Supplementary Information

Tetrasaccharide iteration synthesis of a heparin-like dodecasaccharide and radiolabelling for *in vivo* tissue distribution studies

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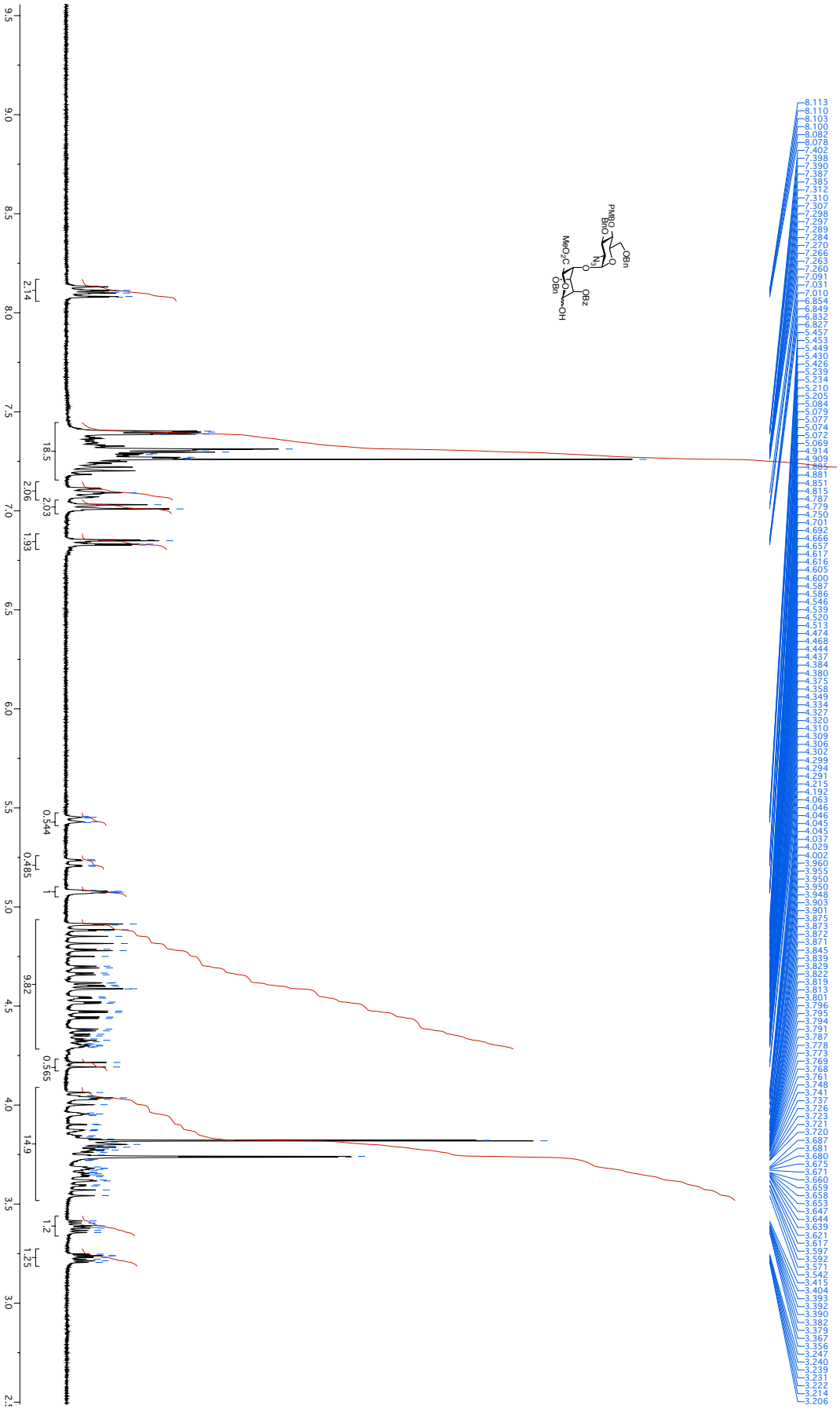
Supplementary figures

NMR and Mass spectra

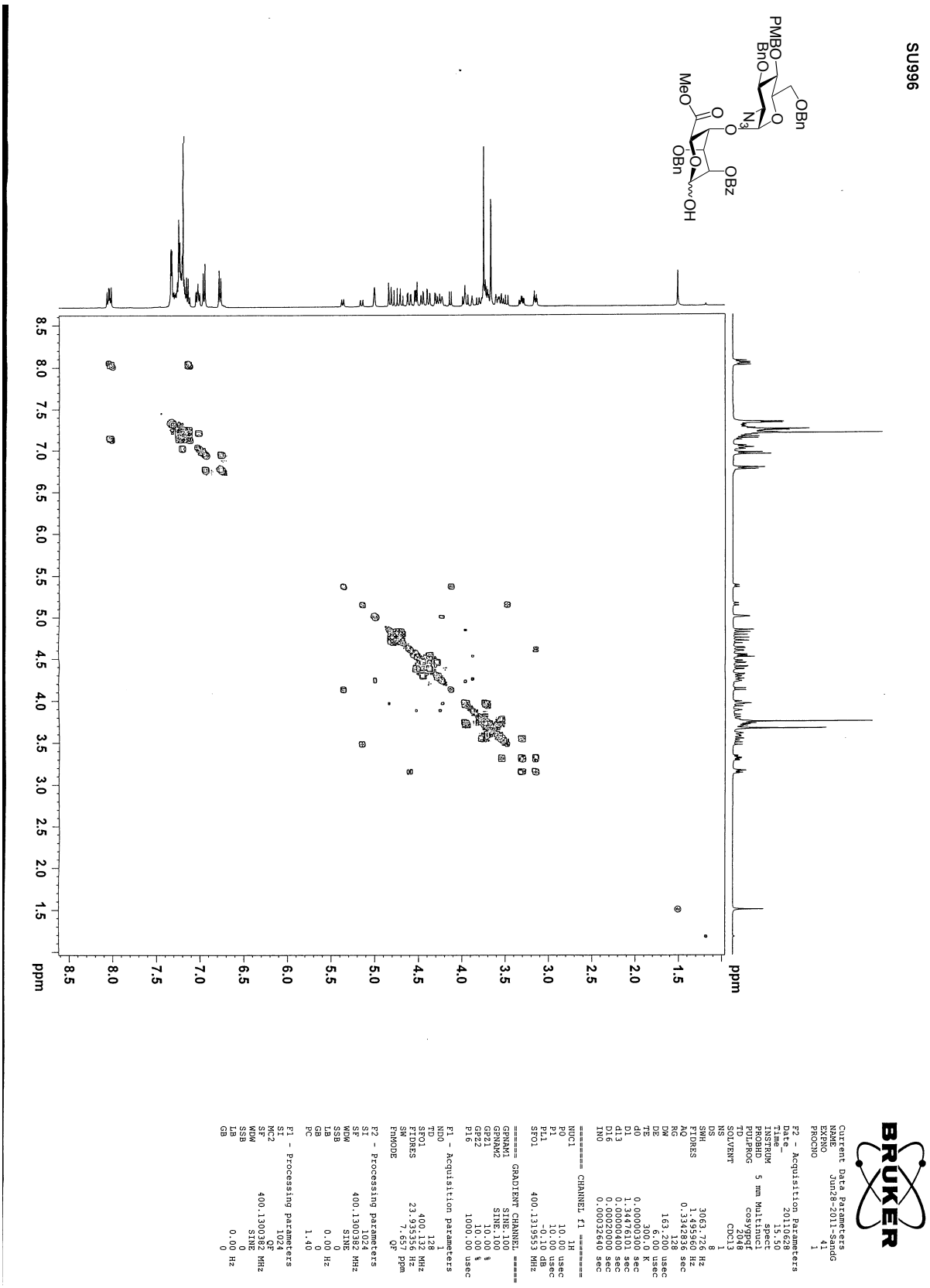
Supplementary methods

Synthesis of oligosaccharides

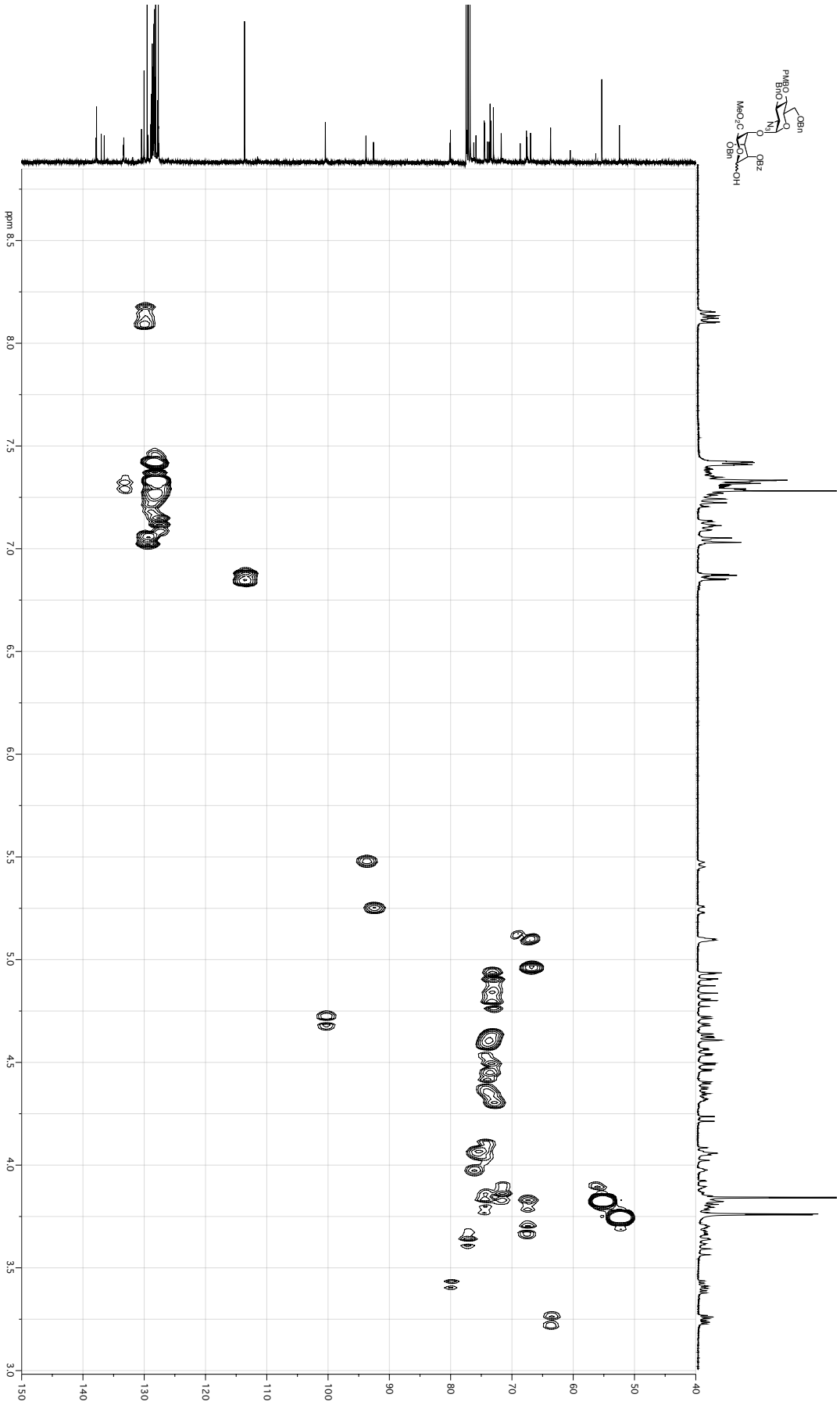
Supplementary figures



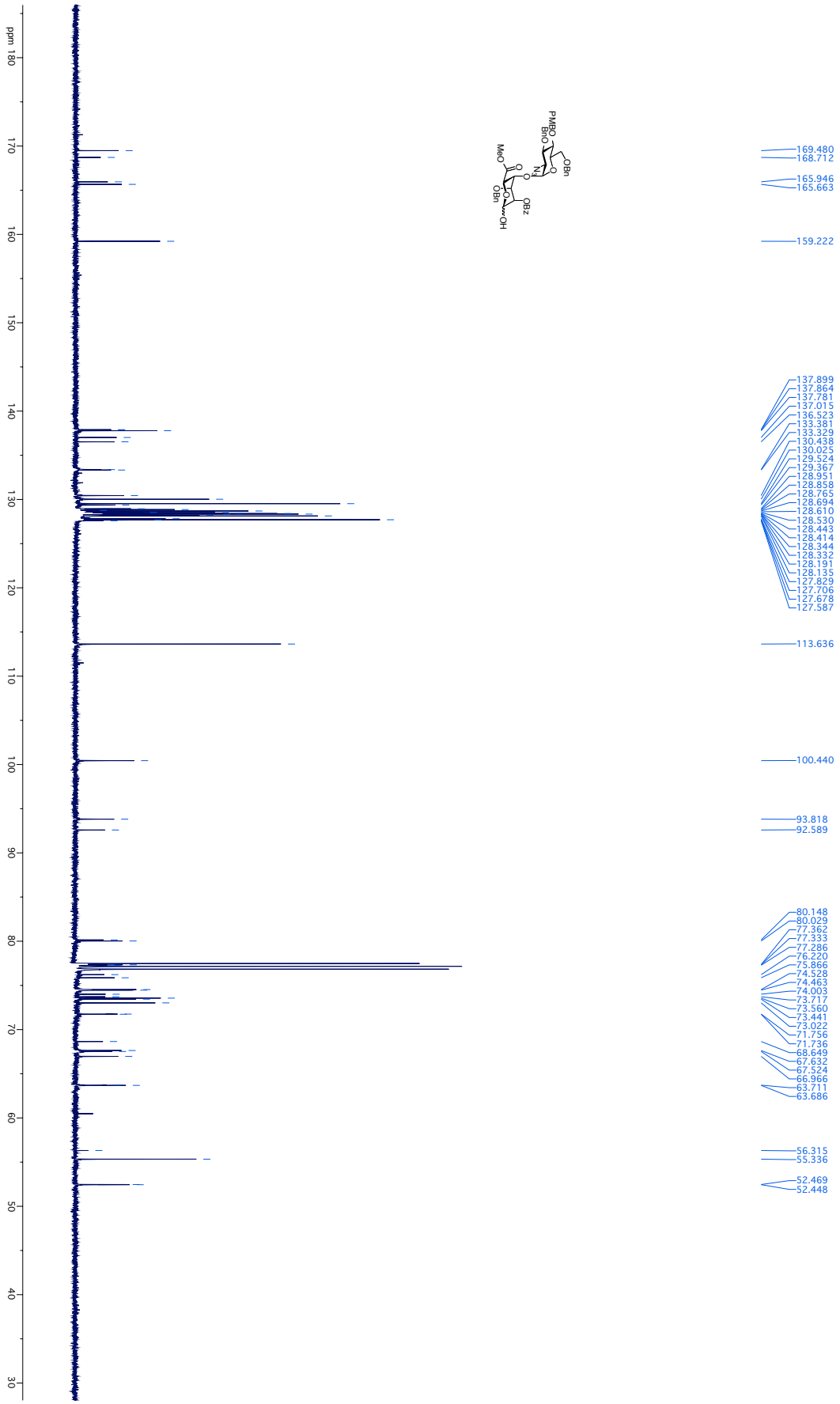
Supplementary Figure S1. ^{1}H NMR (400 MHz; $CDCl_3$) spectrum for **3**.



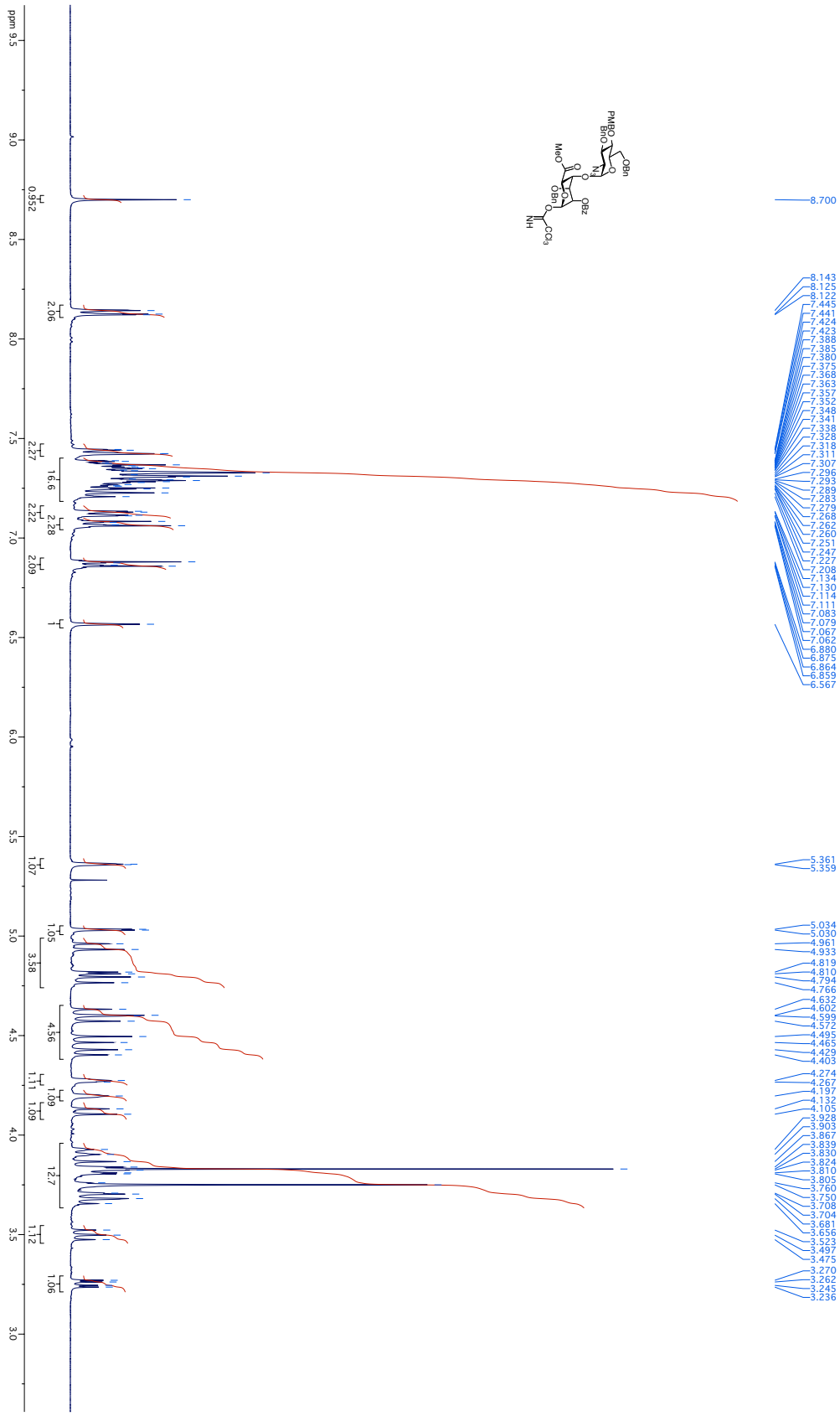
Supplementary Figure S2. COSY NMR spectrum for **3**.



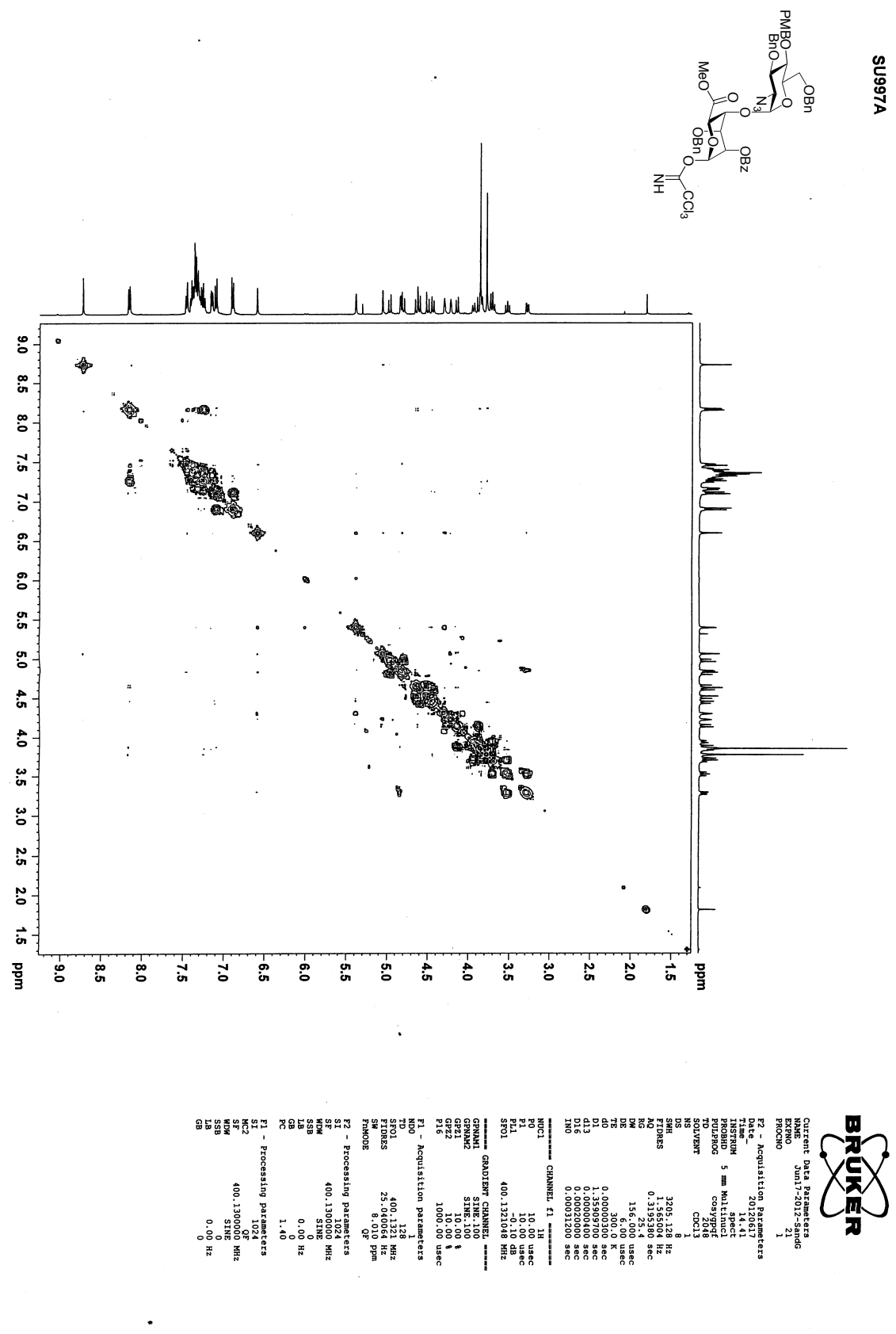
Supplementary Figure S3. HMQC NMR spectrum for **3**.



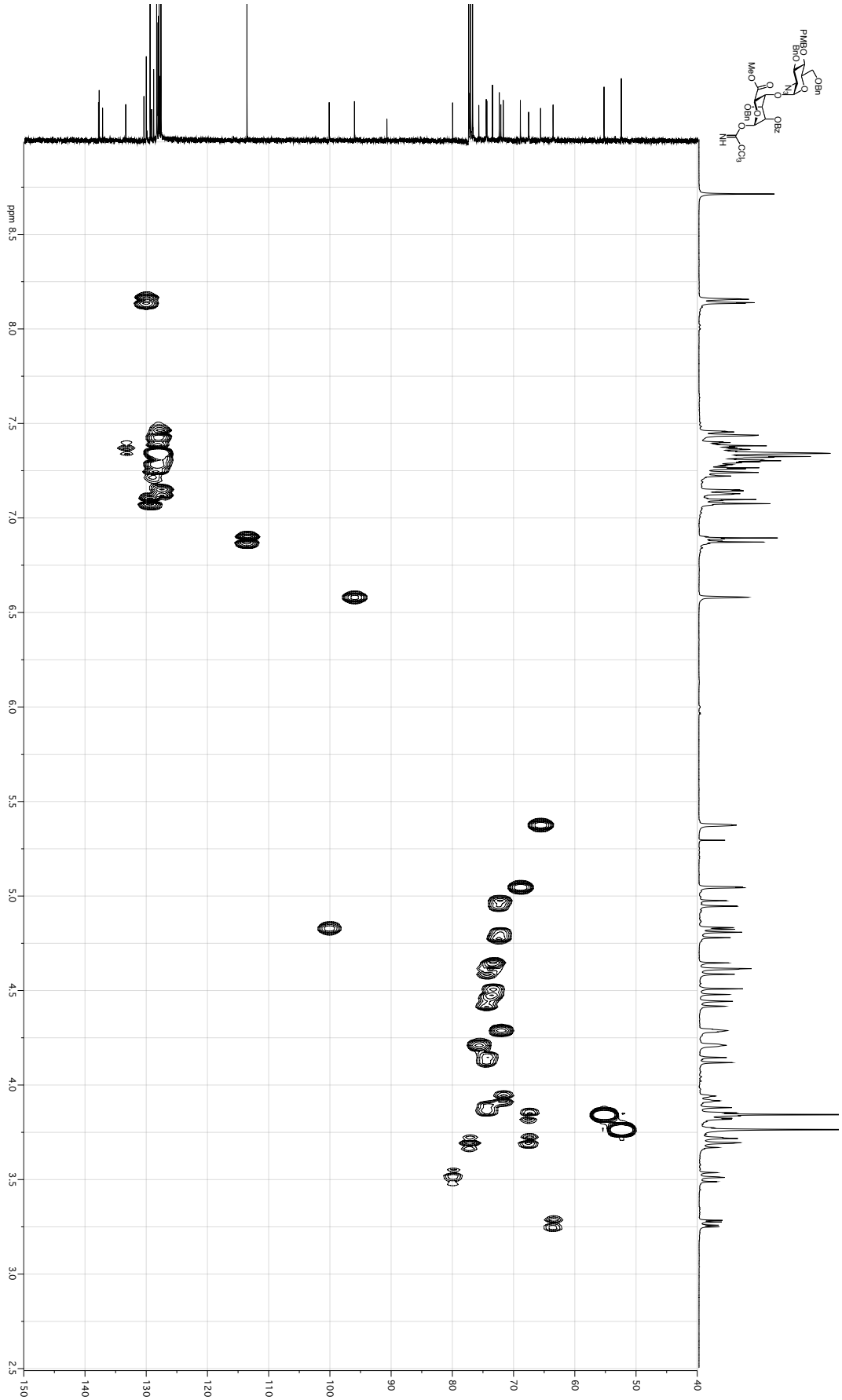
Supplementary Figure S4. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for **3**.



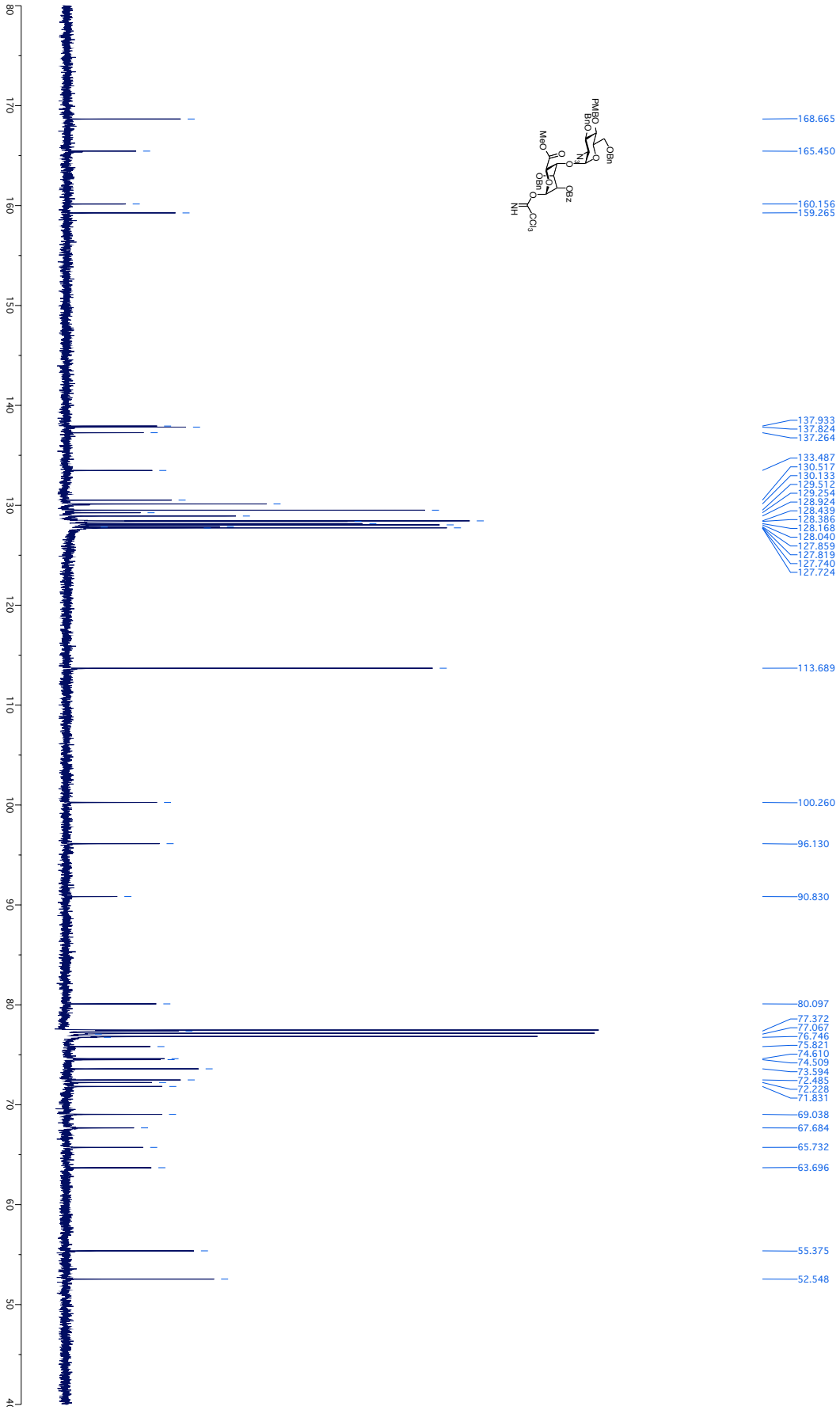
Supplementary Figure S5. ^{1}H NMR (400 MHz; $CDCl_3$) spectrum for α-**4**.



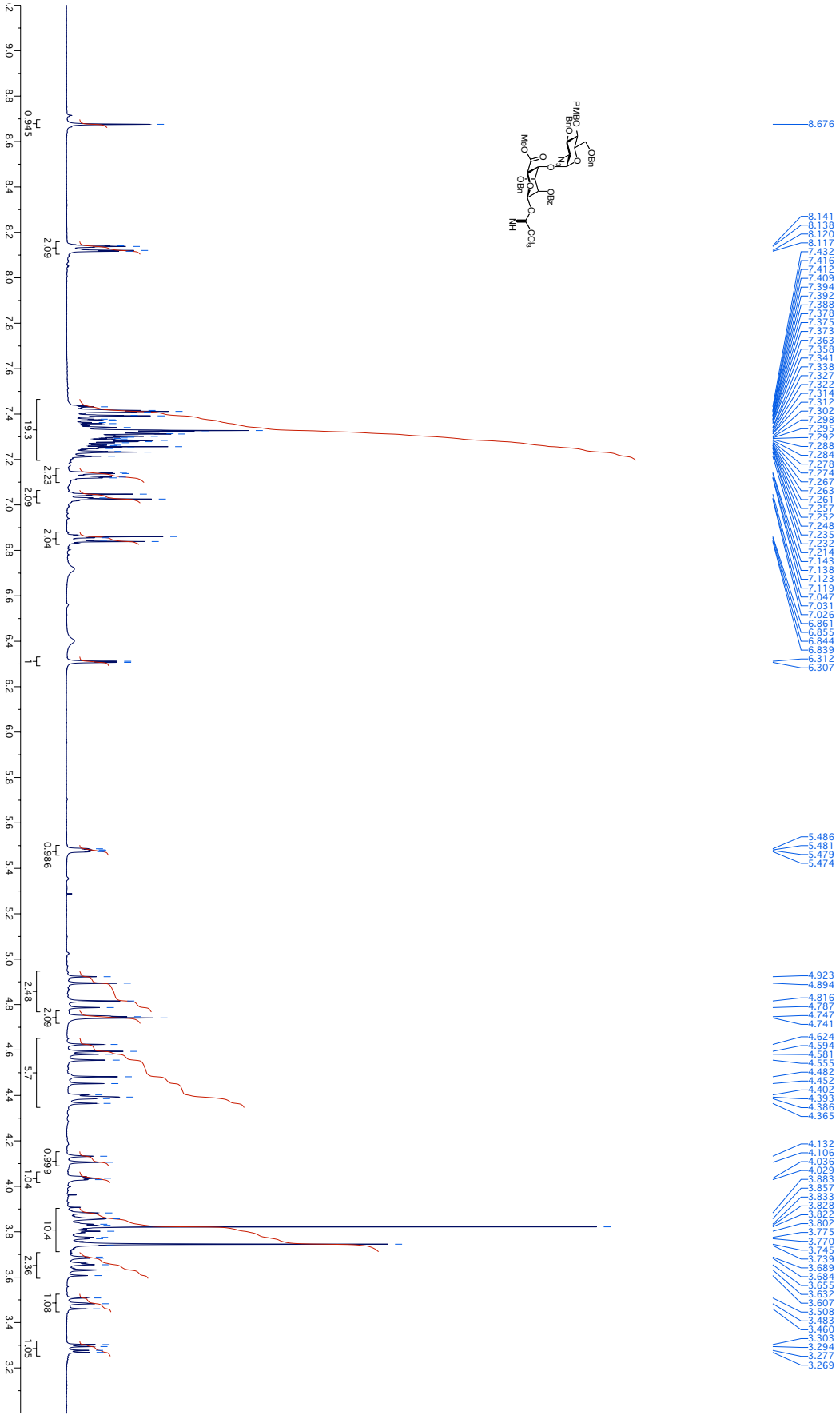
Supplementary Figure S6. COSY NMR spectrum for α-**4**.



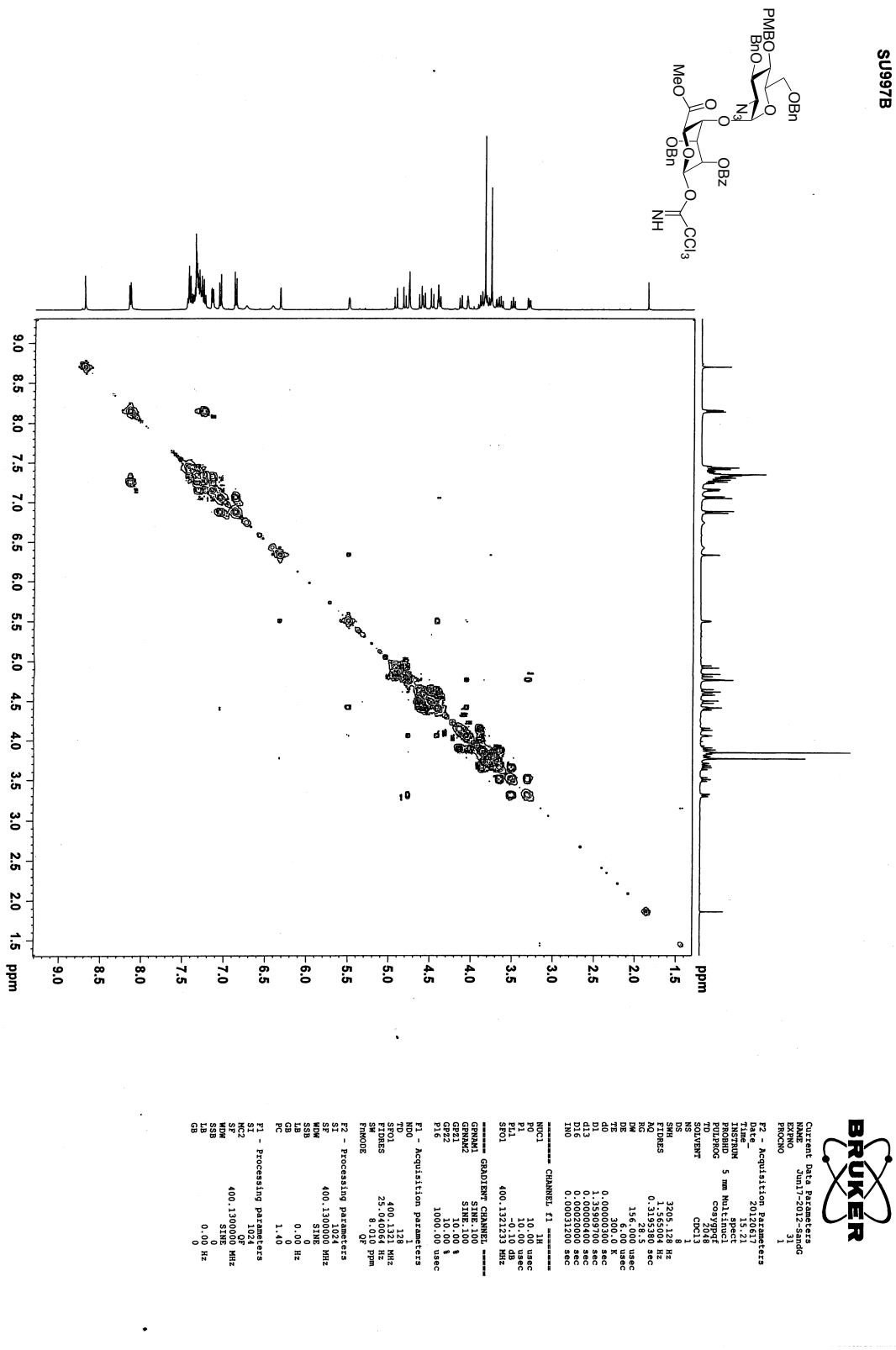
Supplementary Figure S7. HMQC NMR spectrum for α-**4**.



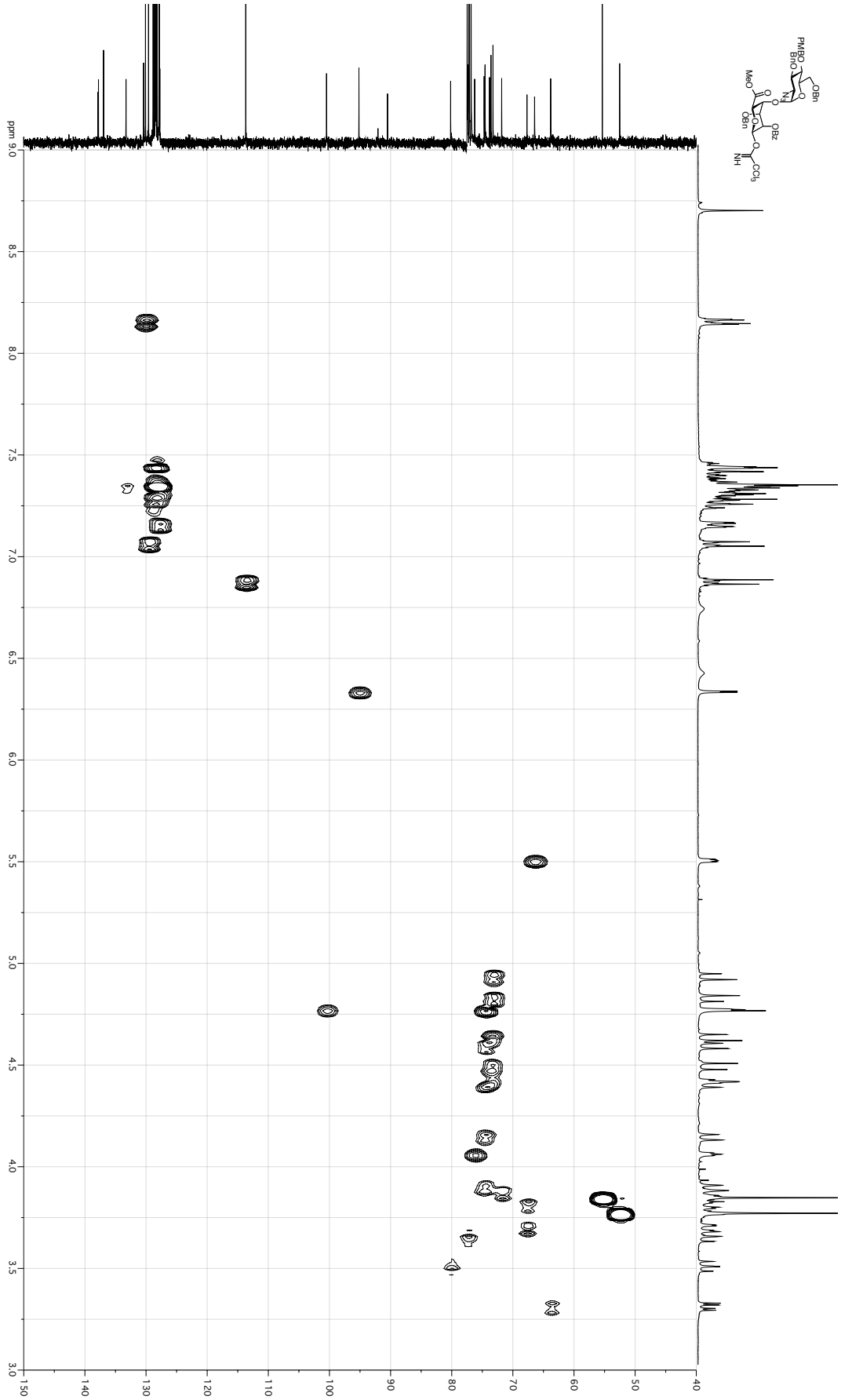
Supplementary Figure S8. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for α-**4**.



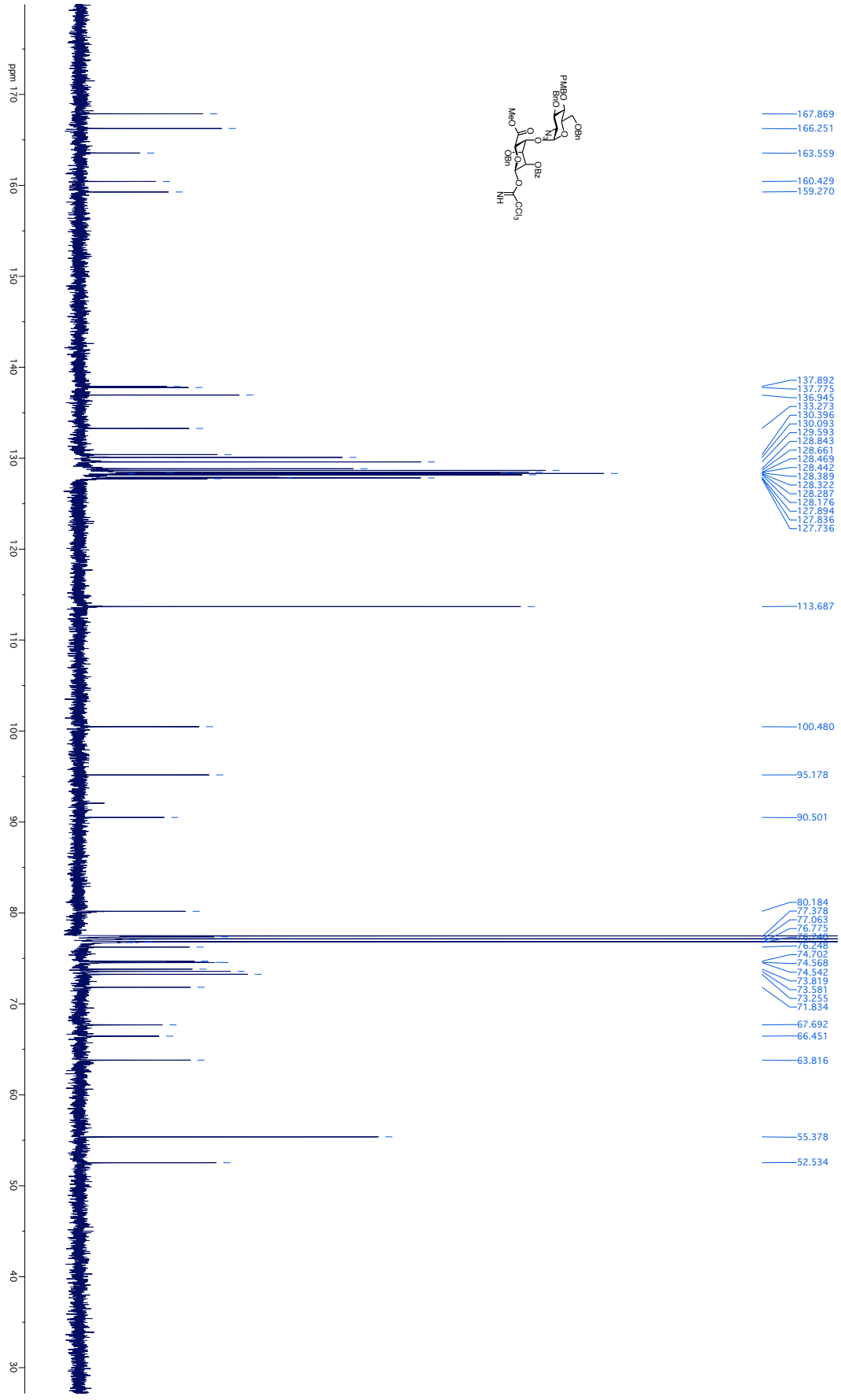
Supplementary Figure S9. ^{1}H NMR (400 MHz; $CDCl_3$) spectrum for β-**4**.



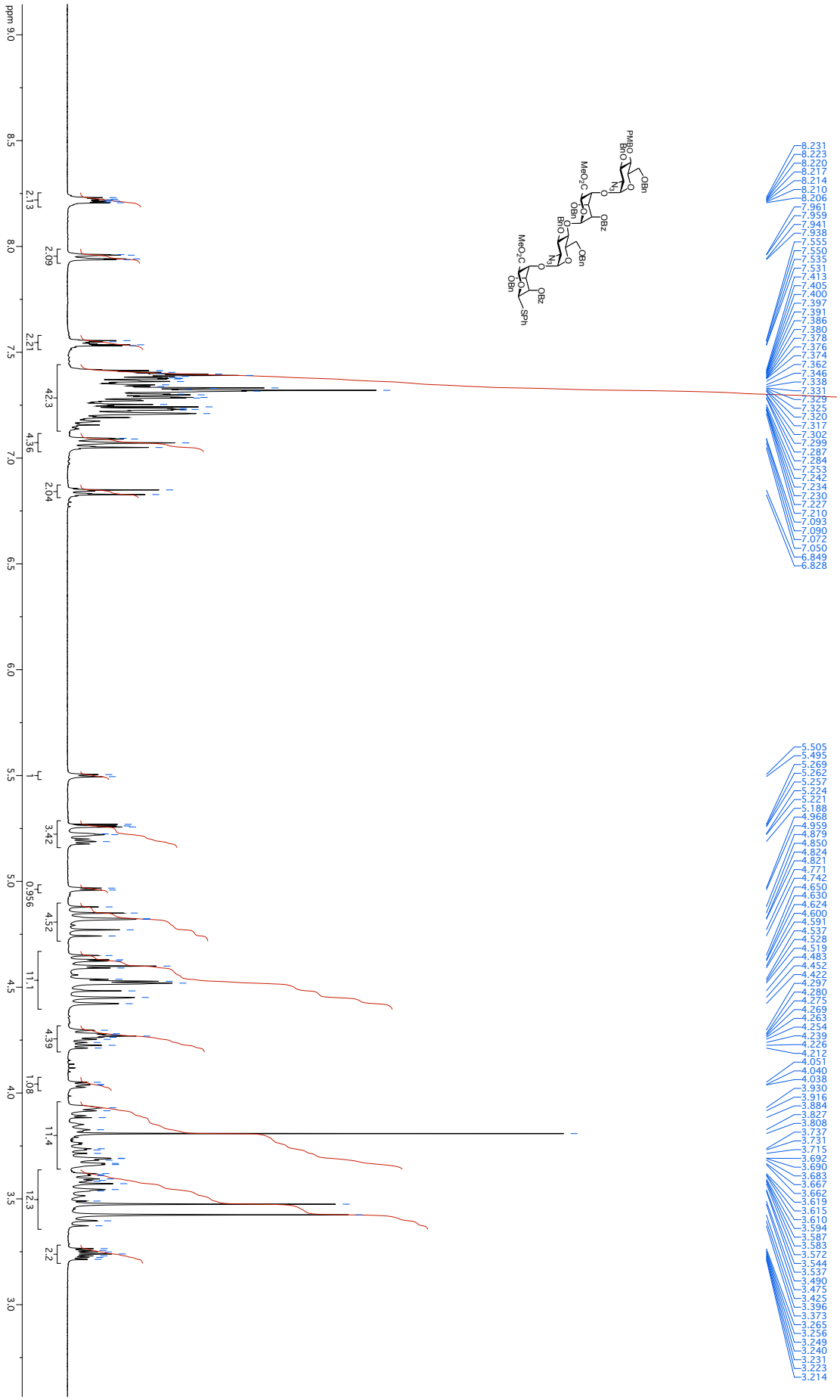
Supplementary Figure S10. COSY NMR spectrum for β-**4**



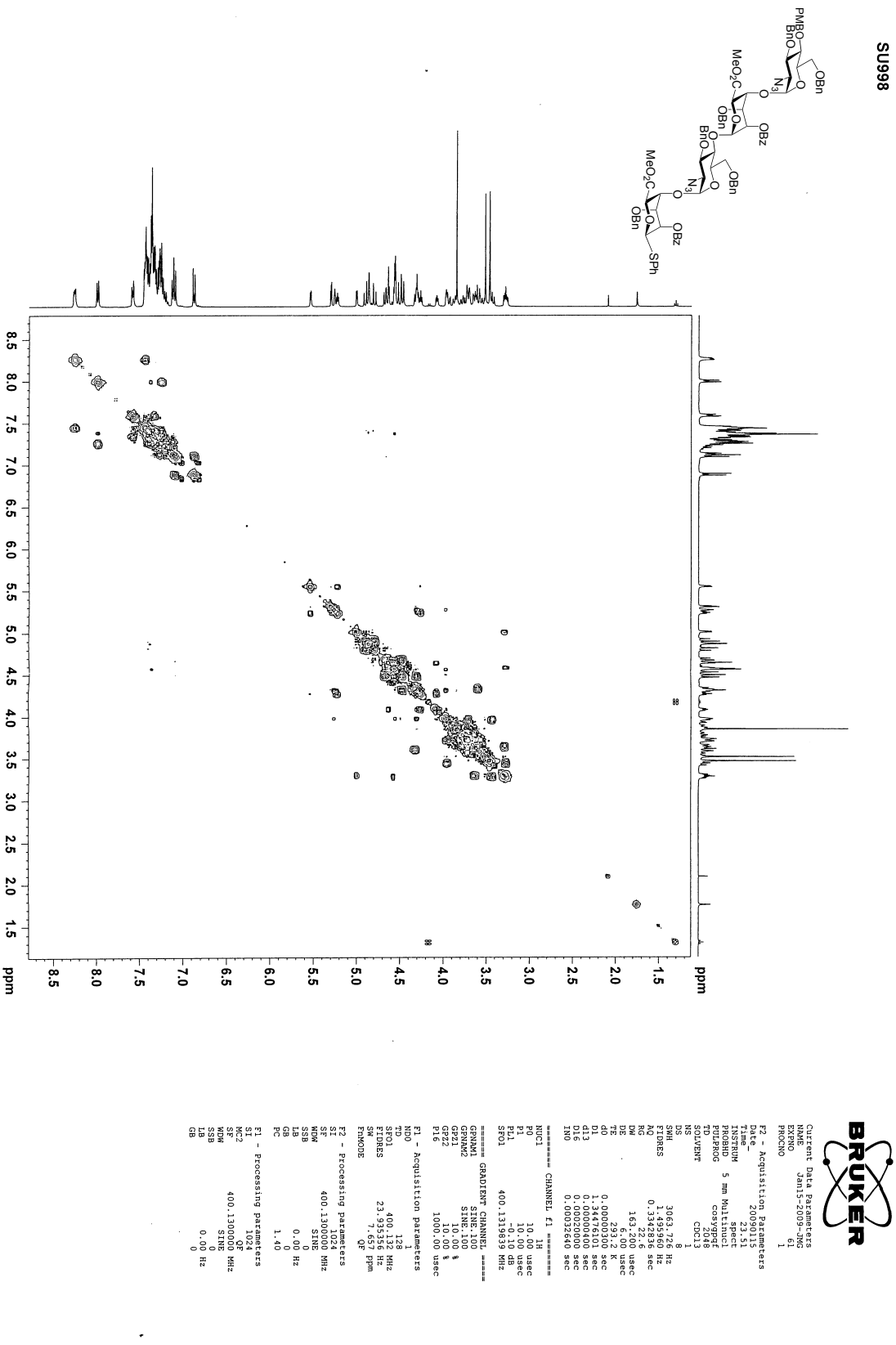
Supplementary Figure S11. HMQC NMR spectrum for β**-4**



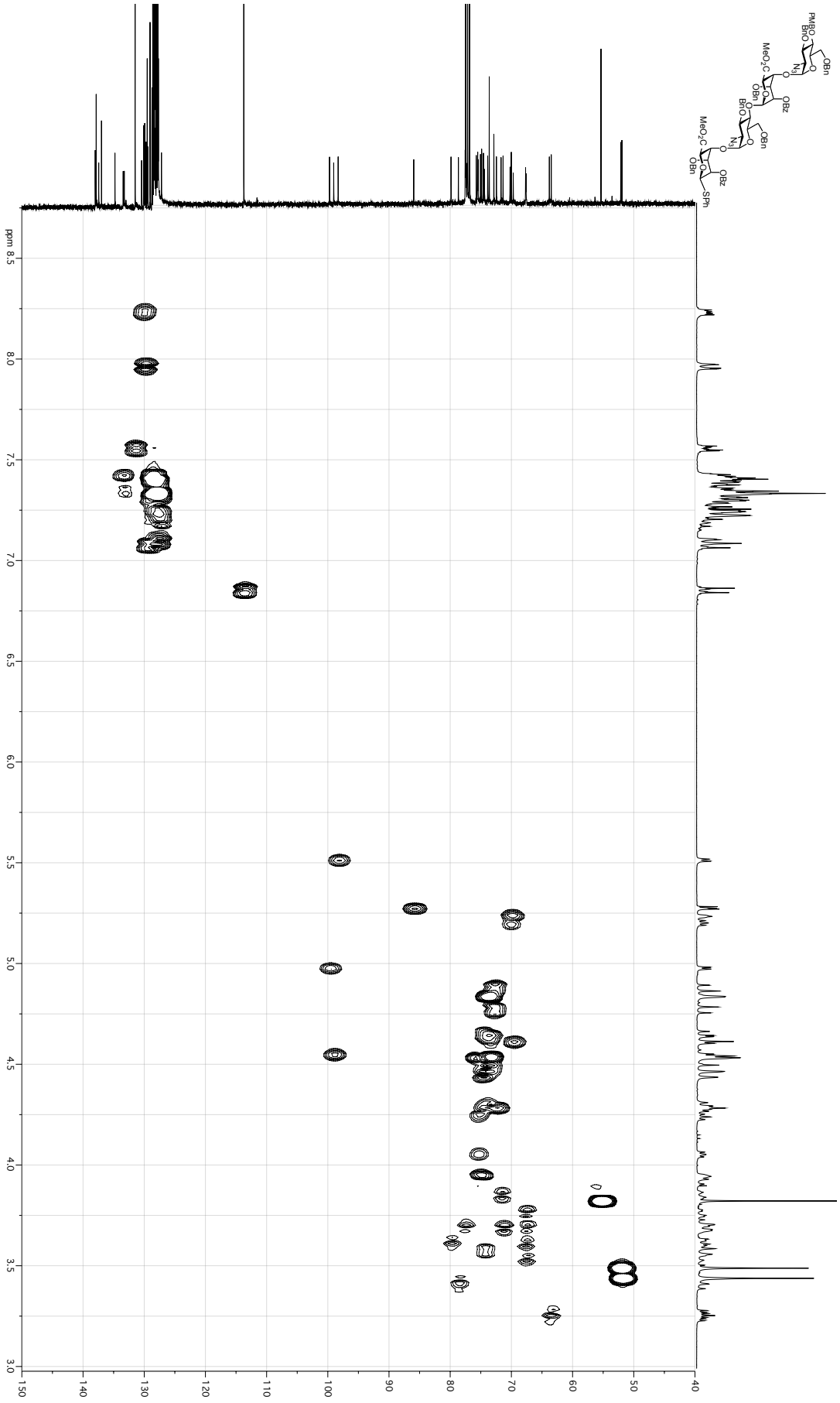
Supplementary Figure S12. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for β-**4**



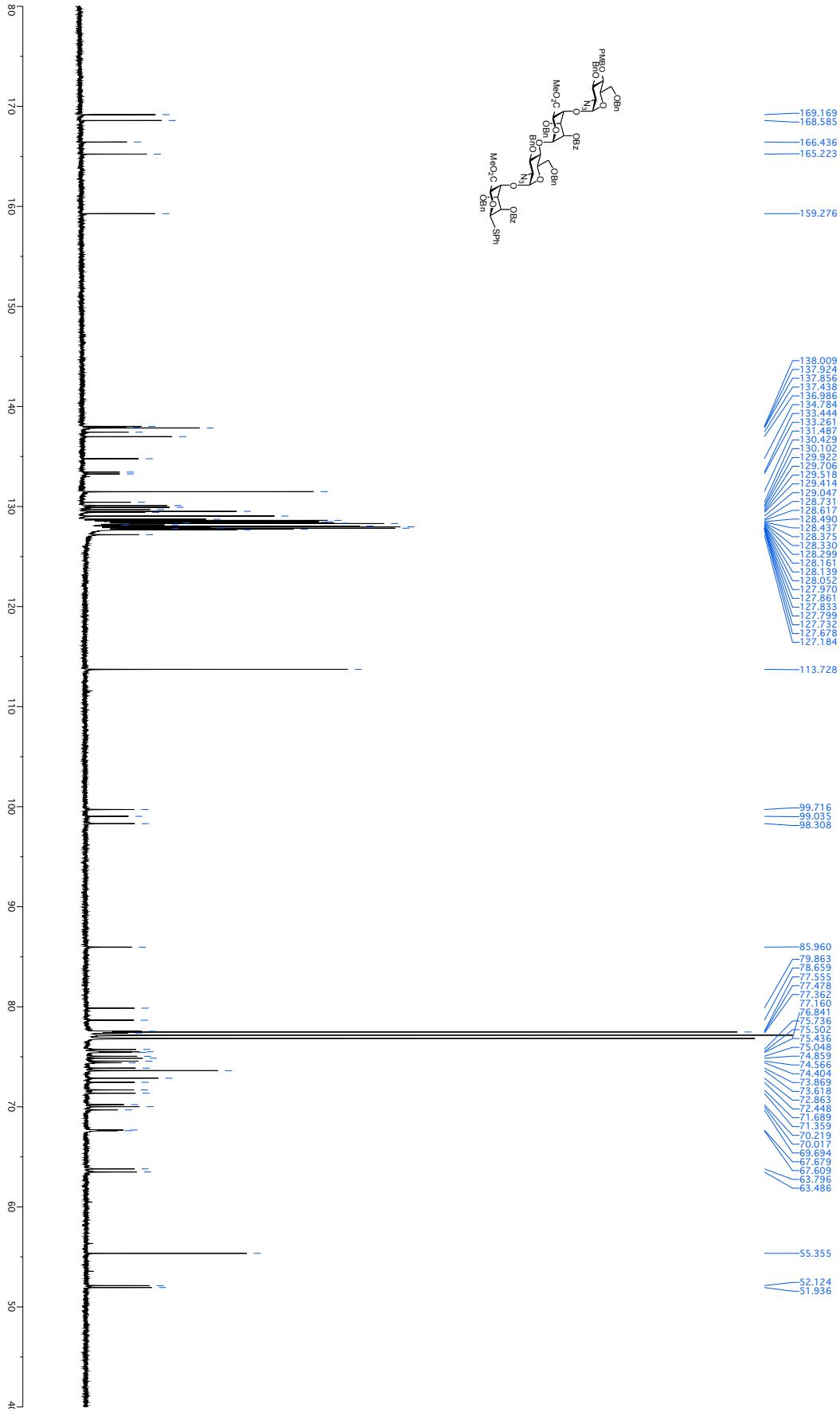
Supplementary Figure S13. ^{1}H NMR (400 MHz; $CDCl_3$) spectrum for β-**6**



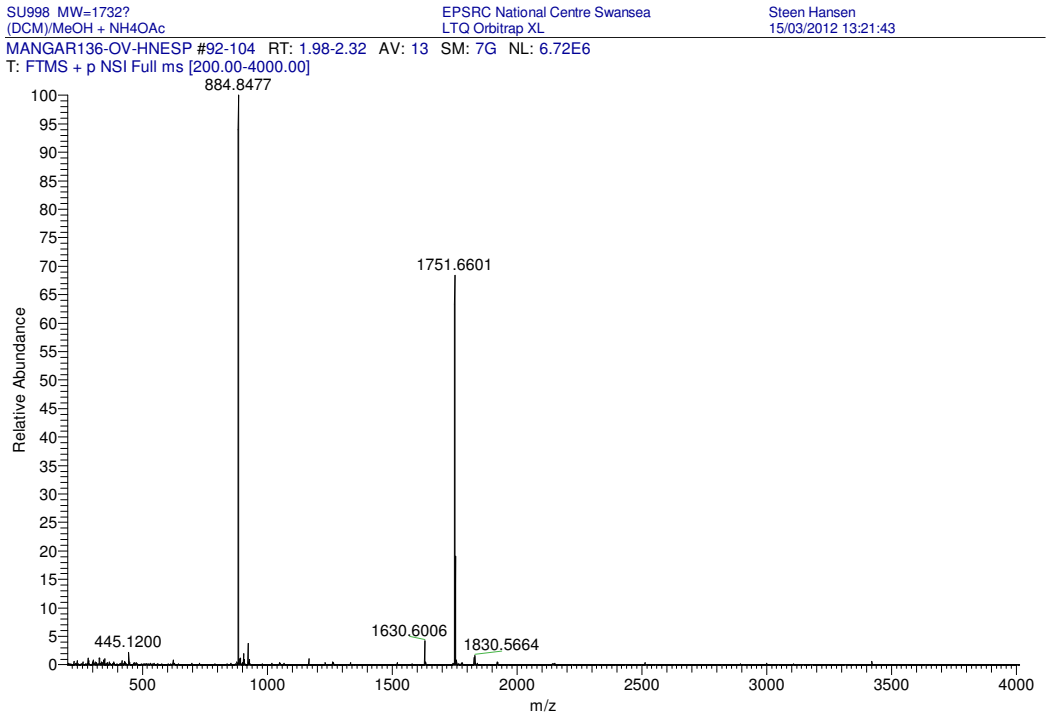
Supplementary Figure S14. COSY NMR spectrum for β-**6**

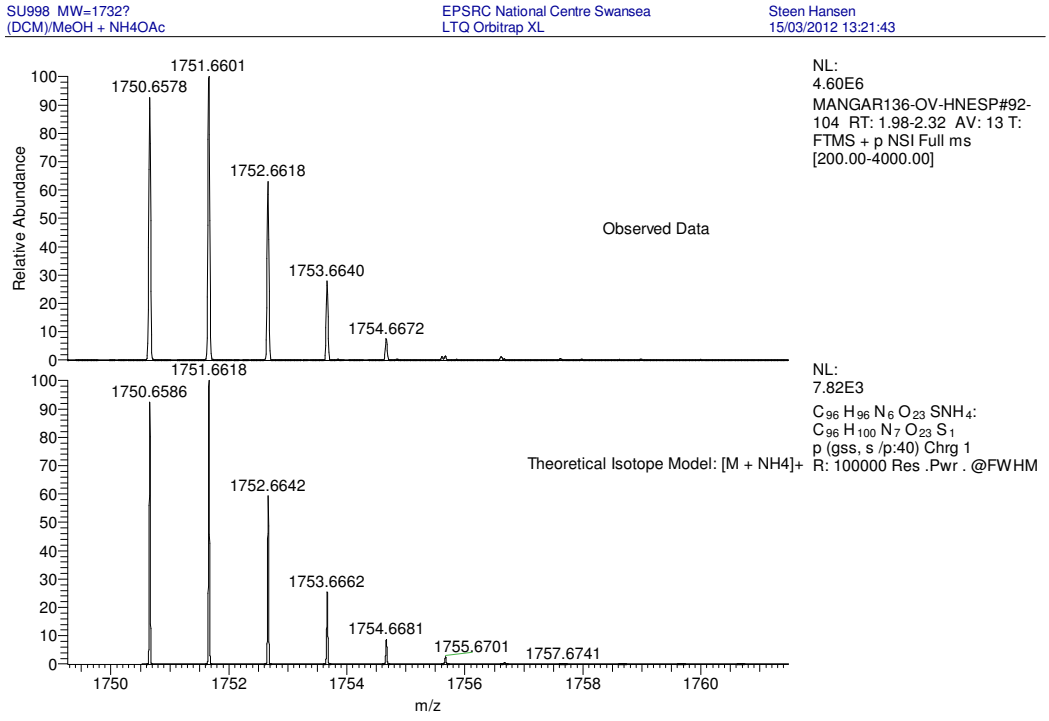


Supplementary Figure S15. HMQC NMR spectrum for β-**6**

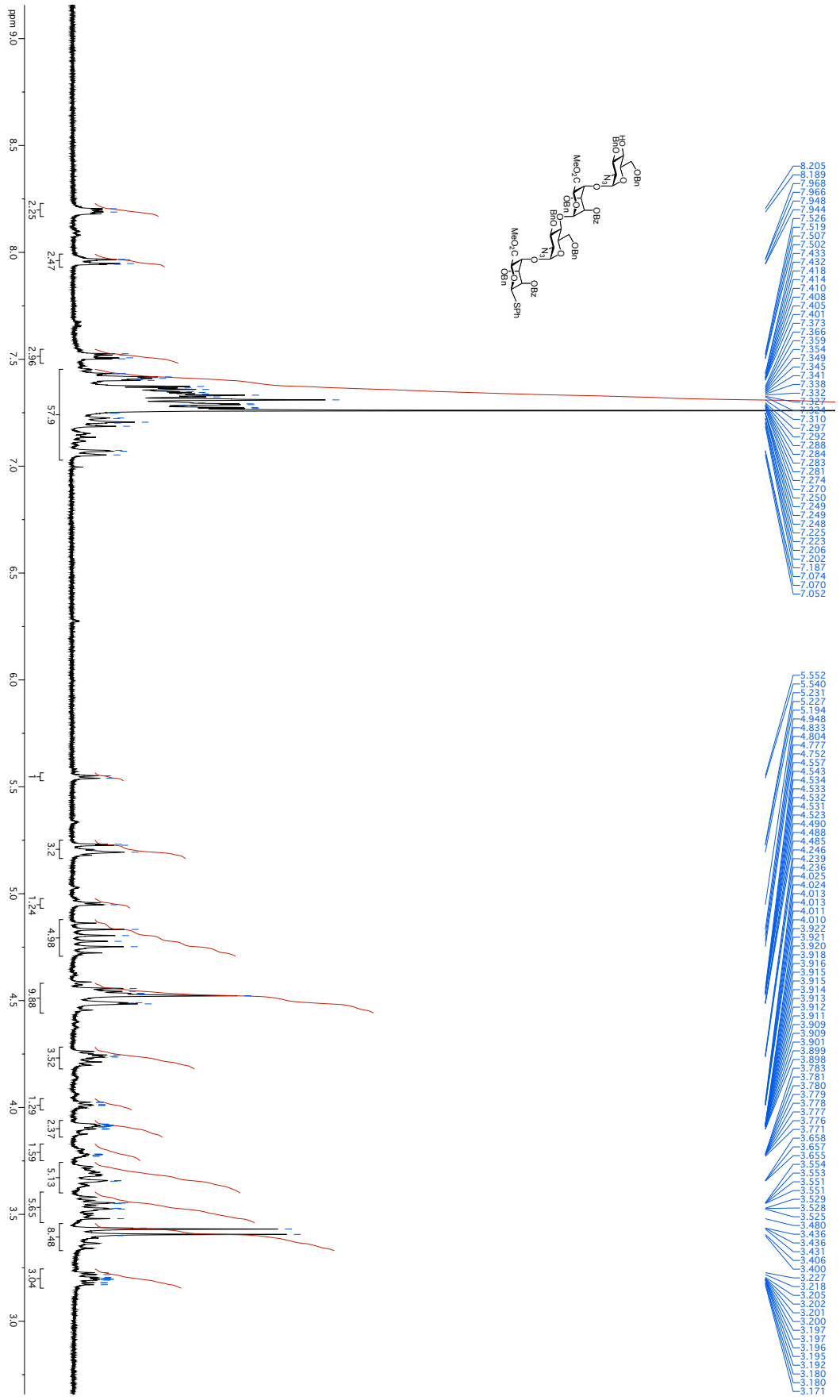


[1] **Supplementary Figure S16.** [3]C NMR (100 MHz; $CDCl_3$) spectrum for β-**6**

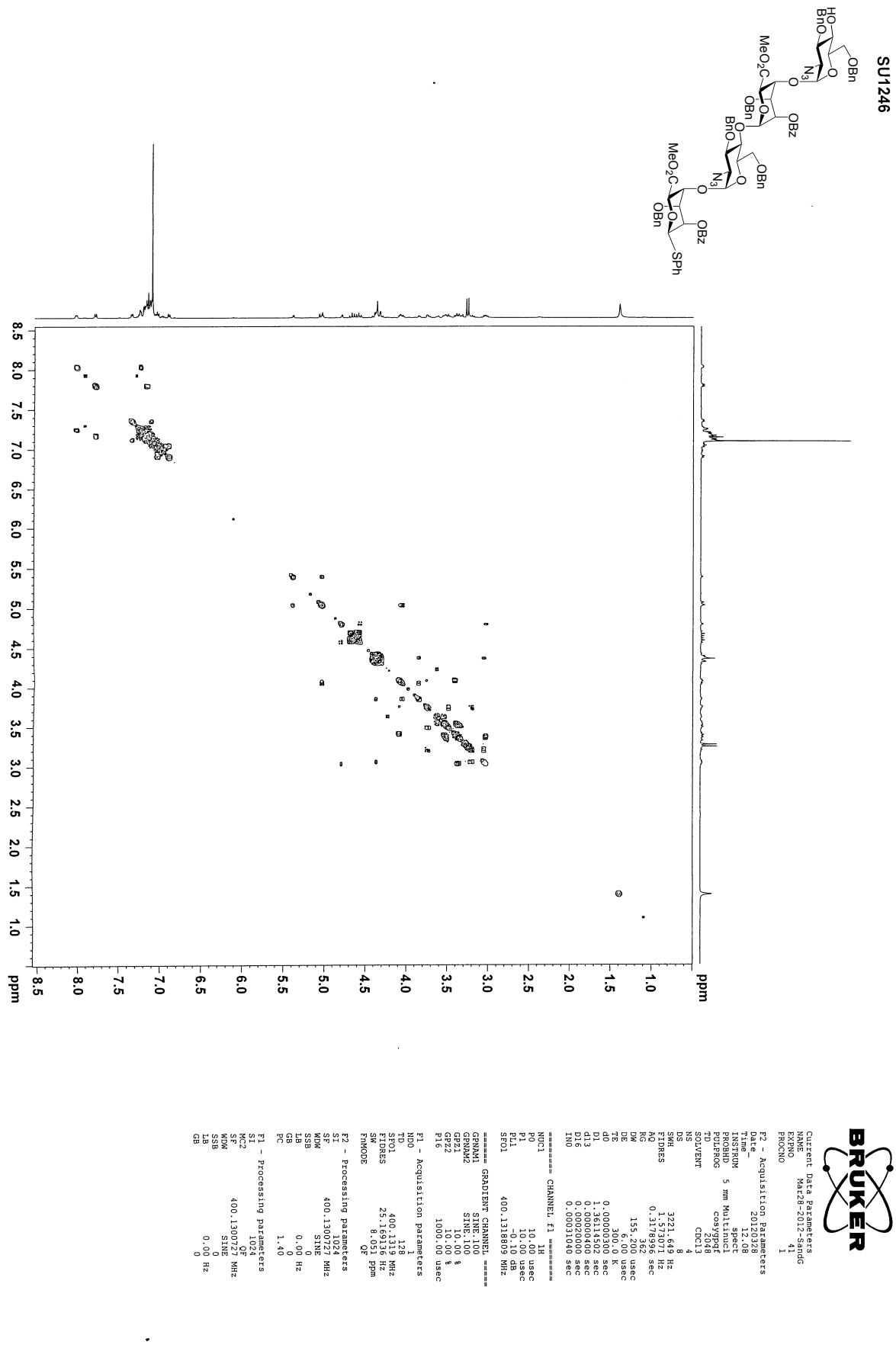




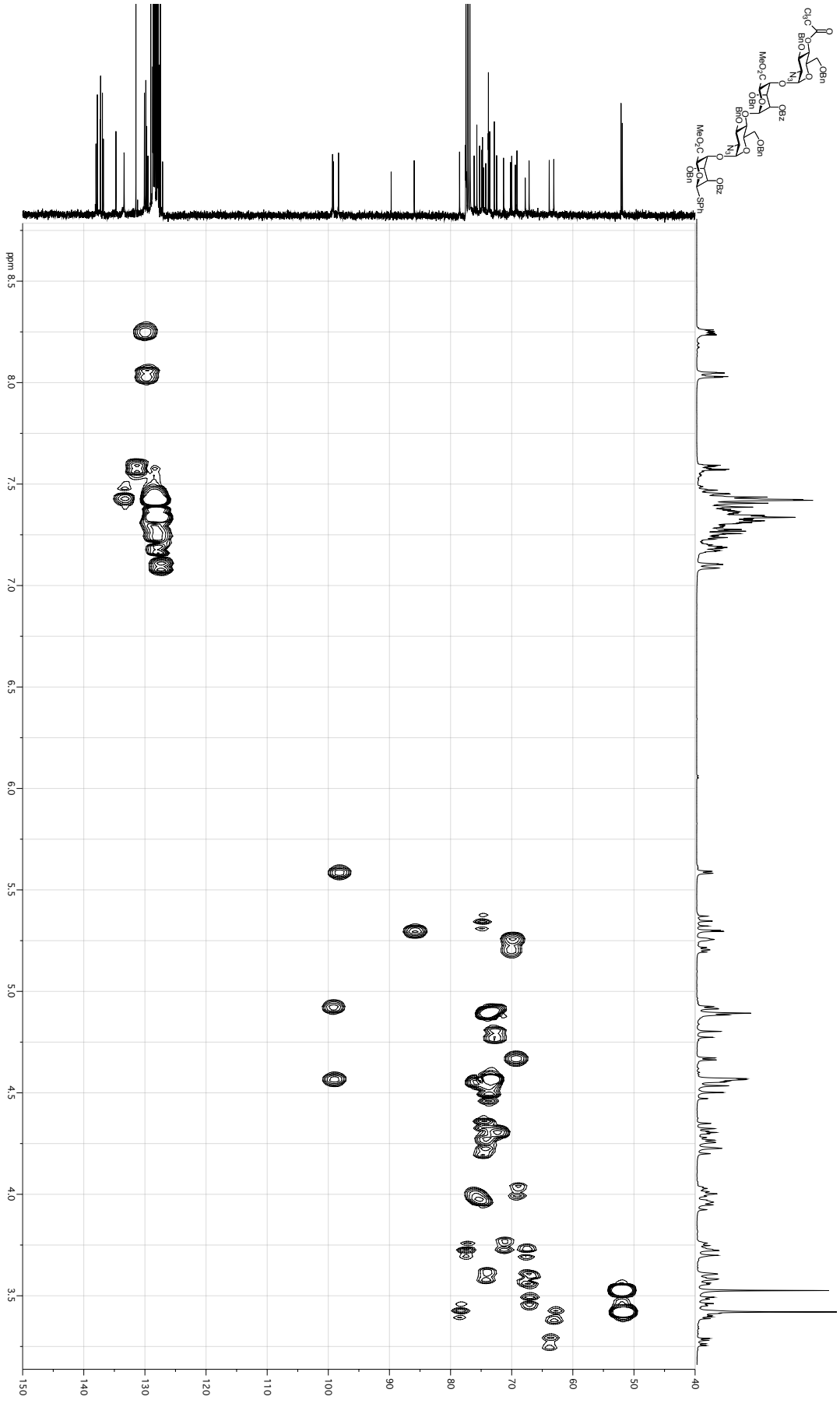
Supplementary Figure S17. HFT MS spectrum for β-**6**



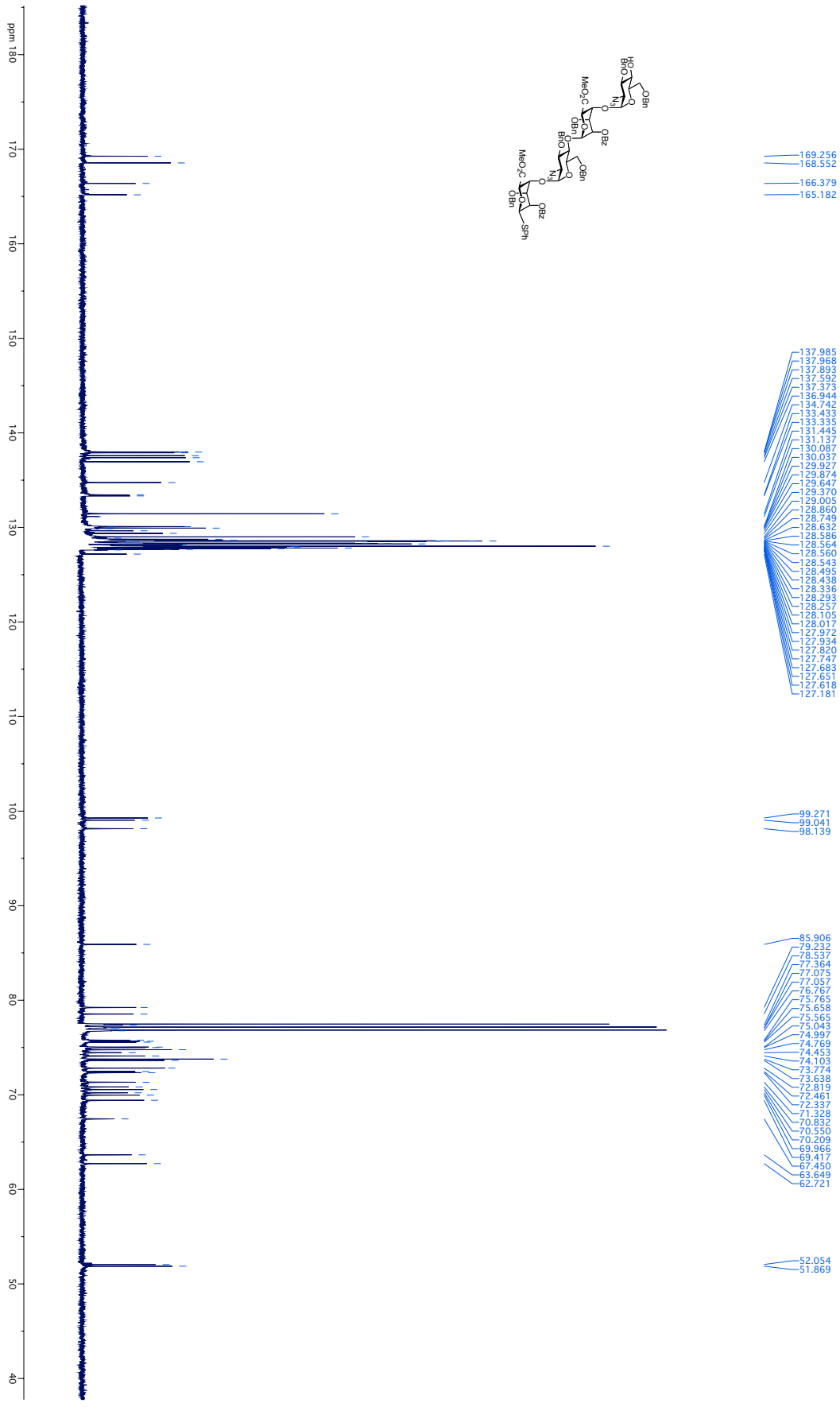
Supplementary Figure S18. ^{1}H (400 MHz, $CDCl_3$) NMR spectrum for β-**7**



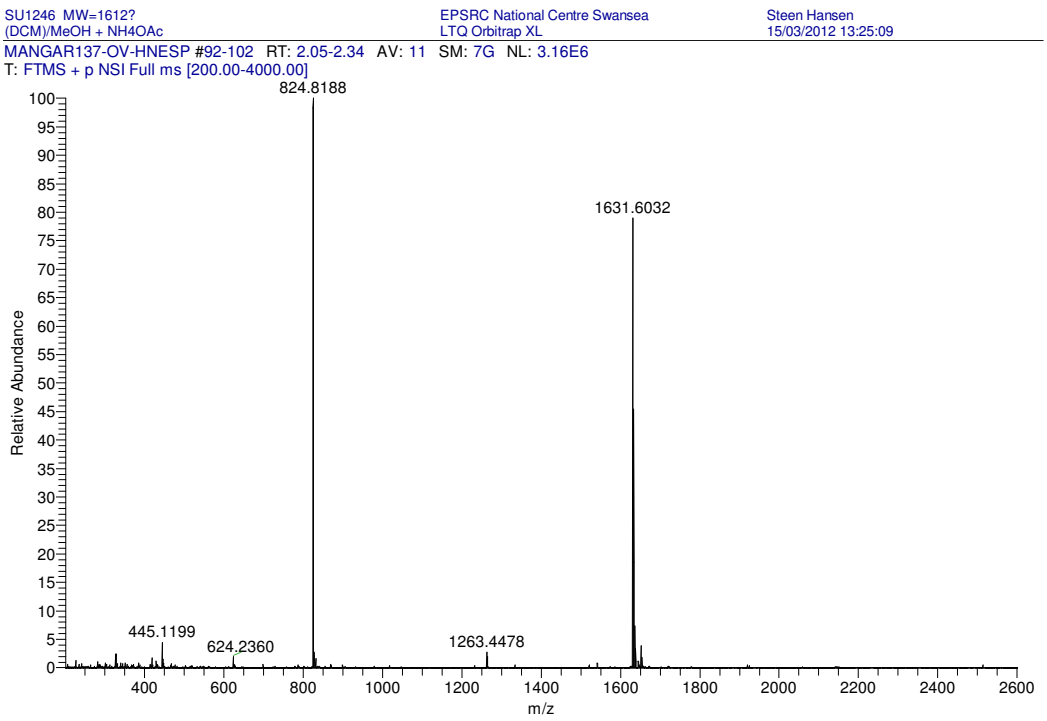
Supplementary Figure S19. COSY NMR spectrum for β-**7**

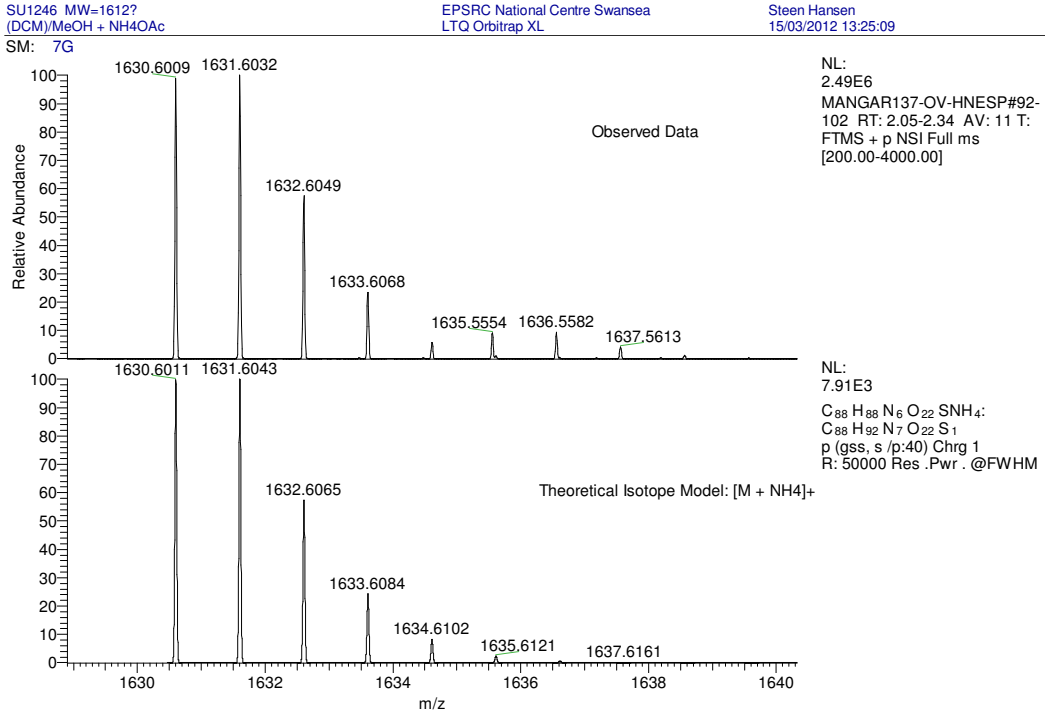


Supplementary Figure S20. HMQC NMR spectrum for β-**7**

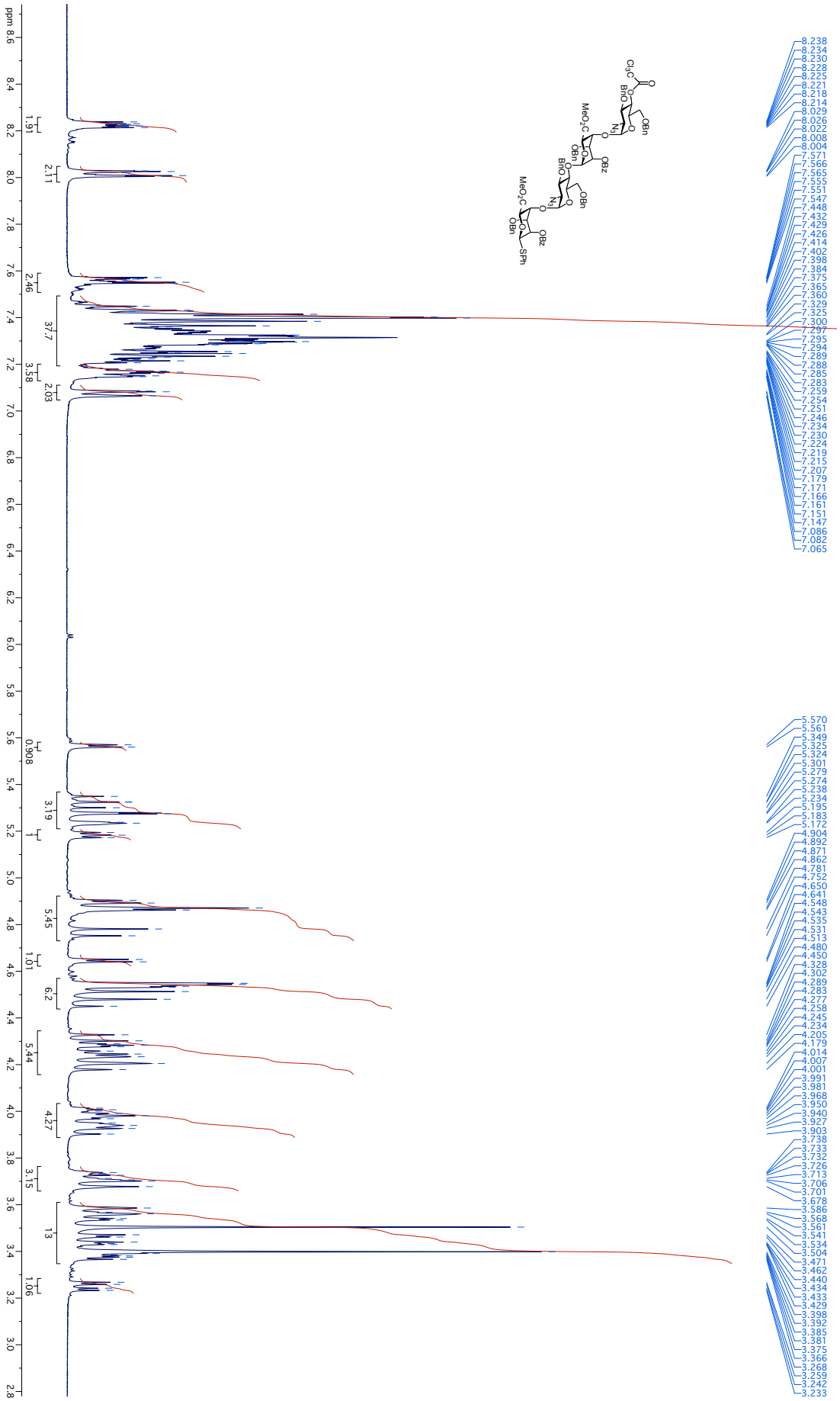


Supplementary Figure S21. $H^{13}C$ NMR (100 MHz; $CDCl_3$) spectrum for **β-7**

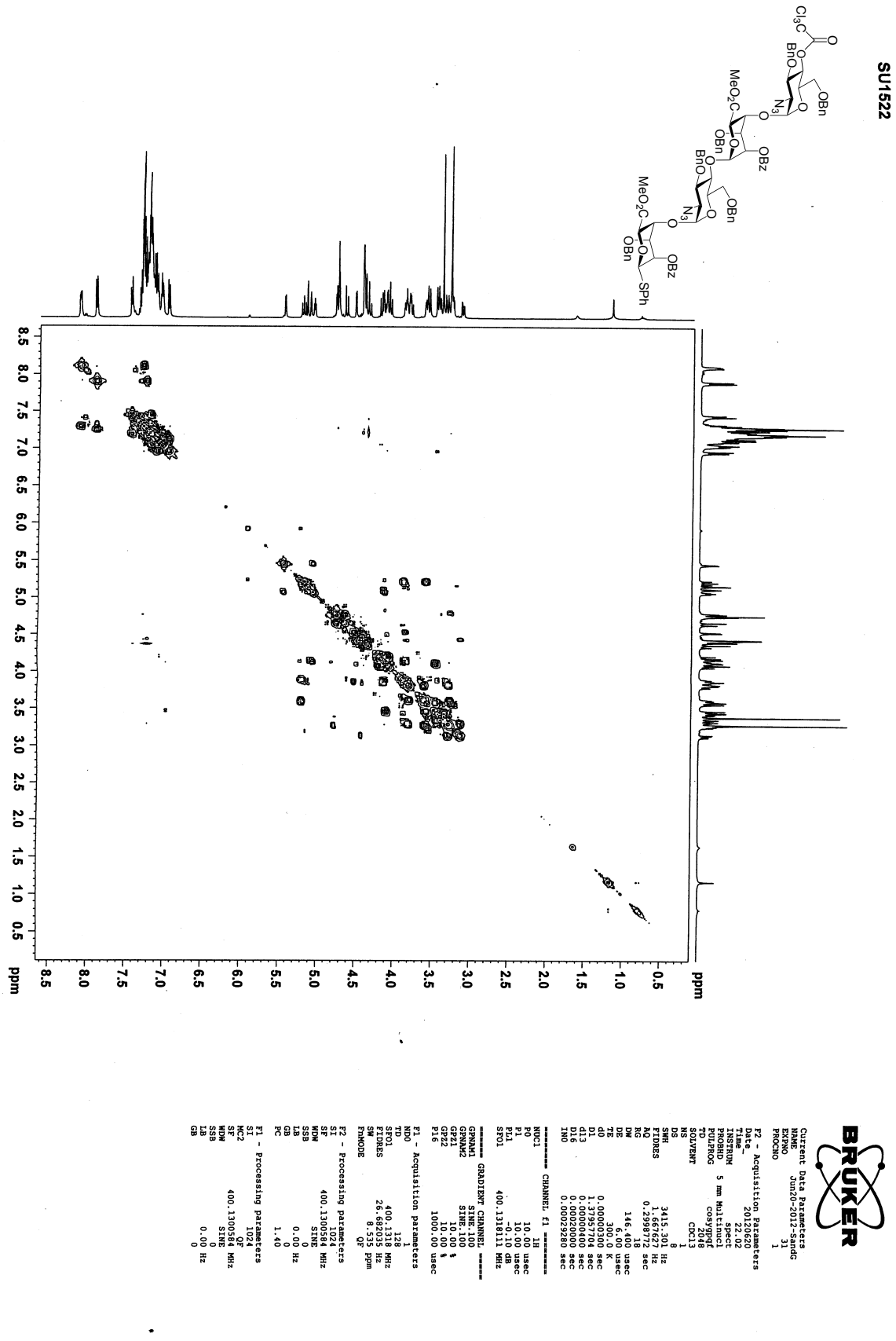




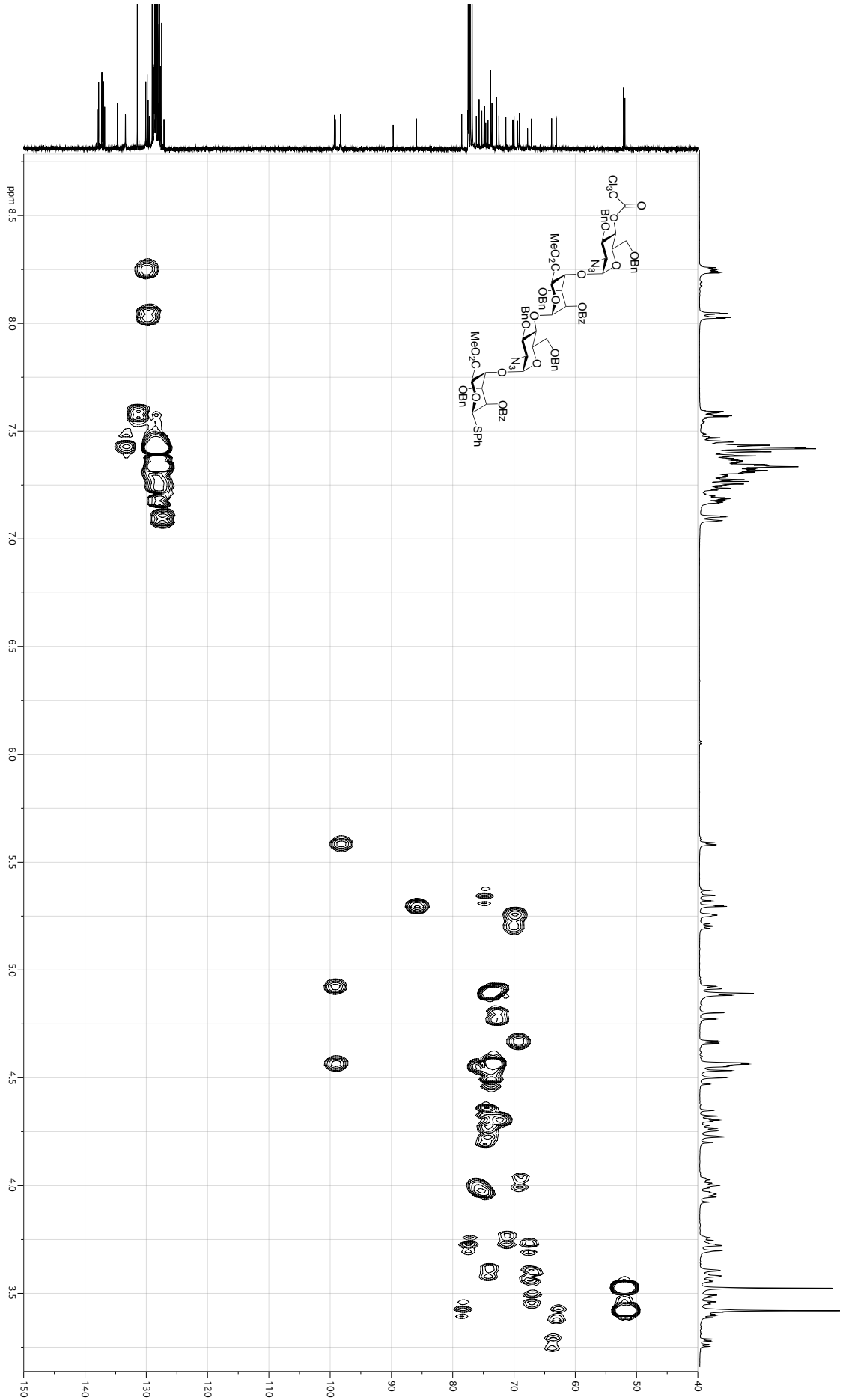
Supplementary Figure S22. HFT MS spectrum for β-**7**.



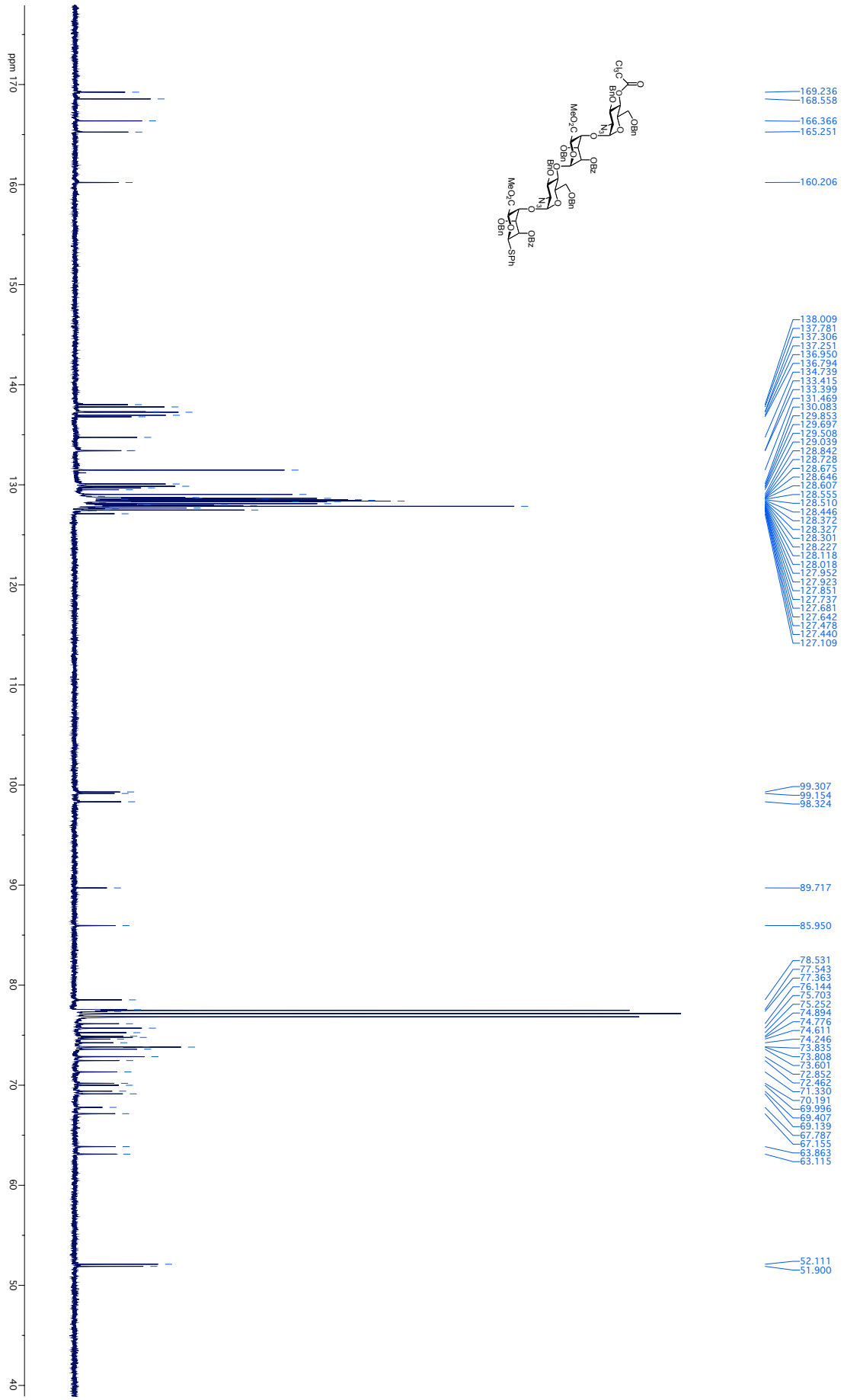
Supplementary Figure S23. H^{1}H NMR (400 MHz; $CDCl_3$) spectrum for β-**8**



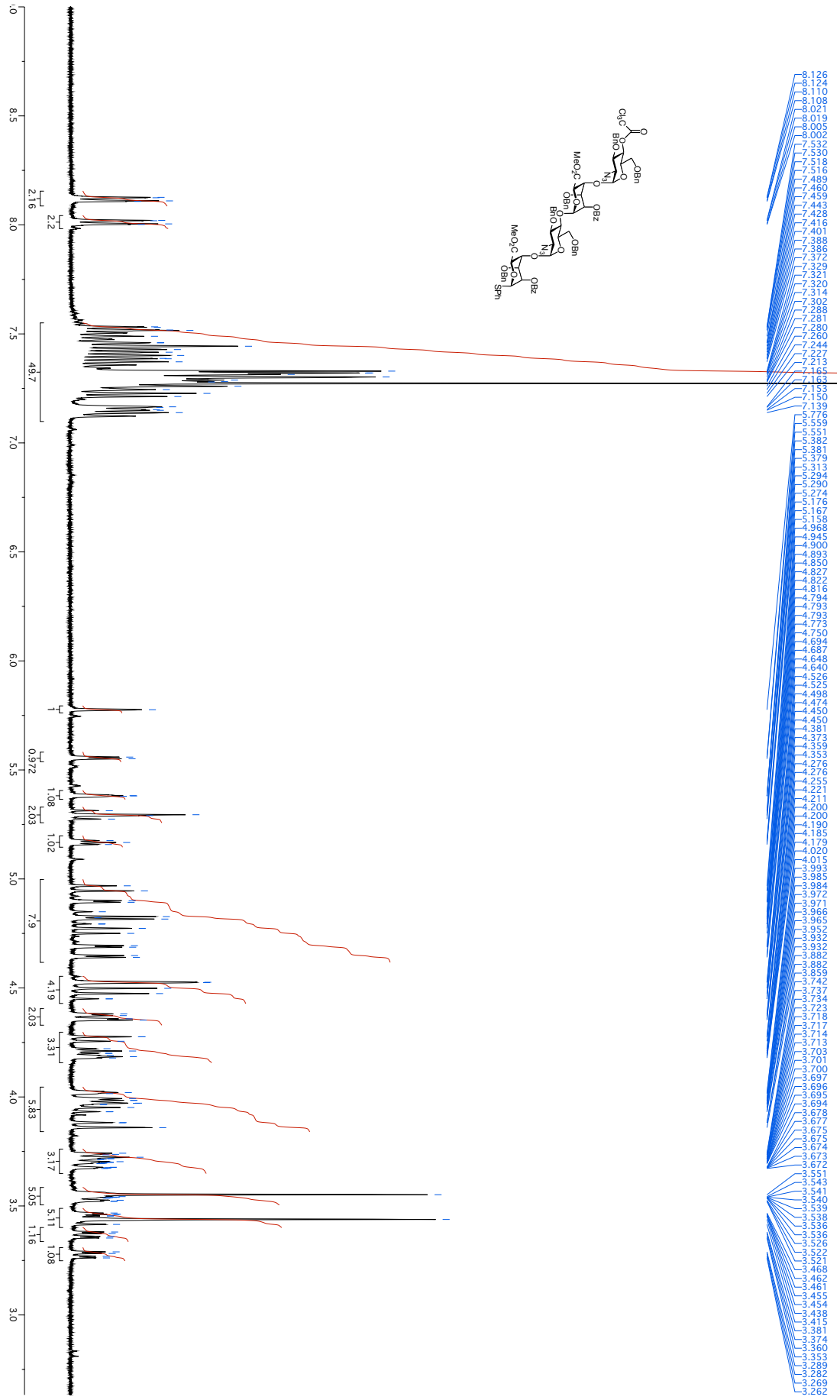
Supplementary Figure S24. COSY NMR spectrum for β-**8**



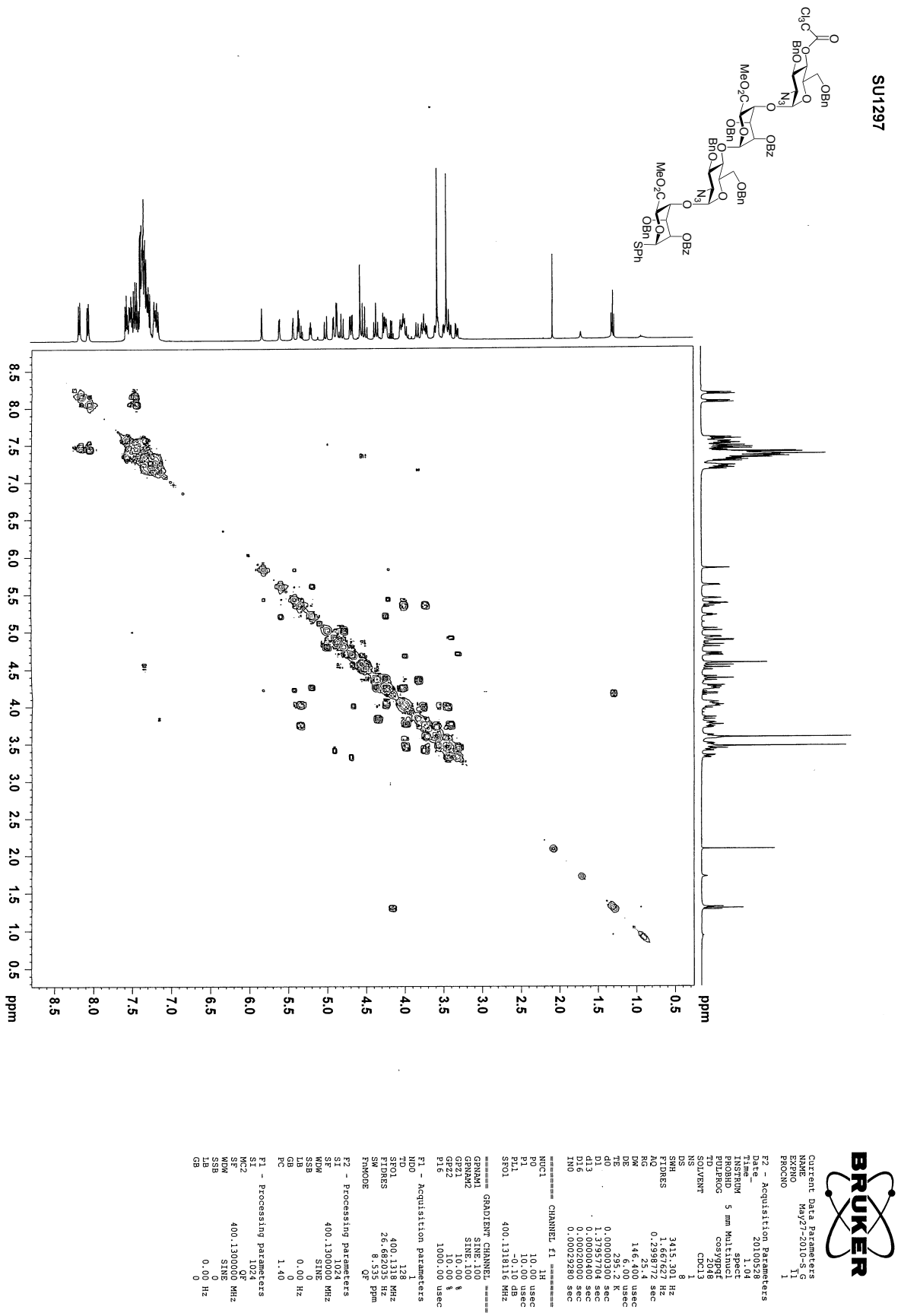
Supplementary Figure S25. HMQC NMR spectrum for β-**8**



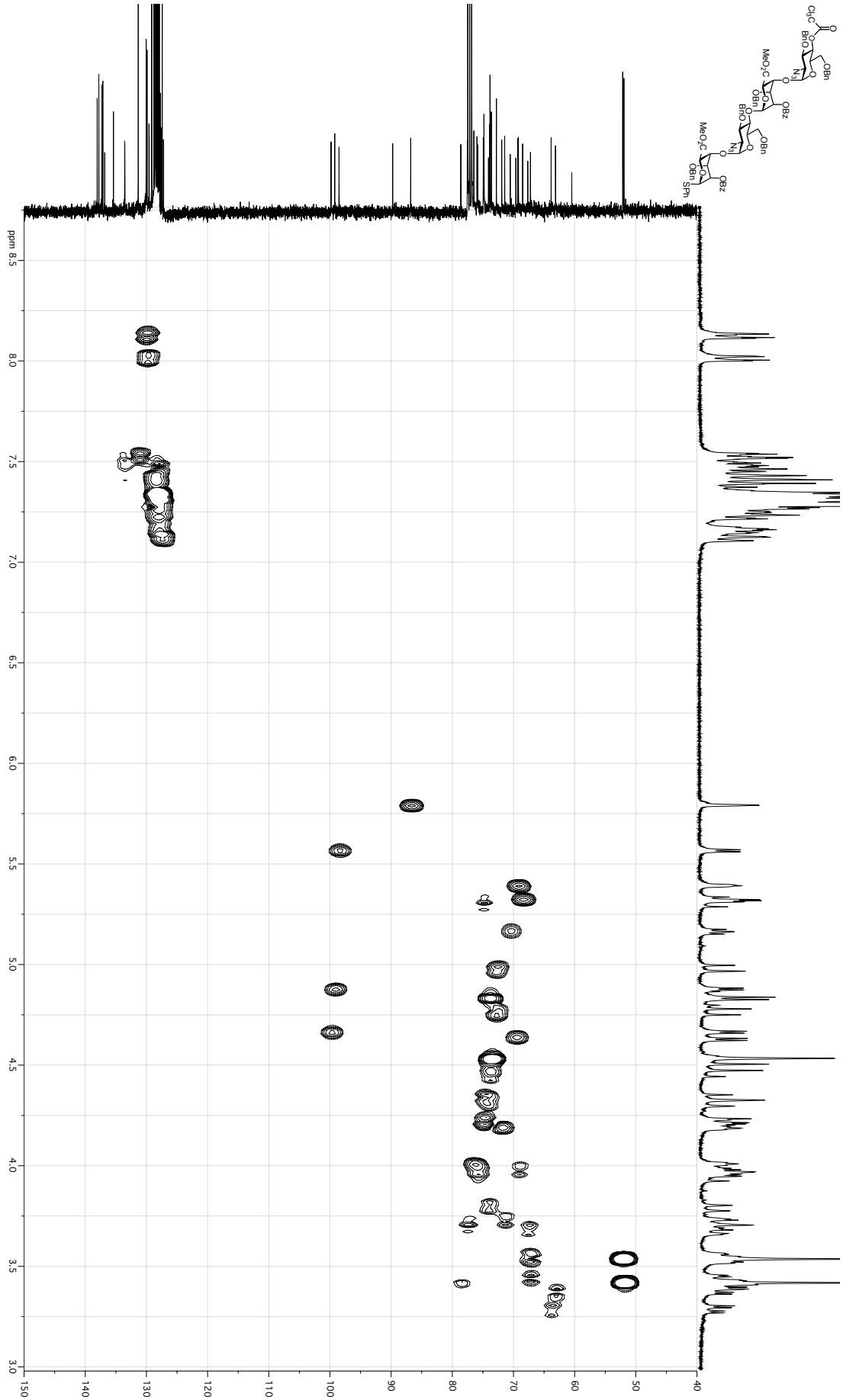
Supplementary Figure S26. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for β-**8**



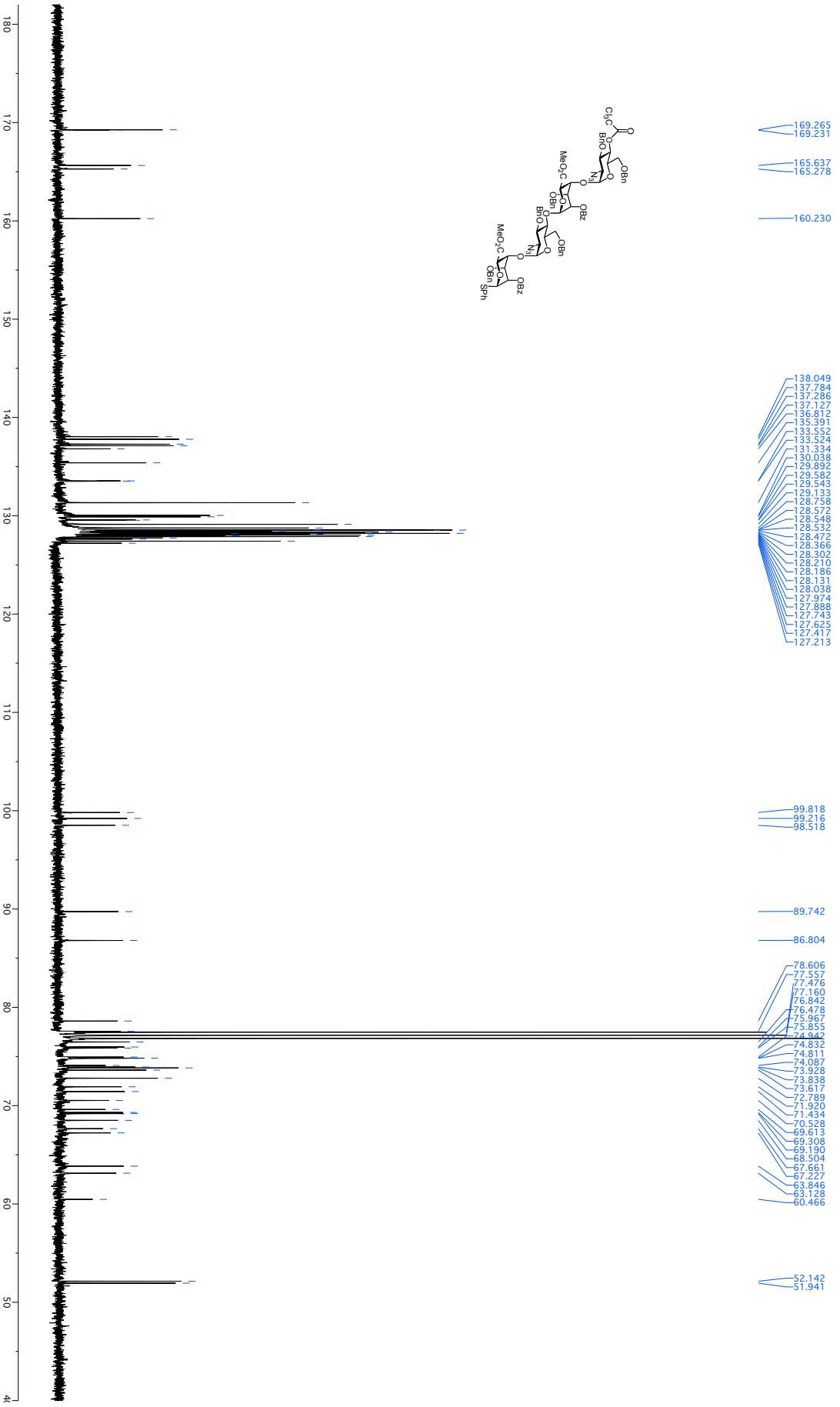
Supplementary Figure S27. ^{1}H NMR (500 MHz; $CDCl_3$) spectrum for **α-8**



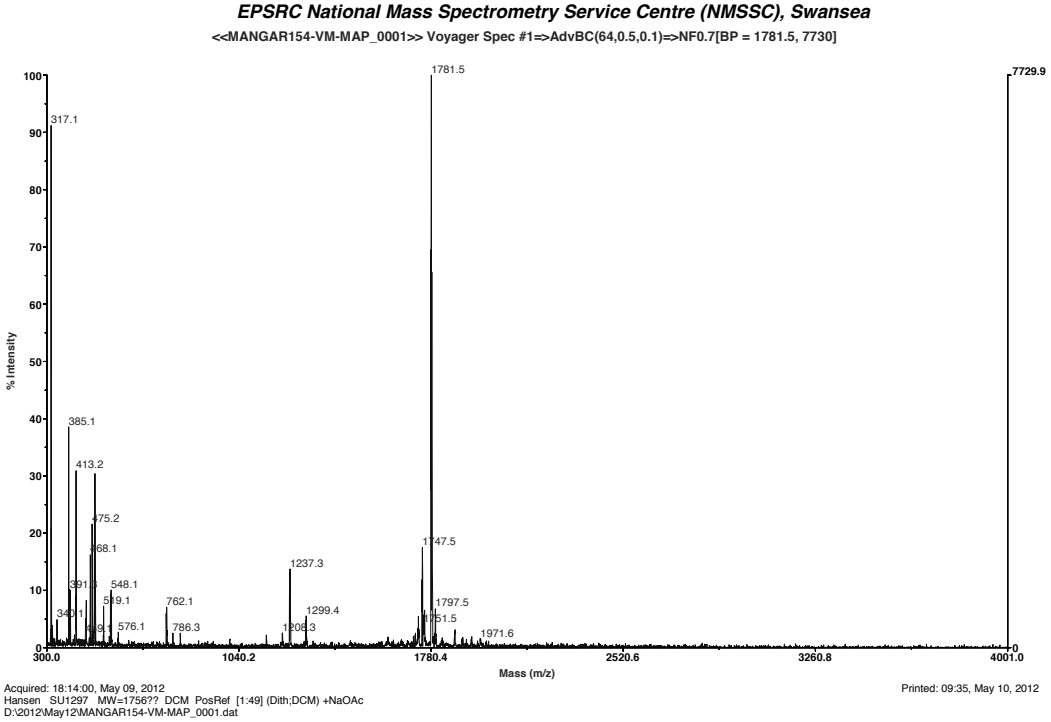
Supplementary Figure S28. COSY NMR spectrum for α-**8**

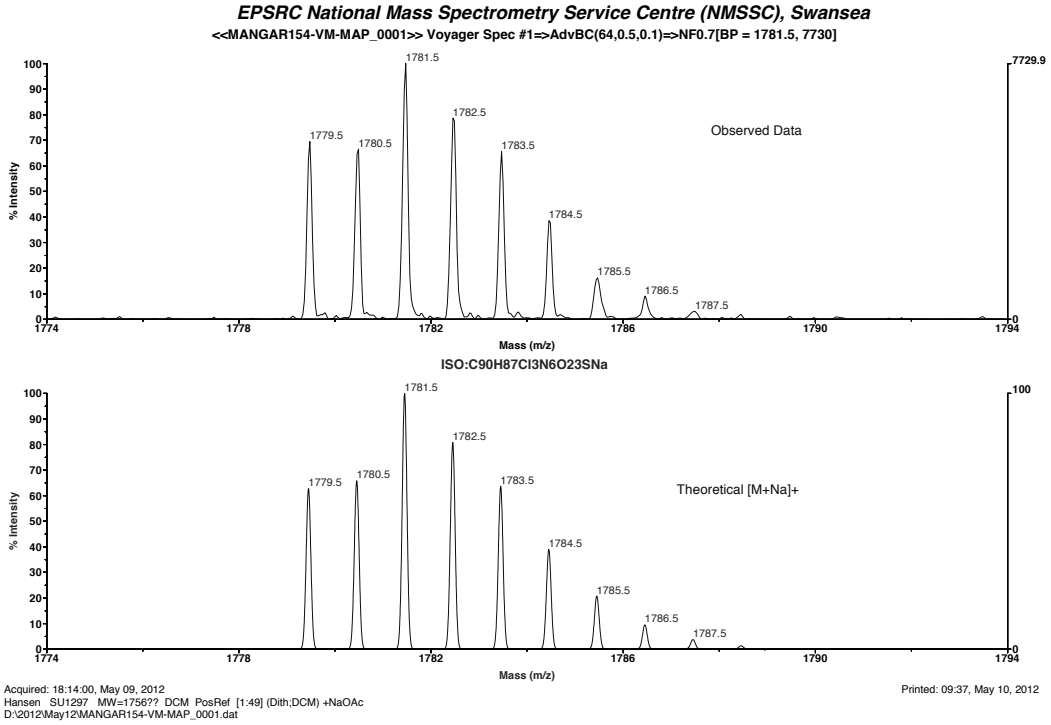


Supplementary Figure S29. HMQC NMR spectrum for α-**8**

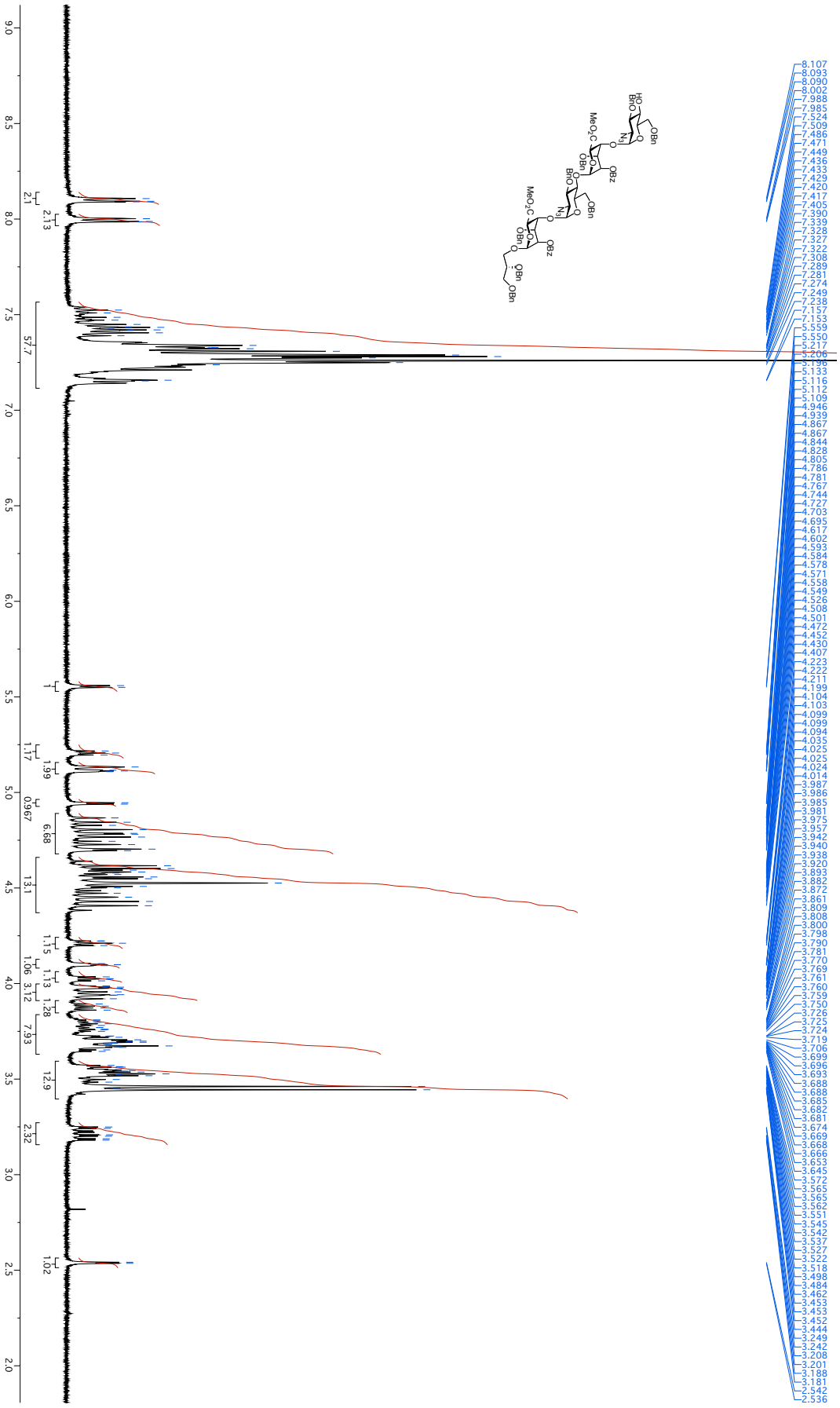


Supplementary Figure S30. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for α-**8**

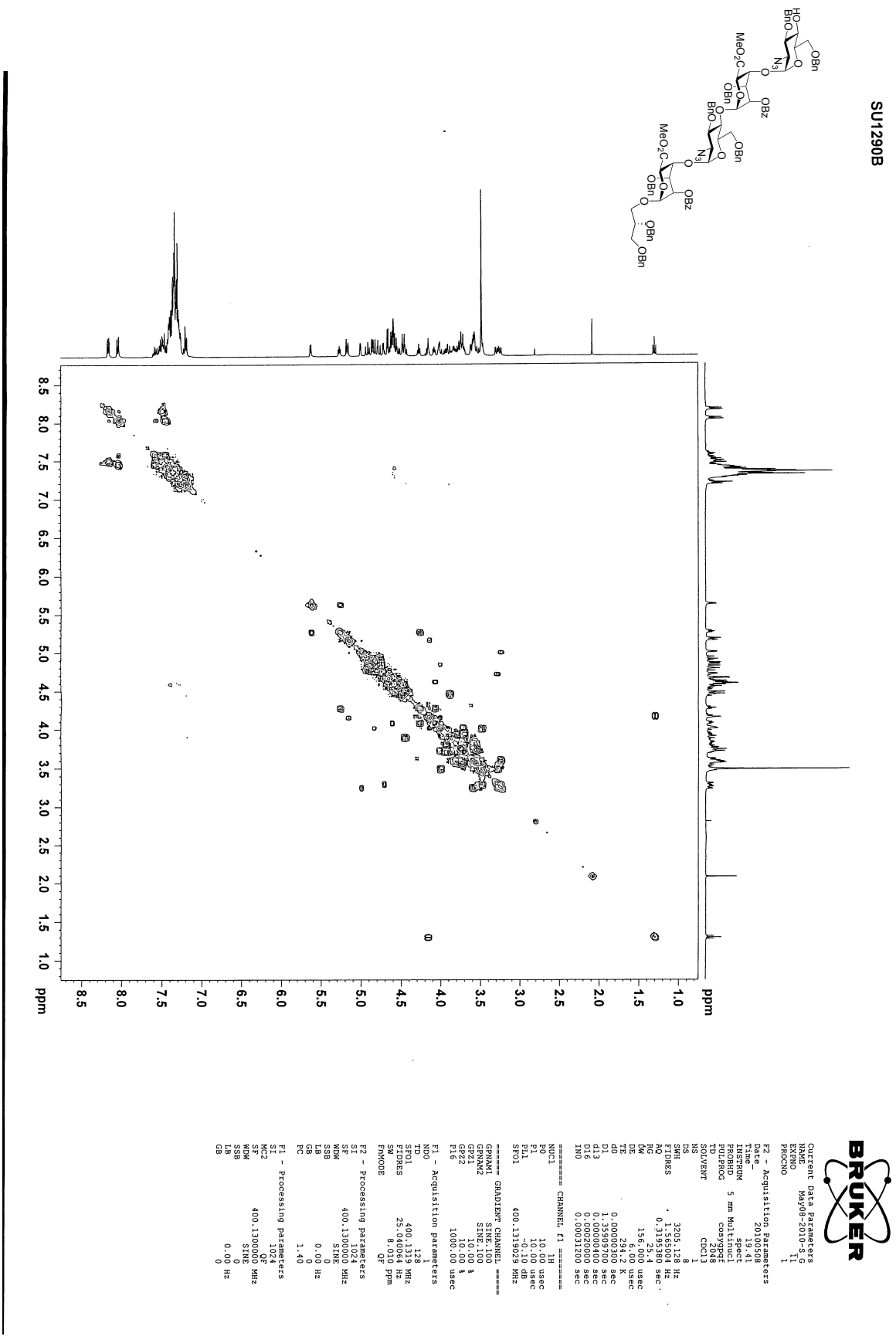




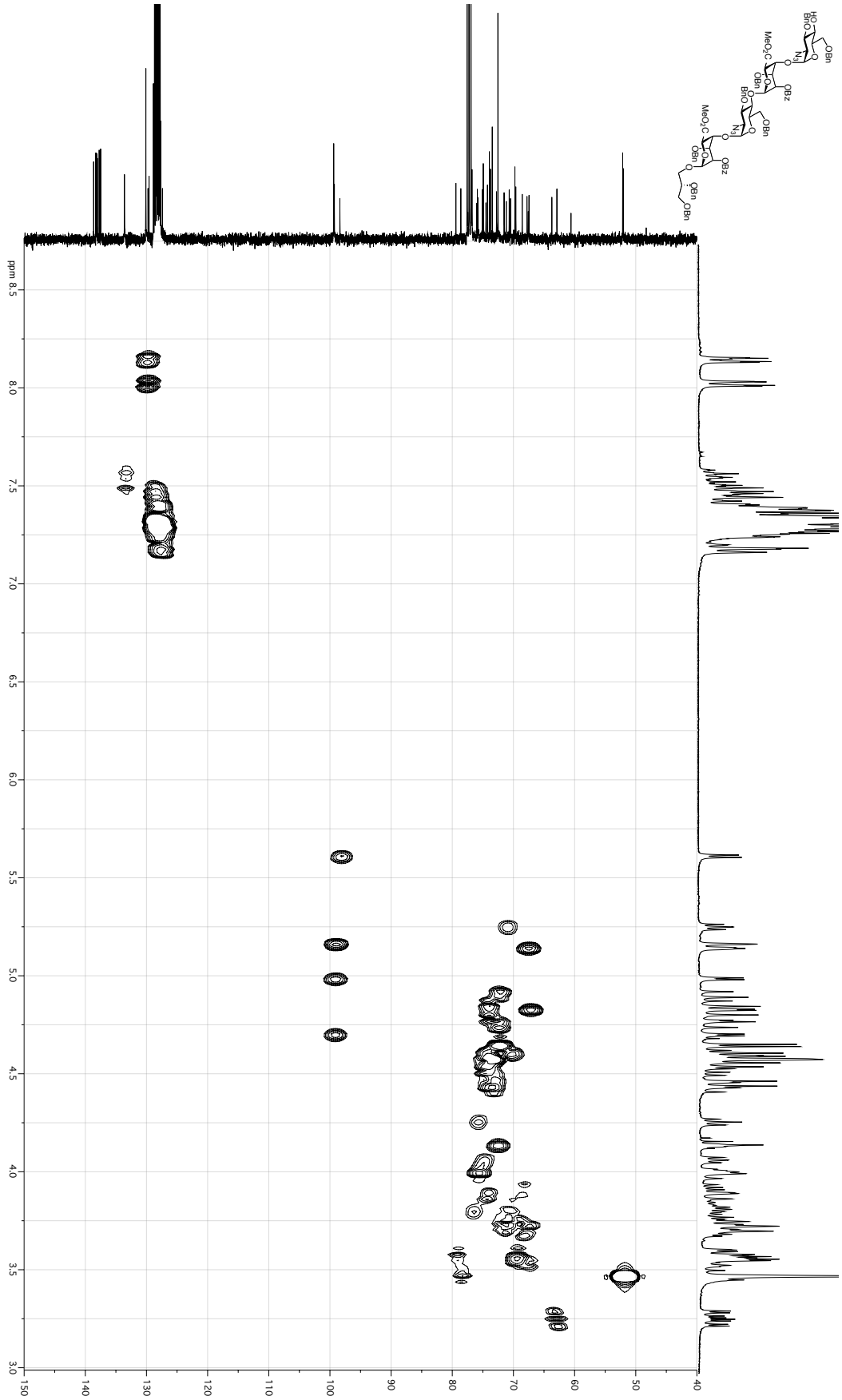
Supplementary Figure S31. MALDI-TOF spectrum for α**-8**



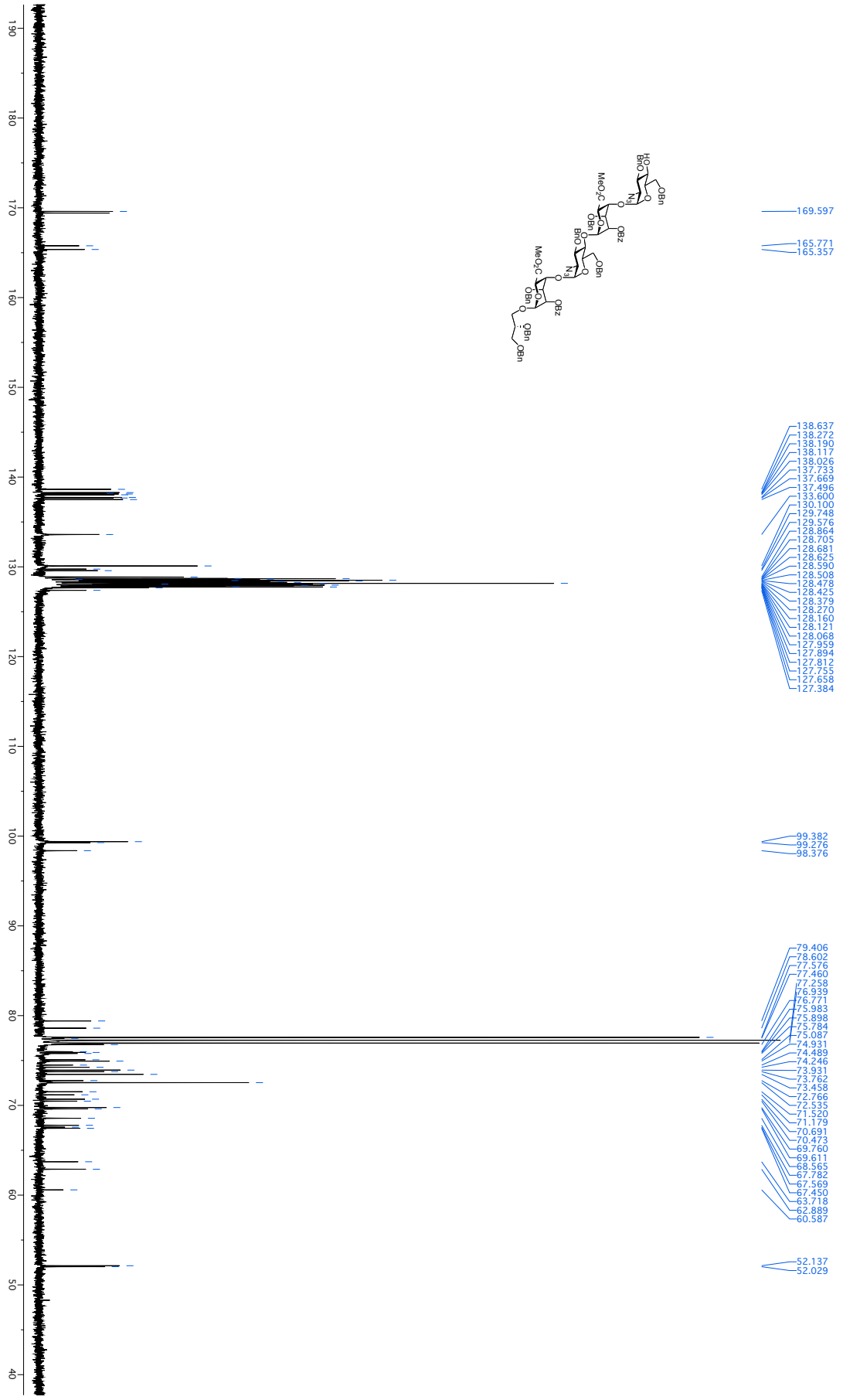
Supplementary Figure S32. ^{1}H NMR (500 MHz; $CDCl_3$) spectrum for **9**



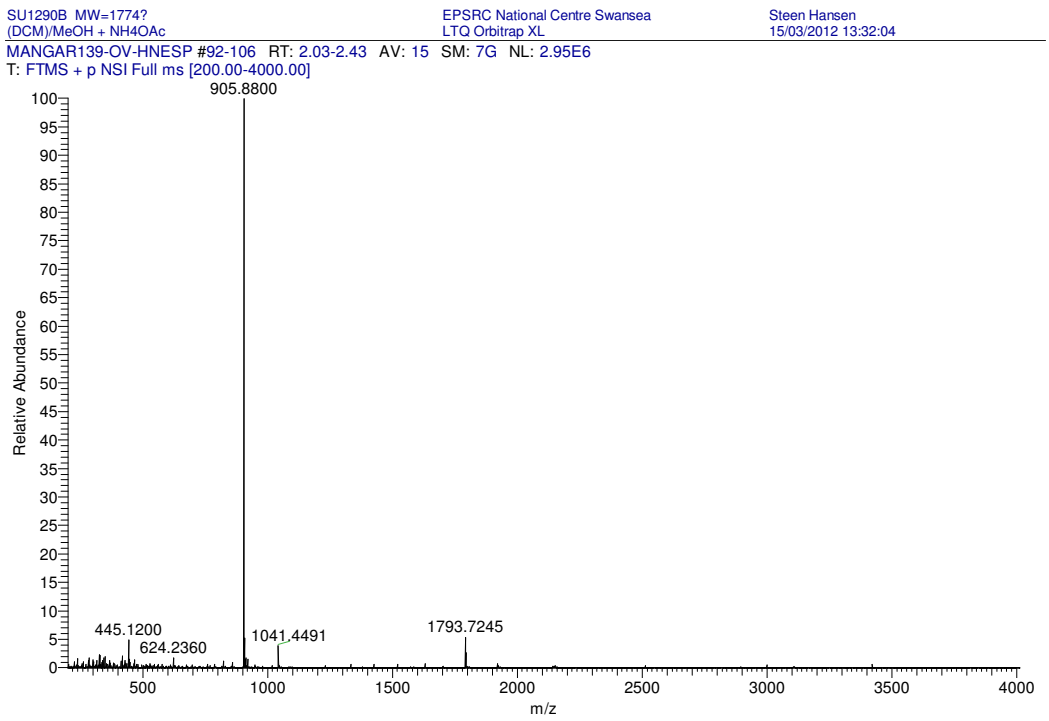
Supplementary Figure S33. COSY NMR spectrum for **9**

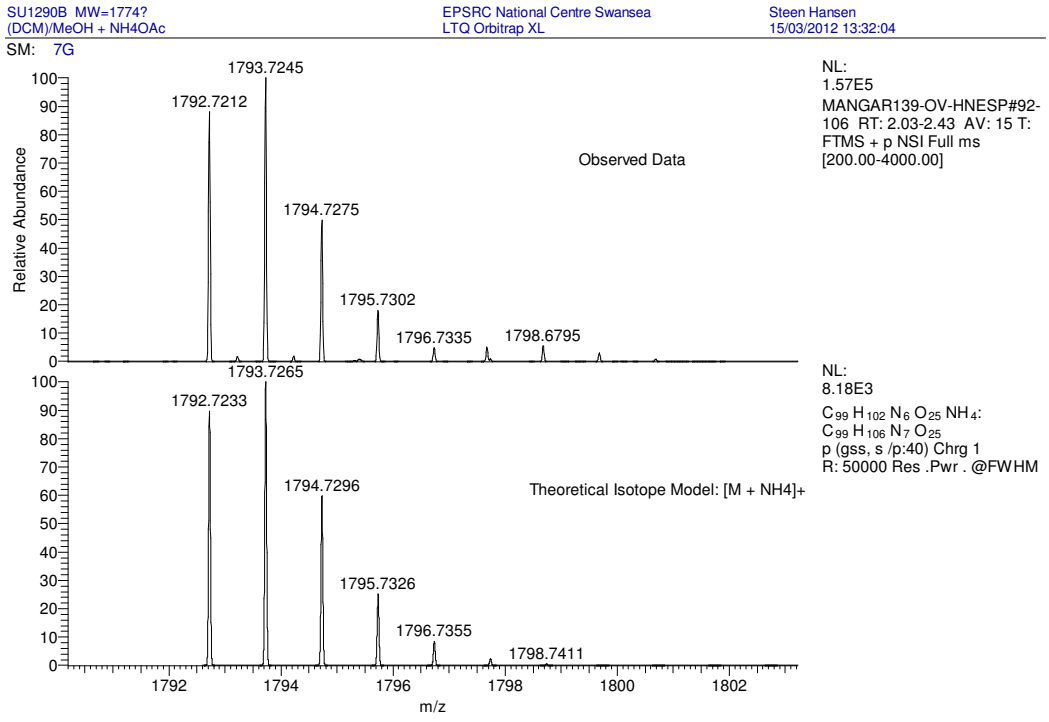


Supplementary Figure S34. HMQC NMR spectrum for **9**

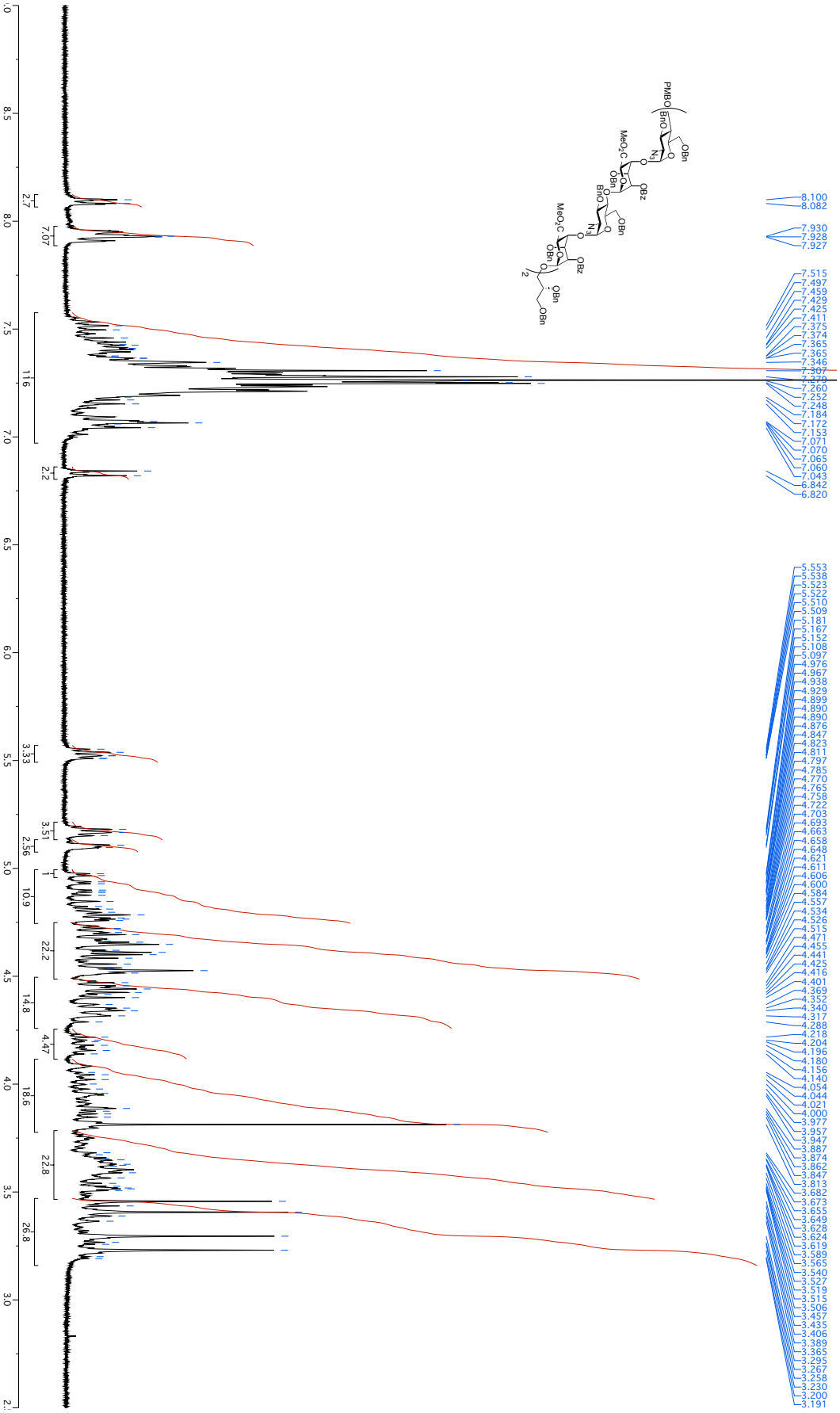


Supplementary Figure S35. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for **9**

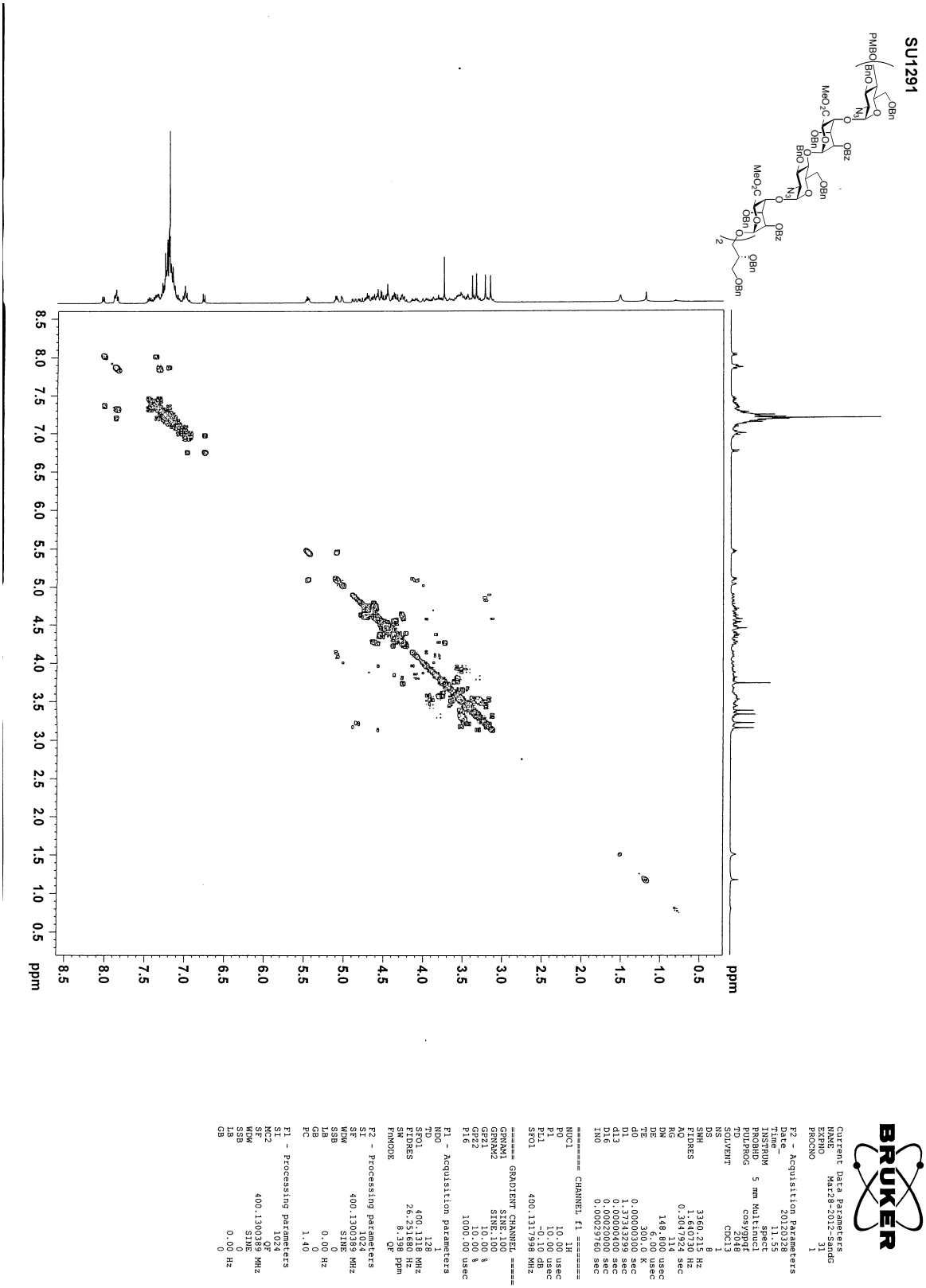




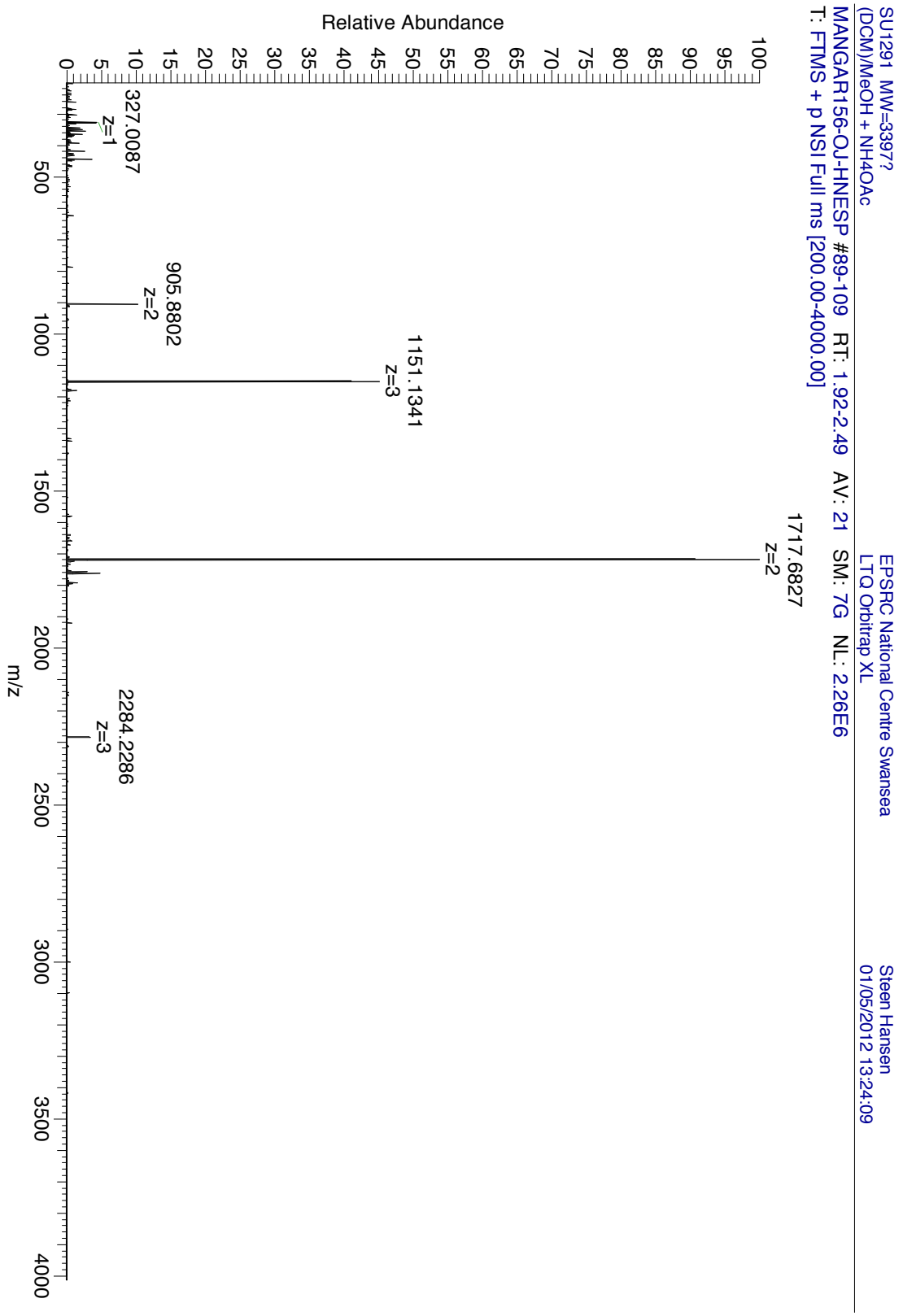
Supplementary Figure S36. FT MS spectrum for **9**



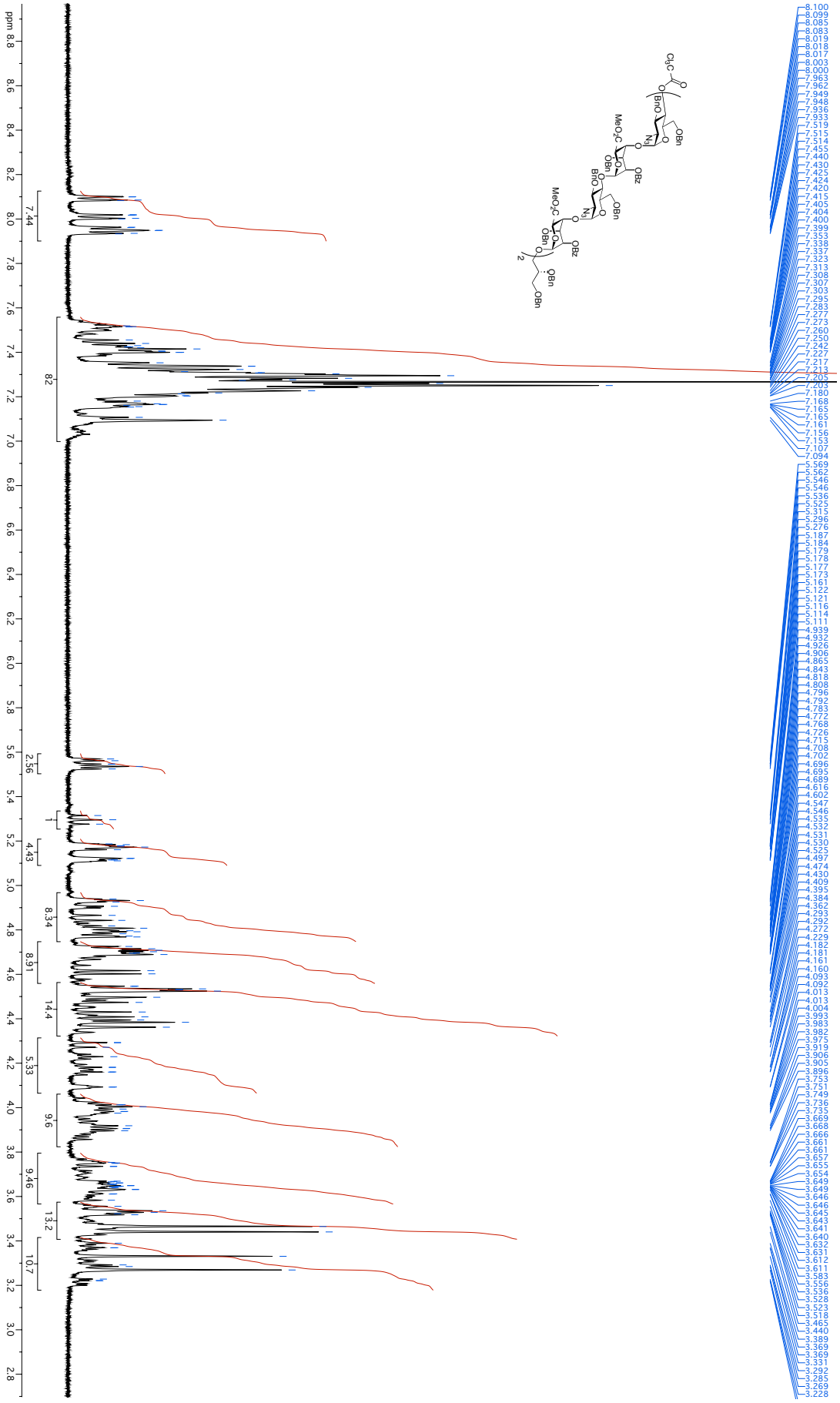
Supplementary Figure S37. ^{1}H NMR (400 MHz; $CDCl_3$) spectrum for **10**



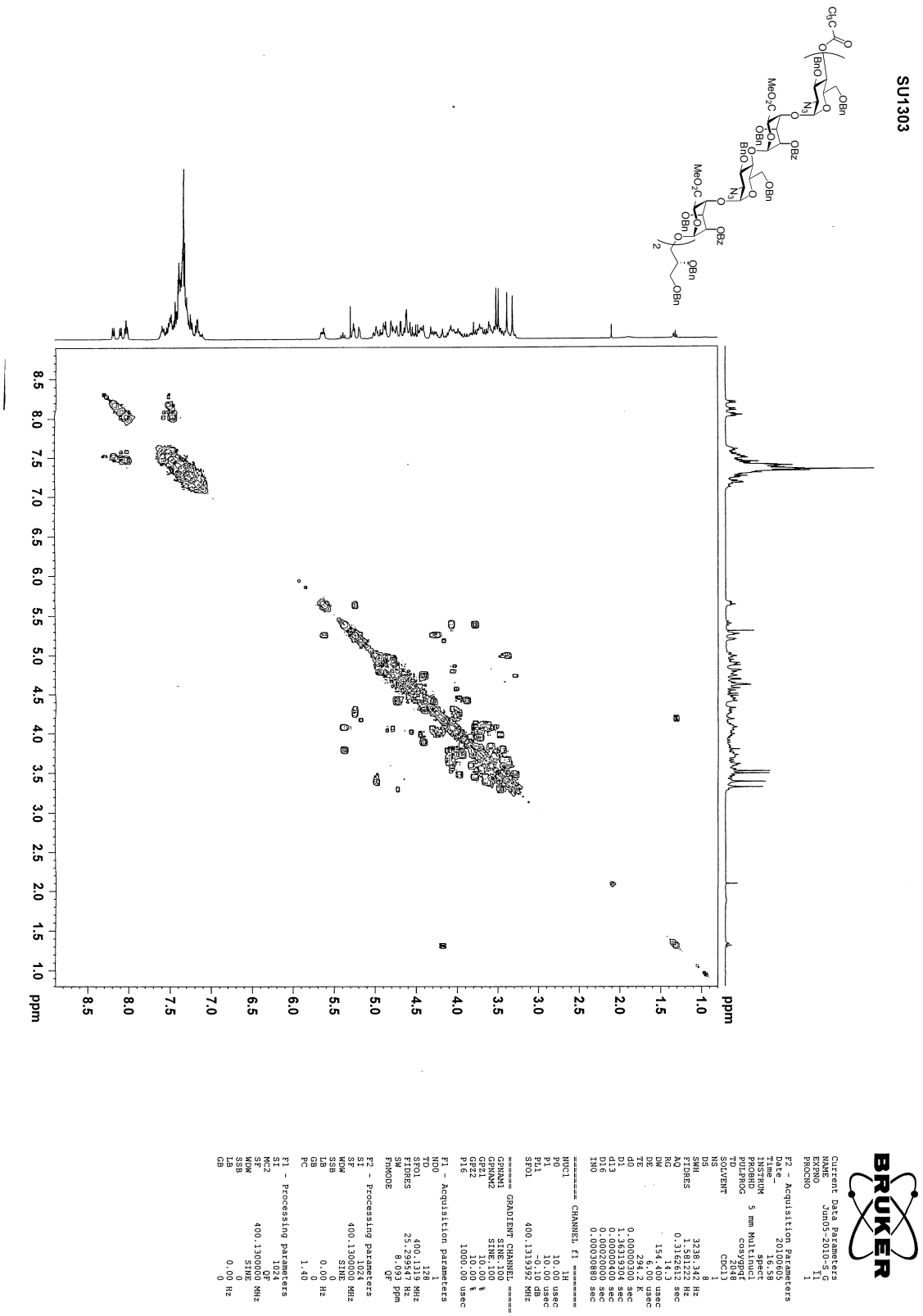
Supplementary Figure S38. COSY NMR spectrum for **10**



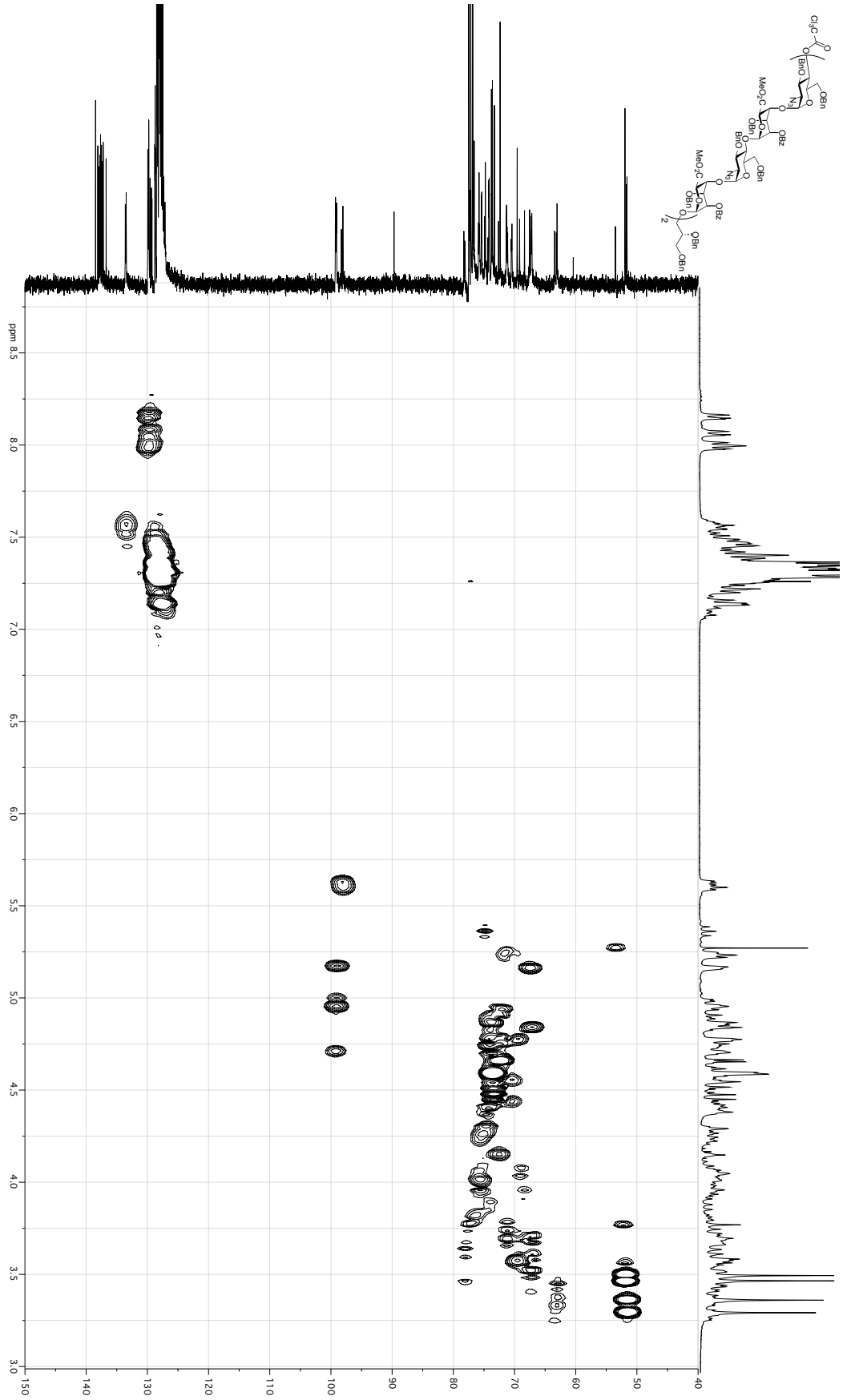
Supplementary Figure S39. FT MS spectrum for **10**



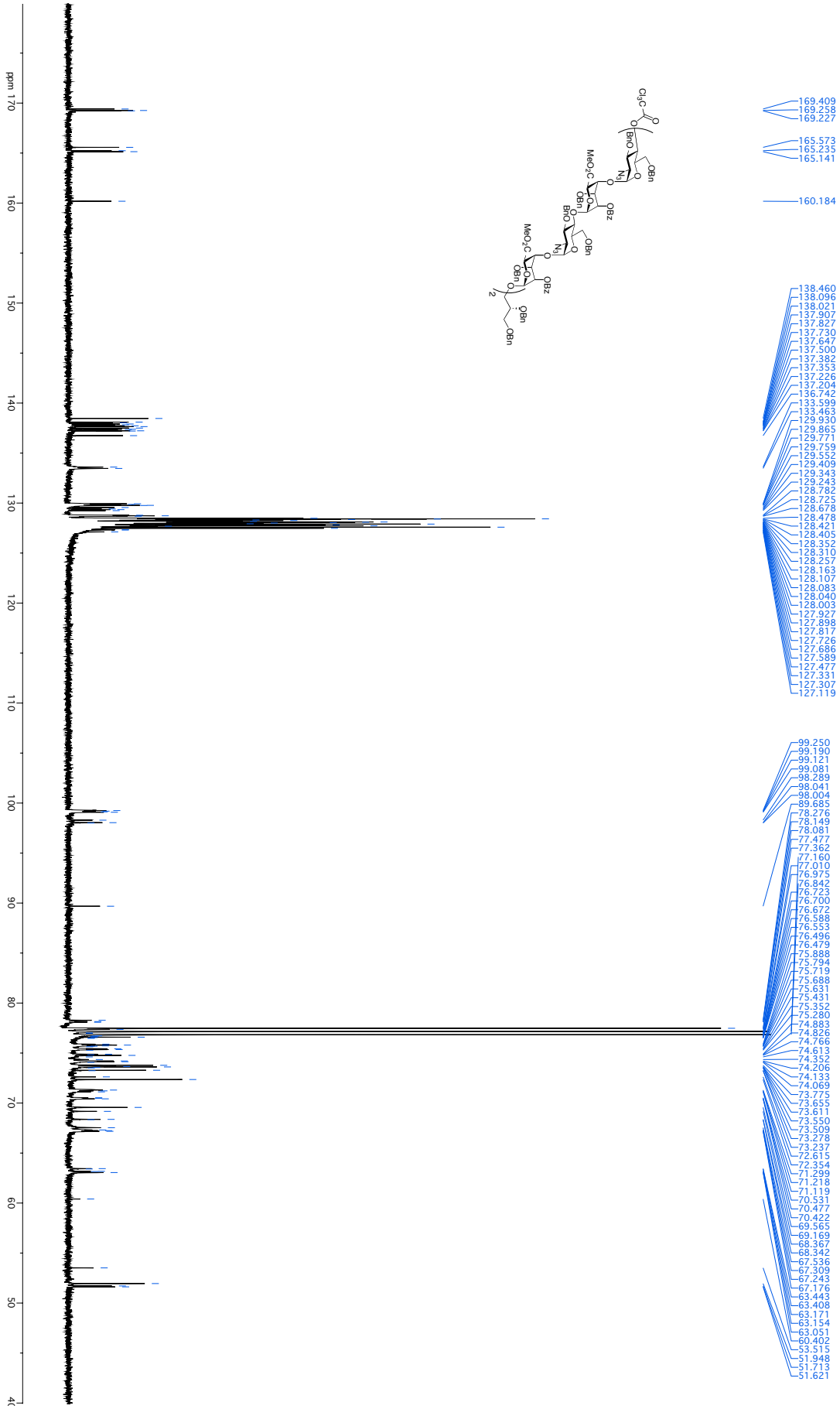
Supplementary Figure S40. ^{1}H NMR (500 MHz; $CDCl_3$) spectrum for **11**



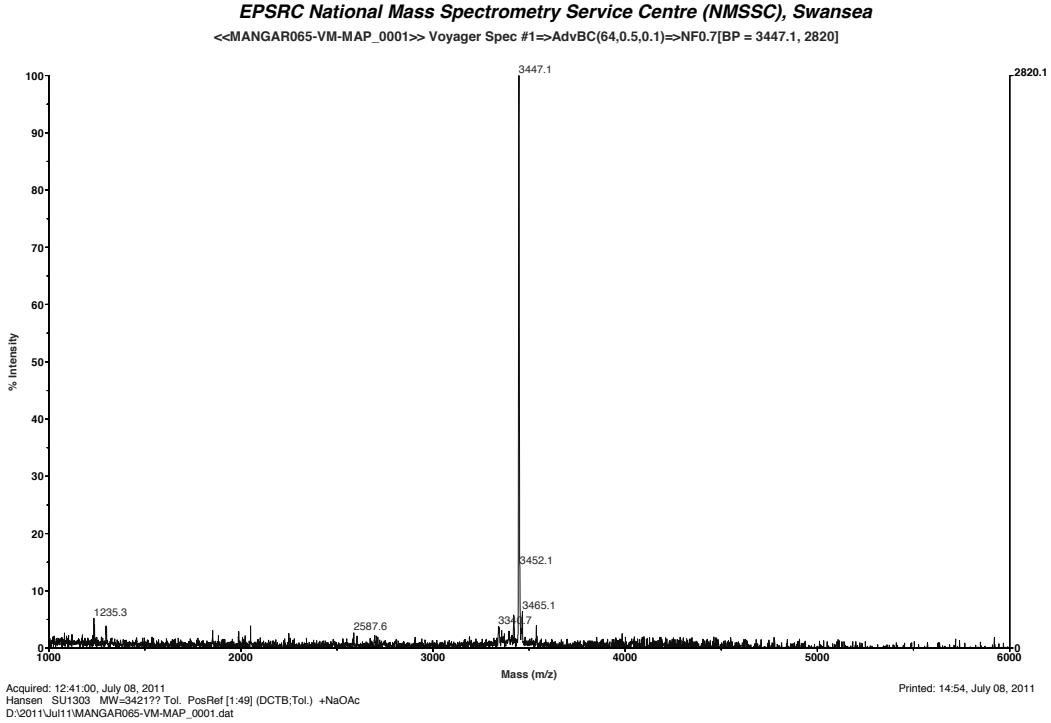
Supplementary Figure S41. COSY NMR spectrum for **11**

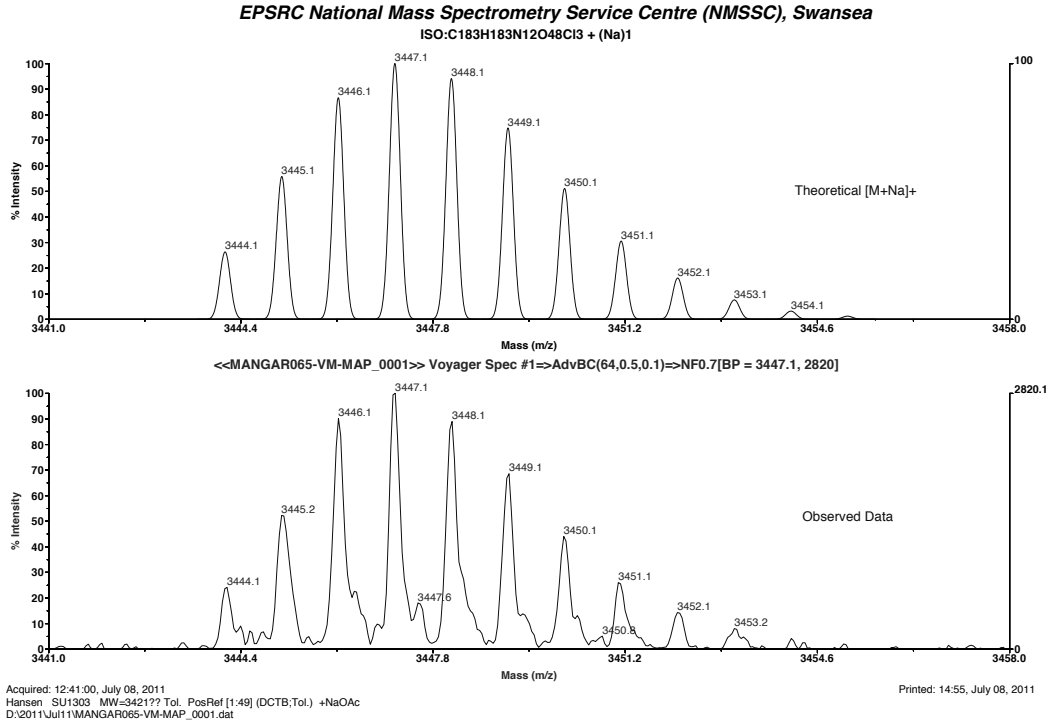


Supplementary Figure S42. HMQC NMR spectrum for **11**

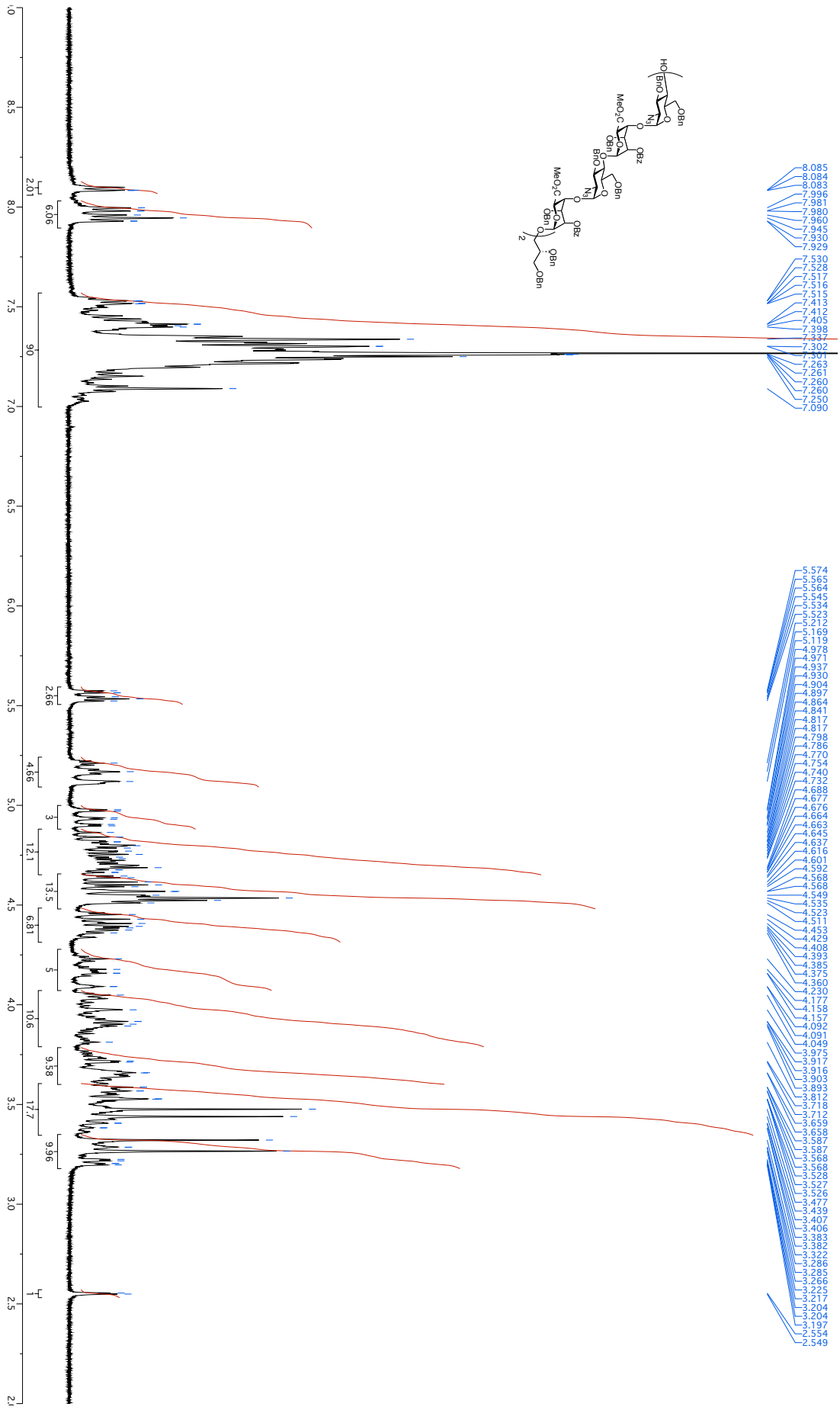


Supplementary Figure S43. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for **11**

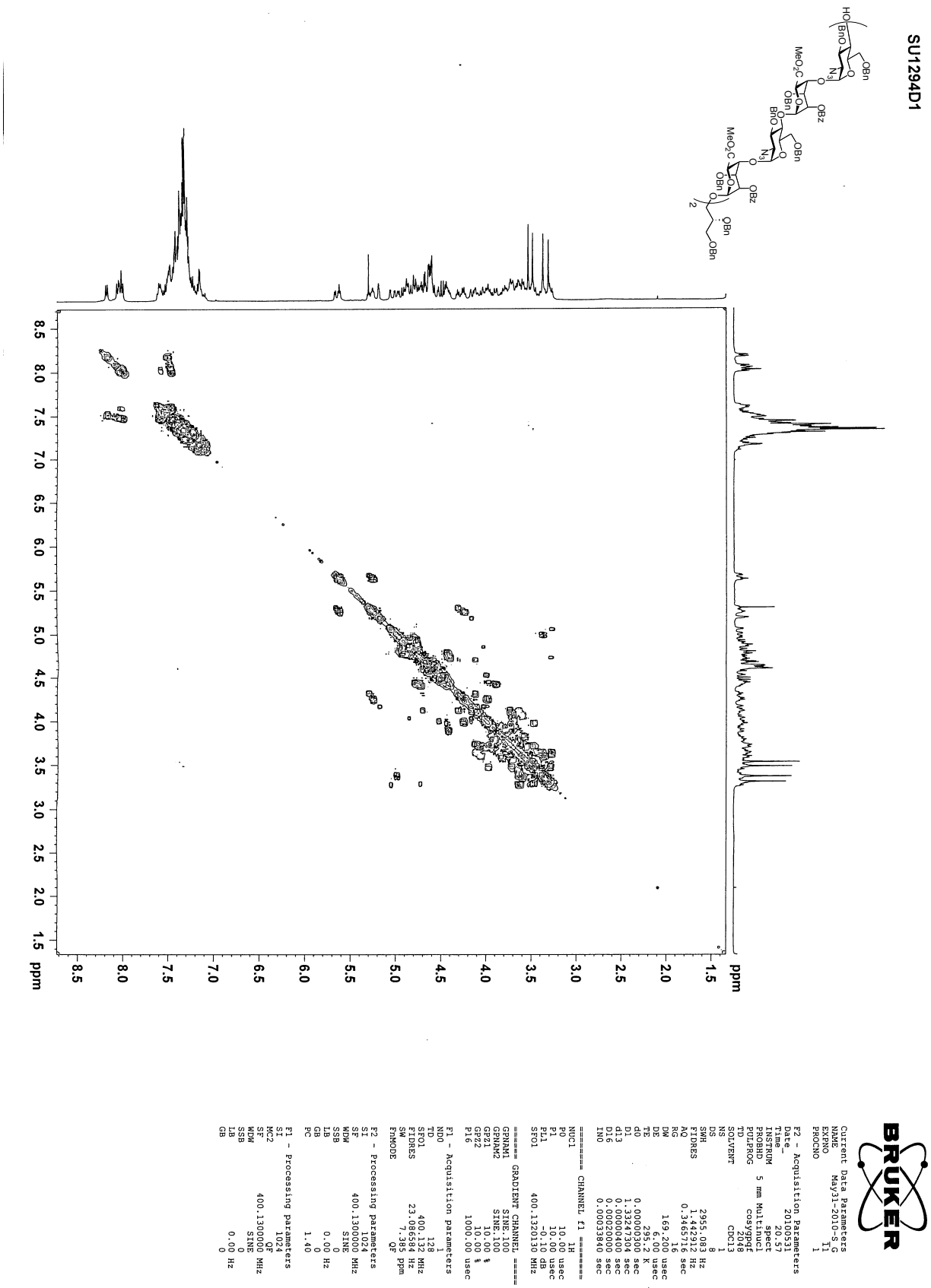




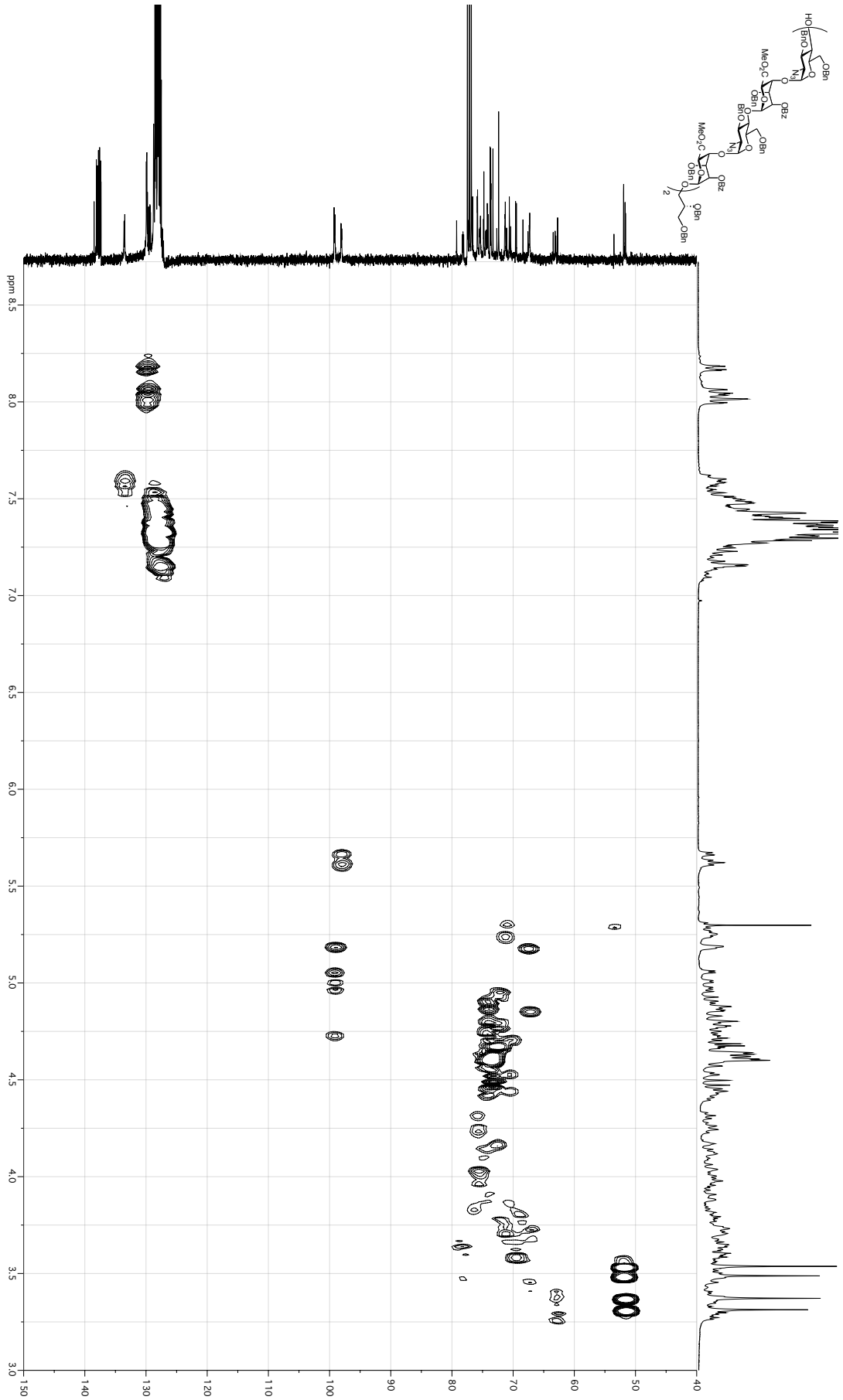
Supplementary Figure S44. MALDI-TOF MS spectrum for **11**



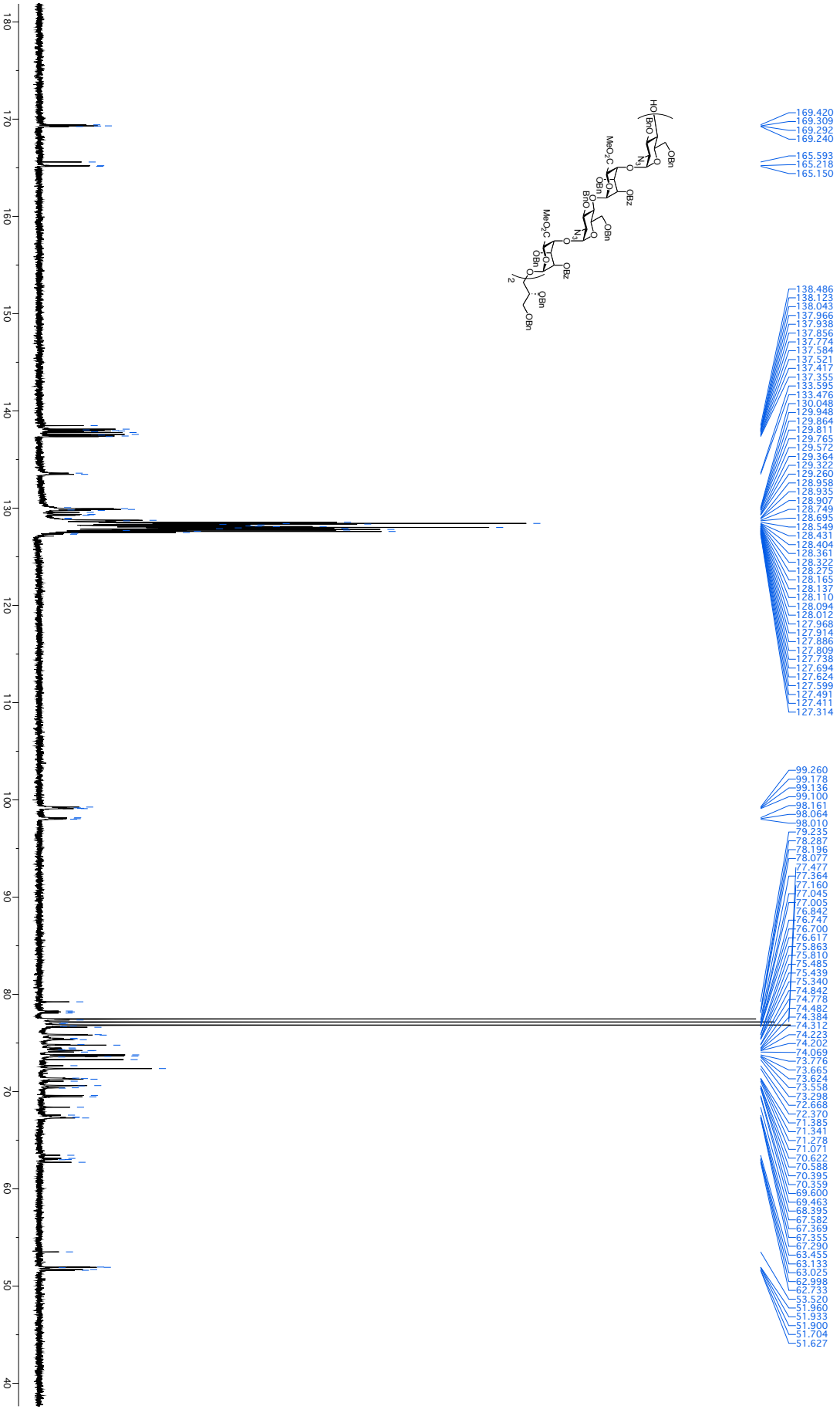
Supplementary Figure S45. ^{1}H NMR (500 MHz; $CDCl_3$) spectrum for **12**



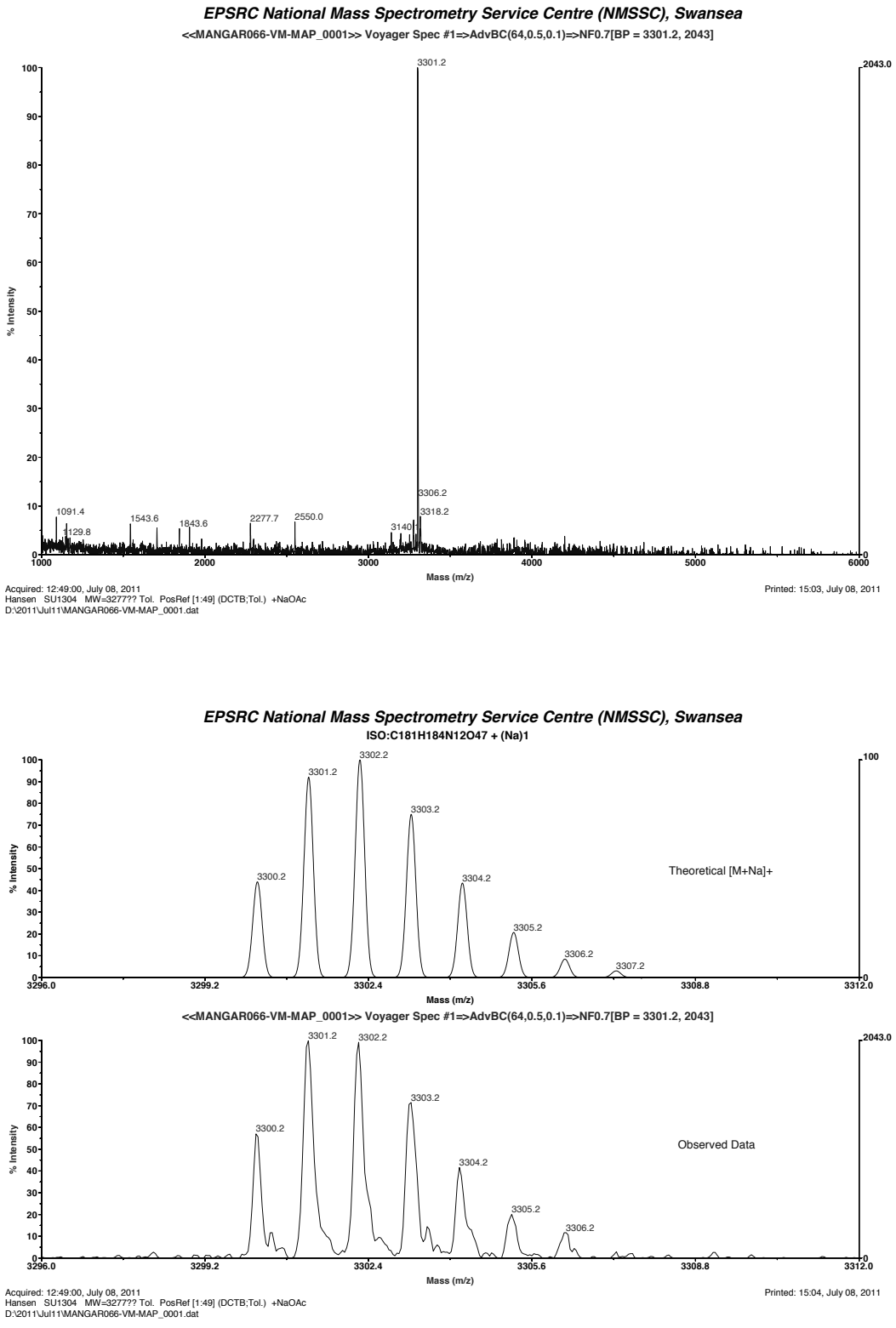
Supplementary Figure S46. COSY NMR spectrum for **12**



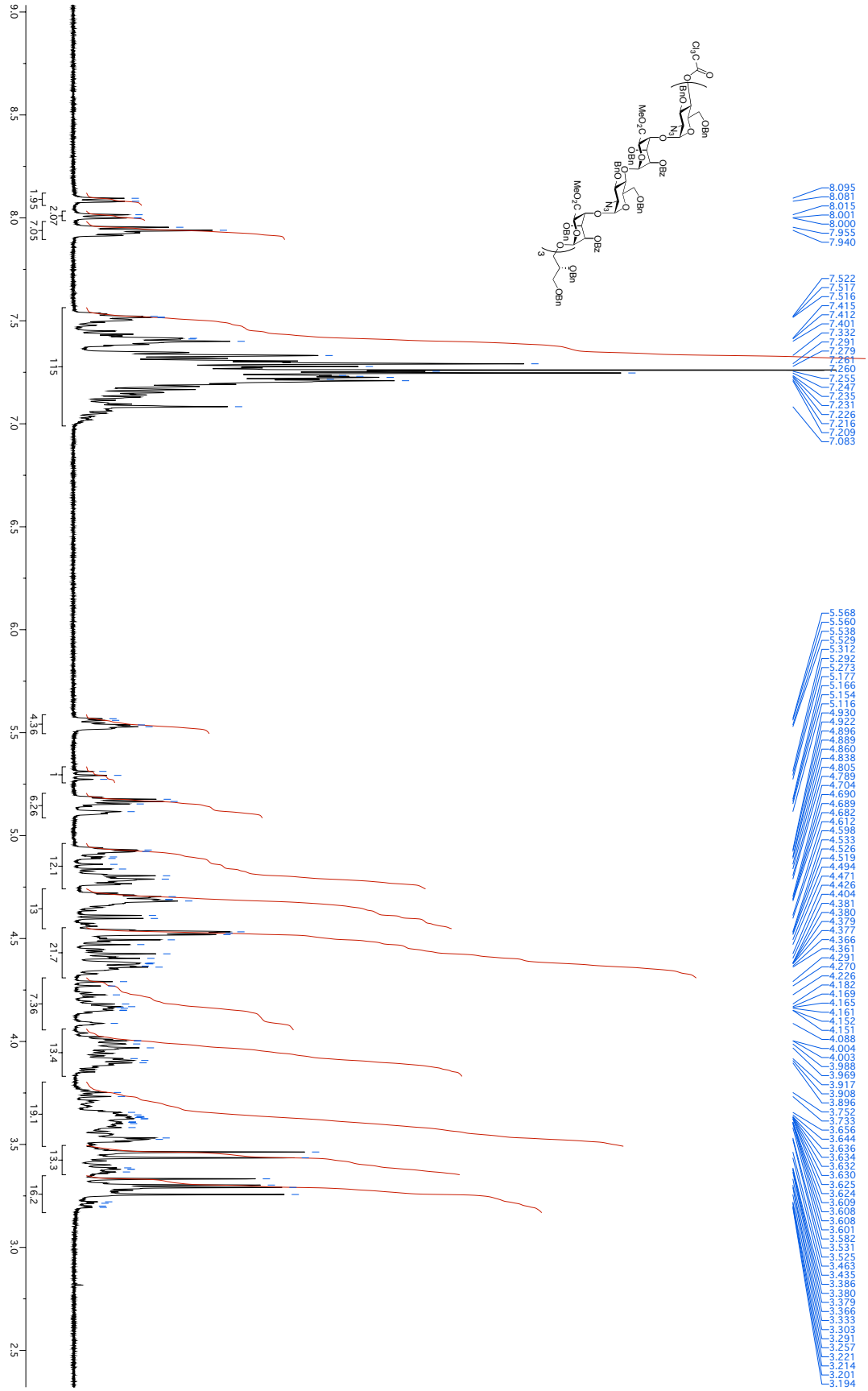
Supplementary Figure S47. HMQC NMR spectrum for **12**



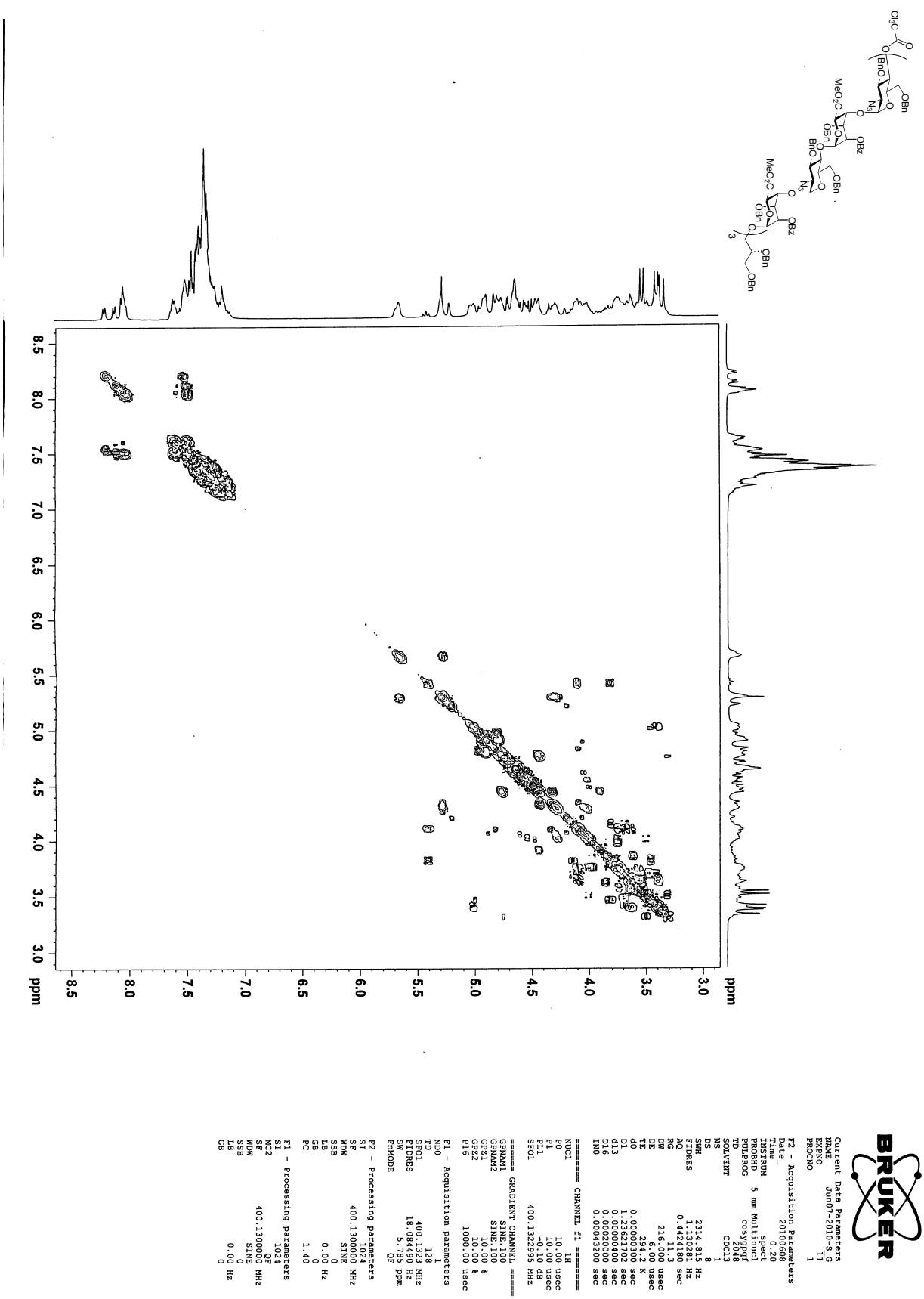
Supplementary Figure S48. HMQC NMR spectrum for **12** ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for **12**



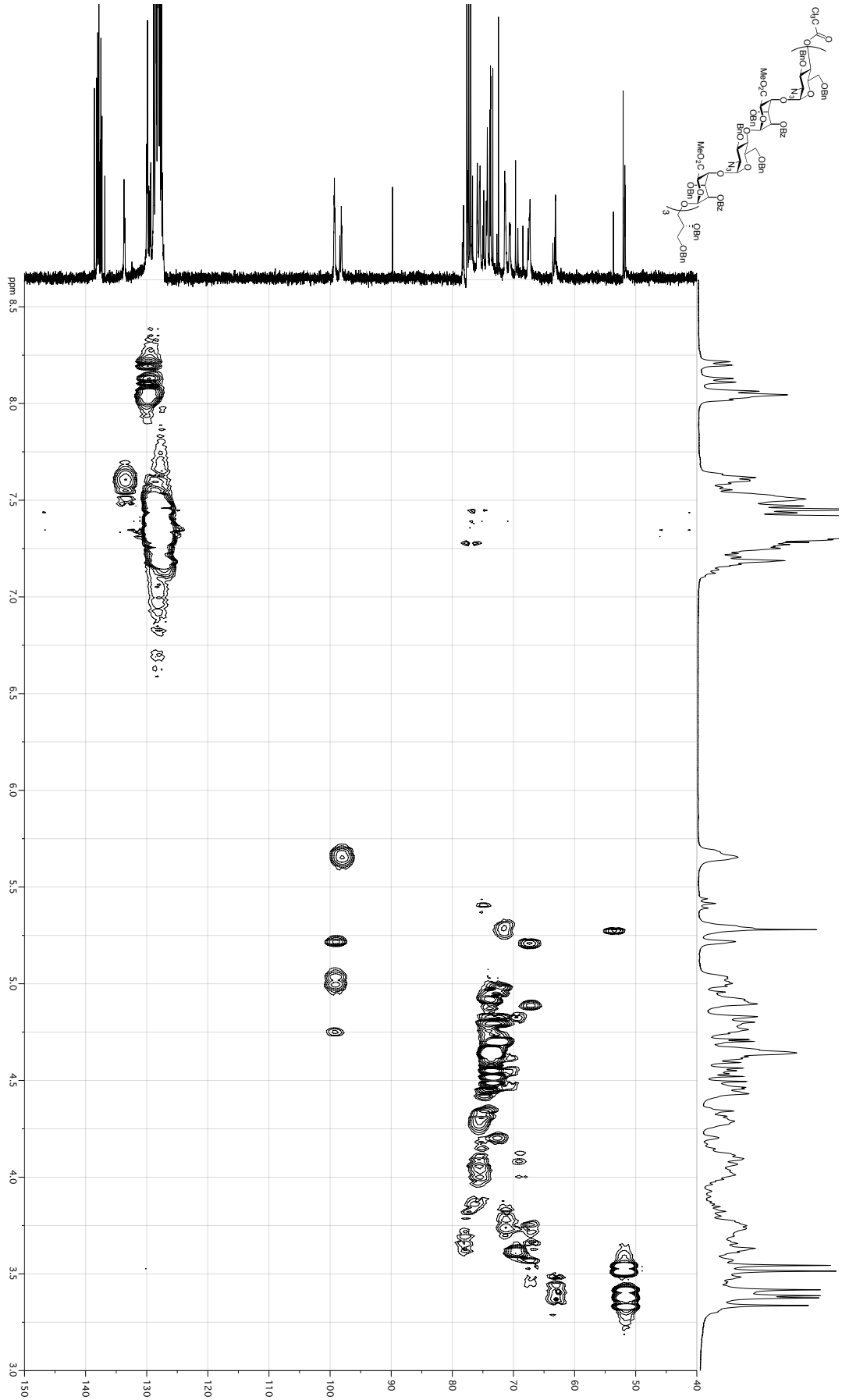
Supplementary Figure S49. MALDI-TOF MS spectrum for **12**



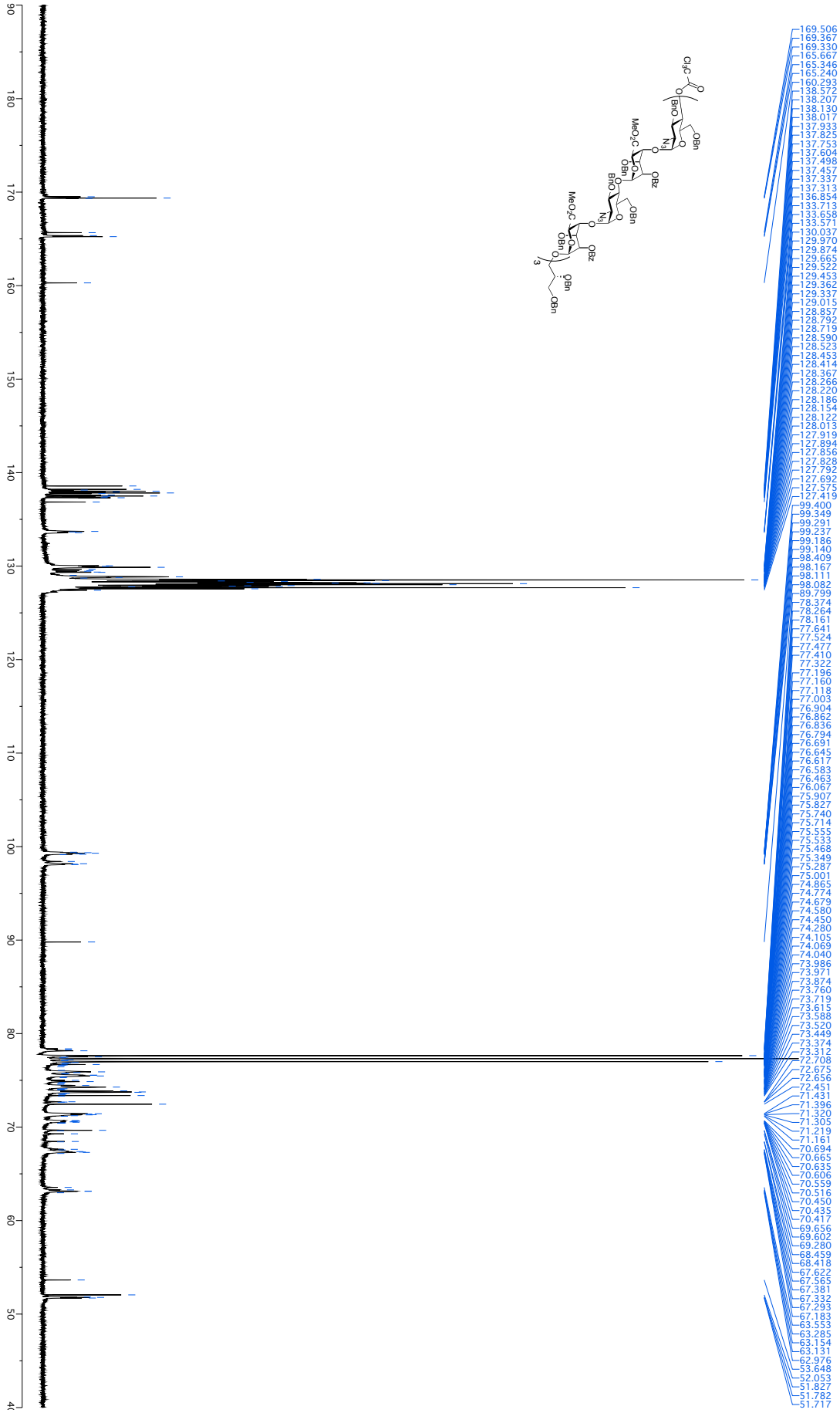
Supplementary Figure S50. ^{1}H NMR (500 MHz; $CDCl_3$) spectrum for **13**



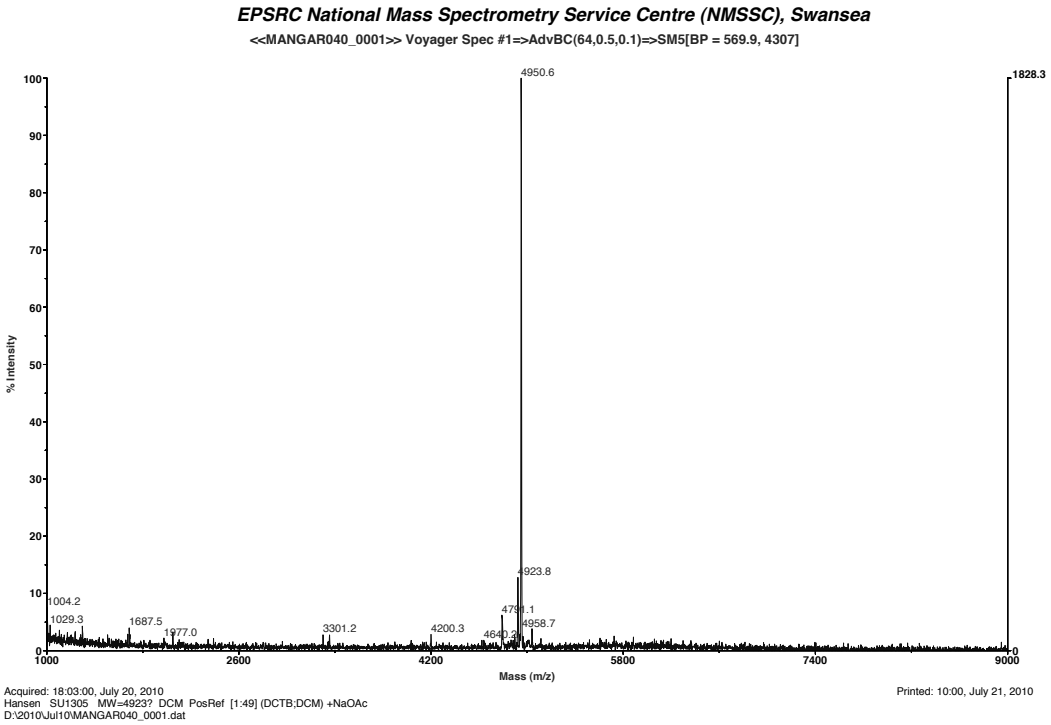
Supplementary Figure S51. COSY NMR spectrum for **13**

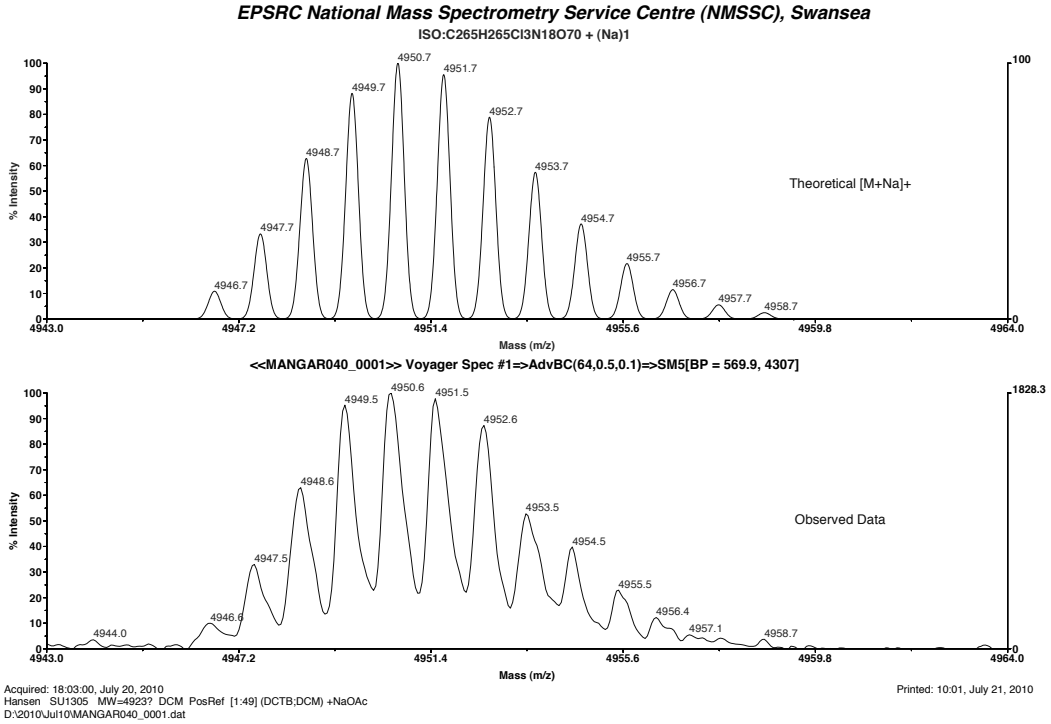


Supplementary Figure S52. HMQC NMR spectrum for **13**

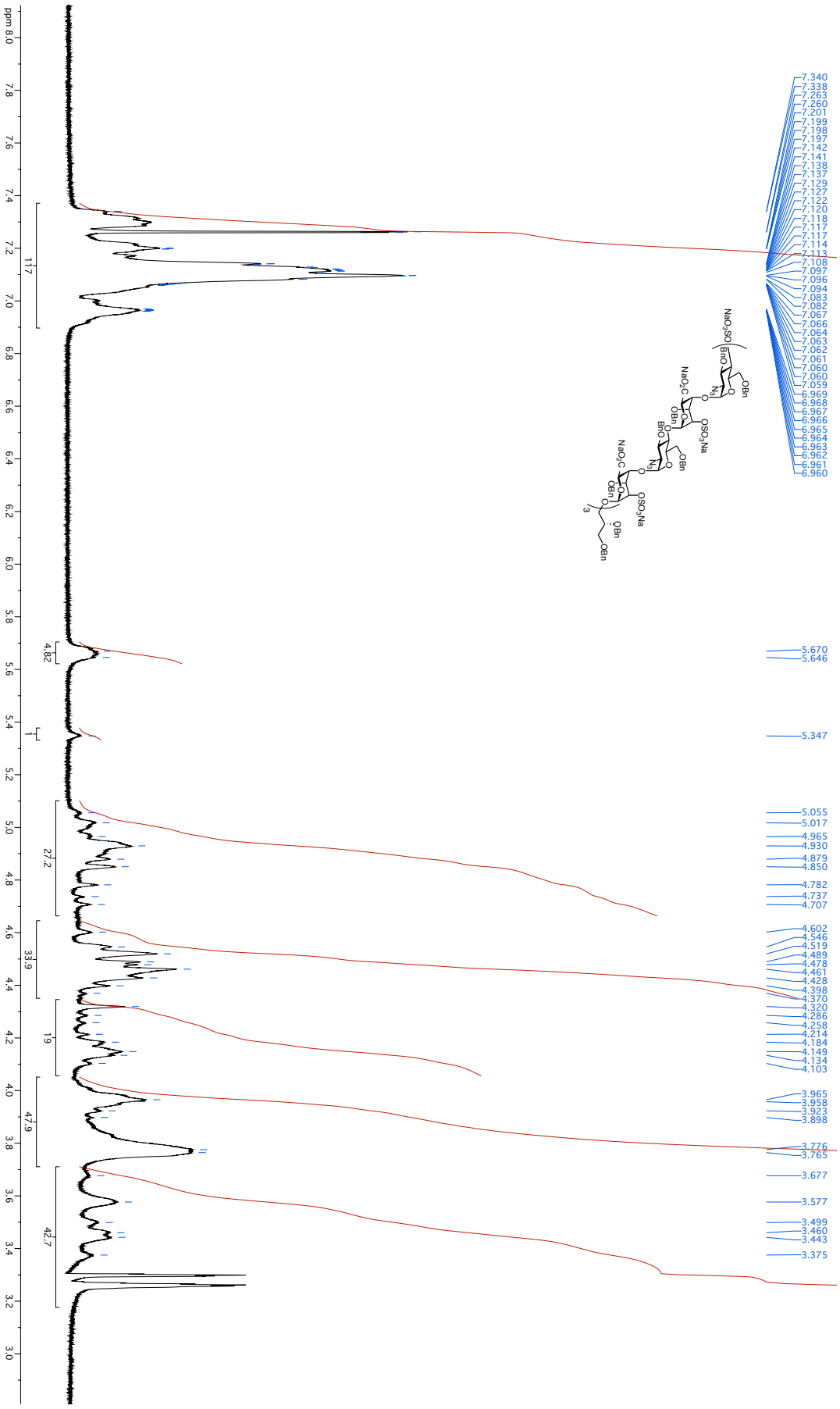


Supplementary Figure S53. ^{13}C NMR (100 MHz; $CDCl_3$) spectrum for **13**

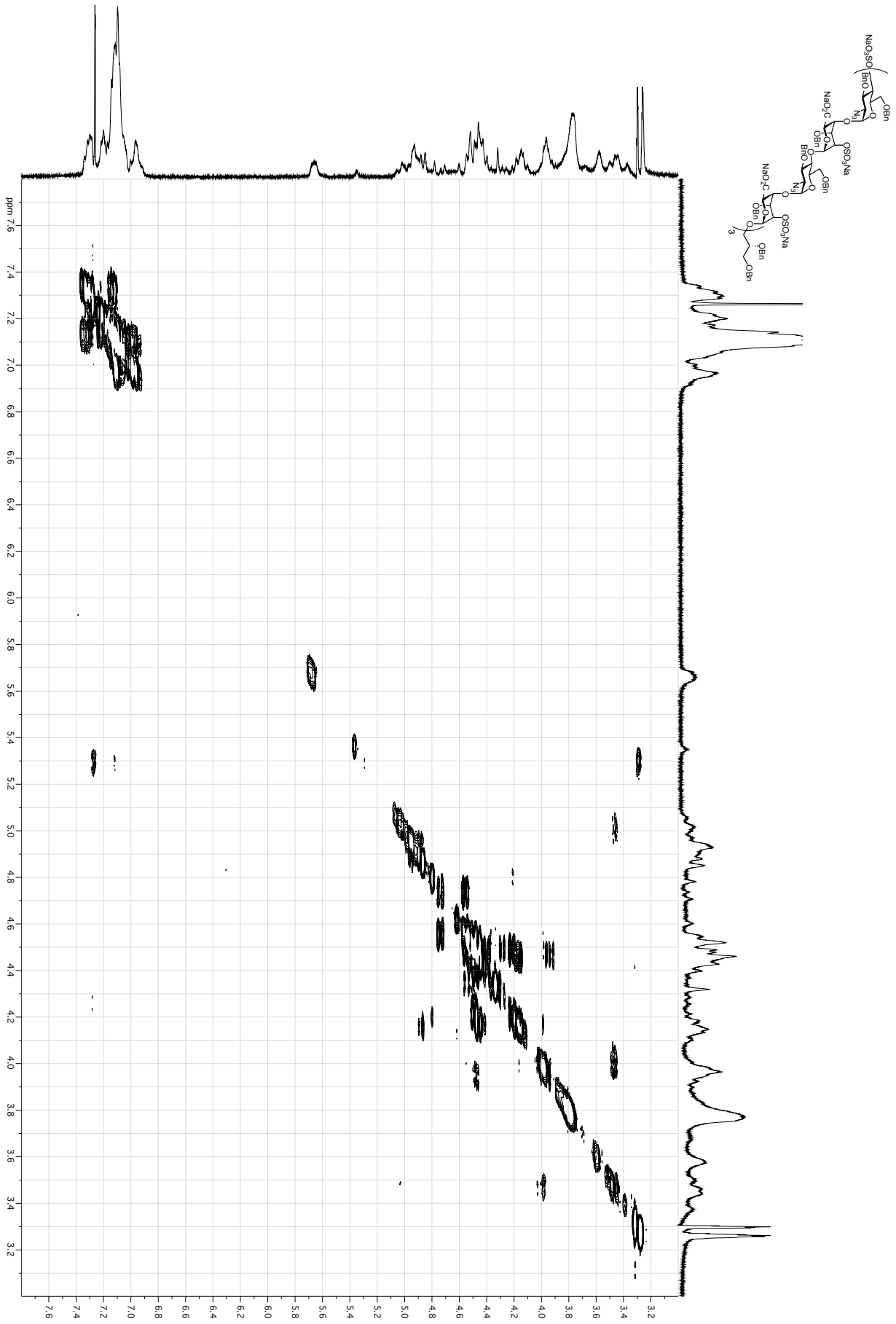




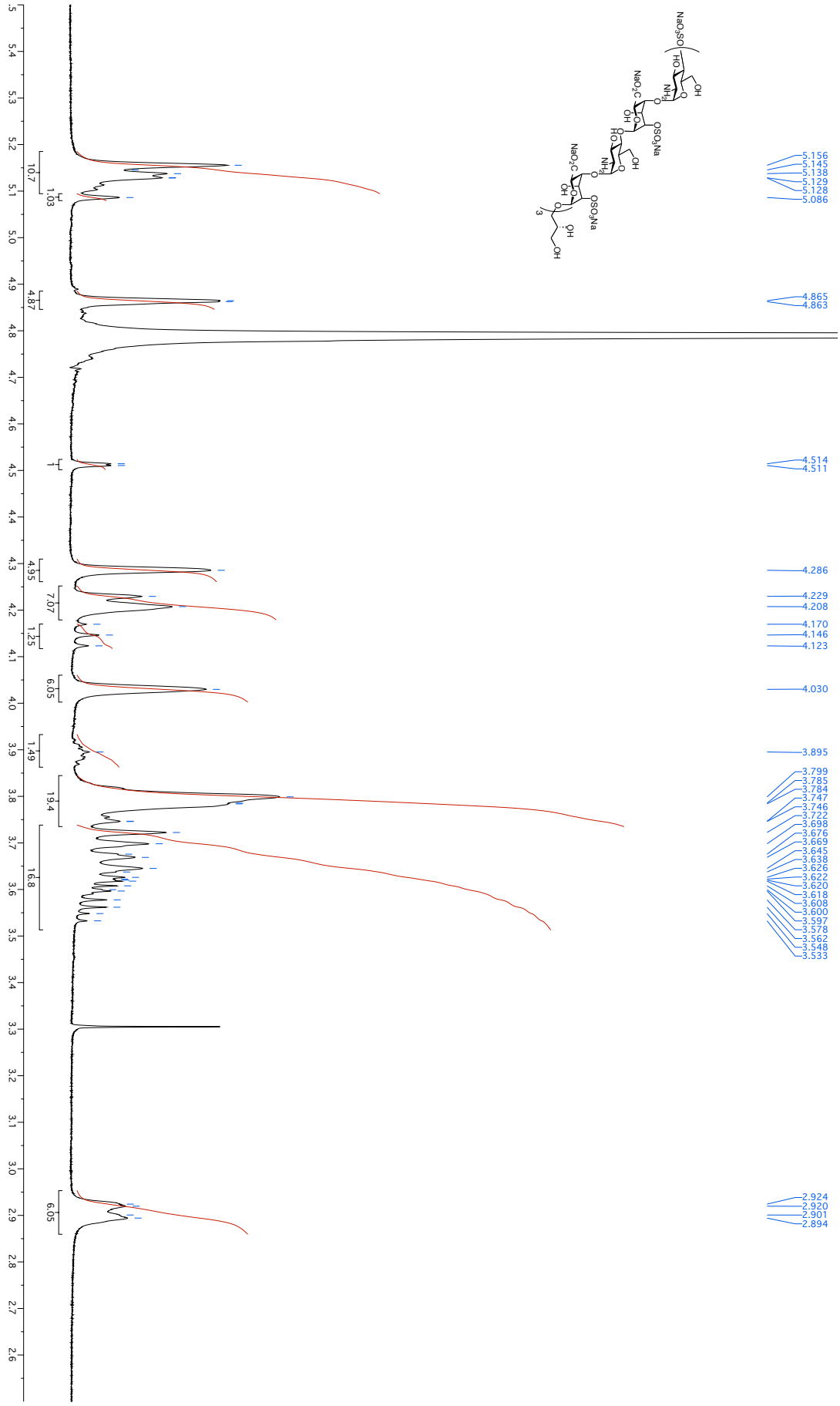
Supplementary Figure S54. MALDI-TOF MS spectrum for **13**



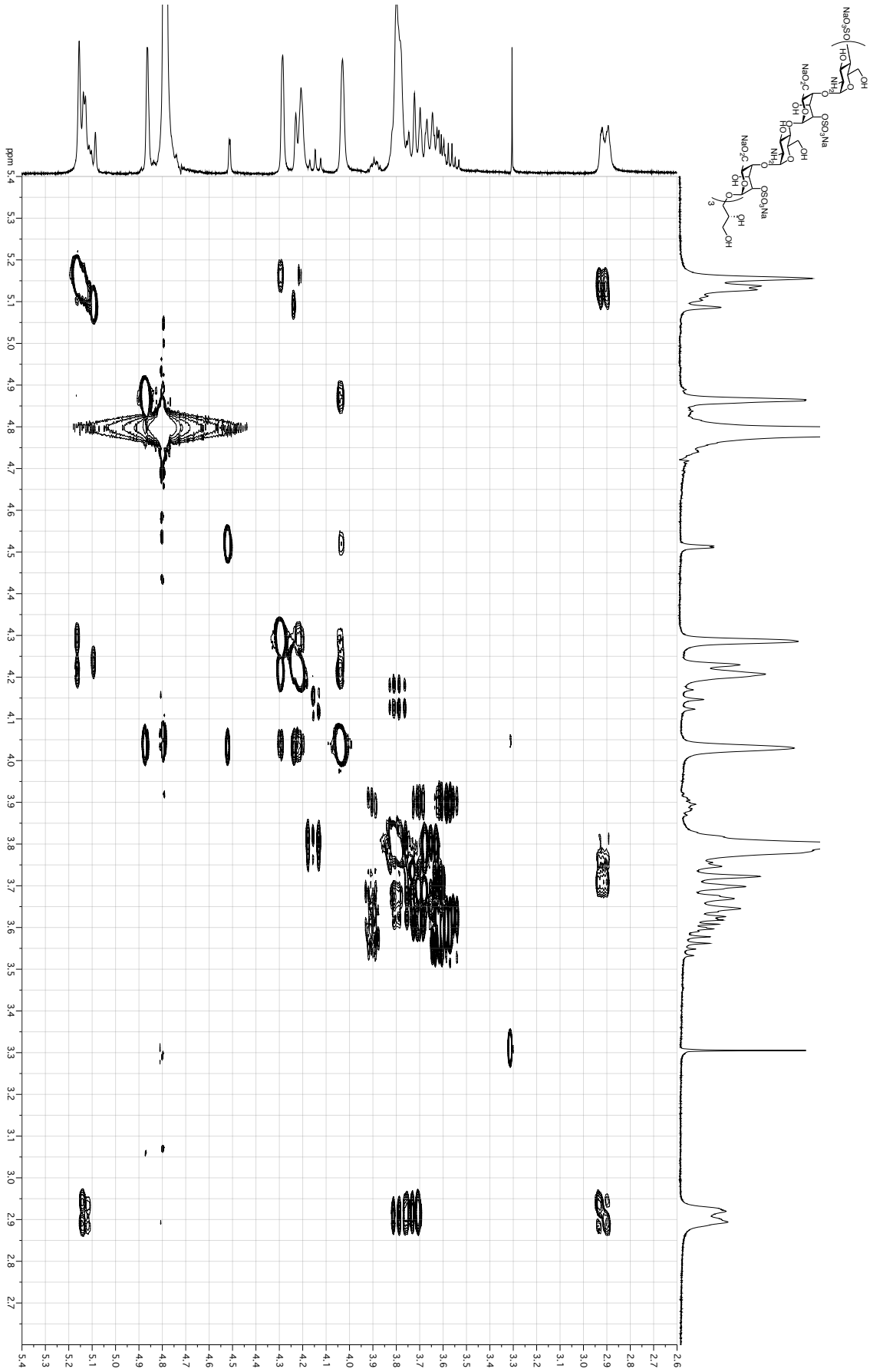
Supplementary Figure S55. ^{1}H NMR (400 MHz; $CDCl_3/CD_3OD$ 10:1) spectrum for **B**



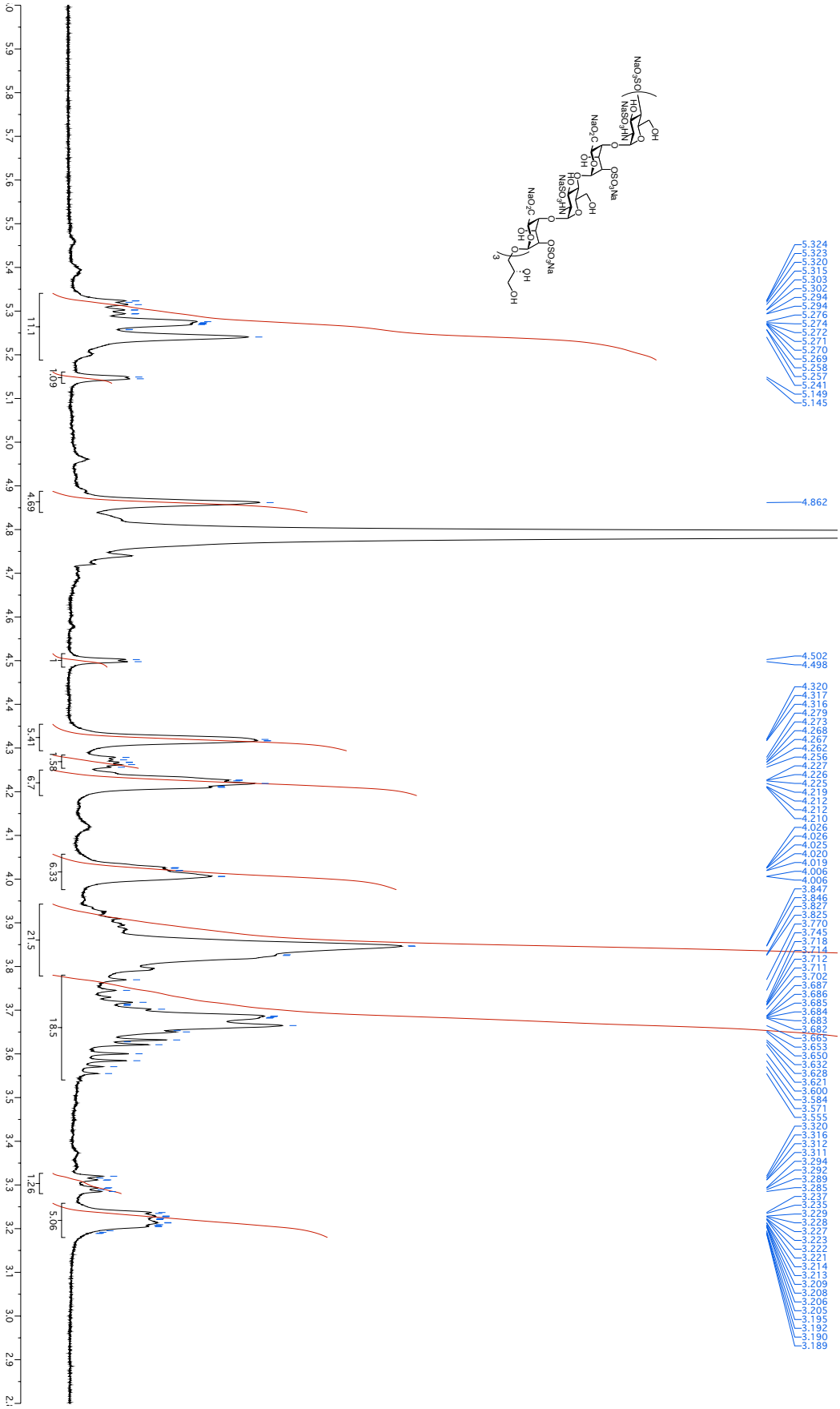
Supplementary Figure S56. COSY NMR spectrum for **B**



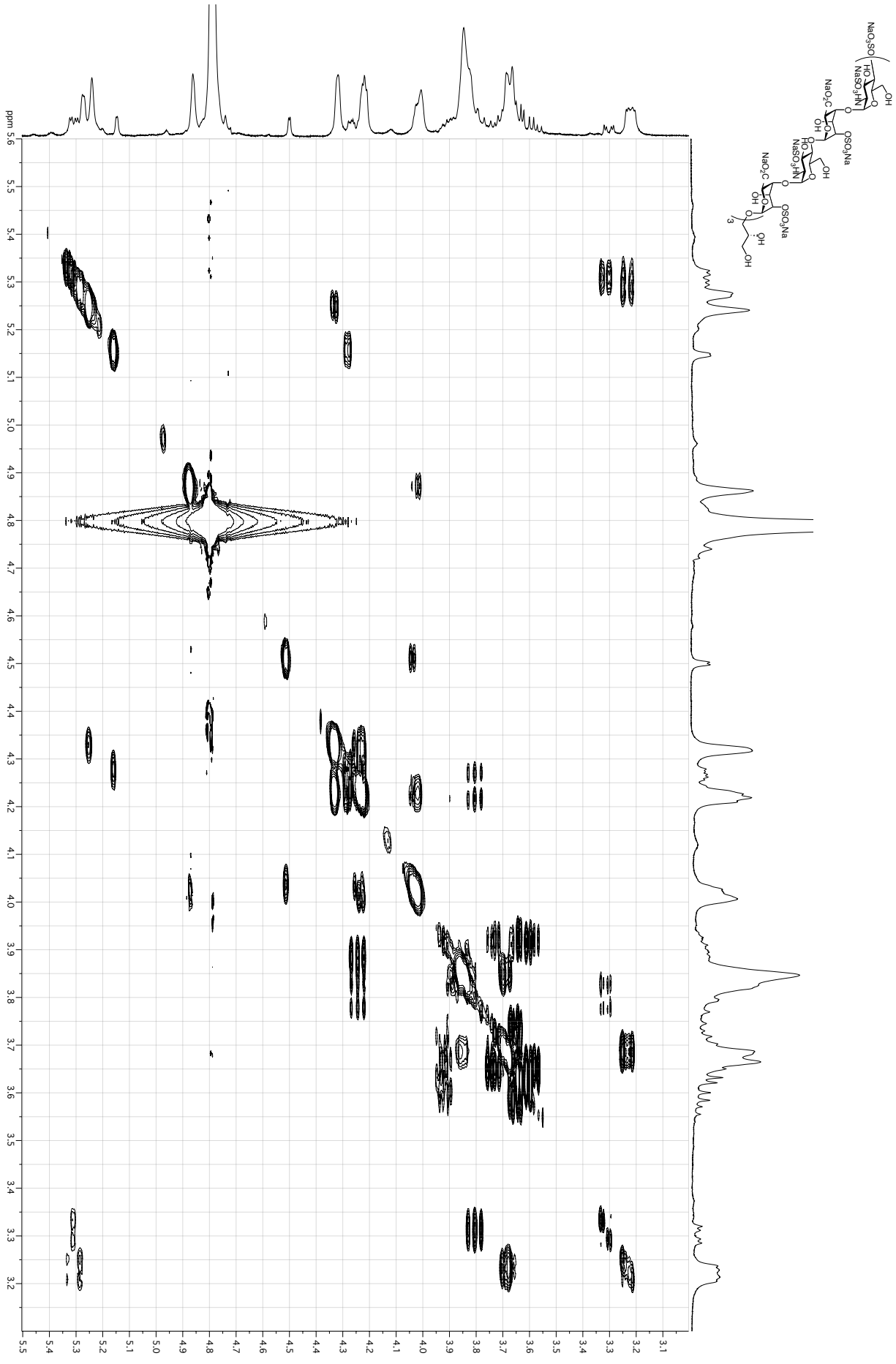
Supplementary Figure S57. ^{1}H NMR (400 MHz; D_2O) spectrum for dodecasaccharide NH_2 intermediate **C**



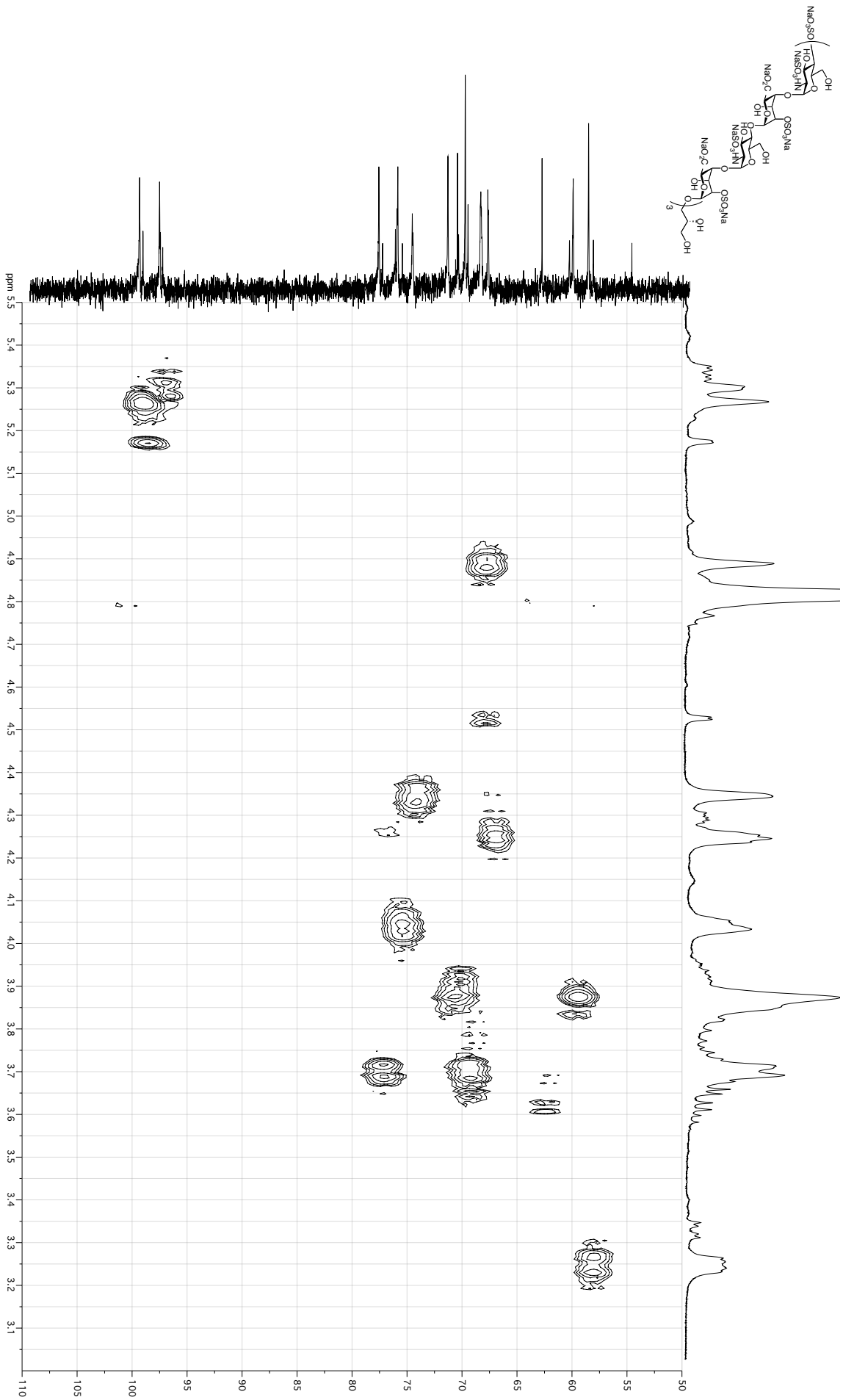
Supplementary Figure S58. COSY NMR spectrum for dodecasaccharide NH_2 intemediate **C**



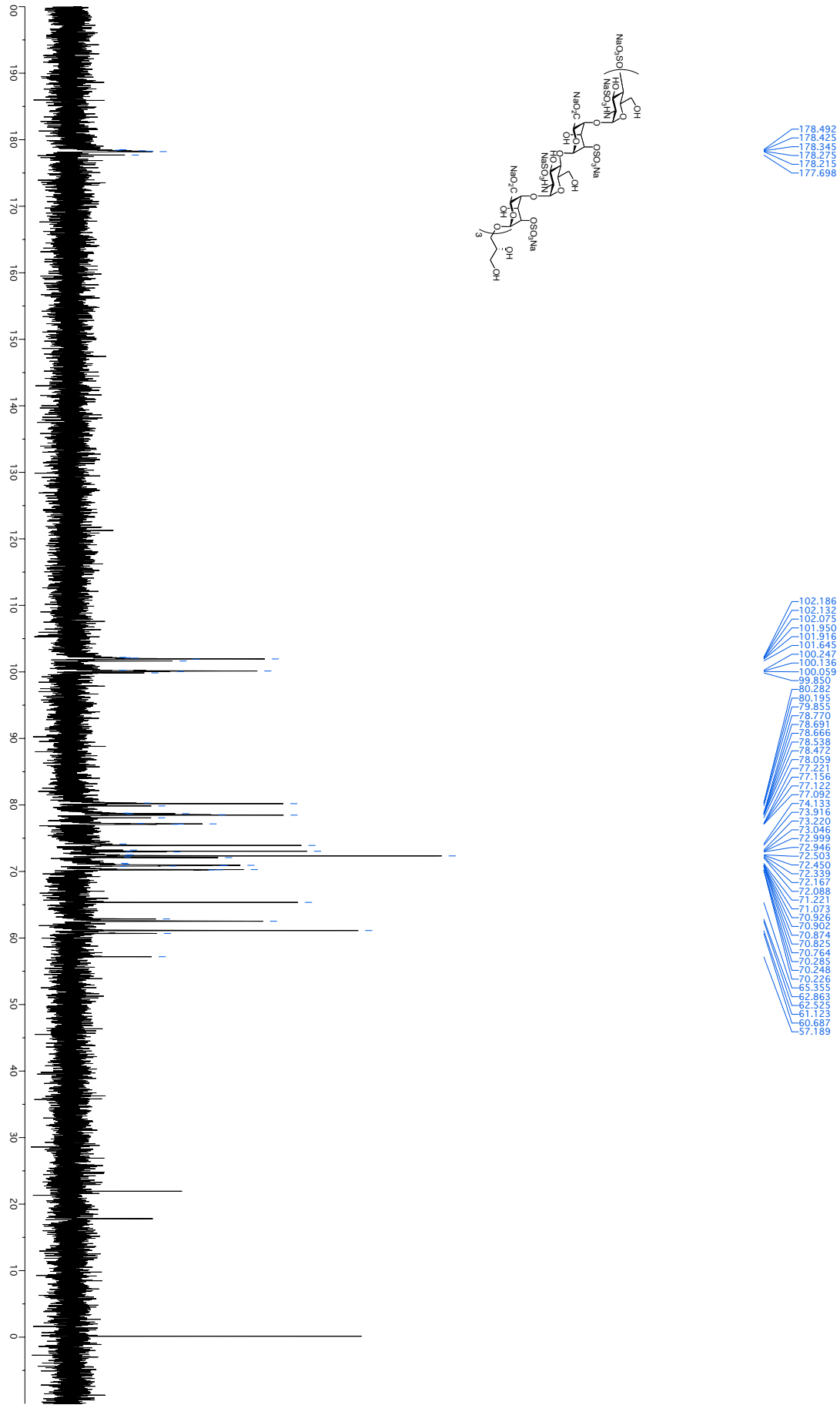
Supplementary Figure S59. ^{1}H NMR (400 MHz; D_2O) spectrum for **14**



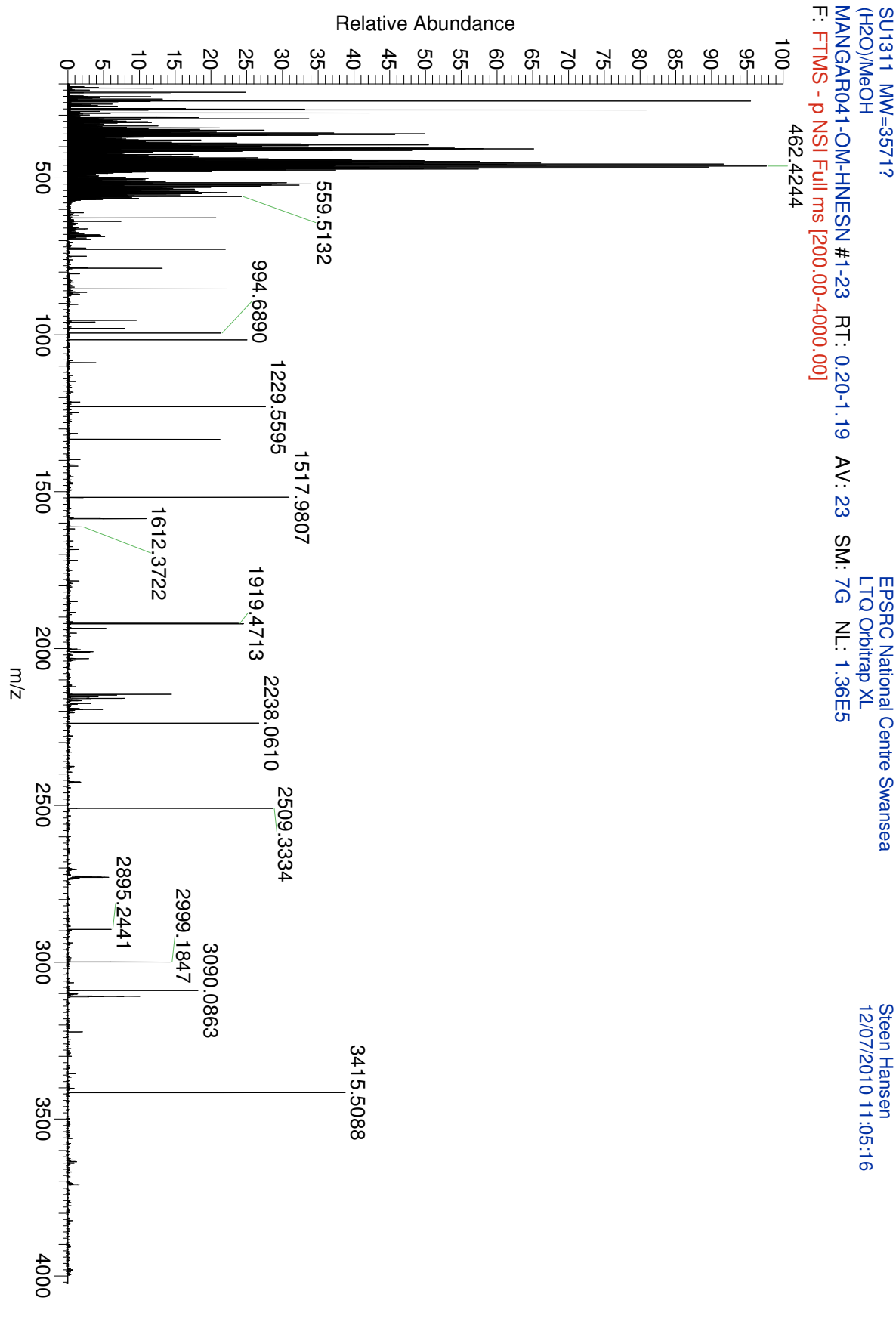
Supplementary Figure S60. COSY NMR spectrum for **14**



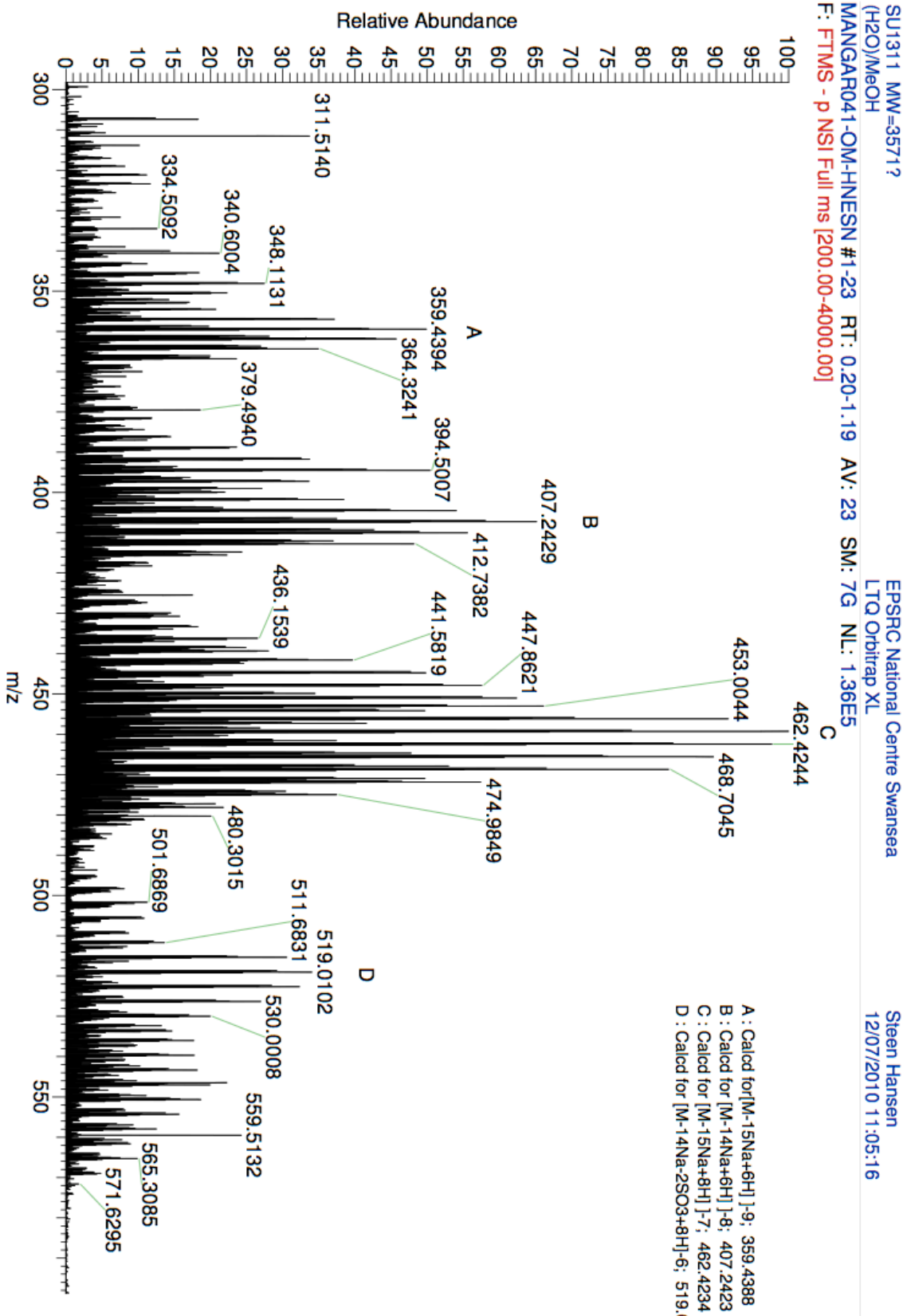
Supplementary Figure S61. HMQC NMR spectrum for **14**



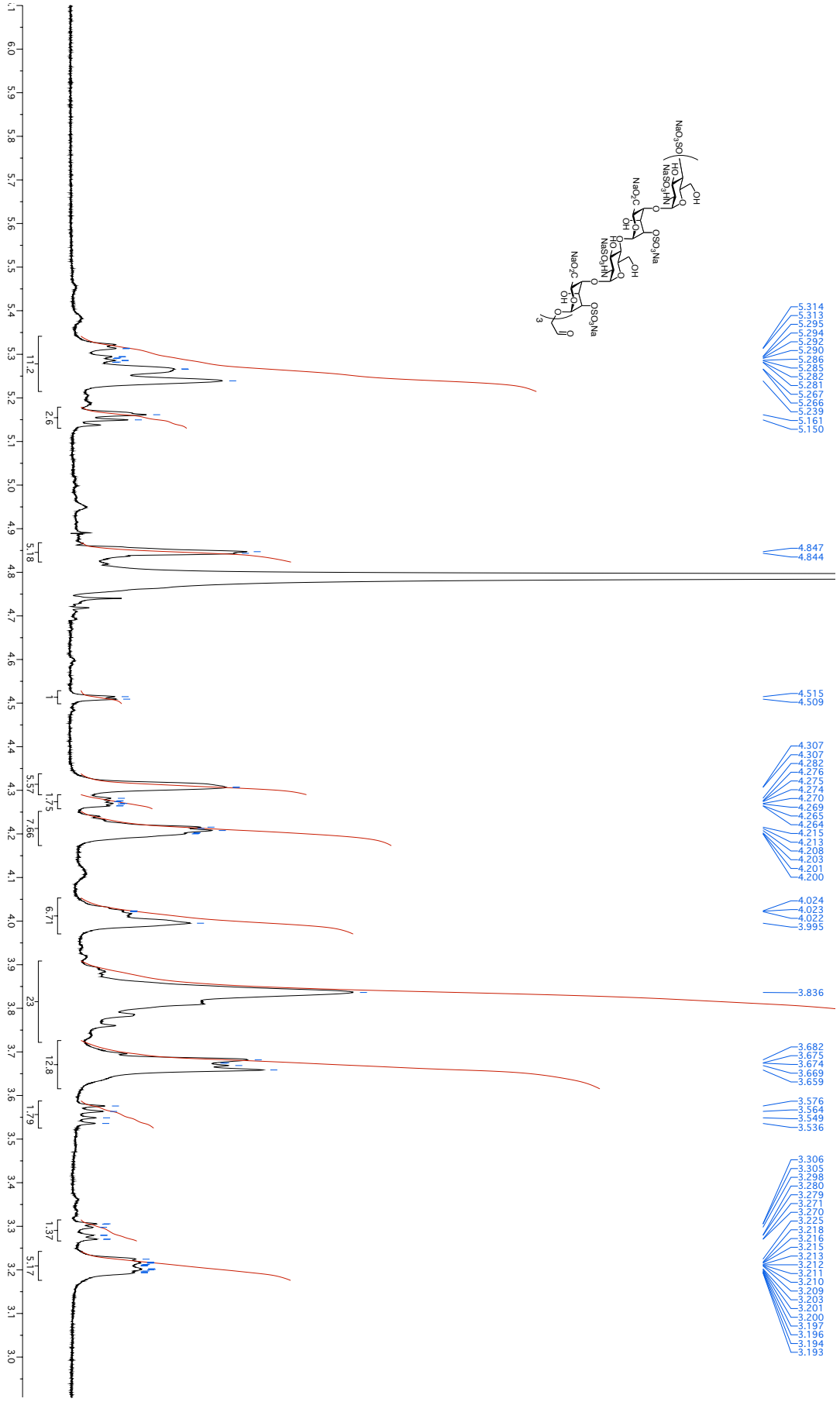
Supplementary Figure S62. ^{13}C NMR (100 MHz; D_2O) spectrum for **14**



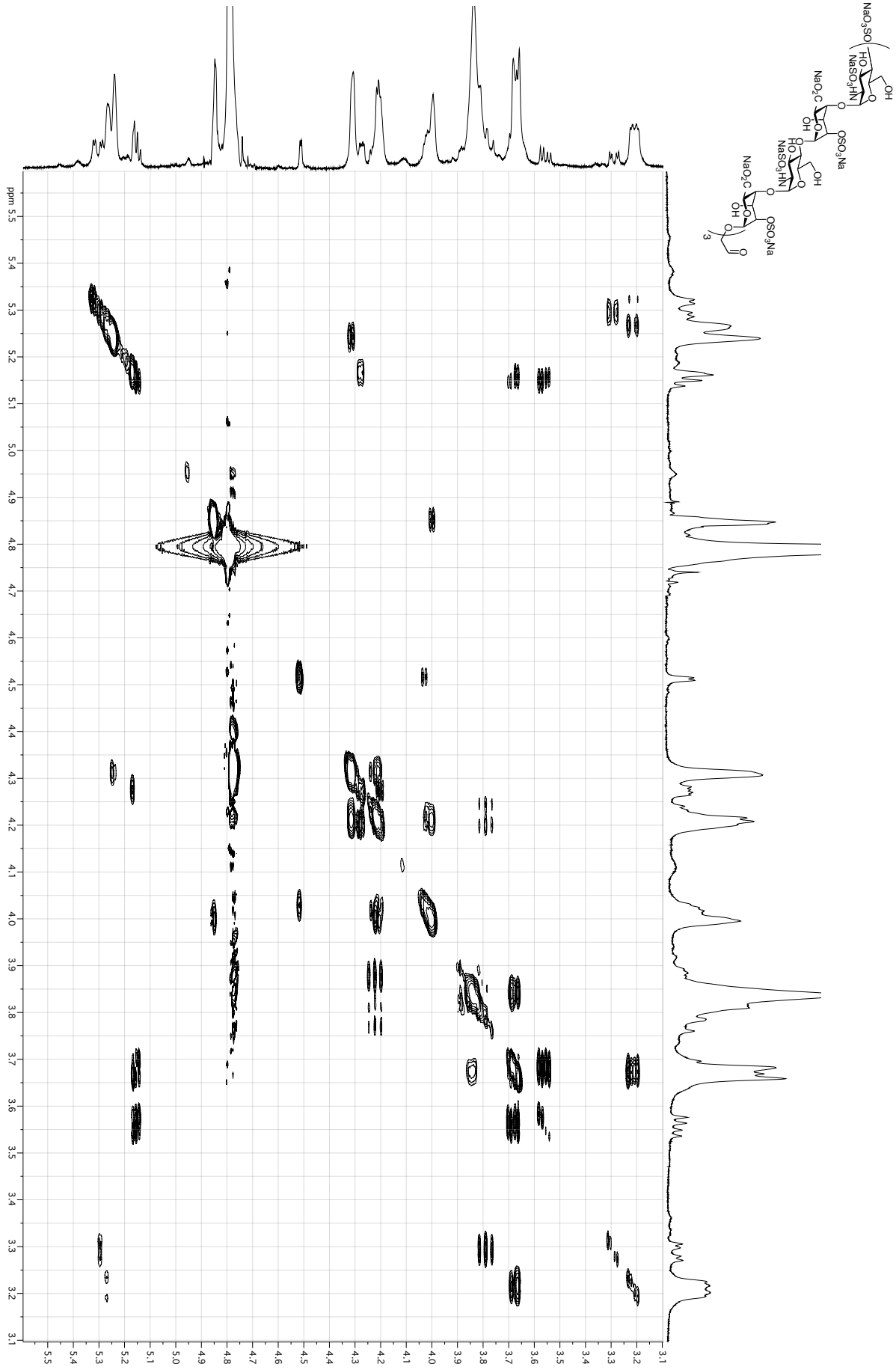
Supplementary Figure S63. FT MS negative mode spectrum for **14**



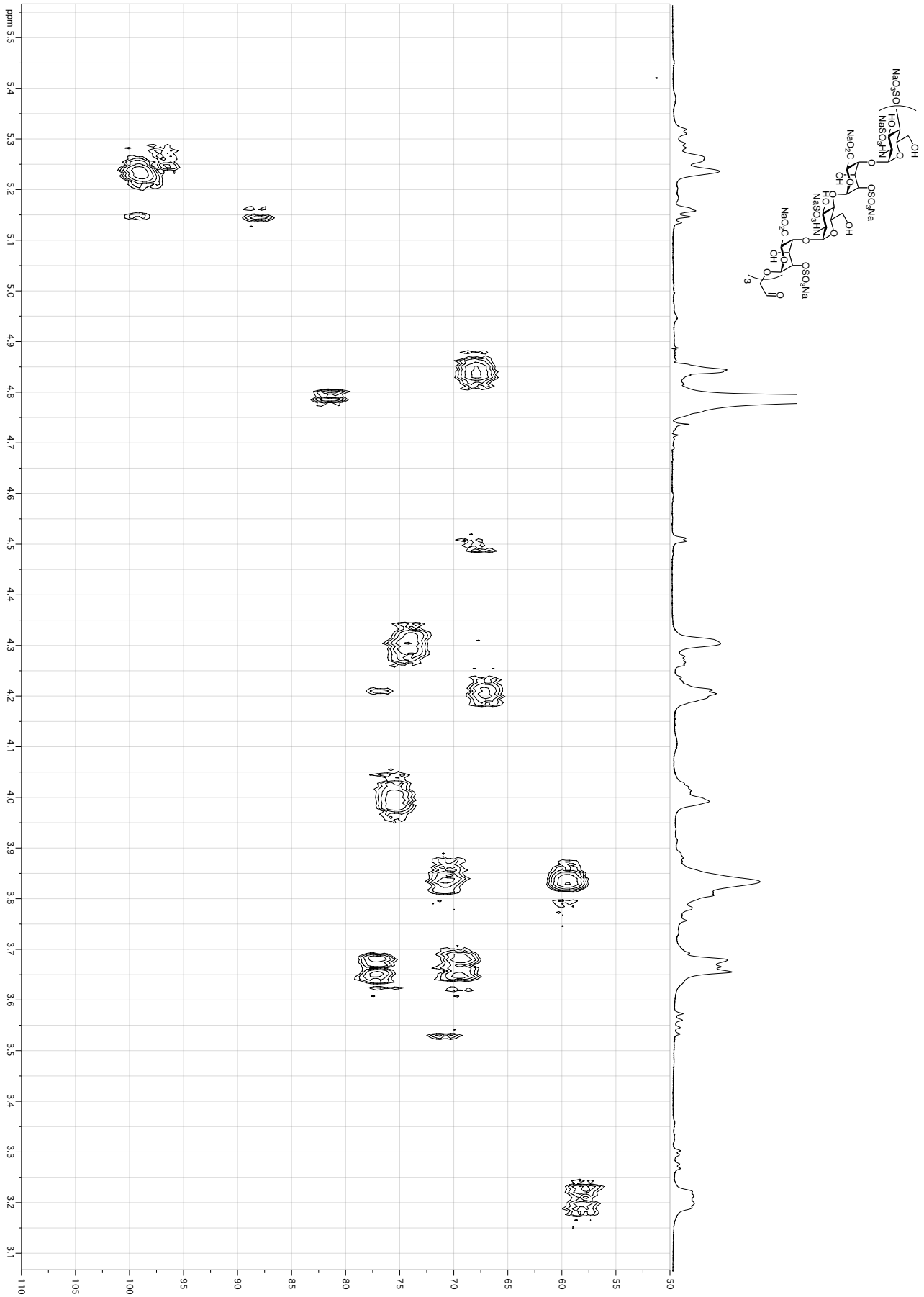
Supplementary Figure S64. FT MS negative mode assigned spectrum for **14**



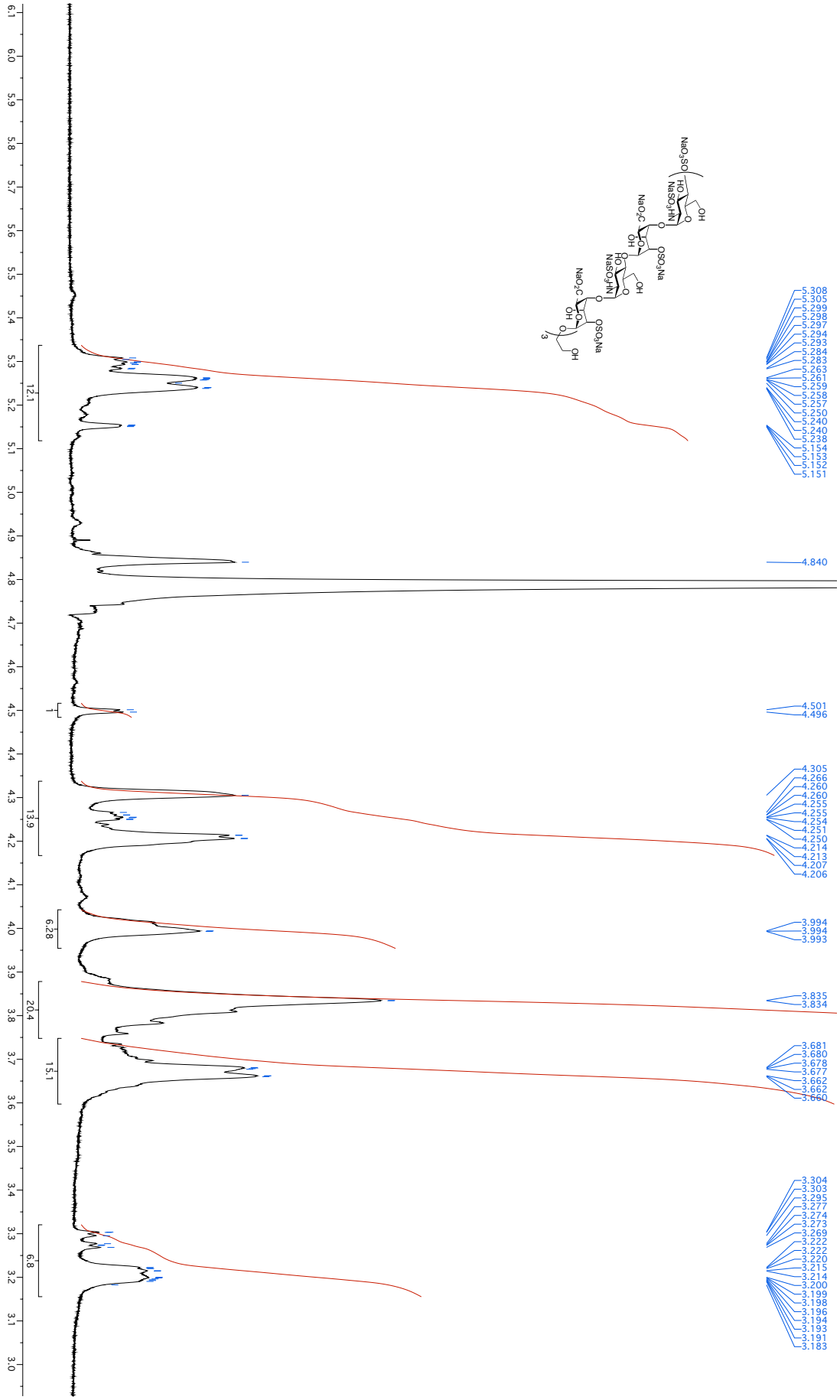
Supplementary Figure S65. ^{1}H NMR (400 MHz; D_2O) spectrum for **15**



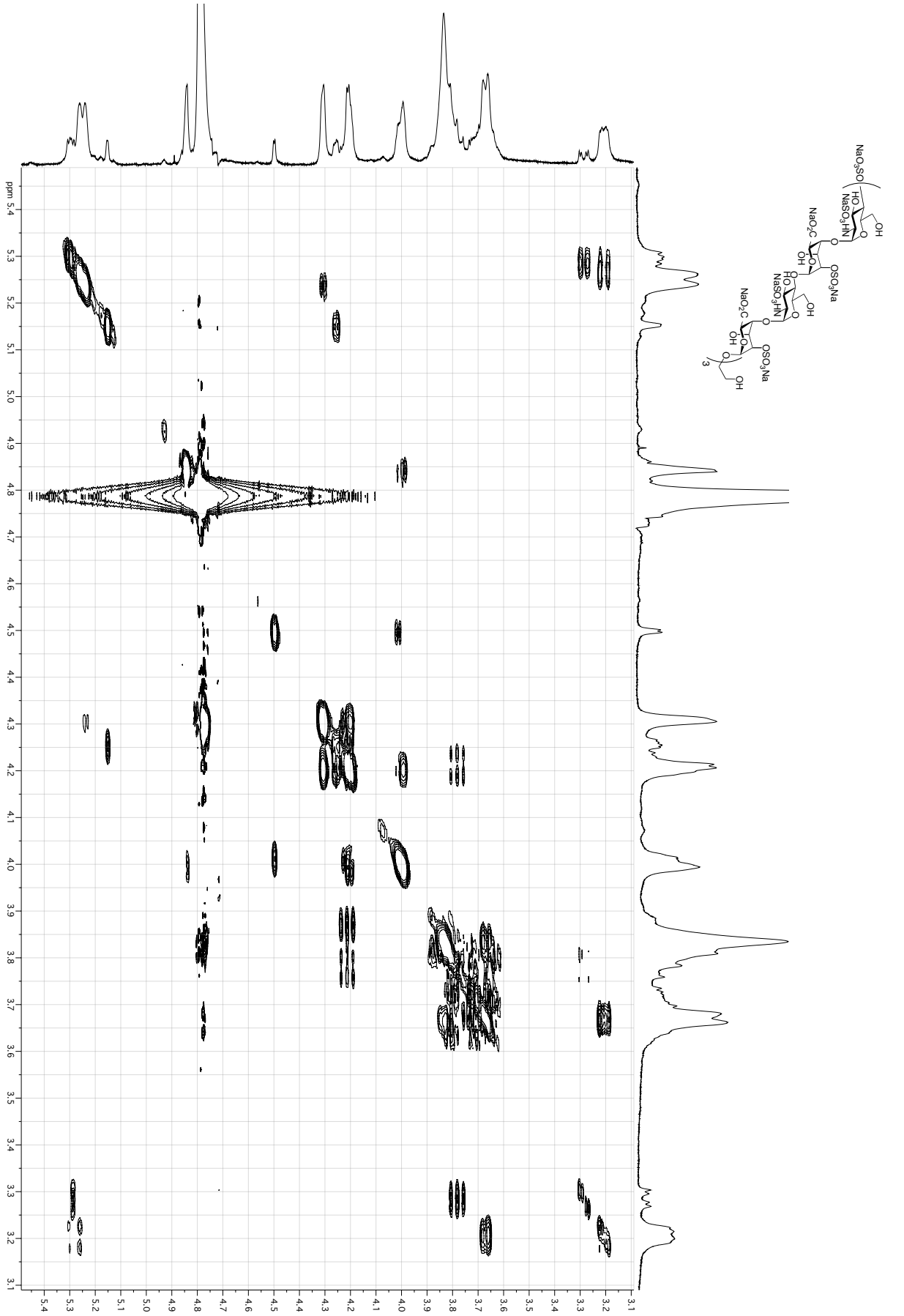
Supplementary Figure S66. COSY NMR spectrum for **15**



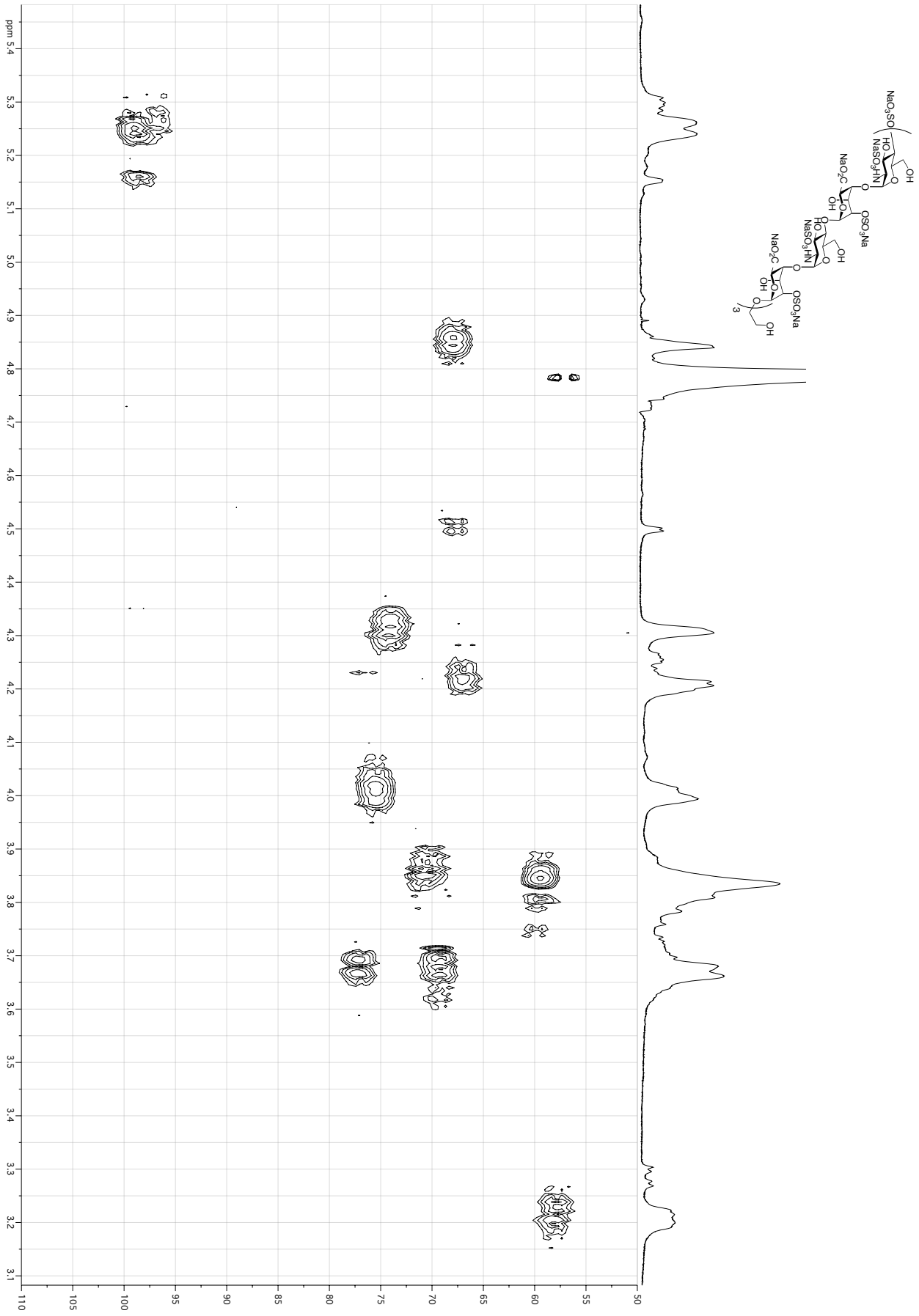
Supplementary Figure S67. HMQC NMR spectrum for **15**



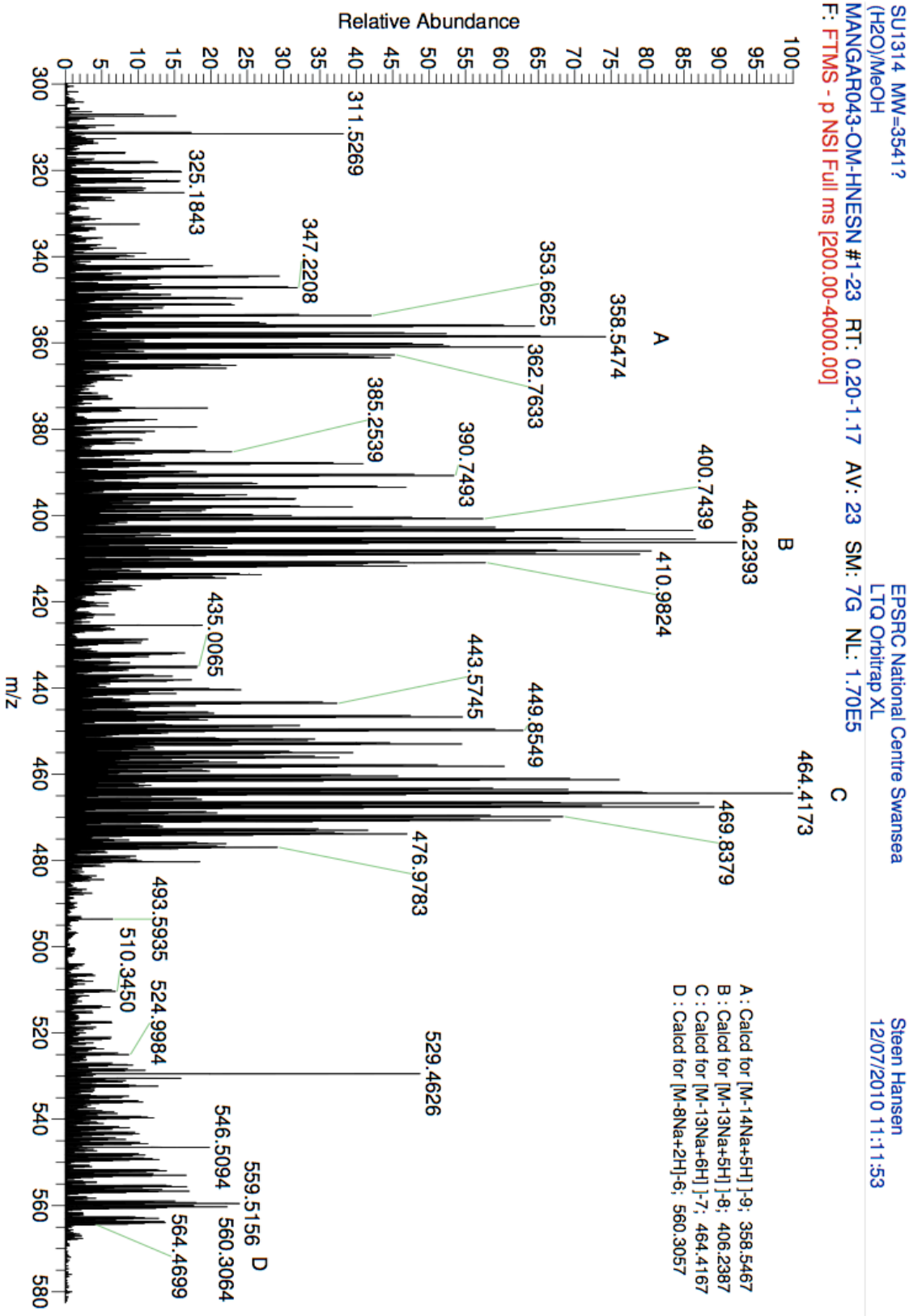
Supplementary Figure S68. ^{1}H NMR (400 MHz; D_2O) spectrum for **16**



Supplementary Figure S69. COSY NMR spectrum for **16**



Supplementary Figure S70. HMQC NMR spectrum for **16**



Supplementary Figure S71. FT MS negative mode assigned spectrum for **16**

Supplementary methods

General methods

All the chemicals used were purchased from commercial sources without further purification. All reactions were monitored by TLC on Merck silica gel plates $^{60}F_{254}$. Silica gel 60 (particle size 0.035-0.070 mm) was used for column chromatography. ^{1}H NMR spectra were recorded at 500 or 400 MHz and ^{13}C spectra at 100 MHz respectively on Bruker DPX spectrometers. Mass spectra (MS) were recorded using a Micromass Platform II spectrometer using an electro spray ionization source or via the EPSRC National Mass Spectrometry Service (Swansea). Isotope patterns for compounds with mass > 1000 are included in the SI. Optical rotations were obtained using an AA-1000 polarimeter. Elemental analyses were performed by Micro Analytical Laboratory, School of Chemistry, The University of Manchester.
NMR Data were reprocessed using iNMR 4 from Nucleomatica.

Synthesis of Oligosaccharides

Methyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-*p*-methoxybenzyl-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-L-idopyranose uronate) (3)
To **2** (1.85 g, 1.88 mmol) was added acetone 50 mL and cooled to 0 °C in an ice-bath. *N*-Bromosuccinimide (335 mg, 1.88 mmol) was then added and the mixture stirred for 45 min. The reaction was quenched by addition of saturated $NaHCO_3$ solution (5 mL), the acetone evaporated and DCM (200 mL) and water (200 mL) added. The organic phase was separated, dried ($MgSO_4$), filtered and evaporated. The crude product was purified using flash column chromatography (EtOAc/hexane 1:2) to yield 1.45 g (87%) of **3** as a white foam (α/β ~ 1:1). R_f 0.17 (EtOAc/ Hexane 1:2). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.11-8.07 (m, 2H, Bz), 7.40-7.17 (m, 16H, Ph), 7.11-7.07 (m, 2H, Bz), 7.02 (d, *J* = 8.8 Hz, 2H, PMB), 6.84 (d, *J* = 8.8 Hz, 2H, PMB), 5.46-5.43 (m, 1H, H-1α), 5.22 (dd, *J* = 11.6 Hz, 2 Hz, 1H, H-1β), 5.08-5.06 (m, 2H, H-2α, H-2β), 4.91-4.90 (m, 1H, H-5α), 4.90-4.75 (m, 2H, C*H*$_2$Ph), 4.69 (d, *J* = 3.6 Hz, 1H, H'-1), 4.66 (d, *J* = 3.6 Hz, 1H, H'-1), 4.62-4.35 (m, 4H, C*H*$_2$Ph, C*H*$_2$PMP), 4.60-4.59 (m, 1H, H-5β), 4.33 (t, *J* = 2.8 Hz, 1H, H-3β), 4.30 (dt, *J* = 2.8 Hz, 1.2 Hz, 1H, H-3α), 4.20 (d, *J* = 9.2 Hz, 1H, O*H*α), 4.06-3.59 (m, 14H, H-4, H'-4, H'-5, H'-6, C*H*$_2$Ph), 3.82 (s, 3H, PhOC*H*$_3$), 3.81 (s, 3H, PhOC*H*$_3$), 3.74 (s, 3H, COOC*H*$_3$), 3.73 (s, 3H, COOC*H*$_3$), 3.41-3.36 (m, 2H, H'-3), 3.25-3.21 (m, 2H, H'-2). ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.5, 168.7, 165.9, 165.7, 159.2, 137.9, 137.9, 137.8, 137.0, 136.5, 133.4, 133.3, 130.4, 130.0, 129.5, 129.4, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 127.7, 127.6, 113.6, 100.4, 93.8, 92.6, 80.2, 80.0, 77.4, 77.3, 77.3, 76.2, 75.9, 74.5, 74.5, 74.0, 73.7, 73.6, 73.4, 73.0, 71.8, 71.7, 68.6, 67.6, 67.5, 67.0, 63.7, 63.7, 56.3, 55.3, 52.5, 52.4. HRMS (FT MS): m/z: calcd for $C_{49}H_{55}N_4O_{13}$ $[M+NH_4]^+$: 907.3760; found: 907.3766.

Methyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-*p*-methoxybenzyl-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-1-trichloroacetimidate-α/β-L-idopyranuronate) (4)
To **3** (505 mg, 0.57 mmol) was added dry DCM (10 mL), CCl_3CN (0.40 mL, 3.99 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (10 μL, 0.07 mmol) and the mixture stirred under N_2 for 1 h. The solution was evaporated and the crude product was purified using flash column

chromatography (EtOAc/hexane 1:3 with 1% NEt_3), yielding 535 mg (91%) of **4** as an oil (α/β ~ 3:1). α-**4**: R_f 0.30 (EtOAc/Hexane 1:3). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.70 (s, 1H, C=N*H*), 8.15-8.12 (m, 2H, Bz), 7.44-7.11 (m, 18H, Ph), 7.07 (d, *J* = 8.6 Hz, 2H, PMB), 6.87 (d, *J* = 8.6 Hz, 2H, PMB), 6.57-6.56 (m, 1H, H-1), 5.36-5.35 (m, 1H, H-2), 5.03 (d, *J* = 2.6 Hz, 1H, H-5), 4.96-4.77 (m, 2H, C*H*$_2$Ph), 4.81 (d, *J* = 3.5 Hz, 1H, H'-1), 4.63-4.40 (m, 4H, C*H*$_2$Ph, C*H*$_2$PMP), 4.27-4.26 (m, 1H, H-3), 4.20-4.19 (m, 1H, H-4), 4.13-4.11 (m, 1H, C*H*$_2$Ph), 3.93-3.81 (m, 4H, H'-5, H'-6a, H'-6b, C*H*$_2$Ph), 3.83 (s, 3H, PhOC*H*$_3$), 3.75 (s, 3H, COOC*H*$_3$), 3.71-3.66 (m, 1H, H'-4), 3.50 (t, *J* = 10.0 Hz, 1H, H'-3), 3.25 (dd, *J* = 10.3 Hz, *J* = 3.5 Hz, 1H, H'-2). ^{13}C NMR (100 MHz; $CDCl_3$) δ 168.7, 165.5, 160.2, 159.3, 137.9, 137.8, 137.3, 133.5, 130.5, 130.1, 129.5, 129.3, 128.9, 128.4, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.7, 113.7, 100.3, 96.1, 90.8, 80.1, 77.4, 77.1, 76.7, 75.8, 74.6, 74.5, 73.6, 72.5, 72.2, 71.8, 69.0, 67.7, 65.7, 63.7, 55.4, 52.5.
β-**4**: R_f 0.16 (EtOAc/Hexane 1:3). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.68 (s, 1H, C=N*H*), 8.14-8.12 (m, 2H, Bz), 7.43-7.12 (m, 18H, Ph), 7.04 (d, *J* = 8.6 Hz, 2H, PMB), 6.85 (d, *J* = 8.6 Hz, 2H, PMB), 6.31 (d, *J* = 1.9 Hz, 1H, H-1), 5.48 (dd, *J* = 3.0 Hz, *J* = 1.9 Hz, 1H, H-2), 4.92-4.79 (m, 2H, C*H*$_2$Ph), 4.62-4.37 (m, 5H, H-3, C*H*$_2$Ph, C*H*$_2$PMP), 4.13-4.11 (m, 1H, C*H*$_2$Ph), 4.04-4.03 (m, 1H, H-4), 3.88-3.61 (m, 5H, H'-4 H'-5, H'-6a, H'-6b, C*H*$_2$Ph), 3.82 (s, 3H, PhOC*H*$_3$), 3.75 (s, 3H, COOC*H*$_3$), 3.48 (t, *J* = 10.2 Hz, 1H, H'-3), 3.28 (dd, *J* = 10.2 Hz, *J* = 3.5 Hz, 1H, H'-2). ^{13}C NMR (100 MHz; $CDCl_3$) δ 167.9, 166.3, 163.6, 160.4, 159.3, 137.9, 137.8, 136.9, 133.3, 130.4, 130.1, 129.6, 128.8, 128.7, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.7, 113.7, 100.5, 95.2, 90.5, 80.2, 77.4, 77.1, 76.8, 76.7, 76.2, 74.7, 74.6, 74.5, 73.8, 73.6, 73.3, 71.8, 67.7, 66.5, 63.8, 55.4, 52.5. HRMS (FT MS): m/z: calcd for $C_{51}H_{51}Cl_3N_4O_{13}$ [*M*+NH_4]$^+$: 1052.2844; found: 1052.2842.

Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-p-methoxybenzyl-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(phenyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-L-idopyranoside)] uronate (β-6)

To **5** (1.05 g, 1.21 mmol) and **4** (1.43 g, 1.38 mmol) was added dry DCM (20 mL), the mixture cooled to -25 °C and TMSOTf (2 μL, 0.01 mmol) added and the mixture stirred under a N_2 atmosphere for 30 min. More TMSOTf (2 μL, 0.01 mmol) was then added, the mixture left another 30 min. and then quenched by addition of a few drops of NEt_3. The solution was evaporated and the crude product was purified using flash column chromatography (EtOAc/hexane 1:3). A second column (DCM/EtOAc 20:1) removed remaining Cl_3CONH_2. This yielded 1.80 g (85%) of the product β-**6** as a foam. R_f 0.16 (EtOAc/Hexane 1:3). $[\alpha]_D^{20}$ = +21.1 (*c* = 0.85, CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.23-8.21 (m, 2H, Bz), 7.96-7.94 (m, 2H, Bz), 7.56-7.53 (m, 2H, Bz), 7.41-7.21 (m, 35H, Ph), 7.09-7.05 (m, 4H, Bz, PMB), 6.84 (d, *J* = 8.4 Hz, 2H, PMB), 5.50 (d, *J* = 4.0 Hz, 1H, H''-1), 5.26 (d, *J* = 2.0 Hz, 1H, H-1), 5.23-5.22 (m, 1H, H-2), 5.19 (t, *J* = 4.4 Hz, 1H, H''-2), 4.96 (d, 1H, *J* = 3.6 Hz, H'-1), 4.88-4.74 (m, 4H, C*H*$_2$Ph, C*H*$_2$PMP), 4.65-4.42 (m, 12H, H'''-1, H-4, H-5, H''-5, 4xC*H*$_2$Ph), 4.62-4.35 (m, 4H, C*H*$_2$Ph, C*H*$_2$PMP), 4.60-4.59 (m, 1H, H-5β), 4.33 (t, *J* = 2.8 Hz, 1H, H-3β), 4.30-4.21 (m, 4H, H-3, H''-3, C*H*$_2$Ph), 4.04 (t, *J* = 4.4 Hz, 1H, H''-4), 3.93-3.37 (m, 10H, H'-3, H'-4, H'-5, H'-6, H'''-3, H'''-4, H'''-5, H'''-6), 3.81 (s, 3H, PhOC*H*$_3$), 3.48 (s, 3H, COOC*H*$_3$), 3.43 (s, 3H, COOC*H*$_3$), 3.27-3.21 (m, 2H, H'-2, H'''-2). ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.2, 168.6, 166.4, 165.2, 159.3, 138.0, 137.9, 137.9, 137.4, 137.0, 134.8, 133.4, 133.3, 131.5, 130.4, 130.1, 129.9, 129.7, 129.5, 129.4, 129.0, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.2, 113.7, 99.7, 99.0, 98.3, 86.0, 79.9, 78.7, 77.6, 77.5, 77.4, 77.2, 76.8, 75.7, 75.5, 75.4, 75.1, 74.9,

74.6, 74.4, 73.9, 73.6, 72.9, 72.4, 71.7, 71.4, 70.2, 70.0, 69.7, 67.7, 67.6, 63.8, 63.5, 55.4, 52.1, 51.9. HRMS (FT MS): m/z: calcd for $C_{96}H_{100}N_7O_{23}S$ [*M*+NH_4]$^+$: 1750.6586; found: 1750.6578.

Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(phenyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-L-idopyranoside)] uronate (β-7)

To β-**6** (952 mg, 0.55 mmol) was added CH_3CN (33 mL) and water (3 mL) followed by ammonium cerium(IV) nitrate (99.99+%, 751 mg, 1.37 mmol). The orange solution was stirred for 90 min and was then extracted with DCM (200 mL, 50 mL) and water (200 mL), dried ($MgSO_4$), filtered and evaporated. The crude product was purified using flash column chromatography (EtOAc/hexane 1:3) yielding β-**7** (596 mg, 67%) as a white foam and recovered starting material (259 mg, 27%). R_f 0.20 (EtOAc/Hexane 1:2). $[\alpha]_D^{20}$ = +10.4 (*c* = 0.12, CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.21-8.18 (m, 2H, Bz), 7.97-7.94 (m, 2H, Bz), 7.53-7.50 (m, 2H, Bz), 7.42-7.05 (m, 35H, Ph), 5.55 (d, *J* = 4.8 Hz, 1H, H''-1), 5.23 (d, *J* = 1.6 Hz, 1H, H-1), 5.21-5.18 (m, 2H, H-2, H''-2), 4.95 (d, 1H, *J* = 3.6 Hz, H'-1), 4.86-4.72 (m, 4H, 2xC*H*$_2$Ph), 4.59-4.46 (m, 9H, H'''-1, H''-5, H-5, 3xC*H*$_2$Ph), 4.26-4.20 (m, 2H, H-3, H''-3), 4.26-3.34 (m, 13H, H-4, H''-4, H'-3, H'-4, H'-5, H'-6, H'''-3, H'''-5, H'''-6, C*H*$_2$Ph), 3.43 (s, 3H, COOC*H*$_3$), 3.41 (s, 3H, COOC*H*$_3$), 3.23-3.17 (m, 3H, H'-2, H'''-2, H'''-4). ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.3, 168.6, 166.4, 165.2, 138.0, 138.0, 137.9, 137.6, 137.4, 136.9, 134.7, 133.4, 133.3, 131.4, 131.1, 130.1, 130.0, 129.9, 129.9, 129.6, 129.4, 129.0, 128.9, 128.8, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.2, 99.3, 99.0, 98.1, 85.9, 79.2, 78.5, 77.4, 77.1, 77.1, 76.8, 75.8, 75.7, 75.6, 75.0, 75.0, 74.8, 74.5, 74.1, 73.8, 73.6, 72.8, 72.5, 72.3, 71.3, 70.8, 70.5, 70.2, 70.0, 69.4, 67.4, 63.6, 62.7, 52.1, 51.9. HRMS (FT MS): m/z: calcd for $C_{88}H_{92}N_7O_{22}S$ [*M*+NH_4]$^+$: 1630.6011; found: 1630.6009.

Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-trichloroacetyl-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(phenyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-L-idopyranoside)] uronate (α-8 and β-8)

The tetrasaccharide α-**7** (596 mg, 0.37 mmol) was dissolved in dry DCM (5 mL), cooled to 0 °C in an icebath, then dry pyridine (0.15 mL, 1.85 mmol) and trichloroacetyl chloride (0.10 mL, 0.93 mmol) was added. The solution was stirred for 1 h. The solution was extracted with DCM (50 mL) and water (50 mL), dried ($MgSO_4$), filtered and evaporated. The crude product was purified using flash column chromatography (EtOAc/hexane 1:3). This yielded α-**8 (**610 mg, 94%) as a white foam. The same procedure was used for converting β-**7** into β-**8**.

α-**8**: R_f 0.23 (EtOAc/Hexane 1:3). $[\alpha]_D^{20}$ = -18.3 (*c* = 0.84, CH_2Cl_2). ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.13-8.11 (m, 2H, Bz), 8.02-8.00 (m, 2H, Bz), 7.53-7.12 (m, 35H, Ph), 5.78-5.77 (m, 1H, H-1), 5.55 (d, *J* = 3.8 Hz, 1H, H''-1), 5.37-5.38 (m, 1H, H-2), 5.31-5.27 (m, 2H, H'''-4, H-5), 5.17 (t, 1H, *J* = 4.4 Hz, H''-2), 4.97-4.75 (m, 4H, 2xC*H*$_2$Ph), 4.90 (d, *J* = 3.6 Hz, 1H, H'-1 or H'''-1), 4.69 (d, *J* = 3.6 Hz, 1H, H'-1 or H'''-1), 4.64 (d, *J* = 4.1 Hz, 1H, H''-5), 4.53-4.25 (m, 6H, 3xC*H*$_2$Ph), 4.21 (t, *J* = 5.2 Hz, 1H, H''-3), 4.19-4.18 (m, 1H, H-3), 4.02-4.01 (m, 1H, H-4), 3.99-3.41 (m, 13H, H''-4, H'-3, H'-4, H'-5, H'-6, H'''-3, H'''-4, H'''-5, H'''-6, C*H*$_2$Ph), 3.55 (s, 3H, COOC*H*$_3$), 3.45 (s, 3H, COOC*H*$_3$), 3.37 (dd, 1H, *J* = 10.1 Hz, 3.4 Hz H'-2 or H'''-2), 3.27 (dd, 1H, *J* = 10.3 Hz, 3.6 Hz H'-2 or H'''-2). ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.3, 169.2, 165.6, 165.3, 160.2, 138.0, 137.8, 137.3, 137.1, 136.8, 135.4, 133.6, 133.5, 131.3, 130.0, 129.9, 129.6, 129.5, 129.1, 128.8, 128.6,

128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.0, 128.0, 127.9, 127.7, 127.6, 127.4, 127.2, 99.8, 99.2, 98.5, 89.7, 86.8, 78.6, 77.6, 77.5, 77.2, 76.8, 76.5, 76.0, 75.9, 74.9, 74.8, 74.8, 74.1, 73.9, 73.8, 73.6, 72.8, 71.9, 71.4, 70.5, 69.6, 69.3, 69.2, 68.5, 67.7, 67.2, 63.8, 63.1, 60.5, 52.1, 51.9. ES MS: m/z: calcd for $C_{90}H_{87}Cl_3N_6O_{23}SNa$ [*M*+Na]$^+$: 1779.5; found: 1779.5. Elemental analysis calcd (%) for $C_{90}H_{87}Cl_3N_6O_{23}S$: C 61.45, H 4.98, N 4.78; found C 61.71, H 5.05, N 4.69. β-**8**: R_f 0.18 (EtOAc/Hexane 1:3). $[\alpha]_D^{20}$ = +32.9 (*c* = 0.61, CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.24-8.21 (m, 2H, Bz), 8.03-8.00 (m, 2H, Bz), 7.57-7.54 (m, 2H, Bz), 7.45-7.07 (m, 35H, Ph), 5.56 (d, *J* = 3.8 Hz, 1H, H''-1), 5.32 (t, *J* = 9.4 Hz, 1H, H'''-4), 5.27 (d, *J* = 1.9 Hz, 1H, H-1), 5.24-5.23 (m, 1H, H-2), 5.18 (t, *J* = 4.4 Hz, H''-2), 4.90-4.75 (m, 5H, H'-1, 2xC*H*$_2$Ph), 4.64 (d, *J* = 4.4 Hz, H-5 or H-5''), 4.55-4.45 (m, 6H, H'''-1, H''-5 or H-5, 2xC*H*$_2$Ph), 4.33-4.18 (m, 4H, H-3, H''-3, C*H*$_2$Ph), 4.01-3.90 (m, 4H, H-4, H''-4, C*H*$_2$Ph), 3.74-3.37 (m, 10H, H'-2, H'-3, H'-4, H'-5, H'-6, H'''-3, H'''-5, H'''-6), 3.50 (s, 3H, COOC*H*$_3$), 3.39 (s, 3H, COOC*H*$_3$), 3.25 (dd, *J* = 10.3 Hz, *J* = 3.6 Hz, 1H, H'''-2). ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.2, 168.6, 166.4, 165.3, 160.2, 138.0, 137.8, 137.3, 137.3, 137.0, 136.8, 134.7, 133.4, 133.4, 131.5, 130.1, 129.9, 129.7, 129.5, 129.0, 128.8, 128.7, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.7, 127.6, 127.5, 127.4, 127.1, 99.3, 99.2, 98.3, 89.7, 85.9, 78.5, 77.5, 77.4, 76.1, 75.7, 75.3, 74.9, 74.8, 74.6, 74.2, 73.8, 73.8, 73.6, 72.9, 72.5, 71.3, 70.2, 70.0, 69.4, 69.1, 67.8, 67.2, 63.9, 63.1, 52.1, 51.9.

Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)- 2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-((*S*)-2,3-bis(benzyloxy)propyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranoside)] uronate (9)

Tetrasaccharide α-**7** (145 mg, 0.082 mmol) was dissolved in dry DCM (2 mL) under N_2. (*S*)-2,3-Bis(benzyloxy)propanol (44 mg, 0.163 mmol) was added and the clear solution cooled to 0 °C. Freshly activated 4Å powdered molecular sieves (137 mg) were added, after 10 min. NIS (50 mg, 2.22 mmol) and after another 10 min. AgOTf (catalytic amount). The suspension changed colour from pale yellow to deep red and was stirred for a further 20 min. The reaction was quenched into $NaHCO_3$ (250 mg) and $Na_2S_2O_3$ (250 mg) in water (5 mL). After stirring for 10 mins and the reaction colour changing to pale yellow the suspension was filtered through a short pad of Celite® washing with water and DCM. The layers were separated and the aqueous extracted with DCM (10 mL). The organics were combined, dried ($MgSO_4$) and solvent removed *in vacuo* to reveal the crude product as a pale yellow oil. This was purified by flash column chromatography (EtOAc/Hexane 3:5) to give **9 (**130 mg, 82%) as a white foam. R_f 0.22 (EtOAc/Hexane 1:2). $[\alpha]_D^{20}$ = +0.7 (*c* = 0.37, CH_2Cl_2). ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.11-8.09 (m, 2H, Bz), 8.00-7.98 (m, 2H, Bz), 7.54-7.14 (m, 40H, Ph), 5.55 (d, *J* = 4.7 Hz, H''-1), 5.21 (t, 1H, *J* = 5.4 Hz, H''-2), 5.14-5.13 (m, 1H, H-1), 5.12-5.11 (m, H-2), 4.94 (d, *J* = 3.6 Hz, 1H, H'-1), 4.87-4.41 (m, 19H, H'''-1, H-5, H''-5, 8xC*H*$_2$Ph), 4.21 (t, *J* = 6.0 Hz, 1H, H''-3), 4.10-4.09 (m, 1H, H-3), 4.04-4.01 (m, 1H, H''-4), 3.99-3.98 (m, 1H, H-4), 3.96-3.42 (m, 15H, H'-3, H'-4, H'-5, H'-6, H'''-3, H'''-4, H'''-5, H'''-6, C*H*$_2$C*H*OBnC*H*$_2$OBn)), 3.46 (s, 3H, COOC*H*$_3$), 3.44 (s, 3H, COOC*H*$_3$), 3.23 (dd, 1H, *J* = 10.2 Hz, 3.6 Hz H'-2 or H'''-2), 3.19 (dd, 1H, *J* = 10.3 Hz, 3.6 Hz H'-2 or H'''-2). ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.6, 169.5, 169.4, 165.8, 165.4, 138.6, 138.3, 138.2, 138.1, 138.0, 137.7, 137.7, 137.5, 133.6, 130.1, 129.8, 129.6, 128.9, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.4, 99.4, 99.3, 98.4, 79.4, 78.6, 77.5, 76.8, 76.0, 75.9, 75.8, 75.1, 74.9, 74.5, 74.2, 73.9, 73.8, 73.5, 72.8, 72.5, 71.5, 71.2, 70.7, 70.5, 69.8, 69.6, 68.6, 67.8, 67.6, 67.5, 63.7, 62.9, 60.6, 52.1, 52.0. HRMS (FT MS): m/z: calcd for

$C_{99}H_{106}N_7O_{25}$ [*M*+NH_4^+]: 1792.7233; found: 1792.7212. Elemental analysis calcd (%) for $C_{99}H_{102}N_6O_{25}$: C 66.96, H 5.79, N 4.73; found C 66.71, H 5.69, N 4.68.

Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-*p*-methoxybenzyl-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate))-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-((*S*)-2,3-bis(benzyloxy)propyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranoside)] uronate (10)

Tetrasaccharide **9** (55 mg, 0.031 mmol) and donor β-**6** (65 mg, 0.037 mmol) was dissolved in dry DCM (1 mL) under N_2. Freshly activated 4Å powdered molecular sieves (100 mg) were added and the solution cooled to 0 °C in an ice-bath. After 10 min. NIS (13 mg, 0.046 mmol) was added, and after another 10 min. AgOTf (catalytic amount) was added. The suspension changed colour from pale yellow to deep red and was stirred for a further 35 min. The reaction was quenched by pouring into a separating funnel containing a mixture of DCM (20 mL), saturated aqueous $NaHCO_3$ (20 mL) and $Na_2S_2O_3$ (2 mL, 10% aqueous). After shaking until the iodine colour was removed the suspension was filtered through a short pad of Celite® washing with water and DCM. The layers were separated and the aqueous extracted with DCM (10 mL). The organic layers were combined, dried ($MgSO_4$) and solvent removed *in vacuo*. The crude product was purified by silica gel flash column chromatography (EtOAc/hexane 3:7) to give **10 (**85 mg, 81%) as a white foam. R_f 0.24 (EtOAc/Hexane 1:2). $[\alpha]_D^{20}$ = +9.1 (*c* = 0.78, CH_2Cl_2). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.10-8.08 (m, 2H, Bz), 7.95-7.91 (m, 6H, Bz), 7.55-7.00 (m, 84H, Ph, PMB), 6.83 (d, 1H, *J* = 8.8 Hz, PMB), 5.55-5.51 (m, 3H, H''-1, H''''-1, H''''''-1), 5.19-5.15 (m, 3H, H''-2, H''''-2, H''''''-2), 5.11-5.10 (m, 2H, H-1, H-2), 4.97 (d, 1H, *J* = 3.5 Hz, H'-1 or H'''-1 or H'''''-1), 4.93 (d, 1H, *J* = 3.5 Hz, H'-1 or H'''-1 or H'''''-1), 4.89 (d, 1H, *J* = 3.8 Hz, H'-1 or H'''-1 or H'''''-1), 4.88-4.29 (m, 33H, H'''''''-1, H-5, H''-5, H''''-5, H''''''-5, 14xCH_2Ph), 4.23-4.07 (m, 4H, H-3, H''-3, H''''-3, H''''''-3), 4.05-3.19 (m, 32H, H'-2, H'''-2, H'''''-2, H'''''''-2, H'-3, H'''-3, H-3''''', H'''''''-3, H-4, H''-4, H''''-4, H''''''-4, H'-4, H'''-4, H'''''-4, H'-5, H'''-5, H'''''-5, H'''''''-5, H'-6, H'''-6, H'''''-6, H'''''''-6, CH_2CHOBnCH_2OBn), 3.81 (s, 3H, PhOCH_3), 3.46 (s, 3H, COOCH_3), 3.41 (s, 3H, COOCH_3), 3.30 (s, 3H, COOCH_3), 3.23 (s, 3H, COOCH_3). HRMS (FTMS) : m/z: calcd for $C_{189}H_{200}N_{14}O_{48}$ [*M* +2NH_4]$^{2+}$: 1717.6848; found: 1717.6827.

Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-trichloroacetyl-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-((*S*)-2,3-bis(benzyloxy)propyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranoside)] uronate (11)

Tetrasaccharide **9** (68 mg, 0.038 mmol) and donor α-**8** (81 mg, 0.046 mmol) was dissolved in dry DCM (1.5 mL) under N_2. Freshly activated 4Å powdered molecular sieves (111 mg) were added and the solution cooled to 0 °C in an icebath. After 10 min. NIS (17 mg, 0.076 mmol) was added, and after another 10 min. AgOTf (catalytic amount) was added. The suspension changed colour from pale yellow to deep red and was stirred for a further 45 min. The reaction was quenched into a

separating funnel containing a mixture of DCM (30 mL), saturated aqueous $NaHCO_3$ (25 mL) and $Na_2S_2O_3$ (2 mL, 10% aqueous). After shaking until the iodine colour was removed the suspension was filtered through a short pad of Celite® washing with water and DCM. The layers were separated and the aqueous extracted with DCM (10 mL). The organic layers were combined, dried ($MgSO_4$) and solvent removed *in vacuo*. The crude was purified by silica gel flash column chromatography (toluene/acetone 20:1) to give **11 (**120 mg, 92%) of as a white foam. R_f 0.23 (EtOAc/Hexane 1:2). $[\alpha]_D^{20}$ = +12.9 (*c* = 0.35, CH_2Cl_2). ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.10-8.08 (m, 2H, Bz), 8.02-8.00 (m, 2H, Bz), 7.96-7.93 (m, 4H, Bz), 7.53-7.03 (m, 82H, Ph), 5.57-5.52 (m, 3H, H''-1, H''''-1, H''''''-1), 5.30 (t, 1H, *J* = 9.8 Hz, H'''''''-4), 5.19-5.16 (m, 3H, H''-2, H''''-2, H''''''-2), 5.12-5.11 (m, 2H, H-1, H-2), 4.94-4.90 (m, 3H, H'-1, H'''-1, H'''''-1), 4.87-4.24 (m, 33H, H'''''''-1, H-5, H''-5, H''''-5, H''''''-5, 14xCH_2Ph), 4.24-4.09 (m, 4H, H-3, H''-3, H''''-3, H''''''-3), 4.04-3.20 (m, 32H, H'-2, H'''-2, H'''''-2, H'''''''-2, H'-3, H'''-3, H-3''''', H'''''''-3, H-4, H''-4, H''''-4, H''''''-4, H'-4, H'''-4, H'''''-4, H'-5, H'''-5, H'''''-5, H'''''''-5, H'-6, H'''-6, H'''''-6, H'''''''-6, CH_2CHOBnCH_2OBn), 3.47 (s, 3H, COOCH_3), 3.44 (s, 3H, COOCH_3), 3.33 (s, 3H, COOCH_3), 3.27 (s, 3H, COOCH_3). ^{13}C NMR (100 MHz; $CDCl_3$) δ 169.4, 169.3, 169.2, 165.6, 165.2, 165.1, 160.2, 138.5, 138.1, 138.0, 137.9, 137.8, 137.7, 137.7, 137.5, 137.4, 137.4, 137.2, 137.2, 136.7, 133.6, 133.5, 129.9, 129.9, 129.8, 129.8, 129.6, 129.4, 129.3, 129.2, 128.8, 128.7, 128.7, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 127.3, 127.3, 127.1, 99.3, 99.3, 99.2, 99.1, 99.1, 98.3, 98.0, 98.0, 89.7, 78.3, 78.2, 78.1, 77.5, 77.4, 77.2, 77.0, 77.0, 76.8, 76.7, 76.7, 76.7, 76.6, 76.6, 76.5, 76.5, 75.9, 75.8, 75.7, 75.7, 75.6, 75.4, 75.4, 75.3, 74.9, 74.8, 74.8, 74.6, 74.4, 74.2, 74.1, 74.1, 73.8, 73.7, 73.6, 73.6, 73.5, 73.3, 73.2, 72.6, 72.4, 71.3, 71.2, 71.1, 70.5, 70.5, 70.4, 69.6, 69.2, 68.4, 68.3, 67.5, 67.3, 67.2, 67.2, 63.4, 63.4, 63.2, 63.2, 63.1, 60.4, 53.5, 51.9, 51.7, 51.6. MS (MALDI-TOF): m/z: calcd for $C_{183}H_{183}Cl_3N_{12}NaO_{48}$ [*M*+Na]$^+$: 3444.1; found: 3444.1. Elemental analysis calcd (%) for $C_{183}H_{183}Cl_3N_{12}O_{48}$: C 64.18, H 5.39, N 4.91; found C 64.10, H 5.32, N 4.89.

Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate))-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-((*S*)-2,3-bis(benzyloxy)propyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranoside)] uronate (12)

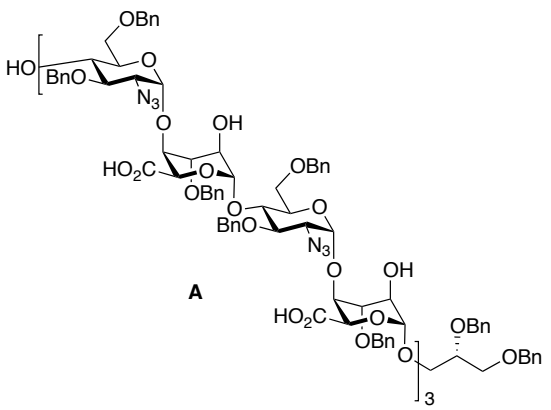
The octasaccharide **11** (346 mg, 0.10 mmol) was dissolved in a mixture of MeOH/pyridine (5 mL/2 mL) and heated to 50 °C for 4 h. The solvents were evaporated and co-evaporated with toluene (2x20 mL). The crude product was purified using flash column chromatography (EtOAc/hexane 1:2 and 3:5). This yielded **12** (300 mg, 91%) as a white foam, along with recovered starting material (20 mg, 5%). R_f 0.10 (EtOAc/Hexane 1:2). $[\alpha]_D^{20}$ = +9.8 (*c* = 0.32, CH_2Cl_2). ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.10-8.08 (m, 2H, Bz), 8.00-7.93 (m, 6H, Bz), 7.54-7.03 (m, 82H, Ph), 5.57-5.52 (m, 3H, H''-1, H''''-1, H''''''-1), 5.22-5.15 (m, 3H, H''-2, H''''-2, H''''''-2), 5.12-5.11 (m, 2H, H-1, H-2), 4.97 (d, 1H, *J* = 3.5 Hz, H'-1 or H'''-1 or H'''''-1), 4.93 (d, 1H, *J* = 3.6 Hz, H'-1 or H'''-1 or H'''''-1), 4.90 (d, 1H, *J* = 3.6 Hz, H'-1 or H'''-1 or H'''''-1), 4.86-4.34 (m, 33H, H'''''''-1, H-5, H''-5, H''''-5, H''''''-5, 14xCH_2Ph), 4.24-4.08 (m, 4H, H-3, H''-3, H''''-3, H''''''-3), 4.05-3.20 (m, 32H, H'-2, H'''-2, H'''''-2, H'''''''-2, H'-3, H'''-3, H-3''''', H'''''''-3, H-4, H''-4, H''''-4, H''''''-4, H'-4, H'''-4, H'''''-4, H'-5, H'''-5, H'''''-5, H'''''''-5, H'-6, H'''-6, H'''''-6, H'''''''-6, CH_2CHOBnCH_2OBn), 3.48 (s, 3H, COOCH_3), 3.44 (s, 3H, COOCH_3), 3.32 (s, 3H, COOCH_3), 3.27

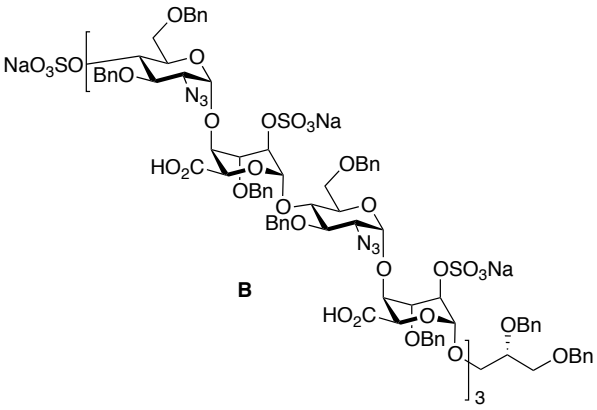
(s, 3H, COOCH_3), 2.55 (d, 1H, J = 2 Hz, OH). ^{13}C NMR (100 MHz; CDCl3): δ 169.4, 169.3, 169.3, 169.2, 165.6, 165.2, 165.2, 138.5, 138.1, 138.0, 138.0, 137.9, 137.9, 137.8, 137.6, 137.5, 137.4, 137.4, 133.6, 133.5, 130.0, 130.0, 129.9, 129.8, 129.8, 129.6, 129.4, 129.3, 129.3, 129.0, 128.9, 128.9, 128.8, 128.7, 128.6, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.4, 127.3, 99.3, 99.2, 99.1, 99.1, 98.2, 98.1, 98.1, 98.0, 79.2, 78.3, 78.2, 78.1, 77.5, 77.4, 77.2, 77.1, 77.0, 76.8, 76.8, 76.7, 76.6, 75.9, 75.8, 75.5, 75.4, 75.3, 74.8, 74.8, 74.5, 74.4, 74.3, 74.2, 74.2, 74.1, 73.8, 73.7, 73.6, 73.6, 73.3, 72.7, 72.4, 71.4, 71.3, 71.3, 71.1, 70.6, 70.6, 70.4, 70.4, 69.6, 69.5, 68.4, 67.6, 67.4, 67.4, 67.3, 63.5, 63.1, 63.0, 63.0, 62.7, 53.5, 52.0, 51.9, 51.9, 51.7, 51.6. MS (MALDI-TOF): m/z: calcd for $C_{181}H_{184}N_{12}NaO_{47}$ [M+Na]$^+$: 3300.2; found: 3300.2. Elemental analysis calcd (%) for $C_{181}H_{184}N_{12}O_{47}$: C 66.29, H 5.66, N 5.13; found C 66.57, H 5.98, N 4.96.

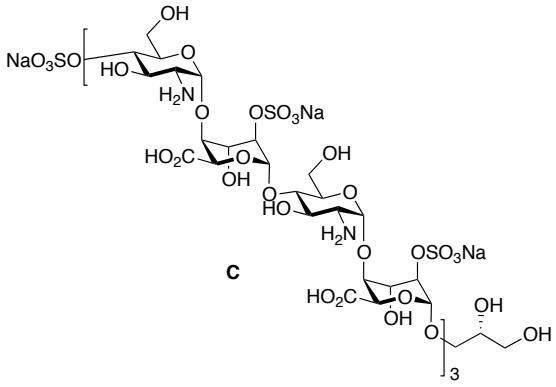
Methyl [2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-trichloroacetyl-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate))-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyl uronate)-(1⟶4)-2-azido-3,6-di-*O*-benzyl-2-deoxy-α-D-glucopyranosyl-(1⟶4)-((*S*)-2,3-bis(benzyloxy)propyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranoside)] uronate (13)

For experimental procedure see main manuscript. R_f 0.17 (EtOAc/Hexane 7:13). $[\alpha]_D^{20}$ = +18.1 (c = 0.68, CH_2Cl_2). ^{1}H NMR (500 MHz; $CDCl_3$) δ 8.10-8.08 (m, 2H, Bz), 8.02-8.00 (m, 2H, Bz), 7.96-7.91 (m, 8H, Bz), 7.53-7.02 (m, 118H, Ph), 5.57-5.52 (m, 5H, H''-1, H''''-1, H''''''-1, H''''''''-1, H''''''''''-1), 5.29 (t, 1H, J = 9.7 Hz, H'''''''''''-4), 5.19-5.14 (m, 5H, H''-2, H''''-2, H''''''-2, H''''''''-2, H''''''''''-2), 5.12-5.11 (m, 2H, H-1, H-2), 4.94-4.89 (m, 5H, H'-1, H'''-1, H'''''-1, H'''''''-1, H'''''''''-1), 4.86-4.27 (m, 47H, H'''''''''''-1, H-5, H''-5, H''''-5, H''''''-5, H''''''''-5, H''''''''''-5, 20xCH_2Ph), 4.24-4.08 (m, 6H, H-3, H''-3, H''''-3, H''''''-3, H''''''''-3, H''''''''''-3), 4.04-3.19 (m, 45H, H'-2, H'''-2, H'''''-2, H'''''''-2, H'''''''''-2, H'''''''''''-2, H'-3, H'''-3, H-3''''', H'''''''-3, H'''''''''-3, H'''''''''''-3, H-4, H''-4, H''''-4, H''''''-4, H''''''''-4, H''''''''''-4, H'-4, H'''-4, H'''''-4, H'''''''-4, H'''''''''-4, H'-5, H'''-5, H'''''-5, H'''''''-5, H'''''''''-5, H'''''''''''-5, H'-6, H'''-6, H'''''-6, H'''''''-6, H'''''''''-6, H'''''''''''-6, CH_2CHOBnCH_2OBn), 3.46 (s, 3H, COOCH_3), 3.44 (s, 3H, COOCH_3), 3.33 (s, 3H, COOCH_3), 3.30 (s, 3H, COOCH_3), 3.29 (s, 3H, COOCH_3), 3.26 (s, 3H, COOCH_3). ^{13}C NMR (100 MHz; CDCl3): δ 169.5, 169.4, 169.3, 165.7, 165.4, 165.3, 165.2, 160.3, 138.6, 138.2, 138.1, 138.0, 137.9, 137.8, 137.8, 137.6, 137.5, 137.5, 137.3, 137.3, 136.9, 133.7, 133.7, 133.6, 130.0, 130.0, 129.9, 129.7, 129.5, 129.5, 129.4, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.7, 127.6, 127.4, 99.4, 99.4, 99.3, 99.2, 99.2, 99.1, 98.4, 98.2, 98.1, 98.1, 89.8, 78.4, 78.3, 76.8, 76.7, 76.7, 76.6, 76.6, 76.5, 76.1, 75.9, 75.8, 75.7, 75.7, 75.6, 75.5, 75.5, 75.4, 75.3, 75.0, 74.9, 74.8, 74.7, 74.6, 74.5, 74.3, 74.1, 74.1, 74.0, 74.0, 74.0, 73.9, 73.8, 73.7, 73.6, 73.6, 73.5, 73.5, 73.4, 73.3, 72.7, 72.7, 72.7, 72.5, 71.4, 71.4, 71.3, 71.3, 71.2, 71.2, 70.7, 70.7, 70.6, 70.6, 70.6, 70.5, 70.5, 70.4, 70.4, 69.7, 69.6, 69.3, 68.5, 68.4, 67.6, 67.6, 67.4, 67.3, 67.3, 67.2, 63.6, 63.3, 63.2, 63.1, 63.0, 53.6, 52.1, 51.8, 51.8, 51.7. MS (MALDI-TOF): m/z: calcd for $C_{265}H_{265}Cl_3N_{18}NaO_{70}$ [M+Na]$^+$: 4946.7; found: 4946.6. Elemental analysis calcd (%) for $C_{265}H_{265}Cl_3N_{18}O_{70}$: C 64.58, H 5.42, N 5.12; found C 63.91, H 5.41, N 5.06.

(*S*)-2,3-dihydroxypropyl 4-*O*-sulfonato-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate -(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranoside uronate nonadecasodium salt (14)







Dodecasaccharide **A** was used directly.

Sulfation of hydroxyls: Dodecasaccharide **B** R_f 0.29 (DCM/MeOH 5:1). ^{1}H NMR (400 MHz; $CDCl_3/CD_3OD$ 10:1) δ 7.34-6.96 (m, 100H, Ph), 5.68-5.64 (m, 5H, H''-1, H''''-1, H''''''-1, H''''''''-1, H''''''''''-1), 5.36-5.34 (m, 1H, H-1), 5.06-3.36 (m, 104H, H'-1, H'''-1, H'''''-1, H''''''''-1, H''''''''''-1, H''''''''''-1, H-5, H''-5, H''''-5, H''''''-5, H''''''''-5, H''''''''''-5, H-3, H''-3, H''''-3, H''''''-3, H''''''''-3, H''''''''''-3, H'-2, H''-2, H'''-2, H''''-2, H'''''-2, H''''''-2, H''''''''-2, H''''''''''-2, H''''''''''-2, H'''''''''''-2, H'-3, H'''-3, H-3''''', H''''''''-3, H''''''''''-3, H'''''''''''-3, H-4, H''-4, H''''-4, H''''''-4, H''''''''-4, H''''''''''-4, H'-4, H'''-4, H'''''-4, H''''''''-4, H''''''''''-4, H'''''''''''-4, H'-5, H'''-5, H'''''-5, H''''''''-5, H''''''''''-5, H'''''''''''-5, H'-6, H'''-6, H'''''-6, H''''''''-6, H''''''''''-6, H'''''''''''-6, CH_2CHOBnCH_2OBn, 20xCH_2Ph).

Hydrogenolysis of benzyls and azides: Dodecasaccharide **C** ^{1}H NMR (400 MHz; D_2O) δ 5.16-5.09 (m, 11H, H'-1,H''-1, H'''-1, H''''-1, H'''''-1, H''''''-1, H''''''''-1, H''''''''''-1, H''''''''''-1, H'''''''''''-1), 5.09-5.08 (m, 1H, H-1), 4.88-4.85 (m, 5H, H'''-5, H'''''-5, H''''''''-5, H''''''''''-5, H'''''''''''-5), 4.51 (d, J = 1.2 Hz, 1H, H-5'), 4.30-4.27 (m, 5H, H-2''', H-2''''', H-2''''''', H-2''''''''',

H-2’’’’’’’’’’’’), 4.24-4.18 (m, 7H, H-2’, H-3’, H-3’’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’’’), 4.15 (t, *J* = 9.6 Hz, 1H, H-4’’’’’’’’’’’’), 4.05-4.01 (m, 6H, H-4’’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’’’), 3.92-3.87 (m, 1H, $CH_2CHOHCH_2OH$), 3.83-3.75 (m, 18H, H-5’’, H-5’’’’, H-5’’’’’’, H-5’’’’’’’’, H-5’’’’’’’’’’, H-5’’’’’’’’’’’’, H-6’’, H-6’’’’, H-6’’’’’’, H-6’’’’’’’’, H-6’’’’’’’’’’, H-6’’’’’’’’’’’’), 3.75-3.53 (m, 15H, H-3’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’, H-3’’’’’’’’’’’’, H-4’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’, $CH_2CHOHCH_2OH$), 2.93-2.89 (m, 6H, H-2’’, H-2’’’’, H-2’’’’’’, H-2’’’’’’’’, H-2’’’’’’’’’’, H-2’’’’’’’’’’’’).

S*ulfation of amines*: Dodecasaccharide **14 (**78 mg, 100%) of as a glassy solid. ^{1}H NMR (400 MHz; D_2O) δ 5.32-5.16 (m, 11H, H’-1,H’’-1, H’’’-1, H’’’’-1, H’’’’’-1, H’’’’’’-1, H’’’’’’’-1, H’’’’’’’’-1, H’’’’’’’’’-1, H’’’’’’’’’’-1, H’’’’’’’’’’’-1), 5.15 (d, *J* = 1.6 Hz, 1H, H-1’), 4.88-4.85 (m, 5H, H’’’-5, H’’’’-5, H’’’’’’-5, H’’’’’’’’-5, H’’’’’’’’’’-5), 4.50 (d, *J* = 1.6 Hz, 1H, H-5’), 4.34-4.30 (m, 5H, H-2’’’, H-2’’’’, H-2’’’’’’, H-2’’’’’’’’, H-2’’’’’’’’’’), 4.28-4.21 (m, 8H, H-2’, H-3’, H-3’’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’, H-4’’’’’’’’’’), 4.05-3.98 (m, 6H, H-4’’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’), 3.94-3.88 (m, 1H, $CH_2CHOHCH_2OH$), 3.87-3.76 (m, 18H, H-5’’, H-5’’’’, H-5’’’’’’, H-5’’’’’’’’, H-5’’’’’’’’’’, H-5’’’’’’’’’’’’, H-6’’, H-6’’’’, H-6’’’’’’, H-6’’’’’’’’, H-6’’’’’’’’’’, H-6’’’’’’’’’’’’), 3.75-3.55 (m, 15H, H-3’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’, H-3’’’’’’’’’’’’, H-4’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’, $CH_2CHOHCH_2OH$), 3.32-3.18 (m, 6H, H-2’’, H-2’’’’, H-2’’’’’’, H-2’’’’’’’’, H-2’’’’’’’’’’, H-2’’’’’’’’’’’’).

^{13}C NMR (100 MHz; D2O): δ 178.5, 178.4, 178.4, 178.3, 178.2, 177.7, 102.2, 102.1, 102.1, 102.01, 102.0, 101.9, 101.6, 100.3, 100.2, 100.1, 100.1, 99.8, 80.3, 80.2, 79.9, 78.8, 78.7, 78.7, 78.5, 78.5, 78.1, 77.2, 77.2, 77.1, 77.1, 74.1, 73.9, 73.2, 73.1, 73.0, 73.0, 72.5, 72.5, 72.3, 72.2, 72.1, 71.2, 71.1, 70.9, 70.9, 70.9, 70.8, 70.8, 70.3, 70.3, 70.2, 65.4, 62.9, 62.5, 61.1, 60.7, 57.2.

HRMS (FT MS): m/z: calcd for $C_{75}H_{111}N_6Na_4O_{102}S_{13}$ [*M*-15Na+8H]$^{-7}$: 462.4234; found: 462.4244

(Note on MS characterisation of sulfated oligosaccharides: Sulfate groups are not stable when exposed to a variety of standard MS techniques, thus making negative mode ESI the only reliable method for collecting data. The main drawback of this method is the possibility of having multiple regions with increasing charges, exchange of sodium with hydrogen and other cations and complex isotope patterns. Overall the appearance of the spectra looks highly complex, but on closer examination reveals well defined clusters that correspond well with the expected m/z. The comparison with theoretical values in each section, is in this case not based on the mono isotopic structure, but the highest intensity peak (3rd peak in each cluster).).

2-Oxoethyl 4-*O*-sulfonato-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate -(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranoside uronate nonadecasodium salt (15)

For experimental procedure see main manuscript. ^{1}H NMR (400 MHz; D_2O) δ 5.33-5.23 (m, 11H, H’-1,H’’-1, H’’’-1, H’’’’-1, H’’’’’-1, H’’’’’’-1, H’’’’’’’-1, H’’’’’’’’-1, H’’’’’’’’’-1, H’’’’’’’’’’-1, H’’’’’’’’’’’-1), 5.17-5.16 (m, 1H, H-1’), 5.15 (t, *J* = 4.8 Hz, 1H, $CH_2CH(OH)_2$), 4.86-4.3 (m, 5H, H’’’-5, H’’’’-5, H’’’’’’-5, H’’’’’’’’-5, H’’’’’’’’’’-5), 4.51 (d, *J* = 2.4 Hz, 1H, H-5’), 4.34-4.30 (m, 5H, H-2’’’, H-2’’’’, H-2’’’’’’, H-2’’’’’’’’, H-2’’’’’’’’’’), 4.28-4.20 (m, 8H, H-2’, H-3’, H-3’’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’, H-4’’’’’’’’’’), 4.03-3.98 (m, 6H, H-4’’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’), 3.87-3.76 (m, 18H, H-5’’, H-5’’’’, H-5’’’’’’, H-5’’’’’’’’, H-5’’’’’’’’’’,

H-5’’’’’’’’’’’’, H-6’’, H-6’’’’, H-6’’’’’’, H-6’’’’’’’’, H-6’’’’’’’’’’, H-6’’’’’’’’’’’’), 3.70-3.62 (m, 11H, H-3’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’, H-3’’’’’’’’’’’’, H-4’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’,), 3.55 (dd, J = 10.9 Hz, J = 5.0 Hz, 2H, CH_2CH(OH)$_2$), 3.31-3.19 (m, 6H, H-2’’, H-2’’’’, H-2’’’’’’, H-2’’’’’’’’, H-2’’’’’’’’’’, H-2’’’’’’’’’’’’).

2-Hydroxyethyl 4-*O*-sulfonato-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate -(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranosyl uronate-(1⟶4)-2-*N*-sulfonato-α-D-glucosaminopyranosyl-(1⟶4)-2-*O*-sulfonato-α-L-idopyranoside uronate nonadecasodium salt (16)

The dodecasaccharide **15** (41 mg, 0.012 mmol) was dissolved in water (1 mL), Sodium borohydride (0.44 mg, 0.012 mmol) was added and stirred 2 h. Then more $NaBH_4$ (1.0 mg, 0.026 mmol) was added and stirred another 3 h. The crude was purified by passage through a Sephadex G-25 column by eluting with water. The fractions containing oligosaccharide were pooled and evaporated to yield 40 mg (98%) of **16** as a glassy solid. ^{1}H NMR (400 MHz; D_2O) δ 5.32-5.23 (m, 11H, H’-1,H’’-1, H’’’-1, H’’’’-1, H’’’’’-1, H’’’’’’-1, H’’’’’’’-1, H’’’’’’’’-1, H’’’’’’’’’-1, H’’’’’’’’’’-1, H’’’’’’’’’’’-1), 5.16-5.15 (m, 1H, H-1’), 4.87-4.84 (m, 5H, H’’’-5, H’’’’-5, H’’’’’’-5, H’’’’’’’’-5, H’’’’’’’’’’-5), 4.50 (d, J = 2.0 Hz, 1H, H-5’), 4.33-4.29 (m, 5H, H-2’’’, H-2’’’’, H-2’’’’’’, H-2’’’’’’’’, H-2’’’’’’’’’’’), 4.27-4.18 (m, 8H, H-2’, H-3’, H-3’’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’’, H-4’’’’’’’’’’’), 4.03-3.97 (m, 6H, H-4’’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’’), 3.87-3.75 (m, 18H, H-5’’, H-5’’’’, H-5’’’’’’, H-5’’’’’’’’, H-5’’’’’’’’’’, H-5’’’’’’’’’’’, H-6’’, H-6’’’’, H-6’’’’’’, H-6’’’’’’’’, H-6’’’’’’’’’’, H-6’’’’’’’’’’’), 3.74-3.62 (m, 14H, H-3’’, H-3’’’’, H-3’’’’’’, H-3’’’’’’’’, H-3’’’’’’’’’’, H-3’’’’’’’’’’’, H-4’’, H-4’’’’, H-4’’’’’’, H-4’’’’’’’’, H-4’’’’’’’’’’, CH_2CH_2OH), 3.30-3.18 (m, 6H, H-2’’, H-2’’’’, H-2’’’’’’, H-2’’’’’’’’, H-2’’’’’’’’’’, H-2’’’’’’’’’’’). HRMS (FT MS): m/z: calcd for $C_{74}H_{107}N_6Na_6O_{101}S_{13}$ [M-13Na+6H]$^{-7}$: 464.4167; found: 464.4173 (See note 2).