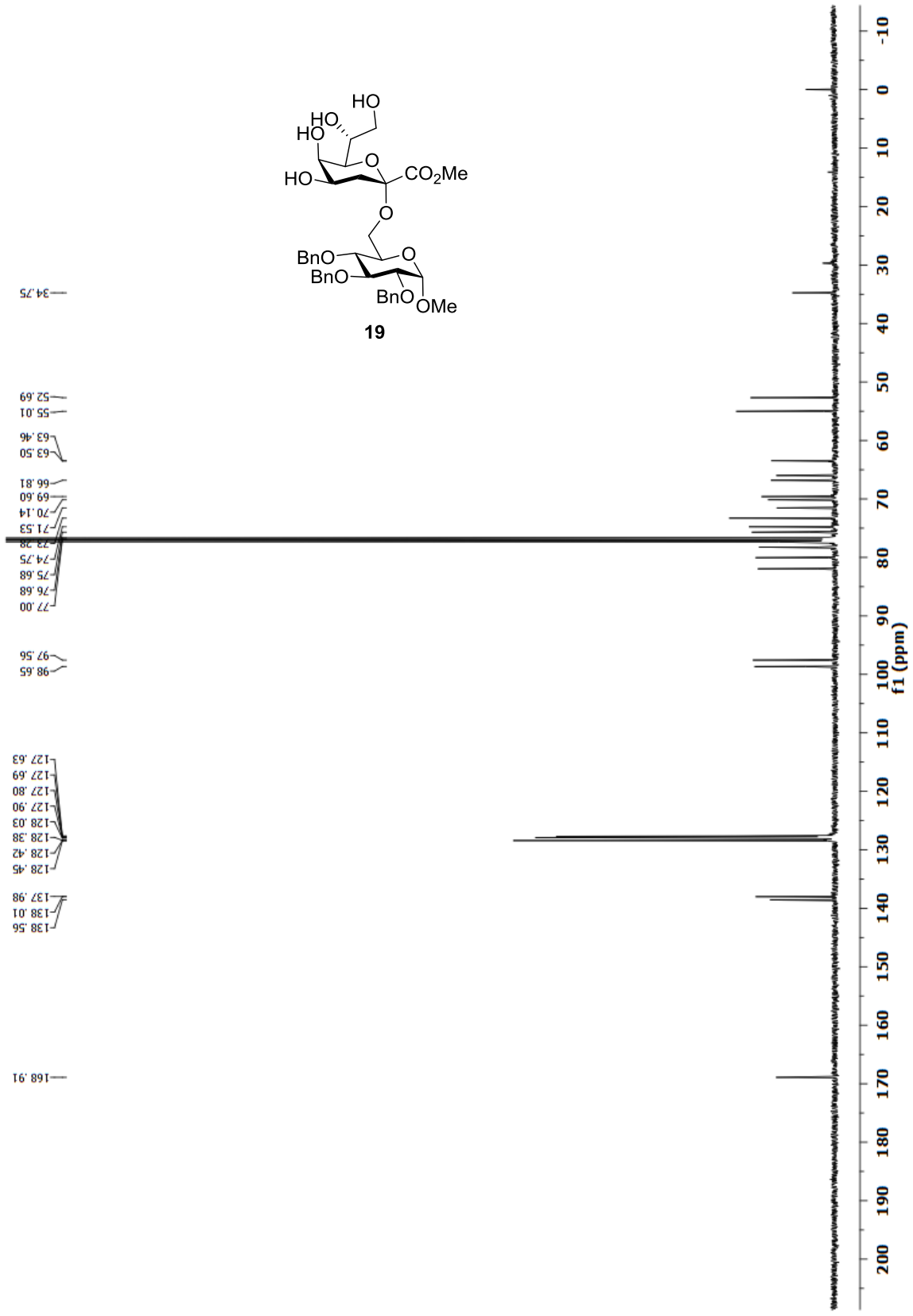
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-phenoxythiocarbonyl-D-glycero-*α*-D-talo-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**S11**)



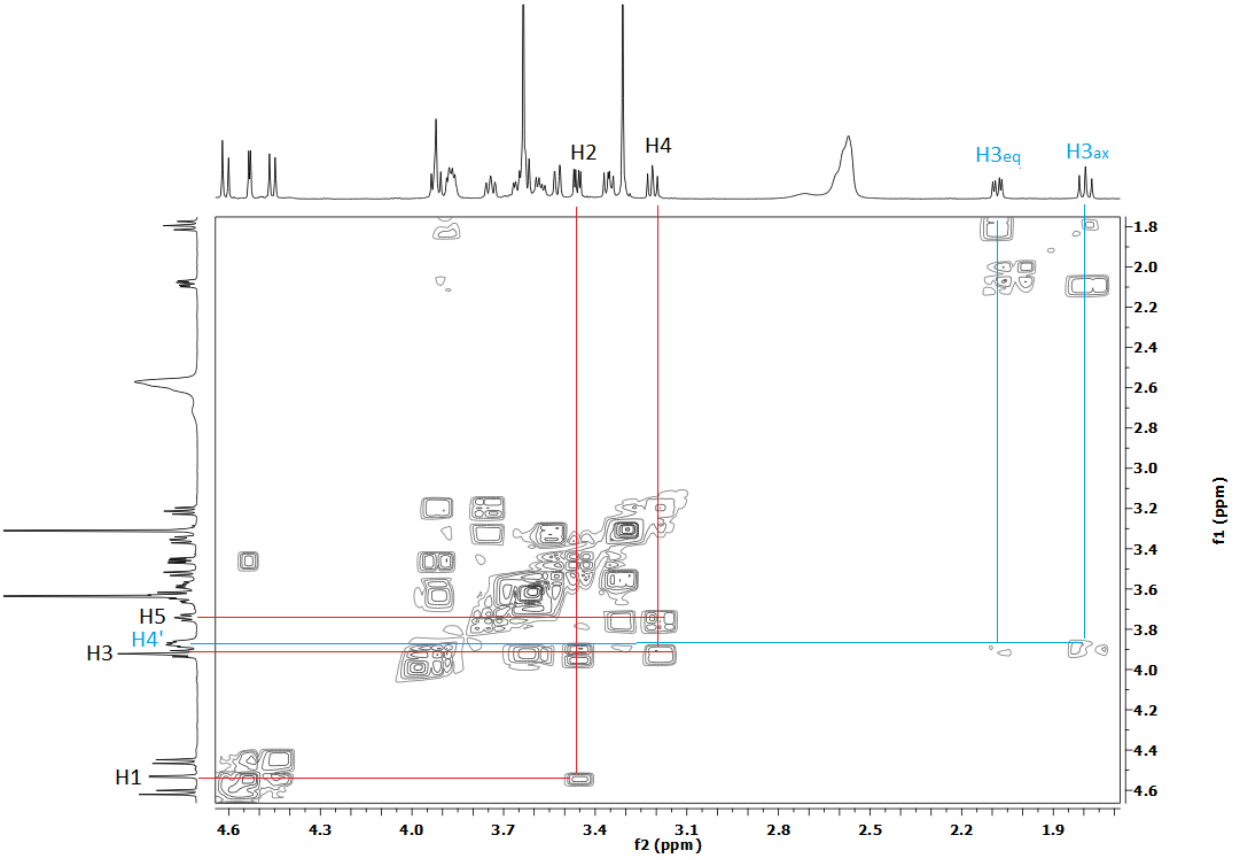
^{1}H NMR (600 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (3-deoxy-α-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**19**)



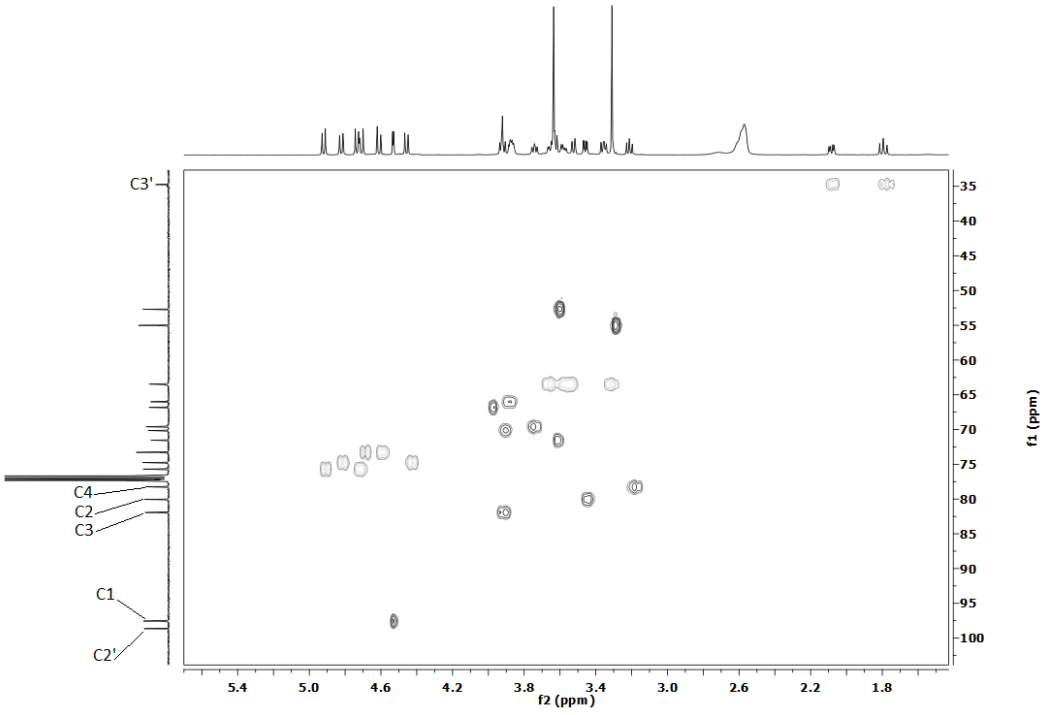
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**19**)



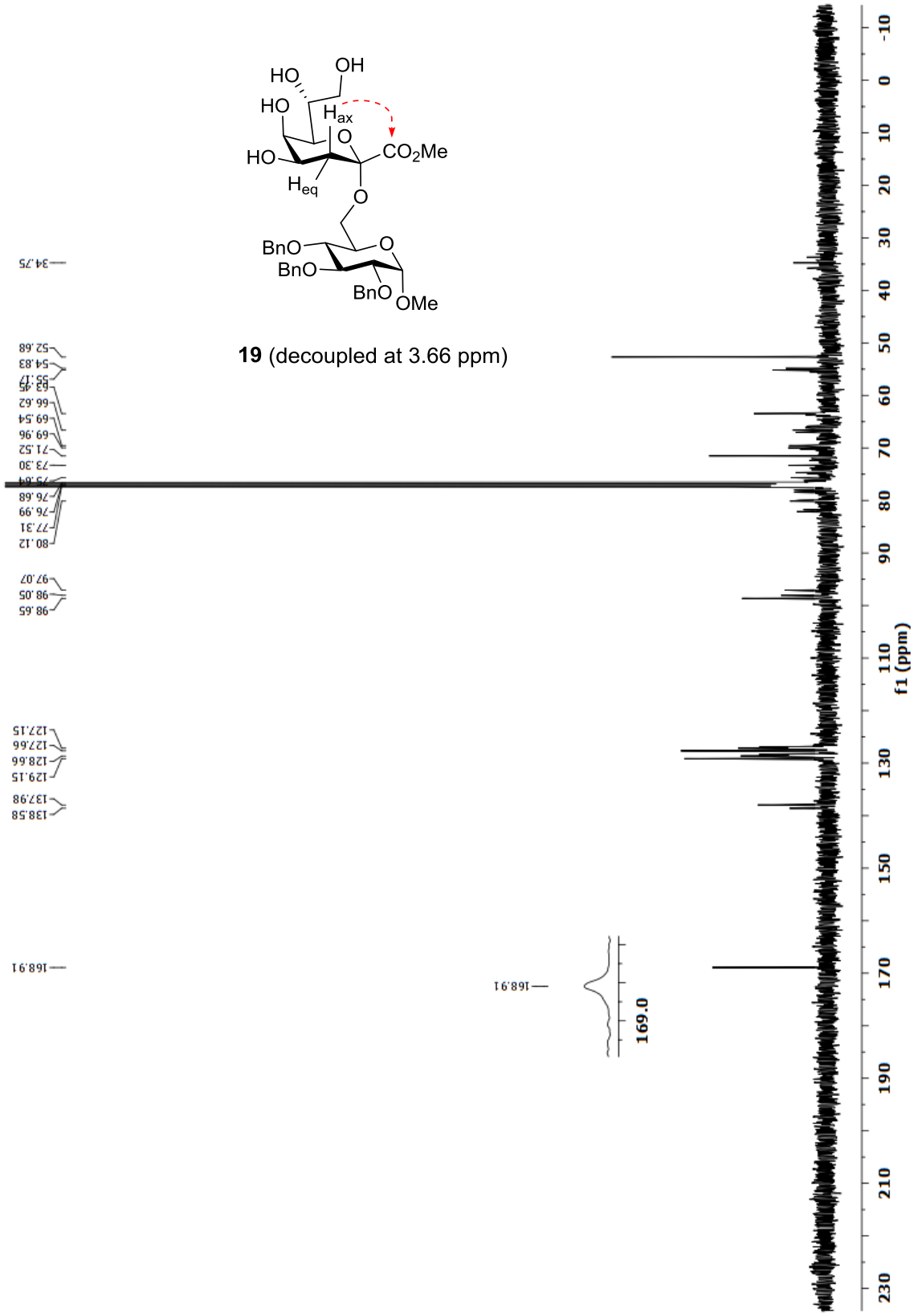
^{1}H-^{1}H GCOSY NMR (400 MHz, $CDCl_3$) of disaccharide (**19**)



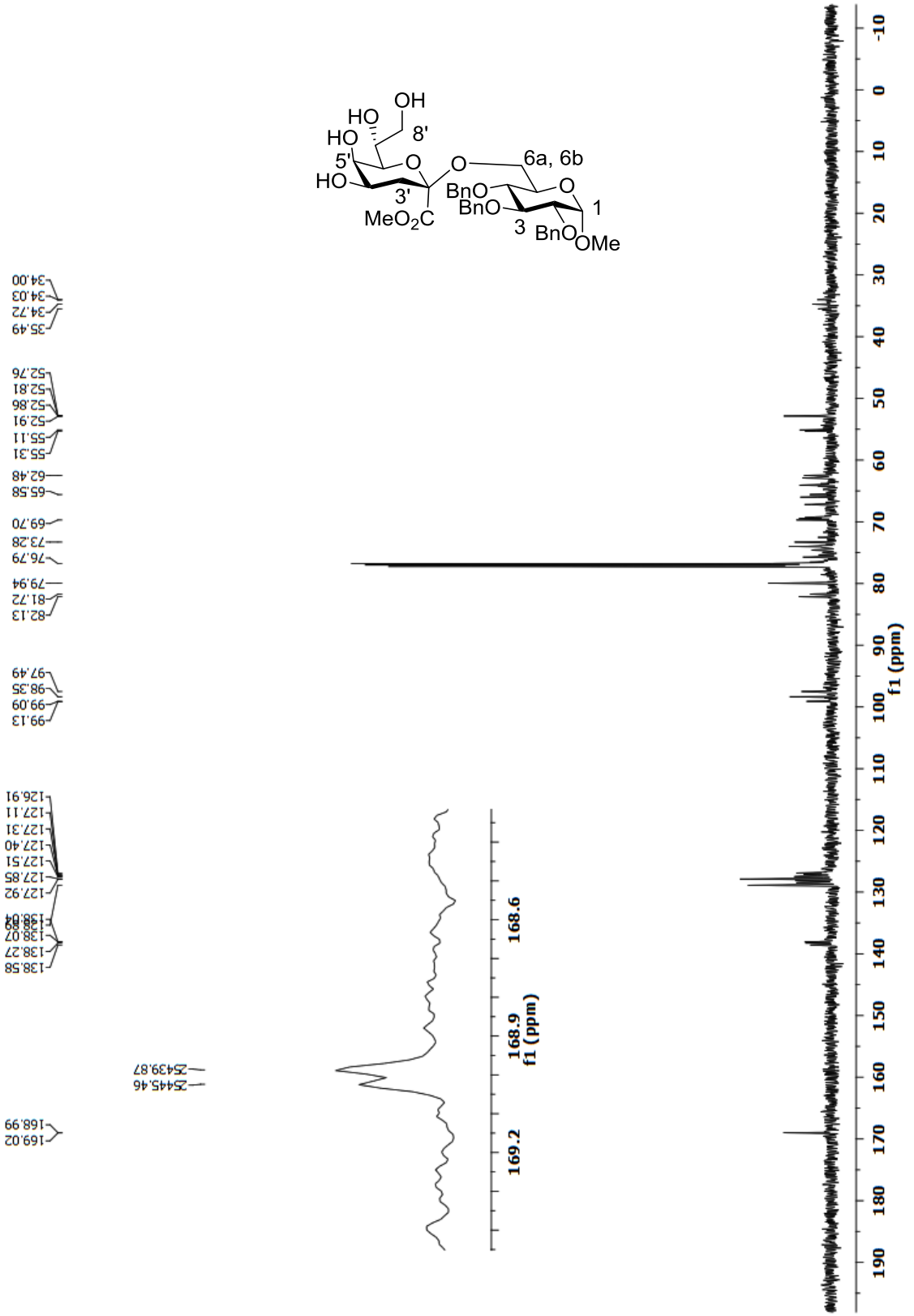
^{1}H-^{13}C HMQC NMR (100 MHz, $CDCl_3$) of disaccharide (**19**)



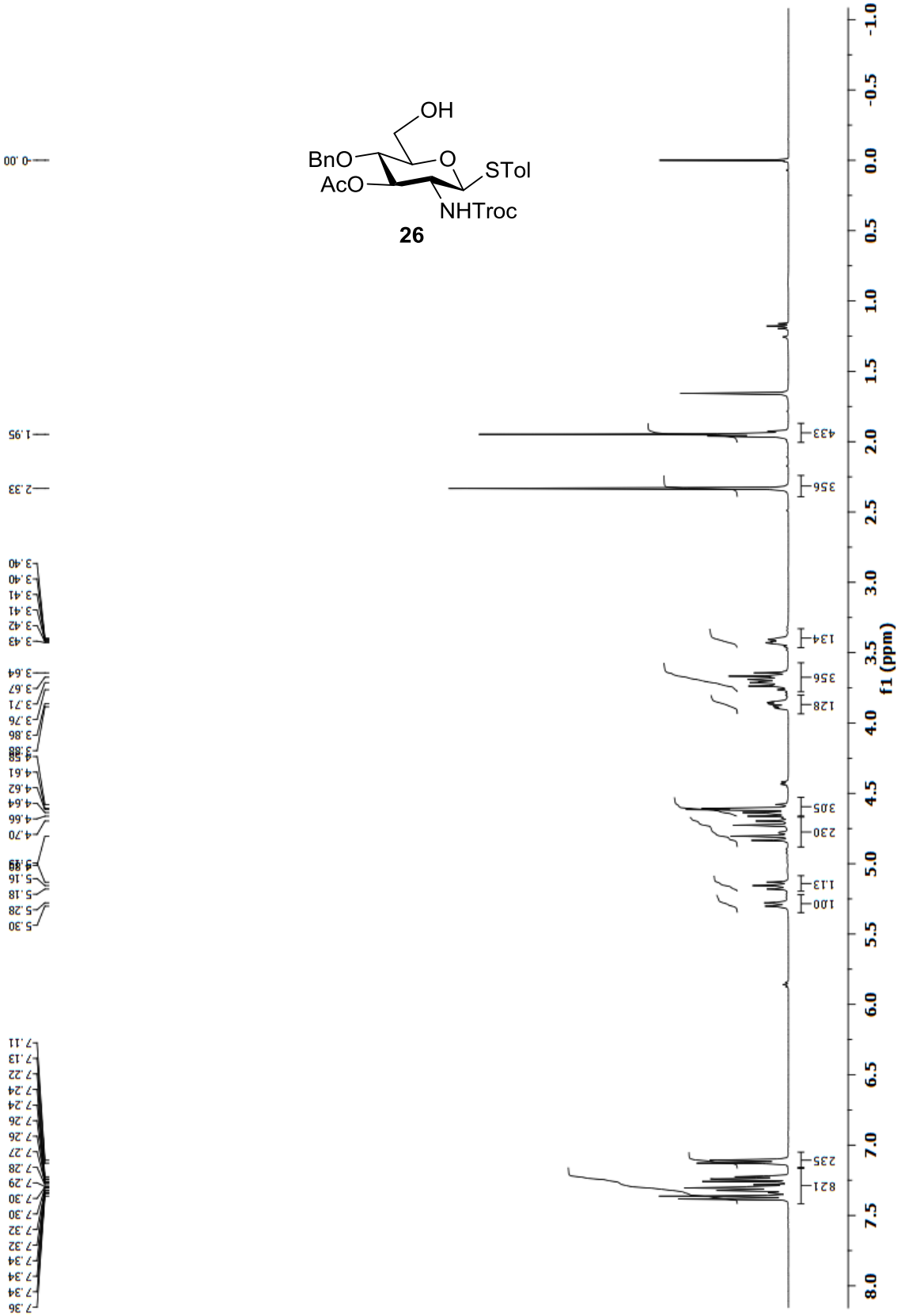
Non-decoupling ($^3J_{C1\text{-}Hax}$) ^{13}C NMR (100 MHz, $CDCl_3$) of disaccharide (**19**) with decoupling at ^1H chemical shift of 3.66 ppm



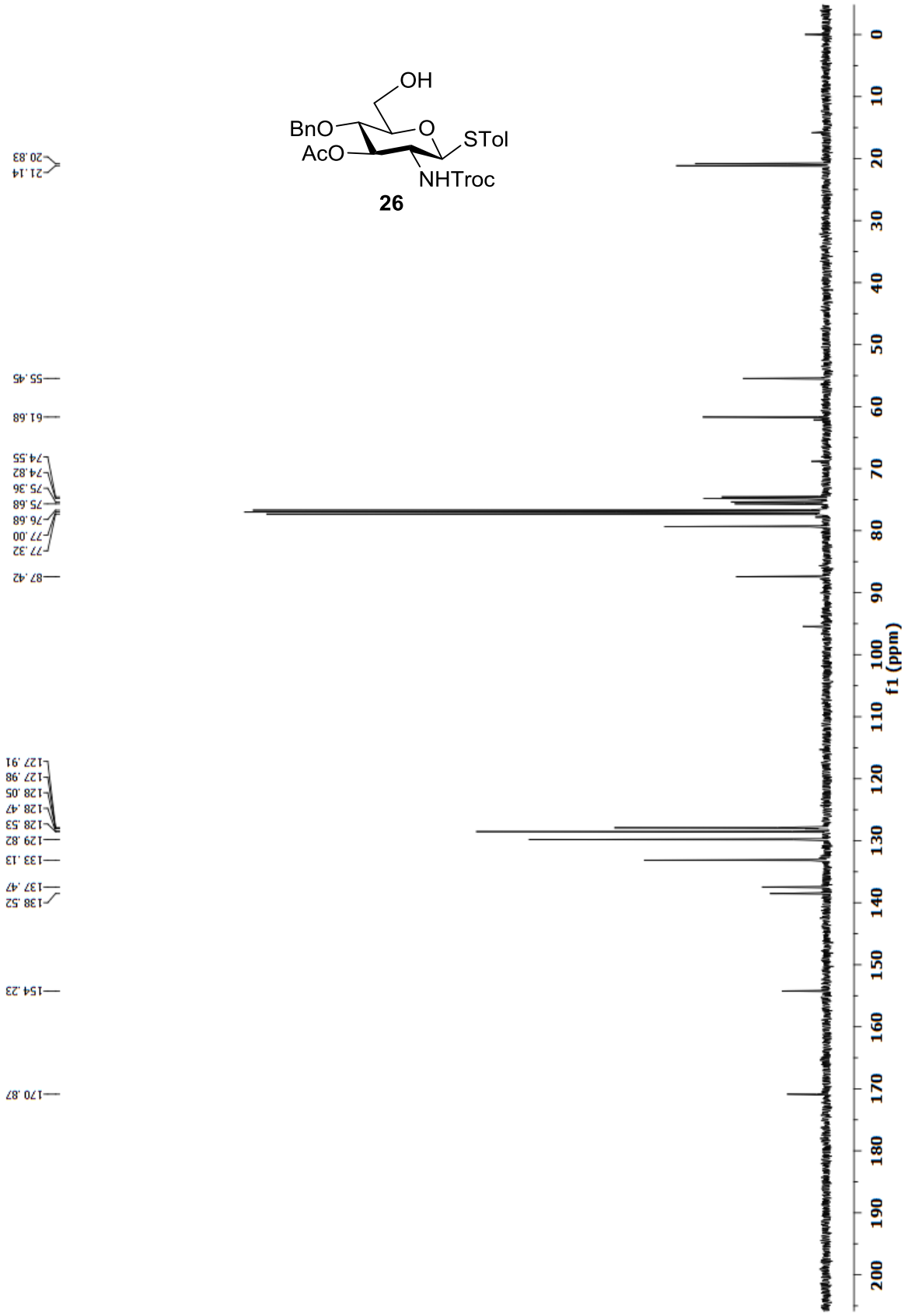
Non-decoupling ^{13}C NMR (150 MHz, $CDCl_3$) of β-anomer of disaccharide (**19**) with decoupling at ^{1}H chemical shift of 3.35 ppm (from ref S7)



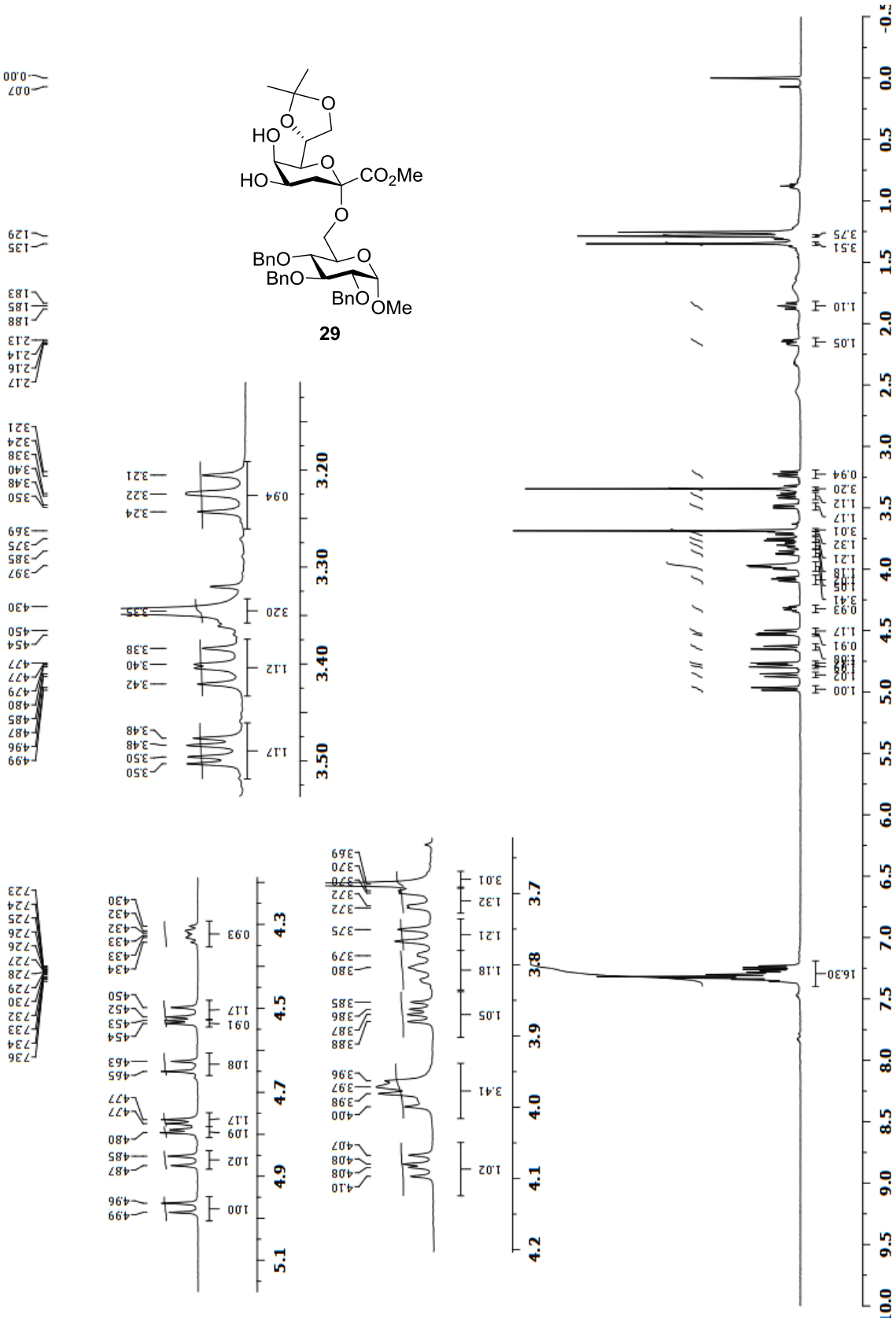
^{1}H NMR (400 MHz, $CDCl_3$) of *p*-totyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-trichloroethyoxycarbonylamino-thioglucosamine (**26**)



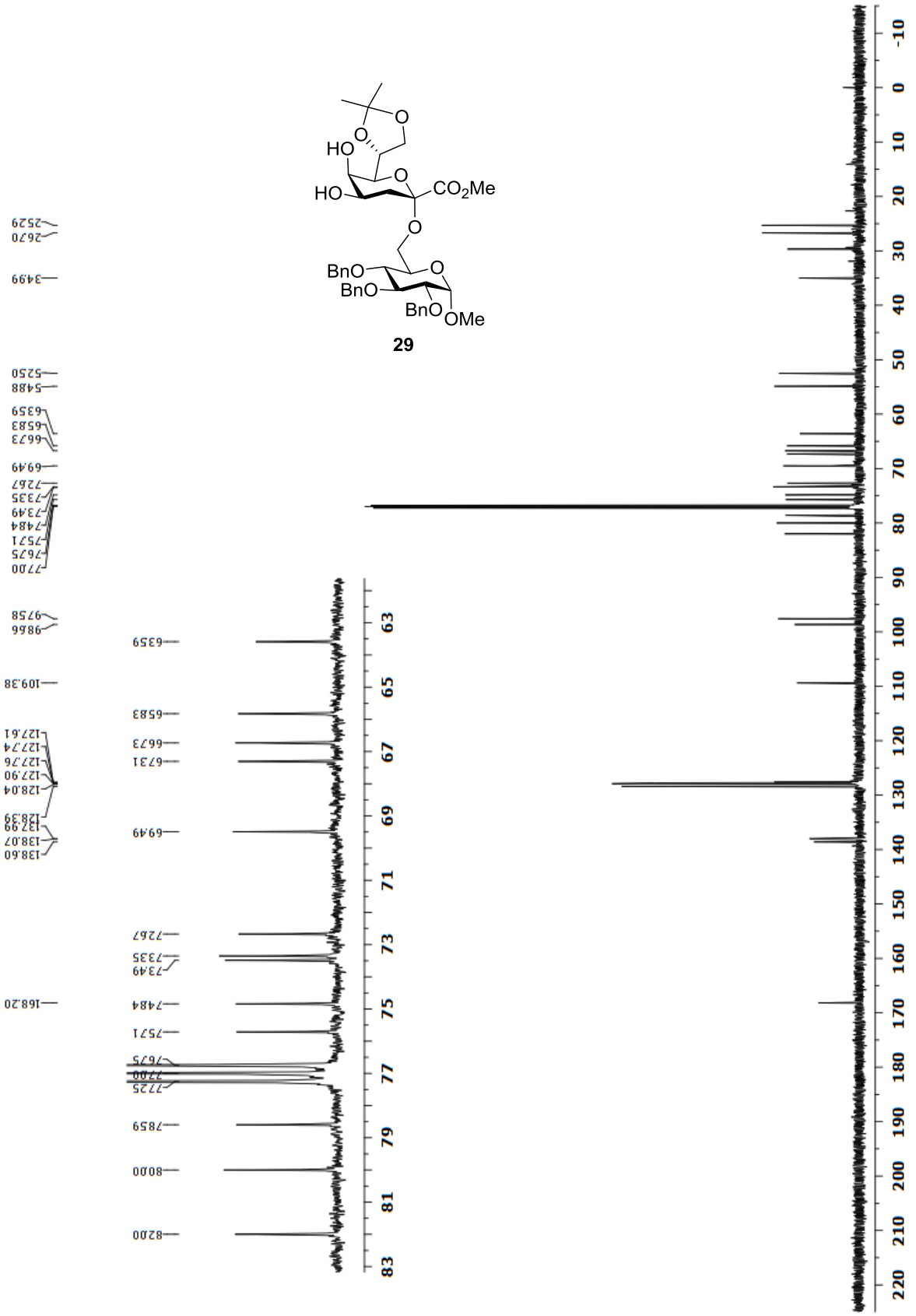
^{13}C NMR (100 MHz, $CDCl_3$) of *p*-totyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-trichloroethyoxycarbonylamino-thioglucosamine (**26**)



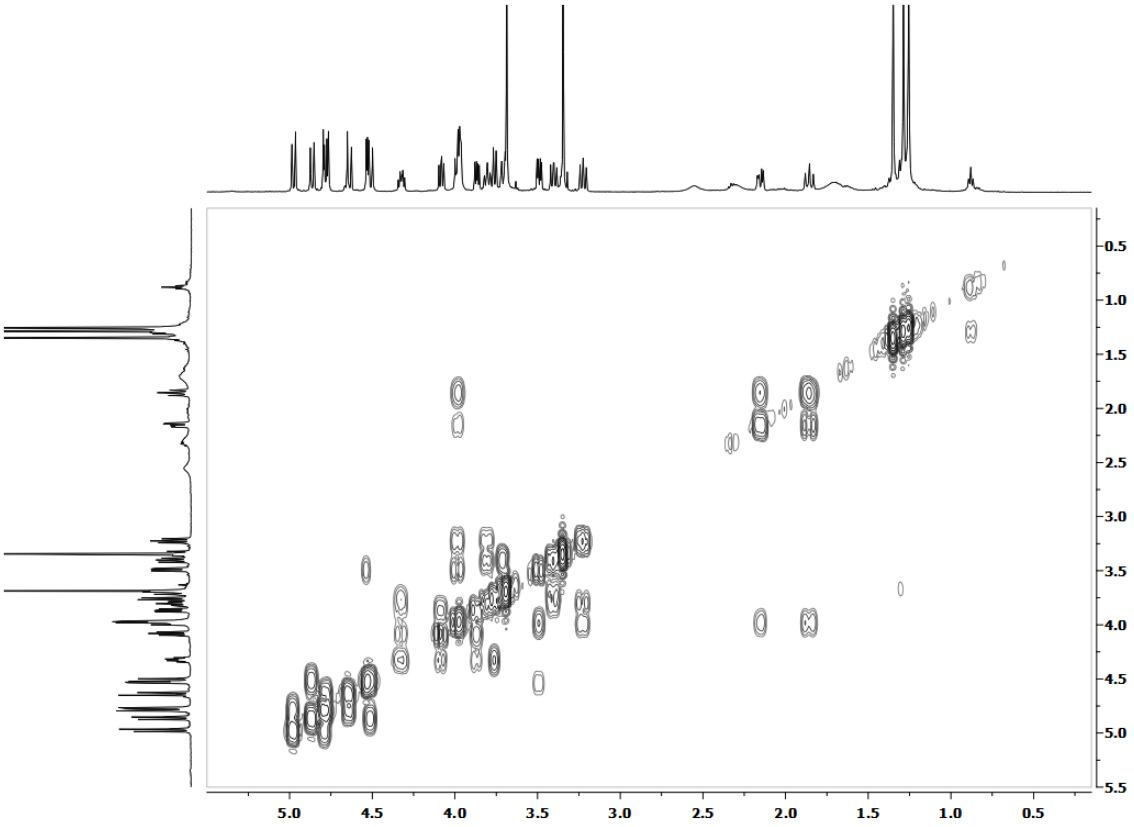
^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**29**)



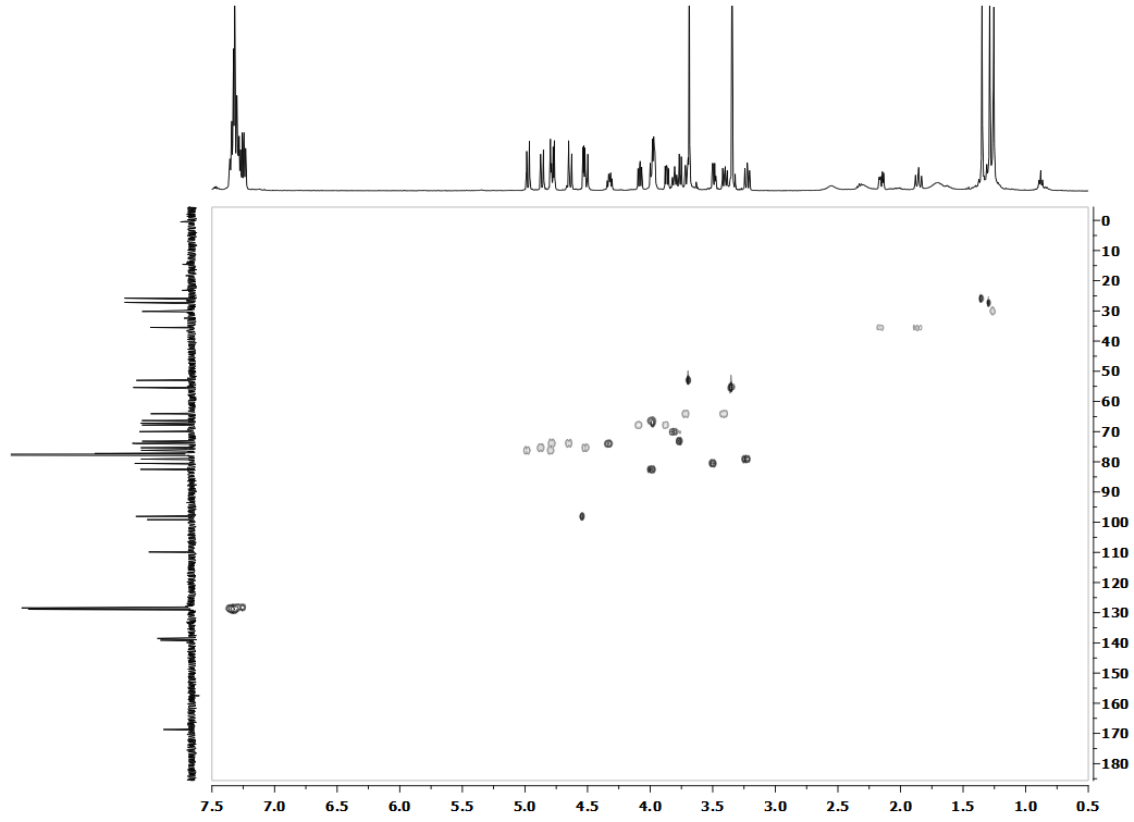
^{13}C NMR (125 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7,8-*O*-isopropylidene-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**29**)



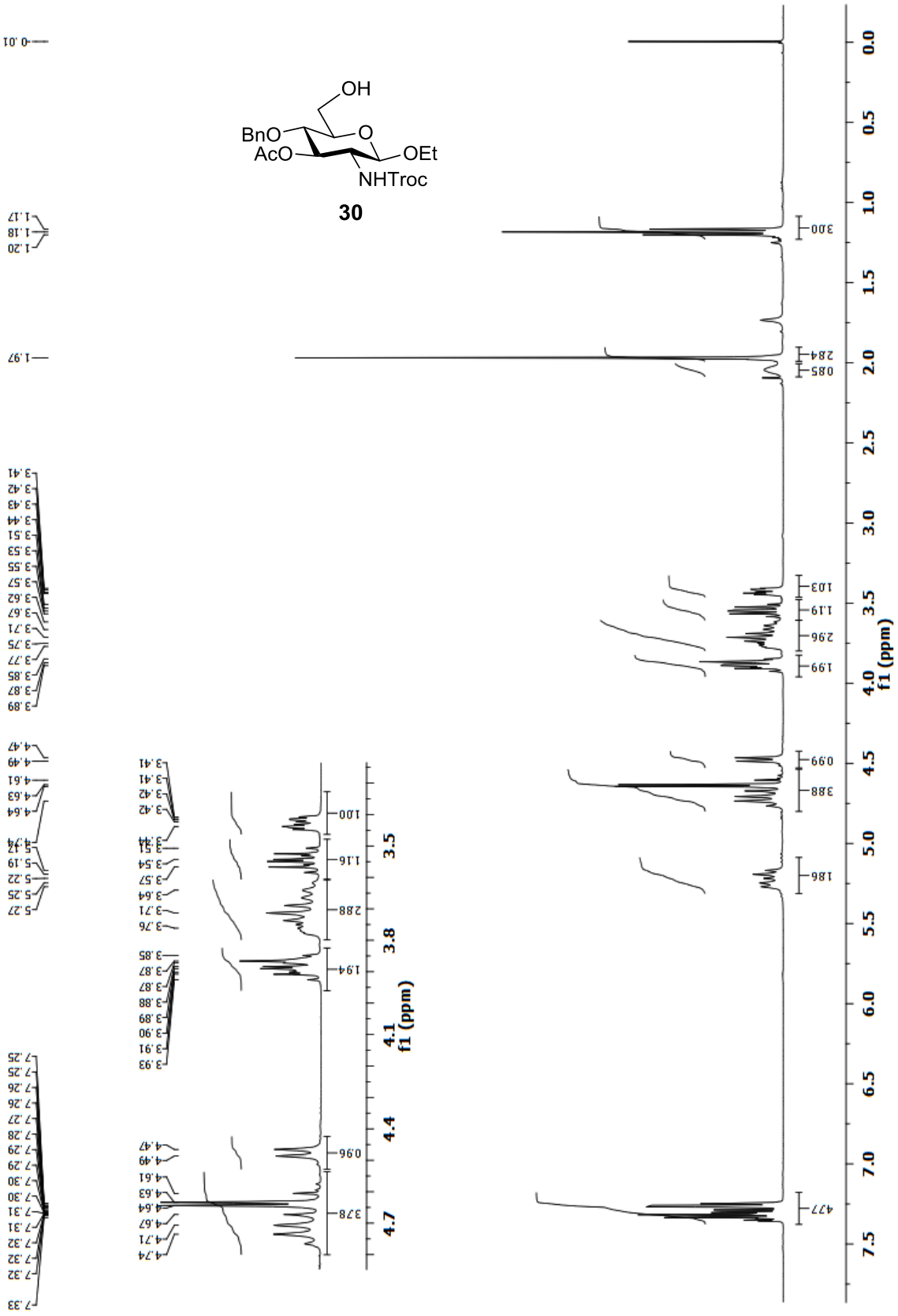
^{1}H-^{1}H GCOSY NMR (600 MHz, $CDCl_3$) of disaccharide (**29**)



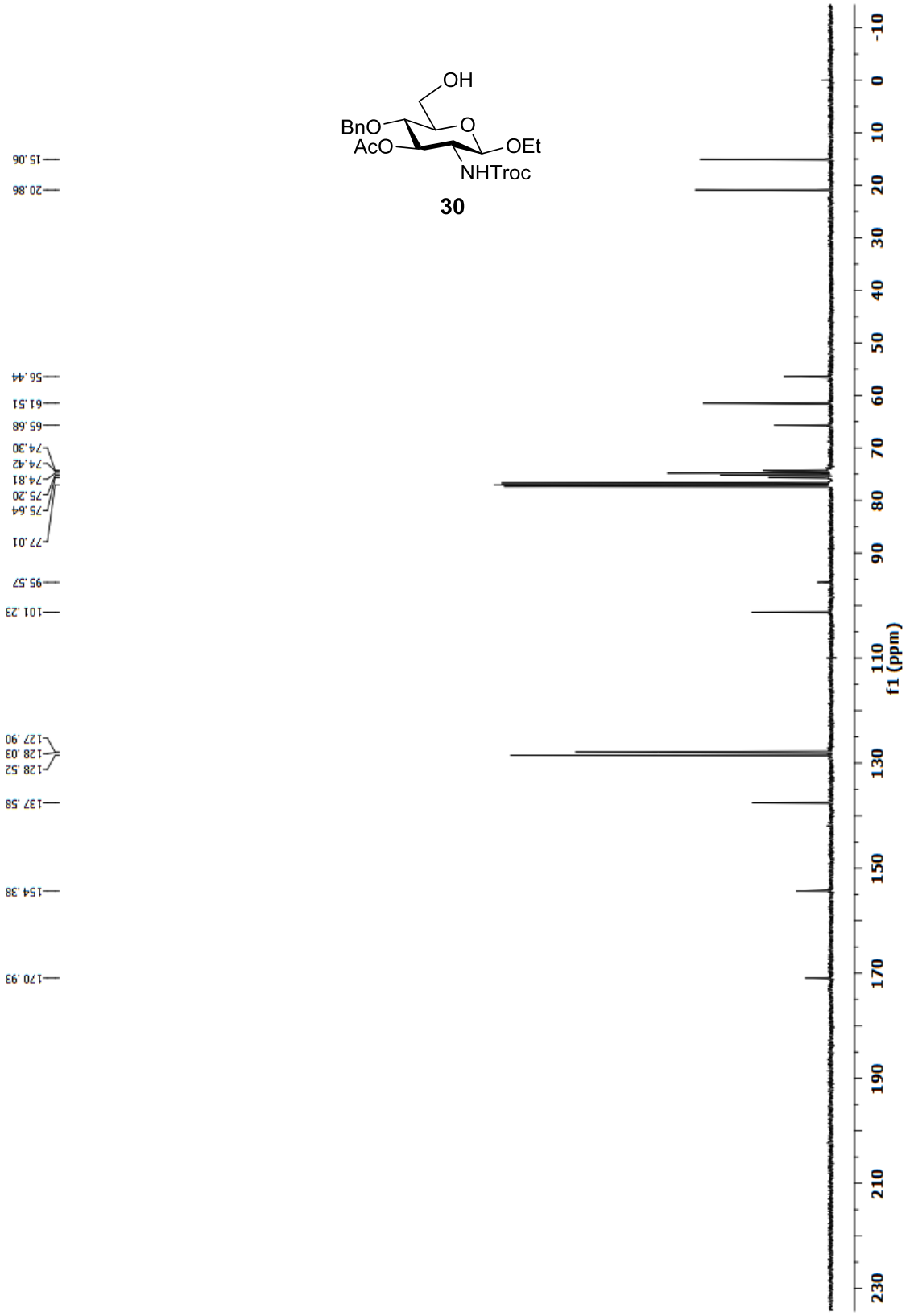
^{1}H-^{13}C HMQC NMR (150 MHz, $CDCl_3$) of disaccharide (**29**)



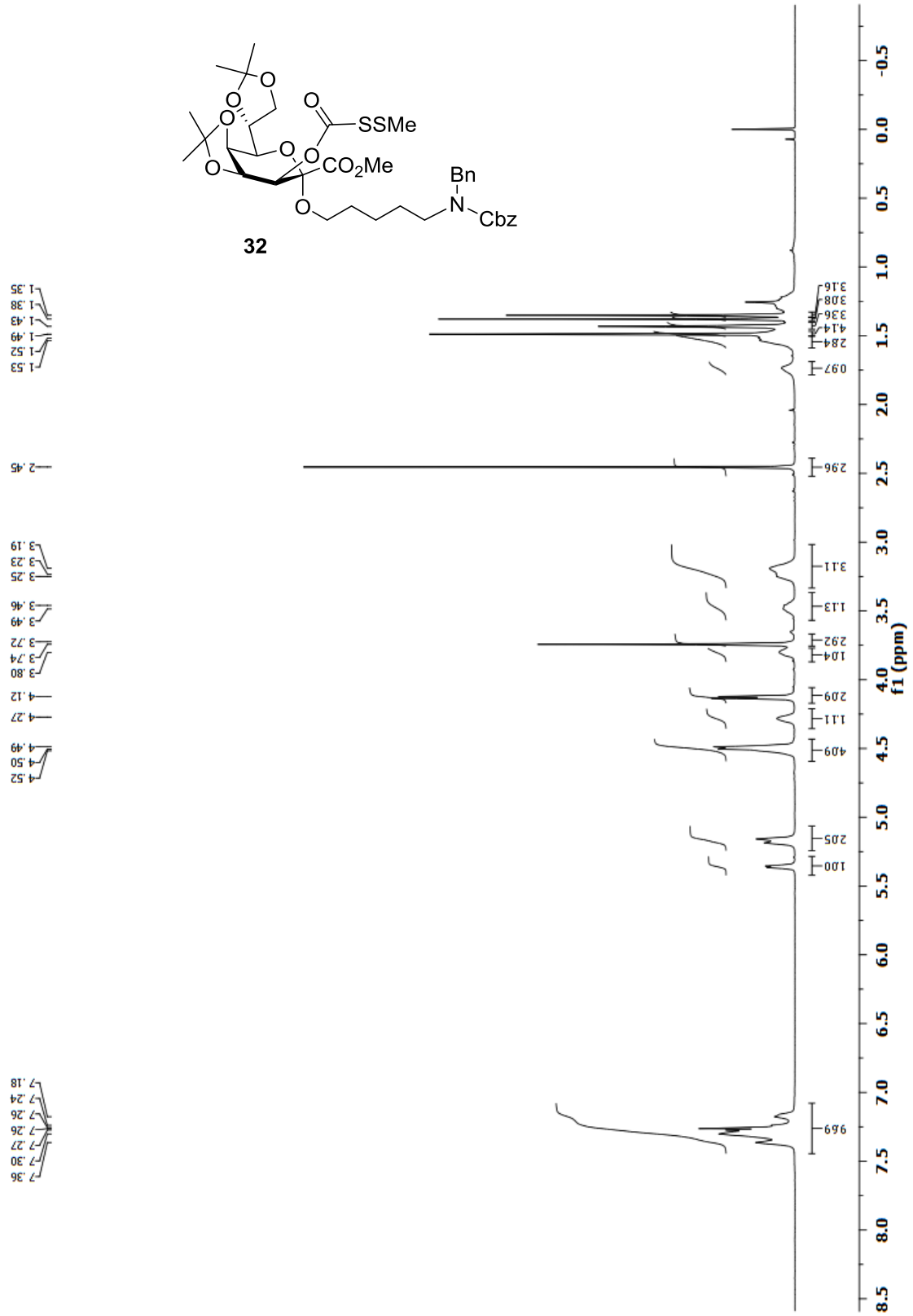
^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-*N*-(trichloroethoxycarbonyl)-*β*-D-glucopyranoside **(30)**



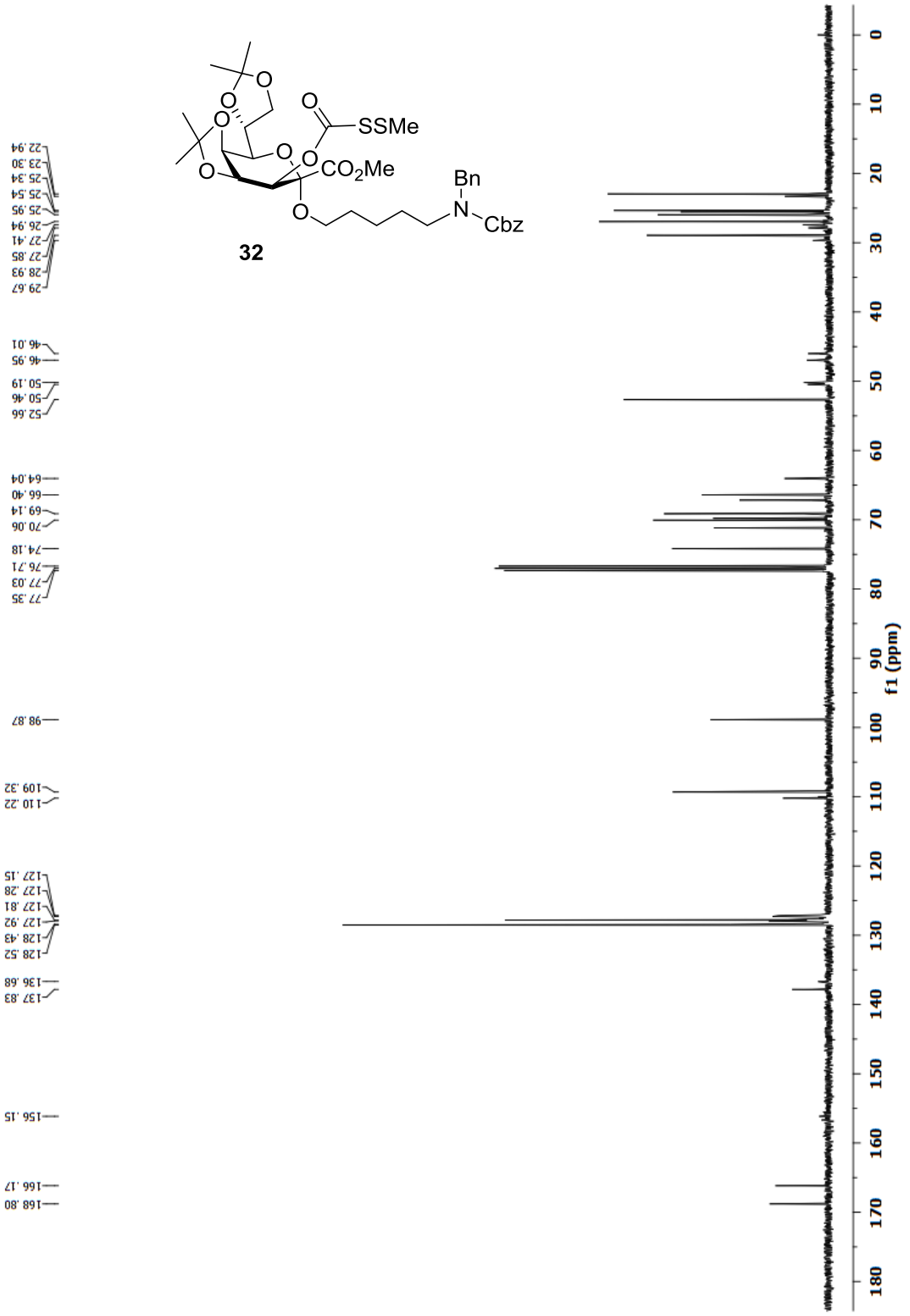
^{13}C NMR (100 MHz, $CDCl_3$) of ethyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-*N*-(trichloroethoxycarbonyl)-*β*-D-glucopyranoside (**30**)



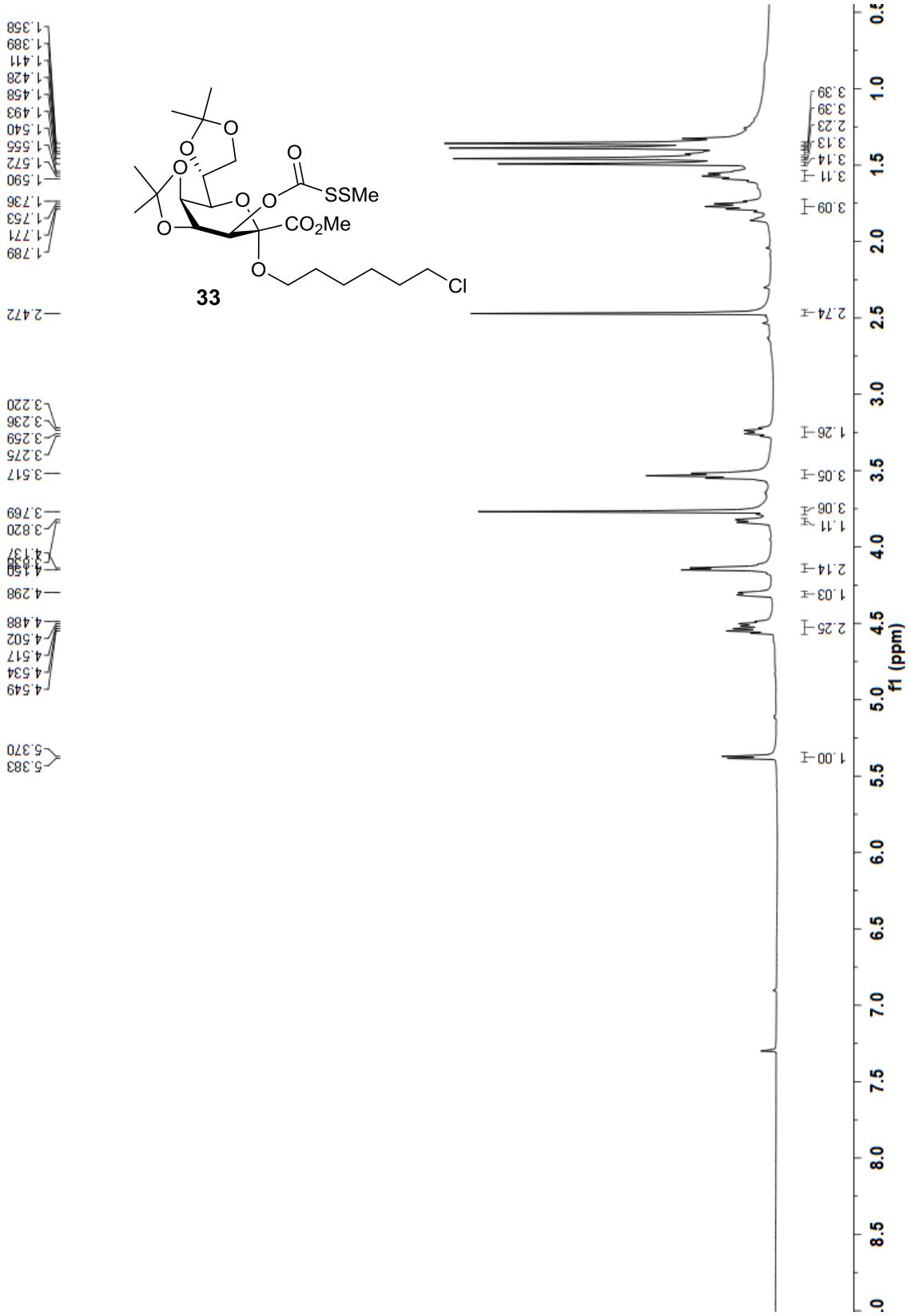
^{1}H NMR (400 MHz, $CDCl_3$) of methyl *N*-benzyl-*N*-benzyloxycarbonyl-5-aminopentyl-(4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate (**32**)



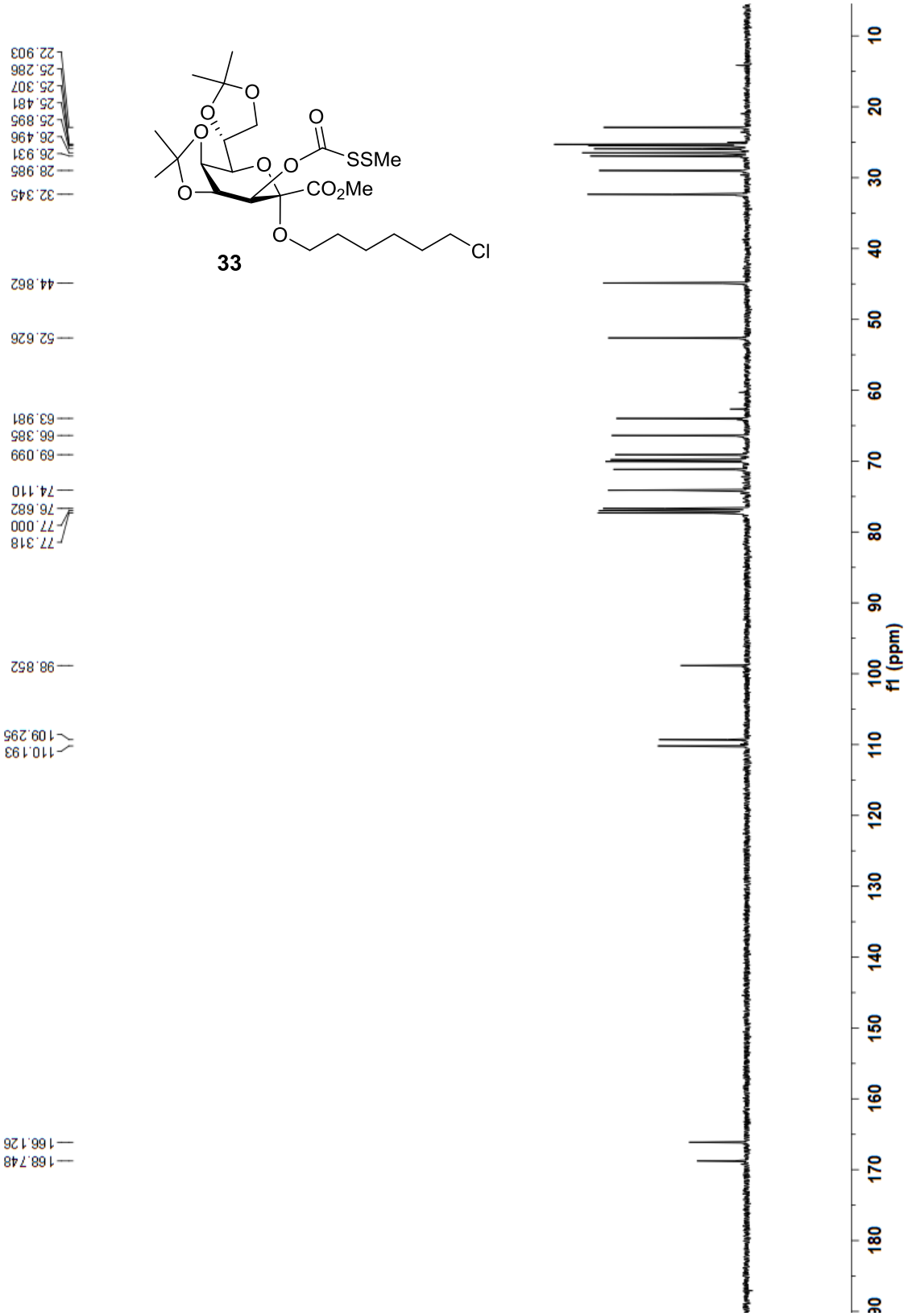
^{13}C NMR (100 MHz, $CDCl_3$) of methyl *N*-benzyl-*N*-benzyloxycarbonyl-5-aminopentyl-(4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate (**32**)



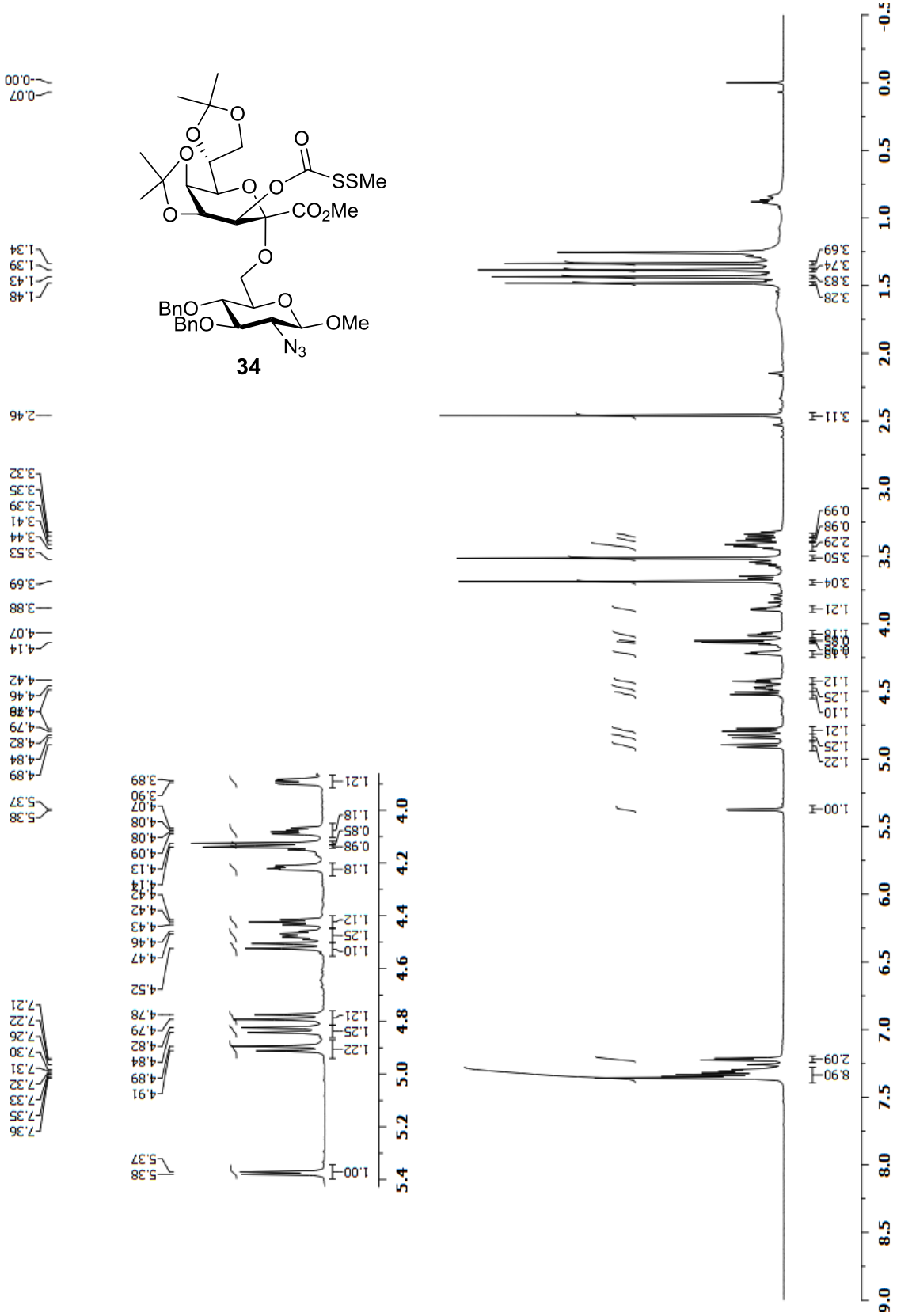
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 6-chlorohexyl-(4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate (**33**)



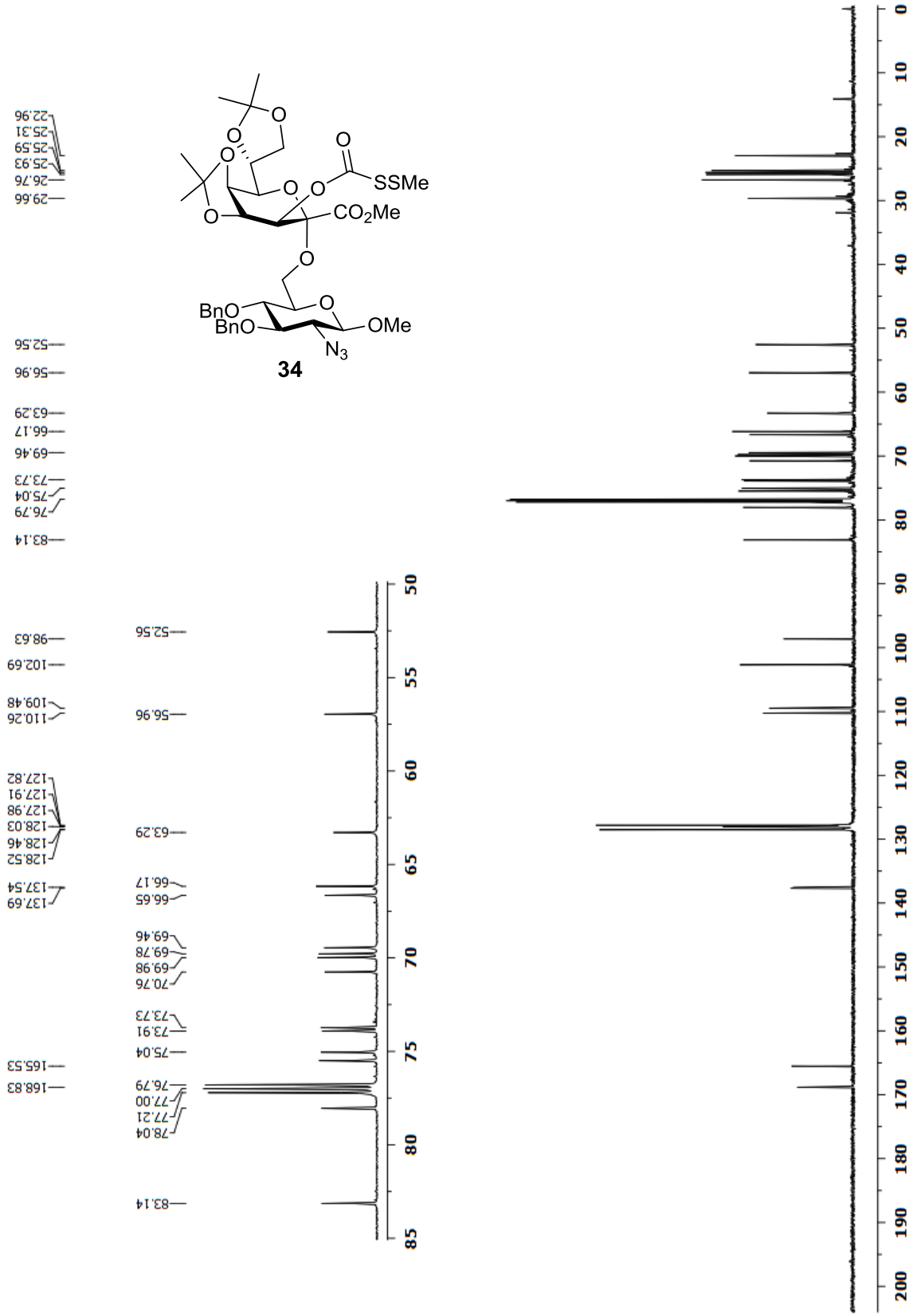
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 6-chlorohexyl-(4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate (**33**)



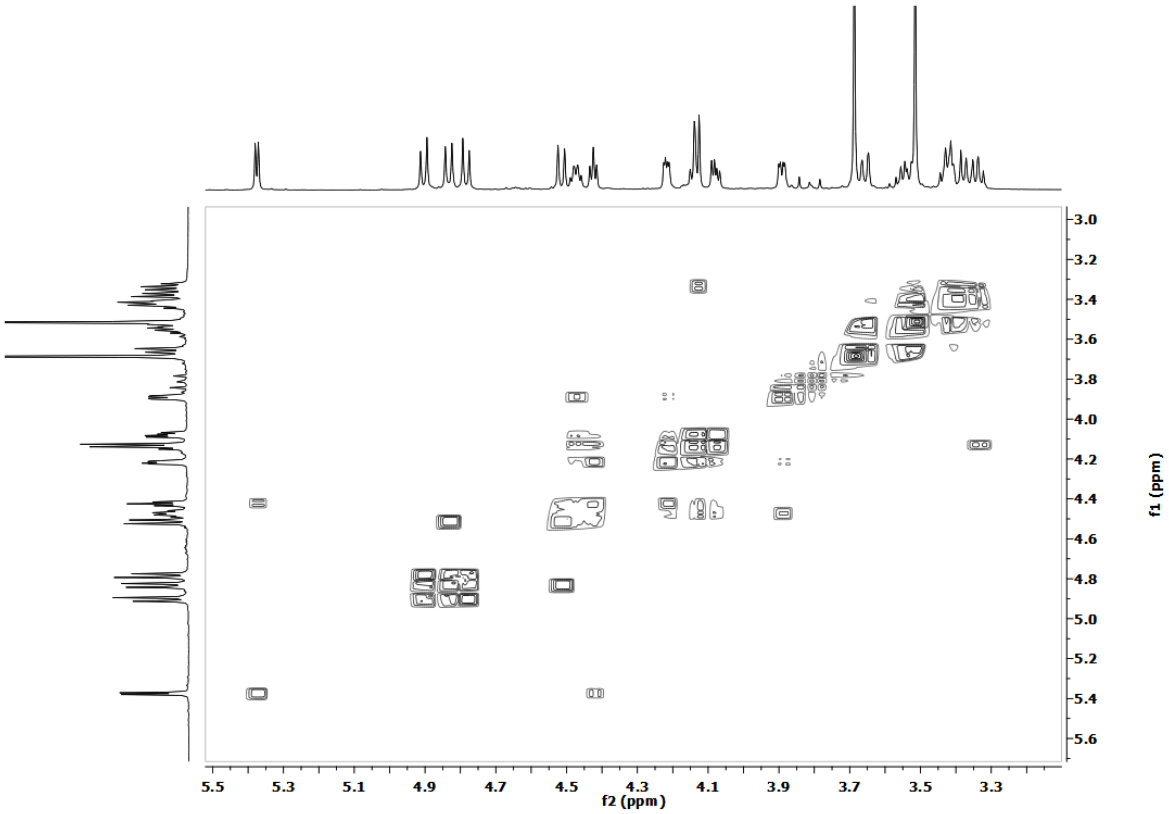
^{1}H NMR (500 MHz, $CDCl_3$) of methyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-glucopyranoside (**34**)



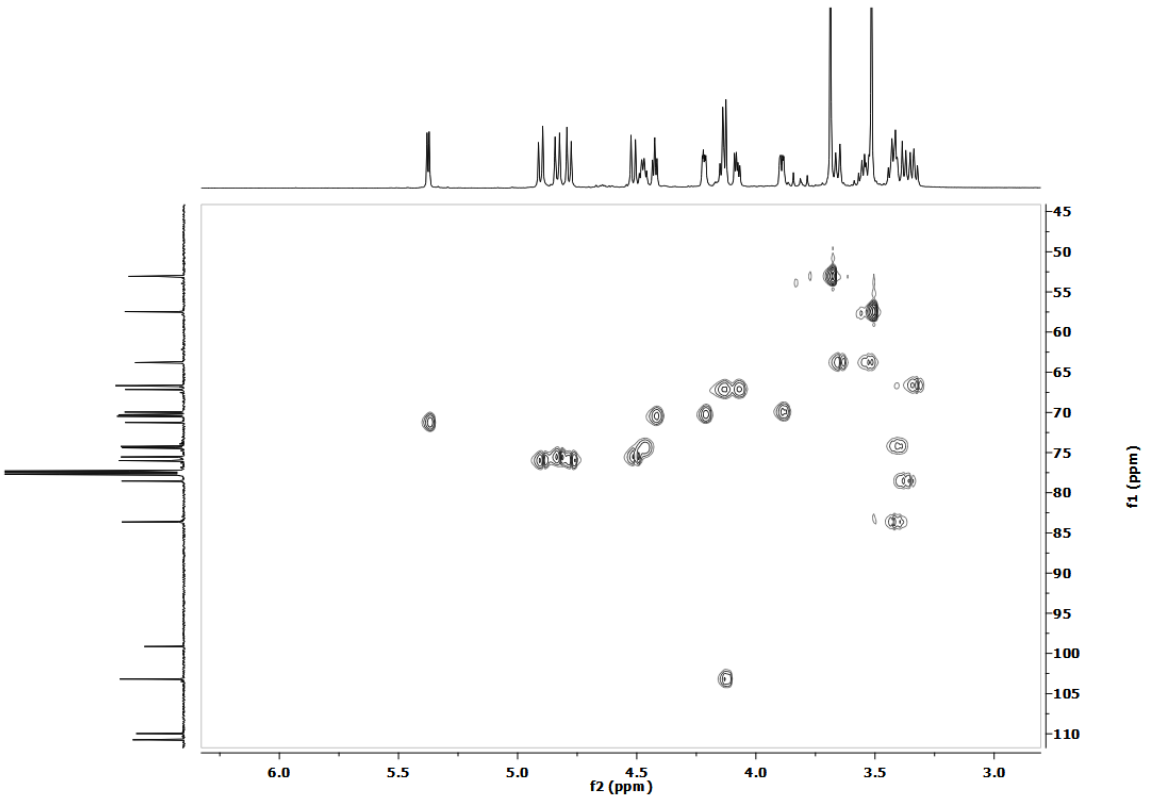
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-glucopyranoside (**34**)



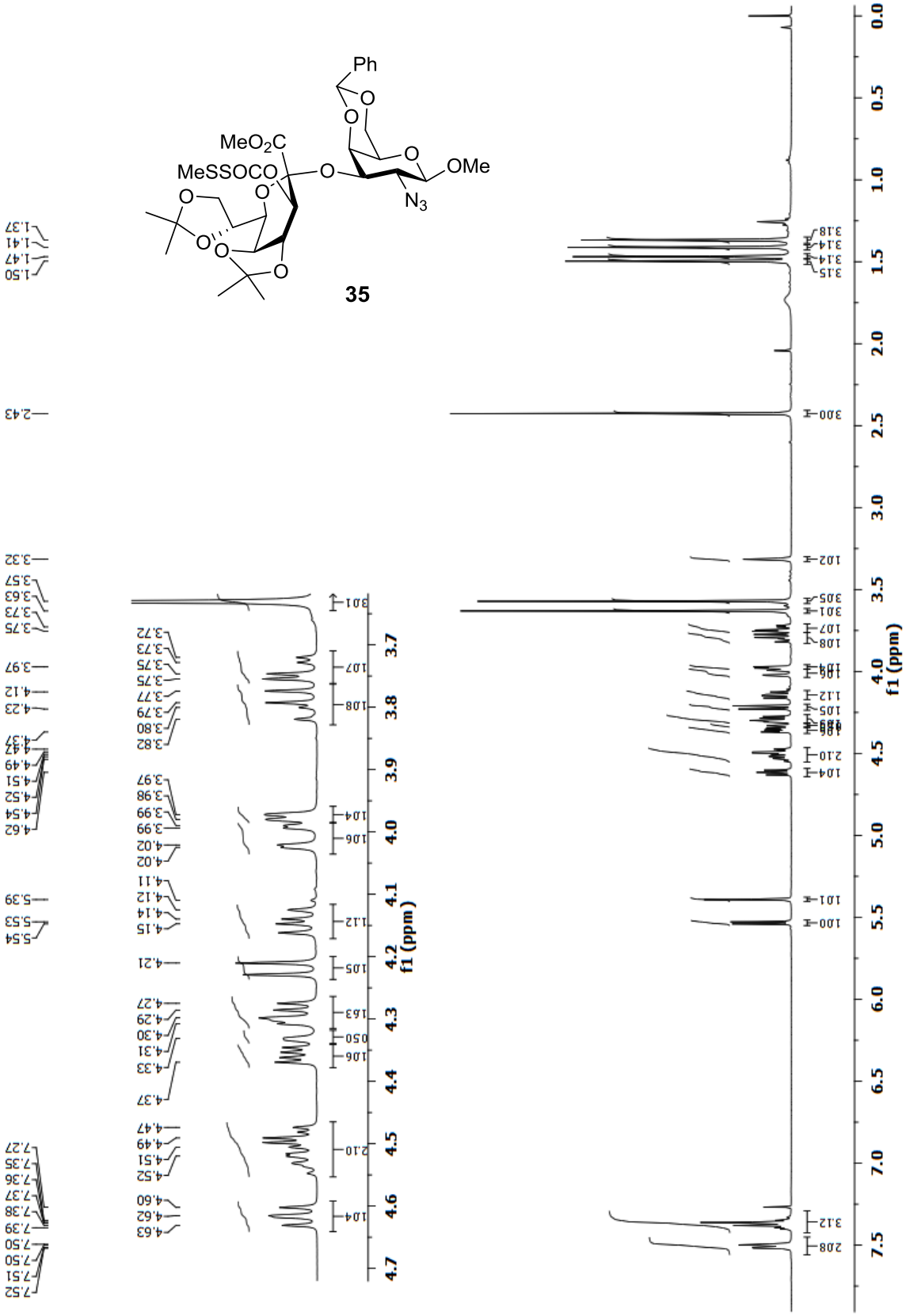
^{1}H-^{1}H GCOSY NMR (500 MHz, $CDCl_3$) of disaccharide **34**



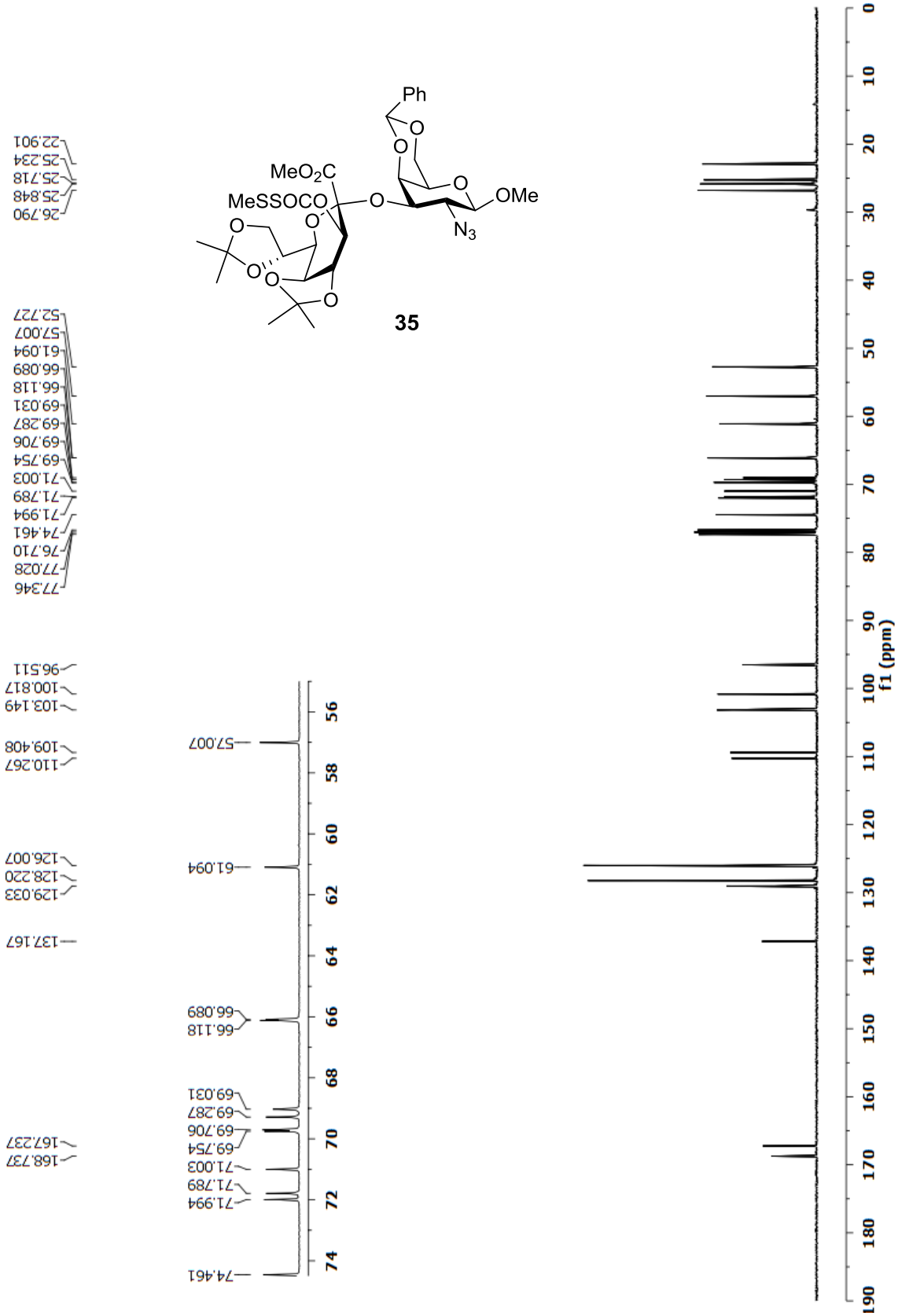
^{1}H-^{13}C HMQC NMR (125 MHz, $CDCl_3$) of disaccharide **34**



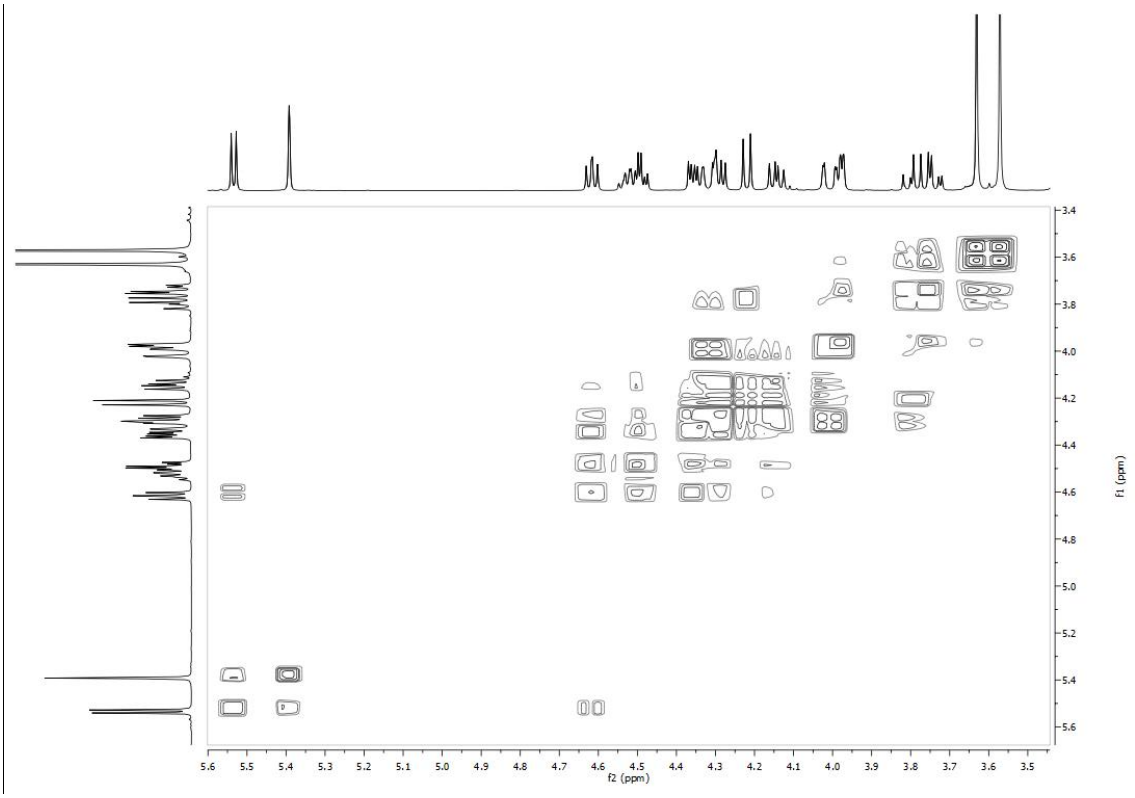
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2-azido-2-deoxy-4,6-*O*-benzylidene-3-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O* (*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-galactopyranoside (**35**)



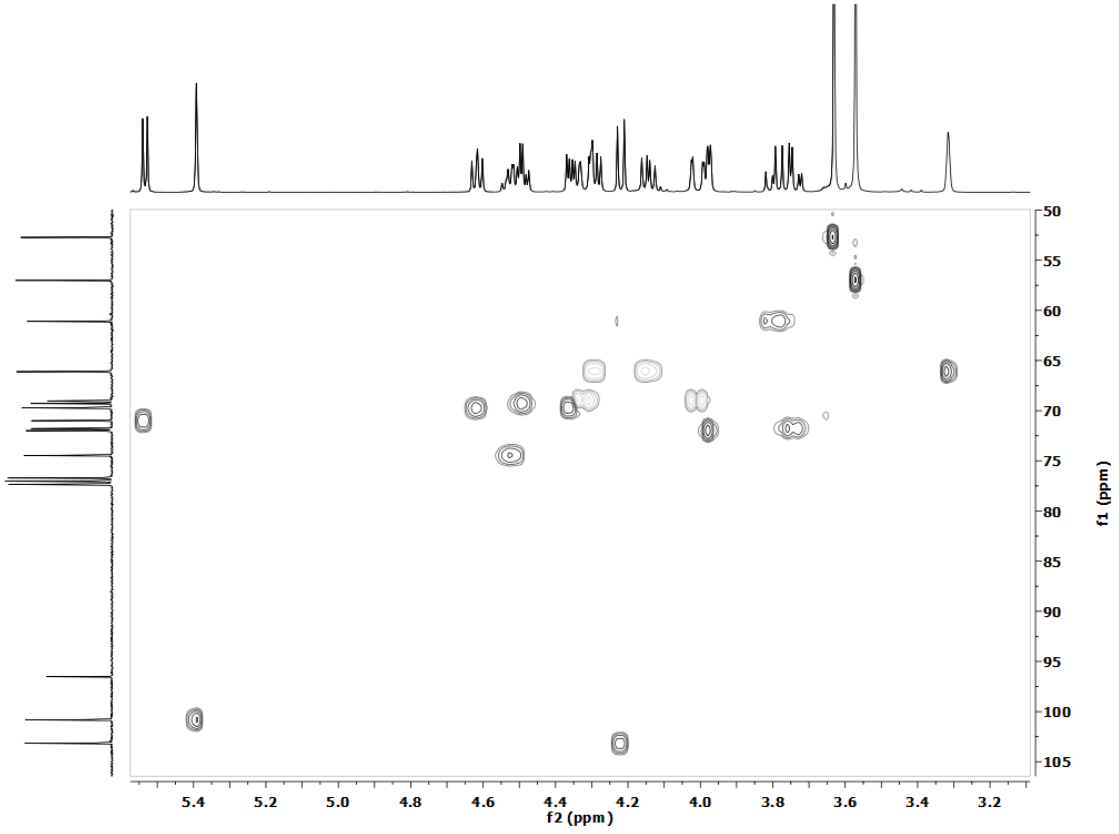
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2-azido-2-deoxy-4,6-*O*-benzylidene-3-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O* (*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-galactopyranoside (**35**)



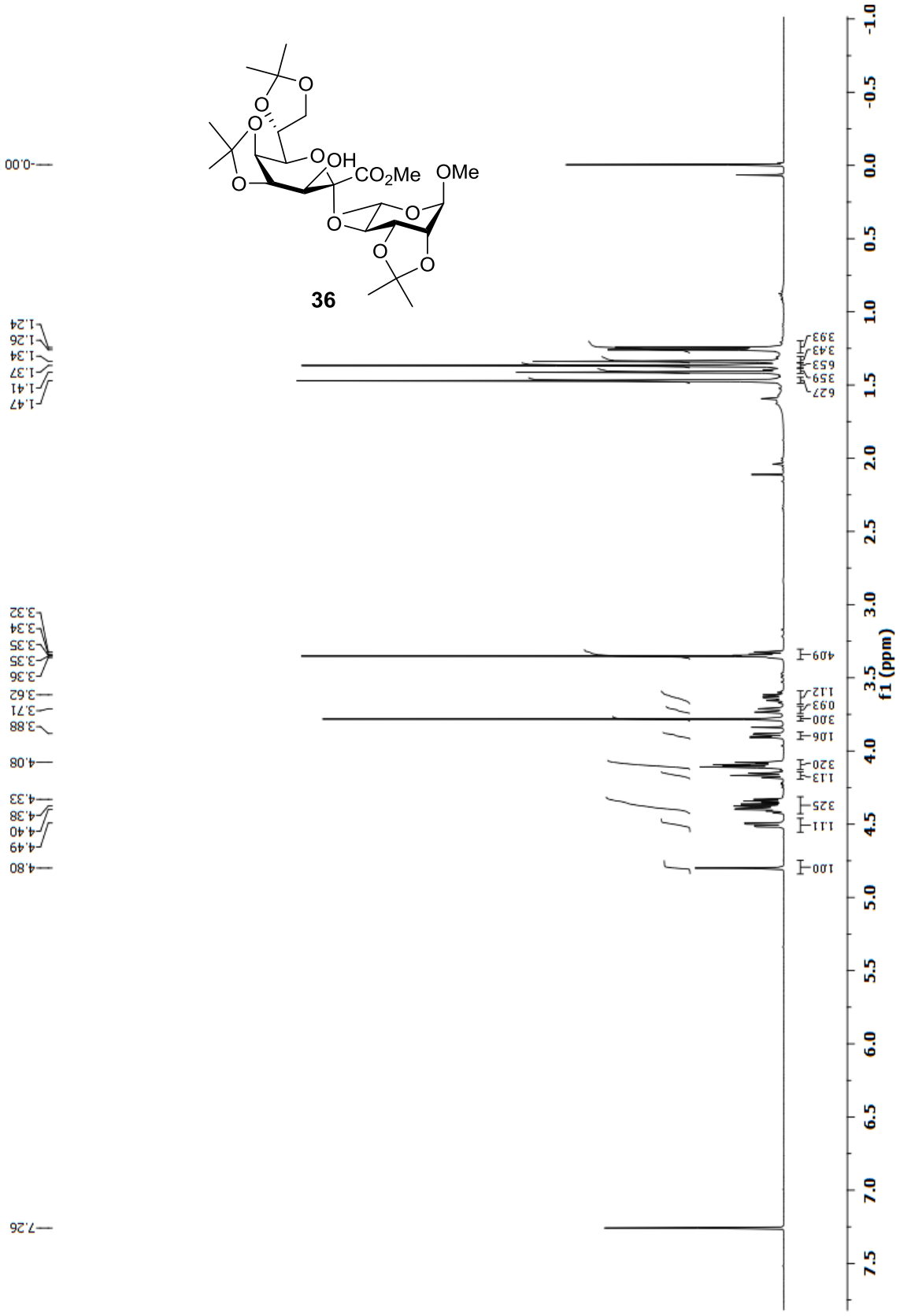
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**35**)



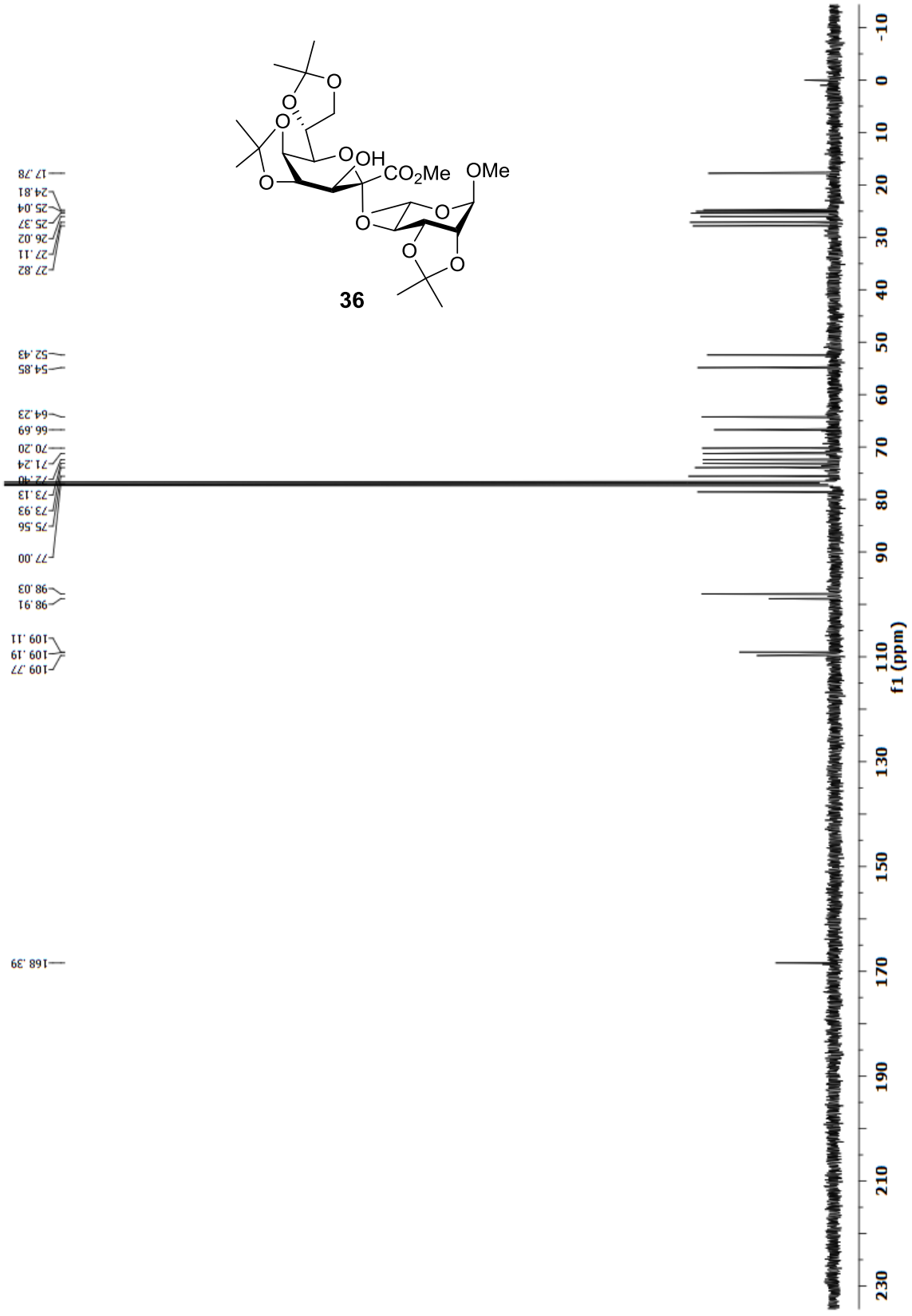
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**35**)



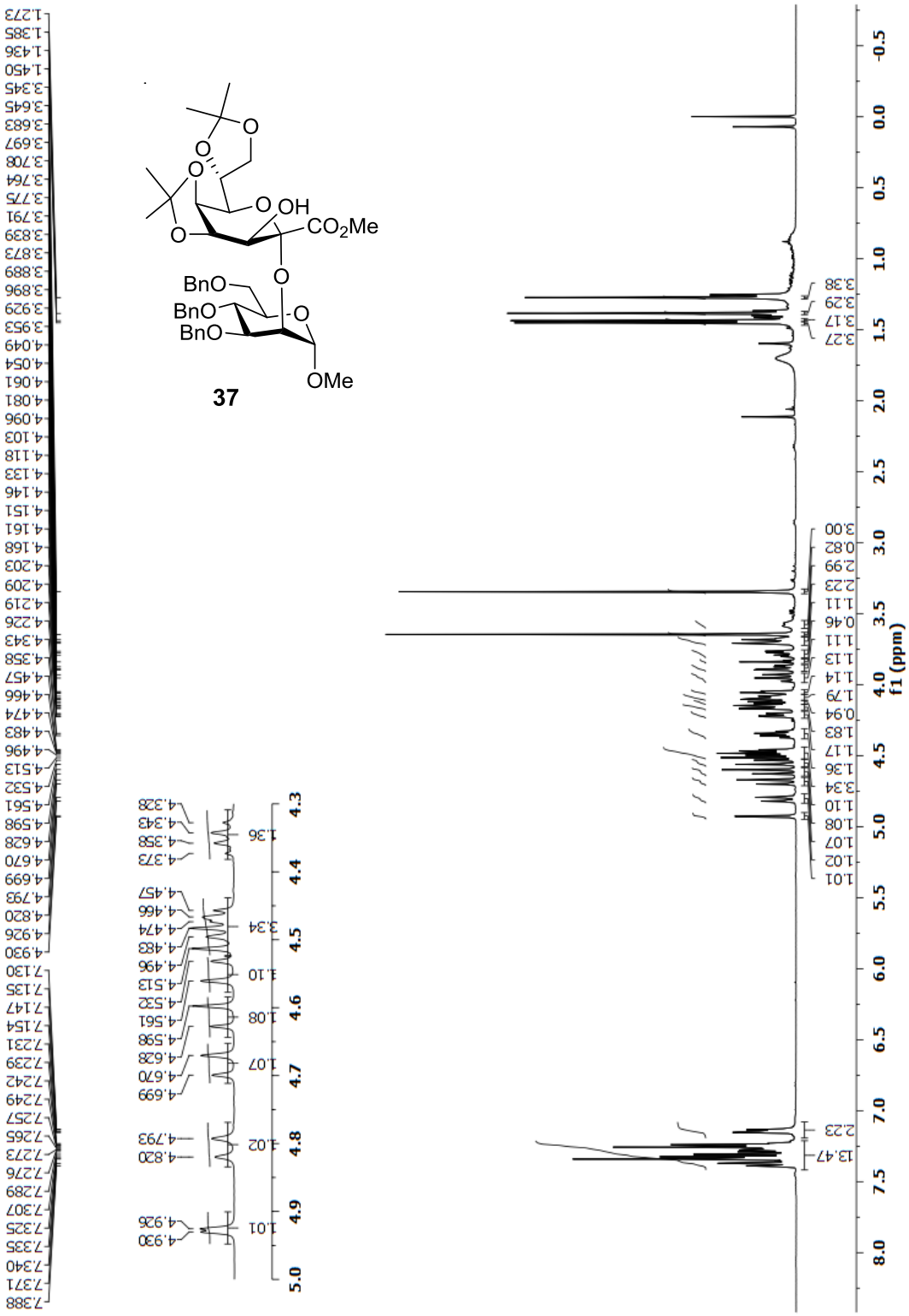
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3-*O*-isopropylidene-4-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-rhamnopyranoside **(36)**



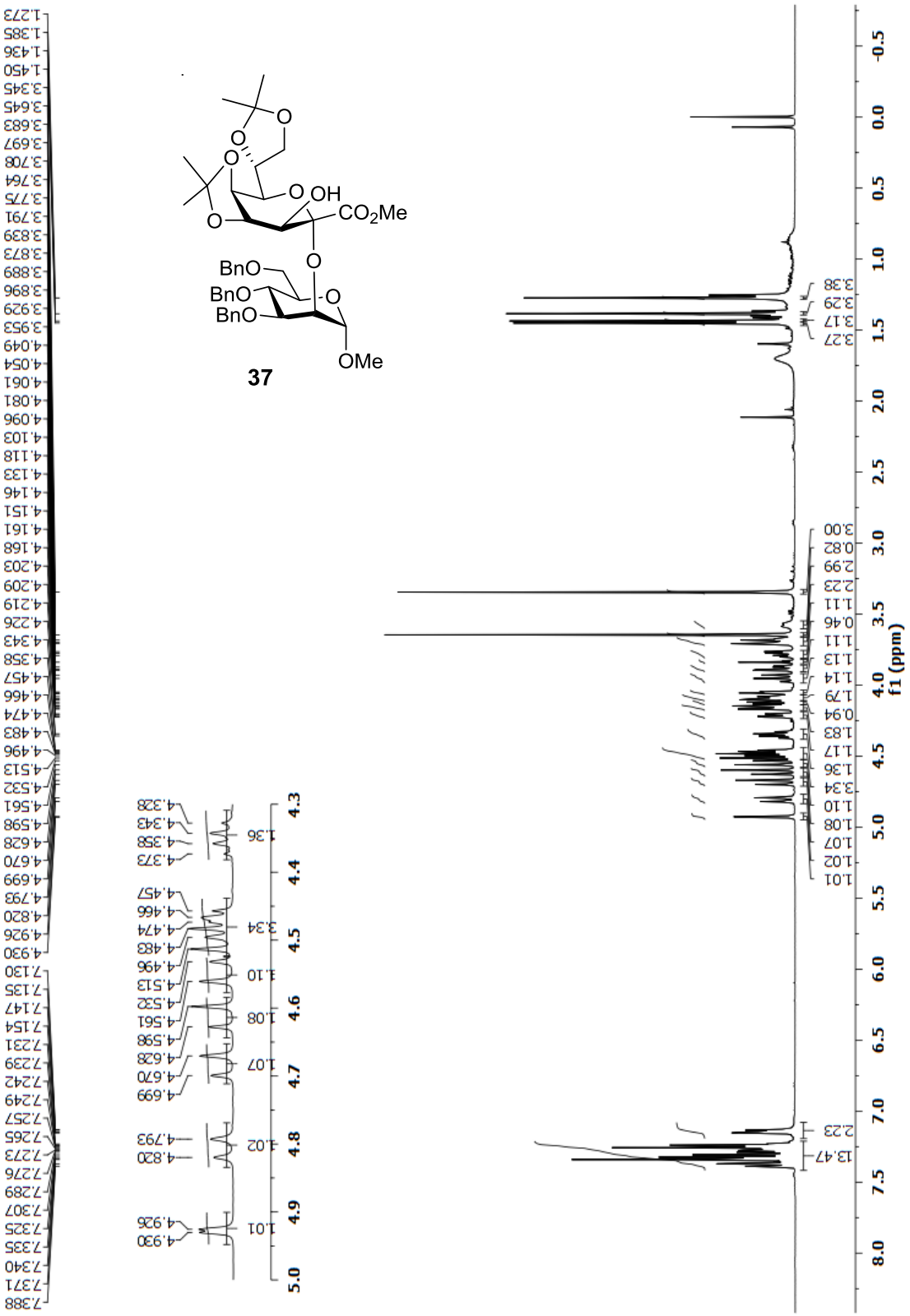
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3-*O*-isopropylidene-4-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-rhamnopyranoside (**36**)



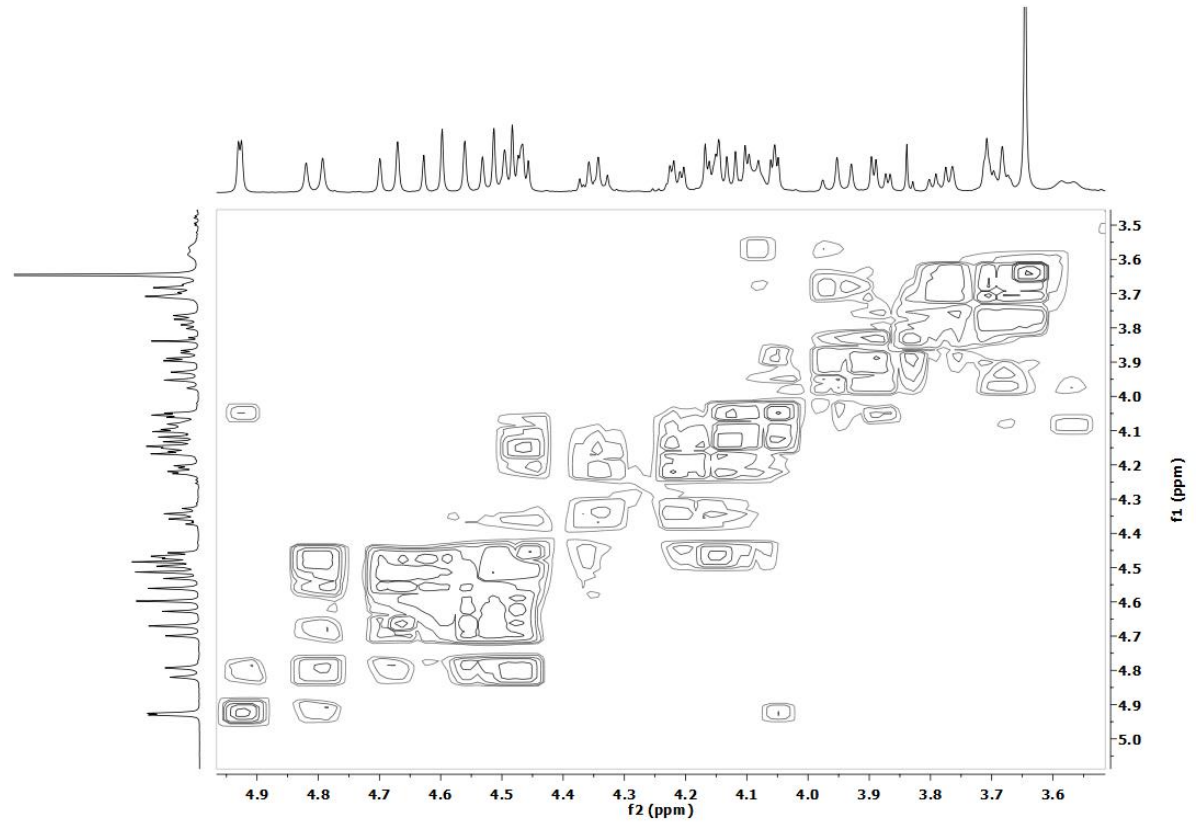
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 3,4,6-tri-*O*-benzyl-2-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-mannopyranoside (**37**)



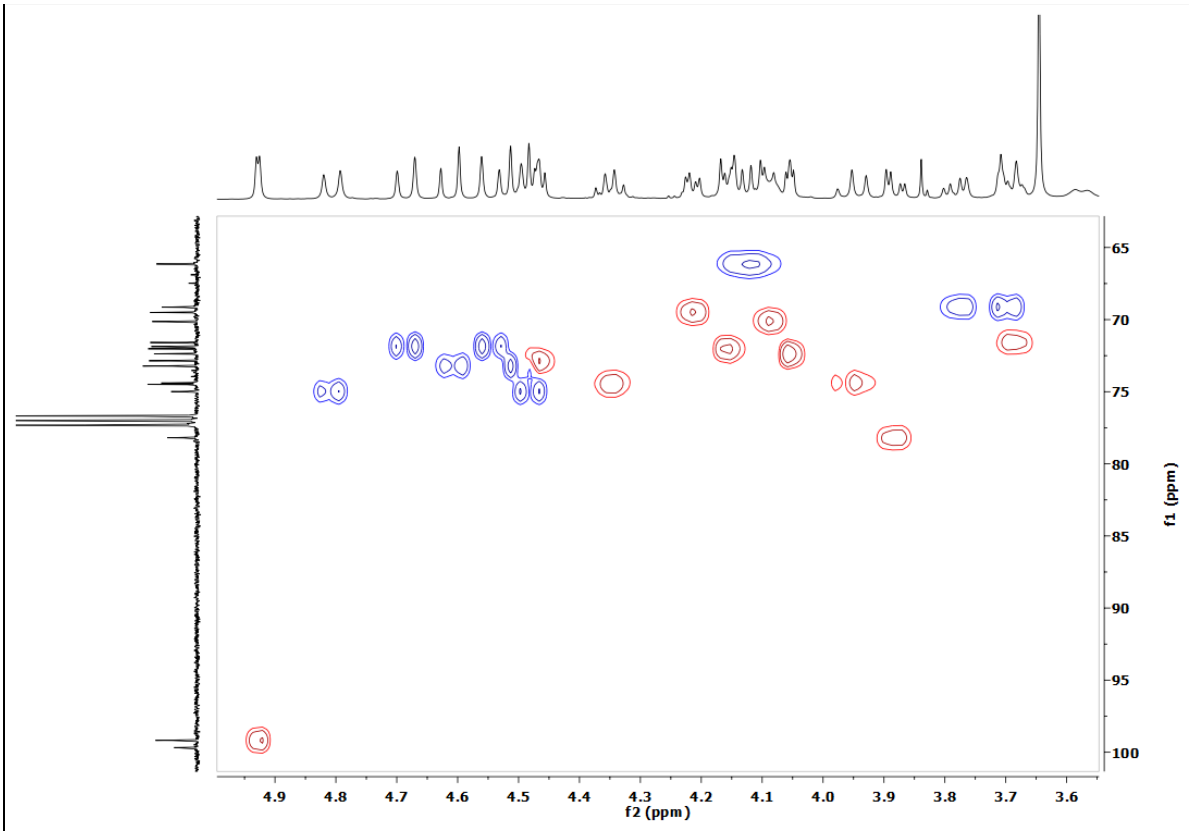
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 3,4,6-tri-*O*-benzyl-2-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-α-D-mannopyranoside (**37**)



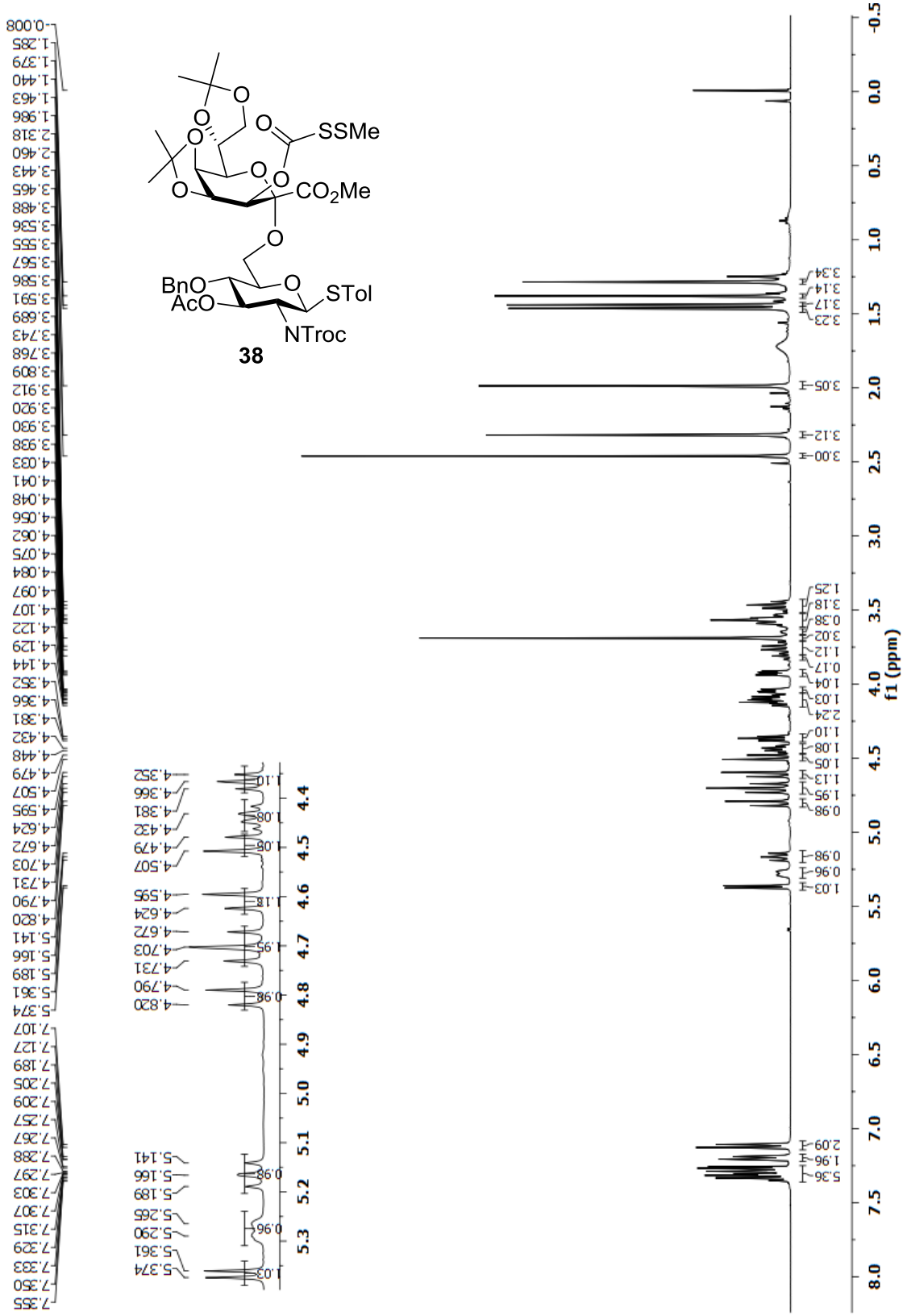
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide **37**



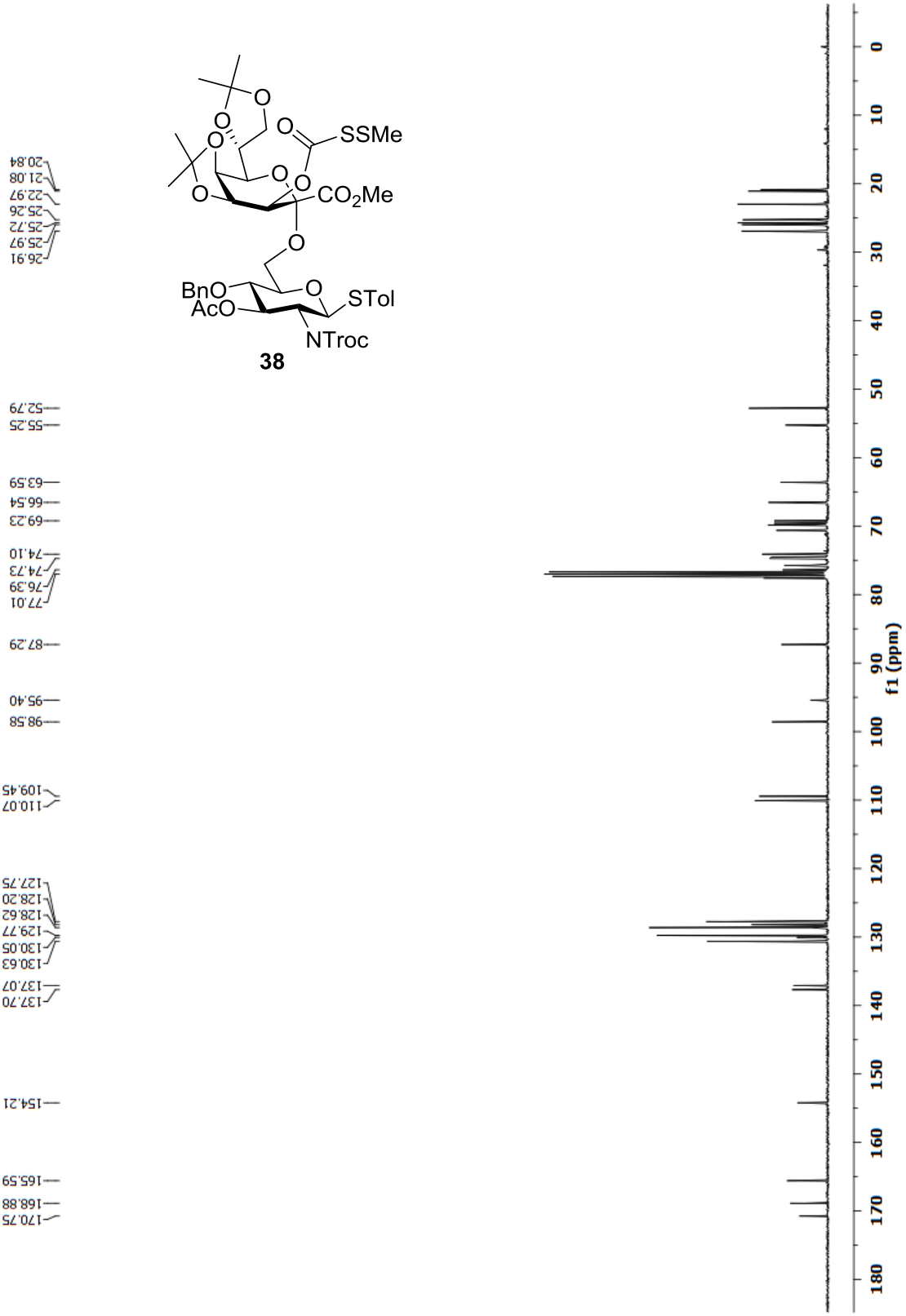
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide **37**



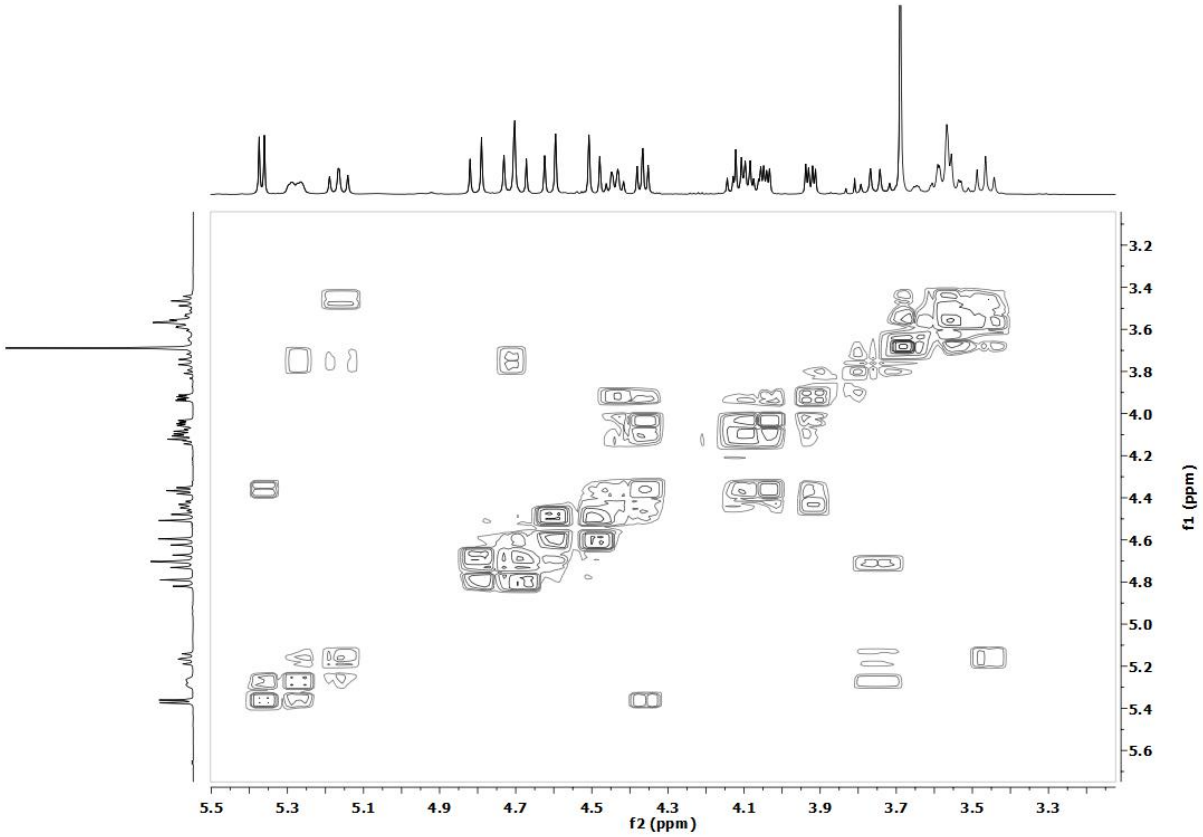
^{1}H NMR (400 MHz, $CDCl_3$) of *p*-tolyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-trichloroethoxycarbonylamino-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-thioglucopyranoside (**38**)



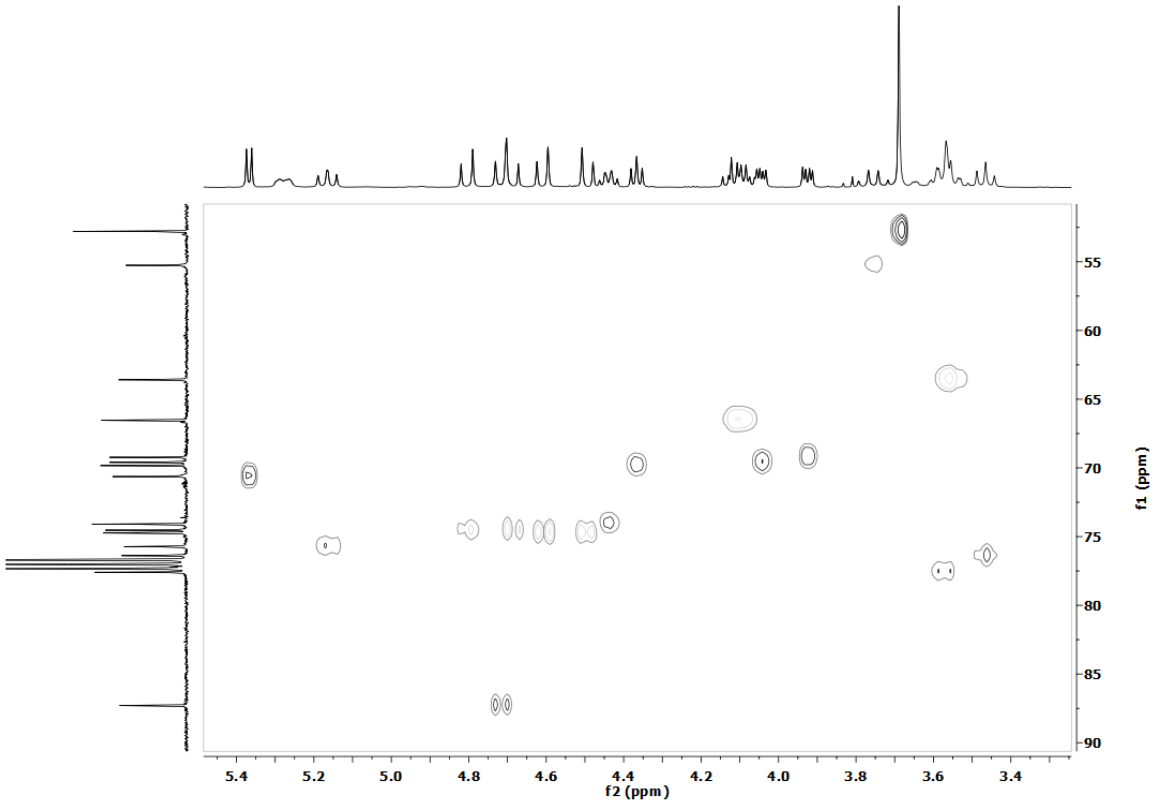
^{13}C NMR (100 MHz, $CDCl_3$) of *p*-tolyl 3-*O*-acetyl-4-*O*-benzyl-2-deoxy-2-trichloroethoxycarbonylamino-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-thioglucopyranoside (**38**)



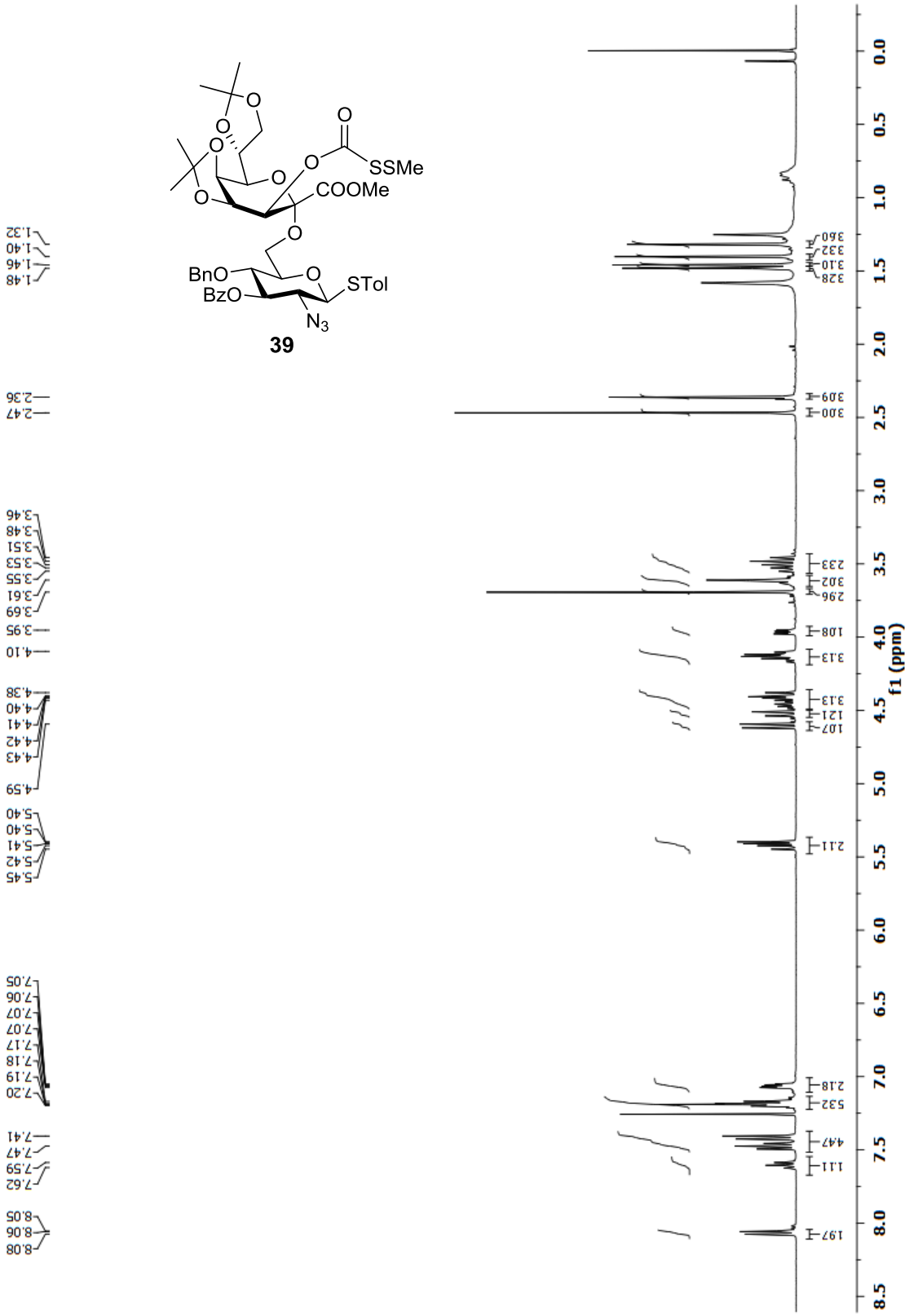
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**38**)



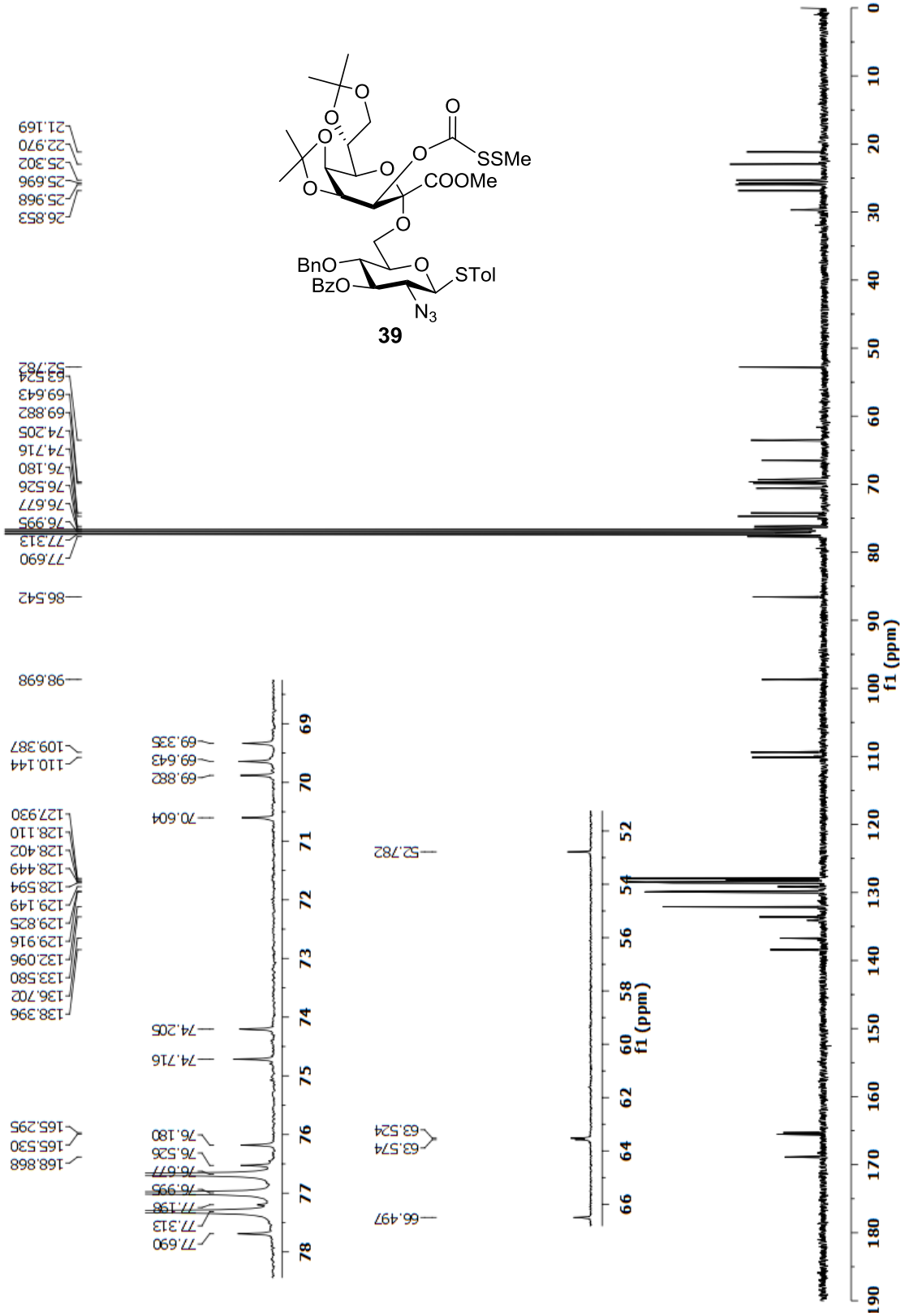
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**38**)



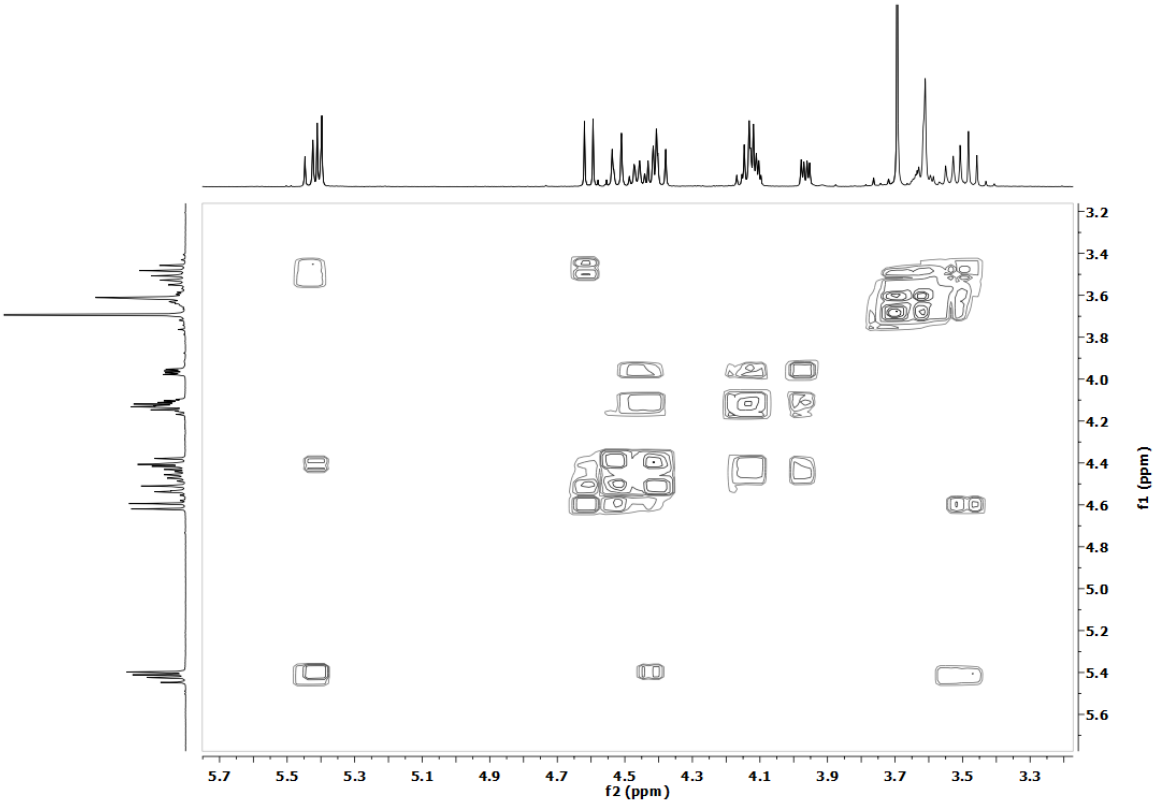
^{1}H NMR (400 MHz, $CDCl_3$) of *p*-tolyl 2-azido-3-benzoyl-4-*O*-benzyl-2-deoxy-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-thioglucopyranoside (**39**)



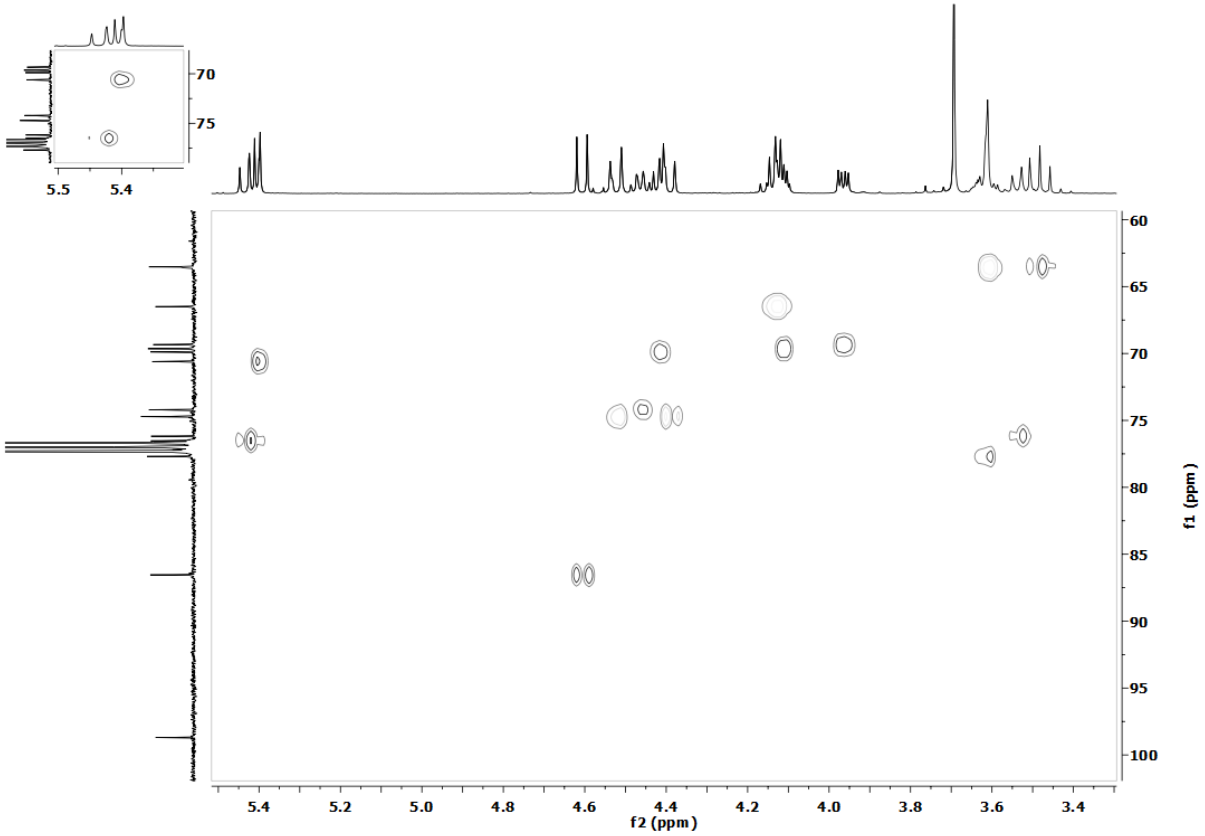
^{13}C NMR (100 MHz, $CDCl_3$) of *p*-tolyl 2-azido-3-benzoyl-4-*O*-benzyl-2-deoxy-6-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-thioglucopyranoside (**39**)



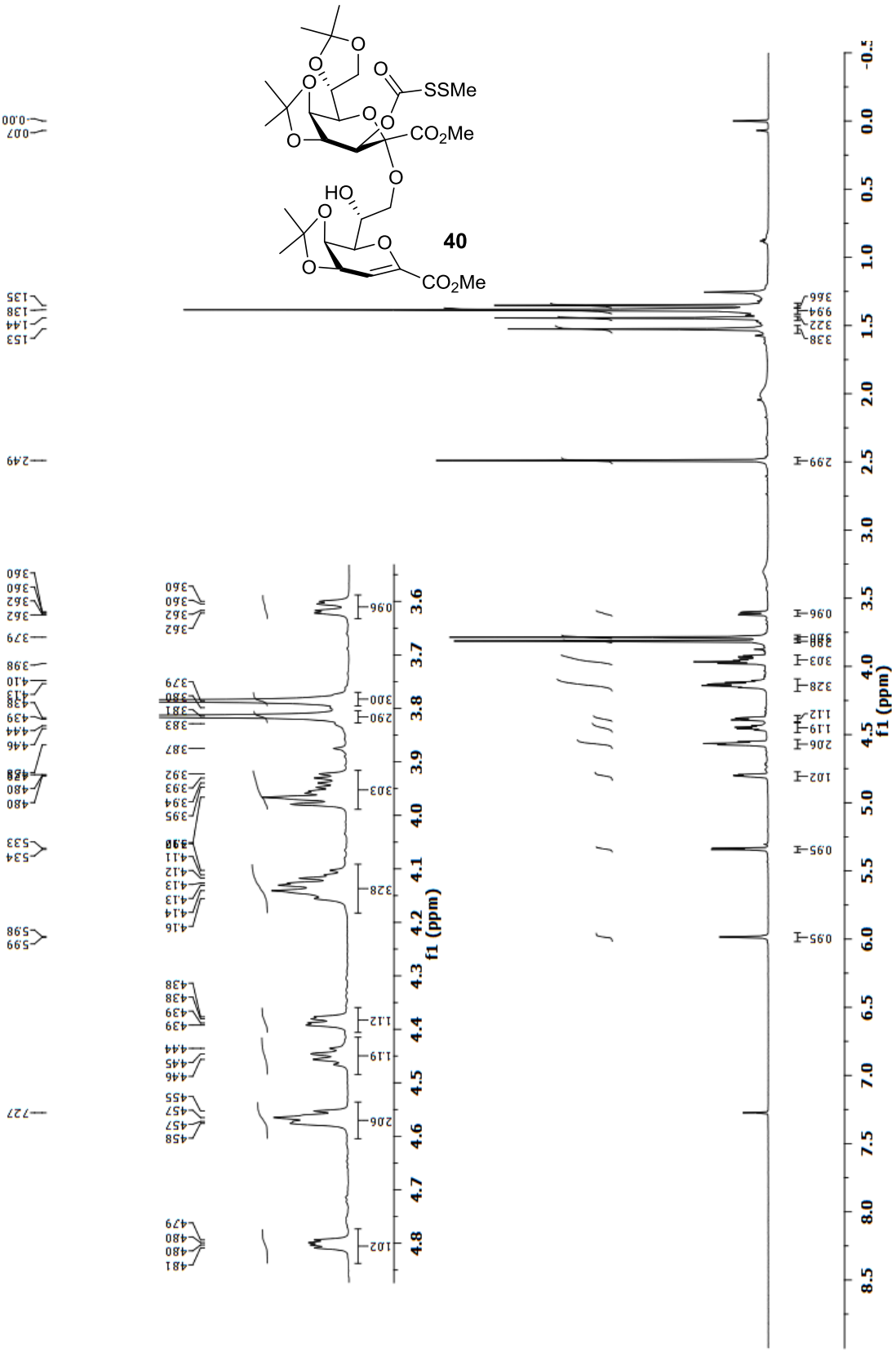
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**39**)



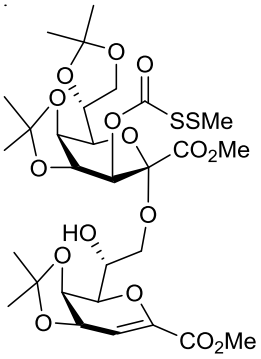
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide **39**



^{1}H NMR (600 MHz, $CDCl_3$) of methyl {2,6-anhydro-3-deoxy-4,5-*O*-isopropylidene-8-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-D-*manno*-2-octulopyranosonyl}onate (**40**)

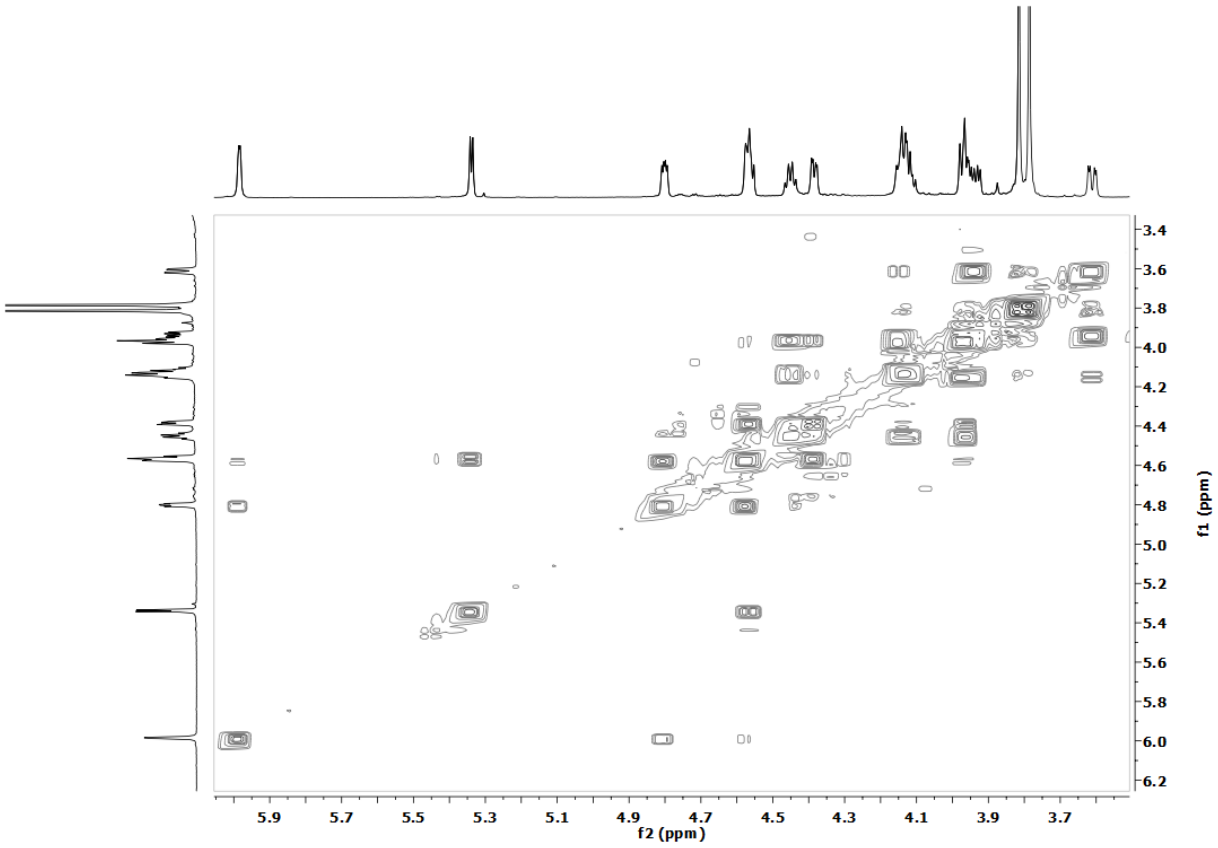


^{13}C NMR (150 MHz, $CDCl_3$) of methyl {2,6-anhydro-3-deoxy-4,5-*O*-isopropylidene-8-*O*-[methyl (4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-α-D-*talo*-2-octulopyranosonyl)onate]-D-*manno*-2-octulopyranosonyl}onate (**40**)

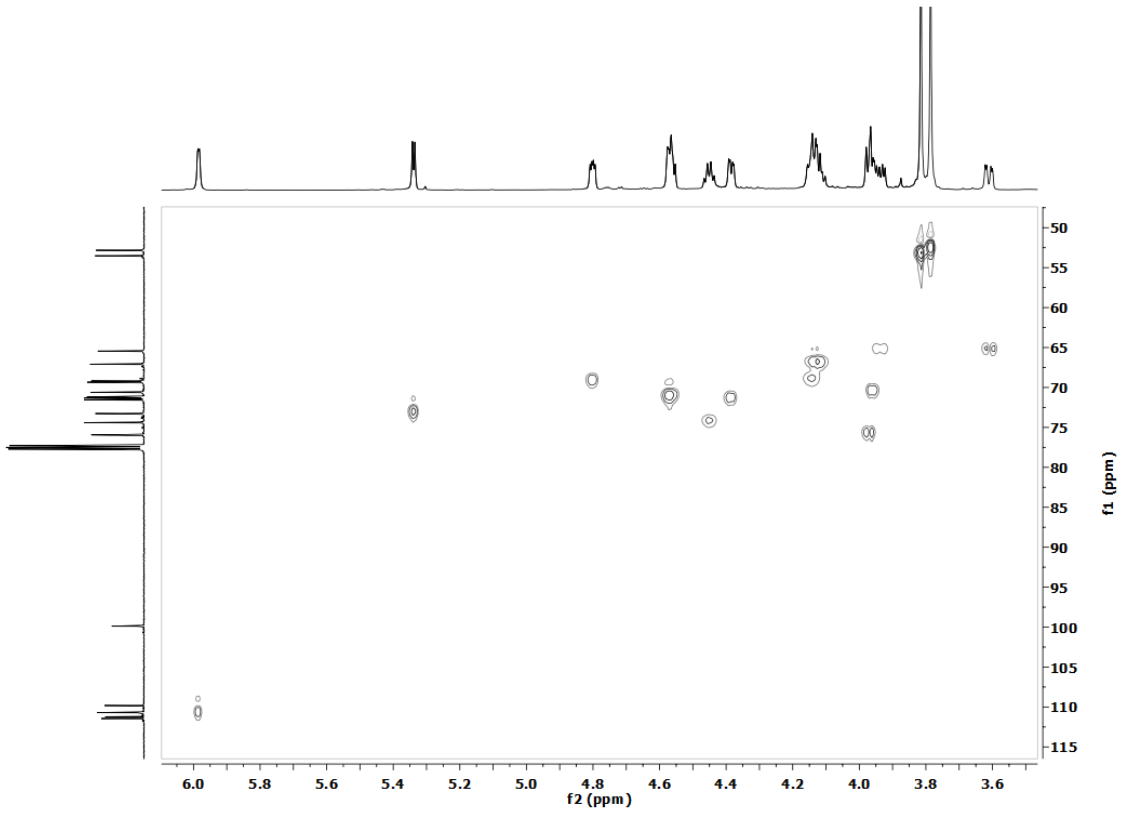


40

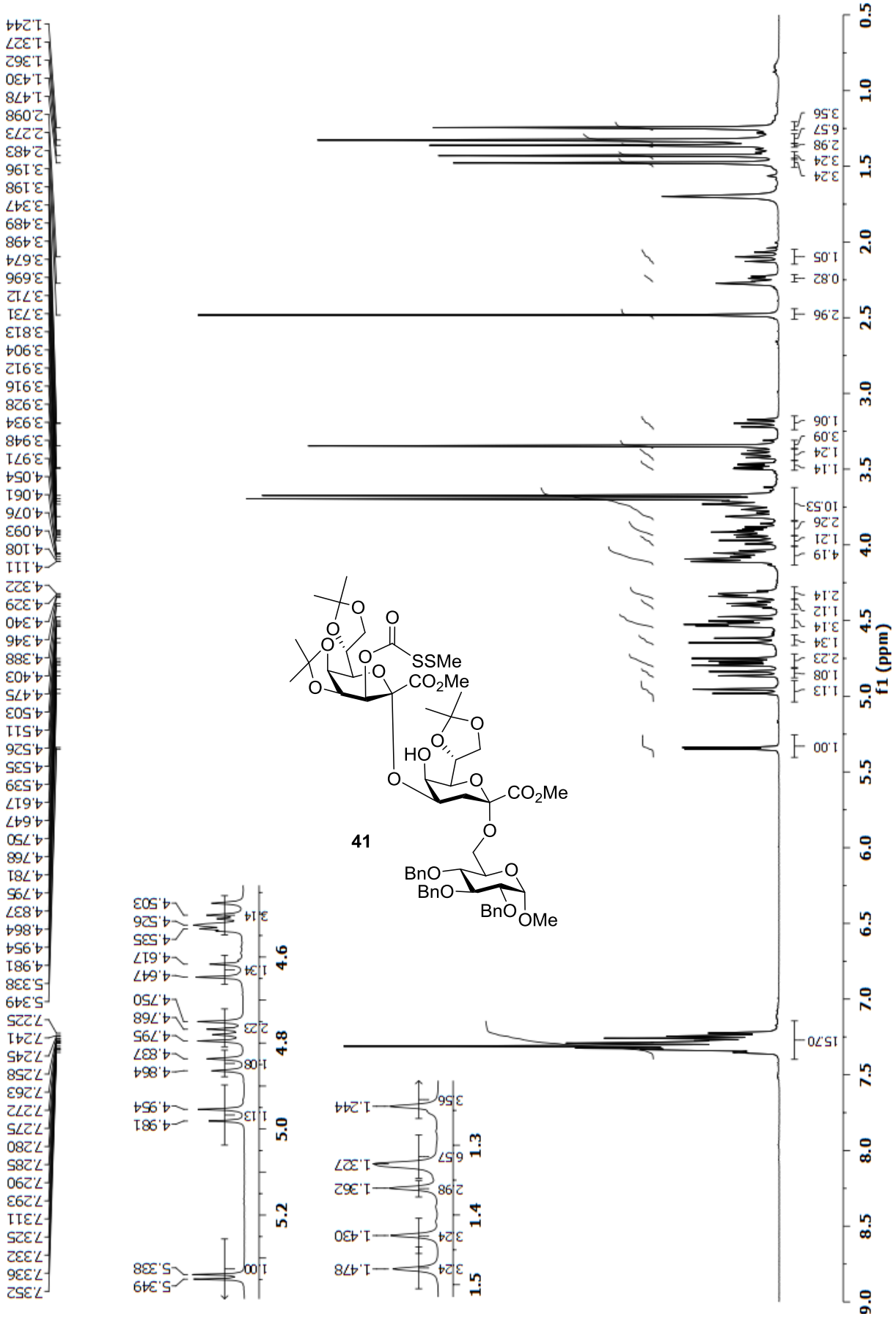
^{1}H-^{1}H GCOSY (600 MHz, $CDCl_3$) of disaccharide (**40**)



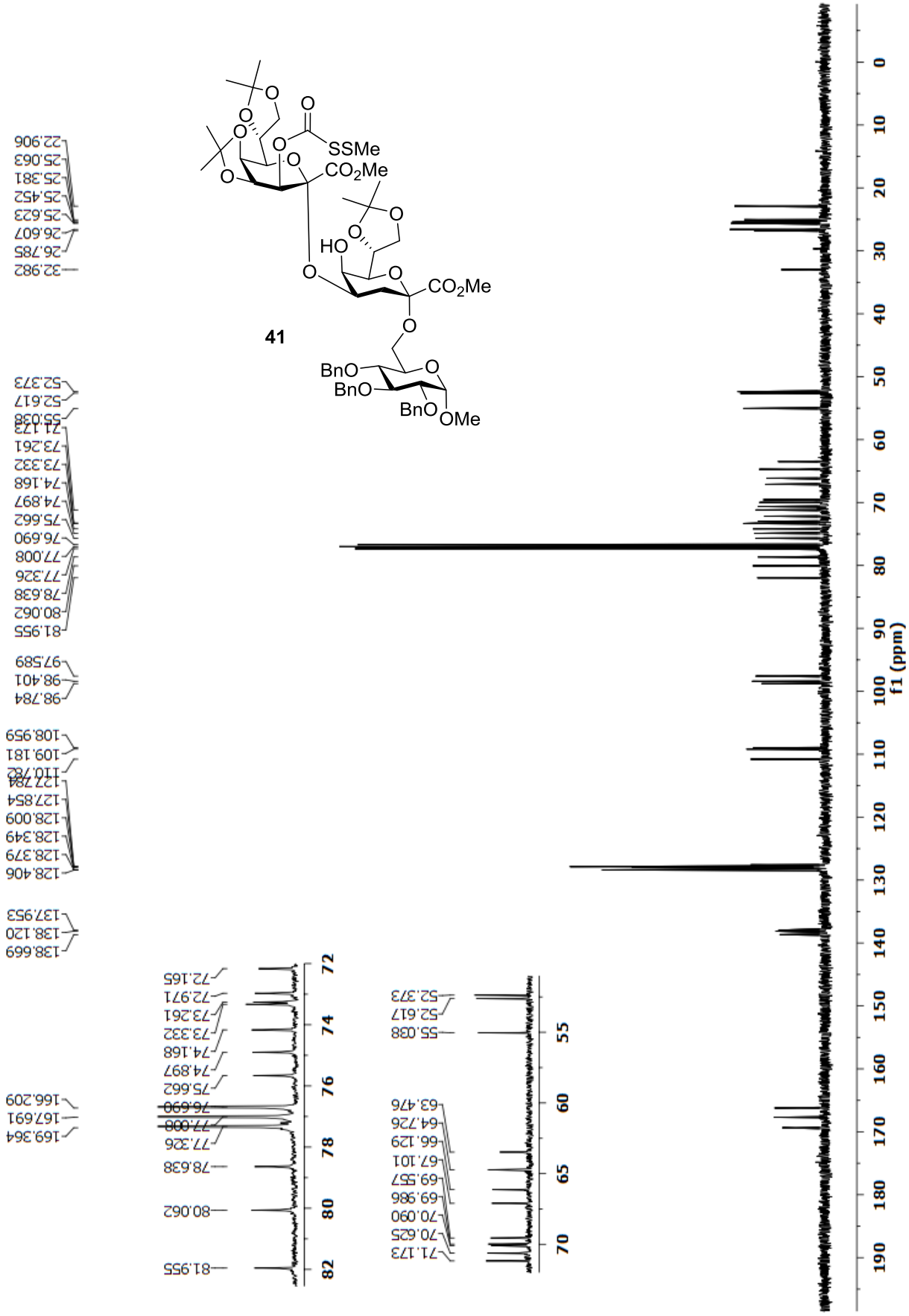
^{1}H-^{13}C HMQC NMR (150 MHz, $CDCl_3$) of disaccharide (**40**)



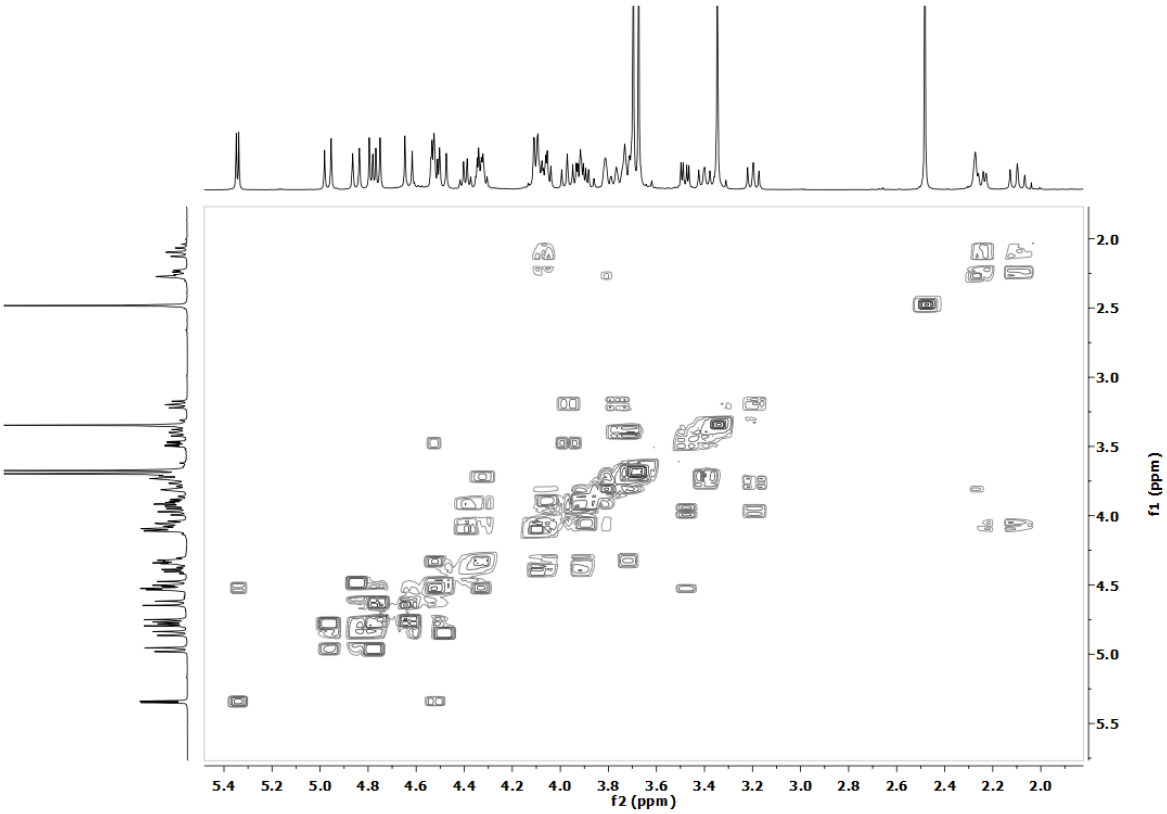
^{1}H NMR (400 MHz, $CDCl_3$) of trisaccharide (**41**)



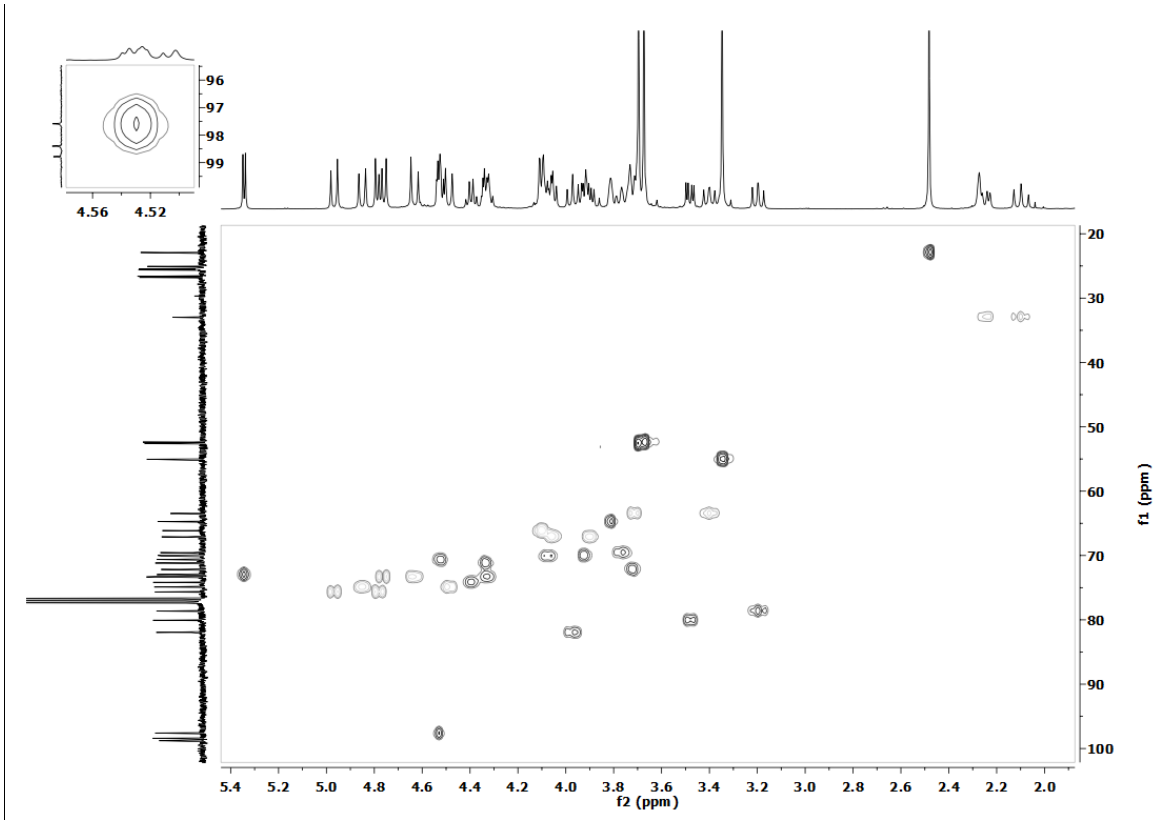
^{13}C NMR (100 MHz, $CDCl_3$) of trisaccharide (**41**)



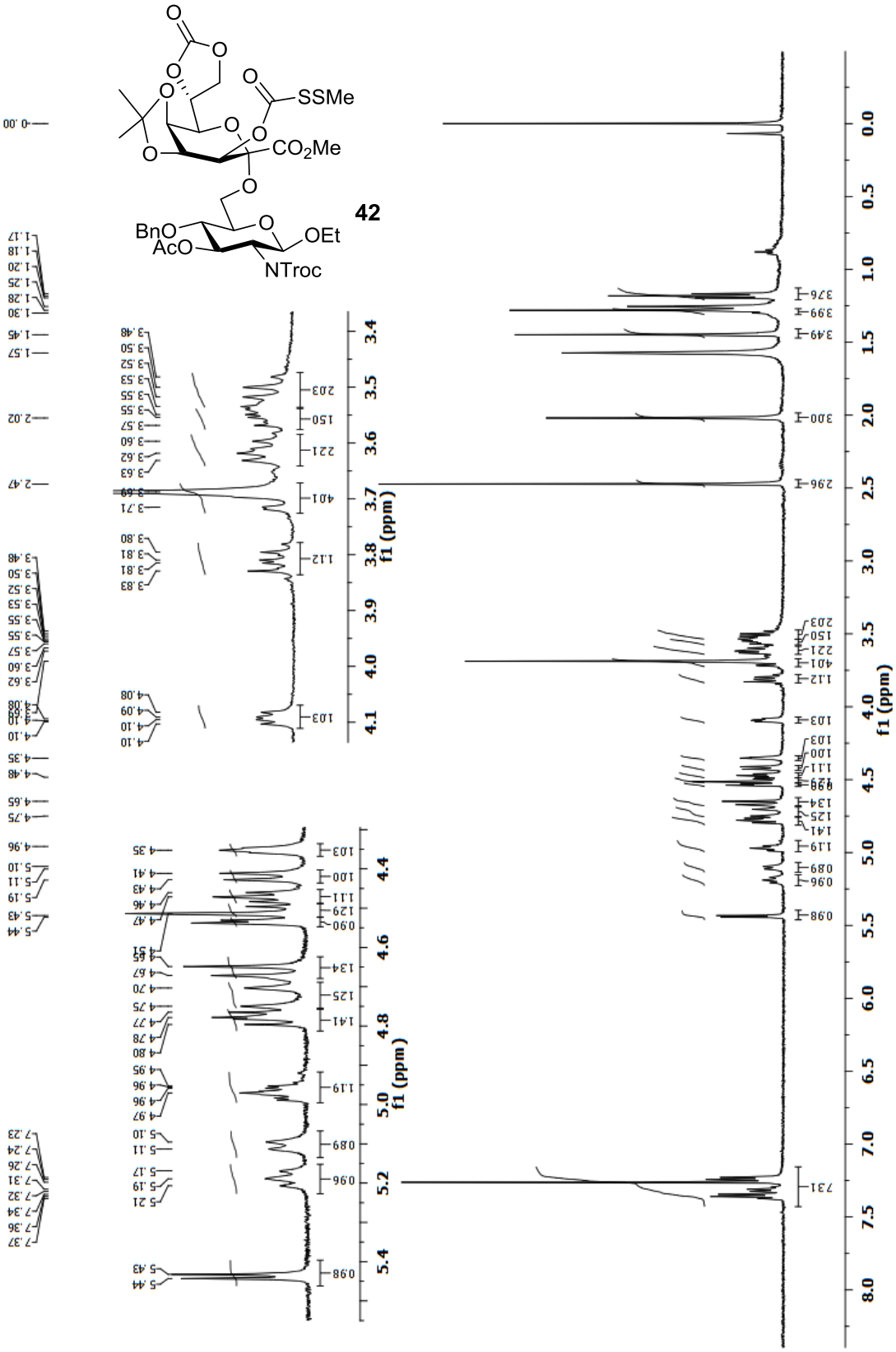
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of trisaccharide (**41**)



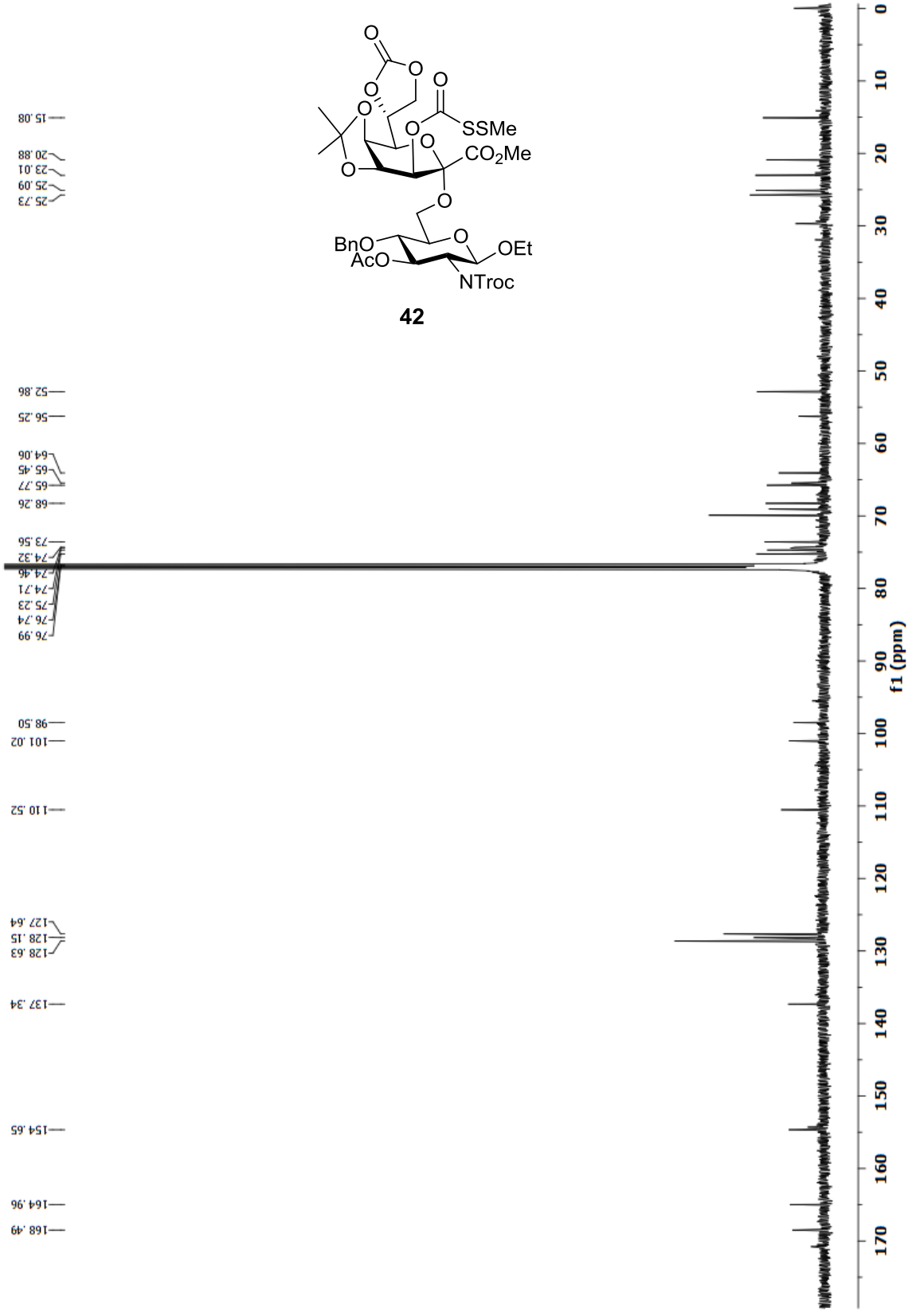
^{1}H-^{13}C HSQC (100 MHz, $CDCl_3$) of trisaccharide (**41**)



^{1}H NMR (500 MHz, $CDCl_3$) of ethyl {3-*O*-acetyl-4-*O*-benzyl-2-trichloroethoxycarbonyamino-2-deoxy-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-glucopyranoside (**42**)

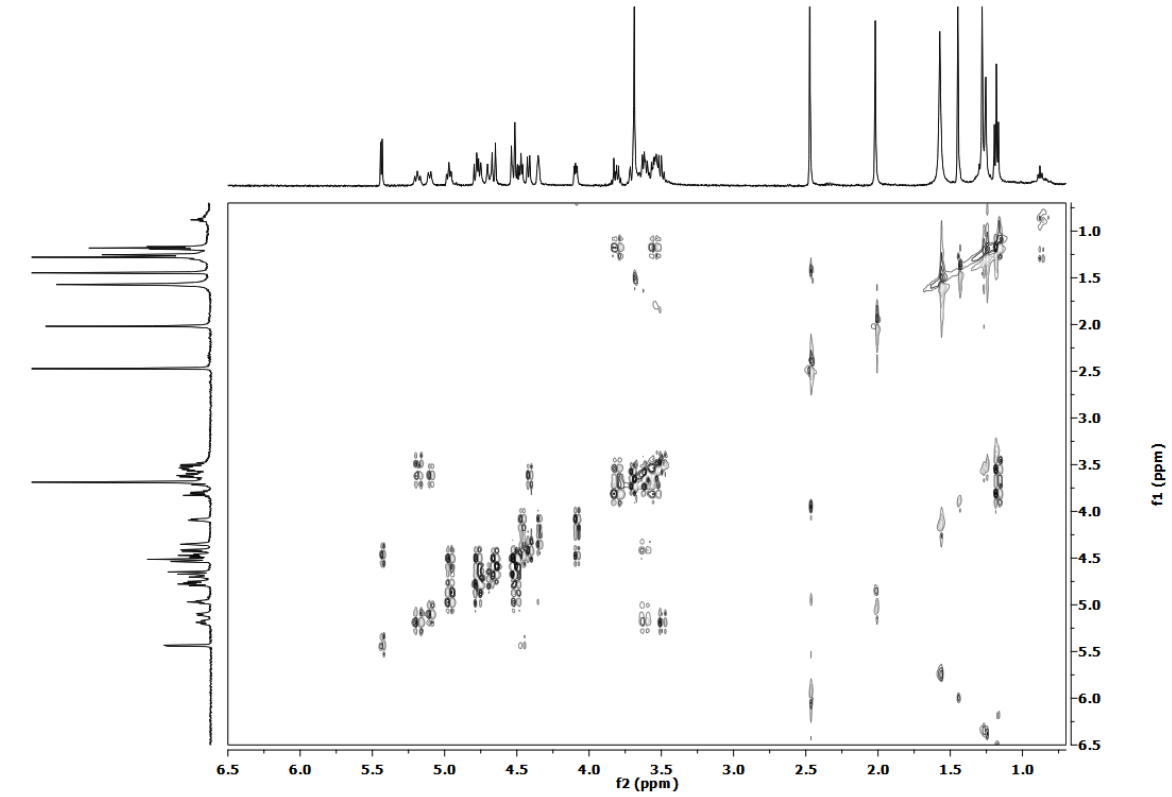


^{13}C NMR (125 MHz, $CDCl_3$) of ethyl {3-*O*-acetyl-4-*O*-benzyl-2-trichloroethoxycarbonylamino-2-deoxy-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*β*-D-glucopyranoside (**42**)

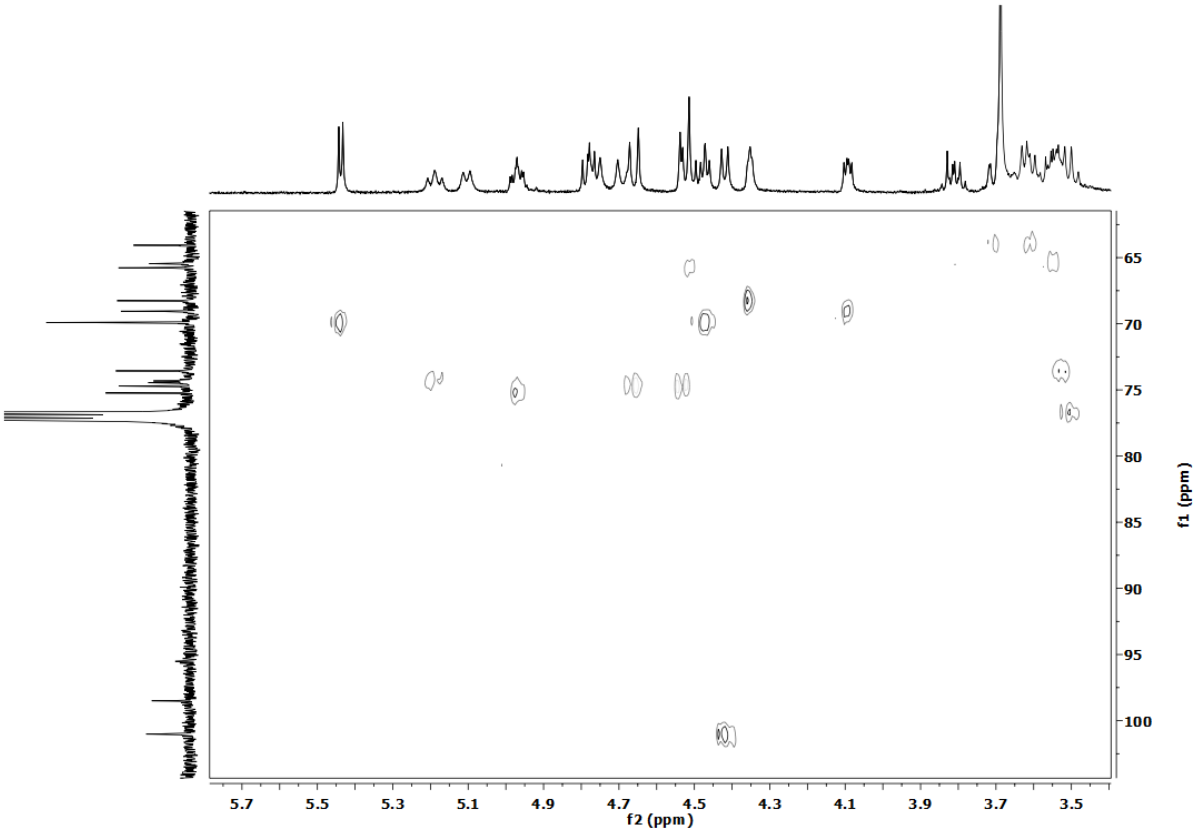


42

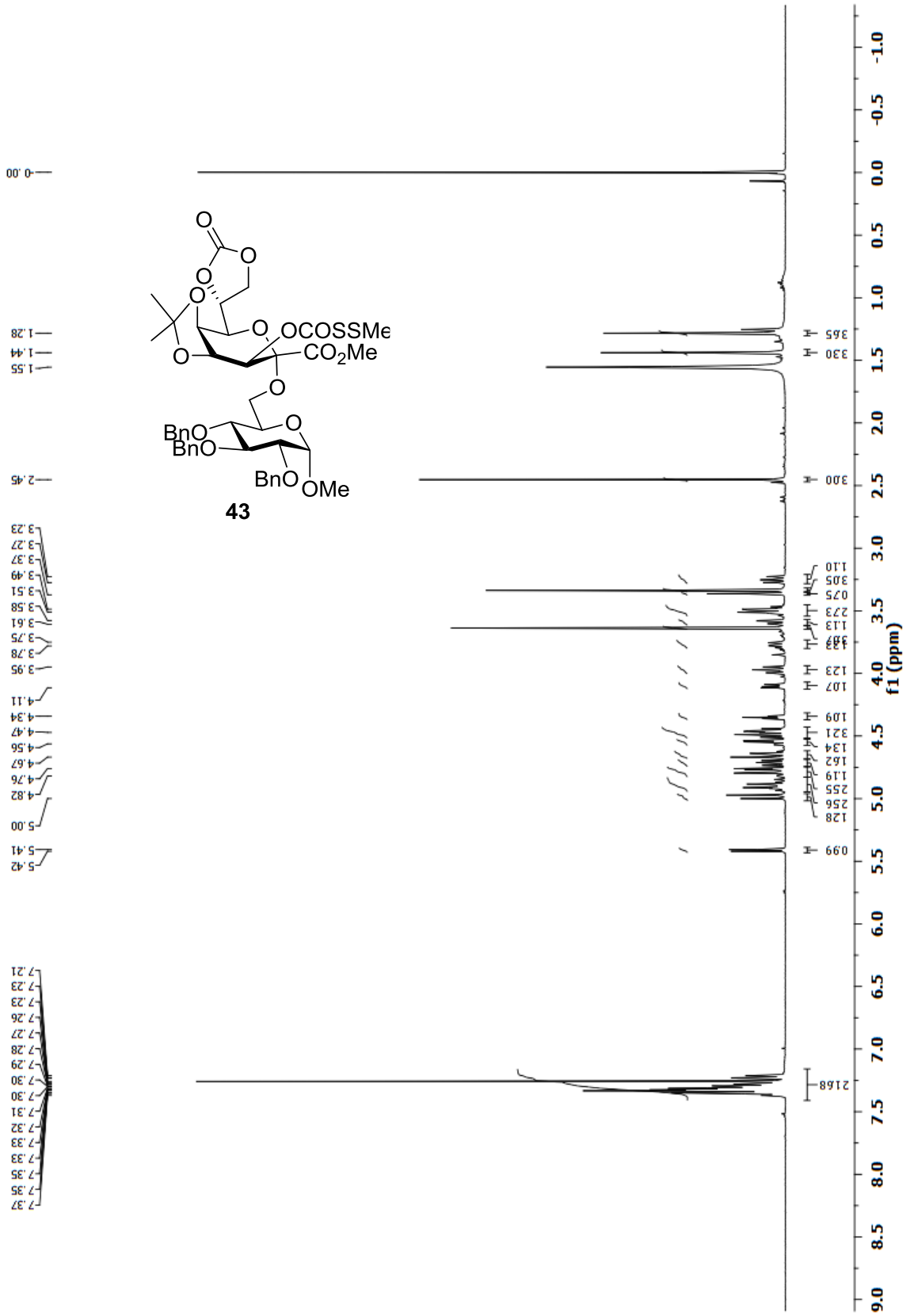
^{1}H-^{1}H GCOSY (500 MHz, $CDCl_3$) of disaccharide (**42**)



^{1}H-^{13}C HSQC NMR (125 MHz, $CDCl_3$) of disaccharide (**42**)

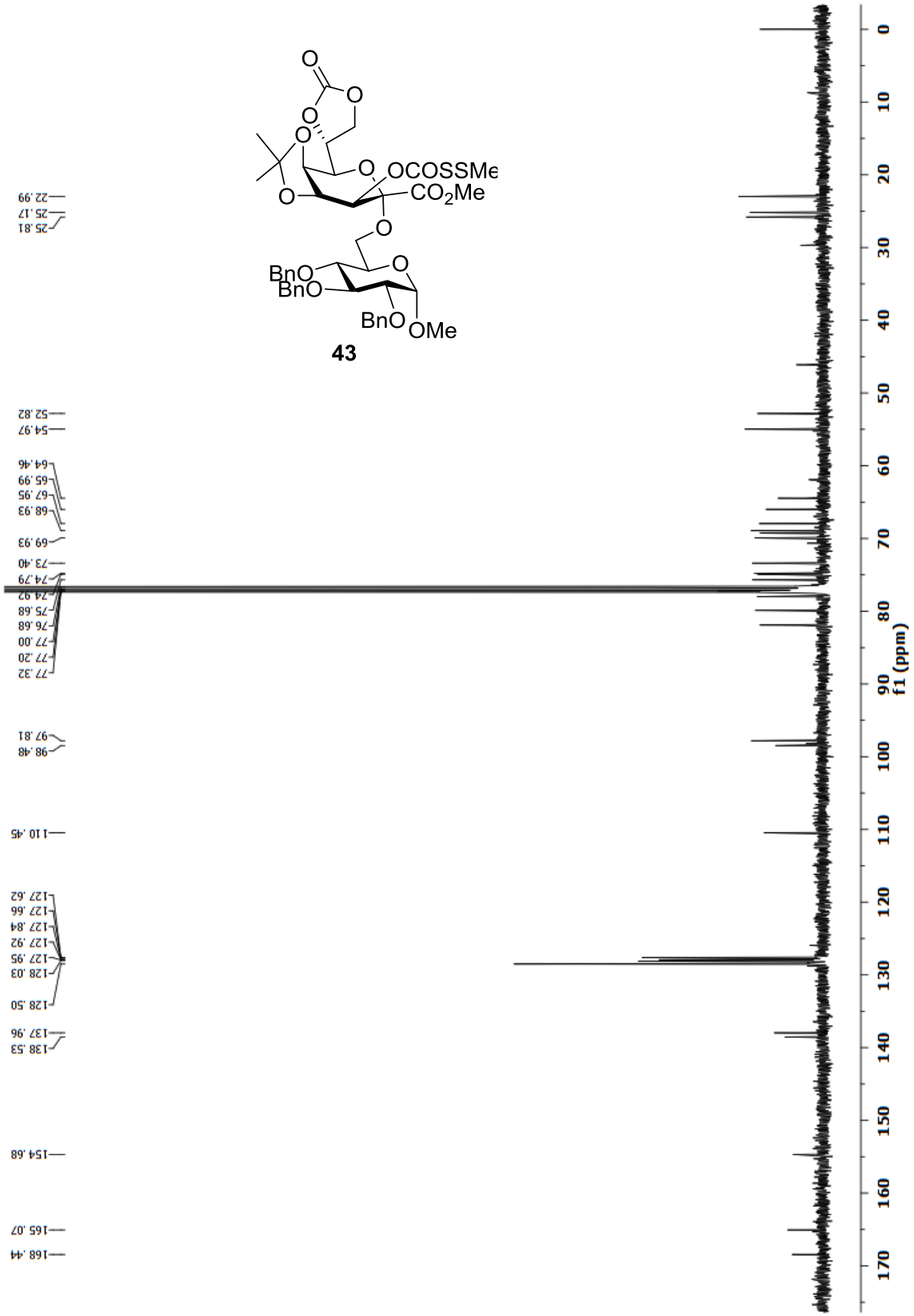


^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**43**)

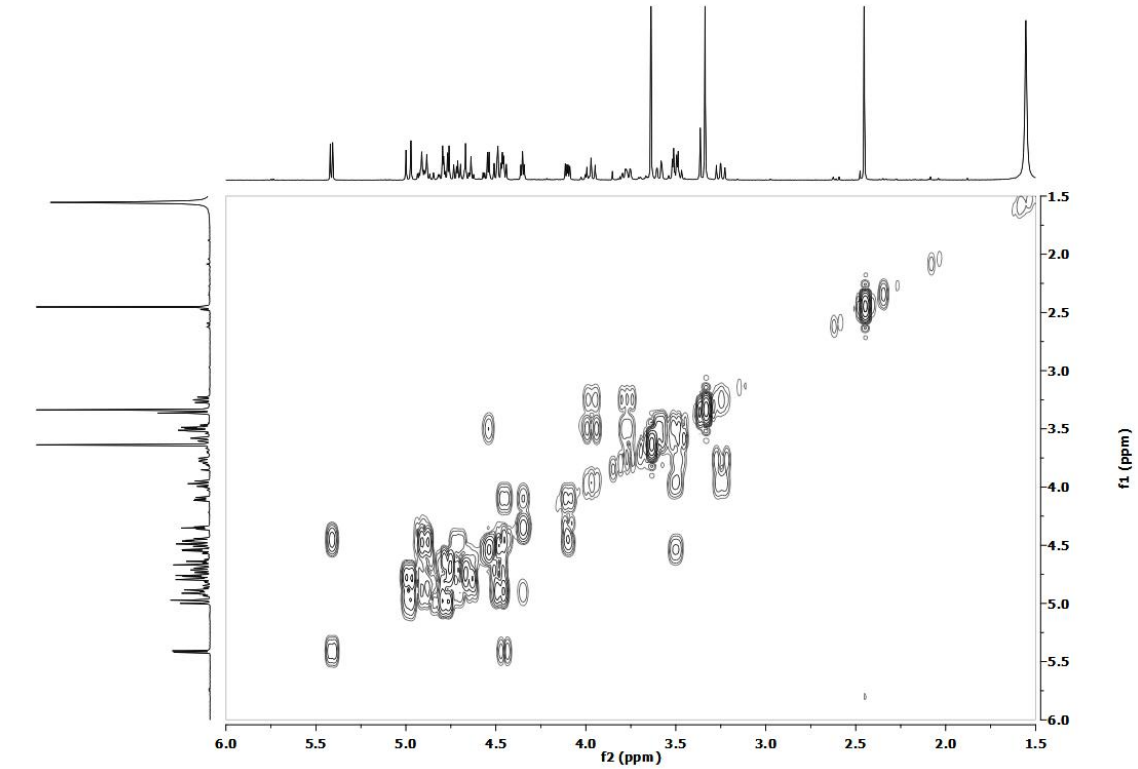


43

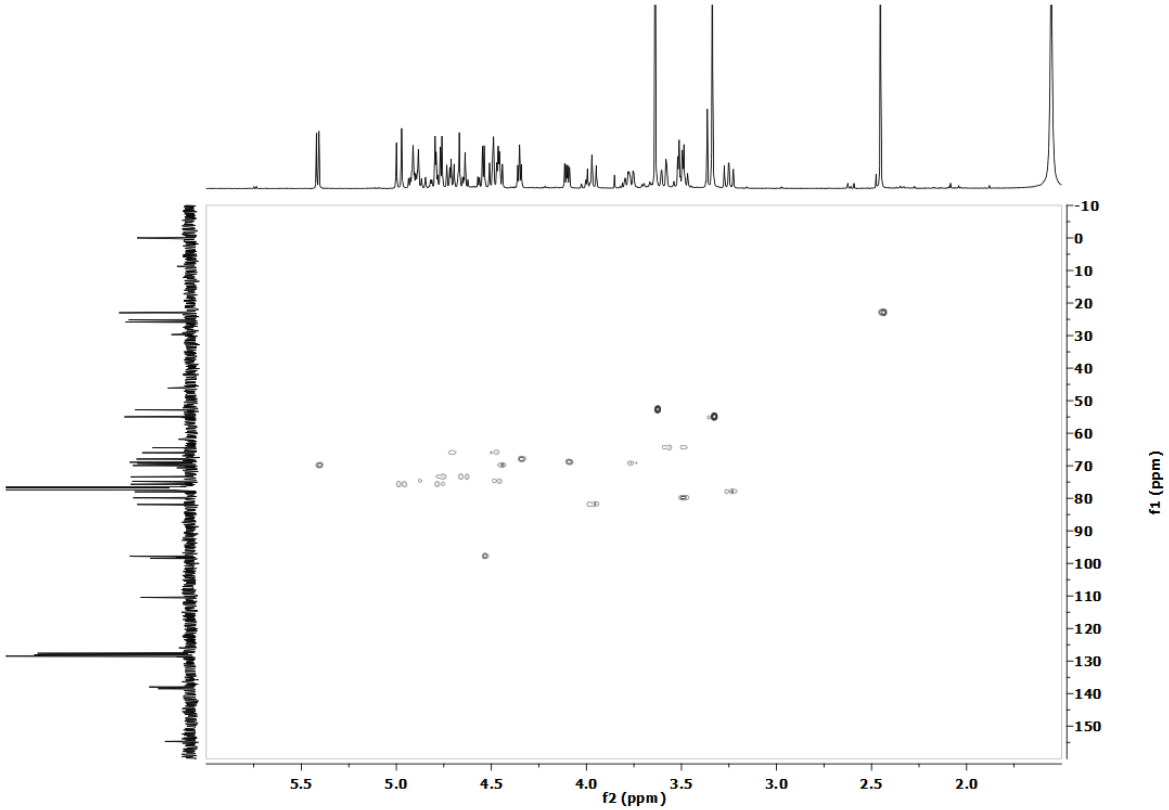
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7,8-*O*-carbonyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**43**)



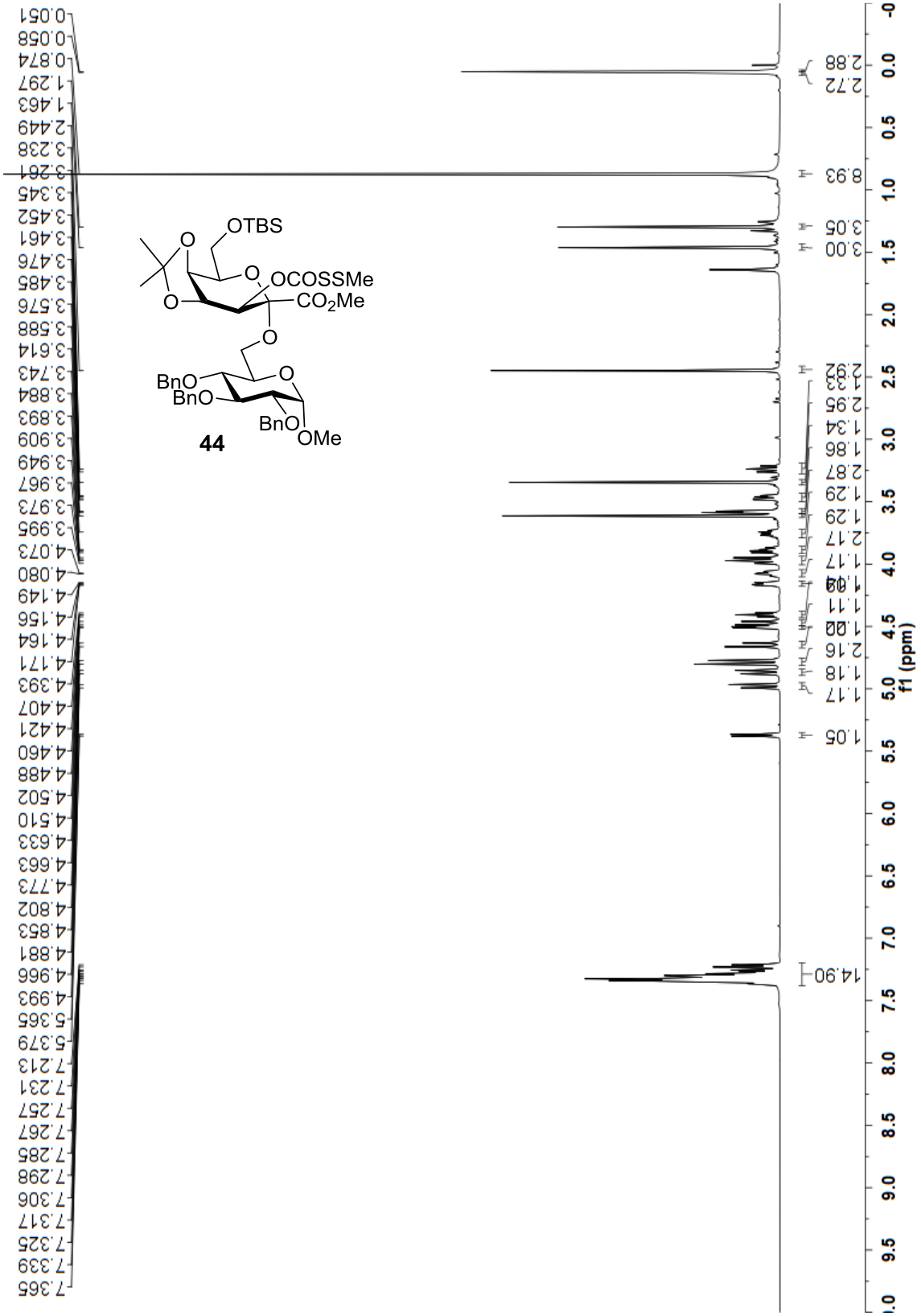
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**43**)



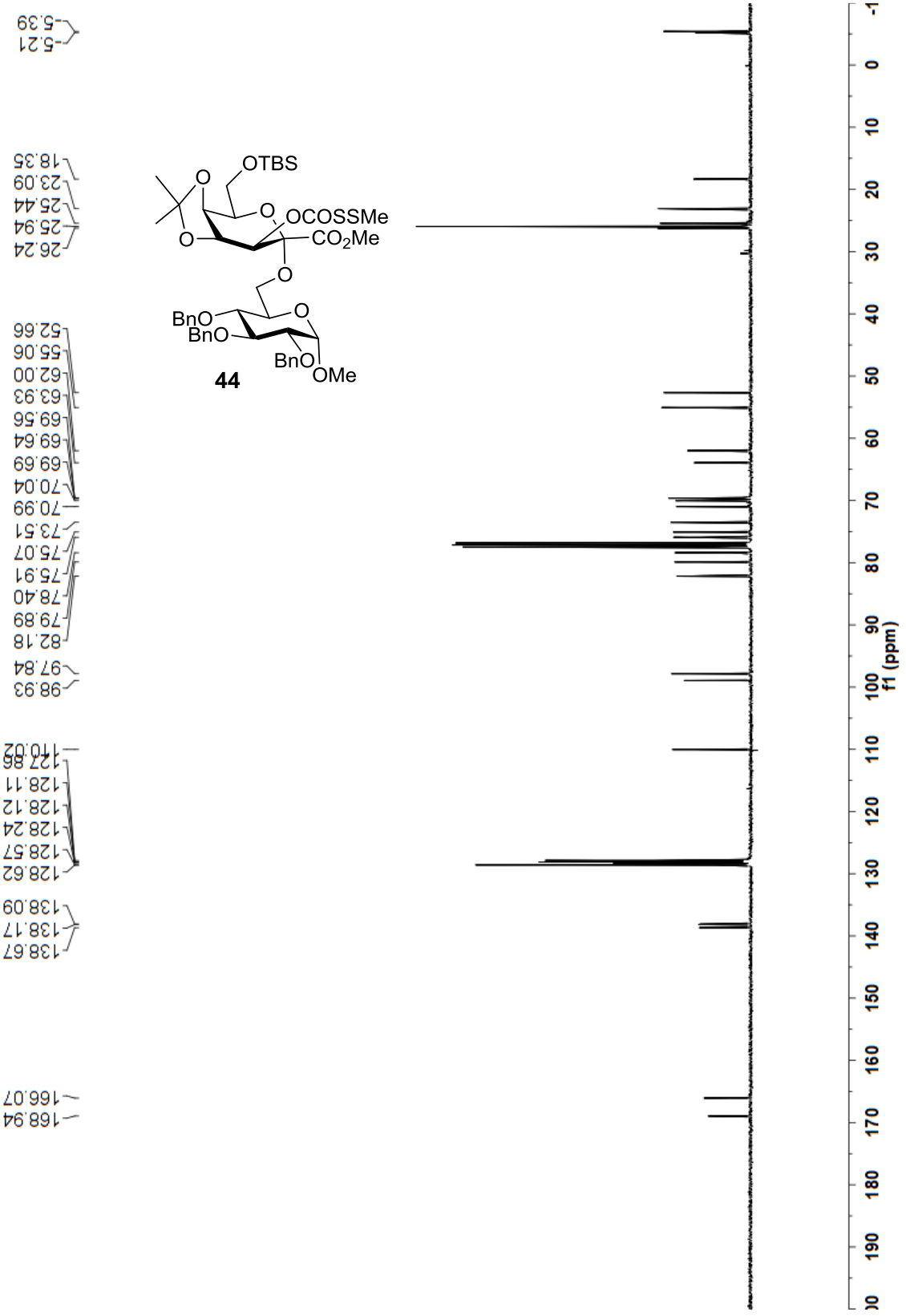
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**43**)



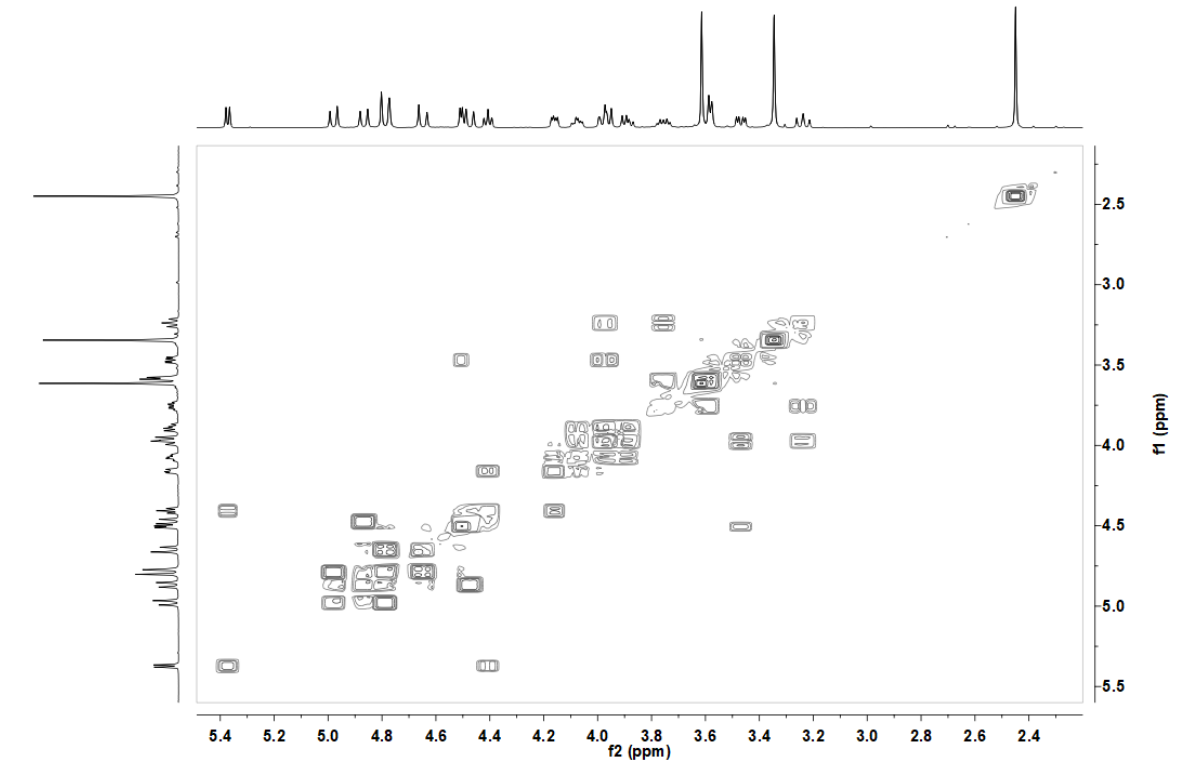
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**44**)



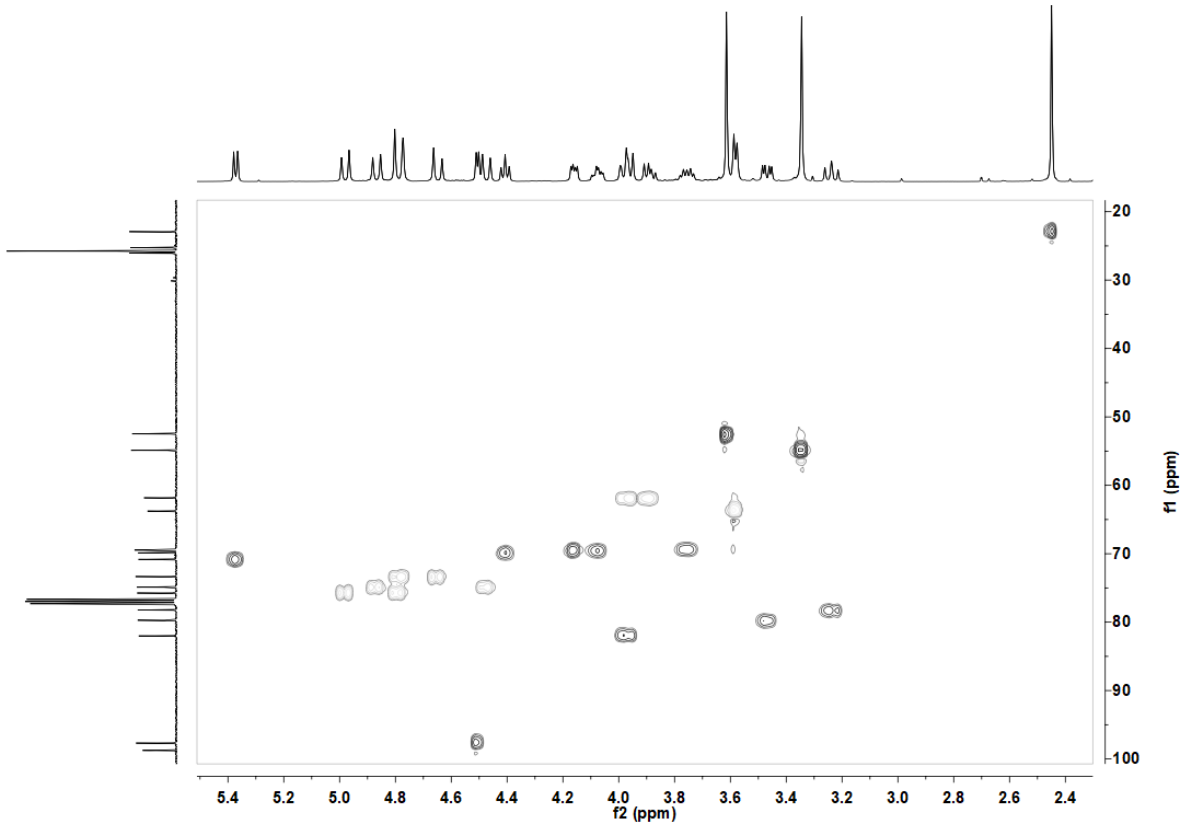
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-tbutyldimethylsilyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**44**)



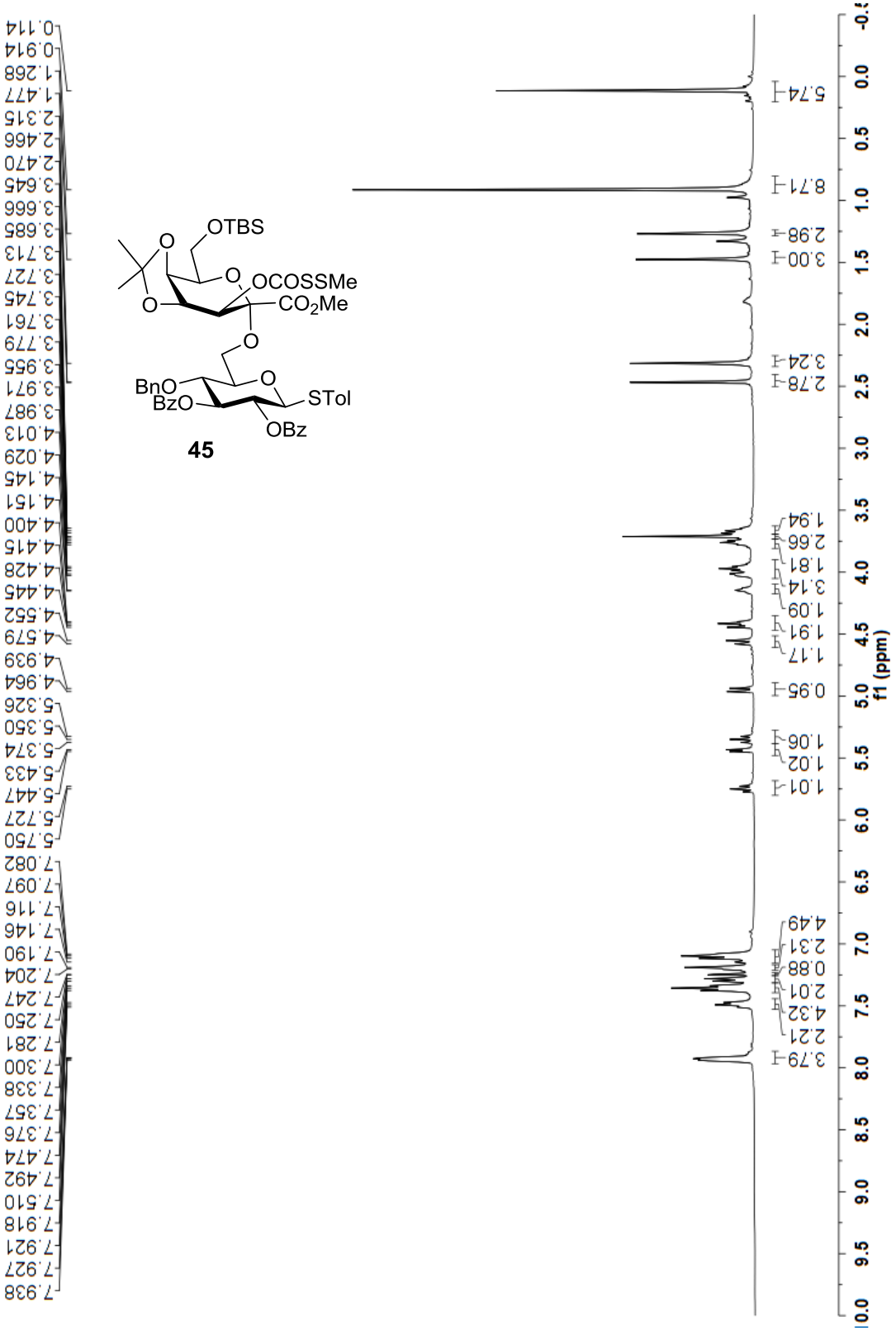
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**44**)



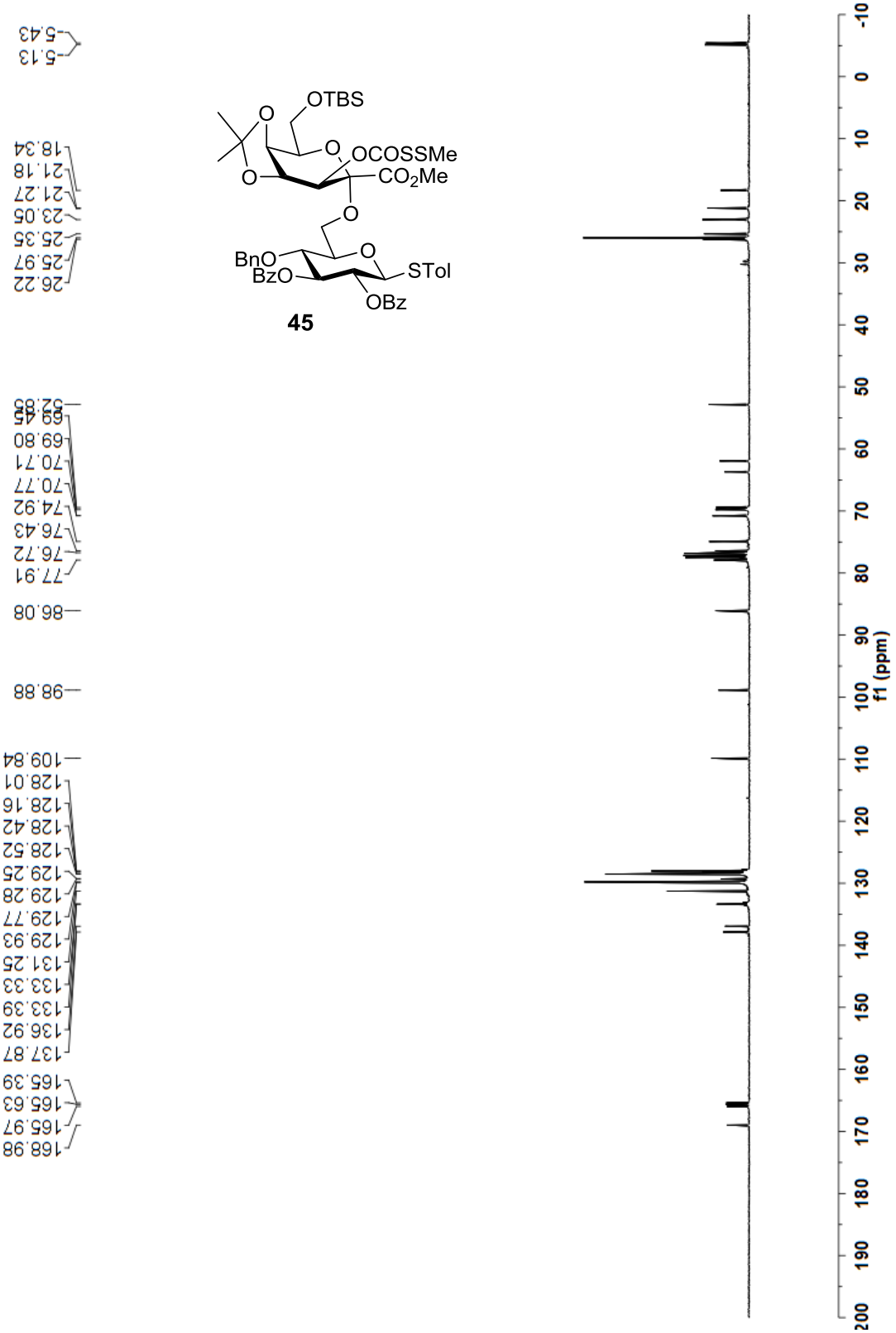
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**44**)



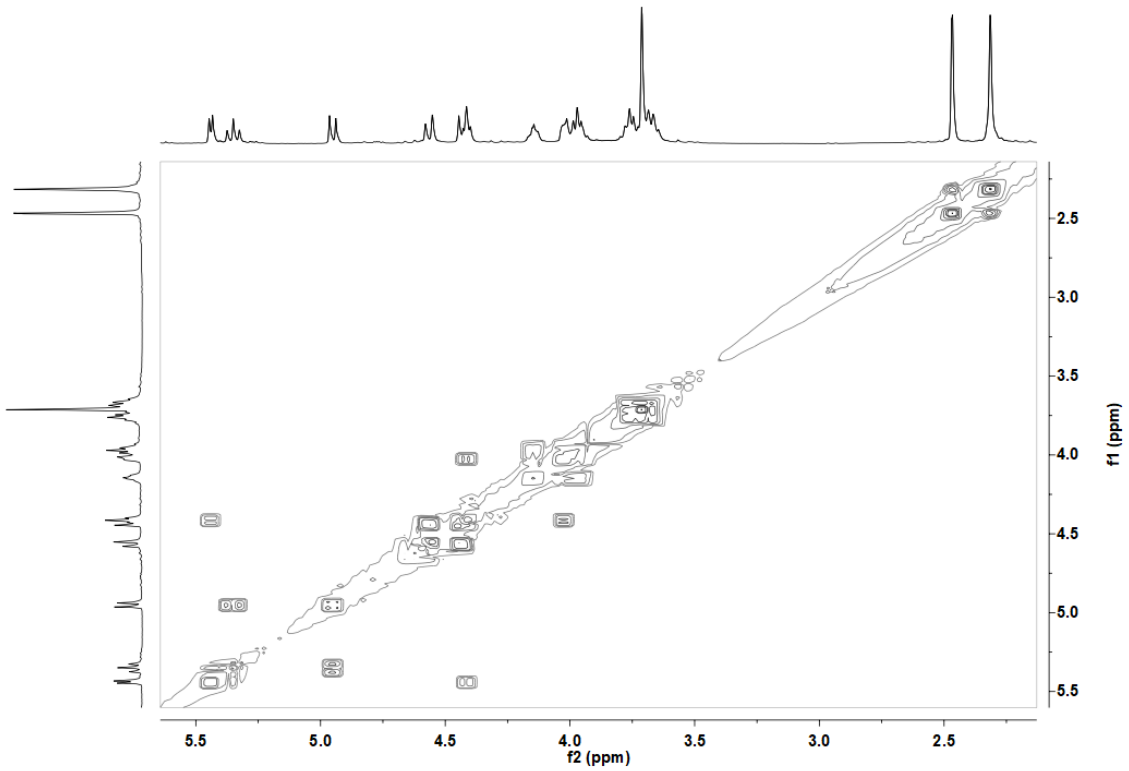
^{1}H NMR (400 MHz, $CDCl_3$) of *p*-tolyl 4-*O*-benzyl-2,3-di-*O*-benzoyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-*α*-D-*talo*-2-heptulopyranosonyl)onate]-thio-*α*-D-glucopyranoside (**45**)



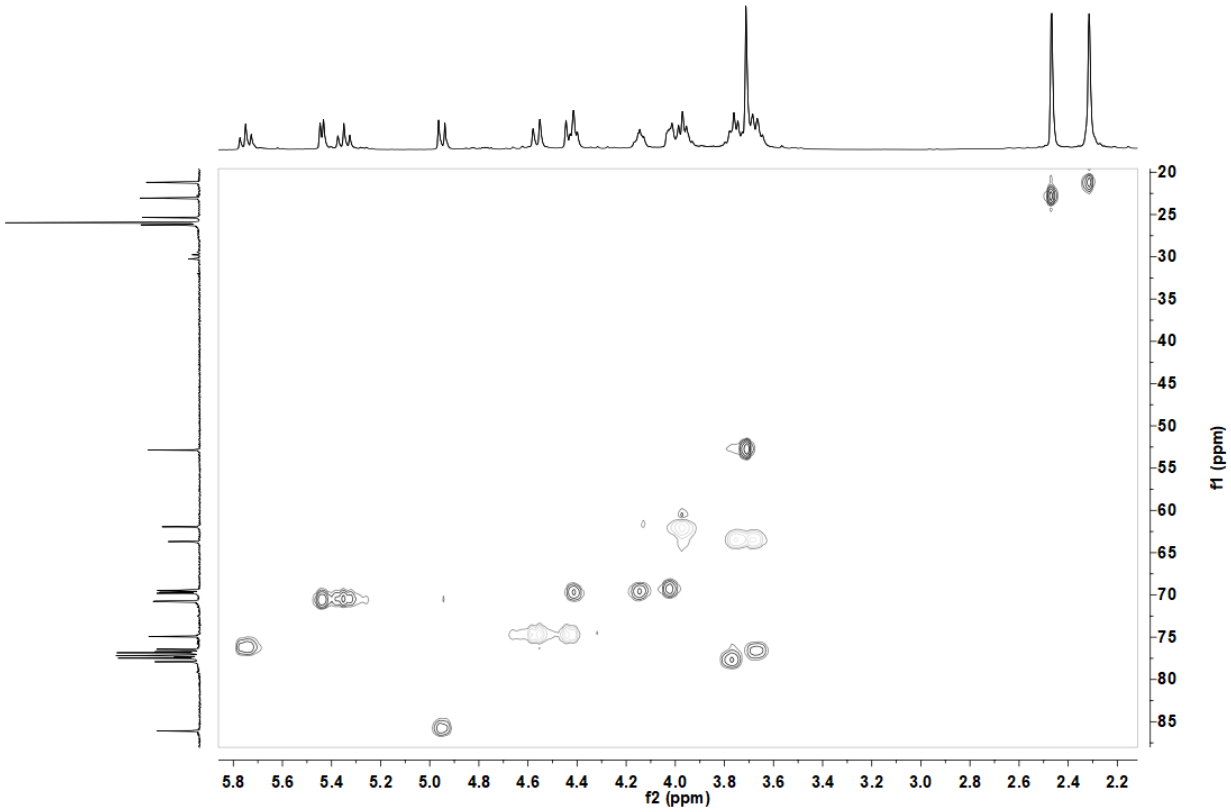
^{13}C NMR (100 MHz, $CDCl_3$) of *p*-**t**olyl 4-*O*-benzyl-2,3-di-*O*-benzoyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl**)**-*α*-D-*talo*-2-heptulopyranosonyl)onate]-thio-*α*-D-glucopyranoside (**45**)



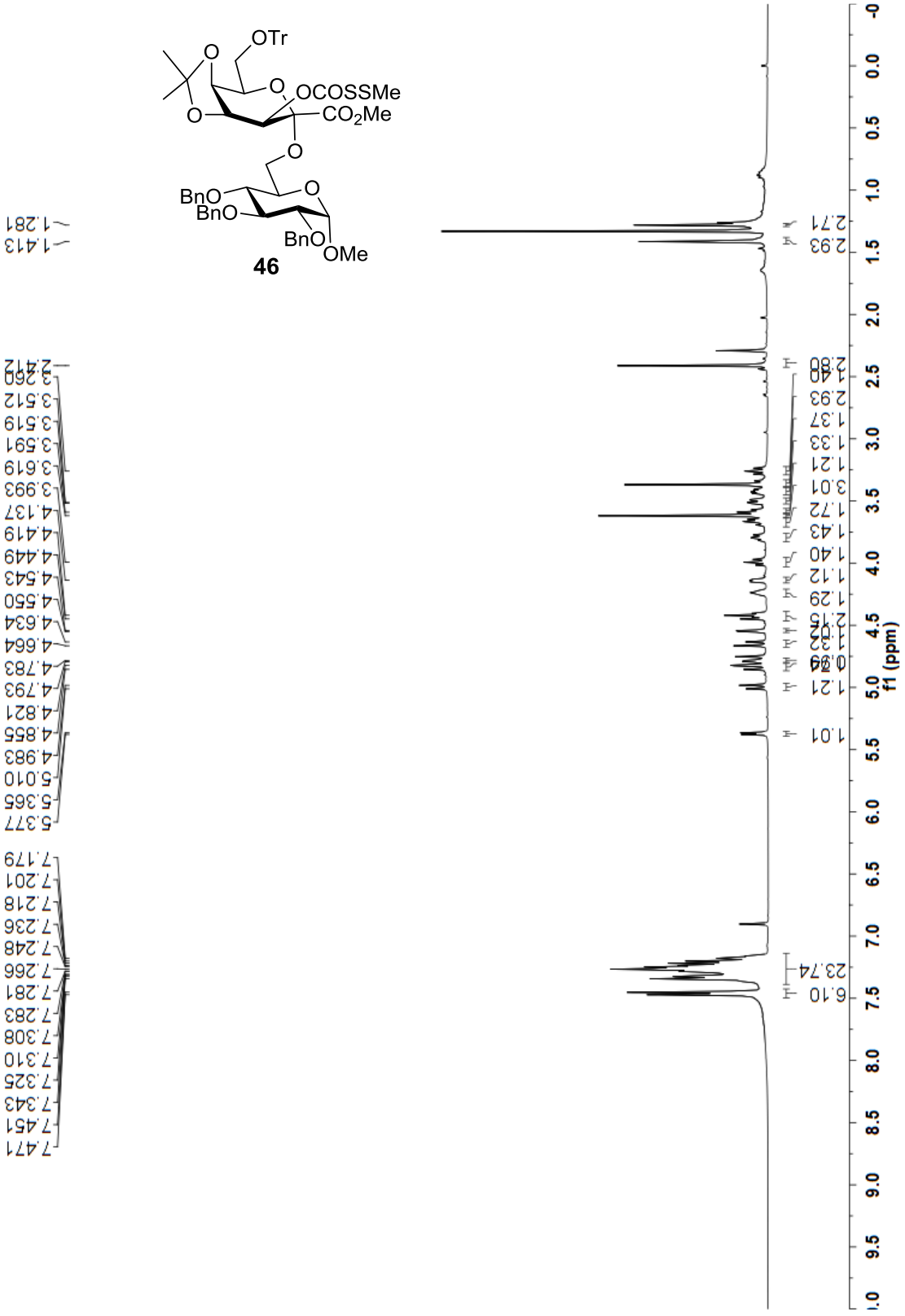
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**45**)



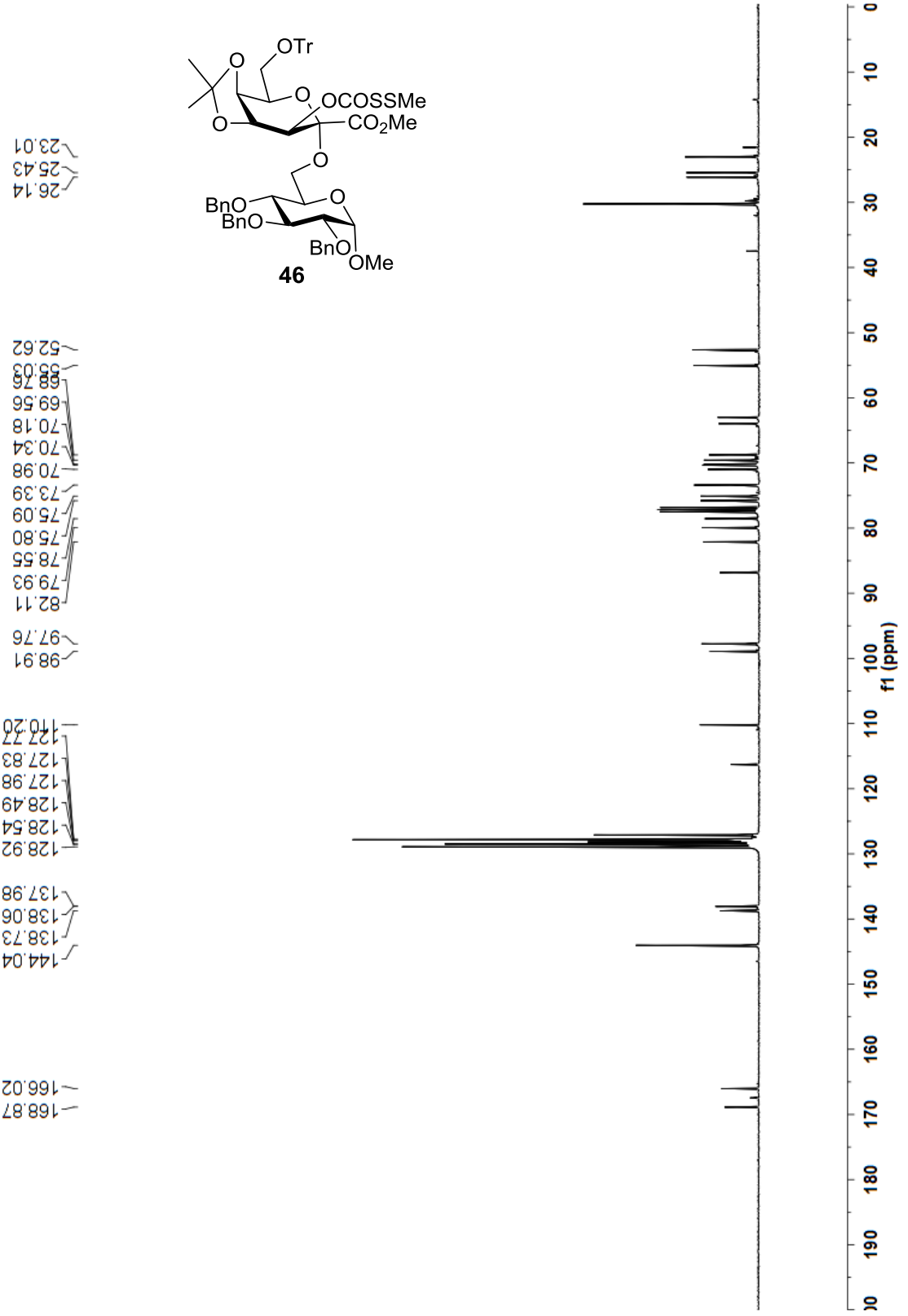
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**45**)



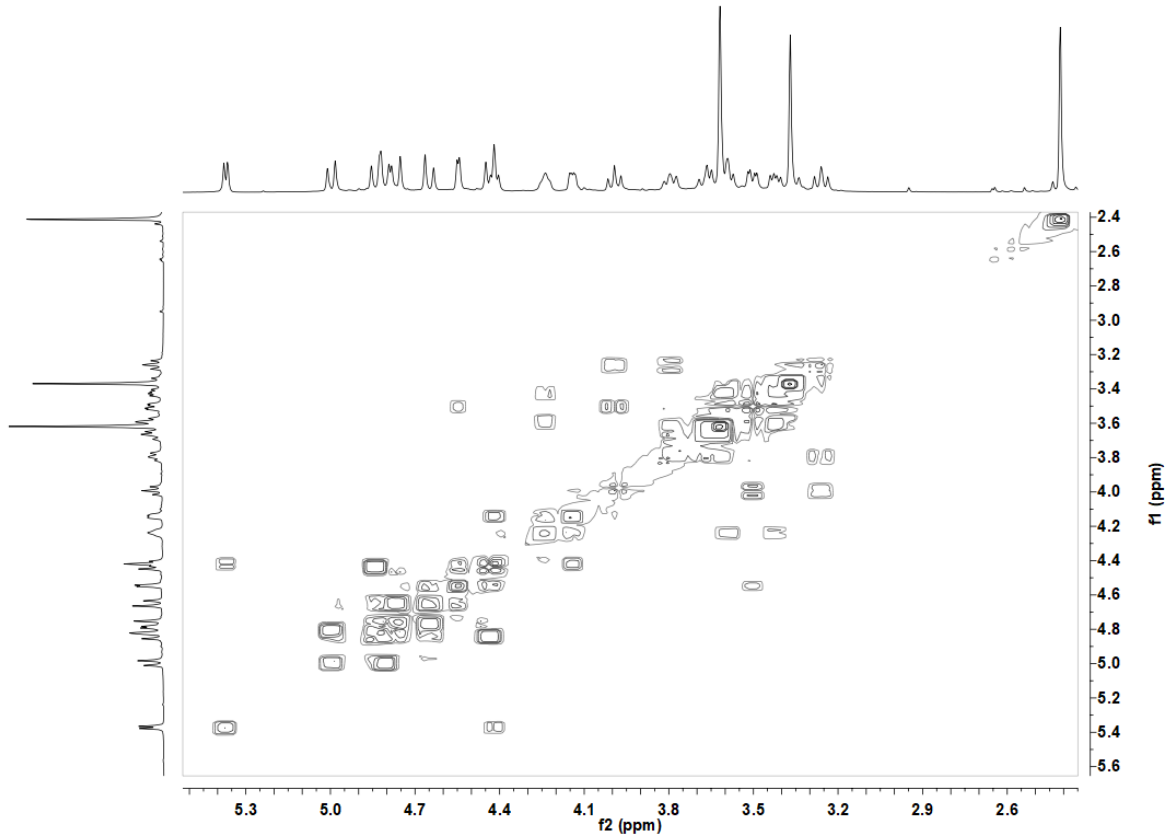
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-7-*O*-trityl-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**46**)



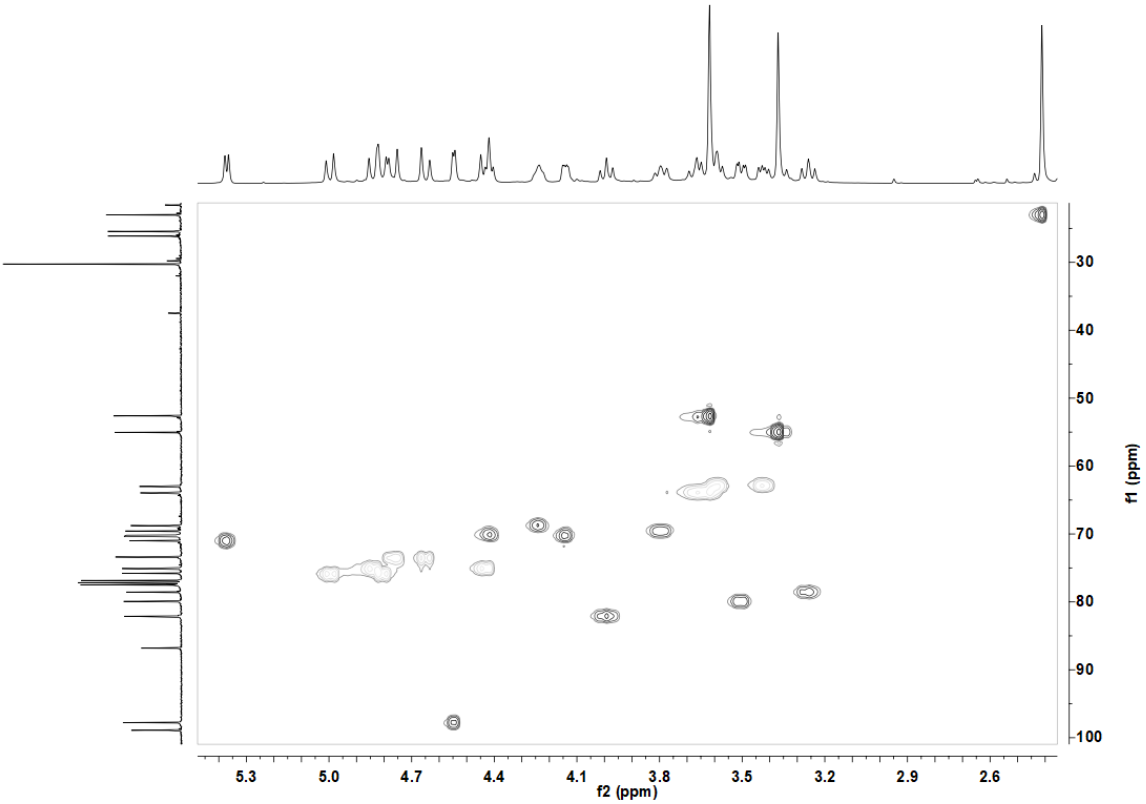
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-7-*O*-trityl-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**46**)



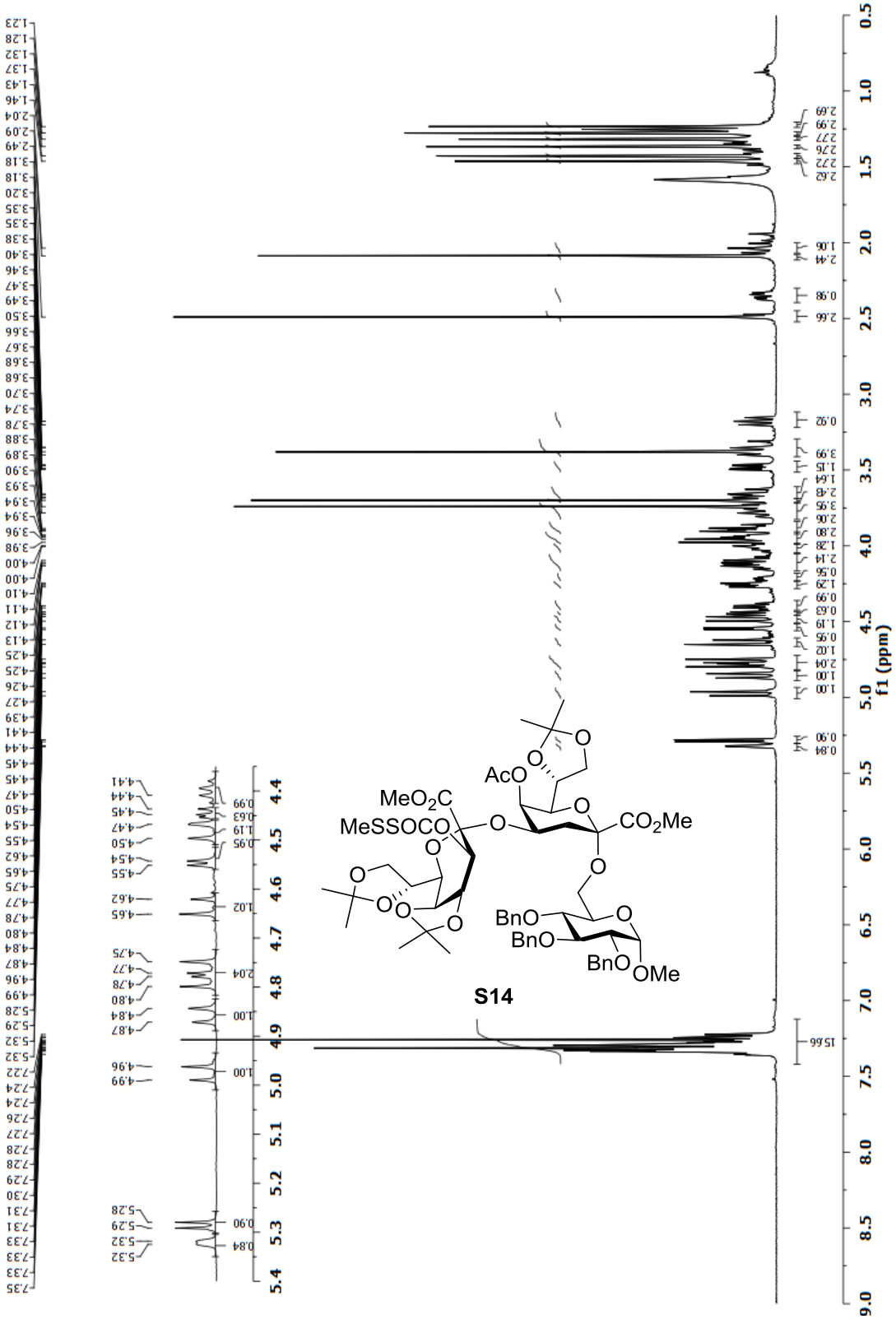
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide **(46)**



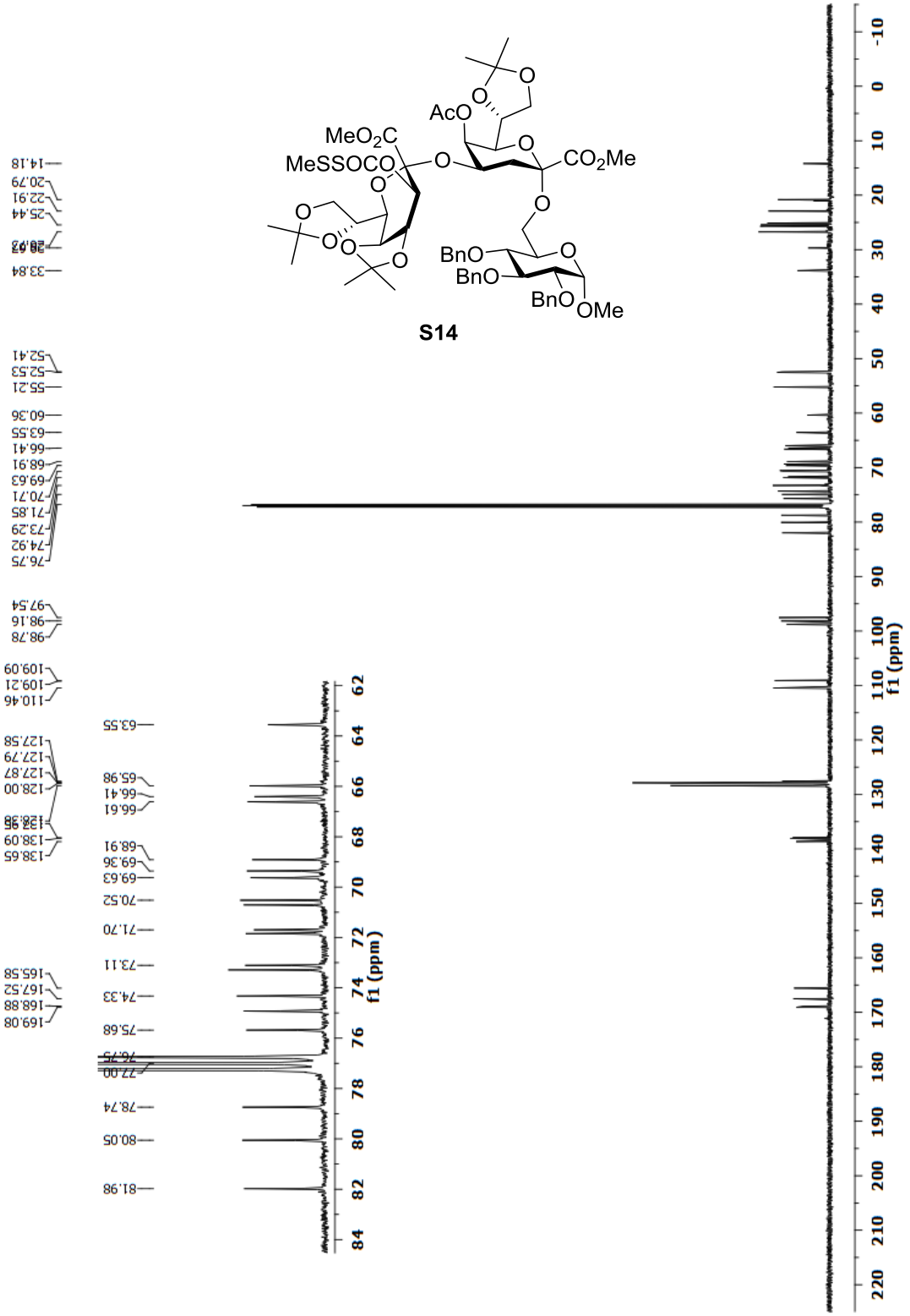
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**46**)



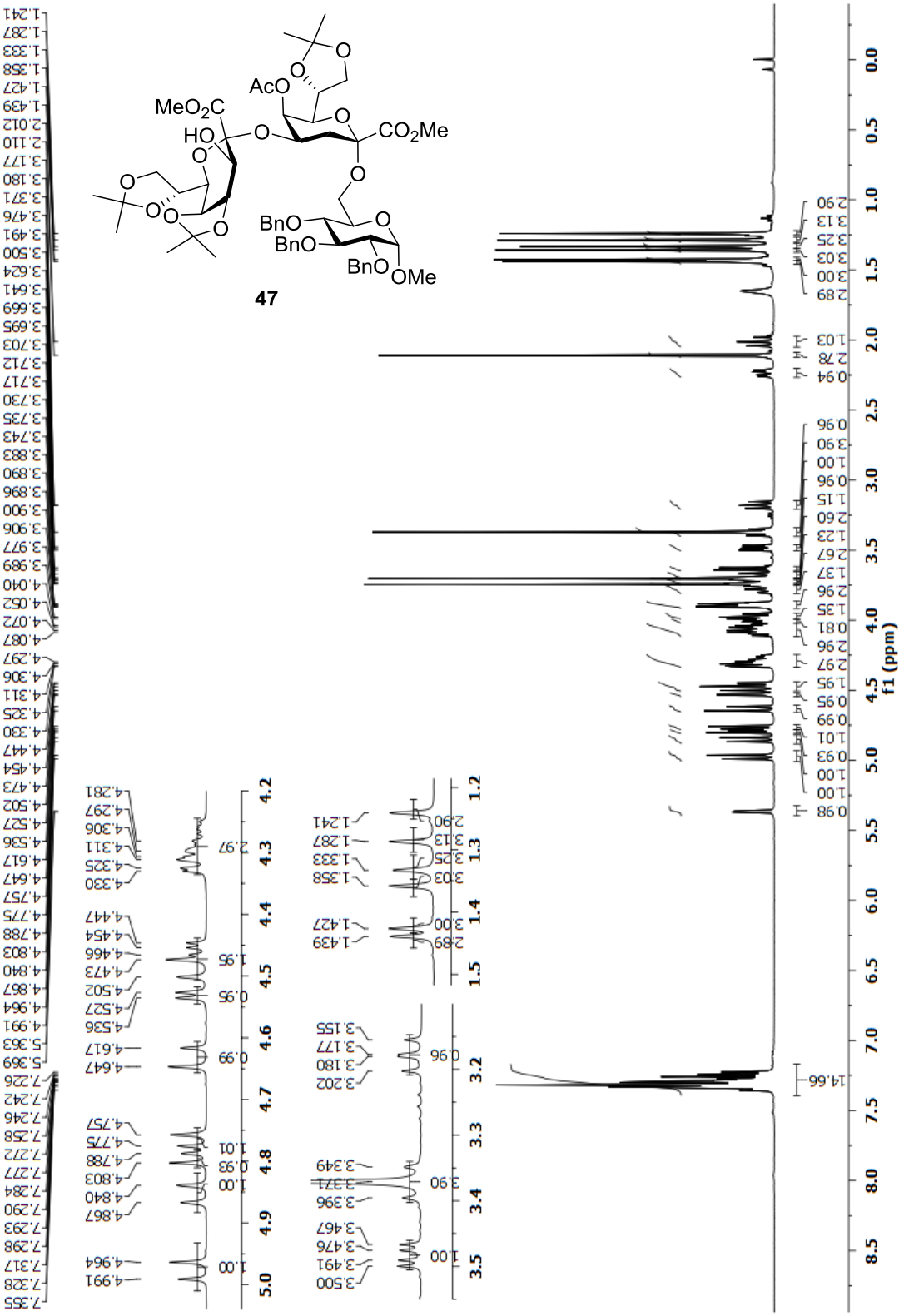
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (**S14**)



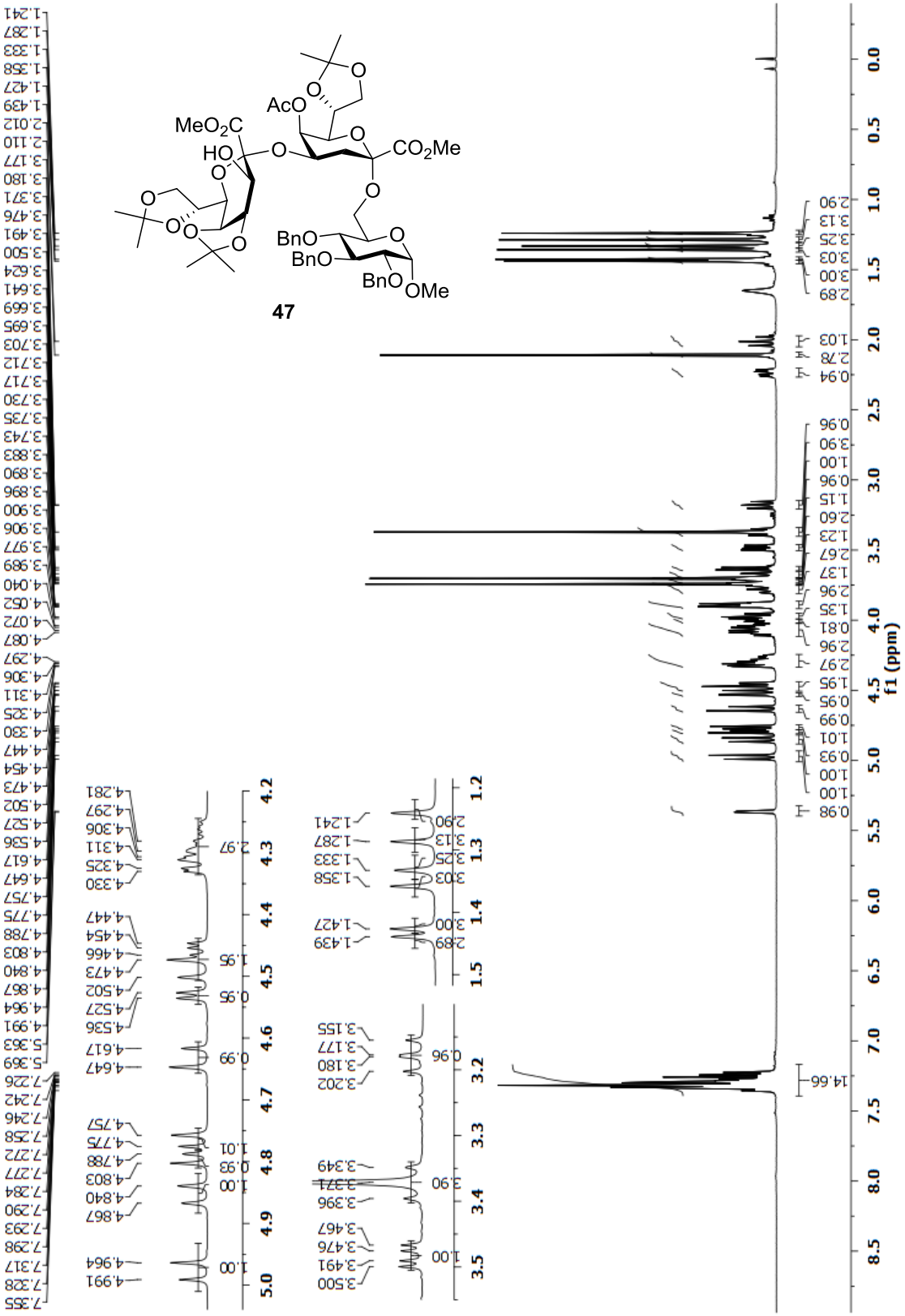
^{13}C NMR (125 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-3-*O*-(*S*-methylperoxycarbonyl)-D-*glycero*-*α*-D-*talo*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (**S14**)



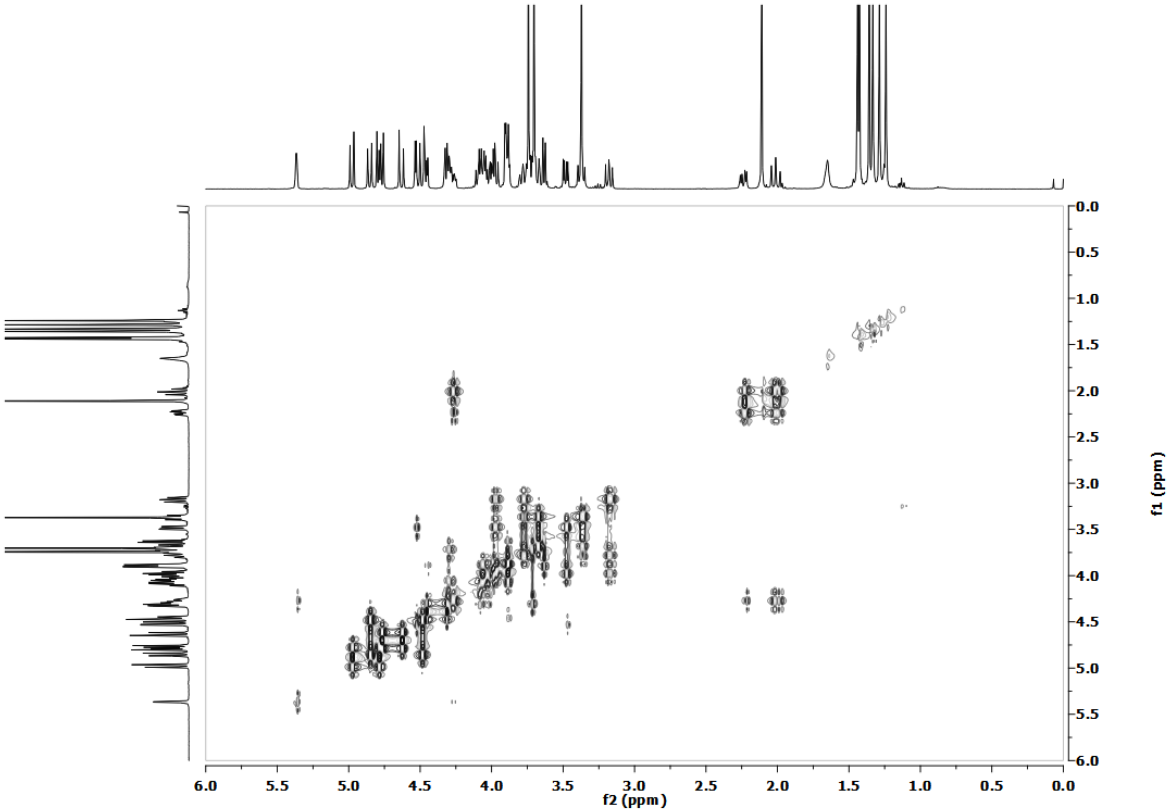
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (**47**)



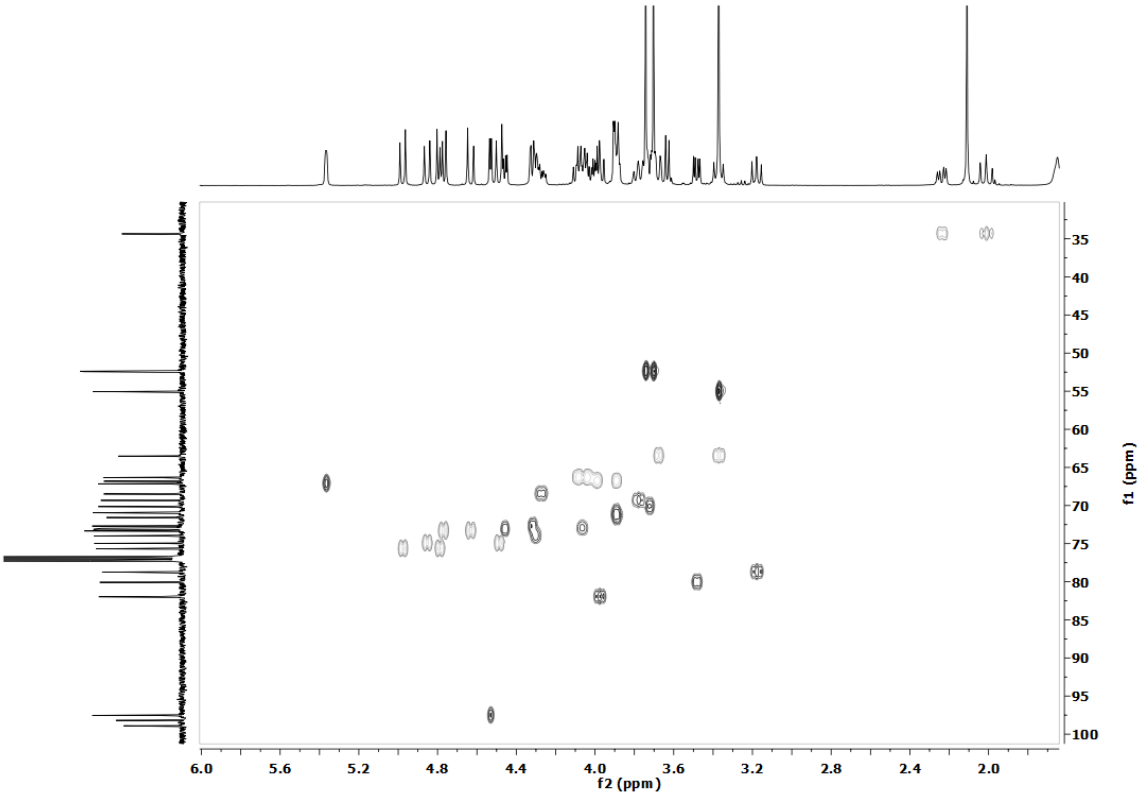
^{13}C NMR (125 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-D-*glycero*-α-D-*talo*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (**47**)



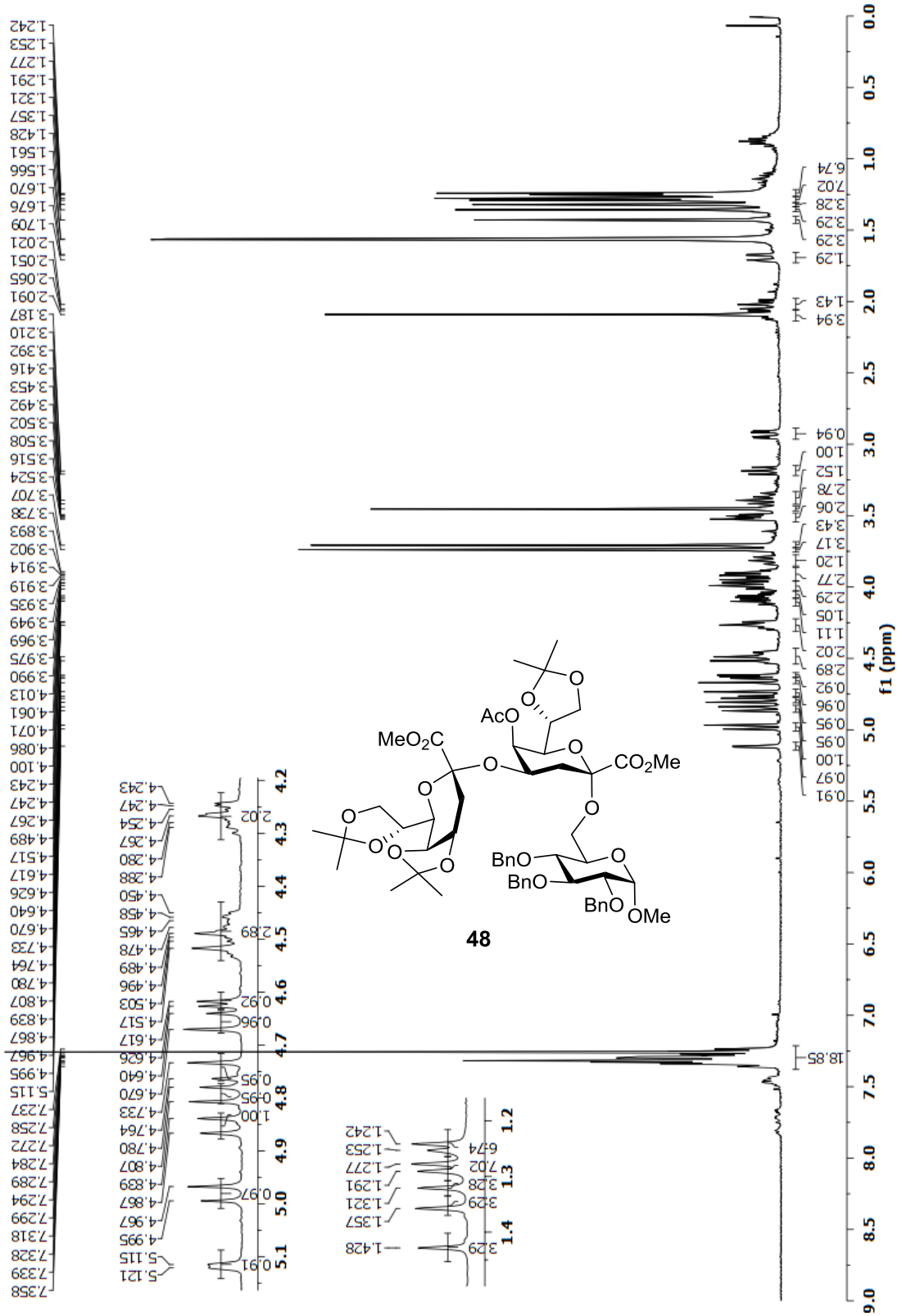
^{1}H-^{1}H GCOSY (500 MHz, $CDCl_3$) of trisaccharide (**47**)



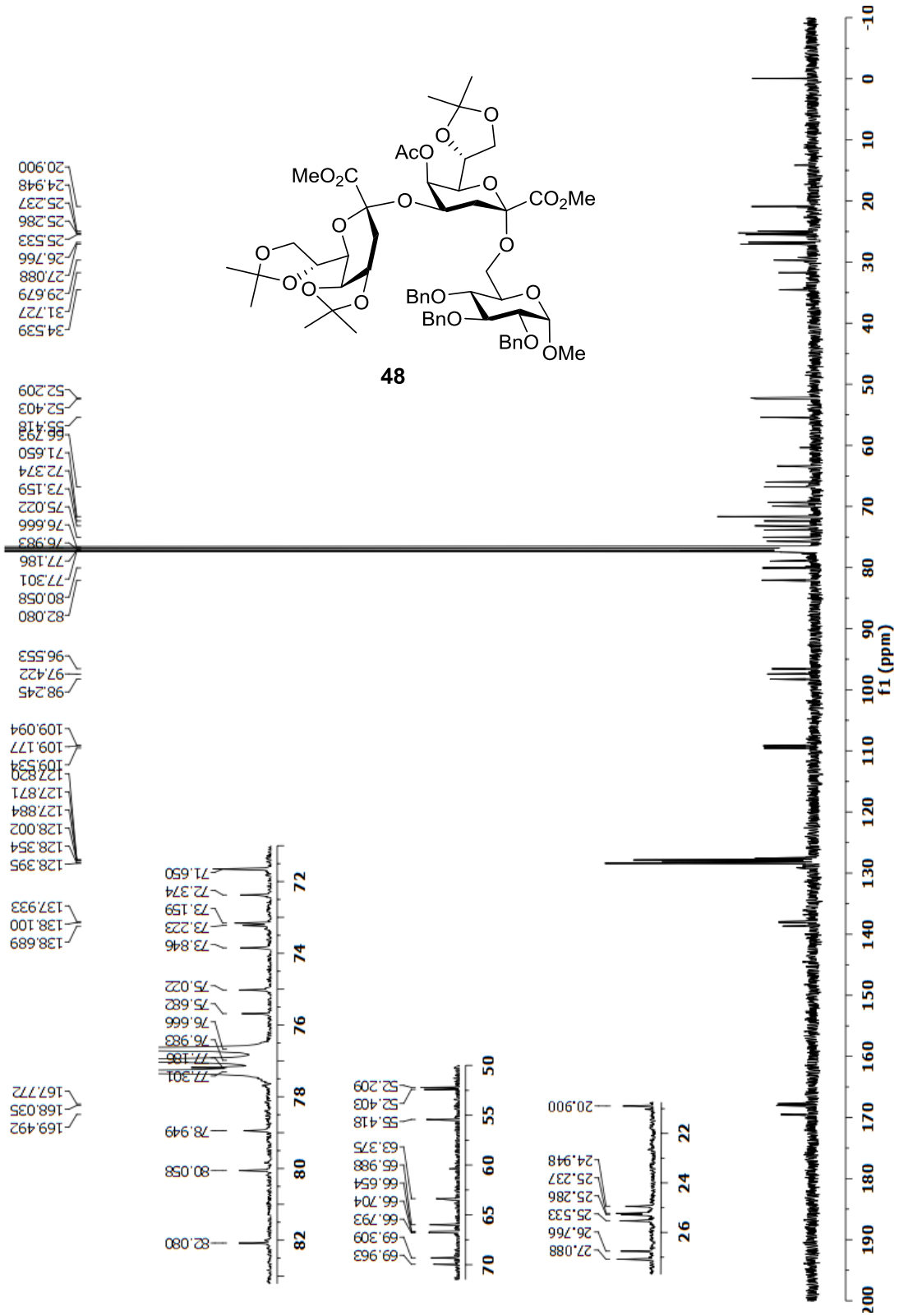
^{1}H-^{13}C HSQC (125 MHz, $CDCl_3$) of trisaccharide (**47**)



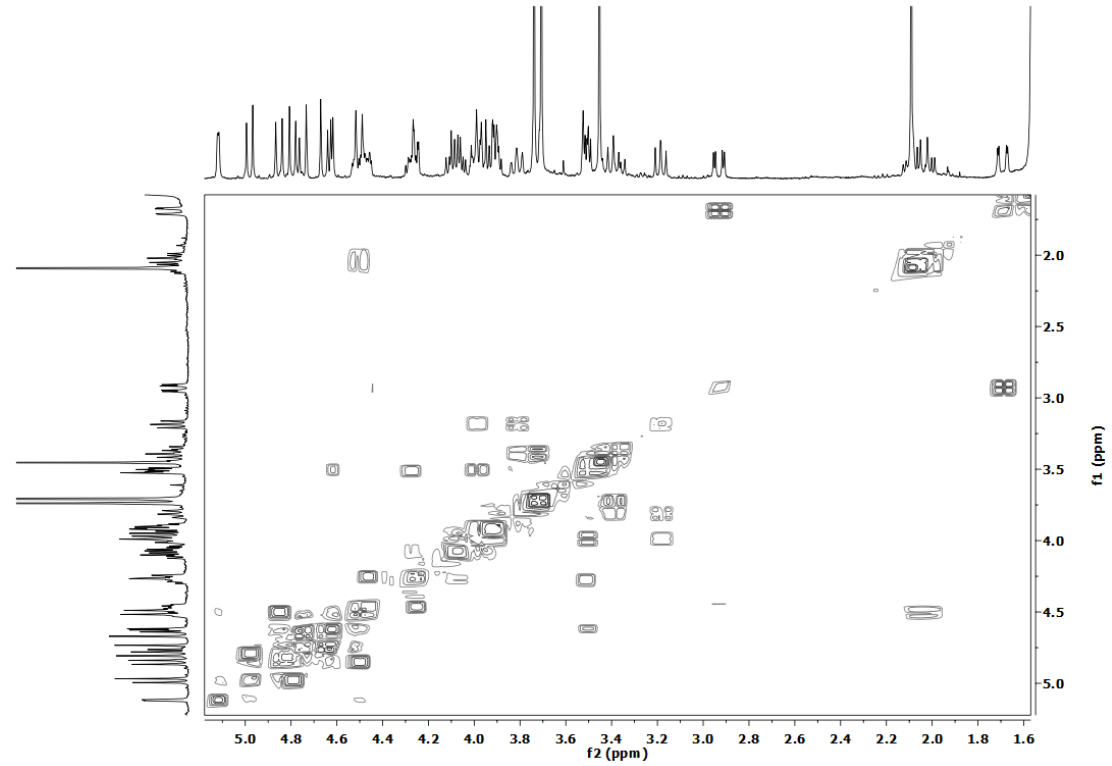
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-3-deoxy-D-*glycero*-*α*-D-*manno*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (**48**)



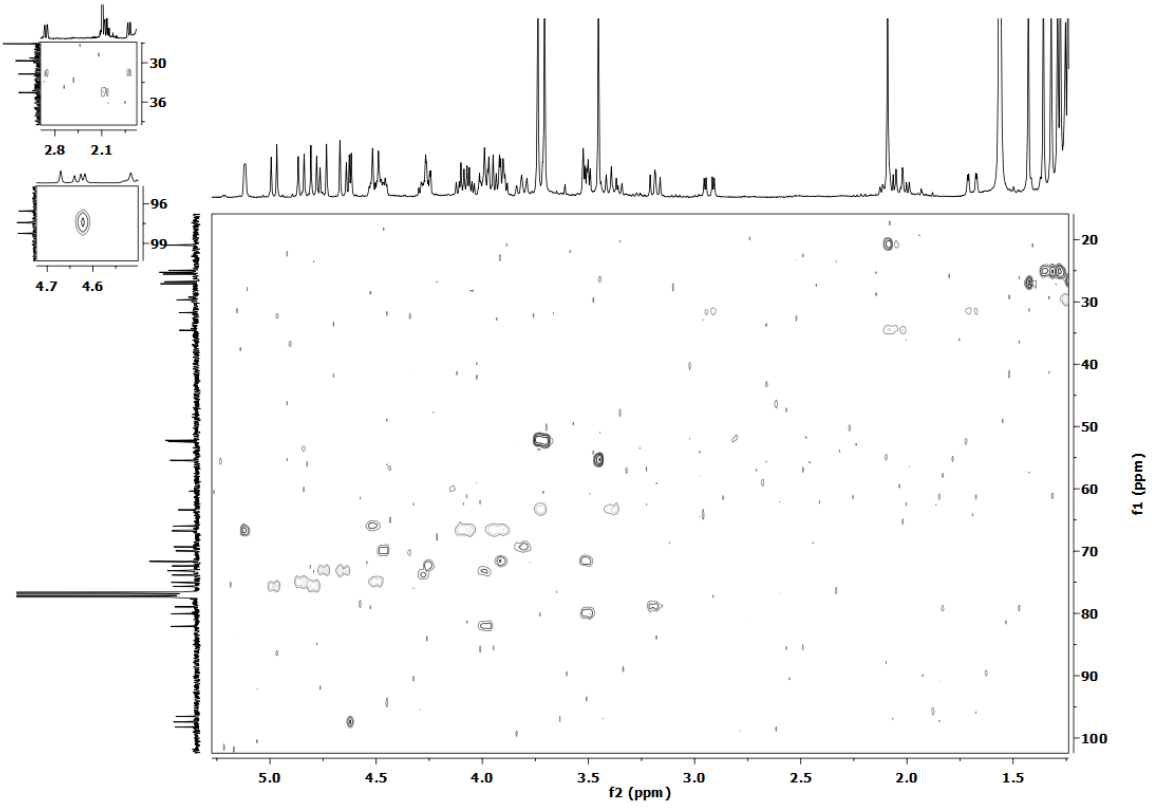
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-{methyl 5-*O*-acetyl-7,8-*O*-isopropylidene-4-*O*-[methyl 4,5:7,8-di-*O*-isopropylidene-3-deoxy-D-*glycero*-*α*-D-*manno*-2-octulopyranosonyl]onate-3-deoxy-*α*-D-*manno*-2-octulopyranosonyl}onate-*α*-D-glucopyranoside (**48**)



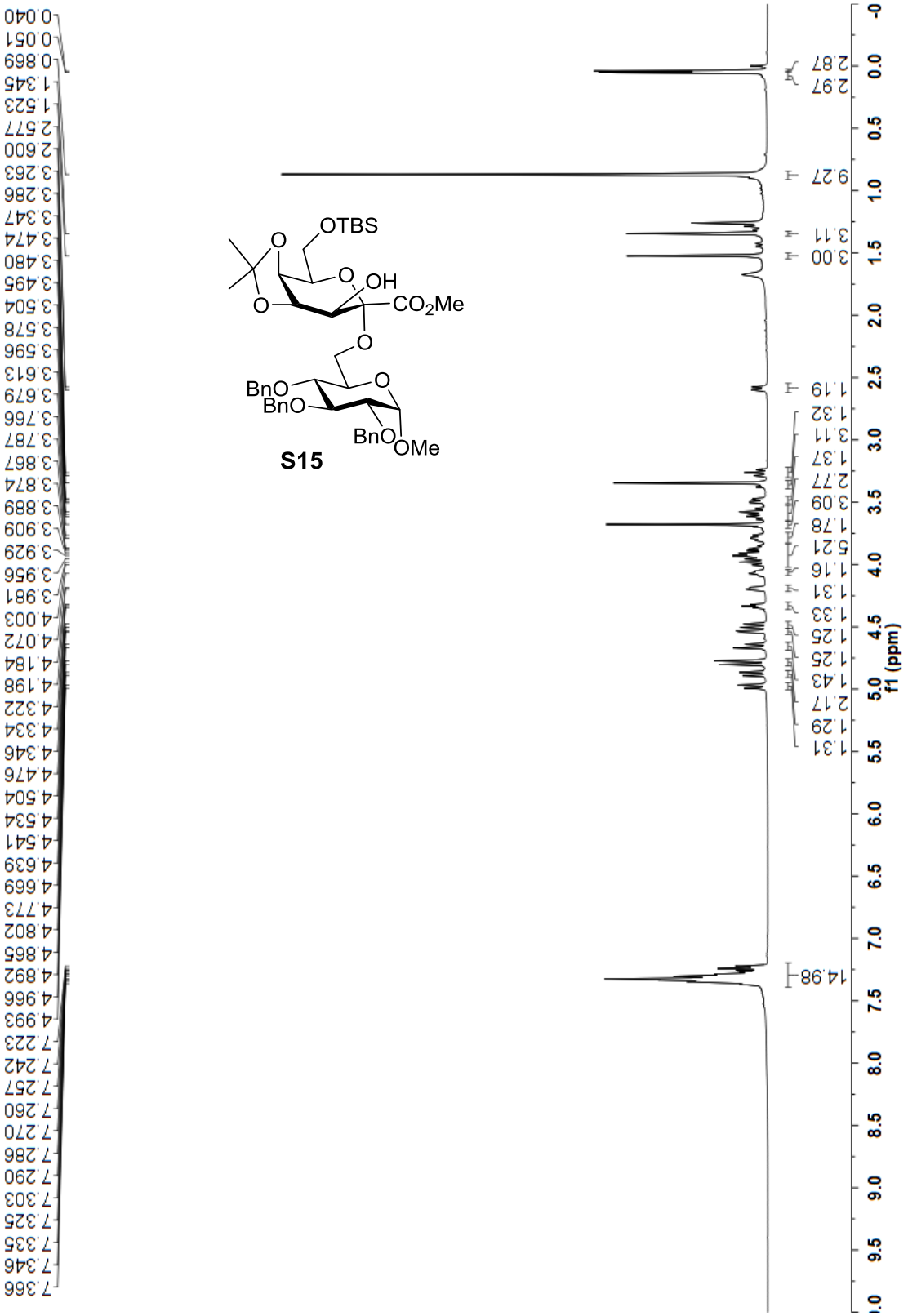
^{1}H-^{1}H GCOSY (500 MHz, $CDCl_3$) of trisaccharide (**48**)



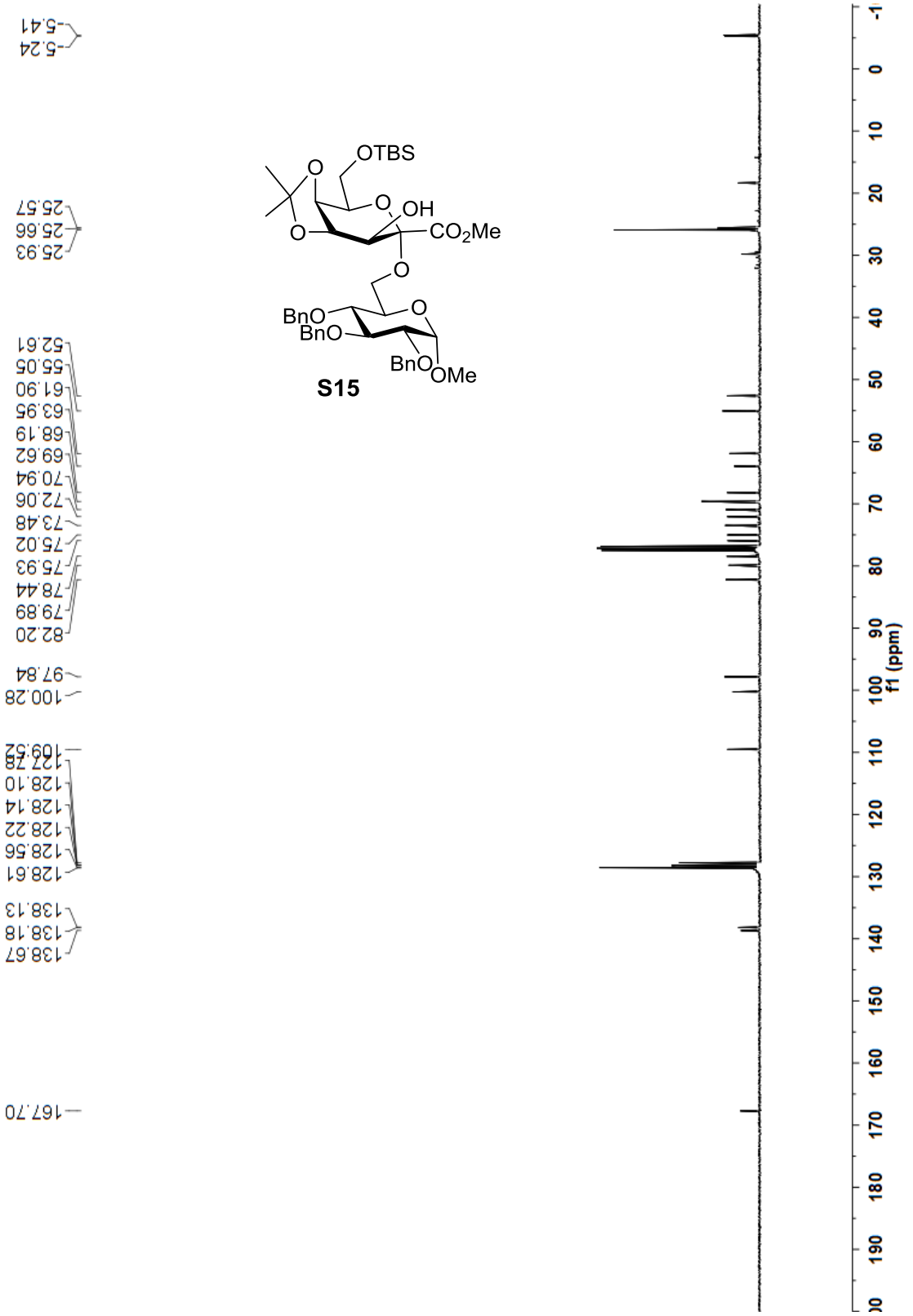
^{1}H-^{13}C HSQC (500 MHz, $CDCl_3$) of trisaccharide (**48**)



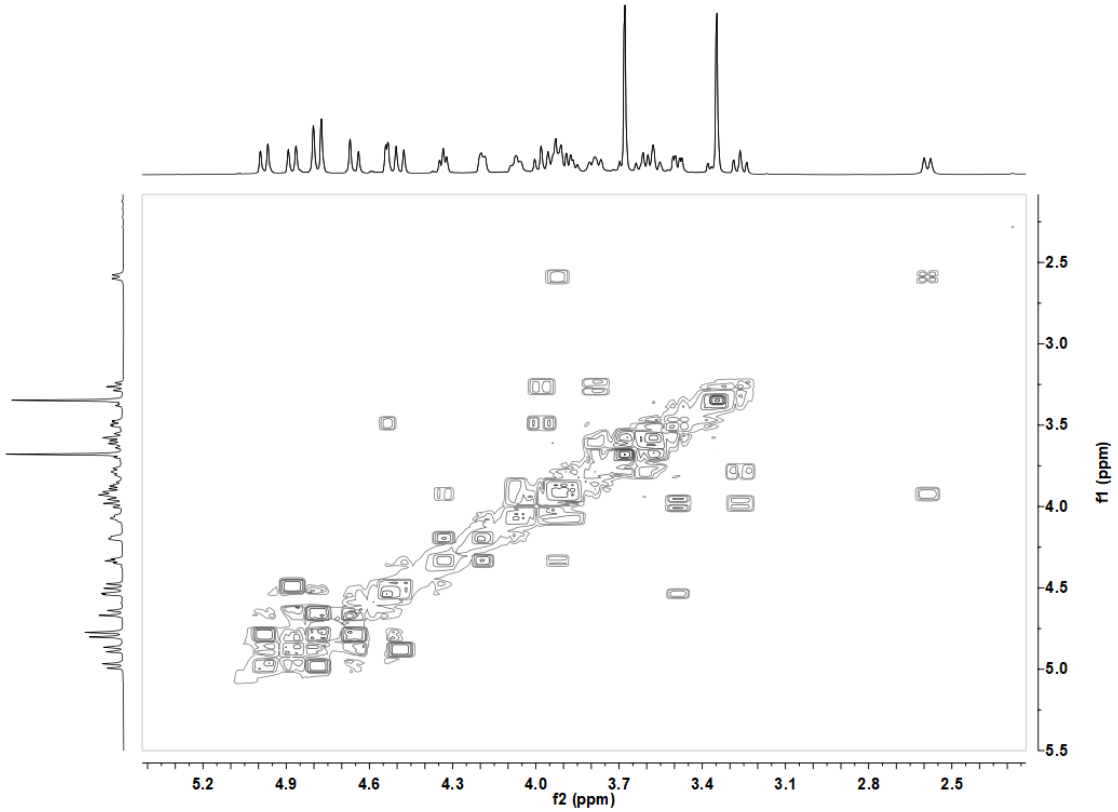
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5-*O*-isopropylidene-7-*O*-*t*butyldimethylsilyl-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**S15**)



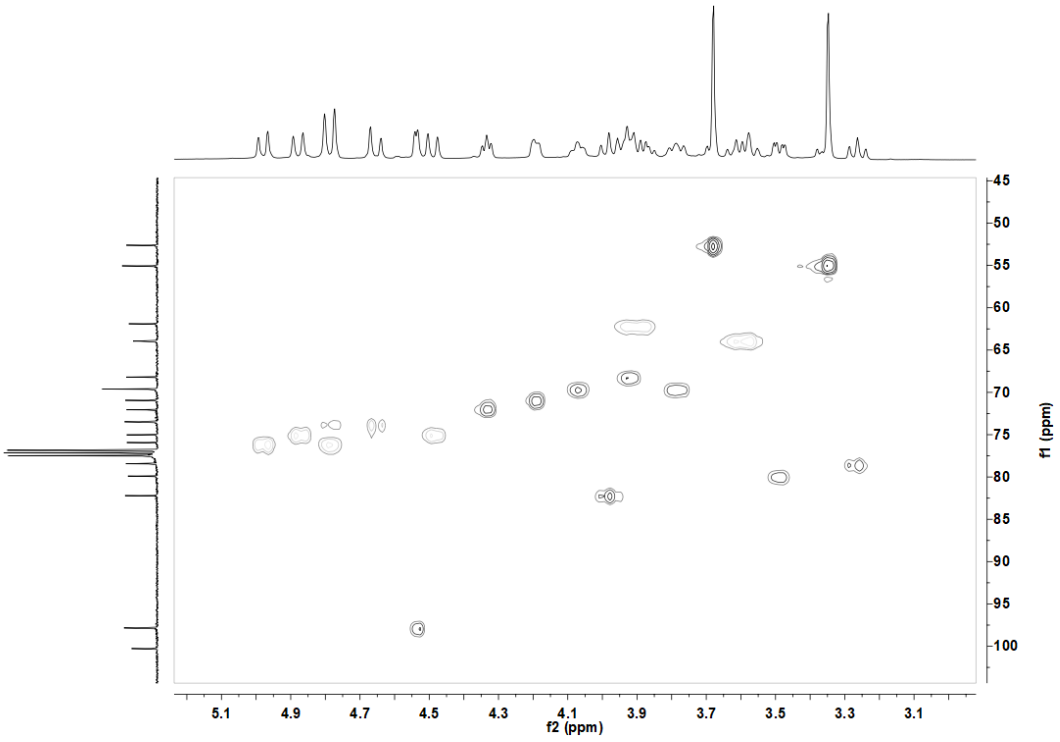
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4,5-*O*-isopropylidene-7-*O*-*t*butyldimethylsilyl-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**S15**)



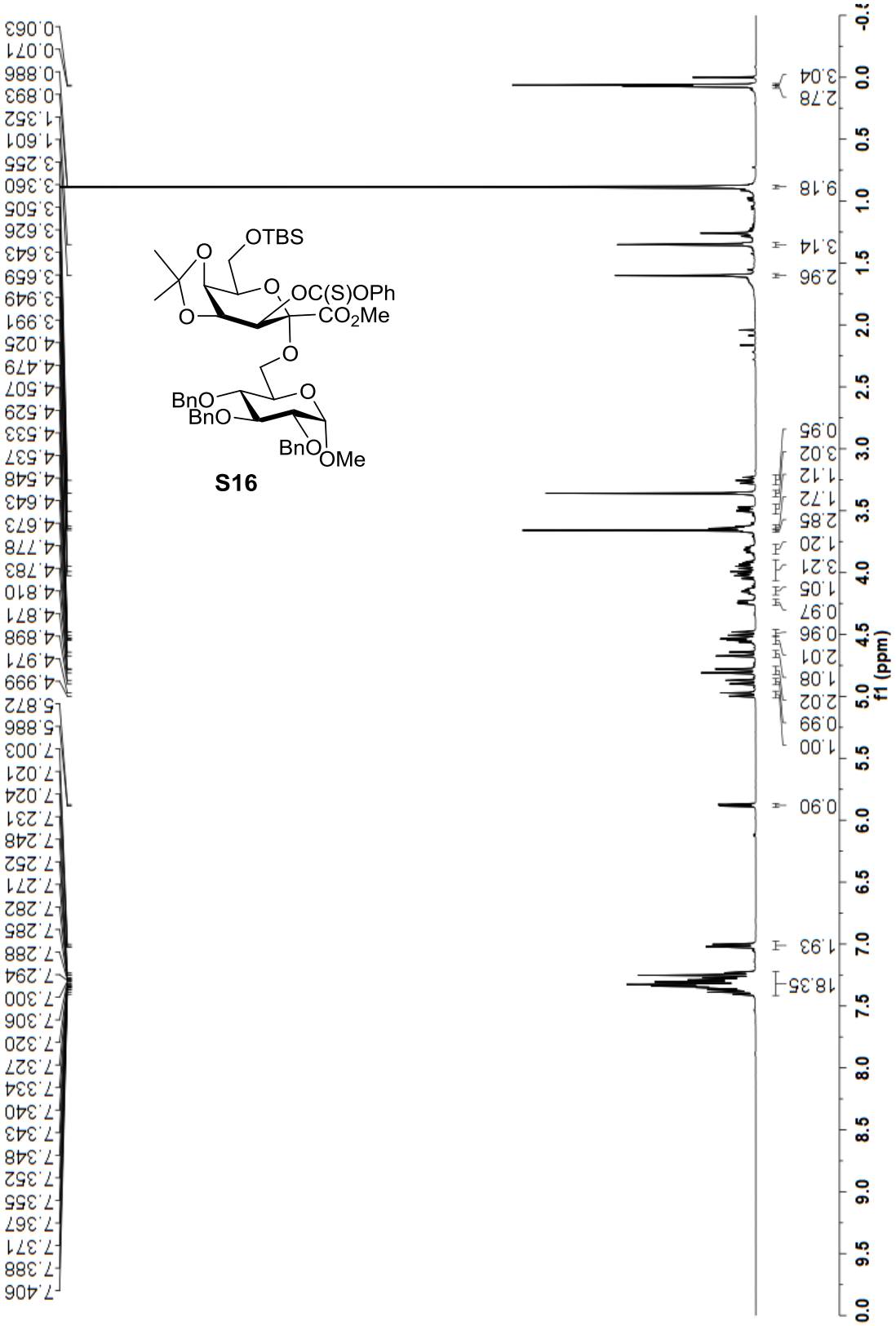
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**S15**)



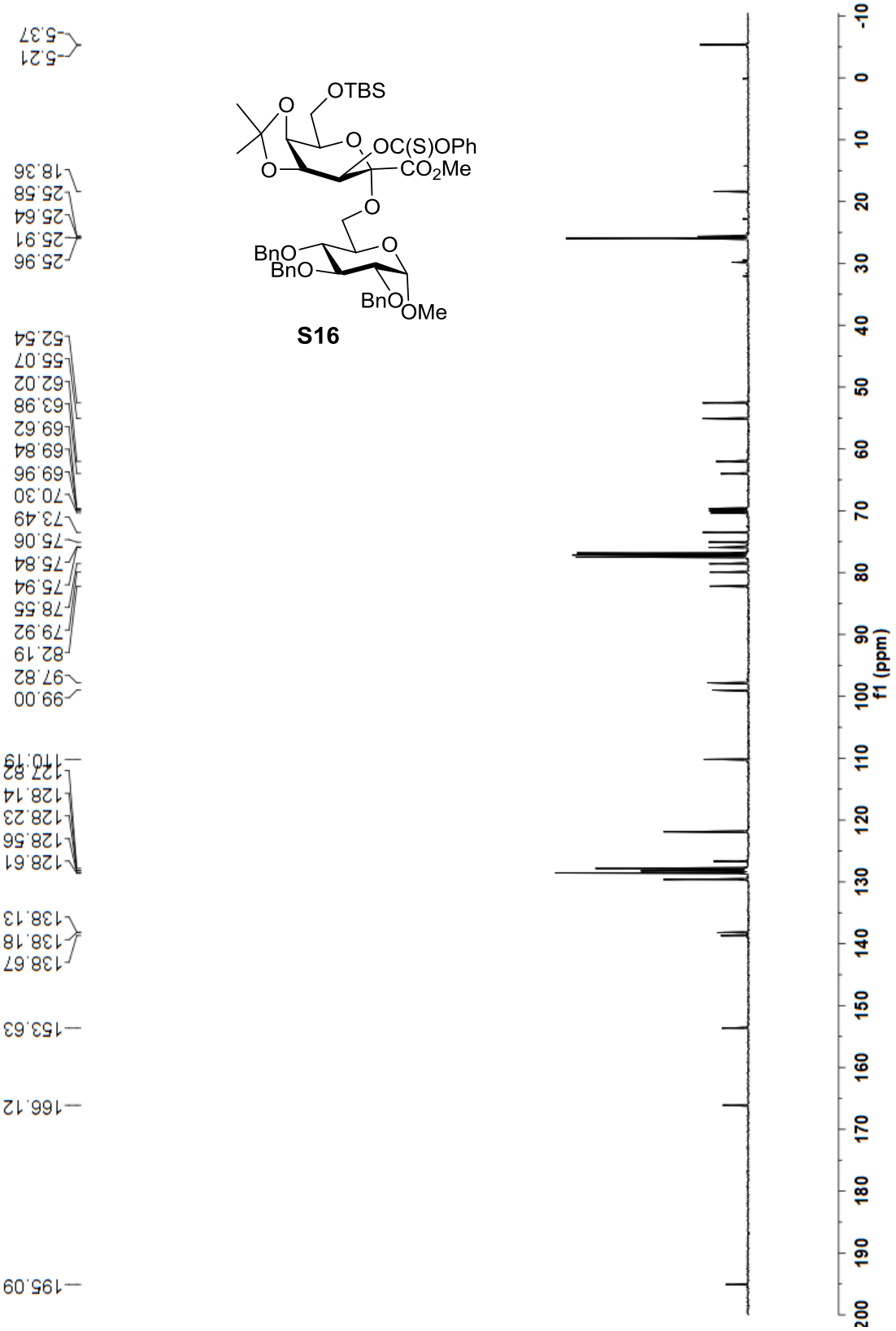
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**S15**)



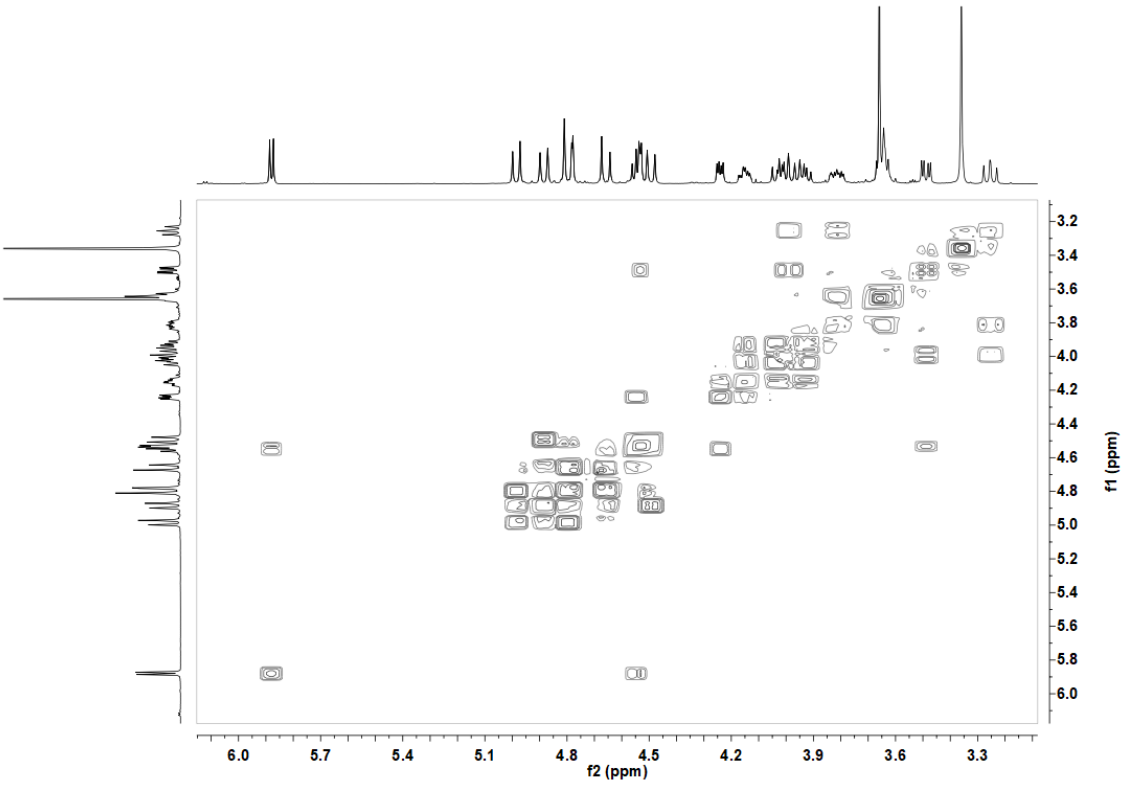
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-4,5-*O*-isopropylidene-3-*O*-phenoxythiocarbonyl)-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**S16**)



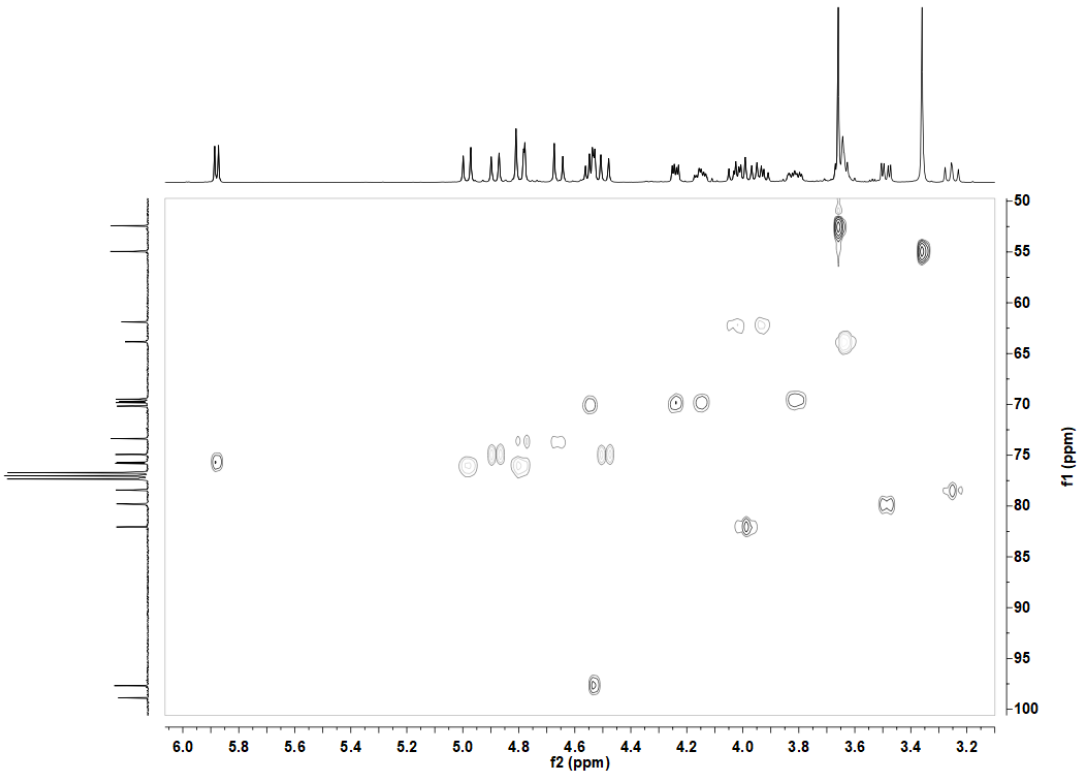
^{13}C NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-4,5-*O*-isopropylidene-3-*O*-phenoxythiocarbonyl)-*α*-D-*talo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**S16**)



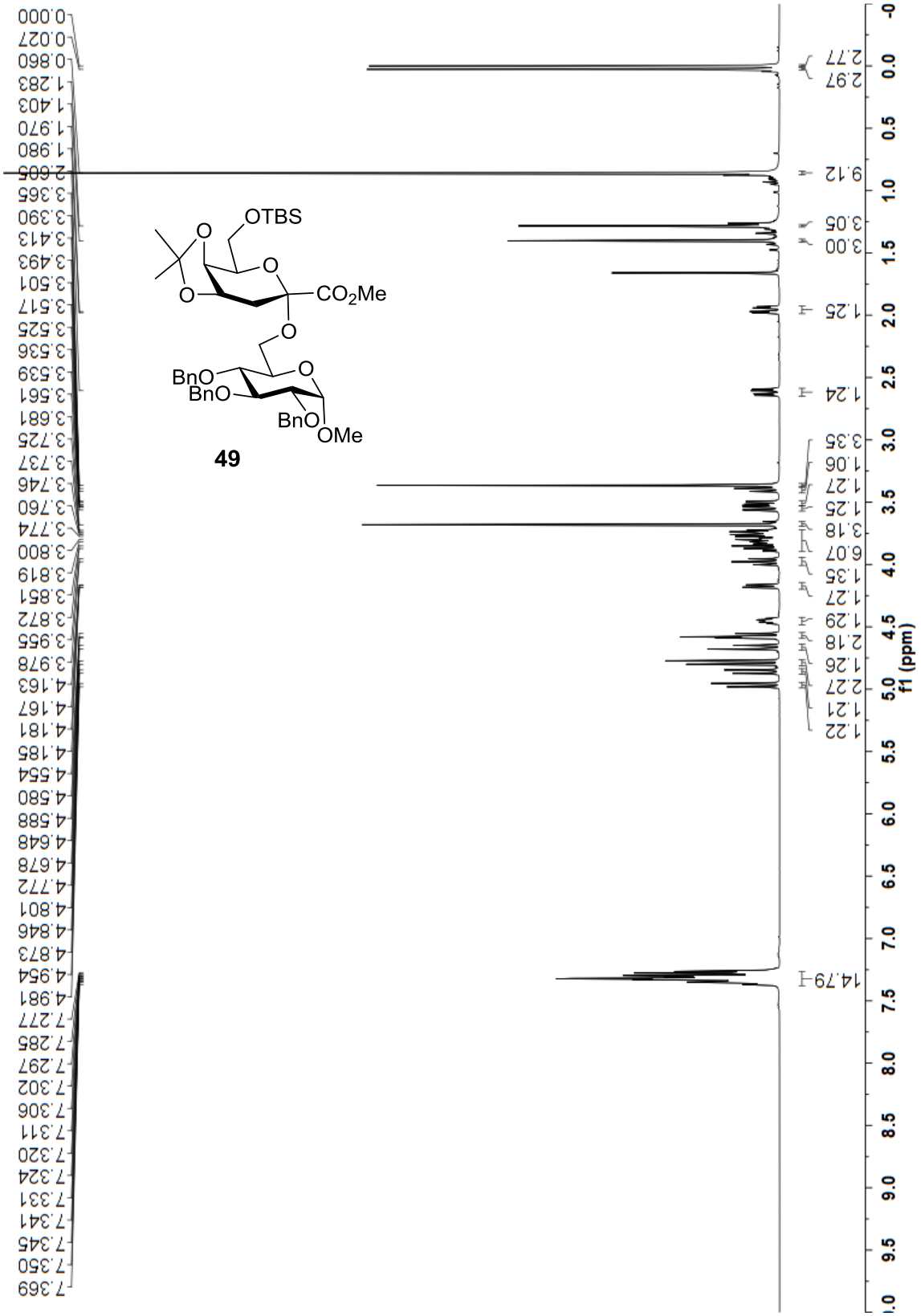
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**S16**)



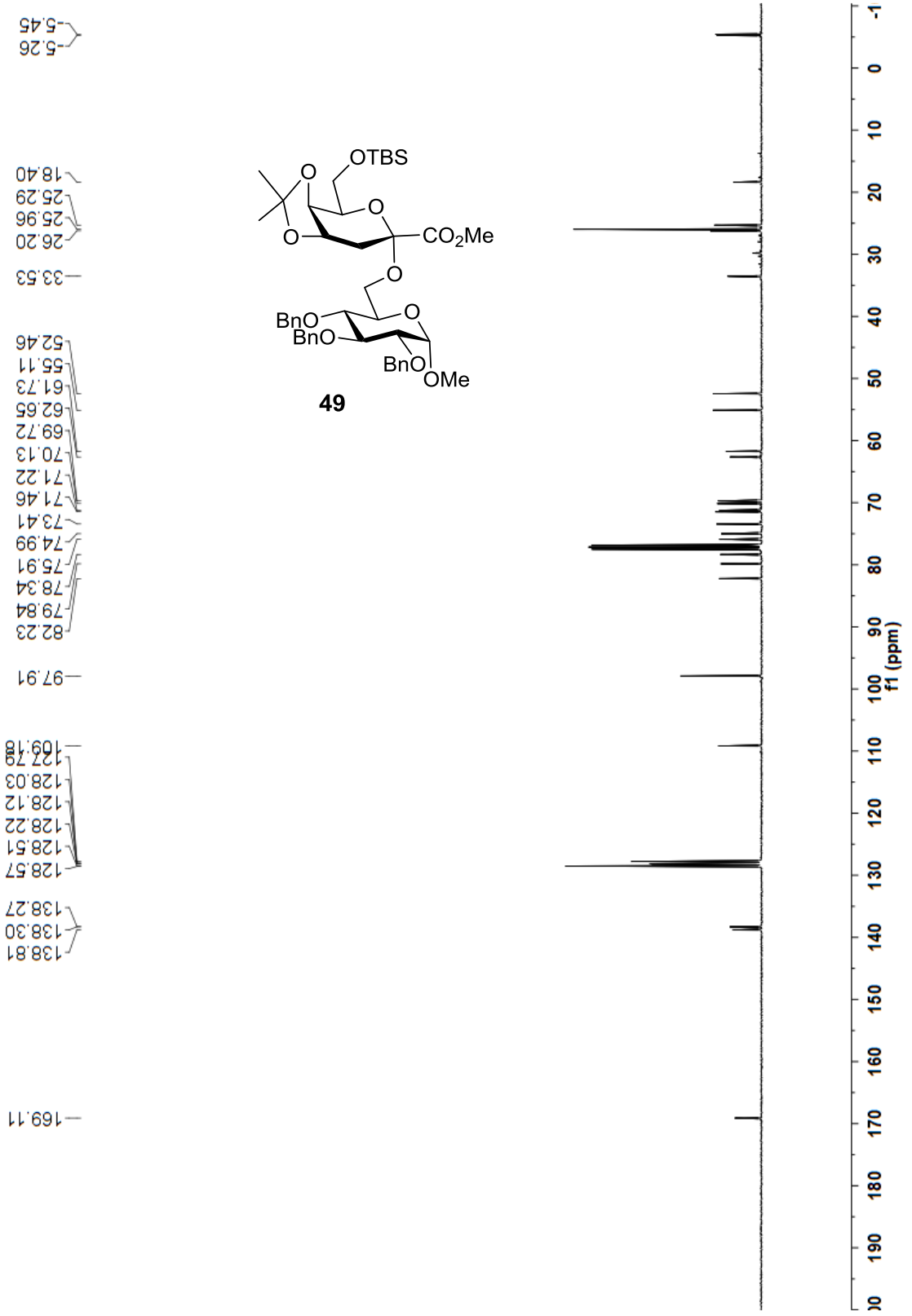
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**S16**)



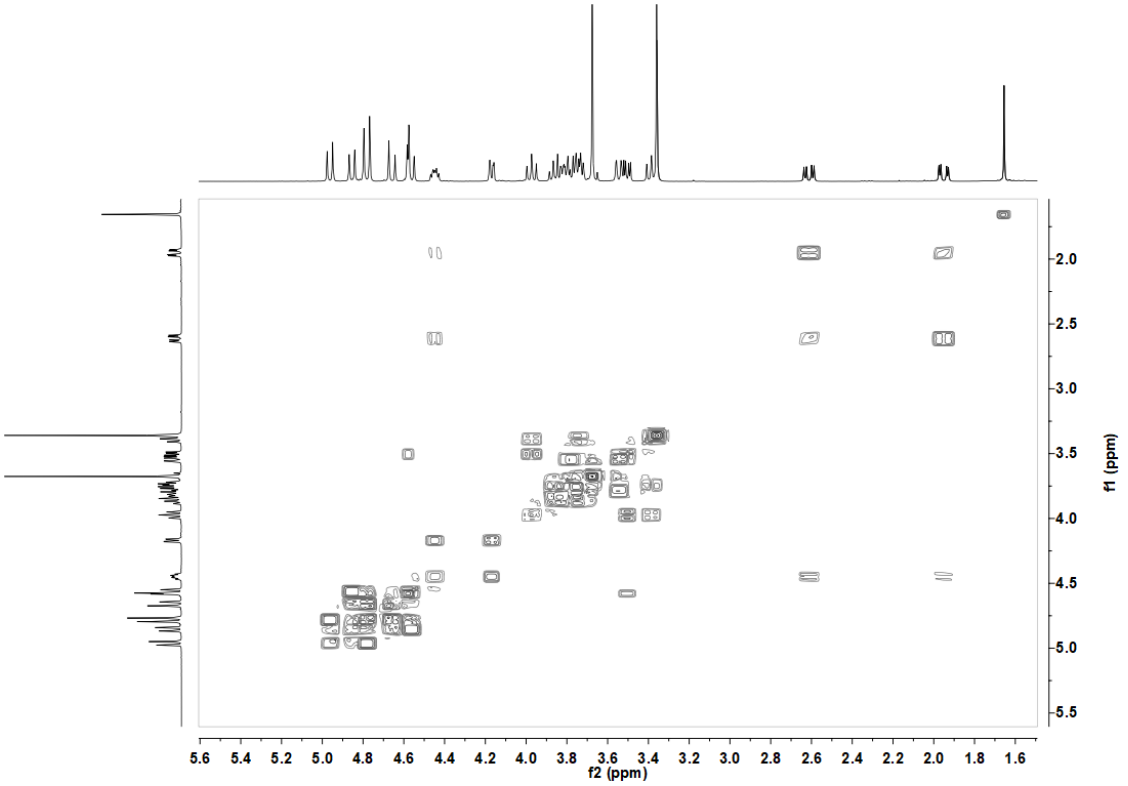
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-tbutyldimethylsilyl-3-deoxy-4,5-*O*-isopropylidene-α-D-*lyxo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**49**)



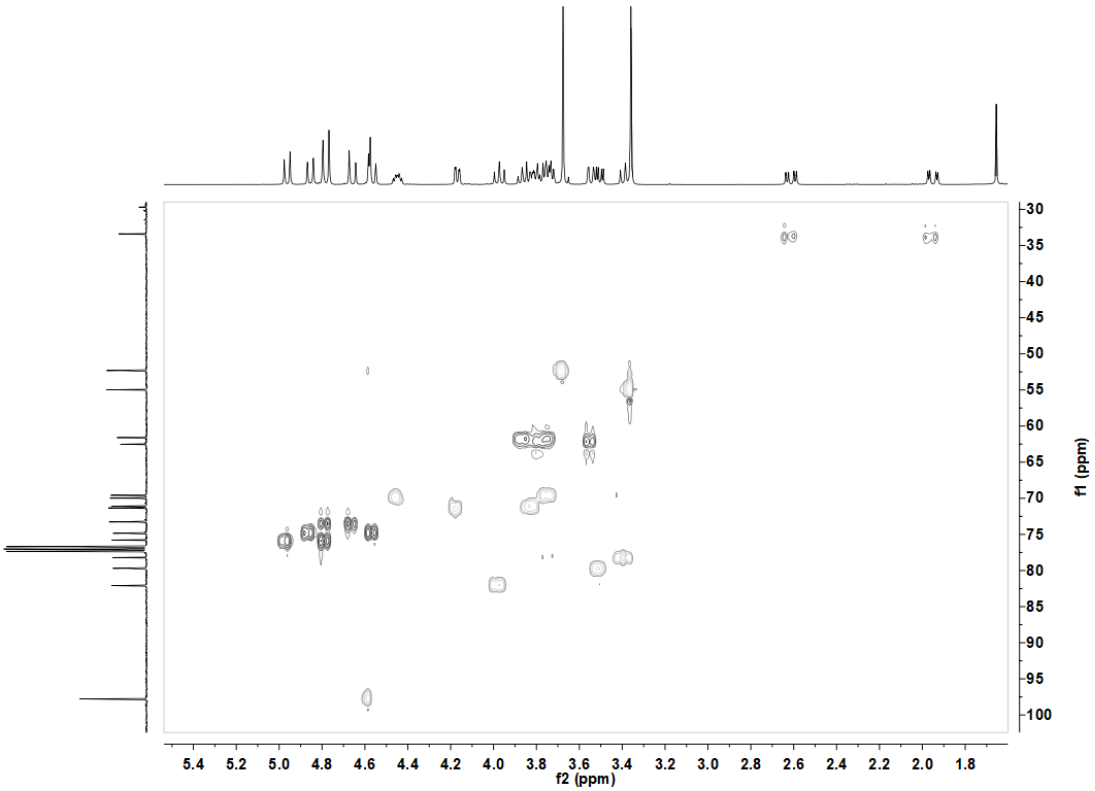
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-*O*-*t*butyldimethylsilyl-3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**49**)



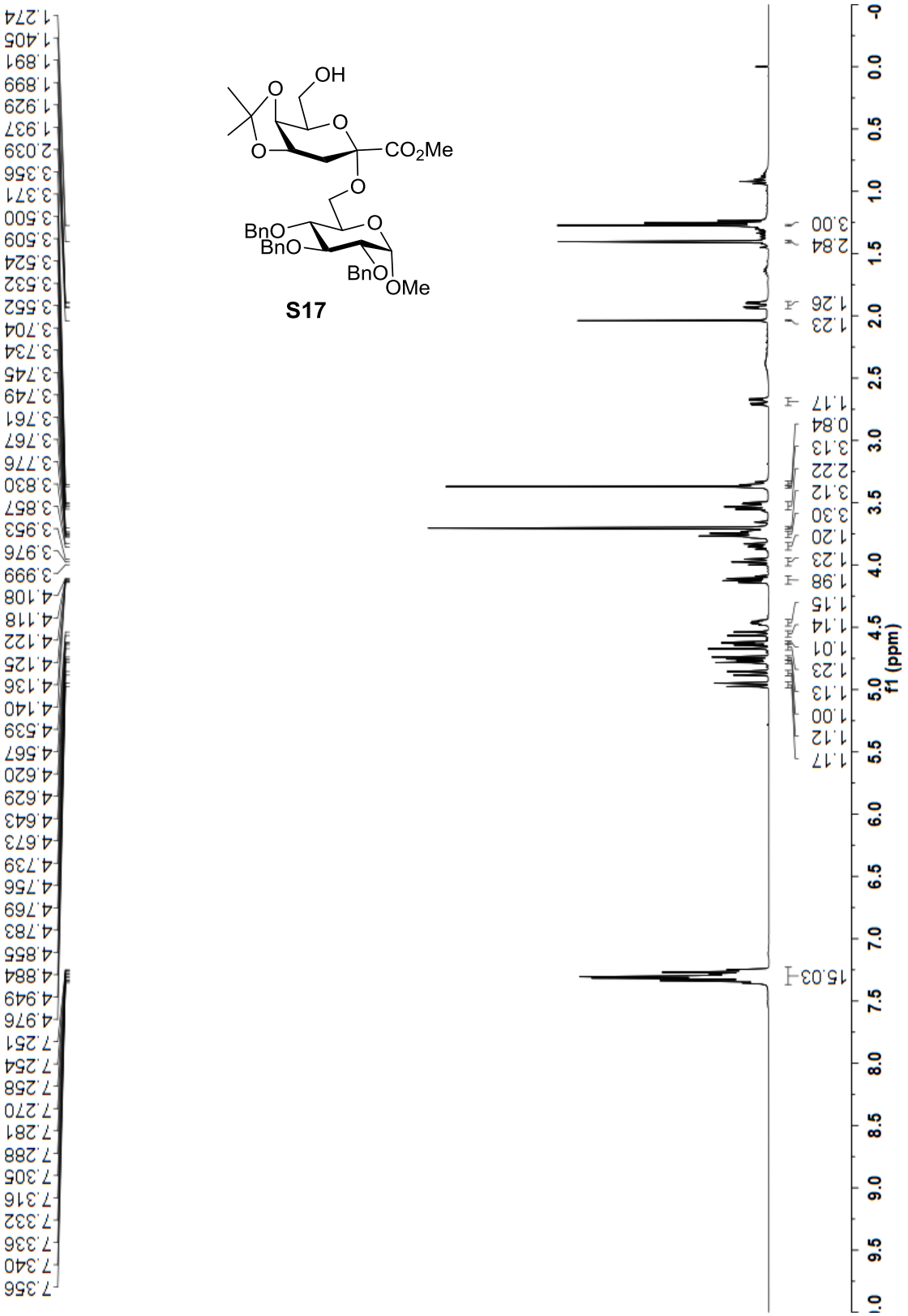
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**49**)



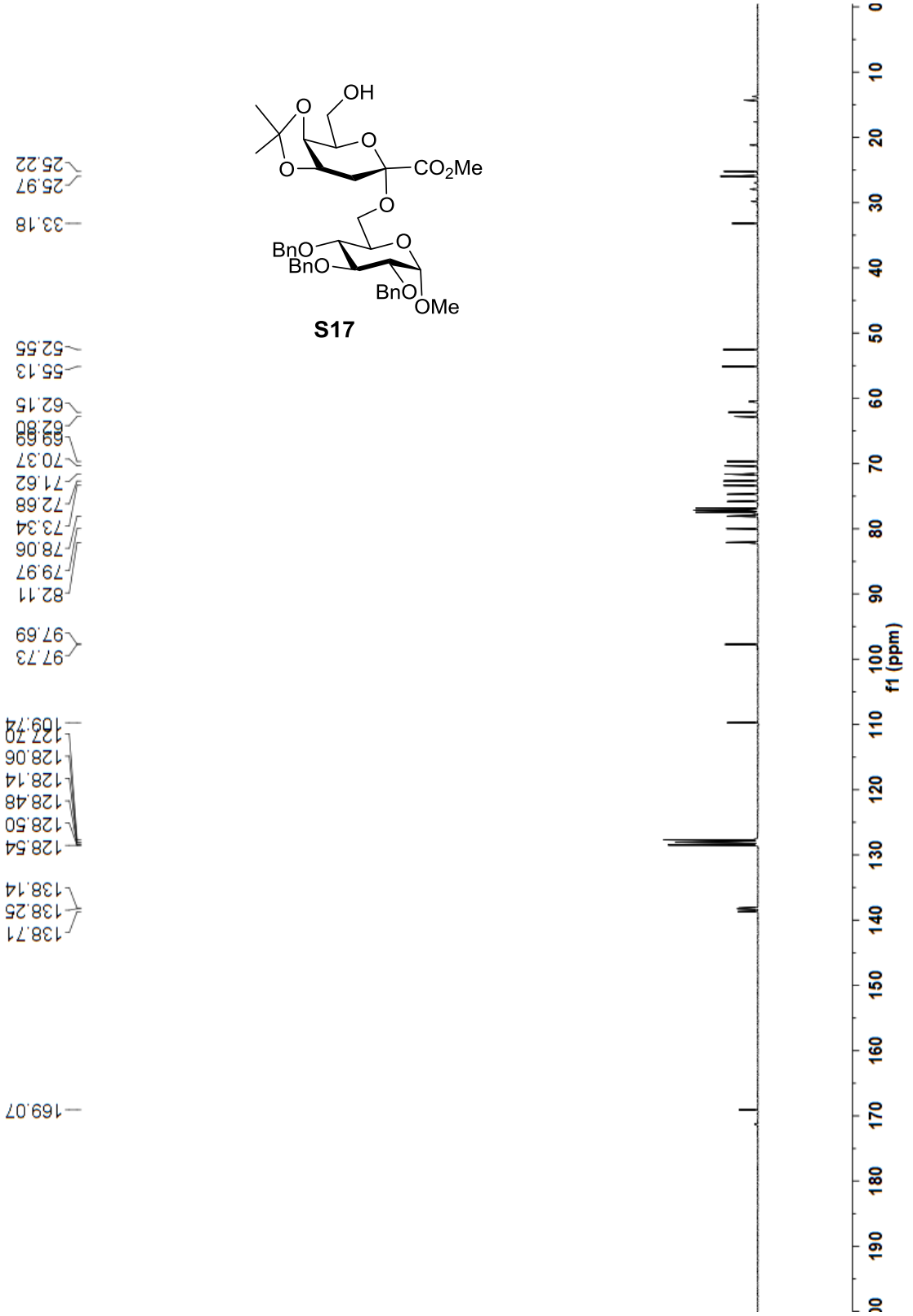
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**49**)



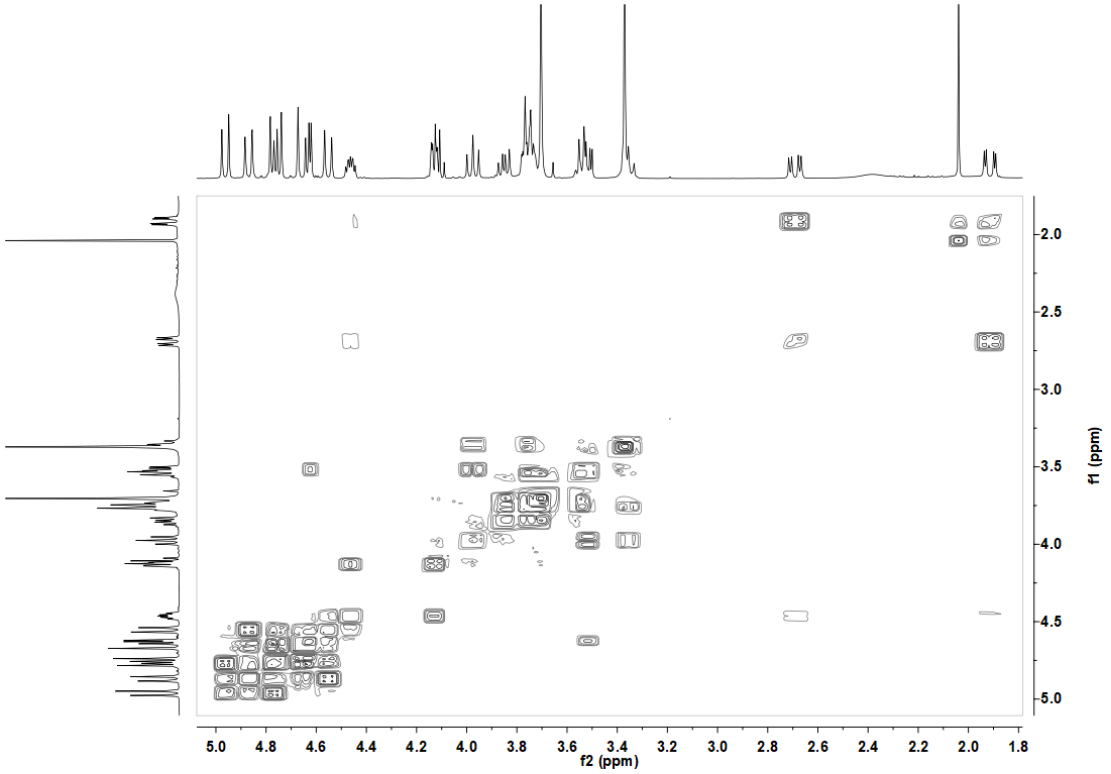
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**S17**)



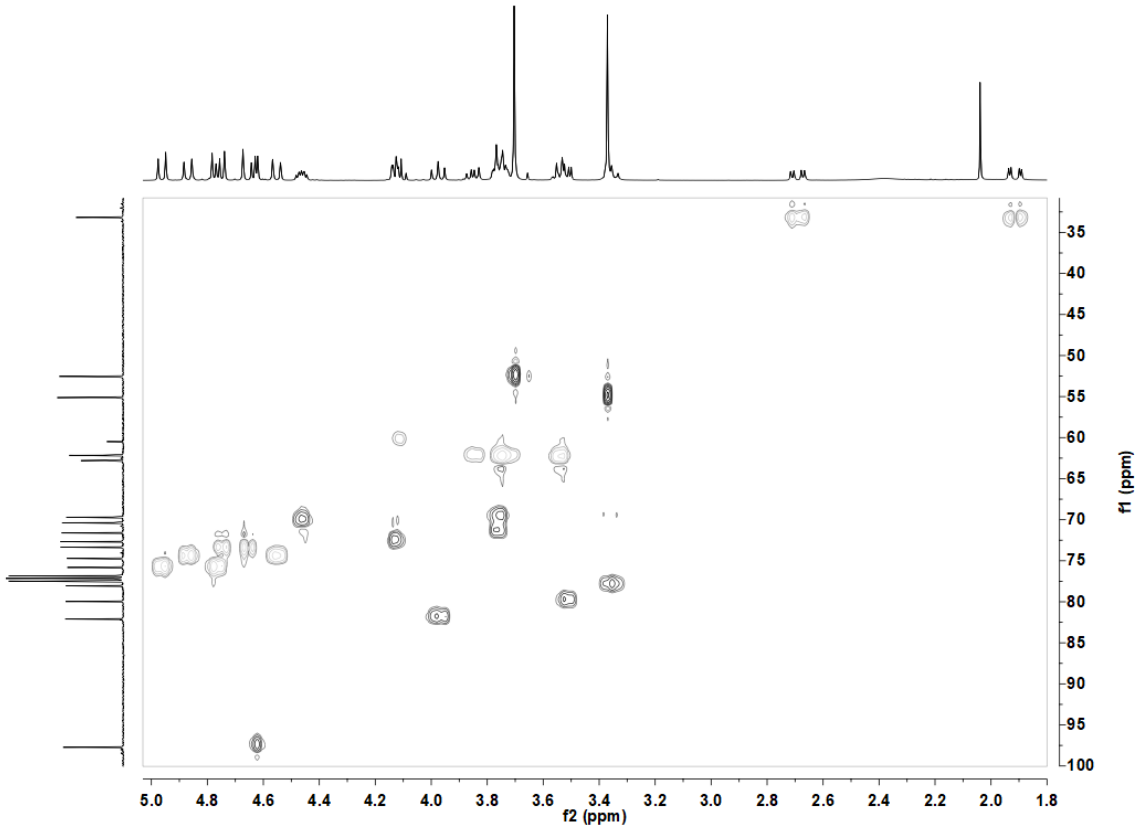
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-2-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**S17**)



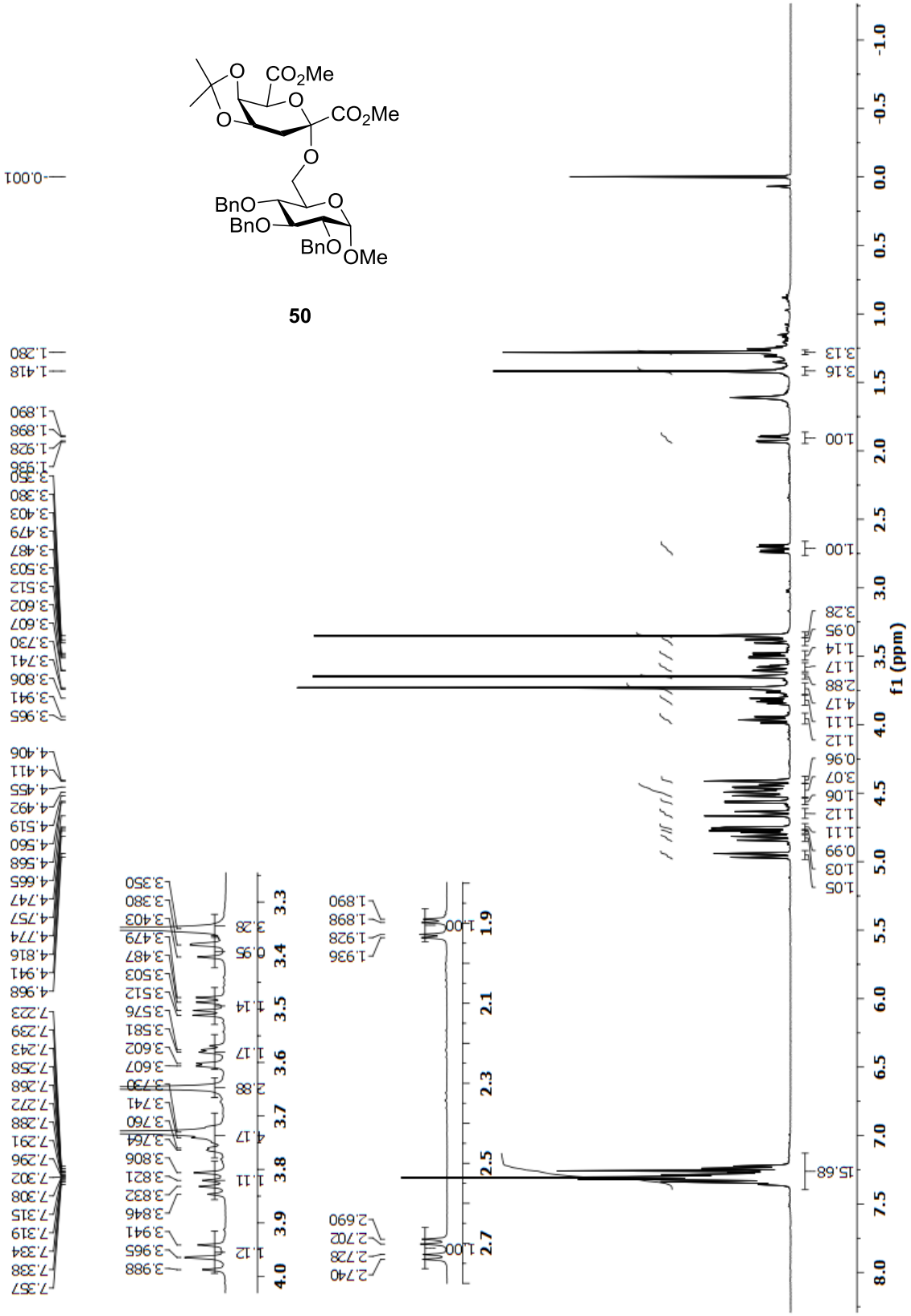
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**S17**)



^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**S17**)

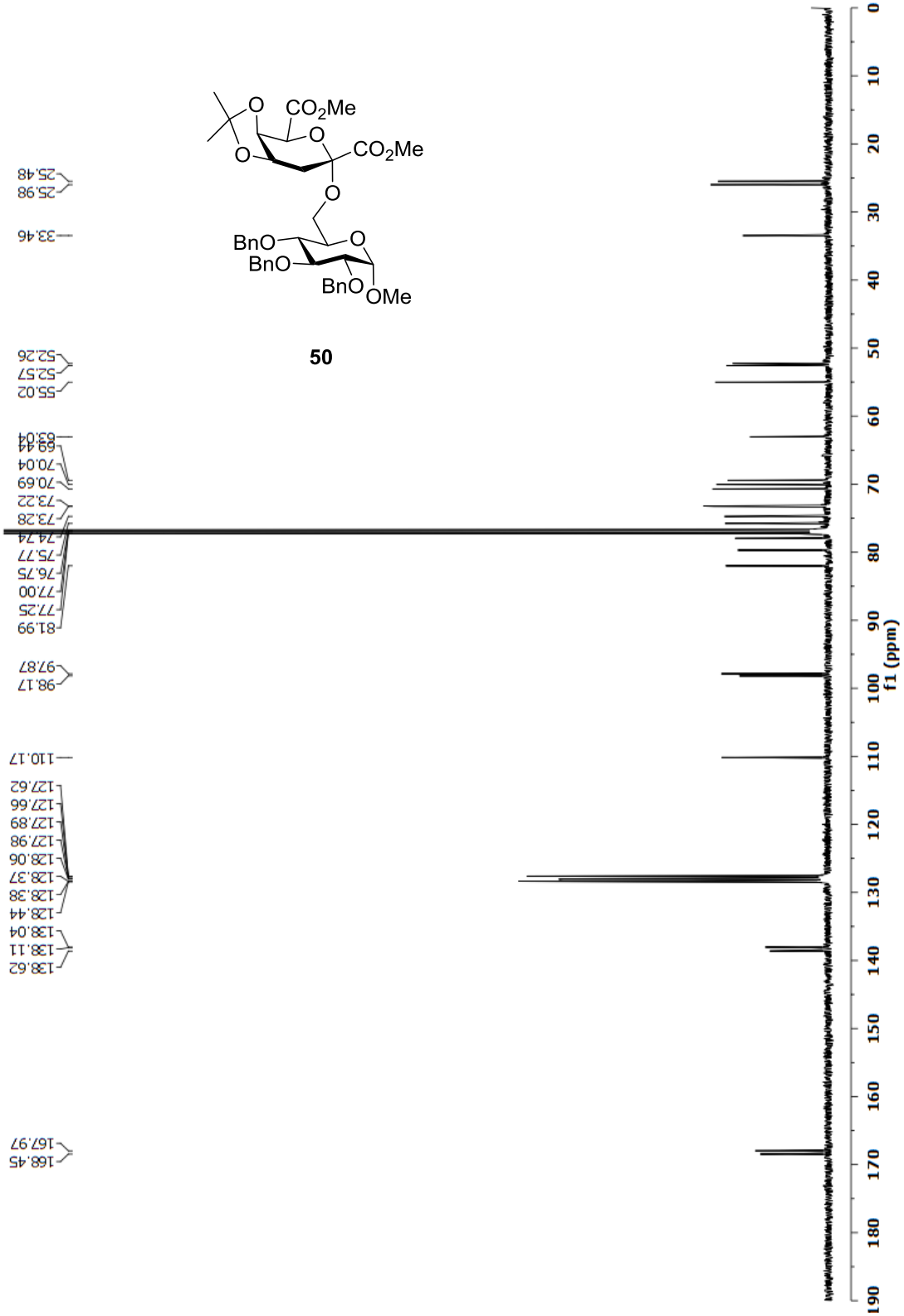


^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-carbomethoxy-3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**50**)

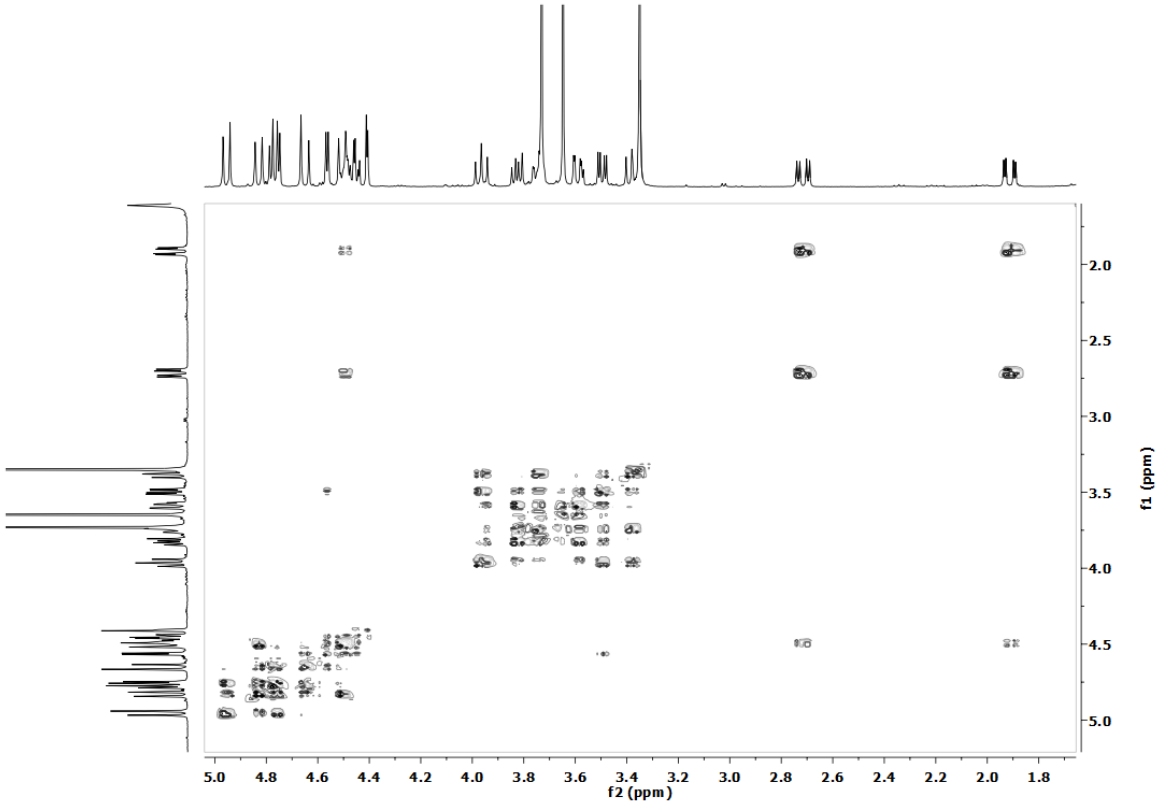


50

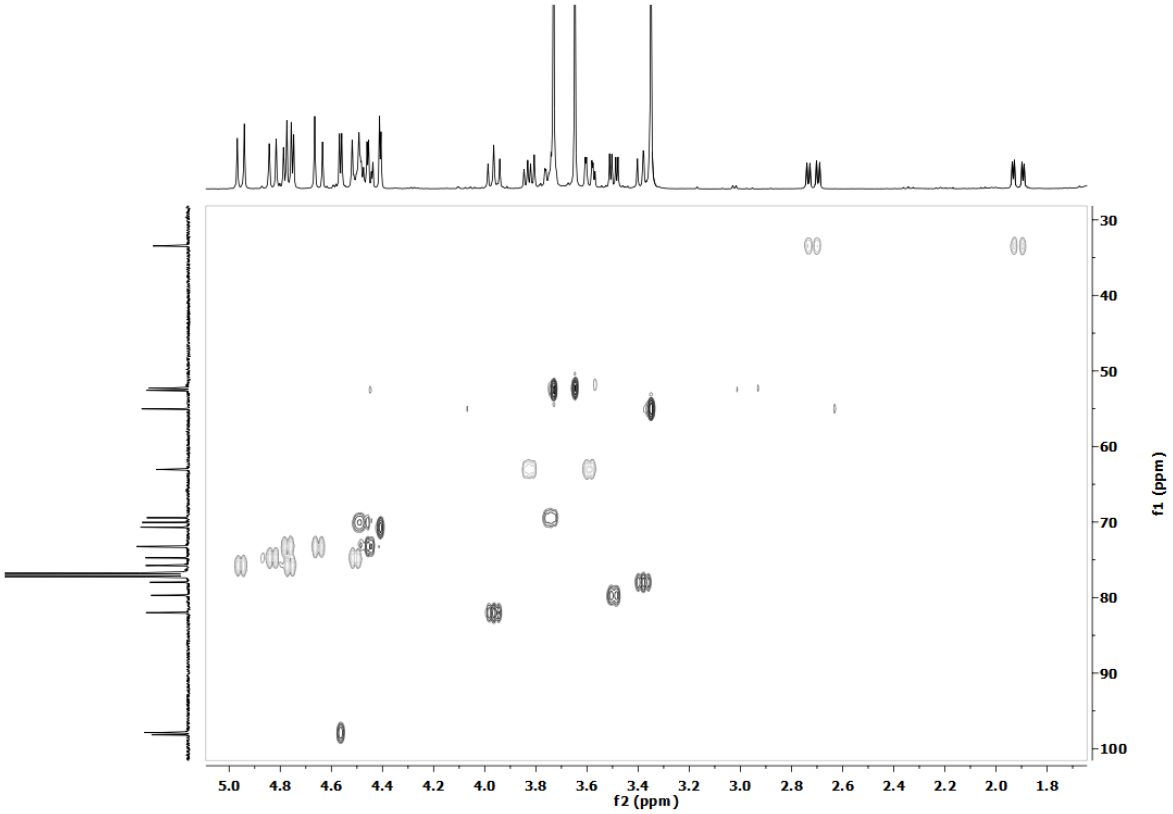
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (7-carbomethoxy-3-deoxy-4,5-*O*-isopropylidene-*α*-D-*lyxo*-heptulopyranosonyl)onate]-*α*-D-glucopyranoside (**50**)



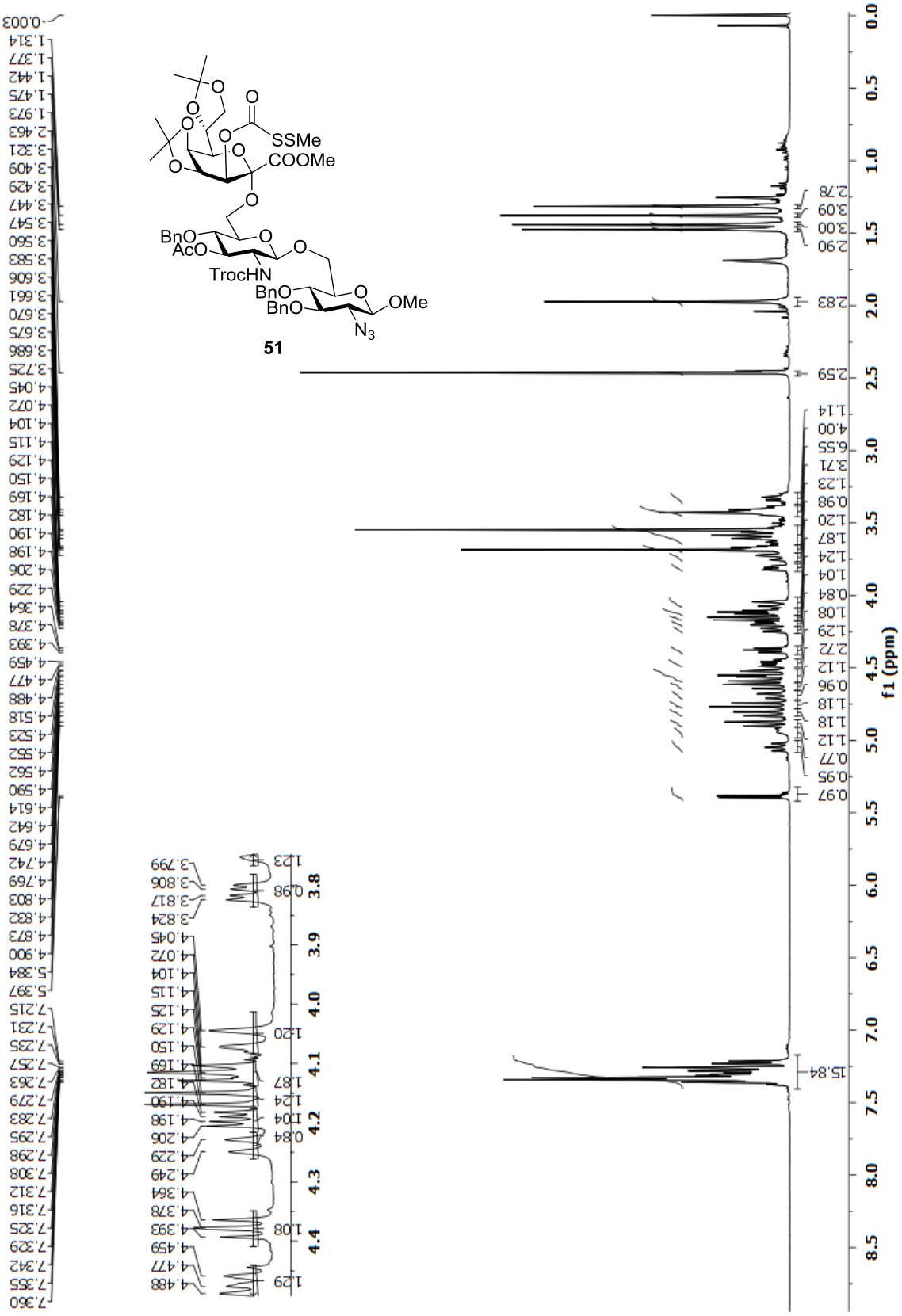
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of disaccharide (**50**)



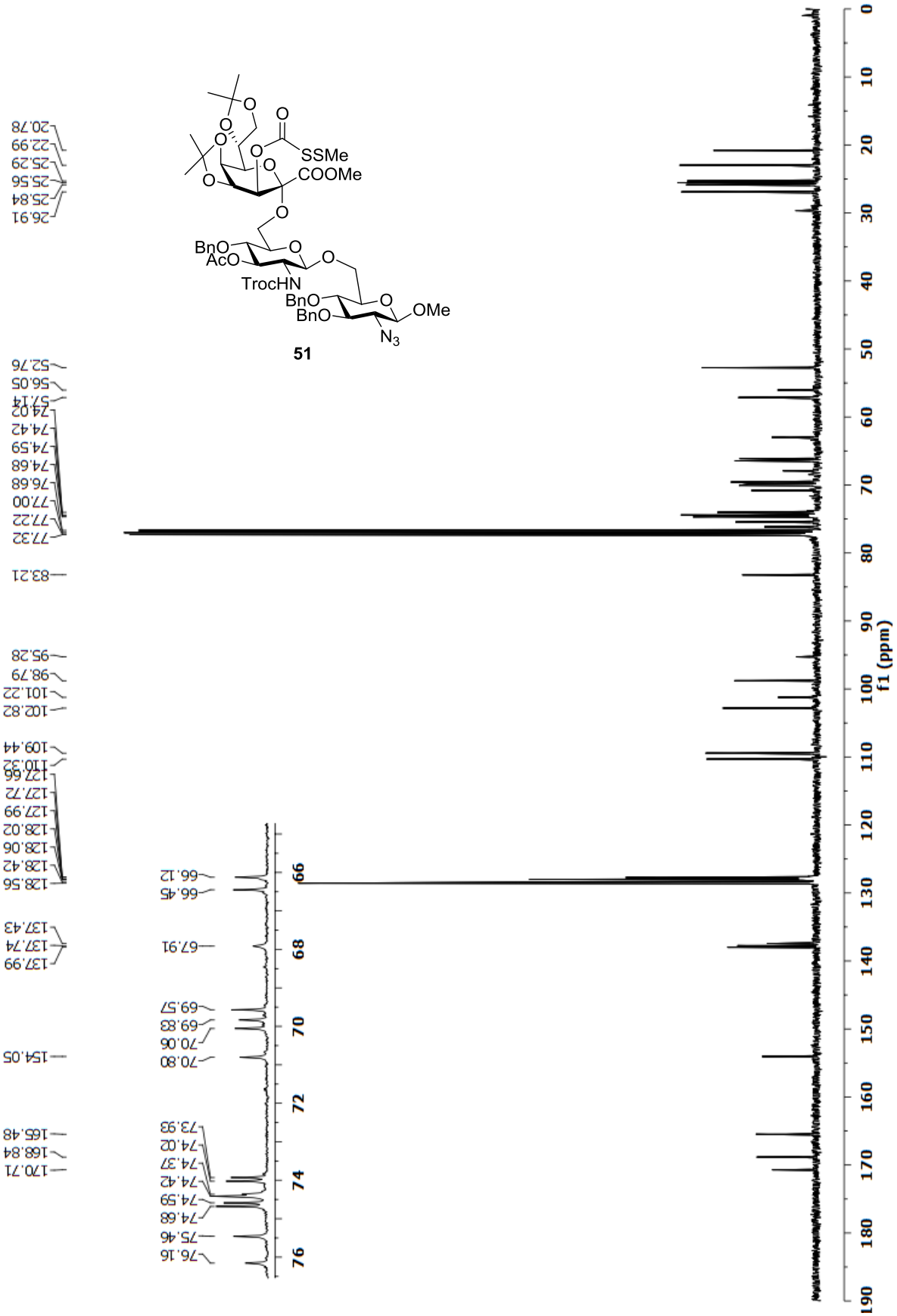
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**50**)



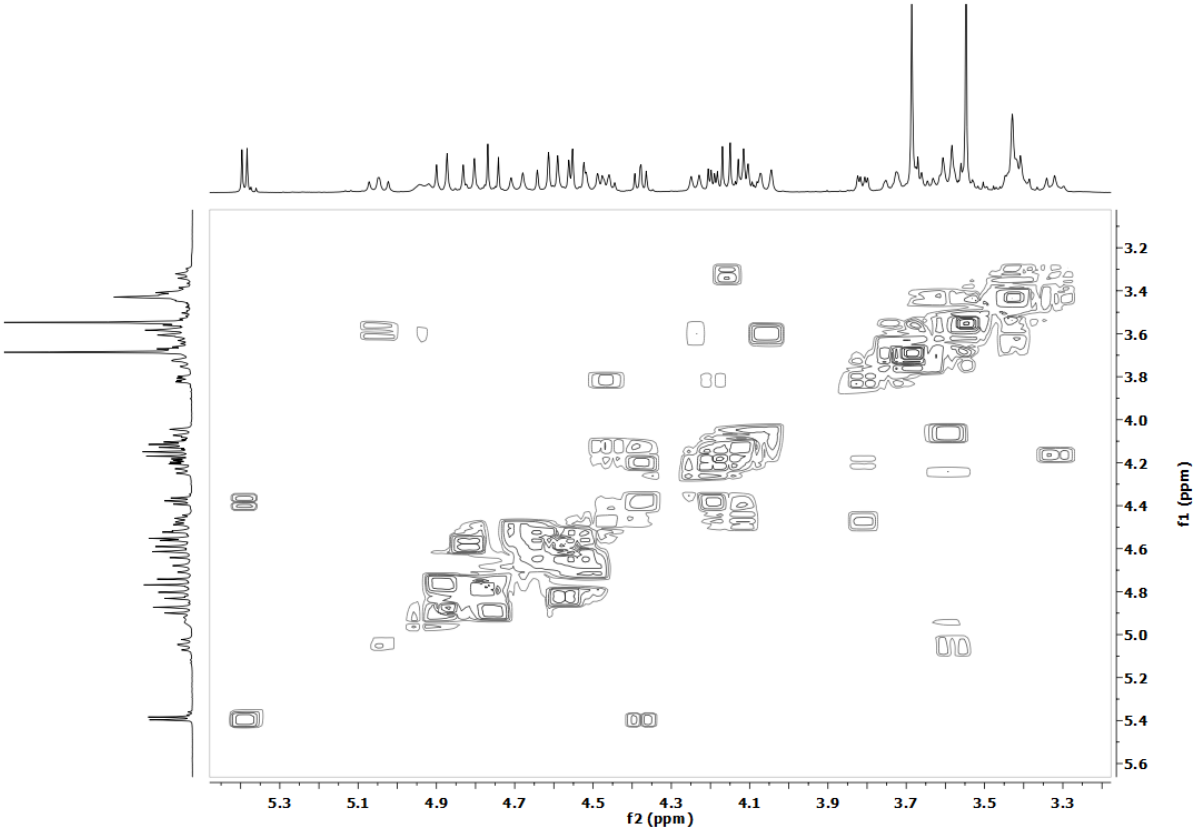
^{1}H NMR (400 MHz, $CDCl_3$) of trisaccharide (**51**)



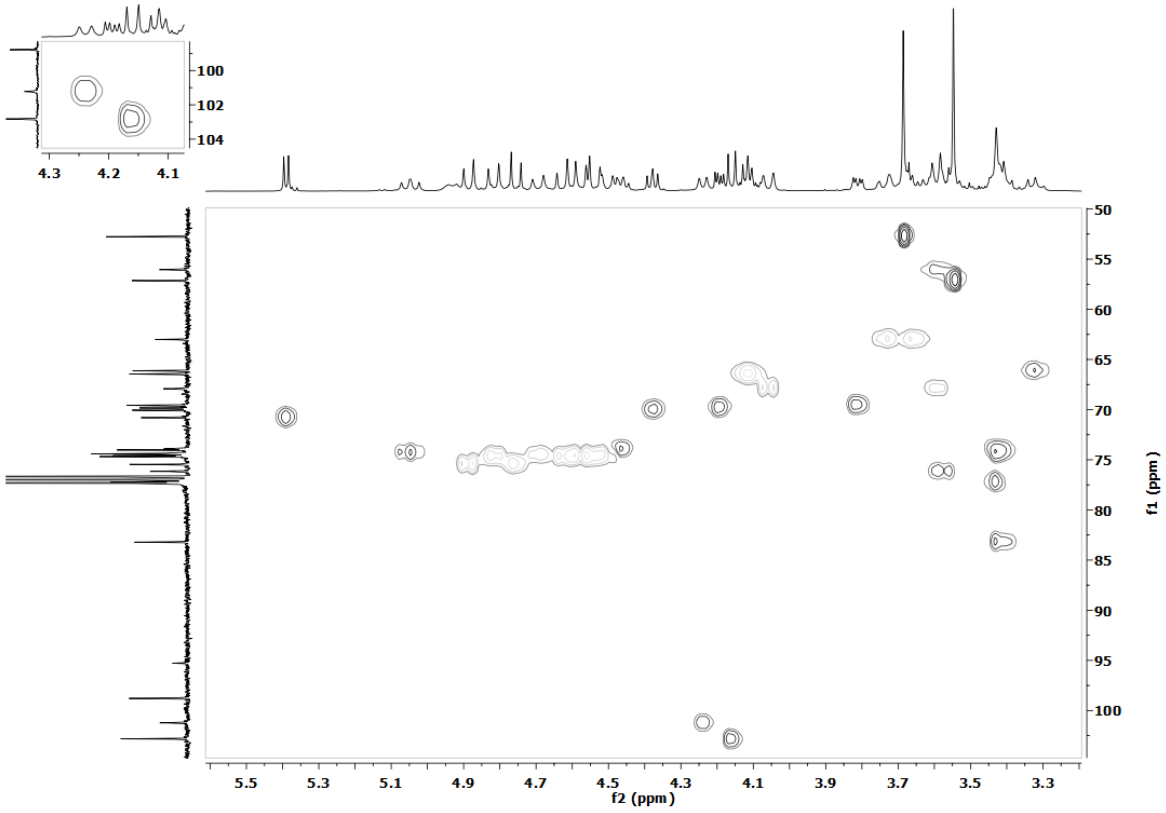
^{13}C NMR (100 MHz, $CDCl_3$) of trisaccharide (**51**)



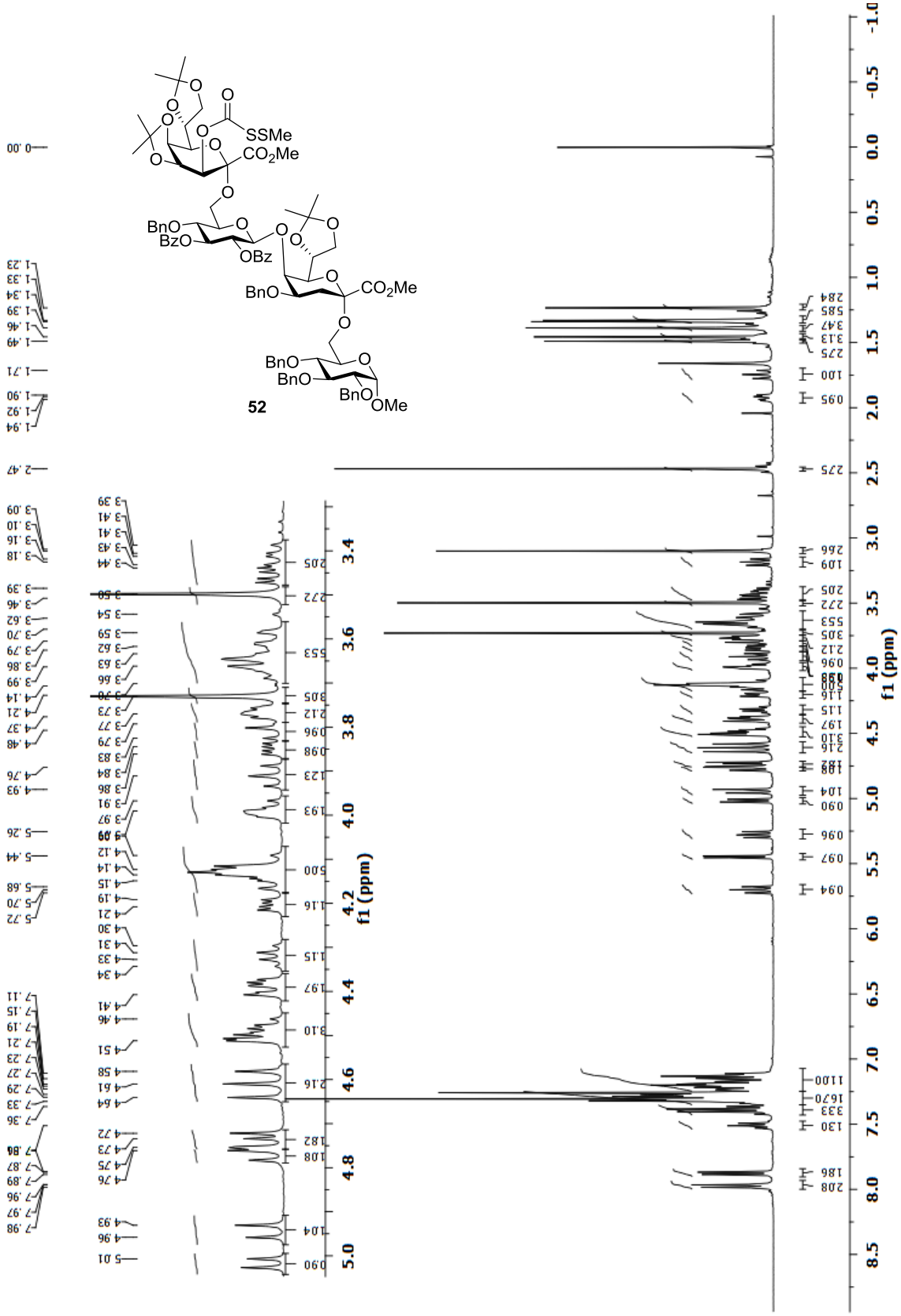
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of trisaccharide (**51**)



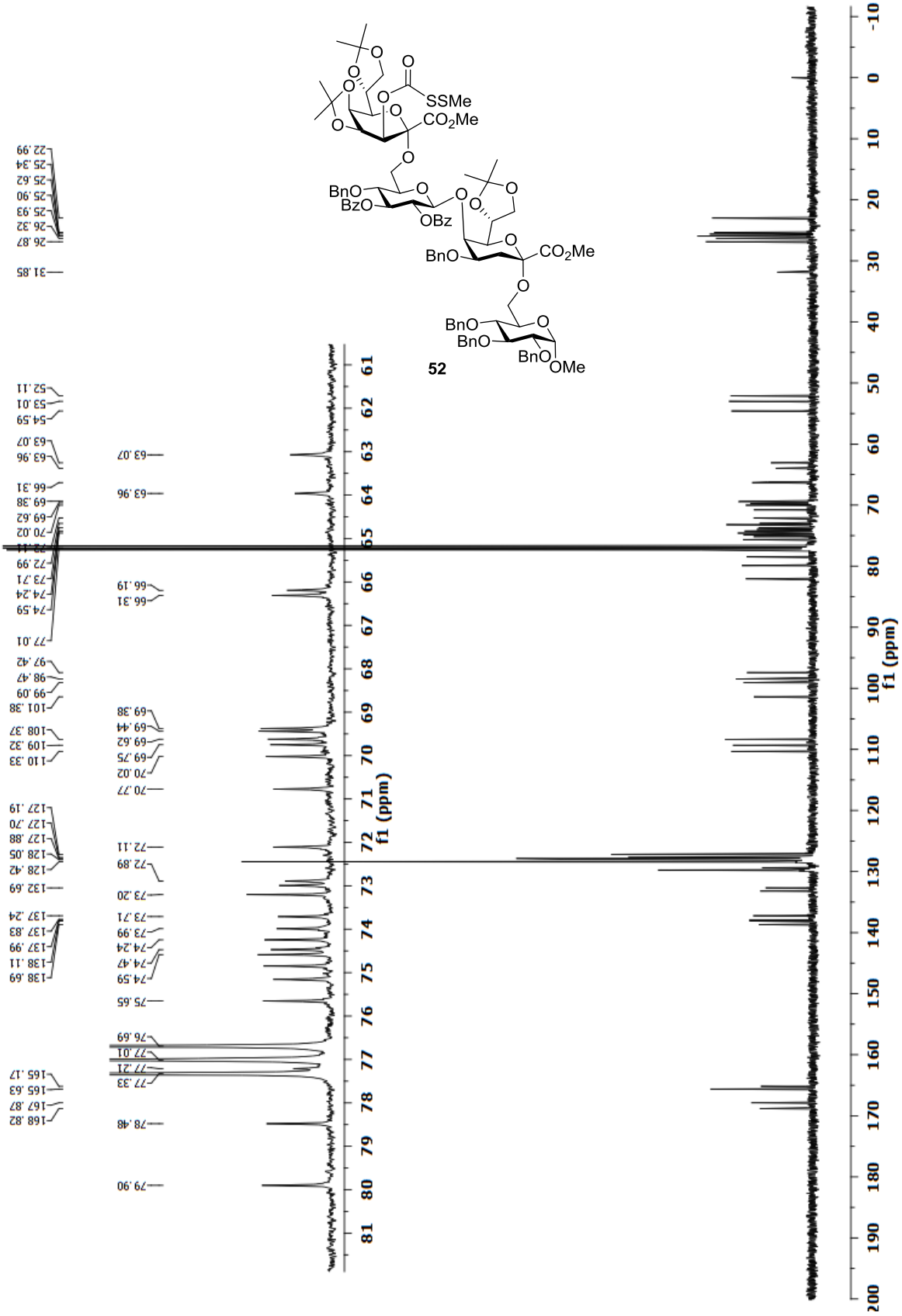
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of trisaccharide (**51**)



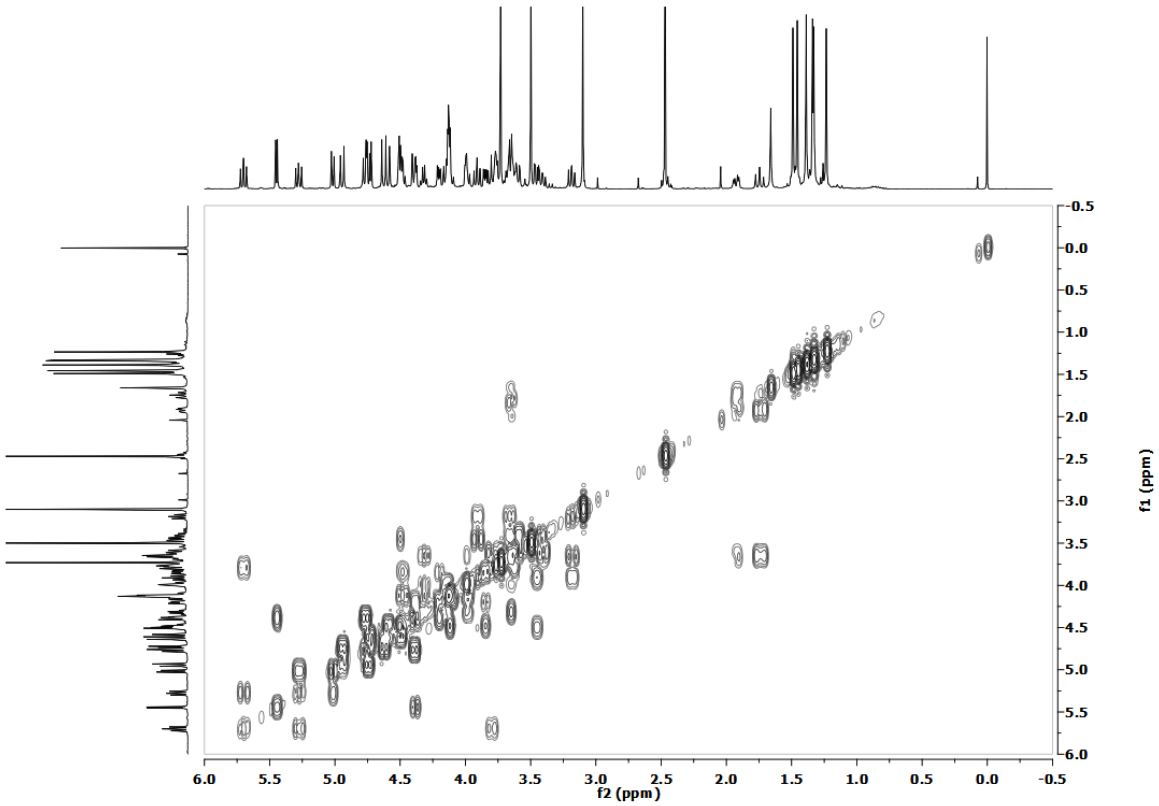
^{1}H NMR (400 MHz, $CDCl_3$) of tetrasaccharide (**52**)



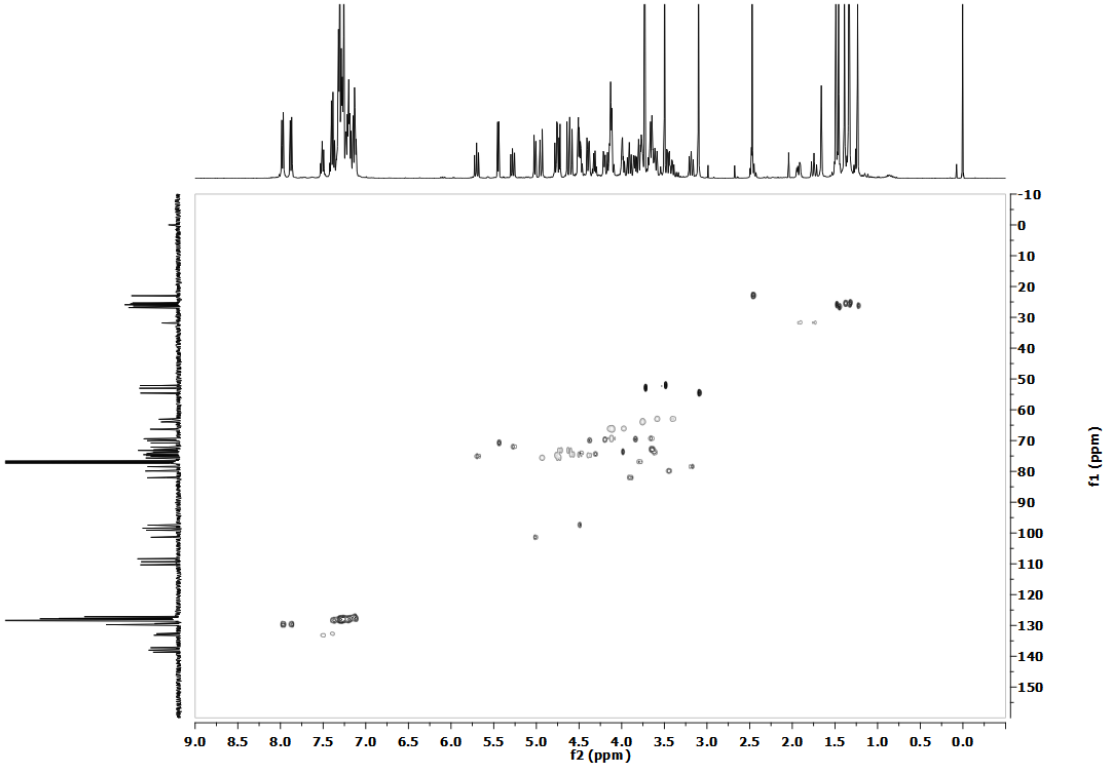
^{13}C NMR (100 MHz, $CDCl_3$) of tetrasaccharide (**52**)



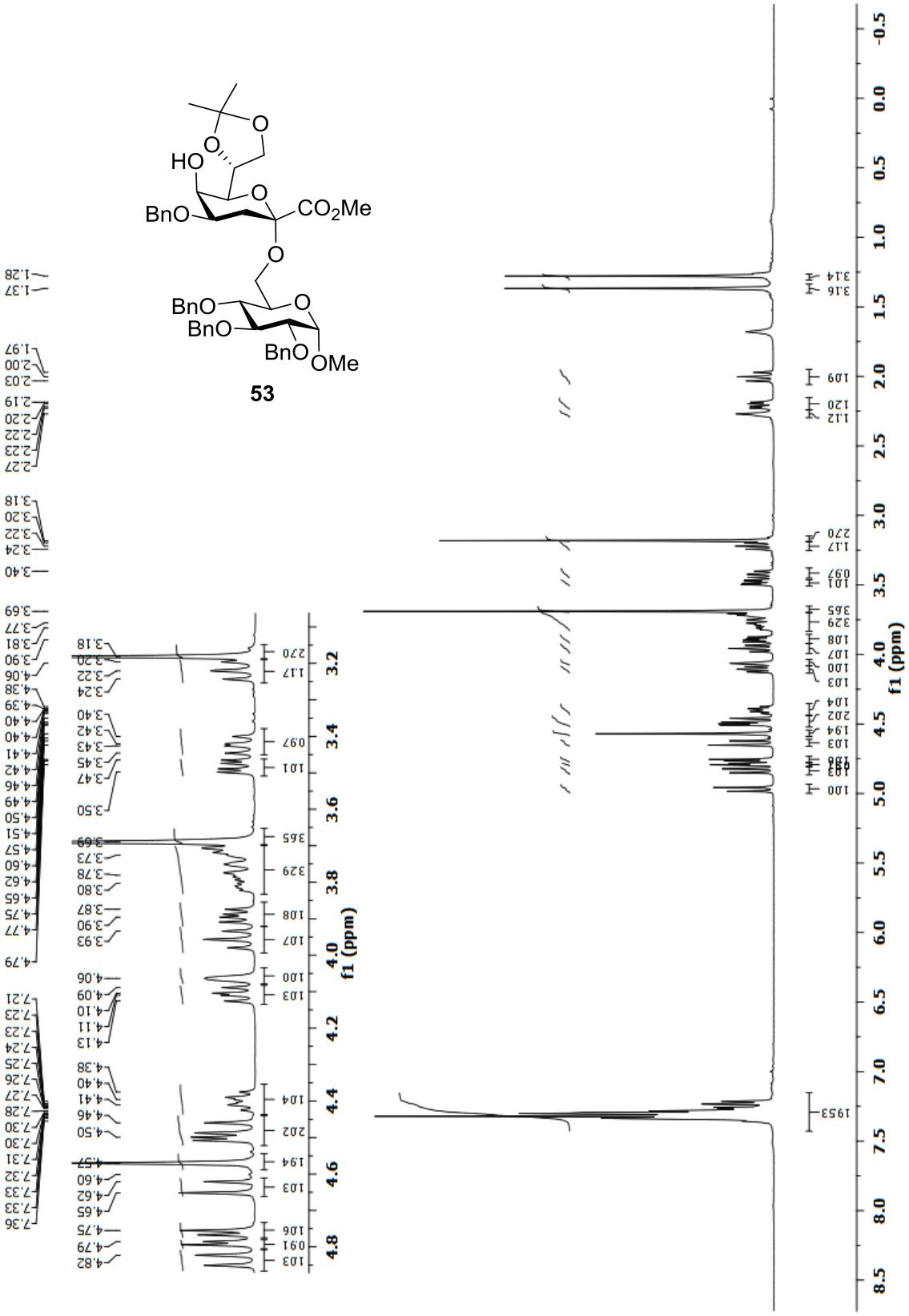
^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of tetrasaccharide (**52**)



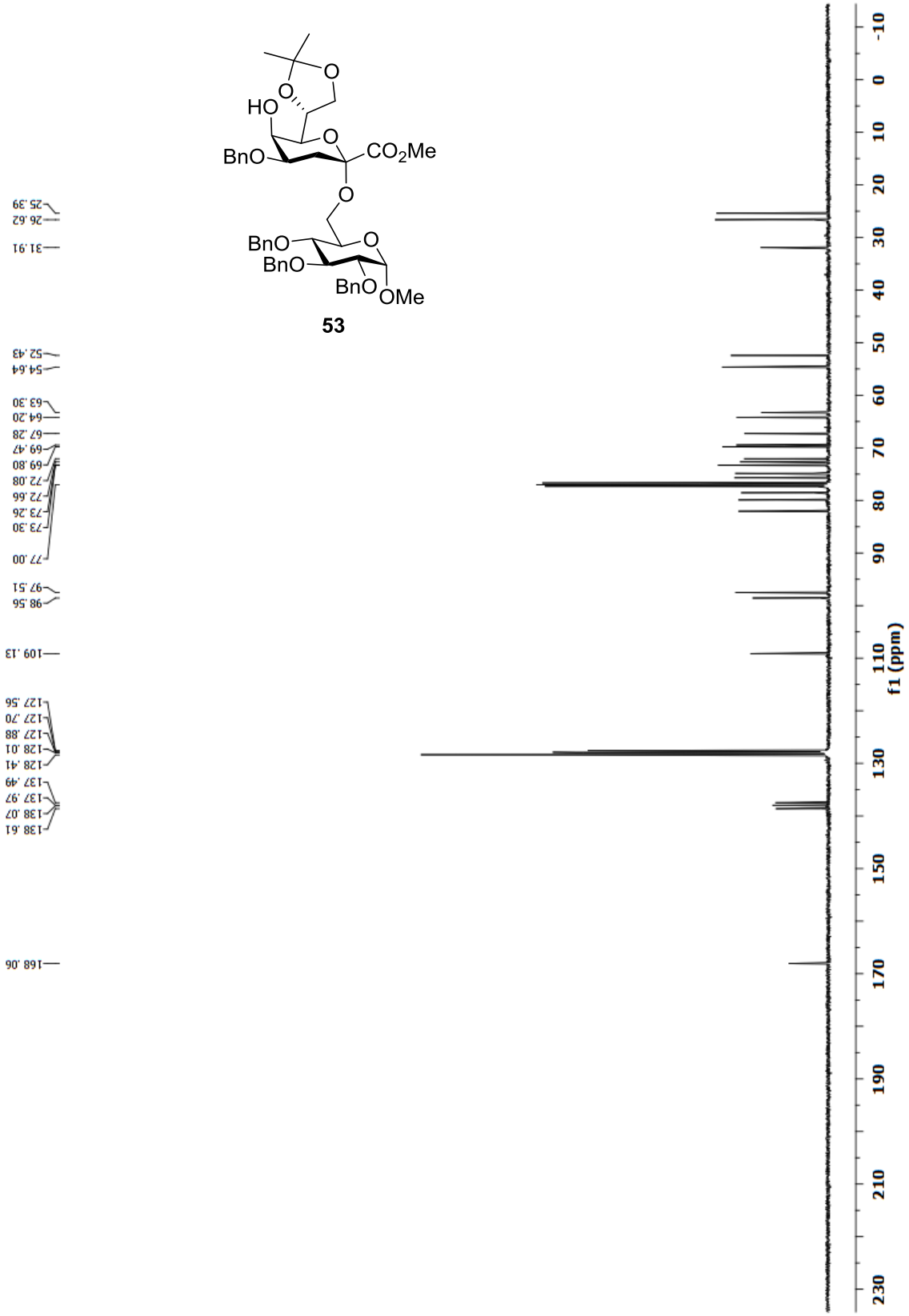
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of tetrasaccharide (**52**)



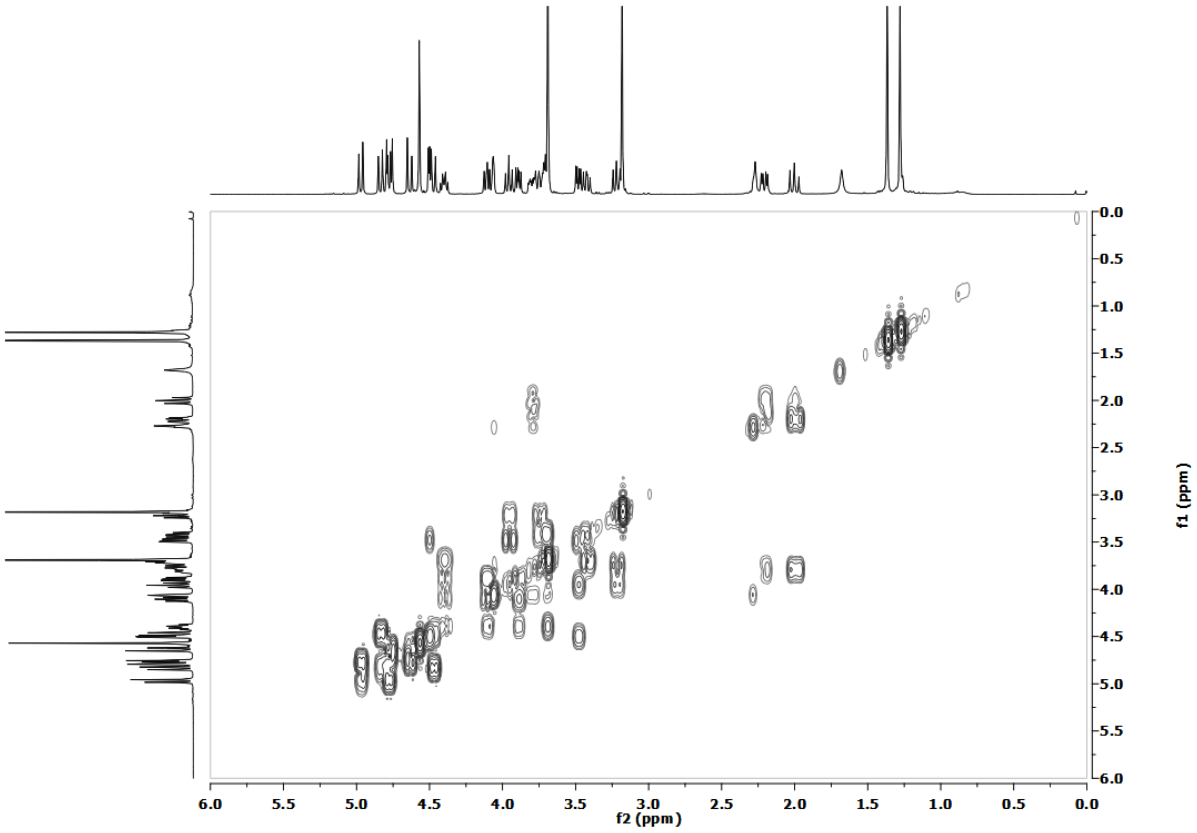
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4-*O*-benzyl-3-deoxy-7,8-*O*-isopropylidene-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**53**)



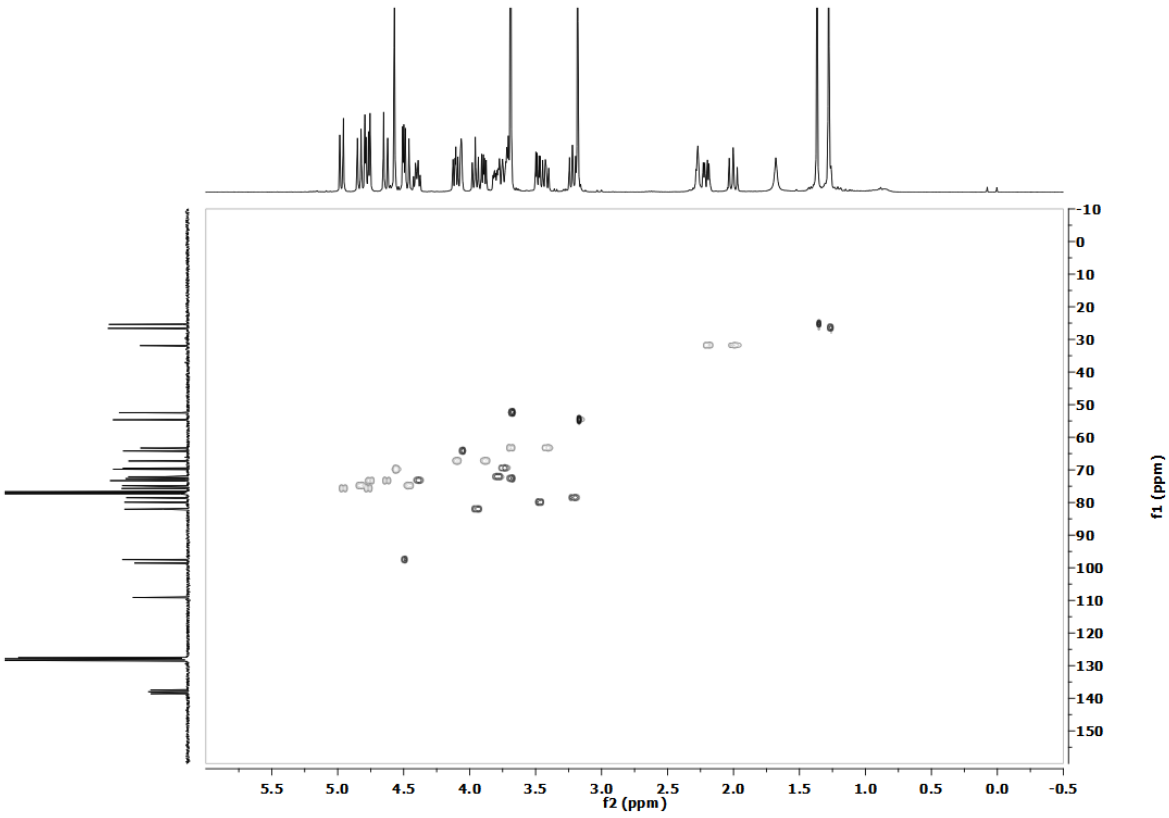
^{13}C NMR (100 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[methyl (4-*O*-benzyl-3-deoxy-7,8-*O*-isopropylidene-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**53**)



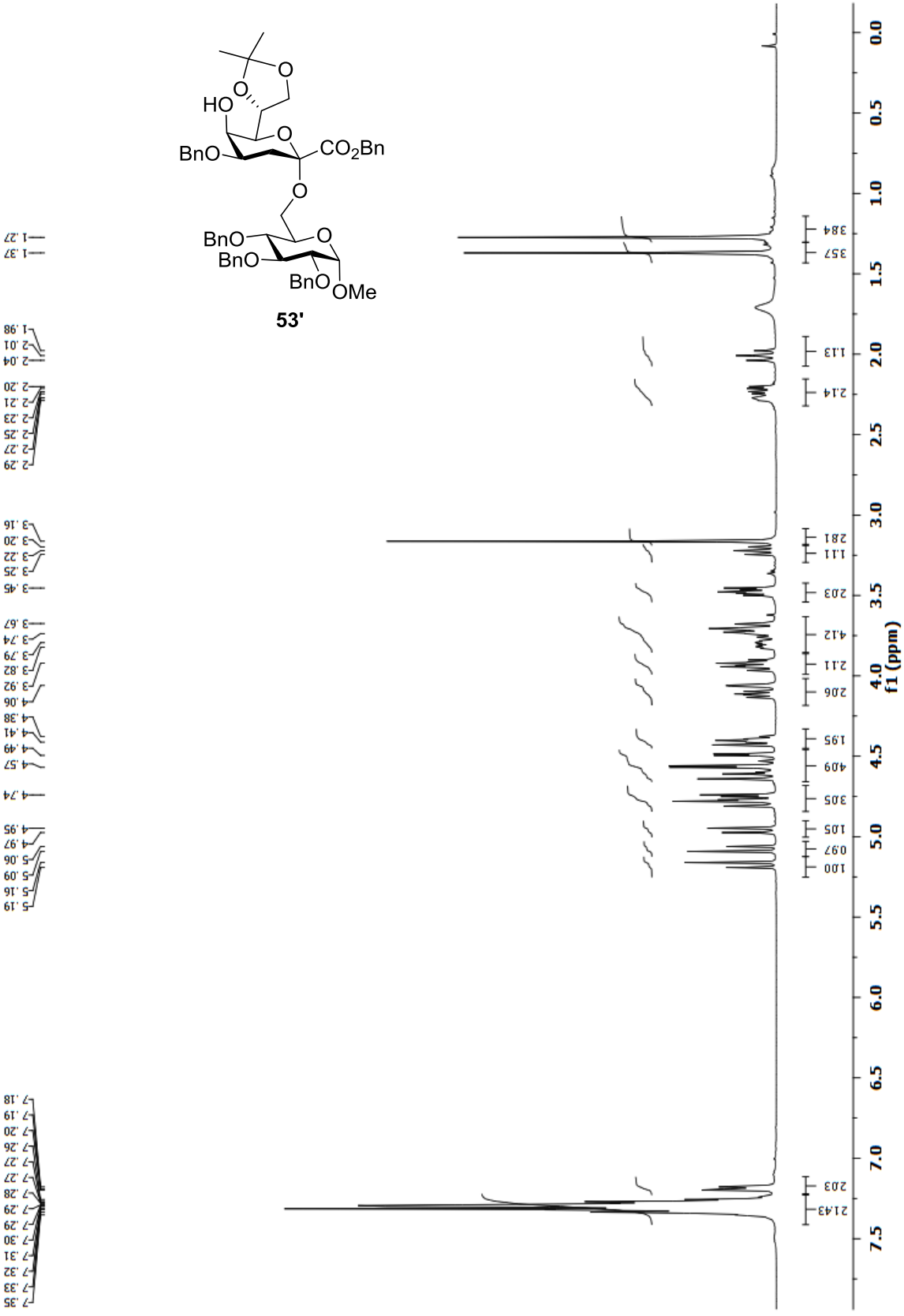
^{1}H-^{1}H GCOSY NMR (400 MHz, $CDCl_3$) of disaccharide (**53**)



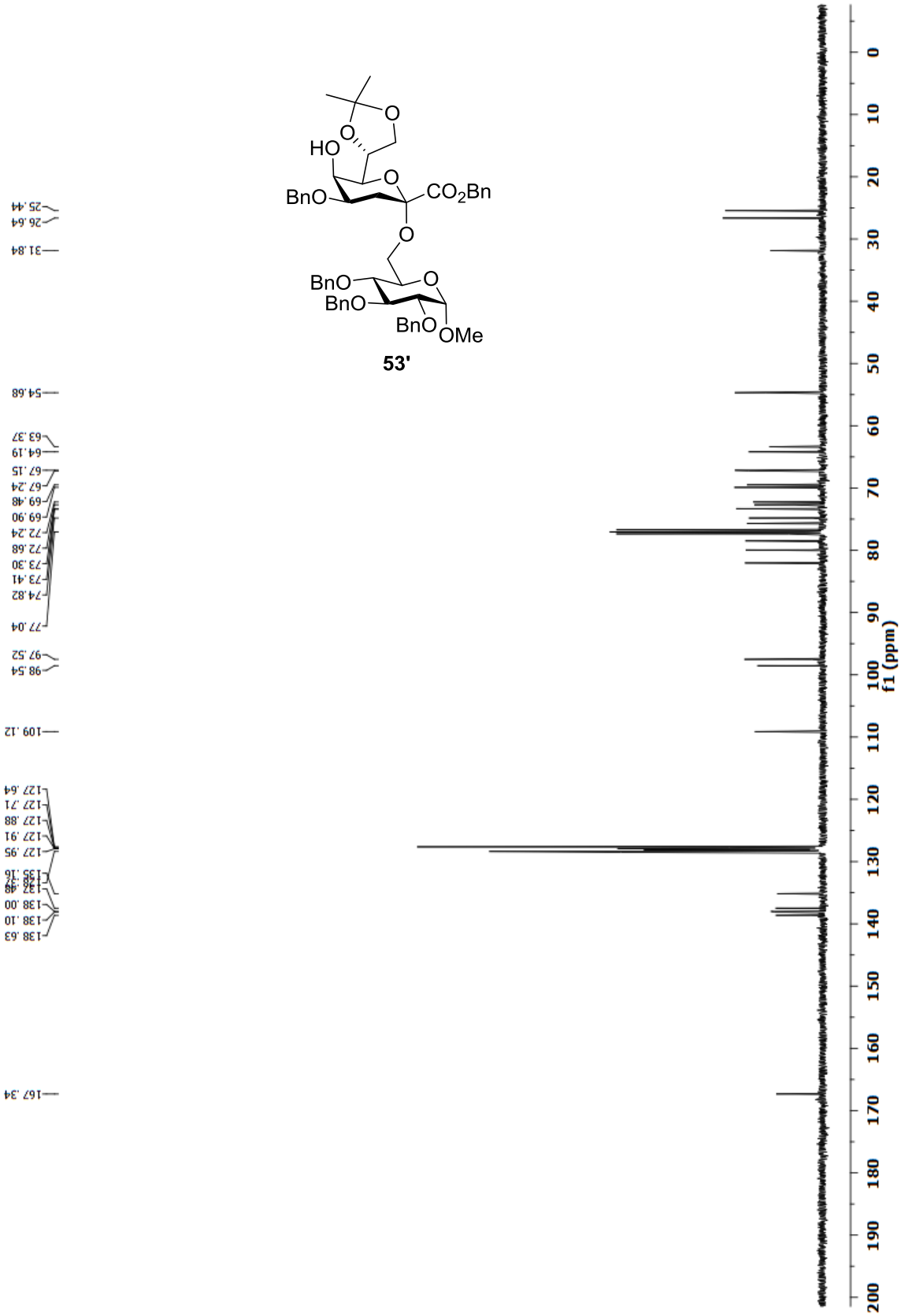
^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of disaccharide (**53**)



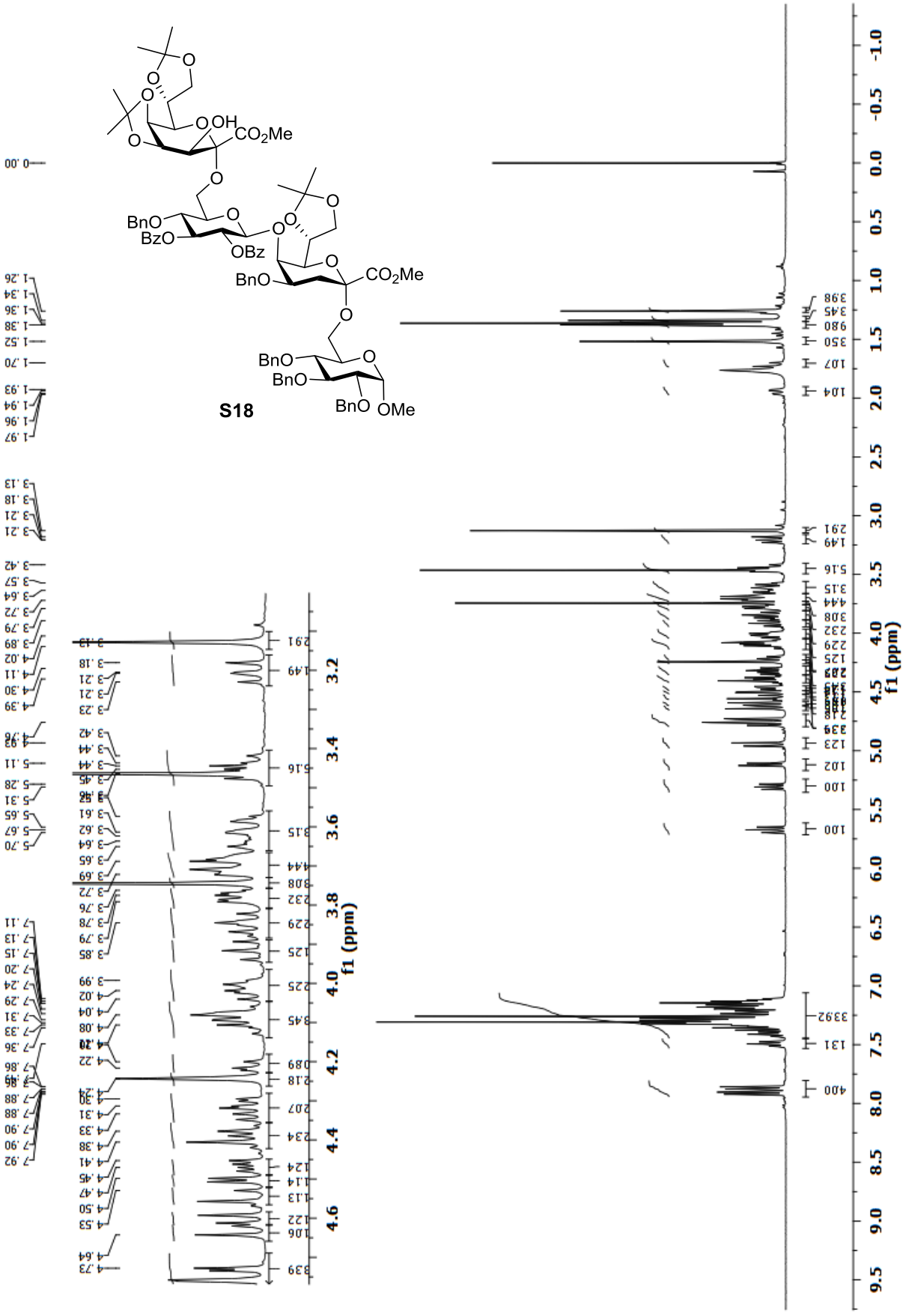
^{1}H NMR (400 MHz, $CDCl_3$) of methyl 2,3,4-tri-*O*-benzyl-6-*O*-[benzyl (4-*O*-benzyl-3-deoxy-7,8-*O*-isopropylidene-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**53′**)



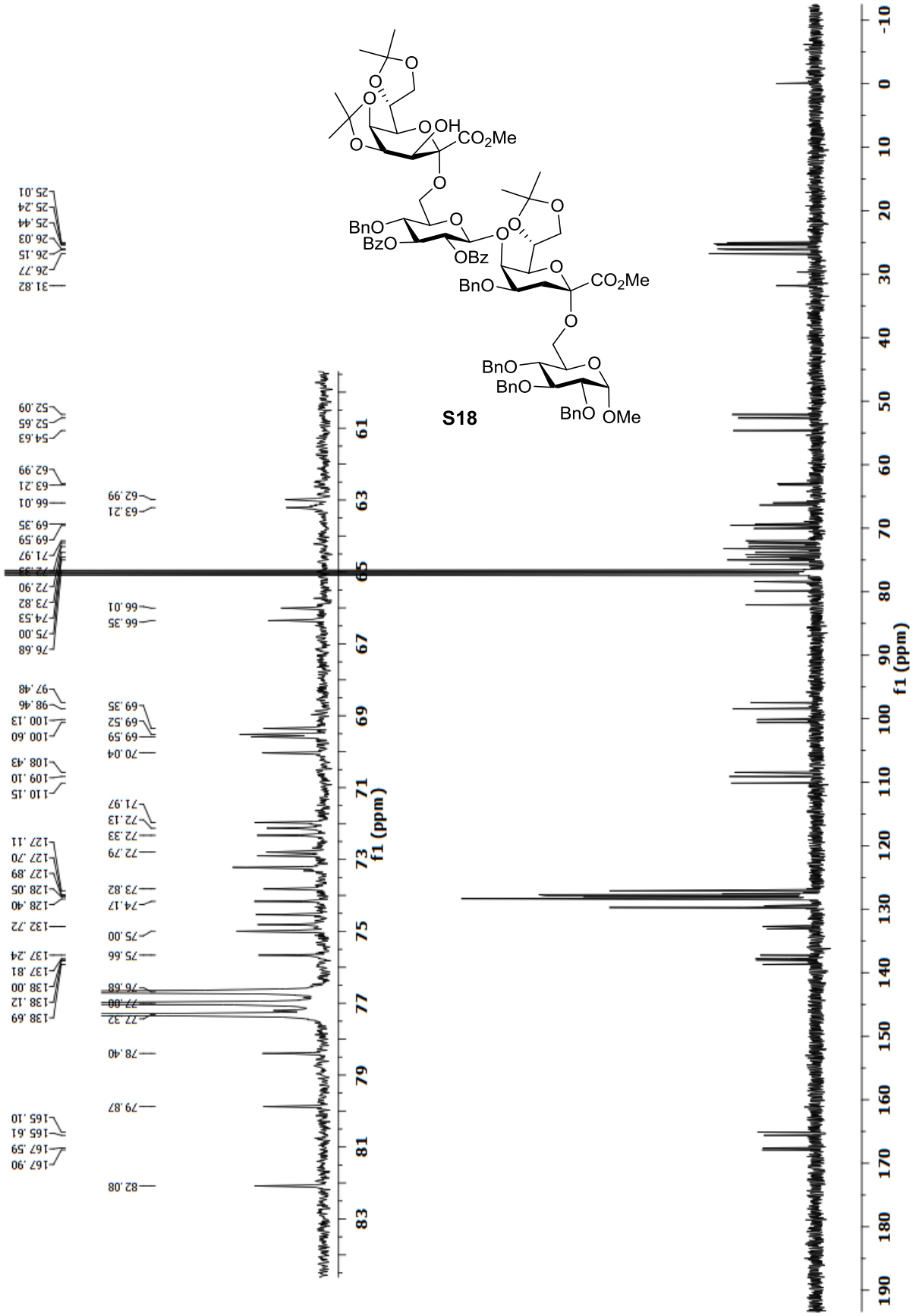
^{13}C NMR (100 MHz, $CDCl_3$) of d methyl 2,3,4-tri-*O*-benzyl-6-*O*-[benzyl (4-*O*-benzyl-3-deoxy-7,8-*O*-isopropylidene-*α*-D-*manno*-2-octulopyranosonyl)onate]-*α*-D-glucopyranoside (**53′**)



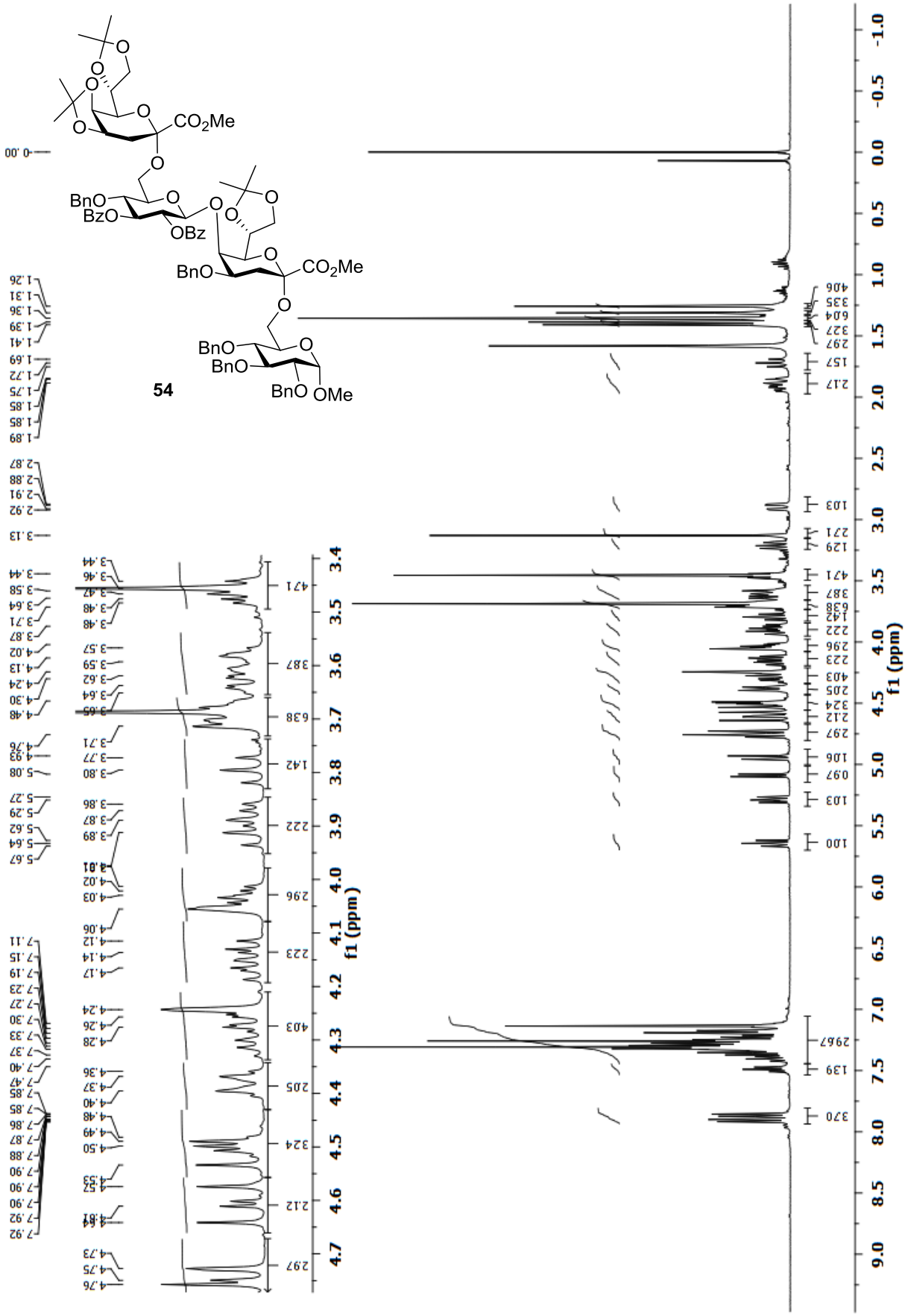
^{1}H NMR (400 MHz, $CDCl_3$) of tetrasaccharide (**S18**)



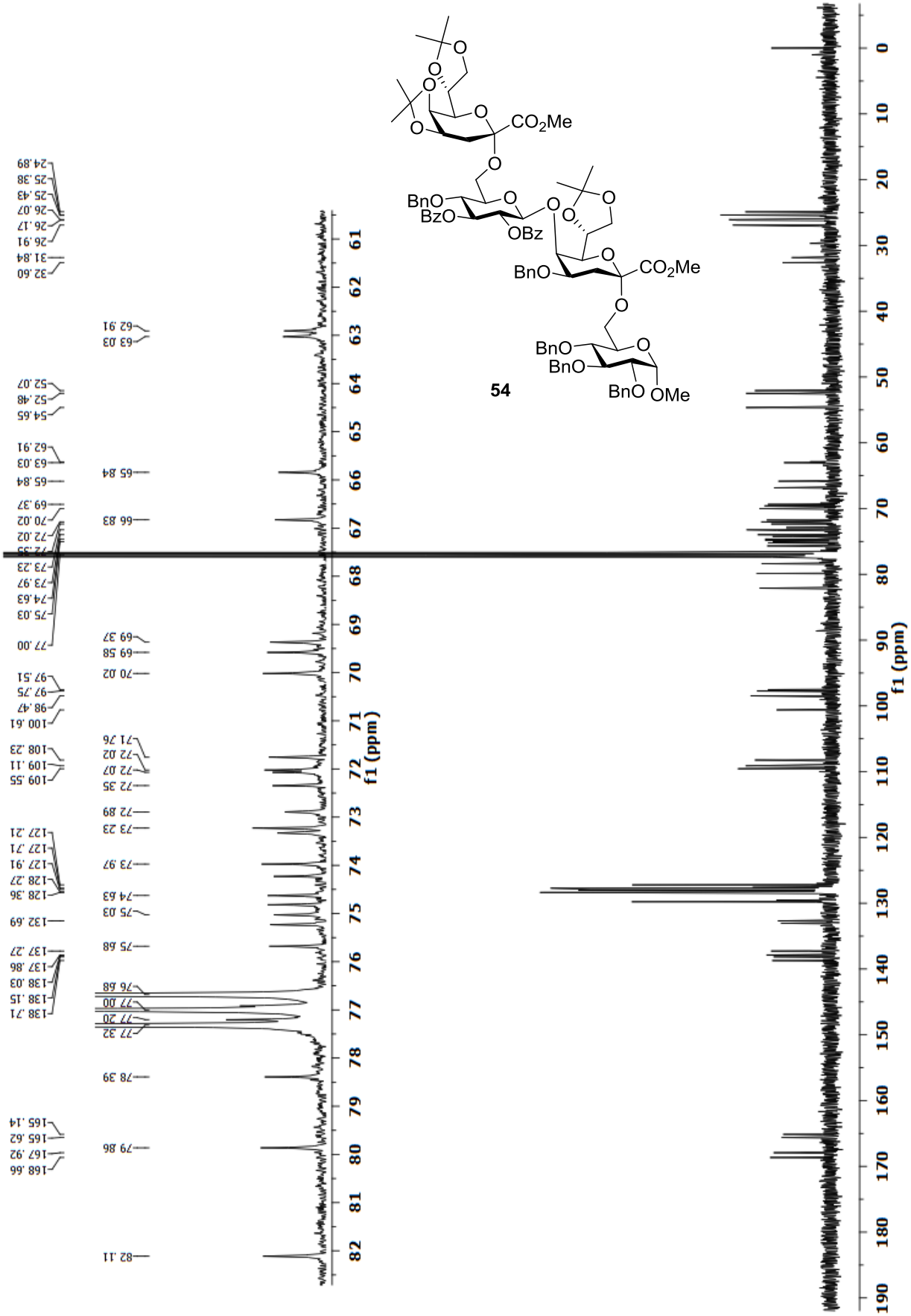
^{13}C NMR (100 MHz, $CDCl_3$) of tetrasaccharide (**S18**)



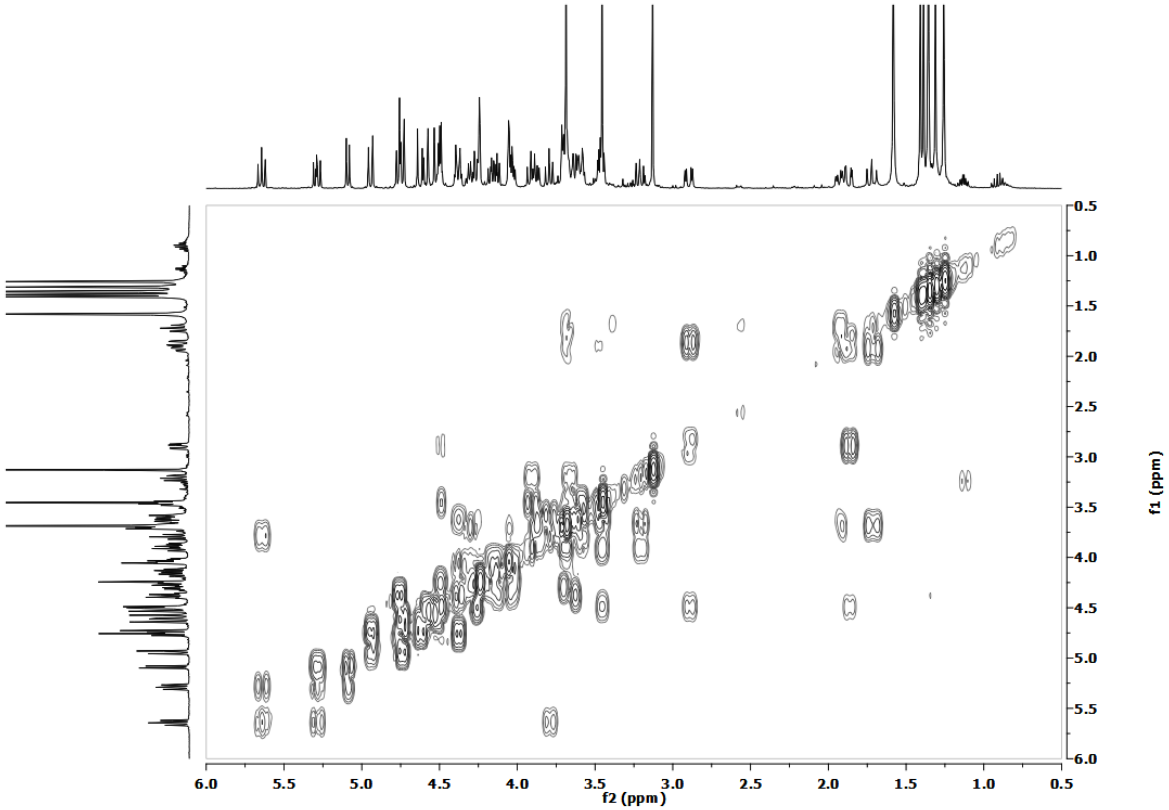
^{1}H NMR (400 MHz, $CDCl_3$) of tetrasaccharide (**54**)



^{13}C NMR (100 MHz, $CDCl_3$) of tetrasaccharide (**54**)



^{1}H-^{1}H GCOSY (400 MHz, $CDCl_3$) of tetrasaccharide (**54**)



^{1}H-^{13}C HSQC NMR (100 MHz, $CDCl_3$) of tetrasaccharide (**54**)