Supporting information

for

Synthesis of Bradyrhizose from D-Glucose

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General Experimental

All reactions were carried out under argon unless otherwise stated. Solvents used for column chromatography were analytical grade and were purchased from commercial suppliers. Thin-layer chromatography was carried out with 250 μm glass backed silica (XHL) plates. Detection of compounds was achieved by UV absorption (254 nm) and by staining with 10% sulfuric acid in ethanol. Purification of crude residues was performed over silica gel chromatography using 230–400 mesh grade 60 silica unless otherwise stated. Specific rotations were measured in chloroform on an automatic polarimeter with a path length of 10 cm. NMR spectra were recorded in acetonitrile-d_3, $CDCl_3$, D_2O or CD_3OD using a 400 or 600 MHz Varian spectrometers and EZC500 JEOL instrument (500 MHz). High-resolution (HRMS) mass spectra were recorded in the electrospray mode using a time of flight mass analyzer (ESI-TOF). Heating of reaction mixtures were carried out on an aluminum heating block of appropriate size. volumetric glass. The chemical shifts (δ) were recorded in ppm and the multiplicity were abbreviated as follows: s (singlet), m (multiplet), br (broad), d (doublet), t (triplet) and q (quartet).

Benzyl α,β-D-glucopyranoside (2). This compound was prepared according to the literature method in 89% yield as a white solid (26.7g) in the form of a 12.5:1 α:β mixture. ^{1}H NMR (400 MHz, CD_3OD) δ 7.47 – 7.16 (m, 10H), 4.94-4.90 (m, 2H), 4.76 (d, *J* = 11.9 Hz, 1H), 4.66 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.36 (d, *J* = 7.8 Hz, 1H), 3.93 – 3.88 (m, 1H), 3.82 – 3.77 (m, 1H), 3.75 – 3.58 (m, 5H), 3.42 (dd, *J* = 9.7, 3.8 Hz, 1H), 3.41 – 3.21 (m, 5H). ^{13}C NMR (101 MHz, CD_3OD) δ 140.4, 137.6, 128.4, 127.92, 127.88, 127.86, 127.8, 127.3, 125.6, 101.9, 97.8, 76.7, 76.6, 73.71, 73.68, 72.5, 72.1, 70.4, 70.34, 70.27, 68.8, 61.4, 61.2. HRMS (ESI): m/z calcd for $C_{13}H_{18}O_6Na$ [M + Na] 293.0957, found 293.0952.

Benzyl 4,6-*O*-benzylidene-α,β-D-glucopyranoside (3). To a solution of **2** (25 g, 92.5 mmol) in DMF (500 mL) was added benzaldehyde dimethyl acetal (17.3 mL, 111.0 mmol) and *p*-TsOH monohydrate (3.5 g, 18.0 mmol). The mixture was stirred at rt till completion. The solvent was then removed at reduced pressure and the residual crude dissolved in ethyl acetate (100 mL) and washed with saturated sodium bicarbonate (2 × 30 mL). The aqueous layer was extracted twice with ethyl acetate and the combined organic layer dried in $MgSO_4$, filtered, and concentrated under reduced pressure. The residual crude in the form of 13.6:1 α:β mixture was purified by silica gel column chromatography (hexane:ethyl acetate 3:1) to give first compound **3β** as a white solid (2.1 g, 6%) and then **3α** as a white solid (28 g, 85%)

3α. Mp 155 -162 °C $[\alpha]_D^{23}$ = +103 (*c* = 0.98, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.16 (m, 10H), 5.48 (s, 1H, benzylidene), 4.95 (d, *J* = 3.9 Hz, 1H, H-1), 4.73 (d, *J* = 11.8 Hz, 1H, $PhCH_2$), 4.53 (d, *J* = 11.8 Hz, 1H, $PhCH_2$), 4.19 (dd, *J* = 10.1, 4.8 Hz, 1H, H-6_{eq}), 3.94 (t, *J* = 9.3 Hz, 1H, H-3), 3.82 (td, *J* = 9.9, 4.8 Hz, 1H, H-5), 3.69 (q, *J* = 10.4 Hz, 1H, H-6_{ax}), 3.60 (dd, *J* = 9.2, 3.9 Hz, 1H, H-2), 3.46 (t, *J* = 9.4 Hz, 1H, H-4). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 137.1, 136.8, 129.1, 128.5, 128.2, 128.12, 128.08, 126.3, 101.8, 98.3, 81.0, 72.9, 71.4, 70.0, 68.9, 62.7. HRMS (ESI): m/z calcd for $C_{20}H_{22}O_6Na$ [M + Na] 381.1314, found 381.1316.

3β. Mp 120 -125 °C $[\alpha]_D^{23}$ = +98 (*c* = 1.0, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.30 (m, 10H), 5.50 (s, 1H, benzylidene), 4.91 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.61 (d, *J* = 11.6 Hz, 1H, $PhCH_2$), 4.45 (d, *J* = 7.7 Hz, 1H, H-1), 4.34 (dd, *J* = 10.5, 5.0 Hz, 1H, H-6_{eq}), 3.84 – 3.70 (m, 2H, H-6_{ax}, H-3), 3.60 – 3.47 (m, 2H, H-2, H-4), 3.39 (td, *J* = 9.7, 4.9 Hz, 1H, H-5). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 136.7, 129.3, 128.6, 128.4, 128.18, 128.16, 126.3, 102.1, 101.9, 80.5, 74.5, 73.1, 71.4, 68.7, 66.4. HRMS (ESI): m/z calcd for $C_{20}H_{22}O_6Na$ [M + Na] 381.1314, found 381.1319.

Benzyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (4). A solution of **3** (8 g, 22.2 mmol) in dry DMF (222 mL) was placed in an ice bath at 0 °C under argon. Sodium hydride (2.7 g, 66.7 mmol) and benzyl bromide were then added. The reaction mixture was stirred at 0 °C for 3 h then at ambient temperature for 4 h, with monitoring by TLC (hexane:ethyl acetate 6:1, R_f = 0.6). After completion, the reaction mixture was quenched with methanol (10 mL) followed by water (100 mL) and extracted with ethyl acetate (100 mL). The aqueous layer was extracted with ethyl acetate thrice and the combined organic layer

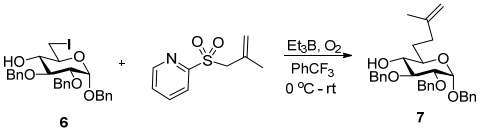
dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane:ethyl acetate 6:1) to give **4** as a white amorphous solid (11.3 g, 94%). Mp 114 -117 °C. $[\alpha]_D^{23}$ = +21.9 (*c* = 0.54, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 6.96 (m, 20H), 5.56 (s, 1H, benzylidene), 4.94 (d, *J* = 11.2 Hz, 1H, $PhCH_2$), 4.86 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.84 (d, *J* = 3.8 Hz, 1H, H-1), 4.77 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.74 (d, *J* = 12.3 Hz, 1H, $PhCH_2$), 4.60 (d, *J* = 12.2 Hz, 2H, $2PhCH_2$), 4.21 (dd, *J* = 10.2, 4.9 Hz, 1H, H-6_{eq}), 4.12 (t, *J* = 9.3 Hz, 1H, H-3), 3.92 (dt, *J* = 9.9, 4.8 Hz, 1H, H-5), 3.70 (t, *J* = 10.3 Hz, 1H, H-6_{ax}), 3.63 (t, *J* = 9.4 Hz, 1H, H-4), 3.57 (dd, *J* = 9.3, 3.8 Hz, 1H, H-2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.1, 137.4, 136.9, 128.9, 128.5, 128.41, 128.36, 128.3, 128.2, 127.97, 127.9, 127.8, 127.6, 126.0, 101.2, 96.5, 82.2, 79.2, 78.7, 75.4, 73.5, 69.3, 69.0, 62.6. HRMS (ESI): m/z calcd for $C_{34}H_{34}O_6Na$ [M + Na] 561.2253, found 561.2258.

Benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside (5). A solution of **4** (19.0 g, 35.2 mmol) in methanol:chloroform 2:1 (300 mL), was treated with *p*-TsOH monohydrate (2.7 g, 14.07 mmol) at rt. The reaction was monitored by TLC (hexane:ethyl acetate 2:1, R_f =0.3). After completion, the reaction mixture was concentrated under reduced pressure, diluted with ethyl acetate (250 mL) and neutralized with saturated aqueous sodium bicarbonate (100 mL). The aqueous layer was extracted with ethyl acetate twice and the combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residual syrup was purified by silica gel column chromatography (hexane:ethyl acetate 2:1) to give **5** (13.3 g, 84%) as white amorphous solid. Mp 95-98 °C. $[\alpha]_D^{23}$ = +53.6 (*c* = 0.64, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 6.96 (m, 15H), 5.05 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.85 (d, *J* = 3.6 Hz, 1H, H-1), 4.75 (d, *J* = 11.4 Hz, 1H, $PhCH_2$), 4.72 (d, *J* = 12.3 Hz, 1H, $PhCH_2$), 4.64 (d, *J* = 11.9 Hz, 1H, $PhCH_2$), 4.57 (d, *J* = 12.3 Hz, 1H, $PhCH_2$), 4.54 (d, *J* = 11.9 Hz, 1H, $PhCH_2$), 3.89 (t, *J* = 9.2 Hz, 1H, H-3), 3.75-3.73 (m, 2H, H-6, H-6'), 3.72 – 3.66 (m, 1H, H-5), 3.57 (t, *J* = 9.2 Hz, 1H, H-4), 3.51 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 138.0, 137.1, 128.6, 128.5, 128.43, 128.39, 127.8, 127.91, 127.85, 95.5, 81.4, 79.8, 75.4, 72.7, 71.1, 70.3, 69.2, 62.2. HRMS (ESI): m/z calcd for $C_{27}H_{30}O_6Na$ [M + Na] 473.1940, found 473.1947.

Benzyl 2,3-di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside (6). A solution of **5** (8.6 g, 19.0 mmol) in toluene:acetonitrile 1:1 (190 mL), was treated with triphenyl phosphine (5.5 g, 20.9 mmol), iodine (5.3 g, 20.9 mmol), and imidazole (3.9 g, 57.1 mmol). The mixture was heated at 40 °C and monitored by TLC (hexane:ethyl acetate 6:1, R_f =0.6). After completion, the reaction mixture was concentrated under reduced pressure. The residual syrup was purified by silica gel column chromatography (hexane:ethyl acetate 6:1) to give **6** (9.3 g, 87%) as a colorless syrup. $[\alpha]_D^{23}$ = +46.6 (*c* = 0.98, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.03 (m, 15H), 5.06 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 3.6 Hz, 1H, H-1), 4.81 (d, *J* = 12.1 Hz, 1H, $PhCH_2$), 4.69 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.63 (d, *J* = 12.7 Hz, 2H, $2PhCH_2$), 4.55 (d, *J* = 11.9 Hz, 1H, $PhCH_2$), 3.87 (t, *J* = 9.2 Hz, 1H, H-3), 3.57 – 3.46 (m, 3H, H-2, H-4, H-6), 3.33 (td, *J* = 9.2, 2.5 Hz, 1H, H-5), 3.26 (dd, *J* = 10.9, 7.5 Hz, 1H, H-6'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 137.8, 136.8, 128.70, 128.65, 128.5, 128.04, 128.01, 128.0, 127.9, 94.97, 80.8, 79.8, 75.4, 73.7, 72.6, 70.1, 68.99, 7.3. HRMS (ESI): m/z calcd for $C_{27}H_{29}IO_5Na$ [M + Na] 583.0957, found 583.0953.

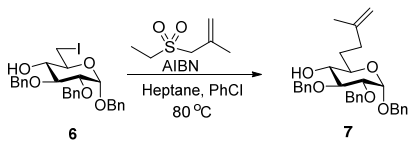
Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-α-D-non-8-enoglucopyranoside (7). Compound **6** (5.89 g, 10.5 mmol) was dissolved in dry α,α,α-trifluorotoluene (117 mL) and treated with 2-pyridyl methallylsulfone (7.3 g, 36.8 mmol). Lauroyl peroxide (20.9 g, 52.6 mmol) was added to the reaction mixture in two portions at 80 °C. The reaction mixture was stirred at 80 °C for 2 h with monitoring by TLC (hexane:ethyl acetate 6:1, R_f =0.6). After completion, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (hexane:ethyl acetate 15:1 to 10:1 to 6:1) to give **7** (2.7 g, 54%) as a colorless syrup and **8** (1.6g, 36%) also as a colorless syrup. $[\alpha]_D^{23}$ = +60.1 (*c* = 0.57, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.22 (m, 15H), 5.06 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.81 (d, *J* = 3.6 Hz, 1H, H-1), 4.76 – 4.68 (m, 4H, $2PhCH_2$, 2H-vinyl), 4.62 (d, *J* = 11.9 Hz, 1H, $PhCH_2$), 4.53 - 48 (m, 2H, $2PhCH_2$), 3.83 (t, *J* = 9.3 Hz, 1H, H-3), 3.65 (t, *J* = 8.8 Hz, 1H, H-5), 3.52 (dd, *J* = 9.5, 3.6 Hz, 1H, H-2), 3.27 (t, *J* = 9.3 Hz, 1H, H-4), 2.26 – 2.18 (m, 1H, H-7), 2.07 – 1.98 (m, 2H, H-7', H-6), 1.74 (s, 3H, methyl), 1.56 – 1.46 (m, 1H, H-6'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 138.8, 138.0, 137.1, 128.6, 128.42, 128.39, 127.93, 127.89, 127.8, 110.1, 94.8, 81.5, 79.9, 75.3, 73.8, 72.5, 70.4, 68.7, 33.5, 29.9, 22.5. HRMS (ESI): m/z calcd for $C_{31}H_{36}O_5Na$ [M + Na] 511.2460, found 511.2459.

Benzyl 2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (8). $\alpha]_D^{23}$ = +19.5 (*c* = 1.1, $CHCl_3$)^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 15H), 5.05 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 3.6 Hz, 1H, H-1), 4.71 (dd, *J* = 11.9, 5.5 Hz, 2H, $PhCH_2$), 4.62 (d, *J* = 11.9 Hz, 1H, $1PhCH_2$), 4.55 (d, *J* = 12.0 Hz, 2H), 3.81 (t, *J* = 9.2 Hz, 1H, H-3), 3.76 – 3.68 (m, 1H, H-5), 3.52 (dd, *J* = 9.5, 3.7 Hz, 1H, H-2), 3.18 (t, *J* = 9.2 Hz, 1H, H-4), 1.21 (d, *J* = 6.3 Hz, 3H, CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 138.2, 137.4, 128.7, 128.50, 128.45, 128.0, 95.4, 81.5, 80.2, 75.5, 75.4, 72.7, 69.1, 67.3, 17.8. HRMS (ESI): m/z calcd for $C_{27}H_{30}O_5Na$ [M + Na] 457.1963, found 457.1968.



6 7

Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-α-D-non-8-enoglucopyranoside (7). Prepared by coupling of **6** (0.16 g, 0.3 mmol) with 2-pyridyl methallylsulfone (57 mg, 0.7 mmol) in α,α,α-trifluorotoluene (3.2 mL) and initiation with triethylborane (1.45 mL, 1.5 mmol) and air (Table 1, entry 1). After completion, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (hexane:ethyl acetate 6:1) to give **7** (57 mg, 40%) as a colorless syrup and **8** (64 mg, 51%) as a colorless syrup. The spectral data were consistent with the data acquired from allylation procedure utilizing lauroyl peroxide as the initiator



Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl- α-D-non-8-enoglucopyranoside (7). Compound **6** (50 mg, 0.1 mmol) was dissolved in a solvent mixture of heptane:PhCl 1:1 (2 mL) and treated with ethyl methallylsulfone (26 mg, 0.2 mmol).and AIBN (3 mg, 0.02 mmol) (Table 1, entry 3). The reaction mixture was stirred at 80 °C for 2 h with monitoring by TLC (hexane:ethyl acetate 3:1, R_f =0.6). After completion, the reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (hexane:ethyl acetate 3:1) to give **7** (4 mg, 10%) as a colorless syrup and **8** (2.6 mg, 6%). The spectral data were consistent with the data acquired from allylation procedure utilizing lauroyl peroxide as the initiator.

Photocatalyzed allylation using *fac*-Ir(ppy)$_3$ catalyst

Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl- α-D-non-8-enoglucopyranoside (7). To an oven-dried 100 mL Pyrex volumetric flask was added compound **6** (0.23 g, 0.4 mmol), 2-pyridyl methallylsulfone (0.16 g, 0.8 mmol) and tributylamine (0.2 mL, 0.8 mmol). Ir(ppy)$_3$ catalyst (5 mol%, 14 mg, 0.02 mmol), purified according to the literature protocol[2]and anhydrous acetonitrile (41 mL) were then added, and the mixture degassed with argon for 30 minutes. The flask was then placed in a 600 mL beaker lined with 12V blue LED strips and covered with aluminum foil. The reaction mixture was irradiated with a blue LED light till completion with monitoring by TLC (hexane:ethyl acetate 5:1, R_f =0.5). The mixture was then diluted with acetonitrile, concentrated at reduced pressure and the residue purified via silica gel chromatography (5:1) to give **7** (0.14 g, 68%) as a colorless syrup and **8** (23 mg, 13%). The spectral data were consistent with the data acquired from allylation procedure utilizing lauroyl peroxide as the initiator.

Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-4-keto-α-D-non-8-enoglucopyranoside (9). Compound **7** (1.85 g, 3.8 mmol) was dried under vaccum overnight and dissolved in anhydrous solution of DMSO:dichloromethane 2:1 (10.8 mL) under argon. The mixture was cooled to 0 °C. A solution of sulfur trioxide pyridine complex (1.81 g, 11.4 mmol) in DMSO (2 mL) was stirred at rt for 20 minutes then added dropwise to the sugar solution at 0 °C. The reaction mixture was allowed to come to rt and stirred till completion with monitoring by TLC (hexane:ethyl acetate 4:1, R_f =0.5). The reaction mixture was concentrated under reduced pressure and the residue diluted with dichloromethane (50 mL) and water (50 mL). The aqueous layer was extracted with dichloromethane twice and the combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane:ethyl acetate 4:1) to give **9** (1.50 g, 81%) as a colorless syrup. $[\alpha]_D^{23}$ = +135.1 (*c* = 1.2, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.20 (m, 15H), 5.03 – 4.94 (m, 2H, $PhCH_2$, H-1), 4.84 – 4.57 (m, 7H, $5PhCH_2$, $2H_{gem}$), 4.52 (d, *J* = 10.1 Hz, 1H, H-3), 4.16 (dd, *J* = 8.4, 3.4 Hz, 1H, H-5), 3.78 (dd, *J* = 10.1, 3.6 Hz, 1H, H-2), 2.21 – 2.01 (m, 3H, H-7, H-7', H-6), 1.80 – 1.63 (m, 4H, H-6', CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 144.9, 138.0, 137.9, 136.8, 128.5, 128.40,

128.38, 128.3, 128.2, 128.1, 128.0, 127.9, 127.83, 127.79, 110.6, 95.7, 82.98, 80.6, 74.4, 73.6, 72.5, 69.8, 33.2, 26.3, 22.4. HRMS (ESI): m/z calcd for $C_{31}H_{34}O_5Na$ [M + Na] 509.2304, found 509.2310.

Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-4-*C*-vinyl-α-D-non-8-enogalactopyranoside (10). A solution of **9** (0.86 g, 1.8 mmol) in dry THF (18 mL) was cooled to -78 °C under argon and treated with vinylmagnesium bromide (5.32 mL, 5.3 mmol). The reaction mixture was stirred at -78 °C for 2 h with monitoring by TLC (hexane:ethyl acetate 6:1, R_f = 0.6). After completion, the reaction mixture was concentrated and the residue purified by silica gel column chromatography (hexane:ethyl acetate 6:1) to give **10** (0.86 g, 97%) as a colorless syrup. $[\alpha]_D^{23}$ = +89.3 (*c* = 1.35, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.22 (m, 15H), 5.82 (dd, *J* = 17.2, 10.6 Hz, 1H, H-vinyl), 5.52 (dd, *J* = 17.2, 1.1 Hz, 1H, H-vinyl), 5.38 (dd, *J* = 10.7, 1.0 Hz, 1H, H-vinyl), 4.94 (d, *J* = 3.6 Hz, 1H, H-1), 4.88 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.80 (d, *J* = 12.3 Hz, 1H, $PhCH_2$), 4.77 – 4.73 (m, 2H), 4.69 (d, *J* = 11.9 Hz, 1H, $PhCH_2$), 4.66 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.59 (d, *J* = 12.3 Hz, 1H, $PhCH_2$), 4.56 (d, *J* = 11.9 Hz, 1H, $PhCH_2$), 3.92 (d, *J* = 9.6 Hz, 1H, H-3), 3.85 (dd, *J* = 9.6, 3.7 Hz, 1H, H-2), 3.78 (dt, *J* = 9.8, 3.51 Hz, 1H, H-5), 2.63 (s, 1H, OH), 2.35 – 2.28 (m, 1H), 2.07 – 2.00 (m, 1H), 1.83 – 1.65 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 139.7, 138.3, 138.2, 137.2, 128.5, 128.4, 128.3, 128.24, 128.17, 127.93, 127.87, 127.8, 127.7, 116.6, 110.3, 95.1, 80.1, 72.9, 71.0, 68.7, 34.6, 25.6, 22.5. HRMS (ESI): m/z calcd for $C_{33}H_{38}O_5Na$ [M + Na] 537.2617, found 537.2622.

Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-α-D-non-8-enogalactopyranoside (11). A solution of **10** (0.76 g, 1.5 mmol) in dry dichloromethane (4 mL) was treated with 2nd gen. Grubbs catalyst (0.1 g, 0.2 mmol). The reaction mixture was heated at 40 °C till completion with monitoring by TLC (hexane:ethyl acetate 3:1, R_f = 0.5). After completion, the reaction mixture was concentrated and the concentrate purified by silica gel column chromatography (hexane:ethyl acetate 3:1) to give **11** (0.62 g, 85%) as a light brown syrup. $[\alpha]_D^{23}$ = +65.6 (*c* = 0.8, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.04 (m, 15H), 5.55 (s, 1H), 5.08 (d, *J* = 11.2 Hz, 1H), 4.93 (d, *J* = 3.9 Hz, 1H, H-1), 4.71 (d, *J* = 12.2 Hz, 2H, $PhCH_2$), 4.69 – 4.60 (m, 2H, $PhCH_2$), 4.55 (d, *J* = 11.8 Hz, 1H, $PhCH_2$), 4.01 (dd, *J* = 9.4, 4.0 Hz, 1H, H-2), 3.74 (dd, *J* = 11.9, 3.7 Hz, 1H, H-5), 3.68 (d, *J* = 9.4 Hz, 1H, H-3), 2.15 – 1.94 (m, 3H, H-7, H-7', H-6), 1.74 – 1.53 (m, 4H, CH_3, H-6'). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.6, 138.3, 137.5, 128.5, 128.39, 128.35, 128.1, 128.0, 127.80, 127.75, 127.7, 122.1, 96.2, 80.2, 78.6, 75.96, 72.9, 70.7, 69.3, 69.3, 30.3, 23.3, 21.7. HRMS (ESI): m/z calcd for $C_{31}H_{34}O_5Na$ [M + Na] 509.2304, found 509.2316.

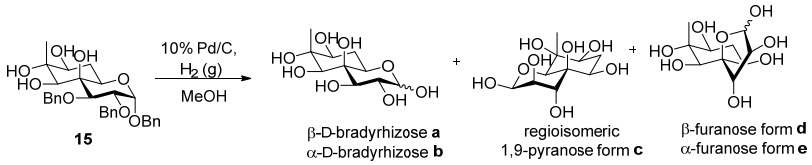
Benzyl 2,3-di-*O*-benzyl-6,8,9-trideoxy-8-methyl-7-keto-α-D-non-8-enogalactopyranoside (12). A solution of **11** (0.48 g, 1.0 mmol) in dry 1.4 dioxane (10 mL) was treated with selenium dioxide (0.11 g, 1.0 mmol) added in four portions over the period of the reaction. The reaction mixture was heated at 80 °C till completion with monitoring by TLC (hexane:ethyl acetate 4:1, R_f = 0.3). After completion, the reaction mixture was concentrated and the residue purified by silica gel column chromatography (hexane:ethyl acetate 4:1 to 2:1) to give **12** (0.34 g, 70%) as an off white crystalline solid. Mp 117-120 °C. $[\alpha]_D^{23}$ = +64.6 (*c* = 0.35, $CHCl_3$), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.20 (m, 15H), 6.47 (s, 1H), 5.12 (d, *J* = 11.3 Hz, 1H,

$PhCH_2$), 4.94 (d, J = 3.8 Hz, 1H, H-1), 4.74 (d, J = 11.4 Hz, 1H, $PhCH_2$), 4.68 (d, J = 12.2 Hz, 1H, $PhCH_2$), 4.63 (d, J = 11.7 Hz, 1H, $PhCH_2$), 4.57 (d, J = 12.2 Hz, 1H, $PhCH_2$), 4.54 (d, J = 11.7 Hz, 1H, $PhCH_2$), 4.10 (dd, J = 12.8, 4.9 Hz, 1H, H-5), 4.03 (dd, J = 9.3, 3.9 Hz, 1H, H-2), 3.78 (d, J = 9.3 Hz, 1H, H-3), 2.91 (dd, J = 16.5, 12.8 Hz, 1H, H-6_{ax}), 2.48 (dd, J = 16.5, 4.9 Hz, 1H, H-6_{eq}), 1.70 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 141.2, 137.9, 137.8, 136.9, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 96.2, 78.4, 78.3, 75.9, 72.9, 70.5, 69.6, 67.0, 37.99, 15.6. HRMS (ESI): m/z calcd for $C_{31}H_{32}O_6Na$ [M + Na] 523.2097, found 523.2096.

Benzyl 2,3-di-*O*-benzyl-6,8,9-trideoxy -8-methyl-α-D-non-8-enogalactopyranoside (13). A solution of **12** (0.39 g, 0.8 mmol) in dry methanol (7 mL) was treated with cerium (III) chloride heptahydrate (0.44 g, 1.2 mmol) and stirred at rt for 1 h. The reaction mixture was cooled to -78 °C and sodium borohydride (50 mg, 1.3 mmol) was added, with monitoring by TLC (hexane:ethyl acetate 1:1, R_f = 0.3). After completion, the reaction mixture was concentrated and the crude diluted with ethyl acetate (50 mL) and washed with water (20 mL). The aqueous layer was extracted with ethyl acetate and the combined organic layer dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography (hexane:ethyl acetate 1:1) to give **13** (0.34 g, 86%) as a colorless liquid. $[\alpha]_D^{23}$ = +55.5 (c = 0.95, $CHCl_3$), ^{1}H NMR (400 MHz, CD_3OD) δ 7.51 – 7.13 (m, 15H), 5.50 (s, 1H, H-9), 5.01 – 4.92 (m, 2H, $PhCH_2$, H-1), 4.69 – 4.63 (m, 2H, $2PhCH_2$), 4.63 – 4.52 (m, 3H, $3PhCH_2$), 4.05 – 3.94 (m, 2H, H-2, H-7), 3.62 (dd, J = 12.2, 4.1 Hz, 1H, H-5), 3.54 (d, J = 9.6 Hz, 1H, H-3), 2.02 – 1.86 (m, 2H, H-6, H-6'), 1.66 (s, 3H, CH_3). ^{13}C NMR (101 MHz, CD_3OD) δ 141.4, 138.6, 138.3, 137.6, 128.2, 128.1, 128.0, 127.96, 127.9, 127.8, 127.5, 127.4, 127.3, 122.9, 96.5, 79.7, 78.4, 75.3, 72.4, 70.5, 69.1, 69.0, 67.7, 31.4, 17.96. HRMS (ESI): m/z calcd for $C_{31}H_{34}O_6Na$ [M + Na] 525.2253, found 525.2252.

Benzyl 8,9-anhydro-2,3-di-*O*-benzyl-6-deoxy-8-methyl-α-D-nonagalactopyranoside (14). A solution of **13** (0.34 g, 0.7 mmol) in dry THF (6.7 mL) was treated with *m*-chloroperoxybenzoic acid (72 mg, 0.4 mmol) and stirred at rt, with monitoring by TLC (hexane:ethyl acetate:methanol 1:1:0.1, R_f = 0.3). After completion, the reaction mixture was concentrated under reduced pressure, diluted with ethyl acetate (50 mL) and neutralized with 0.2 M aqueous sodium bicarbonate (100 mL). The aqueous layer was extracted with ethyl acetate twice and the combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate:methanol 1:1:0.1) to give **14** (0.29 g, 83%) as a syrup. $[\alpha]_D^{23}$ = +28.9 (c = 0.7, $CHCl_3$), ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.16 (m, 15H), 5.09 (d, J = 11.7 Hz, 1H, $PhCH_2$), 4.85 (d, J = 3.9 Hz, 1H, H-1), 4.72 (d, J = 11.7 Hz, 1H, $PhCH_2$), 4.69 (d, J = 11.8 Hz, 1H, $PhCH_2$), 4.62 – 4.59 (m, 2H, $2PhCH_2$), 4.56 (d, J = 11.8 Hz, 1H, $PhCH_2$), 4.07 (dd, J = 9.4, 3.9 Hz, 1H, H-2), 3.73 (dd, J = 10.4, 6.3 Hz, 1H, H-7), 3.69 (d, J = 9.4 Hz, 1H, H-3), 3.19 (dd, J = 12.7, 2.7 Hz, 1H, H-5), 2.78 (s, 1H, H-9), 1.63 (ddd, J = 12.3, 6.3, 2.8 Hz, 1H, H-6_{eq}), 1.48 (td, J = 12.6, 10.4 Hz, 1H, H-6_{ax}), 1.24 (s, 3H, methyl). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.0, 137.3, 128.7, 128.5, 128.41, 128.39, 127.99, 127.97, 127.8, 96.7, 78.3, 75.3, 73.1, 70.8, 69.9, 69.6, 67.4, 63.4, 62.95, 28.5, 19.1. HRMS (ESI): m/z calcd for $C_{31}H_{34}O_7Na$ [M + Na] 541.2202, found 541.2210.

Benzyl 2,3-di-*O*-benzyl-8-α-D-bradyrhizopyranoside (15). A solution of **14** (135 mg, 0.3 mmol) in 1,4 dioxane:water 05:1.5 (5 mL), was treated with concentrated sulphuric acid (30 µL, 0.6 mmol) added dropwise in three portions at 65 °C. The reaction was monitored by TLC (hexane:ethyl acetate:methanol 1:1:0.2, R_f =0.2). After completion, the mixture was diluted with ethyl acetate (20 mL) and neutralized with saturated aqueous sodium bicarbonate (50 mL). The aqueous layer was extracted with ethyl acetate twice and the combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate:methanol 1:1:0.2) to give **15** (70 mg, 50%) as a white amorphous solid. Mp, 148-152 °C. $[\alpha]_D^{23}$ = +66.3 (*c* = 0.75 , $CHCl_3$), ^{1}H NMR (600 MHz, CD_3OD) δ 7.49 – 7.11 (m, 15H), 4.95 – 4.92 (m, 2H, $PhCH_2$, H-1), 4.78 (d, *J* = 10.4 Hz, 1H, $PhCH_2$), 4.66 (d, *J* = 12.2 Hz, 1H, $PhCH_2$), 4.57 (d, *J* = 12.2 Hz, 1H, $PhCH_2$), 4.55 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 4.52 (d, *J* = 11.5 Hz, 1H, $PhCH_2$), 3.93 (dd, *J* = 9.5, 3.7 Hz, 1H, H-2), 3.89 (d, *J* = 9.6 Hz, 1H, H-3), 3.70 (dd, *J* = 12.4, 4.0 Hz, 1H, H-5), 3.48 (s, 1H, H-9), 3.43 (dd, *J* = 12.2, 4.3 Hz, 1H, H-7), 1.82 (q, *J* = 12.2 Hz, 1H, H-6_{ax}), 1.64 (dt, *J* = 11.9, 4.2 Hz, 1H, H-6_{eq}), 1.22 (s, 3H, methyl). ^{13}C NMR (151 MHz, CD_3OD) δ 138.14, 138.08, 137.5, 128.14, 128.09, 128.0, 127.99, 127.96, 127.9, 127.8, 127.54, 127.47, 127.4, 95.97, 82.7, 78.8, 78.0, 77.2, 74.95, 73.8, 72.5, 72.3, 69.2, 66.6, 31.1, 14.0. HRMS (ESI): m/z calcd for $C_{31}H_{36}O_8Na$ [M + Na] 559.2308, found 559.2311.



α,β-D-Bradyrhizose (16). Compound **15** (45 mg, 0.08 mmol) was dissolved in dry methanol (5 ml) then 10% Pd/C (79 mg, 0.1 mmol) was added and the mixture degassed with argon. The reaction mixture was then purged with H_2 gas then put under H_2 gas at rt till completion. The palladium on carbon was filtered and the filtrate concentrated at reduced pressure. The residual crude was purified by reversed phase column chromatography (on a C-18 silica gel) using H_2O as the eluent yielding compound **16** (21 mg, 100% , as an equilibrium mixture of α-D-bradyrhizose, β-D-bradyrhizose, α,β-furanoses and a regioisomeric 1,9-pyranose) as a white foam with spectral data consistent with the literature.[3] ^{1}H NMR (900 MHz, D_2O) δ 5.25 (d, *J* = 3.7 Hz, 0.08H, H-1**e**), 5.23 (d, *J* = 4.1 Hz, 0.08H), 5.21 (d, *J* = 4.3 Hz, 0.42H, H-1**b**), 5.05 (s, 0.03H, H-1**d**), 5.04 (s, 0.17H, H-1**c**), 4.61 (d, *J* = 8.1 Hz, 1H, H-1**a**), 4.37 – 4.25 (m, 0.28H), 4.18 – 4.08 (m, 0.24H), 4.06 – 3.96 (m, 0.53H), 3.94 - 3.91 (m, 0.57H), 3.85 – 3.77 (m, 3.14H), 3.78 – 3.67 (m, 4.83H), 3.50 – 3.42 (m, 0.98H), 2.02 – 1.92 (m, 0.17H), 1.92 – 1.82 (m, 0.40H), 1.34 – 1.30 (m, 0.55H), 1.25 - 1.21 (m, 3.09H), 1.19 – 1.15 (m, 0.80H). ^{13}C NMR (151 MHz, D_2O) δ96.5, 93.6, 93.2, 92.2, 78.4, 78.2, 77.6, 77.3, 74.4, 72.8, 72.6, 72.2, 71.99, 70.5, 69.0, 65.4, 30.9, 30.8, 14.0, 13.99. HRMS (ESI): m/z calcd for $C_{10}H_{18}O_8Na$ [M + Na] 289.0899, found 289.0900.

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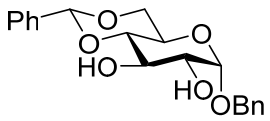
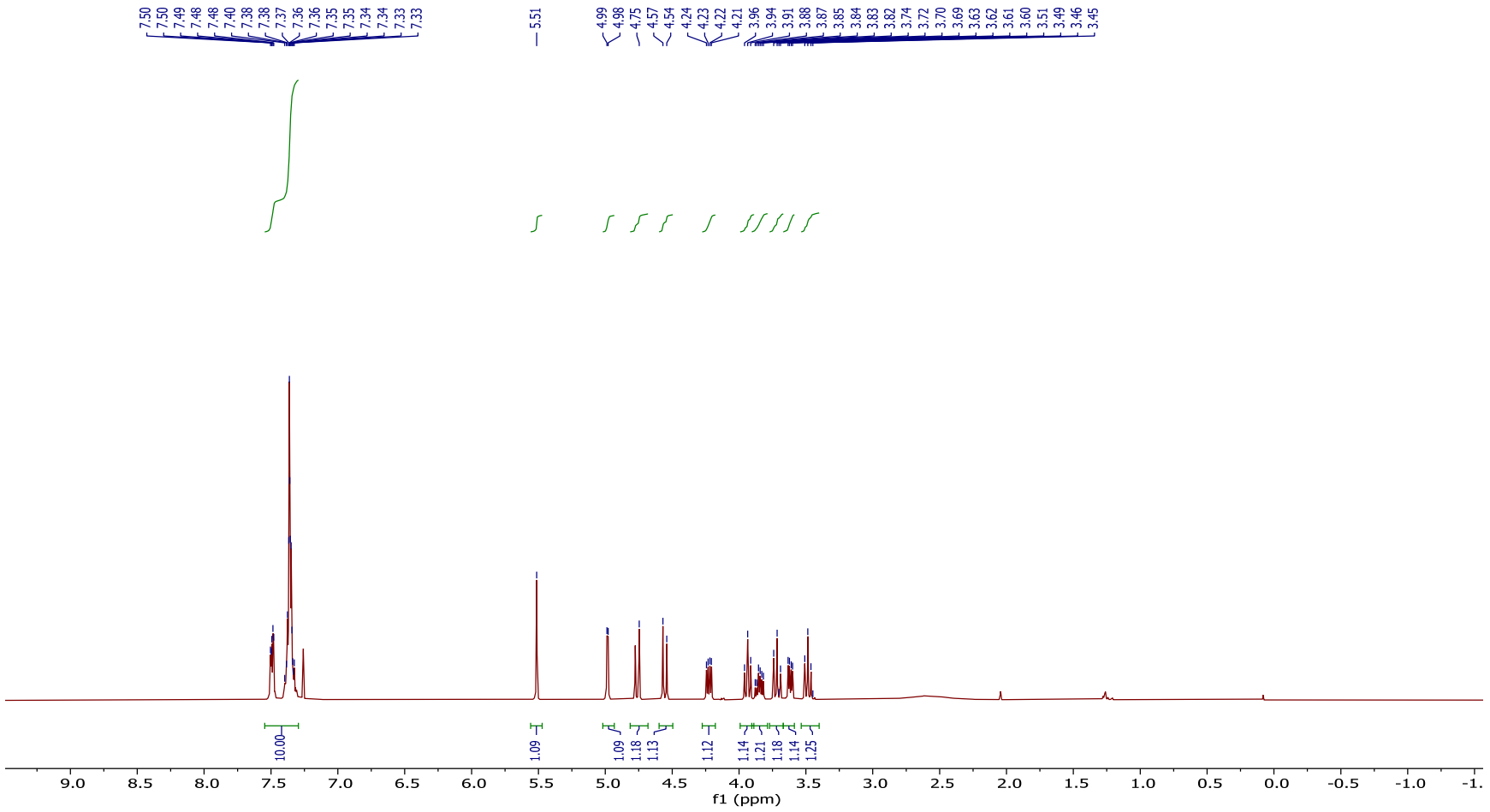
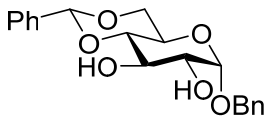
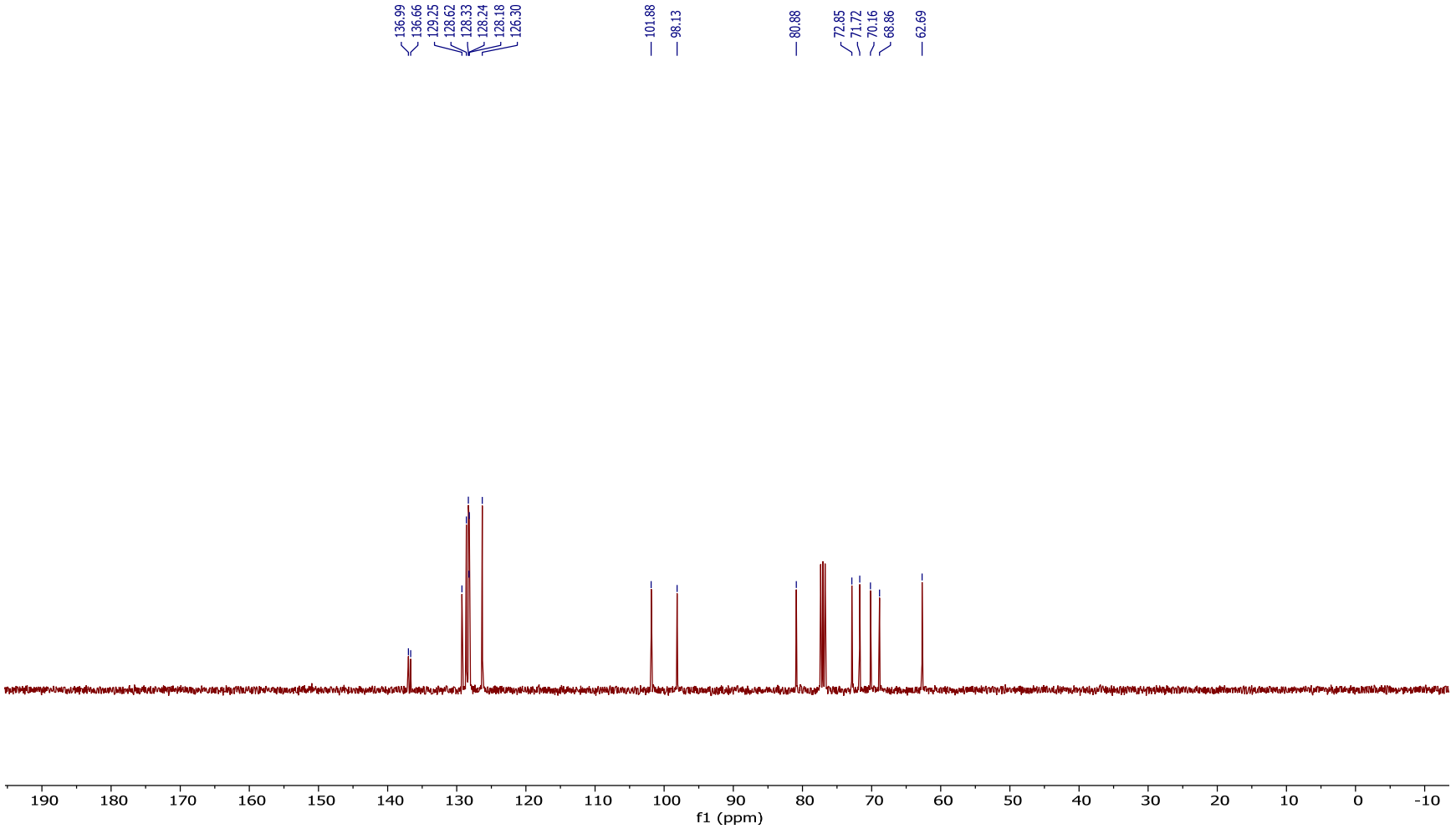
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside **(3)**



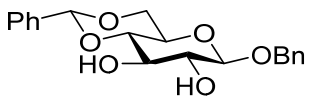


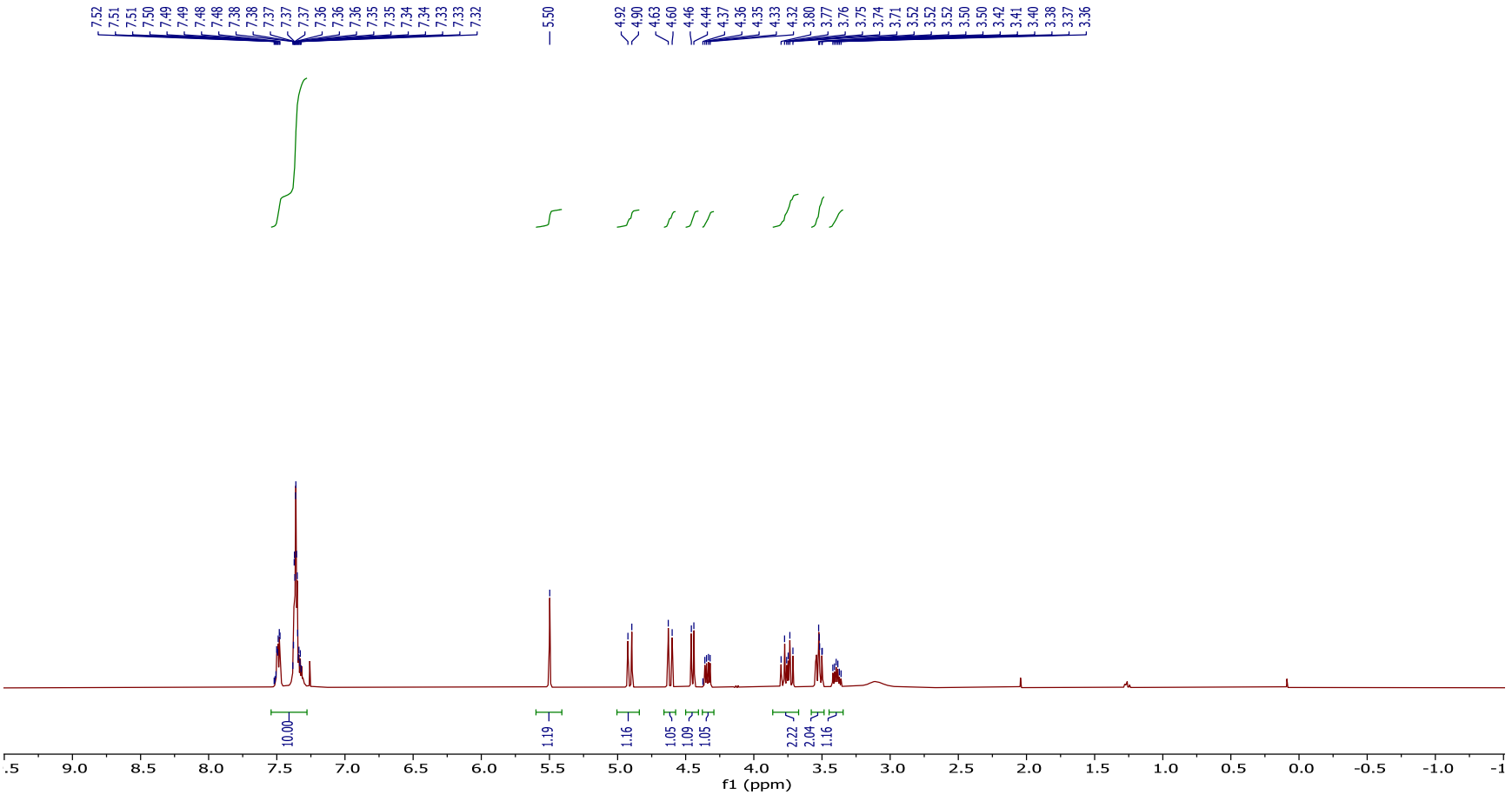
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside **(3)**



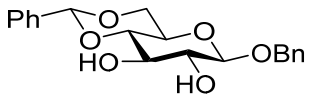


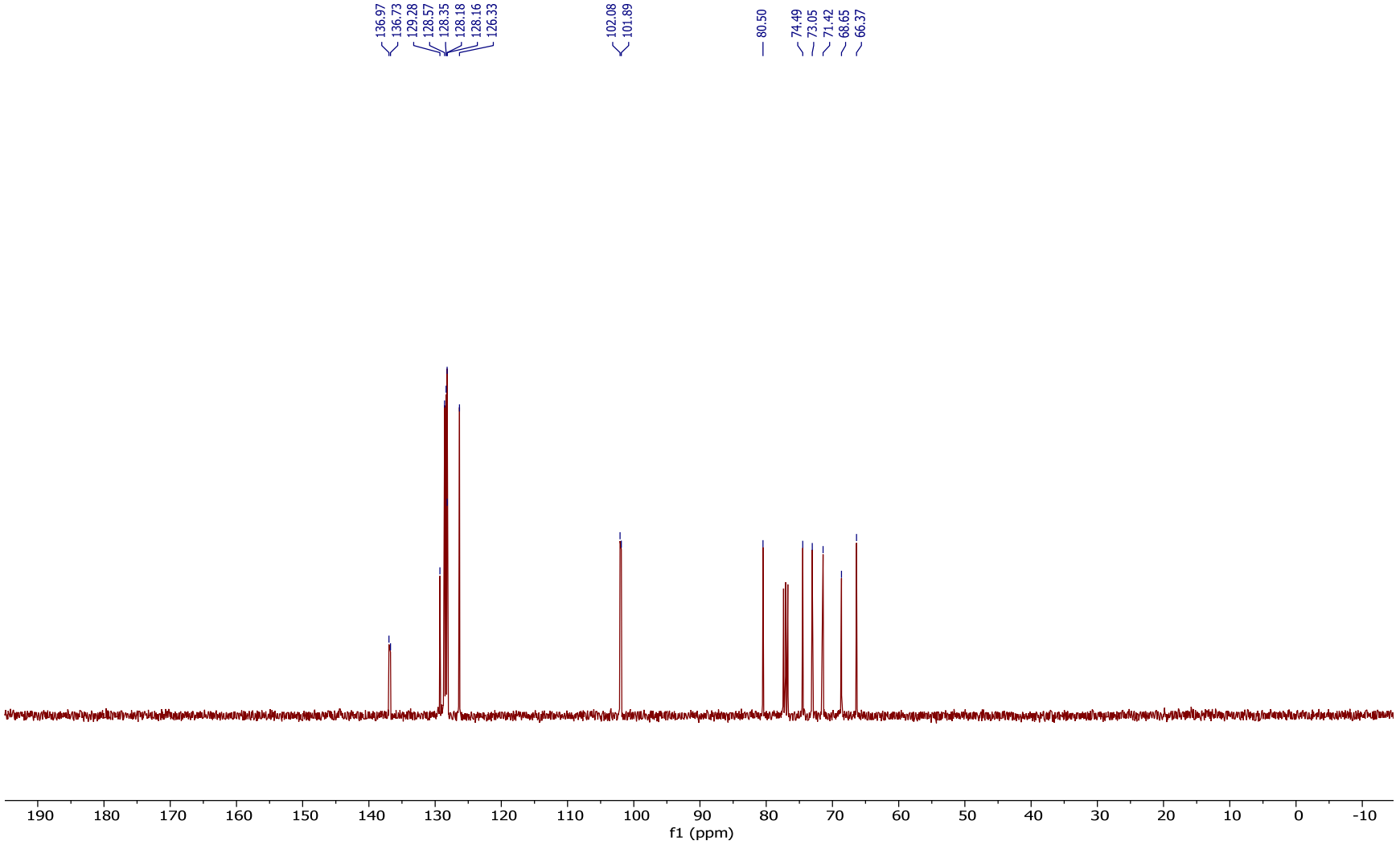
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 4,6-*O*-benzylidene-β-D-glucopyranoside **(3)**



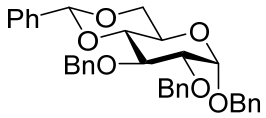


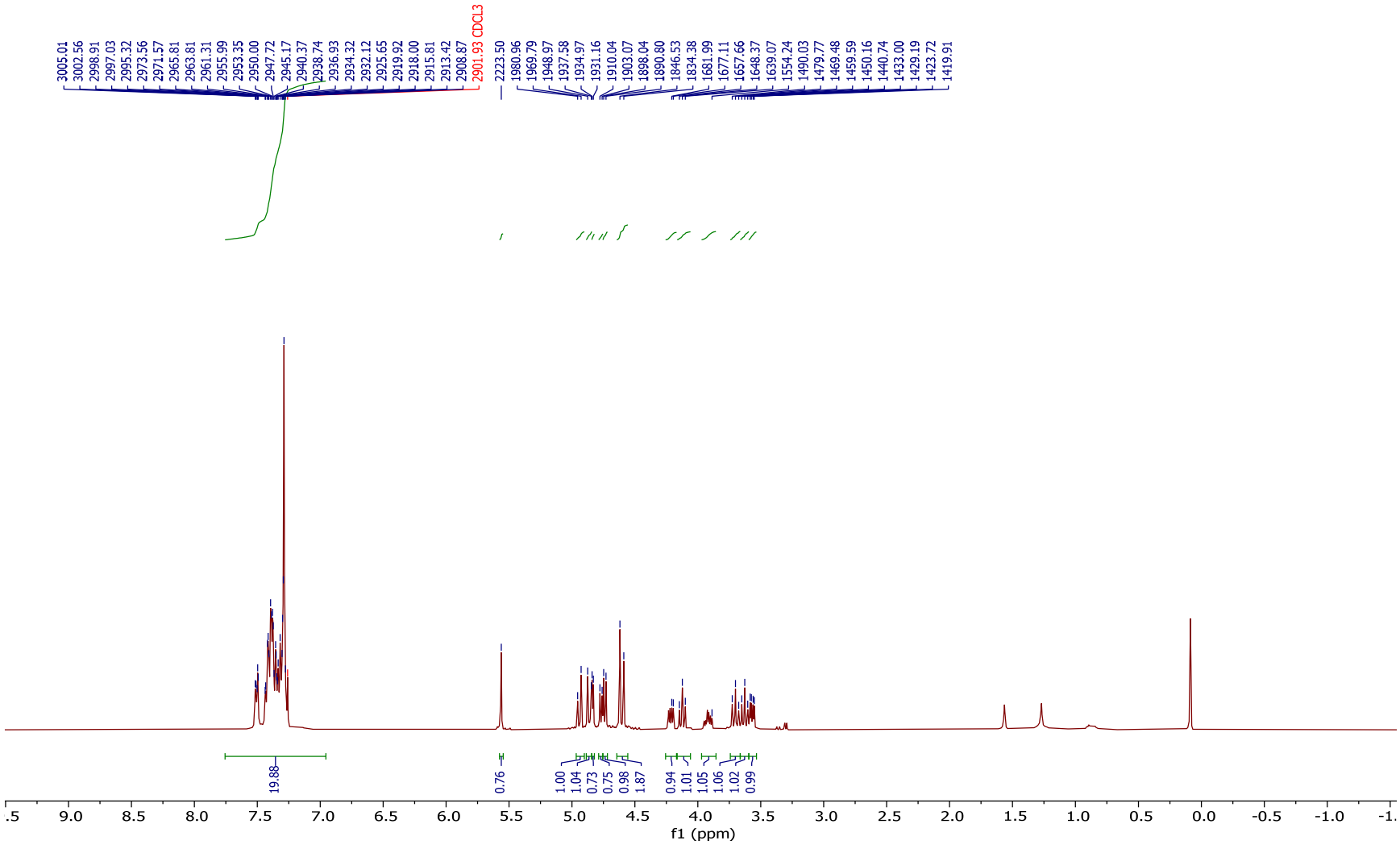
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 4,6-*O*-benzylidene-β-D-glucopyranoside **(3)**



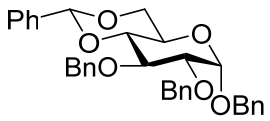


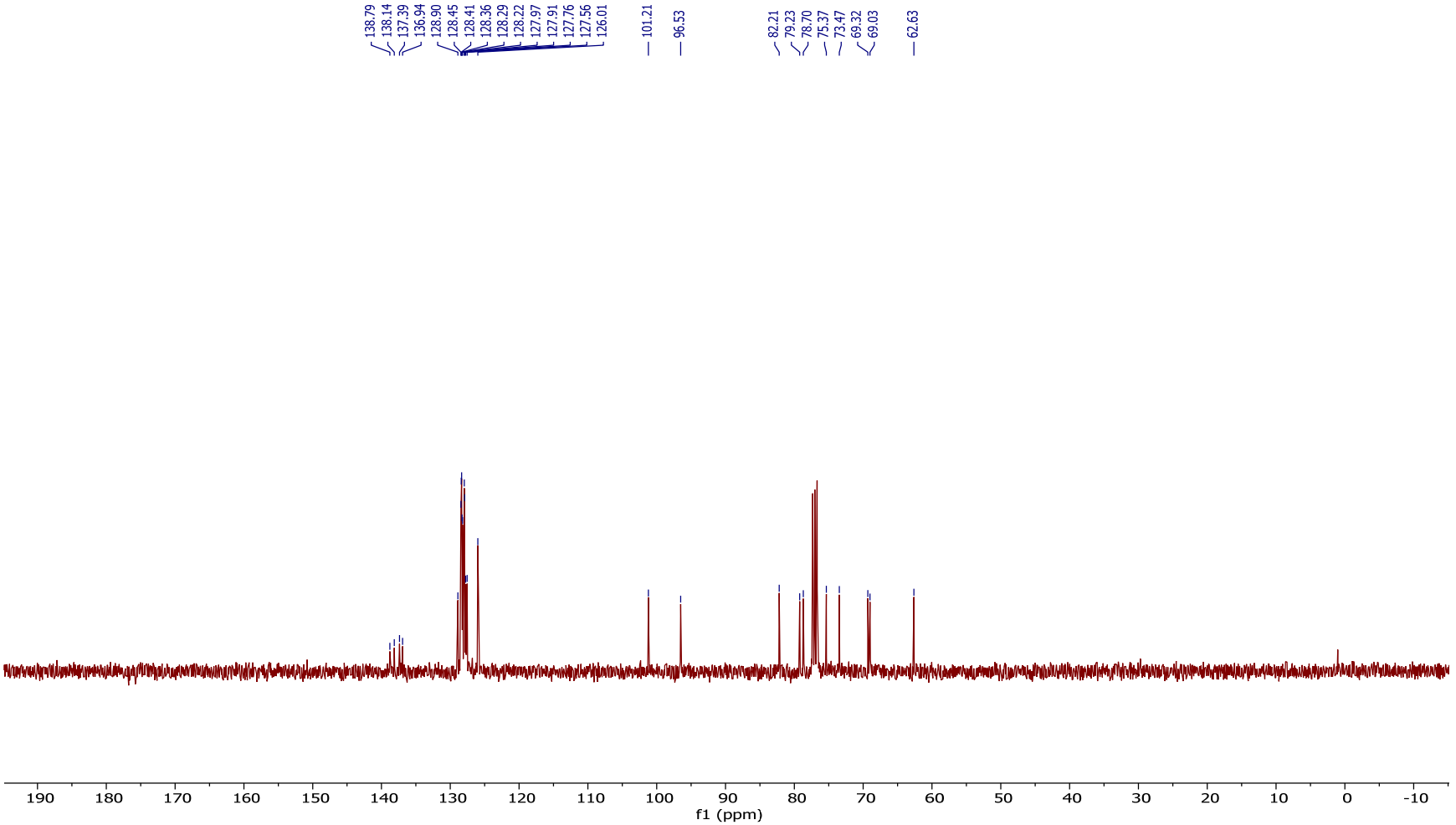
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside **(4)**



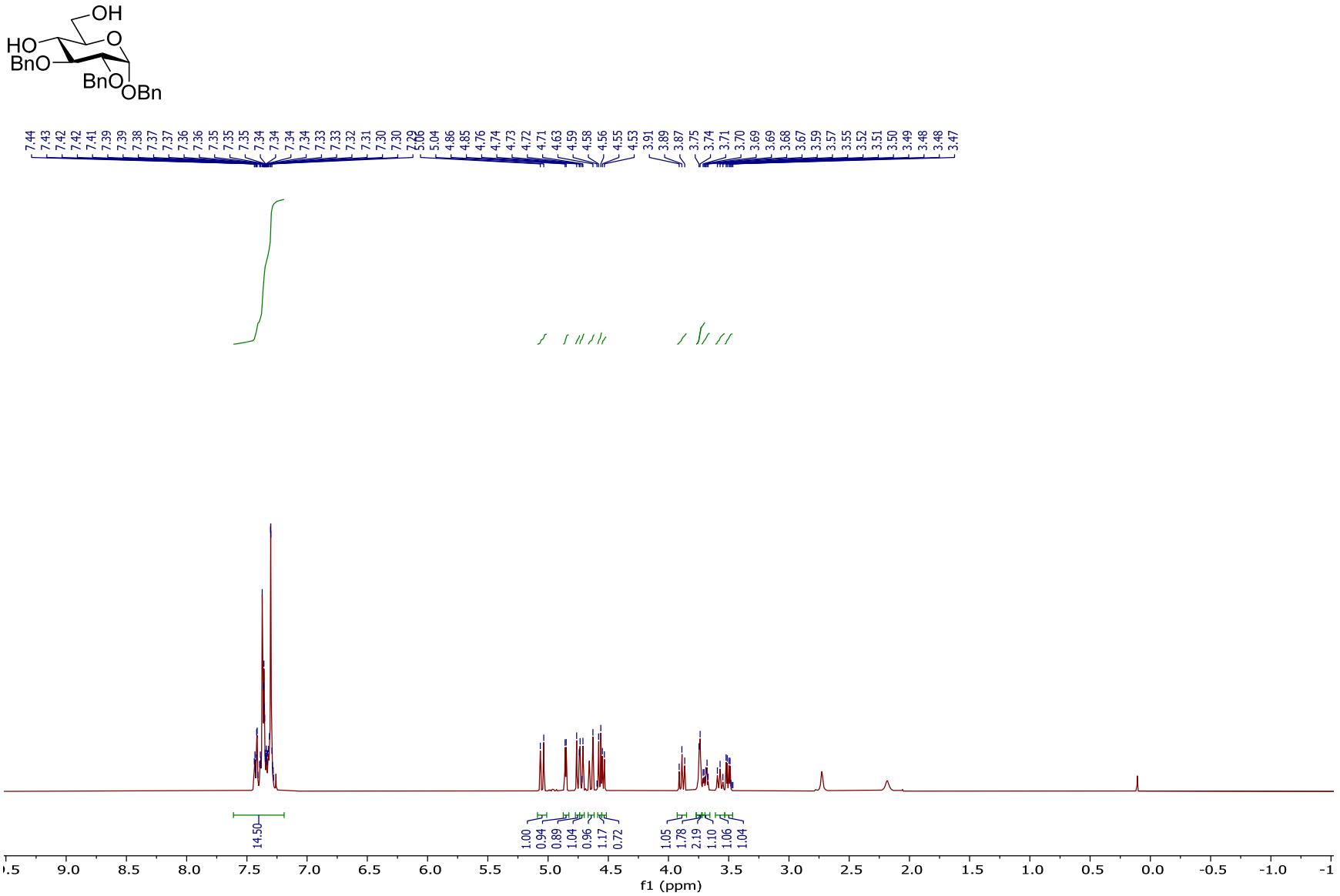


^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside **(4)**

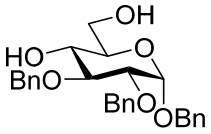


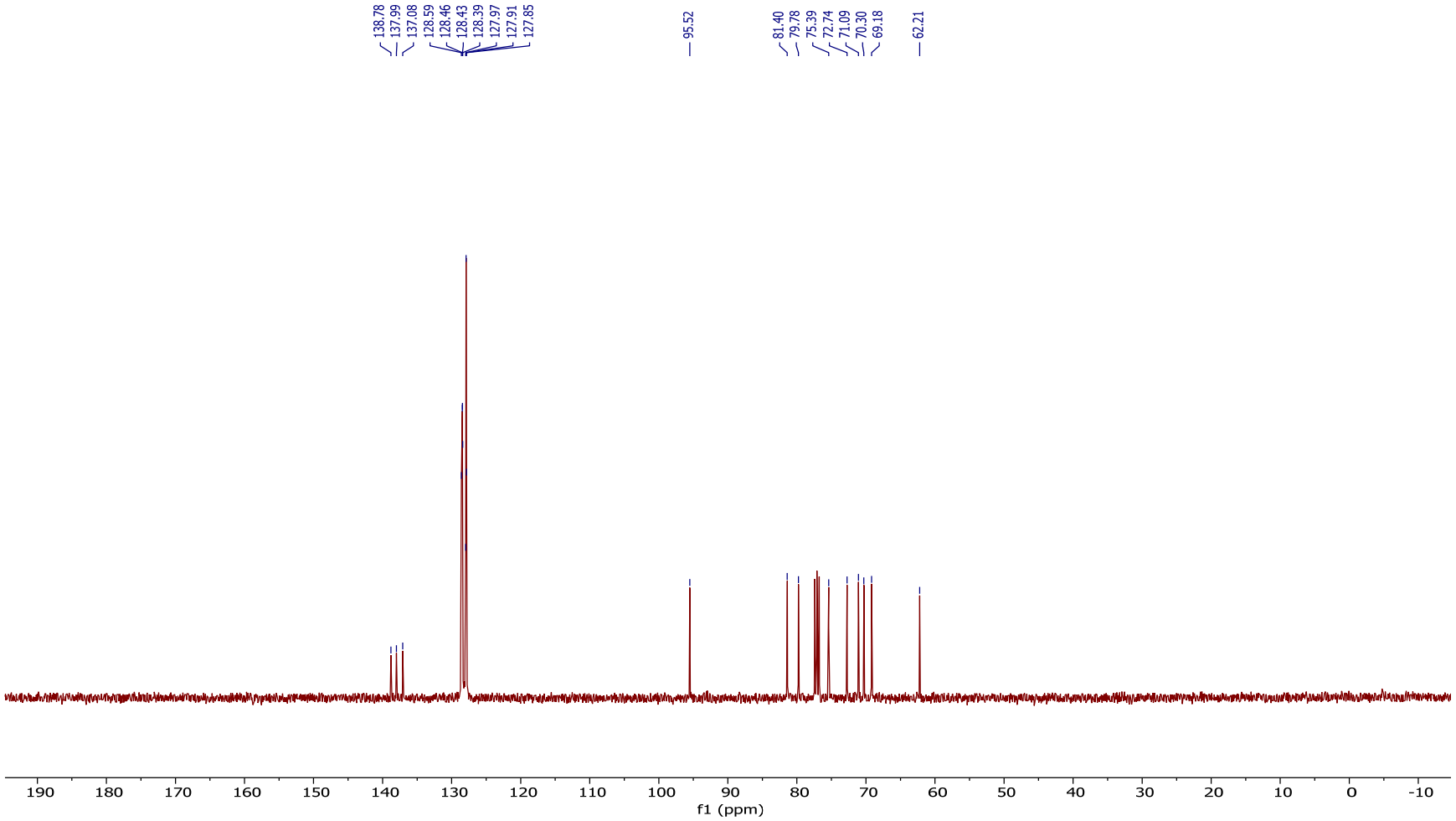


^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside **(5)**

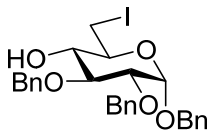


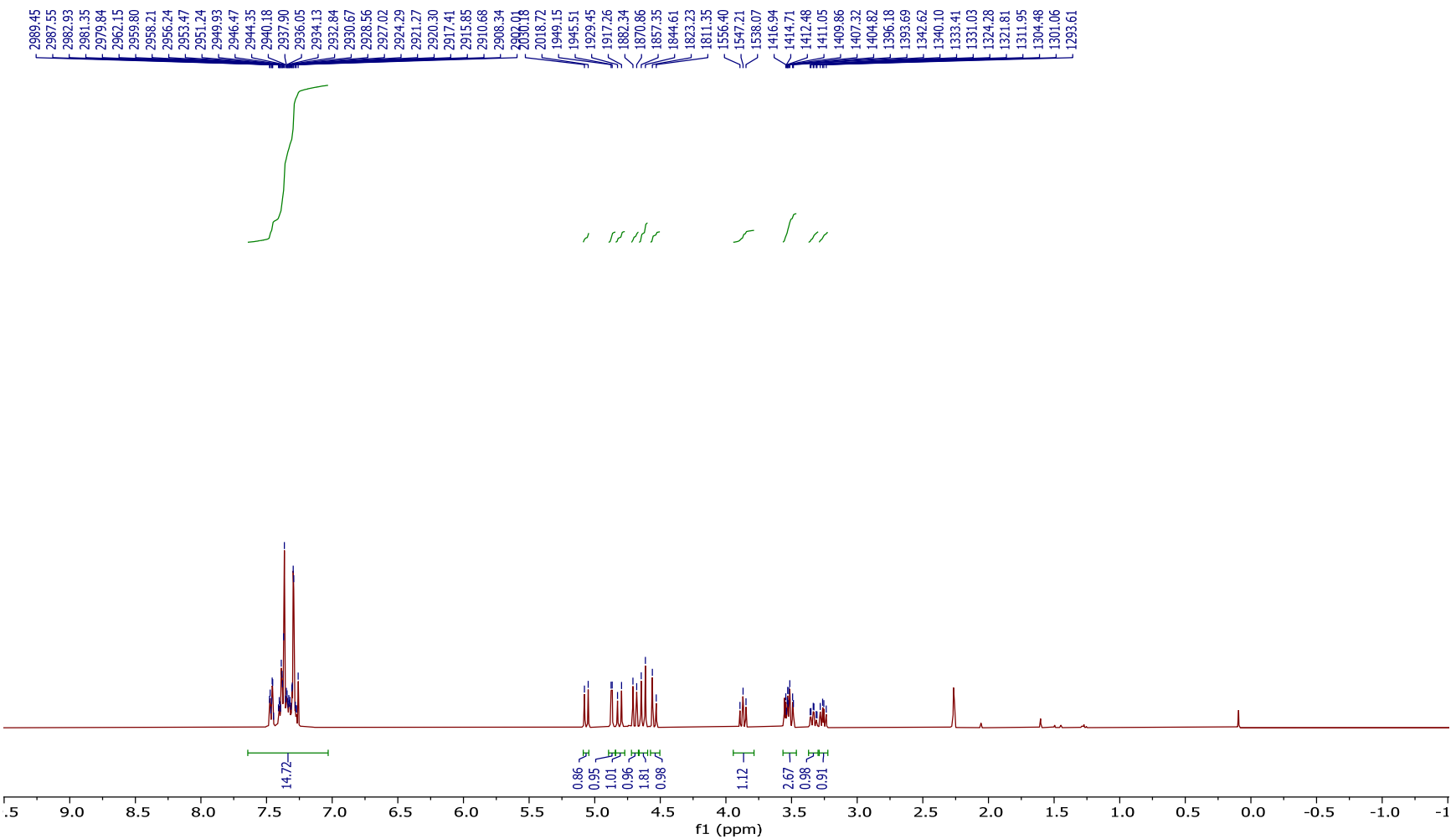
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-α-D-glucopyranoside **(5)**



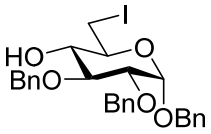


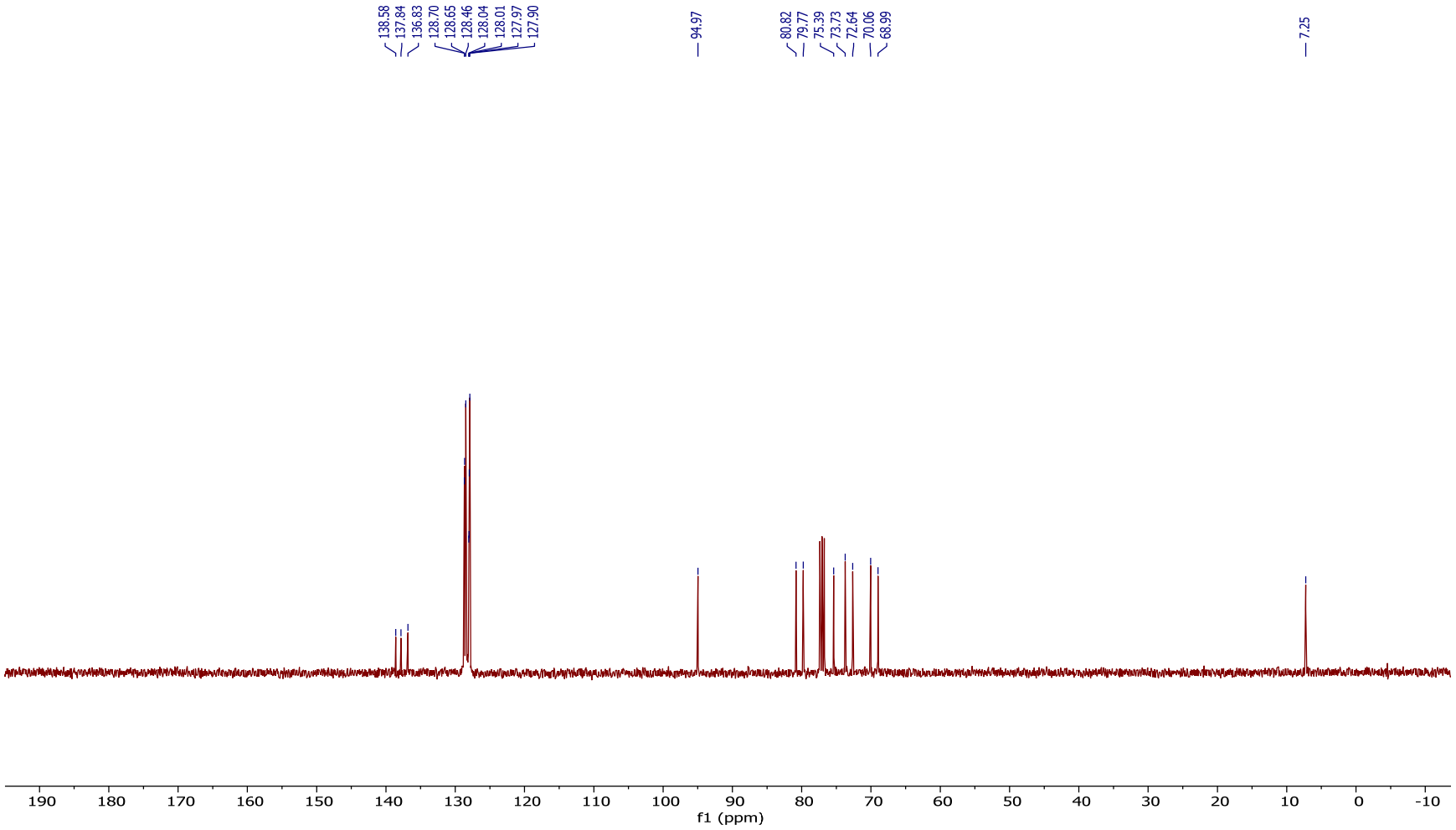
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside **(6)**



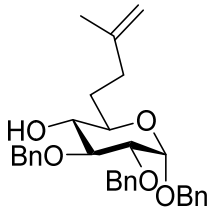


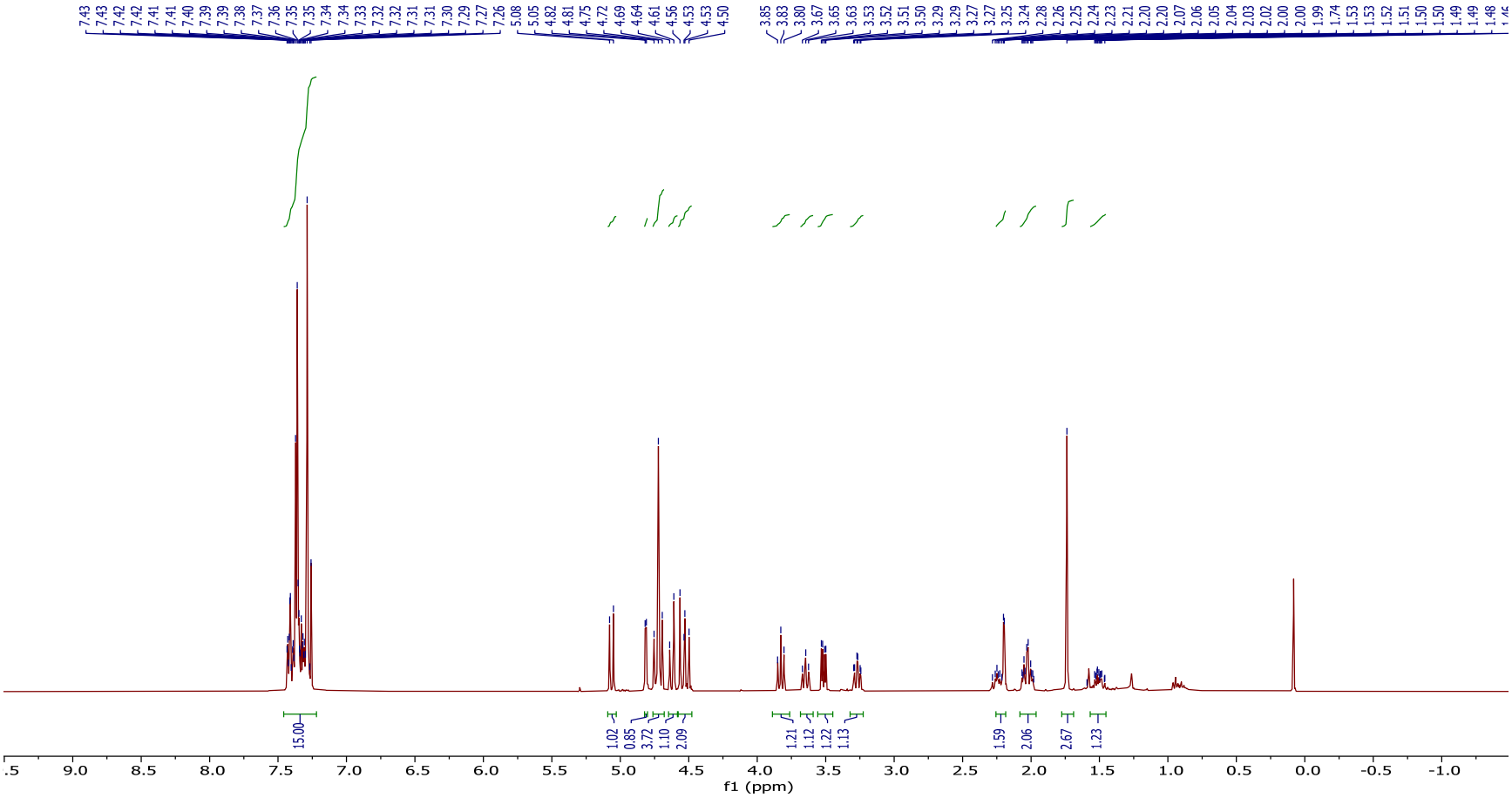
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6-deoxy-6-iodo-α-D-glucopyranoside **(6)**



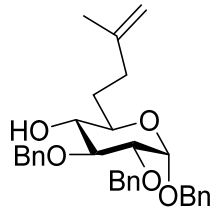


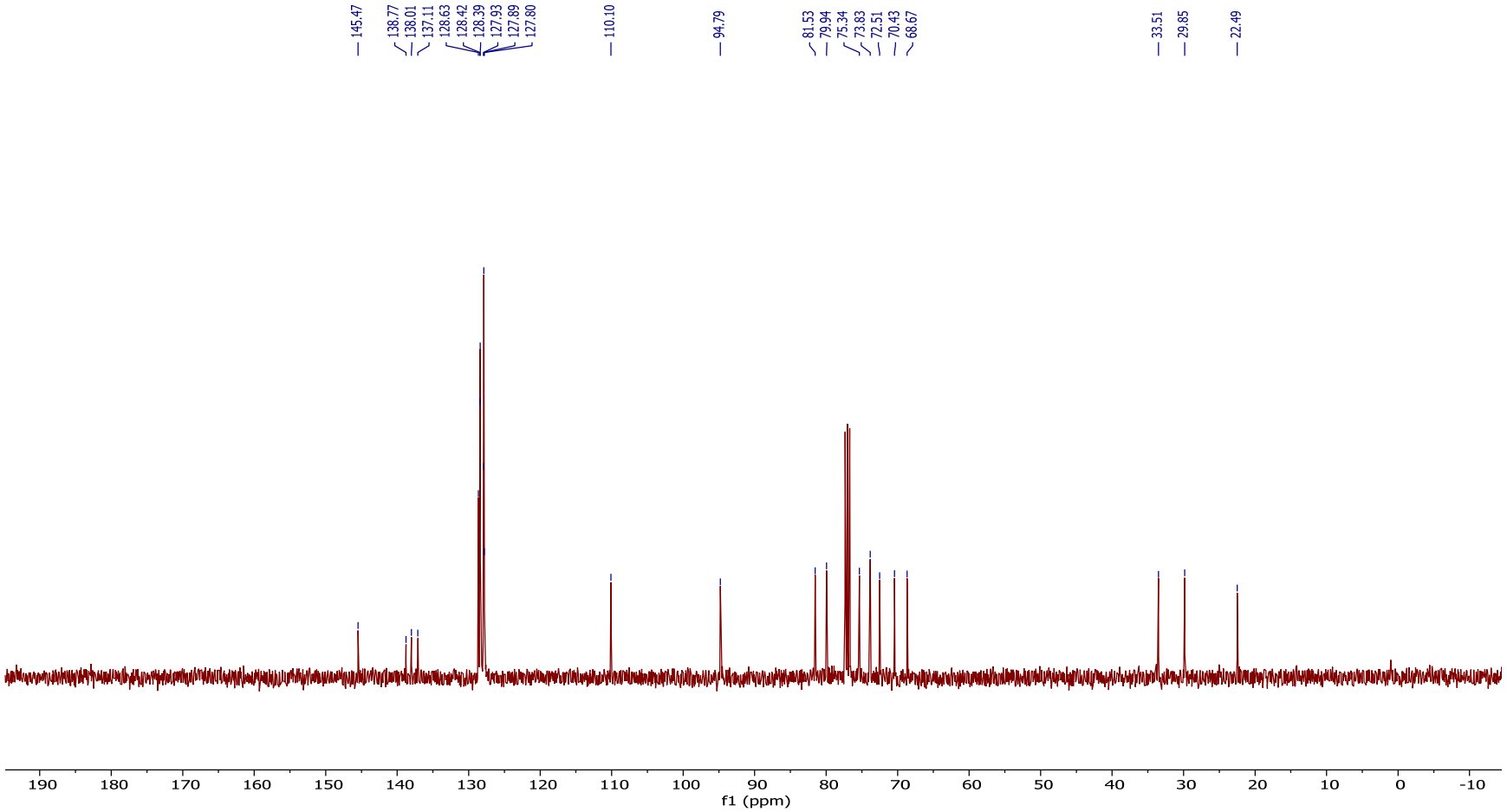
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-α-D-non-8-enoglucopyranoside **(7).**



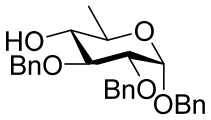


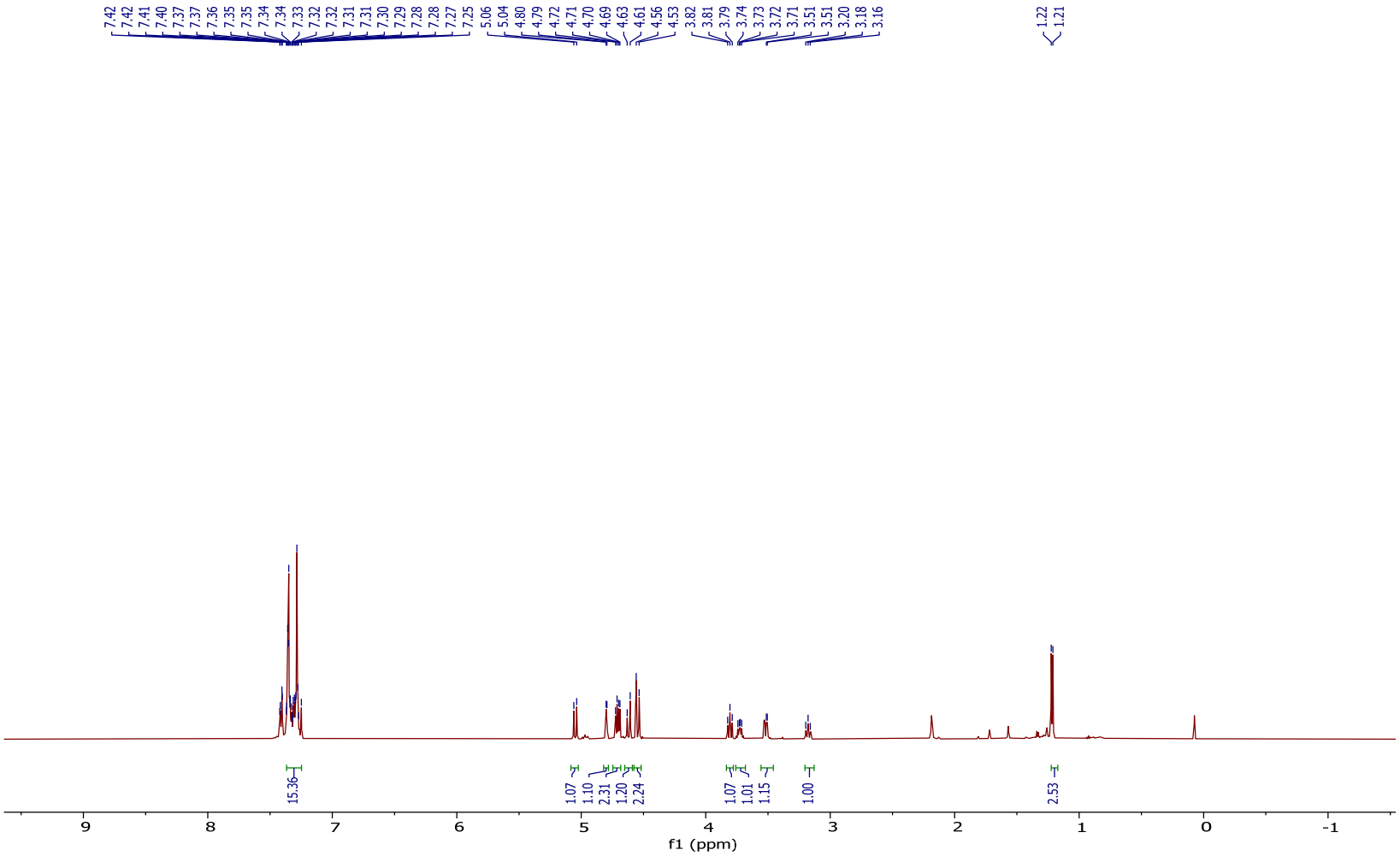
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-α-D-non-8-enoglucopyranoside **(7)**.



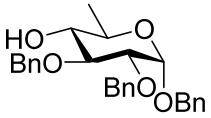


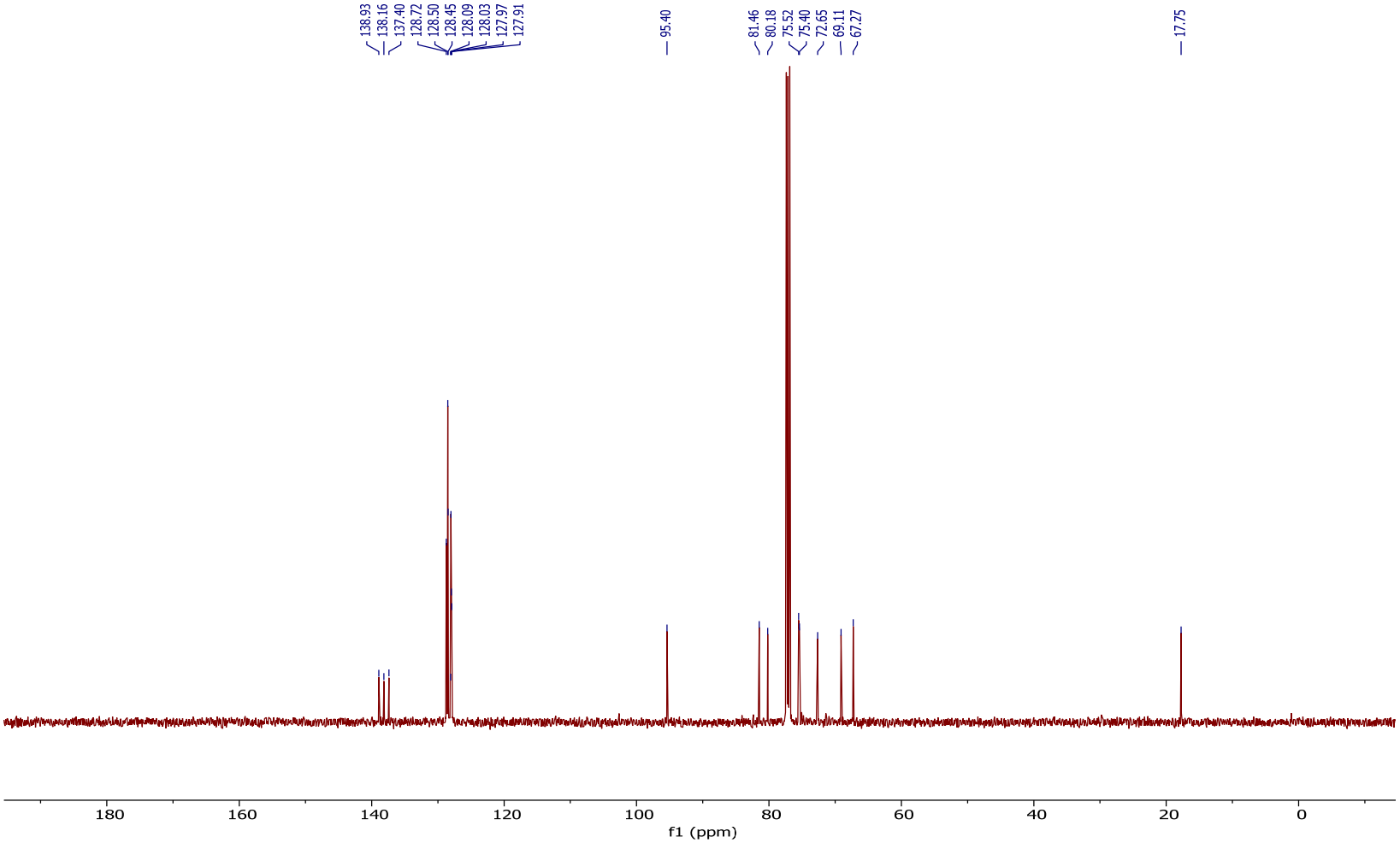
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside **(8)**



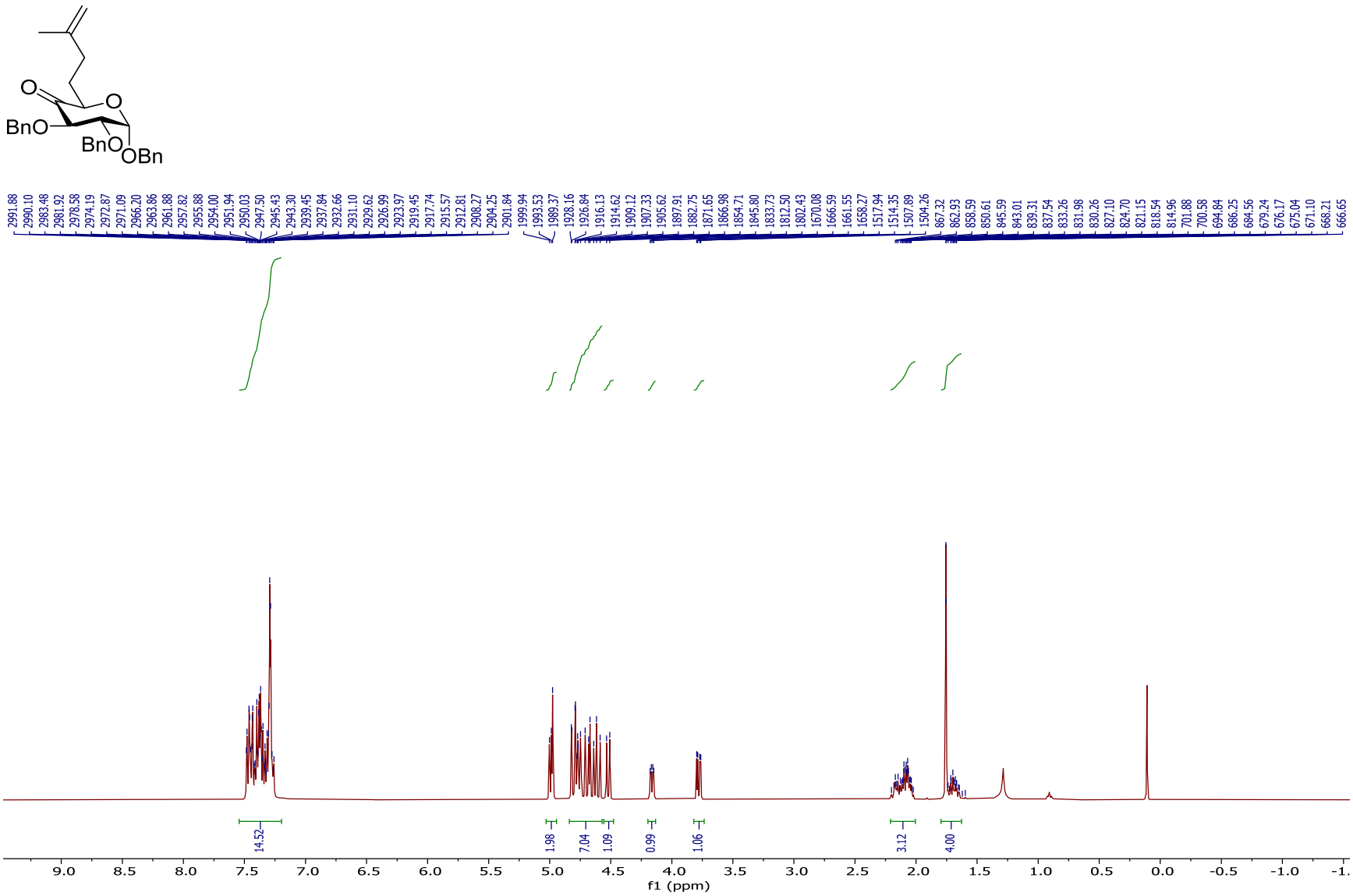


^{13}C NMR (126 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside **(8)**

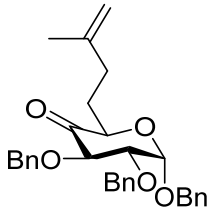


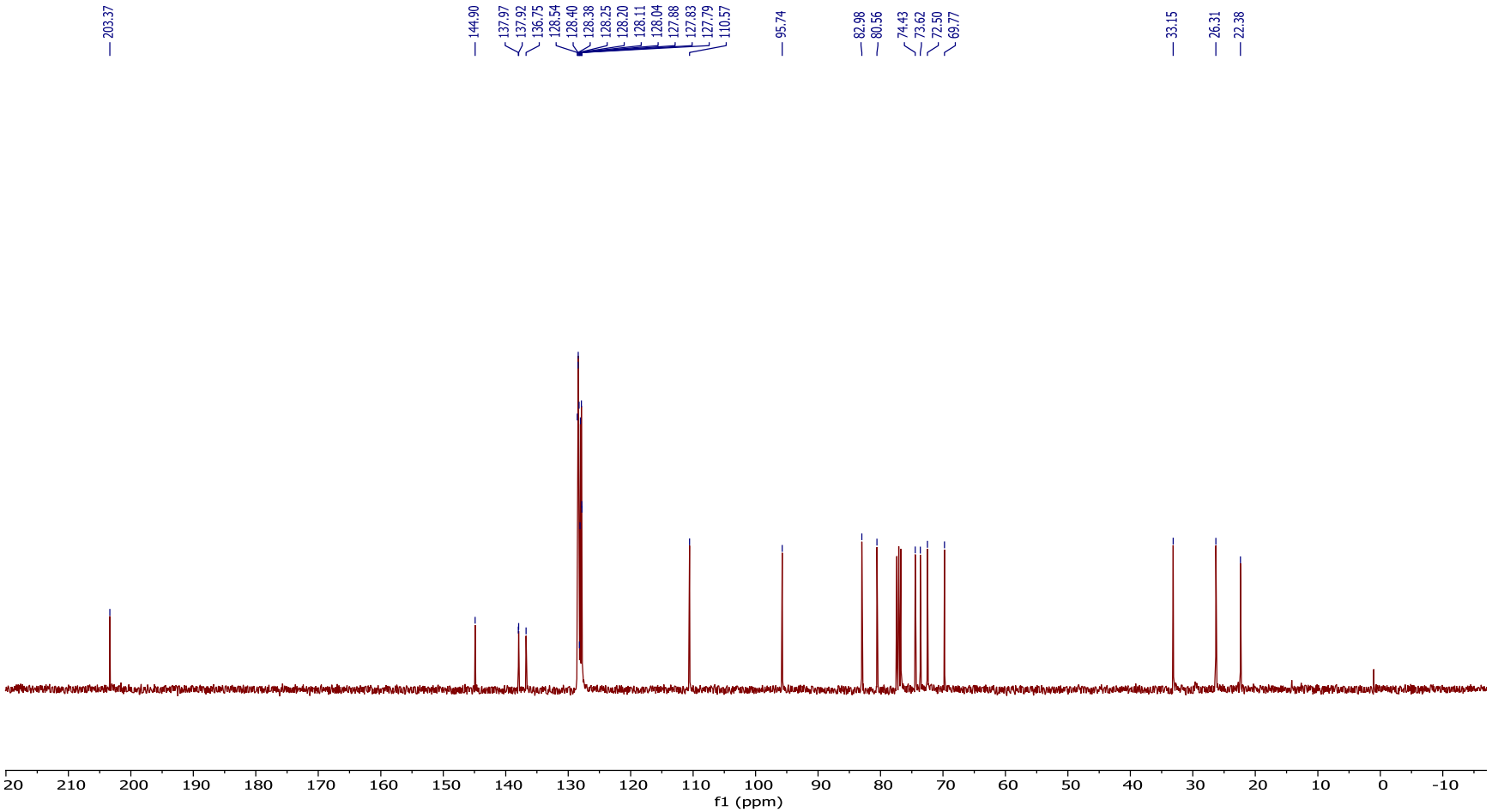


^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-4-keto-α-D-non-8-enoglucopyranoside **(9)**

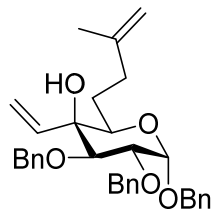


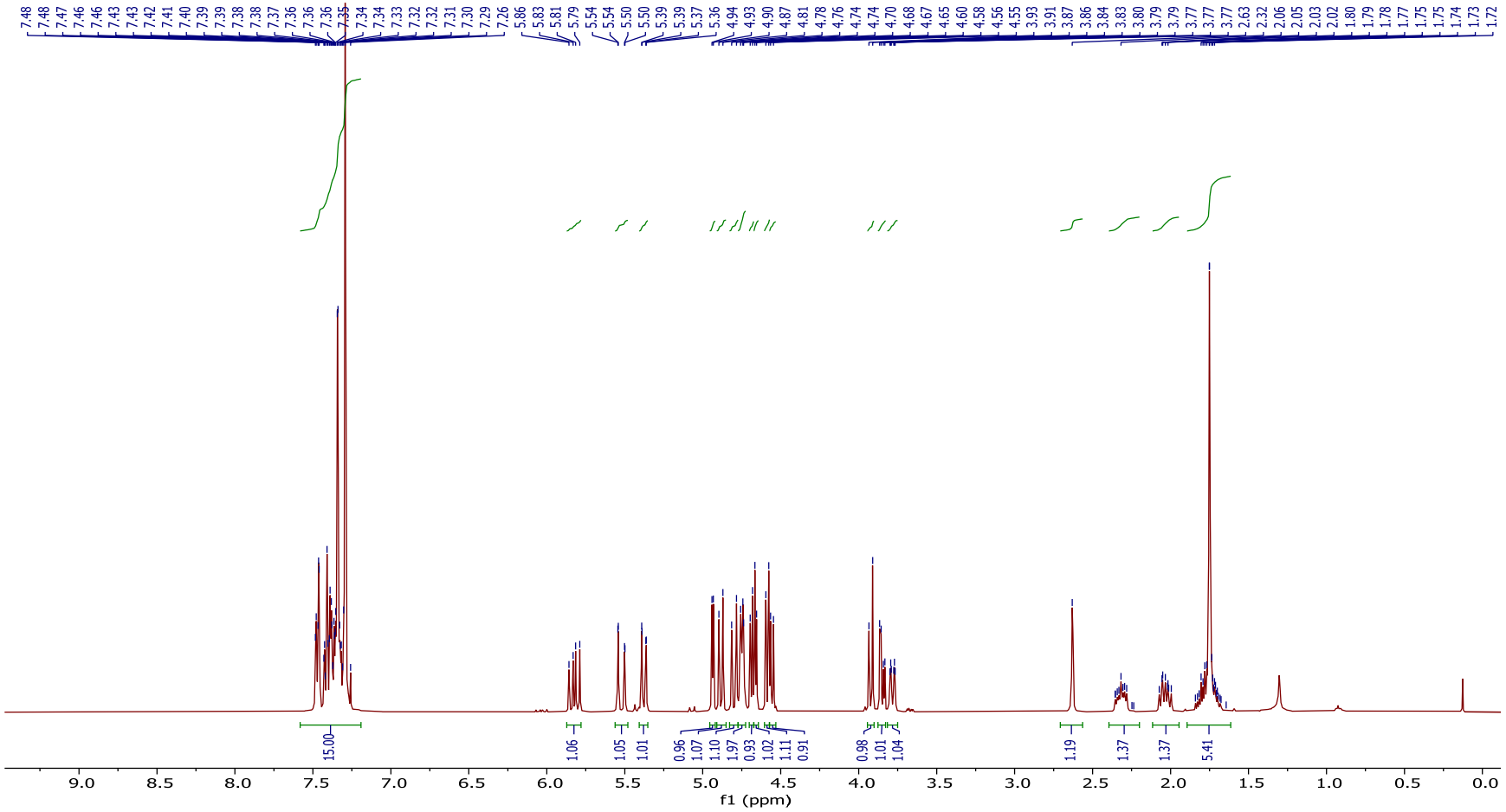
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-4-keto-α-D-non-8-enoglucopyranoside **(9)**



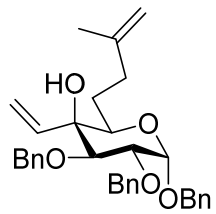


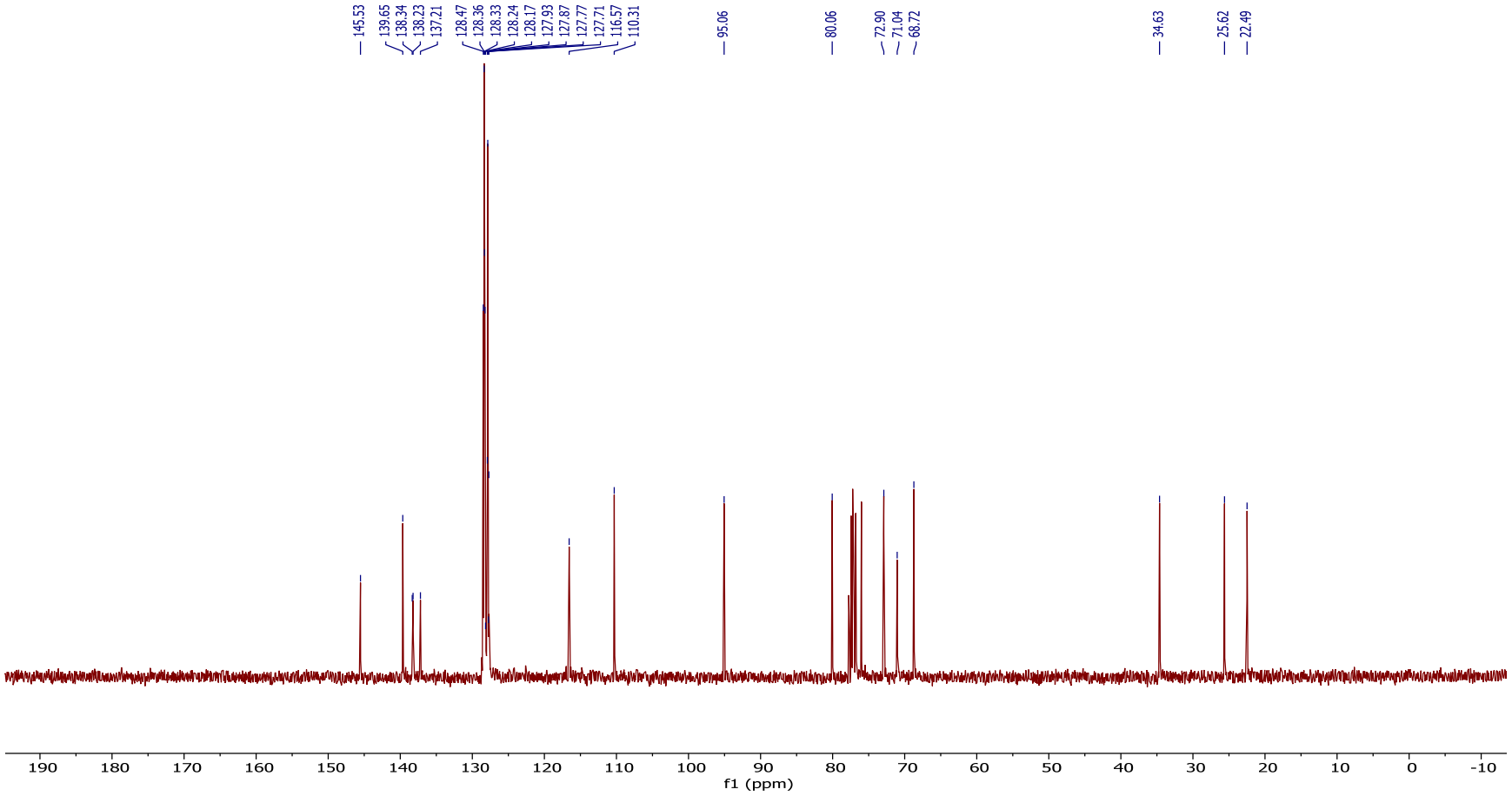
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-4-*C*-vinyl-α-D-non-8-enogalactopyranoside **(10)**



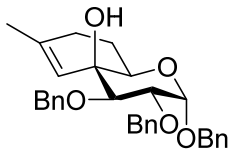


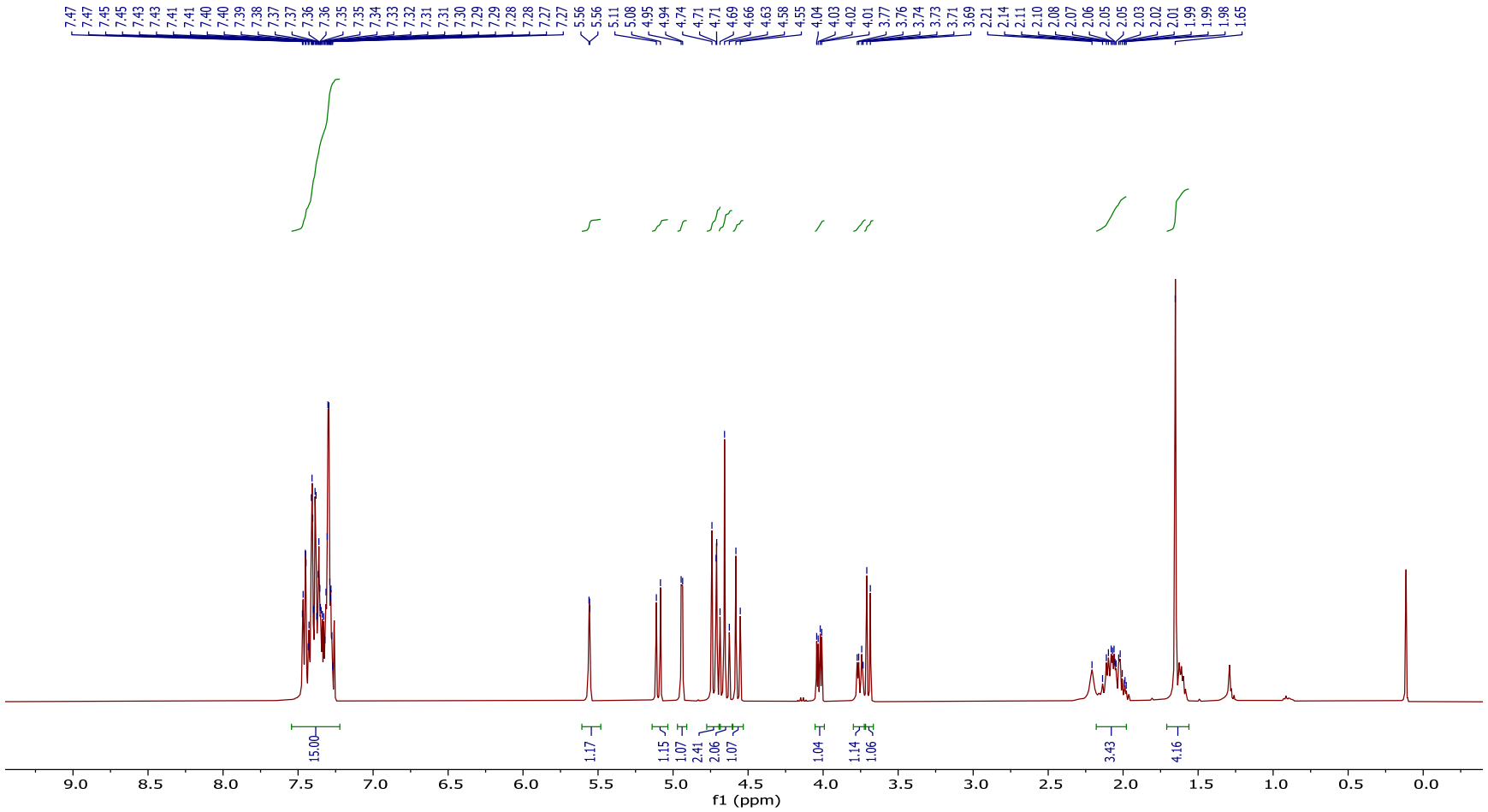
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-4-*C*-vinyl-α-D-non-8-enogalactopyranoside **(10)**



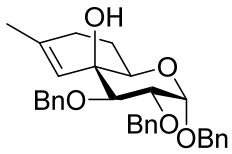


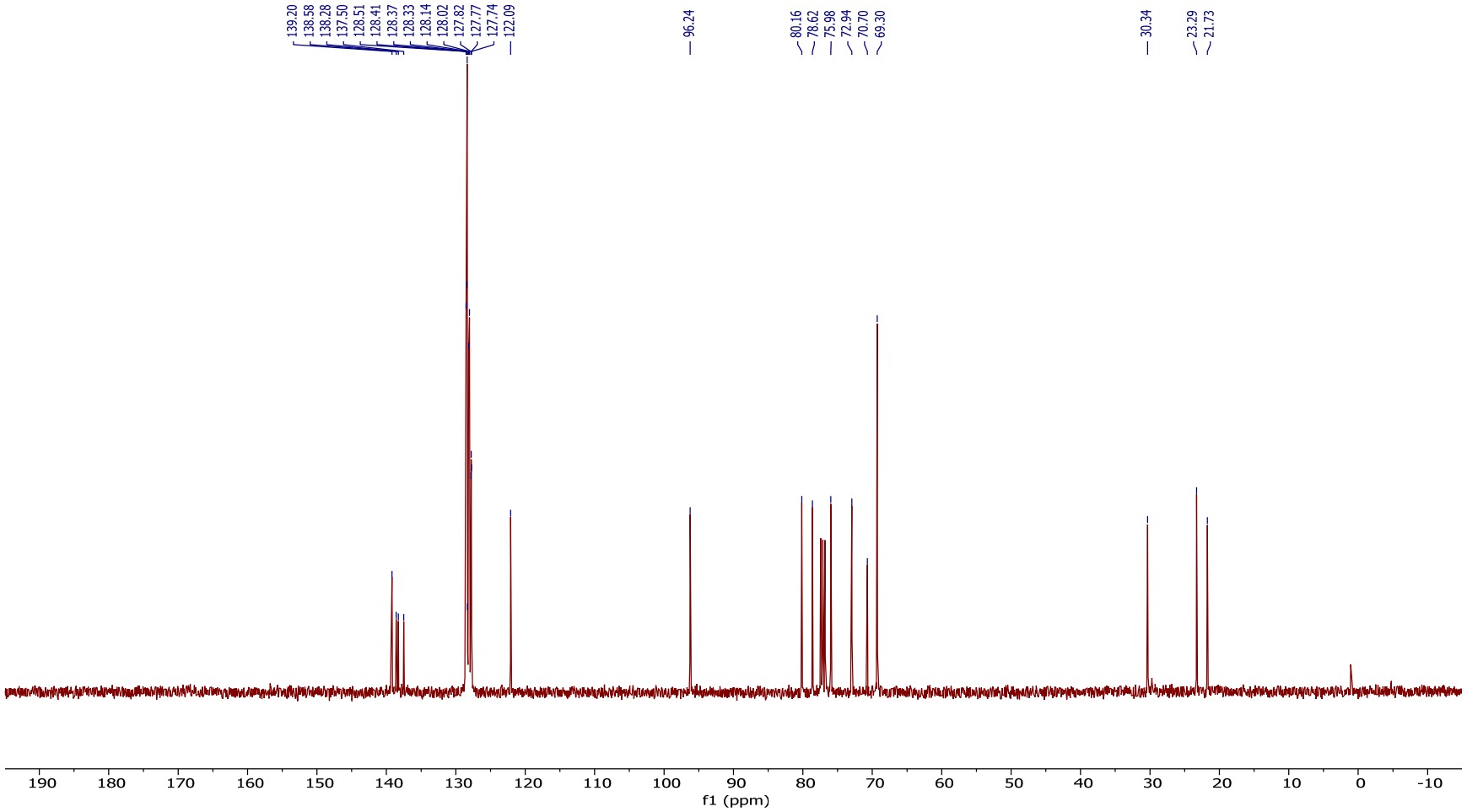
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-α-D-non-8-enogalactopyranoside **(11)**



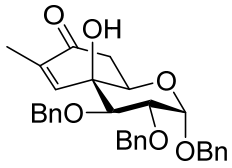


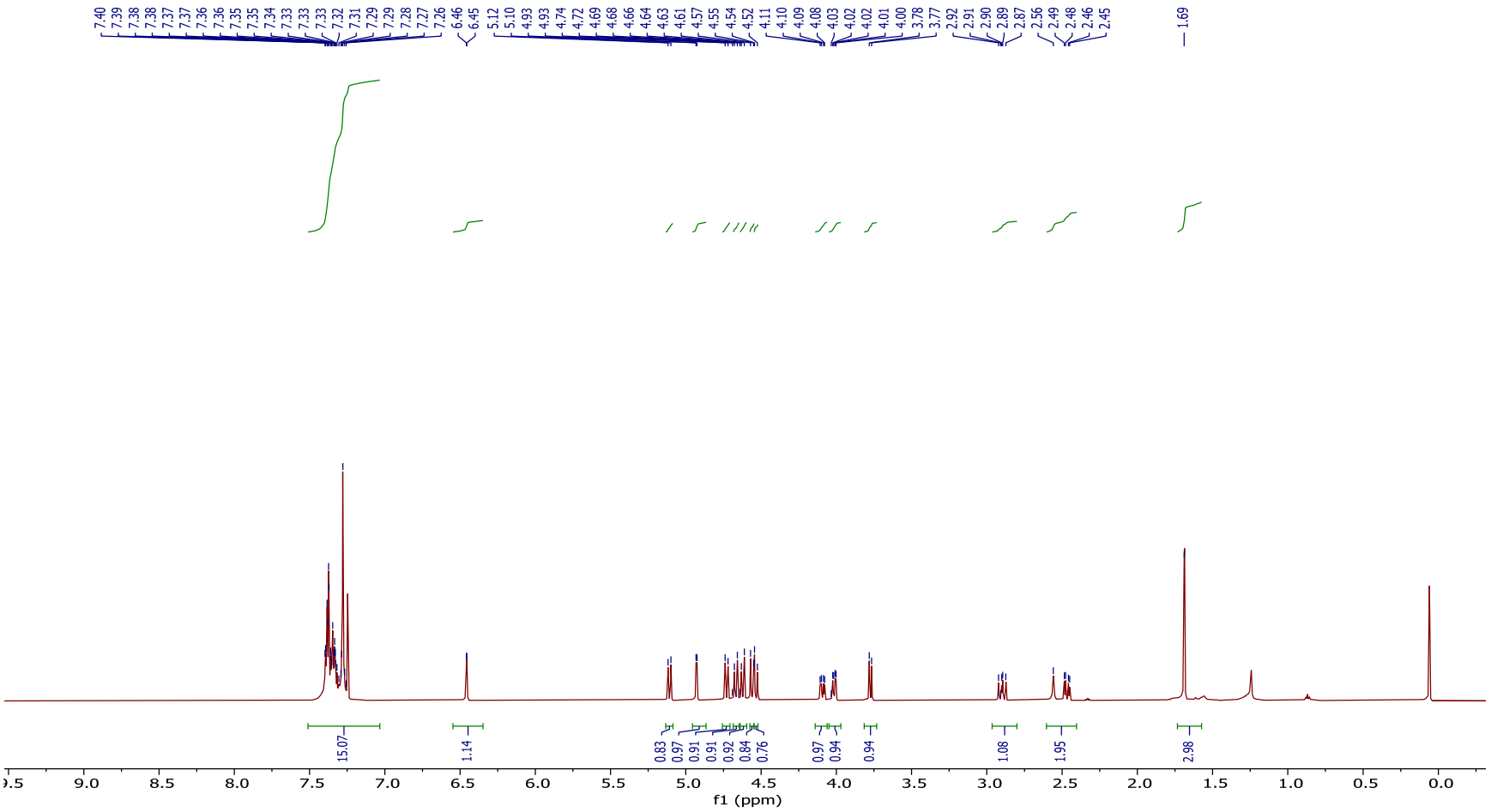
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,7,8,9-tetradeoxy-8-methyl-α-D-non-8-enogalactopyranoside **(11)**



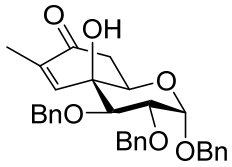


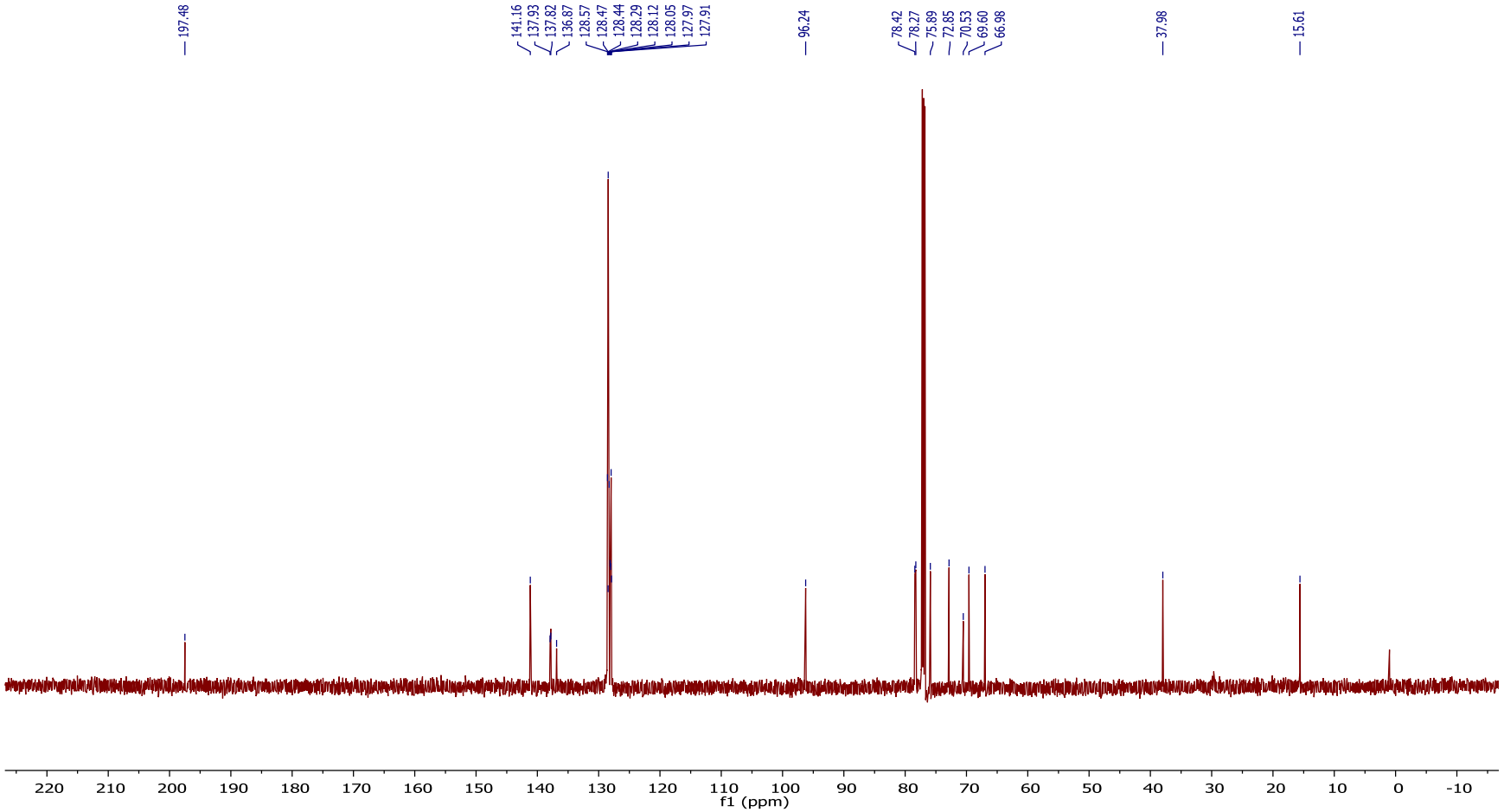
^{1}H NMR (400 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,8,9-trideoxy-8-methyl-7-keto-α-D-non-8-enogalactopyranoside **(12)**



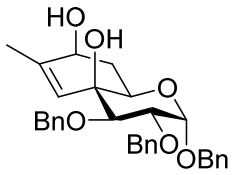


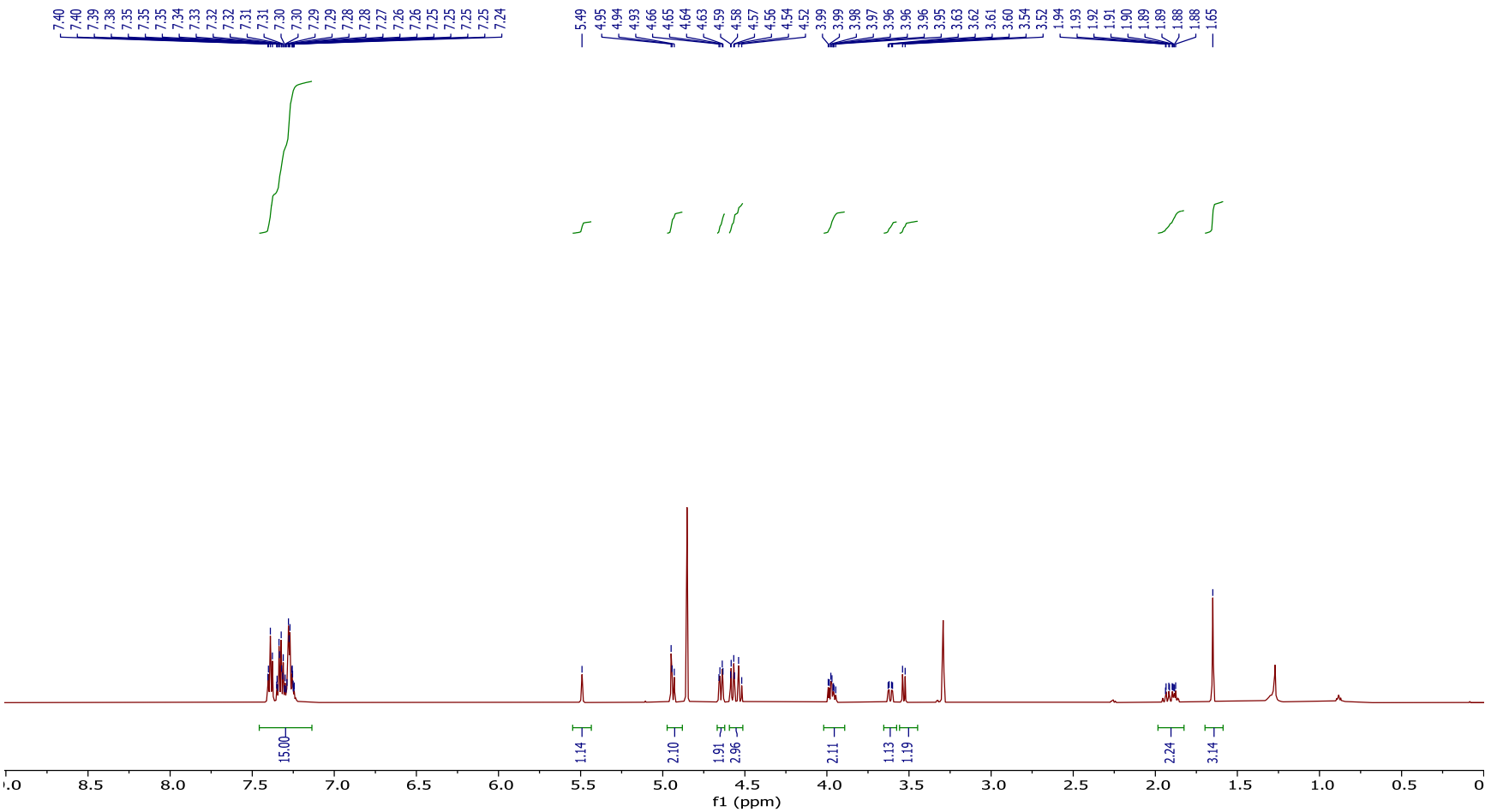
^{13}C NMR (101 MHz, $CDCl_3$) of Benzyl 2,3-di-*O*-benzyl-6,8,9-trideoxy-8-methyl-7-keto-α-D-non-8-enogalactopyranoside **(12)**



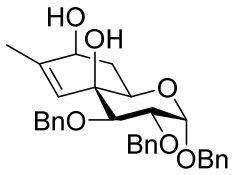


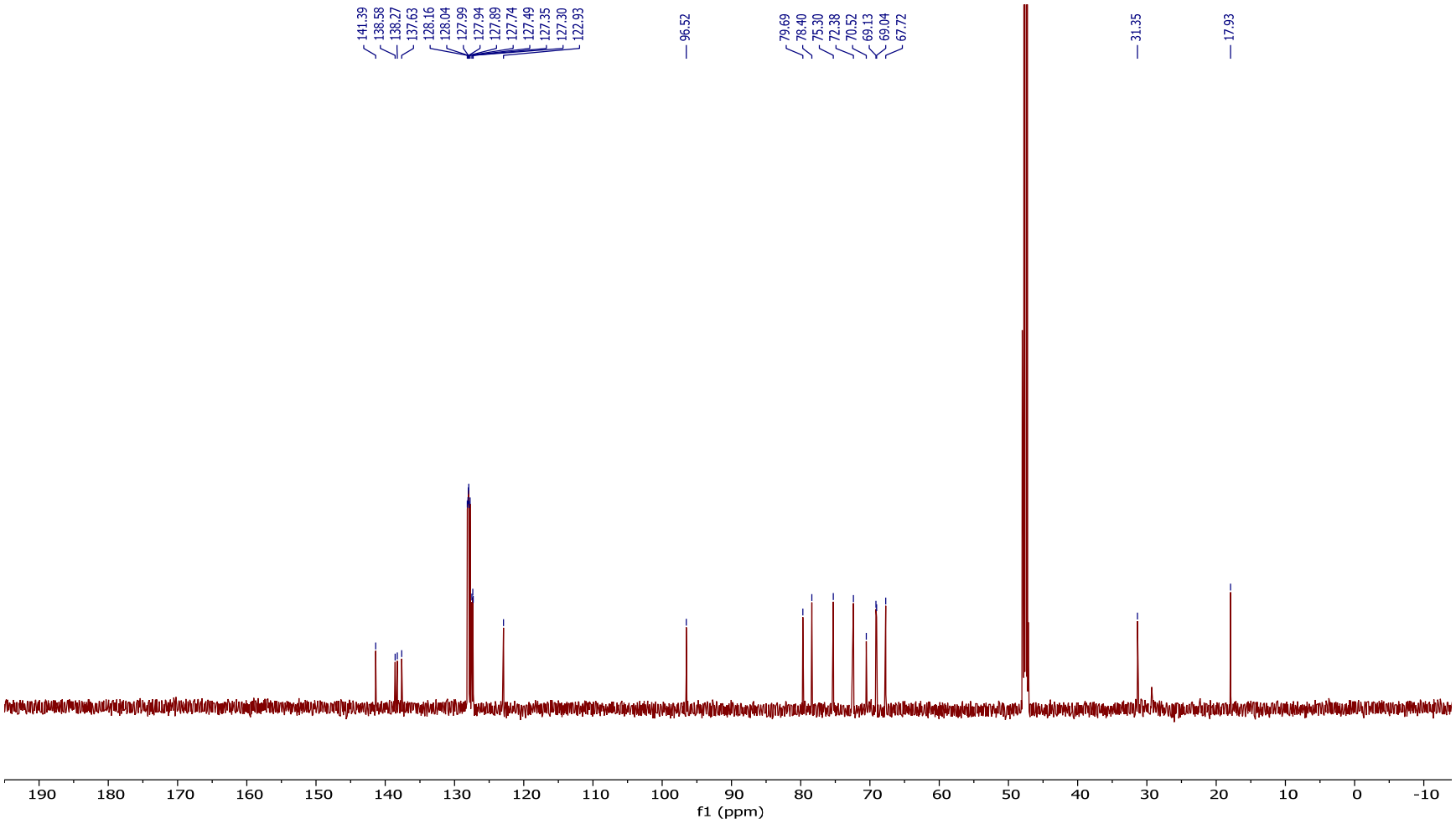
^{1}H NMR (400 MHz, CD_3OD) of Benzyl 2,3-di-*O*-benzyl-6,8,9-trideoxy-8-methyl-α-D-non-8-enogalactopyranoside **(13)**



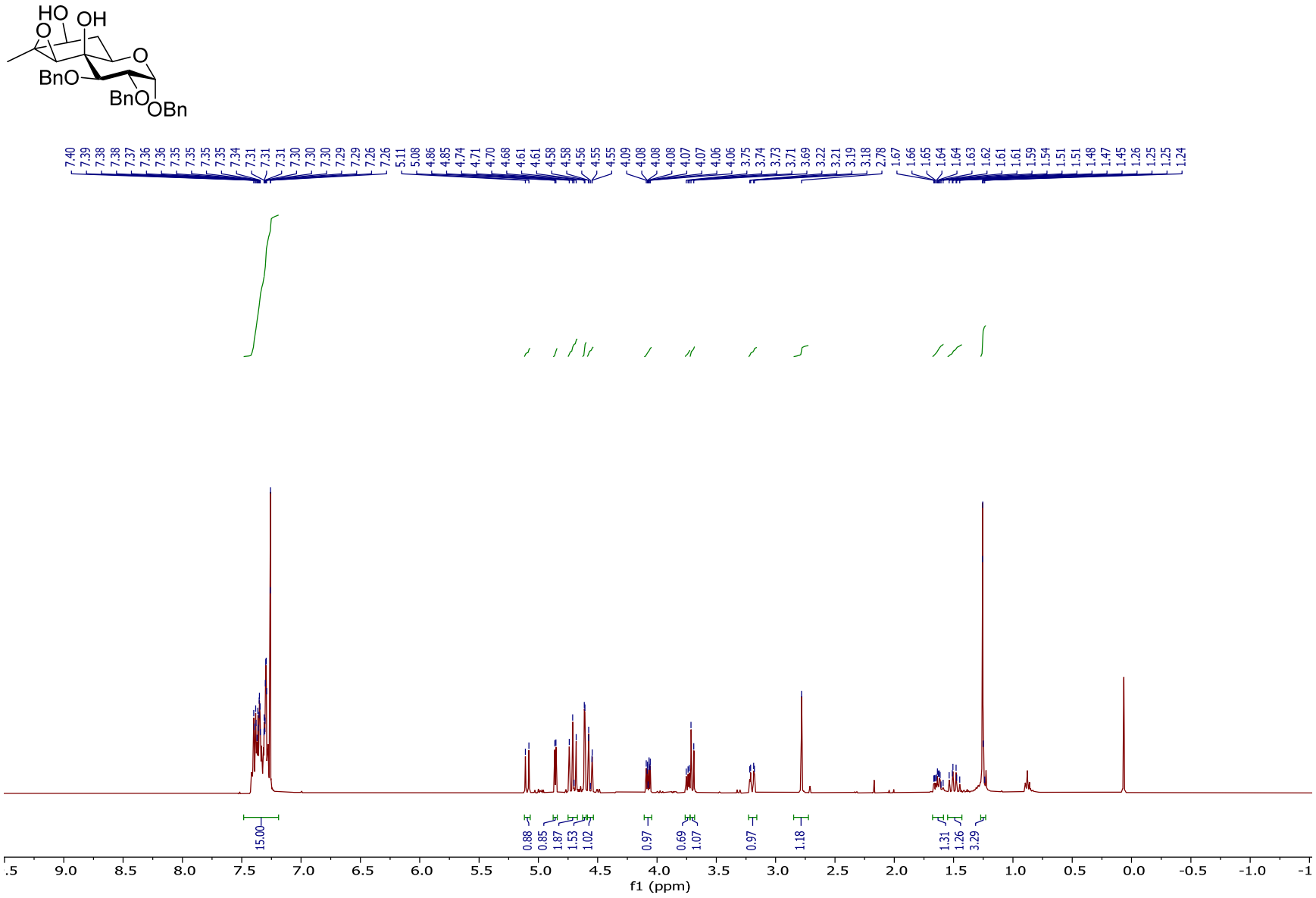


^{13}C NMR (101 MHz, CD_3OD) of Benzyl 2,3-di-*O*-benzyl-6,8,9-trideoxy-8-methyl-α-D-non-8-enogalactopyranoside **(13)**

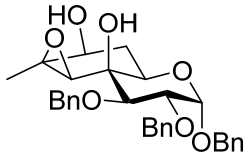


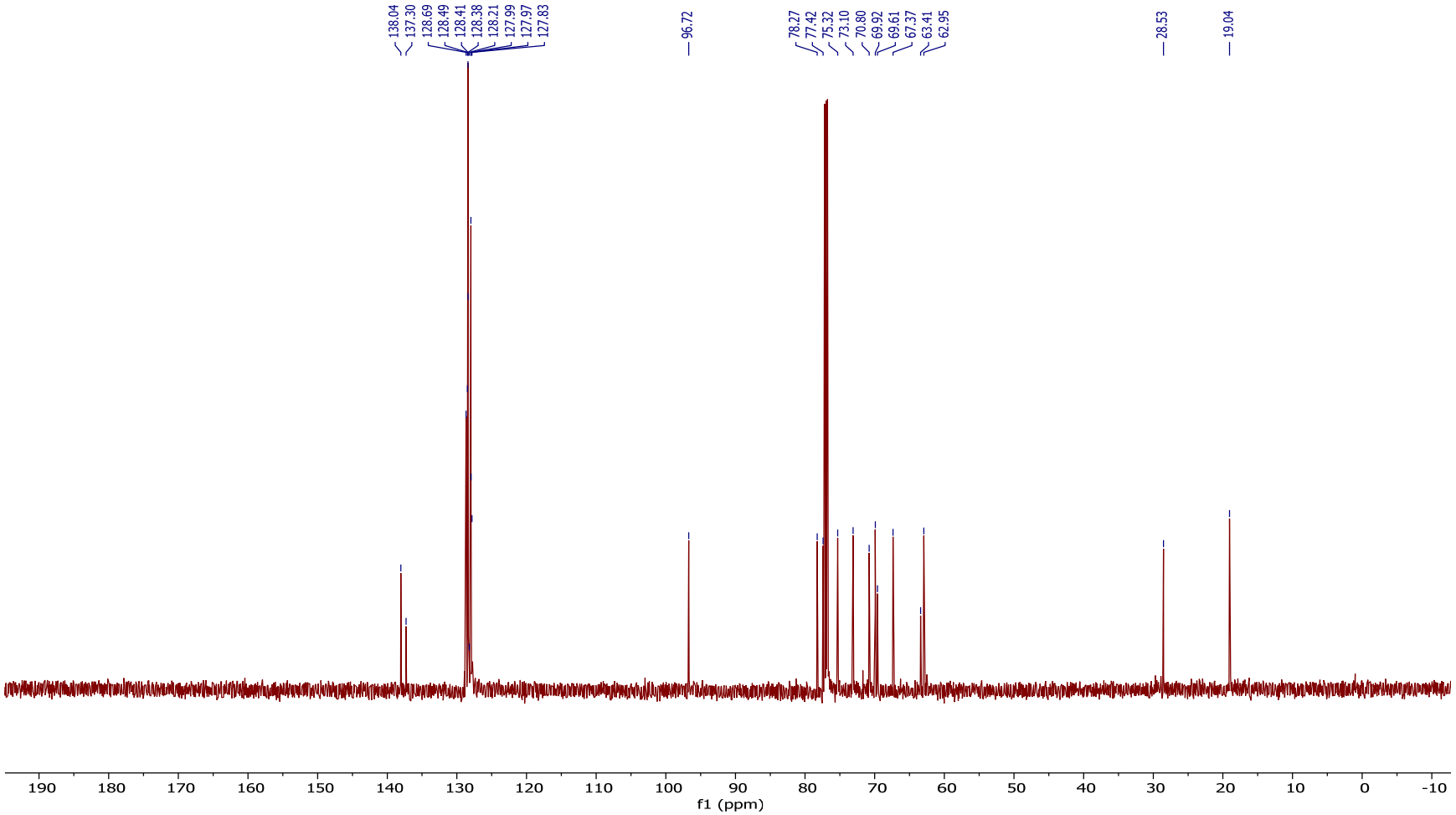


^{1}H NMR (600 MHz, $CDCl_3$) of Benzyl 8,9-anhydro-2,3-di-*O*-benzyl-6-deoxy-8-methyl-α-D-nonagalactopyranoside **(14)**

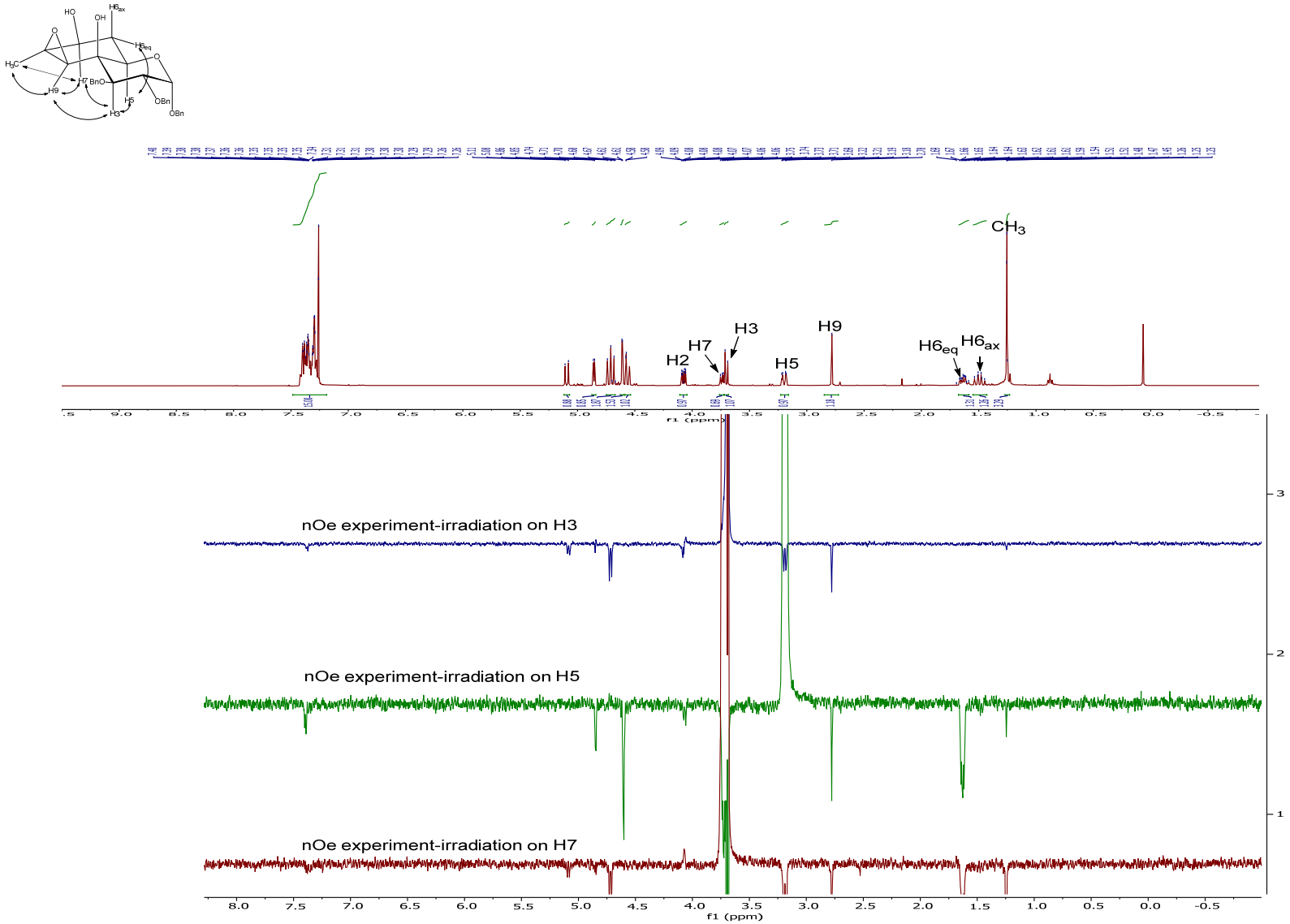


^{13}C NMR (151 MHz, $CDCl_3$) of Benzyl 8,9-anhydro-2,3-di-*O*-benzyl-6-deoxy-8-methyl-α-D-nonagalactopyranoside **(14)**

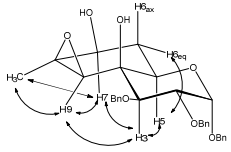


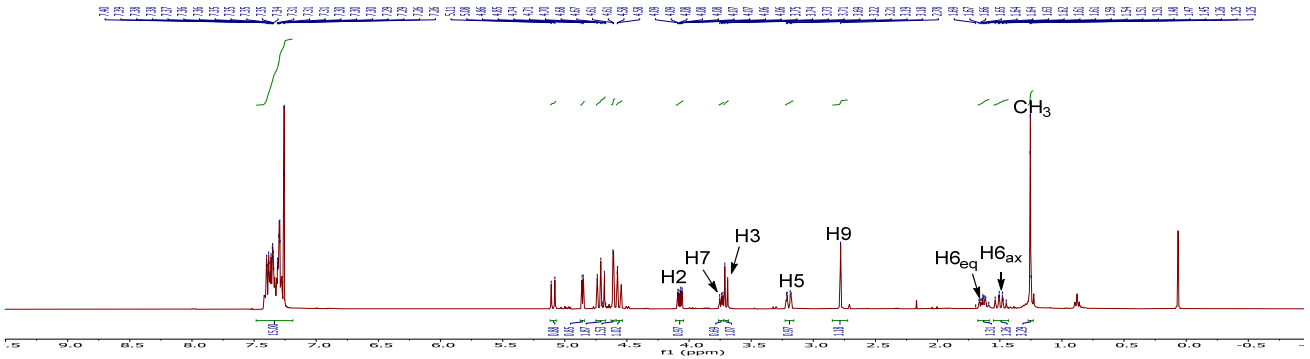


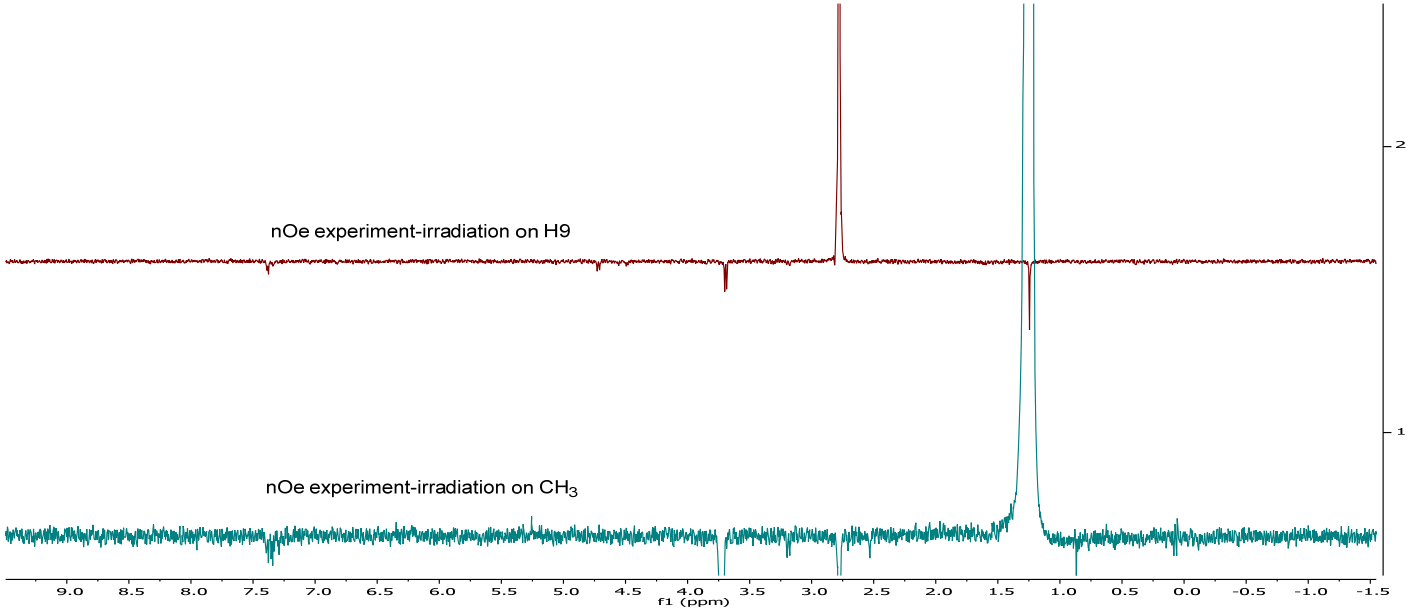
nOe (600 MHz, $CDCl_3$) of Benzyl 8,9-anhydro-2,3-di-*O*-benzyl-6-deoxy-8-methyl-α-D-nonagalactopyranoside **(14)**



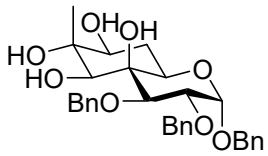
nOe (600 MHz, $CDCl_3$) of Benzyl 8,9-anhydro-2,3-di-*O*-benzyl-6-deoxy-8-methyl-α-D-nonagalactopyranoside **(14)**

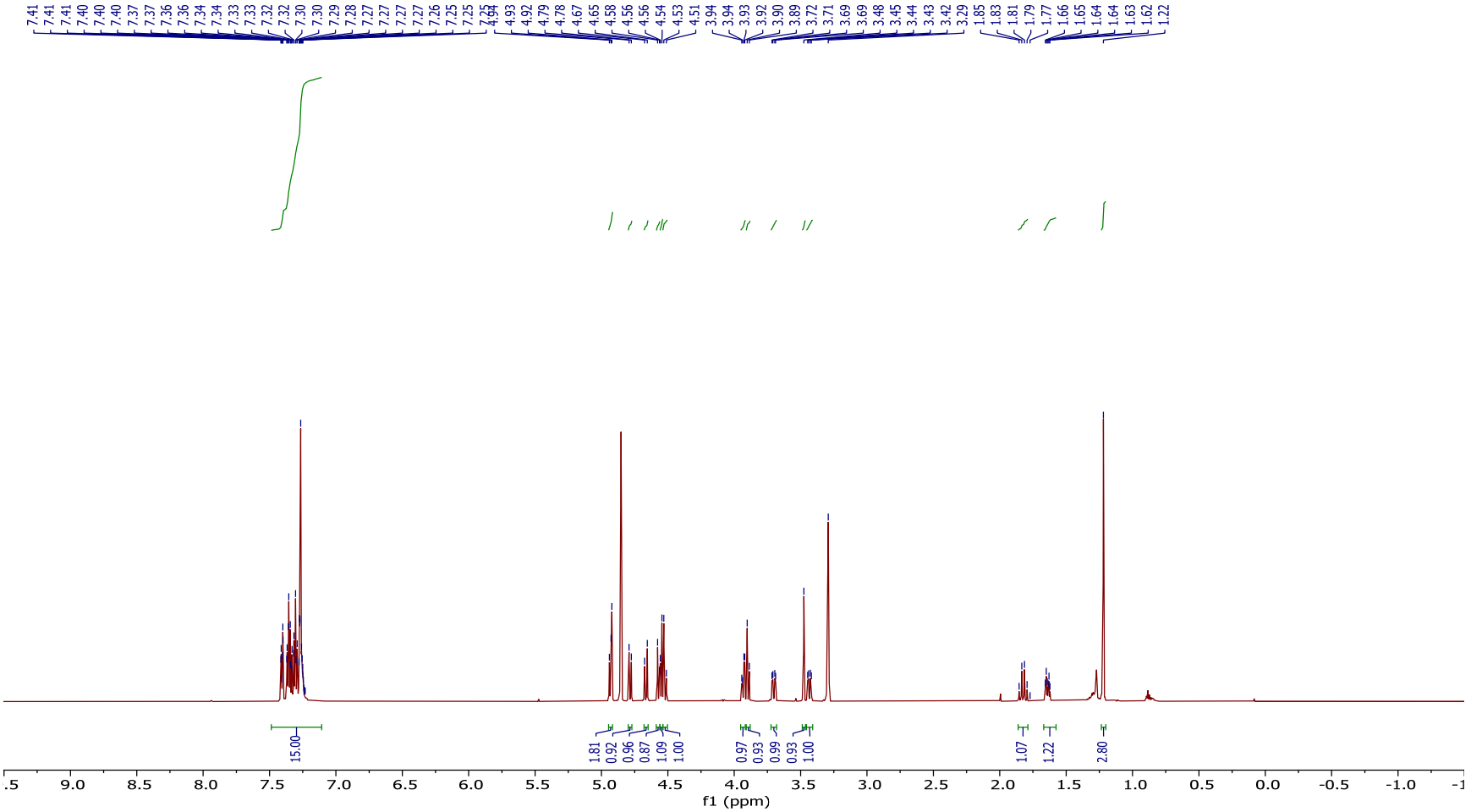




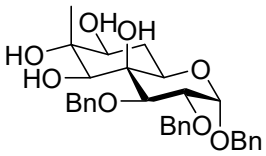


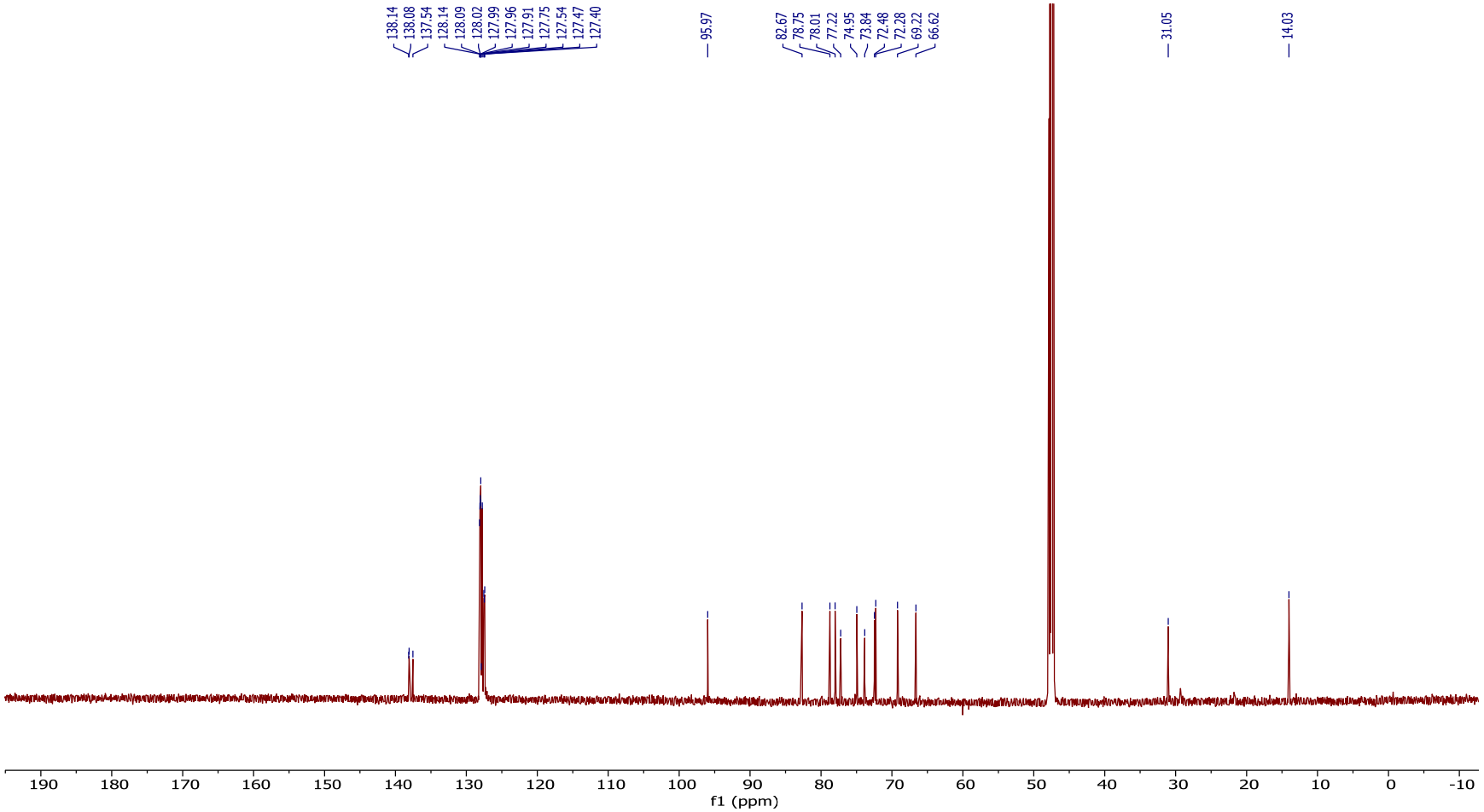
^{1}H NMR (400 MHz, CD_3OD) of Benzyl 2,3-di-*O*-benzyl-α-D-bradyrhizopyranoside **(15)**



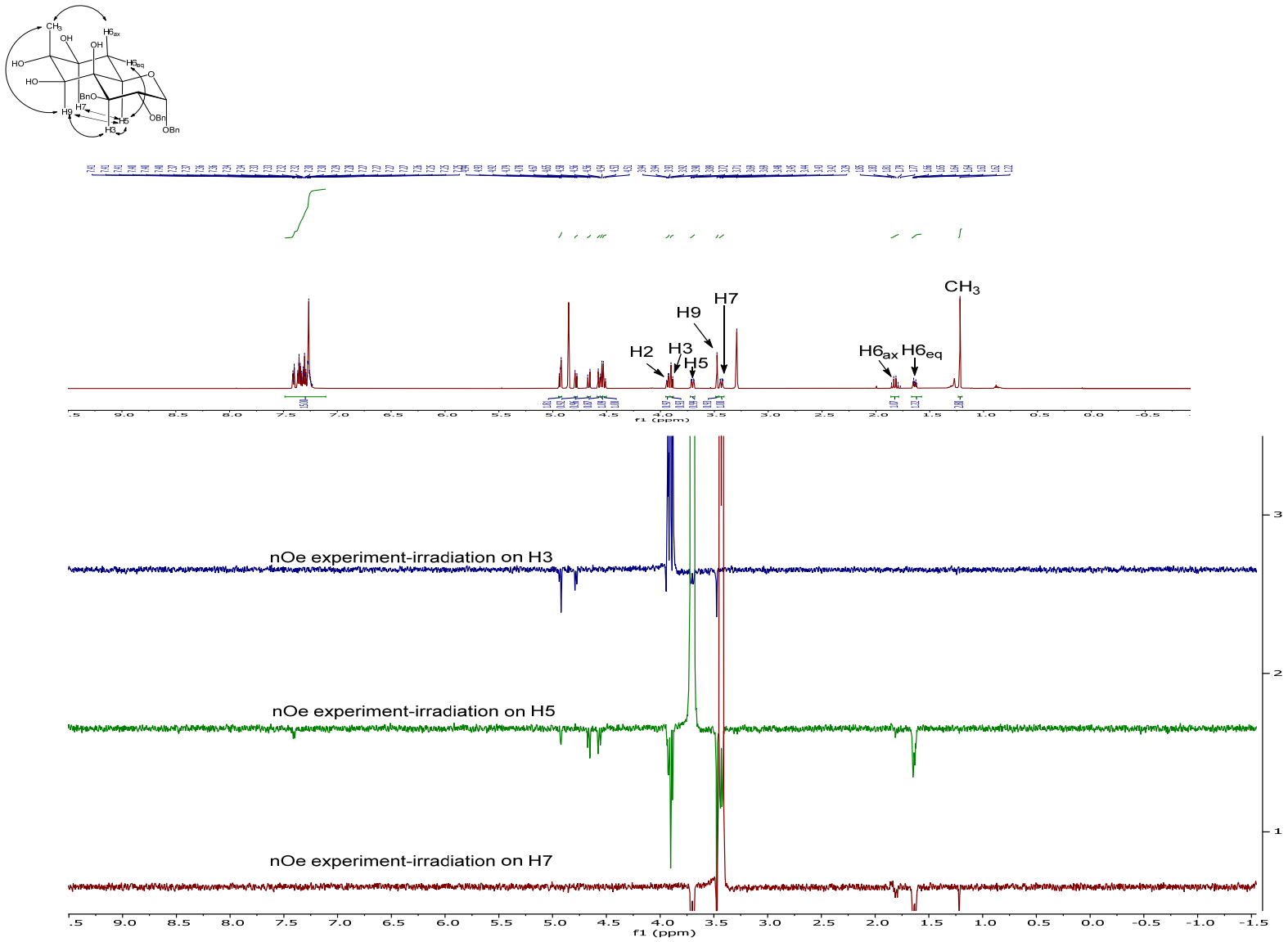


^{13}C NMR (101 MHz, CD_3OD) of Benzyl 2,3-di-*O*-benzyl-α-D-bradyrhizopyranoside **(15)**

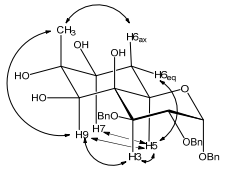


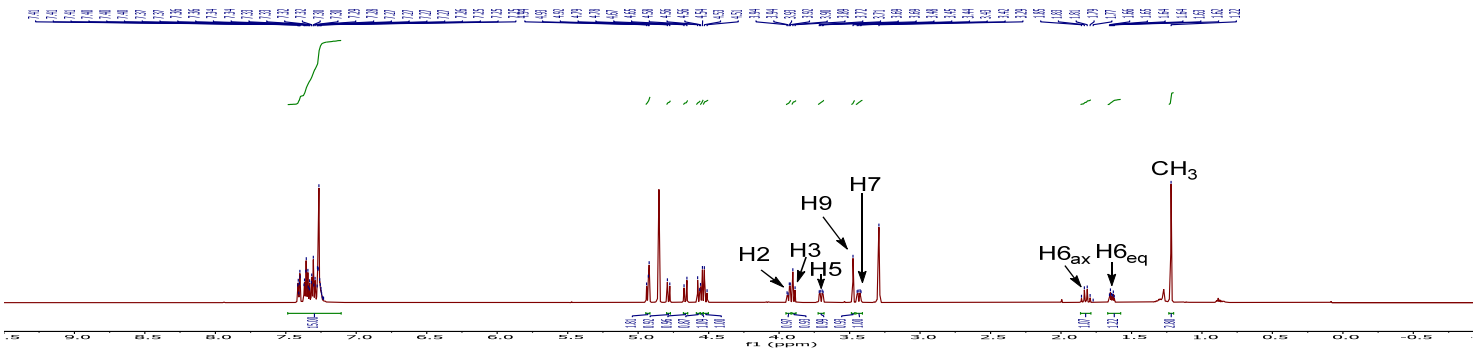


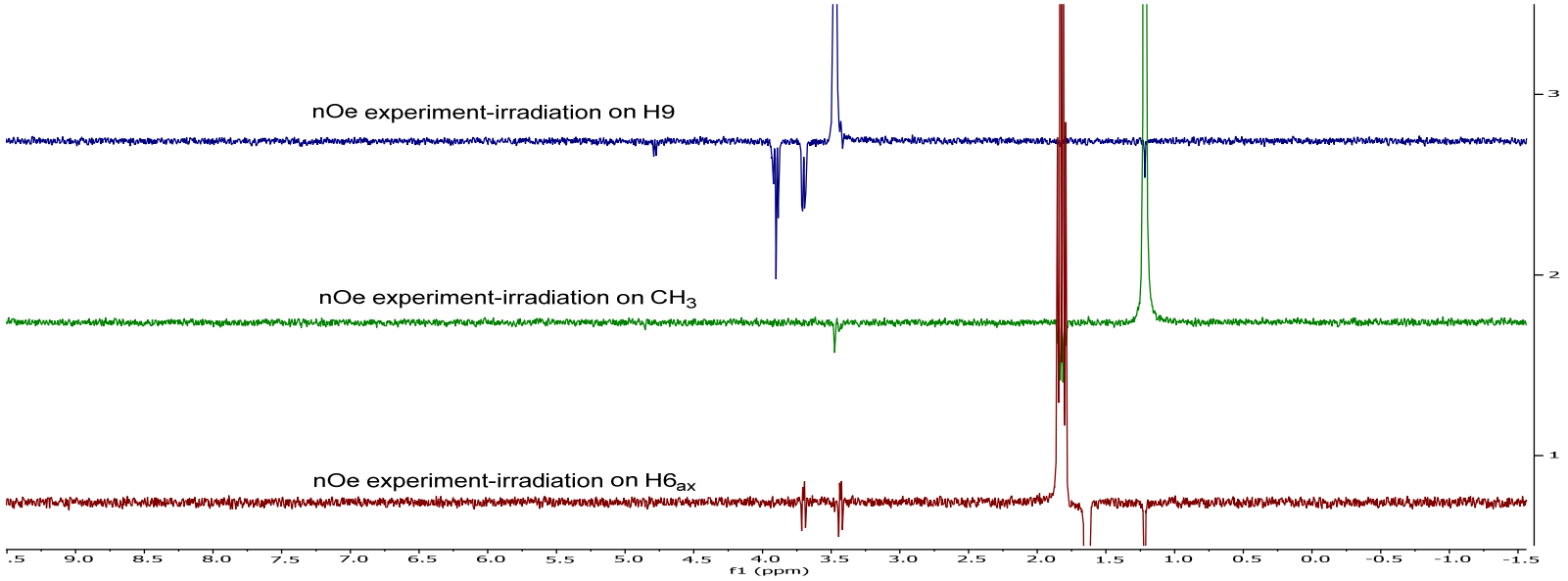
nOe (600 MHz, CD_3OD) of Benzyl 2,3-di-*O*-benzyl-α-D-bradyrhizopyranoside **(15)**



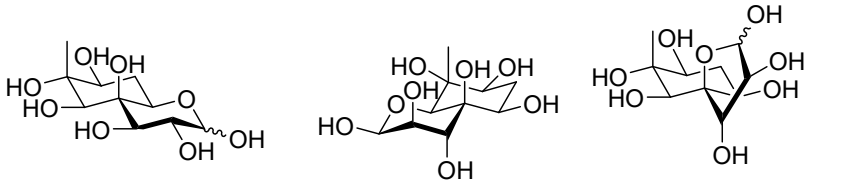
nOe (600 MHz, CD_3OD) of Benzyl 2,3-di-*O*-benzyl-α-D-bradyrhizopyranoside **(15)**







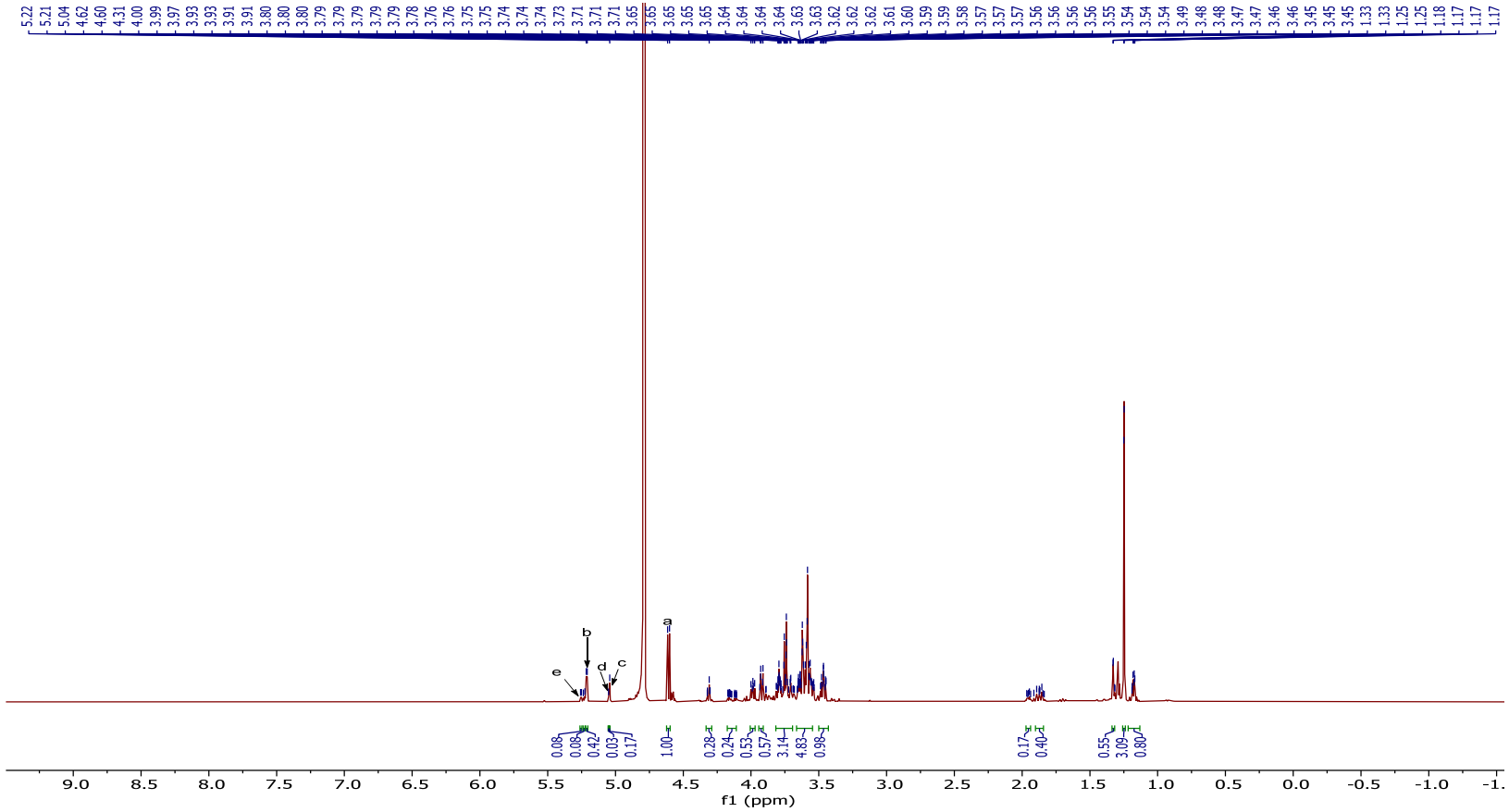
^{1}H NMR (600 MHz, D_2O (ref. to HOD @ 4.79 ppm)) of α,β-D-Bradyrhizose **(16)**



β-D-bradyrhizose **a**
α-D-bradyrhizose **b**

regioisomeric
1,9-pyranose form **c**

β-furanose form **d**
α-furanose form **e**



^{13}C NMR (151 MHz, D_2O) of α,β-D-Bradyrhizose **(16)**

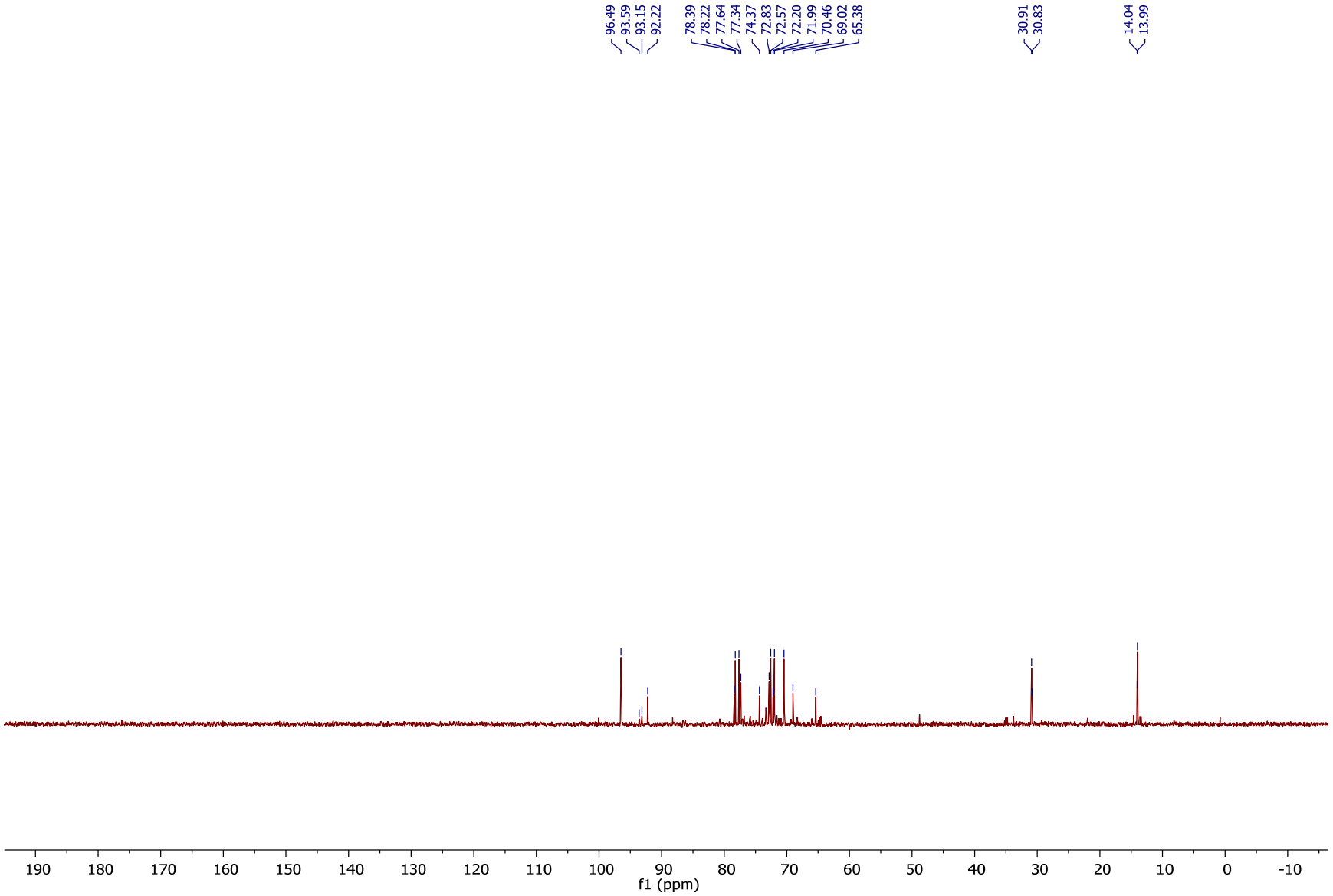


Figure S1. ^{1}H NMR (600 MHz, D_2O) of (a) α,β-D-Bradyrhizose **(16)** and (b) Yu literature spectrum [a, 3]

a)

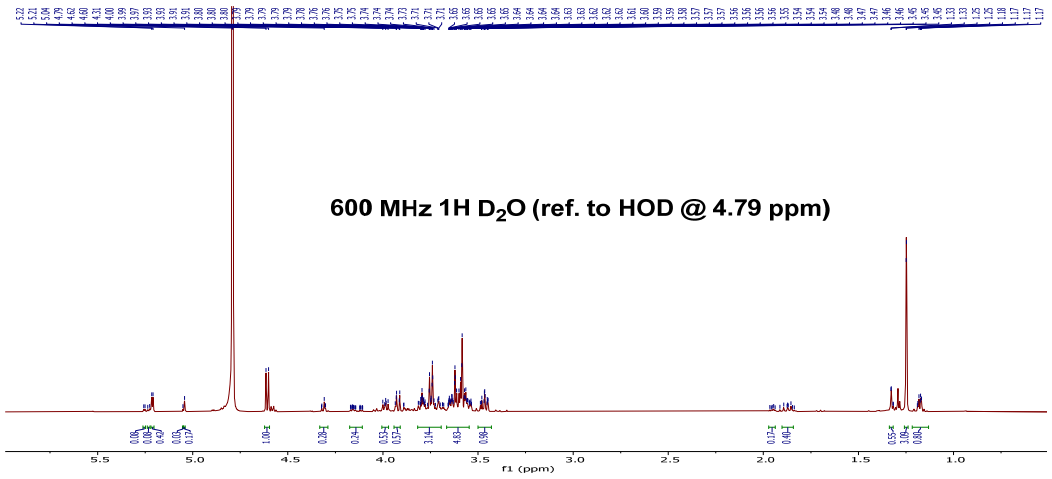
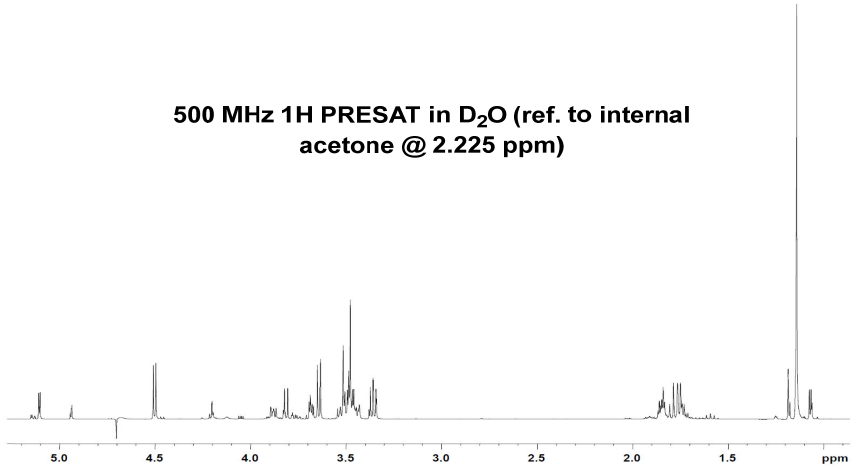


Figure SB: ^{1}H NMR spectrum of bradyrhizose in D_2O

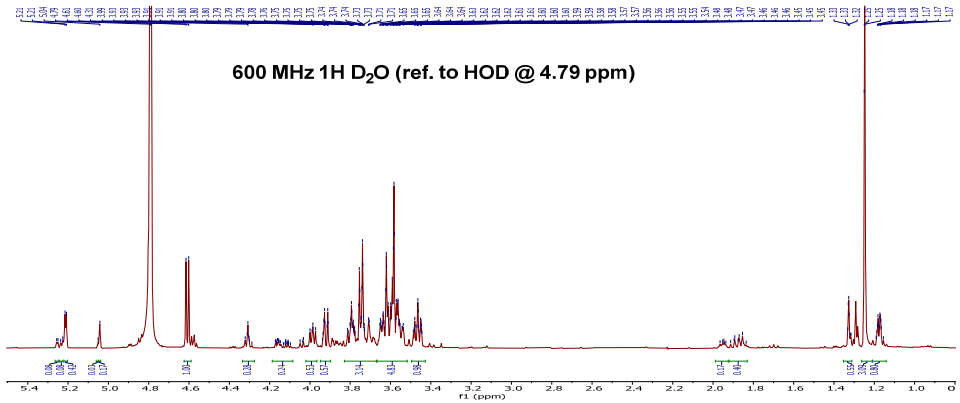
b)



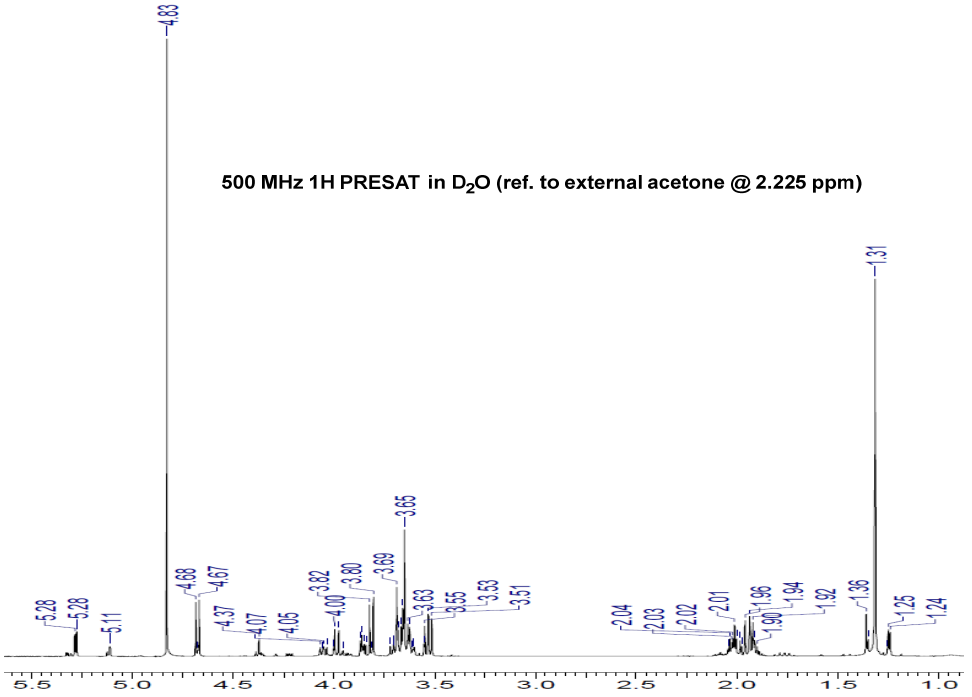
a) Alignment of peaks is perfect. Chemical shift differences are due to referencing of spectra to different standards.

Figure S2. ^{1}H NMR (600 MHz, D_2O) of (a) α,β-D-Bradyrhizose **(16)** and (b) Lowary literature spectrum[c, 3]

a)

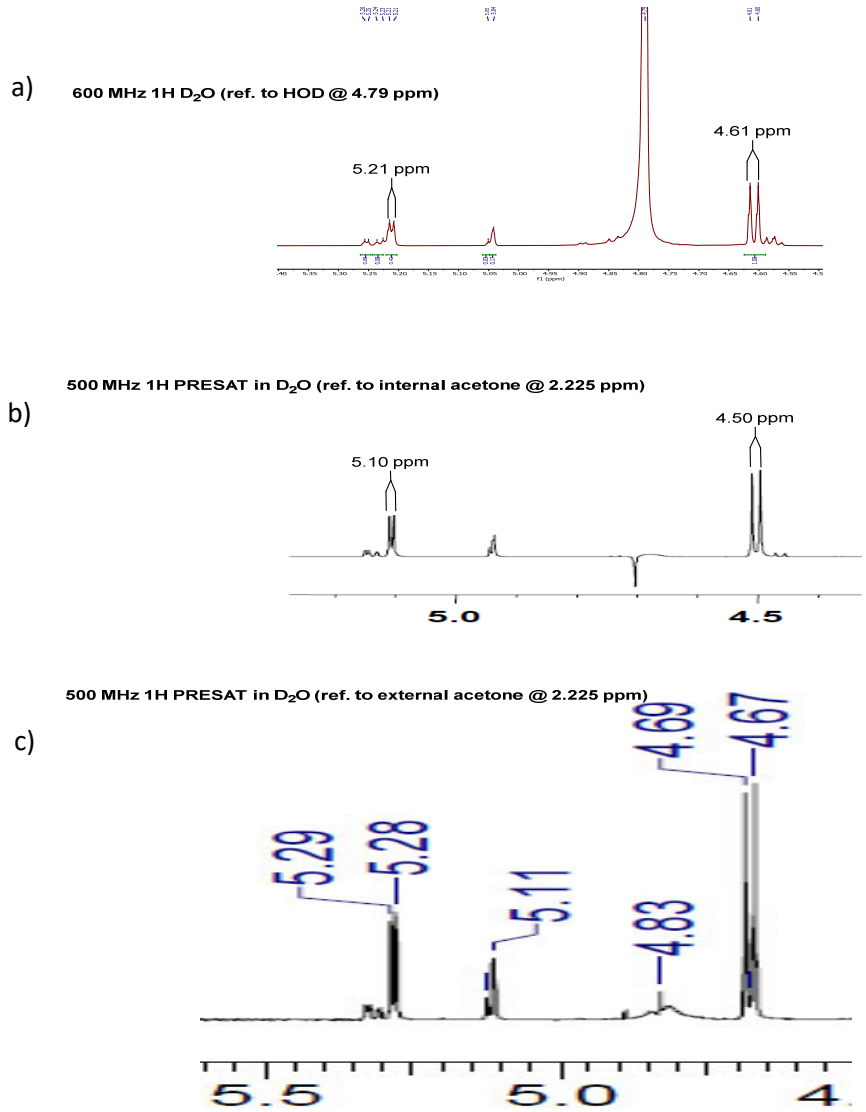


b)



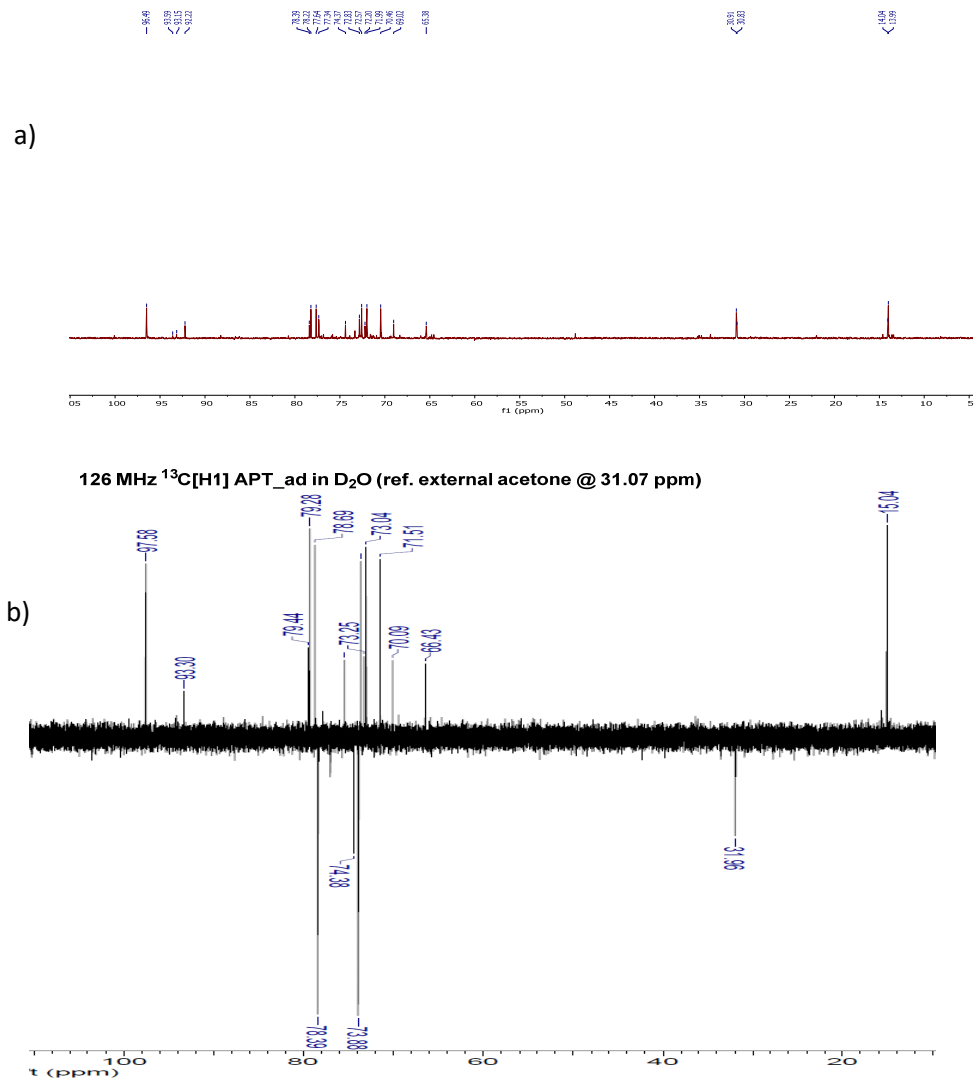
c) Alignment of peaks is perfect. Chemical shift differences are due to referencing of spectra to different standards

Figure S3. Comparison of ^{1}H NMR spectral data of the anomeric region of (a) bradyrhizose **(16)** with Yu and Lowary literature spectra [a, 3] **(b** and **c)** respectively



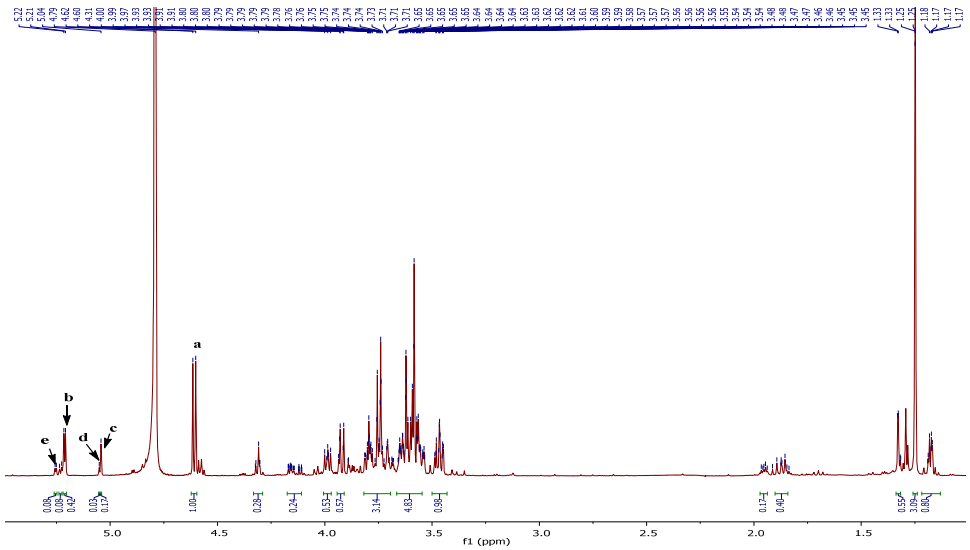
d) Alignment of peaks is perfect. Chemical shift differences are due to referencing of spectra to different standards

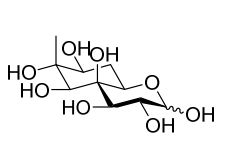
Figure S4. Comparison of ^{13}C NMR spectral data of (a) bradyrhizose **(16)** with (b) Lowary literature spectrum[b, 3]



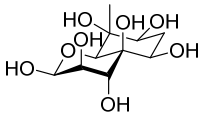
b) Alignment of peaks is perfect. Chemical shift differences are due to referencing of spectra to different standards.

Table S1. Comparison of ^{1}H and ^{13}C chemical shifts and coupling constants $^{3}J_{H,H}$, of bradyrhizose **(16)** with the Yu[3], the Lowary[3] and the Molinaro[4] respectively

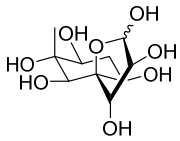




β-D-bradyrhizose **a**
α-D-bradyrhizose **b**



regioisomeric
1,9-pyranose form **c**



β-furanose form **d**
α-furanose form **e**

data source	**H-1, C-1, 16a**	**H-1, C-1, 16b**	**H-1, C-1, 16c**	**H-1, C-1, 16d**	**H-1, C-1, 16e**		**solvent**	**Chemical shift reference**
Our data	δ_H 4.61 (d, $^{3}J_{H1, H2}$ = 8.1 Hz), δ_C 96.5	δ_H 5.21 (d, $^{3}J_{H1, H2}$ =4.3 Hz), δ_C 92.2	δ_H 5.04 (br, s), δ_C 100.1	δ_H 5.05 (br, s) δ_C 93.2	δ_H 5.25 (d, $^{3}J_{H1, H2}$ = 3.7 Hz), δ_C 93.6	δ_H 5.23 (d, $^{3}J_{H1,H2}$ = 4.1 Hz)	D_2O	HOD @ δ_H 4.79
Yu data[3]	δ_H 4.50 (d, $^{3}J_{H1, H2}$ = 8.07 Hz), δ_C 96.5	δ_H 5.10 (d, $^{3}J_{H1, H2}$ = 3.9 Hz), δ_C 92.2	δ_H 4.93 (d, $^{3}J_{H1, H2}$ = 5.0 Hz), δ_C 100.0	δ_H 4.93 (d, $^{3}J_{H1, H2}$ = 1.9 Hz), δ_C 93.2	δ_H 5.14, δ_C 93.6		D_2O	internal acetone @ δ_H 2.225, δ_C 31.45
Lowary data[3]	δ_H 4.62 (d, $^{3}J_{H1, H2}$ = 8.1 Hz), δ_C 97.6	δ_H 5.23 (d, $^{3}J_{H1, H2}$ = 4.0 Hz), δ_C 93.3	δ_H 5.07-5.05 (m)	δ_H 5.07-5.05 (m)	δ_H 5.27 (d, $^{3}J_{H1, H2}$ = 5.3 Hz)	5.23 (br)	D_2O	external acetone @ δ_H 2.225, δ_C 31.07
Molinaro data[4]	δ_H 4.97 (d, $^{3}J_{H1, H2}$ = 3.9 Hz), δ_C 96.6						D_2O	internal acetone @ δ_H 2.225, δ_C 31.45

Figure S5. Comparison of HSQC NMR spectral data of (a) bradyrhizose **(16)** with (b) Yu literature spectrum[3]

a)

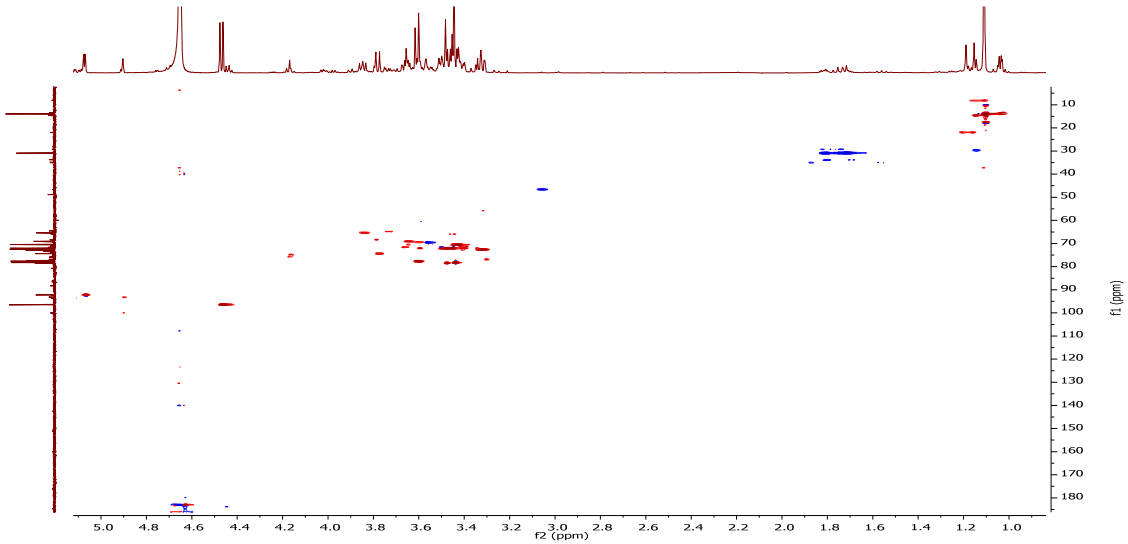


Figure SC: HSQC NMR spectrum of bradyrhizose in D_2O. Cross peaks are labelled as indicated in Table S1

b)