## ***Supporting Information***

# Programmable One-pot Synthesis of Heparin Pentasaccharides Enabling Access to Regiodefined Sulfate Derivatives

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**A. General Procedures**. All chemicals were purchased as reagent grade and used without further purification. The ACS grade solvents used for reactions were purchased from commercial source and further dried in accordance with standard procedures.[1] Molecular sieves (MS) AW-300 (for glycosylation) and MS 4 Å (for *O*-benzylation), were purchased from Aldrich, ground into powdered form and activated using standard procedure prior to use in the reaction. Reactions were performed under an inert atmosphere and strictly anhydrous conditions and monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F254 plates and visualized under UV (254 nm) and/or by spraying with 20% anisaldehyde in ethanol or with a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 25 g/L. $^1$H NMR spectra were recorded on a 600 MHz and 900 MHz NMR spectrometer. Chemical shifts (in ppm) were determined relative to tetramethylsilane in deuterated chloroform (δ 0 ppm). Coupling constant(s) in hertz (Hz) were measured from one-dimensional spectra. Mass spectra were obtained by the analytical services of the department.

**General Procedure for Silyl Ether Cleavage.** A pentasaccharide (0.025 mmol) was dissolved in pyridine (1.1 mL) followed by addition of HF·pyridine (30-40 equiv) at 0 °C. After stirring for 12 h, the solvent was evaporated in *vacuo* and the crude mixture was diluted with $CH_2Cl_2$ (50 mL) and washed with water (50 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL). The organic phase was dried over $MgSO_4$, filtered, concentrated in *vacuo*. The residue was purified by silica gel column chromatography using a gradient of toluene and EtOAc to give the product with 6-OH group at the non-reducing end.

**General Procedure for Lev Esters Cleavage.** To a solution of pentasaccharide (0.03 mmol) in a mixture of THF and MeOH (1/1, v/v, 1.5 mL), hydrazine acetate (5 equiv per Lev group) was added at 0 °C. After stirring for 2 h, acetone (1 mL) was added and the reaction mixture was stirred for additional 30 min at the room temperature. The reaction mixture was diluted with EtOAc (30 mL) and washed with 25 mL of each of the water, saturated $NaHCO_3$ and then brine. The organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography using a gradient of toluene and EtOAc to give the product.

**General Procedure for $Ag_2O$-mediated *O*-benzylation:** To a solution of 6-hydroxyl-pentasaccharide (0.025 mmol) in a co-solvent (*n*-Hexane: $CH_2Cl_2$, 4/1, v/v, 2 mL) in a glass tube was added 4Å molecular sieves (200 mg). After stirring for 30 min under $N_2$-atmosphere, benzyl bromide (2.0 equiv per OH group) and, $Ag_2O$ (3.0 equiv per OH group) were added, sequentially. The glass tube was sealed and the reaction mixture was heated to 70 °C in the dark for 12 h. After the complete conversion of the starting material, the mixture was filtered by a Celite pad and concentrated. The crude residue was purified by a silica gel column chromatography using a gradient of toluene and EtOAc to afford the corresponding *O*-benzyl pentasaccharide.

**General Procedure for Saponification:**

To a solution of the pentasaccharide (0.02 mmol) in THF (1 mL, for 20-30 mg), 30% solution of $H_2O_2$ (100 per ester) and 1 M LiOH (20 per ester) were added dropwise at -5 °C, sequentially. After stirring at room temperature for 8 h, a solution of NaOH (4N, 1.0 mL) was added until pH 14. The reaction mixture was stirred for 18 h at room temperature, then acidified by dropwise addition of AcOH to bring the pH to 8-8.5. It was diluted with $CH_2Cl_2$ (15 mL) and washed with 10 mL of each of the 10 % $Na_2S_2O_3$, $H_2O$ and brine. The organic layer was dried over $MgSO_4$, filtered and concentrated in *vacuo* to give the product as a powder.

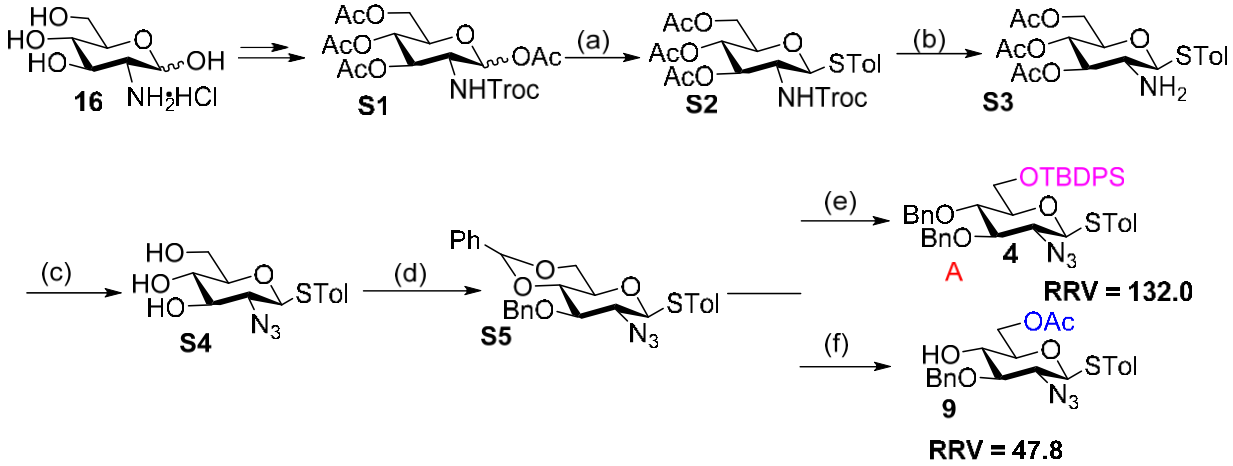
**General Procedure for *O*-Sulfation.** Sulfur trioxide-pyridine complex (10 equiv per OH) was added to a solution of the pentasaccharide in DMF (1.0 mL for 0.02 mmol). The mixture was stirred at 55 °C for 12 h under $N_2$ atmosphere. The reaction flask was cooled down to room temperature, a solution of phosphate buffer (pH 7.5, 1 mL) was added and the mixture was kept stirring for an additional 1 h. The resulting reaction mixture was concentrated in *vacuo* and passed through a LH-20 gel using MeOH as solvent to remove the impurities. The resulting *O*-sultated pentasaccharide was used as such without further purification.

**General Procedure for Hydrogenolysis.** Pd $(OH)_2$/C (20%, 5 equi per OBn) was added to a solution of the starting material (0.02 mmol) in $CH_3OH$. The mixture was equipped with a $H_2$-ballon, and stirred for 36 h at room temperature, then filtered through a pad of Celite and concentrated in *vacuo* to give a white powder. The $^1H$ NMR of the crude mixture showed the absence of the signals of benzyl groups. The hydrogenolysis reaction cleaved all the *O*-Bn groups and reduced $N_3$ to $NH_2$. The crude powder was used as such for the next step without further purification.

**General Procedure for Selective *N*-Sulfation**. The amino-alochol containing pentasaccharide (0.015 mmol) was dissolved in water (1-1.5 mL). The sulfur trioxide-pyridine complex (5 equi per $NH_2$ group) was added in five equal portions in half-hour intervals at room temperature. The pH value of the solution was adjusted to 9.5 by dropwise addition of 1N NaOH (aq). The pH was checked several times within 2-3 h and additional amount of 1N NaOH (aq) was added if pH drops below 9.5. After stirring for 38 h at room temperature, the reaction mixture was concentrated in *vacuo*. The residue was purified by column chromatography on Sephadex G-25 using water as an eluent. The desired fractions were collected, concentrated and passed through an ion exchange column of DOWEX 50WX8$^-Na^+$ using water as eluent. The desired fractions were collected and lyophilized to give the *N*-sulfated pentasaccharide product.

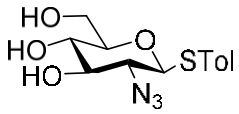
**B. Experimental procedure and characterization data of monosaccharides**

**Scheme S1**. Synthesis of 2-azido thioglycoside donors



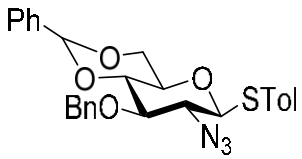

Reaction conditions:(a) p-CrSH, $BF_3$-$Et_2O$, $CH_2Cl_2$, 0 °C-rt, 12 h, 86%; (b) Zn-dust, AcOH : $CH_2Cl_2$ (1:2), rt, 12 h, 83% (c) $TfN_3$, EtOAc: MeOH (1:1), $CuSO_4$, $K_2CO_3$, rt, 12 h, 69%; (d) (i) $PhH(OMe)_2$, CSA, DMF, rt, 12 h, 81%; (ii) NaH, BnBr, DMF, 0 °C-rt, 2 h, 79%; (e) (i) $BH_3$-THF, $^nBu_2BOTf$, 0 °C, 2 h, 82%; (ii) TBDPSCl, Imidazole, rt, 12 h, 92%; (f) (i)TFA : $CH_2Cl_2$ : $H_2O$ (1:10:0.1), 0 °C-rt, 30 min, 81%; (ii) $Ac_2O$, $Et_3N$, $CH_2Cl_2$, 0 °C, 30 min, 88%

**4-Methylphenyl 2-azido-2-deoxy-1-thio-β-D-glucopyranoside (S4)**




Compound **S3** was prepared from D-glucosamine hydrochloride **16** using known procedures.[2] A solution of **S3** (10 g, 24.33 mmol) in MeOH: EtOAc (50:50 mL) was added $CuSO_4 \cdot 5H_2O$ (0.6 g, 0.2433 mmol), and $K_2CO_3$ (3.35 g, 24.27 mmol). The mixture was cooled to 0 °C and treated with a freshly prepared $TfN_3$ solution. It was kept stirring at room temperature for overnight. After that the solvents were evaporated in *vacuo* and the crude mixture was purified by column chromatography on silica gel ($PhCH_3$: EtOAc 6:4) to furnish **S4** (5.25 g, 69%). $R_f$ 0.25 ($PhCH_3$/EtOAc 6:4); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.8 Hz, 2 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 4.45 (d, *J* = 10.2 Hz, 1 H), 3.89 (dd, *J* = 12.0, 3.0 Hz, 1 H), 3.82 (dd, *J* = 12.0, 4.2 Hz, 1 H), 3.54 (t, *J* = 9.6 Hz, 1 H), 3.48 (t, *J* = 9.0 Hz, 1 H), 3.32-3.30 (m, 1 H), 3.26 (t, *J* = 9.6 Hz, 1 H), 2.33 (s, 3 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 138.9, 133.7, 130.0, 127.6, 86.8, 79.2, 69.6, 65.1, 62.1, 57.0, 21.2; m/z (HRMS) calcd for $C_{13}H_{17}N_3O_4SNa$ $[M+Na]^+$: 334.0837, found:.334.0844.

**4-Methylphenyl 2-azido-3-benzyl-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (S5)**



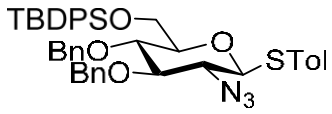

Compound **S4** (5.25 g, 16.88 mmol) in anhydrous DMF (40 mL) was treated with benzaldehyde dimethyl acetal (3.1 mL, 20.3 mmol) and camphor sulphonic acid (3.92 g, 16.88 mmol). The reaction mixture was stirred for 12 h at room temperature and then quenched with $Et_3N$. It was concentrated and diluted with EtOAc (2 × 100 mL), washed with water (2 ×50 mL), brine (50 mL), dried over $MgSO_4$ and filtered. The organic layer was concentrated in *vacuo* and the resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 1:1) to furnish **4-Methylphenyl-2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside** (4.71 g, 81%). $R_f$ 0.41 (Hexane/EtOAc 9:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.11-8.09 (m, 1 H), 7.62-7.60 (m, 1 H), 7.49-7.44 (m, 4 H), 7.38-7.35 (m, 2 H), 7.16 (d, *J* = 8.4 Hz, 2 H), 5.52 (s, 1 H), 4.49 (d, *J* = 10.2 Hz, 1 H), 4.36 (dd, *J* = 4.8, 10.8 Hz, 1 H), 3.78-3.75 (m, 2 H), 3.46-3.44 (m, 2 H), 3.32 (dd, *J* = 9.0, 10.2 Hz, 1 H), 2.37 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 139.4, 134.3, 133.7, 130.1, 129.9, 129.4-126.7, 101.9, 86.8, 80.2, 74.1, 70.2, 68.4, 65.0, 21.2; m/z (HRMS) calcd for $C_{20}H_{21}N_3O_4S$ $[M+H]^+$: 400.1326, found: 401.2591. The purified compound (4.71 g,

11.8 mmol) was dissolved in anhydrous DMF (40 mL) and NaH (0.944 g, 23.60 mmol of 60% dispersion in mineral oil) and benzyl bromide (1.69 mL, 14 mmol) were added at 0 °C. After 2 h, it was quenched with methanol and concentrated in *vacuo*, diluted with EtOAc (2 × 100 mL), washed with water (2 ×75 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by flash column chromatography (Hexane: EtOAc, 8:2) to furnish **S5** (4.56 g, 79%) as yellow oil. $R_f$ 0.51 (Hexane/EtOAc 9:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.39-7.36 (m, 4 H), 7.29-7.19 (m, 8 H), 7.01 (d, *J* = 7.8 Hz, 2 H), 5.46 (s, 1 H), 4.81 (d, *J* = 10.8 Hz, 1 H), 4.69 (d, *J* = 11.4 Hz, 1 H), 4.32 (d, *J* = 10.2 Hz, 1 H), 4.28 (dd, *J* = 10.2, 4.8 Hz, 1 H), 3.67 (t, *J* = 10.2 Hz, 1 H), 3.56 (t, *J* = 9.0 Hz, 1 H), 3.51 (t, *J* = 9.0 Hz, 1 H), 3.35 (td, *J* = 4.8, 9.6 Hz, 1 H), 3.24 (dd, *J* = 9.0, 10.2 Hz, 1 H), 2.26 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 139.1, 137.5, 137.1, 134.5,129.9-128.0, 126.5, 125.9, 101.2, 86.5, 81.2, 81.0, 75.2, 70.4, 68.5, 64.5, 21.2; m/z (HRMS) calcd for $C_{27}H_{27}N_3O_4SNa$ $[M+Na]^+$: 512.1614, found:.512.1634.

**4-Methylphenyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-β-D-glucopyranoside (9)**

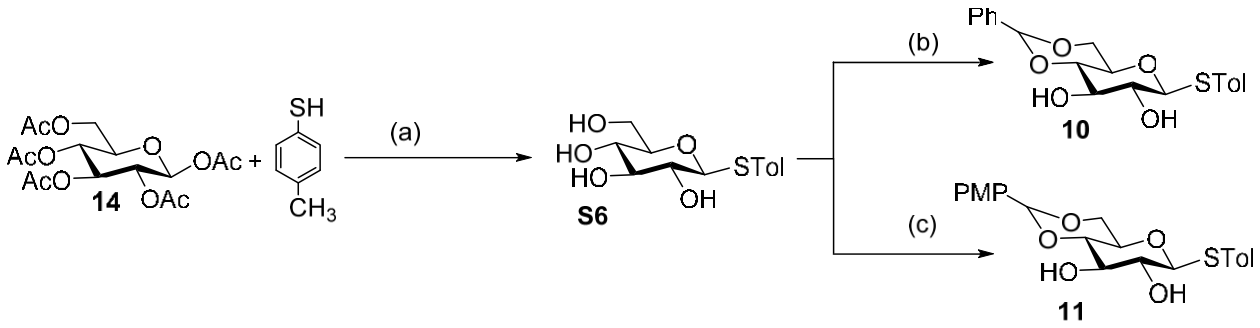

A solution of a compound **S5** (4.56 g, 9.32 mmol) in a mixture of solvents ($CH_2Cl_2$: TFA: $H_2O$ =10/1/0.1 v/v/v) was stirred at room temperature for 30 min. It was then concentrated in *vacuo*, and later co-evaporated with toluene to remove traces of water. The crude diol was further dissolved in anhydrous $CH_2Cl_2$ (25 mL) and treated with $Ac_2O$ (0.96 mL, 9.41 mmol) and $Et_3N$ (11.68 mL, 115.68 mmol) at 0 °C under argon atmosphere for 30 min. After the complete conversion of starting material, it was diluted with $CH_2Cl_2$ (100 mL), washed with saturated $NaHCO_3$ (2 × 50 mL), brine (75 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel coulmn chromatography (Hexane: EtOAc, 6:4) to afford **9** as gum (3.63 g, 88%). $R_f$ 0.38 (hexane/EtOAc, 6:4); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2 H), 7.37-7.34 (m, 4 H), 7.32-7.30 (m, 1 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 4.90 (d, *J* = 11.4 Hz, 1 H), 4.80 (d, *J* = 11.1 Hz, 1 H), 4.42 (dd, *J* = 12.0, 4.8 Hz, 1 H), 4.36 (d, *J* = 10.2 Hz, 1 H), 4.30 (dd, *J* = 12.0, 2.0 Hz, 1 H), 3.40-3.39 (m, 1 H), 3.36 (app dd, *J* = 10.2, 11.6 Hz, 2 H), 3.25 (t, *J* = 9.6 Hz, 1 H), 2.34 (s, 3H), 2.10 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 171.7, 138.9, 137.7, 134.4, 129.8-127.0, 86.2, 84.3, 77.8, 75.7, 69.8, 64.5, 63.1, 21.2, 20.9; m/z (HRMS) calcd for $C_{22}H_{25}N_3O_5SNa$ $[M+Na]^+$: 466.1407, found: 466.1431.

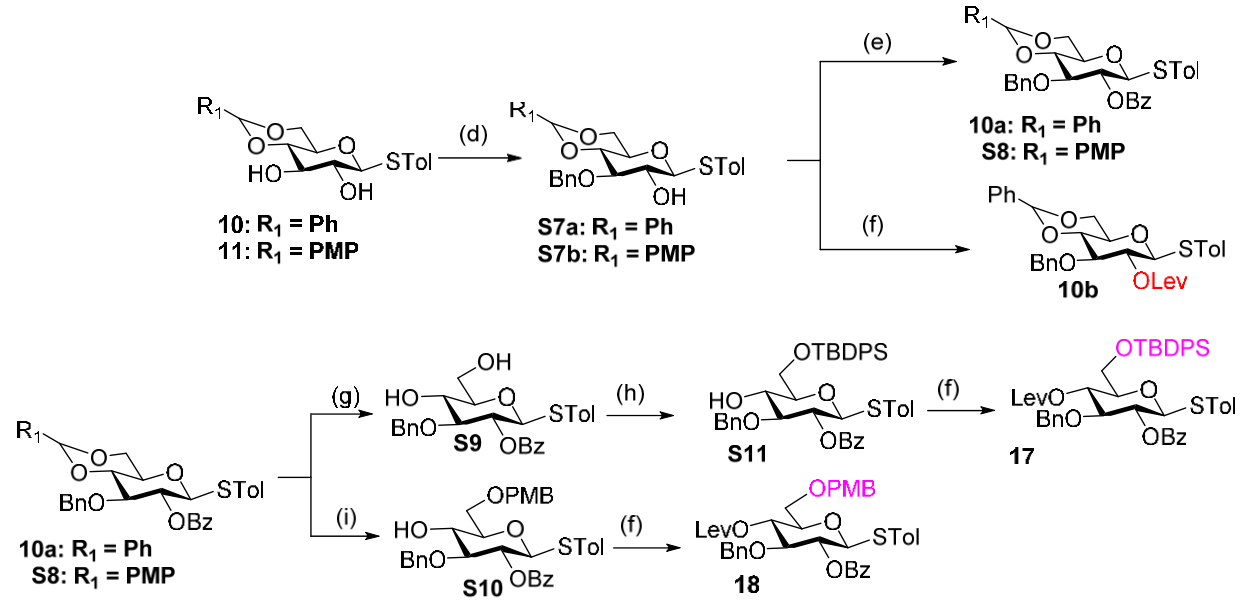
**4-Methylphenyl 2-azido-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-1-thio-β-D-glucopyranoside (4).**




To a solution of compound **S5** (2.0 gm, 4.08 mmol) in anhydrous THF (25 mL) was added $BH_3$·THF complex (15 mL of a 1M solution in THF) followed by $Bu_2BOTf$ (0.500 g of a 1M solution in $CH_2Cl_2$) at 0 °C. After 2 h, the reaction mixture was quenched by a slow addition of MeOH at 0 °C. When no further evolution of hydrogen was found, it was concentrated in *vacuo* and residue was purified by flash column chromatography (hexane/EtOAc, 9:1) to afford the 6-hydroxy derivative (1.64 g, 82%) as a colourless gum. The 6-hydroxy derivative (3.36 mmol) was dissolved in anhydrous $CH_2Cl_2$ (20 mL) and *tert*-butyl diphenyl silyl chloride (1.08 mL, 4.00 mmol) and imidazole (0.332 g, 4.88 mmol) were added under $N_2$ atmosphere. It was stirred over night at room temperature and quenched with MeOH. The solvent was evaporated in *vacuo* and the crude mixture was purified by silica gel column chromatography (Hexane: EtOAc, 20:1) to afford **4** as a gum (2.24 g, 92%). $R_f$ 0.58 (hexane/EtOAc, 20:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.44-7.26 (m, 14 H), 7.16 (app d, 2H), 7.05 (d, *J* = 7.8 Hz, 2 H), 4.86 (app t, *J* = 6.0 Hz, 3H), 4.70 (d, *J* = 10.8 Hz, 1H), 4.38 (d, *J* = 10.2 Hz, 1H), 4.02 (d, *J* = 11.4 Hz, 1H), 3.94 (dd, *J* = 11.4, 3.0 Hz, 1 H), 3.78 (t, *J* = 9.6 Hz, 1 H), 3.54 (t, *J* = 9.6 Hz, 1H), 3.36 (app t, *J* = 9.6 Hz, 2H), 2.32 (s, 3H), 1.10 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 138.0, 137.6, 135.9, 134.2, 133.4, 132.8, 129.8-127.7, 127.2, 86.1, 85.3, 80.0, 76.1, 75.1, 64.8, 62.3, 26.9, 21.2, 19.3; m/z (HRMS) calcd for $C_{43}H_{47}N_3O_4SSiNa$ $[M+Na]^+$: 752.2949, found:.752.2984.

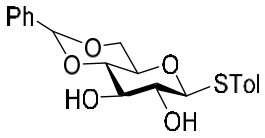
**Scheme S2**. Synthesis of thioglycoside donors (**Building Block B)**






Reaction conditions: (a) (i) $BF_3{\cdot}OEt_2$, $CH_2Cl_2$, 0 °C-rt, 12 h, 94.5%; (ii) NaOMe, MeOH : $CH_2Cl_2$ (3:1), rt, 2 h; (b) $PhH(OMe)_2$,CSA DMF, rt, 12 h, 86%; (c) $PhOMe(OMe)_2$, CSA, DMF, rt, 12 h, 81%; (d) (i) $Bu_2SnO$, $PhCH_3$, 110 °C, 12 h; (ii) CSF, BnBr, DMF, 80 °C, 12 h, 82% (for **S7b**), 80 % (for **S7a**); (e) BzCl, Py, 0 °C-rt, 12 h, 80% (for **10a**), 81 % (for **S8**); (f) $CH_3CO(CH_2)_2COOH$, EDCI, DMAP, $CH_2Cl_2$, rt, 12 h, 81% (for **10b**), 83 % (for **17**), 81% (for **18**); (g) $CH_2Cl_2$ : $CF_3COOH$ : $H_2O$ (10:1:0.1), rt, 1 h, 78%. (h) TBDPSCl, Py, rt, 12 h, 89%; (i) $NaCNBH_3$, TFA, DMF, 0 °C-rt, 12 h, 76 %.

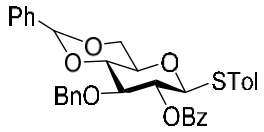
**4-Methylphenyl-4,6-*O*-benzylidine-1-thio-β-D-glucopyranoside (10)**



To a solution of commercially available *per-O-acetyl*-β-D-glucopyranose **14** (20 g, 51.28 mmol) in $CH_2Cl_2$ (100 mL) was treated with *p*-toluenethiol (7.5 g, 60.38 mmol) followed by $BF_3{\cdot}OEt_2$ (16.5 mL, 128 mmol) at 0 °C. After stirring for 12 h, the reaction mixture was washed with saturated $NaHCO_3$ (3 x 100 mL). The aqueous layer was further extracted with $CH_2Cl_2$ (3 x 150 mL). The combined organic layers were washed with a brine solution (200 mL), dried over $MgSO_4$, filtered and concentrated in *vacuo*. The residue was re-dissolved in a minimum amount of EtOAc and hexane was added until it solidified to give the desired derivative (22 g, 94.5%). The analytical data is well in agreement with the reported values. A solution of tri-acetate (10 g, 8.05 mmol) was dissolved in a mixture of MeOH: $CH_2Cl_2$ (60:20 mL) and a catalytic amount of NaOMe (0.650 g) was added. The mixture was stirred for 2 h at room temperature , and after that it was neutralized with amberlite 120 $H^+$ resin. The resin was filtered and the solvent was evaporated to furnish the tri-hydroxyl derivative **S6**. Compound **S6** (5.98 g, 20.90 mmol) in anhydrous DMF (40 mL) was treated with benzaldehyde dimethyl acetal (3.81 mL, 25.1 mmol) and camphor

sulphonic acid (4.85 g, 20.90 mmol). The reaction mixture was stirred for 12 h at room temperature and then quenched with $Et_3N$. It was concentrated and diluted with EtOAc (2 × 100 mL), washed with water (2 × 50 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 1:1) to furnish compound **10** (6.72 g, 86%). $R_f$ 0.52 (hexane/EtOAc 1:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.48-7.44 (m, 2H), 7.42-7.36 (m, 5H), 7.35-7.14 (m, 2H), 5.52 (s, 1H), 4.55 (d, *J* = 9.6 Hz, 1H), 4.36 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.83 (t, *J* = 8.4 Hz, 1H), 3.78 (td, *J* = 3.0, 7.2 Hz, 1H), 3.51-3.49 (m, 1H), 3.48 (br s, 1H), 3.42 (t, *J* = 9.0 Hz, 1H), 2.89 (s, 1H), 2.61 (s, 1H), 2.36 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 138.9, 136.9, 133.7, 129.8-127.2, 126.3, 102.0, 88.7, 80.3, 74.6, 72.5, 70.6, 68.6, 21.2; m/z (HRMS) calcd for $C_{20}H_{22}O_5SNa$ $[M+Na]^+$: 397.1080, found: 397.1097.

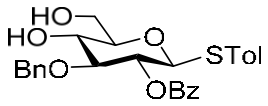
**4-Methylphenyl-2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidine-1-thio-β-D-glucopyranoside (10a)**




A mixture of compound **10** (6.72 g, 17.96 mmol) and dibutyltin oxide (6.71 g, 26.95 mmol) was stirred in toluene (60 mL) at 110 °C by using a dean-stark apparatus for 12 h. The reaction mixture was cooled down to room temperature and concentrated in *vacuo*. The residue was dissolved in anhydrous DMF (40 mL) and BnBr was added (2.79 mL, 23.34 mmol) followed by CsF (3.27 g, 21.3 mmol). The reaction mixture was heated at 80 °C for overnight. Solvents were removed in *vacuo*. It was diluted with EtOAc (2 × 150 mL), washed with water (2 × 70 mL), brine (80 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 8:2) to furnish the compound **S7a** (6.83 g, 82%) as an yellow oil. $R_f$ 0.52 (hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.48-7.44 (m, 2H), 7.43-7.26 (m, 10H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.56 (s, 1H), 4.93 (d, *J* = 11.4 Hz, 1H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 3.86 (dd, *J* = 4.8, 10.2 Hz, 1H), 3.80 (t, *J* = 10.2 Hz, 1H), 3.70 (t, *J* = 9.0 Hz, 1H), 3.64 (t, *J* = 9.0 Hz, 1H), 3.51-3.48 (m, 2H), 2.34 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ δ 138.9, 136.9, 133.8, 130.0, 129.4, 128.5, 127.3, 126.4, 102.0, 88.8, 80.3, 74.6, 72.6, 70.6, 68.7, 21.3; m/z (HRMS) calcd for $C_{27}H_{28}O_5SNa$ $[M+Na]^+$: 487.1555, found:.487.1578. A solution of copound **S7a** (6.83 g, 14.71 mmol) in pyridine (40 mL) was treated with BzCl (3.41 mL, 24.33 mmol) at 0 °C. The reaction mixture was allowed to warm up slowly to room temperature over a period of 12 h. It was diluted with EtOAc (2 × 100 mL), washed with water (2 ×50 mL), brine (80 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 8:2) to furnish the compound **10a** (6.67

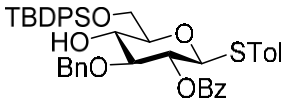
g, 80%). $R_f$ 0.57 (hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.17 (app d, *J* = 2.0, 8.4 Hz, 2 H), 8.02 (d, *J* = 7.2 Hz, 2H), 7.68-7.59 (m, 2H), 7.53-7.50 (m, 2H), 7.40-7.38 (m, 3H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.11-7.04 (m, 6H), 5.59 (s, 1 H), 5.25 (dd, *J* = 10.2, 9.0 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 2H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.40 (dd, *J* = 8.4, 10.8 Hz, 1H), 3.89-3.85 (m, 1H), 3.80 (dd, *J* = 4.8, 9.6 Hz, 2H), 3.54 (td, *J* = 5.4, 10.2 Hz, 1H), 2.32 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 180.0, 137.7, 133.6, 133.1, 130.0, 129.8-128.0, 127.6, 126.0, 101.2, 87.1, 81.4, 79.3, 74.2, 72.0, 70.5, 68.6, 21.3;m/z (HRMS) calcd for $C_{34}H_{32}O_6SNa$ $[M+Na]^+$: 591.1812, found:591.1827.

**4-Methylphenyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-β-D-glucopyranoside (S9)**




A solution of a compound **10a** (4.56 g, 9.32 mmol) in a mixture of solvents ($CH_2Cl_2$: TFA: $H_2O$ = 10:1:0.1, v/v/v) was stirred at room temperature for 1 h. The reaction mixture was quenched with solid $NaHCO_3$, filtered and then concentrated in *vacuo.* The crude reaction mixture was purified by silica gel column chromatography ($CH_2Cl_2$: Hexane, 3:7) to afford **S9** (3.0 g, 78%) as white solid. $R_f$ 0.51 ($CH_2Cl_2$: Hexane, 3:7); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.11-8.00 (m, 3H), 7.62-7.59 (m, 2H), 7.49-7.40 (m, 3H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.19-7.17 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 5.23 (t, *J* = 9.6 Hz, 1H), 4.78 (t, *J* = 10.2 Hz, 1H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 3.92 (dd, *J* = 12.0, 3.0 Hz, 1H), 3.82 (dd, *J* = 4.8, 12.0 Hz, 1H), 3.72 (q, *J* = 7.8 Hz, 2H), 3.47 (q, *J* = 4.2 Hz, 1 H), 2.31 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 165.1, 138.5, 137.7, 133.5, 133.4, 133.2, 130.3, 130.0, 129.9, 129.8, 128.8, 128.6, 128.5, 128.1, 128.0, 86.7, 83.93, 79.5, 74.8, 72.5, 70.4, 62.6, 21.2; m/z (HRMS) calcd for $C_{27}H_{28}O_6SNa$ $[M+Na]^+$: 503.1504, found:503.1521.

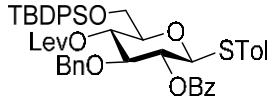
**4-Methylphenyl-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (S11)**




Compound **S9** (3.0 g, 6.25 mmol) was dissolved in anhydrous pyridine (20 mL) and *tert*-butyl diphenyl silyl chloride (2.1 mL, 7.4 mmol) was added under $N_2$ atmosphere. It was stirred overnight at room temperature and quenched with MeOH. The solvents were evaporated in *vacuo* and crude mixture was purified by silica gel column chromatography (Hexane: EtOAc, 9:1) to afford **S11** as colourless gum (3.99 g, 89%). $R_f$ 0.65 (hexane/EtOAc 9:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.21 – 8.13 (m, 1H), 8.13 –

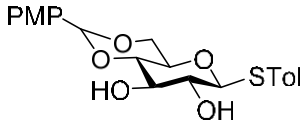
8.08 (m, 1H), 7.79-7.77 (m, 4H), 7.66 – 7.59 (m, 2H), 7.52 – 7.44 (m, 12H), 7.44 – 7.37 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 5.30 – 5.25 (m, 1H), 4.80 (d, *J* = 10.0 Hz, 1H), 4.76 – 4.70 (m, 2H), 4.03 (dd, *J* = 11.0, 3.7 Hz, 1H), 3.99 (dd, *J* = 11.0, 4.6 Hz, 1H), 3.93 – 3.88 (m, 1H), 3.77 (t, *J* = 9.0 Hz, 1H), 3.57 – 3.53 (m, 1H), 2.31 (s, 3H), 1.11 (s, 9H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 165.2, 138.0, 137.9, 135.7, 133.2, 133.1, 132.9, 130.0, 129.8-127.8, 86.6, 84.0, 79.4, 74.7, 72.2, 71.3, 64.1, 31.6, 26.9, 22.7, 21.1, 19.3; m/z (HRMS) calcd for $C_{43}H_{46}O_6SSiNa$ $[M+Na]^+$: 741.2677, found:.741.2701.

**4-Methylphenyl-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-levulinyl-1-thio-β-D-glucopyranoside (17).**




To a solution of **S11** (3.99 g, 5.55 mmol) in $CH_2Cl_2$ (35 mL) was added levulinic acid (0.892 mL, 11.02 mmol), EDCI (2.15 g, 13.89 mmol), DMAP (0.340 g, 2.77 mmol) and the mixture was stirred for overnight at room temperature. It was diluted with EtOAc (2 × 50 mL), washed with water (2 ×25 mL), brine (40 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 8:2) to furnish compound **17** (3.76 g, 83%). $R_f$ 0.48 (hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.08-8.06 (m, 2H), 7.77-7.72 (m, 4H), 7.62-7.60 (m, 2H), 7.49-7.45 (m, 2H), 7.47-7.37 (m, 8H), 7.16-7.11 (m, 4H), 7.01 (d, *J* = 7.8 Hz, 2H), 5.31 (t, *J* = 9.6 Hz, 1H), 5.20 (t, *J* = 9.6 Hz, 1H), 4.81 (d, *J* = 9.6 Hz, 1H), 4.53 (s, 2 H), 3.92 (t, *J* = 9.6 Hz, 1H), 3.82-3.76 (m, 2H), 3.64-3.61 (m, 1H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.38-2.33 (m, 2H), 2.29 (s, 3H), 2.12 (s, 3H), 1.10 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 206.0, 171.2, 165.0, 138.0, 137.7, 135.8, 135.8, 135.6, 134.8, 133.3, 133.3, 133.3, 133.0, 129.9, 129.7, 129.6, 129.2, 128.5, 128.2, 127.9, 127.8, 127.7, 127.7, 127.7, 127.6, 86.8, 81.7, 79.4, 74.1, 72.3, 70.0, 63.0, 37.8, 29.8, 27.8, 26.8, 21.2, 19.3; m/z (HRMS) calcd for $C_{48}H_{52}O_8SSiNa$ $[M+Na]^+$: 839.3044, found: 839.3088.

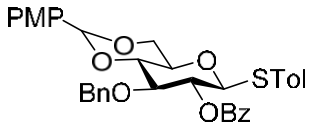
**4-Methylphenyl-4,6-*O*-*p*-methoxybenzylidine-1-thio-β-D-glucopyranoside (11).**




Compound **S6** (6 g, 20.90 mmol) was treated with *p*-anisaldehyde dimethyl acetal (4.28 mL, 25.17 mmol) and camphor sulphonic acid (4.87 g, 20.90 mmol) in anhydrous DMF (40 mL). The reaction mixture was stirred for 12 h at room temperature and then quenched with $Et_3N$. The solvent was removed in *vacuo*. And it was diluted with EtOAc (2 × 100 mL), washed with water (2 × 50 mL), brine (50 mL), then dried

($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 1:1) to furnish compound **11** (6.86 g, 81%). $R_f$ 0.39 (hexane/EtOAc 1:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 12.0 Hz, 2 H), 7.12 (d, *J* = 12.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 5.43 (s, 1H), 4.51 (d, *J* = 9.6 Hz, 1 H), 4.32 (dd, *J* = 10.8, 4.8 Hz, 1H), 3.82-3.77 (m, 1H), 3.76 (s, 3H), 3.74 (d, *J* = 8.4 Hz, 1H), 3.70 (t, *J* = 9.6 Hz, 1H), 3.44-3.41 (m, 2H), 3.39-3.36 (m, 1H), 3.16 (app d, *J* = 2.0 Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 160.2, 138.7, 133.5, 129.8-127.8, 113.7, 101.8, 88.6, 80.1, 74.5, 72.5, 70.4, 68.5, 55.3, 21.2;m/z (HRMS) calcd for $C_{21}H_{24}O_6SNa$ $[M+Na]^+$: 427.1186, found:.427.1209.

**4-Methylphenyl-2-*O*-benzoyl-3-*O*-benzyl-4,6-*p*-methoxybenzylidine-1-thio-β-D-glucopyranoside (S8).**

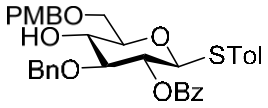



A mixture of compound **11** (6.86 g, 16.98 mmol) and dibutyltin oxide (5.07 g, 20.37 mmol) was stirred in toluene (60 mL) at 110 °C by using dean-stark apparatus for 12 h. The reaction mixture was cooled down to room temperature and solvent was removed in *vacuo*. The residue was dissolved in anhydrous DMF (40 mL) and BnBr was added (2.43 mL, 20.37 mmol) followed by CsF (3.10 g, 20.37 mmol). The reaction mixture was heated at 80 °C and stirred continuously for 12 h. The solvent was removed in *vacuo.* And it was diluted with EtOAc (2 × 150 mL), washed with water (2 × 70 mL), brine (80 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 7:3) to furnish compound **S7b** (6.87 g, 82%) as yellow oil. $R_f$ 0.48 (hexane/EtOAc 7:3); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.2 Hz, 2 H), 7.35 (d, *J* = 6.6 Hz, 2 H), 7.33-7.30 (m, 2 H), 7.28-7.27 (m, 2 H), 7.12 (d, *J* = 8.4 Hz, 2 H), 6.90 (app d, *J* = 6.6 Hz, 2 H), 5.51 (s, 1 H), 4.93 (d, *J* = 11.4 Hz, 1 H), 4.78 (d, *J* = 11.4 Hz, 1 H), 4.56 (d, *J* = 9.6 Hz, 1 H), 4.36 (dd, *J* = 4.8, 10.2 Hz, 1 H), 3.81 (s, 3 H), 3.76 (t, *J* = 10.8 Hz, 1 H), 3.66 (t, *J* = 4.8 Hz, 1 H), 3.60 (t, *J* = 9.6 Hz, 1 H), 3.50-3.48 (m, 1 H), 3.46 (dd, *J* = 9.6, 3.6 Hz, 1 H), 2.51 (s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 160.0, 155.0, 138.7, 138.2, 133.8, 129.8-127.2, 113.6, 101.2, 88.5, 81.6, 81.1, 74.8, 72.1, 70.7, 68.6, 55.3, 21.1; m/z (HRMS) calcd for $C_{28}H_{30}O_6SNa$ $[M+Na]^+$: 517.1655, found:.517.1686.

A solution of compound **S7b** (6.87 g, 14.07 mmol) in pyridine (40 mL) was treated with BzCl (3.41 mL, 24.33 mmol) at 0 °C. The reaction mixture was allowed to warm up slowly to room temperature over a period of 12 h. It was diluted with EtOAc (2 × 100 mL), washed with water (2 ×50 mL), brine (80 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 8:2) to furnish compound **S8** (6.65 g, 81%). $R_f$ 0.5

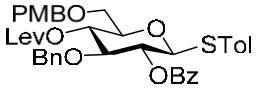
(hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$):δ 8.00 (dd, *J* = 7.8, 1.2 Hz, 2 H), 7.63-7.59 (m, 2 H), 7.47 (t, *J* = 6.6 Hz, 2 H), 7.42 (d, *J* = 4.8 Hz, 2 H), 7.33 (d, *J* = 6.6 Hz, 2 H), 7.11-7.04 (m, 7 H), 6.91 (d, *J* = 7.2 Hz, 2 H), 5.55 (s, 1 H), 5.26 (app d, *J* = 9.6, 9.0 Hz, 1 H), 4.78 (app d, *J* = 12.0, 7.2 Hz, 2 H), 4.64 (d, *J* = 11.4 Hz, 1 H), 4.38 (dd, *J* = 10.2, 5.4 Hz, 1 H), 3.86 (q, *J* = 9.0 Hz, 1 H), 3.83 (s, 3 H), 3.80-3.76 (m, 1 H), 3.52 (td, *J* = 9.6, 4.8 Hz, 1 H), 2.32 (s, 3 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 165.3, 160.2, 138.6, 137.8, 133.7, 133.2, 130.0, 129.8-127.2, 113.7, 101.3, 87.2, 81.4, 79.4, 74.3, 72.1, 70.7, 68.6, 55.4, 21.2; m/z (HRMS) calcd for $C_{35}H_{34}O_7SNa$ $[M+Na]^+$: 621.1917, found: 621.1958.

**4-Methylphenyl-2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-1-thio-β-D-glucopyranoside (S10)**




A solution of compound **S8** (6.65 g, 11.12 mmol) in anhydrous DMF (40 mL) was cooled to 0 °C. It was then treated with solid $NaCNBH_3$ (7.0 g, 111.25 mmol) and TFA (8.52 mL, 111.20 mmol), sequentially. The resulting suspension was stirred at room temperature for 12 h until consumption of starting material was observed. It was neutralized by solid $NaHCO_3$, and the solution was filtered and diluted with EtOAc (2 × 100 mL), washed with water (2 ×50 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 7:3) to furnish compound **S10** (5.07 g, 76%). The ring opening of the acetal was stereoselective and gave only 4-OH derivative. $R_f$ 0.4 (hexane/EtOAc 7:3); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.16-8.14 (m, 2 H), 7.69-7.67 (m, 1 H), 7.56 (t, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 7.8 Hz, 2 H), 7.39-7.34 (m, 5 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 6.99-6.97 (m, 4 H), 5.31 (t, *J* = 9.6 Hz, 1 H), 4.82 (d, *J* = 9.6 Hz, 1 H), 4.80 (d, *J* = 11.4 Hz, 1 H), 4.71 (s, 2 H), 4.60 (d, *J* = 9.6 Hz, 1 H), 3.90 (s, 3 H), 3.87 (d, *J* = 4.8 Hz, 2 H), 3.77 (t, *J* = 9.0 Hz, 1 H), 3.64 (q, *J* = 4.8 Hz, 2 H), 2.42 (s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 165.3, 159.4, 159.3, 138.2, 137.9, 133.6, 133.3, 133.1, 133.0, 130.0, 130.0, 129.8-127.9, 114.0, 113.9, 86.7, 83.7, 78.3, 74.9, 73.5, 72.2, 72.1, 70.2, 65.1, 55.4, 21.2; m/z (HRMS) calcd for $C_{35}H_{36}O_7SNa$ $[M+Na]^+$: 623.2074, found: 623.2102.

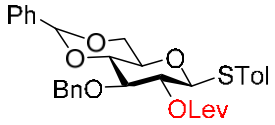
**4-Methylphenyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-levulinyl-6-*O*-*p*-methoxybenzyl-1-thio-β-D-glucopyranoside (18).**




Compound **S10** (5.07 g) was treated as described for preparation of **17**. Compound **18** (4.78 g) was obtained in 81% yield. $R_f$ 0.5 (hexane/EtOAc 6:4); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.04-8.02 (m, 2 H),

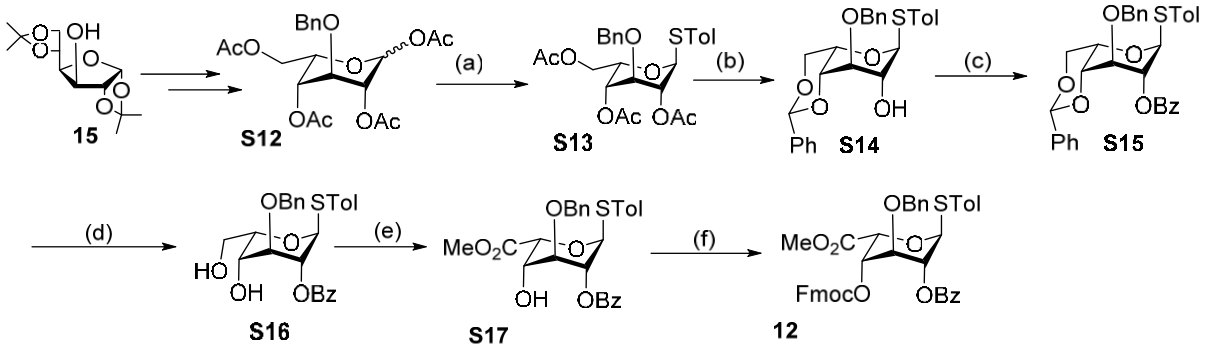
7.59-7.58 (m, 2 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 7.35 (d, *J* = 6.8 Hz, 2 H), 7.28-7.26 (m, 2 H), 7.13-7.08 (m, 4 H), 7.00 (d, *J* = 7.8 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 5.26 (t, *J* = 9.6 Hz, 1 H), 5.09 (t, *J* = 9.6 Hz, 1 H), 4.74 (d, *J* = 10.2 Hz, 1 H), 4.58 (s, 2 H), 4.46 (s, 2 H), 3.86 (t, *J* = 9.0 Hz, 1 H), 3.81 (s, 3 H), 3.69 (td, *J* = 4.2, 5.4 Hz, 1 H), 3.60-3.59 (m, 2 H), 2.64-2.54 (m, 2 H), 2.44-2.39 (m, 2 H), 2.28 (s, 3 H), 2.12 (s, 3 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 206.2, 177.5, 165.0, 159.2, 138.0, 137.6, 133.7, 133.2, 133.0, 130.2, 130.1, 129.8-127.9, 113.7, 86.5, 81.4, 77.9, 74.1, 73.2, 72.1, 71.0, 69.4, 55.2, 37.7, 29.7, 27.8, 21.2; m/z (HRMS) calcd for $C_{40}H_{42}O_9SNa$ $[M+Na]^+$: 721.2442, found:721.2482.

**4-Methylphenyl-3-*O*-benzyl-4,6-*O*-benzylidine-2-*O*-levulinyl-1-thio-β-D-glucopyranoside (10b)**



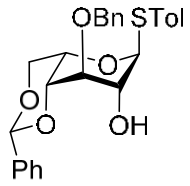

To a solution of compound **S7b** (4.0 g, 8.59 mmol) in $CH_2Cl_2$ (35 mL) was added levulinic acid (0.895 mL, 11.1 mmol), EDCI (3.33 g, 21.4 mmol), DMAP (0.526 g, 4.30 mmol) and the mixture was stirred for overnight at room temperature. It was diluted with EtOAc (2 × 100 mL), washed with water (2 × 50 mL), brine (40 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 7:3) to furnish compound **10b** (3.92 g, 81%). $R_f$ 0.51 (hexane/EtOAc 7:3); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.49 – 7.46 (m, 2H), 7.39 – 7.36 (m, 5H), 7.31 – 7.28 (m, 4H), 7.28 – 7.27 (m, 1H), 7.13 – 7.11 (m, 2H), 5.57 (s, 1H), 4.99 (dd, *J* = 10.1, 8.4 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 10.1 Hz, 1H), 4.38 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.82 – 3.73 (m, 2H), 3.71 (t, *J* = 9.2 Hz, 2H), 3.48 (ddd, *J* = 10.1, 9.0, 5.0 Hz, 1H), 2.75 (td, *J* = 6.8, 2.3 Hz, 2H), 2.66 – 2.58 (m, 1H), 2.58 – 2.51 (m, 1H), 2.34 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 206.2, 171.3, 138.6, 138.2, 137.2, 133.6, 129.7-126.0, 101.3, 87.1, 81.3, 79.8, 76.9, 74.4, 71.8, 70.5, 68.6, 37.9, 29.9, 28.1, 21.2; m/z (HRMS) calcd for $C_{32}H_{35}O_7S$ $[M+H]^+$: 563.2098, found: 563.2077.

**Scheme S3**. Synthesis of thioglycoside donors (**Building Block D**)



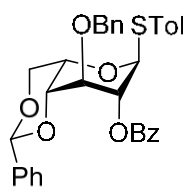
Reaction conditions:(a) (i) *p*-CrSH, $BF_3$-$Et_2O$, $CH_2Cl_2$, 0 °C-rt, 12 h, 90%; (b) (i) NaOMe, MeOH : $CH_2Cl_2$ (3:1), rt, 5 h; (ii) $PhH(OMe)_2$, CSA, DMF, rt, 12 h, 81%; (c) BzCl, Py, 0 °C-rt, 12 h, 80%; (d) TFA: $CH_2Cl_2$:$H_2O$ (1:10:0.1), rt, 1 h, 79%; (e) (i) BAIB, TEMPO, $CH_2Cl_2$:$H_2O$ (2:1), rt, 2 h; (ii) $CH_3I$, $KHCO_3$, DMF, 0 °C-rt, 4 h, 59%; (f) FmocCl, Py, $CH_2Cl_2$, 0 °C-rt, 4 h, 80%.

**4-Methylphenyl 3-*O*-benzyl-4,6-*O*-benzylidine-1-thio-α-L-idopyranoside (S14)**



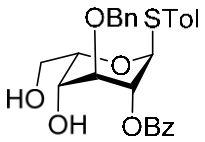

1,2,4,6-Tetra-*O*-acetyl-3-*O*-benzyl-α/β-D-idopyranoside **S12** was prepared from diacetone α-D-glucose **15** using known procedures.[3] It was further treated with *p*-toluenethiol in the presence of $BF_3 \cdot OEt_2$ to furnish **S13** in 90% yield using a reported procedure.[2c] Compound **S13** (3.0 g, 5.97 mmol) was dissolved in a mixture of MeOH : $CH_2Cl_2$ (30:10 mL) and a catalytic amount of NaOMe (100 mg) was added. The mixture was stirred for 5 h at room temperature and it was neutralized with amberlite 120 $H^+$ resin. The resin was filtered and the solvents were evaporated in *vacuo*. The crude mixture dissolved in anhydrous DMF (30 mL) was treated with benzaldehyde dimethyl acetal (0.96 mL, 6.4 mmol) and camphor sulphonic acid (1.23 g, 5.31 mmol). The reaction mixture was stirred for 12 h at room temperature and then quenched with $Et_3N$. Solvents were removed in *vacuo* and diluted with EtOAc (2 × 100 mL), washed with water (2 × 50 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 1:1) to furnish **S14 (**1.99 g, 81%). $R_f$ 0.41 (hexane/EtOAc 1:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.47-7.43 (m, 4 H), 7.42-7.32 (m, 8 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 5.59 (s, 1H), 5.55 (s, 1H), 4.85 (d, *J* = 12.0 Hz, 1 H), 4.60 (d, *J* = 12.0 Hz, 1 H), 4.47 (s, 1 H), 4.34 (d, *J* = 12.0 Hz, 1 H), 4.15-4.10 (m, 3 H), 3.80 (app d, *J* = 2.4 Hz, 2 H), 2.32 (s, 3 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 137.4, 137.3, 136.9, 133.5, 130.8, 129.7-127.8, 126.0, 101.6, 89.5, 74.5, 73.9, 72.4, 70.2, 67.7, 60.6, 21.1; m/z (HRMS) calcd for $C_{27}H_{28}O_5SNa$ $[M+Na]^+$: 487.1555, found: 487.1550.

**4-Methylphenyl 2-*O*-benzoyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-α-L-idopyranoside (S15)**



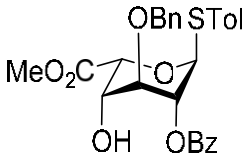
A solution of **S14** (1.99 g, 4.30 mmol) in pyridine (25 mL) was treated with BzCl (0.99 mL, 8.57 mmol) at 0 °C. The reaction mixture was allowed to warm up slowly to room temperature over a period of 12 h. It was diluted with EtOAc (2 × 100 mL), washed with water (2 × 50 mL), brine (80 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane/EtOAc 9:1) to furnish compound **S15** (1.94 g, 80%). $R_f$ 0.57 (hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.2 Hz, 2 H), 7.53-7.48 (m, 5 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 7.40 (t, *J* = 8.4 Hz, 2 H ), 7.35 (t, *J* = 6.0 Hz, 2 H), 7.30 (t, *J* = 7.8 Hz, 2 H), 7.24 (t, *J* = 7.2 Hz, 2 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 5.77 (s, 1 H), 5.61 (s, 1 H), 5.56 (app d, *J* = 1.2 Hz, 1 H), 5.01 (d, *J* = 11.4 Hz, 1 H), 4.74 (d, *J* = 12.0 Hz, 1 H), 4.55 (s, 1 H), 4.42 (d, *J* = 12.6 Hz, 1 H), 4.24 (d, *J* = 12.6 Hz, 1 H), 4.14 (s, 1 H), 3.94 (s, 1 H), 2.34 (s, 3 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 165.7, 137.9, 137.3, 137.2, 133.1, 132.8, 131.0, 130.1, 129.7-127.9, 126.4, 101.1, 86.4, 73.3, 72.5, 70.0, 67.9, 60.2, 21.1; m/z (HRMS) calcd for $C_{34}H_{32}O_6SNa$ $[M+Na]^+$: 591.1812, found, 591.1827.

**4-Methylphenyl 2-*O*-benzoyl-3-*O*-benzyl-1-thio-α-L-idopyranoside (S16)**



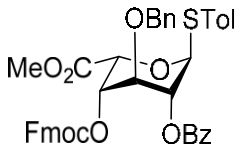

A solution of a compound **S15** (1.94 g, 3.41 mmol) in a mixture of solvents ($CH_2Cl_2$: TFA: $H_2O$ = 10/1/0.1, v/v/v) was stirred at room temperature for 1 h. It was neutralized by solid $NaHCO_3$, filtered and then concentrated in *vacuo*, and later co-evaporated with toluene to remove traces of water. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc 7:3) to furnish **S16** (1.58 g, 79%). $R_f$ 0.28 (hexane/EtOAc 7:3); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.4 Hz, 2 H), 7.58 (t, *J* = 7.8 Hz, 1 H), 7.46-7.43 (m, 6 H), 7.38 (t, *J* = 7.8 Hz, 2 H), 7.33-7.31 (m, 1 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 5.56 (s, 1 H), 5.52 (app s, 1 H), 4.91 (d, *J* = 11.4 Hz, 1 H), 4.81 (d, *J* = 5.4 Hz, 1 H), 4.66 (d, *J* = 10.2 Hz, 1 H), 3.98 (dd, *J* = 12.0, 6.0 Hz, 1 H), 3.88 (dd, *J* = 12.0, 4.2 Hz, 1 H), 3.85 (app s, 2 H), 2.32 (s, 3 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 165.1, 138.1, 137.3, 133.7, 131.9, 129.8-128.1, 127.9, 87.2, 74.1, 72.4, 69.9, 68.4, 68.2, 63.4, 21.2; m/z (HRMS) calcd for $C_{27}H_{28}O_6SNa$ $[M+Na]^+$: 503.1504, found, 503.1532.

**Methyl *p*-tolyl-2-*O*-benzoyl-3-*O*-benzyl-1-thio-α-L-idopyranosyl uronate (S17)**




To a vigorously stirred solution of the diol derivative **S16** (1.58 g, 3.29 mmol) in a mixture of $CH_2Cl_2$: $H_2O$ (2:1) was added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 0.154 g, 0.987 mmol) in the presence of iodobenzene diacetate (BAIB, 2.65 g, 8.21 mmol) as the cooxidant at 0 °C. The reaction mixture was allowed to warm up to room temperature and continued to stir until the complete conversion of the starting material was observed. After 2 h, it was diluted with $CH_2Cl_2$ (2 × 50 mL), washed with 10% $Na_2S_2O_3$ (2 × 30 mL), brine (40 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. It was co-evaporated with toluene to remove traces of water. The resulting residue was dissolved in anhydrous DMF (15 mL) and cooled to 0 °C. Methyl iodide ($CH_3I$, 0.47 mL, 7.54 mmol) and $KHCO_3$ (0.345 g, 3.42 mmol) were added to the mixture under $N_2$ atmosphere. It was stirred for a period of 4 h allowing the reaction mixture to warm up to room temperature, slowly. After 4 h, it was diluted with EtOAc (2 × 50 mL), washed with water (2 × 30 mL), brine (40 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc 7:3) to furnish **S17** (0.986 g, 59%) as colorless gum. $R_f$ 0.46 (hexane/EtOAc 7:3); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.97-7.95 (m, 2 H), 7.58 (t, *J* = 7.2 Hz, 1 H), 7.46-7.37 (m, 8 H), 7.33-7.31 (m, 1 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 5.67 (s, 1 H), 5.50 (app s, 1 H), 5.42 (app s, 1 H), 4.92 (d, *J* = 12.0 Hz, 1 H), 4.70 (d, *J* = 12.0 Hz, 1 H), 4.15 (d, *J* = 11.4 Hz, 1 H), 3.98 (s, 1 H), 3.84 (s, 3 H), 2.83 (d, *J* = 12.0 Hz, 1 H), 2.32 (s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 169.7, 165.0, 137.9, 137.1, 133.8, 132.0, 131.8, 129.5-127.9, 87.3, 73.6, 72.5, 69.7, 69.0, 68.4, 52.5, 21.1;m/z (HRMS) calcd for $C_{28}H_{28}O_7SNa$ $[M+Na]^+$: 531.1448, found, 531.1479.

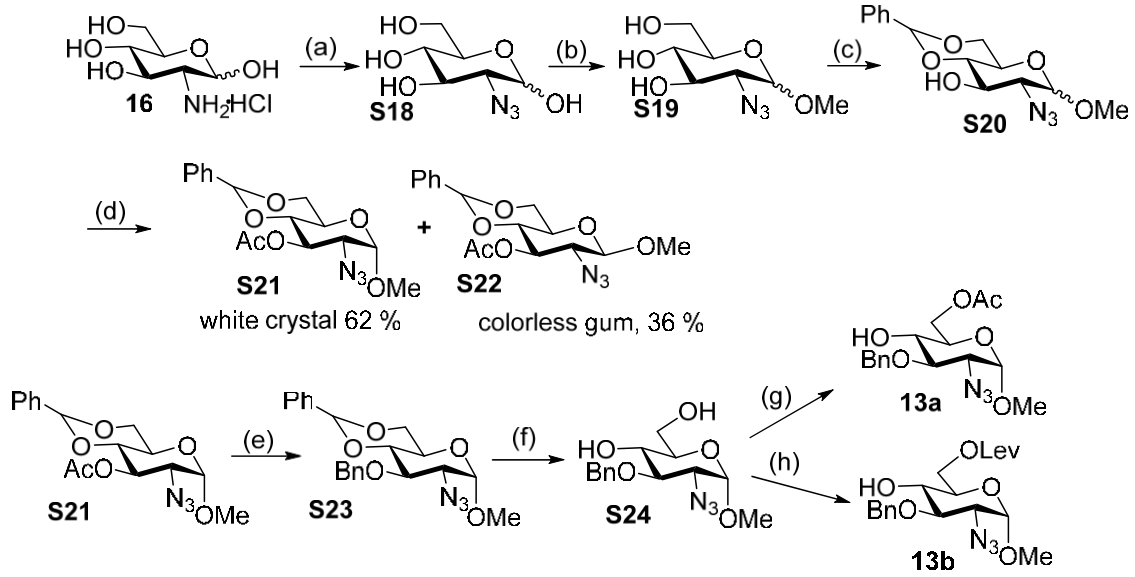
**Methyl *p*-tolyl-2-*O*-benzoyl-3-*O*-benzyl-4-*O*-(9-fluorenylmethoxycarbonyl)-1-thio-α-L-idopyranosyl uronate (12)**




To a solution of the **S17** (0.986 g, 1.94 mmol) in anhydrous $CH_2Cl_2$ was added 9-fluroenylmethoxycarbonyl chloride (0.754 g, 2.91 mmol) in the presence of pyridine (1.56 mL, 19.45 mmol) at 0 °C. It was stirred for a period of 4 h allowing the reaction mixture to warm up to room temperature, slowly. After 4 h, the reaction mixture was diluted with EtOAc (2 × 50 mL), washed with

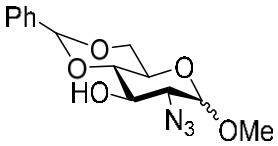
water (2 × 30 mL), brine (40 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (hexane/EtOAc 8:2) to furnish **12** (1.13 g, 80%) as solid. $R_f$ 0.56 (hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.2 Hz, 2 H), 7.75 (d, *J* = 7.8 Hz, 2 H), 7.58 (d, *J* = 7.8 Hz, 2 H), 7.47-7.39 (m, 12 H), 7.34 (t, *J* = 7.2 Hz, 1 H), 7.28-7.21 (m, 2 H), 7.19 (t, *J* = 7.2 Hz, 1 H), 5.71 (s, 1 H), 5.53 (s, 1 H), 5.49 (s, 1 H), 5.26 (s, 1 H), 4.92 (d, *J* = 12.0 Hz, 1 H), 4.81 (d, *J* = 12.6 Hz, 1 H), 4.33 (t, *J* = 9.6 Hz, 1 H), 4.23 (t, *J* = 7.2 Hz, 1 H), 4.11-4.08 (m, 2 H), 3.82 (s, 3 H), 2.32 (s, 3 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 168.7, 165.4, 154.4, 143.3, 142.9, 141.3, 141.2, 137.8, 136.9, 133.5, 131.8, 130.2, 129.6-127.3, 125.3, 125.2, 120.1, 86.2, 72.9, 71.8, 71.2, 70.3, 68.5, 66.9, 52.7, 46.6, 21.1; m/z (HRMS) calcd for $C_{43}H_{38}O_9SNa$ $[M+Na]^+$: 753.2129, found: 753.2166.

**Scheme S4**. Synthesis of α-methyl-2-azido acceptors (**Building Block E)**



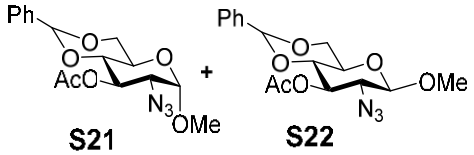

Reaction conditions: (a) $TfN_3$, MeOH, $CuSO_4$, $Et_3N$, rt, 12 h, 69 %; (b) 10 % HCl/MeOH, 90 °C, 7 h, 82%; (c) $PhH(OMe)_2$, CSA, DMF, rt, 12 h, 73%; (d) $Ac_2O$, Py, 0 °C-rt, 5 h; (e) (i) NaOMe, MeOH : $CH_2Cl_2$ (3:1), rt, 2 h; (ii) NaH, BnBr, THF, 0 °C-rt, 12 h, 92%; (f) 80% AcOH, 60 °C, 5h, 86%; (g) $Ac_2O$ (1.1), $Et_3N$ (9), $CH_2Cl_2$, 0 °C, 1 h, 86%; (h) CMPI, $CH_3CO(CH_2)_2COOH$, $CH_2Cl_2$, rt, 15 min; then DABCO, -20 °C -rt, 81%

**Methyl-2-azido-4,6-*O*-benzylidene-2-deoxy-α/β-D-glucopyranoside (S20)**



A solution of sodium azide (20 g, 307.7 mmol) and pyridine (25 mL, 316.45 mmol) in MeCN (100 mL) at 0 °C was treated with trifluoromethanesulfonic anhydride ($Tf_2O$, 40 mL, 235 mmol) slowly from an addition funnel. It was stirred at the same temperature for 2 h and the mixture was filtered through Celite pad with the temperature of the filtrate maintained at 0 °C. In a separate flask, D-glucosamine hydrochloride (**16**, 25 g, 121.95 mmol), $CuSO_4 \cdot 5H_2O$ (0.195 g, 1.21 mmol), and $Et_3N$ (34.0 mL, 243 mmol) were dissolved in MeOH (80 mL) and it was cooled to 0 °C. A freshly prepared cold $TfN_3$ solution was sequentially added and the reaction was stirred at room temperature for 12 h.[2] After the complete conversion of the starting material, the reaction mixture was concentrated in *vacuo* and the crude **S18** was obtained in 69% yield. The crude mixture was treated with 10% HCl in MeOH (100 mL) and heated at 90 °C for a period of 7 h.[3a] After 7 h, the solvents were evaporated in *vacuo* and the mixture was redissolved in MeOH and treated with solid $NaHCO_3$ till the pH of the solution is 7. The crude mixture was filtered and concentrated to give crude methyl glycosides **S19** (8 g, 82%). The crude reaction mixture was co-evaporated with toluene to remove traces of water and then dried for 2-3 h in *vaccum*. To a solution of compound **S19** (8 g, 36.52 mmol) in anhydrous DMF (40 mL) was added benzaldehyde dimethyl acetal (6.7 mL, 43.82 mmol) and camphor sulphonic acid (8.48 gm, 36.52 mmol). The reaction was continued with stirring for 12 h at room temperature and then quenched with $Et_3N$. The solvents were removed in *vacuo* and the crude product was diluted with EtOAc (2 × 200 mL), washed with water (2 × 100 mL), brine (50 mL), dried ($MgSO_4$), filtered. The organic layer was concentrated in *vacuo* and the resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 8:2) to afford **S20** (8.18 g, 73%) as anomeric mixture (α:β = 1:1). $R_f$ 0.58 (hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.49-7.47 (m, 4H), 7.39-7.37 (m, 6H), 5.53 (s, 1H), 4.79 (d, *J* = 3.6 Hz, 1H), 4.34 (dd, *J* = 10.2, 4.8 Hz, 1H), 4.30 (d, *J* = 8.4 Hz, 1H), 4.27 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.16 (t, *J* = 9.0 Hz, 1H), 4.11 (d, *J* = 7.2 Hz, 1H), 3.81 (td, *J* = 10.2, 4.8 Hz, 1H), 3.75 (td, *J* = 10.2, 3.0 Hz, 2H), 3.65 (t, *J* = 9.0 Hz, 1 H), 3.59 (s, 3 H), 3.51 (td, *J* = 9.0, 2.4 Hz, 1H), 3.44 (s, 3H), 3.41-3.35 (m, 3H), 3.30 (dd, *J* = 10.2, 3.6 Hz, 1H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 136.9, 136.8, 129.5, 128.5, 126.3, 126.3, 103.5, 102.2, 102.0, 99.5, 81.8, 80.7, 72.1, 69.1, 68.9, 68.5, 66.4, 66.2, 63.3, 62.3, 57.6, 55.6; m/z (HRMS) calcd for $C_{14}H_{18}N_3O_5[M+H]^+$: 308.1241, found:308.1269.

**Methyl 3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (S21)**
**Methyl 3-*O*-acetyl-2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (S22)**

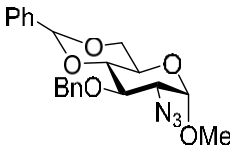



A solution of **S20** (4.0 g, 13.01 mmol) in pyridine (30 mL) was treated with $Ac_2O$ (15 mL) at 0 °C. The reaction mixture was stirred at room temperature for 5 h. The reaction mixture was concentrated in *vacuo* and diluted with EtOAc (2 × 100 mL), washed with water (2 × 50 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 7:3) to furnish crystalline α-anomer **S21** in (2.81 g, 62%) and β-anomer **S22** as colorless gum (1.63 g, 36%). $R_f$ 0.62 (hexane/EtOAc 7:3);

**S21**:$^1$H NMR (600 MHz, $CDCl_3$): δ 7.44-7.43 (m, 2H), 7.36-7.34 (m, 3H), 5.59 (t, *J* = 10.2 Hz, 1H), 5.50 (s, 1H), 4.86 (d, *J* = 3.0 Hz, 1H), 4.30 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.95 (td, *J* = 10.2, 4.8 Hz, 1H), 3.76 (d, *J* = 10.2 Hz, 1H), 3.62 (d, *J* = 9.6 Hz, 1H), 3.48 (s, 3H), 3.27 (dd, *J* = 10.2, 3.6 Hz, 1H), 2.16 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 169.8, 136.9, 129.2, 128.3, 126.2, 101.7, 99.9, 79.5, 69.1, 68.9, 62.7, 61.8, 55.5, 20.9; m/z (HRMS) calcd for $C_{16}H_{19}N_3O_6Na$ $[M+Na]^+$: 372.1166, found:.372.1187.

**S22**:$^1$H NMR (600 MHz, $CDCl_3$): δ 7.43-7.36 (m, 2H), 7.36-7.26 (m, 3H), 5.50 (s, 1H), 5.17 (t, *J* = 9.6 Hz, 1H), 4.38 (d, *J* = 7.8 Hz, 1H), 4.36 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.80 (t, *J* = 10.2 Hz, 1H), 3.62 (d, *J* = 12.0 Hz, 1H), 3.60 (s, 3H), 3.50-3.47 (m, 1H), 3.46-3.45 (m, 1H), 2.13 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 169.7, 136.8, 129.1, 128.3, 126.1, 103.6, 101.5, 78.7, 71.2, 68.5, 66.4, 64.7, 57.6, 20.9; m/z (HRMS) calcd for $C_{16}H_{19}N_3O_6Na$ $[M+Na]^+$: 372.1166, found: 372.1187.

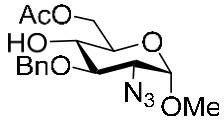
**Methyl 2-azido-3-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (S23).**




Compound **S21** (2.81 g, 8.05 mmol) was dissolved in a mixture of MeOH : $CH_2Cl_2$ (30:10 mL) and a catalytic amount of NaOMe (100 mg) was added. The mixture was stirred for 2 h at room temperature after that it was neutralized with amberlite 120 $H^+$ resin. The resin was filtered and the solvents were evaporated to give the crude mixture which was co-evaporated with toluene and dissolved in THF (20 mL). It was cooled to 0 °C and NaH (0.651 g, 17.5 mmol) was added. After the mixture was stirred for 1h, BnBr (1.17 mL, 9.77 mmol) was added to it and the reaction mixture was further stirred for a period of 12 h at room temperature. The resulting mixture was filtered through a Celite pad and the filtrate was concentrated in *vacuo*. It was diluted with EtOAc (100 mL), washed with water (2 × 50 mL), brine (50

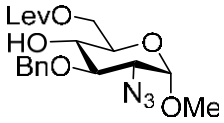
mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 8:2) to furnish **S23** as gum (2.94 g, 92%). $R_f$ 0.46 (hexane/EtOAc 8:2); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2 H), 7.41-7.37 (m, 5 H), 7.33-7.24 (m, 3 H), 5.59 (s, 1 H), 4.94 (d, *J* = 10.8 Hz, 1 H), 4.81 (s, 1 H), 4.78 (dd, *J* = 10.8, 4.2 Hz, 1 H), 4.30 (dd, *J* = 10.8, 4.2 Hz, 1 H), 4.06 (t, *J* = 9.6 Hz, 1 H), 3.88 (td, *J* = 10.2, 4.8 Hz, 1 H), 3.77 (t, *J* = 10.2 Hz, 1 H), 3.72 (t, *J* = 6.0 Hz, 1 H), 3.45 (app d, *J* = 3.6 Hz, 1 H), 3.44 (app s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 137.9, 137.3, 129.1-126.1, 101.5, 99.5, 82.8, 76.4, 75.1, 69.0, 63.2, 62.7, 55.5; m/z (HRMS) calcd for $C_{21}H_{23}N_3O_5Na$ $[M+Na]^+$: 420.1530, found: 420.1547.

**Methyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranoside (13a).**



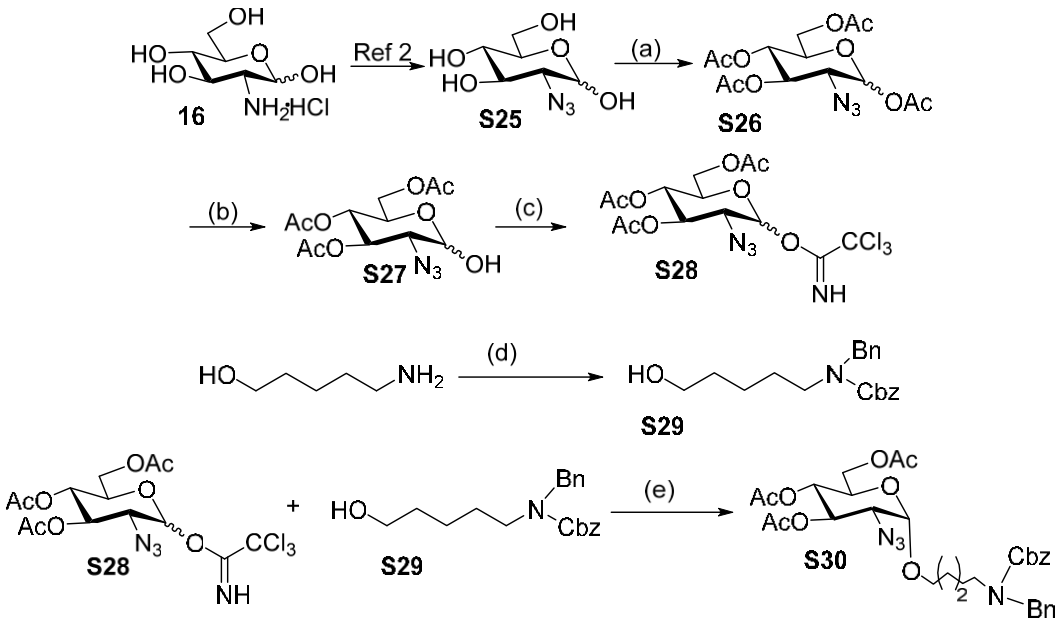

Compound **S23** (2.94 g, 7.40 mmol) was dissolved in 80% AcOH-$H_2O$ and the mixture was stirred at 60 °C for a period of 5 h, then concentrated and the residue was co-evaporated with toluene to remove traces of water to generate the 4,6-diol derivative **S24**. Then, it was dissolved in anhydrous $CH_2Cl_2$ (25 mL) and treated with $Ac_2O$ (0.85 mL, 8.88 mmol) and $Et_3N$ (9.28 mL, 91.96 mmol) at 0 °C under argon atmosphere for 1 h. After complete conversion of the starting material, it was diluted with $CH_2Cl_2$ (100 mL), washed with saturated $NaHCO_3$ (2 × 50 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 6:4) to furnish **13a** as gum (2.23 g, 86%). $R_f$ 0.38 (hexane/EtOAc 6:4); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.42-7.32 (m, 5 H), 4.92 (d, *J* = 10.8 Hz, 1 H), 4.81 (s, 1H), 4.80 (app d, *J* = 3.0 Hz, 1 H), 4.51 (dd, *J* = 12.0, 4.2 Hz, 1 H), 4.19 (dd, *J* = 11.4, 2.4 Hz, 1 H), 3.82 (app dd, *J* = 10.2, 9.0 Hz, 1 H), 3.76-3.74 (m, 1 H), 3.48 (td, *J* = 10.8, 3.0 Hz, 1 H), 3.43 (s, 3 H), 3.36 (dd, *J* = 10.2, 3.6 Hz, 1 H), 2.63 (s, 1 H), 2.09 (s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 171.9, 137.9, 128.8, 128.3, 128.2, 98.9, 79.7, 75.4, 70.6, 69.9, 63.2, 55.4, 20.9; m/z (HRMS) calcd for $C_{16}H_{21}N_3O_6Na$ $[M+Na]^+$: 374.1323, found:.374.1345.

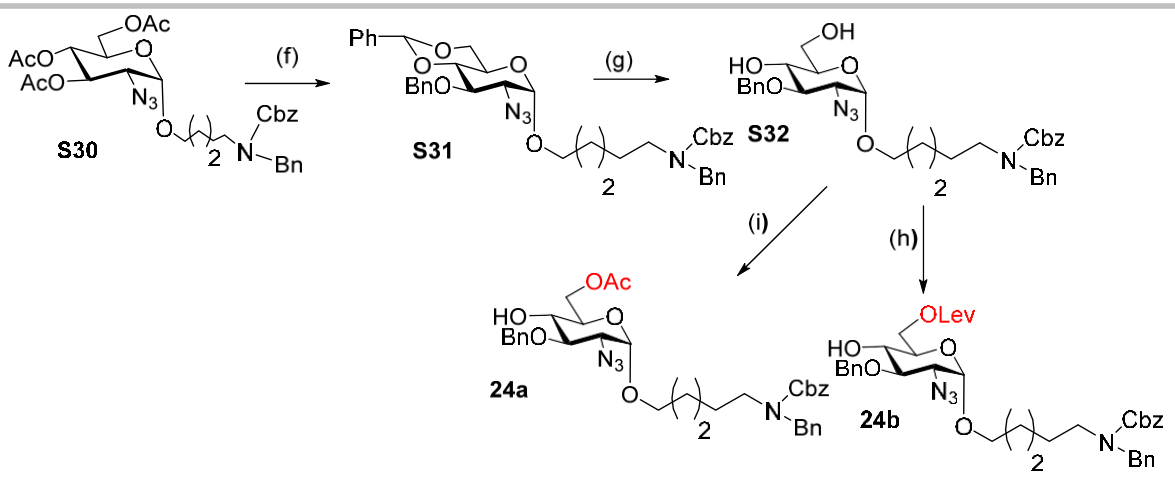
**Methyl 2-azido-3-*O*-benzyl-6-*O*-levulinyl-2-deoxy-α-D-glucopyranoside (13b).**



To a solution of **S24** (1.5 g, 4.85 mmol) in $CH_2Cl_2$ (20 mL) was added levulinic acid (0.741, 7.27 mmol) and 2-chloromethyl pyridinium chloride (CMPI) (3.10 g, 12.13 mmol). The reaction mixture was stirred for 15 min at room temperature and then cooled to -20 $^oC$. And 1,4-diazabicyclo[2,2,2] octane (1.90 g, 16.97 mmol) was added to the mixture at the same temperature. The reaction mixture was allowed to warm up to room temperature slowly with a period of 90 min. It was filtered through celite, diluted with EtOAc (2 × 50 mL), washed with brine (2 × 50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 6:4) to furnish **13b** as colorless oil (1.60 g, 81%). $R_f$ 0.42 (hexane/EtOAc 6:4); $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.43 – 7.39 (m, 2H), 7.37 (ddd, *J* = 7.5, 6.7, 1.2 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.21 – 7.15 (m, 1H), 4.92 (d, *J* = 11.1 Hz, 1H), 4.83 (d, *J* = 11.1 Hz, 1H), 4.79 (d, *J* = 3.6 Hz, 1H), 4.56 (dd, *J* = 12.2, 4.1 Hz, 1H), 4.19 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.82 (dd, *J* = 10.1, 8.7 Hz, 1H), 3.76 (ddd, *J* = 9.9, 4.1, 2.2 Hz, 1H), 3.54 (ddd, *J* = 9.9, 8.7, 3.9 Hz, 1H), 3.43 (s, 3H), 3.37 (dd, *J* = 10.2, 3.6 Hz, 1H), 2.82 – 2.77 (m, 1H), 2.79 – 2.75 (m, 2H), 2.61 (dd, *J* = 6.8, 6.0 Hz, 1H), 2.19 (s, 3H);$^{13}C$ NMR (150 MHz, $CDCl_3$): δ 206.7, 173.5, 138.1, 129.1, 128.2, 98.9, 79.7, 75.3, 70.6, 70.0, 63.2, 63.1, 55.4, 38.0, 29.9, 27.9;m/z (HRMS) calcd for $C_{19}H_{25}N_3O_7Na$ $[M+Na]^+$: 430.1585, found: 430.1594.

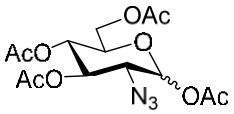
**Scheme S5**. Synthesis of 2-azido acceptors (**Building Block E)**






Reaction conditions: (a) (i) $Ac_2O$, DMAF, 0 $^oC$-rt, 16 h, 84%; (b) $NH_2(CH_2)_2NH_2$, AcOH, THF, rt, 16 h, 87 %; (c) $CCl_3CN$, DBU, $CH_2Cl_2$, 0 $^oC$-rt, 90 min, 74%; (d) (i) benzaldehyde (1.0 eq.), EtOH, 50 °C, reduced pressure; (ii) $NaBH_4$ (1.2 eq.), MeOH, 0 °C to r.t.; (iii) Benzyl chloroformate (1.0 eq.), $Et_2O/H_2O$, $NaHCO_3$, 0° C to r.t., 89% over three steps. (e) TMSOTf, $CH_2Cl_2$:$Et_2O$ (1:5), MS, -20 $^oC$, 1 h, 84%; (f) (i) NaOMe/ MeOH, rt, 12 h; (ii) $PhH(OMe)_2$, CSA, DMF, rt, 12 h, 81 %; (iii) NaH, BnBr, DMF, 12 h, 95%; (g) 80% AcOH, 5 h, 60 $^oC$; (h) CMPI, $CH_3CO(CH_2)_2COOH$, $CH_2Cl_2$, rt, 15 min, DABCO, -20 $^o$C –rt, 81%; (i) $Ac_2O$ (1.1), $Et_3N$ (9), $CH_2Cl_2$, 0 $^oC$, 1 h, 82%.

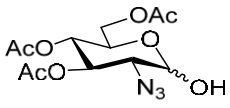
**1,3,4,6-Tetra-*O*-acetyl -2-azido-2-deoxy-D-glucopyranose (S26).**




Compound **S25** can be easily prepared from the readily available D-glucosamine hydrochloride **16** based on previously reported method.[2] After the complete conversion of the starting material, the reaction mixture was concentrated in *vacuo* and the crude **S25** (4.0 g, 19.55 mmol) was dissolved in acetic anhydride (30 mL). The reaction mixture was cooled to 0 °C and N,N-dimethyl amino pyridine (DMAP, 0.235 g, 1.95 mmol) was added. The mixture was stirred for 16 h allowing to warm up to room temperature. The solvents were evaporated in *vacuo* and the crude mixture was diluted with EtOAc (200 mL), washed with water (2 × 50 mL), brine (75 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 7:3) to furnish **S26** as gum (α:β =4:1, 6.12 g, 84%). $R_f$ 0.46 (hexane/EtOAc 7:3); $^1$H NMR (600 MHz, $CDCl_3$):δ 6.24 (d, *J* = 3.6 Hz, 0.25 H), 5.52 (d, *J* = 8.6 Hz, 1H), 5.40 (dd, *J* = 10.5, 9.4 Hz, 0.3H), 5.26 (s, 0.4H), 5.05 (dd, *J* = 10.1, 9.3 Hz, 1H), 4.99 (t, *J* = 9.7 Hz, 1H), 4.24 (ddd, *J* = 12.4, 5.8, 4.2 Hz, 1H), 4.08 – 4.04 (m, 1H), 4.05 – 4.00 (m, 2H), 3.78 (ddd, *J* = 10.0, 4.5, 2.2 Hz, 1H), 3.64 – 3.59 (m, 1H), 2.14 (app d, *J* = 1.7 Hz, 4H), 2.05 (s, 1H), 2.04 (s, 3H), 2.02 (s, 4H), 1.99 (s, 1H), 1.98 (s, 1H), 1.97 (s, 3H). $^{13}$C NMR

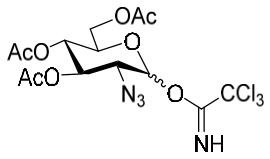
(150 MHz, $CDCl_3$): δ 171.1, 170.5, 170.0, 169.7, 169.6, 169.5, 168.5, 168.4, 92.5, 89.9, 77.3, 76.9, 72.6, 72.6, 70.7, 69.7, 67.9, 67.8, 62.5, 61.4, 61.4, 60.3, 60.2, 53.5, 21.0, 20.8, 20.8, 20.6, 20.6, 20.5, 20.4; m/z (HRMS) calcd for $C_{21}H_{23}N_3O_5Na$ $[M+Na]^+$: 420.1530, found:.420.1547.

**3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-D-glucopyranose (S27)**



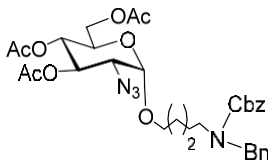

In a round bottom flask, ethylene diamine (1.31 mL, 19.65 mmol) and AcOH (1.37 mL, 22.4 mmol) were added in THF (100 mL) under argon atmosphere. To this suspension, compound **S26** was added (6.12 g, 16.1 mmol) and the reaction mixture was stirred for 16 h at room temperature. The crude mixture was diluted with $CH_2Cl_2$ (200 mL), washed with water (2 × 50 mL), brine (75 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (Hexane: EtOAc, 6:4) to furnish **S27** as white gum (4.71 g, 87%). The spectroscopic data was in agreement with that in the literature.[4]

**3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl trichloroacetimidate (S28)**



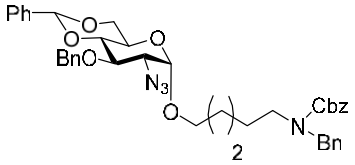

To a solution of compound **S27** (4.71 g, 14.22 mmol) in anhydrous $CH_2Cl_2$ (30 mL) at 0 °C was added trichloroacetonitrile (14.27 mL, 142.2 mmol) and 1,8-diazabicyclo-[5.4.0]undec-7-ene (0.324 mL, 2.13 mmol) under argon atmosphere. The reaction mixture was stirred for 90 min at 0 °C. Then the solvent was evaporated in *vacuo* and crude residue was purified by silica gel chromatography (hexane: EtOAc, 8:2) to furnish **S28** (4.99 gm, 74%) as a colorless foam. The spectroscopic data was in agreement with that in the literature.[5]

**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranoside (S30)**



Glycosyl donor **S28** (2.5 g, 5.26 mmol), acceptor **S29** (2.06 g, 6.31 mmol) and flame activated AW-300 MS (6.0 g) were suspended in $CH_2Cl_2$:$Et_2O$ (1:5, 40 mL) for 1 h at room temperature under argon atmosphere. The mixture was cooled to -25 $^oC$. After then, TMSOTf (95 µL, 0.526 mmol) was added and the mixture was stirred at the same temperature for 1h. It was warmed to room temperature slowly. Triethylamine (1 mL) was added and the mixture was filtered using Celite pad and the filtrate was diluted with $CH_2Cl_2$ (2 × 30 mL), washed with saturated $NaHCO_3$ (40 mL), brine (30 mL), then dried ($MgSO_4$) and filtered. Then, the solvent was evaporated in *vacuo* and the crude residue was purified by silica gel column chromatography (hexane: EtOAc, 8:2) to furnish **S30** (2.70 gm, 84%) as an oil. The spectroscopic data was in agreement with that in the literature.[5]

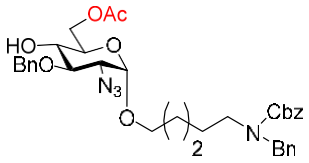
**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-2-azido-4-*O*-benzyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (S31)**




A solution of **S30** (2.70 g, 4.31 mmol) was dissolved in MeOH (25 mL) and a catalytic amount of NaOMe (0.100 g) was added. The mixture was stirred for 12 h at room temperature, and after that it was neutralized with amberlite 120 $H^+$ resin. The resin was filtered and the solvents were evaporated to furnish the triol derivative which was dissolved in anhydrous DMF (40 mL) and benzaldehyde dimethyl acetal (0.9 mL, 5.55 mmol) and camphor sulphonic acid (1.06 g, 4.6 mmol) were added. The reaction was continued with stirring for 12 h at room temperature and then quenched with $Et_3N$. The solvents were removed in *vacuo* and the mixture was diluted with EtOAc (2 × 100 mL), washed with water (2 × 50 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 1:1) to furnish the 4,6-*O*-benzylidene derivative (2.20 g, 81 %). The spectroscopic data was in agreement with that in the literature. The 4,6-*O*-benzylidene derivative (2.20 g, 3.74 mmol) was dissolved in DMF (25 mL) and cooled to 0 °C.Then, NaH (0.3 g, 7.48 mmol) and BnBr (1.17 mL, 9.77 mmol) were added. The reaction mixture was further stirred for a period of 12 h at room temperature. The resulting mixture was filtered through a Celite and was concentrated in *vacuo*. It was diluted with EtOAc (100 mL), washed with water (2 × 50 mL), brine (50 mL), then dried ($MgSO_4$), and the filtrate was concentrated in *vacuo*. The resulting residue was purified by silica gel chromatography (hexane: EtOAc, 8:2) to give **S31** as gum (2.40 g, 95%). $^1H$ NMR (600 MHz, $CDCl_3$):δ 7.51 (dd, *J* = 7.5, 2.1 Hz, 2H), 7.41-7.36 (m, 8H), 7.34-7.29 (m, 5H), 7.28-7.25 (m, 2H), 7.20-7.16 (m, 2H), 5.60 (s, 1H), 5.19-5.17 (m, 2H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.85-4.83 (m, 1H), 4.81 (d, *J* = 11.0 Hz,

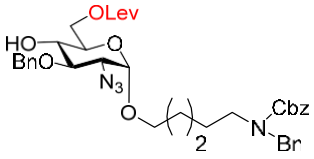
1H), 4.51 (d, *J* = 11.8 Hz, 2H), 4.28 (app d, *J* = 9.6 Hz, 1H), 4.07 (app t, *J* = 10.1 Hz, 1H), 3.88 (br s, 1H), 3.76 (t, *J* = 10.3 Hz, 1H), 3.71 (t, *J* = 9.3 Hz, 1H), 3.47 – 3.36 (m, 2H), 3.34 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.29-3.22 (m, 1H), 1.60-1.52 (m, 4H), 1.43 – 1.28 (m, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 156.8, 156.3, 138.0, 137.2, 136.9, 129.9-126.0, 101.5, 98.6, 82.9, 76.1, 75.1, 69.0, 67.2, 63.0, 62.8, 50.6, 50.3, 47.1, 46.2, 29.8, 29.1, 27.9, 27.5, 23.4; (HRMS) calcd for $C_{39}H_{42}N_4O_7Na$ [M+Na]$^+$: 678.3053, found, 678.3094.

**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-α-D-glucopyranoside (24a)**




Compound **S32** (1.20 g, 2.03 mmol) was dissolved in 80 % AcOH-$H_2O$ and was stirred at 60 °C for a period of 5 h. It was concentrated and the residue was co-evaporated with toluene to remove the last traces of water. It was then dissolved in anhydrous $CH_2Cl_2$ (15 mL) and treated with $Ac_2O$ (0.24 mL, 2.23 mmol) and $Et_3N$ (2.6 mL, 18.3 mmol) at 0 °C under argon atmosphere for 30 min. The reaction mixture was diluted with $CH_2Cl_2$ (50 mL), washed with saturated $NaHCO_3$ (2 × 30 mL), brine (50 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel chromatography (Hexane: EtOAc, 6:4) to generate **24a** as gum (1.06 g, 82%). The spectroscopic data was the same as that in the literature.[6]

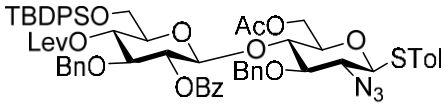
**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-2-azido-3-*O*-benzyl-6-*O*-levulinyl-2-deoxy-α-D-glucopyranoside (24b)**




To a solution of **S32** (1.20 g, 2.03 mmol) in $CH_2Cl_2$ (15 mL) was added levulinic acid (0.353 g, 3.05 mmol) and 2-chloromethyl pyridinium chloride (CMPI) (1.29 g, 5.07 mmol). It was stirred for 15 min at room temperature and then cooled to -20 $^o$C. 1,4-diazabicyclo[2,2,2] octane (0.797 g, 7.1 mmol) was added to The mixture at the same temperature. The reaction mixture was allowed to warm up to room temperature slowly in a period of 90 min and then filtered through Celite pad, diluted with EtOAc (2 × 50 mL), washed with brine (2 × 50 mL), dried ($MgSO_4$), filtered and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography (hexane: EtOAc, 6:4) to generate **24b** as colourless oil (1.13 g, 81%). The spectroscopic data was in agreement with that in the literature.[6]

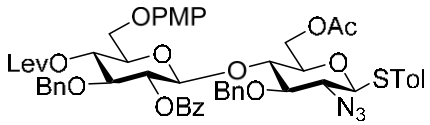
## C. Experimental procedure and characterization data of disaccharides

**4-Methylphenyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-4-*O*-levulinyl-β-D-glucopyranosyl)-β-D-glucopyranoside (19)**



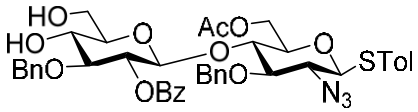

Glucosyl donor **17** (0.6 g, 0.74 mmol), azidoglucosyl acceptor **9** (0.325 g, 0.74 mmol) and flame activated AW-300 MS (2.0 g) were suspended in anhydrous $CH_2Cl_2$ (8 mL) for 1 h at room temperature under argon atmosphere. The mixture was cooled to -45 °C and then *N*-iodosuccinimide (NIS) (0.198 g, 0.88 mmol) and trifluoromethanesulfonic acid (TfOH) (21 μL, 0.22 mmol) were added. After 1 h, the reaction mixture was warmed up to -30 °C and stirred for another 1 h. The mixture was quenched with $Et_3N$ and filtered, diluted with $CH_2Cl_2$ (2 × 30 mL), washed with saturated $NaHCO_3$ (25 mL), $Na_2S_2O_3$ (25 mL) and brine (20 mL). It was dried over $MgSO_4$ and concentrated in *vacuo*. The crude residue was purified by silica gel column chromatography ($PhCH_3$: EtOAc, 20:1) to furnish **19** (0.634 g, 76%) as yellow oil. $R_f$ 0.48 ($PhCH_3$/EtOAc 9:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, *J* = 1.2 Hz, 2 H), 7.69 (d, *J* = 7.2 Hz, 2 H), 7.66-7.58 (m, 4 H), 7.46 (t, *J* = 7.8 Hz, 2 H), 7.43-7.37 (m, 6 H), 7.35-7.33 (m, 4 H), 7.27-7.24 (m, 4 H), 7.22-7.18 (m, 3 H), 7.12 (d, *J* = 7.2 Hz, 2 H), 5.32 (t, *J* = 9.0 Hz, 1 H), 5.10 (t, *J* = 9.0 Hz, 1 H), 4.93 (d, *J* = 12.0 Hz, 1 H), 4.76 (d, *J* = 11.4 Hz, 1 H), 4.64 (t, *J* = 7.8 Hz, 1 H), 4.55 (q, *J* = 11.4 Hz, 2 H), 4.32 (d, *J* = 11.4 Hz, 1 H), 4.20 (d, *J* = 10.8 Hz, 1 H), 4.10 (dd, *J* = 11.4, 4.8 Hz, 1 H), 3.82 (t, *J* = 9.0 Hz, 1 H), 3.77 (t, *J* = 9.6 Hz, 1 H), 3.64 (app q, *J* = 6.6 Hz, 2 H), 3.46-3.45 (m, 1 H), 3.43 (t, *J* = 9.6 Hz, 1 H), 3.30 (app dd, *J* = 10.2, 4.2 Hz, 1 H), 3.16 (t, *J* = 9.0 Hz, 1 H), 2.60-2.50 (m, 2 H), 2.34-2.31 (m, 1 H), 2.29 (s, 3 H), 2.25- 2.23 (m, 1 H), 2.10 (s, 3 H), 1.96 (s, 3 H), 0.99 (s, 9 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 205.9, 171.3, 170.5, 164.7, 138.7, 138.0, 137.9, 137.6, 135.8(3), 135.7(2), 134.3, 133.5, 133.4, 133.1, 129.6-127.5, 125.3, 100.6, 85.8, 81.8, 80.2, 76.2, 75.8, 75.0, 74.0, 73.9, 70.6, 64.6, 63.0, 62.4, 37.8, 29.8, 27.8, 26.8, 21.2, 20.8, 19.2; m/z (HRMS) calcd for $C_{63}H_{69}N_3O_{13}SSiNa$ $[M+Na]^+$: 1158.4218, found, 1158.4211.

**4-Methylphenyl-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(2-*O*-benzoyl-3-*O*-benzyl-4-*O*-levulinyl-6-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (20)**



Glucosyl donor **18** (0.5 g, 0.716 mmol), azidoglucosyl acceptor **9** (0.317 g, 0.716 mmol) and flame activated AW-300 MS (2.0 g) were suspended in anhydrous $CH_2Cl_2$ (8 mL) for 1 h at room temperature under argon atmosphere. It was cooled to -45 $^oC$ and then *N*-iodosuccinimide (NIS) (0.193 g, 0.86 mmol) and trifluoromethanesulfonic acid (TfOH) (20 μL, 0.21 mmol) were added. After 1 h, the reaction mixture was warmed up to -30 $^oC$ and stirred for another 1 h. It was quenched with $Et_3N$. It was filtered, diluted with $CH_2Cl_2$ (2 × 30 mL), washed with saturated $NaHCO_3$ (25 mL), $Na_2S_2O_3$ (25 mL), brine (20 mL) and then dried ($MgSO_4$). The solvent was removed in *vacuo*, and the residue was purified by silica gel column chromatography ($PhCH_3$: EtOAc, 9:1) to afford **20** (0.531 g, 73 %) as yellow oil. $R_f$ 0.42 ($PhCH_3$/EtOAc 9:1); $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.01-7.99 (m, 2 H), 7.60 (d, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.41-7.36 (m, 4 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.15-7.08 (m, 5H), 7.06 (d, *J* = 8.4 Hz, 4 H), 6.80 (d, *J* = 9.0 Hz, 2 H), 5.31 (dd, *J* = 9.6, 7.2 Hz, 1 H), 5.12 (t, *J* = 9.6 Hz, 1 H), 5.00 (d, *J* = 10.8 Hz, 1 H), 4.72 (d, *J* = 10.8 Hz, 1 H), 4.56 (dd, *J* = 2.4, 6.0 Hz, 2 H), 4.53 (d, *J* = 11.4 Hz, 1 H), 4.24-4.22 (m, 1 H), 4.17 (t, *J* =12.0 Hz, 2 H), 4.10 (dd, *J* = 12.0, 4.8 Hz, 1 H), 3.80 (t, *J* =9.6 Hz, 1 H), 3.72 (s, 3 H), 3.68 (t, *J* =9.6 Hz, 1 H), 3.52 (dt, *J* =9.6, 4.2 Hz, 1 H), 3.44 (dd, *J* =10.8, 4.2 Hz, 1 H), 3.40 (d, *J* =9.0 Hz, 1 H), 3.30 (dd, *J* =10.8, 5.4 Hz, 1 H), 3.29-3.26 (m, 1 H), 3.18 (t, *J* =10.2 Hz, 1 H), 2.79 (app d, *J* =1.2 Hz, 1 H), 2.55 (t, *J* =6.6 Hz, 2 H), 2.35-2.33 (m, 2 H), 2.30 (s, 3 H), 2.11 (s, 3 H), 1.95 (s, 3 H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 206.2, 171.6, 170.5, 164.7, 159.2, 138.8, 138.1, 137.6, 134.4, 133.5, 130.5, 130.1, 129.6-127.0, 113.7, 101.0, 85.8, 82.8, 80.0, 75.8, 74.2, 73.8, 73.7, 73.2, 71.6, 69.7, 64.7, 62.3, 55.3, 37.7, 29.8, 27.9, 21.2, 20.8; m/z (HRMS) calcd for $C_{55}H_{59}N_3O_{14}SNa$ $[M+Na]^+$: 1040.3615, found:1040.3632.

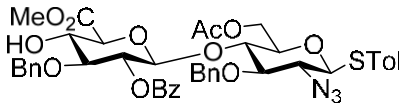
**4-Methylphenyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (22a)**




To a solution of **19** (0.634 mg, 0.55 mmol) in pyridine/AcOH (3:2) (2.5 mL) was added 1M hydrazine hydrate ($NH_2NH_2\,H_2O$, 0.8 mL).The reaction mixture was stirred at room temperature for 2 h and the solvent was removed; the residue was diluted with $H_2O$ and the mixture was extracted by EtOAc (2 x 25 mL). The combined organic layers were washed with saturated $NaHCO_3$ (25 mL), brine (25 mL), then dried ($MgSO_4$) and concentrated. It was further dried under vacuum for 2-3 h. The crude compound **21** was dissolved in pyridine (6 mL), and HF-Pyridine (0.7 mL) was added at 0 $^oC$. It was stirred for overnight at room temperature under nitrogen atmosphere. The solvent was evaporated under *vacuum*. The residue was dissolved in $CH_2Cl_2$ (50 mL) and washed with saturated $NaHCO_3$ (25 mL), brine (25 mL), then dried ($MgSO_4$). The residue was purified by flash column chromatography on silica gel (toluene/EtOAc = 8:2 )

to furnish diol **22a** (0.32 g, 81%) as colorless oil. $R_f$ 0.42 ($PhCH_3$/EtOAc 8:2); $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 7.8 Hz, 2 H), 7.60 (t, *J* = 7.8 Hz, 2 H), 7.48 (t, *J* = 7.8 Hz, 1 H), 7.40-7.36 (m, 6 H), 7.21-7.16 (m, 6 H), 7.10 (d, *J* = 7.8 Hz, 2 H), 5.26 (t, *J* = 8.4 Hz, 1 H), 4.96 (d, *J* = 10.8 Hz, 1 H), 4.80 (d, *J* = 10.8 Hz, 1 H), 4.69 (d, *J* = 11.4 Hz, 1 H), 4.58 (d, *J* = 12.0 Hz, 1 H), 4.48 (d, *J* = 8.4 Hz, 1 H), 4.42 (d, *J* = 10.2 Hz, 2 H), 4.12 (dd, *J* = 12.0, 6.0 Hz, 1 H), 3.64-3.59 (m, 4 H), 3.44 (t, *J* = 9.0 Hz, 1 H), 3.32 (dd, *J* = 12.0, 5.4 Hz, 1 H), 3.29-3.25 (m, 2 H), 3.22 (d, *J* = 10.2 Hz, 1 H), 2.33 (s, 3 H), 1.99 (s, 3 H);$^{13}C$ NMR (150 MHz, $CDCl_3$): δ 170.5, 164.9, 138.9, 138.1, 137.7, 134.4, 133.6, 129.9-127.4, 101.2, 85.7, 82.9, 82.7, 75.7, 75.6, 74.9, 73.8, 70.8, 64.5, 62.2, 21.2, 20.8; m/z (HRMS) calcd for $C_{42}H_{45}N_3O_{11}SNa$ $[M+Na]^+$: 822.2672, found, 822.2678.

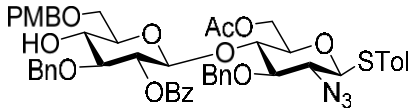
**4-Methylphenyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-β-D-glucopyranosyluronate)-β-D-glucopyranoside (5a)**




To a vigorously stirred solution of the diol derivative **22a** (0.32 g, 0.5 mmol) in a mixture of $CH_2Cl_2$:$H_2O$ (2:1, 9 mL) was added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 0.018 g, 0.15 mmol) in the presence of iodobenzene diacetate (BAIB, 0.32 g, 1.25 mmol) as the cooxidant at 0 °C. The reaction mixture was allowed to warm up to room temperature and continued to stir until a complete conversion of the starting material was observed. After 2 h, it was diluted with $CH_2Cl_2$ (2 × 25 mL), washed with 10% $Na_2S_2O_3$ (2 × 15 mL), brine (30 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. It was co-evaporated with toluene to remove trace of waters. The resulting residue was dissolved in anhydrous DMF (6 mL) and cooled to 0 °C. Methyl iodide ($CH_3I$, 0.1 mL) and $KHCO_3$ (0.05 g, 0.48 mmol) were added to the reaction mixture under $N_2$ atmosphere. It was stirred for a period of 4 h allowing the reaction mixture to warm up to room temperature, slowly. After 4 h, it was diluted with EtOAc (2 × 25 mL), washed with water (2 × 20 mL), brine (30 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography (toluene/EtOAc 8:2) to furnish **5** (0.21 g, 63 %) as colorless gum. $R_f$ 0.41 (toluene/EtOAc 8:2); $^1H$ NMR (600 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.8 Hz, 2 H), 7.78 (t, *J* = 7.2 Hz, 1 H), 7.58 (t, *J* = 7.8 Hz, 2 H), 7.50-7.44 (m, 7 H), 7.40-7.38 (m, 2 H), 7.28-7.26 (m, 3 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 5.40 (t, *J* = 8.4 Hz, 1 H), 5.20 (d, *J* = 11.4 Hz, 1 H), 4.88 (d, *J* = 12.0 Hz, 2 H), 4.82 (d, *J* = 11.4 Hz, 1 H), 4.77 (d, *J* = 7.8 Hz, 1 H), 4.38-4.36 (m, 1 H), 4.32 (d, *J* = 10.2 Hz, 1 H), 4.22 (dd, *J* = 12.0, 4.8 Hz, 1 H), 4.14 (t, *J* = 9.0 Hz, 1 H), 3.90 (d, *J* = 9.6 Hz, 1 H), 3.81-3.77 (m, 2 H), 3.65 (s, 3 H), 3.55 (t, *J* = 9.0 Hz, 1 H), 3.40-3.34 (m, 2 H), 3.16 (s, 1H), 2.44 (s, 3 H), 2.05 (s, 3 H); $^{13}C$ NMR (150 MHz, $CDCl_3$): δ 170.4, 169.3, 164.8, 138.9, 138.3, 137.7, 134.6, 133.5, 129.9-

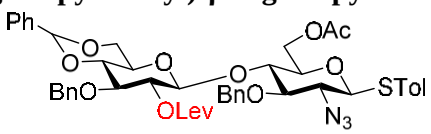
126.6, 101.4, 85.7, 83.0, 80.9, 77.6, 76.8, 75.7, 74.7, 74.4, 73.1, 72.3, 64.6, 62.1, 52.8, 21.2, 20.8; m/z (HRMS) calcd for $C_{43}H_{45}N_3O_{12}SNa$ $[M+Na]^+$: 850.2622, found, 850.2627.

**4-Methylphenyl-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(2-*O*-benzoyl-3-*O*-benzyl-6-*O*-*p*-methoxybenzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (6)**




A solution of **20** (0.531 mg, 0.55 mmol) in pyridine/AcOH (3:2, 2.5 mL), 1M hydrazine hydrate ($NH_2NH_2$ $H_2O$, 0.8 mL) was added. The reaction mixture was stirred at room temperature for 2 h and the solvent was removed; the residue was diluted with $H_2O$ and the mixture was extracted by EtOAc (2 x 20 mL). The combined organic layers were washed with saturated $NaHCO_3$ (30 mL), brine (30 mL) and dried over ($MgSO_4$). The solvents were removed in *vacuo* and the residue was purified by flash column chromatography on silica gel (toluene/EtOAc 9:1) to furnish disaccharide **6** (0.43 g, 90%) as colorless oil. $R_f$ 0.36 (toluene/EtOAc 9:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 2 H), 7.70 (t, *J* = 7.8 Hz, 2 H), 7.58 (t, *J* = 7.8 Hz, 2 H), 7.50 (t, *J* = 8.4 Hz, 2 H), 7.47 (d, *J* = 7.8 Hz, 2 H), 7.41 (t, *J* = 6.6 Hz, 2 H), 7.38 (t, *J* = 7.2 Hz, 2 H), 7.28-7.24 (m, 5 H), 7.18 (d, *J* = 7.8 Hz, 2 H), 6.97 (d, *J* = 8.4 Hz, 2 H), 5.36 (t, *J* = 8.4 Hz, 1 H), 5.12 (t, *J* = 10.8 Hz, 1 H), 4.85 (dd, *J* = 10.8, 5.4 Hz, 1 H), 4.79 (d, *J* = 12.0 Hz, 1 H), 4.66 (d, *J* = 7.8 Hz, 1 H), 4.36 (s, 2 H), 4.35 (app dd, *J* = 11.4, 1.2 Hz, 1 H), 4.32 (d, *J* = 10.2 Hz, 1 H), 4.22 (dd, *J* = 12.0, 5.4 Hz, 1 H), 3.92 (s, 3 H), 3.89 (d, *J* = 9.0 Hz, 1 H), 3.76 (q, *J* = 9.0 Hz, 2 H), 3.62 (dd, *J* = 9.6, 4.8 Hz, 1 H), 3.56 (app dd, *J* = 9.6, 6.0 Hz, 1 H), 3.35-3.52 (m, 2 H), 3.39-3.36 (m, 2 H), 3.32 (t, *J* = 9.6 Hz, 1 H), 2.43 (s, 3H), 1.99 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 170.5, 164.9, 159.4, 138.8, 138.2, 137.9, 134.4, 133.4, 129.6-127.6, 126.8, 113.9, 101.1, 85.6, 82.8, 81.8, 75.6, 74.6, 73.8, 73.5, 73.4, 70.7, 64.5, 62.2, 55.3, 21.2, 20.8; m/z (HRMS) calcd for $C_{50}H_{53}N_3O_{12}SNa$ $[M+Na]^+$: 942.3248, found, 942.3244.

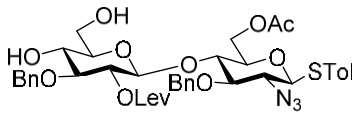
**4-Methylphenyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-levulinyl-β-D-glucopyranosyl)-β-D-glucopyranoside (23b)**




Glucosyl donor **10b** (0.5 g, 0.89 mmol), azidoglucosyl acceptor **9** (0.33 g, 0.746 mmol) and flame activated AW-300 MS (2.0 g) were suspended in anhydrous $CH_2Cl_2$ (8 mL) for 1 h at room temperature under argon atmosphere. The mixture was cooled to -20 °C and then *N*-iodosuccinimide (NIS) (0.240 g,

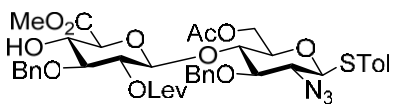
1.06 mmol) and tri methylsilyl trifluoromethanesulfonic acid (TMSOTf) (16 μL, 0.09 mmol) were added. After 5 min, the reaction mixture was warmed up to 0 °C and stirred for another 10 min. It was quenched with $Et_3N$. The mixture was filtered, diluted with $CH_2Cl_2$ (2 × 30 mL), washed with saturated. $NaHCO_3$ (25 mL), $Na_2S_2O_3$ (25 mL) and brine (20 mL). It was dried over $MgSO_4$. Solvents were removed in *vacuo* and the residue was purified by silica gel column chromatography ($PhCH_3$: EtOAc, 9:1) to furnish **23b** (0.697 g, 89%) as yellow oil. $^1$H NMR (600 MHz, $CDCl_3$): 7.38-7.37 (m, 4 H), 7.30-7.27 (m, 9 H), 7.23-7.21 (m, 3 H), 7.00 (d, *J* = 7.8 Hz, 3 H), 5.41 (s, 1 H), 5.00 (s, 1 H), 4.96-4.93 (m, 1 H), 4.84 (d, *J* = 8.4 Hz, 1 H), 4.78 (d, *J* = 10.2 Hz, 1 H), 4.66 (d, *J* = 10.2 Hz, 1 H), 4.56 (d, *J* = 12.0 Hz, 1 H), 4.52 (dd, *J* = 12.0, 1.8 Hz, 1 H), 4.42 (d, *J* = 7.8 Hz, 1 H), 4.26 (d, *J* = 10.2 Hz, 1 H), 4.14 (dd, *J* = 12.0, 4.2 Hz, 1 H), 4.04 (dd, *J* = 10.2, 4.8 Hz, 1 H), 3.63-3.57 (m, 3 H), 3.40 (t, *J* = 9.0 Hz, 1 H), 3.32 (t, *J* = 10.2 Hz, 1 H), 3.25-3.22 (m, 1 H), 3.18 (t, *J* = 9.6 Hz, 1 H), 2.78-2.74 (m, 1 H), 2.56 (dd, *J* = 13.2, 6.6 Hz, 1 H), 2.53-2.48 (m, 2 H), 2.27 (s, 3 H), 2.09 (s, 3 H), 2.02 (s, 3 H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 206.1, 171.4, 170.5, 139.0, 138.2, 138.1, 137.0, 134.8, 129.6-126.0, 101.5, 101.2, 85.2, 82.8, 81.5, 78.8, 75.3, 74.4, 73.4, 68.4, 66.4, 64.3, 62.3, 38.0, 37.6, 29.8, 27.7, 21.2, 21.0; m/z (HRMS) calcd for $C_{47}H_{51}N_3O_{12}SNa$ $[M+Na]^+$: 904.3091, found, 904.3099.

**4-Methylphenyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(3-*O*-benzyl-2-*O*-levulinyl-β-D-glucopyranosyl)-β-D-glucopyranoside (22b)**




A solution of a compound **23b** (0.672 g, 0.762 mmol) was treated with 80% AcOH at 70 °C for 3 h. It was neutralized by solid $NaHCO_3$, filtered and then concentrated in *vacuo*, and later co-evaporated with toluene to remove traces of water. The crude mixture was purified by silica gel column chromatography ($PhCH_3$: EtOAc, 7:3) to furnish **22b** (0.447 g, 79%) as colorless gum. $R_f$ 0.3 ($PhCH_3$/EtOAc 7:3); The spectroscopic data was in agreement with that in the literature.[3c]

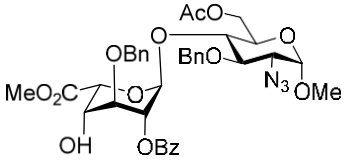
**4-Methylphenyl-6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-1-thio-4-*O*-(methyl-3-*O*-benzyl-2-*O*-levulinyl-β-D-glucopyranosyl)-β-D-glucopyranoside (5b)**




To a vigorously stirred solution of the diol derivative **22b** (0.477 g, 0.60 mmol) in a mixture of $CH_2Cl_2$:$H_2O$ (2:1, 9 mL) was added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)(0.037 g, 0.24mmol)

in the presence of iodobenzene diacetate (BAIB) (0.484 g, 1.50 mmol) as the cooxidant at 0 °C. The reaction mixture was allowed to warm up to room temperature and continued to stir until complete conversion of the starting material was observed. After 2 h, it was diluted with $CH_2Cl_2$ (2 × 25 mL), washed with 10 % $Na_2S_2O_3$ (2 × 15 mL), brine (30 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. It was co-evaporated with toluene to remove traces of water. The resulting residue was dissolved in anhydrous DMF (6 mL) and cooled to 0 °C. Methyl iodide ($CH_3I$, 0.1 mL) and $KHCO_3$ (0.07 g, 0.65 mmol) were added under $N_2$ atmosphere. It was stirred for a period of 2 h, allowing the reaction mixture to warm up to room temperature slowly. After 2 h, it was diluted with EtOAc (2 × 25 mL), washed with water (2 ×20 mL), brine (30 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography ($PhCH_3$/EtOAc 9:1) to furnish **5b** (0.307 g, 61%) as colorless gum. $R_f$ 0.37 ($PhCH_3$/EtOAc 9:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.47 – 7.42 (m, 2H), 7.36 – 7.31 (m, 5H), 7.31 – 7.23 (m, 5H), 7.13 – 7.10 (m, 2H), 5.05 (d, *J* = 11.2 Hz, 1H), 4.99 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.82 (d, *J* = 11.8 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.69 (d, *J* = 11.1 Hz, 1H), 4.57 (dd, *J* = 12.1, 2.1 Hz, 1H), 4.52 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 10.2 Hz, 1H), 4.22 (dd, *J* = 12.1, 4.5 Hz, 1H), 3.93 (ddd, *J* = 9.7, 8.7, 2.4 Hz, 1H), 3.77 – 3.71 (m, 1H), 3.74-3.71 (m, 2H), 3.64 (ddd, *J* = 9.9, 4.6, 2.1 Hz, 1H), 3.56 – 3.51 (m, 1H), 3.50 (s, 3H), 3.47 (dd, *J* = 9.4, 8.6 Hz, 1H), 3.27 (dd, *J* = 10.2, 9.4 Hz, 1H), 2.83 – 2.74 (m, 1H), 2.64 – 2.53 (m, 2H), 2.35 (s, 3H), 2.34 – 2.29 (m, 1H), 2.16 (s, 3H), 2.11 (s, 3H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 206.1, 171.3, 170.5, 169.2, 138.9, 138.3, 138.2, 134.6, 129.9-126.5, 101.2, 85.5, 82.9, 81.4, 77.6, 76.7, 75.6, 74.7, 74.3, 72.7, 72.0, 64.5, 62.3, 52.7, 37.6, 29.7, 27.7, 21.2, 20.9; m/z (HRMS) calcd for $C_{41}H_{47}N_3O_{13}SNa$ $[M+Na]^+$: 844.2727, found, 844.2738.

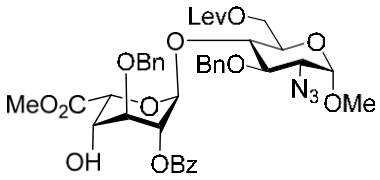
**Methyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside (7a)**




Iodopyranosyl donor **12** (0.748 g, 1.02 mmol), azidoglucosyl acceptor **13a** (0.3 g, 0.85 mmol) and flame activated AW-300 MS (2.0 g) were suspended in anhydrous $CH_2Cl_2$ (10 mL) for 1 h at room temperature under argon atmosphere. The mixture was cooled to -60 °C and then *N*-iodosuccinimide (NIS, 0.345 g, 1.53 mmol), trifluoromethanesulfonic acid (TfOH, 28 μL, 0.3 mmol) were added. After 30 min, the reaction mixture was warmed up to -30 °C and stirred for another 30 min. It was quenched with excess of $Et_3N$ and stirred for another 1 h at room temperature. The mixture was filtered, diluted with $CH_2Cl_2$ (2 × 40 mL), washed with saturated $NaHCO_3$ (35 mL), $Na_2S_2O_3$ (40 mL) and brine (40 mL). It was dried over $MgSO_4$ and concentrated in *vacuo*. The resulting mixture was purified by silica gel column

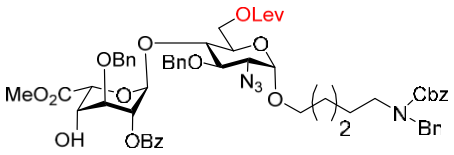
chromatography ($PhCH_3$: EtOAc, 8:2) to furnish **7a** (0.655 g, 87%) as colorless gum. $R_f$ 0.38 ($PhCH_3$/EtOAc 8:2); $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.97 (m, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 7.40-7.22 (m, 9 H), 7.28-7.15 (m, 1 H), 5.27 (s, 1 H), 5.16 (br s, 1 H), 4.94 (d, *J* = 2.4 Hz, 1 H), 4.81 (d, *J* = 4.8 Hz, 1 H), 4.80-4.78 (m, 2 H), 4.71-4.67 (m, 2 H), 4.43 (dd, *J* = 12.6, 1.8 Hz, 1 H), 4.32 (dd, *J* = 12.0, 4.2 Hz, 1 H), 4.00 (app dd, *J* = 10.2, 2.4 Hz, 1 H), 3.94-3.92 (m, 1 H), 3.90 (app t, *J* = 3.0 Hz, 1 H), 3.86-3.83 (m, 2 H), 3.53-3.51 (m, 1 H), 3.50 (s, 3 H), 3.43 (app s, 3 H), 2.66 (app d , *J* = 10.8 Hz, 1 H), 2.07 (s, 3 H);$^{13}C$ NMR (150 MHz, $CDCl_3$): δ 170.7, 169.7, 165.1, 137.9, 137.8, 137.5, 133.9, 129.9-125.4, 98.7, 98.2, 78.8, 75.4, 75.1, 74.7, 72.7, 69.0, 68.9, 68.1, 68.0, 63.8, 62.3, 55.5, 52.1, 20.9;m/z (HRMS) calcd for $C_{37}H_{41}N_3O_{13}Na$ $[M+Na]^+$: 758.2537, found 758.2548.

**Methyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinyl-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside (7b)**



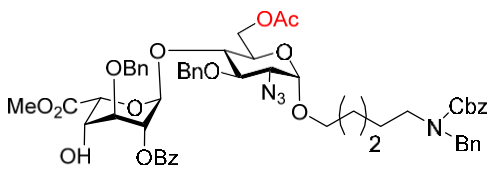

Iodopyranosyl donor **12** (0.310 g, 0.424 mmol), azidoglucosyl acceptor **13b** (0.15 g, 0.354 mmol) and flame activated AW-300 MS (1.5 g) were suspended in anhydrous $CH_2Cl_2$ (5 mL) for 1 h at room temperature under argon atmosphere. The mixture was cooled to -60 °C and then *N*-iodosuccinimide (NIS, 0.115 g, 0.5 mmol) and trifluoromethanesulfonic acid (TfOH, 16 μL, 0.17 mmol) were added. After 30 min, the reaction mixture was warmed up to -30 °C and stirred for another 30 min. It was quenched with excess of $Et_3N$ and stirred for another 1 h in room temperature. The mixture was filtered, diluted with $CH_2Cl_2$ (2 × 40 mL), washed with saturated $NaHCO_3$ (35 mL), $Na_2S_2O_3$ (40 mL) and brine (40 mL). It was dried over $MgSO_4$ and concentrated in *vacuo*. The resulting mixture was purified by silica gel column chromatography ($PhCH_3$: EtOAc, 8:2) to furnish **7b** (0.268 g, 80%) as light-yellow gum. $R_f$ 0.32 ($PhCH_3$/EtOAc 8:2); $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.95 – 7.90 (m, 2H), 7.55 – 7.49 (m, 1H), 7.39 – 7.36 (m, 2H), 7.34 – 7.30 (m, 4H), 7.30 – 7.27 (m, 2H), 7.24 (dt, *J* = 7.5, 1.8 Hz, 1H), 7.23 – 7.20 (m, 2H), 7.18 – 7.14 (m, 1H), 5.18 (d, *J* = 1.5 Hz, 1H), 5.10 (s, 1H), 4.94 (s, 1H), 4.87 (d, *J* = 2.3 Hz, 1H), 4.75 (d, *J* = 2.1 Hz, 1H), 4.73 (dd, *J* = 5.5, 3.2 Hz, 3H), 4.62 (dd, *J* = 11.1, 8.1 Hz, 2H), 4.36 (dd, *J* = 12.4, 2.2 Hz, 1H), 4.27 (dd, *J* = 12.4, 3.8 Hz, 1H), 3.88 (t, *J* = 9.6 Hz, 1H), 3.83 (t, *J* = 3.0 Hz, 1H), 3.79– 3.76 (m, 2H), 3.44 (s, 3H), 3.38 (d, *J* = 3.6 Hz, 1H), 3.37 (s, 3H), 2.65 (m, 2H), 2.60 – 2.53 (m, 1H), 2.50 (m, 1H), 2.02 (s, 3H);$^{13}C$ NMR (150 MHz, $CDCl_3$): δ 206.5, 177.0, 172.4, 169.7, 165.1, 137.9, 137.3, 133.7, 129.9-127.4, 98.6, 98.0, 79.3, 78.7, 75.1, 75.0, 74.8, 72.6, 69.1, 68.9, 68.1, 68.0, 63.8, 62.5, 55.5, 52.1, 37.9, 29.7, 29.6, 27.6;m/z (HRMS) calcd for $C_{40}H_{45}N_3O_{14}Na$ $[M+Na]^+$: 814.2799, found. 814.2792.

**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinyl-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside (8b)**




Iodopyranosyl donor **12** (0.436 g, 0.597 mmol), azidoglucosyl acceptor **24b** (0.35 g, 0.498 mmol) and flame activated AW-300 MS (1.5 g) were suspended in anhydrous $CH_2Cl_2$ (8 mL) for 1 h at room temperature under argon atmosphere. The mixture was cooled to -60 °C and then *N*-iodosuccinimide (NIS, 0.161 g, 0.72 mmol) and trifluoromethanesulfonic acid (TfOH, 20 µL, 0.238 mmol) were added. After 30 min, the reaction mixture was warmed up to -30 °C and stirred for another 30 min. It was quenched with excess of $Et_3N$ and stirred for another 1 h in room temperature. The mixture was filtered, diluted with $CH_2Cl_2$ (2 × 40 mL), washed with saturated $NaHCO_3$ (35 mL), $Na_2S_2O_3$ (35 mL) and brine (40 mL). It was dried over $MgSO_4$ and concentrated in *vacuo*. The resulting mixture was purified by silica gel column chromatography ($PhCH_3$: EtOAc, 8:2) to furnish **8b** (0.44 g, 82%) as yellow oil. $R_f$ 0.38($PhCH_3$/EtOAc 7:3); $^1$H NMR (600 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.5 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 7.36 (d, *J* = 15.5 Hz, 2H), 7.32–7.14 (m, 14H), 7.10 (d, *J* = 7.1 Hz, 4H), 5.18 (s, 1H), 5.14–5.07 (m, 4 H), 4.92–4.86 (m, 1 H), 4.77 – 4.70 (m, 2H), 4.60 (dd, *J* = 11.4, 2.6 Hz, 2H), 4.43 (d, *J* = 9.8 Hz, 2H), 4.36–4.30 (m, 1H), 4.29–4.19 (m, 1H), 3.99 –3.94 (m, 2H), 3.87 (t, *J* = 9.4 Hz, 1H), 3.82 (t, *J* = 3.4 Hz, 1H), 3.78 (d, *J* = 10.5 Hz, 3H), 3.61-3.50 (m, 1 H), 3.42 (s, 3H), 3.36-3.30 (m, 1 H), 3.26 (dd, *J* = 10.2, 3.4 Hz, 1H), 3.21-3.14 (m, 1H), 2.73 (d, *J* = 10.6 Hz, 1H), 2.65 – 2.61 (m, 2H), 2.58-2.52 (m, 1H), 2.50-2.45 (m, 1H), 2.00 (s, 3H), 1.53–1.45 (m, 4H), 1.29-1.17 (m, 2H); $^{13}$C NMR (150 MHz, $CDCl_3$): $^{13}$C NMR (151 MHz, $CDCl_3$) δ 206.5, 172.5, 169.7, 165.2, 156.8, 156.3, 138.0, 137.9, 137.4, 133.8, 130.0, 129.1- 127.3, 125.4, 98.1, 97.7, 78.5, 75.1, 74.5, 72.6, 69.2, 68.9, 68.3, 68.1, 67.3, 63.5, 62.6, 52.2, 50.7, 50.4, 47.2, 46.3, 38.0, 29.8, 29.7, 29.1, 28.0, 28.0, 27.5, 23.4, 21.6;m/z (HRMS) calcd for $C_{59}H_{66}N_4O_{16}Na$ $[M+Na]^+$: 1109.4372, found. 1109.4398.

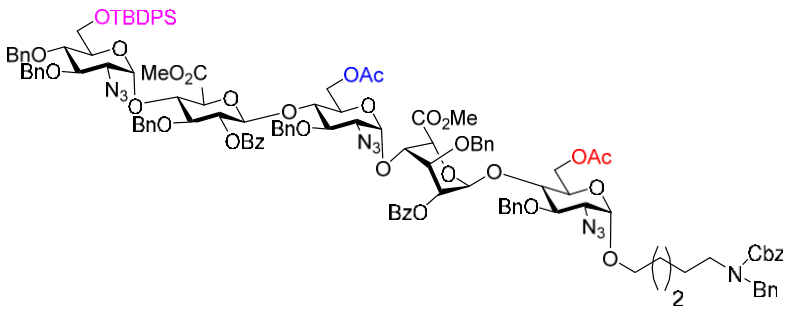
**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside (8a)**



Iodopyranosyl donor **12** (0.406 g, 0.557 mmol), azidoglucosyl acceptor **24a** (0.30 g, 0.464 mmol) and flame activated AW-300 MS (1.5 g) were suspended in anhydrous $CH_2Cl_2$ (8 mL) for 1 h at room temperature under argon atmosphere. The mixture was cooled to -60 °C and then *N*-iodosuccinimide (NIS, 0.150 g, 0.667 mmol) and trifluoromethanesulfonic acid (TfOH, 20 µL, 0.228 mmol) were added. After 30 min, the reaction mixture was warmed up to -30 °C and stirred for another 30 min. It was quenched with excess of $Et_3N$ and stirred for another 1 h in room temperature. The mixture was filtered, diluted with $CH_2Cl_2$ (2 × 40 mL), washed with saturated $NaHCO_3$ (35 mL), $Na_2S_2O_3$ (35 mL), and brine (40 mL). It was dried over $MgSO_4$ and concentrated in *vacuo*. The resulting mixture was purified by silica gel column chromatography ($PhCH_3$: EtOAc, 8:2) to furnish **8a** (0.378 g, 86%) as an oil. $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 3H), 7.43 – 7.25 (m, 17H), 7.18 – 7.16 (m, 2H), 5.27 (s, 1H), 5.19–5.17 (m, 4 H), 4.95 (s, 1 H), 4.87-4.83 (m, 1 H), 4.80 (d, *J* = 10.8 Hz, 2H), 4.70–4.66 (m, 2H), 4.50 (d, *J* = 9.0 Hz, 2H), 4.43 (dd, *J* = 12.6, 1.8 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.05 (dt, *J* = 10.8, 3.2 Hz, 1H), 3.92 (t, *J* = 9.0 Hz, 1H), 3.90–3.86 (m, 2H), 3.70–3.61 (m, 1H), 3.49 (s, 3H), 3.47–3.38 (m, 1H), 3.32 (dd, *J* = 10.2, 3.6 Hz, 1H), 3.30-3.21 (m, 1H), 2.65 (t, *J* = 10.2 Hz, 1H), 2.35 (d, *J* = 2.4 Hz, 1H), 2.06 (s, 3H), 1.65–1.54 (m, 4H), 1.40–1.29 (m, 2H);$^{13}C$ NMR (150 MHz, $CDCl_3$): δ 170.7, 169.9, 165.2, 156.8, 156.3, 138.0-137.3, 133.8-133.5, 130.0, 129.9-127.9, 98.2, 97.7, 78.4, 75.4, 75.0, 74.5, 72.6, 69.1, 69.0, 68.7, 68.4, 68.3, 68.1, 67.8, 67.2, 63.4, 62.3, 52.1, 50.6, 50.3, 47.1, 46.2, 29.0, 28.2, 27.9, 27.4, 23.2, 20.8; m/z (HRMS) calcd for $C_{56}H_{62}N_4O_{15}Na$ $[M+Na]^+$: 1053.4109, found. 1053.4106.

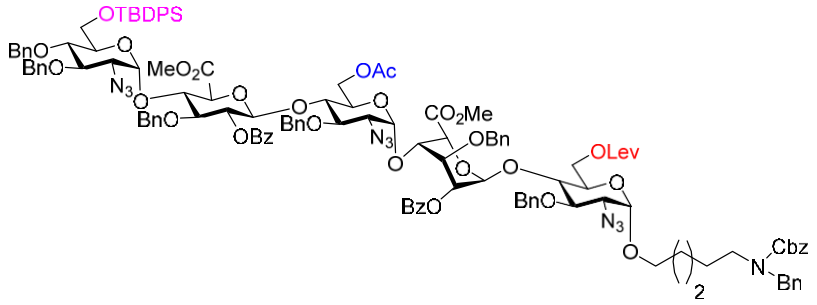
## D. Experimental procedure and characterization data of pentasaccharides

**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-α-D-glucopyranoside}- β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (25a)**



Glucosyl donor **4** (0.040 g, 0.054 mmol), azidoglucosyl acceptor **5a** (0.037 g, 0.045 mmol) and flame activated AW-300 MS (0.5 g) were suspended in anhydrous $CH_2Cl_2$ (1 mL) for 1 h at room temperature under $N_2$ atmosphere. The mixture was then cooled to to -45°C. NIS (0.015 g, 0.064 mmol) and TfOH (2 μL, 0.021 mmol) were added and the reaction mixture was allowed to warm to -30°C. The disaccharide acceptor **8a** (0.046 g, 0.045 mmol) in anhydrous $CH_2Cl_2$ (1 mL) and MS AW-300 (0.1 g) were stirred for 30 min at room temperature. After consumption of donor **4** and acceptor **5a** (TLC, $PhCH_3$/EtOAc, 20:1), the mixture was again cooled to -45°C and acceptor **8a** was added to it. Then, an additional amount of NIS (0.015 g, 0.066 mmol) and TfOH (3 μL, 0.040 mmol) was added and the reaction mixture was allowed to warm up to -25 °C. After complete consumption of the starting materials, it was quenched with saturated $NaHCO_3$ and solid $Na_2S_2O_3$. The mixture was filtered and washed with 25 mL each of the saturated $NaHCO_3$, saturated $Na_2S_2O_3$, $H_2O$, brine, then dried ($MgSO_4$) and concentrated in *vacuo*. The residue was purified by silica gel column chromatography ($PhCH_3$/EtOAc, 20:1) to give pentasaccharide (0.051 g, 50%) as yellow gum. $R_f$ 0.43 ($PhCH_3$/EtOAc 20:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.04 – 7.96 (m, 6H), 7.57 (ddd, *J* = 18.9, 8.0, 1.4 Hz, 6 H), 7.52–7.44 (m, 4 H), 7.41–7.35 (m, 7 H), 7.33–7.29 (m, 5H), 7.28–7.25 (m, 4H), 7.24–7.19 (m, 12H), 7.14–7.06 (m, 16H), 5.47 (d, *J* = 6.0 Hz, 1H), 5.46 – 5.44 (m, 1H), 5.43 – 5.41 (m, 2H), 5.23 – 5.17 (m, 4H), 4.92 (dd, *J* = 10.9, 2.1 Hz, 3H), 4.88 (dd, *J* = 10.5, 4.5 Hz, 4H), 4.79 (d, *J* = 11.1 Hz, 2H), 4.74 (dd, *J* = 14.9, 2.7 Hz, 2H), 4.72 – 4.66 (m, 4H), 4.55 – 4.49 (m, 4H), 4.36 – 4.28 (m, 2H), 4.26 – 4.21 (m, 2H), 4.21 – 4.15 (m, 2H), 4.06 (td, *J* = 5.8, 5.3, 2.9 Hz, 2H), 4.01 – 3.99 (m, 1H), 3.98 (dd, *J* = 8.7, 2.4 Hz, 2H), 3.96 – 3.94 (m, 1H), 3.94 – 3.90 (m, 3H), 3.86 (ddd, *J* = 11.6, 9.9, 2.6 Hz, 2H), 3.80 – 3.74 (m, 1H), 3.73 – 3.69 (m, 1H), 3.58 – 3.51 (m, 2H), 3.45 – 3.42 (m, 2H), 3.37 – 3.34 (m, 1H), 3.33 – 3.29 (m, 2H), 3.26 (app s, 3H), 3.22 (dt, *J* = 10.4, 3.5 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H), 1.60 – 1.37 (m, 2H), 1.29 – 1.09 (m, 4H), 0.96 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.5, 169.6, 167.6, 165.3, 164.8, 138.3-137.3, 136.0-135.7, 133.7, 133.1, 130.0-129.7, 128.9-127.5, 101.1, 98.6, 98.1, 97.9, 97.6, 82.6, 80.1, 77.9, 77.8, 76.3, 75.7, 75.3, 75.2, 75.0, 74.9, 74.7, 73.6, 72.5, 69.5, 68.9, 68.8, 68.3, 67.2, 63.6, 63.1, 62.1, 61.8, 61.6, 52.4, 51.9, 50.6, 50.3, 47.1, 46.2, 32.0, 31.5, 30.4, 29.8, 29.7, 29.4, 29.0, 27.8, 27.5, 27.0, 26.8, 23.3, 22.8, 20.9, 20.9 (2), 19.4; m/z (HRMS) calcd for $C_{128}H_{138}N_{10}O_{31}Si$ $[M+H]^+$: 2339.9377, found 2339.9319.

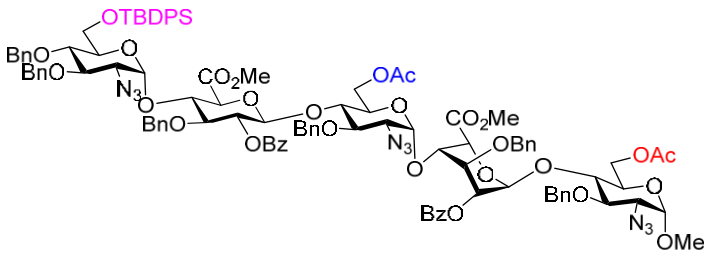
**N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinyl-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α- D-glucopyranoside (25b)**




Glucosyl donor **4** (0.040 g, 0.054 mmol), azidoglucosyl acceptor **5a** (0.037 g, 0.045 mmol) and flame activated AW-300 MS (0.5 g) were suspended in anhydrous $CH_2Cl_2$ (1 mL) for 1 h at room temperature under $N_2$ atmosphere. The mixture was then cooled to -45°C. NIS (0.015 g, 0.064 mmol) and TfOH (2 μL, 0.021 mmol) were added and the reaction mixture was allowed to warm to -30°C. The disaccharide acceptor **8b** (0.048 g, 0.045 mmol) in anhydrous $CH_2Cl_2$ (1 mL) and MS AW-300 (0.1 g) were stirred for 30 min at room temperature. After consumption of donor **4** and acceptor **5a** (TLC, $PhCH_3$/EtOAc, 20:1), the mixture was again cooled to -45°C and acceptor **8b** was added to it. Then, an additional amount of NIS (0.015 g, 0.066 mmol) and TfOH (3 μL, 0.040 mmol) was added and the reaction mixture was allowed to warm up to -25 °C. After complete consumption of the starting materials, it was quenched with solid $NaHCO_3$ and solid $Na_2S_2O_3$. The mixture was filtered and washed with 25 mL of each of the saturated $NaHCO_3$, saturated $Na_2S_2O_3$, $H_2O$, brine, then dried ($MgSO_4$) and concentrated in *vacuo*. The resulting residue was purified by silica gel column chromatography ($PhCH_3$/EtOAc, 20:1) to give pentasaccharide (0.044 g, 42%) as colourless oil. $R_f$ 0.37 ($PhCH_3$/EtOAc 20:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.04 – 7.98 (m, 5H), 7.61 – 7.53 (m, 7H), 7.53 – 7.45 (m, 4H), 7.43 – 7.35 (m, 4H), 7.34 – 7.19 (m, 20H), 7.18 – 7.05 (m, 20H), 5.35 (d, *J* = 8.6 Hz, 1H), 5.34 – 5.30 (m, 4H), 5.08 (td, *J* = 11.6, 10.5, 6.7 Hz, 5H), 4.87 – 4.83 (m, 1H), 4.82 (dd, *J* = 10.9, 2.0 Hz, 3H), 4.79 – 4.75 (m, 3H), 4.75 – 4.71 (m, 1H), 4.71 – 4.66 (m, 2H), 4.66 – 4.61 (m, 2H), 4.59 (d, *J* = 10.7 Hz, 2H), 4.56 (d, *J* = 7.9 Hz, 1H), 4.41 (d, *J* = 10.7 Hz, 3H), 4.15 (d, *J* = 14.0 Hz, 1H), 4.11 (td, *J* = 9.1, 2.8 Hz, 1H), 4.07 – 4.04 (m, 1H), 3.97 (t, *J* = 5.9 Hz, 1H), 3.90 – 3.85 (m, 2H), 3.84 (d, *J* = 7.7 Hz, 1H), 3.82 – 3.78 (m, 3H), 3.74 (dt, *J* = 11.7, 3.1 Hz, 2H), 3.67 – 3.63 (m, 1H), 3.60 – 3.55 (m, 2H), 3.45 – 3.39 (m, 1H), 3.34 – 3.31 (m, 1H), 3.28 (d, *J* = 8.7 Hz, 3H), 3.24 (tt, *J* = 7.6, 3.3 Hz, 1H), 3.19 (dd, *J* = 9.8, 4.2 Hz, 1H), 3.14 (s, 3H), 3.10 (dd, *J* = 10.3, 3.4 Hz, 2H), 2.70 – 2.57 (m, 2H), 2.57 – 2.47 (m, 2H), 2.06 (s, 3H), 2.06 – 1.99 (m, 2H), 1.93 (s, 3H), 1.55-1.50 (m, 4H), 1.35-1.27 (m, 2H), 1.04 (s, 9H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 206.5, 172.4, 170.5, 169.5, 167.6, 165.4, 164.8, 156.8, 156.2, 138.3-137.3, 136.0-135.7, 133.6-133.0, 130.0-129.7, 129.1-127.6, 125.4, 101.1, 98.5, 98.1, 97.8, 97.6, 82.5, 80.1, 77.8, 77.5, 75.7, 75.3, 75.2, 75.0, 74.9, 74.7, 73.6, 72.6, 69.4, 68.9, 68.2, 67.2, 63.6, 63.2, 62.9, 62.3, 61.8, 61.5, 52.4, 51.8, 50.6, 50.3, 47.1, 46.2, 38.0,

32.6, 29.9, 29.8, 29.0, 28.3, 27.9, 27.0, 26.8, 23.3, 22.8, 21.5, 20.9, 19.4; m/z (HRMS) calcd for $C_{131}H_{142}N_{10}O_{32}Si$ $[M]^+$: 2396.9717, found 2396.9635.

**Methyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (3a)**

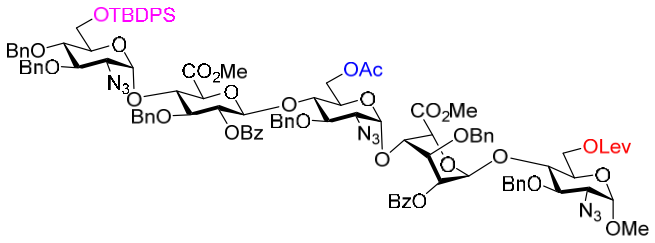



**Method A**: Glucosyl donor **4** (0.038 g, 0.052 mmol), azidoglucosyl acceptor **6** (0.04 g, 0.043 mmol) and flame activated AW-300 MS (0.3 g) were suspended in anhydrous $CH_2Cl_2$ (1 mL) for 1 h at room temperature under $N_2$ atmosphere. The mixture was then cooled to to -45°C. NIS (0.014 g, 0.062 mmol) and TfOH (3 µL, 0.016 mmol) were added and the reaction mixture was allowed to warm to -30°C. The disaccharide acceptor **7a** (0.031 g, 0.043 mmol) in anhydrous $CH_2Cl_2$ (1 mL) and MS AW-300 (0.1 g) were stirred for 30 min at room temperature. After consumption of donor **4** (TLC, $PhCH_3$/EtOAc, 20:1), the mixture was again cooled to -45°C followed acceptor **7a** was added to it. Then, an additional amount of NIS (0.013 g, 0.06 mmol) and TfOH (3 µL, 0.032 mmol) was added and the reaction mixture was allowed to warm up to -25 °C. After the complete consumption of the starting materials, it was quenched with solid $NaHCO_3$ and solid $Na_2S_2O_3$. The mixture was filtered and washed with 25 mL of each of the saturated $NaHCO_3$, saturated $Na_2S_2O_3$, $H_2O$, brine, then dried ($MgSO_4$) and concentrated in *vacuo*. The resulting mixture was purified by silica gel column chromatography ($PhCH_3$/EtOAc, 20:1) to give pentasaccharide. It was dissolved in a mixture of $CH_2Cl_2$: $H_2O$ (1:0.1 mL) and DDQ (4 mg, 0.018 mmol) was added. It was stirred for 1h at room temperature and diluted with $CH_2Cl_2$ (20 mL), washed with $H_2O$ (15 mL) to make the organic phase colourless. The crude 6-hydroxy derivative was re dissolved in $CH_2Cl_2$:$H_2O$ (2:1, 2 mL) and was added 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1.5 mg) in the presence of iodobenzene diacetate (BAIB, 0.013 g, 0.043 mmol) as the cooxidant at 0 °C. It was stirred at room temperature for 2 h. The reaction mixture was diluted with $CH_2Cl_2$ (20 mL), washed with 10% $Na_2S_2O_3$ (15 mL) and brine, then dried ($MgSO_4$) and concentrated in *vacuo*. It was also co-evaporated with toluene to remove traces of water. The crude carboxyl acid was dissolved in anhydrous DMF and cooled to 0 °C. After then, methyl iodide ($CH_3I$, 5 µL) and $KHCO_3$ (2 mg) were added under $N_2$ atmosphere. It was stirred for a period of 4 h allowing the reaction mixture to warm up to room

temperature, slowly. After 4 h, it was diluted with EtOAc (2 × 15 mL), washed with water (10 mL), brine (10 mL), then dried ($MgSO_4$), filtered and concentrated in *vacuo*. The crude mixture was purified by silica gel column chromatography ($PhCH_3$/EtOAc 20:1) to furnish **3a** (0.035 g) as colourless gum in 42% yield over three steps.

**Method B**: Glucosyl donor **4** (0.042 g, 0.058 mmol), azidoglucosyl acceptor **5a** (0.04 g, 0.048 mmol) and flame activated AW-300 MS (0.3 g) were suspended in anhydrous $CH_2Cl_2$ (1 mL) for 1 h at room temperature under argon atmosphere. The mixture was then cooled to -45°C. NIS (0.019 g, 0.087 mmol) and 1 M TfOH in $CH_2Cl_2$ (12 μL, 0.018 mmol) were added and the reaction was allowed to warm up to -30°C. The disaccharide acceptor **7a** (0.035 g, 0.043 mmol) in anhydrous $CH_2Cl_2$ (1 mL) and MS AW-300 (0.1 g) were stirred for 30 min at room temperature. After consumption of donor **4** and acceptor **5a** (TLC, $PhCH_3$/EtOAc, 20:1), the mixture was again cooled to -45°C and acceptor **7a** was added. Then, an additional amounts of NIS (0.017 g, 0.072 mmol) and TfOH (3 μL, 0.040 mmol) were added and the mixture was allowed to warm up to -25 °C. After complete consumption of the starting materials, it was quenched with $Et_3N$. The mixture was filtered and washed with 25 mL each of saturated $NaHCO_3$, saturated $Na_2S_2O_3$, $H_2O$, brine, then dried ($MgSO_4$) and concentrated in *vacuo*. The resulting mixture was purified by silica gel column chromatography ($PhCH_3$/EtOAc, 20:1) to give pentasaccharide **3a** (0.054 g, 54%) as colourless gum. $R_f$ 0.41 ($PhCH_3$/EtOAc 20:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.09-8.07 (m, 4 H), 7.65 (dd, *J* = 7.8, 1.2 Hz, 2 H), 7.62 (dd, *J* = 7.8, 1.2 Hz, 2 H), 7.57 (d, *J* = 7.2 Hz, 1 H), 7.54 (d, *J* = 7.2 Hz, 1 H), 7.46 (td, *J* = 7.8, 3.6 Hz, 4 H), 7.39-7.35 (m, 5 H), 7.34 (d, *J* = 5.4 Hz, 2 H), 7.29-7.26 (m, 10 H), 7.25-7.22 (m, 6 H), 7.21-7.17 (m, 9 H), 7.15-7.13 (m, 4 H), 5.42 (app t, *J* = 4.8 Hz, 1 H), 5.40 (d, *J* = 9.0 Hz, 1 H), 5.38 (d, *J* = 3.6 Hz, 1 H), 5.14 (t, *J* = 5.4 Hz, 1 H), 4.94 (d, *J* = 10.8 Hz, 1 H), 4.88 (dd, *J* = 10.8, 2.4 Hz, 2 H), 4.86-4.83 (m, 4 H), 4.76-4.72 (m, 2 H), 4.70 (dd, *J* = 10.2, 3.0 Hz, 3 H), 4.68-4.67 (m, 2 H), 4.63 (t, *J* = 7.2 Hz, 2 H), 4.40 (d, *J* = 5.4 Hz, 1 H), 4.27 (dd, *J* = 10.8, 3.6 Hz, 2 H), 4.21-4.18 (m, 2 H), 4.16 (app d, *J* = 3.6 Hz, 1 H), 4.12 (app dd, *J* = 12.0, 1.8 Hz, 2 H), 4.02 (t, *J* = 6.6 Hz, 1 H), 3.97-3.96 (m, 1 H), 3.94-3.93 (m, 1 H), 3.91 (app d, *J* = 5.4 Hz, 1 H), 3.90-3.85 (m, 3 H), 3.80 (ddd, *J* = 3.6, 6.6, 10.2 Hz, 2 H), 3.72 (q, *J* = 8.4 Hz, 1 H), 3.69-3.67 (m, 2 H), 3.53-3.49 (m, 2 H), 3.43 (dd, *J* = 9.6, 3.6 Hz, 2 H), 3.34 (s, 3 H), 3.15-3.12 (m, 1 H), 3.23 (s, 3 H), 3.18 (dd, *J* = 3.6, 10.2 Hz, 1 H), 2.35 (s, 3 H), 2.05 (s, 3 H), 1.03 (s, 9 H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.5, 169.6, 167.8, 165.4, 164.8, 138.2, 138.1, 138.0, 138.0, 137.9, 137.2, 134.0, 133.7, 130.0, 129.9-127.5, 125.4, 101.3, 98.6, 98.6, 98.1, 97.9, 82.6, 80.2, 78.5, 77.9, 77.8, 77.7, 76.3, 75.9, 75.5, 75.4, 75.2, 75.2 (2), 75.1, 75.1 (2), 74.9, 74.7, 74.2, 73.7, 71.5, 71.2, 70.8, 69.5, 68.9, 67.7, 63.4, 63.0, 62.1, 61.6, 55.5, 52.6, 51.9, 31.0, 29.8, 20.9, 20.8.; m/z (HRMS) calcd for $C_{109}H_{117}N_9O_{29}SiNa$ $[M+Na]^+$: 2066.7618, found 2066.7584.

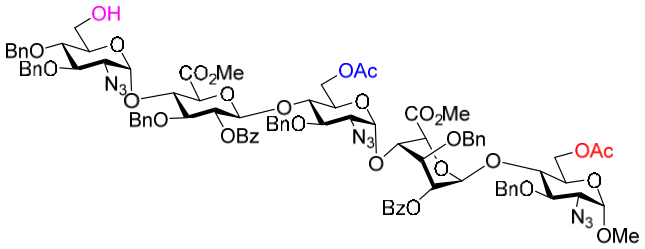
**Methyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinyl-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4-di-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (3b)**




Glucosyl donor **4** (0.134 g, 0.183 mmol), azidoglucosyl acceptor **5a** (0.105 g, 0.127 mmol) and flame activated AW-300 MS (1.5 g) were suspended in anhydrous $CH_2Cl_2$ (4 mL) for 1 h at room temperature under argon atmosphere. The mixture was then cooled to -45°C. NIS (0.052 g, 0.227 mmol) and TfOH (8 μL, 0.073 mmol) were added and the reaction mixture was allowed to warm up to -30°C. The disaccharide acceptor **7b** (0.100 g, 0.127 mmol) in anhydrous $CH_2Cl_2$ (2 mL) and MS AW-300 (0.5 g) were stirred for 30 min at room temperature. After consumption of donor **4** and acceptor **5a** (TLC, $PhCH_3$/EtOAc, 20:1), the mixture was again cooled to -45°C and acceptor **7b** was added. Then, an additional amounts of NIS (0.052 g, 0.227 mmol) and TfOH (8 μL, 0.073 mmol) were added and the reaction mixture was allowed to warm up to -25 °C. After complete consumption of the starting materials, it was quenched with $Et_3N$. The mixture was filtered and washed with 25 mL of each of saturated $NaHCO_3$, saturated $Na_2S_2O_3$, $H_2O$, brine, then dried ($MgSO_4$) and concentrated in *vacuo*. The resulting mixture was purified by silica gel column chromatography ($PhCH_3$/EtOAc, 20:1) to give pentasaccharide **3b** (0.133 g, 48%) as yellow oil. $R_f$ 0.36 ($PhCH_3$/EtOAc 9:1); $^1$H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.7 Hz, 4H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.52 (q, *J* = 8.1 Hz, 4H), 7.43 (m, 4H), 7.41 – 7.33 (m, 10H), 7.33 – 7.28 (m, 6H), 7.27 – 7.18 (m, 16H), 5.47 – 5.45 (m, 2H), 5.44 (d, *J* = 3.7 Hz, 1H), 5.19 (t, *J* = 5.4 Hz, 1H), 4.98 (d, *J* = 11.0 Hz, 1H), 4.96 – 4.92 (m, 2H), 4.90 (dd, *J* = 6.7, 3.9 Hz, 2H), 4.88 (t, *J* = 3.1 Hz, 2H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.78 – 4.76 (m, 2H), 4.73 (d, *J* = 10.1 Hz, 2H), 4.71 – 4.67 (m, 2H), 4.50 (d, *J* = 4.8 Hz, 1H), 4.31 – 4.26 (m, 4H), 4.25 – 4.17 (m, 3H), 4.10 (t, *J* = 5.8 Hz, 1H), 4.03 – 3.95 (m, 3H), 3.95 – 3.91 (m, 3H), 3.91 – 3.84 (m, 3H), 3.80 – 3.72 (m, 2H), 3.70 (dt, *J* = 10.0, 2.6 Hz, 1H), 3.57-3.52 (m, 1H), 3.46 – 3.43 (m, 1H), 3.43 (s, 3H), 3.41 (s, 3H), 3.39-3.35 (m, 1H), 3.27 (s, 3H), 3.22 (dd, *J* = 10.2, 3.8 Hz, 1H), 2.85-2.73 (m, 2H), 2.71-2.61 (m, 2H), 2.20 (s, 3H), 2.06 (s, 3H), 1.09 (s, 9H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 206.4, 172.4, 170.4, 169.5, 167.6, 165.3, 164.8, 138.9-137.2, 135.9-135.6, 133.9, 133.6, 133.5, 132.9, 129.8-127.4, 125.3, 101.0, 98.5, 98.5, 98.0, 97.7, 82.5, 80.1, 78.4, 77.8, 77.7, 77.5, 75.9, 75.7, 75.2, 75.1, 75.0, 74.9, 74.8, 74.7, 74.6, 73.9, 73.5, 72.5, 70.6, 70.3, 69.4, 68.8, 63.5,

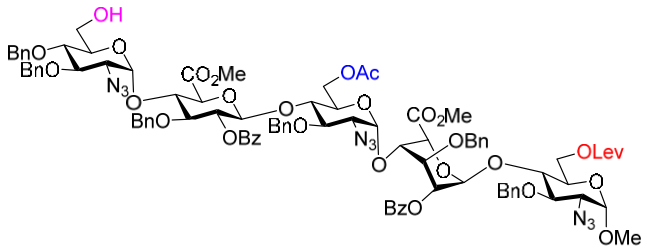
63.4, 62.8, 62.3, 61.8, 61.3, 55.4, 52.4, 51.8, 37.9, 29.9, 27.9, 26.8, 21.5, 20.8, 19.4;m/z (HRMS) calcd for $C_{112}H_{121}N_9O_{30}SiNa$ $[M+Na]^+$: 2122.7886, found 2122.7909.

**Methyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (26a)**



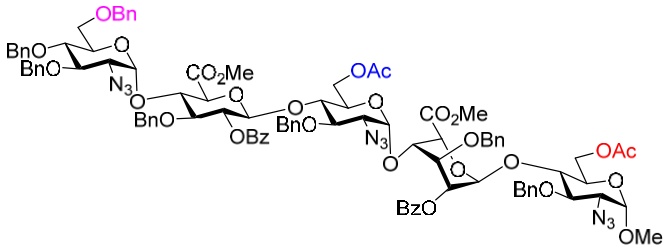

Pentasaccharide **26a** was prepared from **3a** (0.05 g, 0.024 mmol) using the general procedure for silyl ether cleavage, followed by purification by silica gel column chromatography ($PhCH_3$: EtOAc = 75:25) to furnish the product (0.036 g) in 83% yield.$^1$H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.10 (m, 2H), 8.10 – 8.07 (m, 3H), 7.62 – 7.56 (m, 2H), 7.48 (td, *J* = 7.9, 7.5, 1.6 Hz, 5H), 7.38 – 7.36 (m, 1H), 7.35 (dd, *J* = 3.2, 1.2 Hz, 2H), 7.34 – 7.33 (m, 2H), 7.32 (d, *J* = 2.3 Hz, 1H), 7.31 (t, *J* = 1.6 Hz, 3H), 7.29 (d, *J* = 1.9 Hz, 2H), 7.27 (dd, *J* = 2.9, 1.7 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.23 – 7.21 (m, 4H), 7.21 – 7.19 (m, 2H), 7.19 (d, *J* = 1.9 Hz, 3H), 7.18 (d, *J* = 1.2 Hz, 2H), 7.17 – 7.15 (m, 2H), 7.12 (dd, *J* = 7.5, 2.0 Hz, 2H), 5.45 (d, *J* = 5.1 Hz, 1H), 5.44 – 5.41 (m, 2H), 5.16 (t, *J* = 5.6 Hz, 1H), 4.95 (dd, *J* = 10.8, 5.8 Hz, 1H), 4.89 (d, *J* = 10.7 Hz, 1H), 4.88 – 4.84 (m, 2H), 4.82 (d, *J* = 10.4 Hz, 2H), 4.74 – 4.71 (m, 3H), 4.71 – 4.69 (m, 1H), 4.67 (dd, *J* = 5.4, 2.5 Hz, 2H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.43 (d, *J* = 5.1 Hz, 1H), 4.31 – 4.26 (m, 2H), 4.23 (dd, *J* = 12.5, 3.2 Hz, 2H), 4.18 (dd, *J* = 12.4, 2.4 Hz, 1H), 4.16 – 4.12 (m, 1H), 4.05 (td, *J* = 6.1, 2.2 Hz, 1H), 3.96 (d, *J* = 9.1 Hz, 2H), 3.95 – 3.90 (m, 1H), 3.90 – 3.88 (m, 1H), 3.89 – 3.87 (m, 1H), 3.86 (d, *J* = 2.2 Hz, 1H), 3.82 (dd, *J* = 10.0, 8.9 Hz, 1H), 3.77 (ddd, *J* = 11.0, 9.1, 2.2 Hz, 2H), 3.70 (dt, *J* = 10.0, 2.8 Hz, 2H), 3.65 (dd, *J* = 11.9, 3.9 Hz, 1H), 3.55 (d, *J* = 1.6 Hz, 1H), 3.54 – 3.51 (m, 1H), 3.51 (s, 3H), 3.45 (ddd, *J* = 10.2, 3.9, 2.8 Hz, 1H), 3.42 (s, 3H), 3.41 (d, *J* = 4.6 Hz, 1H), 3.39 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.36 (s, 3H), 3.31 (dd, *J* = 10.4, 3.8 Hz, 1H), 3.22 (ddd, *J* = 10.1, 3.8, 2.1 Hz, 1H), 2.08 (s, 3H), 2.04 (s, 3H);$^{13}$C NMR (150 MHz, $CDCl_3$): δ 170.8, 170.4, 169.6, 167.9, 165.4, 164.8, 138.1, 138.0, 137.9, 137.8, 137.5, 137.2, 134.5, 134.0, 133.7, 133.7, 130.1, 129.9, 129.2-127.6, 127.1, 125.4, 101.2, 98.6, 98.5, 98.1, 97.8, 82.6, 80.1, 78.4, 77.9, 77.8, 77.6, 76.2, 75.6, 75.5, 75.4, 75.2, 75.1, 75.1, 75.0, 74.7, 74.1, 73.7, 72.3, 71.1, 70.7, 69.5, 68.9, 63.5, 63.4, 62.9, 62.1, 61.6, 61.4, 55.5, 52.9, 52.0, 21.0, 20.9; m/z (HRMS) calcd for $C_{93}H_{99}N_9O_{29}SiNa$ $[M+Na]^+$: 1828.6441, found1828.6441.

**Methyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinyl-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (26b)**



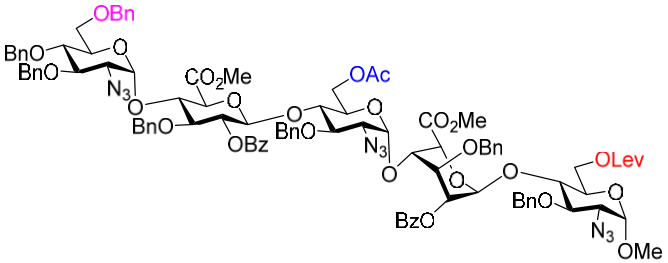

Pentasaccharide **26b** was prepared from **3b** (0.05 g, 0.024 mmol) using t he general procedure for silyl ether cleavage, and then purification by silica gel column chromatography ($PhCH_3$: EtOAc = 8:2) to give the product (0.037 g) in 85% yield.$^1$H NMR (600 MHz, $CDCl_3$) δ 8.11 – 8.07 (m, 4H), 7.62 – 7.53 (m, 3H), 7.48 (app td, *J* = 7.9, 4.0 Hz, 4H), 7.38 – 7.29 (m, 8H), 7.29 – 7.24 (m, 9H), 7.24 –7.19 (m, 4H), 7.19 – 7.13 (m, 6H), 7.11 (app dd, *J* = 7.3, 2.1 Hz, 2H), 5.45 – 5.37 (m, 4H), 5.13 (dt, *J* = 12.8, 5.2 Hz, 1H), 4.95 – 4.89 (m, 1H), 4.85 – 4.79 (m, 4H), 4.73 (d, *J* = 3.0 Hz, 3H), 4.70 – 4.63 (m, 4H), 4.47 (d, *J* = 4.8 Hz, 1H), 4.28 (d, *J* = 9.0 Hz, 1H), 4.27 – 4.20 (m, 4H), 4.16 – 4.11 (m, 1H), 4.10 – 4.04 (m, 1H), 3.94 (dd, *J* = 9.1, 7.6 Hz, 2H), 3.90 – 3.85 (m, 3H), 3.84 – 3.78 (m, 1H), 3.78 – 3.72 (m, 2H), 3.71 (dt, *J* = 9.8, 3.1 Hz, 1H), 3.69 – 3.59 (m, 2H), 3.53 (td, *J* = 10.1, 2.4 Hz, 2H), 3.50 (app s, 4H), 3.45 (ddt, *J* = 10.0, 6.3, 3.2 Hz, 1H), 3.38 (app s, 4H), 3.36 (s, 3H), 3.33 – 3.27 (m, 1H), 3.20 (dt, *J* = 10.4, 2.6 Hz, 1H), 2.81 – 2.67 (m, 2H), 2.61-2.54 (m, 2H), 2.15 (d, *J* = 3.9 Hz, 3H), 2.04 (d, *J* = 1.5 Hz, 3H);$^{13}$C NMR (150 MHz, $CDCl_3$) δ 206.5, 172.5, 170.6, 169.6, 168.0, 164.8, 138.1, 138.0, 138.0 (2), 137.3, 137.7, 137.4, 137.2, 134.0, 133.7, 130.1, 129.9, 129.3, 129.1, 129.0, 129.0 (2), 128.8, 128.7, 128.6 (2), 128.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.9 (2), 127.9 (3), 127.8, 127.6, 127.5, 125.4, 101.2, 98.6, 98.5, 98.1, 97.8, 82.6, 80.1, 78.5, 77.9, 77.8, 77.6, 76.0, 75.6, 75.5, 75.3, 75.2, 75.1, 75.0, 74.8, 74.0, 73.7, 72.3, 70.6, 70.30, 69.5, 68.9, 63.5, 63.5 (2), 63.0, 62.3, 61.6, 61.4, 55.5, 52.9, 51.9, 38.0, 29.9, 27.7, 21.6, 20.1; m/z (HRMS) calcd for $C_{96}H_{103}N_9O_{30}Na$ $[M+Na]^+$: 1884.6703, found 1884.6763.

**Methyl 6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (27a)**



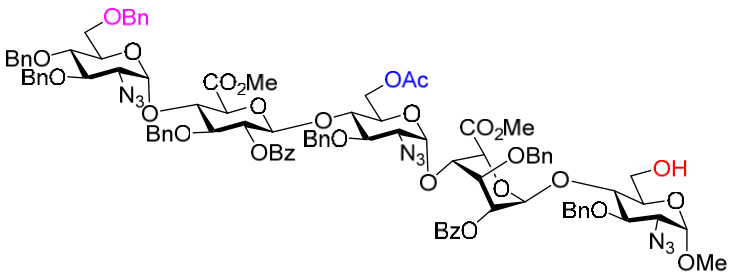
Pentasaccharide **27a** was prepared from **26a** (0.025 g, 0.014 mmol) using the general procedure for $Ag_2O$-mediated *O*-benzylation, and then purification by silica gel column chromatography ($PhCH_3$: EtOAc = 8:2) to furnish the product (0.021 g) in 82% yield. $^1$H NMR (600 MHz, $CDCl_3$): δ 8.14 – 8.06 (m, 7H), 7.61 – 7.56 (m, 6H),7.50 – 7.44 (m, 7H), 7.36 – 7.33 (m, 7H), 7.31- (m, 4 H), 7.29 – 7.28 (m, 4H), 7.22 – 7.19 (m, 4H), 7.20 – 7.17 (m, 4H), 7.12 – 7.10 (m, 2H), 5.47 (dd, *J* = 8.3, 4.5 Hz, 2H), 5.45 – 5.40 (m, 1H), 5.38 (s, 1H), 5.17 (dd, *J* = 11.4, 5.7 Hz, 1H), 4.99 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.87-4.84 (m, 4H), 4.82 – 4.77 (m, 2H), 4.76 (d, *J* = 6.2 Hz, 1H), 4.74 – 4.68 (m, 4H), 4.66 (t, *J* = 9.3 Hz, 2H), 4.60 (d, *J* = 12.2 Hz, 1H), 4.54 – 4.50 (m, 1H), 4.47 – 4.43 (m, 1H), 4.42 (d, *J* = 5.2 Hz, 1H), 4.33 – 4.30 (m, 2H), 4.28 (d, *J* = 9.1 Hz, 1H), 4.24 (dd, *J* = 5.4, 3.1 Hz, 1H), 4.20 (dd, *J* = 14.2, 2.8 Hz, 1H), 4.18 – 4.12 (m, 1H), 4.06 – 4.03 (m, 1H), 3.96 – 3.92 (m, 2H), 3.92 – 3.89 (m, 1H), 3.89 – 3.84 (m, 1H), 3.84 – 3.81 (m, 1H), 3.77 – 3.74 (m, 2H), 3.73 – 3.72 (m, 1H), 3.72 – 3.68 (m, 1H), 3.62 – 3.58 (m, 1H), 3.54 (ddd, *J* = 10.8, 8.4, 2.9 Hz, 1H), 3.51 – 3.47 (m, 2H), 3.45 (s, 3H), 3.43 (s, 3H), 3.39 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.35 (s, 3H), 3.24 – 3.18 (m, 1H), 2.09 (s, 3H), 2.02 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 170.8, 170.5, 169.6, 167.9, 165.4, 164.8, 138.2, 138.1, 138.0, 137.9, 137.5, 133.7, 133.1, 130.1, 129.9, 129.8, 129.1, 128.9-127.7, 101.3, 98.6, 98.6, 98.1, 97.9, 82.6, 80.2, 78.4, 77.9, 77.9 (2), 77.7, 76.3, 75.6, 75.4, 75.2, 75.2, 75.1 (2), 75.1, 74.9, 74.7, 74.2, 73.7, 73.7, 71.5, 71.2, 70.7, 69.8, 69.5, 68.9, 67.7, 66.8, 63.4, 63.0, 62.2, 55.5, 52.6, 51.9, 20.9, 20.9(2); m/z (HRMS) calcd for $C_{100}H_{105}N_9O_{29}Na$ $[M+Na]^+$: 1918.6912, found 1918.6849.

**Methyl 2-azido-3-*O*-benzyl-2-deoxy-6-*O*-levulinyl-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4,6-tri-*O*-benzyl-2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (27b)**



Pentasaccharide **27b** was prepared from **26b** (0.030 g, 0.016 mmol) using the general procedure for $Ag_2O$-mediated *O*-benzylation, and then purification by silica gel column chromatography ($PhCH_3$: EtOAc = 75:25) to give the product (0.024 g) in 78% yield. $^1$H NMR (600 MHz, $CDCl_3$): δ 8.09 (tt, *J* = 8.4, 1.5 Hz, 5H), 7.61–7.55 (m, 3H), 7.50–7.46 (m, 5H), 7.38 –7.32 (m, 6H), 7.31–7.27 (m, 12H), 7.24–7.17 (m, 9H), 7.14 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.10 (dd, *J* = 7.4, 2.3 Hz, 3H), 5.47 (d, *J* = 3.7 Hz, 1H), 5.43–5.39 (m, 2H), 5.16–5.11 (m, 2H), 4.96 (d, *J* = 10.7 Hz, 1H), 4.88–4.83 (m, 2H), 4.84–4.81 (m, 1H), 4.80–4.75 (m, 1H), 4.73 (d, *J* = 2.6 Hz, 2H), 4.70 (dd, *J* = 10.1, 3.7 Hz, 1H), 4.68–4.63 (m, 2H), 4.61–4.57 (m, 2H), 4.52 (d, *J* = 10.9 Hz, 2H), 4.47–4.43 (m, 2H), 4.30–4.27 (m, 1H), 4.27–4.23 (m, 2H), 4.23–4.19 (m, 1H), 4.14 (d, *J* = 12.8 Hz, 1H), 4.10–4.05 (m, 2H), 3.94 (ddd, *J* = 8.8, 5.0, 3.3 Hz, 2H), 3.90–3.87 (m, 1H), 3.86–3.83 (m, 1H), 3.83–3.80 (m, 1H), 3.80–3.75 (m, 1H), 3.75 –3.73 (m, 1H), 3.72 (dd, *J* = 5.6, 3.0 Hz, 1H), 3.67 (d, *J* = 10.0 Hz, 1H), 3.60 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.54 – 3.49 (m, 2H), 3.50–3.46 (m, 1H), 3.44 (s, 3H), 3.39 (s, 3H), 3.38 (d, *J* = 6.7 Hz, 1H), 3.36 (s, 3H), 3.35 –3.32 (m, 1H), 3.19 (ddd, *J* = 10.2, 3.7, 1.6 Hz, 1H), 3.19 (ddd, *J* = 10.2, 3.7, 1.6 Hz, 1H), 2.80 – 2.69 (m, 2H), 2.67–2.56 (m, 2H), 2.16 (app s, 3H), 2.02 (app s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 206.5, 172.5, 170.5, 169.6, 165.4, 164.8, 138.2, 138.2 (2), 138.0, 138.0, 137.9, 137.9 (2), 137.5, 137.5 (2), 137.2, 134.0, 133.7, 130.1, 129.9-127.7, 101.3, 98.6, 98.6, 98.1, 97.9, 82.6, 80.2, 78.5, 78.0, 77.9, 77.7, 76.1, 75.6, 75.3, 75.2, 75.1, 75.1 (2), 75.0, 74.9, 74.7, 74.0, 73.8, 73.7, 71.5, 69.5, 68.9, 67.7, 63.5, 63.4, 63.0, 62.35, 61.61, 55.5, 52.6, 51.9, 38.0, 29.9, 29.8, 28.0, 22.8, 20.9; m/z (HRMS) calcd for $C_{103}H_{109}N_9O_{30}Na$ $[M+Na]^+$: 1974.7172, found 1974.7160.

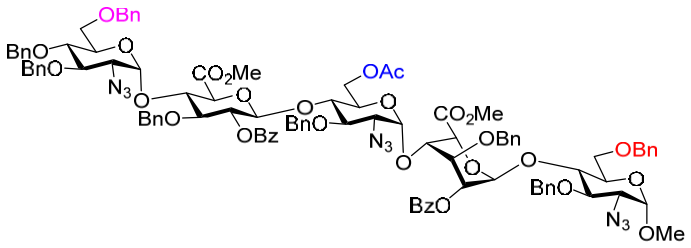
**Methyl 2-azido--3-*O*-benzyl-2-deoxy-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4,6-tri-*O*-benzyl -2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (28)**




Pentasaccharide **28** was prepared from **27b** (0.024 g, 0.012 mmol) using the general procedure cleavage of Lev esters, followed by purification using silica gel column chromatography ($PhCH_3$: EtOAc = 7:3) to furnish the product (0.019 g) in 85% yield.$^1$H NMR (600 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 12.8, 7.7 Hz, 5H), 7.62–7.55 (m, 4H), 7.52–7.38 (m, 6H), 7.33 (d, *J* = 6.9 Hz, 6H), 7.31–7.26 (m, 12H), 7.25–7.22 (m, 2H), 7.21–7.15 (m, 5H), 7.15–7.07 (m, 5H), 5.45 (dd, *J* = 7.1, 4.0 Hz, 2H), 5.41 (t, *J* = 8.5 Hz, 1H), 5.14 (t, *J*

= 4.1 Hz, 1H), 4.88 (d, *J* = 10.6 Hz, 1H), 4.85 – 4.83 (m, 2H), 4.80 (dd, *J* = 10.5, 5.0 Hz, 2H), 4.77–4.70 (m, 4H), 4.69–4.62 (m, 3H), 4.62–4.58 (m, 2H), 4.51 (d, *J* = 11.0 Hz, 1H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.27 (t, *J* = 8.9 Hz, 1H), 4.21 (app d, *J* = 12.3 Hz, 1H), 4.17 (app d, *J* = 11.8 Hz, 1H), 4.10–4.04 (m, 3H), 3.98–3.89 (m, 4H), 3.82 (app dt, *J* = 15.3, 9.5 Hz, 2H), 3.76–3.70 (m, 5H), 3.67 (d, *J* = 10.2 Hz, 1H), 3.62–3.54 (m, 3H), 3.54–3.45 (m, 3H), 3.42 (s, 3H), 3.38 (app s, 3H), 3.33 (s, 3H), 3.20 (dd, *J* = 10.2, 3.8 Hz, 1H), 2.03 (s, 3H); $^{13}$C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.3, 167.9, 165.6, 164.9, 138.2, 137.9, 137.4, 137.2, 133.9, 133.8, 129.9-127.5, 101.2, 98.7, 98.7, 97.9, 97.9 (2), 82.7, 80.2, 78.5, 78.0, 77.9, 77.7, 75.6, 75.3, 75.2, 75.1, 75.1, 74.9, 74.7, 73.7, 73.7 (2), 73.3, 71.5, 71.4, 70.3, 69.9, 69.6, 63.7, 63.4, 63.2, 61.6, 61.2, 55.4, 52.6, 52.0, 21.0; m/z (HRMS) calcd for $C_{98}H_{103}N_9O_{28}Na$ $[M+Na]^+$: 1876.6810, found 1877.6826.

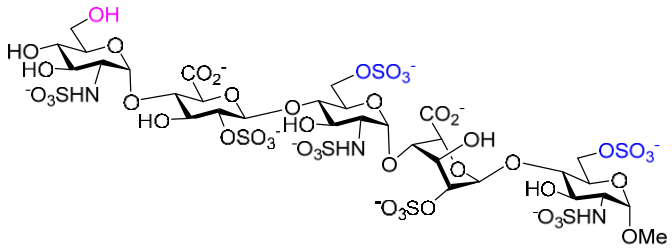
**Methyl 2-azido-3,6-di-*O*-benzyl-2-deoxy-4-*O*-{methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-[6-*O*-acetyl-2-azido-3-*O*-benzyl-2-deoxy-4-*O*-(methyl 2-*O*-benzoyl-3-*O*-benzyl-4-*O*-{2-azido-3,4,6-tri-*O*-benzyl -2-deoxy-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (29)**




Pentasaccharide **29** was prepared from **28** (0.019 g, 0.010 mmol) using the general procedure for $Ag_2O$-mediated *O*-benzylation, followed by purification using silica gel column chromatography ($PhCH_3$: EtOAc = 9:1) to give the product (0.016 g) in 81% yield. $^1$H NMR (600 MHz, $CDCl_3$): δ 8.11–8.08 (m, 2H), 8.00–7.95 (m, 3H), 7.62–7.54 (m, 3H), 7.50–7.42 (m, 5H), 7.36–7.32 (m, 5H), 7.32–7.27 (m, 10H), 7.26–7.16 (m, 18H), 7.15 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.11 (dd, *J* = 7.4, 2.1 Hz, 2H), 5.47 (d, *J* = 3.9 Hz, 2H), 5.42 (dd, *J* = 9.1, 7.9 Hz, 1H), 5.15 – 5.13 (m, 1H), 4.94 – 4.87 (m, 1H), 4.86 (d, *J* = 6.8 Hz, 2H), 4.82 – 4.79 (m, 2H), 4.78 (d, *J* = 6.3 Hz, 1H), 4.75 (app dd, *J* = 12.6, 2.4 Hz, 2H), 4.70 – 4.66 (m, 2H), 4.65 (d, *J* = 3.9 Hz, 1H), 4.62–4.58 (m, 1H), 4.55–4.47 (m, 2H), 4.46 (d, *J* = 12.1 Hz, 1H), 4.28 (t, *J* = 8.9 Hz, 1H), 4.22 (dd, *J* = 12.4, 3.1 Hz, 1H), 4.18–4.13 (m, 2H), 4.13–4.07 (m, 2H), 4.00–3.95 (m, 1H), 3.93 (dd, *J* = 9.2, 3.5 Hz, 2H), 3.94 (s, 1H), 3.88 – 3.86 (m, 1H), 3.86–3.77 (m, 2H), 3.77–3.72 (m, 3H), 3.69–3.62 (m, 3H), 3.62– 3.57 (m, 2H), 3.54–3.51 (m, 1H), 3.50–3.47 (m, 2H), 3.43 (app s, 3H), 3.41 (dd, *J* = 10.3, 3.6 Hz, 1H), 3.36 (s, 3H), 3.34 (d, *J* = 3.8 Hz, 1H), 3.28 (s, 3H), 3.27 (d, *J* = 2.8 Hz, 1H), 3.20 (dd, *J* = 10.3, 3.8 Hz, 1H), 2.01 (s, 3H);$^{13}$C NMR (150 MHz, $CDCl_3$) δ 170.5, 169.2, 167.9, 165.4, 164.8,

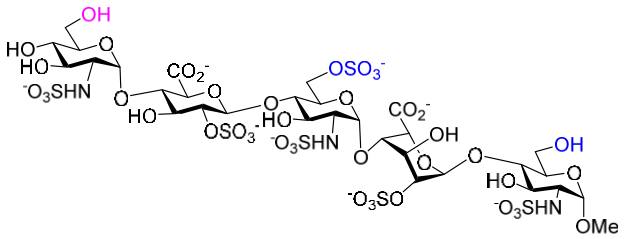
138.1, 138.1 (2), 138.0, 137.9, 137.9 (2), 137.8, 137.5, 137.2, 133.9, 133.6, 129.9, 129.9 (2), 128.5-127.6, 101.2, 98.9, 98.7, 98.2, 97.9, 82.7, 80.2, 78.6, 77.9, 77.7, 75.9, 75.6, 75.4, 75.3, 75.2, 75.1, 74.9, 74.7, 73.7, 73.7, 73.7, 73.7, 71.5, 70.5 (2), 70.1, 69.5, 67.7, 63.5, 63.4, 63.1, 55.4, 52.6, 51.9, 20.95; m/z (HRMS) calcd for $C_{105}H_{109}N_9O_{28}Na$ $[M+Na]^+$: 1966.7274, found 1966.7273.

**Methyl 2-deoxy-2-sulfoamino-6-*O*-sulfonate-4-*O*-{2-*O*-sulfonate-4-*O*-[2-deoxy-2-sulfoamino-6-*O*-sulfonate-4-*O*-(2-*O*-sulfonate-4-*O*-{2-deoxy-2-sulfoamino-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (1a)**




Pentasaccharide **27a** and **27b** were converted to **2a** *via* saponification and *O*-sulfation. The resulting *O*-sultated **2a** was used as such without further purification. Pentasaccharide **1a** was prepared from **2a** (0.012 g) *via* a two-step sequences: (i) hydrogenolysis (ii) selective *N*-sulfation. The crude *O*-and *N*-sulfated pentasaccharide was purified by a column of Sephadex G-25 using water as eluent. The appropriate fractions were concentrated and passed through a column of Dowex 50WX8-$Na^+$ with water. The product protion was collected and lyophilized to furnish the protecting group free pentasaccharide **1a** (0.0036 g, 40%). $^1$H NMR (900 MHz, $D_2O$) δ 5.64 (d, *J* = 4.0 Hz, 1H), 5.45 – 5.39 (m, 1H), 5.27 – 5.18 (m, 1H), 5.05 – 4.99 (m, 1H), 4.56 (d, *J* = 11.4 Hz, 2H), 4.40 – 4.35 (m, 1H), 4.34 – 4.28 (m, 2H), 4.25 – 4.20 (m, 1H), 4.20 – 4.12 (m, 1H), 4.08 (m, 1H), 4.05 – 3.95 (m, 1H), 3.86 (d, *J* = 3.1 Hz, 2H), 3.84 – 3.76 (m, 3H), 3.76 – 3.69 (m, 6H), 3.65 – 3.57 (m, 1H), 3.49 – 3.45 (m, 2H), 3.42 (s, 3H), 3.40 (d, *J* = 3.1 Hz, 1H), 3.31 – 3.24 (m, 2H), 3.21 (dt, *J* = 10.4, 3.3 Hz, 1H), 2.92 – 2.86 (m, 1H), 2.83 – 2.77 (m, 2H);$^{13}$C NMR (151 MHz, $D_2O$) δ 174.3, 174.0, 99.5, 97.8, 97.6, 97.2, 96.6, 79.3, 77.4, 76.6, 76.2, 75.9, 75.8, 74.6, 71.2, 70.9, 69.5, 69.4, 69.2, 68.8, 68.6, 68.5, 68.4, 68.0, 67.1, 66.4, 65.4, 59.7, 57.6, 57.3, 57.2, 57.1, 54.9, 54.9 (2); m/z (HRMS) calcd for $C_{31}H_{52}N_3O_{46}S_7$ $[M-Na-H]^{2-}$: calcd for 701.4983, found 701.4982; $C_{31}H_{51}N_3O_{46}S_7$ $[M-2H]^{2-}$ calcd for 712.4892, found 712.4907; $C_{31}H_{49}N_3O_{46}S_7$ $[M+2Na-4H]^{2-}$: calcd for 734.4710, found 734.4729; $C_{31}H_{53}N_3O_{46}S_7$ $[M-3Na]^{3-}$:calcd for 452.6750, found 452.6770; $C_{31}H_{52}N_3O_{46}S_7$ $[M-2Na-H]^{3-}$: calcd for 460.0023, found 460.0049; $C_{31}H_{51}N_3O_{46}S_7$ $[M-Na-2H]^{3-}$: calcd for 467.3295, found 467.3321; $C_{31}H_{51}N_3O_{46}S_7$ $[M-3H]^{3-}$: calcd for 474.6568, found 474.6586.

**Methyl 2-deoxy-2-sulfoamino-4-*O*-{2-*O*-sulfonate-4-*O*-[2-deoxy-2-sulfoamino-6-*O*-sulfonate-4-*O*-(2-*O*-sulfonate-4-*O*-{2-deoxy-2-sulfoamino-α-D-glucopyranoside}-β-D-glucopyranosyluronate)-α-D-glucopyranoside]-α-L-idopyranosyluronate}-α-D-glucopyranoside (1b)**




Pentasaccharide **29** was converted to **2b** *via* saponification and *O*-sulfation. The resulting *O*-sultated **2b** was used as such without further purification. Pentasaccharide **1b** was prepared from **2b** (0.014 g) *via* a two-step sequences: (i) hydrogenolysis (ii) selective *N*-sulfation. The crude *O*-and *N*-sulfated pentasaccharide was purified by a column of Sephadex G-25 using water as eluent. The appropriate fractions were collected, concentrated and passed through a column of Dowex 50WX8$^{-}Na^{+}$ with water as eluent. The product protion was lyophilized to furnish the protecting group free pentasaccharide **1a** (0.0048 g, 47%) $^{1}$H NMR (900 MHz, $D_2O$) δ 5.65 – 5.60 (m, 1H), 5.44 – 5.33 (m, 1H), 5.26 – 5.18 (m, 1H), 5.03 (d, *J* = 4.5 Hz, 1H), 5.01 – 4.92 (m, 1H), 4.57 (d, *J* = 10.3 Hz, 1H), 4.34 – 4.25 (m, 1H), 4.22 – 4.12 (m, 3H), 4.03 – 3.94 (m, 1H), 3.93 –3.85 (m, 3H), 3.83 – 3.78 (m, 4H), 3.79 – 3.72 (m, 2H), 3.72 – 3.64 (m, 2H), 3.63 – 3.58 (m, 1H), 3.49 – 3.47 (m, 3H), 3.46 (app d, *J* = 9.3 Hz, 2H), 3.41 (app d, *J* = 10.3 Hz, 3H), 3.33 – 3.23 (m, 2H), 3.21 (dd, *J* = 10.4, 3.5 Hz, 1H), 3.05 – 2.96 (m, 2H), 2.92 – 2.87 (m, 2H), 2.79 (d, *J* = 7.3 Hz, 2H);$^{13}$C NMR (151 MHz, $D_2O$) δ 174.2, 174.0, 101.3, 99.5, 97.8, 97.2, 95.6 79.2, 77.2, 75.8, 75.6, 75.3, 74.4, 71.3, 71.2, 70.8, 70.7, 70.2, 70.0, 69.1, 68.6, 66.3, 65.2, 64.9, 60.55, 59.6, 59.5, 59.2, 57.55, 57.5(2), 57.0, 56.8, 54.8, 54.5, 54.2, 53.6; m/z (HRMS) calcd for $C_{31}H_{48}N_3O_{43}S_6$ [M-H]$^{-}$: calcd for 1340.9933, found 1340.9834.

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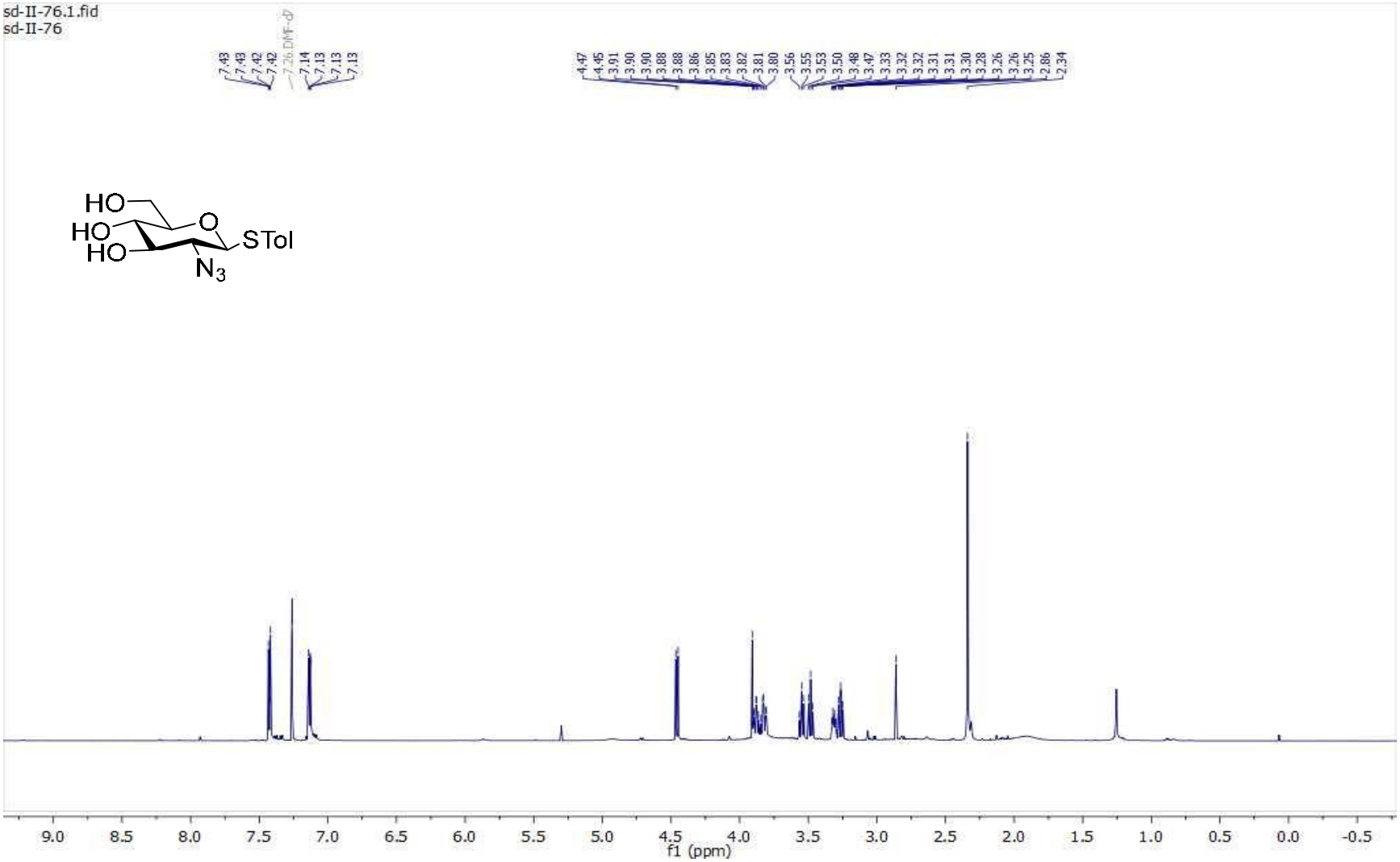


Figure 1.[1]H NMR spectrum of 4-Methylphenyl 2-azido-2-deoxy-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$)

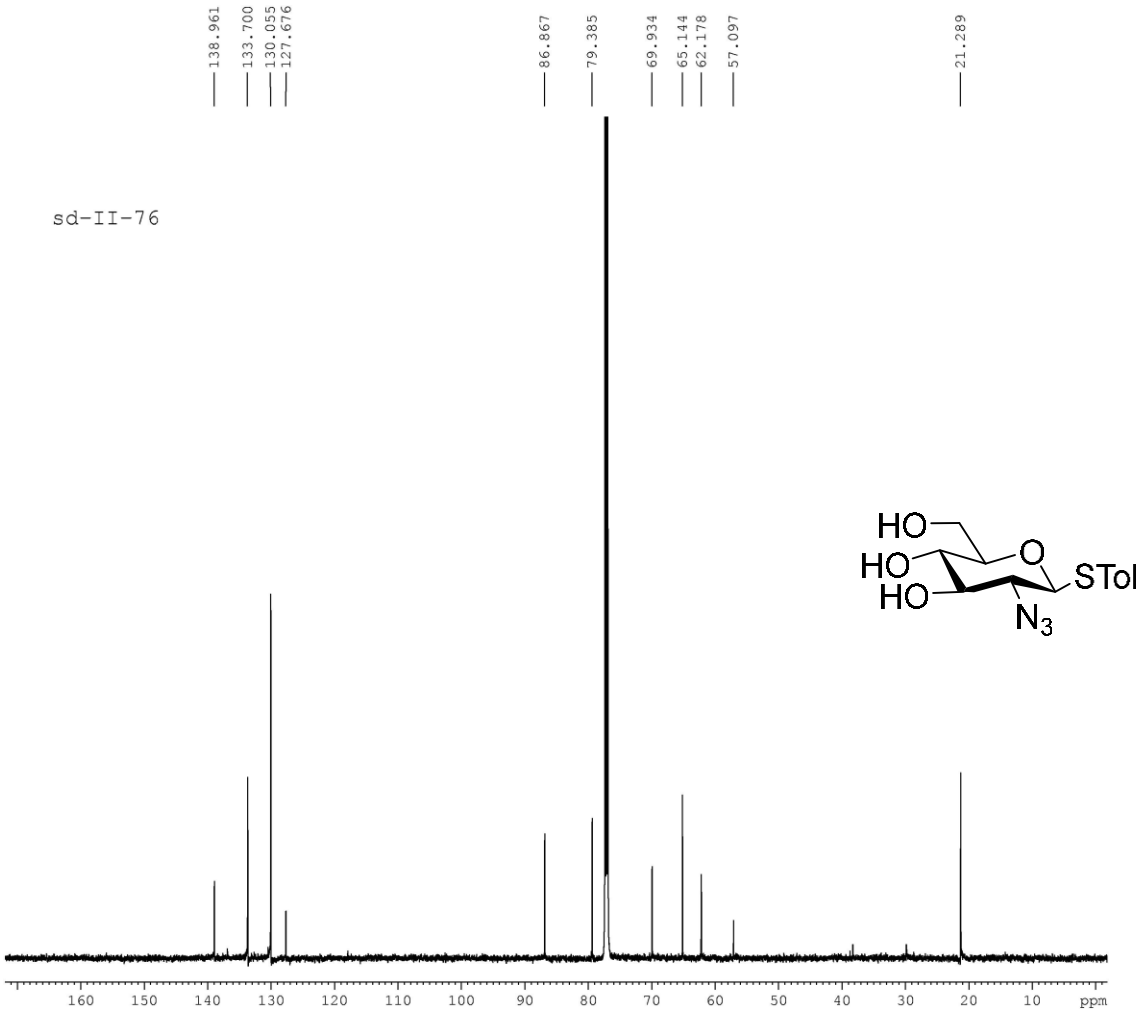


Figure 2. $^{13}$C NMR spectrum of 4-Methylphenyl 2-azido-2-deoxy-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

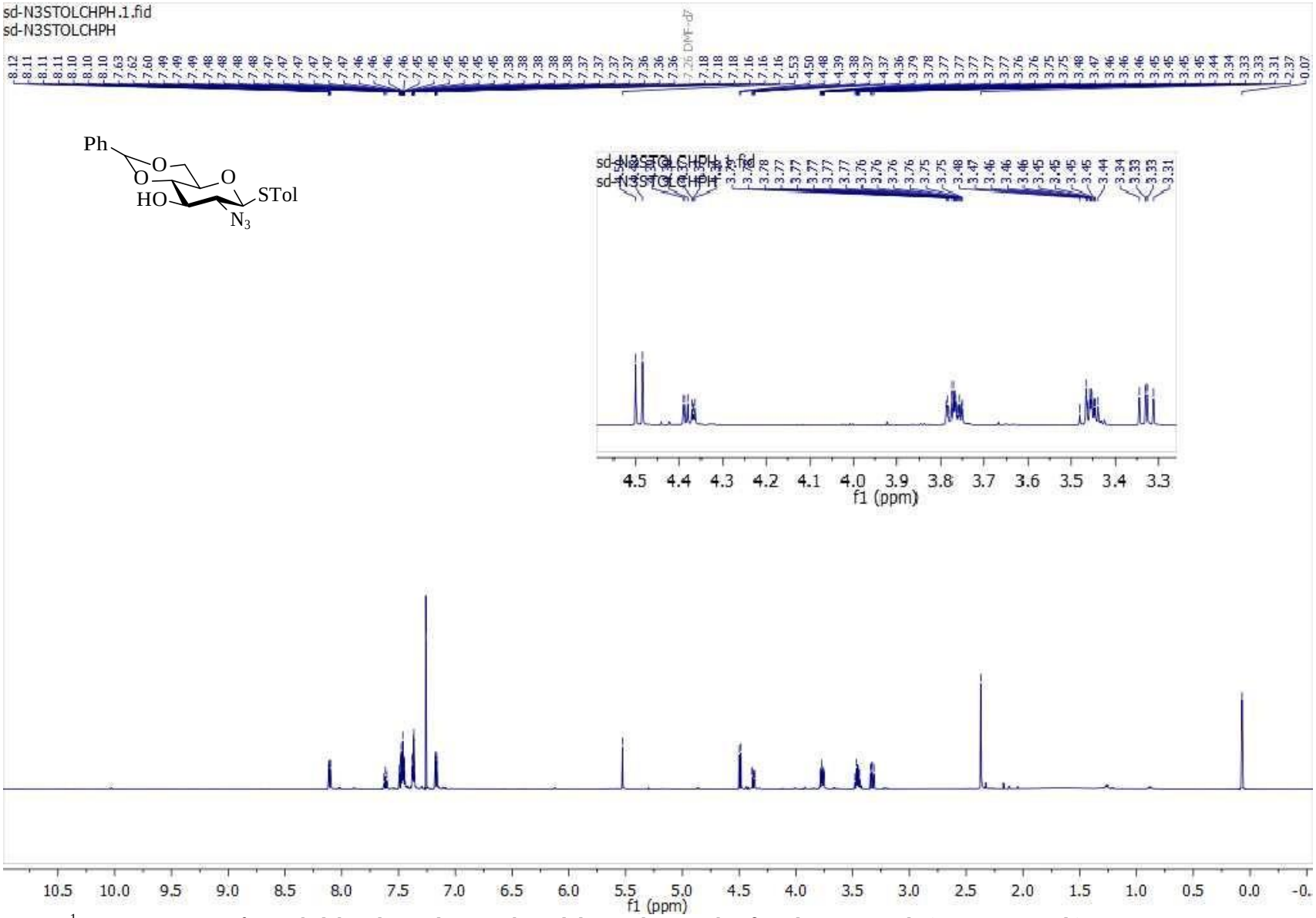


Figure 3. $^{1}$H NMR spectrum of 4-Methylphenyl-2-azido-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

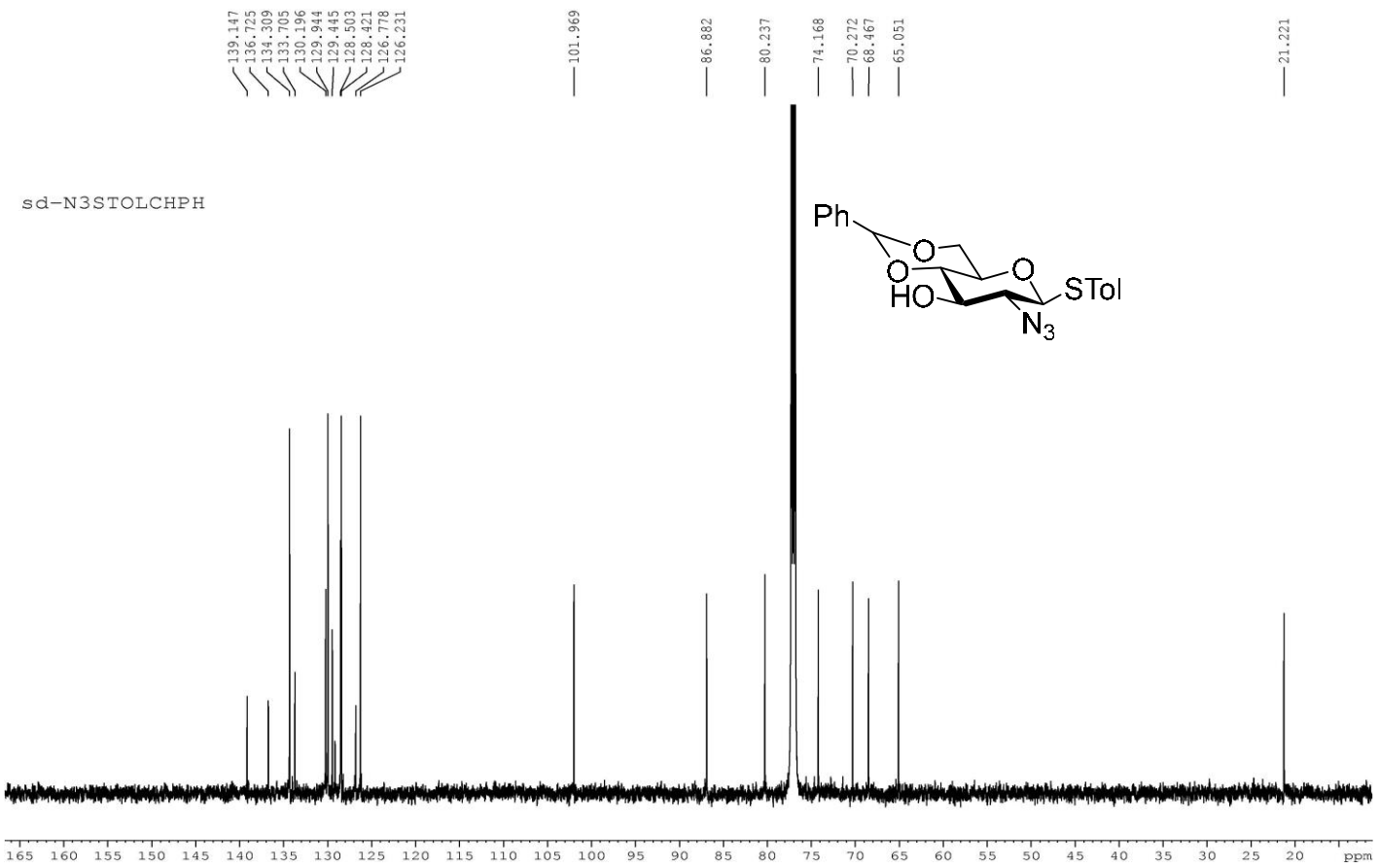


Figure 4.[13]C NMR spectrum of 4-Methylphenyl-2-azido-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

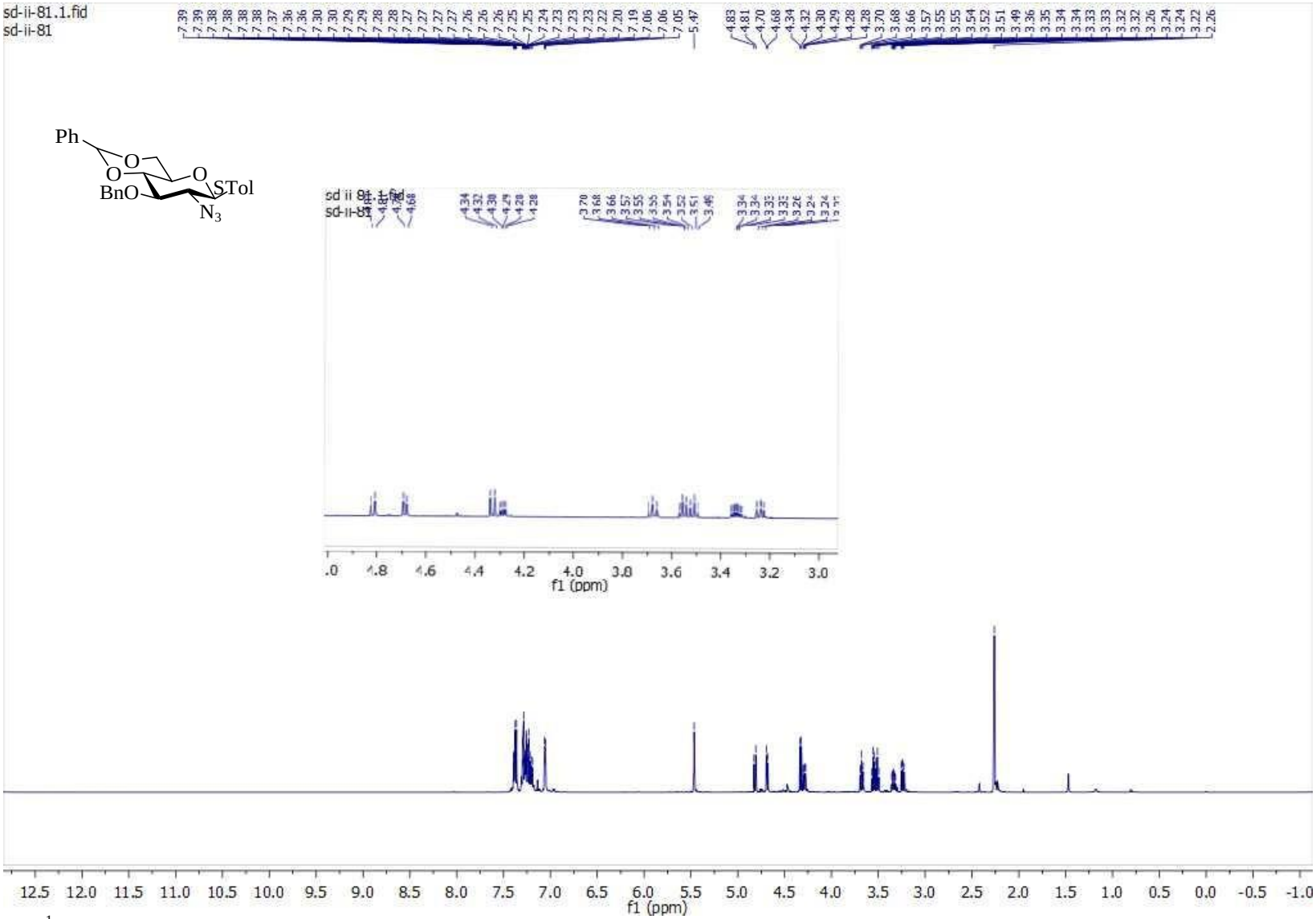


Figure 5.[1]H NMR spectrum of 4-Methylphenyl 2-azido-3-benzyl-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

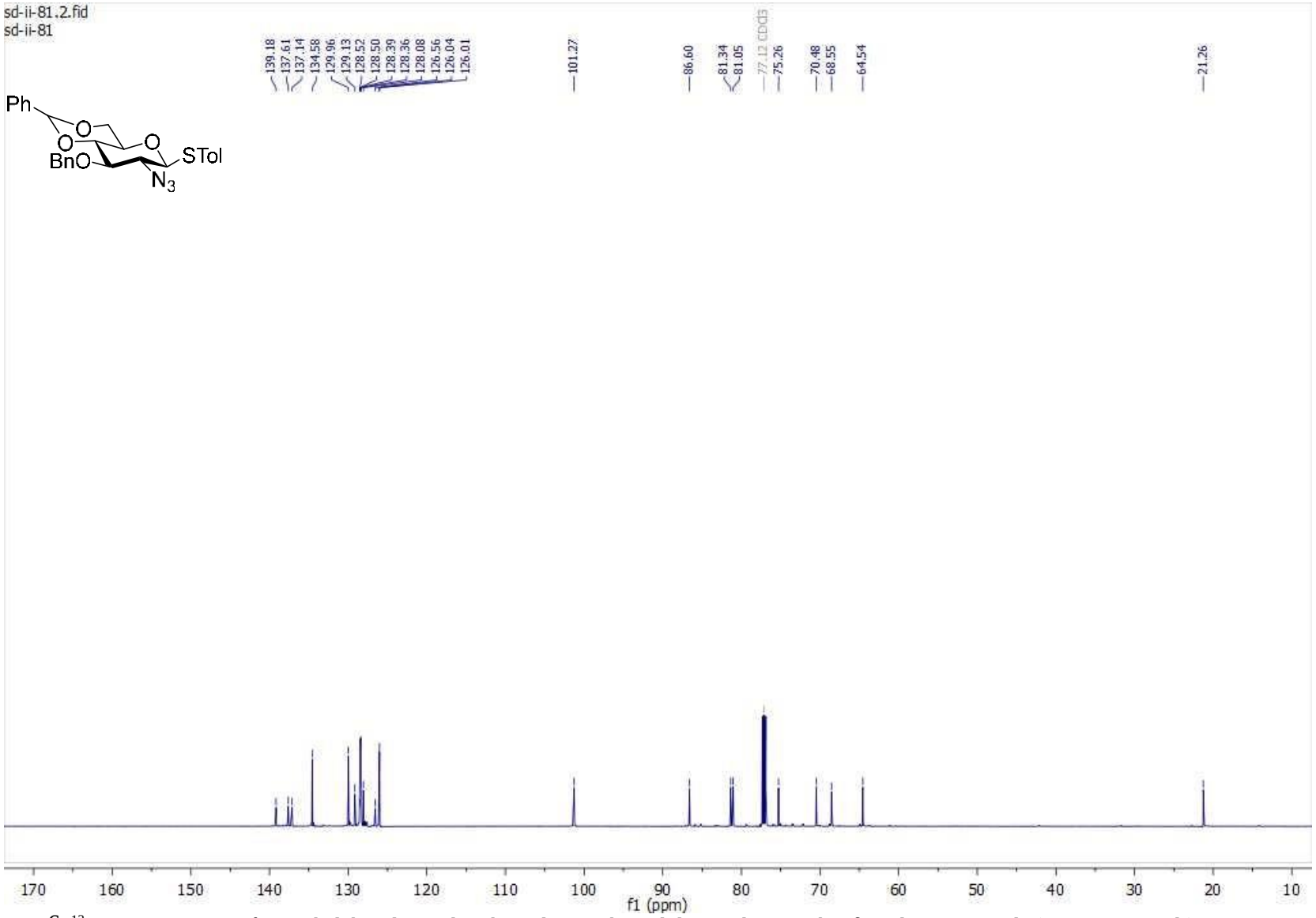


Figure 6. $^{13}$C NMR spectrum of 4-Methylphenyl 2-azido-3-benzyl-4,6-O-benzylidene-2-deoxy-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

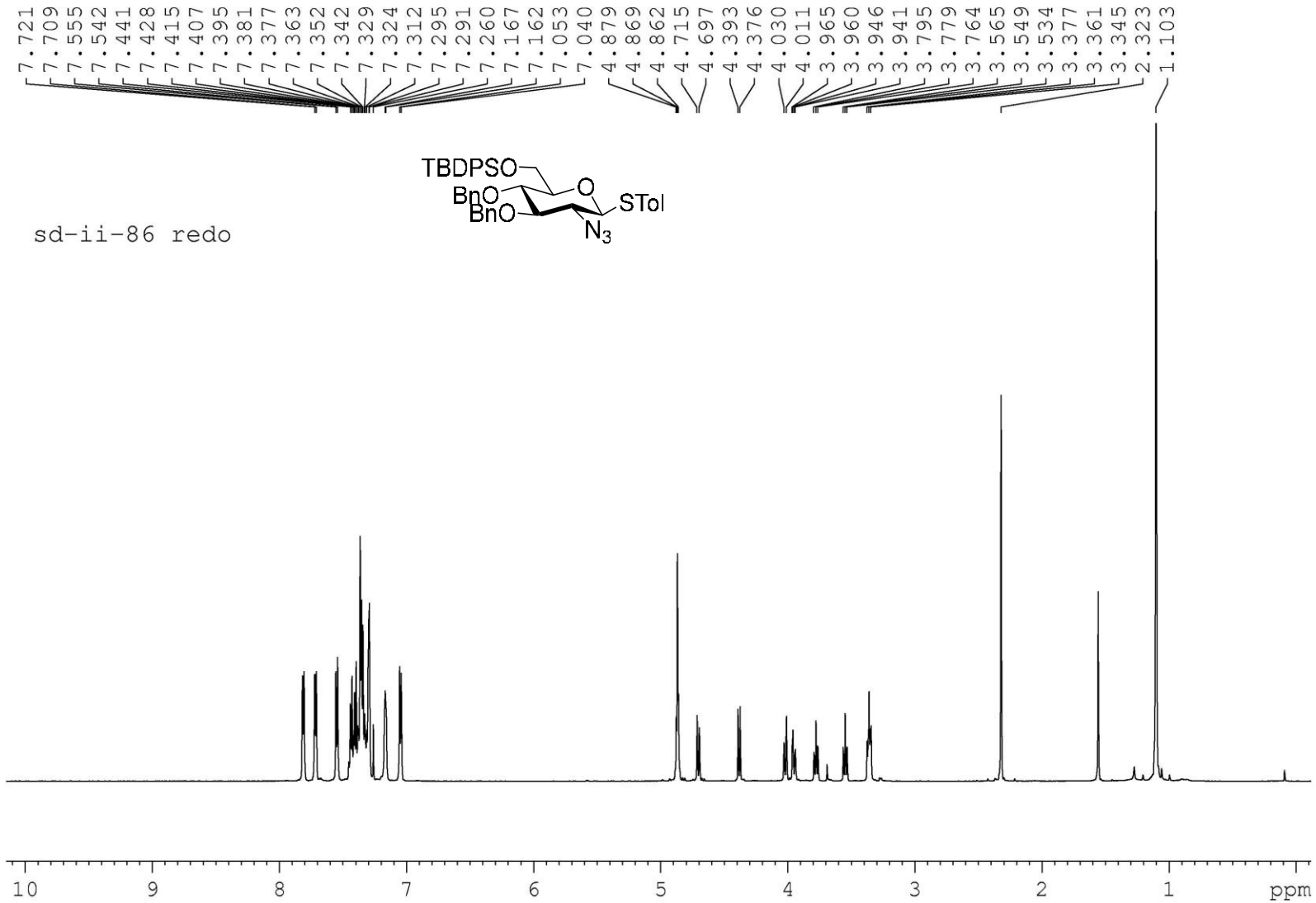


Figure 7. $^{1}$H NMR spectrum of 4-Methylphenyl 2-azido-3,4-di-O-benzyl-2-deoxy-6-O-tert-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

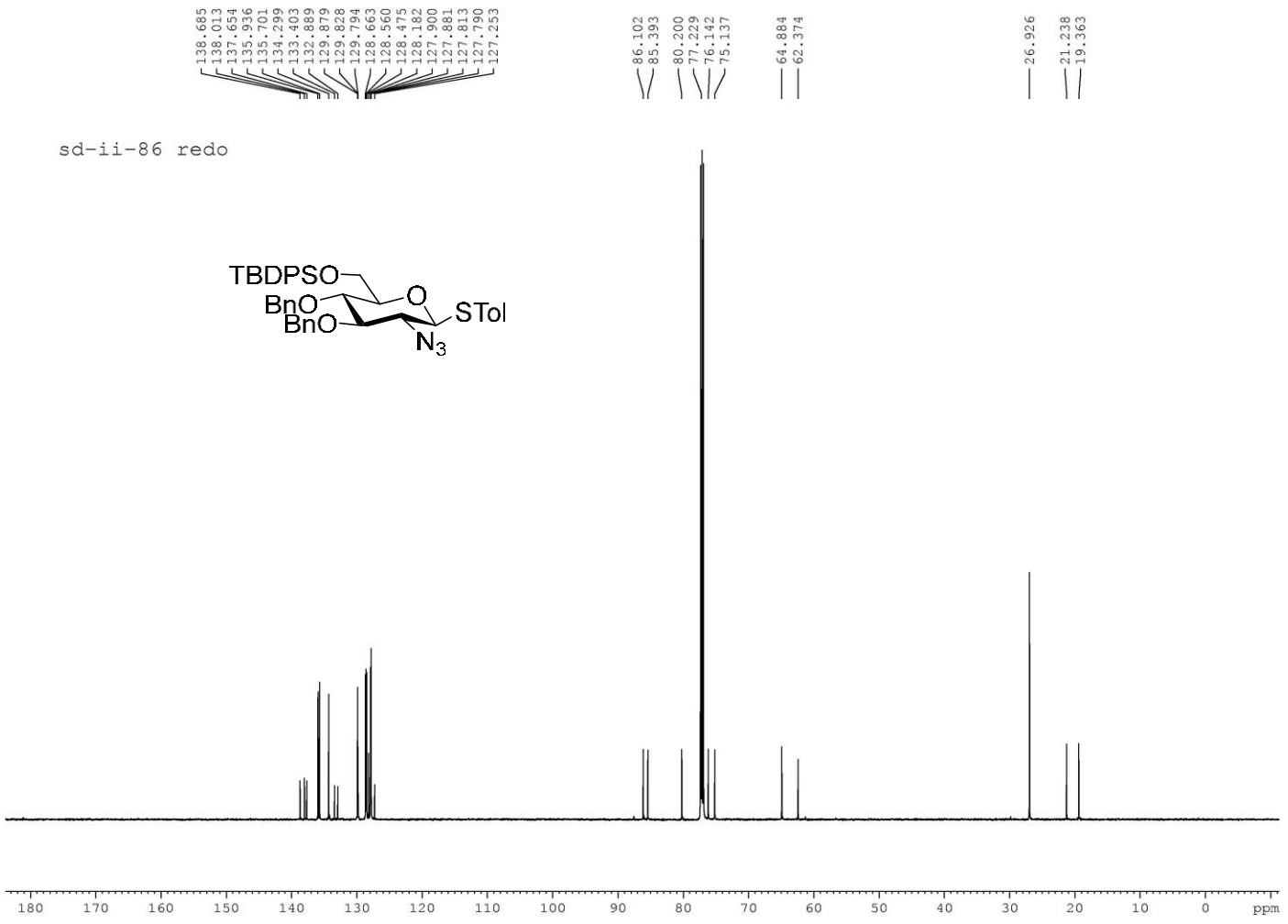


Figure 8.[13]C NMR spectrum of 4-Methylphenyl 2-azido-3,4-di-O-benzyl-2-deoxy-6-O-tert-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$). (150 MHz, $CDCl_3$).

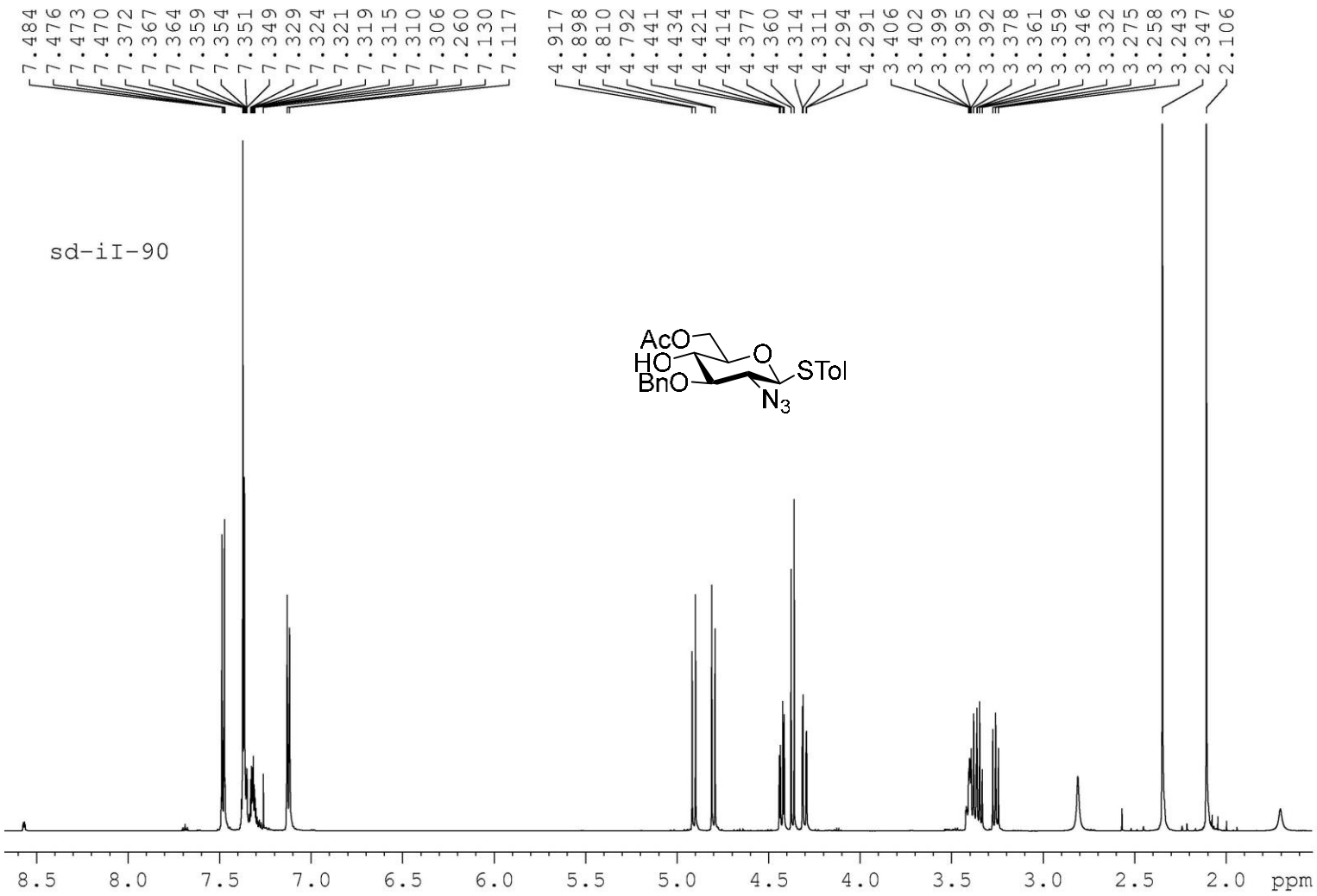


Figure 9. $^{1}$H NMR spectrum of 4-Methylphenyl-2-azido-6-O-acetyl-3-O-benzyl-2-deoxy-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

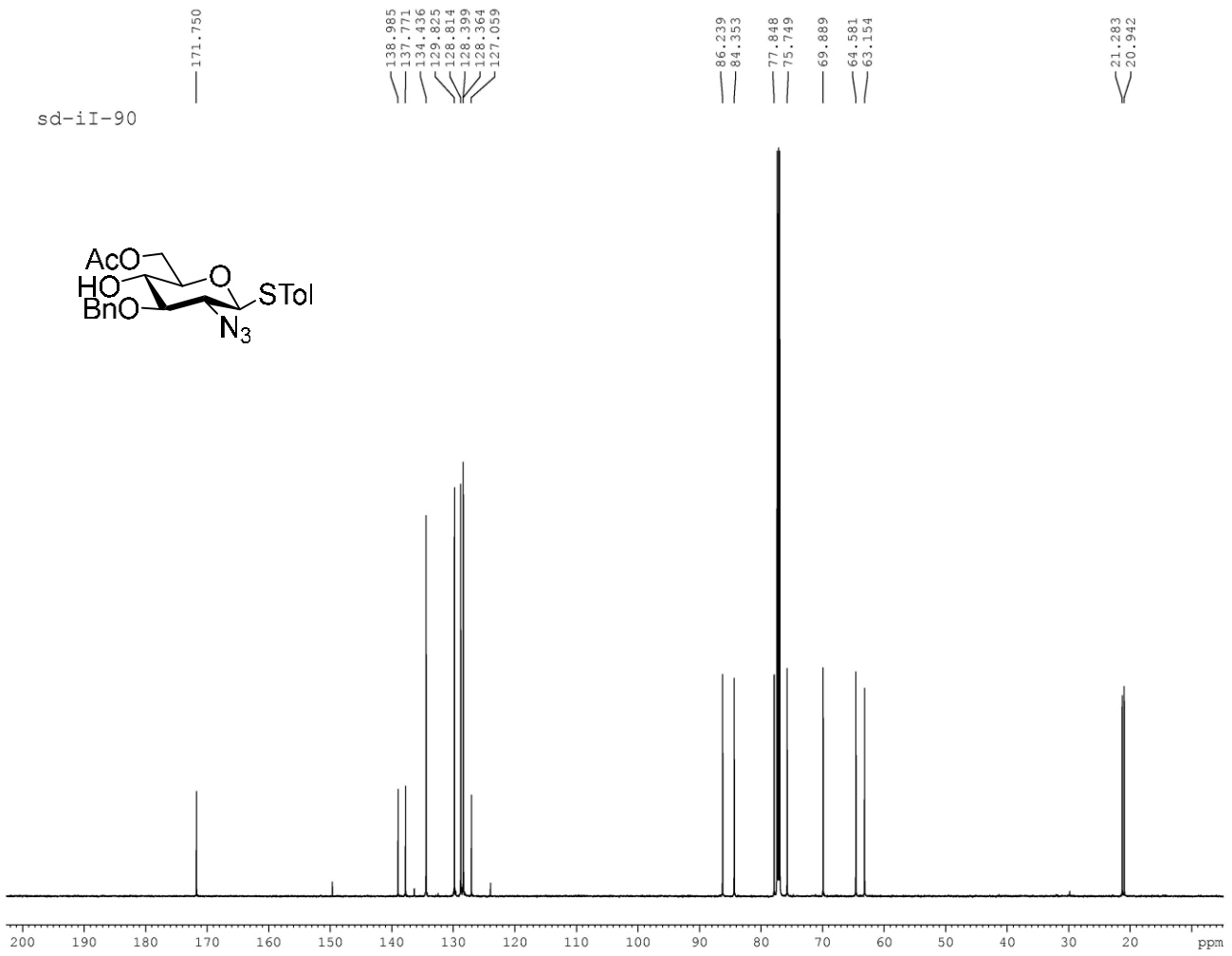


Figure 10. $^{13}C$ NMR spectrum of 4-Methylphenyl-2-azido-6-O-acetyl-3-O-benzyl-2-deoxy-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

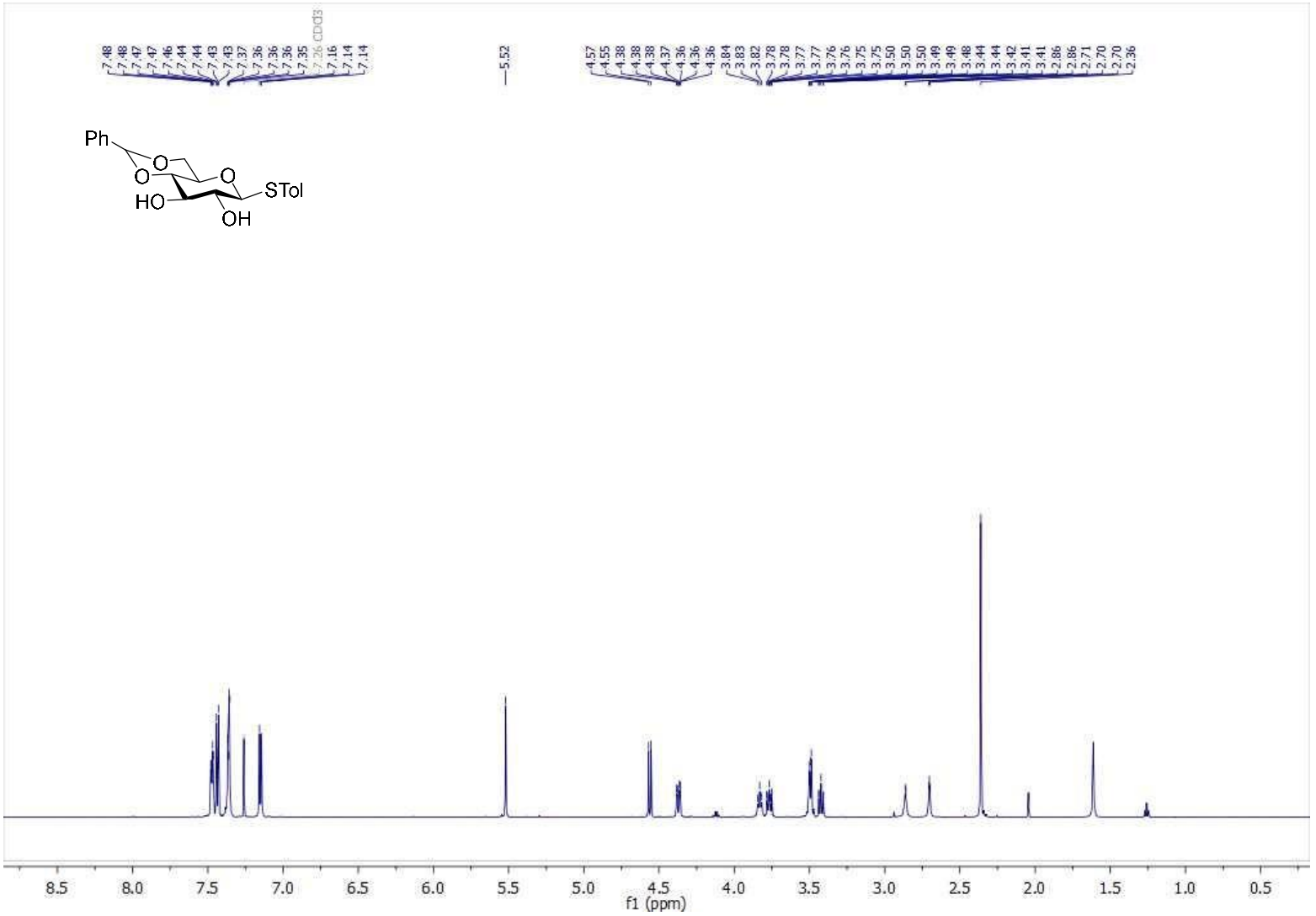


Figure 11. $^{1}$H NMR spectrum of 4-Methylphenyl-4,6-O-benzylidine-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

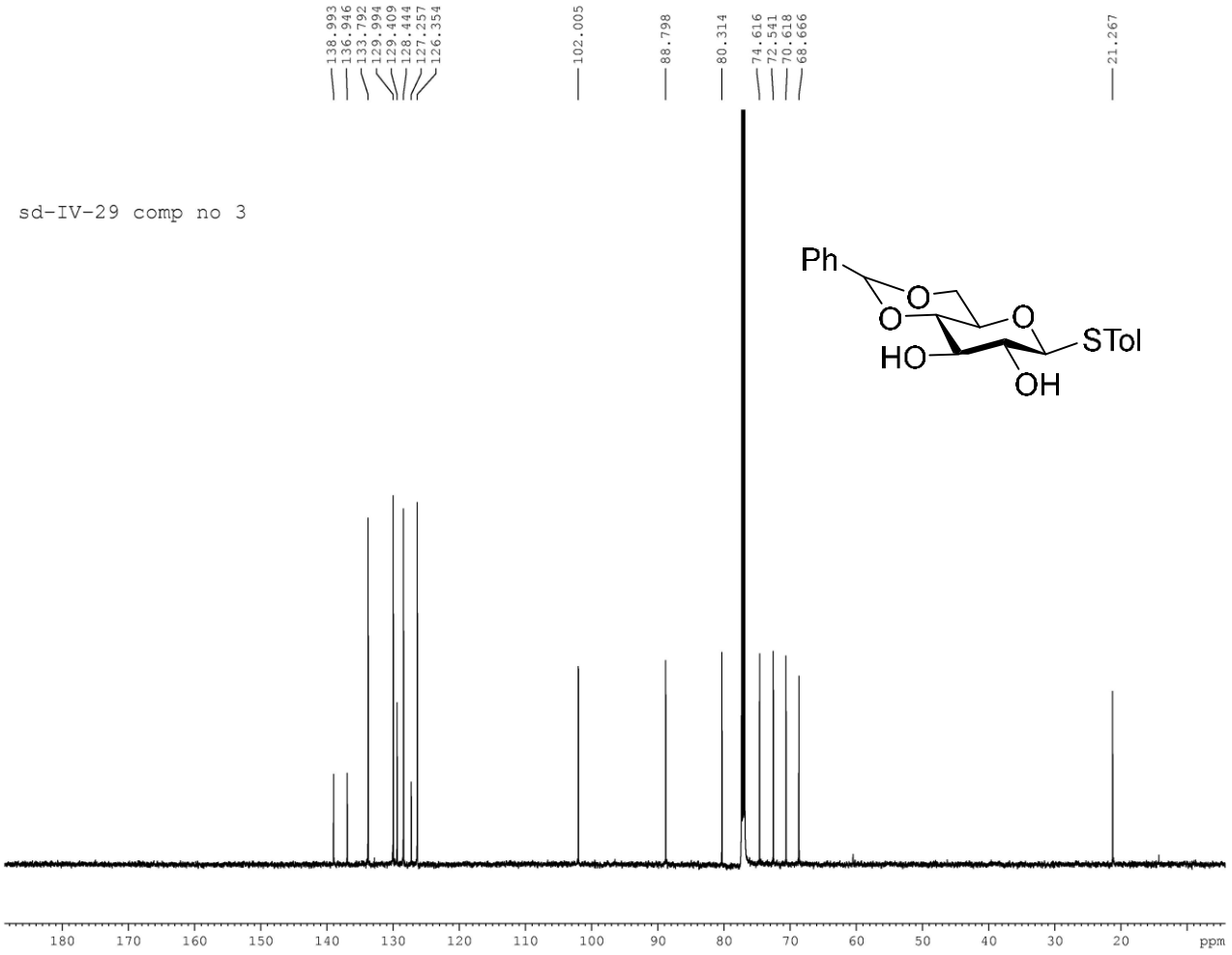


Figure 12.· $^{13}C$ NMR spectrum of 4-Methylphenyl-4,6-O-benzylidine-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

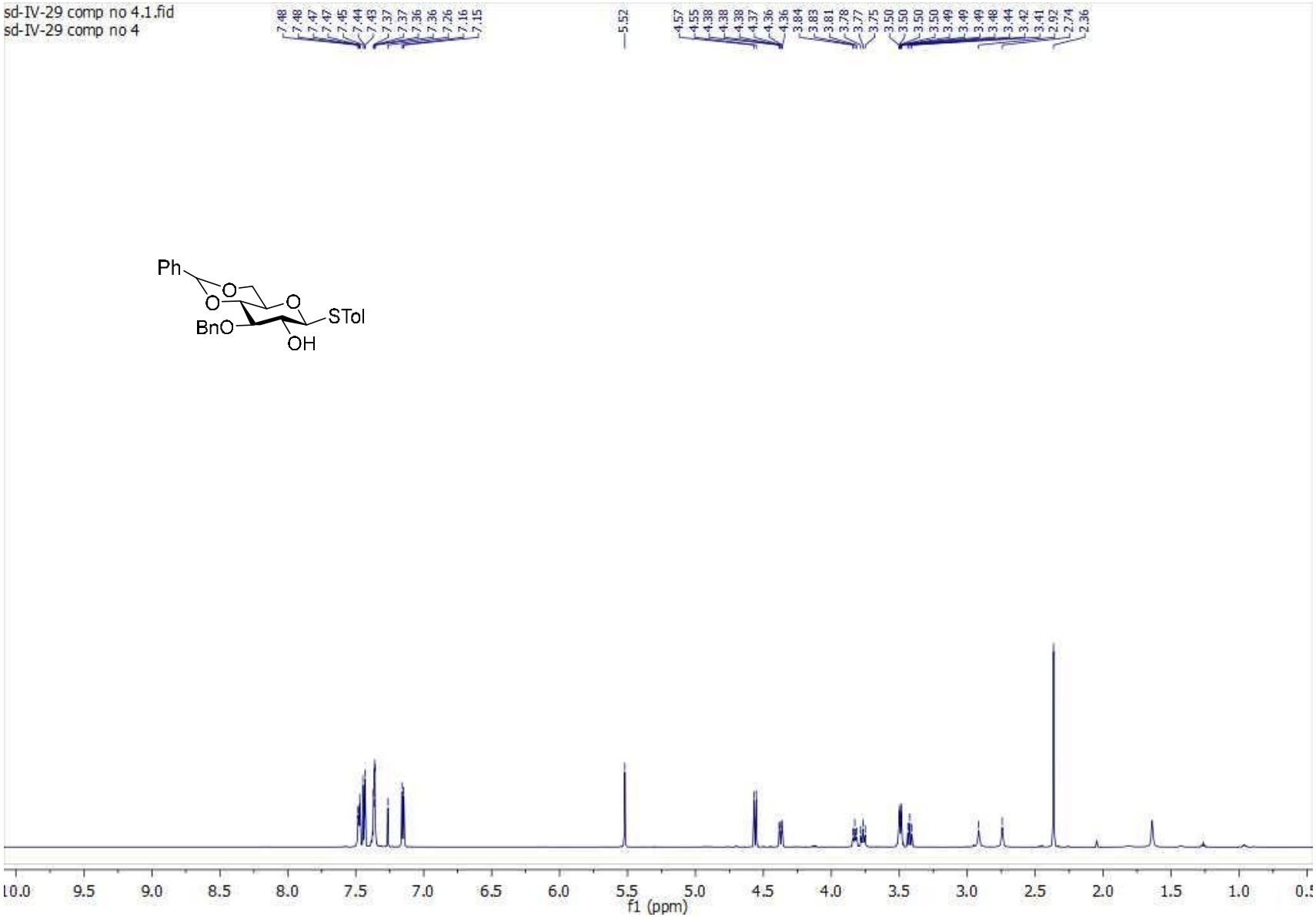


Figure 13. $^{1}$H NMR spectrum of 4-methylphenyl 3-O-benzyl-4,6-O-benzylidine-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

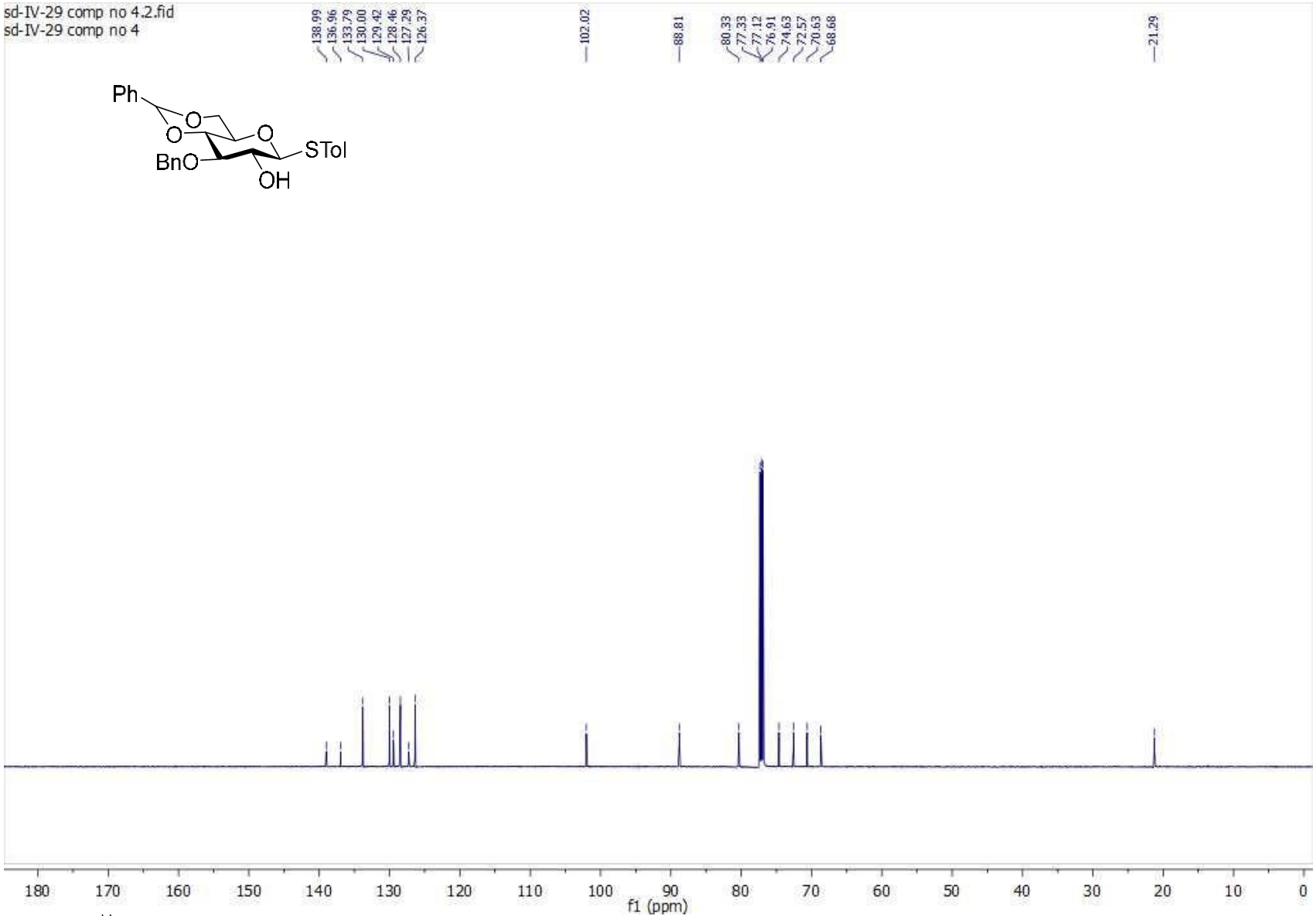


Figure 14. $^{13}$C NMR spectrum of 4-methylphenyl 3-O-benzyl-4,6-O-benzylidine-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

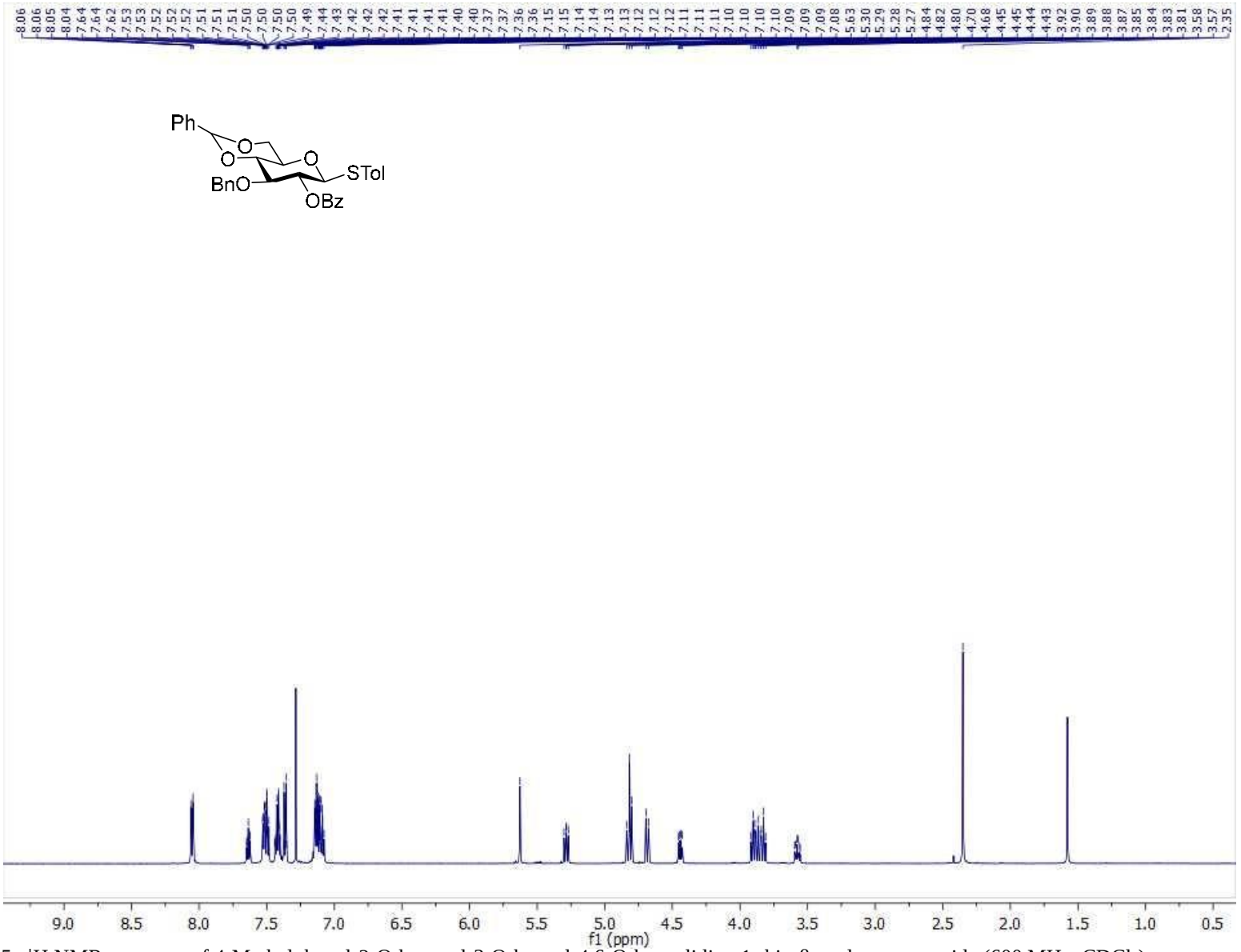


Figure 15. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4,6-O-benzylidine-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

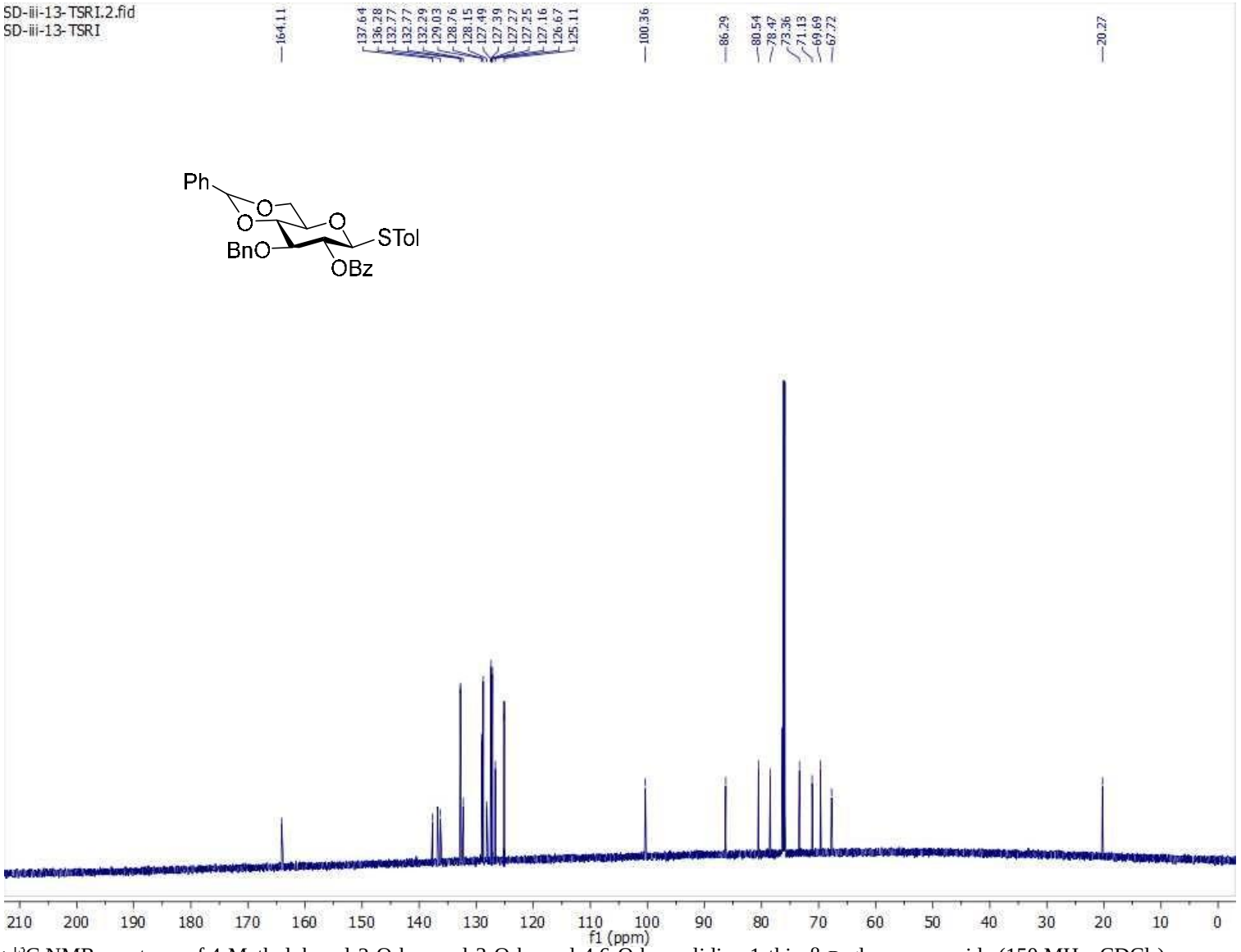


Figure 16. $^{13}$C NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4,6-O-benzylidine-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

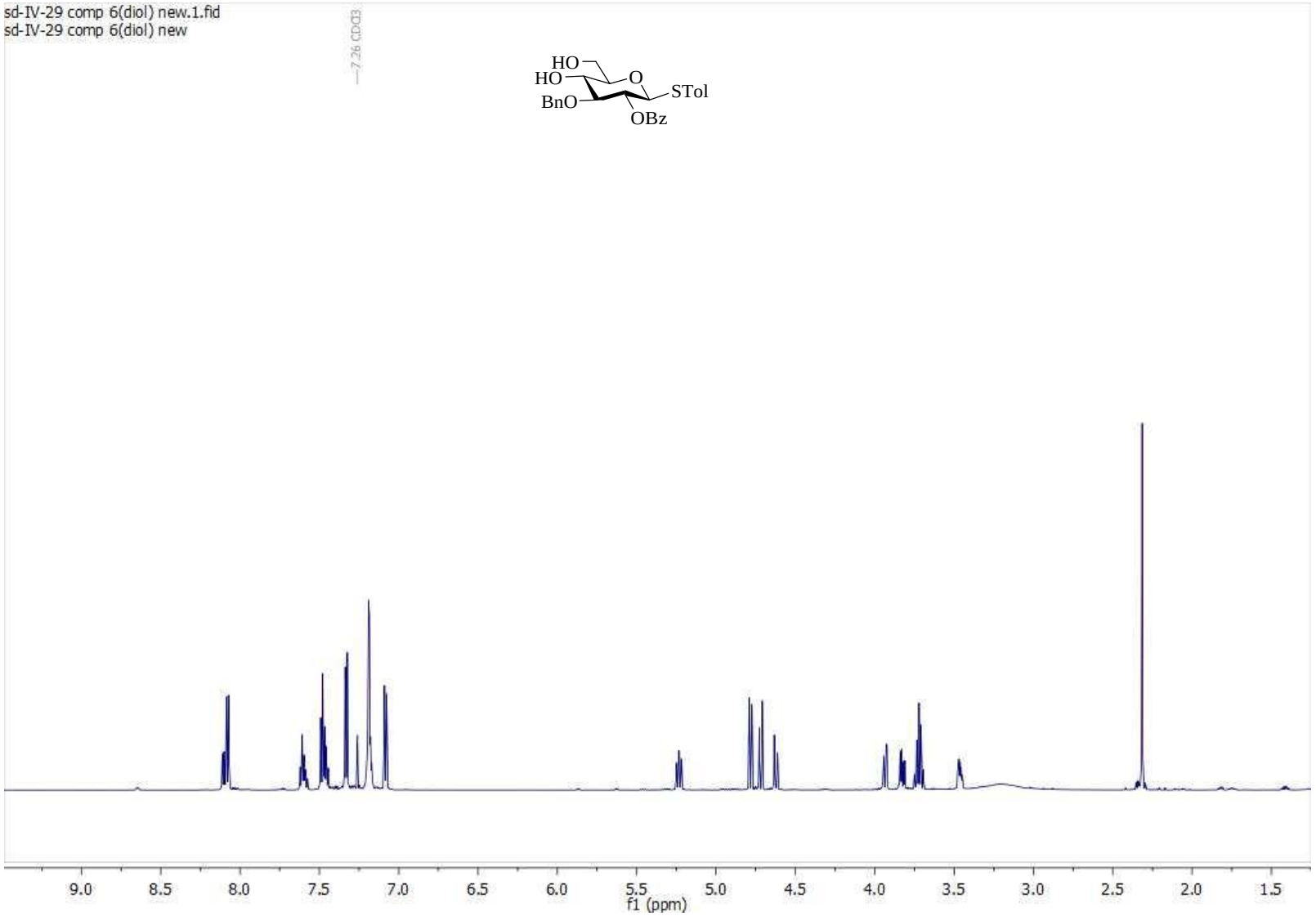


Figure 17. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

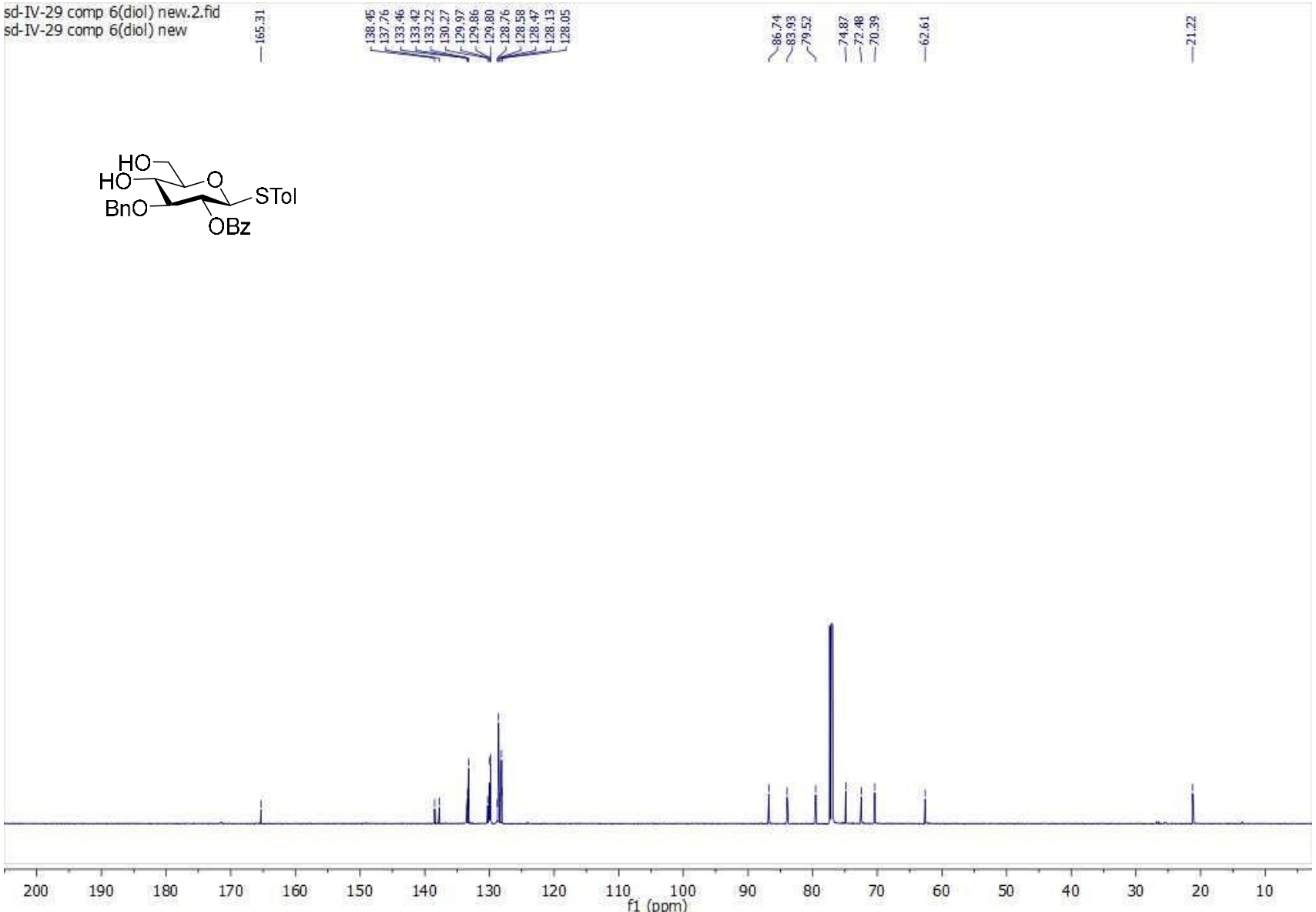


Figure 18. $^{13}$C NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

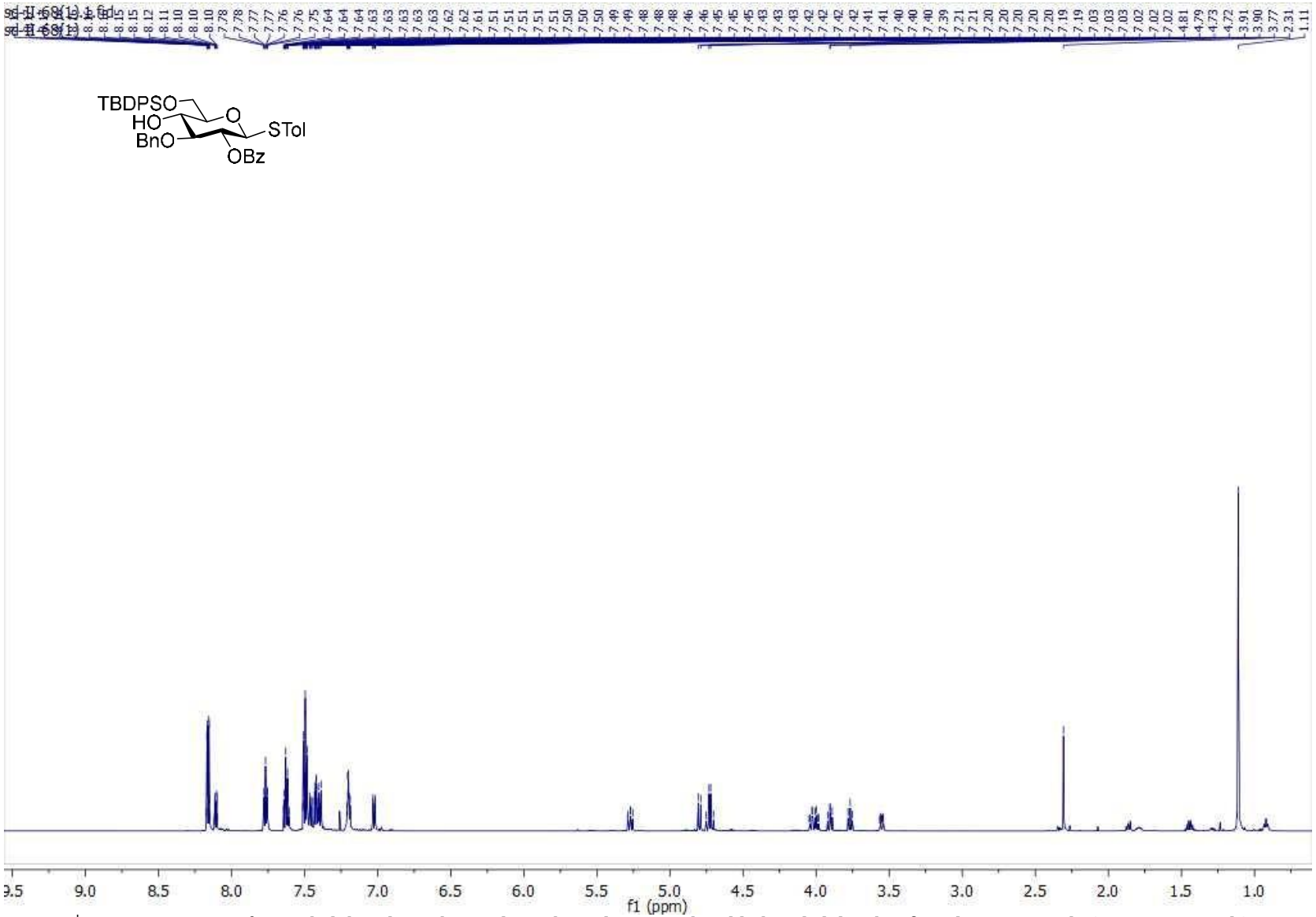


Figure 19. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-6-O-tert-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

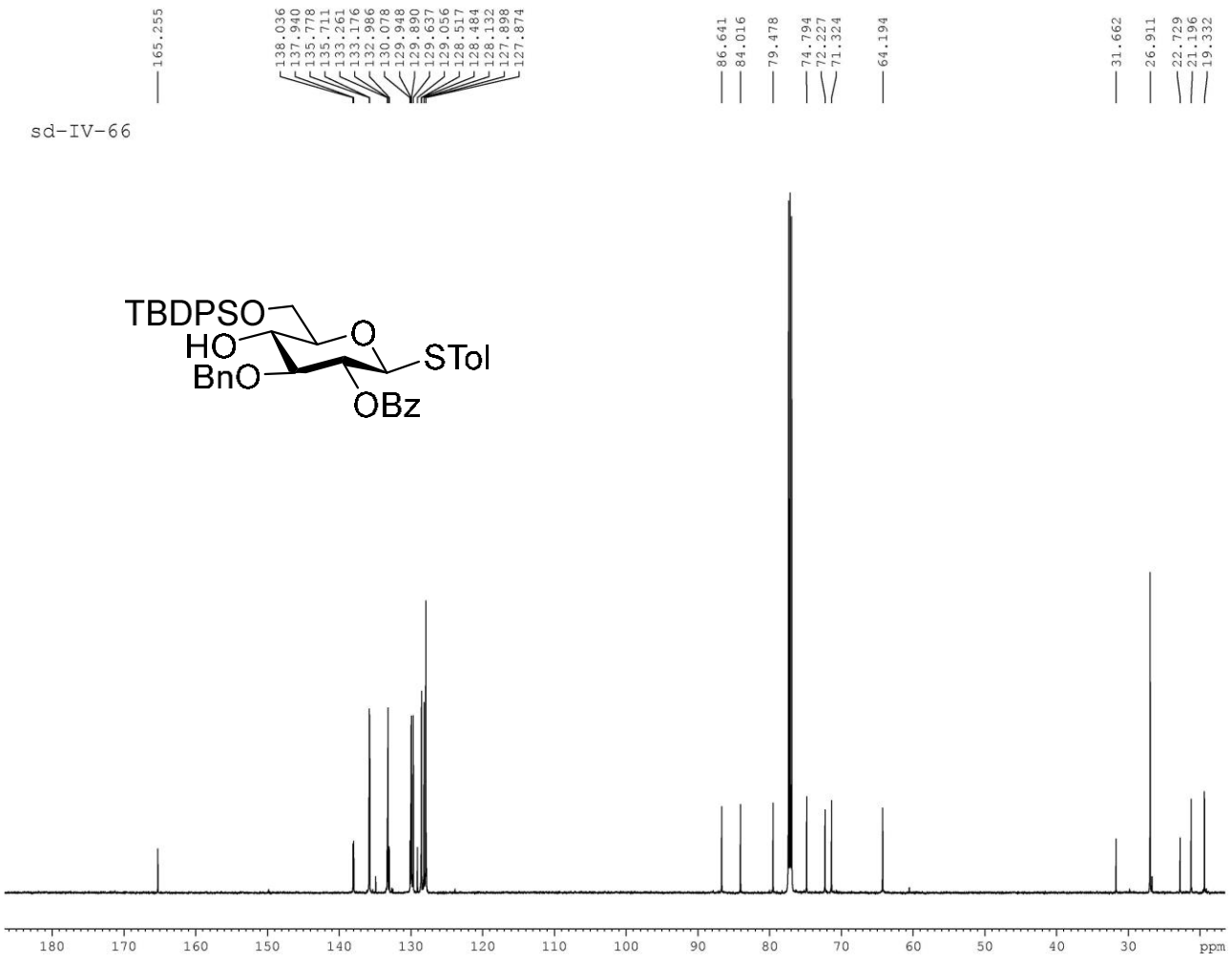


Figure 20. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-6-O-tert-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

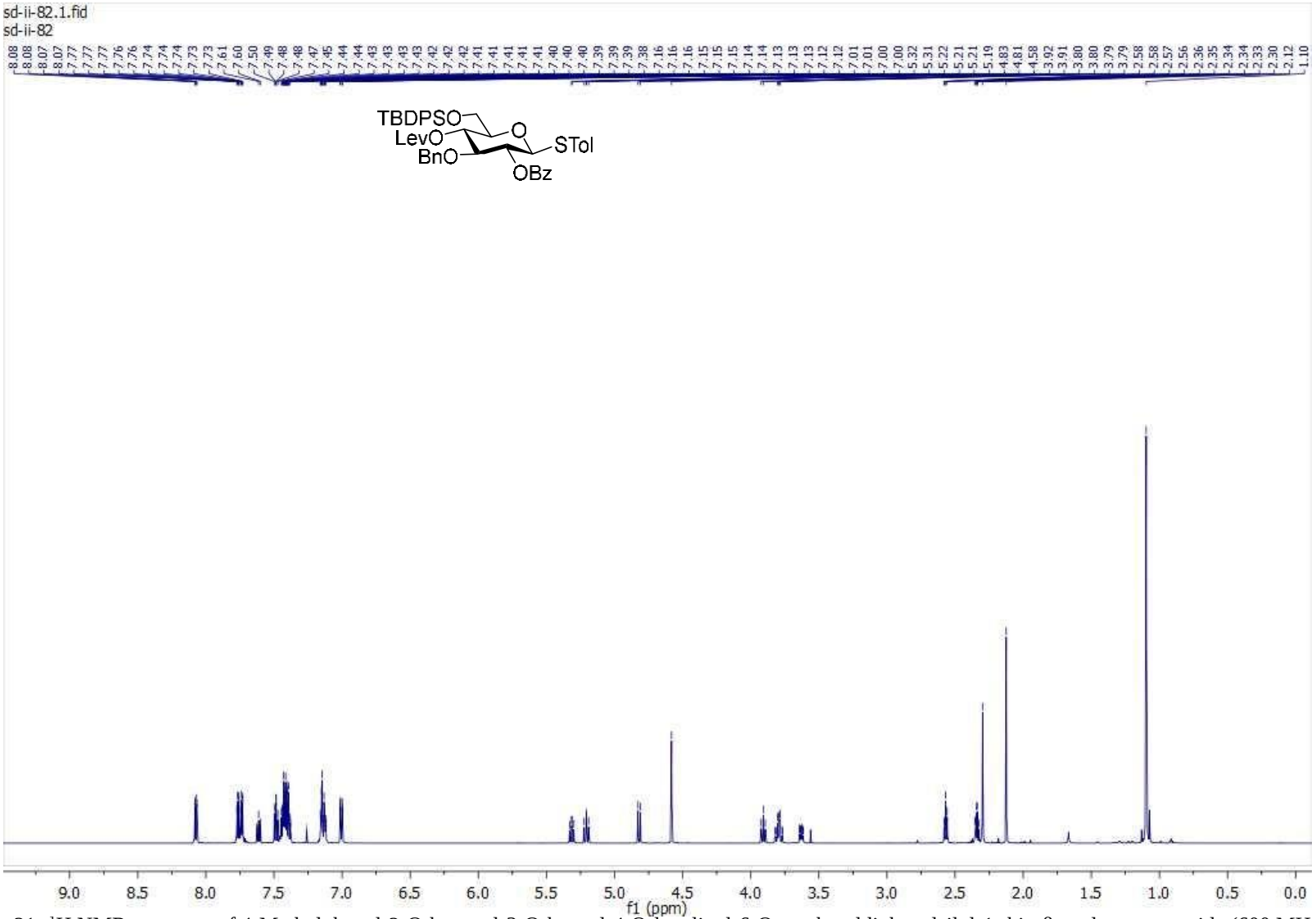


Figure 21. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4-O-levulinyl-6-O-tert-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

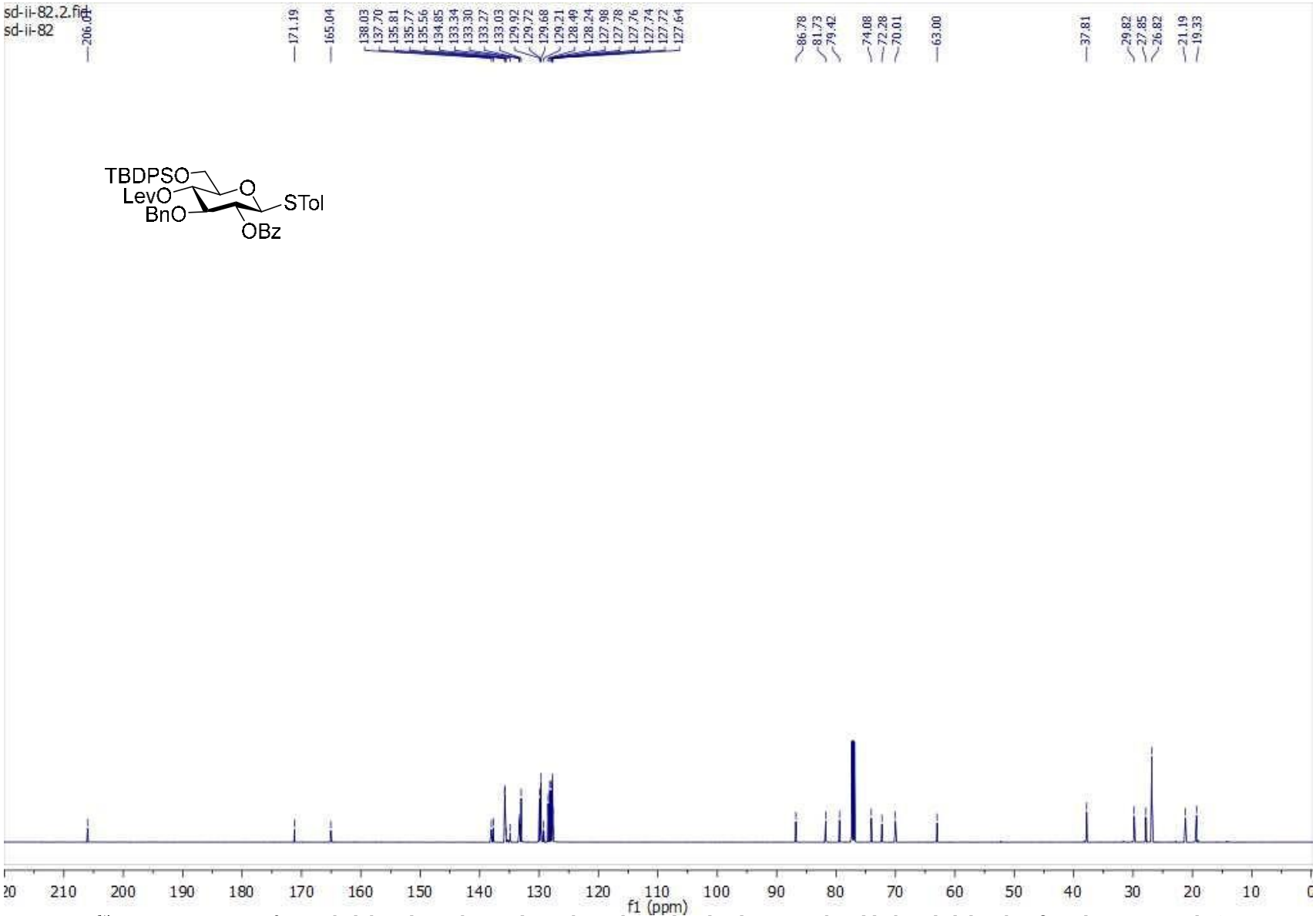


Figure 22. $^{13}$C NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4-O-levulinyl-6-O-tert-butyldiphenylsilyl-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

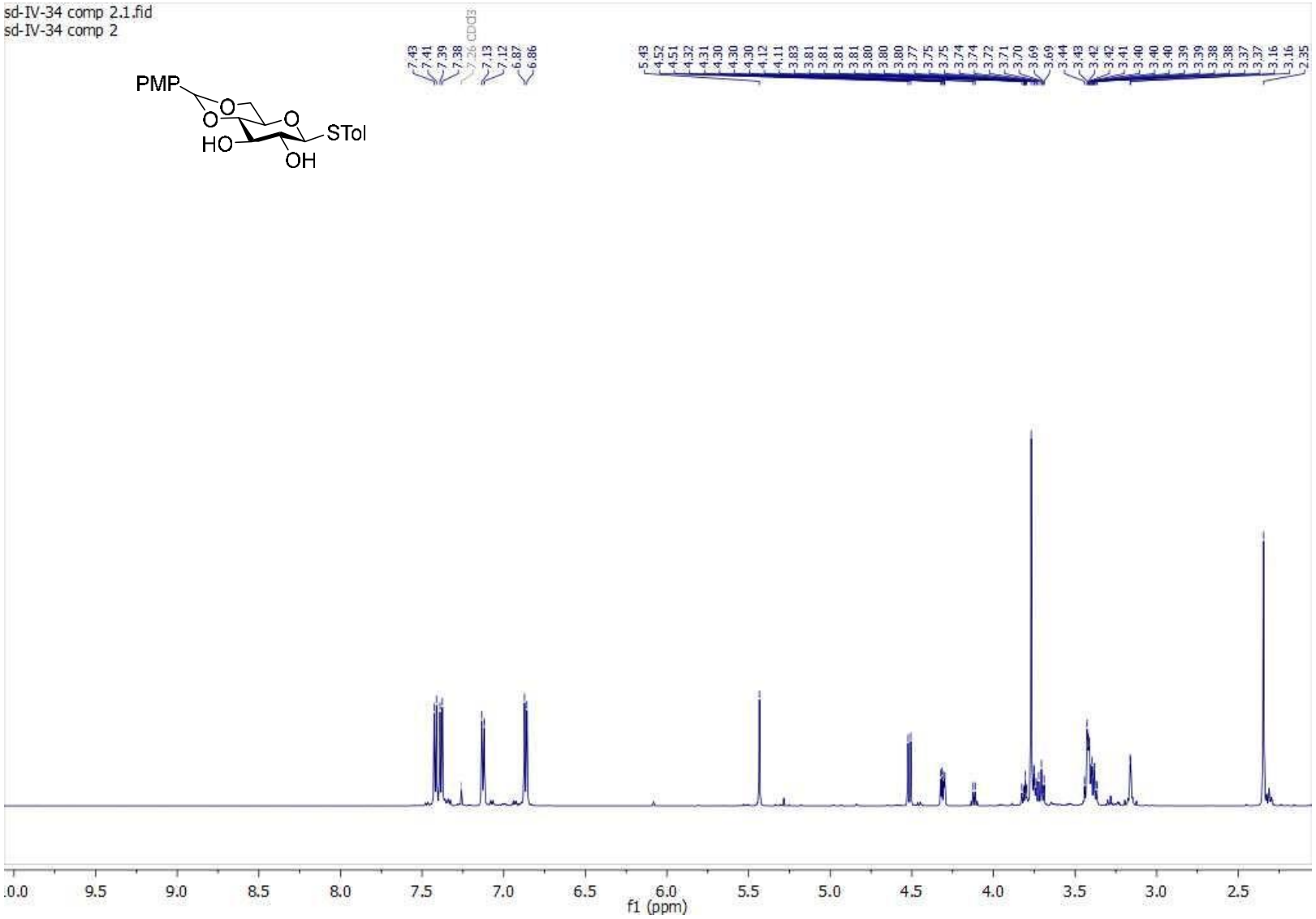


Figure 23. $^{1}$H NMR spectrum of 4-Methylphenyl-4,6-O-p-methoxybenzylidine-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

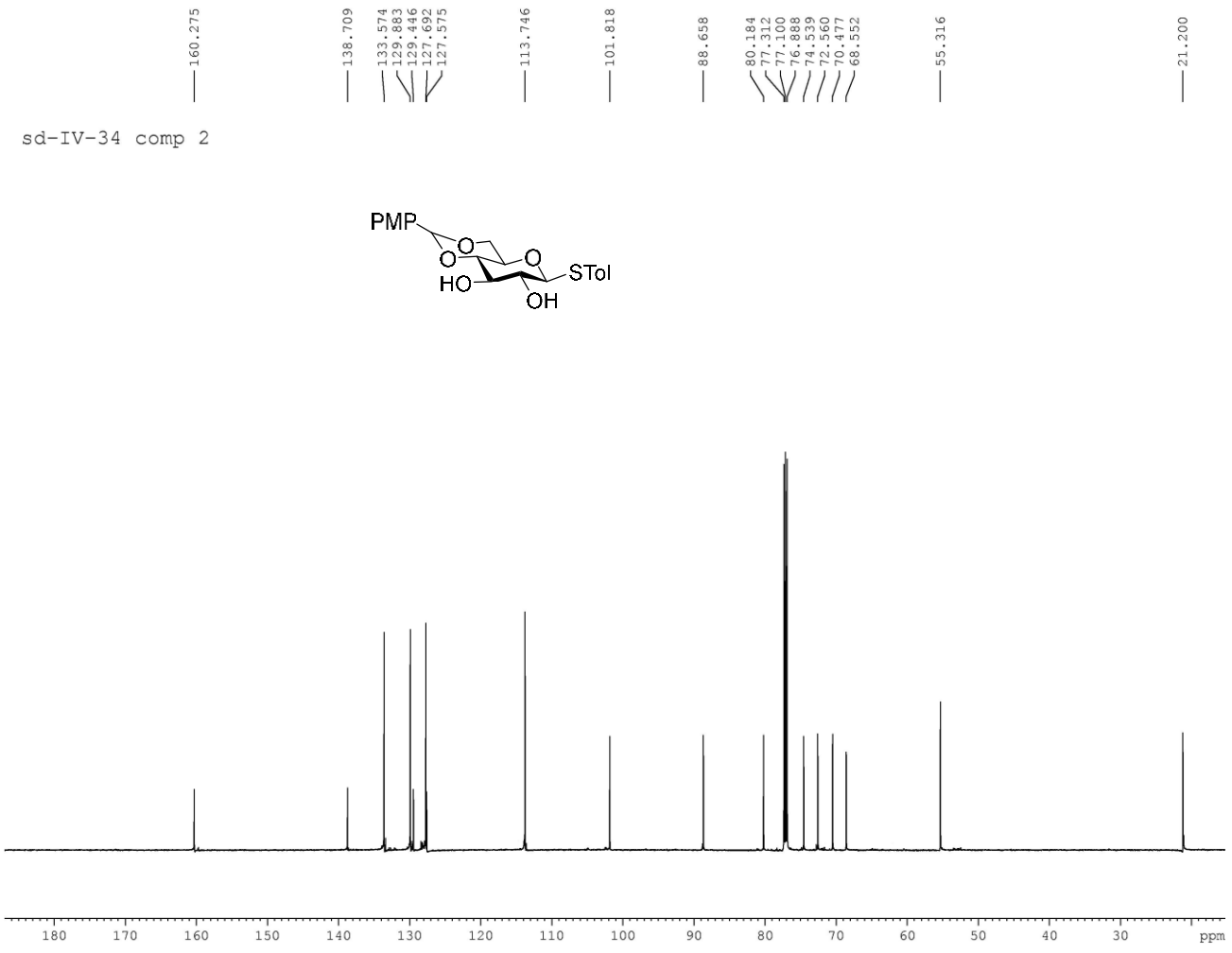


Figure 24. $^{13}C$ NMR spectrum of 4-Methylphenyl-4,6-O-p-methoxybenzylidine-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

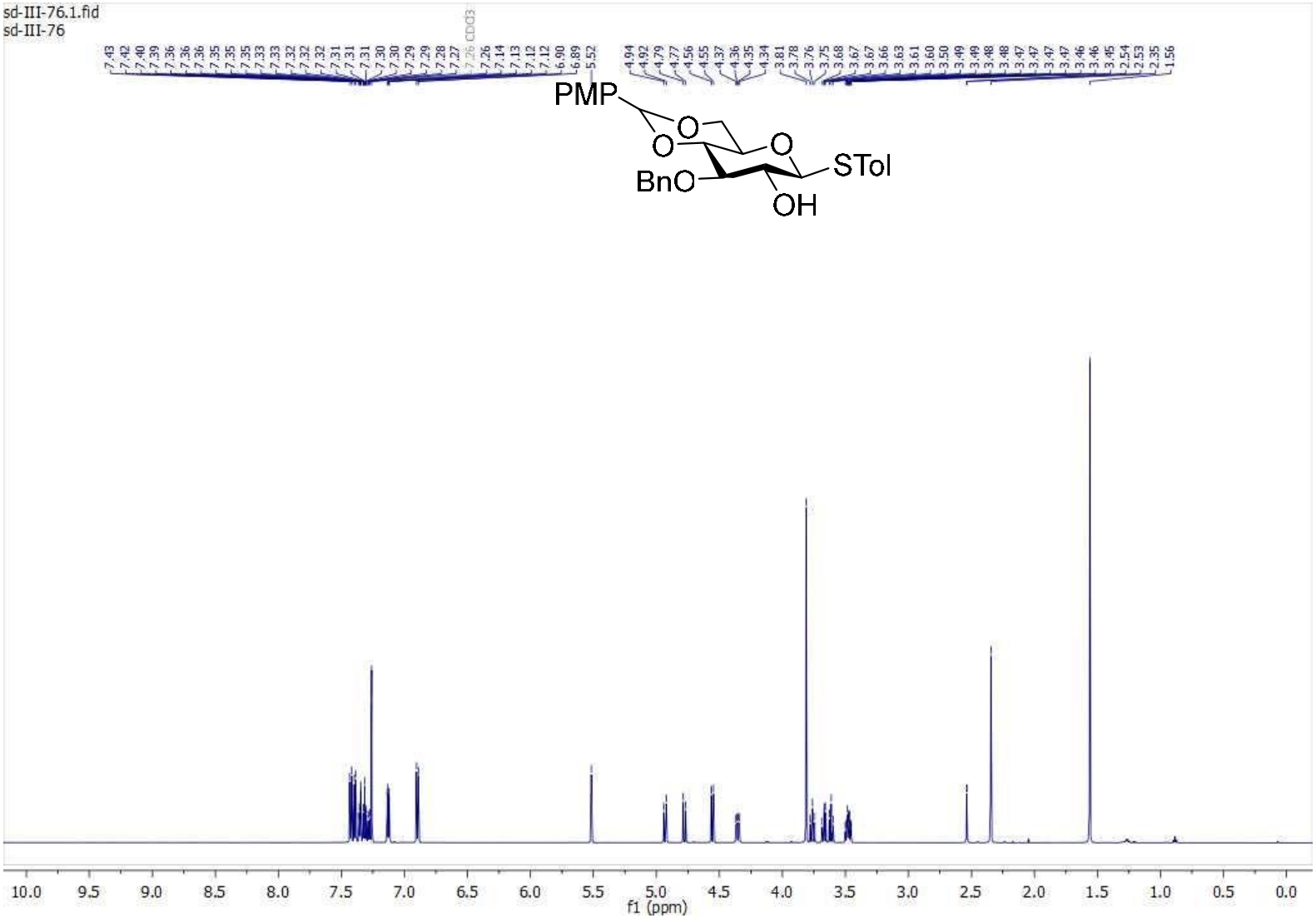


Figure 25. $^{1}$H NMR spectrum of 4-methylphenyl-3-O-benzyl-4,6-O-p-methoxybenzylidine-1-thio-β-D-gluco-pyranoside (600 MHz, $CDCl_3$).

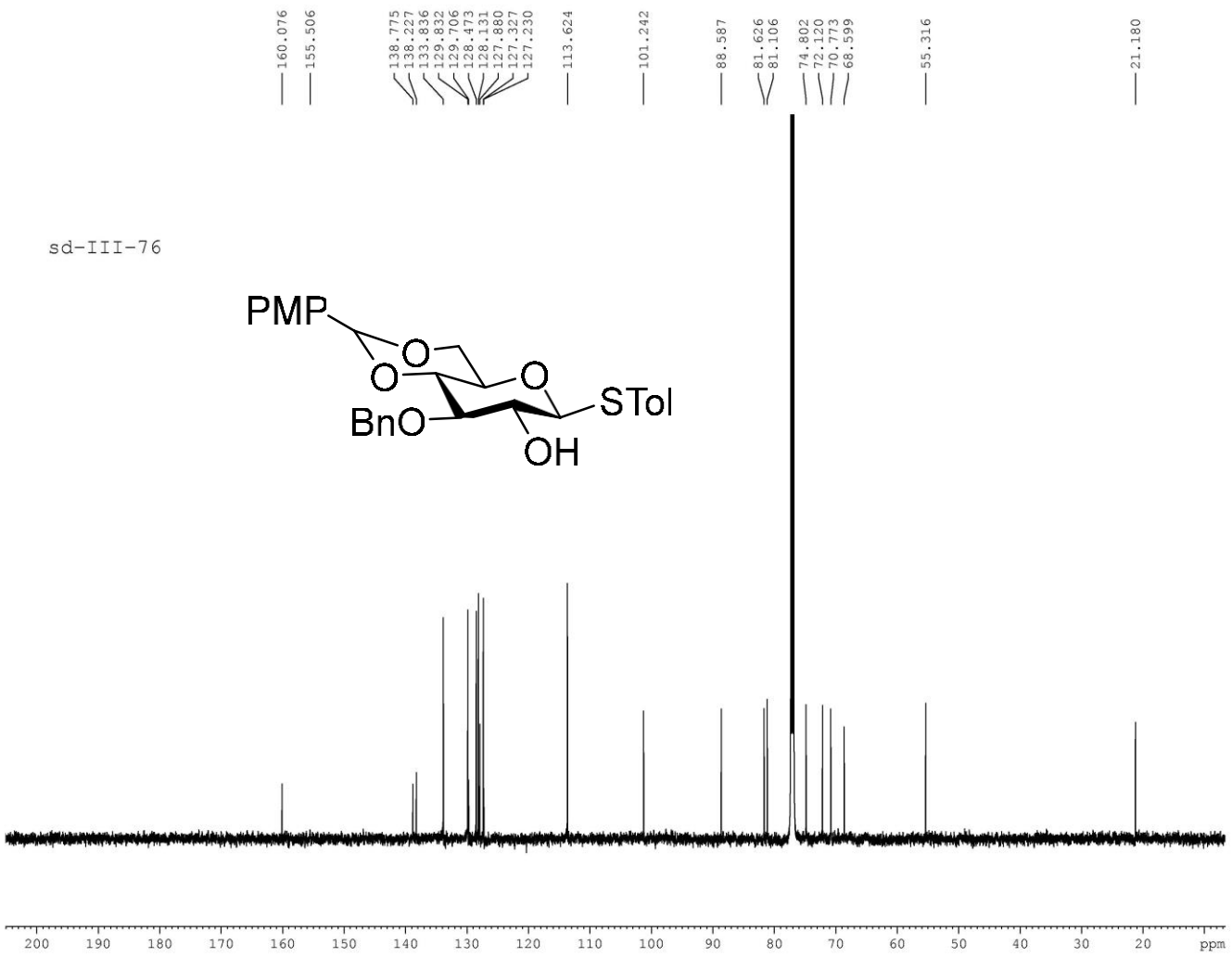


Figure 26. $^{13}$C NMR spectrum of 4-methylphenyl-3-O-benzyl-4,6-O-p-methoxybenzylidine-1-thio-β-D-gluco-pyranoside (150 MHz, $CDCl_3$).

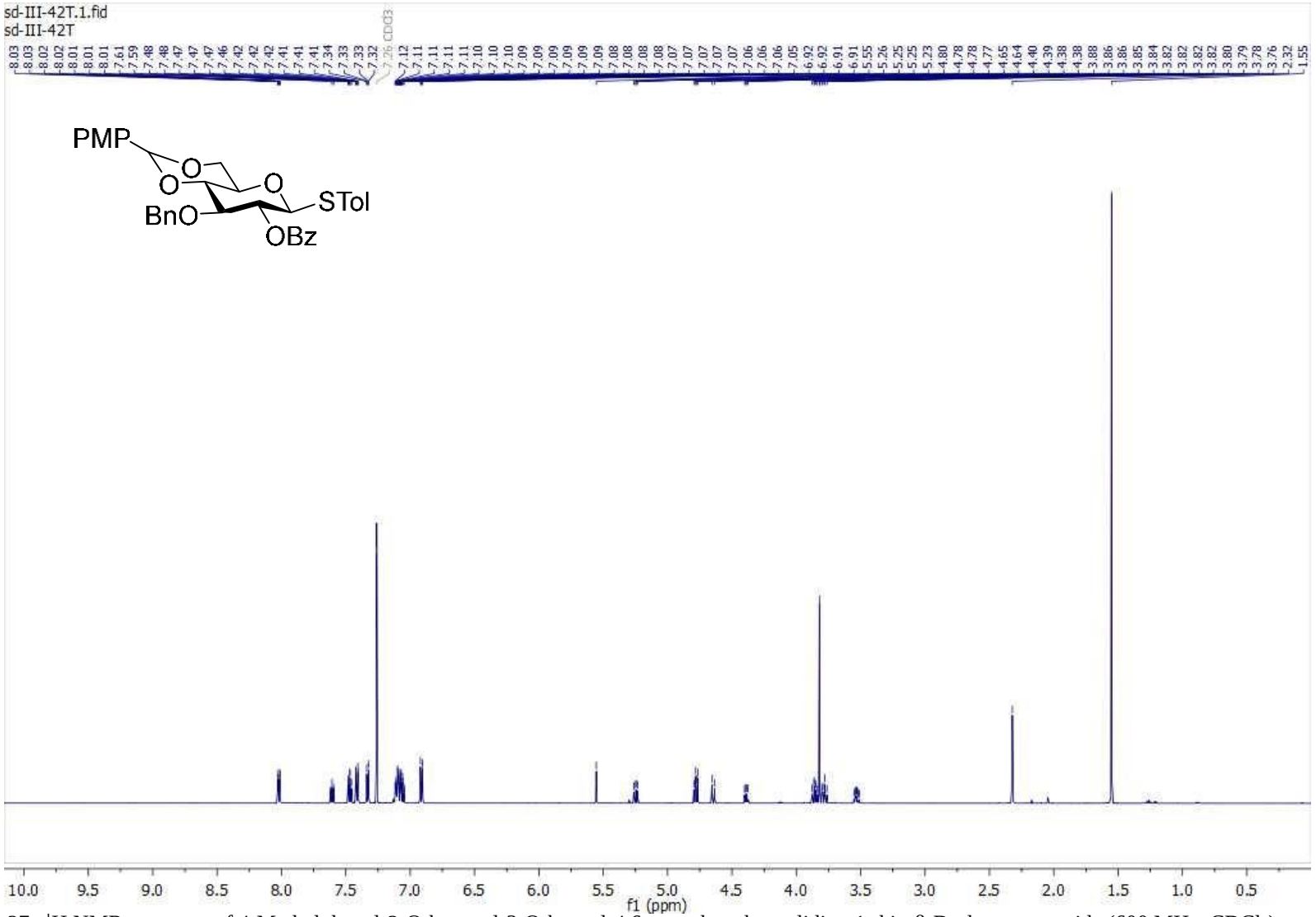


Figure 27. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4,6-p-methoxybenzylidine-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

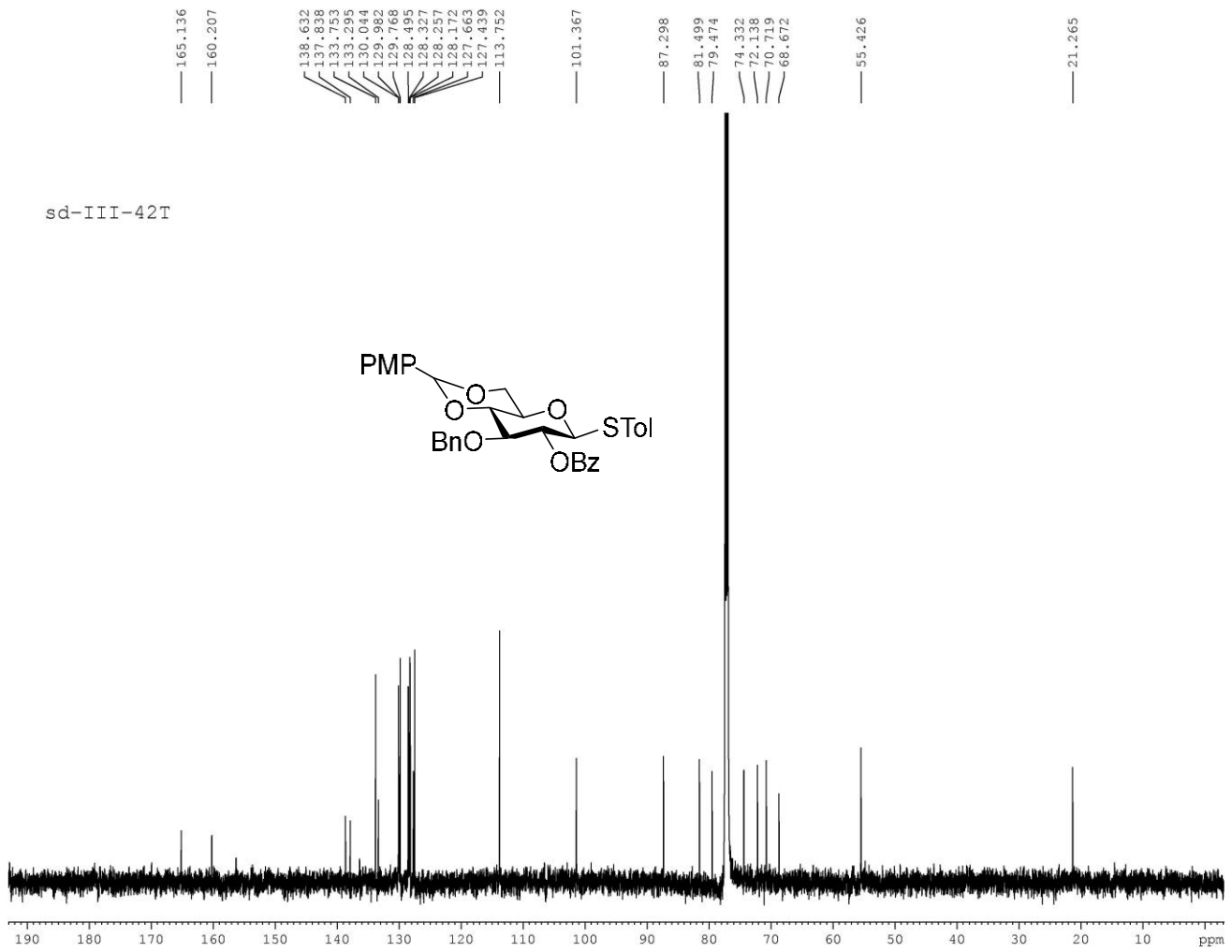


Figure 28. $^{13}C$ NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4,6-p-methoxybenzylidine-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

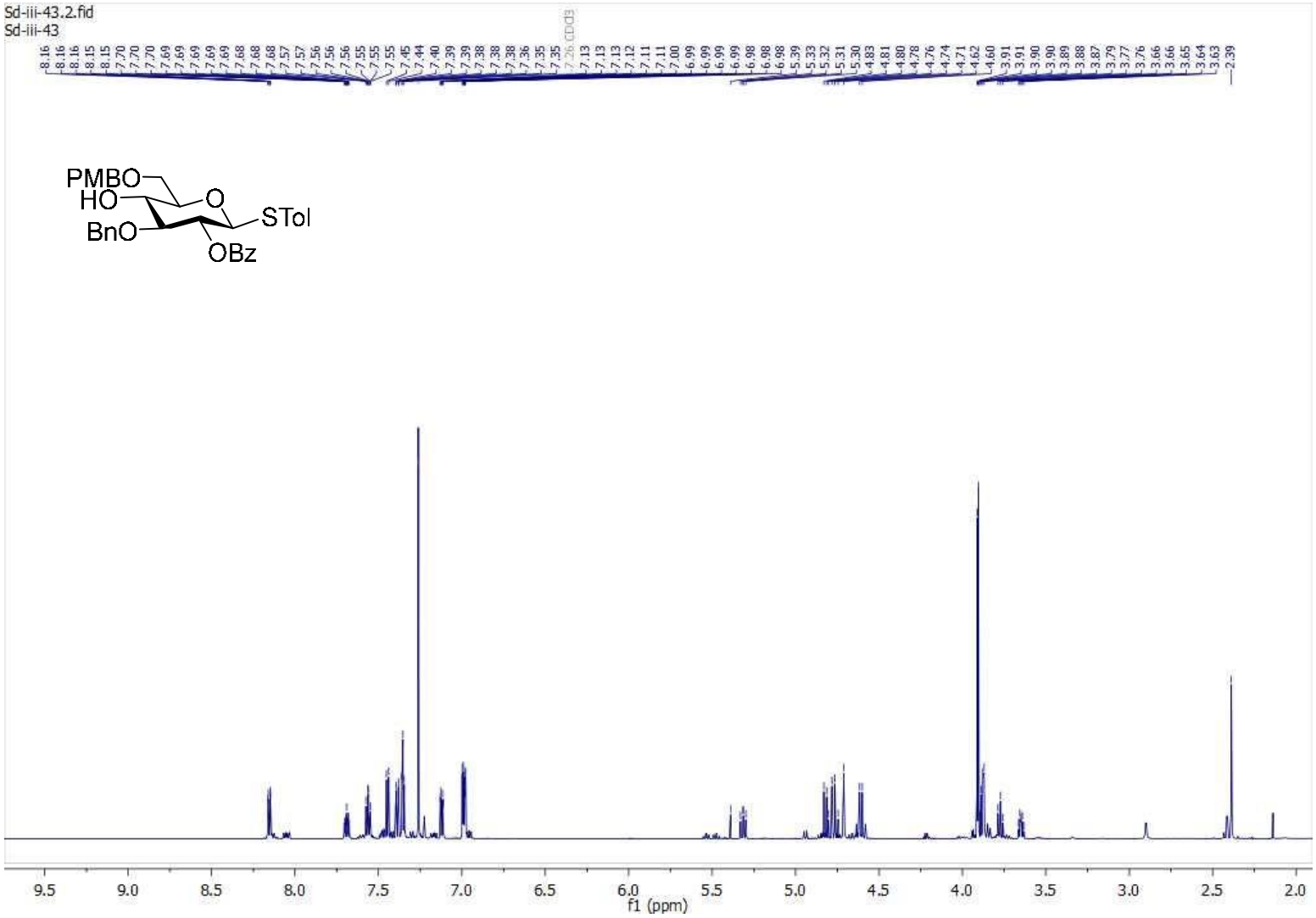


Figure 29. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-6-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

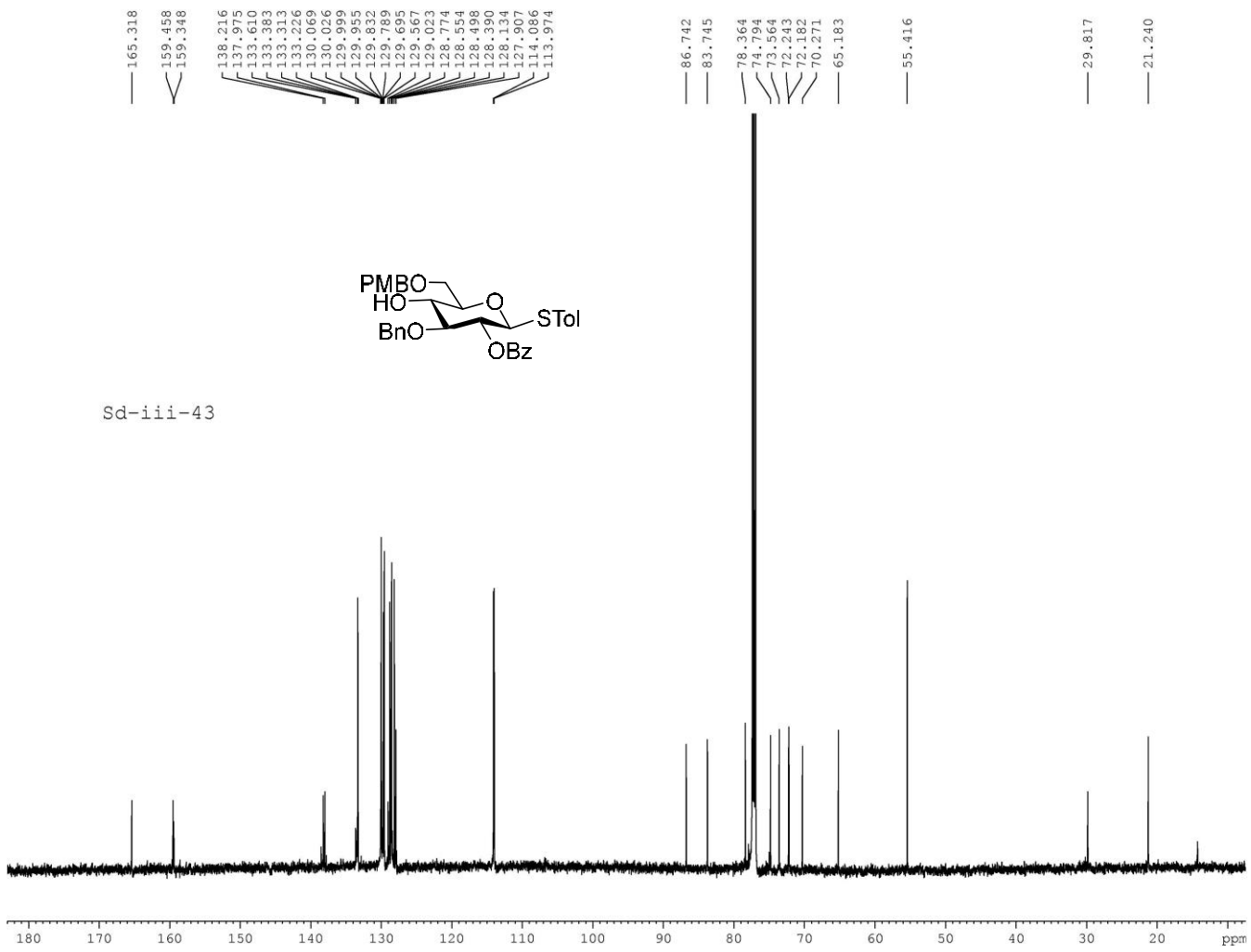


Figure 30. $^{13}C$ NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-6-O-p-methoxybenzyl1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

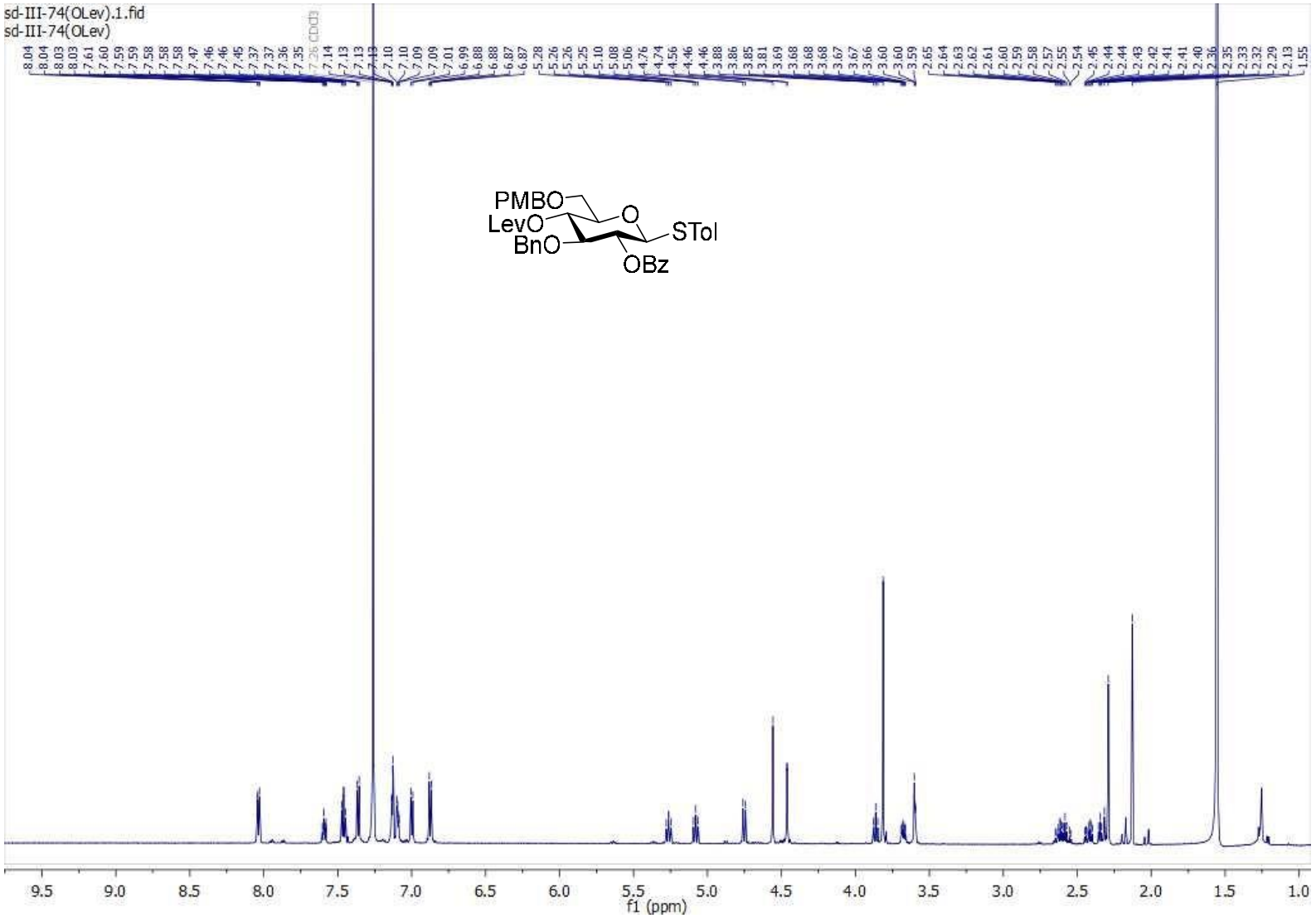


Figure 31. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4-O-levulinyl-6-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

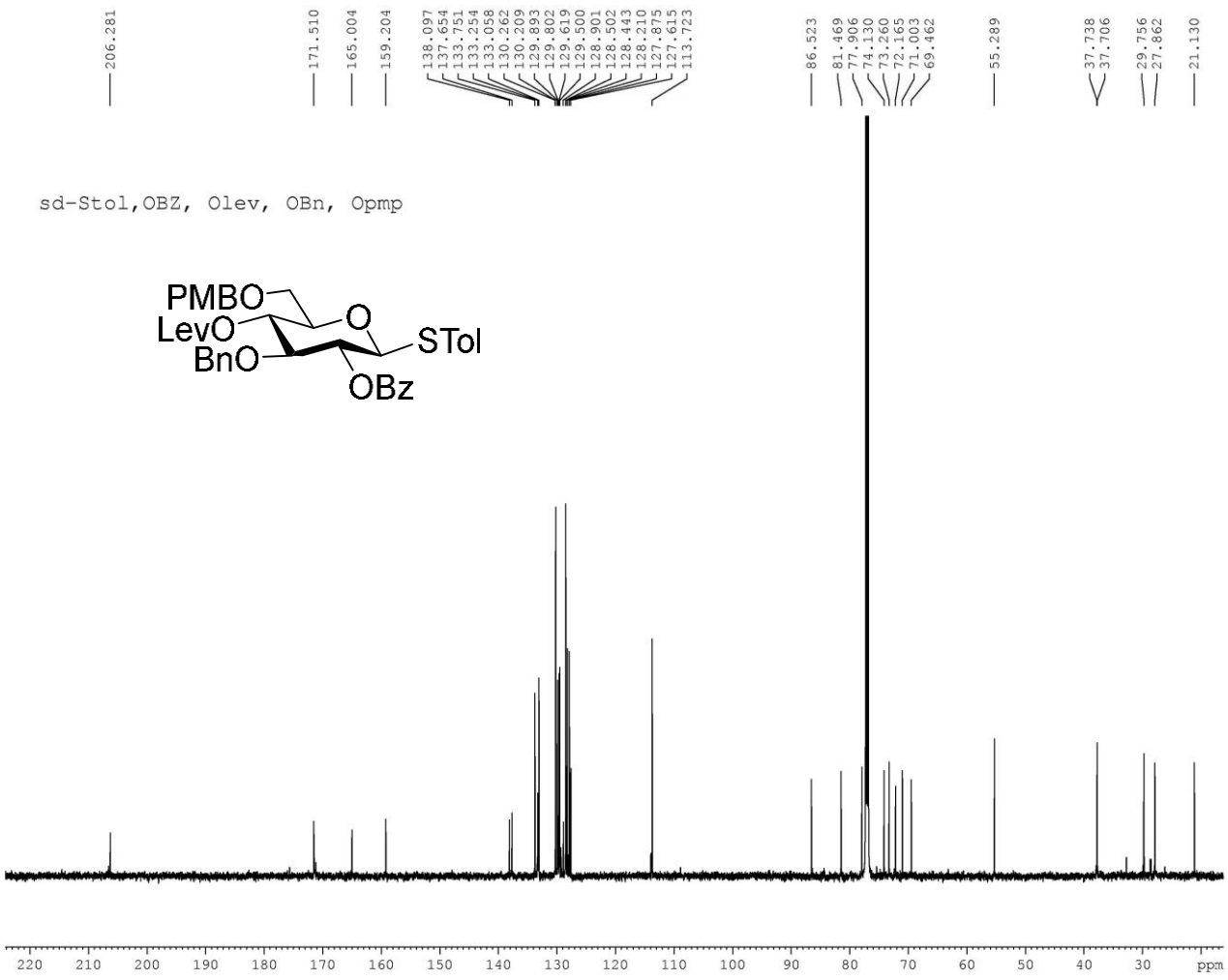


Figure 32. $^{13}$C NMR spectrum of 4-Methylphenyl-2-O-benzoyl-3-O-benzyl-4-O-levulinyl-6-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

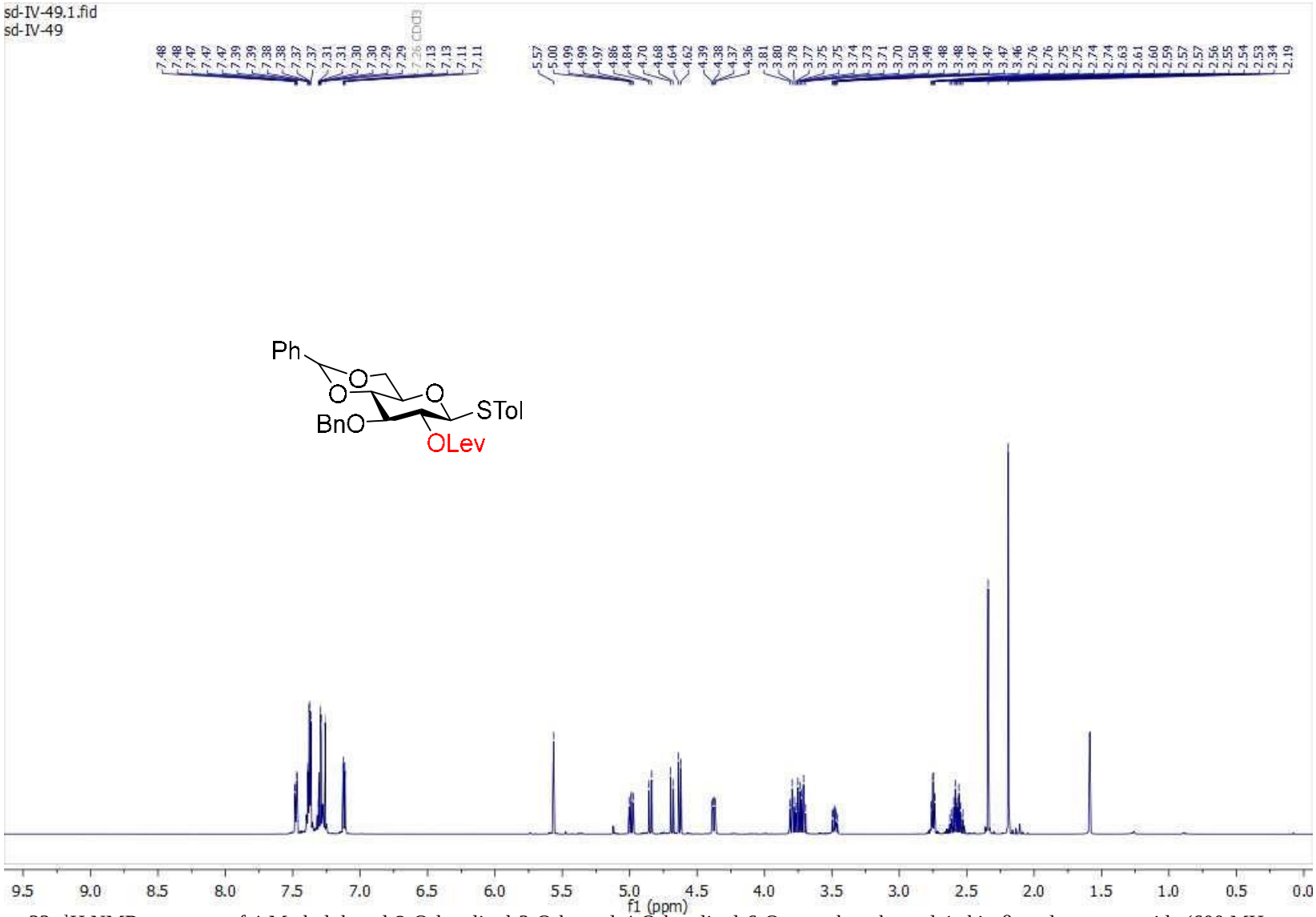


Figure 33. $^{1}$H NMR spectrum of 4-Methylphenyl-2-O-levulinyl-3-O-benzyl-4-O-levulinyl-6-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (600 MHz, $CDCl_3$).

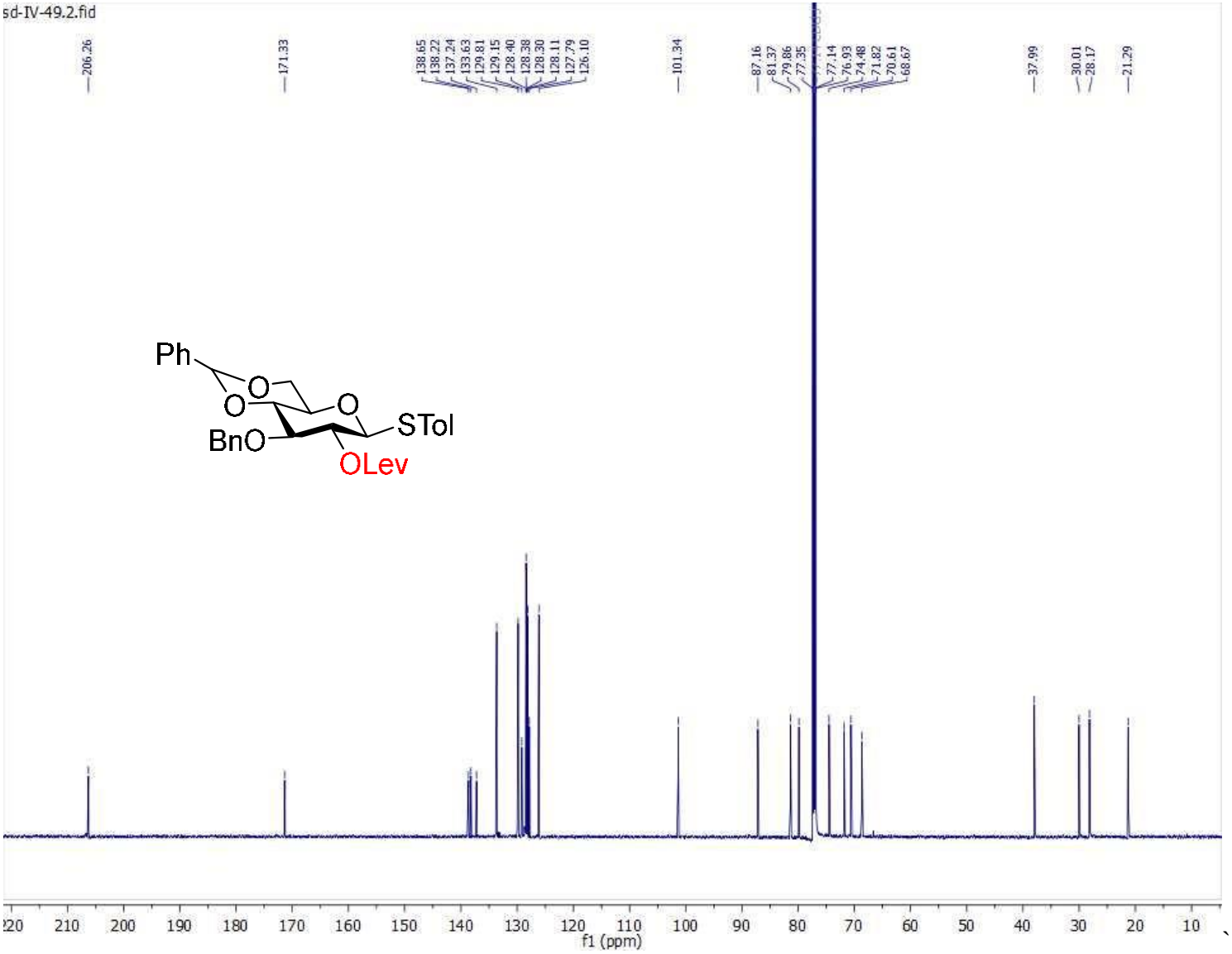


Figure 34. $^{13}C$ NMR spectrum of 4-Methylphenyl-2-O-levulinyl-3-O-benzyl-4-O-levulinyl-6-O-p-methoxybenzyl-1-thio-β-D-glucopyranoside (150 MHz, $CDCl_3$).

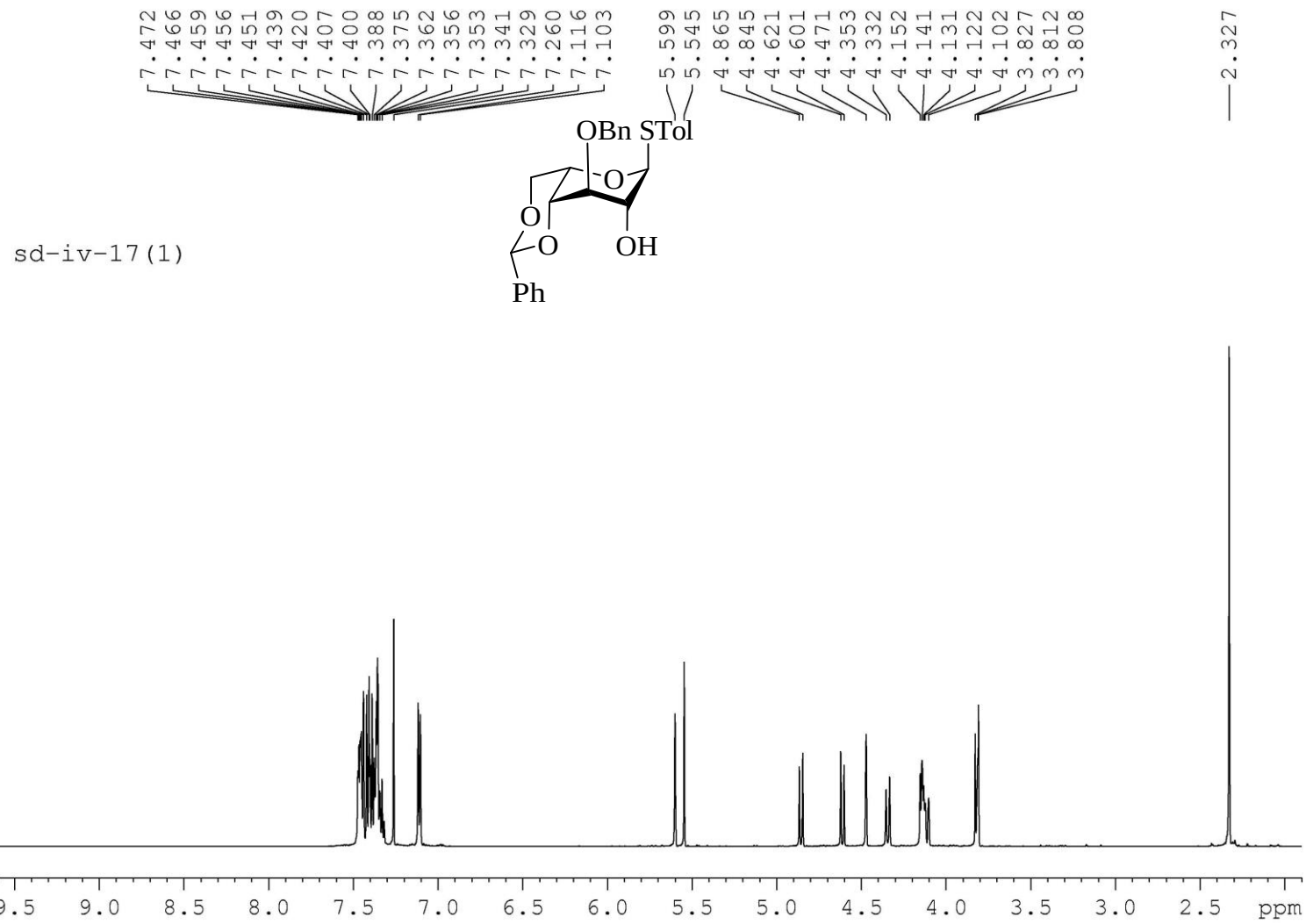


Figure 35. $^{1}$H NMR spectrum of 4-Methylphenyl 3-O-benzyl-4,6-O-benzylidine-1-thio-α-L-idopyranoside (600 MHz, $CDCl_3$).

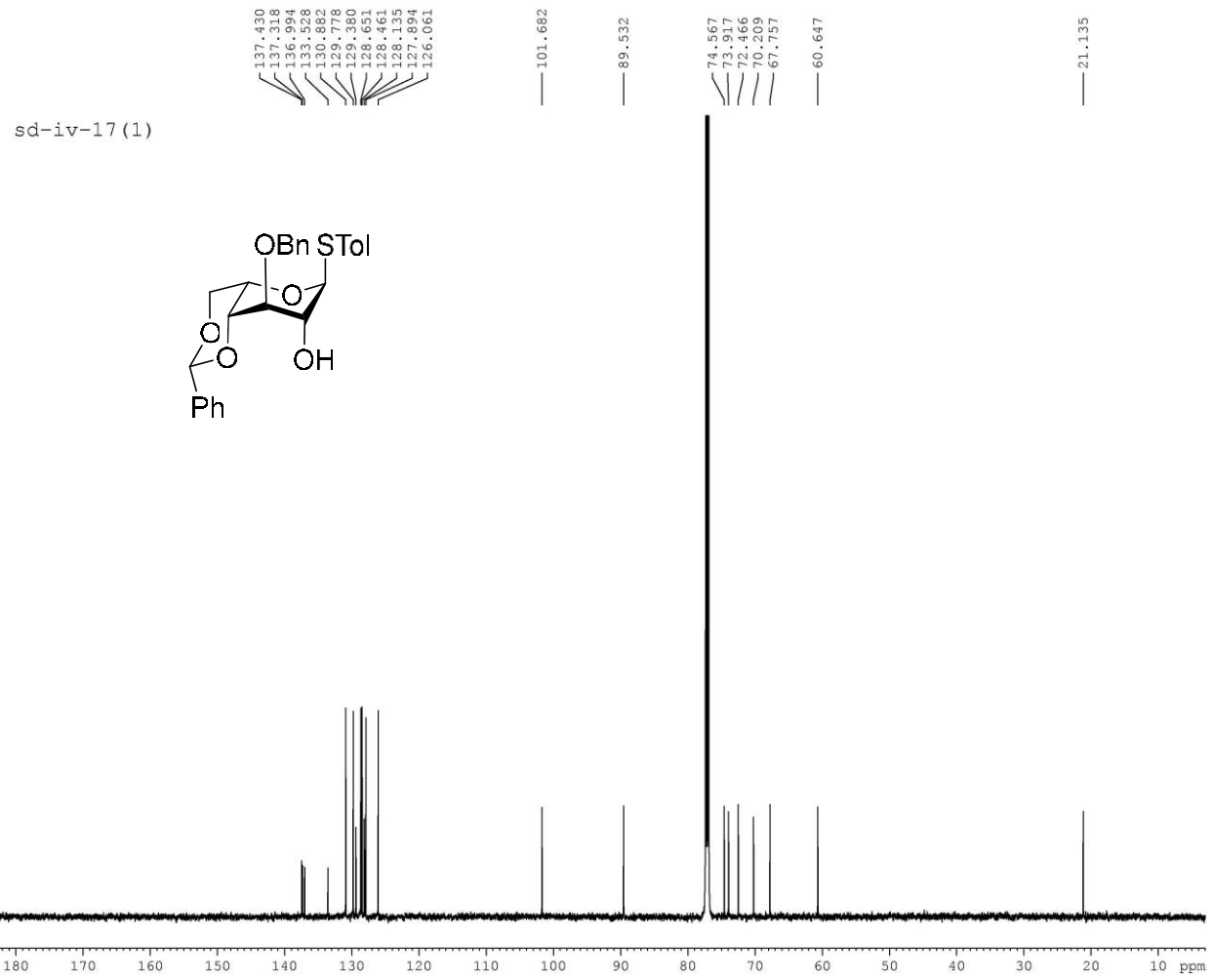


Figure 36. $^{13}C$ NMR spectrum of 4-Methylphenyl 3-O-benzyl-4,6-O-benzylidine-1-thio-α-L-idopyranoside (150 MHz, $CDCl_3$).

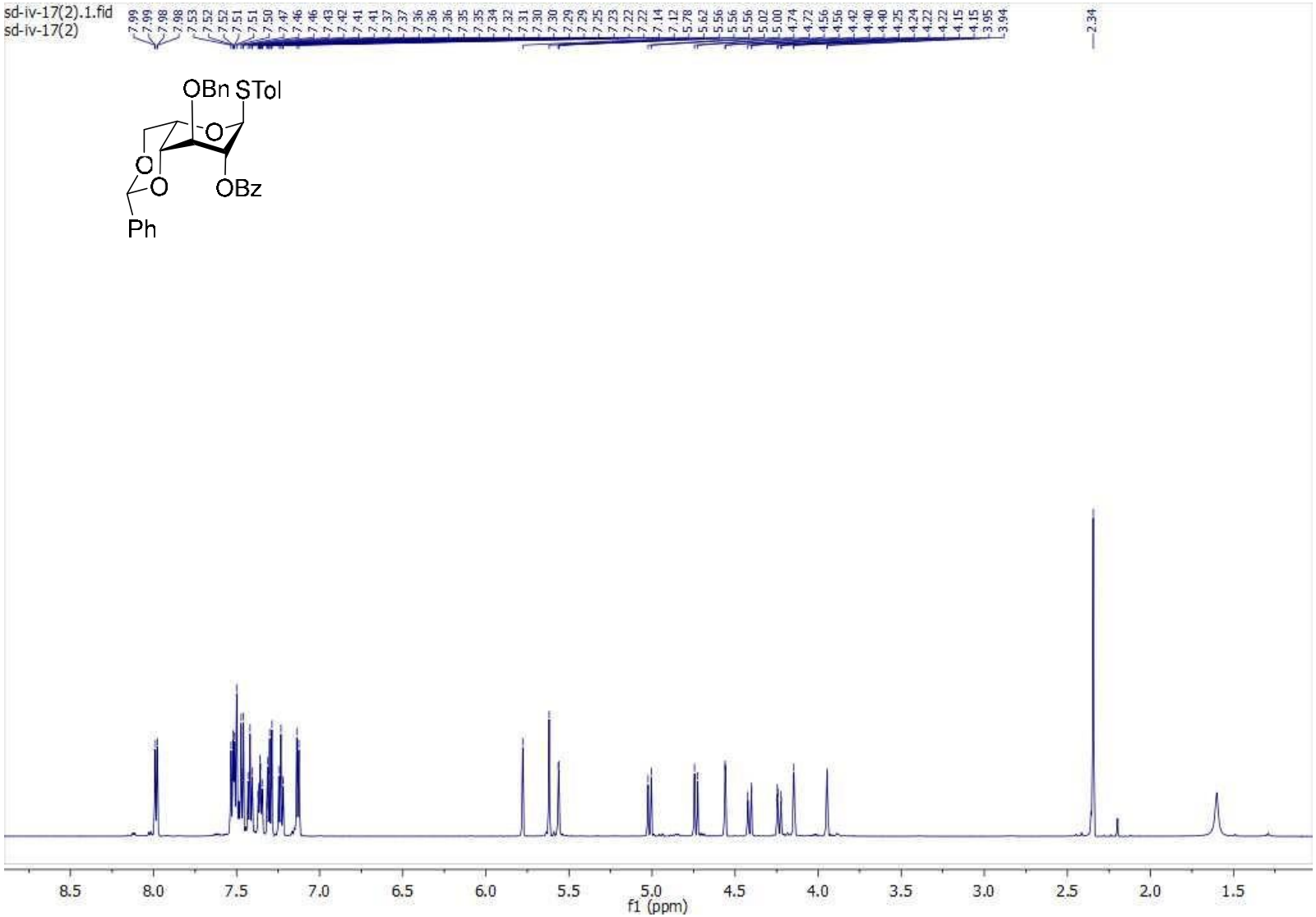


Figure 37. $^{1}$H NMR spectrum of 4-Methylphenyl 2-O-benzoyl-3-O-benzyl-4,6-O-benzylidene-1-thio-α-L-idopyranoside (600 MHz, $CDCl_3$).

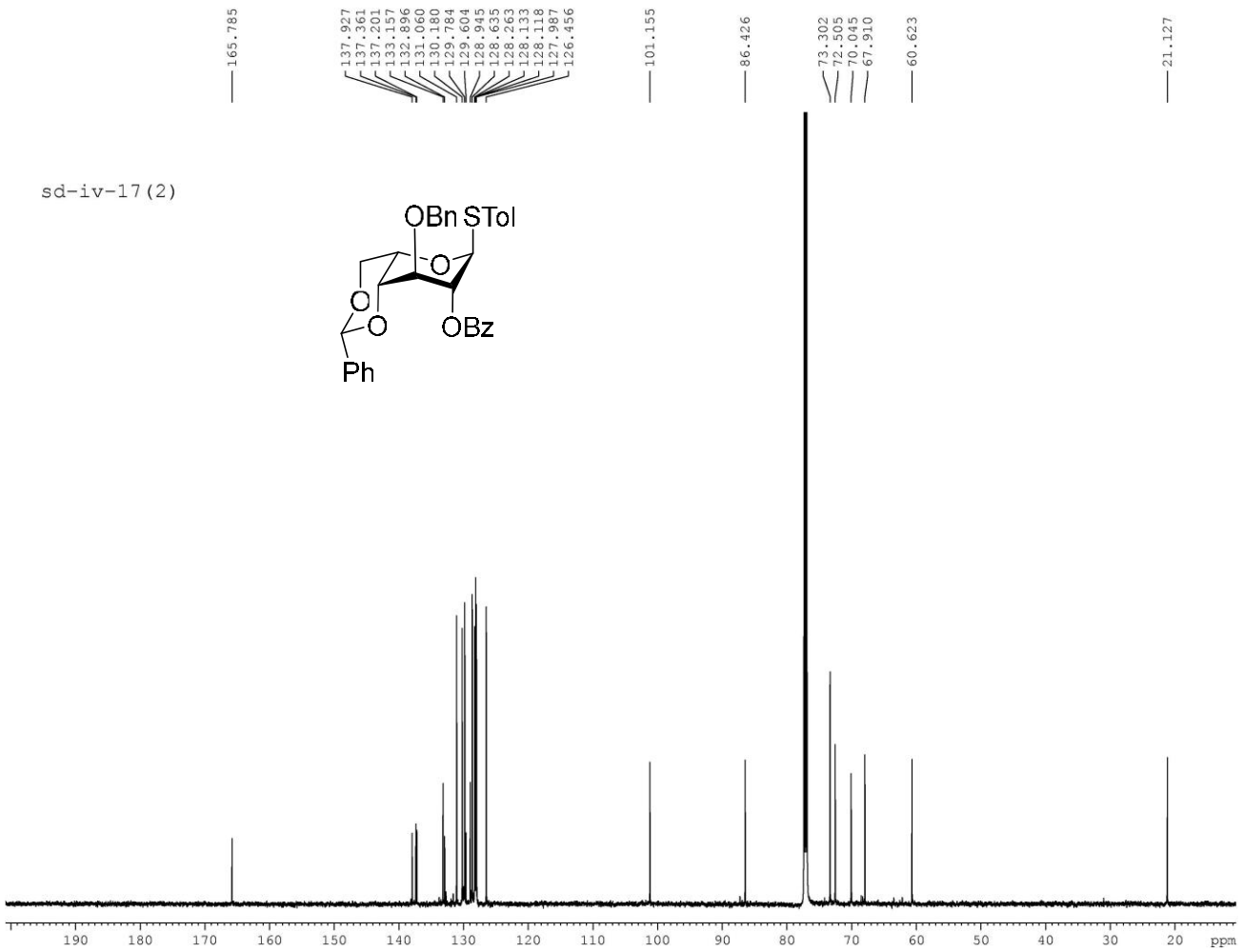


Figure 38. $^{13}C$ NMR spectrum of 4-Methylphenyl 2-O-benzoyl-3-O-benzyl-4,6-O-benzylidene-1-thio-α-L-idopyranoside (150 MHz, $CDCl_3$).

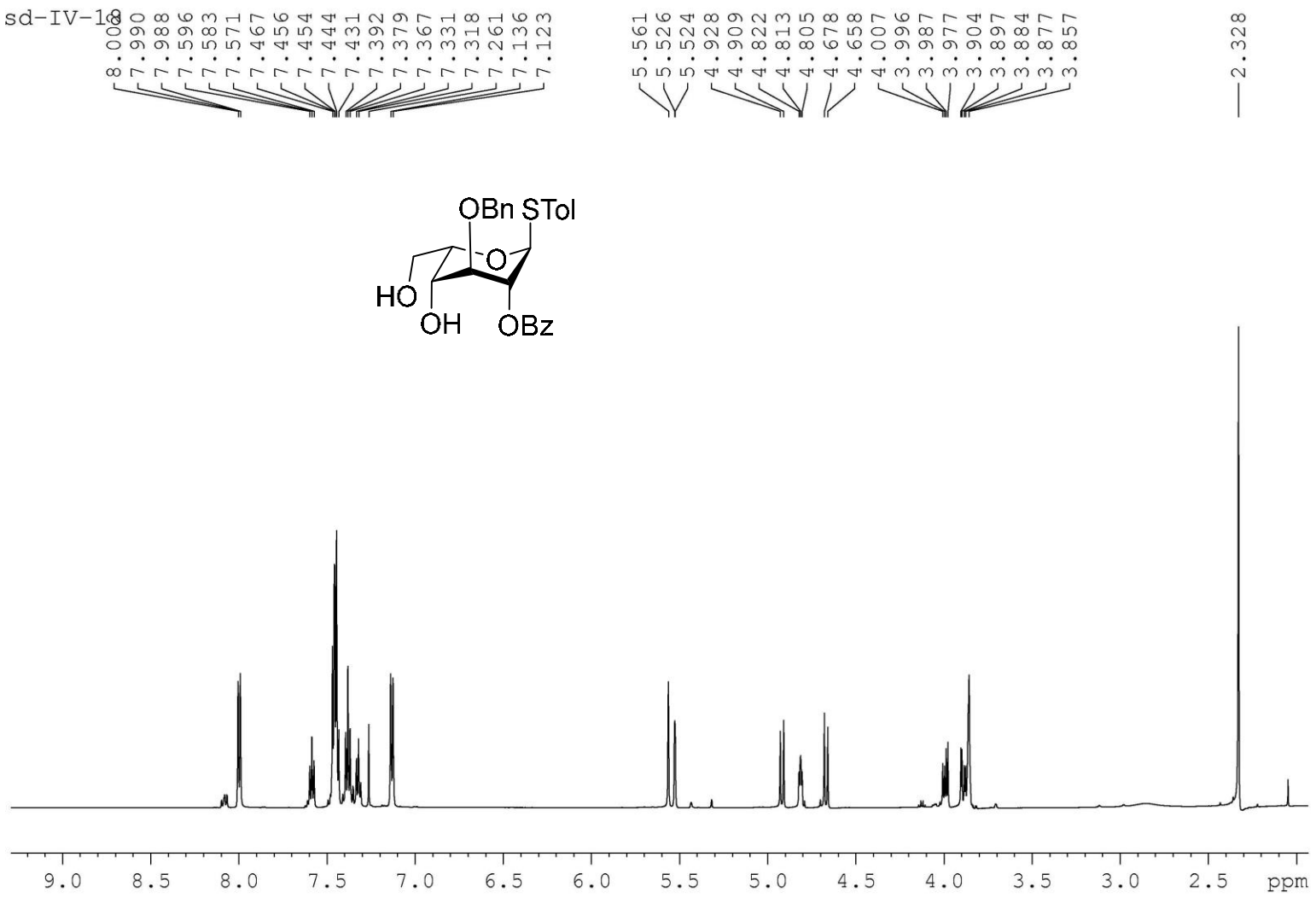


Figure 39. $^{1}$H NMR spectrum of 4-Methylphenyl 2-O-benzoyl-3-O-benzyl-1-thio-α-L-idopyranoside (600 MHz, $CDCl_3$).

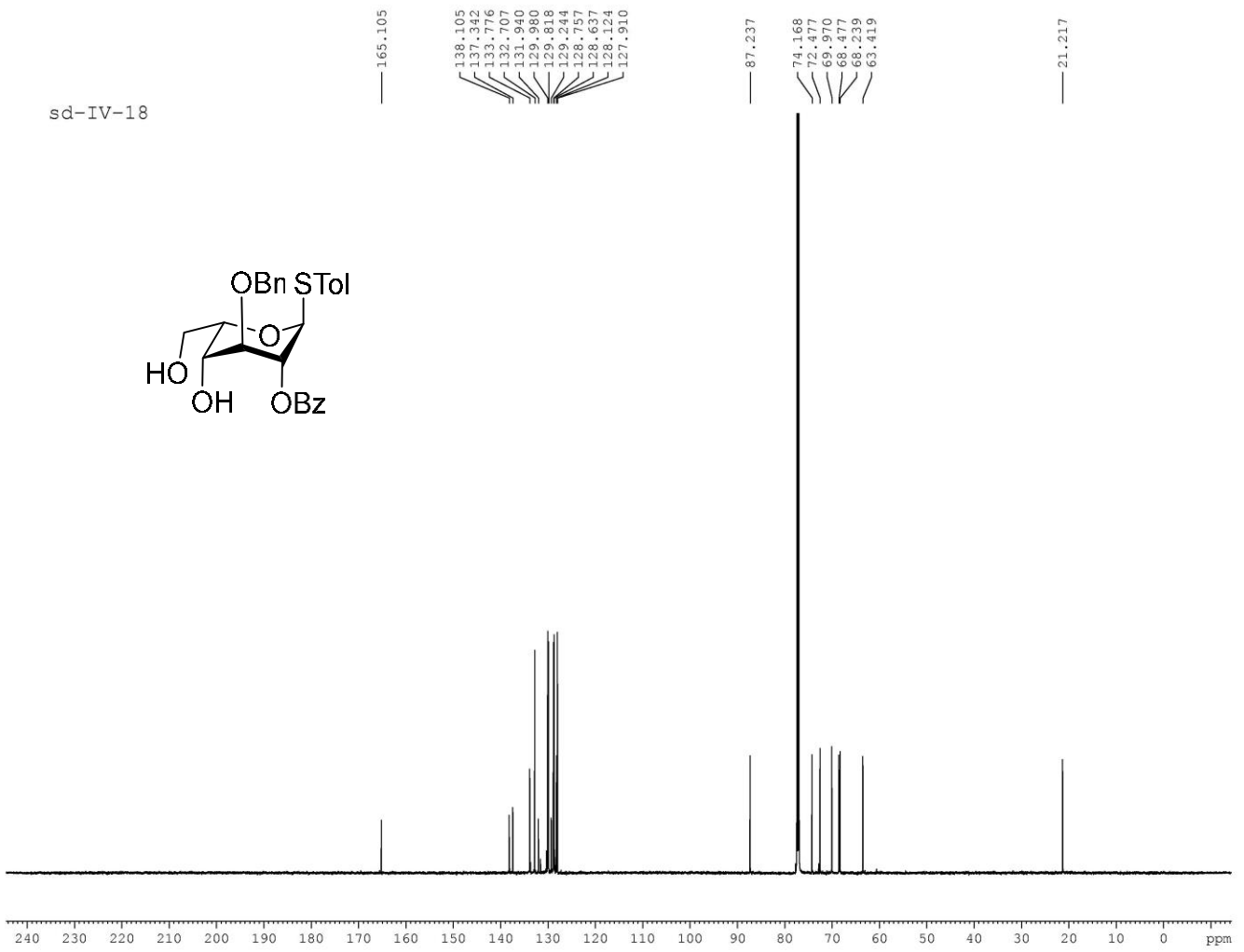


Figure 40. $^{13}$C NMR spectrum of 4-Methylphenyl 2-O-benzoyl-3-O-benzyl-1-thio-α-L-idopyranoside (150 MHz, $CDCl_3$).

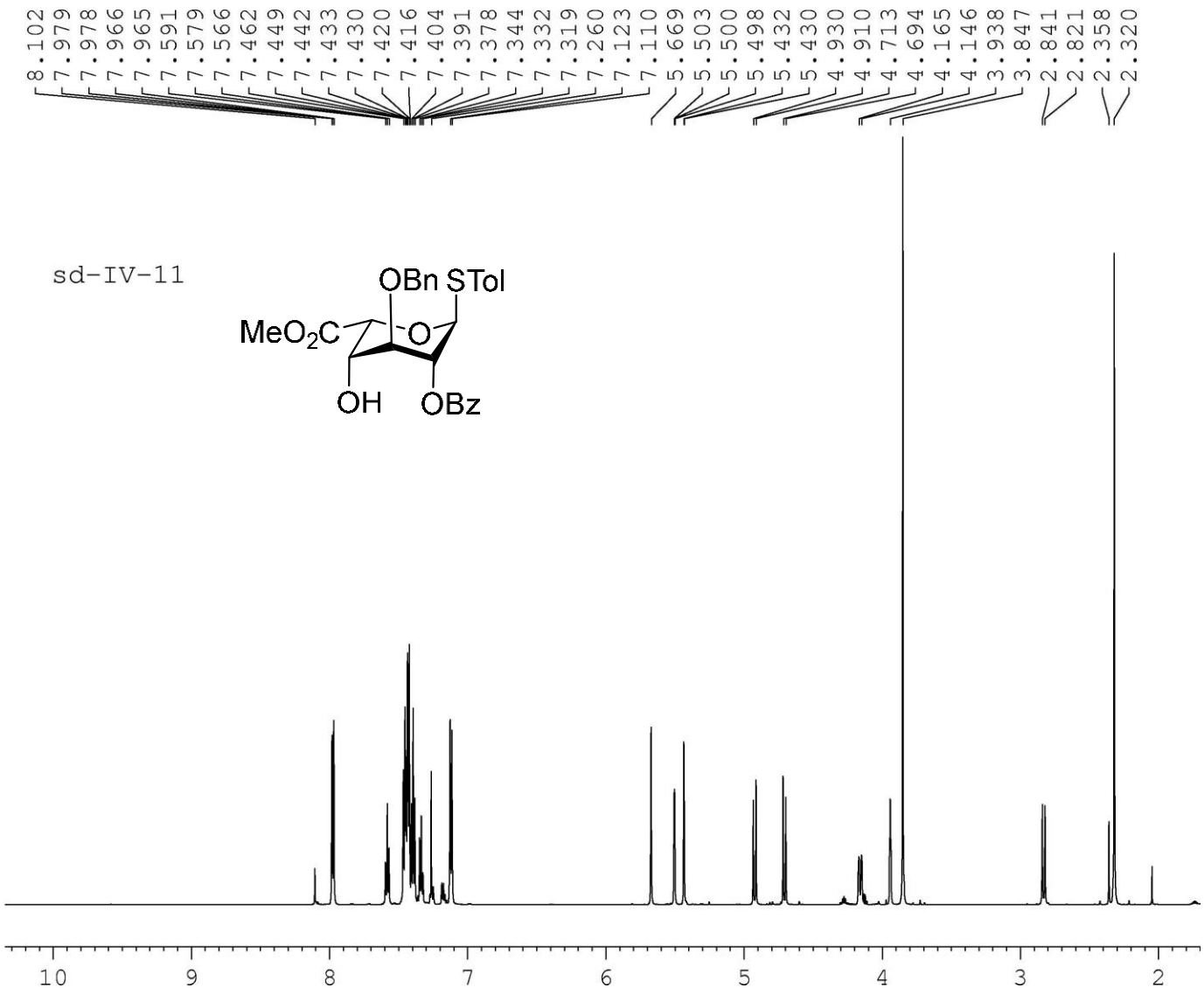


Figure 41. $^{1}$H NMR spectrum of Methyl p-methylphenyl-2-O-benzoyl-3-O-benzyl-1-thio-α-L-idopyranosyl uronate (600 MHz, $CDCl_3$).

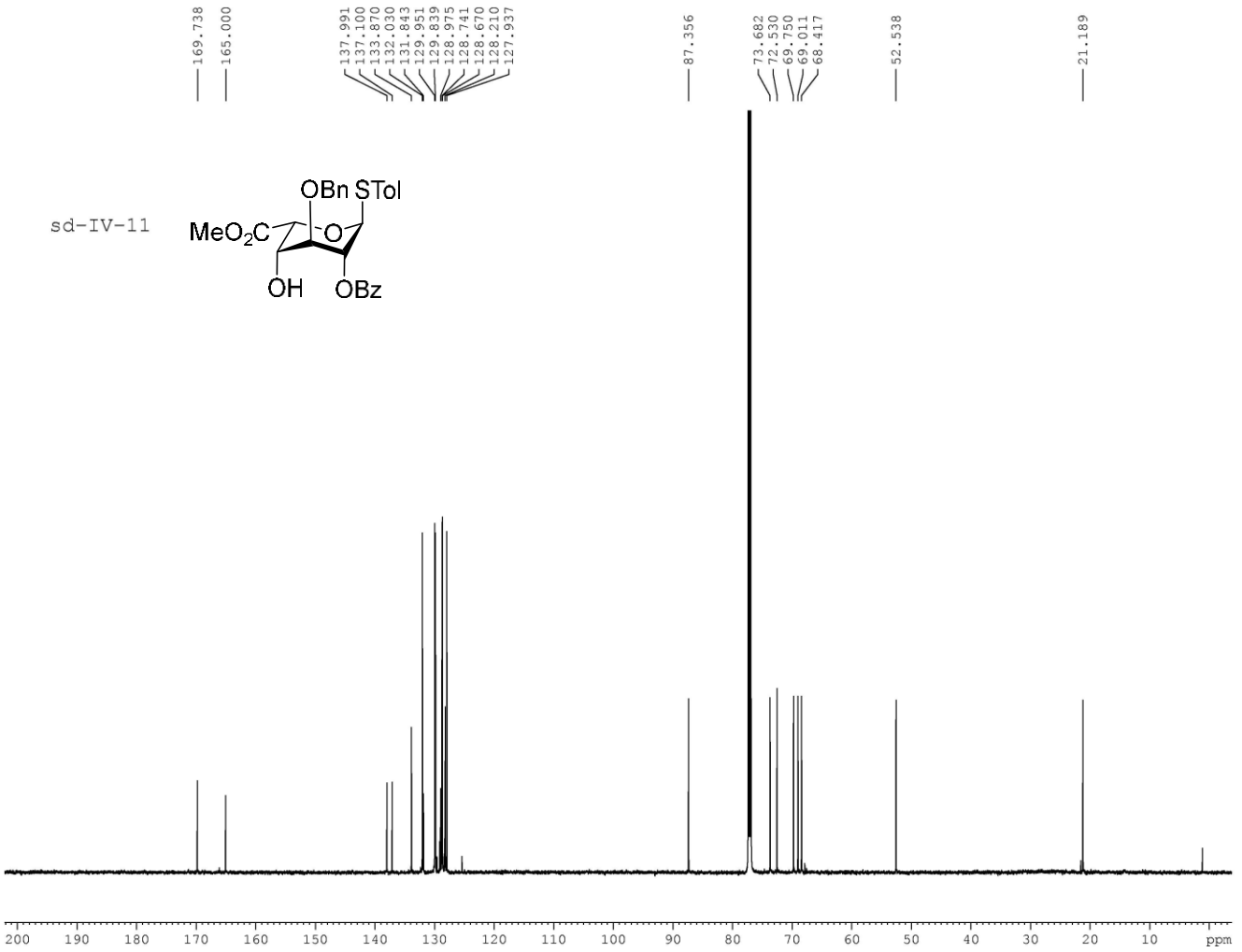


Figure 42. $^{13}$C NMR spectrum of Methyl p-methylphenyl-2-O-benzoyl-3-O-benzyl-1-thio-α-L-idopyranosyl uronate (600 MHz, $CDCl_3$).

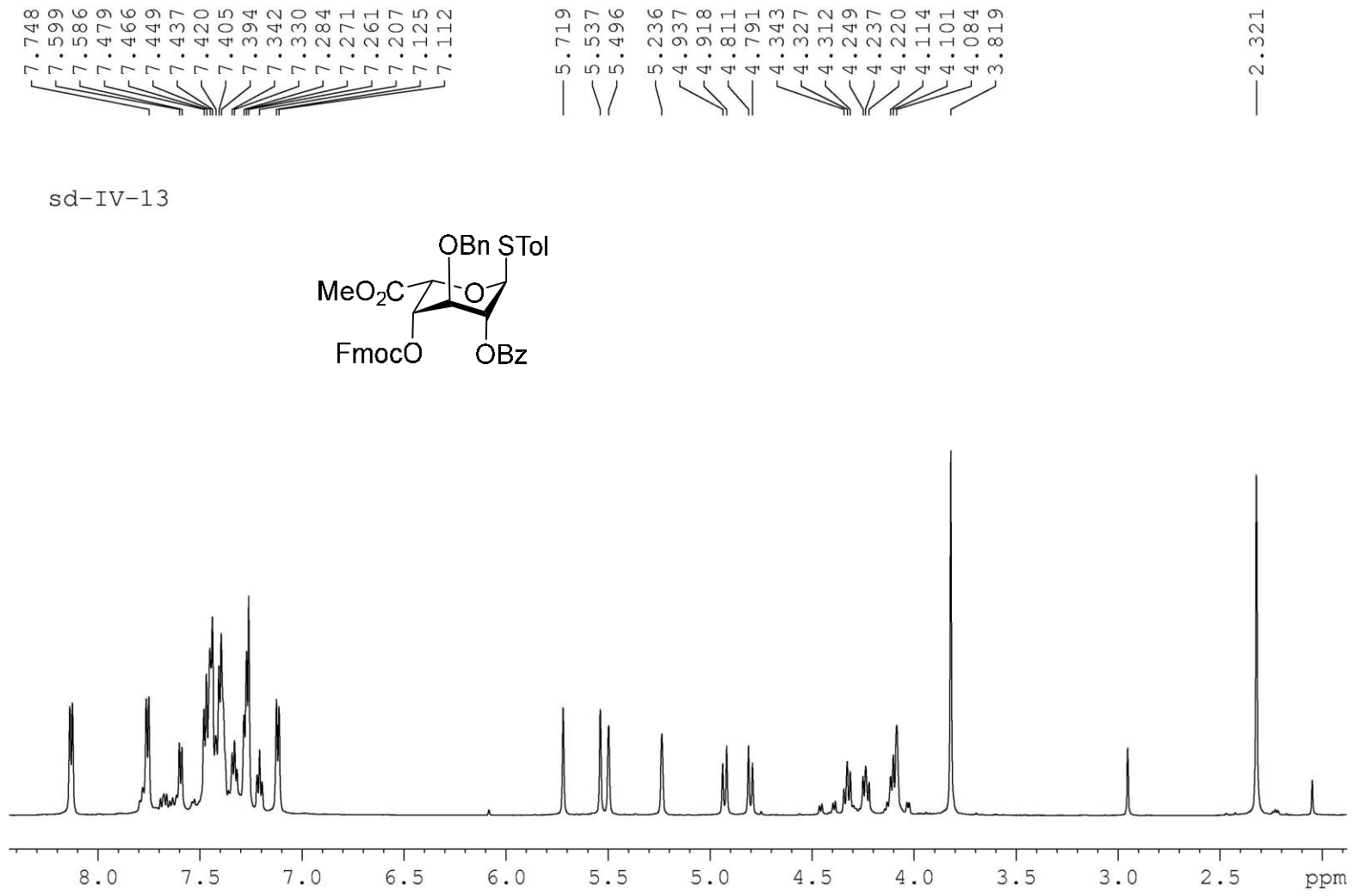


Figure 43. $^{1}$H NMR spectrum of Methyl p-methylphenyl-2-O-benzoyl-3-O-benzyl-4-O-(9-fluorenylmethoxycarbonyl)-1-thio-α-L-idopyranosyl uronate (600 MHz, $CDCl_3$).

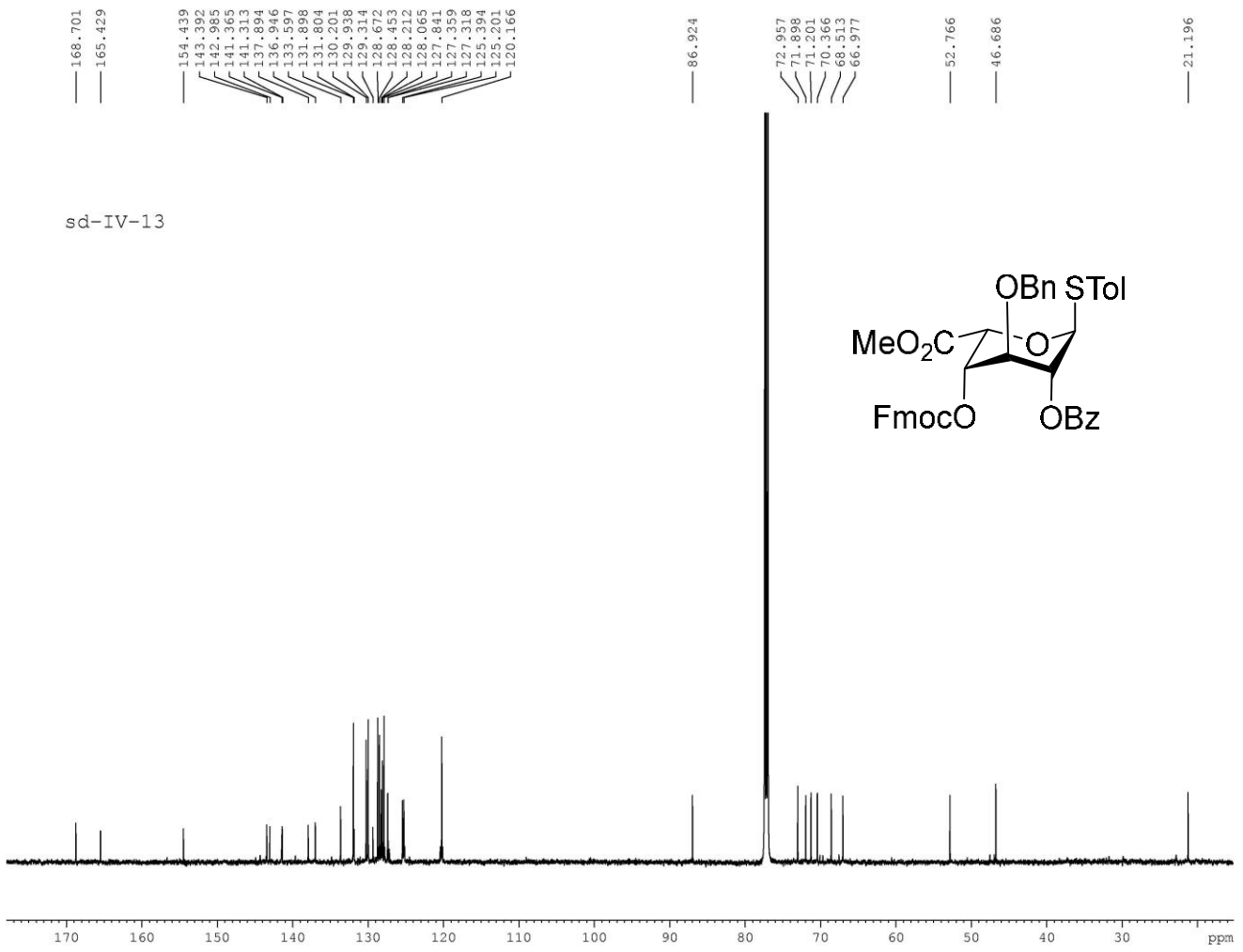


Figure 44. $^{13}$C NMR spectrum of Methyl p-methylphenyl-2-O-benzoyl-3-O-benzyl-4-O-(9-fluorenylmethoxycarbonyl)-1-thio-α-L-idopyranosyl uronate (150 MHz, $CDCl_3$).

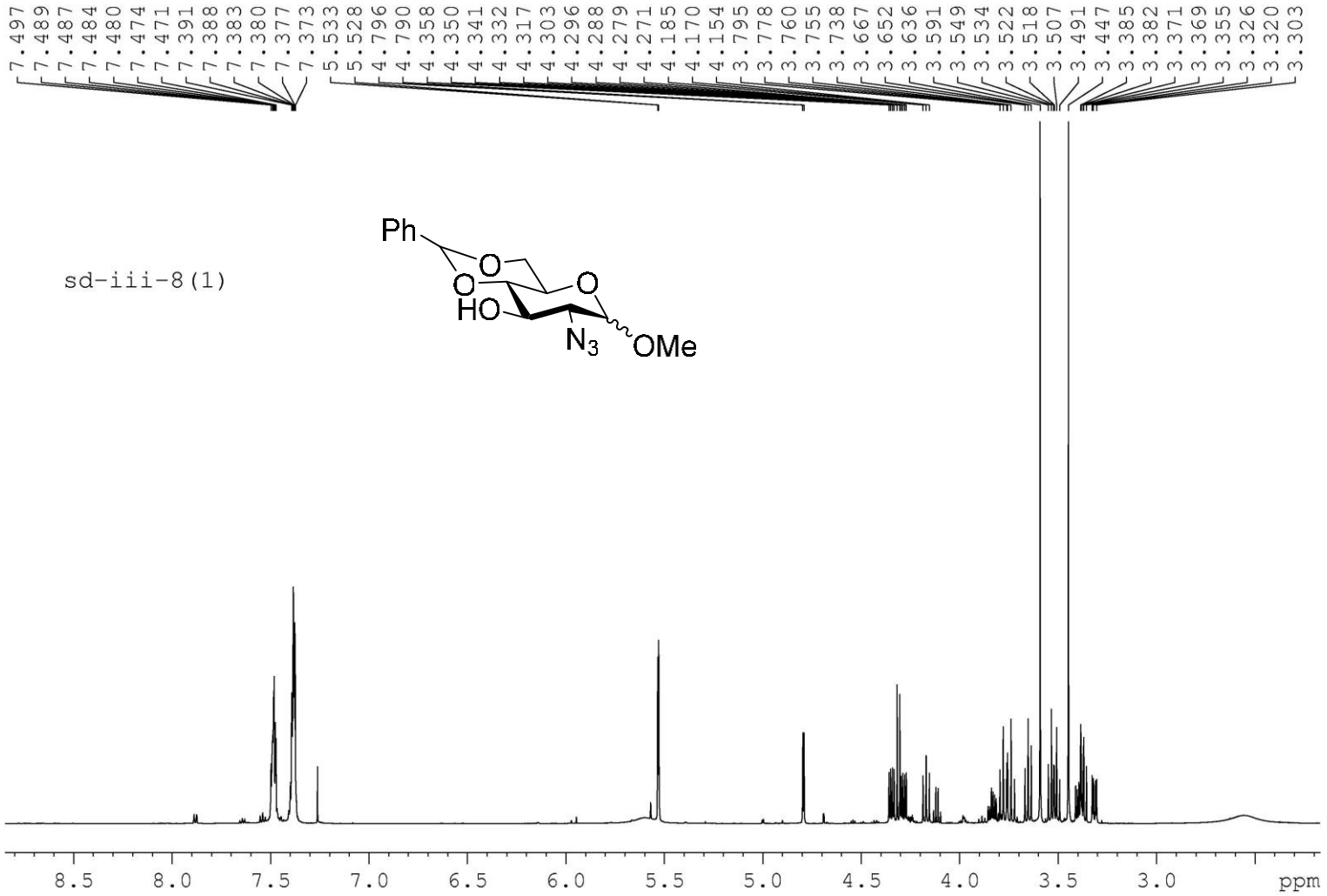


Figure 45. $^{1}$H NMR spectrum of Methyl-2-azido-4,6-O-benzylidene-2-deoxy-D-glucopyranoside (600 MHz, $CDCl_3$).

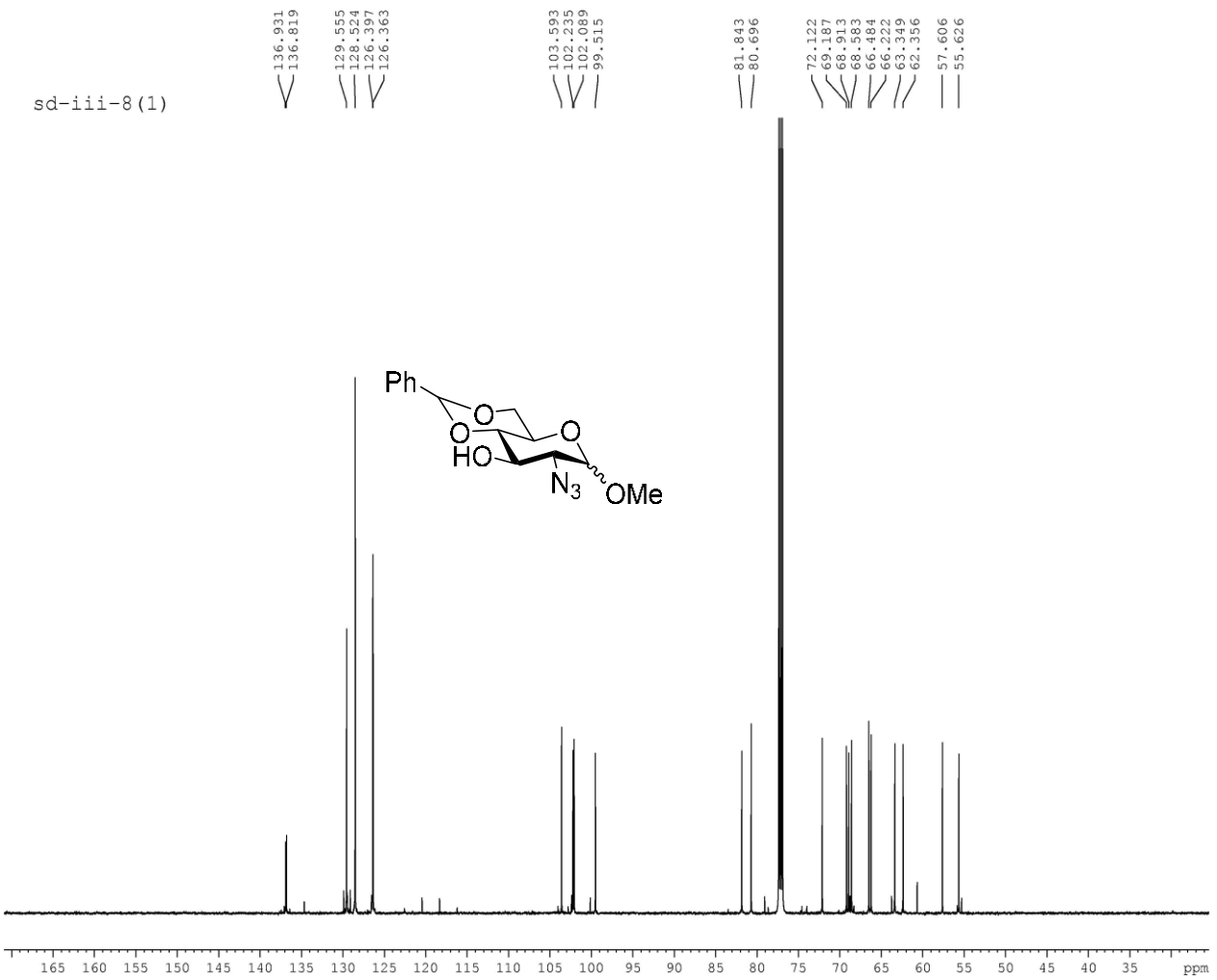


Figure 46. $^{13}C$ NMR spectrum of Methyl-2-azido-4,6-O-benzylidene-2-deoxy-D-glucopyranoside (150 MHz, $CDCl_3$).

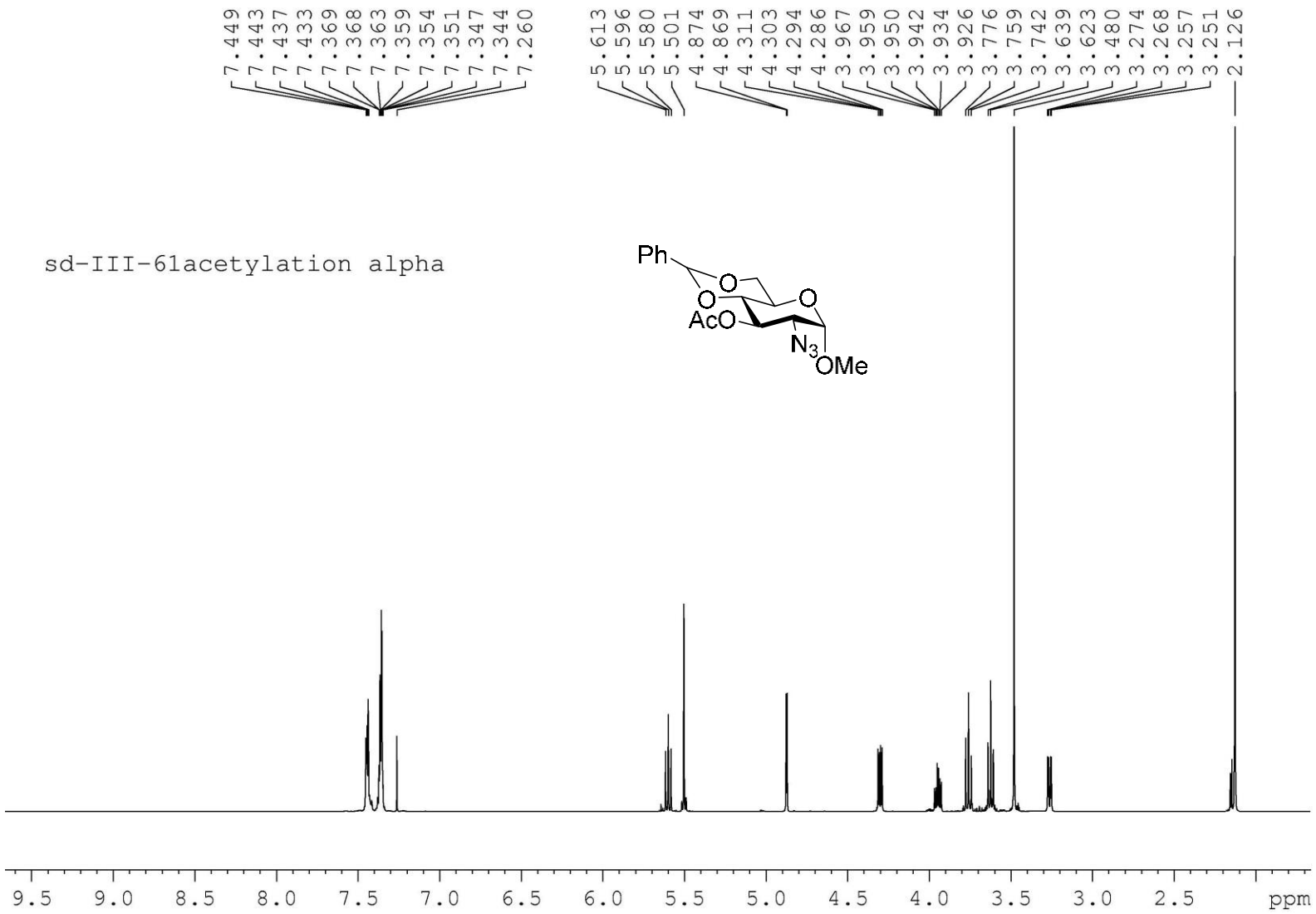


Figure 47. $^{1}$H NMR spectrum of Methyl-2-azido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (600 MHz, $CDCl_3$).

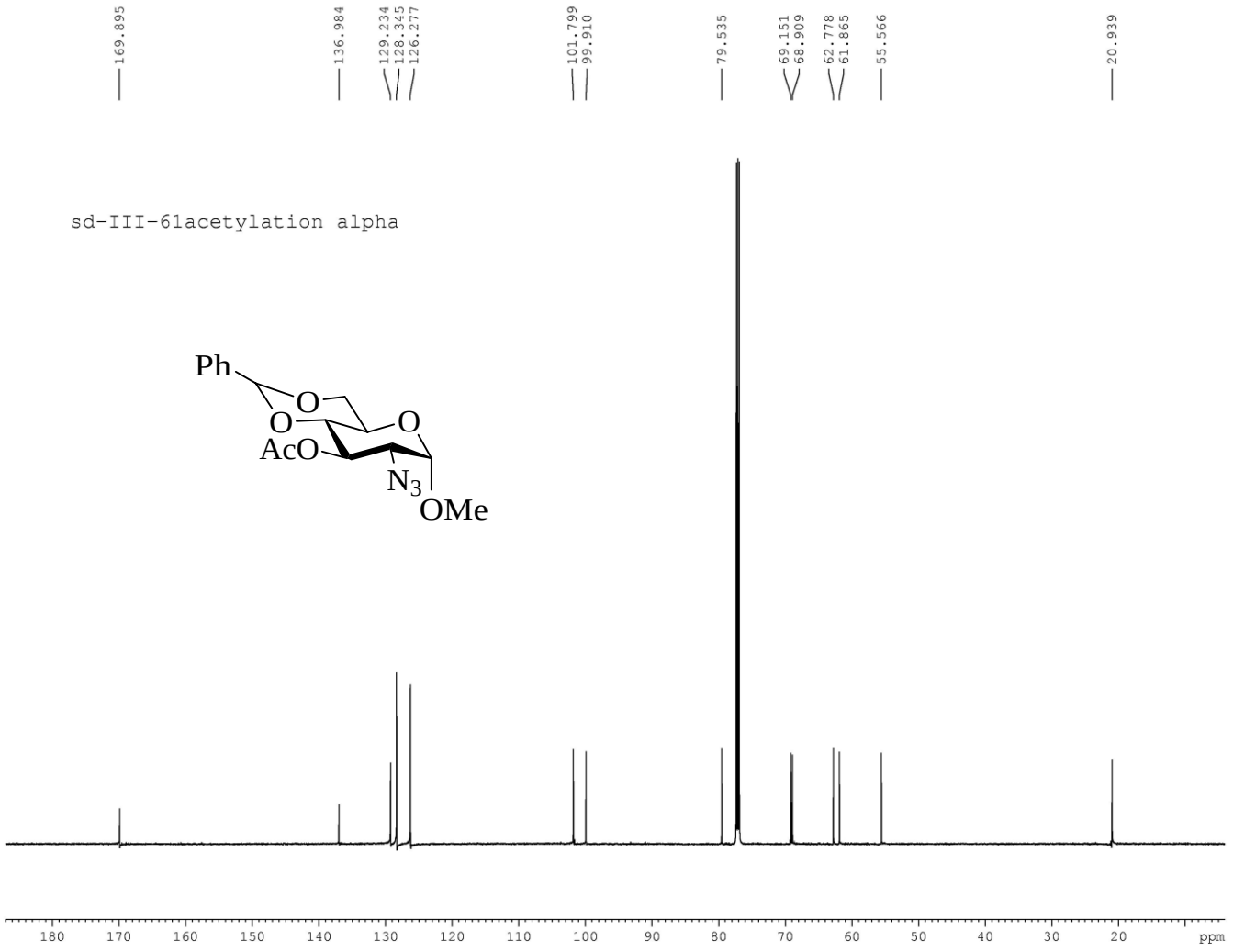


Figure 48. $^{13}$C NMR spectrum of Methyl-2-azido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (150 MHz, $CDCl_3$).

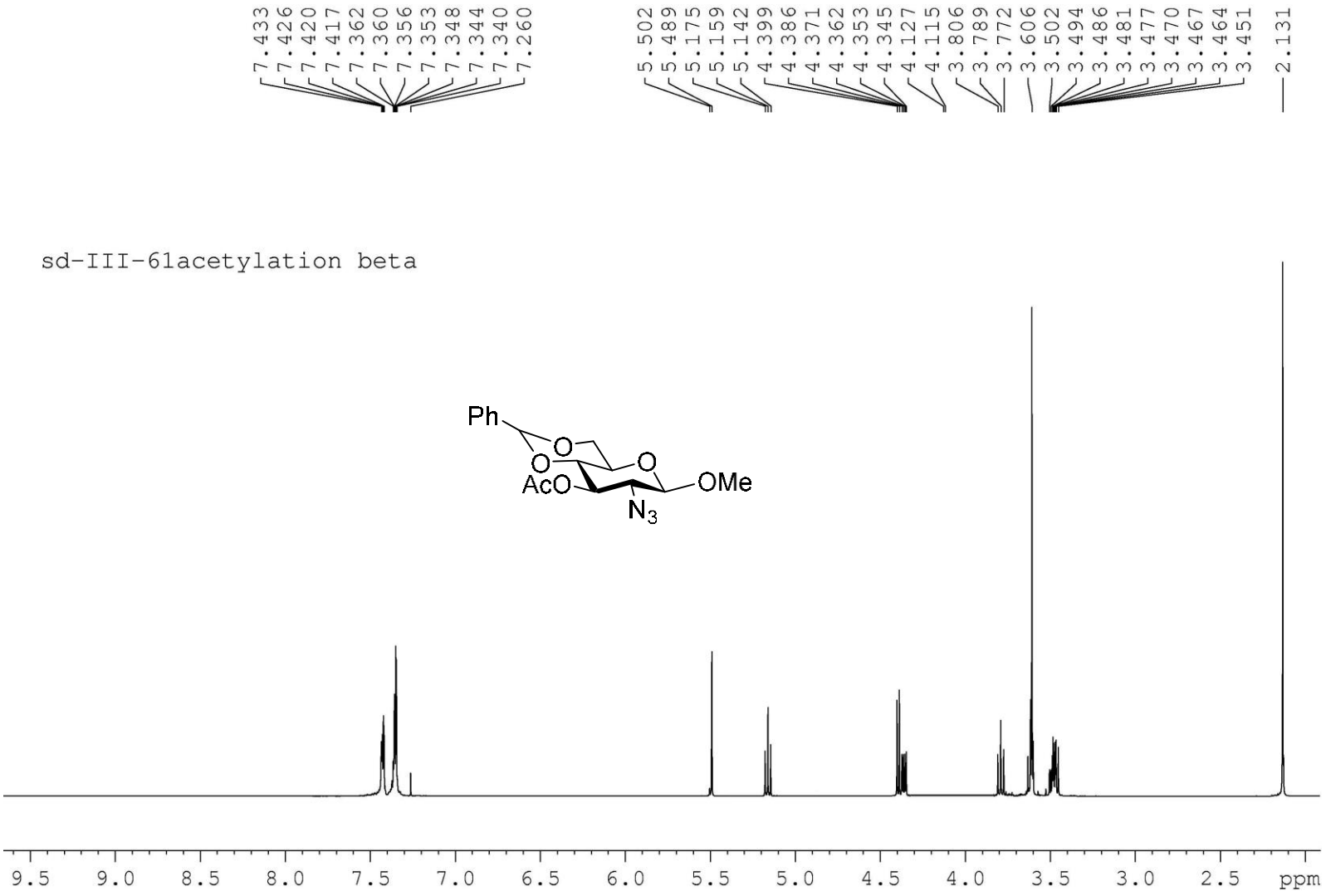


Figure 49. $^{1}$H NMR spectrum of Methyl-2-azido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (600 MHz, $CDCl_3$).

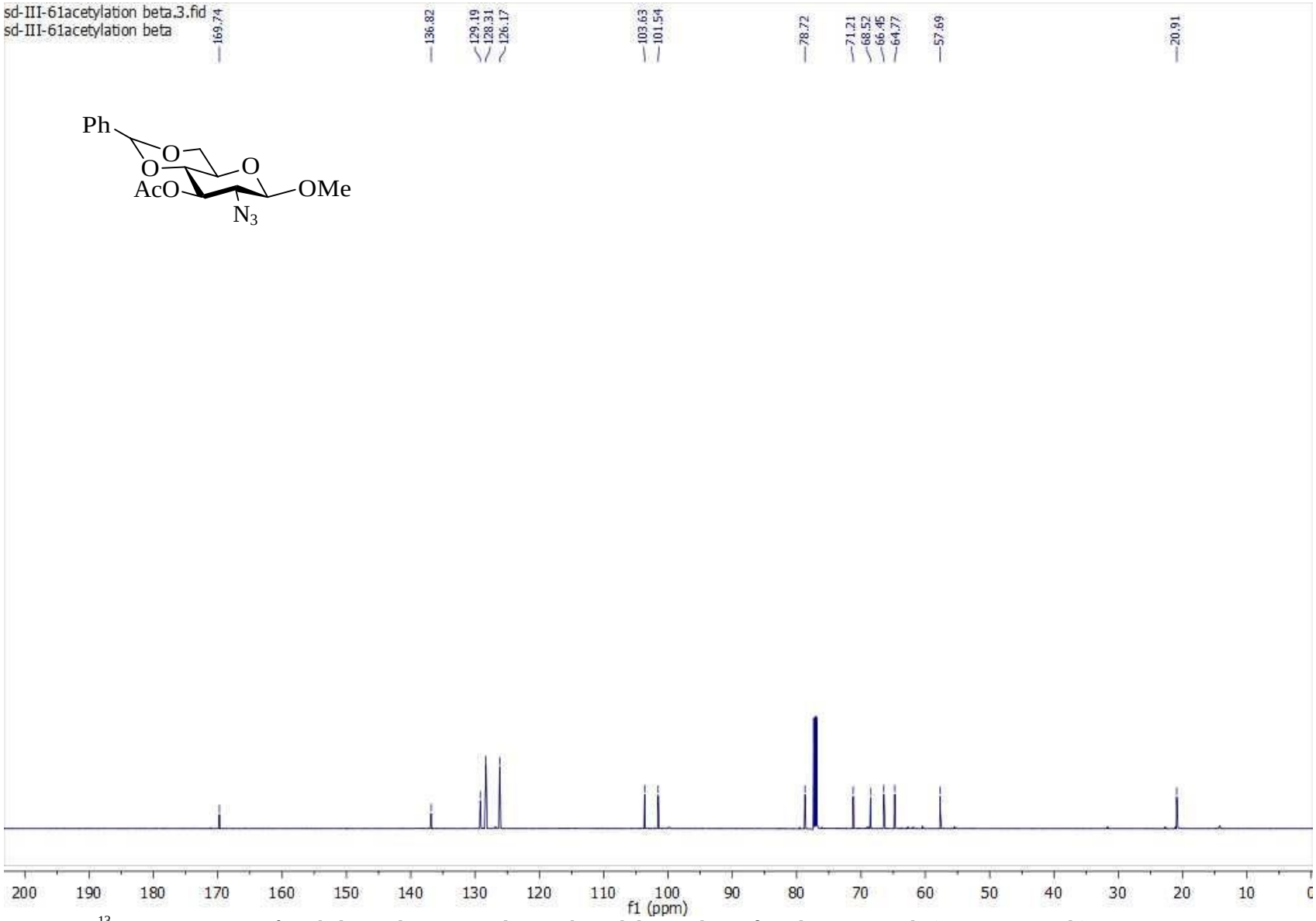


Figure 50. $^{13}$C NMR spectrum of Methyl-2-azido-3-O-acetyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside (150 MHz, $CDCl_3$).

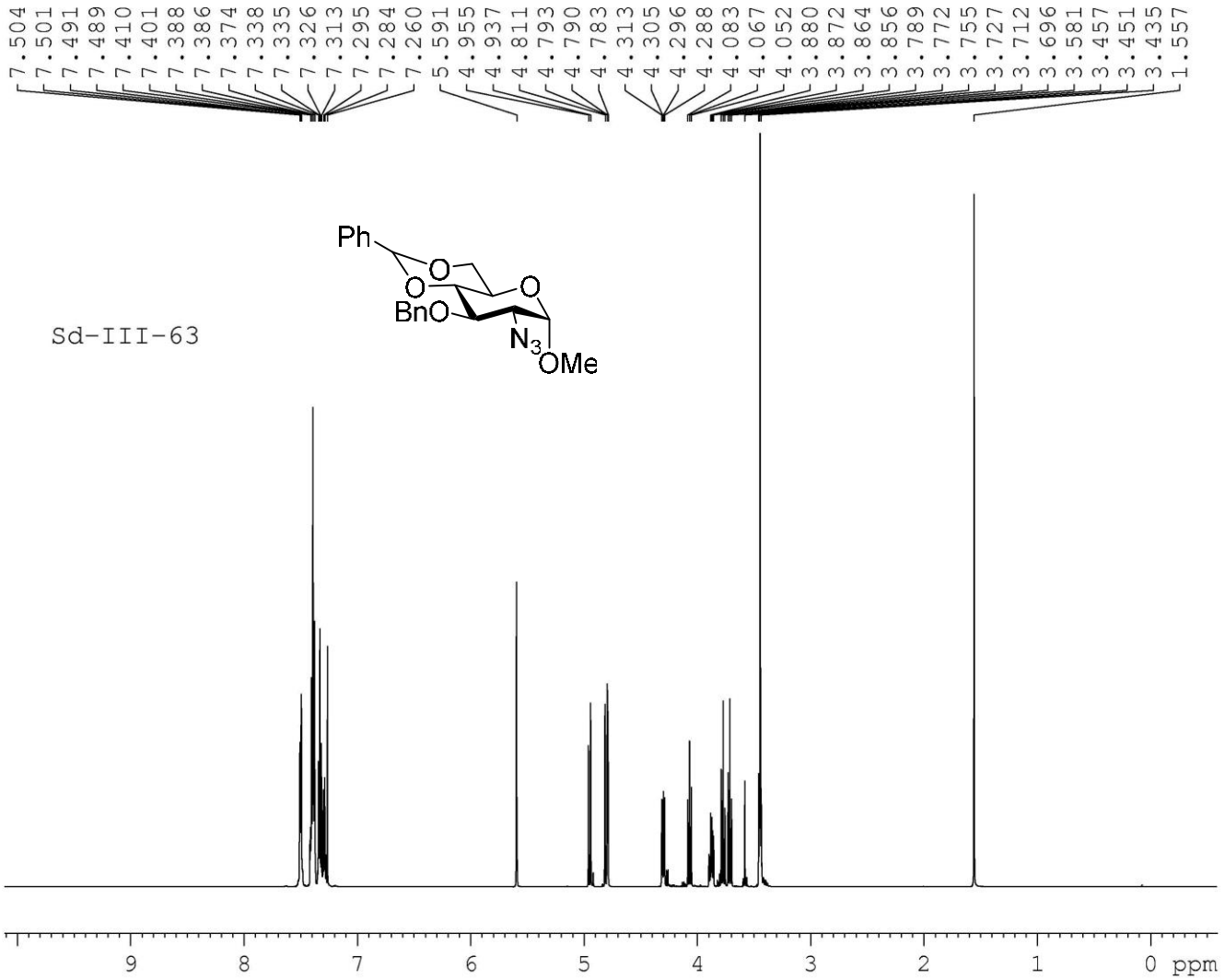


Figure 51. $^{1}$H NMR spectrum of Methyl-2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (600 MHz, $CDCl_3$).

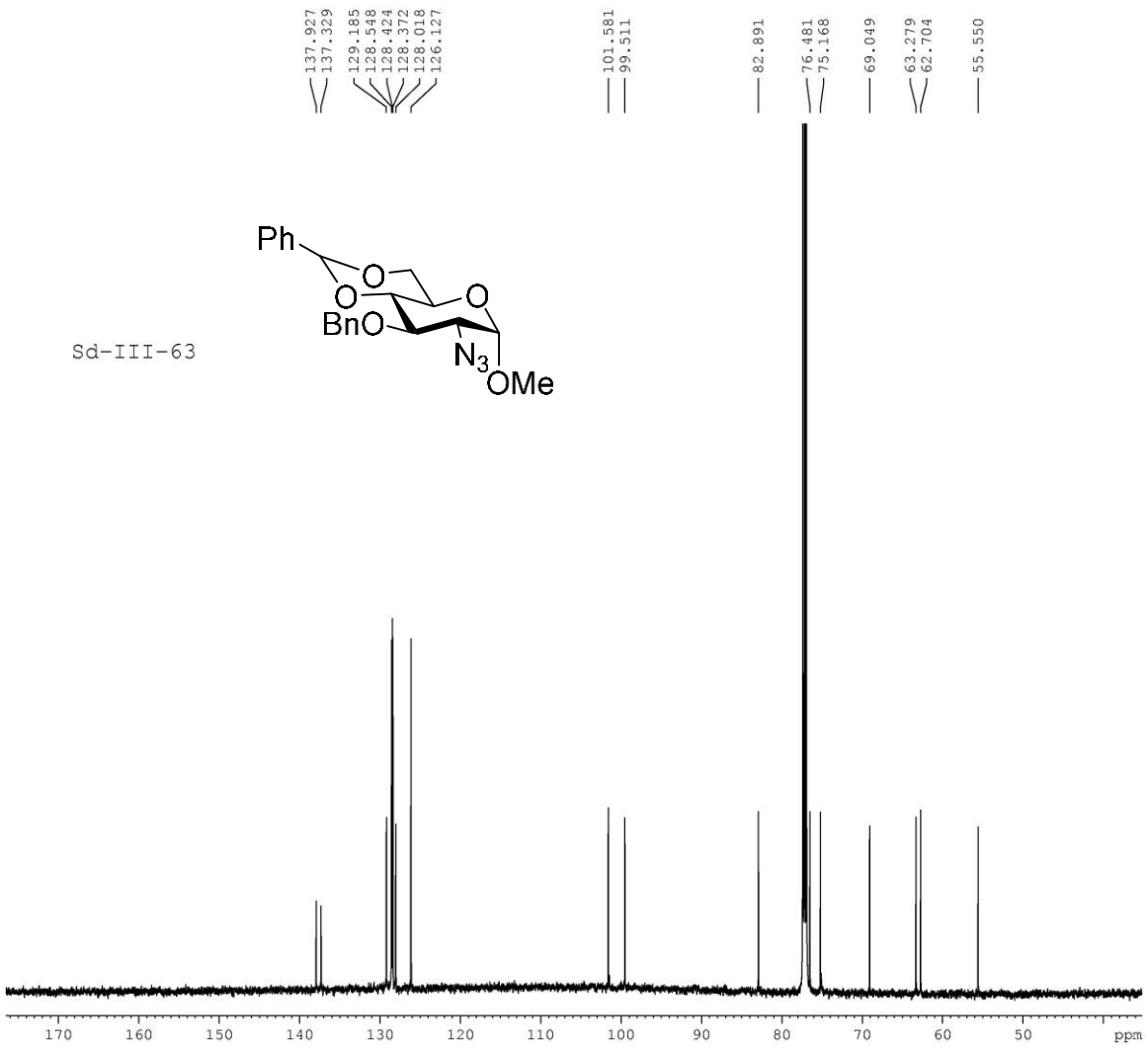


Figure 52. $^{13}$C NMR spectrum of Methyl-2-azido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (150 MHz, $CDCl_3$).

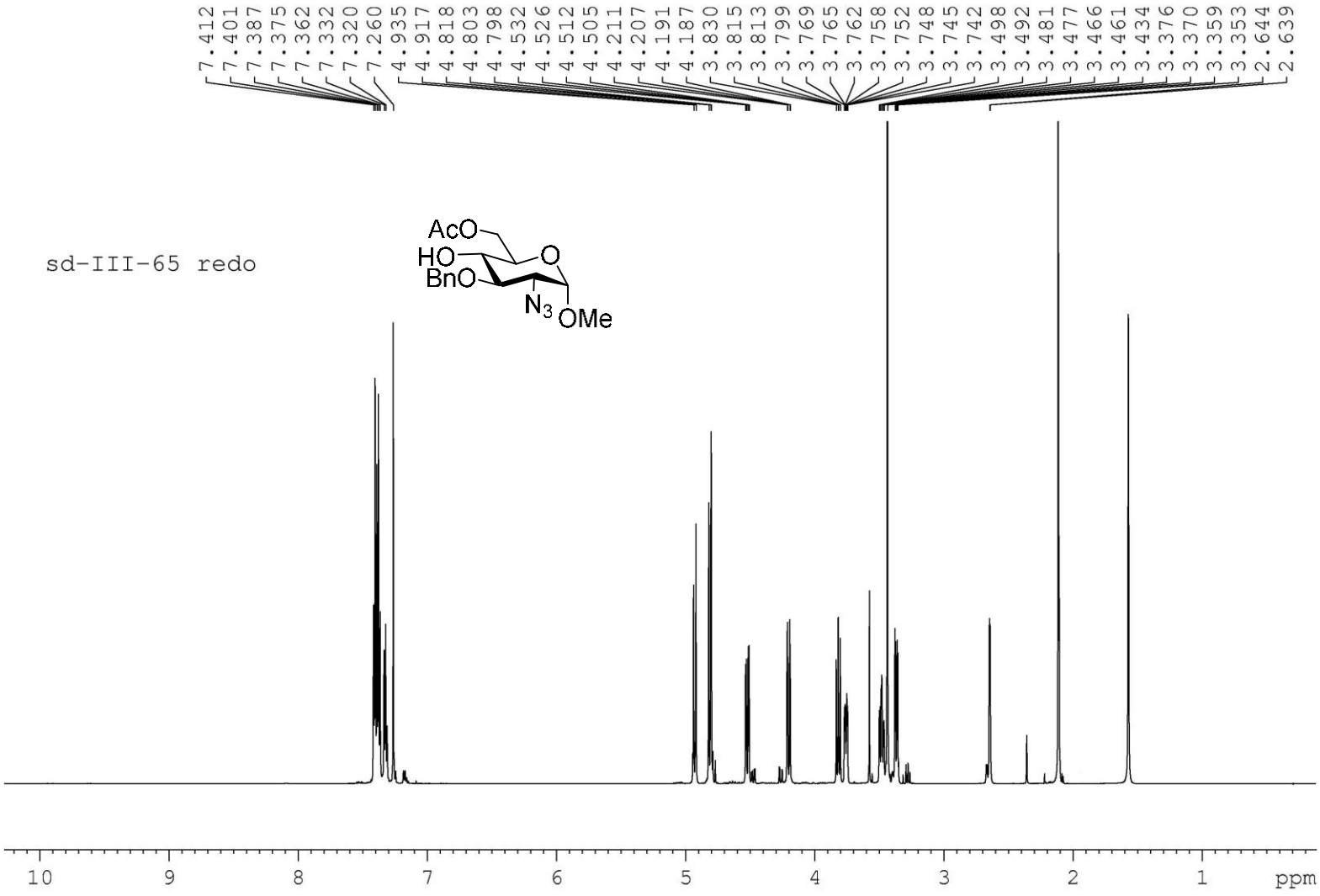


Figure 53. $^{1}$H NMR spectrum of Methyl-2-azido-6-O-acetyl-3-O-benzyl-2-deoxy-α-D-glucopyranoside (600 MHz, $CDCl_3$).

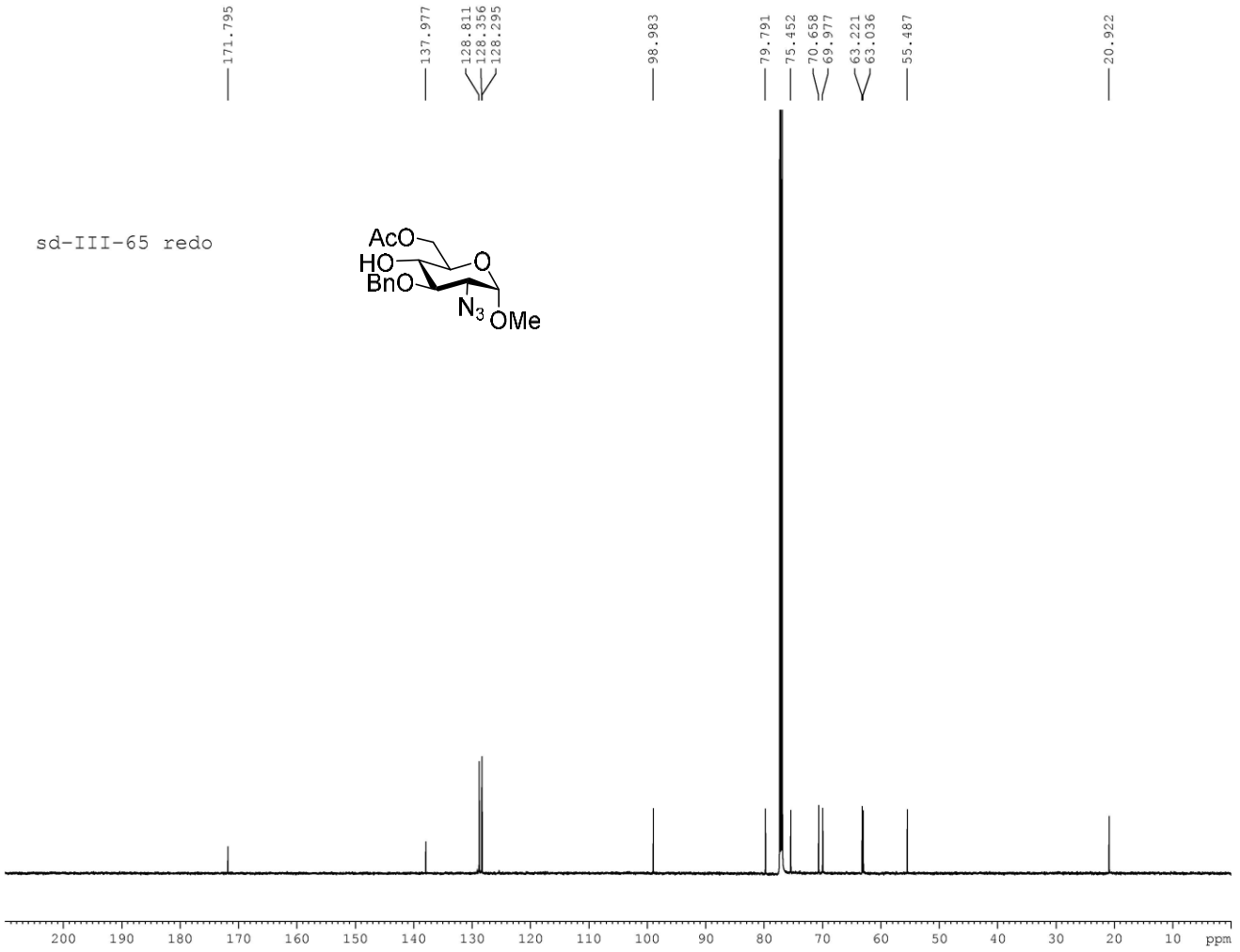


Figure 54. $^{13}$C NMR spectrum of Methyl-2-azido-6-O-acetyl-3-O-benzyl-2-deoxy-α-D-glucopyranoside (150 MHz, $CDCl_3$).

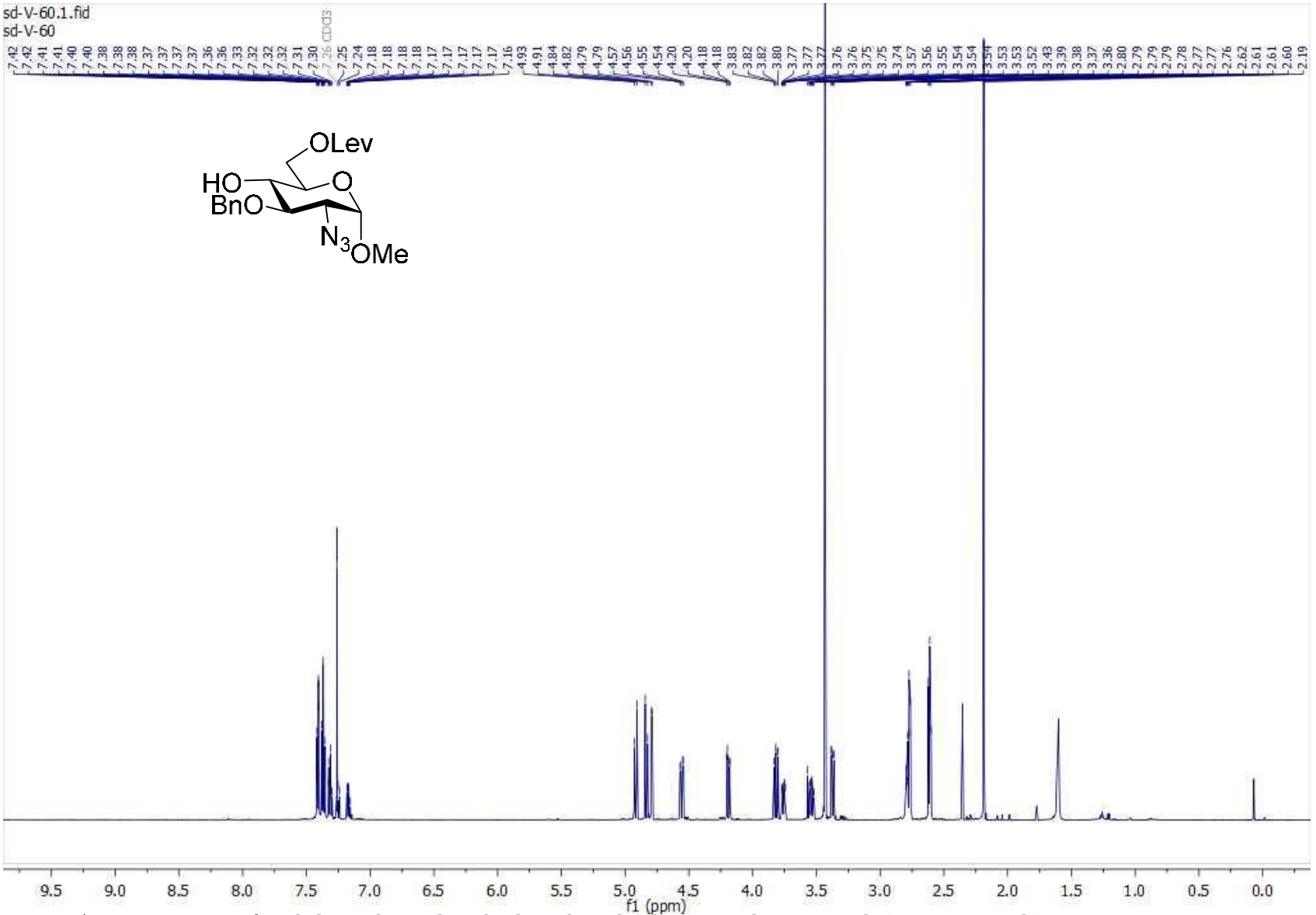


Figure 55. $^{1}$H NMR spectrum of Methyl-2-azido-6-O-levunlinyl-3-O-benzyl-2-deoxy-α-D-glucopyranoside (600 MHz, $CDCl_3$).

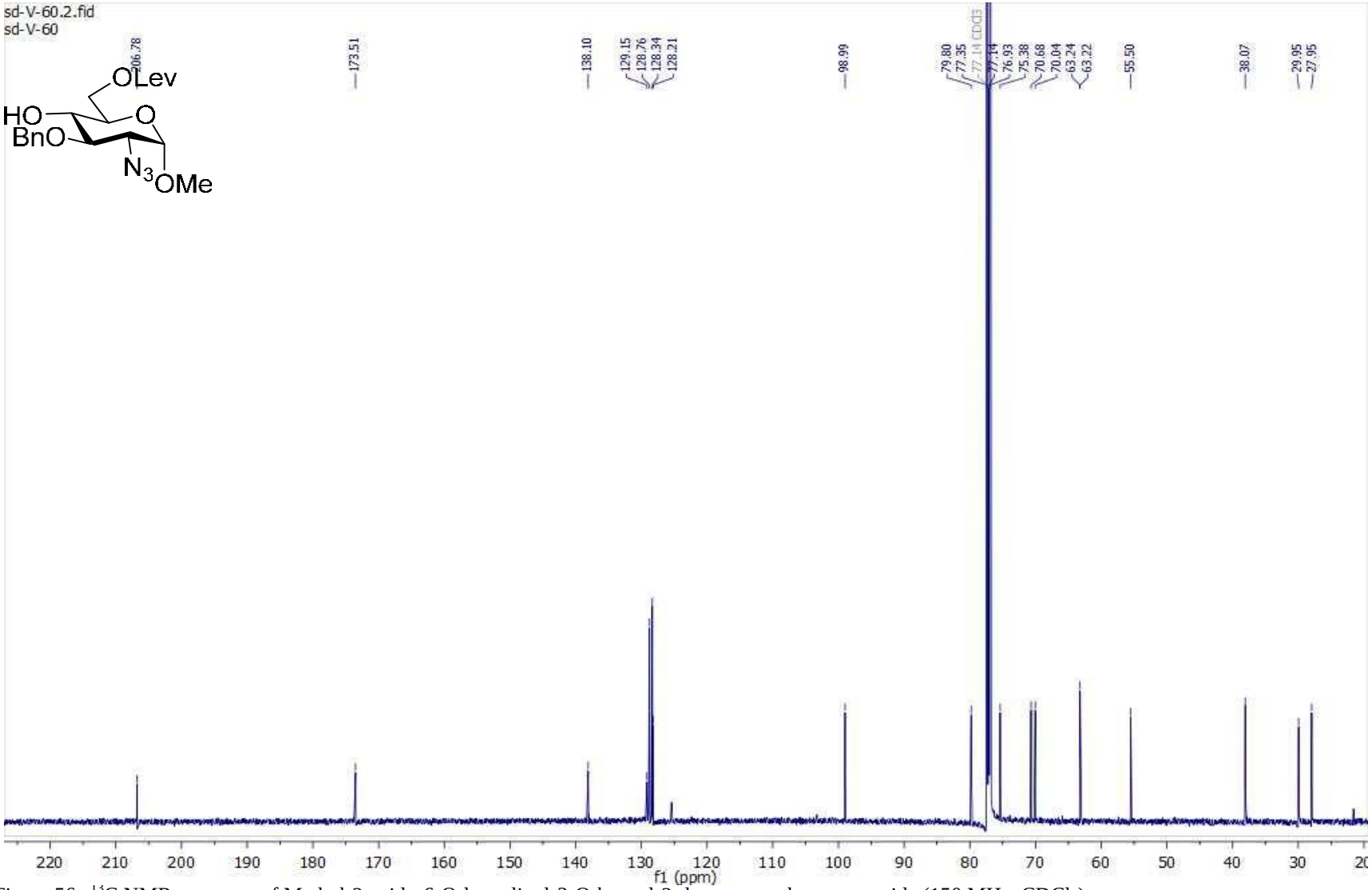


Figure 56. $^{13}C$ NMR spectrum of Methyl-2-azido-6-O-levunlinyl-3-O-benzyl-2-deoxy-α-D-glucopyranoside (150 MHz, $CDCl_3$).

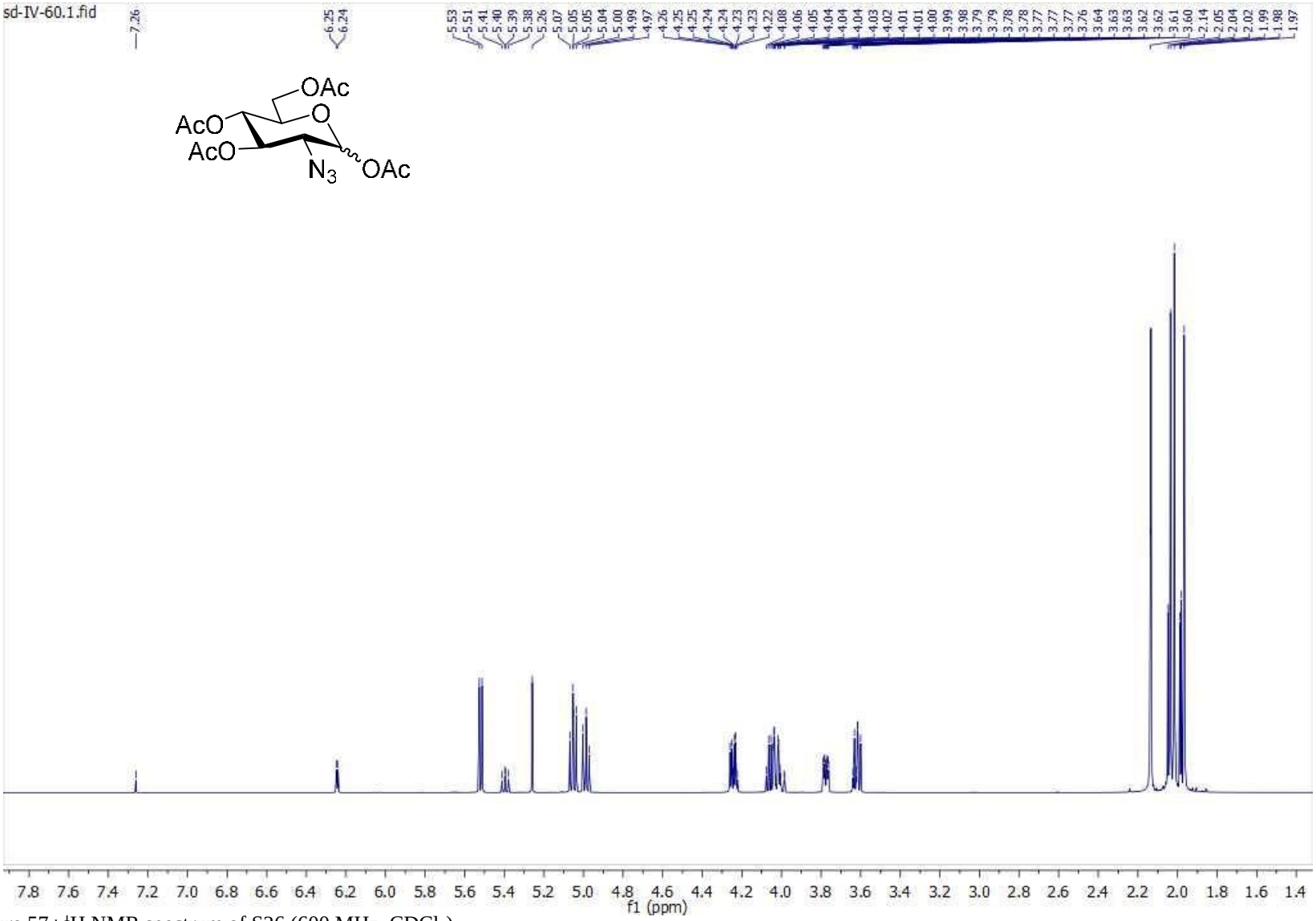


Figure 57. $^{1}$H NMR spectrum of S26 (600 MHz, $CDCl_3$).

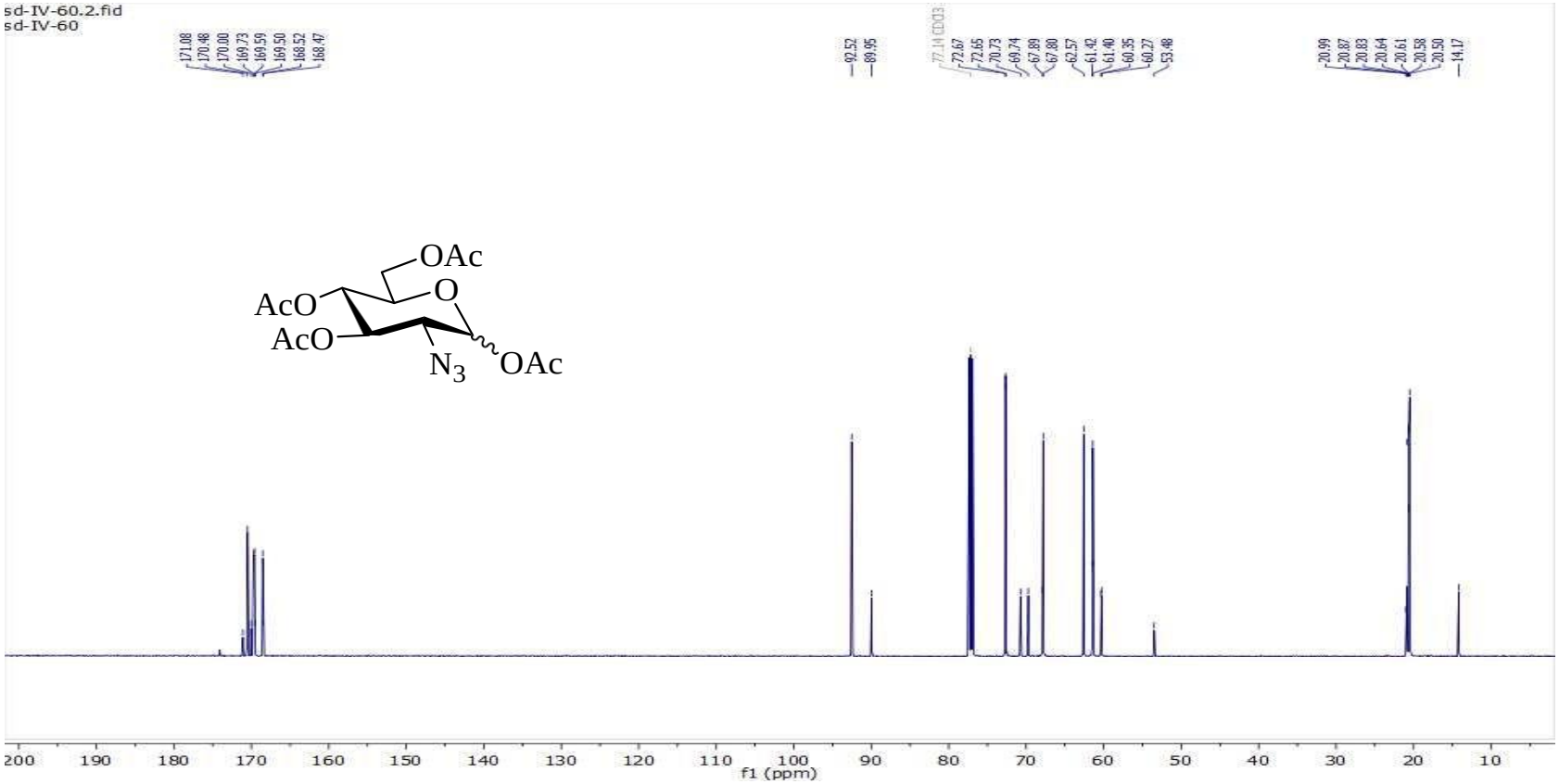


Figure 58. $^{13}C$ NMR spectrum of S26 (150 MHz, $CDCl_3$).

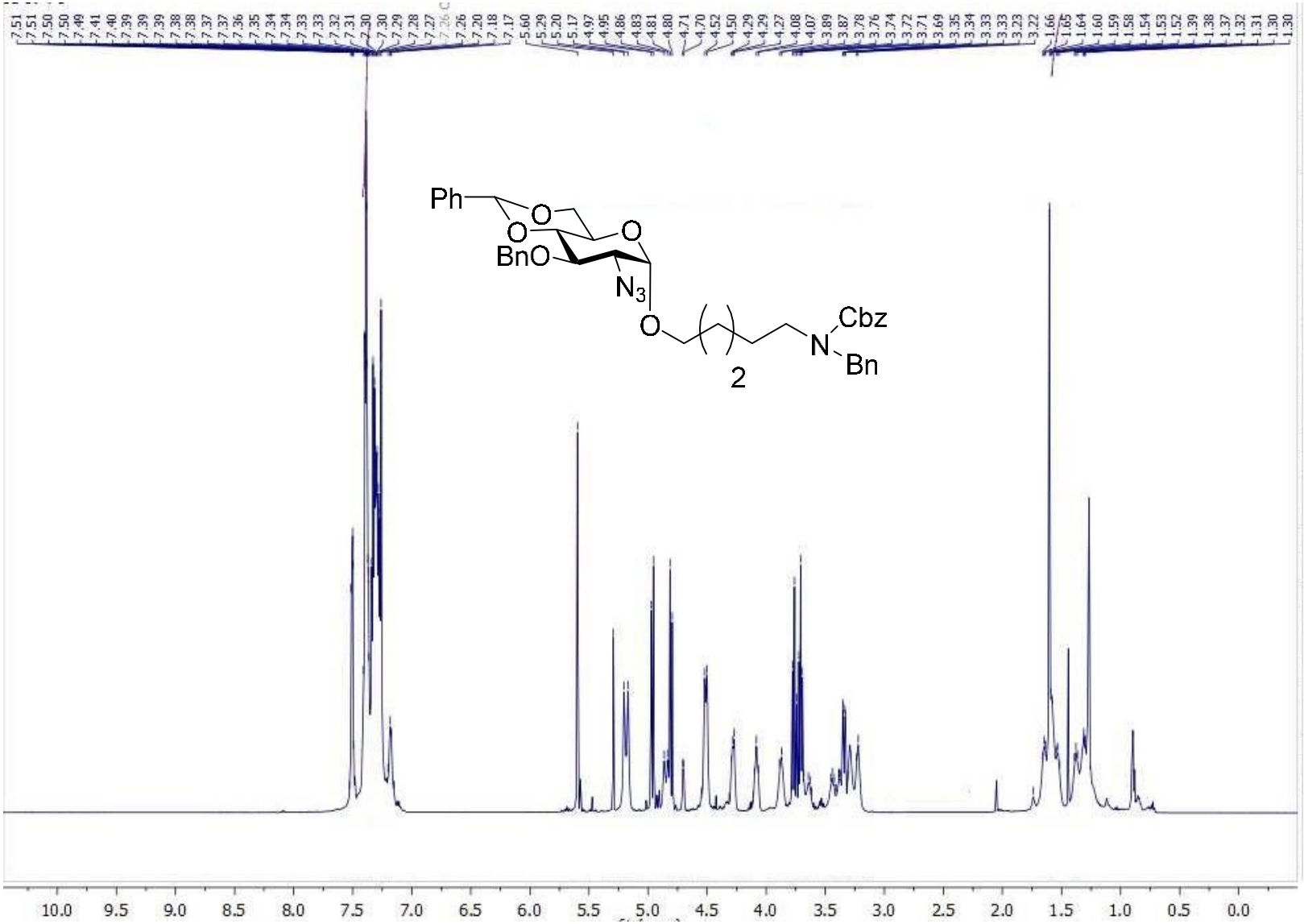


Figure 59. $^{1}H$ NMR spectrum of S31 (600 MHz, $CDCl_3$).

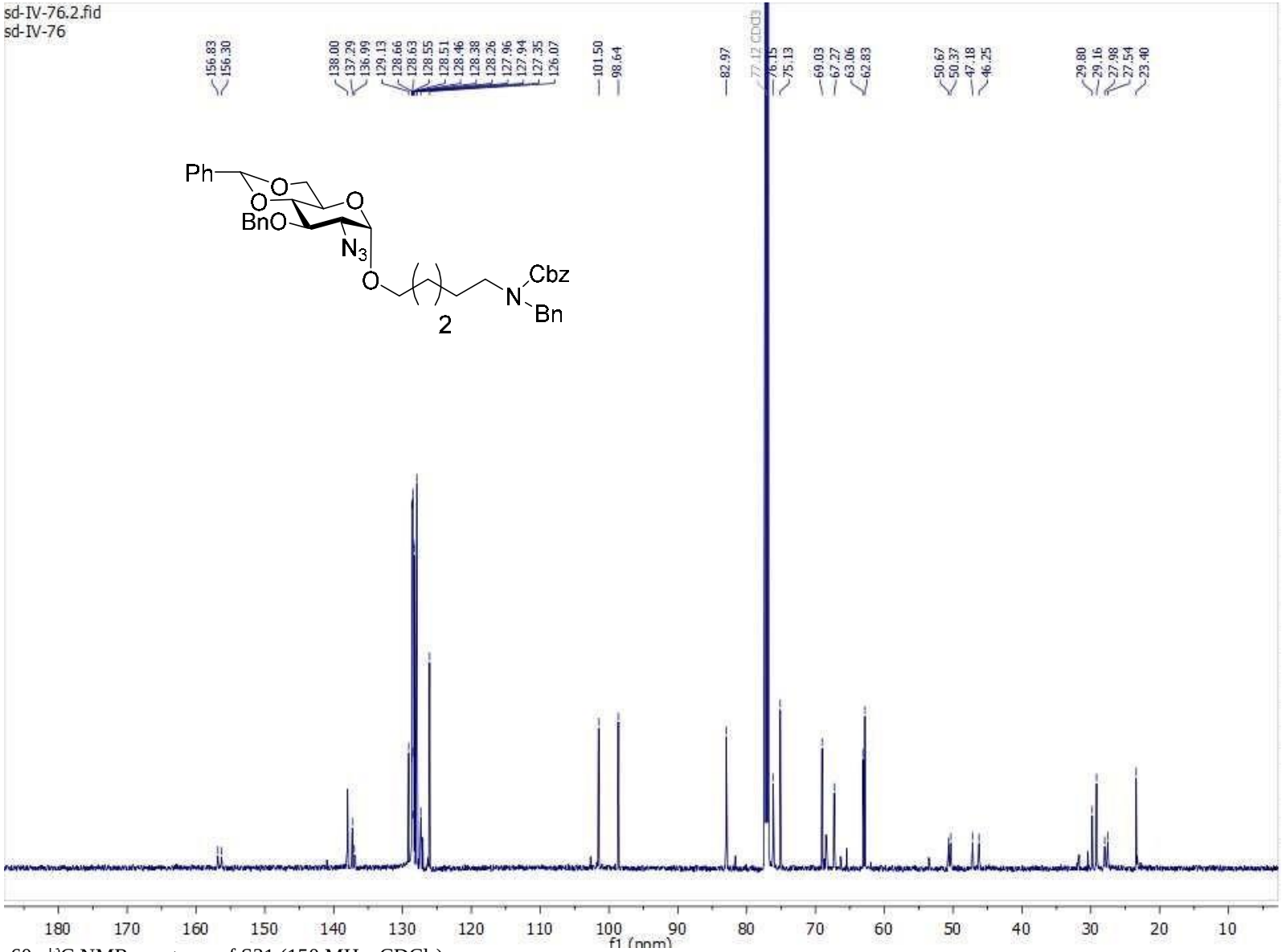


Figure 60. $^{13}C$ NMR spectrum of S31 (150 MHz, $CDCl_3$).

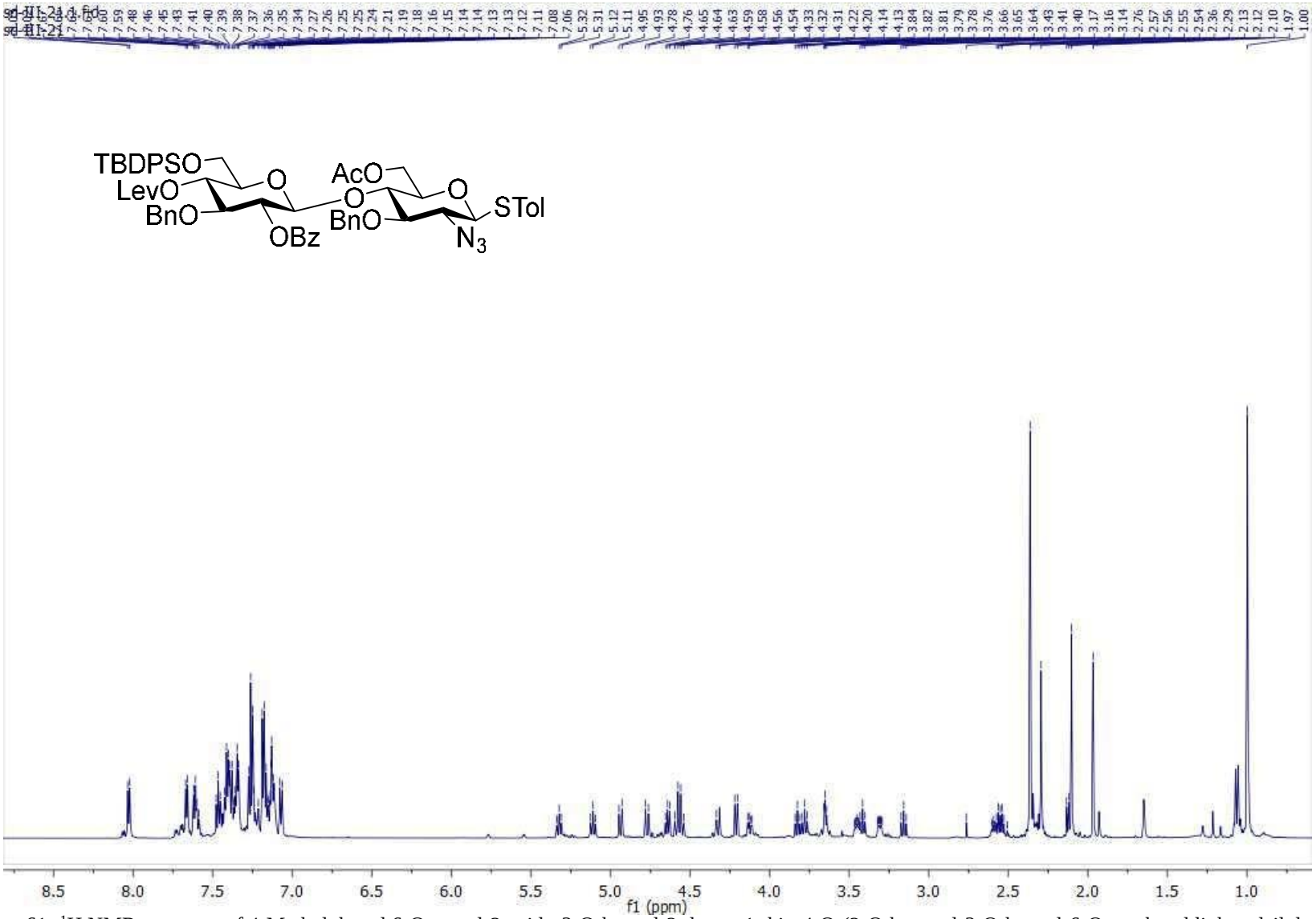


Figure 61. $^{1}$H NMR spectrum of 4-Methylphenyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-6-O-tert-butyldiphenylsilyl-4-O-levunlinyl-β-D-glucopyranosyl)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

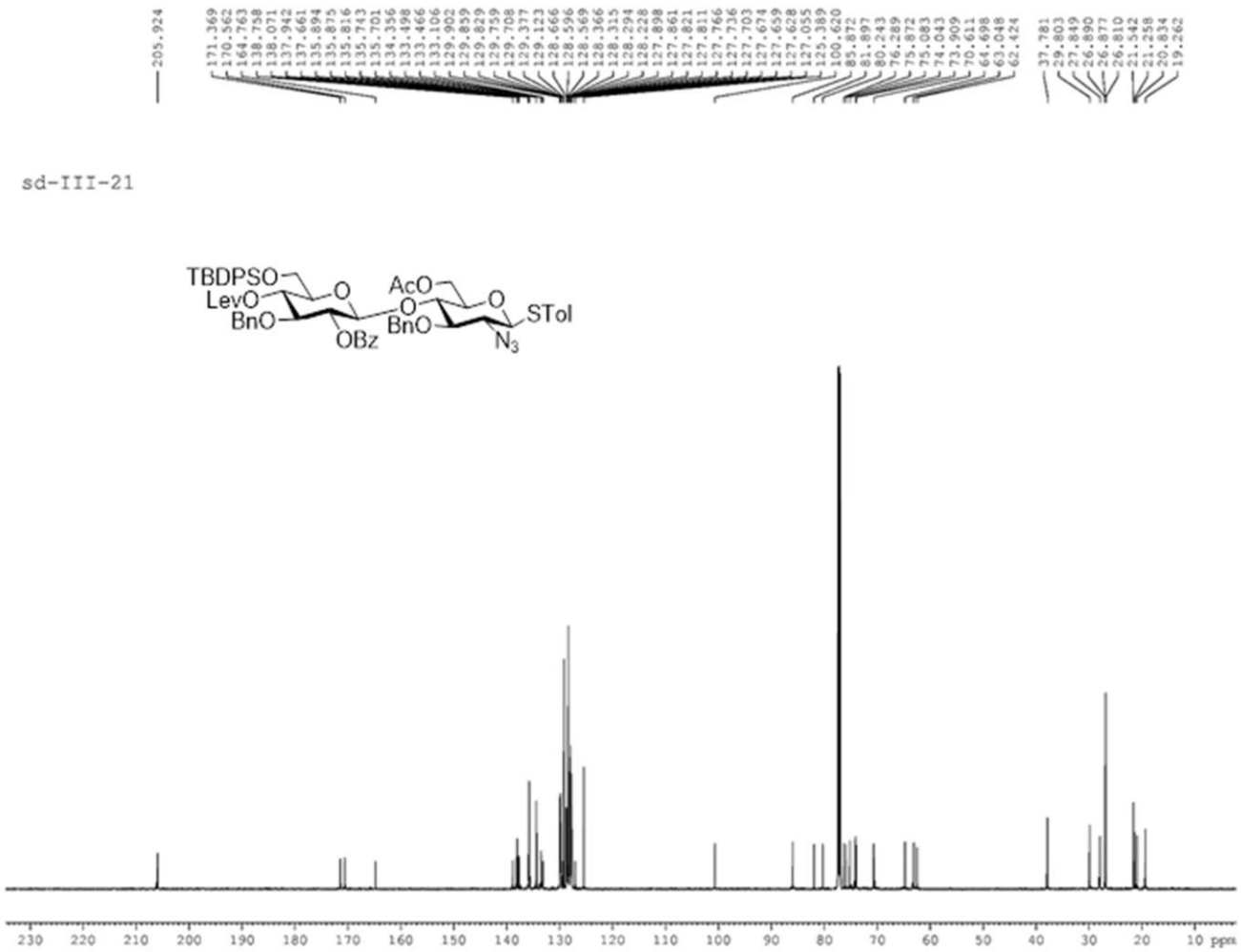


Figure 62. $^{13}$C NMR spectrum of 4-Methylphenyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-6-O-tert-butyldiphenylsilyl-4-O-levunlinyl-β-D-glucopyranosyl)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

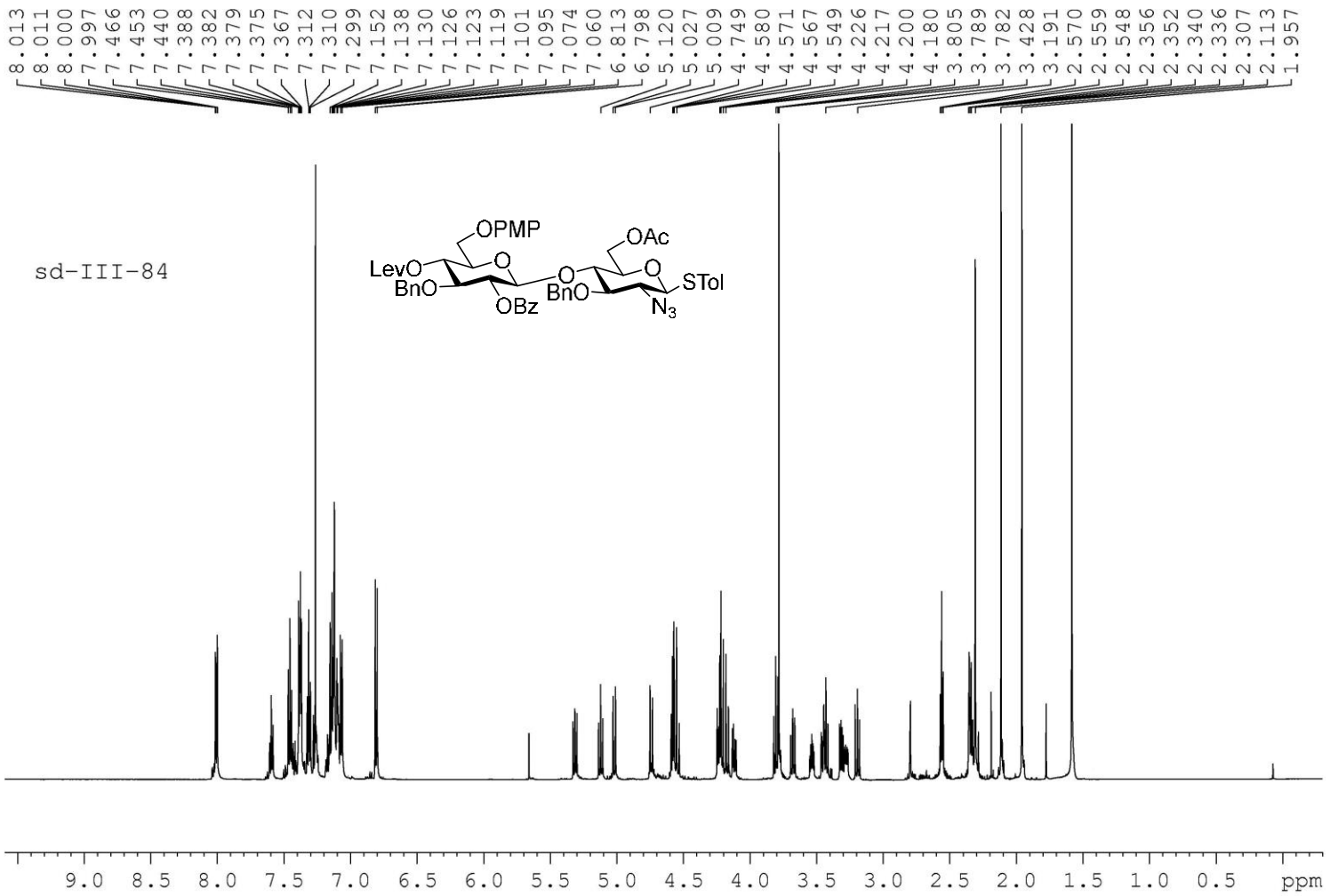


Figure 63. $^{1}$H NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-4-O-levunlinyl-6-O-p-methoxybenzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

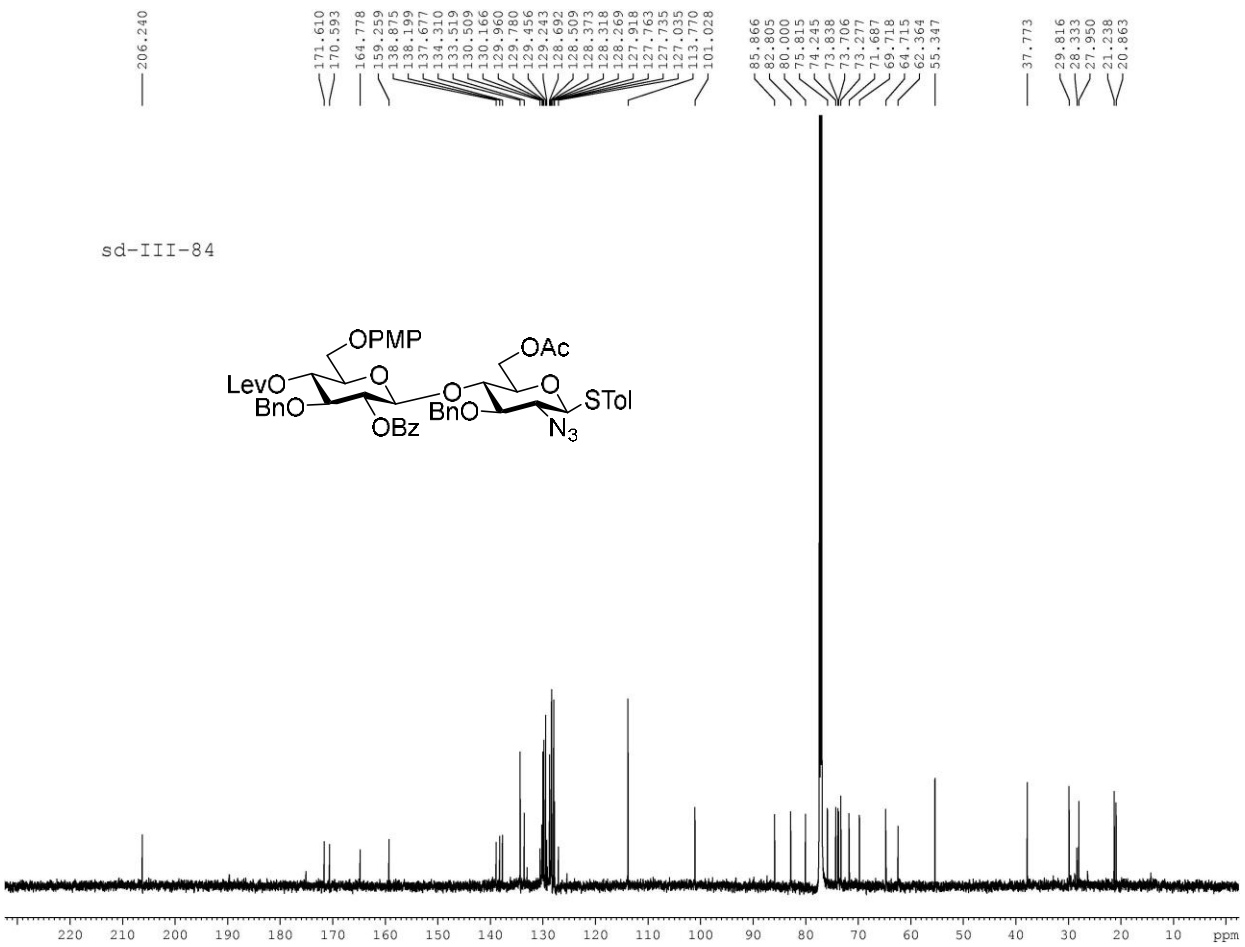


Figure 64. $^{13}C$ NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-4-O-levunlinyl-6-O-p-methoxybenzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

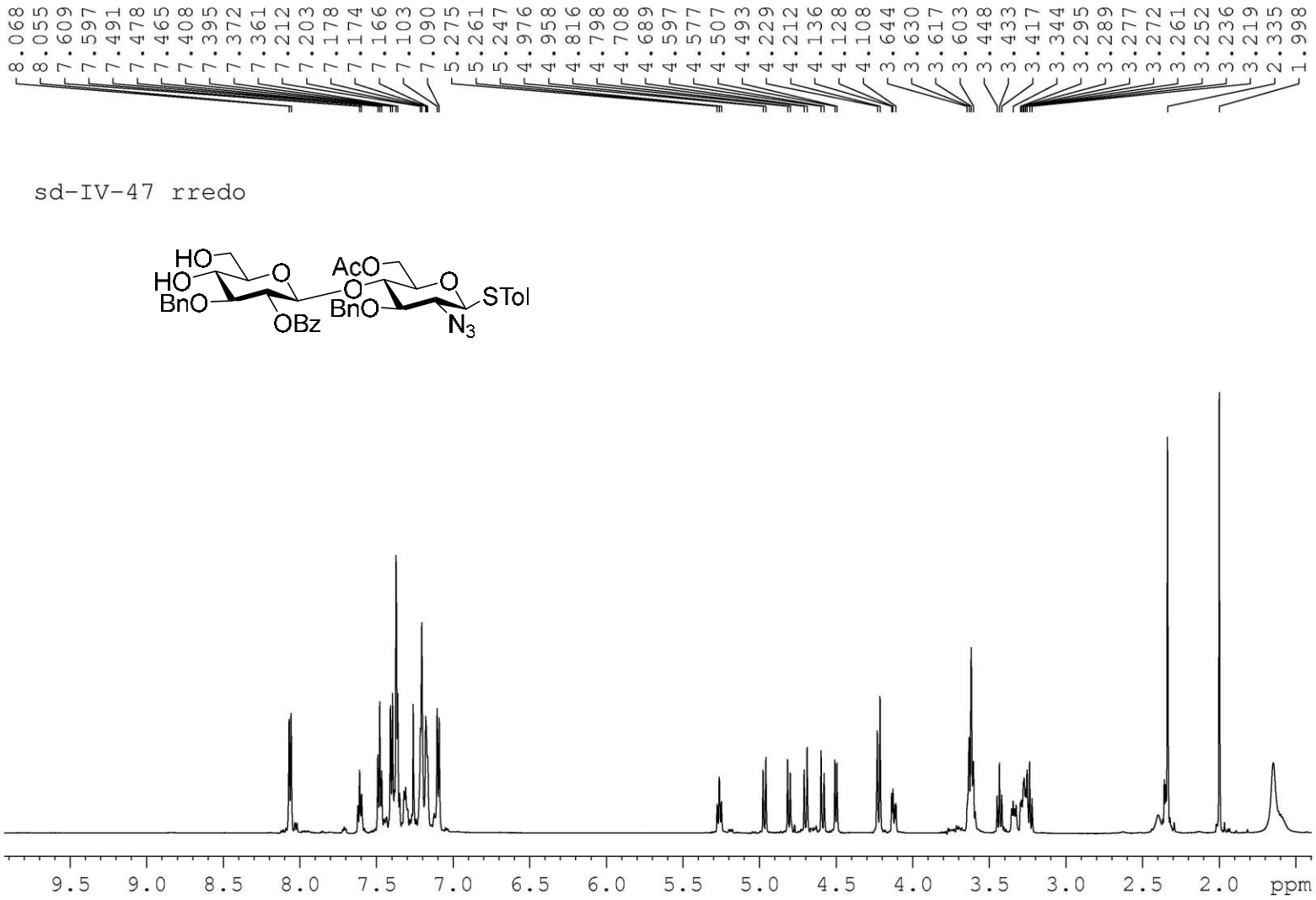


Figure 65. $^{1}$H NMR spectrum of 4-Methylphenyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

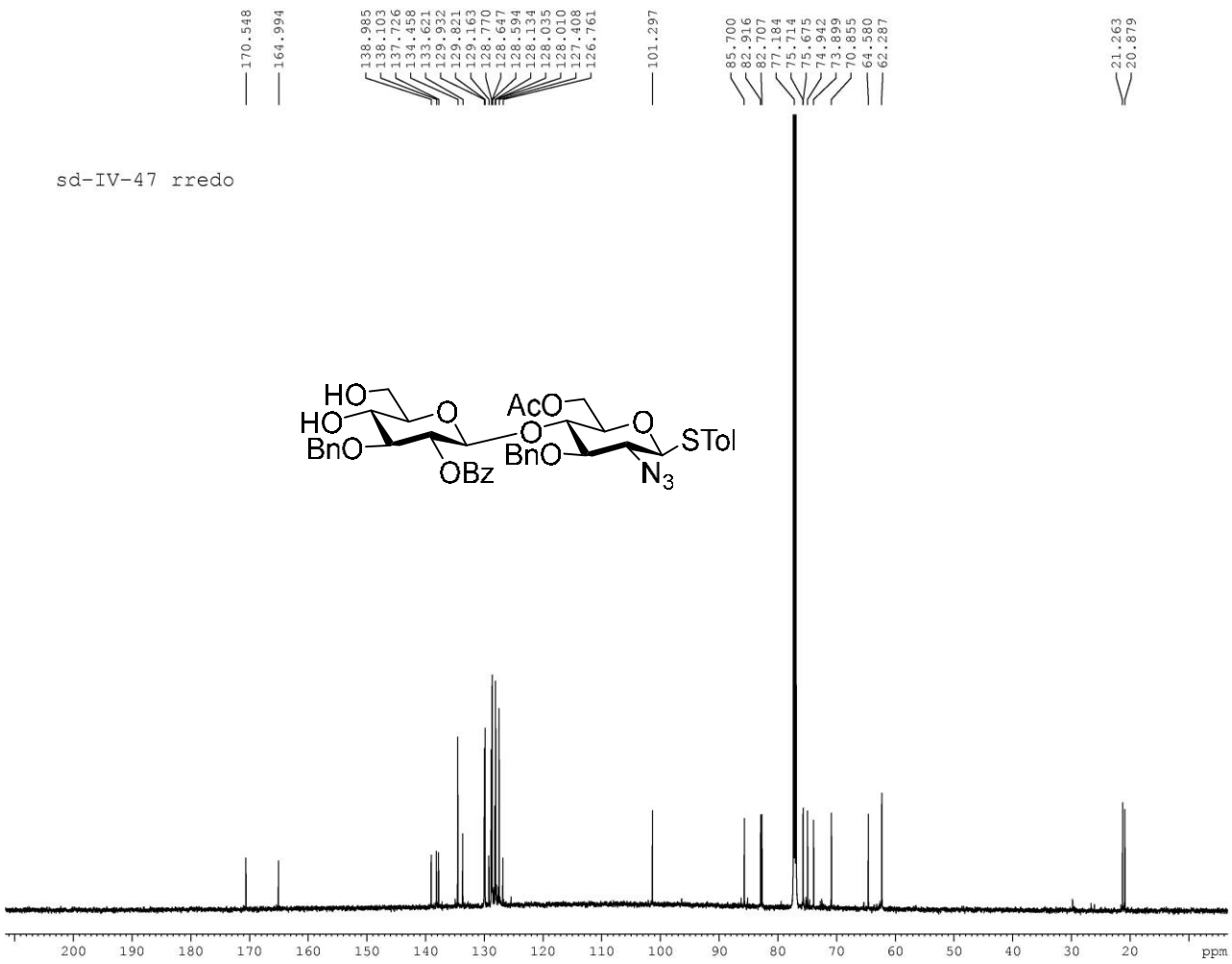


Figure 66. $^{13}C$ NMR spectrum of 4-Methylphenyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

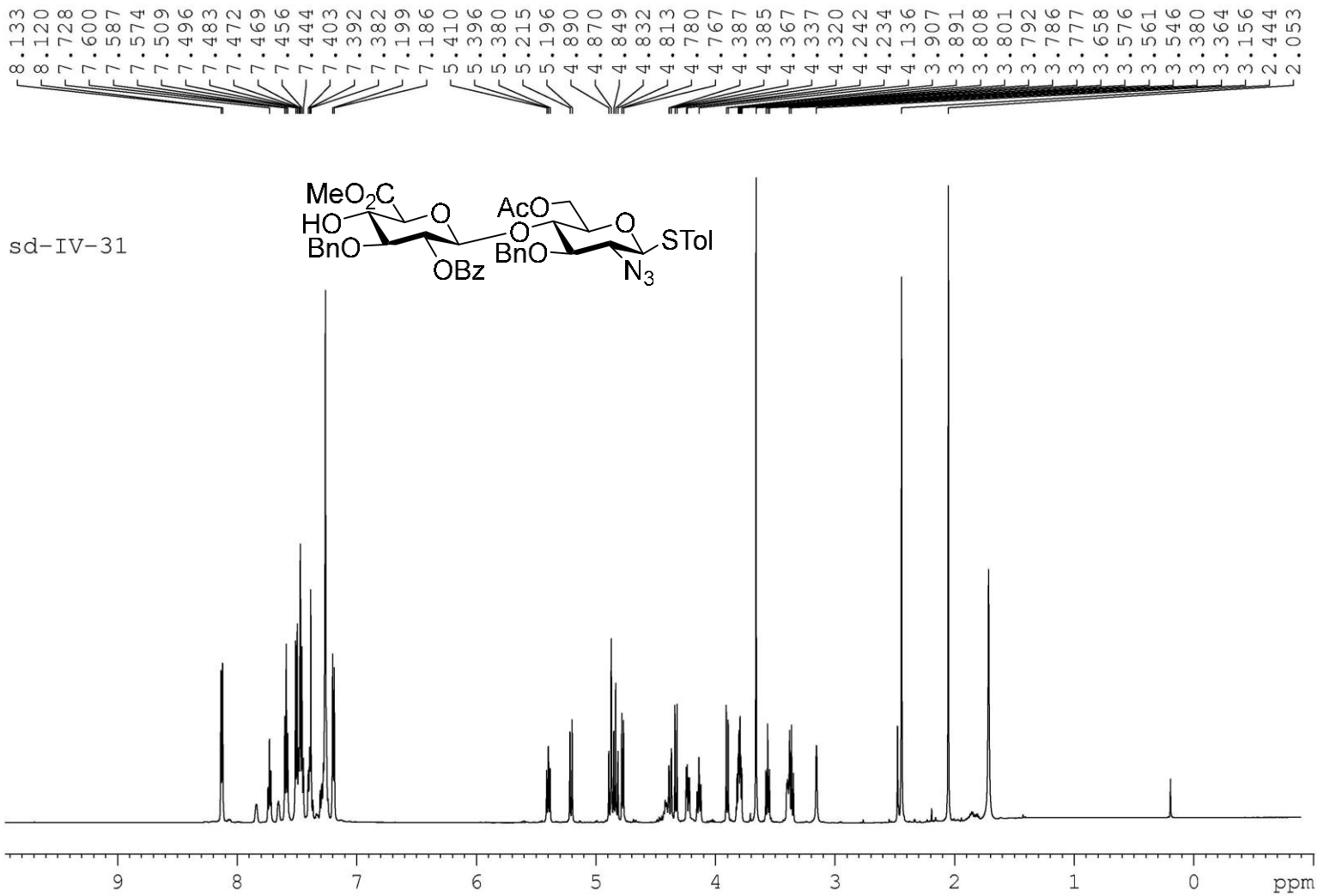


Figure 67. $^{1}$H NMR spectrum of 4-Methylphenyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(methyl 2-O-benzoyl-3-O-benzyl-β-D-glucopyranosyluronate)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

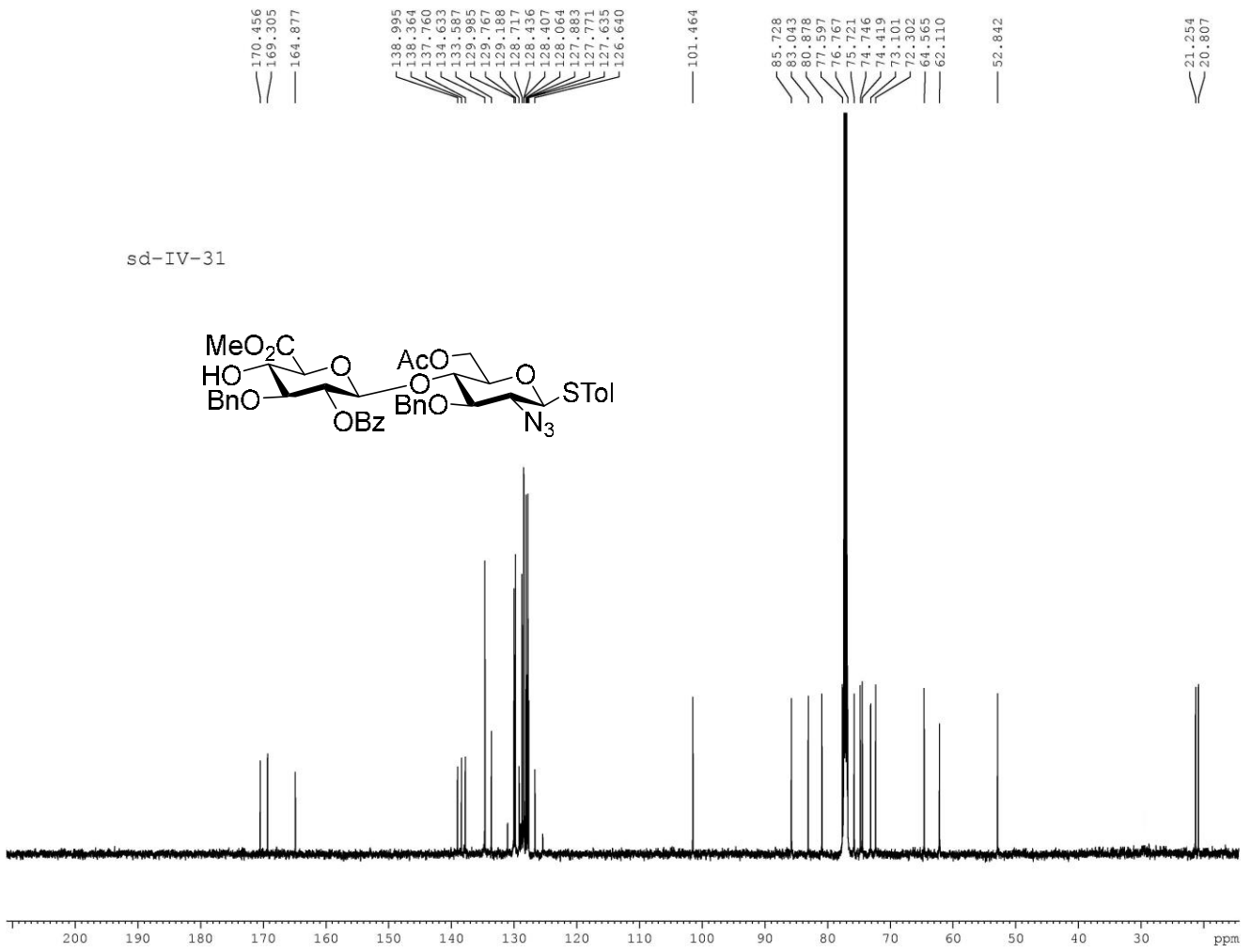


Figure 68. $^{13}C$ NMR spectrum of 4-Methylphenyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(methyl 2-O-benzoyl-3-O-benzyl-β-D-glucopyranosyluronate)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

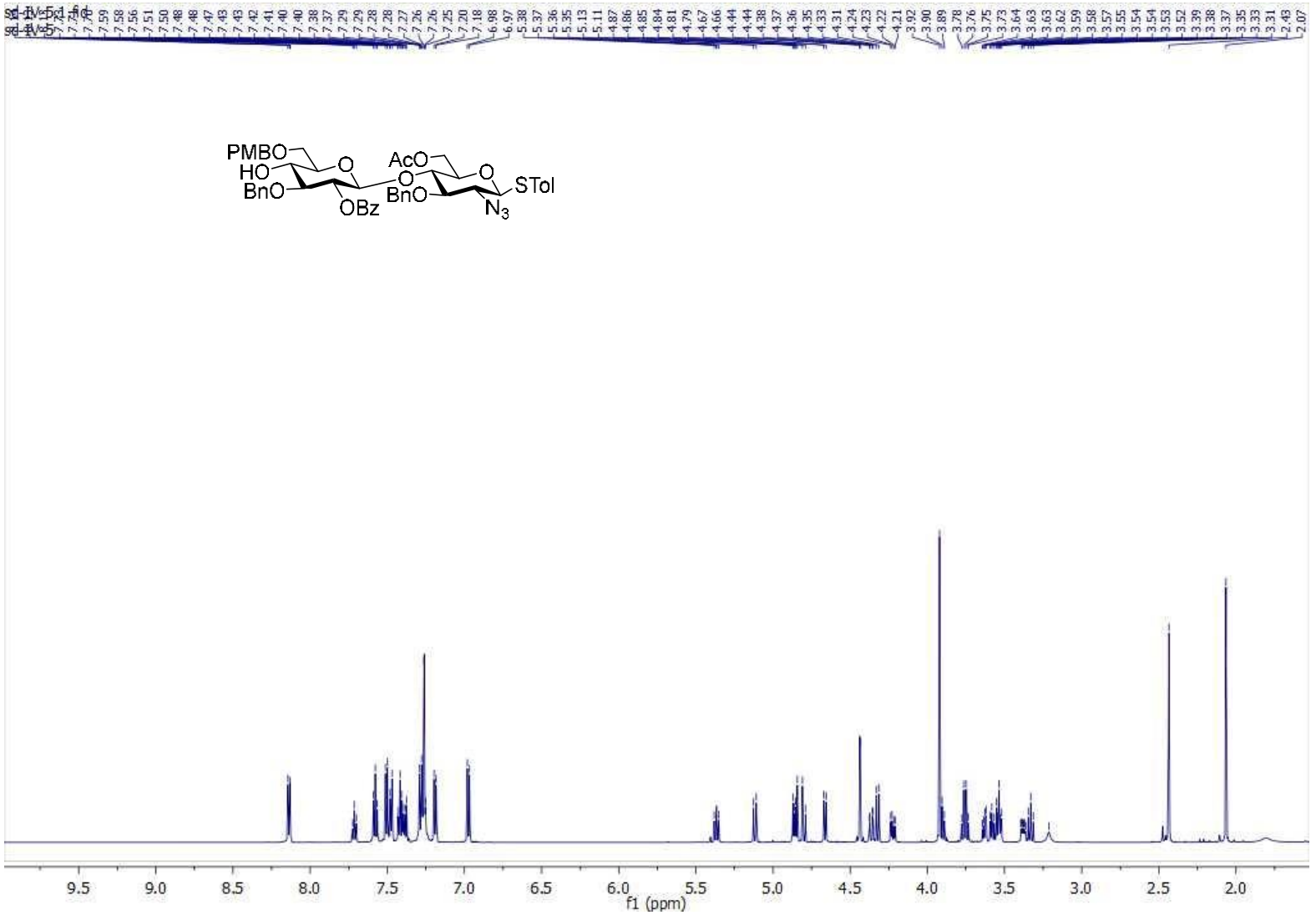


Figure 69. $^{1}$H NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-6-O-p-methoxybenzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (600 MHz, $CDCl_3$)

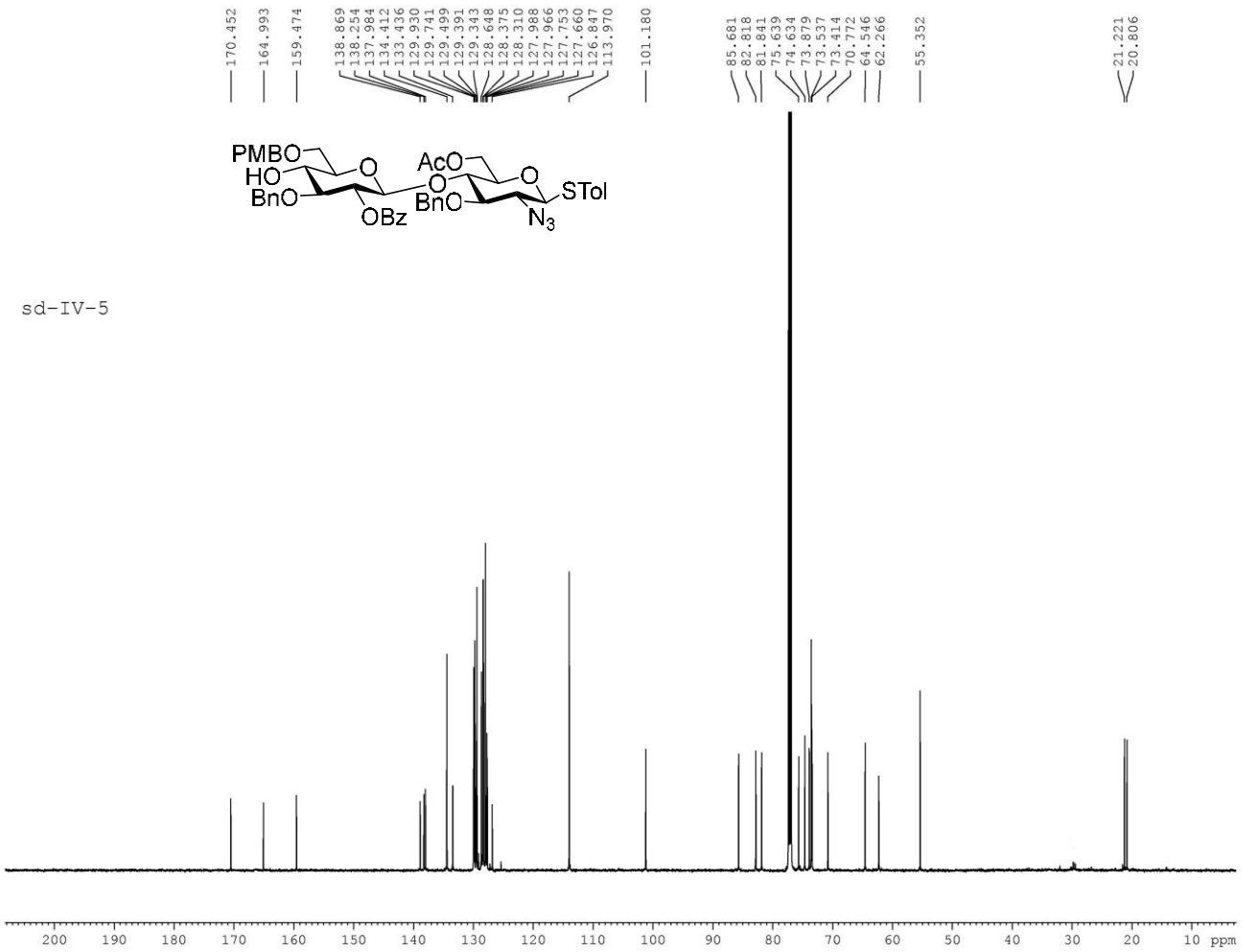


Figure 70. $^{13}$C NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-benzoyl-3-O-benzyl-6-O-p-methoxybenzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

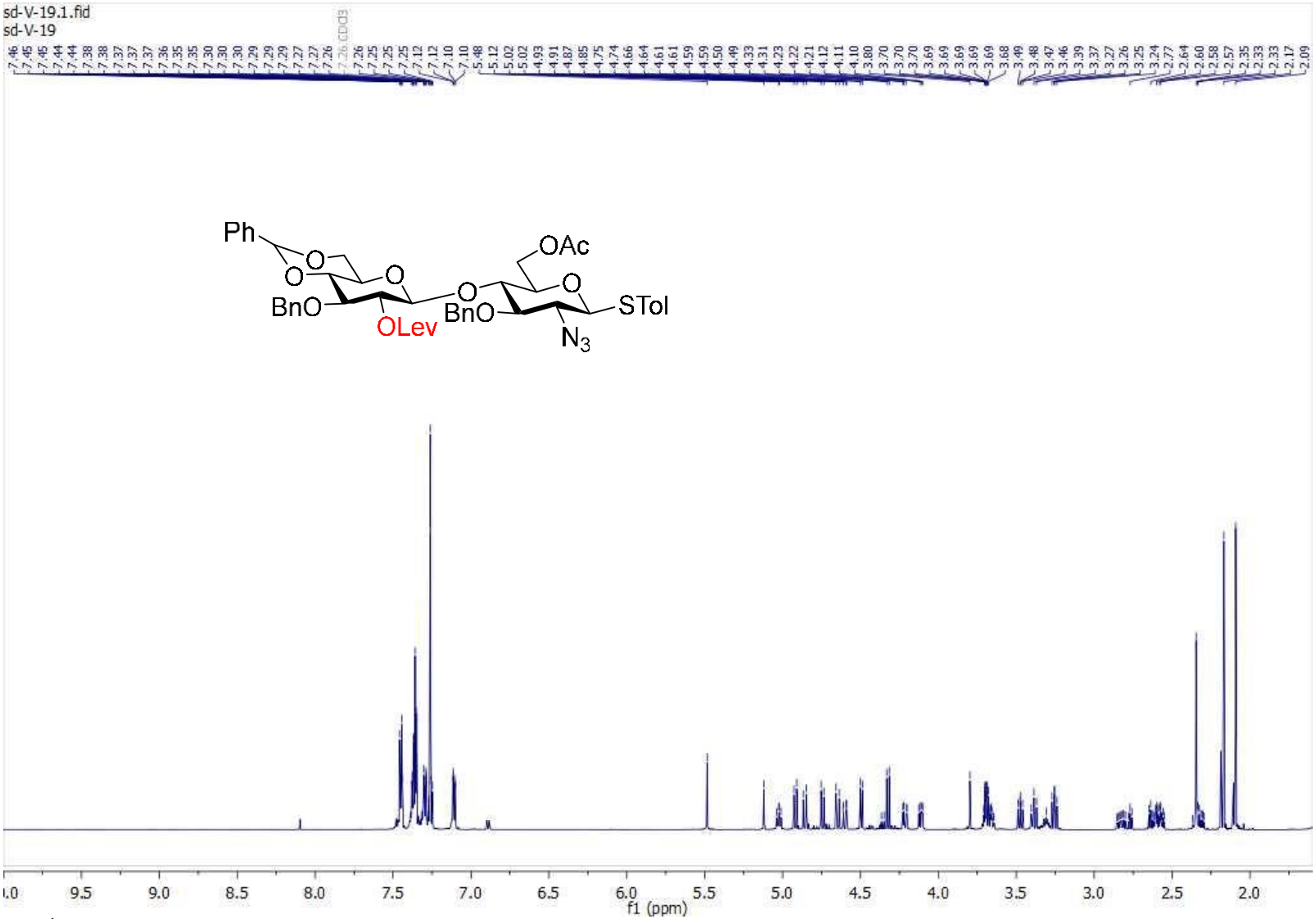


Figure 71. $^{1}$H NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-levunlinyl-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

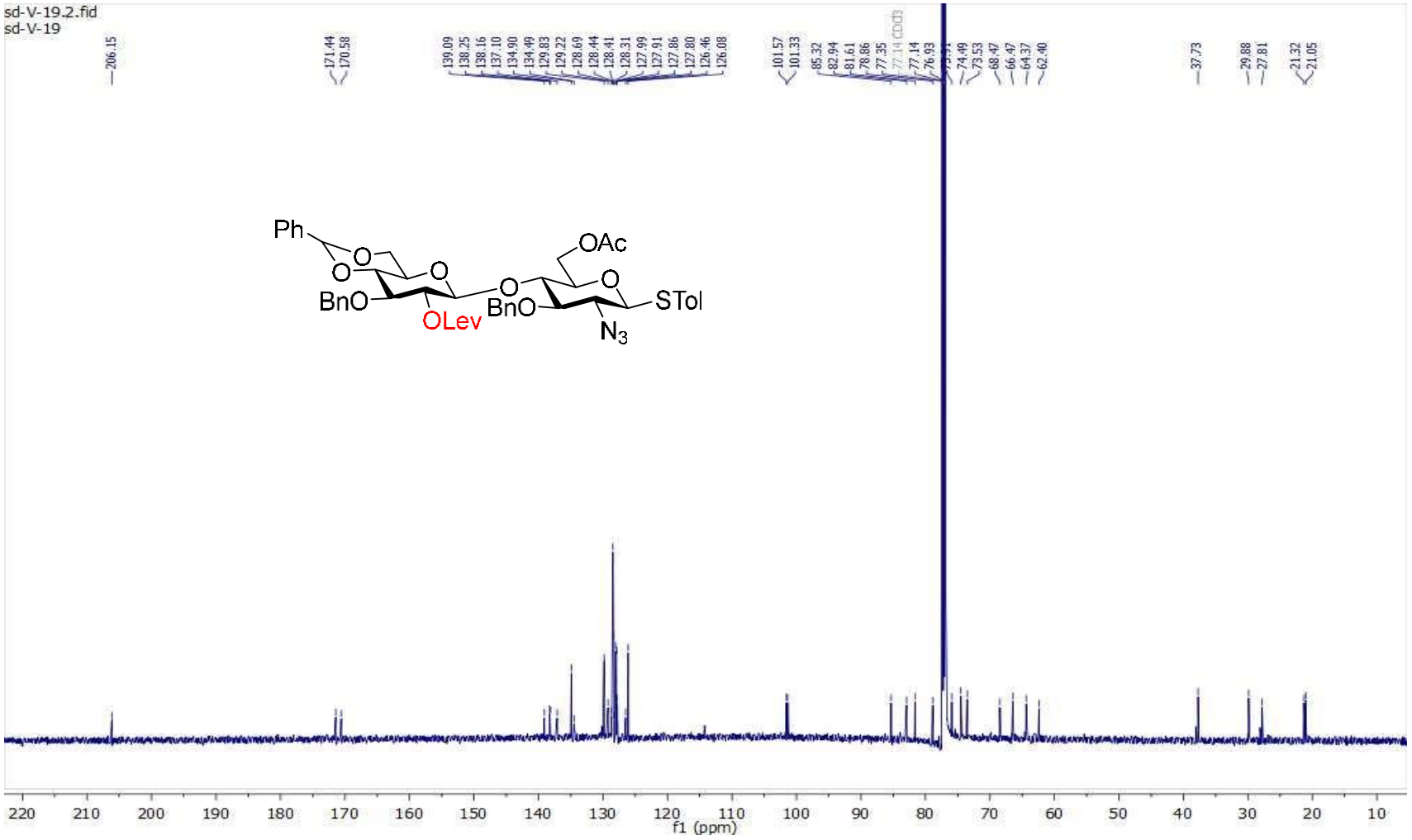


Figure 72. $^{13}$C NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(2-O-levunlinyl-3-O-benzyl-4,6-O-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

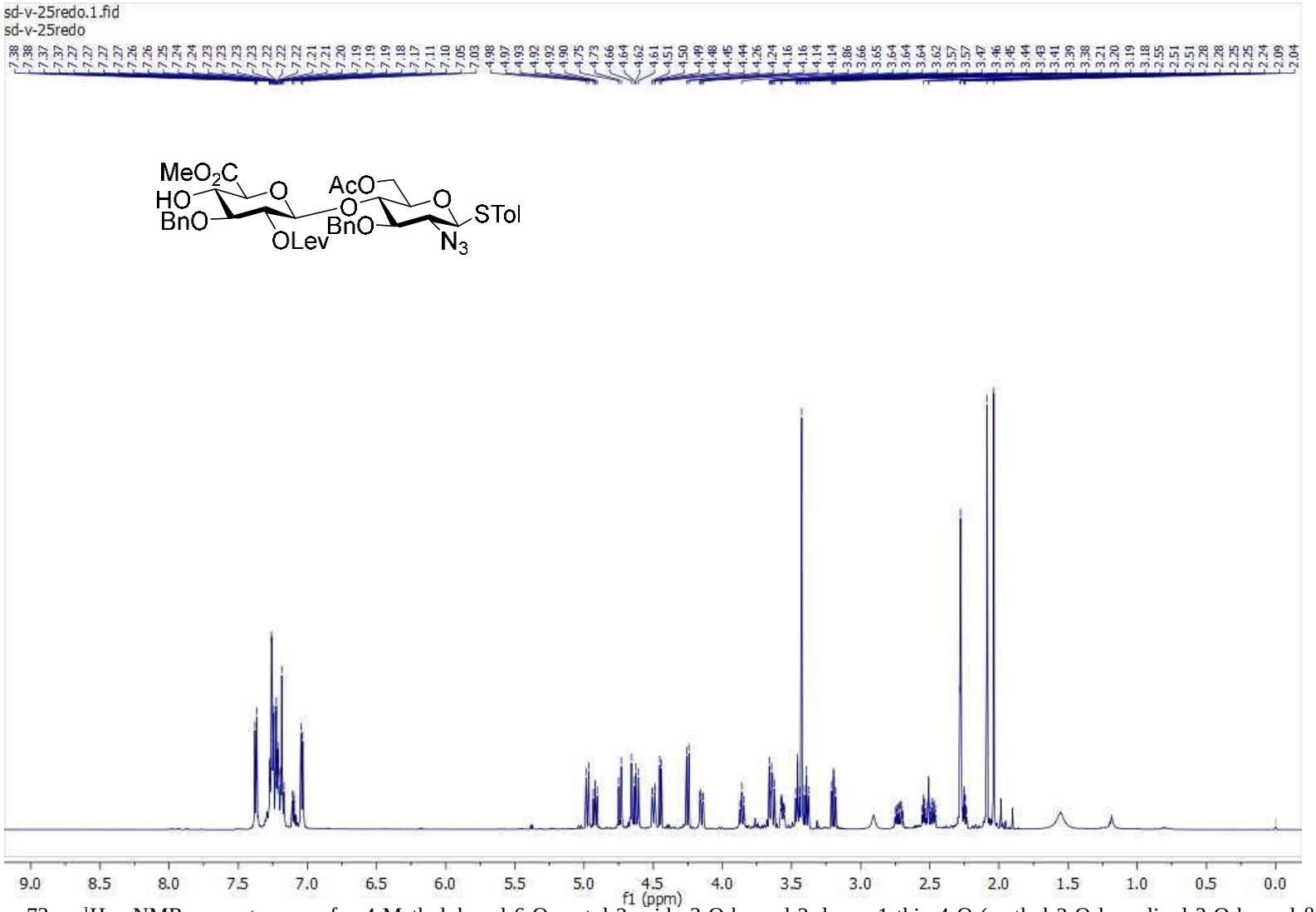


Figure 73. $^{1}$H NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(methyl-2-O-levunlinyl-3-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

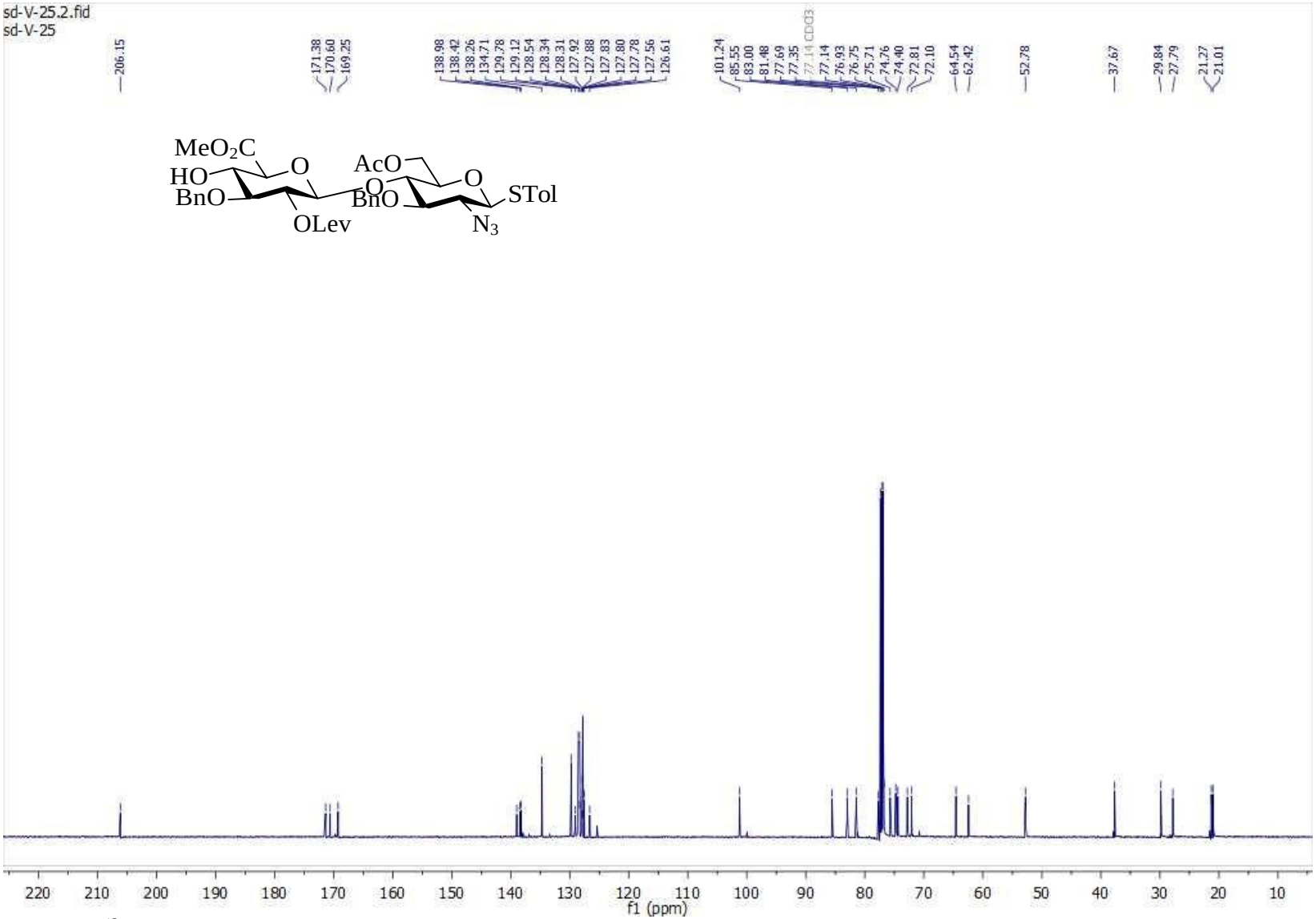


Figure 74. $^{13}C$ NMR spectrum of 4-Methylphenyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-1-thio-4-O-(methyl-2-O-levunlinyl-3-O-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

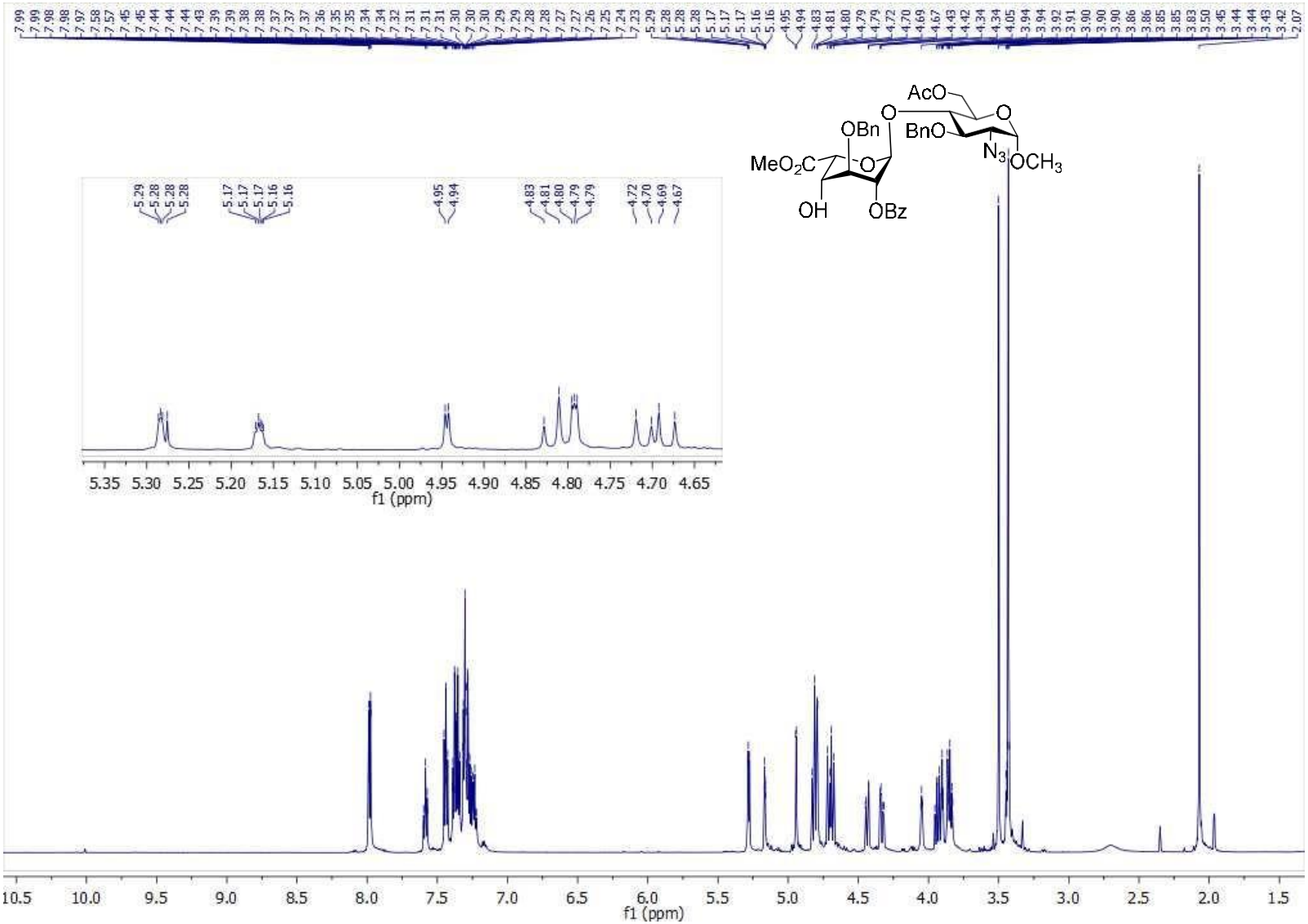


Figure 75. $^{1}$H NMR spectrum of Methyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl-2-O-benzoyl-3-O-benzyl-α-L-idopyranosyluronate)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

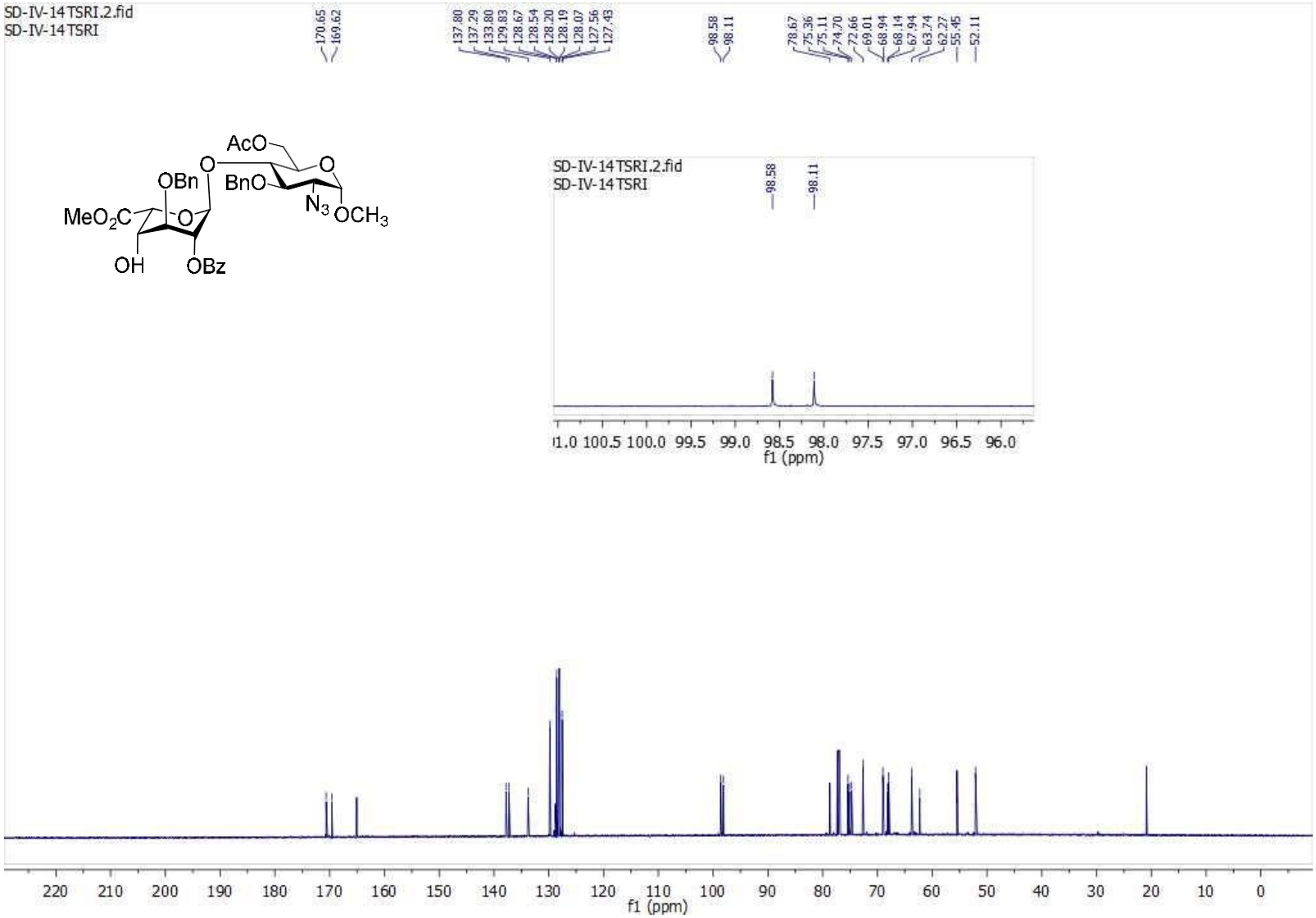


Figure 76. $^{13}C$ NMR spectrum of Methyl 6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl 2-O-benzoyl-3-O-benzyl-α-L-idopyranosyluronate)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

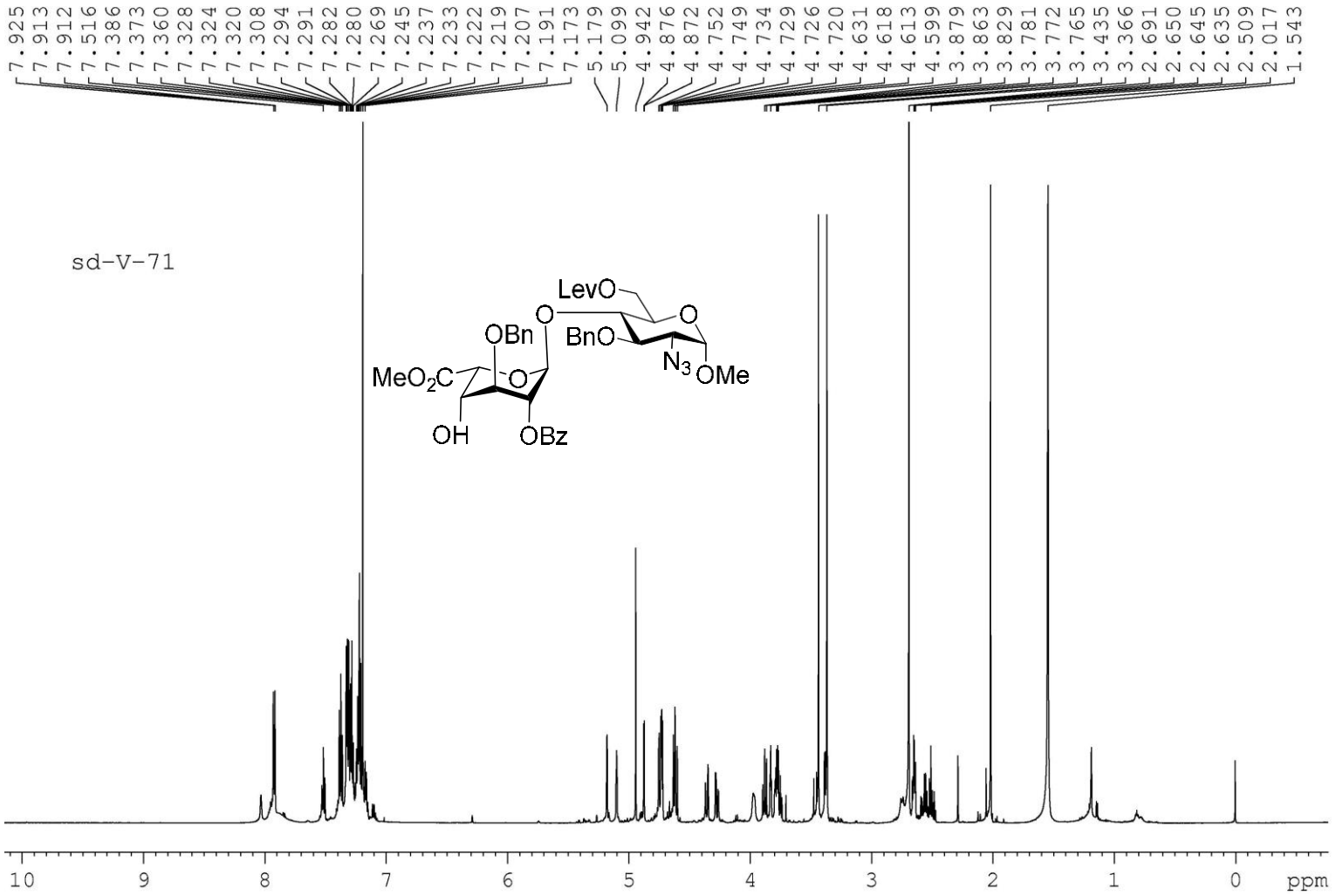


Figure 77. $^{1}$H NMR spectrum of Methyl 6-O-levunlinyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl 2-O-benzoyl-3-O-benzyl-α-L-idopyranosyluronate)-β-D-glucopyranoside (600 MHz, $CDCl_3$).

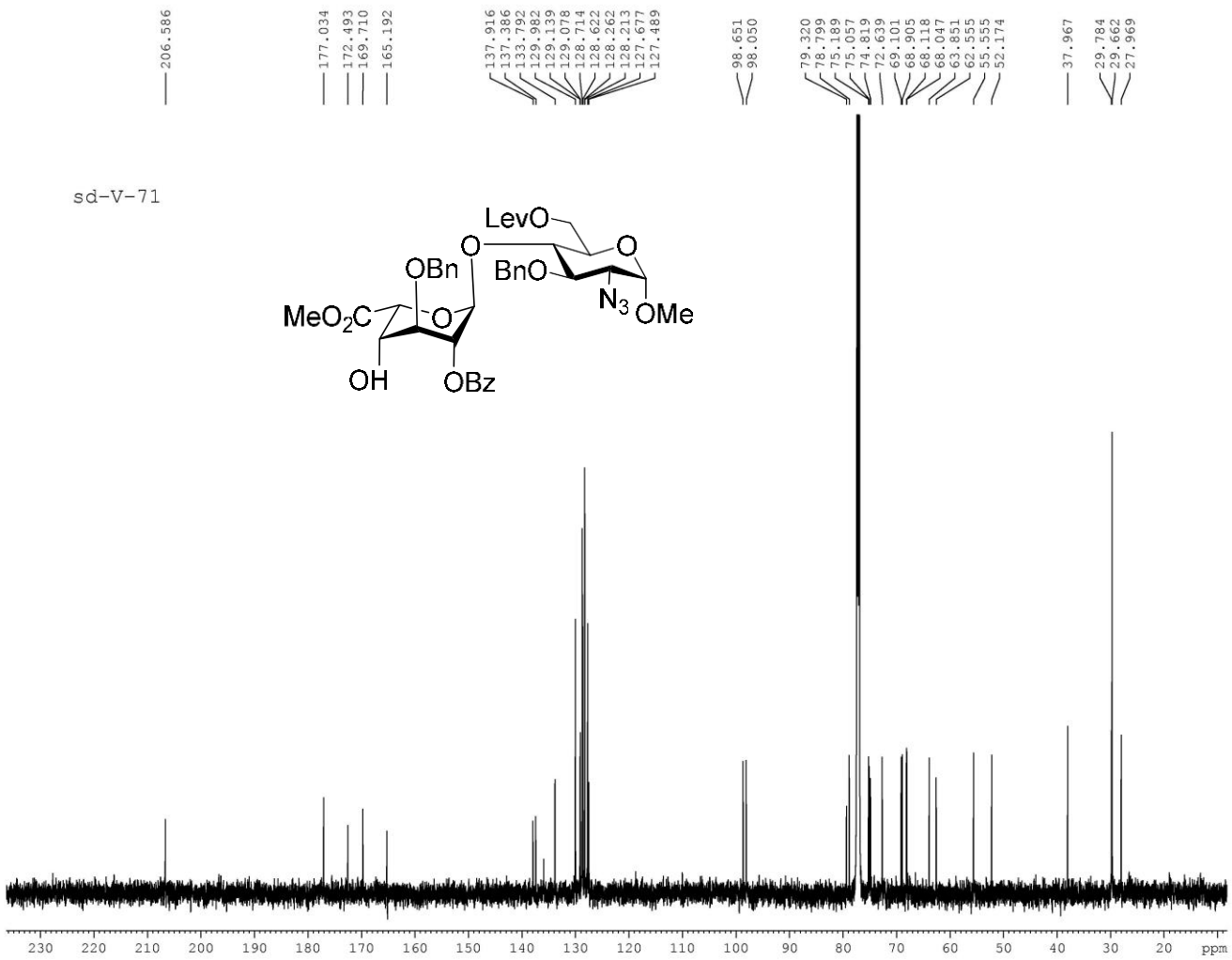


Figure 78. $^{13}$C NMR spectrum of Methyl 6-O-levunlinyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl 2-O-benzoyl-3-O-benzyl-α-L-idopyranosyluronate)-β-D-glucopyranoside (150 MHz, $CDCl_3$).

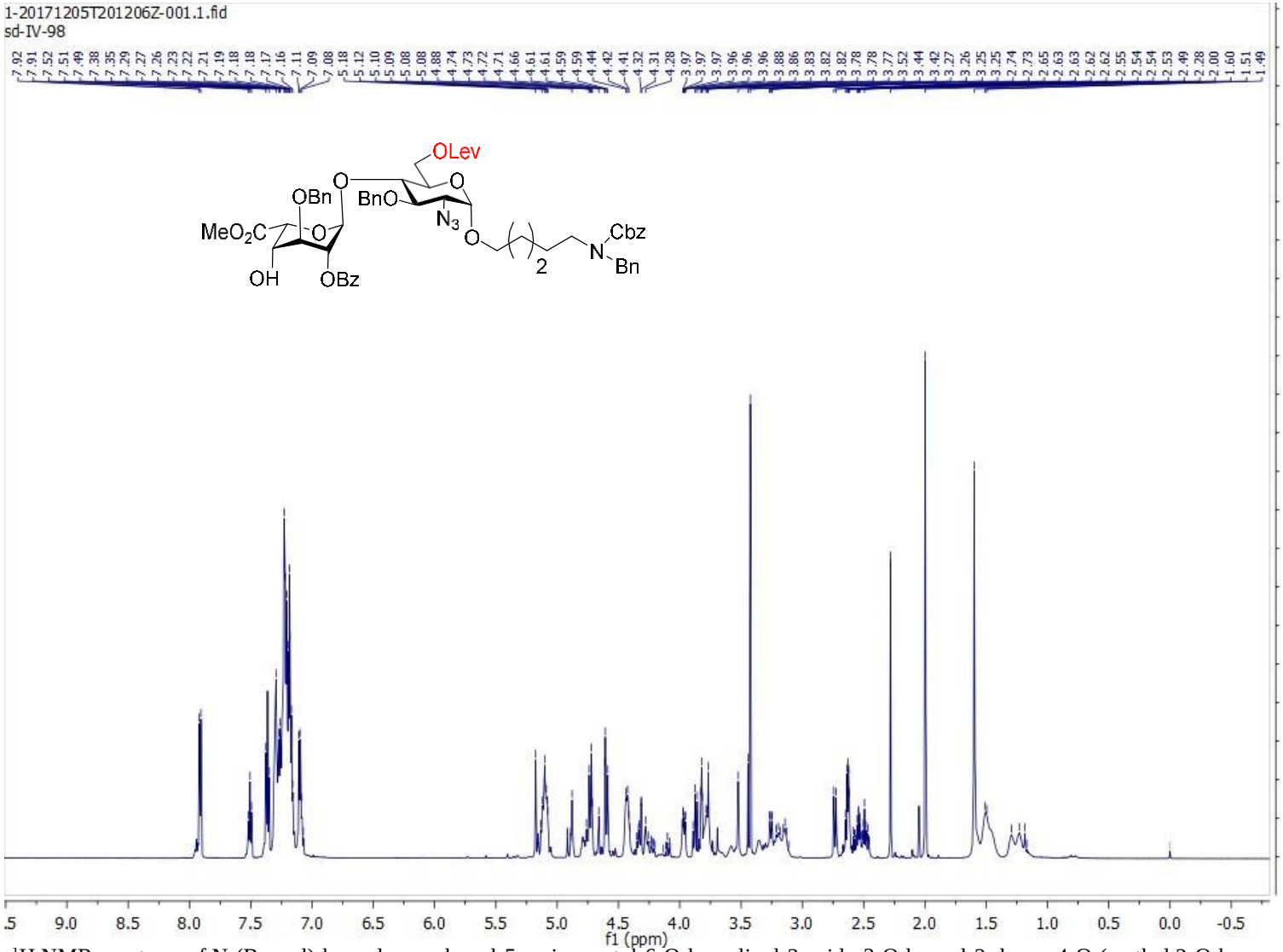


Figure 79. $^{1}$H NMR spectrum of N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-6-O-levunlinyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl 2-O-benzoyl-3-O-benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside (600 MHz, $CDCl_3$).

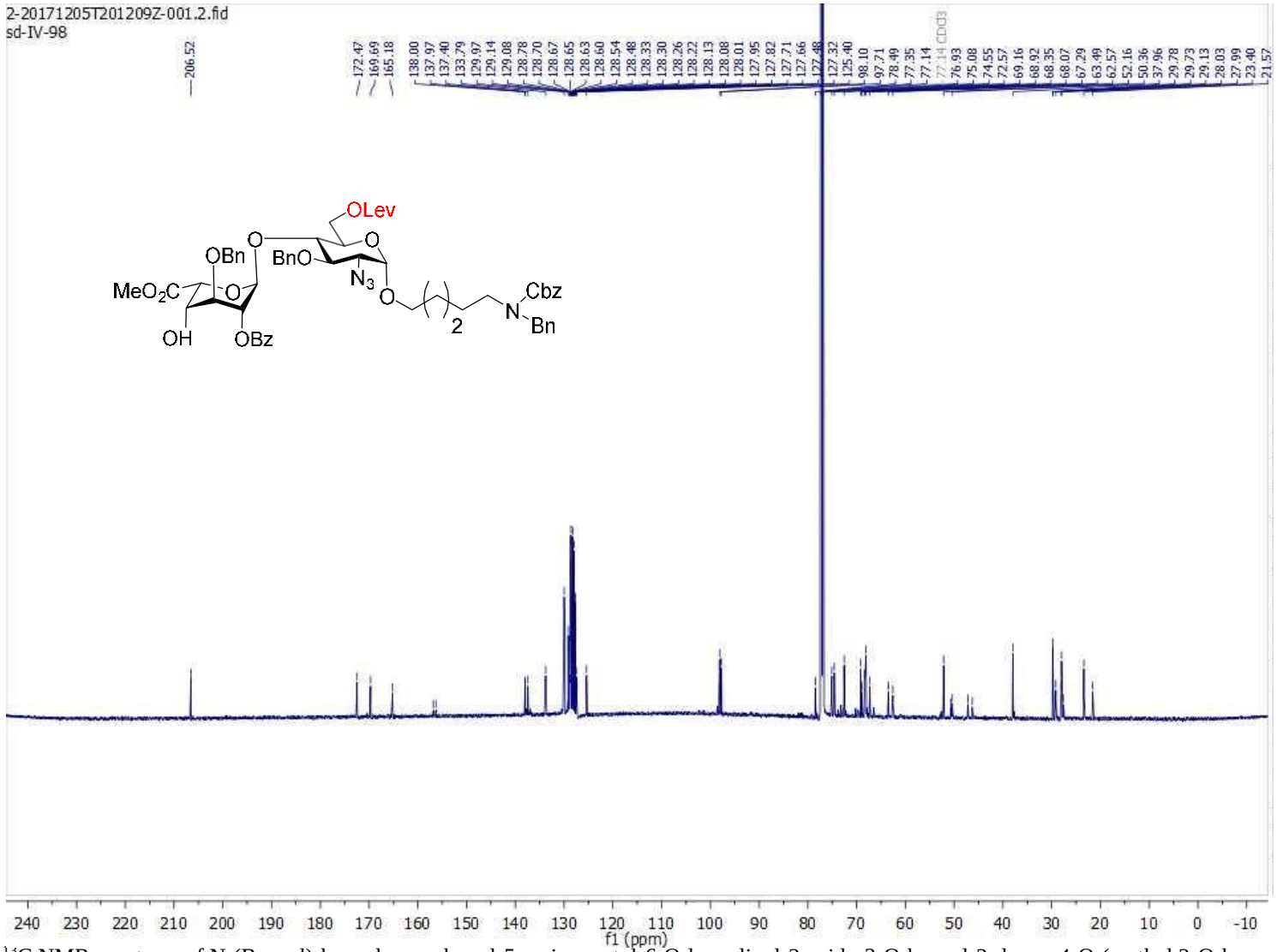


Figure 80. $^{13}$C NMR spectrum of N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-6-O-levunlinyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl 2-O-benzoyl-3-O-benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside (150MHz, $CDCl_3$).

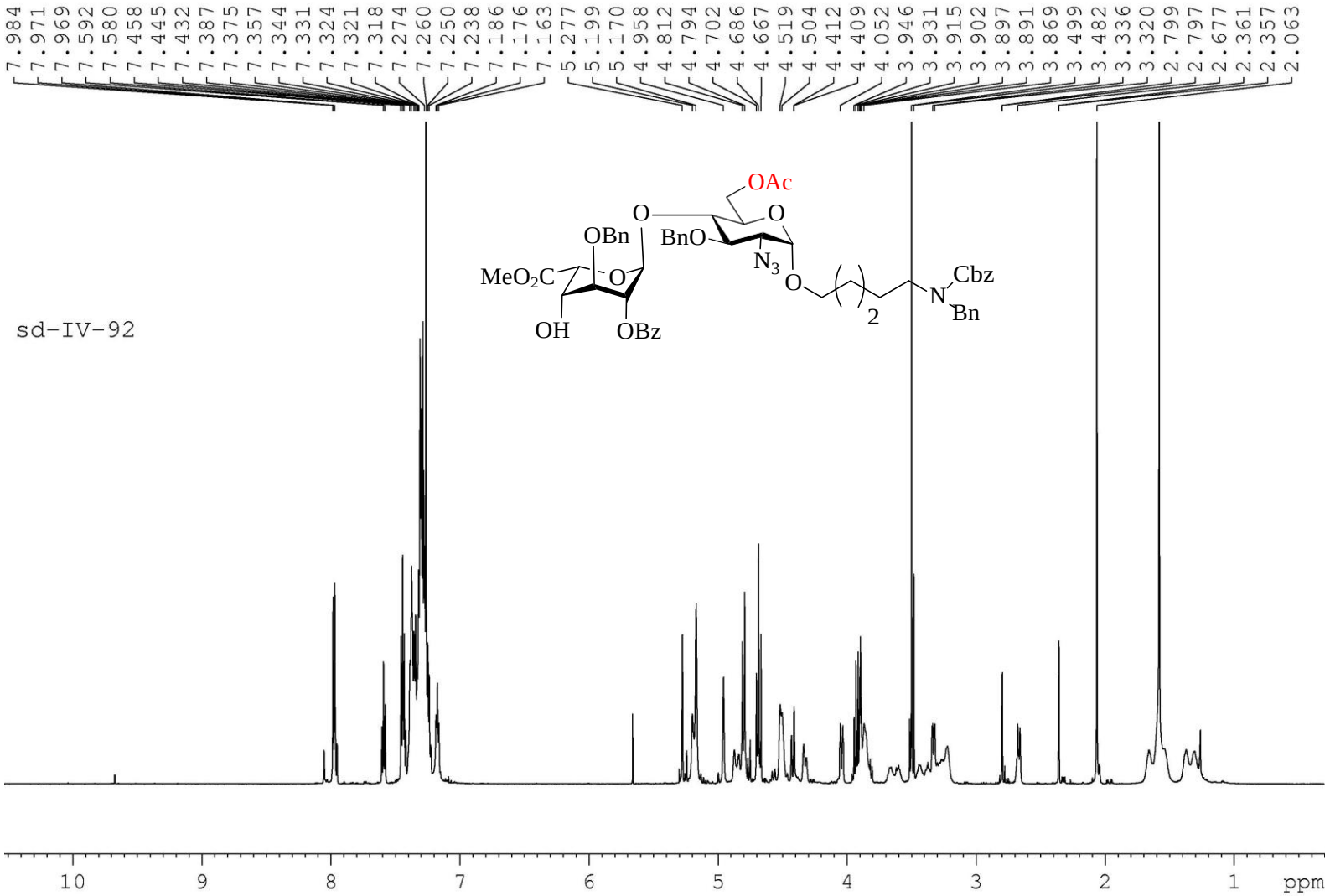


Figure 81. $^{1}$H NMR spectrum of N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl-2-O-benzoyl-3-O-benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside(600 MHz, $CDCl_3$).

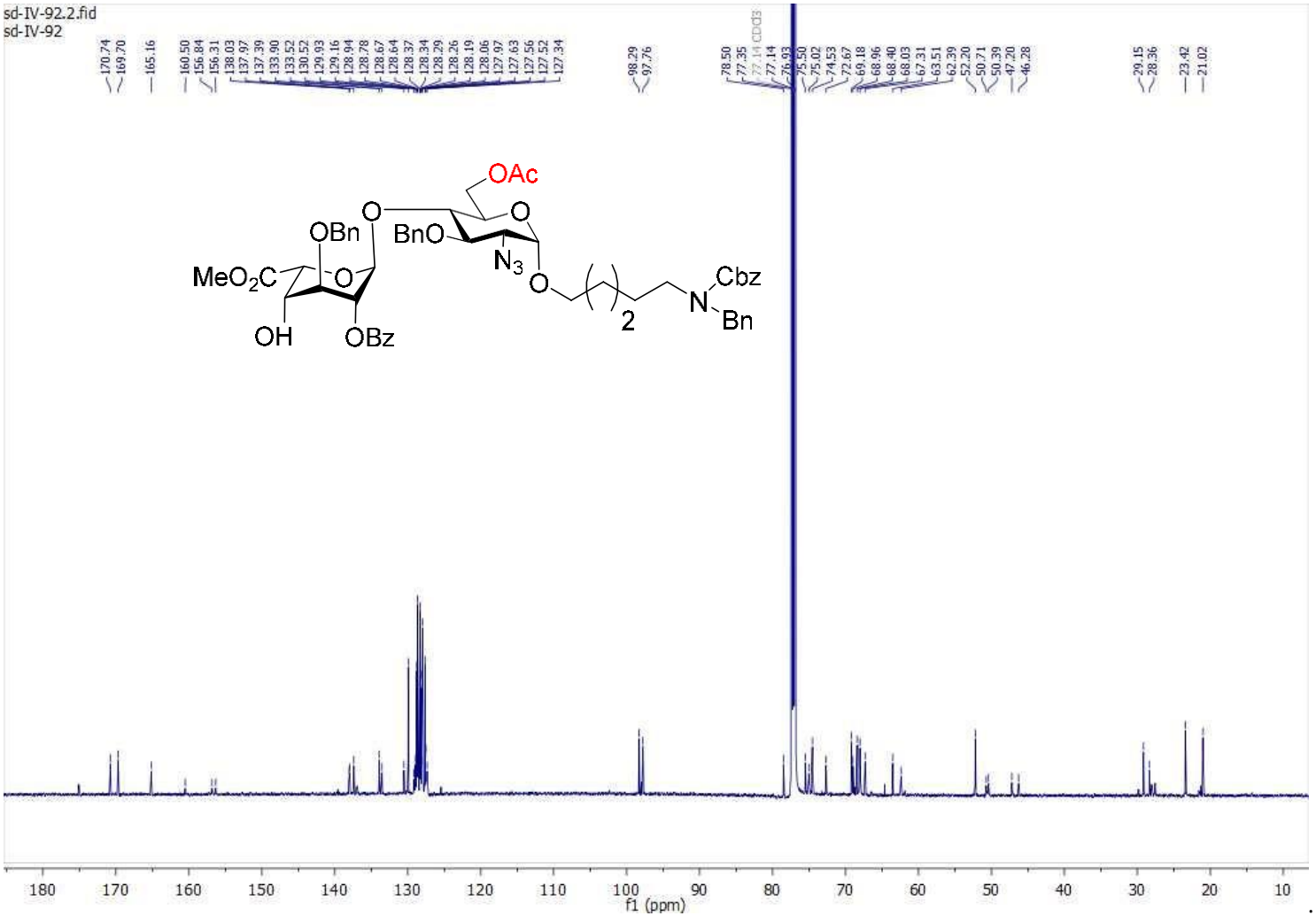


Figure 82. $^{13}$C NMR spectrum of N-(Benzyl)-benzyloxycarbonyl-5-aminopentyl-6-O-acetyl-2-azido-3-O-benzyl-2-deoxy-4-O-(methyl 2-O-benzoyl-3-O- benzyl-α-L-idopyranosyluronate)-α-D-glucopyranoside (150 MHz, $CDCl_3$).

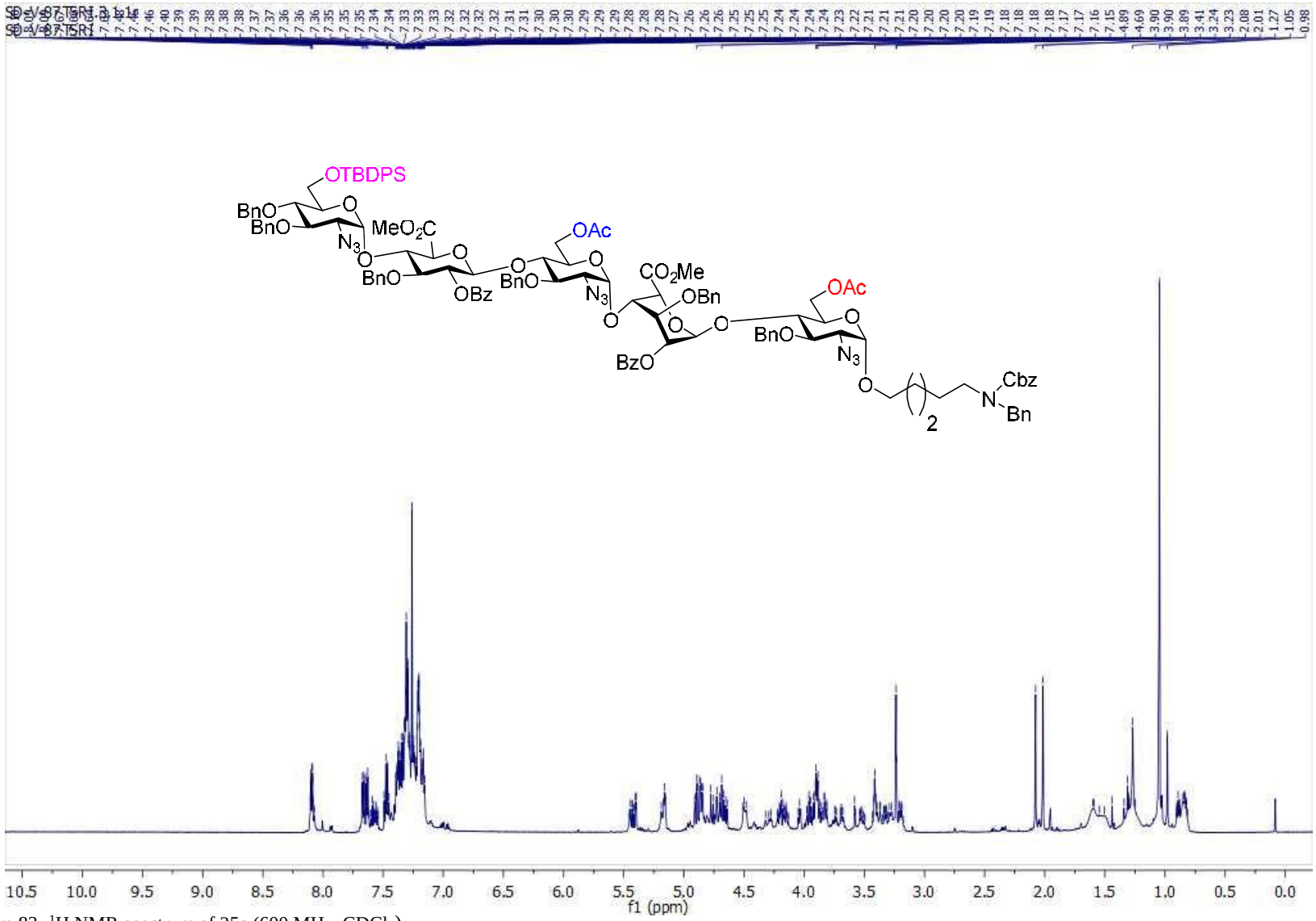


Figure 83. $^{1}H$ NMR spectrum of 25a (600 MHz, $CDCl_3$).

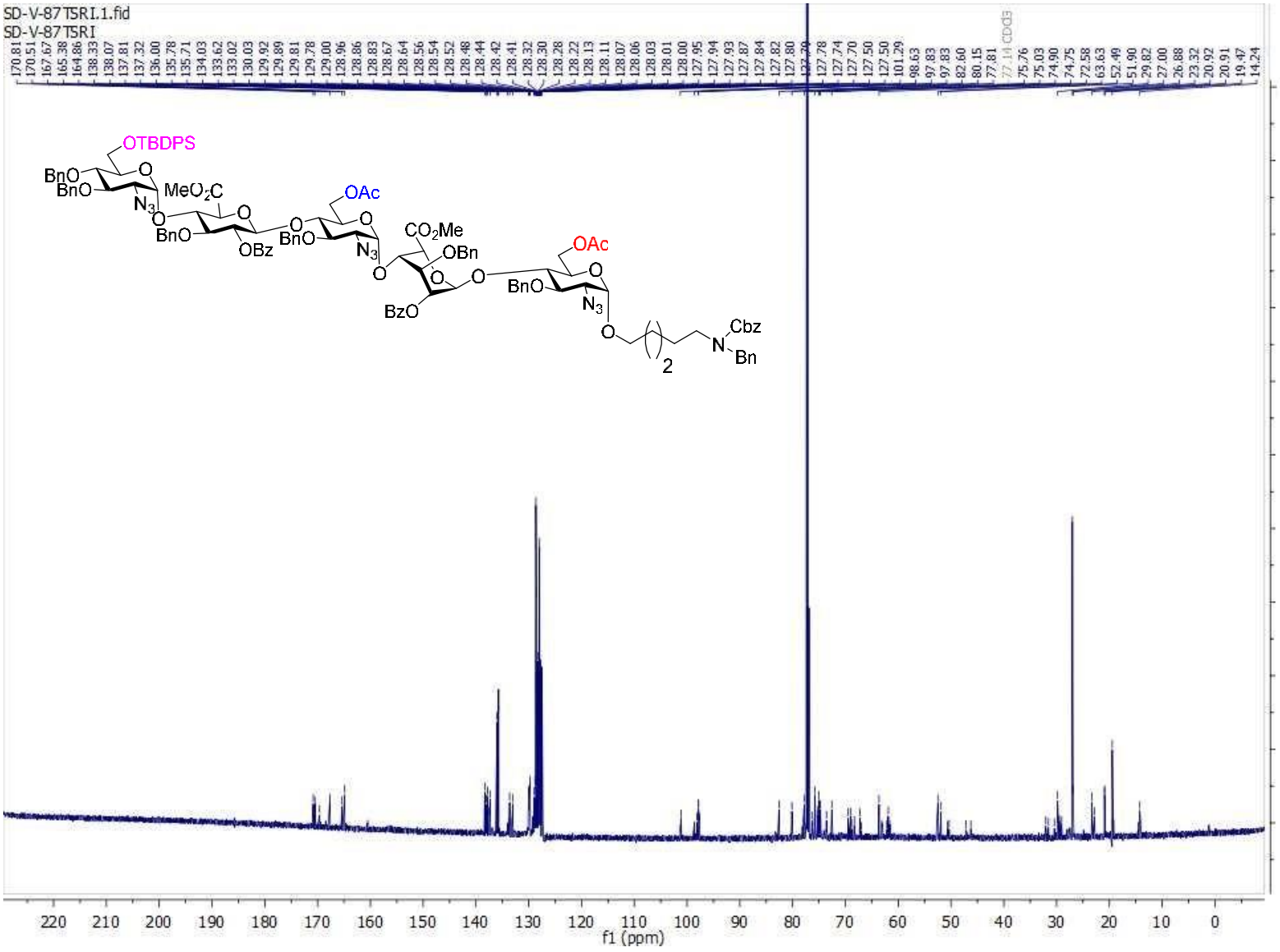


Figure 84. $^{13}C$ NMR spectrum of 25a (150 MHz, $CDCl_3$).

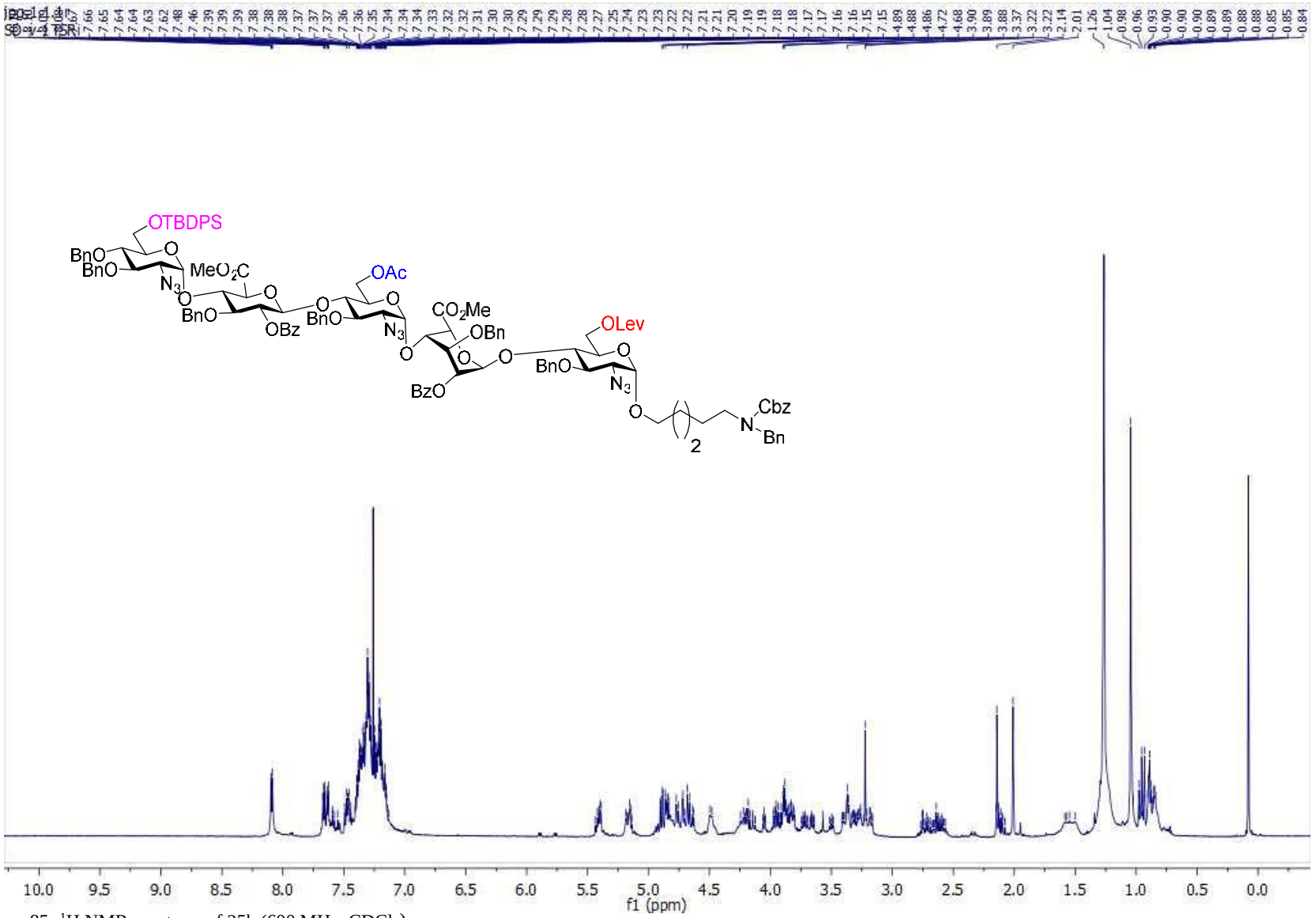


Figure 85. $^{1}H$ NMR spectrum of 25b (600 MHz, $CDCl_3$).

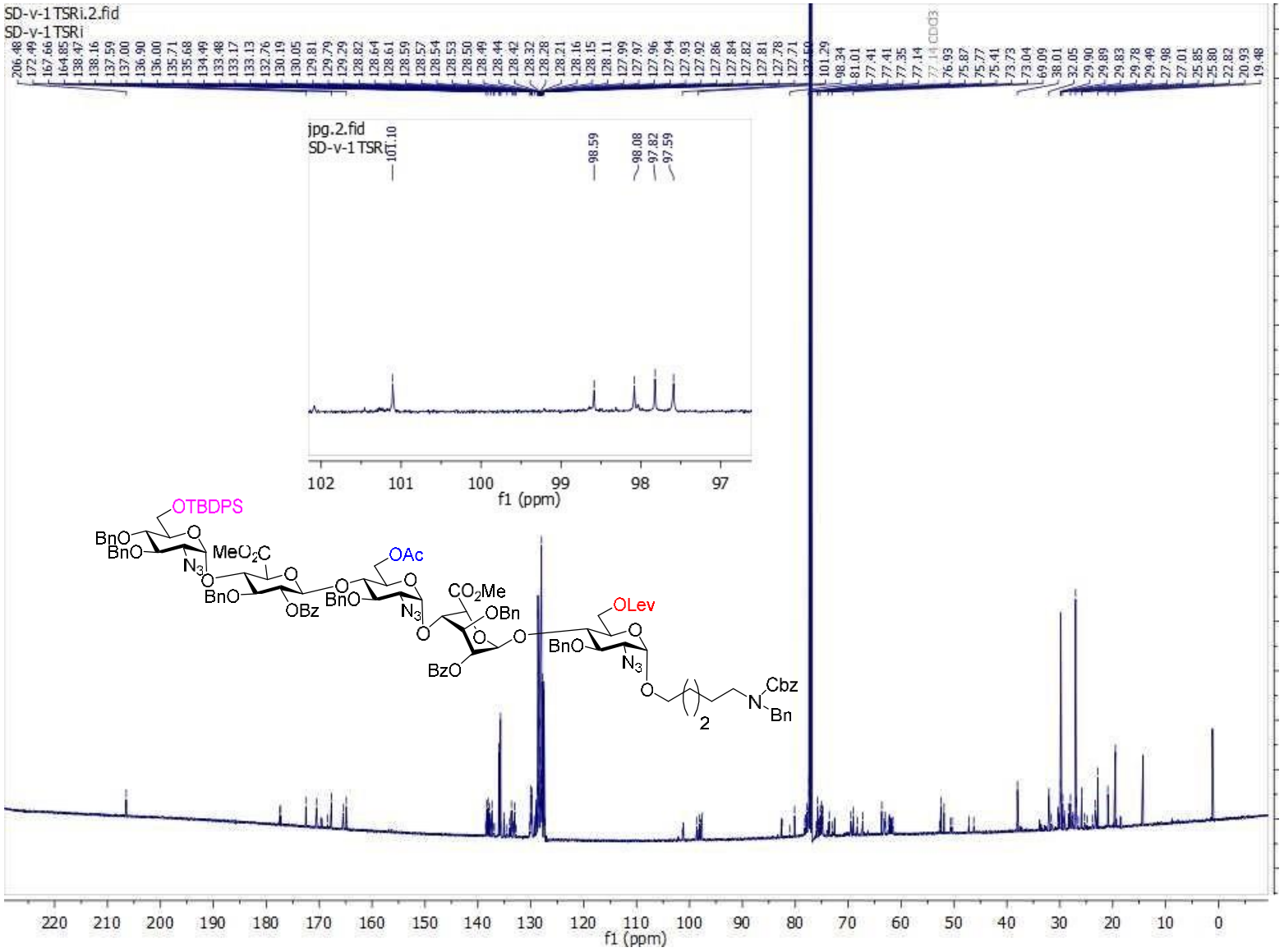


Figure 86. $^{13}C$ NMR spectrum of 25b (150 MHz, $CDCl_3$).

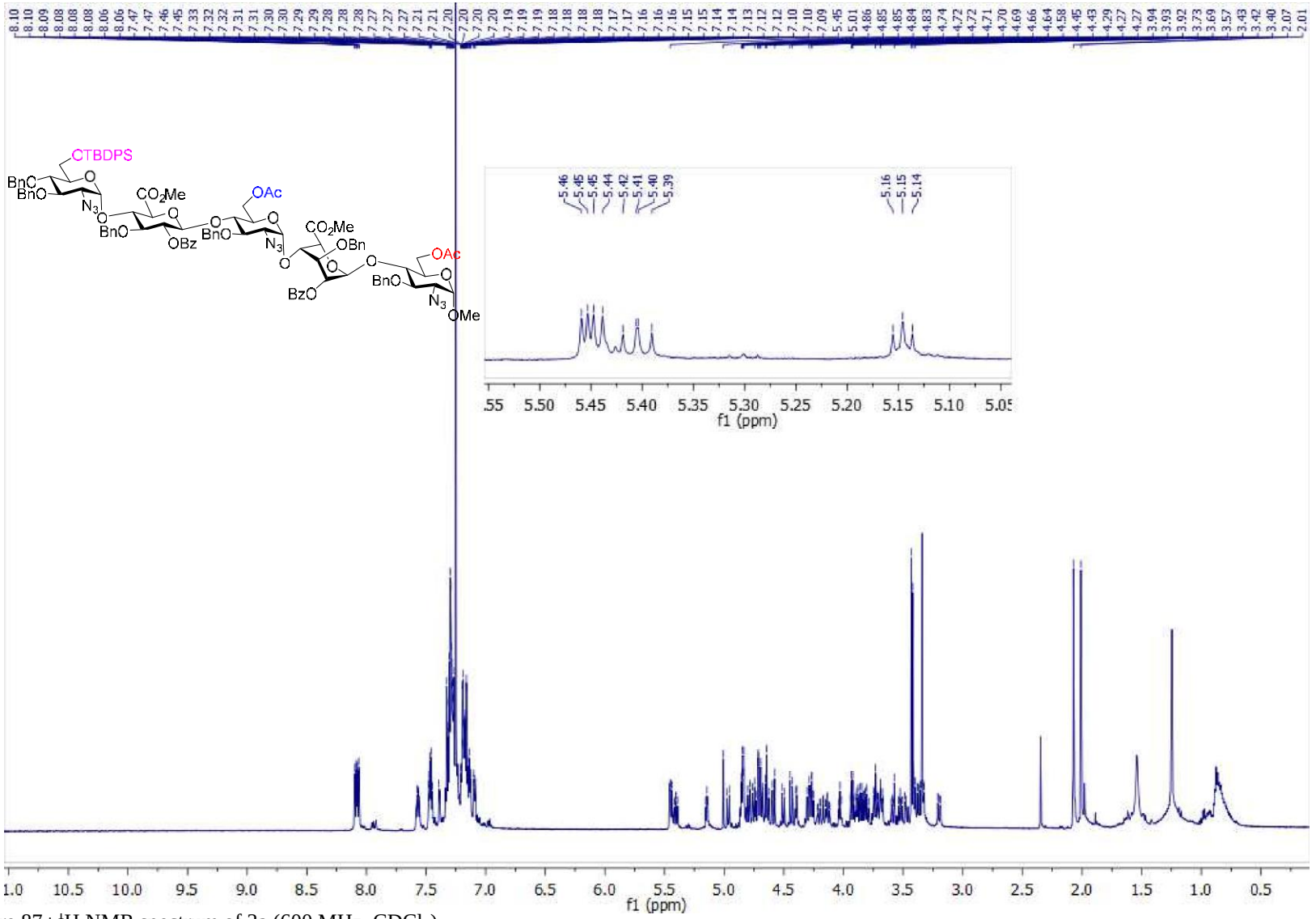


Figure 87. $^{1}$H NMR spectrum of 3a (600 MHz, $CDCl_3$).

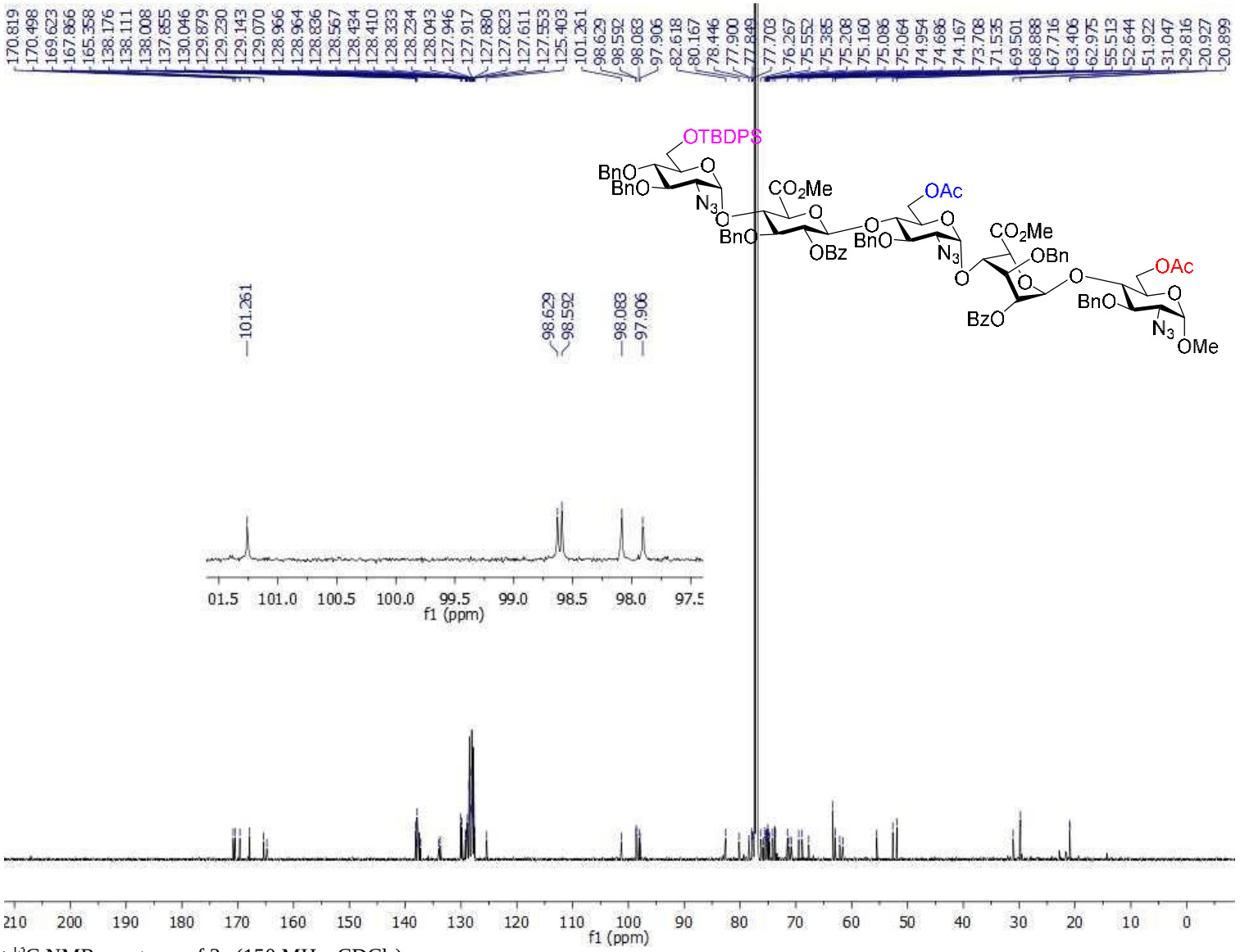


Figure 88. $^{13}$C NMR spectrum of 3a (150 MHz, $CDCl_3$).

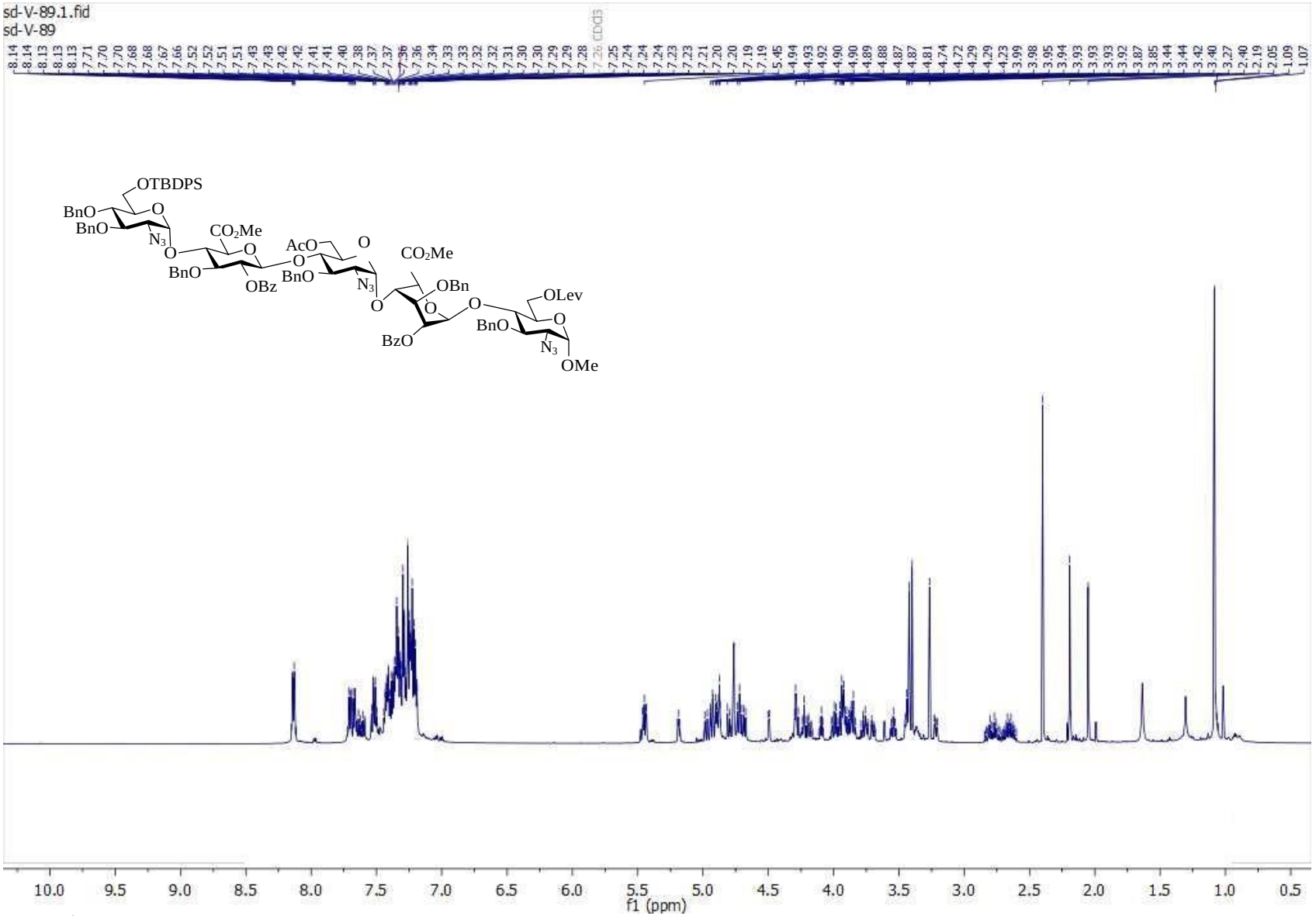


Figure 89. $^{1}$H NMR spectrum of 3b (600 MHz, $CDCl_3$).

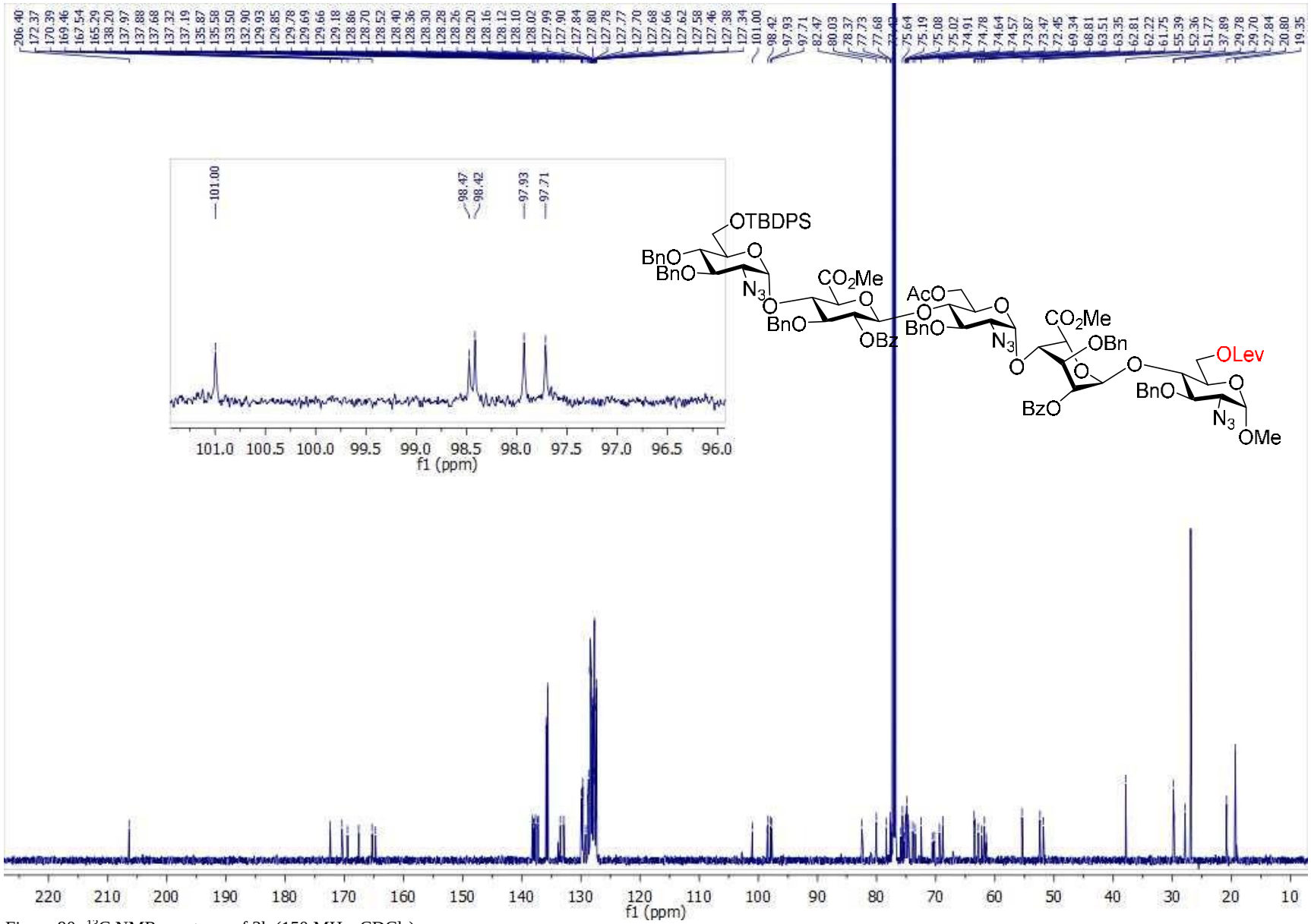


Figure 90. $^{13}C$ NMR spectrum of 3b (150 MHz, $CDCl_3$).

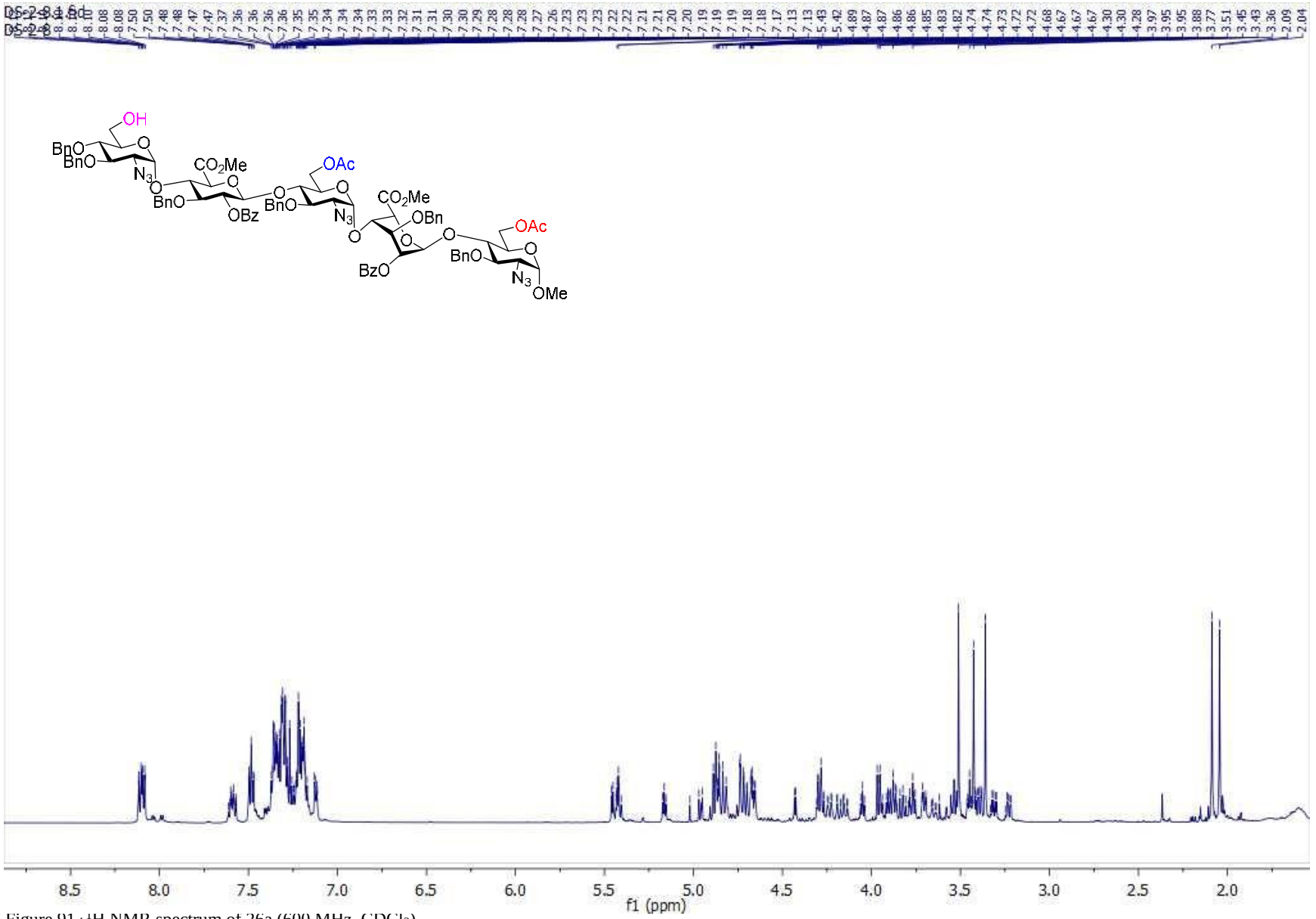


Figure 91. $^1$H NMR spectrum of 26a (600 MHz, $CDCl_3$).

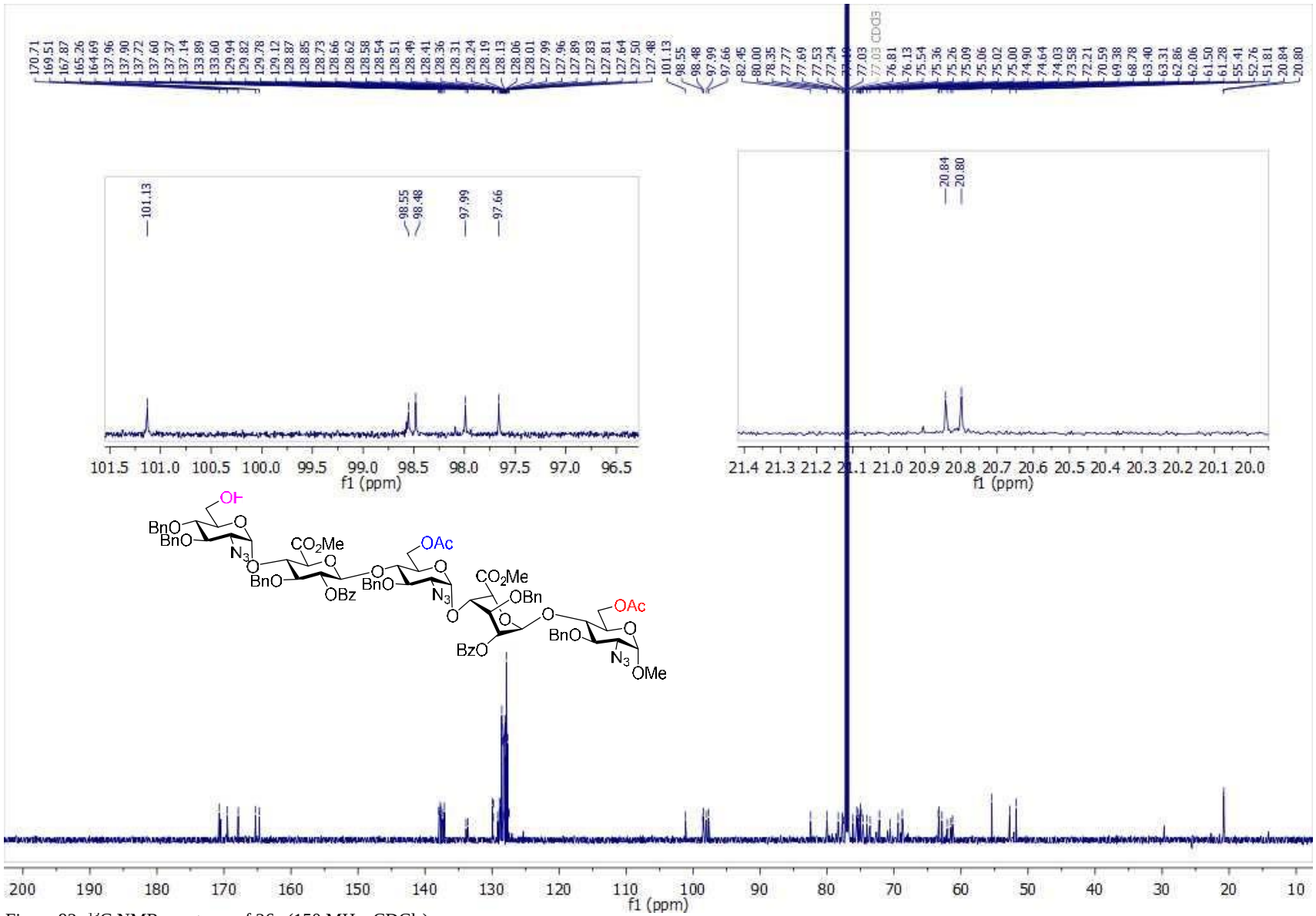


Figure 92. $^{13}$C NMR spectrum of 26a (150 MHz, $CDCl_3$).

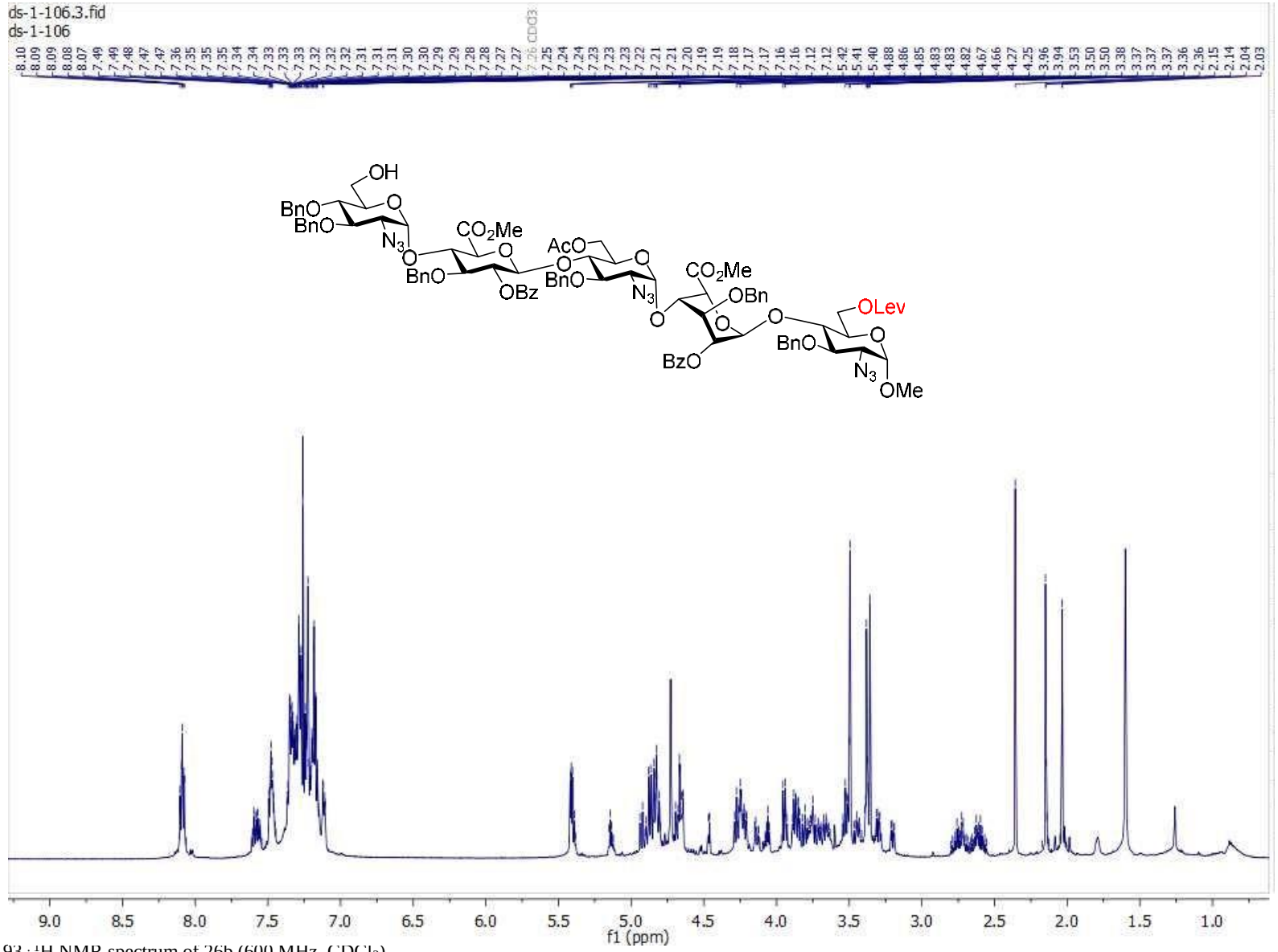


Figure 93. $^1$H NMR spectrum of 26b (600 MHz, $CDCl_3$).

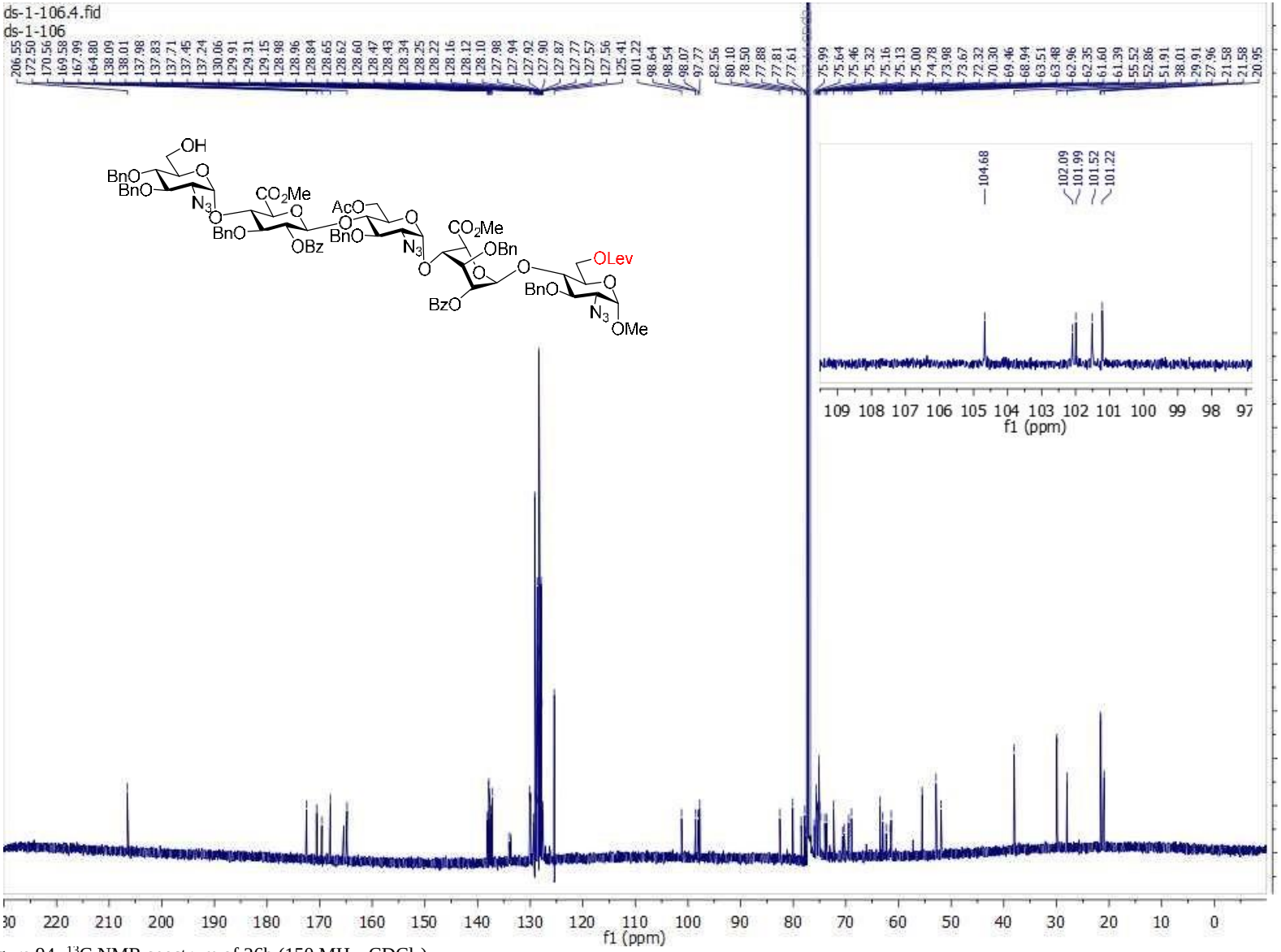


Figure 94. $^{13}C$ NMR spectrum of 26b (150 MHz, $CDCl_3$).

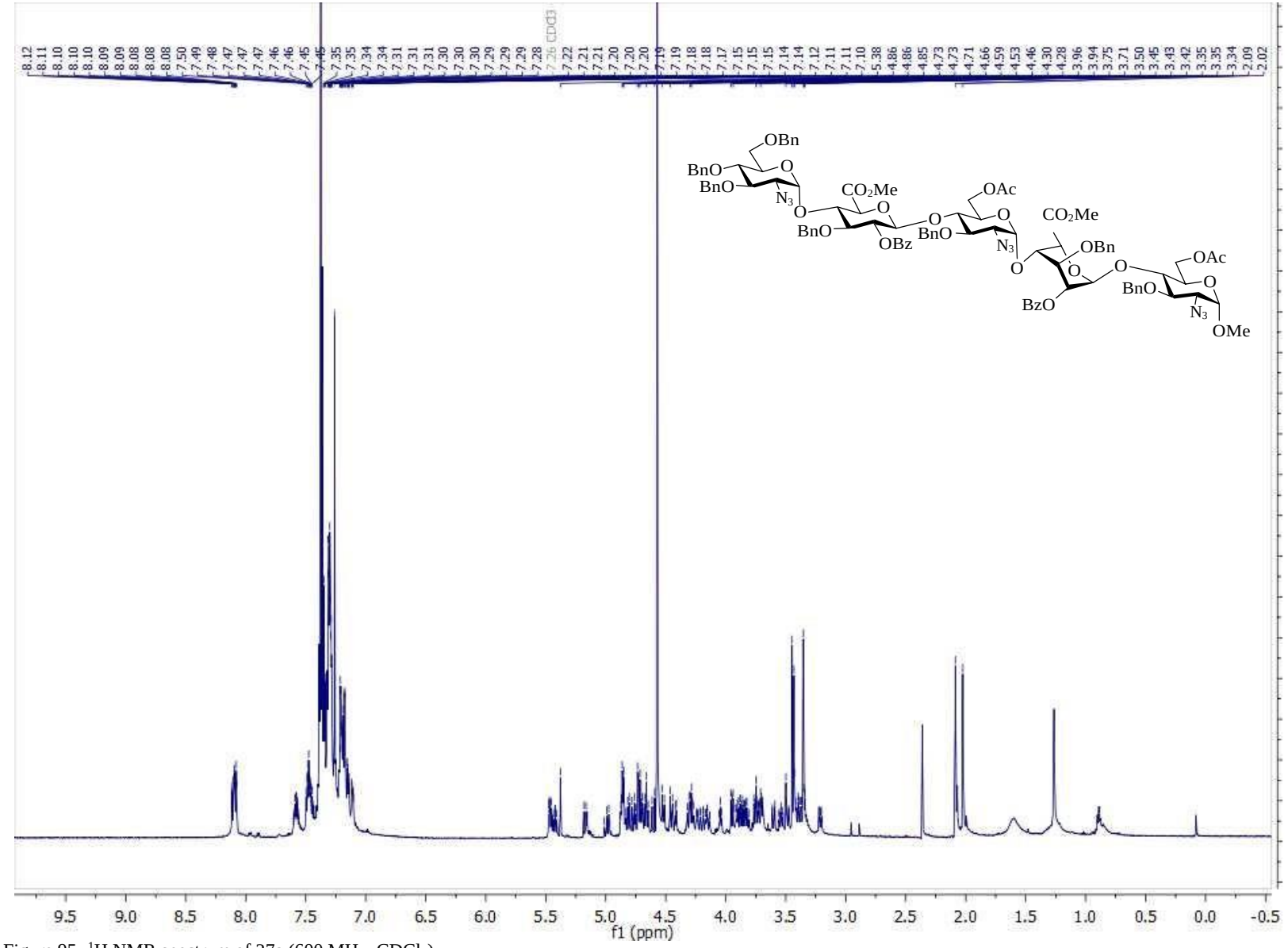


Figure 95. $^{1}$H NMR spectrum of 27a (600 MHz, $CDCl_3$).

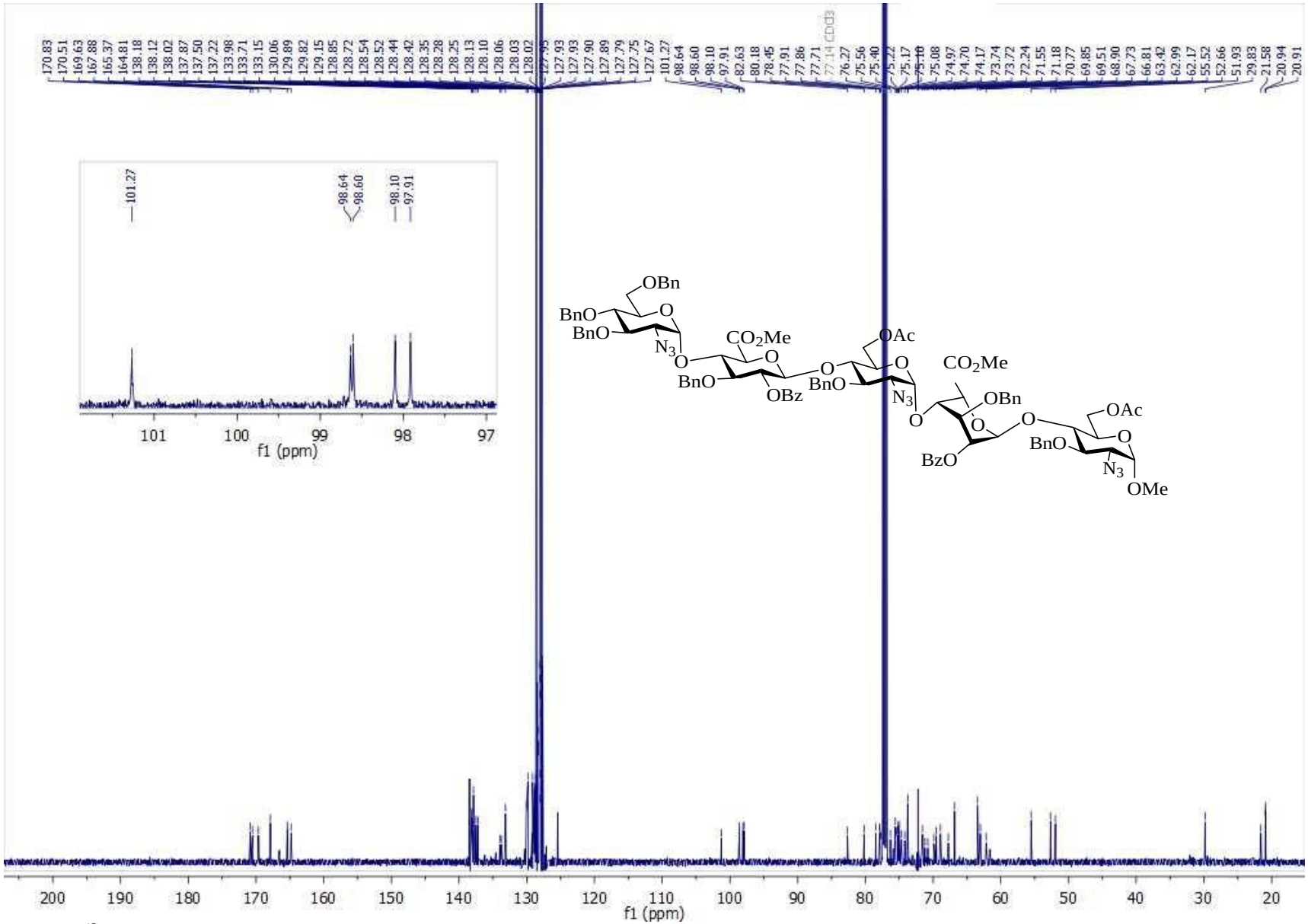


Figure 96. $^{13}C$ NMR spectrum of 27a (150 MHz, $CDCl_3$).

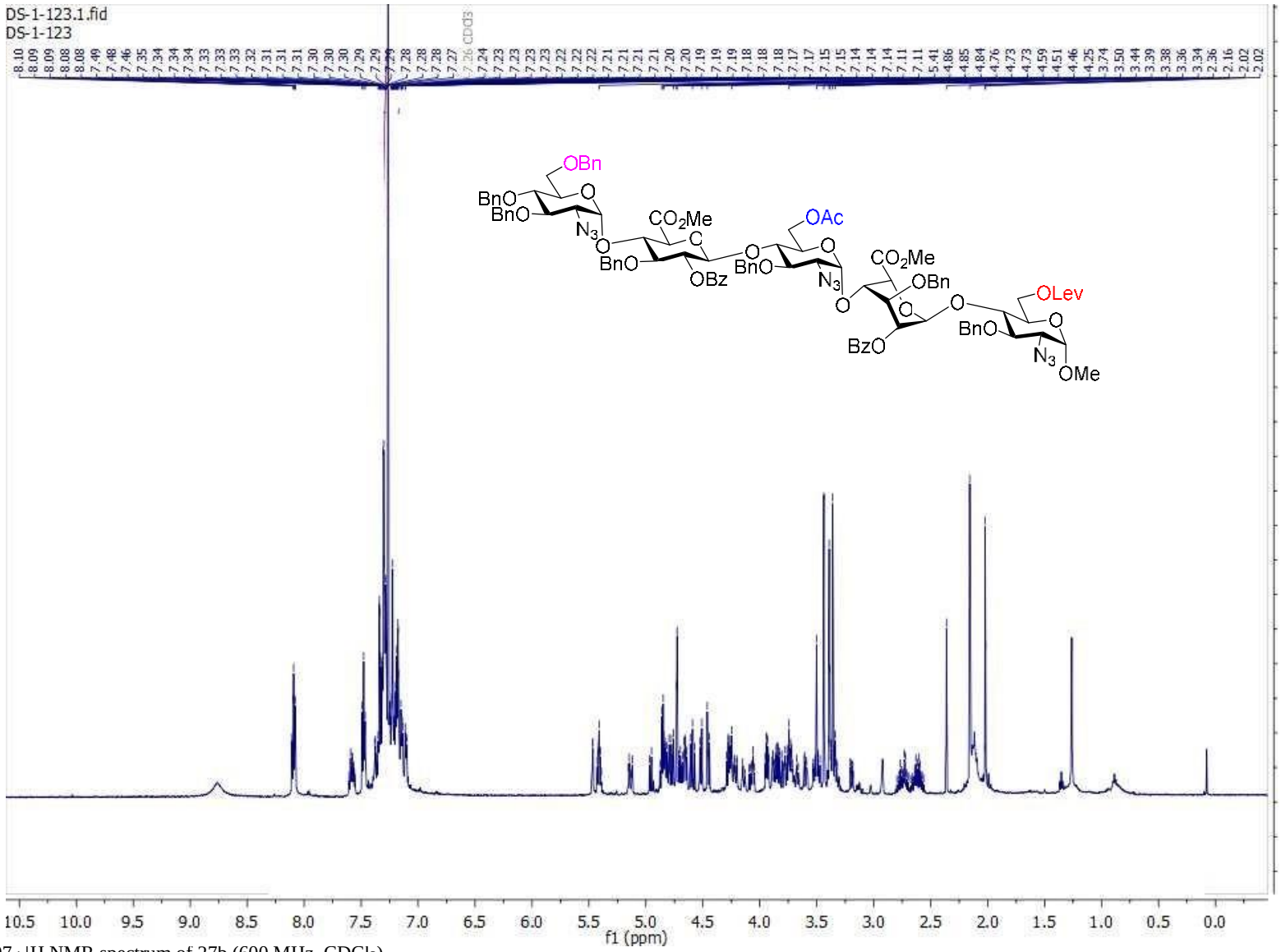


Figure 97. $^{1}$H NMR spectrum of 27b (600 MHz, $CDCl_3$).

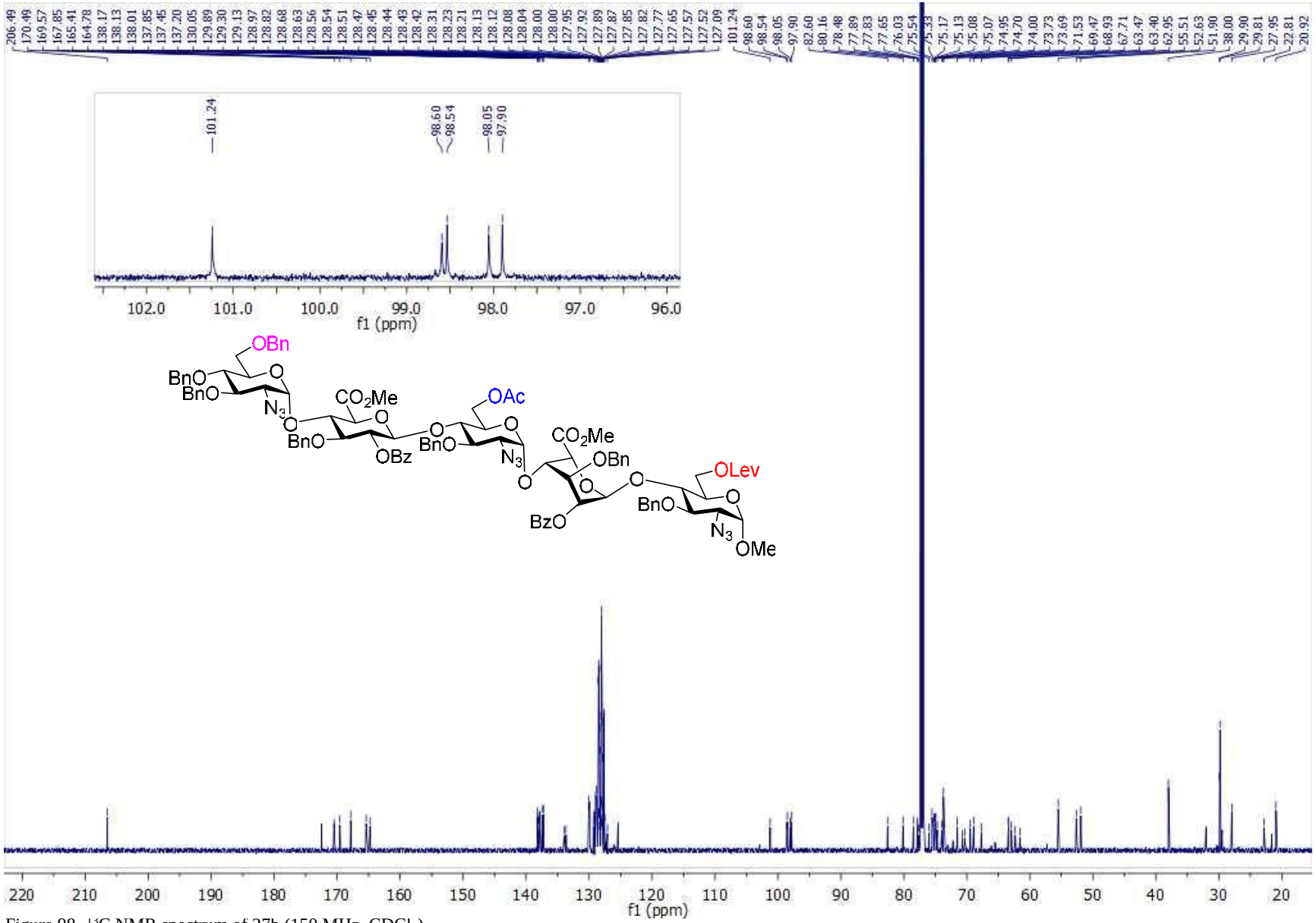


Figure 98. $^{13}C$ NMR spectrum of 27b (150 MHz, $CDCl_3$).

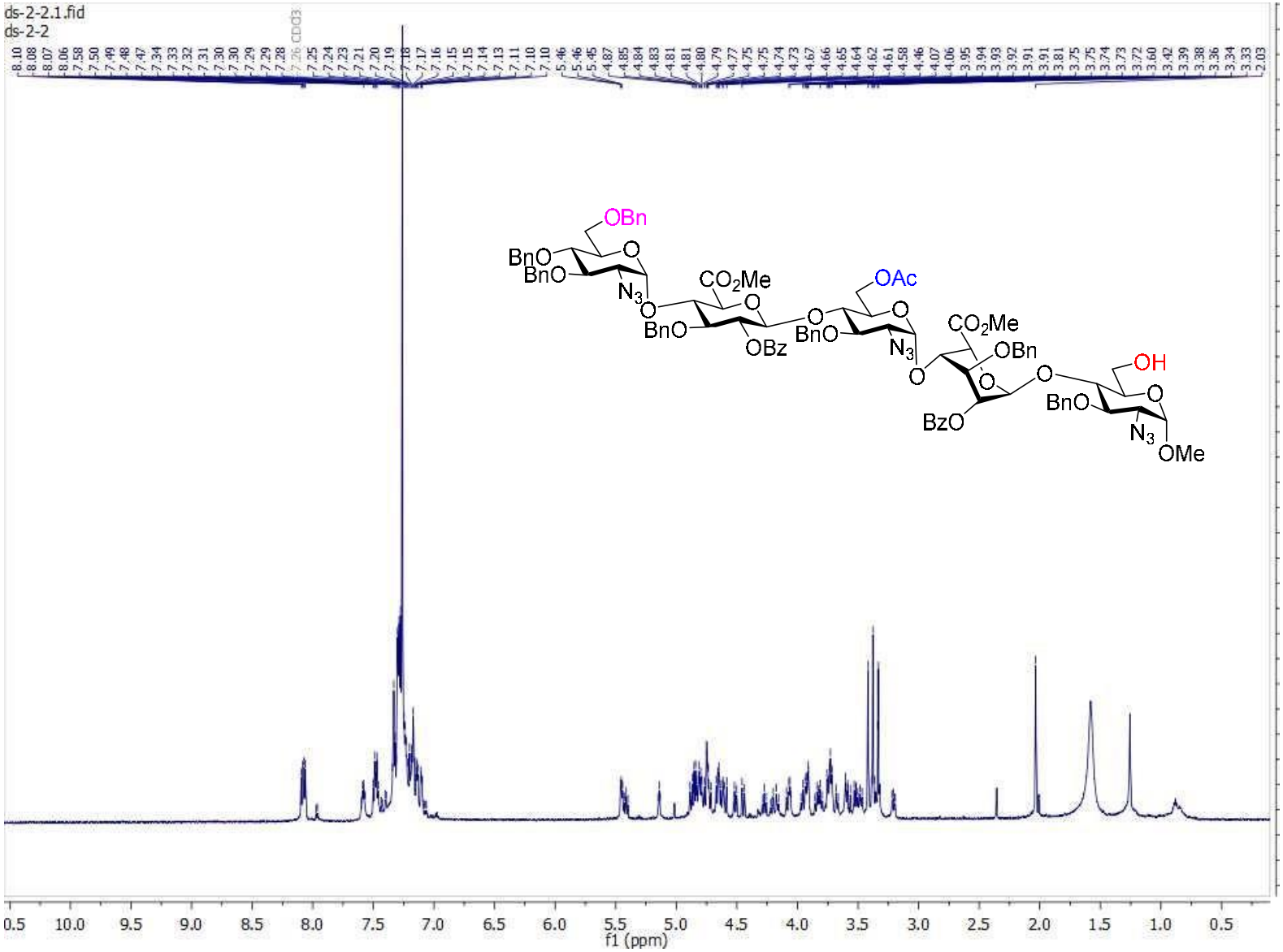


Figure 99. $^{1}$H NMR spectrum of 28 (600 MHz, $CDCl_3$).

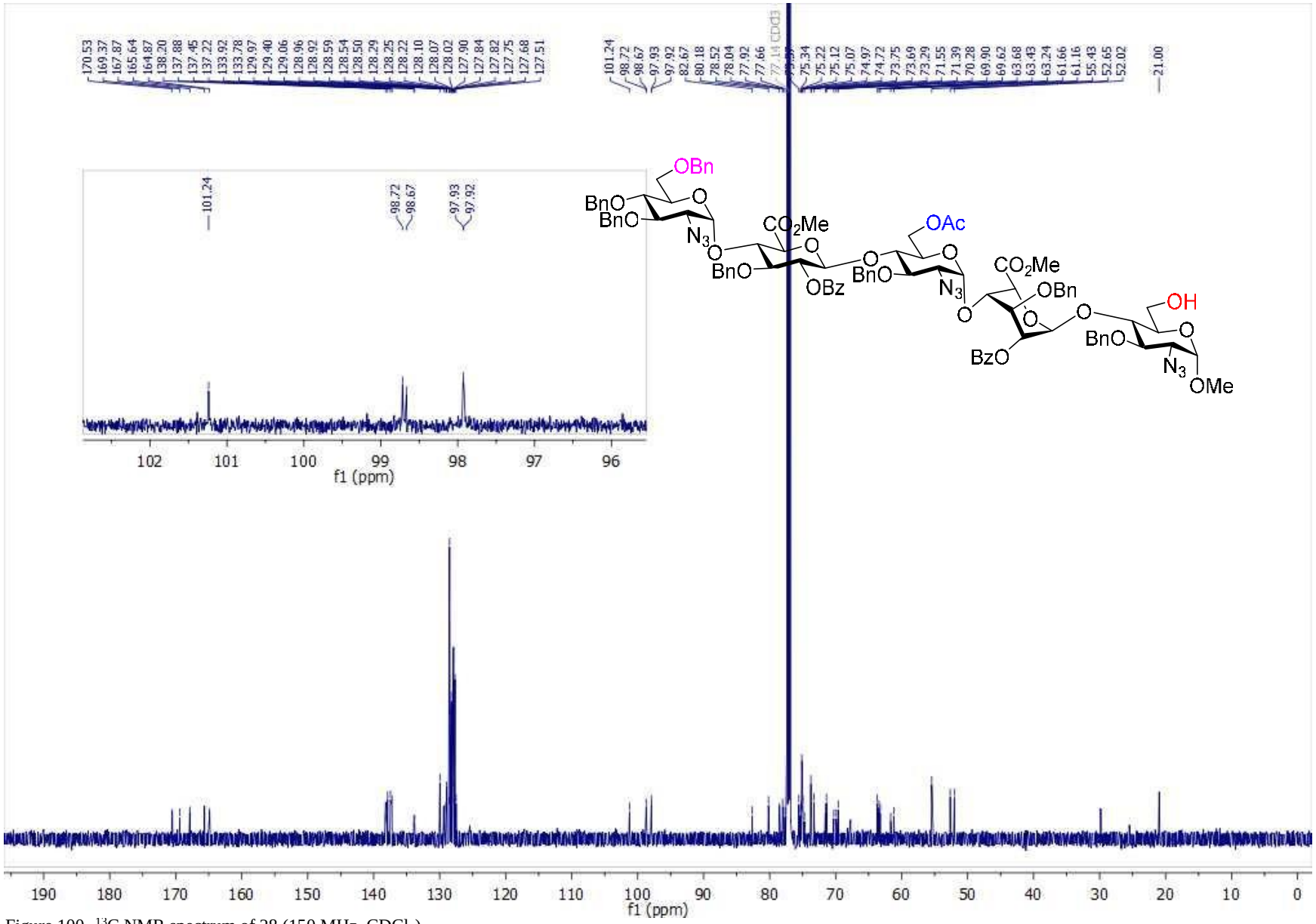


Figure 100. $^{13}$C NMR spectrum of 28 (150 MHz, $CDCl_3$).

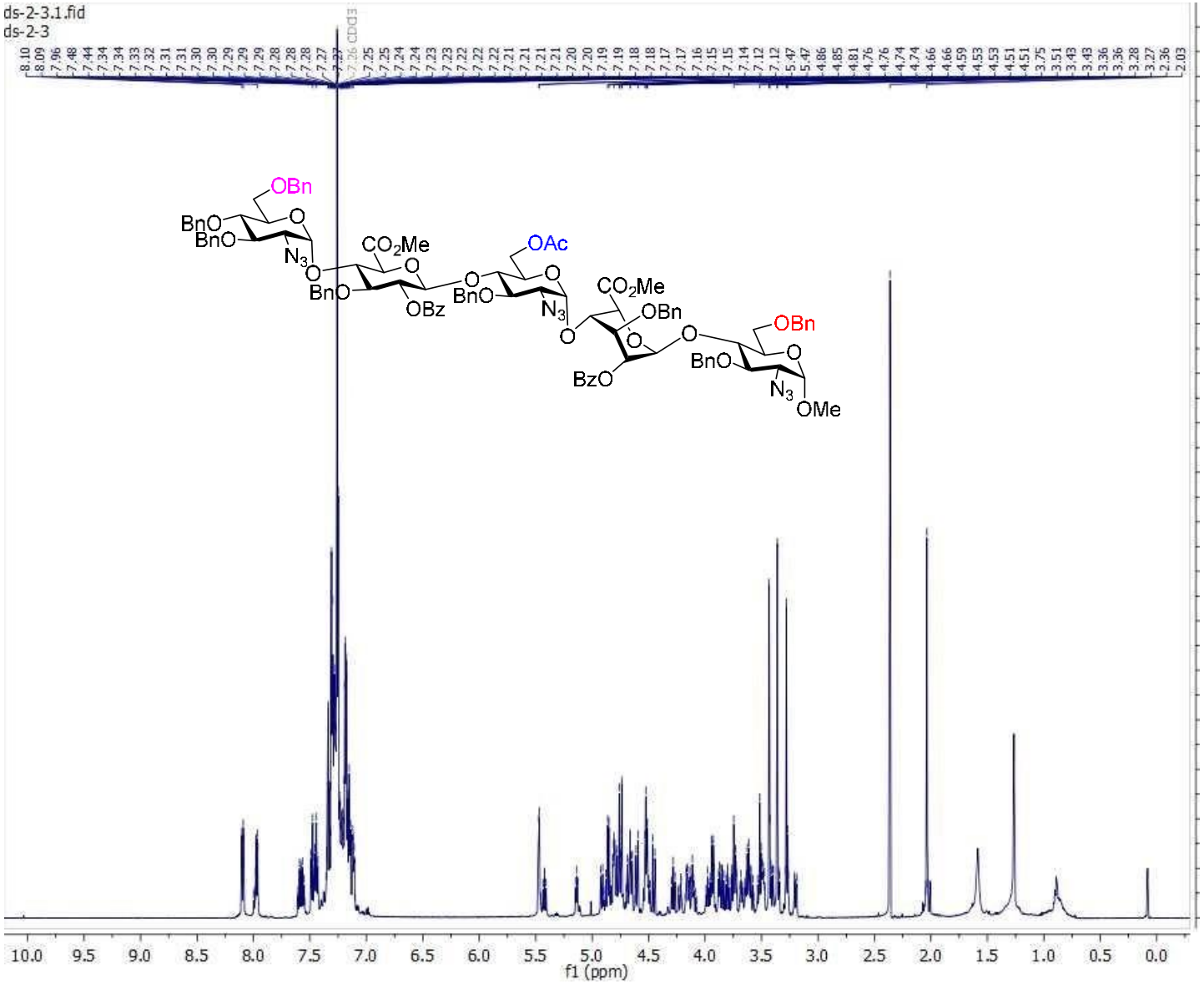


Figure 101. $^{1}H$ NMR spectrum of 29 (600 MHz, $CDCl_3$).

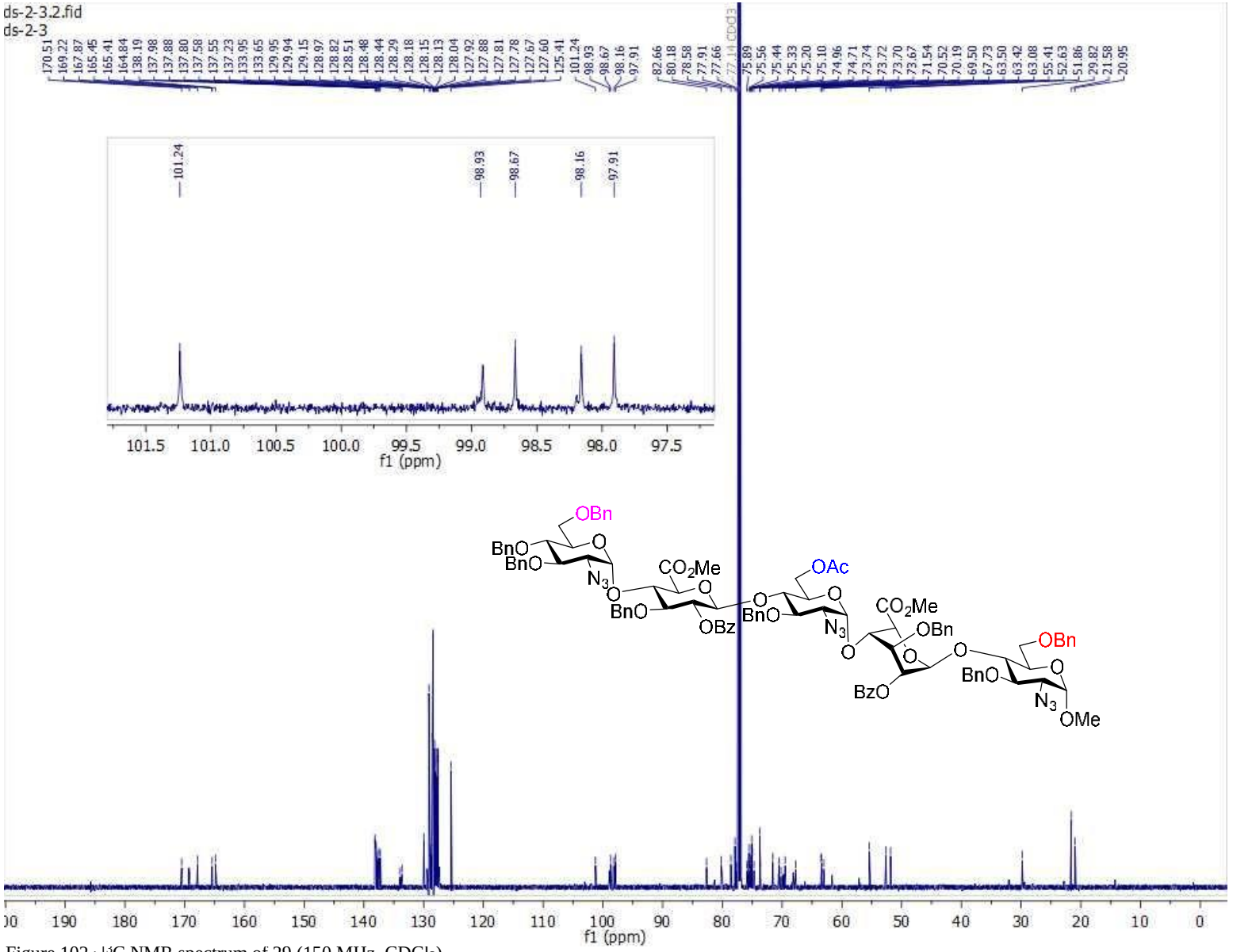


Figure 102. $^{13}$C NMR spectrum of 29 (150 MHz, $CDCl_3$).

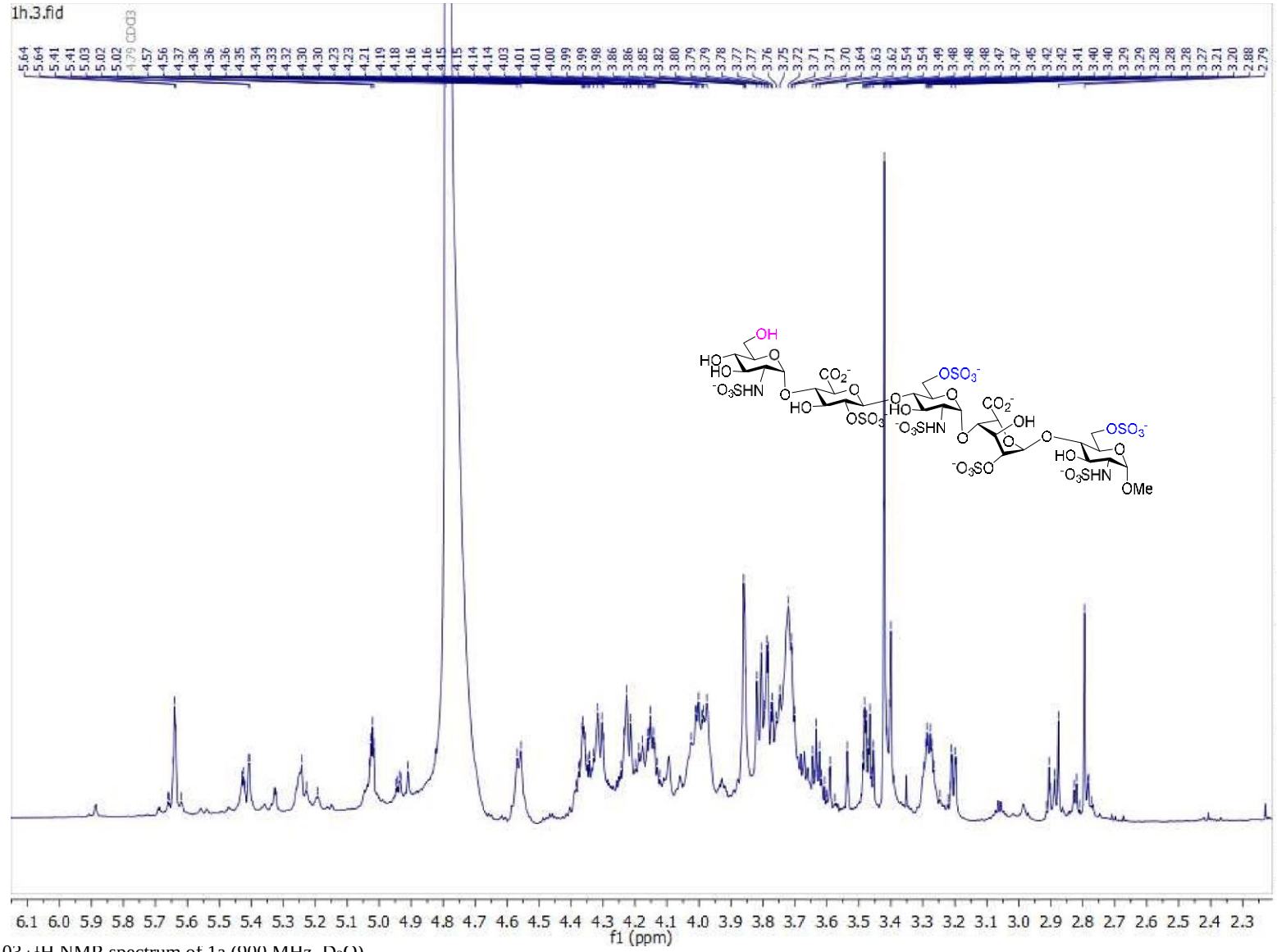


Figure 103. $^1$H NMR spectrum of 1a (900 MHz, $D_2O$).

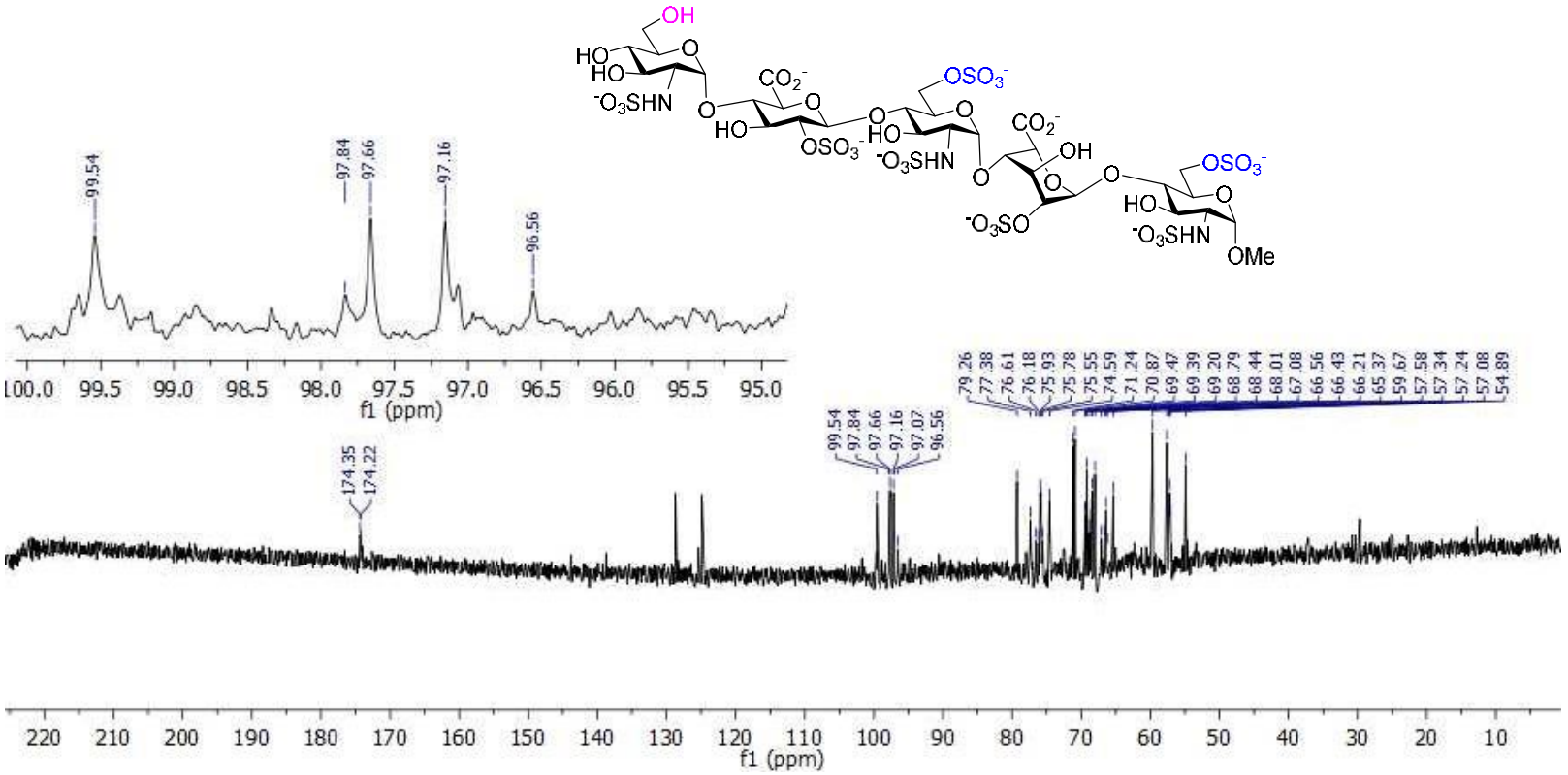


Figure 104.· $^{13}$C NMR spectrum of 1a (150 MHz, $D_2O$).

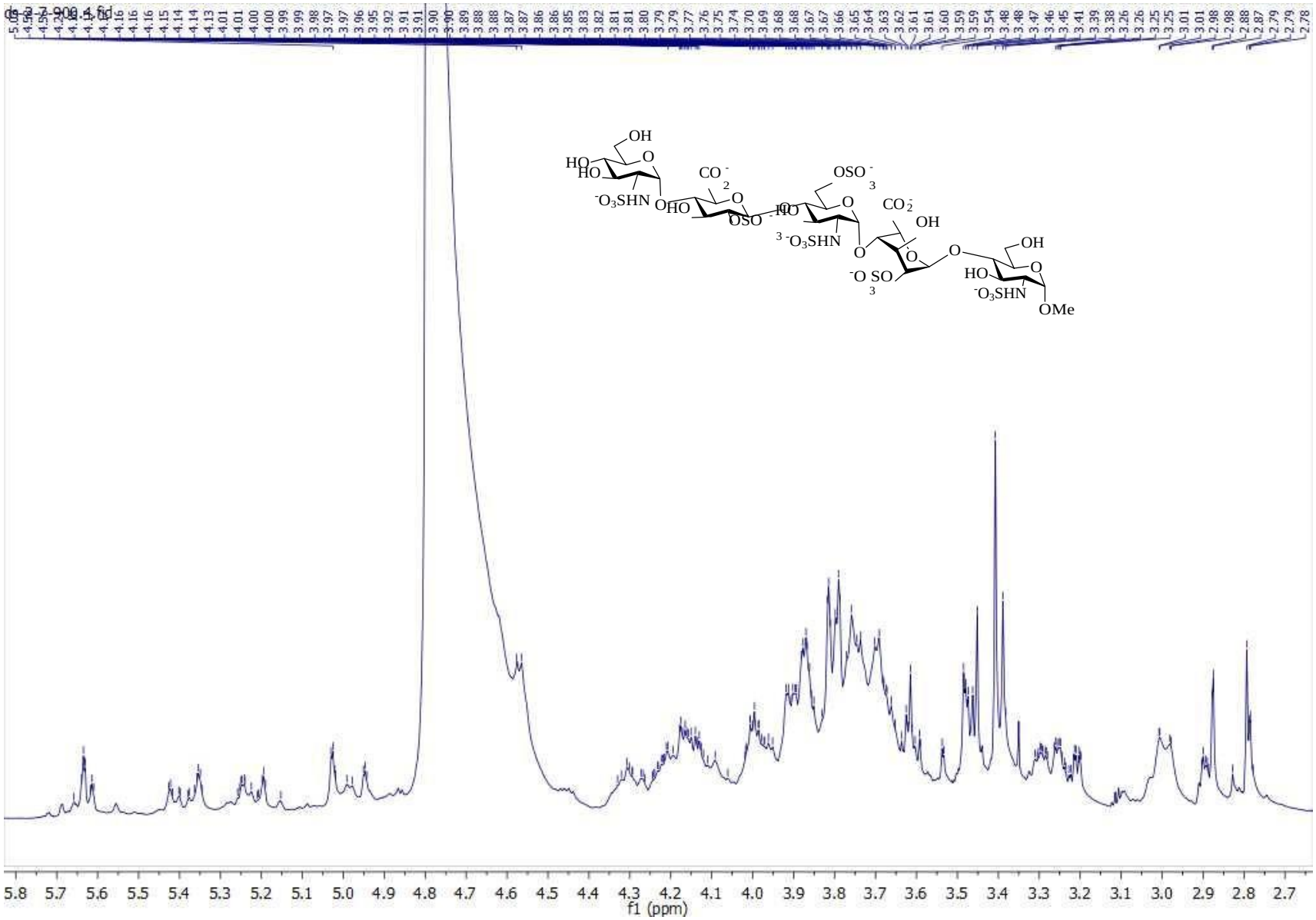


Figure 105. $^{1}$H NMR spectrum of 1b (900 MHz, $D_2O$).

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ds-2-7ionexchange

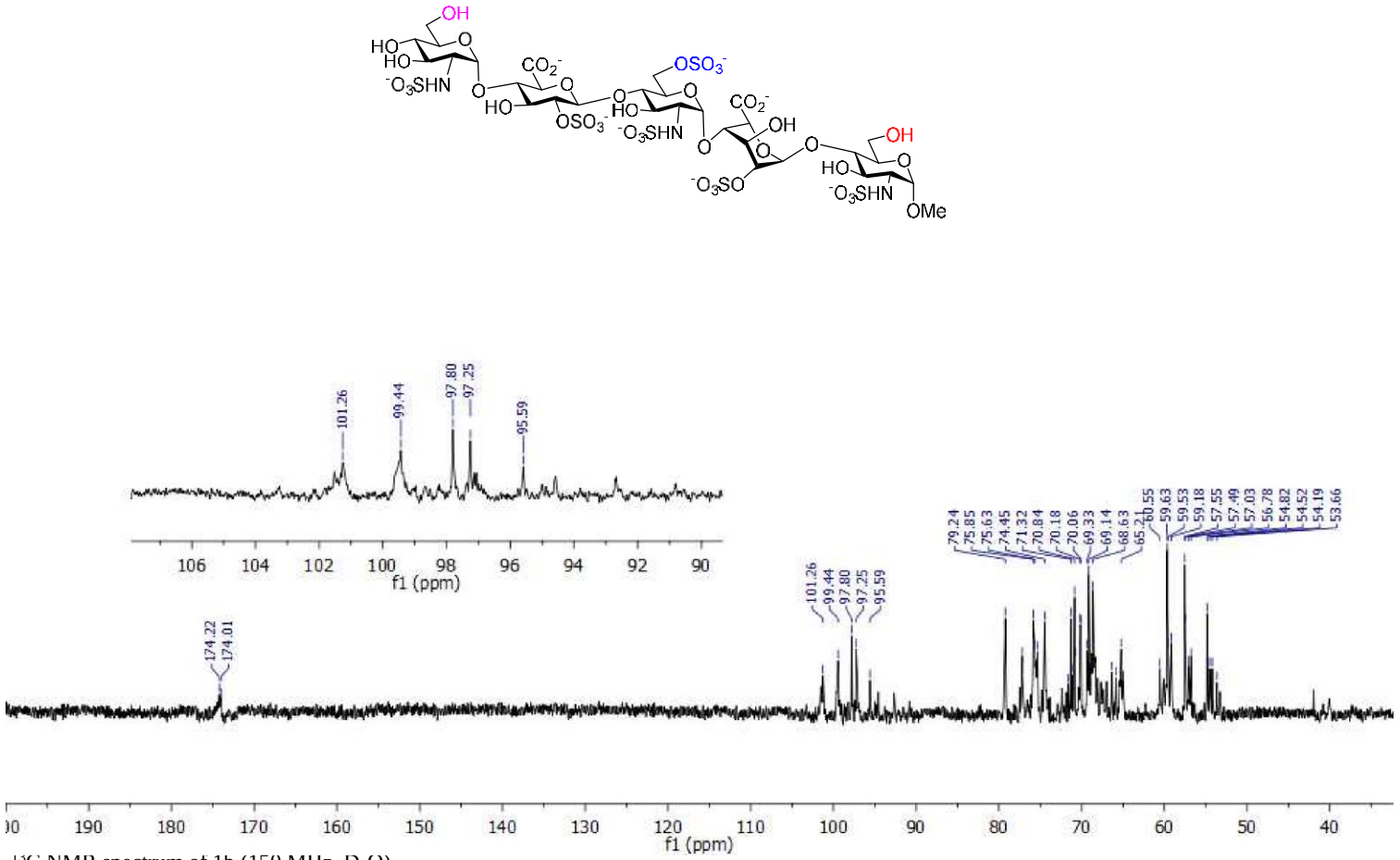


Figure 106. $^{13}C$ NMR spectrum of 1b (150 MHz, $D_2O$).

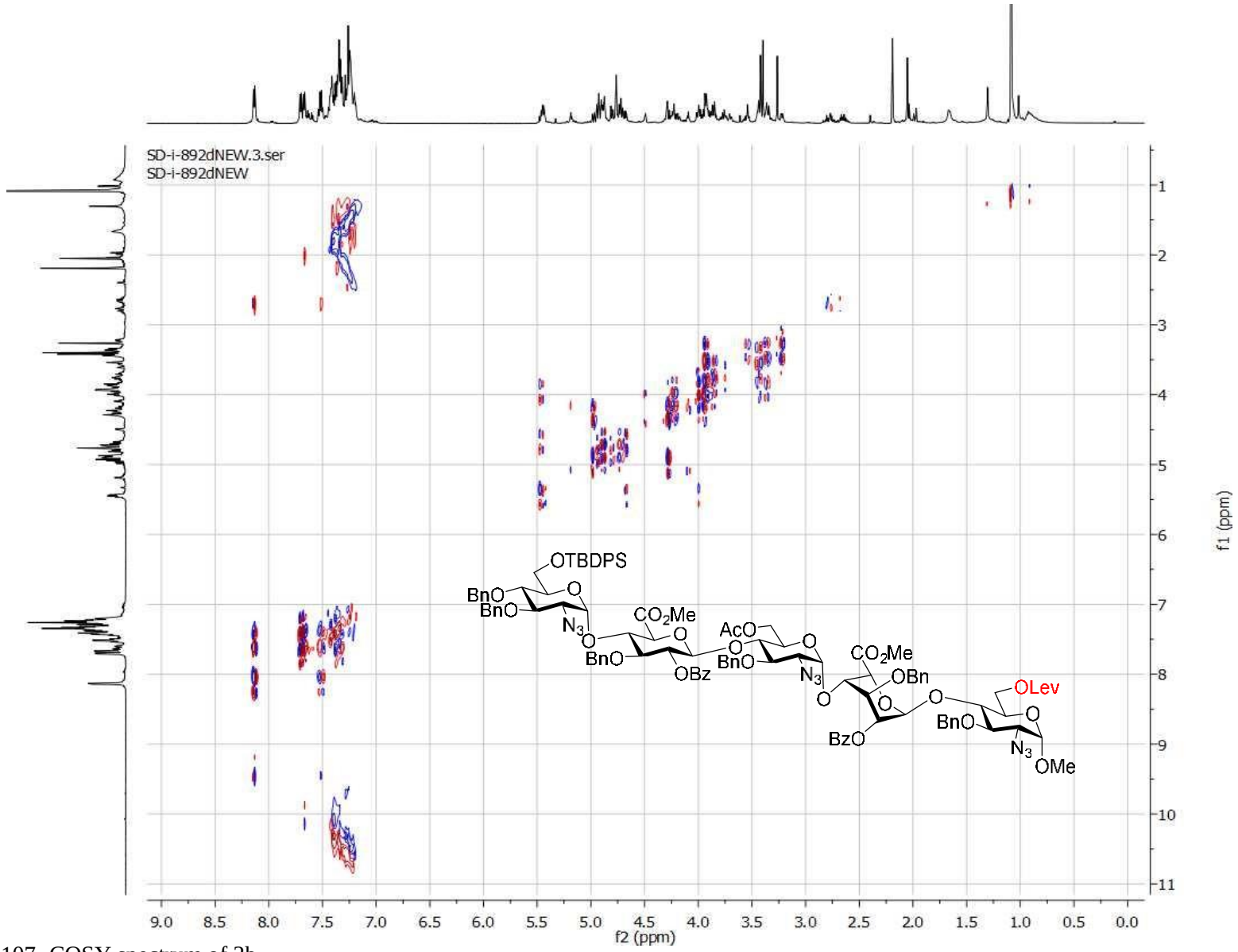


Figure 107. COSY spectrum of 3b.

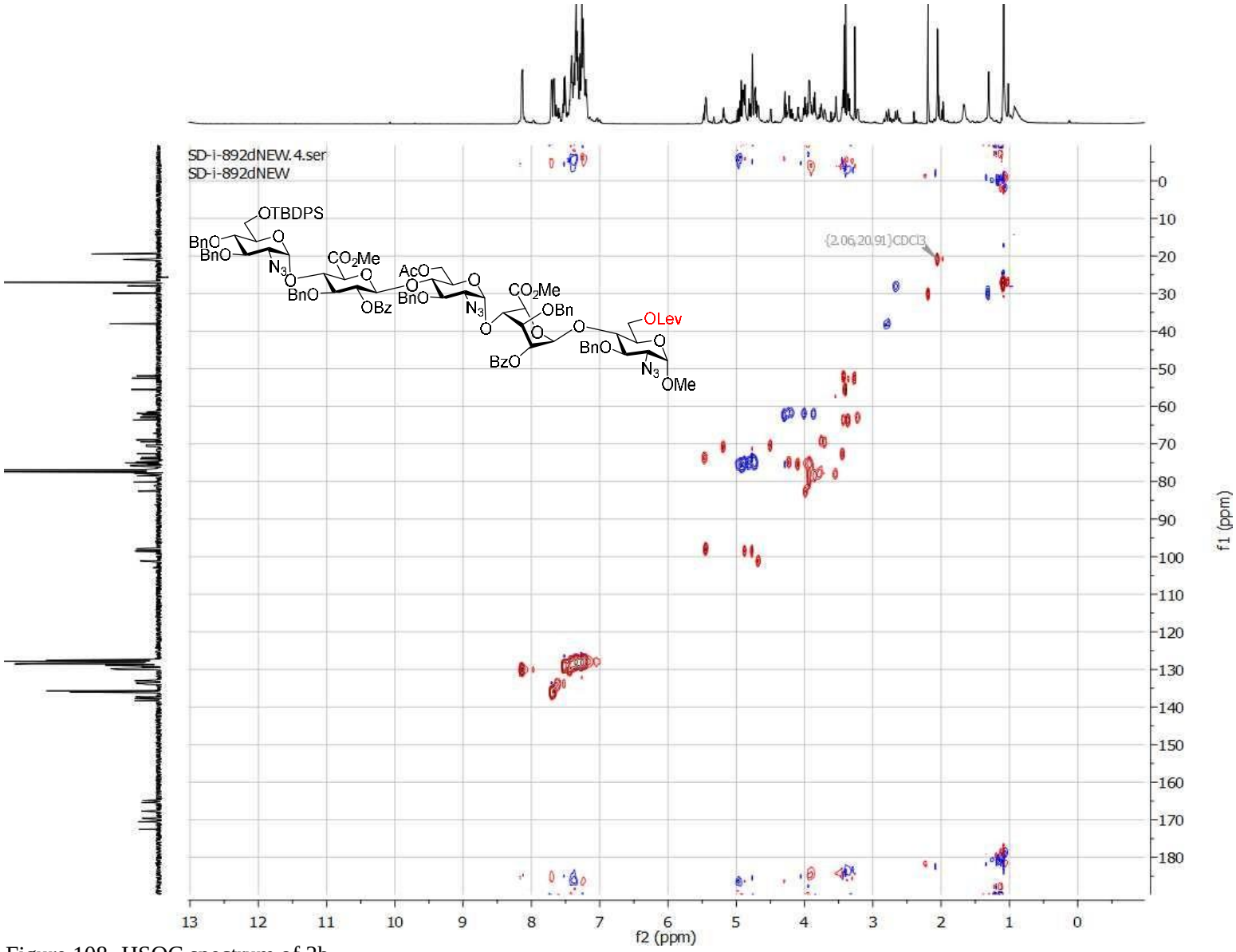


Figure 108. HSQC spectrum of 3b.

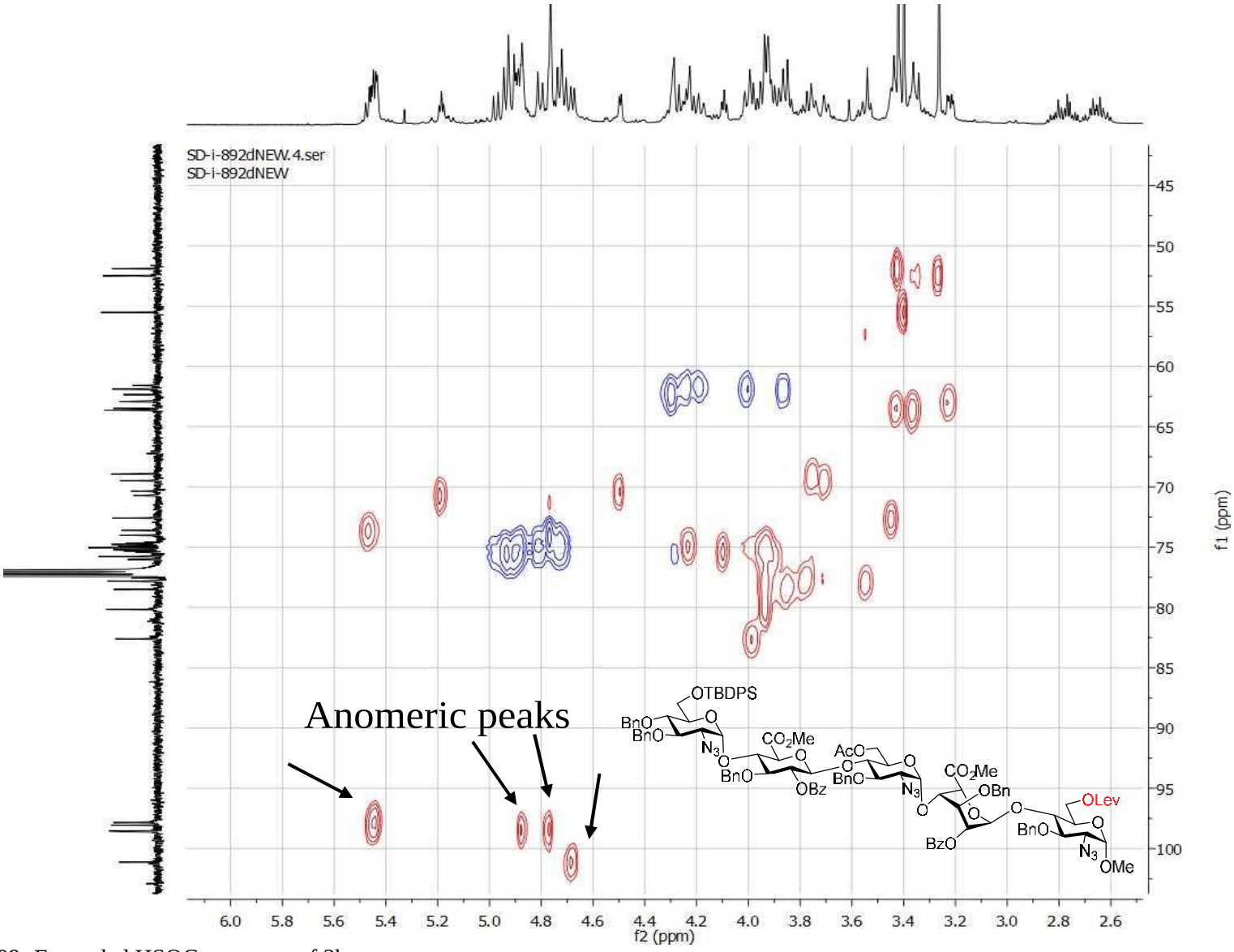


Figure 109. Expanded HSQC spectrum of 3b.

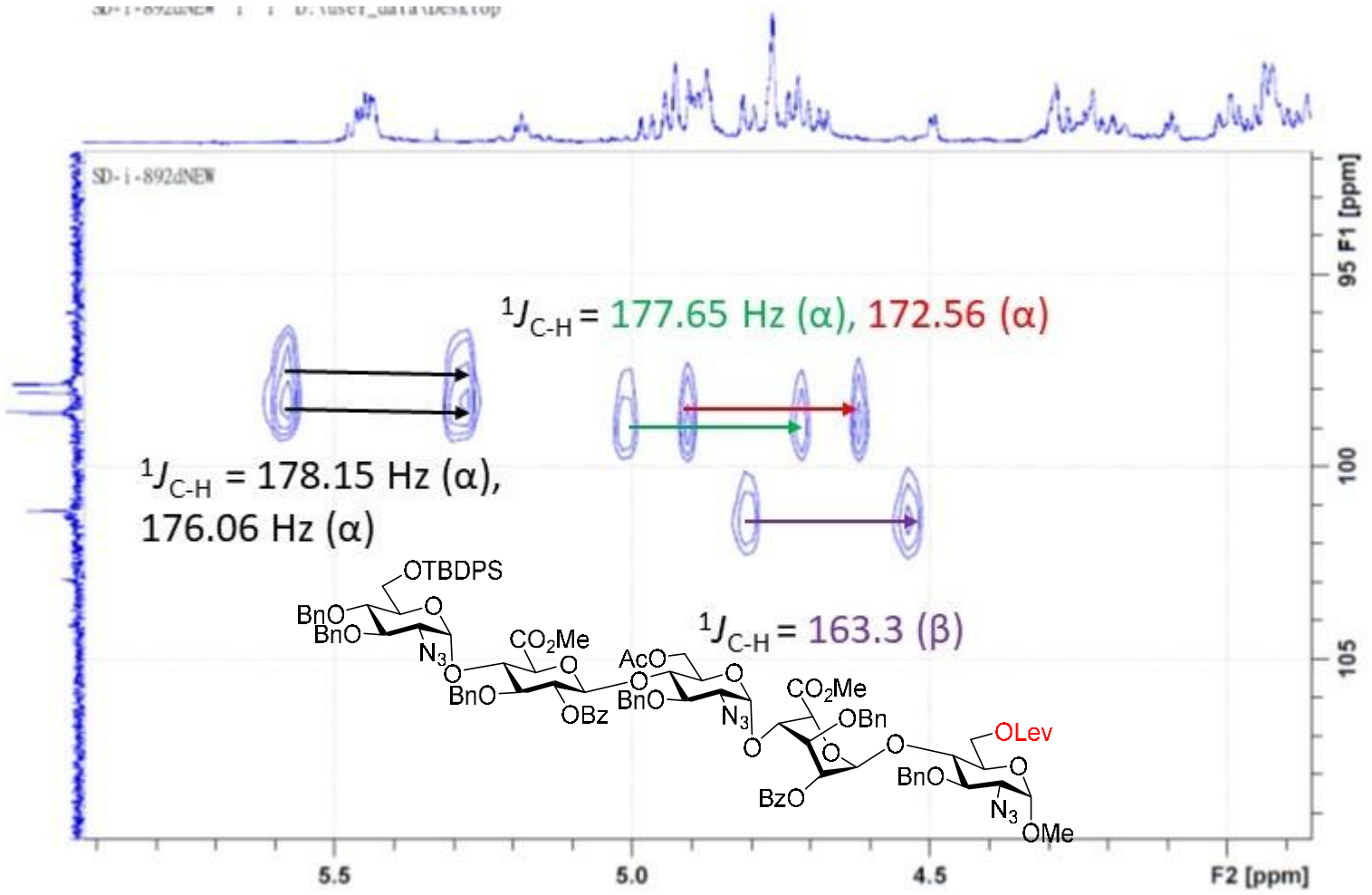


Figure 109. $^{13}C$ coupled HSQC spectrum of 3b.

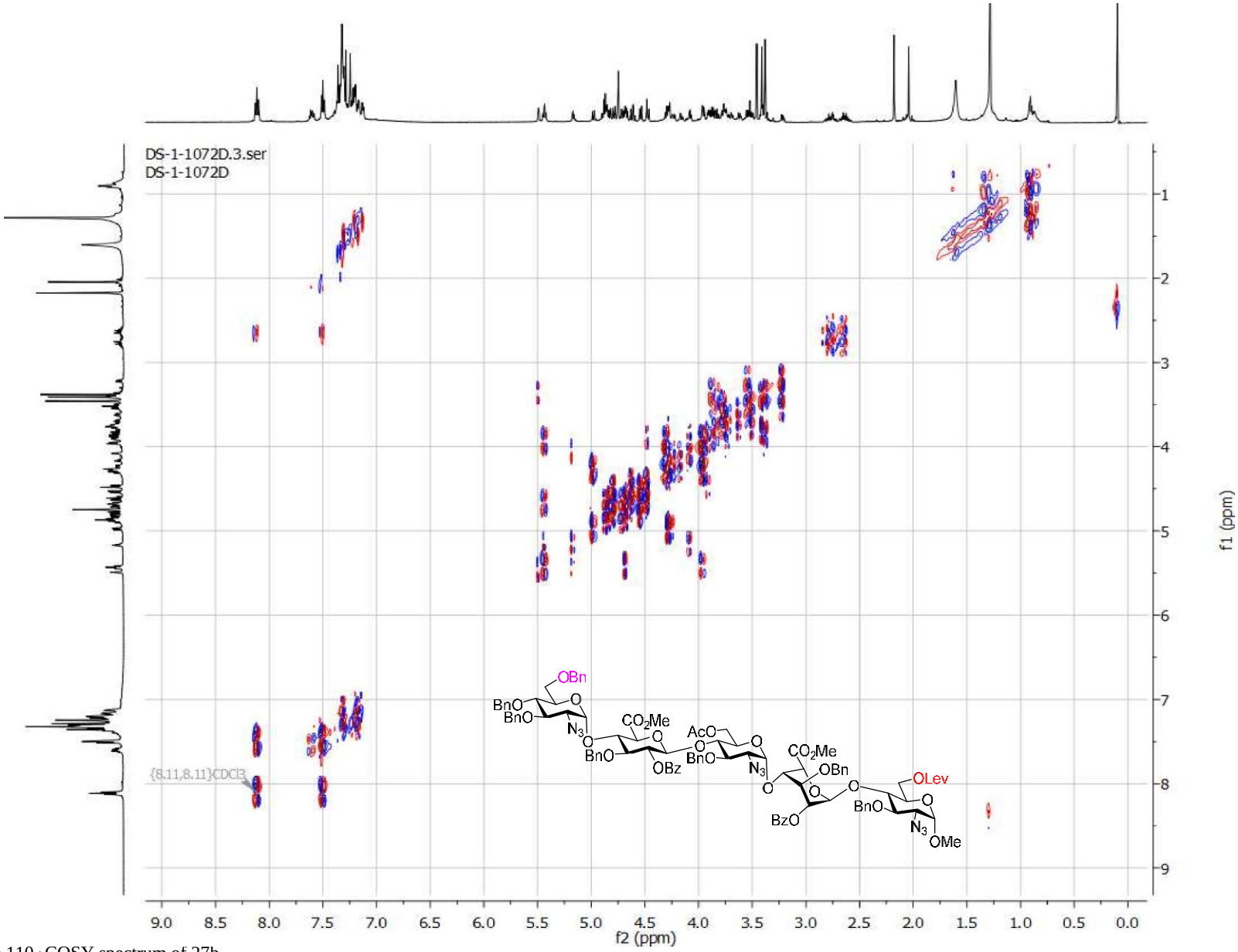


Figure 110. COSY spectrum of 27b.

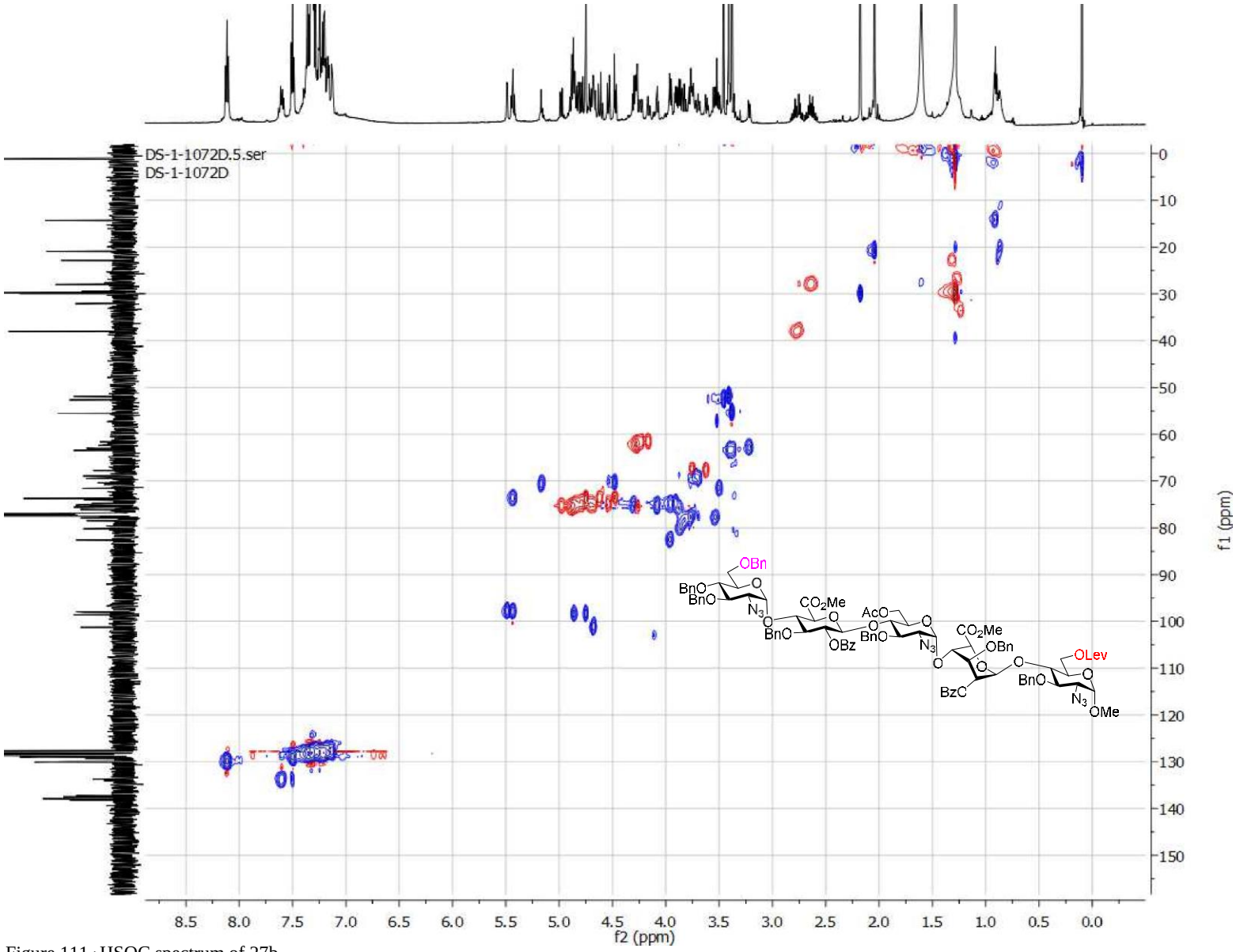


Figure 111. HSQC spectrum of 27b.

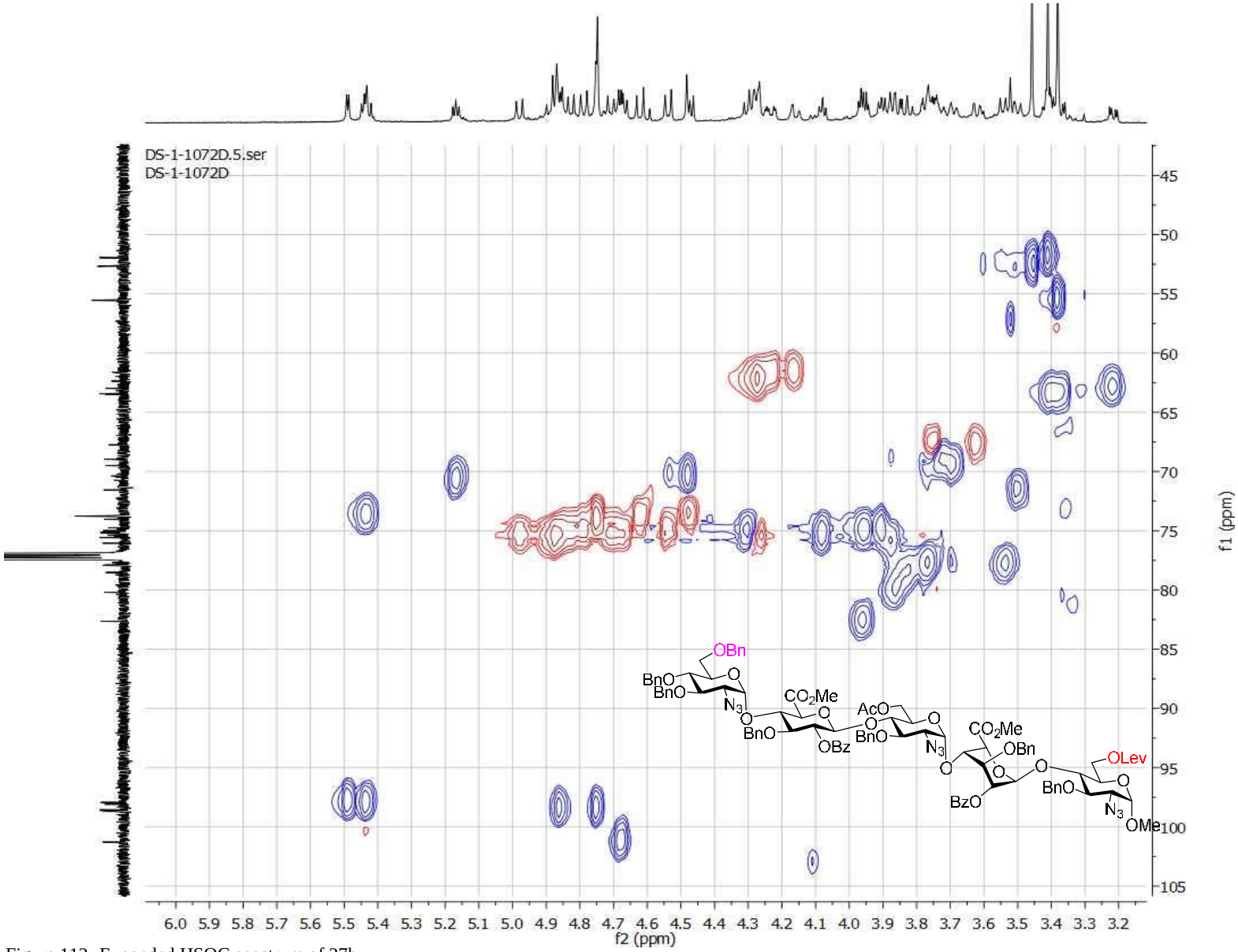


Figure 112. Expanded HSQC spectrum of 27b.

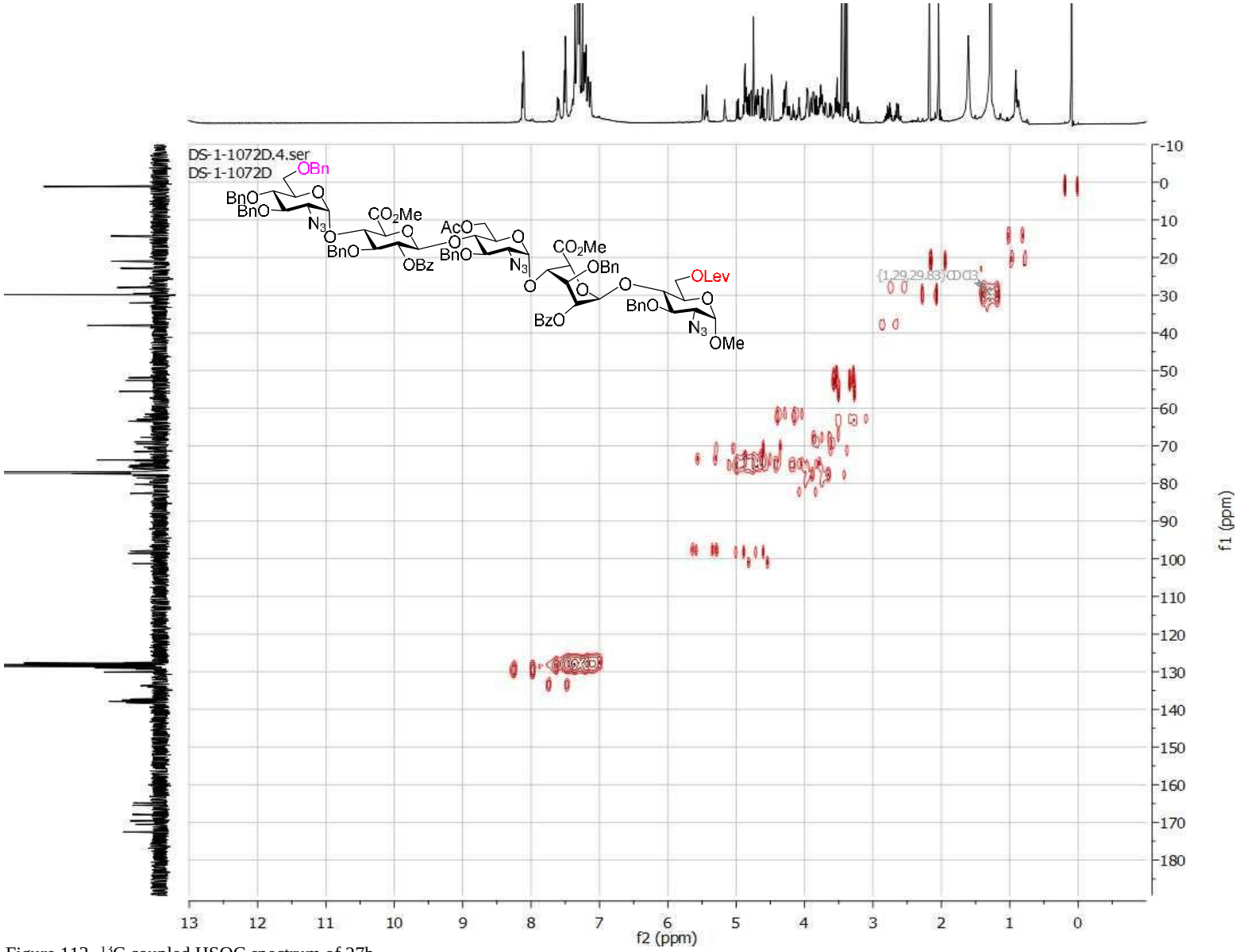


Figure 113. $^{13}$C coupled HSQC spectrum of 27b.

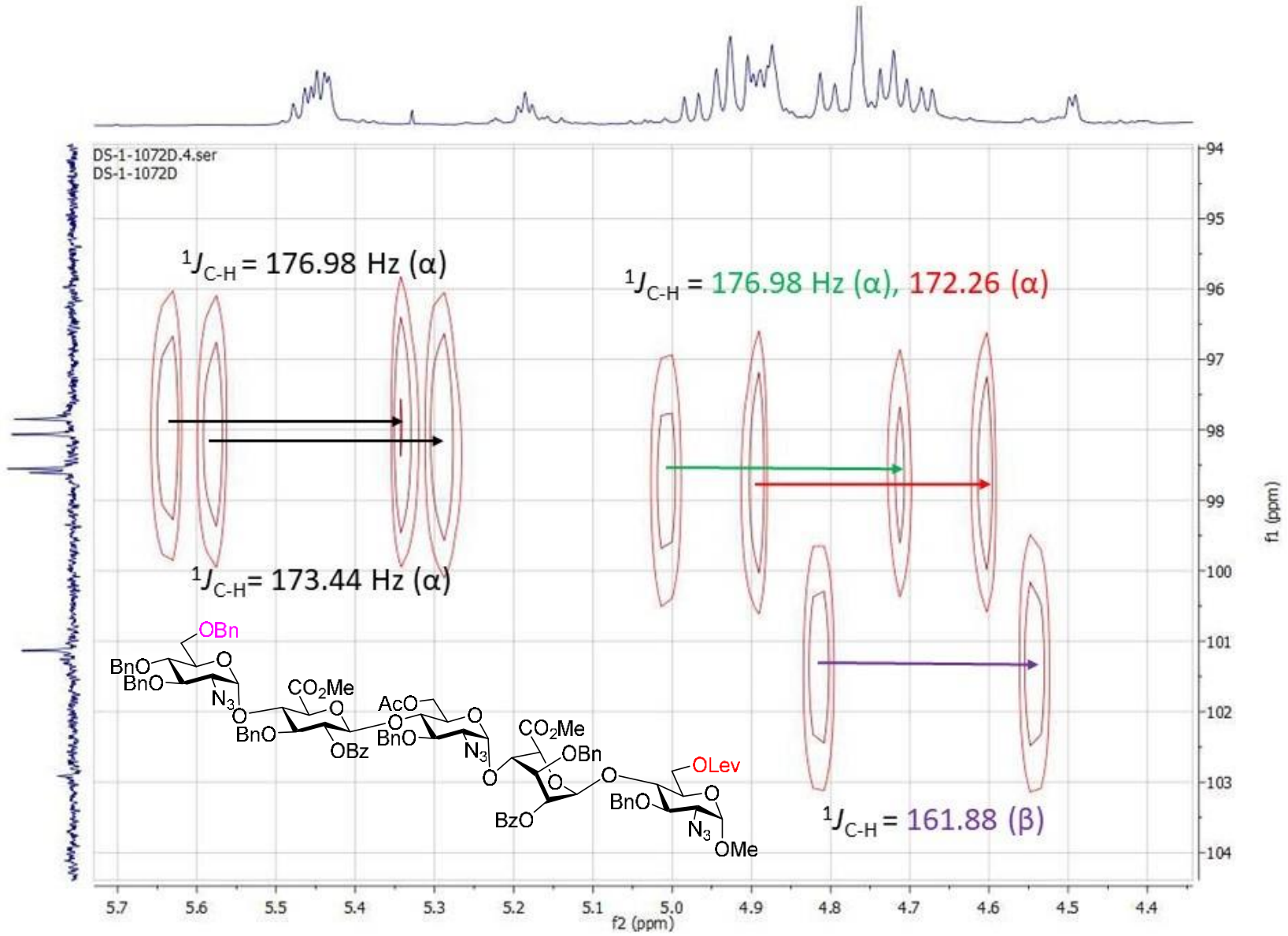


Figure 114. Expanded $^{13}C$ coupled HSQC spectrum of 27b.

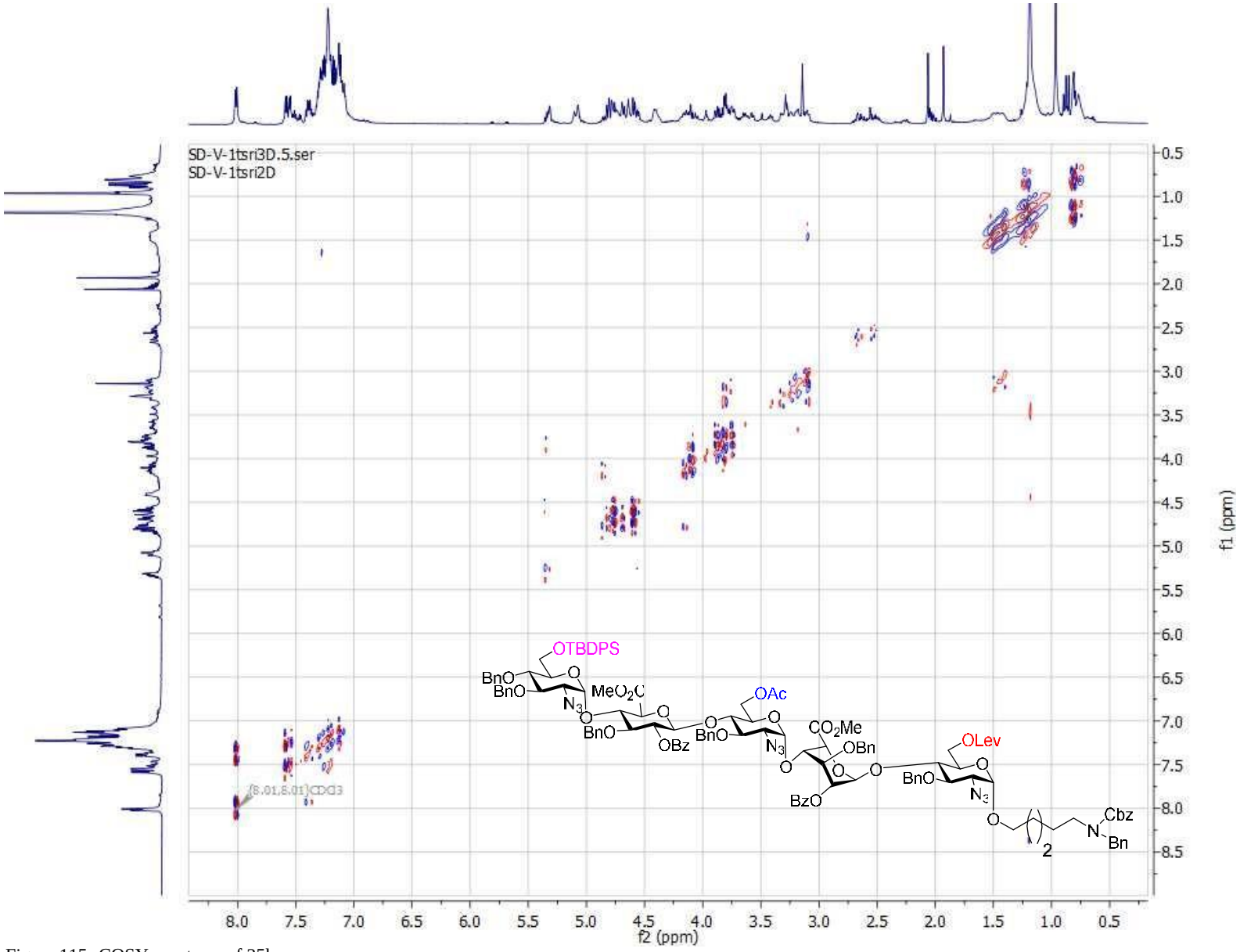


Figure 115. COSY spectrum of 25b.

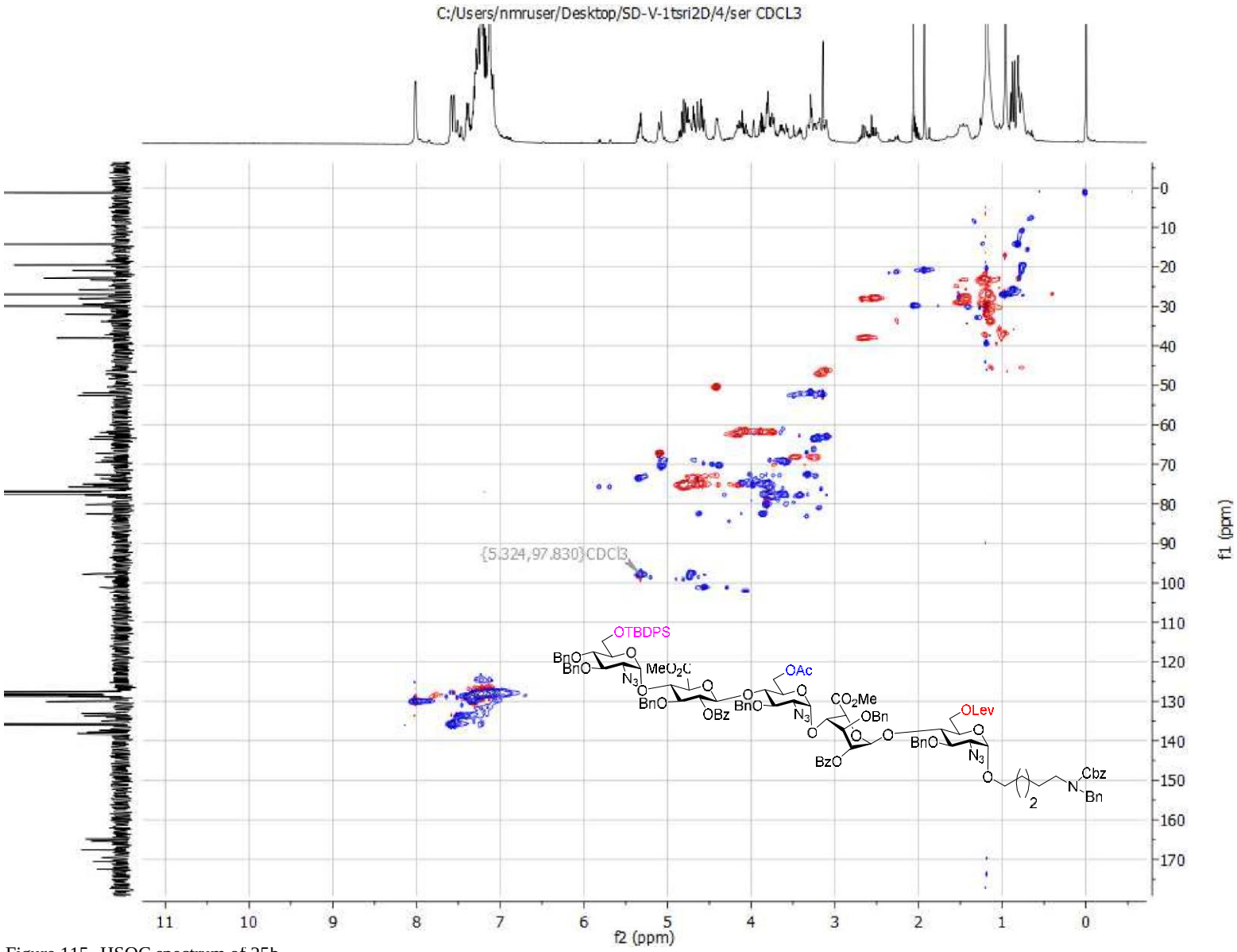


Figure 115. HSQC spectrum of 25b.

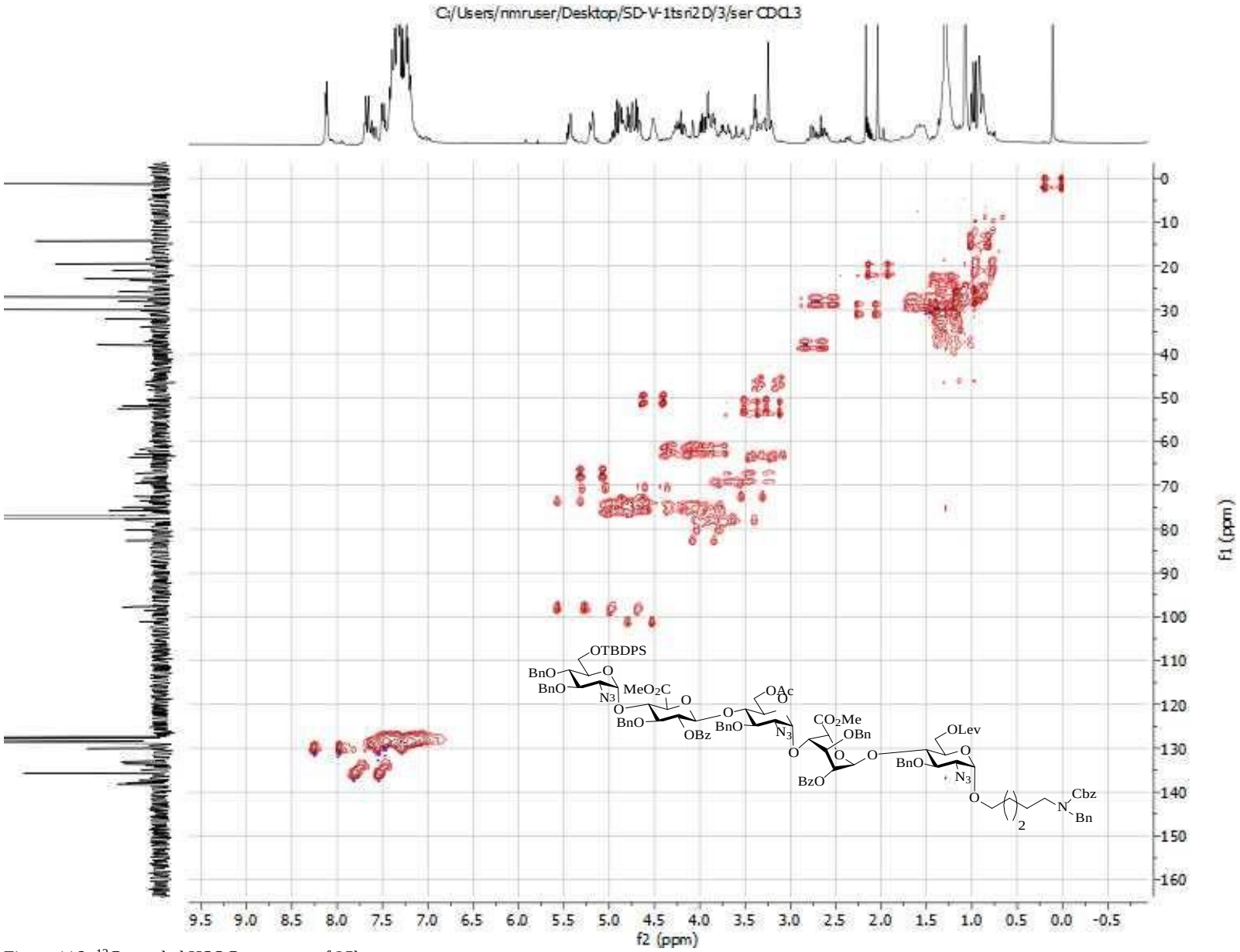


Figure 116. $^{13}$C coupled HSQC spectrum of 25b.

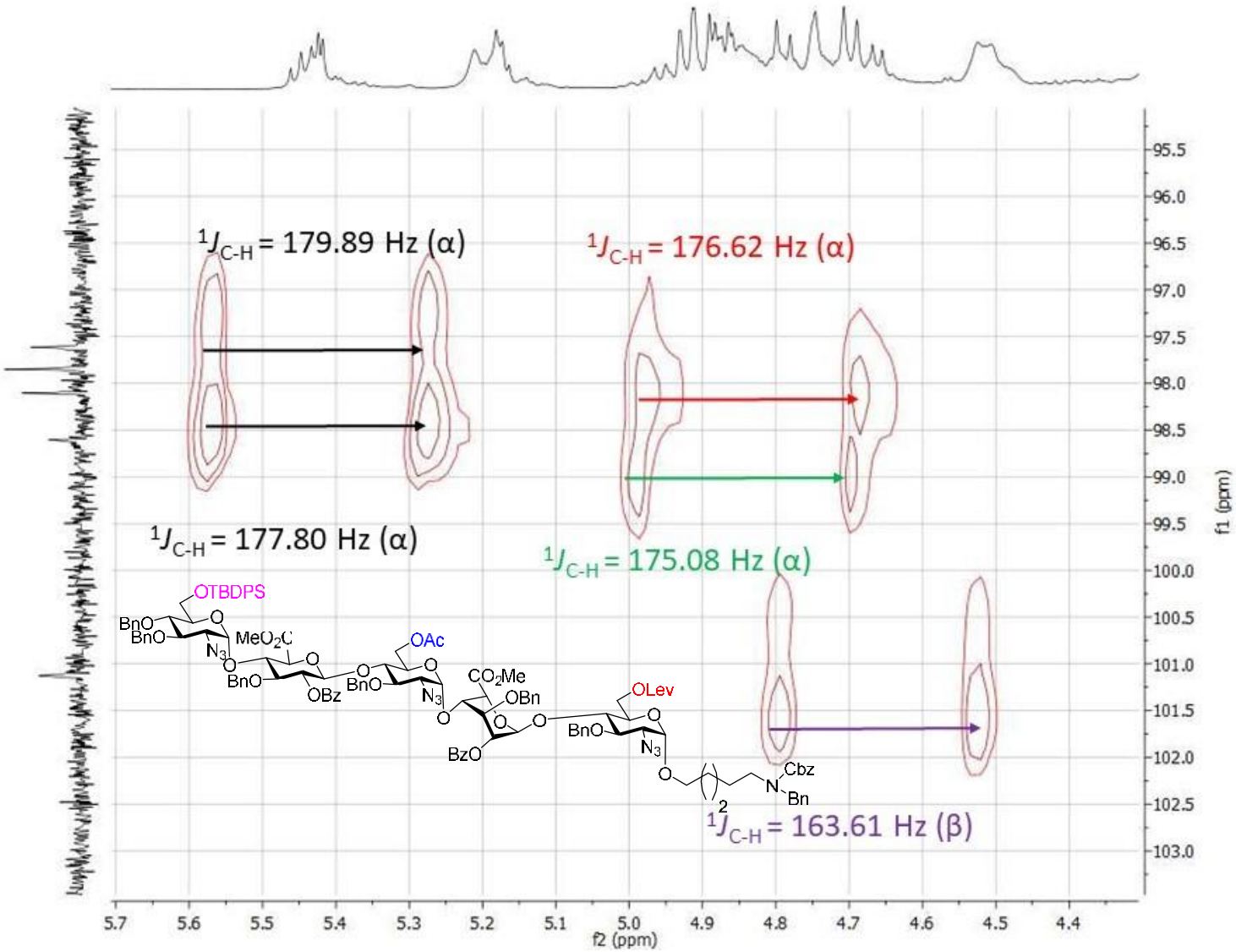


Figure 117. Expanded $^{13}C$ coupled HSQC spectrum of 25b.

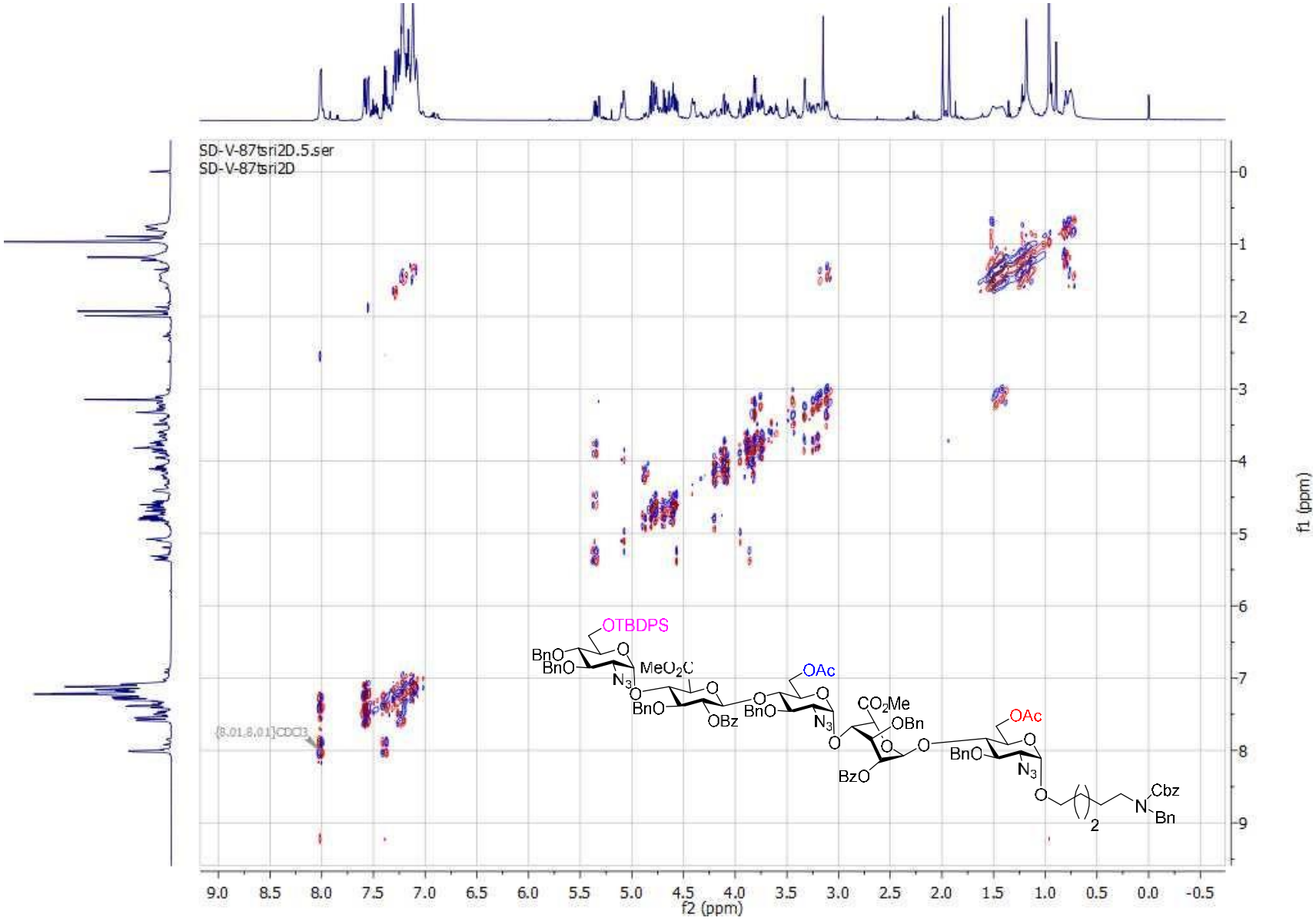


Figure 118. COSY spectrum of 25a.

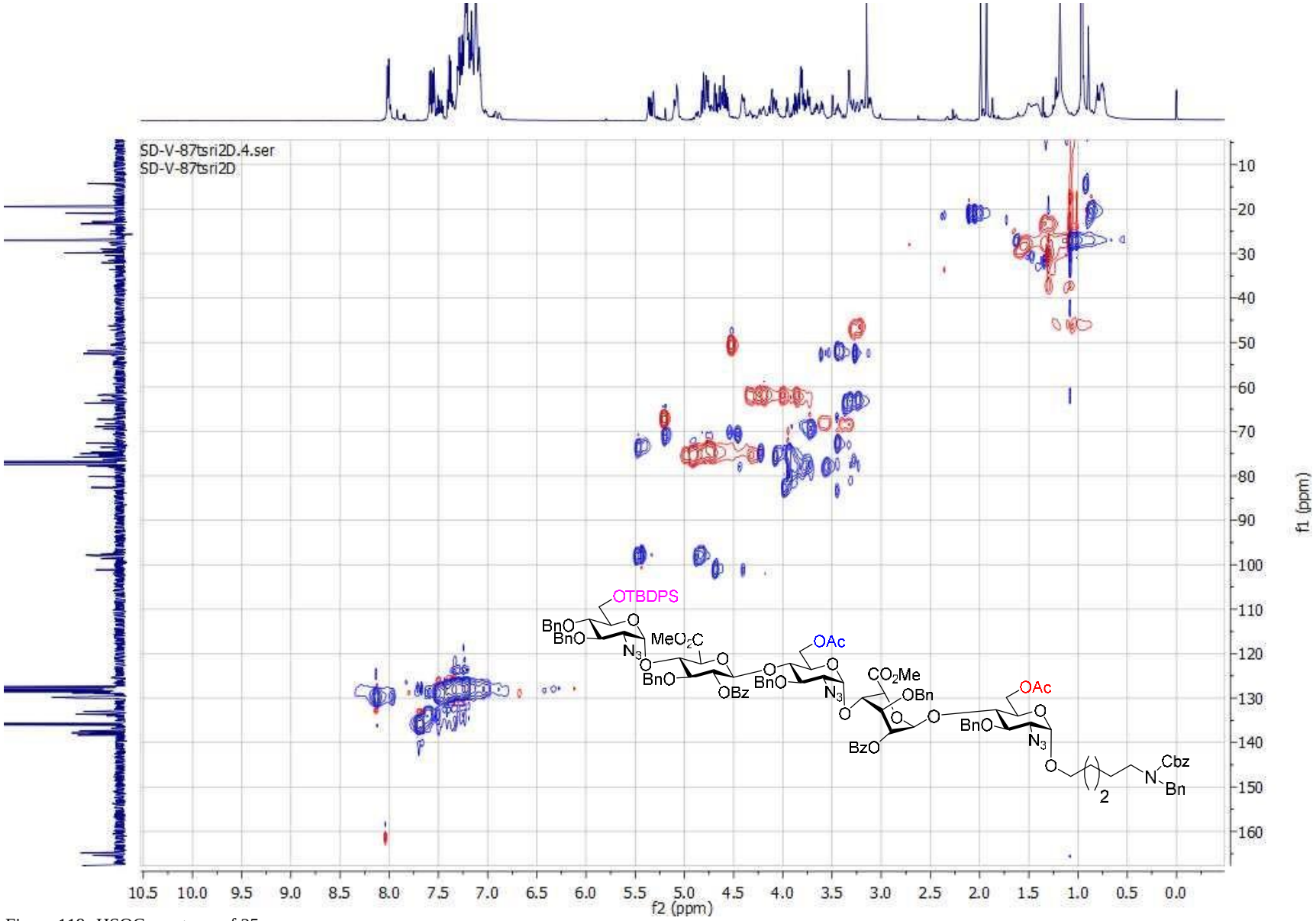


Figure 119. HSQC spectrum of 25a.

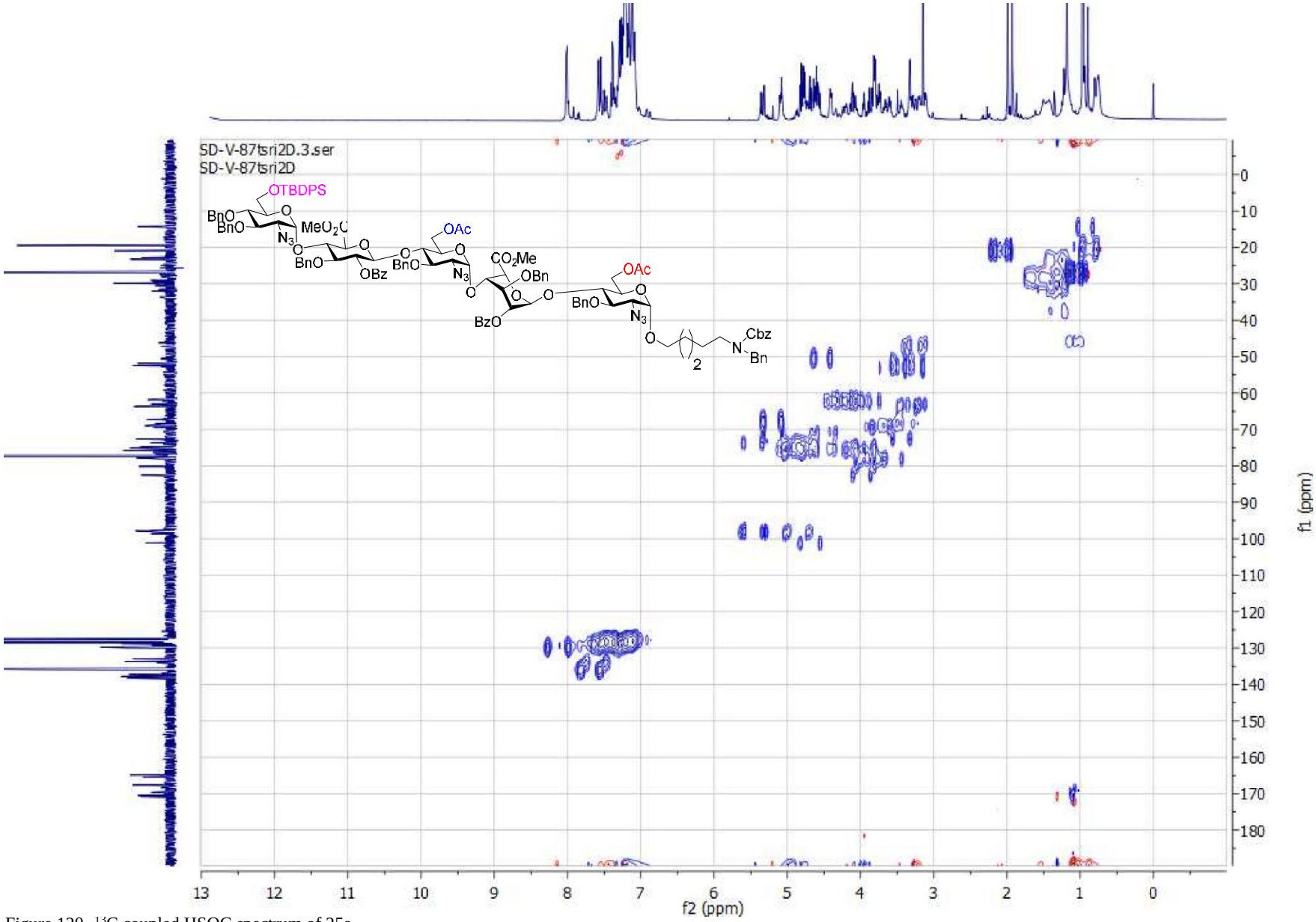


Figure 120. $^{13}C$ coupled HSQC spectrum of 25a.

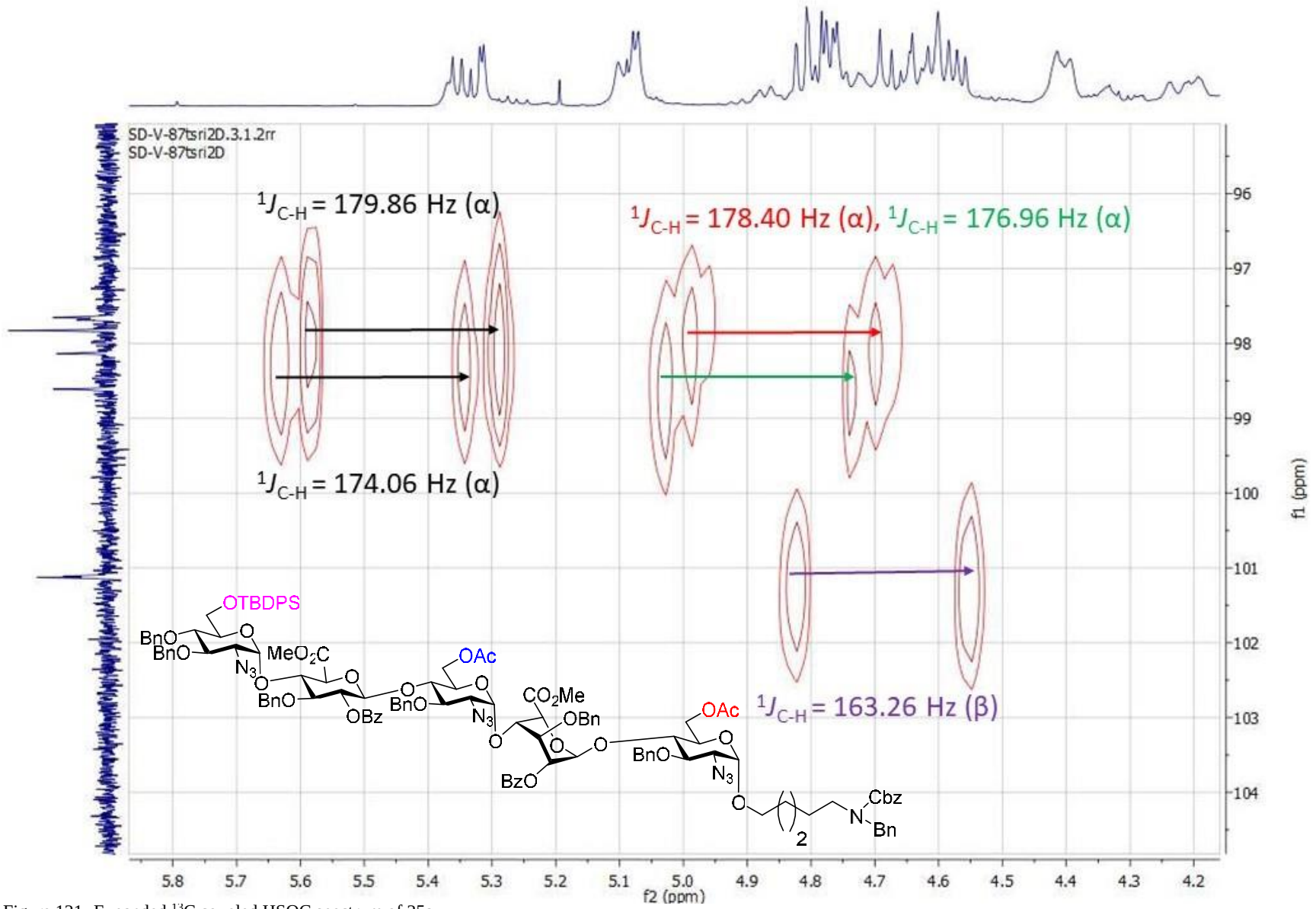


Figure 121. Expanded $^{13}C$ coupled HSQC spectrum of 25a.

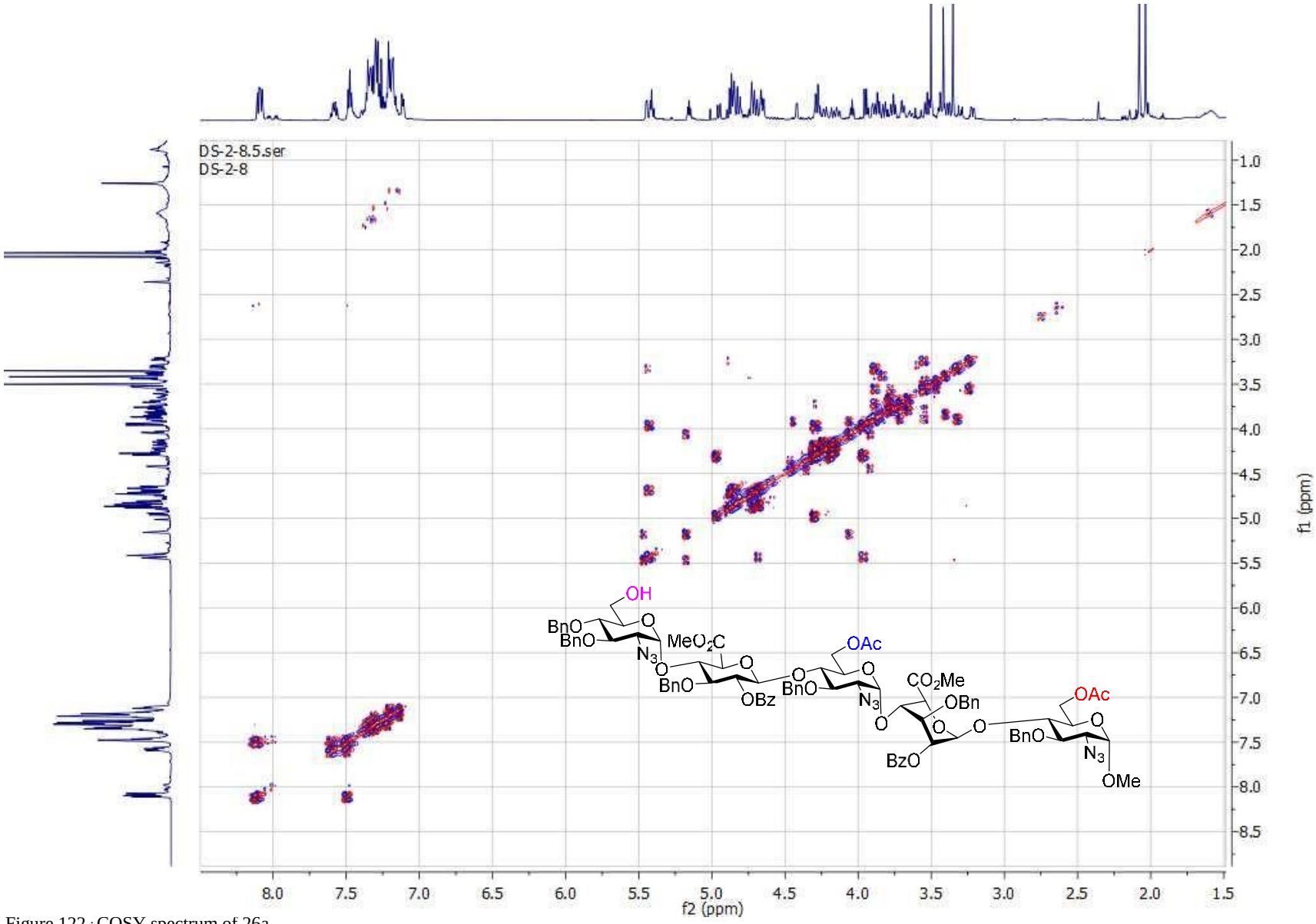


Figure 122. COSY spectrum of 26a.

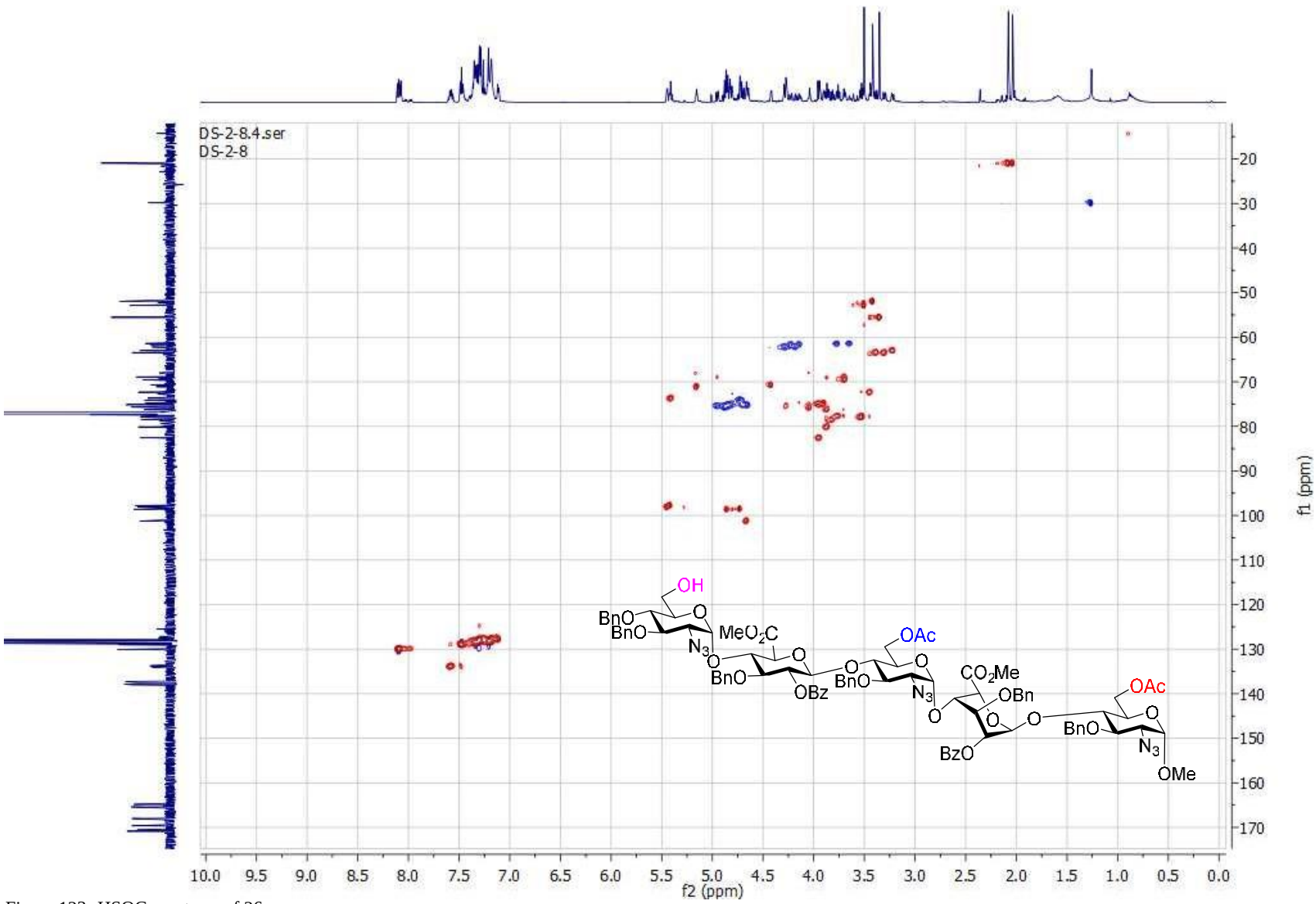


Figure 123. HSQC spectrum of 26a.

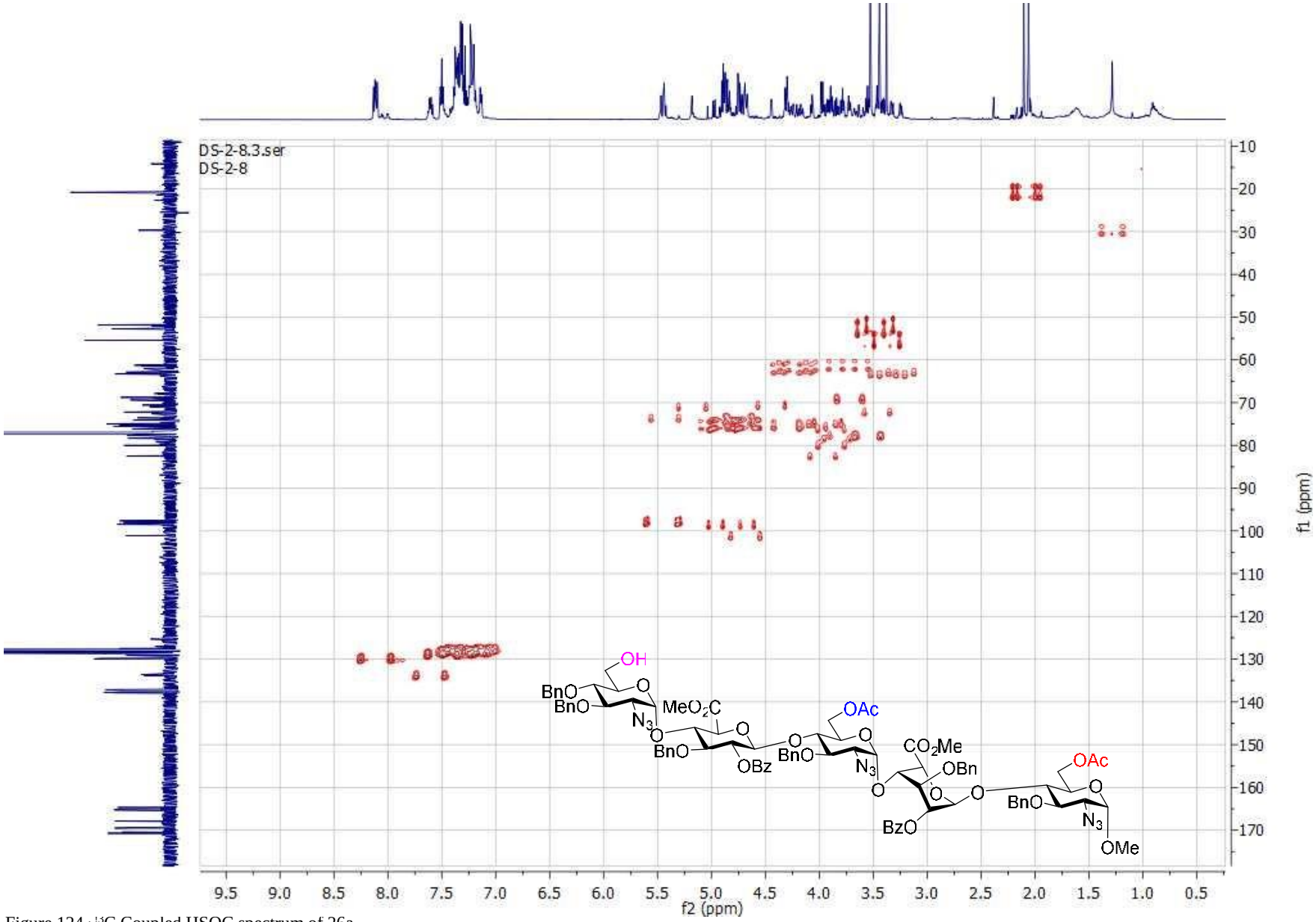


Figure 124. $^{13}$C Coupled HSQC spectrum of 26a.

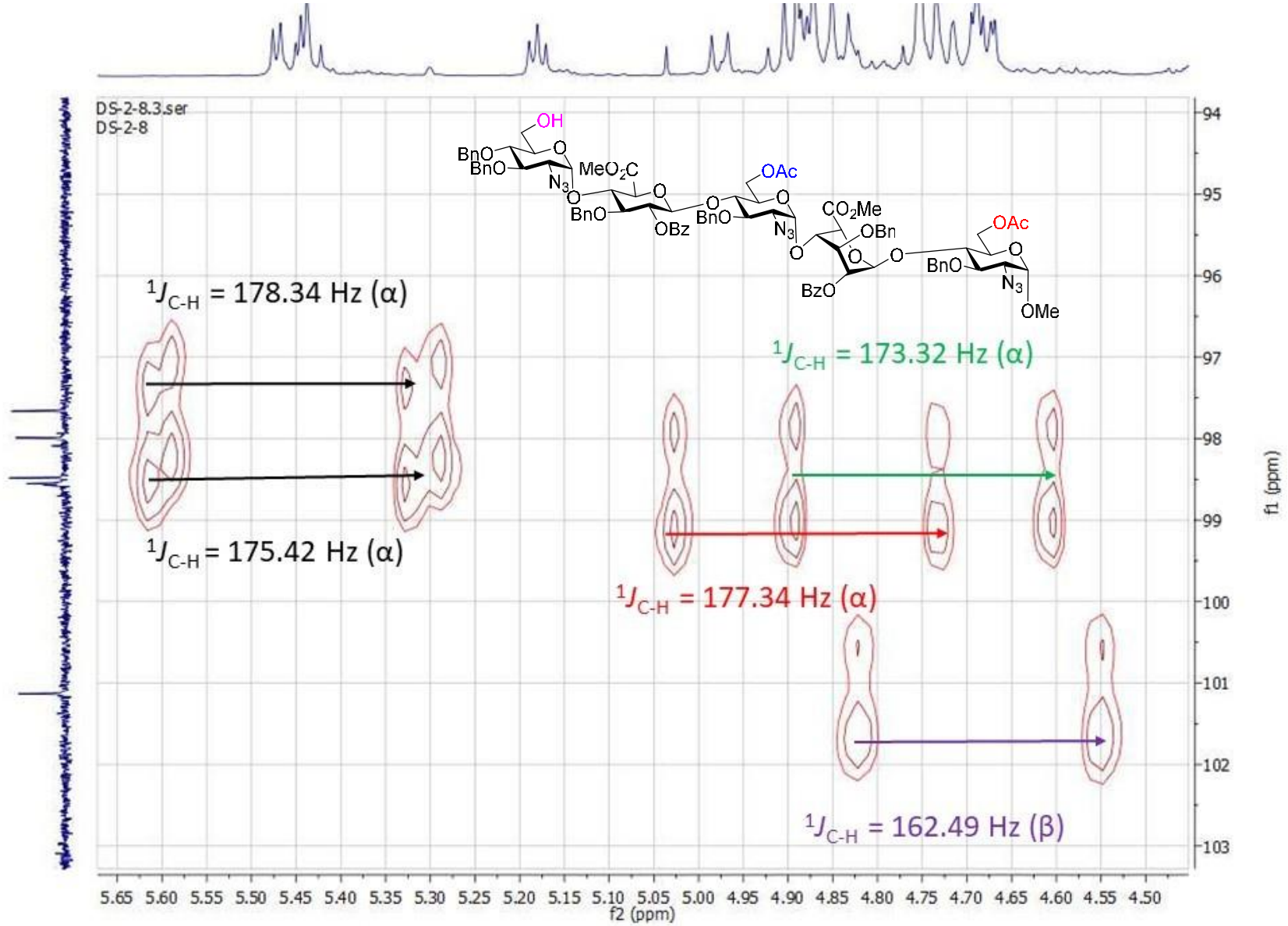


Figure 125. Expanded $^{13}C$ Coupled HSQC spectrum of 26a.