I. Supplementary Methods

II. Supplementary Results

Supplementary Figures

Supplementary Tables

III. Supplementary reference

1. General materials and methods.

1.1. General Materials. Unless otherwise stated, all chemicals and reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA) and utilized as received. Compound **1** was previously synthesized from glucose,[S1] Compound **22**[S2], **24**,[S3] **26**,[S4] **28**,[S5] were synthesized following prior published protocols.

1.2. General Methods. High resolution mass spectrometric data were obtained on a Waters (Milford, MA) LCT time-of-flight spectrometer for electrospray ionization (ESI) or AB SCIEX TripleTOF® 5600 System. NMR spectra were obtained on either a Varian Unity Inova 400 or 500 MHz instrument (Palo Alto, CA) using 99.8% $CDCl_3$ with 0.05% v/v TMS or 99.8% CD_3OD from Cambridge isotopes (Cambridge Isotope Laboratories, MA, USA). ^1H and ^{13}C chemical shifts were referenced to internal solvent resonances. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet) and br (broad). Chemical shifts are reported in parts per million (ppm) and coupling constants *J* are given in Hz. Routine ^{13}C NMR spectra were fully decoupled by broad-broad WALTZ decoupling. All NMR spectra were recorded at ambient temperature. Normal phase flash chromatography was performed on 40 – 63 µm, 60 A silica gel (from Silicycle, Quebec, Canada). Analytical TLC was performed on silica gel glass TLC plates (from EMD chemical Inc). TLC visualization was accomplished with UV light (254 nm) followed by staining with diluted sulfuric acid (5% in ethanol) solution and heating.

2. Synthesis of 2-chloro-4-nitrophenyl glycosides (2-20).

2.1. General procedure of bromination with $TiBr_4$/EtOAc. The per-*O*-acylated glycoside (1 eq) was dissolved in CH_2Cl_2/EtOAc (100/1) to a final concentration of 200 mM. To this solution was added $TiBr_4$ (2 eq) and the reaction was stirred under room temperature for 12 h or until TLC indicated completion of the reaction. The reaction was quenched by adding NaOAc (1 eq) and stirred for 15 mins, then filtered through celite and washed with CH_2Cl_2 (50 mL, x3). The brown filtrate was washed with water until the organic layer became colorless. The organic layer was then washed with brine and dried over Na_2SO_4. After the removal of the solvent, the per-*O*-acetylated-1-bromo-glycosides were purified by normal phase column chromatography (using a gradient from 100:0 to 40:60 hexanes:EtOAc) and subjected to glycosylation reaction immediately upon isolation.

2.2. General procedure for Koenigs-Knorr glycosylation reaction. To the per-*O*-acylated glycosyl bromide (1.0 eq) in anhydrous 150 mM CH_3CN solution was added 2-chloro-4-nitrophenol (2.0 eq) and 4 Å molecular sieves. The mixture was stirred for 30 min before Ag_2O (1.5 eq) was added to the solution. The reaction was stirred under room temperature for 12 h or until TLC indicated the completion of the reaction. The reaction was quenched by filtering through celite and was subsequently washed with EtOAc to recover all material. After the removal of the solvent under vacuum, the 2-chloro-4-nitrophenyl glycoside was purified by normal phase column chromatography (using a gradient from 100:0 to 40:60 hexanes:EtOAc) to afford the desired per-*O*-acylated 2-chloro-nitrophenyl glycoside as the pure product.

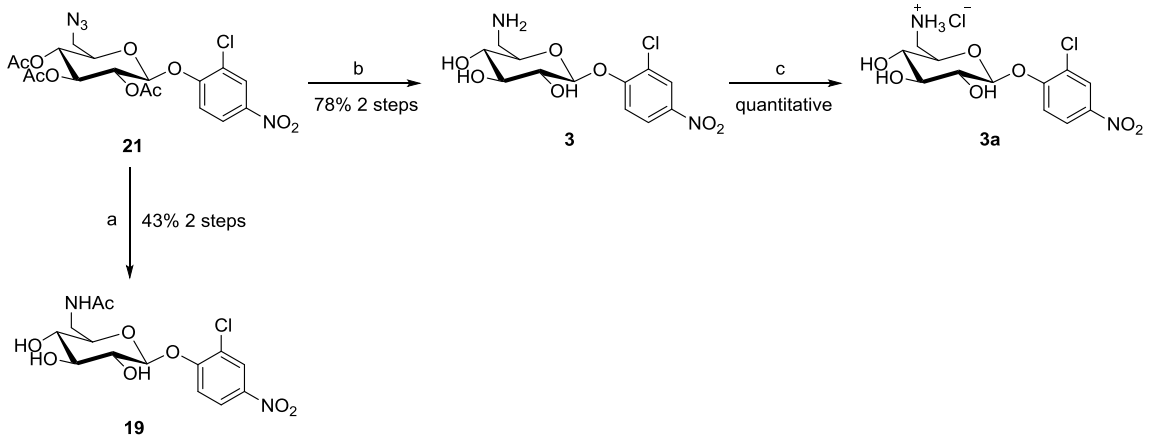
2.3. General procedure for deacetylation. A solution of per-*O*-acylated 2-chloro-4-nitrophenyl glycoside (100 mM) and NaOMe (2 eq) in MeOH was stirred at room temperature until the complete consumption of starting material (~ 2 h). The reaction was quenched by adding Amberlite 120 (H^+) (4 eq) and stirred for 30 min. The reaction mixture was filtered through celite and and was subsequently washed with EtOAc to recover all material. After the removal of solvent under vacuum, the desired 2-chloro-4-nitrophenyl glycoside was purified by normal phase column chromatography (using a gradient from 100:0 to 80:20 CH_2Cl_2:MeOH) to afford the 2-chloro-4-nitrophenyl glycoside as the pure product.

2.4. General procedure for azide reduction. To a 100 mM solution of 2-chloro-4-nitrophenyl azidosugar glycoside (1 eq) in THF was added PPh_3 (1.2 eq) or PMe_3 in THF (1.2 eq) and the reaction was stirred at 50 ^oC for 1 h. After removal of the solvent under reduced pressure, the residue was purified by normal-phase column chromatography (using a gradient from 100:0 CH_2Cl_2:MeOH to 80:20 CH_2Cl_2:MeOH) to afford the desired 2-chloro-4-nitrophenyl aminosugar glycoside as the pure product.

2.5. General procedure for 2-chloro-4-nitrophenyl aminosugar glycoside HCl formation. The purified 2-chloro-4-nitrophenyl aminosugar glycoside was dissolved into water (4 mM) and acidified to pH 4 using 1 M HCl solution. After the removal of the solvent by reduced pressure, the 2-chloro-4-nitrophenyl aminosugar glycoside hydrochloride salt was obtained and used without further purification.

2.6. General procedure azidosugar formation. Tf_2O (1.5 eq) was slowly added to a 125 mM CH_2Cl_2 solution of suitably-protected glycoside (1.0 eq) and pyridine (1.6 eq) under 0 ^oC and the reaction was stirred at 0 ^oC for 30 min. The reaction was diluted with CH_2Cl_2 and washed with water, sat. $NaHCO_3$, and brine and dried over Na_2SO_4. After filtration, the CH_2Cl_2 solution was concentrated in *vacuo* to less than 4 mL and transferred to 100 mL DMF solution containing NaN_3 (2.0 eq). The reaction mixture was stirred at room temperature for 12 h and filtered through a celite pad. The filtrate was concentrated under reduced pressure and purified by normal-phase column chromatography (using a gradient from 90:10 to 30:70 hexanes:EtOAc).

2.7. Synthesis of (2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (2).



(a) (1) PPh_3, CH_3CN/water=10/1, (2) NaOMe, MeOH; (b) (1) NaOMe, MeOH, (2) PMe_3 in toluene, THF; (c) HCl, Water

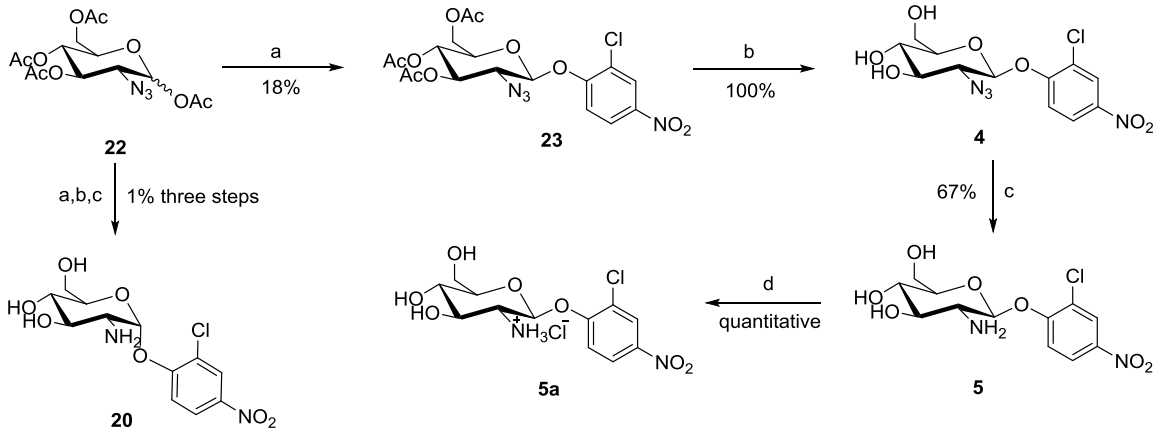
(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (3). To a 10 mL MeOH solution of **21**[S1] (58.3 mg, 0.12 mmol) was added 80 µl 1 M NaOMe/MeOH solution and according to general protocol **2.3**, (2-chloro-4-nitrophenyl)-6-deoxy-6-azido-β-D-glucopyranoside **2** [S1] (43.0 mg, 0.12 mmol) was obtained. The subsequent **2.4** general protocol for reduction of **2** yielded **3** (33.2 mg, 78% yield after 2 steps) as a white solid. ^1H NMR (CD_3OD, 500 MHz) δ ppm 8.32 (d, *J* = 2.7 Hz, 1 H), 8.19 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.41 (d, *J* = 9.3 Hz, 1 H), 5.20 (d, *J* = 7.6 Hz, 1 H), 3.57 (dd, *J* = 9.5, 7.6 Hz, 1 H), 3.42 - 3.52 (m, 3 H), 3.09 (dd, *J* = 13.6, 3.1 Hz, 1 H), 2.79 (dd, *J* = 13.7, 7.6 Hz, 1 H). ^{13}C NMR (D_2O, 125 MHz) δ ppm 157.4, 142.7, 126.5, 124.5, 123.6, 115.6, 99.9, 76.1, 75.4, 72.8, 71.1, 41.5. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{15}ClN_2O_7Na$, 357.0460; found 357.0457.

(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside hydrochloride (3a). According to general protocol **2.5**, **3** (30.0 mg, 0.08 mmol) yielded **3a** (33 mg, quantitative yield as a light yellow solid. ^1H NMR (D_2O, 500 MHz) δ ppm 8.48 (dd, *J* = 2.8, 1.3 Hz, 1 H), 8.27 (dd, *J* = 9.3, 2.9 Hz, 1 H), 7.41 (d, *J* = 9.3 Hz, 1 H), 5.44 (d, *J* = 7.8 Hz, 1 H), 3.8 - 4.0 (m, 1 H), 3.79 (t, *J* = 8.3 Hz, 1 H), 3.70 (t, *J*

= 9.3 Hz, 1 H), 3.5 (m, 2 H), 3.21 (dd, *J* = 13.7, 8.5 Hz, 1 H). ^{13}C NMR (D_2O, 125 MHz) δ 157.3, 142.6, 126.5, 124.5, 123.6, 115.6, 99.9, 75.1, 72.6, 71.1, 62.8, 40.6. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{12}H_{16}ClN_2O_7$, 335.0646; found 335.0647.

(2-chloro-4-nitrophenyl)-6-deoxy-6-*N*-acetylamino-β-D-glucopyranoside (19). To a 10 mL CH_3CN/H_2O (10/1) solution of (2-chloro-4-nitrophenyl)-2,3,4-triacetyl-6-deoxy-6-azido-glucoside **21** [S1] (30 mg, 0.06 mmol) was added PPh_3 (25 mg, 0.09 mmol) and the reaction was stirred under room temperature for 12 h. The solvent was removed in *vacuo* and the residue was purified by column chromatography (using a gradient from 50:50 to 90:10 EtOAc:MeOH) to give the amine. To a 10 mL MeOH solution of this amine was added 60 µl 1 M NaOMe/MeOH solution and according to **2.3** general protocol for deacetylation reaction **19** (10 mg, 0.03 mmol) was obtained in 43% after two steps. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.31 (d, *J* = 2.7 Hz, 1 H), 8.18 (dd, *J* = 9.5, 3.0 Hz, 1 H), 7.38 (d, *J* = 9.4 Hz, 1 H), 5.18 (d, *J* = 7.6 Hz, 1 H), 3.5 - 3.6 (m, 3 H), 3.4 - 3.5 (m, 2 H), 3.25 (t, *J* = 9.0 Hz, 1 H), 1.94 (s, 3 H). ^{13}C NMR (CD_3OD, 100 MHz) δ 172.5, 157.7, 142.1, 125.3, 123.34, 123.31, 115.2, 100.0, 75.9, 74.8, 73.1, 70.9, 39.9, 20.9. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{14}H_{17}ClN_2O_8Na$, 399.0566; found 399.0566.

2.8. Synthesis of (2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (5).



(a) (1) $TiBr_4$, CH_2Cl_2/EtOAc, (2) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., R. T., 12 hours; (b) NaOMe, MeOH; (c) PMe_3 in toluene, THF; (d) HCl, Water

(2-chloro-4-nitrophenyl)-3,4,6-tri-*O*-acetyl-2-deoxy-2-azido-β-D-glucopyranoside (23). According to general procedure **2.1** and **2.2**, **22** (1.42 g, 3.81 mmol) yielded **23** (0.33g, 18% yield after two steps) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (d, *J* = 2.7 Hz, 1 H), 8.15 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.18 (d, *J* = 9.2 Hz, 1 H), 5.1 (m, 2 H), 5.05 (d, *J* = 8.0 Hz, 1 H), 4.30 (dd, *J* = 12.4, 5.6 Hz, 1 H), 4.17 (dd, *J* = 12.4, 2.4 Hz, 1 H), 3.8 (m, 2 H), 2.13 (s, 3 H), 2.09 (s, 3 H), 2.05 - 2.07 (m, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 170.5, 170.0, 169.7, 157.0, 143.5, 126.6, 125.0, 123.7, 115.9, 99.9, 72.8, 72.2, 68.2, 64.0, 61.9, 20.9, 20.9, 20.8. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{19}ClN_4O_{10}Na$, 509.0682; found 509.0679.

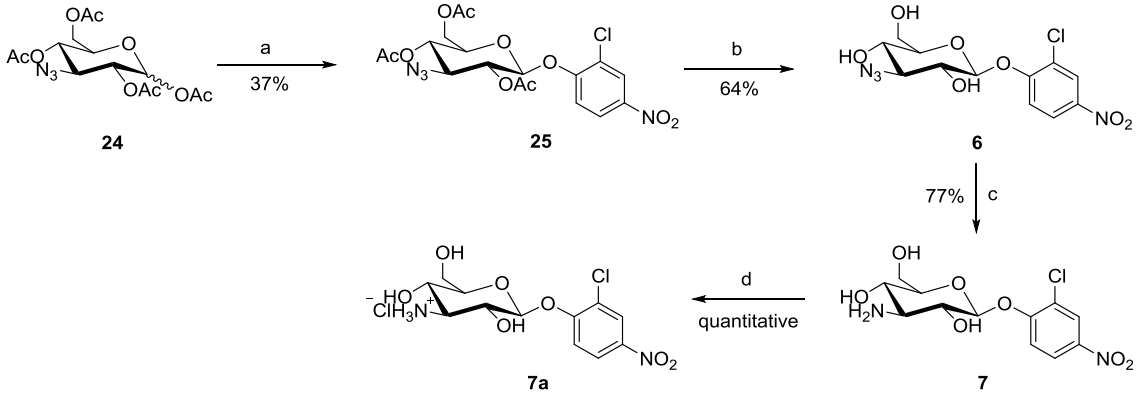
(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-glucopyranoside (4). According to general procedure **2.3**, **23** (0.16 g, 0.33 mmol) yielded **4** (0.13 g, 100% yield) as a light yellow solid. ^{1}H NMR (CD_3OD, 500 MHz) δ ppm 8.33 (d, *J* = 2.7 Hz, 1 H), 8.19 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.44 (d, *J* = 9.3 Hz, 1 H), 5.21 (d, *J* = 7.8 Hz, 1 H), 3.91 (dd, *J* = 12.2, 2.2 Hz, 1 H), 3.71 (dd, *J* = 12.2, 5.6 Hz, 1 H), 3.5 (m, 2 H), 3.4 - 3.5 (m, 2 H). ^{13}C NMR (CD_3OD, 125 MHz) δ 157.5, 142.7, 125.5, 123.8, 123.4, 115.8, 99.4, 77.4, 75.0, 69.8, 66.9, 61.0. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}ClN_4O_7Na$, 383.0365; found 383.0385.

(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (5). According to general procedure **2.4**, **4** (62.3 mg, 0.17 mmol) yielded **5** (39.8 mg, 67% yield) as a yellow solid**.** ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.33 (d, *J* = 2.7 Hz, 1 H), 8.20 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.49 (d, *J* = 9.4 Hz, 1 H), 5.05 (d, *J* = 8.0 Hz, 1 H), 3.92 (dd, *J* = 12.1, 2.1 Hz, 1 H), 3.72 (dd, *J* = 12.2, 5.8 Hz, 1 H), 3.5 (m, 1 H), 3.40 (dd, *J* = 9.4, 8.2 Hz, 2 H), 2.99 (dd, *J* = 9.4, 8.0 Hz, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ 157.9, 142.6, 125.4, 123.8, 123.5, 116.1, 101.9, 77.6, 75.8, 70.0, 61.1, 56.8. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{12}H_{16}ClN_2O_7$, 335.0641; found 335.0622.

(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside hydrochloride (5a). According to general procedure **2.5**, **5** (17 mg, 0.05 mmol) yielded **5a** (18.8 mg, quantitative yield) as a yellow oil. ^{1}H NMR (D_2O, 500 MHz) δ ppm 8.43 (d, *J* = 2.9 Hz, 1 H), 8.24 (dd, *J* = 9.3, 2.7 Hz, 1 H), 7.45 (d, *J* = 9.3 Hz, 1 H), 5.66 (d, *J* = 8.5 Hz, 1 H), 3.97 (dd, *J* = 12.5, 2.2 Hz, 1 H), 3.9 (m, 2 H), 3.77 (d, *J* = 2.2 Hz, 1 H), 3.65 (t, *J* = 9.8 Hz, 1 H), 3.57 (dd, *J* = 10.6, 8.4 Hz, 1 H). ^{13}C NMR (D_2O, 125 MHz) δ 156.3, 143.2, 126.5, 124.5, 124.0, 116.6, 96.7, 77.0, 72.1, 69.6, 60.3, 55.5. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{12}H_{16}ClN_2O_7$, 335.0641; found 335.0642.

(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-α-D-glucopyranoside (20). According to general procedure **2.1-2.4**, **22** (1.42 g, 3.81 mmol) yielded **20** (5.7 mg, 1% yield after three steps) as minor product. ^{1}H NMR (CD_3OD, 500 MHz) δ ppm 8.34 (d, *J* = 2.7 Hz, 1 H), 8.20 (dd, *J* = 9.3, 2.7 Hz, 1 H), 7.60 (d, *J* = 9.3 Hz, 1 H), 5.74 (d, *J* = 3.4 Hz, 1 H), 3.75 (dd, *J* = 12.2, 2.4 Hz, 1 H), 3.7 (m, 2 H), 3.57 (ddd, *J* = 5.2, 2.3,2.0 Hz, 1 H), 3.42 (dd, *J* = 10.0, 8.8 Hz, 1 H), 2.85 (dd, *J* = 10.0, 3.4 Hz, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ 157.1, 142.3, 125.2, 125.1, 123.6, 115.6, 99.3, 74.5, 74.4, 69.8, 60.8, 55.5. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{12}H_{16}ClN_2O_7$, 335.0641; found 335.0622.

2.9. Synthesis of (2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (7).



(a) (1) $TiBr_4$, CH_2Cl_2/EtOAc; (2) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., R. T., 12 hours; (b) NaOMe, MeOH; (c) PMe_3 in toluene, THF; (d) HCl, Water

(2-chloro-4-nitrophenyl)-2,4,6-tri-*O*-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (25). According to general procedure **2.1** and **2.2**, **24** (0.40 g, 1.07 mmol) yielded **25** (0.19 g, 37% yield for two steps) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30 (d, *J* = 2.5 Hz, 1 H), 8.12 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.24 (d, *J* = 9.0 Hz, 1 H), 5.32 (dd, *J* = 10.2, 7.9 Hz, 1 H), 5.07 (d, J = 7.8 Hz, 1H), 5.09 (t, J = 9.2 Hz, 1H), , 4.1 - 4.2 (m, 2 H), 3.8 (m, 1 H), 3.77 (t, *J* = 10.0 Hz, 1 H), 2.17 (s, 3 H), 2.16 (s, 3 H), 2.11 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.6, 169.3, 168.9, 157.4, 143.5, 126.4, 125.3, 123.7, 116.8, 99.8, 73.6, 70.4, 68.3, 64.0, 61.9, 20.9, 20.82, 20.80. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{19}ClN_4O_{10}Na$, 509.0682; found 509.0692.

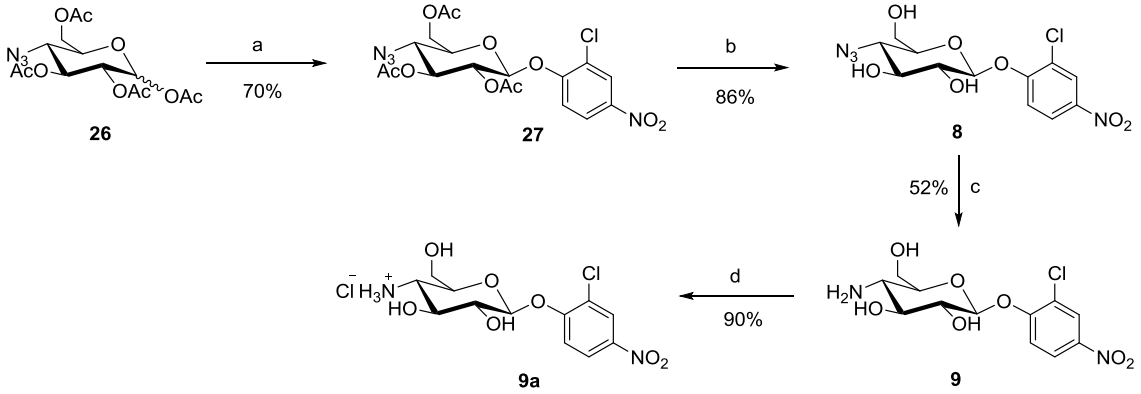
(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-glucopyranoside (6). According to general procedure **2.3**, **25** (0.19 g, 0.39 mmol) yielded **6** (0.09 g, 64% yield) as a white solid. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.30 (d, *J* = 2.7 Hz, 1 H), 8.18 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.43 (d, *J* = 9.2 Hz, 1 H), 5.24 (d, *J* = 7.6

Hz, 1 H), 3.88 (dd, *J* = 12.1, 2.1 Hz, 1 H), 3.70 (dd, *J* = 12.1, 5.5 Hz, 1 H), 3.5 (m, 2 H), 3.4 - 3.5 (m, 2 H). ^{13}C NMR (CD_3OD, 100 MHz) δ 157.9, 142.4, 125.5, 123.7 (2 carbons), 115.6, 100.5, 77.8, 72.1, 69.9, 68.4, 60.8. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}ClN_4O_7Na$, 383.0365; found 383.0348.

(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (7). According to general protocol **2.4**, **6** (35.7 mg, 0.096 mmol) yielded **7** (25.6 mg, 77% yield) as a yellow solid**.** ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.28 (d, *J* = 2.7 Hz, 1 H), 8.14 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.42 (d, *J* = 9.4 Hz, 1 H), 5.18 (d, *J* = 7.8 Hz, 1 H), 4.66 (br. s., 1 H), 3.44 (t, *J* = 6.8 Hz, 3 H), 3.24 (t, *J* = 8.6 Hz, 1 H), 3.09 (t, *J* = 9.2 Hz, 1 H), 2.64 (t, *J* = 9.5 Hz, 1 H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 158.3, 142.1, 126.1, 124.8, 122.9, 116.3, 100.7, 78.8, 73.3, 69.9, 61.0, 59.8. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{12}H_{16}ClN_2O_7$, 335.0641; found 335.0626.

(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (7a). According to general procedure **2.5**, **7** (8.9 mg, 0.03 mmol) yielded **7a** (12.0 mg, quantitative yield) as a white solid. ^{1}H NMR (D_2O, 500 MHz) δ ppm 8.43 (d, *J* =2.7 Hz, 1 H), 8.24 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.43 (d, *J* = 9.3 Hz, 1 H), 5.44 (d, *J* = 7.6 Hz, 1 H), 3.9 (m, *J* = 10.5 Hz, 2 H), 3.8 - 3.9 (m, 3 H), 3.42 - 3.49 (m, 1 H). ^{13}C NMR (D_2O, 100 MHz) δ 157.2, 142.8, 126.4, 124.5, 123.6, 115.9, 100.2, 77.4, 69.2, 65.7, 60.0, 57.7. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{12}H_{16}ClN_2O_7$, 335.0646; found 335.0628.

2.10. Synthesis of (2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (9).



(a) (1) $TiBr_4$, CH_2Cl_2/EtOAc, (2) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., R. T., 12 hours; (b) NaOMe, MeOH; (c) PPh_3 , THF; (d) HCl, Water

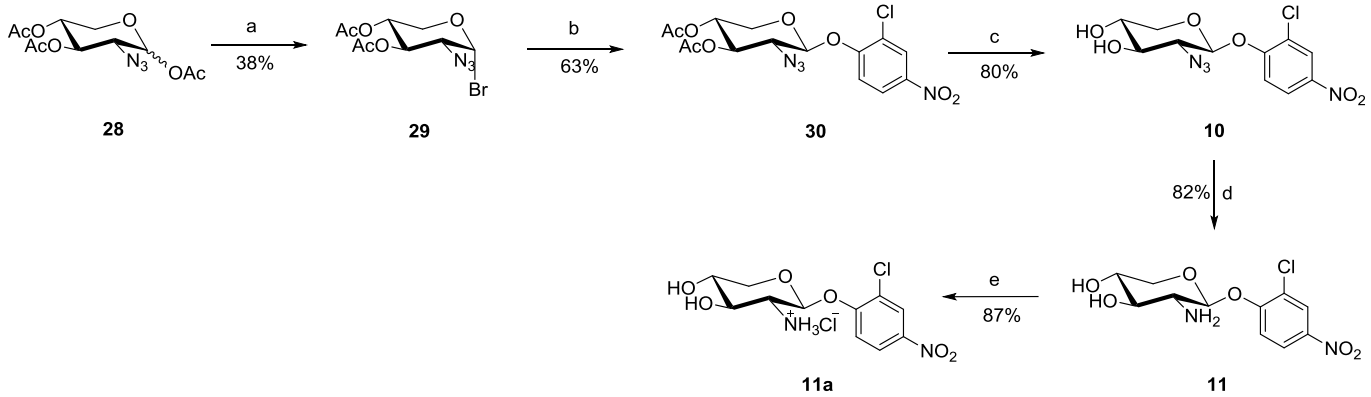
(2-chloro-4-nitrophenyl)-2,3,6-tri-*O*-acetyl-4-deoxy-4-azido-β-D-glucopyranoside (27). According to general procedure **2.1** and **2.2**, **26** (1.38 g, 3.7 mmol) yielded **27** (1.26 g, 70% yield for two steps) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.29 (d, *J* = 2.7 Hz, 1 H), 8.13 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.23 (d, *J* = 9.0 Hz, 1 H), 5.2 - 5.3 (m, 2 H), 5.13 (d, *J* = 7.6 Hz, 1 H), 4.50 (dd, *J* = 12.2, 2.2 Hz, 1 H), 4.31 (dd, *J* = 12.3, 5.0 Hz, 1 H), 3.81 (t, *J* = 10.0 Hz, 1 H), 3.70 (ddd, *J* = 5.1, 2.6, 1.8 Hz, 1 H), 2.15 (s, 3 H), 2.12 (s, 3 H), 2.09 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 170.5, 170.0, 169.5, 157.4, 143.5, 126.4, 125.2, 123.8, 116.7, 99.5, 73.3, 73.1, 71.0, 62.6, 59.8, 20.9, 20.83, 20.81. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{19}ClN_4O_{10}Na$, 509.0682; found m/z 509.0699.

(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-glucopyranoside (8). According to general procedure **2.3**, **27** (1.26 g, 2.59 mmol) yielded **8** (0.80 g, 86% yield) as a white solid. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.33 (d, *J* = 2.7 Hz, 1 H), 8.17 (dd, *J* = 9.2, 3.7 Hz, 1 H), 7.40 (d, *J* = 8.8 Hz, 1 H), 5.18 (d, *J* = 7.0 Hz, 1 H), 3.8 (m, 1 H), 3.73 (dd, *J* = 12.1, 4.1 Hz, 1 H), 3.65 (t, *J* = 8.8 Hz, 1H), 3.61 (t, *J* = 9.2 Hz, 1 H), 3.4 - 3.5 (m, 2 H). ^{13}C NMR (CD_3OD, 100 MHz) δ 157.9, 142.4, 125.5, 123.6 (2 carbons), 115.5, 100.3, 76.0, 75.4, 73.4, 61.5, 60.8. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{13}ClN_4O_6Na$, 383.0365; found 383.0344.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (9). According to general procedure **2.4**, **8** (130 mg, 0.36 mmol) yielded **9** (62.1 mg, 52% yield) as a white solid**.** ^{1}H NMR (CD_3OD, 400 MHz) δ 8.30 (d, *J* = 2.7 Hz, 1 H), 8.18 (dd, *J* = 9.3, 2.8 Hz, 1 H), 7.42 (d, *J* = 9.2 Hz, 1 H), 5.17 (d, *J* = 7.8 Hz, 1 H), 3.85 (dd, *J* = 12.2, 2.8 Hz, 1 H), 3.71 (dd, *J* = 12.3, 5.3 Hz, 1 H), 3.57 (dd, *J* = 9.1, 7.7 Hz, 1 H), 3.48 (ddd, *J* = 8.0, 5.3, 2.7 Hz, 1 H), 3.38 (d, *J* = 9.7 Hz, 1 H), 2.79 (t, *J* = 9.8 Hz, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ 158.1, 142.3, 125.4, 123.6 (2 carbons), 115.5, 100.7, 77.6, 76.5, 73.6, 61.5, 53.0. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{12}H_{16}ClN_2O_7$, 335.0641; found 335.0626.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside hydrochloride (9a). According to general procedure **2.5**, **9** (36.0 mg, 0.11 mmol) yielded **9a** (36.0 mg, 90% yield) as a yellow solid. ^{1}H NMR (D_2O, 500 MHz) δ ppm 8.32 (d, *J* = 2.7 Hz, 1 H), 8.15 (dd, *J* = 9.3, 2.7 Hz, 1 H), 7.35 (d, *J* = 9.3 Hz, 1 H), 5.36 (d, *J* = 7.6 Hz, 1 H), 4.07 (ddd, *J* = 10.3, 9.3, 4.9 Hz, 1 H), 3.97 (dd, *J* = 12.7, 3.9 Hz, 1 H), 3.8 - 3.9 (m, 2 H), 3.81 (t, *J* = 8.1 Hz, 1 H), 3.43 (t, *J* = 10.3 Hz, 1 H). ^{13}C NMR (D_2O, 125 MHz) δ 157.3, 142.6, 126.4, 124.5, 123.6, 115.8, 100.0, 73.0, 72.7, 71.9, 60.7, 52.6. HRMS-ESI (m/z): $[M]^+$) calcd for $C_{12}H_{16}ClN_2O_7Na$, 335.0646; found 335.0628.

2.11. Synthesis of (2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (11).



(a) $TiBr_4$, CH_2Cl_2/EtOAc; (b) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., R. T., 12 hours; (c) NaOMe, MeOH; (d) PMe_3 in toluene, THF; (e) HCl, Water

1-bromo-3,4-di-*O*-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (29). According to general procedure **2.1**, **28** (0.20 g, 0.66 mmol) yielded **29** (0.08 g, 38% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 6.39 (d, *J* = 3.7 Hz, 1 H), 5.51 (t, *J* = 9.8 Hz, 1 H), 5.04 (ddd, *J* = 10.9, 9.4, 6.0 Hz, 1 H), 4.04 (dd, *J* = 11.5, 6.0 Hz, 1 H), 3.91 (t, *J* = 11.3 Hz, 1 H), 3.71 (dd, *J* = 10.1, 3.9 Hz, 1 H), 2.13 (s, 3 H), 2.06 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 170.1, 169.7, 88.6, 71.1, 68.4, 63.0, 62.7, 20.8, 20.8. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_9H_{12}ClN_3O_5Na$, 343.9853; found 343.9865.

(2-chloro-4-nitrophenyl)-3,4-di-*O*-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (30). According to general procedure **2.2**, **29** (80 mg, 0.25 mmol) yielded **30** (64.9 mg, 63% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.34 (d, *J* = 2.7 Hz, 1 H), 8.15 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.21 (d, *J* = 9.2 Hz, 1 H), 5.15 (t, *J* = 6.44 Hz, 1H), 5.12 (d, *J* = 8.0 Hz,,1H), 5.03 (td, *J* = 7.8, 4.8 Hz, 1 H), 4.23 (dd, *J* = 12.2, 4.8 Hz, 1 H), 3.90 (dd, *J* = 9.0, 6.6 Hz, 1 H), 3.57 (dd, *J* = 12.1, 7.8 Hz, 1 H), 2.17 (s, 3 H), 2.09 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 170.0, 169.8, 156.9, 143.2, 126.5, 124.7, 123.8, 115.9, 99.8, 70.7, 68.5, 62.8, 62.3, 20.92, 20.91. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{15}ClN_4O_8Na$, 437.0471; found 437.0459.

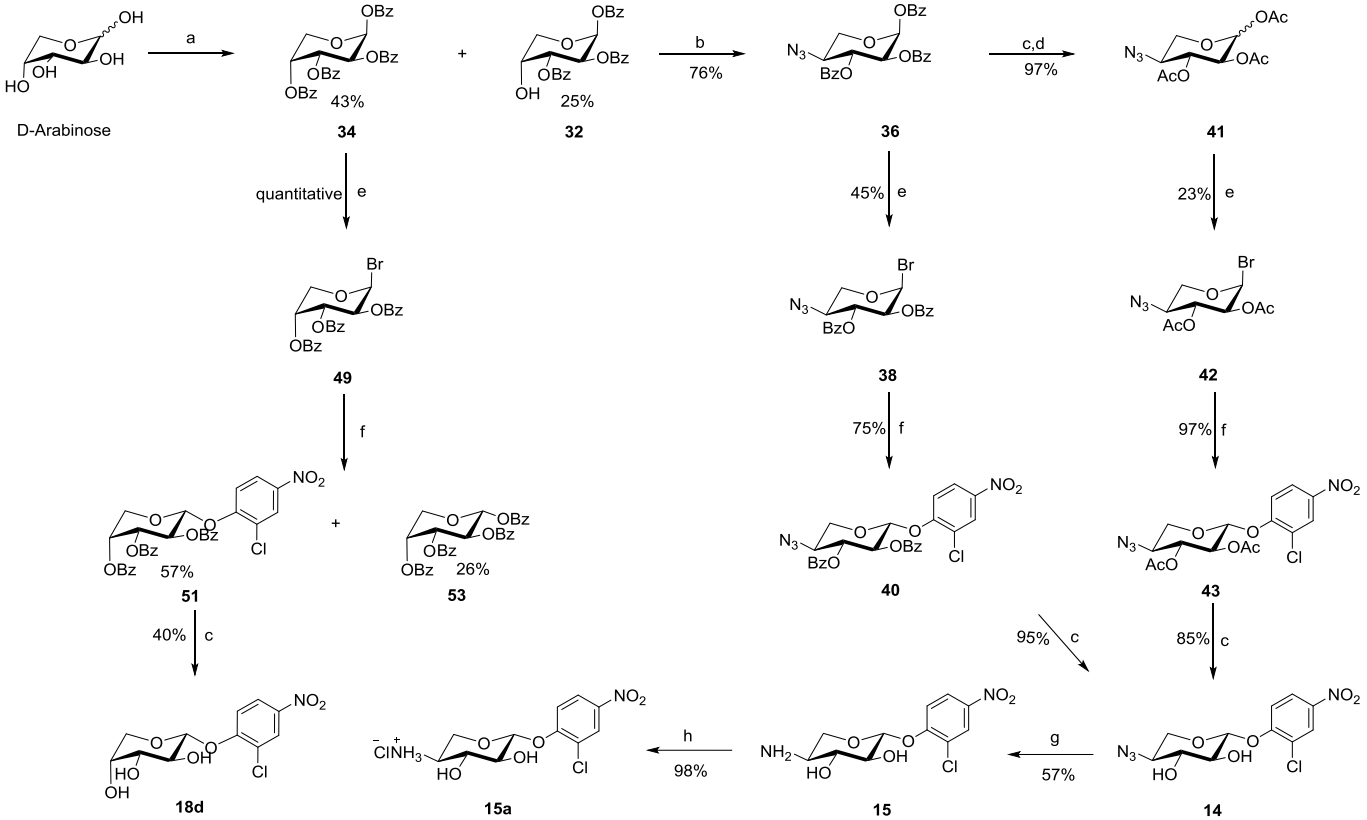
(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (10). According to general procedure **2.3**, **30** (65 mg, 0.16 mmol) yielded **10** (41.4 mg, 80% yield) as a light yellow solid. ^{1}H NMR (CD_3OD, 500 MHz) δ ppm 8.32 (d, *J* = 2.7 Hz, 1 H), 8.17 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.36 (d, *J* = 9.3 Hz, 1 H),

5.13 (d, *J* = 7.8 Hz, 1 H), 3.98 (dd, *J* = 11.5, 5.4 Hz, 1 H), 3.64 (ddd, *J* = 10.4, 8.9, 5.4 Hz, 1 H), 3.53 (dd, *J* = 9.8, 7.8 Hz, 1 H), 3.3 (m, 2 H). ^{13}C NMR (CD_3OD, 125 MHz) δ ppm 157.4, 142.8, 125.6, 123.7 (2 carbons), 115.6, 100.0, 75.0, 69.5, 66.8, 66.1. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{11}ClN_4O_6Na$, 353.0259; found 353.0276.

(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (11). According to general procedure **2.4**, **10** (26.5 mg, 0.08 mmol) yielded **11** (20.0 mg, 82% yield) as a white solid. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.32 (d, *J* = 2.7 Hz, 1 H), 8.19 (dd, *J* = 9.2, 2.9 Hz, 1 H), 7.41 (d, *J* = 9.2 Hz, 1 H), 5.04 (d, *J* = 7.8 Hz, 1 H), 4.00 (dd, *J* = 11.4, 5.2 Hz, 1 H), 3.6 (m, 1 H), 3.45 (dd, *J* = 11.4, 10.0 Hz, 1 H), 3.3 (m, 1 H), 2.98 (dd, *J* = 9.6, 7.7 Hz, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ ppm 157.7, 142.6, 125.5, 123.7 (2 carbons), 115.9, 102.3, 75.4, 69.6, 66.1, 56.5. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{14}ClN_2O_6$, 305.0535; found 305.0543.

(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (11a). According to general procedure **2.5**, **11** (13.3 mg, 0.08 mmol) yielded **11a** (13.0 mg, 87% yield) as a white solid. ^{1}H NMR (D_2O, 400 MHz) δ ppm 8.36 (d, *J* = 2.7 Hz, 1 H), 8.16 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.37 (d, *J* = 9.2 Hz, 1 H), 5.56 (d, *J* = 7.8 Hz, 1 H), 4.11 (dd, *J* = 12.0, 4.2 Hz, 1 H), 3.7 (m, 2 H), 3.5 (m, 2 H). ^{13}C NMR (D_2O, 100 MHz) δ ppm 156.1, 143.2, 126.5, 124.4, 124.0, 116.6, 97.1, 71.6, 69.1, 65.7, 55.0. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{11}H_{14}ClN_2O_6Na$, 305.0535; found 305.0544.

2.12. Synthesis of (2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (15).



(a) BzCl, Pyridine, -78°C-RT; (b) (1) Tf_2O, pyridine, CH_2Cl_2, (2) NaN_3, DMF; (c) NaOMe, MeOH; (d) Ac_2O, Et_3N, DMAP, CH_2Cl_2; (e) $TiBr_4$, CH_2Cl_2/EtOAc
(f) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., R. T., 12 hours; (g) PPh_3, THF; (h) HCl, Water

1,2,3-tri-*O*-benzoyl-α-D-arabinopyranoside (32). To a solution of D-arabinose (1.0 g, 6.7 mmol) in anhydrous pyridine (20 mL) at -50 °C with stirring was added benzoyl chloride (2.48 mL, 21.3 mmol) in a dropwise fashion. The reaction was held below -20 °C for 2 h and then allowed to slowly warm to

room temperature. The reacion was quenched by removing pyridine in *vacuo* and the residue was diluted with EtOAc and washed with 1N HCl, $NaHCO_3$ (sat), water, and brine. The organic phase was dried over Na_2SO_4 and purified by normal-phase column chrotomagraphy (using a gradient from 100:0 Hexanes:EtOAc to 70:30 Hexanes:EtOAc). Compound **32** (0.76 g, 1.64 mmol) was obtained in 25% as a white solid along with **34** (1.62 g, 2.86 mmol, 43% yield). **32:** ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.1 (m, 2 H), 8.0 (m, 2 H), 7.9 (m, 2 H), 7.6 (m, 2 H), 7.4 - 7.5 (m, 5 H), 7.3 (m, 2 H), 6.76 (d, *J* = 3.7 Hz, 1 H), 6.03 (dd, *J* = 10.5, 3.7 Hz, 1 H), 5.85 (dd, *J* = 10.5, 3.2 Hz, 1 H), 4.49 (br. s., 1 H), 4.26 (dd, *J* = 12.9, 1.2 Hz, 1 H), 4.04 (dd, *J* = 12.8, 2.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 166.14, 165.79, 164.96, 133.94, 133.84, 133.55, 130.09 (3 carbons), 130.05 (3 carbons), 129.95 (3 carbons), 128.91, 128.78 (2 carbons), 128.59 (3 carbons), 91.56, 71.08, 68.00, 67.58, 64.99. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{22}O_8Na$, 485.1207; found 485.1232.

1,2,3,4-tetra-*O*-benzoyl-α-D-arabinopyranoside (34). ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.15 (ddd, *J* = 8.1, 4.0, 1.1 Hz, 3 H), 7.8 (m, 3 H), 7.5 - 7.6 (m, 2 H), 7.3 - 7.5 (m, 10 H), 7.26 (t, *J* = 7.6 Hz, 2 H), 6.95 (d, *J* = 2.3 Hz, 1 H), 6.3 (m, 2 H), 5.97 (s, 1 H), 4.46 (d, *J* = 12.5 Hz, 1 H), 4.21 (dd, *J* = 13.5, 1.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.97, 165.94, 165.83, 164.93, 134.08, 133.80, 133.70 (2 carbons), 133.65 (3 carbons), 130.15 (3 carbons), 129.98 (3 carbons), 129.41, 129.23, 129.07, 129.00 (2 carbons), 128.88 (2 carbons), 128.67 (2 carbons), 128.64 (2carbons), 91.41, 69.81, 68.53, 68.15, 63.34. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{33}H_{26}O_9Na$, 589.1469; found 589.1491.

1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (36). According to general procedure **2.6**, **32** (0.76 g,1.64 mmol) yielded **36** (0.61 g, 76% yield) as a white oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.1 (m, 2 H), 8.0 (m, 2 H), 7.9 (m, 2 H), 7.63 (tt, *J* = 7.5, 1.3 Hz, 2 H), 7.4 - 7.6 (m, 5 H), 7.2 - 7.3 (m, 2 H), 6.70 (d, *J* = 3.7 Hz, 1 H), 6.01 (t, *J* = 9.6 Hz, 1 H), 5.50 (dd, *J* = 10.0, 3.7 Hz, 1 H), 4.0 (m, 2 H), 3.90 (d, *J* = 12.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.97, 165.70, 164.78, 134.18(3 carbons), 133.88 (3 carbons), 133.79, 130.23, 130.10, 129.17, 129.12, 129.04, 128.82 (2 carbons), 128.77 (2 carbons), 128.70 (2 carbons), 90.50, 71.33, 70.69, 62.26, 59.76. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{21}N_3O_7Na$, 510.1272; found 510.1279.

1-bromo-2,3-di-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (38). According to general procedure **2.1**, **36** (27 mg, 0.054 mmol) yielded **38** (11 mg, 45 % yield) as a white oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.0 (m, 3 H), 7.6 (m, 3 H), 7.4 (m, 4 H), 6.74 (d, *J* = 3.9 Hz, 1 H), 5.96 (t, *J* = 9.6 Hz, 1 H), 5.15 (dd, *J* = 9.9, 3.9 Hz, 1 H), 4.0 (m, 1 H), 3.9 - 4.0 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.56 (2 carbons), 134.02, 133.80, 130.27 (2 carbons), 130.03 (2 carbons), 129.02, 128.77 (2 carbons), 128.73 (2 carbons), 128.53, 87.83, 71.58, 71.36, 63.98, 59.07. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{16}BrN_3O_5Na$, 468.0166; found 408.0176.

(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-*O*-benzoyl-β-L-xylopyranoside (40). According to general procedure **2.2**, **38** (11 mg, 0.025 mmol) yielded **40** (10.0 mg, 75% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.26 (d, *J* = 2.7 Hz, 1 H), 8.0 - 8.1 (m, 5 H), 7.6 (m, 3 H), 7.4 (m, 3 H), 7.34 (d, *J* = 9.0 Hz, 1 H), 5.63 (dd, *J* = 5.9, 4.4 Hz, 1 H), 5.58 (t, *J* = 6.2 Hz, 1 H), 5.54 (d, *J* = 4.4 Hz, 1 H), 4.41 (dd, *J* = 12.5, 3.9 Hz, 1 H), 3.97 (td, *J* = 6.3, 3.9 Hz, 1 H), 3.80 (dd, *J* = 12.3, 6.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 167.32, 167.15, 159.23, 145.04, 135.91, 135.80, 132.18 (2 carbons), 132.15 (2 carbons), 132.03, 132.00, 130.83, 130.68, 130.65, 130.61, 128.28, 126.84, 125.79, 118.19, 100.54, 72.12, 71.12, 63.71, 59.00. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{25}H_{19}ClN_4O_8Na$, 561.0784; found 561.0802.

1,2,3-tri-*O*-acetyl-4-deoxy-4-azido-L-xylopyranoside (41). To a solution of **36** (0.55g, 1.13 mmol) in 20 mL was added MeOH 1 M NaOMe in MeOH (2 mL, 2 mmol) and the reaction was stirred at room temperature for 2 h. The reaction was quenched by adding Amberlite 120 (H^+) (0.1 g) and stirred for 30 min. The reaction mixture was filtered through celite and the celite subsequently washed with MeOH (5 mL, x3). After removal of solvent from collected organics, the residue was dried under vacuum. The

dried residue was dissolved into 40 mL CH_2Cl_2 solution and to this Et_3N (1.27 mL, 9.04 mmol), DMAP (34 mg, 0.28 mmol), Ac_2O (0.53 mL, 5.64 mmol) were added and the reaction was stirred at room temperature for 6 h. To the reaction was added 50 mL ethyl acetate and 50 mL $NaHCO_3$ (sat) solution and it was stirred vigorously until the evolution of gas halted. The organic layer was washed with water, brine and dried over Na_2SO_4. After the removal of the solvent under vacuum the recovered material was purified by normal phase column chromatography (using a gradient from 100:0 Hexanes:EtOAc to 70:30 Hexanes:EtOAc) to give **41** (0.30 g, 1.1 mmol, 97%) as a white powder. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 6.24 (d, *J* = 3.7 Hz, 1 H), 5.64 (d, *J* = 7.6 Hz, 1 H), 5.39 (t, *J* = 9.8 Hz, 1 H), 5.14 (t, *J* = 9.0 Hz, 1 H), 4.9 (m, 2 H), 4.09 (dd, *J* = 12.1, 5.2 Hz, 1 H), 3.88 (dd, *J* = 11.2, 5.4 Hz, 1 H), 3.7 (m, 2 H), 3.65 (t, *J* = 11.5 Hz, 1 H), 3.43 (dd, *J* = 12.0, 10.3 Hz, 1 H), 2.17 (s, 3 H), 2.12 (s, 3 H), 2.11 (s, 3 H), 2.10 (s, 3H), 2.05 (s, 3 H), 2.02 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 170.11, 170.09, 170.01, 169.76, 169.26, 169.16, 92.45, 89.64, 73.29, 70.70, 70.33, 69.71, 64.29, 61.86, 59.36, 58.76, 21.13, 21.02, 20.98, 20.91, 20.83, 20.74. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{15}N_3O_7Na$, 324.0802; found 324.0809.

1-bromo-2,3-di-*O*-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (42). According to general procedure **2.1**, **41** (0.30 g, 1.1 mmol) yielded **42** (80 mg, 23 % yield) as a white oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 6.55 (d, *J* = 3.9 Hz, 1 H), 5.50 (t, *J* = 9.7 Hz, 1 H), 4.75 (dd, *J* = 9.9, 3.9 Hz, 1 H), 4.00 (dd, *J* = 10.9, 5.5 Hz, 1 H), 3.84 (t, *J* = 11.5 Hz, 1 H), 37 (m, 1 H), 2.13 (s, 3 H), 2.10 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 170.1, 169.6, 87.6, 71.0, 70.7, 63.7, 58.7, 20.8 (2 carbons). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_9H_{12}BrN_3O_5Na$, 343.9853; found 343.9863.

(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-*O*-acetyl-β-L-xylopyranoside (43). According to general procedure **2.2**, **42** (80 mg, 0.25 mmol) yielded **43** (100 mg, 97% yield) as a yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.30 (d, *J* = 2.7 Hz, 1 H), 8.14 (dd, *J* = 9.0, 2.7 Hz, 2 H), 7.25 (d, *J* = 9.0 Hz, 1 H), 5.27 (d, *J* = 5.6 Hz, 1 H), 5.23 (dd, *J* = 7.3, 5.6 Hz, 1 H), 5.19 (d, *J* = 7.3 Hz, 1 H), 4.22 (dd, *J* = 12.2, 4.4 Hz, 1 H), 3.76 (td, *J* = 7.6, 4.6 Hz, 1 H), 3.57 (dd, *J* = 12.2, 8.1 Hz, 1 H), 2.16 (s, 3 H), 2.13 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 169.95, 169.62, 157.23, 143.26, 126.48, 124.88, 123.99, 116.20, 98.78, 71.06, 69.45, 62.70, 57.46, 20.99, 20.91. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{15}ClN_4O_8Na$, 437.0471; found 437.0485.

1-bromo-2,3,4-tri-*O*-benzoyl-α-D-arabinopyranoside (49). According to general procedure **2.1**, **34** (0.40 g, 0.71 mmol) yielded **49** (0.47 g, quantitative yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.1 (m, 3 H), 8.0 (m, 2 H), 7.8 (m, 2 H), 7.4 - 7.6 (m, 6 H), 7.2 (m, 2 H), 6.96 (d, *J* = 3.9 Hz, 1 H), 6.04 (dd, *J* = 10.4, 3.4 Hz, 1 H), 5.9 (m, 1 H), 5.75 (dd, *J* = 10.5, 3.9 Hz, 1 H), 4.47 (d, *J* = 12.9 Hz, 1 H), 4.24 (dd, *J* = 13.5, 1.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.82, 165.78, 165.67, 133.99, 133.97, 133.87, 133.63, 130.44, 130.25 (2 carbons), 130.13 (2 carbons), 129.99 (2 carbons), 129.63, 129.49, 129.17, 128.89, 128.80, 128.71, 128.62, 90.14, 69.18, 68.98, 68.86, 65.29. HRMS-ESI (m/z): ($[M+Na]^+$ calcd for $C_{26}H_{21}ClO_7Na$, 547.0363; compound decomposed during MS analysis.

(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-β-D-arabinopyranoside (51). According to general procedure **2.2**, **49** (0.47 g, 0.90 mmol) yielded **51** (0.29 g, 57% yield) and **53** (0.12 g, 26%) both as white crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.23 (d, *J* = 2.7 Hz, 1 H), 8.12 (dd, *J* = 9.3, 2.7 Hz, 1 H), 8.0 (m, 3 H), 7.5 - 7.6 (m, 4 H), 7.4 - 7.5 (m, 9 H), 5.98 (dd, *J* = 6.1, 4.2 Hz, 1 H), 5.8 (m, 2 H), 5.61 (d, *J* = 4.2 Hz, 1 H), 4.47 (dd, *J* = 12.2, 6.3 Hz, 1 H), 4.1 (m, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 165.84, 165.81, 165.34, 157.70, 143.12, 134.07, 133.90, 130.32 (2 carbons), 130.21 (2 carbons), 130.13 (2 carbons), 129.36, 129.25, 129.06, 128.89, 128.85 (2 carbons), 128.75 (2 carbons), 126.41, 124.99, 124.71, 124.01, 116.54, 116.45, 98.70, 69.56, 69.29, 67.09, 61.38. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{32}H_{24}ClNO_{10}Na$, 640.0981; found 640.0989.

1,2,3,4-tetra-*O*-benzoyl-β-D-arabinopyranoside (53). According to general procedure **2.2**, **49** (0.47 g, 0.90 mmol) yielded **51** (0.29 g, 57% yield) and **53** (0.12 g, 26%) both as white crystals. ^{1}H NMR ($CDCl_3$,

500 MHz) δ ppm 8.0 (m, 7 H), 7.5 - 7.6 (m, 4 H), 7.3 - 7.5 (m, 9 H), 6.27 (d, *J* = 5.4 Hz, 1 H), 5.95 (dd, *J* = 7.2, 5.5 Hz, 1 H), 5.8 (m, 2 H), 4.43 (dd, *J* = 12.5, 5.1 Hz, 1 H), 4.14 (dd, *J* = 12.6, 2.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 165.82, 165.73, 165.38, 165.00, 133.98, 133.87, 133.78, 133.76, 130.41, 130.17, 129.54, 129.35, 129.11, 129.05, 128.82 (2 carbons), 128.79 (2 carbons), 128.76 (2 carbons), 128.74, 92.68, 70.18, 69.17, 67.83, 63.01. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{33}H_{26}O_9Na$, 589.1469; found 589.1477.

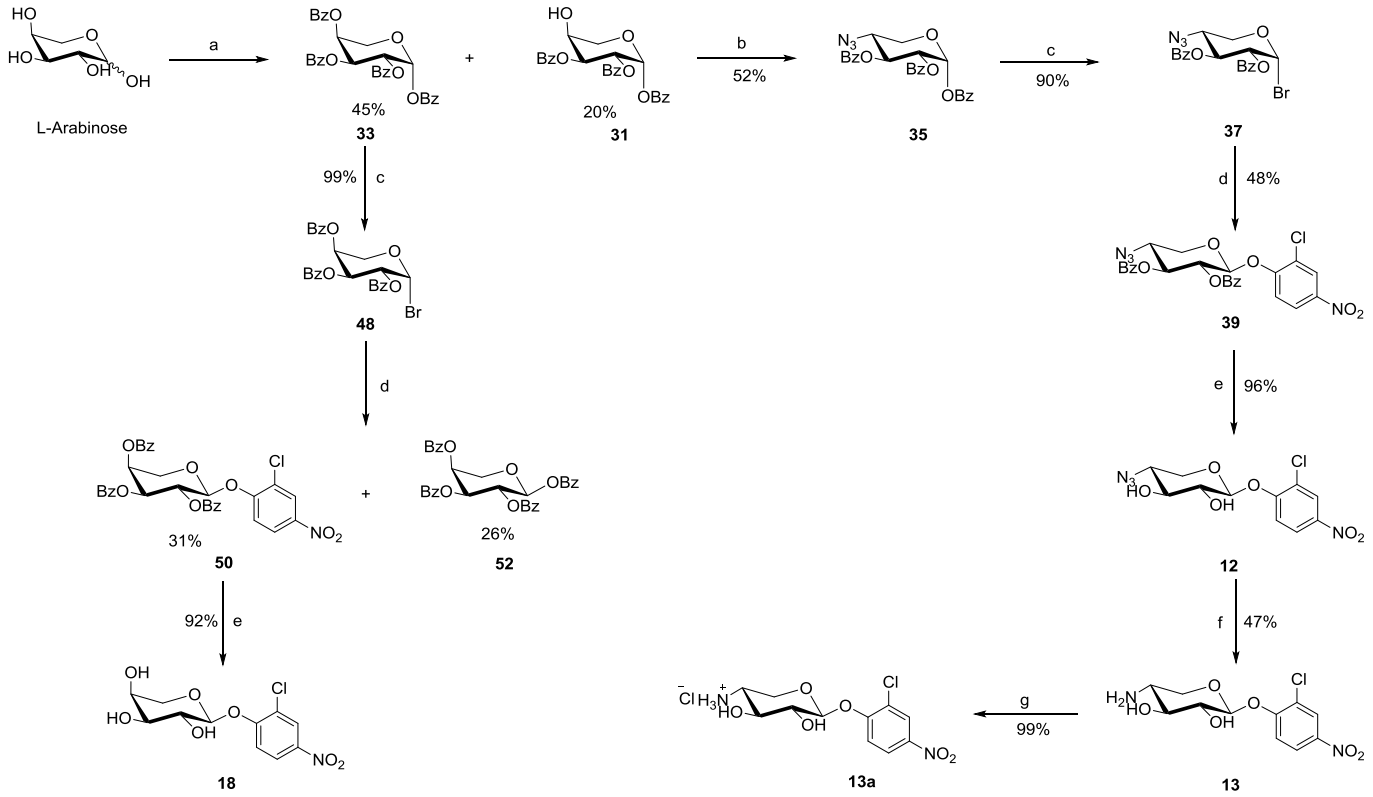
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (14). According to general procedure **2.3**, **43** (100 mg, 0.24 mmol) yielded **14** (67 mg, 85% yield) or with **40** (10 mg,0.018 mmol) yielded **14** (5.8 mg, 95% yield) as a light yellow solid. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.29 (d, *J* = 2.7 Hz, 1 H), 8.16 (dd, *J* = 9.2, 2.7 Hz, 1 H), 7.35 (d, *J* = 9.4 Hz, 1 H), 5.12 (d, *J* = 7.0 Hz, 1 H), 4.00 (dd, *J* = 11.1, 4.9 Hz, 1 H), 3.5 - 3.6 (m, 3 H), 3.4 (m, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ ppm 157.8, 142.4, 125.5, 123.6 (2 carbons), 115.5, 101.0, 75.7, 73.3, 63.9, 61.3. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{11}ClN_4O_6Na$, 353.0259; found 353.0270.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (15). According to general procedure **2.4**, **14** (49.2 mg, 0.15 mmol) yielded **15** (25.6 mg, 57% yield) as a yellow solid. ^{1}H NMR (CD_3OD, 500 MHz) δ ppm 8.31 (d, *J* = 2.7 Hz, 1 H), 8.18 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.38 (d, *J* = 9.3 Hz, 1 H), 5.15 (d, *J* = 7.3 Hz, 1 H), 3.98 (dd, *J* = 11.5, 4.9 Hz, 1 H), 3.57 (dd, *J* = 8.7, 7.2 Hz, 1 H), 3.43 (dd, *J* = 11.6, 10.1 Hz, 1 H), 3.37 (t, *J* = 8.9 Hz, 1 H), 2.89 (ddd, *J*=10.0, 9.0, 5.1 Hz, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ ppm 157.9, 142.4, 125.5, 123.7, 123.6, 115.5, 101.3, 76.0, 73.3, 65.8, 52.1. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{14}ClN_2O_6$, 305.0535; found m/z 305.0548.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (15a). According to general procedure **2.5**, **15** (8.6 mg, 0.02 mmol) yielded **15a** (9.0 mg, 98% yield) as a yellow solid. ^{1}H NMR (D_2O, 400 MHz) δ ppm 8.3 (m, 1 H), 8.1 (m, 1 H), 7.34 (d, *J* = 9.4 Hz, 1 H), 5.33 (d, *J* = 5.5 Hz, 1 H), 4.26 (dd, *J* = 12.0, 4.8 Hz, 1 H), 3.7 - 3.8 (m, 3 H), 3.4 (m, 1 H). ^{13}C NMR (DMSO-d_6, 100 MHz) δ ppm 157.9, 142.5, 126.3, 124.9, 123.2, 116.6, 100.9, 73.3, 72.3, 62.3, 51.2. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{11}H_{14}ClN_2O_6Na$, 305.0535; found 305.0550.

(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (18d). According to general procedure **2.2**, **51** (140 mg, 0.25 mmol) yielded **18d** (30 mg, 40% yield) as a yellow solid. ^{1}H NMR (CD_3OD, 500 MHz) δ ppm 8.31 (d, *J* = 2.7 Hz, 1 H), 8.18 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.40 (d, *J* = 9.3 Hz, 1 H), 5.14 (d, *J* = 6.8 Hz, 1 H), 3.9 (m, 1 H), 3.9 (m, 2 H), 3.77 (dd, *J* = 12.0, 1.5 Hz, 1 H), 3.67 (m, *J* = 3.4 Hz, 1 H).^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 8.35 (d, *J* = 2.7 Hz, 1 H), 8.23 (dd, *J* = 9.3, 2.9 Hz, 1 H), 7.5 (m, 1 H), 5.37 (br. s., 1 H), 5.22 (d, *J* = 6.6 Hz, 1 H), 4.93 (br. s., 1 H), 4.77 (br. s., 1 H), 3.6 - 3.8 (m, 4 H), 3.53 (d, *J* = 8.1 Hz, 1 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ ppm 158.4, 142.1, 126.2, 124.9, 123.1, 116.4, 101.2, 72.9, 70.6, 67.8, 66.4. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}ClNO_7Na$ 328.0195; found 328.0210.

2.13. Synthesis of (2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside (13).



(a) BzCl, Pyridine, -78°C-RT; (b) (1) Tf_2O, pyridine, CH_2Cl_2, (2) NaN_3, DMF; (c) $TiBr_4$, CH_2Cl_2/EtOAc; (d) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., R. T., 12 hours; (e) NaOMe, MeOH; (f) PMe_3 in toluene, THF; (g) HCl, Water

1,2,3-tri-*O*-benzoyl-β-L-arabinopyranoside (31). To a magnetically-stirred solution of L-arabinose (2.0 g, 13.3 mmol) in anhydrous pyridine (40 mL) at -50 °C was added benzoyl chloride (4.64 mL, 40.0 mmol) in a dropwise fashion with stirring. The reaction temperature held below -20 °C for 2 h and was slowly allowed to room temperature. The reacion was quenched by removing pyridine in *vacuo* and the residue was diluted with EtOAc and was washed with 1N HCl, $NaHCO_3$ (sat), water, and brine. The organic phase was dried over Na_2SO_4 and resulting residue was purified by normal phase column chromatography (using a gradient from 100:0 to70:30 hexanes:EtOAc). Compound **31** (1.22 g, 2.64 mmol) was obtained with a yield of 20% as a white solid along with **33** (3.36 g, 5.94 mmol, 45% yield). **31**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.12 (d, *J* = 7.3 Hz, 2 H), 8.03 (d, *J* = 7.3 Hz, 2 H), 7.87 (d, *J* = 7.3 Hz, 2 H), 7.5 (m, 1 H), 7.3 - 7.5 (m, 4 H), 7.2 - 7.3 (m, 4 H), 6.79 (d, *J* = 3.7 Hz, 1 H), 6.12 (dd, *J* = 10.5, 3.7 Hz, 1 H), 5.88 (dd, *J* = 10.5, 2.9 Hz, 1 H), 4.55 (br. s., 1 H), 4.26 (d, *J* = 12.5 Hz, 1 H), 4.0 - 4.1 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 166.1, 165.6, 164.9, 133.7, 133.5, 133.3, 129.9 (2 carbons), 129.8 (2 carbons), 129.7 (2 carbons), 129.2, 129.0, 128.8, 128.7 (2 carbons), 128.4 (2 carbons), 128.3 (2 carbons), 91.4, 70.9, 67.6, 67.5, 65.0. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{22}O_8Na$, 485.1207; found 485.1238.

1,2,3,4-tetra-*O*-benzoyl-β-L-arabinopyranoside (33). ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.28 (d, *J* = 2.0 Hz, 1 H), 7.9 - 8.2 (m, 8 H), 7.2 - 7.6 (m, 10 H), 7.11 (d, *J* = 9.0 Hz, 1 H), 6.27 (d, *J* = 5.4 Hz, 1 H), 5.95 (t, *J* = 6.0 Hz, 1 H), 5.7 (m, 2 H), 4.44 (dd, *J* = 12.3, 5.3 Hz, 1 H), 4.15 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.75, 165.71, 165.6, 164.7, 133.8, 133.59, 133.49, 133.44, 129.9 (3 carbons), 129.7 (3 carbons), 129.3, 129.1, 128.9, 128.8 (2 carbons), 128.7 (2 carbons), 128.6 (3 carbons), 128.44 (2 carbons), 128.42 (2 carbons), 91.1, 69.5, 68.2, 67.9, 63.1. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{33}H_{26}O_9Na$, 589.1469; found 589.1481.

1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (35). According to general procedure **2.6**, **31** (1.22 g,2.64 mmol) yielded **35** (0.67 g, 52% yield) as a white oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.1 (m, 2 H), 8.0 (m, 2 H), 7.8 - 7.9 (m, 2 H), 7.6 (m, 1 H), 7.5 (m, 3 H), 7.4 (m, 3 H), 7.30 (t, *J* = 7.8 Hz, 2 H), 6.73 (d, *J* = 3.7 Hz, 1 H), 6.04 (t, *J* = 9.7 Hz, 1 H), 5.53 (dd, *J* = 10.0, 3.7 Hz, 1 H), 4.0 - 4.2 (m, 2 H), 3.9 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.7, 165.4, 164.5, 133.9, 133.6, 133.5, 129.94 (4 carbons), 129.81 (3 carbons), 128.77 (3 carbons), 128.8, 128.55 (2 carbons), 128.43 (2 carbons), 90.2, 71.0, 70.4, 61.9, 59.4. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{21}N_3O_7Na$, 510.1272; found 510.1273.

1-bromo-2,3-di-*O*-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (37). According to general procedure **2.1**, **35** (0.67 g, 1.18 mmol) yielded **37** (0.47 mg, 90 % yield) as a white oil. ^{1}H NMR (CD_3Cl, 400 MHz) δ ppm 7.9 - 8.0 (m, 5 H), 7.5 (m, 2 H), 7.3 - 7.4 (m, 3 H), 6.74 (d, *J* = 3.9 Hz, 1 H), 5.9 (m, 1 H), 5.16 (dd, *J* = 9.8, 3.9 Hz, 1 H), 4.1 (m, 1 H), 3.9 - 4.0 (m, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.3, 133.8, 133.6, 130.0 (2 carbons), 129.8 (2 carbons), 128.7 (2 carbons), 128.6 (2 carbons), 128.5 (2 carbons), 128.2, 87.6, 71.3, 71.1, 63.7, 58.7. HRMS-ESI (m/z): compound decomposed during MS analysis.

(2-chloro-4-nitrophenyl)-2,3-di-*O*-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (39). According to general procedure **2.2**, **37** (0.38 mg, 0.85 mmol) yielded **39** (0.22 g, 48% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.21 (dd, *J* = 2.7, 1.2 Hz, 1 H), 7.9 - 8.1 (m, 5 H), 7.5 - 7.6 (m, 2 H), 7.3 - 7.4 (m, 5 H), 5.63 (dd, *J* = 5.5, 4.3 Hz, 1 H), 5.58 (t, *J* = 6.3 Hz, 1 H), 5.53 (d, *J* = 4.3 Hz, 1 H), 4.39 (dd, *J* = 12.5, 3.5 Hz, 1 H), 3.9 - 4.0 (m, 1 H), 3.78 (dd, *J* = 12.5, 6.3 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.2, 165.0, 157.1, 142.8, 133.8, 133.7, 130.03 (2 carbons), 129.87 (2 carbons), 129.8, 129.8, 128.5 (2 carbons), 128.5 (2 carbons), 126.1, 124.6, 123.7, 116.0, 98.4, 70.1, 69.0, 61.6, 56.9. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{25}H_{19}ClN_4O_8Na$, 561.0784; found 561.1366.

1-bromo-2,3,4-tri-*O*-benzoyl-β-L-arabinopyranoside (48). According to general procedure **2.1**, **33** (0.65 g, 1.15 mmol) yielded **48** (0.60 g, 100% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.1 (m, 1 H), 8.05 (d, *J* = 8.3 Hz, 1 H), 7.88 (d, *J* = 8.3 Hz, 1 H), 7.62 (d, *J* = 0.7 Hz, 2 H), 7.3 - 7.6 (m, 8 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 6.97 (d, *J* = 3.7 Hz, 1 H), 6.04 (dd, *J* = 10.5, 3.4 Hz, 1 H), 5.87 (d, *J* = 1.7 Hz, 1 H), 5.75 (dd, *J* = 10.3, 3.9 Hz, 1 H), 4.49 (d, *J* = 13.4 Hz, 1 H), 4.26 (d, *J* = 13.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 172.2, 165.6, 165.55, 165.4, 133.77, 133.6, 133.4, 130.20 (2 carbons), 130.0, 129.87 (2 carbons), 129.7, 129.3, 129.2, 128.9, 128.63, 128.58, 128.55, 128.47, 128.37, 89.8, 68.9, 68.9, 68.7, 65.0. HRMS-ESI (m/z): compound decomposed during MS analysis.

(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-α-L-arabinopyranoside (50). According to general procedure **2.2**, **48** (0.60 g, 1.15 mmol) yielded **50** (0.22 g, 31% yield) and **52** (0.17 g, 26%) both as white crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.2 - 8.3 (m, 1 H), 7.9 - 8.2 (m, 7 H), 7.3 - 7.6 (m, 9 H), 7.1 (m, 1 H), 5.96 (dd, *J* = 4.9, 3.7 Hz, 1 H), 5.8 (m, 2 H), 5.59 (d, *J* = 3.7 Hz, 1 H), 4.47 (dd, *J* = 11.7, 6.6 Hz, 1 H), 4.1 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.54, 165.51, 165.0, 157.4, 156.9, 142.81, 133.79, 133.6, 130.02 (2 carbons), 129.90 (2 carbons), 129.85 (2 carbons), 129.8, 128.7, 128.6, 128.54, 128.50, 128.44, 126.1, 125.3, 124.7, 124.5, 123.7, 116.2, 116.1, 98.3, 69.2, 68.9, 66.7, 60.9. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{32}H_{24}ClNO_{10}Na$, 640.0981; found 640.0995.

1,2,3,4-tetra-*O*-benzoyl-α-L-arabinopyranoside (52). According to general procedure **2.2**, **48** (0.60 g, 1.15 mmol) yielded **50** (0.22 g, 31% yield) and **52** (0.17 g, 26%) both as white crystals. ^{1}H NMR ($CDCl_3$, 500 MHz) ^{1}H NMR δ ppm 8.2 (m, 1 H), 7.9 - 8.2 (m, 8 H), 7.2 - 7.6 (m, 10 H), 7.1 (m, 1 H), 6.27 (d, *J* = 5.4 Hz, 1 H), 5.95 (t, *J* = 6.0 Hz, 1 H), 5.7 - 5.8 (m, 2 H), 4.44 (dd, *J* = 12.6, 5.0 Hz, 1 H), 4.08 - 4.19 (m, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 165.6, 165.5, 165.2, 164.8, 156.9, 133.8, 133.64, 133.55, 133.53, 130.10 (2 carbons), 129.86 (3 carbons), 129.13 (2 carbons), 128.94 (2 carbons), 128.69 (2 carbons), 128.6, 128.5, 128.51, 128.48, 128.46, 125.4, 124.5, 116.2, 92.3, 69.9, 68.8, 67.5, 62.7. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{33}H_{26}O_9Na$, 589.1469; found m/z 589.1479.

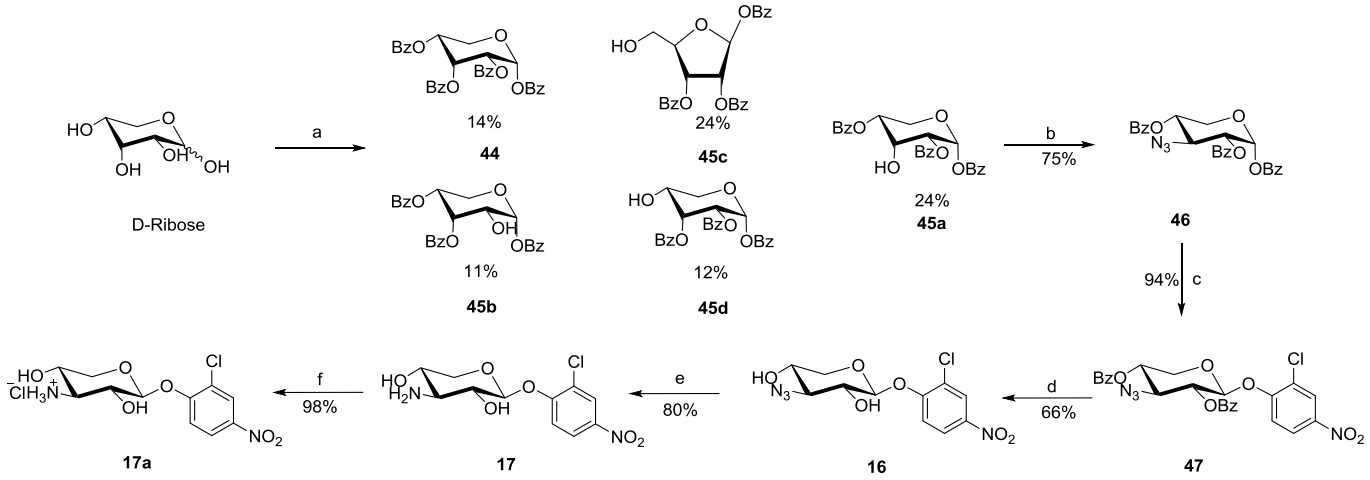
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (12). According to general procedure **2.3**, **39** (0.22 g, 0.41 mmol) yielded **12** (0.13 g, 96% yield) as a light yellow solid. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.27 (d, *J* = 2.7 Hz, 1 H), 8.14 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.33 (d, *J* = 9.4 Hz, 1 H), 5.09 (d, *J* = 7.0 Hz, 1 H), 3.98 (dd, *J* = 11.5, 4.5 Hz, 1 H), 3.5 - 3.6 (m, 3 H), 3.3 (m, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ ppm 157.6, 142.2, 125.3, 123.4, 123.3, 115.2, 100.7, 75.5, 73.1, 63.6, 61.1. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{11}ClN_4O_6Na$, 353.0259; found 353.0234.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside (13). According to general procedure **2.4**, **12** (70 mg, 0.19 mmol) yielded **13** (27.6 mg, 47% yield) as a yellow solid. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.29 (d, *J* = 2.7 Hz, 1 H), 8.16 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.36 (d, *J* = 9.4 Hz, 1 H), 5.12 (d, *J* = 7.0 Hz, 1 H), 3.95 (dd, *J* = 11.5, 4.9 Hz, 10 H), 3.54 (dd, *J* = 8.8, 7.2 Hz, 1 H), 3.40 (dd, *J*= 11.5, 10.4 Hz, 1 H), 3.3 (m, 1 H), 2.85 (ddd, *J* = 10.3, 9.3, 5.1 Hz, 1 H). ^{13}C NMR (CD_3OD, 100 MHz) δ ppm 157.7, 142.1, 125.3, 123.4, 123.3, 115.2, 101.1, 76.1, 73.1, 65.8, 51.9. HRMS-ESI (m/z): $[M+H]^+$ Calcd for $C_{11}H_{14}ClN_2O_6$, 305.0535; found 305.0545.

(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside hydrochloride (13a). According to general procedure **2.5**, **13** (8.3 mg, 0.03 mmol) yielded **13a** (10.0 mg, 100% yield) as a yellow solid. ^{1}H NMR (D_2O, 400 MHz) δ ppm 8.22 (d, *J* = 2.7 Hz, 1 H), 8.03 (dd, *J* = 9.4, 2.7 Hz, 1 H), 7.22 (d, *J* = 9.0 Hz, 1 H), 5.21 (d, *J* = 6.7 Hz, 1 H), 4.15 (dd, *J* = 12.1, 4.7 Hz, 1 H), 3.6 - 3.7 (m, 3 H), 3.32 (td, *J*=9.3, 4.5 Hz, 1 H). ^{13}C NMR (D_2O, 100 MHz) δ ppm 156.8, 142.3, 126.0, 124.1, 123.4, 115.5, 99.9, 71.8, 70.7, 61.4, 50.4. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{11}H_{14}ClN_2O_6$, 305.0535; found 305.0847.

(2-chloro-4-nitrophenyl)-α-L-arabinopyranoside (18). According to general procedure **2.2**, **50** (0.22 g, 0.36 mmol) yielded **18** (0.10 g, 92% yield) as a yellow solid. ^{1}H NMR (CD_3OD, 400 MHz) δ ppm 8.32 (d, *J* = 2.4 Hz, 1 H), 8.18 (dd, *J* = 9.3, 2.4 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 1 H), 5.14 (d, *J* = 6.6 Hz, 1 H), 3.9 (m, 3 H), 3.8 (m, 1 H), 3.67 (dd, *J* = 8.6, 2.9 Hz, 1 H). ^{13}C NMR (DMSO-*d6*, 100 MHz) δ ppm 158.1, 141.8, 125.9, 124.6, 122.8, 116.0, 100.9, 72.6, 70.3, 67.5, 66.1. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}ClNO_7Na$, 328.0195; found 328.0192.

2.14. Synthesis of (2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (17).



(a) BzCl(3.2eq) , Pyridine, -50°C-R. T.; (b) (1) Tf_2O, Pyridine, CH_2Cl_2, (2) NaN_3, DMF; (c) (1) $TiBr_4$, CH_2Cl_2/EtOAc, (2) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., R. T., 12 hours; (d) NaOMe, MeOH; (e) PPh_3 THF, 50°C; (f) HCl, Water

1,2,3,4-tetra-*O*-benzoyl-α-D-ribopyranoside (44). To a solution of D-ribose (1.1 g, 7.33 mmol) in anhydrous pyridine (10 ml) at -50 °C with stirring was added benzoyl chloride (2.72 ml, 23.5 mmol) in

dropwise fashion. The reaction temperature held below -20 ^{o}C for 2 h and then allowed to slowly warm to room temperature. The solvent was removed in *vacu* and the residue was diluted with EtOAc and was washed with 1N HCl, $NaHCO_3$, water, and brine. The organic phase was dried over Na_2SO_4 and purified by normal phase chromotography (using a gradient of 100:0 Hexanes:EtOAc to 70:30 Hexanes:EtOAc) to afford **44** (0.56 g, 0.99 mmol, 14%) as a white solid, together with **45a** (0.82 g, 1.77 mmol, 24%), **45b** (0.37 g, 0.80 mmol, 11%)**, 45c** (0.82 g, 1.77 mmol, 24%)**,** and **45d** (0.40 g, 0.86 mmol, 12%). **48**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.1 (m, 3 H), 8.0 (m, 3 H), 7.8 - 7.9 (m, 3 H), 7.4 - 7.6 (m, 7 H), 7.3 - 7.4 (m, 4 H), 6.63 (d, *J* = 3.4 Hz, 1 H), 6.06 (t, *J* = 3.8 Hz, 1 H), 5.74 (td, *J* = 3.8, 0.7 Hz, 1 H), 5.71 (q, *J* = 3.3 Hz, 1 H), 4.41 (dd, *J* = 12.9, 2.9 Hz, 1 H), 4.29 (dd, *J* = 12.9, 4.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 166.18, 165.81, 165.57, 164.56, 134.17, 133.68, 133.65, 133.52 (2 carbons), 130.40 (2 carbons), 130.28 (4 carbons), 130.18 (3carbons), 130.02, 128.93, 128.72, 128.69, 128.64 (3 carbons), 128.61 (3 carbons), 92.39, 68.04, 67.38, 66.90, 63.41. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{33}H_{26}O_9Na$, 589.1469; found 589.1498.

1,2,4-tri-*O*-benzoyl-α-D-ribopyranoside (45a). ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.0 (m, 3 H), 7.5 (m, 5 H), 7.4 (m, 2 H), 7.3 - 7.4 (m, 5 H), 6.42 (d, *J* = 3.2 Hz, 1 H), 5.5 (m, 1 H), 5.34 (dt, *J* = 7.5, 3.9 Hz, 1 H), 4.65 (q, *J* = 3.6 Hz, 1 H), 4.41 (dd, *J* = 11.7, 7.8 Hz, 1 H), 4.20 (d, *J* = 3.2 Hz, 1 H), 3.92 (dd, *J* = 11.6, 3.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 166.10, 165.93, 165.04, 134.05, 133.86, 133.71, 133.67, 133.60, 130.34 (2 carbons), 130.25 (2 carbons), 130.19 (2 carbons), 130.15, 129.63, 129.43, 129.41, 128.87 (2 carbons), 128.79 (2 carbons), 128.69 (2 carbons), 128.65,128.59, 90.52, 69.42, 68.83, 67.55. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{22}O_8Na$, 485.1207; found 485.1216.

1,3,4-tri-*O*-benzoyl-α-D-ribopyranoside (45b). ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.1 (m, 3 H), 8.0 (m, 3 H), 7.9 (m, 2 H), 7.3 - 7.7 (m, 7 H), 6.49 (d, *J* = 3.2 Hz, 1 H), 5.79 (t, *J* = 3.5 Hz, 1 H), 5.7 (m, 1 H), 4.32 (dd, *J* = 13.1, 2.3 Hz, 1 H), 4.25 (dt, *J* = 3.4, 1.7 Hz, 1 H), 4.20 (dd, *J* = 13.1, 3.5 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 165.85, 165.65, 164.71, 134.10, 133.90, 133.78, 130.36, 130.27, 130.20, 130.13, 130.10, 130.03, 129.91, 129.18 (2 carbons), 128.96 (2 carbons), 128.74 (2 carbons), 128.67, 128.63, 94.67, 69.25, 68.42, 68.04, 63.29. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{26}H_{22}O_8Na$, 485.1207; found 485.1212.

1,2,3-tri-*O*-benzoyl-α-D-ribofuranoside (45c). ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.9 - 8.1 (m, 3 H), 7.5 - 7.6 (m, 5 H), 7.4 (m, 2 H), 7.0 - 7.4 (m, 5 H), 6.57 (d, *J* = 3.2 Hz, 1 H), 5.50 (t, *J* = 3.8 Hz, 1 H), 5.45 (q, *J* = 3.2 Hz, 1 H), 4.66 (t, *J* = 3.8 Hz, 1 H), 4.20 (m, *J*=2.9 Hz, 2 H), 3.6 (s, broad, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 167.03, 166.63, 164.57, 134.10, 133.75, 133.64, 130.39 (3 carbons), 130.29 (3 carbons), 130.22, 129.86, 129.56, 129.24, 128.92 (2 carbons), 128.67 (2 carbons), 128.64, 92.29, 70.31, 69.95, 65.53, 63.18. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{26}H_{22}O_8Na$, 485.1207; found 485.1217.

1,2,3-tri-*O*-benzoyl-α-D-ribopyranoside (45d). ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 7.9 - 8.1 (m, 4 H), 7.5 - 7.8 (m, 4 H), 7.3 - 7.5 (m, 7 H), 6.53 (d, *J* = 3.9 Hz, 1 H), 5.81 (t, *J* = 3.4 Hz, 1 H), 5.66 (td, *J* = 3.8, 1.0 Hz, 1 H), 4.3 (m, 1 H), 4.23 (dd, *J* = 12.3, 2.6 Hz, 1 H), 4.1 (m, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 166.07, 165.46, 164.65, 134.19, 133.98, 133.84, 130.30 (2 carbons), 130.15 (2 carbons), 130.11 (2 carbons), 129.49, 129.26, 129.05, 128.96 (2 carbons), 128.95 (2 carbons), 128.82 (2 carbons), 92.20, 69.37, 69.03, 66.93, 66.08. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{26}H_{22}O_8Na$, 485.1207; found 485.1221.

3-deoxy-3-azido-1,2,4-tri-*O*-benzoyl-D-xylopyranoside (46). According to general procedure **2.6**, **45a** (0.82 g, 1.77 mmol) yielded **46** (0.65 g, 75% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm (α/β=2/1) ppm 8.1 (m, 5 H), 7.3 - 7.7 (m, 10 H), 6.70 (d, *J* = 3.7 Hz, 0.7 H), 6.21 (d, *J* = 6.1 Hz, 0.3 H), 5.46 (dd, *J* = 8.1, 6.1 Hz, 0.3 H), 5.34 (dd, *J* = 10.5, 3.7 Hz, 0.7 H), 5.27 (td, *J* = 10.3, 5.7 Hz, 0.7 H), 5.22 (td, *J* = 7.6, 4.4 Hz, 0.3 H), 4.4 (m, 1 H), 4.2 (m, 1 H), 3.94 (m, *J* = 11.0, 11.0 Hz, 0.7 H), 3.81 (dd, *J* = 12.2, 7.6 Hz, 0.3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 165.53, 165.42, 164.69, 134.18, 134.05, 133.95 (2 carbons), 130.39 (2 carbons), 130.19, 130.15, 129.03, 128.93, 128.91, 128.89, 128.86 (2

carbons), 128.83 (2 carbons), 128.80 (2 carbons), 89.89, 70.98, 70.20, 61.84, 61.32. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{26}H_{21}N_3O_7Na$, 510.1272; found 510.1281.

(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-*O*-benzoyl-β-D-xylopyranoside (47). According to general procedure **2.2**, **46** (0.26 g, 0.53 mmol) yielded **47** (0.27 g, 94% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ ppm 8.28 (d, *J* = 2.7 Hz, 1 H), 8.13 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.9 (m, 2 H), 7.6 (m, 2 H), 7.4 (m, 3 H), 7.3 (m, 3 H), 7.32 (d, *J* = 9.3 Hz, 1 H), 5.60 (d, *J* = 4.4 Hz, 1 H), 5.52 (dd, *J* = 6.3, 4.2 Hz, 1 H), 5.14 (td, *J* = 5.9, 3.7 Hz, 1 H), 4.43 (dd, *J* = 12.5, 3.7 Hz, 1 H), 4.31 (t, *J* = 6.3 Hz, 1 H), 3.83 (dd, *J* = 12.5, 5.1 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ ppm 165.69, 165.23, 157.16, 143.20, 134.05, 134.01, 130.20 (2 carbons), 130.18 (2 carbons), 129.20, 128.95, 128.85 (2 carbons), 128.80 (2 carbons), 126.51, 125.26, 123.88, 116.26, 98.33, 69.10, 68.94, 61.72, 59.69. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{25}H_{19}ClN_4O_8Na$, 561.0784; found 561.0801.

(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-xylopyranoside (16). According to general procedure **2.3**, **47** (270 mg, 0.50 mmol) yielded **16** (119.5 mg, 66% yield) as a light yellow solid. ^{1}H NMR (CD_3OD, 500 MHz) δ ppm 8.31 (d, *J* = 2.7 Hz, 1 H), 8.18 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.38 (d, *J* = 9.3 Hz, 1 H), 5.18 (d, *J* = 7.6 Hz, 1 H), 3.95 (dd, *J* = 11.2, 5.1 Hz, 1 H), 3.5 (m, 2 H), 3.50 (dd, *J* = 11.2, 10.0 Hz, 1 H), 3.40 (t, *J* = 9.5 Hz, 1 H). ^{13}C NMR (CD_3OD, 125 MHz) δ ppm 157.9, 142.5, 125.6, 123.7, 123.6, 115.6, 101.1, 71.9, 69.6, 68.3, 66.6. HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{11}ClN_4O_6Na$, 353.0259; found 353.0268.

(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (17). According to general procedure **2.4**, **16** (56 mg, 0.16 mmol) yielded **17** (41.8 mg, 80% yield) as a white solid. ^{1}H NMR (CD_3OD, 500 MHz) δ ppm 8.32 (d, *J* = 2.7 Hz, 1 H), 8.19 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.40 (d, *J* = 9.3 Hz, 1 H), 5.17 (d, *J* = 7.3 Hz, 1 H), 3.94 (dd, *J* = 10.9, 4.5 Hz, 1 H), 3.4 - 3.5 (m, 3 H), 2.81 (t, *J* = 9.0 Hz, 1 H).^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 8.35 (d, *J* = 2.9 Hz, 1 H), 8.22 (dd, *J* = 9.3, 2.7 Hz, 1 H), 7.51 (d, *J* = 9.3 Hz, 1 H), 5.49 (br. s., 1 H), 5.26 (d, *J* = 7.3 Hz, 1 H), 5.15 (br. s., 1 H), 3.79 (dd, *J* = 11.0, 5.1 Hz, 1 H), 3.43 (t, *J* = 10.5 Hz, 1 H), 3.3 (m, 1H), 3.29 (t, *J* = 8.5 Hz, 1 H), 3.19 (s, 1 H), 3.19 (s, 1 H), 2.64 (t, *J* = 9.3 Hz, 1 H), 1.84 (s, 1 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ ppm 158.3, 142.2, 126.2, 124.9, 123.1, 116.4, 101.4, 73.4, 70.0, 67.5, 60.0. HRMS-ESI (m/z): $[M+H]^+$ calcd for $C_{11}H_{14}ClN_2O_6$, 305.0535; found 305.0536.

(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (17a). According to general procedure **2.5**, **17** (2 mg, 0.006 mol) yielded **17a** (2 mg, 98% yield) as a yellow solid. ^{1}H NMR (D_2O, 500 MHz) δ ppm 8.42 (d, *J* = 2.7 Hz, 1 H), 8.23 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.42 (d, *J* = 9.3 Hz, 1 H), 5.37 (d, *J* = 7.3 Hz, 1 H), 4.19 (dd, *J* = 11.5, 5.4 Hz, 1 H), 4.03 (td, *J* = 10.1, 5.4 Hz, 1 H), 3.97 (dd, *J* = 10.6, 7.4 Hz, 1 H), 3.68 (dd, *J* = 11.5, 10.5 Hz, 1 H), 3.38 (t, *J* = 10.4 Hz, 1 H). ^{13}C NMR (D_2O, 125 MHz) δ ppm 157.2, 142.9, 126.5, 124.5, 123.7, 115.9, 100.7, 69.1, 66.6, 65.7, 57.8. HRMS-ESI (m/z): $[M]^+$ calcd for $C_{11}H_{14}ClN_2O_6$, 305.0535; found 305.0539.

3. 2-chloro-4-nitrophenyl glycoside library screening

***In Vitro* 2-chloro-4-nitrophenyl glycoside screening with OleD variant** Reactions containing 10 µM purified wtOleD, OleD TDP-16, or OleD Loki, 2 mM UDP or 5 mM TDP, and 2 mM of (2-chloro-4-nitophenol)-glycosides (**1**-**20**) in Tris-HCl (50 mM, pH 8.0) with a final volume of 100 µL were incubated at 25°C for 12 h and the absorbance of the reactions were monitored at 410 nm using a Fluostar Omega microplate reader (BMG LABTECH GmbH, Ortenberg, Germany). Reactions noted as positives based upon absorbance change where subsequently analyzed via HPLC as follows. To the reaction was added 50 µL MeOH and 50 µL H_2O and the mixture filtered through MultiScreen Filter Plate (from Millipore, Billerica, MA, USA) according to manufacturer's instructions. Sugar nucleotide formation was assessed by analytical reverse-phase HPLC using an Agilent 1260 system equipped with a DAD detector with a 250 mm x 4.6 mm Gemini-NX 5µ C18 column (Phenomenex, Torrance, CA, USA) and a

linear gradient of 1% B to 71% B over 30 min, 71% B for 5 min, 71% B to 1% B over 1 min, 1% B for 4 min (Solvent A = 50 mM PO_4^{2-}, 5 mM tetrabutylammonium bisulfate, 2% acetonitrile, pH adjusted to 6.0 with KOH; Solvent B = acetonitrile); flow rate = 1 mL min^{-1}; A_{254} nm; injection volume 10 µL. The percent conversion was calculated based on the peak area of NDP and NDP-sugar integrated with Agilent 1260 workstation and each assay was repeated at least two times. The percentage conversion with the three enzymes and the retention time of the NDP-sugars are presented in Table S2. All 2-chloro-4-nitrophenyl aminosugar glycoside hydrochloride salts (**3a**, **5a**, **7a**, **9a**, **11a**, **13a**) were tested with OleD Loki iva the same protocol above and the percentage conversion was listed in Table S2.

Purification and characterization of NDP-sugars. Reactions containing 10 µM purified OleD Loki, 2 mM UDP or 2 mM TDP, and 2 mM of 2-chloro-4-nitophenyl glycoside (**3, 5, 7, 9, 11, 13, 18, 19**) in Tris-HCl (50 mM, pH 8.0) with a final volume of 100 µL were incubated at 25°C for 6 h. To the reactions was added 50 µL MeOH and 50 µL H_2O and the mixtures filtered through Vivaspin 500 centrifugal concentrators. The recovered filtrate from each reaction was completely injected into reverse-phase HPLC using an Agilent 1260 system equipped with a DAD detector with a 250 mm x 4.6 mm Gemini-NX 5µ C18 column (Phenomenex, Torrance, CA, USA) with a gradient of 1% B for 4min, 1% B to 20% B over 9 min, 20% B to 80% B over 2 min, 80% B for 7 min, 80% B to 1% B over 2 min, 1% B for 4 min (Solvent A = 50 mM triethylammonium acetate buffer, pH 7.0; Solvent B = acetonitrile; flow rate = 1 mL min^{-1}; A_{254} nm). The sugar nucleotide peak was collected automatically by Agilent sample collector. The desired fractions were frozen at -80 °C, and lyophilized. The following samples were dissolved into 200 µL 70% acetonitrile/ H_2O and submitted for mass analysis. The high resolution mass data are presented in Table S3.

4. Single enzyme coupled reaction of 4-methylumbelliferone 54. Reactions containing 10 µM of purified OleD Loki, 0.1 mM UDP, 1 mM 4-methylumbelliferone **54**, and 1 mM 2-chloro-4-nitophenyl glycosides (**1**, **2, 3, 5, 7, 9, 11, 13, 18**) in Tris-HCl (50 mM, pH 8.0) with a final volume of 100 µL were incubated at 25°C for 8 h and the fluorescence of the reactions were monitored (λ_{ex}=355 nm; I_{em}=460 nm) using a Fluostar Omega microplate reader (BMG LABTECH GmbH, Ortenberg, Germany). To the reaction was added 50 µL MeOH and 50 µL H_2O and the mixture filtered through a MultiScreen Filter Plate (from Millipore, Billerica, MA, USA) according to manufacturer's instructions. The filtrate was analyzed for the formation of related glycosylated 4-methylumbelliferone by analytical reverse-phase HPLC using an Agilent 1260 system equipped with a DAD detector with a 250 mm x 4.6 mm Gemini-NX 5µ C18 column (Phenomenex, Torrance, CA, USA) with a linear gradient of 1% B to 71% B over 30 min, 71% B for 5 min, 71% B to 1% B over 1 min, 1% B for 4 min (Solvent A = 50 mM PO_4^{2-}, 5 mM tetrabutylammonium bisulfate, 2% acetonitrile, pH adjusted to 6.0 with KOH; Solvent B = acetonitrile; flow rate = 1 mL min^{-1}; A_{254} nm; injection volume 10 µL). Percent conversion was calculated based on the peak area of glycosylated 4-methylumbelliferone and 4-methylumbelliferone integrated with Agilent 1260 workstation and was repeated at least two times for each glycoside donor. Retention times for the glycosylated 4-methylumbelliferones are listed in Table S4.

Purification and characterization of 4-methylumbelliferone glycosides. Reactions containing 2.6 µM of purified OleD Loki, 0.2 mM UDP, 2 mM 4-methylumbelliferone **54**, and 2 mM of (2-chloro-4-nitophenyl)-glycoside (**1**, **2, 3, 5, 7, 9, 13**) in Tris-HCl (50 mM, pH 8.0) with a final volume of 200 µl were incubated at 25°C for 12 h. To the reactions was added 10 µL 5/1 MeOH/HCl, 40 µL MeOH and 50 µL H_2O and the mixture filtered through Vivaspin 500 centrifugal concentrators. The entire filtrate was purified by semi-preparative reverse-phase HPLC with a Gemini C-18 (5 µm, 250 × 10 mm) column (from Phenomenex, Torrance, California, USA) using a gradient of 5% B to 55% B over 27 min, 55% B to 100% B over 1 min, 100% B for 5 min, 100% B to 5% B over 1 min, 5% B for 4 min (A = ddH_2O with 0.1% TFA; B = acetonitrile; flow rate = 5 mL min^{-1}; A_{254} nm). The desired fractions were collected, frozen at -80 °C, and lyophilized. The recovered samples were dissolved into 200 µL 70% acetonitrile/H_2O and submitted for mass analysis. The high resolution mass data for all glycosylated 4-methylumbelliferones is presented in Table S4.

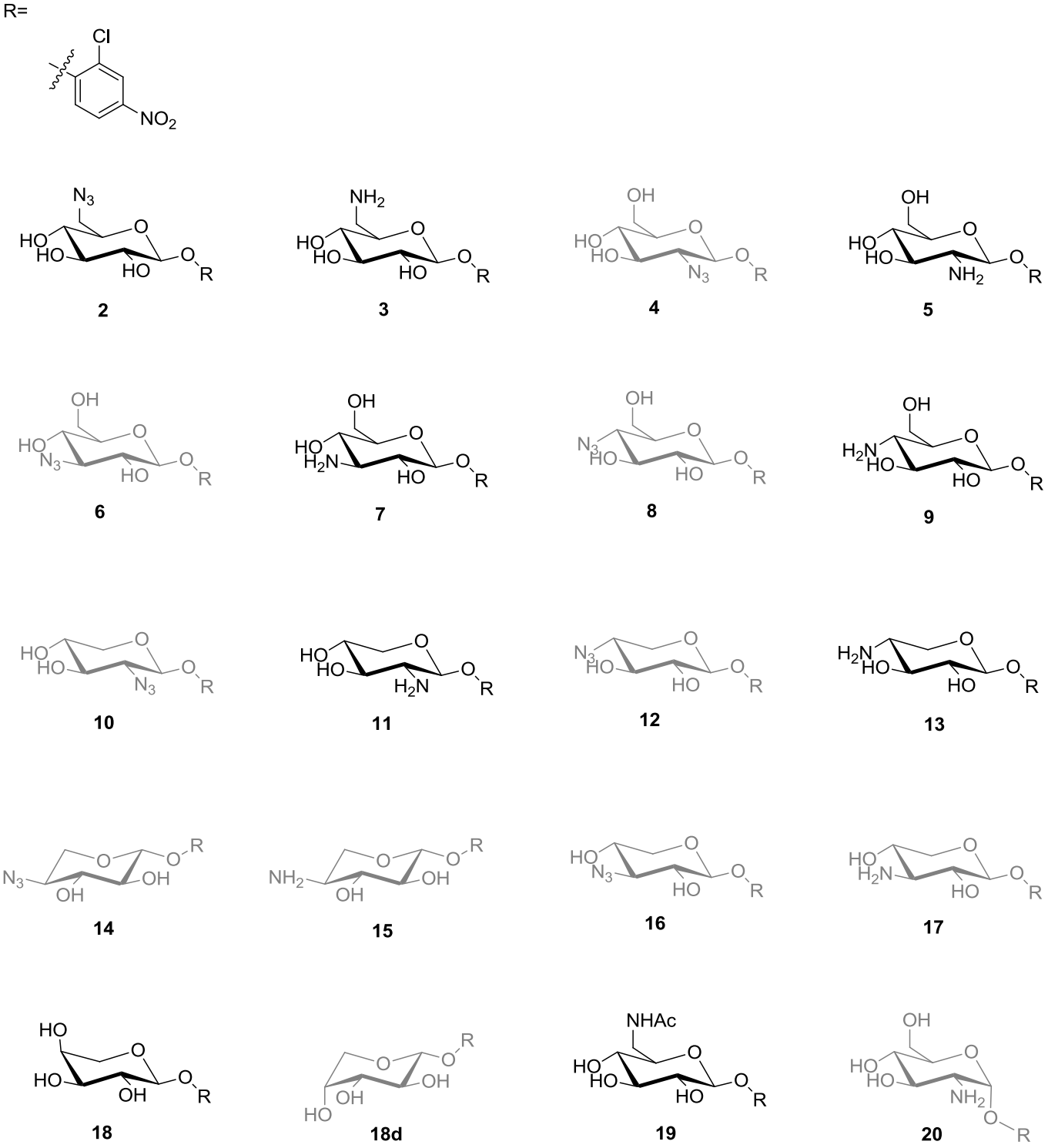


Figure S1. Library of synthesized 2-chloro-4-nitrophenyl glycoside donors (grey indicates no detectable turn-over in wtOleD-, OleD TDP-16-, or OleD Loki-catalyzed reactions).

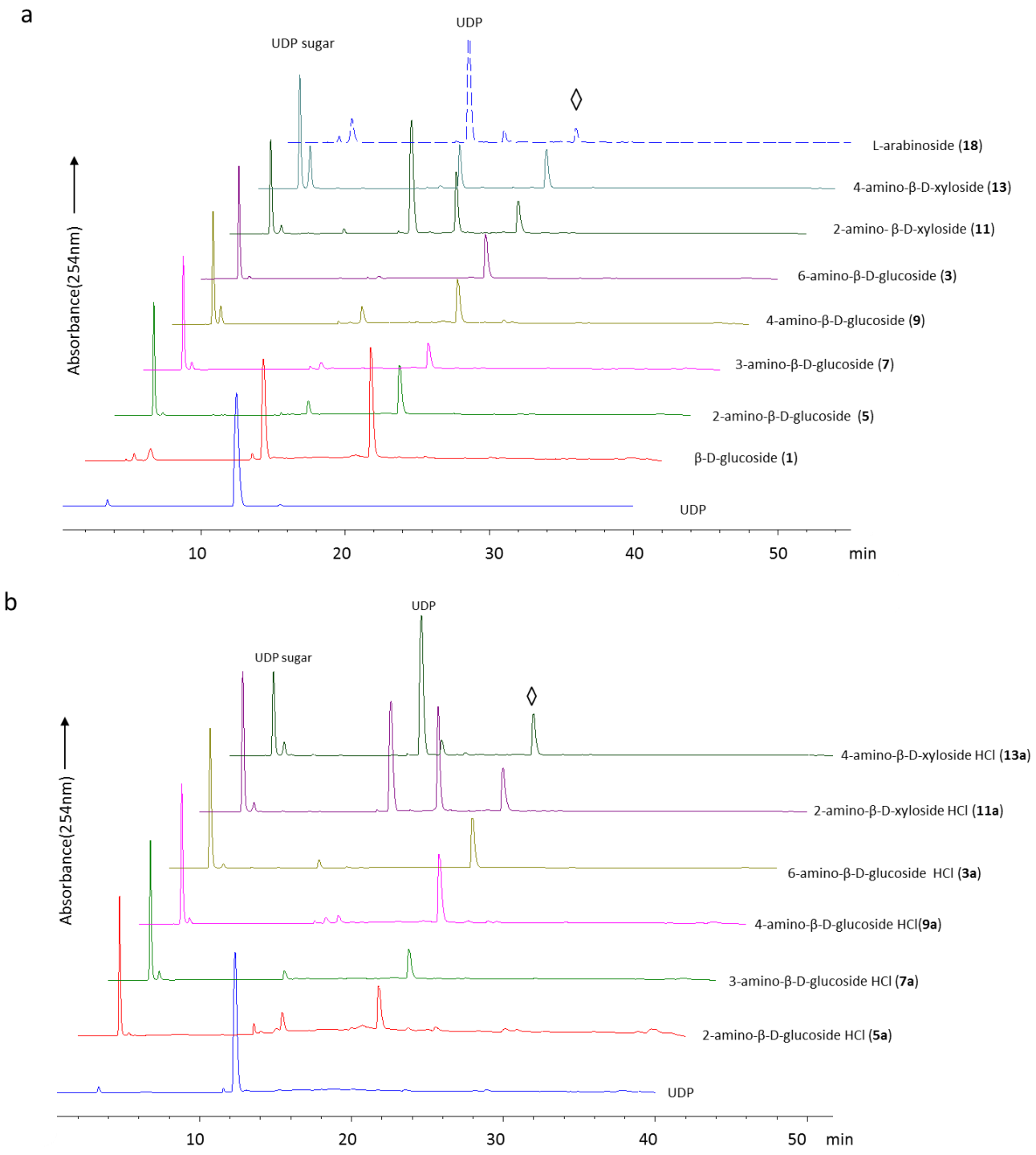


Figure S2. HPLC chromatograms of UDP-sugar forming reactions. Reactions contained 10 µM purified OleD Loki, 2 mM UDP, and 2 mM of 2-chloro-4-nitrophenyl glycoside in Tris-HCl (50 mM, pH 8.0) in a final volume of 100 µl. (a) reaction of (2-chloro-4-nitrophenyl)-β-D-glucoside (**1**) and 2-chloro-4-nitrophenyl glucosamino/xylosaminosides (**5, 7, 9, 3, 11, 13, 18**) with UDP. (b) reaction of 2-chloro-4-nitrophenyl glucosamino/xylosaminoside hydrochloride salts (**5a, 7a, 9a, 3a, 11a, 13a**) with UDP. (◊) denotes the corresponding phenolate by product.

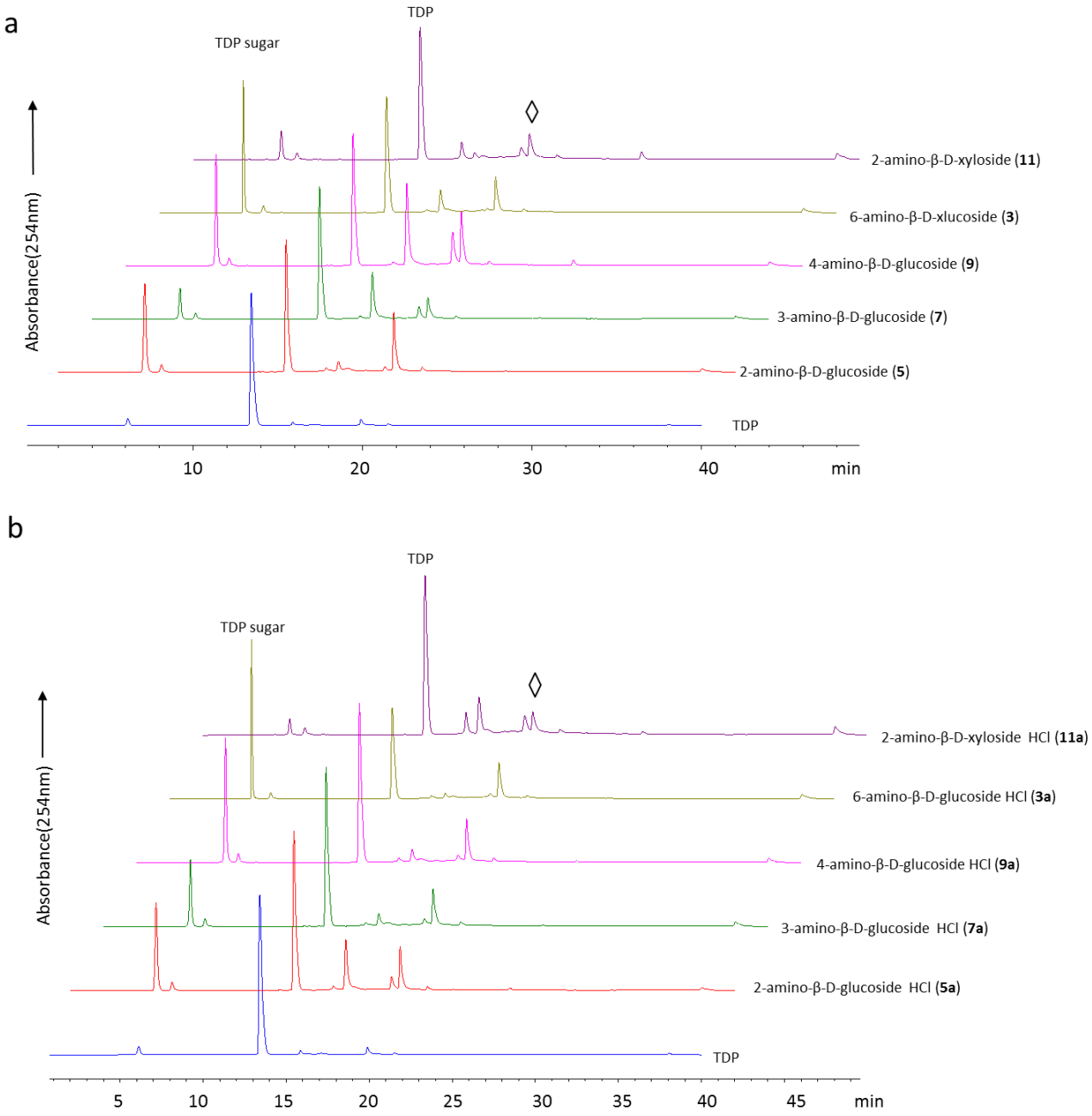


Figure S3. HPLC chromatograms of TDP-sugar forming reactions. Reactions contained 10 µM purified OleD Loki, 5 mM TDP, and 2 mM of 2-chloro-4-nitrophenyl glycoside in Tris-HCl (50 mM, pH 8.0) with a final volume of 100 µl. (a) reaction of 2-chloro-4-nitrophenyl glucosamino/xylosaminosides (**5, 7, 9, 3, 11**) with TDP; (b) reaction of 2-chloro-4-nitrophenyl glucosamino/xylosaminoside hydrochloride salts (**5a, 7a, 9a, 3a, 11a**) with TDP. (◊) denotes the phenolate by product.

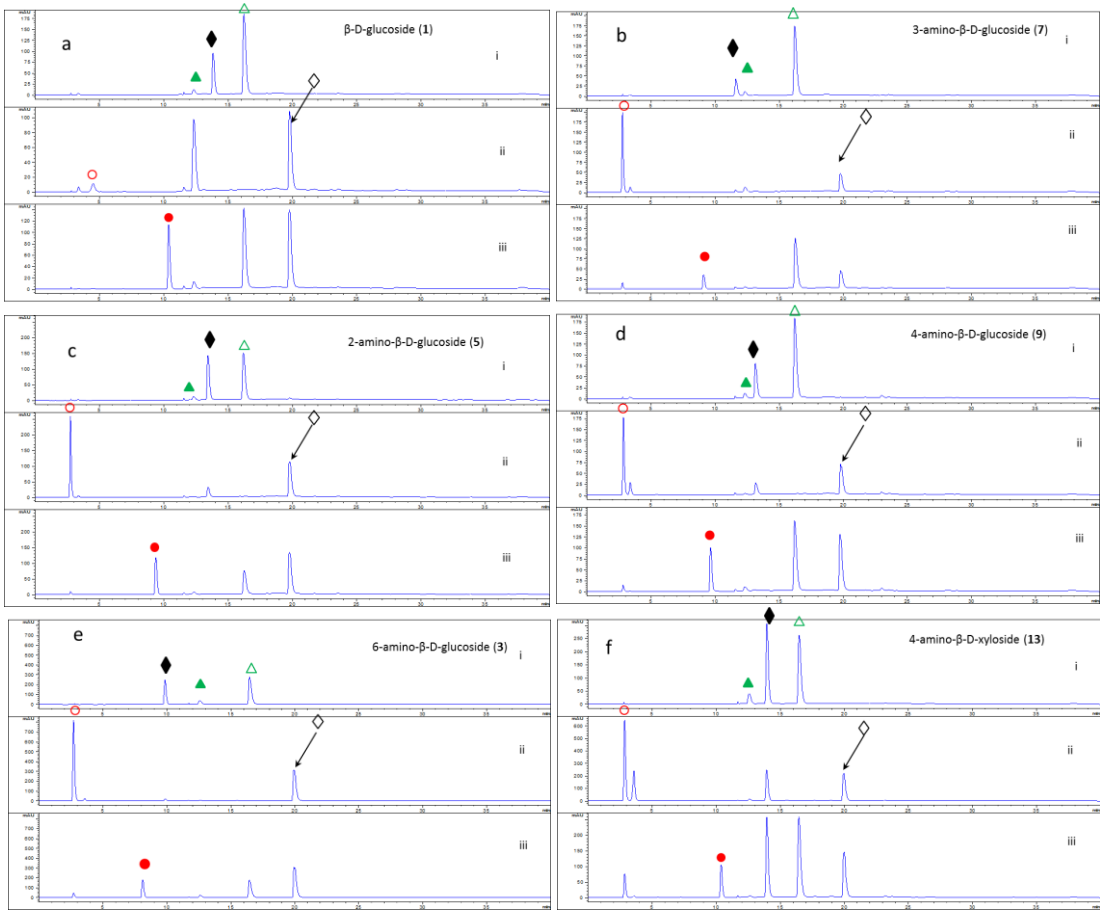


Figure S4. HPLC of OleD Loki-catalyzed transglycosylation reactions. For each representative series: (i) control lacking enzyme; (ii) reaction of 2 mM 2-chloro-4-nitrophenyl glycoside, 2 mM UDP, 10 μM Loki lacking 4-methylumbelliferone in 100 μl Tris solution (50 mM, pH 8.0); (iii) full reaction of 2 mM 2-chloro-4-nitrophenyl glycoside, 0.2 mM UDP, 2 mM 4-methylumbelliferone, and 10 μM Loki in 100 μl Tris solution (50 mM, pH 8.0). The series includes: (a) β-D-glucoside (**1**); (b) 3-amino-β-D-glucoside (**7**); (c) 2-amino-β-D-glucoside (**5**); (d) 4-amino-β-D-glucoside (**9**); (e) 6-amino-β-D-glucoside (**3**); and (f) 4-amino-β-D-xyloside (**13**). Black closed diamonds (♦) denote 2-chloro-4-nitrophenyl glycosides, black open diamonds (◊) denote 2-chloro-4-nitrophenolate, red open circles (○) denote UDP sugar, red closed circles (●) denote 4-methylumbelliferone glycosides, green open triangles (△) denote 4-methylumbelliferone (**54**) and green closed triangles (▲) denote UDP.

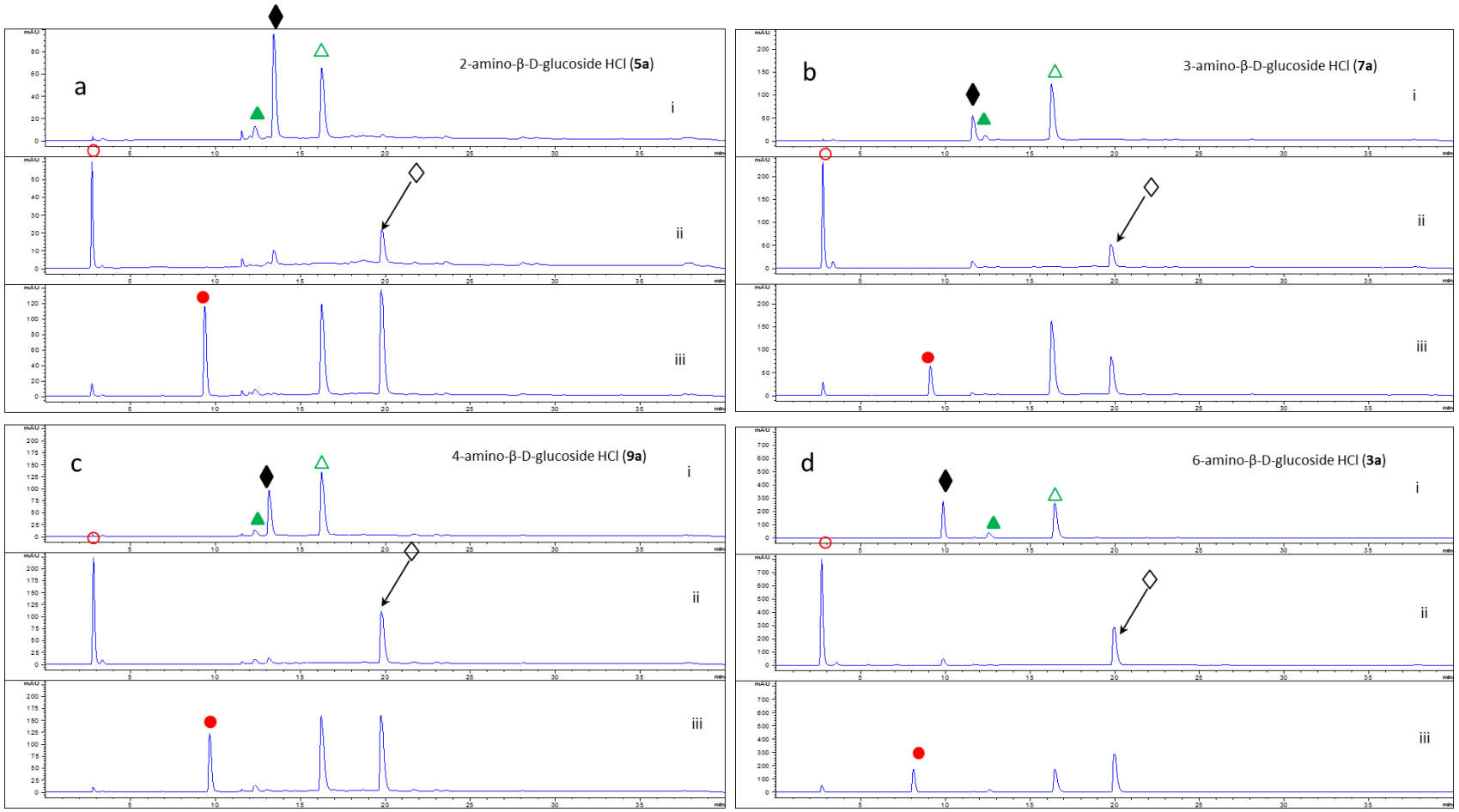
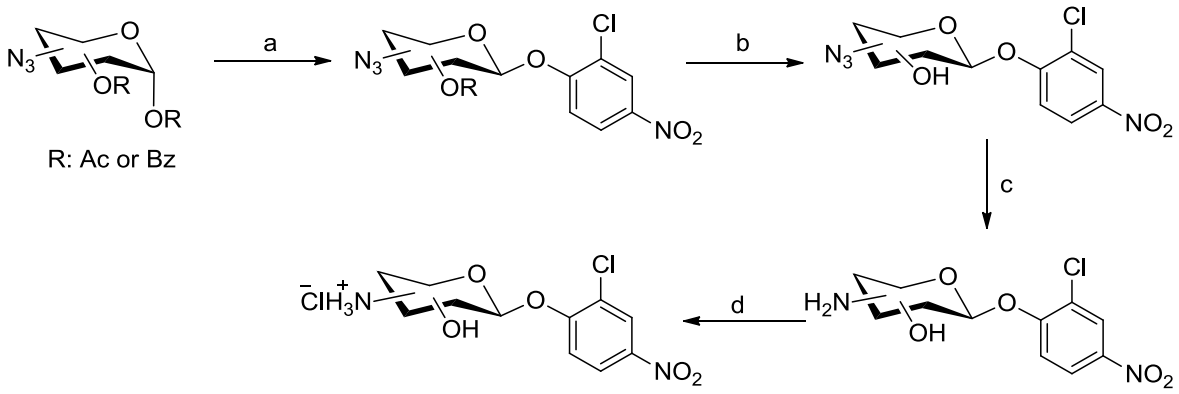


Figure S5. HPLC of OleD Loki-catalyzed transglycosylation with 2-chloro-4-nitrophenyl glycoside HCl salts. For the representative reaction, (i) control lacking enzyme; (ii) reaction with 2 mM 2-chloro-4-nitrophenyl glycoside HCl, 2 mM UDP, 10 μM Loki lacking 4-methylumbelliferone in 100 μl 50 mM Tris, pH 8.0; (iii) full reaction with 2 mM 2-chloro-4-nitrophenyl glycoside HCl, 0.2 mM UDP, 2 mM 4-methylumbelliferone, and 10 μM Loki in 100 μl 50 mM Tris, pH 8.0. The series includes: (a) 2-amino-β-D-glucoside HCl (**5a**); (b) 3-amino-β-D-glucoside HCl (**7a**); (c) 4-amino-β-D-glucosidide HCl (**9a**); (d) 6-amino-β-D-glucoside HCl (**3a**); Black closed diamonds (♦) denote 2-chloro-4-nitrophenyl glycosides HCl, black open diamonds (◊) denote 2-chloro-4-nitrophenolate, red open circles (○) denote **UDP sugar**, and red closed circles (●) denote **glycosylated-4-methylumbelliferone** in their respective panels. Green open triangle (△) denote 4-methylumbelliferone (**54**)and green closed triangle (▲) denote UDP.

Table S1. Summary of 2-chloro-4-nitrophenyl aminosugar donors syntheses.



(a) (1) $TiBr_4$, CH_2Cl_2/EtOAc; (2) 2-chloro-4-nitrophenol, Ag_2O, CH_3CN, M.S., r t, 12 h;
(b) NaOMe, MeOH; (c) PMe_3, THF, 50°C or PPh_3, THF, 50°C; (d) HCl, Water.

Entry	Starting material	step a[a]	step b[a]	step c[a]	step d[a]
1	**22**: 2-deoxy-azido-D-glucoside (OAc)	**23**: 18%	**4**: 99%	**5**: 67%	**5a**: 99%
2	**24**: 3-deoxy-3-azido-D-glucoside (OAc)	**25**: 37%	**6**: 64%	**7**: 77%	**7a**: 99%
3	**26**: 4-deoxy-4-azido-D-glucoside (OAc)	**27**: 70%	**8**: 86%	**9**: 52%	**9a**: 90%
4	**28**: 2-deoxy-2-azido-D-xyloside (OAc)	**30**: 24%	**10**: 80%	**11**: 82%	**11a**: 87%
5	**46**: 3-deoxy-3-azido-D-xyloside (OBz)	**47**: 94%	**12**: 66%	**13**: 80%	**13a**: 98%
6	**35**: 4-deoxy-4-azido-D-xyloside (OBz)	**39**: 43%	**16**: 96%	**17**: 47%	**17a**: 99%
7	**36**: 4-deoxy-4-azido-L-xyloside (OBz)	**40**: 13%	**14**: 95%	**15**: 57%	**15a**: 98%
18	**41**: 4-deoxy-4-azido-L-xyloside (OAc)	**43**: 22%	**14**: 85%	**15**: 57%	**15a**: 98%

[a]isolated yield

Table S2. Percentage conversion and retention time of the NDP-sugars.

Entry	Compound	OleD Loki		OleD TDP-16	wtOleD	Retention time (min)
		A[a]	B[b]			
1U	UDP-α -D-glucose	25%	-	97%	81%	4.9
2U	UDP-α-6-deoxy-6-azido-D-glucose	92%	-	96%	90%	11.7
3U	UDP-α-6-deoxy-6-amino-D-glucose	96%	100%	22%	77%	2.7
5U	UDP-α-2-deoxy-2-amino-D-glucose	100%	100%	72%	68%	2.7
7U	UDP-α-3-deoxy-3-amino-D-glucose	87%	90%	24%	1%	2.7
9U	UDP-α-4-deoxy-4-amino-D-glucose	96%	97%	58%	72%	2.8
11U	UDP-α-2-deoxy-2-amino-D-xylose	54%	54%	6%	28%	2.8
13U	UDP-α-4-deoxy-4-amino-D-xylose	88%	82%	1%	5%	2.8
18U	UDP-β-L-arabinose	13%	-	5%	7%	4.5
19U	UDP-α-6-deoxy-*N*-acetyamino-D-glucose	39%	-	11%	12%	5.8
1T	TDP-α -D-glucose	27%	-	87%	84%	7.7
2T	TDP-α-6-deoxy-6-azido-D-glucose	56%	-	93%	34%	11.9
3T	TDP-α-6-deoxy-6-amino-D-glucose	92%	100%	21%	2%	4.9
5T	TDP-α-2-deoxy-2-amino-D-glucose	97%	89%	52%	61%	5.1
7T	TDP-α-3-deoxy-3-amino-D-glucose	64%	60%	9%	7%	5.2
9T	TDP-α-4-deoxy-4-amino-D-glucose	94%	88%	52%	14%	5.3
11T	TDP-α-2-deoxy-2-amino-D-xylose	72%	76%	2%	46%	5.2
13T	TDP-α-4-deoxy-4-amino-D-xylose	69%	47%	1%	9%	5.1
18T	TDP-β-L-arabinose	7%	-	2%	6%	8.4
19T	TDP-α-6-deoxy-*N*-acetyamino-D-glucose	48%	-	1%	4%	9.4

[a]2-chloro-4-nitrophenyl aminosugar glycoside; [b]2-chloro-4-nitrophenyl aminosugar glycoside hydrochloride salt

Table S3. HRMS of the synthesized NDP-sugars.

Entry	Compound	Elemental Composition $[M+Na]^+$	Calculated Theoretical Mass (m/z) $[M+Na]^+$	Observed Mass (m/z) $[M+Na]^+$
3U	UDP-α-6-deoxy-6-amino-D-glucose	$C_{15}H_{25}N_3O_{16}P_2Na^+$	588.0602	588.0600
5U	UDP-α-2-deoxy-2-amino-D-glucose	$C_{15}H_{25}N_3O_{16}P_2Na^+$	588.0602	588.0601
7U	UDP-α-3-deoxy-3-amino-D-glucose	$C_{15}H_{25}N_3O_{16}P_2Na^+$	588.0602	588.0598
9U	UDP-α-4-deoxy-4-amino-D-glucose	$C_{15}H_{25}N_3O_{16}P_2Na^+$	588.0602	588.0600
11U	UDP-α-2-deoxy-2-amino-D-xylose	$C_{14}H_{23}N_3O_{15}P_2Na^+$	558.0497	558.0493
13U	UDP-α-4-deoxy-4-amino-D-xylose	$C_{14}H_{23}N_3O_{15}P_2Na^+$	558.0497	558.0495
18U	UDP-β-L-arabinose	$C_{14}H_{22}N_2O_{16}P_2Na^+$	559.0337	559.0336
19U	UDP-α-6-deoxy-6-acetyamino-D-glucose	$C_{17}H_{27}N_3O_{17}P_2Na^+$	630.0708	630.0704
3T	TDP-α-6-deoxy-6-amino-D-glucose	$C_{16}H_{27}N_3O_{15}P_2Na^+$	586.0810	586.0797
5T	TDP-α-2-deoxy-2-amino-D-glucose	$C_{16}H_{27}N_3O_{15}P_2Na^+$	586.0810	586.0809
7T	TDP-α-3-deoxy-3-amino-D-glucose	$C_{16}H_{27}N_3O_{15}P_2Na^+$	586.0810	586.0811
9T	TDP-α-4-deoxy-4-amino-D-glucose	$C_{16}H_{27}N_3O_{15}P_2Na^+$	586.0810	586.0795
11T	TDP-α-2-deoxy-2-amino-D-xylose	$C_{15}H_{25}N_3O_{14}P_2Na^+$	556.0704	556.0692
13T	TDP-α-4-deoxy-4-amino-D-xylose	$C_{15}H_{25}N_3O_{14}P_2Na^+$	556.0704	556.0693
18T	TDP-β-L-arabinose	$C_{15}H_{24}N_2O_{15}P_2Na^+$	557.0544	557.0531
19T	TDP-α-6-deoxy-6-acetyamino-D-glucose	$C_{18}H_{29}N_3O_{16}P_2Na^+$	628.0915	628.0911

	Compound	Elemental Composition $[M-H]^-$	Calculated Theoretical Mass (m/z) $[M-H]^-$	Observed Mass (m/z) $[M-H]^-$
3U	UDP-α-6-deoxy-6-amino-D-glucose	$C_{15}H_{24}N_3O_{16}P_2^-$	564.0637	564.0642
5U	UDP-α-2-deoxy-2-amino-D-glucose	$C_{15}H_{24}N_3O_{16}P_2^-$	564.0637	564.0648
7U	UDP-α-3-deoxy-3-amino-D-glucose	$C_{15}H_{24}N_3O_{16}P_2^-$	564.0637	564.0649
9U	UDP-α-4-deoxy-4-amino-D-glucose	$C_{15}H_{24}N_3O_{16}P_2^-$	564.0637	564.0642
11U	UDP-α-2-deoxy-2-amino-D-xylose	$C_{14}H_{22}N_3O_{15}P_2^-$	534.0532	534.0534
13U	UDP-α-4-deoxy-4-amino-D-xylose	$C_{14}H_{22}N_3O_{15}P_2^+$	534.0532	534.0535
18U	UDP-β-L-arabinose	$C_{14}H_{21}N_2O_{16}P_2^-$	535.0372	535.0372
19U	UDP-α-6-deoxy-6-acetyamino-D-glucose	$C_{17}H_{26}N_3O_{17}P_2^-$	606.0743	606.0751
3T	TDP-α-6-deoxy-6-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2^-$	562.0845	562.0853
5T	TDP-α-2-deoxy-2-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2^-$	562.0845	562.0849
7T	TDP-α-3-deoxy-3-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2^-$	562.0845	562.0849
9T	TDP-α-4-deoxy-4-amino-D-glucose	$C_{16}H_{26}N_3O_{15}P_2^-$	562.0845	562.0851
11T	TDP-α-2-deoxy-2-amino-D-xylose	$C_{15}H_{24}N_3O_{14}P_2^-$	532.0739	532.0746
13T	TDP-α-4-deoxy-4-amino-D-xylose	$C_{15}H_{24}N_3O_{14}P_2^-$	532.0739	532.0747
18T	TDP-β-L-arabinose	$C_{15}H_{23}N_2O_{15}P_2^-$	533.0579	533.0586
19T	TDP-α-6-deoxy-6-acetyamino-D-glucose	$C_{18}H_{28}N_3O_{16}P_2^-$	604.0950	604.0955

Table S4. Characterization data of the glycosylated 4-methylumbelliferone.

					HRMS-ESI(m/z)	
Entry	Conjugated sugars	Percentage conversion	Retention time(min)	Chemical formula	Calculated Theoretical Mass	Observed Mass (m/z)
54a	β-D-glucose	36%	10.4	$C_{16}H_{18}O_8$	339.1074 $[M+H]^+$	339.1072 $[M+H]^+$
54b	β-D-6-deoxy-6-amino-glucose	43%	8.1	$C_{16}H_{19}NO_7$	338.1234 $[M+H]^+$	338.1231 $[M+H]^+$
54c	β-D-6-deoxy-6-azido-glucose	42%	15.8	$C_{16}H_{17}N_3O_7$	364.1139 $[M+H]^+$	364.1144 $[M+H]^+$
54d	β-D-2-deoxy-2-amino-glucose	53%	9.4	$C_{16}H_{19}NO_7$	338.1234 $[M+H]^+$	338.1232 $[M+H]^+$
54e	β-D-3-deoxy-3-amino-glucose	22%	9.1	$C_{16}H_{19}NO_7$	338.1234 $[M+H]^+$	338.1210 $[M+H]^+$
54f	β-D-4-deoxy-4-amino-glucose	37%	9.4	$C_{16}H_{19}NO_7$	338.1234 $[M+H]^+$	338.1231 $[M+H]^+$
54g	β-D-4-deoxy-4-amino-xylose	23%	10.4	$C_{15}H_{17}NO_6$	308.1129 $[M+H]^+$	308.1126 $[M+H]^+$

Table S5. ^{1}H NMR, gCOSY, ^{13}C NMR of the synthesized compounds

Supplementary References.

[S1] R. W. Gantt, P. Peltier-Pain, W. J. Cournoyer, J. S. Throson, *Nat. Chem. Biol.* **2011**, *7*, 685-691.

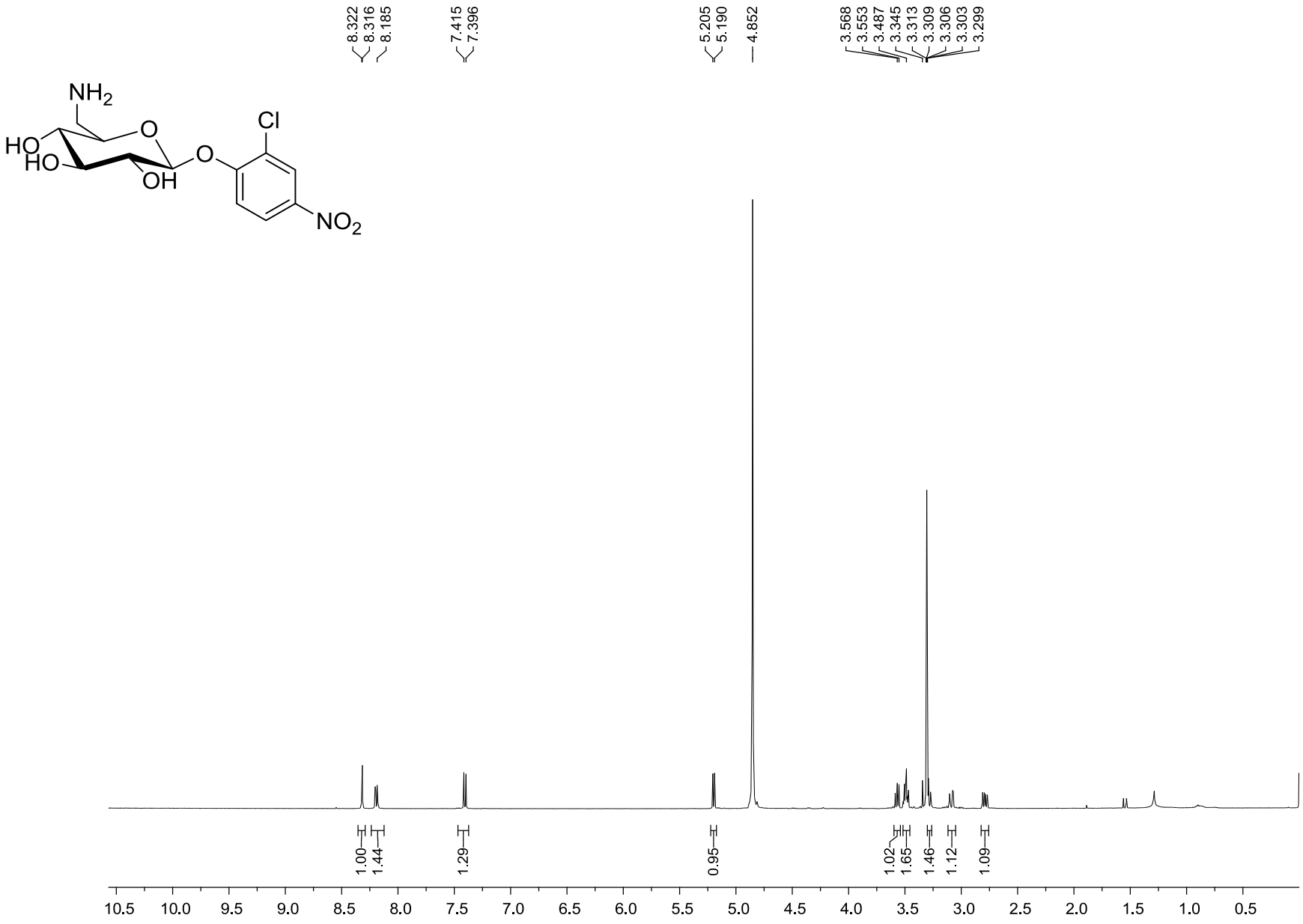
[S2] S. Masuko, S. Bera, D. E. Green, M. Weiwer, J. Liui, P. L. DeAngelis, R. J. Linhardt, *J. Org. Chem.* **2012**, *77*, 1449-1456.

[S3] V. L. Campo, R. Sesti-Costa, Z. A. Carneiro, J. S. Silva, S. Schenkman, I. Carvalho. *Bioorg. Med. Chem.* **2012**, *20*, 145-156.

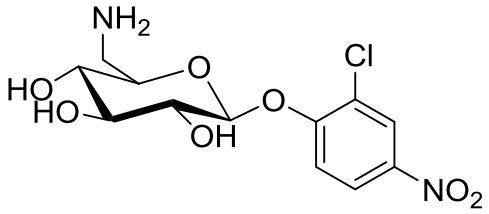
[S4] E. V. Dijkum, R. Danac, D. J. Hughes, R. Wood, A. Rees, B. L. Wilkinson, A. J. Fairbanks, *Org. Biolmol. Chem.* **2009**, *7*, 1097-1105.

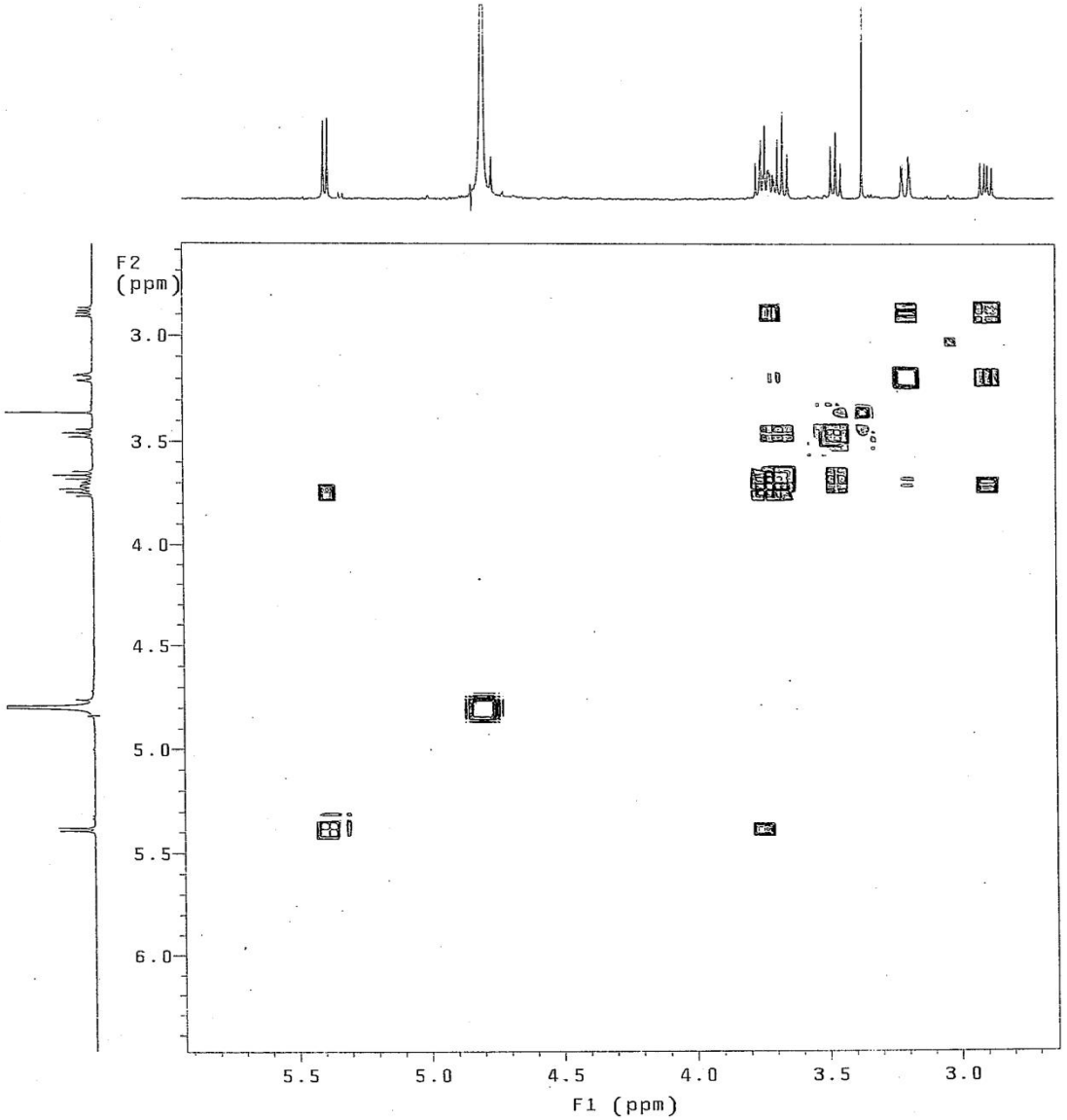
[S5] J. Zhang, J. S. Thorson, Unpublished result.

(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (**3**): ^{1}H NMR (CD_3OD, 500 MHz)

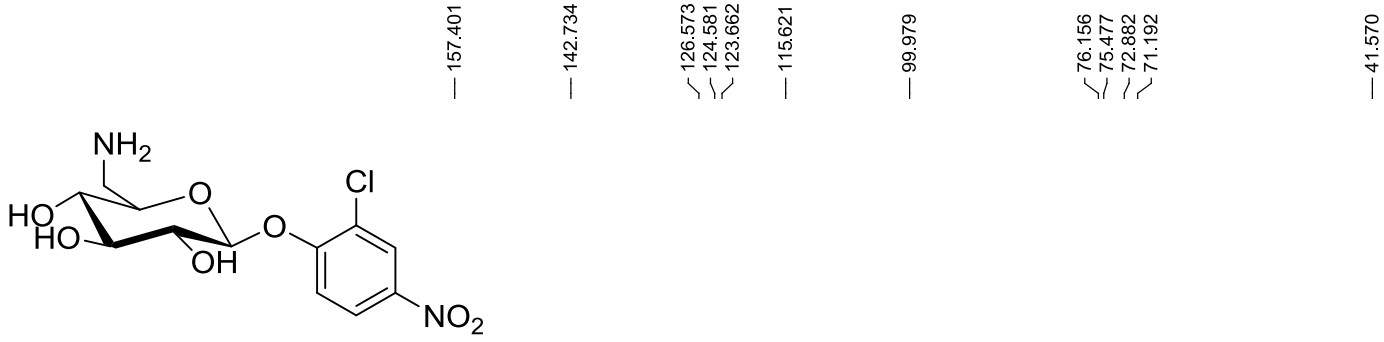


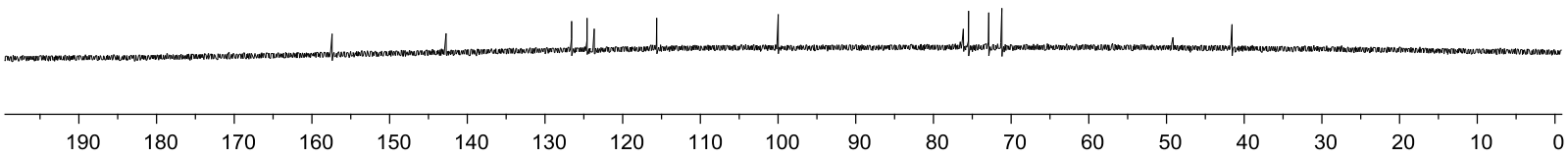
(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (**3**): gCOSY (CD_3OD, 500 MHz)



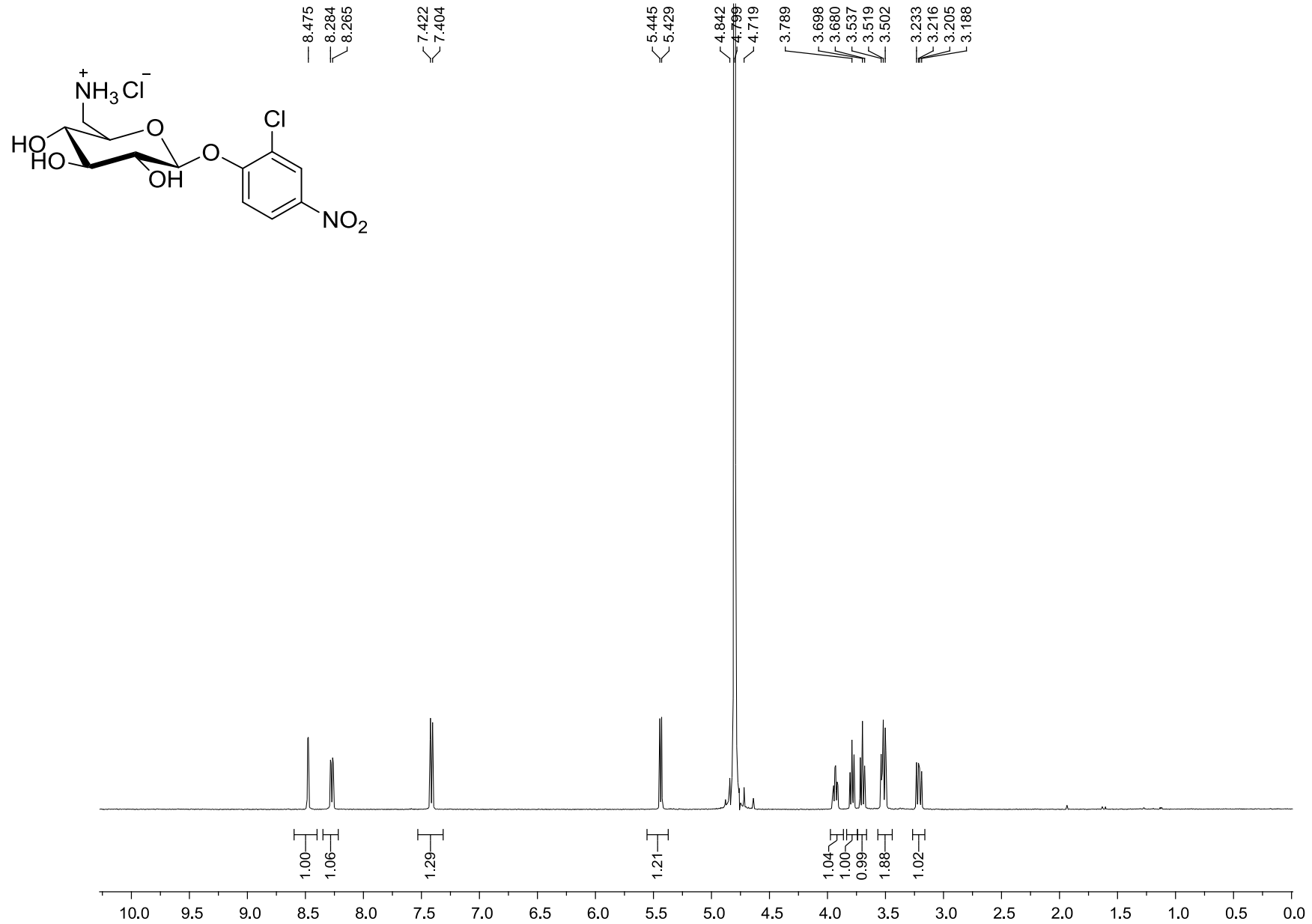


(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside (**3**): ^{13}C NMR (D_2O, 125 MHz)

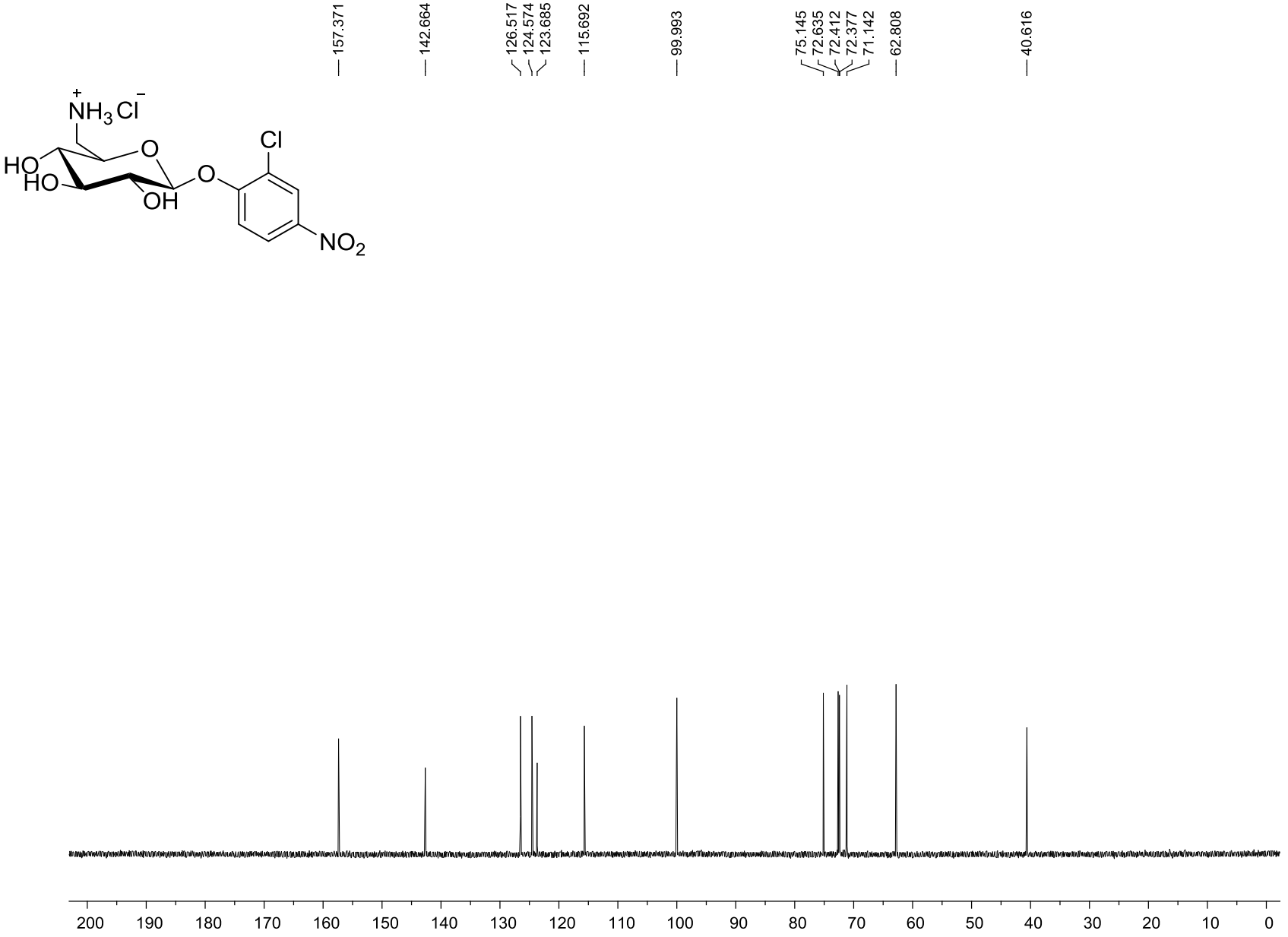




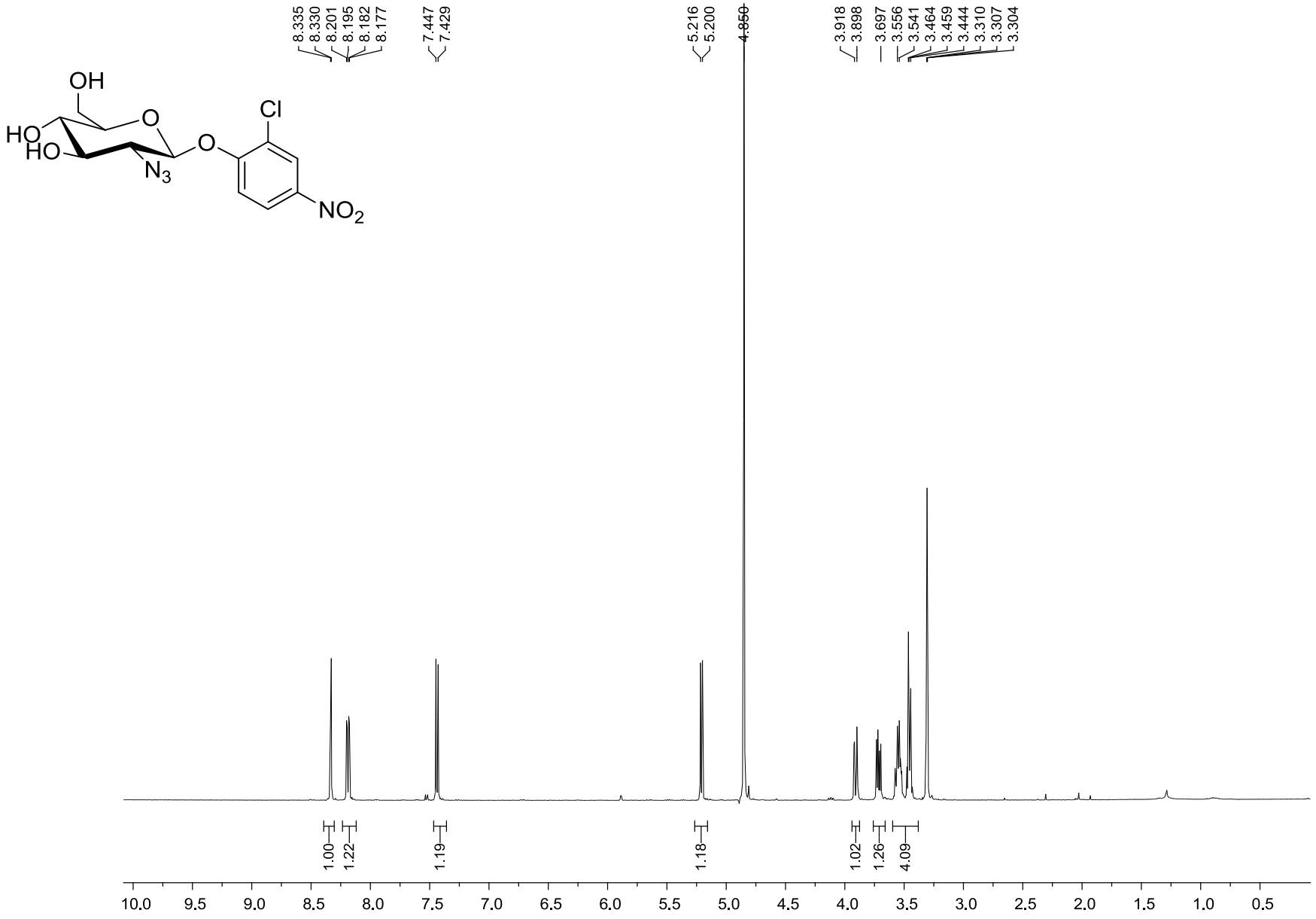
(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside hydrochloride (**3a**): ^{1}H NMR (D_2O, 500 MHz)



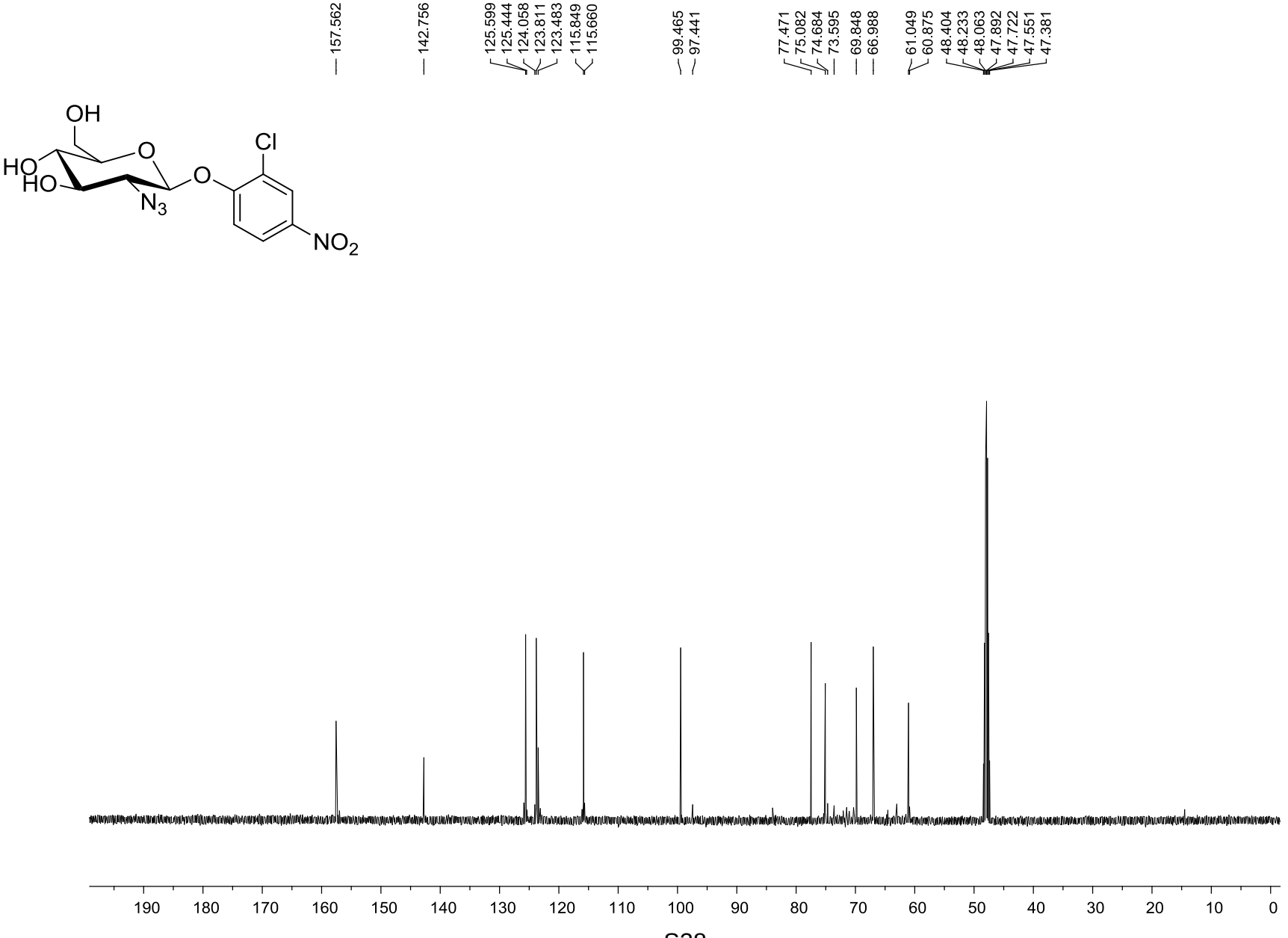
(2-chloro-4-nitrophenyl)-6-deoxy-6-amino-β-D-glucopyranoside hydrochloride (**3a**): ^{13}C NMR (D_2O, 125 MHz)



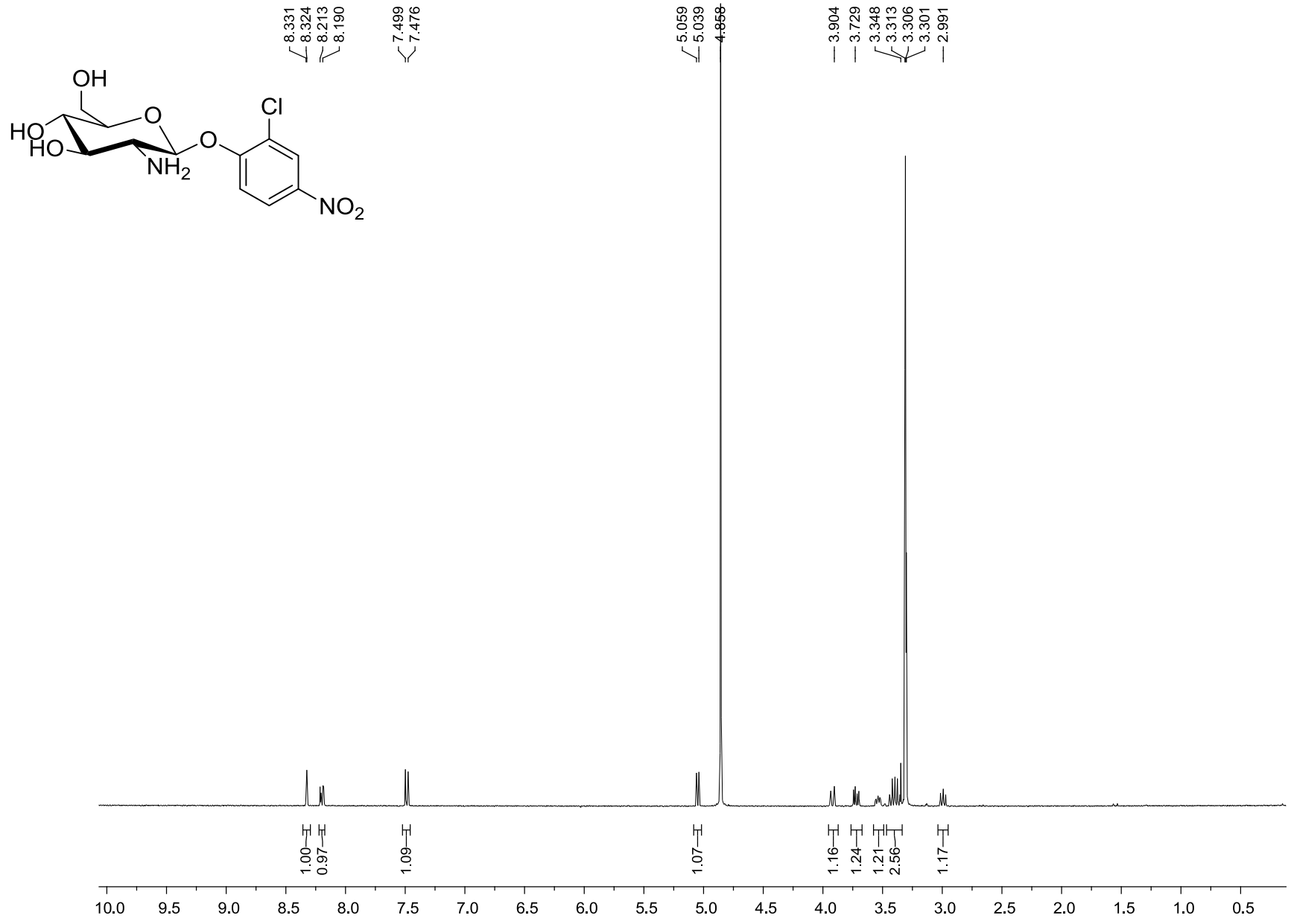
(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-glucopyranoside (**4**): ^{1}H NMR (CD_3OD, 500 MHz)



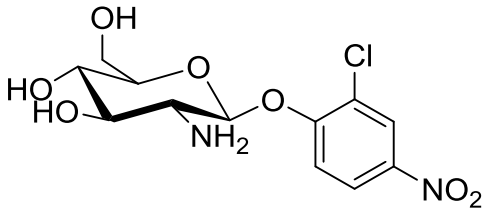
(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-glucopyranoside (**4**): ^{13}C NMR (CD_3OD, 125 MHz)

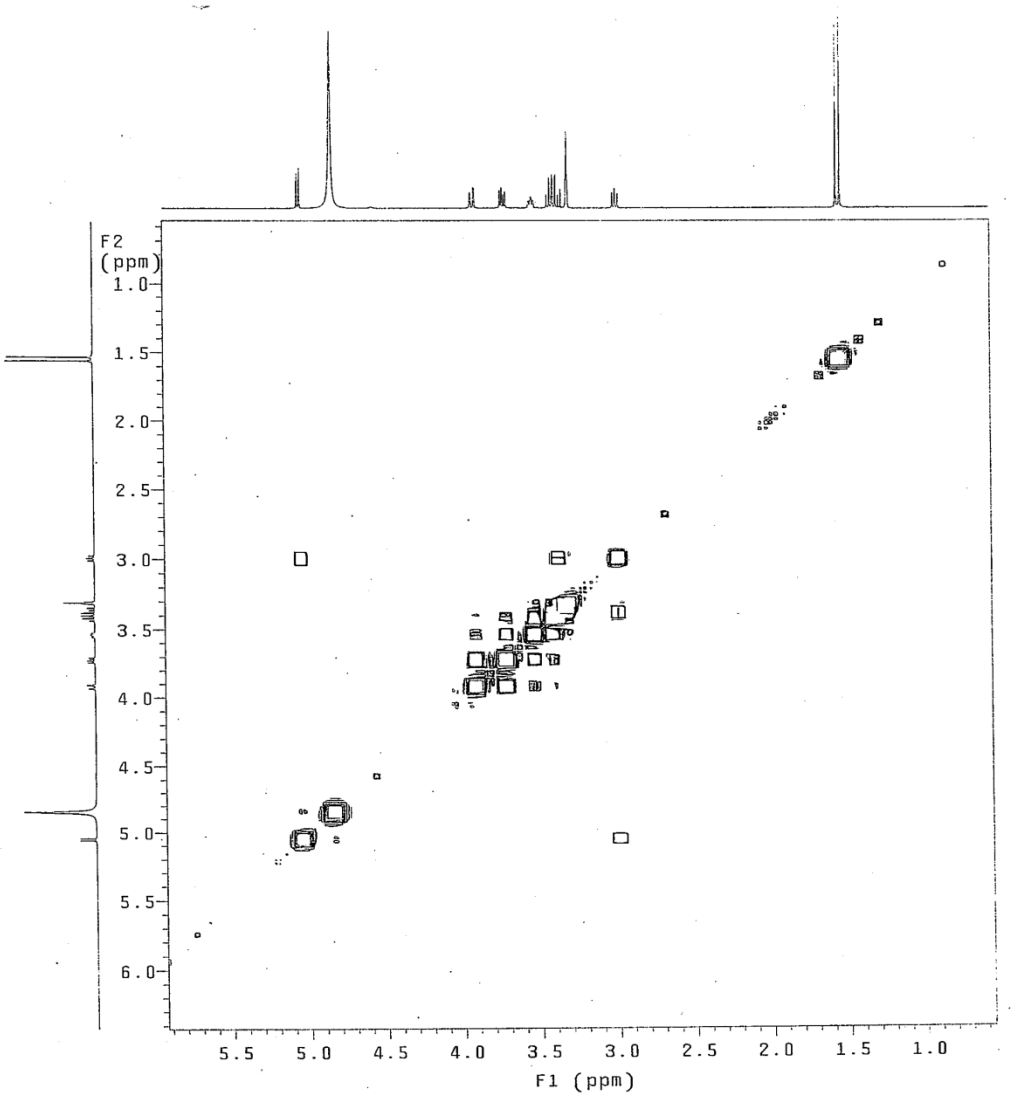


(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (**5**): ^{1}H NMR (CD_3OD, 400 MHz)

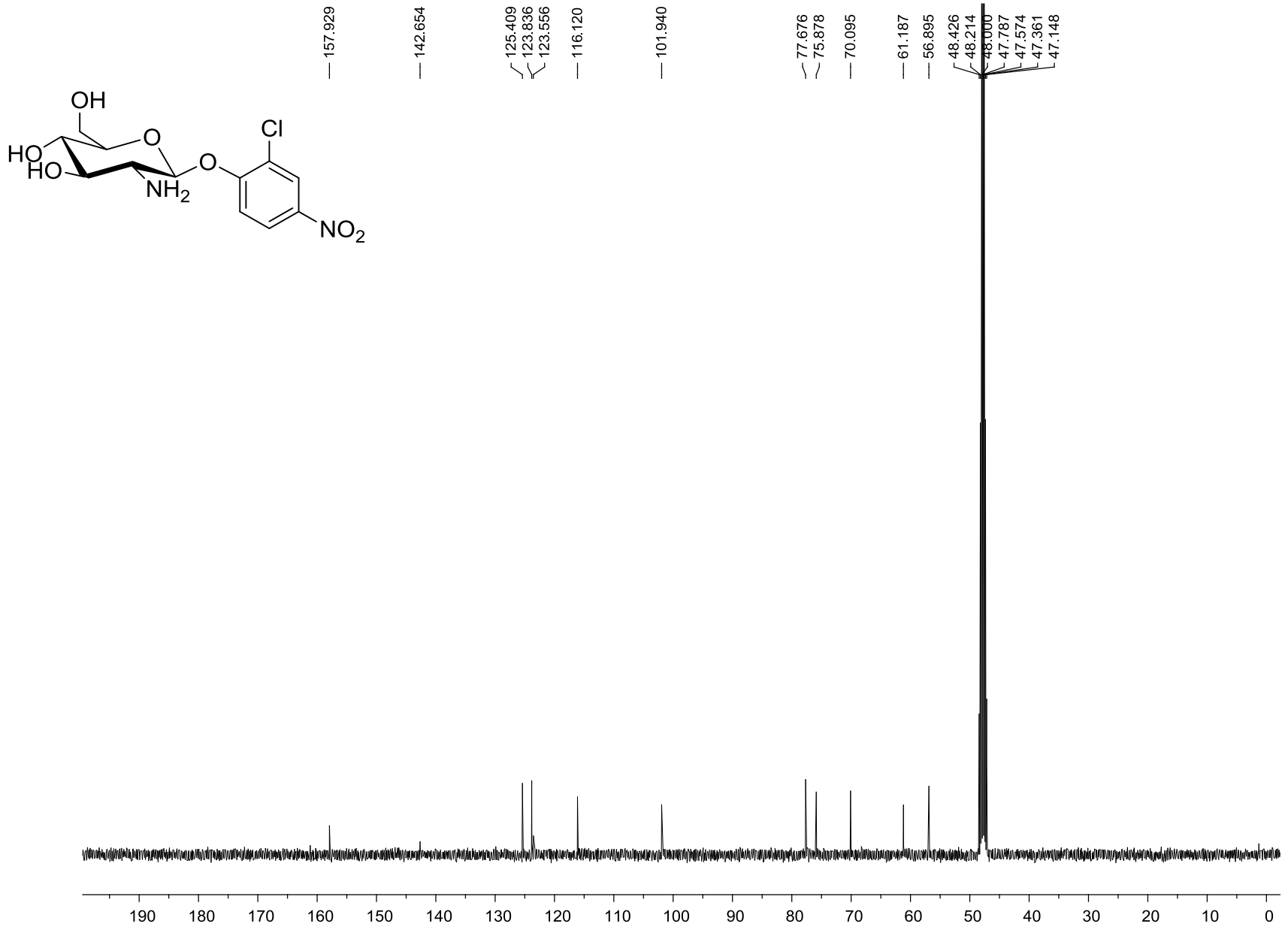


(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (**5**): gCOSY NMR (CD_3OD, 400 MHz)

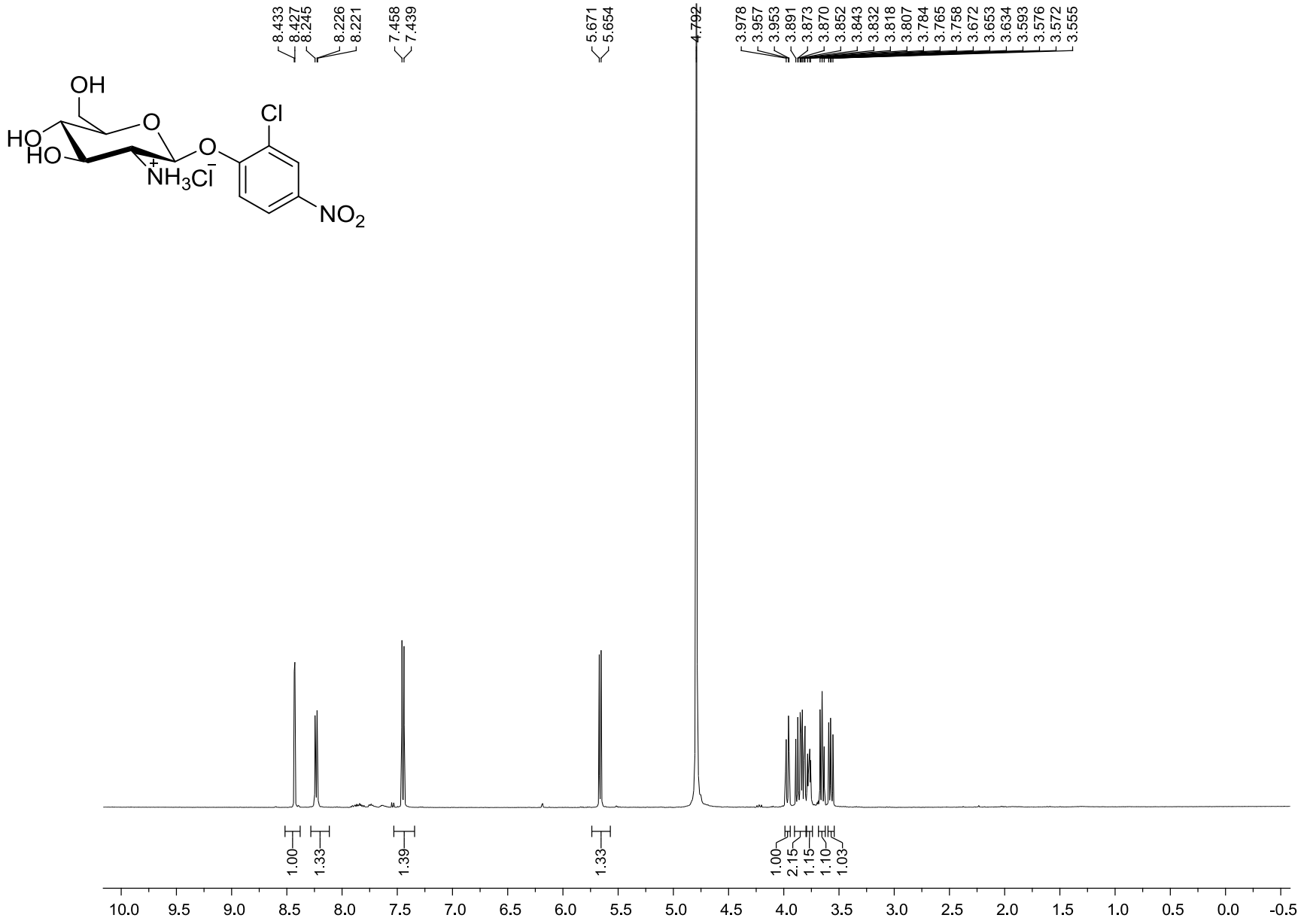




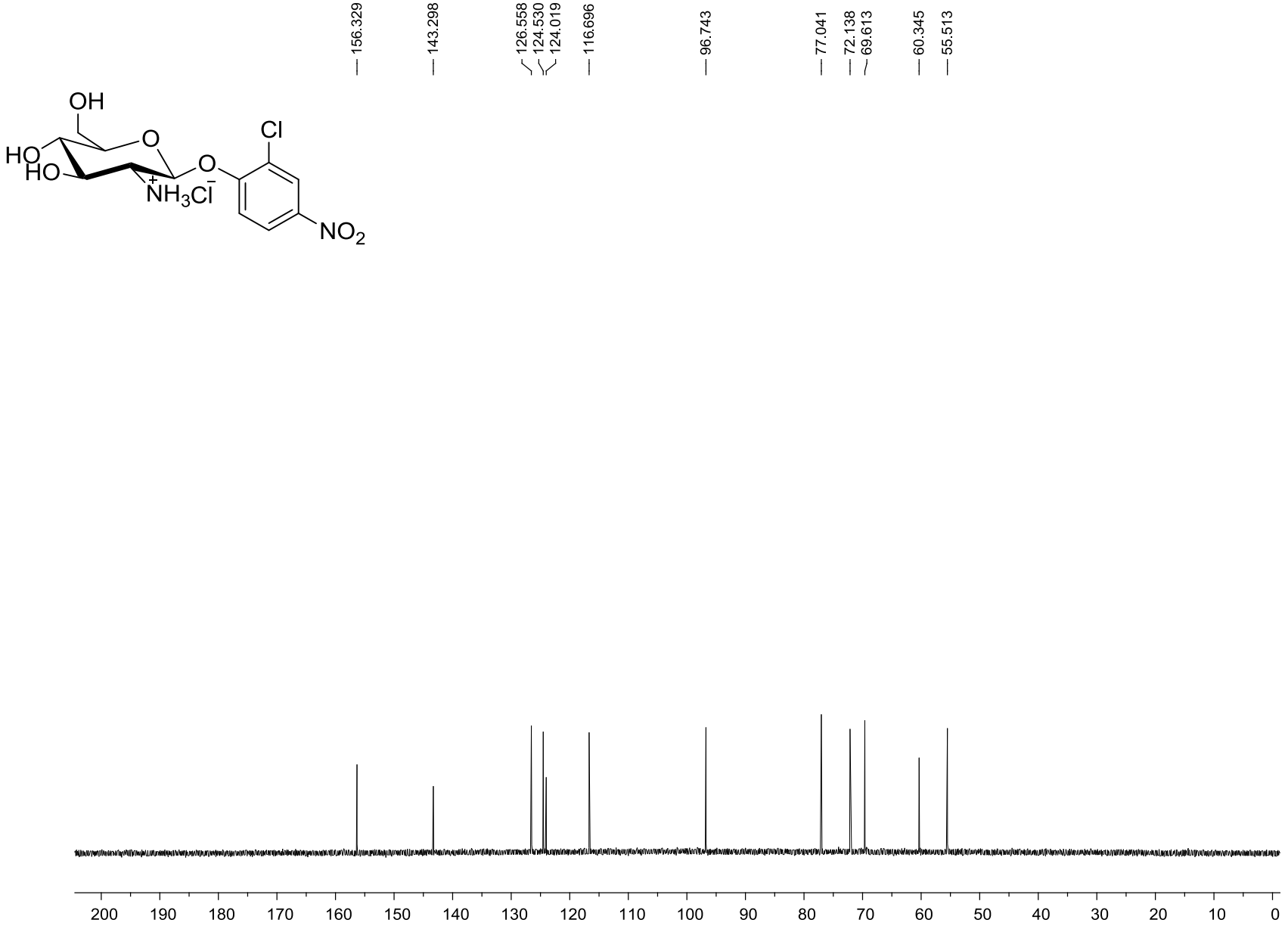
(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside (**5**): ^{13}C NMR (CD_3OD, 100 MHz)



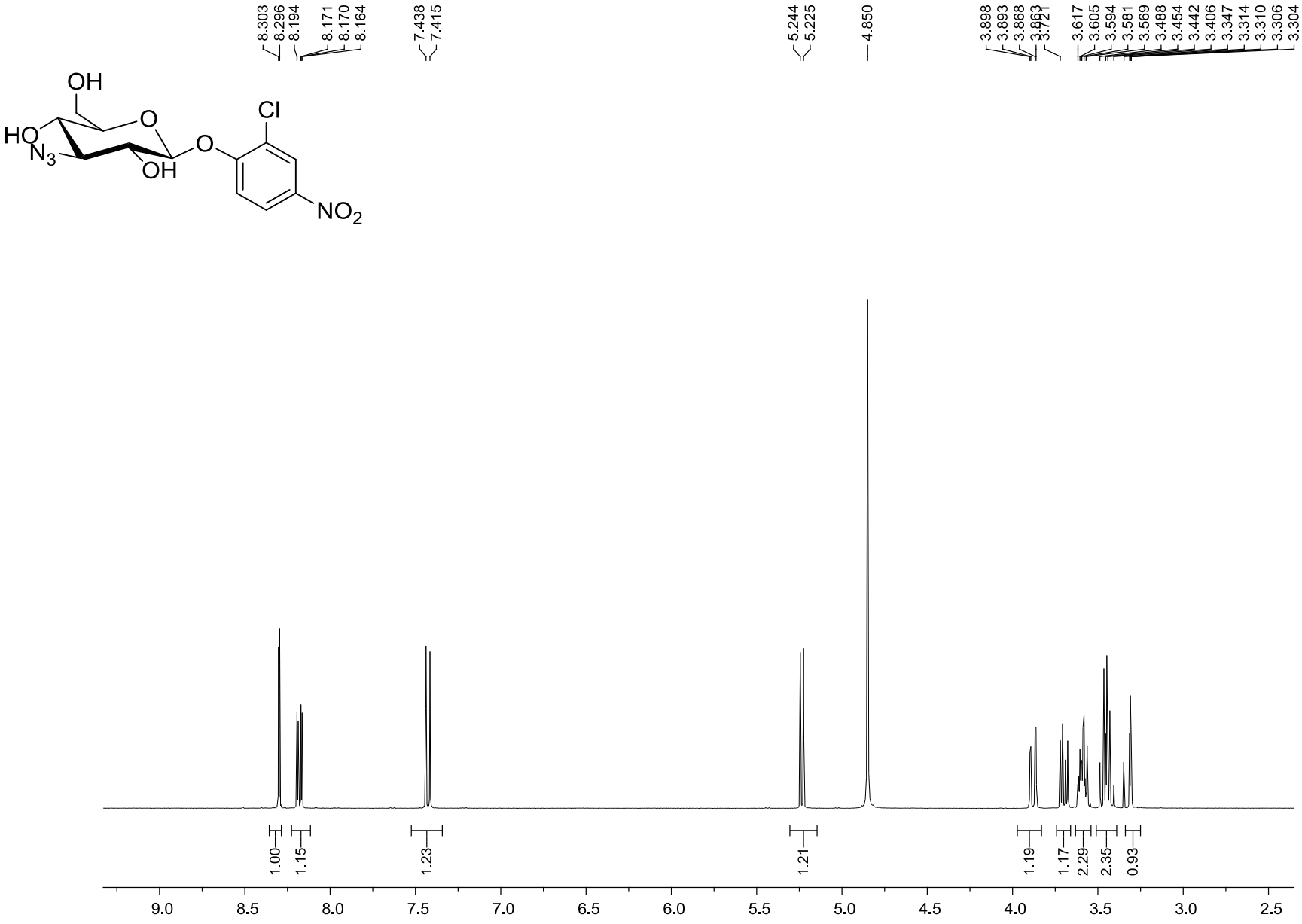
(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside hydrochloride (**5a**): ^{1}H NMR (CD_3OD, 500 MHz)



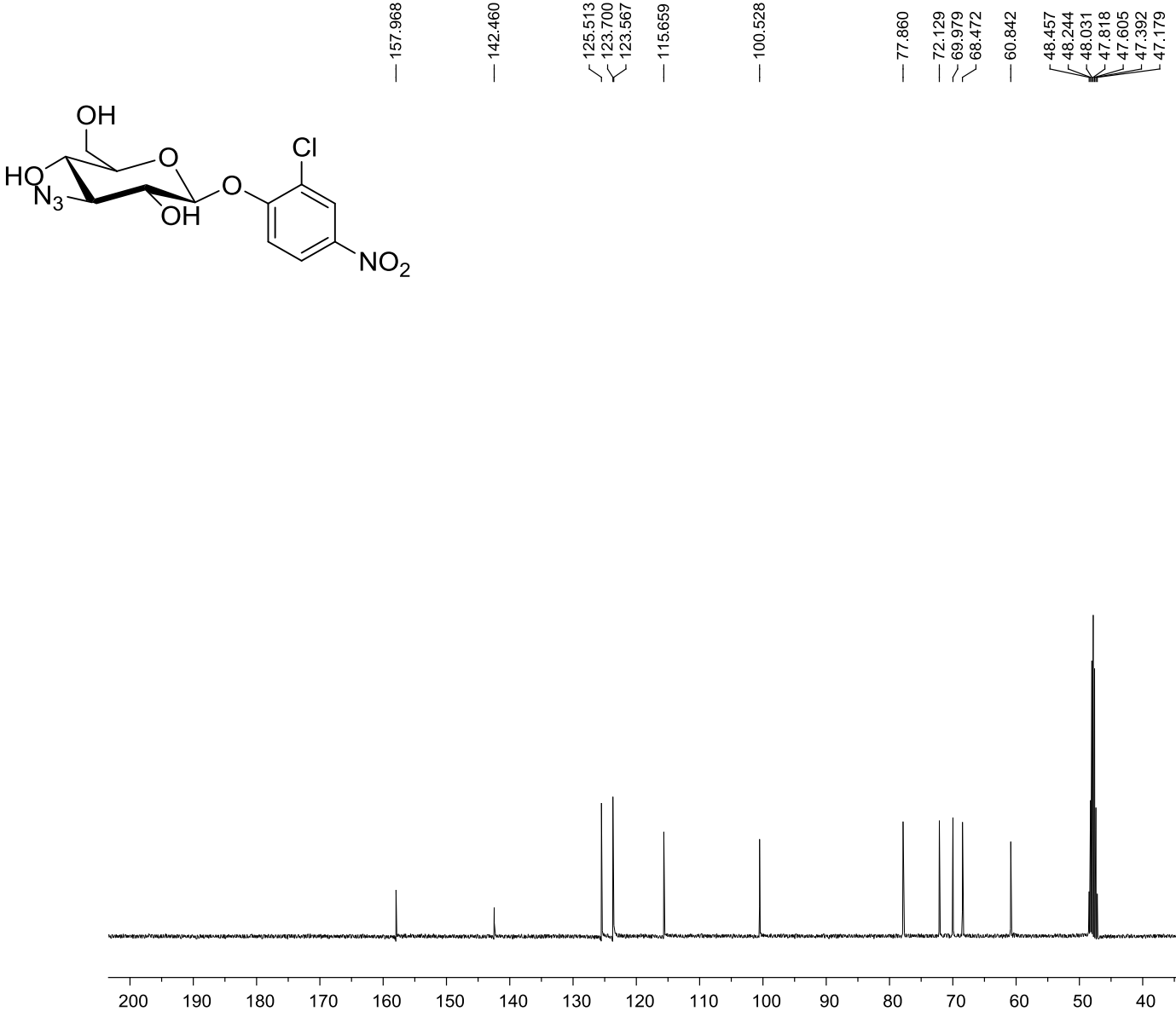
(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-glucopyranoside hydrochloride (**5a**): ^{13}C NMR (CD_3OD, 125 MHz)



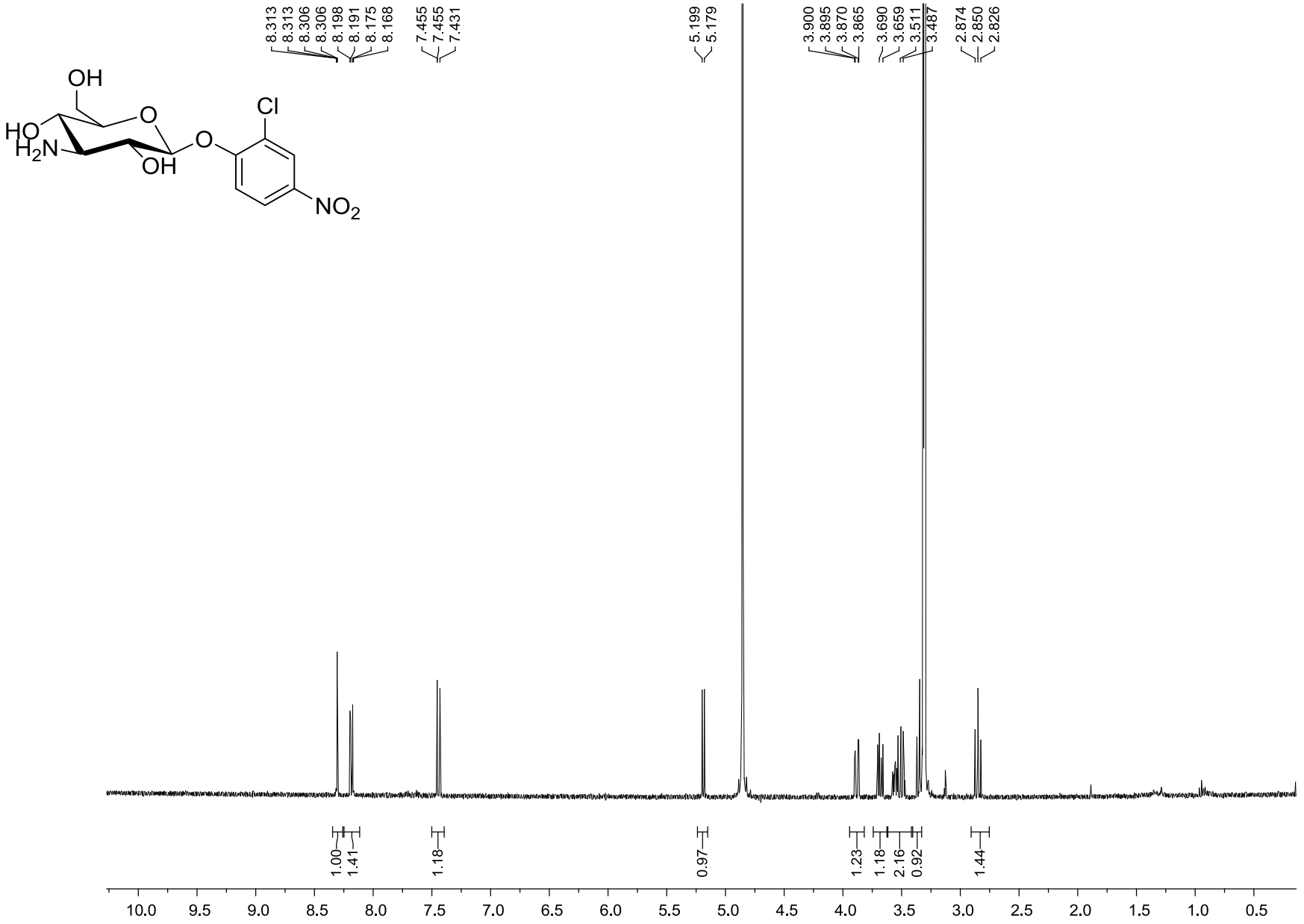
(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-glucopyranoside (**6**): ^{1}H NMR (CD_3OD, 400 MHz)



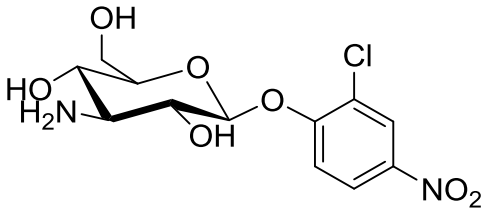
(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-glucopyranoside (**6**): ^{13}C NMR (CD_3OD, 100 MHz)

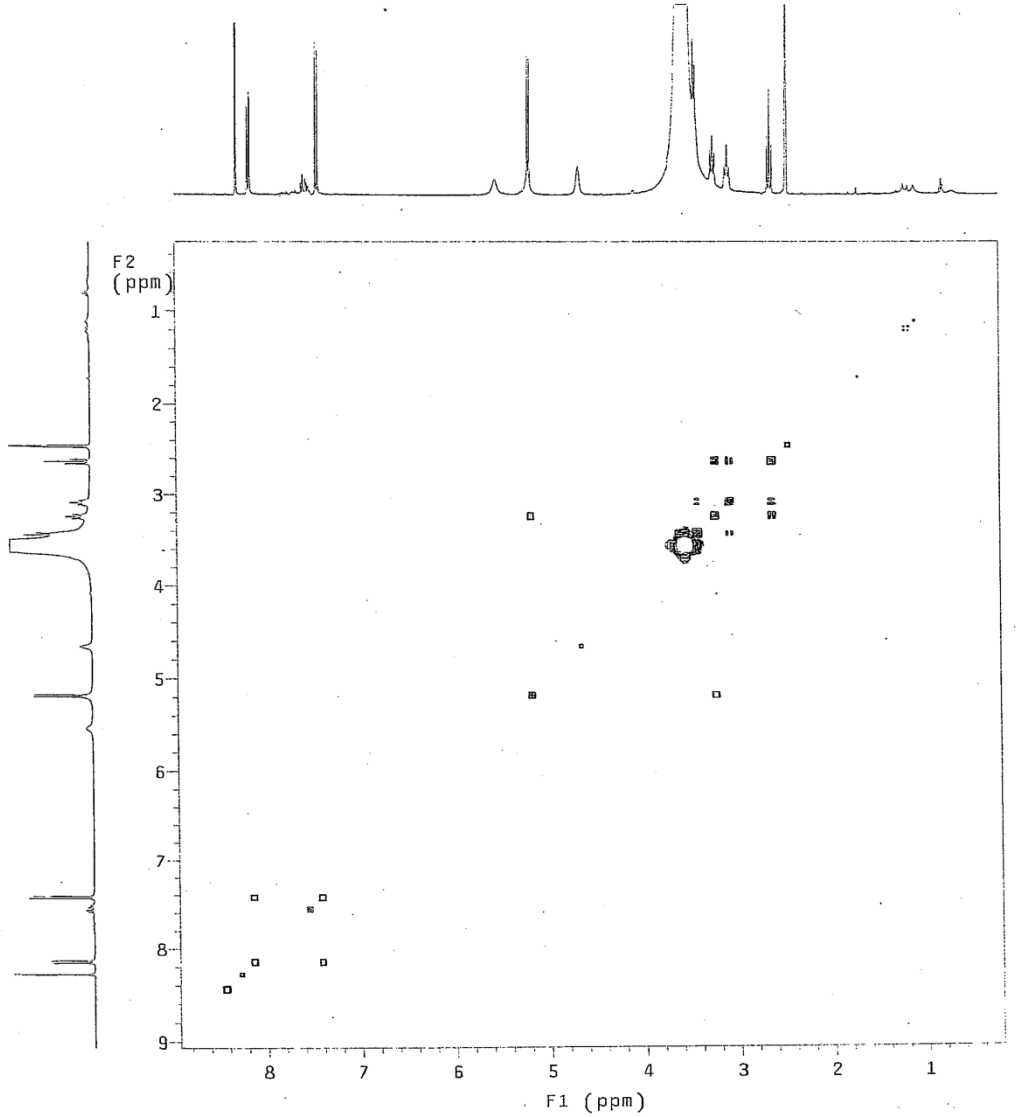


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (**7**): ^{1}H NMR (CD_3OD, 400 MHz)

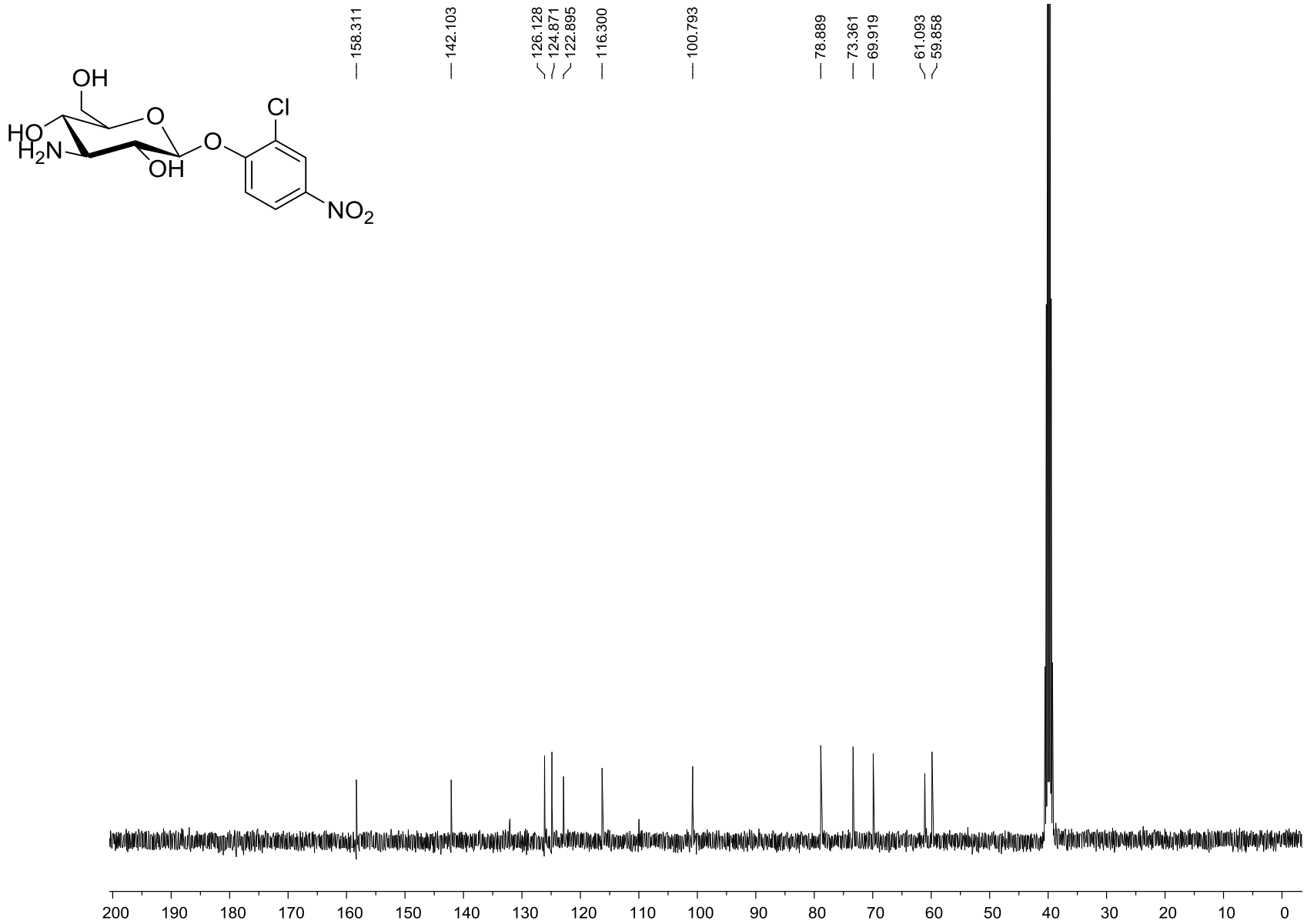


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (**7**): gCOSY NMR (CD_3OD, 500 MHz)

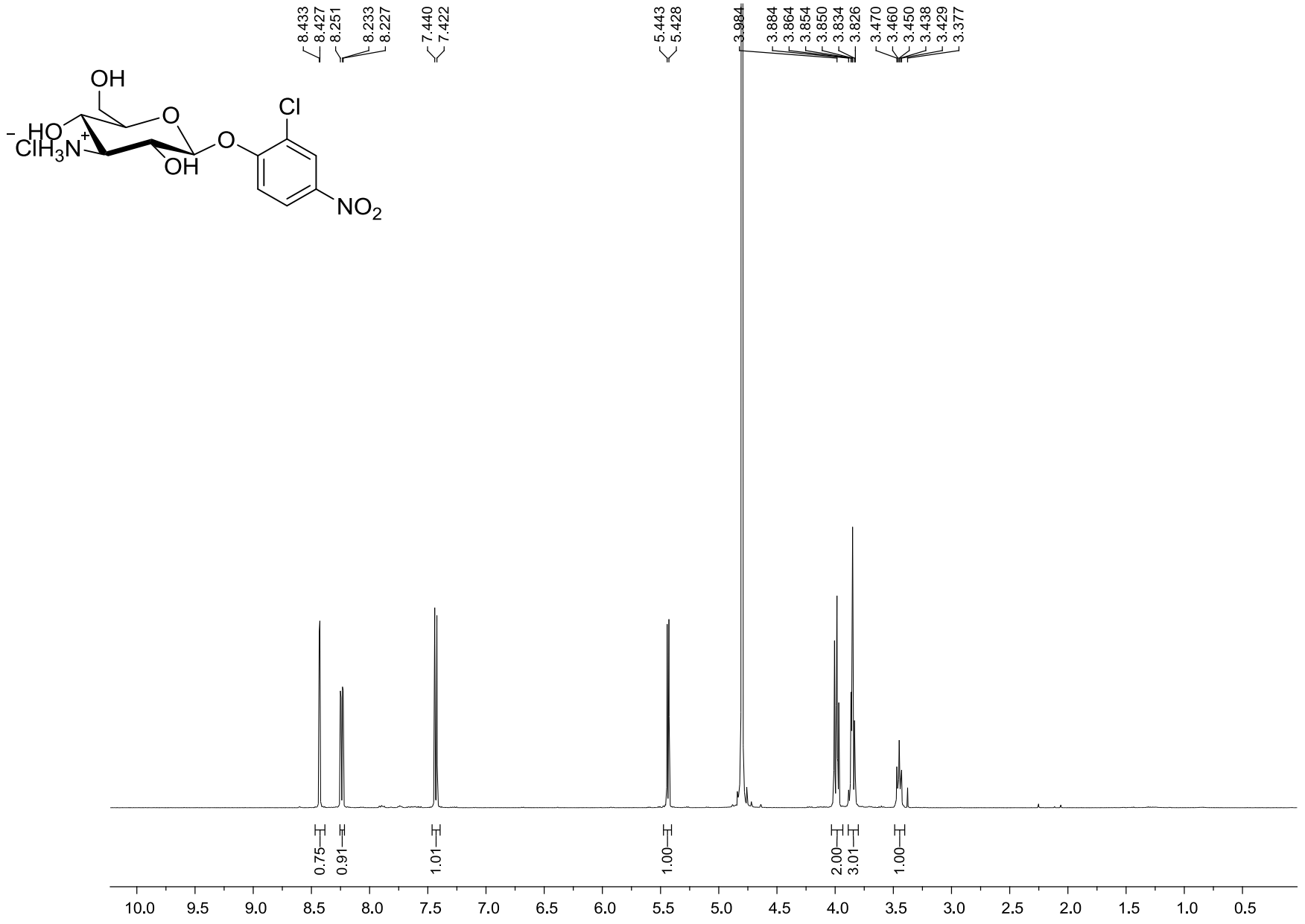




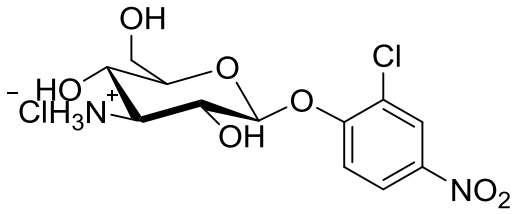
(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside (**7**): ^{13}C NMR (DMSO-d_6, 100 MHz)

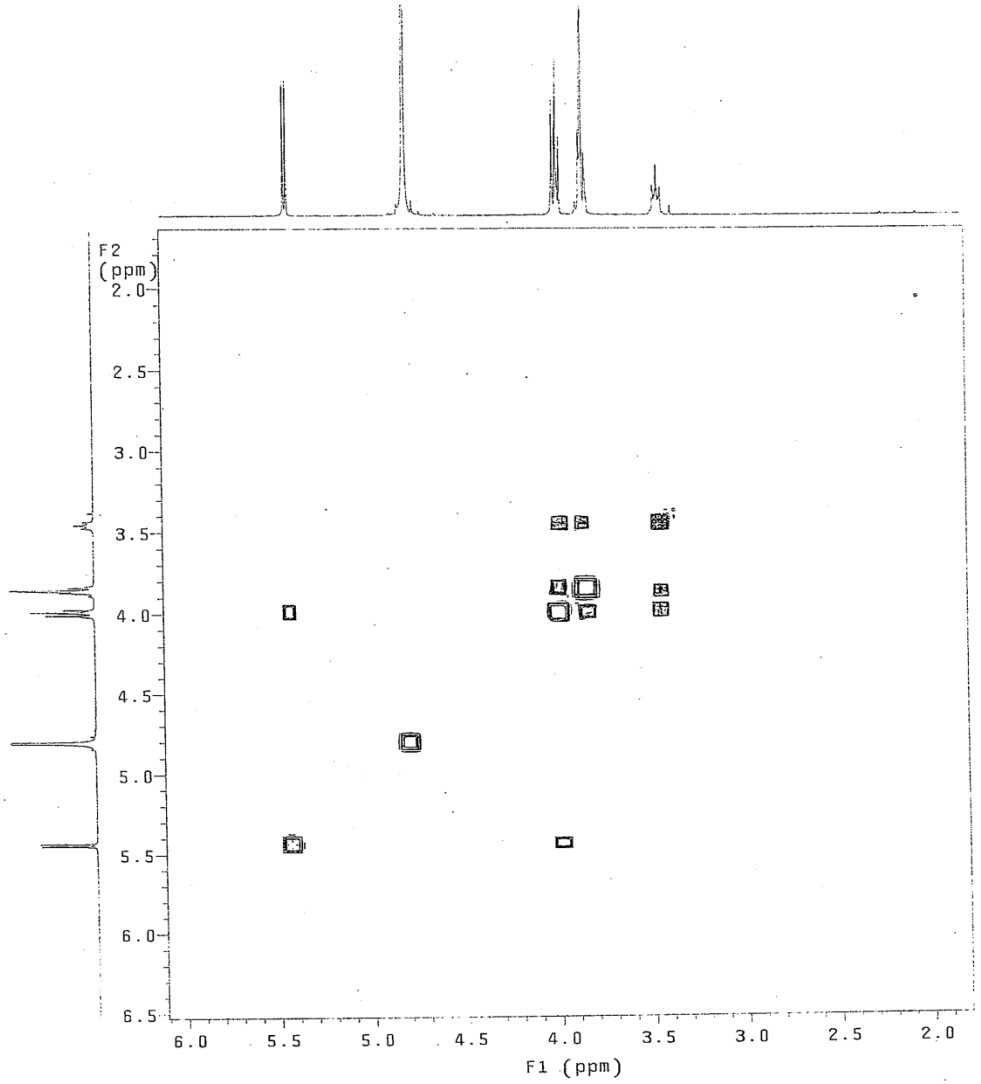


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (**7a**): ^{1}H NMR (D_2O, 500 MHz)

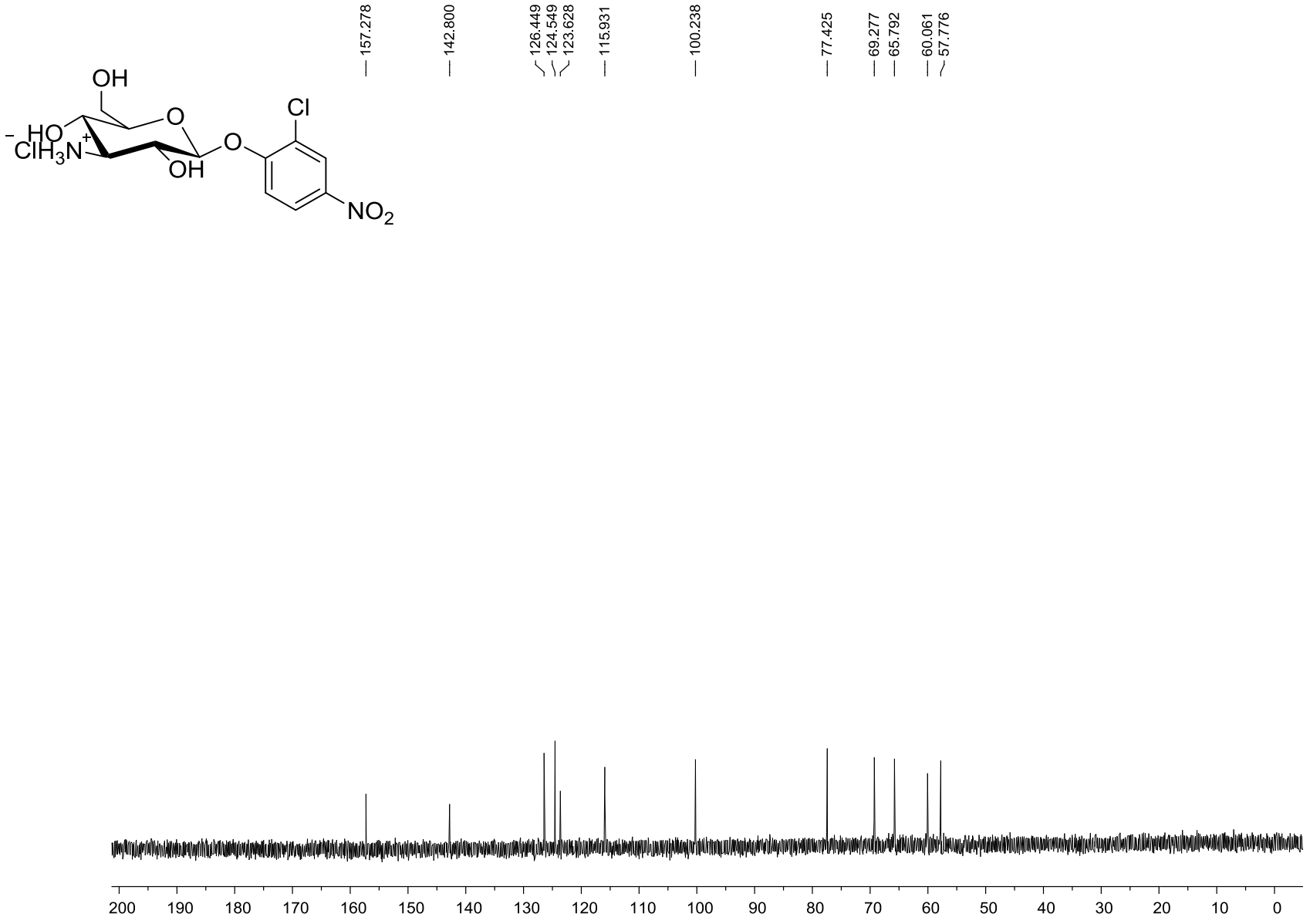


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (**7a**): gCOSY NMR (D_2O, 500 MHz)

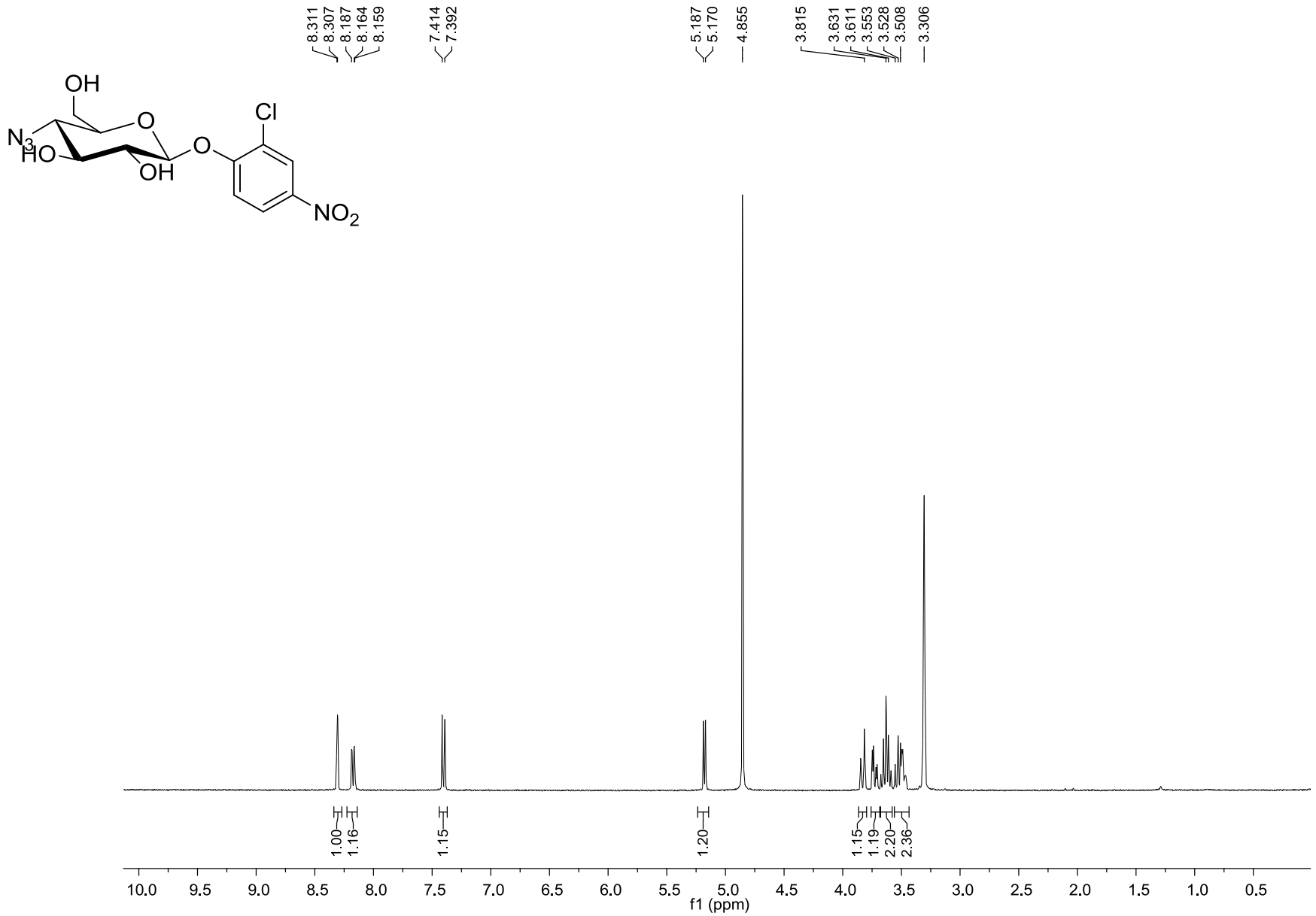




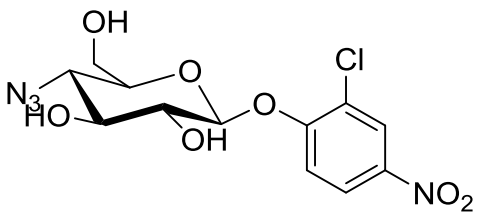
(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-glucopyranoside hydrochloride (**7a**): ^{13}C NMR (D_2O, 100 MHz)

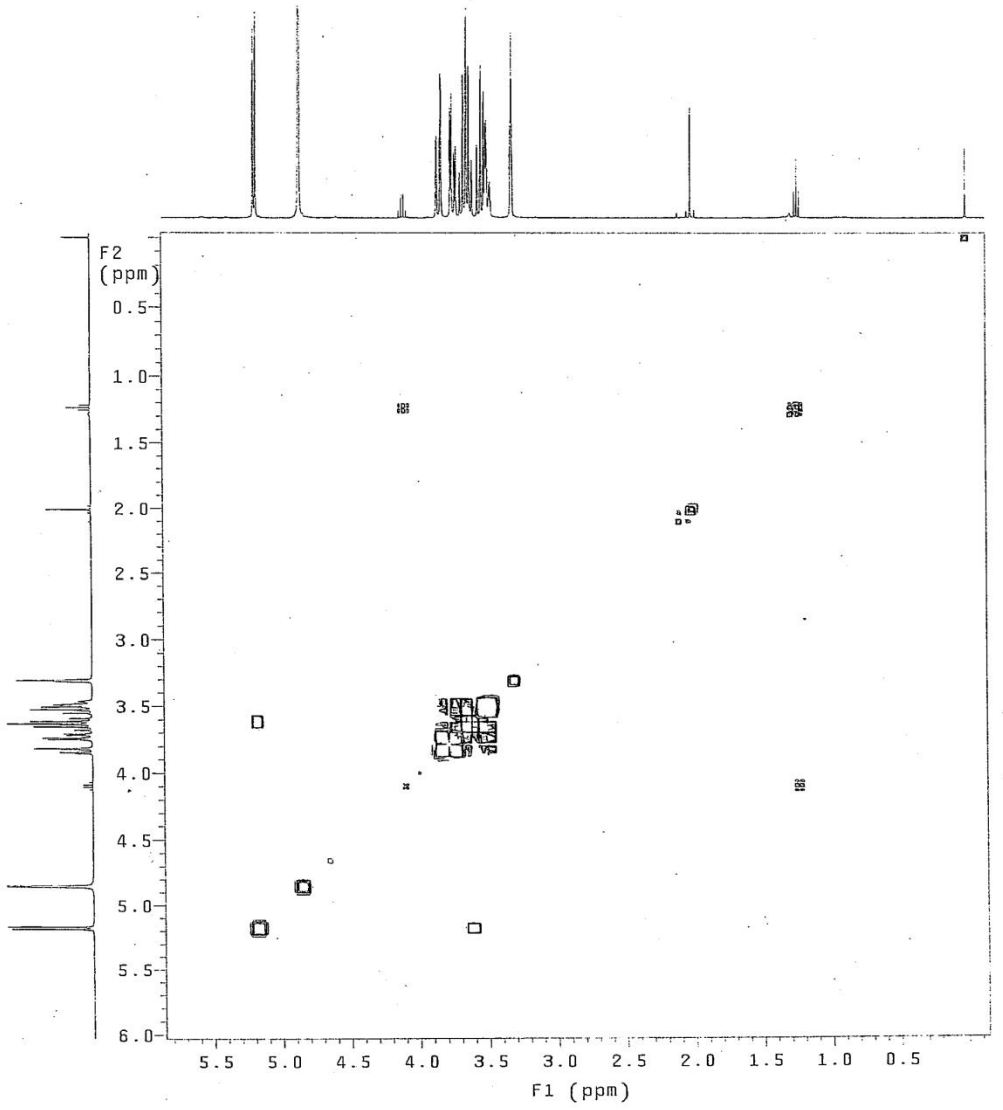


(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-glucopyranoside (**8**): ^{1}H NMR (CD_3OD, 400 MHz)

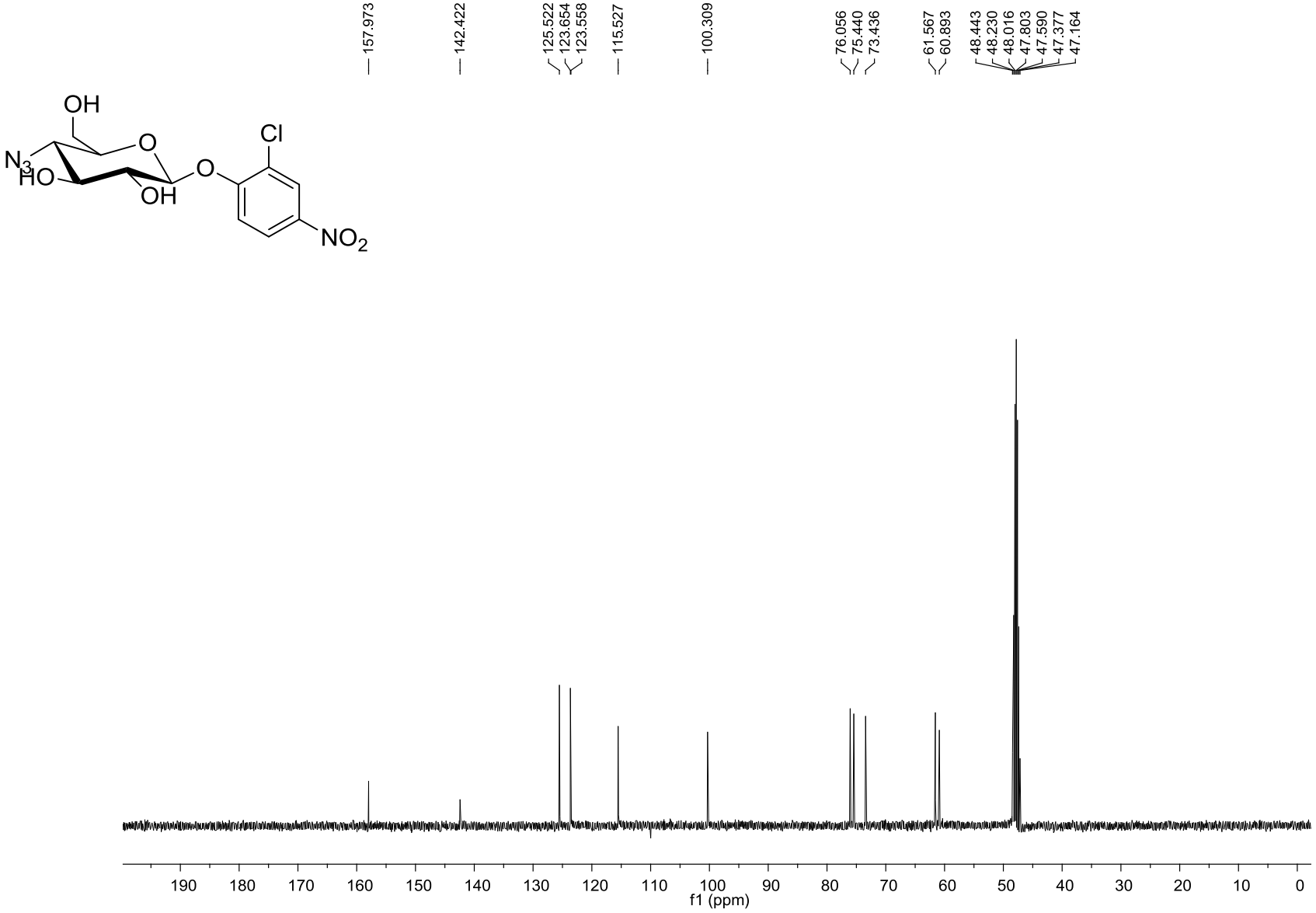


(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-glucopyranoside (**8**): gCOSY NMR (CD_3OD, 400 MHz)

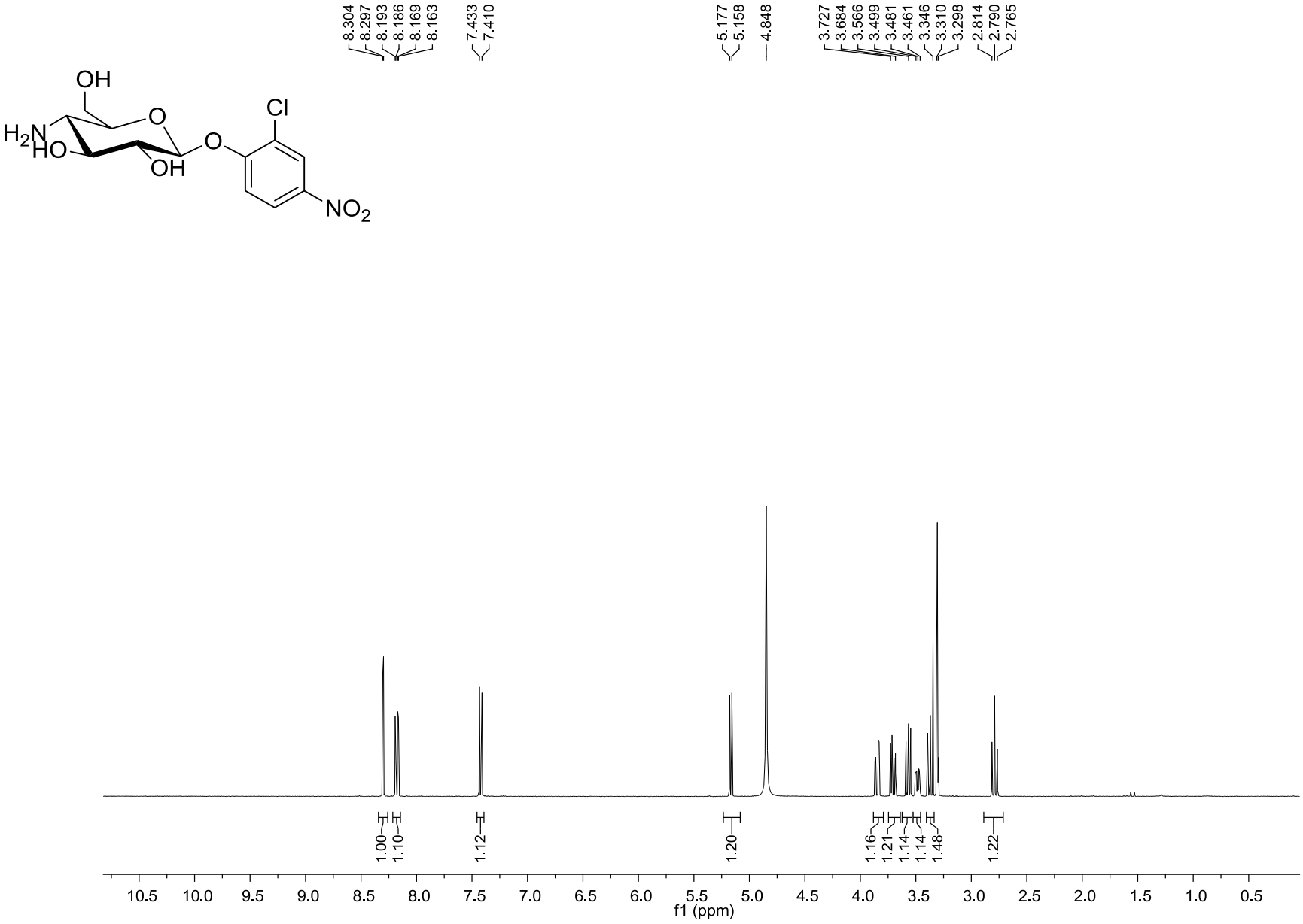




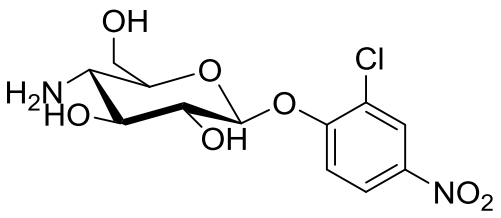
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-glucopyranoside (**8**): ^{13}C NMR (CD_3OD, 100 MHz)

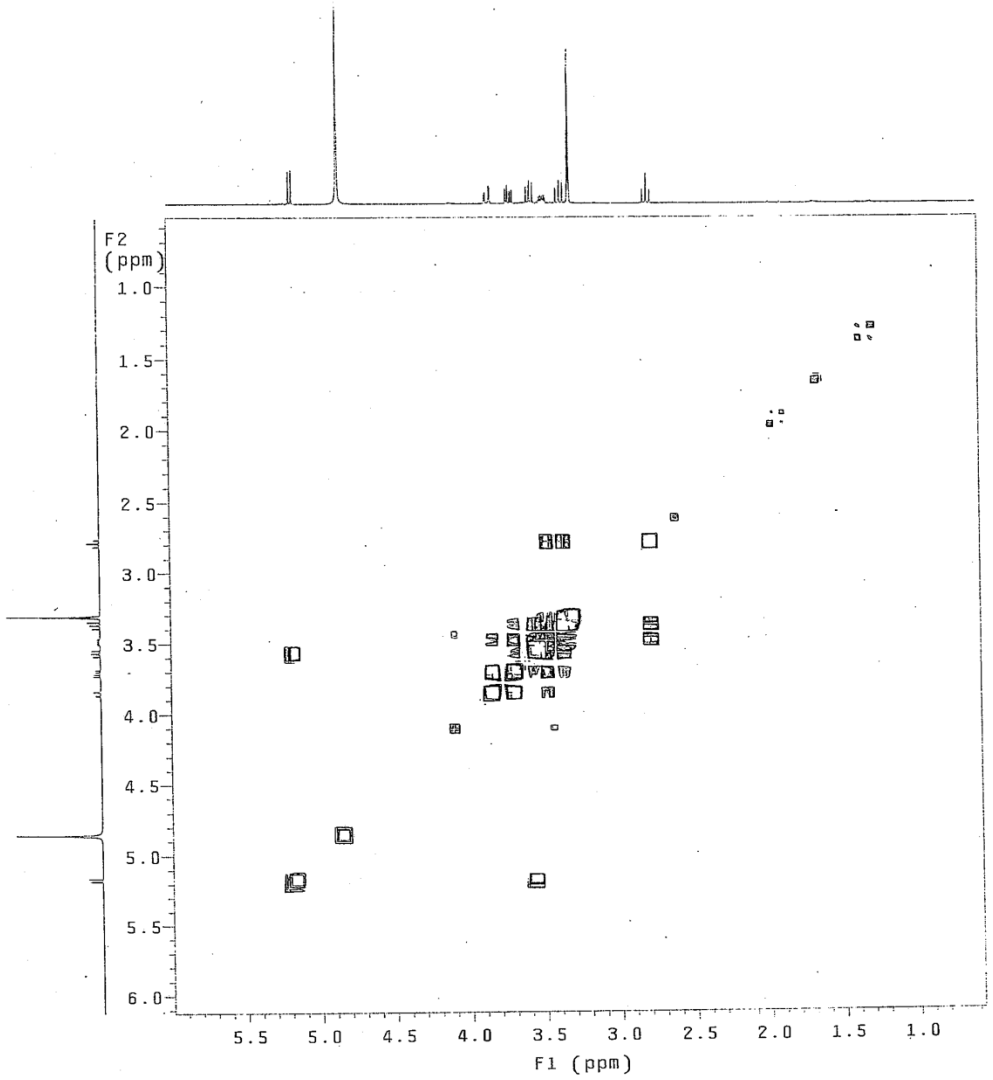


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (**9**): ^{1}H NMR (CD_3OD, 400 MHz)

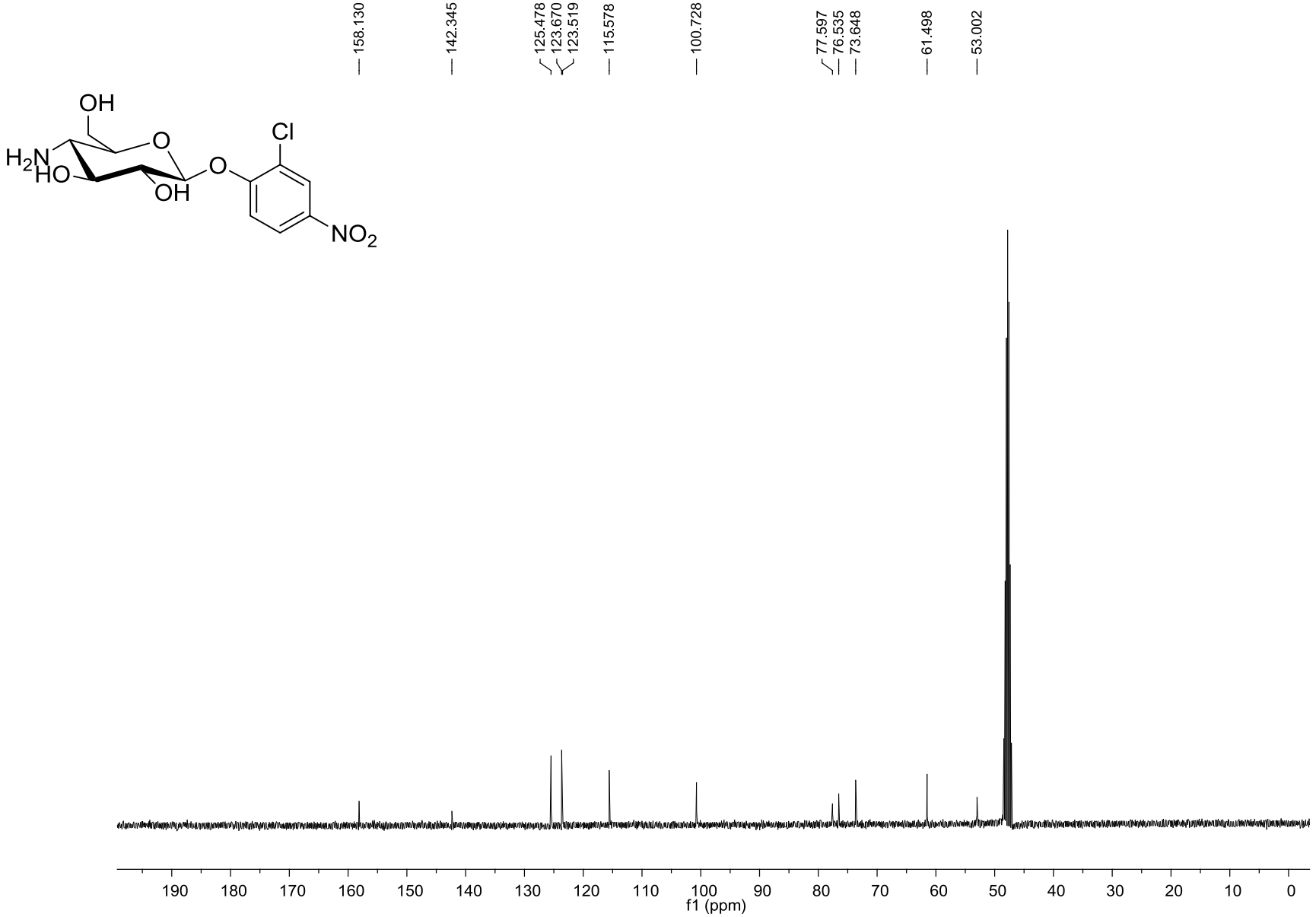


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (**9**): gCOSY NMR (CD_3OD, 400 MHz)

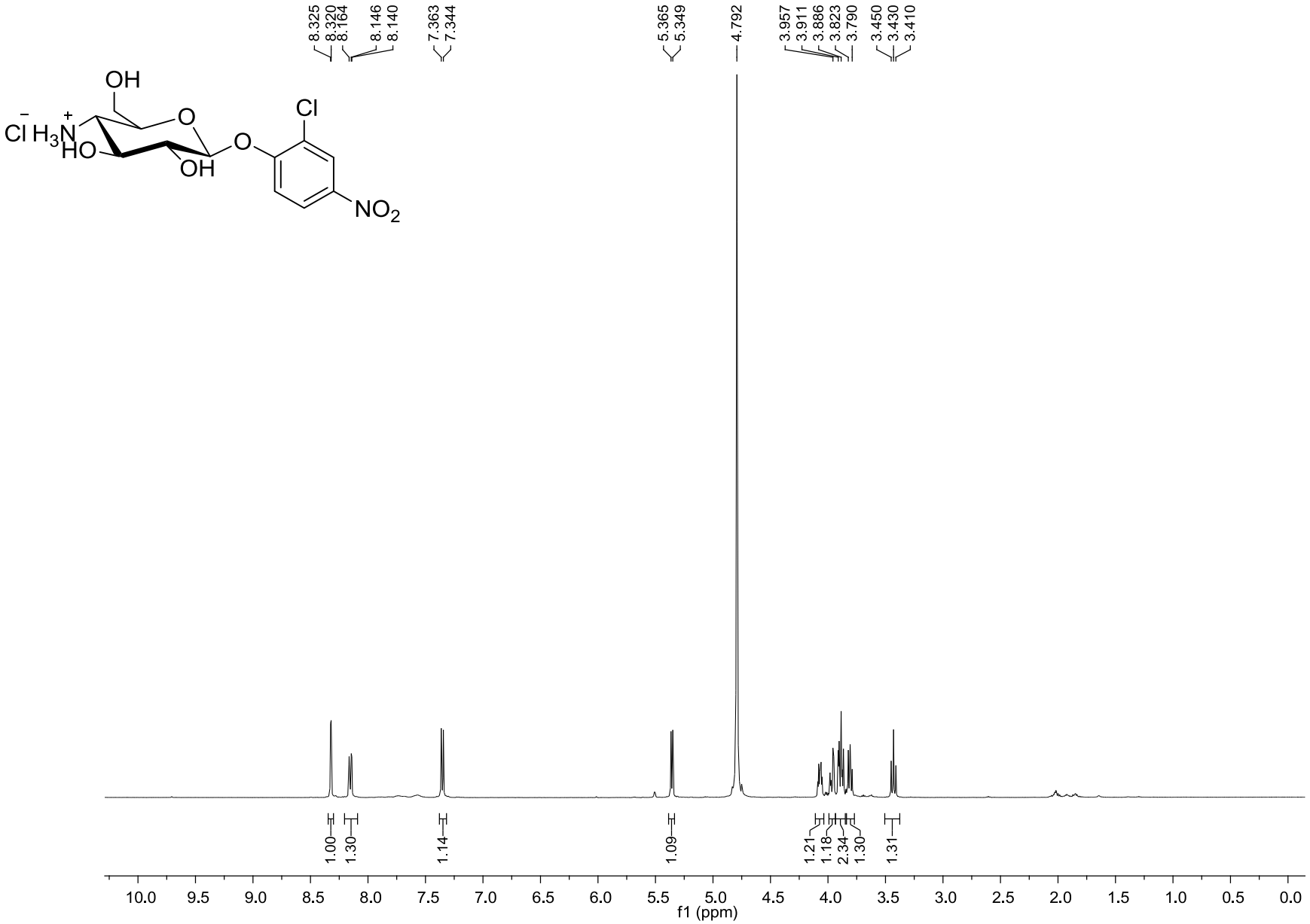




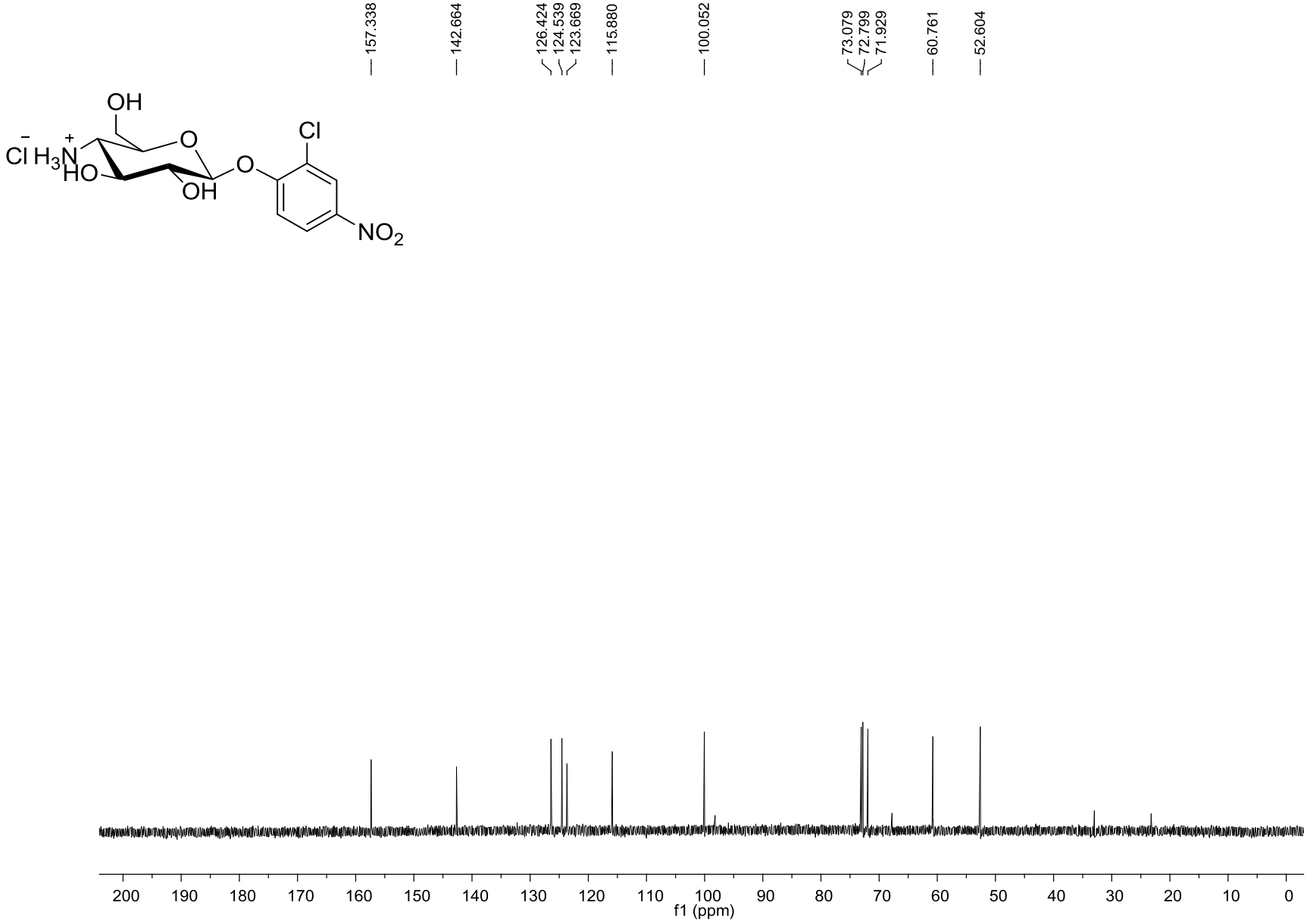
(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside (**9**): ^{13}C NMR (CD_3OD, 100 MHz)



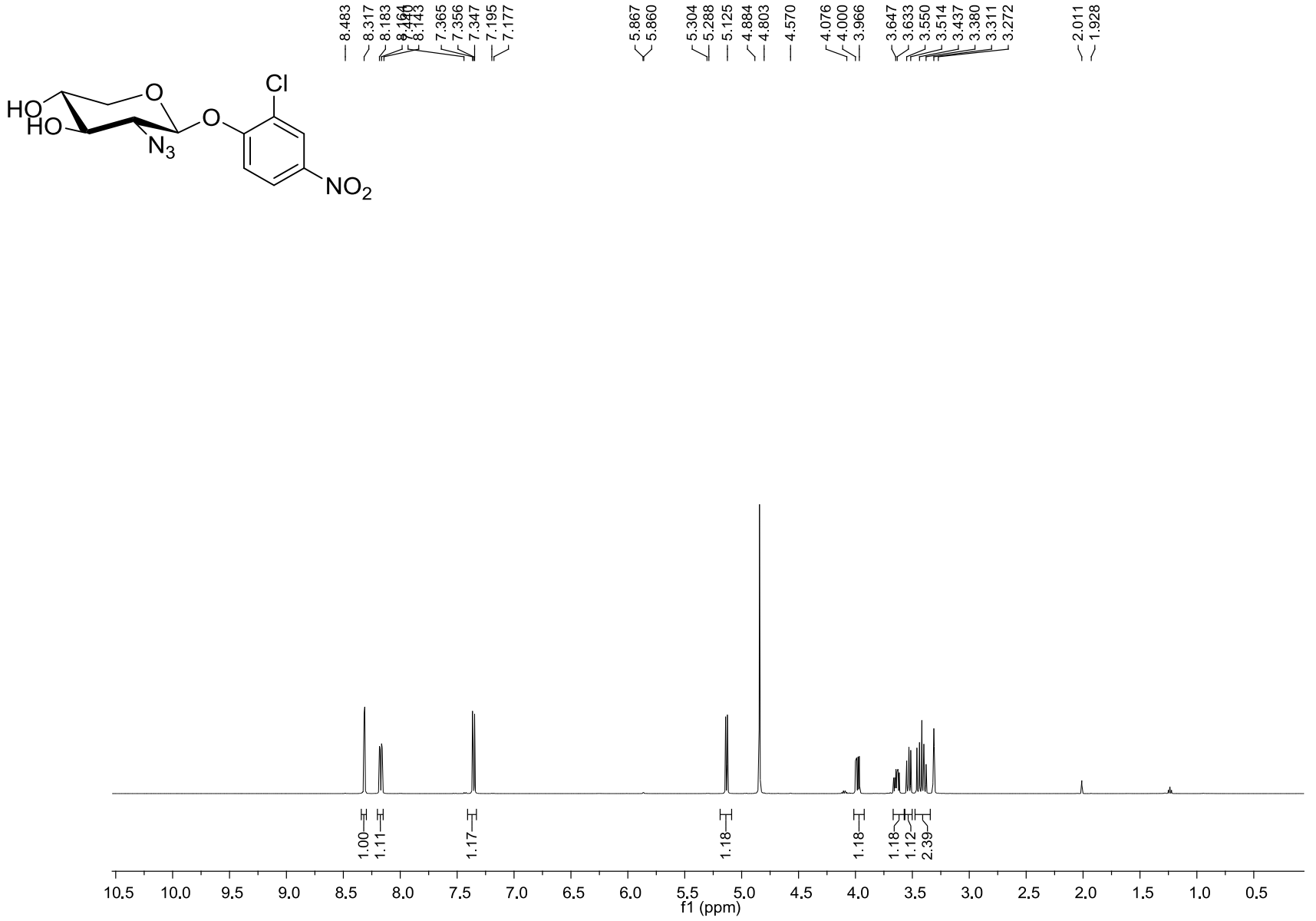
(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside hydrochloride (**9a**): ^{1}H NMR (D_2O, 500 MHz)



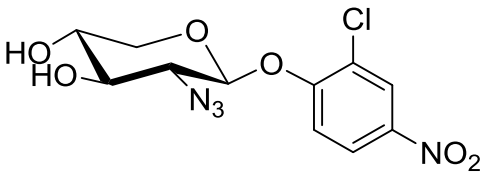
(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-glucopyranoside hydrochloride (**9a**): ^{13}C NMR (D_2O, 125 MHz)

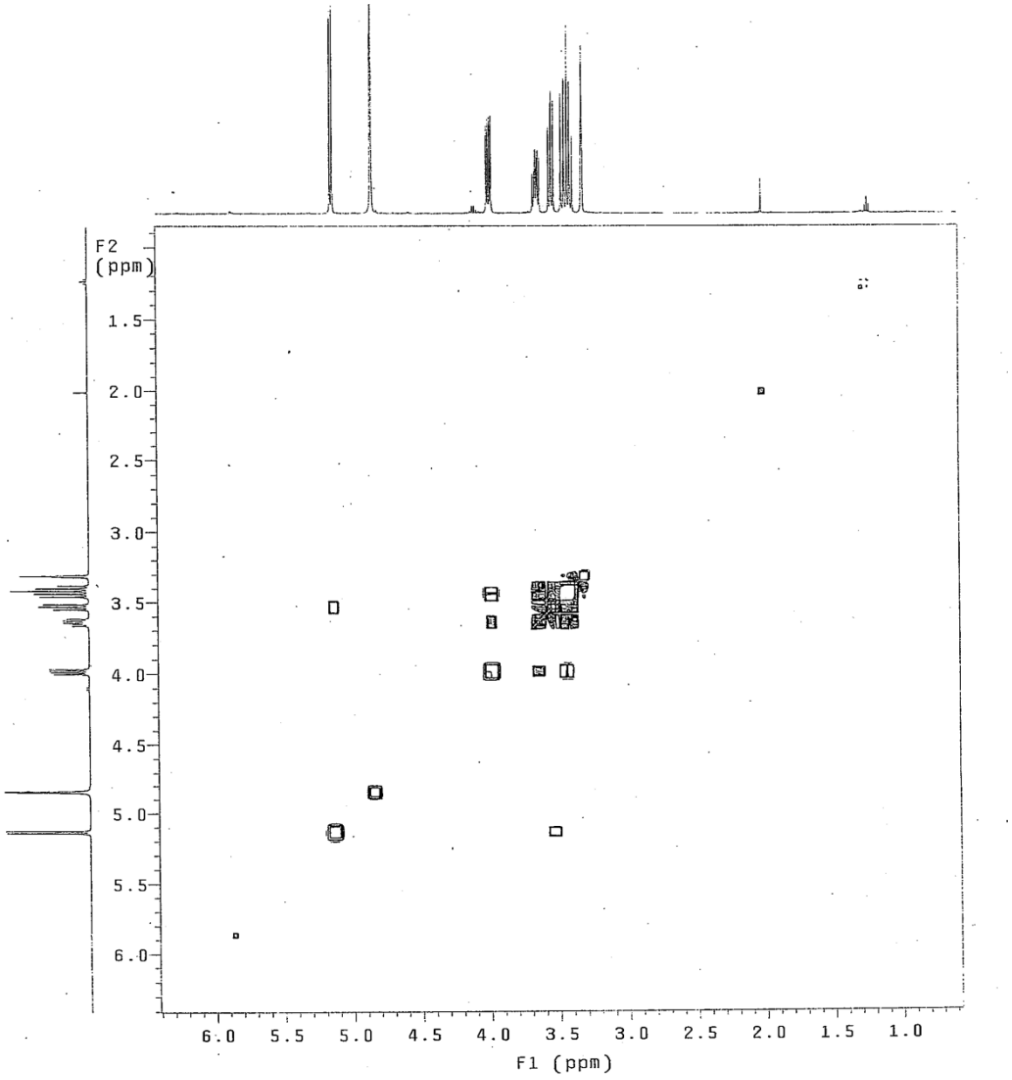


(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (**10**): ^{1}H NMR (CD_3OD, 500 MHz)

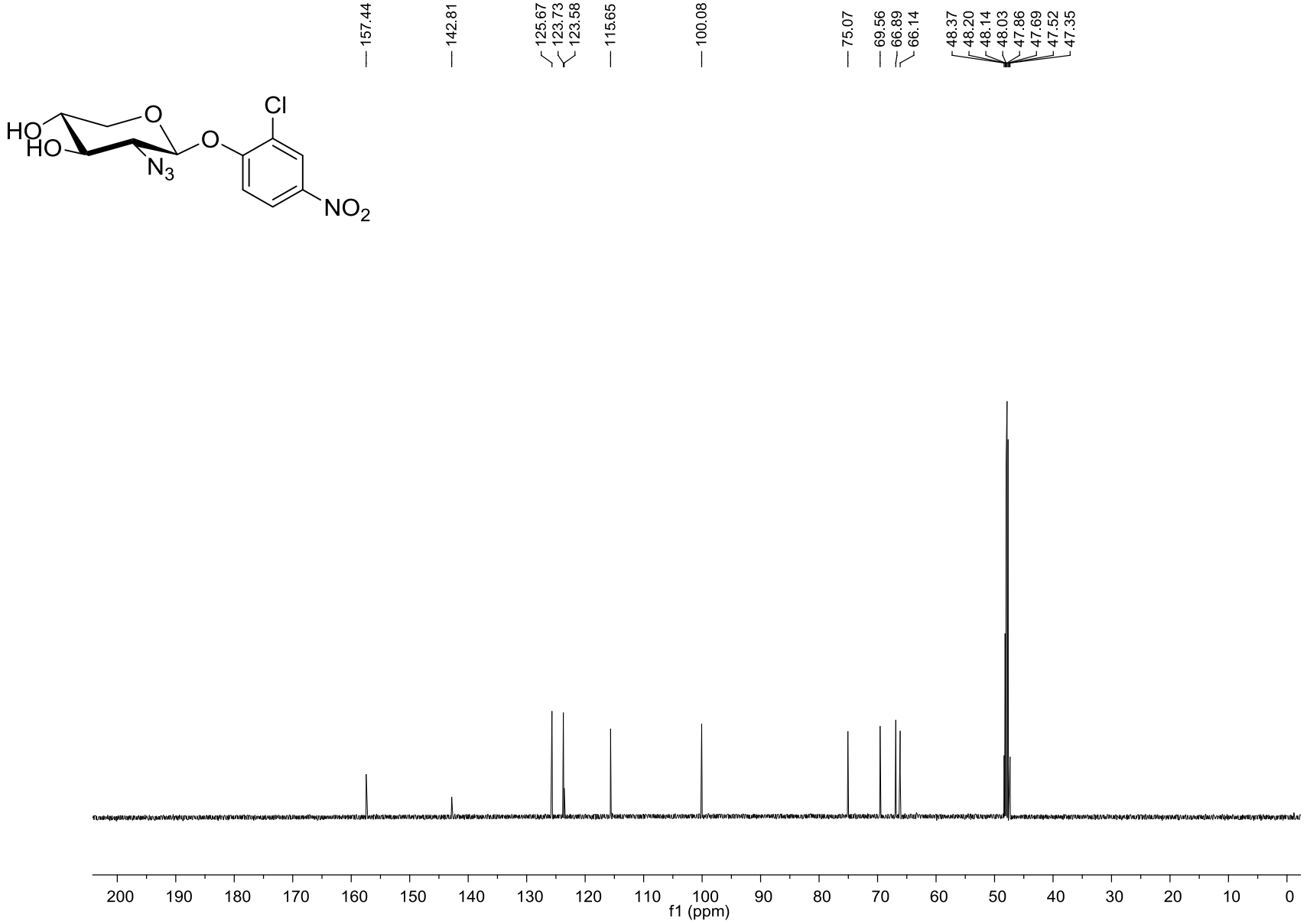


(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (**10**): gCOSY NMR (CD_3OD, 500 MHz)

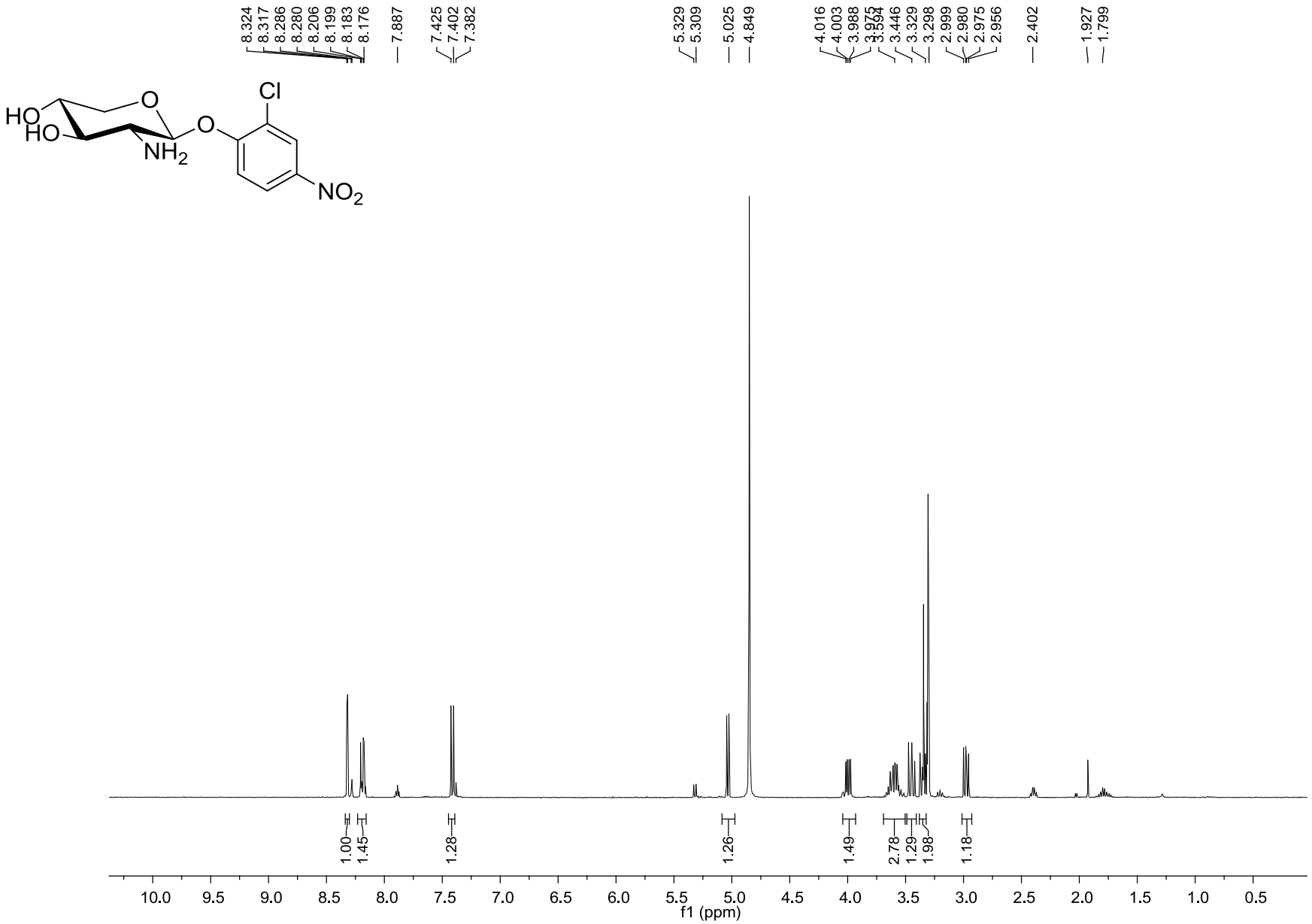




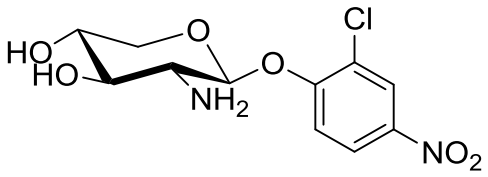
(2-chloro-4-nitrophenyl)-2-deoxy-2-azido-β-D-xylopyranoside (**10**): ^{13}C NMR (CD_3OD, 125 MHz)

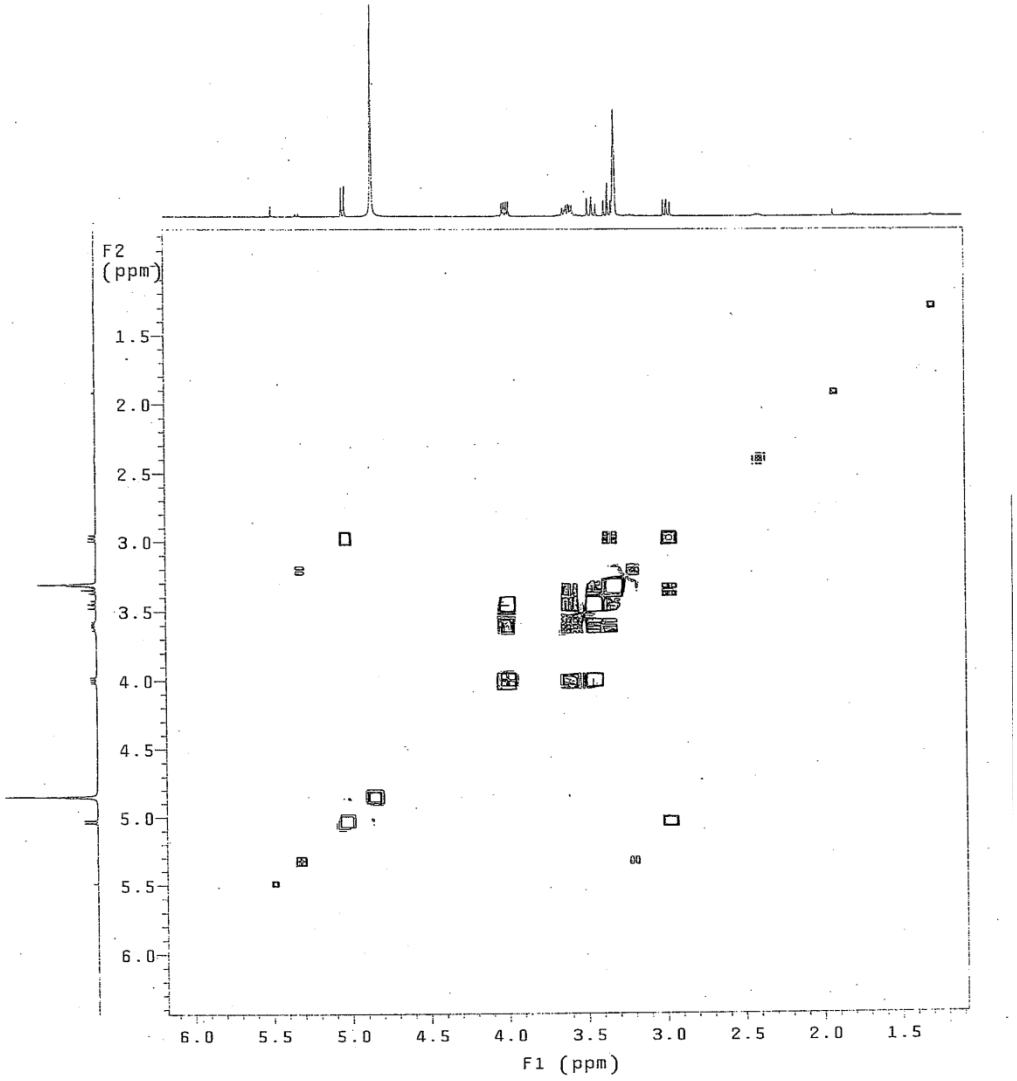


(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (**11**): ^{1}H NMR (CD_3OD, 400 MHz)

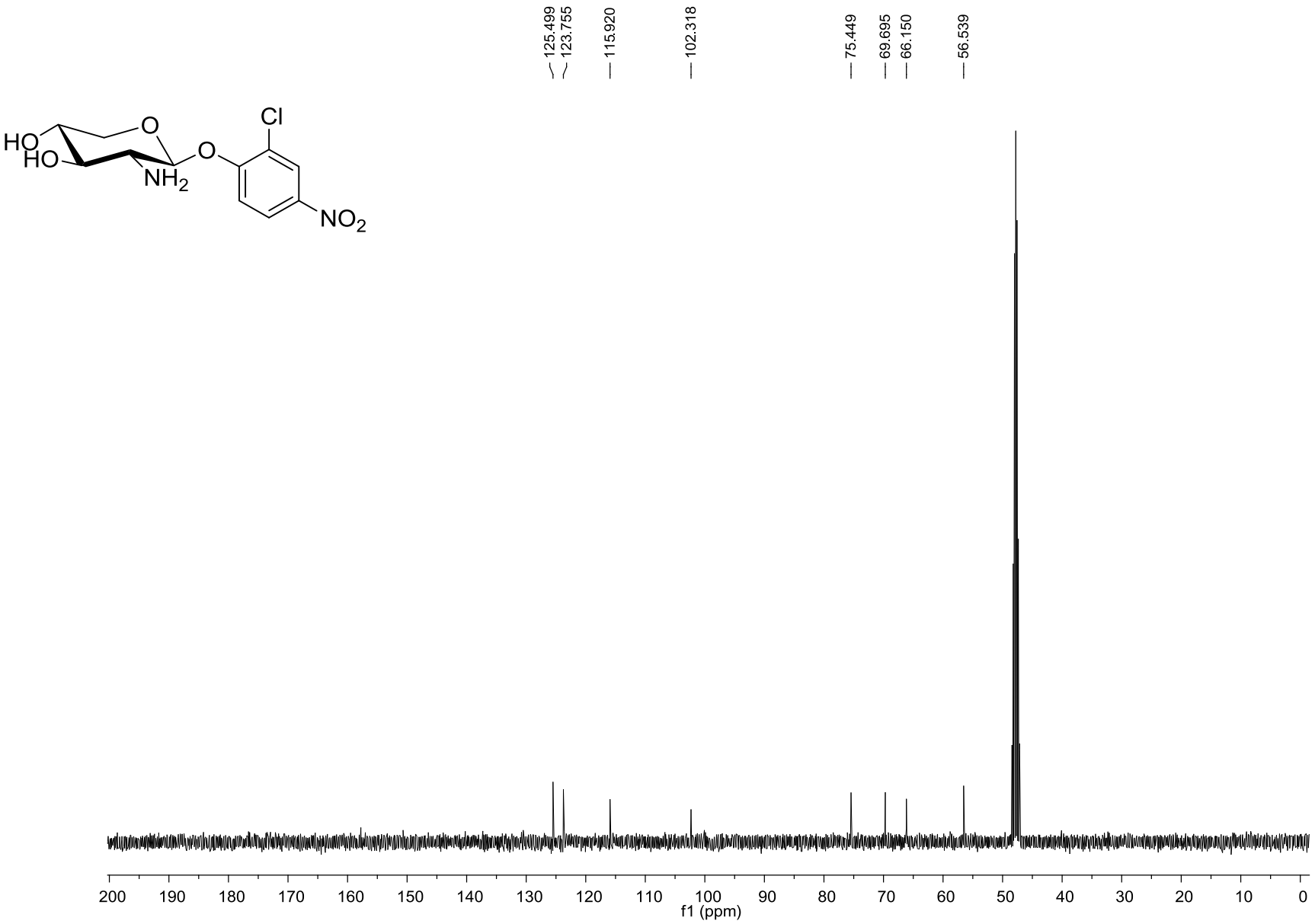


(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (**11**): gCOSY (CD_3OD, 400 MHz)

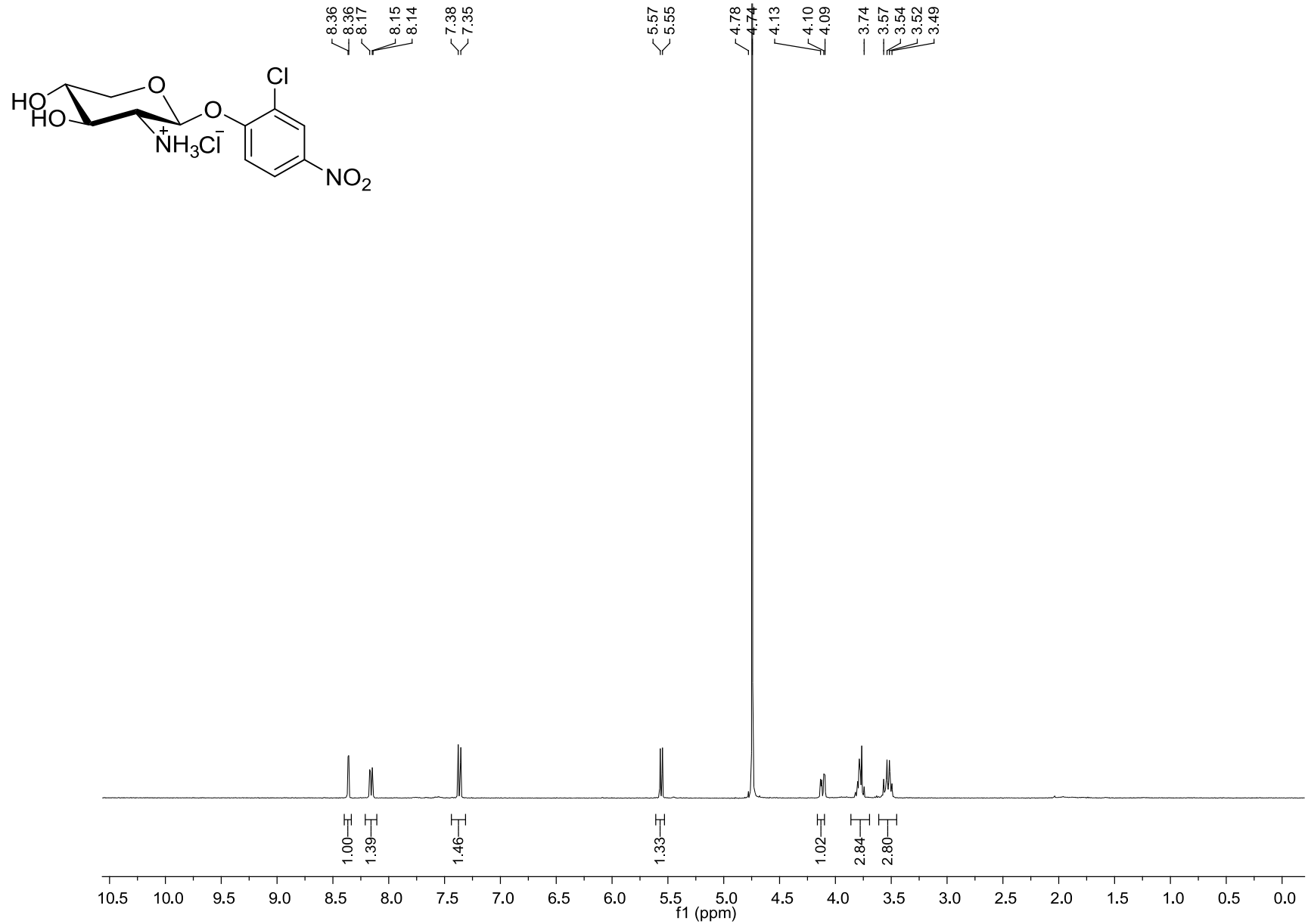




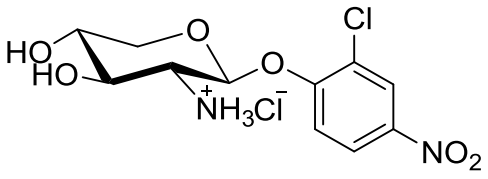
(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside (**11**): ^{13}C NMR (CD_3OD, 100 MHz)

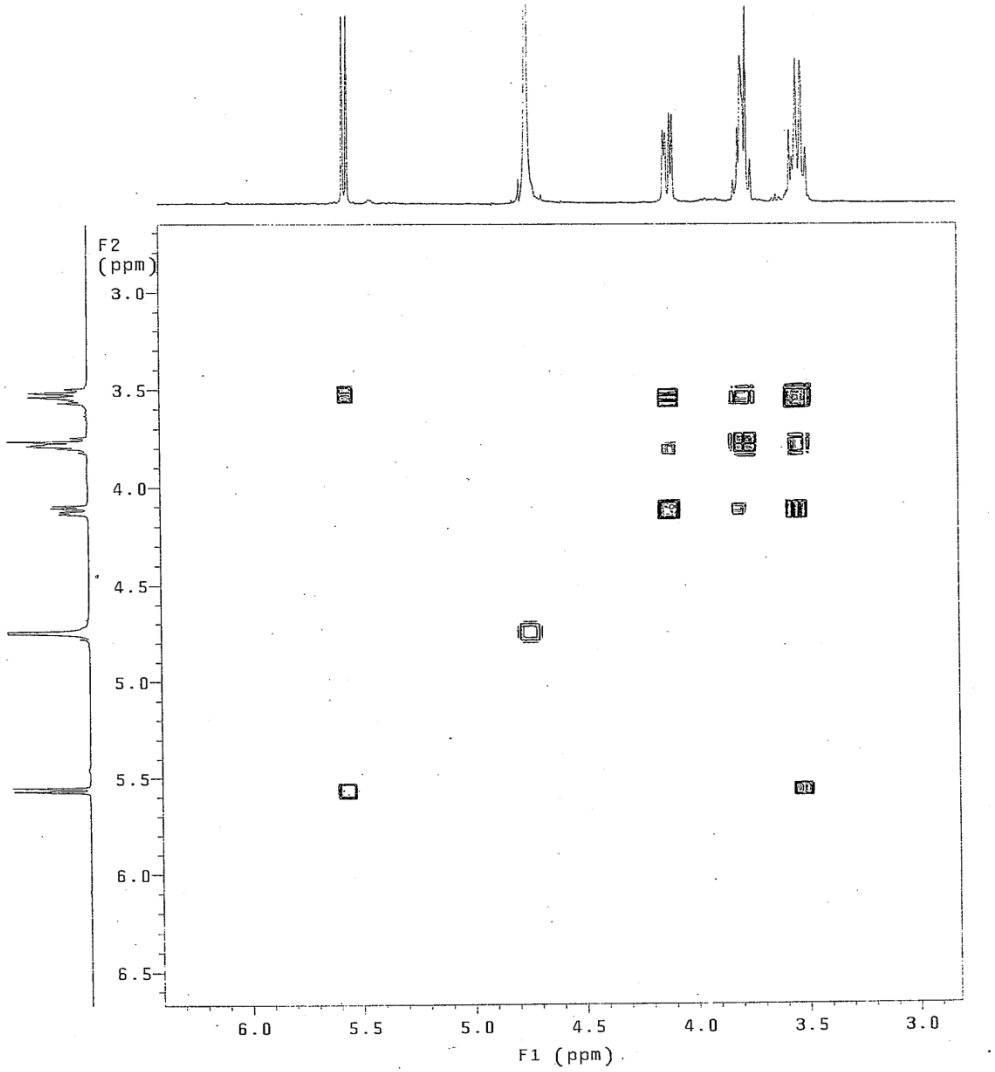


(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (**11a)**: ^{1}H NMR (D_2O, 400 MHz)

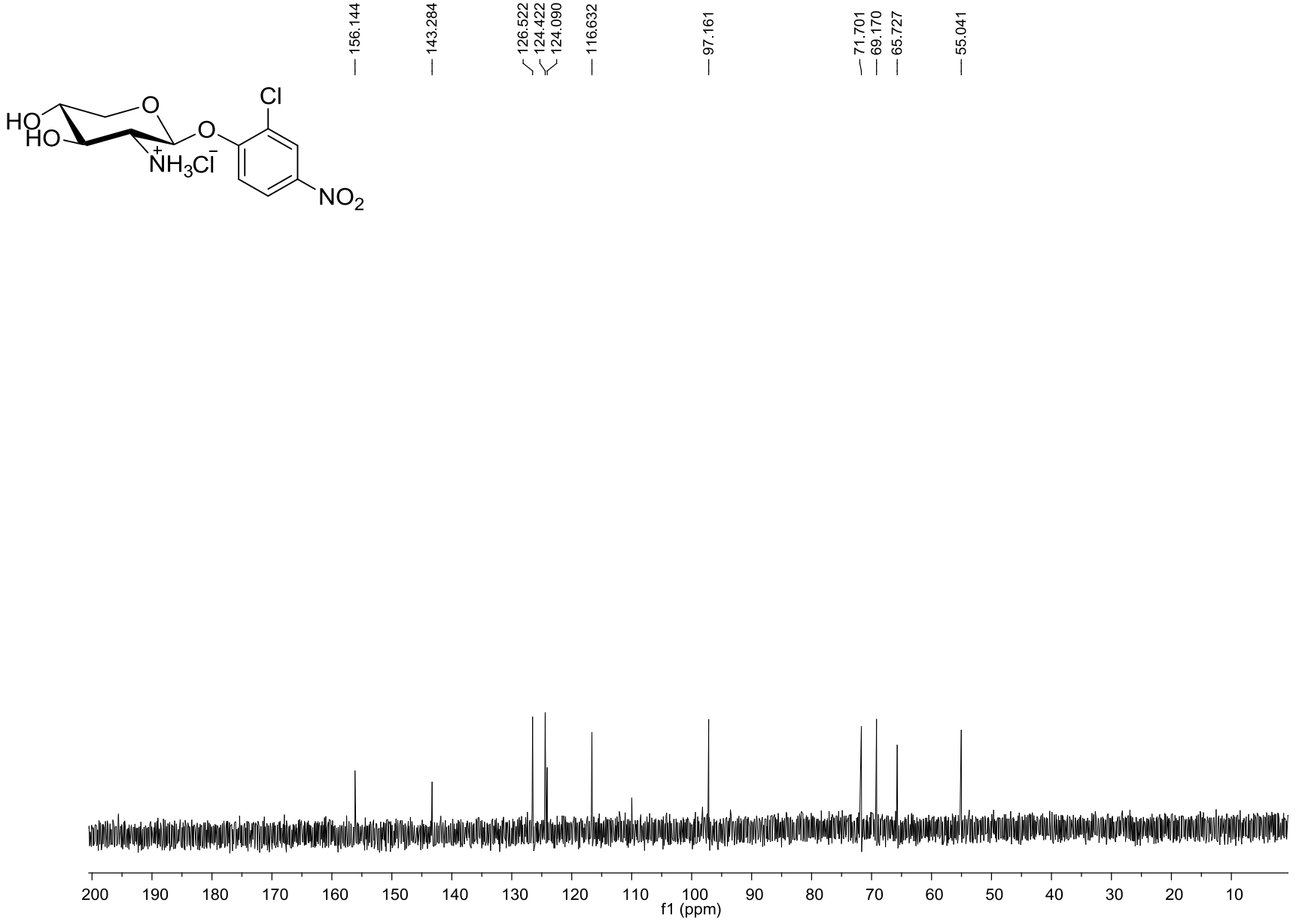


(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (**11a)**: gCOSY NMR (D_2O, 400 MHz)

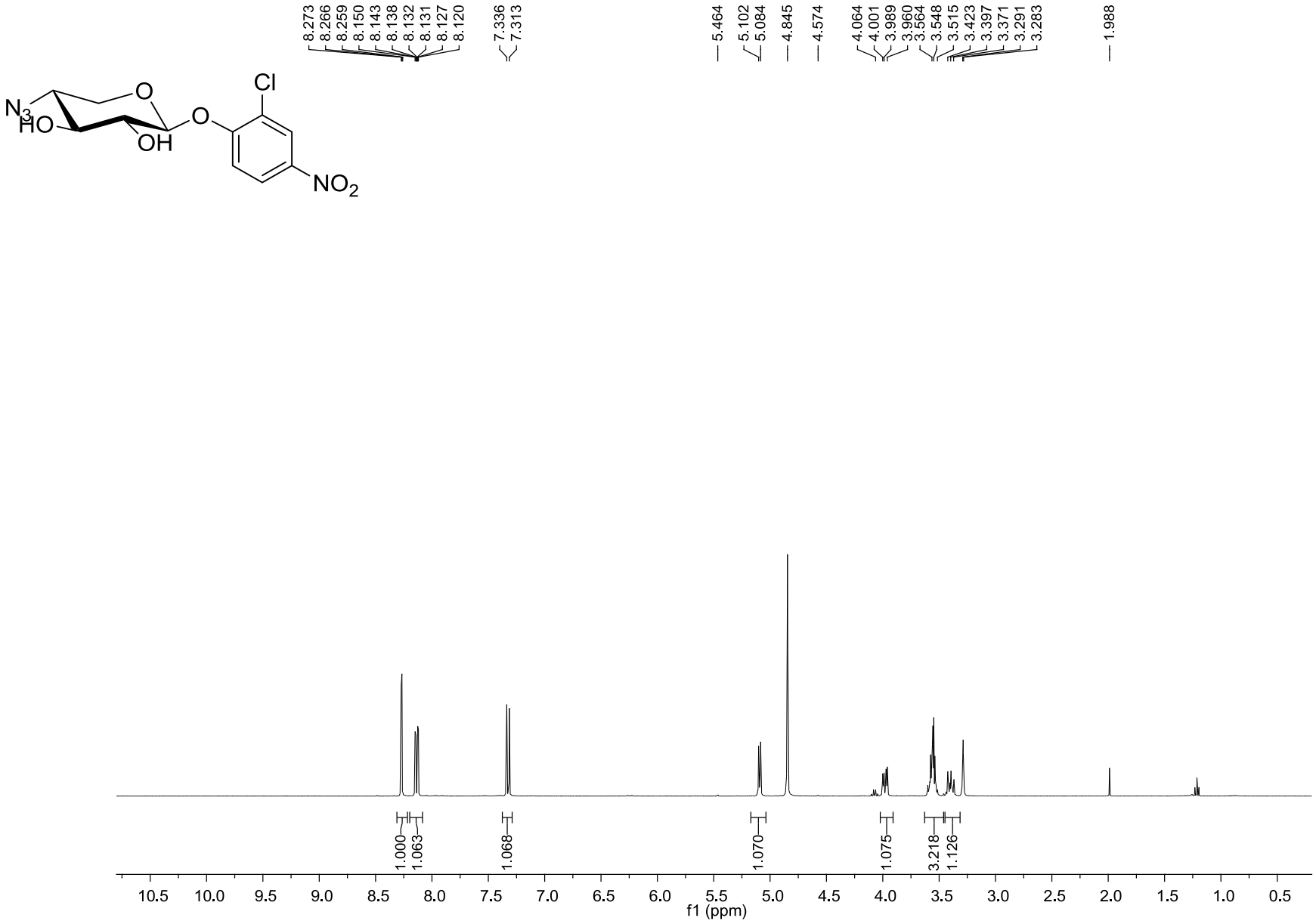




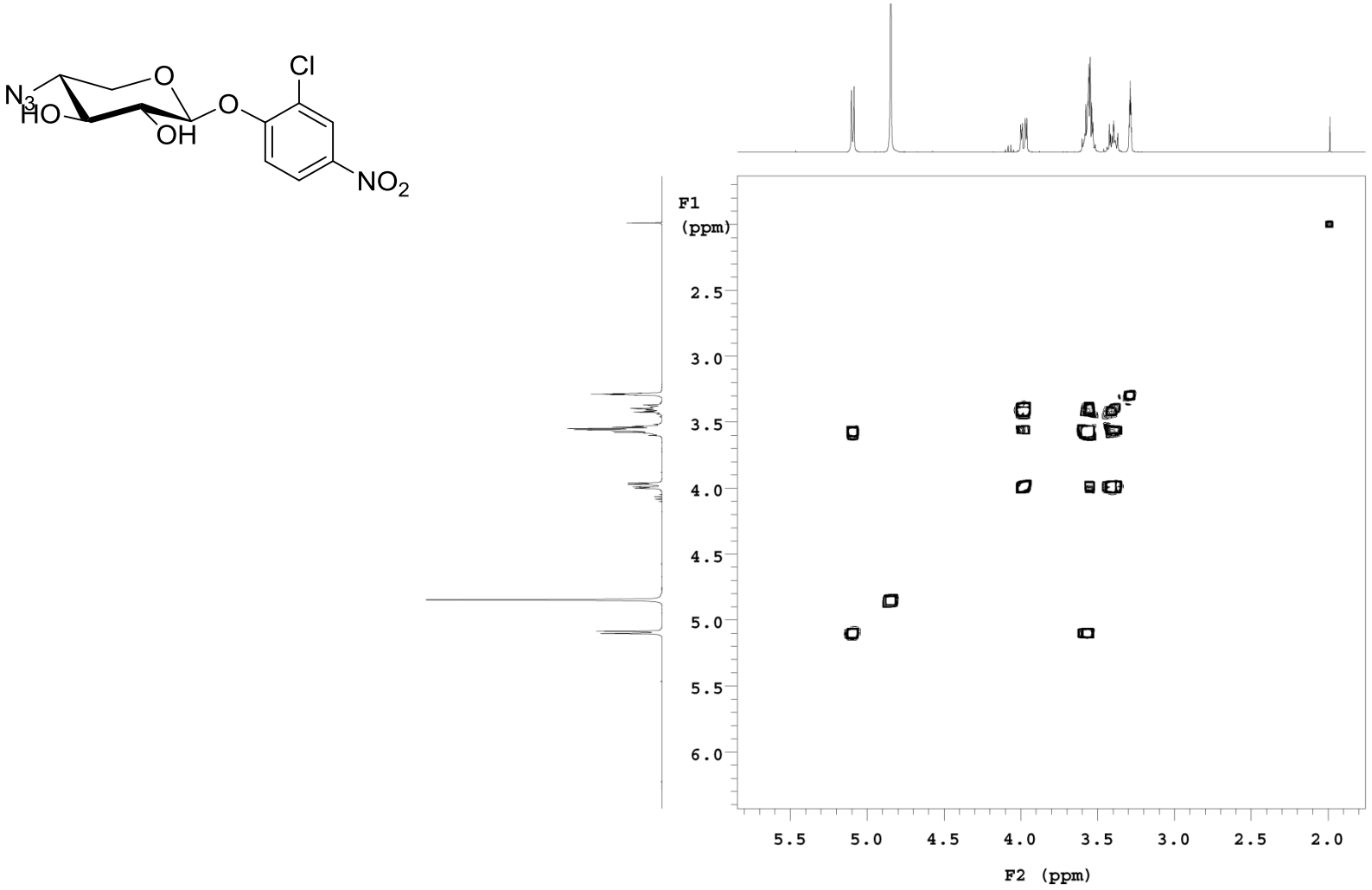
(2-chloro-4-nitrophenyl)-2-deoxy-2-amino-β-D-xylopyranoside hydrochloride (**11a)**: ^{13}C NMR (D_2O, 100 MHz)



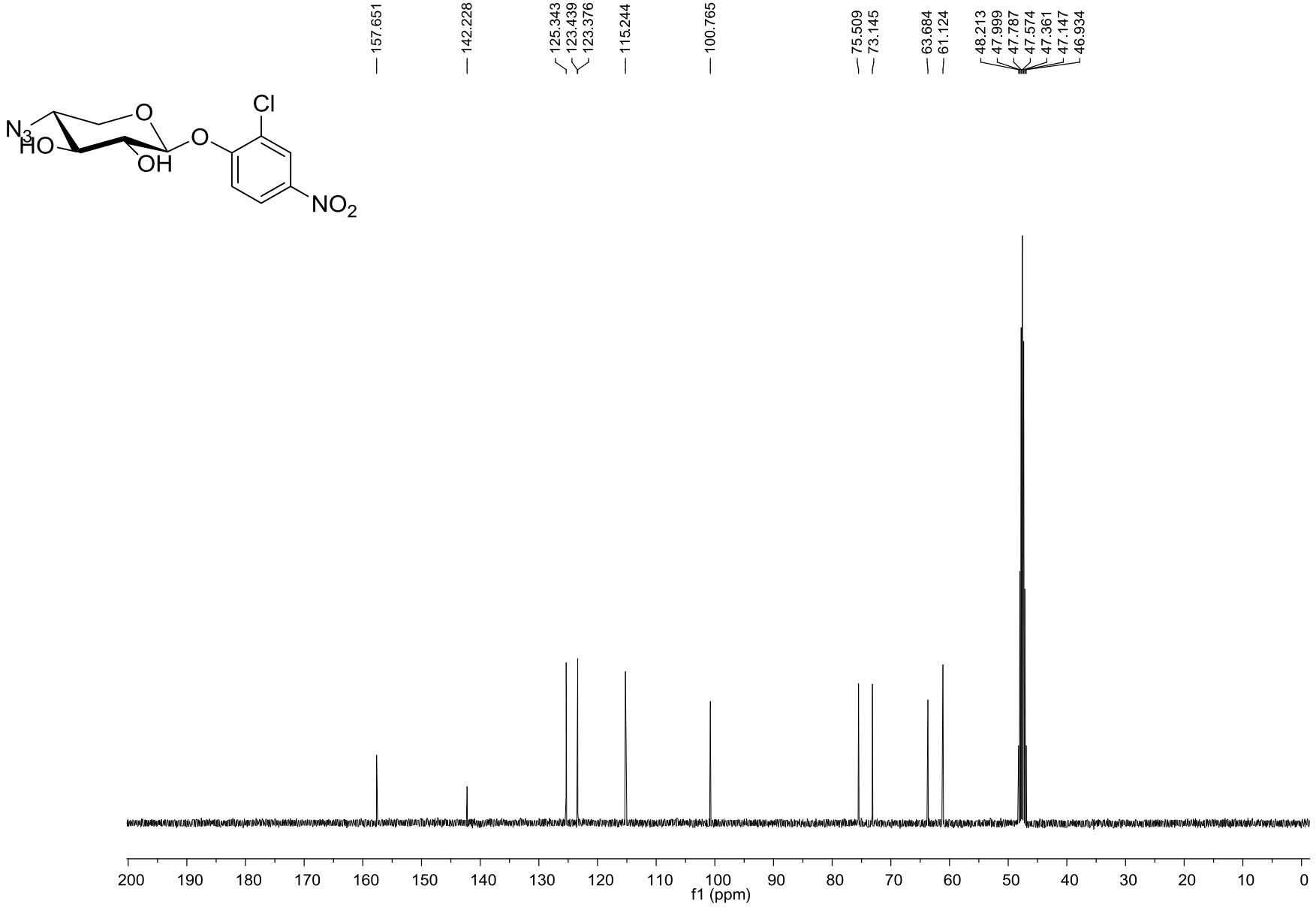
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (**12**): ^{1}H NMR (CD_3OD, 400 MHz)



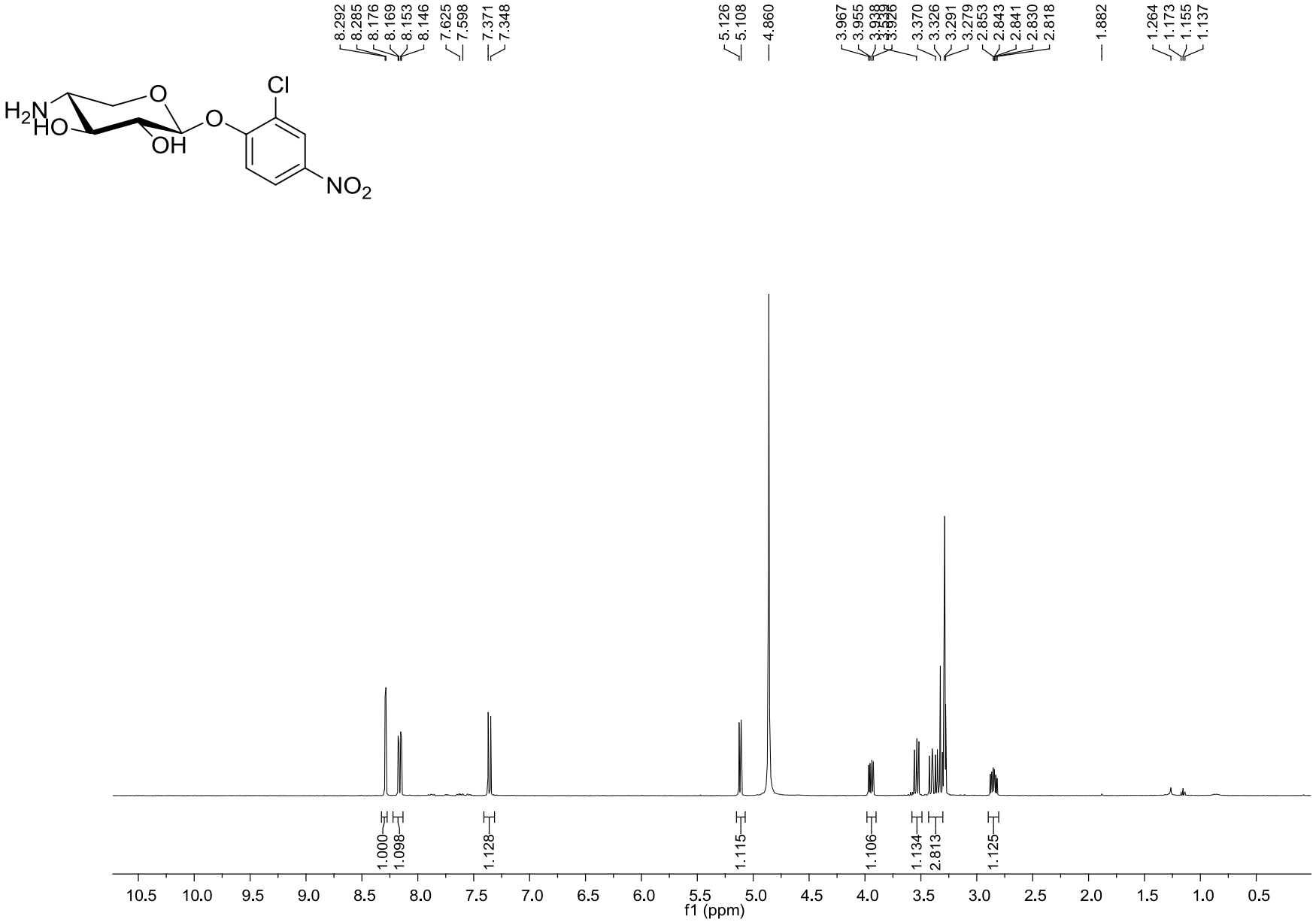
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (**12**): gCOSY NMR (CD_3OD, 400 MHz)



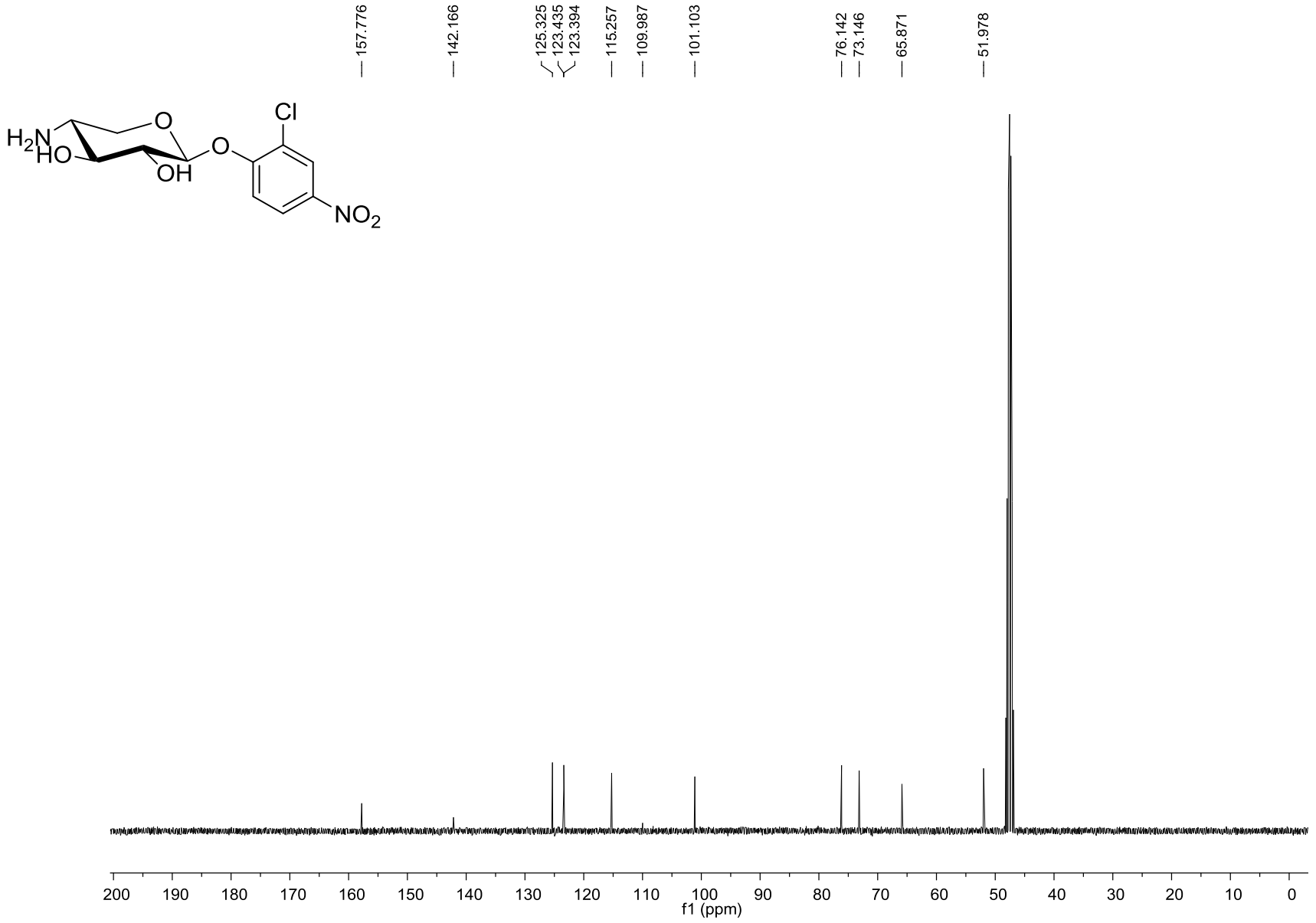
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-D-xylopyranoside (**12**): ^{13}C NMR (CD_3OD, 400 MHz)



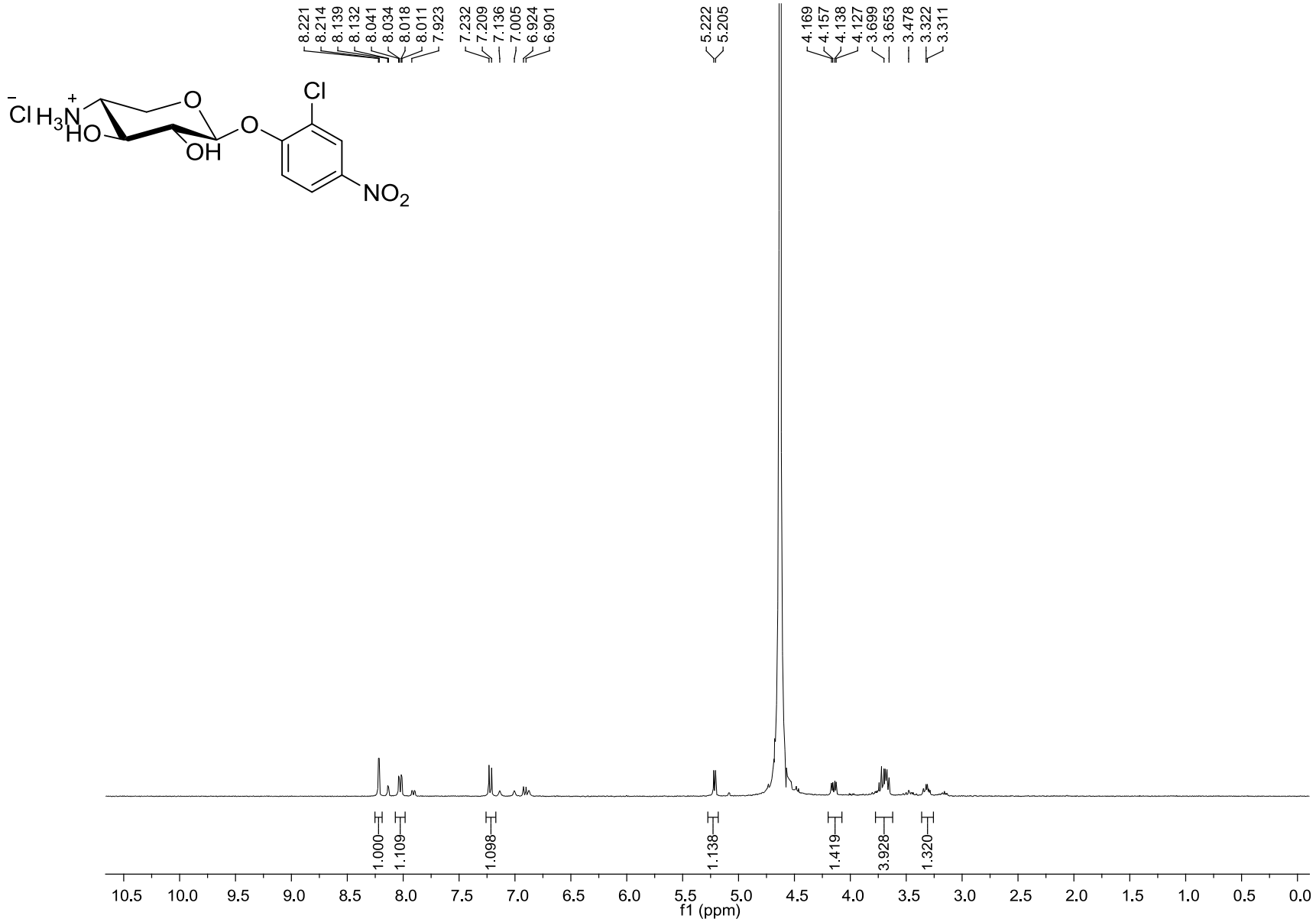
(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside (**13**): ^{1}H NMR (CD_3OD, 400 MHz)



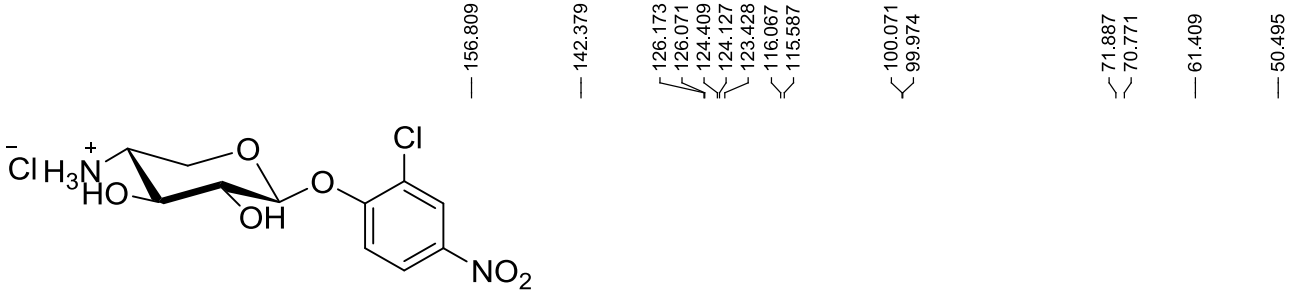
(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside (**13**): ^{13}C NMR (CD_3OD, 400 MHz)

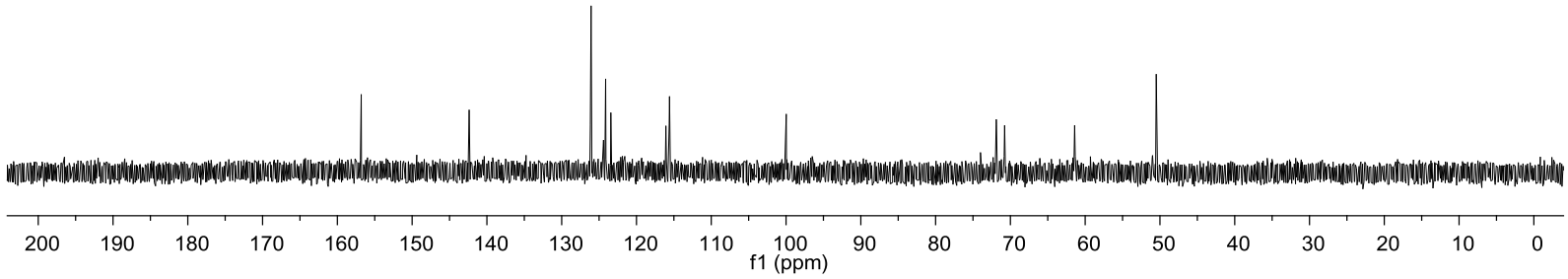


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside hydrochloride (**13a**): ^{1}H NMR (D_2O, 400 MHz)

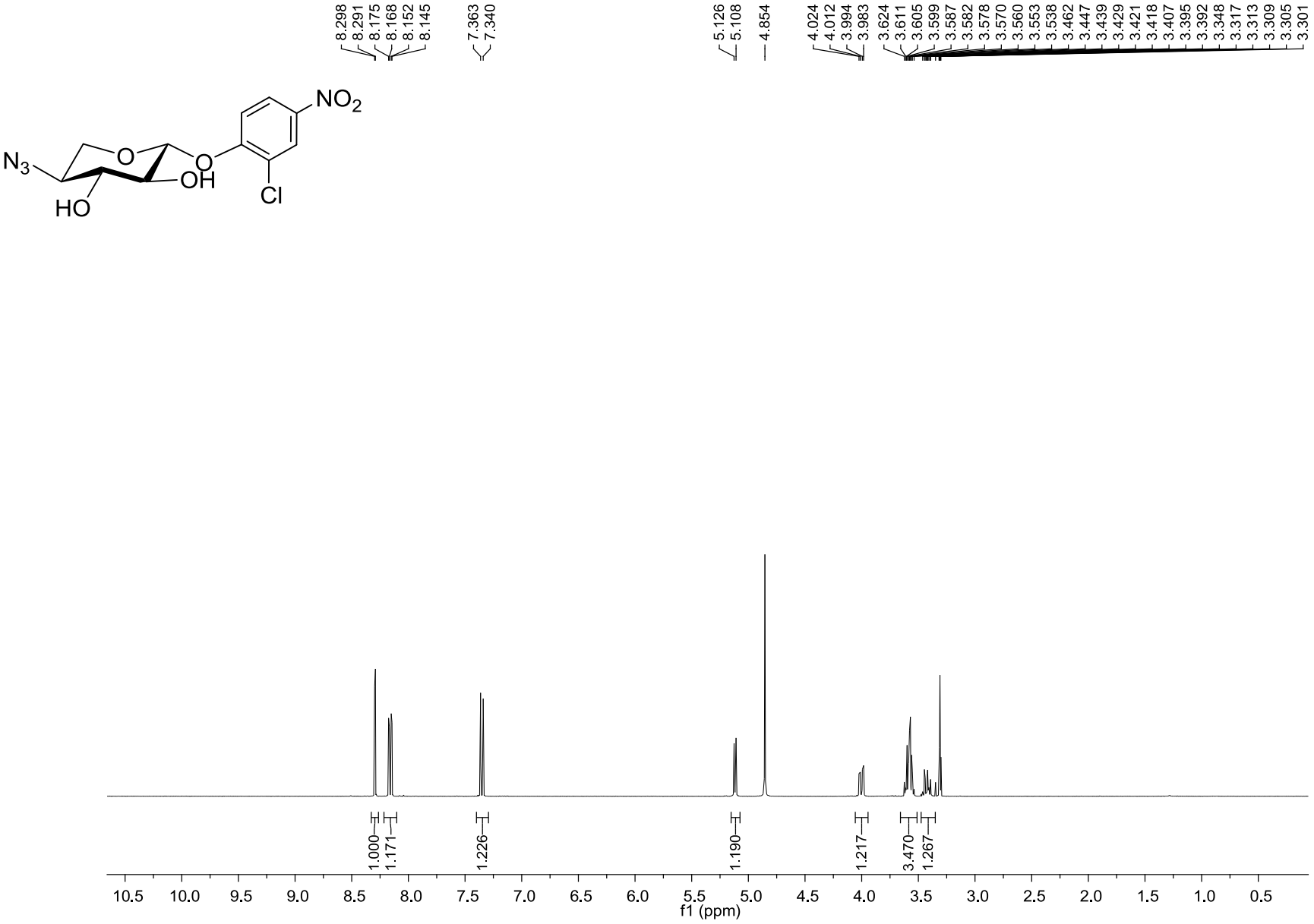


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-D-xylopyranoside hydrochloride (**13a**): ^{13}C NMR (D_2O, 100 MHz)

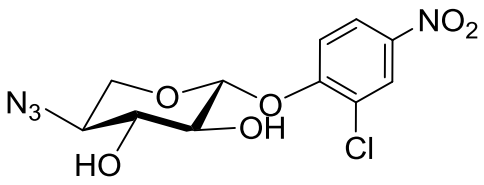


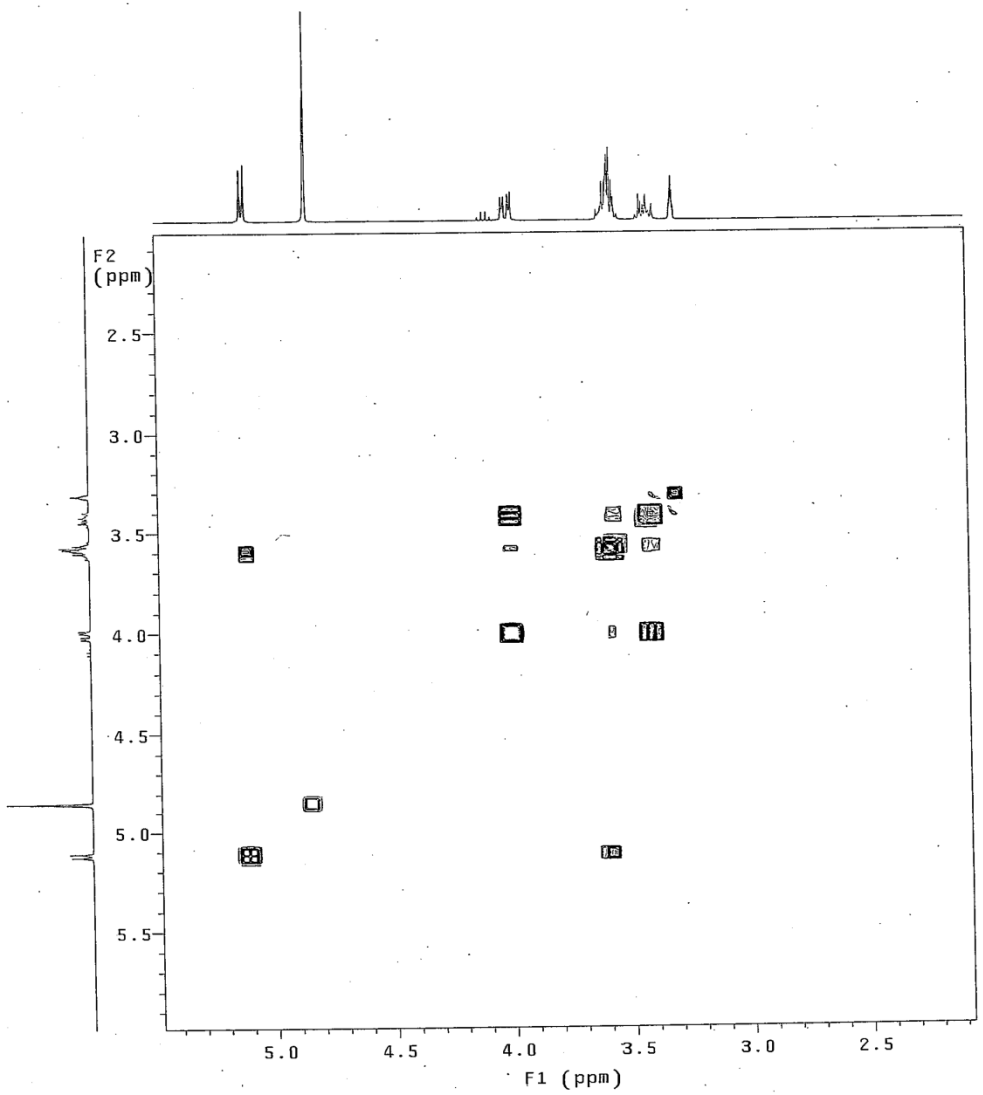


(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (**14**): ^{1}H NMR (CD_3OD, 400 MHz)

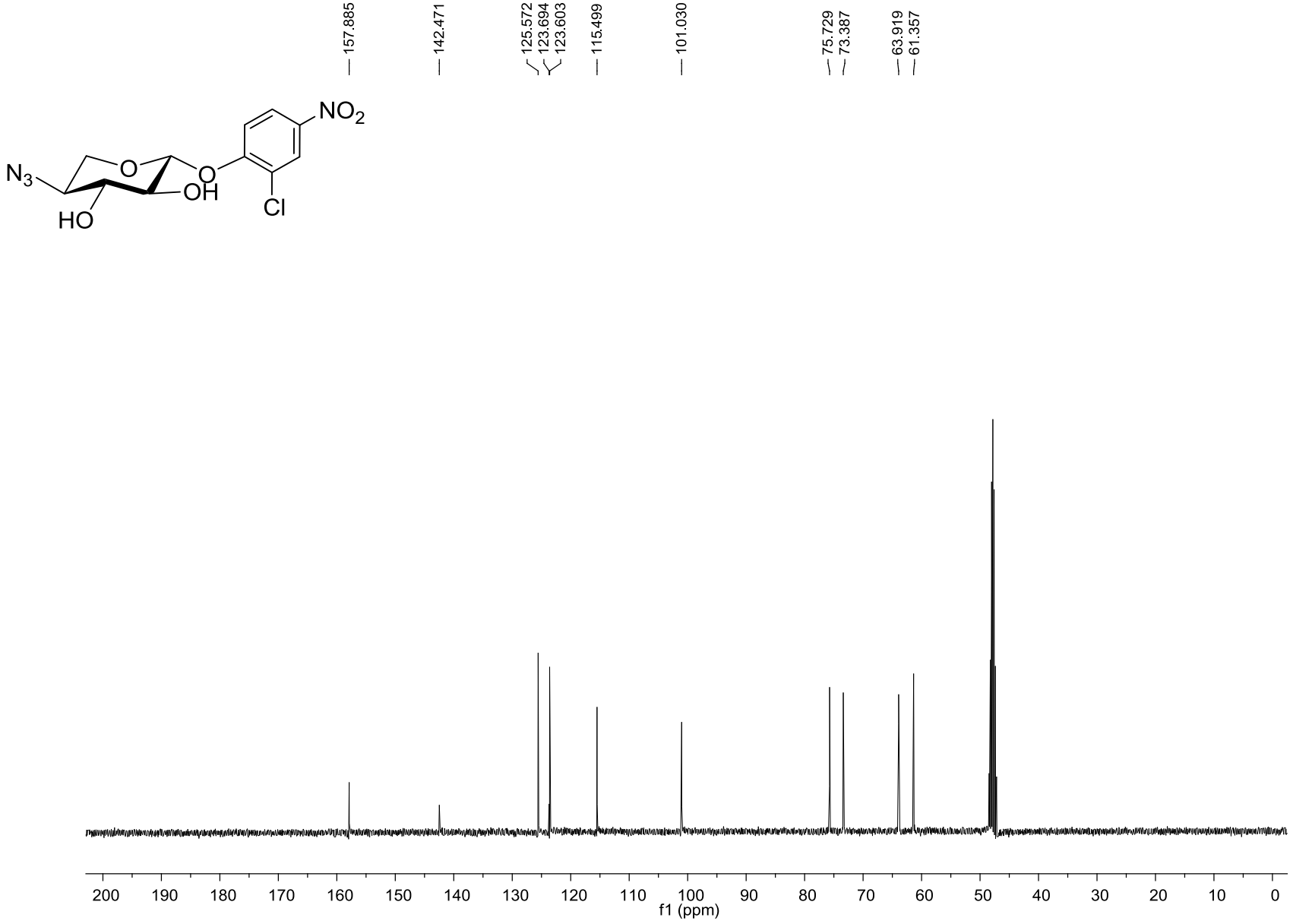


(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (**14**): gCOSY NMR (CD_3OD, 400 MHz)

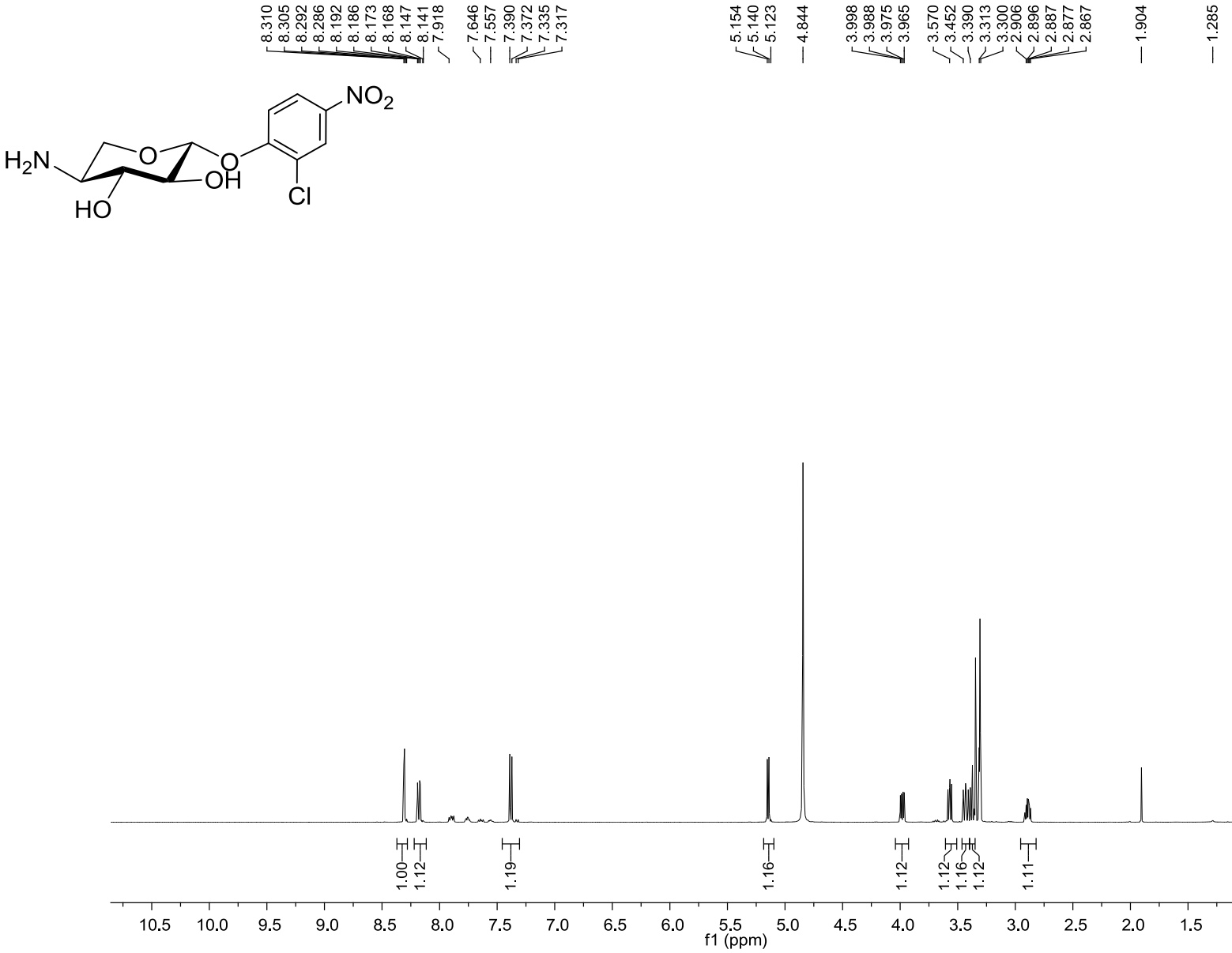




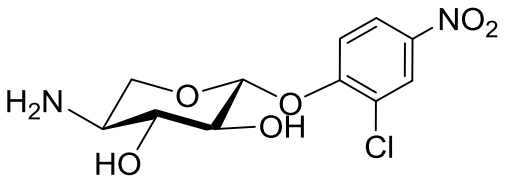
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-β-L-xylopyranoside (**14**): ^{13}C NMR (CD_3OD, 400 MHz)

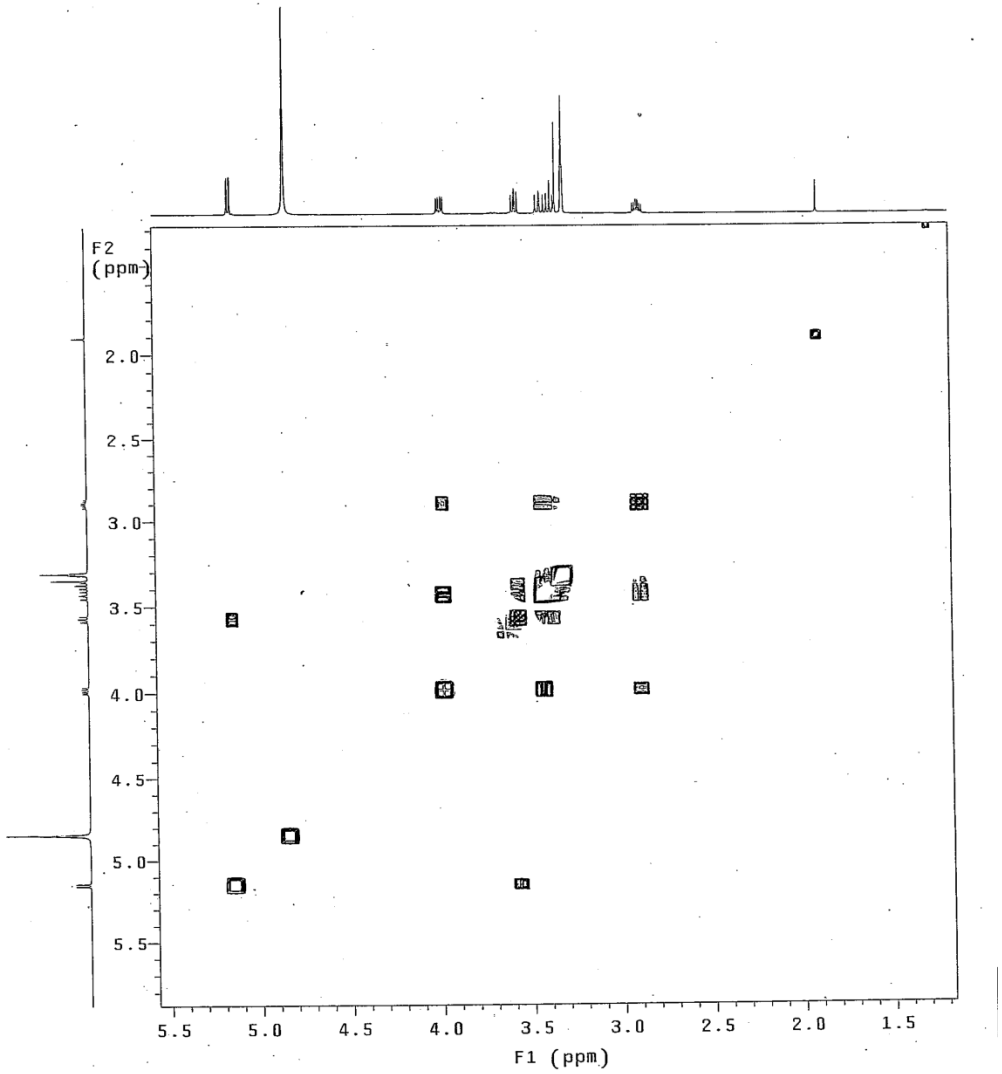


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (**15**): ^{1}H NMR (CD_3OD, 500 MHz)

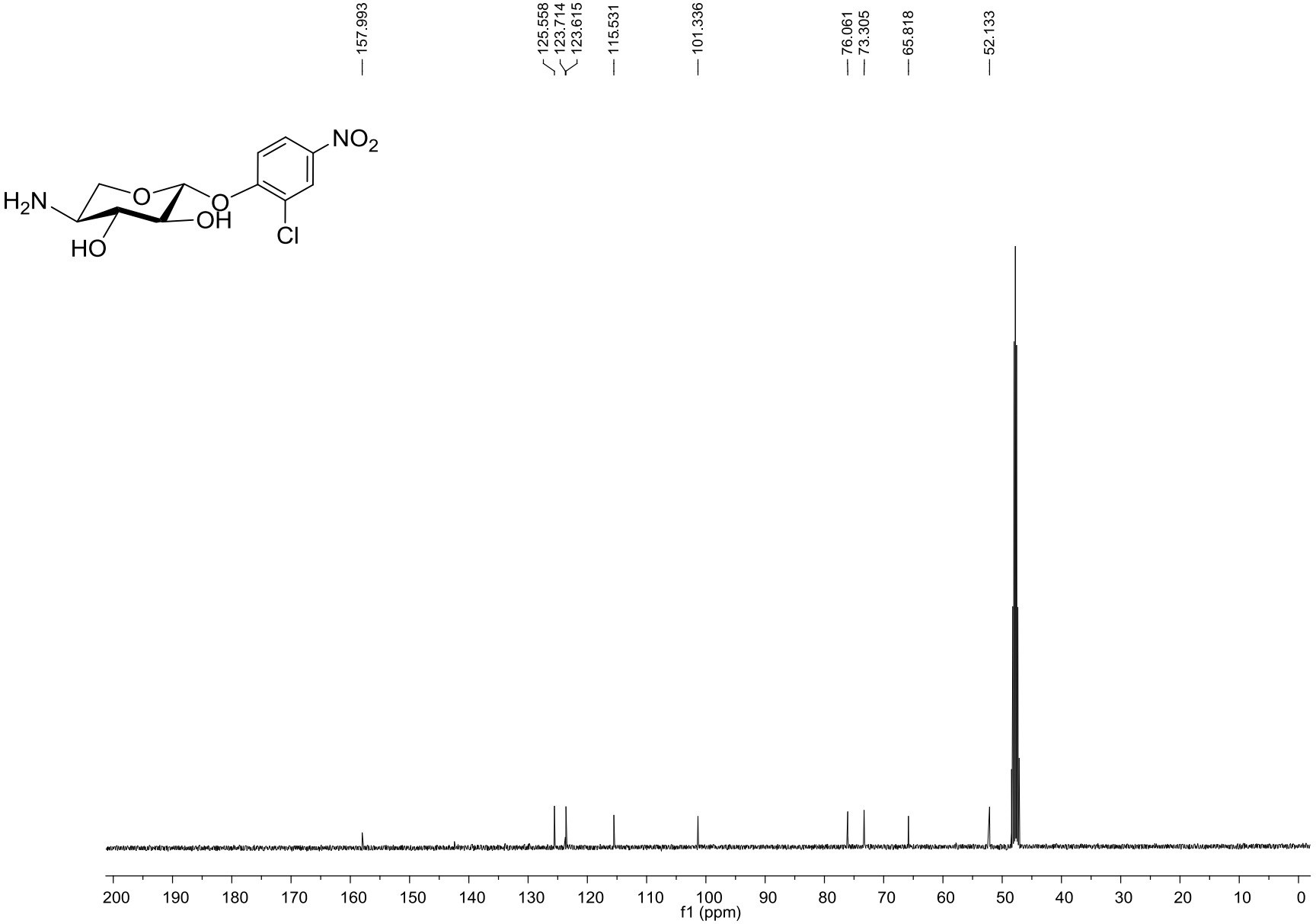


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (**15**): gCOSY NMR (CD_3OD, 500 MHz)

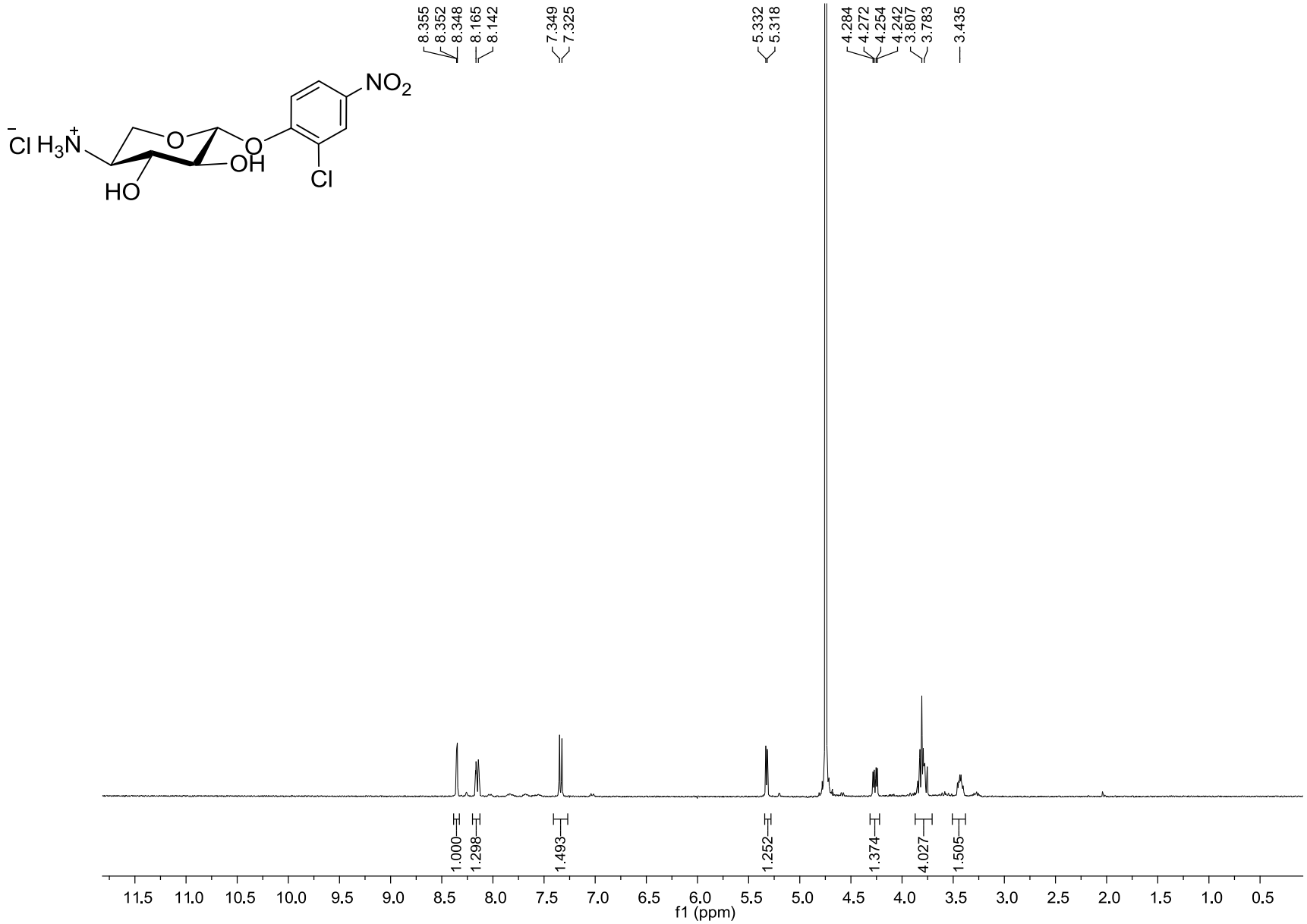




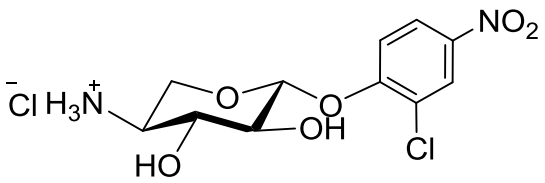
(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside (**15**): ^{13}C NMR (CD_3OD, 100 MHz)

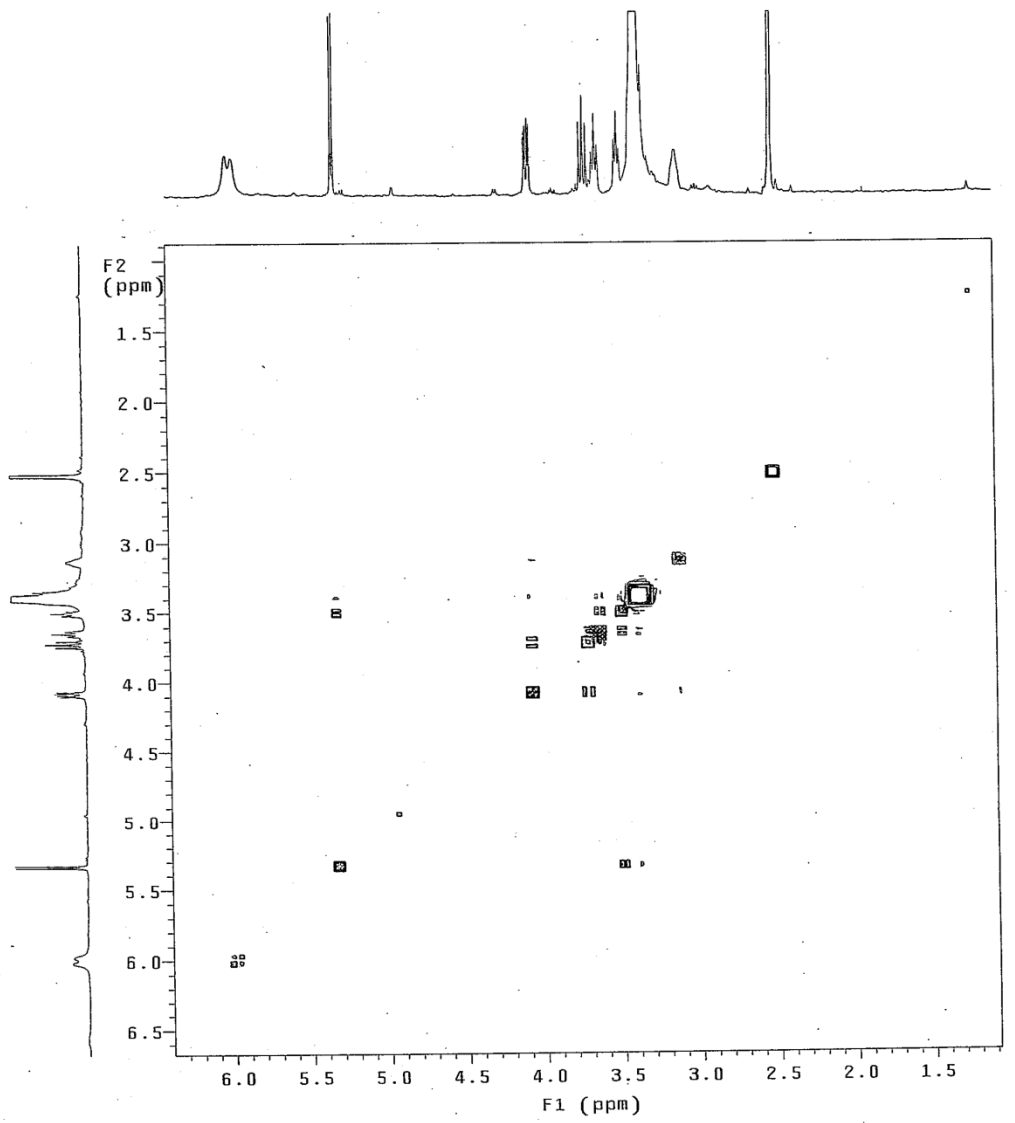


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (**15a**): ^{1}H NMR (D_2O, 400 MHz)

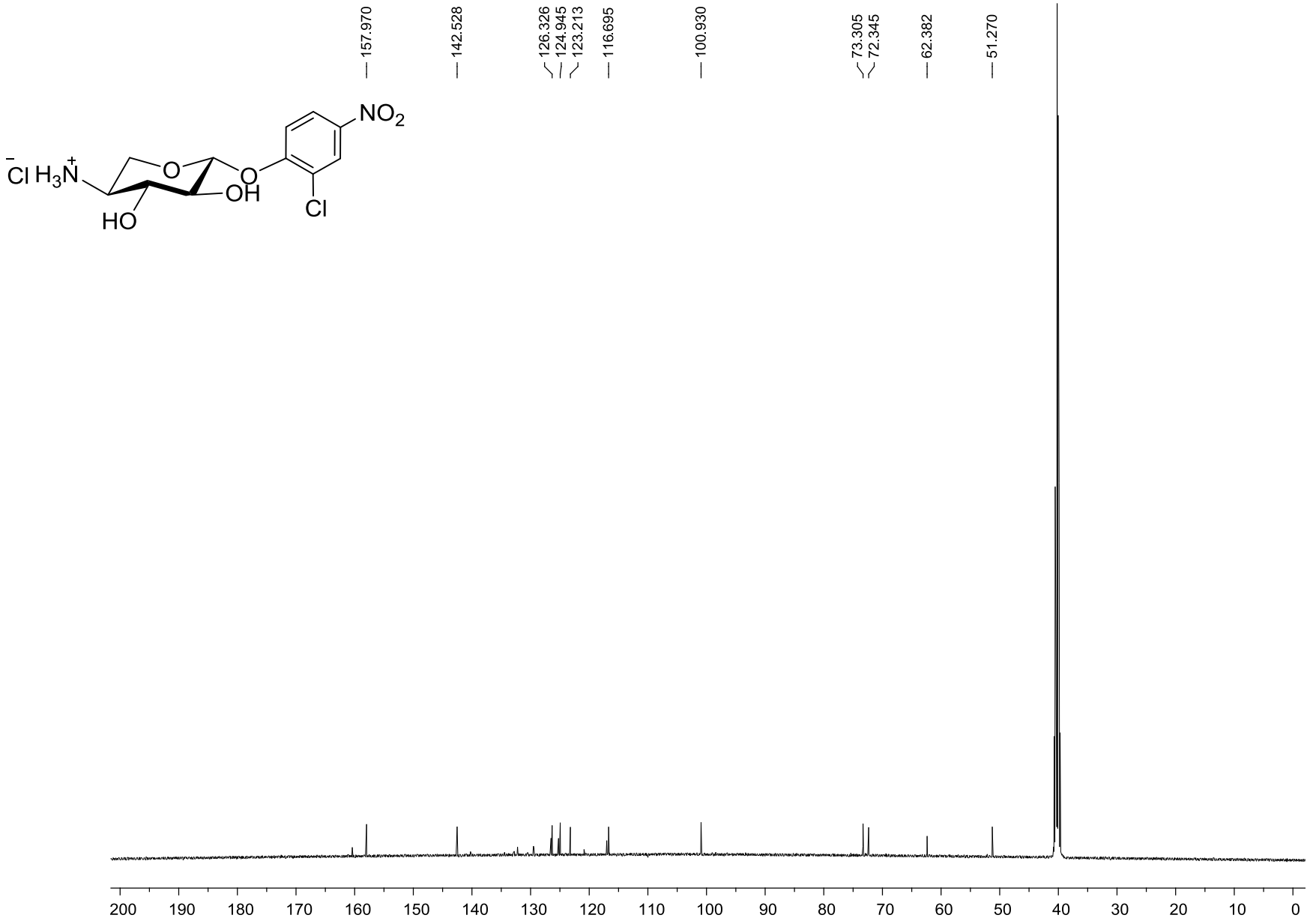


(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (**15a**): gCOSY NMR (DMSO-*d6*, 500 MHz)

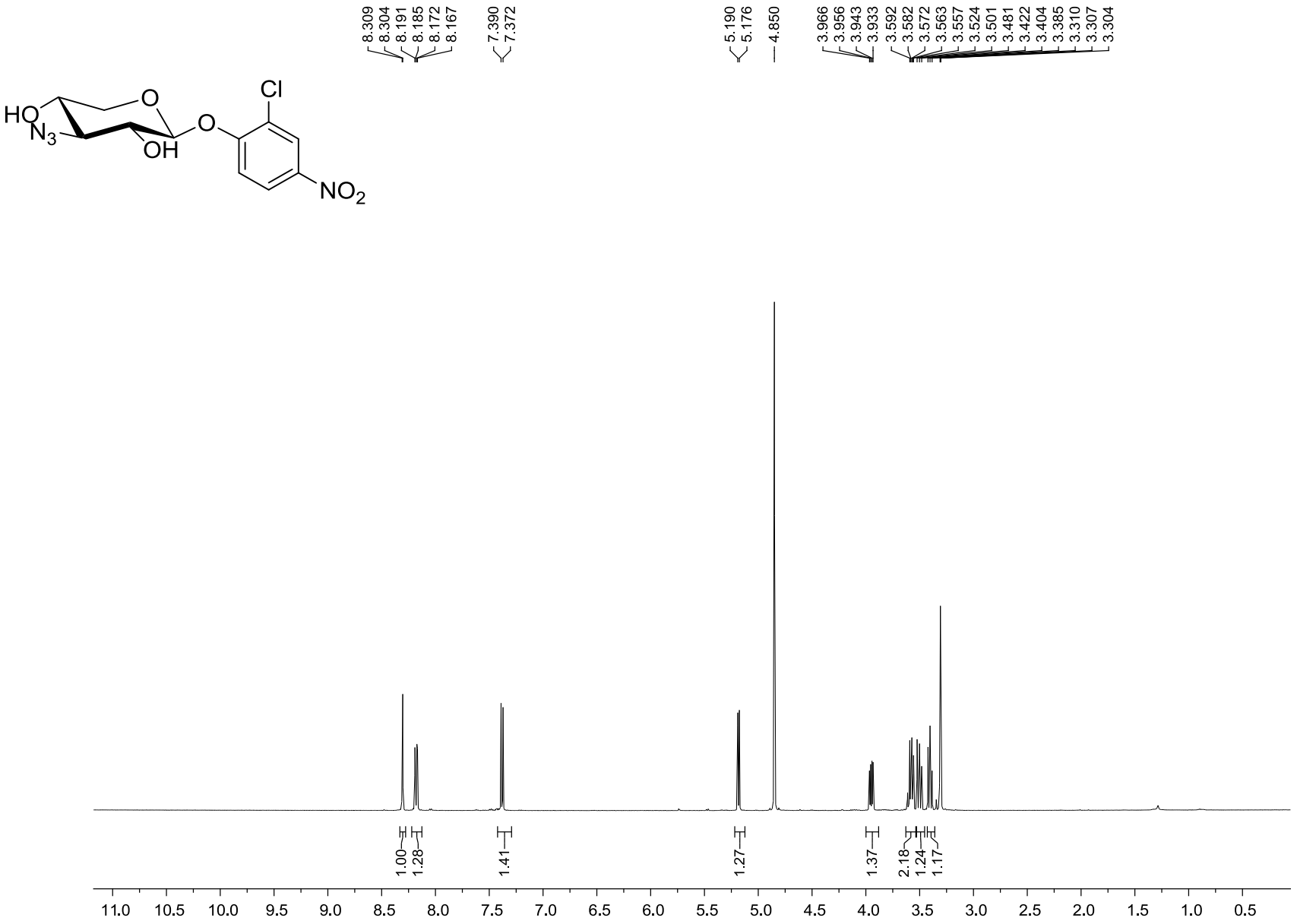




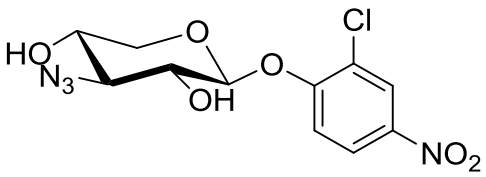
(2-chloro-4-nitrophenyl)-4-deoxy-4-amino-β-L-xylopyranoside hydrochloride (**15a**): ^{13}C NMR (DMSO-*d6*, 500 MHz)

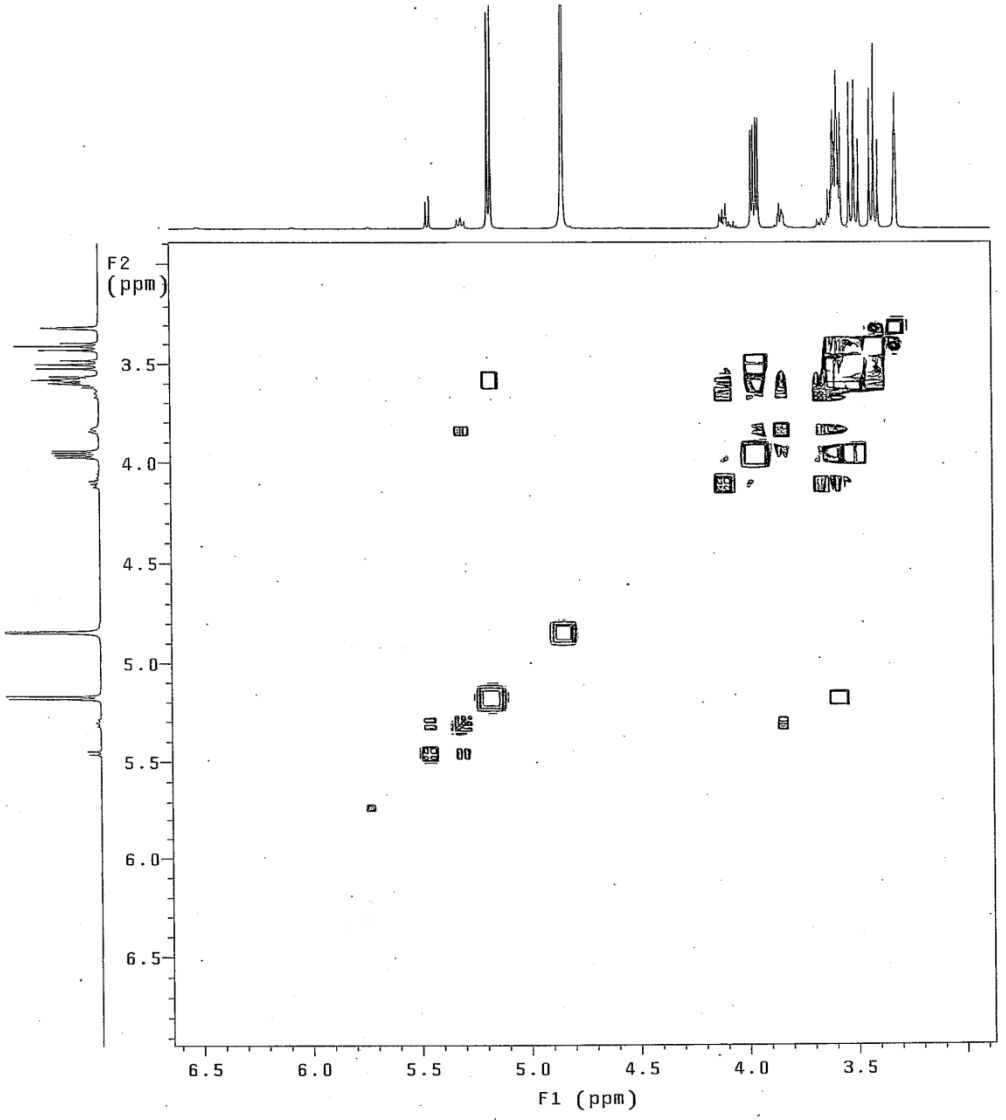


(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-xylopyranoside (**16**): ^{1}H NMR (CD_3OD, 500 MHz)

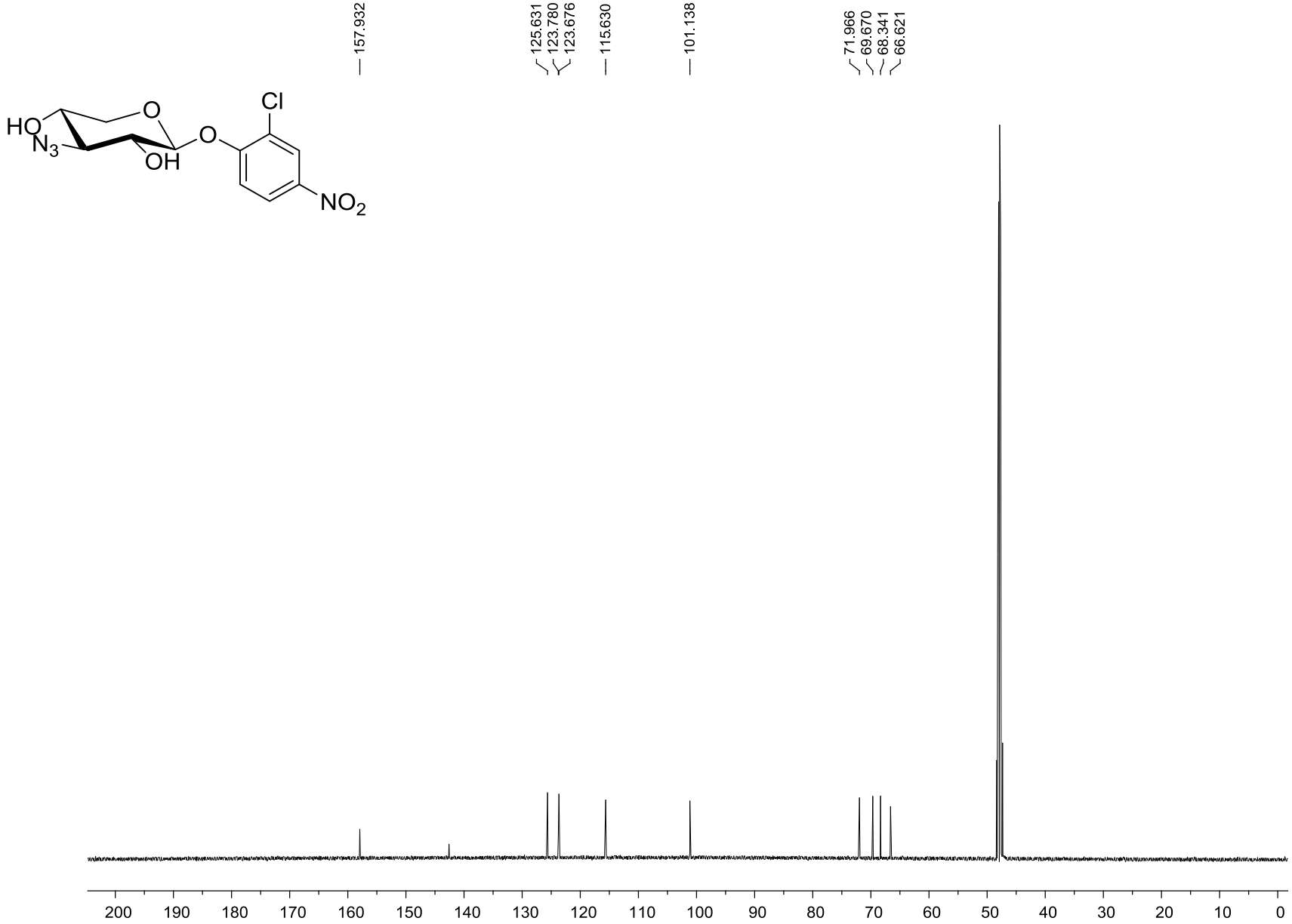


(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-xylopyranoside (**16**): gCOSY NMR (CD_3OD, 500 MHz)

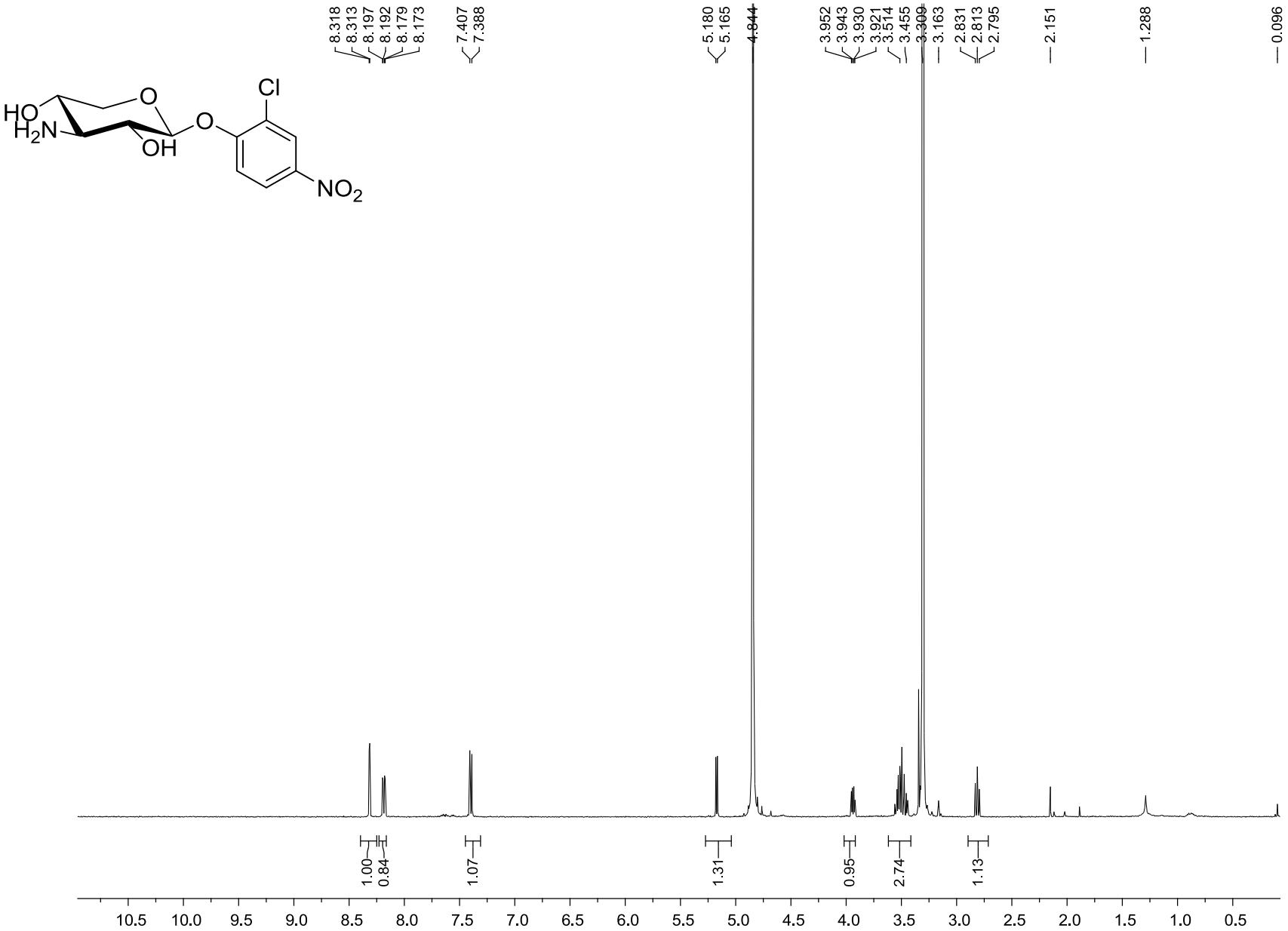




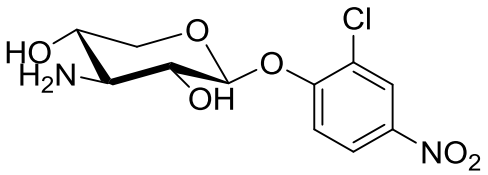
(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-β-D-xylopyranoside (**16**): ^{13}C NMR (CD_3OD, 125 MHz)

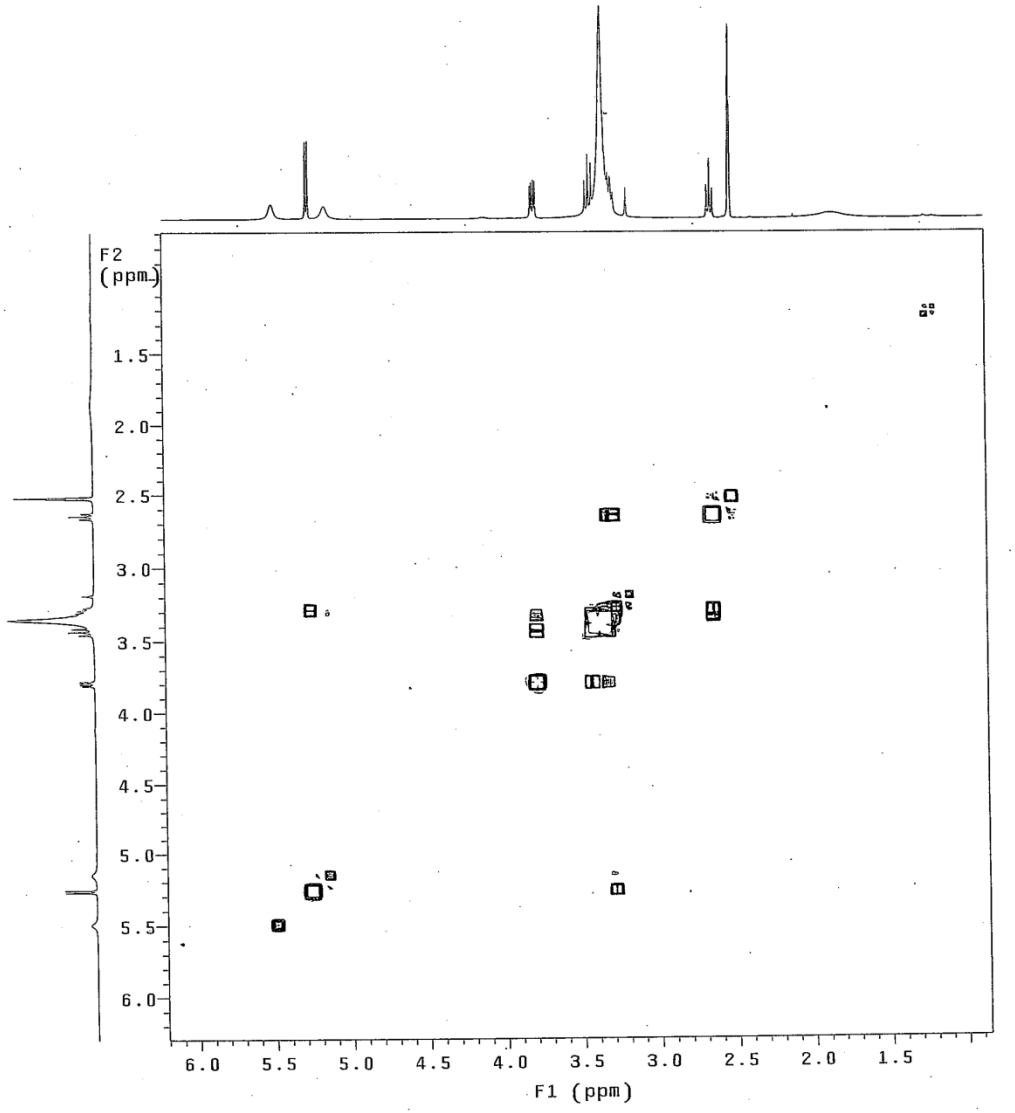


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (**17**): ^{1}H NMR (CD_3OD, 500 MHz)

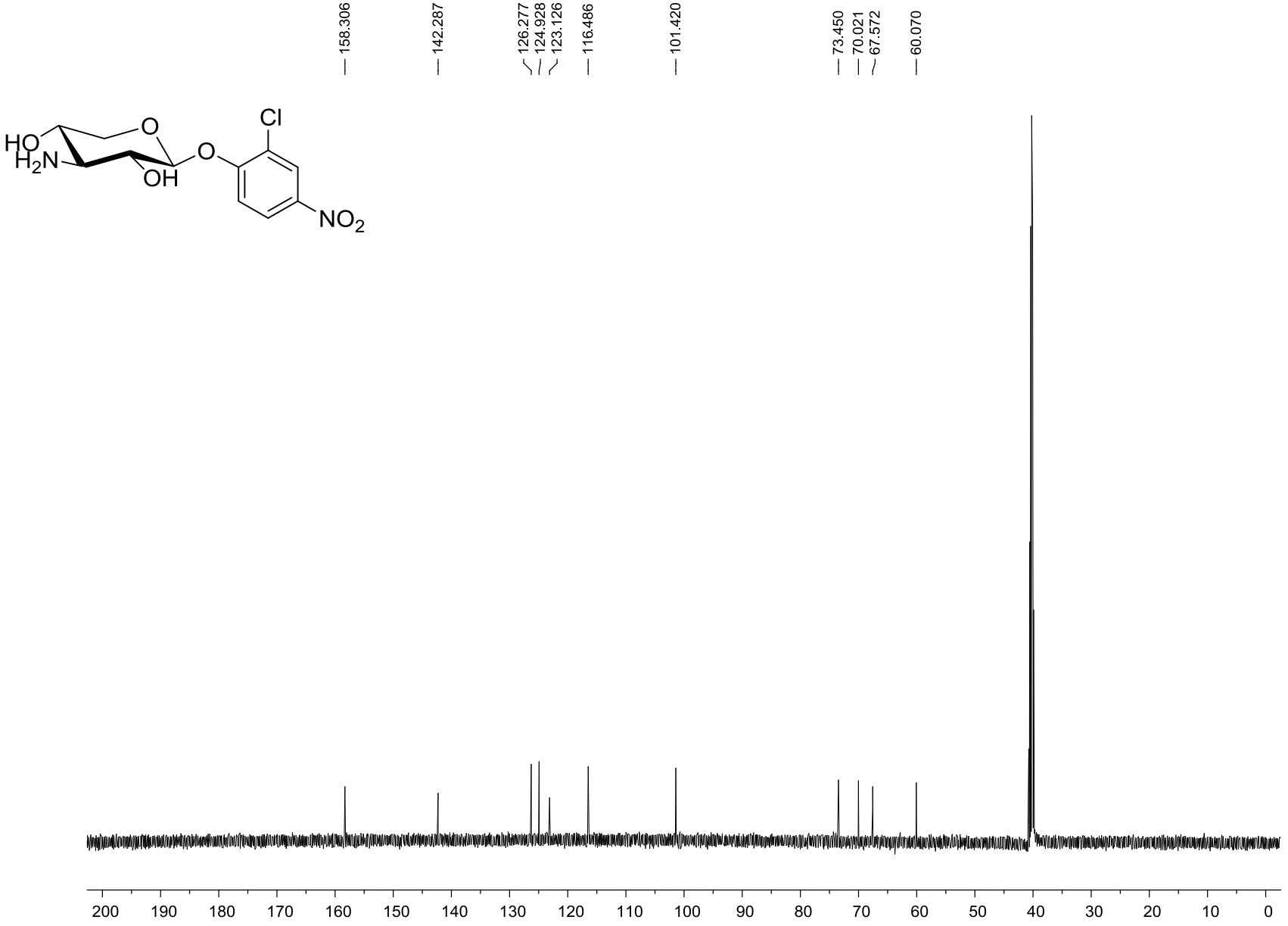


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (**17**): gCOSY NMR (DMSO-*d6*, 500 MHz)

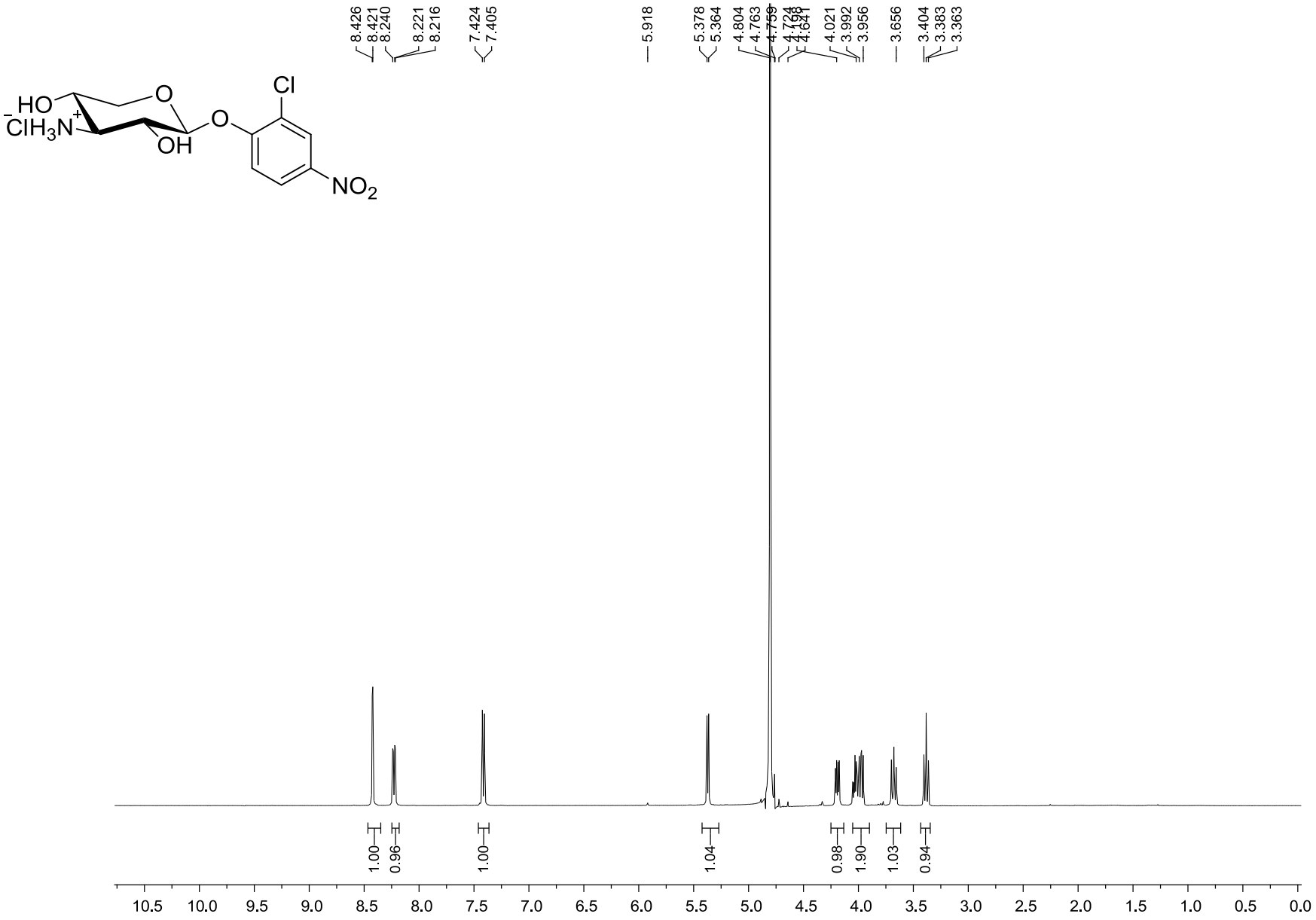




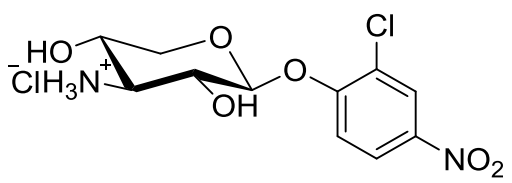
(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside (**17**): ^{13}C NMR (DMSO-*d6*, 500 MHz)

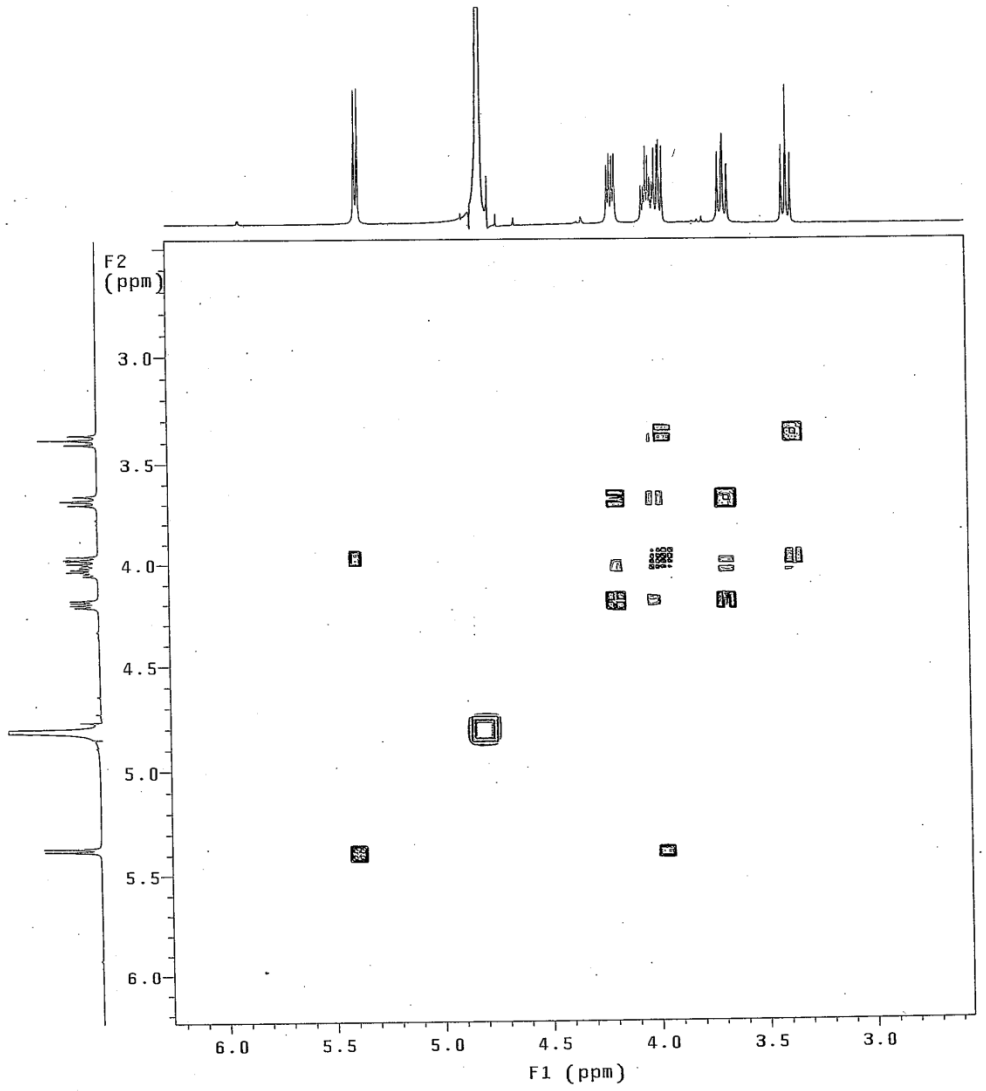


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (**17a**): ^{1}H NMR (D_2O, 500 MHz)

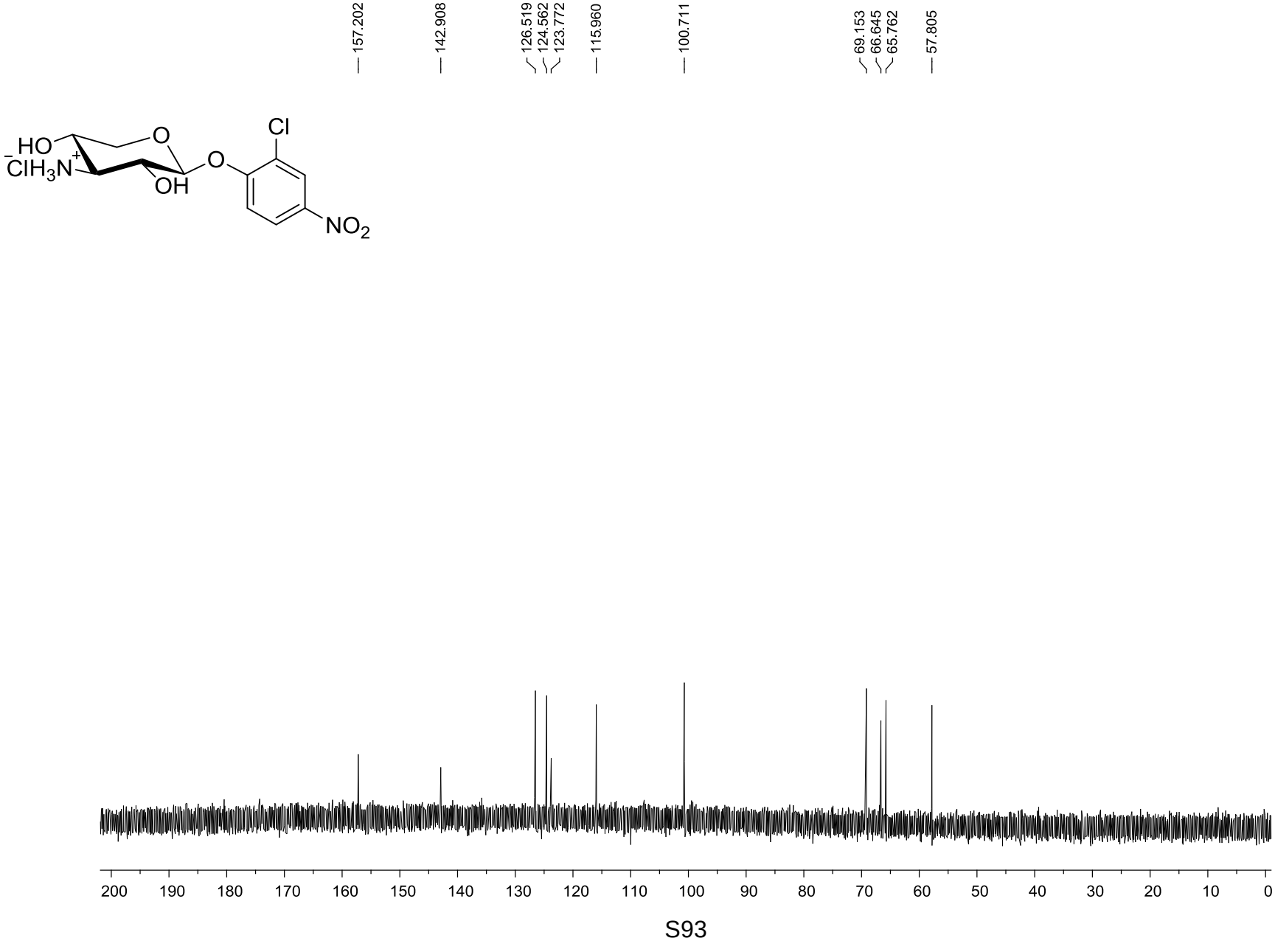


(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (**17a**): gCOSY NMR (D_2O, 500 MHz)

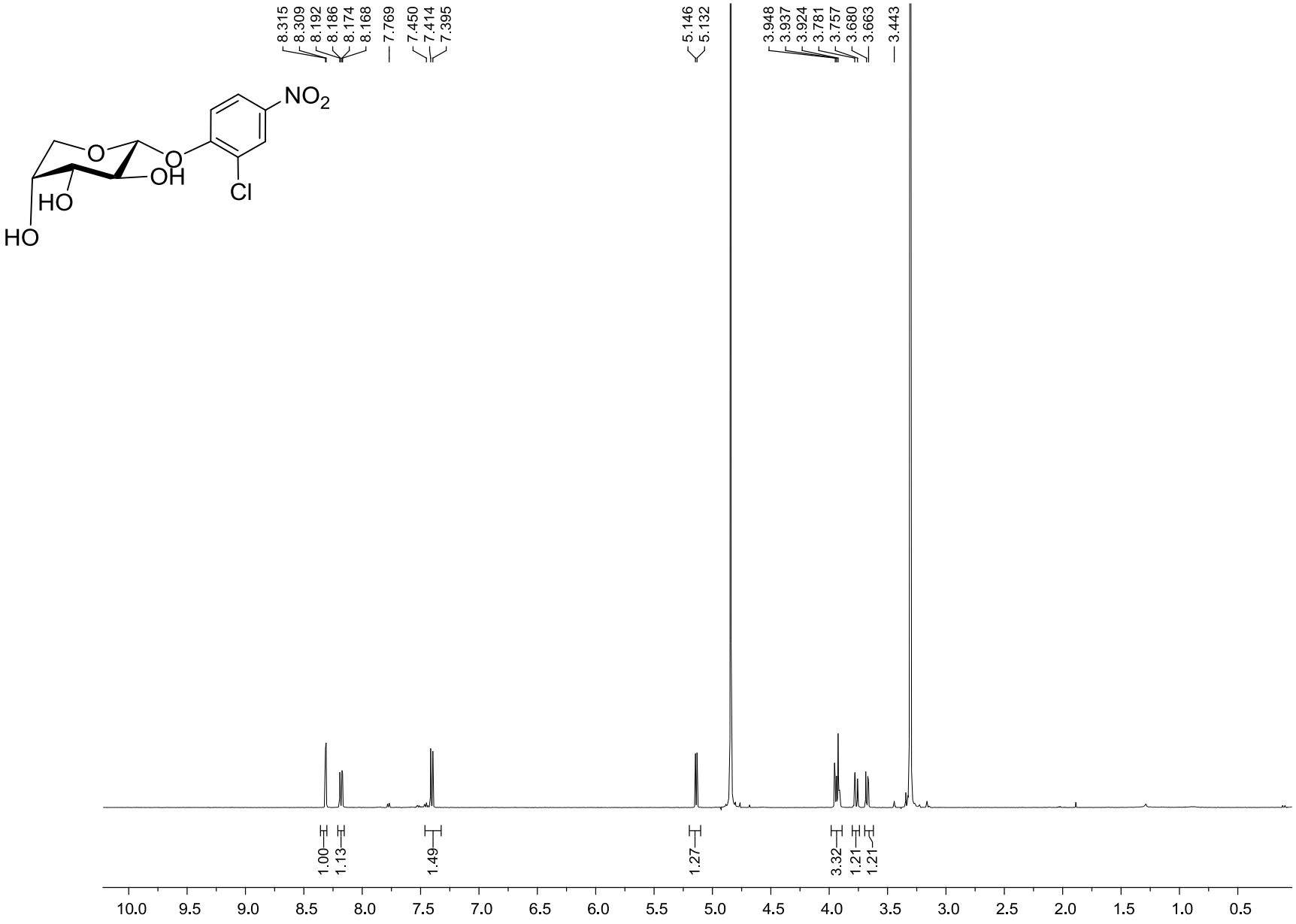




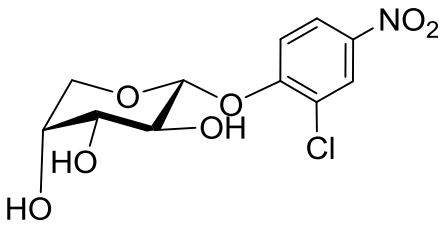
(2-chloro-4-nitrophenyl)-3-deoxy-3-amino-β-D-xylopyranoside hydrochloride (**17a**): ^{13}C NMR (D_2O, 125 MHz)

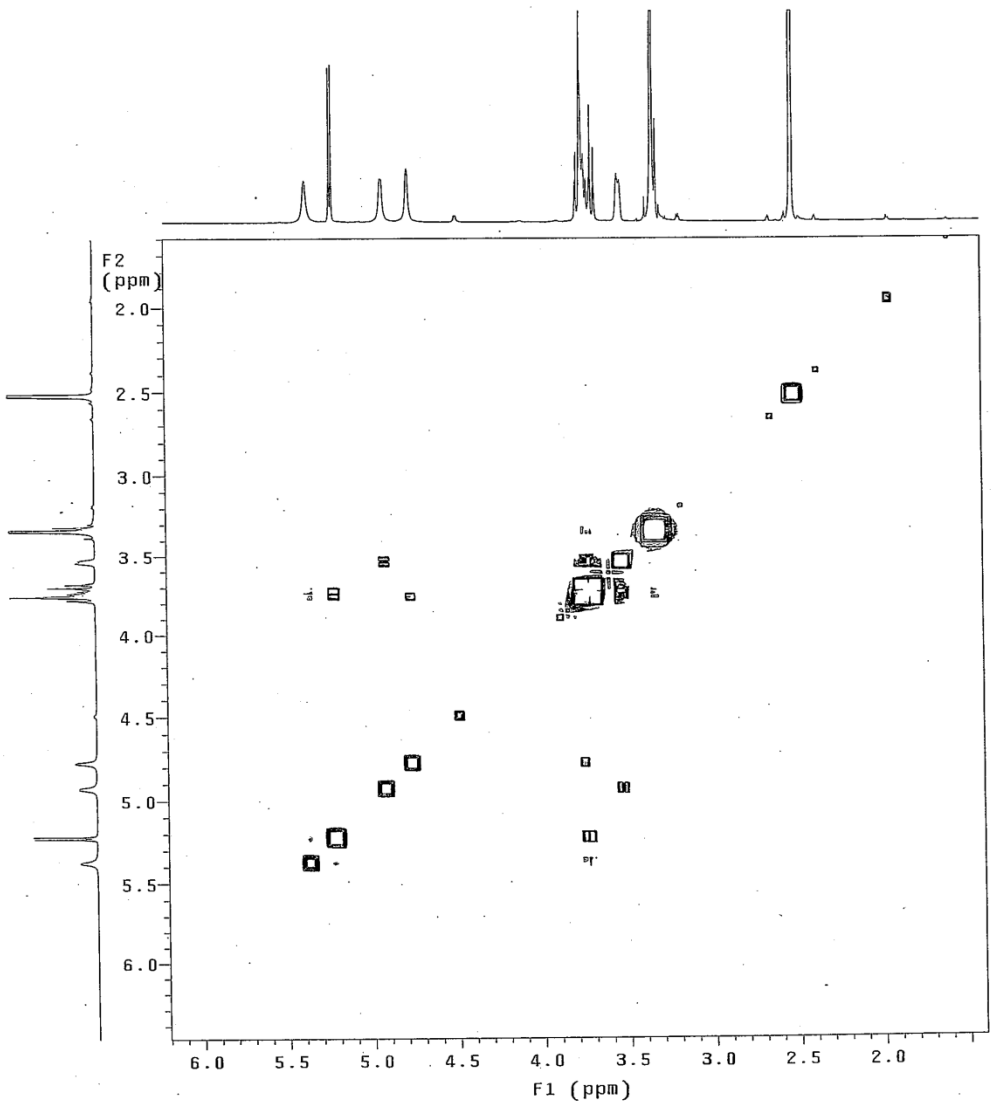


(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (**18d**): ^{1}H NMR (CD_3OD, 500 MHz)

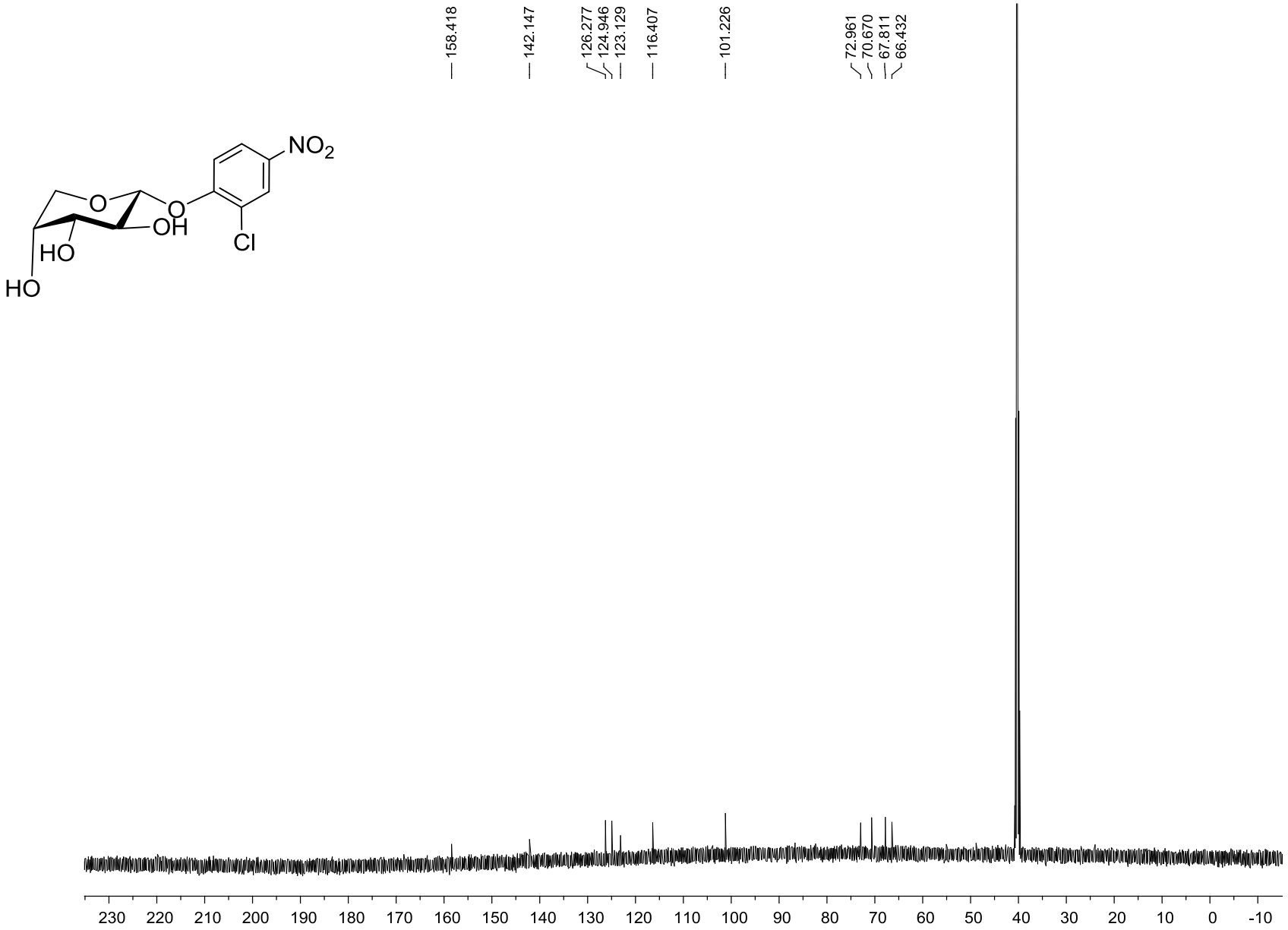


(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (**18d**): gCOSY NMR (DMSO-*d6*, 500 MHz)

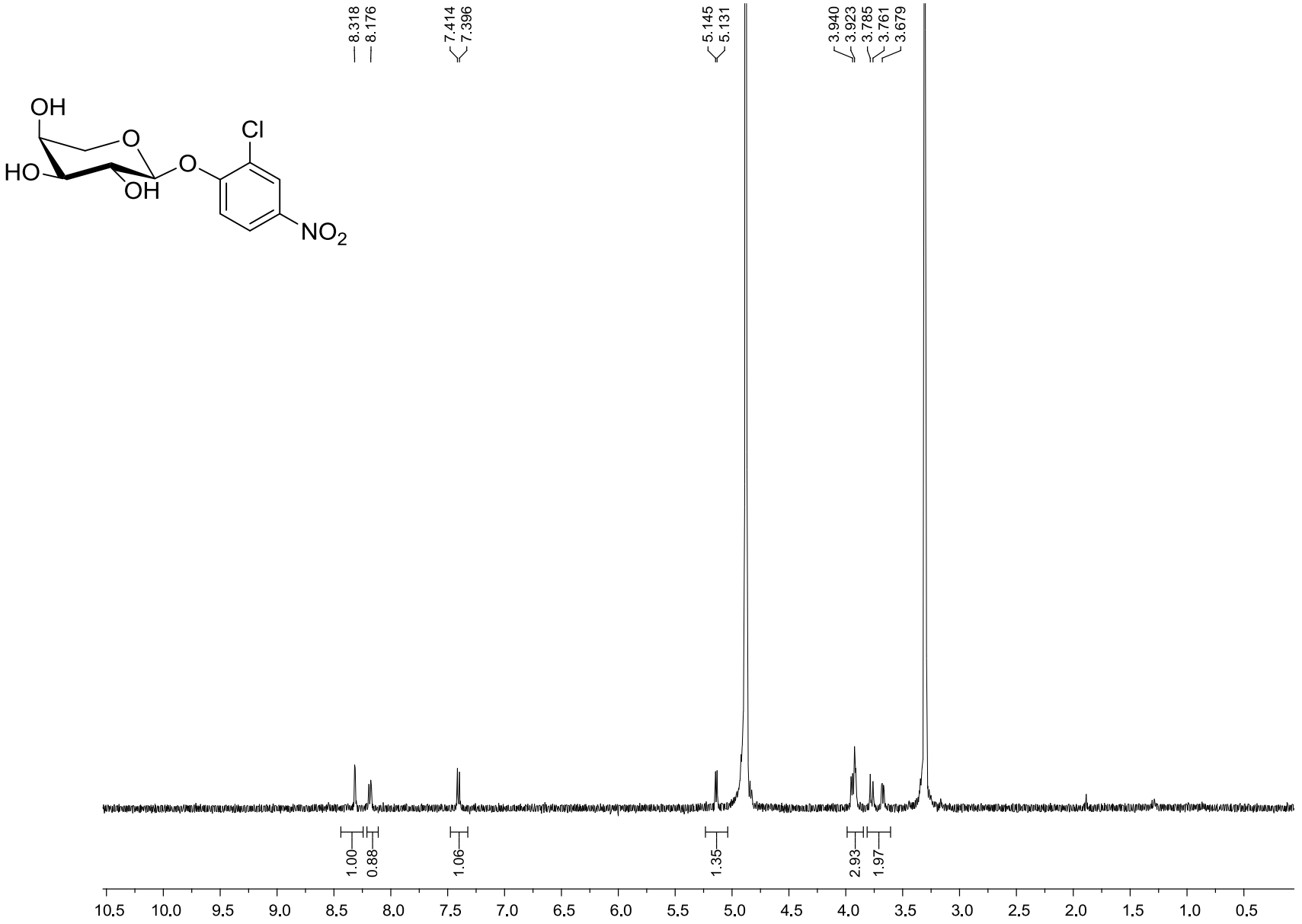




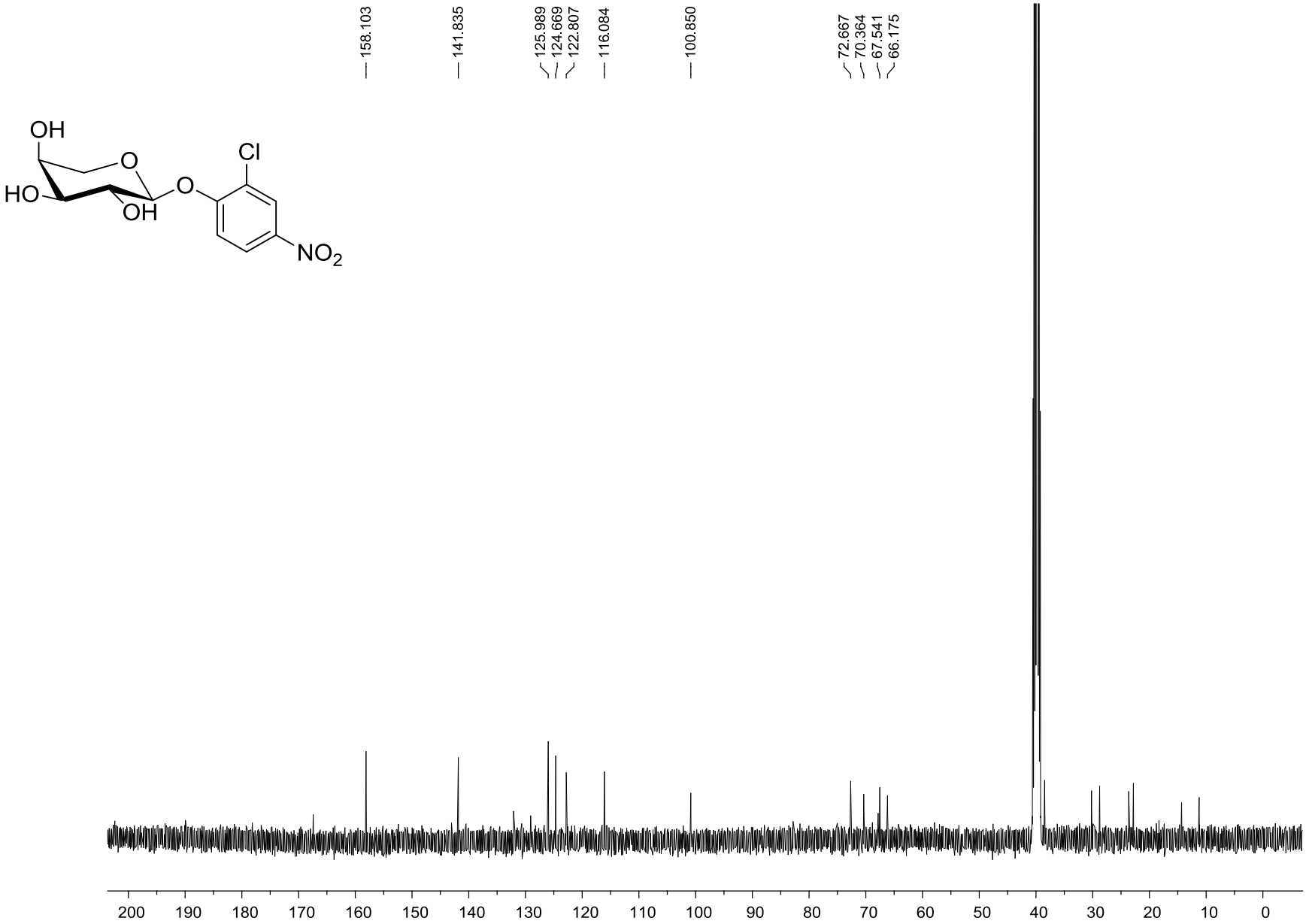
(2-chloro-4-nitrophenyl)-β-D-arabinopyranoside (**18d**): ^{13}C NMR (DMSO-*d6*, 500 MHz)



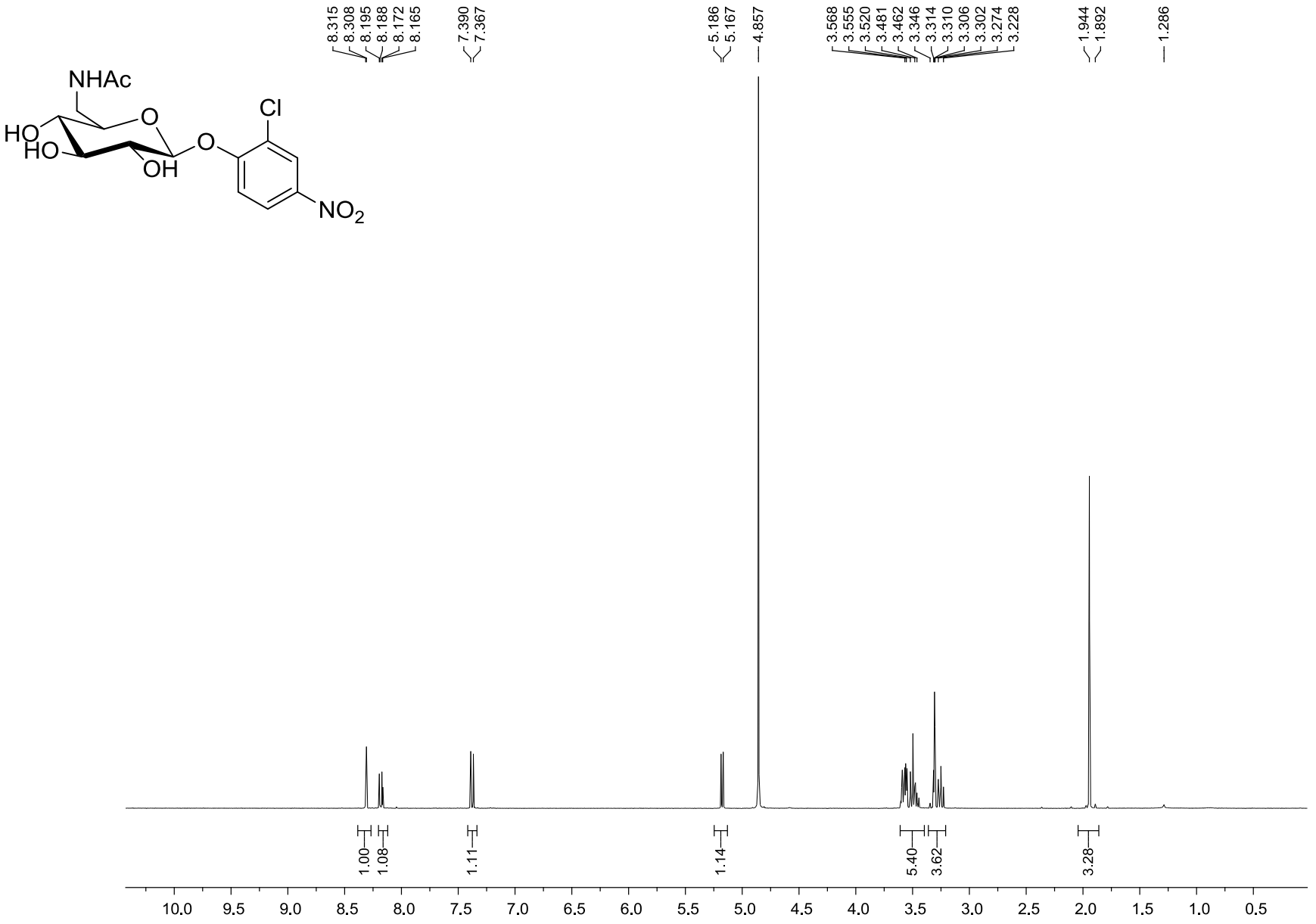
(2-chloro-4-nitrophenyl)-α-L-arabinopyranoside (**18**): ^{1}H NMR (CD_3OD, 400 MHz)



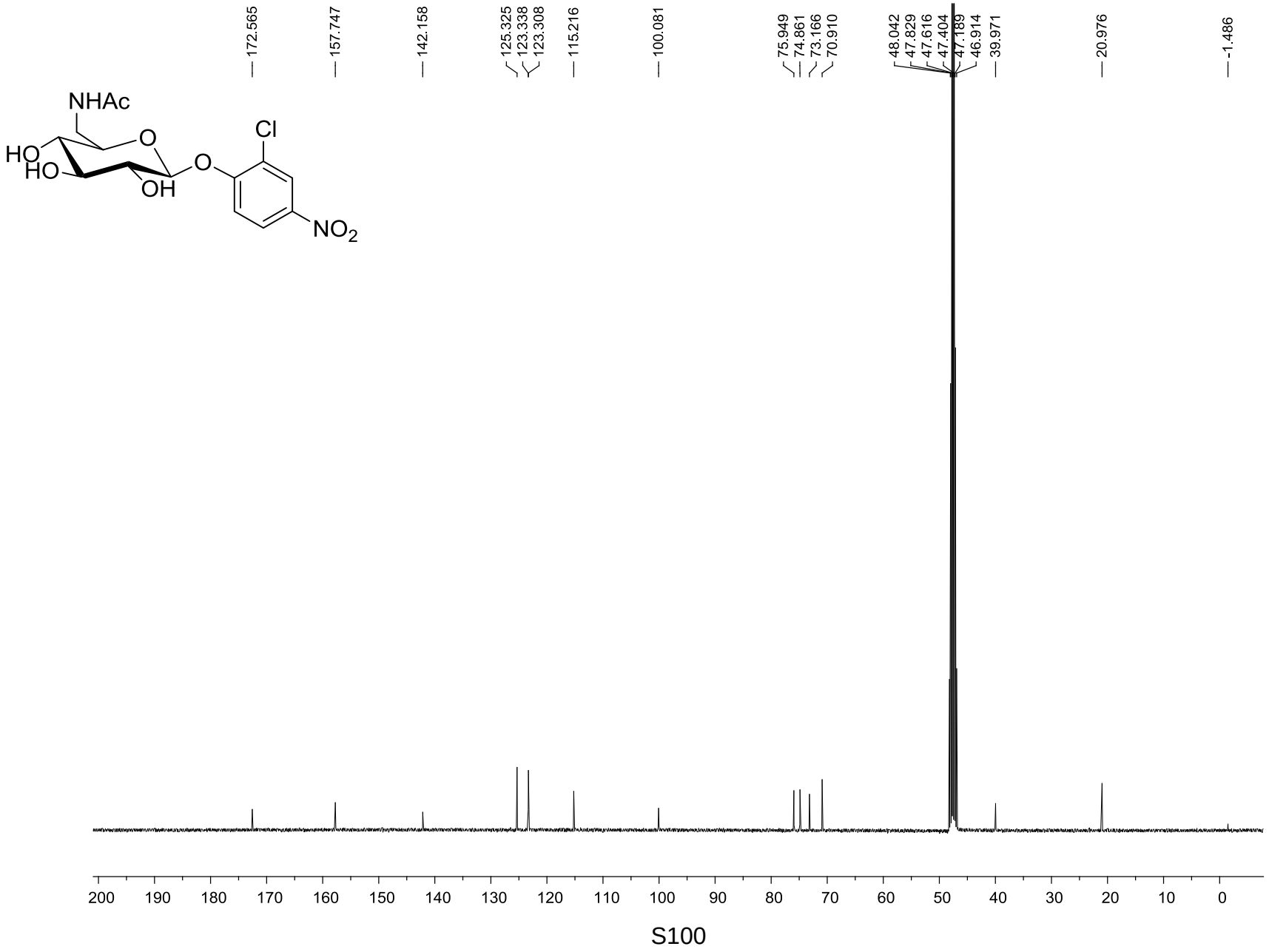
(2-chloro-4-nitrophenyl)-α-L-arabinopyranoside (**18**): ^{13}C NMR (DMSO-*d6*, 100 MHz)



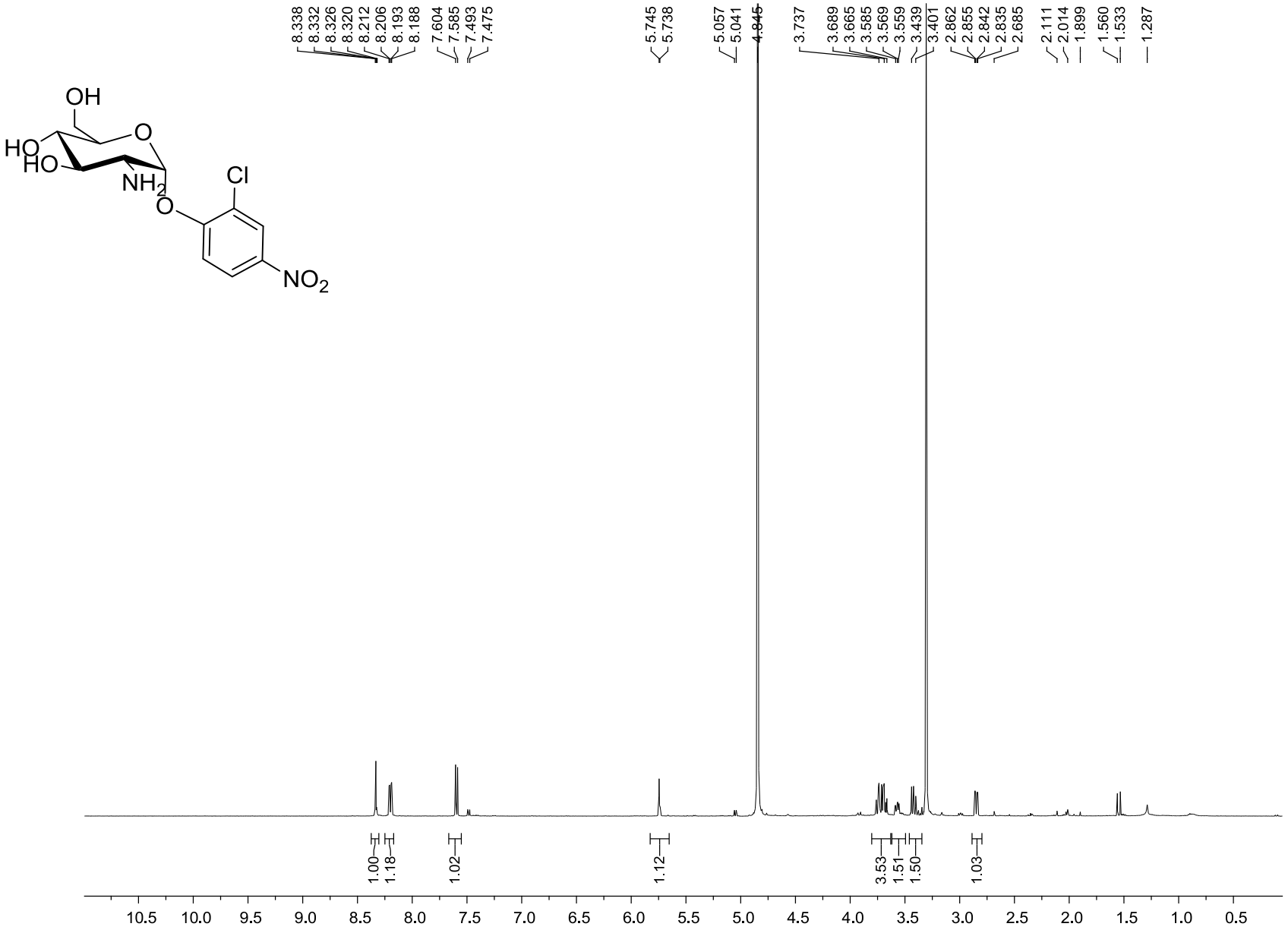
(2-chloro-4-nitrophenyl)-6-deoxy-6-aminoacetyl-β-D-glucopyranoside (**19**): ^{1}H NMR (CD_3OD, 400 MHz)



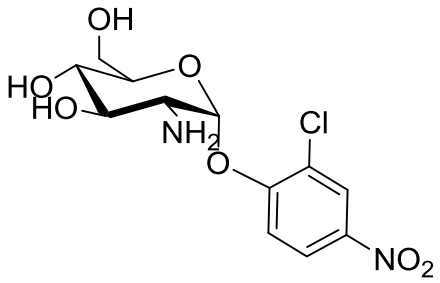
(2-chloro-4-nitrophenyl)-6-deoxy-6-aminoacetyl-β-D-glucopyranoside (**19**): ^{13}C NMR (CD_3OD, 100 MHz)

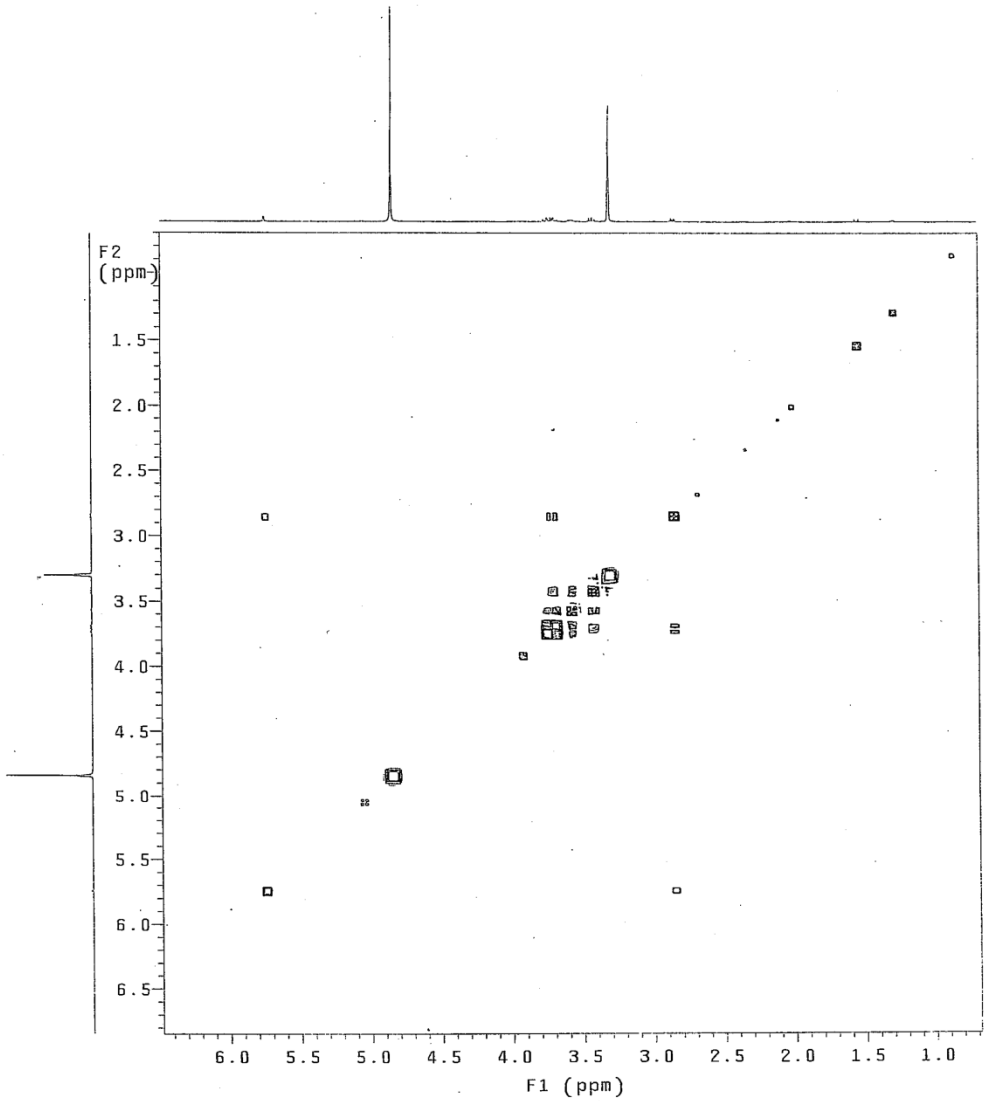


(2-chloro-4-nitrophenyl)-2-amino-α-D-glucopyranoside (**20**): ^{1}H NMR (CD_3OD, 500 MHz)

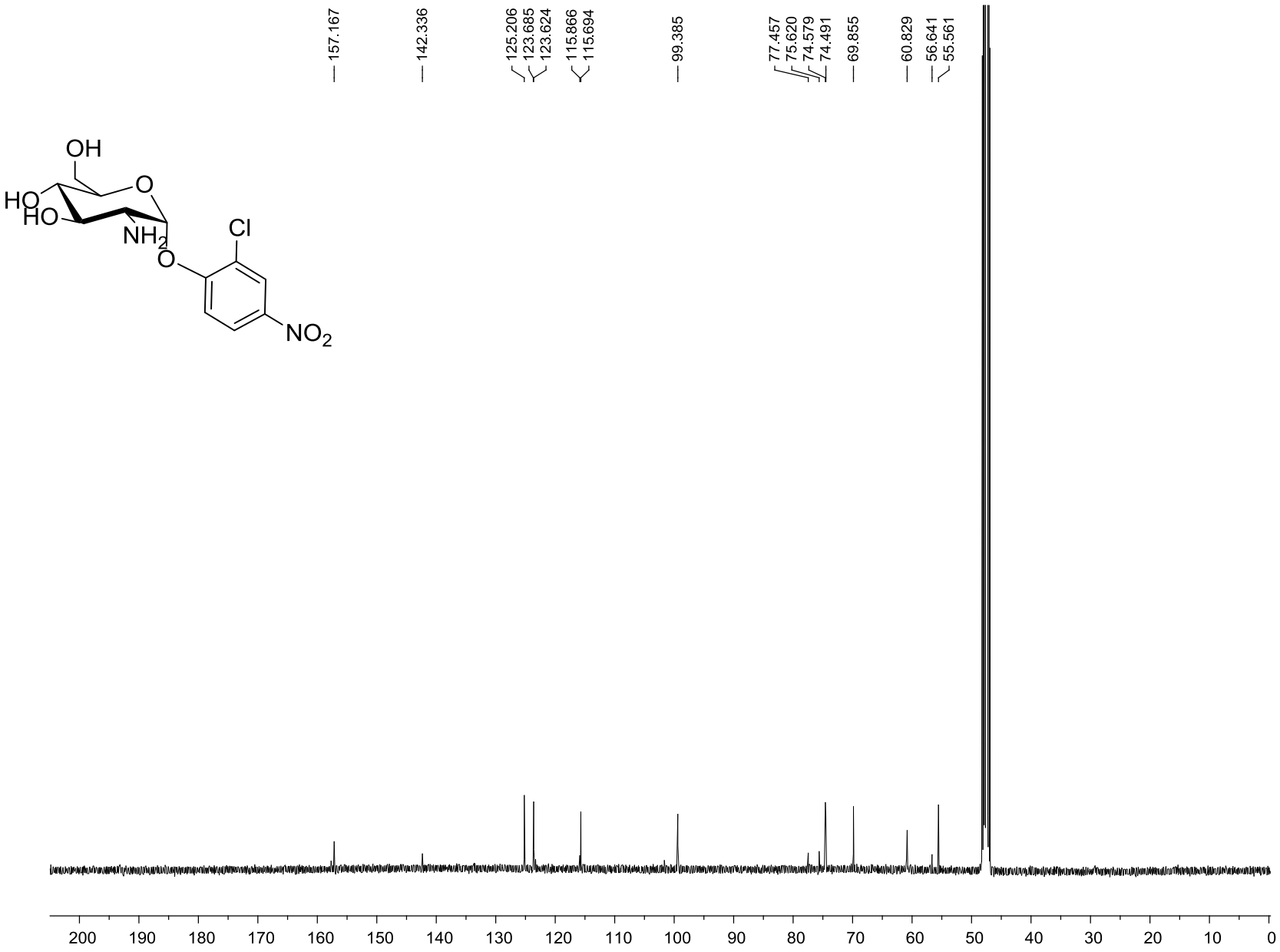


(2-chloro-4-nitrophenyl)-2-amino-α-D-glucopyranoside (**20**): gCOSY NMR (CD_3OD, 500 MHz)

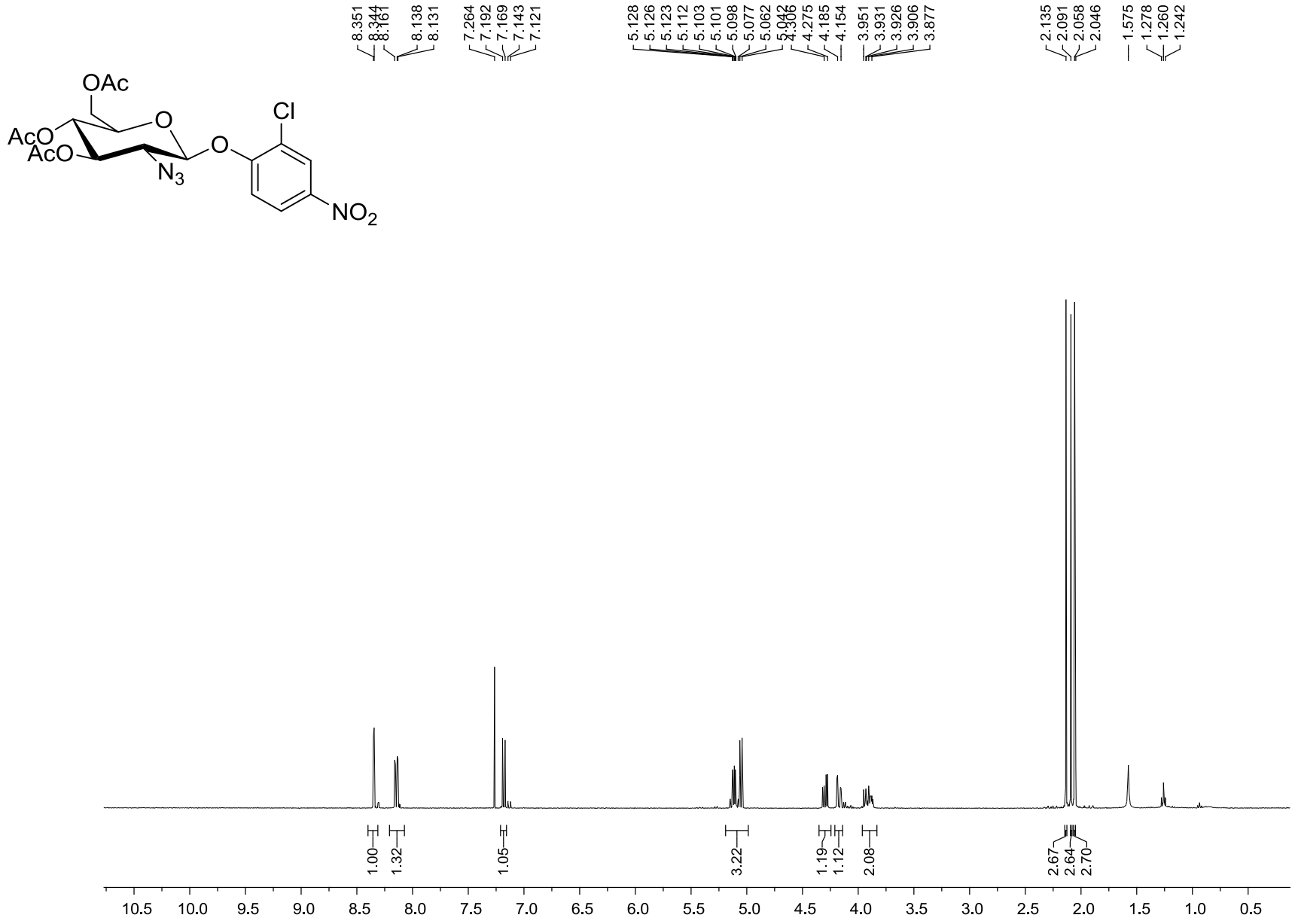




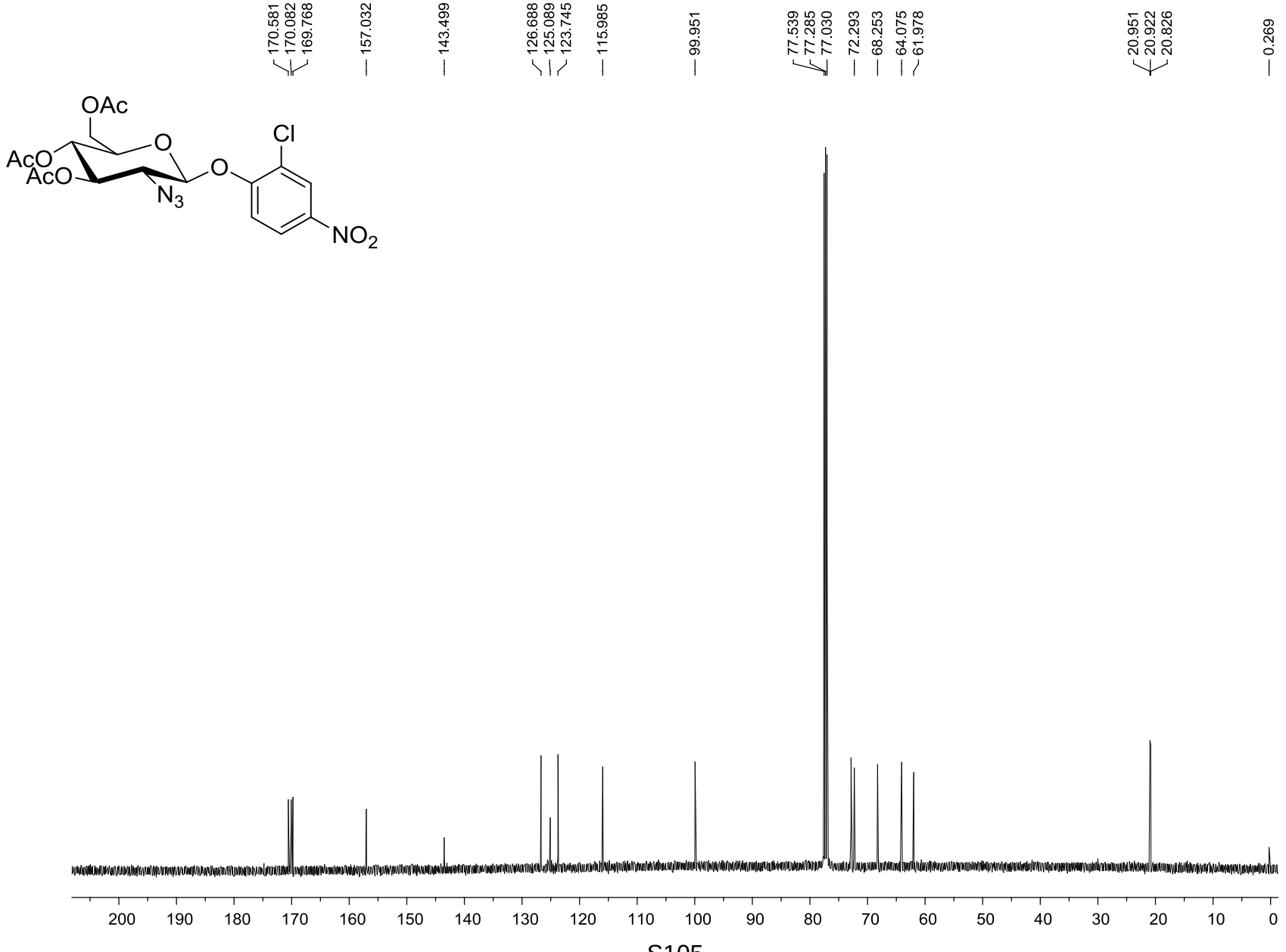
(2-chloro-4-nitrophenyl)-2-amino-α-D-glucopyranoside (**20**): ^{13}C NMR (CD_3OD, 100 MHz)



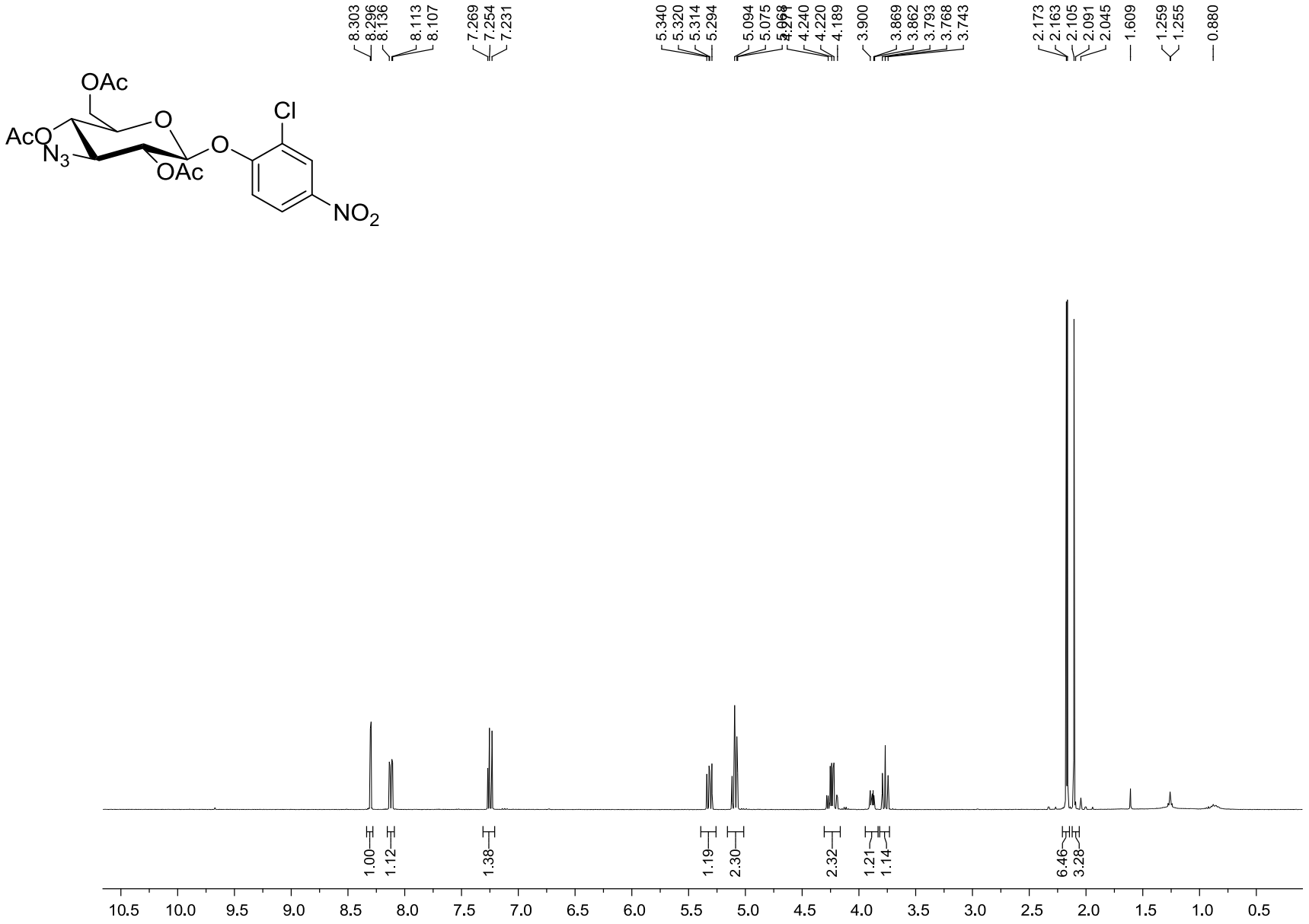
(2-chloro-4-nitrophenyl)-3,4,6-tri-*O*-acetyl-2-deoxy-2-azido-β-D-glucopyranoside (**23**): ^{1}H NMR ($CDCl_3$, 400 MHz)



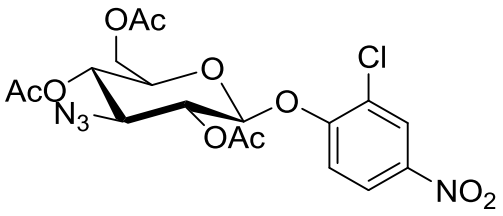
(2-chloro-4-nitrophenyl)-3,4,6-tri-*O*-acetyl-2-deoxy-2-azido-β-D-glucopyranoside (**23**): ^{13}C NMR ($CDCl_3$, 125 MHz)

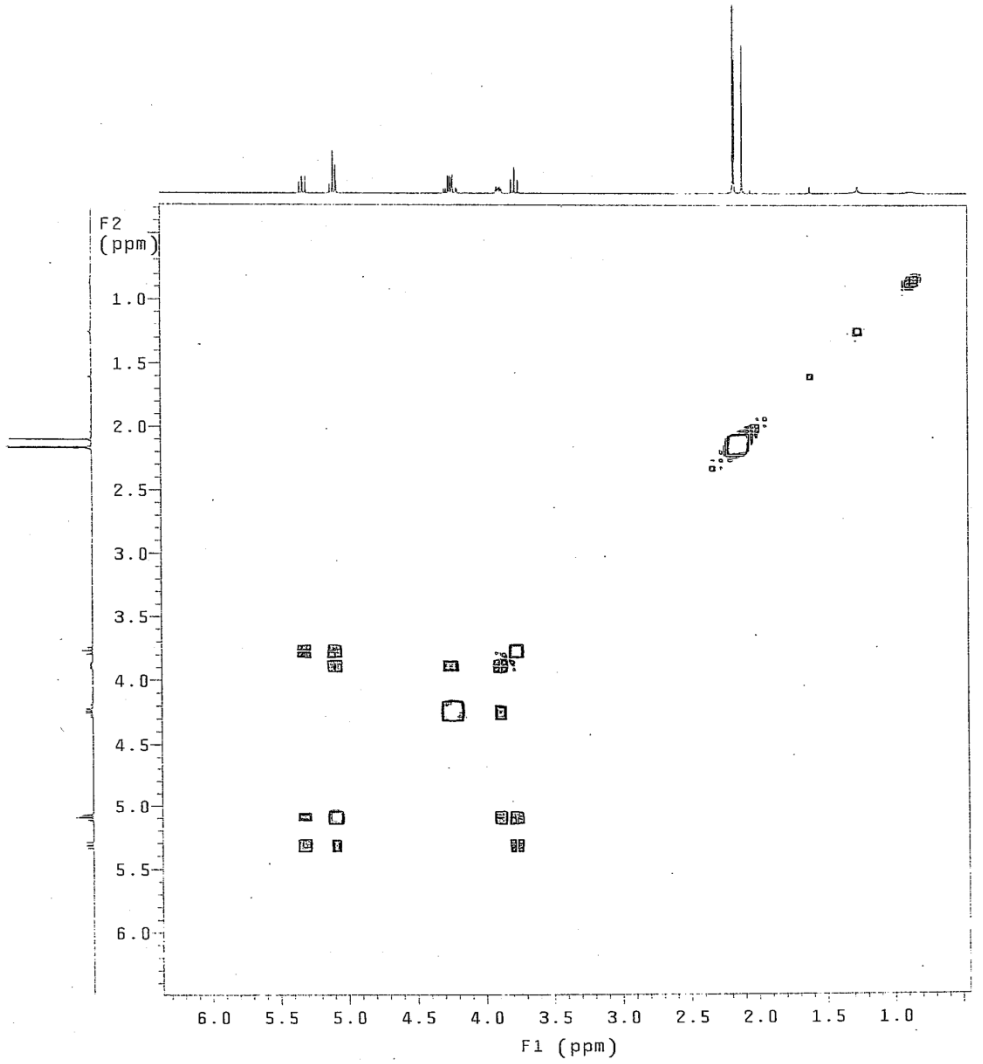


(2-chloro-4-nitrophenyl)-2,4,6-tri-*O*-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (**25**): ^{1}H NMR ($CDCl_3$, 400 MHz)

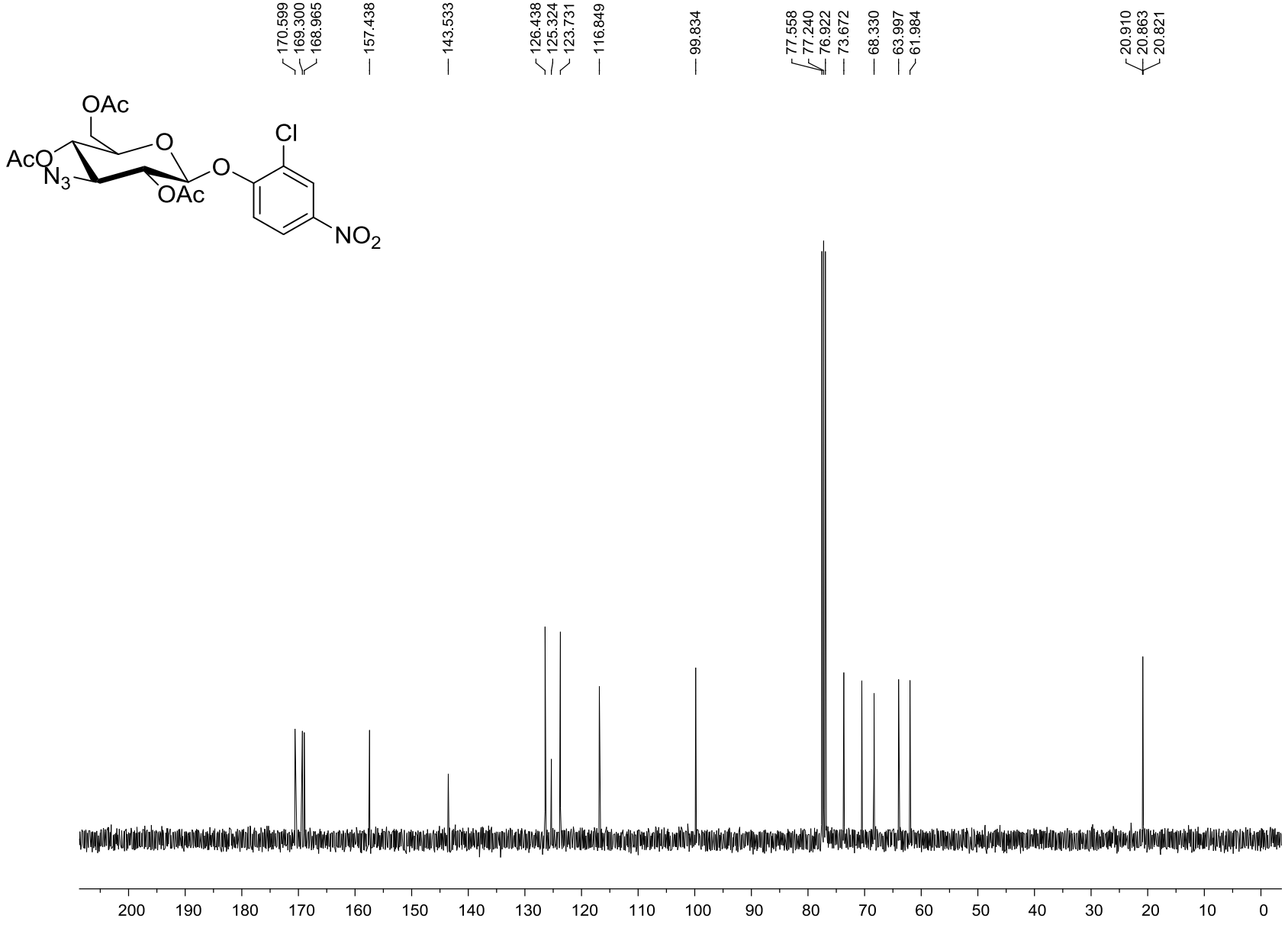


(2-chloro-4-nitrophenyl)-2,4,6-tri-*O*-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (**25**): gCOSY NMR ($CDCl_3$, 400 MHz)

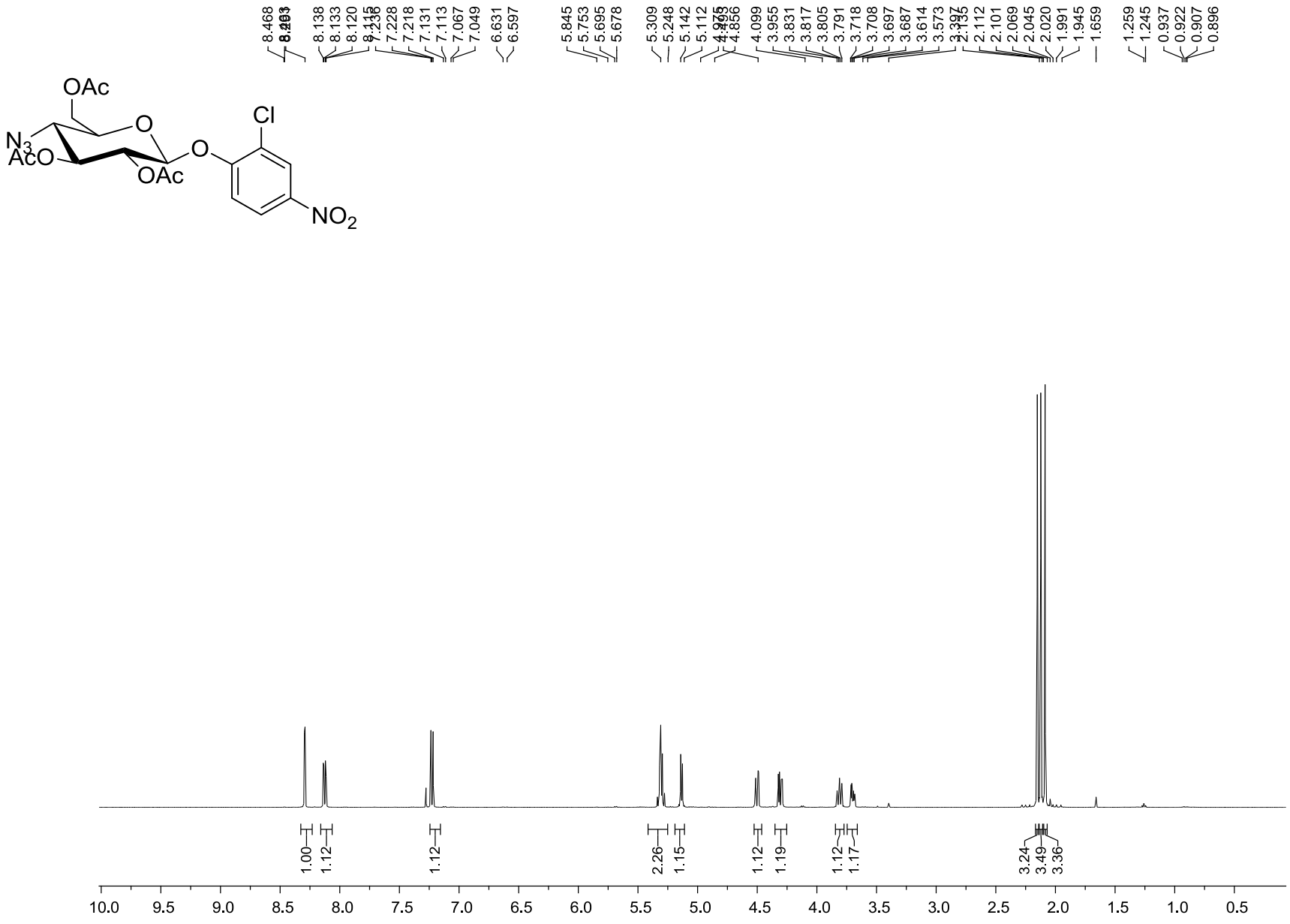




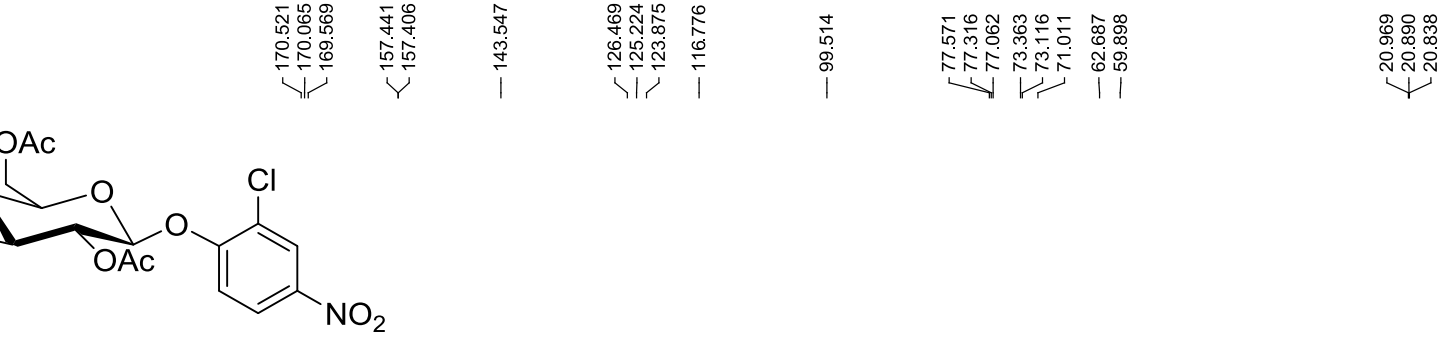
(2-chloro-4-nitrophenyl)-2,4,6-tri-*O*-acetyl-3-deoxy-3-azido-β-D-glucopyranoside (**25**): ^{13}H NMR ($CDCl_3$, 100 MHz)

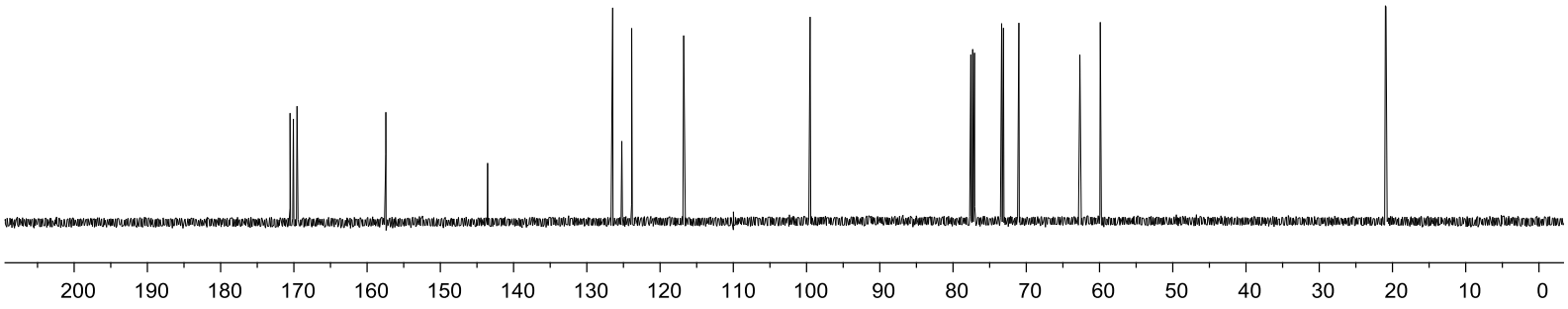


(2-chloro-4-nitrophenyl)-2,3,6-tri-*O*-acetyl-4-deoxy-4-azido-β-D-glucopyranoside (**27**): ^{1}H NMR ($CDCl_3$, 500 MHz)

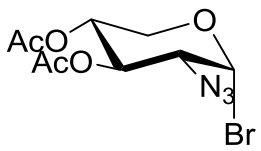


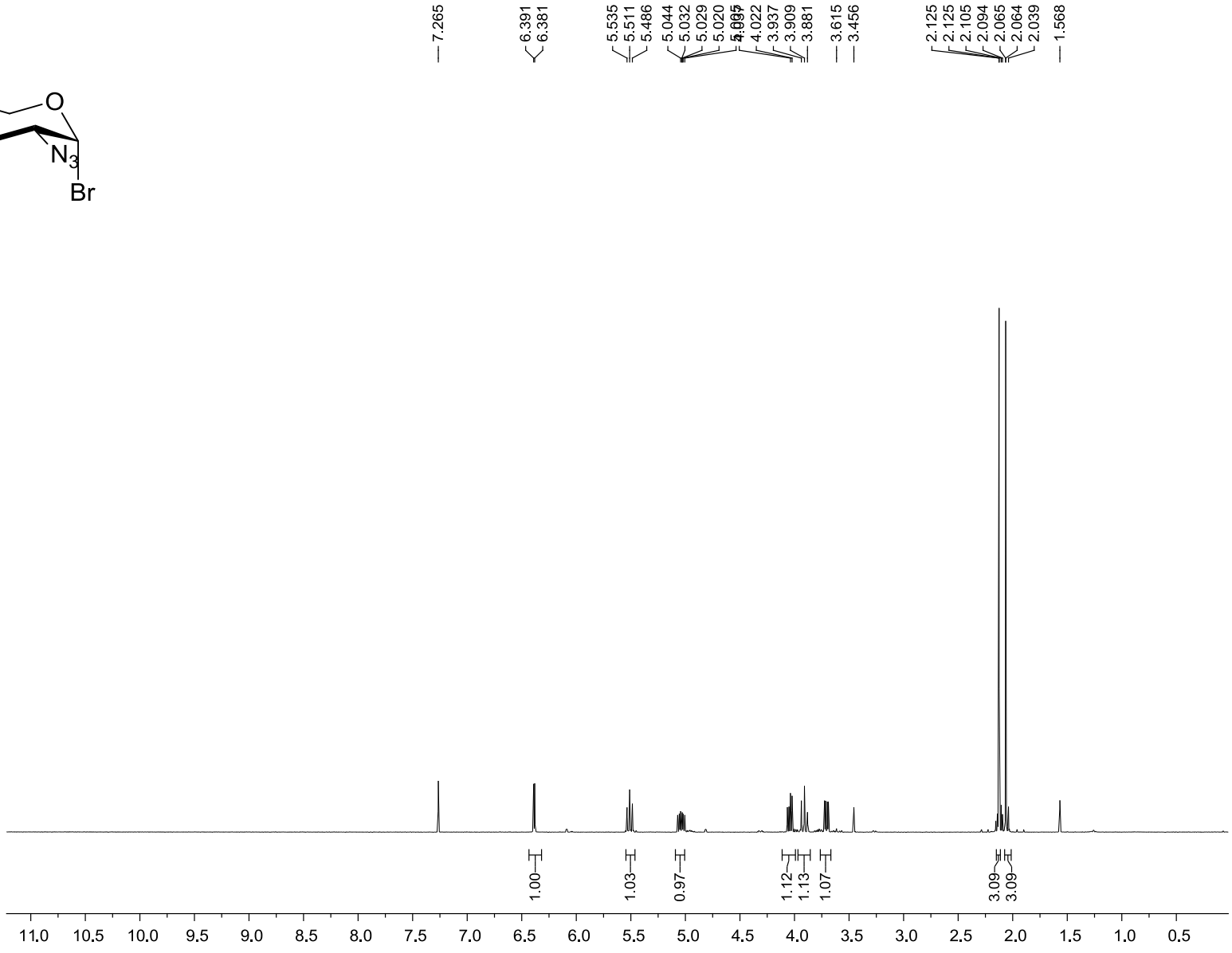
(2-chloro-4-nitrophenyl)-2,3,6-tri-*O*-acetyl-4-deoxy-4-azido-β-D-glucopyranoside (**27**): ^{13}C NMR ($CDCl_3$, 500 MHz)



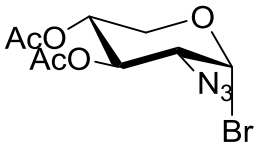


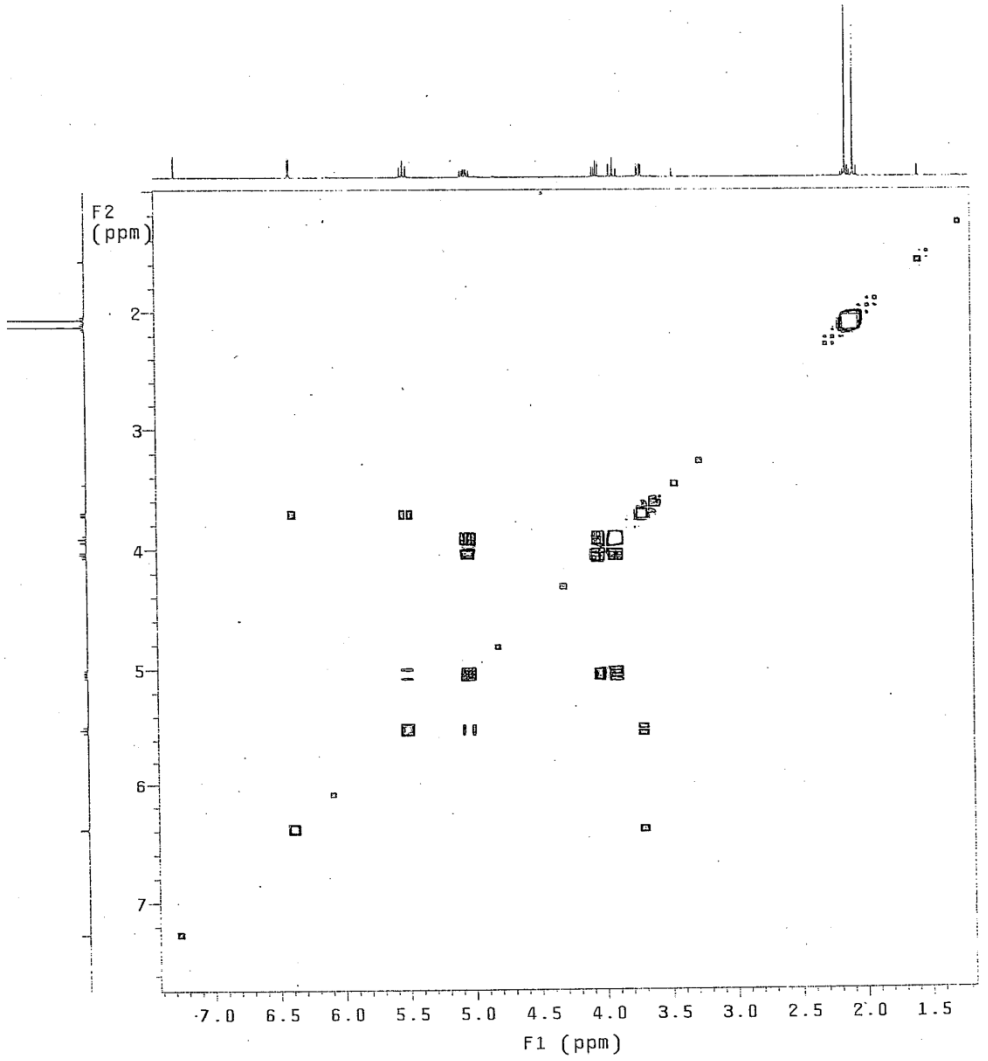
1-bromo-3,4-di-*O*-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (**29**): ^{1}H NMR ($CDCl_3$, 400 MHz)



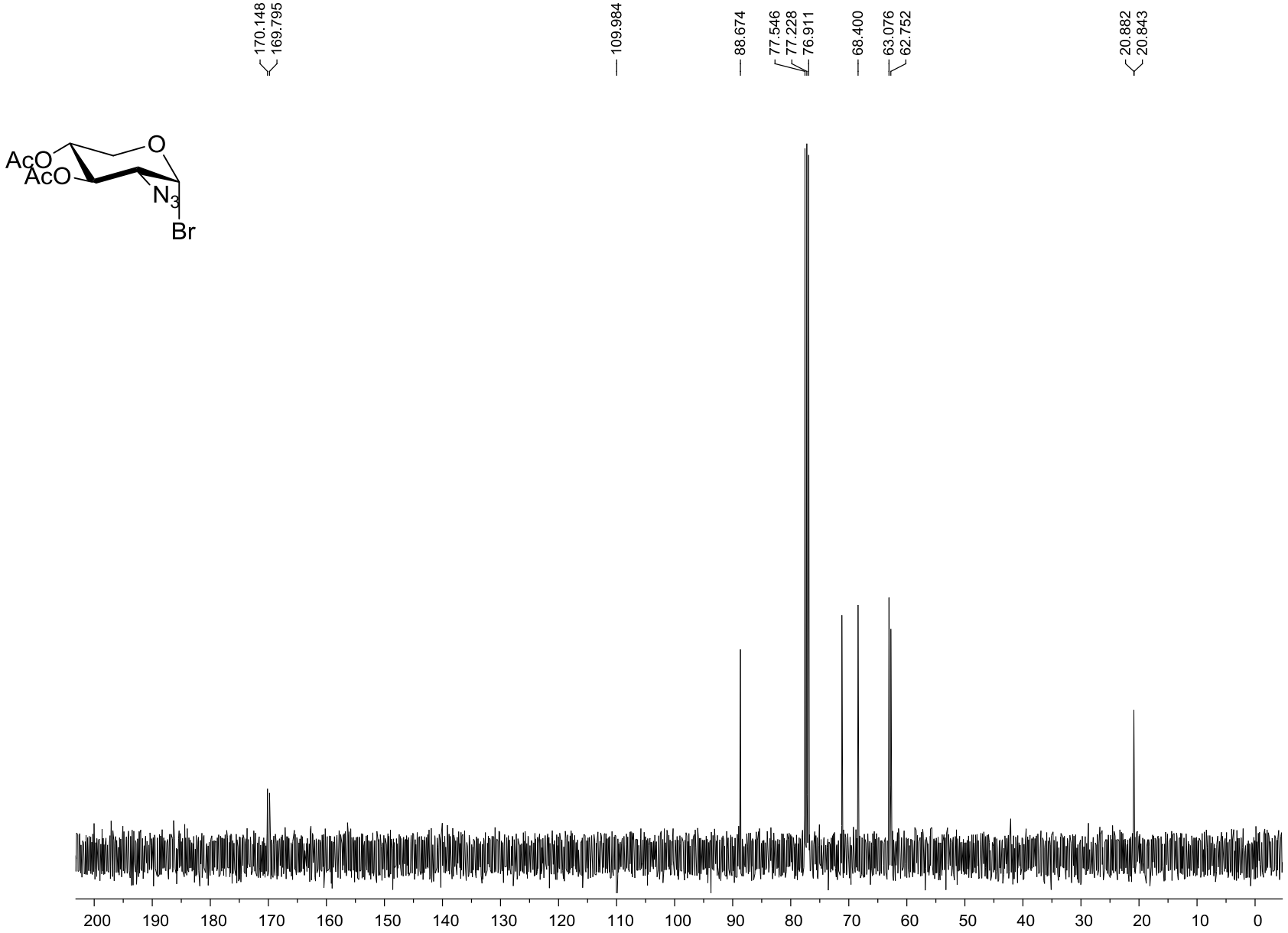


1-bromo-3,4-di-*O*-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (**29**): gCOSY NMR ($CDCl_3$, 400 MHz)

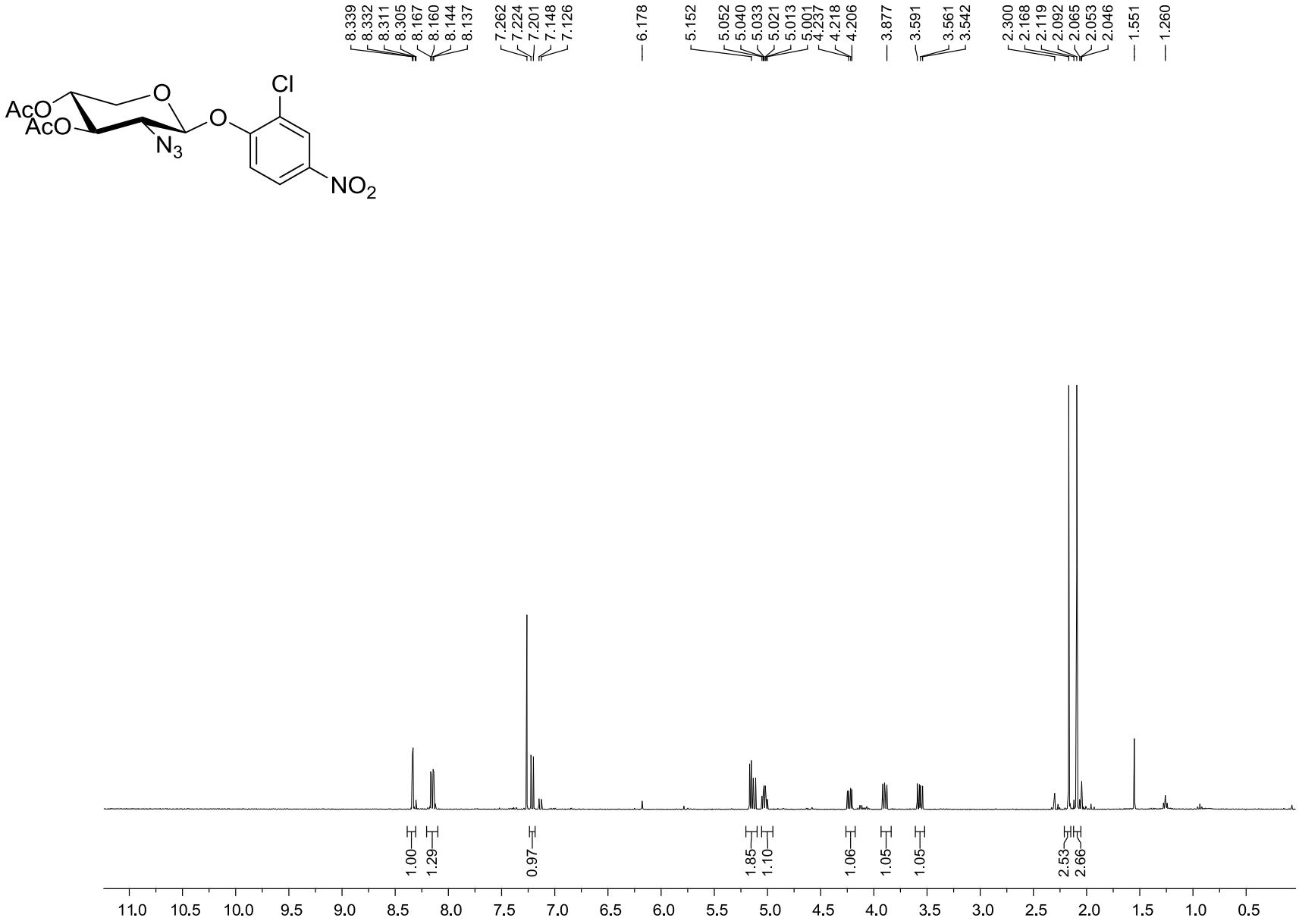




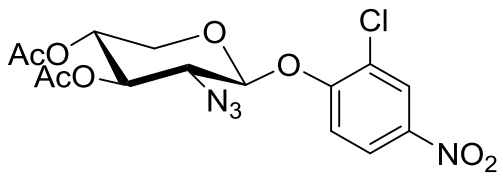
1-bromo-3,4-di-*O*-acetyl-2-deoxy-2-azido-α-D-xylopyranoside (**29**): ^{13}C NMR ($CDCl_3$, 100 MHz)

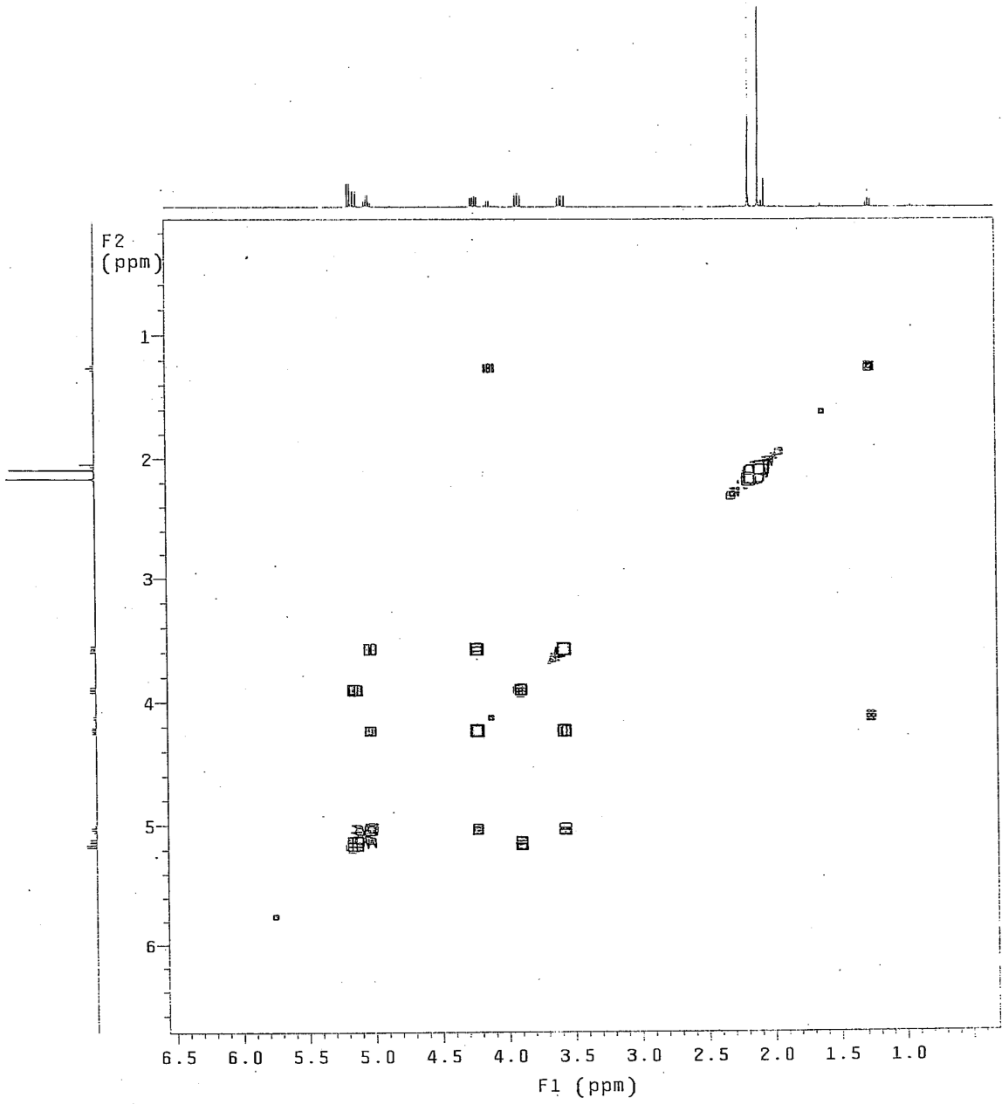


(2-chloro-4-nitrophenyl)-3,4-di-*O*-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (**30**): ^{1}H NMR ($CDCl_3$, 400 MHz)

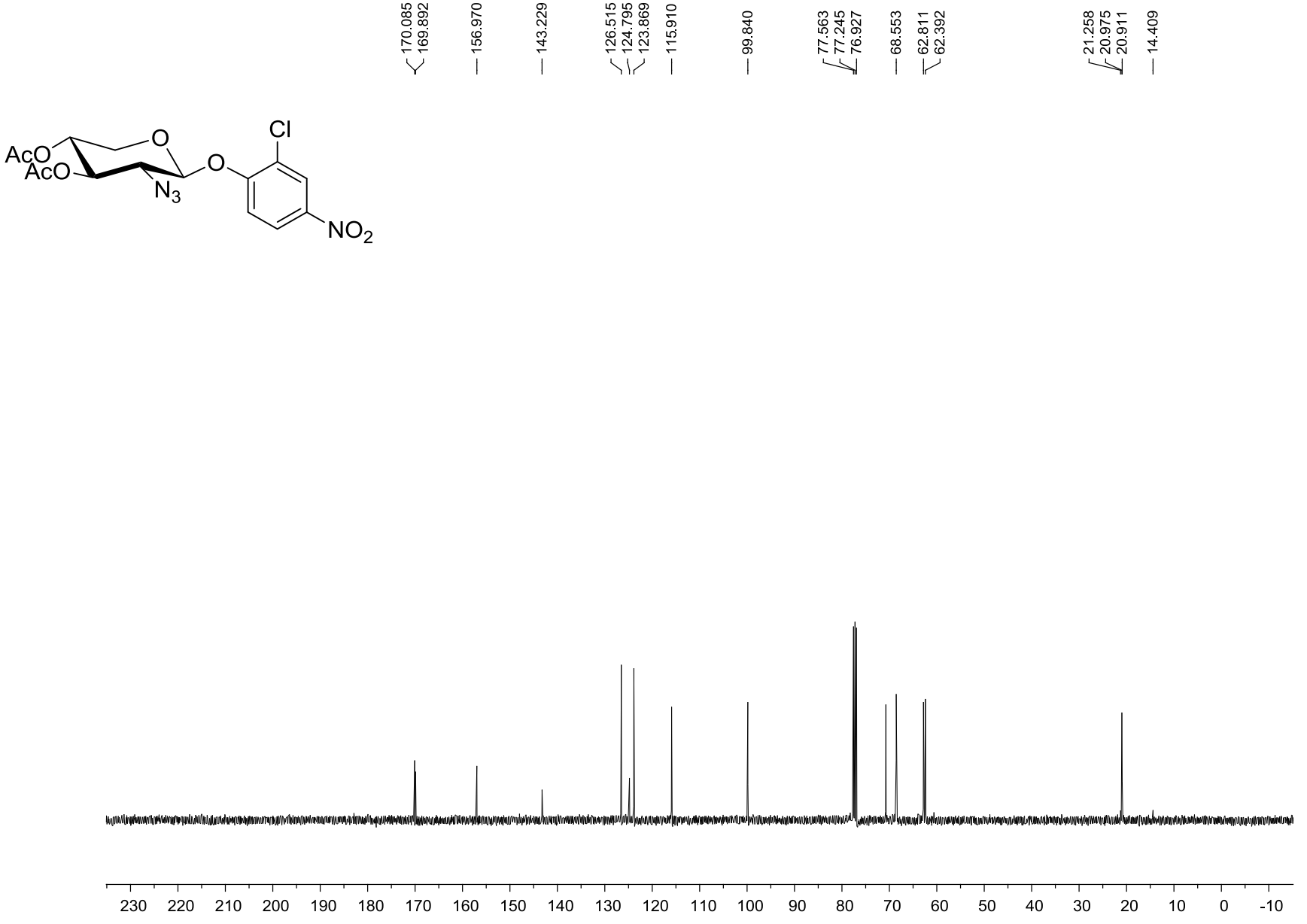


(2-chloro-4-nitrophenyl)-3,4-di-*O*-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (**30**): gCOSY NMR ($CDCl_3$, 400 MHz)

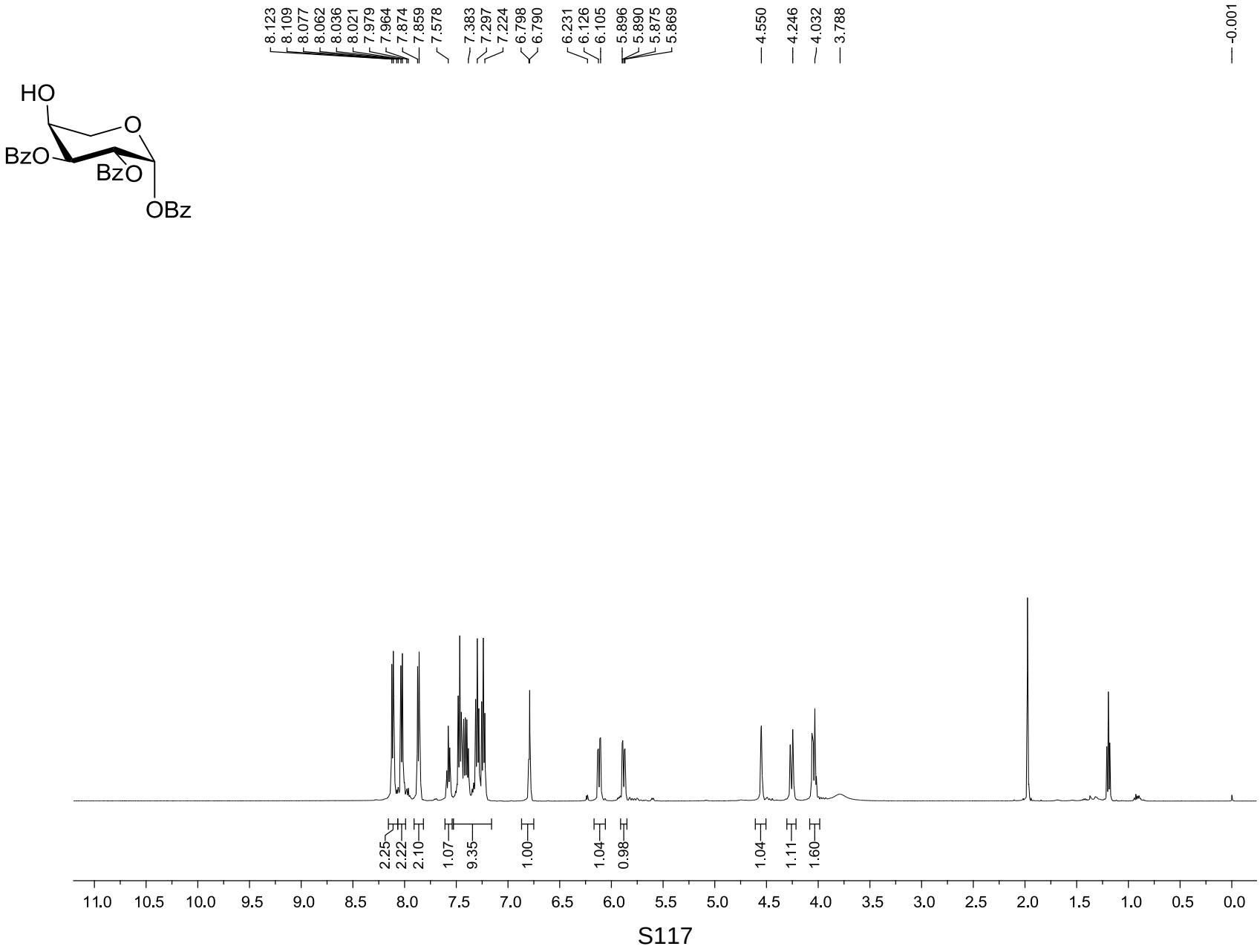




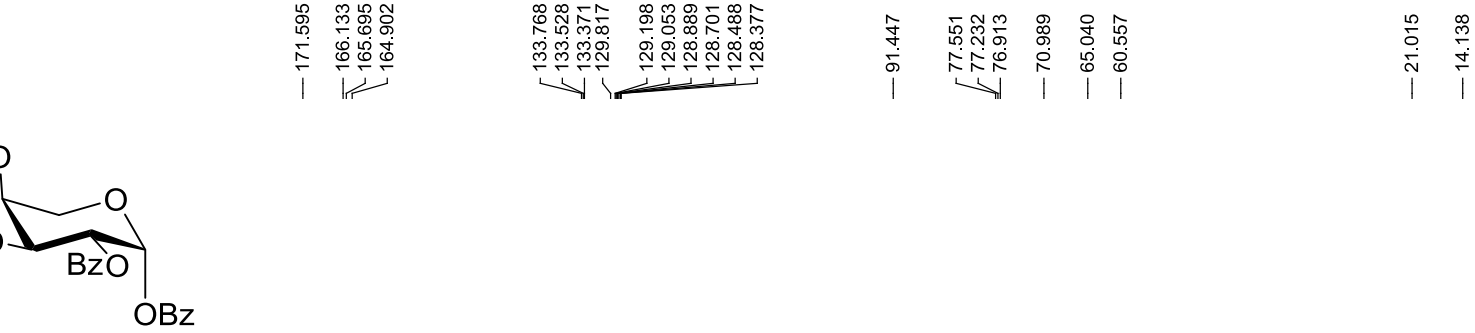
(2-chloro-4-nitrophenyl)-3,4-di-*O*-acetyl-2-deoxy-2-azido-β-D-xylopyranoside (**30**): ^{13}C NMR ($CDCl_3$, 100 MHz)

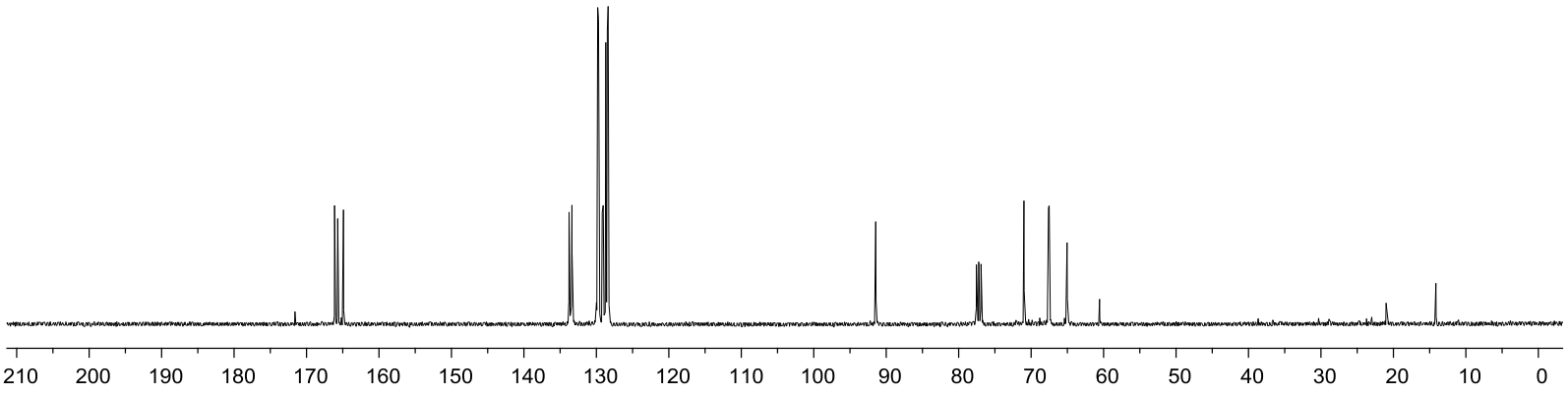


1,2,3-tri-*O*-benzoyl-β-L-arabinopyranoside (**31**): ^{1}H NMR ($CDCl_3$, 500 MHz)

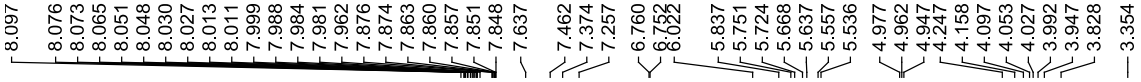


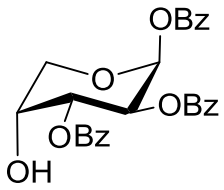
1,2,3-tri-*O*-benzoyl-β-L-arabinopyranoside (**31**): ^{13}C NMR ($CDCl_3$, 100 MHz)

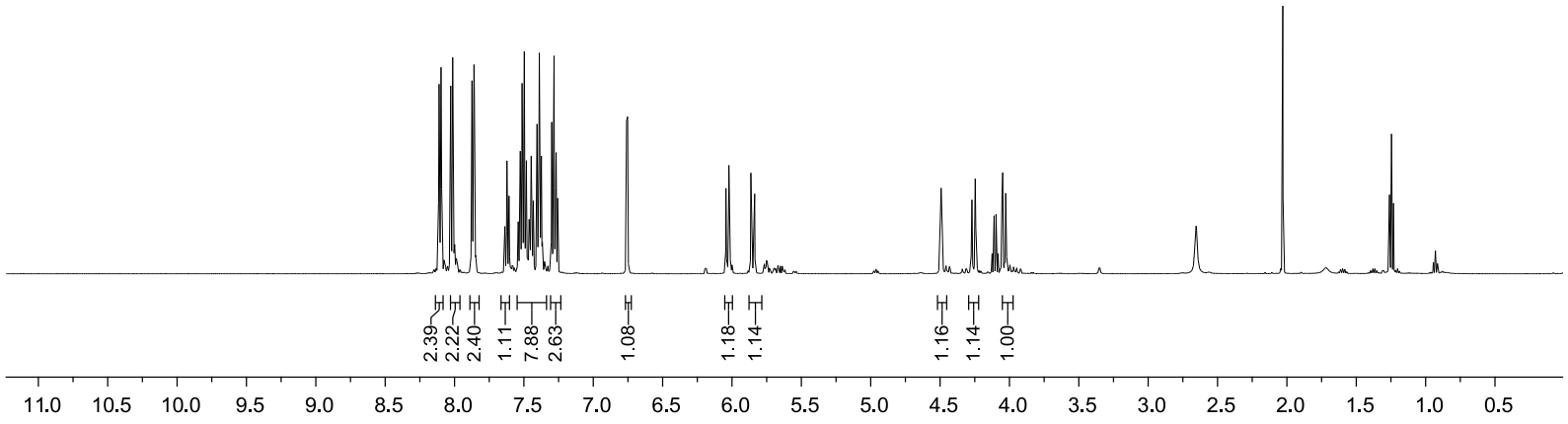




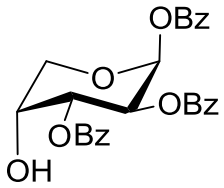
1,2,3-tri-*O*-benzoyl-β-D-arabinopyranoside (**32**): ^{1}H NMR ($CDCl_3$, 500 MHz)

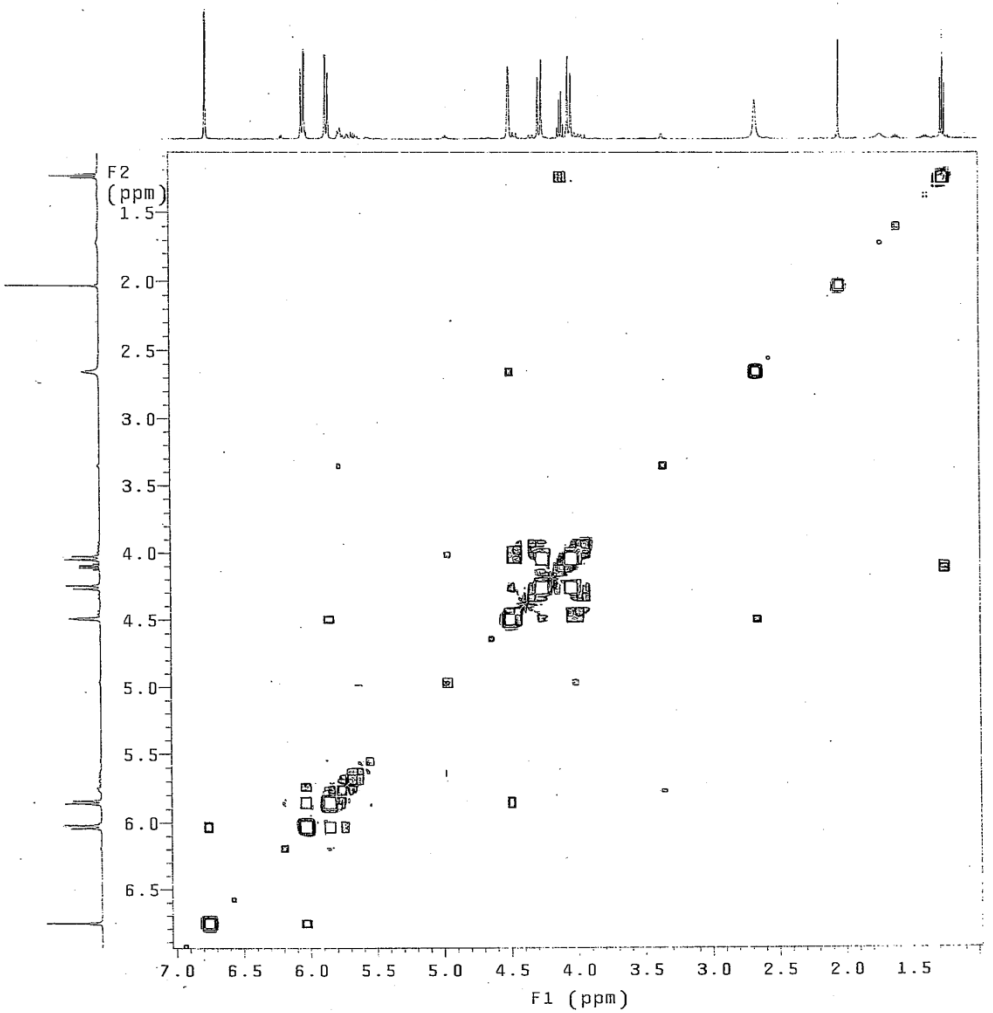






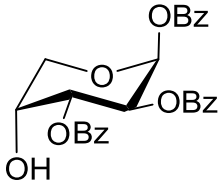
1,2,3-tri-*O*-benzoyl-β-D-arabinopyranoside (**32**): gCOSY NMR ($CDCl_3$, 500 MHz)

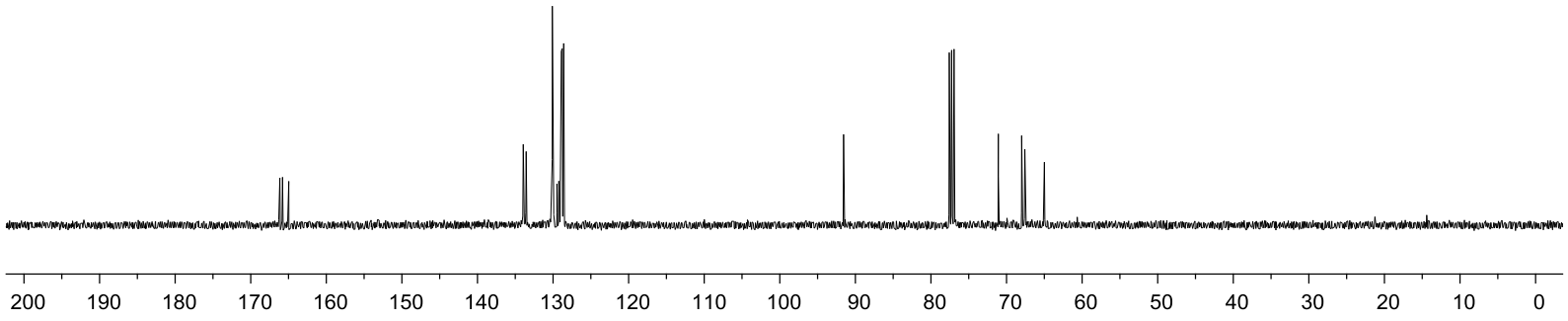




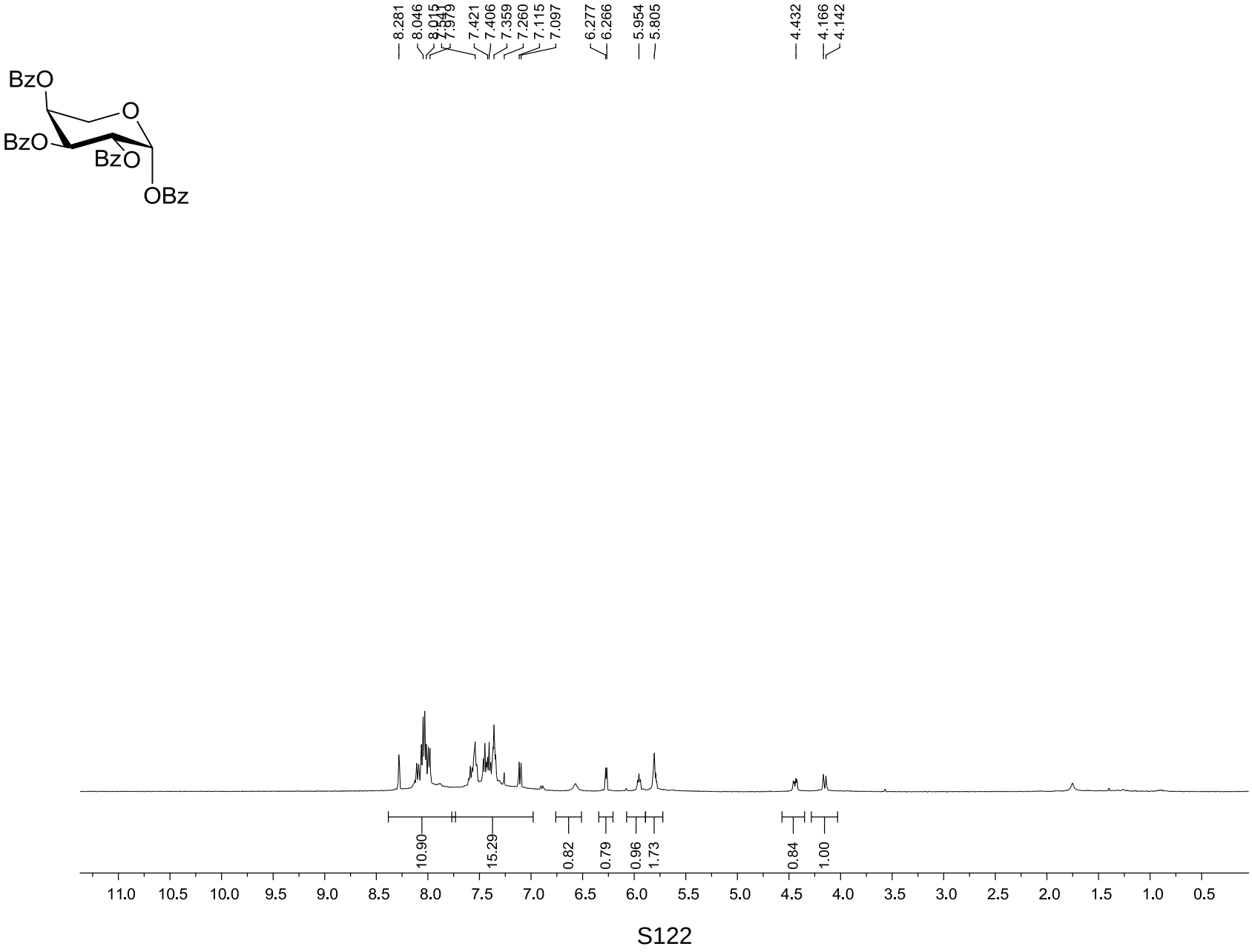
1,2,3-tri-*O*-benzoyl-β-D-arabinopyranoside (**32**): ^{13}C NMR ($CDCl_3$, 100 MHz)

166.147
165.794
164.966
133.942
133.845
133.557
130.096
129.164
128.910
128.784
128.681
128.592
128.528
91.560
77.580
77.262
76.944
64.993
60.646
21.258
14.405

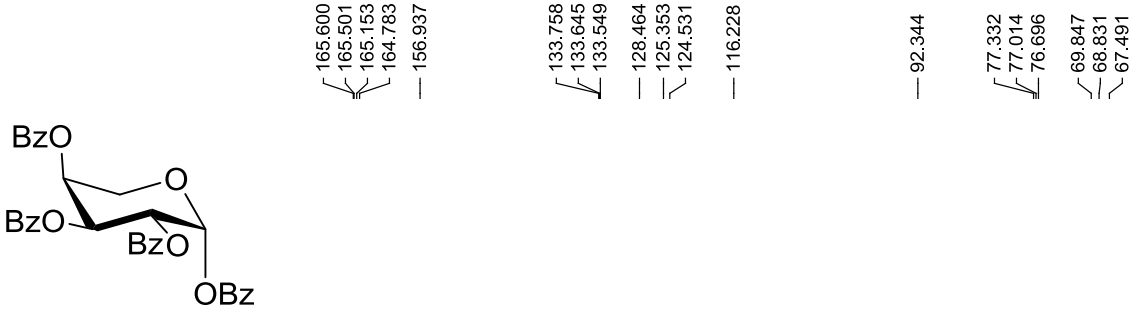


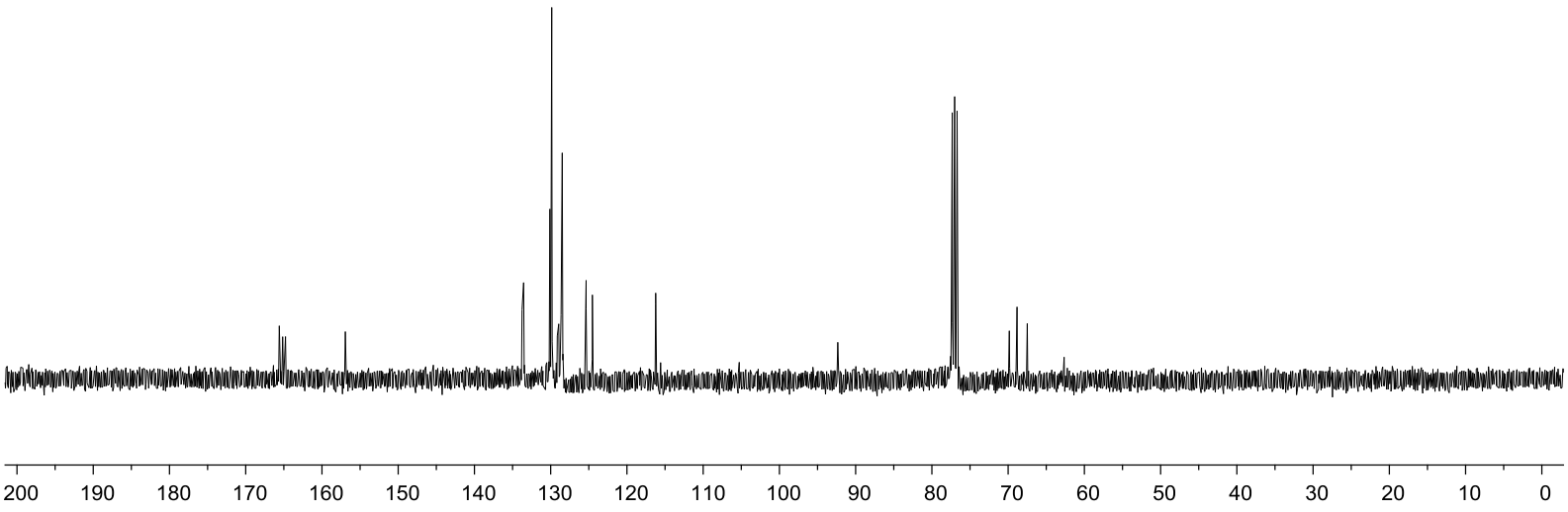


1,2,3,4-tetra-*O*-benzoyl-β-L-arabinopyranoside (**33**): ^{1}H NMR ($CDCl_3$, 500 MHz)

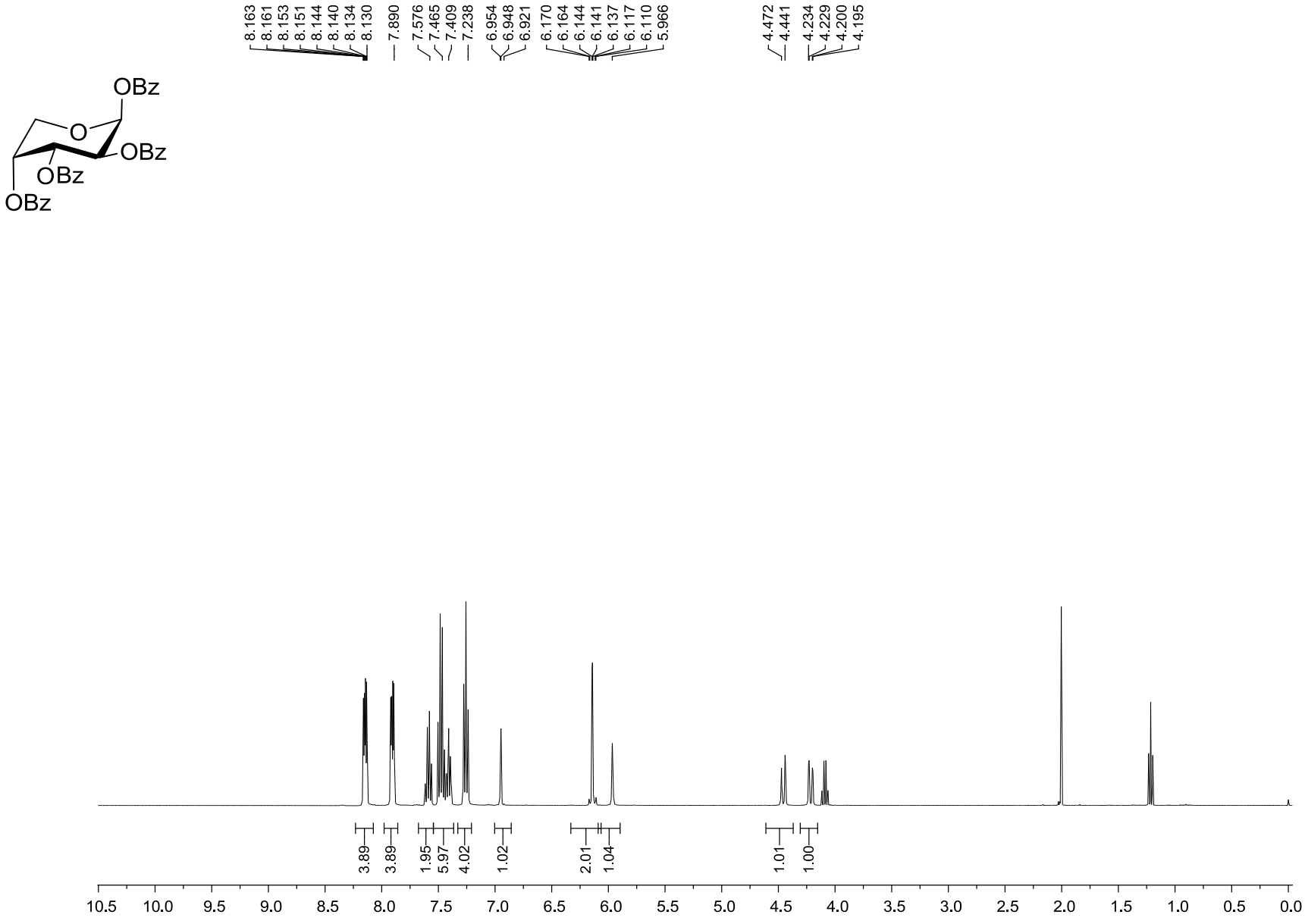


1,2,3,4-tetra-*O*-benzoyl-β-L-arabinopyranoside (**33**): ^{13}C NMR ($CDCl_3$, 100 MHz)

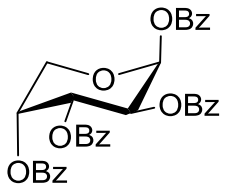


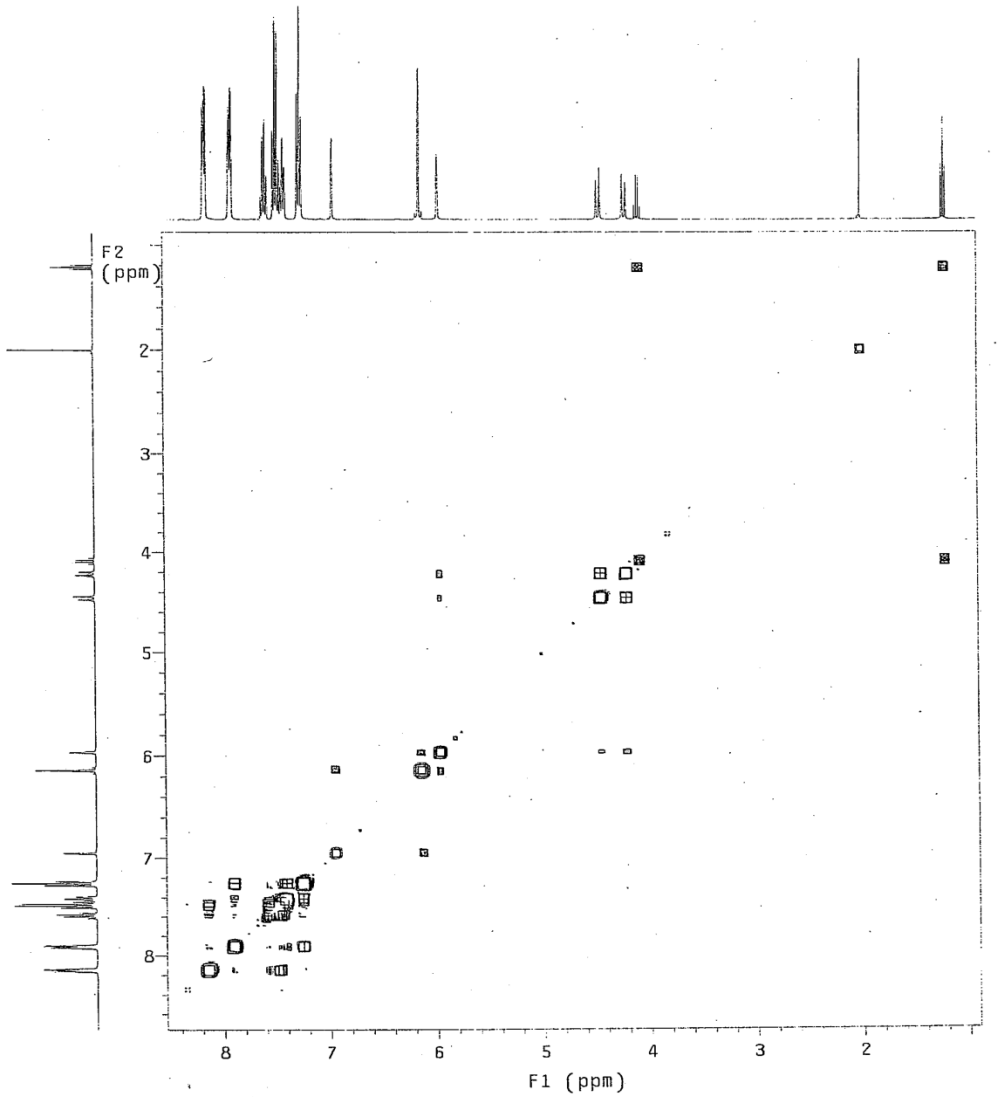


1,2,3,4-tetra-*O*-benzoyl-α-D-arabinopyranoside (**34**): ^{1}H NMR ($CDCl_3$, 400 MHz)



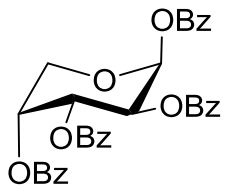
1,2,3,4-tetra-*O*-benzoyl-α-D-arabinopyranoside (**34**): gCOSY NMR ($CDCl_3$, 400 MHz)

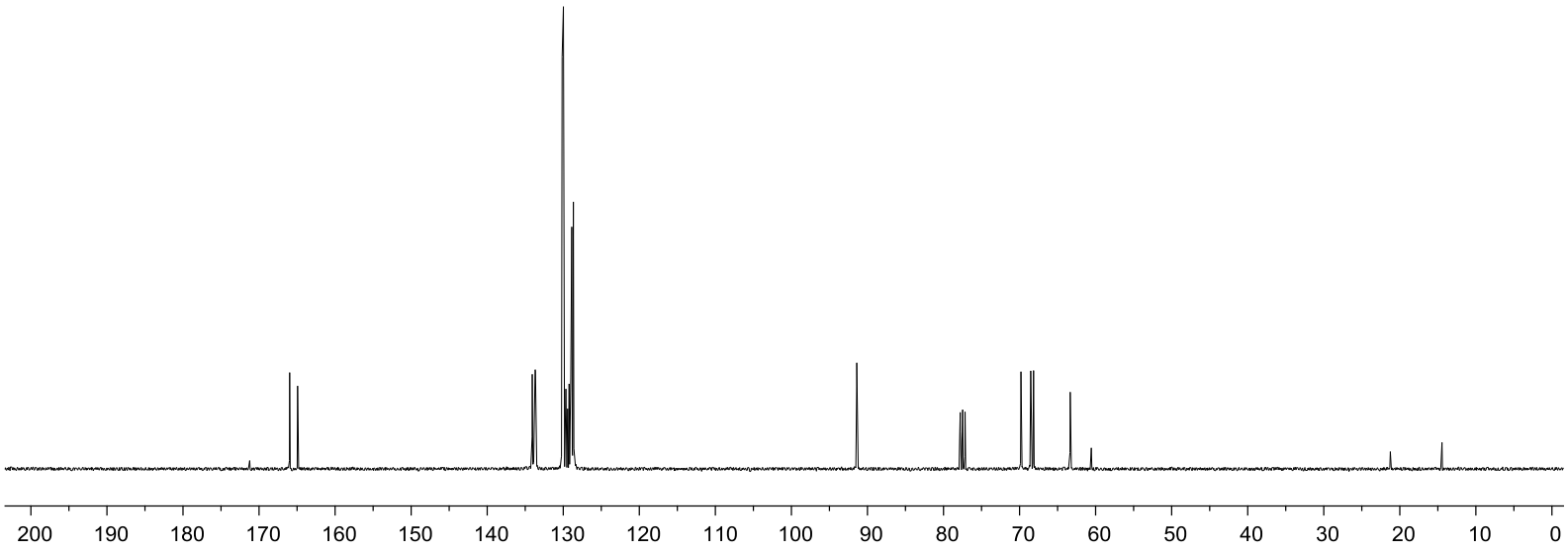




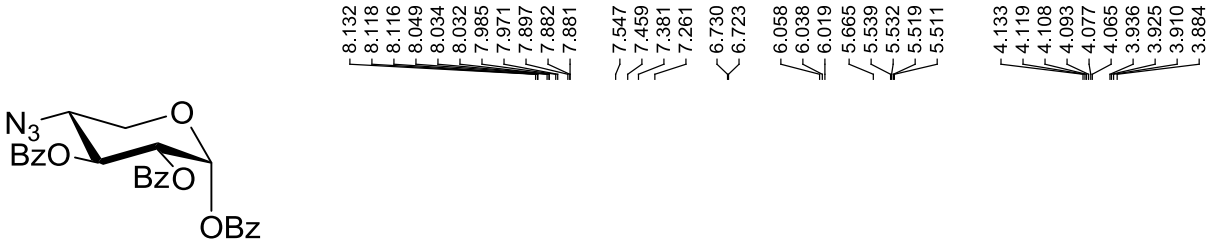
1,2,3,4-tetra-*O*-benzoyl-α-D-arabinopyranoside (**34**): ^{13}C NMR ($CDCl_3$, 100 MHz)

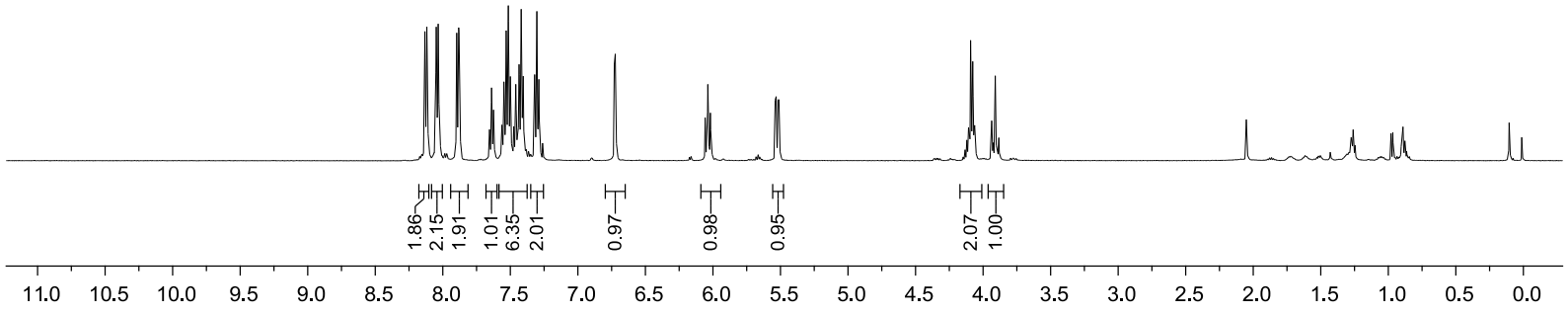
171.231
165.974
165.942
165.832
164.930
134.079
133.807
133.700
129.416
129.229
129.078
129.001
128.881
128.669
128.644
91.408
77.803
77.484
77.165
68.533
68.157
63.339
60.567
21.246
14.454



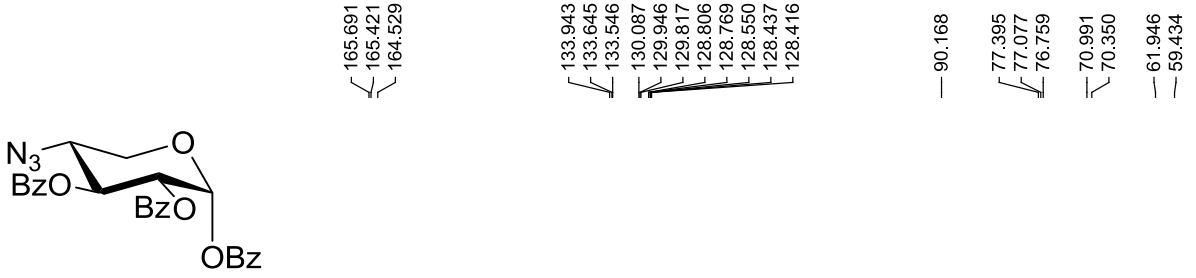


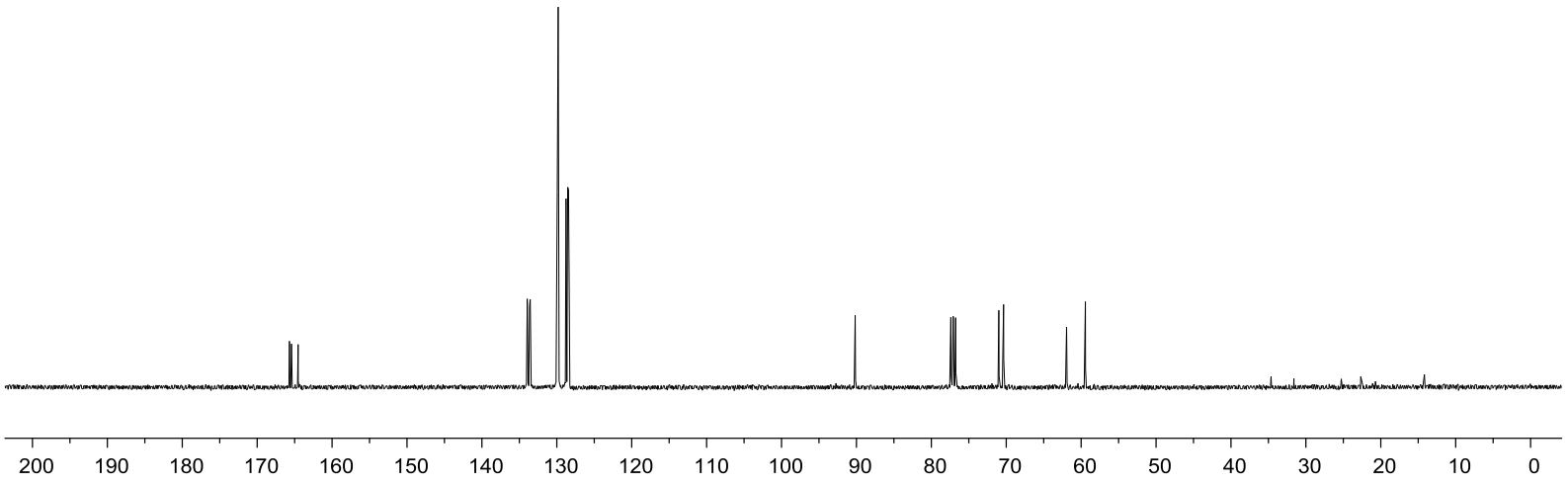
1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (**35**)**:** ^{1}H NMR ($CDCl_3$, 500 MHz)



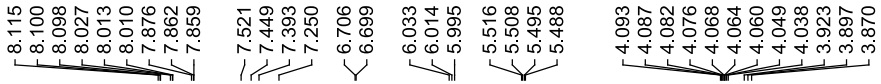


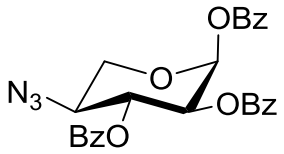
1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (**35**)**:** ^{13}C NMR ($CDCl_3$, 100 MHz)

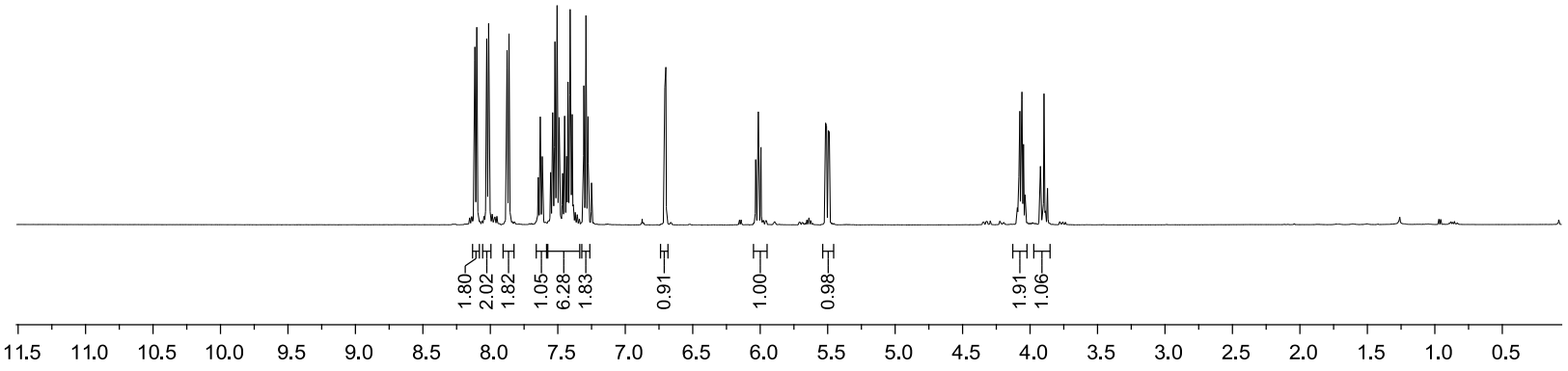




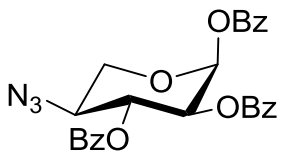
1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**36**): ^{1}H NMR ($CDCl_3$, 500 MHz)

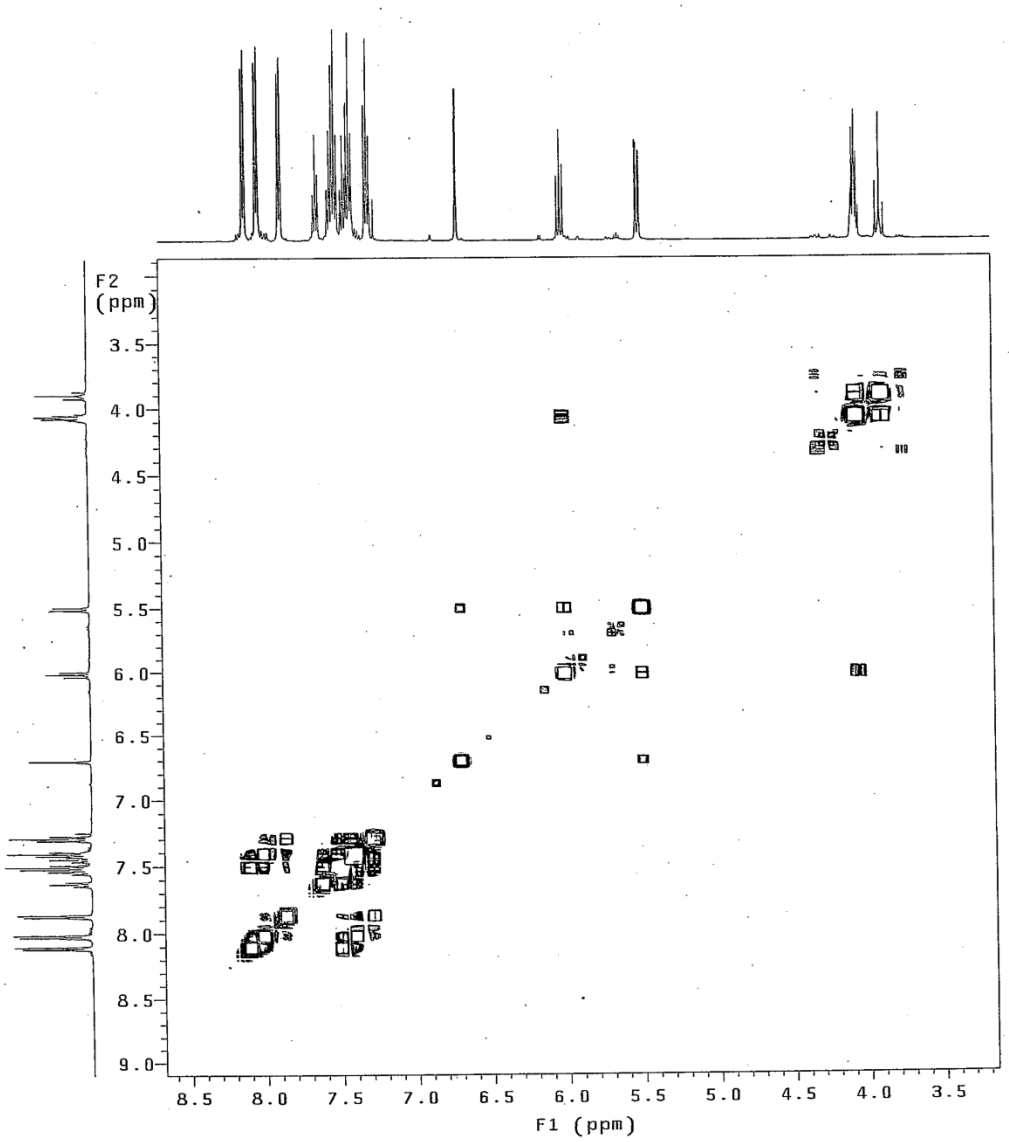




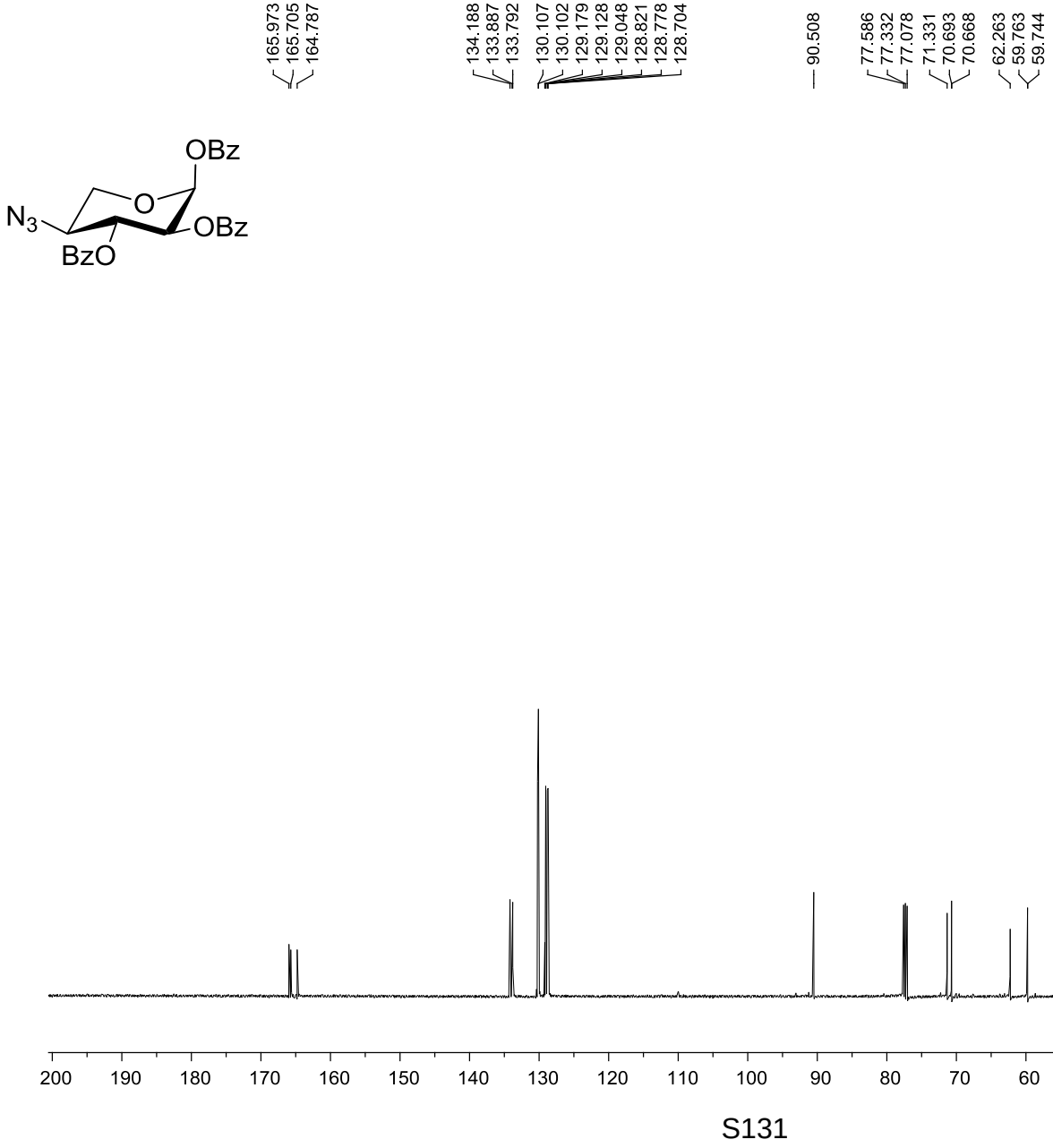


1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**36**): gCOSY NMR ($CDCl_3$, 500 MHz)

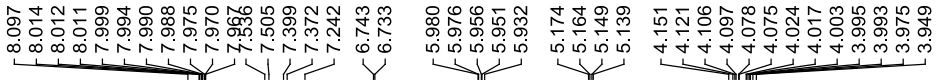


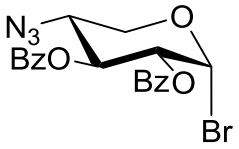


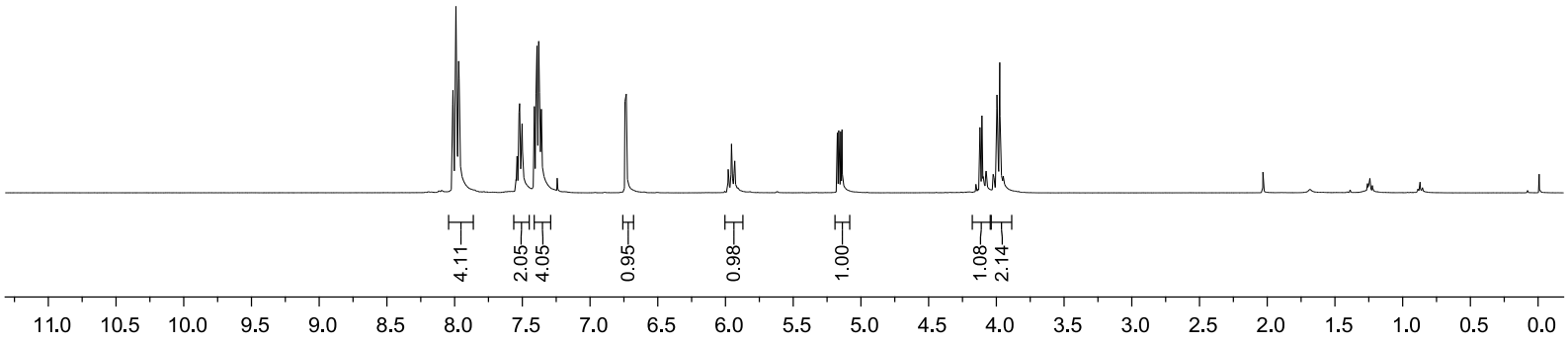
1,2,3-tri-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**36**): ^{13}C NMR ($CDCl_3$, 125 MHz)



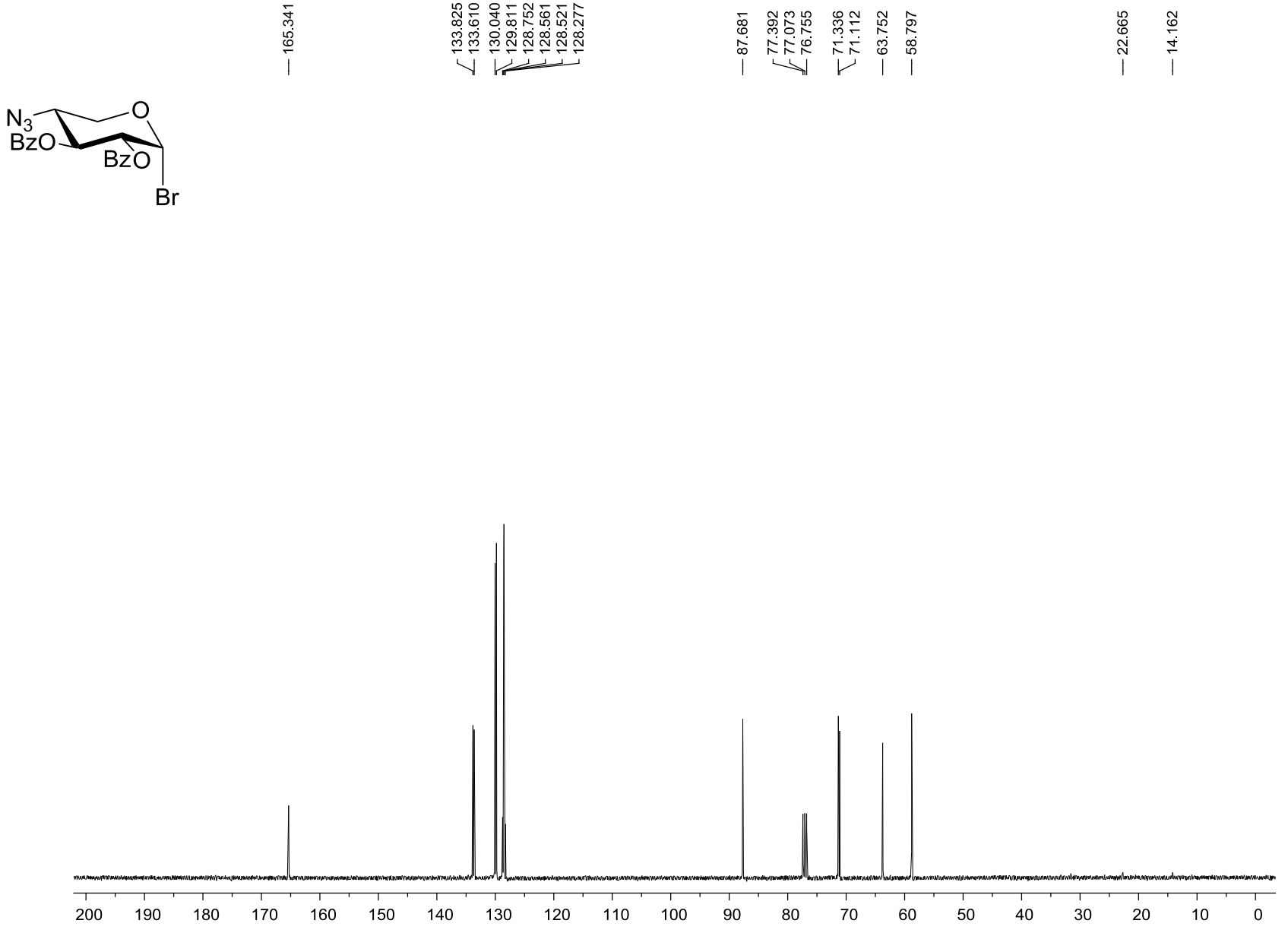
1-bromo-2,3-di-*O*-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (**37**): ^{1}H NMR (CD_3Cl, 400 MHz)



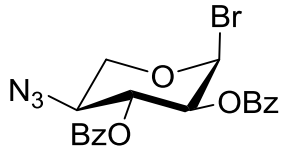




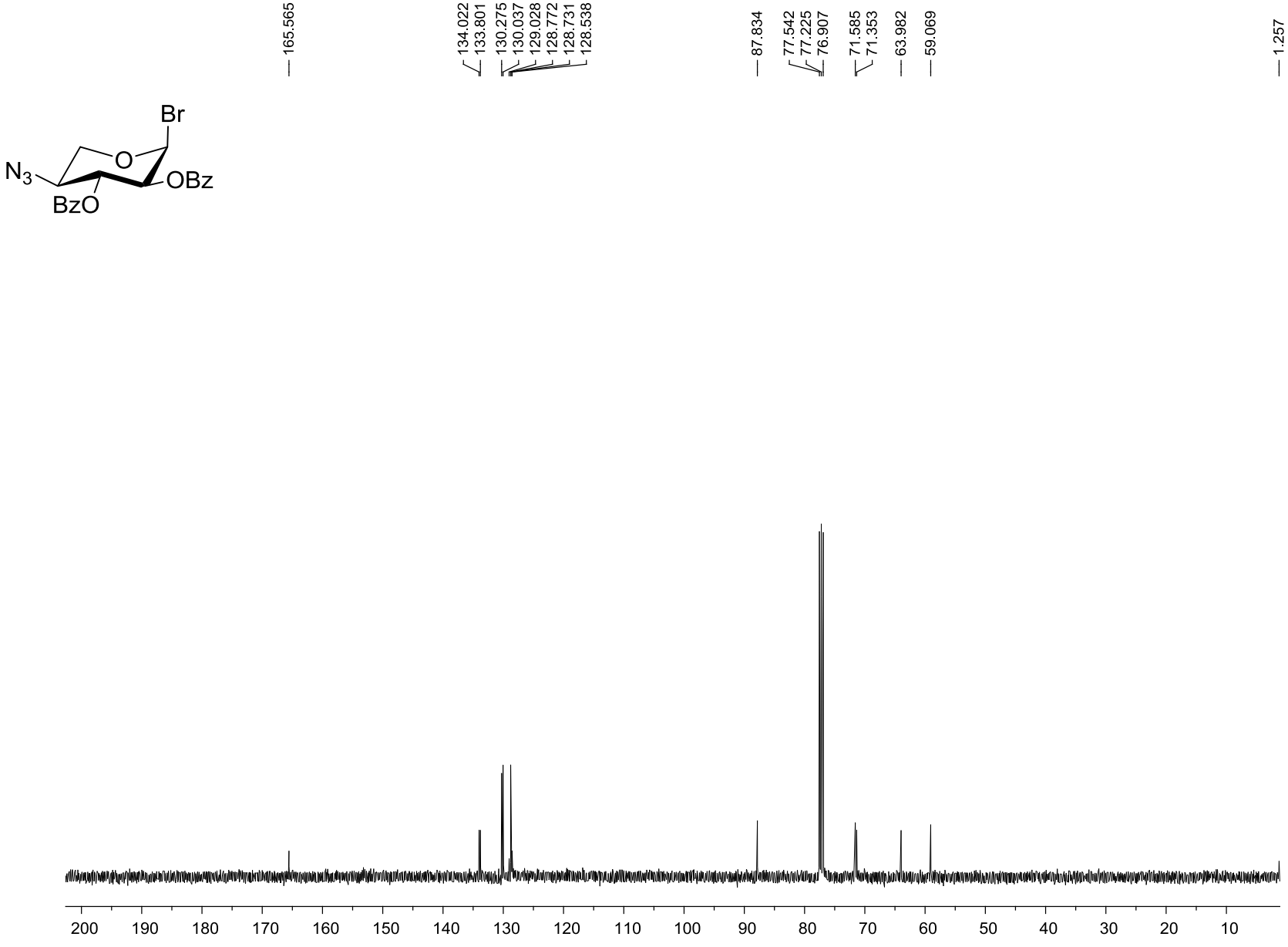
1-bromo-2,3-di-*O*-benzoyl-4-deoxy-4-azido-α-D-xylopyranoside (**37**): ^{13}C NMR (CD_3Cl, 100 MHz)



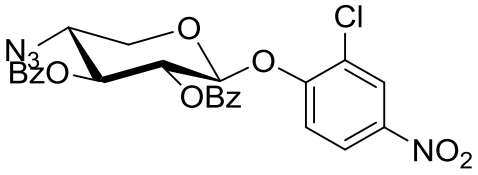
1-bromo-2,3-di-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**38**): ^{1}H NMR ($CDCl_3$, 400 MHz)

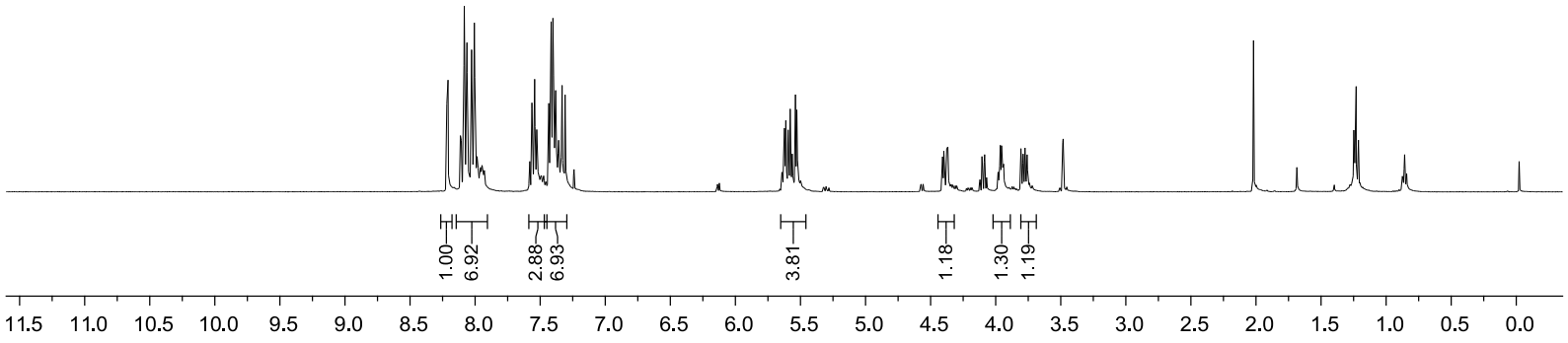


1-bromo-2,3-di-*O*-benzoyl-4-deoxy-4-azido-α-L-xylopyranoside (**38**): ^{13}C NMR ($CDCl_3$, 100 MHz)

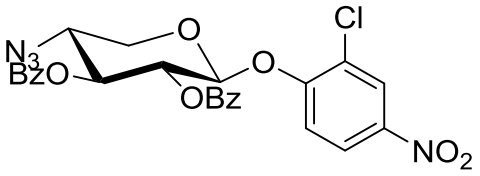


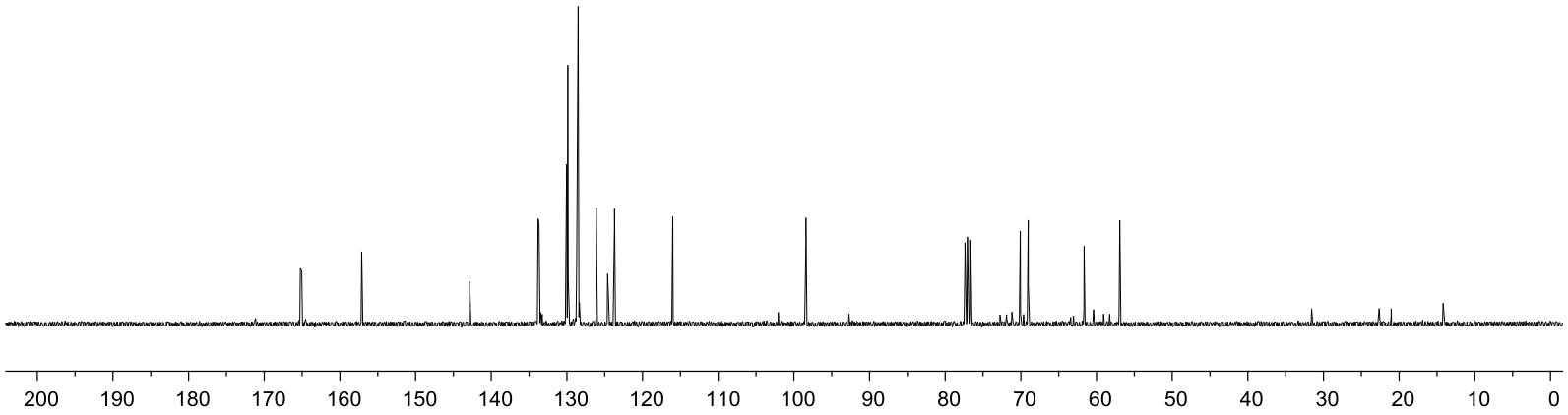
(2-chloro-4-nitrophenyl)-2,3-di-*O*-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (**39**): ^{1}H NMR ($CDCl_3$, 400 MHz)



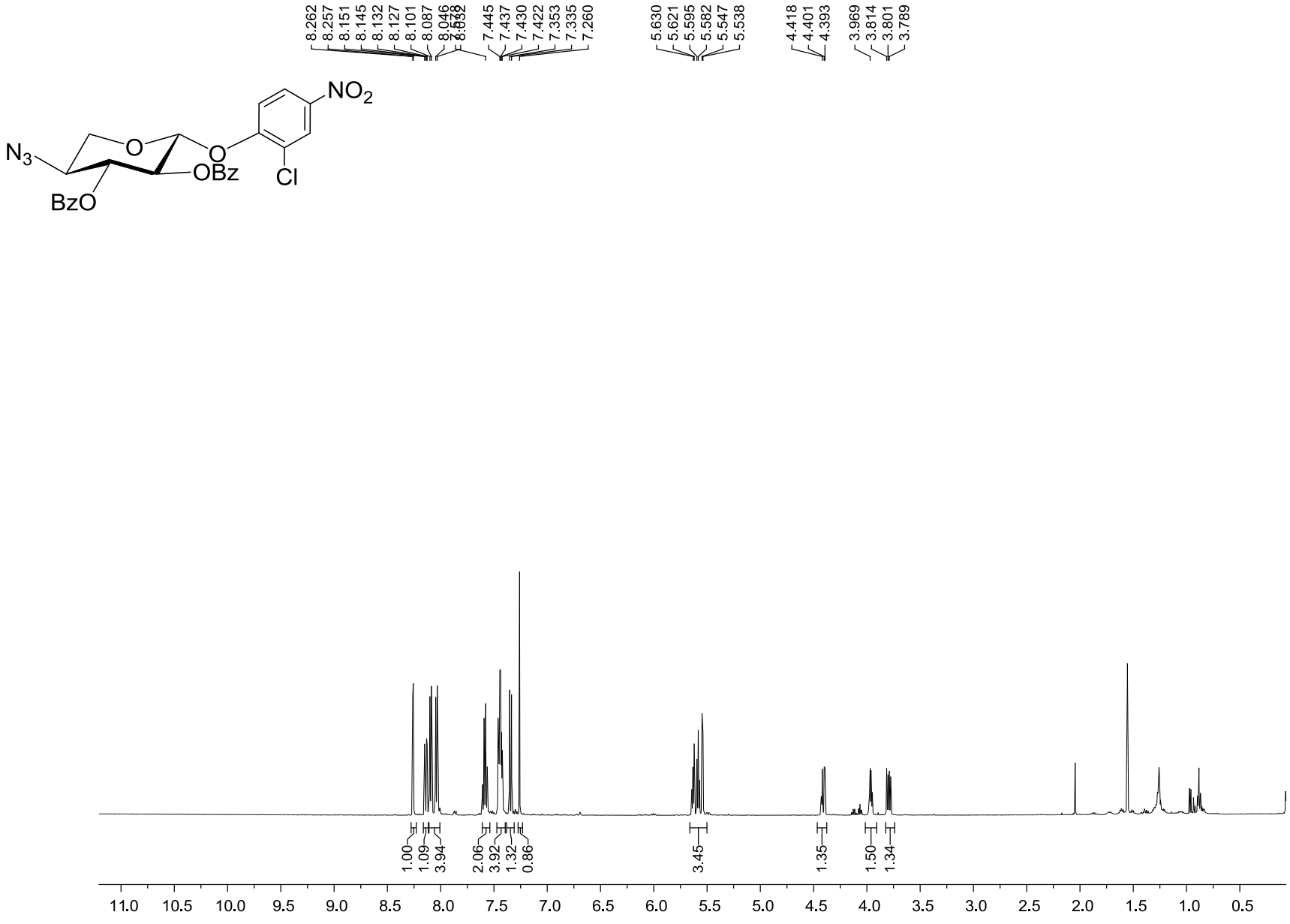


(2-chloro-4-nitrophenyl)-2,3-di-*O*-benzoyl4-deoxy-4-azido-β-D-xylopyranoside (**39**): ^{13}H NMR ($CDCl_3$, 100 MHz)

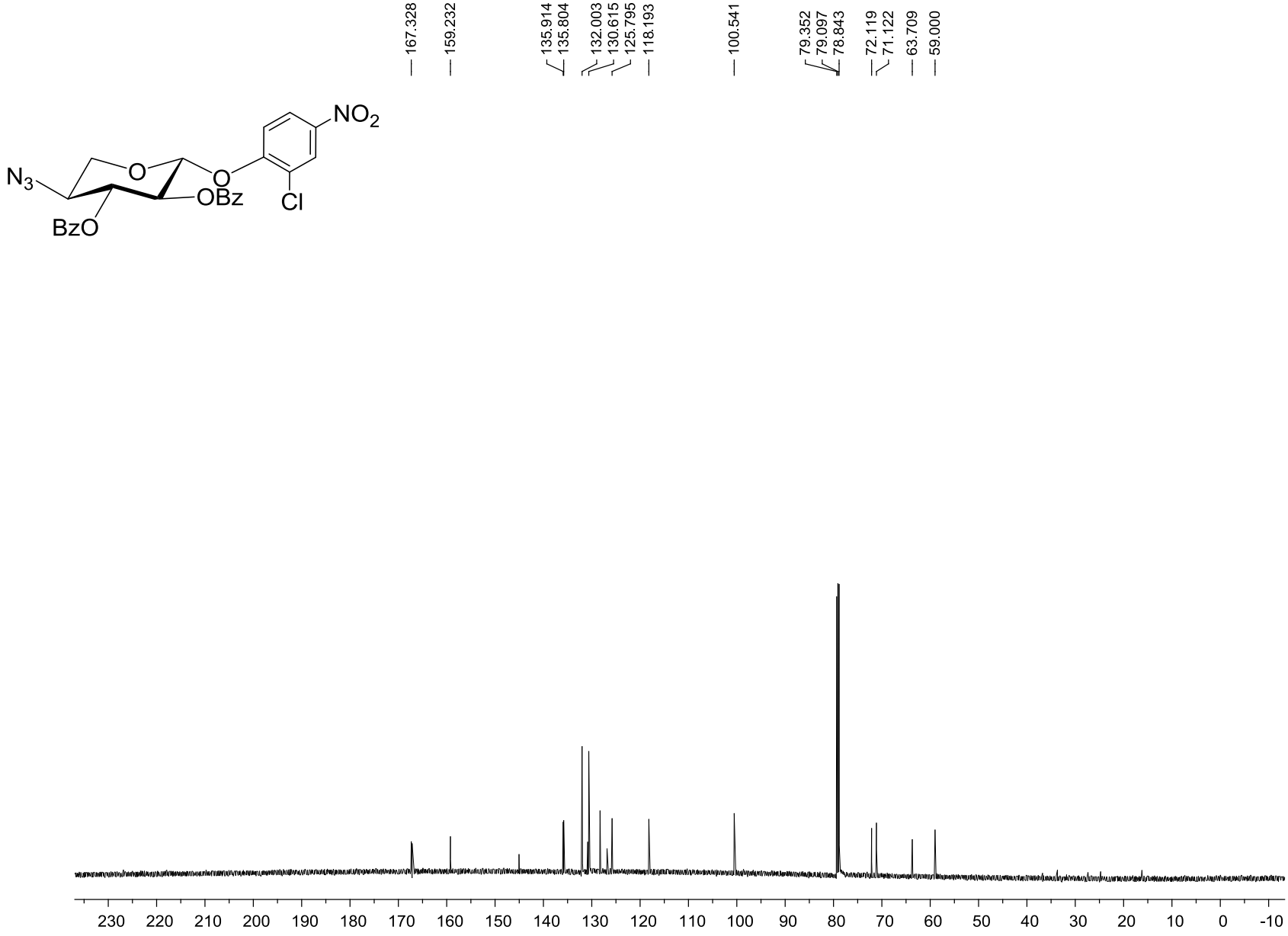




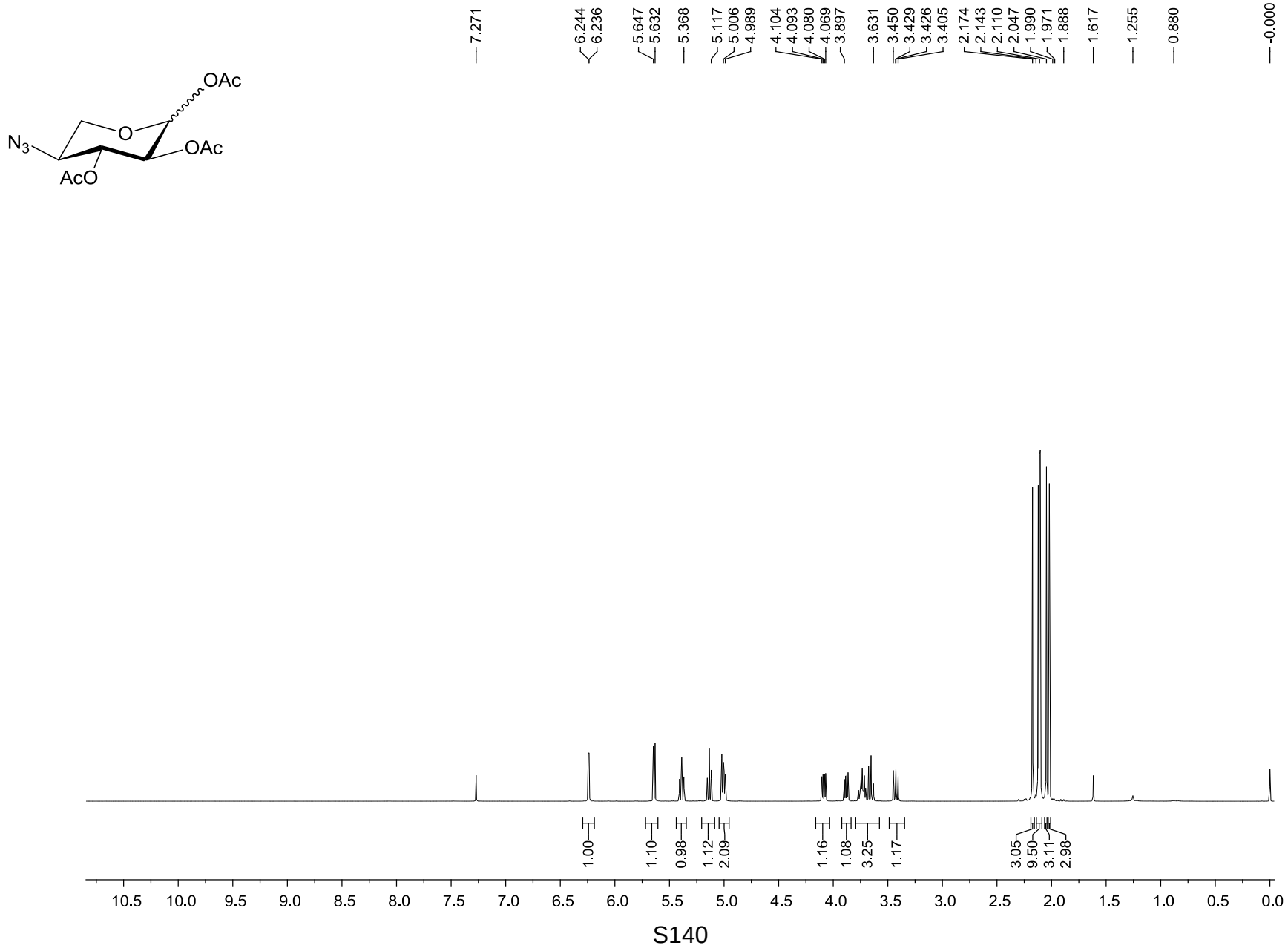
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-*O*-benzoyl-β-L-xylopyranoside (**40**): ^{1}H NMR ($CDCl_3$, 500 MHz)



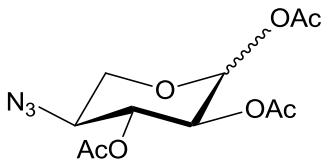
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-*O*-benzoyl-β-L-xylopyranoside (**40**): ^{13}C NMR ($CDCl_3$, 125 MHz)

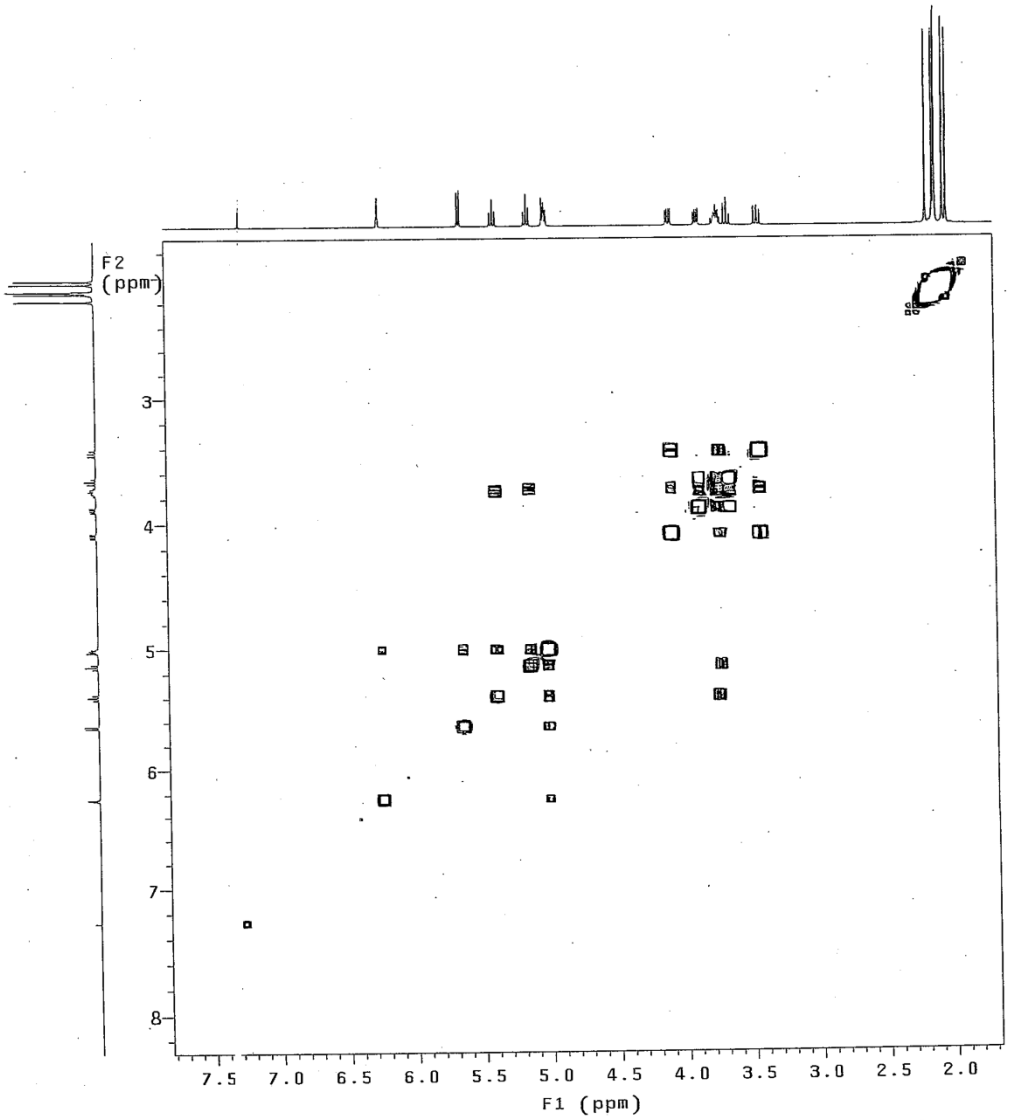


1,2,3-tri-*O*-acetyl-4-deoxy-4-azido-L-xylopyranoside (**41**): ^{1}H NMR ($CDCl_3$, 500 MHz)

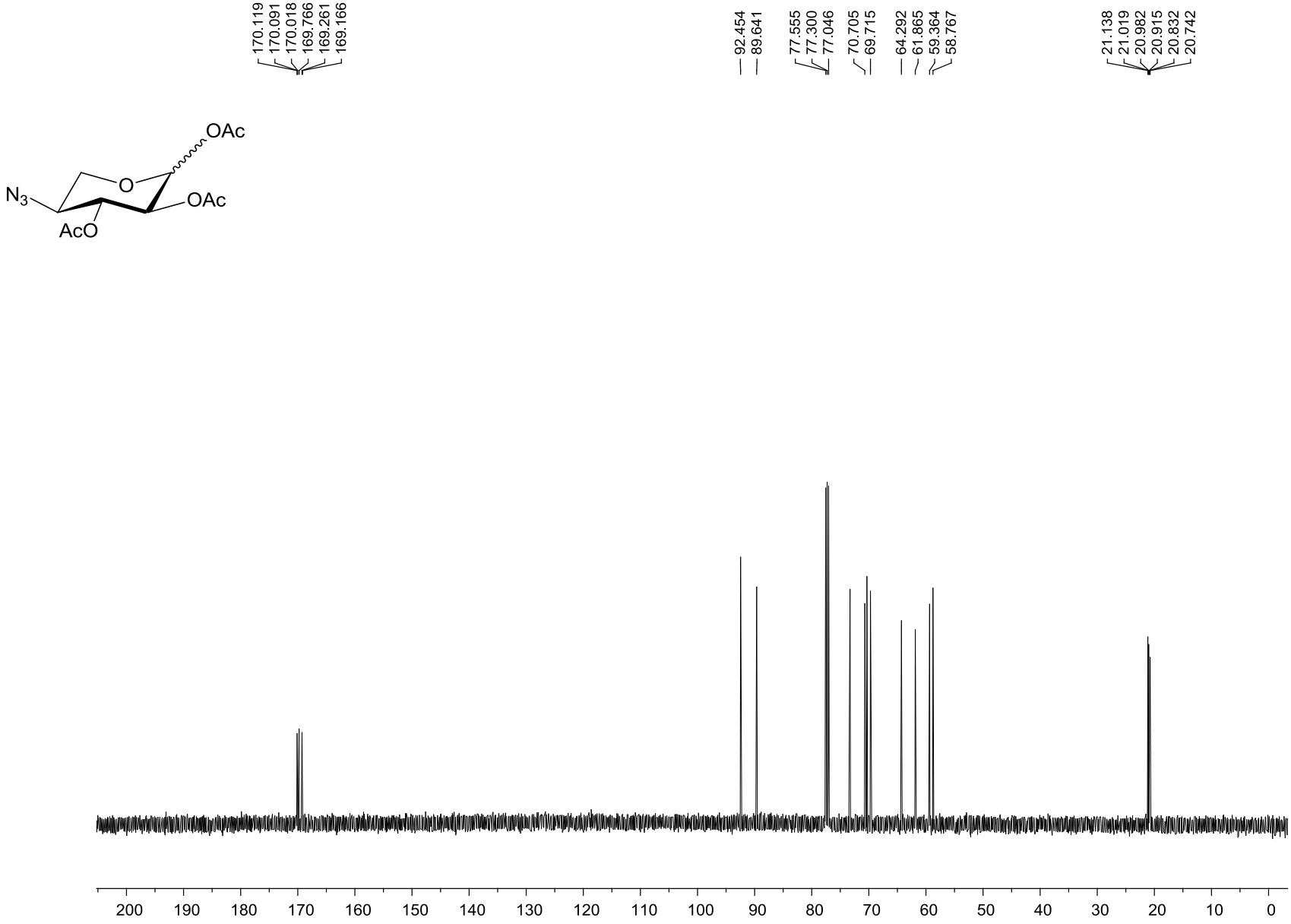


1,2,3-tri-*O*-acetyl-4-deoxy-4-azido-L-xylopyranoside (**41**): gCOSY NMR ($CDCl_3$, 500 MHz)

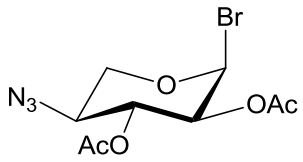




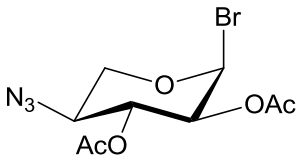
1,2,3-tri-*O*-acetyl-4-deoxy-4-azido-L-xylopyranoside (**41**): ^{13}C NMR ($CDCl_3$, 125 MHz)

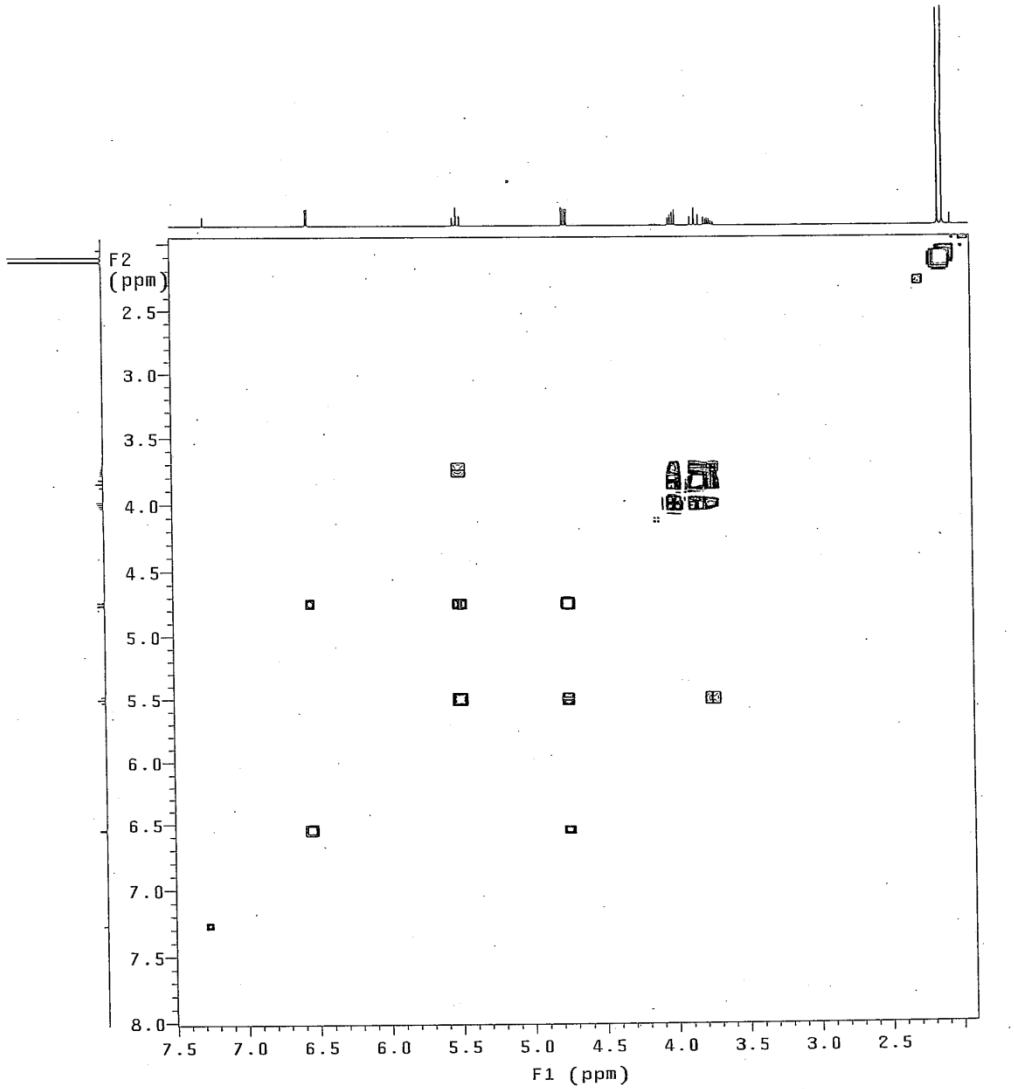


1-bromo-2,3-di-*O*-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (**42**): ^{1}H NMR ($CDCl_3$, 400 MHz)

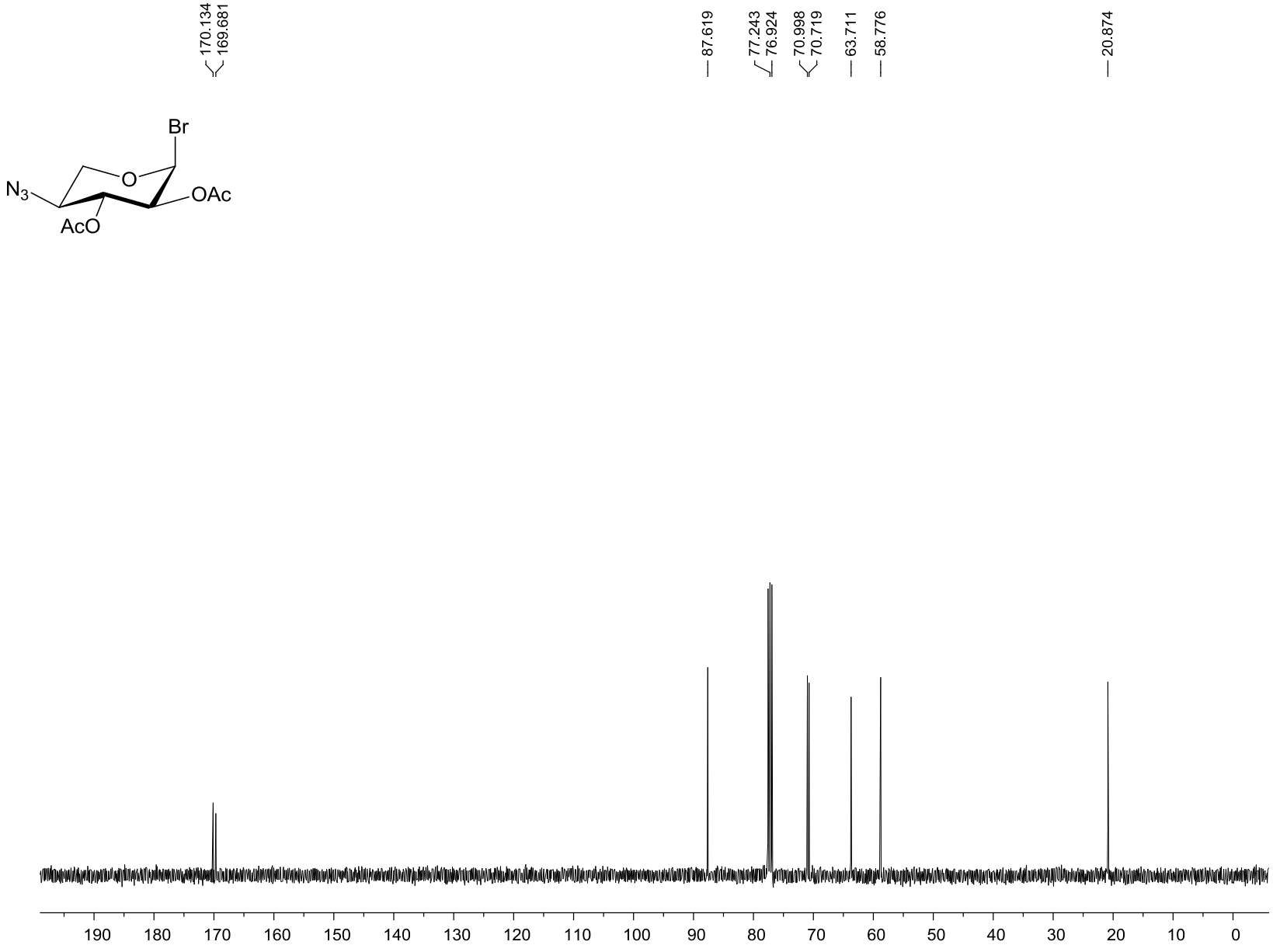


1-bromo-2,3-di-*O*-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (**42**): gCOSY NMR ($CDCl_3$, 400 MHz)

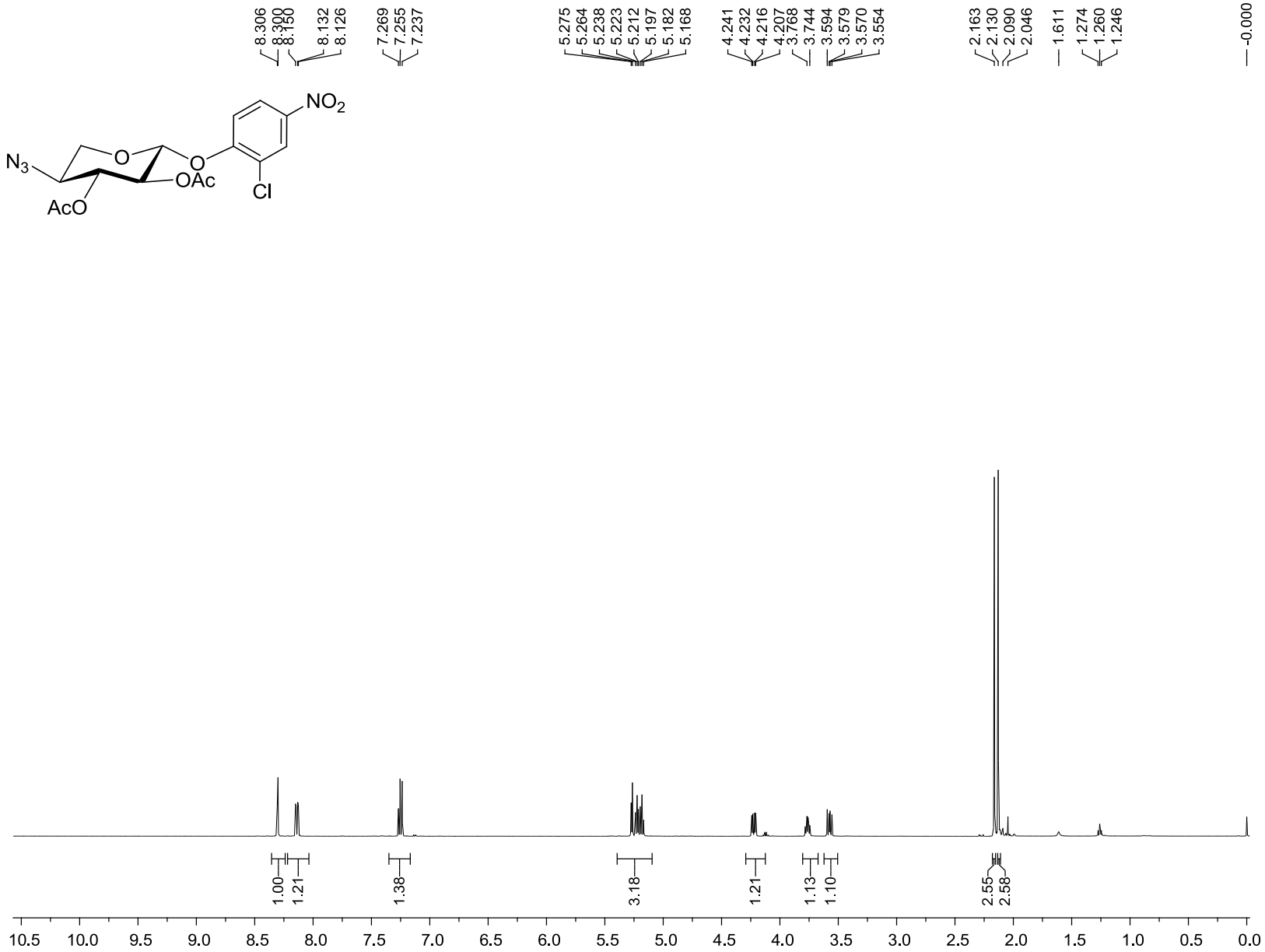




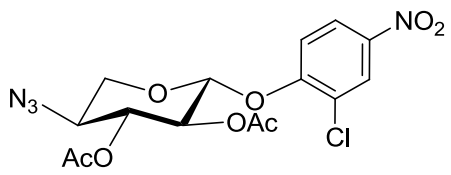
1-bromo-2,3-di-*O*-acetyl-4-deoxy-4-azido-α-L-xylopyranoside (**42**): ^{13}C NMR ($CDCl_3$, 100 MHz)

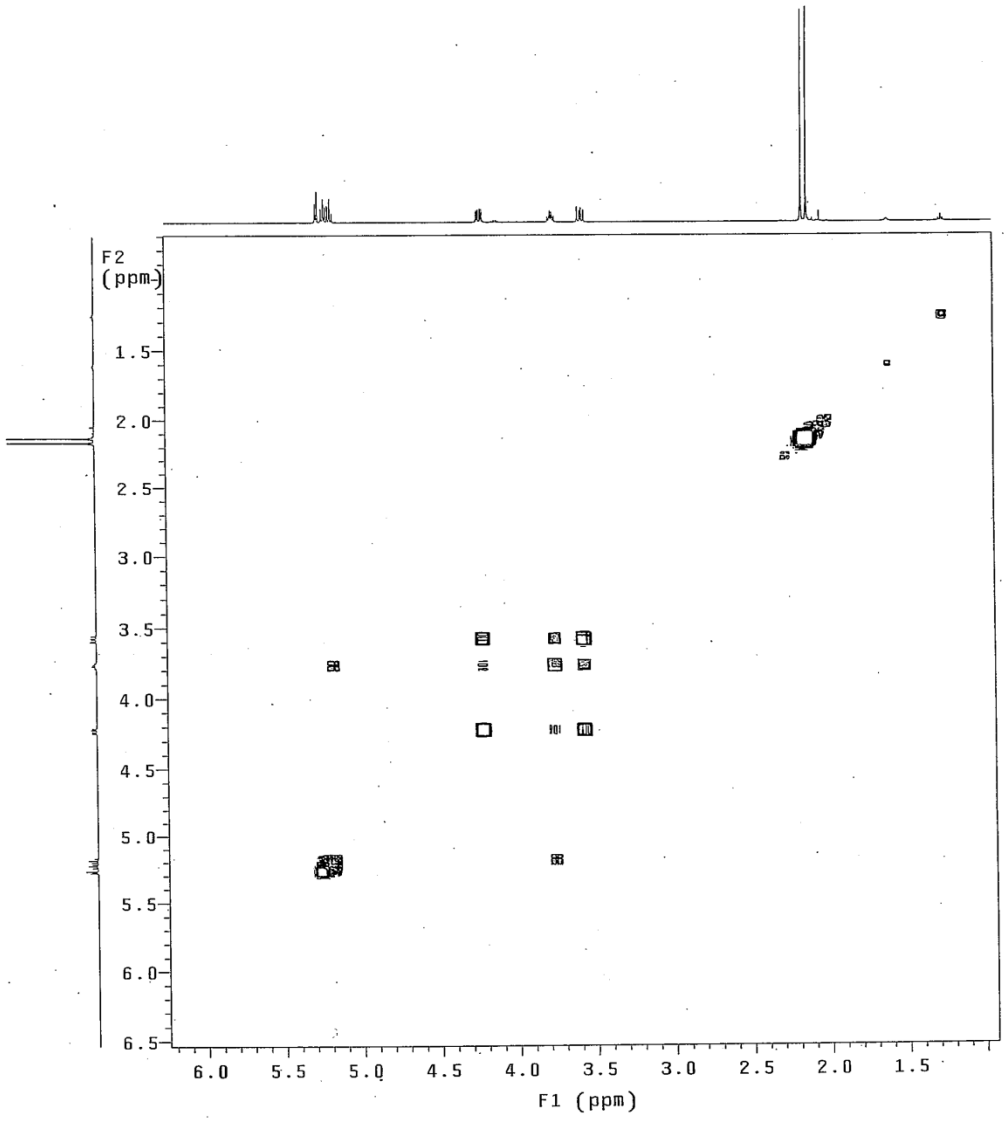


(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-*O*-acetyl-β-L-xylopyranoside (**43**): ^{1}H NMR ($CDCl_3$, 500 MHz)

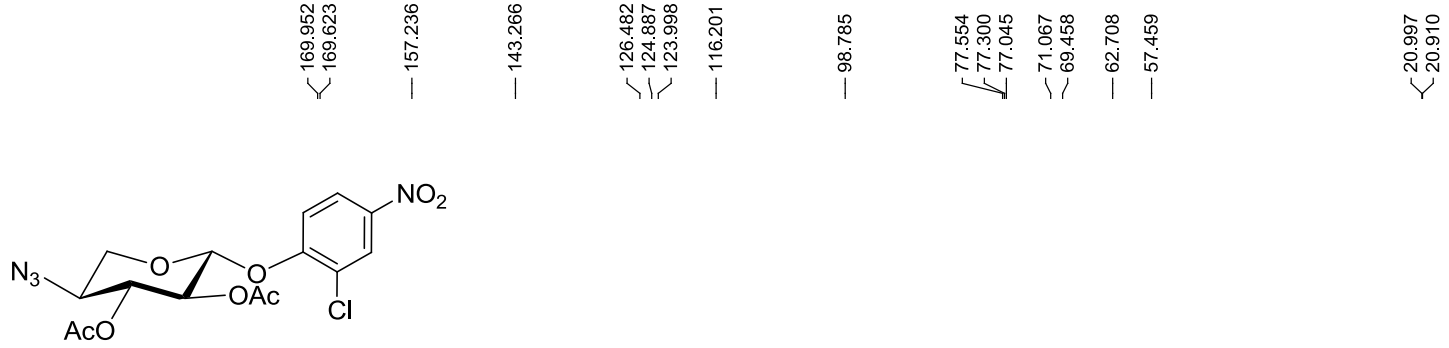


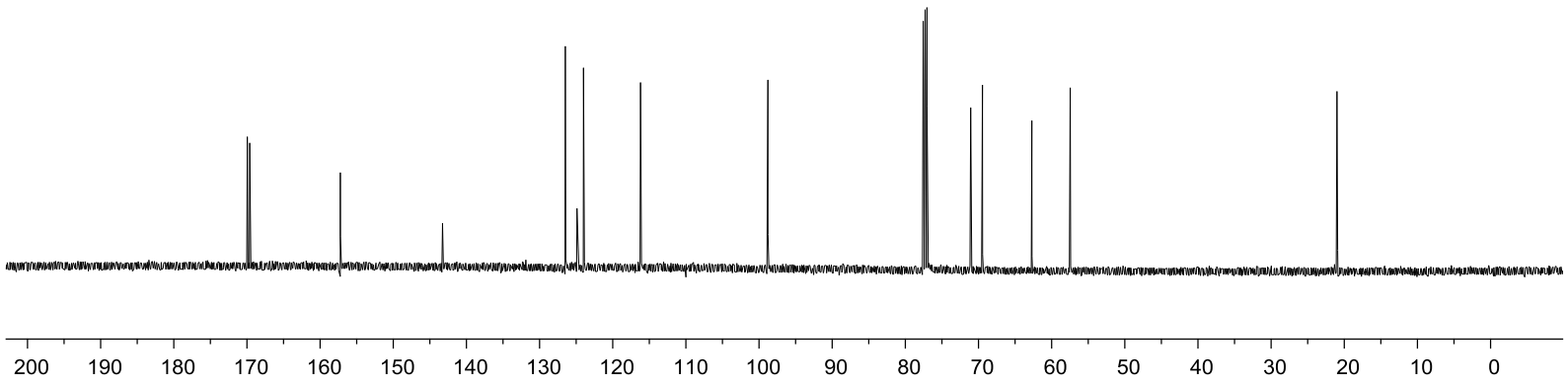
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-*O*-acetyl-β-L-xylopyranoside (**43**): gCOSY NMR ($CDCl_3$, 500 MHz)



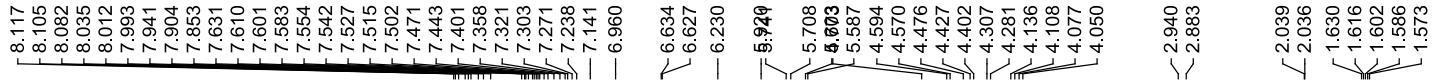


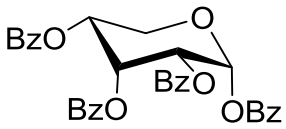
(2-chloro-4-nitrophenyl)-4-deoxy-4-azido-2,3-di-*O*-acetyl-β-L-xylopyranoside (**43**): ^{13}C NMR ($CDCl_3$, 125 MHz)

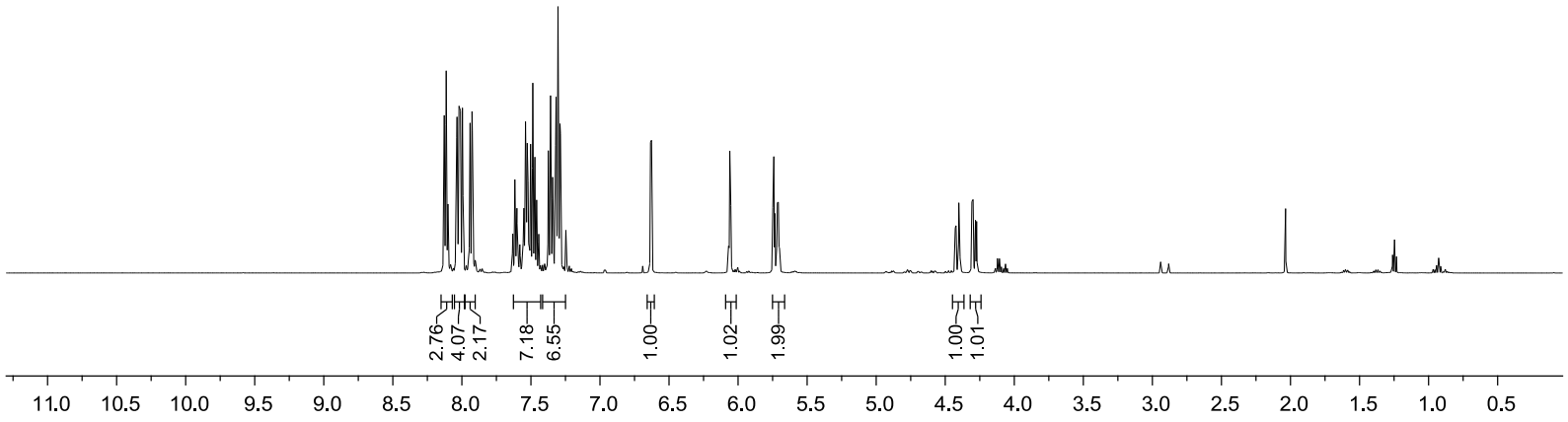




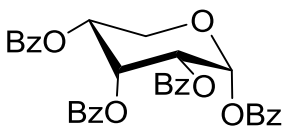
1,2,3,4-tetra-*O*-benzoyl-α-D-ribopyranoside (**44**): ^{1}H NMR ($CDCl_3$, 500 MHz)

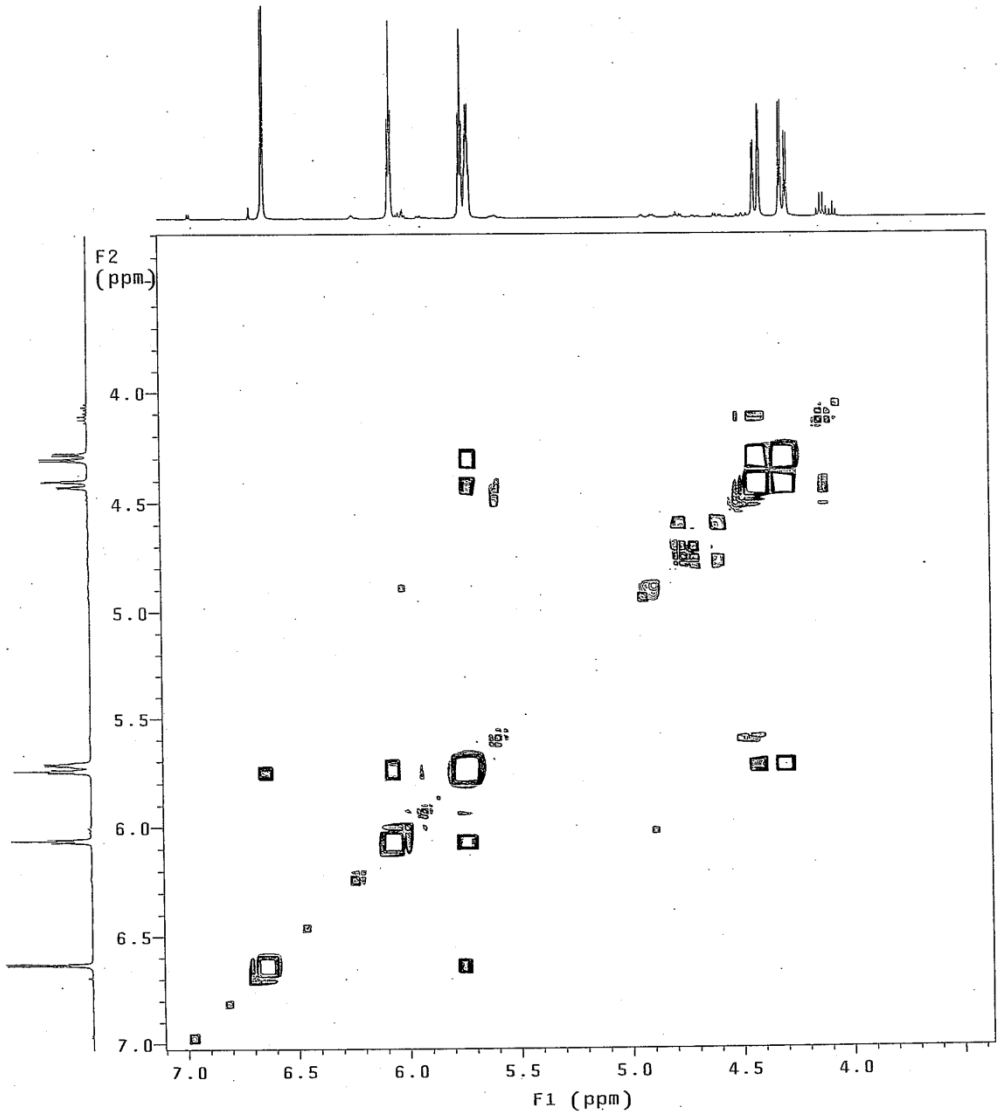






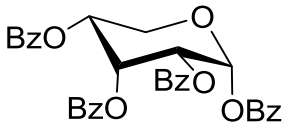
1,2,3,4-tetra-*O*-benzoyl-α-D-ribopyranoside (**44**): gCOSY NMR ($CDCl_3$, 500 MHz)

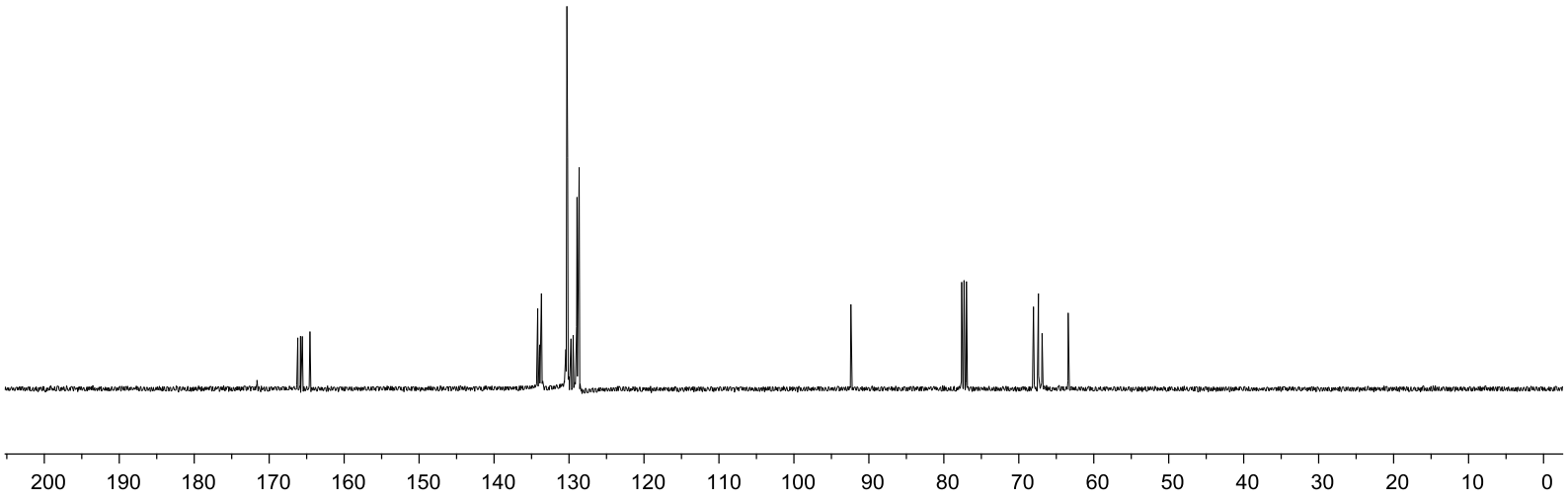




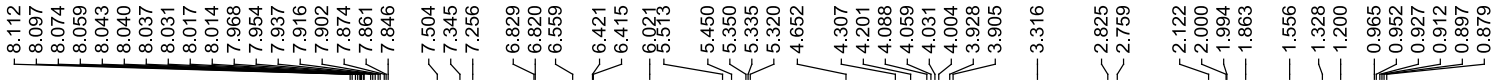
1,2,3,4-tetra-*O*-benzoyl-α-D-ribopyranoside (**44**): ^{13}C NMR ($CDCl_3$, 100 MHz)

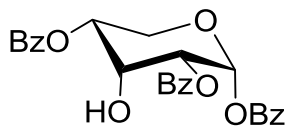
171.624
166.184
165.817
165.575
164.561
134.178
133.923
133.682
133.649
133.528
130.283
130.027
129.577
129.419
128.935
128.691
128.615
92.397
77.622
77.304
76.986
67.381
66.899
63.415

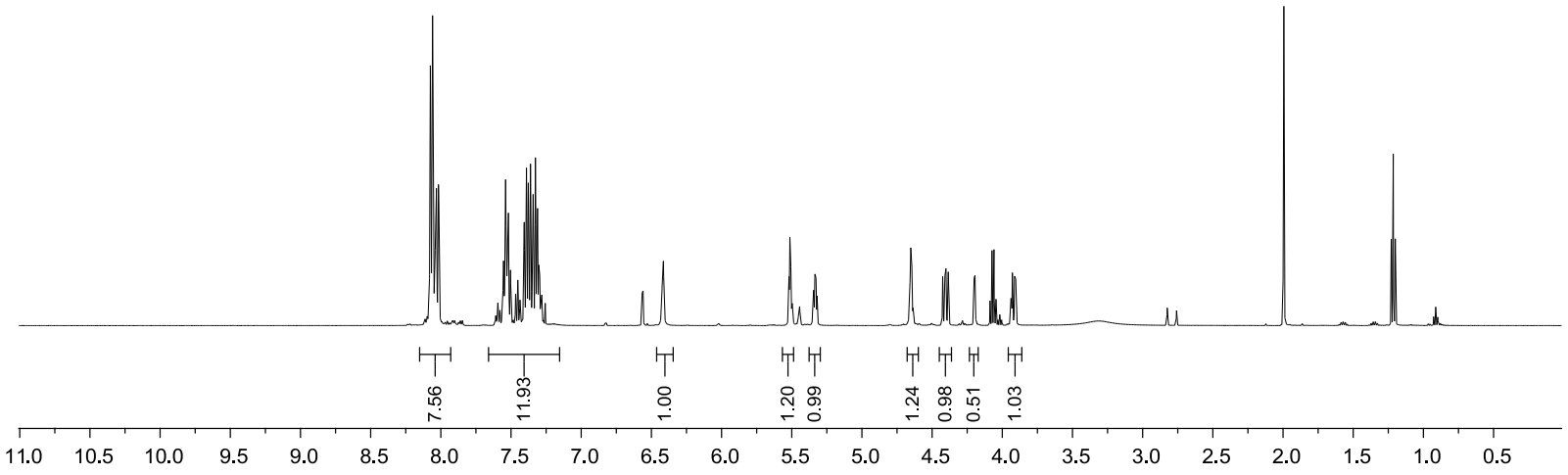




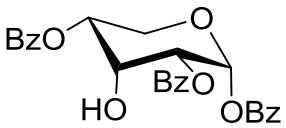
1,2,4-tri-*O*-benzoyl-α-D-ribopyranoside (**45a**): ^{1}H NMR ($CDCl_3$, 500 MHz)

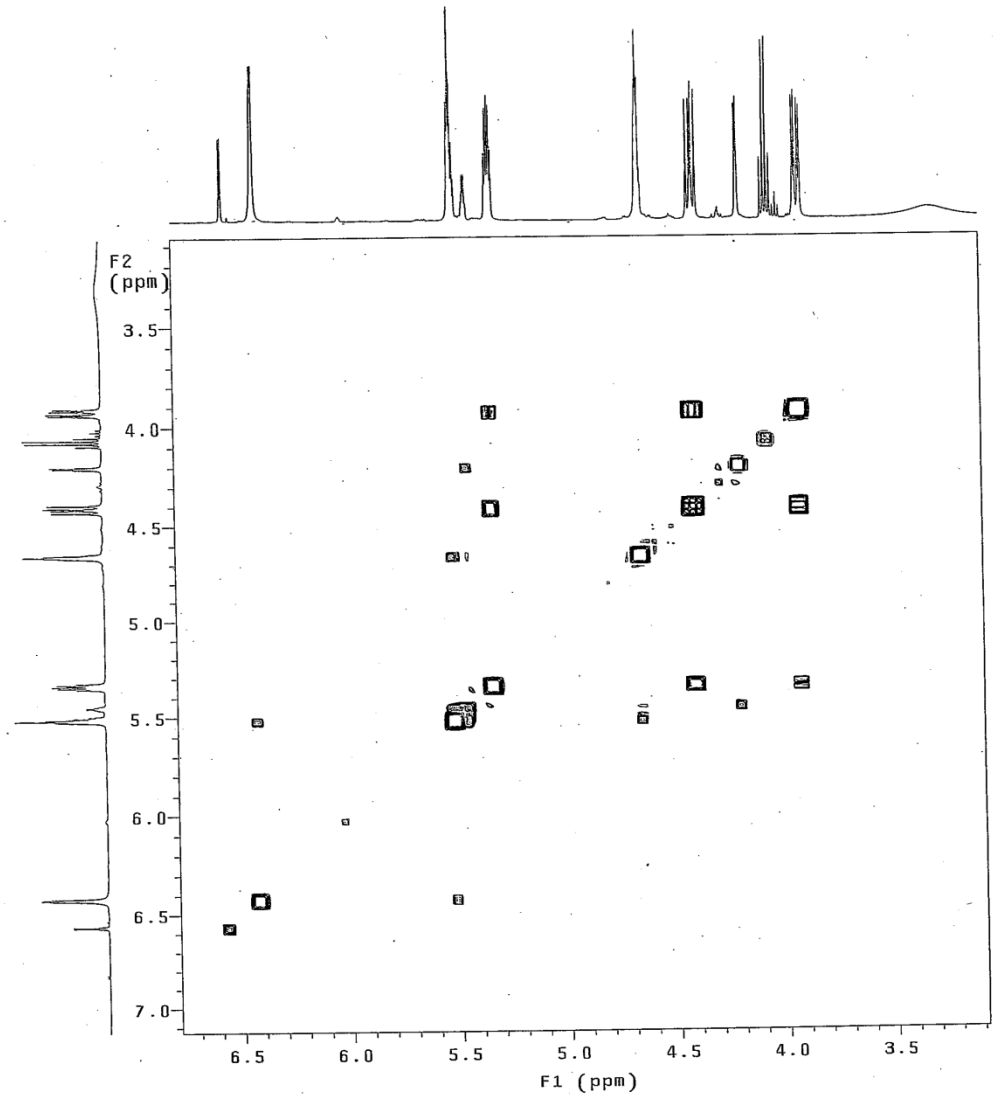






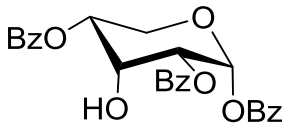
1,2,4-tri-*O*-benzoyl-α-D-ribopyranoside (**45a**): gCOSY NMR ($CDCl_3$, 500 MHz)

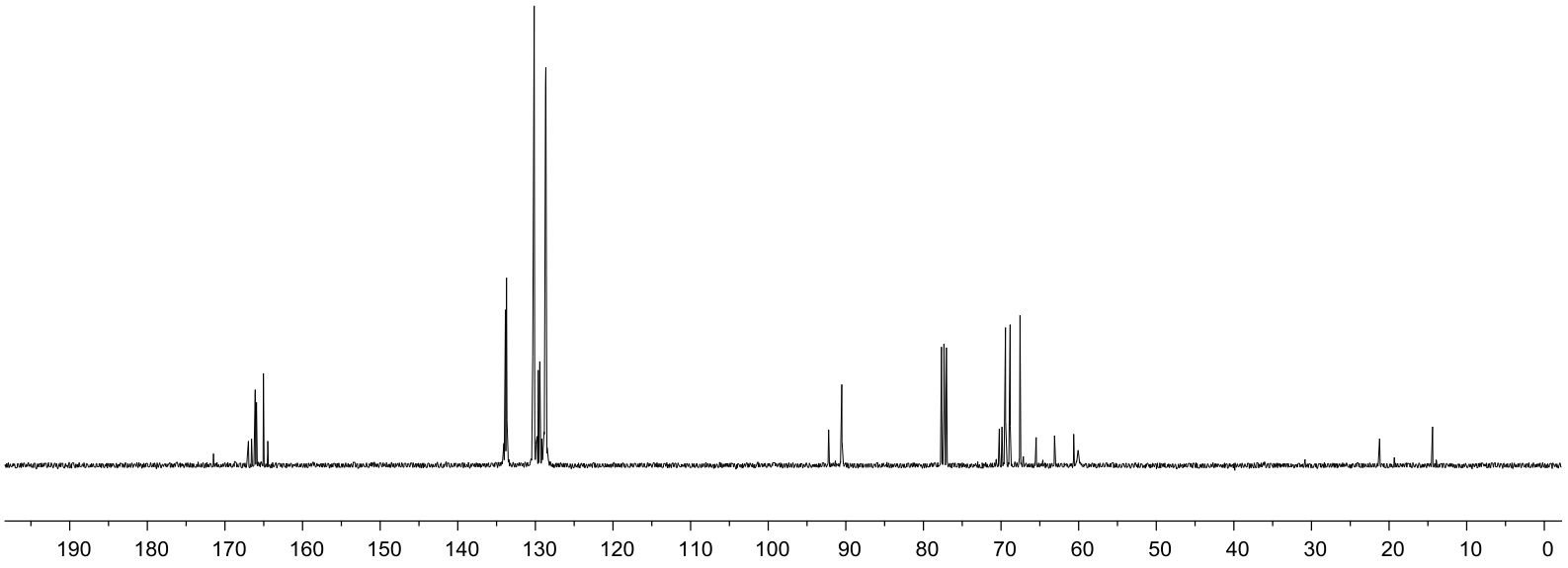




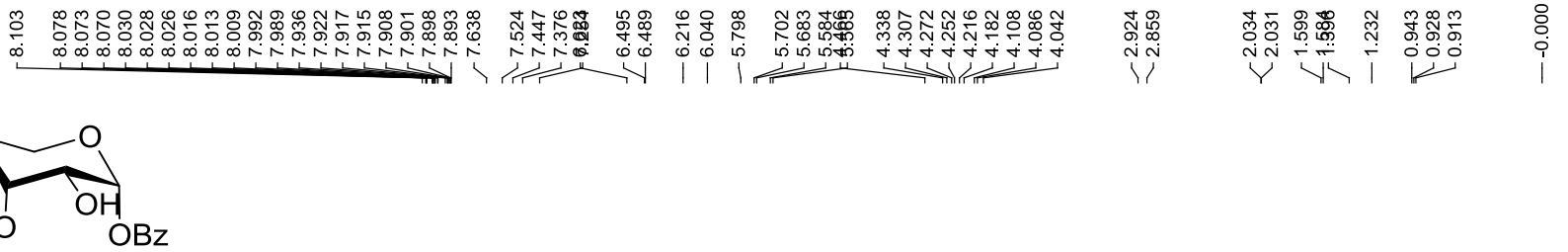
1,2,4-tri-*O*-benzoyl-α-D-ribopyranoside (**45a**): ^{13}C NMR ($CDCl_3$, 100 MHz)

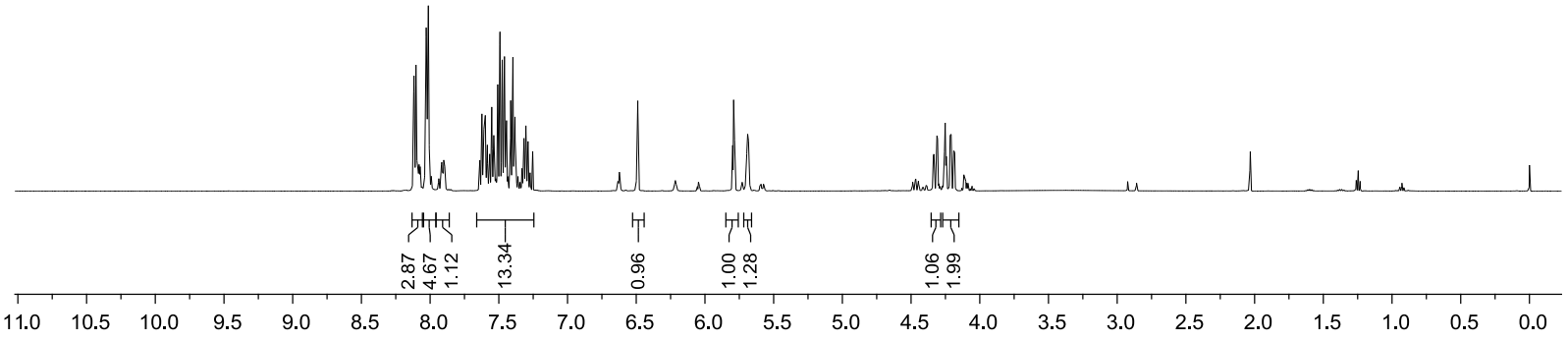
171.480
166.572
166.104
165.934
165.042
164.485
134.051
133.861
133.718
133.675
133.606
130.153
129.782
129.478
129.413
128.870
128.690
128.627
128.491
92.216
90.521
77.677
77.359
77.040
70.225
69.881
69.427
68.830
67.554
67.126
65.474
63.108
60.641
60.079
21.225
19.331
14.396



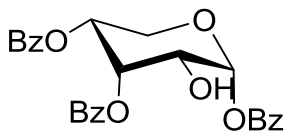


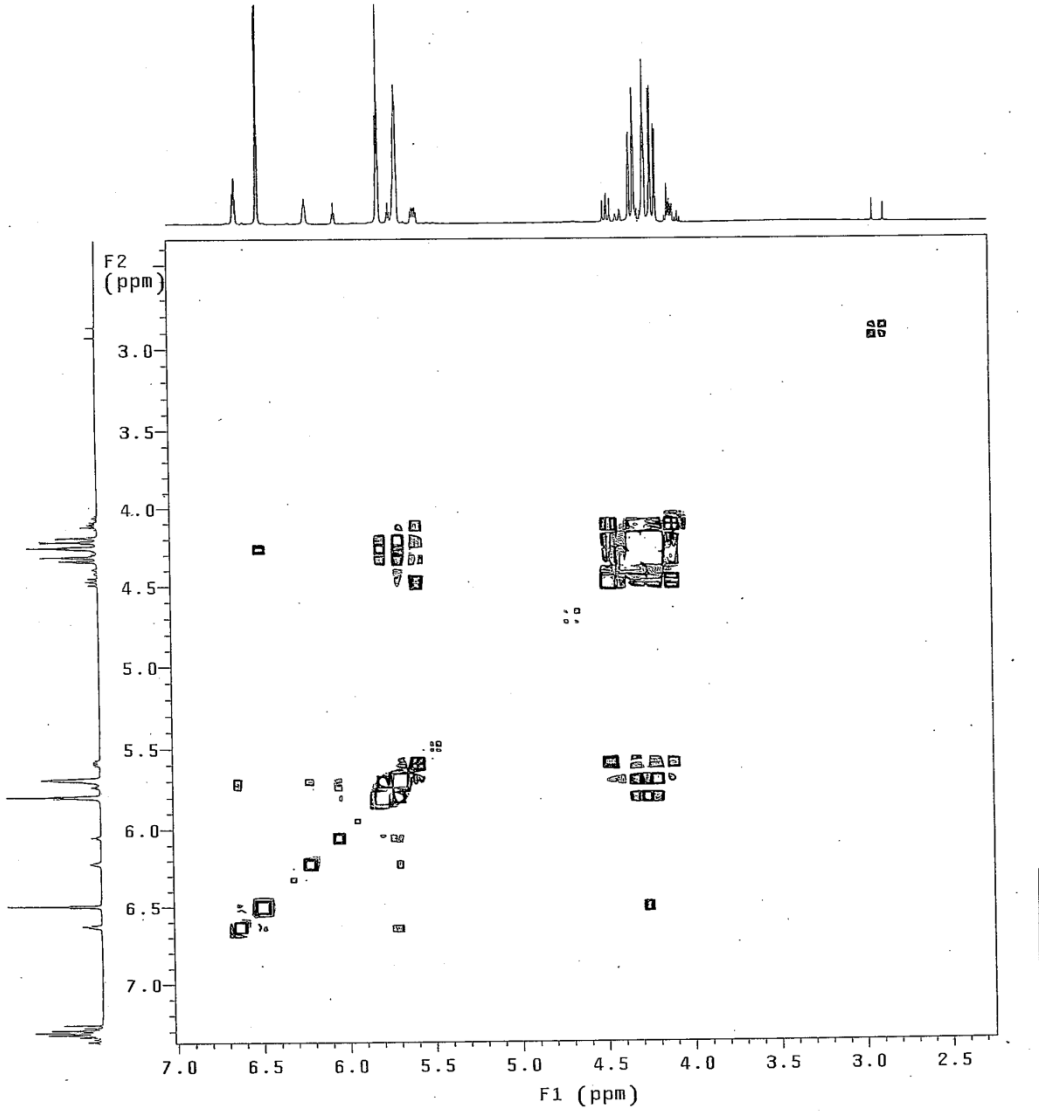
1,3,4-tri-*O*-benzoyl-α-D-ribopyranoside (**45b**): ^{1}H NMR ($CDCl_3$, 500 MHz)



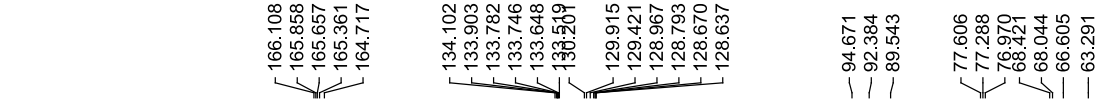


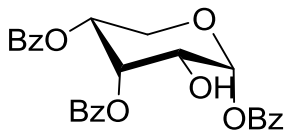
1,3,4-tri-*O*-benzoyl-α-D-ribopyranoside (**45b**): gCOSY NMR ($CDCl_3$, 500 MHz)

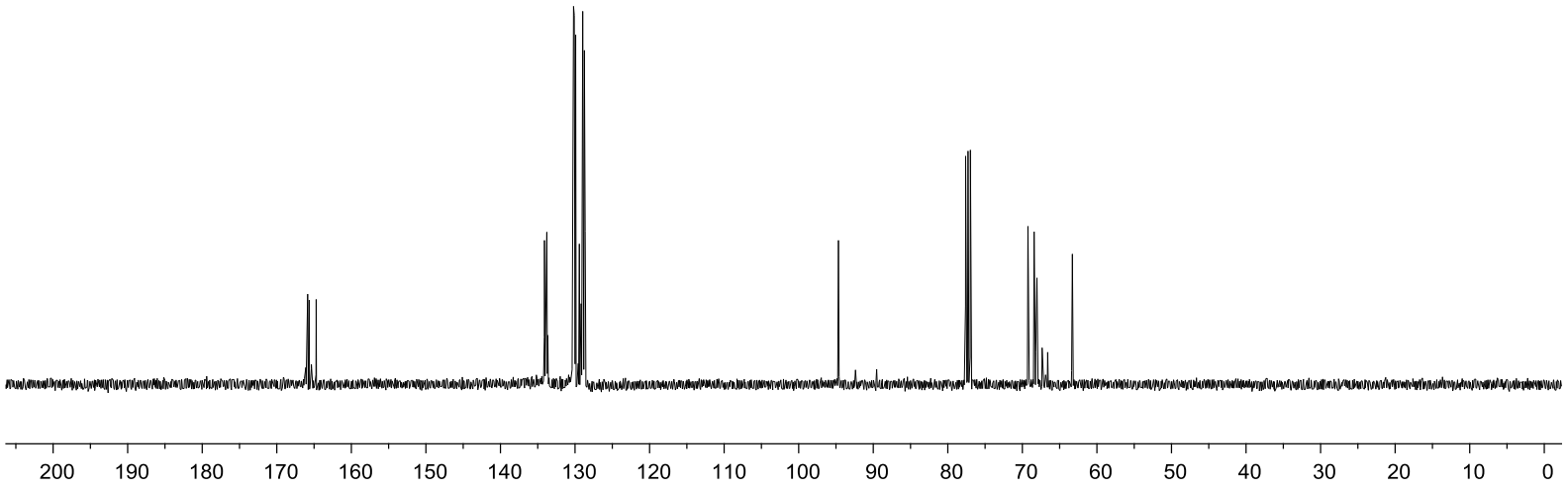




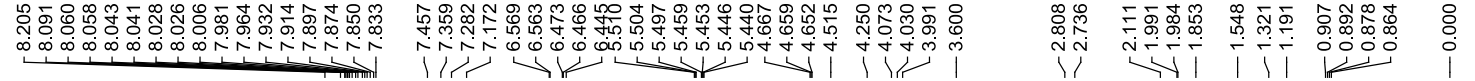
1,3,4-tri-*O*-benzoyl-α-D-ribopyranoside (**45b**): ^{13}C NMR ($CDCl_3$, 125 MHz)

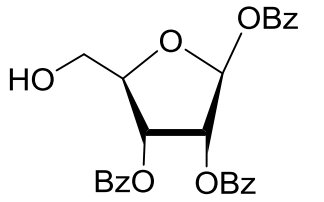


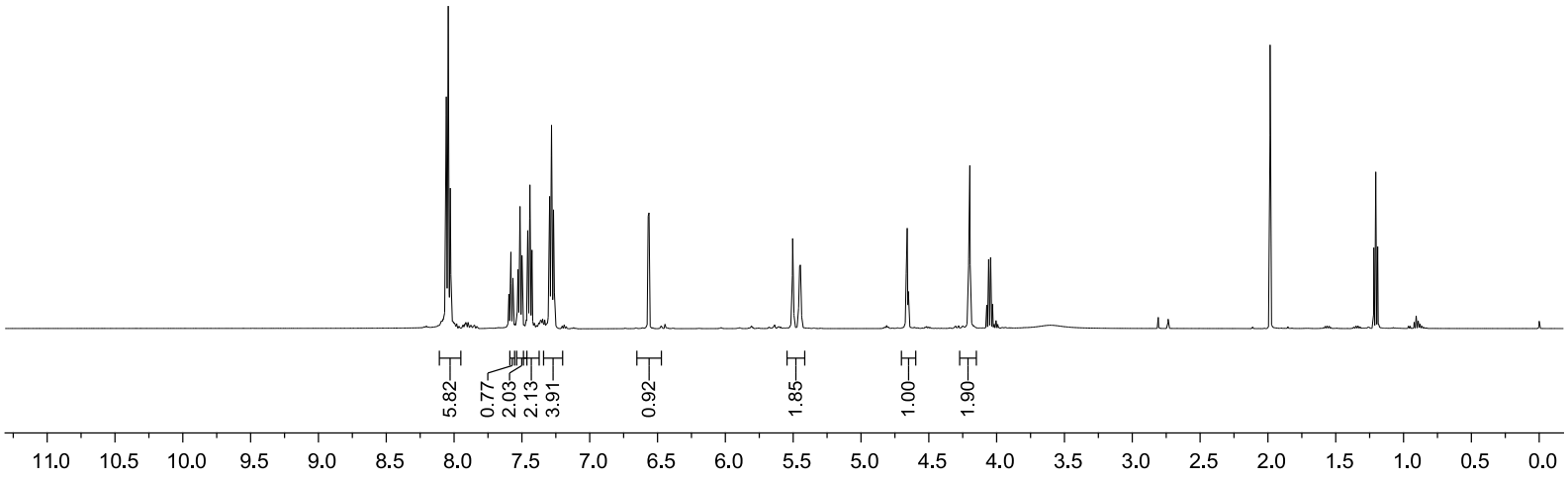




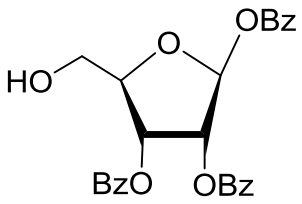
1,2,3-tri-*O*-benzoyl-α-D-ribofuranoside (**45c**): ^{1}H NMR ($CDCl_3$, 500 MHz)

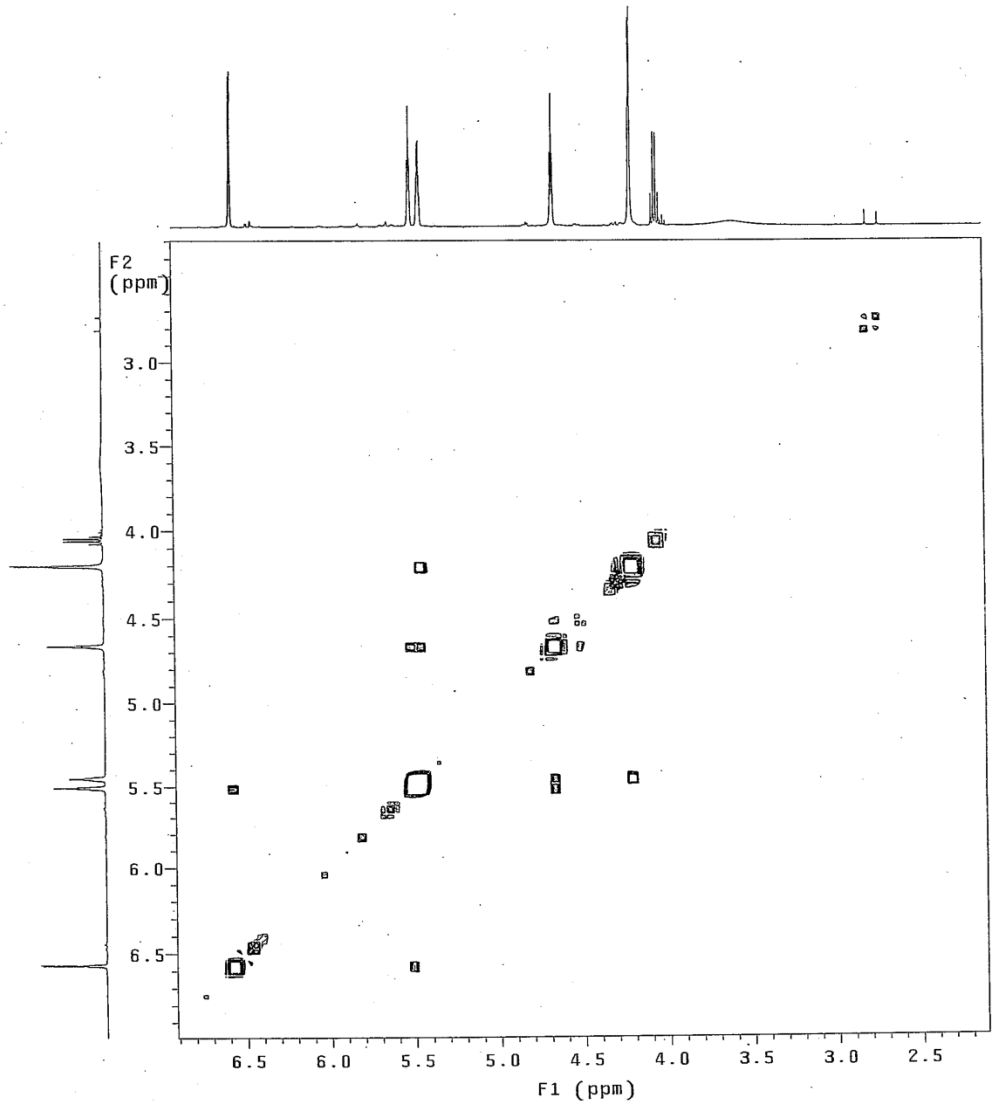




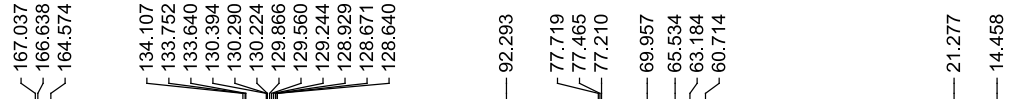


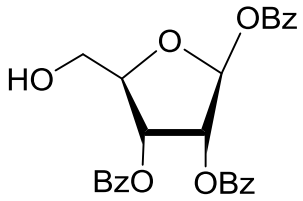
1,2,3-tri-*O*-benzoyl-α-D-ribofuranoside (**45c**): gCOSY NMR ($CDCl_3$, 500 MHz)

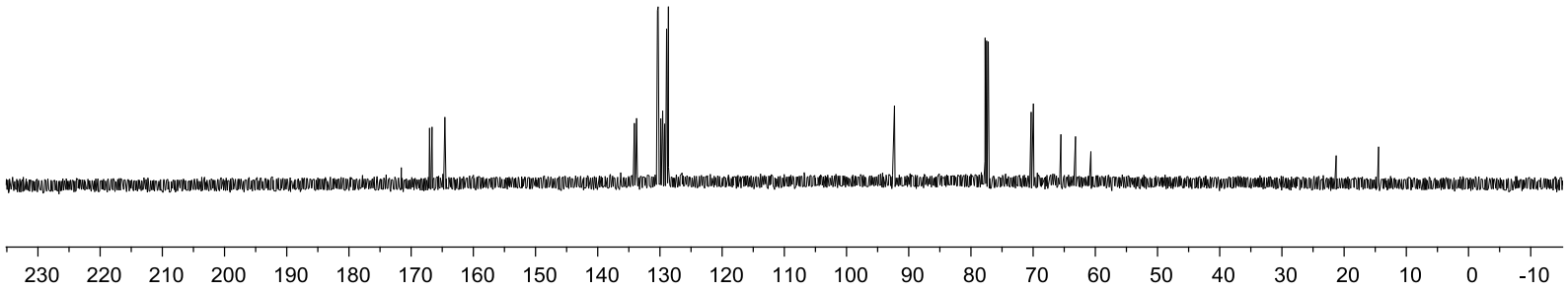




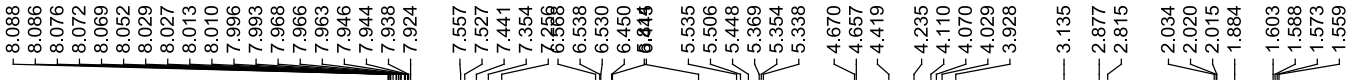
1,2,3-tri-*O*-benzoyl-α-D-ribofuranoside (**45c**): ^{13}C NMR ($CDCl_3$, 125 MHz)

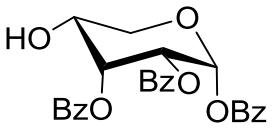


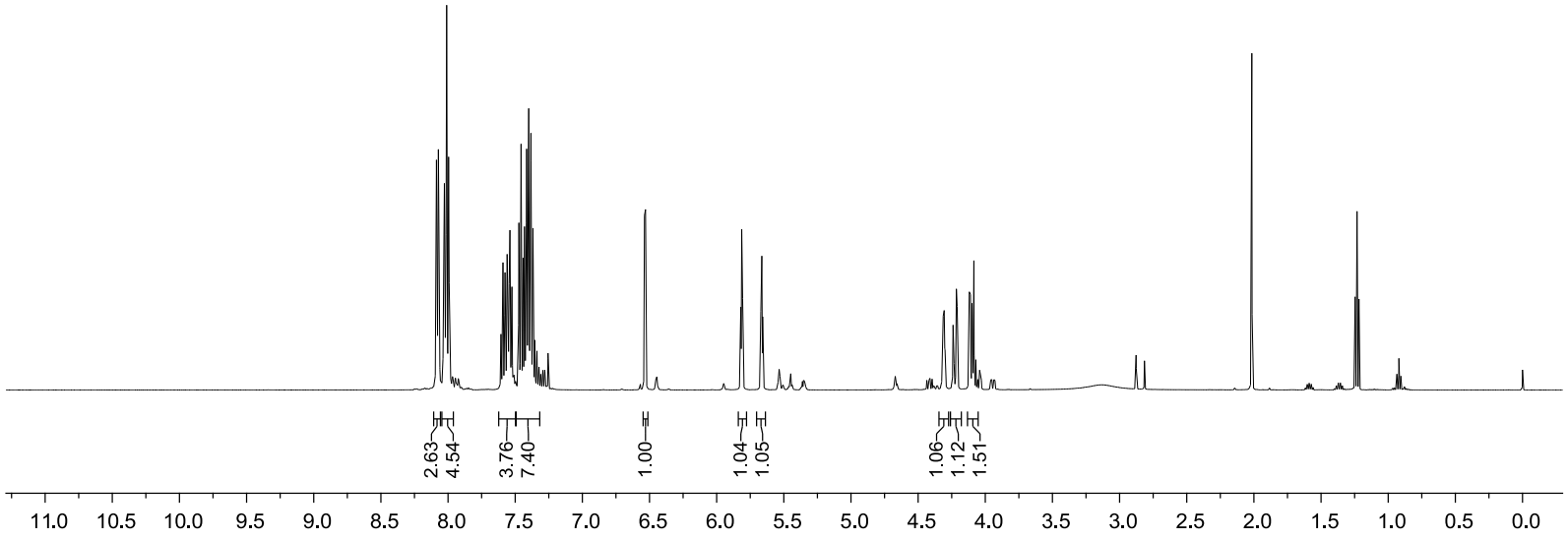




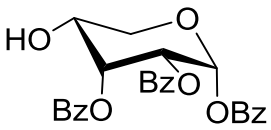
1,2,3-tri-*O*-benzoyl-α-D-ribopyranoside (**45d**): ^{1}H NMR ($CDCl_3$, 500 MHz)

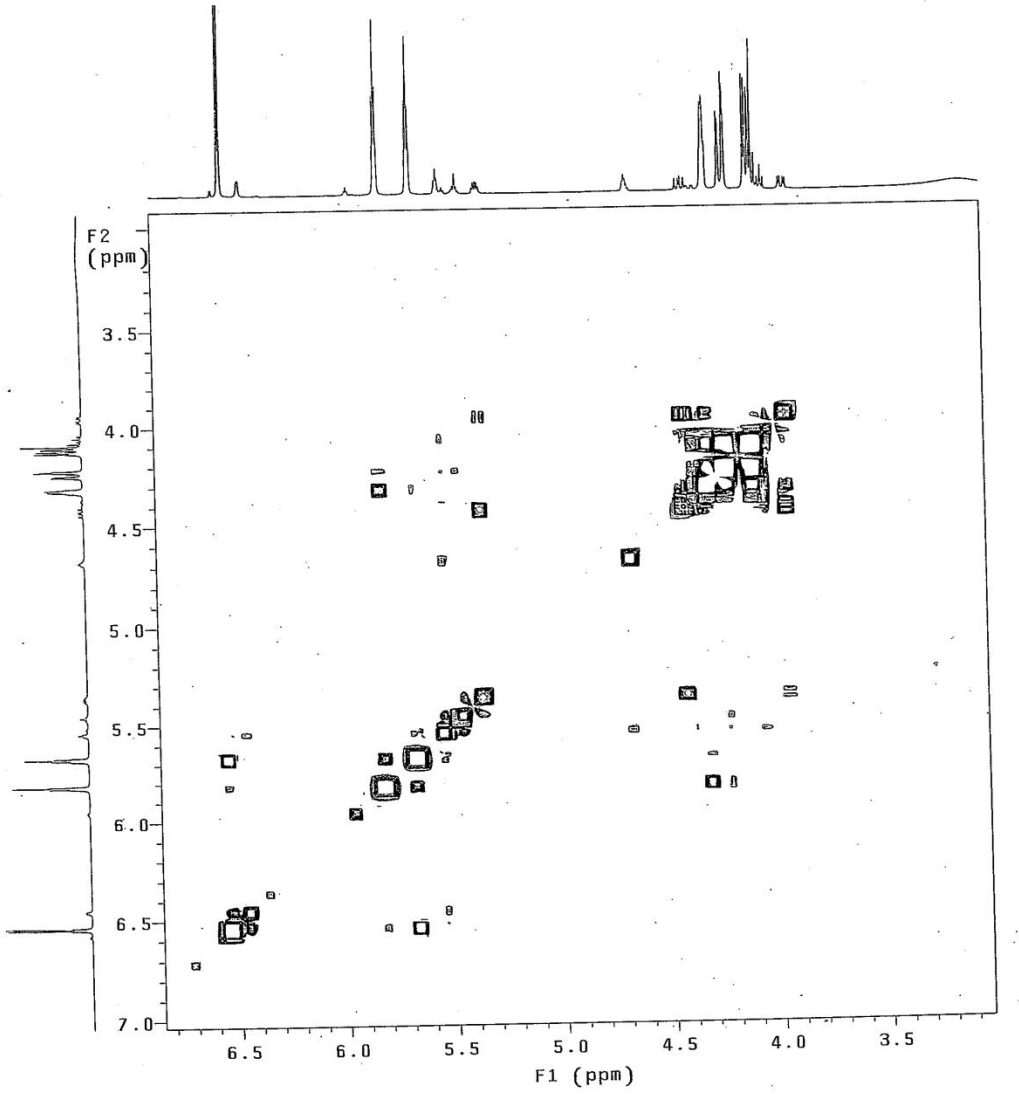




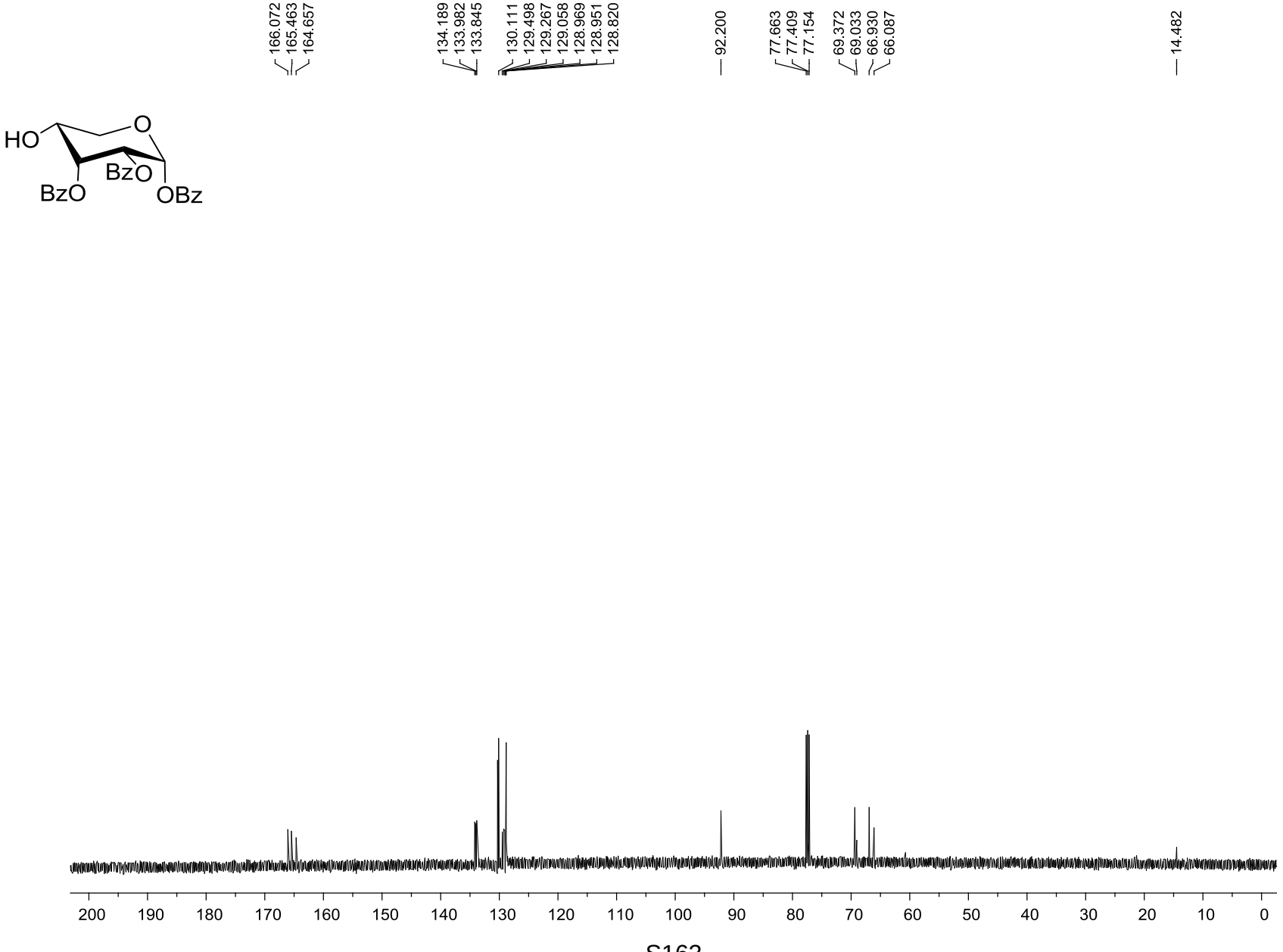


1,2,3-tri-*O*-benzoyl-α-D-ribopyranoside (**45d**): gCOSY NMR ($CDCl_3$, 125 MHz)

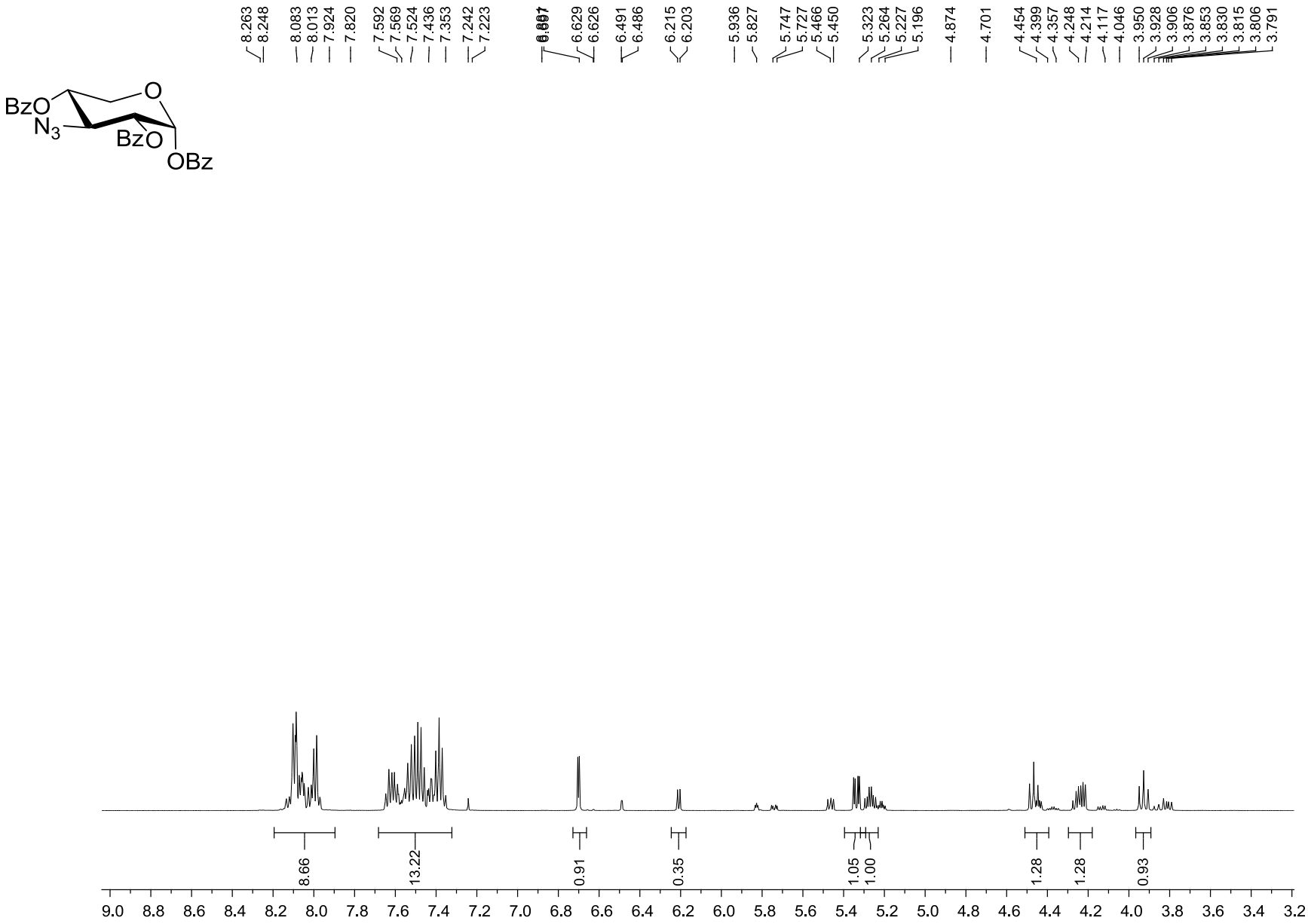




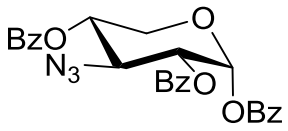
1,2,3-tri-*O*-benzoyl-α-D-ribopyranoside (**45d**): ^{13}C NMR ($CDCl_3$, 125 MHz)

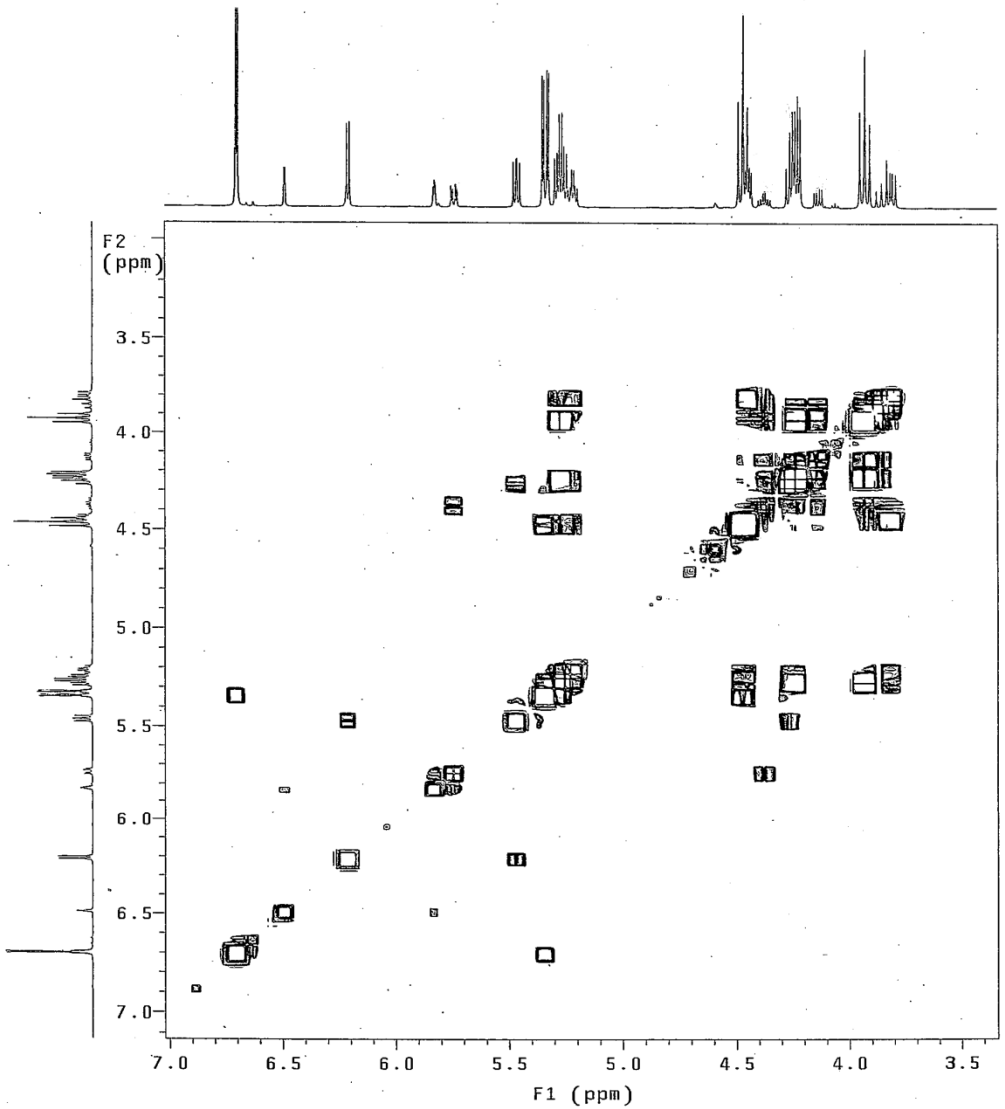


3-deoxy-3-azido-1,2,4-tri-*O*-benzoyl-D-xylopyranoside (**46**): ^{1}H NMR ($CDCl_3$, 500 MHz)

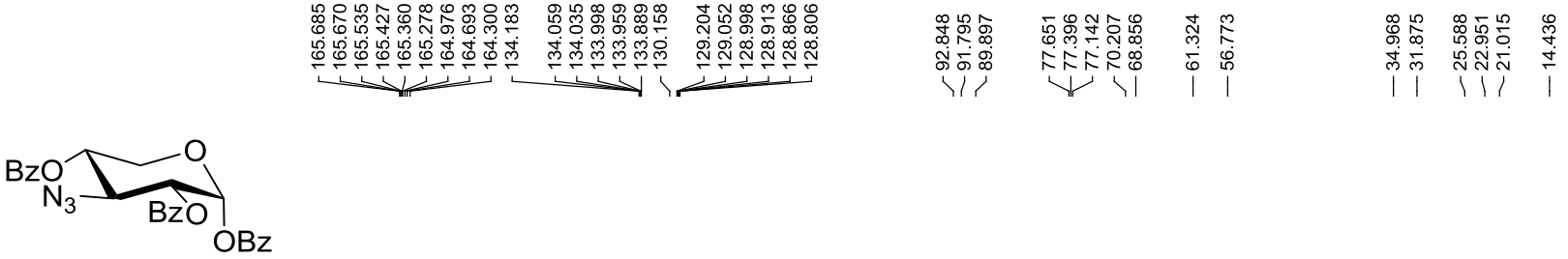


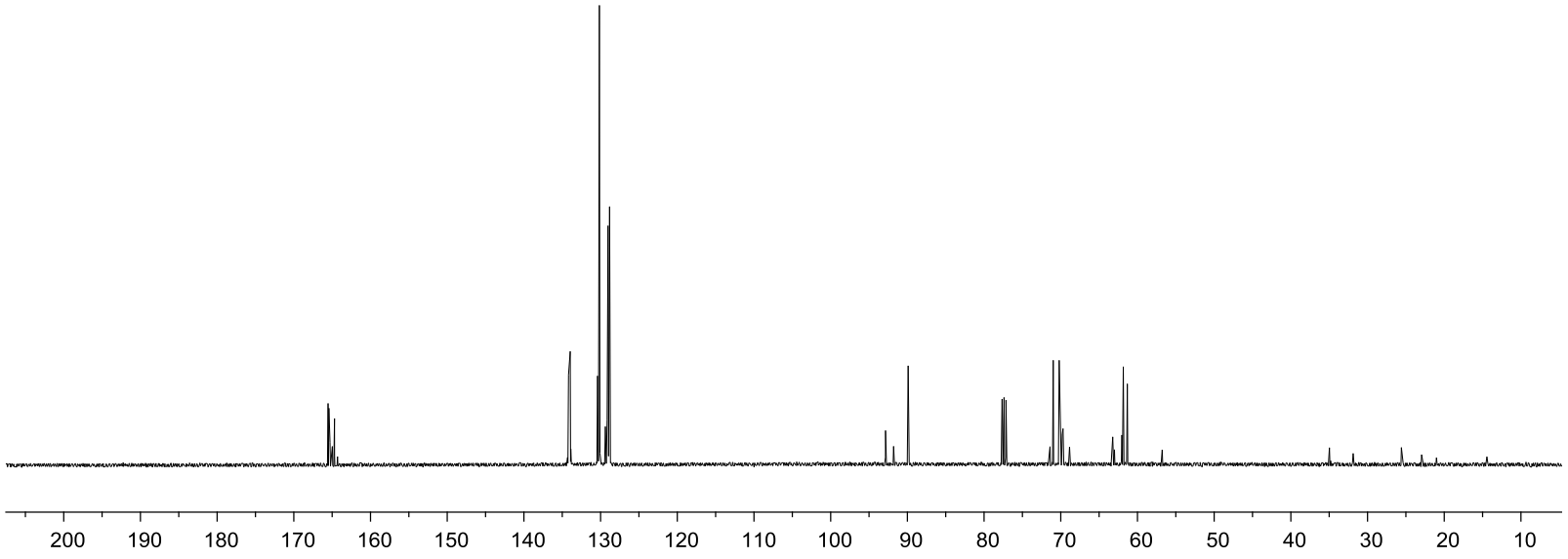
3-deoxy-3-azido-1,2,4-tri-*O*-benzoyl-D-xylopyranoside (**46**): gCOSY NMR ($CDCl_3$, 500 MHz)



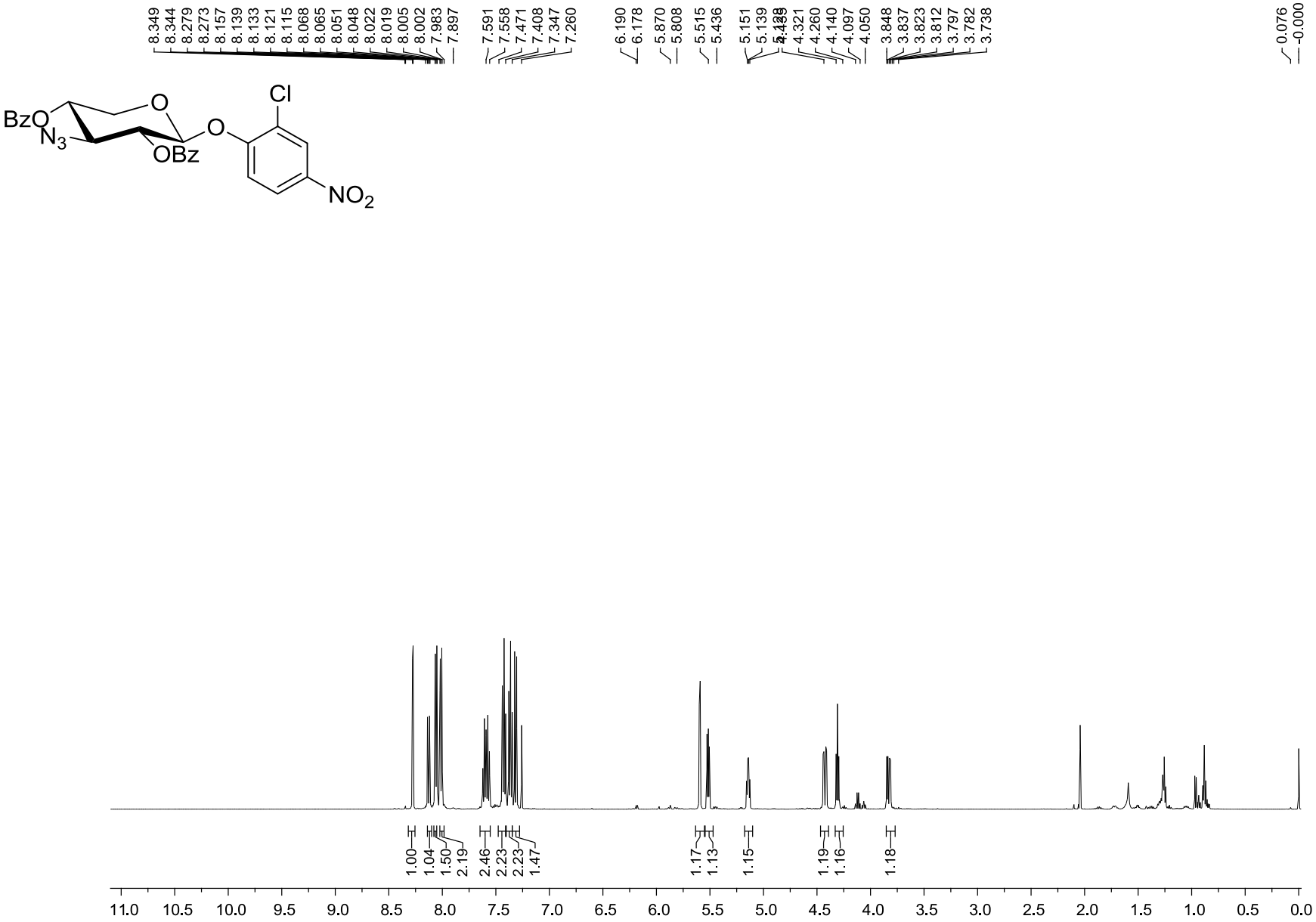


3-deoxy-3-azido-1,2,4-tri-*O*-benzoyl-D-xylopyranoside (**46**): ^{13}C NMR ($CDCl_3$, 125 MHz)

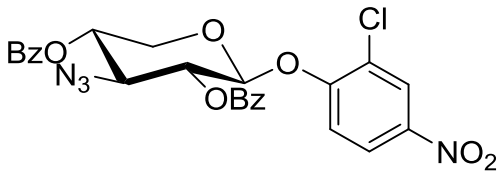


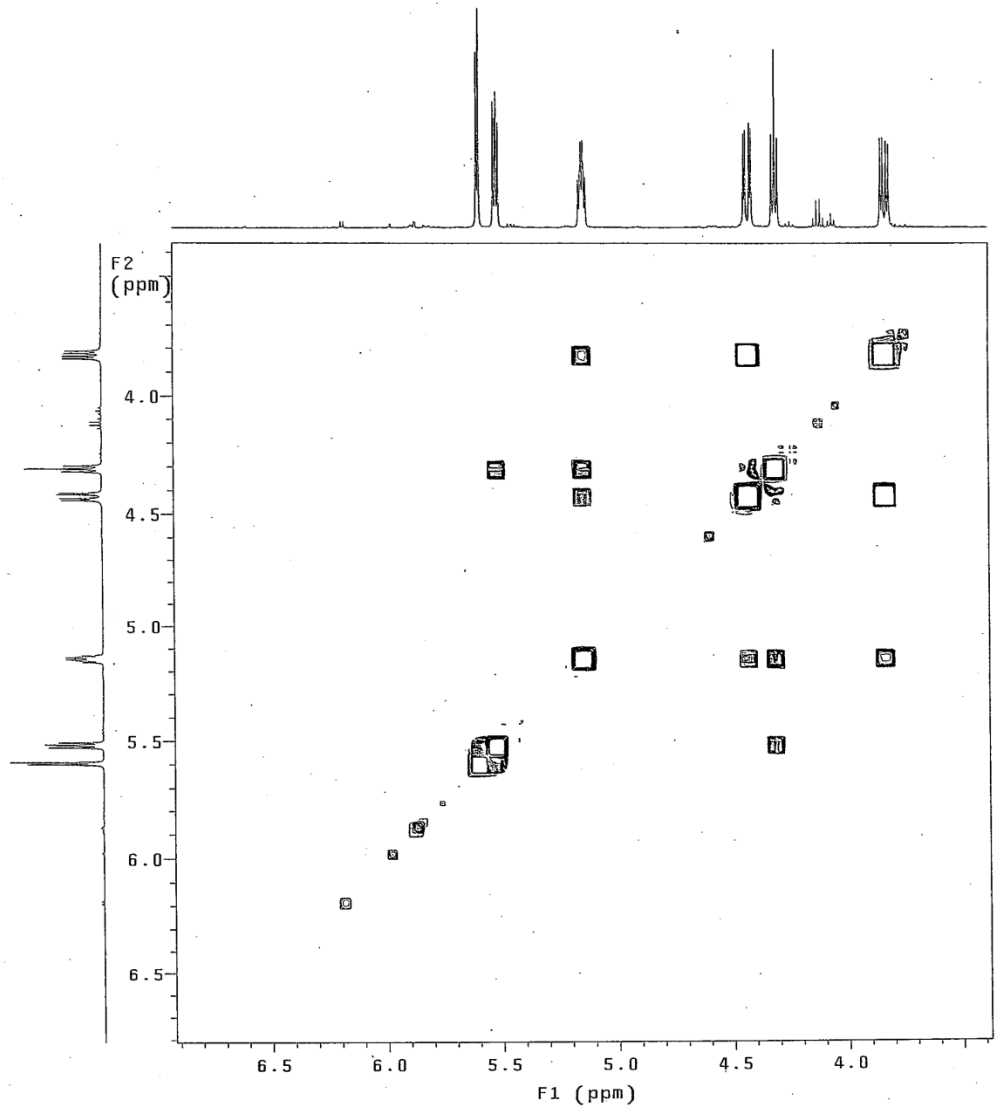


(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-*O*-benzoyl-β-D-xylopyranoside (**47**): ^{1}H NMR ($CDCl_3$, 500 MHz)



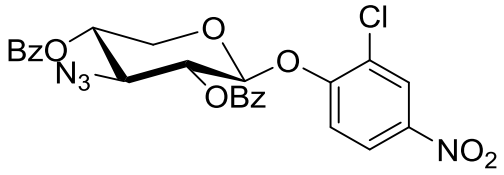
(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-*O*-benzoyl-β-D-xylopyranoside (**47**): gCOSY NMR ($CDCl_3$, 500 MHz)

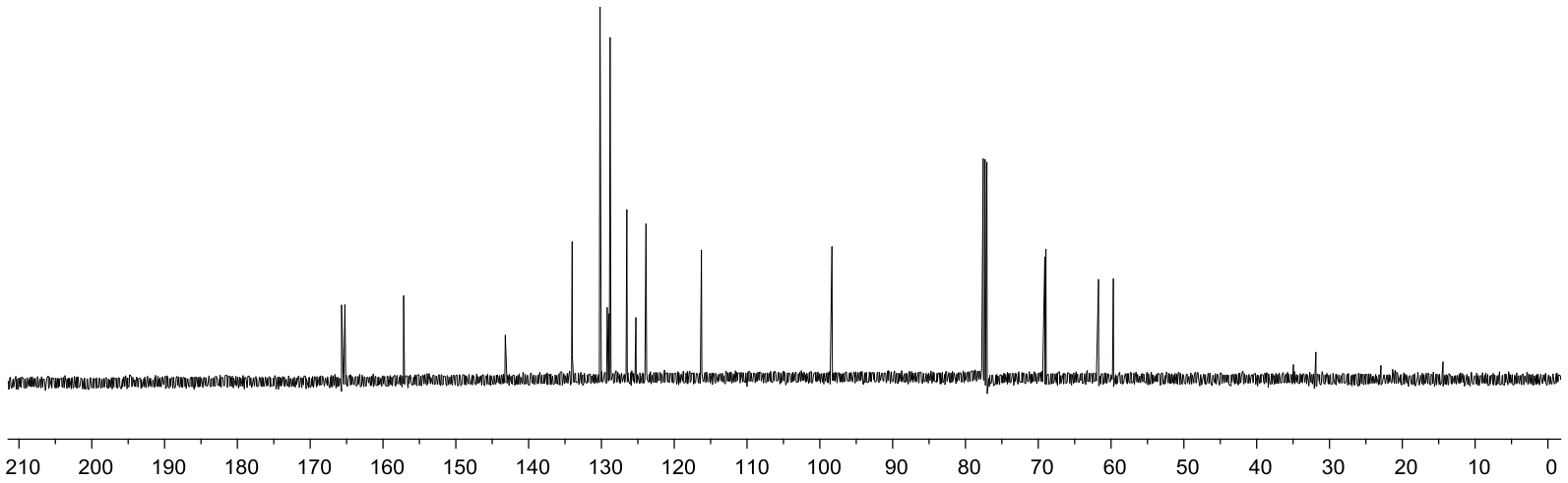




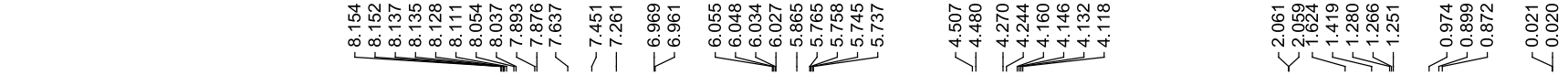
(2-chloro-4-nitrophenyl)-3-deoxy-3-azido-2,4-di-*O*-benzoyl-β-D-xylopyranoside (**47**): ^{13}C NMR ($CDCl_3$, 125 MHz)

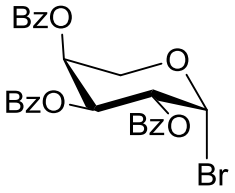
165.693
165.236
157.167
143.208
134.052
134.015
130.206
128.858
126.509
123.880
116.263
98.336
77.564
77.310
77.055
69.102
68.949
61.723
59.690
31.866
14.403

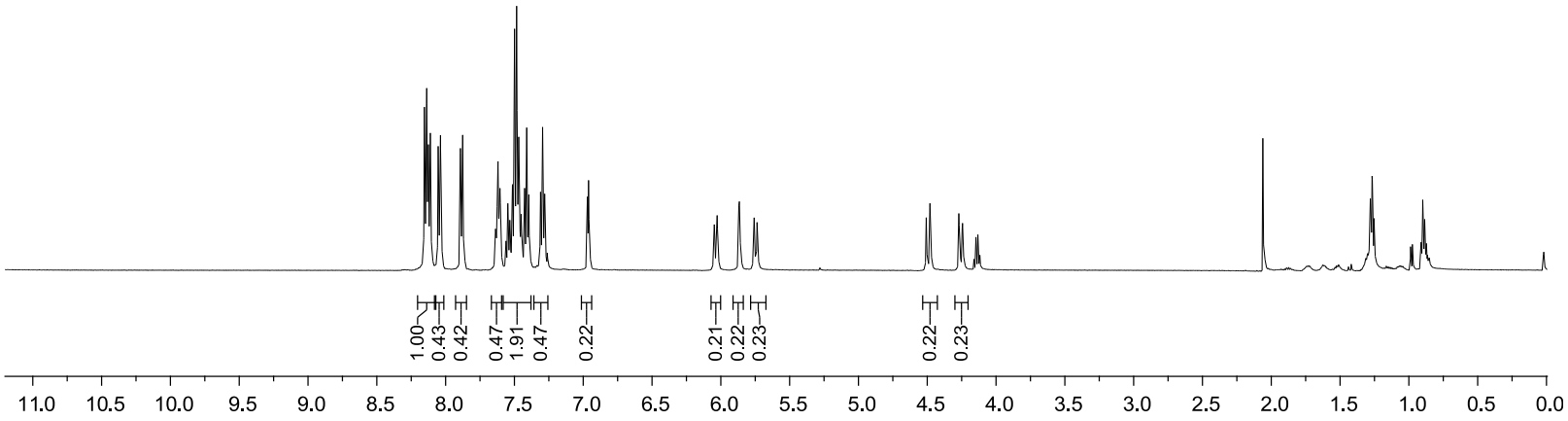




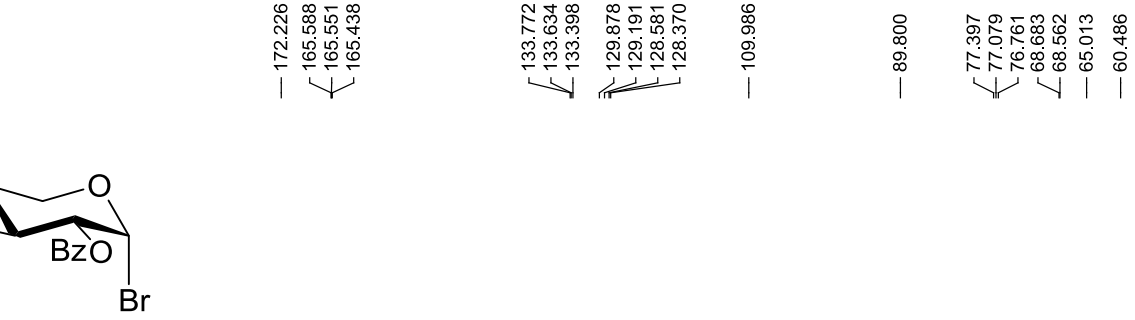
1-bromo-2,3,4-tri-*O*-benzoyl-β-L-arabinopyranoside (**48**): ^{1}H NMR ($CDCl_3$, 500 MHz)

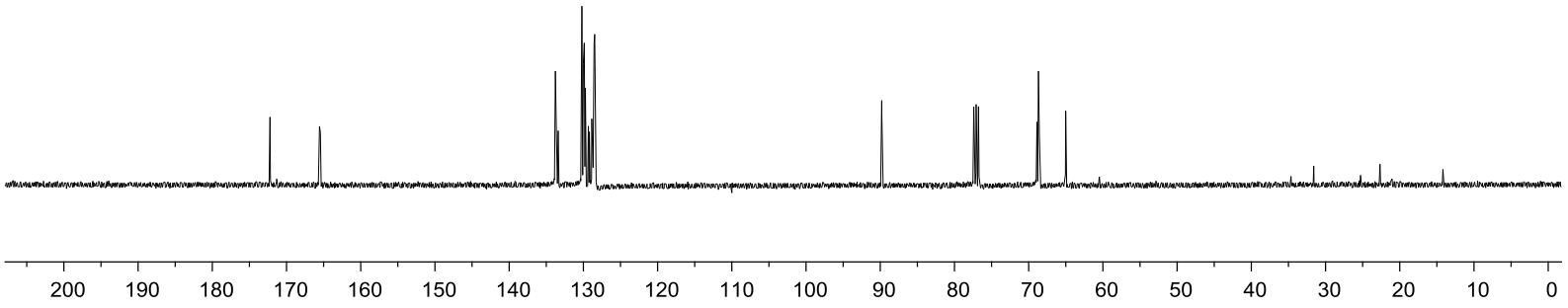




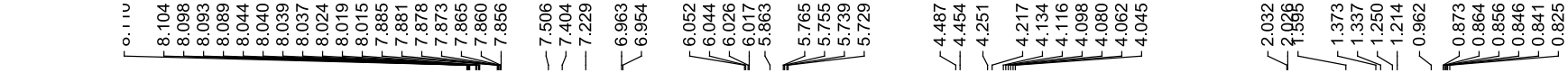


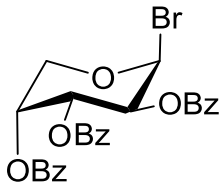
1-bromo-2,3,4-tri-*O*-benzoyl-β-L-arabinopyranoside (**48**): ^{13}C NMR ($CDCl_3$, 100 MHz)

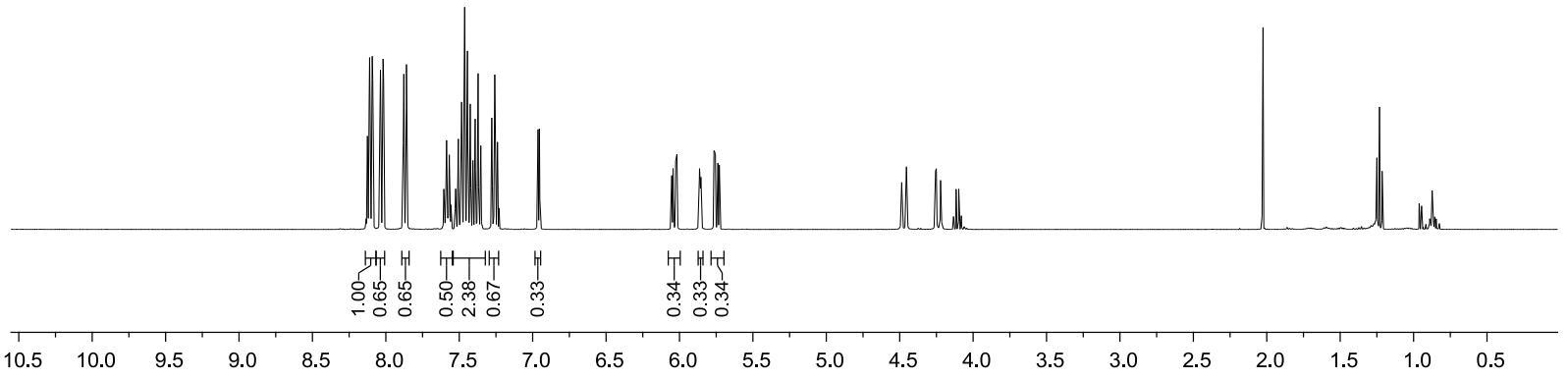




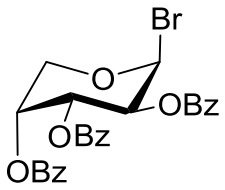
1-bromo-2,3,4-tri-*O*-benzoyl-α-D-arabinopyranoside (**49**): ^{1}H NMR ($CDCl_3$, 400 MHz)

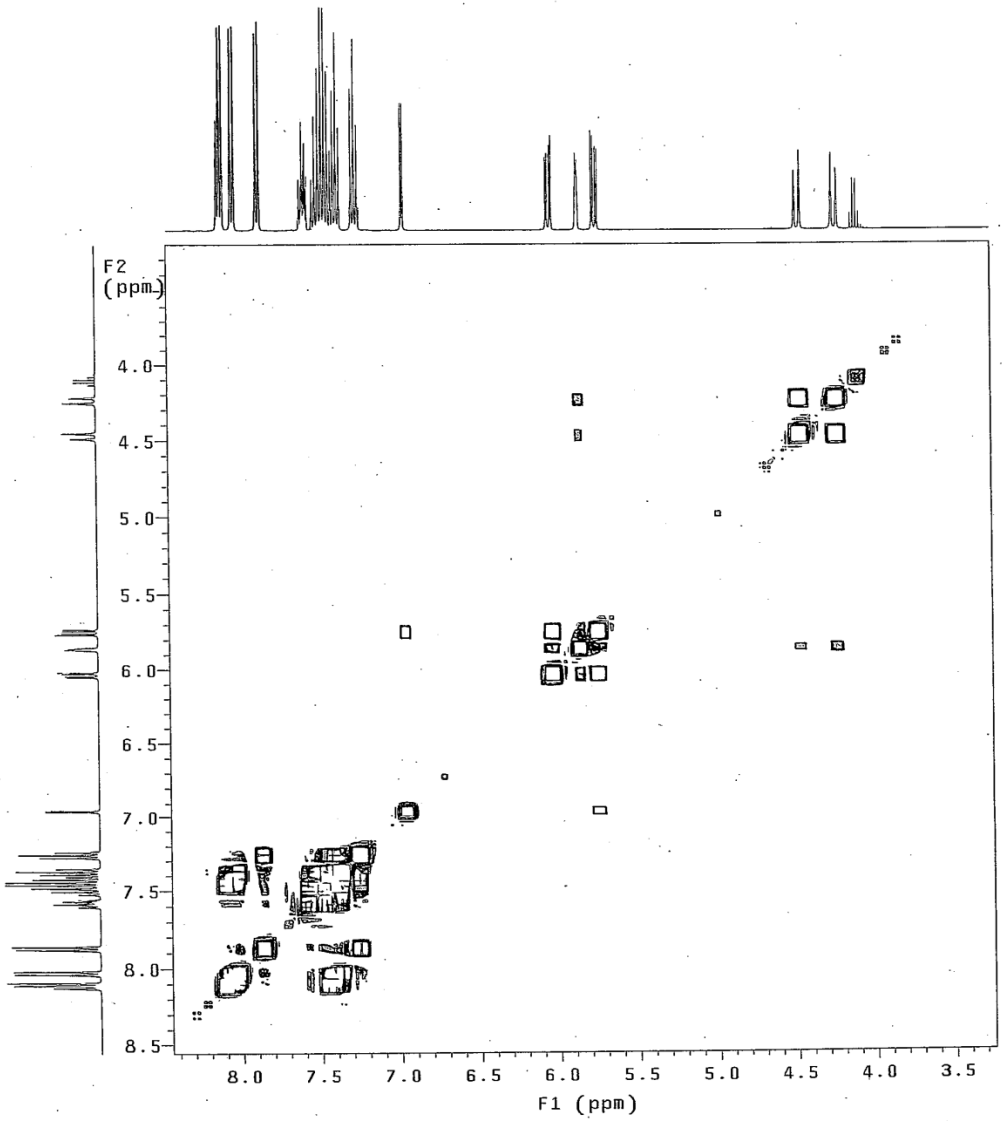






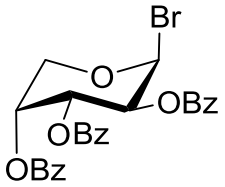
1-bromo-2,3,4-tri-*O*-benzoyl-α-D-arabinopyranoside (**49**): gCOSY NMR ($CDCl_3$, 400 MHz)

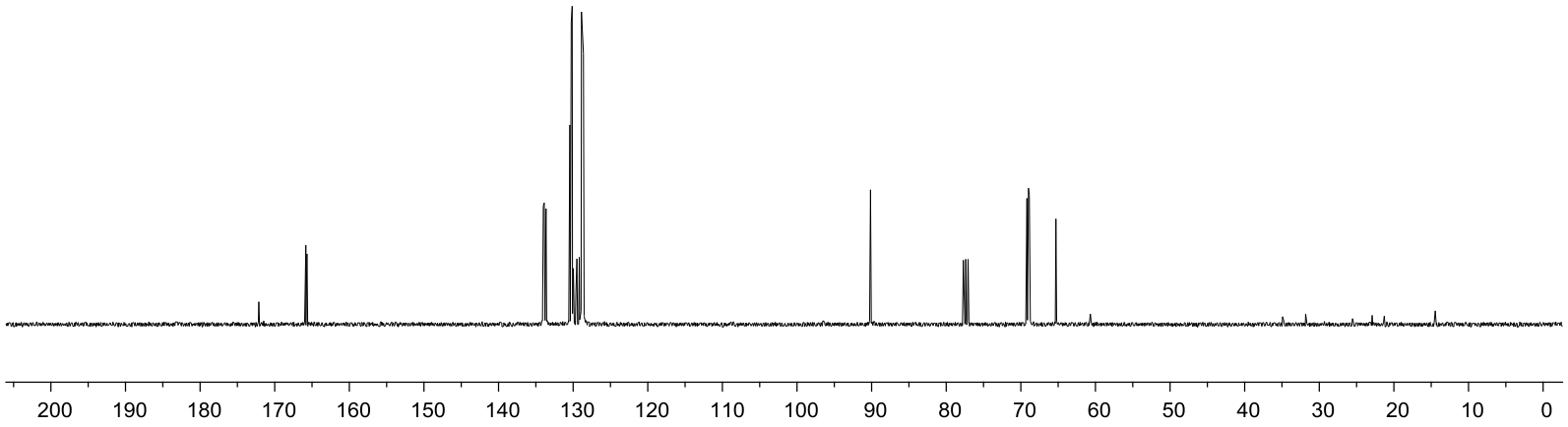




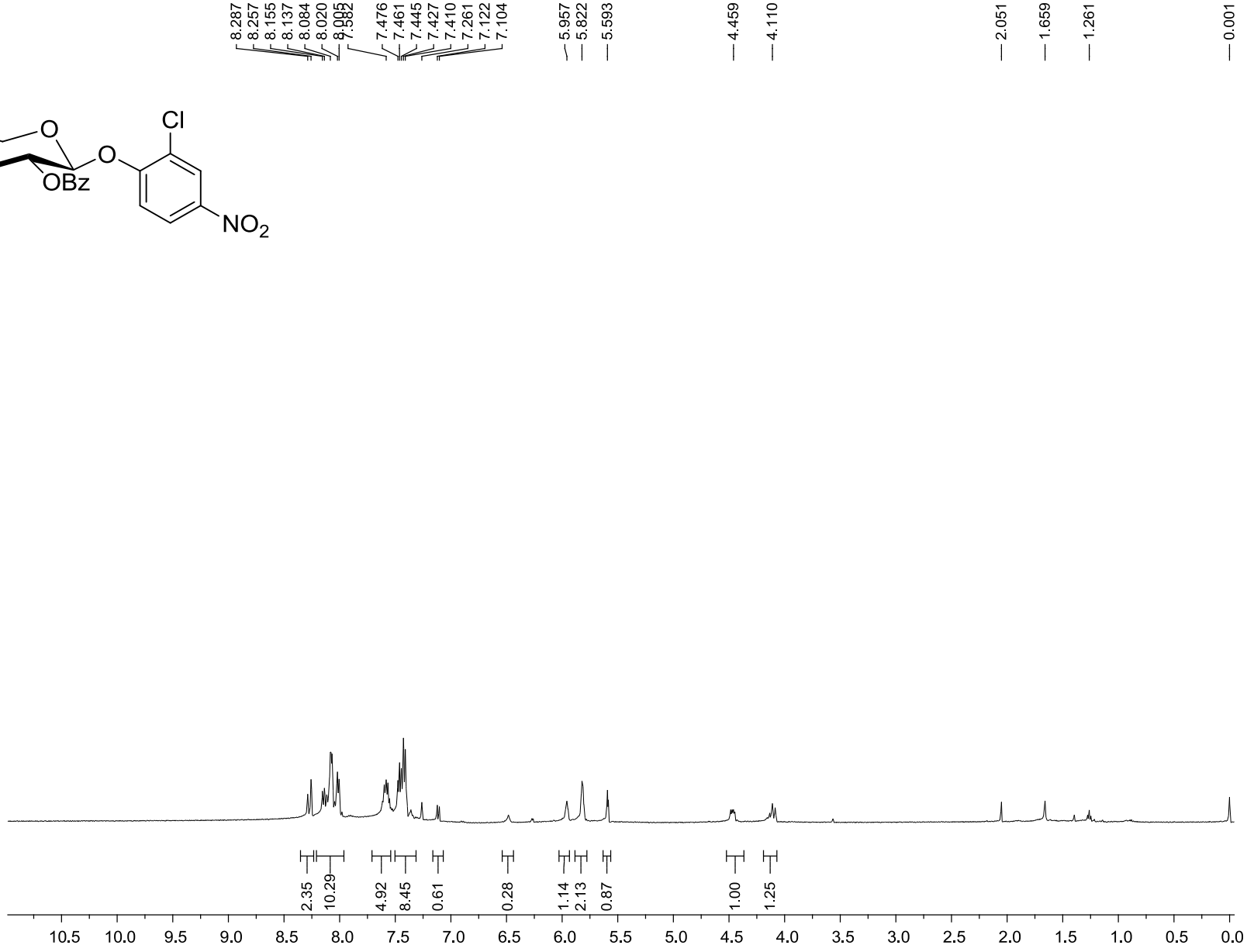
1-bromo-2,3,4-tri-*O*-benzoyl-α-D-arabinopyranoside (**49**): ^{13}C NMR ($CDCl_3$, 100 MHz)

172.135
165.829
165.789
165.676
133.997
133.976
133.875
133.632
130.132
129.631
129.498
129.177
128.890
128.805
128.712
128.621
90.145
77.706
77.388
77.069
68.979
68.863
65.296
60.683

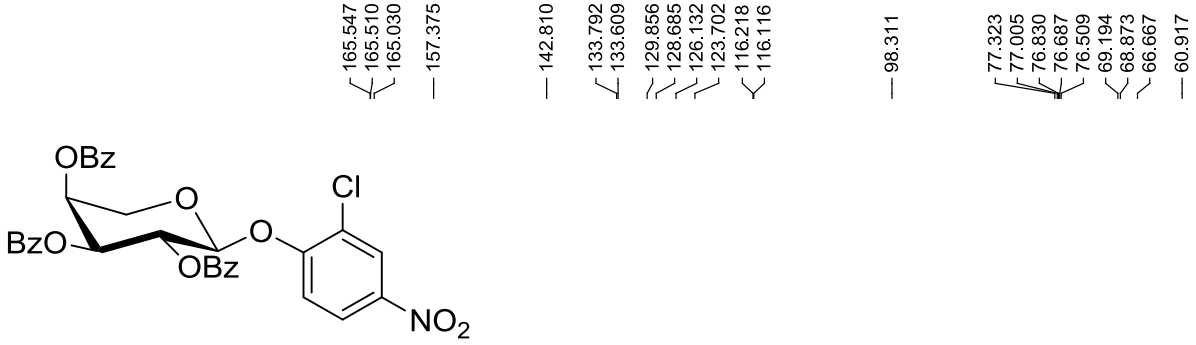


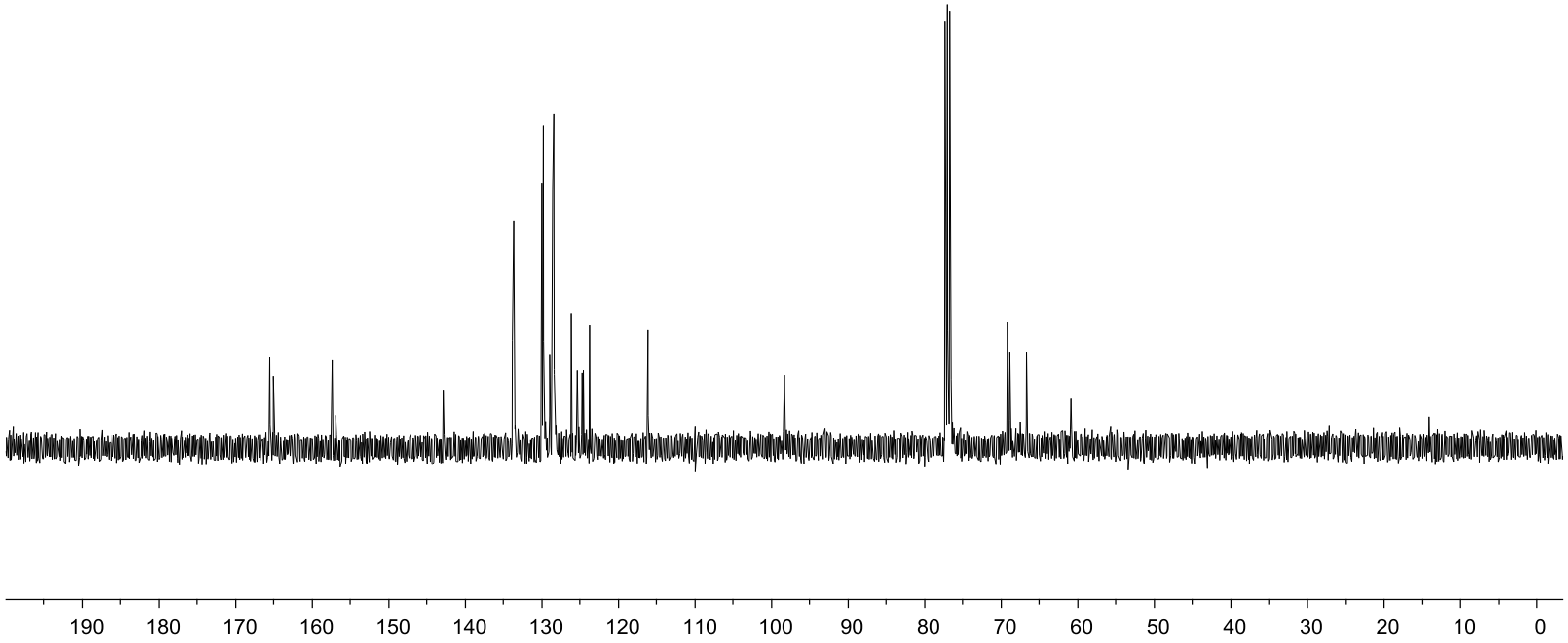


(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-α-L-arabinopyranoside (**50**): ^{1}H NMR ($CDCl_3$, 500 MHz)

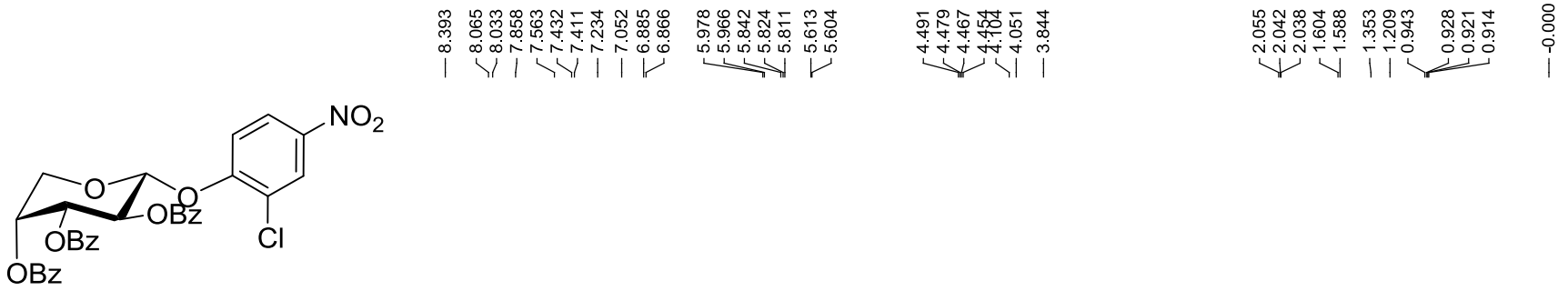


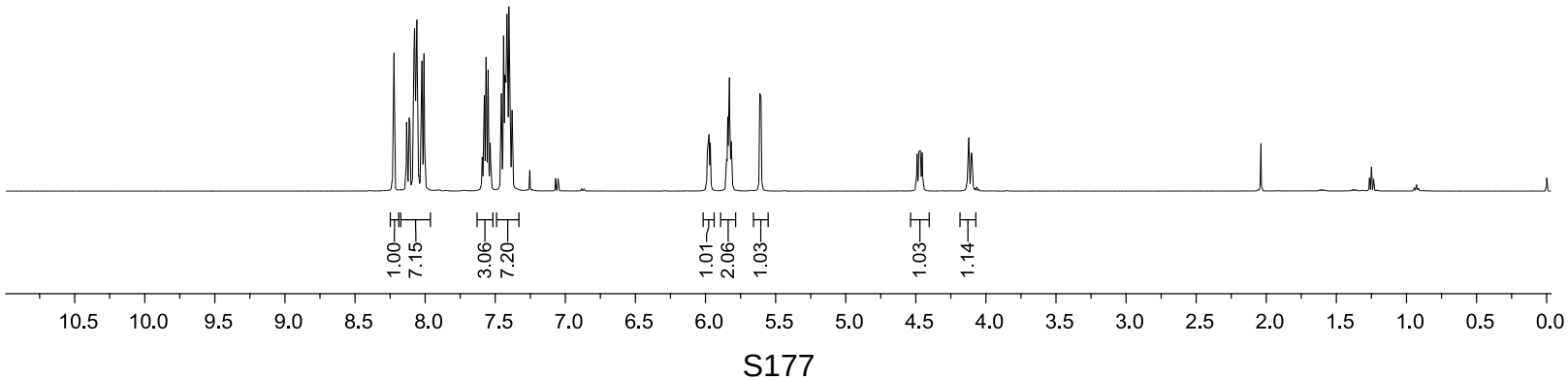
(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-α-L-arabinopyranoside (**50**): ^{13}C NMR ($CDCl_3$, 100 MHz)



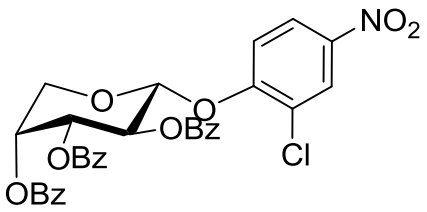


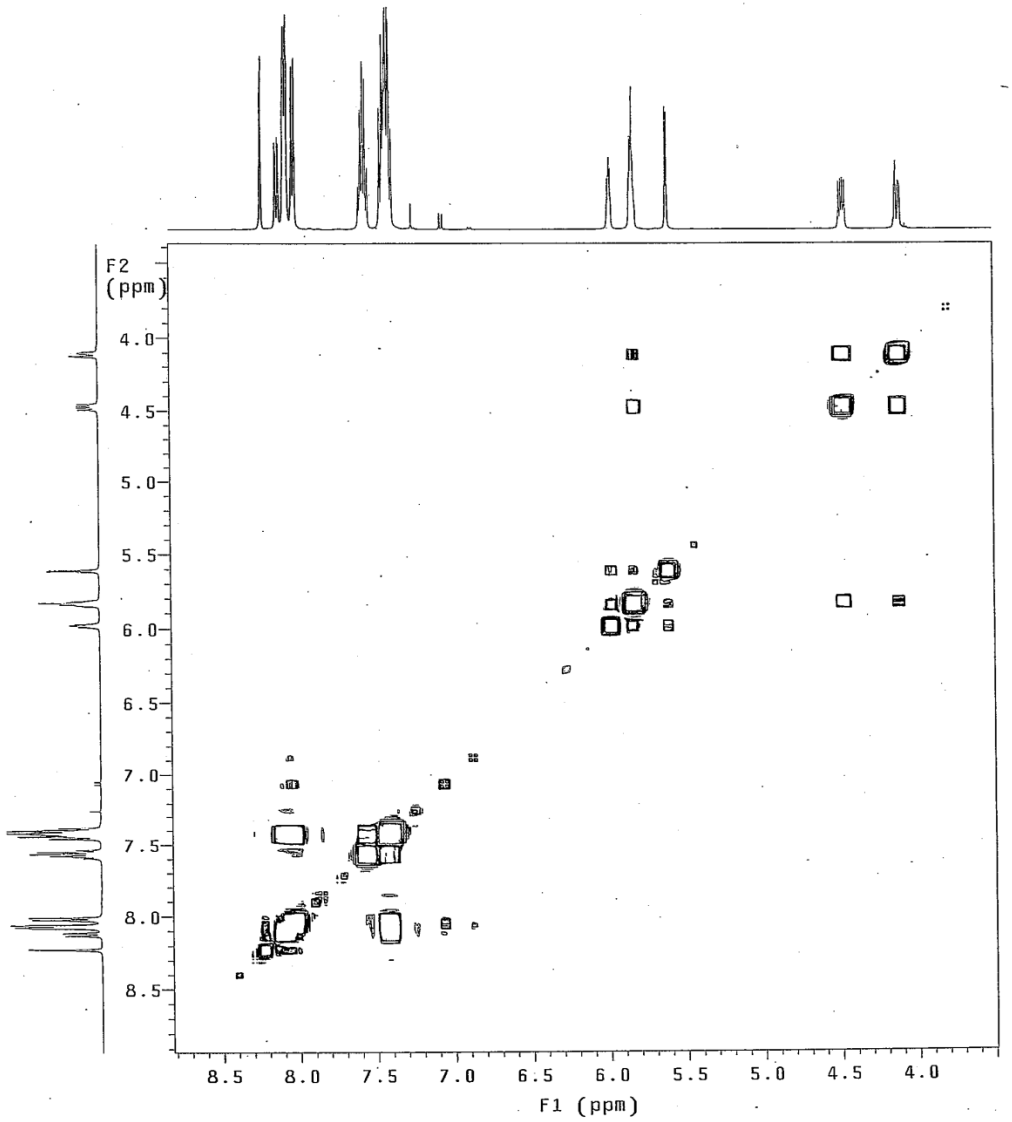
(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-β-D-arabinopyranoside (**51**)**:** ^{1}H NMR ($CDCl_3$, 500 MHz)



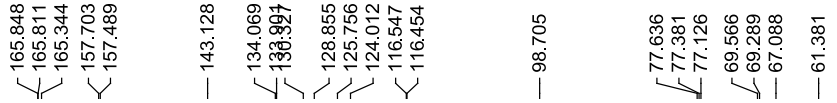


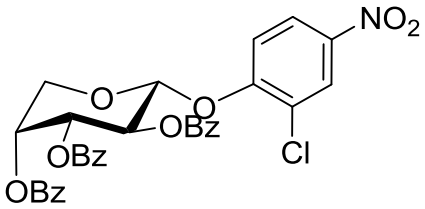
(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-β-D-arabinopyranoside (**51**)**:** gCOSY ($CDCl_3$, 500 MHz)

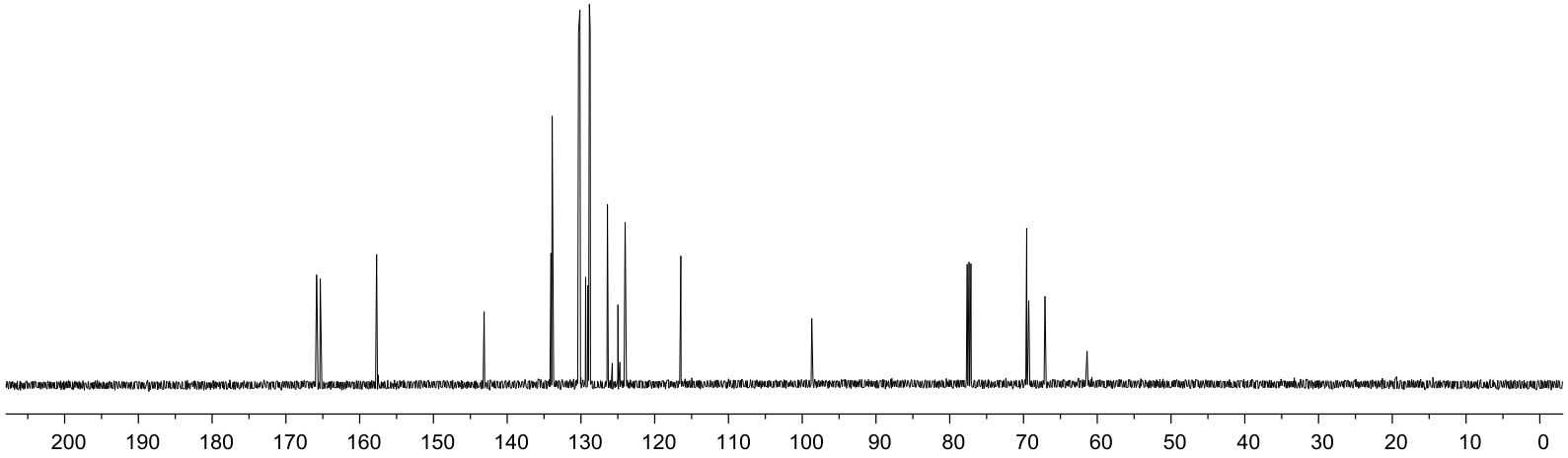




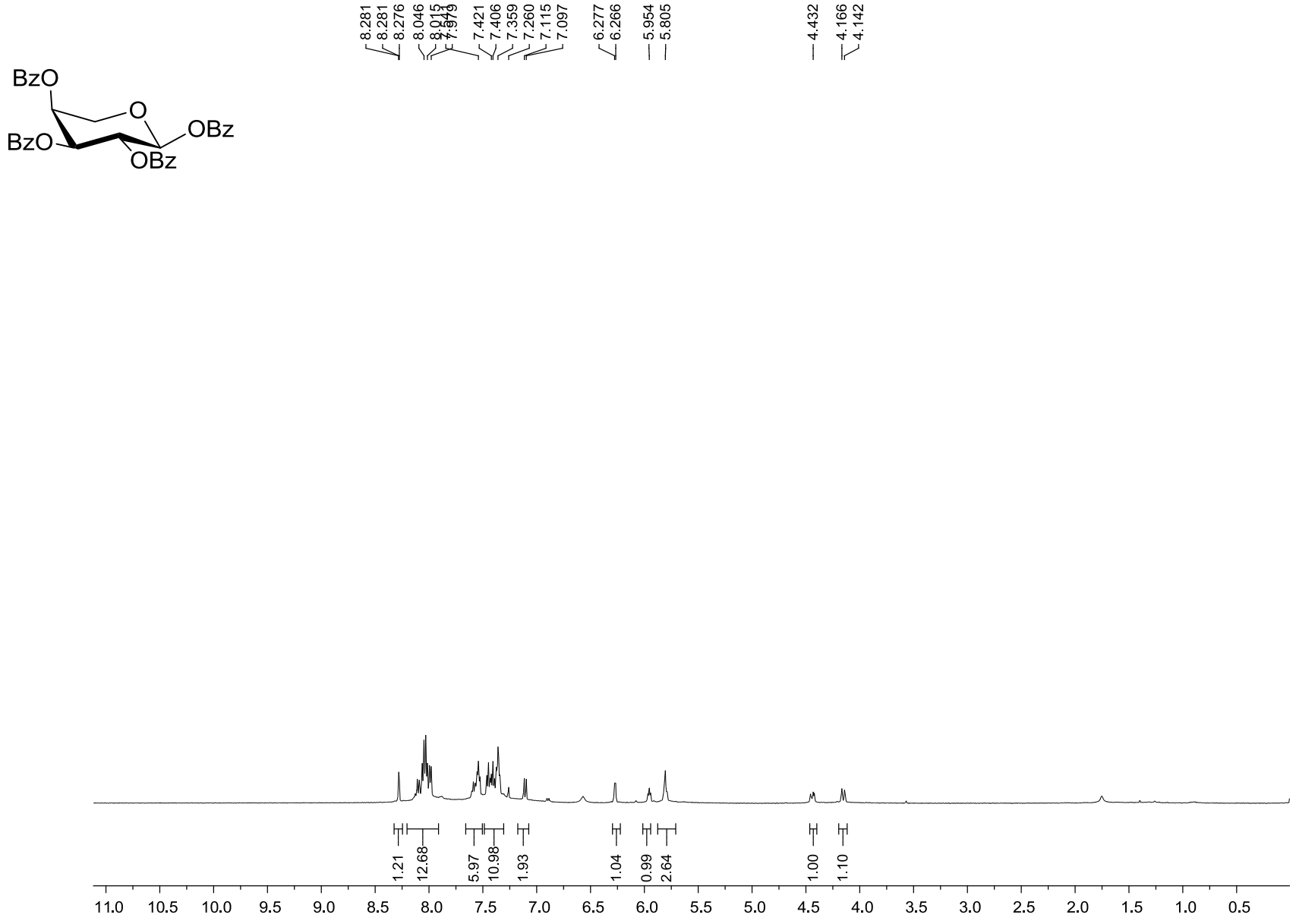
(2-chloro-4-nitrophenyl)-2,3,4-tri-*O*-benzoyl-β-D-arabinopyranoside (**51**)**:** ^{13}C NMR ($CDCl_3$, 125 MHz)



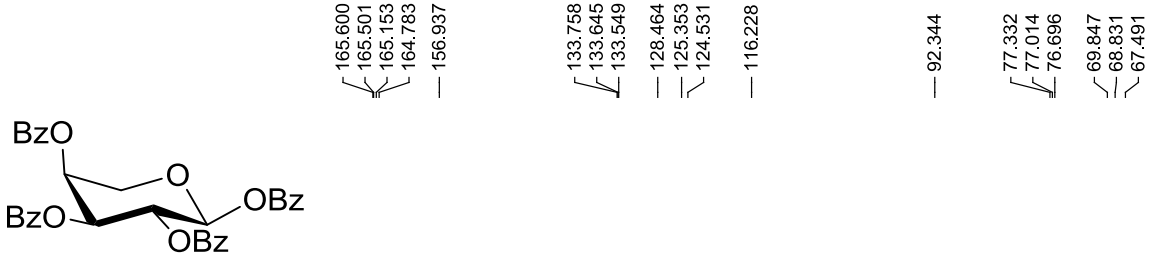


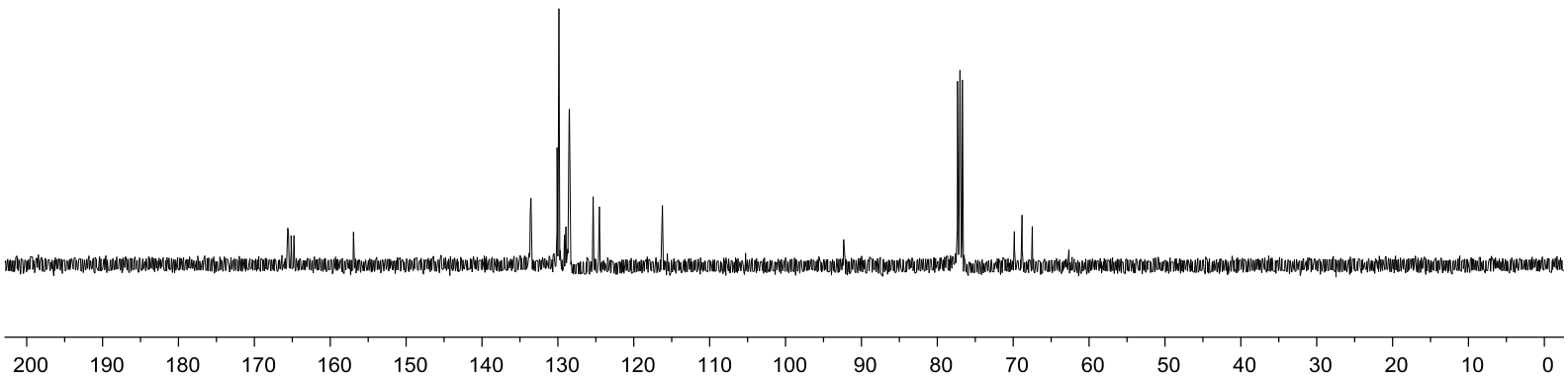


1,2,3,4-tetra-*O*-benzoyl-α-L-arabinopyranoside (**52**): ^{1}H NMR ($CDCl_3$, 500 MHz)

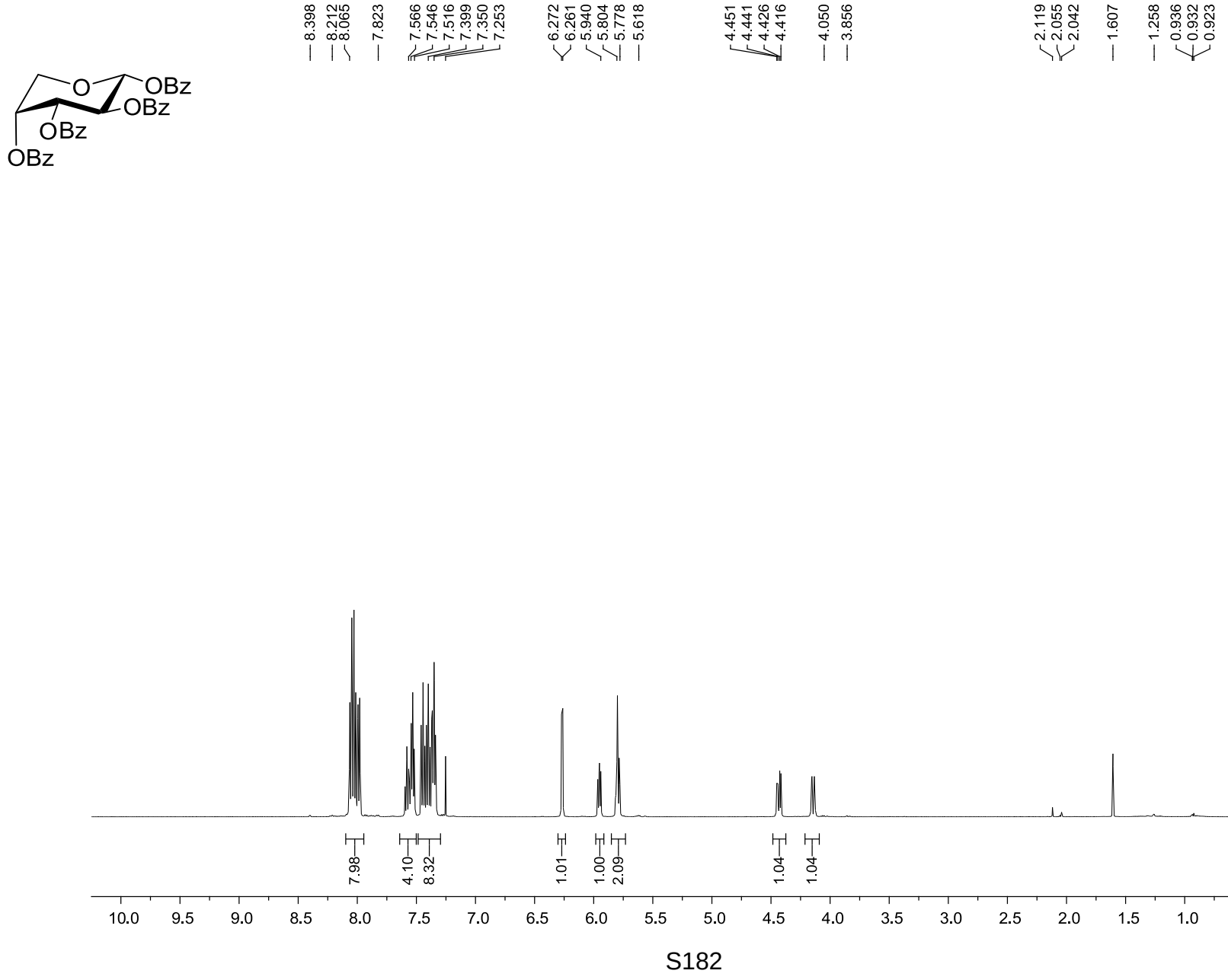


1,2,3,4-tetra-*O*-benzoyl-α-L-arabinopyranoside (**52**): ^{13}C NMR ($CDCl_3$, 100 MHz)

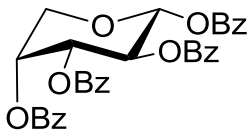


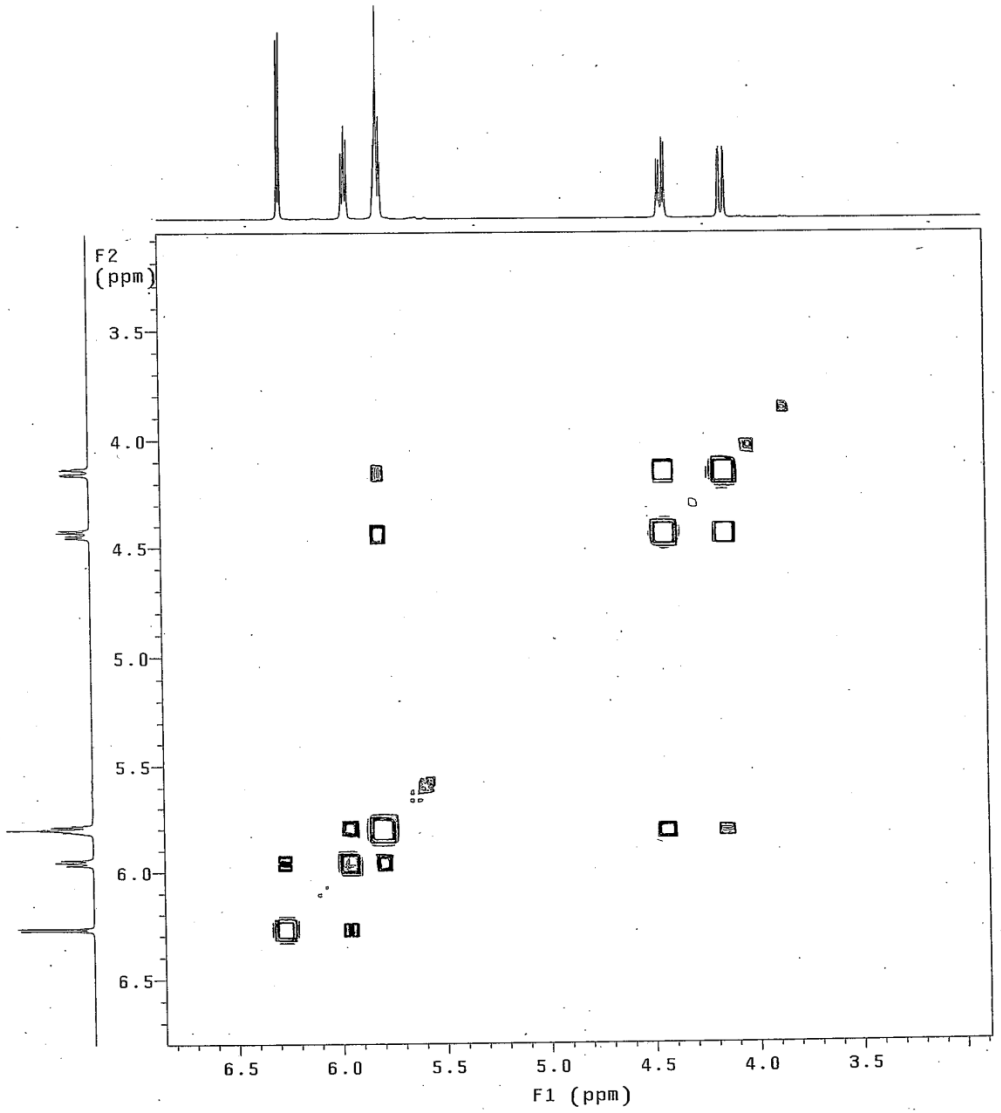


1,2,3,4-tetra-*O*-benzoyl-β-D-arabinopyranoside (**53**): ^{1}H NMR ($CDCl_3$, 500 MHz)



1,2,3,4-tetra-*O*-benzoyl-β-D-arabinopyranoside (**53**): gCOSY NMR ($CDCl_3$, 500 MHz)





1,2,3,4-tetra-*O*-benzoyl-β-D-arabinopyranoside (**53**): ^{13}C NMR ($CDCl_3$, 125 MHz)