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Supporting Information

Influence of Side Chain Conformation on the Activity of Glycosidase Inhibitors

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Supplementary Figures

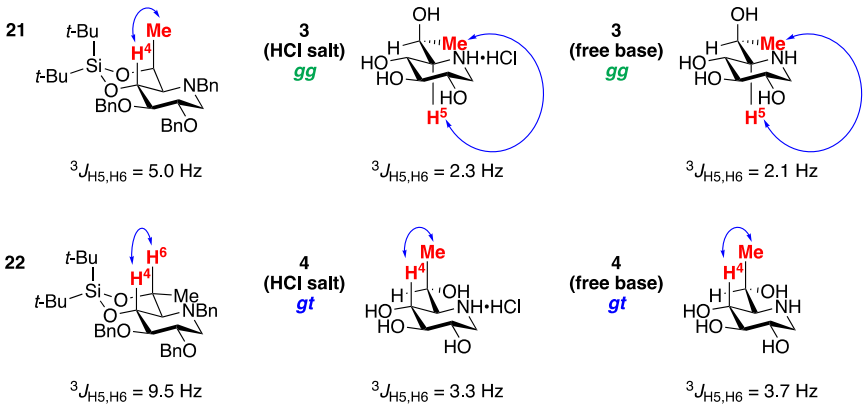


Figure S1. Diagnostic NOE correlations (blue arrows) and coupling constants for *gluco* iminosugars.

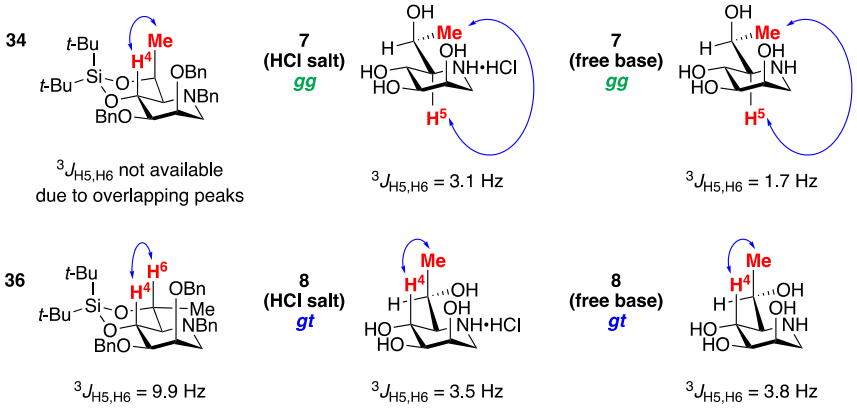


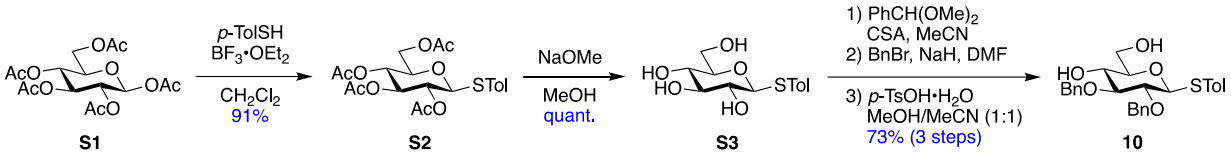
Figure S2. Diagnostic NOE correlations (blue arrows) and coupling constants for *manno* iminosugars.

General Methods

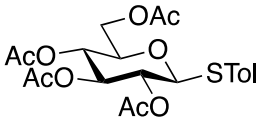
All reagents were purchased from commercial sources and used without further purification unless noted. All reactions were carried out in oven-dried round-bottom flasks and were performed under a positive pressure of argon or nitrogen. Reactions were monitored by thin-layer chromatography (TLC) on Sorbtech silica XHL 250 µm glass-backed plates with UV254 (catalog # 4115126). TLC spots were detected under UV light and by charring with a 20:80 v/v solution of sulfuric acid in ethanol or with a ceric ammonium molybdate solution containing 4 g of cerium(IV) sulfate, 10 g of ammonium molybdate, 40 mL of concentrated sulfuric acid and 360 mL of water. In the reaction work-up involving extractions, solutions of organic solvents were washed with equal amounts of aqueous solutions. Organic solvents were removed under reduced pressure at 40 ºC on a rotary evaporator. All column chromatography was performed on silica gel 60 (40–60 µm). Optical rotations were measured on a Rudolph Research Analytical AUTOPOL® III automatic polarimeter at 22 ± 1 ºC at the sodium D line (589 nm) and are in units of (deg·mL)/(dm·g). All NMR spectra were acquired on a JEOL JNM-ECZ500R 500 MHz spectrometer. ^{1}H NMR spectra were recorded at 500 MHz, and chemical shifts are referenced to residual $CHCl_3$ (7.26 ppm, $CDCl_3$), CD_2HOD (3.31 ppm, CD_3OD), C_6HD_5 (7.16 ppm, C_6D_6), or HOD (4.79 ppm, D_2O). ^{13}C NMR spectra were ^{1}H decoupled and were recorded at 126 MHz, and chemical shifts are referenced to internal $CDCl_3$ (77.16 ppm, $CDCl_3$), CD_3OD (49.00 ppm, CD_3OD), or C_6D_6 (128.06 ppm, C_6D_6). Peak assignments were based on two-dimensional NMR (COSY and HSQC) experiments, and the configurational or conformational assignments were determined with the aid of selective 1D NOESY NMR experiments. High-resolution electrospray ionization (ESI) mass spectrometry spectra were recorded using a Thermo Scientific Orbitrap mass analyzer.

Experimental Procedures and Characterization Data

Scheme S1. Preparation of Compound 10



p-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (S2)[1,2]



To a solution of commercially available 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose **S1** (10.0 g, 25.6 mmol) and *p*-thiocresol (3.82 g, 30.7 mmol) in CH_2Cl_2 (128 mL) at 0 ºC was added boron trifluoride diethyl etherate (4.74 mL, 38.4 mmol) dropwise. The reaction mixture was warmed slowly to rt and stirred for 22 h. Excess boron trifluoride diethyl etherate was quenched by the addition of saturated aqueous $NaHCO_3$ solution (10 mL) at 0 ºC. The organic layer was washed with saturated aqueous $NaHCO_3$ solution, water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (30% EtOAc/hexanes) to afford **S2** (10.6 g, 91%) as a white solid. Spectroscopic data were consistent with those reported.[2]

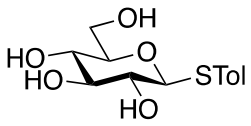
***R*$_f$** 0.58 (1:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.36 (m, 2H, ArH), 7.14 – 7.09 (m, 2H, ArH), 5.20 (dd, *J* = 9.5, 9.3 Hz, 1H, H-3), 5.01 (dd, *J* = 10.1, 9.5 Hz, 1H, H-4), 4.92 (dd, *J* = 10.0, 9.3 Hz, 1H, H-2), 4.63 (d, *J* = 10.0 Hz, 1H, H-1), 4.21 (dd, *J* = 12.3, 5.0 Hz, 1H, H-6a), 4.16 (dd, *J* = 12.3, 2.6 Hz, 1H, H-6b), 3.69 (ddd, *J* = 10.1, 5.0, 2.6 Hz, 1H, H-5), 2.34 (s, 3H, $ArCH_3$), 2.08 (d, *J* = 4.2 Hz, 6H, $C(O)CH_3$), 2.00 (s, 3H, $C(O)CH_3$), 1.97 (s, 3H, $C(O)CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7 (C=O), 170.3 (C=O), 169.5 (C=O), 169.3 (C=O), 138.9 (Ar), 134.0 (Ar), 129.8 (Ar), 127.7 (Ar), 85.9 (C-1), 75.9 (C-5), 74.1 (C-3), 70.0 (C-2), 68.3 (C-4), 62.2 (C-6), 21.3 ($ArCH_3$), 20.9 ($C(O)CH_3$), 20.8 ($C(O)CH_3$), 20.70 ($C(O)CH_3$), 20.68 ($C(O)CH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{21}H_{26}NaO_9S$, 477.1190; found, 477.1187.

***p*-Methylphenyl 1-Thio-β-D-glucopyranoside (S3)[1,2]**



To a solution of **S2** (9.22 g, 20.3 mmol) in MeOH (135 mL) at 0 ºC was added sodium methoxide (219 mg, 4.06 mmol). The reaction mixture was stirred at rt for 1 h before being neutralized with Amberlite® IR-120 (H^+) resin, filtered, and concentrated to give **S3** (5.81 g, quantitative) as a white solid. Spectroscopic data were consistent with those reported.[2]

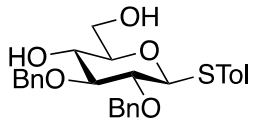
***R*$_f$** 0.29 (10:1 EtOAc/MeOH)

^{1}H NMR (500 MHz, CD_3OD): δ 7.48 – 7.44 (m, 2H, ArH), 7.14 – 7.10 (m, 2H, ArH), 4.51 (d, *J* = 9.7 Hz, 1H, H-1), 3.85 (dd, *J* = 12.1, 2.0 Hz, 1H, H-6a), 3.66 (dd, *J* = 12.1, 5.4 Hz, 1H, H-6b), 3.38 (dd, *J* = 8.7, 8.5 Hz, 1H, H-3), 3.30 – 3.24 (m, 2H, H-5 and H-4), 3.18 (dd, *J* = 9.7, 8.7 Hz, 1H, H-2), 2.31 (s, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, CD_3OD): δ 138.8 (Ar), 133.5 (Ar), 131.2 (Ar), 130.5 (Ar), 89.6 (C-1), 82.0 (C-5), 79.7 (C-3), 73.7 (C-2), 71.4 (C-4), 62.9 (C-6), 21.1 ($ArCH_3$).

HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{13}H_{18}NaO_5S$, 309.0767; found, 309.0764.

***p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-β-D-glucopyranoside (10)[3]**



To a solution of **S3** (2.77 g, 9.67 mmol) and benzaldehyde dimethyl acetal (2.90 mL, 19.3 mmol) in MeCN (48 mL) at 0 ºC was added camphorsulfonic acid (674 mg, 2.90 mmol). The reaction mixture was stirred at rt for 6 h. Excess camphorsulfonic acid was quenched by the addition of saturated aqueous $NaHCO_3$ solution (5 mL) at 0 ºC and the solution was diluted with EtOAc. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. To a solution of the crude product in DMF (39 mL) at 0 ºC were added sodium hydride (60% dispersion in mineral oil; 1.16 g, 29.0 mmol) and benzyl bromide (3.45 mL, 29.0 mmol). The reaction mixture was stirred at rt. After 6 h, ice was added, and the solution was diluted with EtOAc. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (10% EtOAc/hexanes). To a solution of the product (4.68 g, 8.44 mmol) in a mixture of MeOH (40 mL) and MeCN (40 mL) was added *p*-toluenesulfonic acid monohydrate (321 mg, 1.69 mmol). The reaction mixture was stirred at 50 ºC. After 5 h, Et_3N (2 mL) was added, and the solution was concentrated. The crude

residue was purified by column chromatography (60% EtOAc/hexanes) to afford **10** (3.29 g, 73% over three steps) as a white solid. Peak assignments for spectroscopic data[3] were corrected as reported below.

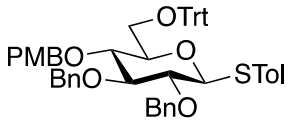
***R*$_f$** 0.28 (1:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.40 (m, 4H, ArH), 7.39 – 7.29 (m, 8H, ArH), 7.15 – 7.10 (m, 2H, ArH), 4.97 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 4.96 (d, *J* = 11.4 Hz, 1H, OCH_2Ar), 4.75 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 4.72 (d, *J* = 11.4 Hz, 1H, OCH_2Ar), 4.66 (d, *J* = 9.4 Hz, 1H, H-1), 3.87 (dd, *J* = 11.9, 3.5 Hz, 1H, H-6a), 3.75 (dd, *J* = 11.9, 5.4 Hz, 1H, H-6b), 3.57 (dd, *J* = 9.2, 9.0 Hz, 1H, H-4), 3.51 (dd, *J* = 9.0, 8.6 Hz, 1H, H-3), 3.46 (dd, *J* = 9.4, 8.6 Hz, 1H, H-2), 3.33 (ddd, *J* = 9.2, 5.4, 3.5 Hz, 1H, H-5), 2.34 (s, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.5 (Ar), 138.2 (Ar), 138.0 (Ar), 132.7 (Ar), 130.0 (Ar), 129.7 (Ar), 128.9 (Ar), 128.6 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 88.2 (C-1), 86.2 (C-3), 81.0 (C-2), 79.2 (C-5), 75.6 (OCH_2Ar), 75.5 (OCH_2Ar), 70.6 (C-4), 62.9 (C-6), 21.3 ($ArCH_3$).

HRMS–ESI (*m*/*z*): $[M + Na]^+$ calcd for $C_{27}H_{30}NaO_5S$, 489.1706; found, 489.1687.

p-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-β-D-glucopyranoside (11)



To a solution of **10** (3.27 g, 7.01 mmol) in CH_2Cl_2 (35 mL) were added Et_3N (1.95 mL, 14.0 mmol), 4-(dimethylamino)pyridine (85.6 mg, 0.701 mmol) and triphenylmethyl chloride (3.13 g, 11.2 mmol). The reaction mixture was stirred at rt for 13 h. Excess triphenylmethyl chloride was quenched by the addition of MeOH (2 mL). The resulting solution was concentrated before being diluted with EtOAc and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. To a solution of the crude product in DMF (35 mL) at 0 ºC were added sodium hydride (60% dispersion in mineral oil; 420 mg, 10.5 mmol), 4-methoxybenzyl chloride (1.43 mL, 10.5 mmol) and tetrabutylammonium iodide (259 mg, 0.701 mmol). The reaction mixture was stirred at rt for 2 h. Excess 4-methoxybenzyl chloride was quenched by the addition of MeOH (2 mL) and the solution was diluted with EtOAc. The organic layer was washed with ice-cold water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (15% EtOAc/hexanes, containing 1% Et_3N) to afford **11** (5.74 g, 98% over two steps) as a white foam.

***R*$_f$** 0.37 (5:1 hexanes/EtOAc)

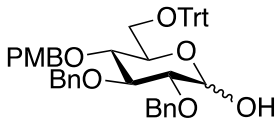
$[\alpha]_D^{23}$ –23.0 (*c* 0.8, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.59 (m, 2H, ArH), 7.54 – 7.49 (m, 6H, ArH), 7.45 – 7.41 (m, 2H, ArH), 7.37 – 7.22 (m, 17H, ArH), 7.08 – 7.04 (m, 2H, ArH), 6.75 – 6.66 (m, 4H, ArH), 4.91 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 4.87 – 4.81 (m, 2H, OCH_2Ar), 4.75 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 4.64 (d, *J* = 9.6 Hz, 1H, H-1), 4.57 (d, *J* = 10.0 Hz, 1H, OCH_2Ar), 4.24 (d, *J* = 10.0 Hz, 1H, OCH_2Ar), 3.76 (s, 3H, $ArOCH_3$), 3.72 (dd, *J* = 9.8, 9.4 Hz, 1H, H-4), 3.65 – 3.58 (m, 2H, H-3 and H-6a), 3.55 (dd, *J* = 9.6, 9.2 Hz, 1H, H-2), 3.42 (ddd, *J* = 9.8, 4.3, 1.9 Hz, 1H, H-5), 3.25 (dd, *J* = 10.1, 4.3 Hz, 1H, H-6b), 2.31 (s, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.4 (Ar), 144.1 (Ar), 138.6 (Ar), 138.4 (Ar), 137.8 (Ar), 132.9 (Ar), 130.1 (Ar), 129.94 (Ar), 129.88 (Ar), 129.0 (Ar), 128.64 (Ar), 128.58 (Ar), 128.4 (Ar), 128.08 (Ar), 128.06 (Ar), 128.0 (Ar), 127.9 (Ar), 127.1 (Ar), 113.8 (Ar), 87.8 (C-1), 87.0 (C-3), 86.6 ($OC(C_6H_5)_3$), 80.9 (C-2), 79.0 (C-5), 77.7 (C-4), 76.1 (OCH_2Ar), 75.5 (OCH_2Ar), 74.7 (OCH_2Ar), 62.6 (C-6), 55.4 ($ArOCH_3$), 21.3 ($ArCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{54}H_{52}NaO_6S$, 851.3377; found, 851.3369.

2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-glucopyranose (12)



To a solution of **11** (2.05 g, 2.47 mmol) in a mixture of acetone (25 mL) and water (2.5 mL) at 0 ºC was added *N*-iodosuccinimide (1.11 g, 4.94 mmol). The reaction mixture was stirred at 0 ºC for 1 h before being diluted with EtOAc. The resulting solution was washed with saturated aqueous $Na_2S_2O_3$ solution, water and brine, dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (30% EtOAc/hexanes, containing 1% Et_3N) to afford **12** (1.60 g, 90%, α:β = 2:1) as a white foam.

α-anomer: ***R*$_f$** 0.21 (3:1 hexanes/EtOAc)

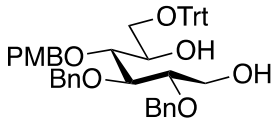
β-anomer: ***R*$_f$** 0.34 (3:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 – 7.44 (m, 10H, ArH), 7.41 – 7.19 (m, 37H, ArH), 6.79 – 6.74 (m, 3H, ArH), 6.72 – 6.67 (m, 3H, ArH), 5.37 (d, *J* = 3.6 Hz, 1H, H-1α), 4.94 – 4.88 (m, 2H, OCH_2Ar), 4.86 – 4.79 (m, 3H, OCH_2Ar), 4.78 – 4.73 (m, 2H, OCH_2Ar and H-1β), 4.64 – 4.59 (m, 2H, OCH_2Ar), 4.30 – 4.24 (m, 2H, OCH_2Ar), 4.03 (ddd, *J* = 10.0, 3.7, 2.0 Hz, 1H, H-5α), 3.92 (dd, *J* = 9.4, 9.2 Hz, 1H, H-3α), 3.81 – 3.72 (m, 6H, $ArOCH_3$ and H-4α), 3.68 (dd, *J* = 9.4, 3.6 Hz, 1H, H-2α), 3.63 – 3.52 (m, 3H, H-3β, H-6aβ, H-6bβ and H-6aα), 3.50 – 3.44 (m, 1H, H-2β), 3.21 (dd, *J* = 10.0, 3.7 Hz, 1H, H-6bα).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3 (Ar), 144.1 (Ar), 144.0 (Ar), 138.8 (Ar), 138.2 (Ar), 130.4 (Ar), 129.9 (Ar), 129.8 (Ar), 129.0 (Ar), 128.8 (Ar), 128.7 (Ar), 128.60 (Ar), 128.57 (Ar), 128.3 (Ar), 128.2 (Ar), 128.11 (Ar), 128.08 (Ar), 127.96 (Ar), 127.94 (Ar), 127.85 (Ar), 127.13 (Ar), 127.08 (Ar), 113.8 (Ar), 113.7 (Ar), 97.8 (C-1β), 91.4 (C-1α), 86.6 ($OC(C_6H_5)_3$), 86.4 ($OC(C_6H_5)_3$), 84.8 (C-3β), 83.6 (C-2β), 82.0 (C-3α), 80.6 (C-2α), 77.7 (C-4α), 77.4 (C-4β), 76.1 (OCH_2Ar), 76.0 (OCH_2Ar), 75.1 (OCH_2Ar), 75.0 (OCH_2Ar), 74.7 (OCH_2Ar), 73.5 (OCH_2Ar), 70.8 (C-5α), 62.7 (C-5β), 62.4 (C-6α), 58.2 (C-6β), 55.4 ($ArOCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{47}H_{46}NaO_7$, 745.3136; found, 745.3132.

2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (13)



To a solution of **12** (2.52 g, 3.49 mmol) in THF (23 mL) at 0 ºC was added lithium aluminum hydride (397 mg, 10.5 mmol) in portions. The reaction mixture was stirred at rt for 2 h. Excess lithium aluminum hydride was quenched by the addition of EtOAc (2 mL) at 0 ºC. The resulting solution was diluted with EtOAc and washed with saturated aqueous NH_4Cl solution, water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (50% EtOAc/hexanes, containing 1% Et_3N) to afford **13** (2.25 g, 89%) as a white foam.

***R*$_f$** 0.26 (2:1 hexanes/EtOAc)

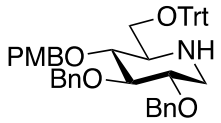
$[\alpha]_D^{23}$ –5.7 (*c* 0.9, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 6H, ArH), 7.33 – 7.21 (m, 19H, ArH), 7.02 – 6.97 (m, 2H, ArH), 6.78 – 6.74 (m, 2H, ArH), 4.66 (d, *J* = 11.3 Hz, 1H, OCH_2Ar), 4.64 (d, *J* = 11.6 Hz, 1H, OCH_2Ar), 4.59 (d, *J* = 11.6 Hz, 1H, OCH_2Ar), 4.51 (d, *J* = 11.3 Hz, 1H, OCH_2Ar), 4.37 – 4.30 (m, 2H, OCH_2Ar), 4.04 (ddd, *J* = 5.3, 4.3, 2.9 Hz, 1H, H-5), 3.83 (dd, *J* = 6.9, 2.9 Hz, 1H, H-4), 3.80 – 3.74 (m, 5H, H-3, H-2 and $ArOCH_3$), 3.69 (dd, *J* = 12.0, 3.8 Hz, 1H, H-1a), 3.54 (dd, *J* = 12.0, 4.0 Hz, 1H, H-1b), 3.35 (dd, *J* = 9.6, 4.3 Hz, 1H, H-6a), 3.27 (dd, *J* = 9.6, 5.3 Hz, 1H, H-6b), 3.10 (s, 1H, OH), 2.14 (s, 1H, OH).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.5 (Ar), 144.0 (Ar), 138.4 (Ar), 137.9 (Ar), 130.1 (Ar), 129.8 (Ar), 128.9 (Ar), 128.62 (Ar), 128.60 (Ar), 128.5 (Ar), 128.10 (Ar), 128.08 (Ar), 128.0 (Ar), 127.9 (Ar), 127.2 (Ar), 113.9 (Ar), 86.8 ($OC(C_6H_5)_3$), 79.6 (C-2), 79.5 (C-3), 76.5 (C-4), 74.5 (OCH_2Ar), 73.2 (OCH_2Ar), 72.6 (OCH_2Ar), 70.9 (C-5), 64.8 (C-6), 62.0 (C-1), 55.4 ($ArOCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{47}H_{48}NaO_7$, 747.3292; found, 747.3279.

2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1,5-dideoxy-1,5-imino-D-glucitol (14)



To a solution of oxalyl chloride (590 µL, 6.98 mmol) in CH_2Cl_2 (7.0 mL) at –78 ºC was added a solution of DMSO (620 µL, 8.73 mmol) in CH_2Cl_2 (4.4 mL) dropwise. The reaction mixture was stirred below –70 ºC for 30 min before a solution of **13** (1.27 g, 1.75 mmol) in CH_2Cl_2 (3.5 mL) was added dropwise. After the reaction mixture was stirred below –60 ºC for 2 h, Et_3N (2.92 mL, 20.9 mmol) was added dropwise. The reaction mixture was allowed to warm to 0 ºC over 2 h before being concentrated and co-evaporated twice with toluene. To a solution of the crude product in MeOH (35 mL) was added ammonium formate (2.20 g, 34.9 mmol). The mixture was stirred at 0 ºC for 10 min before powdered 4 Å acid-washed molecular sieves[4] (1.28 g) were added. After 20 min, sodium cyanoborohydride (439 mg, 6.98 mmol) was added. The reaction mixture was stirred at 0 ºC for 1 h and was then stirred at rt for 20 h before being filtered, diluted with EtOAc, and washed with saturated aqueous $NaHCO_3$ solution and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (30% EtOAc/hexanes, containing 1% Et_3N) to afford **14** (766 mg, 62% over two steps) as a white foam.

***R*$_f$** 0.28 (2:1 hexanes/EtOAc)

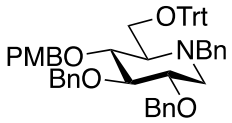
$[\alpha]_D^{23}$ +6.2 (*c* 0.5, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.20 (m, 25H, ArH), 6.80 – 6.77 (m, 2H, ArH), 6.70 – 6.67 (m, 2H, ArH), 4.95 (d, *J* = 10.9 Hz, 1H, OCH_2Ar), 4.81 (d, *J* = 10.9 Hz, 1H, OCH_2Ar), 4.74 – 4.66 (m, 2H, OCH_2Ar), 4.62 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 4.13 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 3.77 (s, 3H, $ArOCH_3$), 3.58 – 3.48 (m, 3H, H-6a, H-2 and H-3), 3.37 – 3.28 (m, 2H, H-1a and H-4), 3.13 (dd, *J* = 8.9, 6.1 Hz, 1H, H-6b), 2.74 (ddd, *J* = 9.3, 6.1, 2.6 Hz, 1H, H-5), 2.56 (dd, *J* = 12.1, 9.9 Hz, 1H, H-1b).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2 (Ar), 143.9 (Ar), 139.1 (Ar), 138.7 (Ar), 130.5 (Ar), 129.8 (Ar), 128.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.2 (Ar), 113.7 (Ar), 87.6 (C-3), 86.7 ($OC(C_6H_5)_3$), 80.8 (C-2), 80.0 (C-4), 75.9 (OCH_2Ar), 74.8 (OCH_2Ar), 73.0 (OCH_2Ar), 63.7 (C-6), 60.5 (C-5), 55.4 ($ArOCH_3$), 48.5 (C-1).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{47}H_{48}NO_5$, 706.3527; found, 706.3524.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (15)



To a solution of **14** (721 mg, 1.02 mmol) in DMF (10 mL) were added potassium carbonate (282 mg, 2.04 mmol) and benzyl bromide (240 µL, 2.04 mmol). The reaction mixture was stirred at rt for 3 h before being filtered, diluted with EtOAc, and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (10% EtOAc/hexanes, containing 1% Et_3N) to afford **15** (708 mg, 87%) as a white foam.

***R*$_f$** 0.23 (9:1 hexanes/EtOAc)

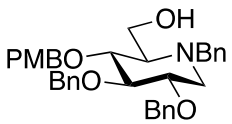
[α]$_D^{23}$ +18.6 (*c* 0.6, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 6H, ArH), 7.35 – 7.12 (m, 24H, ArH), 6.87 – 6.82 (m, 2H, ArH), 6.73 – 6.68 (m, 2H, ArH), 4.96 (d, *J* = 11.0 Hz, 1H, OCH_2Ar), 4.80 (d, *J* = 11.0 Hz, 1H, OCH_2Ar), 4.76 (d, *J* = 10.5 Hz, 1H, OCH_2Ar), 4.53 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.48 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.37 (d, *J* = 10.5 Hz, 1H, OCH_2Ar), 4.15 (d, *J* = 13.8 Hz, 1H, NCH_2Ar), 3.80 (s, 3H, $ArOCH_3$), 3.67 (dd, *J* = 10.3, 1.5 Hz, 1H, H-6a), 3.59 – 3.47 (m, 3H, H-3, H-2 and H-4), 3.15 – 3.05 (m, 2H, H-6b and NCH_2Ar), 3.01 (dd, *J* = 11.4, 4.4 Hz, 1H, H-1a), 2.59 (ddd, *J* = 9.5, 4.6, 1.5 Hz, 1H, H-5), 1.92 (dd, *J* = 11.4, 10.2 Hz, 1H, H-1b).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1 (Ar), 144.1 (Ar), 139.5 (Ar), 139.1 (Ar), 138.5 (Ar), 130.6 (Ar), 129.8 (Ar), 129.0 (Ar), 128.7 (Ar), 128.5 (Ar), 128.4 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 127.1 (Ar), 126.8 (Ar), 113.7 (Ar), 87.8 (C-3), 86.8 ($OC(C_6H_5)_3$), 78.5 (C-2), 78.2 (C-4), 75.4 (OCH_2Ar), 74.4 (OCH_2Ar), 72.5 (OCH_2Ar), 66.5 (C-5), 62.7 (C-6), 57.6 (NCH_2Ar), 55.4 ($ArOCH_3$), 54.1 (C-1).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{54}H_{54}NO_5$, 796.3997; found, 796.3975.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-glucitol (16)



A solution of **15** (245 mg, 0.308 mmol) in a mixture of acetic acid (1.5 mL) and ethanol (1.5 mL) was stirred at 80 ºC. After 10 h, the reaction mixture was concentrated and co-evaporated twice

with toluene. The crude residue was purified by column chromatography (40% EtOAc/hexanes) to afford **16** (118 mg, 69%) as a colorless oil.

***R*$_f$** 0.32 (2:1 hexanes/EtOAc)

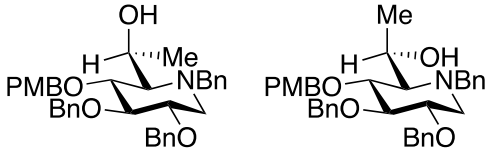
[α]$_D^{23}$ –13.2 (*c* 0.7, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.21 (m, 17H, ArH), 6.89 – 6.84 (m, 2H, ArH), 4.98 (d, *J* = 11.0 Hz, 1H, OCH_2Ar), 4.91 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 4.86 (d, *J* = 11.0 Hz, 1H, OCH_2Ar), 4.63 (d, *J* = 10.3 Hz, 1H, OCH_2Ar), 4.61 (d, *J* = 11.6 Hz, 1H, OCH_2Ar), 4.54 (d, *J* = 11.6 Hz, 1H, OCH_2Ar), 4.05 (d, *J* = 13.7 Hz, 1H, NCH_2Ar), 3.98 (dd, *J* = 11.9, 3.0 Hz, 1H, H-6a), 3.86 (dd, *J* = 11.9, 1.9 Hz, 1H, H-6b), 3.80 (s, 3H, $ArOCH_3$), 3.67 (dd, *J* = 9.1, 8.7 Hz, 1H, H-4), 3.58 – 3.49 (m, 2H, H-2 and H-3), 3.33 (d, *J* = 13.7 Hz, 1H, NCH_2Ar), 3.06 (dd, *J* = 11.5, 3.5 Hz, 1H, H-1a), 2.39 – 2.30 (m, 1H, H-5), 2.14 – 2.08 (m, 1H, H-1b).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.5 (Ar), 139.0 (Ar), 138.4 (Ar), 130.7 (Ar), 129.8 (Ar), 128.8 (Ar), 128.7 (Ar), 128.52 (Ar), 128.50 (Ar), 127.9 (Ar), 127.84 (Ar), 127.79 (Ar), 127.7 (Ar), 127.5 (Ar), 114.0 (Ar), 86.9 (C-3), 78.1 (C-2), 78.0 (C-4), 75.44 (OCH_2Ar), 75.39 (OCH_2Ar), 72.9 (OCH_2Ar), 66.0 (C-5), 58.3 (C-6), 56.8 (NCH_2Ar), 55.4 ($ArOCH_3$), 54.3 (C-1).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{35}H_{40}NO_5$, 554.2901; found, 554.2878.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*gluco*-heptitol (17) and 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-*glycero*-D-*gluco*-heptitol (18)



To a solution of **16** (138 mg, 0.249 mmol) in a mixture of CH_2Cl_2 (2.2 mL) and DMSO (1.1 mL) was added *N*,*N*-diisopropylethylamine (220 µL, 1.25 mmol). The mixture was cooled to 0 ºC, and sulfur trioxide pyridine complex (159 mg, 0.997 mmol) was added. The reaction mixture was stirred at 0 ºC for 15 min and was then stirred at rt for 45 min before being diluted with EtOAc. The resulting solution was washed with saturated aqueous NH_4Cl solution, water and brine, dried over Na_2SO_4, filtered, and concentrated to give the intermediate aldehyde. To a solution of the crude aldehyde in THF (5 mL) at 0 ºC was added a solution of methyl magnesium chloride (3.0 M in THF; 250 µL, 0.748 mmol). The reaction mixture was stirred at 0 ºC for 50 min before saturated aqueous NH_4Cl solution (1 mL) was added. The resulting solution was diluted with EtOAc and washed with saturated aqueous NH_4Cl solution and brine. The organic layer was dried

over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (30% EtOAc/hexanes) to give an inseparable mixture of **17** and **18** (114 mg, 80% over two steps, **17**:**18** = 2:1) as a colorless oil.

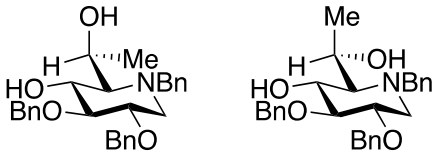
***R*$_f$** 0.44 (2:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.19 (m, 29H, ArH), 6.89 – 6.83 (m, 3H, ArH), 4.98 (d, *J* = 11.0 Hz, 1H, OCH_2Ar), 4.93 (d, *J* = 10.6 Hz, 1H, OCH_2Ar), 4.84 – 4.75 (m, 3H, OCH_2Ar), 4.68 (d, *J* = 11.5 Hz, 1H, OCH_2Ar), 4.61 – 4.48 (m, 5H, OCH_2Ar), 4.19 (qd, *J* = 6.4, 4.4 Hz, 1H, H-6 of **18**), 4.12 – 4.01 (m, 2H, NCH_2Ar and H-6 of **17**), 3.96 (d, *J* = 13.3 Hz, 1H, NCH_2Ar), 3.86 (d, *J* = 13.3 Hz, 1H, NCH_2Ar), 3.80 (s, 3H, $ArOCH_3$), 3.79 (s, 3H, $ArOCH_3$), 3.75 (dd, *J* = 6.5, 6.1 Hz, 1H, H-3 of **17**), 3.71 – 3.64 (m, 4H, H-4 of **17**, H-4, H-3 and H-2 of **18**), 3.62 (ddd, *J* = 7.9, 6.5, 3.6 Hz, 1H, H-2 of **17**), 3.43 (d, *J* = 14.1 Hz, 1H, NCH_2Ar), 3.02 – 2.94 (m, 2H, H-1a of **17** and H-1a of **18**), 2.67 (dd, *J* = 6.2, 6.2 Hz, 1H, H-5 of **17**), 2.56 (dd, *J* = 8.5, 4.4 Hz, 1H, H-5 of **18**), 2.46 (dd, *J* = 12.9, 7.9 Hz, 1H, H-1b of **17**), 2.22 (dd, *J* = 12.4, 9.6 Hz, 1H, H-1b of **18**), 1.28 (d, *J* = 6.4 Hz, 3H, CH_3 of **18**), 1.21 (d, *J* = 6.2 Hz, 3H, CH_3 of **17**).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.5 (Ar), 139.1 (Ar), 138.8 (Ar), 138.5 (Ar), 138.45 (Ar), 138.37 (Ar), 130.2 (Ar), 129.8 (Ar), 129.6 (Ar), 129.0 (Ar), 128.6 (Ar), 128.55 (Ar), 128.49 (Ar), 128.3 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.3 (Ar), 127.2 (Ar), 114.1 (Ar), 87.2 (C-3 of **18**), 83.3 (C-3 of **17**), 78.9 (C-2 of **18**), 77.65 (C-2 of **17**), 77.59 (C-4 of **18**), 77.3 (C-4 of **17**), 75.1 (OCH_2Ar), 74.5 (OCH_2Ar), 73.8 (OCH_2Ar), 73.1 (OCH_2Ar), 72.4 (OCH_2Ar), 72.1 (OCH_2Ar), 69.1 (C-5 of **18**), 68.2 (C-6 of **18**), 67.8 (C-5 of **17**), 65.4 (C-6 of **17**), 59.3 (NCH_2Ar), 55.8 (NCH_2Ar), 55.4 ($ArOCH_3$), 52.3 (C-1 of **18**), 49.3 (C-1 of **17**), 20.0 (CH_3), 19.1 (CH_3).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{36}H_{42}NO_5$, 568.3057; found, 568.3041.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (19) and 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (20)



To a solution of the mixture of **17** and **18** (114 mg, 0.200 mmol) in CH_2Cl_2 (2 mL) at 0 ºC was added trifluoroacetic acid (120 µL, 1.60 mmol). The reaction mixture was stirred at rt for 5 h. Excess trifluoroacetic acid was quenched by the addition of saturated aqueous $NaHCO_3$ solution (1 mL) at 0 ºC. The resulting solution was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was dried over Na_2SO_4, filtered, and

concentrated. The crude residue was purified by column chromatography (40% EtOAc/hexanes) to afford **19** (46.0 mg isolated, 51%) and **20** (23.5 mg isolated, 26%) as colorless oils.

Data for **19**:

***R*$_f$** 0.20 (2:1 hexanes/EtOAc)

[α]$_D^{23}$ –17.6 (*c* 0.6, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 – 7.20 (m, 15H, ArH), 4.92 (d, *J* = 11.5 Hz, 1H, OCH_2Ar), 4.66 (d, *J* = 11.5 Hz, 1H, OCH_2Ar), 4.53 – 4.45 (m, 2H, OCH_2Ar), 4.29 (qd, *J* = 6.4, 4.6 Hz, 1H, H-6), 3.97 (d, *J* = 13.6 Hz, 1H, NCH_2Ar), 3.79 (dd, *J* = 7.8, 7.4 Hz, 1H, H-4), 3.60 – 3.46 (m, 3H, NCH_2Ar, H-2 and H-3), 3.13 (br s, 1H, OH), 3.03 (dd, *J* = 12.5, 3.9 Hz, 1H, H-1a), 2.61 (dd, *J* = 7.8, 4.6 Hz, 1H, H-5), 2.25 (dd, *J* = 12.5, 7.9 Hz, 1H, H-1b), 1.28 (d, *J* = 6.4 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.5 (Ar), 138.0 (Ar), 128.74 (Ar), 128.70 (Ar), 128.59 (Ar), 128.57 (Ar), 128.05 (Ar), 127.97 (Ar), 127.9 (Ar), 127.8 (Ar), 127.3 (Ar), 83.7 (C-3), 77.7 (C-2), 74.5 (OCH_2Ar), 72.1 (OCH_2Ar), 70.9 (C-4), 67.8 (C-5), 66.6 (C-6), 57.9 (NCH_2Ar), 51.5 (C-1), 18.4 (CH_3).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{28}H_{34}NO_4$, 448.2482; found, 448.2473.

Data for **20**:

***R*$_f$** 0.16 (2:1 hexanes/EtOAc)

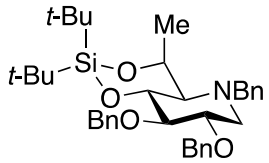
[α]$_D^{23}$ +12.6 (*c* 0.1, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.18 (m, 15H, ArH), 4.93 (d, *J* = 11.5 Hz, 1H, OCH_2Ar), 4.67 (d, *J* = 11.5 Hz, 1H, OCH_2Ar), 4.47 – 4.40 (m, 2H, OCH_2Ar), 4.34 – 4.28 (m, 1H, H-6), 3.98 (d, *J* = 14.0 Hz, 1H, NCH_2Ar), 3.83 (dd, *J* = 7.8, 7.4 Hz, 1H, H-4), 3.62 (ddd, *J* = 8.5, 7.9, 3.9 Hz, 1H, H-2), 3.56 (d, *J* = 14.0 Hz, 1H, NCH_2Ar), 3.50 (dd, *J* = 7.9, 7.4 Hz, 1H, H-3), 3.10 (dd, *J* = 12.9, 3.9 Hz, 1H, H-1a), 3.02 (br s, 1H, OH), 2.58 (dd, *J* = 7.8, 4.5 Hz, 1H, H-5), 2.34 (dd, *J* = 12.9, 8.5 Hz, 1H, H-1b), 1.31 (d, *J* = 6.4 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.3 (Ar), 138.1 (Ar), 128.8 (Ar), 128.57 (Ar), 128.55 (Ar), 128.49 (Ar), 128.2 (Ar), 128.1 (Ar), 127.9 (Ar), 127.8 (Ar), 127.3 (Ar), 83.8 (C-3), 76.1 (C-2), 74.7 (OCH_2Ar), 71.9 (OCH_2Ar), 70.2 (C-4), 68.8 (C-5), 67.6 (C-6), 56.0 (NCH_2Ar), 50.6 (C-1), 20.4 (CH_3).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{28}H_{34}NO_4$, 448.2482; found, 448.2475.

2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (21)



To a solution of **19** (9.4 mg, 0.021 mmol) in pyridine (1 mL) at 0 ºC was added di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (6.8 µL, 0.021 mmol). The reaction mixture was stirred at rt for 2 h before being concentrated and co-evaporated twice with toluene. The residue was dissolved in EtOAc and washed with saturated aqueous NH_4Cl solution, water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (5% EtOAc/hexanes) to afford **21** (8.9 mg, 72%) as a colorless oil.

***R*$_f$** 0.42 (9:1 hexanes/EtOAc)

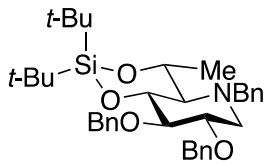
[α]$_D^{23}$ –59.0 (*c* 0.5, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 7.38 (m, 2H, ArH), 7.33 – 7.19 (m, 13H, ArH), 5.00 (d, *J* = 11.1 Hz, 1H, OCH_2Ar), 4.82 (d, *J* = 11.1 Hz, 1H, OCH_2Ar), 4.76 – 4.70 (m, 1H, H-6), 4.65 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.50 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.10 (dd, *J* = 9.3, 8.5 Hz, 1H, H-4), 3.89 (d, *J* = 13.7 Hz, 1H, NCH_2Ar), 3.45 – 3.35 (m, 2H, H-2 and H-3), 3.06 (d, *J* = 13.7 Hz, 1H, NCH_2Ar), 2.94 (dd, *J* = 11.2, 4.0 Hz, 1H, H-1a), 2.67 (dd, *J* = 9.3, 5.0 Hz, 1H, H-5), 1.90 (dd, *J* = 11.2, 10.4 Hz, 1H, H-1b), 1.39 (d, *J* = 6.4 Hz, 3H, CH_3), 1.08 (s, 9H, $SiC(CH_3)_3$), 1.05 (s, 9H, $SiC(CH_3)_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 139.4 (Ar), 138.8 (Ar), 137.9 (Ar), 128.6 (Ar), 128.44 (Ar), 128.39 (Ar), 128.38 (Ar), 128.3 (Ar), 127.7 (Ar), 127.58 (Ar), 127.57 (Ar), 127.3 (Ar), 87.6 (C-3), 76.9 (C-2), 75.7 (OCH_2Ar), 73.3 (C-4), 73.0 (OCH_2Ar), 70.3 (C-6), 65.3 (C-5), 56.4 (NCH_2Ar), 54.8 (C-1), 27.7 ($SiC(CH_3)_3$), 27.5 ($SiC(CH_3)_3$), 21.4 ($SiC(CH_3)_3$), 20.6 ($SiC(CH_3)_3$), 17.6 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{36}H_{50}NO_4Si$, 588.3504; found, 588.3512.

2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (22)



To a solution of **20** (8.8 mg, 0.020 mmol) in pyridine (1 mL) at 0 ºC was added di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (6.4 µL, 0.020 mmol). The reaction mixture was stirred at rt for 2 h

before being concentrated and co-evaporated twice with toluene. The residue was dissolved in EtOAc and washed with saturated aqueous NH_4Cl solution, water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (5% EtOAc/hexanes) to afford **22** (9.0 mg, 78%) as a colorless oil.

***R*$_f$** 0.52 (9:1 hexanes/EtOAc)

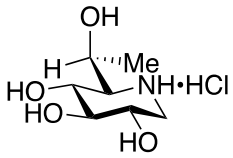
$[\alpha]_D^{23}$ +13.0 (*c* 0.5, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.43 (m, 2H, ArH), 7.37 – 7.22 (m, 11H, ArH), 7.17 – 7.12 (m, 2H, ArH), 5.06 (d, *J* = 10.7 Hz, 1H, OCH_2Ar), 4.84 (d, *J* = 10.7 Hz, 1H, OCH_2Ar), 4.65 (d, *J* = 11.8 Hz, 1H, OCH_2Ar), 4.54 (d, *J* = 11.8 Hz, 1H, OCH_2Ar), 4.40 (dq, *J* = 9.5, 6.0 Hz, 1H, H-6), 4.32 (dd, *J* = 10.7, 8.6 Hz, 1H, H-4), 3.82 (ddd, *J* = 11.2, 9.0, 5.1 Hz, 1H, H-2), 3.68 (d, *J* = 13.4 Hz, 1H, NCH_2Ar), 3.50 (dd, *J* = 9.0, 8.6 Hz, 1H, H-3), 3.49 (d, *J* = 13.4 Hz, 1H, NCH_2Ar), 2.93 (dd, *J* = 14.1, 5.1 Hz, 1H, H-1a), 2.55 (dd, *J* = 10.7, 9.5 Hz, 1H, H-5), 2.41 (dd, *J* = 14.1, 11.2 Hz, 1H, H-1b), 1.42 (d, *J* = 6.0 Hz, 3H, CH_3), 1.10 (s, 9H, $SiC(CH_3)_3$), 1.03 (s, 9H, $SiC(CH_3)_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 139.3 (Ar), 138.8 (Ar), 138.7 (Ar), 128.6 (Ar), 128.51 (Ar), 128.49 (Ar), 128.45 (Ar), 128.3 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.4 (Ar), 89.2 (C-3), 76.3 (OCH_2Ar), 75.7 (C-4), 73.8 (C-2), 73.2 (OCH_2Ar), 71.0 (C-6), 67.6 (C-5), 51.5 (C-1), 50.1 (NCH_2Ar), 27.7 ($SiC(CH_3)_3$), 27.3 ($SiC(CH_3)_3$), 22.8 ($SiC(CH_3)_3$), 22.0 ($SiC(CH_3)_3$), 19.8 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{36}H_{50}NO_4Si$, 588.3504; found, 588.3505.

1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol Hydrochloride (3)

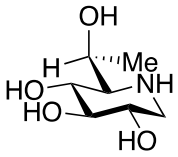


A solution of **19** (30.7 mg, 0.0686 mmol) in ethanol (2 mL) was acidified to pH 2 with 1 N aqueous HCl solution and was stirred under an atmosphere of argon. After 5 min, 10 wt. % of palladium on carbon (30.7 mg) was added. The reaction mixture was stirred under an atmosphere of hydrogen at rt for 14 h before being filtered through a syringe filter (0.22 µm) and rinsed with MeOH. The filtrate was concentrated and co-evaporated twice with toluene. The residue was dissolved in water and the resulting solution was lyophilized to give the HCl salt **3** (14.7 mg, quantitative) as a white solid.

$[\alpha]_D^{21}$ +60.0 (*c* 0.1, H_2O)

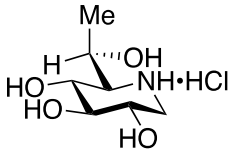
^{1}H NMR (500 MHz, D_2O): δ 4.36 (qd, *J* = 6.8, 2.3 Hz, 1H, H-6), 3.81 (ddd, *J* = 11.5, 9.3, 5.1 Hz, 1H, H-2), 3.65 (dd, *J* = 10.5, 9.3 Hz, 1H, H-4), 3.55 – 3.49 (m, 2H, H-3 and H-1a), 3.08 (dd, *J* = 10.5, 2.3 Hz, 1H, H-5), 2.99 (dd, *J* = 12.6, 11.5 Hz, 1H, H-1b), 1.36 (d, *J* = 6.8 Hz, 3H, CH_3).
^{13}C NMR (126 MHz, D_2O): δ 76.2 (C-3), 68.4 (C-4), 66.7 (C-2), 63.2 (C-5), 62.2 (C-6), 45.9 (C-1), 19.3 (CH_3).
HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1074; found, 178.1072.

1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (3)



The HCl salt **3** (9.8 mg, 0.046 mmol) was dissolved in MeOH (2 mL) and was stirred with Amberlite® HPR550 OH anion exchange resin at rt. After 15 min, the solution was filtered through a syringe filter (0.22 µm), rinsed with MeOH, and concentrated to afford the free base **3** (7.1 mg) as a white solid.
$[\alpha]_D^{21}$ +72.0 (*c* 0.1, H_2O)
^{1}H NMR (500 MHz, D_2O): δ 4.19 (qd, *J* = 6.6, 2.1 Hz, 1H, H-6), 3.48 (ddd, *J* = 10.8, 8.6, 5.2 Hz, 1H, H-2), 3.40 – 3.30 (m, 2H, H-4 and H-3), 3.11 (dd, *J* = 12.8, 5.2 Hz, 1H, H-1a), 2.41 (dd, *J* = 12.8, 10.8 Hz, 1H, H-1b), 2.36 (dd, *J* = 9.6, 2.1 Hz, 1H, H-5), 1.27 (d, *J* = 6.6 Hz, 3H, CH_3).
^{13}C NMR (126 MHz, D_2O): δ 78.5 (C-3), 71.8 (C-4), 71.1 (C-2), 64.7 (C-6), 63.4 (C-5), 48.6 (C-1), 19.3 (CH_3).
HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1074; found, 178.1068.

1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol Hydrochloride (4)



A solution of **20** (10.6 mg, 0.0237 mmol) in ethanol (1 mL) was acidified to pH 2 with 1 N aqueous HCl solution and was stirred under an atmosphere of argon. After 5 min, 10 wt. % of palladium on carbon (10.6 mg) was added. The reaction mixture was stirred under an atmosphere of hydrogen at rt for 11 h before being filtered through a syringe filter (0.22 µm) and rinsed with MeOH. The filtrate was concentrated and co-evaporated twice with toluene. The residue was dissolved in

water and the resulting solution was lyophilized to give the HCl salt **4** (5.1 mg, quantitative) as a white solid.

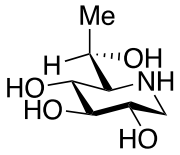
$[\alpha]_D^{21}$ +31.6 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 4.37 (qd, *J* = 6.8, 3.3 Hz, 1H, H-6), 3.82 (ddd, *J* = 11.6, 9.1, 5.2 Hz, 1H, H-2), 3.63 – 3.50 (m, 3H, H-4, H-3 and H-1a), 3.30 (dd, *J* = 10.7, 3.3 Hz, 1H, H-5), 3.00 (dd, *J* = 12.6, 11.6 Hz, 1H, H-1b), 1.30 (d, *J* = 6.8 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, D_2O): δ 76.5 (C-3), 68.6 (C-4), 66.8 (C-2), 63.9 (C-6), 63.1 (C-5), 46.3 (C-1), 15.6 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1074; found, 178.1073.

1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (4)



The HCl salt **4** (4.1 mg, 0.019 mmol) was dissolved in MeOH (2 mL) and was stirred with Amberlite® HPR550 OH anion exchange resin at rt. After 15 min, the solution was filtered through a syringe filter (0.22 µm), rinsed with MeOH, and concentrated to afford the free base **4** (2.7 mg) as a white solid.

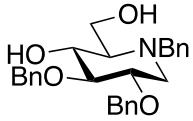
$[\alpha]_D^{21}$ +45.0 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 4.18 (qd, *J* = 6.6, 3.7 Hz, 1H, H-6), 3.51 (ddd, *J* = 10.8, 9.1, 5.1 Hz, 1H, H-2), 3.32 (dd, *J* = 9.1, 8.9 Hz, 1H, H-3), 3.24 (dd, *J* = 9.9, 8.9 Hz, 1H, H-4), 3.15 (dd, *J* = 12.0, 5.1 Hz, 1H, H-1a), 2.62 (dd, *J* = 9.9, 3.7 Hz, 1H, H-5), 2.47 (dd, *J* = 12.0, 10.8 Hz, 1H, H-1b), 1.19 (d, *J* = 6.6 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, D_2O): δ 78.7 (C-3), 72.7 (C-4), 70.6 (C-2), 66.9 (C-6), 64.0 (C-5), 49.2 (C-1), 15.7 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1074; found, 178.1068.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (23)



To a solution of **15** (55.5 mg, 0.0697 mmol) in CH_2Cl_2 (1 mL) at 0 ºC was added trifluoroacetic acid (54 µL, 0.70 mmol). The reaction mixture was stirred at rt for 2 h. Excess trifluoroacetic acid was quenched by the addition of saturated aqueous $NaHCO_3$ solution (0.5 mL) at 0 ºC. The

resulting solution was diluted with EtOAc and washed with saturated aqueous $NaHCO_3$ solution, water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (60% EtOAc/hexanes) to afford **23** (21.9 mg, 72%) as a colorless oil.

***R*$_f$** 0.16 (1:1 hexanes/EtOAc)

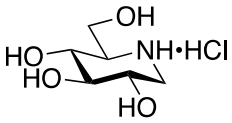
[α]$_D^{23}$ –10.5 (*c* 0.2, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.22 (m, 15H, ArH), 4.99 (d, *J* = 11.6 Hz, 1H, OCH_2Ar), 4.71 (d, *J* = 11.6 Hz, 1H, OCH_2Ar), 4.57 – 4.49 (m, 2H, OCH_2Ar), 4.06 (d, *J* = 13.7 Hz, 1H, NCH_2Ar), 4.01 – 3.93 (m, 2H, H-6a and H-6b), 3.70 (dd, *J* = 8.9, 8.7 Hz, 1H, H-4), 3.54 (ddd, *J* = 9.9, 8.9, 4.4 Hz, 1H, H-2), 3.42 – 3.33 (m, 2H, NCH_2Ar and H-3), 3.10 (dd, *J* = 11.6, 4.4 Hz, 1H, H-1a), 2.38 (ddd, *J* = 9.1, 8.9, 3.0 Hz, 1H, H-5), 2.16 (dd, *J* = 11.6, 9.9 Hz, 1H, H-1b).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.8 (Ar), 138.3 (Ar), 128.9 (Ar), 128.72 (Ar), 128.68 (Ar), 128.5 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.5 (Ar), 85.2 (C-3), 77.7 (C-2), 74.9 (OCH_2Ar), 72.4 (OCH_2Ar), 70.5 (C-4), 65.6 (C-5), 59.3 (C-6), 57.0 (NCH_2Ar), 53.6 (C-1).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{27}H_{32}NO_4$, 434.2326; found, 434.2318.

1,5-Dideoxy-1,5-imino-D-glucitol Hydrochloride (2)



A solution of **23** (14.1 mg, 0.0325 mmol) in ethanol (1 mL) was acidified to pH 2 with 1 N aqueous HCl solution and was stirred under an atmosphere of argon. After 5 min, 10 wt. % of palladium on carbon (14.1 mg) was added. The reaction mixture was stirred under an atmosphere of hydrogen at rt for 10 h before being filtered through a syringe filter (0.22 μm) and rinsed with MeOH. The filtrate was concentrated and co-evaporated twice with toluene. The residue was dissolved in water and the resulting solution was lyophilized to give the HCl salt **2** (6.5 mg, quantitative) as a white solid. Peak assignments for spectroscopic data[5] were corrected as reported below.

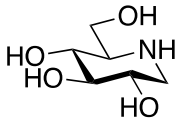
[α]$_D^{21}$ +32.7 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 3.98 (dd, *J* = 12.8, 3.2 Hz, 1H, H-6a), 3.91 (dd, *J* = 12.8, 5.2 Hz, 1H, H-6b), 3.82 (ddd, *J* = 11.6, 9.3, 5.1 Hz, 1H, H-2), 3.63 (dd, *J* = 10.6, 9.2 Hz, 1H, H-4), 3.58 – 3.51 (m, 2H, H-3 and H-1a), 3.24 (ddd, *J* = 10.6, 5.2, 3.2 Hz, 1H, H-5), 3.01 (dd, *J* = 12.6, 11.6 Hz, 1H, H-1b).

^{13}C NMR (126 MHz, D_2O): δ 76.2 (C-3), 67.7 (C-4), 66.9 (C-2), 59.9 (C-5), 57.6 (C-6), 45.8 (C-1).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_6H_{14}NO_4$, 164.0917; found, 164.0911.

1,5-Dideoxy-1,5-imino-D-glucitol (2)



The HCl salt **2** (4.2 mg, 0.021 mmol) was dissolved in MeOH (2 mL) and was stirred with Amberlite® HPR550 OH anion exchange resin at rt. After 15 min, the solution was filtered through a syringe filter (0.22 µm), rinsed with MeOH, and concentrated to afford the free base **2** (2.8 mg) as a white solid. Peak assignments for spectroscopic data[6] were corrected as reported below.

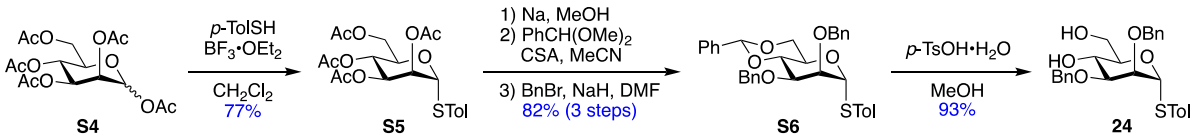
$[\alpha]_D^{21}$ +40.0 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 3.85 (dd, *J* = 11.7, 3.0 Hz, 1H, H-6a), 3.65 (dd, *J* = 11.7, 6.2 Hz, 1H, H-6b), 3.51 (ddd, *J* = 10.8, 9.1, 5.2 Hz, 1H, H-2), 3.34 (dd, *J* = 9.1, 9.1 Hz, 1H, H-3), 3.25 (dd, *J* = 9.9, 9.1 Hz, 1H, H-4), 3.14 (dd, *J* = 12.3, 5.2 Hz, 1H, H-1a), 2.57 (ddd, *J* = 9.9, 6.2, 3.0 Hz, 1H, H-5), 2.48 (dd, *J* = 12.3, 10.8 Hz, 1H, H-1b).

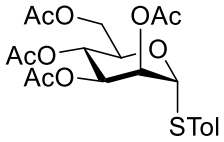
^{13}C NMR (126 MHz, D_2O): δ 78.4 (C-3), 71.6 (C-4), 70.9 (C-2), 61.4 (C-6), 60.5 (C-5), 48.7 (C-1).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_6H_{14}NO_4$, 164.0917; found, 164.0912.

Scheme S2. Preparation of Compound 24



***p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (S5)[7]**



Commercially available 1,2,3,4,6-penta-*O*-acetyl α/β-D-mannopyranose (10.0 g, 25.6 mmol) was dissolved in CH_2Cl_2 (30 mL) and *p*-thiocresol (6.40 g, 51.2 mmol) was added. The mixture was cooled to 0 ºC, followed by addition of BF_3•Et_2O (5.70 mL, 46.1 mmol). The reaction mixture was stirred for 10 h at rt, and after that time saturated aqueous $NaHCO_3$ solution was added to neutralize the mixture at 0 ºC. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 X 100 mL). Combined organic layers were dried over Na_2SO_4 and concentrated. Obtained residue was purified by flash column chromatography (40% EtOAc/hexanes) to obtain **S5** as a clear, colorless syrup (8.96 g, 77%). Spectroscopic data were consistent with those reported.[7]

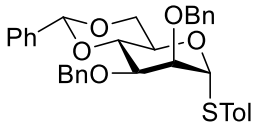
***R*$_f$** 0.60 (2:3 EtOAc/hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.36 (m, 2H, ArH), 7.12 – 7.10 (m, 2H, ArH), 5.48 (dd, *J* = 1.7, 1.0 Hz, 1H, H-2), 5.40 (d, *J* = 1.0 Hz, 1H, H-1), 5.32 – 5.30 (m, 2H, H-4, H-3), 4.57 – 4.50 (m, 1H, H-5), 4.28 (dd, *J* = 12.2, 5.9 Hz, 1H, H-6a), 4.09 (dd, *J* = 12.2, 2.4 Hz, 1H, H-6b), 2.31 (s, 3H, $ArCH_3$), 2.13 (s, 3H, $C(O)CH_3$), 2.06 (s, 3H, $C(O)CH_3$), 2.05 (s, 3H, $C(O)CH_3$), 2.00 (s, 3H, $C(O)CH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6 (C=O), 170.0 (C=O), 169.9 (C=O), 169.8 (C=O), 138.5 (Ar), 132.7 (Ar), 130.1 (Ar), 128.9 (Ar), 86.1 (C-1), 71.0 (C-2), 69.5 (C-5), 69.5 (C-3), 66.5 (C-4), 62.6 (C-6), 21.2 ($ArCH_3$), 20.9 ($C(O)CH_3$), 20.8 ($C(O)CH_3$), 20.8 ($C(O)CH_3$), 20.7 ($C(O)CH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{21}H_{26}NaO_9S$, 477.1189; found, 477.1173.

p-Methylphenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (S6)[8]



Compound **S5** (9.00 g, 19.8 mmol) was suspended in MeOH (90 mL) and treated with sodium (0.14 mg, 5.94 mmol), the resulting mixture was stirred for 1.5 h at rt. Upon complete consumption of starting material (detected by LCMS), the reaction mixture was neutralized with Amberlyst® 15, filtered, and concentrated to give crude product as a thick syrup. The crude product was subsequently dissolved in MeCN (90 mL) and benzaldehyde dimethyl acetal (3.26 mL, 21.7 mmol) was added followed by camphor sulfonic acid (1.15 g, 4.95 mmol). The reaction mixture was allowed to stir at rt for 5 h, neutralized by the addition of Et_3N and the solvent was evaporated. The resulting off-white solid in DMF (90 mL) was cooled to 0 ºC, followed by the addition of sodium hydride (60% dispersion in mineral oil, 1.90 g, 79.2 mmol) and benzyl bromide (5.90 mL, 49.5 mmol). The reaction mixture was stirred at rt for 3 h, before being quenched by addition of MeOH at 0 ºC. After that the solvent was removed under *vacuo* and the crude was diluted with EtOAc (100 mL) and subsequently washed with water (100 mL) and brine (100 mL), dried over Na_2SO_4, and concentrated. Crude product was purified by flash column chromatography (20% EtOAc/hexanes) to obtain **S6** as a colorless oil (9.00 g, 82% over three steps). Spectroscopic data were consistent with those reported.[8]

***R*$_f$** 0.50 (1:4 EtOAc/hexanes)

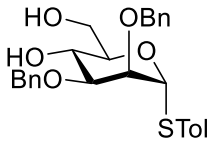
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 – 7.45 (m, 2H, ArH), 7.35 – 7.18 (m, 15H, ArH), 7.03 – 7.04 (m, 2H, ArH), 5.58 (s, 1H, benzylidene C-H), 5.38 (d, *J* = 1.5 Hz, 1H, H-1), 4.76 (d, *J* = 12.2 Hz, 1H, OCH_2Ar), 4.65 (s, 2H, OCH_2Ar), 4.59 (d, *J* = 12.2 Hz, 1H, OCH_2Ar), 4.28 – 4.19 (m, 2H, H-4,

H-5), 4.16 (dd, *J* = 10.2, 4.3 Hz, 1H, H-6a), 3.97 (dd, *J* = 3.3, 1.5 Hz, 1H, H-2), 3.91 (dd, *J* = 9.5, 3.3 Hz, 1H, H-3), 3.85 – 3.78 (m, 1H, H-6b), 2.26 (s, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.5 (Ar), 138.1 (Ar), 137.9 (Ar), 137.8 (Ar), 132.4 (Ar), 130.1 (Ar), 130.0 (Ar), 129.0 (Ar), 128.5 (Ar), 128.5 (Ar), 128.3 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 126.2 (Ar), 101.6 (benzylidene C), 87.6 (C-1), 79.3 (C-4), 78.1 (C-2), 76.3 (C-3), 73.2 (OCH_2Ar), 73.1 (OCH_2Ar), 68.7 (C-6), 65.5 (C-5), 21.2 ($ArCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{34}H_{34}NaO_5S$, 577.2019; found, 577.2029.

p-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-α-D-mannopyranoside (24)[8]



Compound **S6** (9.00 g, 16.2 mmol) was suspended in MeOH (150 mL) and *p*-TsOH•H_2O (0.30 g, 1.62 mmol) was added, the resulting mixture was stirred for 4 h at 50 ºC, followed by the addition of Et_3N until pH>7. The solvent was evaporated, and the crude compound was purified by flash column chromatography (50% EtOAc/hexanes) to obtain **24** as a white solid (7 g, 93%). Spectroscopic data were consistent with those reported.[8]

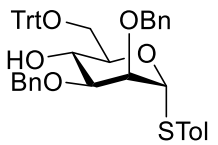
***R*$_f$** 0.34 (1:1 EtOAc/hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.25 (m, 12H, ArH), 7.12 – 7.11 (m, 2H, ArH), 5.48 (d, *J* = 1.5 Hz, 1H, H-1), 4.65 (d, *J* = 12.2 Hz, 1H, OCH_2Ar), 4.60 – 4.53 (m, 2H, OCH_2Ar), 4.47 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.15 – 4.06 (m, 2H, H-4, H-5), 4.00 (dd, *J* = 3.1, 1.5 Hz, 1H, H-2), 3.90 – 3.79 (m, 2H, H-6a, H-6b), 3.69 (dd, *J* = 8.9, 3.1 Hz, 1H, H-3), 2.33 (s, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.2 (Ar), 137.8 (Ar), 137.8 (Ar), 132.6(Ar), 130.1 (Ar), 130.1 (Ar), 128.7 (Ar), 128.6 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 86.5 (C-1), 79.7 (C-3), 75.6 (C-2), 73.3 (C-4), 72.3 (OCH_2Ar), 71.8 (OCH_2Ar), 67.4 (C-5), 62.8 (C-6), 21.2 ($ArCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{27}H_{30}NaO_5S$, 489.1706; found 489.1698.

p-Methylphenyl 2,3-Di-*O*-benzyl-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (25)



Compound **24** (7.00 g, 15.0 mmol) was dissolved in pyridine (50 mL) and triphenylmethyl chloride (6.27 g, 22.5 mmol) was added. The mixture was stirred at 55 °C for 12 h, then cooled to rt and

the solvents were removed and co-evaporated twice with toluene. After dilution with EtOAc (100 mL), the organic phase was washed with aqueous 1M HCl solution (50 mL), water (100 mL) and brine (100 mL), dried over Na_2SO_4, and concentrated to dryness. The crude product was purified by flash column chromatography (20% EtOAc/hexanes, containing 1% Et_3N) to obtain **25** as a white powder (9.03 g, 85%).

***R*$_f$** 0.51 (1:4 EtOAc/hexanes)

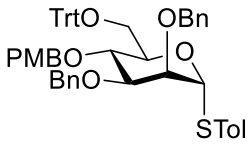
$[\alpha]_D^{23}$ +11.0 (*c* 0.4, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.43 (m, 6H, ArH), 7.43 – 7.39 (m, 2H, ArH), 7.35 – 7.21 (m, 19H, ArH), 7.06 (d, *J* = 7.6 Hz, 2H, ArH), 5.56 (d, *J* = 1.5 Hz, 1H, H-1), 4.68 (d, *J* = 12.2 Hz, 1H, (OCH_2Ar), 4.62 – 4.51 (m, 3H, (OCH_2Ar), 4.27 (ddd, *J* = 9.3, 5.5, 3.4 Hz, 1H, H-5), 4.07 (td, *J* = 9.5, 2.1 Hz, 1H, H-4), 4.01 (dd, *J* = 3.1, 1.5 Hz, 1H, H-2), 3.66 (dd, *J* = 9.5, 3.1 Hz, 1H, H-3), 3.47 (dd, *J* = 10.0, 3.4 Hz, 1H, H-6a), 3.38 (dd, *J* = 10.0, 5.6 Hz, 1H, H-6b), 2.41 (d, *J* = 2.1 Hz, 1H, -OH), 2.32 (s, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.1 (Ar), 138.1 (Ar), 138.1 (Ar), 137.7 (Ar), 132.2 (Ar), 130.9 (Ar), 129.9 (Ar), 129.0 (Ar), 128.7 (Ar), 128.5 (Ar), 128.1 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.1 (Ar), 87.0 ($OC(C_6H_5)_3$), 86.2 (C-1), 79.8 (C-3), 76.0 (C-2), 72.6 (C-5), 72.1 (OCH_2Ar), 72.0 (OCH_2Ar), 68.3 (C-4), 64.3 (C-6), 21.3 ($ArCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{46}H_{44}NaO_5S$, 731.2801; found, 731.2806.

***p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (26)**



The alcohol **25** (9.00 g, 12.7 mmol) was dissolved in DMF (90 mL) and sodium hydride (60% in mineral oil, 0.46 g, 19.0 mmol) was added at 0 °C followed by *p*-methoxybenzyl chloride (2.60 mL, 19.0 mmol). The reaction mixture was stirred for 6 h at rt and then quenched with methanol. The solvents were removed and co-evaporated twice with toluene. After dilution with EtOAc (150 mL), the organic phase was washed with ice cold water (150 mL) and brine (100 mL), dried over Na_2SO_4, and concentrated to dryness. The crude product was purified by flash column chromatography (10% EtOAc/hexanes, containing 1% Et_3N) to obtain **26** as a white foam (8.90 g, 85%).

***R*$_f$** 0.50 (1:9 EtOAc/hexanes)

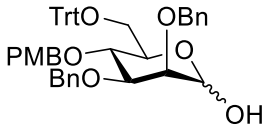
$[\alpha]_D^{23}$ +15.8 (*c* 0.5, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 – 7.45 (m, 6H, ArH), 7.41 – 7.21 (m, 21H, ArH), 7.06 (d, *J* = 8.0 Hz, 2H, ArH), 6.80 (d, *J* = 8.6 Hz, 2H, ArH), 6.70 (d, *J* = 8.6 Hz, 2H, ArH), 5.61 (d, *J* = 1.6 Hz, 1H, H-1), 4.72 4.72 – 4.59 (m, 5H, OCH_2Ar), 4.29 (ddd, *J* = 10.0, 4.9, 1.9 Hz, 1H, H-5), 4.20 (d, *J* = 10.1 Hz, 1H, OCH_2Ar), 4.07 (t, *J* = 9.6 Hz, 1H, H-4), 4.01 (dd, *J* = 3.2, 1.6 Hz, 1H, H-2), 3.81 (dd, *J* = 9.6, 3.2, 1H, H-3), 3.78 (s, 3H, $ArOCH_3$), 3.52 (dd, *J* = 10.0, 1.9 Hz, 1H, H-6a), 3.29 (dd, *J* = 10.0, 4.9 Hz, 1H, H-6b), 2.32 (s, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.2 (Ar), 144.2 (Ar), 138.4 (Ar), 138.4 (Ar), 137.3 (Ar), 131.6 (Ar), 131.4 (Ar), 130.5 (Ar), 130.0 (Ar), 129.8 (Ar), 129.0 (Ar), 128.5 (Ar), 128.5 (Ar), 127.9 (Ar), 127.8 (Ar), 127.8 (Ar), 127.7 (Ar), 127.6 (Ar), 126.9 (Ar), 113.7 (Ar), 86.5 ($OC(C_6H_5)_3$), 85.8 (C-1), 80.4 (C-3), 77.2 (C-2), 74.9 (C-4), 72.9 (C-5), 72.4 (OCH_2Ar), 72.1 (OCH_2Ar), 63.0 (C-6), 55.4 ($ArOCH_3$), 21.2 ($ArCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{54}H_{52}NaO_6S$, 851.3376; found, 851.3392.

2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-mannopyranose (27)



Compound **26** (9.10 g, 10.9 mmol) was dissolved in 9:1 acetone/water (171 mL) and treated with NBS (1.95 g, 10.9 mmol) at 0 °C. After 15 min the reaction was quenched with saturated aqueous $Na_2S_2O_3$ solution and diluted with CH_2Cl_2 (200 mL). The organic layer was separated, and aqueous layer was extracted with CH_2Cl_2 (100 mL). Combined organic layers were washed with water (200 mL) and brine (200 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography (30% EtOAc/hexanes, containing 1% Et_3N) to obtain **27** as a white solid (6.1 g, 77%).

***R*$_f$** 0.37 (3:7 EtOAc/hexanes)

(α:β mixture of anomers ~1:0.2)

Signals observed for both anomers:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 – 7.49 (m, 7H, ArH), 7.49 – 7.41 (m, 3H, ArH), 7.41 – 7.37 (m, 3H, ArH), 7.37 – 7.19 (m, 18H, ArH), 6.85 – 6.80 (m, 2H, ArH), 6.75 – 6.65 (m, 2H, ArH), 4.86 (d, *J* = 12.5 Hz, 1H, OCH_2Ar), 4.77 – 4.58 (m, 5H, OCH_2Ar), 4.25 (d, *J* = 10.1 Hz, 1H, OCH_2Ar).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3 (Ar), 159.2 (Ar), 144.2 (Ar), 144.2 (Ar), 138.9 (Ar), 138.8 (Ar), 138.6 (Ar), 138.3 (Ar), 130.7 (Ar), 130.0 (Ar), 129.0 (Ar), 129.0 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.6 (Ar), 127.0 (Ar), 113.7 (Ar), 113.7 (Ar), 93.7, 83.2, 77.0, 75.3, 74.9, 74.7, 74.3, 73.0, 72.9, 72.5, 62.8.

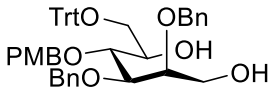
α-anomer:

^{1}H NMR (500 MHz, $CDCl_3$): 5.30 (d, *J* = 1.9 Hz, 1H, H-1), 4.12 (t, *J* = 9.0 Hz, 1H, H-4), 4.01 (dt, *J* = 9.5, 2.4 Hz, 1H, H-5), 3.95 (dd, *J* = 9.0, 3.0 Hz, 1H, H-3), 3.82 (dd, *J* = 3.0, 1.9 Hz, 1H, H-2), 3.79 (s, 3H, $ArOCH_3$), 3.52 (d, *J* = 10.0 Hz, 1H, H-6a), 3.25 (dd, *J* = 10.1, 4.6 Hz, 1H, H-6b).

^{13}C NMR (126 MHz, $CDCl_3$): 92.8 (C-1), 86.5 ($OC(C_6H_5)_3$), 79.7 (C-3), 76.0 (C-2), 74.7 (C-4), 72.3 (C-5), 63.1 (C-6), 55.4 ($ArOCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{47}H_{46}NaO_7$, 745.3135; found, 745.3153.

2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (28)



To a stirred solution of compound **27** (3.50 g, 4.84 mmol) in THF (35 mL) at 0 °C was added $LiAlH_4$ (0.55 g, 14.5 mmol). After stirring 1 h at rt, the mixture was cooled to 0 °C and the excess of $LiAlH_4$ was carefully quenched with a few drops of EtOAc. The mixture was diluted with EtOAc (50 mL), washed with saturated aqueous NH_4Cl solution (50 mL), water (50 mL), dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (50% EtOAc/hexanes, containing 1% Et_3N) to obtain **28** as a colorless syrup (2.89 g, 83%).

***R*$_f$** 0.53 (1:1 EtOAc/hexanes)

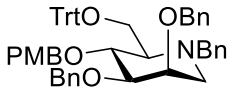
$[\alpha]_D^{23}$ –1.8 (*c* 0.2, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (m, 6H, ArH), 7.33 – 7.23 (m, 19H, ArH), 6.99 – 6.97 (m, 2H, ArH), 6.79 – 6.68 (m, 2H, ArH), 4.67 (d, *J* = 11.3 Hz, 1H, OCH_2Ar), 4.55 (dd, *J* = 11.3, 8.9 Hz, 2H, OCH_2Ph), 4.41 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.32 (s, 2H, OCH_2Ar), 4.08 (dt, *J* = 11.3, 5.7 Hz, 1H, H-5), 3.97 – 3.88 (m, 2H, H-1', H-3), 3.87 – 3.82 (dd, *J* = 7.2, 2.3 Hz, 1H, H-4), 3.76 (m, 4H, $ArOCH_3$, H-1''), 3.70 (dt, *J* = 5.9, 4.0 Hz, 1H, H-2), 3.39 (dd, *J* = 9.5, 4.4 Hz, 1H, H-6a), 3.33 (dd, *J* = 9.5, 5.6 Hz, 1H, H-6b), 2.81 (d, *J* = 5.8 Hz, 1H, 5-OH), 2.15 (dd, *J* = 8.0, 4.5 Hz, 1H, 1-OH).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.4 (Ar), 143.9 (Ar), 138.2 (Ar), 130.1 (Ar), 129.9 (Ar), 128.9 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.0 (Ar), 127.9 (Ar), 127.9 (Ar), 127.8 (Ar), 127.3 (Ar), 113.8 (Ar), 86.9 ($OC(C_6H_5)_3$), 79.7 (C-2), 78.5 (C-3), 77.8 (C-4), 74.4 (OCH_2Ar), 72.8 (OCH_2Ar), 71.6 (OCH_2Ar), 70.4 (C-5), 64.8 (C-6), 60.5 (C-1), 55.4 ($ArOCH_3$).

HRMS–ESI (*m/z*): $[M + Na]^+$ calcd for $C_{47}H_{48}NaO_7$, 747.3292; found, 747.3308.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (29)



Oxalyl chloride (0.24 mL, 2.75 mmol) was dissolved in CH_2Cl_2 (2 mL), and the reaction mixture was cooled to –68 °C. Then DMSO (0.25 mL, 3.44 mmol) in CH_2Cl_2 (1 mL) was added dropwise over 10 minutes. The reaction mixture was stirred for 30 min at –68 °C. Then compound **28** (0.50 g, 0.68 mmol) in CH_2Cl_2 (1 mL) was added dropwise. After this the mixture was stirred at –60 °C for 2 h, followed by dropwise addition of Et_3N (1.70 mL, 8.26 mmol). After that the reaction mixture was then warmed to –5 °C over 2 h and concentrated under reduced pressure (co-evaporated with toluene three times). Crude intermediate was dissolved in MeOH (14 mL), and $BnNH_2$ (1.50 mL, 13.7 mmol) and 3 Å molecular sieves (0.44 g) were subsequently added at 0 °C. The reaction mixture was stirred for 15 minutes, before $NaBH_3CN$ (0.17 g, 2.76 mmol) was added at 0 °C and the reaction mixture was stirred for 17 h at rt. After such time the mixture was filtered, and the filtrate concentrated under reduced pressure. The residue was dissolved in EtOAc (50 mL), washed with aq. saturated aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL), dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (20% EtOAc/hexanes, containing 1% Et_3N) to obtain the **29** as a colorless syrup (0.32 g, 59% over two steps).

***R*$_f$** 0.45 (1:4 EtOAc/hexanes)

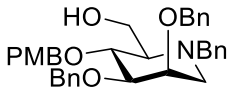
[α]$_D^{23}$ –2.9 (*c* 0.3, $CHCl_3$)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.39 (m, 6H, ArH), 7.30 – 7.18 (m, 24H, ArH), 7.05 – 7.03 (m, 2H, ArH), 6.80 – 6.78 (m, 2H, ArH), 4.63 (d, *J* = 11.1 Hz, 1H, OCH_2Ar), 4.56 (d, *J* = 12.1 Hz, 1H, OCH_2Ar), 4.52 – 4.47 (m, 2H, OCH_2Ar), 4.39 (d, *J* = 11.1 Hz, 1H, OCH_2Ar), 4.33 (d, *J* = 12.4 Hz, 1H, OCH_2Ar), 4.12 (d, *J* = 13.6 Hz, 1H, NCH_2Ar), 3.87 (t, *J* = 6.6 Hz, 1H, H-4), 3.81 (s, 3H, $ArOCH_3$), 3.76 (dt, *J* = 6.3, 2.9 Hz, 1H, H-2), 3.63 (dd, *J* = 7.0, 3.2 Hz,1H, H-3), 3.57 (dd, *J* = 9.9, 3.5 Hz, 1H, H-6a), 3.39 – 3.29 (m, 2H, NCH_2Ar, H-6b), 2.95 (dd, *J* = 12.7, 6.5 Hz, 1H, H-1a), 2.82 (q, *J* = 5.0 Hz, 1H, H-5), 2.14 (d, *J* = 12.2 Hz, 1H, H-1b).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.1(Ar), 144.3 (Ar), 140.0 (Ar), 138.7 (Ar), 130.9 (Ar), 129.6 (Ar), 129.0 (Ar), 128.9 (Ar), 128.4 (Ar), 128.3 (Ar), 128.2 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5 (Ar), 127.4 (Ar), 127.0 (Ar), 126.8 (Ar), 113.8 (Ar), 86.8 ($OC(C_6H_5)_3$), 80.6 (C-3), 75.7 (C-4), 73.2 (OCH_2Ar), 71.8 (C-2), 71.6 (OCH_2Ar), 70.4 (OCH_2Ar), 63.8 (C-5), 62.3 (C-6), 58.7 (NCH_2Ar), 55.4 ($ArOCH_3$), 49.5 (C-1).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{54}H_{54}NO_5$, 796.3996; found, 796.4014.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-mannitol (30)



Compound **29** (0.28 g, 0.35 mmol) was dissolved in pre-mixed solution of 1:1 acetic acid/ethanol (2 mL) and the reaction mixture stirred at 80 °C for 3 h. LCMS and TLC (EtOAc/hexanes 50:50) analysis showed that approximately 90% of product had been formed after such time. The solvents were removed and co-evaporated twice with toluene. The crude product was purified by flash column chromatography on silica (50% EtOAc/hexanes) to obtain **30** as a white solid (0.13 g, 65%).

***R*$_f$** 0.55 (1:1 EtOAc/hexanes)

[α]$_D^{23}$ –4.9 (*c* 0.3, $CHCl_3$)

^{1}H NMR (500 MHz, C_6D_6): δ 7.33 – 7.26 (m, 2H, ArH), 7.25 – 7.18 (m, 6H, ArH), 7.10 – 7.01 (m, 9H, ArH), 6.79 – 6.71 (m, 2H, ArH), 4.83 (d, *J* = 11.0 Hz, 1H, OCH_2Ar), 4.58 (d, *J* = 10.9 Hz, 1H, OCH_2Ar), 4.49 (d, *J* = 12.1 Hz, 1H, OCH_2Ar), 4.43 – 4.33 (m, 2H, OCH_2Ar), 4.23 (d, *J* = 12.3 Hz, 1H, OCH_2Ar), 4.17 (t, *J* = 7.6 Hz, 1H, H-4), 4.04 – 3.93 (m, 2H, NCH_2Ar, H-6a), 3.80 (dd, *J* = 11.4, 2.3 Hz, 1H, H-6b), 3.57 (dt, *J* = 5.5, 2.4 Hz, 1H, H-2), 3.44 (dd, *J* = 8.0, 3.0 Hz, 1H, H-3), 3.24 (s, 3H, $ArOCH_3$), 3.07 (d, *J* = 13.4 Hz, 1H, NCH_2Ar), 3.00 (dd, *J* = 12.9, 5.5 Hz, 1H, H-1a), 2.72 – 2.48 (m, 1H, -OH), 2.39 (dt, *J* = 7.1, 3.5 Hz, 1H, H-5), 1.82 (d, *J* = 15.0 Hz, 1H, H-1b).

^{13}C NMR (126 MHz, C_6D_6): δ 159.7 (Ar), 139.5 (Ar), 139.4 (Ar), 131.7 (Ar), 129.7 (Ar), 129.1 (Ar), 128.7 (Ar), 128.6 (Ar) 128.6 (Ar), 128.4 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 114.1 (Ar), 82.2 (C-3), 76.5 (C-4), 74.6 (OCH_2Ar) , 72.0 (OCH_2Ar), 71.8 (C-2), 71.0 (OCH_2Ar), 65.5 (C-5), 59.1 (NCH_2Ar), 57.8 (C-6), 54.8 ($ArOCH_3$), 50.4 (C-1).

HRMS–ESI (*m*/*z*): $[M + H]^+$ calcd for $C_{35}H_{40}NO_5$, 554.2901; found, 554.2915.

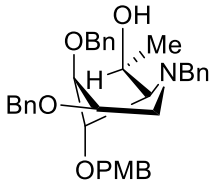
Synthesis of Compounds 31 and 32:

Compound **30** (0.15 g, 0.27 mmol) was dissolved in anhydrous DMSO/dichloromethane 2:1 (2.2 mL) mixture under argon. The reaction mixture then was cooled to 0 °C and diisopropylethylamine (0.24 mL, 1.35 mmol), sulfur trioxide pyridine complex (0.17 g, 1.08 mmol) was added. The reaction mixture was allowed to gradually warm up to the rt and stirred until completion (detected by LCMS and TLC) (Et_2O/CH_2Cl_2: 1:9). After completion the reaction mixture was concentrated under reduced pressure and the residue was diluted with Et_2O (10 mL) and water (10 mL). The organic layer was separated, and aqueous layer was extracted with Et_2O (2 X 10 mL). Combined organic layer was washed with saturated aqueous $NaHCO_3$ solution (10 mL) and brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the intermediate aldehyde

which was used in the next step without purification. MeMgCl (3 M in THF) (0.27 mL, 0.81 mmol) was added to a stirred solution of crude aldehyde in THF (2.20 mL) at 0 °C. After 1 h the reaction was quenched with saturated aqueous NH_4Cl solution, diluted with Et_2O (10 mL), washed with saturated aqueous NH_4Cl solution (10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography (10% Et_2O/CH_2Cl_2) to give mixture of alcohols **31** and **32** (0.14 mg, 90% over two steps, **31**:**32** = 1:3) as a colorless syrup. Since, these two compounds obtained were extremely difficult to separate by chromatography, a small amount of each diastereomer was separated by careful chromatographic purification.

Observed values of coupling constants of compounds **31** ($^3J_{1,2}$ = 13.8 Hz, $^3J_{3,4}$ = 3.3 Hz, $^3J_{4,5}$ = 1.5 Hz) and **32** ($^3J_{1,2}$ = 13.3 Hz, $^3J_{3,4}$ = 5.5 Hz, $^3J_{4,5}$ = 4.0 Hz) are deviated from *J*-values estimated for 1-deoxymanojirimycin derivatives in chair conformation, thus suggesting that both compounds **31** and **32** adopt twist-boat conformations.[9]

2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*manno*-heptitol (31)



***R*$_f$** 0.60 (1:9 Et_2O/CH_2Cl_2)

[α]$_D^{23}$ –7.3 (*c* 0.2, $CHCl_3$)

^{1}H NMR (500 MHz, C_6D_6): δ 7.29 – 7.23 (m, 6H, ArH), 7.16 – 7.08 (m, 11H, ArH), 6.84 – 6.76 (m, 2H, ArH), 4.68 (d, *J* = 12.3 Hz, 1H, OCH_2Ar), 4.57 – 4.48 (m, 2H, H-6, OCH_2Ar), 4.34 – 4.29 (m, 3H, OCH_2Ar), 4.24 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.18 – 4.14 (m, 2H, H-2, -OH), 4.10 – 4.04 (m, 2H, NCH_2Ar), 4.02 (t, *J* = 3.3 Hz, 1H, H-3), 3.80 (dd, *J* = 3.9, 1.5 Hz, 1H, H-4), 3.39 (dd, *J* = 13.8, 11.3 Hz, 1H, H-1a), 3.31 (s, 3H, $ArOCH_3$), 2.75 – 2.68 (m, 2H, H-5, H-1b), 1.29 (d, *J* = 6.0 Hz, 3H, (CH_3).

^{13}C NMR (126 MHz, C_6D_6): δ 160.0 (Ar), 140.3 (Ar), 139.4 (Ar), 139.3 (Ar), 130.6 (Ar), 129.6 (Ar), 129.3 (Ar), 128.8 (Ar), 128.6 (Ar), 128.4 (Ar), 128.2 (Ar), 128.0 (Ar), 127.8 (Ar), 127.7 (Ar), 127.7 (Ar), 127.5 (Ar), 114.3 (Ar), 77.0 (C-4), 76.5 (C-3), 73.5 (OCH_2 Ar), 71.6 (OCH_2Ar), 70.8 (OCH_2Ar), 69.1 (C-2), 68.3 (C-5), 63.2 (C-6), 60.8 (NCH_2Ar), 54.8 (-OCH_3), 43.6 (C-1), 20.5 (CH_3).

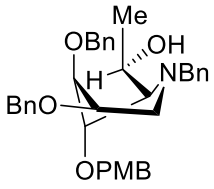
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.25 (m, 13H, ArH), 7.22 – 7.13 (m, 4H, ArH), 6.91 – 6.83 (m, 2H, ArH), 4.68 (d, *J* = 12.2 Hz, 1H, OCH_2Ar), 4.55 – 4.47 (m, 3H, OCH_2Ar), 4.44 (d, *J* = 11.7

Hz, 1H, OCH_2Ar), 4.38 (d, *J* = 11.7 Hz, 1H, OCH_2Ar), 4.14 (m, 2H, H-6, -OH), 4.05 (dt, *J* = 11.4, 3.6 Hz, 1H, H-2), 4.01 (d, *J* = 13.2 Hz, 1H, NCH_2Ar), 3.94 (m, 2H, H-3, NCH_2Ar), 3.82 (s, 3H, $ArOCH_3$), 3.68 (dd, *J* = 3.8, 1.2 Hz, 1H, H-4), 3.10 (dd, *J* = 13.8, 11.5 Hz, 1H, H-1a), 2.60 (dd, *J* = 13.9, 4.0 Hz, 1H, H-1b), 2.54 (d, *J* = 9.6 Hz, 1H, H-5), 1.05 (d, *J* = 6.0 Hz, 3H, $ArCH_3$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.4 (Ar), 139.6 (Ar), 138.7 (Ar), 138.6 (Ar), 130.1 (Ar), 129.3 (Ar), 129.1 (Ar), 128.5 (Ar), 128.5 (Ar), 128.4 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.4 (Ar), 114.0 (Ar), 76.0 (C-4), 75.6 (C-3), 73.2 (OCH_2Ar), 71.5 (OCH_2Ar), 70.8 (OCH_2Ar), 68.1 (C-2), 67.9 (C-5), 62.6 (C-6), 60.5 (NCH_2Ar), 55.4 ($ArOCH_3$), 42.9 (C-1), 19.8 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{36}H_{42}NO_5$, 568.3057; found, 568.3043.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*manno*-heptitol (32)



***R*$_f$** 0.61 (10% Et_2O/CH_2Cl_2)

$[\alpha]_D^{23}$ –25.8 (*c* 0.2, $CHCl_3$)

^{1}H NMR (500 MHz, C_6D_6): δ 7.41 (d, *J* = 6.7 Hz, 2H, ArH), 7.36 – 7.30 (m, 2H, ArH), 7.29 – 7.26 (m, 2H, ArH), 7.22 (dd, *J* = 10.5, 8.2 Hz, 4H, ArH), 7.15 – 6.99 (m, 7H, ArH), 6.87 – 6.78 (m, 2H, ArH), 4.70 (d, *J* = 11.9 Hz, 1H, OCH_2Ar), 4.54 (dd, *J* = 11.4, 3.3 Hz, 2H, OCH_2Ar), 4.47 (d, *J* = 11.4 Hz, 1H), 4.37 (m, 2H, H-6), 4.32 – 4.23 (m, 3H, H-4, OCH_2Ar, NCH_2Ar), 4.00 (dt, *J* = 8.9, 3.3 Hz, 1H, H-2), 3.92 (dd, *J* = 5.5, 2.9 Hz, 1H, H-3), 3.81 (d, *J* = 13.8 Hz, 1H, NCH_2Ar), 3.34 (dd, *J* = 13.3, 9.0 Hz, 1H, H-1a), 3.31 (s, 3H, $ArOCH_3$), 2.68 (dd, *J* = 6.9, 3.8 Hz, 1H, H-5), 2.52 (dd, *J* = 13.2, 3.5 Hz, 1H, H-1b), 2.18 (d, *J* = 4.7 Hz, 1H, -OH), 1.30 (d, *J* = 6.3 Hz, 3H, (CH_3).

^{13}C NMR (126 MHz, C_6D_6): δ 159.8 (Ar), 141.0 (Ar), 139.5 (Ar), 139.2 (Ar), 131.3 (Ar), 129.6 (Ar), 129.1 (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.2 (Ar), 128.1 (Ar), 128.0 (Ar), 128.0 (Ar), 127.7 (Ar), 127.6 (Ar), 127.2 (Ar), 114.2 (Ar), 79.1 (C-3), 76.7 (C-4), 73.1 (OCH_2Ar), 72.6 (OCH_2Ar), 71.3 (OCH_2Ar), 70.9 (C-2), 67.3 (C-5), 67.1 (C-6), 59.8 (NCH_2Ar), 54.8 ($ArOCH_3$), 47.3 (C-1), 21.7 (CH_3).

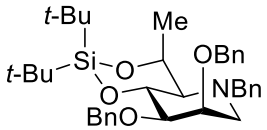
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.19 (m, 17H, ArH), 6.87 – 6.86 (m, 2H, ArH), 4.77 (d, *J* = 11.9 Hz, 1H, OCH_2Ar), 4.63 – 4.57 (m, 2H, OCH_2Ar), 4.55 – 4.48 (m, 2H, OCH_2Ar), 4.44 (d, *J* = 12.1 Hz, 1H, OCH_2Ar), 4.22 (t, *J* = 6.4 Hz, 1H, H-6), 4.13 (d, *J* = 13.8 Hz, 1H, NCH_2Ar), 4.06 (dd, *J* = 5.5, 4.0 Hz, 1H, H-4), 3.94 (dt, *J* = 8.6, 3.3 Hz, 1H, H-2), 3.87 (dd, *J* = 5.6, 2.9 Hz, 1H, H-3),

3.81 (s, 3H, $ArOCH_3$), 3.73 (d, *J* = 13.8 Hz, 1H, NCH_2Ar), 3.17 (dd, *J* = 13.3, 8.7 Hz, 1H, H-1a), 2.57 (dd, *J* = 6.3, 4.0 Hz, 1H, H-5), 2.48 (dd, *J* = 13.3, 3.5 Hz, 1H, H-1b), 1.26 (s, 1H, -OH), 1.21 (d, *J* = 6.4 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.3 (Ar), 140.1 (Ar), 138.7 (Ar), 138.4 (Ar), 130.7 (Ar), 129.3 (Ar), 128.8 (Ar), 128.6 (Ar), 128.4 (Ar), 128.3 (Ar), 127.9 (Ar), 127.9 (Ar), 127.6 (Ar), 127.6 (Ar), 127.0 (Ar), 113.9 (Ar), 78.5 (C-3), 76.1 (C-4), 72.9 (OCH_2Ar), 72.5 (OCH_2Ar), 70.8 (OCH_2Ar), 70.8 (C-2), 67.0 (C-5), 66.8 (C-6), 59.1 (NCH_2Ar), 55.4 ($ArOCH_3$), 46.9 (C-1), 21.1 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{36}H_{42}NO_5$, 568.3057; found, 568.3043.

2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol (34)



TFA (6.0 mL, 0.088 mmol) was added to a stirred solution of compound **31** (5.0 mg, 0.0088 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C. After 1 h the reaction mixture was diluted with CH_2Cl_2 (5 mL) and quenched by addition of saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was separated, and aqueous layer was extracted with CH_2Cl_2 (2 X 5 mL). Combined organic layers were washed with brine (5 mL), then dried over Na_2SO_4, and concentrated to dryness. The crude product was filtered through a short plug of silica gel, concentrated to give compound **33** and used in the next step without further purification. Di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (3.2 mL, 0.010 mmol) was added dropwise to a stirred solution of crude product (3.0 mg, 0.0067 mmol) in pyridine (0.30 mL) at 0 °C. After being stirred at 0 °C for 1.5 h, pyridine was evaporated in *vacuo* (co-evaporating with toluene). The residue was diluted with EtOAc (5 mL) and washed with saturated aqueous NH_4Cl solution (5 mL), brine (5 mL), dried over Na_2SO_4 and concentrated to dryness. Crude product was purified by flash column chromatography (5% EtOAc/hexanes) to afford compound **34** (2.80 mg, 72% over two steps) as a colorless syrup.

***R*$_f$** 0.48 (5:95 EtOAc/hexanes)

$[\alpha]_D^{23}$ –52.5 (*c* 0.2, $CHCl_3$)

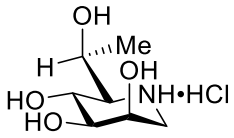
^{1}H NMR (500 MHz, C_6D_6): δ 7.51 – 7.50 (m, 2H, ArH), 7.33 – 7.32 (m, 4H, ArH), 7.28 – 7.18 (m, 4H, ArH), 7.13 – 7.11 (m, 4H, ArH), 7.08 – 7.03 (m, 1H, ArH), 4.90 – 4.82 (m, 2H, OCH_2Ar, H-4), 4.72 (d, *J* = 12.5 Hz, 1H, OCH_2Ar), 4.66 – 4.61 (m, 1H, H-6), 4.54 (d, *J* = 12.7 Hz, 1H, OCH_2Ar), 4.43 (d, *J* = 12.7 Hz, 1H, OCH_2Ar), 3.70 (d, *J* = 13.8 Hz, 1H, OCH_2Ar), 3.43 – 3.42 (m, 1H, H-2), 3.22 (dd, *J* = 9.0, 3.3 Hz, 1H, H-3), 2.88 (dd, *J* = 12.7, 3.6 Hz, 1H, H-1a), 2.65 – 2.58 (m, 2H, H-

5, OCH_2Ar), 1.52 (d, *J* = 6.4 Hz, 3H, CH_3), 1.45 (dd, *J* = 12.6, 1.3 Hz, 1H, H-1b), 1.22 (s, 9H, *t*-Bu), 1.19 (s, 9H, *t*-Bu).

^{13}C NMR (126 MHz, C_6D_6): δ 140.3 (Ar), 139.8 (Ar), 139.1 (Ar), 128.7 (Ar), 128.6 (Ar), 128.4 (Ar), 128.4 (Ar), 127.7 (Ar), 127.6 (Ar), 127.5 (Ar), 127.4 (Ar), 127.4 (Ar), 83.4 (C-3), 73.1 (C-2), 72.8 (OCH_2Ar), 71.3 (OCH_2Ar), 70.8 (C-6), 70.6 (C-4), 66.4 (C-5), 56.7 (OCH_2Ar), 53.2 (C-1), 28.0 (*t*-Bu), 27.7 (*t*-Bu), 21.6 (*t*-Bu), 20.7 (*t*-Bu), 18.1 ($-CH_3$).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{36}H_{50}NO_4Si$, 588.3503; found, 588.3495.

1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol Hydrochloride (7)



TFA (19 mL, 0.24 mmol) was added to a stirred solution of compound **31** (14.0 mg, 0.024 mmol) in CH_2Cl_2 (1.5 mL) at 0 °C. After 1 h the reaction mixture was diluted with CH_2Cl_2 (5 mL) and quenched by addition of saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was separated, and aqueous layer was extracted with CH_2Cl_2 (2 X 5 mL). Combined organic layers were washed with brine (5 mL), dried over Na_2SO_4 and concentrated to dryness. The crude residue was filtered through a short plug of silica gel, concentrated and used in the next step without further purification. To a solution of the crude product **33** (8.0 mg, 0.018 mmol) in ethanol (2 mL) was added 10% Pd/C (8.0 mg), and aqueous 1M HCl solution (36 mL, 0.036 mmol). The suspension was degassed and stirred vigorously under 1 atm of H_2 (balloon) for 14 h. Then it was filtered through a syringe filter (0.22 µm), and the syringe filter was additionally washed with ethanol (2 mL). The filtrate was concentrated to dryness and the crude product was redissolved in deionized water (1 mL). The resulting solution was transferred into a glass vial and lyophilized overnight to afford compound **7** (4.50 mg, 86% over two steps) as a colorless thick syrup.

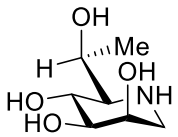
$[\alpha]_D^{23}$ –17.5 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 4.36 (qd, *J* = 6.7, 2.8 Hz, 1H, H-6), 4.30 – 4.28 (m, 1H, H-2), 3.99 (t, *J* = 9.8 Hz, 1H, H-4), 3.73 (dd, *J* = 9.5, 3.0 Hz, 1H, H-3), 3.46 (dd, *J* = 13.6, 3.3 Hz, 1H, H-1a), 3.29 (dd, *J* = 13.6, 1.7 Hz, 1H, H-1b), 3.03 (dd, *J* = 10.2, 3.1 Hz, 1H, H-5), 1.38 (d, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, D_2O): δ 72.5 (C-3), 66.1 (C-4), 65.6 (C-2), 63.5 (C-5), 62.7 (C-6), 47.3 (C-1), 19.5 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1073; found, 178.1066.

1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol (7)



The HCl salt **7** (4.0 mg, 0.020 mmol) was dissolved in 3 mL of ethanol and was stirred with AmberLite® HPR550 OH anion exchange resin. The resin was filtered through a syringe filter (0.22 µm), washed with ethanol, and the filtrate was concentrated to provide the free base **7** (3.0 mg) as a colorless thick syrup.

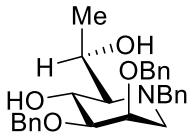
$[\alpha]_D^{23}$ –9.2 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 4.12 (qd, *J* = 6.5, 1.7 Hz, 1H, H-6), 3.87 (td, *J* = 3.0, 1.6 Hz, 1H, H-2), 3.55 (t, *J* = 9.4 Hz, 1H, H-4), 3.45 (dd, *J* = 9.4, 3.2 Hz, 1H, H-3), 2.88 (dd, *J* = 14.6, 2.7 Hz, 1H, H-1a), 2.60 (dd, *J* = 14.6, 1.6 Hz, 1H, H-1b), 2.19 (dd, *J* = 10.0, 1.7 Hz, 1H, H-5), 1.16 (d, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, D_2O): δ 74.7 (C-3), 69.2 (C-4), 68.7 (C-2), 64.4 (C-6), 63.6 (C-5), 48.3 (C-1), 19.5 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1073; found, 178.1068.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (35)



TFA (16 mL, 0.21 mmol) was added to a stirred solution of compound **32** (10 mg, 0.018 mmol) in CH_2Cl_2 (0.50 mL) at 0 °C. After 2 h the reaction mixture was diluted with CH_2Cl_2 (5 mL) and quenched by addition of saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was separated, and aqueous layer was extracted with CH_2Cl_2 (2 X 5 mL). Combined organic layers were washed with brine (5 mL), then dried over Na_2SO_4, and concentrated. The crude residue was purified by flash column chromatography (10% Et_2O/CH_2Cl_2) to afford compound **35** (8.0 mg, 80%) as a white solid.

***R*$_f$** 0.60 (1:9 Et_2O/CH_2Cl_2)

$[\alpha]_D^{23}$ –45.7 (*c* 0.1, $CHCl_3$)

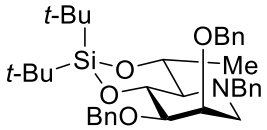
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.24 (m, 15H, ArH), 4.70 (d, *J* = 11.8 Hz, 1H, OCH_2Ar), 4.50 (dd, *J* = 14.8, 11.9 Hz, 2H, OCH_2Ar), 4.42 – 4.36 (m, 1H, H-6), 4.34 (d, *J* = 12.2 Hz, 1H, OCH_2Ar), 4.26 (d, *J* = 13.7 Hz, 1H, NCH_2Ar), 4.19 (t, *J* = 7.4 Hz, H-4), 3.79 (dt, *J* = 5.7, 2.9 Hz, 1H, H-2), 3.55 – 3.45 (m, 2H, H-3, NCH_2Ar), 3.21 (dd, *J* = 13.2, 5.5 Hz, 1H, H-1a), 2.95 (bs, 1H, OH), 2.63

– 2.58 (m, 1H, OH), 2.52 (dd, *J* = 7.1, 4.1 Hz, 1H, H-5), 2.30 (dd, *J* = 13.2, 2.6 Hz, 1H, H-1b), 1.32 (d, *J* = 6.4 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$): δ 139.1 (Ar), 138.3 (Ar), 137.9 (Ar), 128.7 (Ar), 128.6 (Ar), 128.5 (Ar), 128.5 (Ar), 128.1 (Ar), 128.1 (Ar), 127.7 (Ar), 127.7 (Ar), 127.2 (Ar), 81.3 (C-3), 72.0 (OCH_2Ar), 71.8 (C-2), 70.9 (OCH_2Ar), 68.8 (C-5), 67.8 (C-4), 66.8 (C-6), 56.9 (NCH_2Ar), 49.5 (H-1), 20.1 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{28}H_{34}NO_4$, 448.2482; found, 448.2467.

2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (36)



Di-*tert*-butylsilyl bis(trifluoromethanesulfonate) (22 mL, 0.067 mmol) was added dropwise to a stirred solution of compound **35** (0.020 g, 0.044 mmol) in pyridine (1 mL) at 0 °C. After being stirred at 0 °C for 1.5 h, pyridine was evaporated and co-evaporated twice with toluene. The remains were diluted with EtOAc (10 mL), washed with saturated aqueous NH_4Cl solution (10 mL), brine (10 mL), dried over Na_2SO_4 and concentrated to dryness. The crude product was purified by flash column chromatography (5% EtOAc/hexanes) to afford compound **36** (17 mg, 65%) as a colorless syrup.

***R*$_f$** 0.48 (5% EtOAc/hexanes)

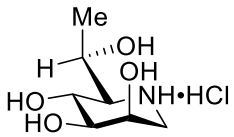
$[\alpha]_D^{23}$ –1.8 (*c* 0.8, $CHCl_3$)

^{1}H NMR (500 MHz, C_6D_6): δ 7.58 – 7.43 (m, 2H, ArH), 7.39 – 7.29 (m, 4H, ArH), 7.26 – 7.24 (m, 4H, ArH), 7.15 – 7.04 (m, 5H, ArH), 5.00 (d, *J* = 12.1 Hz, 1H, OCH_2Ar), 4.86 (dd, *J* = 9.9, 9.1 Hz, 1H, H-4), 4.71 (d, *J* = 12.1 Hz, 1H, OCH_2Ar), 4.63 (d, *J* = 12.0 Hz, 1H, OCH_2Ar), 4.45 (m, 2H, OCH_2Ar, H-6), 4.34 (d, *J* = 13.1 Hz, 1H, OCH_2Ar), 3.55 (d, *J* = 13.2 Hz, 1H, OCH_2Ar), 3.48 (dt, *J* = 3.9, 2.0 Hz, 1H, H-2), 3.23 (dd, *J* = 9.1, 3.6 Hz, 1H, H-3), 3.01 (dd, *J* = 15.1, 2.1 Hz, 1H, H-1a), 2.50 (t, *J* = 9.9 Hz, 1H, H-5), 2.16 – 2.11 (dd, *J* = 15.09, 2.06 Hz, 1H, H-b), 1.45 (d, *J* = 5.9 Hz, 3H, CH_3), 1.19 (s, 9H, *t*-Bu), 1.17 (s, 9H, *t*-Bu).

^{13}C NMR (126 MHz, C_6D_6): δ 140.7 (Ar), 140.4 (Ar), 139.6 (Ar), 129.0 (Ar), 128.6 (Ar), 128.5 (Ar), 128.5 (Ar), 128.4 (Ar), 128.2 (Ar), 128.0 (Ar), 127.7 (Ar), 127.7 (Ar), 127.6 (Ar), 127.1 (Ar), 85.6 (C-3), 79.5 (C-2), 74.1 (OCH_2Ar), 73.8 (OCH_2Ar), 73.3 (C-4), 71.1 (C-6), 69.0 (C-5), 51.0 (OCH_2Ar), 50.3 (C-1), 27.9 (*t*-Bu), 27.6 (*t*-Bu), 22.9 (*t*-Bu), 22.3 (*t*-Bu), 19.93 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{36}H_{50}NO_4Si$, 588.3503; found, 588.3499.

1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)



To a solution of compound **35** (10 mg, 0.022 mmol) in ethanol (2.2 mL) was added 10% Pd/C (10 mg), and 1N aqueous HCl solution (44 mL, 0.044 mmol). The suspension was degassed and stirred vigorously under 1 atm of H_2 (balloon) for 10 h. After such time the reaction mixture was filtered through a syringe filter (0.22 µm), and the syringe filter was additionally washed with ethanol (2 mL). The filtrate was concentrated to dryness and the crude product was redissolved in deionized water (1 mL). The resulting solution was transferred into a glass vial and lyophilized overnight to afford compound **8** (4.3 mg, 90%) as a colorless thick syrup.

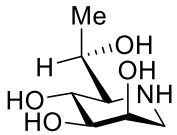
$[\alpha]_D^{23}$ –25.6 (*c* 0.2, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 4.38 (qd, *J* = 6.8, 3.5 Hz, 1H, H-6), 4.30 – 4.29 (m, 1H, H-2), 3.92 (t, *J* = 9.4 Hz, 1H, H-4), 3.73 (dd, *J* = 9.4, 3.1 Hz, 1H, H-3), 3.47 (dd, *J* = 13.6, 3.0 Hz, 1H, H-1a), 3.29 (dd, *J* = 13.6, 1.6 Hz, 1H, H-1b), 3.24 (dd, *J* = 10.8, 3.5 Hz, 1H, H-5), 1.34 (d, *J* = 6.9 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, D_2O): δ 72.9 (C-3), 66.3 (C-4), 65.8 (C-2), 64.0 (C-6), 63.4 (C-5), 48.1 (C-1), 15.7 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1073; found, 178.1069.

1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (8)



The HCl salt **8** (4.0 mg, 0.020 mmol) was dissolved in 3 mL of ethanol and was stirred with AmberLite® HPR550 OH anion exchange resin. The resin was filtered through a syringe filter (0.22 µm), washed with ethanol, and the filtrate was concentrated to provide the free base **8** (3.0 mg) as a colorless thick syrup.

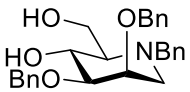
$[\alpha]_D^{23}$ –13.1 (*c* 0.2, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 4.16 (qd, *J* = 6.6, 3.8 Hz, 1H, H-6), 4.00 (td, *J* = 2.6, 1.5 Hz, 1H, H-2), 3.59 – 3.54 (m, 2H, H-3, H-4), 3.02 (dd, *J* = 14.2, 2.7 Hz, 1H, H-1a), 2.74 (dd, *J* = 14.2, 1.7 Hz, 1H, H-1b), 2.53 (dd, *J* = 10.1, 3.8 Hz,1H, H-5), 1.23 (d, *J* = 6.7 Hz, 3H, CH_3).

^{13}C NMR (126 MHz, D_2O): δ 74.8 (C-3), 70.2 (C-4), 69.0 (C-2), 67.4 (C-6), 64.1 (C-5), 48.7 (C-1), 16.5 (CH_3).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_7H_{16}NO_4$, 178.1073; found, 178.1065.

2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-mannitol (37)



TFA (10 mL, 0.120 mmol) was added to a stirred solution of compound **29** (10 mg, 0.012 mmol) in CH_2Cl_2 (0.2 mL) at 0 °C. After 3 h the reaction mixture was diluted with CH_2Cl_2 (5 mL) and quenched by addition of saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was separated, and aqueous layer was extracted with CH_2Cl_2 (2 X 5 mL). Combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. Crude product was purified by flash column chromatography (50% EtOAc/hexanes) to afford compound **37** (3.8 mg, 70%) as a white foam.

$[\alpha]_D^{23}$ –17.8 (*c* 0.4, $CHCl_3$)

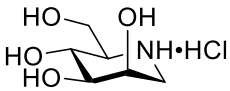
***R*$_f$** 0.26 (50% EtOAc/hexanes)

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 – 7.20 (m, 15H, Ar), 4.64 (d, *J* = 11.8 Hz, 1H, OCH_2Ar), 4.51 (d, *J* = 12.3 Hz, 1H, OCH_2Ar), 4.45 (d, *J* = 11.9 Hz, 1H, OCH_2Ar), 4.31 (d, *J* = 12.3 Hz, 1H, OCH_2Ar), 4.21 (t, *J* = 8.8 Hz, 1H, H-4), 4.15 (d, *J* = 13.6 Hz, 1H, NCH_2Ar), 4.05 – 3.97 (m, 2H, H-6a, H-6b), 3.75 – 3.71 (m, 1H, H-2), 3.36 – 3.26 (m, 2H, NCH_2Ar, H-3), 3.14 (dd, *J* = 13.0, 4.2 Hz, 1H, H-1a), 2.38 (dt, *J* = 8.6, 3.0 Hz, 1H, H-5), 2.09 (d, *J* = 14.8 Hz, 1H, H-1b).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.4 (Ar), 138.1 (Ar), 138.1 (Ar), 129.0 (Ar), 128.6 (Ar), 128.6 (Ar), 128.5 (Ar), 128.0 (Ar), 127.9 (Ar), 127.8 (Ar), 127.7 (Ar), 127.5 (Ar), 82.1 (C-3), 71.3 (OCH_2Ar), 70.6 (OCH_2Ar), 70.6 (C-2), 68.0 (C-4), 65.8 (C-5), 59.3 (C-6), 56.9 (NCH_2Ar), 51.3 (C-1).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_{27}H_{32}NO_4$, 434.2325; found, 434.2321.

1,5-Dideoxy-1,5-imino-D-mannitol Hydrochloride (6)[10]



To a solution of compound **37** (5.0 mg, 0.011 mmol) in ethanol (1 mL) was added 10% Pd/C (5 mg), and 1N aqueous HCl solution (23 mL, 0.023 mmol). The suspension was degassed and stirred vigorously under 1 atm of H_2 (balloon) for 14 h. After such time the reaction mixture was filtered through a syringe filter (0.22 μm), and the syringe filter was additionally washed with ethanol (2 mL). The filtrate was concentrated to dryness and the crude product was redissolved in deionized water (1 mL). The resulting solution was transferred into a glass vial and lyophilized

overnight to afford compound **6** (2.0 mg, 89%) as a colorless thick syrup. Spectroscopic data were consistent with those reported.[10]

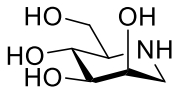
$[\alpha]_D^{23}$ –19.0 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 4.29 (td, *J* = 3.1, 1.5 Hz, 1H, H-2), 4.04 (dd, *J* = 12.6, 3.3 Hz, 1H, H-6a), 3.95 – 3.85 (m, 2H, H-4, H-6b), 3.74 (dd, *J* = 9.6, 3.1 Hz, 1H, H-3), 3.46 (dd, *J* = 13.6, 3.1 Hz, 1H, H-1a), 3.29 (dd, *J* = 13.6, 1.5 Hz, 1H, H-1b), 3.20 (ddd, *J* = 10.3, 6.8, 3.3 Hz, 1H, H-5).

^{13}C NMR (126 MHz, D_2O): δ 72.5 (C-3), 65.9 (C-2), 65.8 (C-4), 60.4 (C-5), 58.2 (C-6), 47.6 (C-1).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_6H_{14}NO_4$, 164.0917; found, 164.0913.

1,5-Dideoxy-1,5-imino-D-mannitol (6)[11]



The HCl salt **6** (5.0 mg, 0.025 mmol) was dissolved in 3 mL of ethanol and was stirred with AmberLite® HPR550 OH anion exchange resin. The resin was filtered through a syringe filter (0.22 µm), washed with ethanol, and the filtrate was concentrated to provide the free base **6** (3.5 mg) as a colorless thick syrup. Spectroscopic data were consistent with those reported.[11]

$[\alpha]_D^{23}$ –6.6 (*c* 0.1, H_2O)

^{1}H NMR (500 MHz, D_2O): δ 3.89 (td, *J* = 2.9, 1.4 Hz, 1H, H-2), 3.66 – 3.65 (m, 2H, H-6a, H-6b), 3.51 – 3.41 (m, 2H, H-3, H-4), 2.94 – 2.84 (m, 1H, H-1a), 2.65 (dt, *J* = 14.4, 1.5 Hz, 1H, H-1b), 2.36 (dt, *J* = 9.4, 4.0 Hz, 1H, H-5).

^{13}C NMR (126 MHz, D_2O): δ 74.6 (C-3), 69.3 (C-2), 68.4 (C-4), 60.8 (C-5), 60.5 (C-6), 48.3 (C-1).

HRMS–ESI (*m/z*): $[M + H]^+$ calcd for $C_6H_{14}NO_4$, 164.0917; found, 164.0910.

Enzyme Kinetics

Biochemical Methods

Gluco iminosugars **2**–**4** were evaluated in their HCl salt forms as inhibitors of *Tm*GH1 and *Ss*GH1 using *p*-nitrophenyl β-D-glucopyranoside as a substrate, and the HCl salts of *manno* compounds **6**–**8** were examined as inhibitors of *Bt*Man2A using *p*-nitrophenyl β-D-mannopyranoside as a substrate. *Tm*GH1 (CZ0211), *Ss*GH1 (CZ0414) and *Bt*Man2A (CZ0810) were purchased from NZYTech in Portugal. *p*-Nitrophenyl β-D-glucopyranoside (487507) and *p*-nitrophenyl β-D-mannopyranoside (N1268) were purchased from Sigma-Aldrich. The UV–visible absorbance of the released *p*-nitrophenolate was monitored at 400 nm in a BioTek Synergy LX multi-mode reader to determine the hydrolysis rate. The K_m values from the Michaelis–Menten equation and the K_i values of competitive inhibition were approximated by GraphPad Prism 9.4 using non-linear regression. All kinetic parameters were determined in duplicate.

*Tm*GH1

The activity of *Tm*GH1 was measured using 0.125 to 4 mM *p*-nitrophenyl β-D-glucopyranoside (*p*NP-Glc) as a substrate (**Figure S3**). All reactions were performed in 50 mM sodium phosphate buffer, pH 6.8, containing 1 mg/mL bovine serum albumin in a total volume of 20 µL. The reaction was initiated by the addition of *Tm*GH1 to give a final concentration of 3.7 nM. The mixture was incubated at 37 ºC for 30 min and the reaction was stopped by the addition of 80 µL of 1 M Na_2CO_3. The absorbance of the resulting mixture was measured at 400 nm to determine a K_m of 0.57 ± 0.08 mM and a k_{cat} of 85 ± 4 s^{-1} (reported K_m = 0.30 mM and k_{cat} = 42 s^{-1} with 2,4-dinitrophenyl β-D-glucopyranoside as a substrate).[12] The K_i determination of **2**, **3** and **4** against *Tm*GH1 was carried out as described above with substrate concentrations ranging from 0.25 to 1 mM and with a range of inhibitor concentrations that spanned the K_i value.

*Ss*GH1

The activity of *Ss*GH1 was measured using 0.0625 to 2 mM *p*-nitrophenyl β-D-glucopyranoside (*p*NP-Glc) as a substrate (**Figure S4**). All reactions were performed in 50 mM sodium phosphate buffer, pH 6.5, containing 1 mg/mL bovine serum albumin in a total volume of 20 µL. The reaction was initiated by the addition of *Ss*GH1 to give a final concentration of 17 nM. The mixture was incubated at 37 ºC for 30 min and the reaction was stopped by the addition of 80 µL of 1 M Na_2CO_3. The absorbance of the resulting mixture was measured at 400 nm to determine a K_m of 0.35 ± 0.02 mM and a k_{cat} of 16 ± 0.3 s^{-1} (reported K_m = 0.16 mM and k_{cat} = 4.2 s^{-1} with *p*NP-Glc as a

substrate).[13] The K_i determination of **2**, **3** and **4** against *Ss*GH1 was carried out as described above with substrate concentrations ranging from 0.125 to 0.5 mM and with a range of inhibitor concentrations that spanned the K_i value.

*Bt*Man2A

The activity of *Bt*Man2A was measured using 0.125 to 2 mM *p*-nitrophenyl β-D-mannopyranoside (*p*NP-Man) as a substrate (**Figure S5**). All reactions were performed in 116 mM Na_2HPO_4 plus 42 mM citric acid buffer, pH 5.6, containing 1 mg/mL bovine serum albumin in a total volume of 20 µL. The reaction was initiated by the addition of *Bt*Man2A to give a final concentration of 5 nM. The mixture was incubated at 37 ºC for 30 min and the reaction was stopped by the addition of 80 µL of 1 M Na_2CO_3. The absorbance of the resulting mixture was measured at 400 nm to determine a K_m of 0.39 ± 0.08 mM and a k_{cat} of 67 ± 5 s^{-1} (reported K_m = 0.19 mM and k_{cat} = 128 s^{-1} with *p*NP-Man as a substrate).[14] The K_i determination of **6**, **7** and **8** against *Bt*Man2A was carried out as described above with substrate concentrations ranging from 0.125 to 0.5 mM and with a range of inhibitor concentrations that spanned the K_i value.

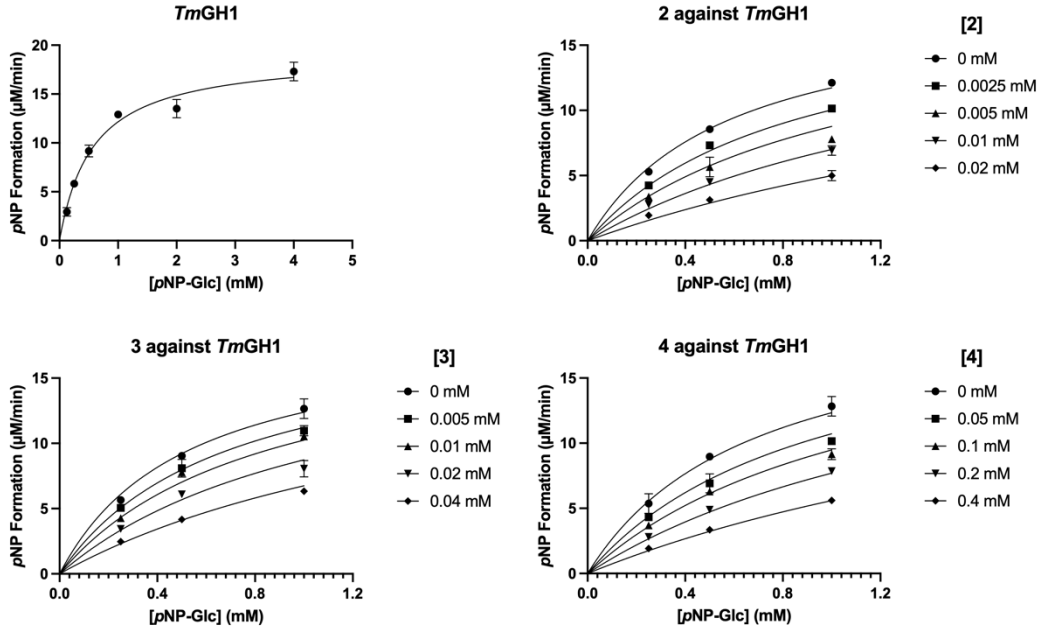


Figure S3. Kinetics of *p*NP-Glc hydrolysis by *Tm*GH1 and K_i determination of **2** (5.4 ± 0.5 µM), **3** (16 ± 2 µM) and **4** (135 ± 11 µM) against *Tm*GH1.

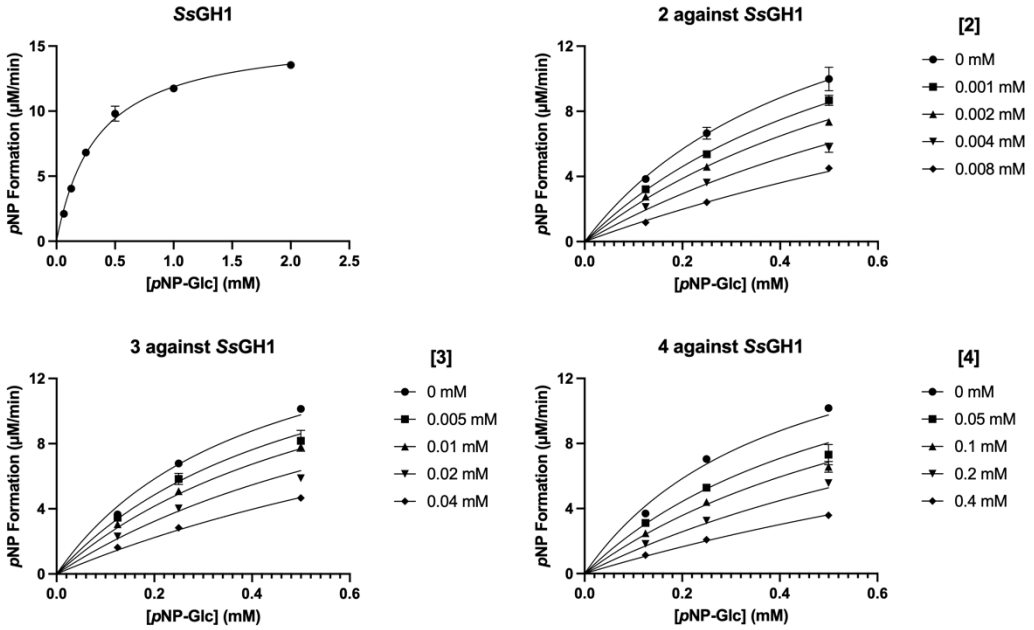


Figure S4. Kinetics of *p*NP-Glc hydrolysis by *Ss*GH1 and K_i determination of **2** (3.1 ± 0.2 µM), **3** (17 ± 1 µM) and **4** (105 ± 10 µM) against *Ss*GH1.

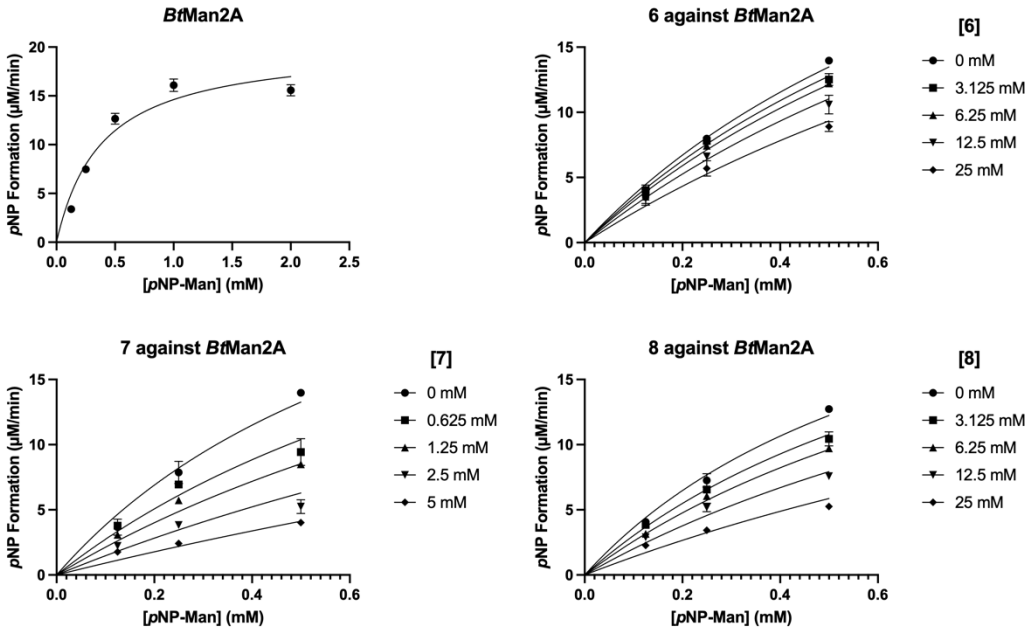


Figure S5. Kinetics of *p*NP-Man hydrolysis by *Bt*Man2A and K_i determination of **6** (38 ± 5 mM), **7** (1.4 ± 0.2 mM) and **8** (14 ± 1 mM) against *Bt*Man2A.

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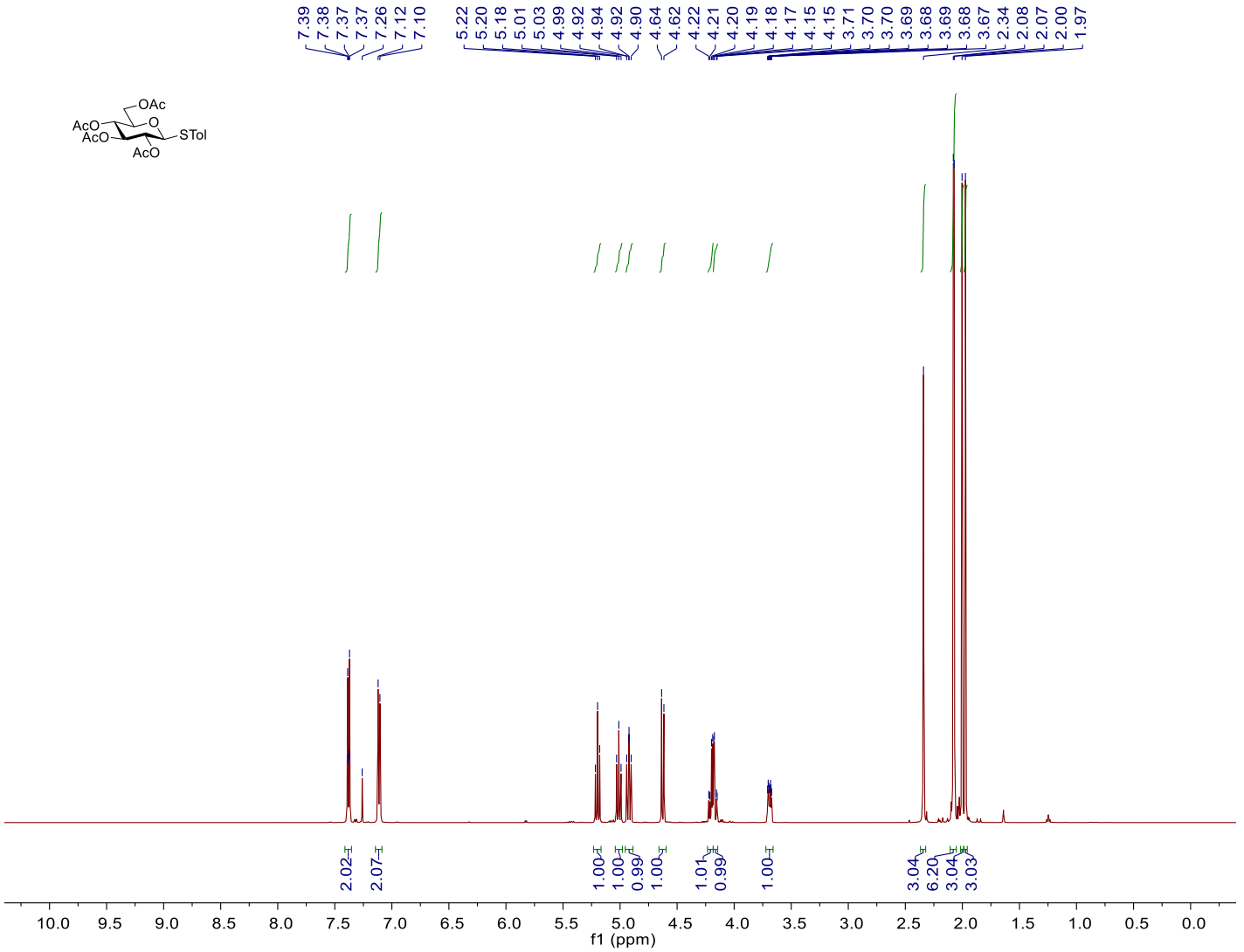
Author Contributions

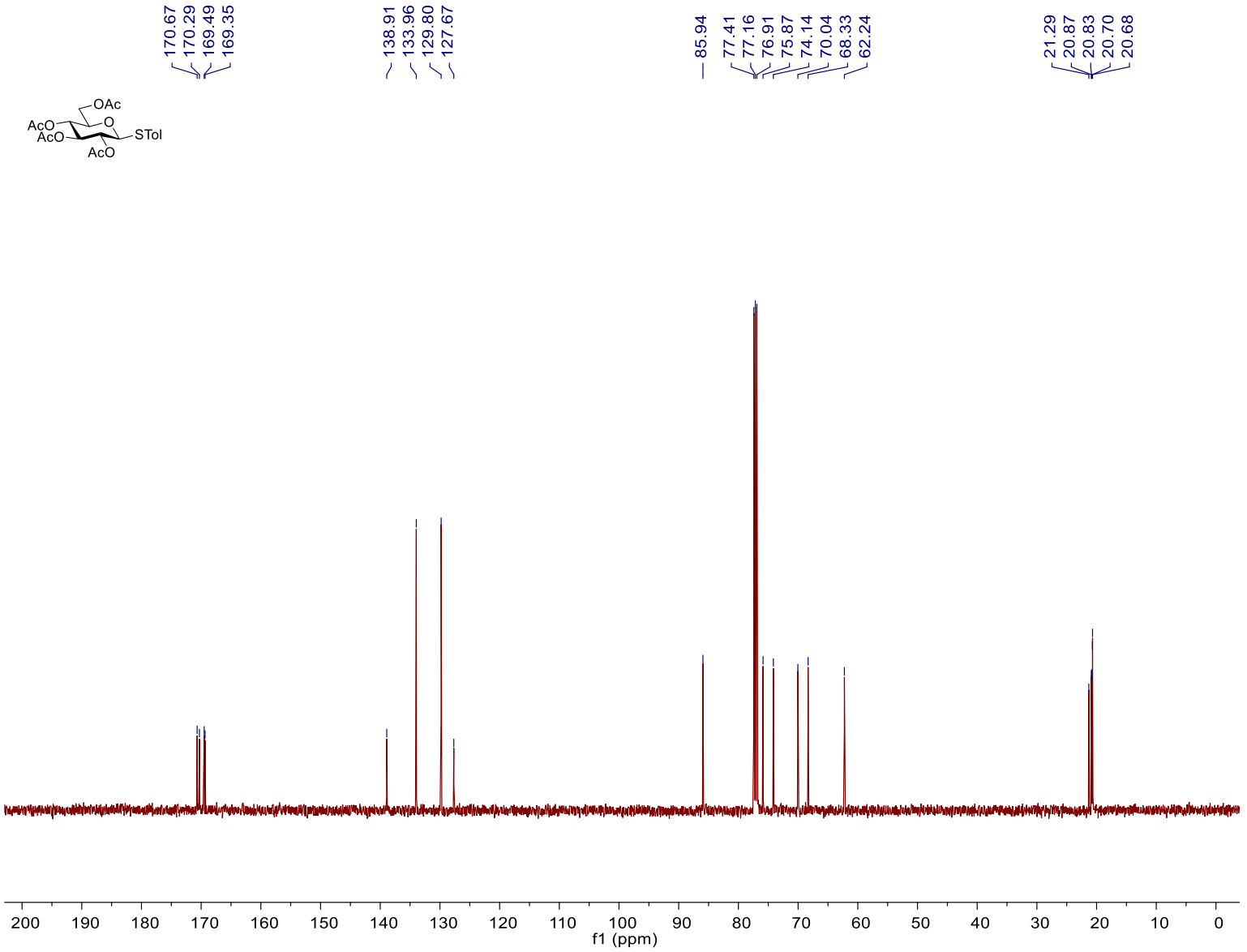
DC conceived the project and obtained funding. PST, CA, KWM and DC designed the experiments. PST and CA synthesized all the compounds, obtained, analyzed and documented the data under the supervision of DC. PST performed all the biochemical experiments under the supervision of KWM and DC. PST and DC wrote the manuscript with input from all authors.

NMR Spectra

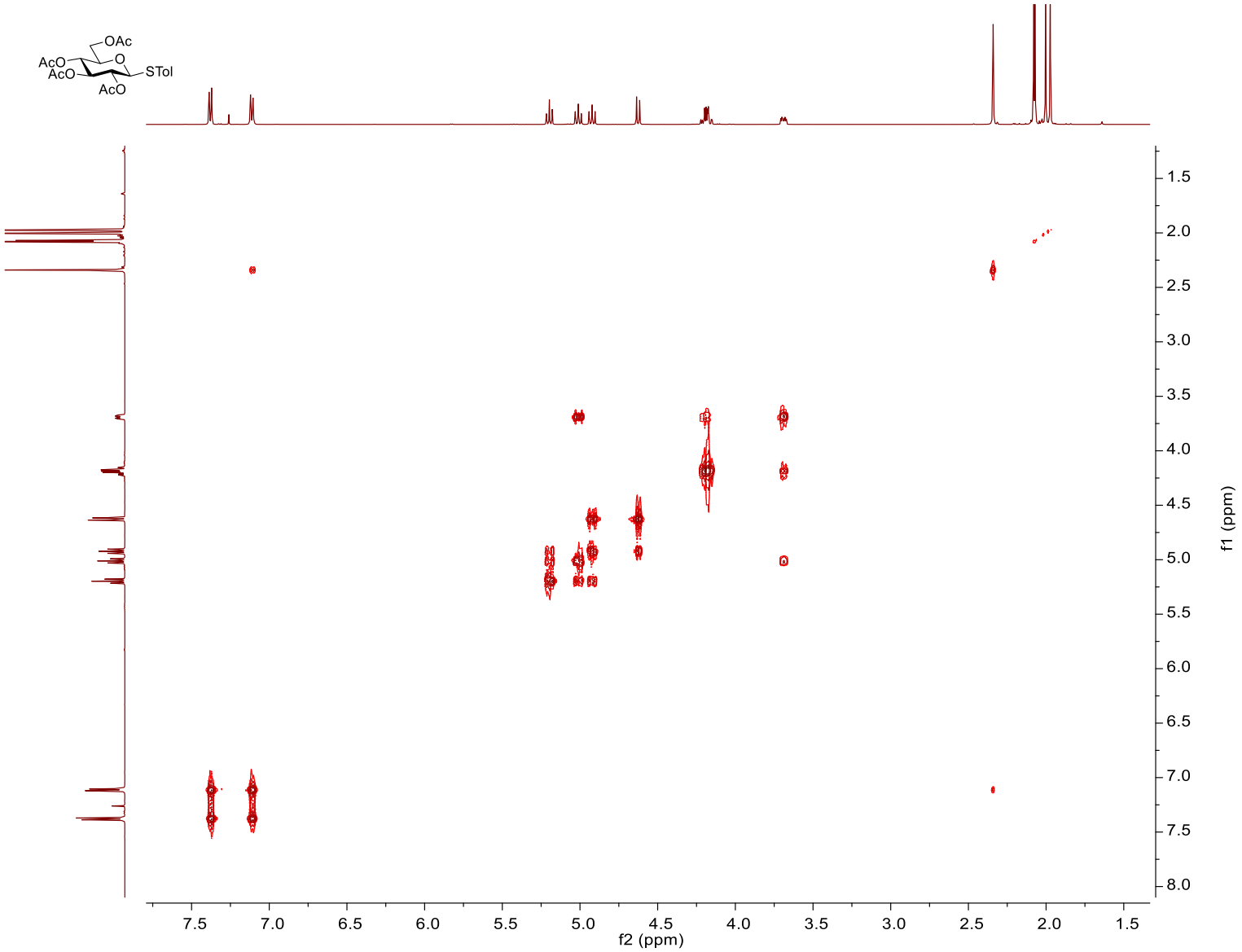
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (S2)



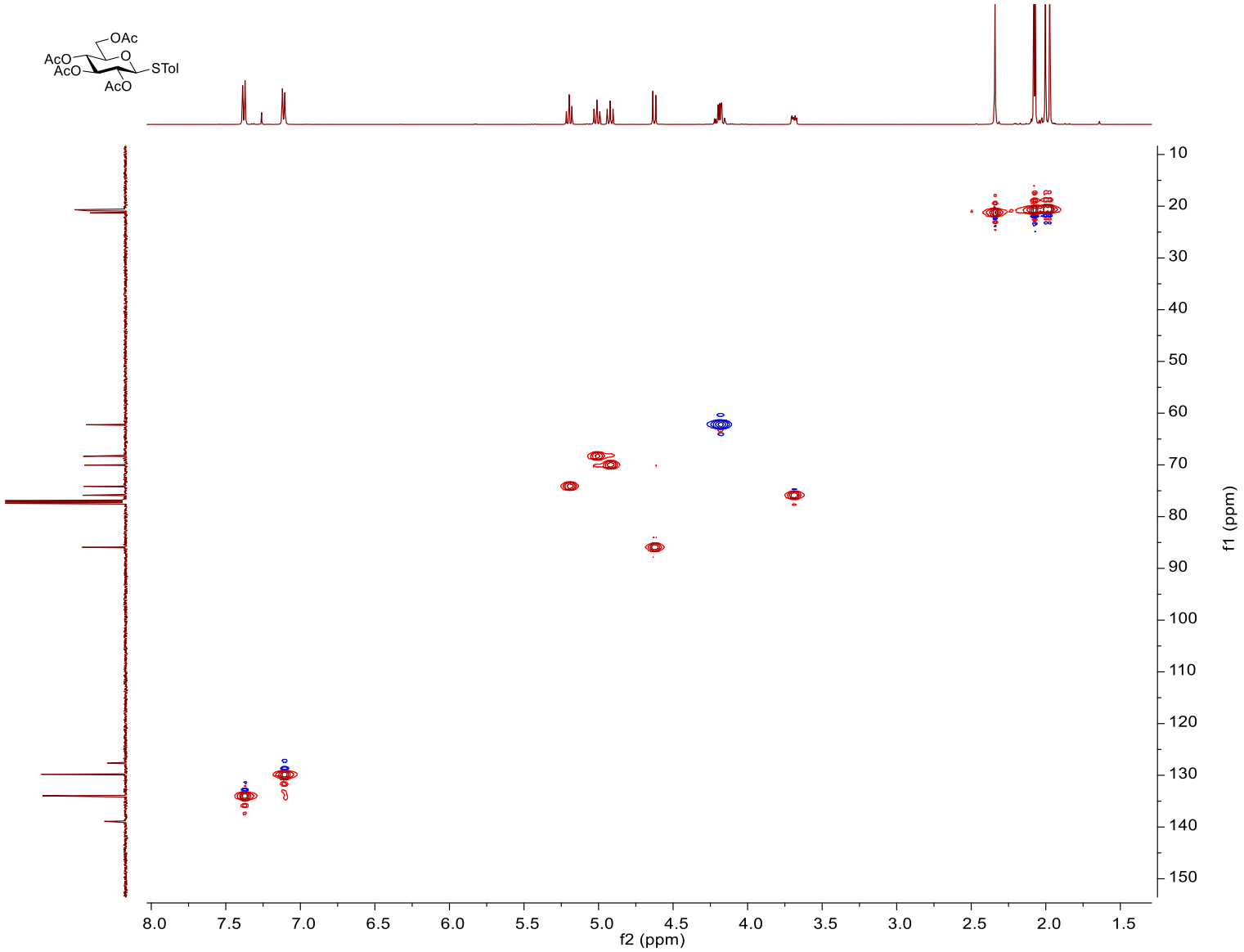
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (S2)



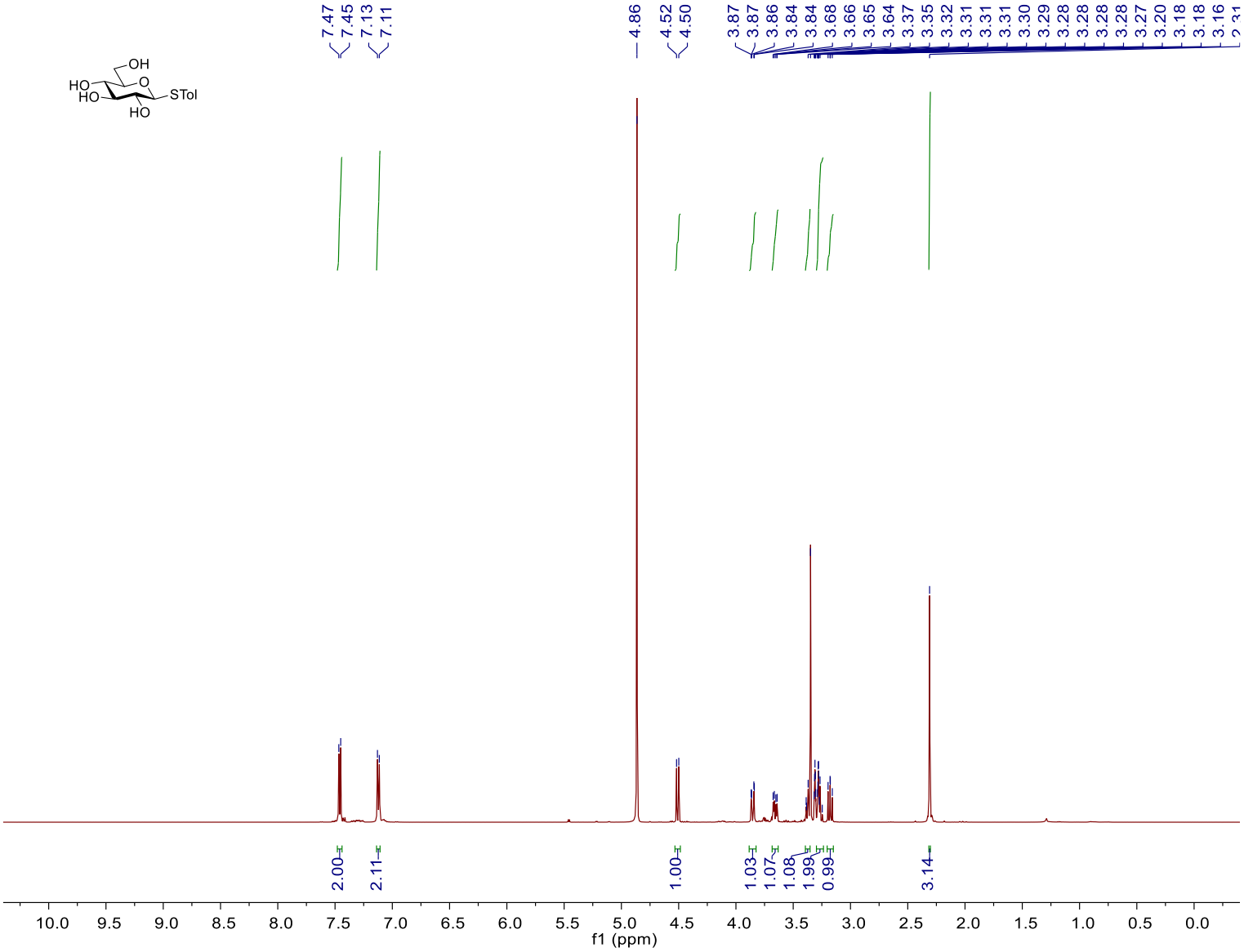
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (S2)



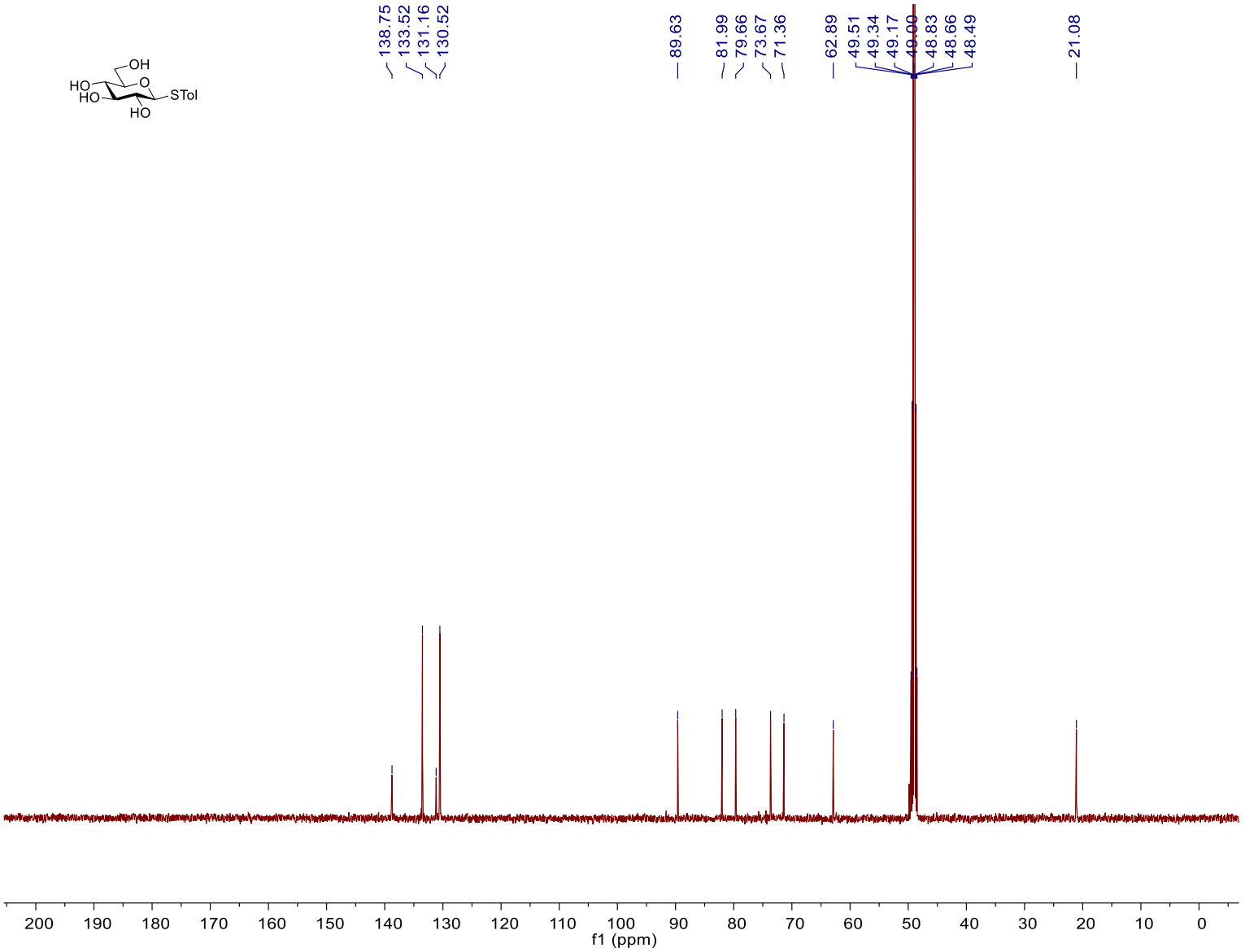
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (S2)



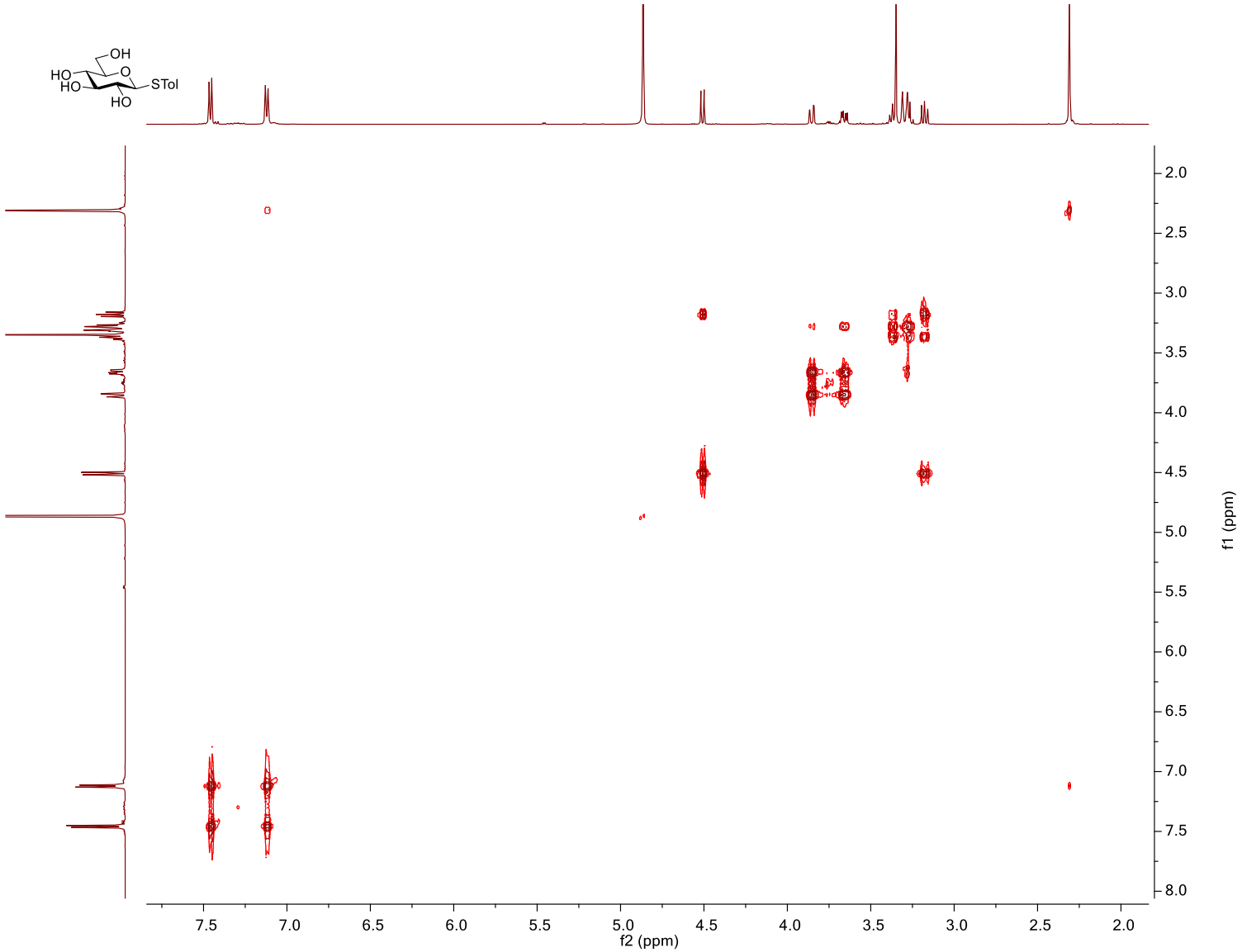
^{1}H NMR (500 MHz, CD_3OD) Spectrum of *p*-Methylphenyl 1-Thio-β-D-glucopyranoside (S3)



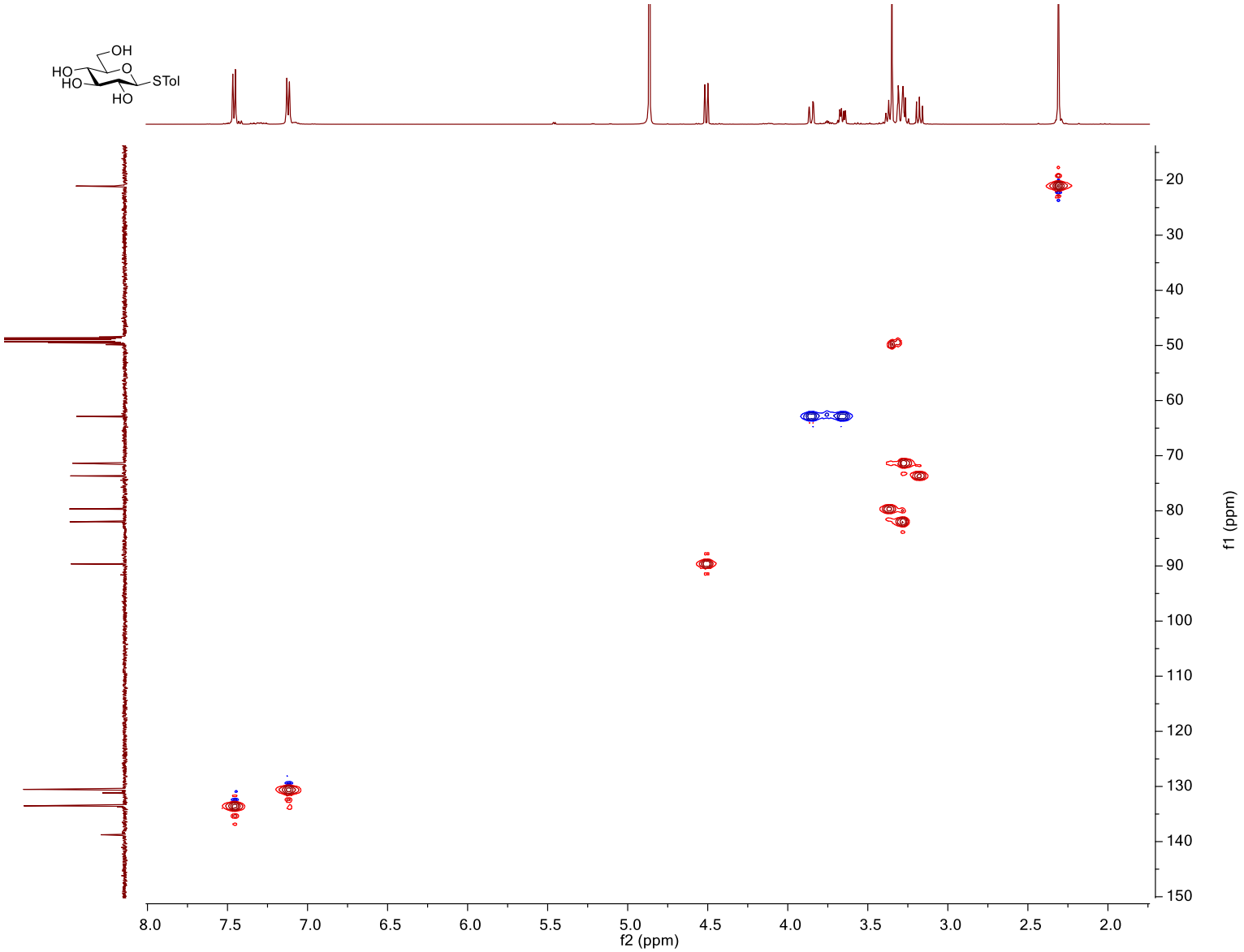
^{13}C NMR (126 MHz, CD_3OD) Spectrum of *p*-Methylphenyl 1-Thio-β-D-glucopyranoside (S3)



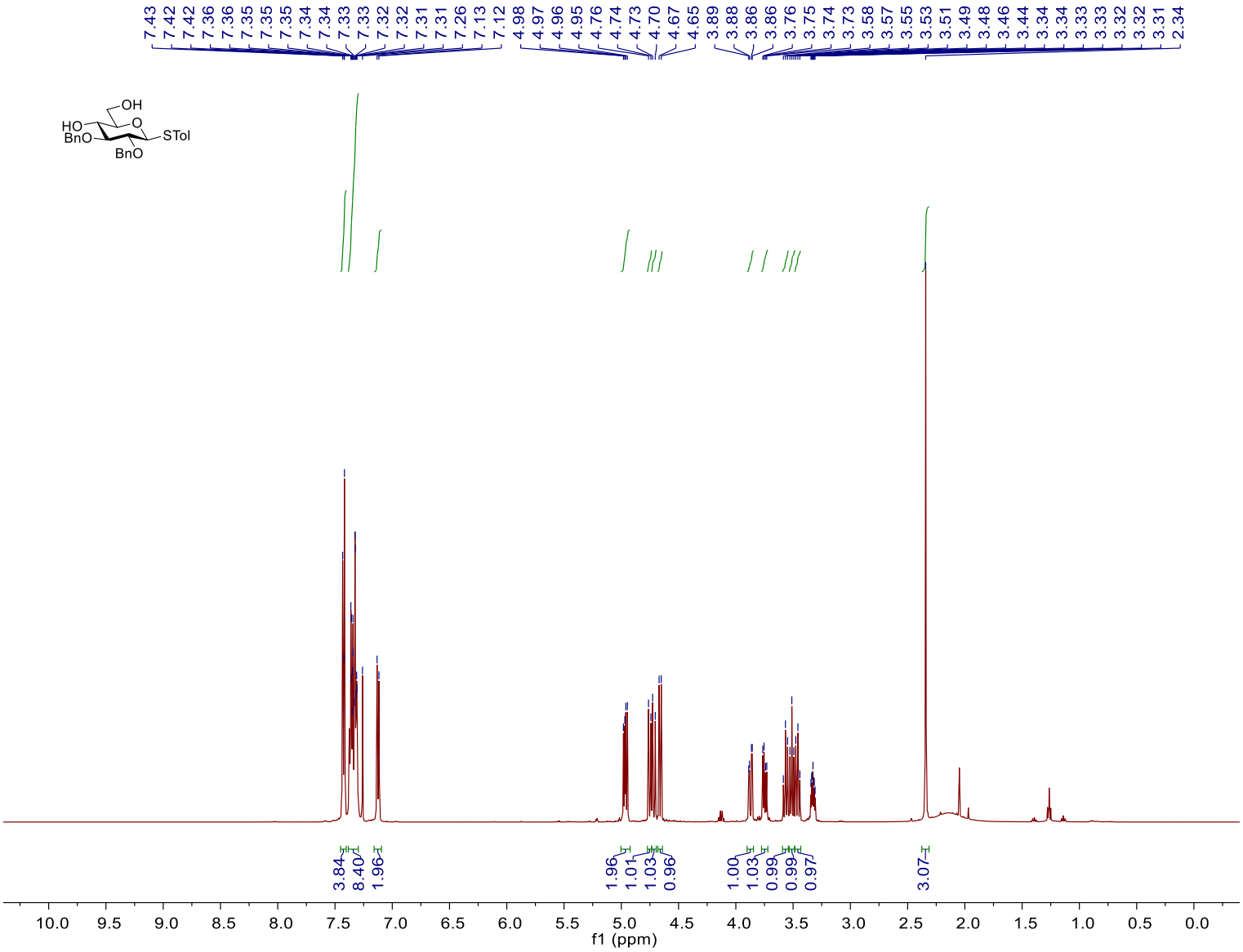
COSY NMR (500 MHz, CD_3OD) Spectrum of *p*-Methylphenyl 1-Thio-β-D-glucopyranoside (S3)



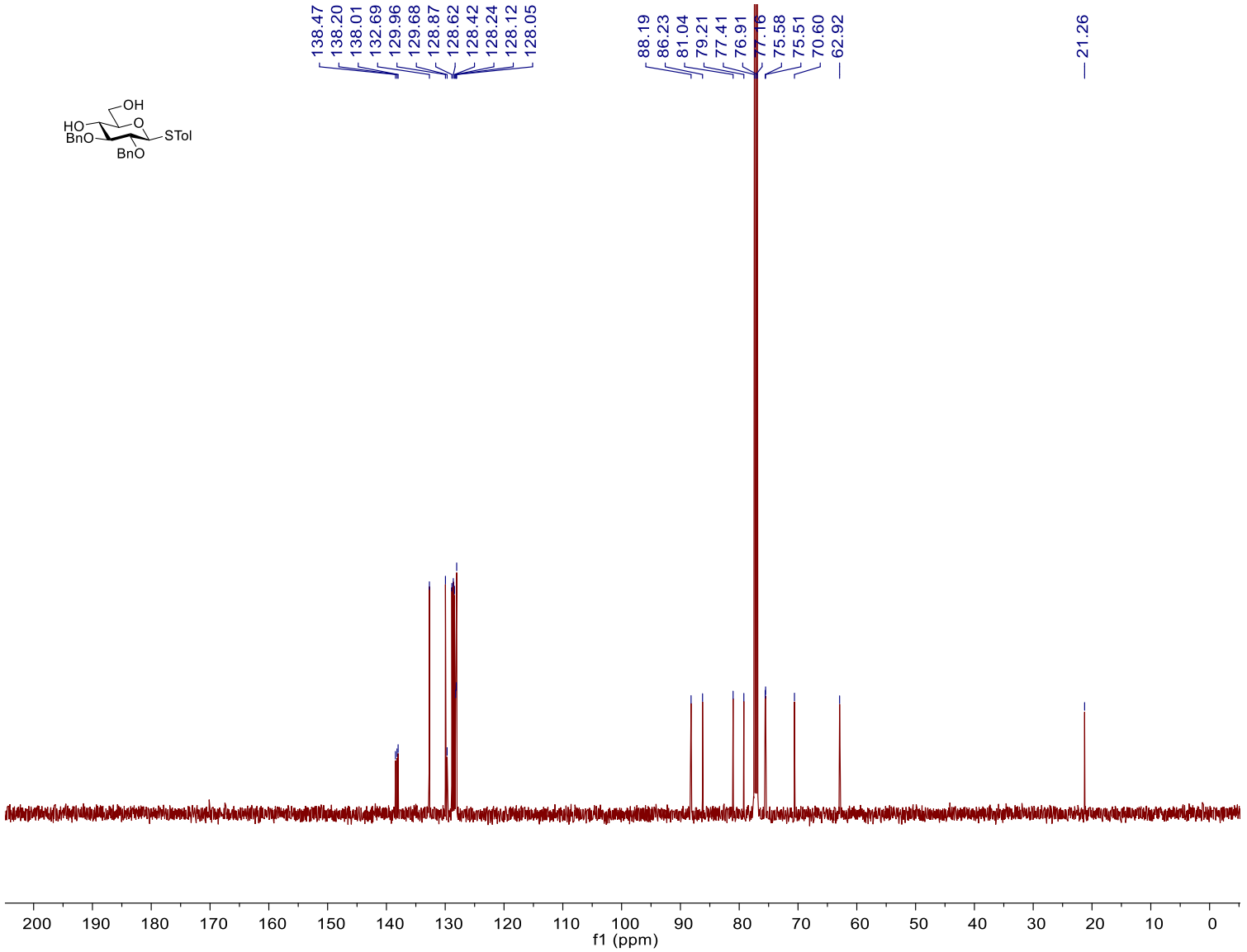
HSQC NMR (500 MHz, CD_3OD) Spectrum of *p*-Methylphenyl 1-Thio-β-D-glucopyranoside (S3)



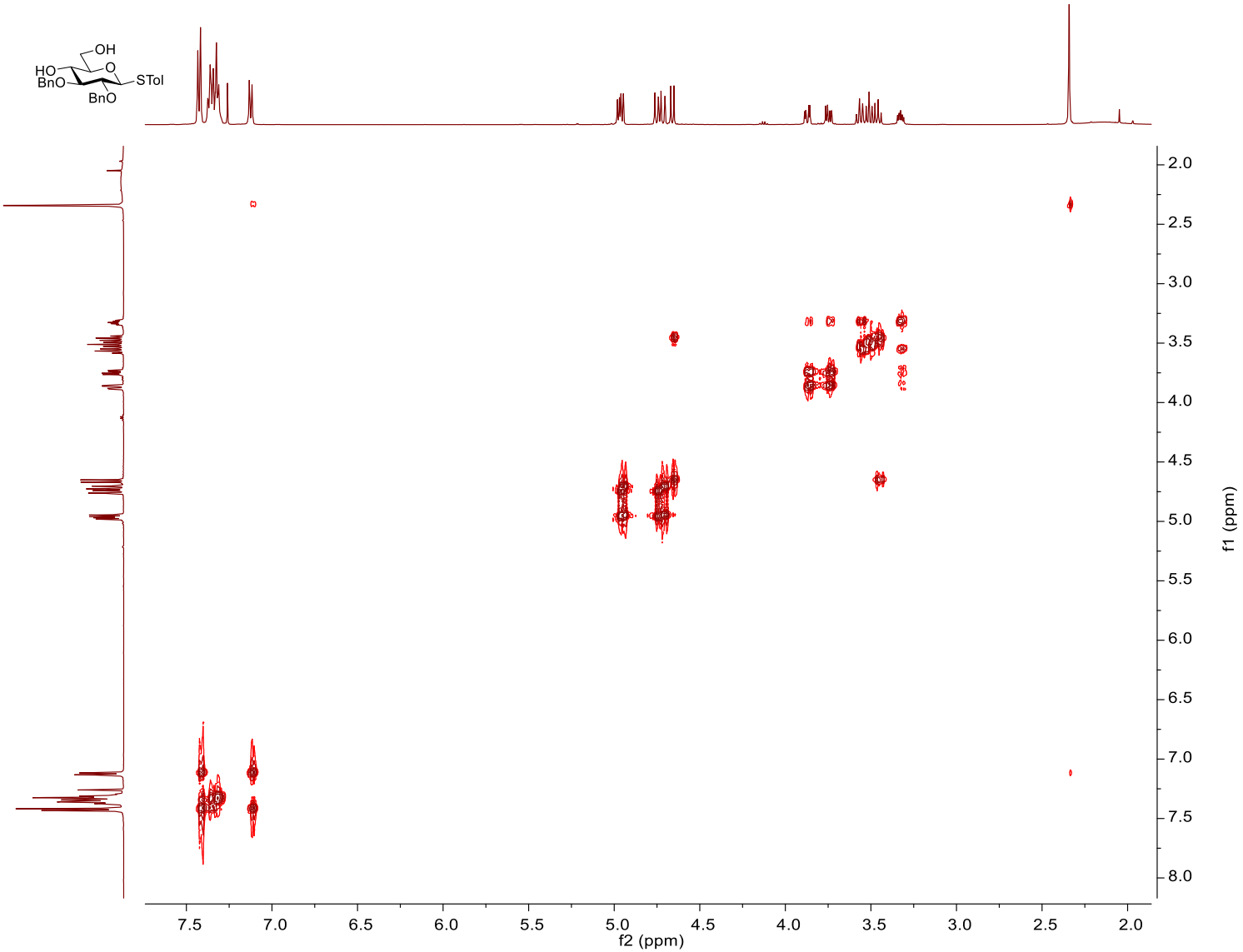
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-β-D-glucopyranoside (10)



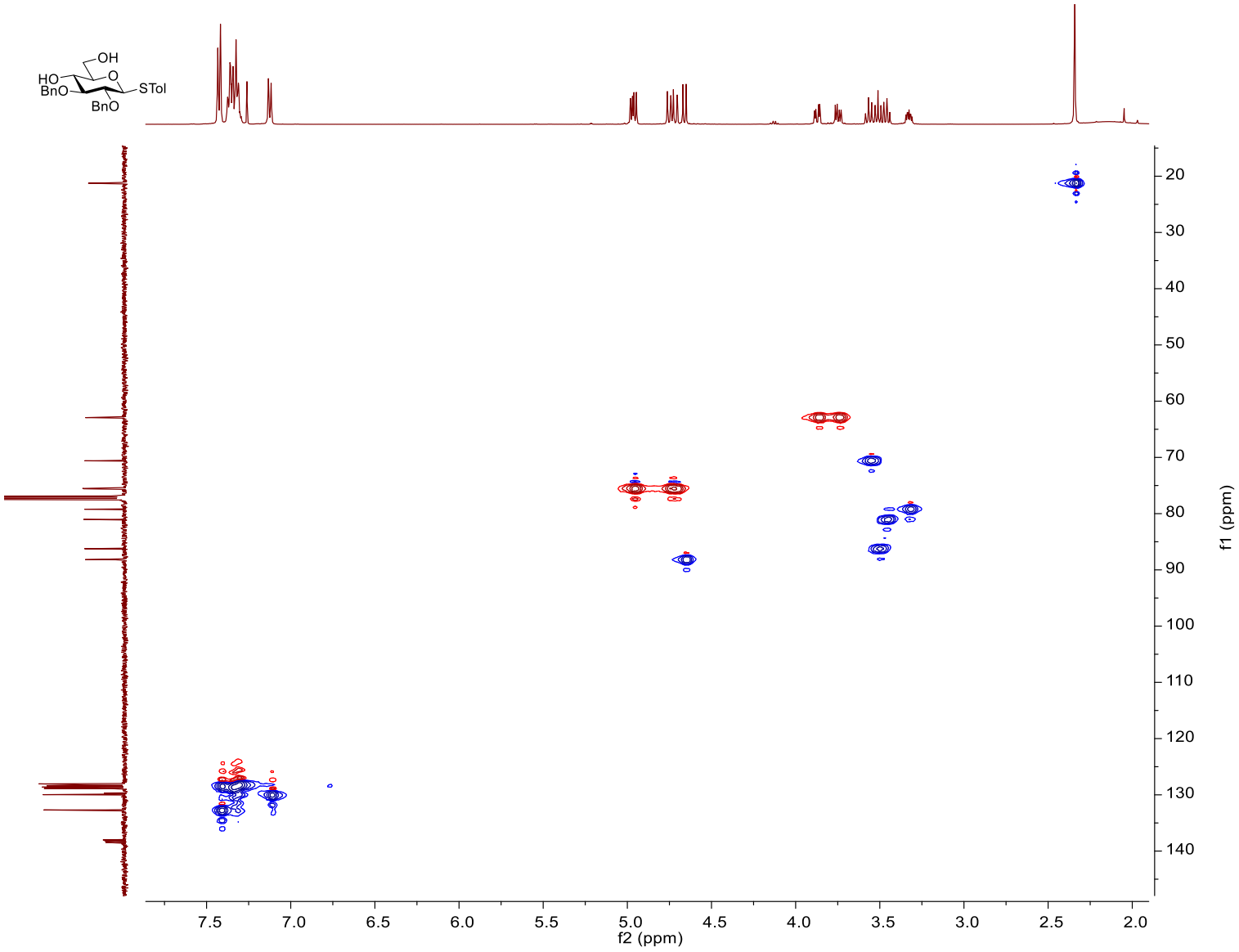
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-β-D-glucopyranoside (10)



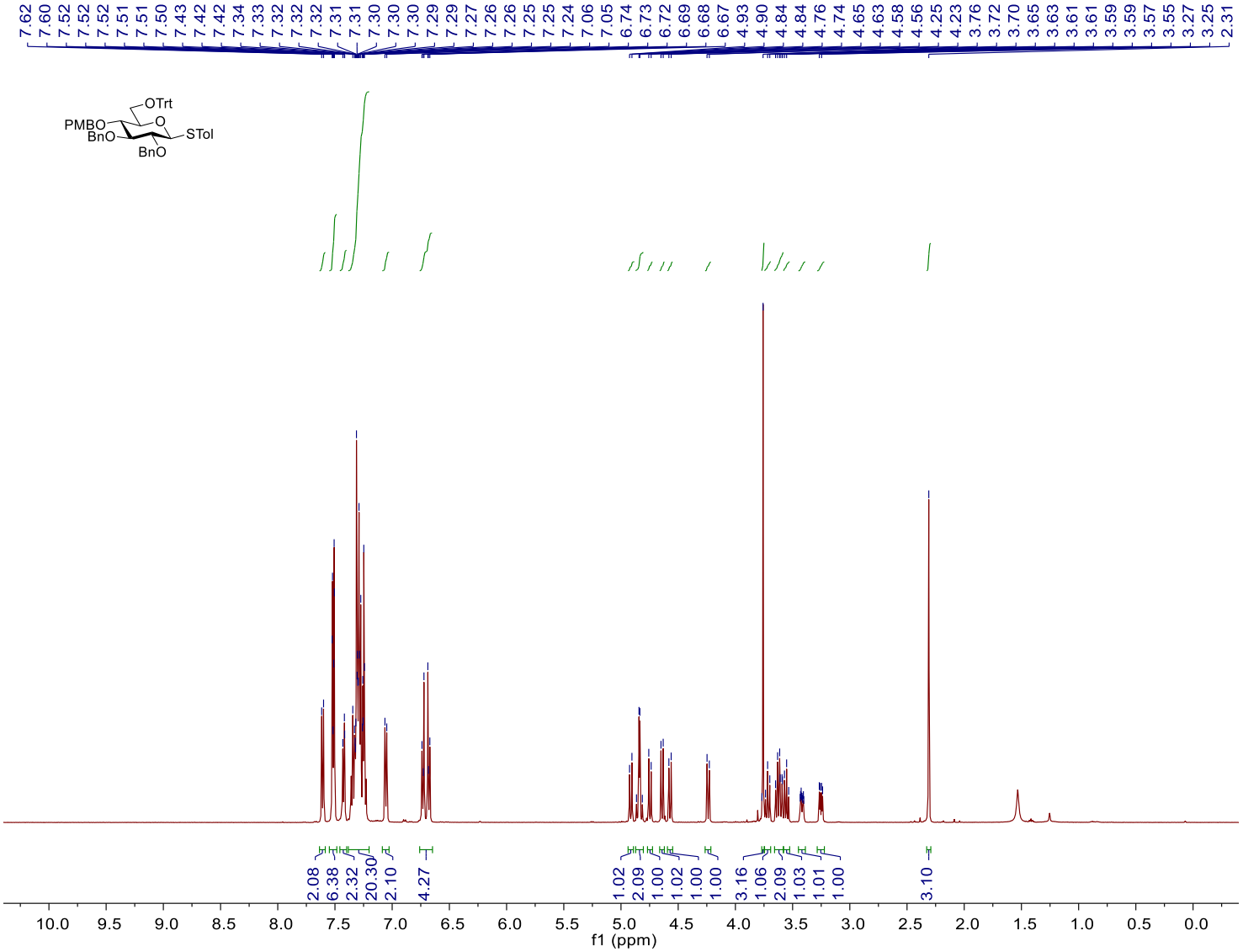
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-β-D-glucopyranoside (10)



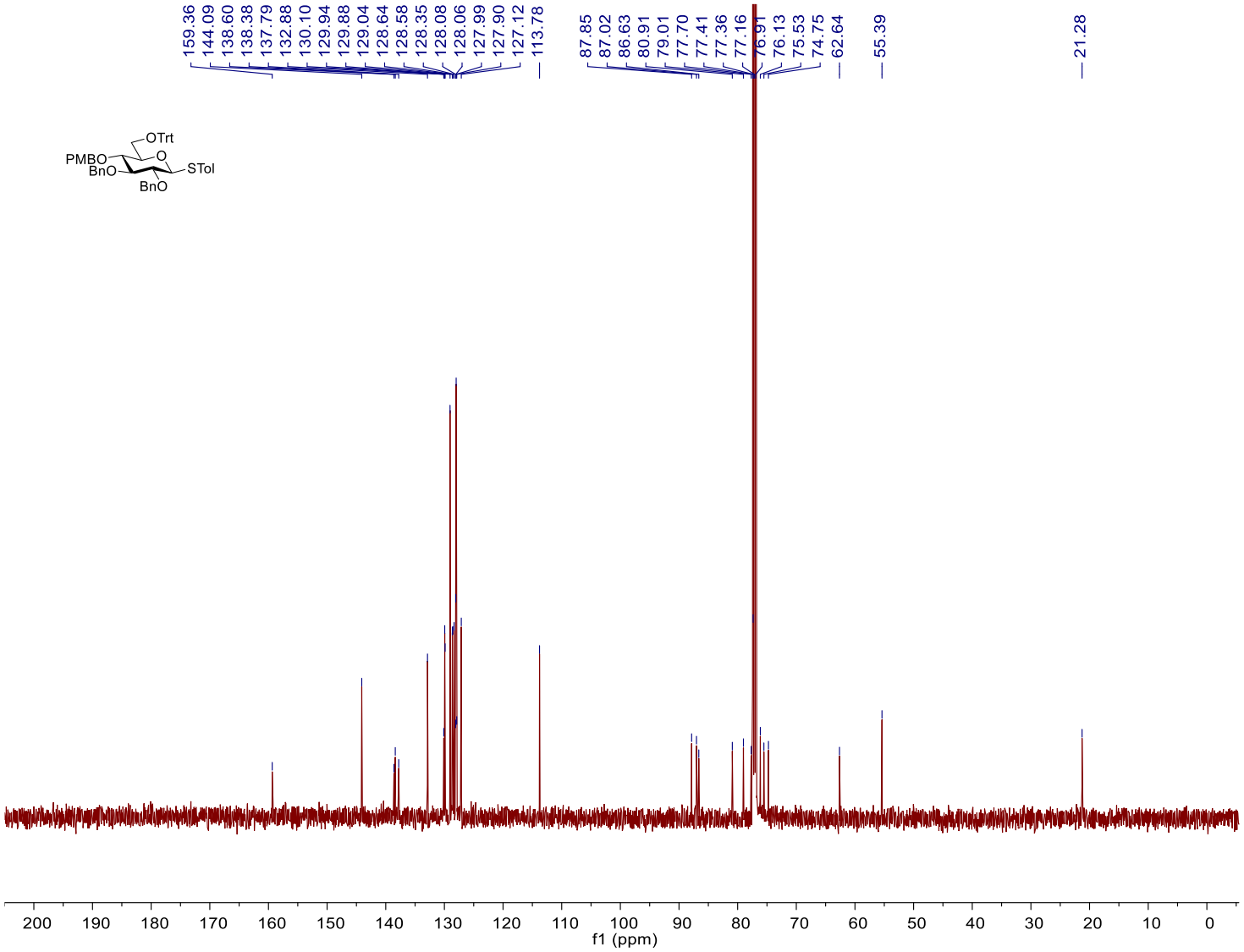
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-β-D-glucopyranoside (10)



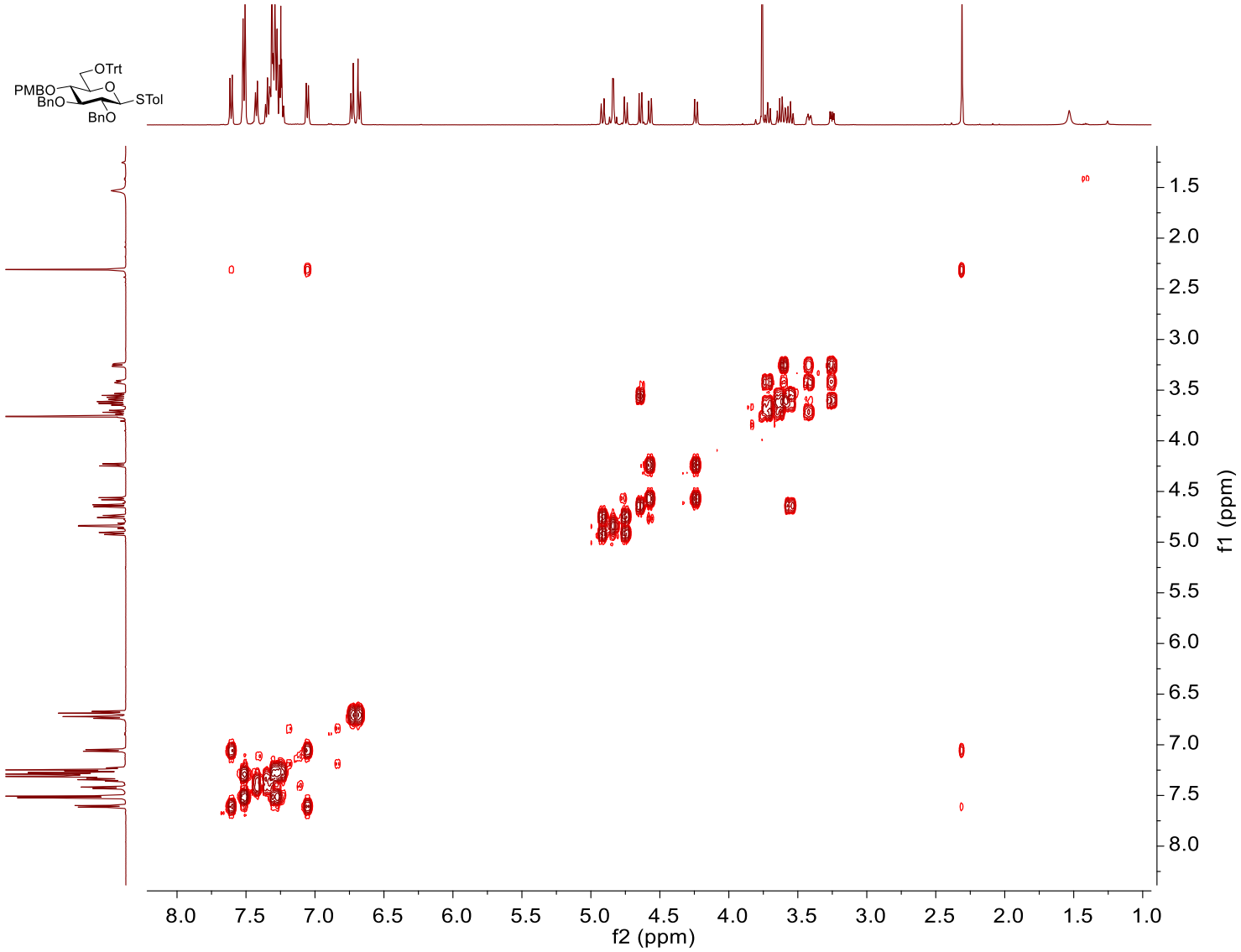
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-β-D-glucopyranoside (11)



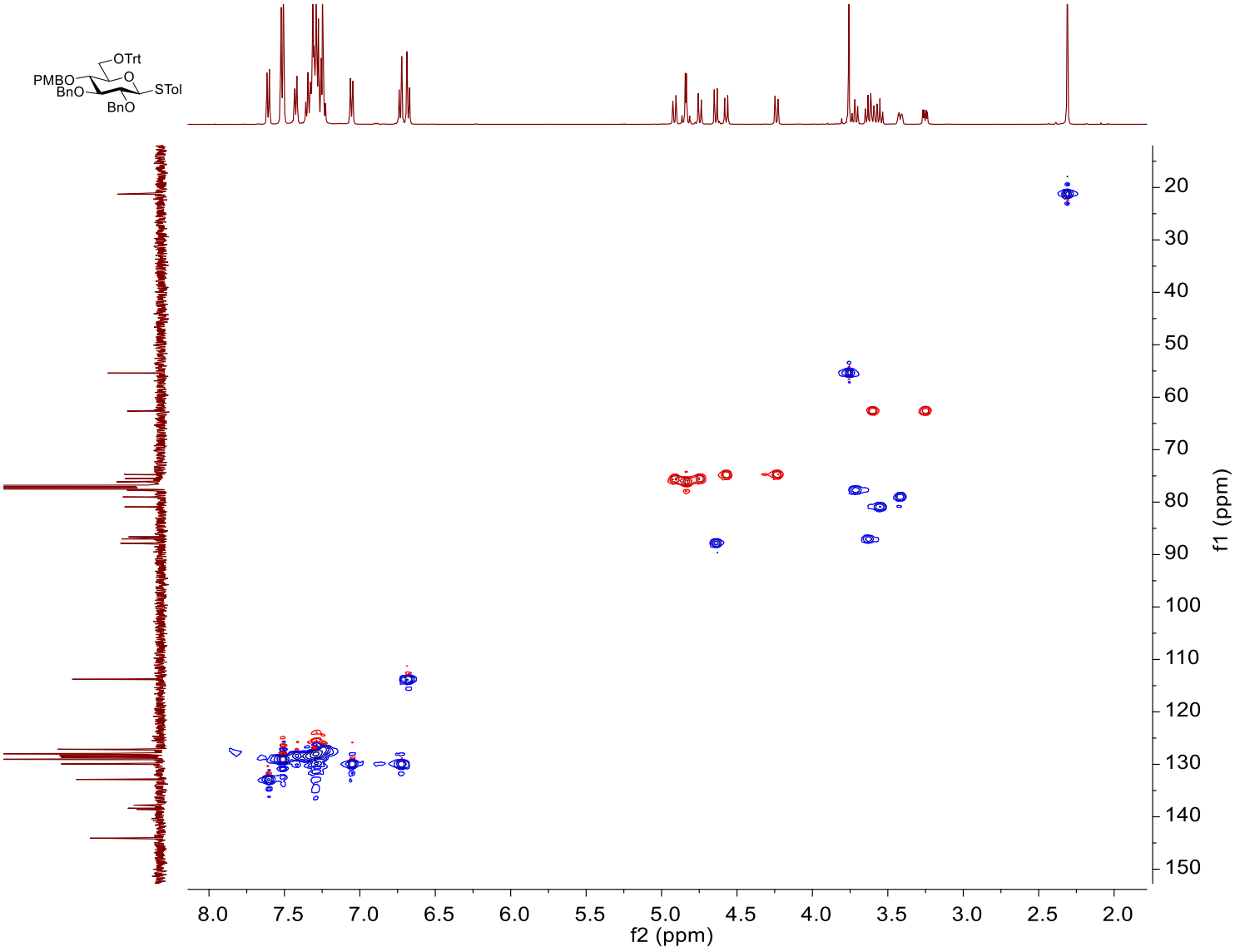
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-β-D-glucopyranoside (11)



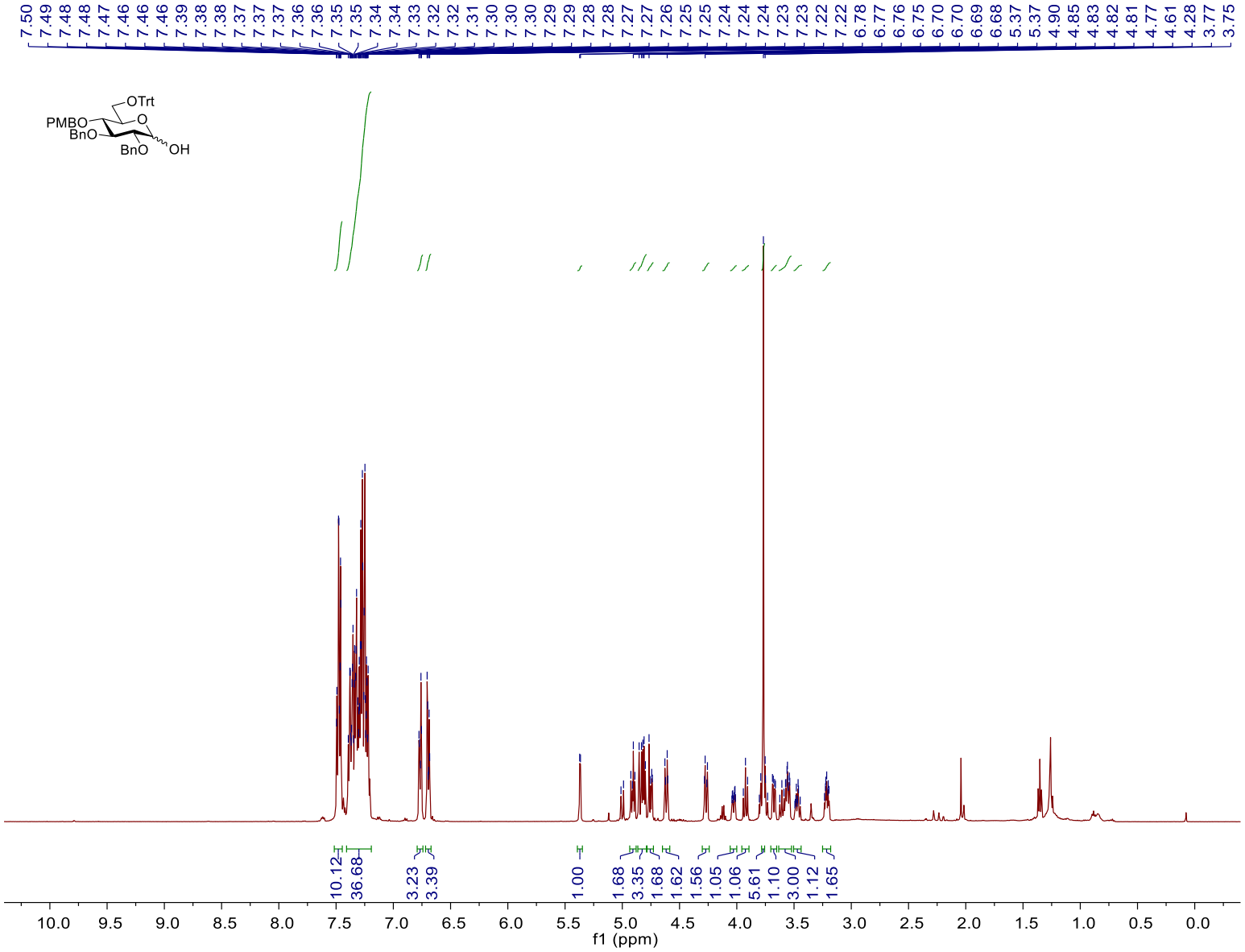
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-β-D-glucopyranoside (11)



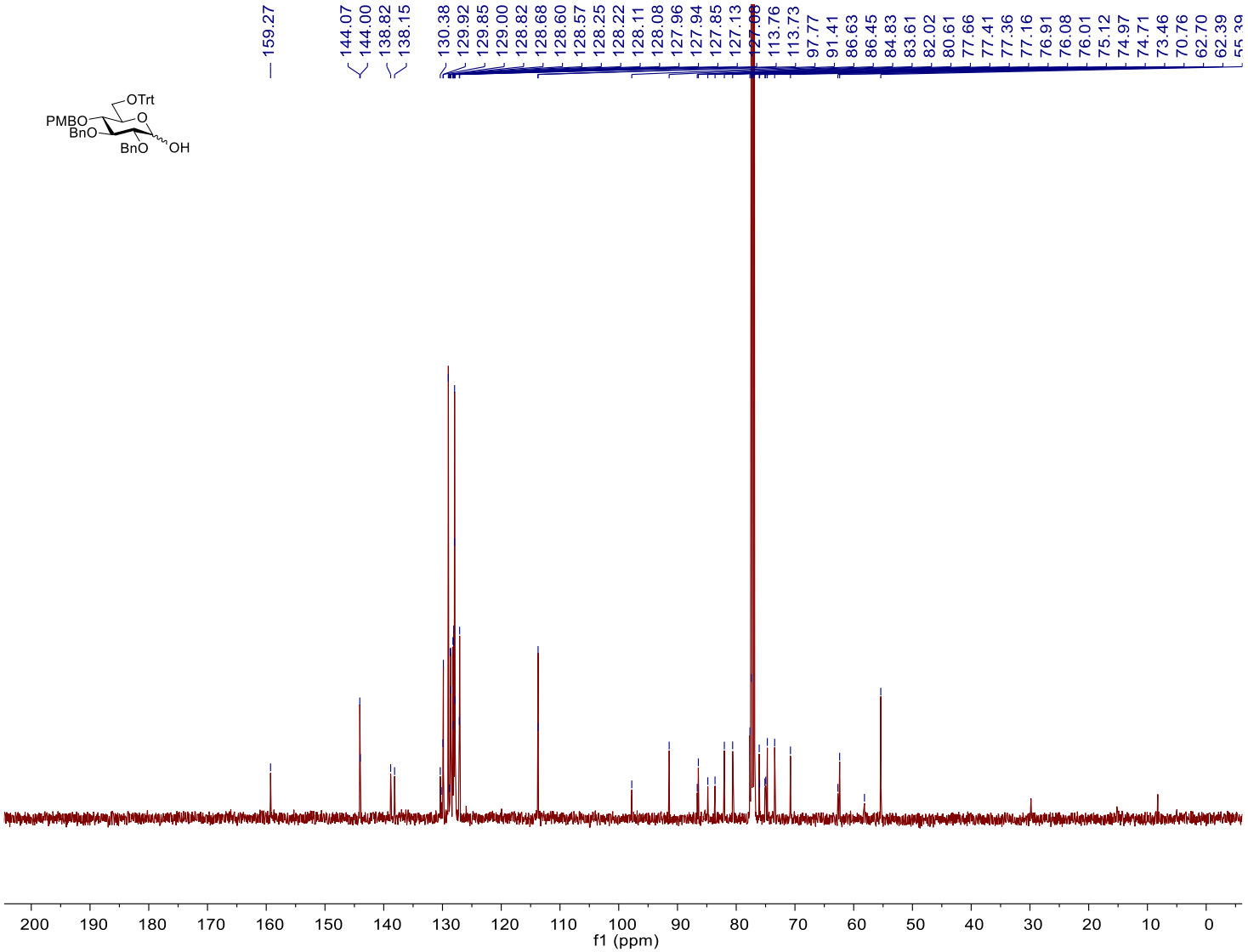
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-β-D-glucopyranoside (11)



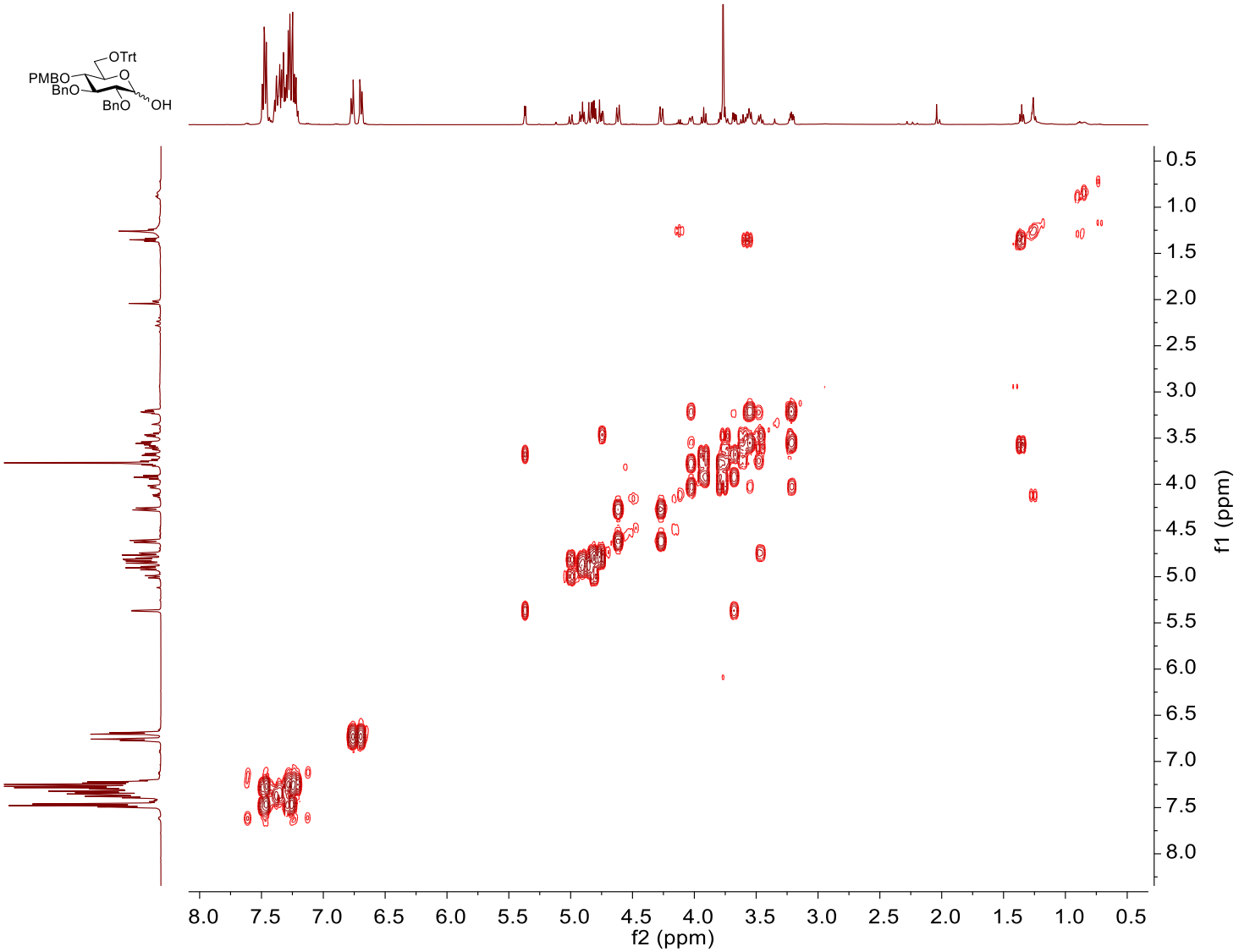
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-glucopyranose (12)



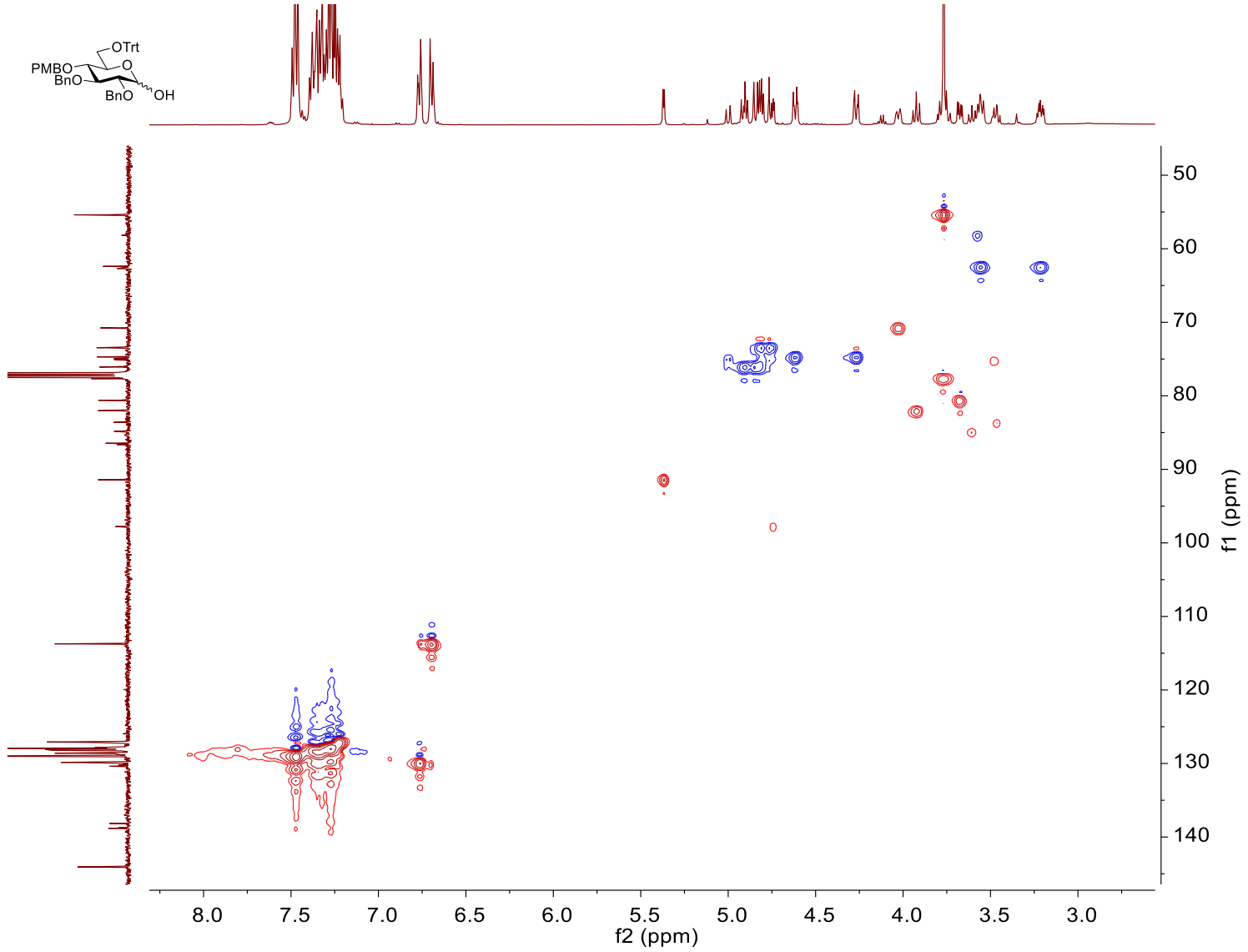
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-glucopyranose (12)



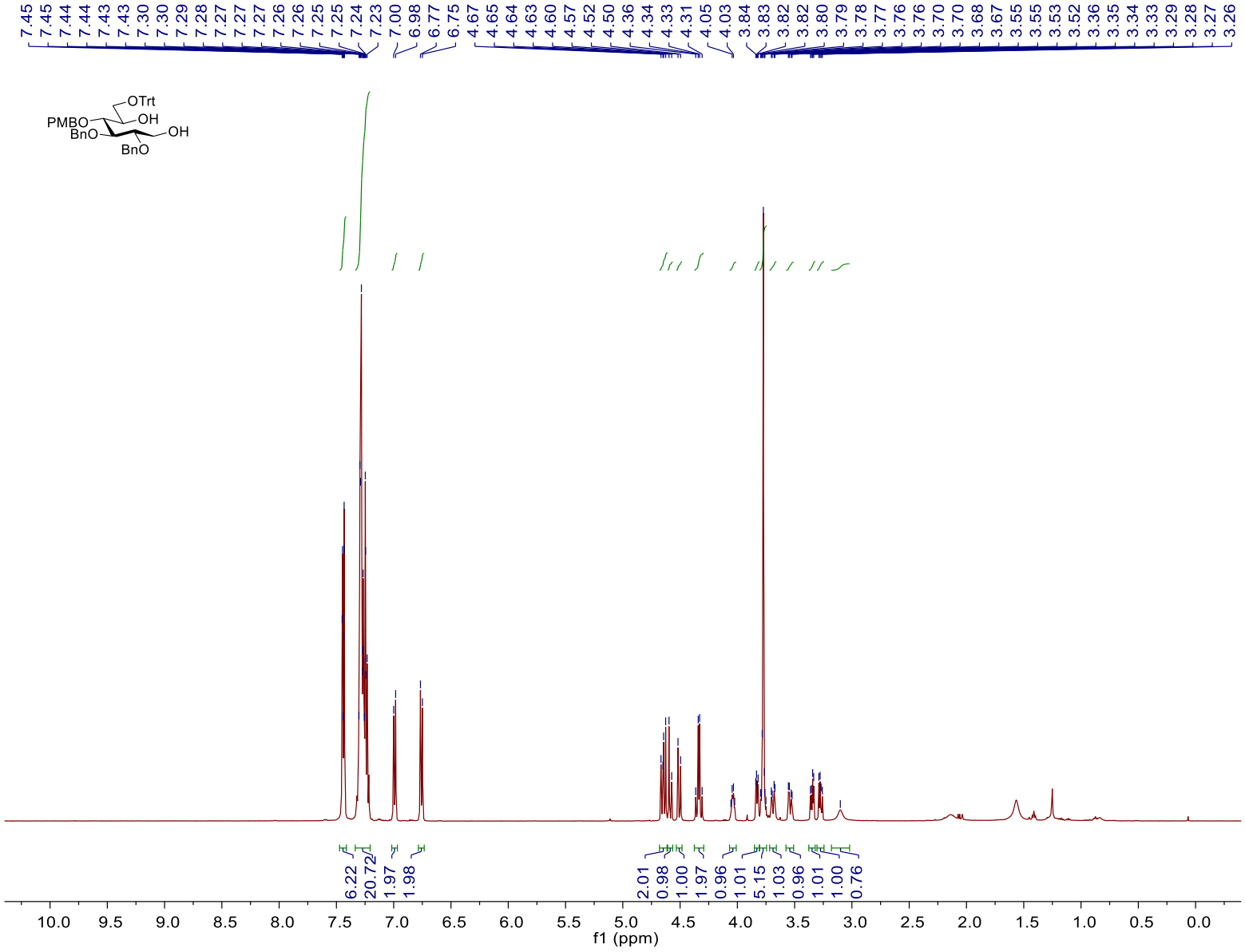
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-glucopyranose (12)



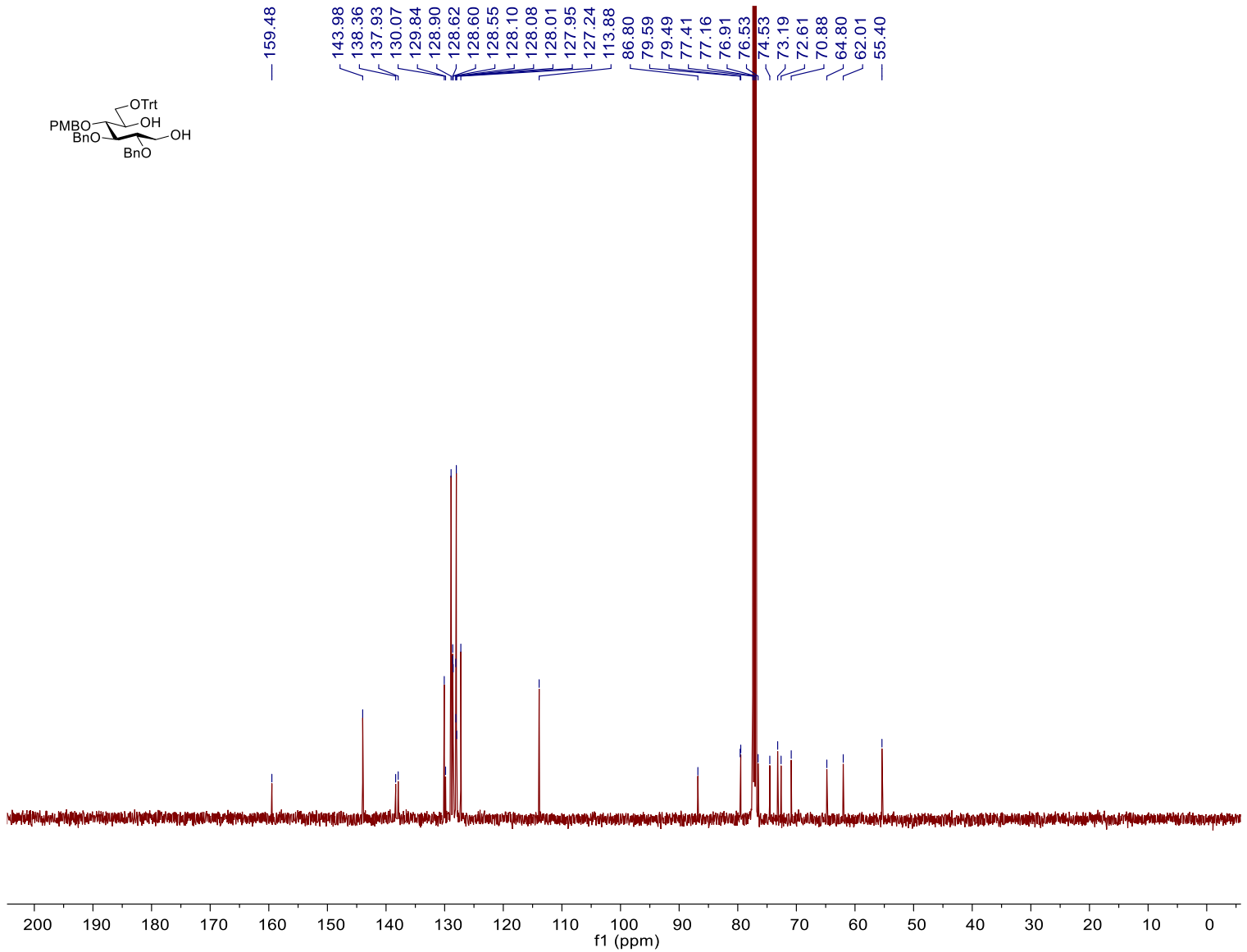
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-glucopyranose (12)



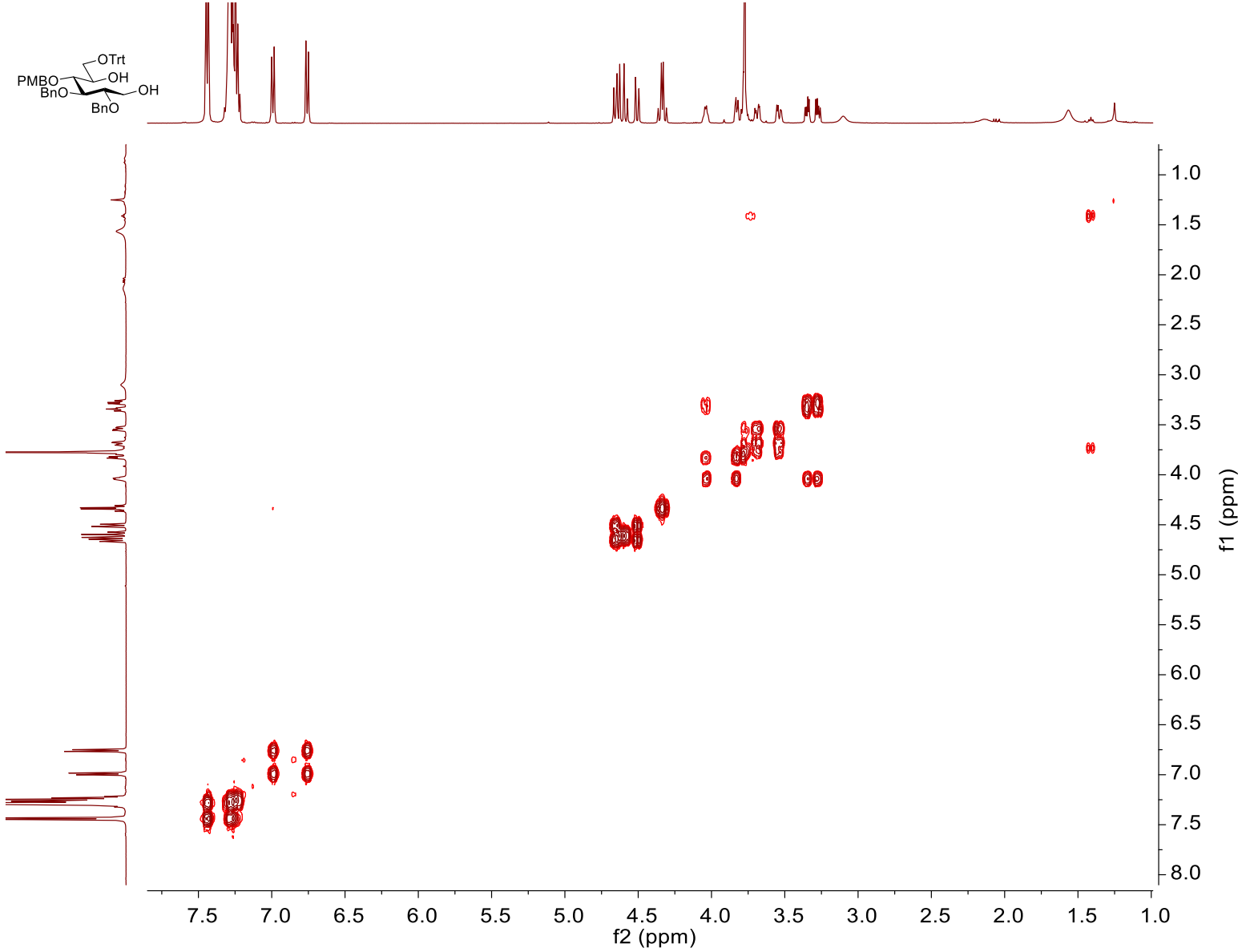
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (13)



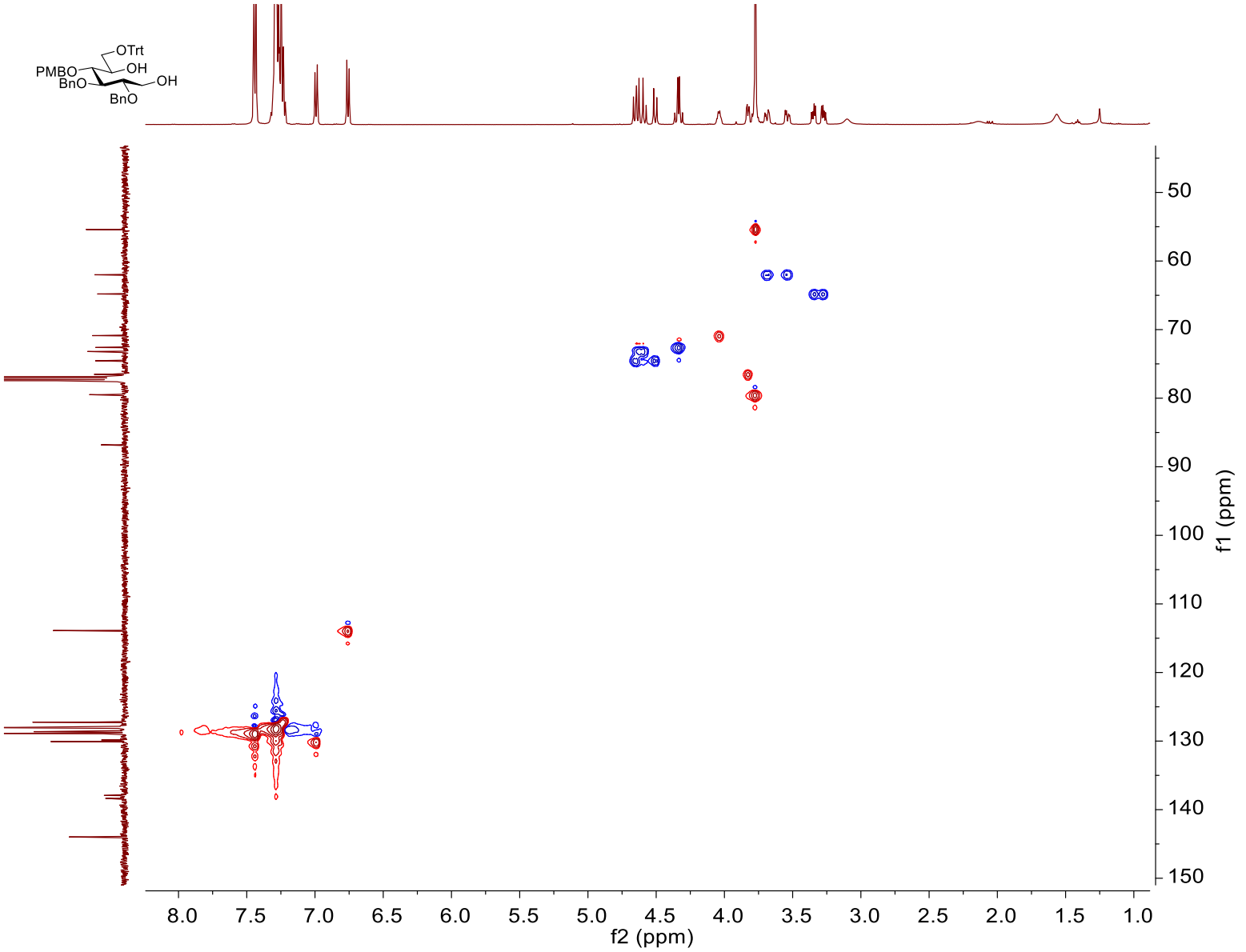
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (13)



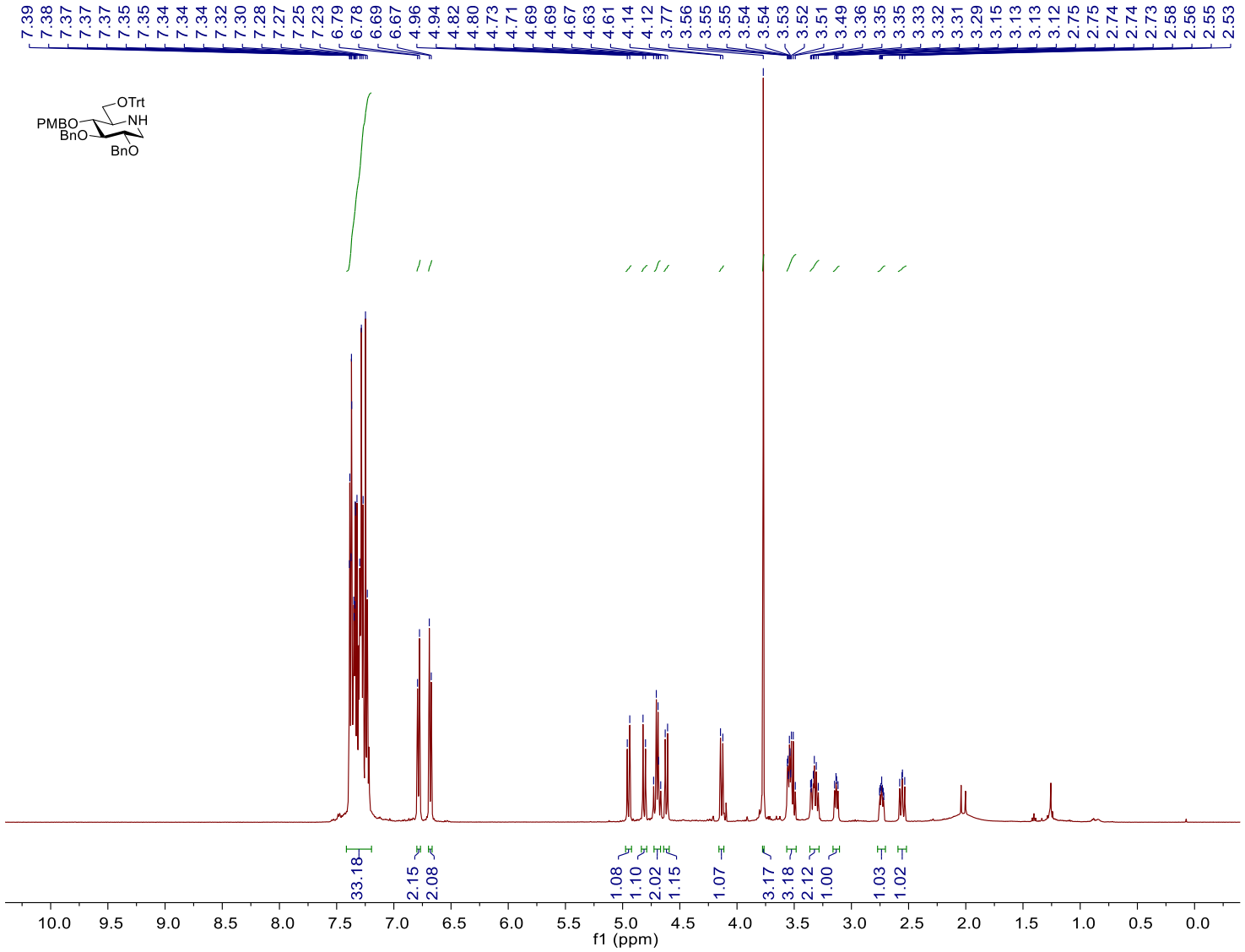
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (13)



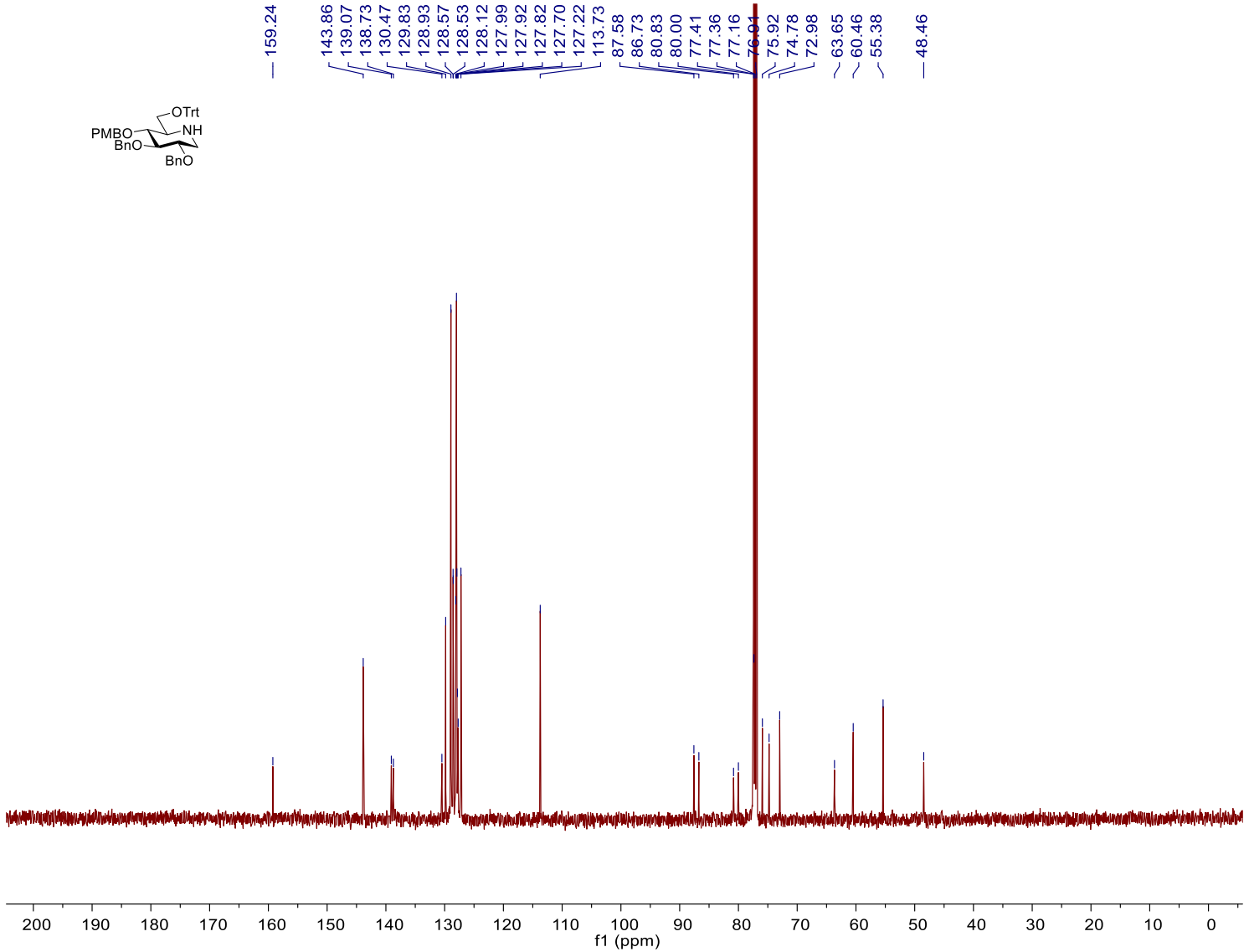
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (13)



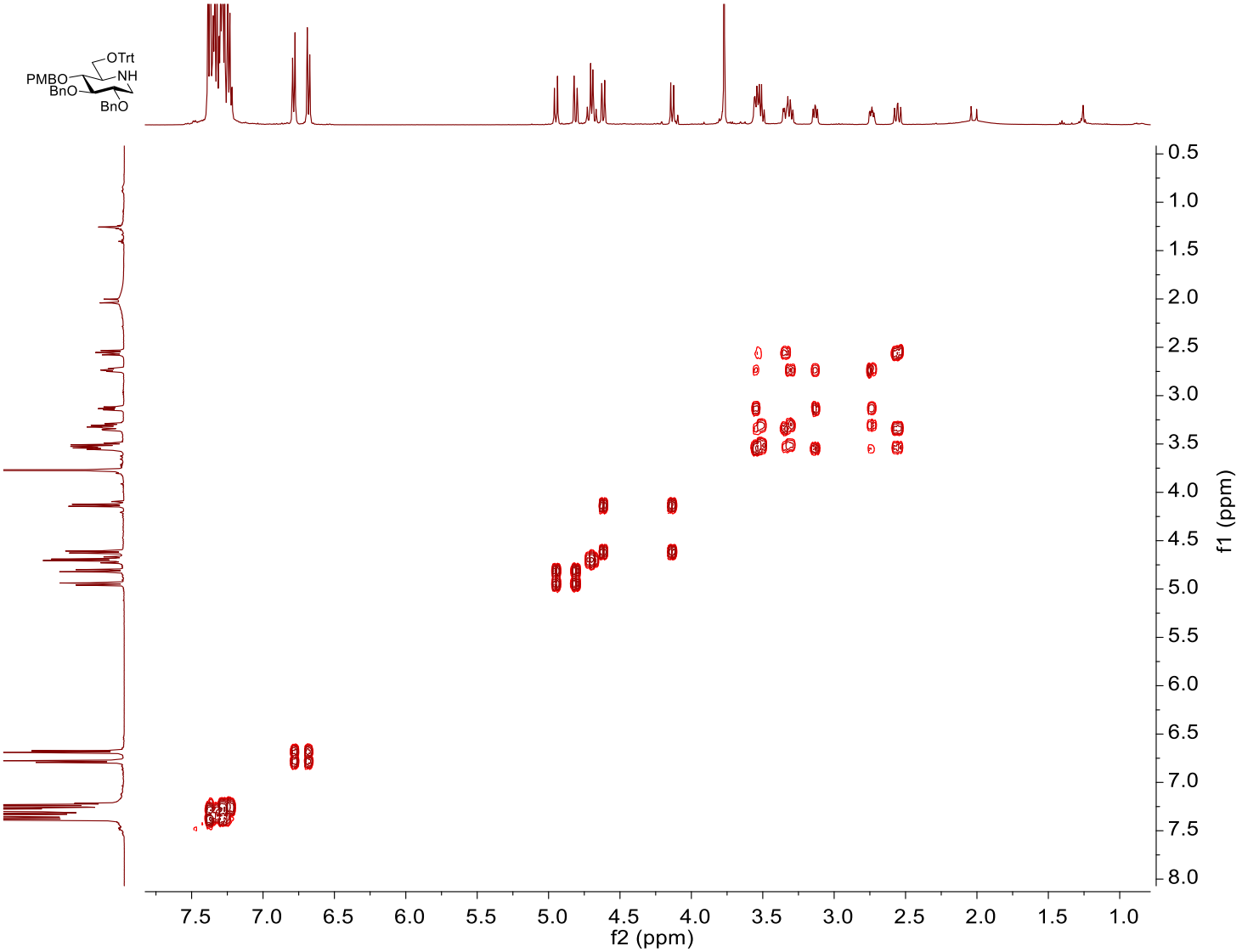
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1,5-dideoxy-1,5-imino-D-glucitol (14)



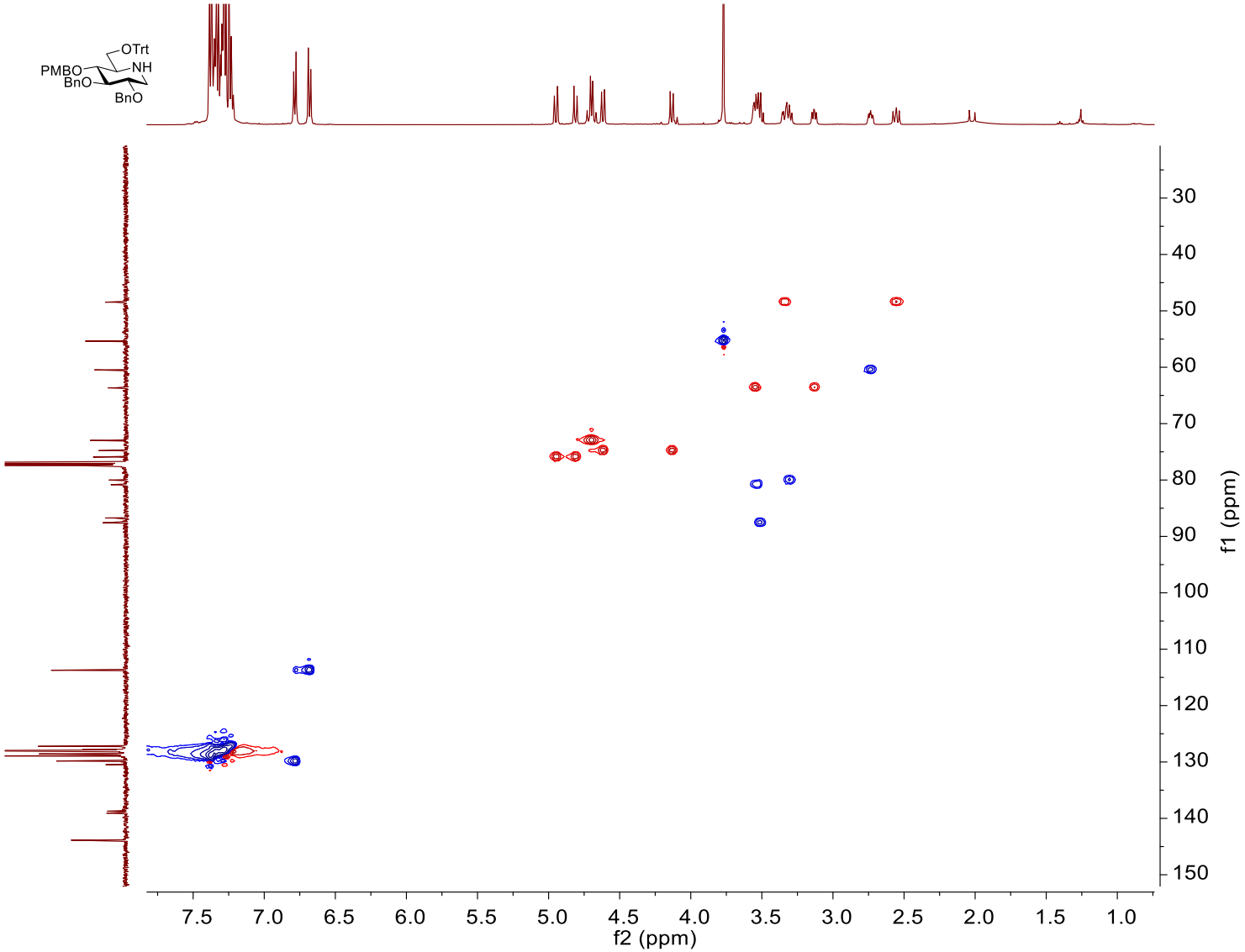
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1,5-dideoxy-1,5-imino-D-glucitol (14)



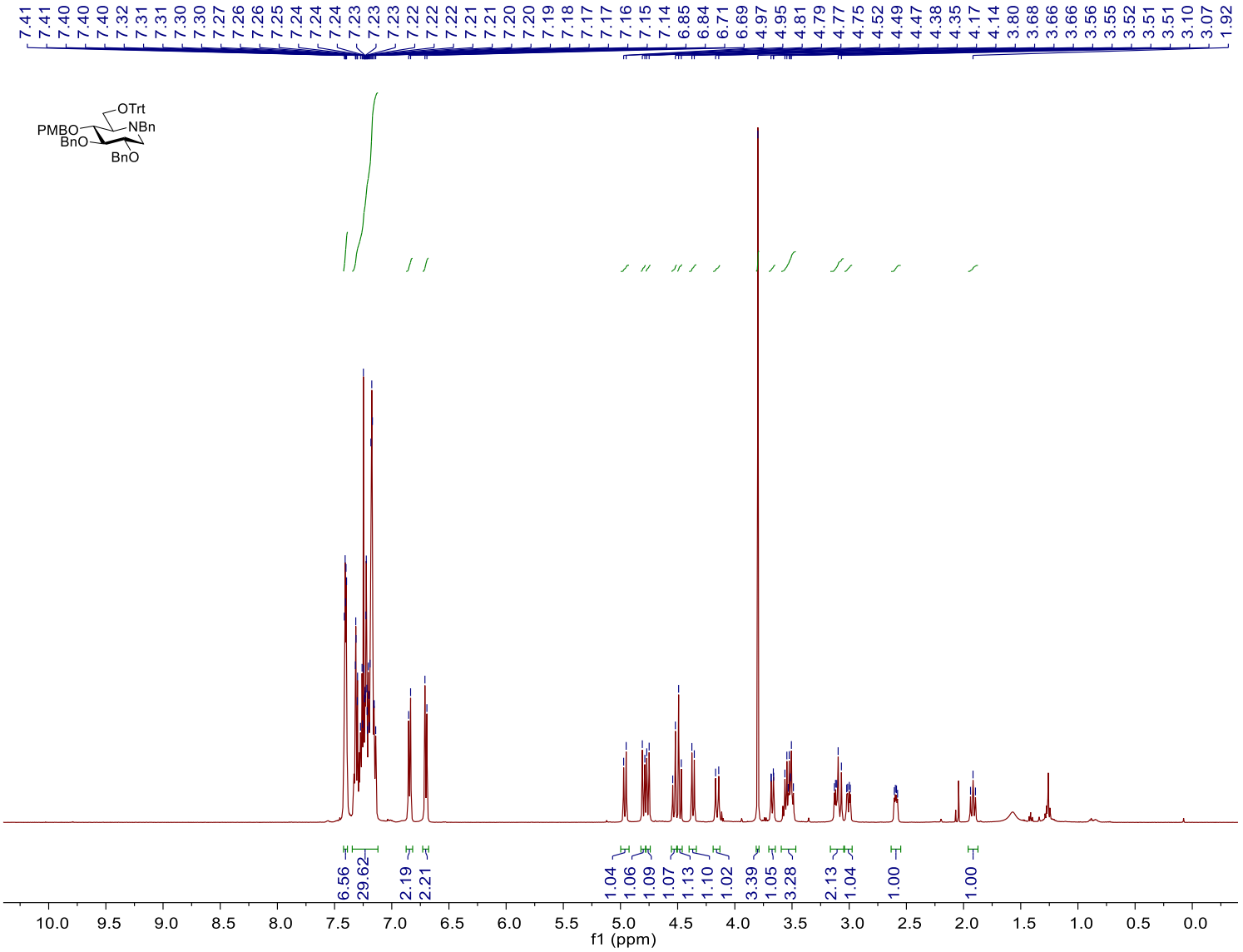
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1,5-dideoxy-1,5-imino-D-glucitol (14)



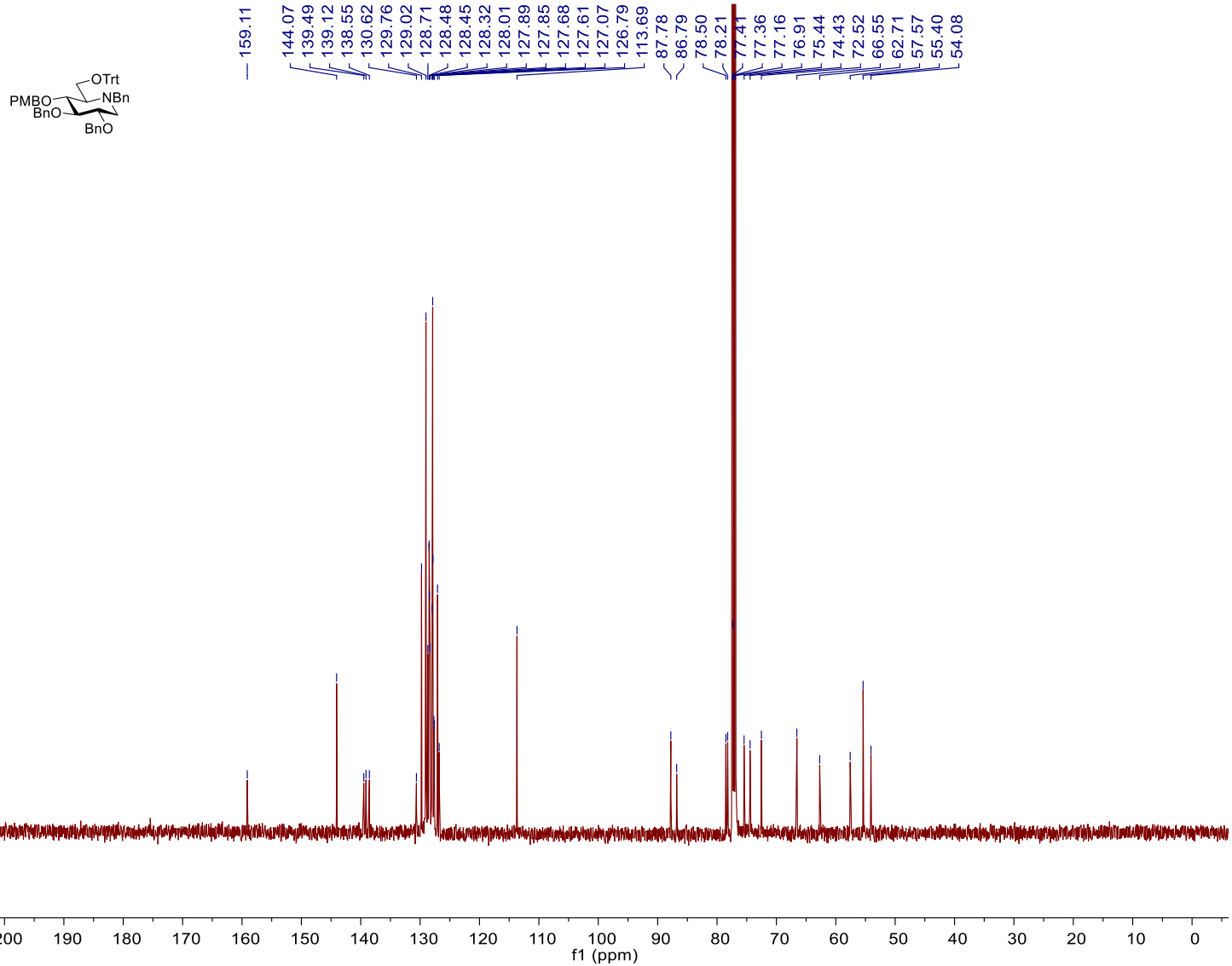
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1,5-dideoxy-1,5-imino-D-glucitol (14)



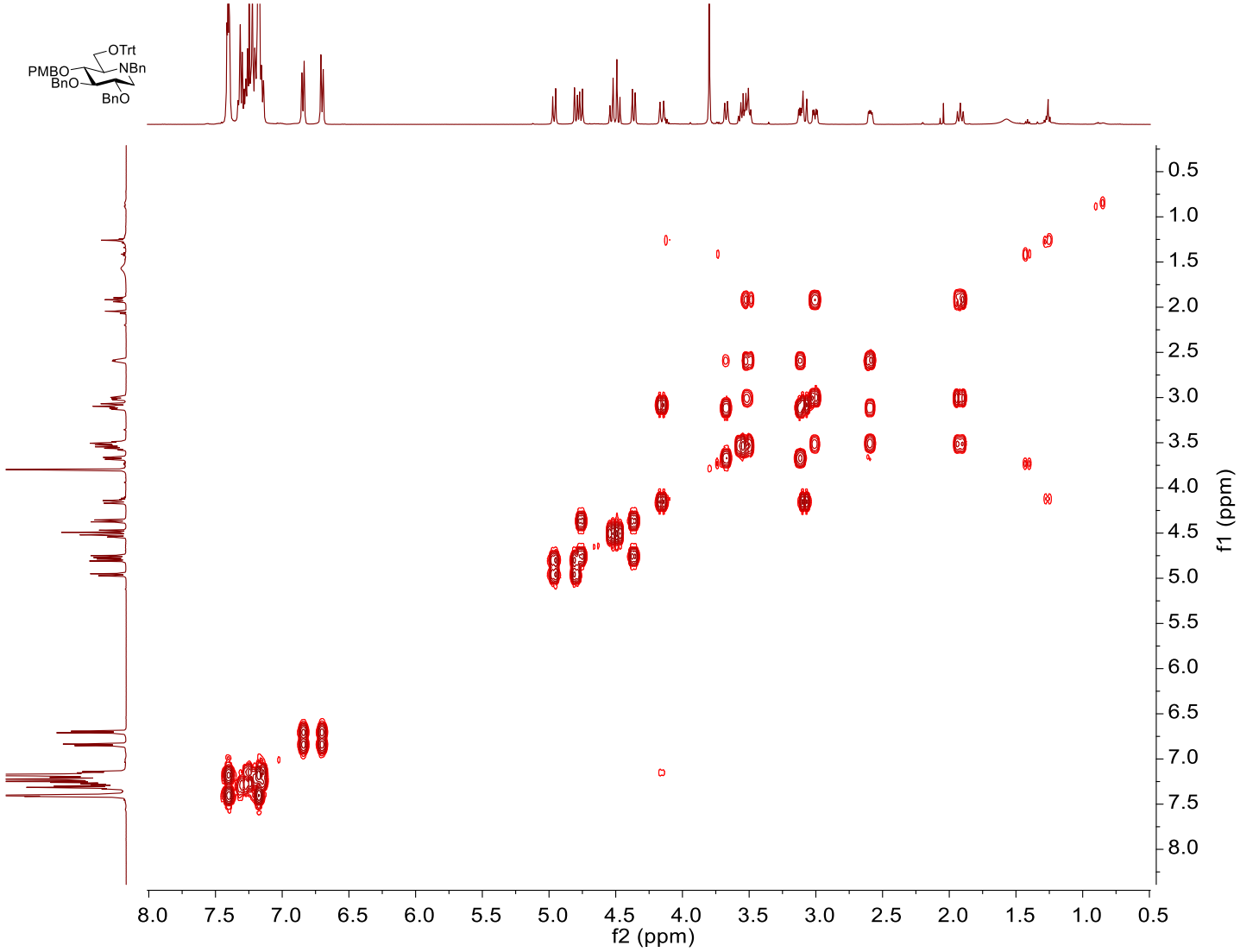
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (15)



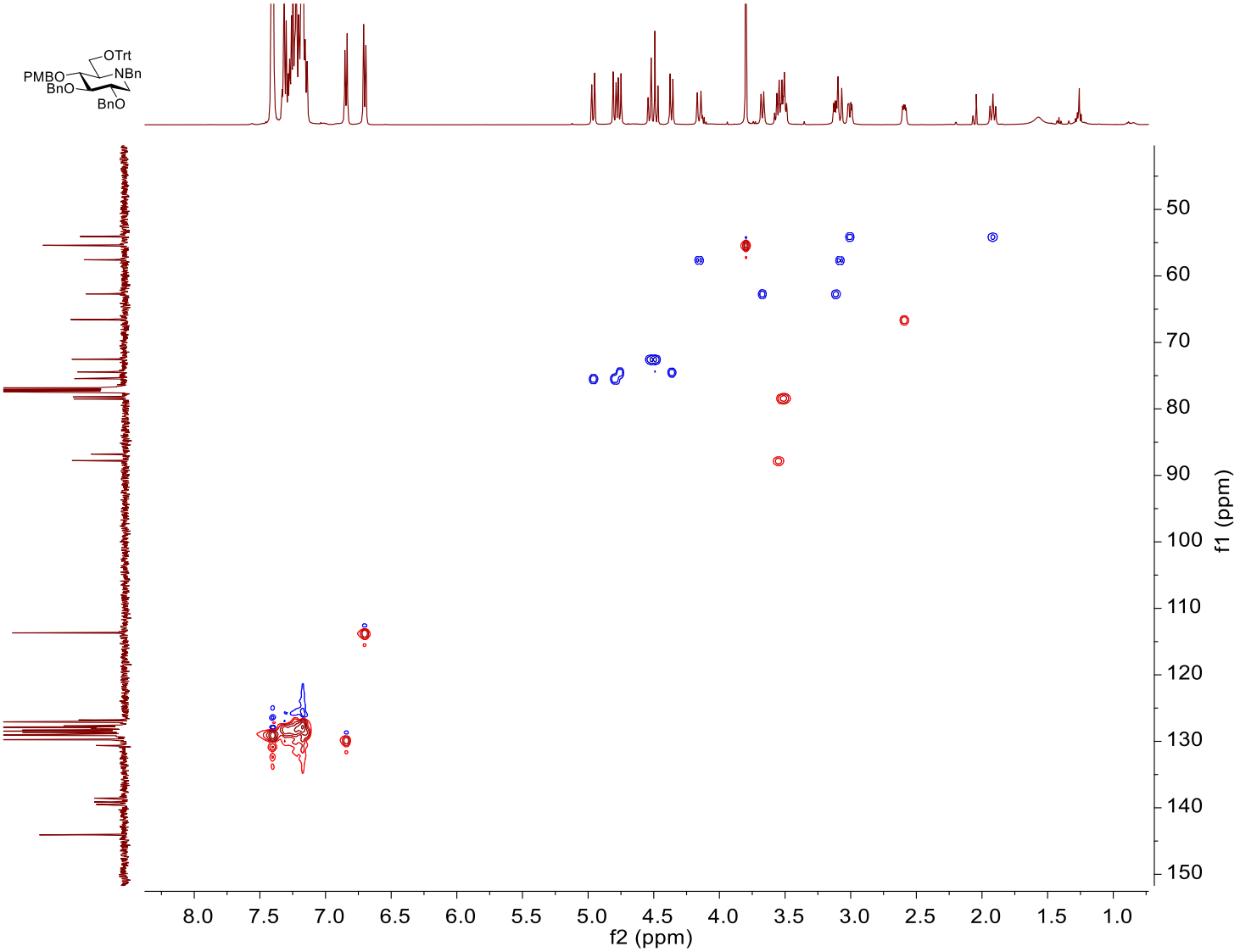
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (15)



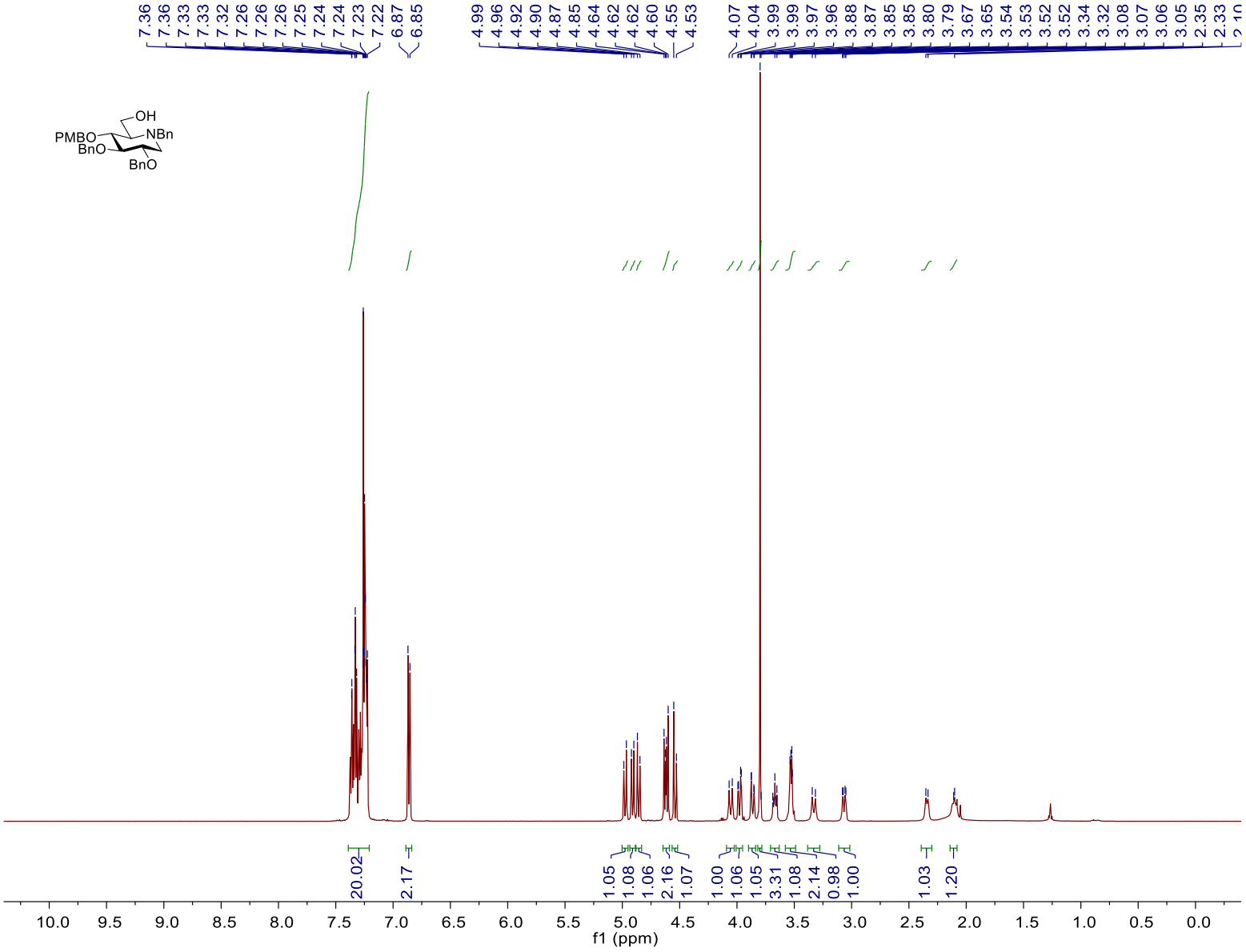
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (15)



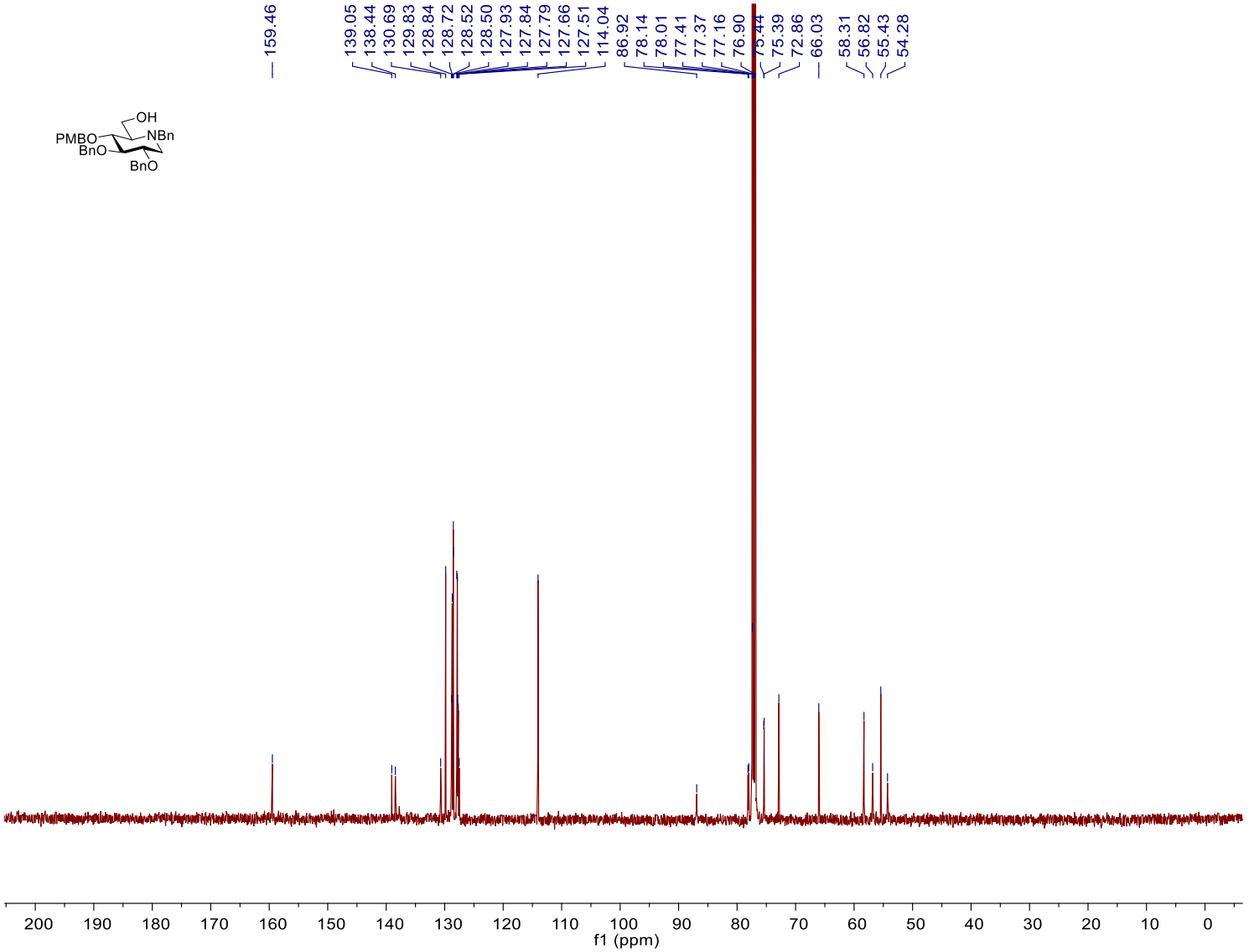
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-glucitol (15)



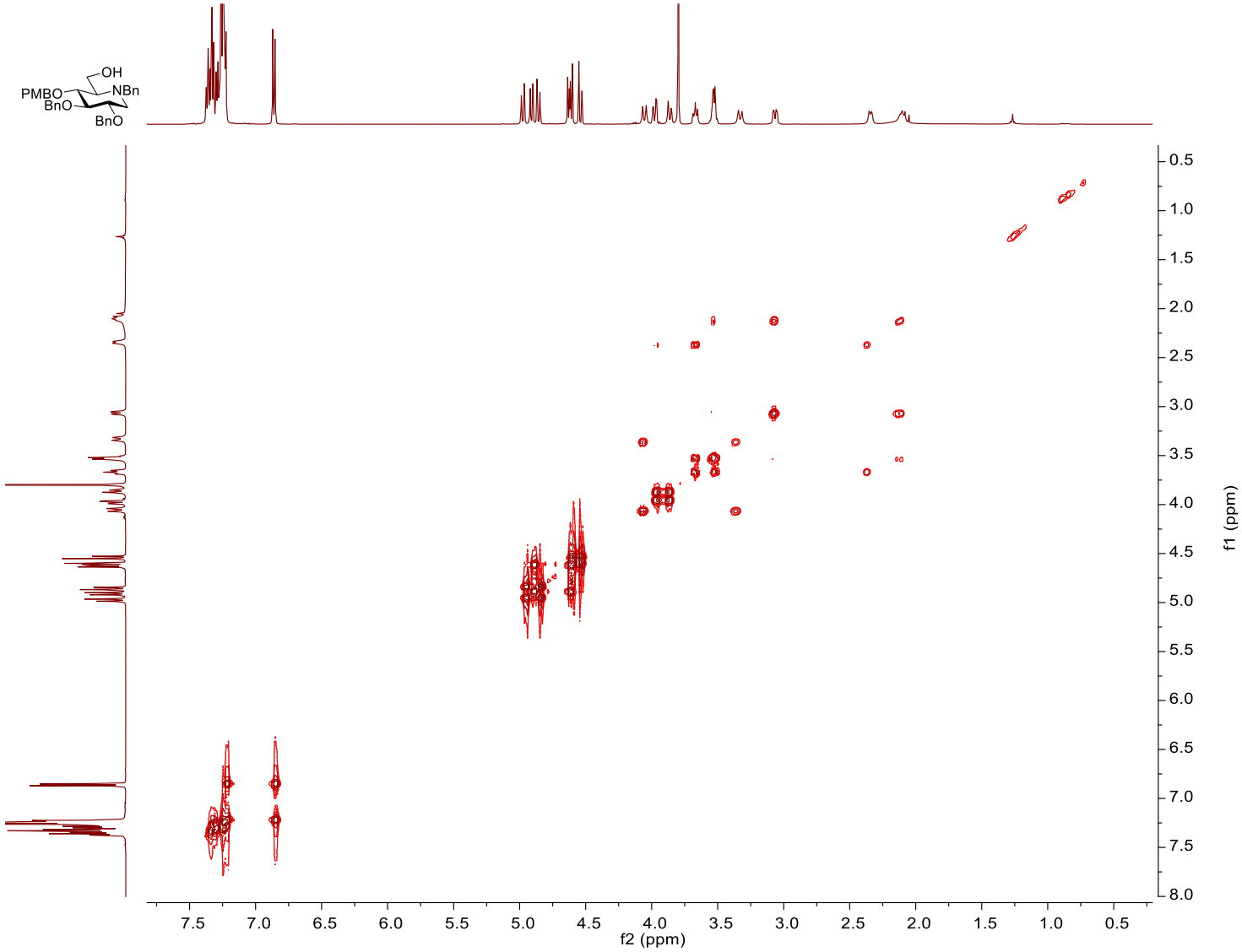
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-glucitol (16)



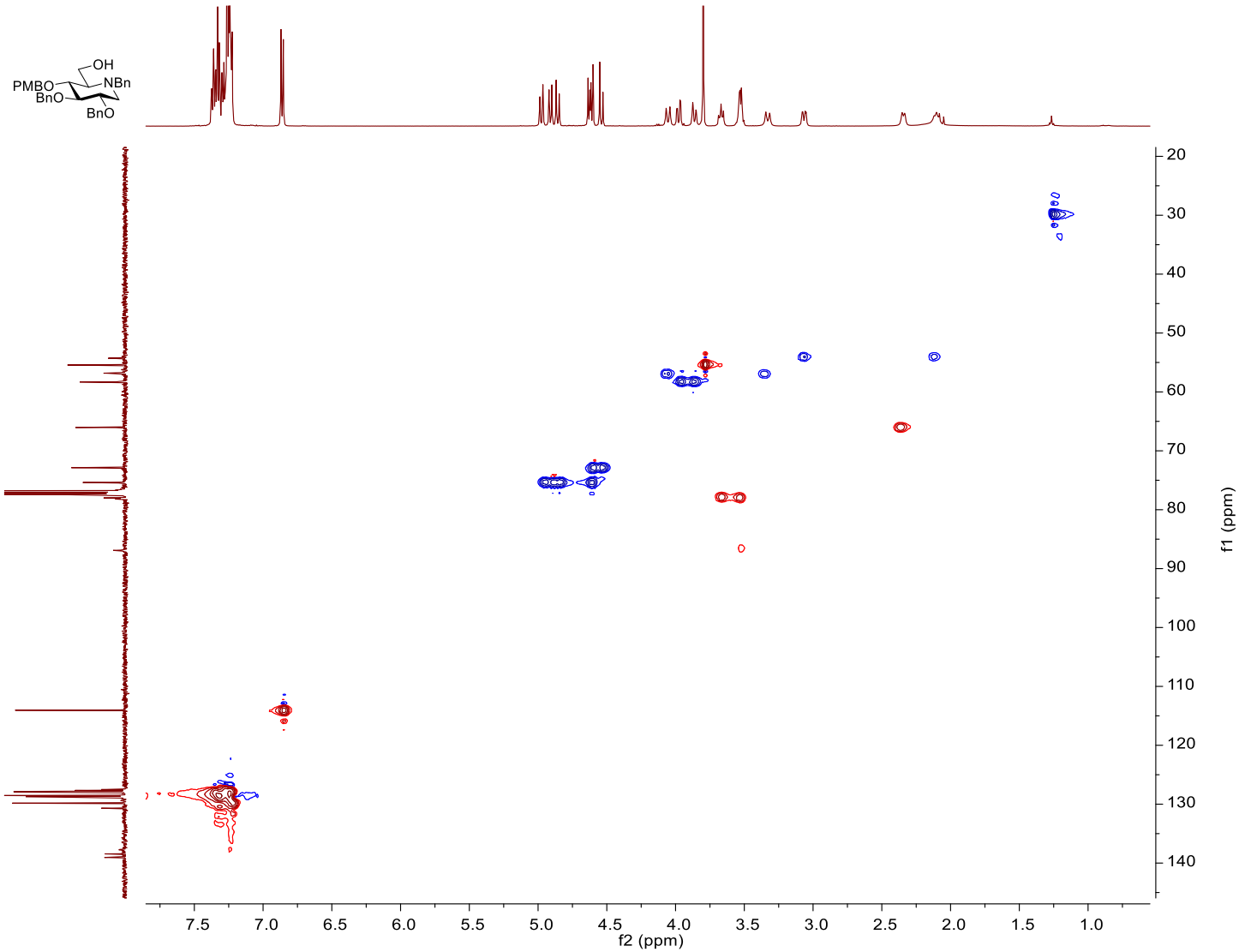
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-glucitol (16)



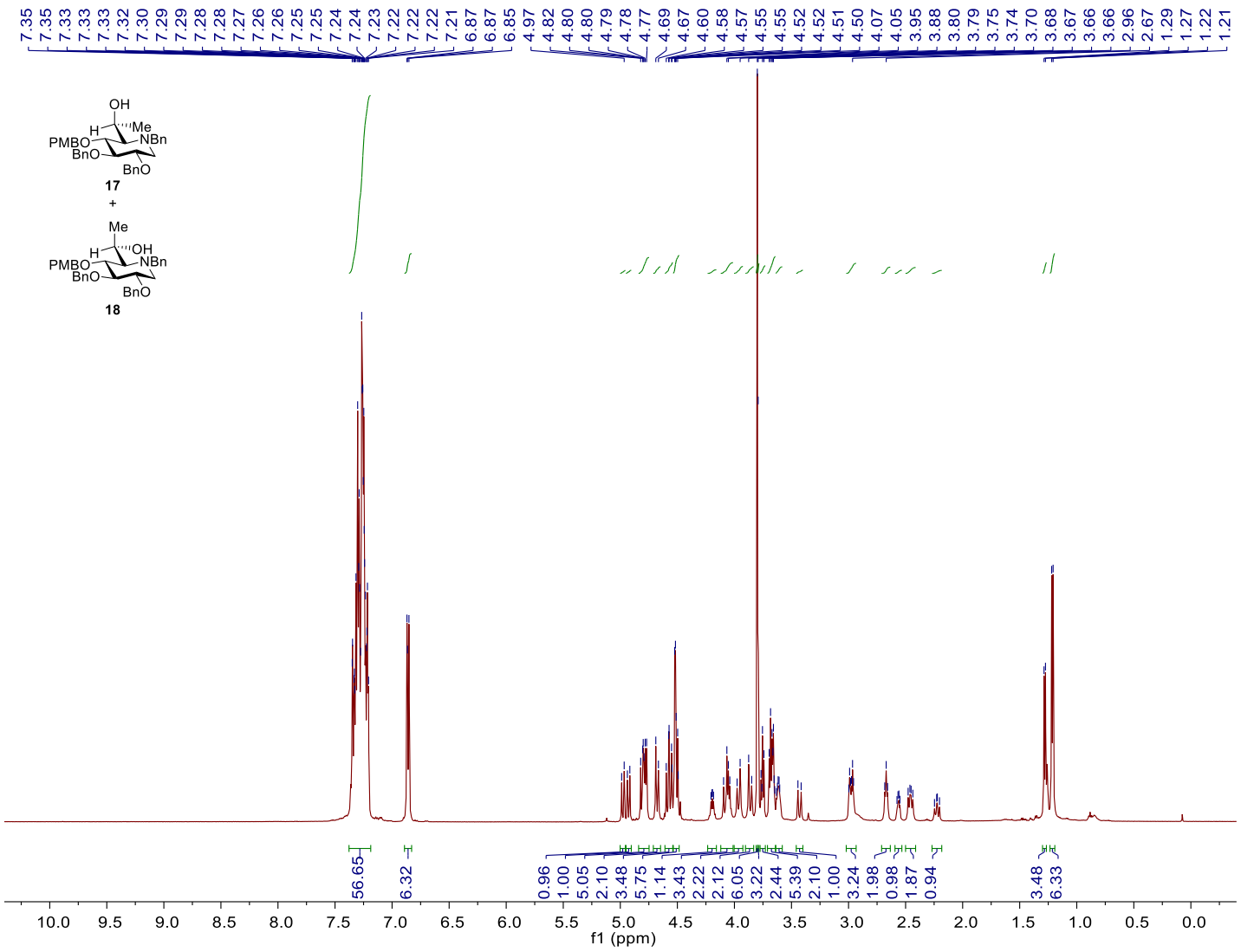
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-glucitol (16)



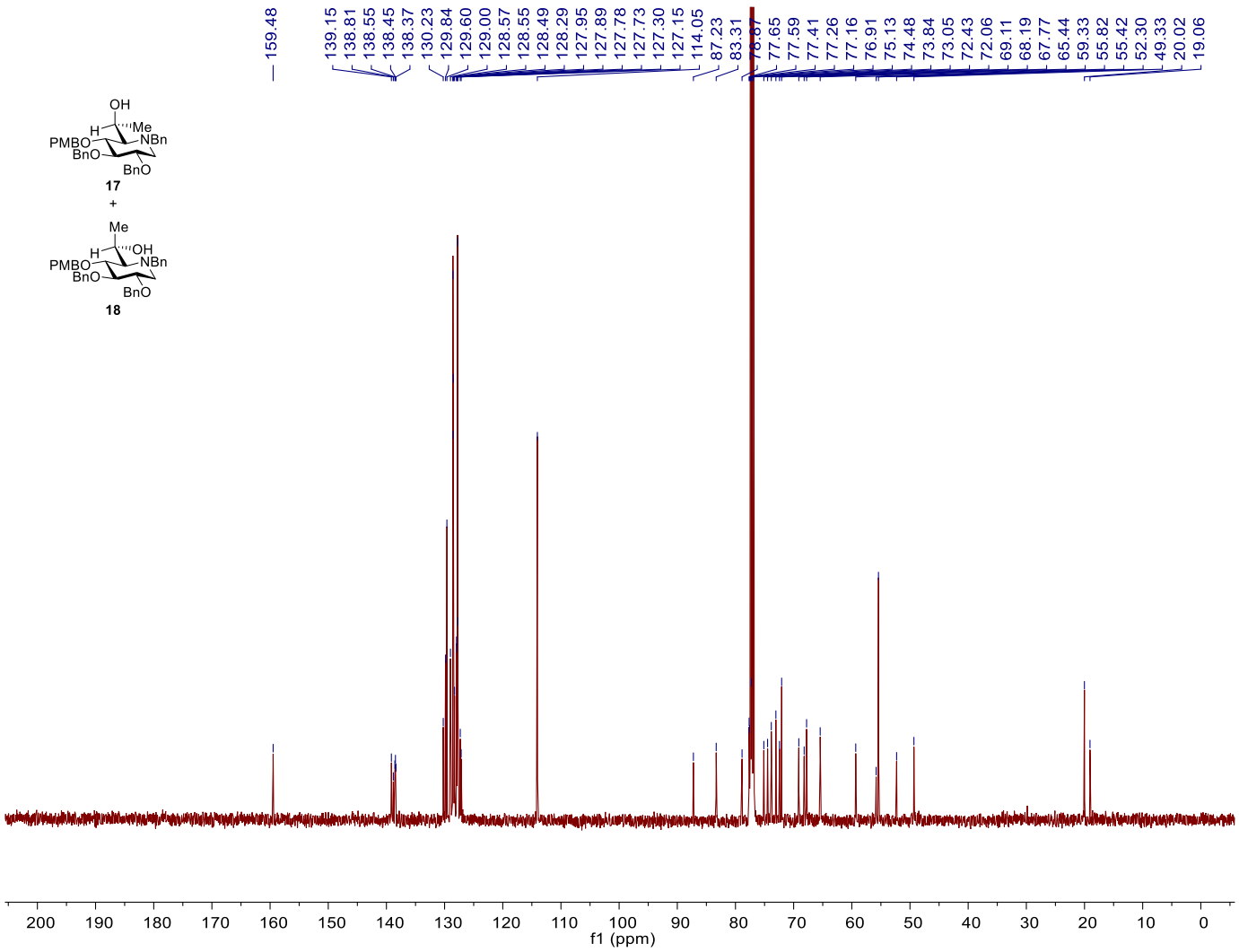
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-glucitol (16)



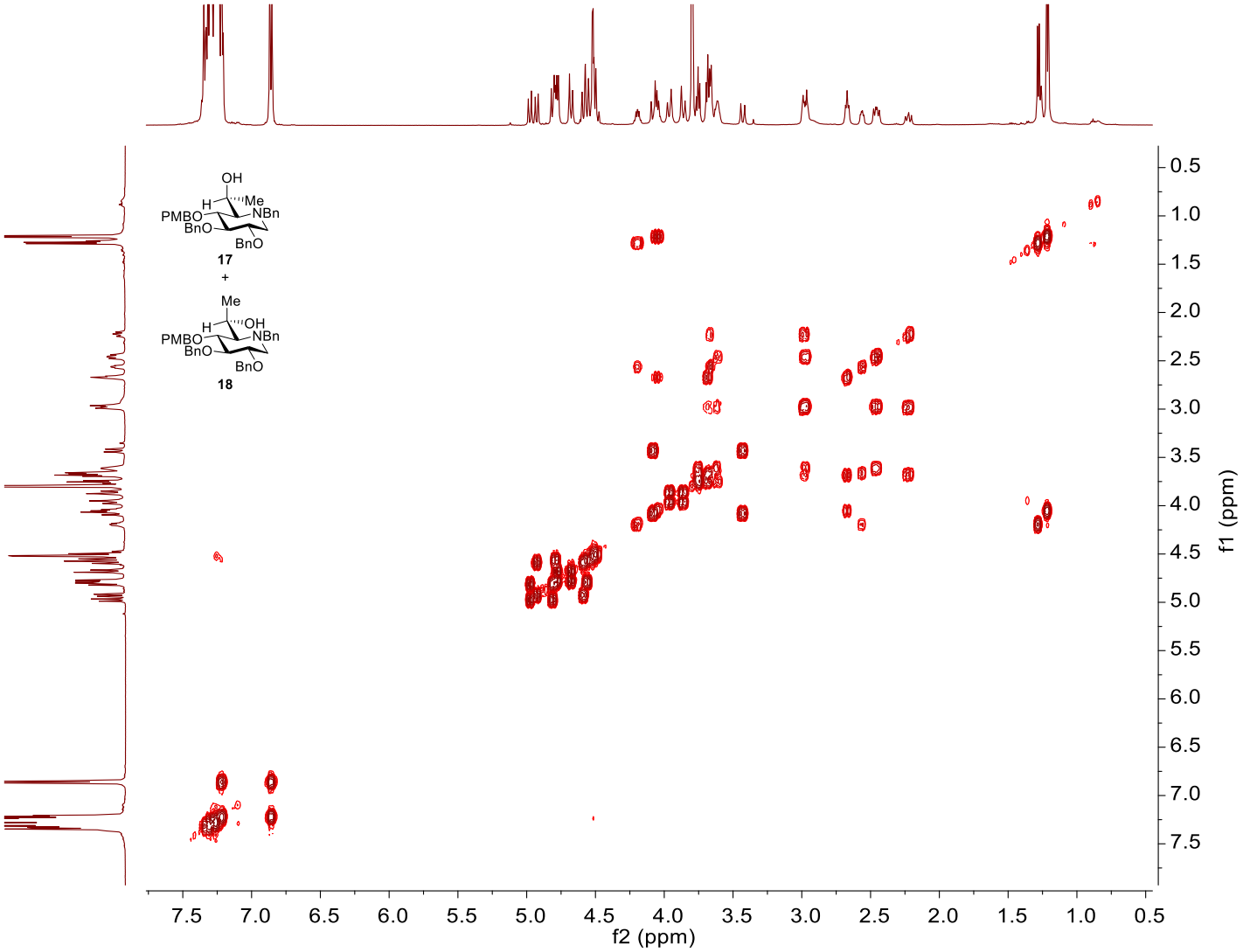
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*gluco*-heptitol (17) and 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*gluco*-heptitol (18)



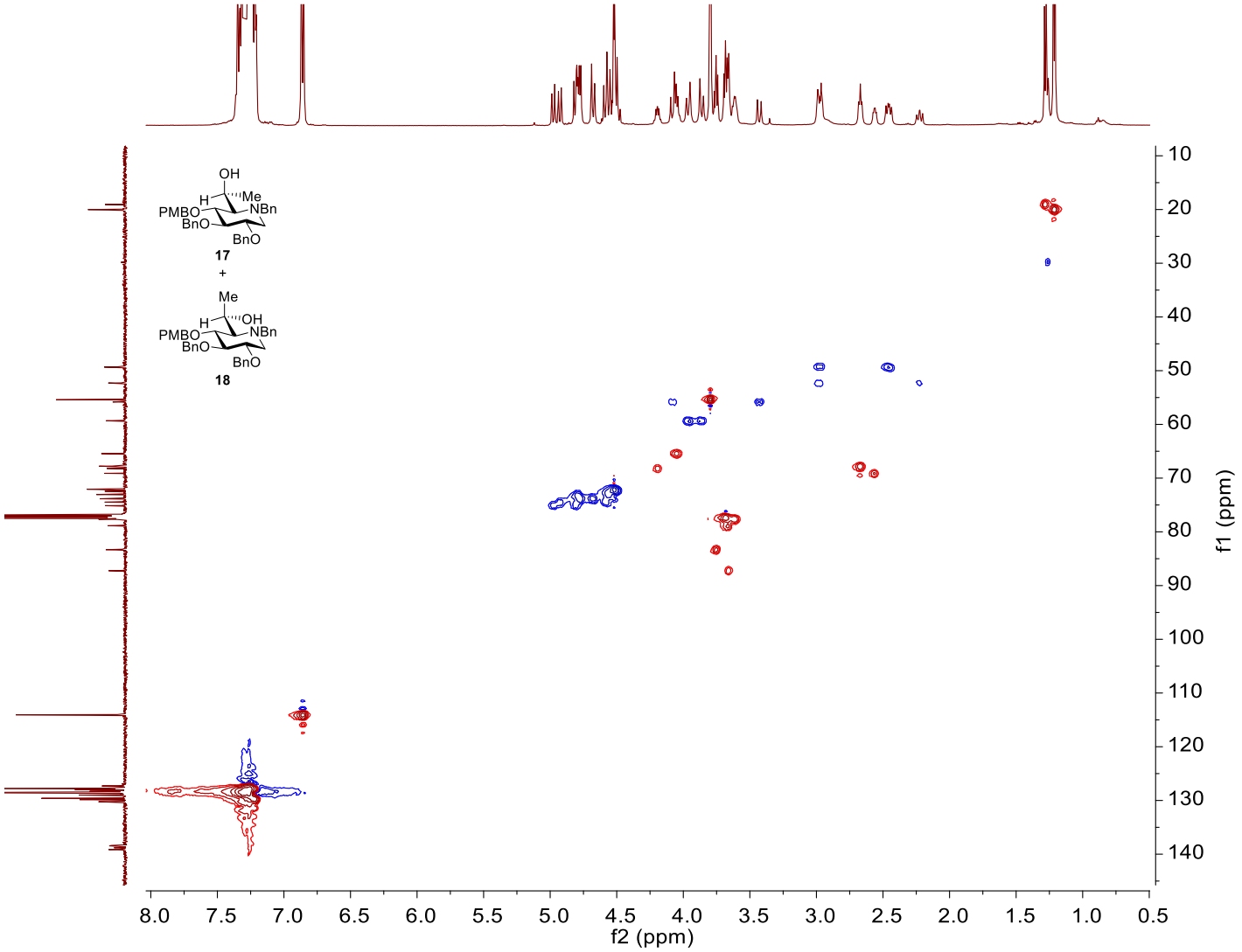
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*gluco*-heptitol (17) and 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*gluco*-heptitol (18)



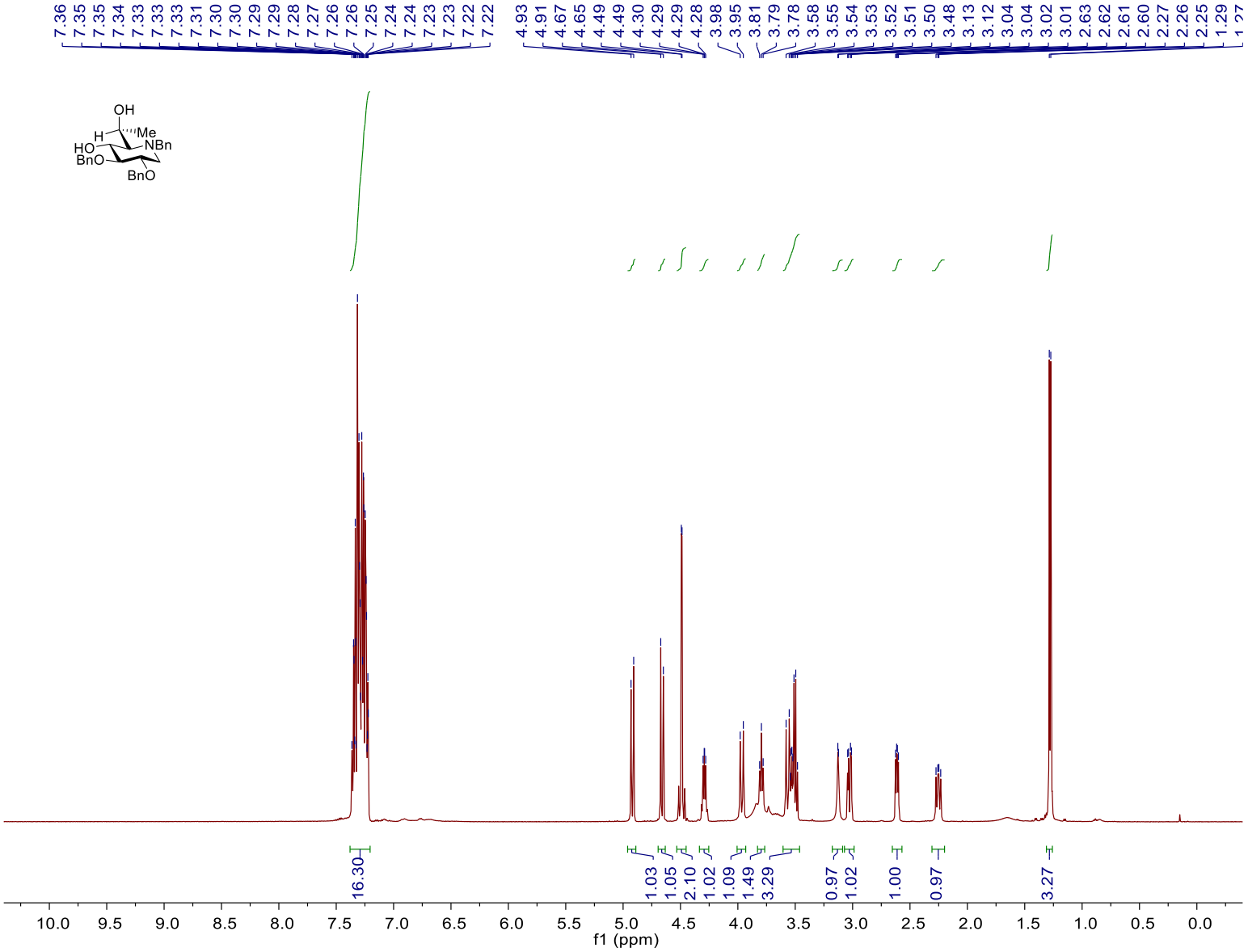
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*gluco*-heptitol (17) and 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*gluco*-heptitol (18)



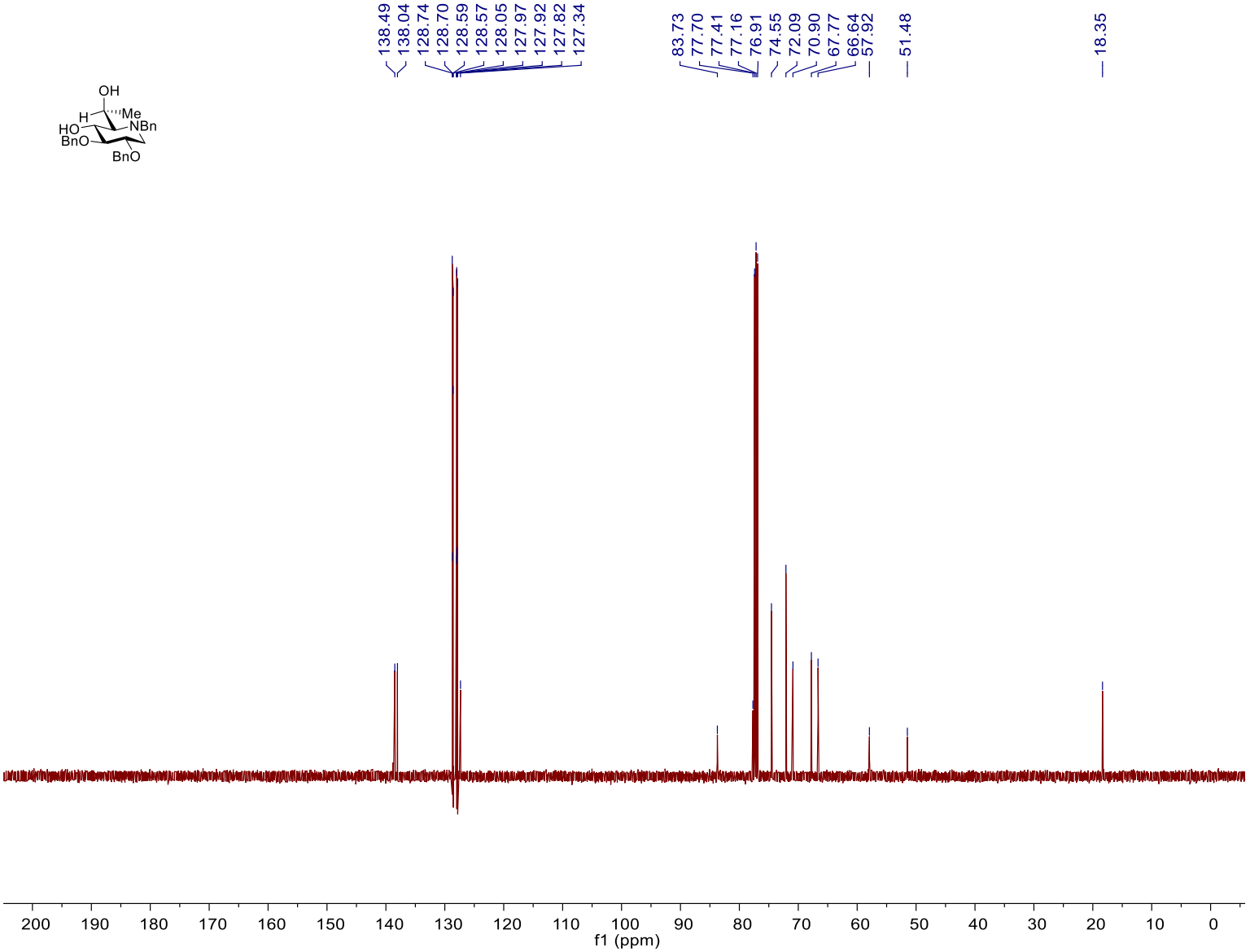
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*gluco*-heptitol (17) and 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*gluco*-heptitol (18)



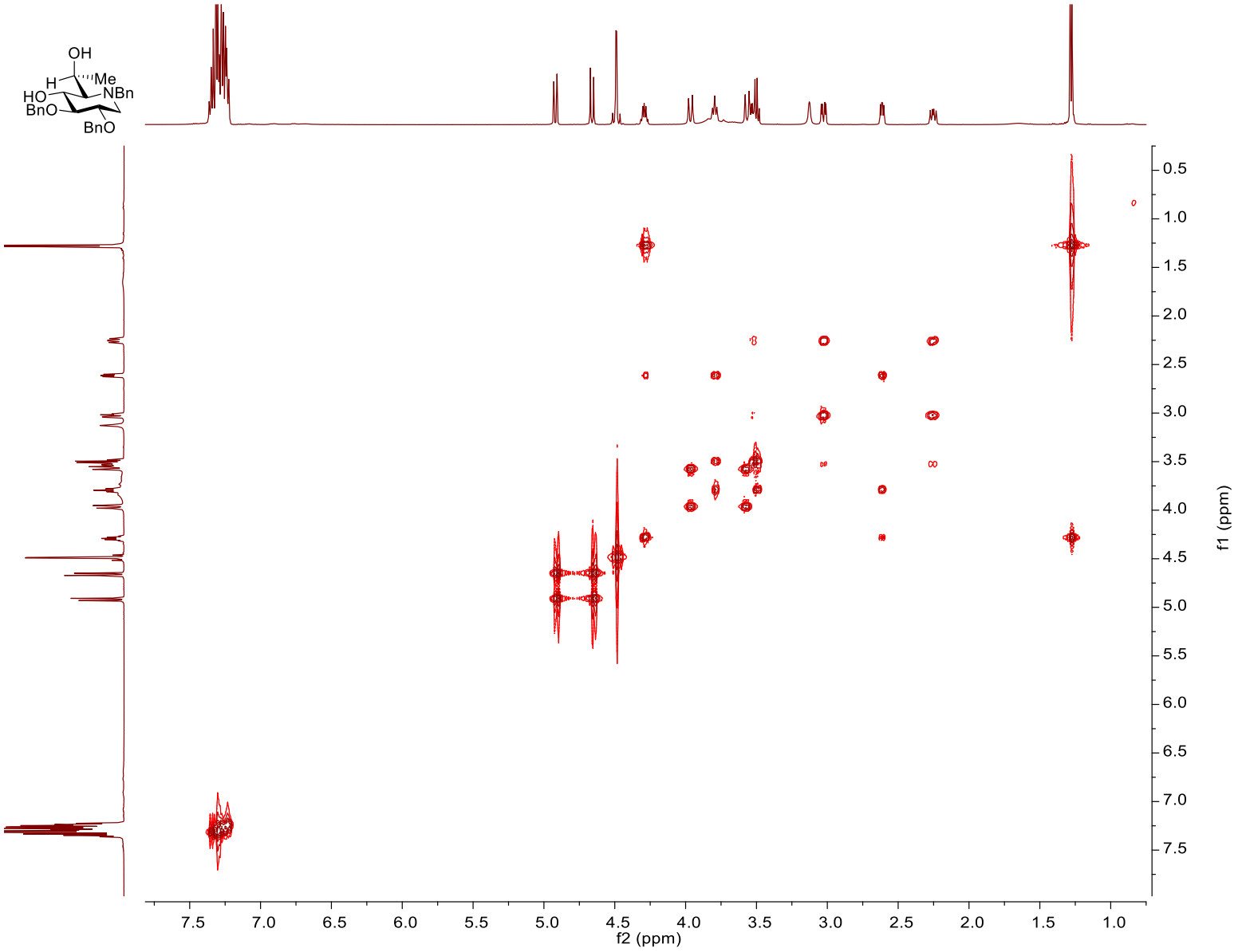
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (19)



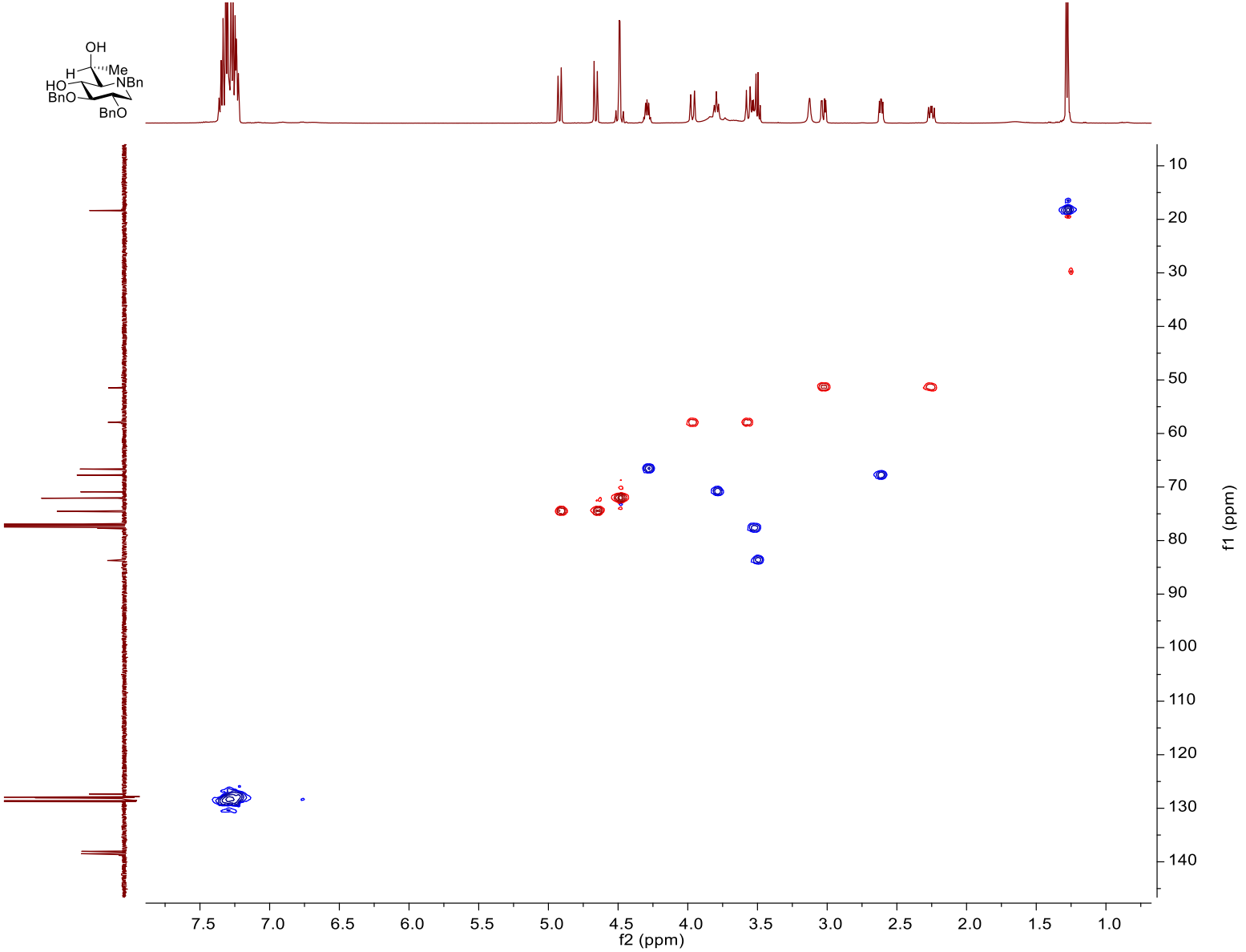
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (19)



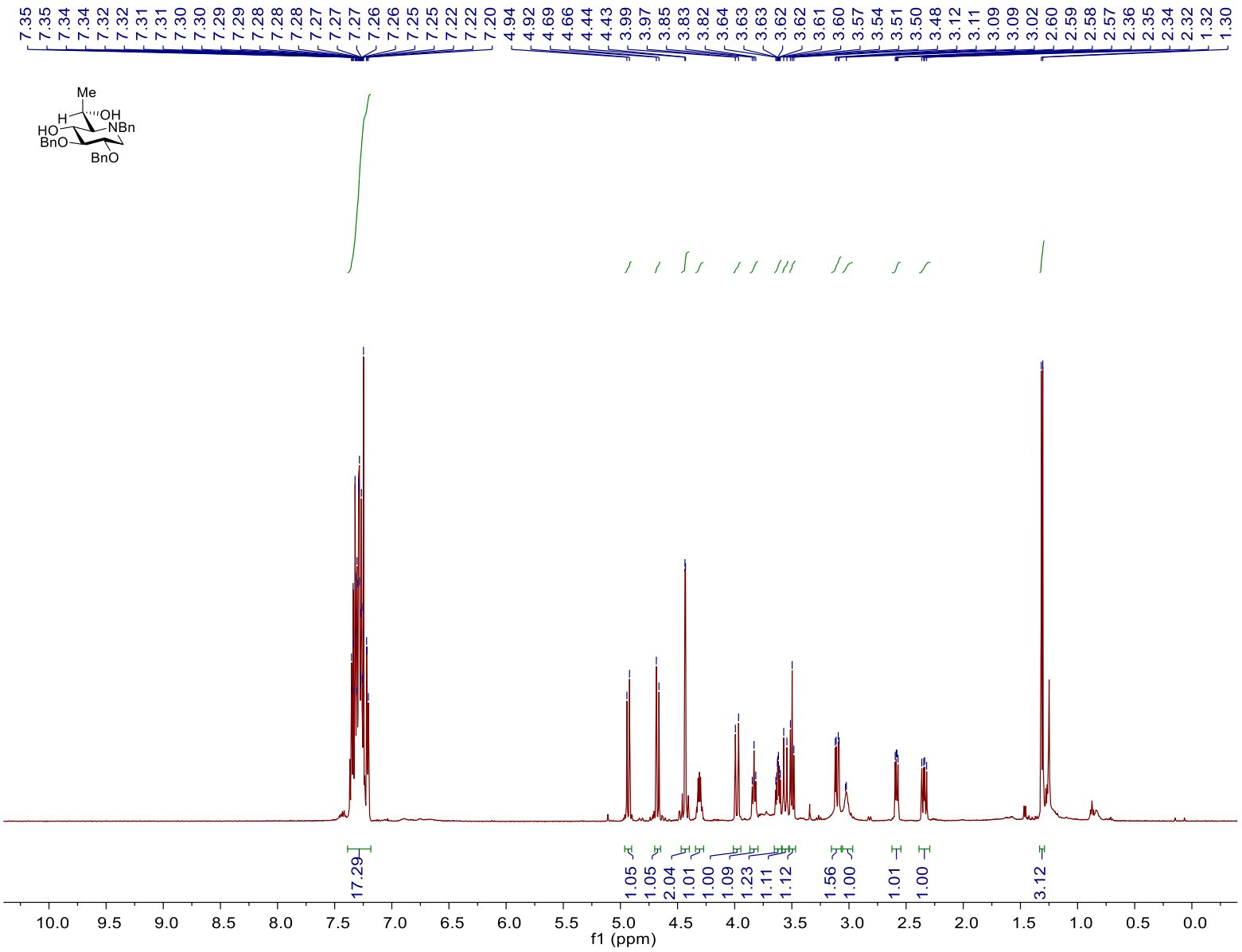
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (19)



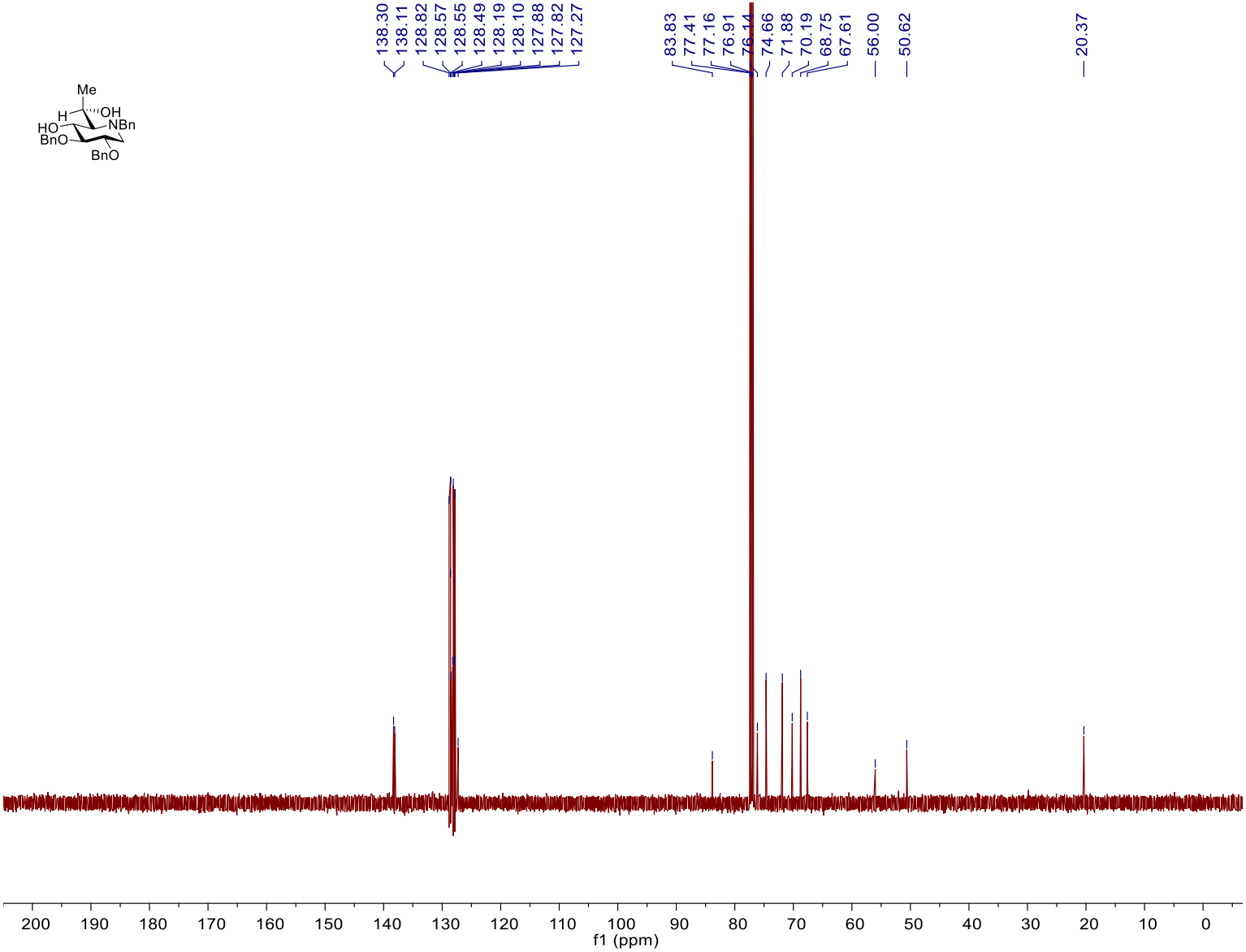
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (19)



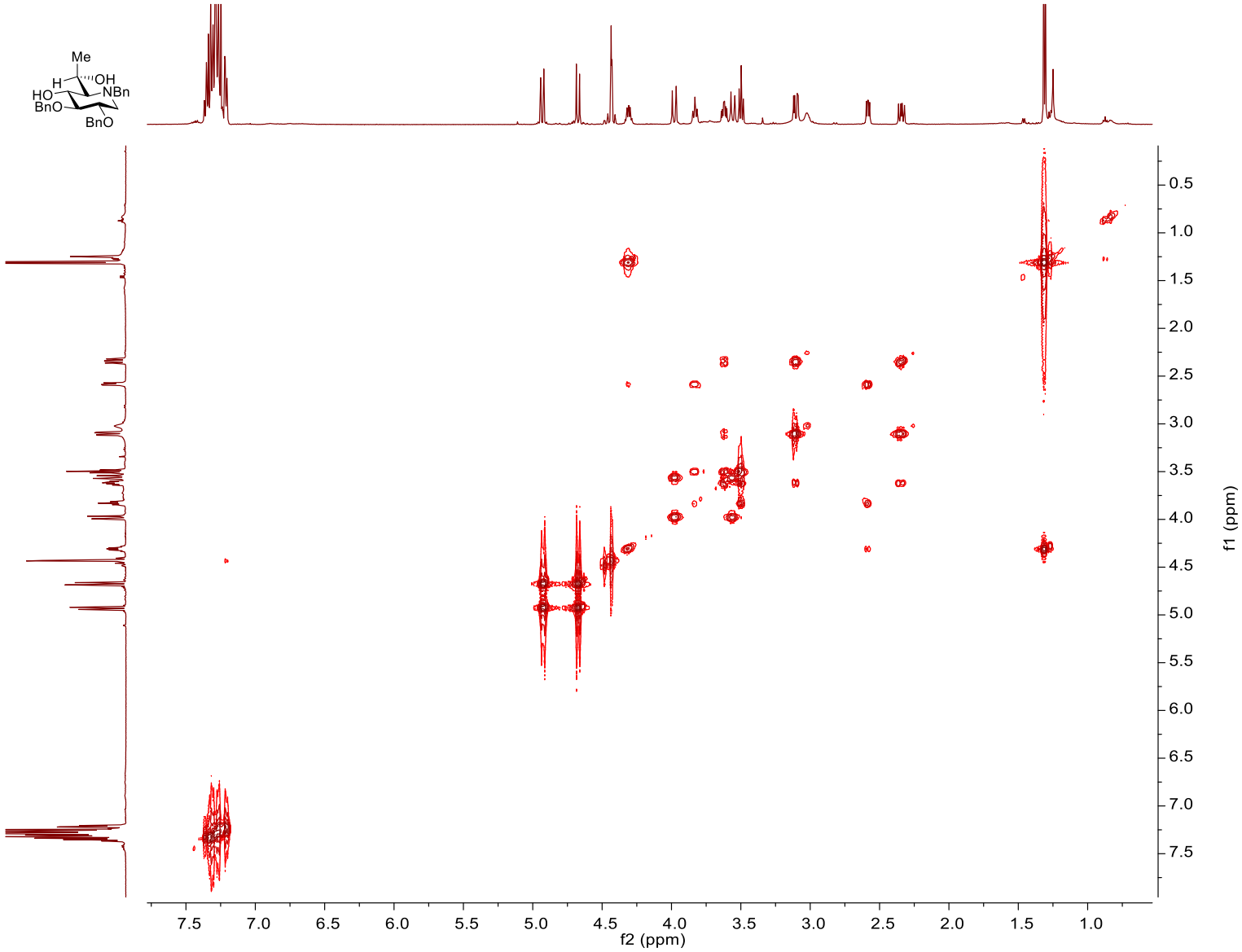
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (20)



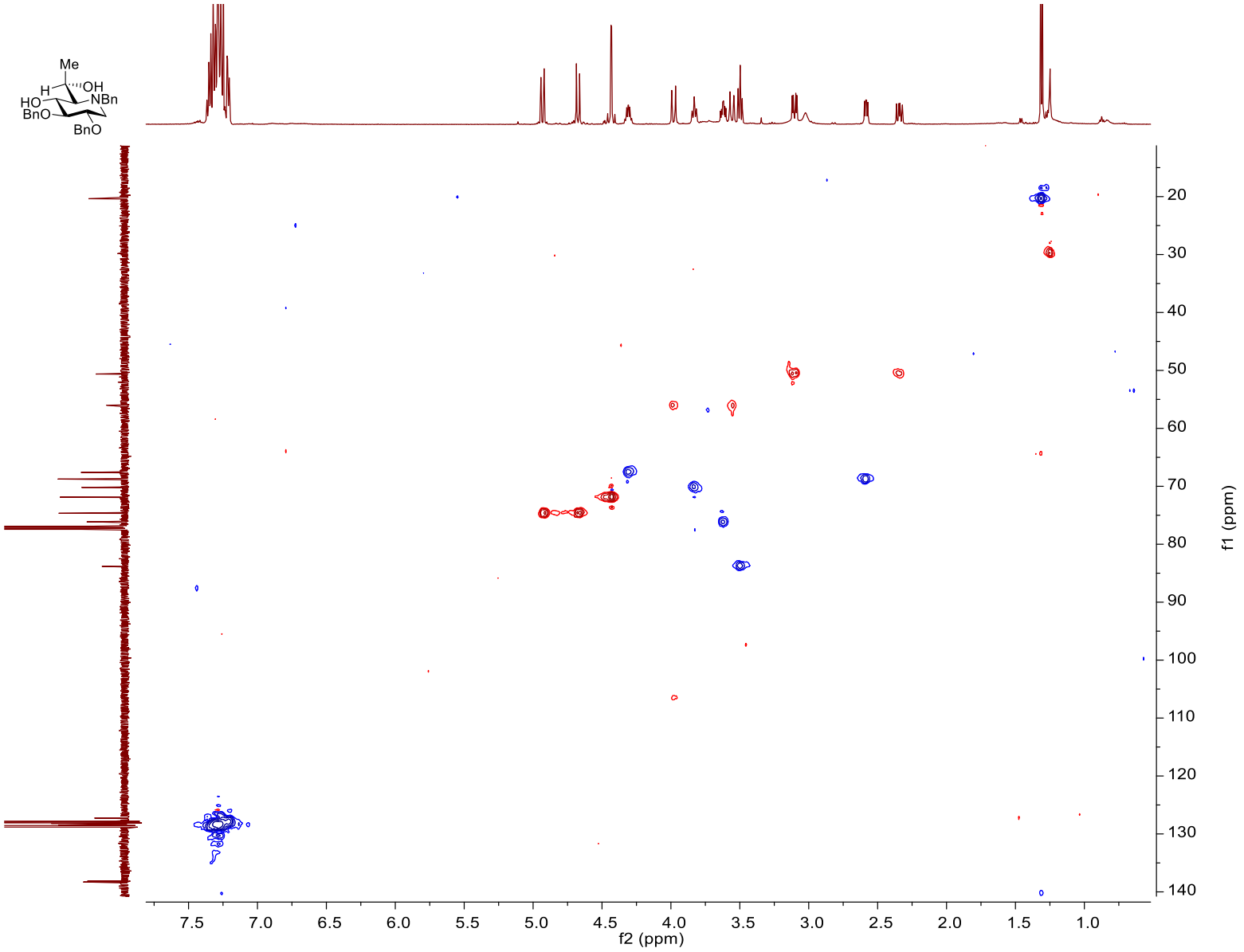
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (20)



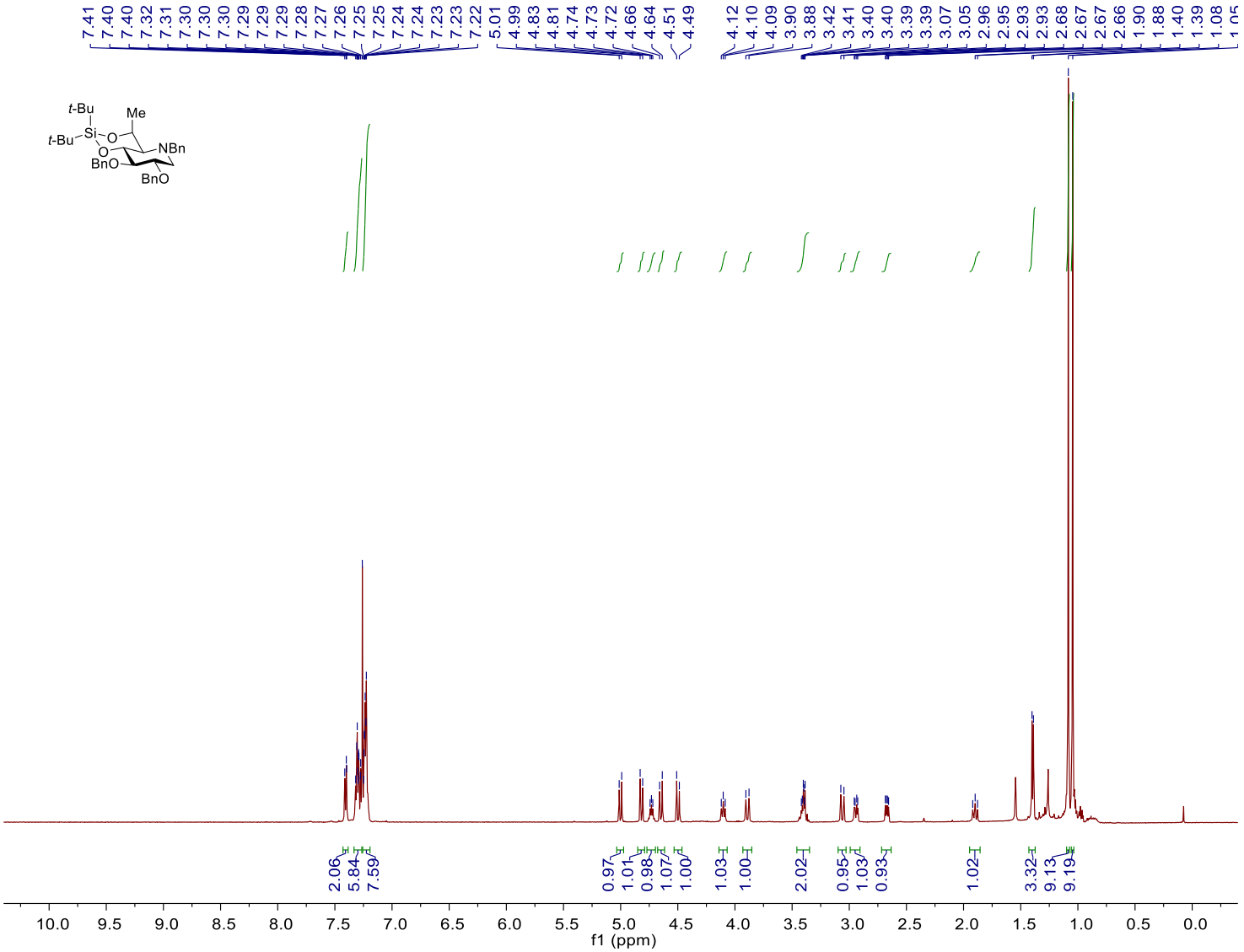
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (20)



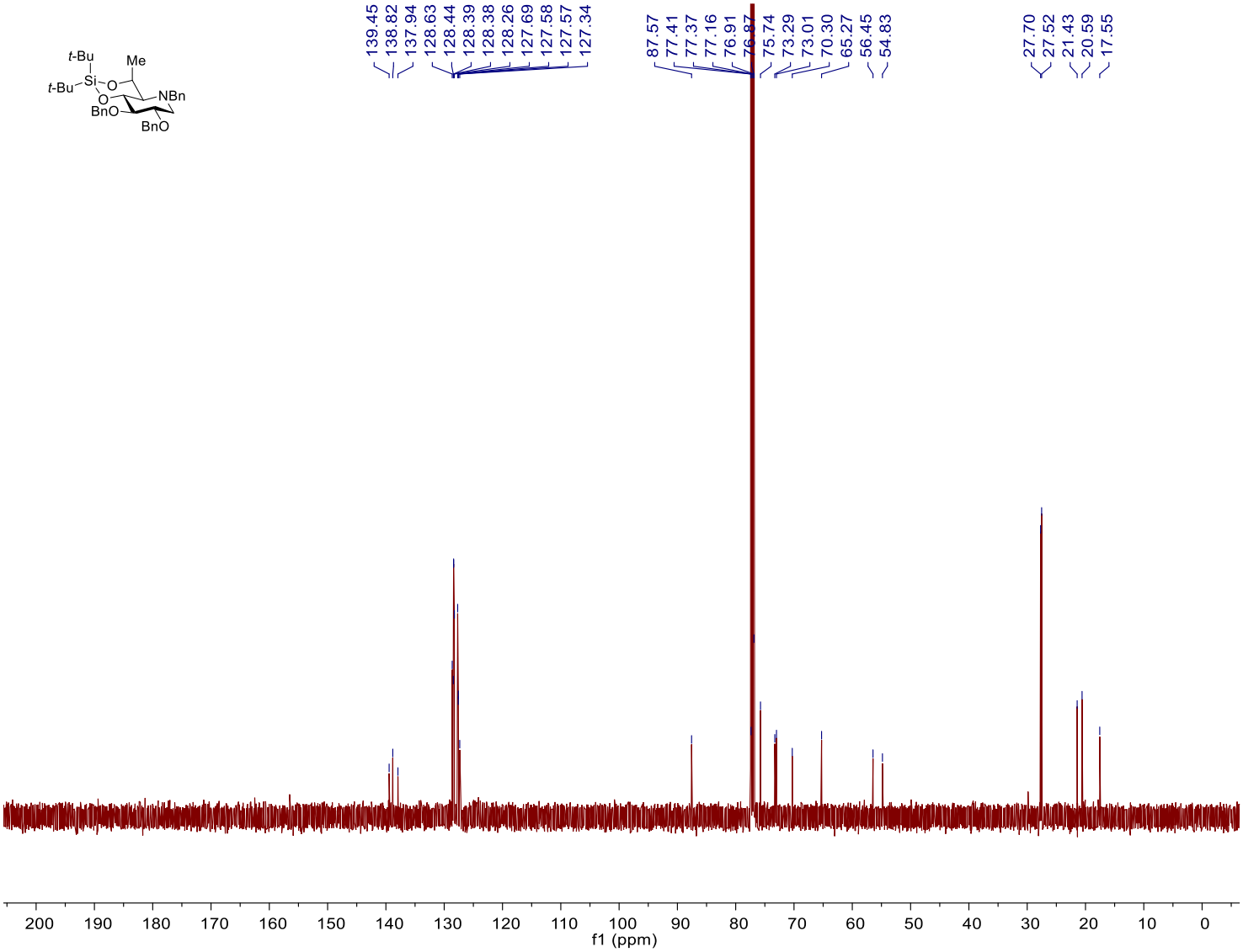
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (20)



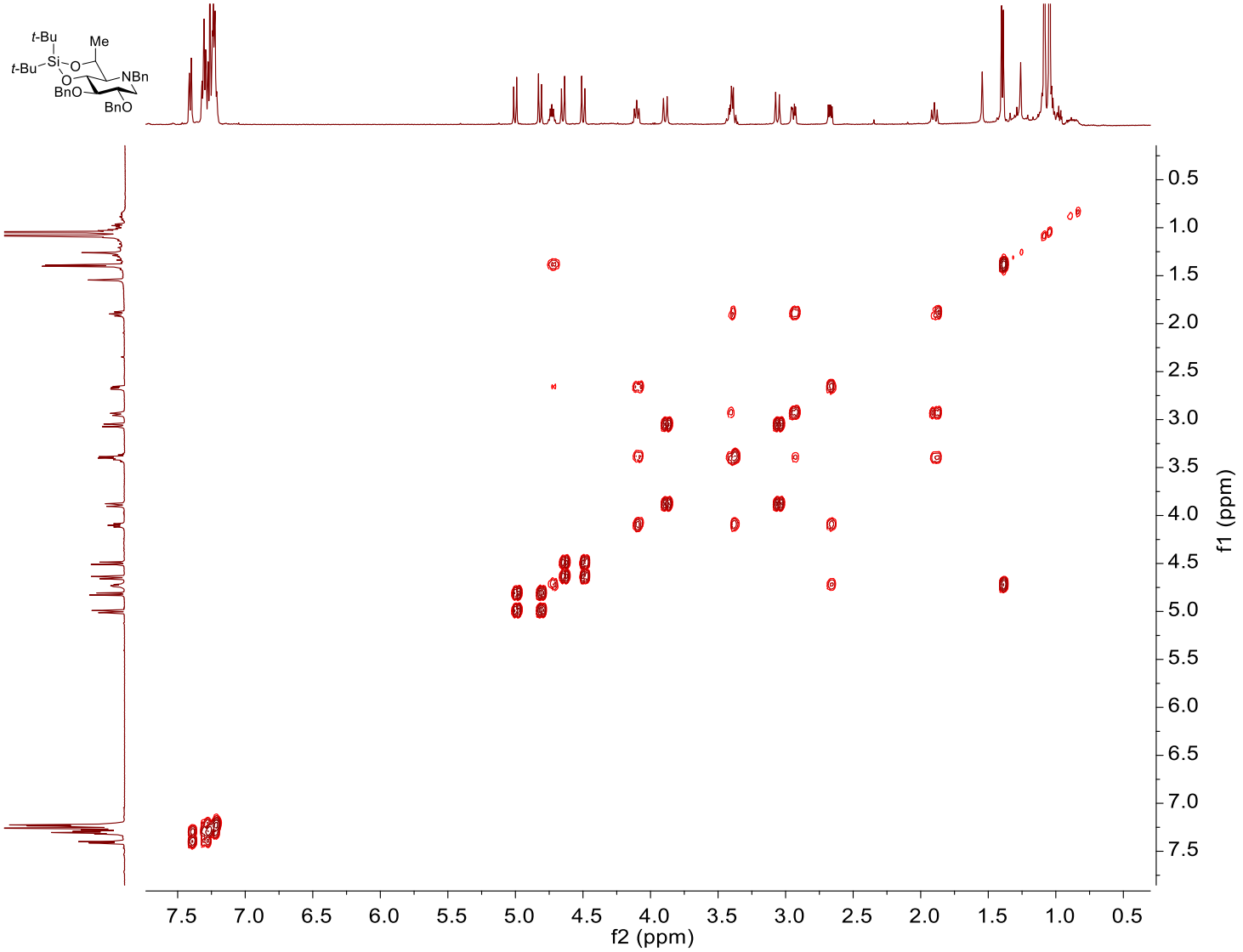
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (21)



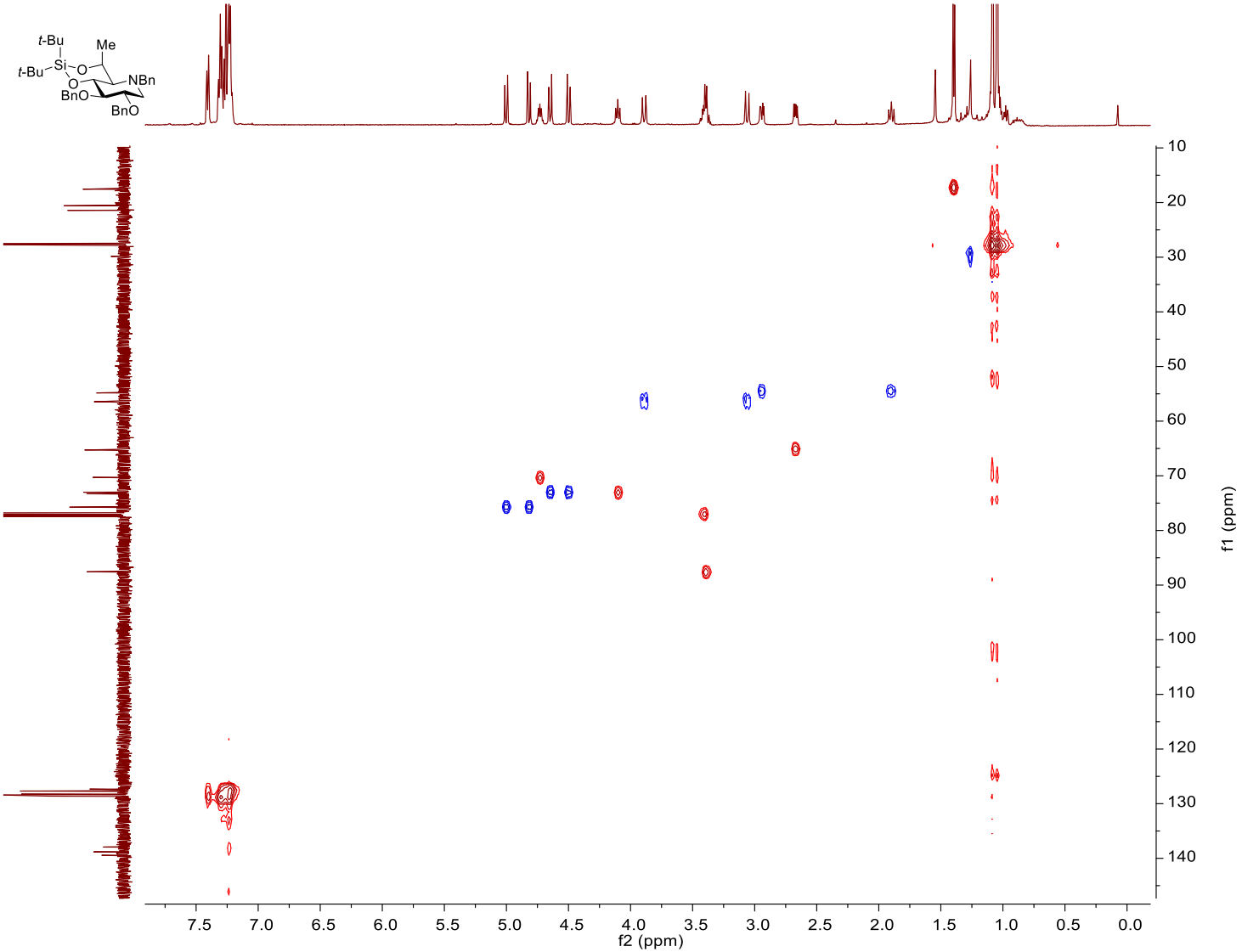
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (21)



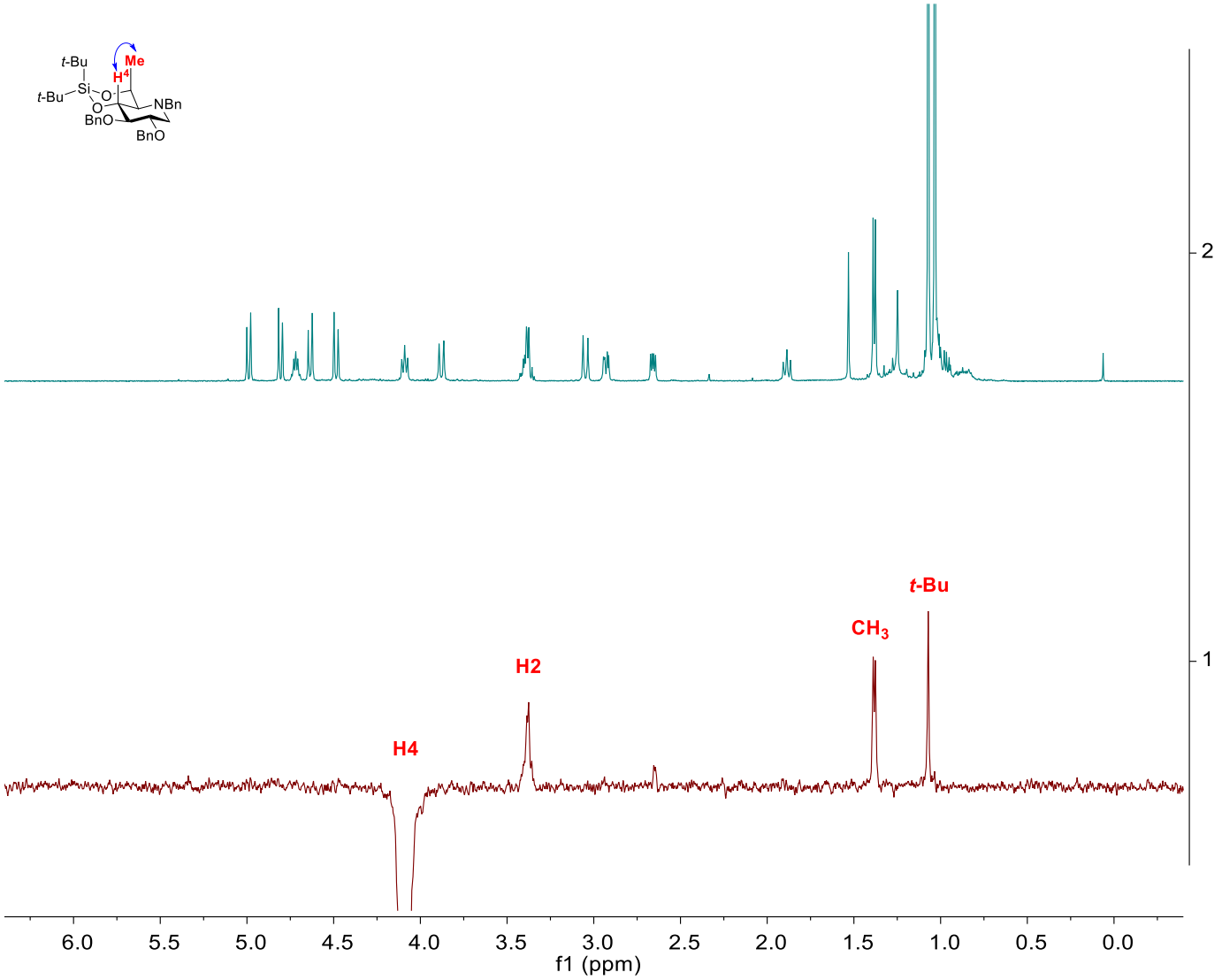
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (21)



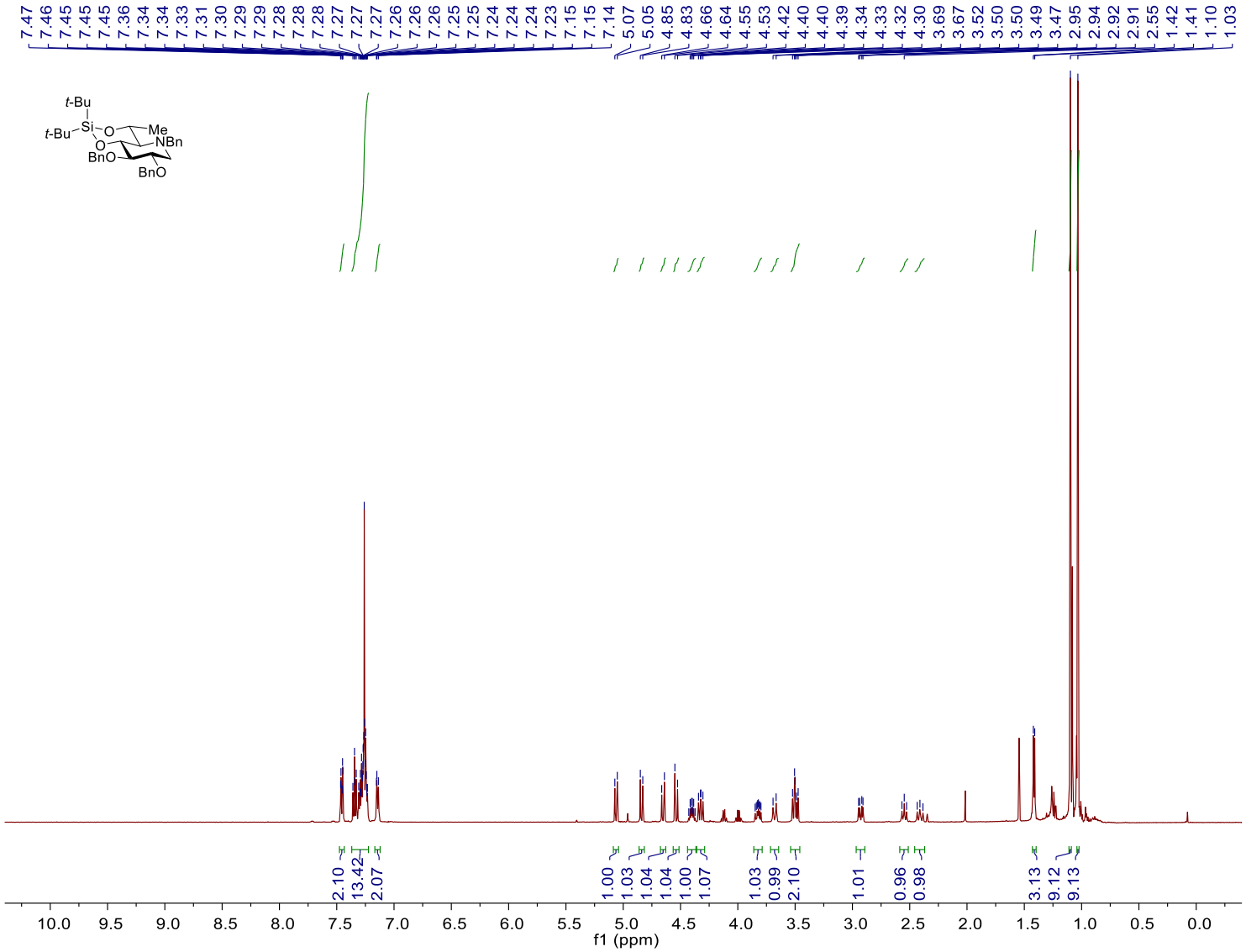
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (21)



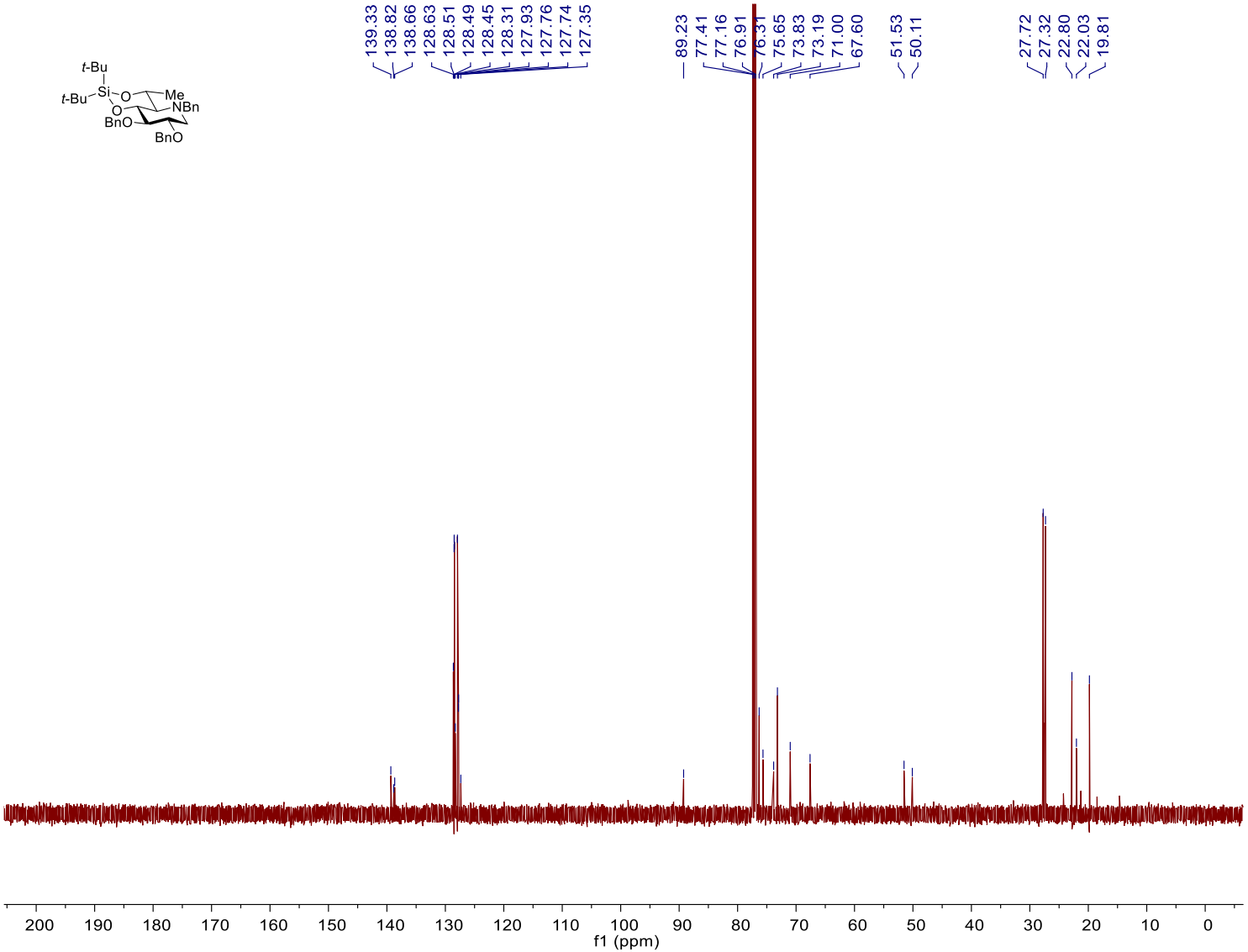
Selective 1D NOESY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (21)



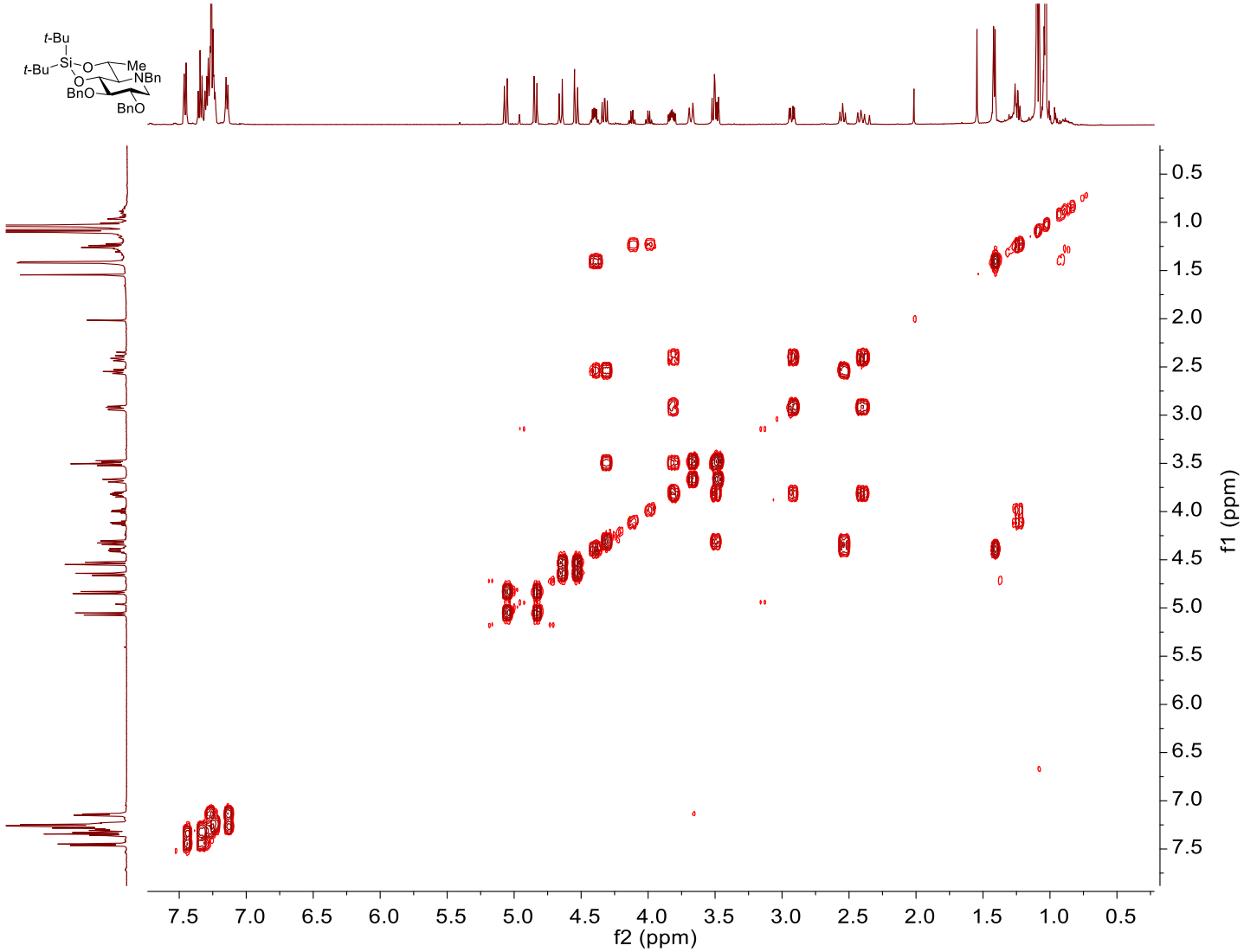
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (22)



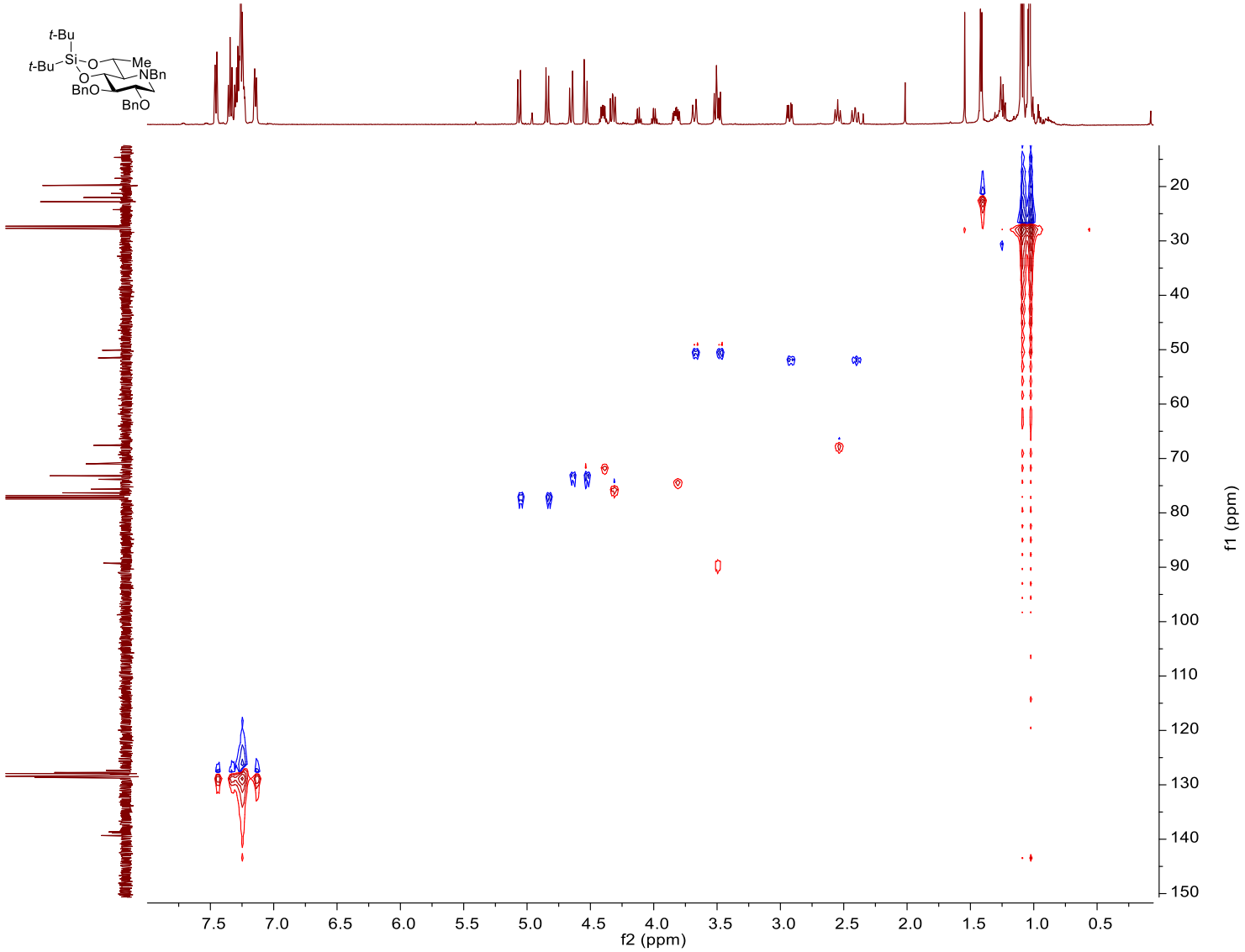
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (22)



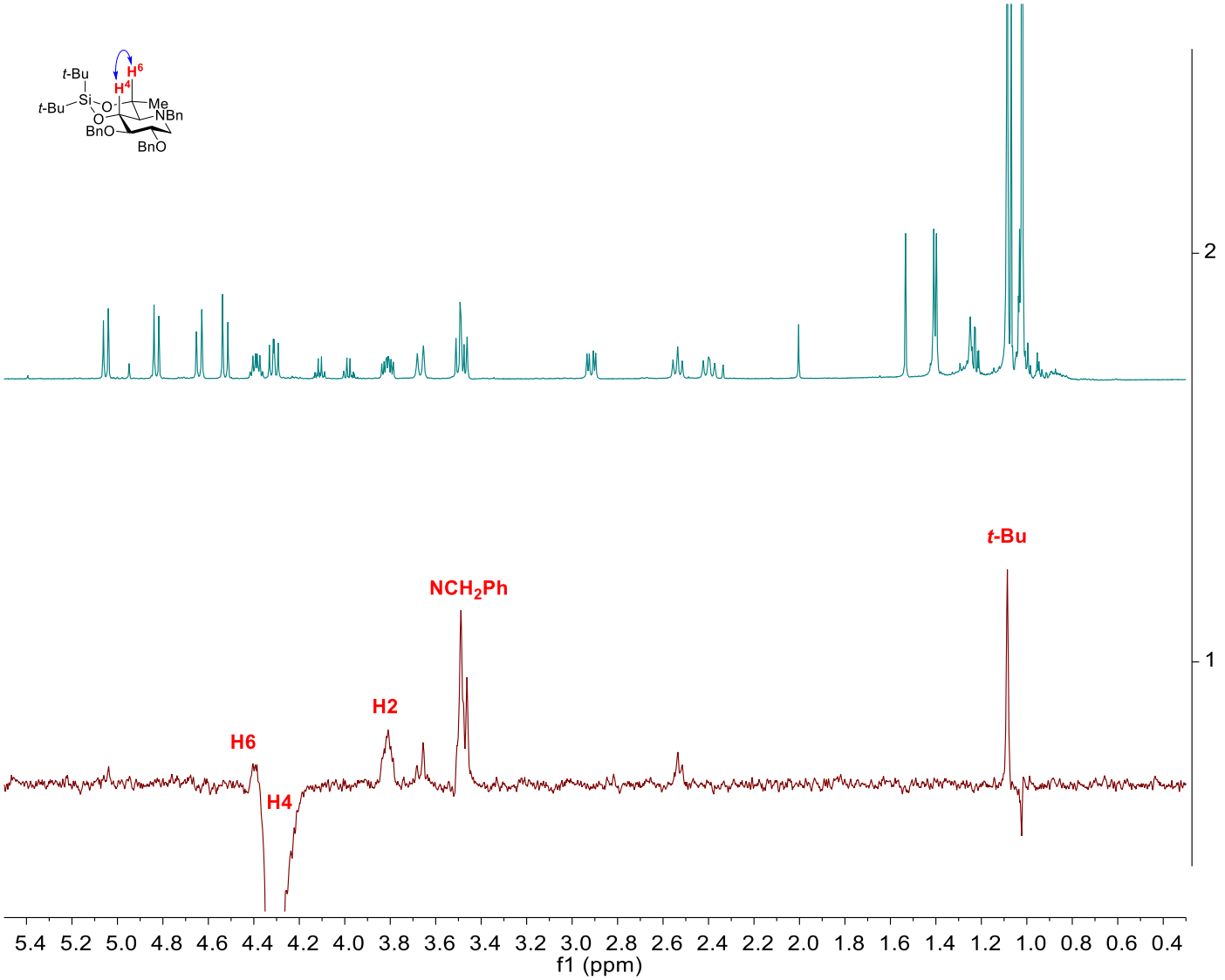
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (22)



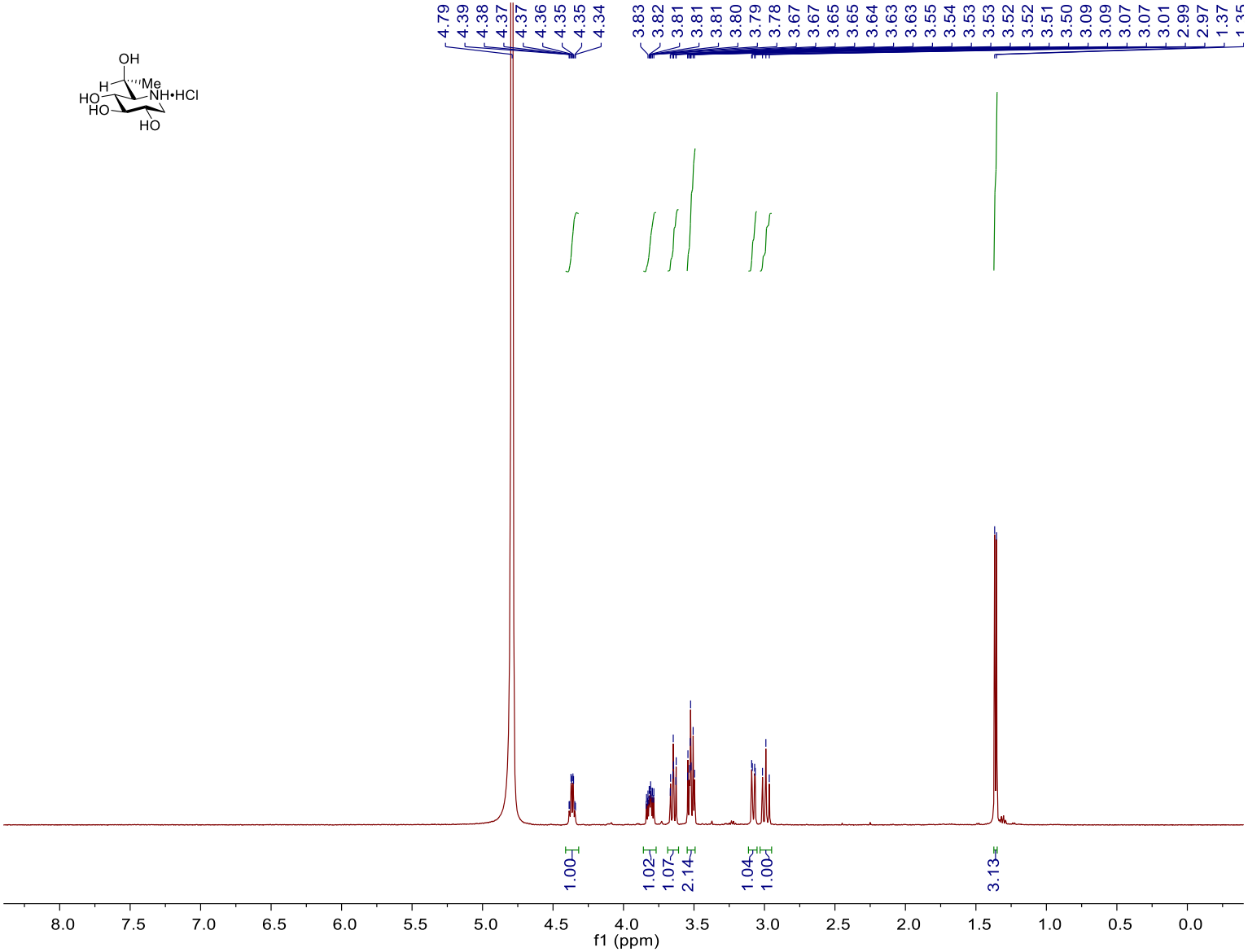
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (22)



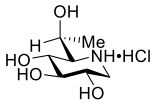
Selective 1D NOESY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (22)



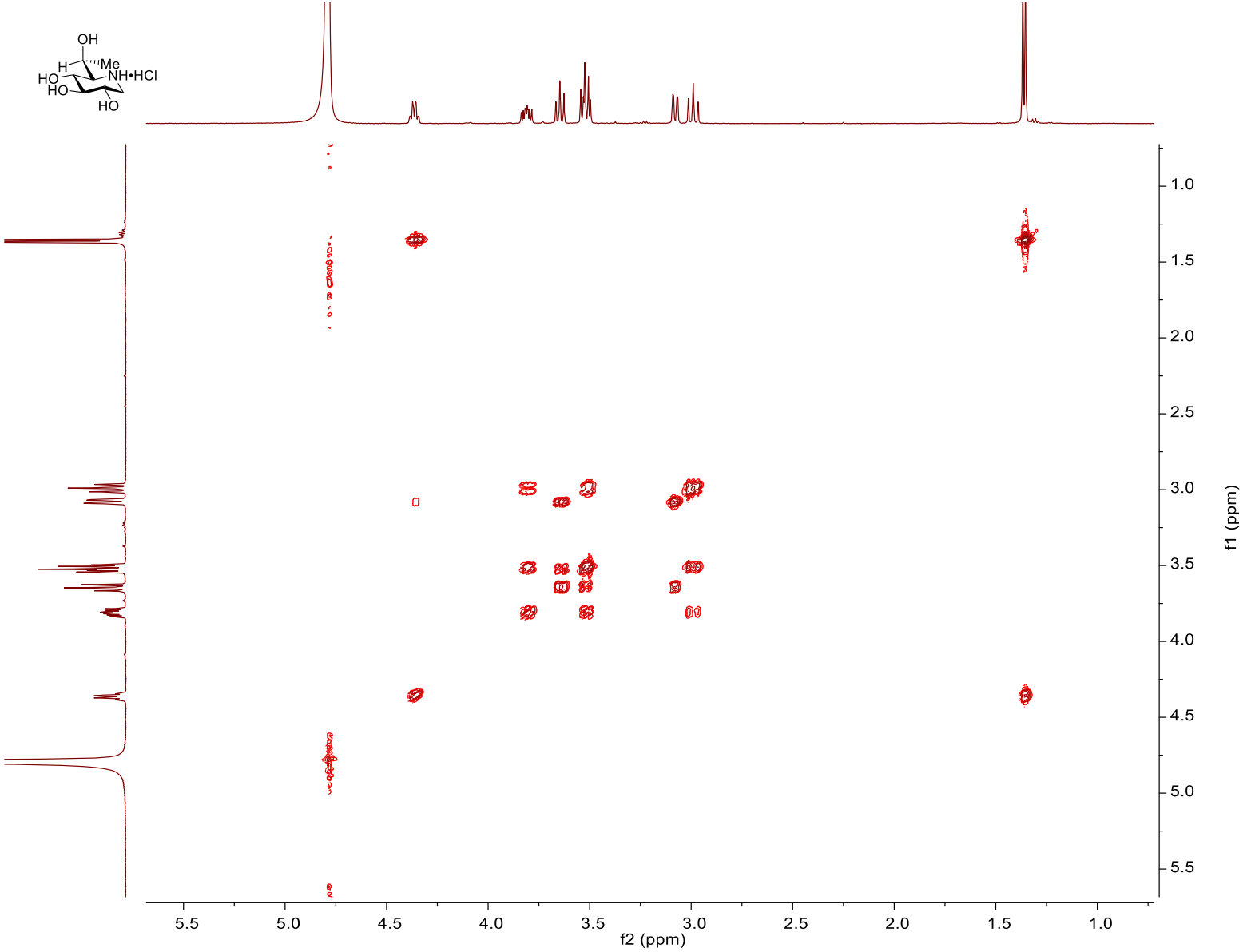
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol Hydrochloride (3)



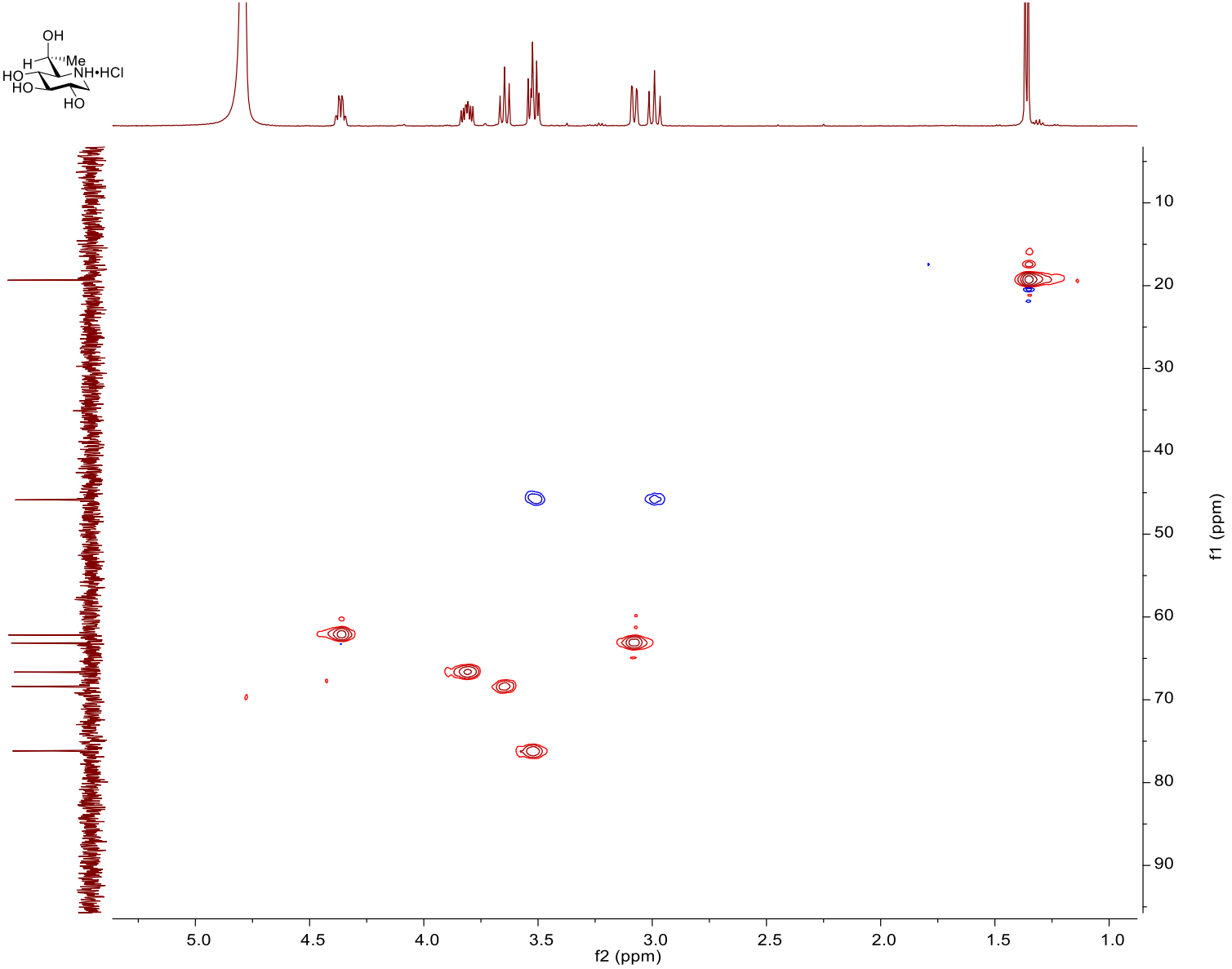
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol Hydrochloride (3)



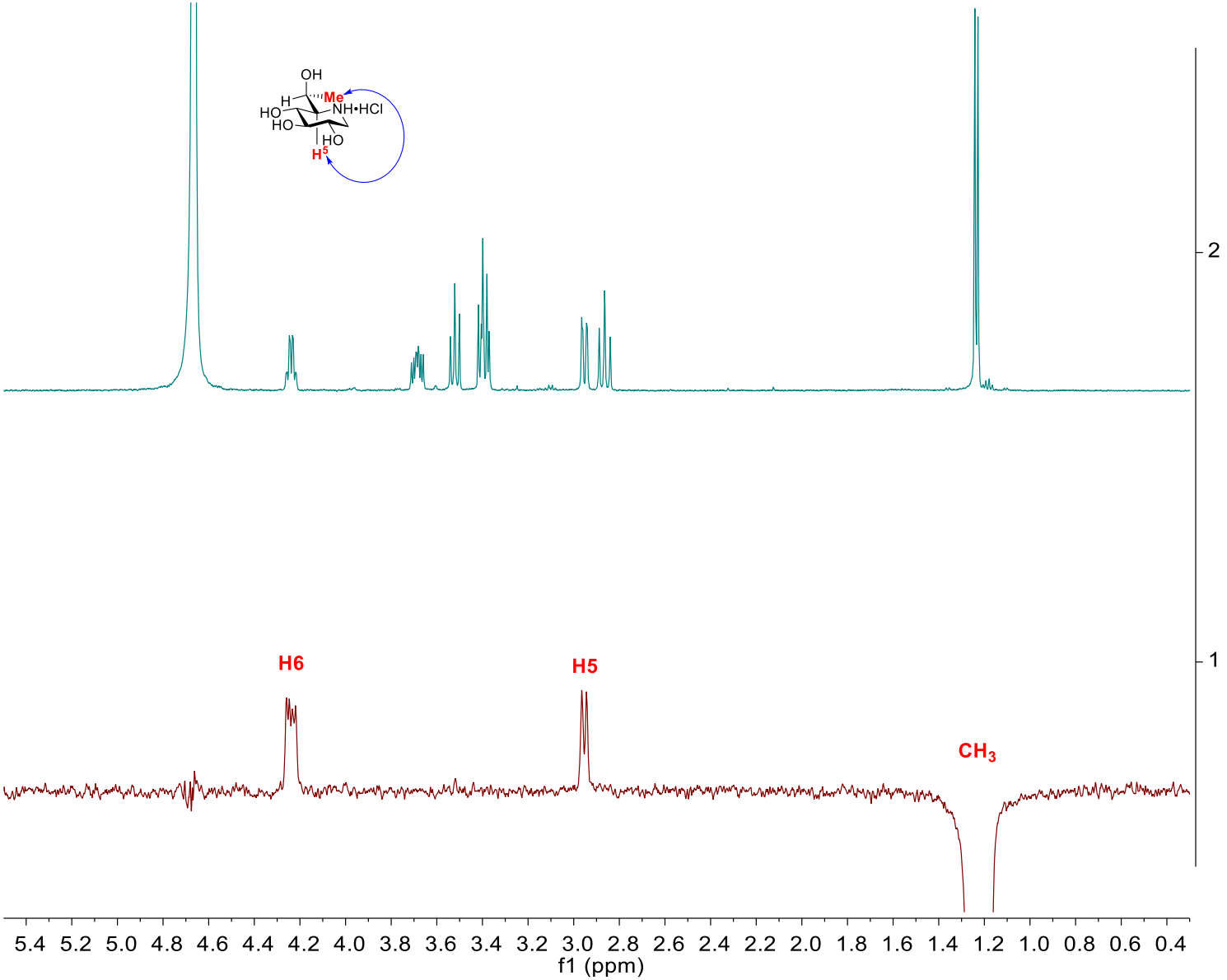
COSY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol Hydrochloride (3)



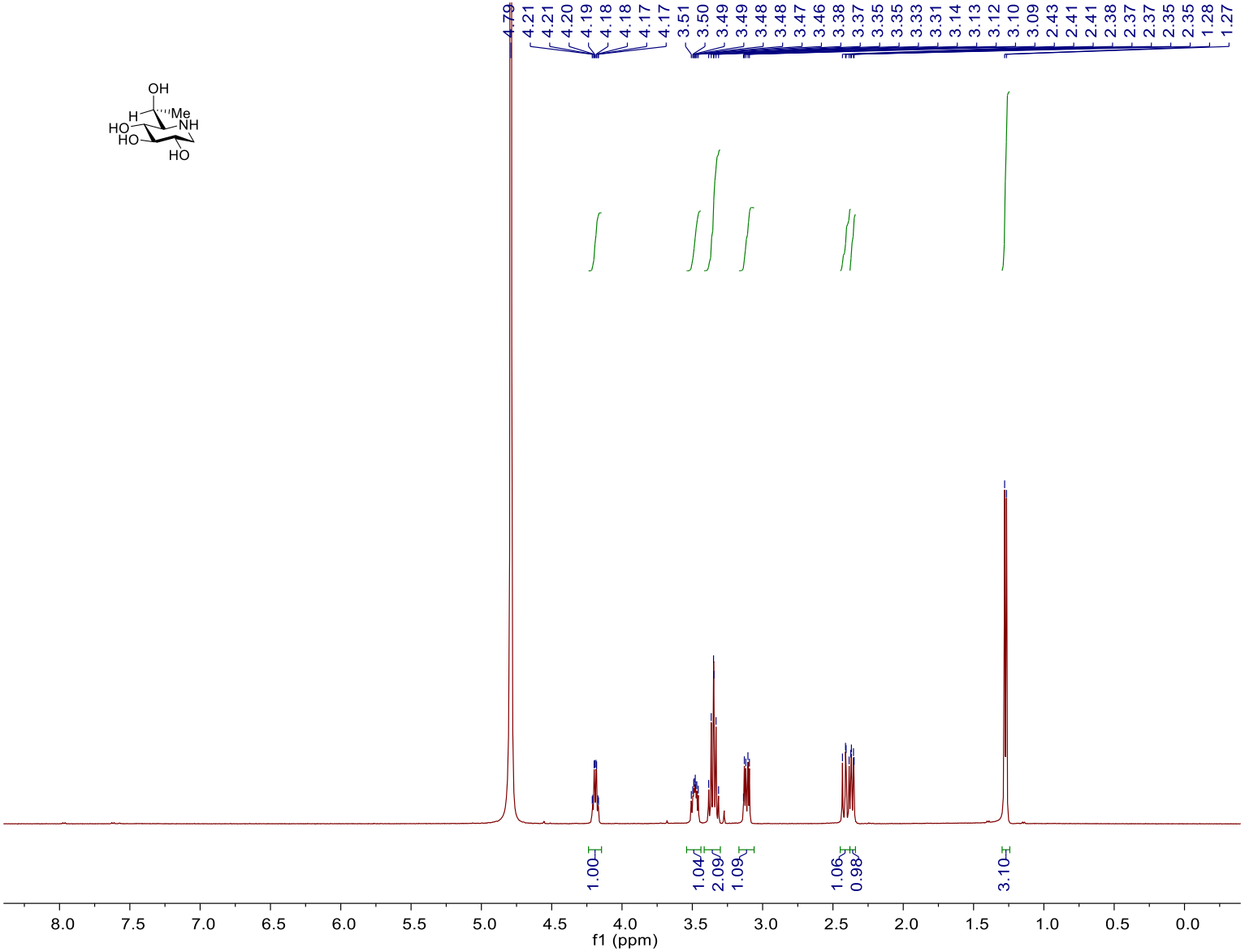
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol Hydrochloride (3)



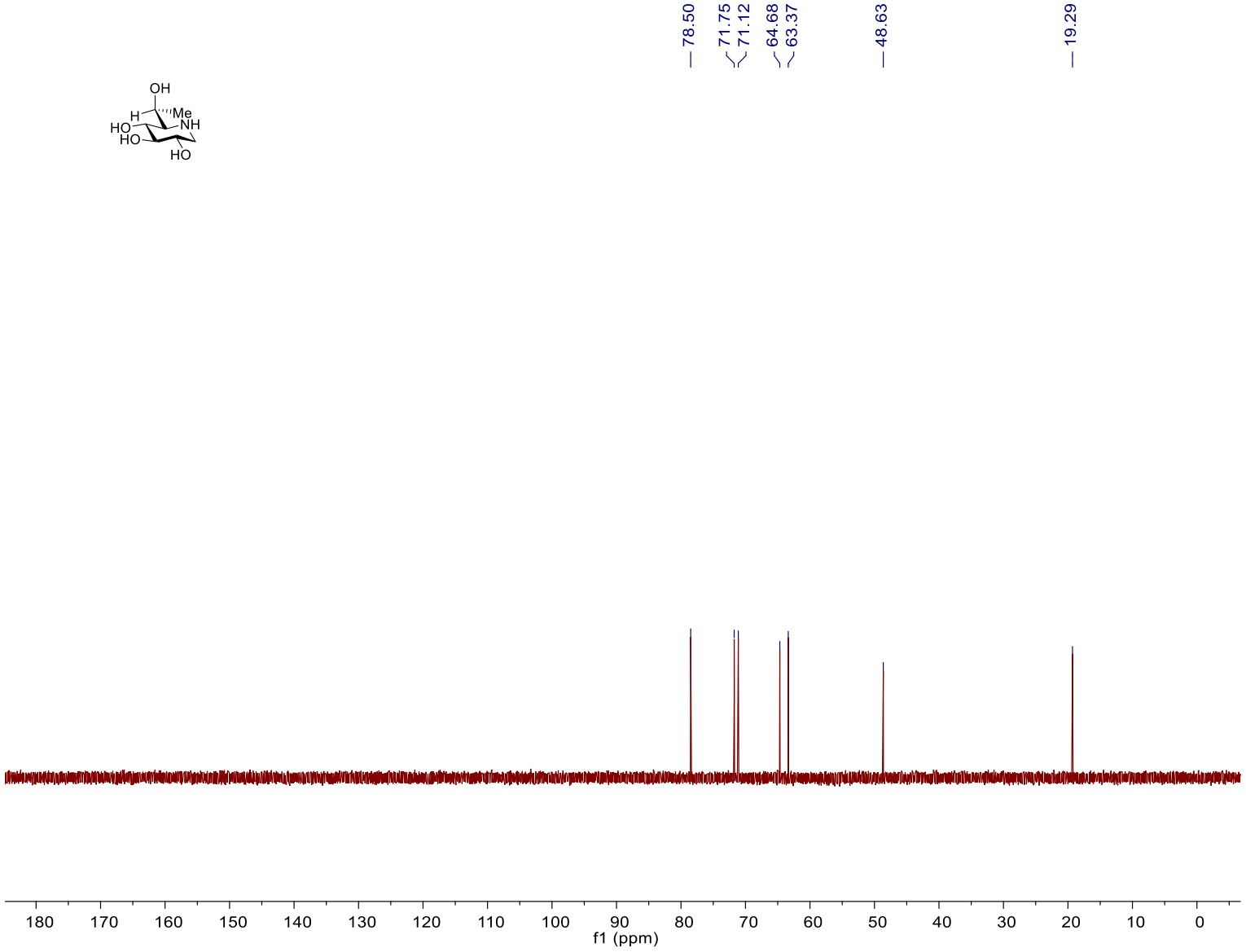
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol Hydrochloride (3)



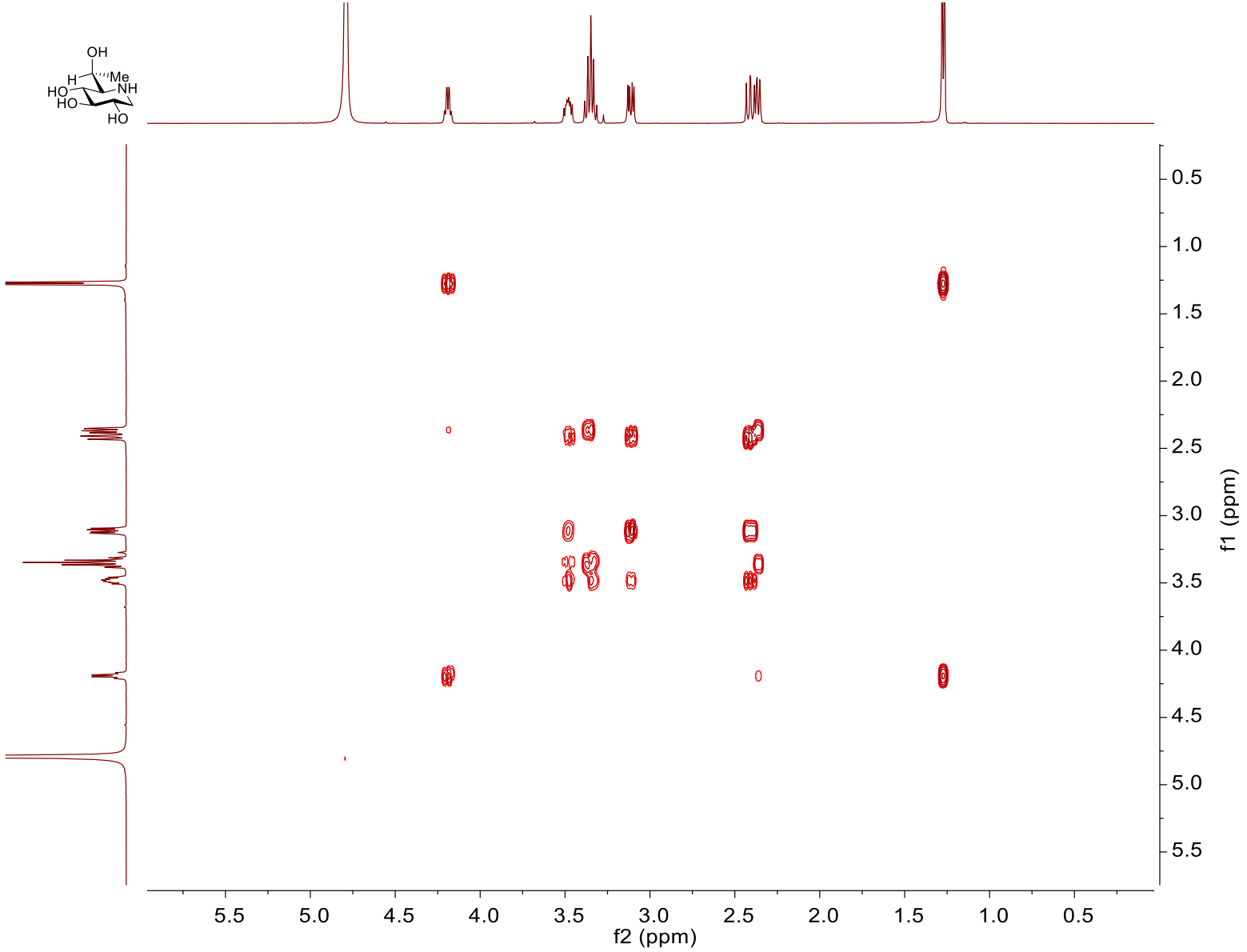
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (3)



^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (3)



COSY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (3)



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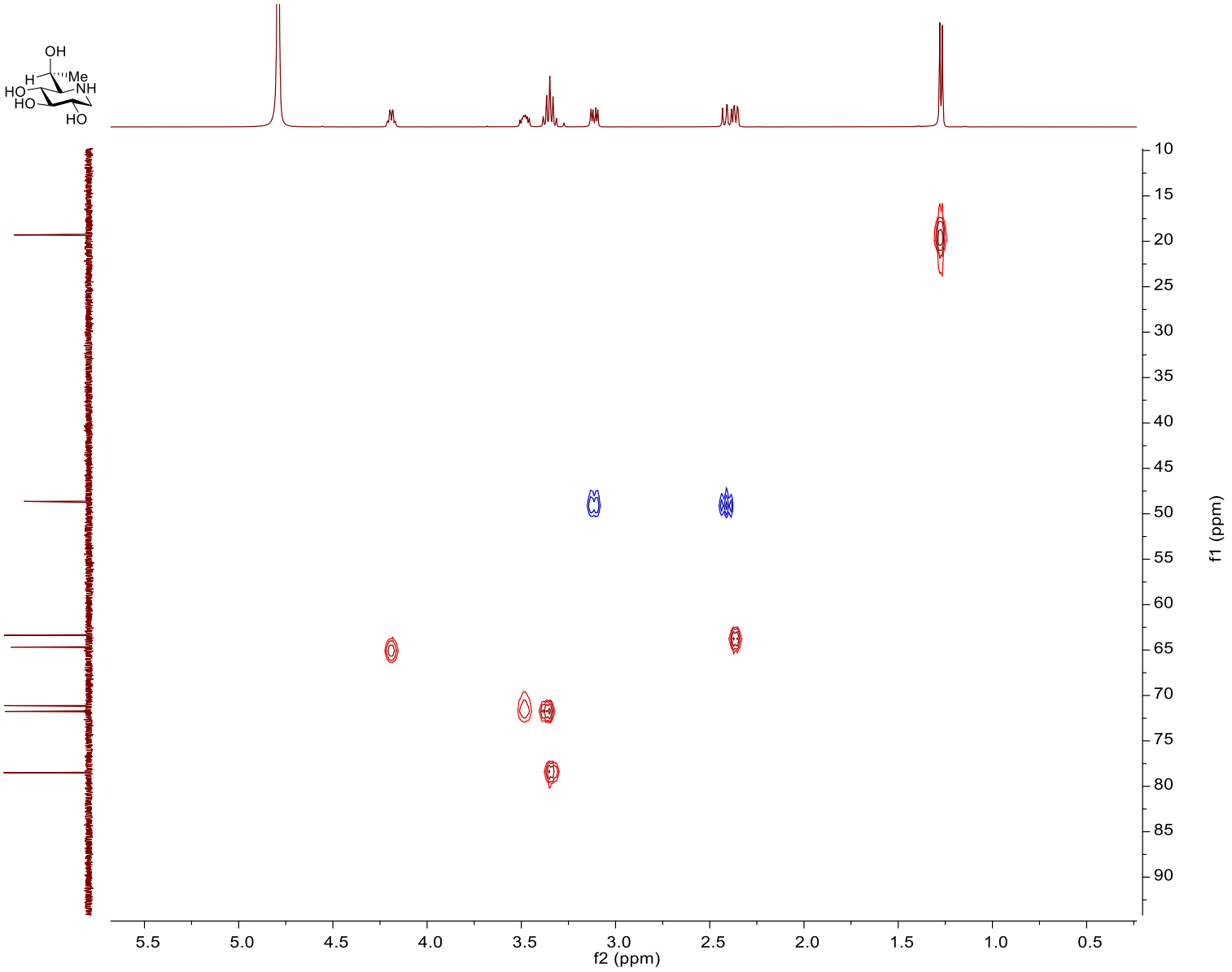
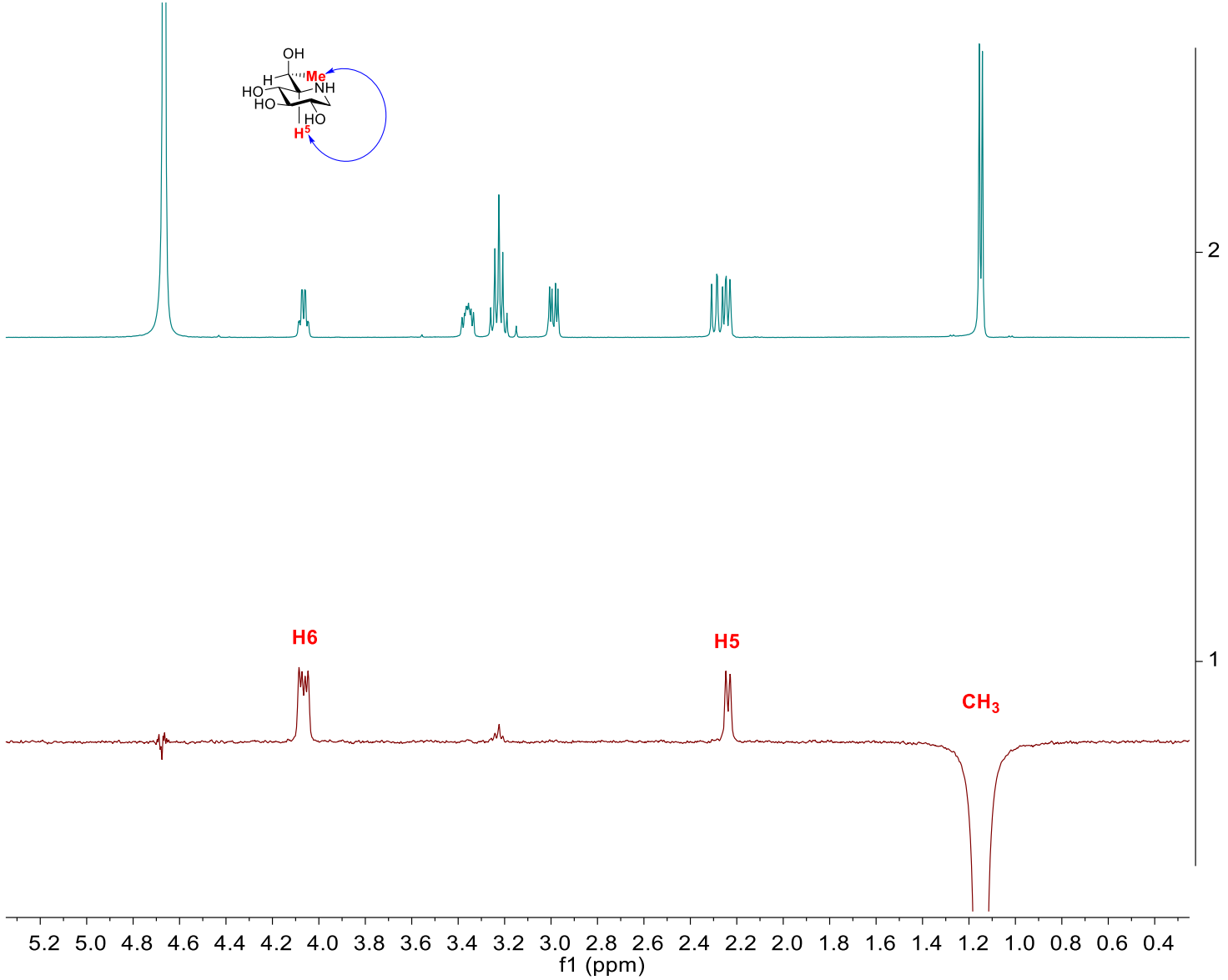
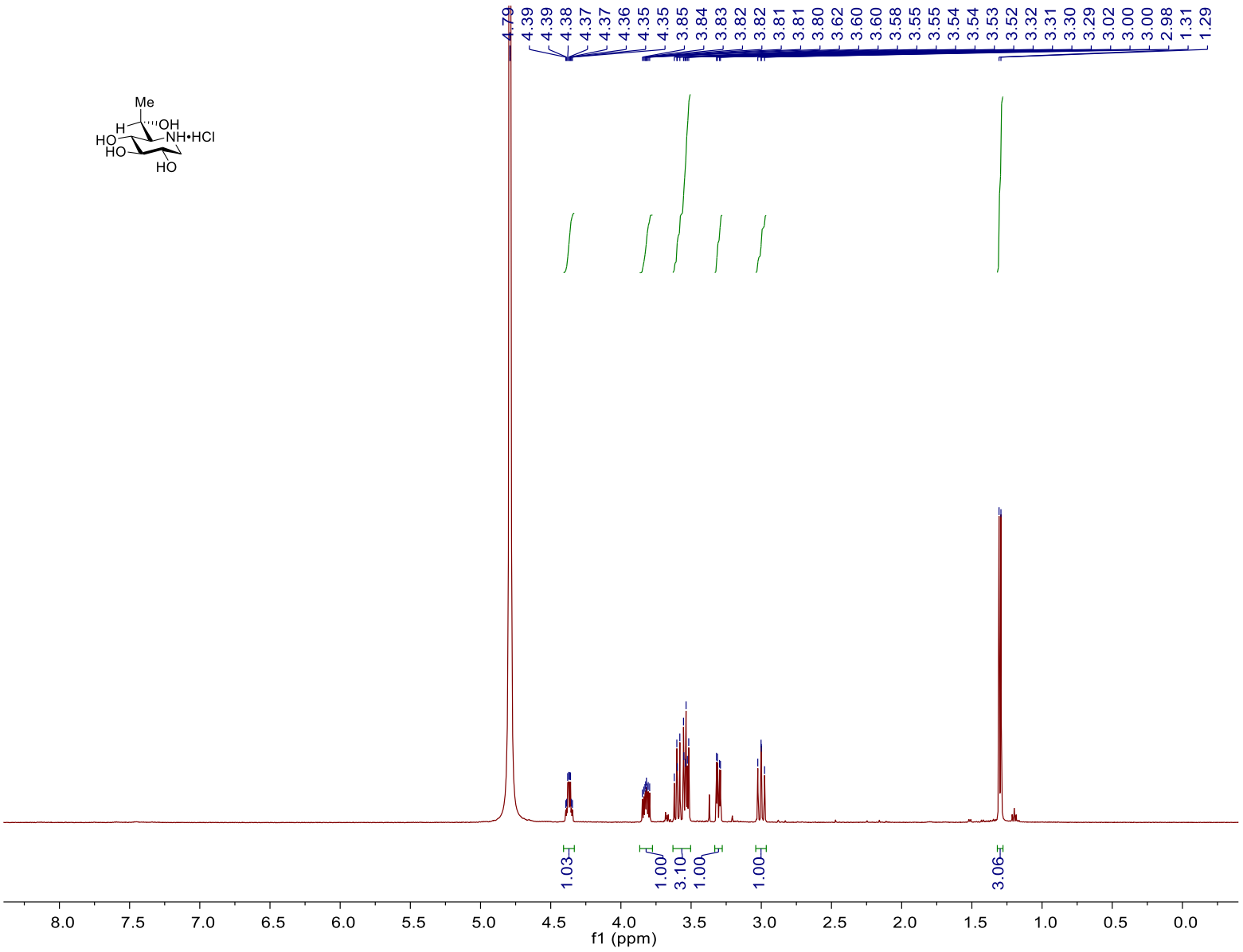


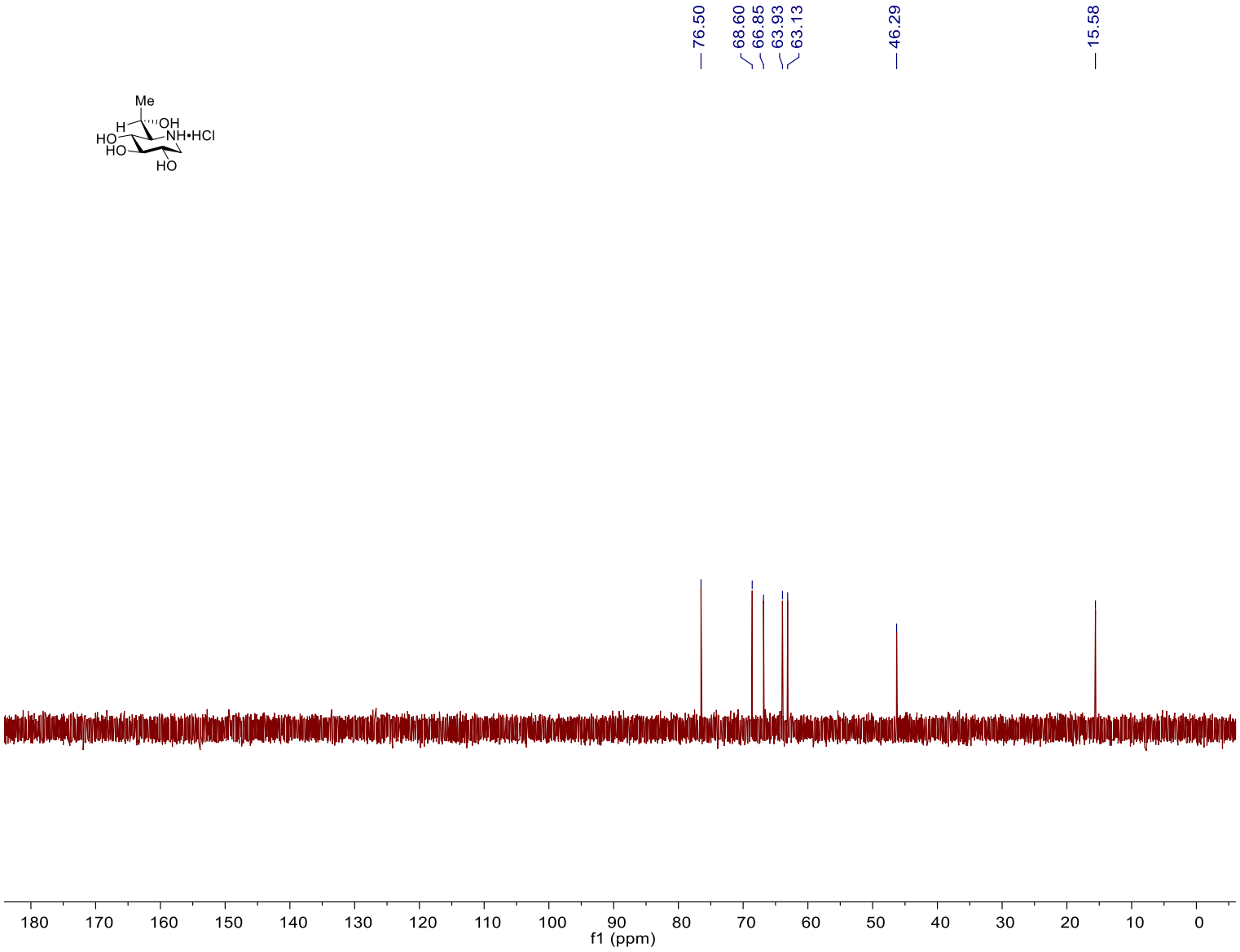
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*gluco*-heptitol (3)



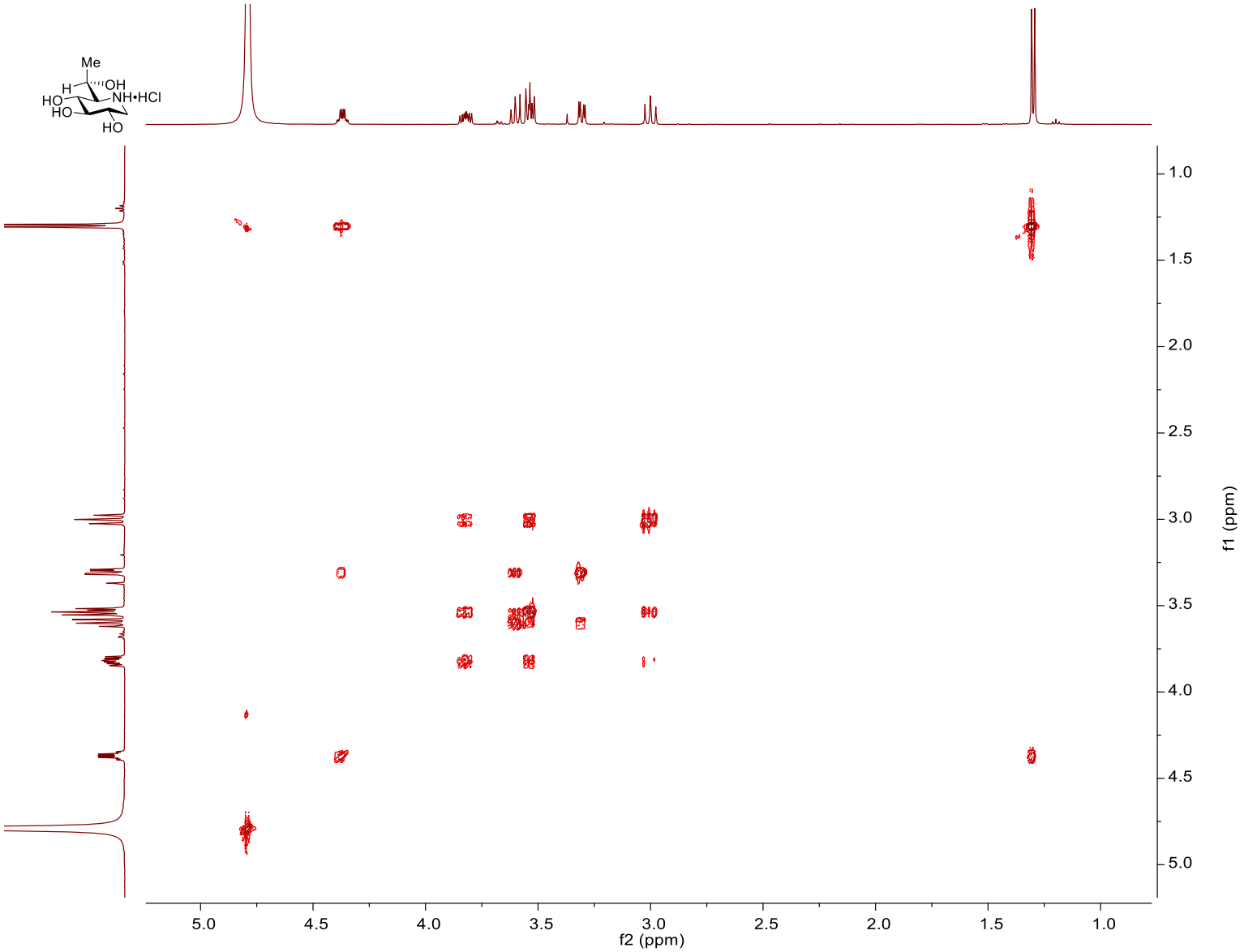
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol Hydrochloride (4)



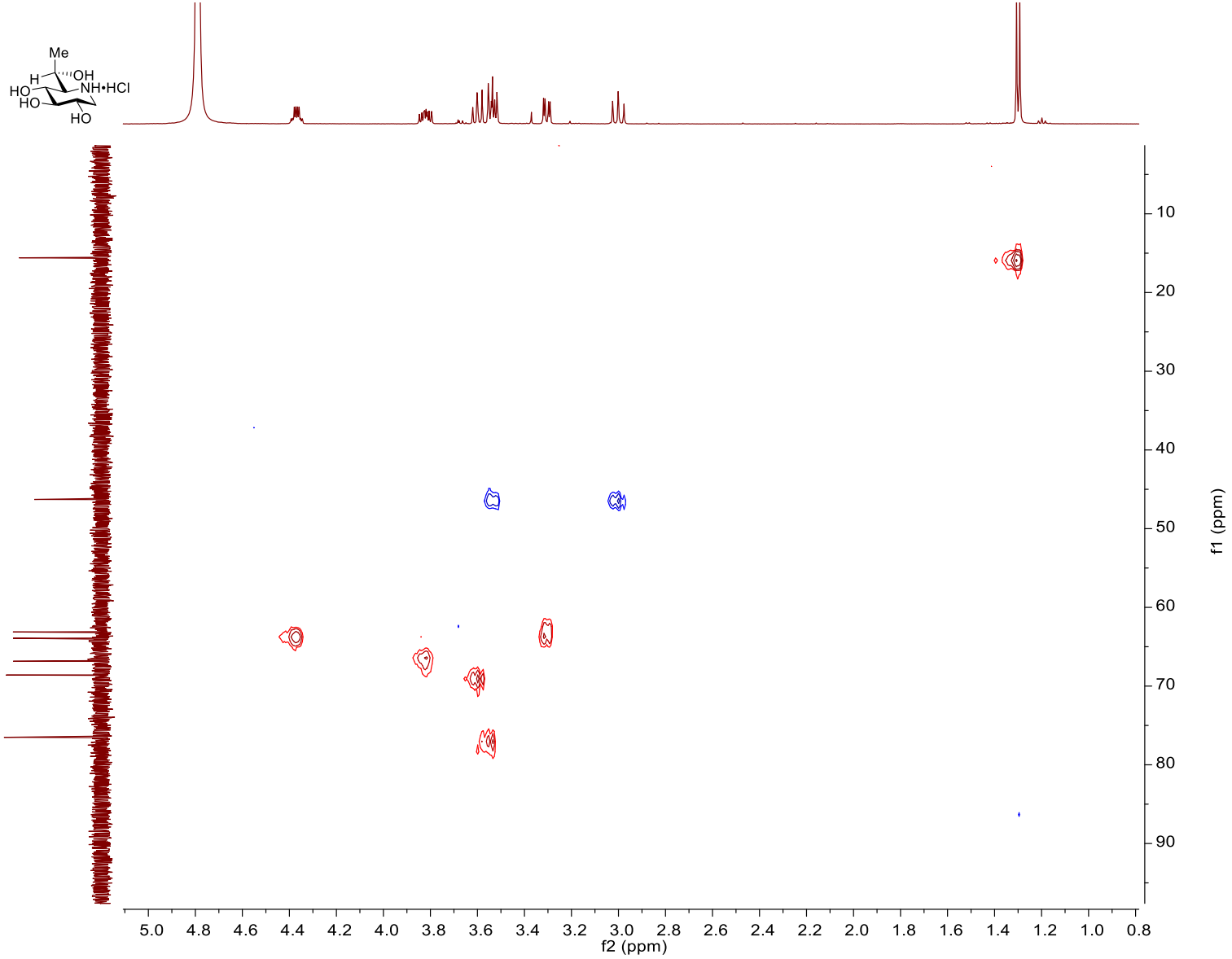
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol Hydrochloride (4)



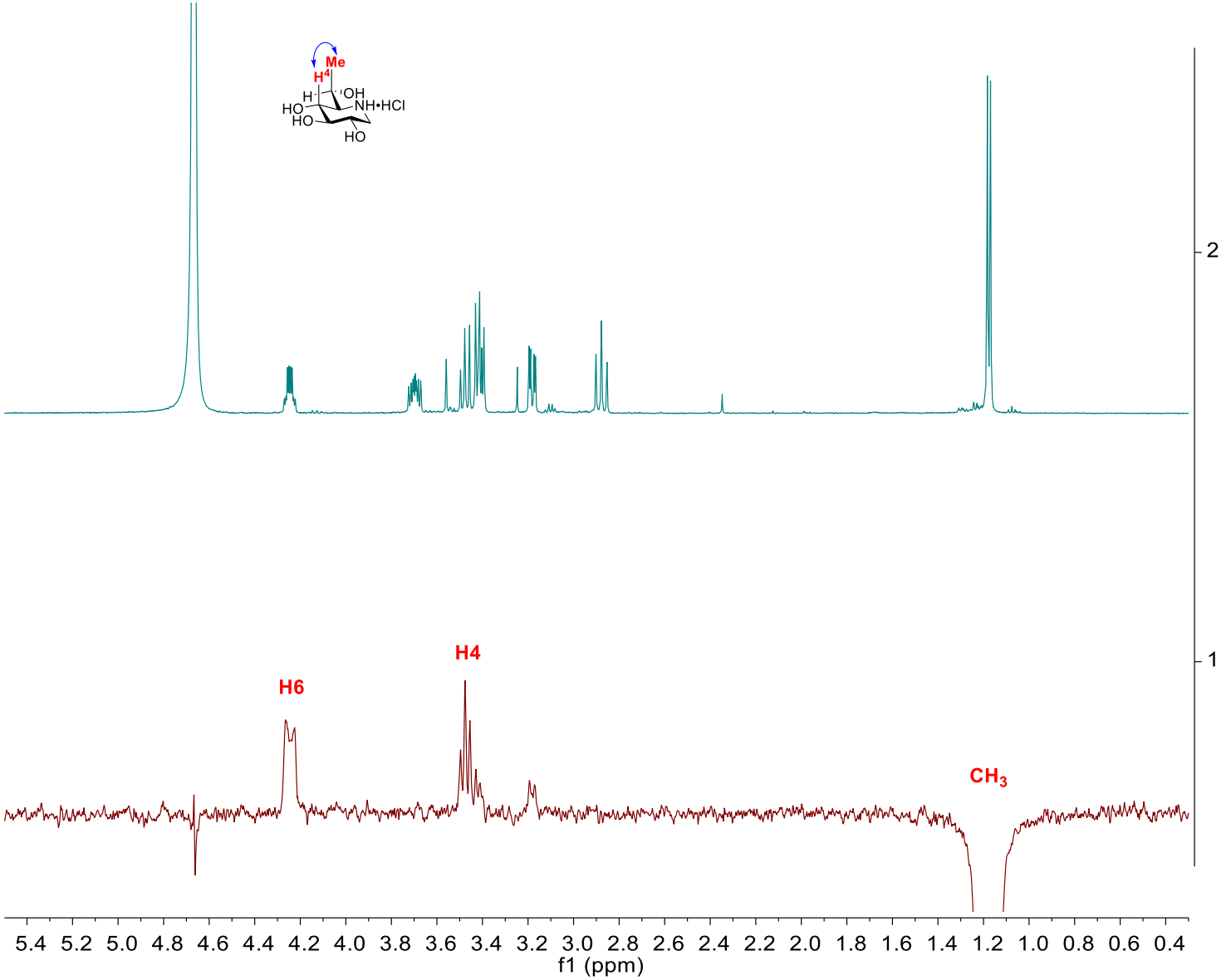
COSY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol Hydrochloride (4)



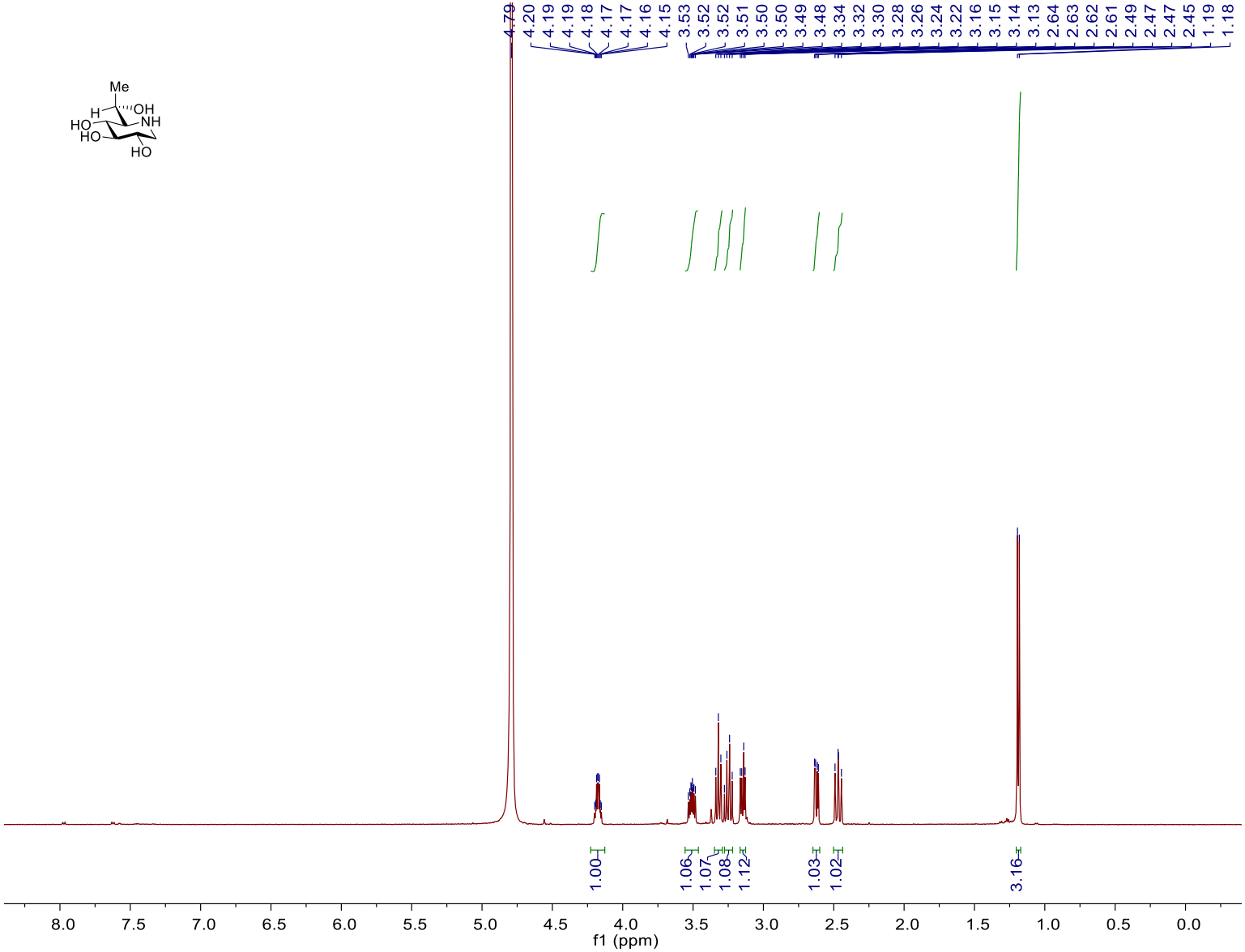
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol Hydrochloride (4)



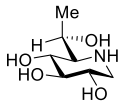
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol Hydrochloride (4)



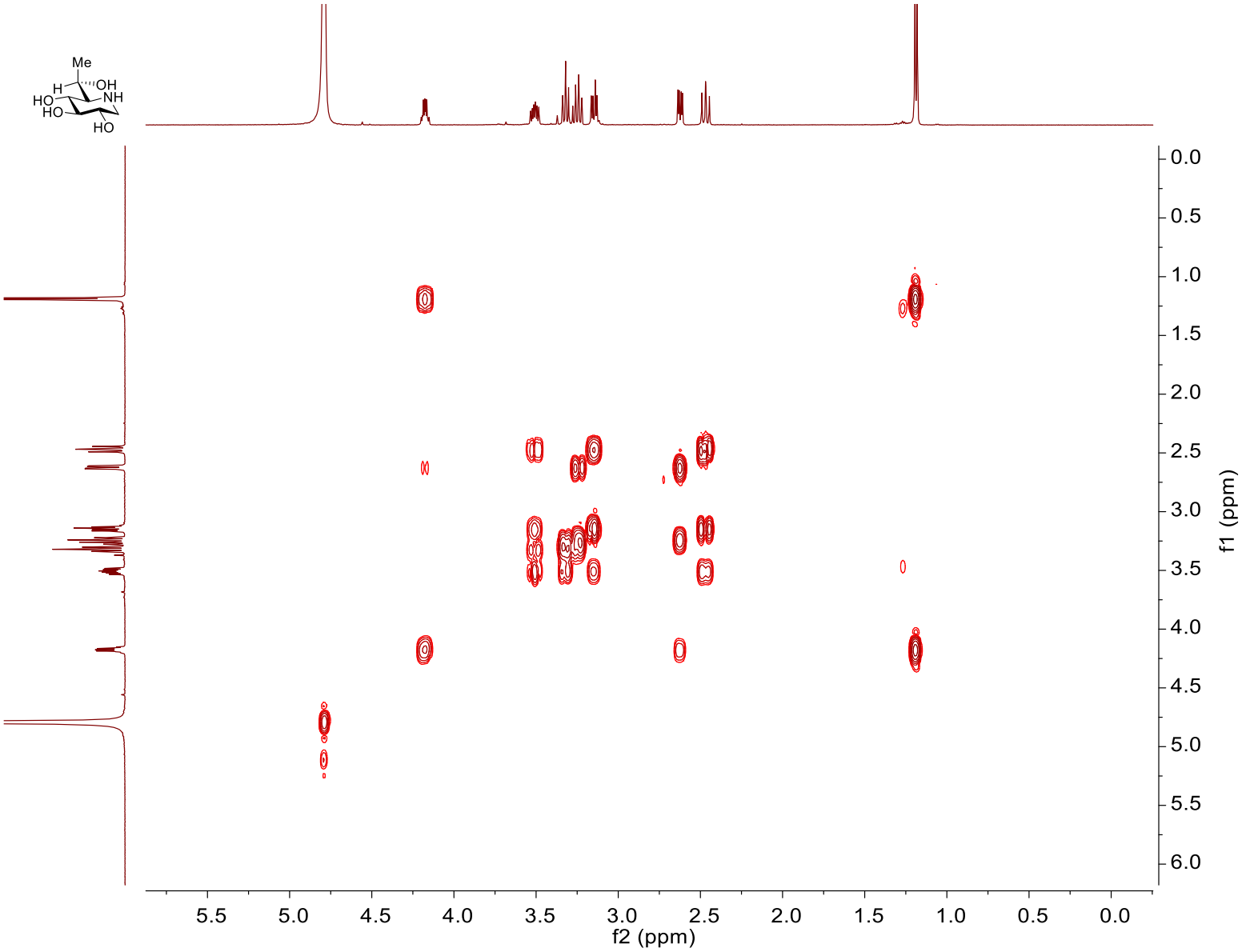
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (4)



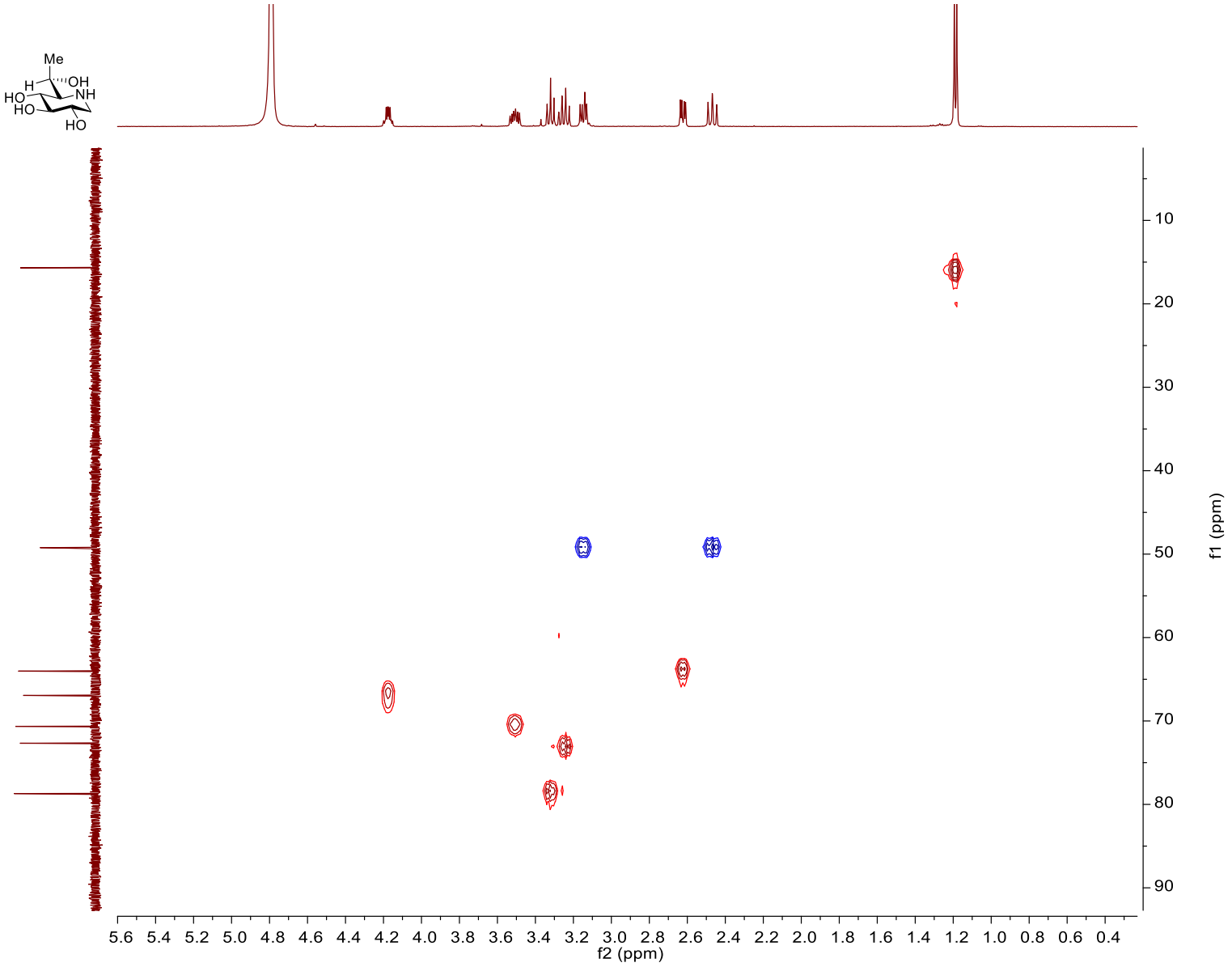
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (4)



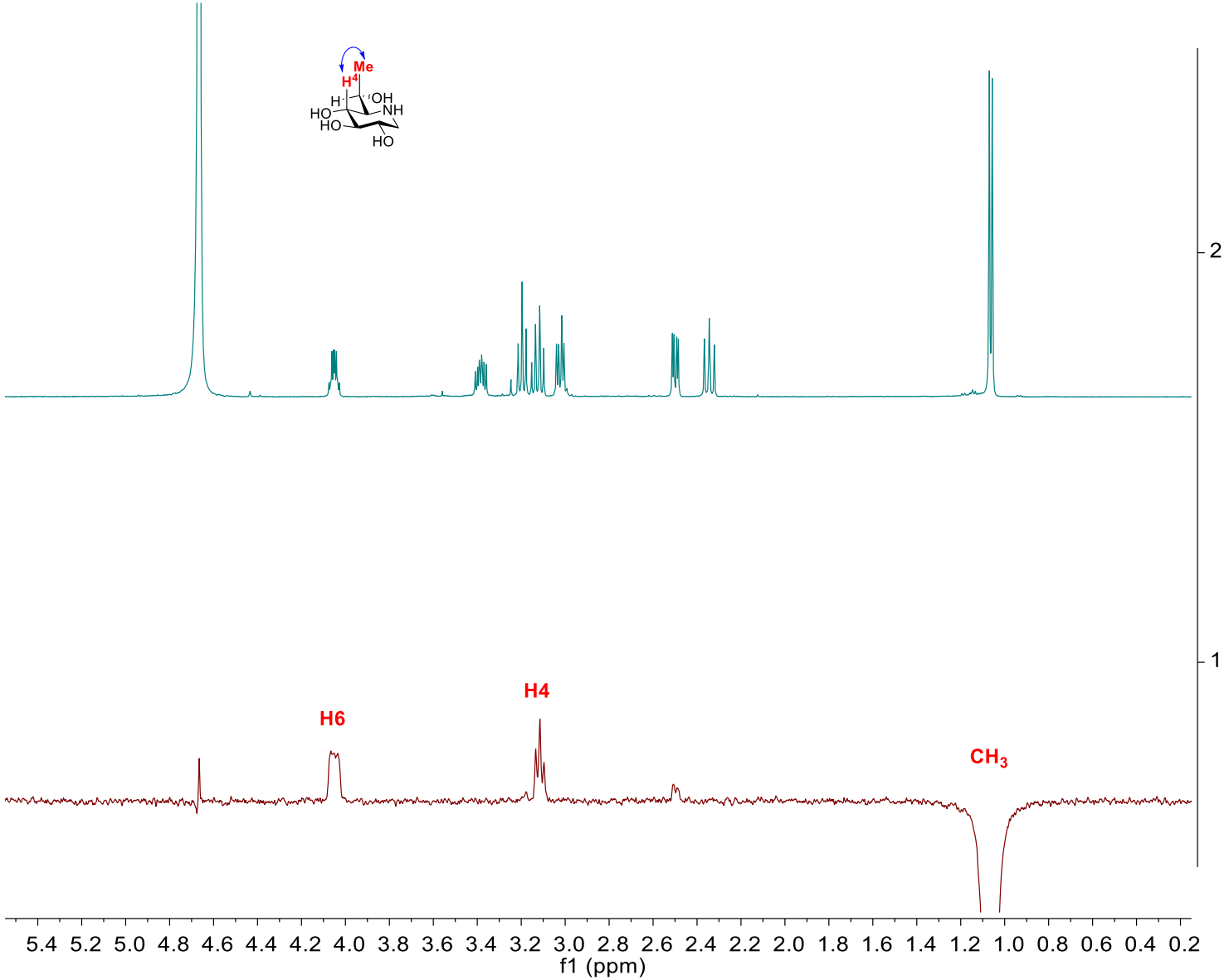
COSY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (*4*)



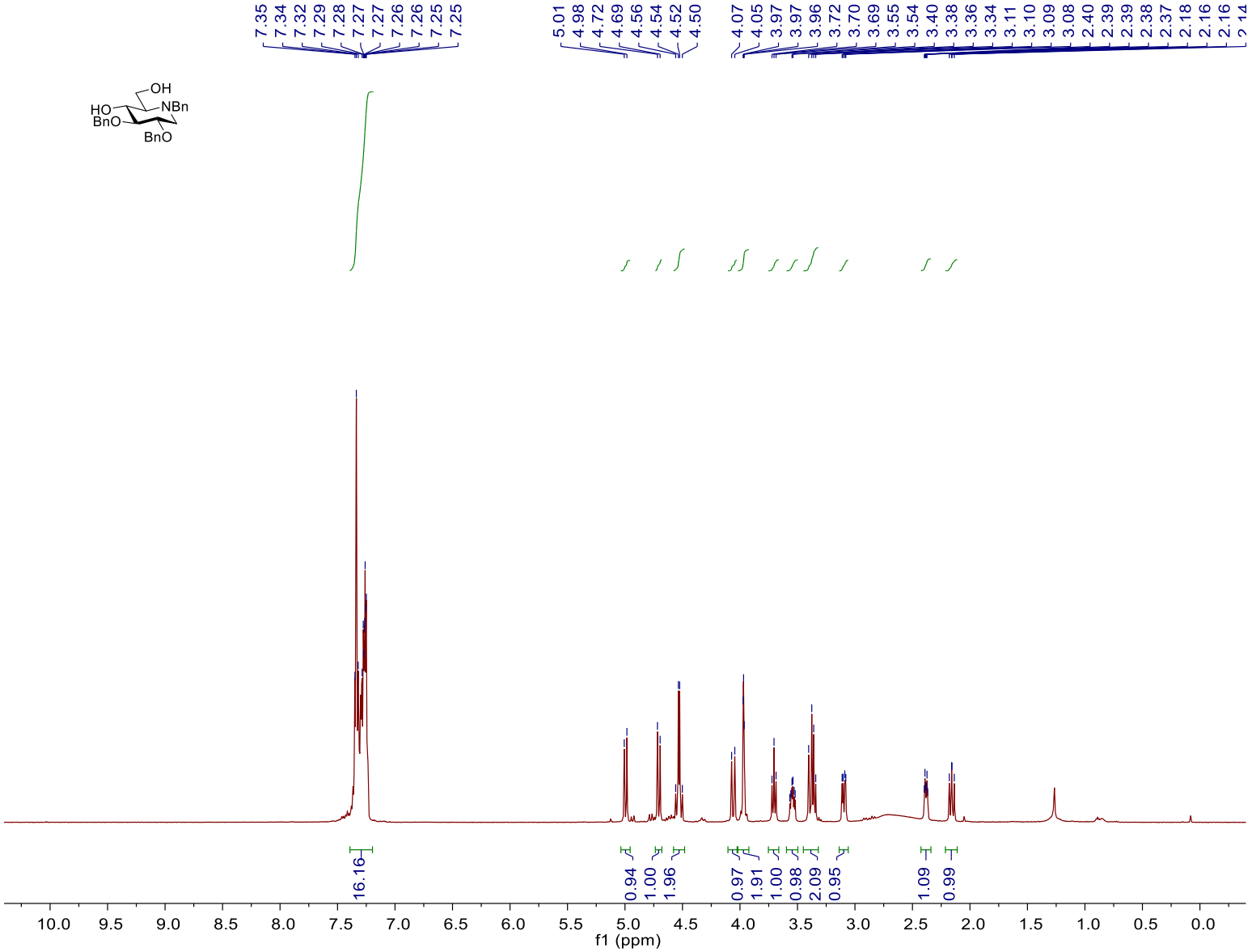
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (*4*)



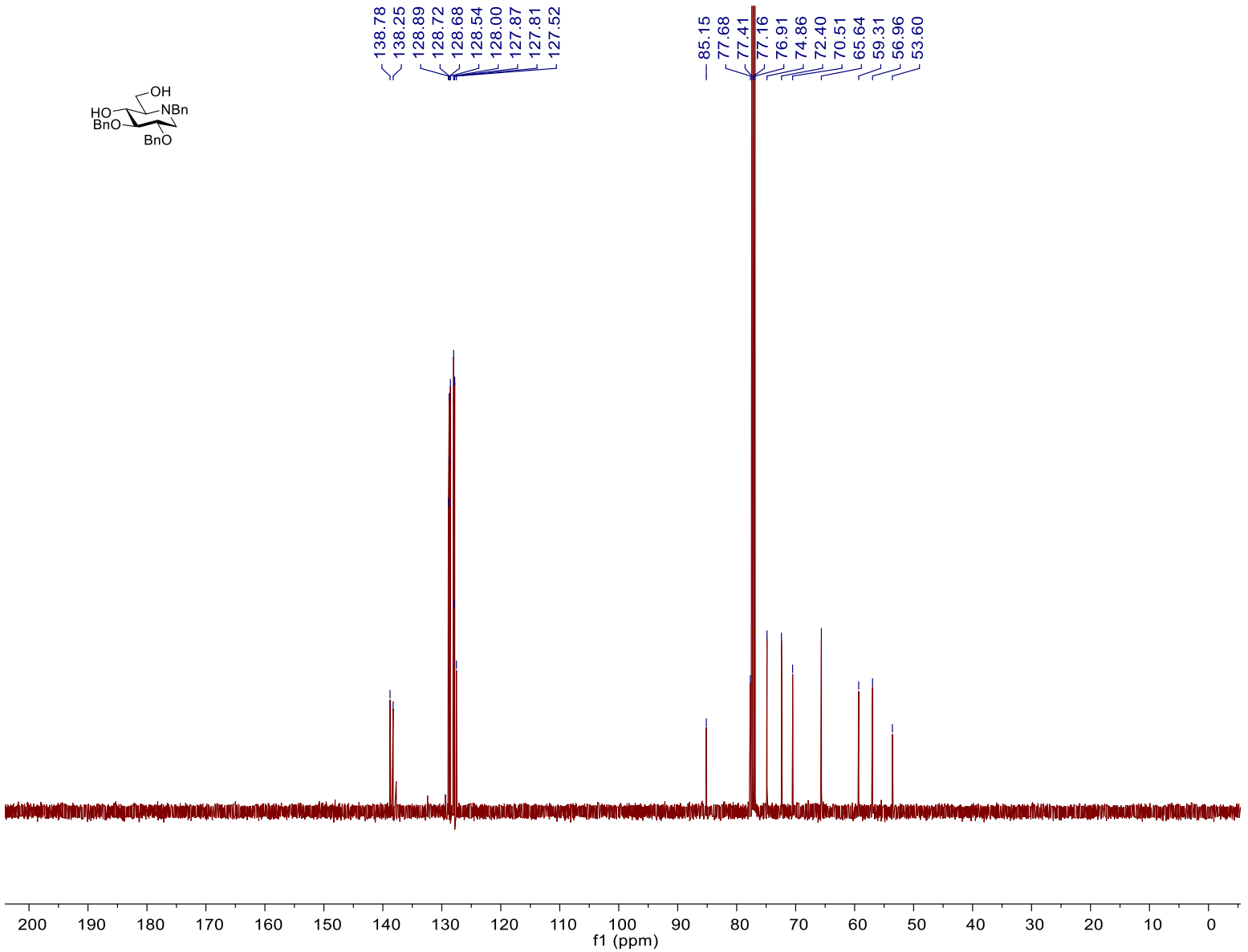
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*gluco*-heptitol (4)



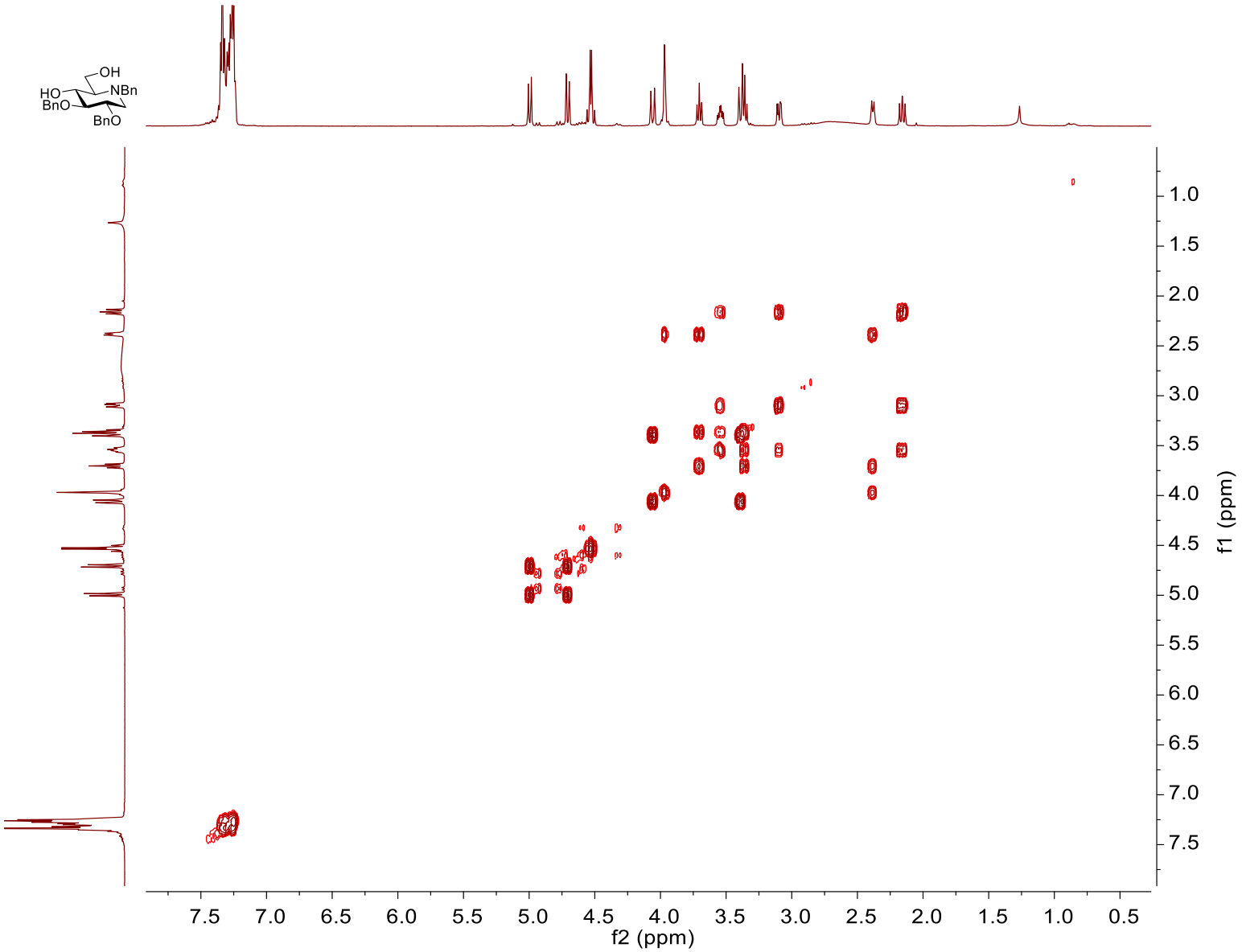
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (23)



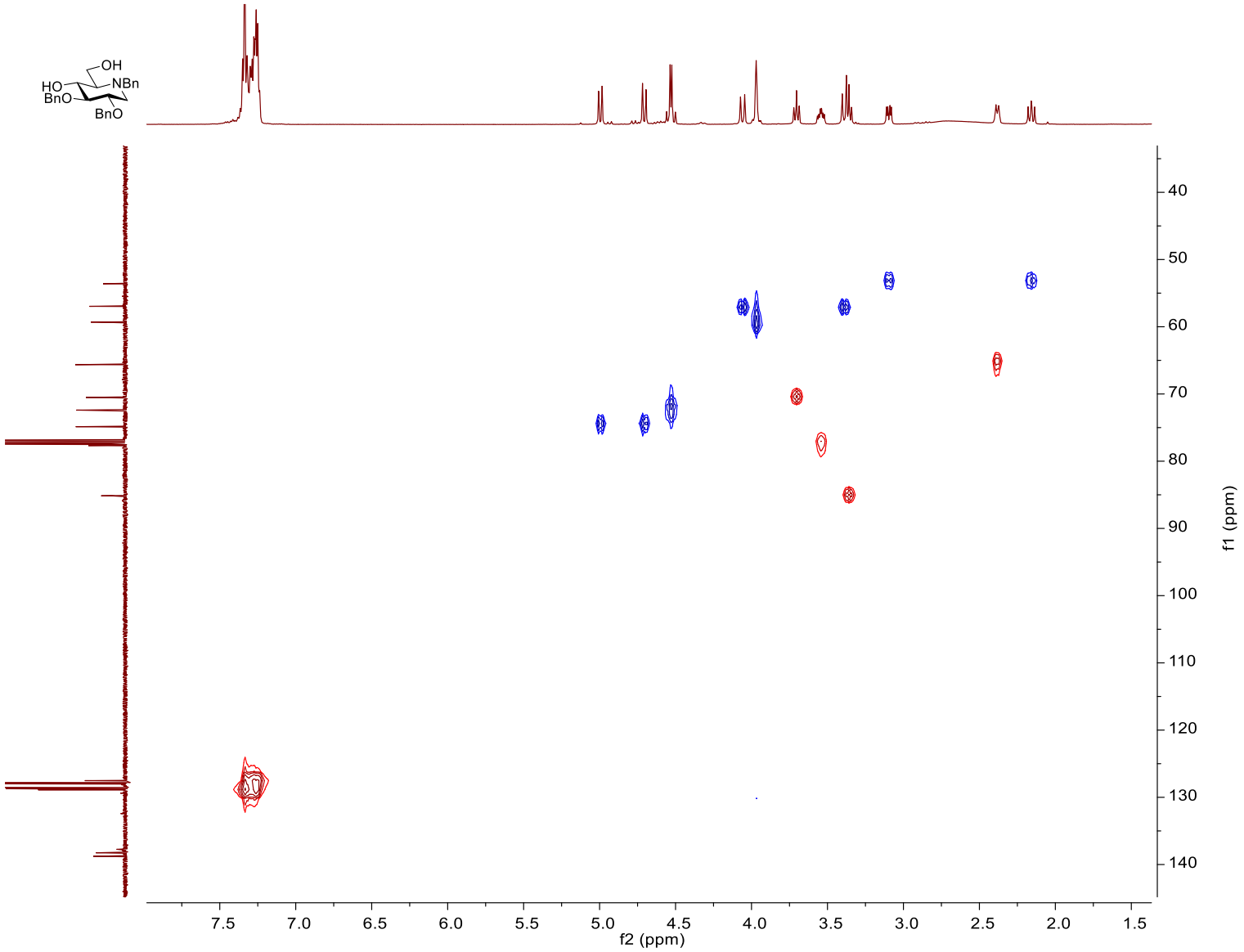
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (23)



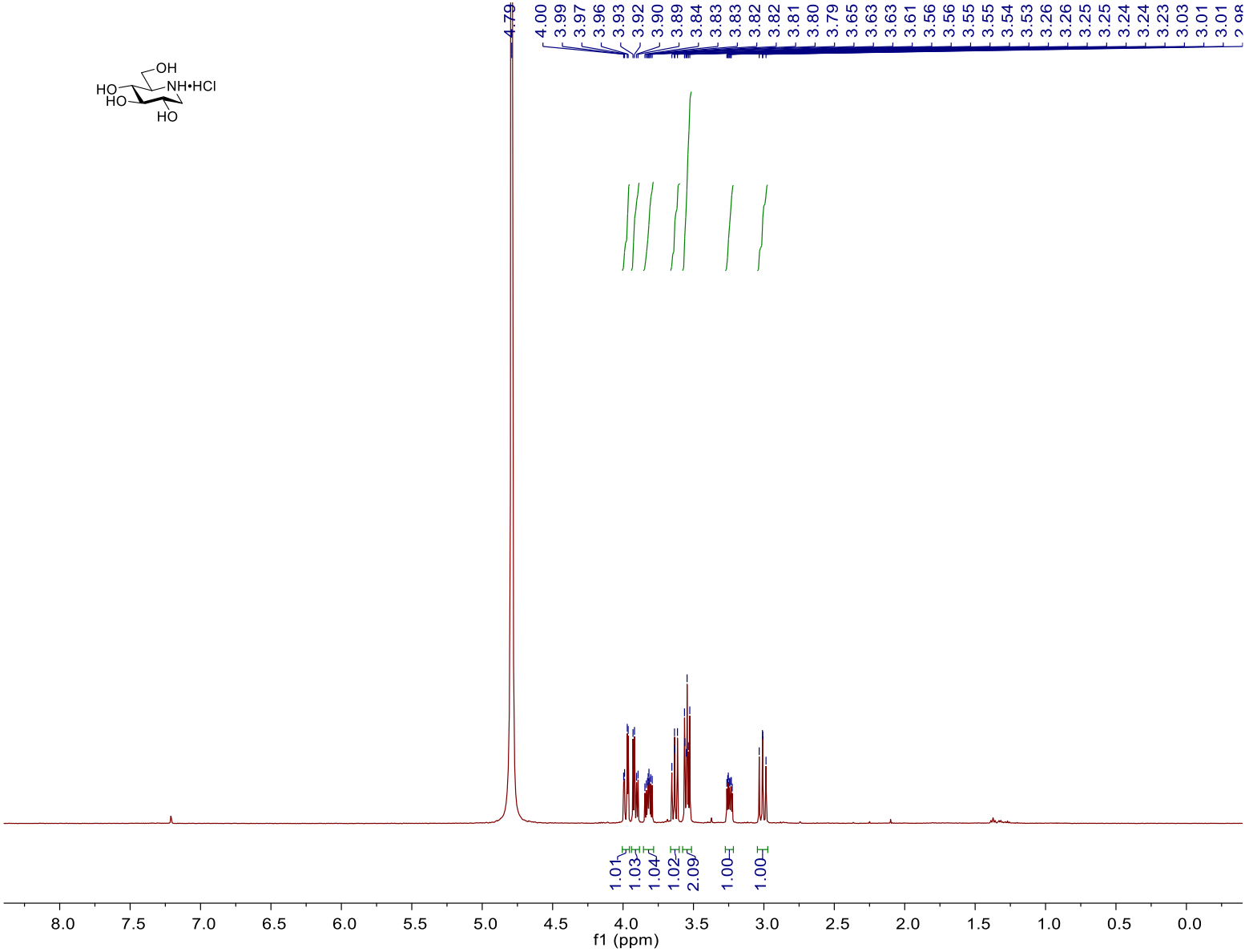
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (23)



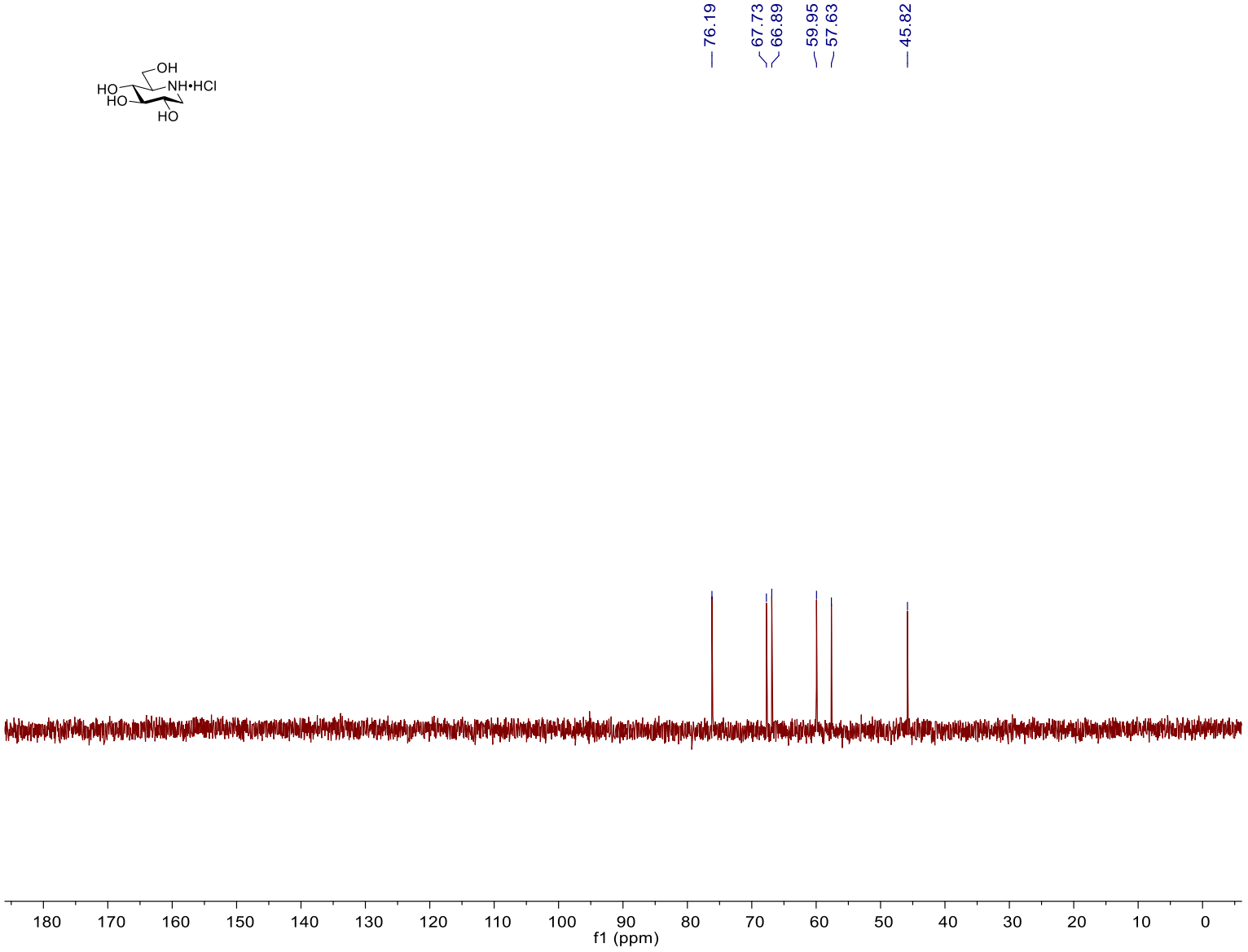
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-glucitol (23)



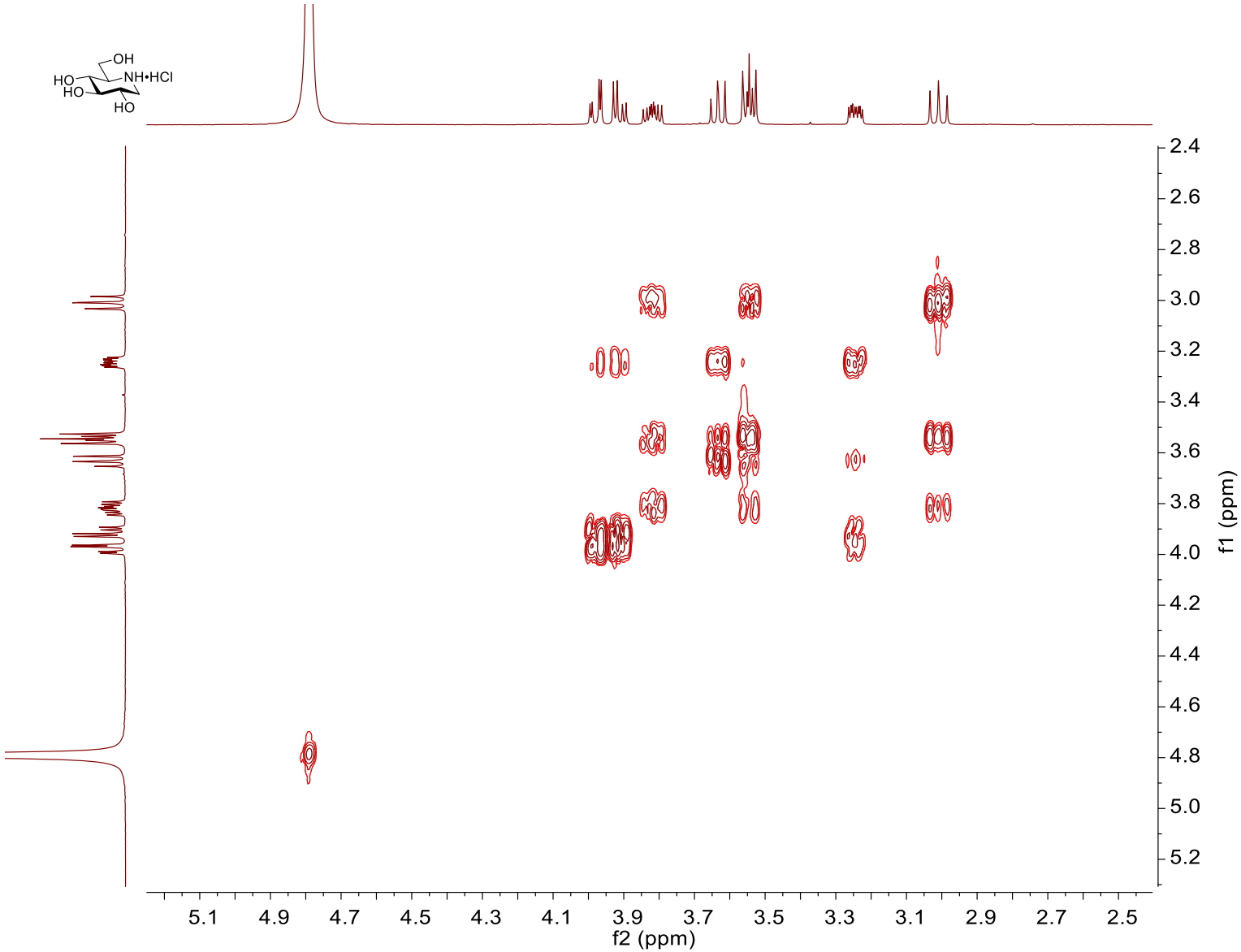
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol Hydrochloride (2)



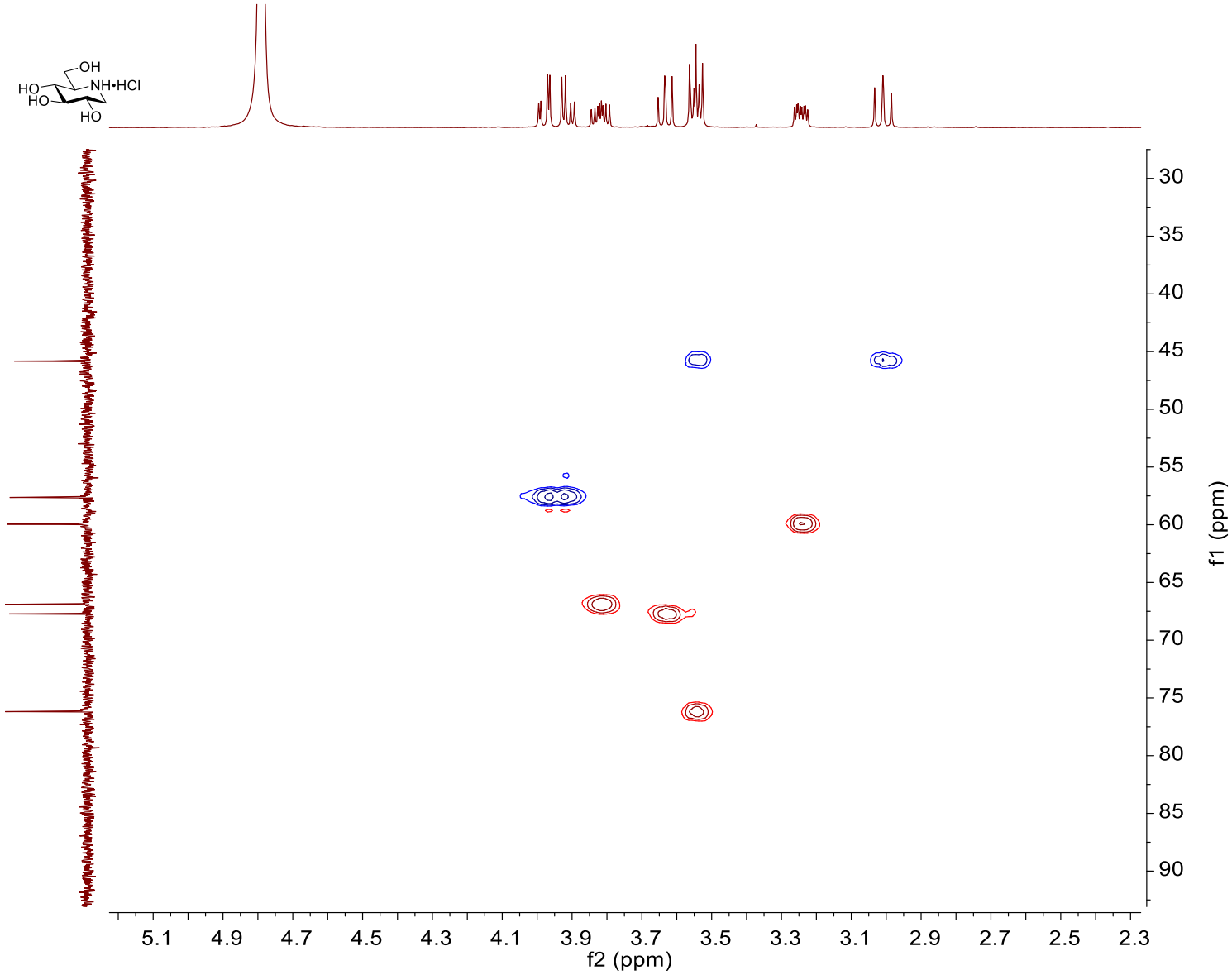
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol Hydrochloride (2)



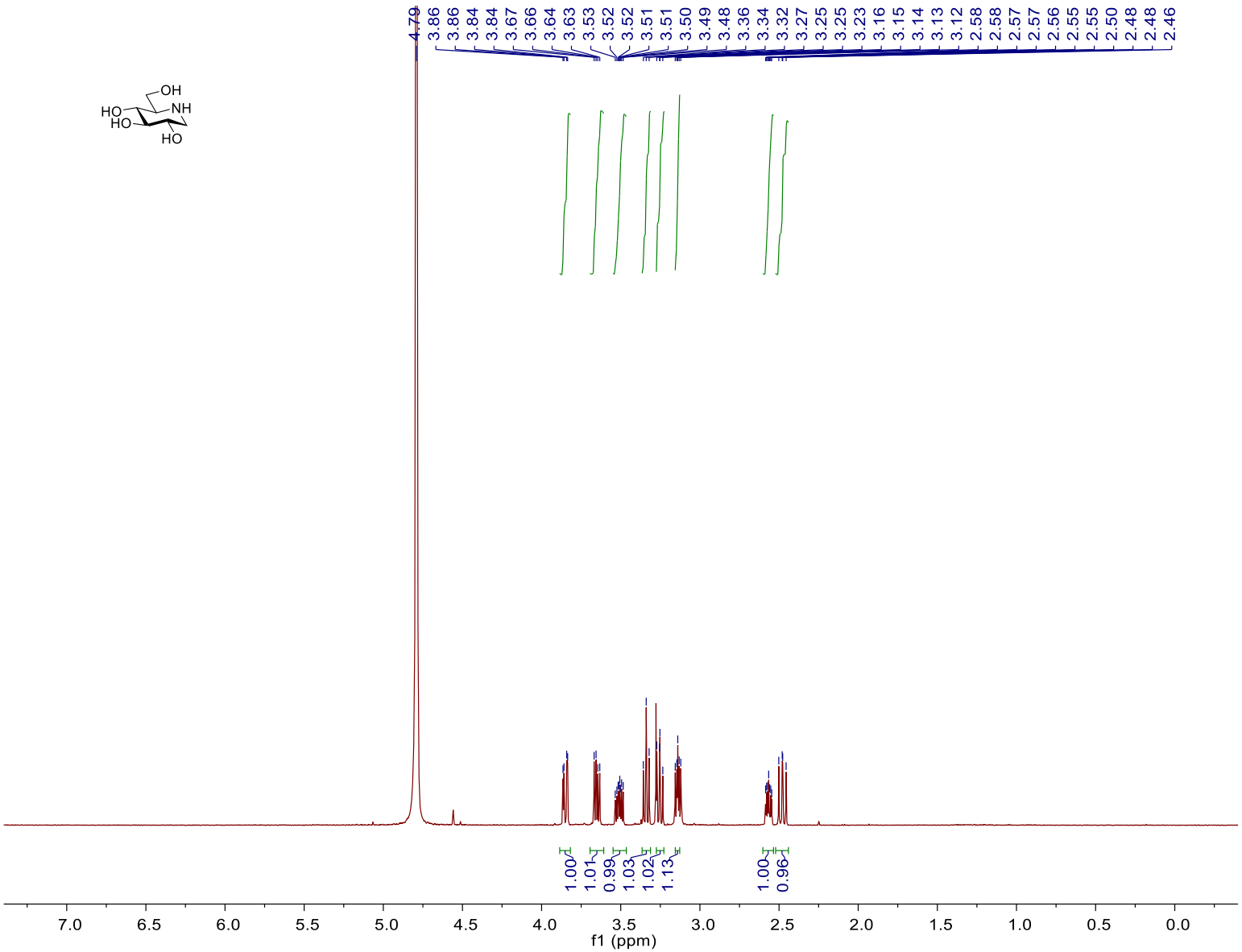
COSY NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol Hydrochloride (2)



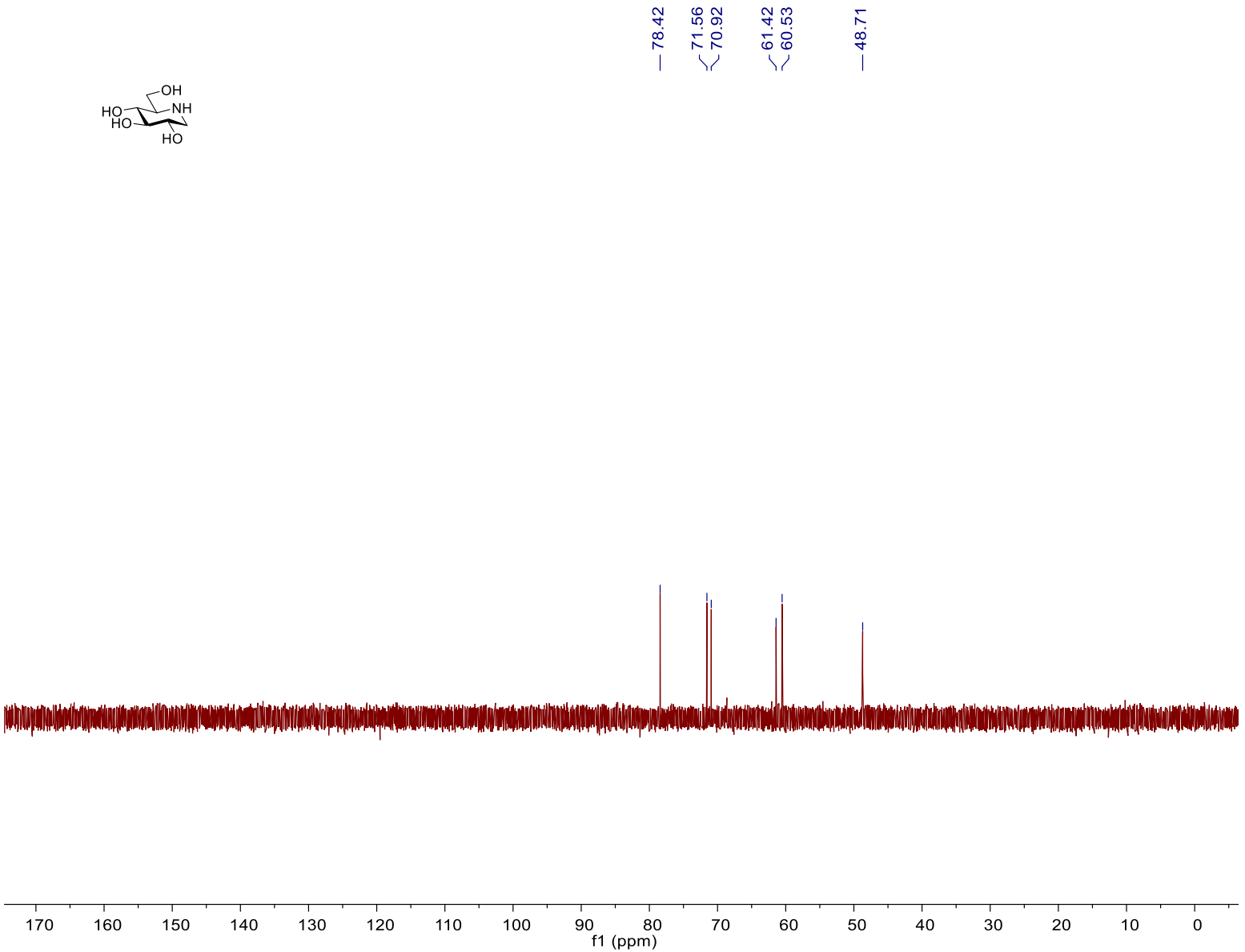
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol Hydrochloride (2)



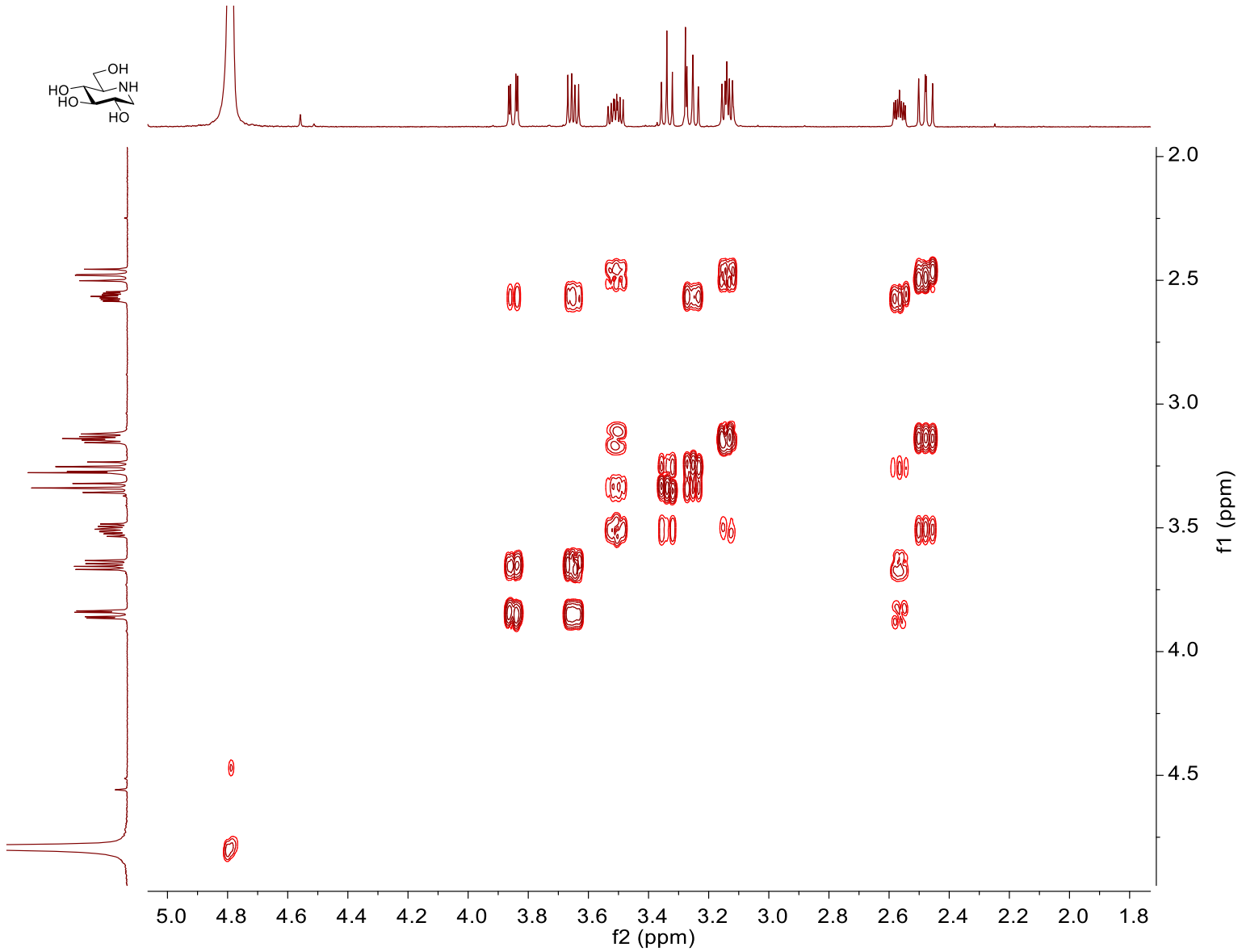
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol (2)



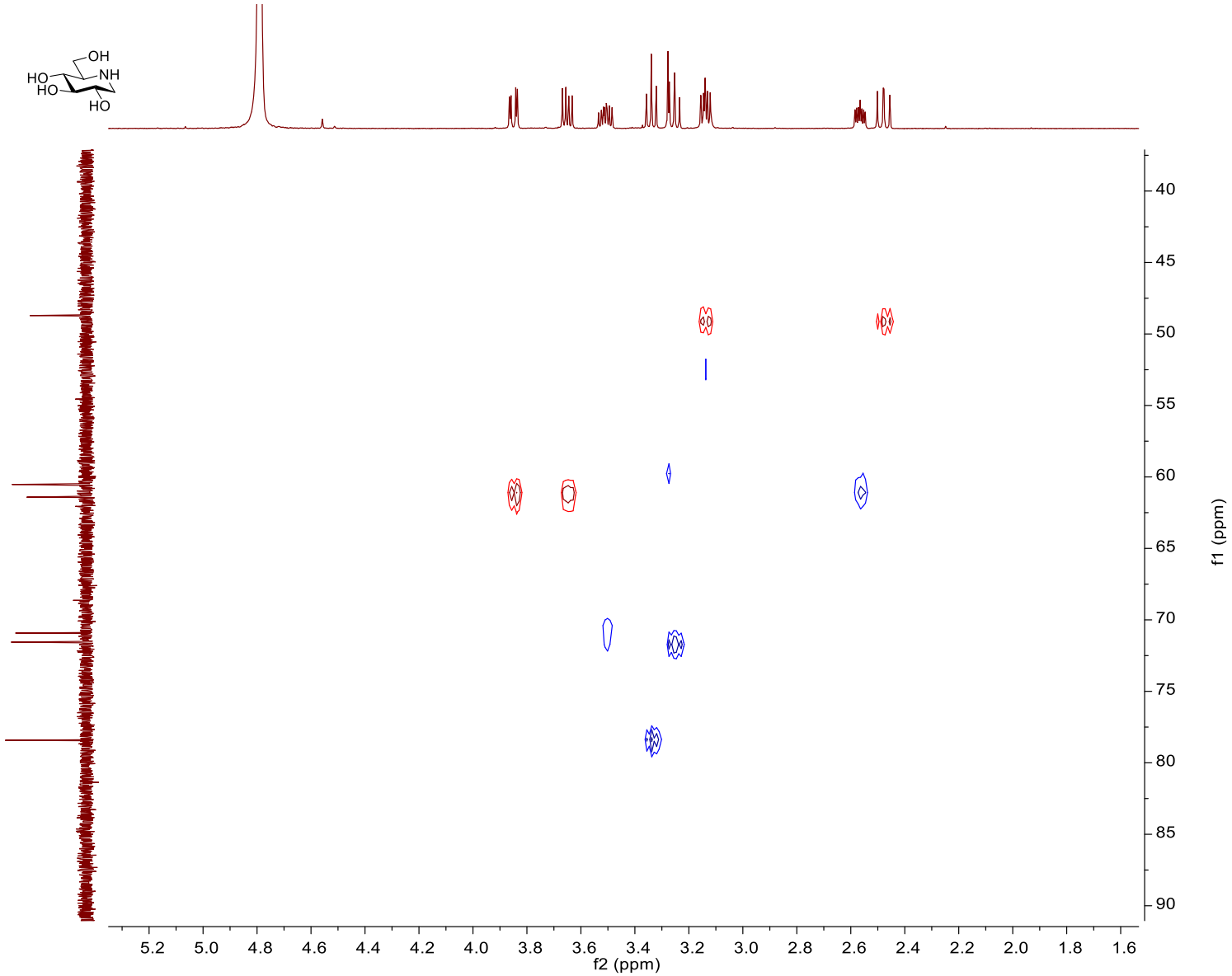
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol (2)



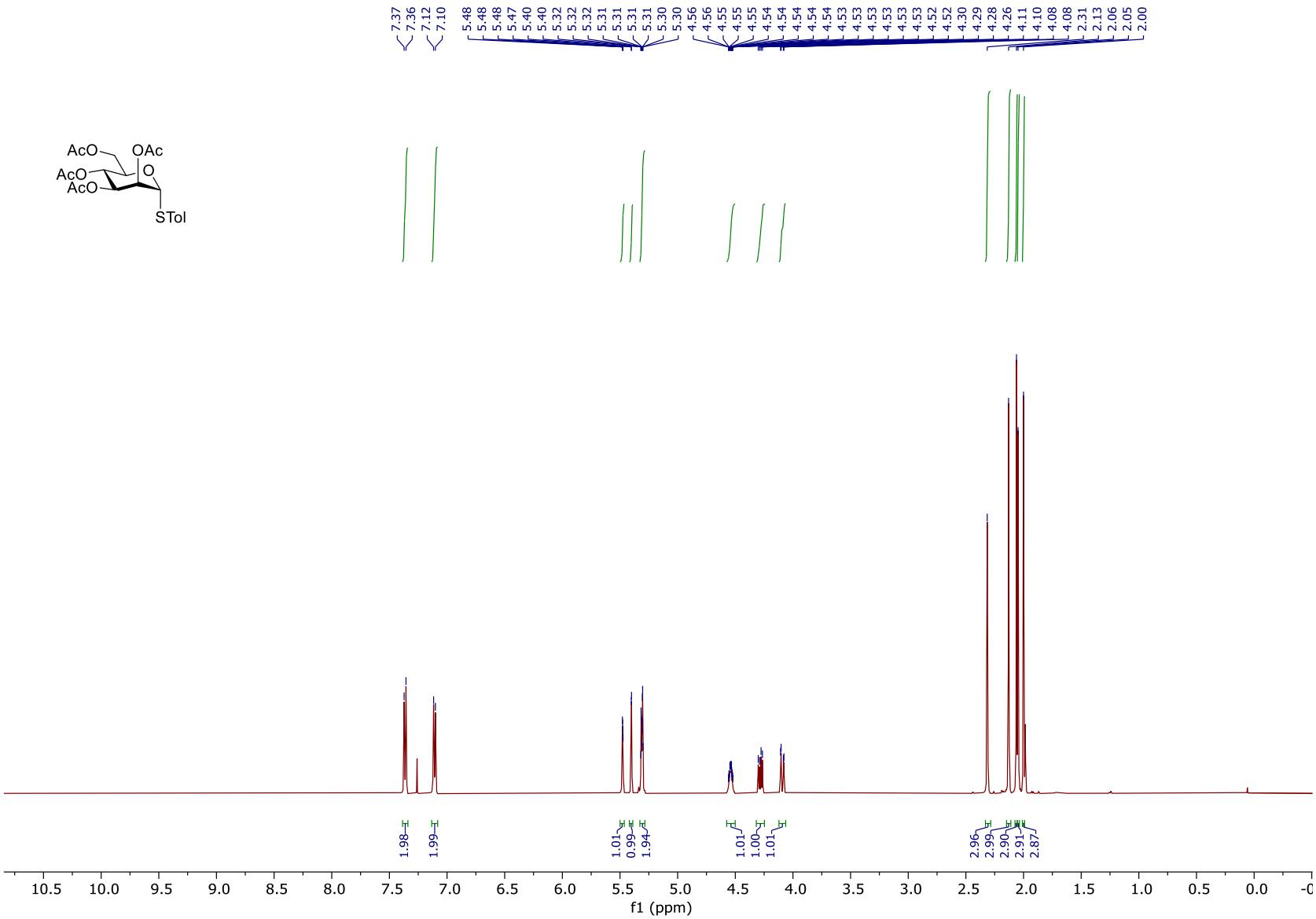
COSY NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol (2)



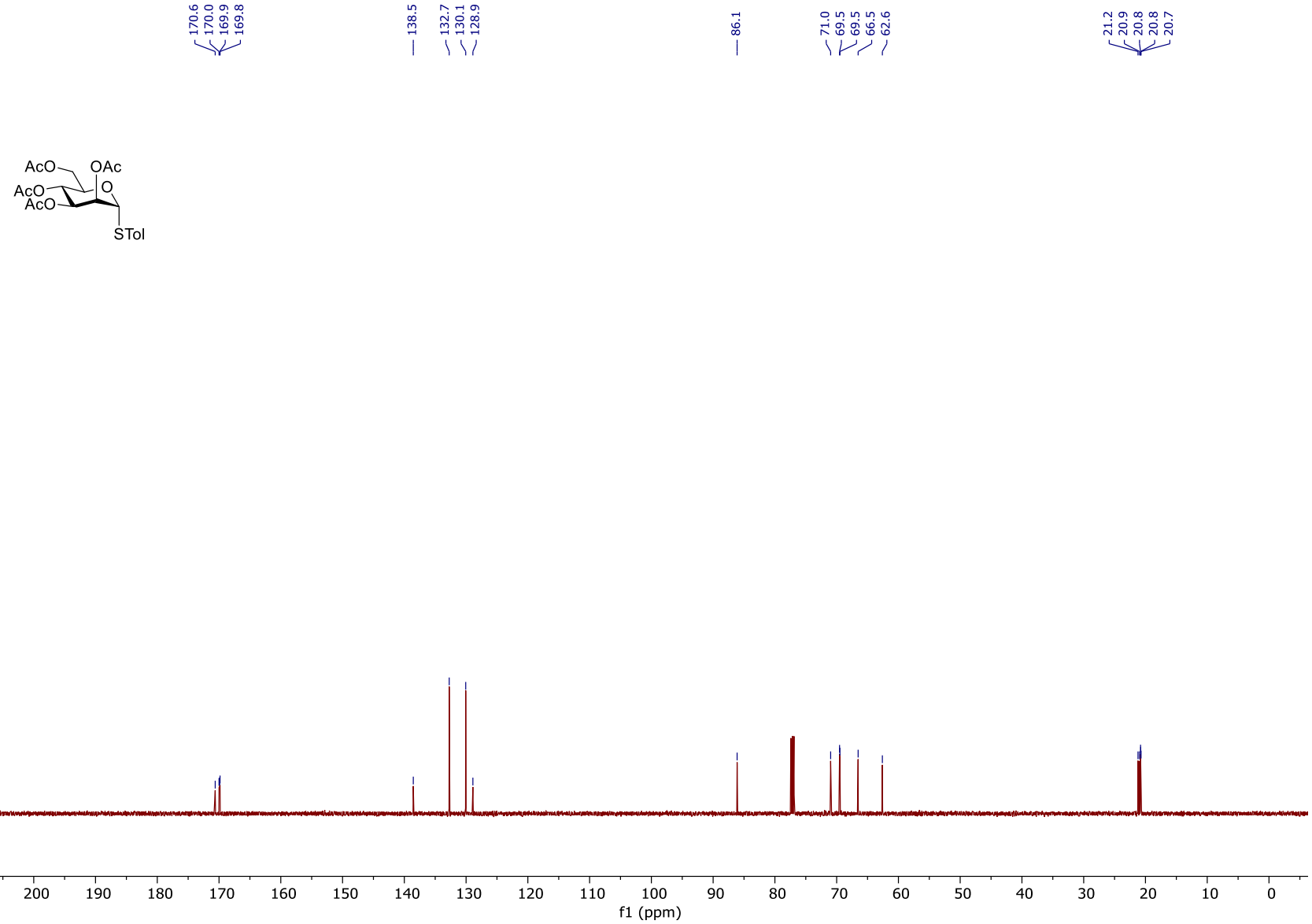
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-glucitol (2)



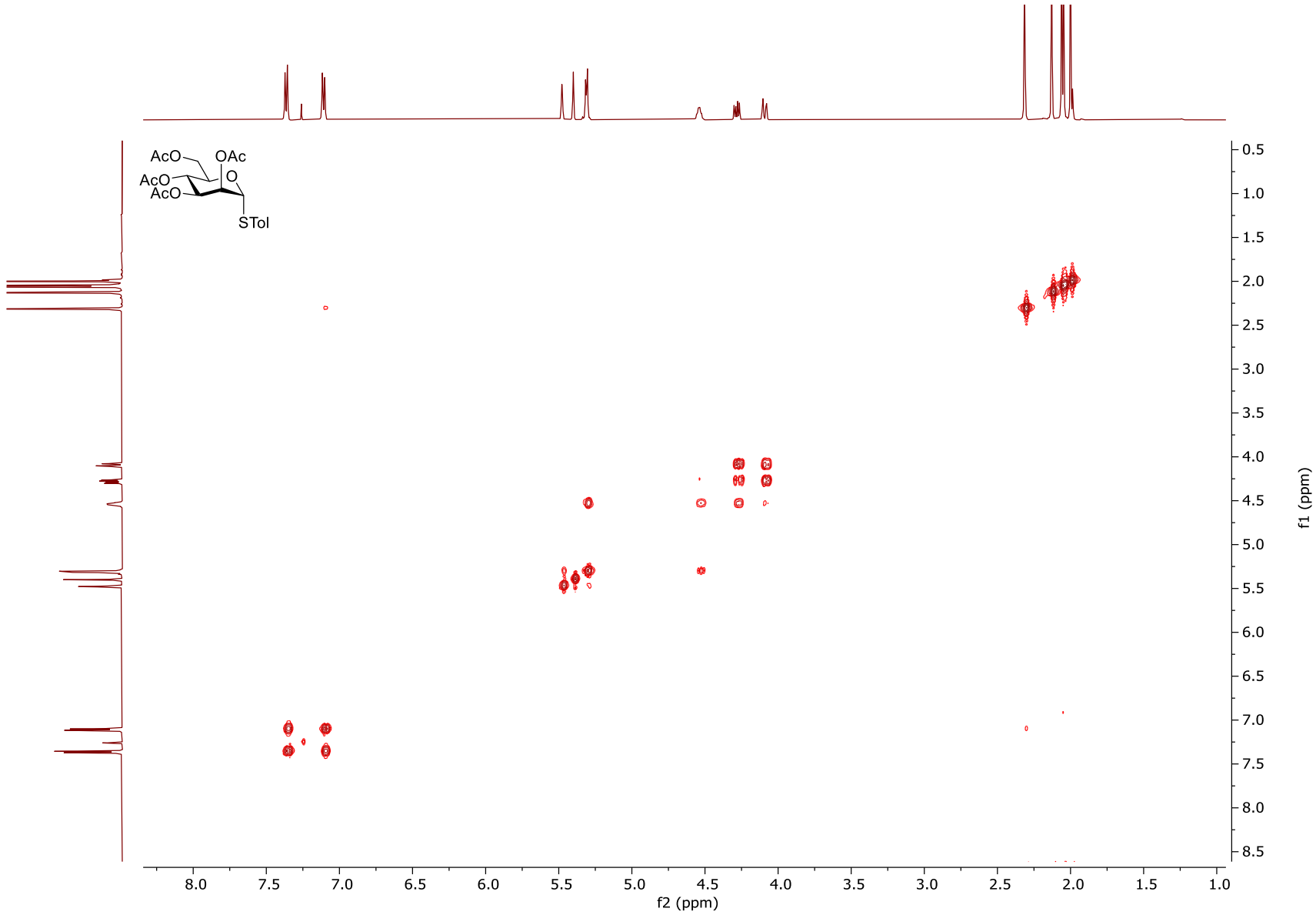
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (S5)



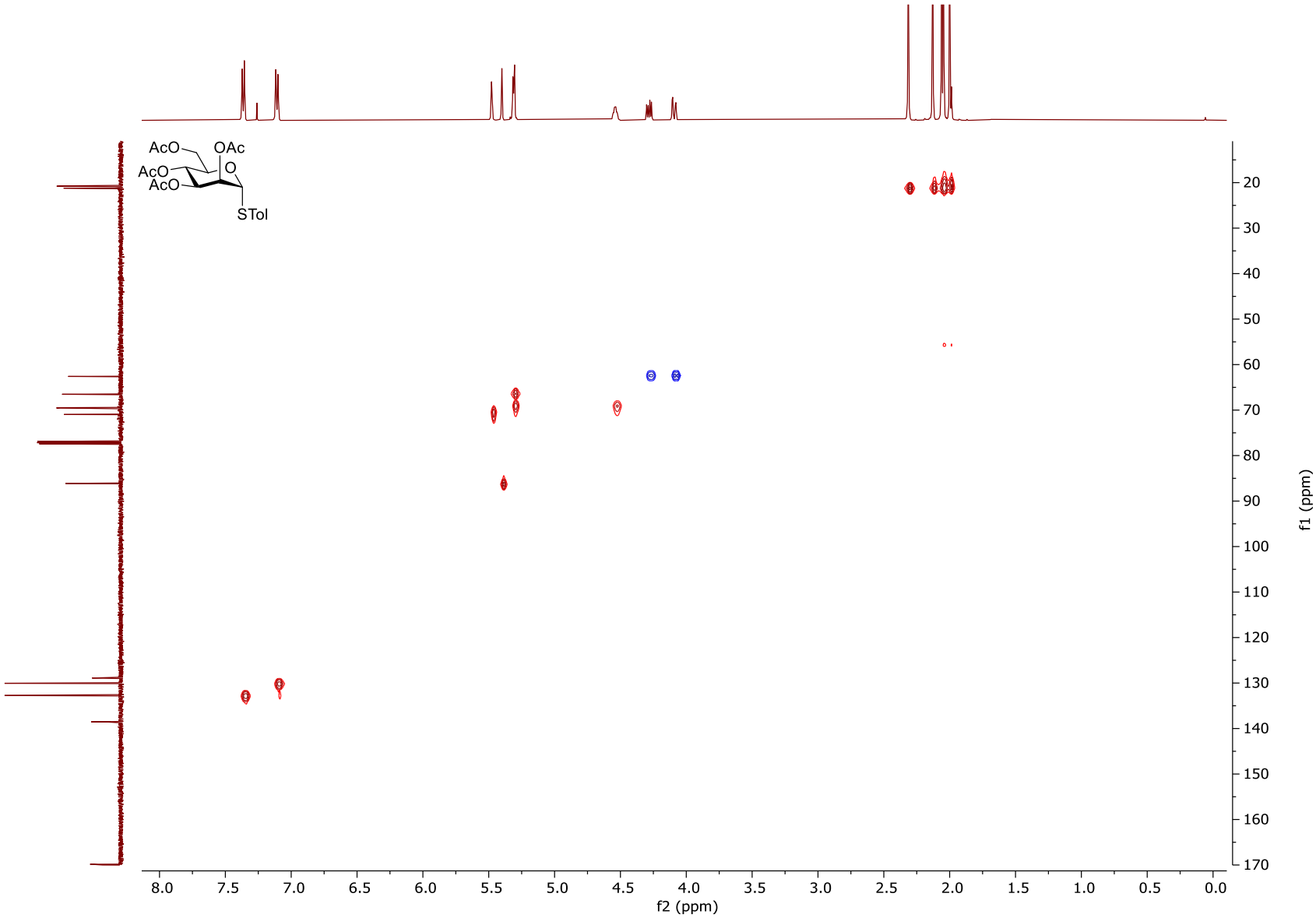
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (S5)



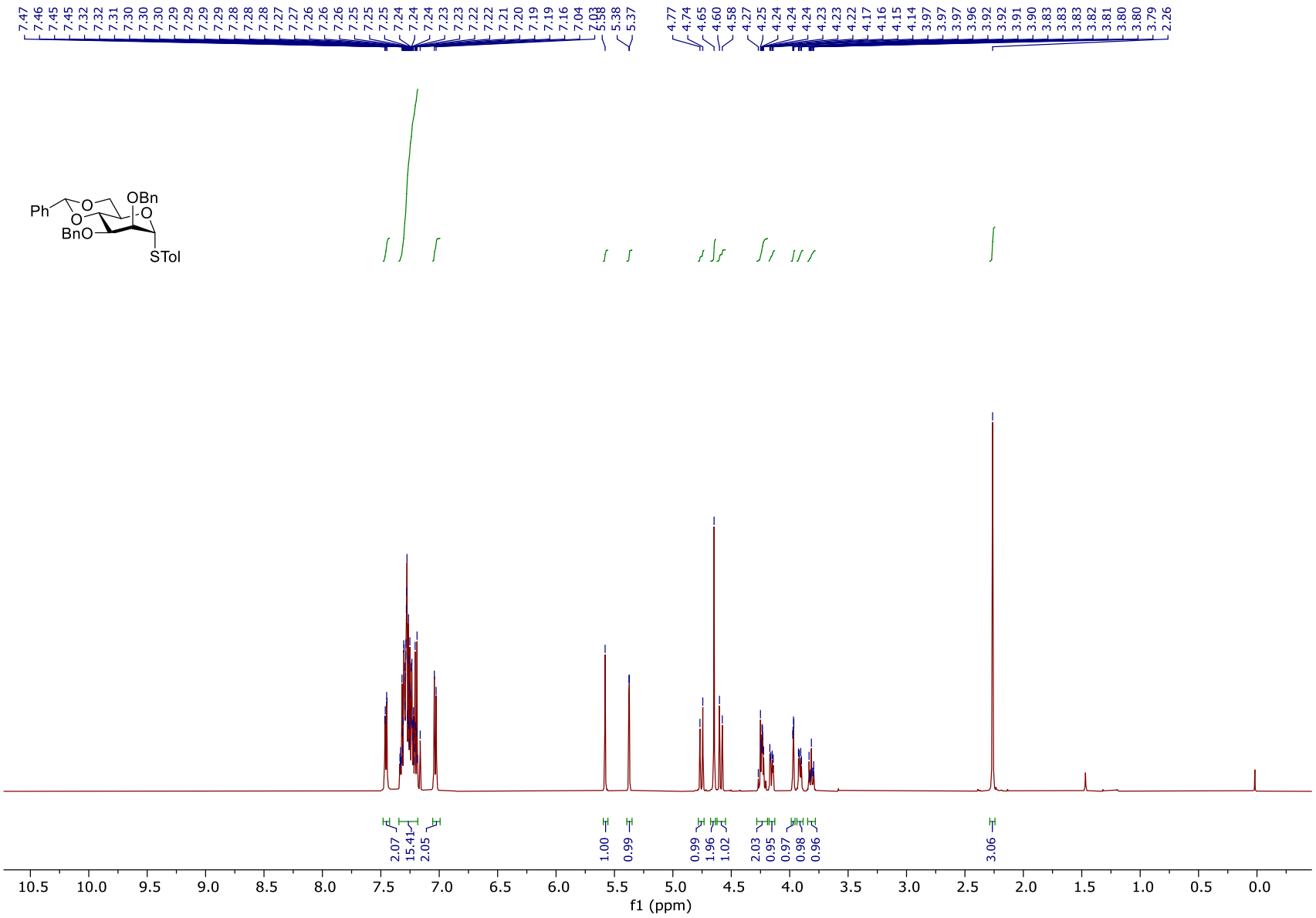
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (S5)



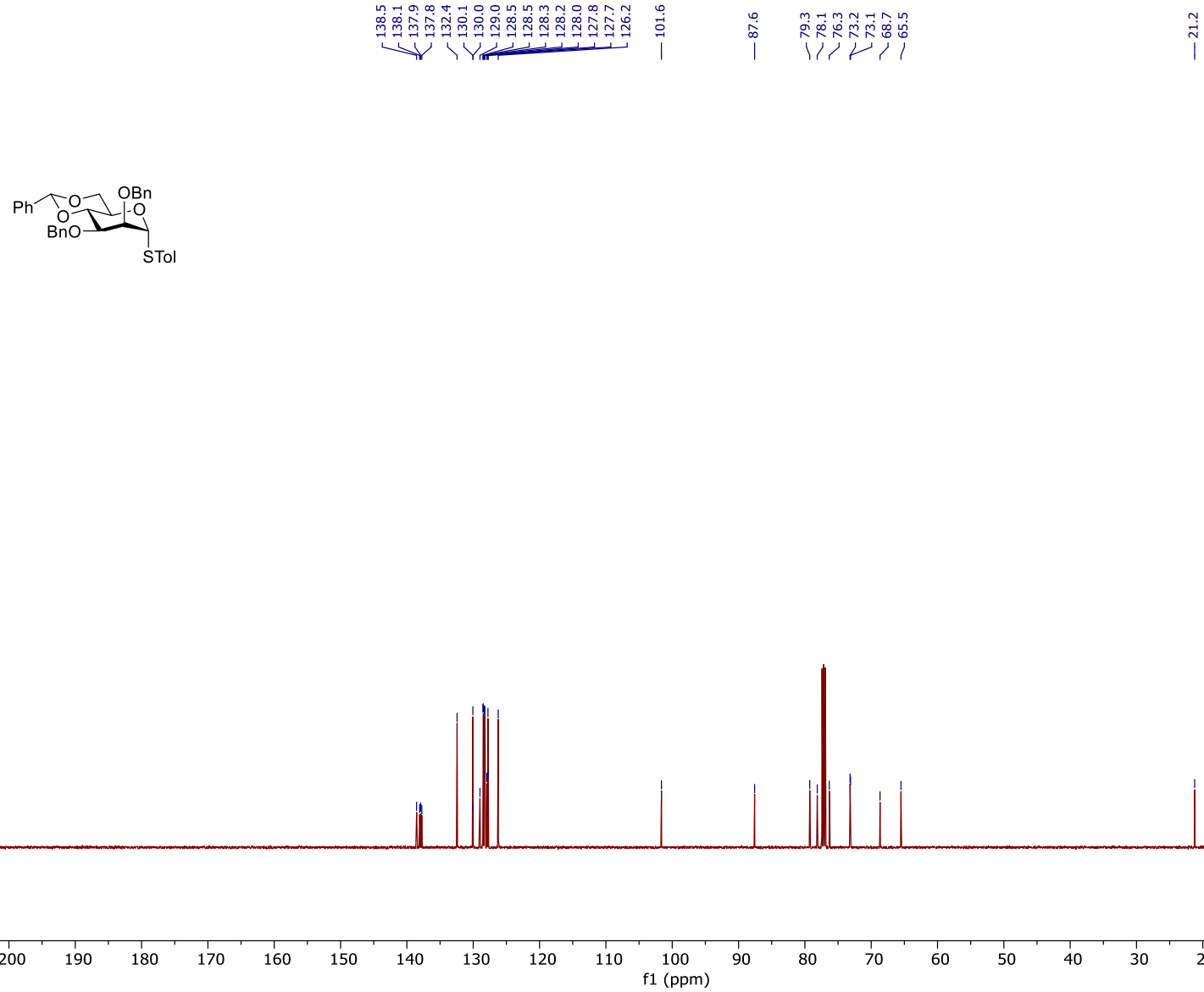
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3,4,6-Tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (S5)



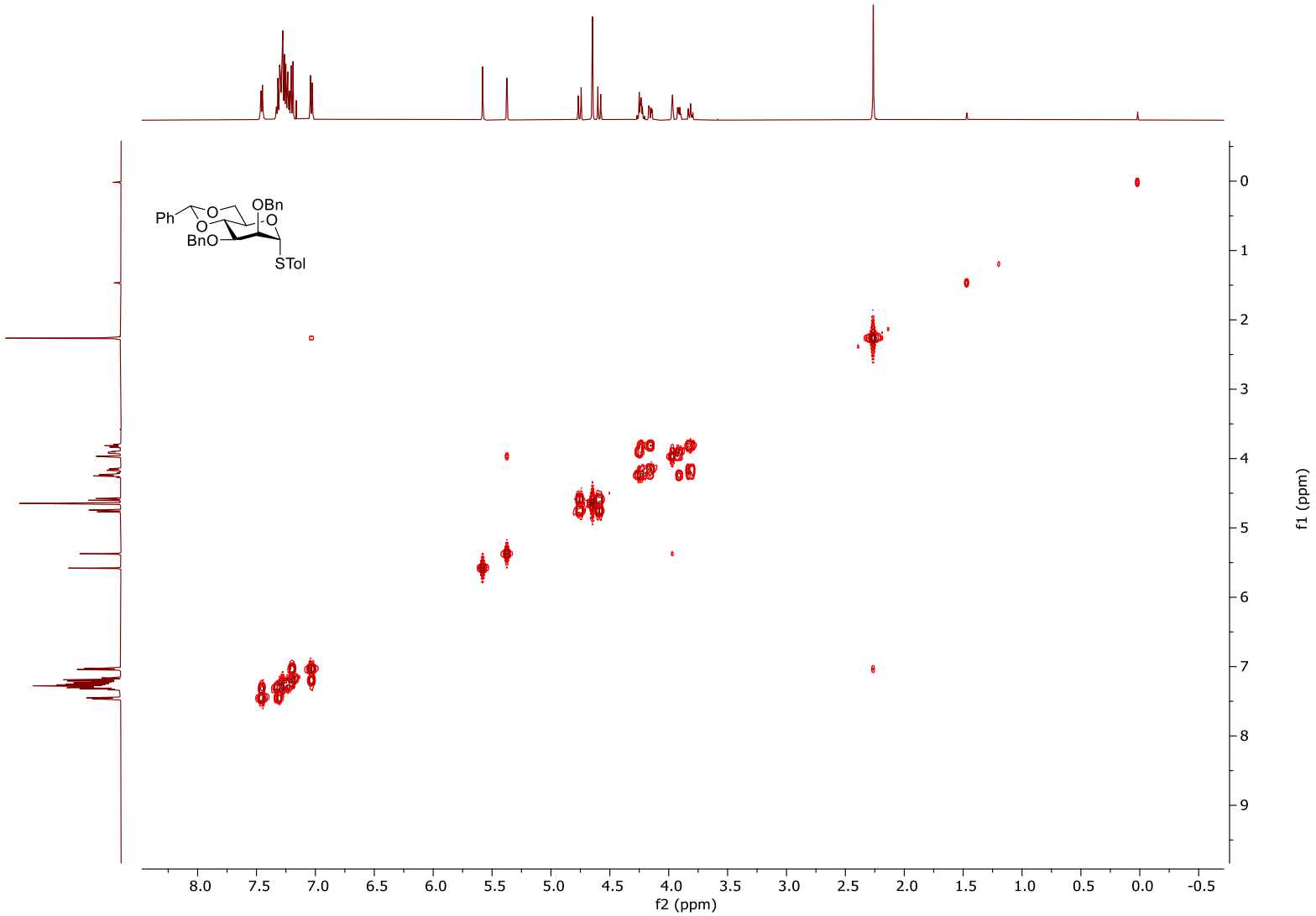
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (S6)



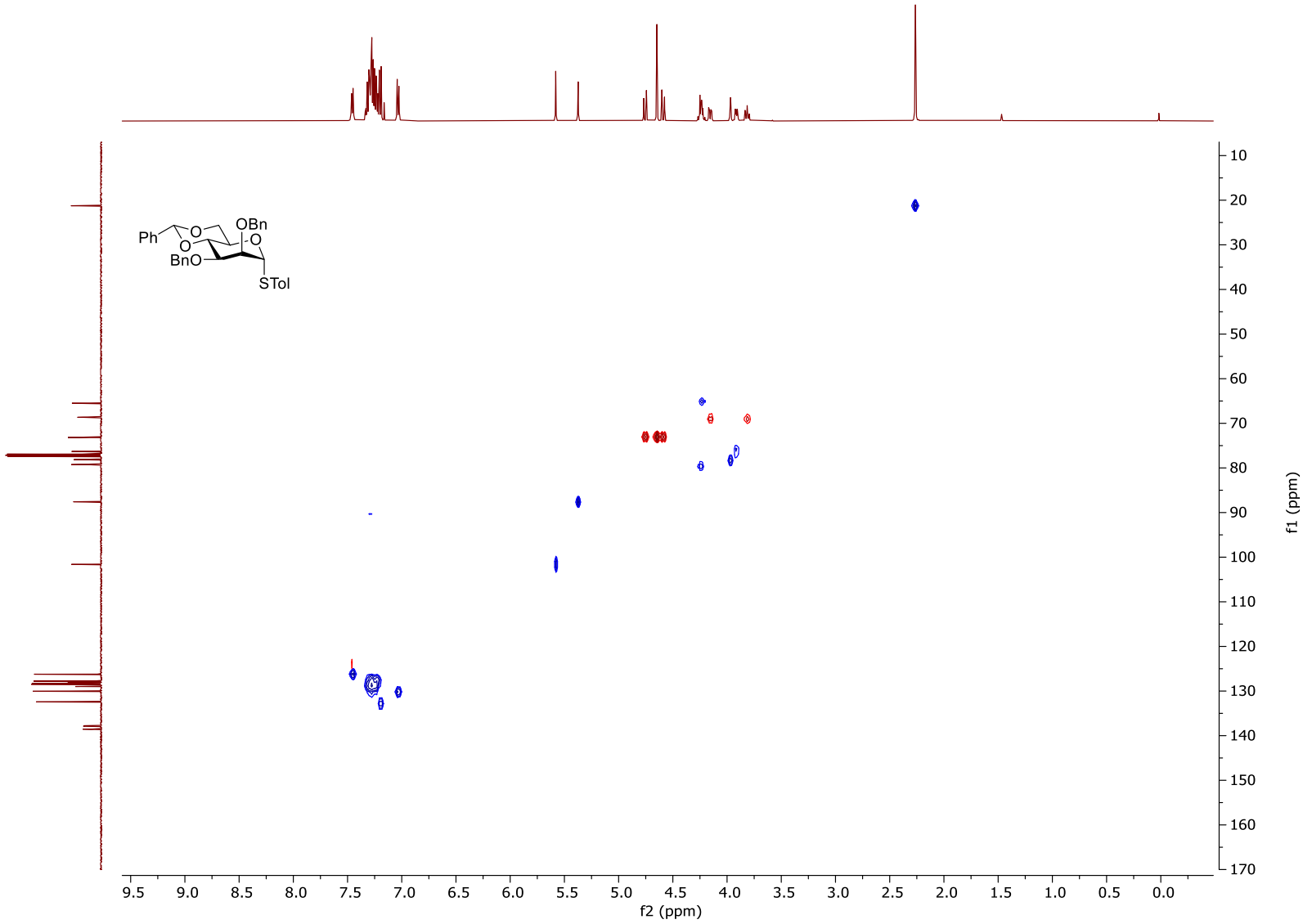
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (S6)



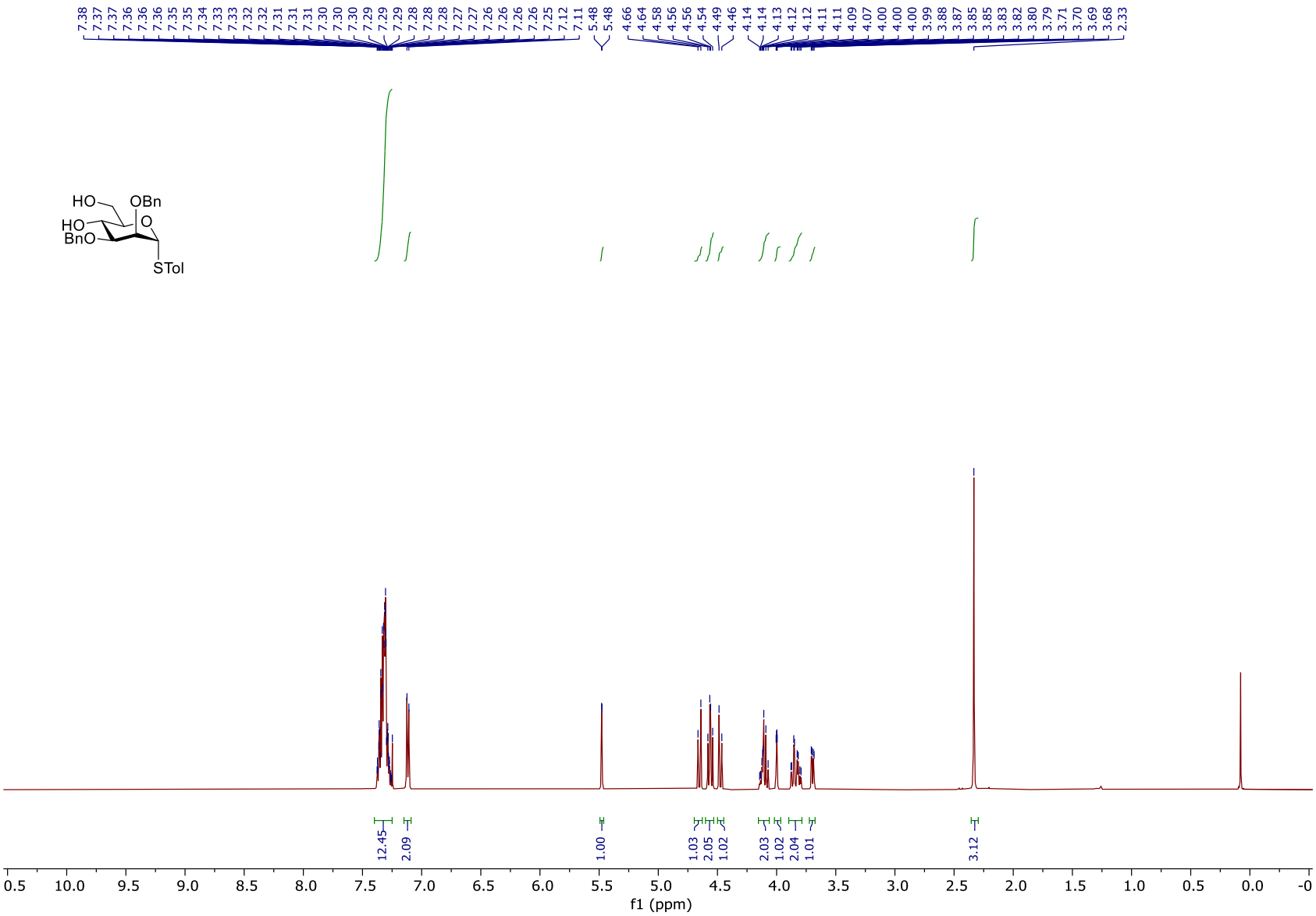
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (S6)



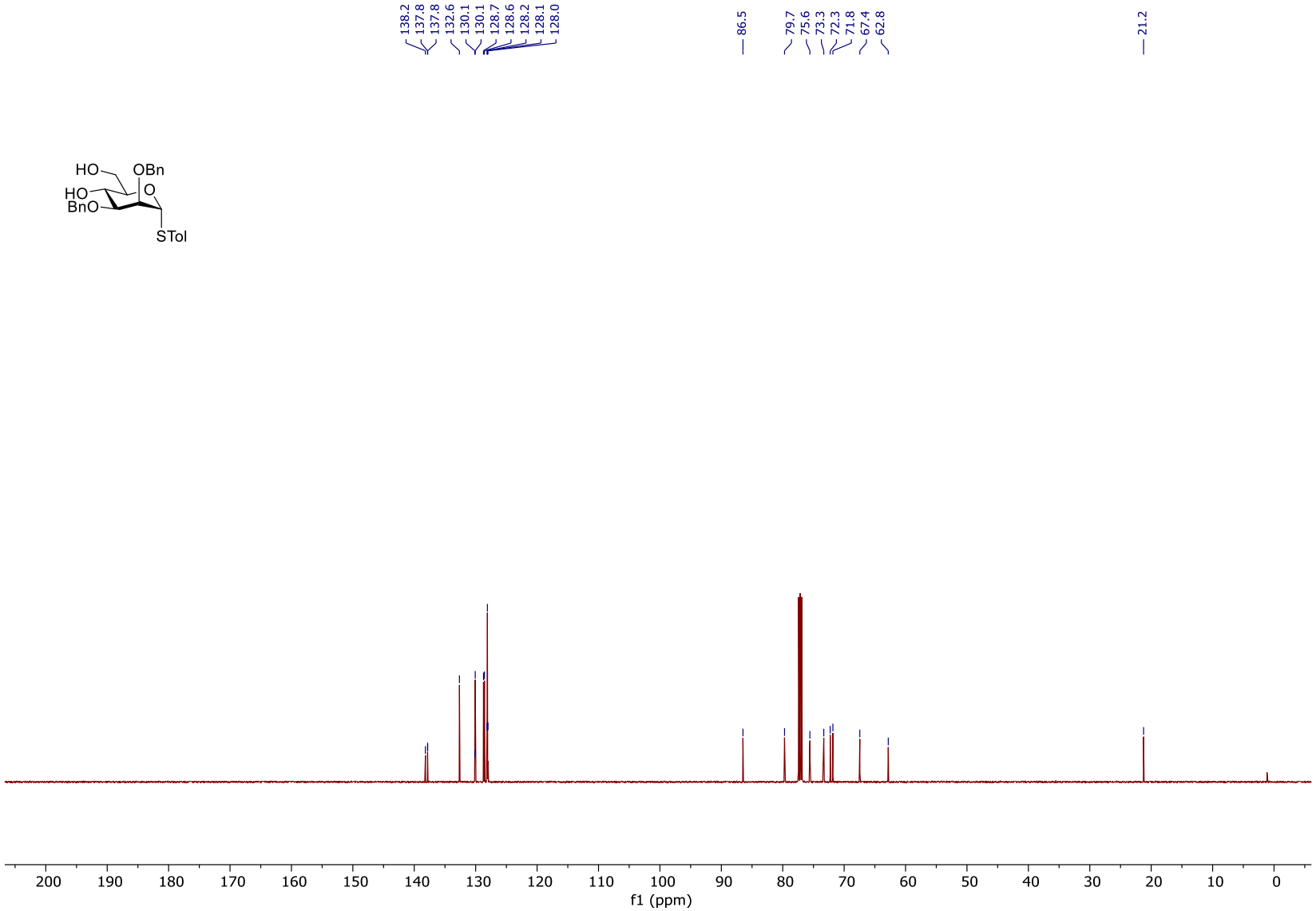
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (S6)



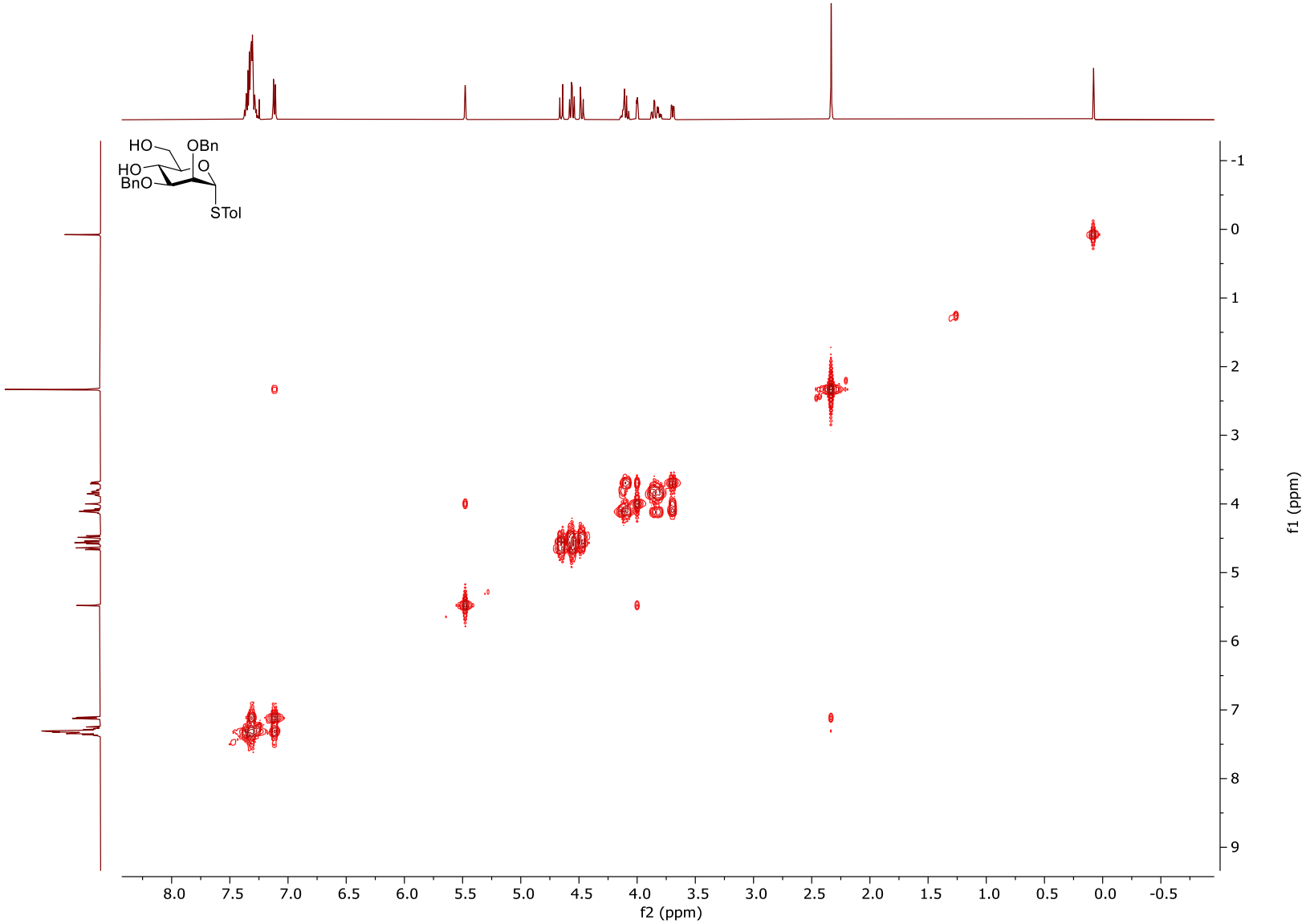
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-α-D-mannopyranoside (24)



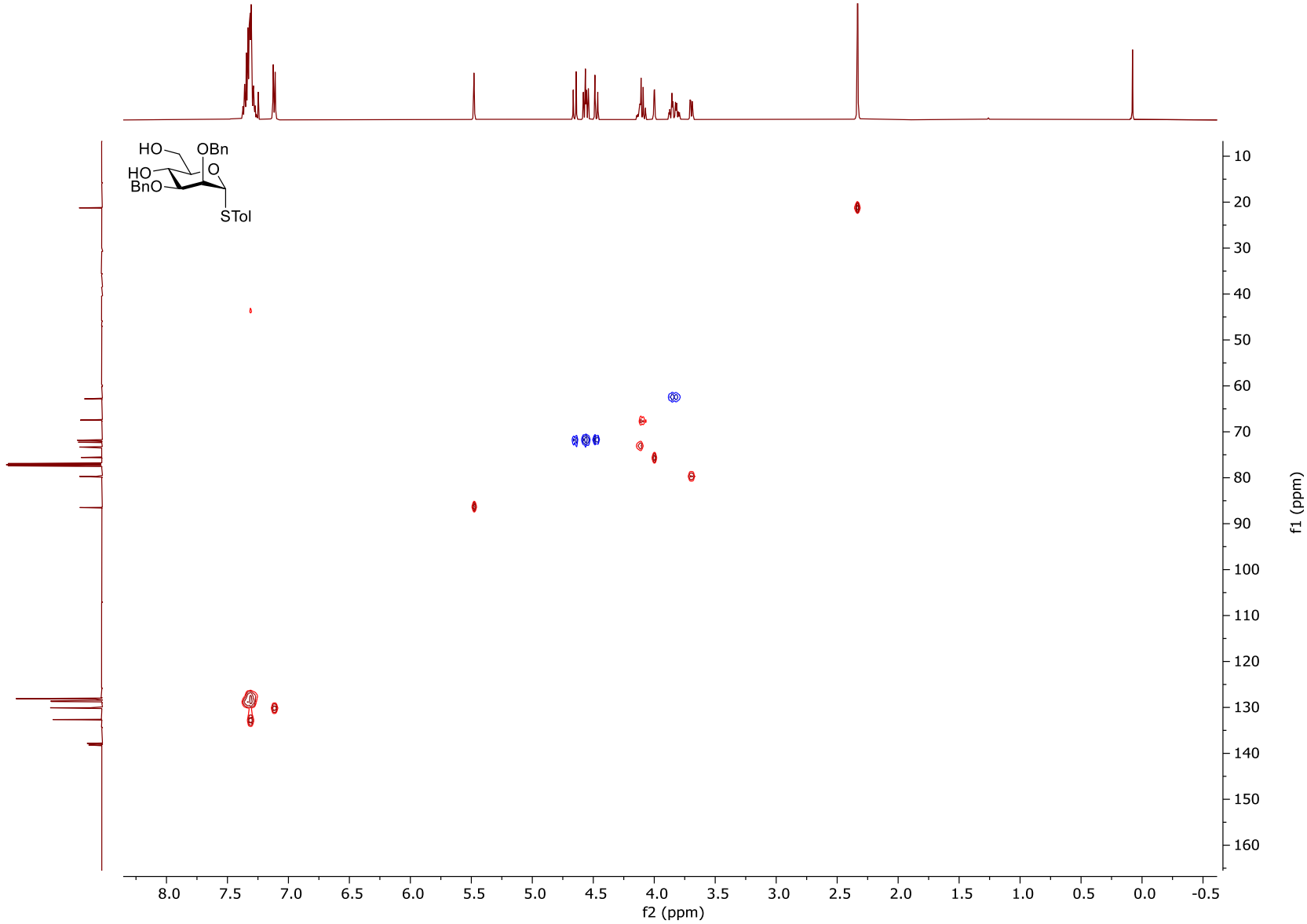
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-α-D-mannopyranoside (24)



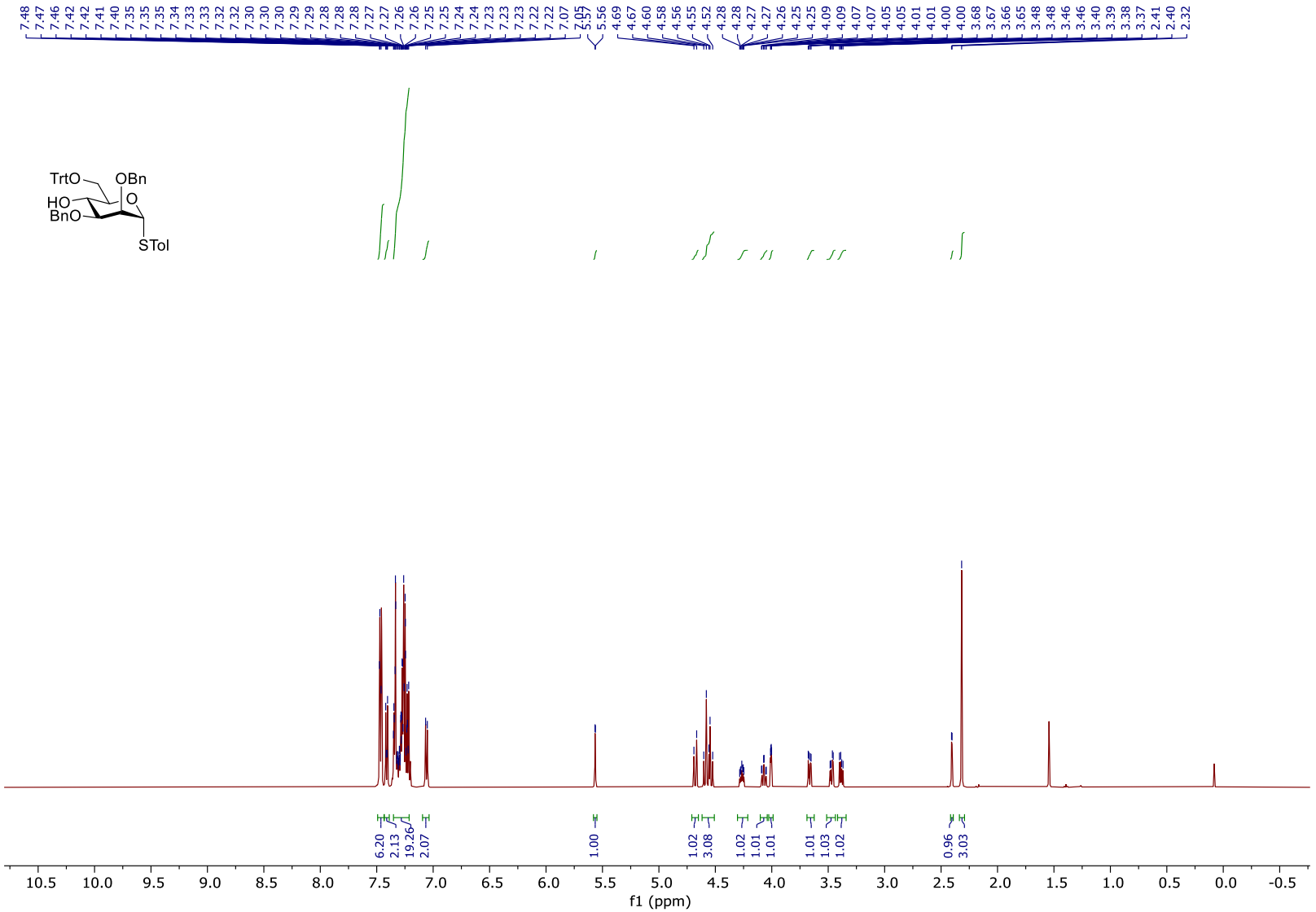
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-α-D-mannopyranoside (24)



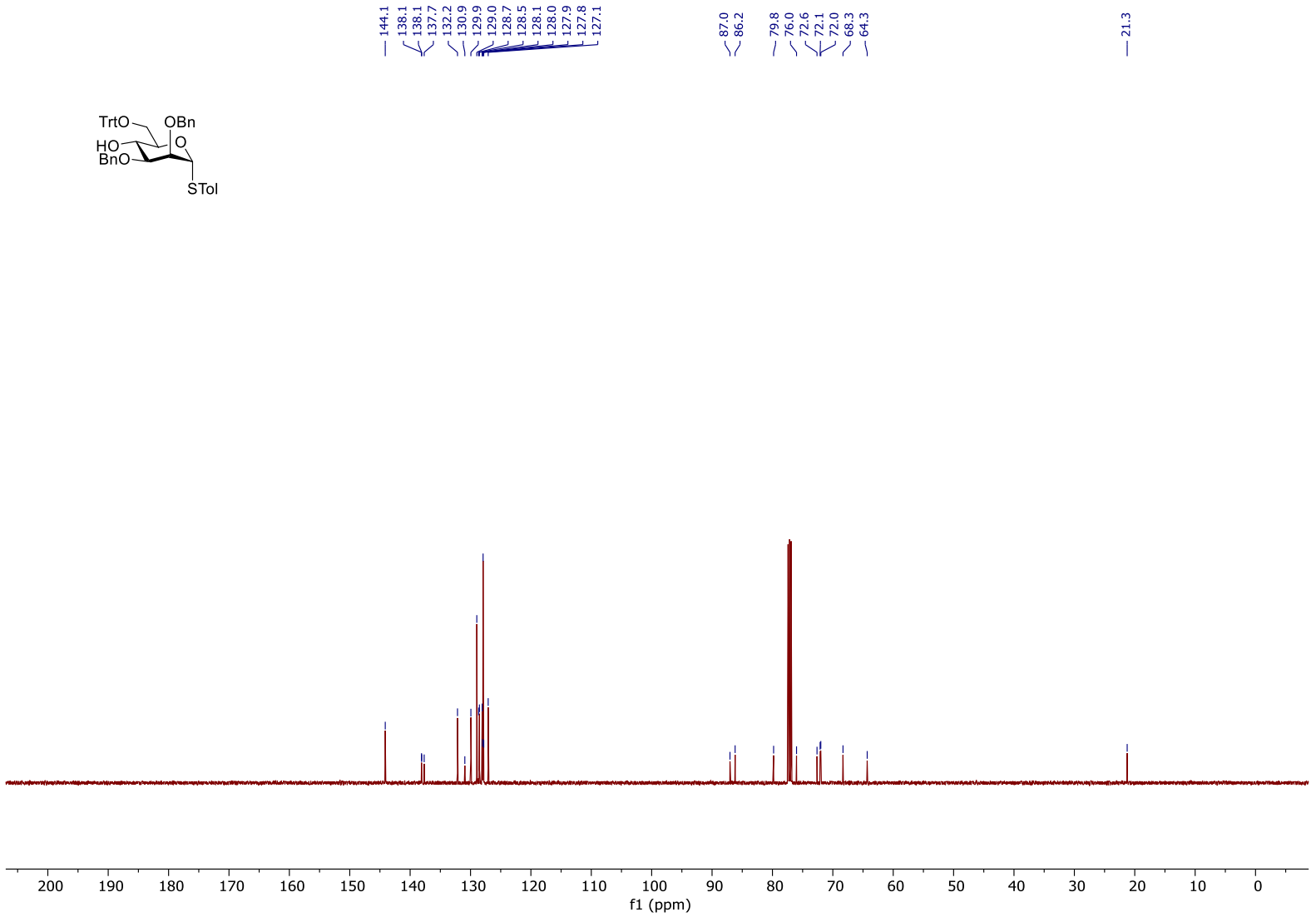
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-1-thio-α-D-mannopyranoside (24)



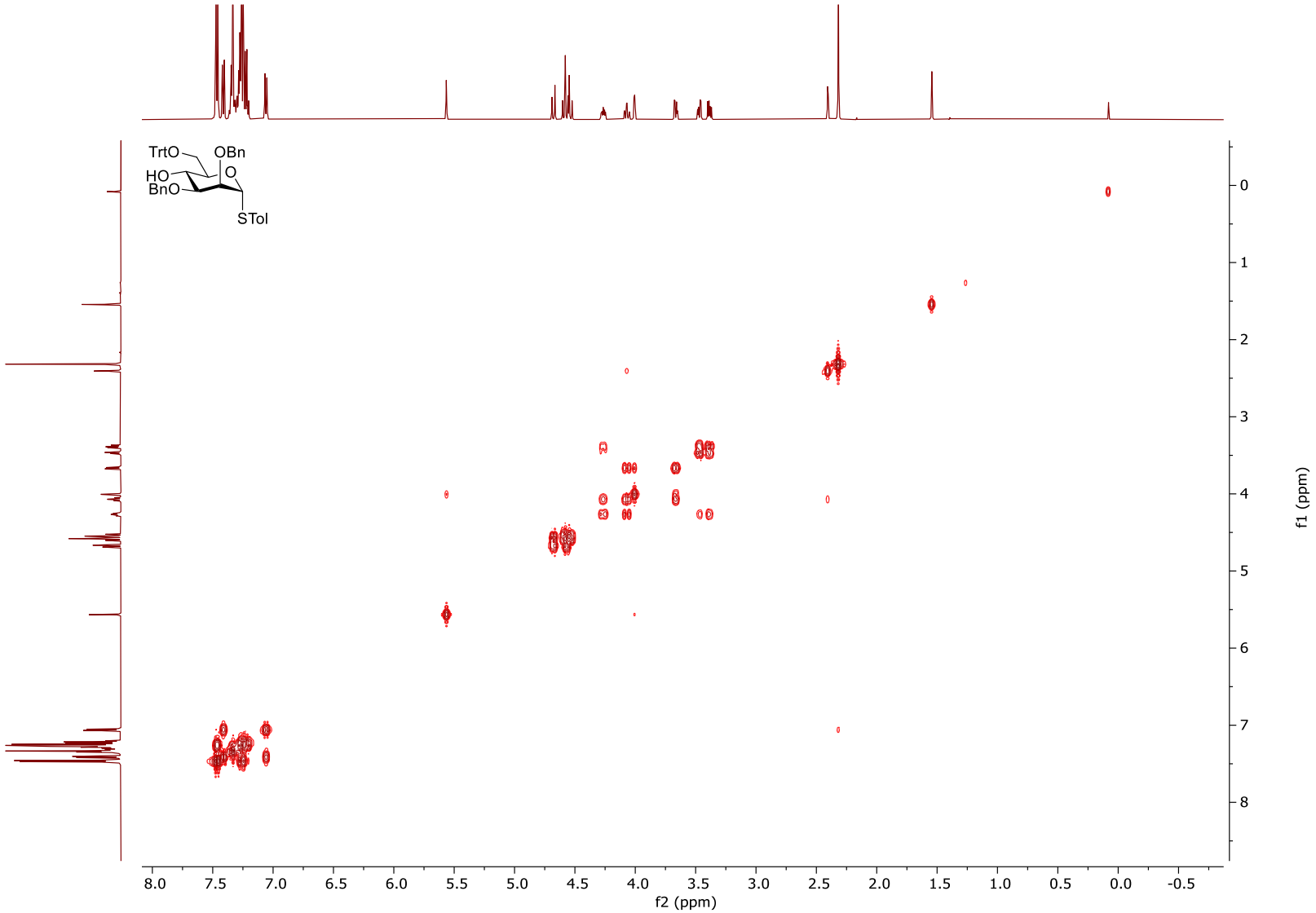
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (25)



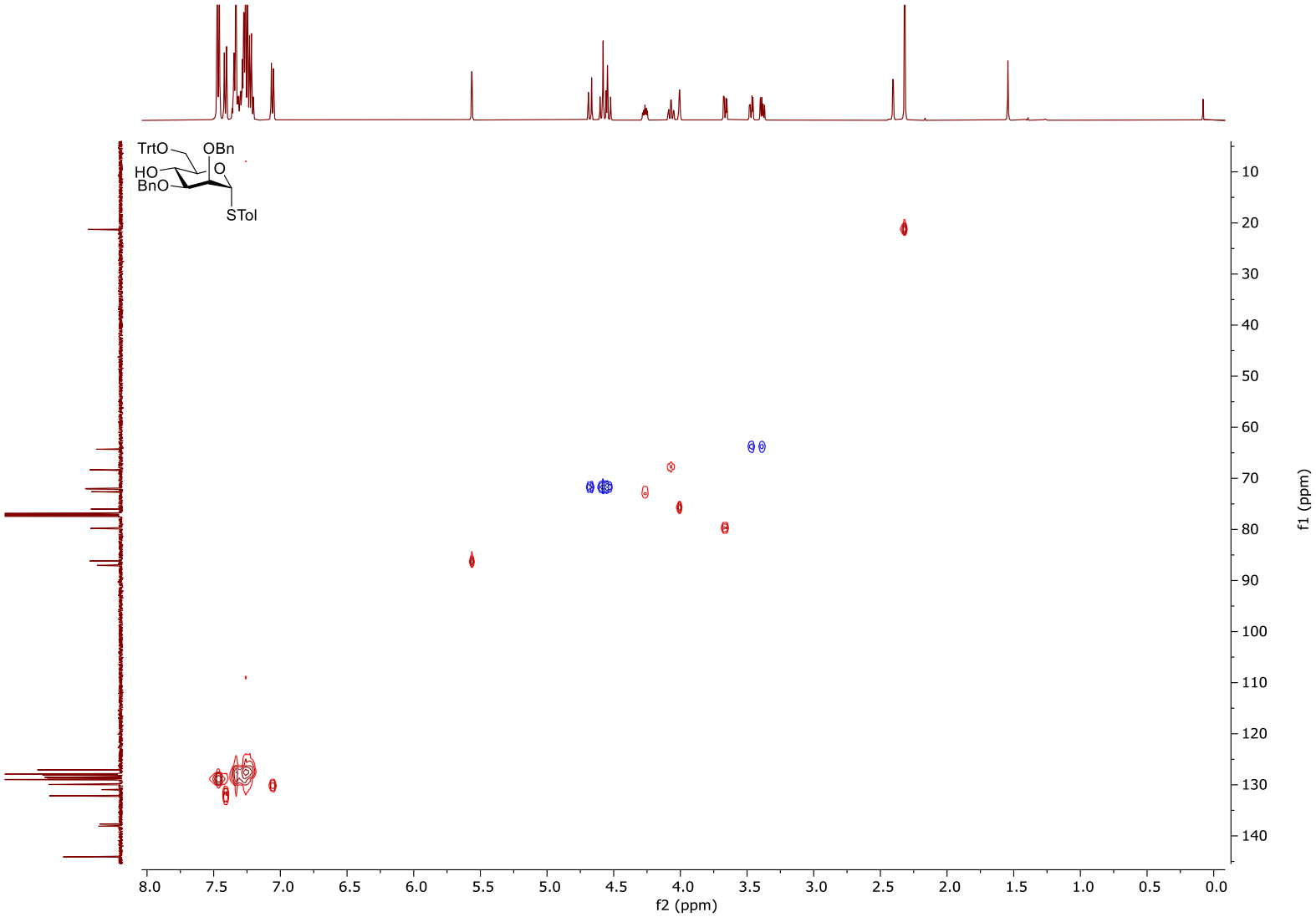
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (25)



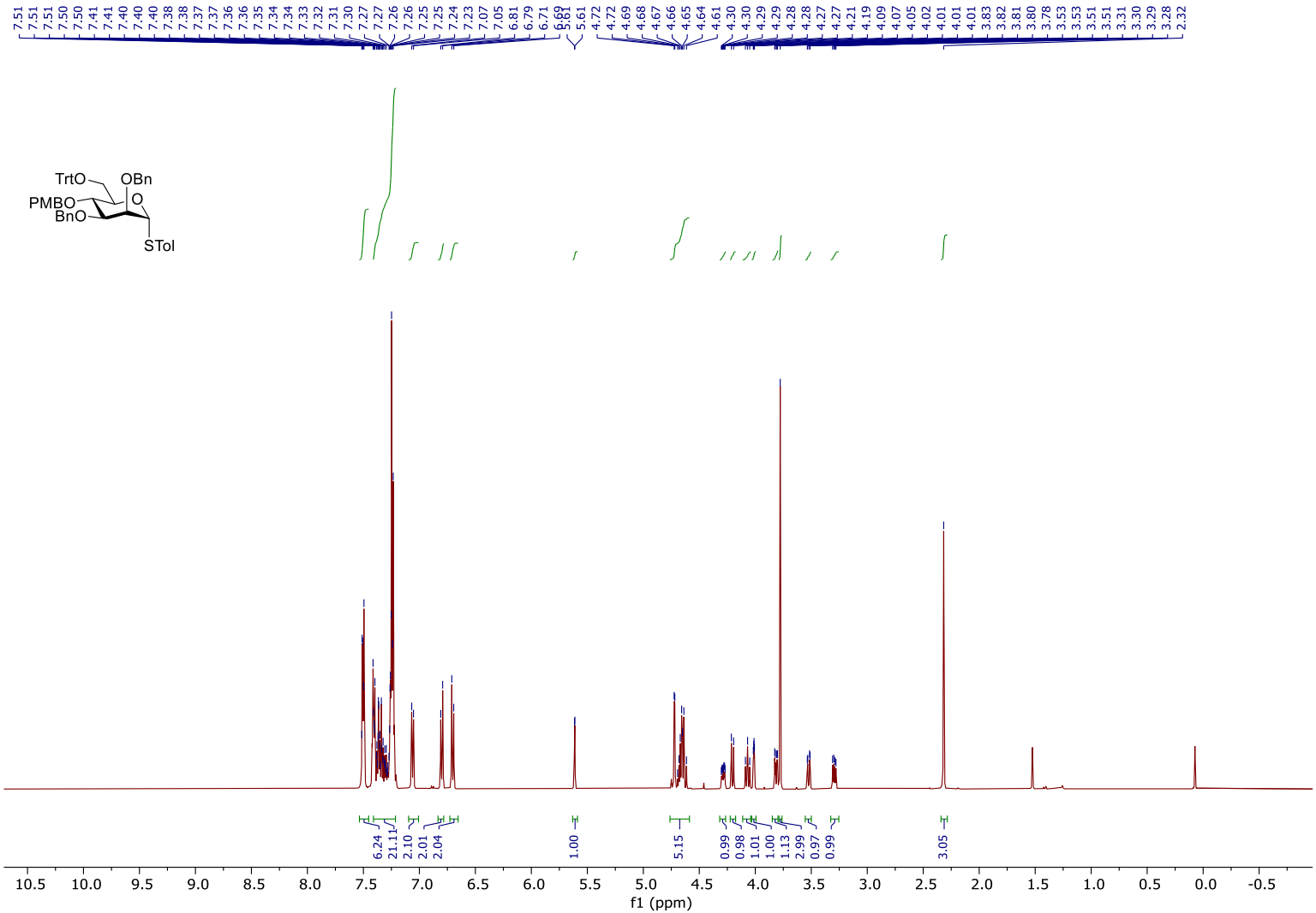
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (25)



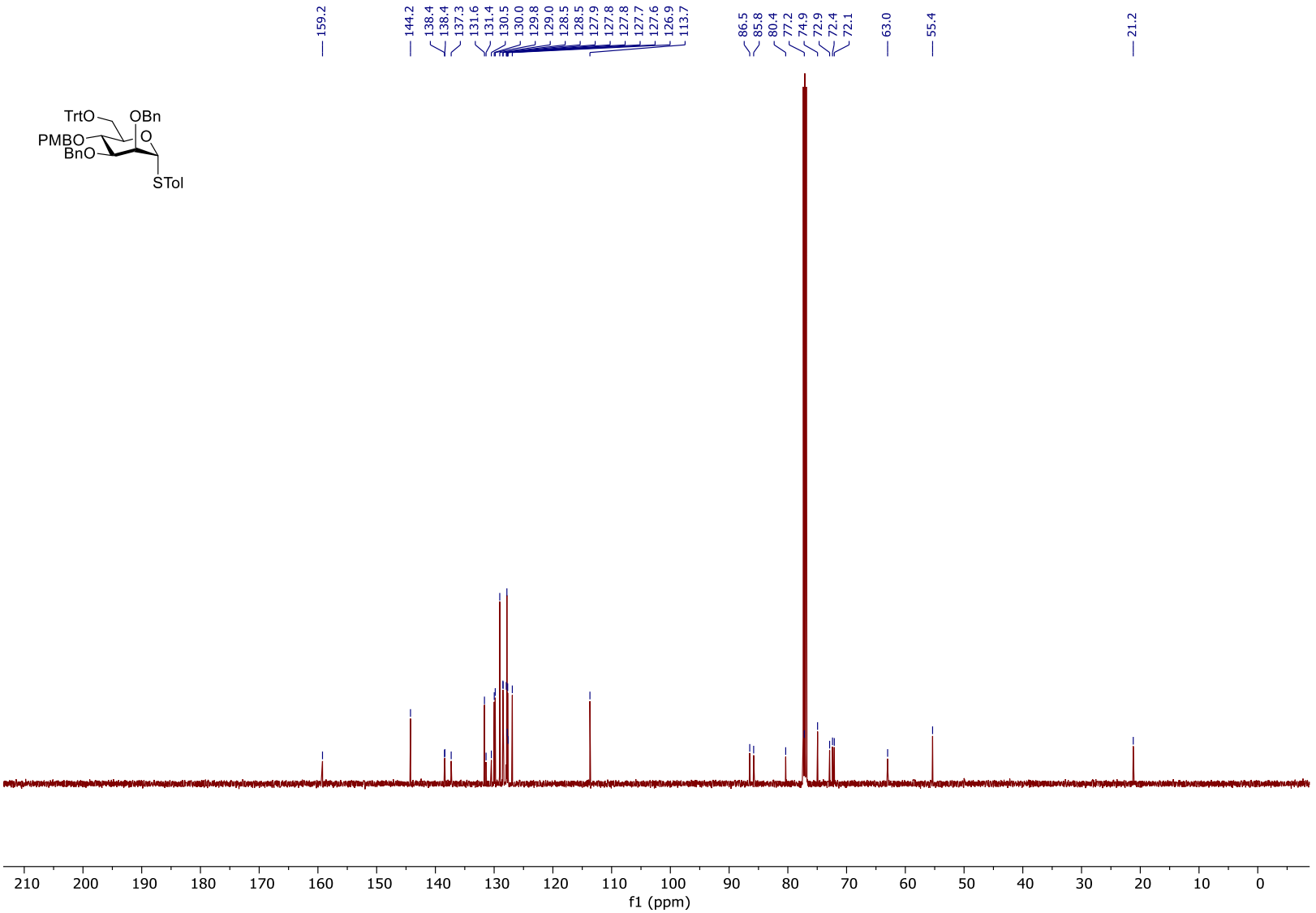
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (25)



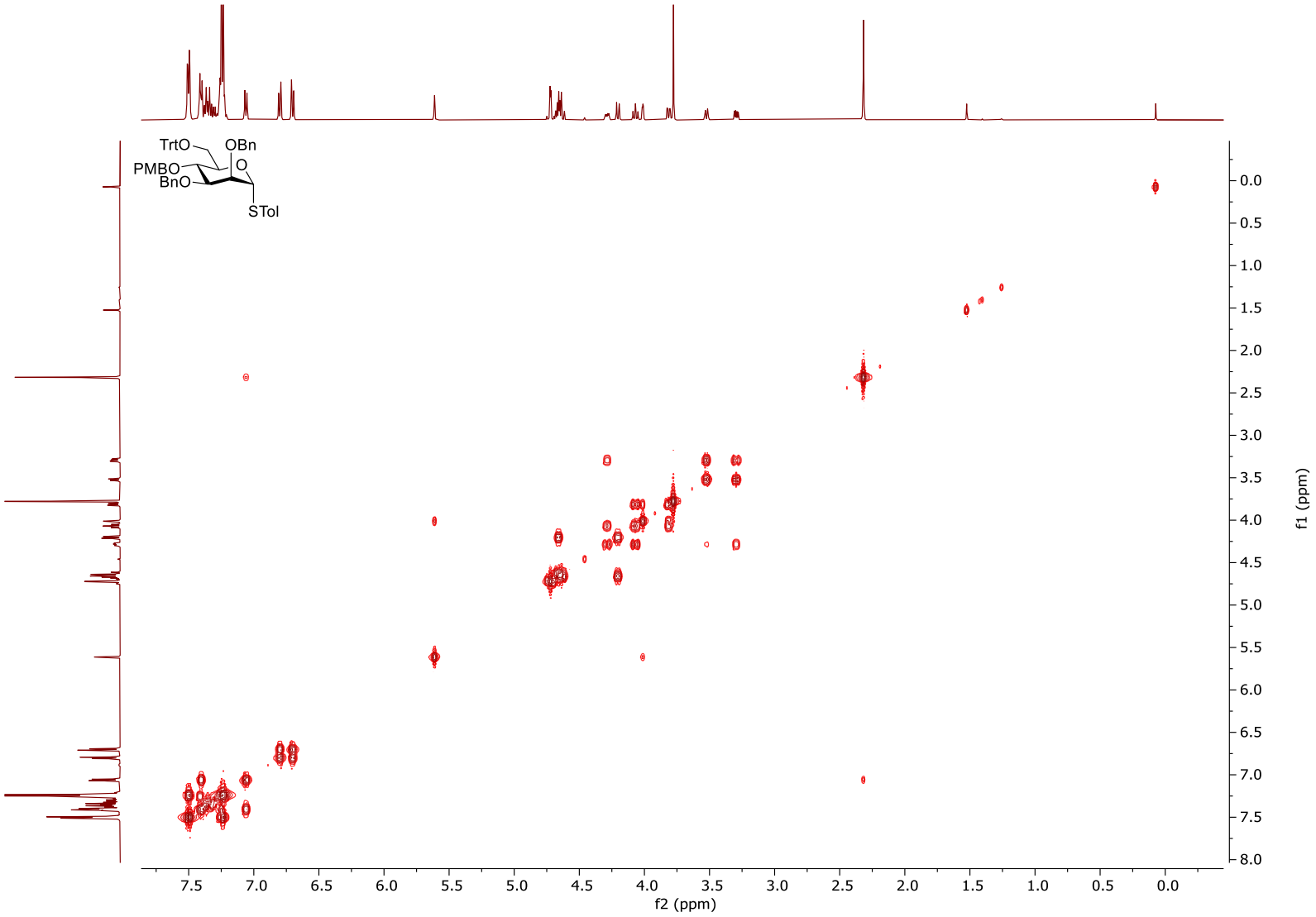
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (26)



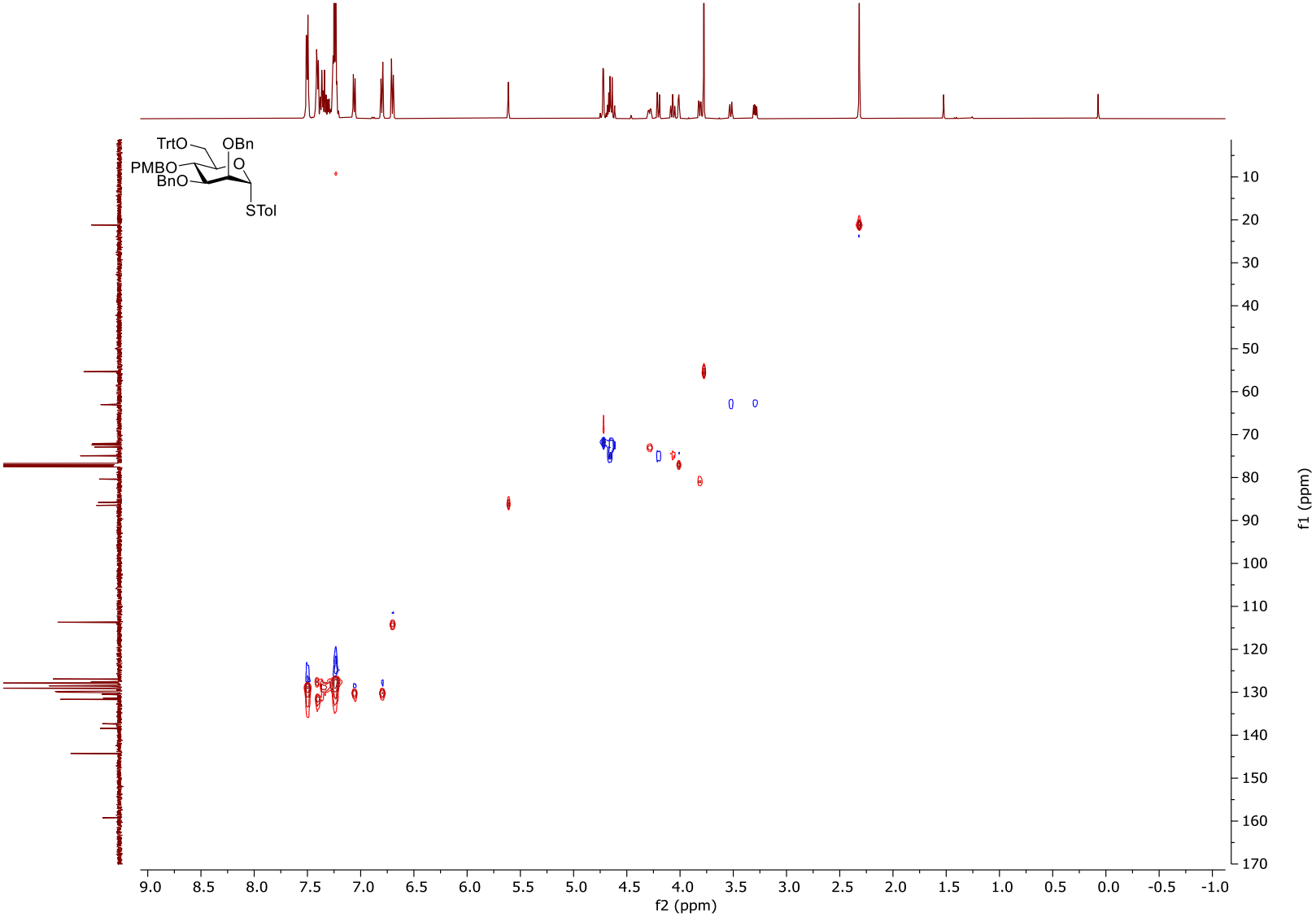
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (26)



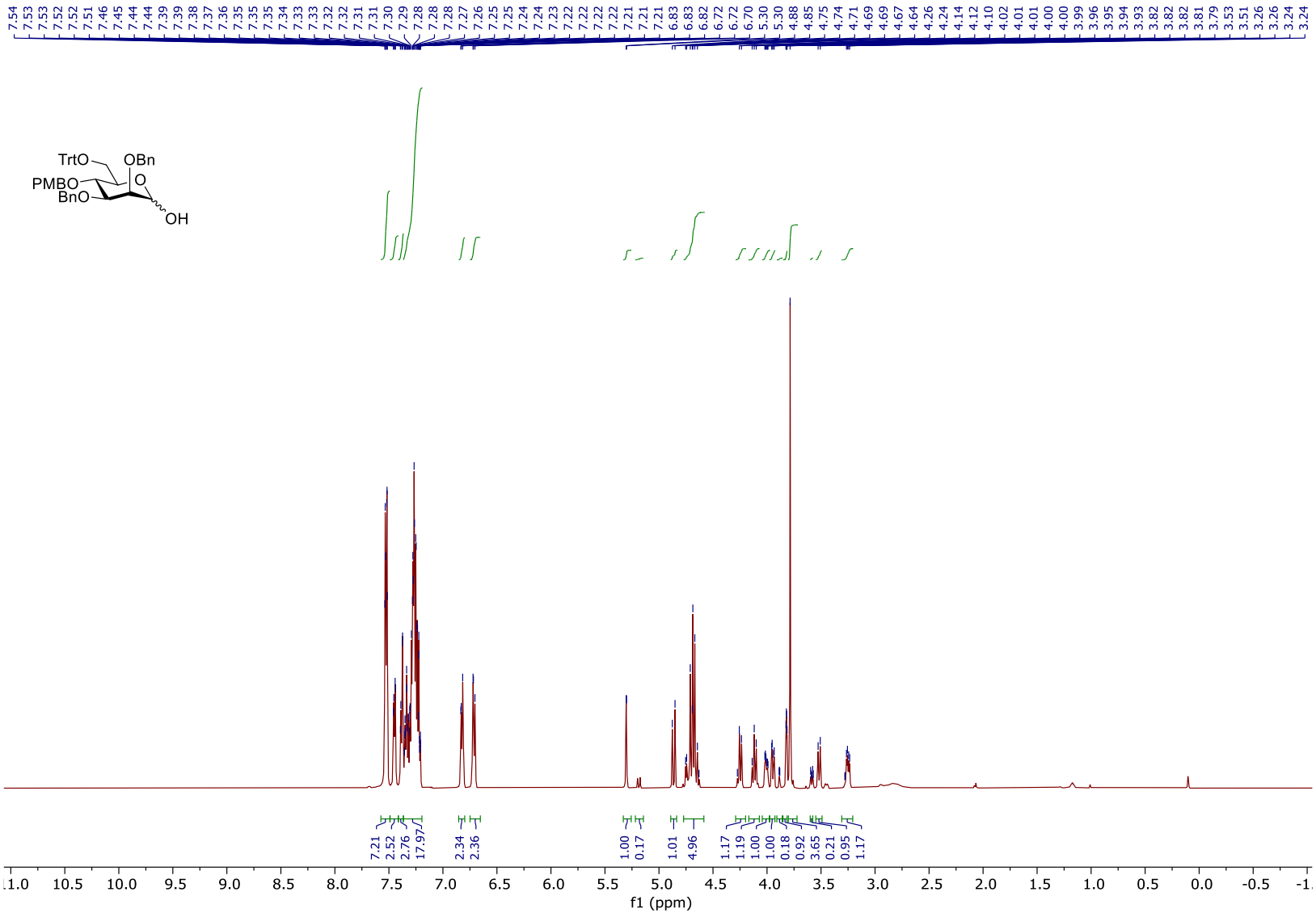
COSY NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (26)



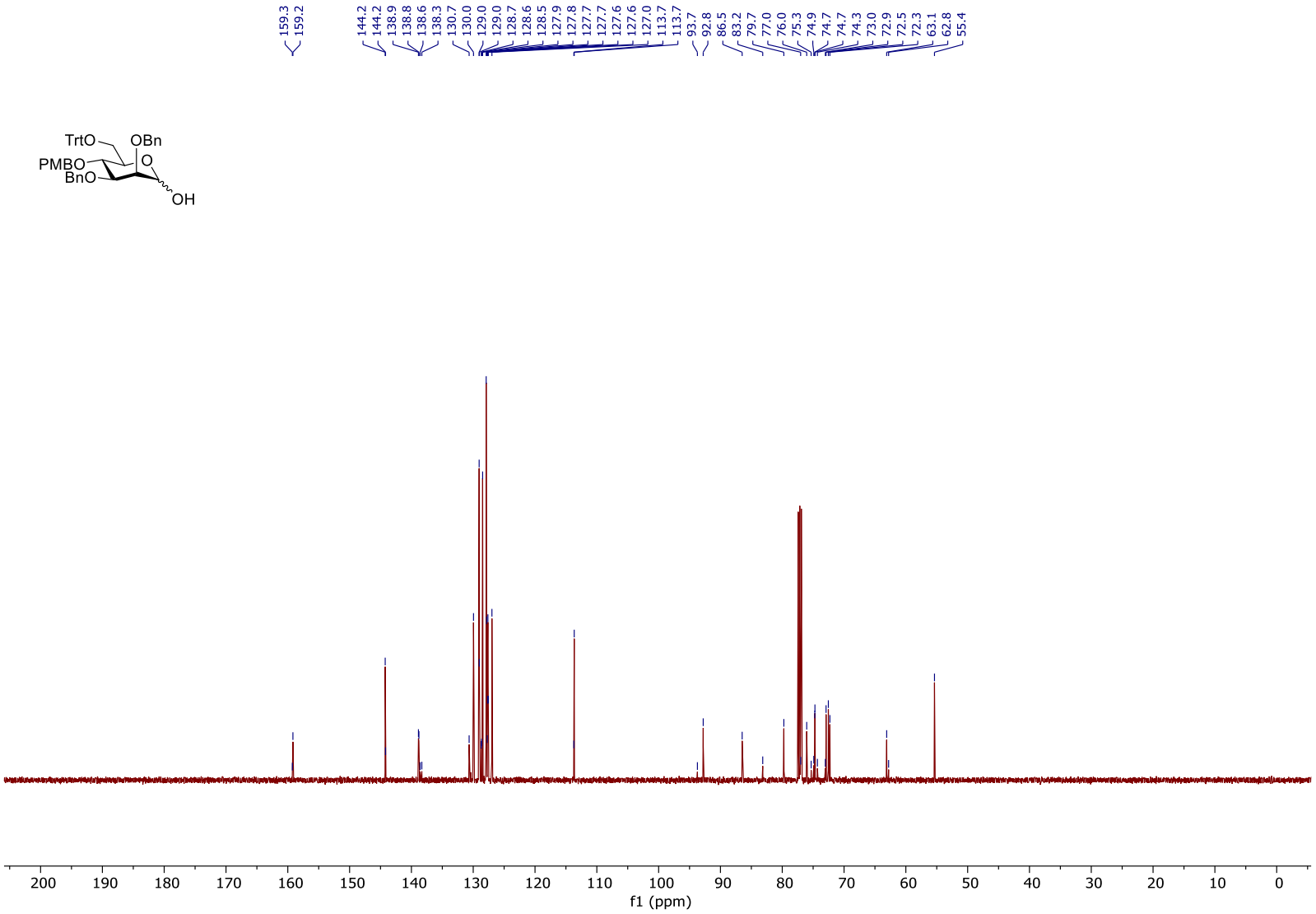
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of *p*-Methylphenyl 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-1-thio-α-D-mannopyranoside (26)



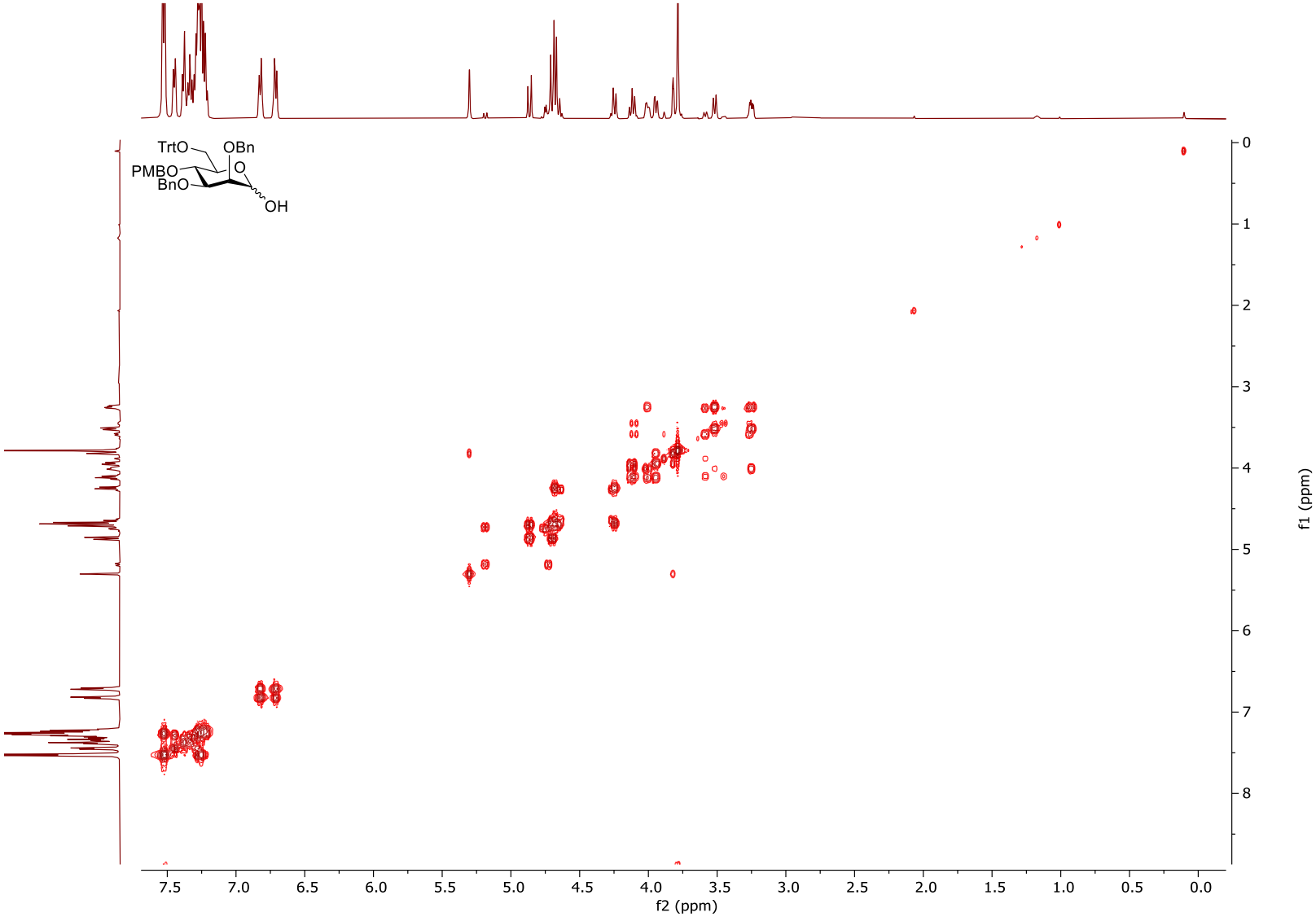
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-mannopyranose (27)



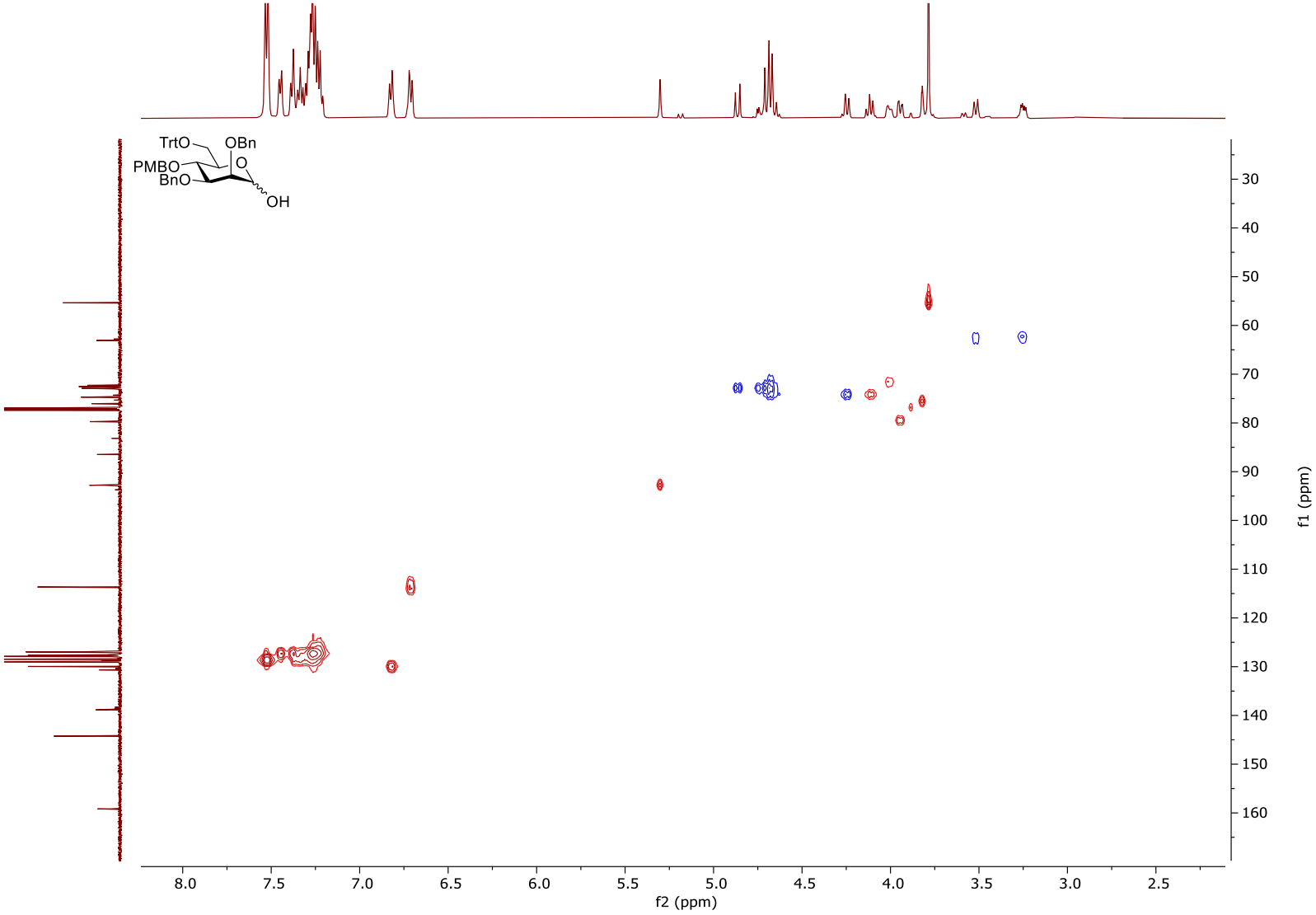
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-mannopyranose (27)



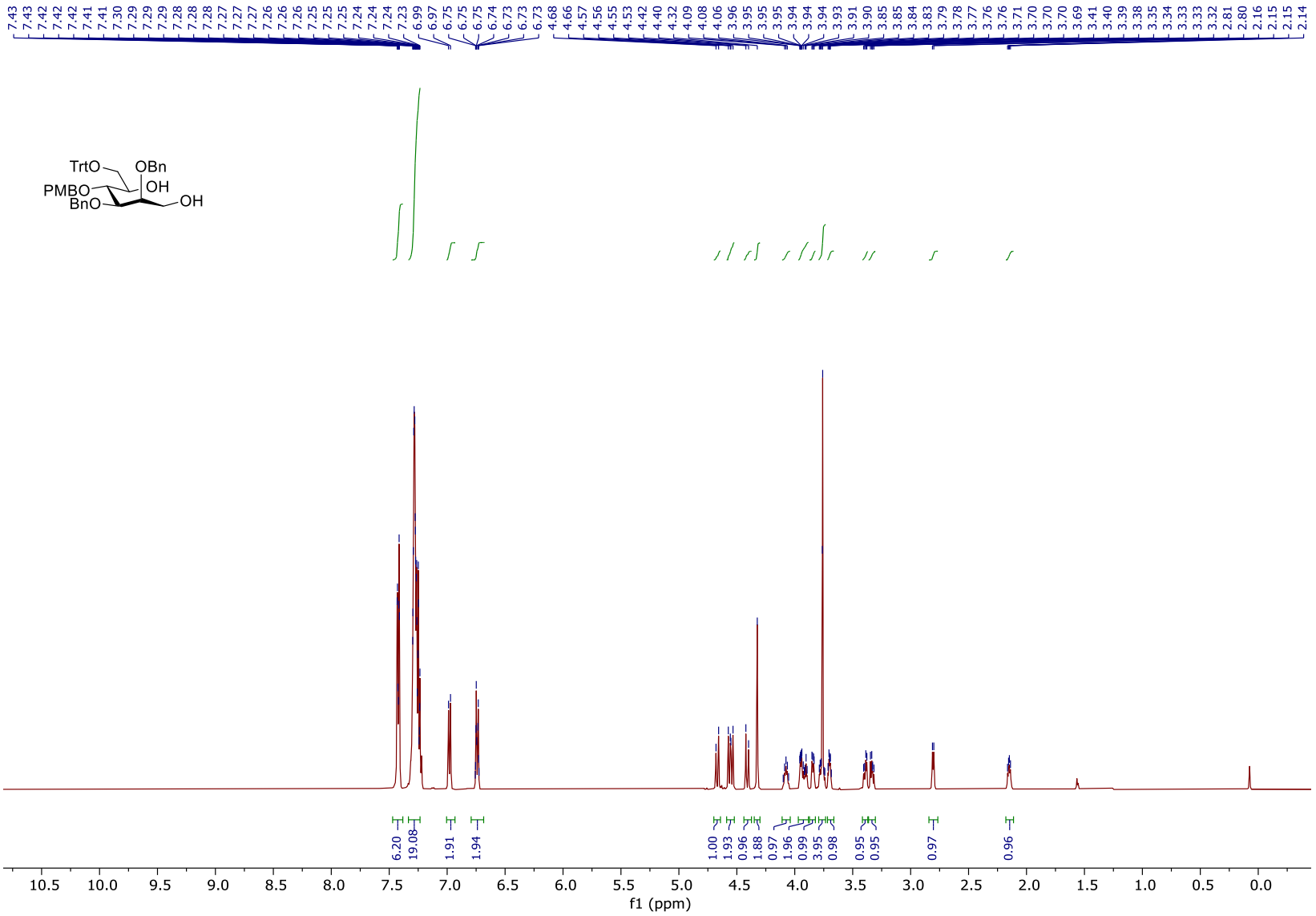
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-mannopyranose (27)



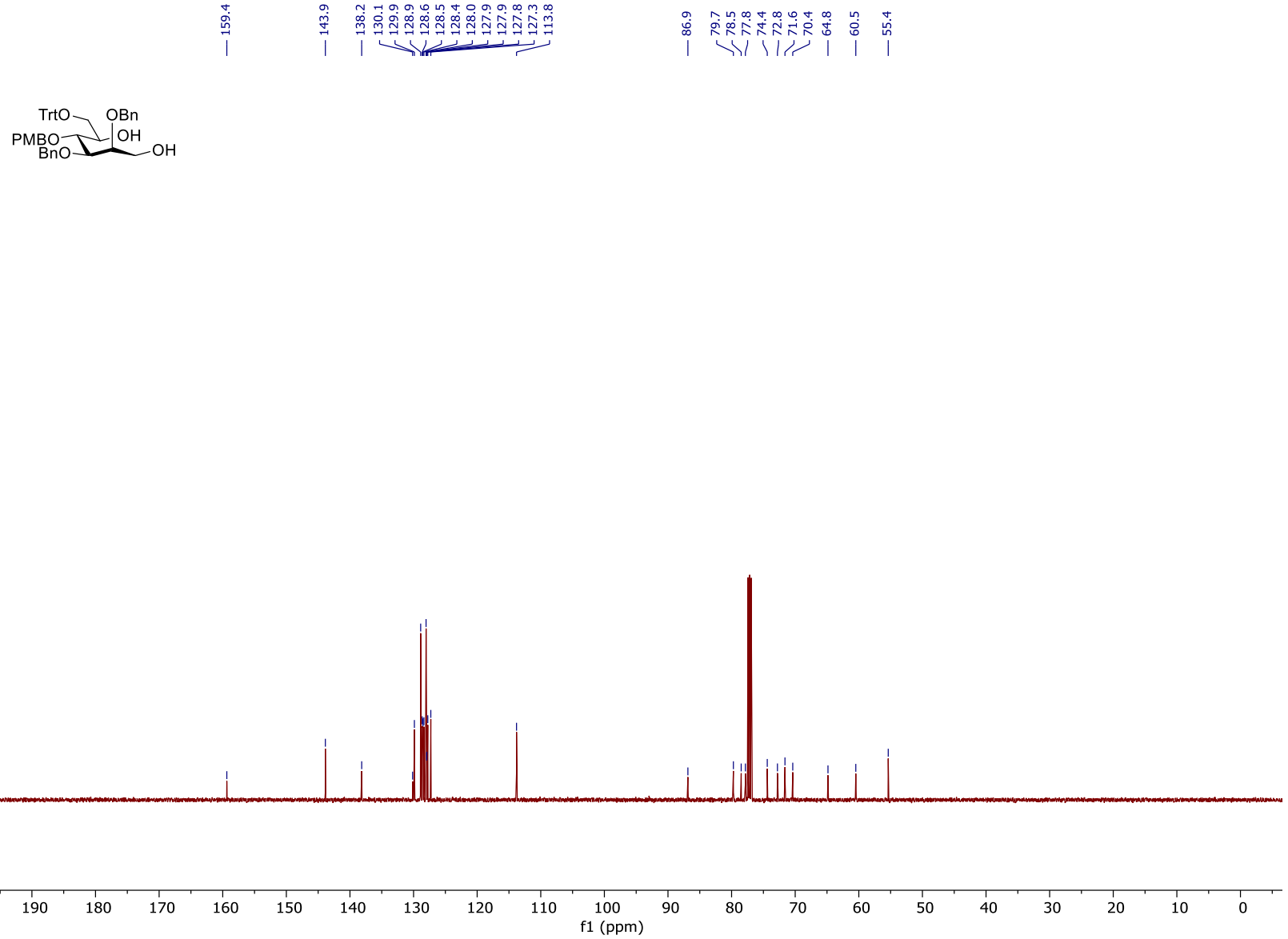
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-α/β-D-mannopyranose (27)



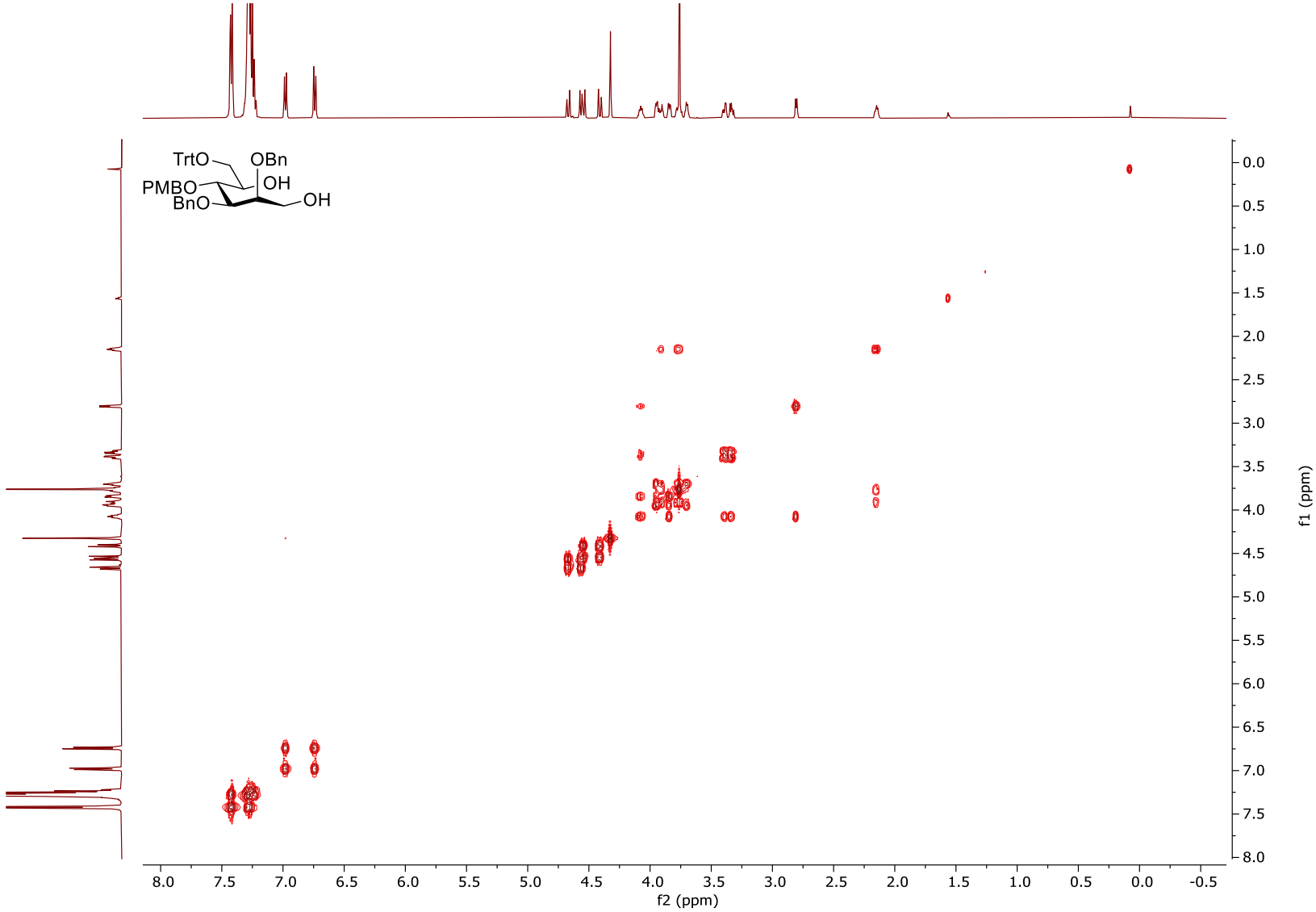
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (28)



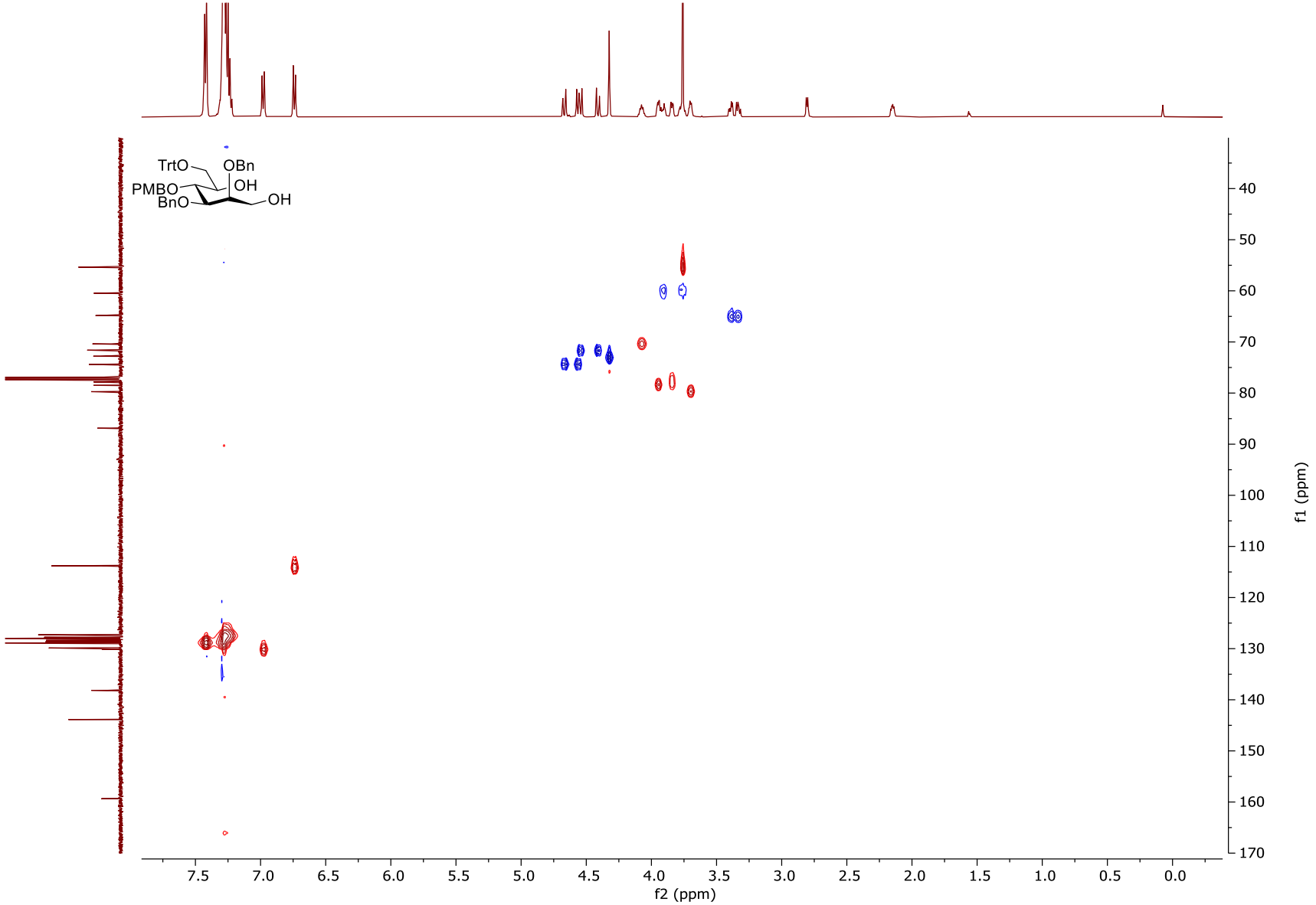
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (28)



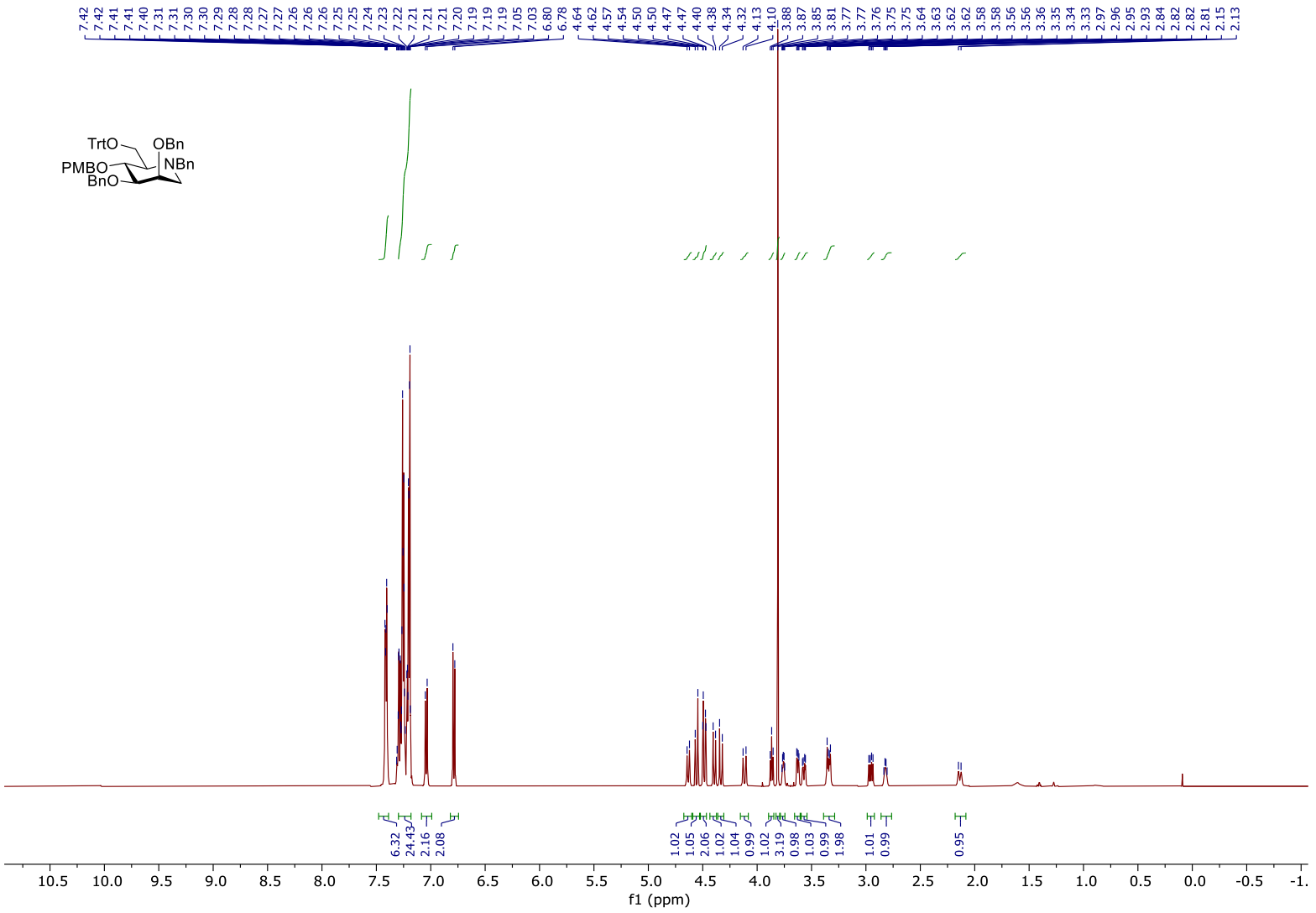
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (28)



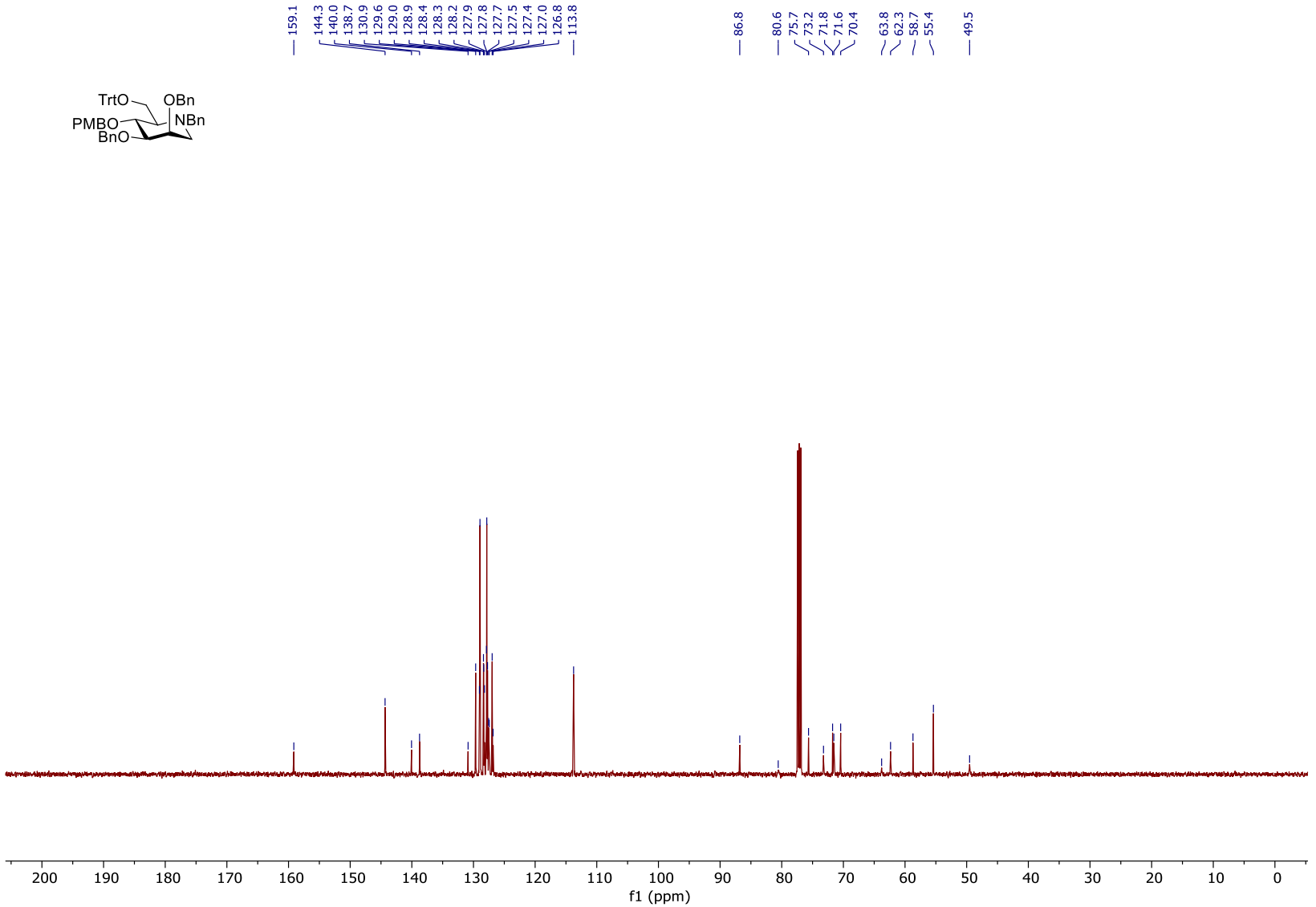
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (28)



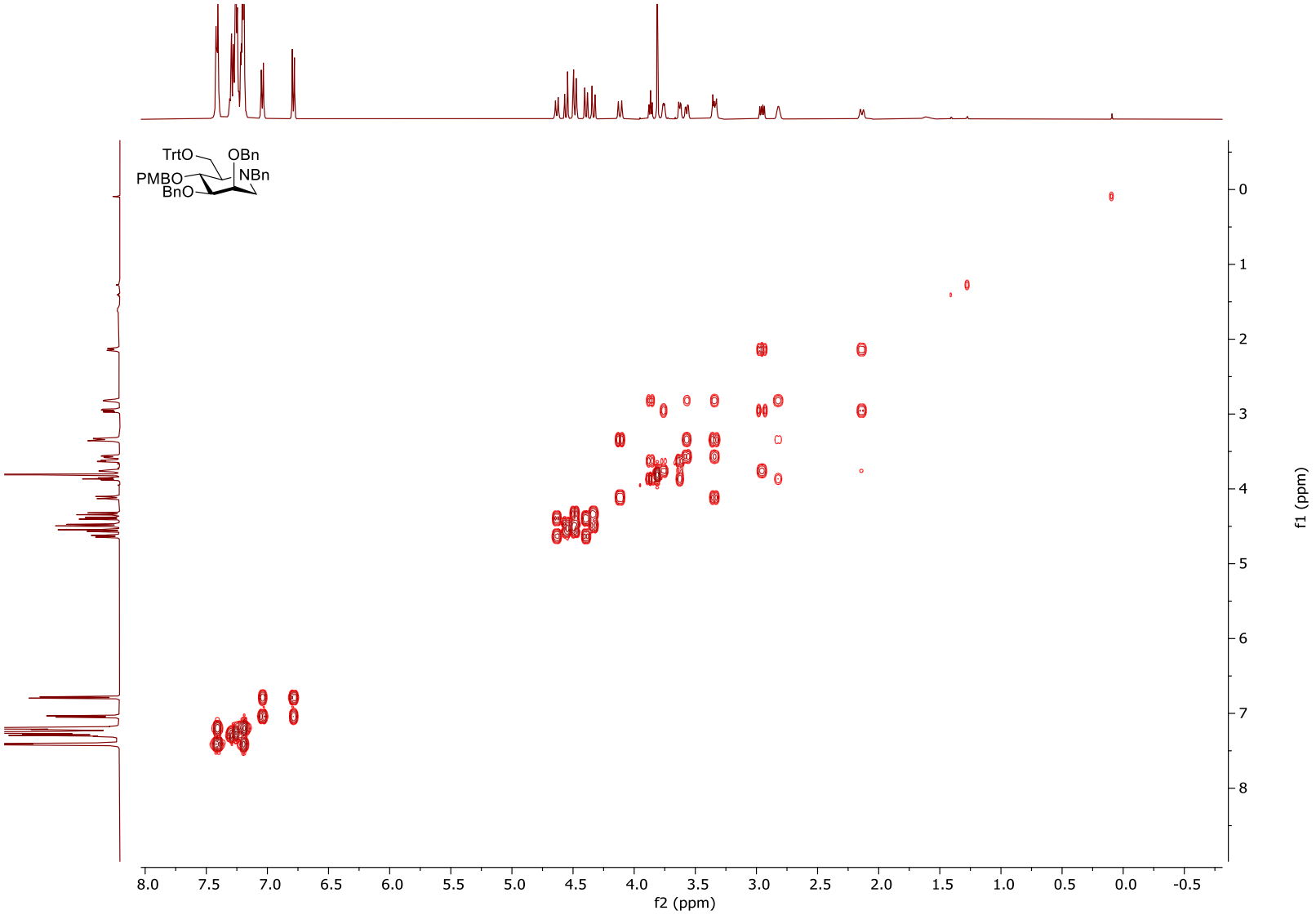
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (29)



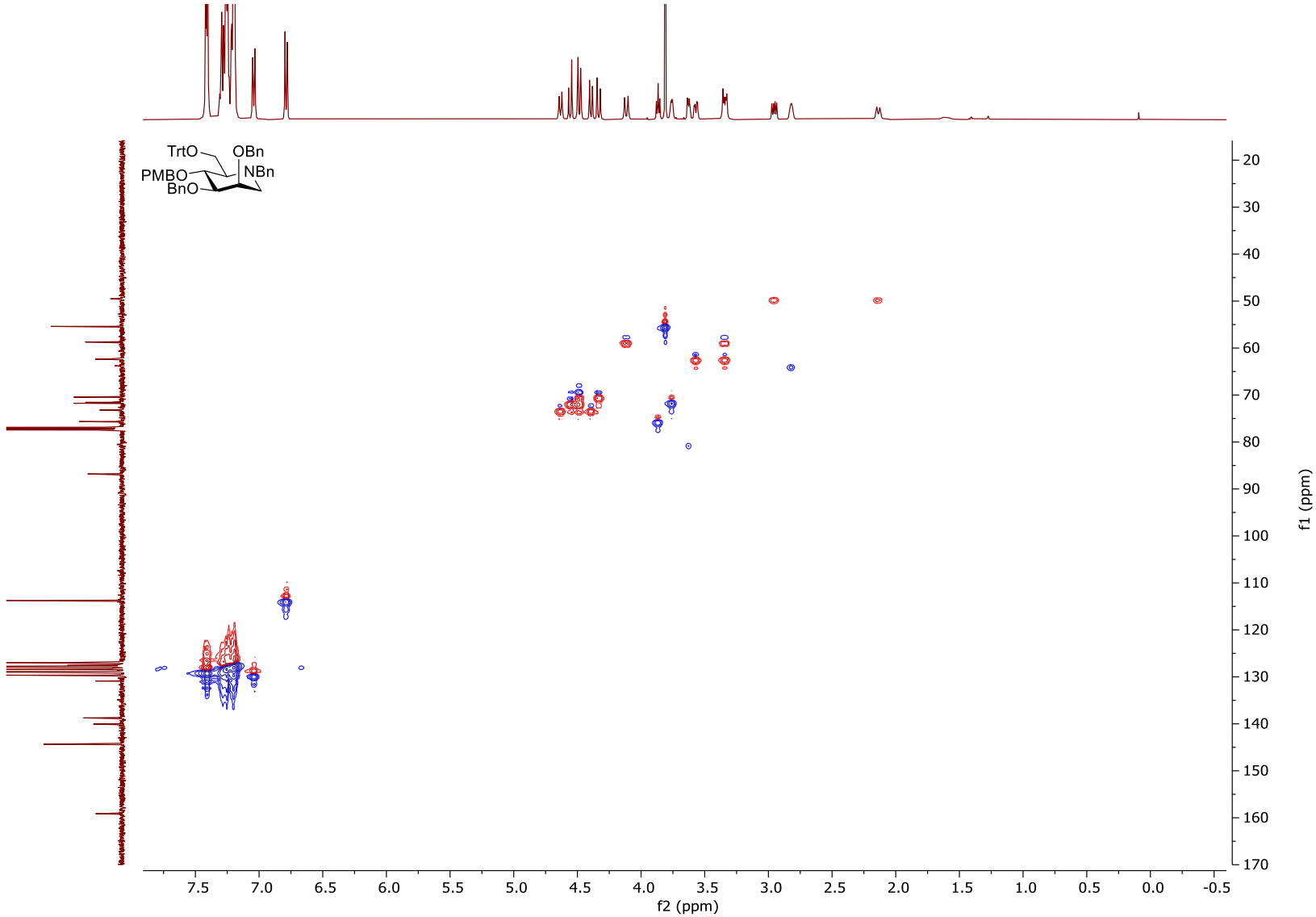
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (29)



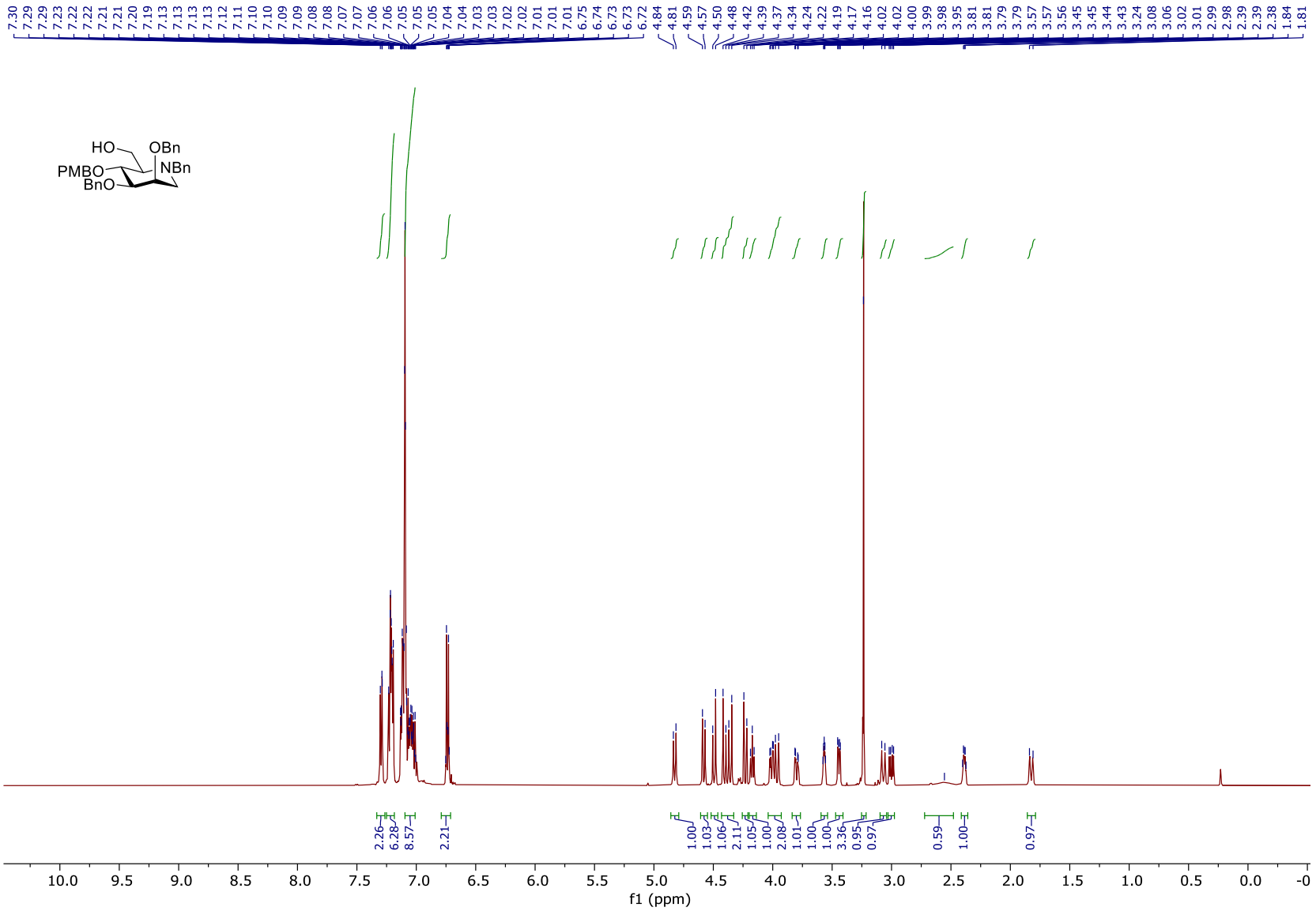
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (29)



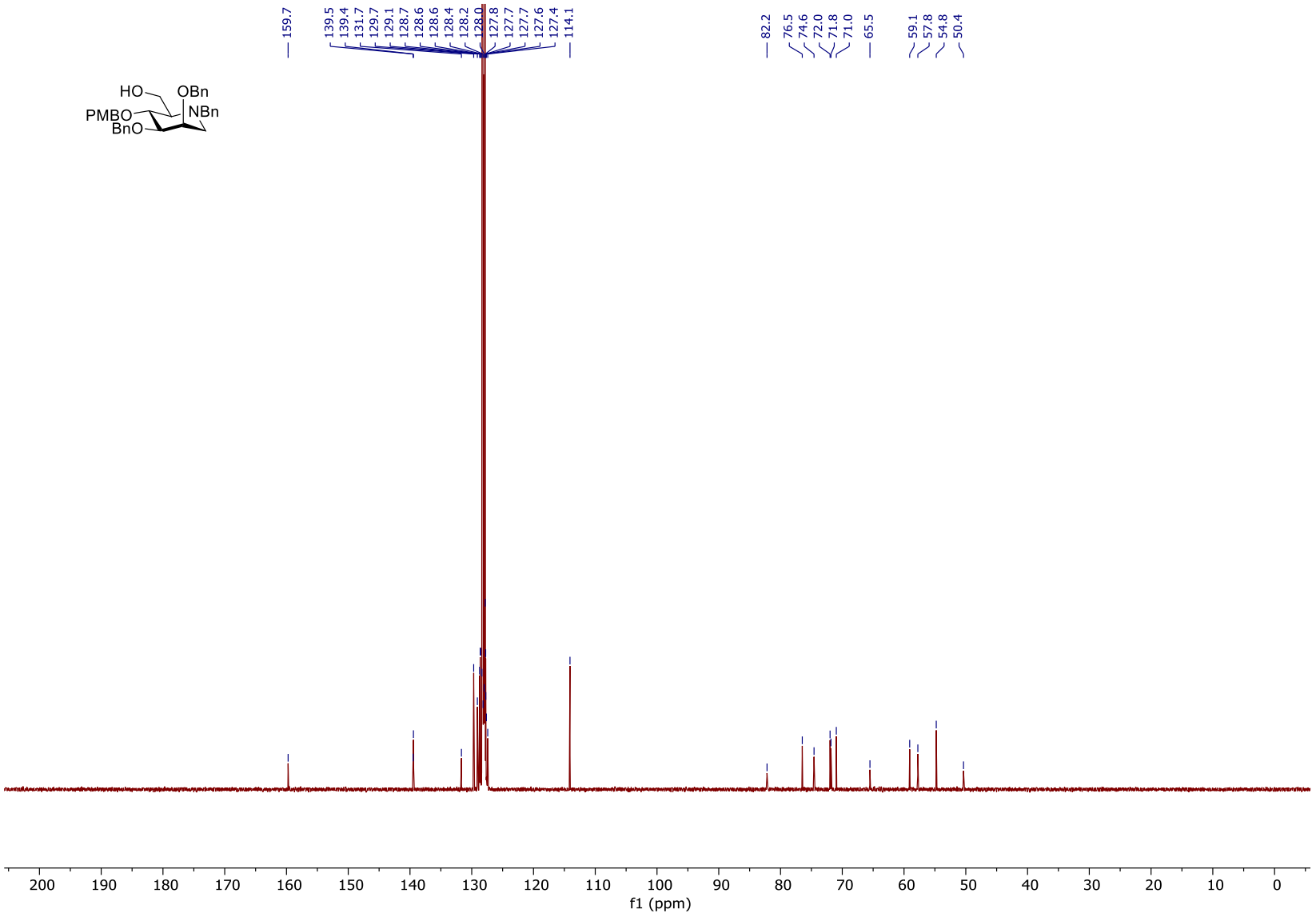
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-6-*O*-triphenylmethyl-D-mannitol (29)



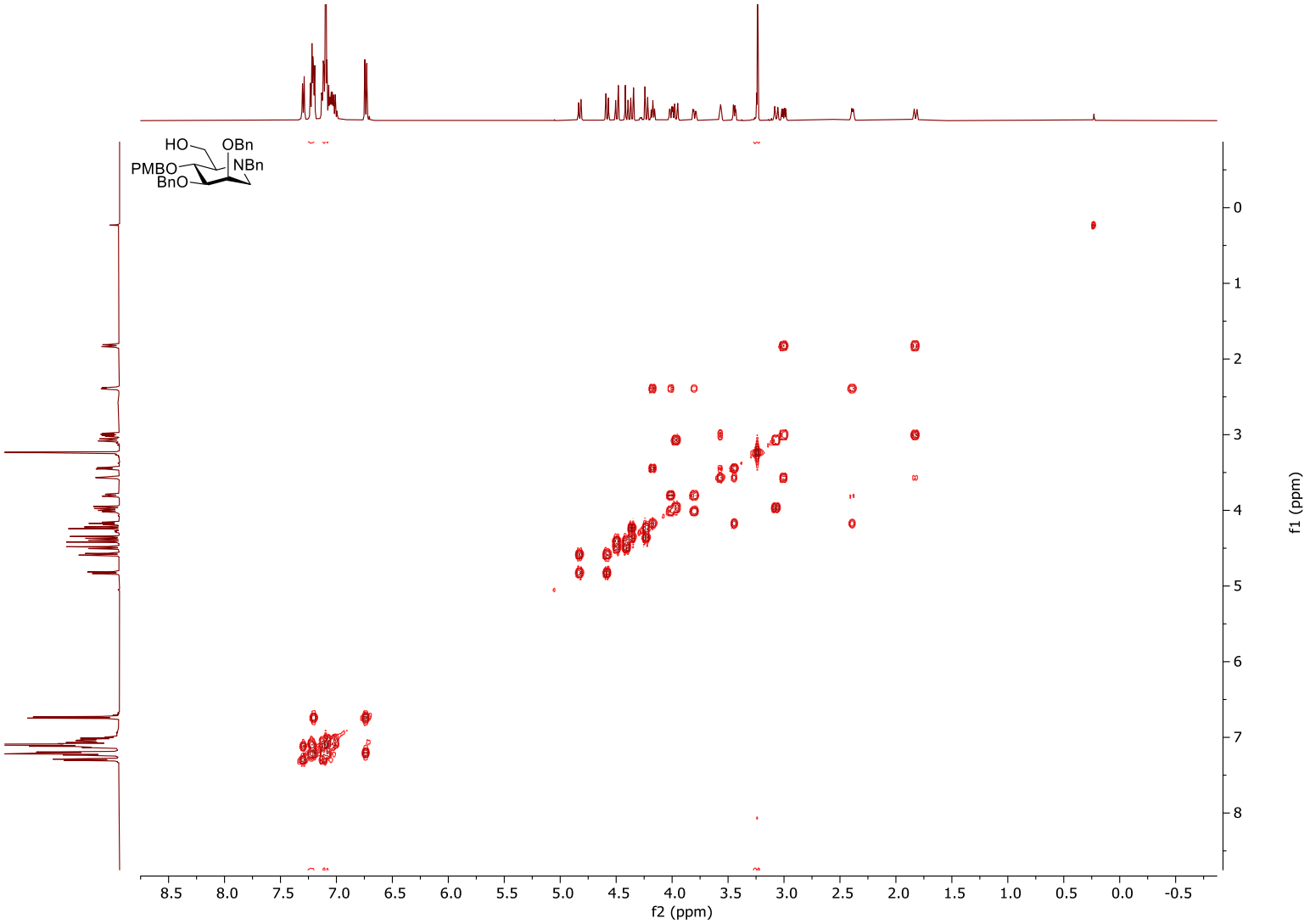
^{1}H NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-mannitol (30)



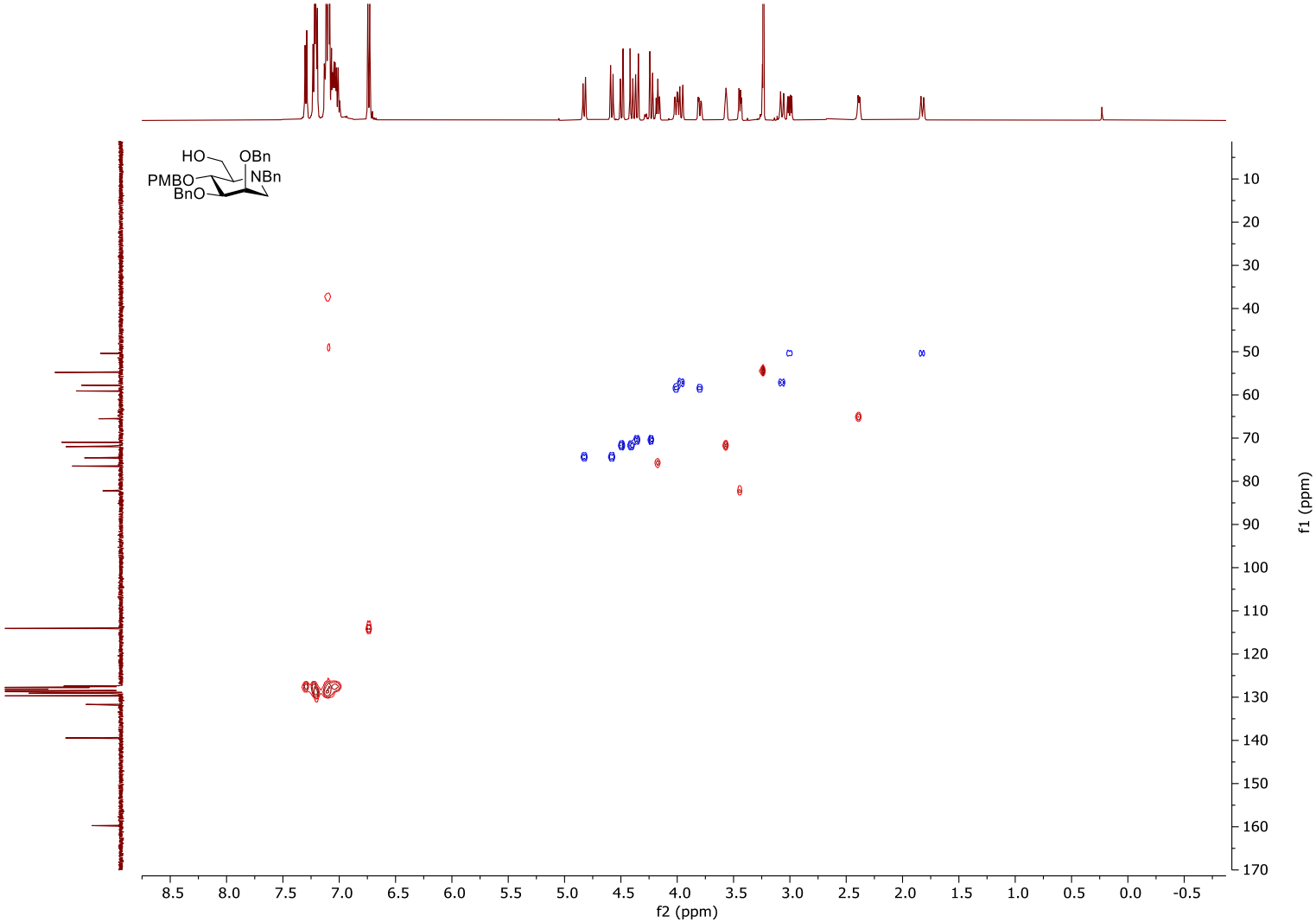
^{13}C NMR (126 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-mannitol (30)



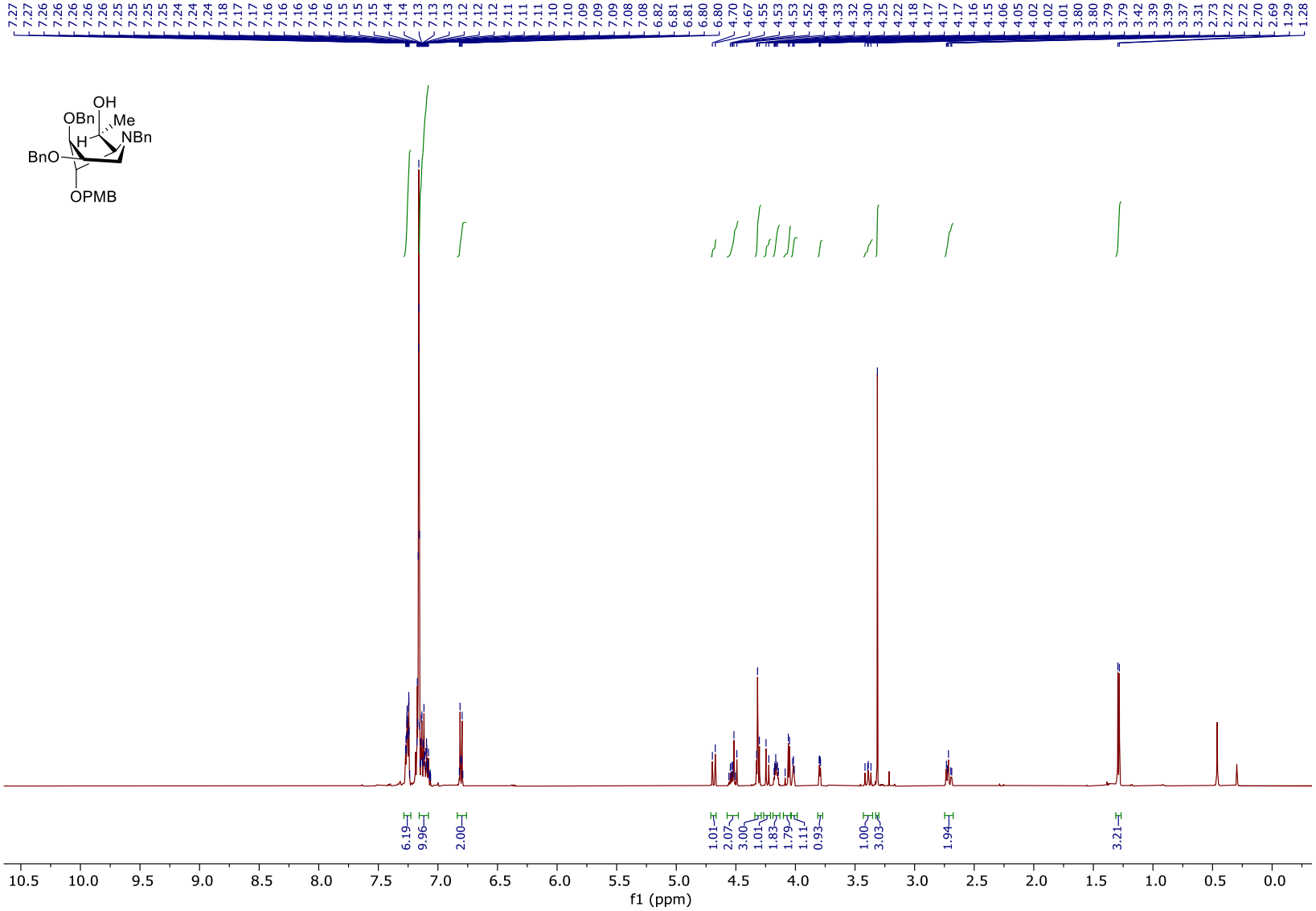
COSY NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-mannitol (30)



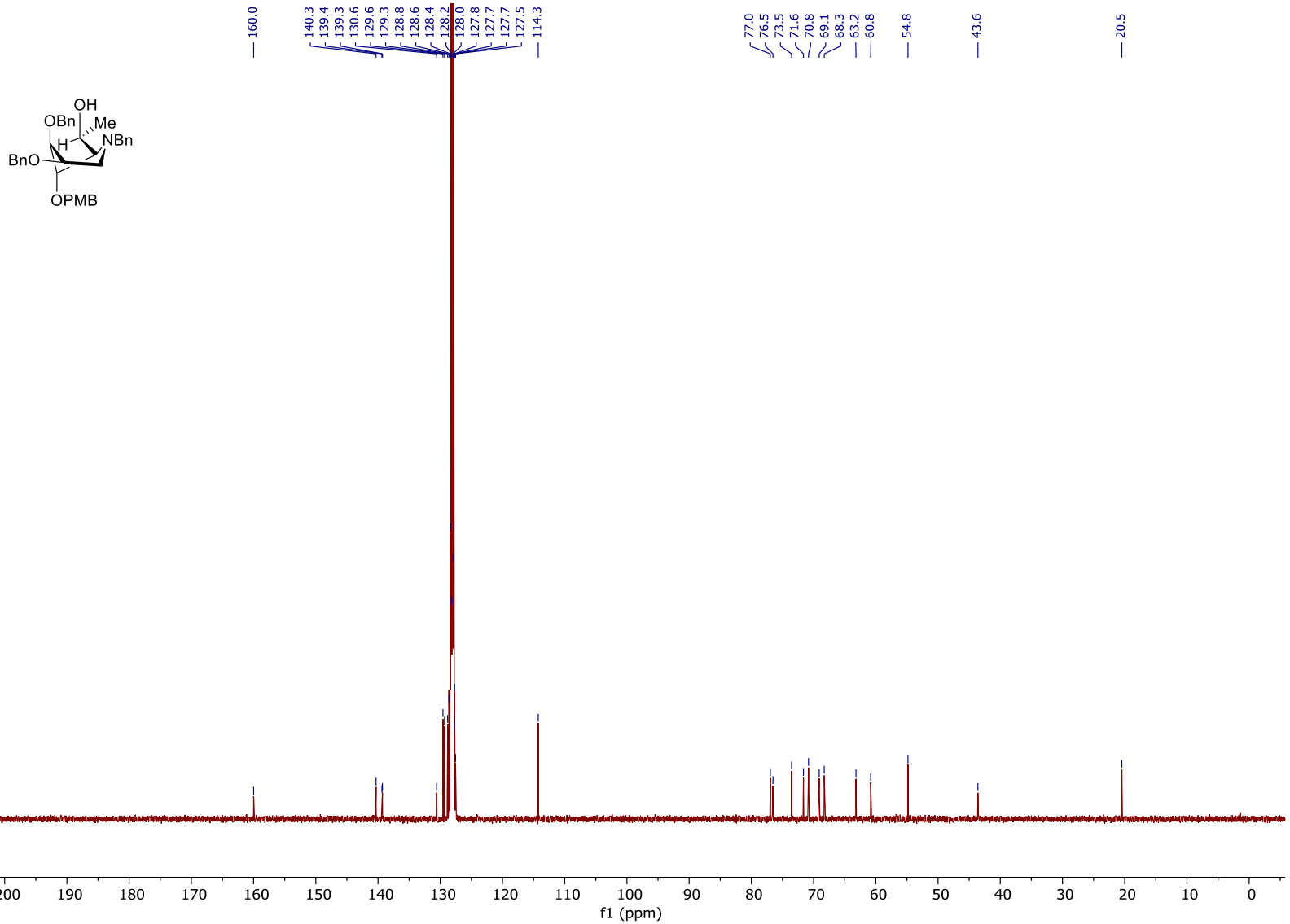
HSQC NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-D-mannitol (30)



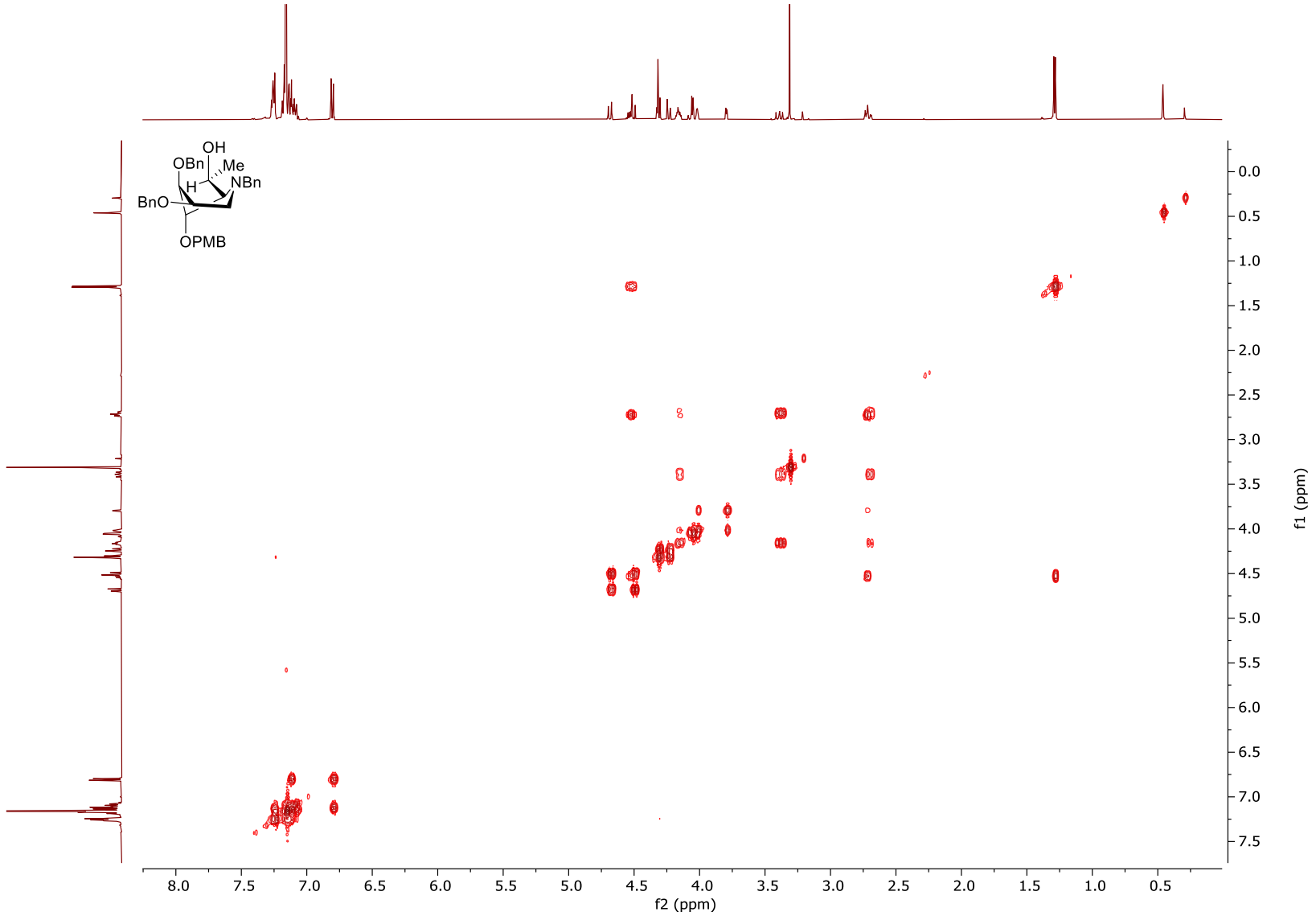
^{1}H NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*manno*-heptitol (31)



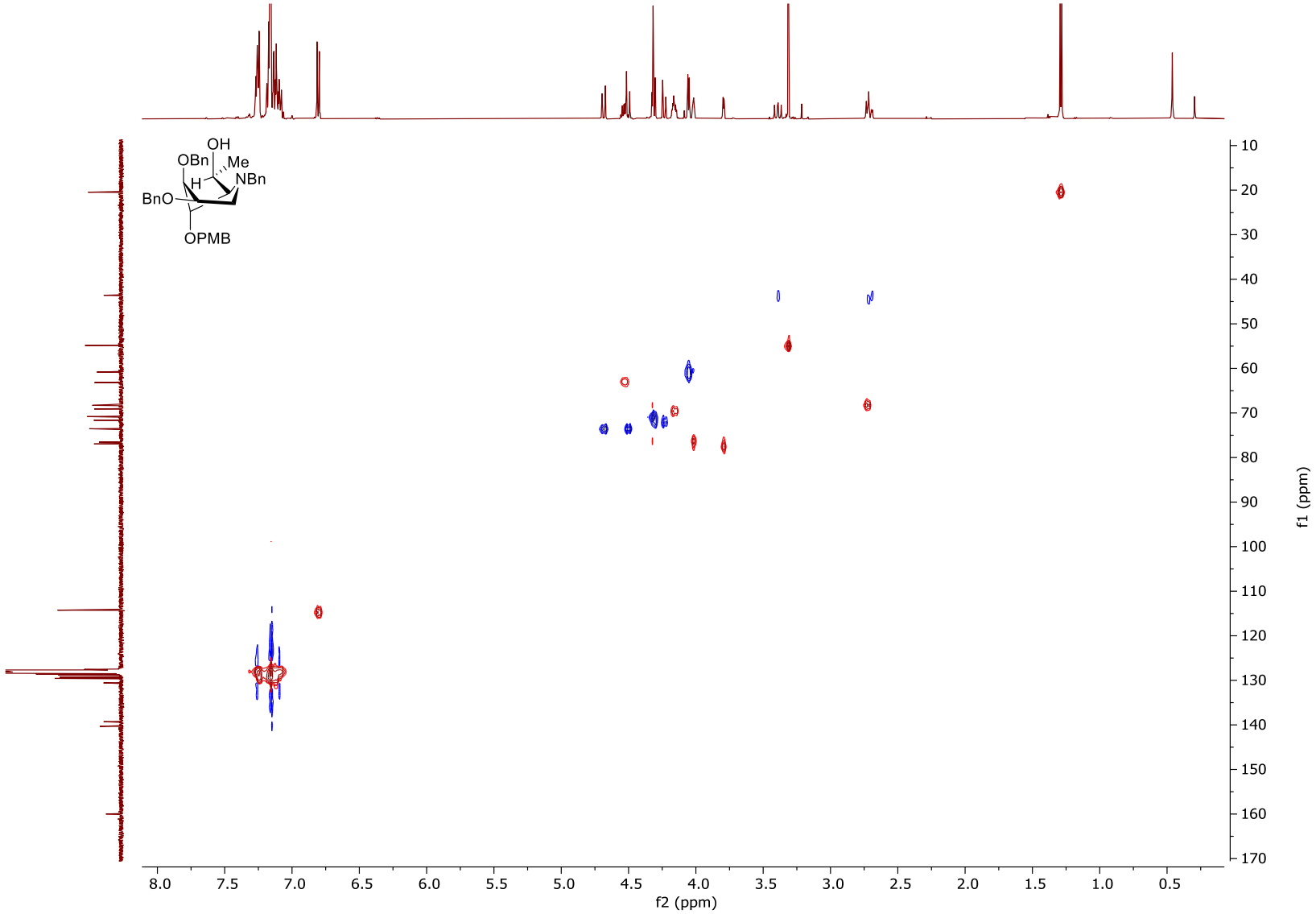
^{13}C NMR (126 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*manno*-heptitol (31)



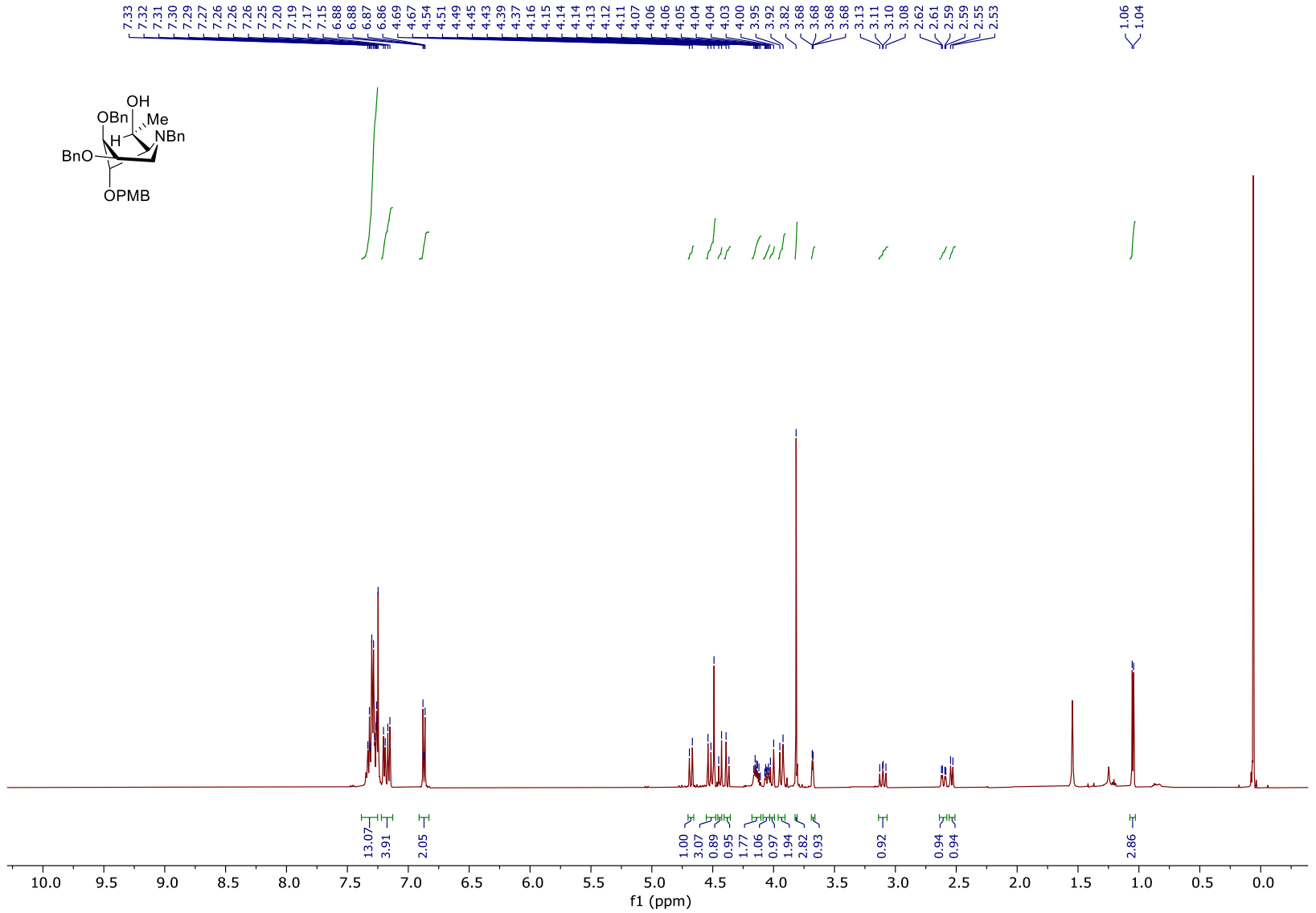
COSY NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*manno*-heptitol (31)



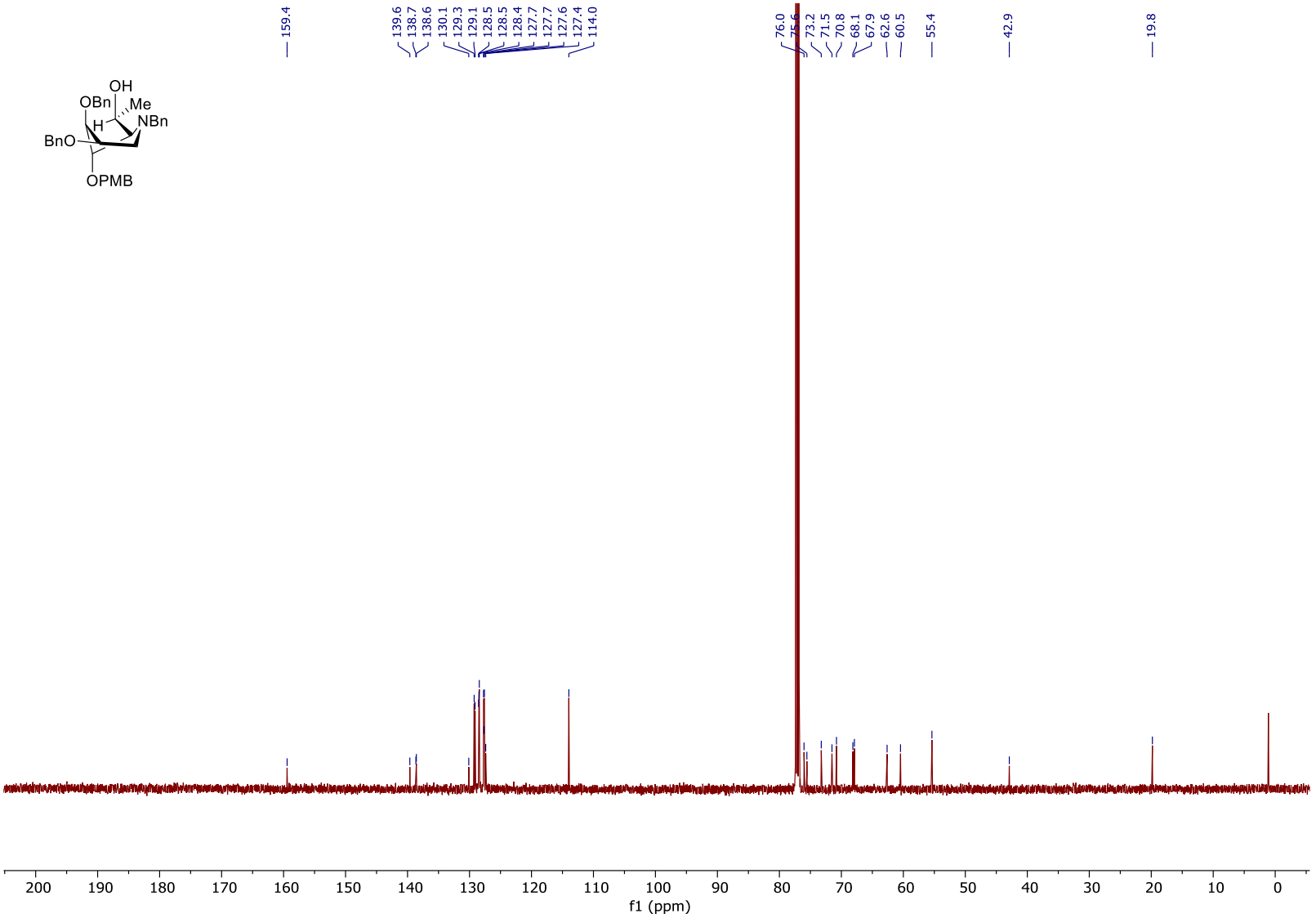
HSQC NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*manno*-heptitol (31)



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*manno*-heptitol (31)



^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxybenzyl)-L-*glycero*-D-*manno*-heptitol (31)



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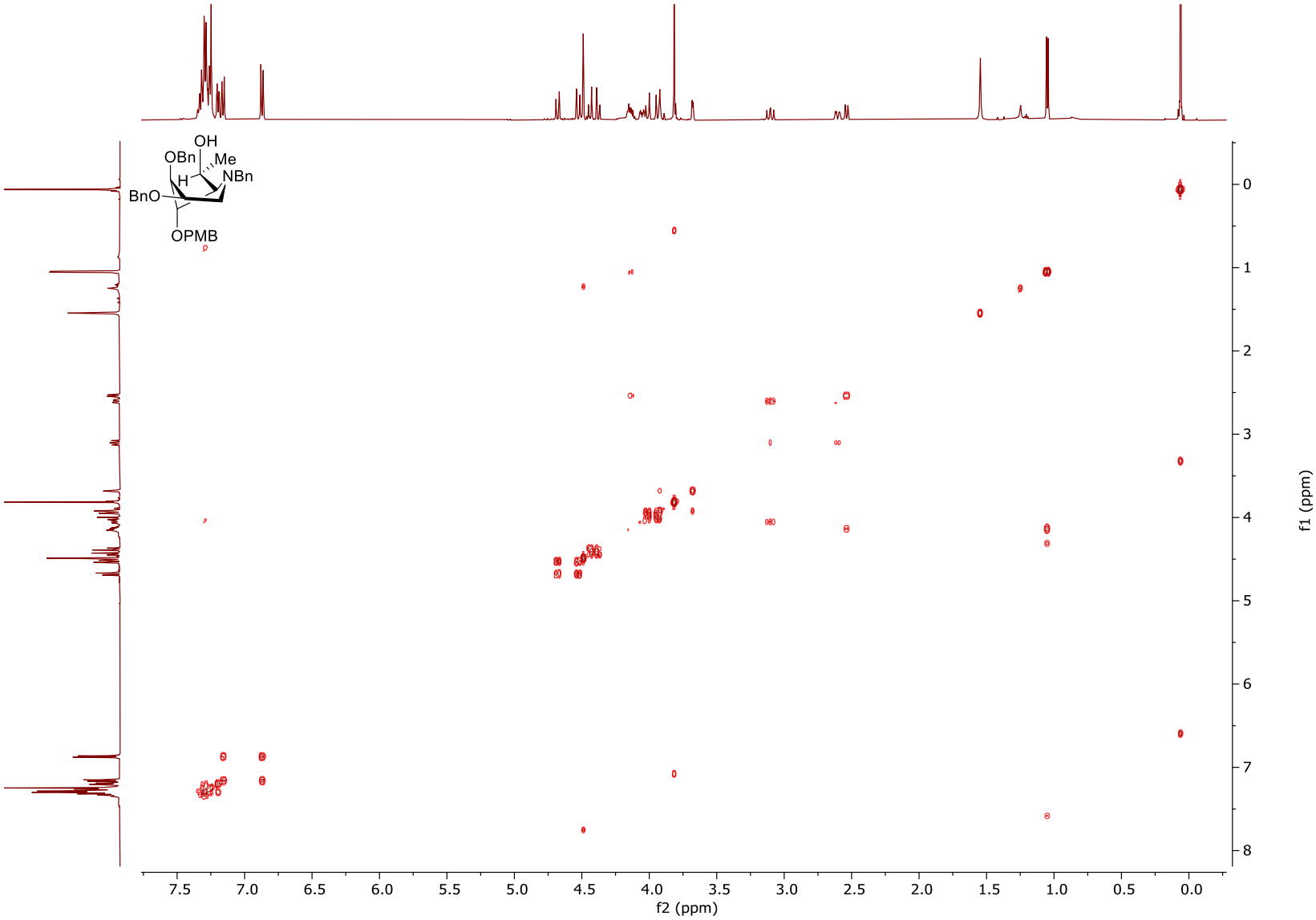

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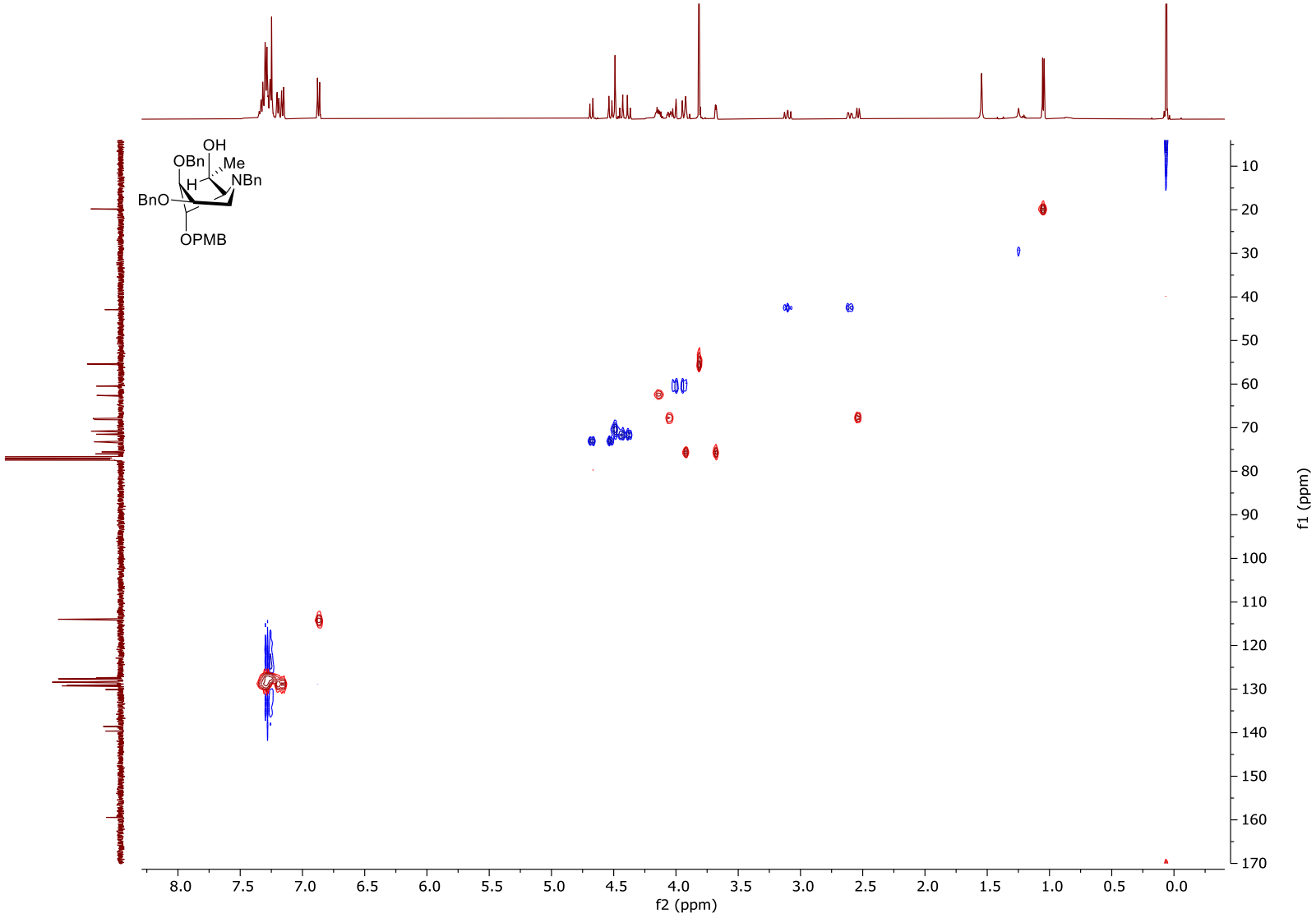
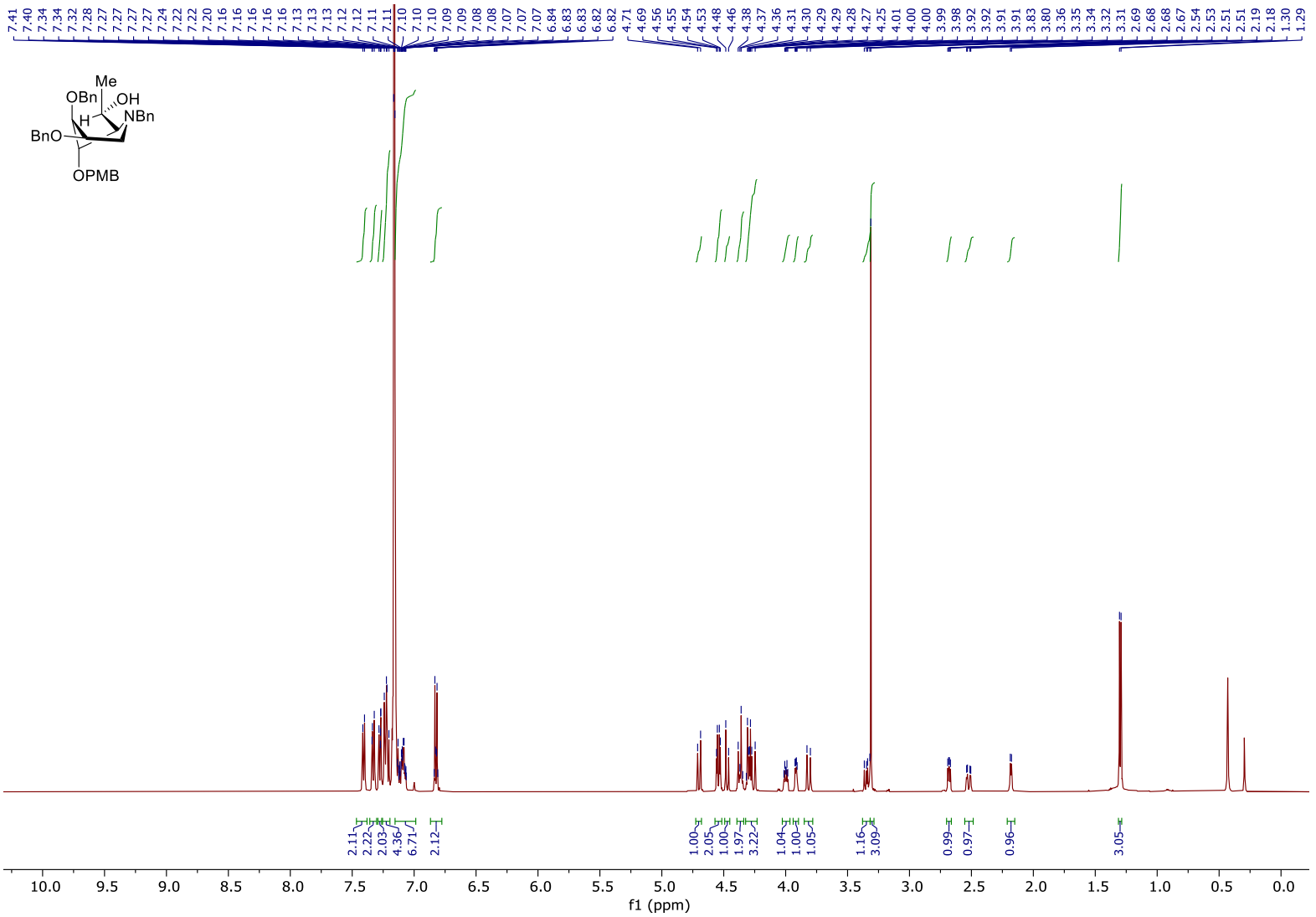
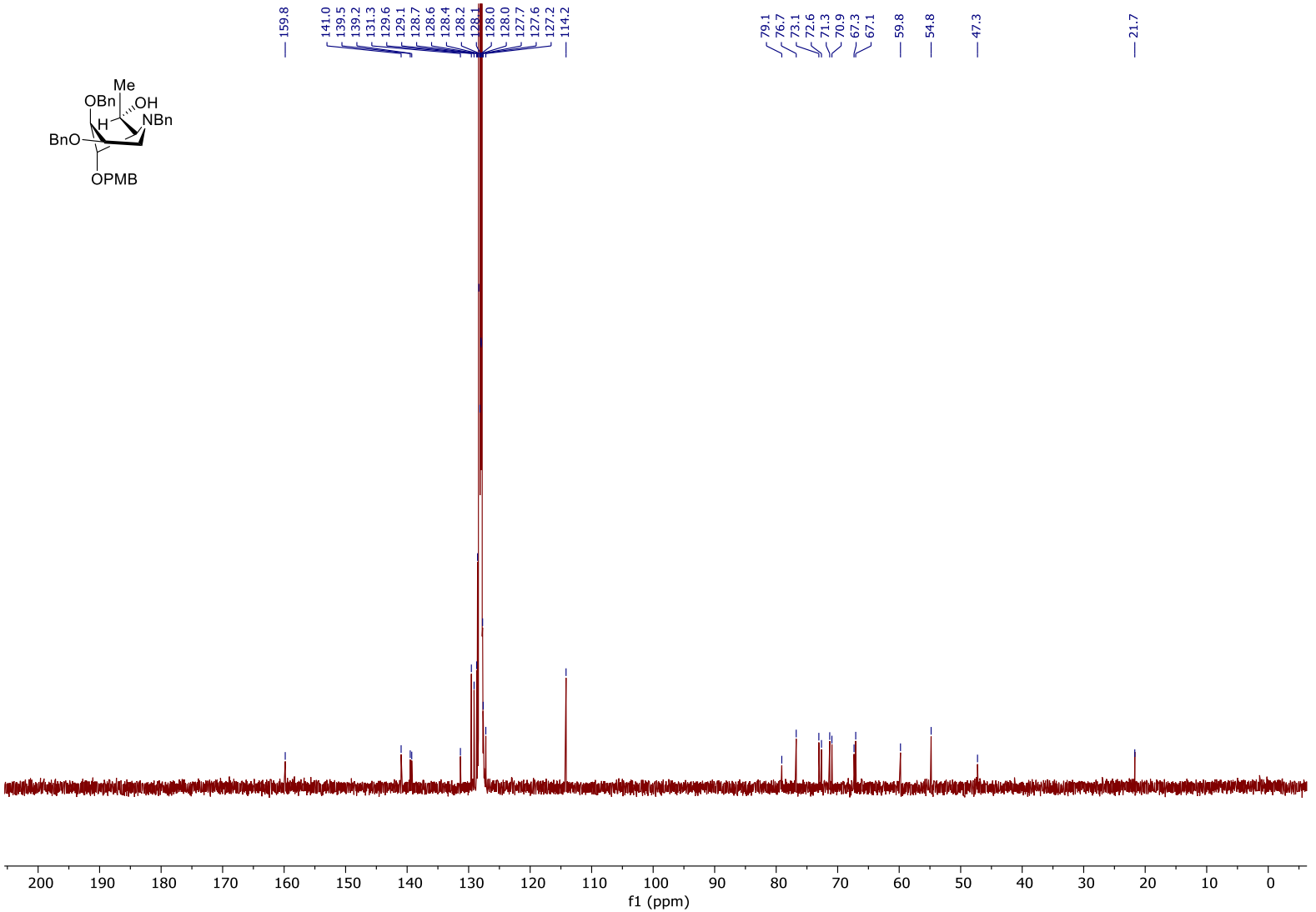


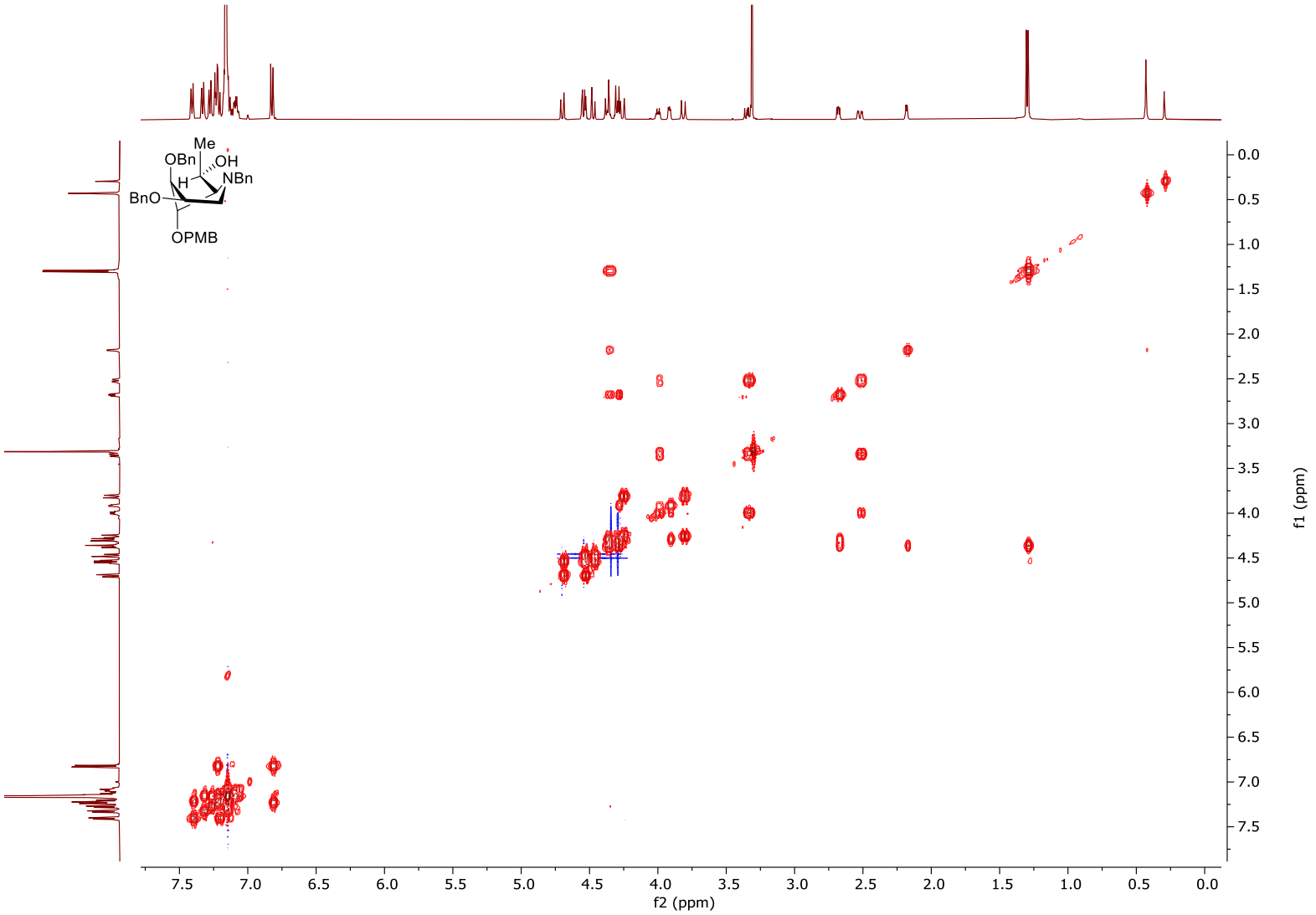
^{1}H NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*manno*-heptitol (32)



^{13}C NMR (126 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*manno*-heptitol (32)



COSY NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5,7-trideoxy-1,5-imino-4-*O*-(4-methoxy-benzyl)-D-*glycero*-D-*manno*-heptitol (32)



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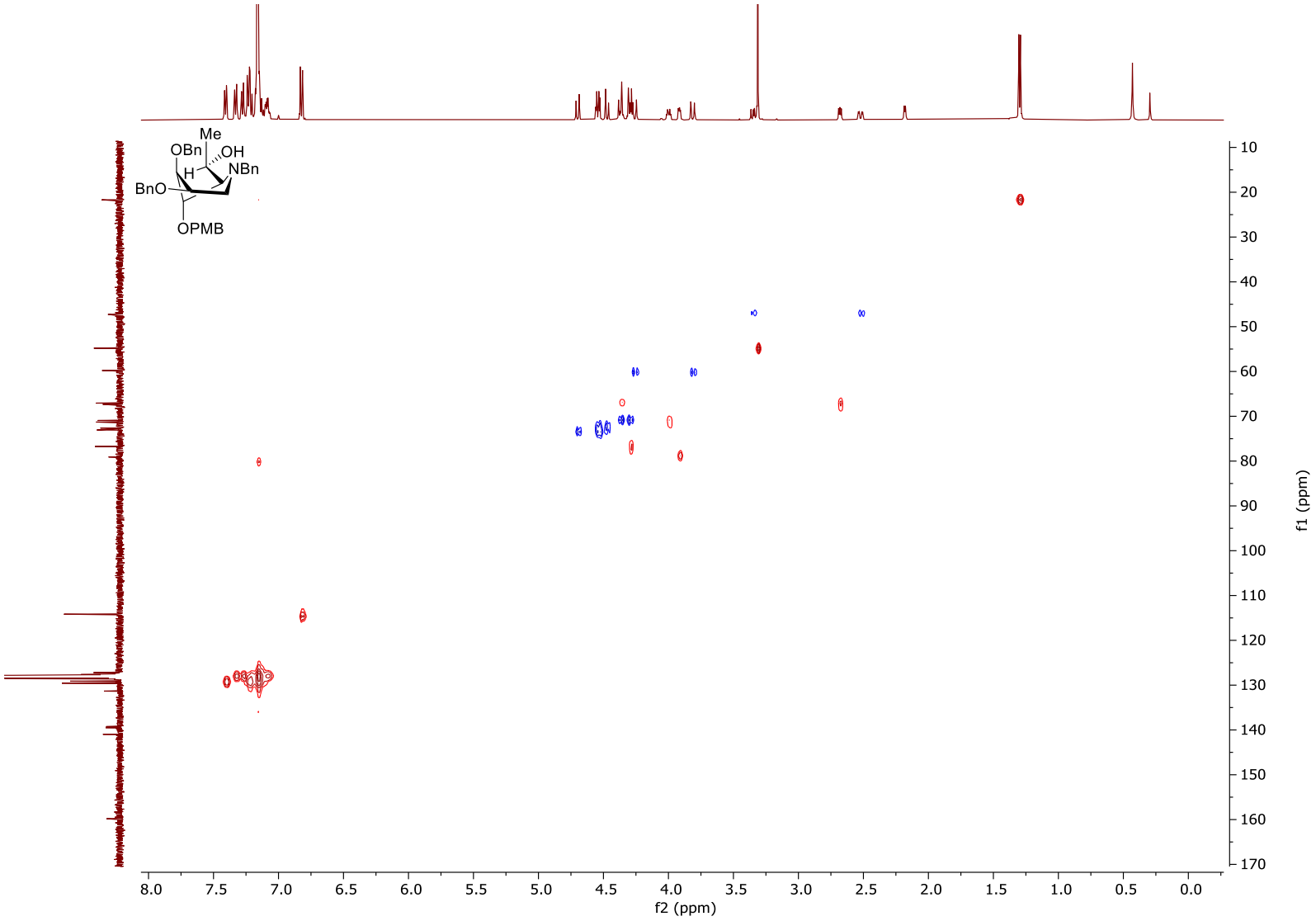

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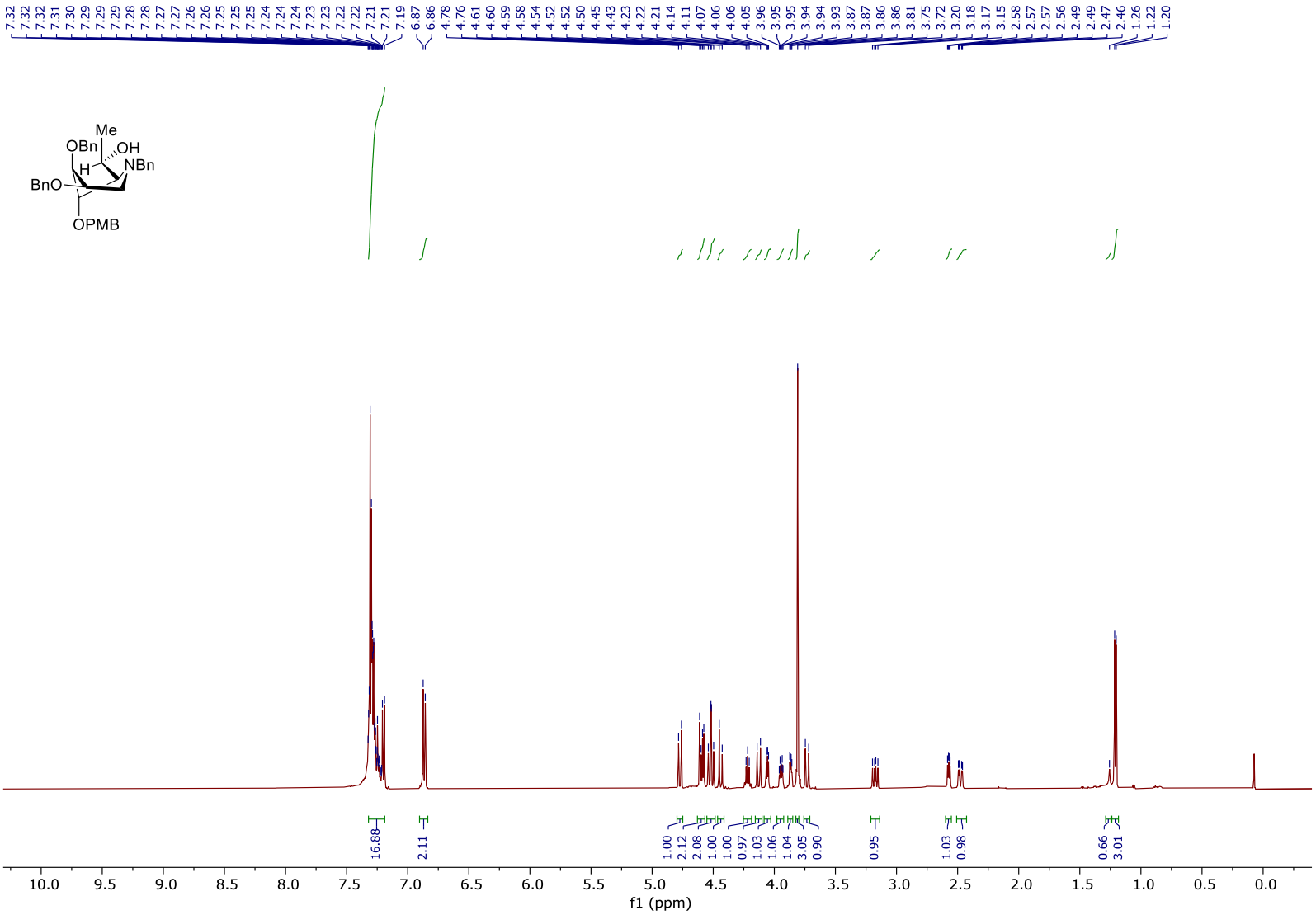

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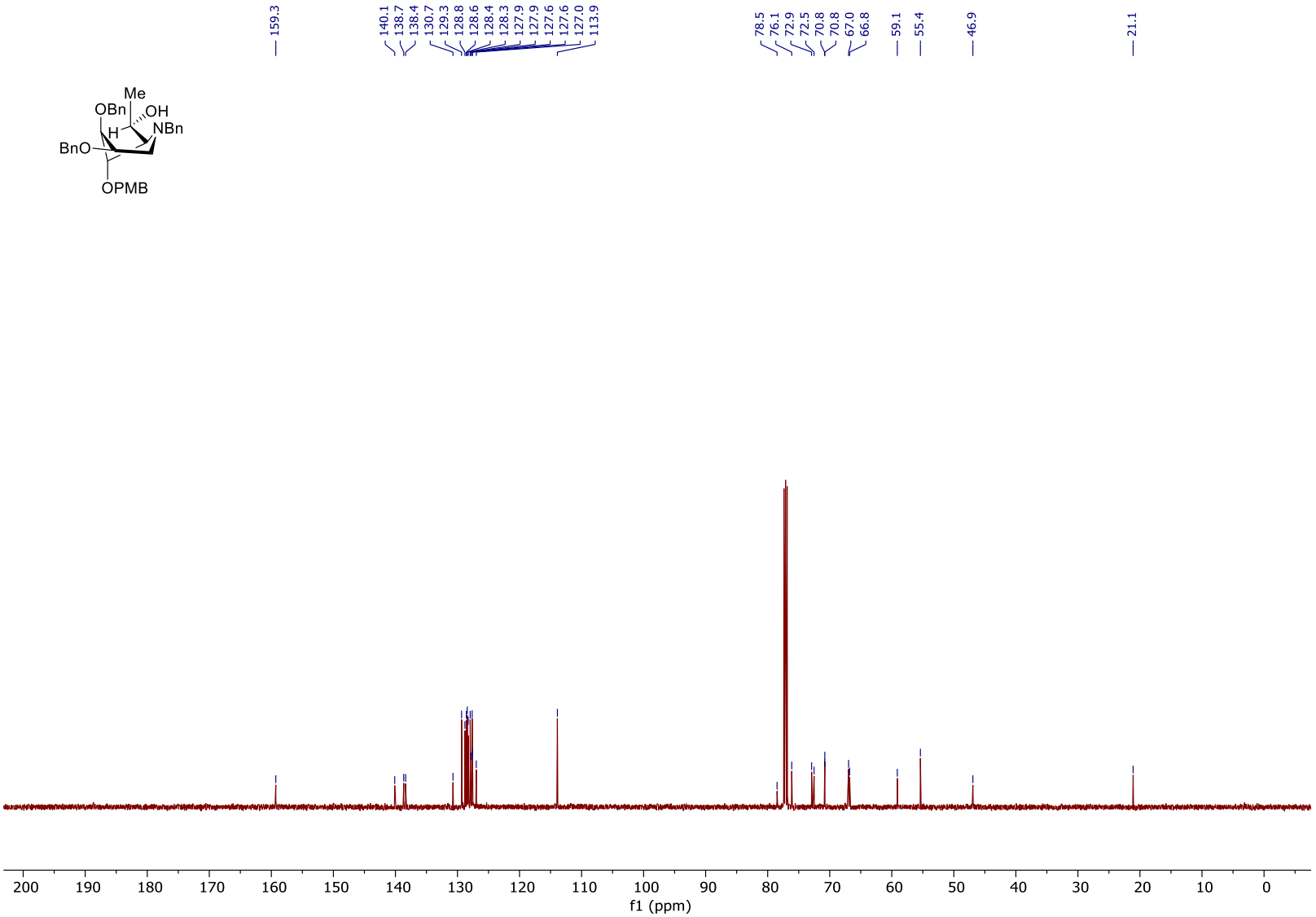

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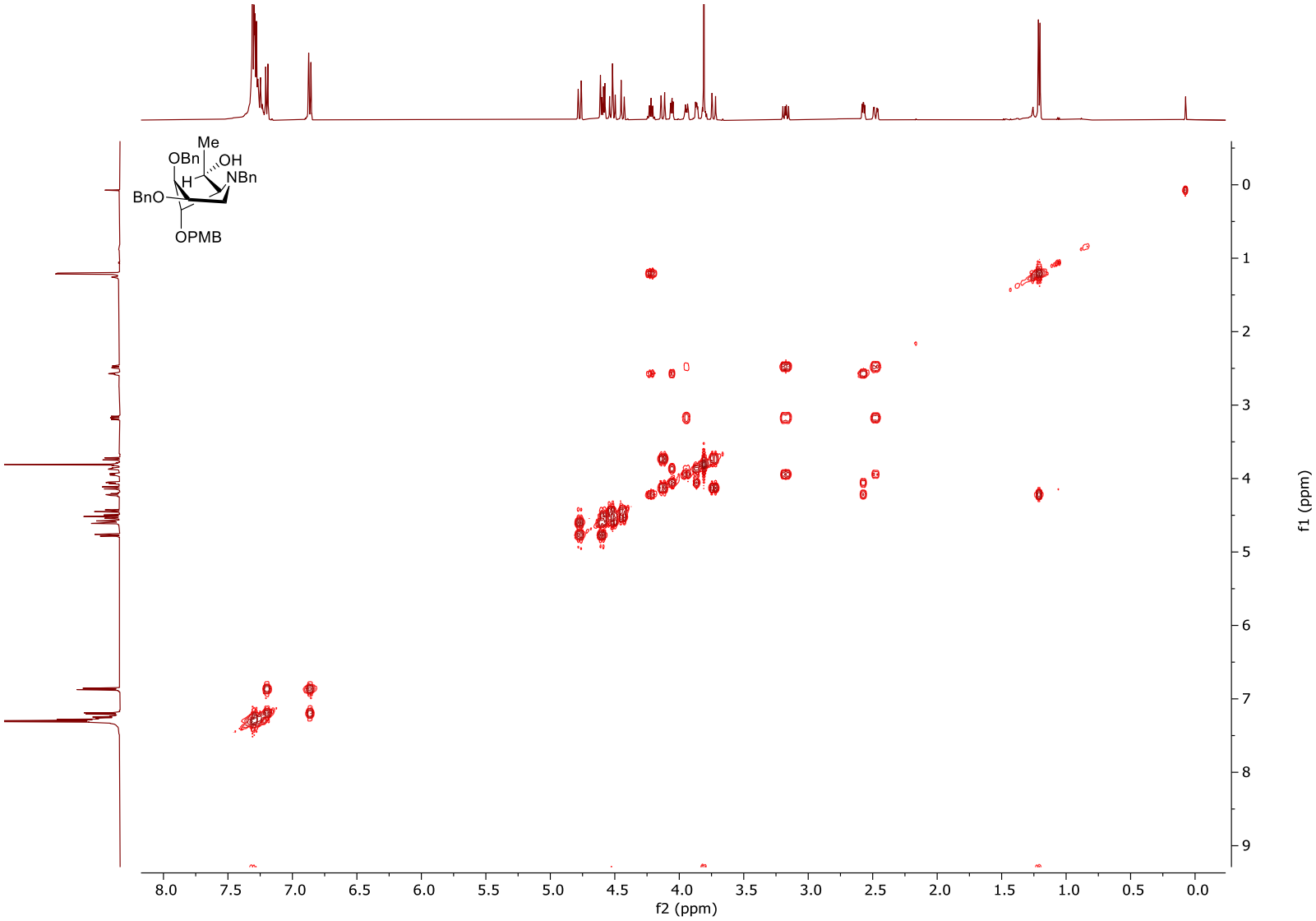

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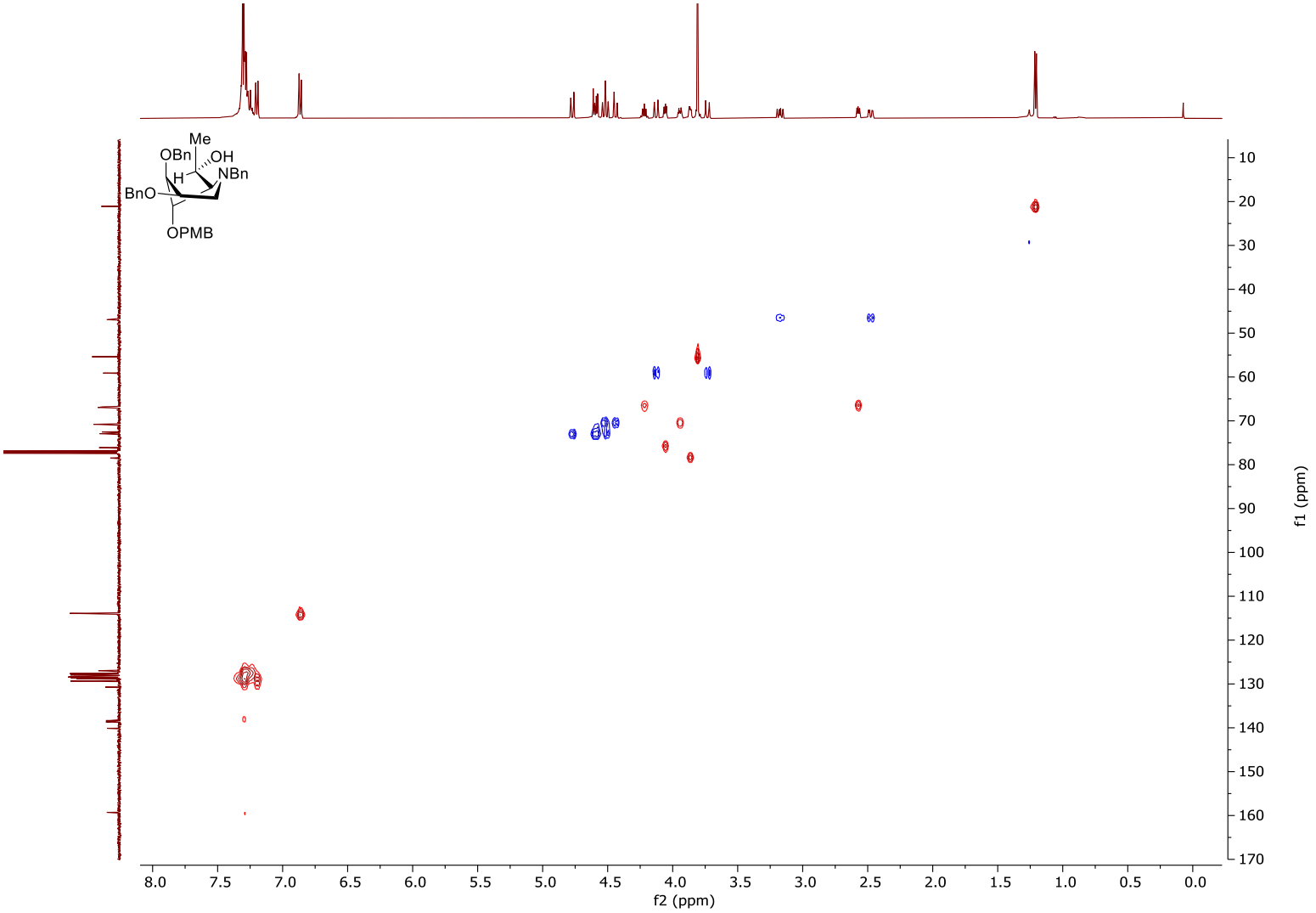
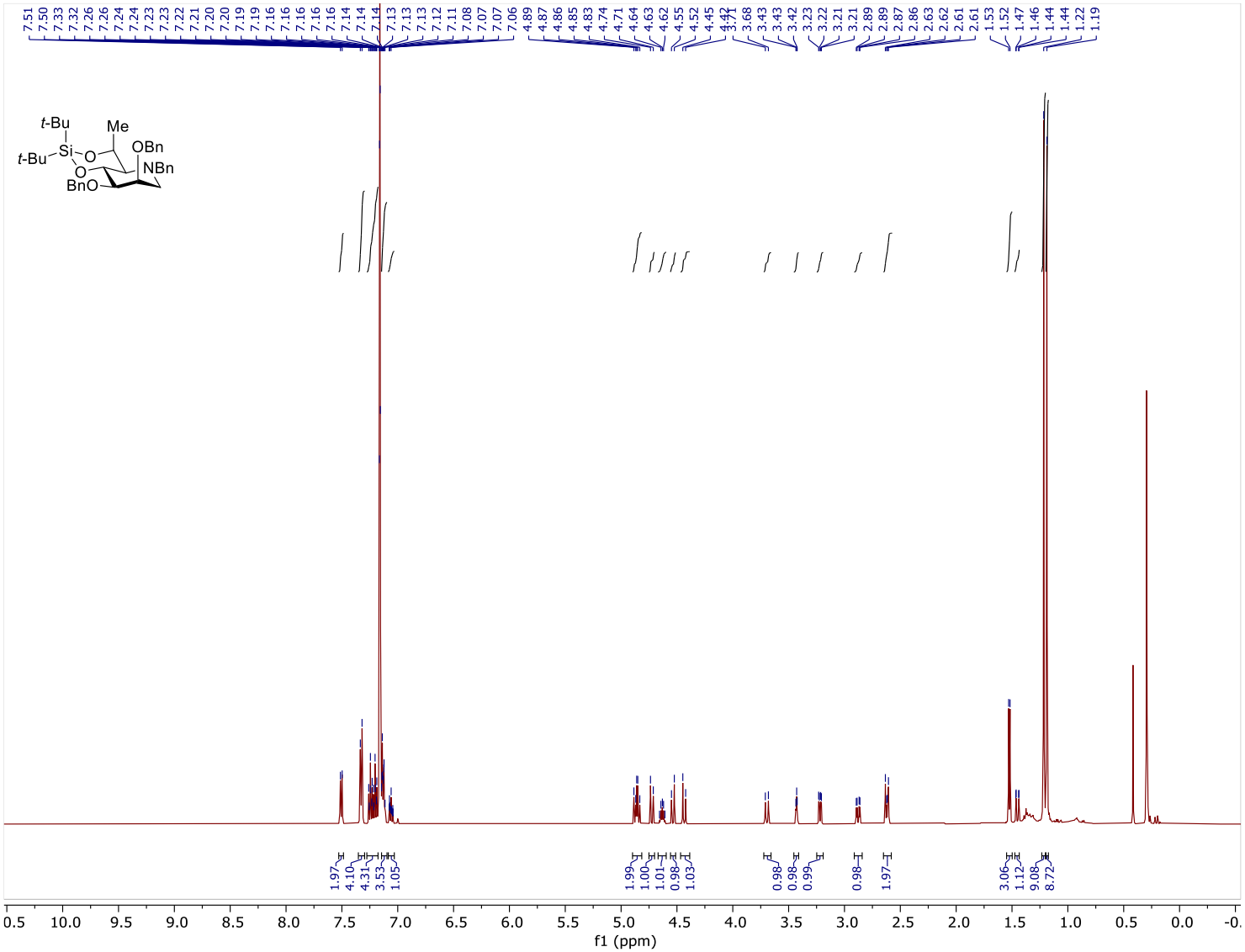
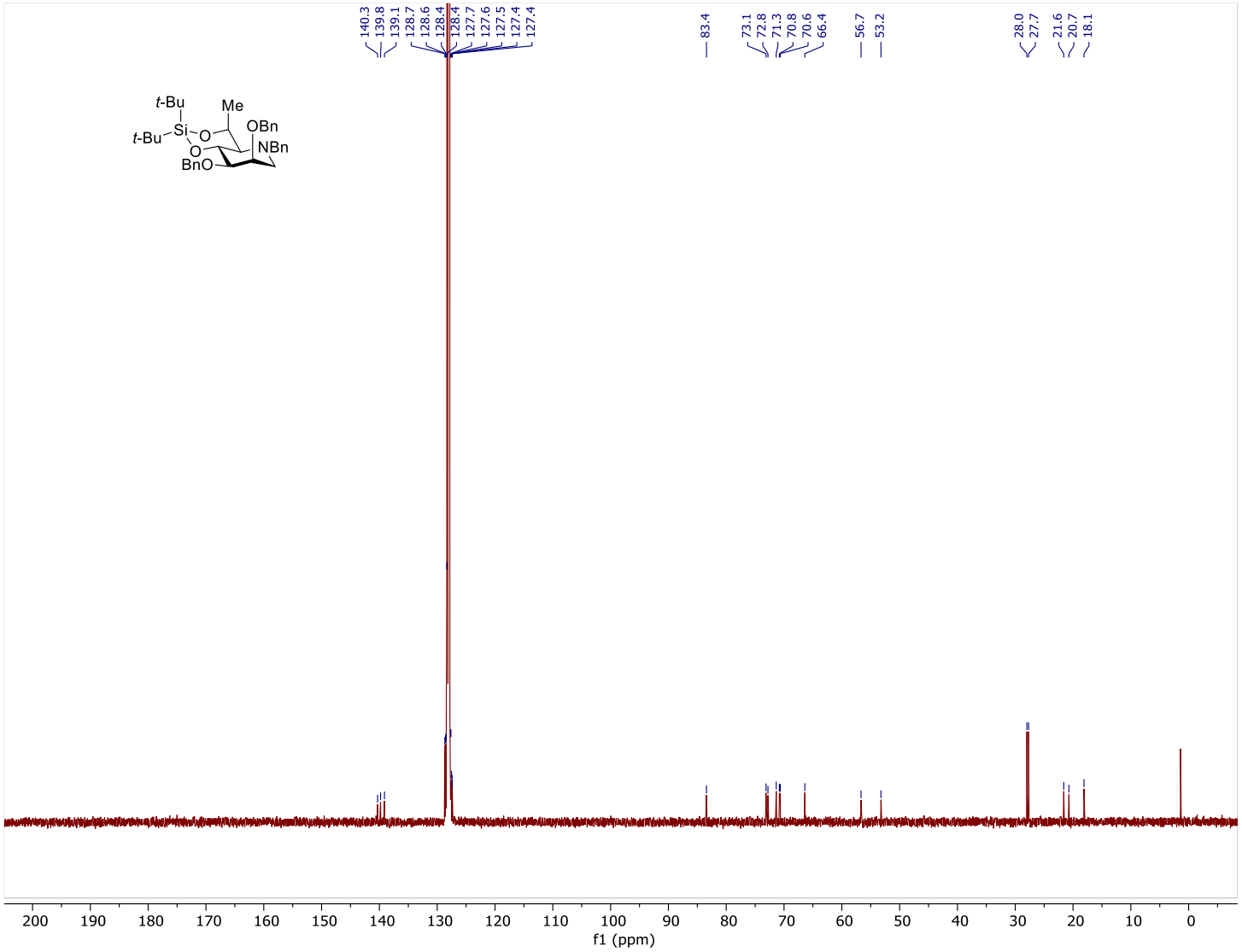


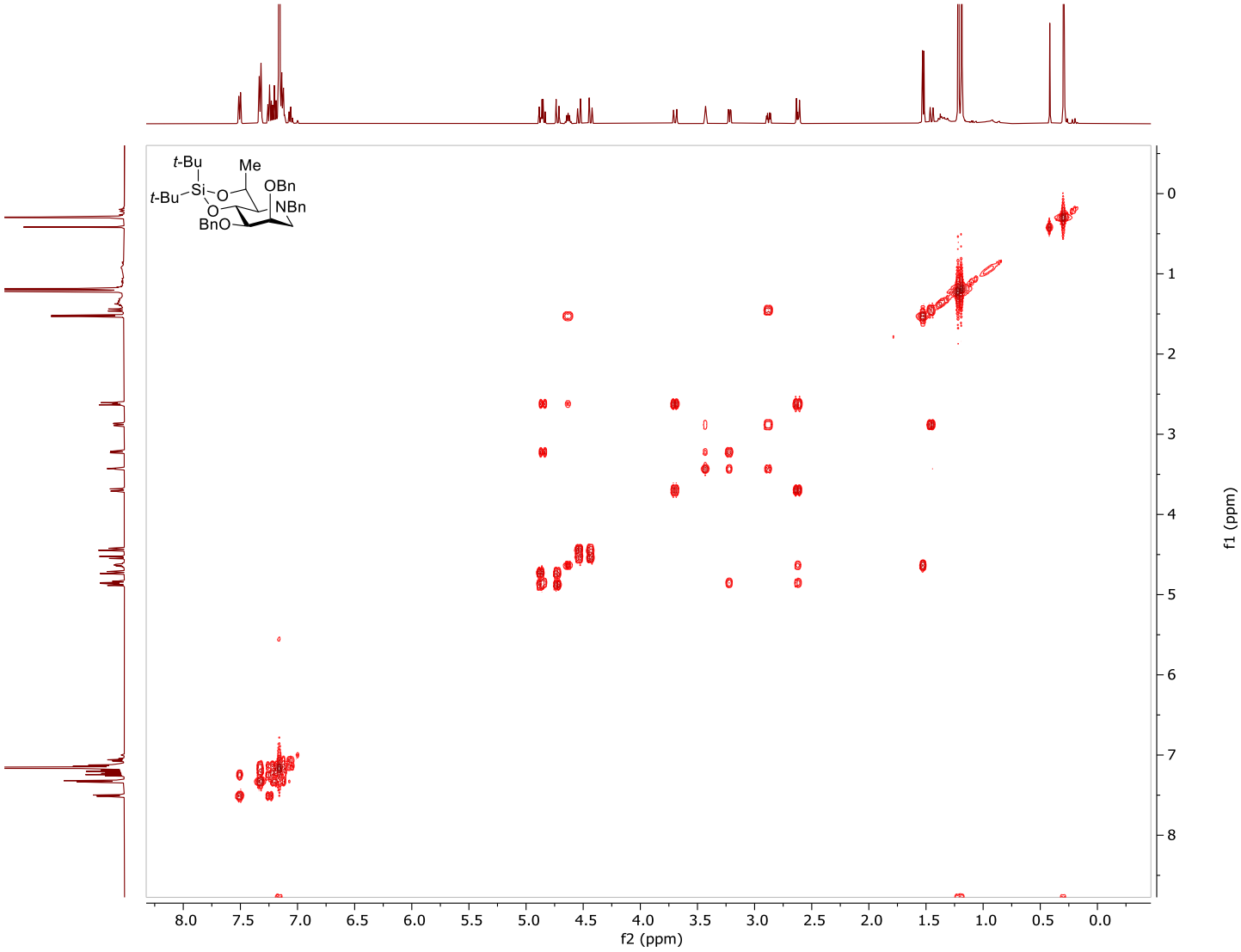
^{1}H NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol (34)



^{13}C NMR (126 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol (34)



COSY NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol (34)



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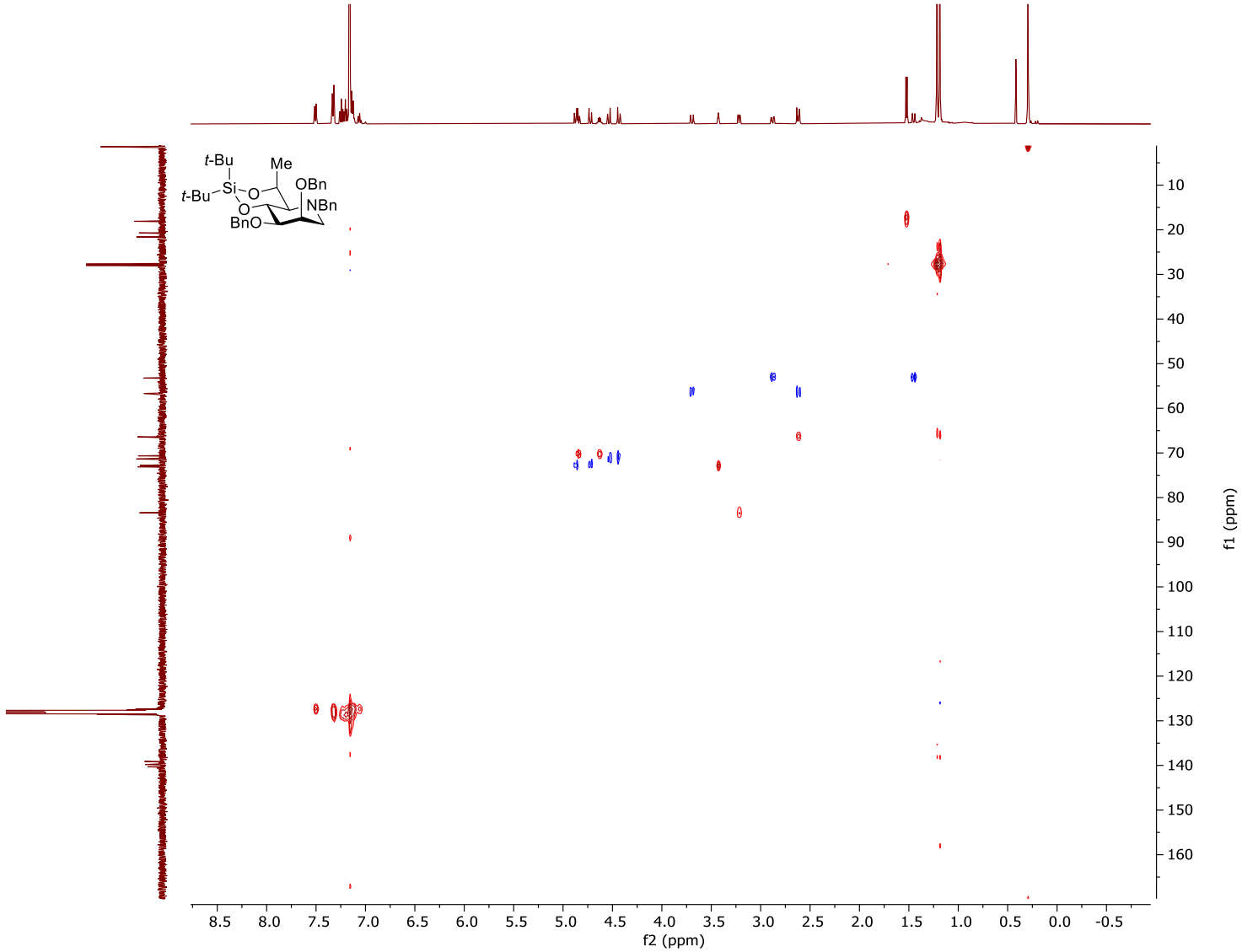
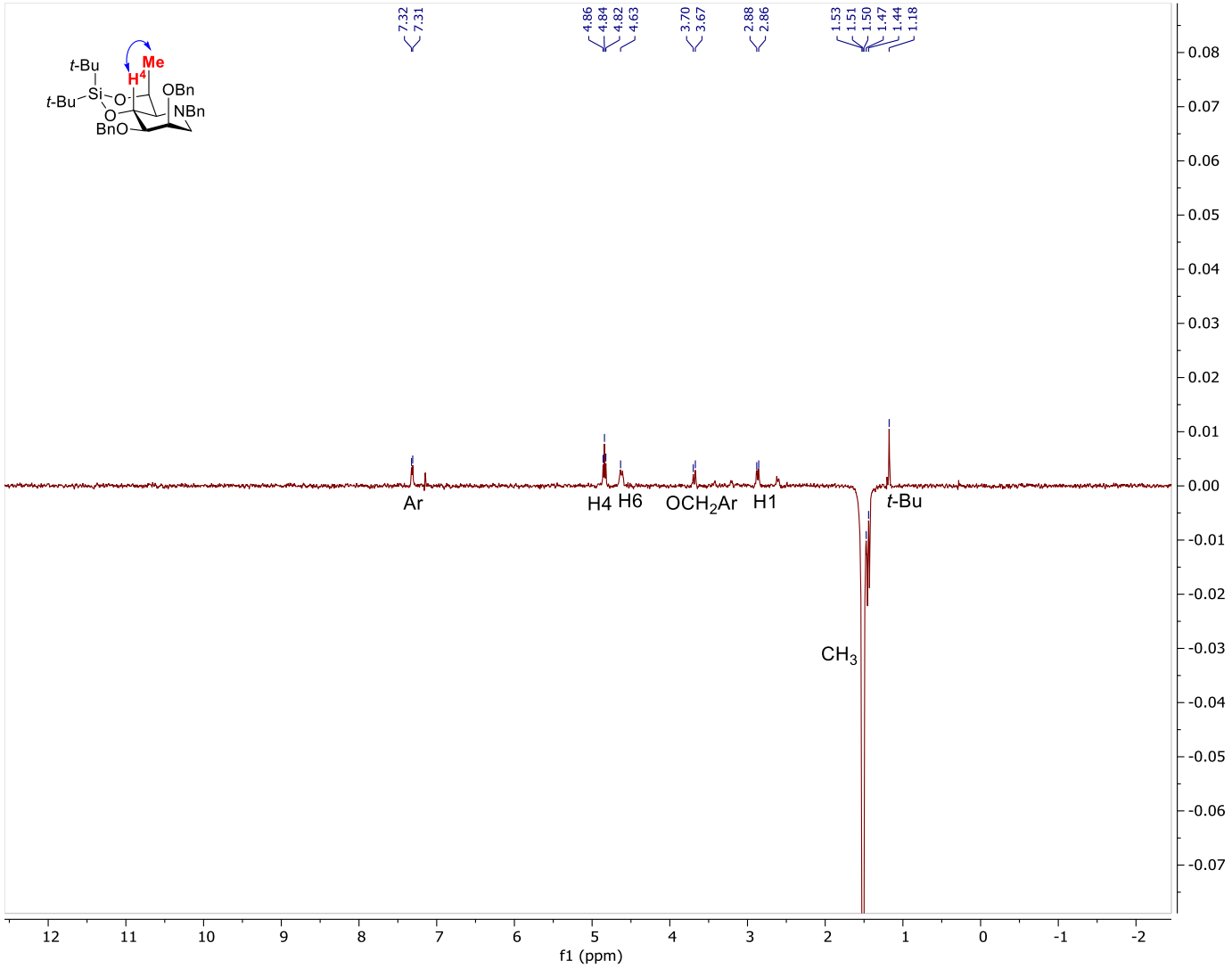


Selective 1D NOESY NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol (34)



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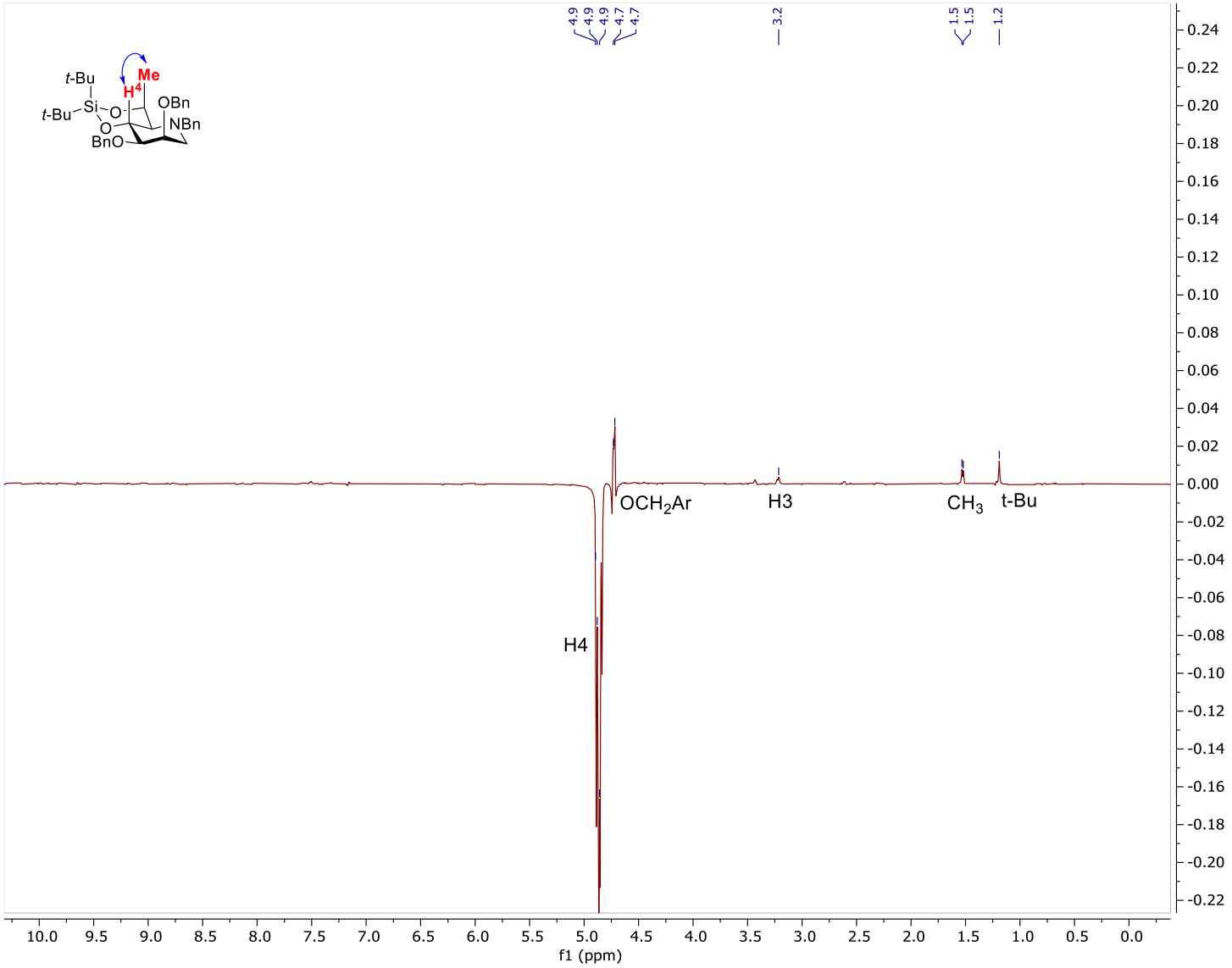
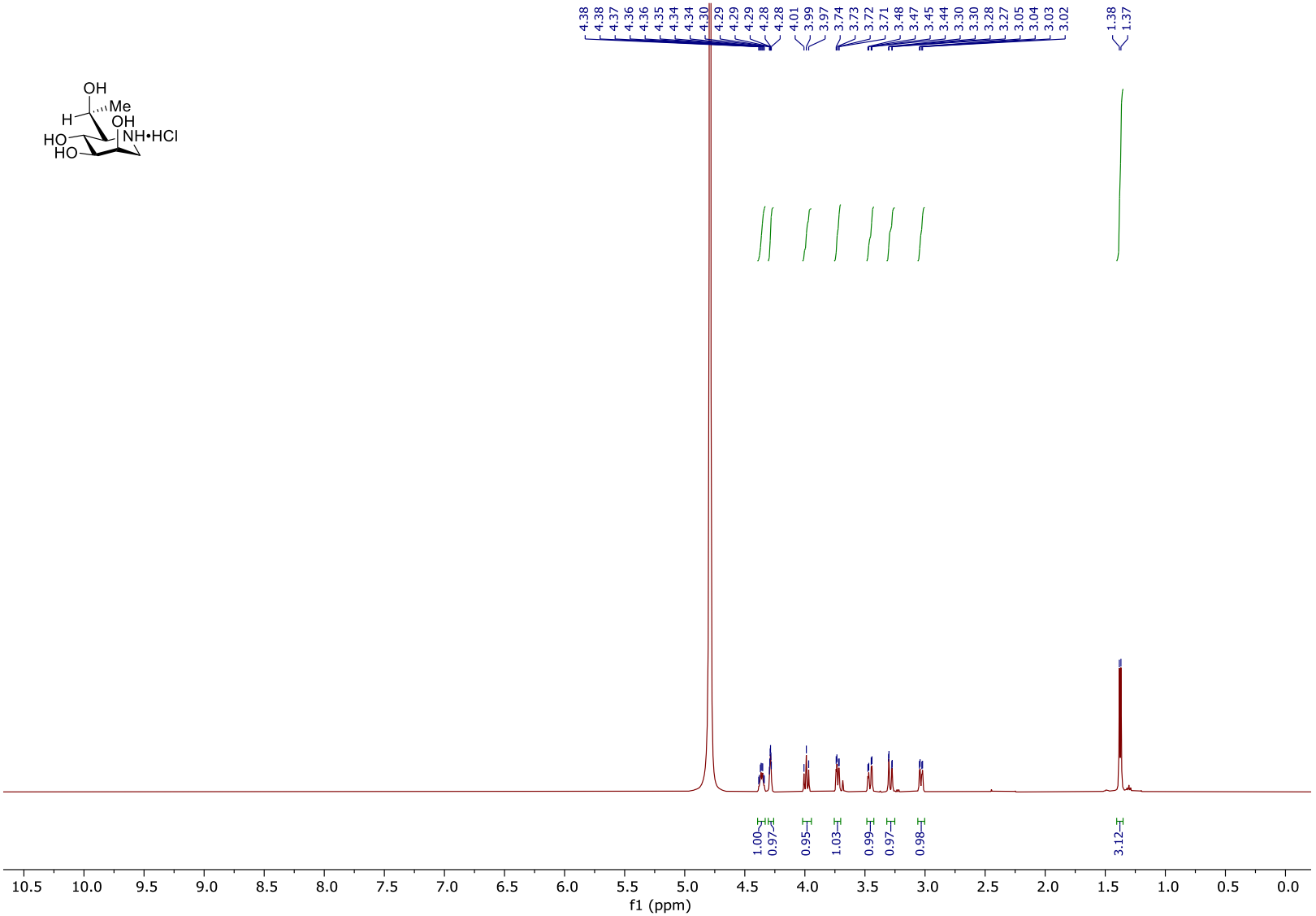
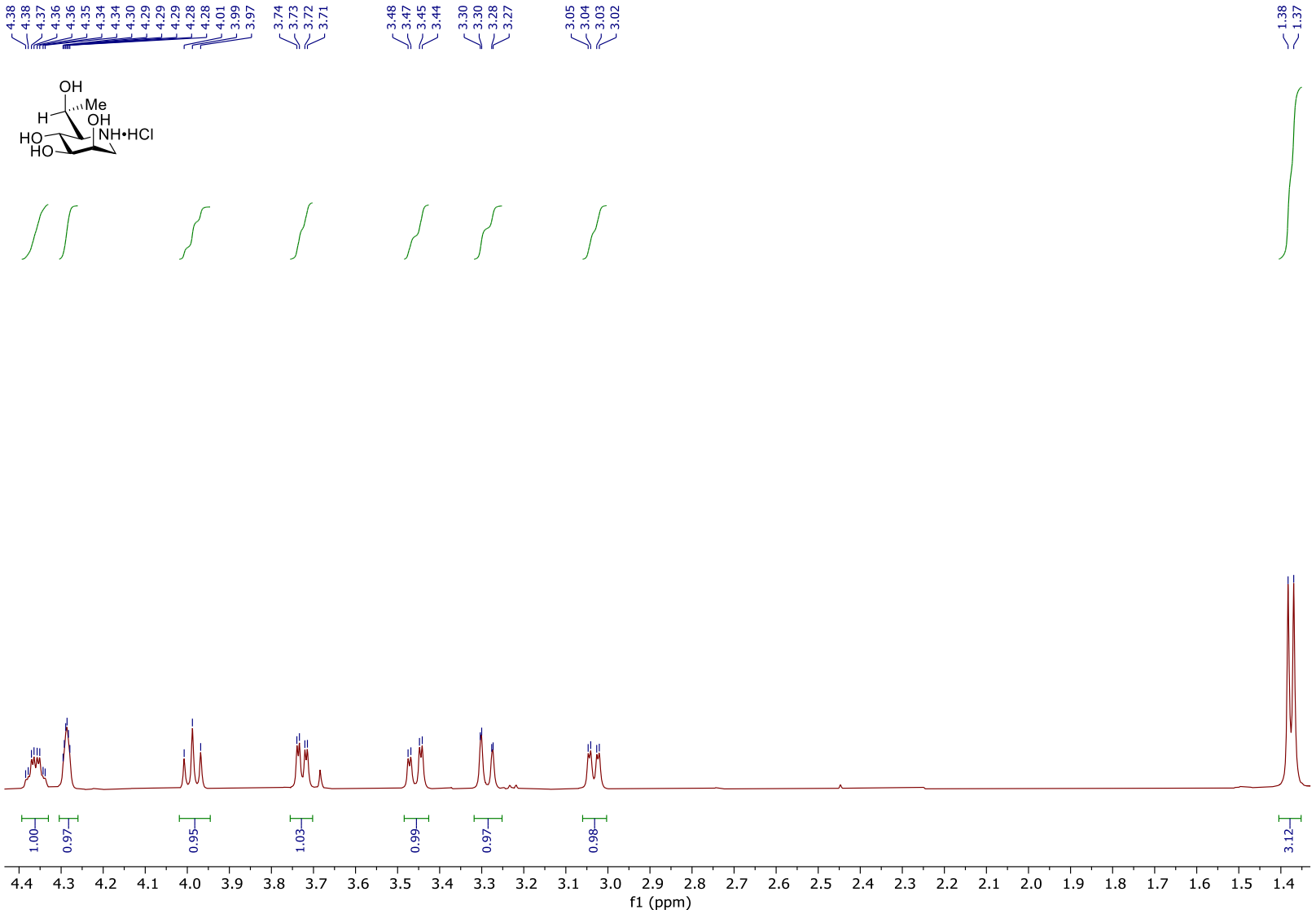


^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol Hydrochloride (7)

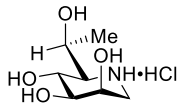


^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol Hydrochloride (7)

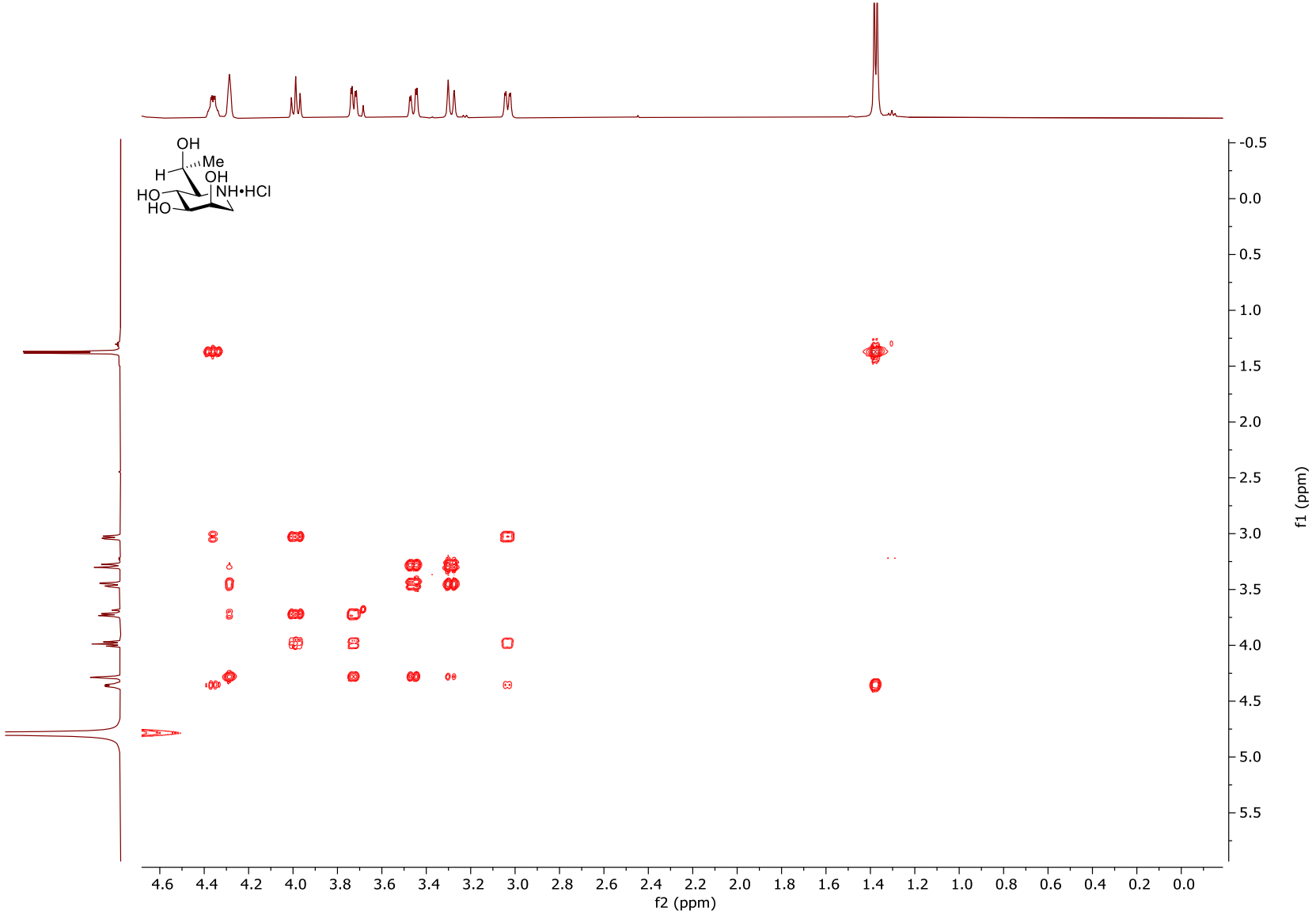
(selected and expanded region from 4.4 to 1.4 ppm)



^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol Hydrochloride (7)



COSY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-L-*glycero*-D-*manno*-heptitol Hydrochloride (7)



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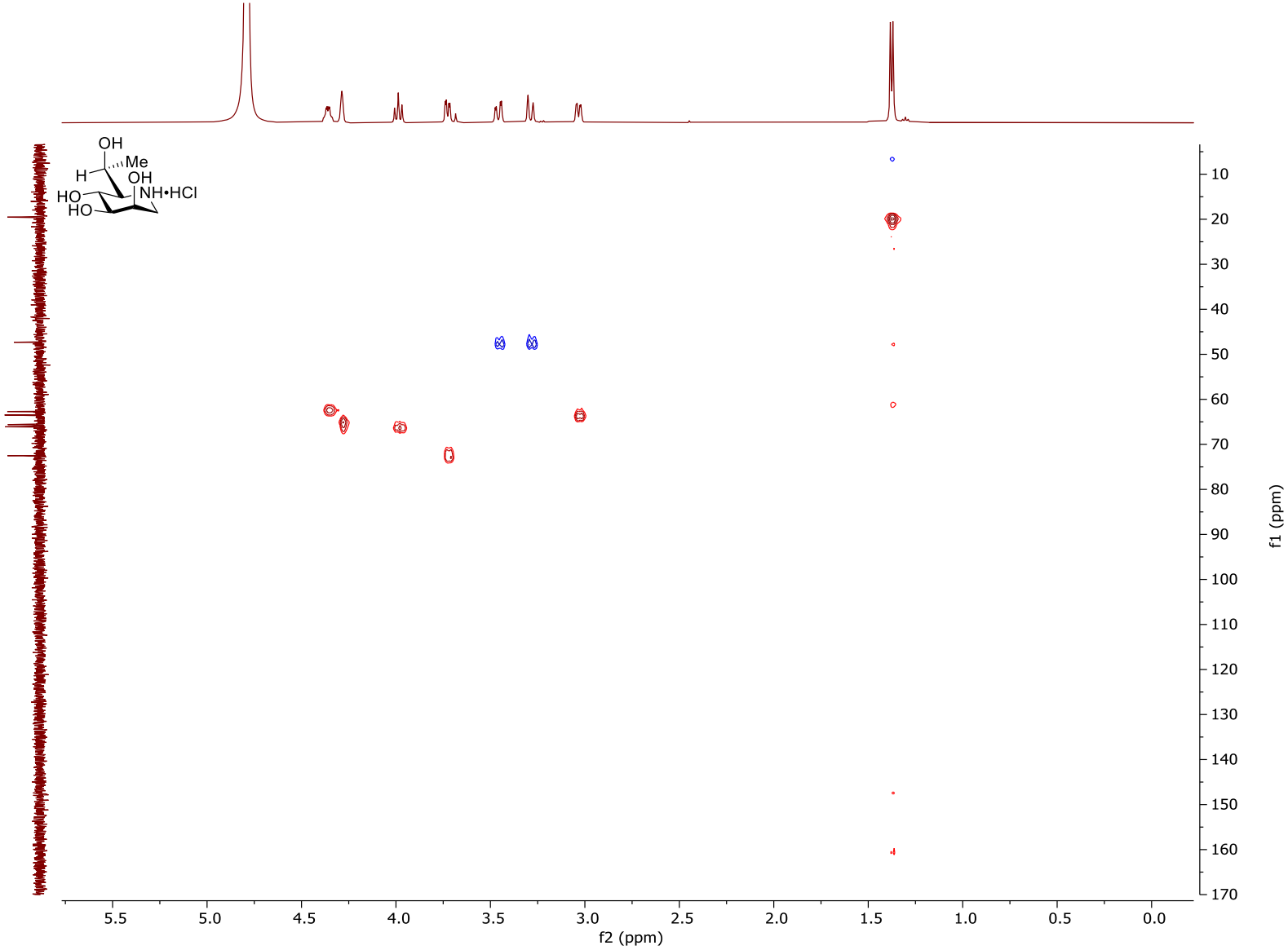

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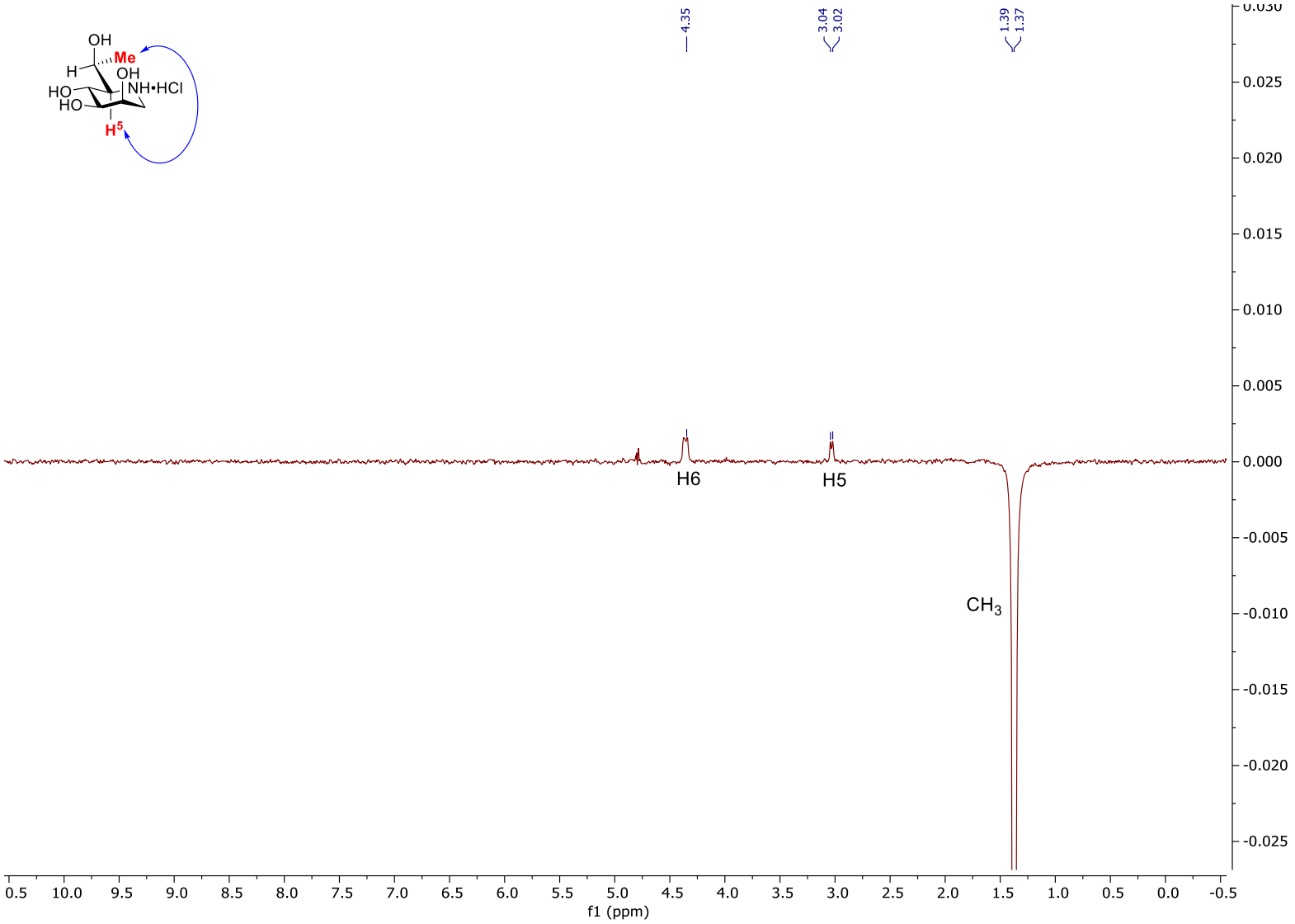

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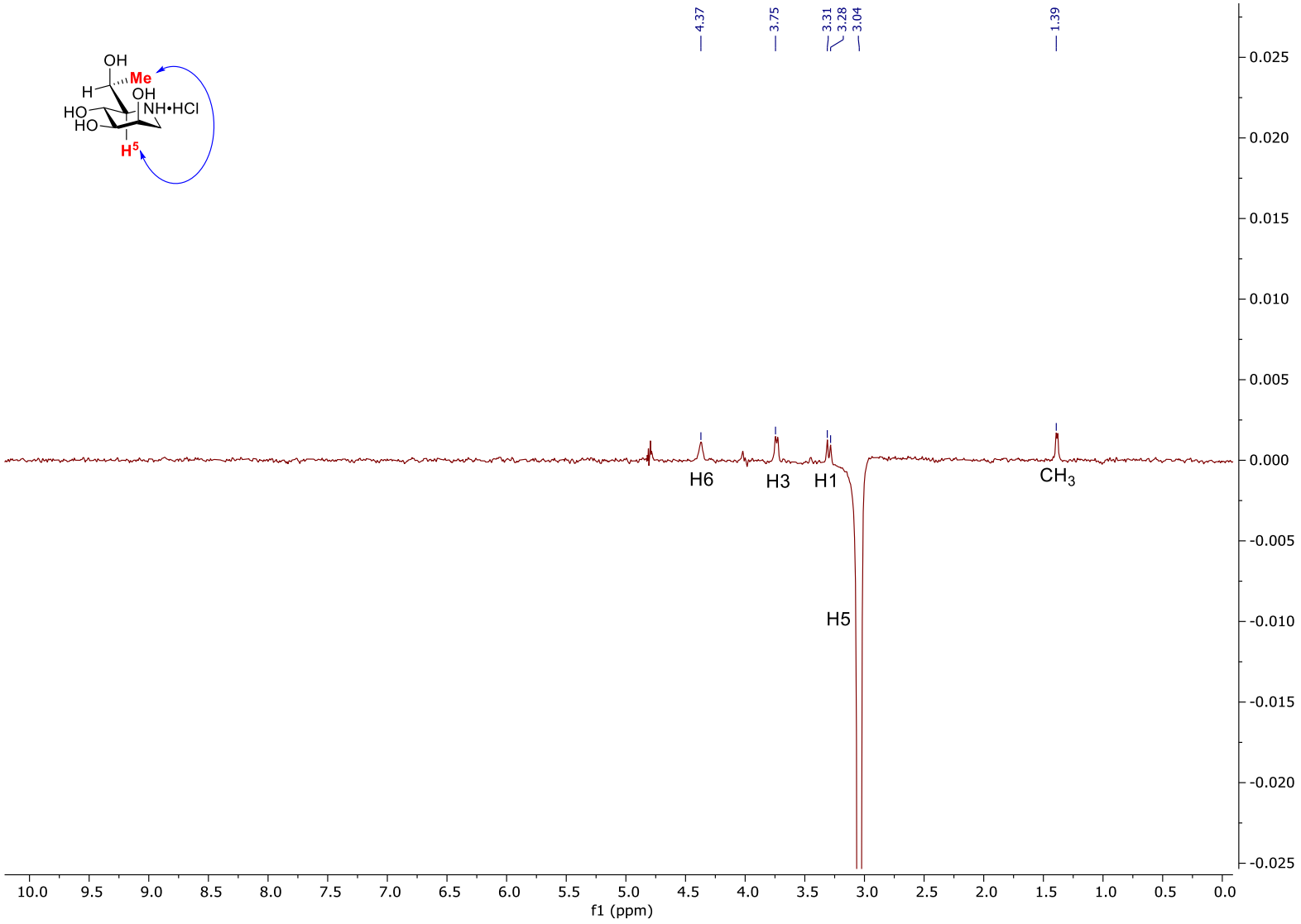

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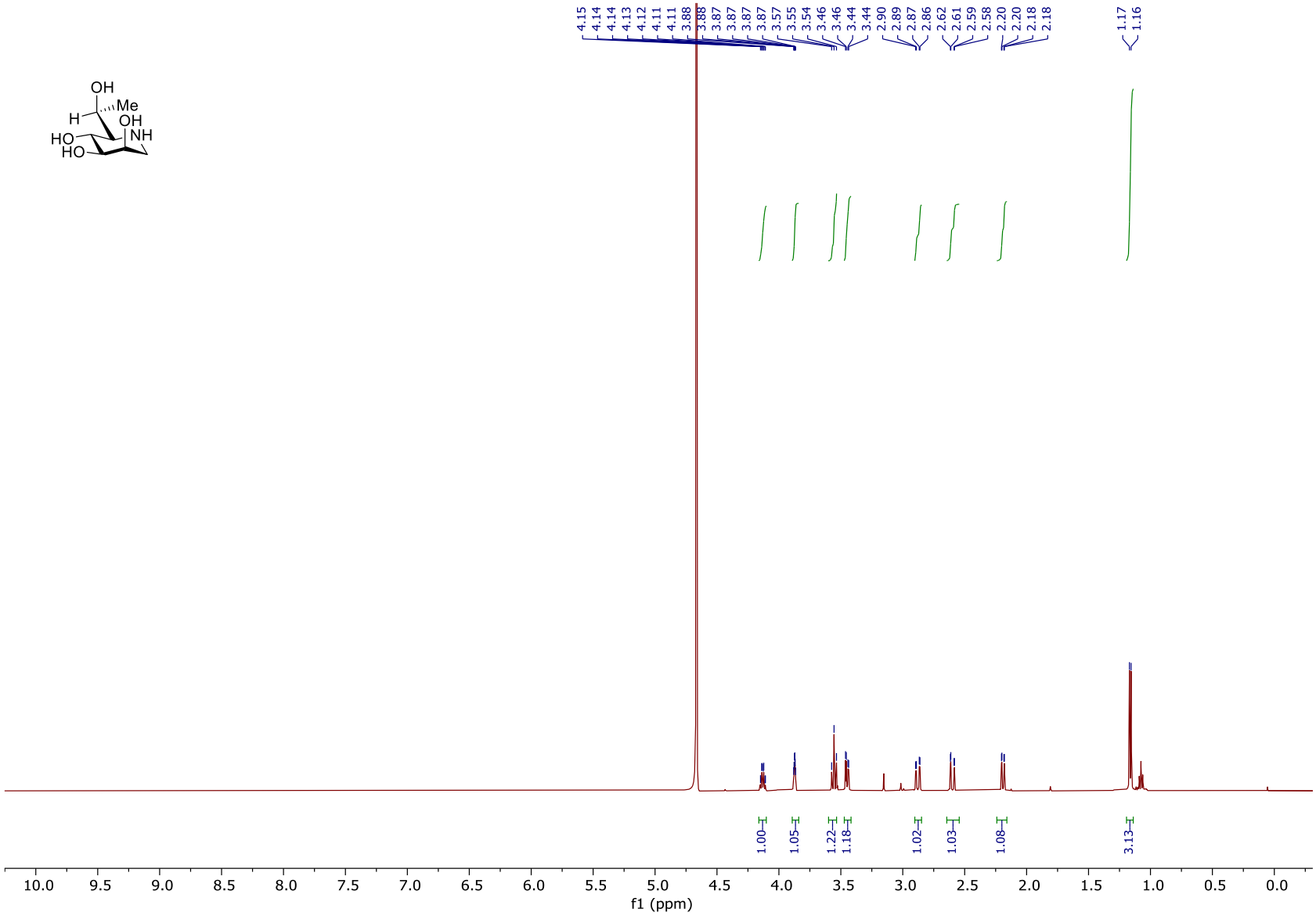

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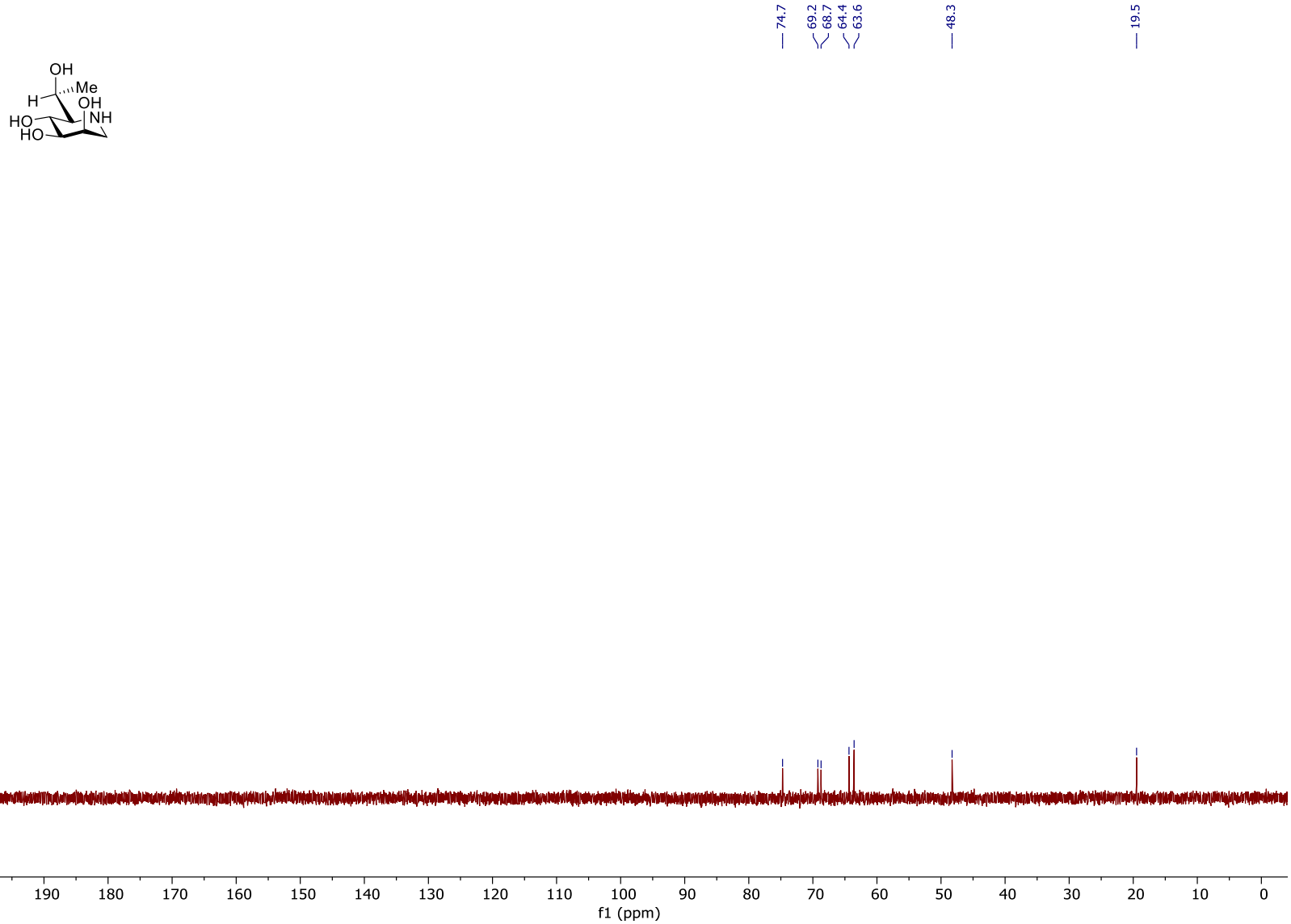

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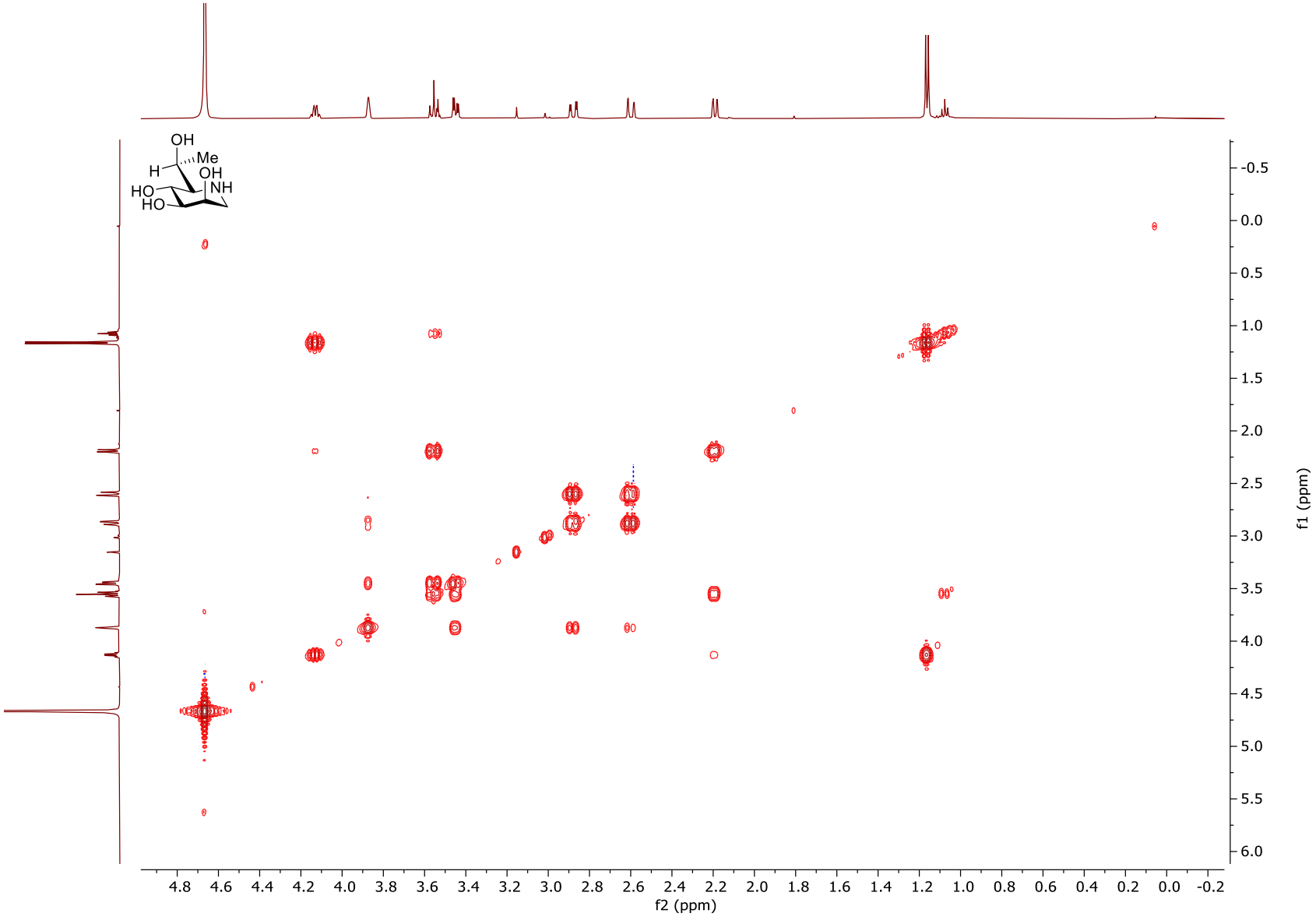

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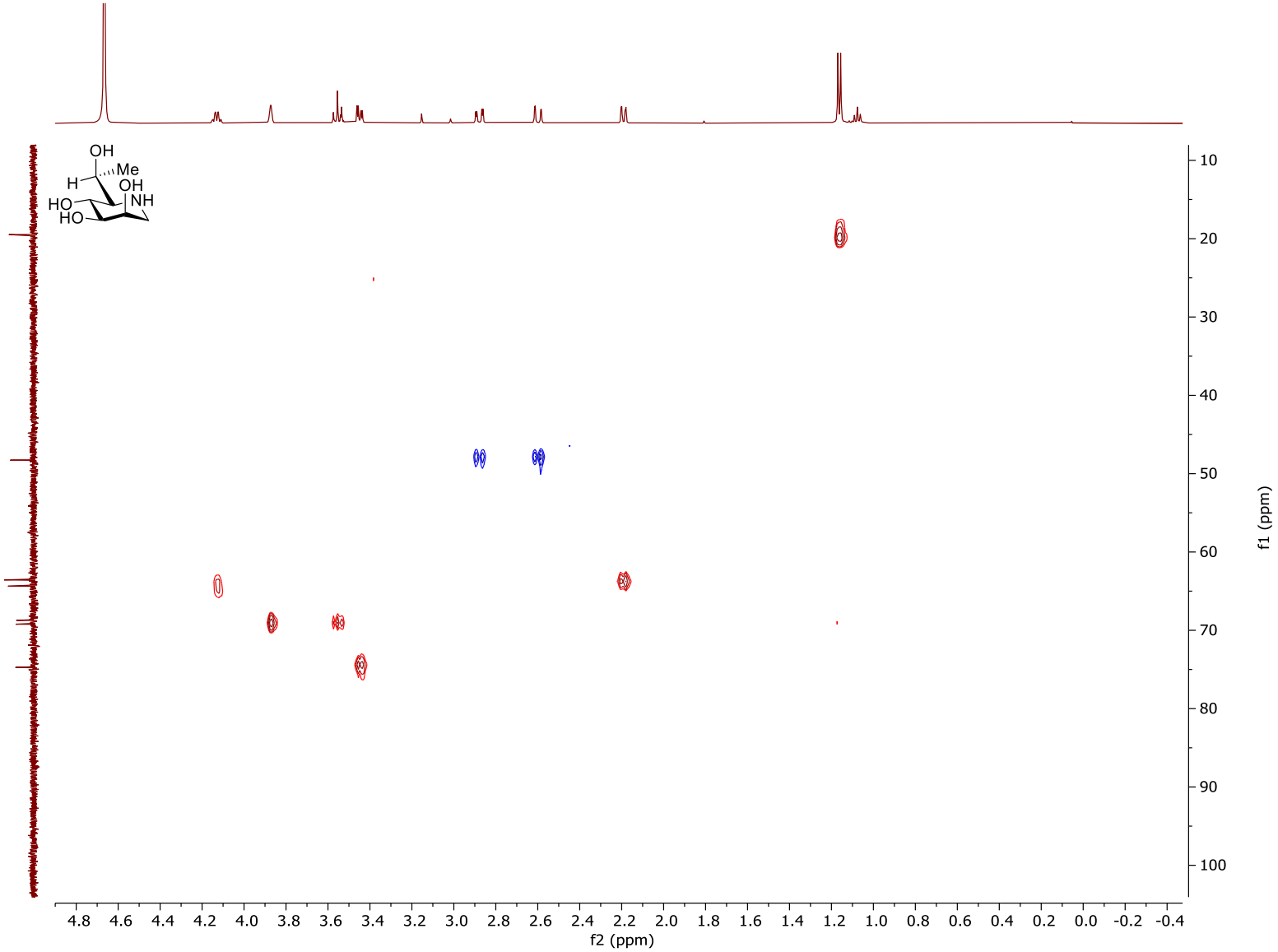

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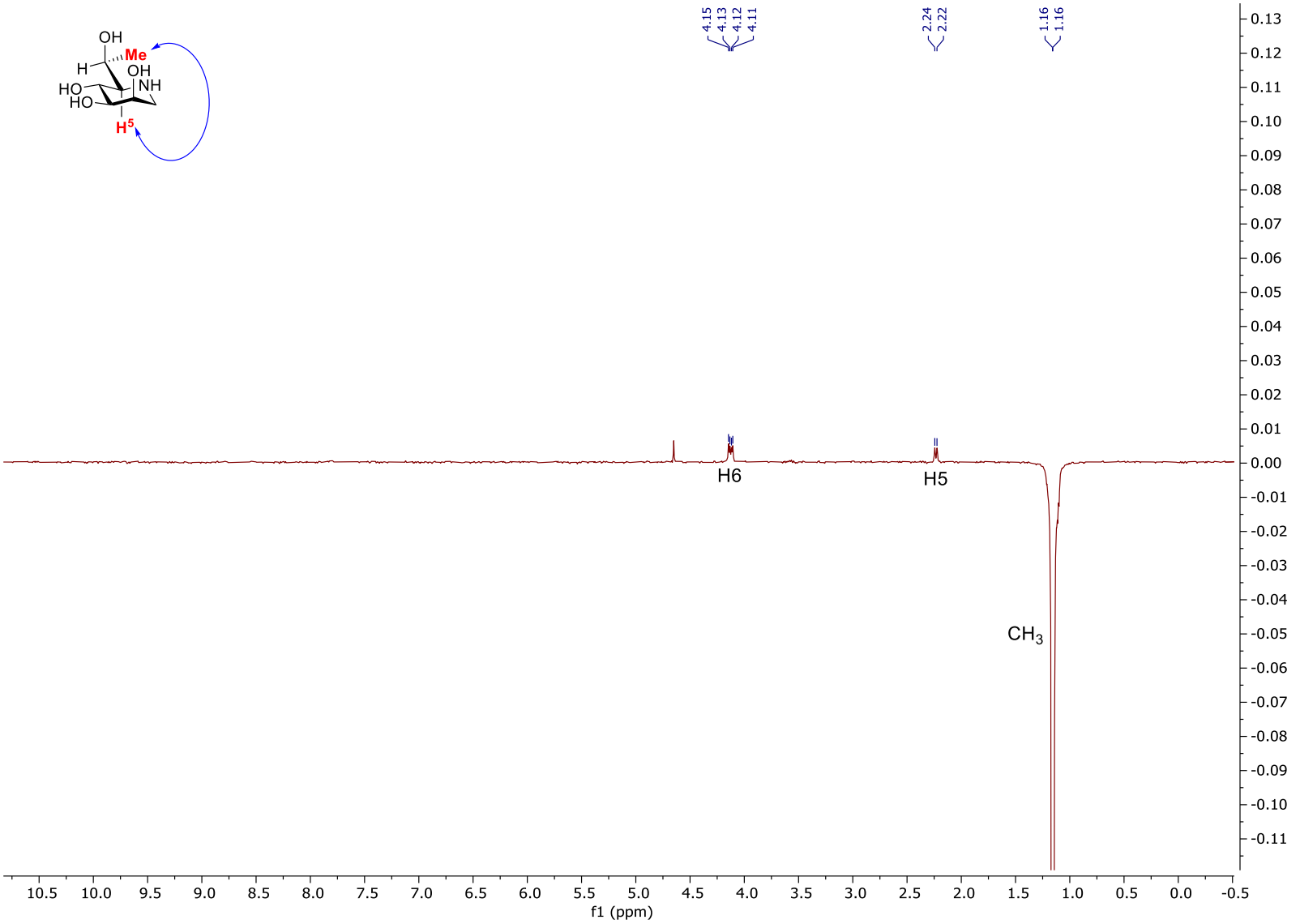

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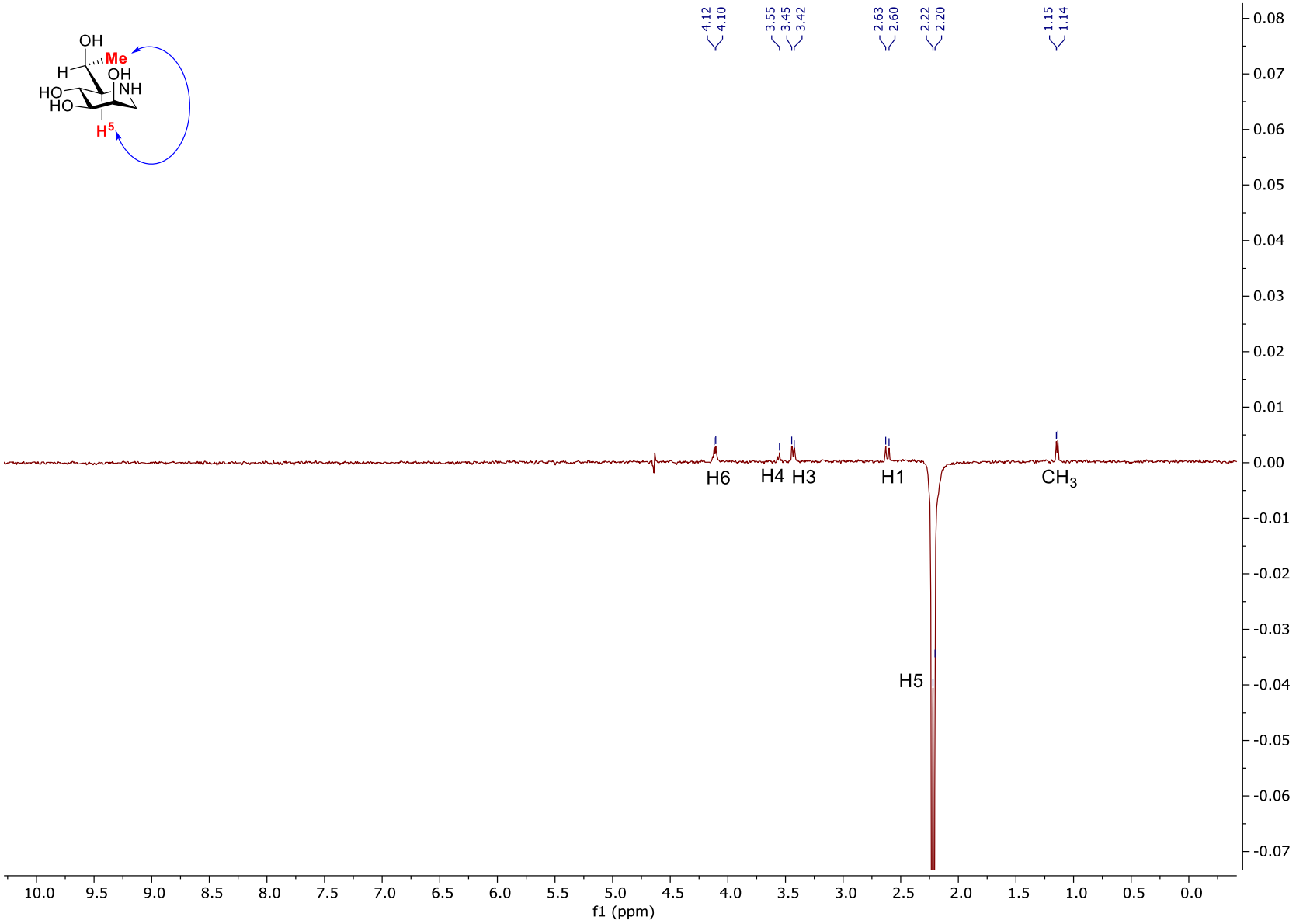

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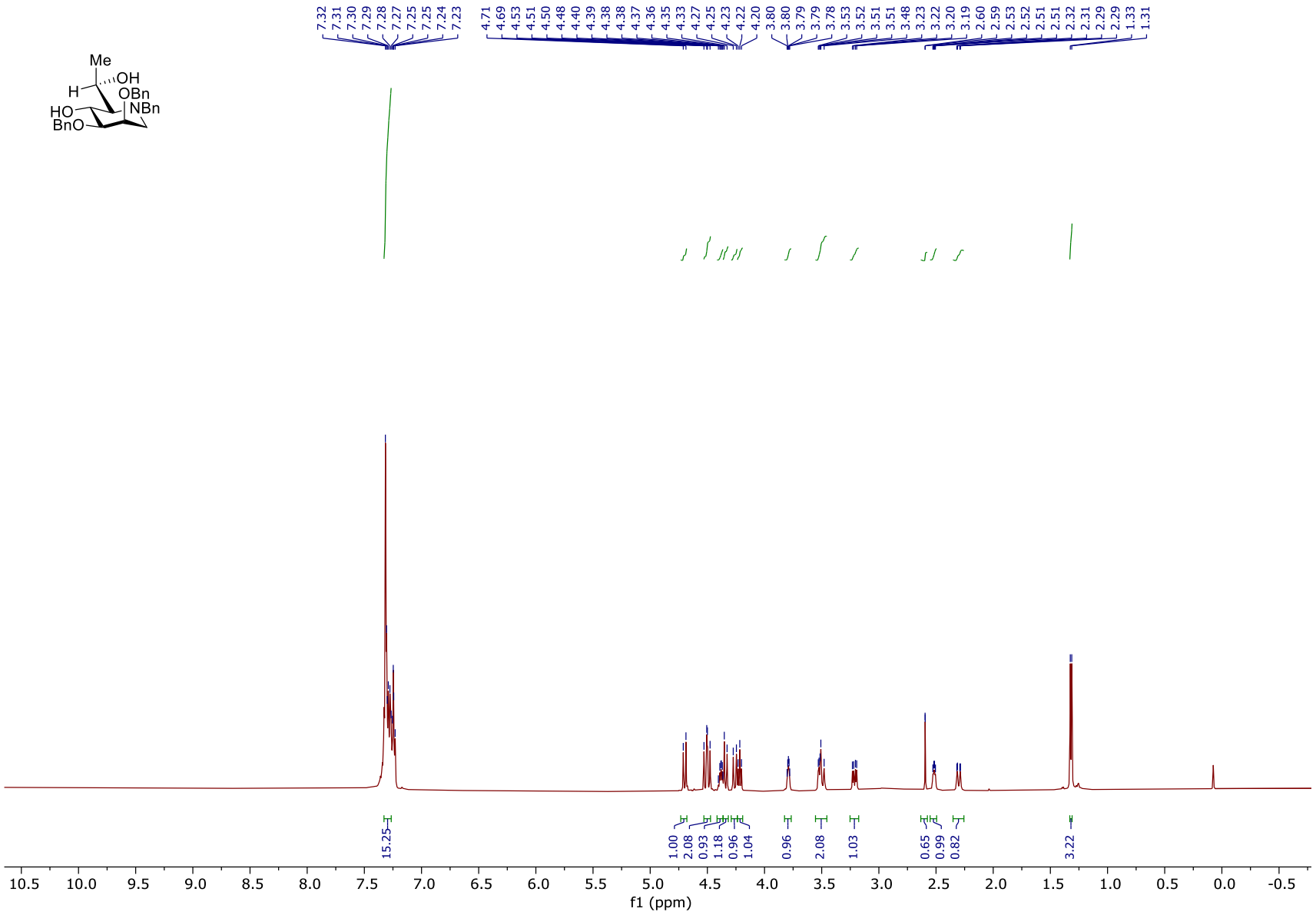

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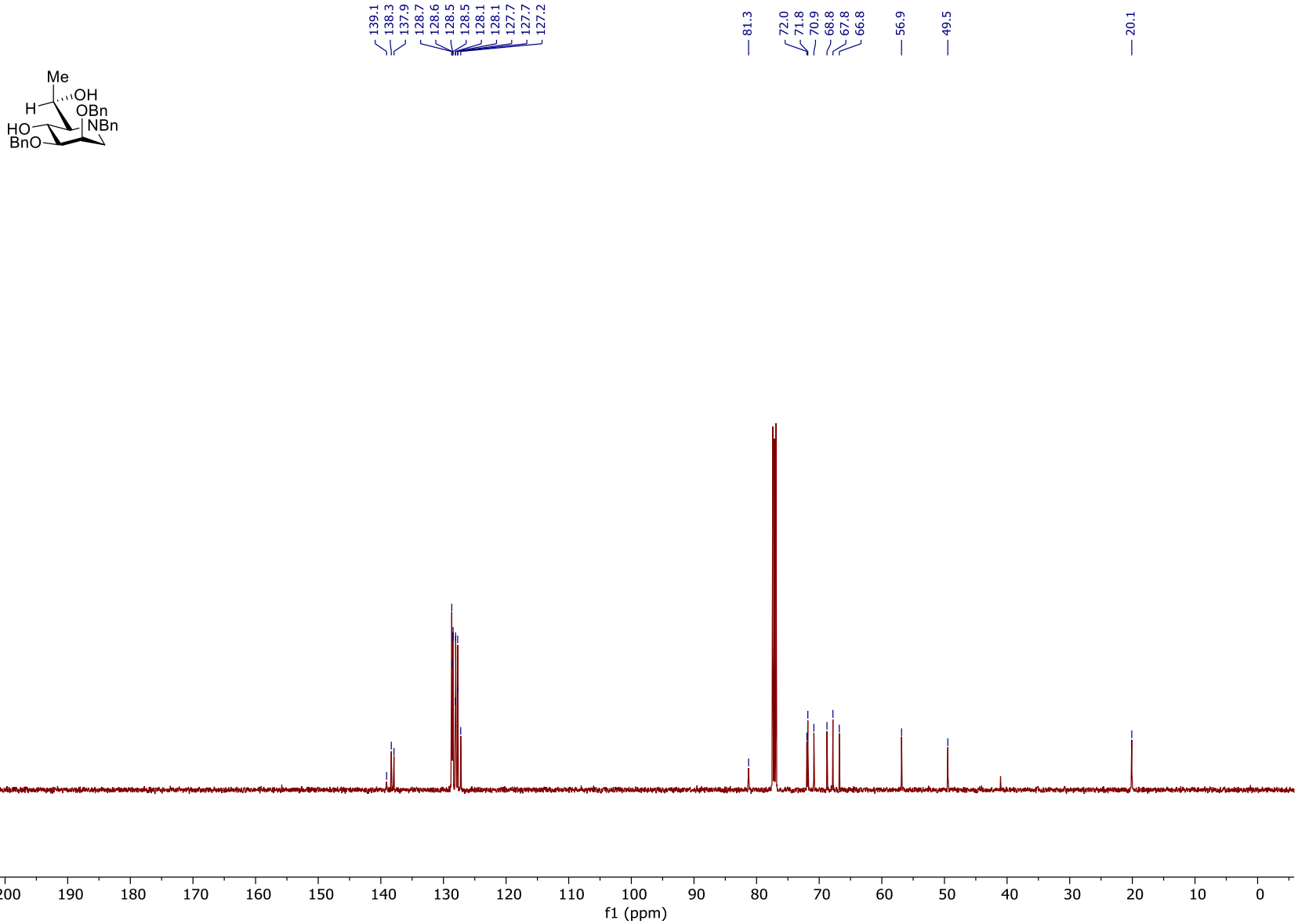

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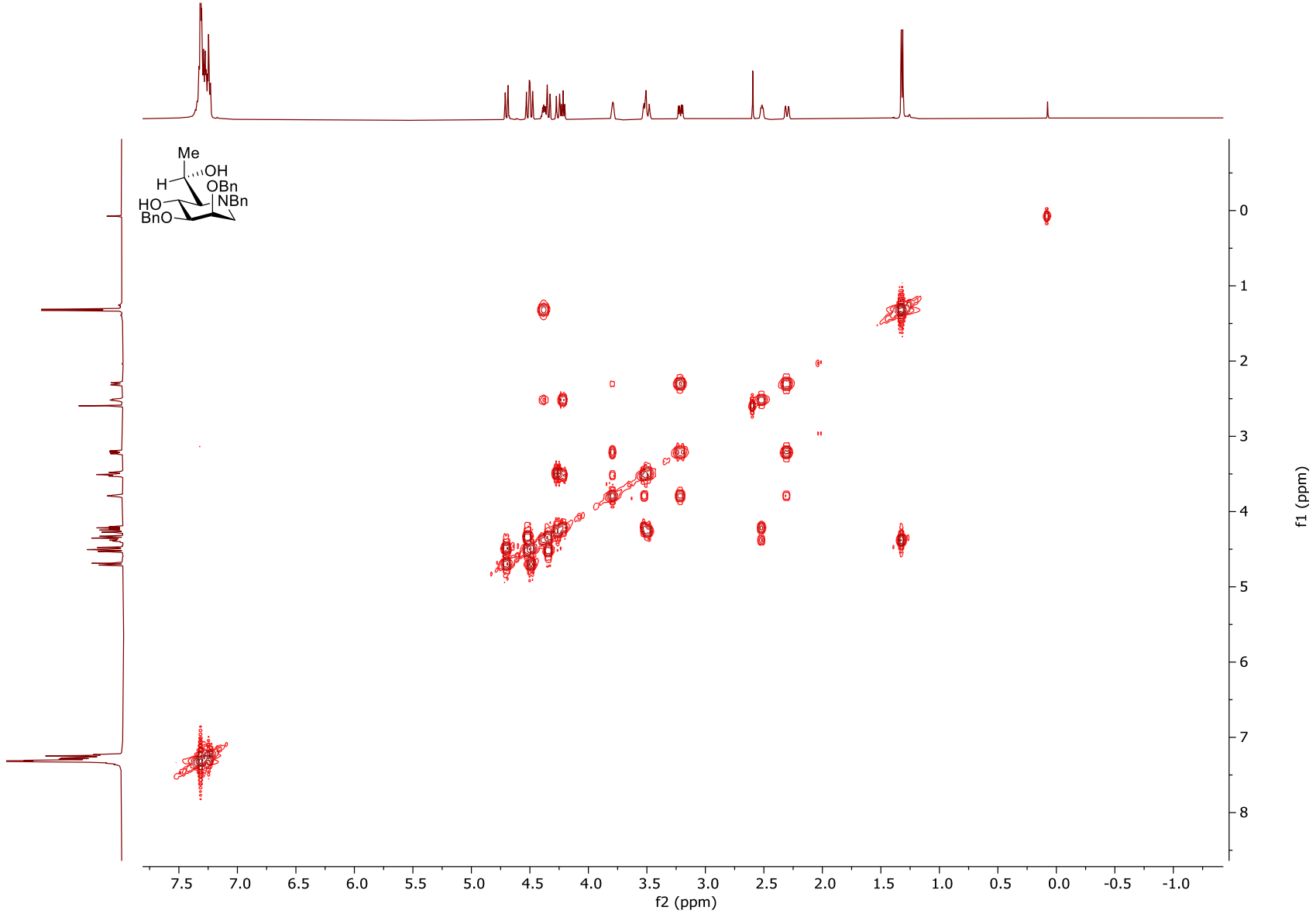

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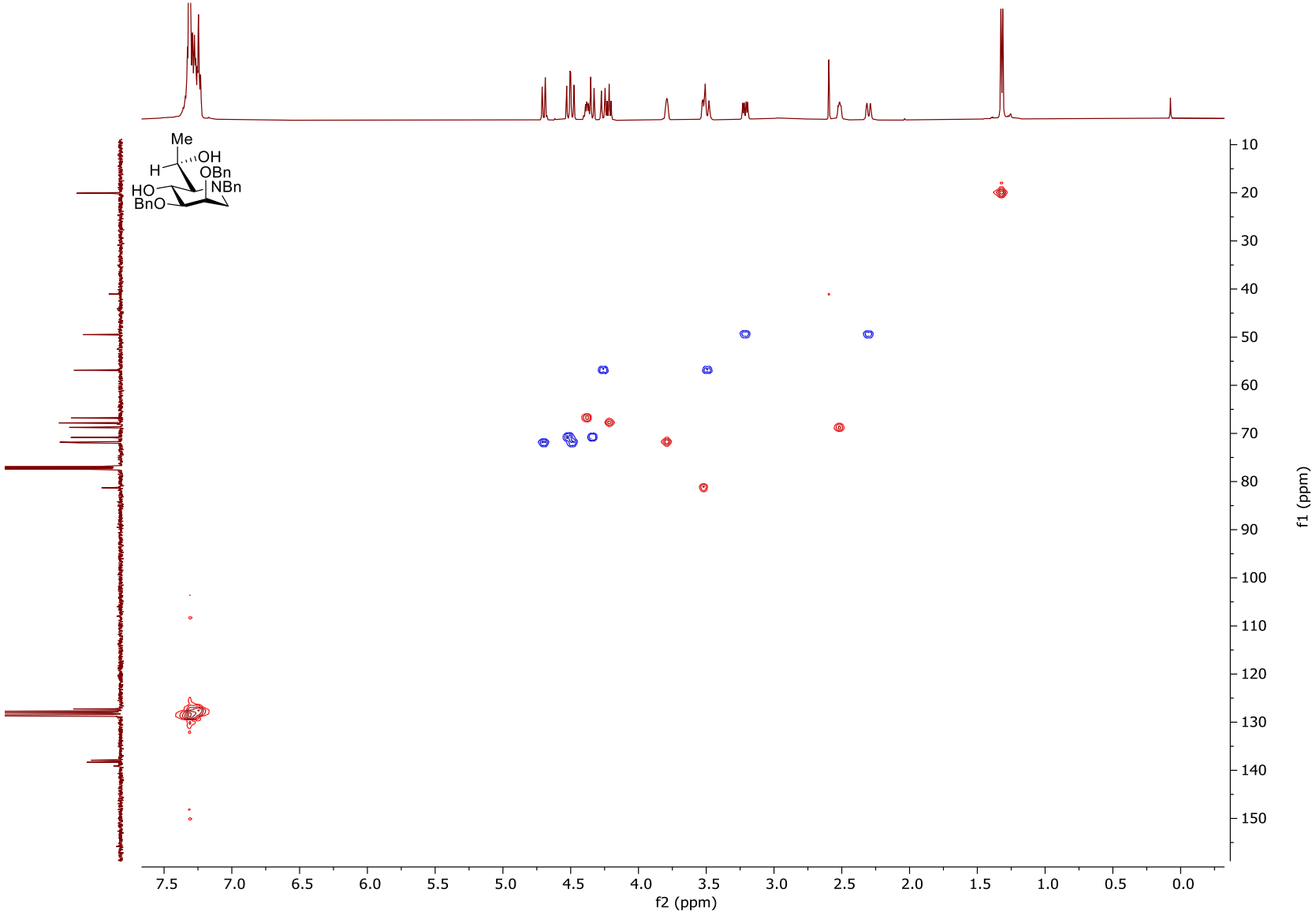
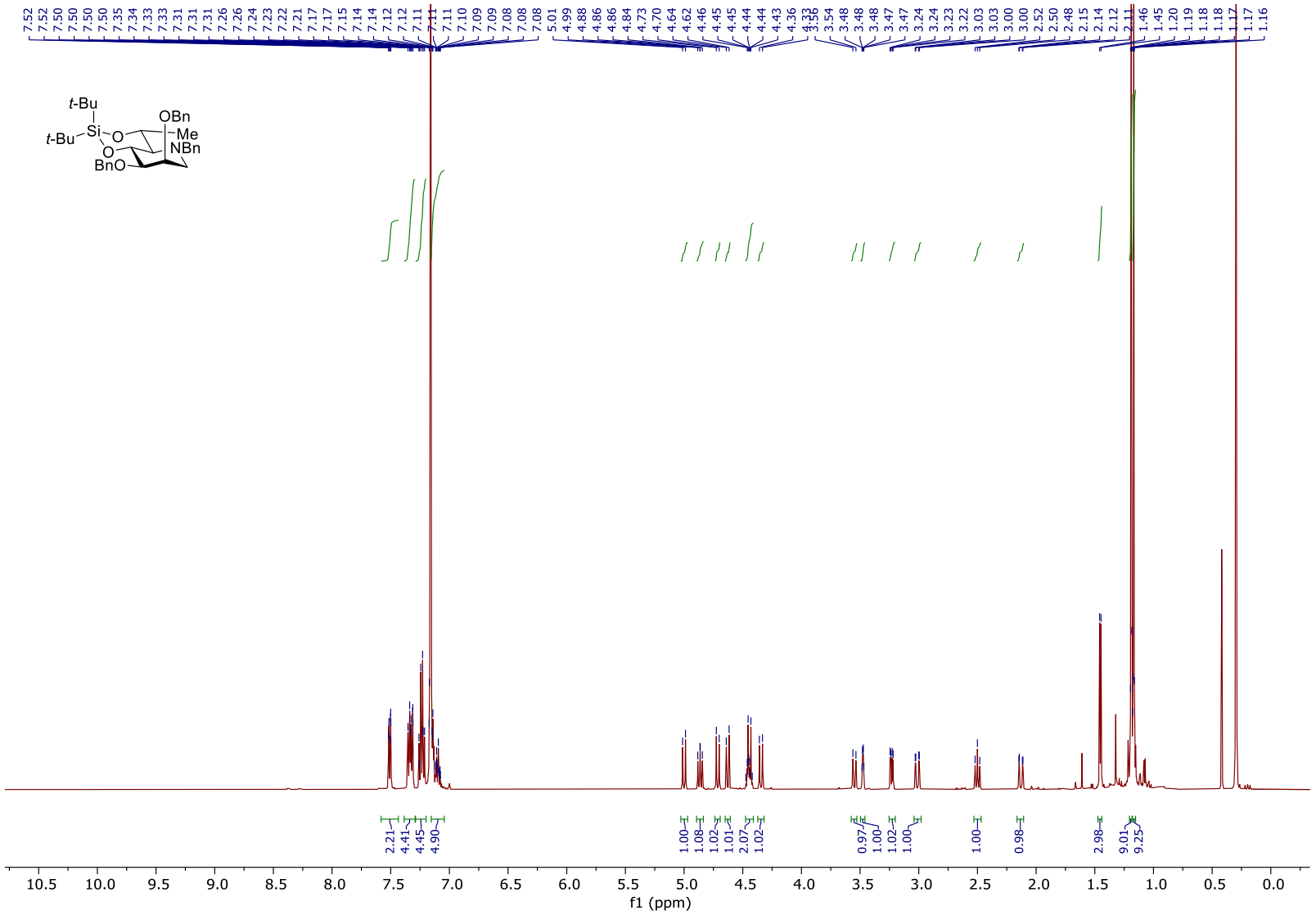
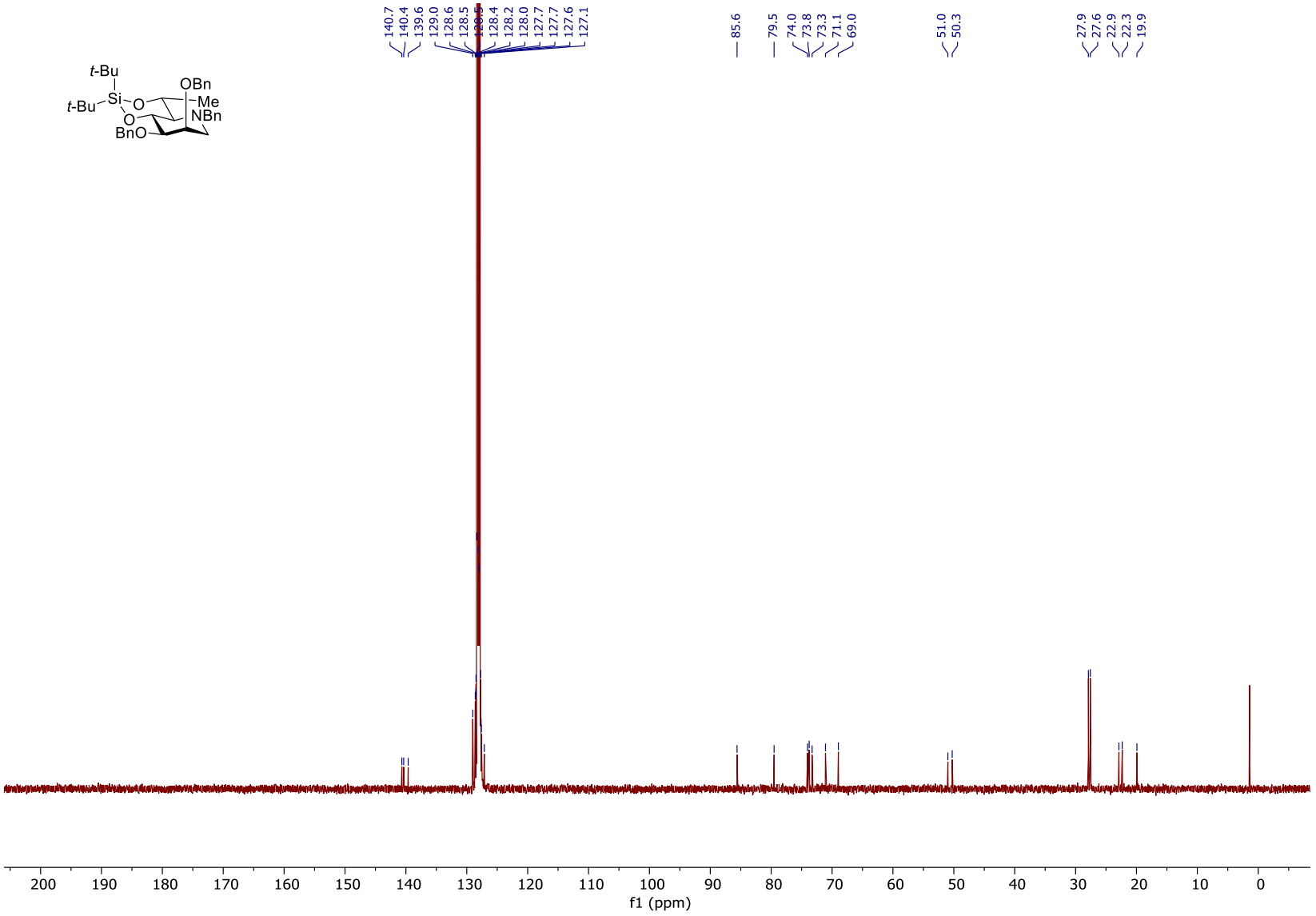


^{1}H NMR (500 MHz C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (36)



^{13}C NMR (126 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (36)



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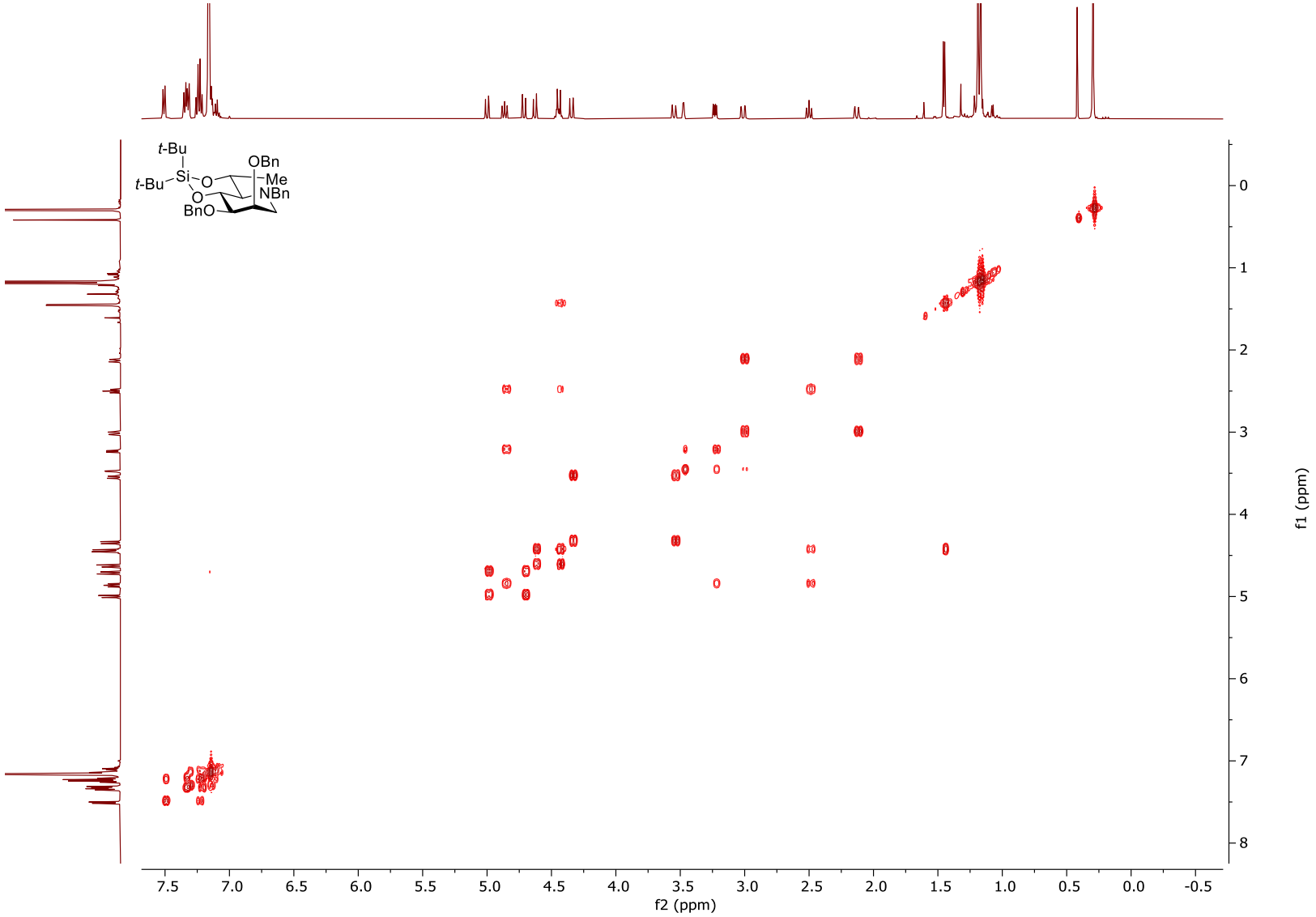
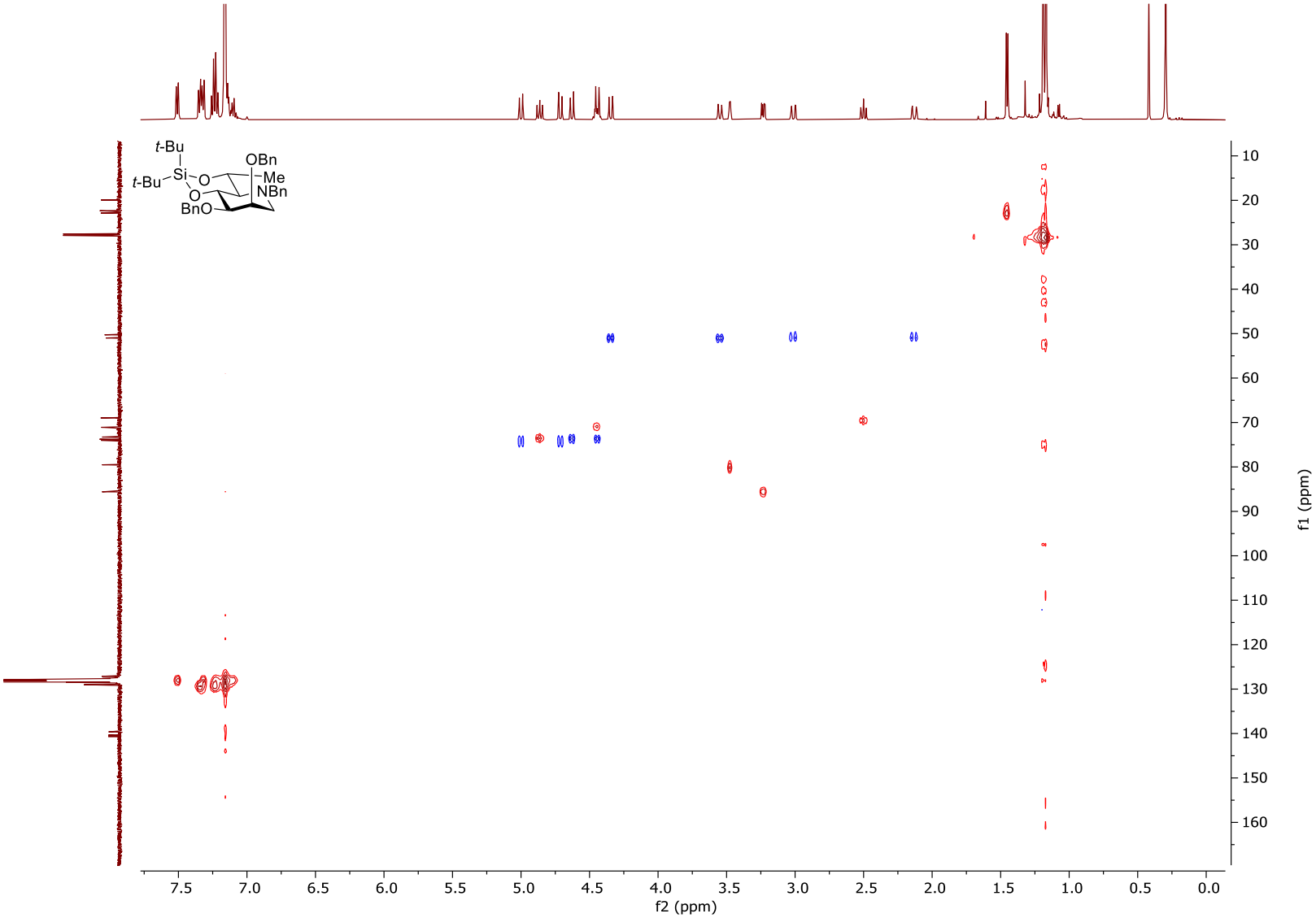
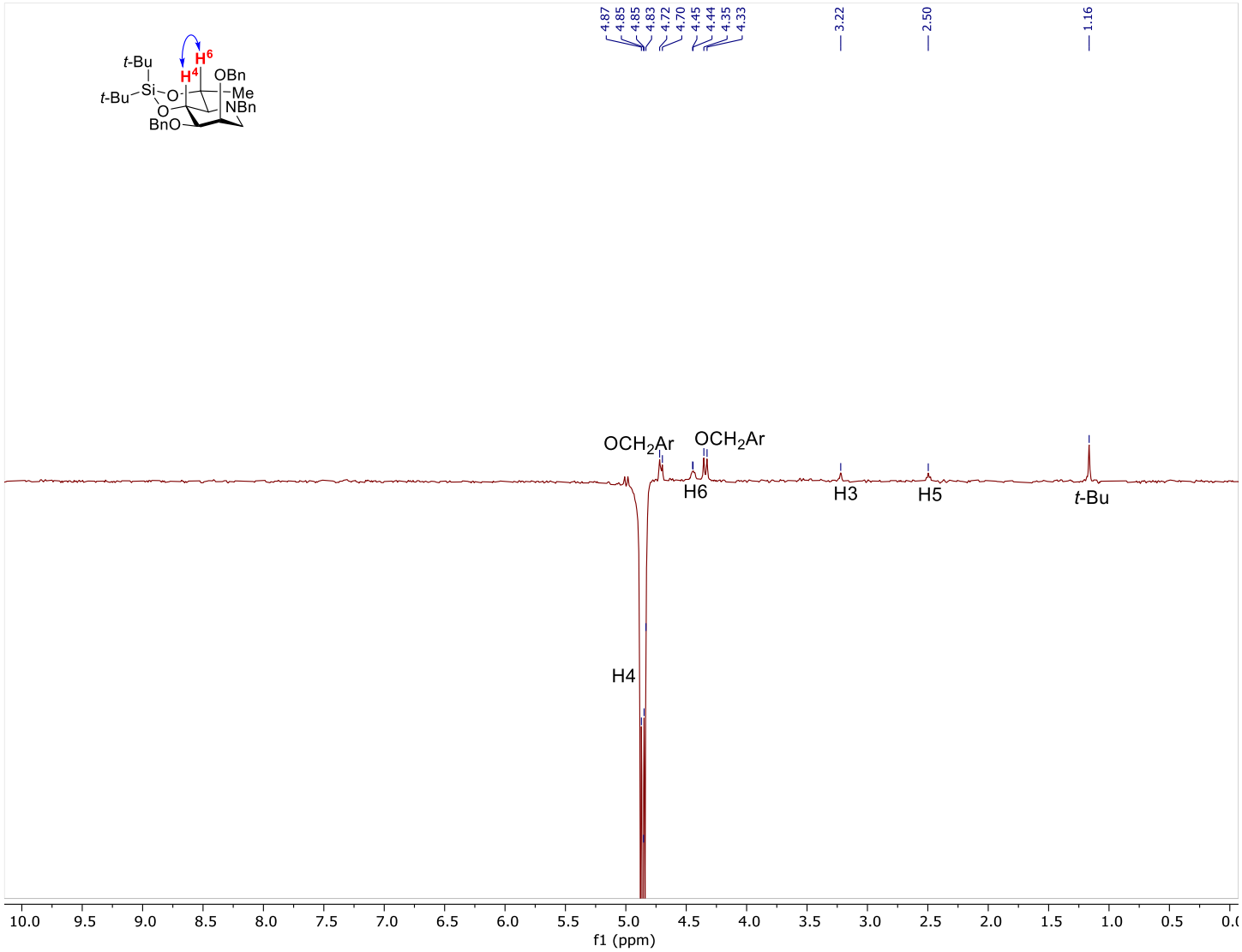


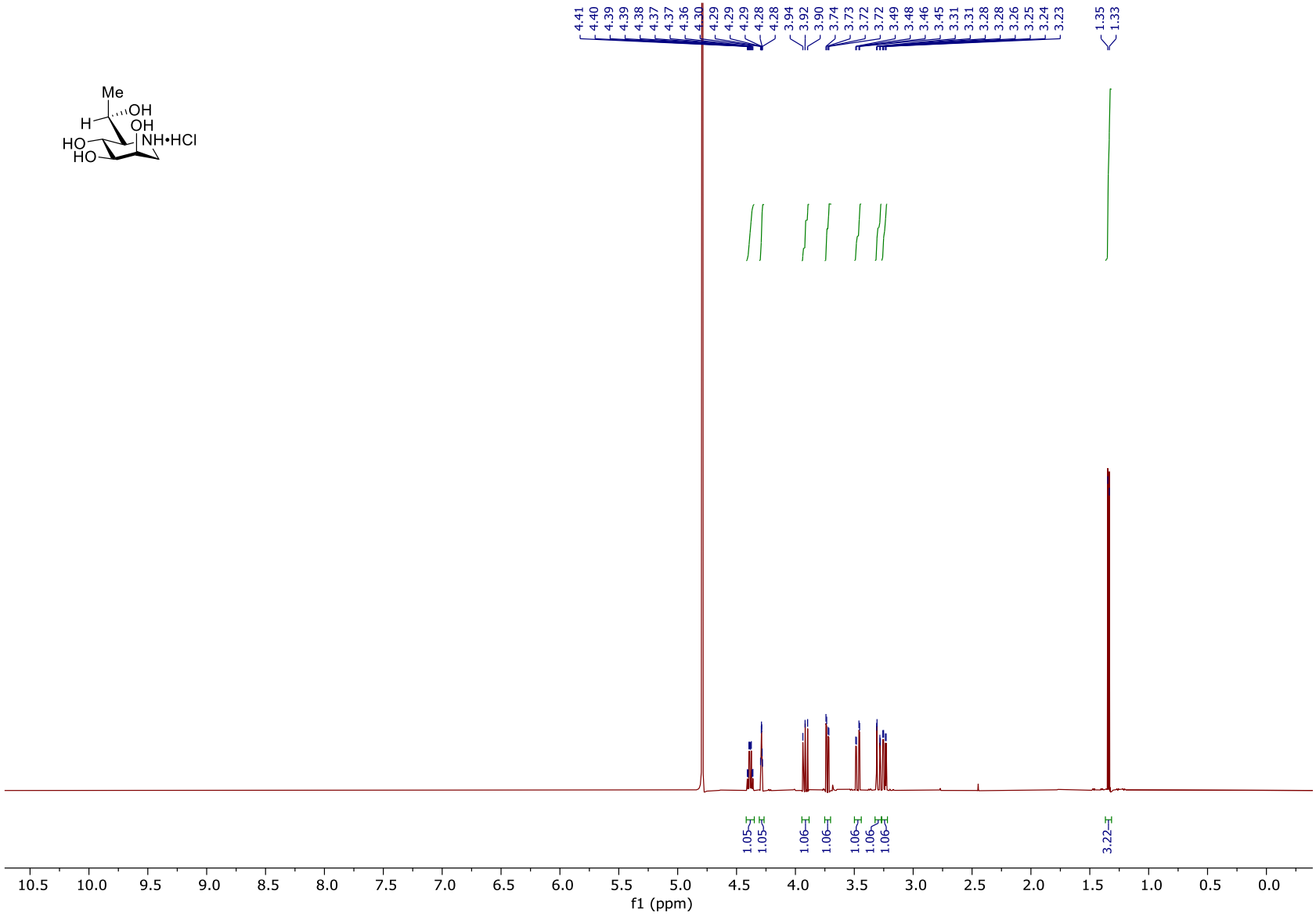
HSQC NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (36)



Selective 1D NOESY NMR (500 MHz, C_6D_6) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-4,6-*O*-di-*tert*-butylsilylene-1,5,7-trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (36)

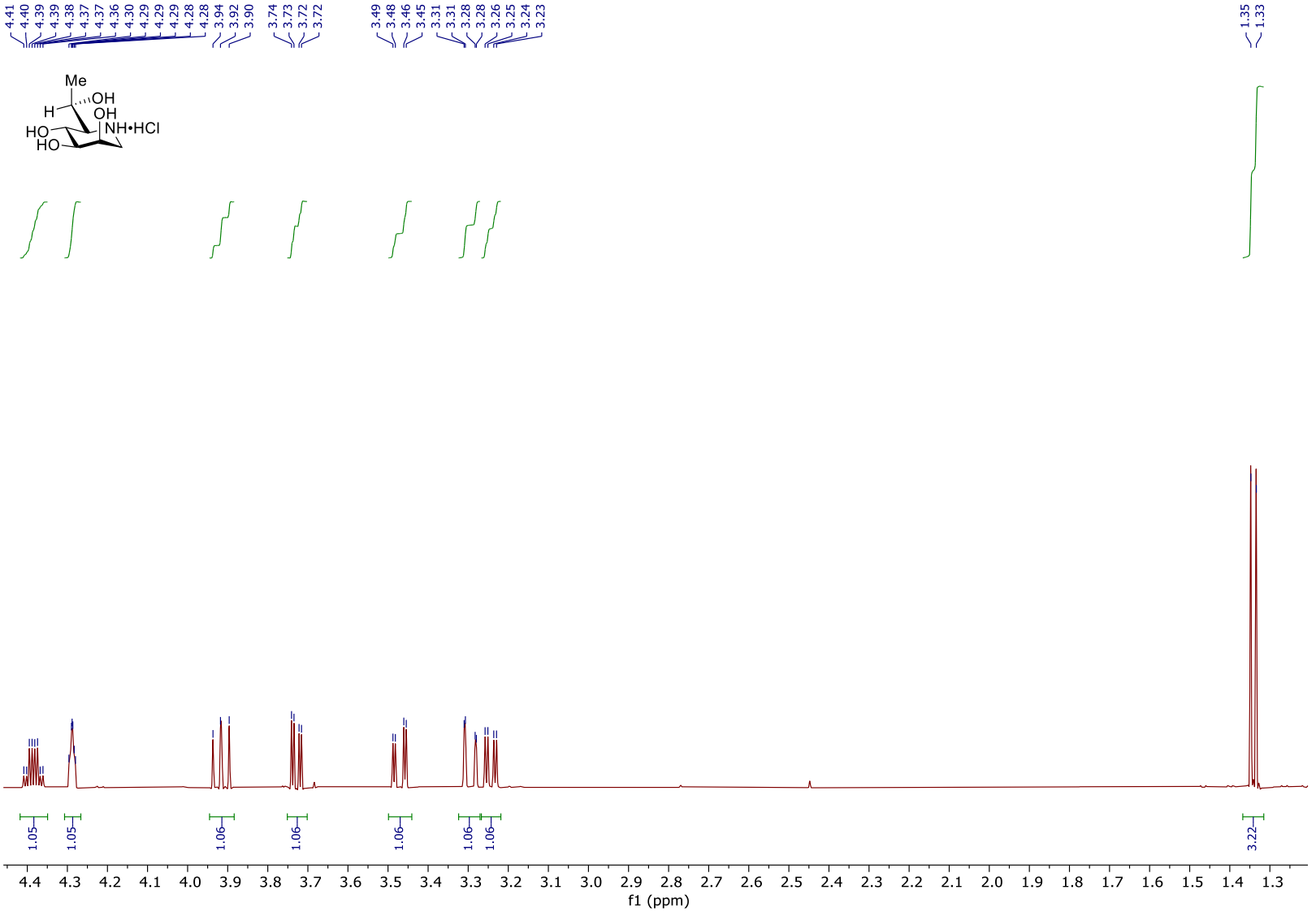


^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)

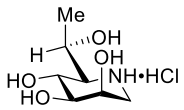


^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)

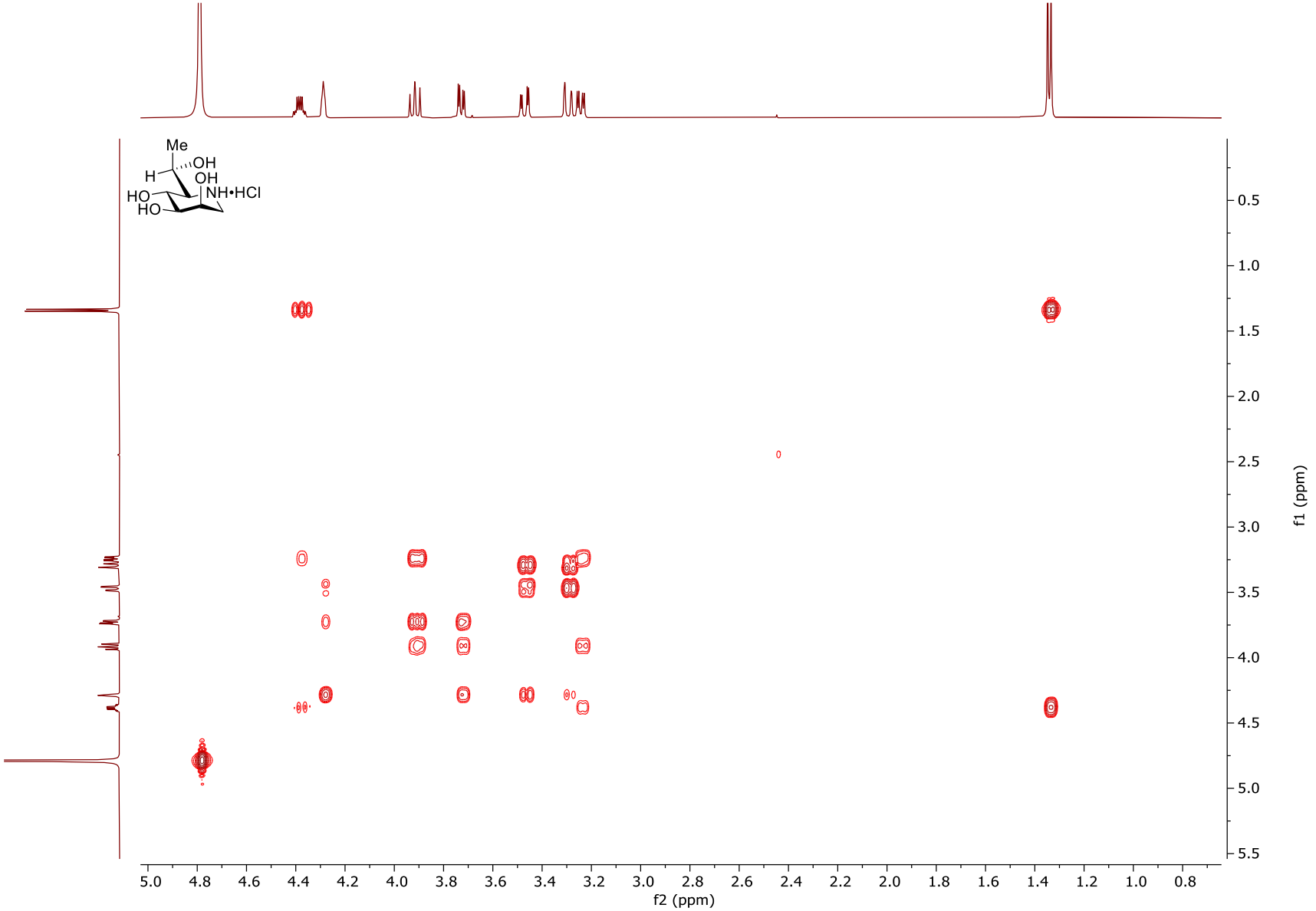
(selected and expanded region from 4.5 to 1.2 ppm)



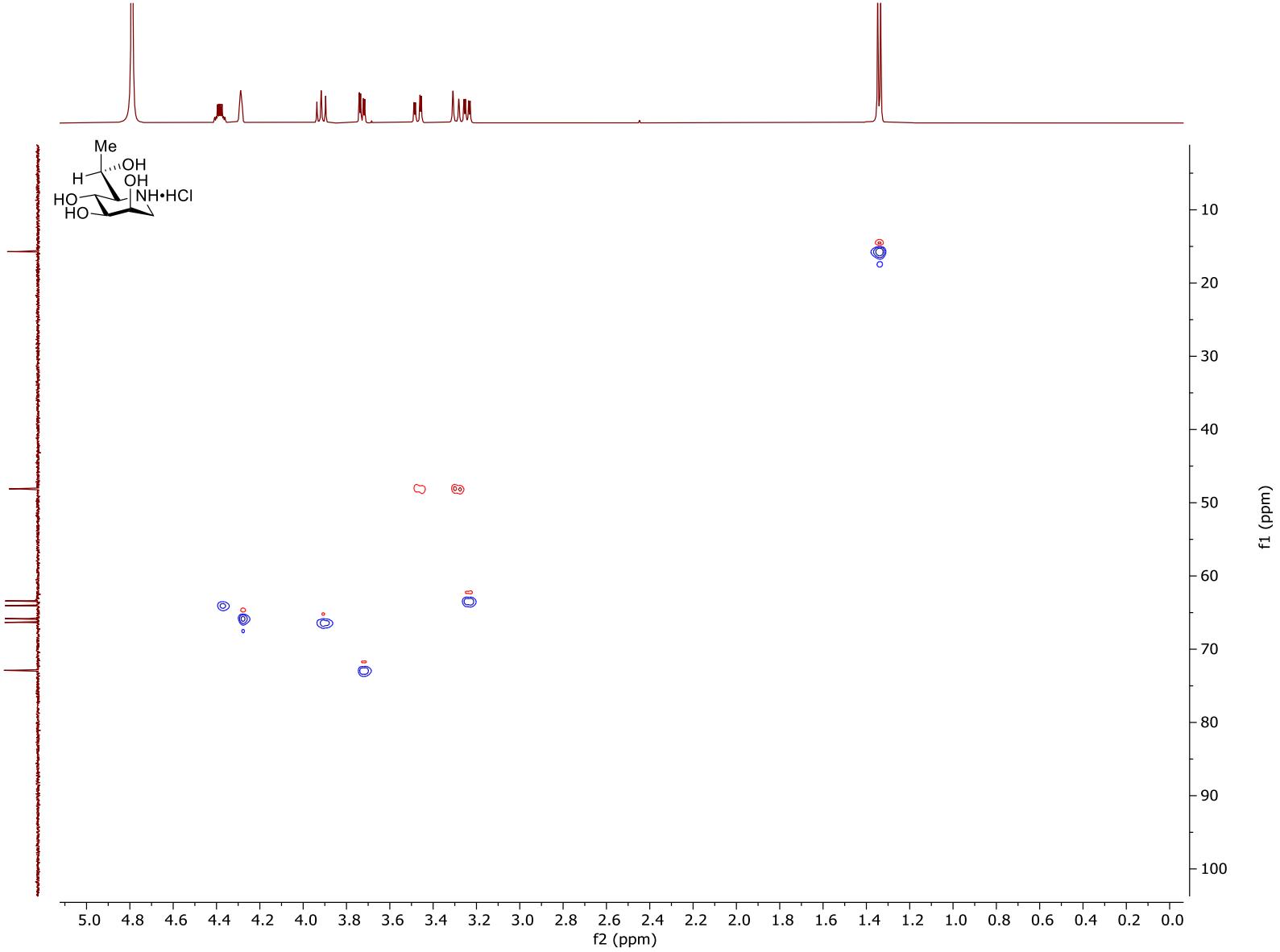
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)



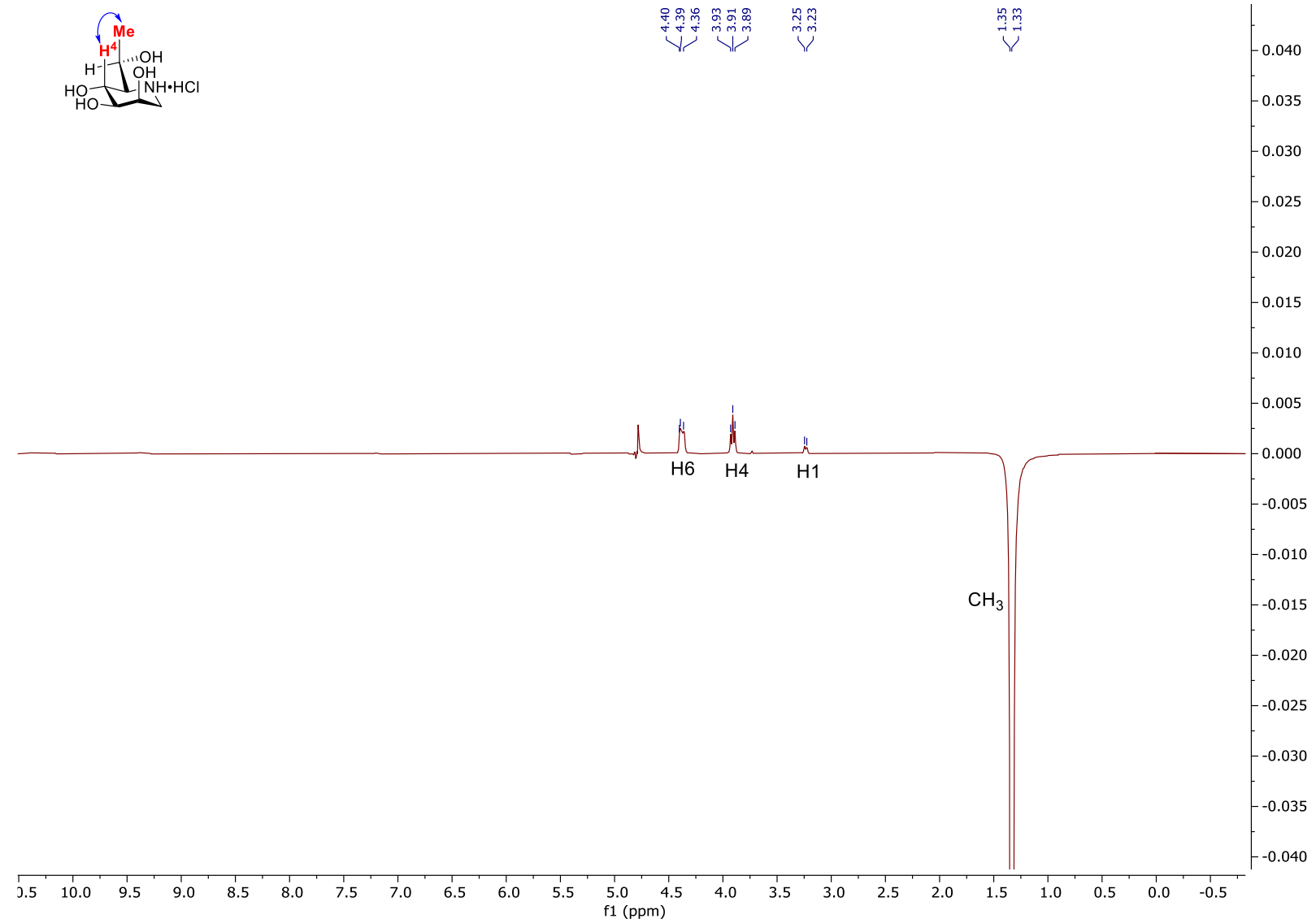
COSY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)



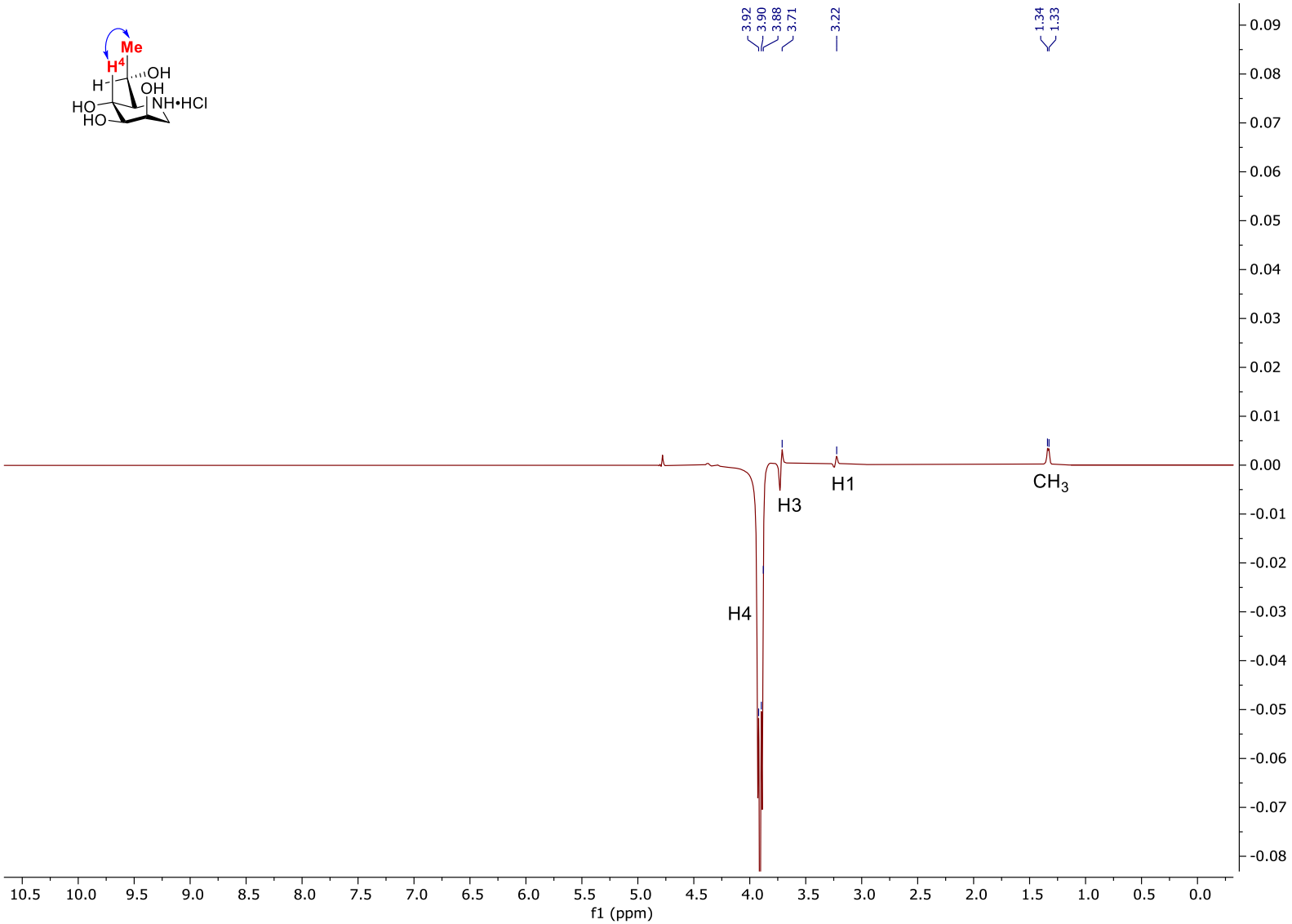
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)



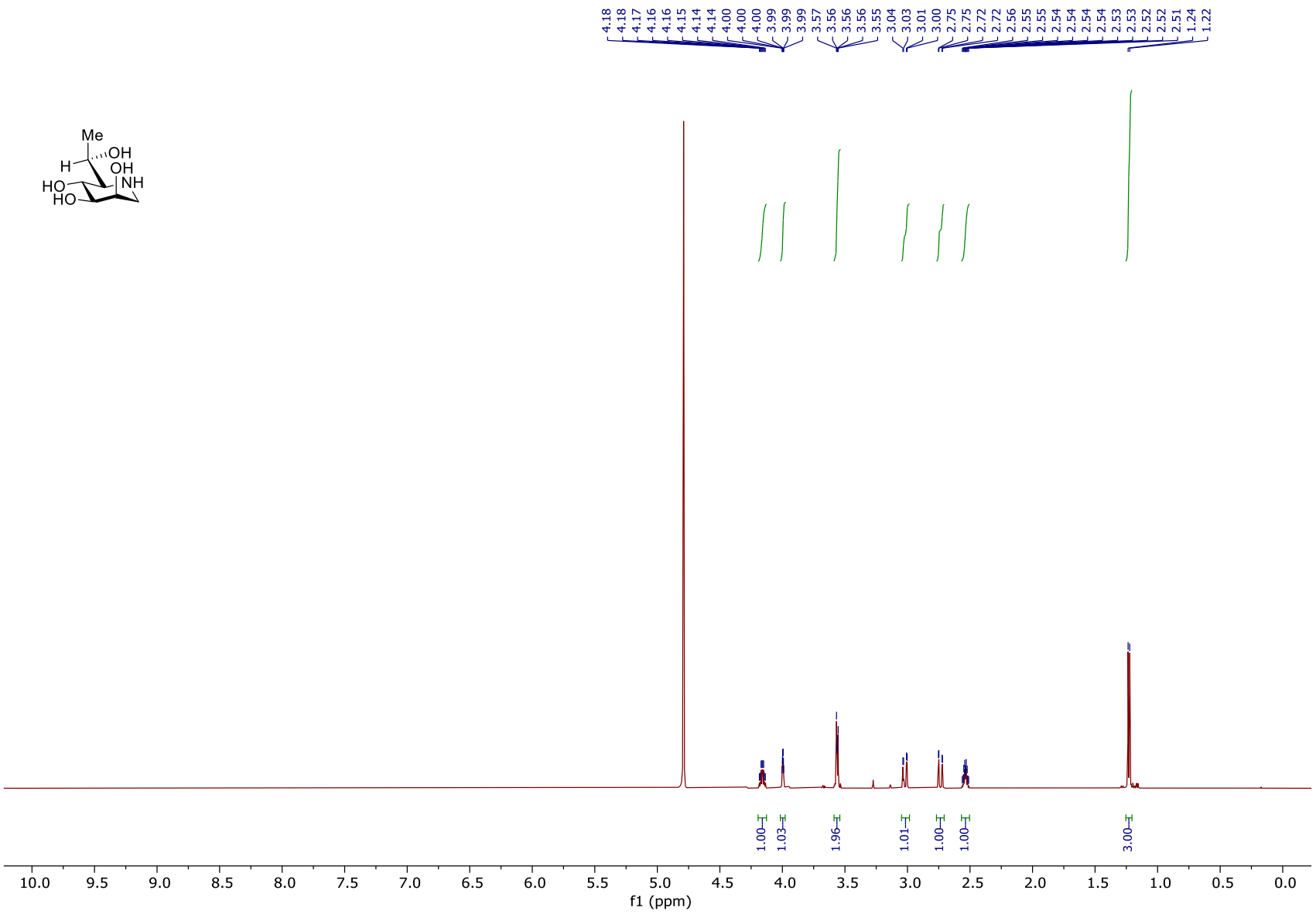
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)



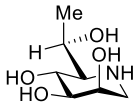
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol Hydrochloride (8)



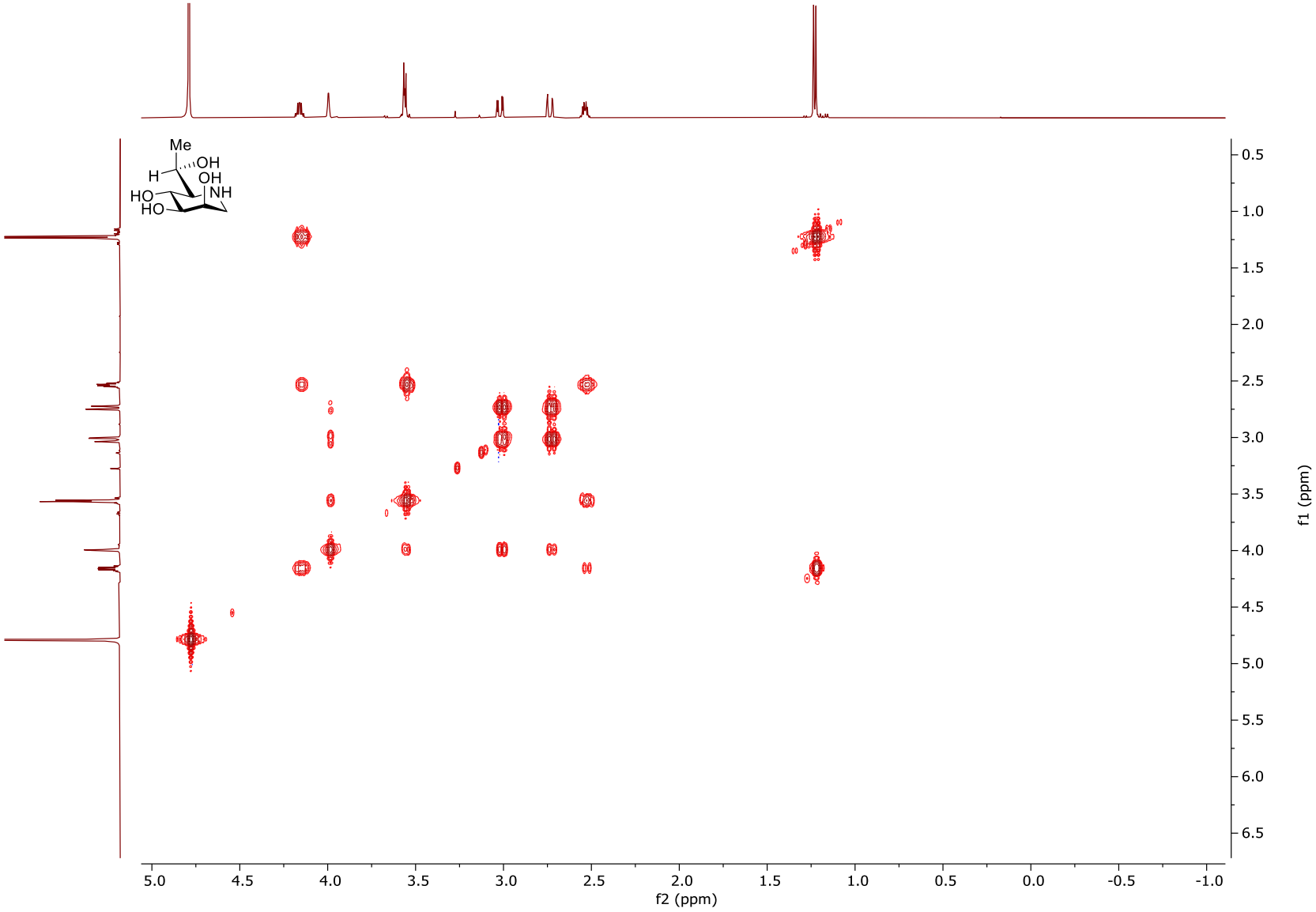
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (8)



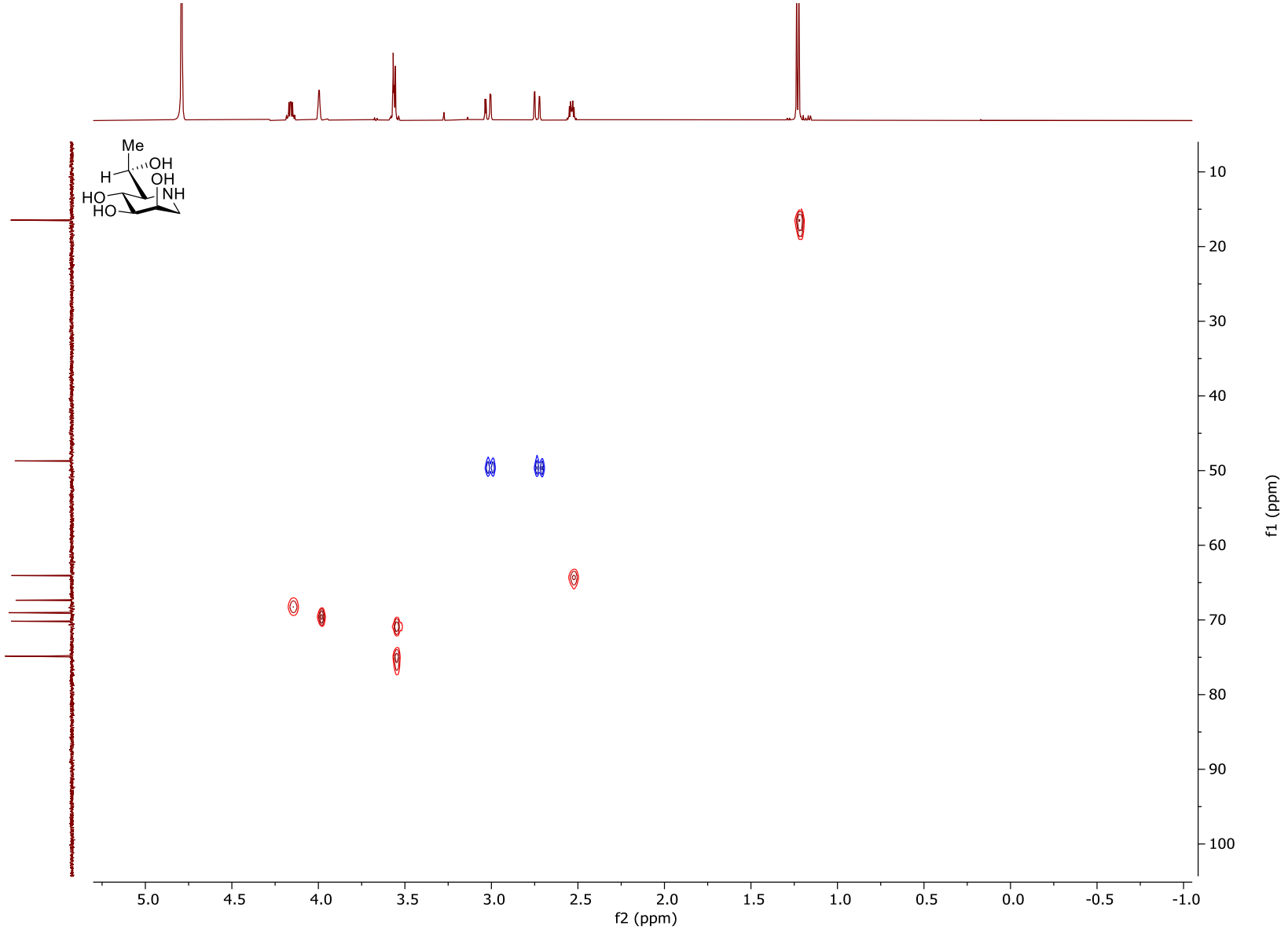
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (8)



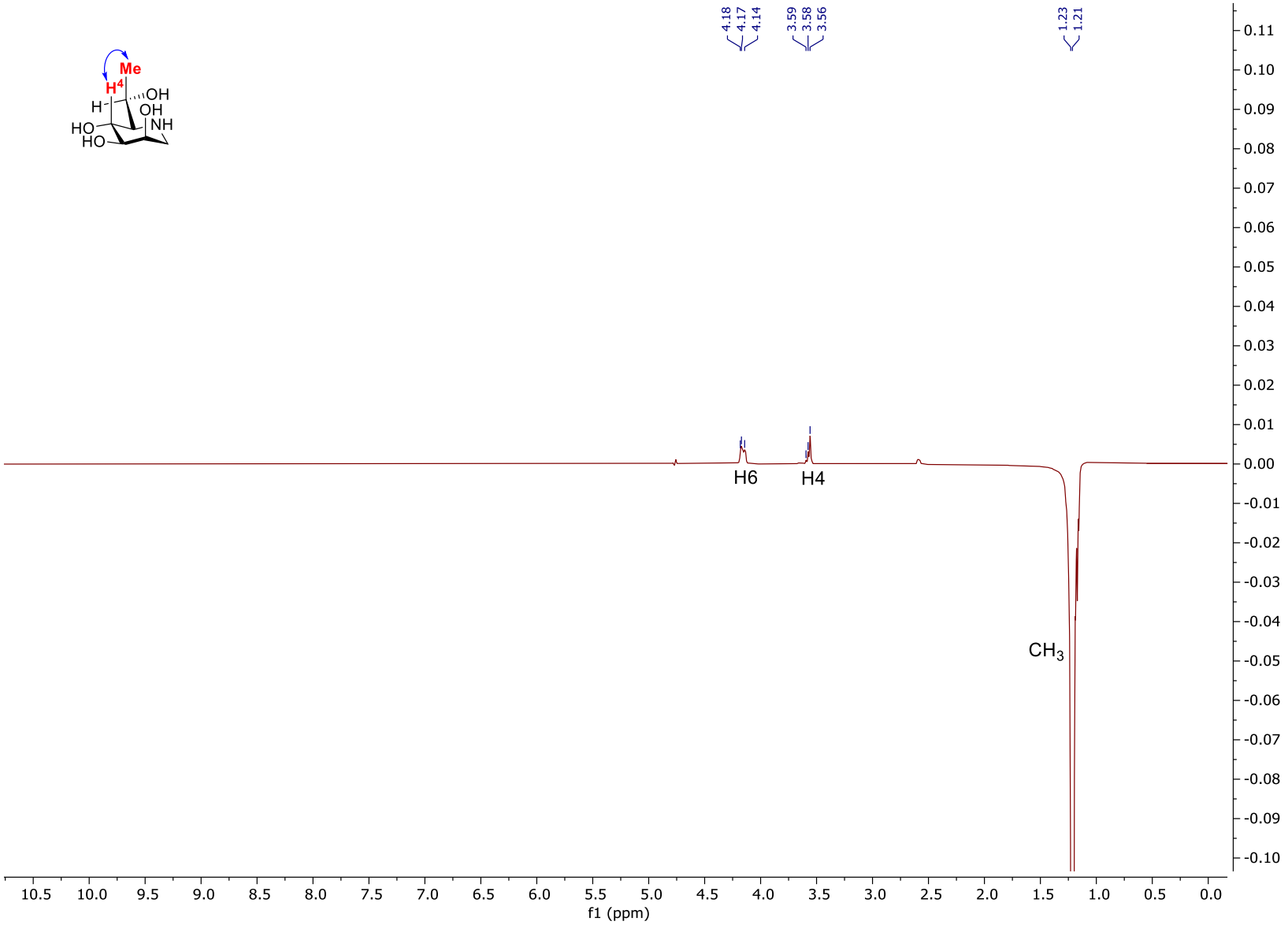
COSY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (8)



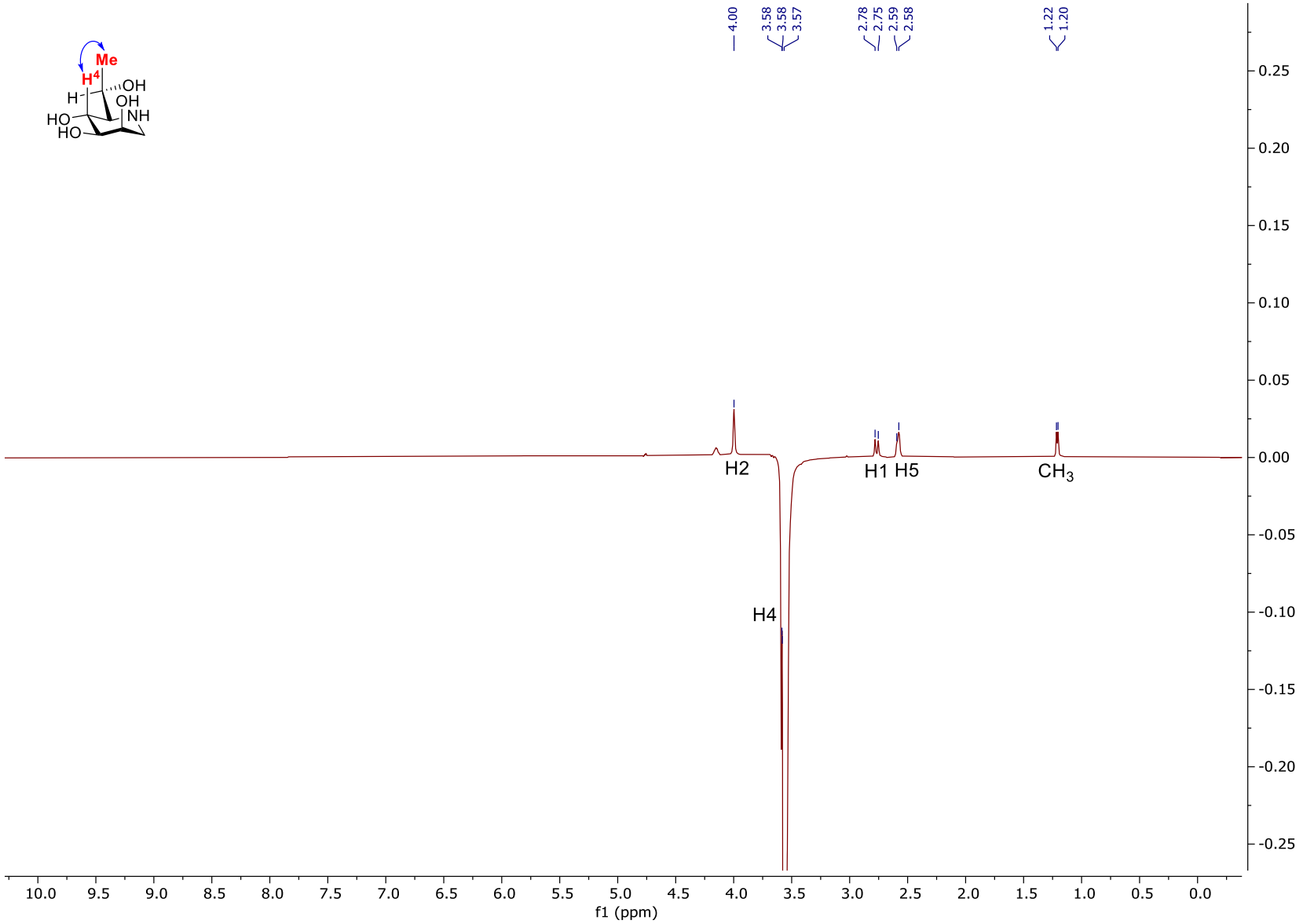
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (8)



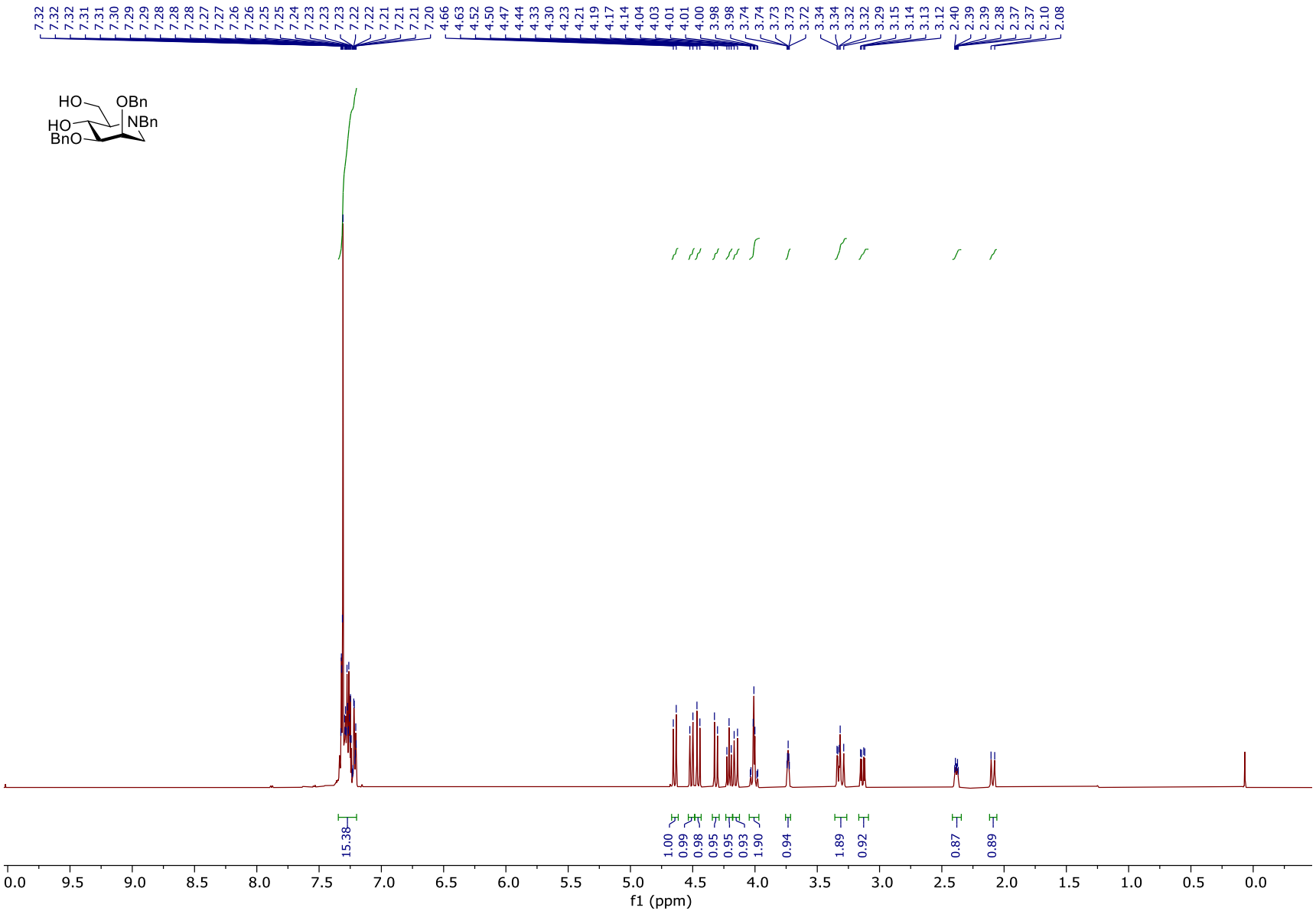
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (8)



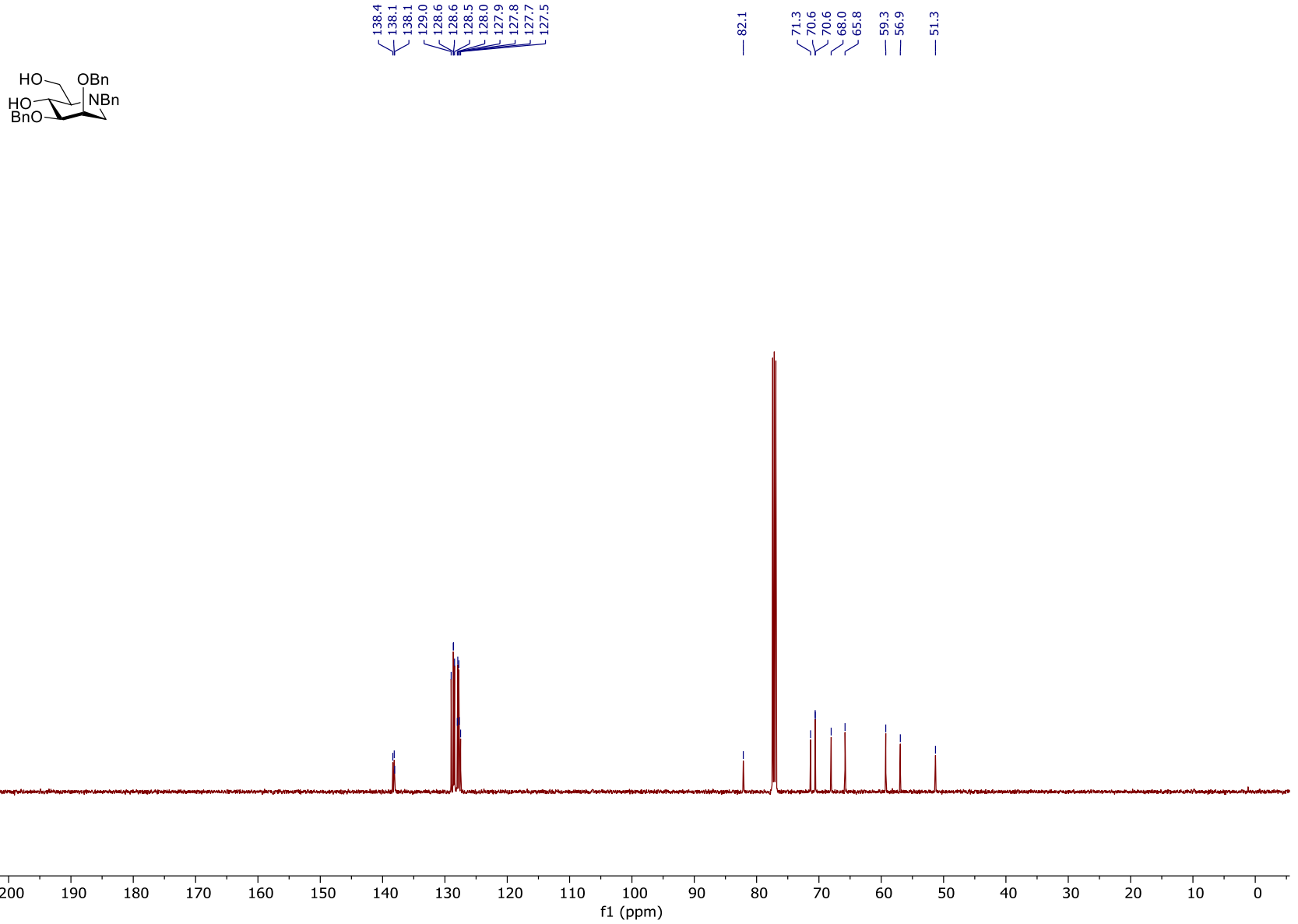
Selective 1D NOESY NMR (500 MHz, D_2O) Spectrum of 1,5,7-Trideoxy-1,5-imino-D-*glycero*-D-*manno*-heptitol (8)



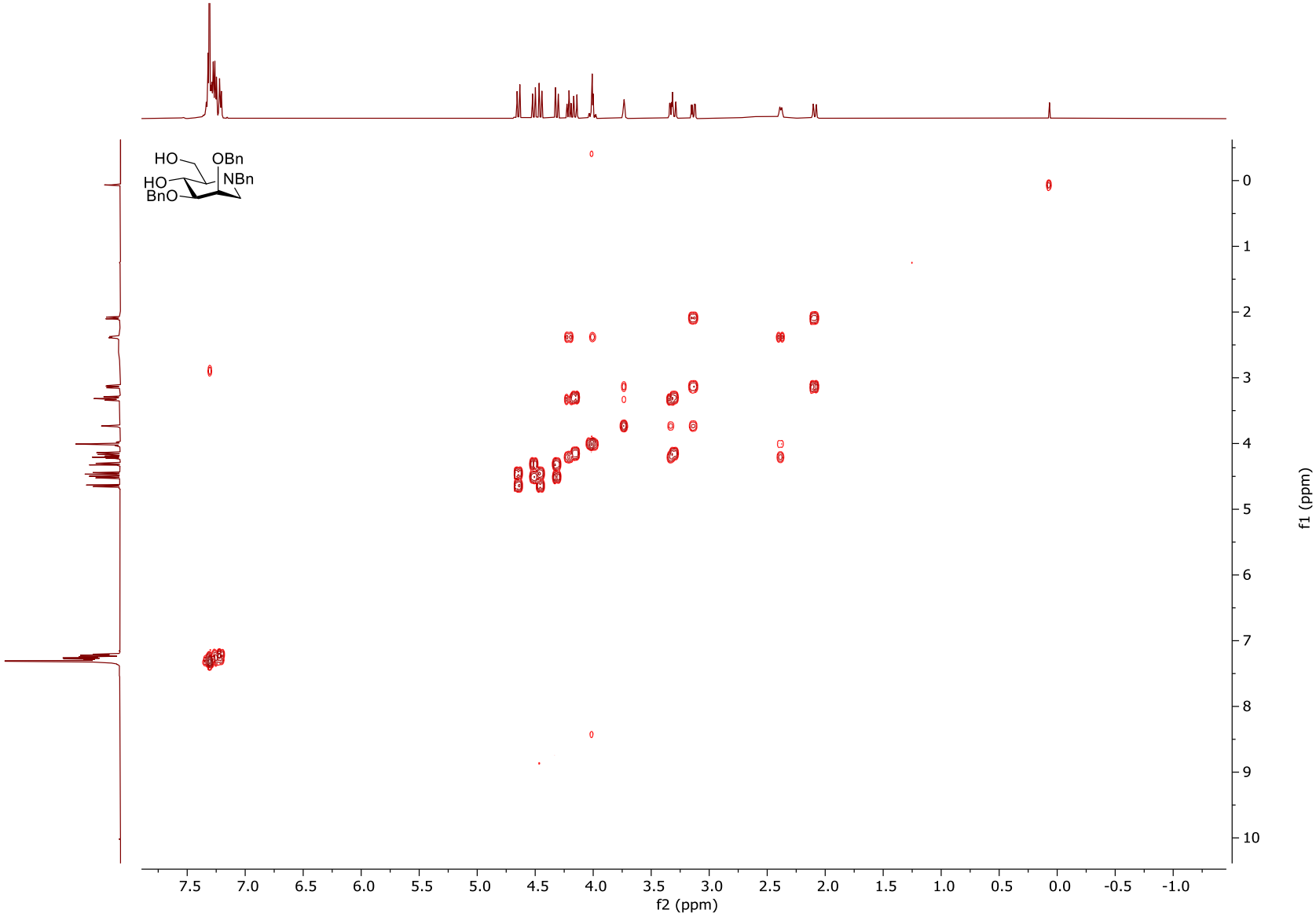
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-mannitol (37)



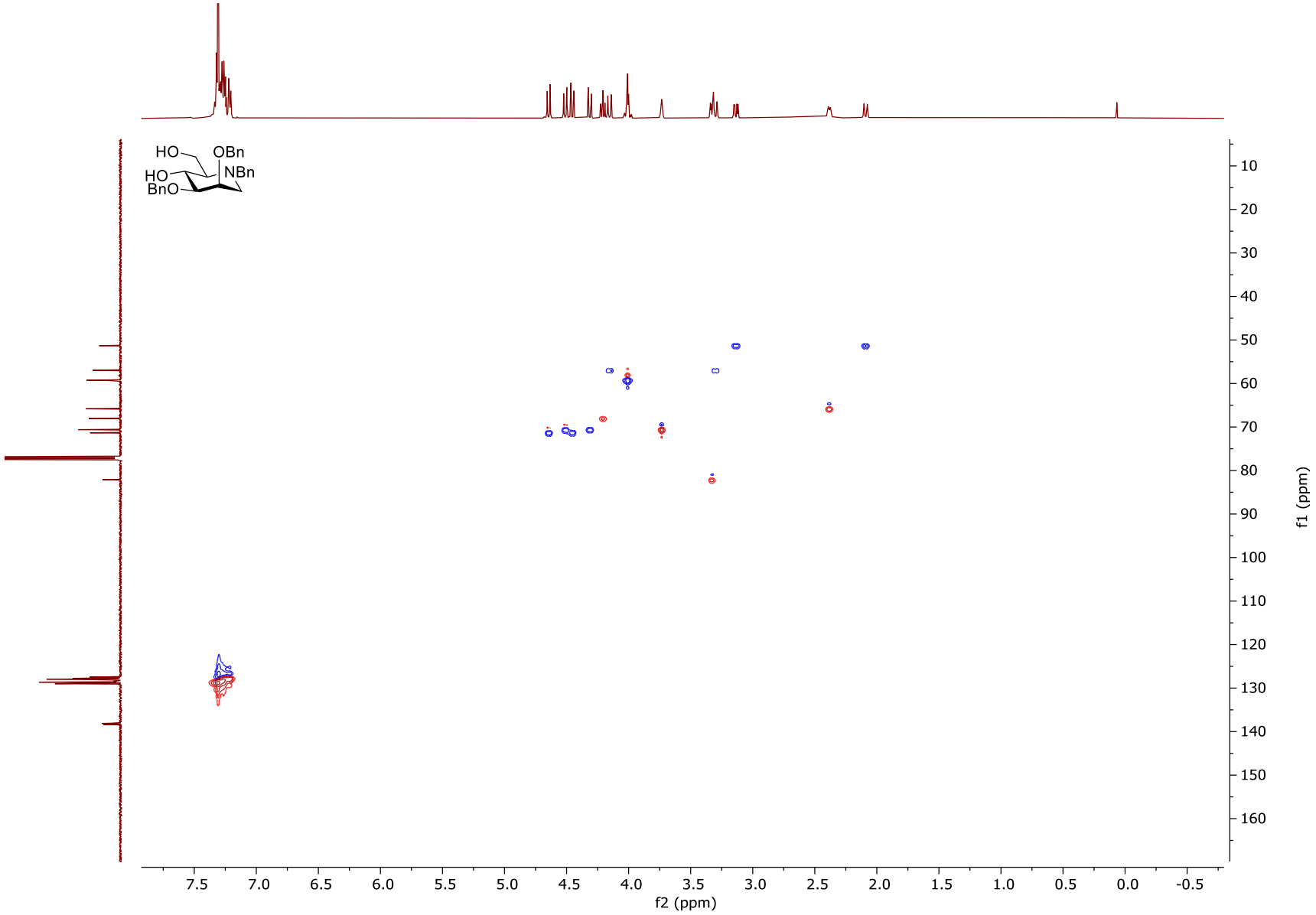
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-mannitol (37)



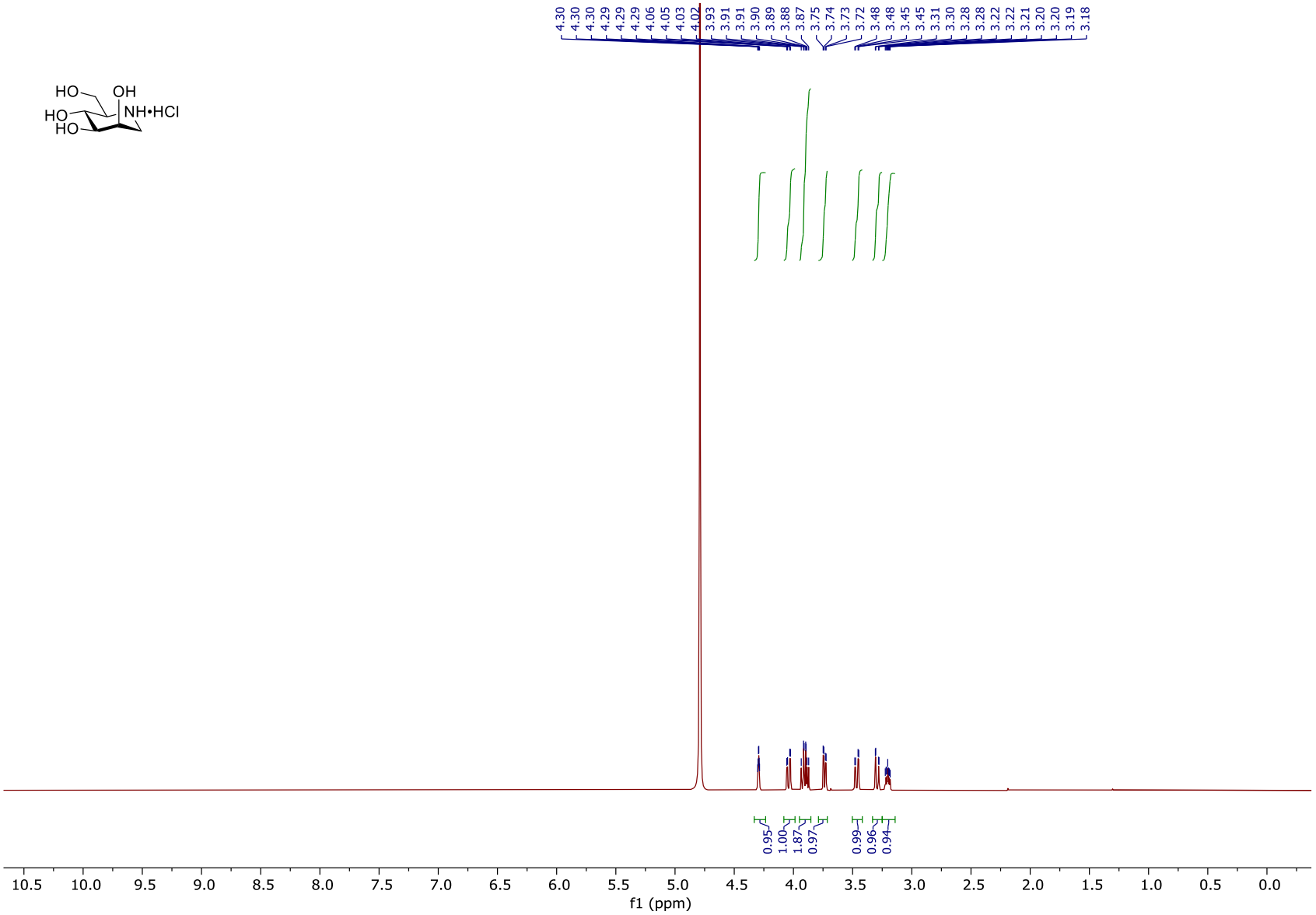
COSY NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-mannitol (37)



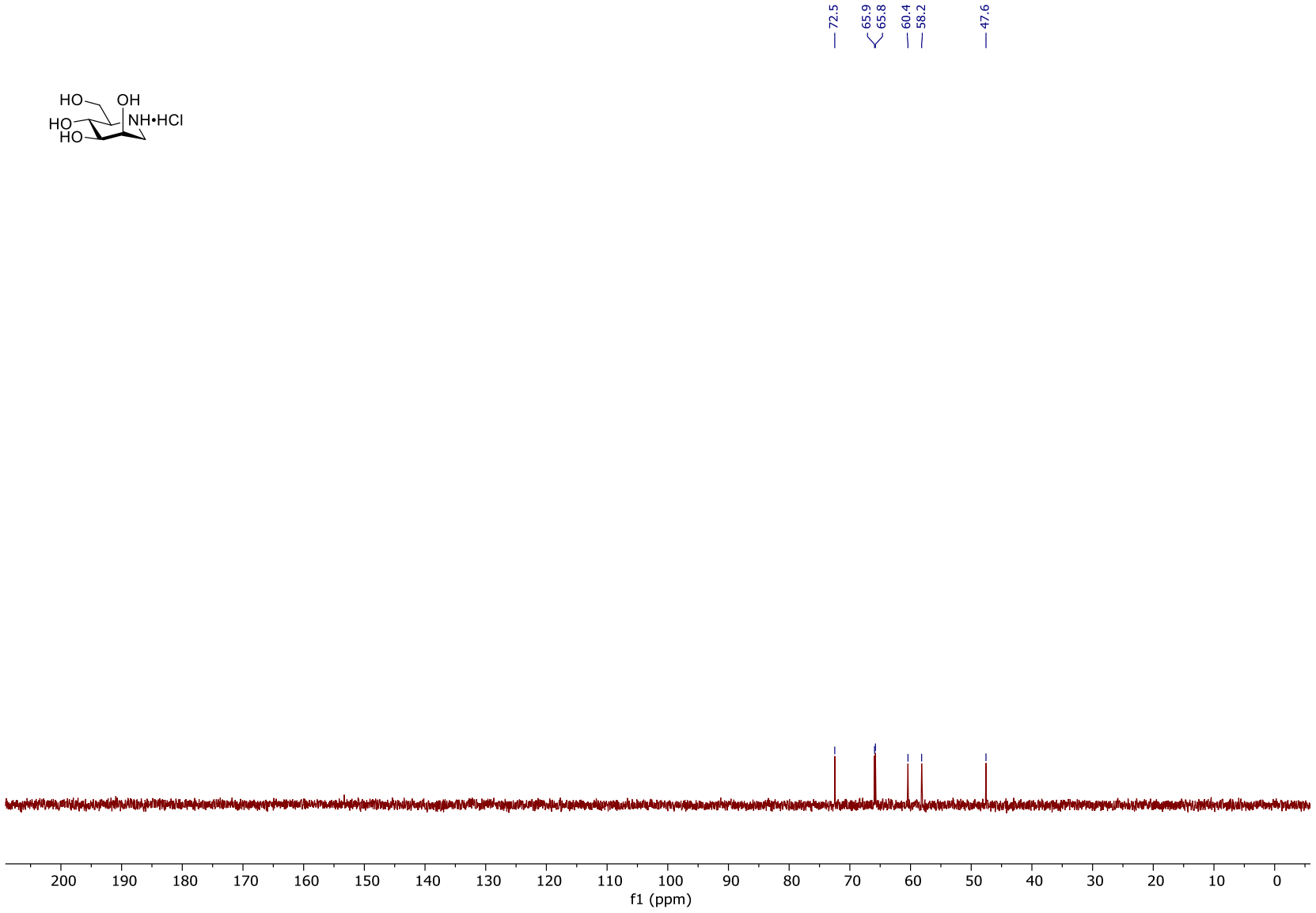
HSQC NMR (500 MHz, $CDCl_3$) Spectrum of 2,3-Di-*O*-benzyl-*N*-benzyl-1,5-dideoxy-1,5-imino-D-mannitol (37)



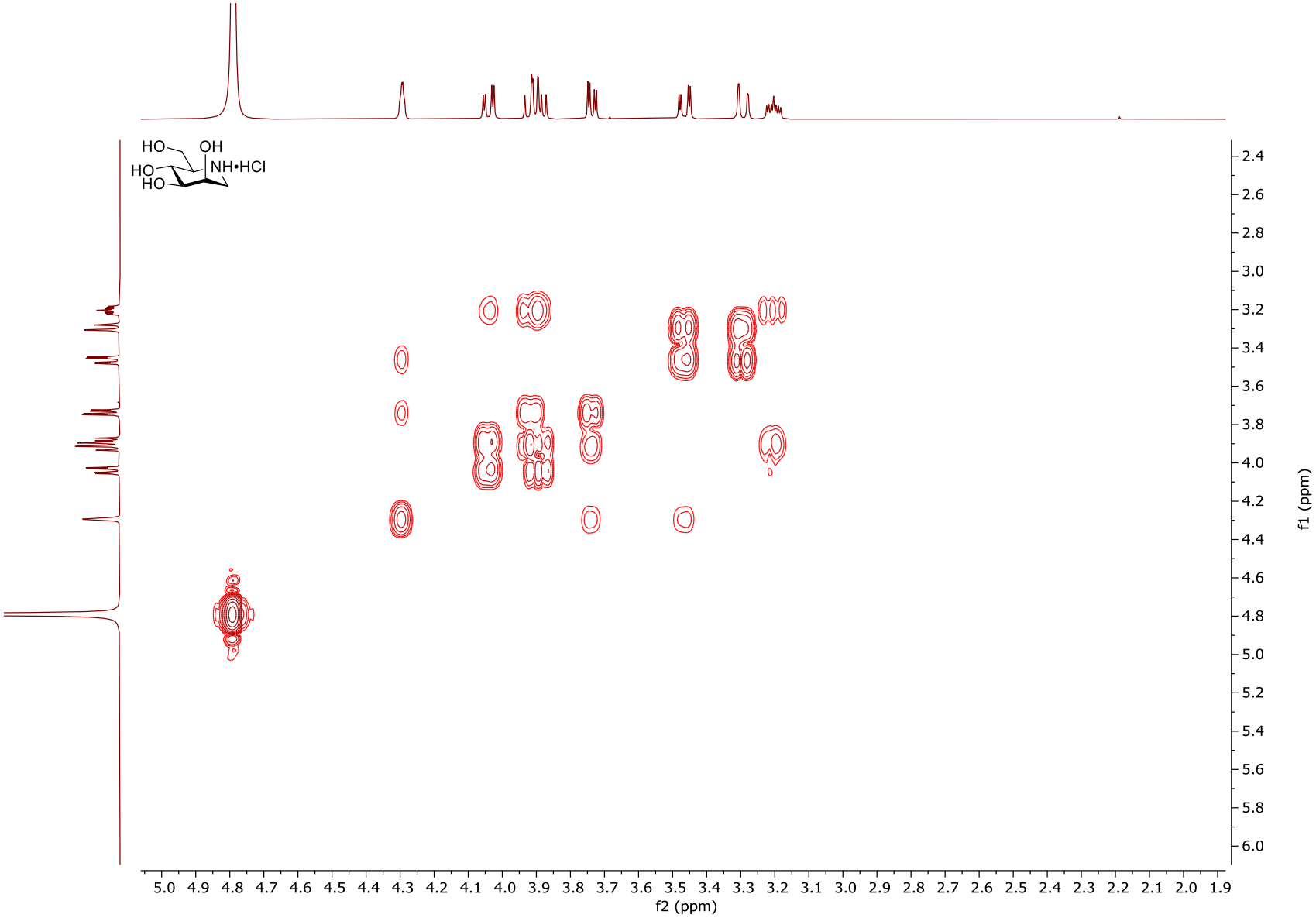
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol Hydrochloride (6)



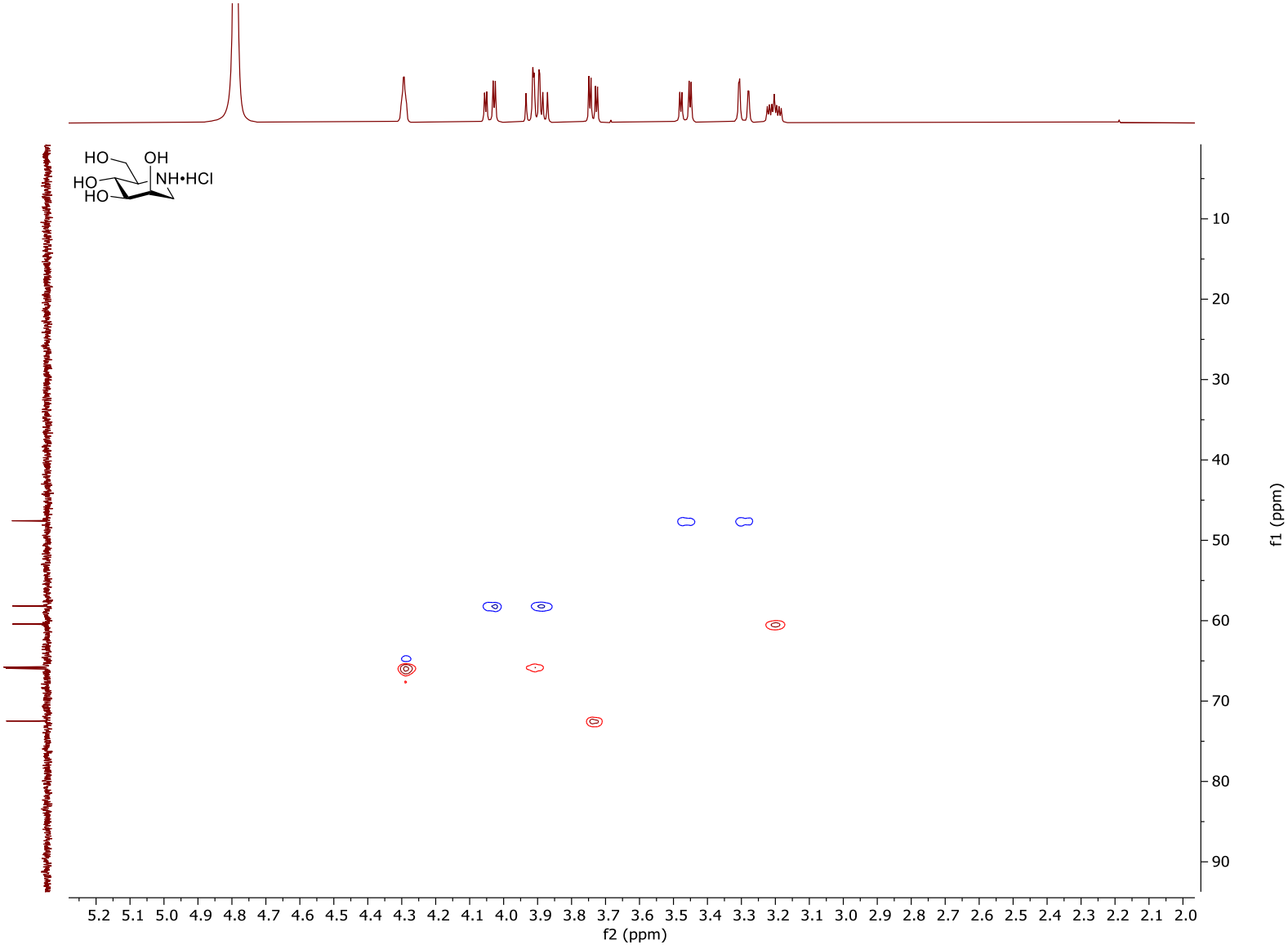
^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol Hydrochloride (6)



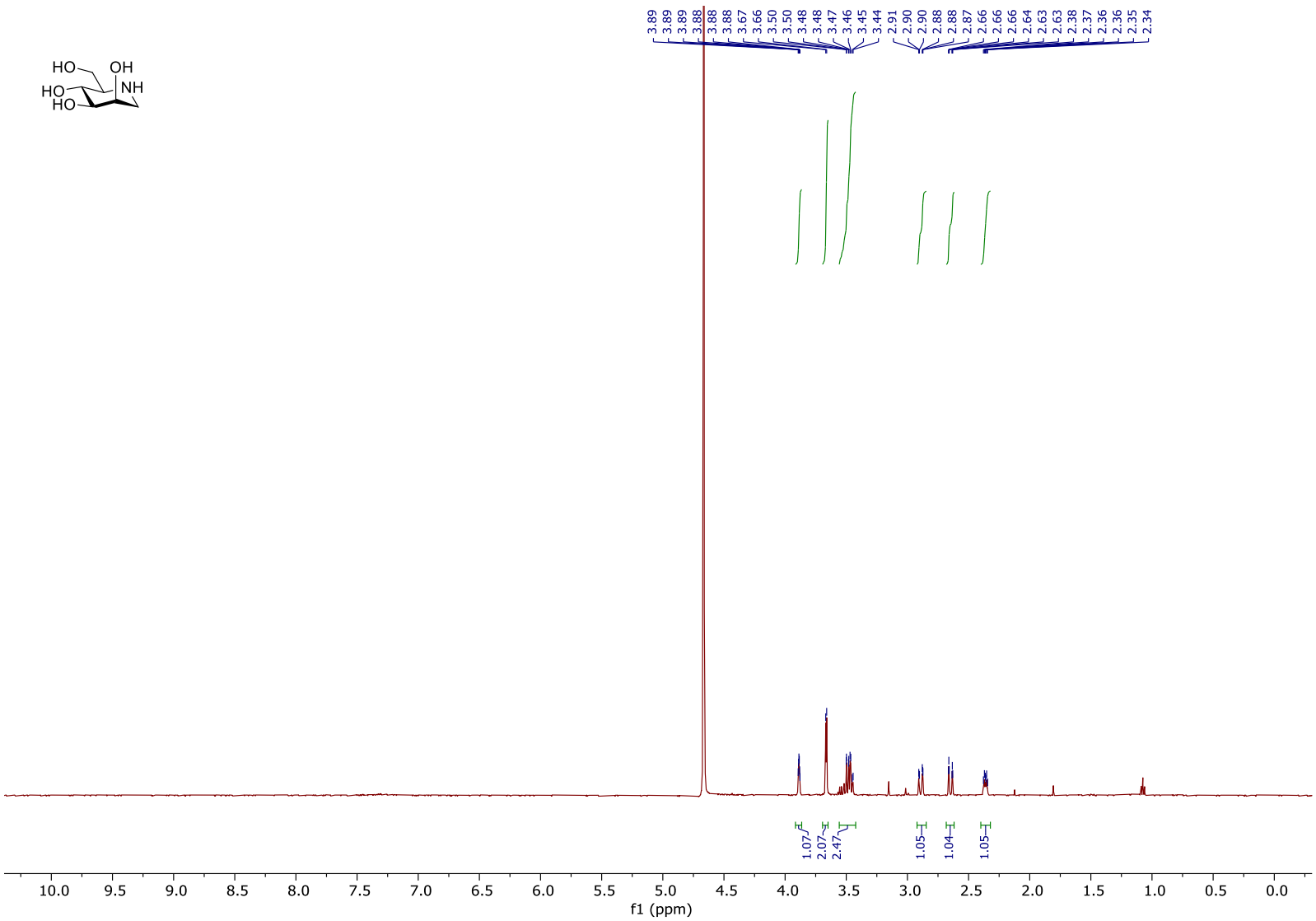
COSY NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol Hydrochloride (6)



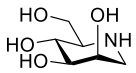
HSQC NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol Hydrochloride (6)



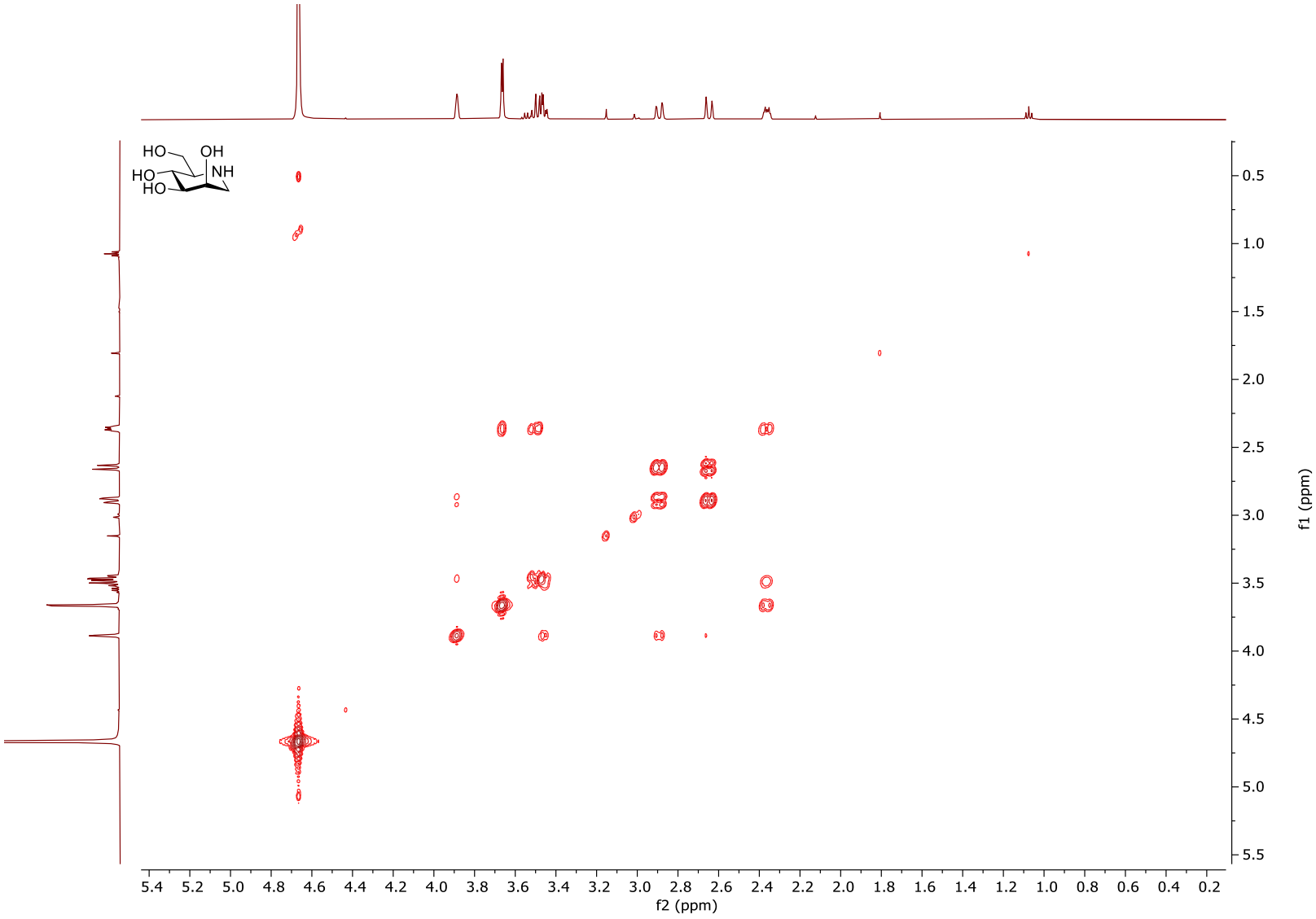
^{1}H NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol (6)



^{13}C NMR (126 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol (6)



COSY NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol (6)



HSQC NMR (500 MHz, D_2O) Spectrum of 1,5-Dideoxy-1,5-imino-D-mannitol (6)