Supplementary Information

[Au]/[Ag]-Catalysed Synthesis of Non-hydrolysable *C*-Glycosides

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General information:

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Gold-phosphite catalyst was purchased from Proactive Molecular Research, Florida (USA) and AgOTf/$AgNTf_2$ were purchased from Sigma-Aldrich. All the moisture sensitive reactions were performed in flame dried glassware under nitrogen or argon atmosphere unless stated otherwise. 4Å molecular sieves were activated by heating at 150-200 °C under high vacuum for 4 h before storing in a dry desiccator. Freshly distilled CH_2Cl_2 was stored over activated 4Å molecular sieves (preheated to 200-250 °C). The reactions were monitored by analytical thin layer chromatography (TLC) performed on 0.25 mm Merck silica gel plates ($60F_{254}$) under 254 nm UV lamp and stained by anisaldehyde stain. Removal of solvent *in vacuo* refers to distillation using a rotary evaporator attached to an efficient vacuum pump. Column chromatography of the crude compounds was performed on silica gel of 100-200 mesh (75-150 μm). Products obtained as solids or syrups were dried under high vacuum. IR spectra were recorded on a FT-IR spectrometer. NMR spectra were recorded either on a 400 or 600 MHz with $CDCl_3$ as the solvent and TMS as the internal standard. High resolution mass spectroscopy (HRMS) was performed using an ESI-TOF mass analyzer or MALDI-TOF mass analyzer.

General procedure for the preparation of glycosyl alkynyl carbonate donors (4a-4g): All the glycosyl donors were prepared by following the previously reported protocol.[6a]

General procedure for the synthesis of C-glycosides with acceptors 5b, 5c, 5d 5f & 5g: Freshly activated 4Å MS powder (30 mg/mL) was added to a solution containing glycosyl carbonate donor (1.0 eqiv.), and the acceptor (**5b, 5c, 5d, 5f, 5g**; 2.5 eqiv.) in anhydrous CH_2Cl_2 (100mM reaction conc.) and stirred under nitrogen atmosphere. After 20 min, gold-phosphite **6** (10 mol%) and AgOTf (10 mol%) were added to the reaction mixture at 25 °C and stirred for 1 h. At the end of the reaction, as monitored by the TLC examination, the reaction mixture was filtered through a bed of Celite® and the filtrate was concentrated in vacuo to obtain a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as mobile phase.

General procedure for the synthesis of C-glycosides with acceptors 5a & 5e: Freshly activated 4Å MS powder (30 mg/mL) was added to a solution containing glycosyl carbonate donor (1.0 eqiv.), and the acceptor (**5a, 5e**; 4.0 eqiv.) in anhydrous CH_2Cl_2 (100mM reaction conc.) and stirred under nitrogen atmosphere. After 20 min, gold-phosphite **6** (10 mol%) and $AgNTf_2$ (10 mol%) were added to the reaction mixture at 25 °C and stirred for 1 h. After the complete consumption of the starting material glycosyl donor as adjudged by the TLC, the reaction mixture was filtered through a bed of Celite® and the filtrate was concentrated in vacuo to obtain a residue that was purified by silica gel column chromatography using ethyl acetate and hexane as mobile phase.

Characterization Data:

1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside (7a): 77 mg isolated from 100 mg **4a** (α:β>20:1**,** 94%) Major α product: White amorphous solid; [α]25 D (CHCl3, c 1.0): +10.0; IR (cm-1, CHCl3): 3067, 3031, 2919, 2862, 1729, 1495, 1453, 1361, 1265, 1210, 1082, 1033, 999, 913, 824, 740, 699; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 20H), 7.15 (dd, *J* = 7.3, 2.2 Hz, 2H), 5.84 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.15 – 5.08 (m, 2H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.83 (dd, *J* = 10.8, 3.3 Hz, 2H), 4.72 – 4.65 (m, 2H), 4.51 – 4.48 (m, 2H), 4.16 (dt, *J* = 10.4, 5.0 Hz, 1H), 3.84 – 3.77 (m, 2H), 3.68 – 3.62 (m, 3H), 2.51 (tdd, *J* = 11.1, 8.5, 3.7 Hz, 2H), ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 138.4, 138.3, 138.2, 134.9, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 117.1, 82.5, 80.2, 78.2, 75.6, 75.2, 73.8, 73.6, 73.2, 71.2, 69.0, 29.9; m/z calculated for $C_{37}H_{40}O_5$ $[M+Na]^+$: 587.2773; Found: 587.2769.

1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl galactopyranoside (7b): 60 mg isolated from 80 mg **4c** (α:β=12:1**,** 91%) Major α product: Syrup; $[\alpha]^{25}{}_{D}$ ($CHCl_3$, c 1.0): +9.2; IR (cm^{-1}, $CHCl_3$): 3019, 2921, 2860, 1731, 1455, 1362, 1214, 1094, 998, 914, 751, 699; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 20H), 5.83 – 5.76 (m, 1H), 5.13 – 5.04 (m, 2H), 4.73 (dd, *J* = 11.9, 4.5 Hz, 2H), 4.64 – 4.51 (m, 6H), 4.04 (t, *J* = 3.4 Hz, 2H), 3.92 – 3.85 (m, 1H), 3.80 – 3.68 (m, 3H), 2.48 – 2.35 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 138.6, 138.6, 138.4, 135.2, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.9, 127.7, 127.7, 127.7, 127.6,

127.6, 116.9, 76.5, 74.3, 73.3, 73.2, 73.2, 73.1, 72.7, 70.9, 70.3, 67.3, 29.8; m/z calculated for $C_{37}H_{40}O_5$ $[M+Na]^+$: 587.2773; Found: 587.2765.

1-Allyl-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside (7c): 80 mg isolated from 100 mg **4e** (α:β=7:1**,** 89%) Major α product: Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +13.1; IR (cm^{-1}, $CHCl_3$): 3607, 3026, 2917, 2855, 1729, 1456, 1361, 1213, 1086, 914, 746, 698; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.27 (m, 15H), 5.95 – 5.76 (m, 1H), 5.15 – 5.07 (m, 2H), 5.00 (dd, *J* = 11.0, 1.7 Hz, 1H), 4.93 (dd, *J* = 10.8, 1.7 Hz, 1H), 4.86 (dd, *J* = 11.0, 1.7 Hz, 1H), 4.73 (dd, *J* = 11.6, 1.5 Hz, 1H), 4.64 (dd, *J* = 11.8, 1.5 Hz, 2H), 4.02 – 3.98 (m, 1H), 3.68 – 3.59 (m, 2H), 3.34 – 3.23 (m, 2H), 3.22 – 3.15 (m, 1H), 2.67 – 2.57 (m, 1H), 2.24 (dt, *J* = 14.8, 7.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.8, 138.3, 138.3, 134.7, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.8, 117.4, 86.5, 81.3, 79.3, 78.9, 75.7, 75.4, 73.4, 68.1, 36.3; HRMS (ESI-MS): m/z calculated for $C_{29}H_{32}O_4$ $[M+Na]^+$: 467.2197; Found: 467.2193.

1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside (7d): 66 mg isolated from 100 mg **4f** (only α**,** 83%), syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +13.7; IR (cm^{-1}, $CHCl_3$): 3067, 3029, 2915, 2862, 1495, 1453, 1358, 1212, 1089, 1035, 995, 916, 743, 700; ^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.36 – 7.25 (m, 15H), 5.79 (ddt, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.14 – 5.01 (m, 2H), 4.80 (d, *J* = 11.7 Hz, 1H), 4.63 – 4.46 (m, 5H), 4.21 (dt, *J* = 7.1, 3.5 Hz, 1H), 4.07 (ddt, *J* = 13.9, 7.1, 3.8 Hz, 2H), 3.97 (t, *J* = 4.1 Hz, 1H), 3.57 (ddd, *J* = 44.0, 10.7, 3.6 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 138.3, 138.0, 135.1, 128.4,

128.4, 128.4, 128.4, 128.3, 128.3, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 127.6, 116.9, 80.1, 80.1, 79.5, 77.7, 73.4, 73.3, 72.7, 70.1, 34.3; m/z calculated for $C_{29}H_{32}O_4$ $[M+Na]^+$: 467.2198; Found: 467.2193.

1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside (7e): 50 mg isolated from 80 mg **4g** (α:β=1:2.5**,** 78%), Syrup; IR (cm^{-1}, $CHCl_3$): 2918, 2862, 1726, 1495, 1453, 1364, 1209, 1079, 915, 739, 696; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.29 (m, 15H), 5.91 – 5.82 (m, 1H), 5.20 – 5.07 (m, 2H), 4.63 – 4.52 (m, 5H), 4.43 – 4.26 (m, 1H), 4.17 – 4.06 (m, 2H), 4.01 – 3.83 (m, 2H), 3.71 – 3.54 (m, 2H), 2.60 – 2.44 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 138.3, 138.1, 138.1, 138.0, 138.0, 135.0, 134.4, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.8, 127.8, 117.7, 117.1, 87.0, 85.5, 83.8, 82.9, 82.8, 82.1, 81.7, 81.1, 73.5, 73.4, 72.0, 71.9, 71.5, 71.5, 70.8, 70.4, 37.8, 33.4; m/z calculated for $C_{29}H_{32}O_4$ $[M+Na]^+$: 467.2198; Found: 467.2201

1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside (8a): 110 mg isolated from 150 mg **4a** (only α**,** 85%), Syrup; [α]25 D (CHCl3, c 1.0): +20.3; IR (cm-1, CHCl3): 3027, 2953, 2920, 2863, 1732, 1456, 1363, 1213, 1090, 910, 742, 698; 1H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.25 (m, 18H), 7.15 – 7.11 (m, 2H), 4.95 (d, *J* = 10.8 Hz, 1H), 4.87 – 4.78 (m, 3H), 4.65 – 4.60 (m, 2H), 4.58 – 4.42 (m, 3H), 3.92 – 3.80 (m, 2H), 3.74 (dd, *J* = 11.0, 3.2 Hz, 1H), 3.68 – 3.62 (m, 3H); ^{13}C NMR (101 MHz, CDCl3) δ 138.3, 137.9, 137.5, 137.2, 128.8, 128.8, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.1, 128.1, 128.0,

128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 115.4, 83.2, 77.2, 76.3, 76.2, 76.0, 75.2, 74.0, 73.6, 67.8, 67.0.; m/z calculated for $C_{35}H_{35}NO_5$ $[M+H]^+$: 550.2593; Found: 550.2598.

1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl galactopyranoside (8b): 68 mg isolated from 100 mg **4c** (α:β>10:1**,** 84%), Major α product: Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +17.7; IR (cm^{-1}, $CHCl_3$): 3030, 2919, 2870, 1495, 1455, 1363, 1211, 1091, 914, 739, 696; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.28 (m, 20H), 4.97 (dd, *J* = 11.3, 3.1 Hz, 1H), 4.88 (dd, *J* = 11.8, 3.5 Hz, 2H), 4.82 – 4.77 (m, 1H), 4.76 – 4.68 (m, 2H), 4.60 (dd, *J* = 11.3, 3.0 Hz, 1H), 4.55 – 4.42 (m, 2H), 4.18 – 4.13 (m, 1H), 4.05 (h, *J* = 3.4 Hz, 2H), 3.86 (dd, *J* = 9.8, 2.8 Hz, 1H), 3.57 (dt, *J* = 10.8, 6.6 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.3, 138.3, 137.8, 137.7, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.7, 127.7, 116.0, 80.4, 75.2, 75.2, 74.2, 74.1, 73.7, 73.6, 73.5, 68.1, 67.7; m/z calculated for $C_{35}H_{35}NO_5$ $[M+H]^+$: 550.2593; Found: 550.2590.

1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl mannopyranoside (8c): 74 mg isolated from 100 mg **4d** (α:β=8:1**,** 92%), Major α product: Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): -1.4; IR (cm^{-1}, $CHCl_3$): 3032, 2921, 2862, 1727, 1495, 1455, 1362, 1283, 1210, 1096, 1035, 912, 742, 700; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.25 (m, 16H), 7.17 – 7.14 (m, 2H), 5.00 – 4.89 (m, 2H), 4.85 – 4.82 (m, 1H), 4.65 – 4.52 (m, 5H), 4.18 (s, 1H), 3.99 (d, *J* = 2.8 Hz, 1H), 3.92 (td, *J* = 9.4, 1.9 Hz, 1H), 3.74 – 3.68 (m, 2H), 3.52 (dd, *J* = 9.3, 2.8 Hz, 1H), 3.45 – 3.41 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.0, 137.9, 137.7,

137.5, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 127.9, 127.7, 127.7, 127.7, 116.1, 82.4, 80.5, 75.4, 74.7, 74.2, 74.1, 73.7, 72.7, 68.9, 67.5; m/z calculated for $C_{35}H_{35}NO_5$ $[M+H]^+$: 550.2593; Found: 550.2595.

1-Cyano-1-*deoxy*-2,3,4-tri-*O*-benzyl xylopyranoside (8d): 62 mg isolated from 90 mg **4e** (only α**,** 90%), Brown amorphous solid; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +8.7; IR (cm^{-1}, $CHCl_3$): 2920, 1456, 1363, 1214, 1087, 1020, 939, 744; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 15H), 4.91 (d, *J* = 1.6 Hz, 2H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.75 (d, *J* = 11.7 Hz, 1H), 4.64 (dd, *J* = 11.8, 8.2 Hz, 2H), 4.55 (dd, *J* = 6.0, 2.1 Hz, 1H), 3.90 (dd, *J* = 11.7, 5.2 Hz, 1H), 3.82 (t, *J* = 9.0 Hz, 1H), 3.66 – 3.51 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 138.0, 137.4, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.2, 128.2, 128.2, 128.2, 128.1, 128.0, 127.9, 127.9, 115.4, 82.3, 76.8, 76.7, 76.1, 74.1, 73.7, 67.4, 65.7; HRMS (ESI-MS): m/z calculated for $C_{27}H_{27}NO_4$ $[M+H]^+$: 430.2018; Found: 430.2017.

1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl arabinofuranoside (8e): 60 mg isolated from 90 mg **4g** (α:β=1:5**,** 87%), Major β product**:**Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): -3.7; IR (cm^{-1}, $CHCl_3$): 3800, 3756, 3649, 3546, 3032, 2924, 2862, 1729, 1498, 1456, 1366, 1270, 1210, 1095, 743, 701, 626; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.39 – 7.31 (m, 13H), 7.27 – 7.24 (m, 2H), 4.75 (d, *J* = 5.0 Hz, 1H), 4.63 – 4.58 (m, 3H), 4.56 – 4.52 (m, 2H), 4.50 (d, *J* = 11.9 Hz, 1H), 4.20 – 4.16 (m, 2H), 4.09 (t, *J* = 3.1 Hz, 1H), 3.67 (dd, *J* = 10.1, 5.9 Hz, 1H), 3.60 (dd, *J* = 10.1, 6.5 Hz, 1H), ^{13}C NMR (101 MHz, Chloroform,-*d*) δ 137.9, 137.2, 136.7, 128.8,

128.8, 128.7, 128.7, 128.5, 128.5, 128.4, 128.2, 128.2, 128.2, 127.9, 127.9, 127.9, 127.9, 127.9, 115.9, 83.5, 82.6, 82.5, 73.6, 72.8, 72.1, 69.8, 69.5; m/z calculated for $C_{27}H_{27}NO_4$ $[M+H]^+$: 430.2018; Found: 430.2016.

1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside (9a): 84 mg isolated from 100 mg **4a** (only α**,** 90%),White amorphous solid; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +12.2; IR (cm^{-1}, $CHCl_3$): 3062, 3031, 2918, 2864, 1726, 1683, 1593, 1496, 1453, 1362, 1276, 1212, 1082, 1019, 745, 697; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.59 – 7.28 (m, 21H), 7.23 – 7.17 (m, 2H), 4.97 (dt, *J* = 10.8, 3.6 Hz, 2H), 4.86 (dt, *J* = 11.0, 2.5 Hz, 2H), 4.74 – 4.59 (m, 3H), 4.54 (dd, *J* = 10.7, 3.1 Hz, 1H), 4.48 (dd, *J* = 12.1, 2.5 Hz, 1H), 3.91 – 3.83 (m, 2H), 3.80 – 3.69 (m, 3H), 3.67 – 3.61 (m, 1H), 3.54 – 3.22 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.7, 138.8, 138.3, 138.2, 138.1, 137.2, 133.2, 128.7, 128.7, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 127.8, 127.8, 82.3, 79.5, 77.9, 75.5, 75.2, 73.6, 73.5, 72.7, 71.1, 68.9, 35.9; m/z calculated for $C_{42}H_{42}O_6$ $[M+H]^+$: 643.3060; Found: 643,3058.

1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,5-tri-*O*-benzyl α/β-D-ribofuranoside (9b): 77 mg isolated from 100 mg **4f** (α:β=3:1**,** 85%), Syrup; IR (cm^{-1}, $CHCl_3$): 3301, 2919, 2863, 1682, 1593, 1495, 1452, 1367, 1292, 1211, 1088, 994, 809, 743, 696; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (td, *J* = 7.8, 2.1 Hz, 2H), 7.41 – 7.27 (m, 12H), 7.27 – 7.21 (m, 2H), 7.16 – 7.13 (m, 1H), 4.73 – 4.69 (m, 1H), 4.66 – 4.55 (m, 4H), 4.53 – 4.46

(m, 1H), 4.36 – 4.34 (m, 1H), 4.26 – 3.95 (m, 3H), 3.69 – 3.40 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.3, 138.4, 138.0, 137.9, 137.1, 133.3, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 84.1, 83.1, 82.7, 78.0, 73.5, 71.8, 71.7, 70.8, 38.3; 70.2; m/z calculated for $C_{34}H_{34}O_5$ $[M+H]^+$: 523.2484; Found: 523.2488.

1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl xylopyranoside (9c): 78 mg isolated from 90 mg **4e** (α:β>15:1**,** 92%), Major α product: Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +21.2; IR (cm^{-1}, $CHCl_3$): 3092, 2915, 2860, 1727, 1682, 1592, 1495, 1452, 1275, 1209, 1071, 741, 693; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 – 7.91 (m, 2H), 7.58 – 7.53 (m, 1H), 7.46 – 7.42 (m, 2H), 7.39 – 7.22 (m, 15H), 4.68 – 4.54 (m, 5H), 4.51 (ddd, *J* = 7.0, 5.9, 2.9 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 3.85 (t, *J* = 3.2 Hz, 2H), 3.75 (t, *J* = 4.4 Hz, 1H), 3.58 (dd, *J* = 4.5, 3.0 Hz, 1H), 3.45 – 3.37 (m, 2H), 3.24 (dd, *J* = 17.1, 5.9 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.2, 138.4, 138.2, 138.0, 137.2, 133.2, 128.7, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 128.0, 128.0, 128.0, 128.0, 127.9, 127.9, 127.9, 75.2, 74.0, 73.3, 72.9, 72.7, 72.0, 71.8, 65.8, 38.6; HRMS (ESI-MS): m/z calculated for $C_{34}H_{34}O_5$ $[M+Na]^+$: 545.2304; Found: 545.2310.

1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl glucopyranoside (10a): 78 mg isolated from 100 mg **4a** (α:β>15:1**,** 87%), Major α product: White amorphous solid; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +7.2; IR (cm^{-1}, $CHCl_3$): 3063, 3031, 2929, 2862, 1709, 1495, 1454, 1362, 1305, 1210, 1084, 909, 742, 700; ^{1}H NMR

(400 MHz, Chloroform-*d*) δ 7.32 – 7.15 (m, 20H), 4.76 – 4.64 (m, 3H), 4.56 (dd, *J* = 11.9, 1.6 Hz, 2H), 4.52 – 4.43 (m, 3H), 4.39 (dd, *J* = 10.4, 4.6 Hz, 1H), 3.94 (dd, *J* = 6.5, 4.6 Hz, 1H), 3.79 (t, *J* = 6.4 Hz, 1H), 3.73 (dt, *J* = 8.1, 4.0 Hz, 1H), 3.67 – 3.58 (m, 3H), 2.96 (td, *J* = 10.2, 4.7 Hz, 1H), 2.34 – 2.20 (m, 3H), 1.99 (t, *J* = 4.7 Hz, 1H), 1.84 (dq, *J* = 8.8, 4.7, 4.2 Hz, 1H), 1.65 – 1.49 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.0, 138.5, 138.3, 138.3, 138.3, 128.5, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 128.0, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 79.7, 77.9, 76.7, 73.9, 73.8, 73.5, 73.5, 73.5, 70.9, 69.4, 49.6, 42.8, 31.3, 29.6, 24.5; m/z calculated for $C_{40}H_{44}O_6$ $[M+Na]^+$: 643.3036; Found: 643.3033.

1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl galactopyranoside (10b): 82 mg isolated from 100 mg **4c** (α:β>10:1**,** 80%), Major α product: Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +36.5; IR (cm^{-1}, $CHCl_3$): 3031, 2925, 2862, 1712, 1494, 1455, 1363, 1270, 1212, 1105, 1026, 914, 742, 701, 630; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.38 – 7.28 (m, 20H), 4.97 – 4.76 (m, 3H), 4.70 – 4.59 (m, 3H), 4.46 (q, *J* = 11.8 Hz, 2H), 4.04 (d, *J* = 2.7 Hz, 1H), 3.91 (dd, *J* = 9.7, 3.4 Hz, 1H), 3.78 (t, *J* = 9.4 Hz, 1H), 2.57 – 2.51 (m, 1H), 2.47 – 2.31 (m, 3H), 2.19 – 2.14 (m, 2H), 1.90 – 1.78 (m, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 210.4, 139.1, 138.4, 138.3, 138.1, 128.5, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.2, 128.2, 127.9, 127.9, 127.7, 127.7, 127.7, 127.7, 127.6, 127.6, 127.6, 127.4, 85.6, 76.7, 75.7, 74.7, 74.6, 74.4, 73.7, 73.4, 72.0, 68.6, 50.8, 41.9, 26.7, 26.0, 23.8; m/z calculated for $C_{40}H_{44}O_6$ $[M+Na]^+$: 643.3036; Found: 643.3043.

1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4-tri-*O*-benzyl α/β-D-xylopyranoside (10c): 60 mg isolated from 80 mg **4e** (α:β=6:1**,** 82%), Major α product: Syrup; IR (cm^{-1}, $CHCl_3$): 3019, 2925, 2859, 1711, 1456, 1216, 1077, 754, 701; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.26 (m, 13H), 7.25 – 7.22 (m, 2H), 4.53 (dd, *J* = 13.1, 2.0 Hz, 4H), 4.43 (d, *J* = 12.1 Hz, 1H), 4.28 (d, *J* = 11.9 Hz, 1H), 4.25 – 4.12 (m, 2H), 3.85 – 3.80 (m, 2H), 3.74 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.31 (q, *J* = 1.9, 1.4 Hz, 1H), 2.52 – 2.46 (m, 1H), 2.37 – 2.32 (m, 1H), 2.20 – 2.01 (m, 4H), 1.86 – 1.81 (m, 1H), 1.71 – 1.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.5, 138.5, 138.3, 138.0, 128.6, 128.6, 128.5, 128.5, 128.3, 128.3, 128.3, 128.3, 127.9, 127.9, 127.9, 127.9, 127.8, 127.7, 127.6, 74.0, 72.9, 72.7, 72.4, 71.8, 71.2, 70.3, 67.2, 50.1, 43.0, 31.9, 31.3, 25.0; m/z calculated for $C_{32}H_{36}O_5$ $[M+Na]^+$: 523.2460; Found: 523.2457.

1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl ribofuranoside (10d): 60 mg isolated from 90 mg **4f** (α:β>15:1**,** 75%), Major α product: White amorphous solid; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +18.6; IR (cm^{-1}, $CHCl_3$): 3031, 2929, 2861, 1705, 1494, 1453, 1354, 1313, 1269, 1209, 1086, 1040, 911, 739, 699; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.24 (m, 15H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 3.0 Hz, 1H), 4.58 – 4.47 (m, 3H), 4.41 – 4.33 (m, 2H), 4.09 – 4.04 (m, 3H), 3.69 – 3.64 (m, 1H), 3.50 (dt, *J* = 10.7, 2.1 Hz, 1H), 2.95 – 2.85 (m, 1H), 2.50 – 2.43 (m, 1H), 2.26 – 2.15 (m, 2H), 2.05 (tt, *J* = 5.8, 2.8 Hz, 1H), 1.87 – 1.82 (m, 1H), 1.60 (td, *J* = 8.6, 7.9, 4.2 Hz, 2H), 1.39 – 1.35 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 213.1, 138.9, 138.5, 138.0, 128.6, 128.6, 128.6, 128.4, 128.4, 128.4, 128.1, 128.0, 127.9, 127.9, 127.8, 127.8, 127.7,

127.7, 127.1, 80.8, 79.8, 78.2, 77.9, 74.4, 73.4, 73.0, 69.9, 51.1, 42.8, 32.0, 28.8, 25.1; m/z calculated for $C_{32}H_{36}O_5$ $[M+Na]^+$: 523.2460; Found: 523.2460.

3,4,6-tri-O-benzoyl-2-benzoyloxy glucal (11b): Data matched with previously reported compound.[6a]

1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α-D-ribofuranoside (12a): 83 mg isolated from 100 mg **4f** (only α**,** 90%), Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +13.4; IR (cm^{-1}, $CHCl_3$): 3064, 3032, 2921, 2864, 1736, 1654, 1494, 1452, 1366, 1233, 1088, 1037, 912, 846, 741, 701; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 7.08 (m, 15H), 4.97 – 4.83 (m, 2H), 4.65 (dd, *J* = 11.7, 2.5 Hz, 1H), 4.49 – 4.30 (m, 7H), 4.05 (dq, *J* = 7.5, 4.0, 3.0 Hz, 2H), 3.96 – 3.93 (m, 1H), 3.89 – 3.83 (m, 1H), 3.40 (ddt, *J* = 36.5, 10.7, 3.1 Hz, 2H), 2.44 – 2.28 (m, 2H), 1.88 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 141.2, 138.4, 138.3, 138.0, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 127.8, 127.8, 127.8, 127.8, 127.8, 127.7, 127.7, 127.7, 127.6, 114.0, 79.9, 79.9, 78.8, 78.0, 73.4, 73.3, 72.7, 70.2, 67.1, 33.4, 21.0; m/z calculated for $C_{32}H_{36}O_6$ $[M+Na]^+$: 539.2410; Found: 539.2403.

1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α/β-D-arabinofuranoside (12b): 66 mg isolated from 100 mg **4g** (α:β=1:3.5**,** 72%), Syrup; IR (cm^{-1}, $CHCl_3$): 3031, 2920, 2862, 1728, 1495, 1452, 1368, 1230, 1087, 909, 847, 739, 698; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.29 (m, 15H), 5.15 (dt, *J* = 3.3, 1.6 Hz, 1H), 5.10 – 5.03 (m, 1H), 4.64 – 4.57 (m, 5H), 4.56 – 4.50 (m, 2H), 4.39 (dd, *J* = 11.9, 1.4 Hz, 1H), 4.30 – 4.20 (m, 1H), 4.18 – 4.09 (m, 1H), 4.00 (t, *J* = 2.4 Hz, 1H), 3.92 – 3.88 (m, 1H), 3.70 – 3.52 (m,

2H), 2.60 – 2.45 (m, 2H), 2.08 (d, *J* = 1.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 141.1, 138.4, 138.0, 138.0, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.0, 128.0, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 114.3, 83.6, 83.2, 82.9, 80.0, 73.4, 71.5, 71.4, 70.7, 67.2, 32.5, 21.1; m/z calculated for $C_{32}H_{36}O_6$ $[M+Na]^+$: 539.2409; Found: 539.2416.

1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside (12c): 82 mg isolated from 100 mg **4a** (α:β=6:1**,** 88%), Major α product: White amorphous solid; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +39.3; IR (cm^{-1}, $CHCl_3$): 3031, 2921, 2863, 1736, 1495, 1452, 1365, 1231, 1082, 910, 832, 741, 700; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 – 7.27 (m, 18H), 7.18 (dd, *J* = 7.5, 2.1 Hz, 2H), 5.20 – 5.10 (m, 2H), 5.00 (d, *J* = 10.9 Hz, 1H), 4.90 – 4.84 (m, 2H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.71 – 4.65 (m, 3H), 4.59 (d, *J* = 13.1 Hz, 1H), 4.51 (t, *J* = 11.2 Hz, 2H), 4.33 – 4.30 (m, 1H), 3.87 – 3.80 (m, 2H), 3.77 (dd, *J* = 10.5, 2.6 Hz, 1H), 3.71 (d, *J* = 5.9 Hz, 2H), 3.67 – 3.64 (m, 1H), 2.63 – 2.52 (m, 2H), 2.10 (s, 3H), ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.8, 140.9, 138.8, 138.3, 138.3, 138.1, 128.6, 128.6, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.2, 128.2, 128.1, 128.1, 128.1, 128.1, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 115.6, 82.4, 80.0, 78.1, 75.6, 75.3, 73.6, 73.3, 72.9, 71.5, 68.9, 66.9, 28.6, 21.1; m/z calculated for $C_{40}H_{44}O_7$ $[M+Na]^+$: 659.2985; Found: 659.2981.

1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranoside (12d): 72 mg isolated from 100 mg **4c** (α:β=4:1**,** 77%), Major α product: Syrup; IR (cm^{-1}, $CHCl_3$): 3031, 2923, 2863, 1737, 1493, 1453, 1367, 1234, 1096, 1036, 912, 741, 700; 1H NMR (400 MHz, Chloroform-*d*) δ

7.45 – 6.95 (m, 20H), 5.05 (s, 1H), 4.96 (s, 1H), 4.76 – 4.62 (m, 2H), 4.60 – 4.50 (m, 4H), 4.49 – 4.44 (m, 2H), 4.40 (d, J = 7.4 Hz, 2H), 4.13 (dt, J = 10.0, 4.1 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.81 – 3.50 (m, 4H), 2.53 – 2.20 (m, 2H), 1.96 (s, 3H); 13C NMR (101 MHz, Chloroform-*d*) δ 170.7, 141.2, 138.6, 138.5, 138.4, 138.3, 128.5, 128.5, 128.4, 128.4, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 127.6, 114.8, 82.6, 79.8, 76.7, 74.3, 73.3, 73.3, 73.2, 73.1, 72.4, 67.4, 67.1, 29.8, 21.0. m/z calculated for $C_{40}H_{44}O_7$ $[M+Na]^+$: 659.2985; Found: 659.2984.

1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside (13a): 70 mg isolated from 90 mg **4a** (α:β=3:1**,** 86%), Major α product: White amorphous solid; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +17.3; IR (cm^{-1}, $CHCl_3$): 3063, 3031, 2917, 2864, 1715, 1494, 1454, 1360, 1319, 1267, 1209, 1083, 910, 741, 699; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.15 (m, 20H), 4.96 – 4.92 (m, 1H), 4.87 – 4.80 (m, 2H), 4.70 (dt, *J* = 7.3, 2.2 Hz, 1H), 4.68 – 4.58 (m, 3H), 4.53 – 4.47 (m, 2H), 3.80 (dd, *J* = 9.1, 5.7 Hz, 1H), 3.76 – 3.62 (m, 5H), 2.89 – 2.83 (m, 1H), 2.75 (dd, *J* = 15.5, 8.5 Hz, 1H), 2.15 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 206.3, 138.7, 138.2, 138.1, 138.0, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.5, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 128.0, 128.0, 128.0, 127.9, 127.8, 127.8, 82.2, 79.5, 77.8, 75.5, 75.1, 73.6, 73.5, 72.5, 71.0, 68.9, 41.1, 30.7; m/z calculated for $C_{37}H_{40}O_6$ $[M+Na]^+$: 603.2723; Found: 603.2729.

1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside (13b): 74 mg isolated from 100 mg **4e** (α:β=5:1**,** 90%), Major α product: Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$,

c 1.0): +18.1; IR (cm^{-1}, $CHCl_3$): 3030, 2917, 2861, 1714, 1496, 1455, 1361, 1261, 1208, 1073, 1028, 740, 697; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.25 (m, 15H), 4.65 – 4.59 (m, 3H), 4.56 (s, 2H), 4.43 (dd, *J* = 11.9, 1.3 Hz, 1H), 4.29 (tt, *J* = 6.2, 2.4 Hz, 1H), 3.78 (dd, *J* = 3.7, 1.7 Hz, 2H), 3.70 (td, *J* = 4.7, 1.8 Hz, 1H), 3.45 – 3.38 (m, 2H), 2.92 (ddd, *J* = 16.4, 8.0, 1.5 Hz, 1H), 2.57 (ddd, *J* = 16.5, 5.2, 1.5 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.2, 138.4, 138.2, 138.1, 128.6, 128.6, 128.5, 128.5, 128.5, 128.5, 128.5, 128.5, 128.0, 128.0, 128.0, 128.0, 128.0, 128.0, 127.9, 75.6, 74.0, 73.7, 73.1, 72.7, 72.0, 71.7, 65.5, 43.5, 31.1; m/z calculated for $C_{29}H_{32}O_5$ $[M+Na]^+$: 483.2147; Found: 483.2137.

3,4,6-tri-*O*-benzyl-2-benzyloxy glucal (15): Syrup; IR (cm^{-1}, $CHCl_3$): 3070, 3031, 2862, 1727, 1492, 1450, 1361, 1265, 1210, 1082, 1037, 999, 913, 824, 740, 699. 1H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.19 (m, 20H), 6.31 (s, 1H), 4.74 (d, J = 11.4 Hz, 2H), 4.70 (s, 2H), 4.60 (dd, J = 11.6, 7.0 Hz, 2H), 4.54 (s, 2H), 4.26 (d, J = 4.6 Hz, 1H), 4.09 (td, J = 6.2, 3.3 Hz, 1H), 3.90 (dd, J = 6.7, 4.7 Hz, 1H), 3.77 (dd, J = 10.7, 6.0 Hz, 1H), 3.68 (dd, J = 10.6, 3.5 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 138.4, 138.1, 137.9, 137.2, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 128.3, 128.0, 127.9, 127.9, 127.9, 127.9, 127.9, 127.8, 127.8, 127.8, 127.8, 127.7, 127.6, 127.6, 76.2, 75.6, 74.3, 73.5, 72.9, 72.3, 71.1, 68.3.

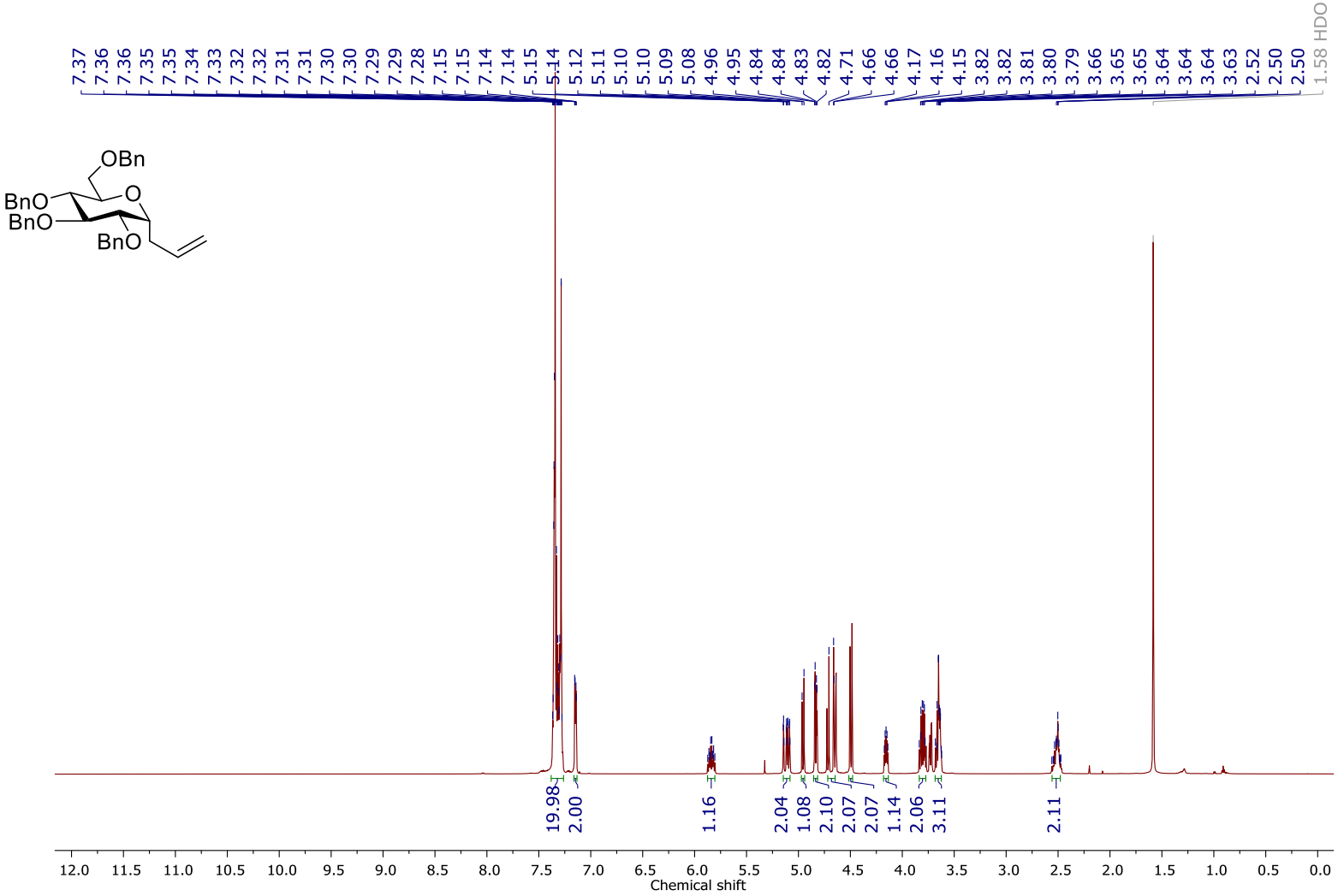
1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl ribofuranoside (16a): 74 mg isolated from 100 mg **4f** (α:β=10:1**,** 86%), Major α product: Syrup; $[\alpha]^{25}{}_D$ ($CHCl_3$, c 1.0): +5.1; IR (cm^{-1}, $CHCl_3$): 3065, 3031, 2921, 2861, 1493, 1454, 1359, 1209,

1129, 1042, 912, 835, 742, 701; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.22 (m, 16H), 7.05 (dt, *J* = 3.5, 1.0 Hz, 1H), 6.95 (dd, *J* = 5.0, 3.5 Hz, 1H), 5.27 (d, *J* = 6.8 Hz, 1H), 4.64 – 4.58 (m, 3H), 4.55 (d, *J* = 4.1 Hz, 1H), 4.51 (d, *J* = 3.6 Hz, 2H), 4.32 (q, *J* = 4.1 Hz, 1H), 4.01 (dd, *J* = 5.2, 3.8 Hz, 1H), 3.91 (dd, *J* = 6.8, 5.1 Hz, 1H), 3.60 (d, *J* = 4.3 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.8, 138.2, 137.9, 137.7, 128.4, 128.4, 128.4, 128.4, 128.4, 128.4, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.6, 127.6, 127.6, 126.7, 125.2, 125.0, 83.9, 82.0, 79.0, 77.6, 73.5, 72.4, 72.0, 70.5; m/z calculated for $C_{30}H_{30}O_4S$ $[M+Na]^+$: 509.1762; Found: 509.1753.

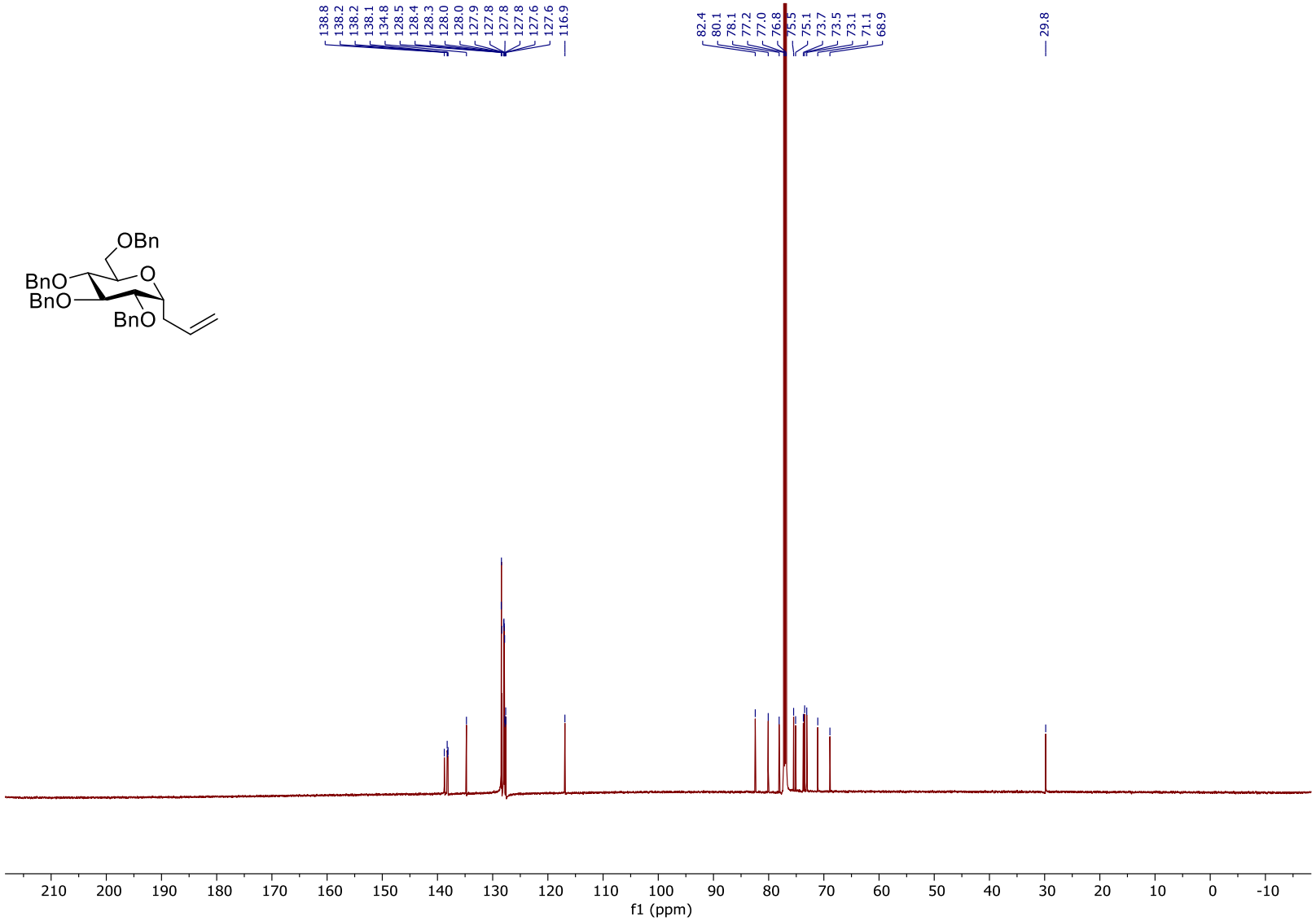
1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside (16b): 56 mg isolated from 190 mg **4g** (α:β=1:2.5, 74%) Syrup; IR (cm^{-1}, $CHCl_3$): 3023, 2921, 2860, 1727, 1454, 1364, 1213, 1087, 749, 700; ^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.34 – 7.23 (m, 16H), 7.12 – 7.07 (m, 1H), 6.99 – 6.95 (m, 1H), 5.36 – 5.21 (m, 1H), 4.63 – 4.46 (m, 6H), 4.36 – 4.19 (m, 3H), 3.64 (dd, *J* = 5.1, 0.8 Hz, 2H; ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 138.0, 137.7, 137.5, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 128.2, 127.7, 127.7, 127.6, 127.6, 127.6, 127.6, 127.5, 127.5, 126.6, 125.2, 125.2, 90.1, 84.6, 81.2, 79.8, 73.3, 72.2, 72.0, 70.0; m/z calculated for $C_{30}H_{30}O_4S$ $[M+Na]^+$: 509.1762; Found: 509.1760.

NMR Spectral charts

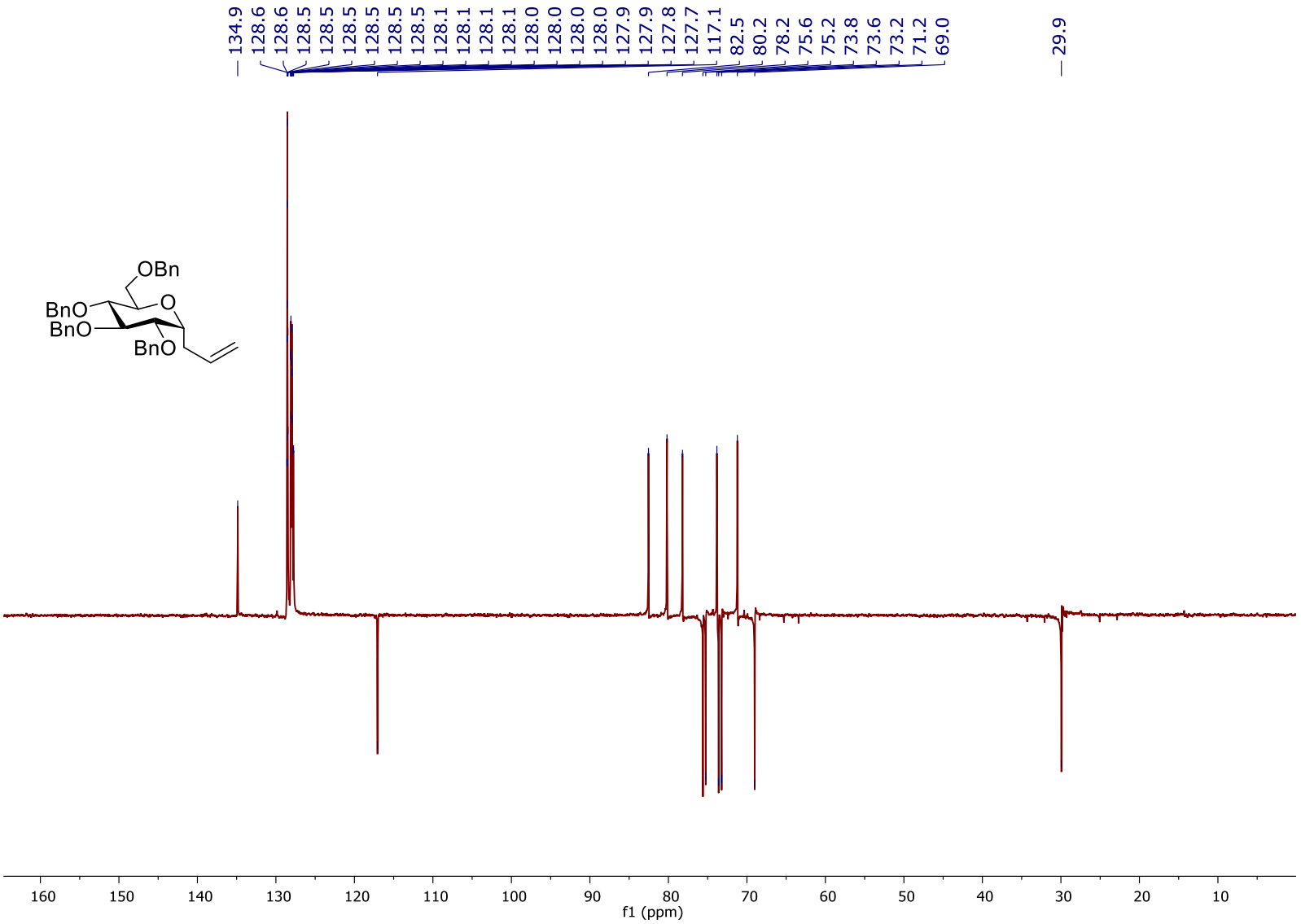
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(7a):**



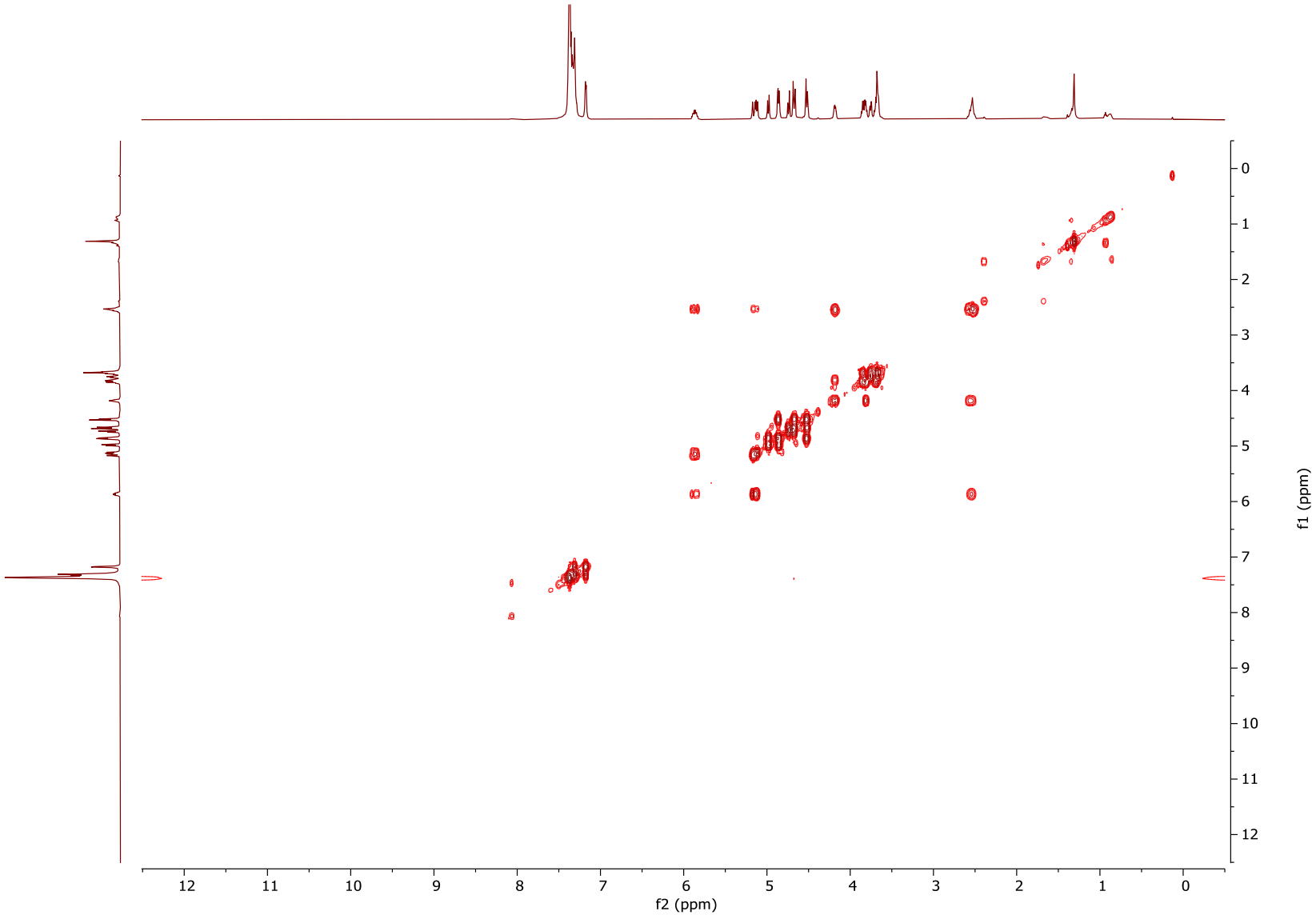
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(7a):**



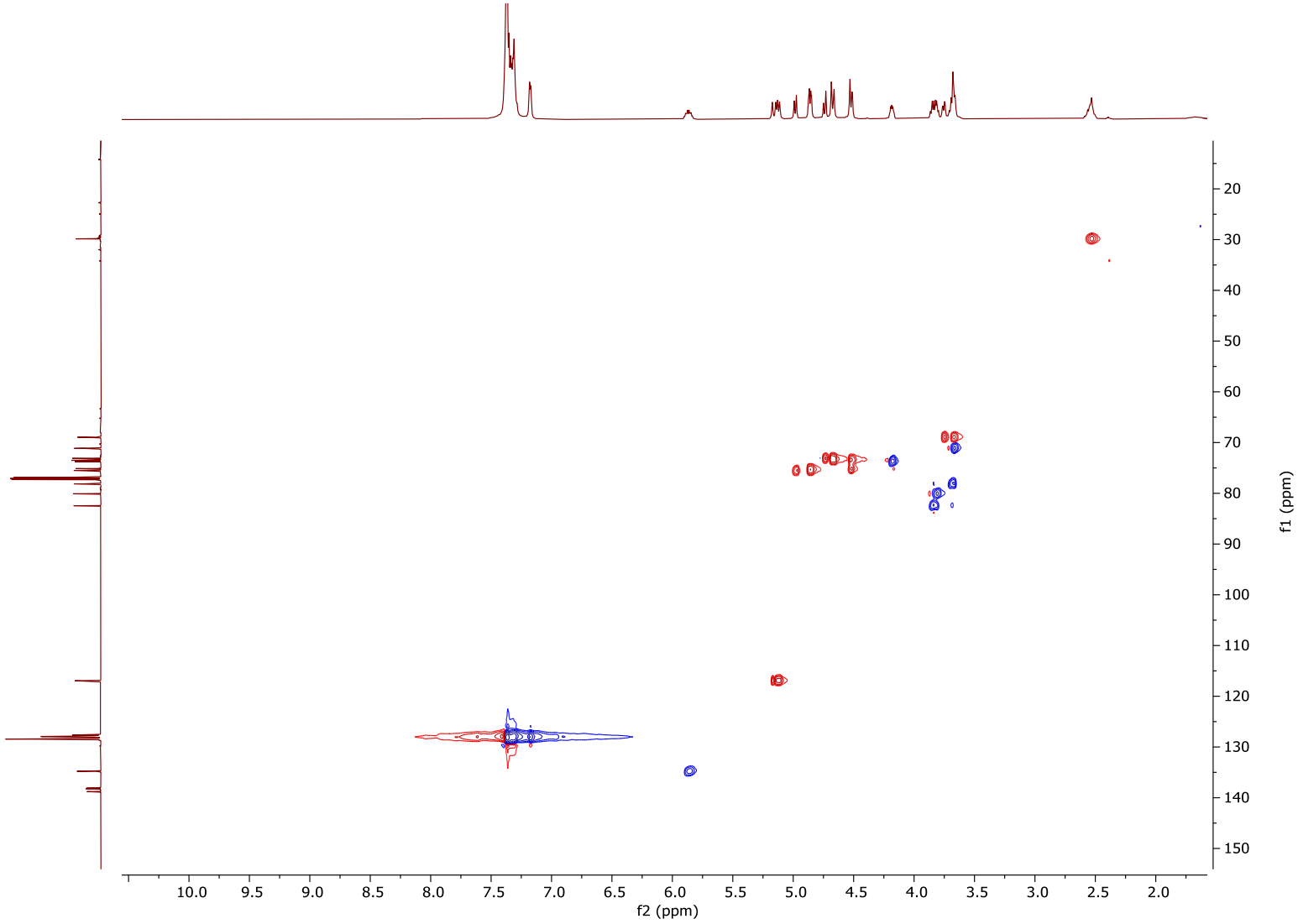
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(7a):**



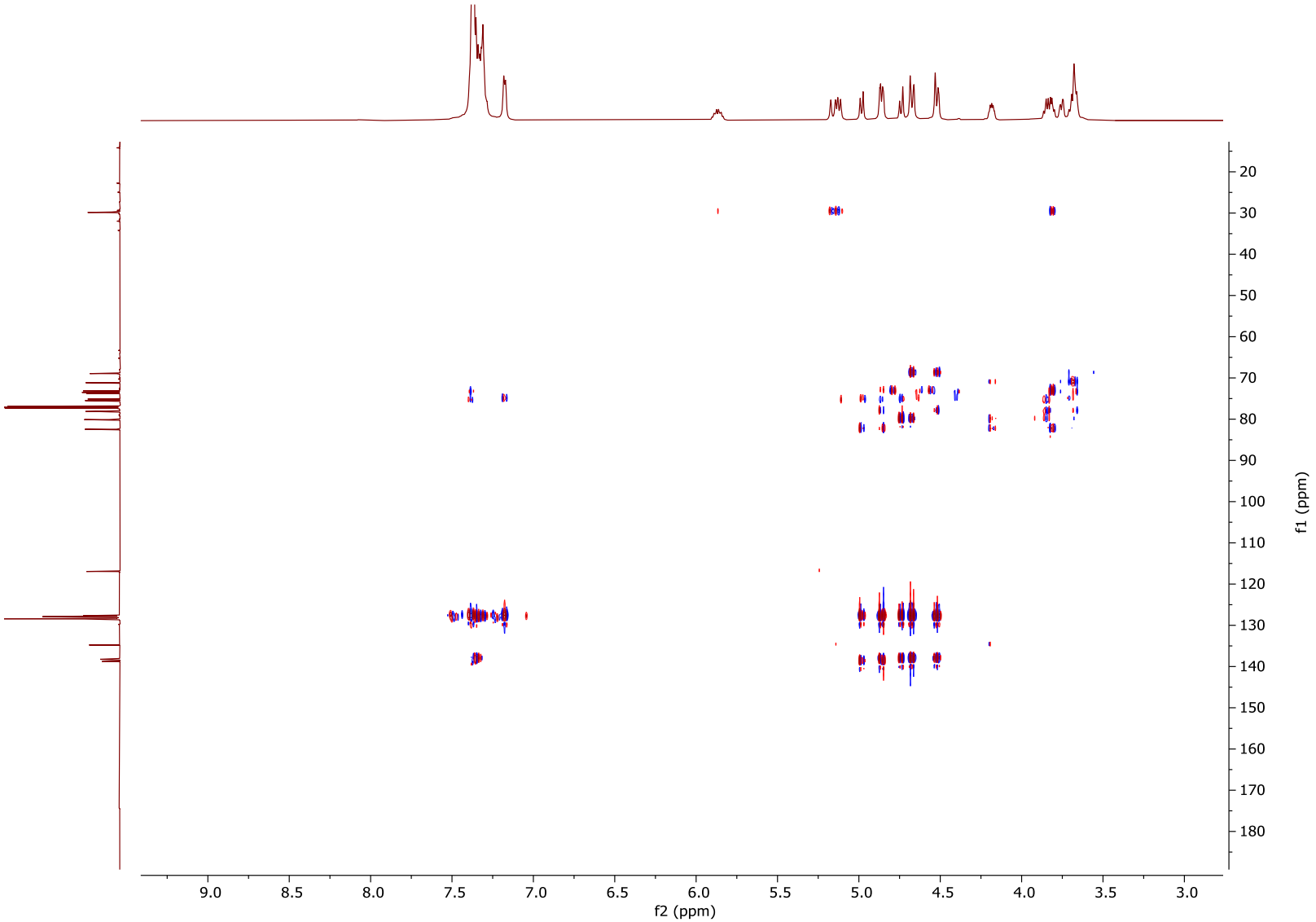
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(7a):**



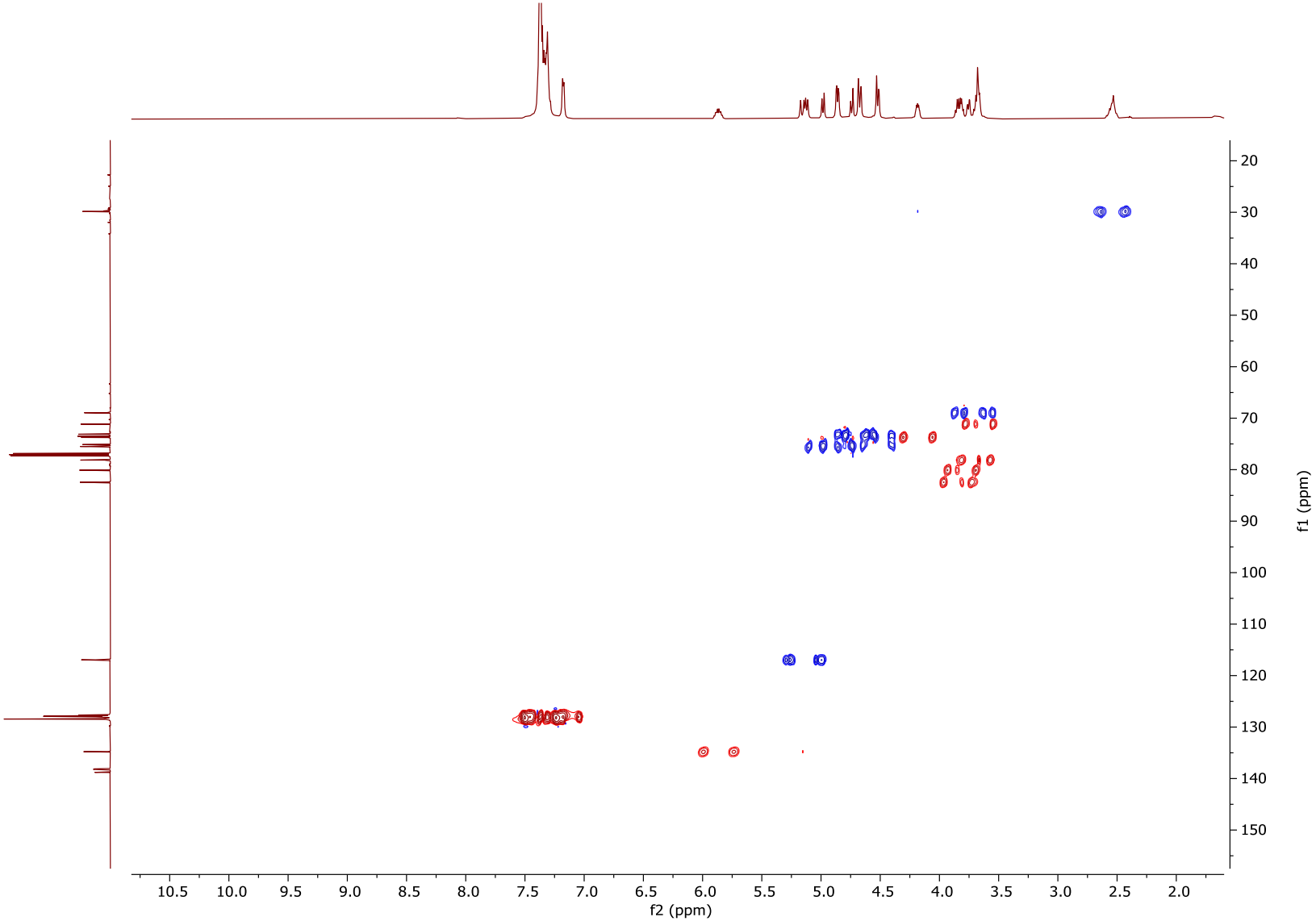
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(7a):**



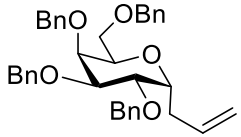
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(7a):**

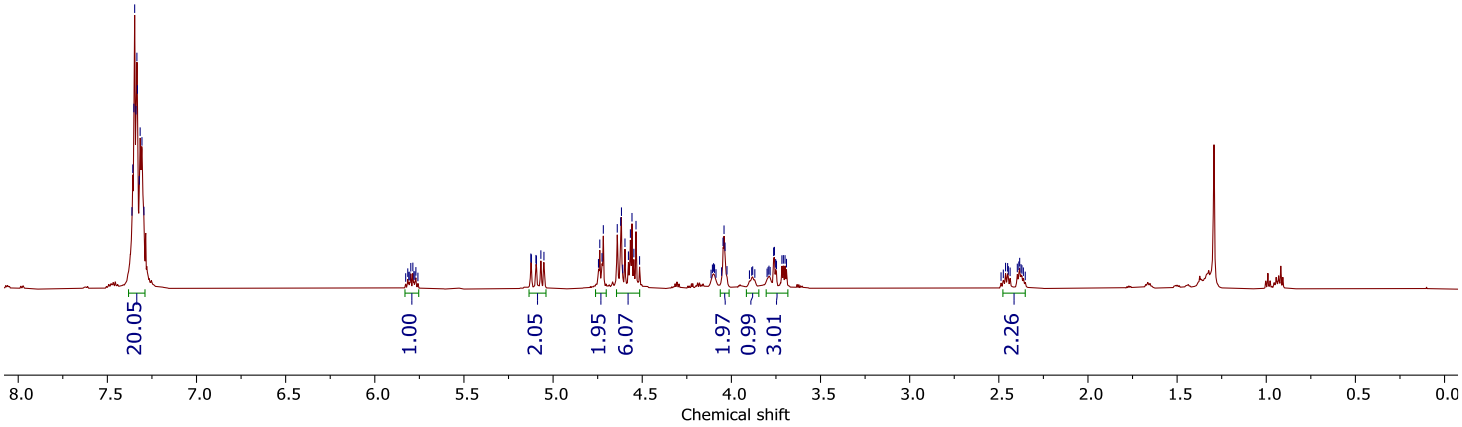


HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(7a):**

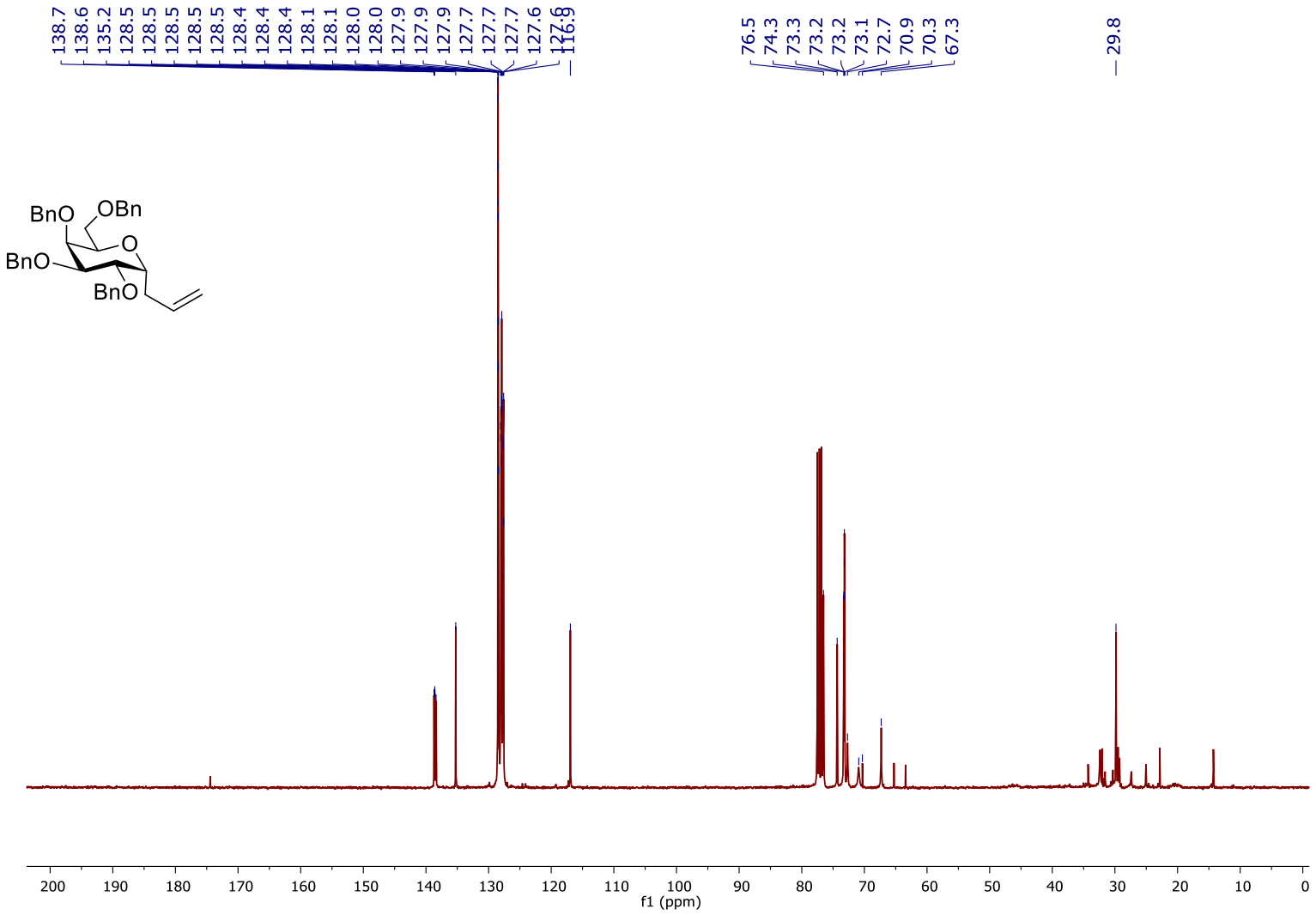


^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(7b):**

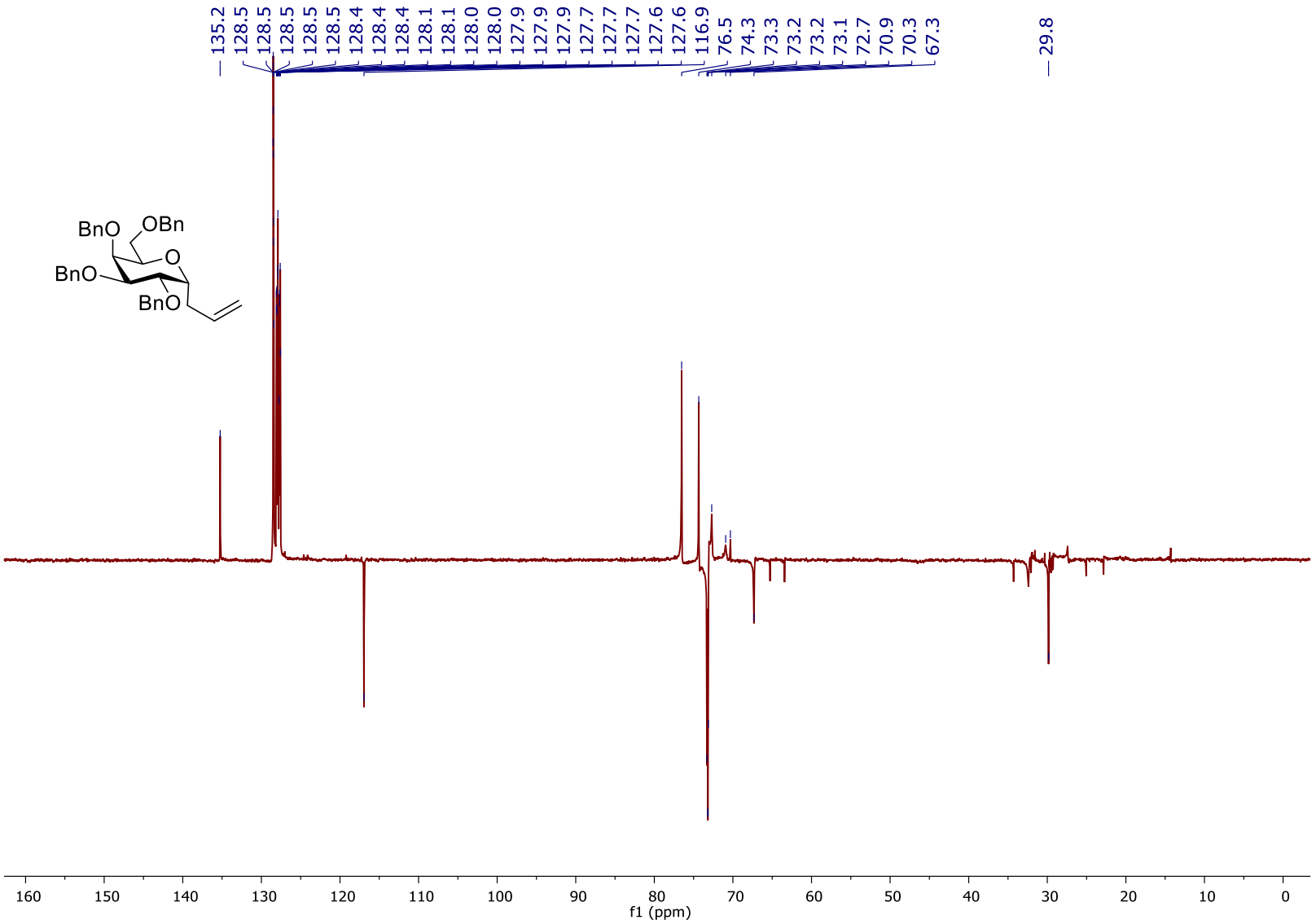




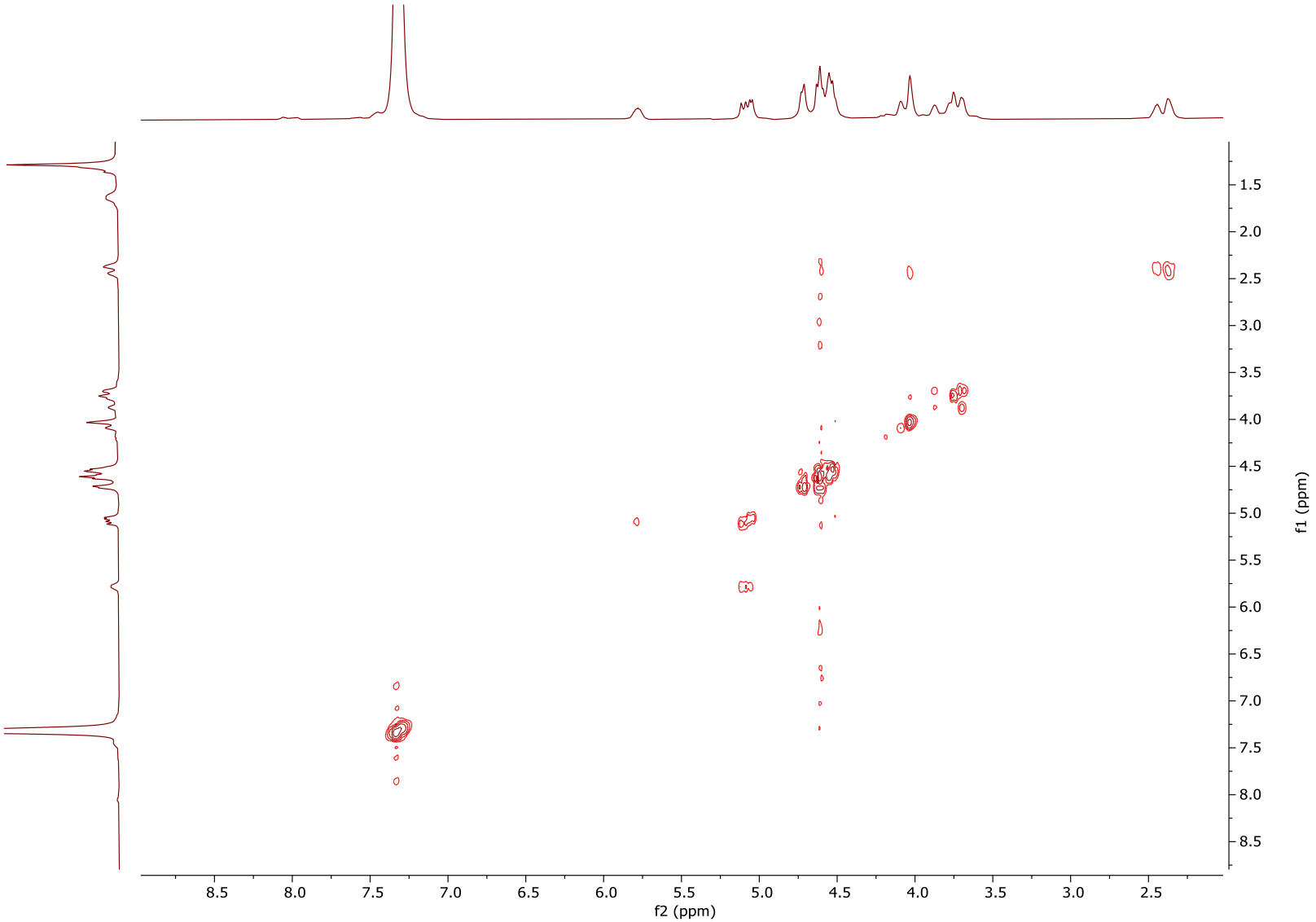
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(7b):**



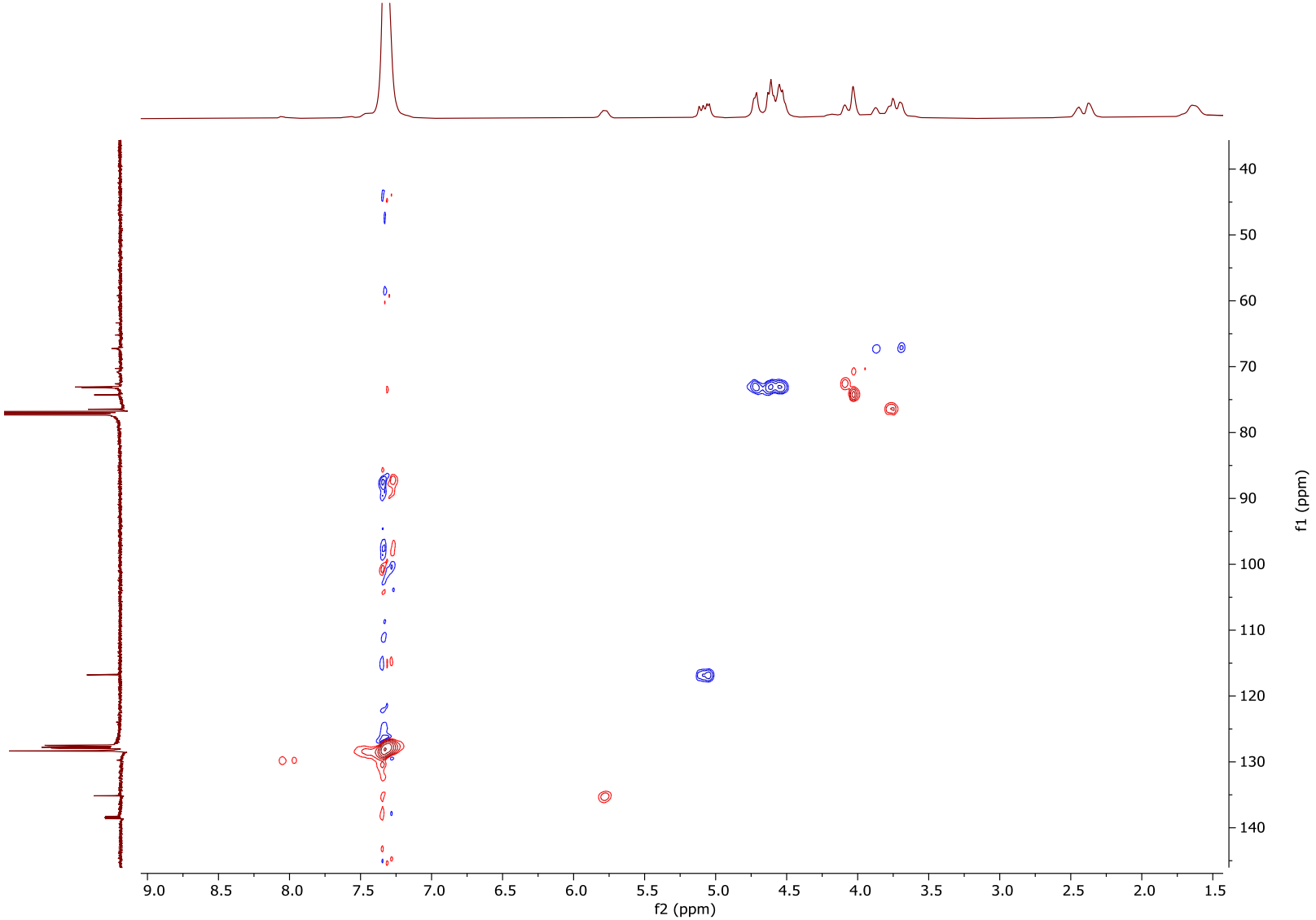
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(7b):**



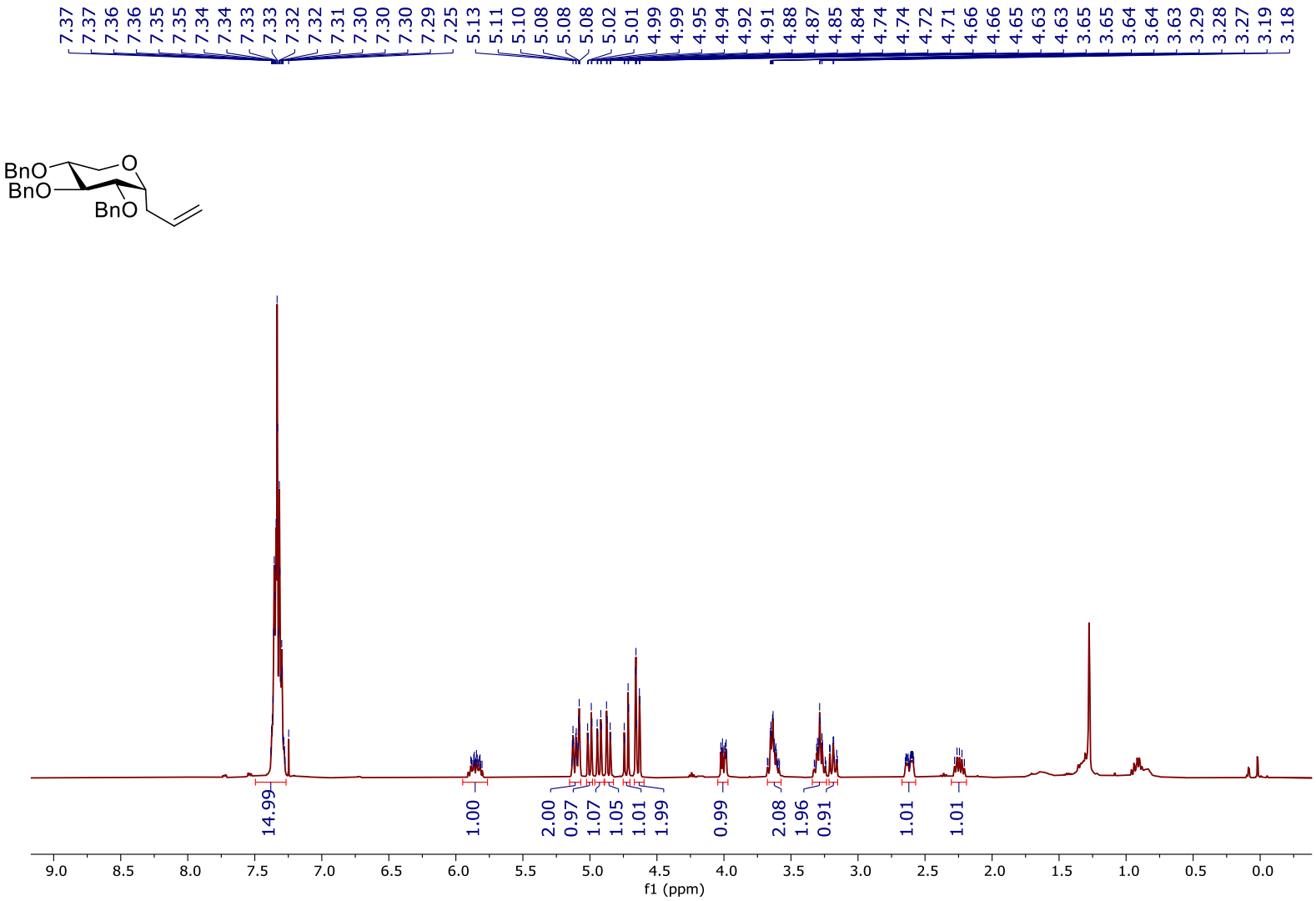
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(7b):**



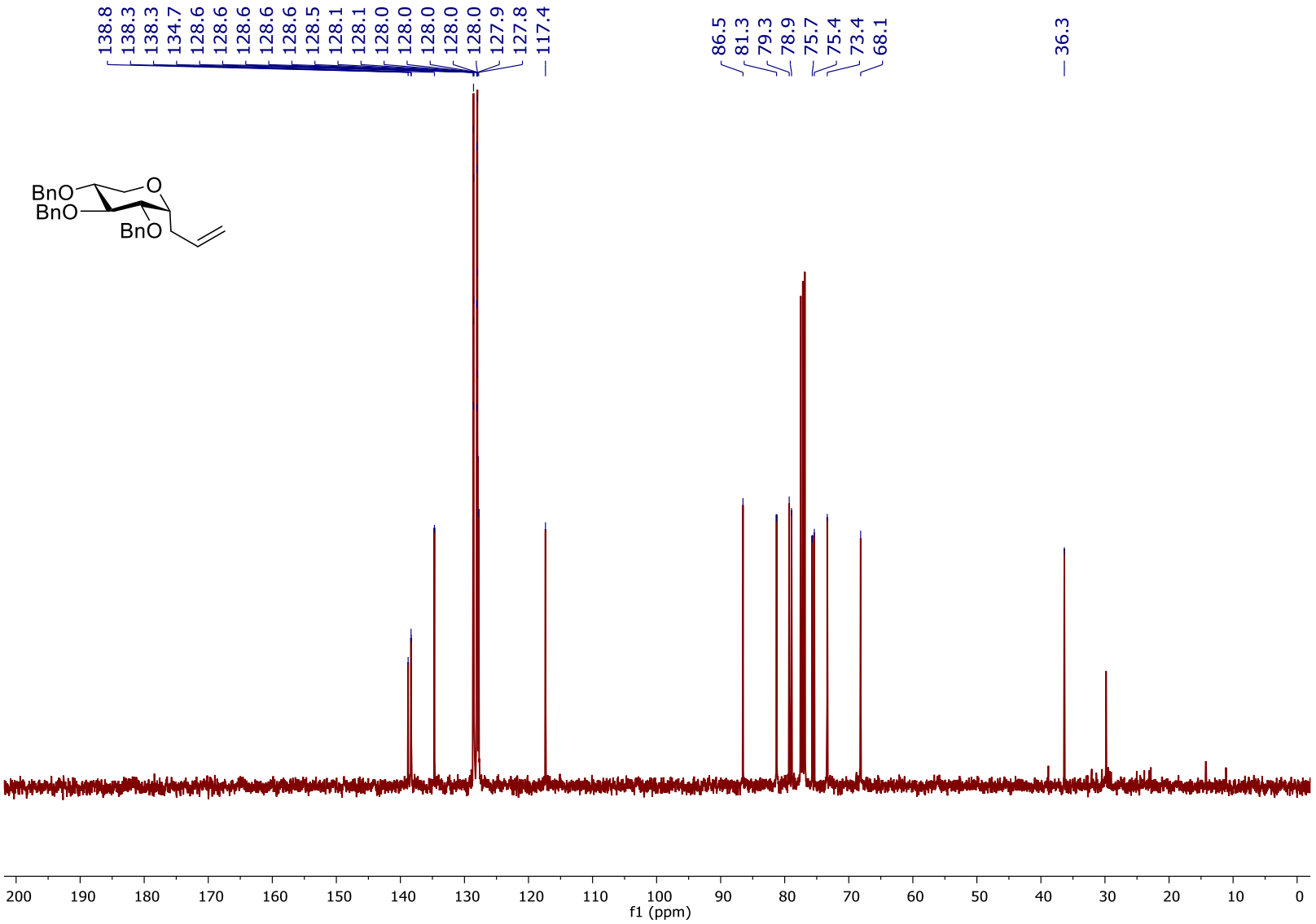
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(7b):**



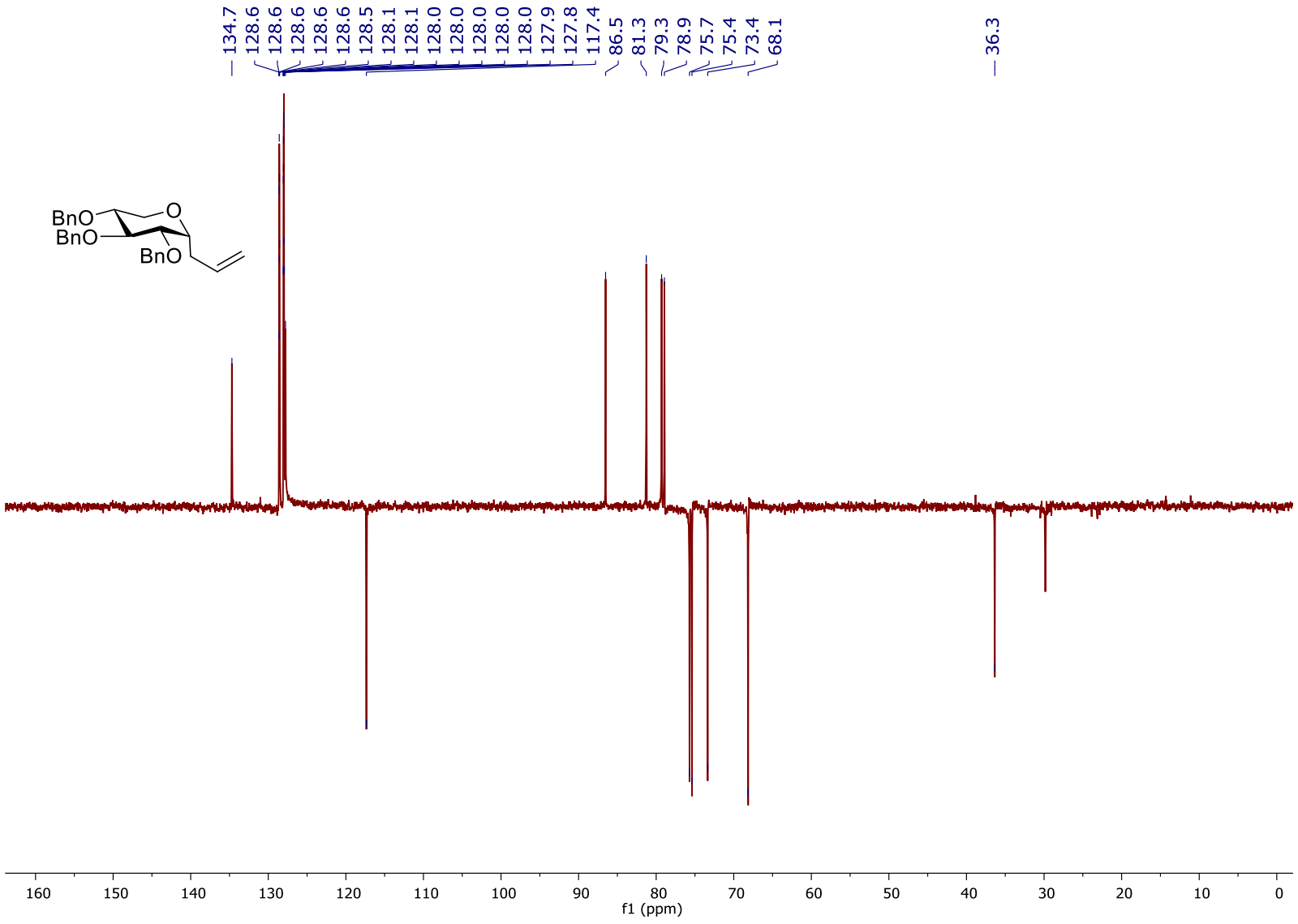
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(7c):**



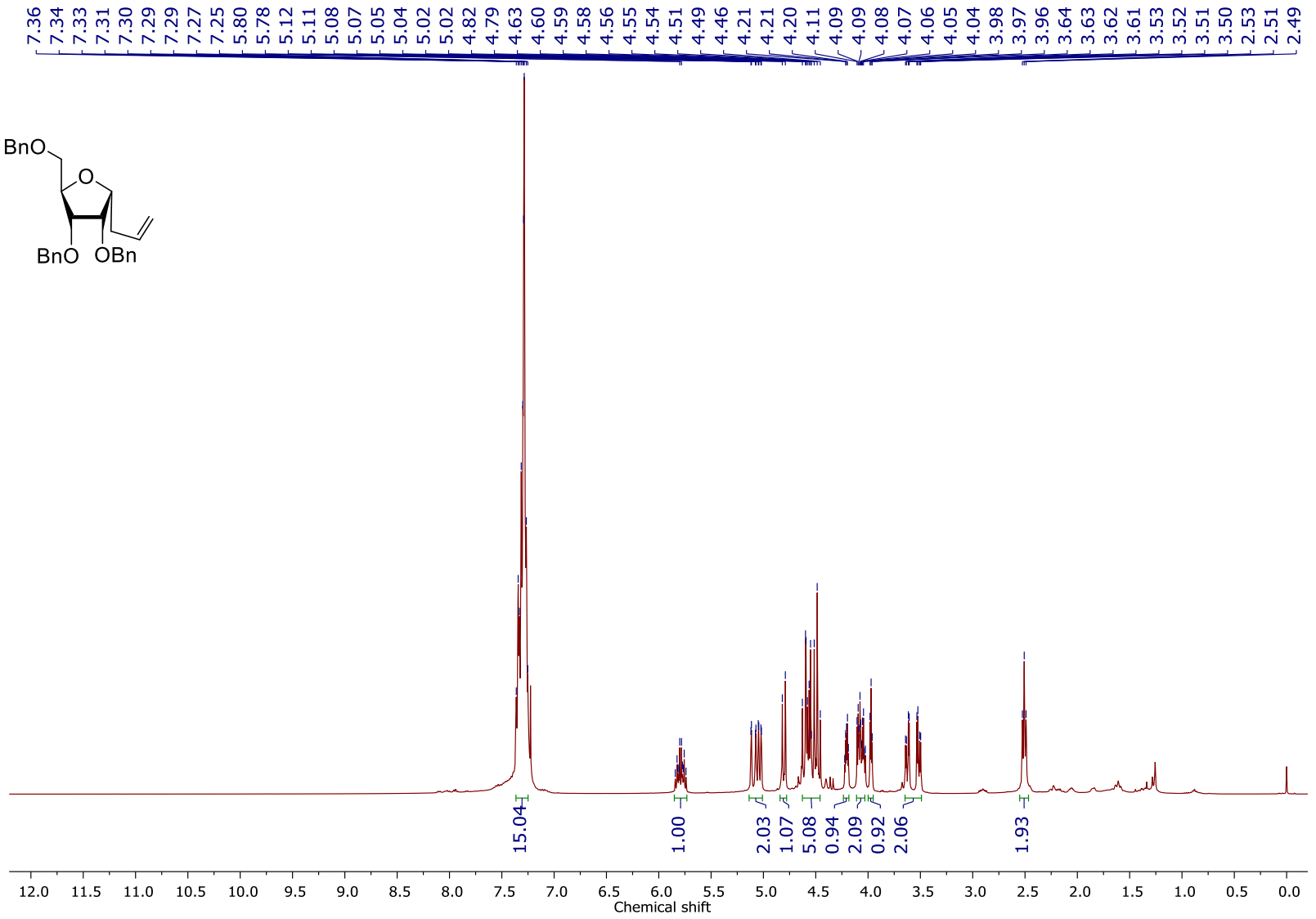
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(7c):**



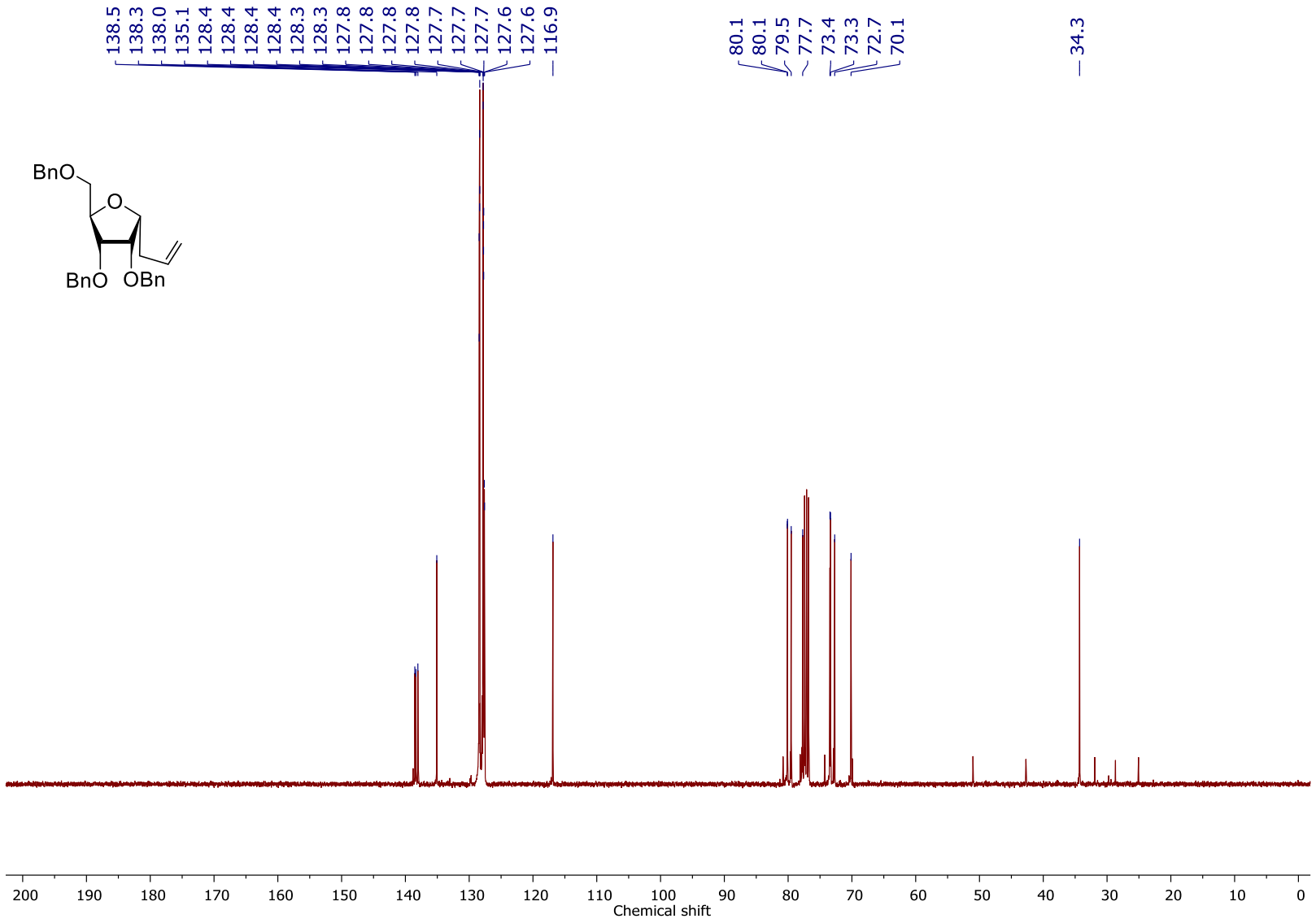
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(7c):**



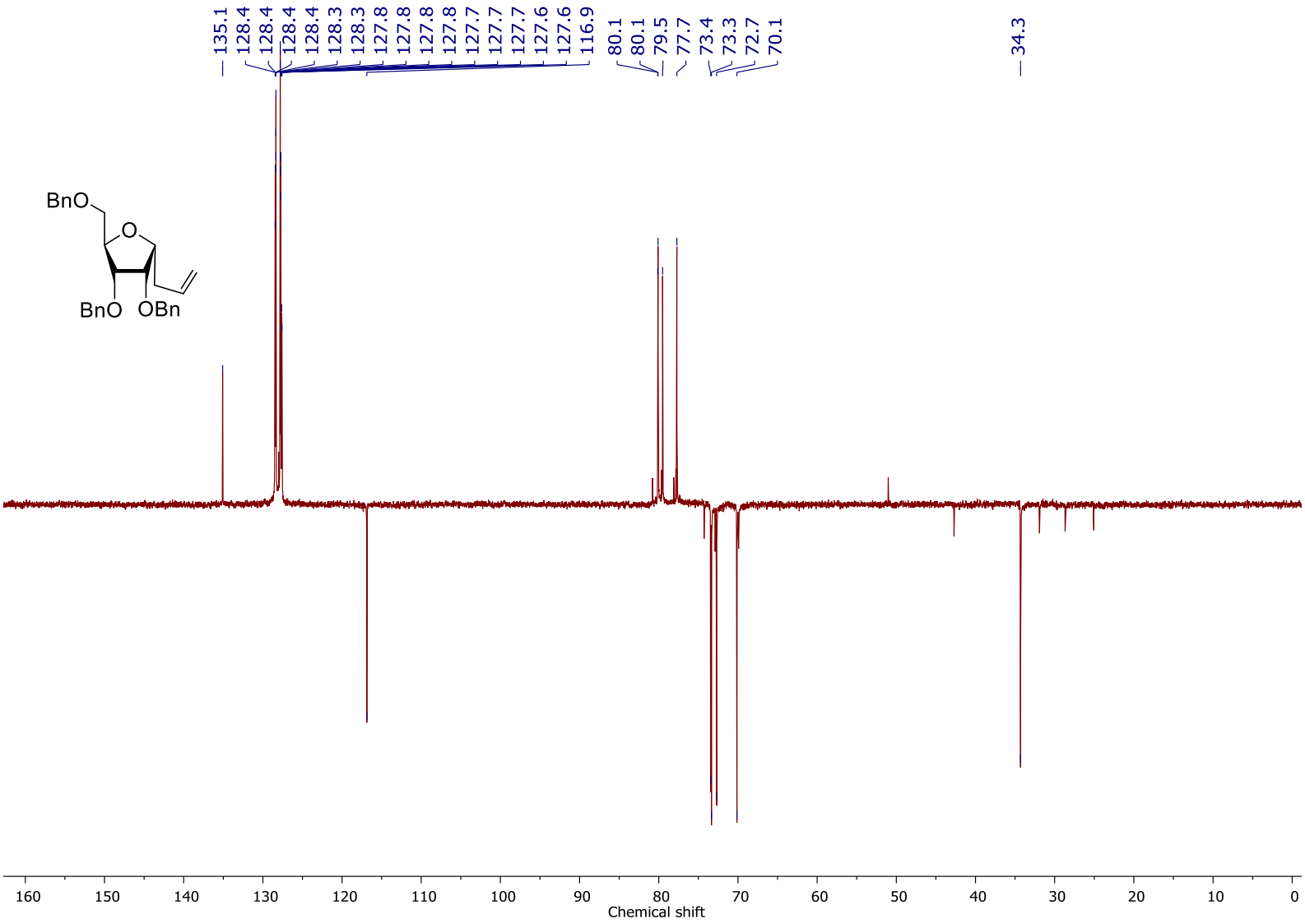
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(7d):**



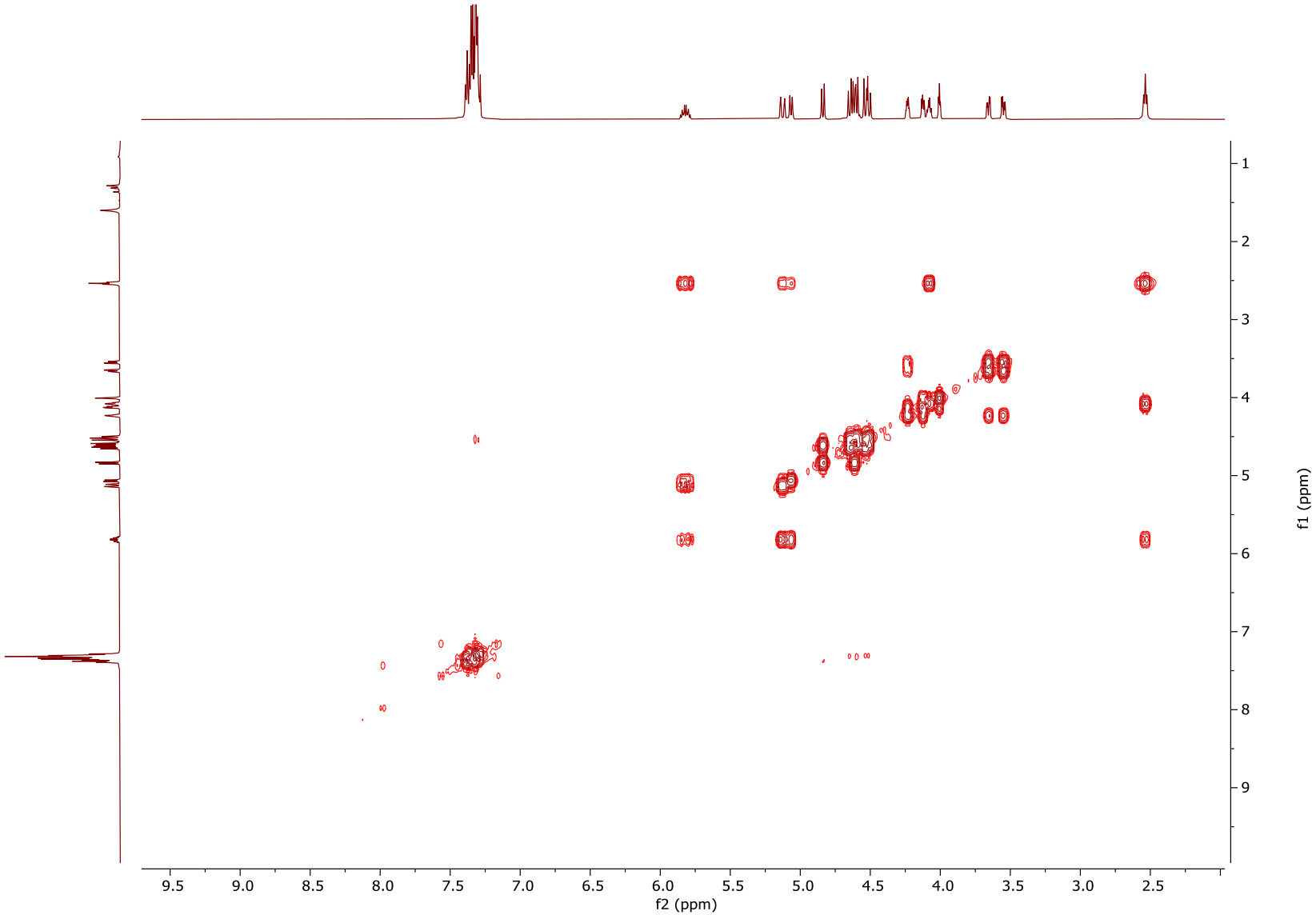
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(7d):**



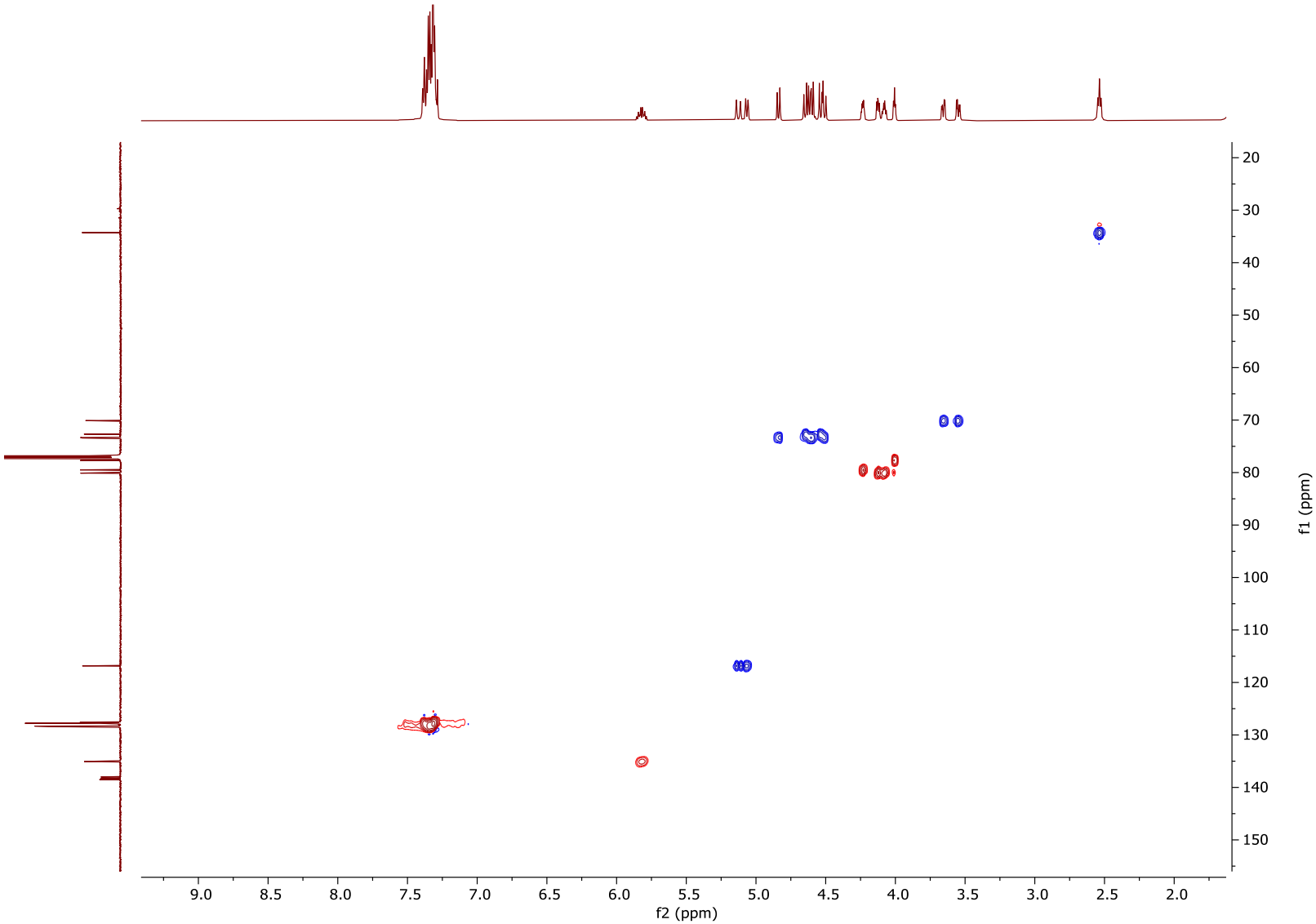
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(7d):**



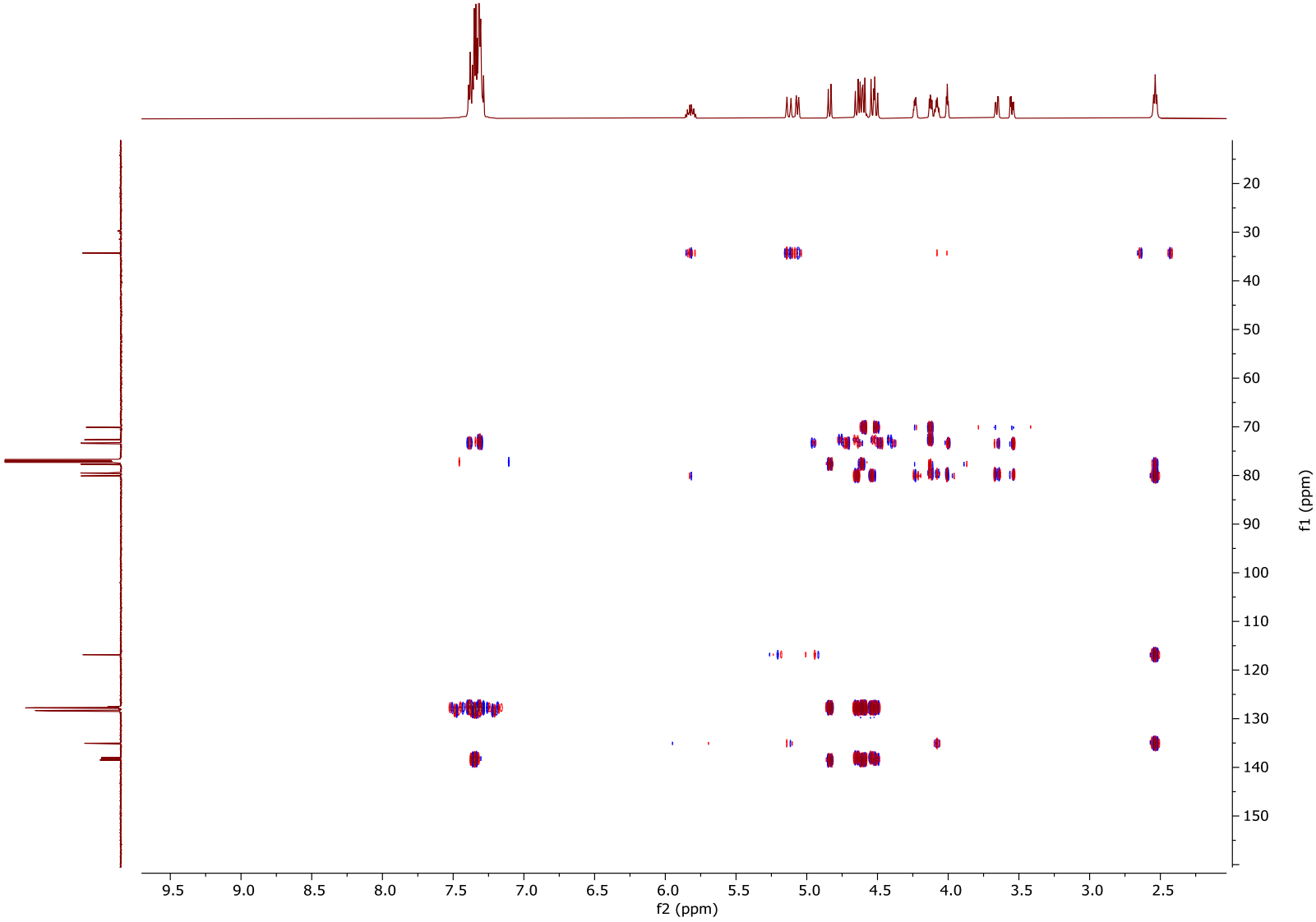
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(7d):**



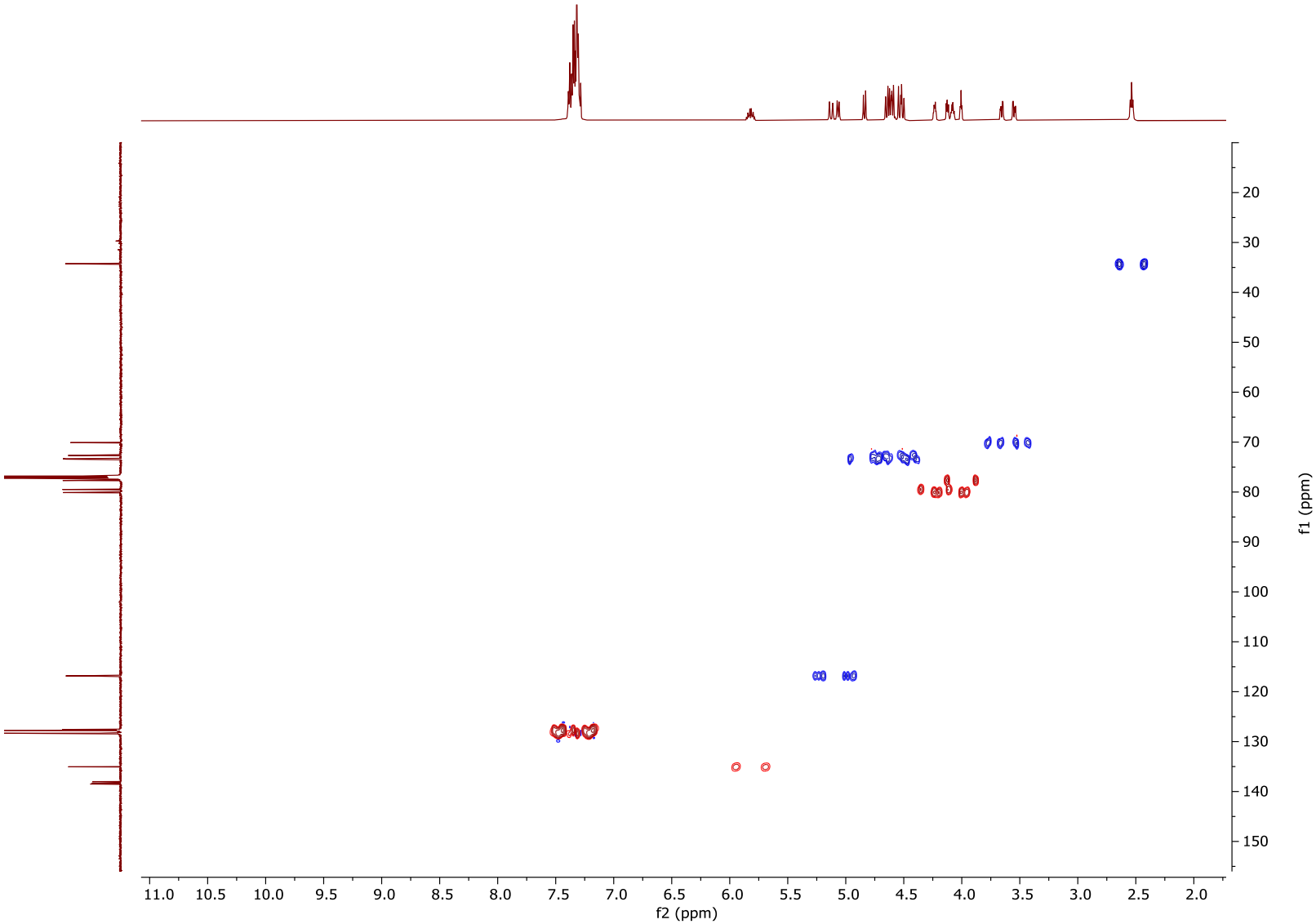
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(7d):**



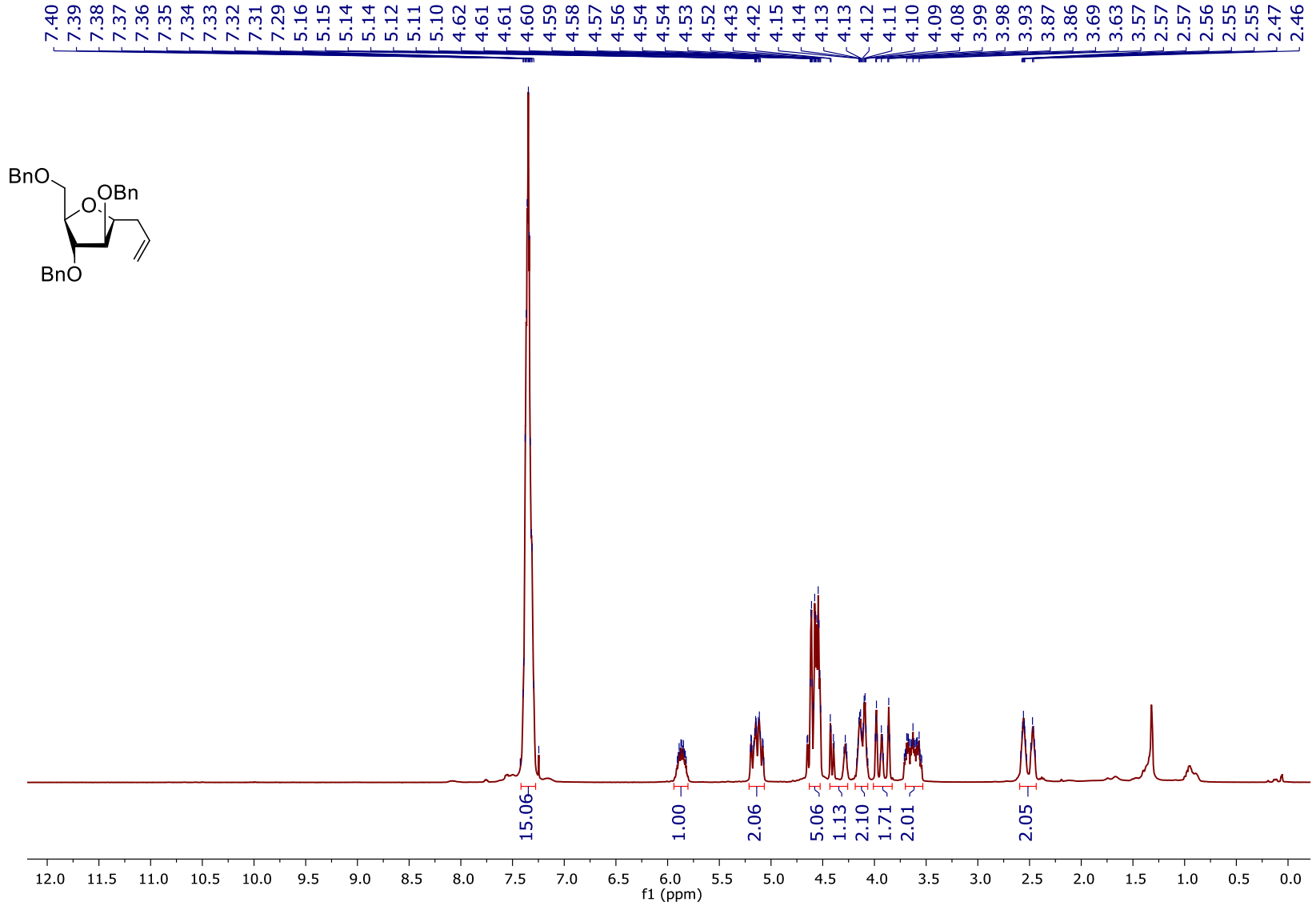
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(7d):**



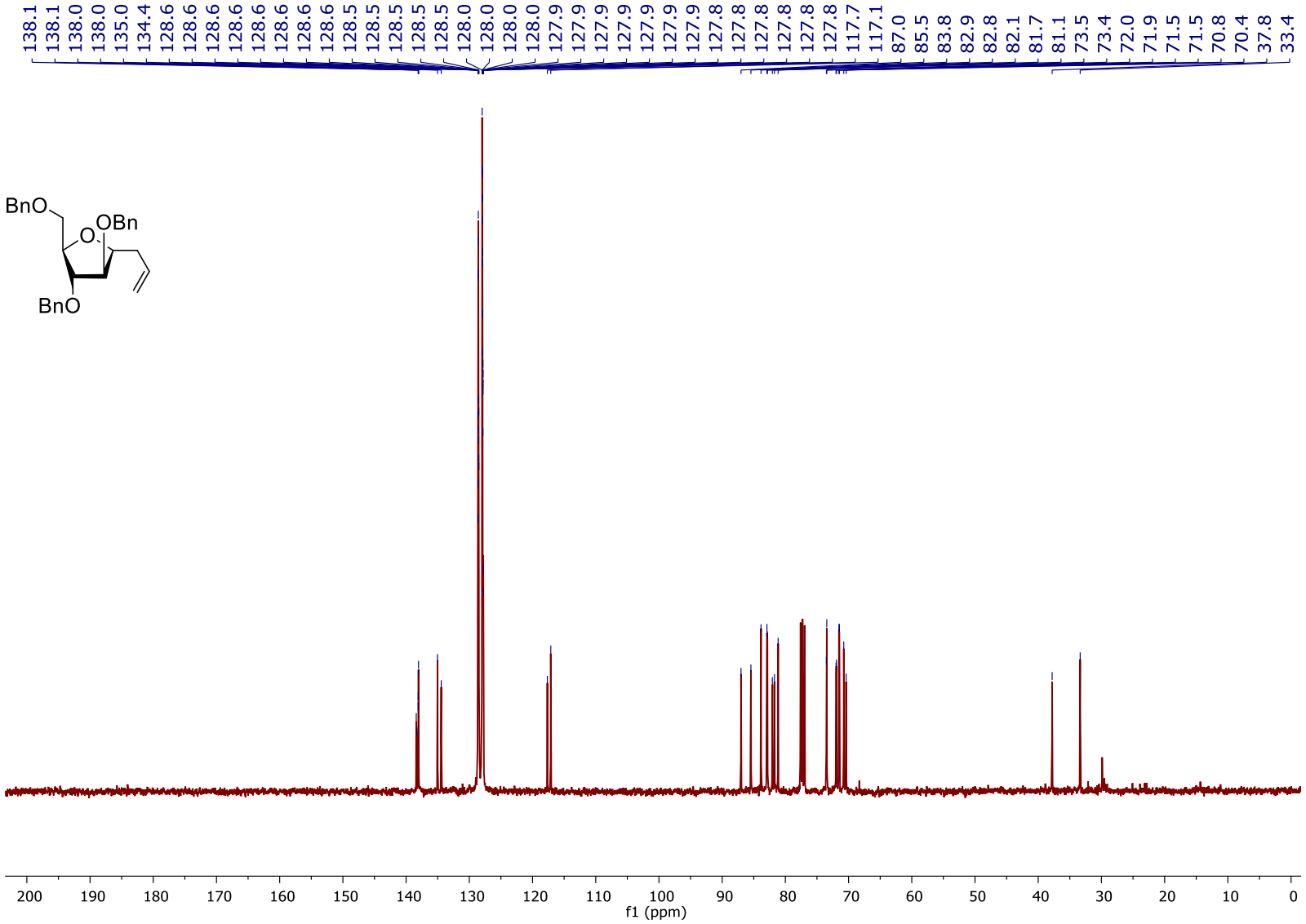
HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(7d):**



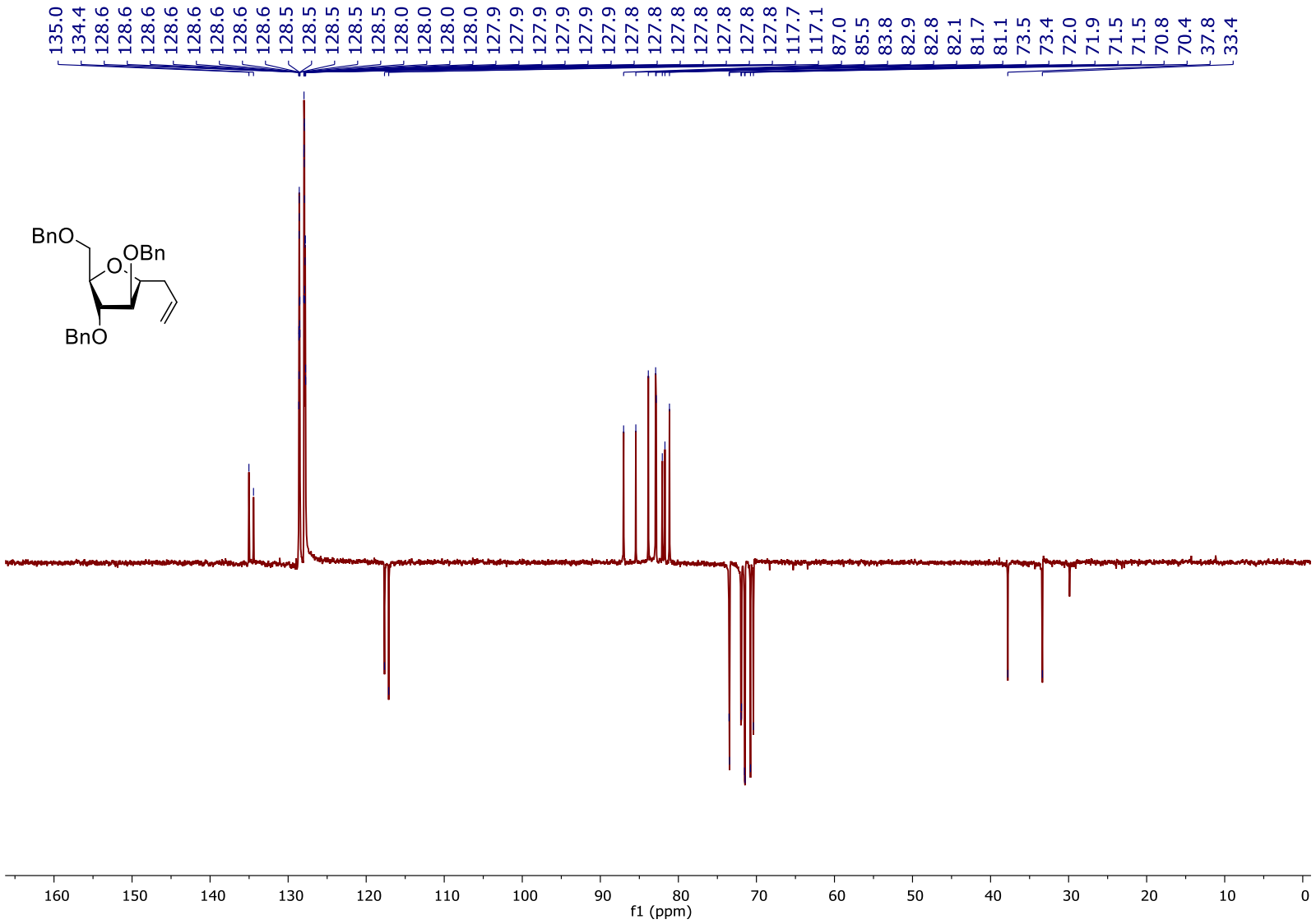
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside **(7e):**



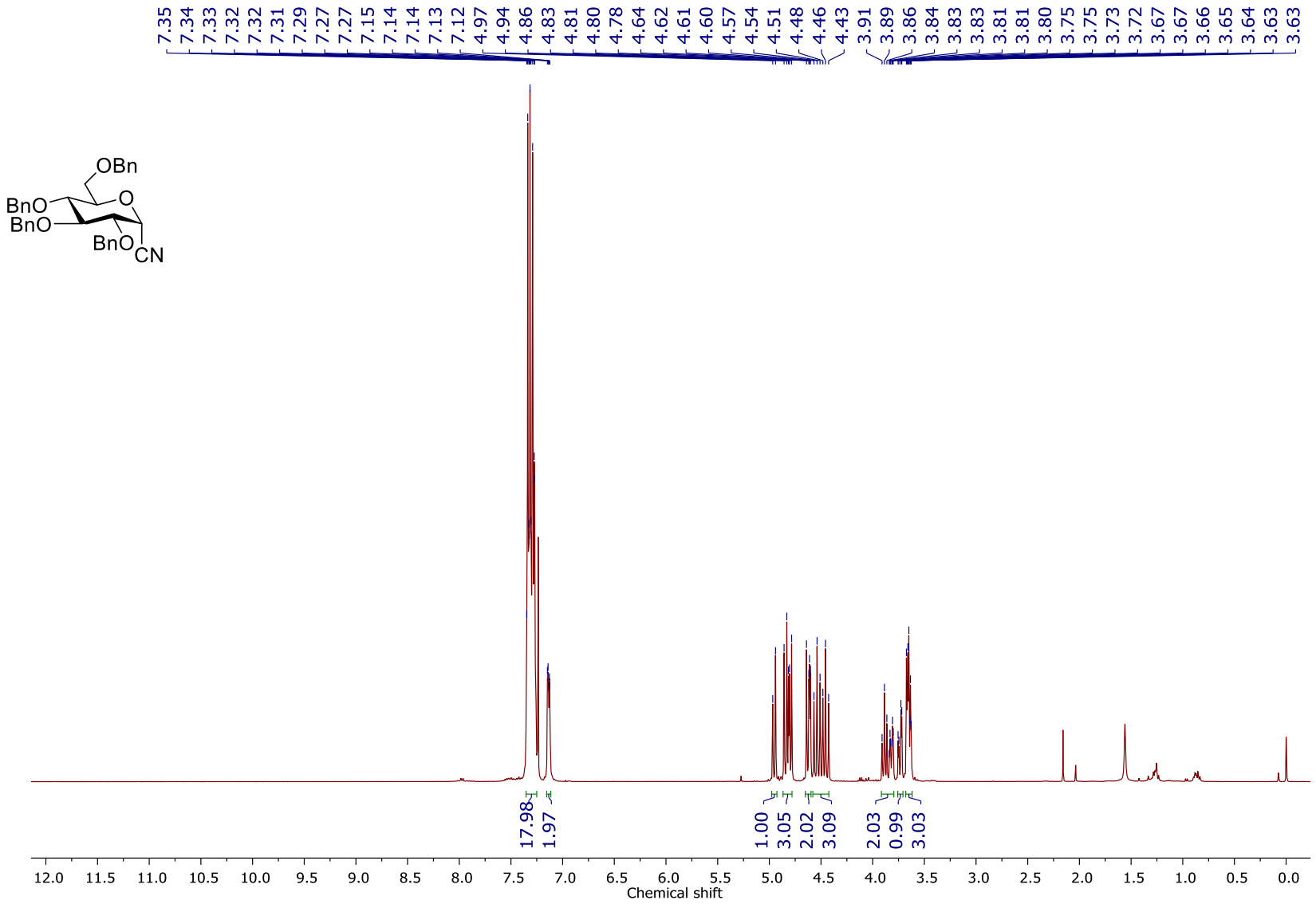
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside **(7e):**



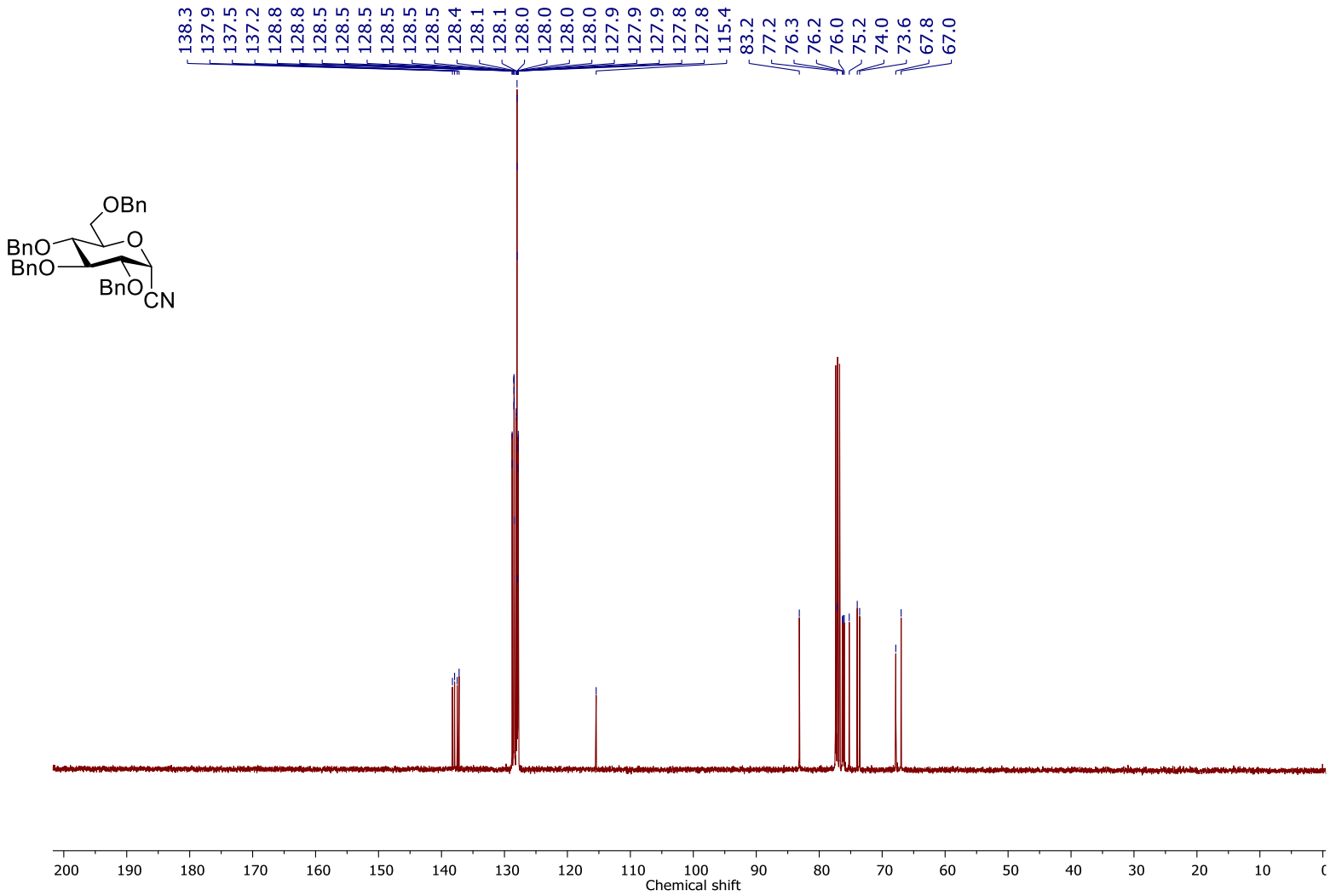
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Allyl-1-*deoxy* 2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside **(7e):**



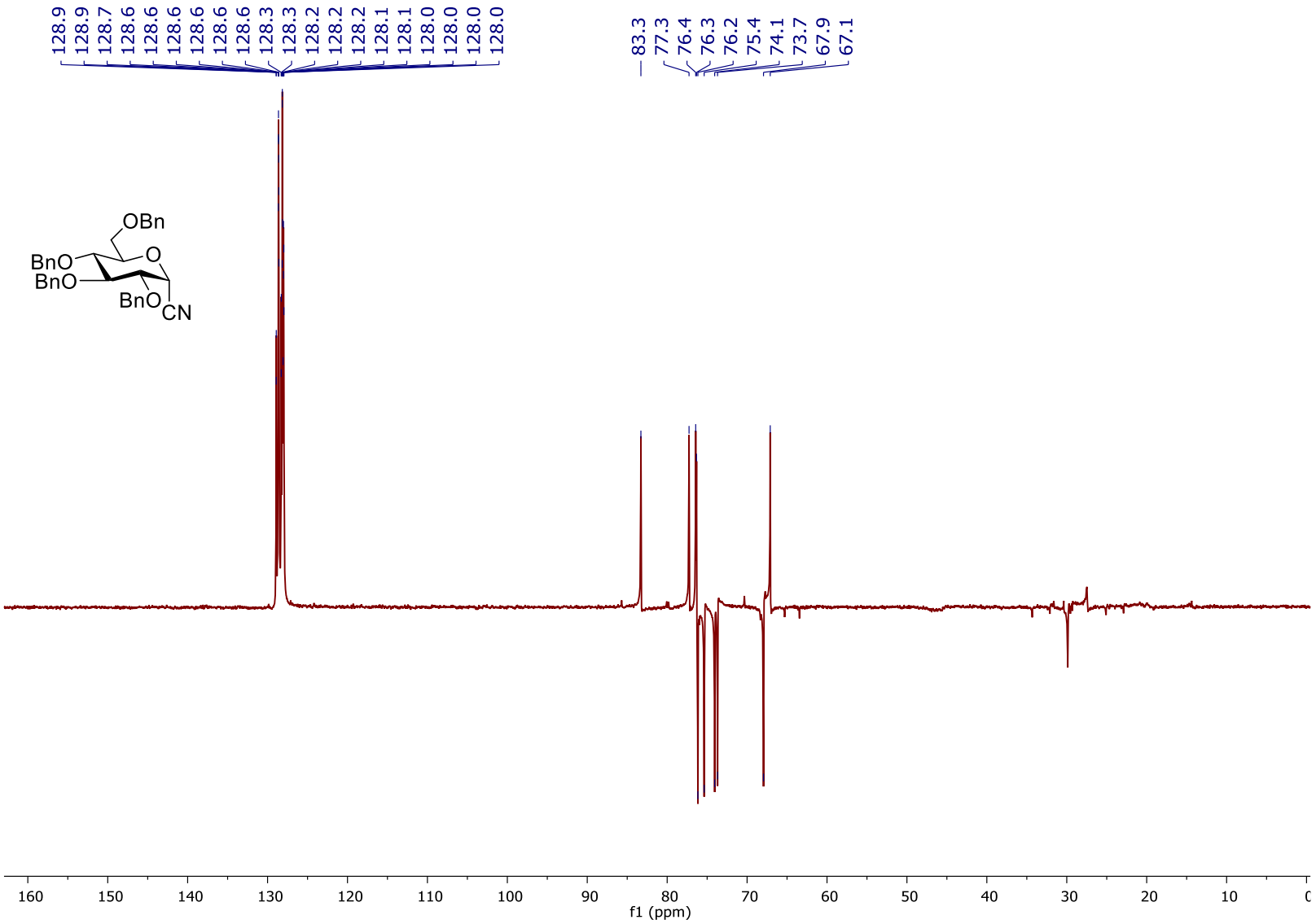
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(8a):**



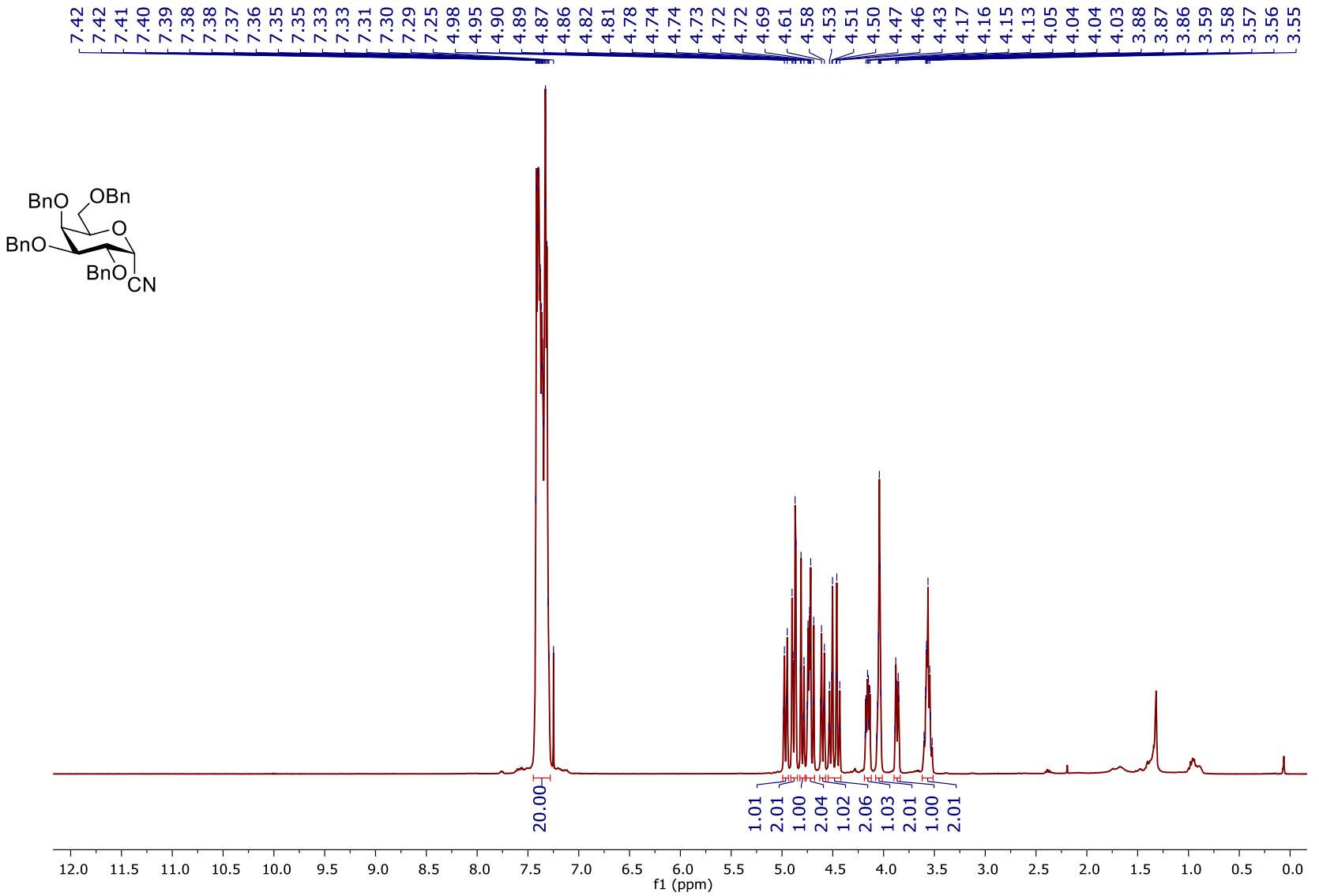
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(8a):**



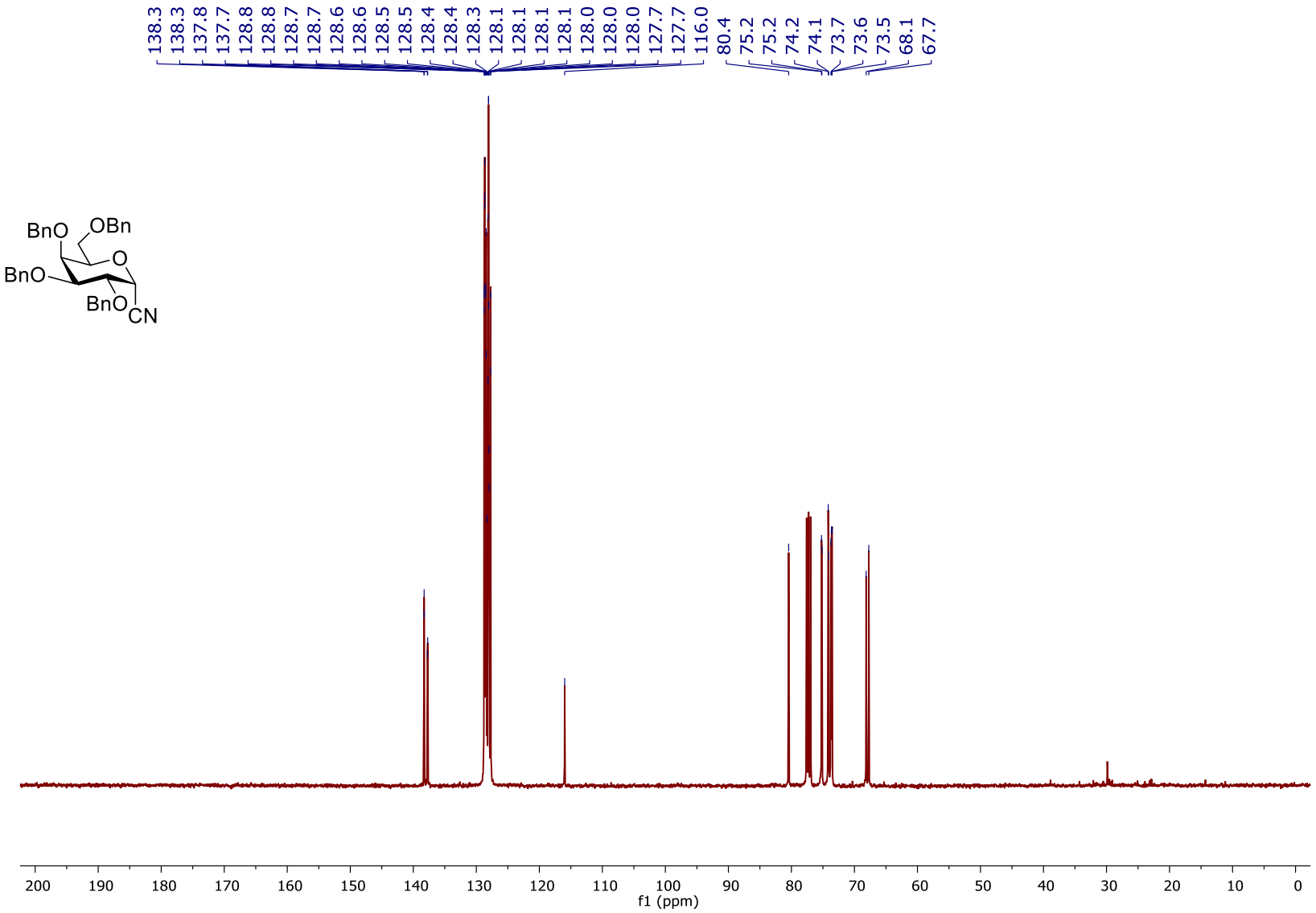
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(8a):**



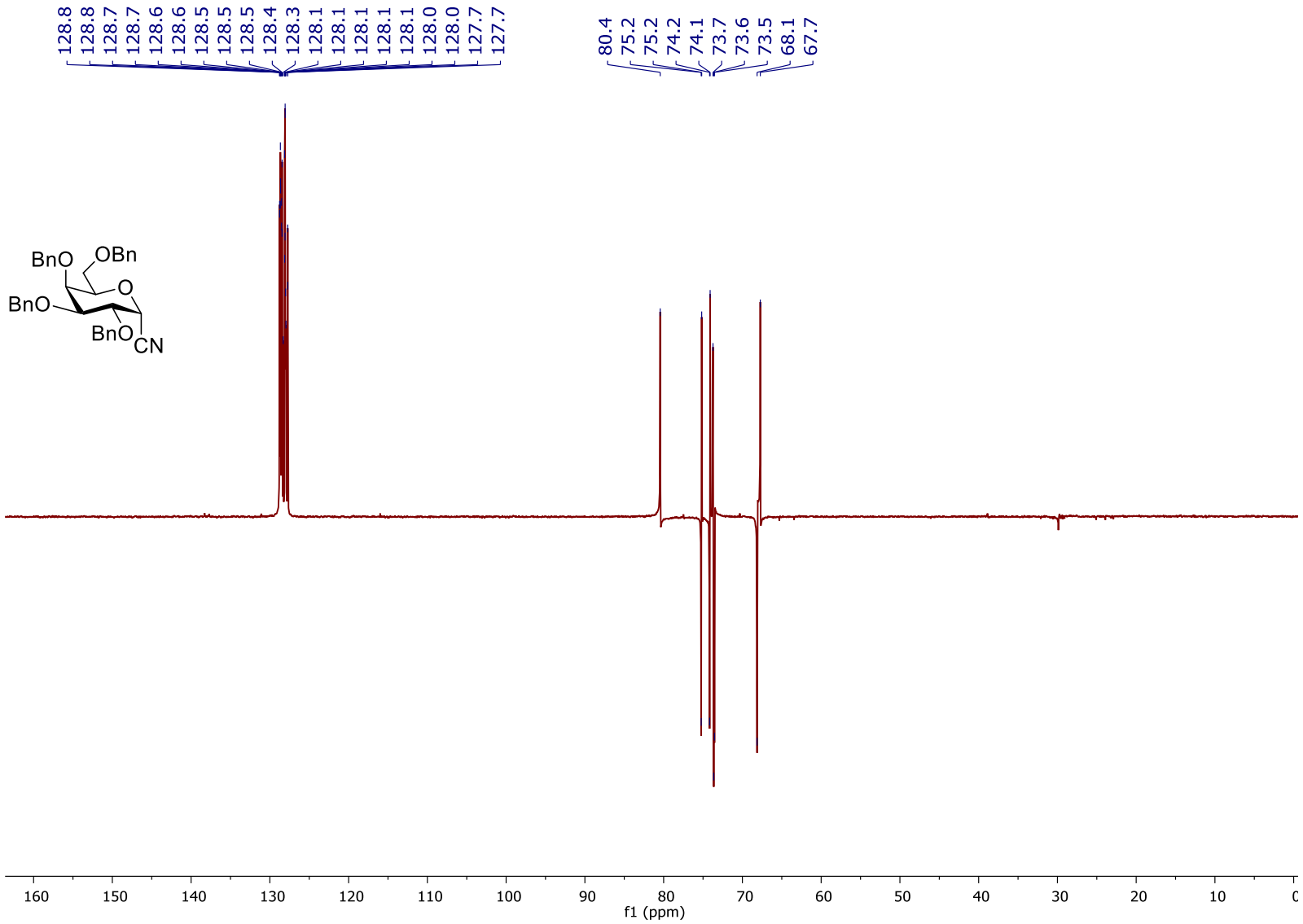
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(8b):**



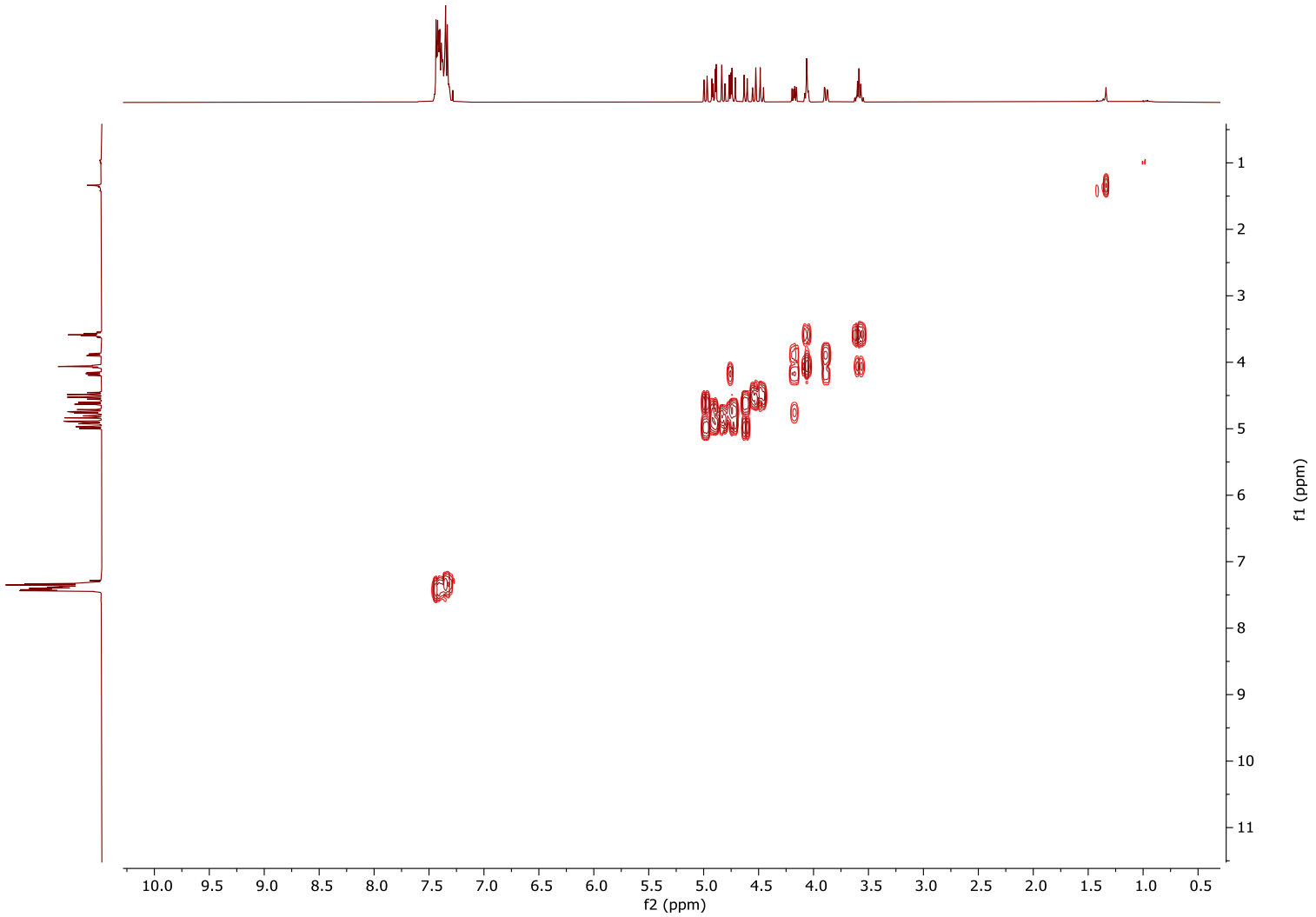
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(8b):**



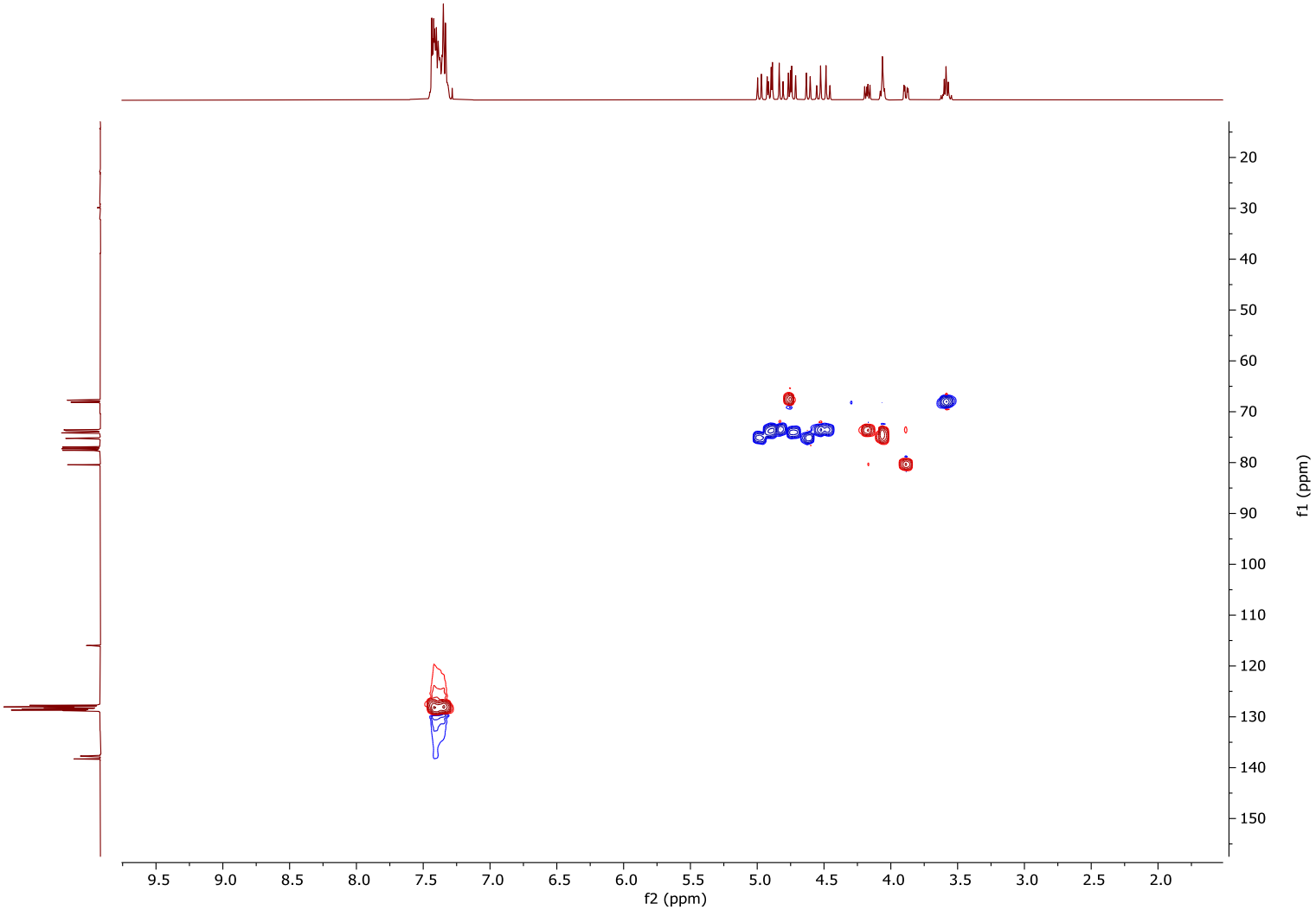
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(8b):**



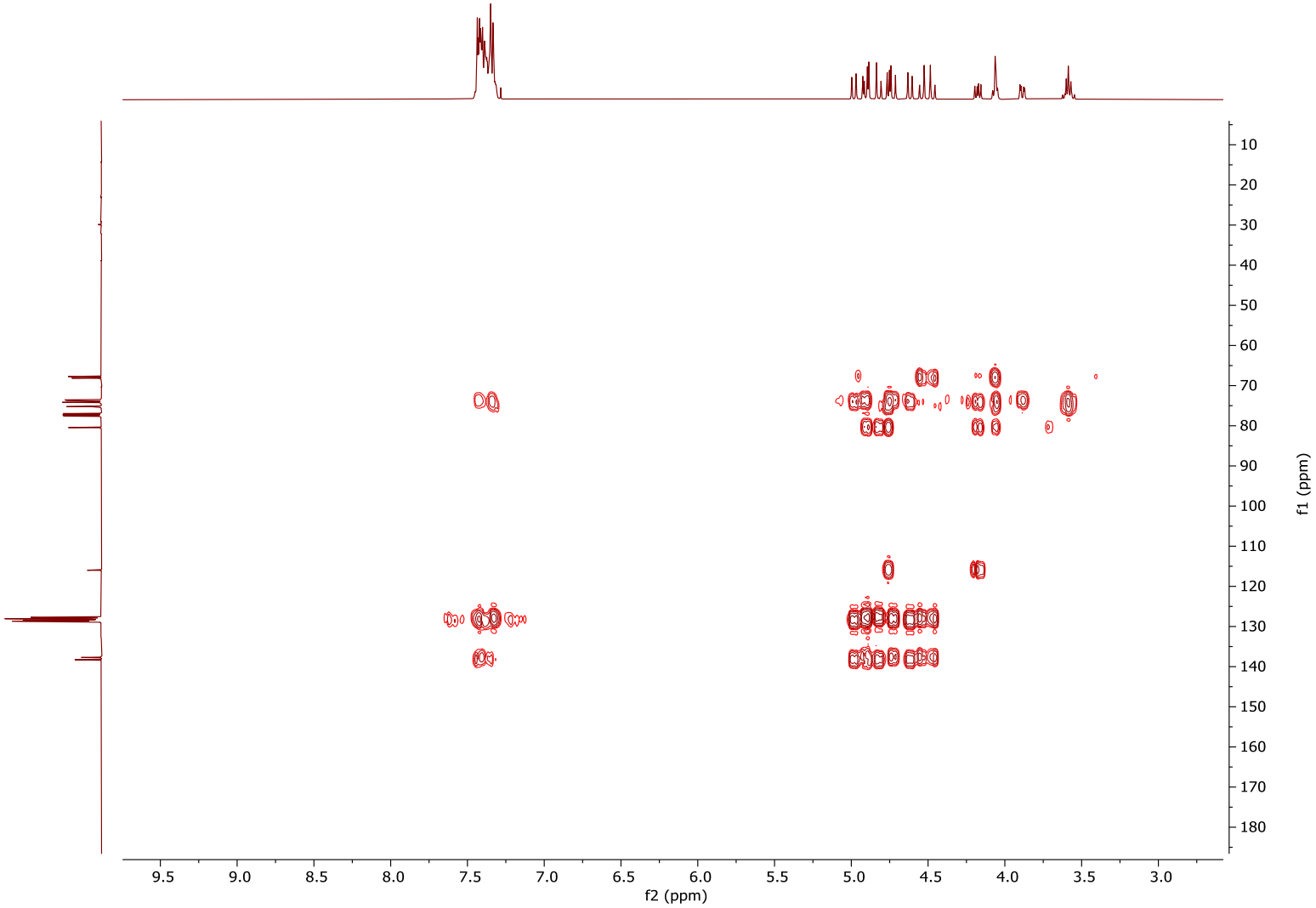
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(8b):**



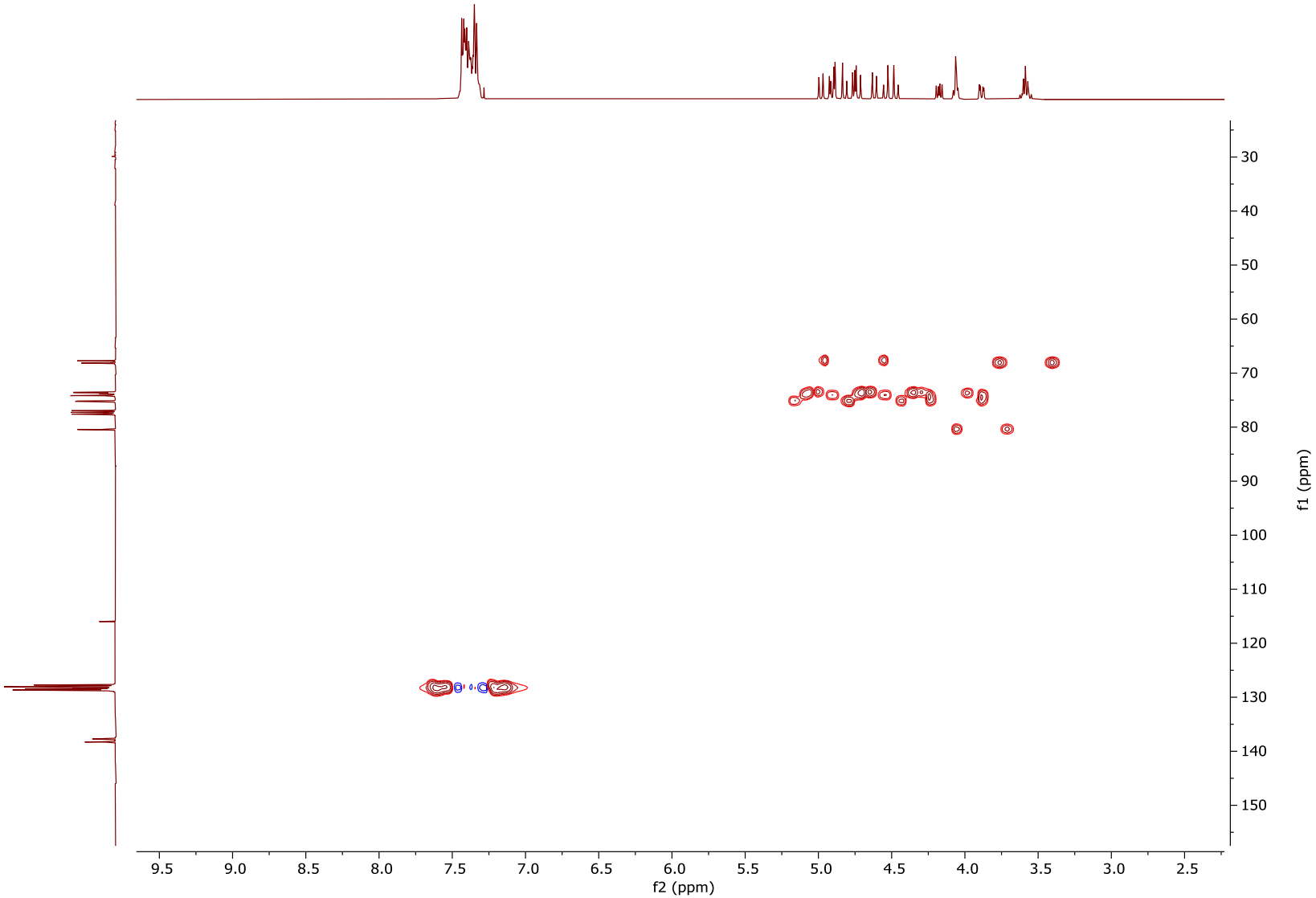
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(8b):**



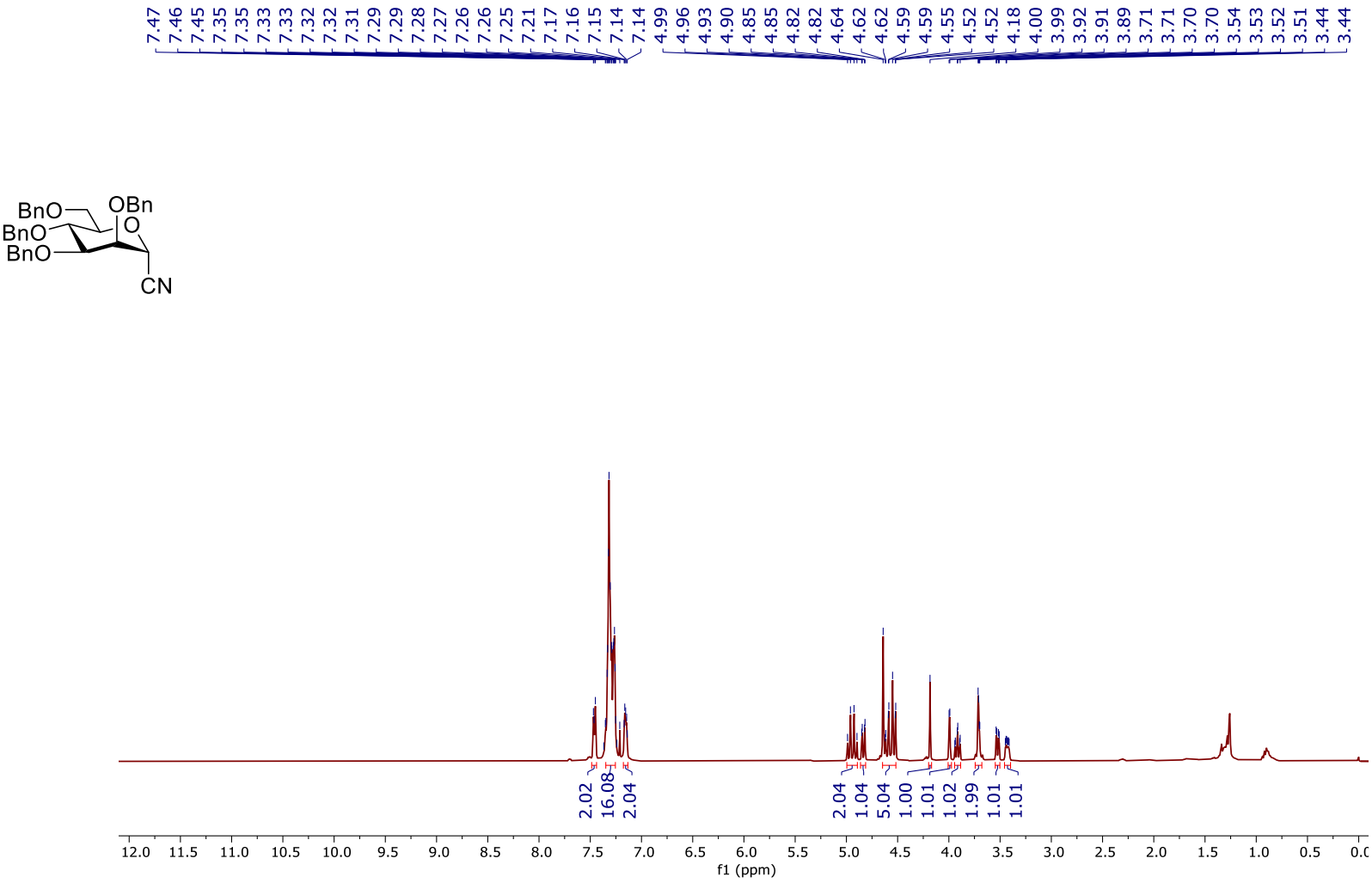
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(8b):**



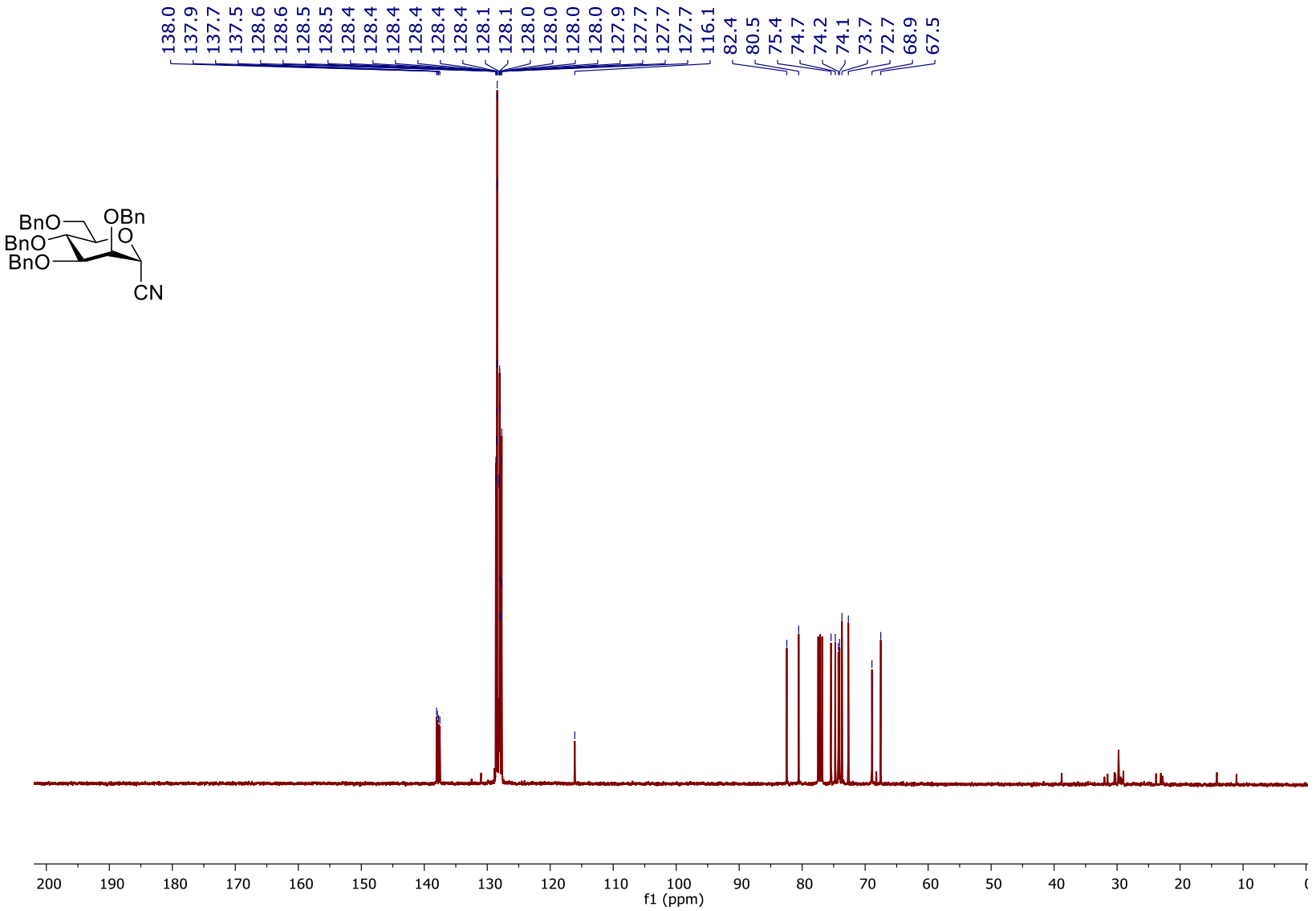
HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(8b):**



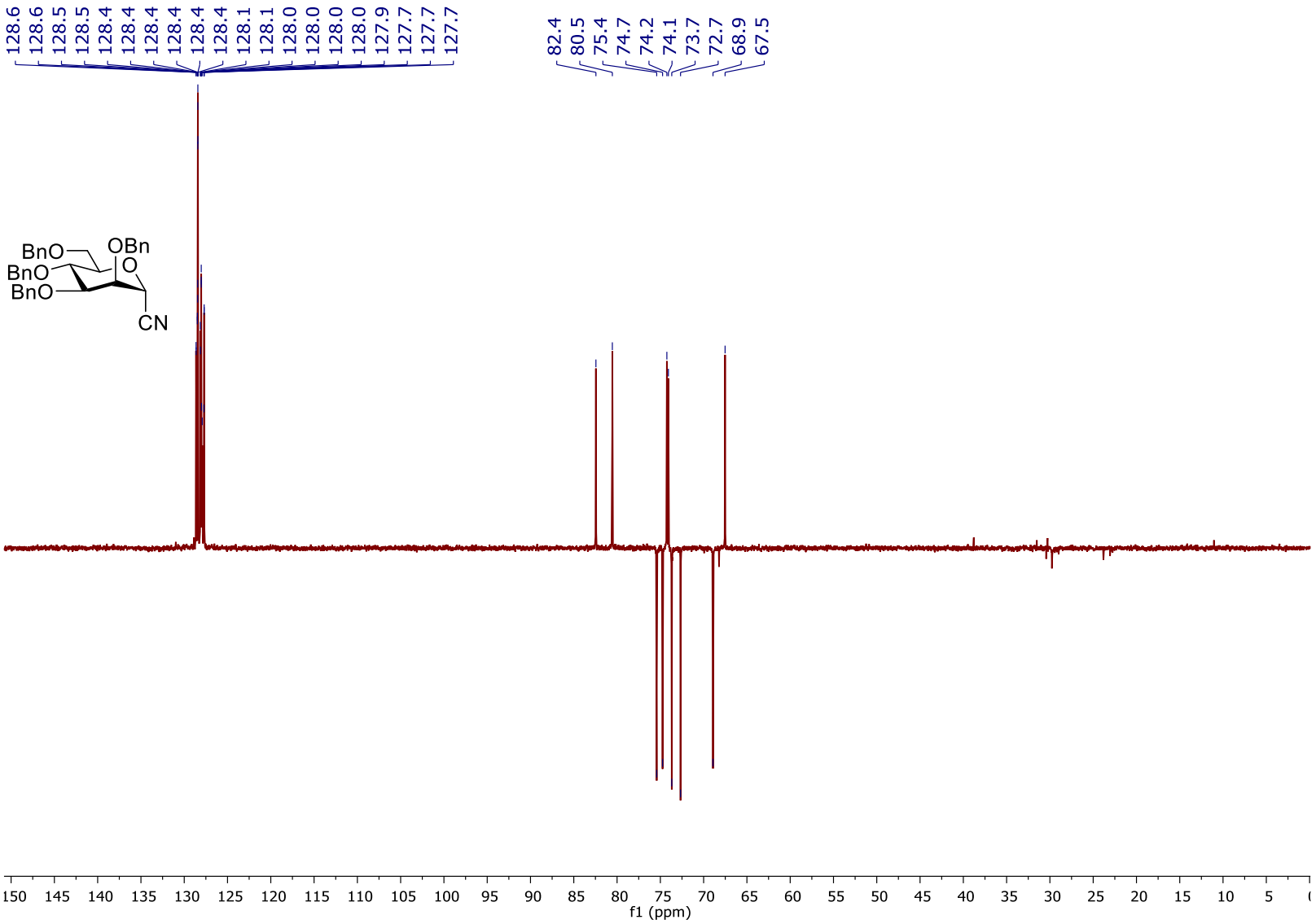
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **(8c):**



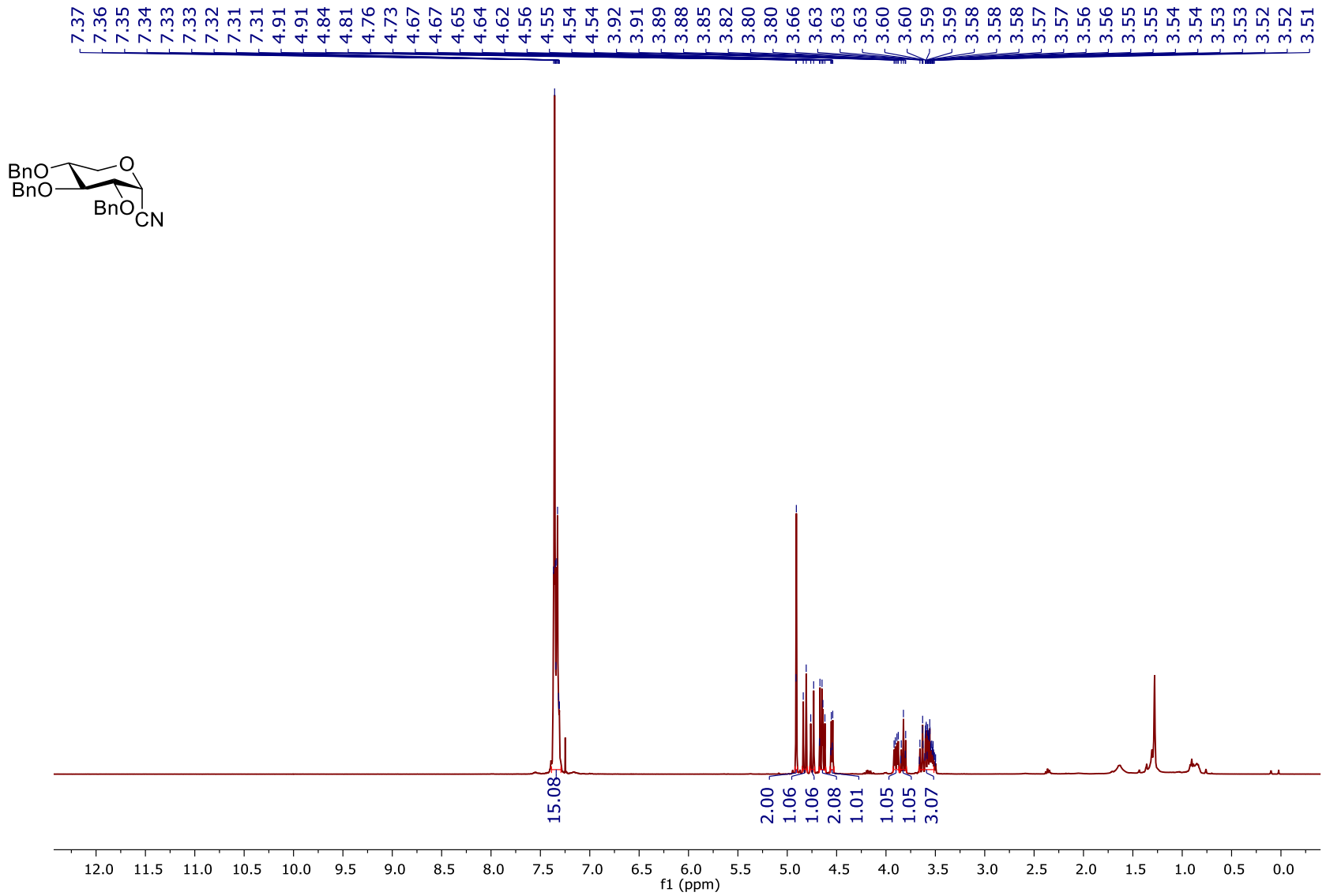
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **(8c):**



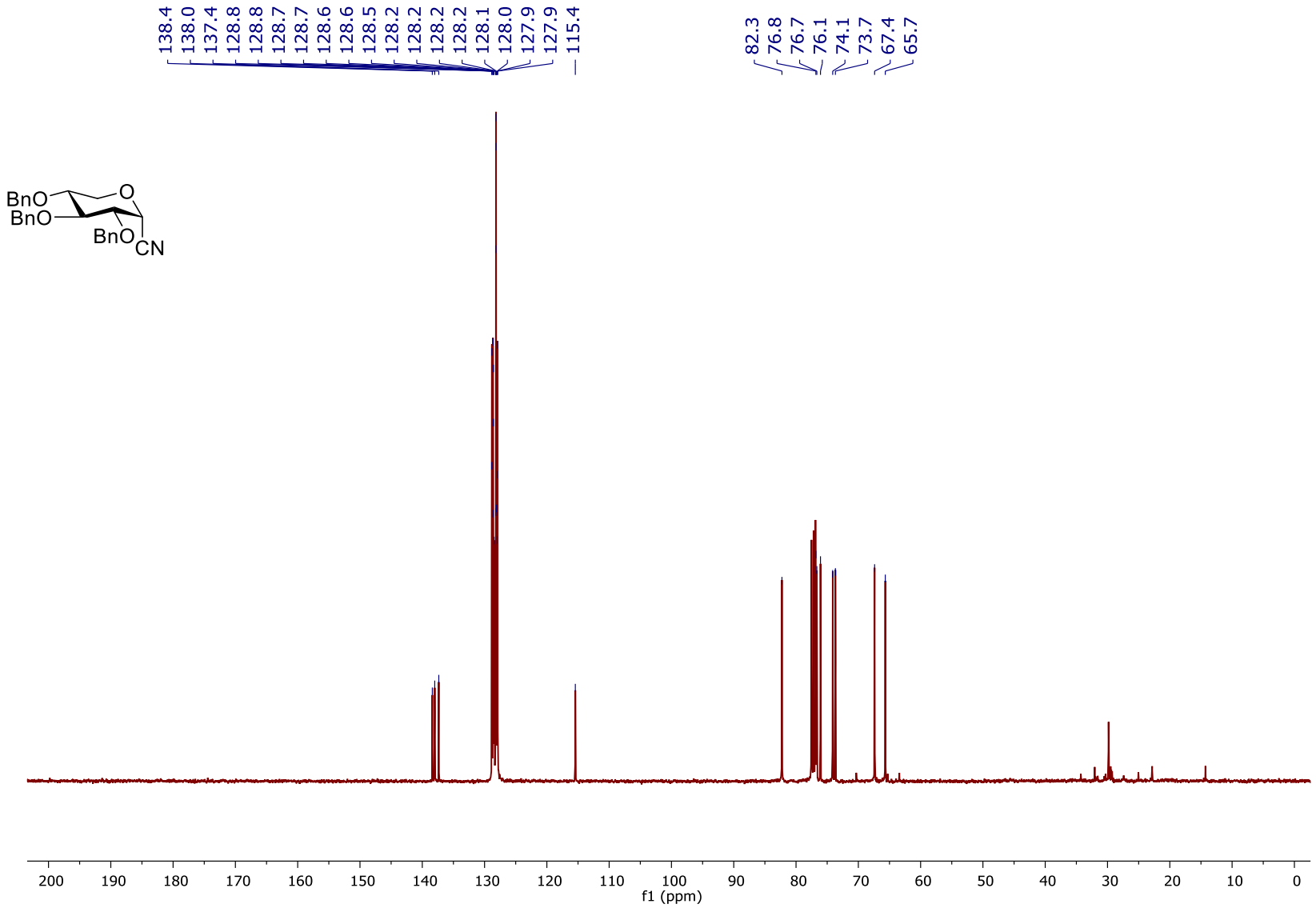
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside **(8c):**



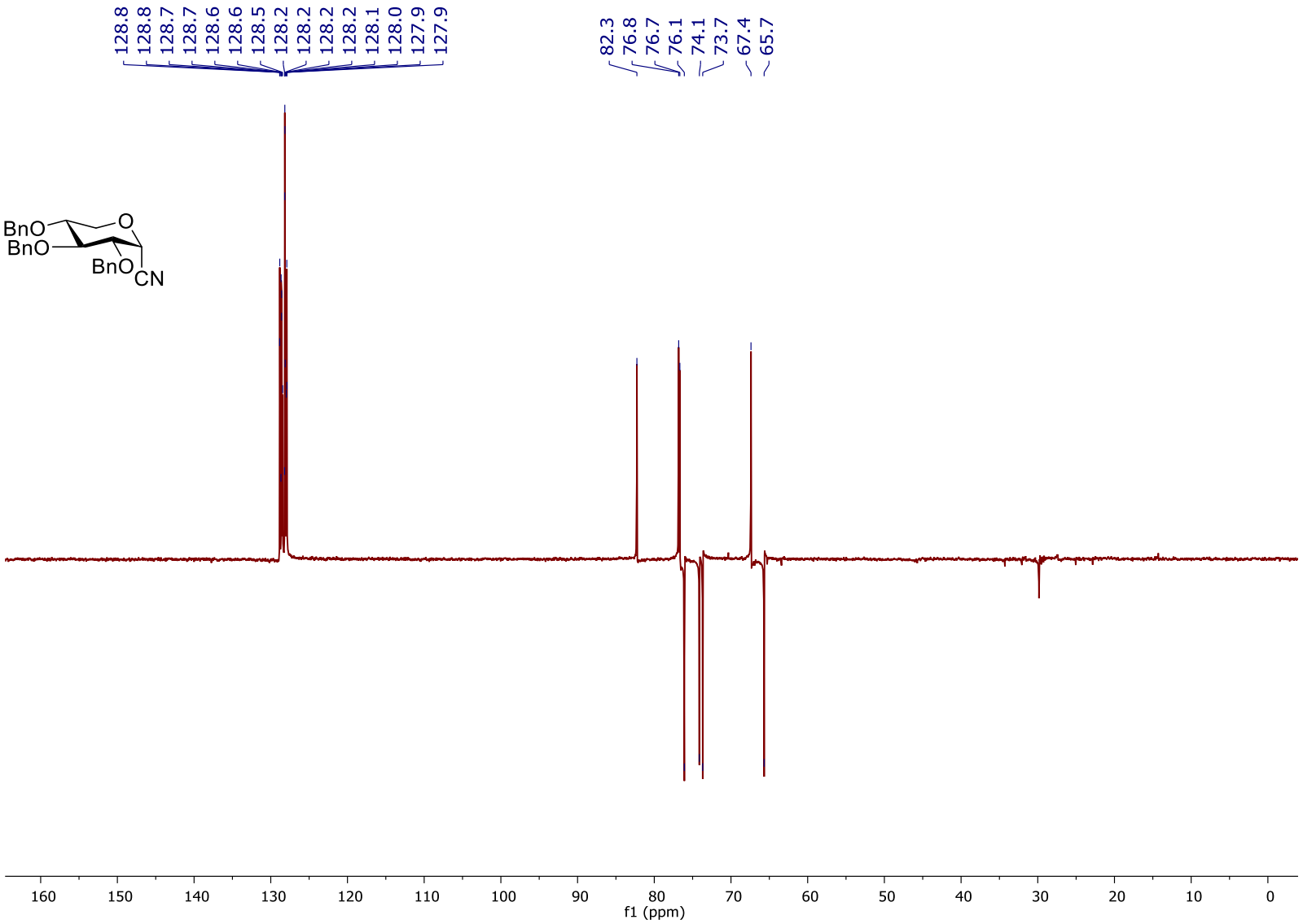
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(8d):**



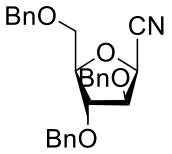
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(8d):**

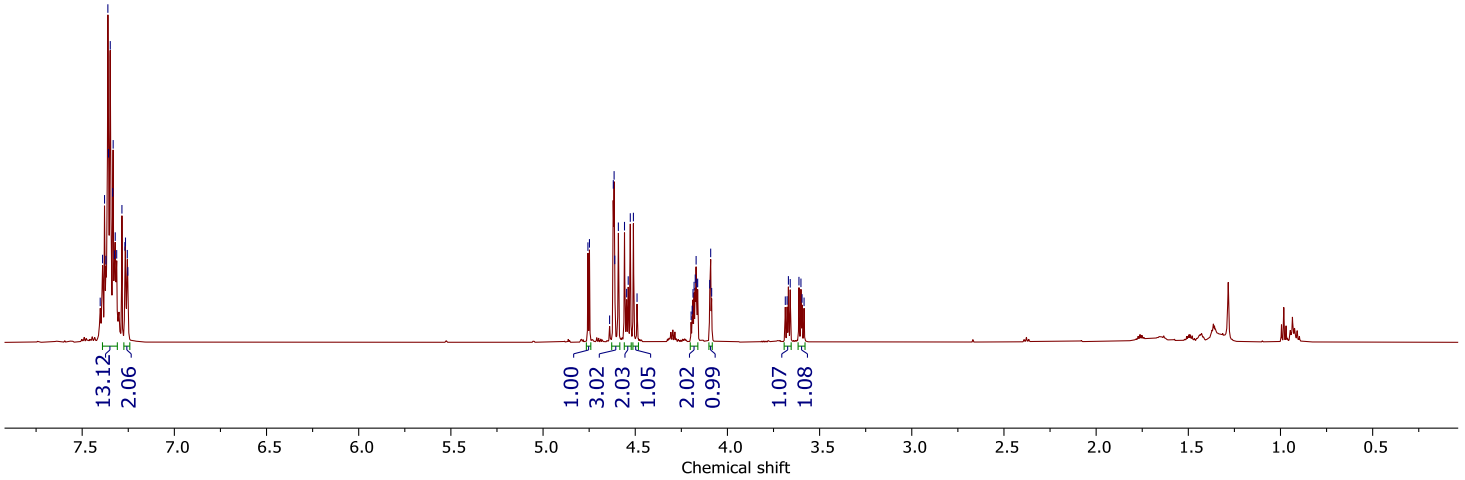


DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(8d):**

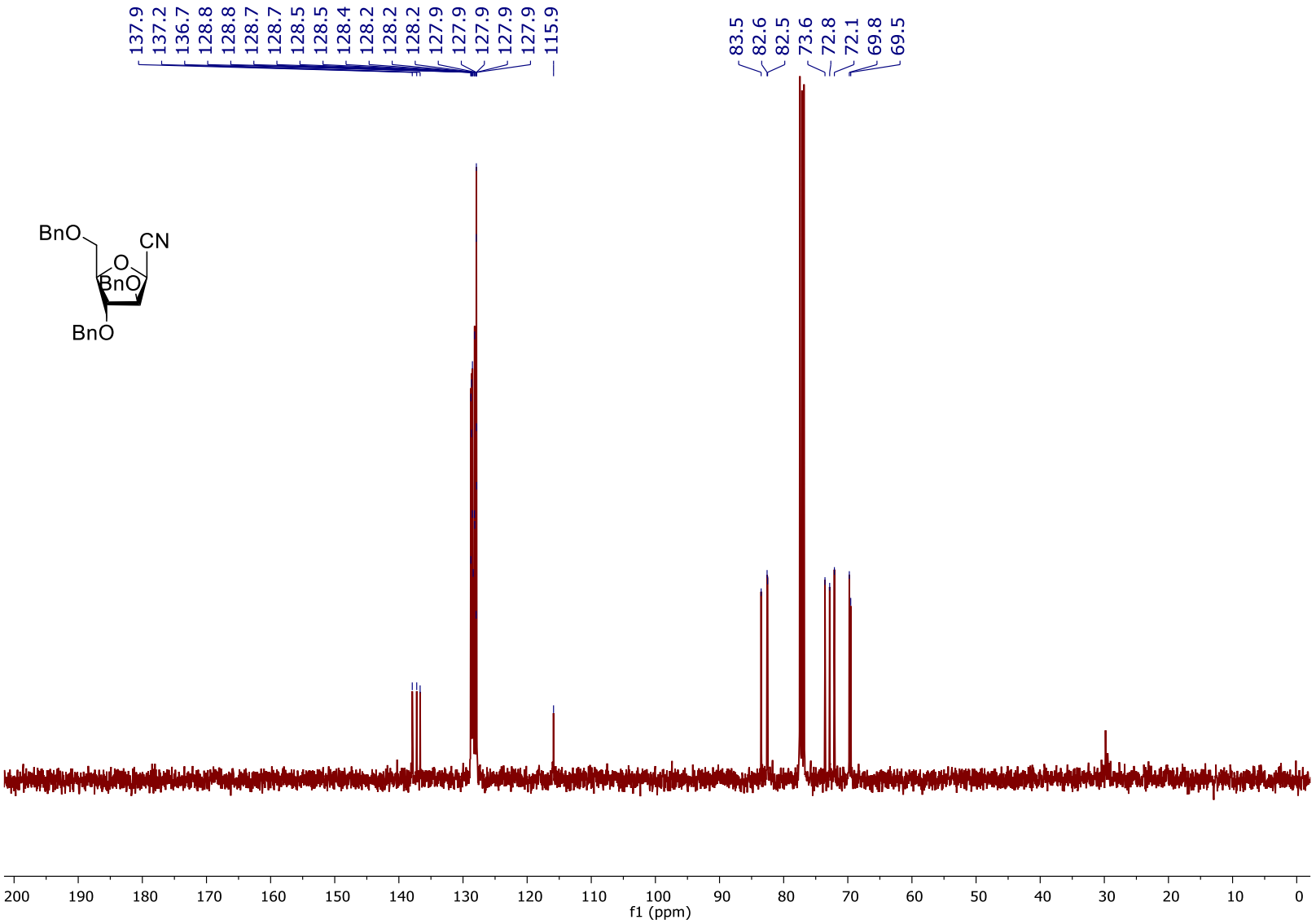


^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl β-D-arabinofuranoside **(8e):**

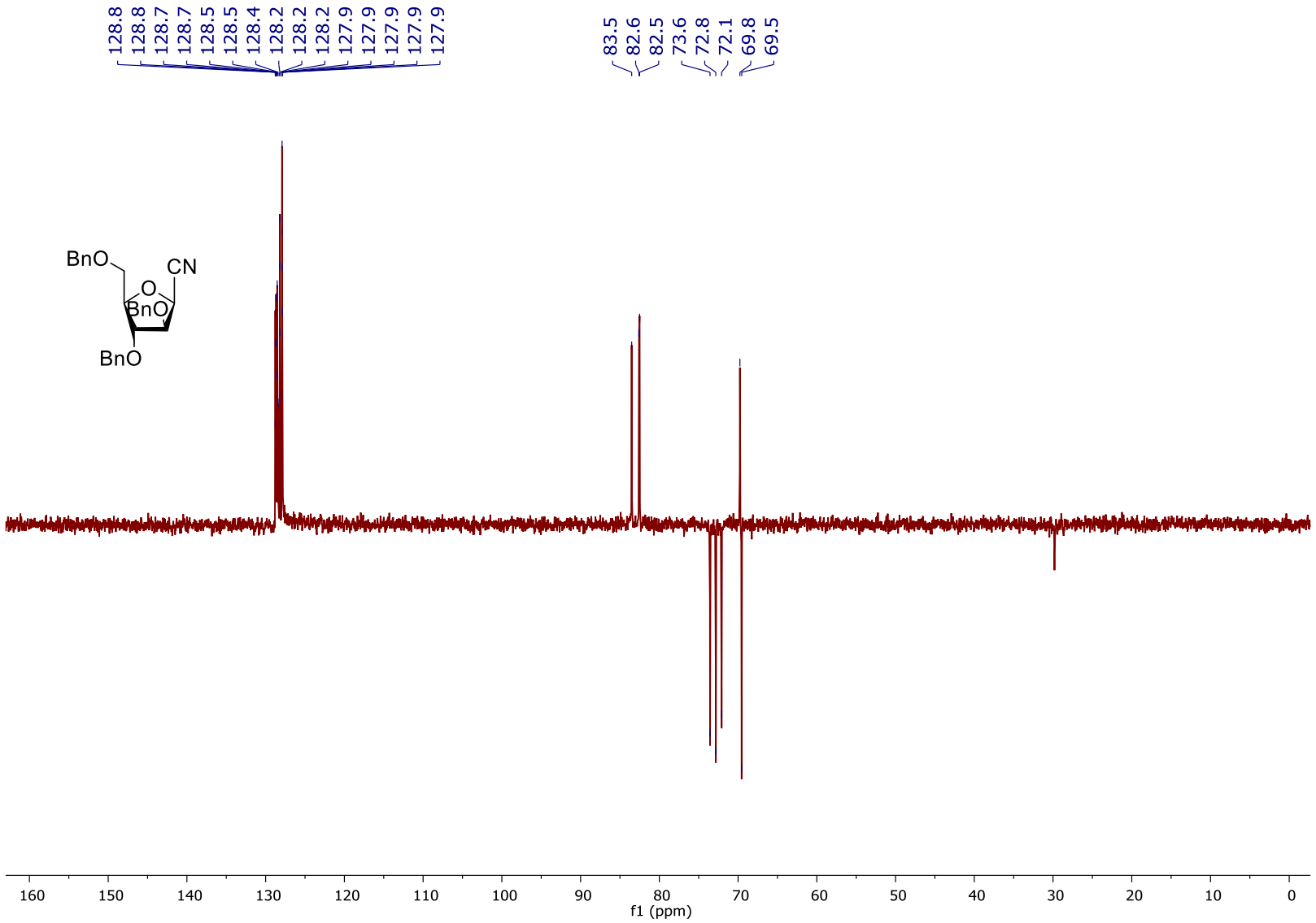




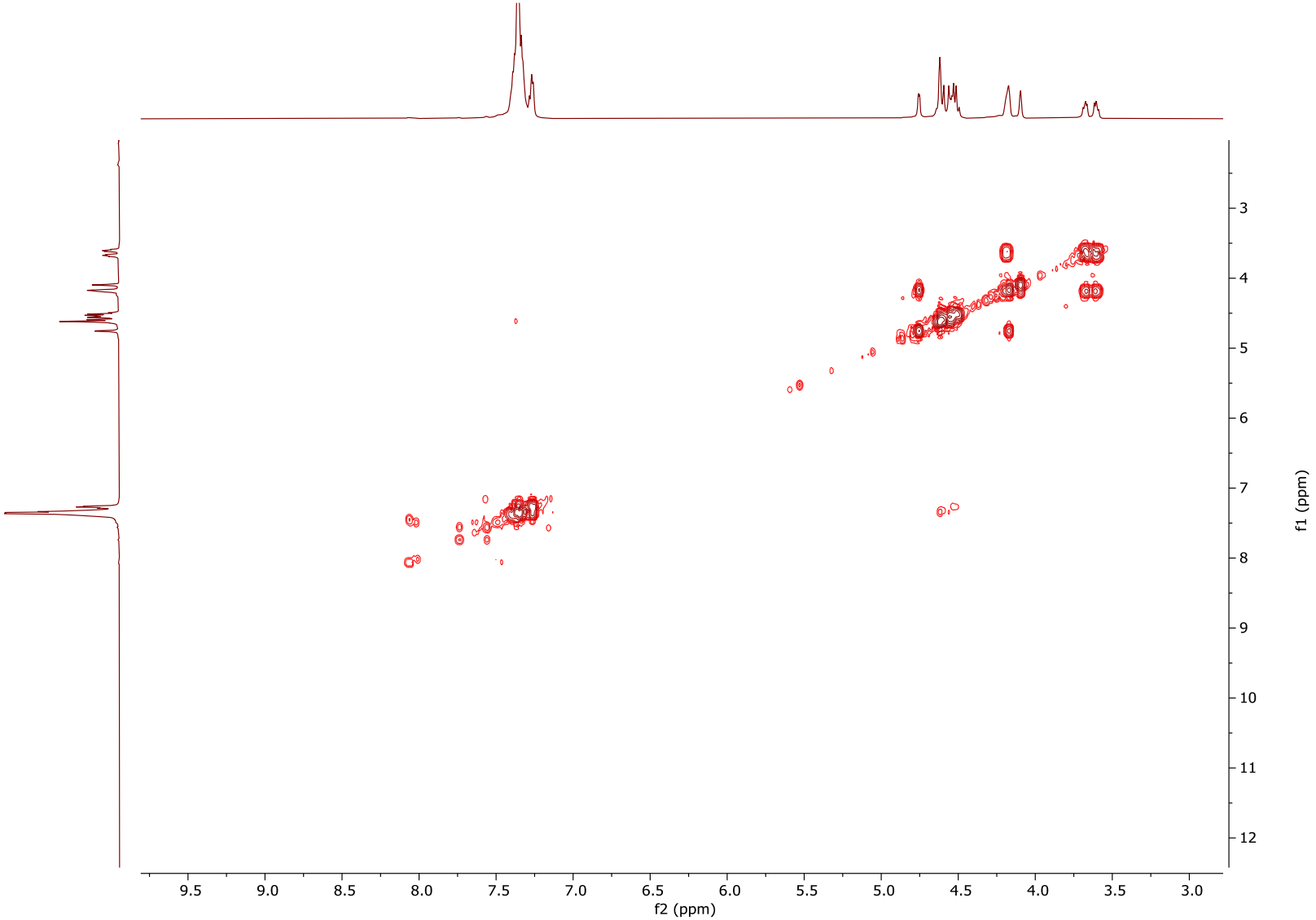
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl β-D-arabinofuranoside **(8e):**



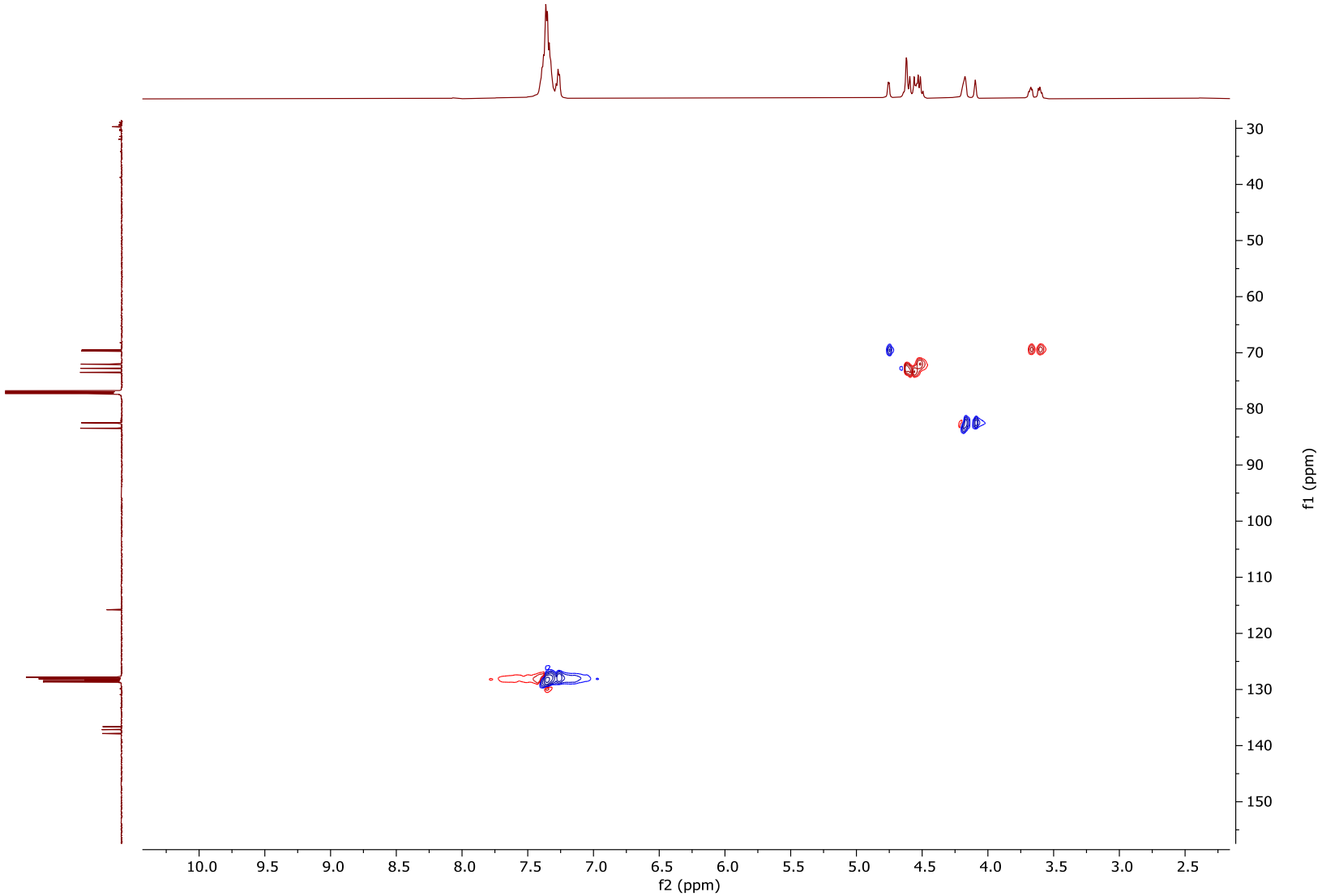
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl β-D-arabinofuranoside **(8e):**



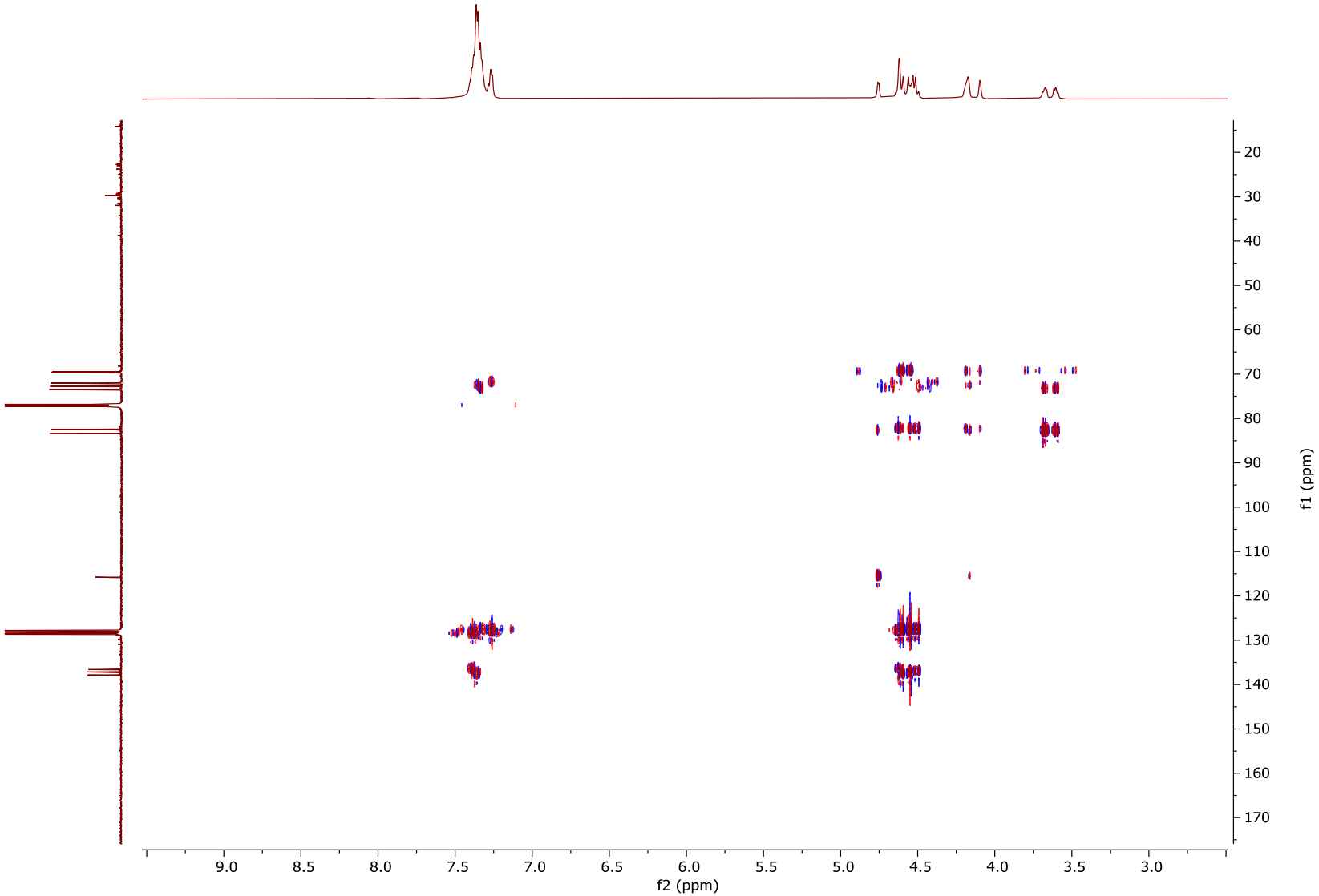
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl β-D-arabinofuranoside **(8e):**



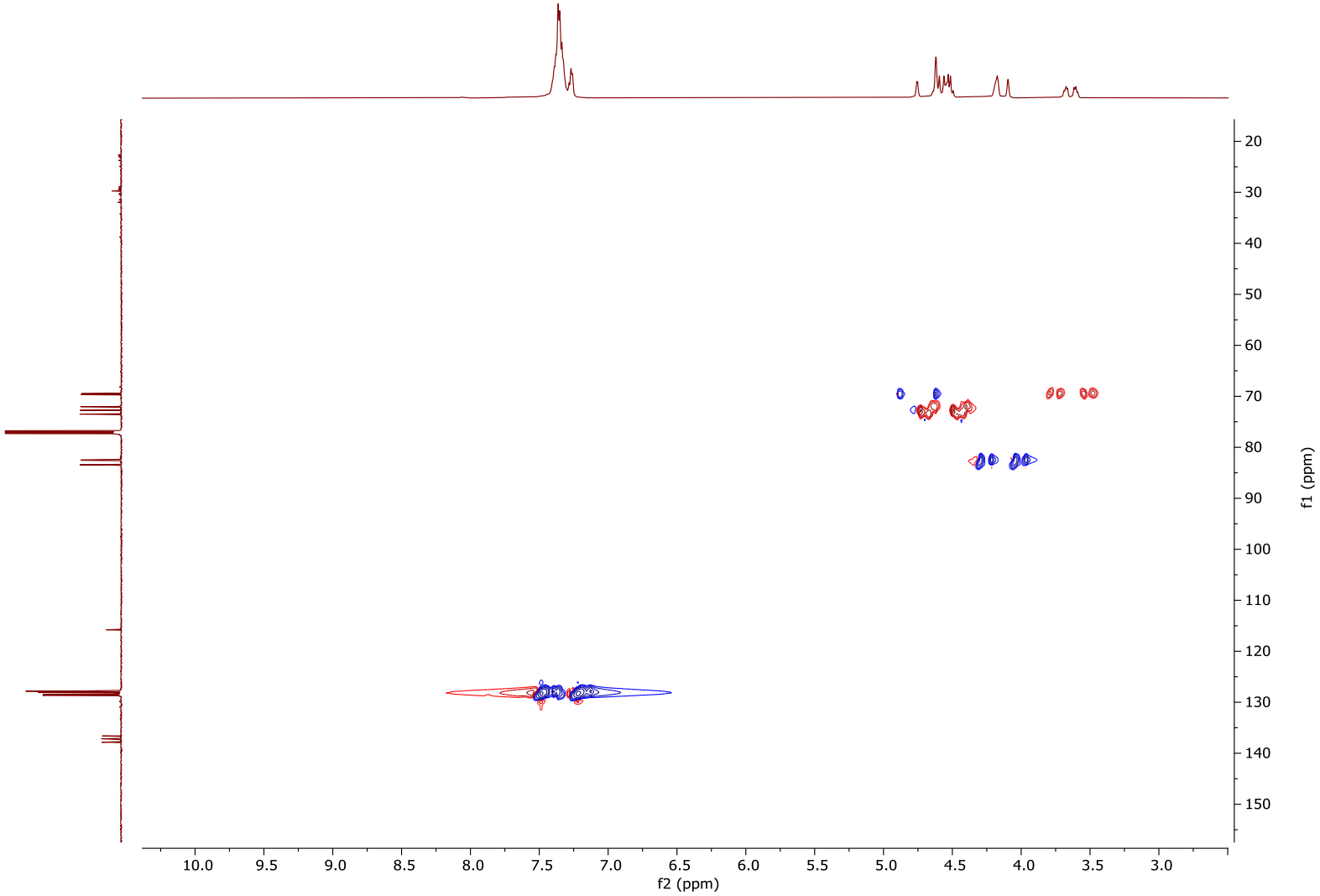
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl β-D-arabinofuranoside **(8e):**



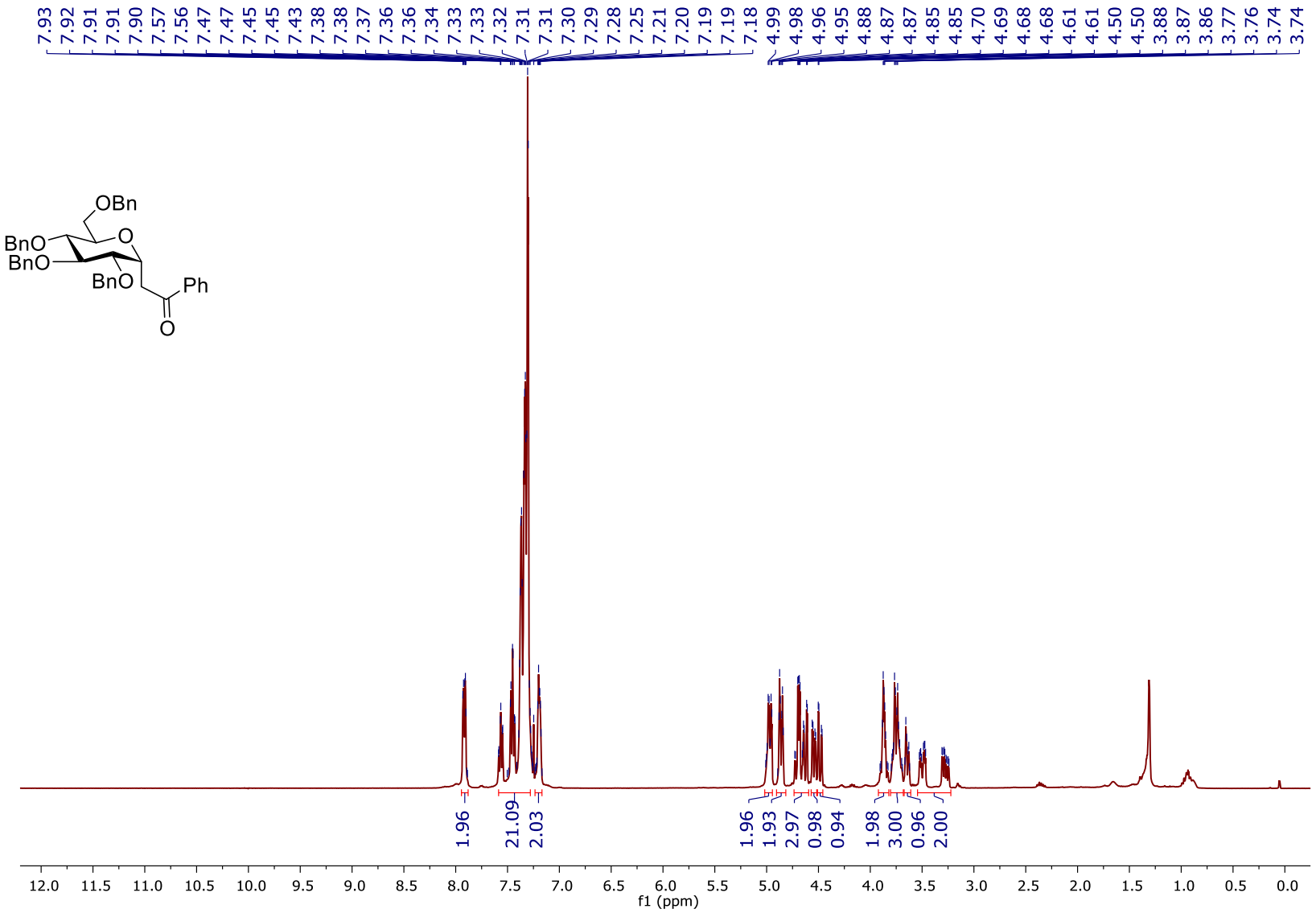
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl β-D-arabinofuranoside **(8e):**



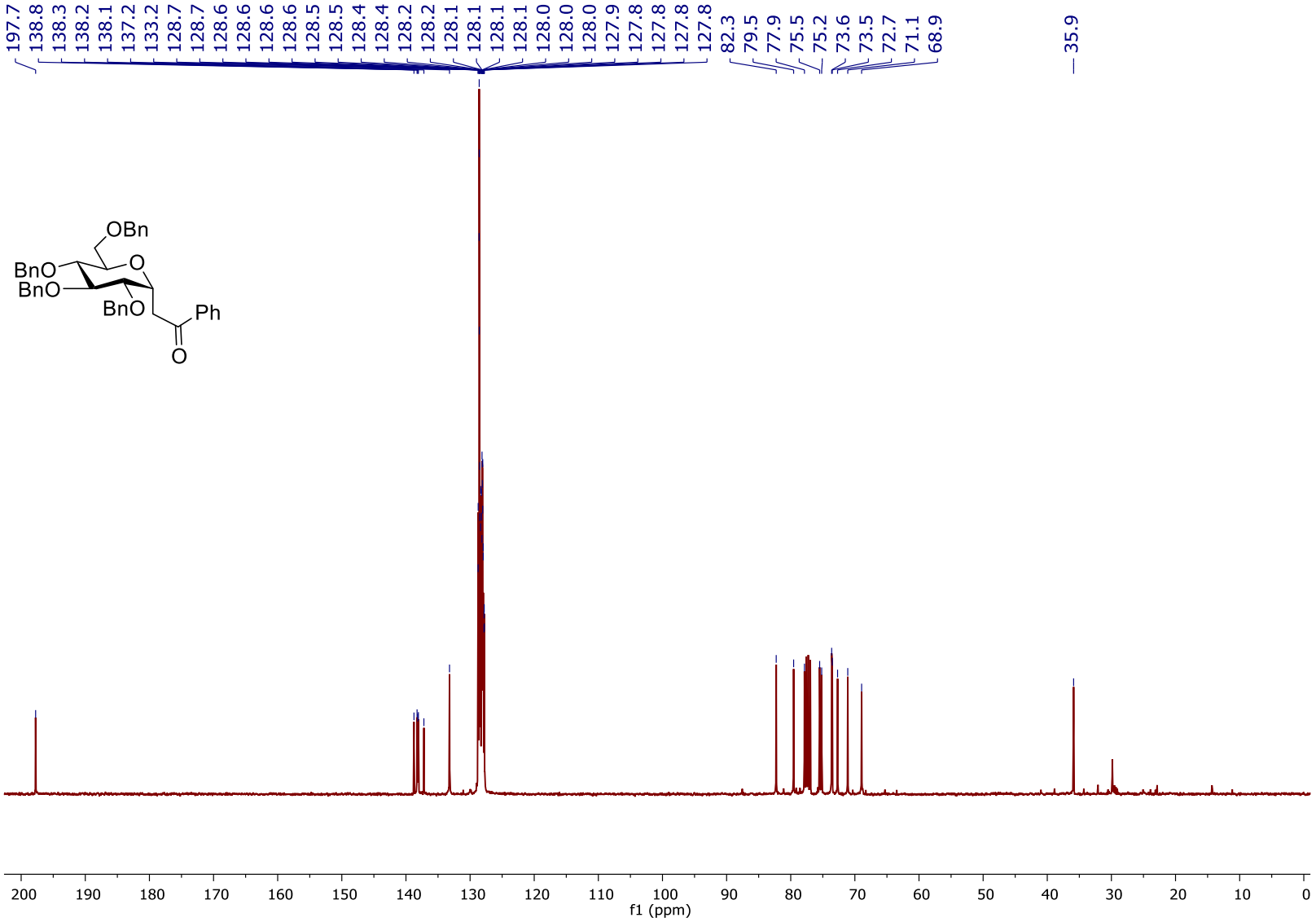
HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-Cyano-1-*deoxy*-2,3,5-tri-*O*-benzyl β-D-arabinofuranoside **(8e):**



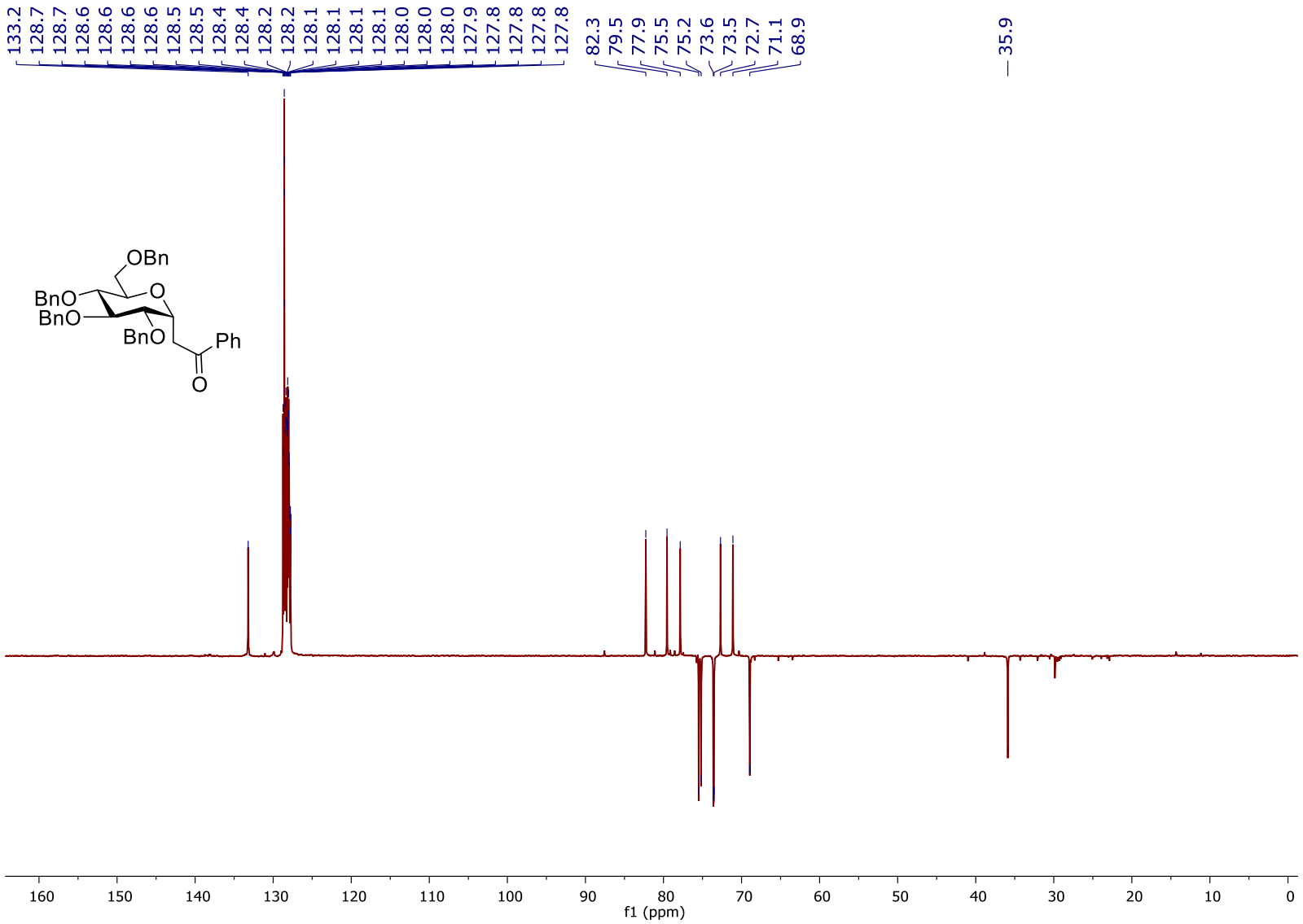
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(9a):**



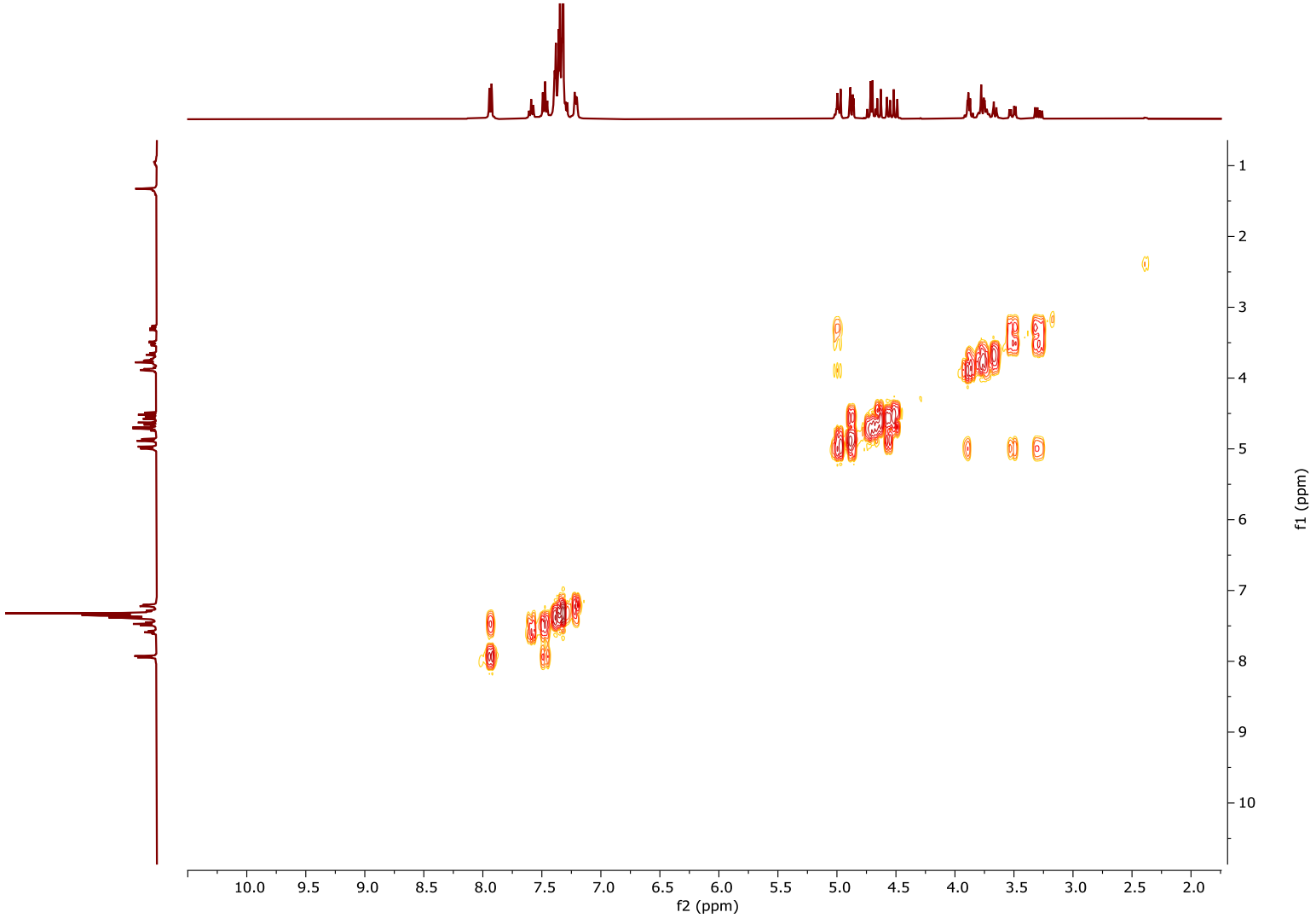
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(9a):**



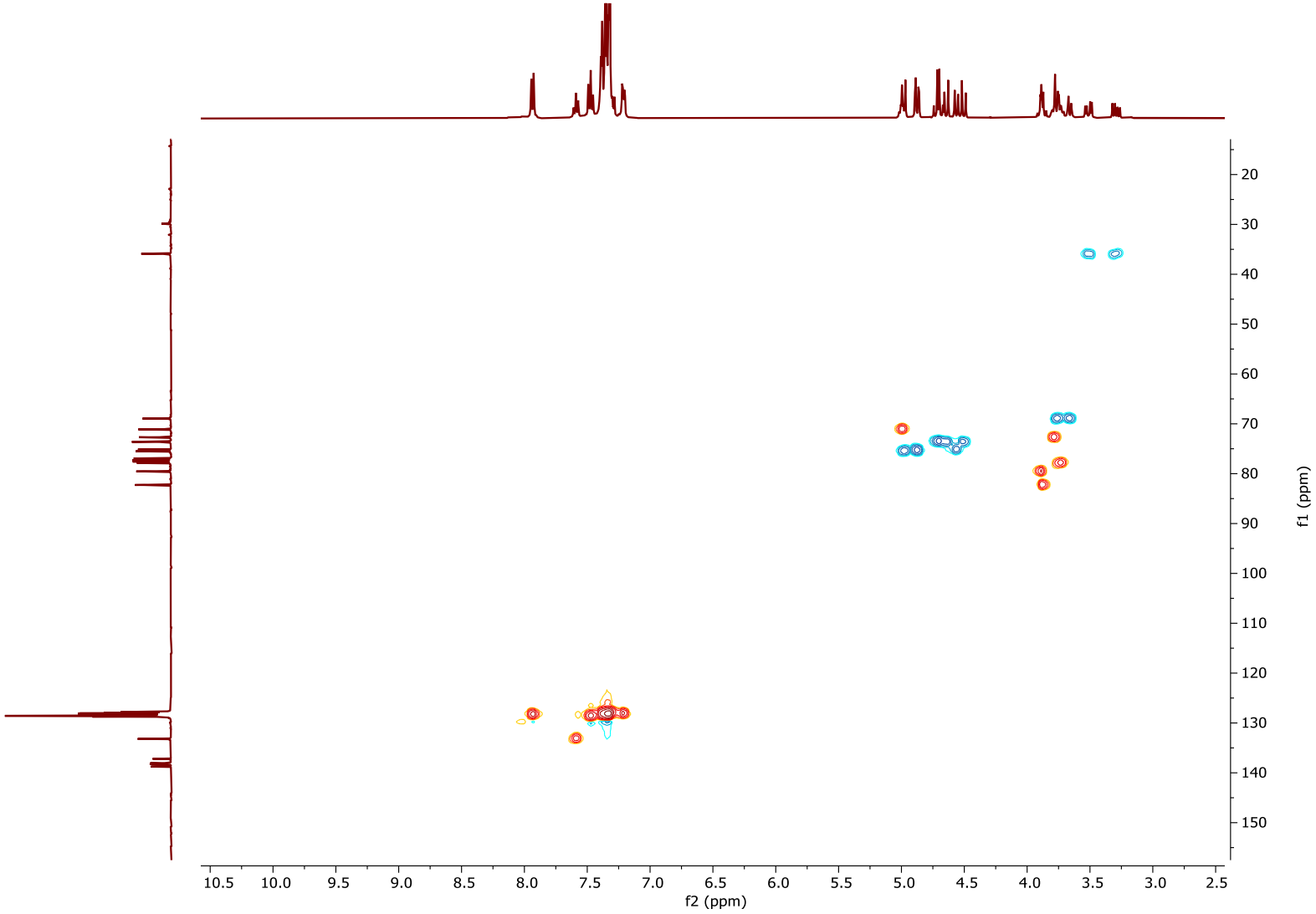
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(9a):**



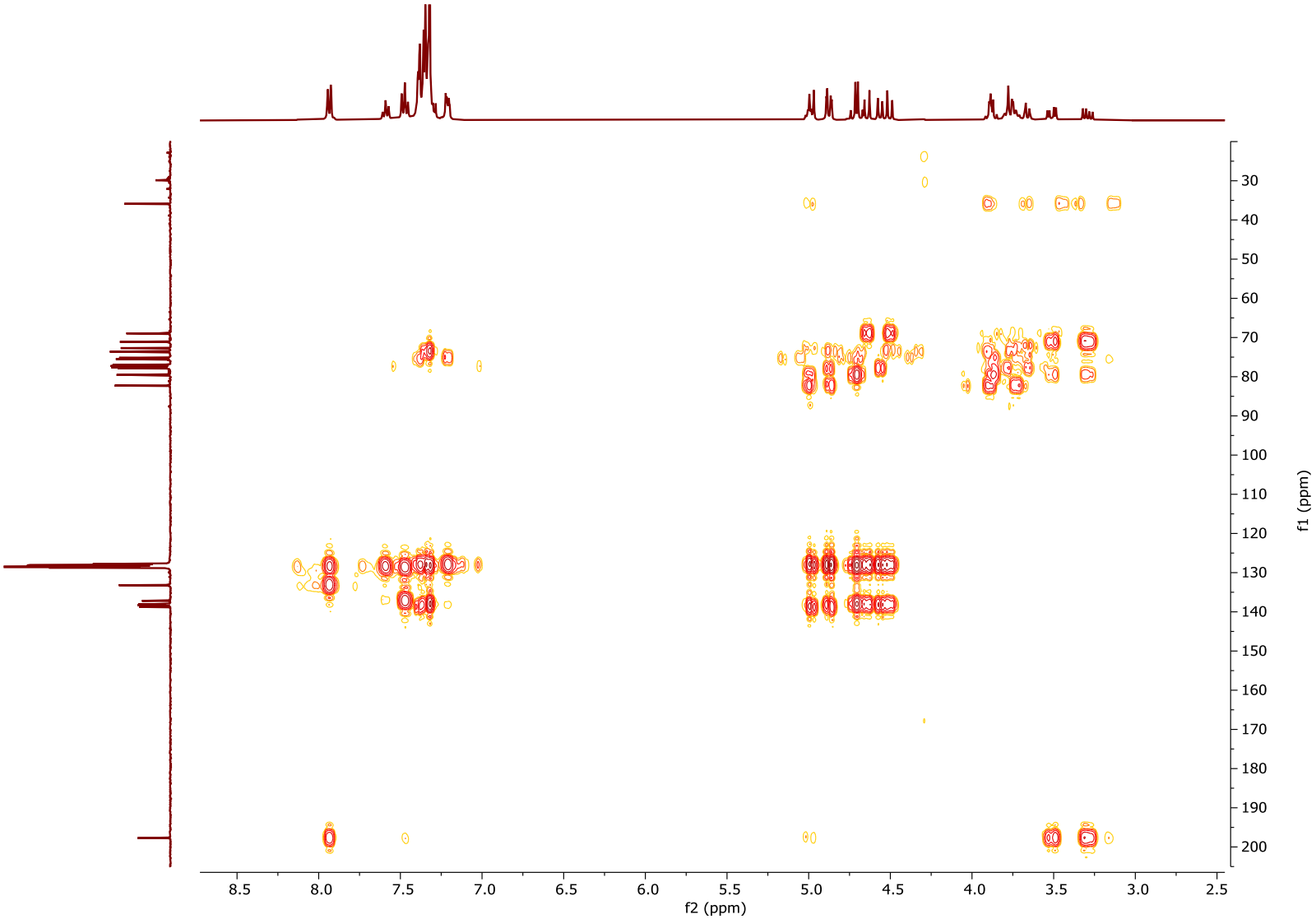
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(9a):**



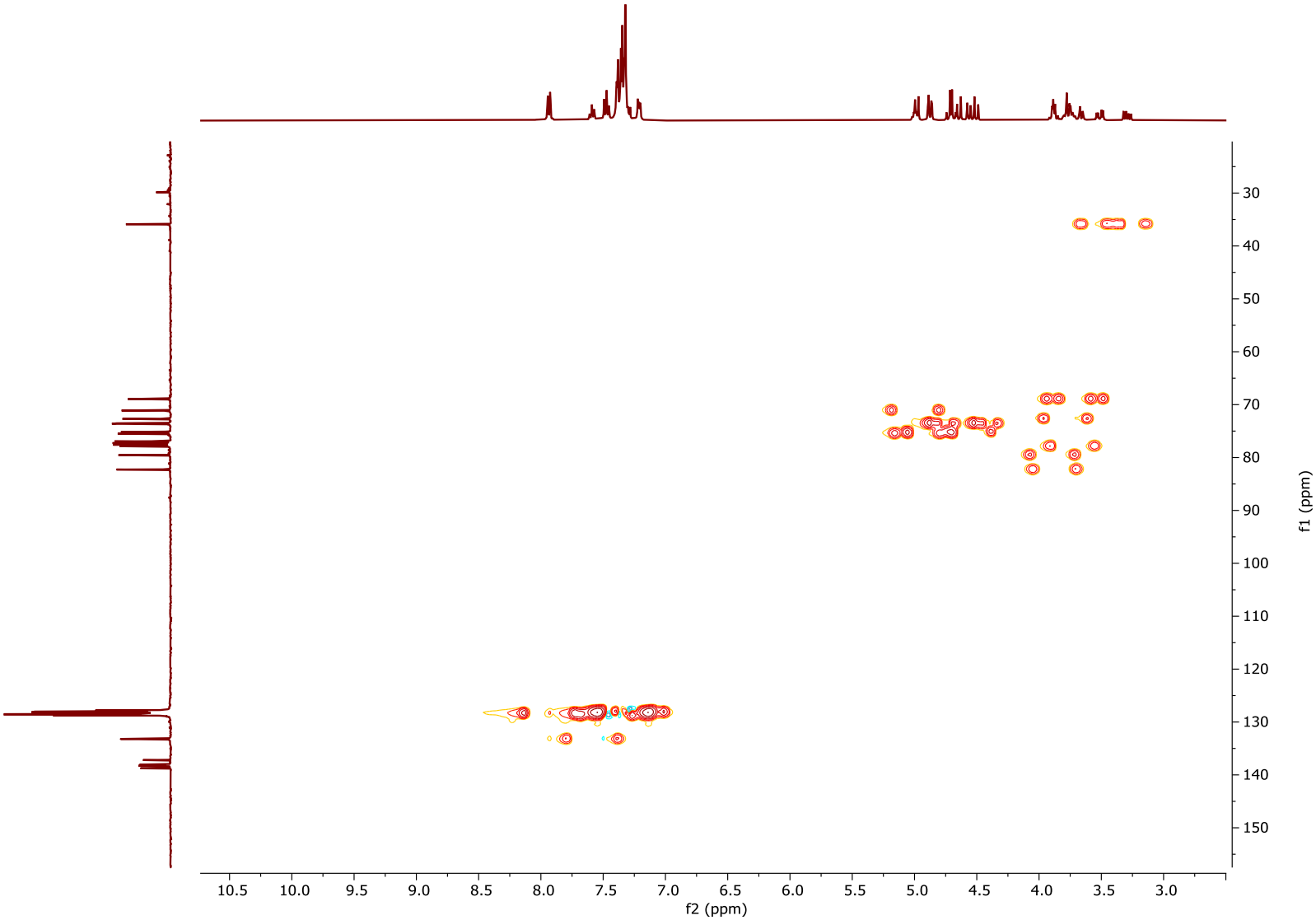
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(9a):**



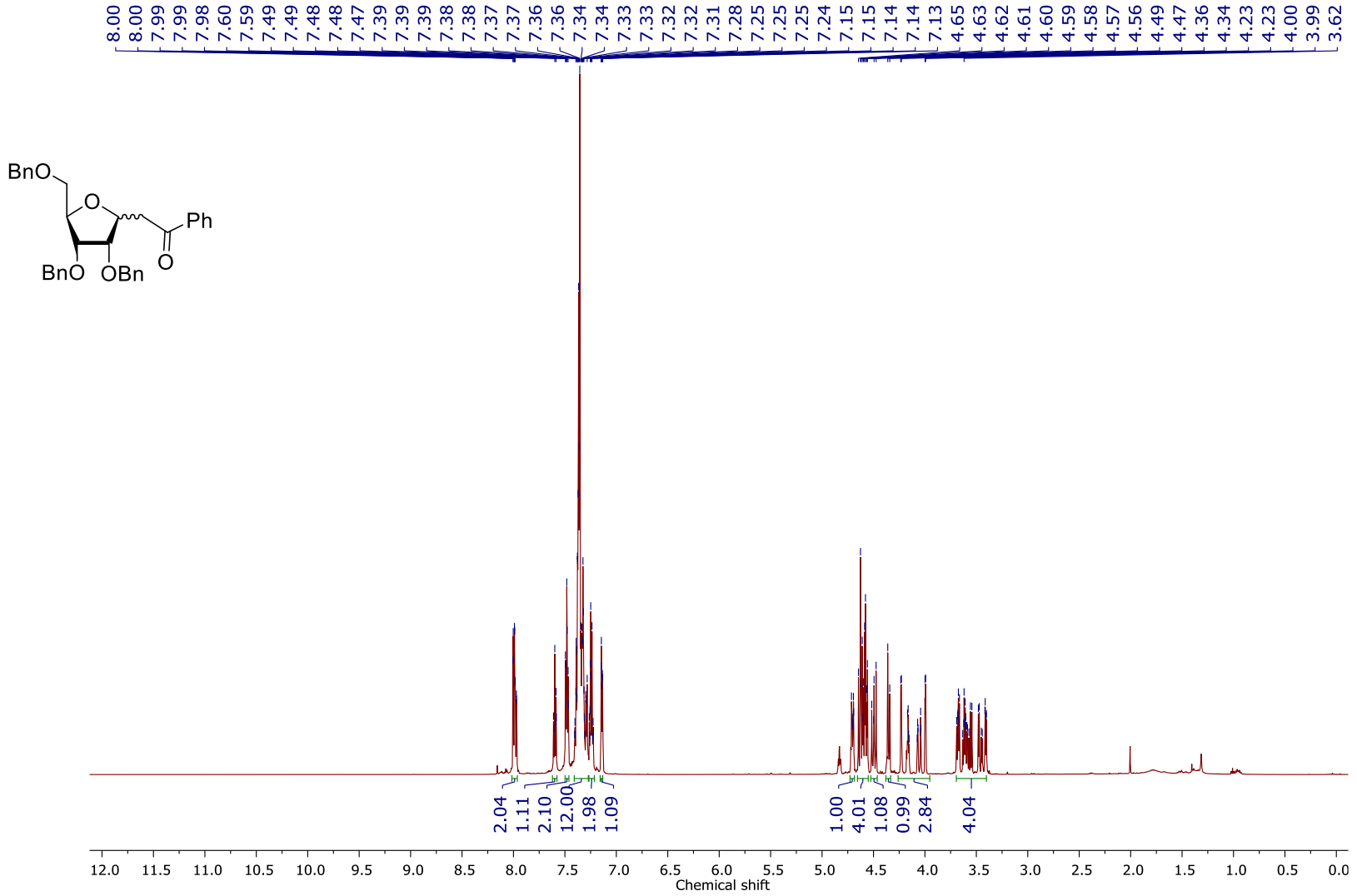
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(9a):**



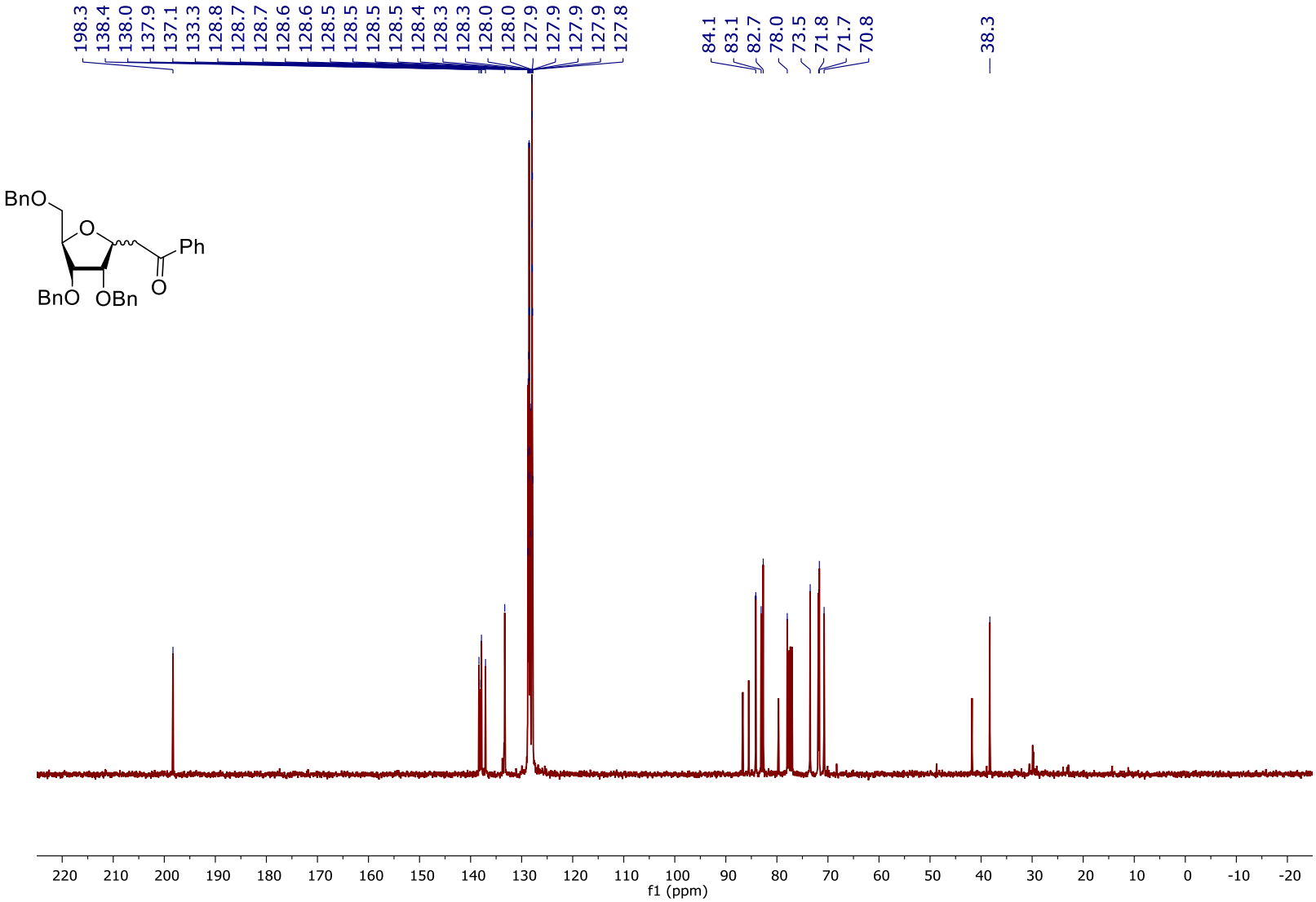
HSQC coupled Spectrum (600 MHz) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(9a):**



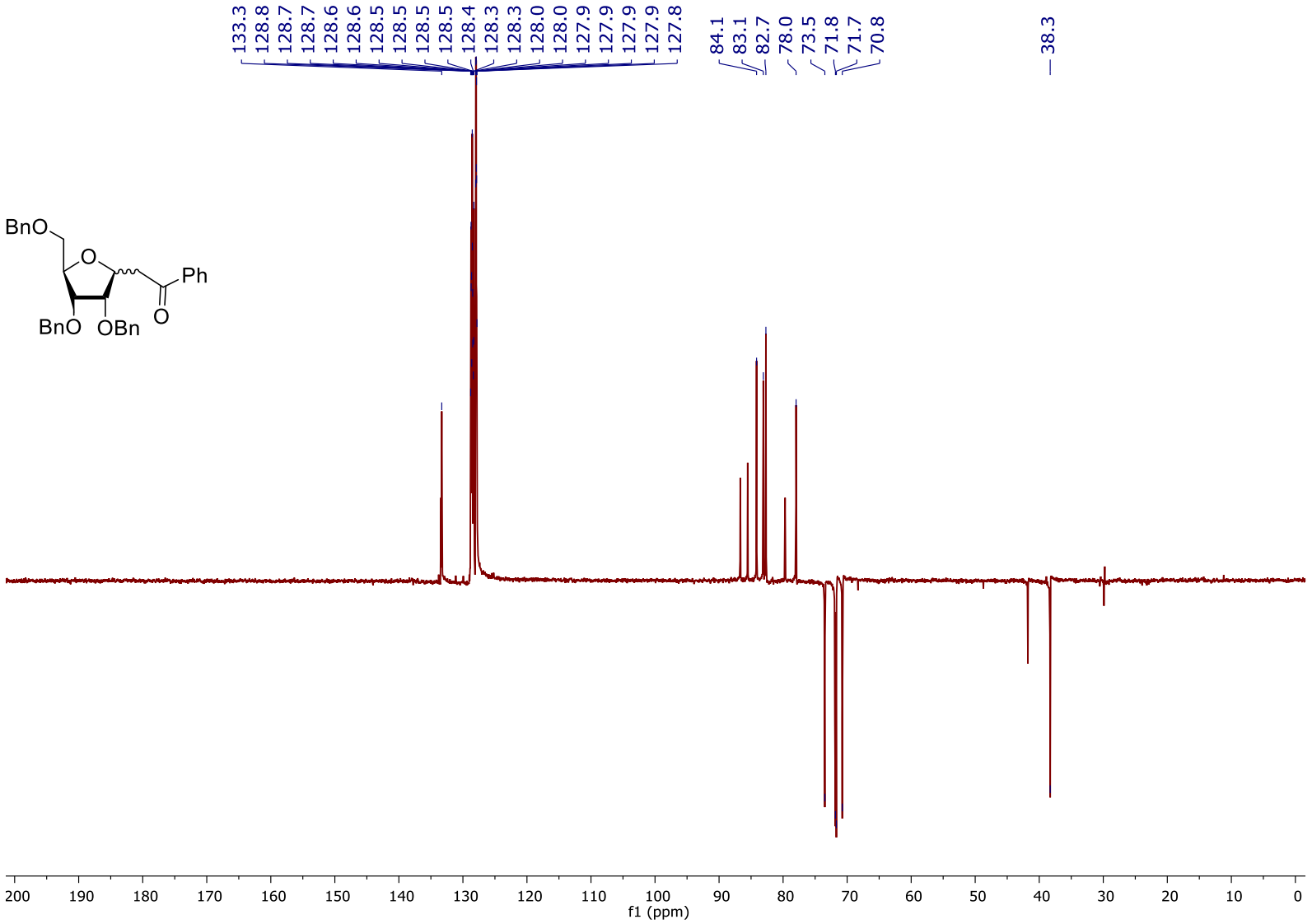
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)- 2,3,5-tri-*O*-benzyl α/β-D-ribofuranoside **(9b):**



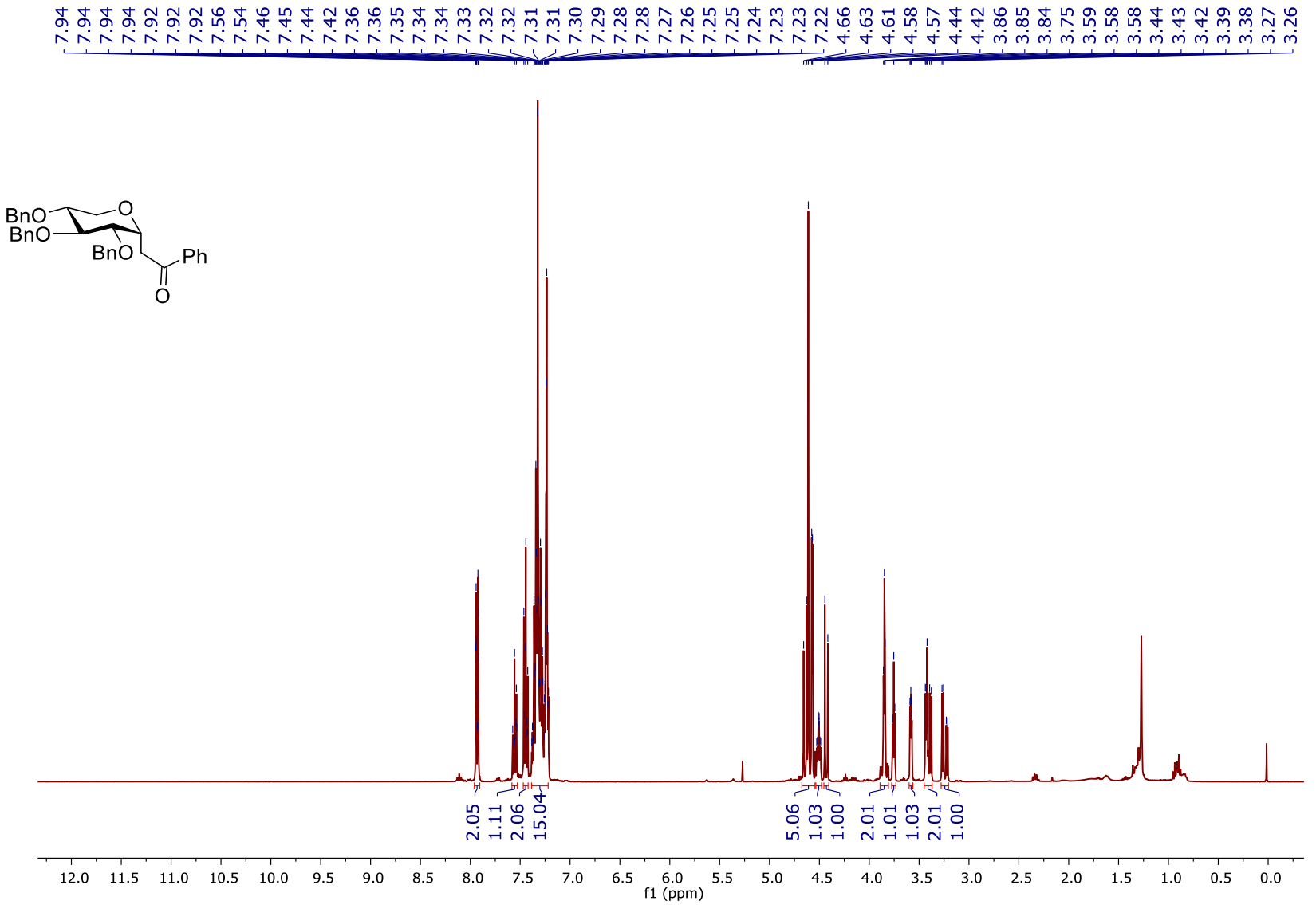
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)- 2,3,5-tri-*O*-benzyl α/β-D-ribofuranoside **(9b):**



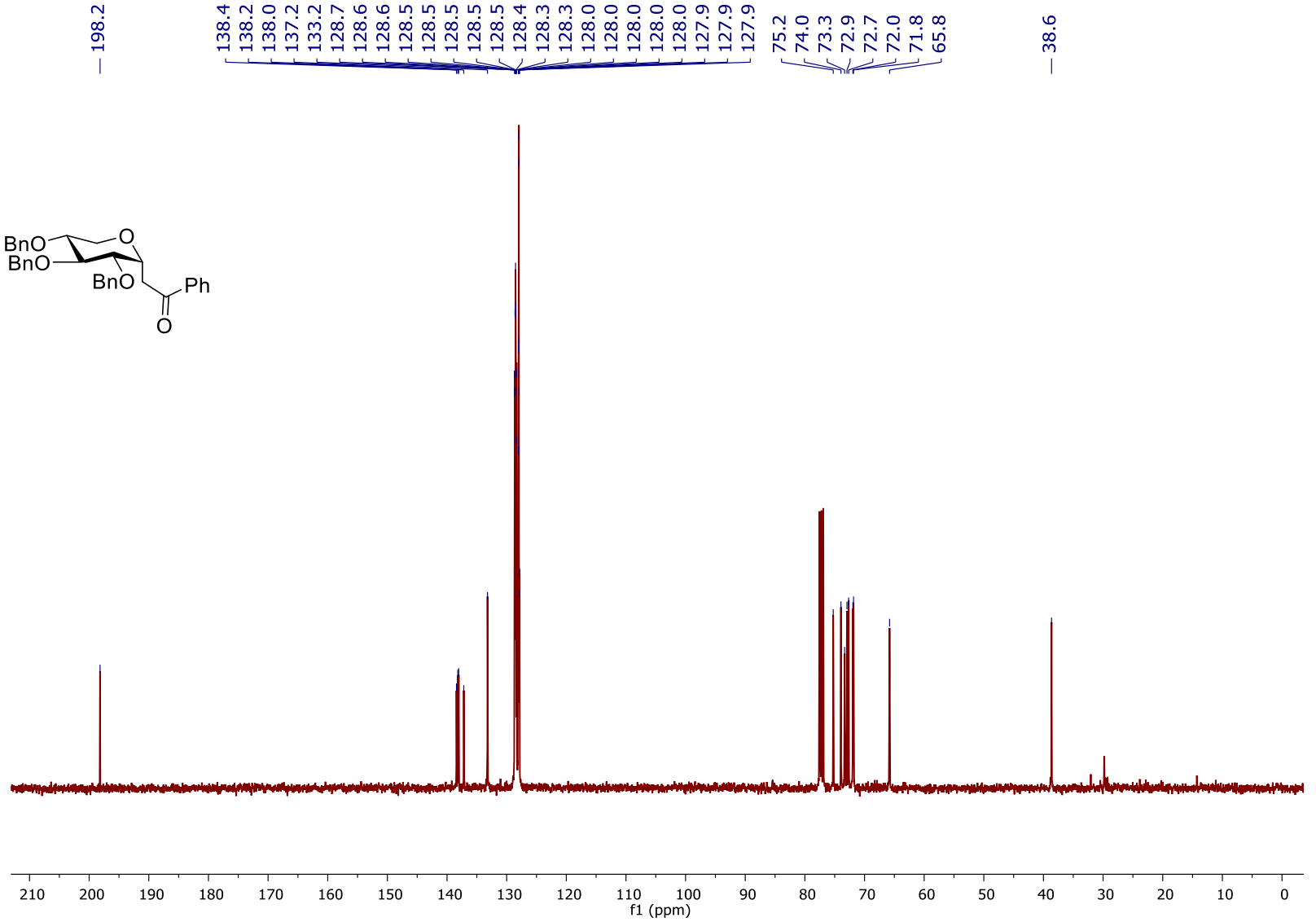
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of **1**-*deoxy*-1-(Phenyl ethan-2-one)- 2,3,5-tri-*O*-benzyl α/β-D-ribofuranoside **(9b):**



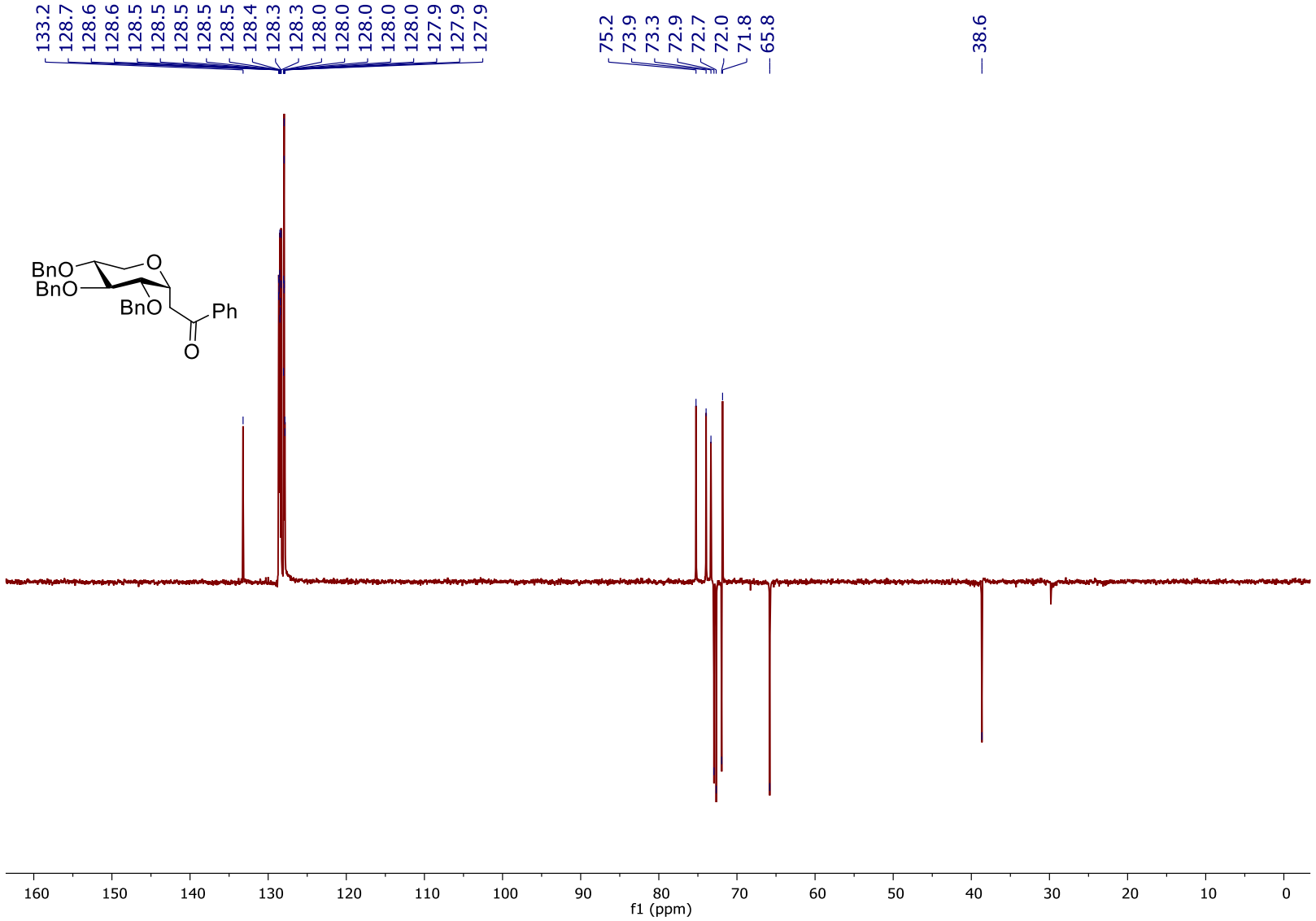
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(9c):**



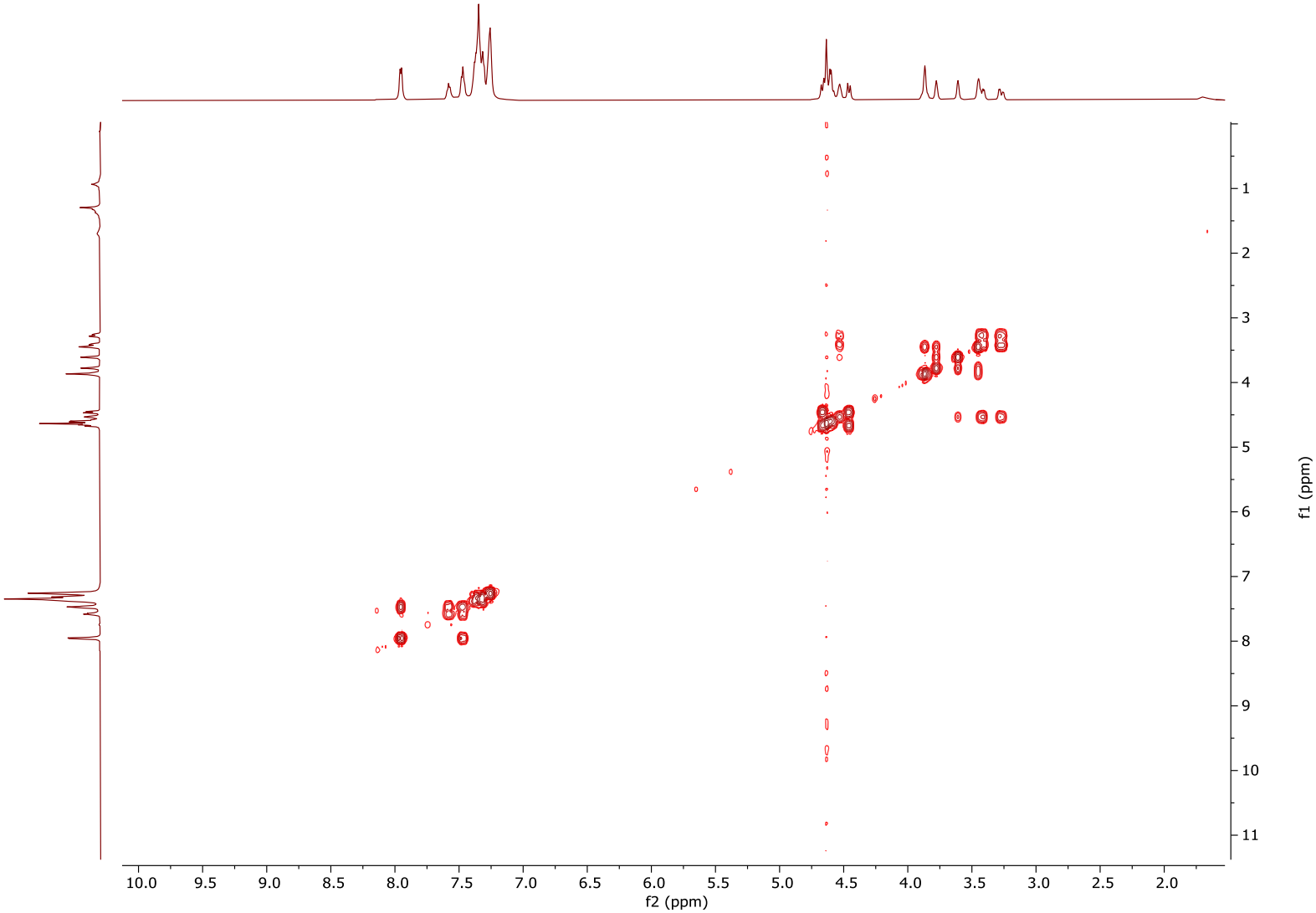
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(9c):**



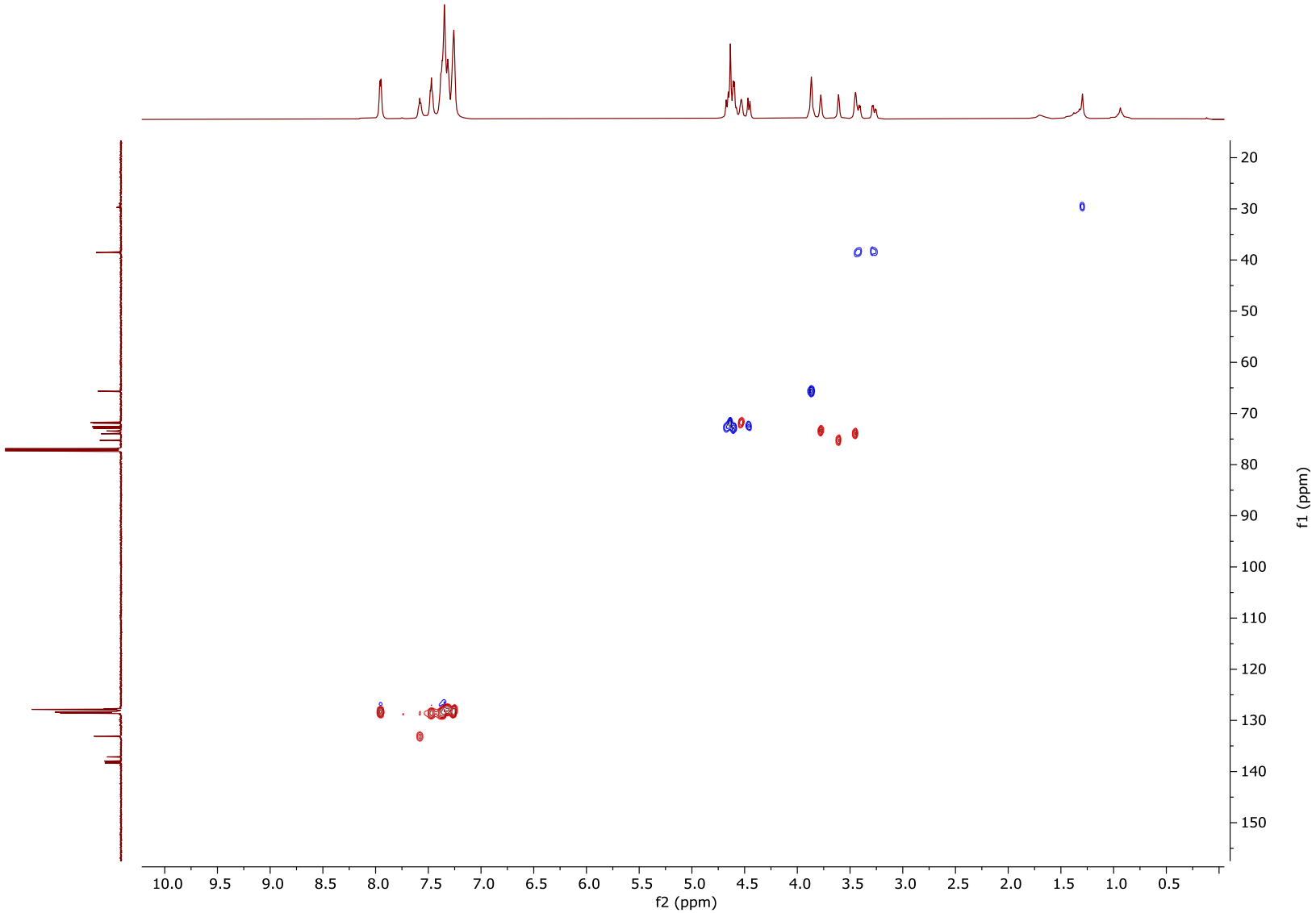
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(9c):**



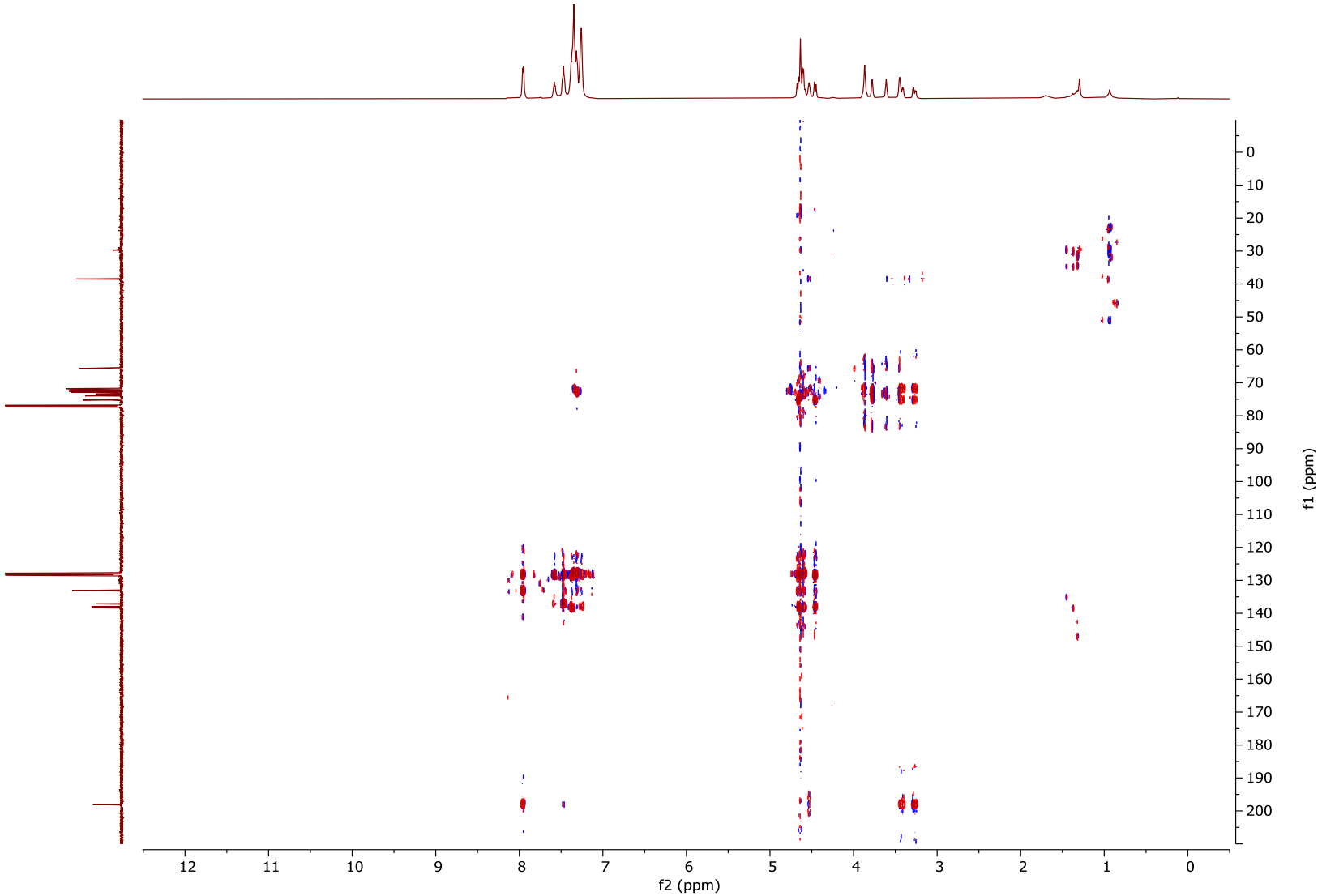
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(9c):**



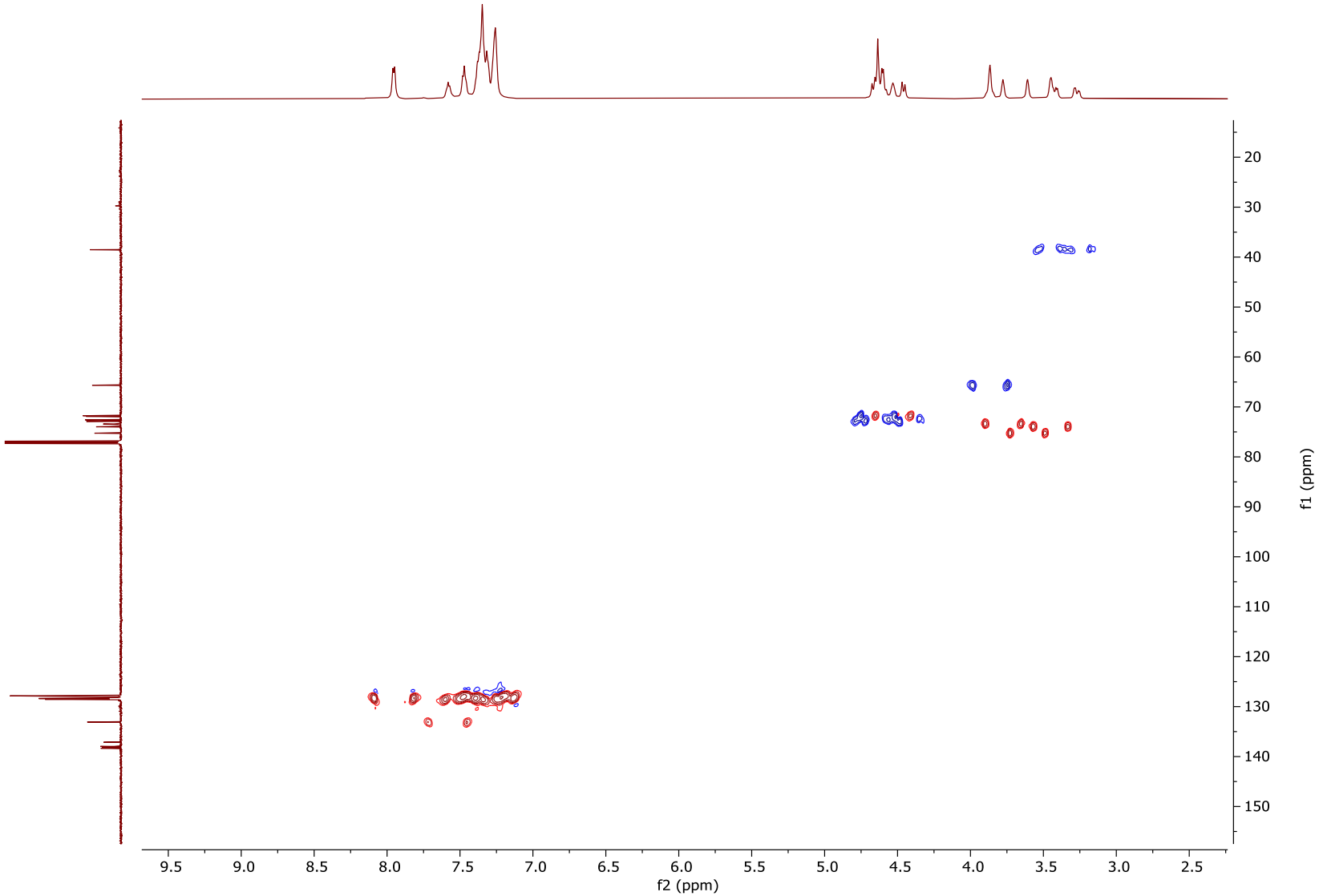
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(9c):**



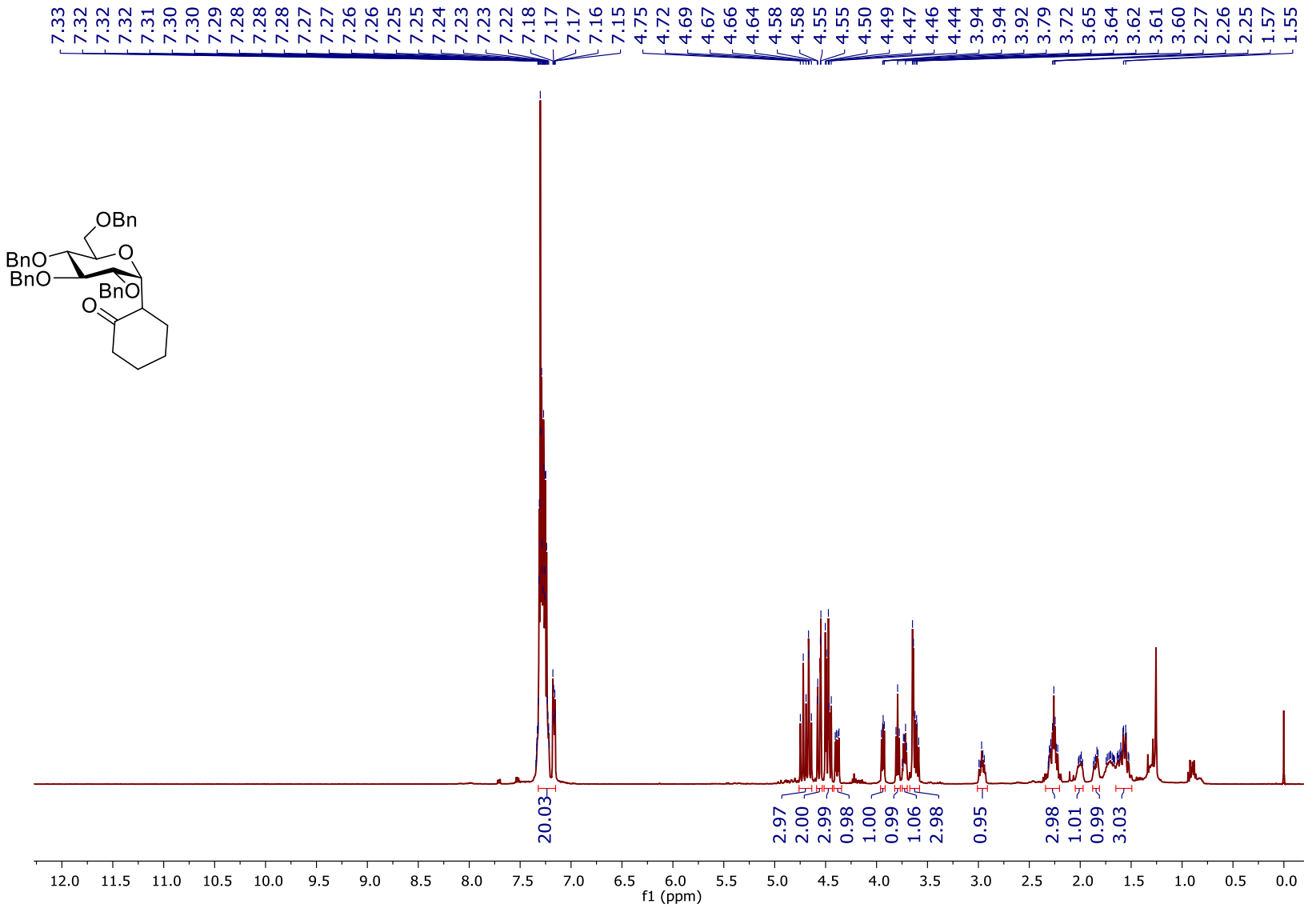
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(9c):**



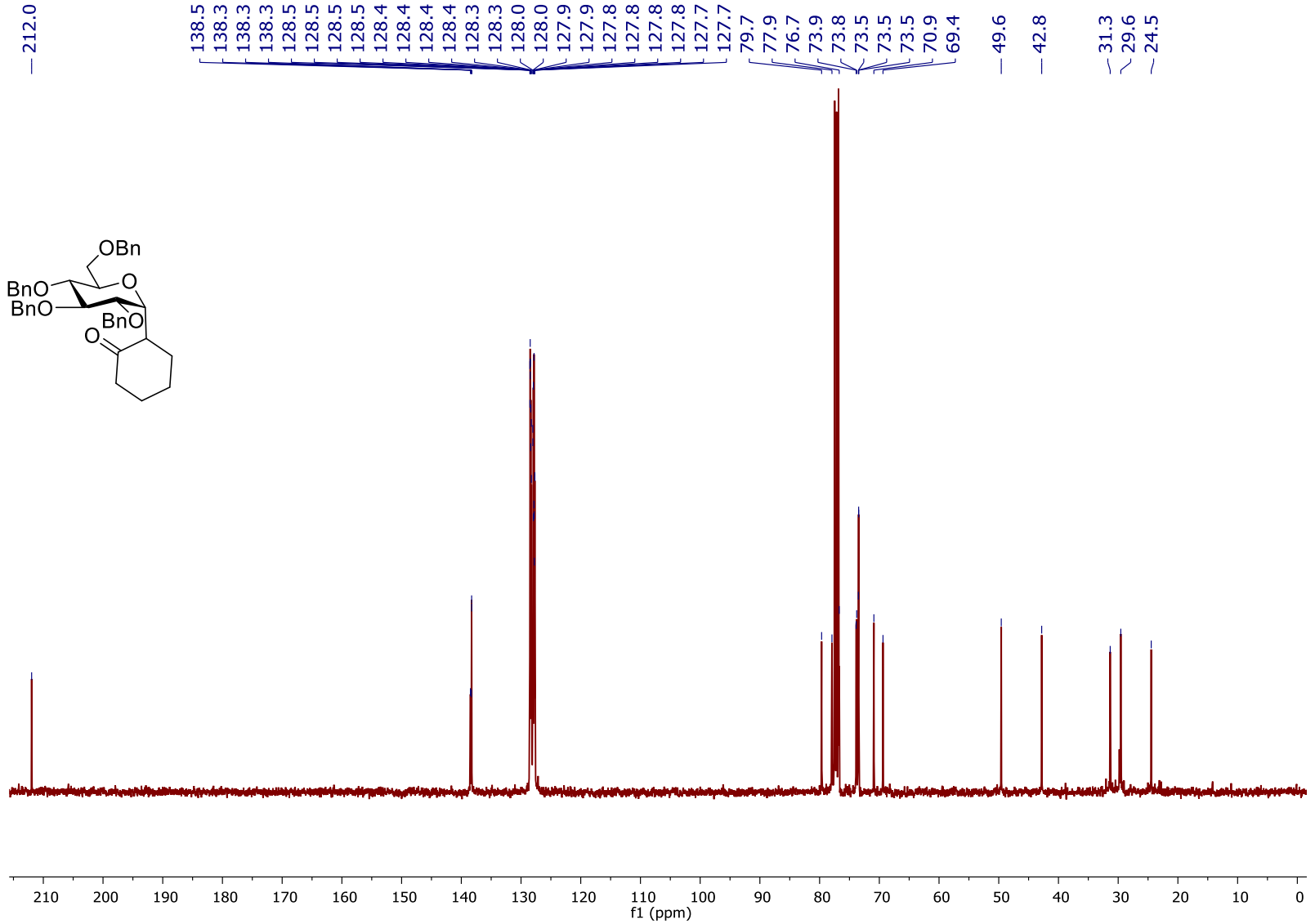
HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Phenyl ethan-2-one)-2,3,4-tri-*O*-benzyl α-D-xylopyranoside **(9c):**



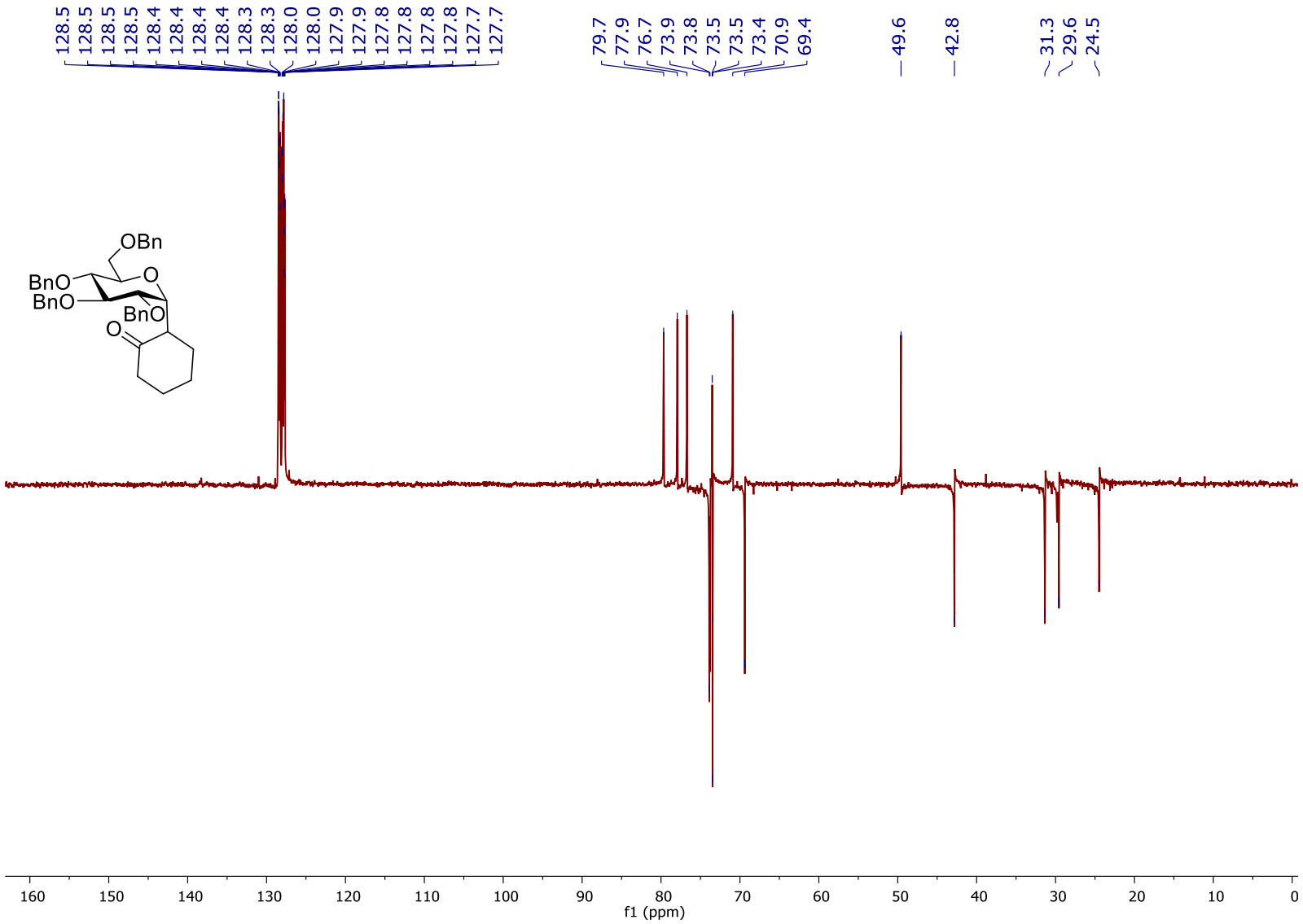
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(10a):**



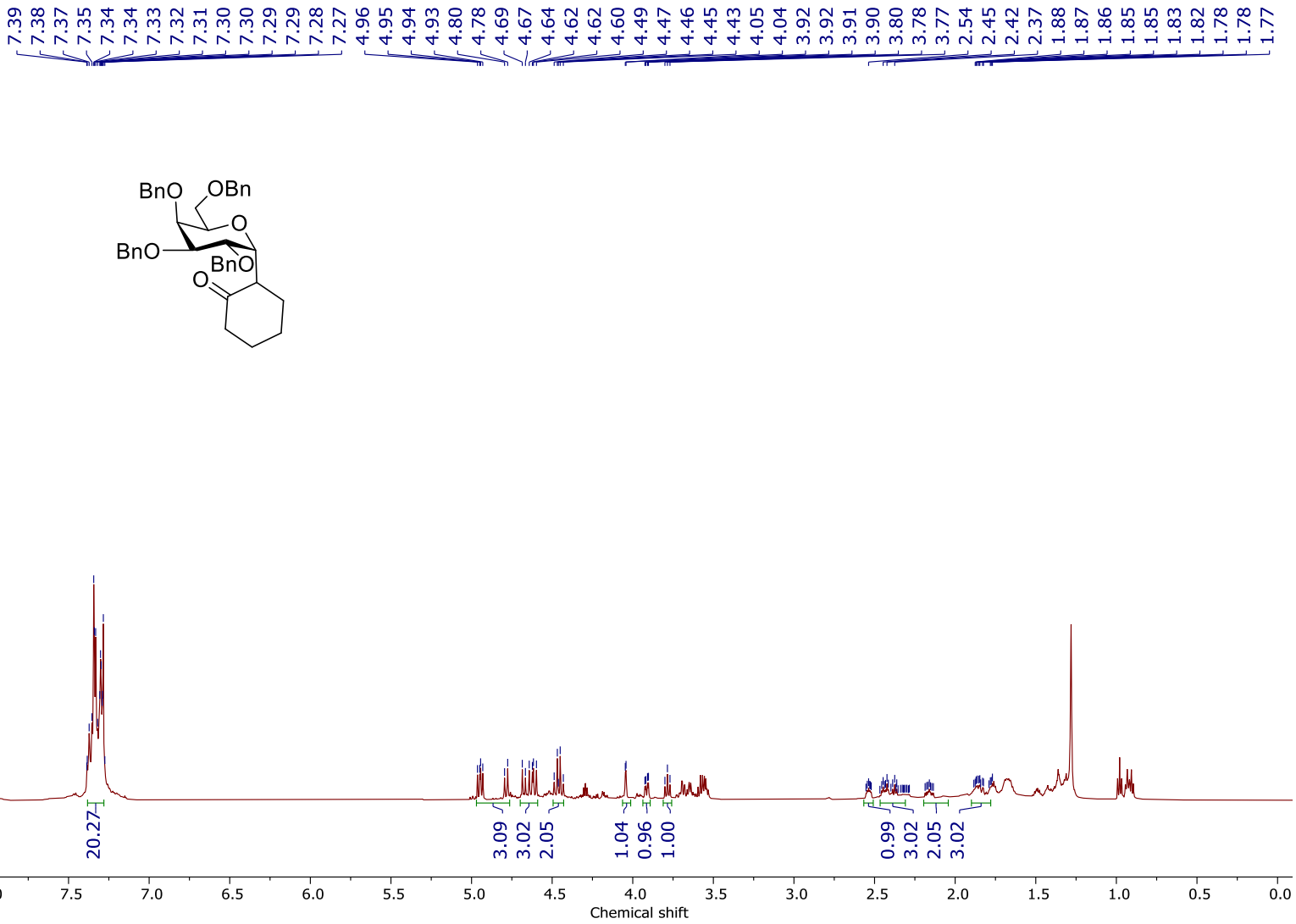
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(10a):**



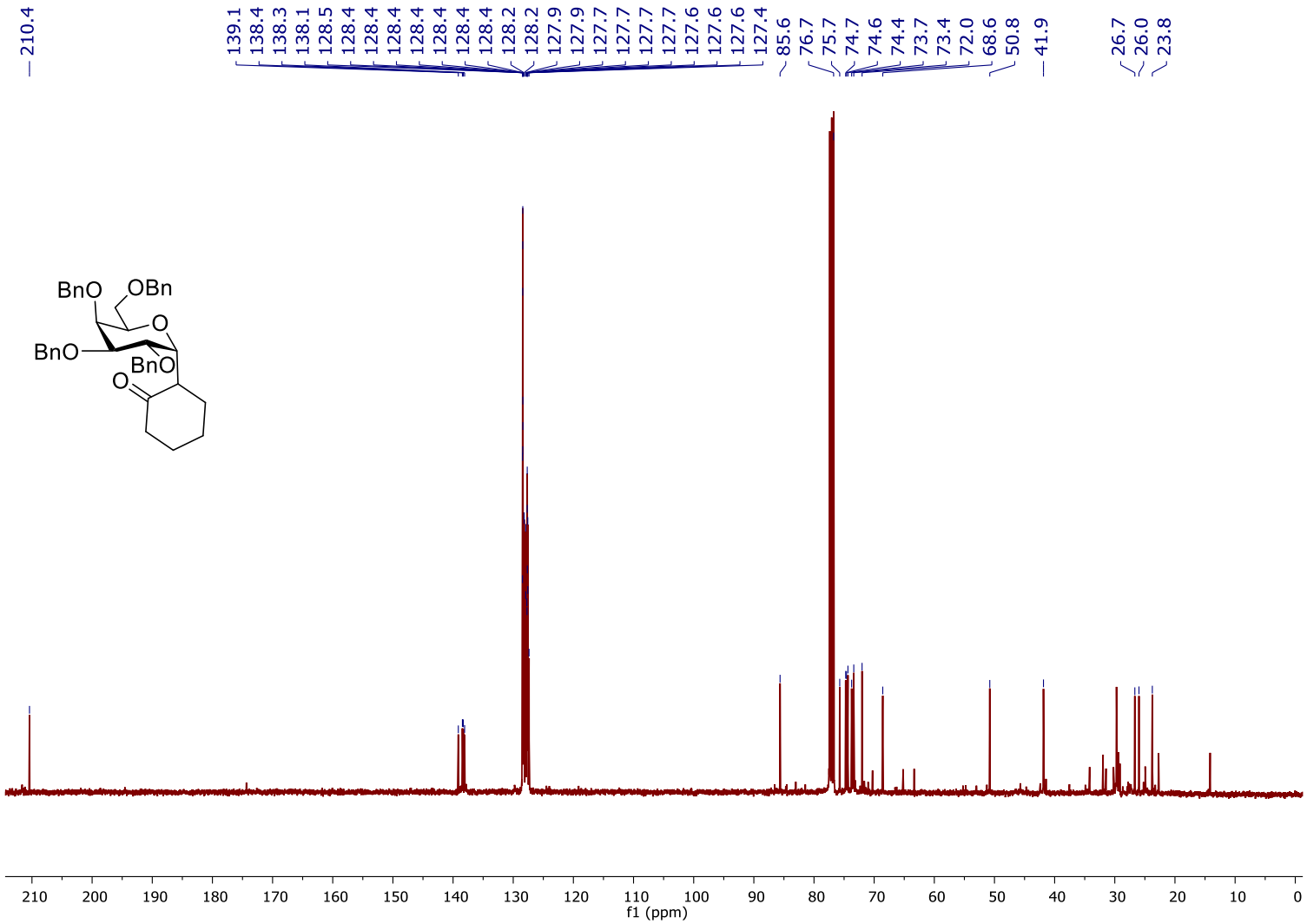
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(10a):**



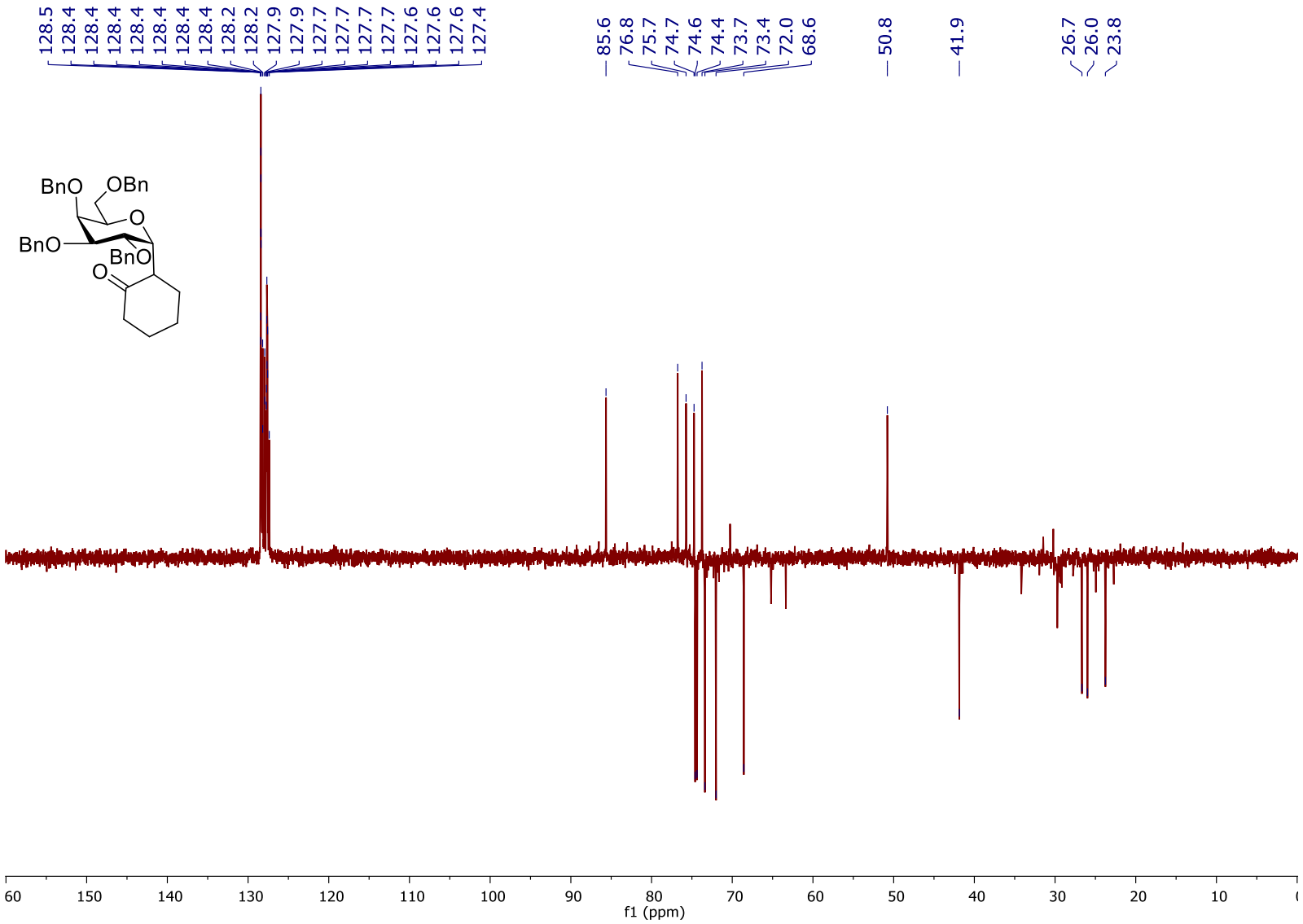
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(10b):**



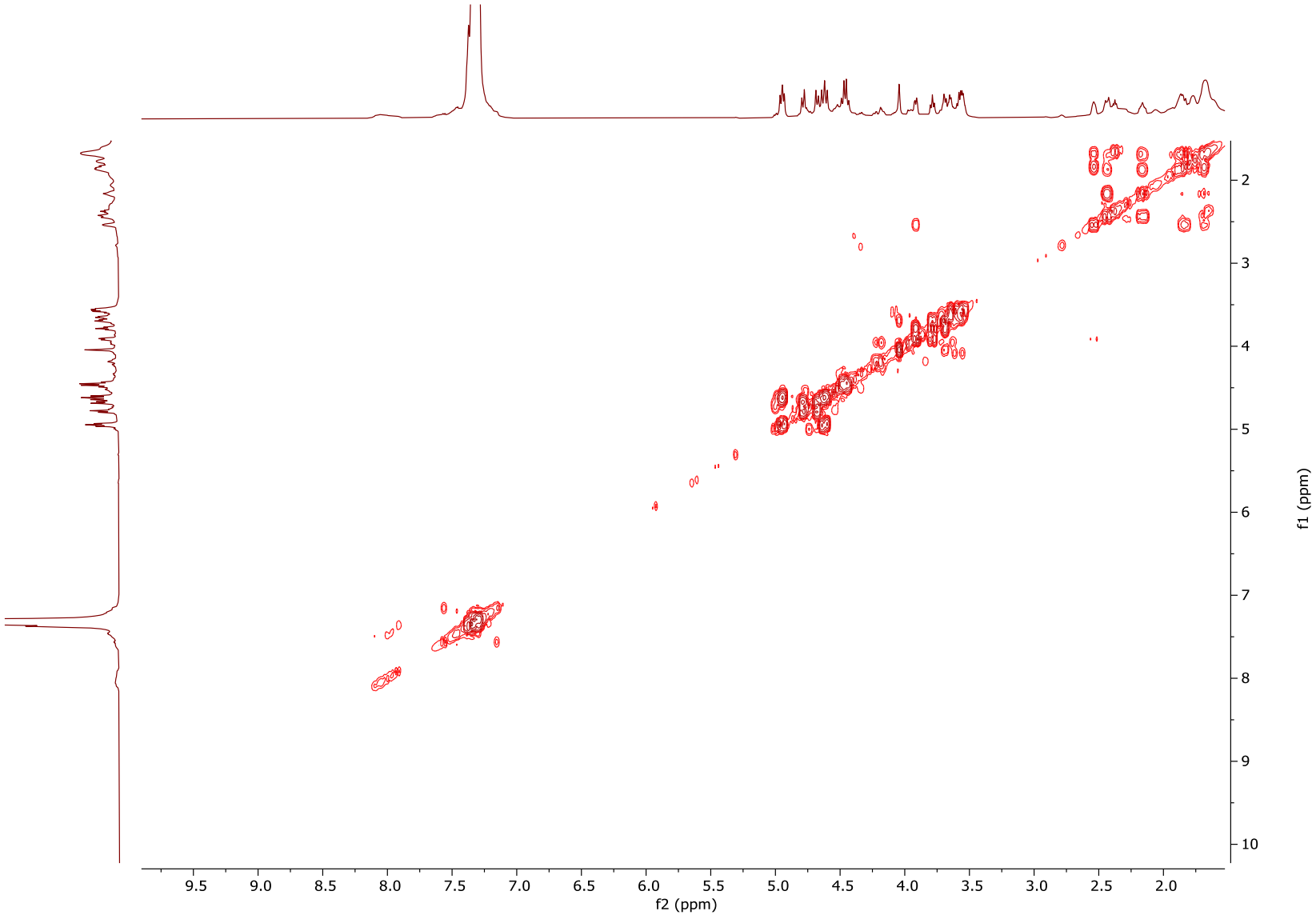
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(10b):**



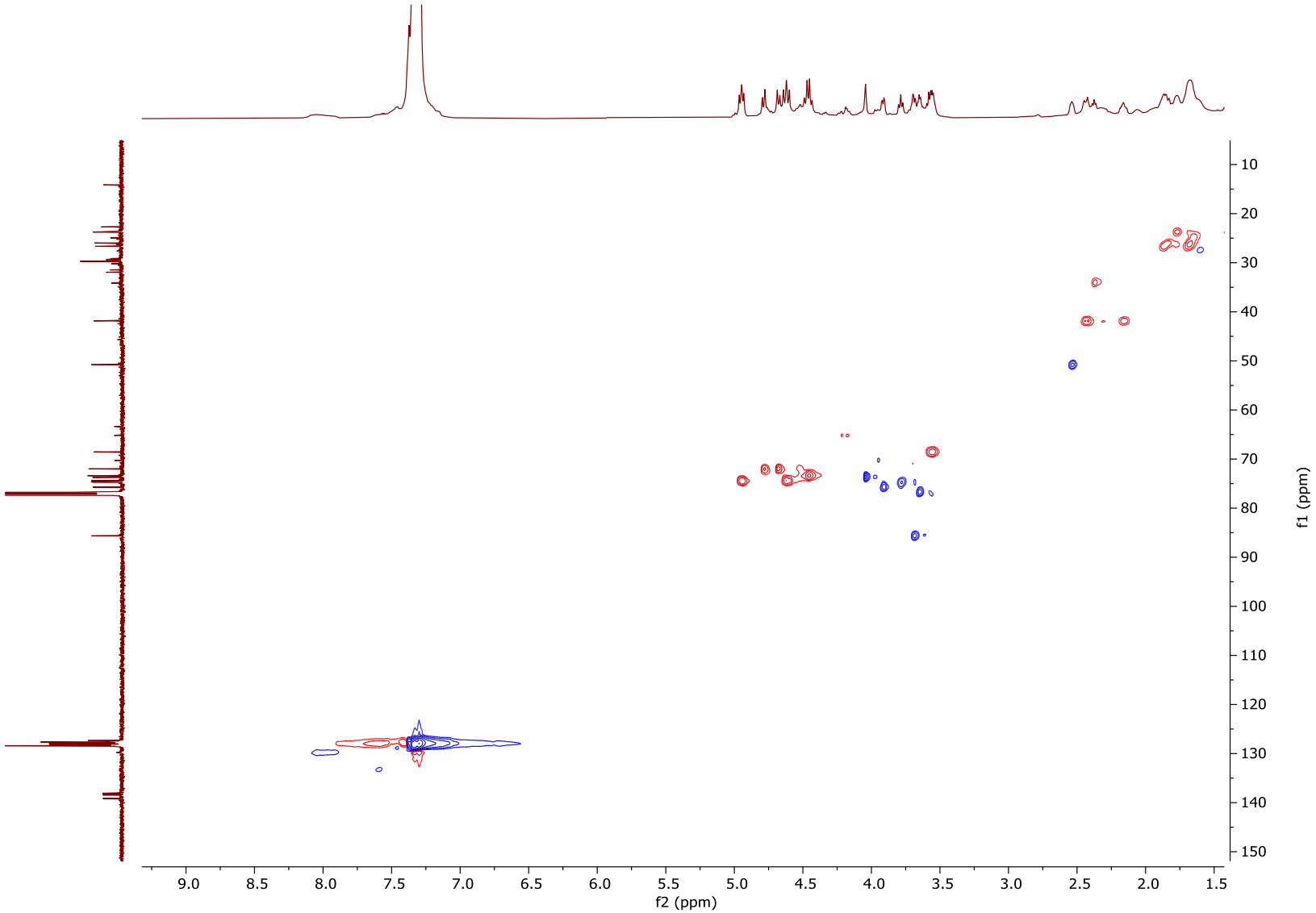
DEPT Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(10b):**



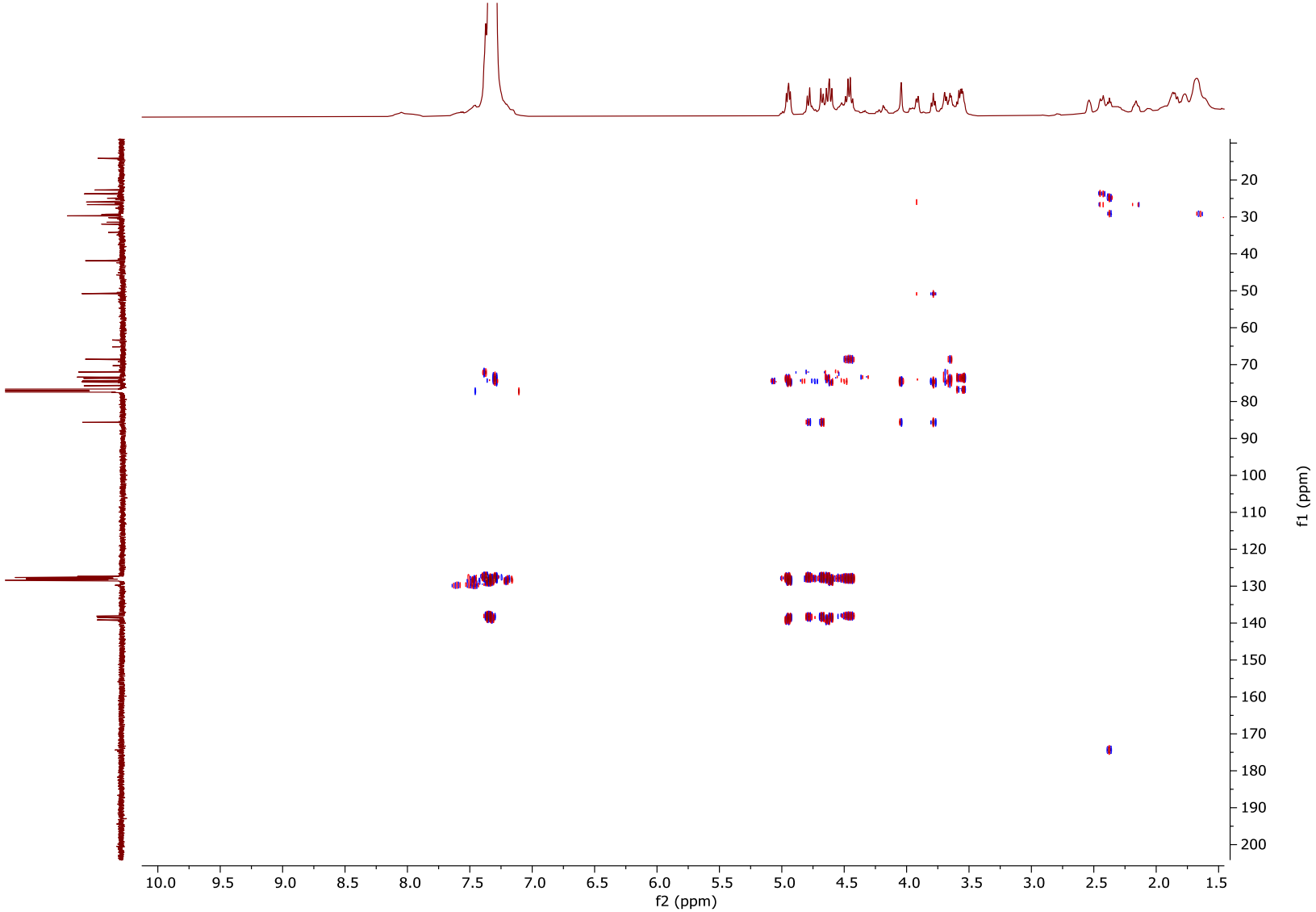
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(10b):**



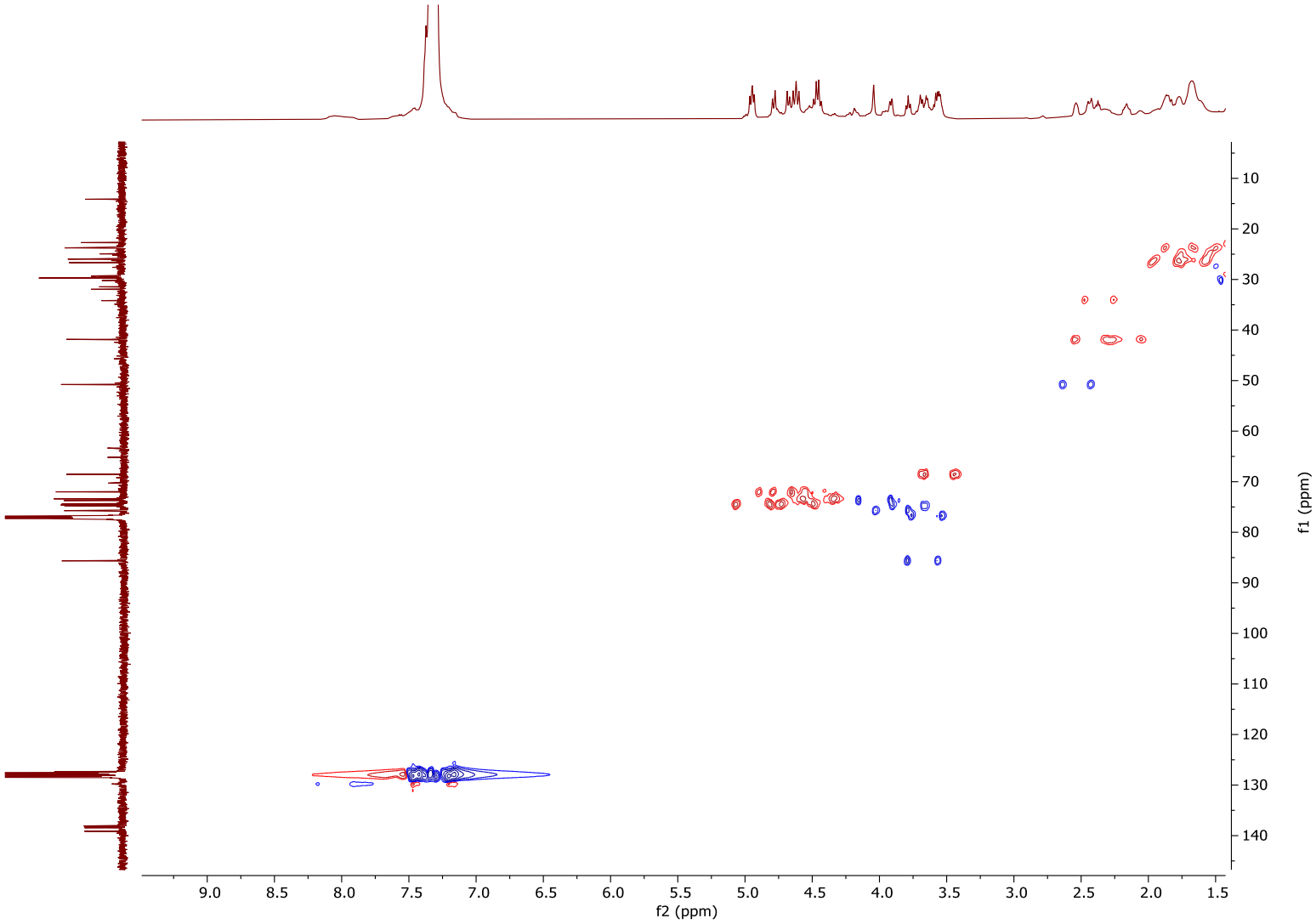
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(10b):**



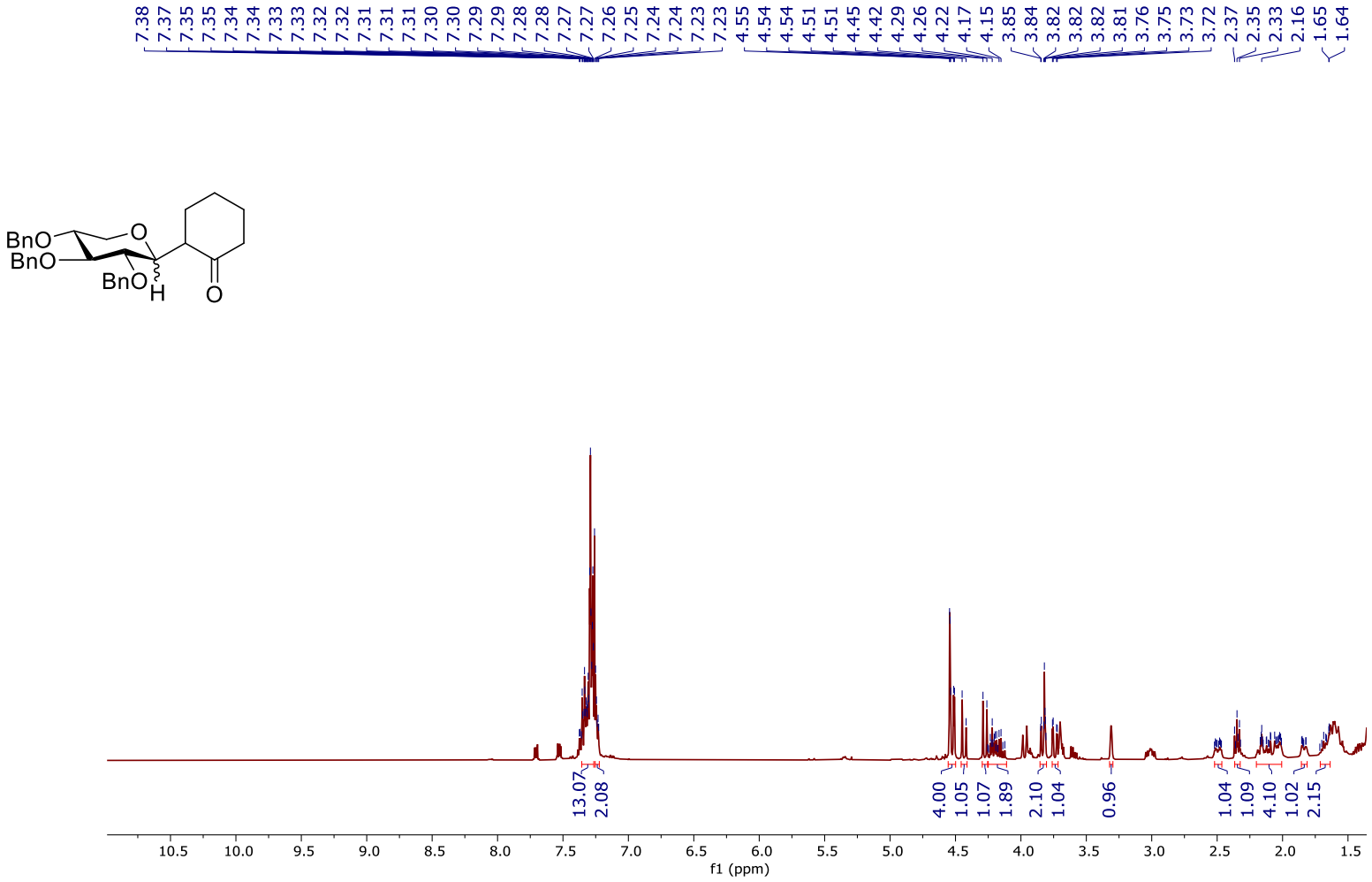
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(10b):**



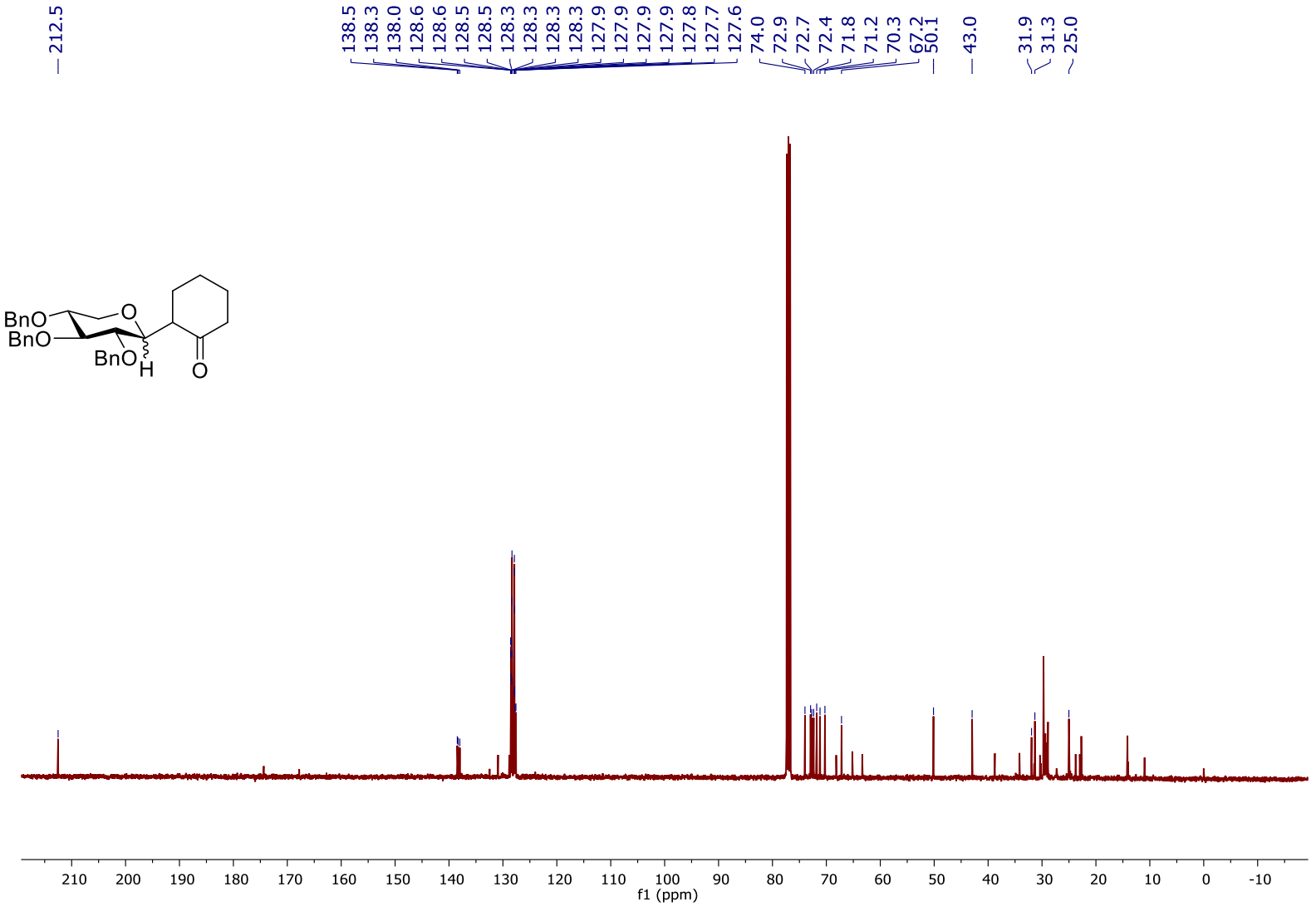
HSQC coupled Spectrum (600 MHz) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4,6-tetra-*O*-benzyl α-D-galactopyranoside **(10b):**



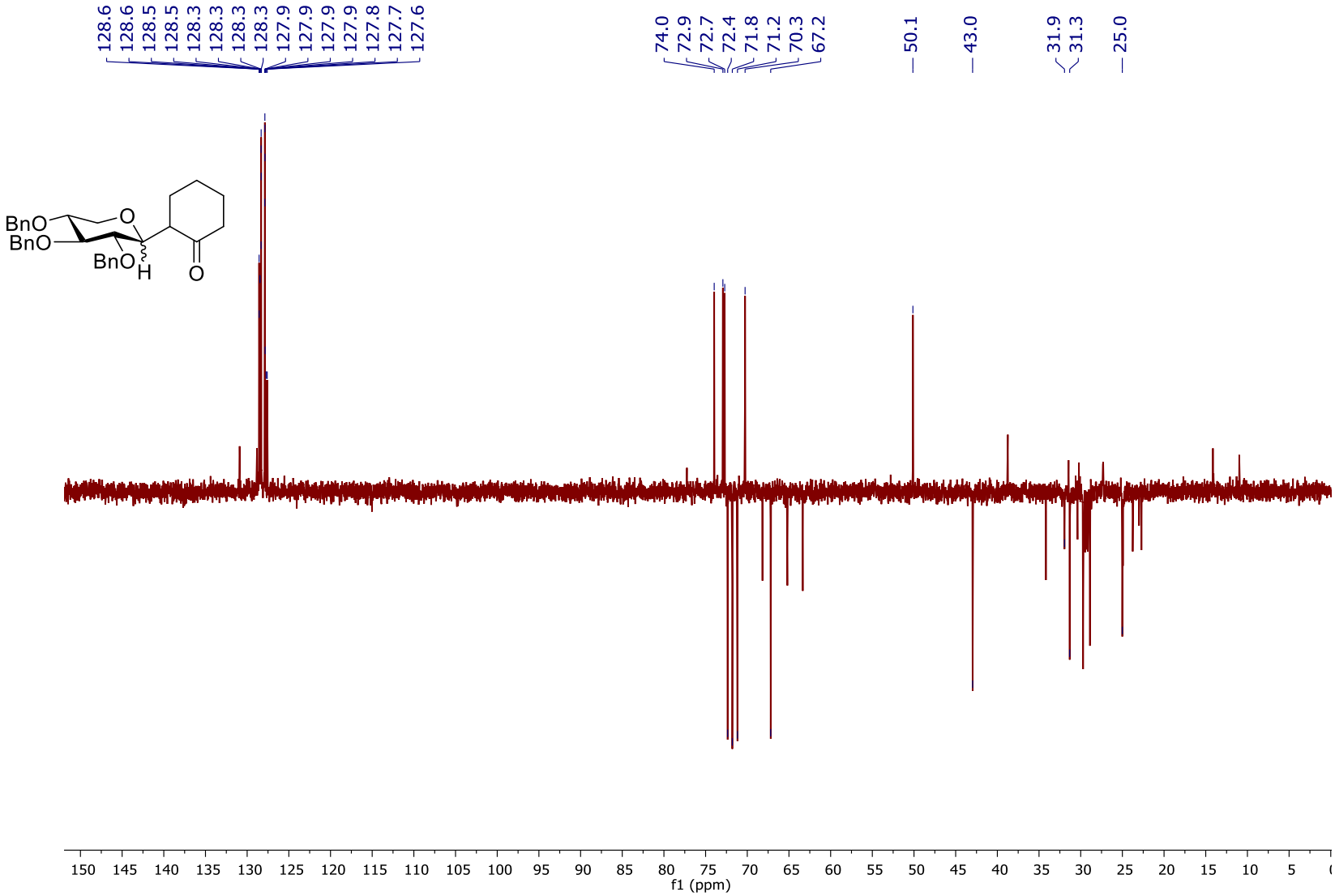
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4-tri-*O*-benzyl α/β-D-xylopyranoside **(10c):**



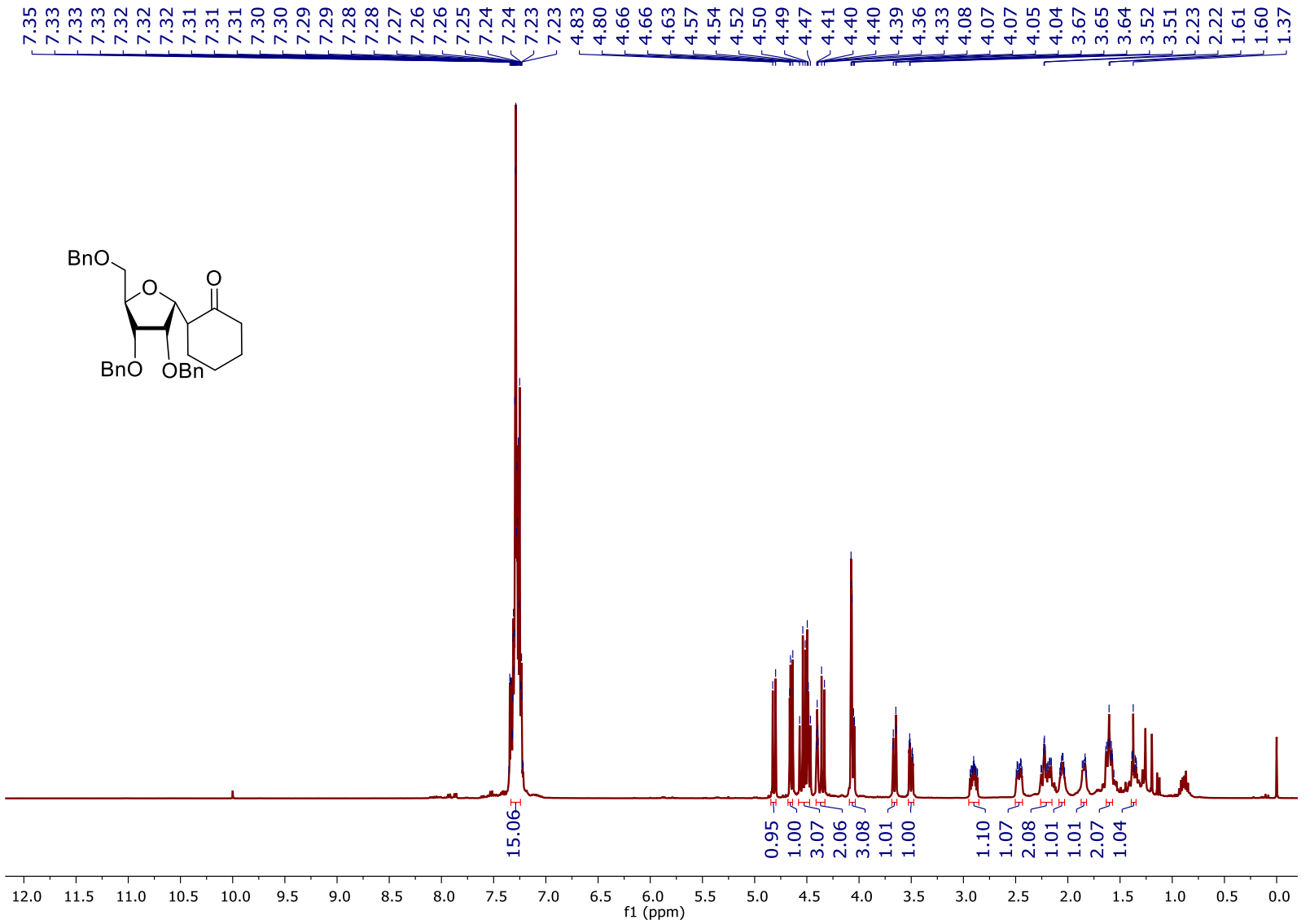
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4-tri-*O*-benzyl α/β-D-xylopyranoside **(10c):**



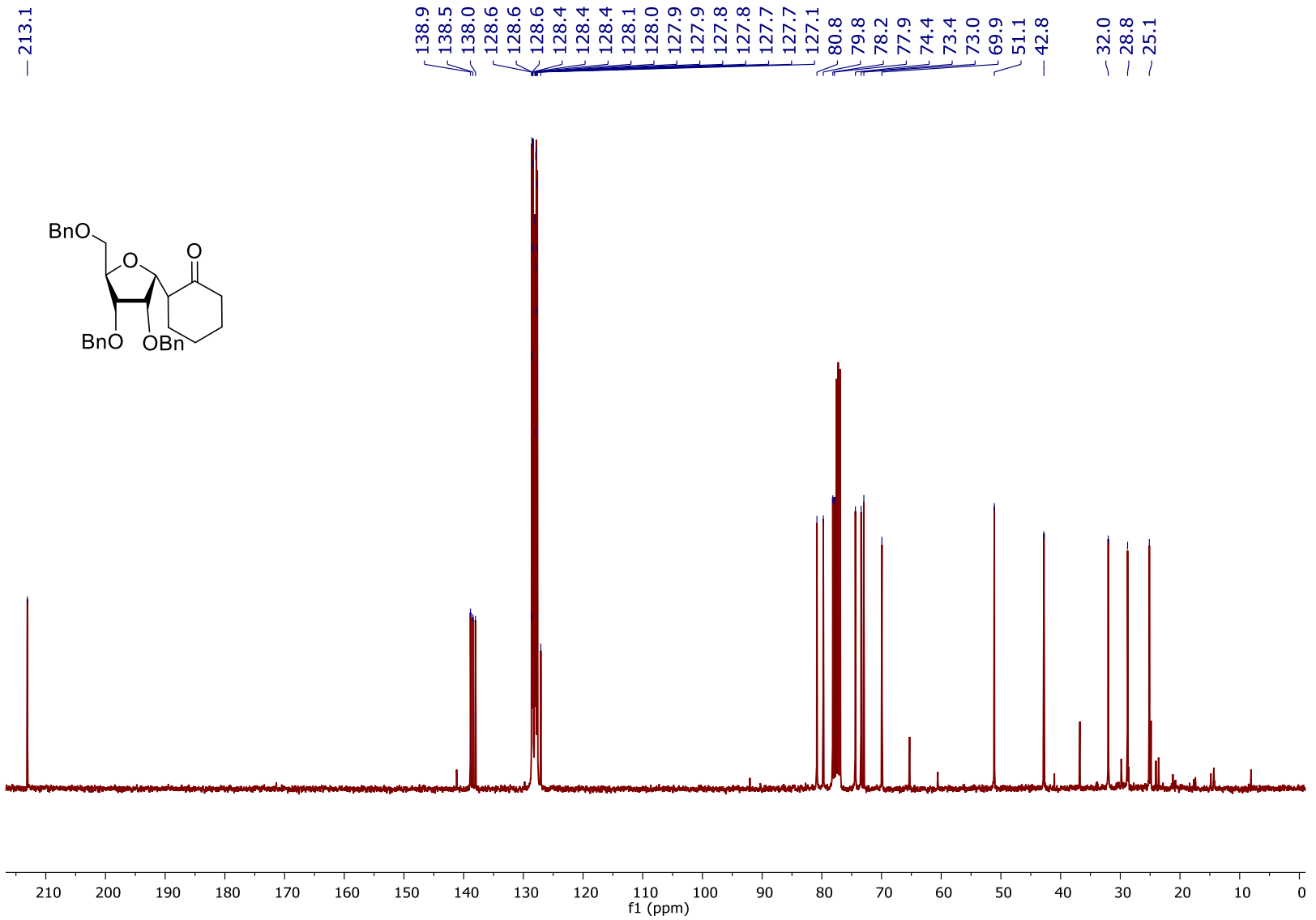
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,4-tri-*O*-benzyl α/β-D-xylopyranoside **(10c):**



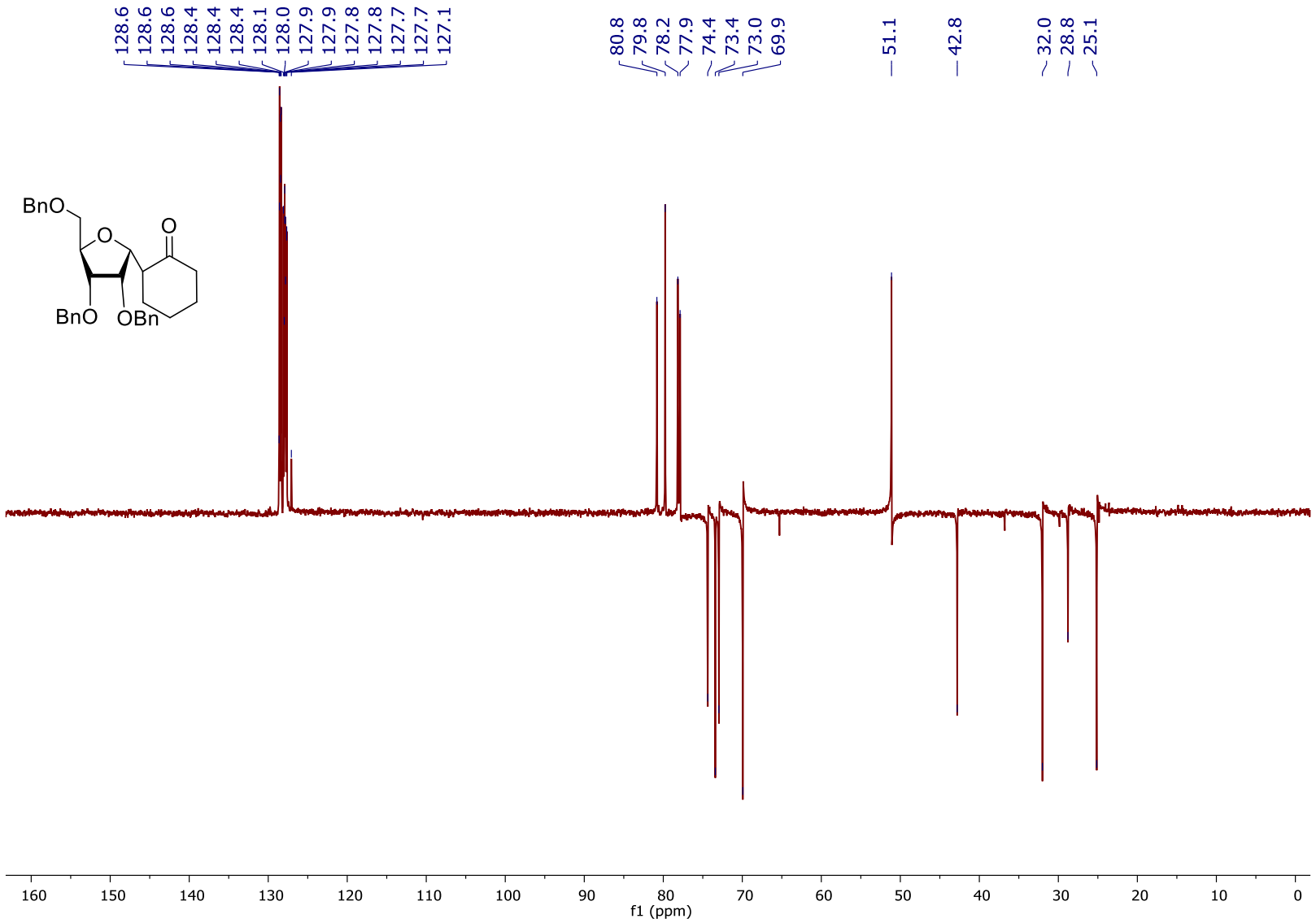
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(10d):**



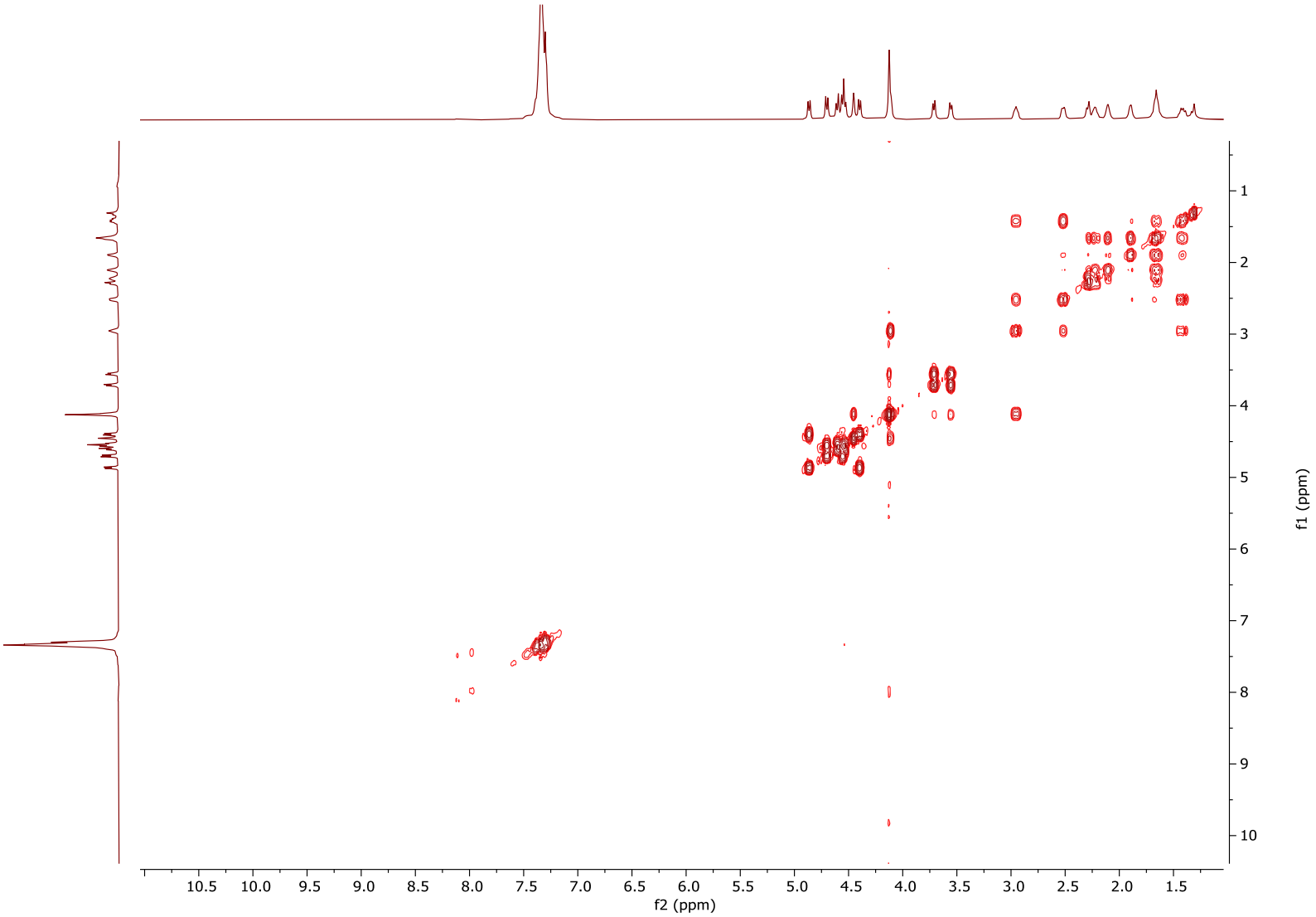
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(10d):**



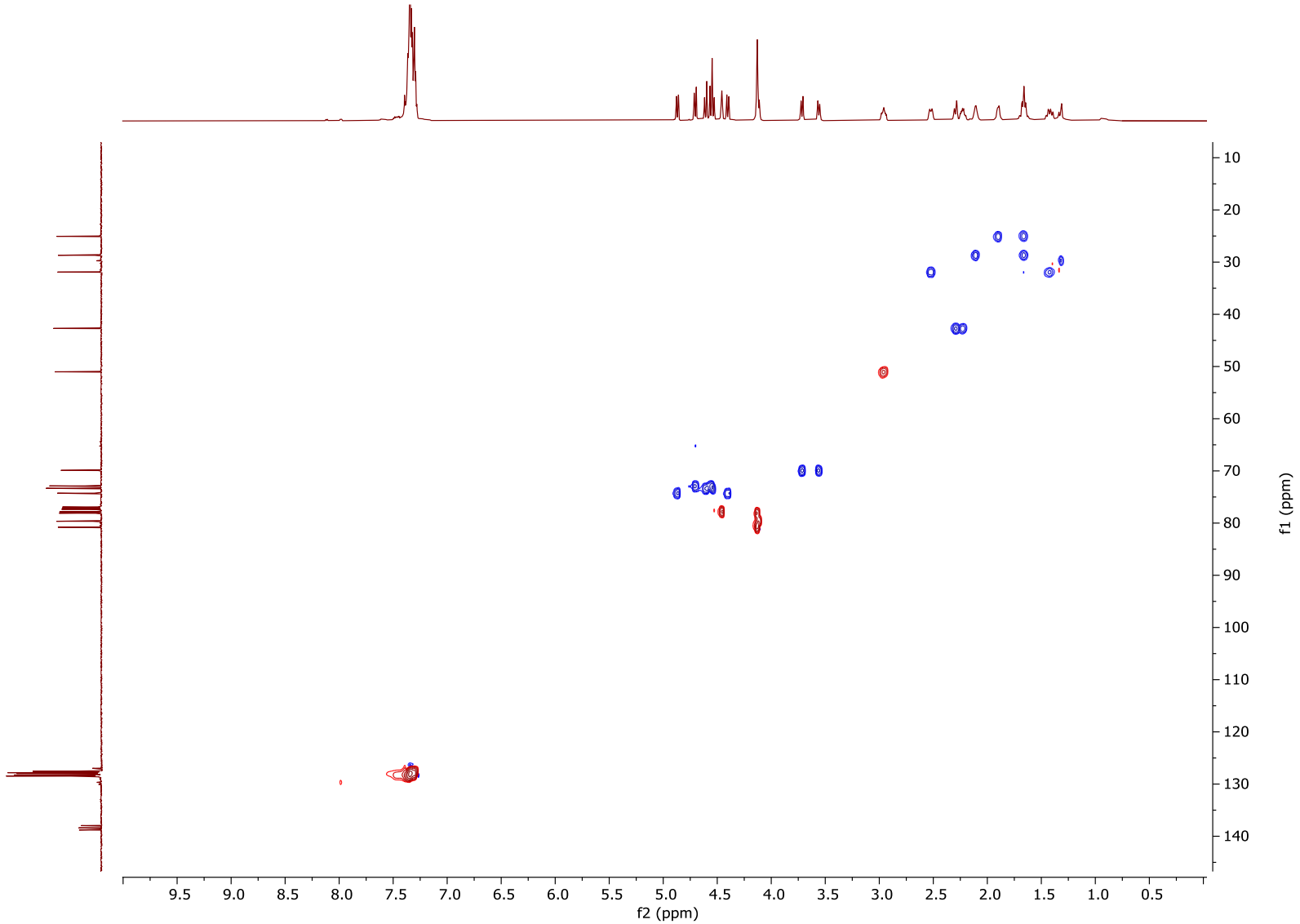
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(10d):**



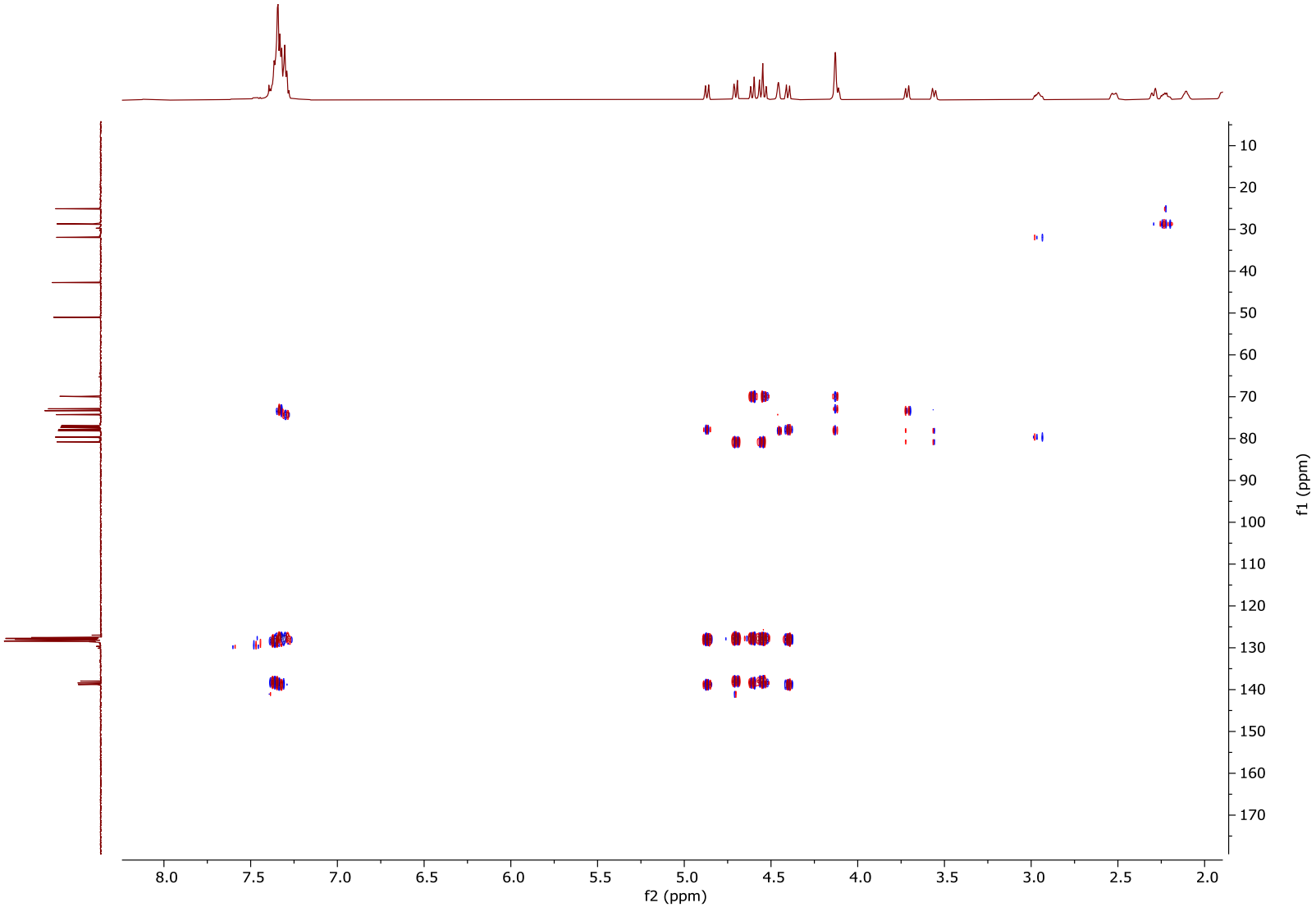
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(10d):**



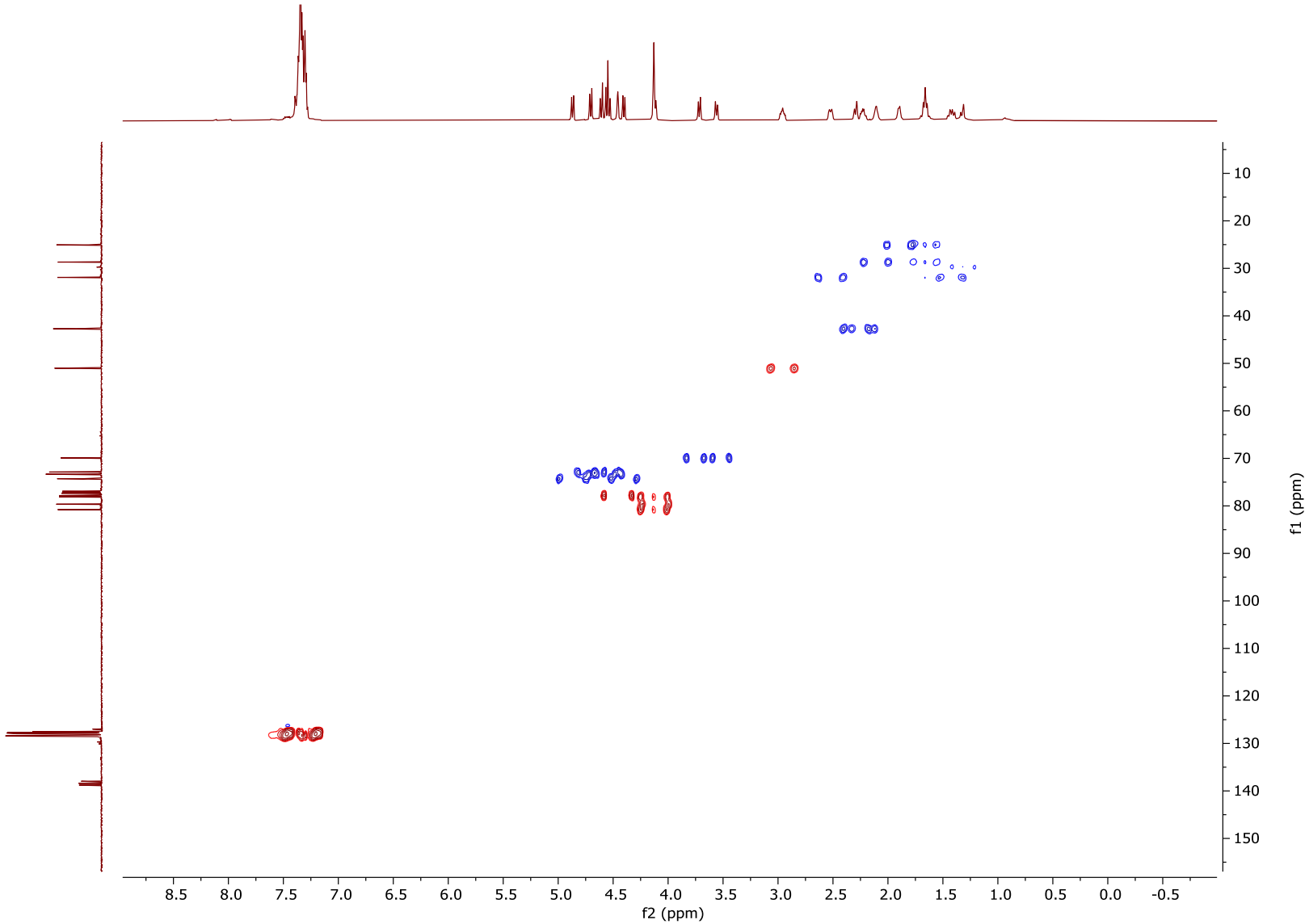
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(10d):**



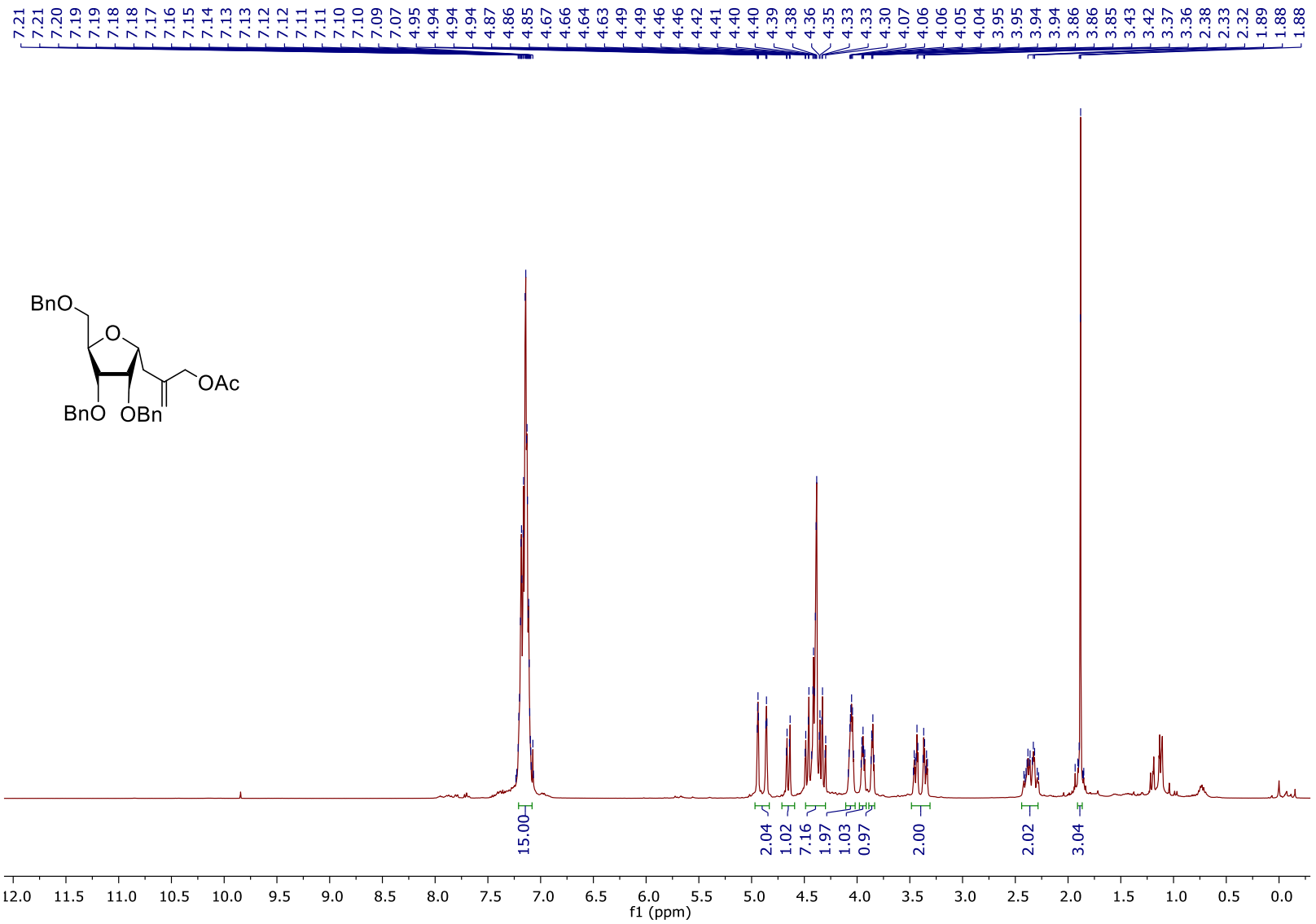
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(10d):**



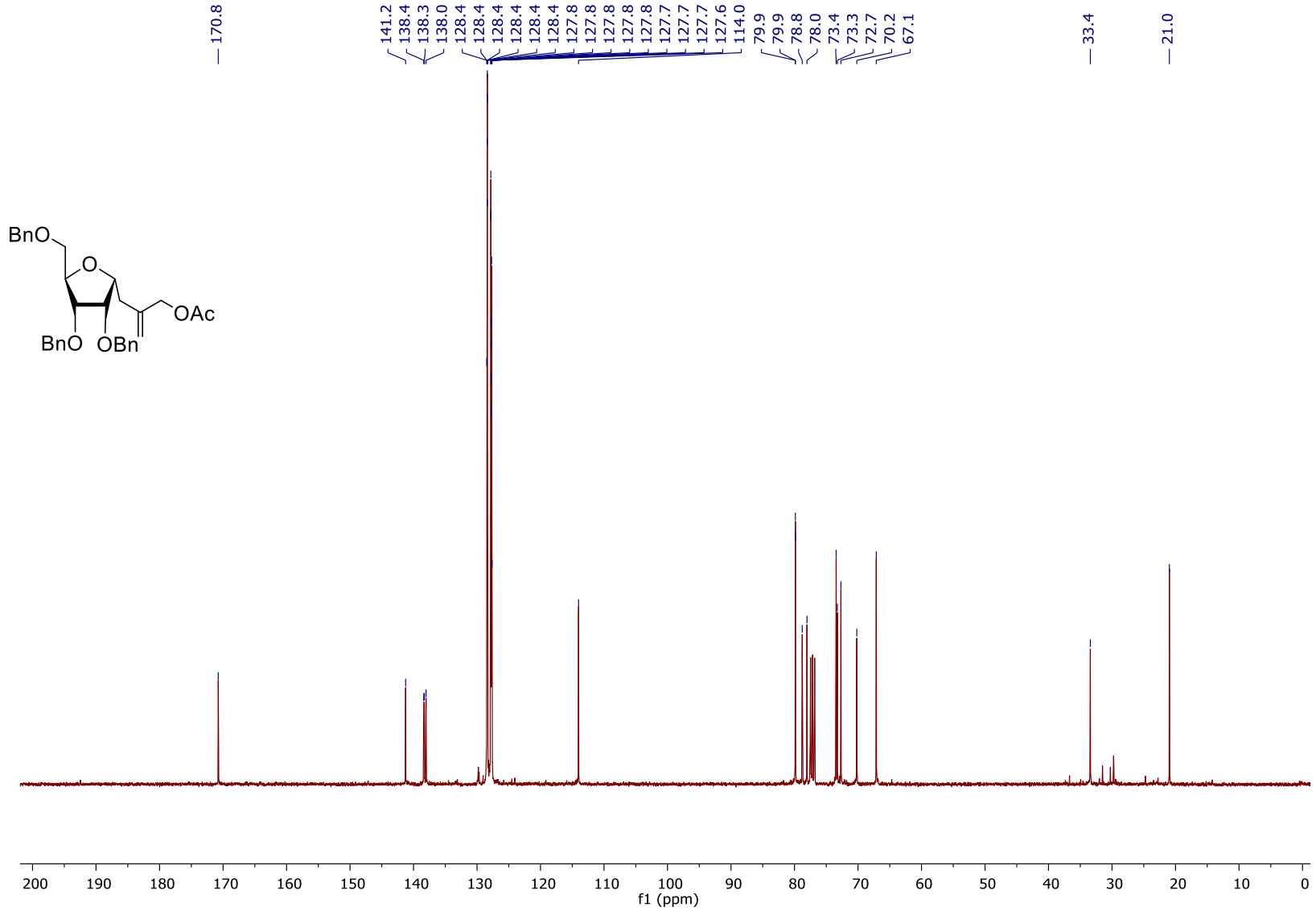
HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-*deoxy*-1-(Cyclohexane-2-one)-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(10d):**



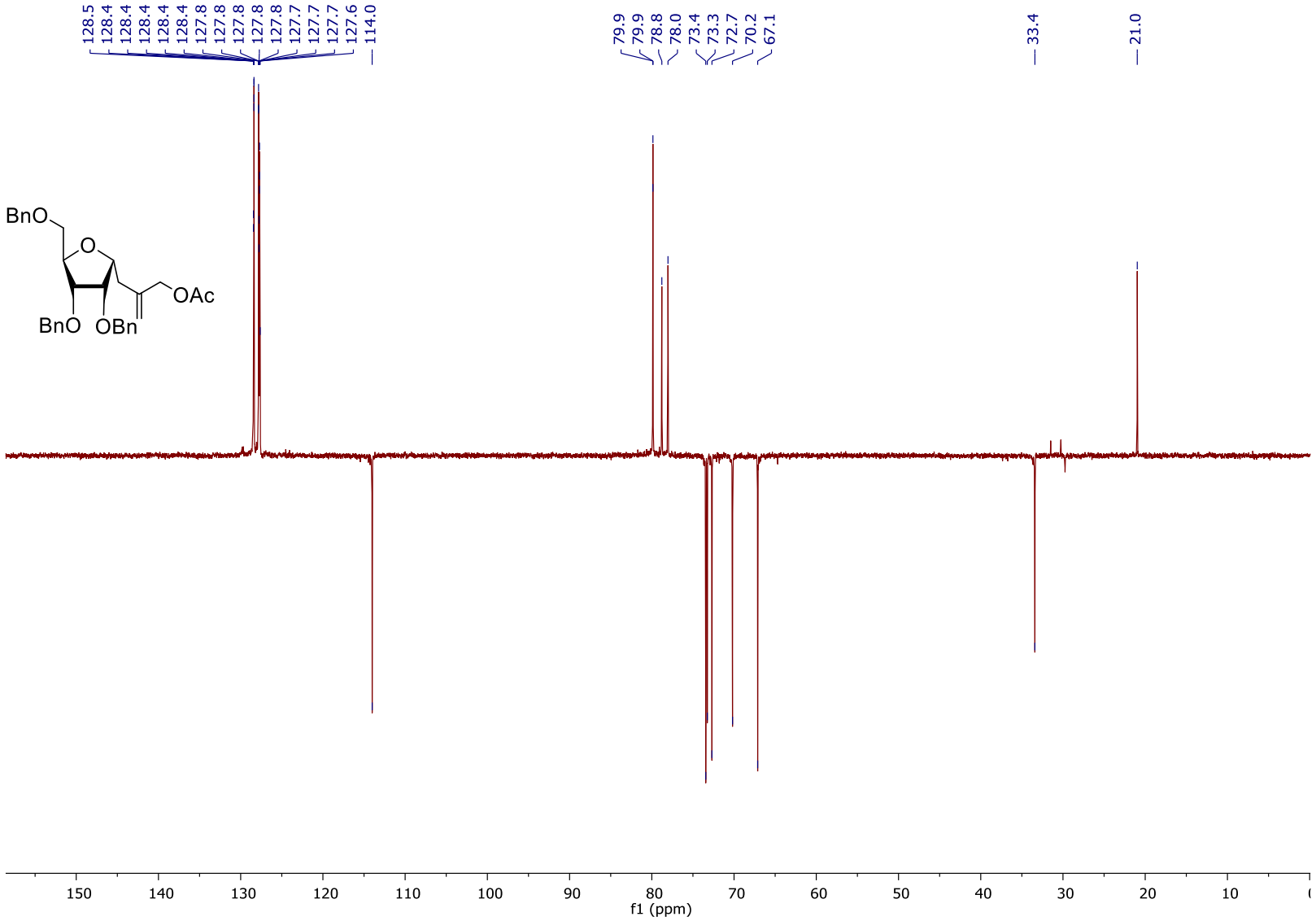
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α-D-ribofuranoside **(12a):**



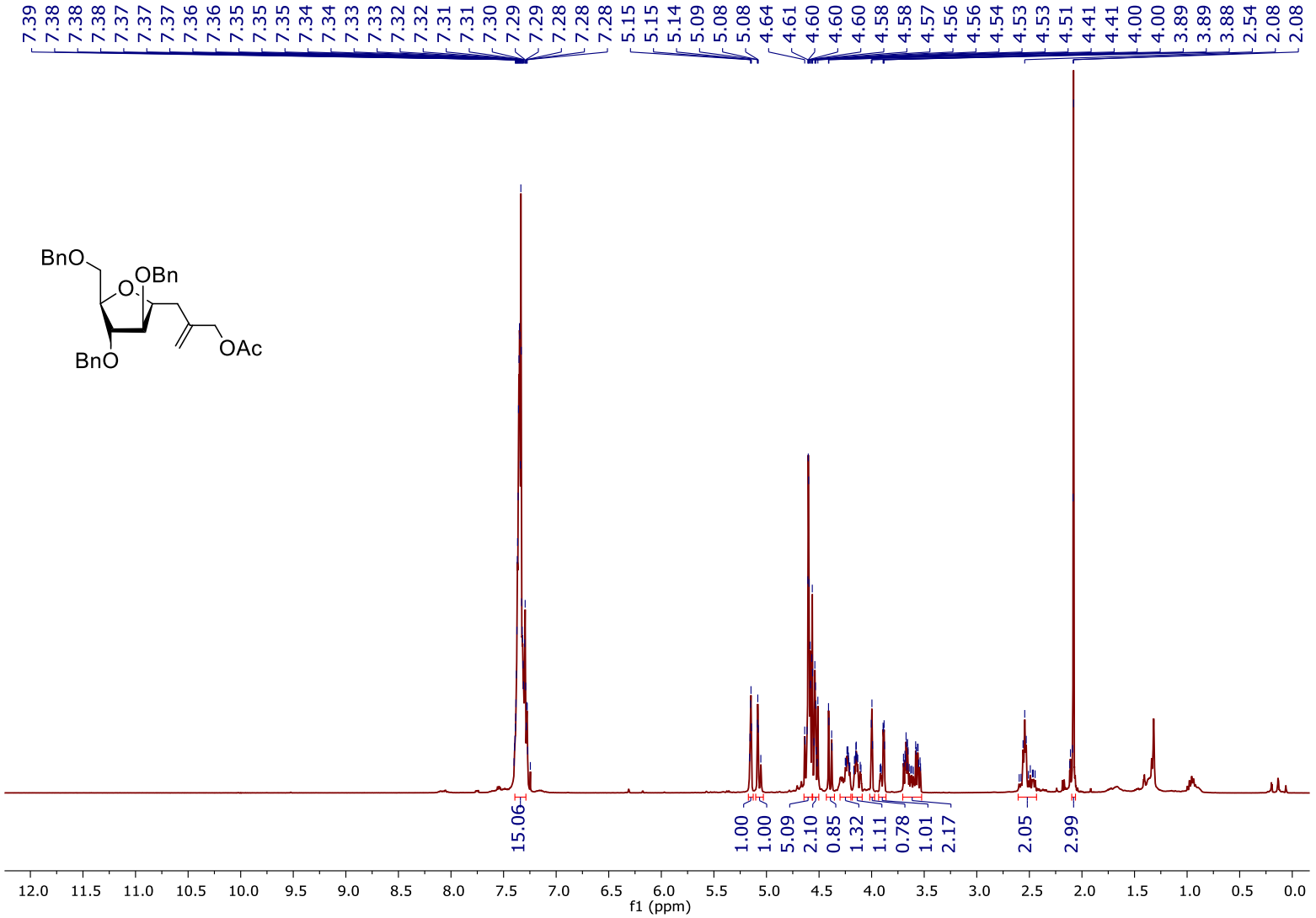
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α-D-ribofuranoside **(12a):**



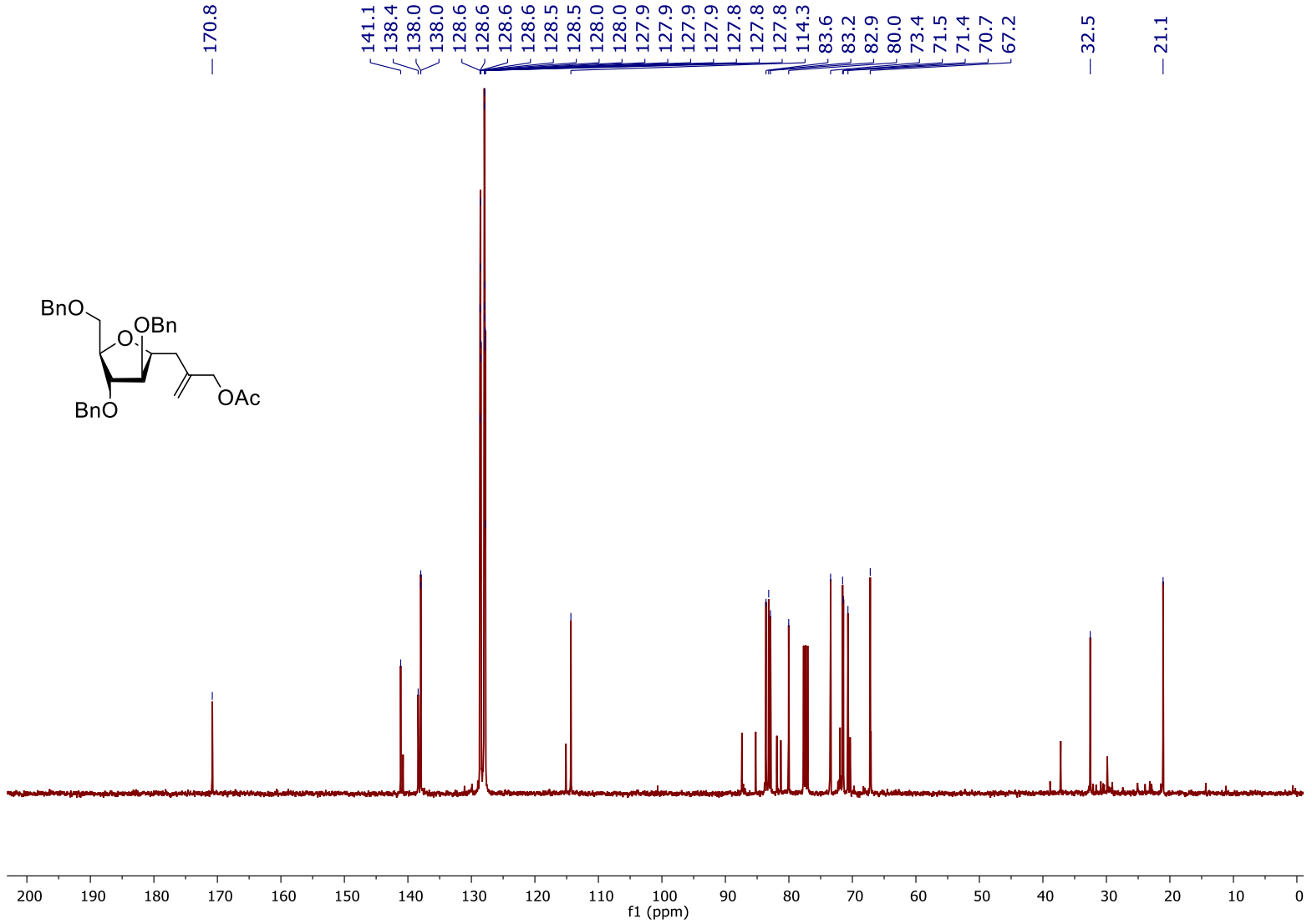
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α-D-ribofuranoside **(12a):**



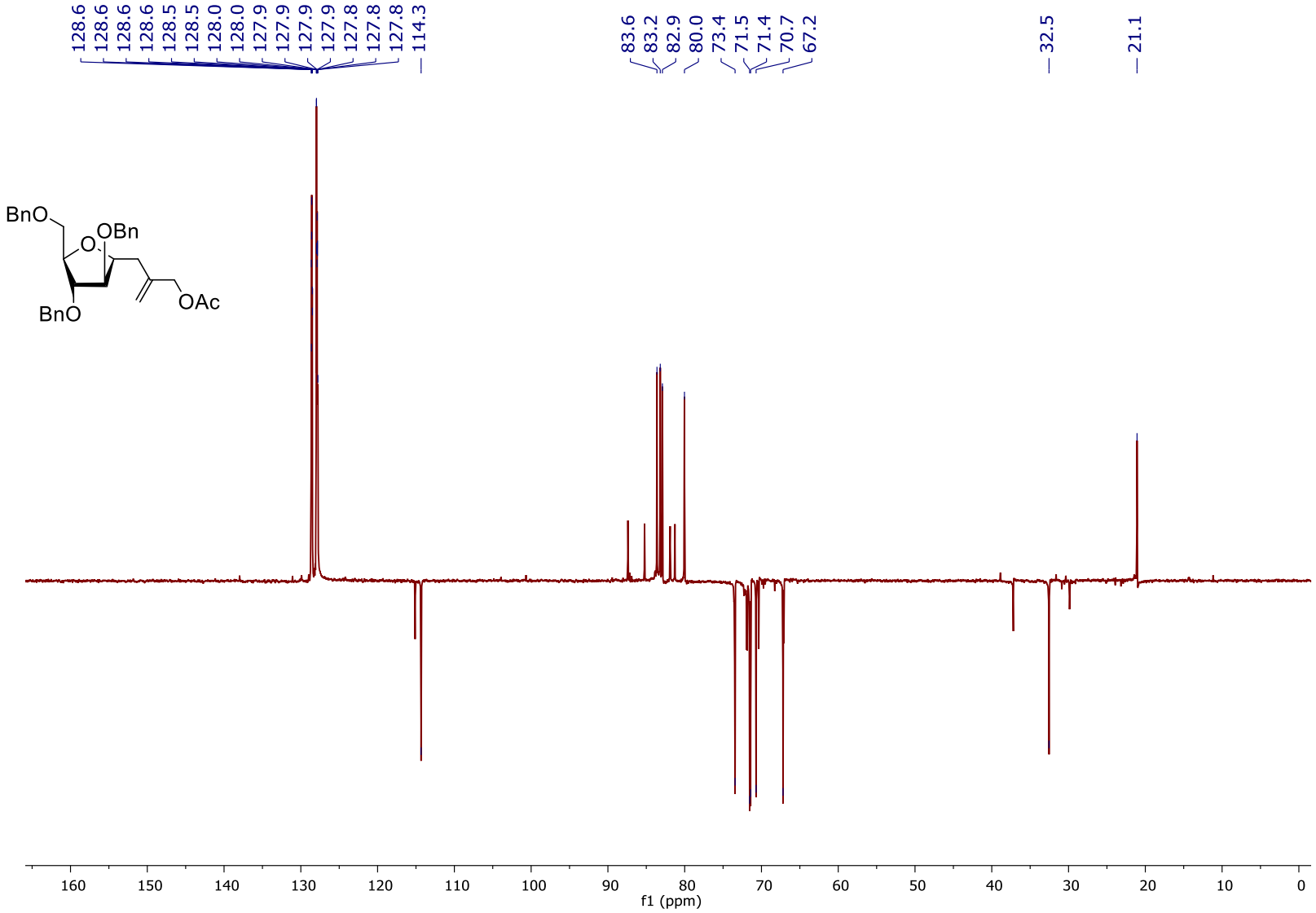
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α/β-D-arabinofuranoside **(12b):**



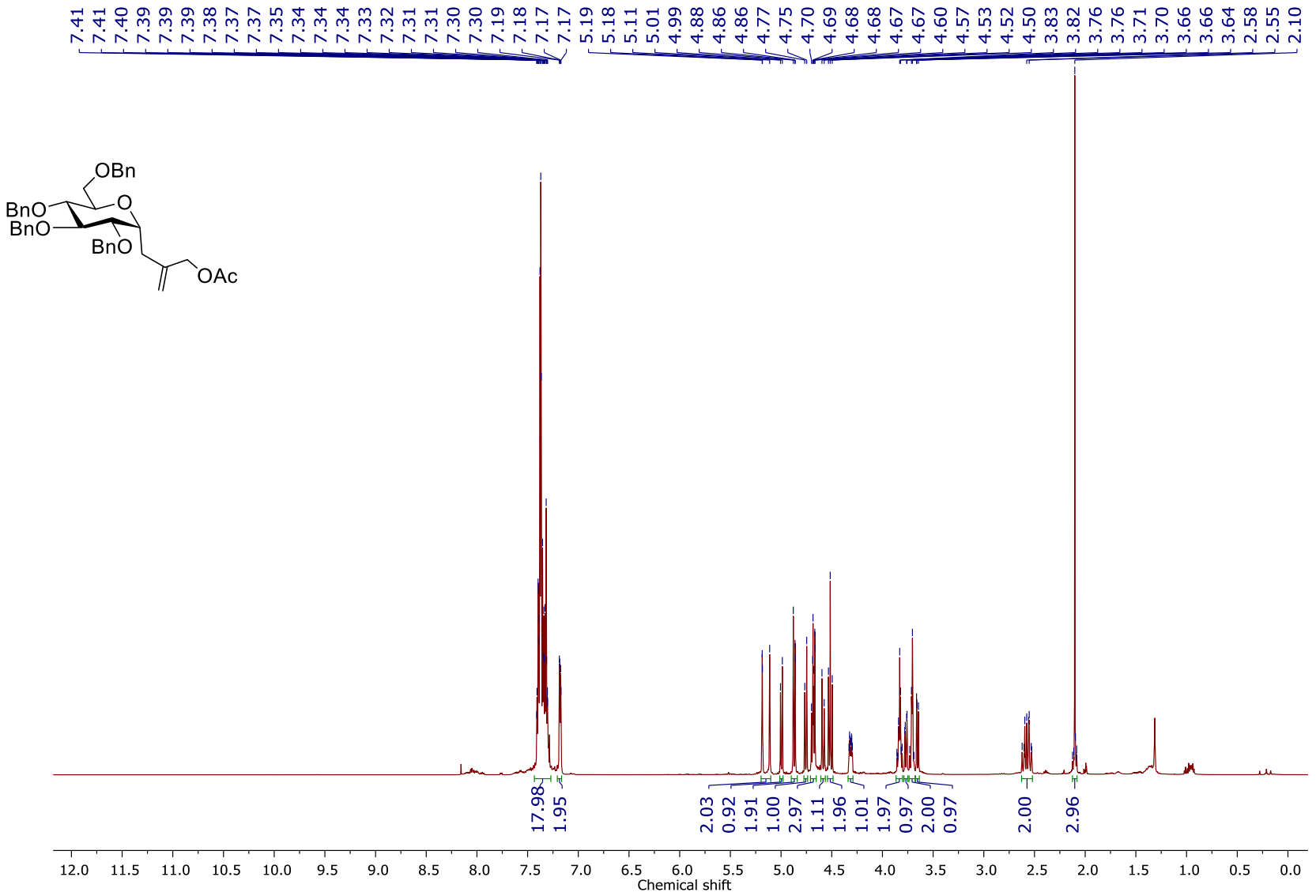
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α/β-D-arabinofuranoside **(12b):**



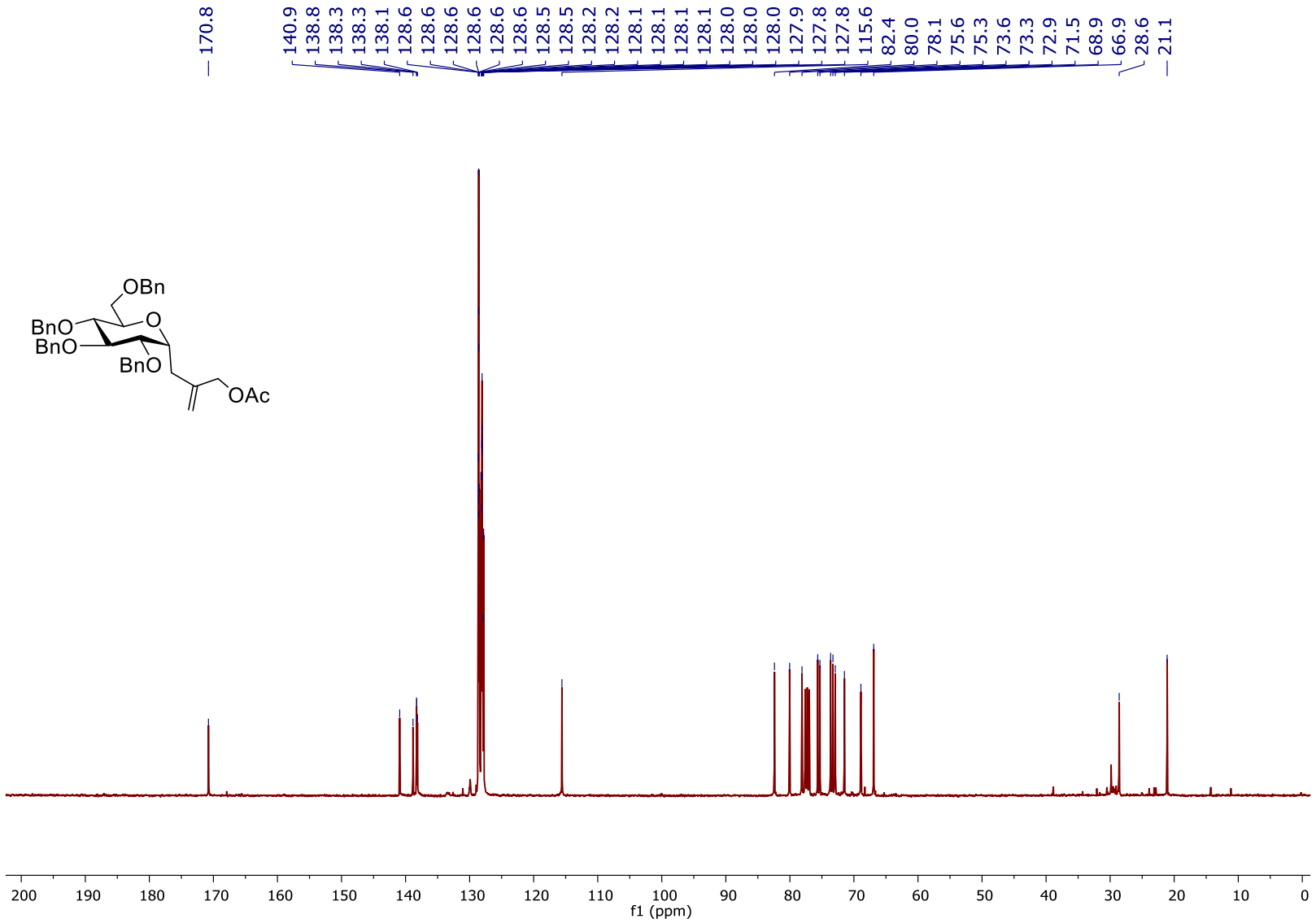
DEPT Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,5-tri-O-benzyl α/β-D-arabinofuranoside **(12b):**



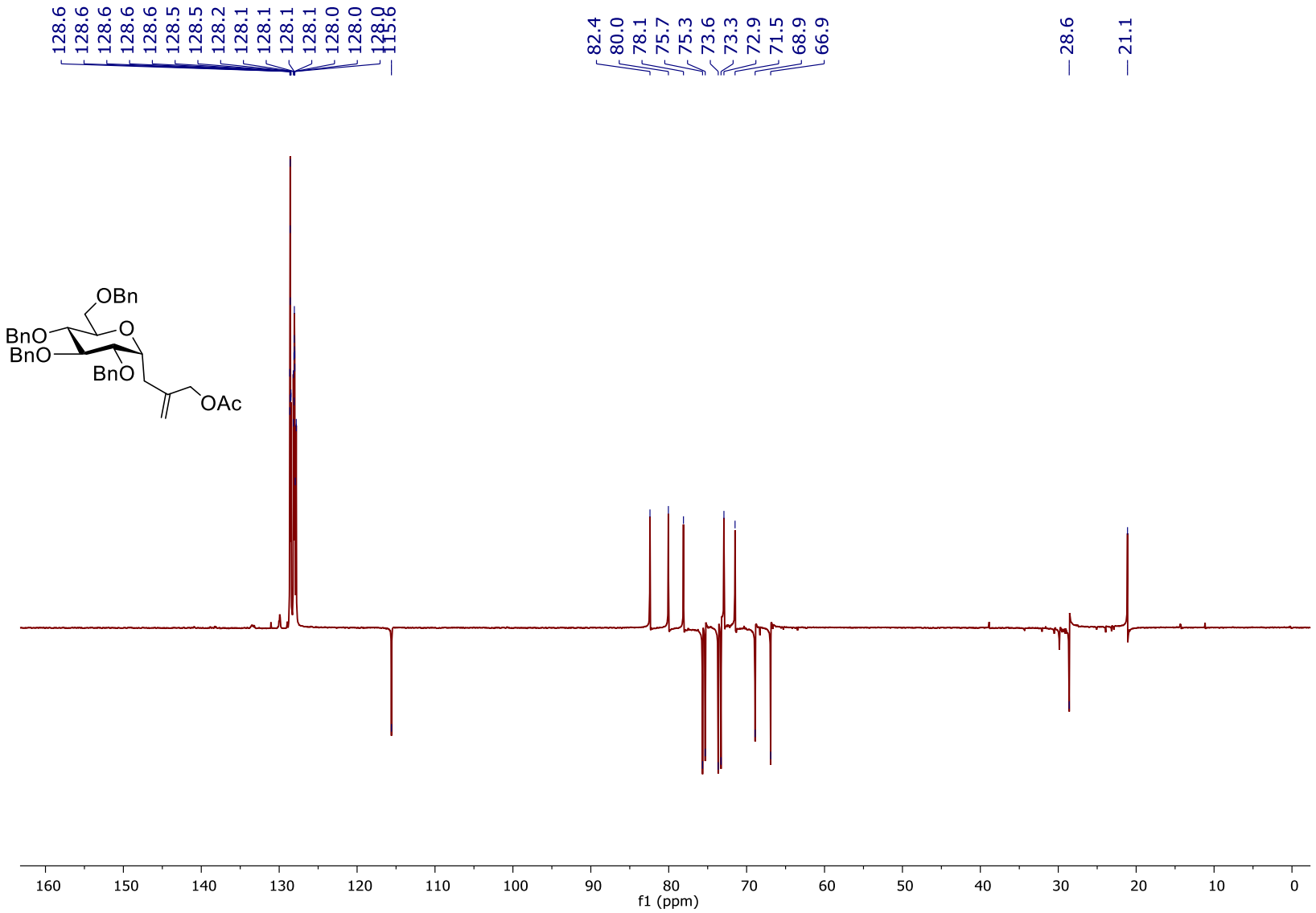
^{1}H NMR Spectrum (600 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(12c):**



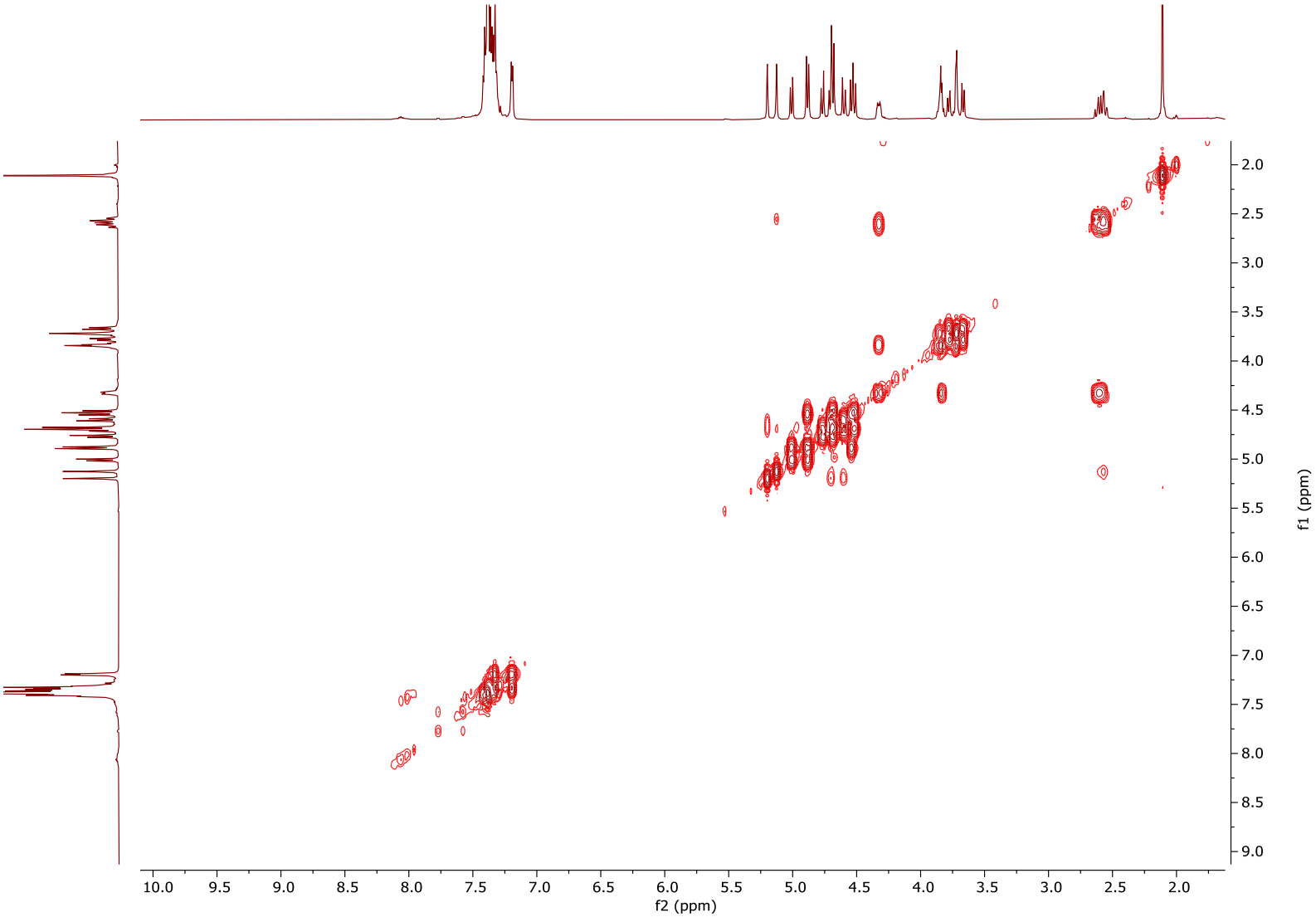
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D-glucopyranoside **(12c):**



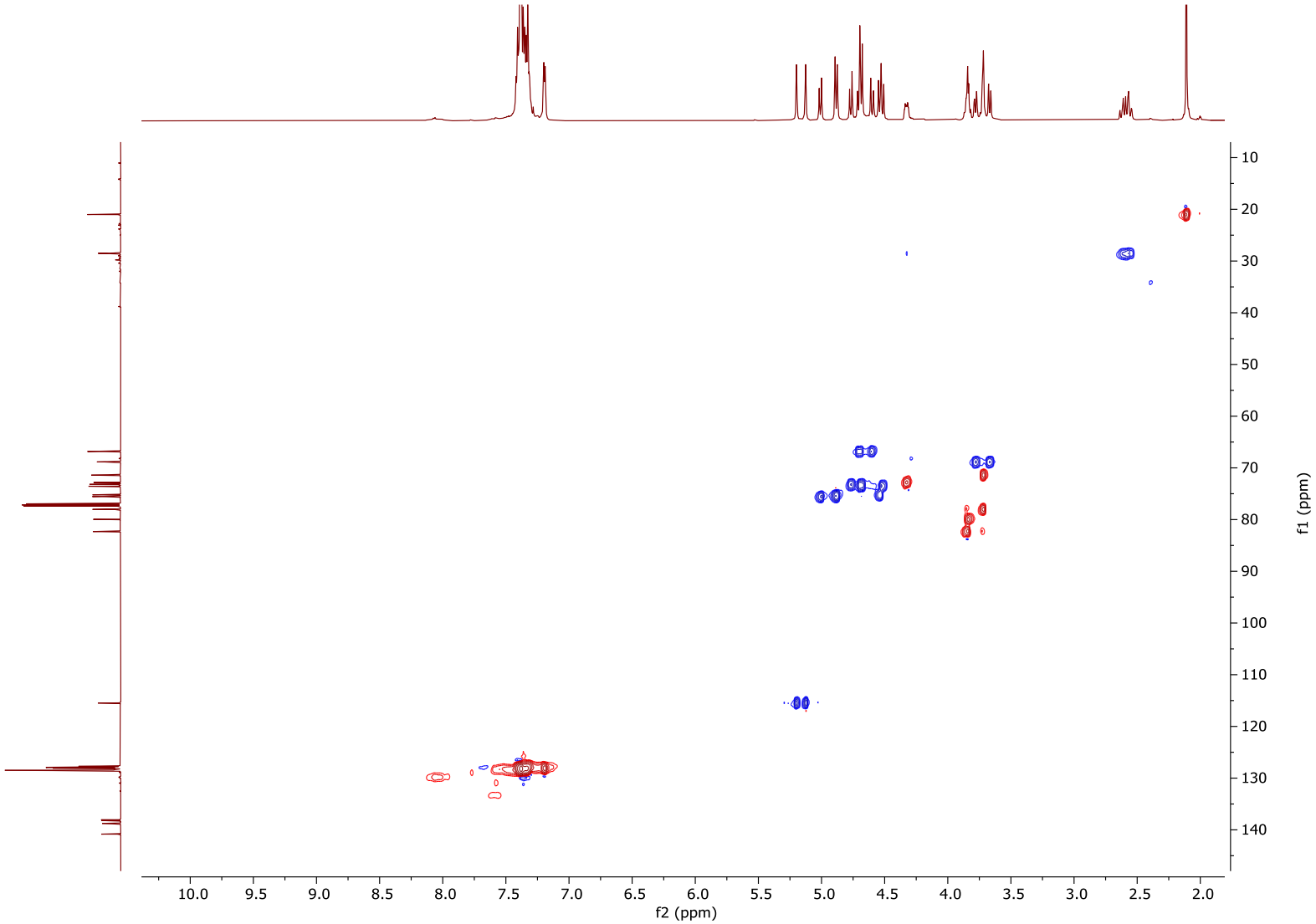
DEPT Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D- glucopyranoside **(12c):**



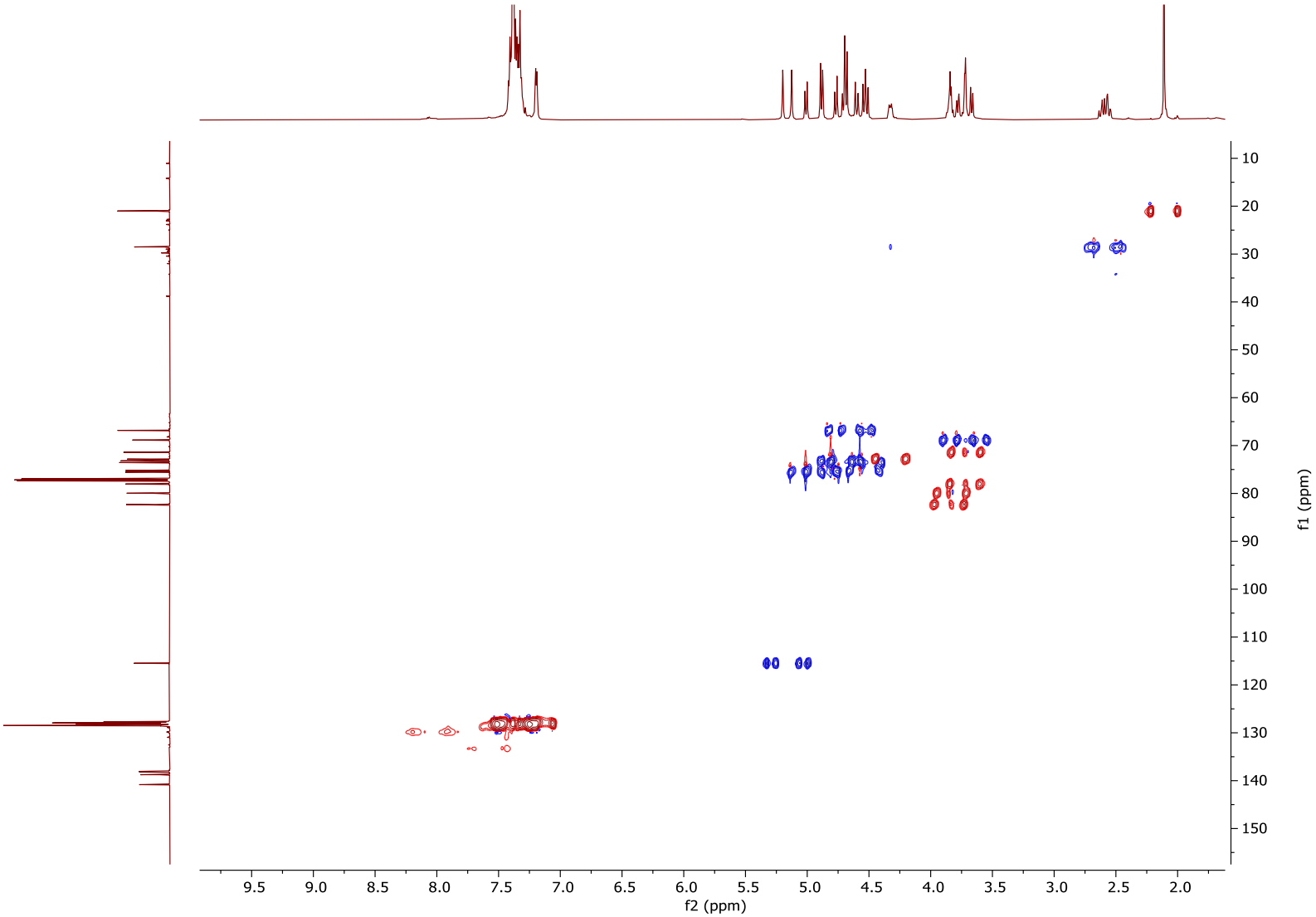
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D- glucopyranoside **(12c):**



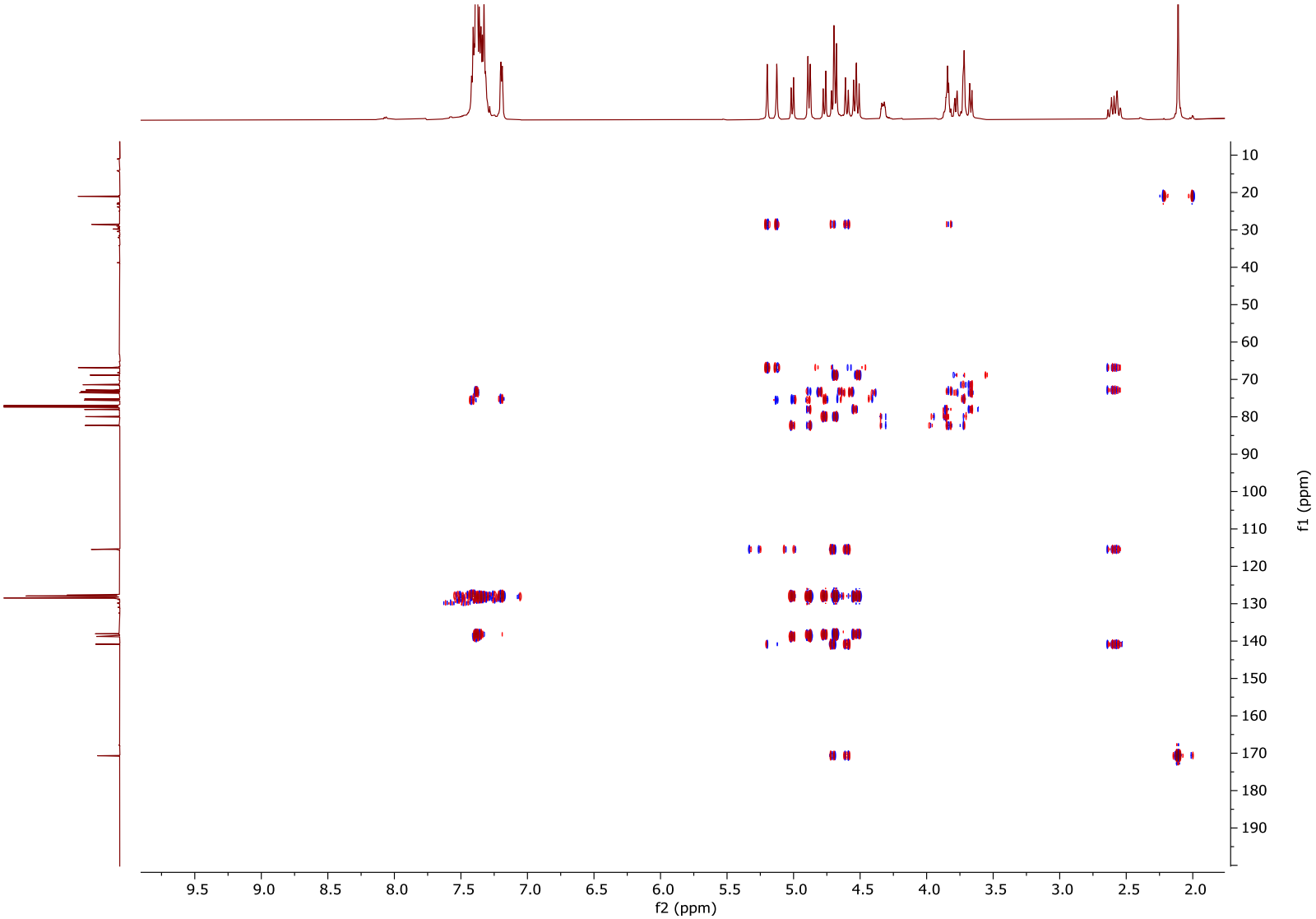
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D- glucopyranoside **(12c):**



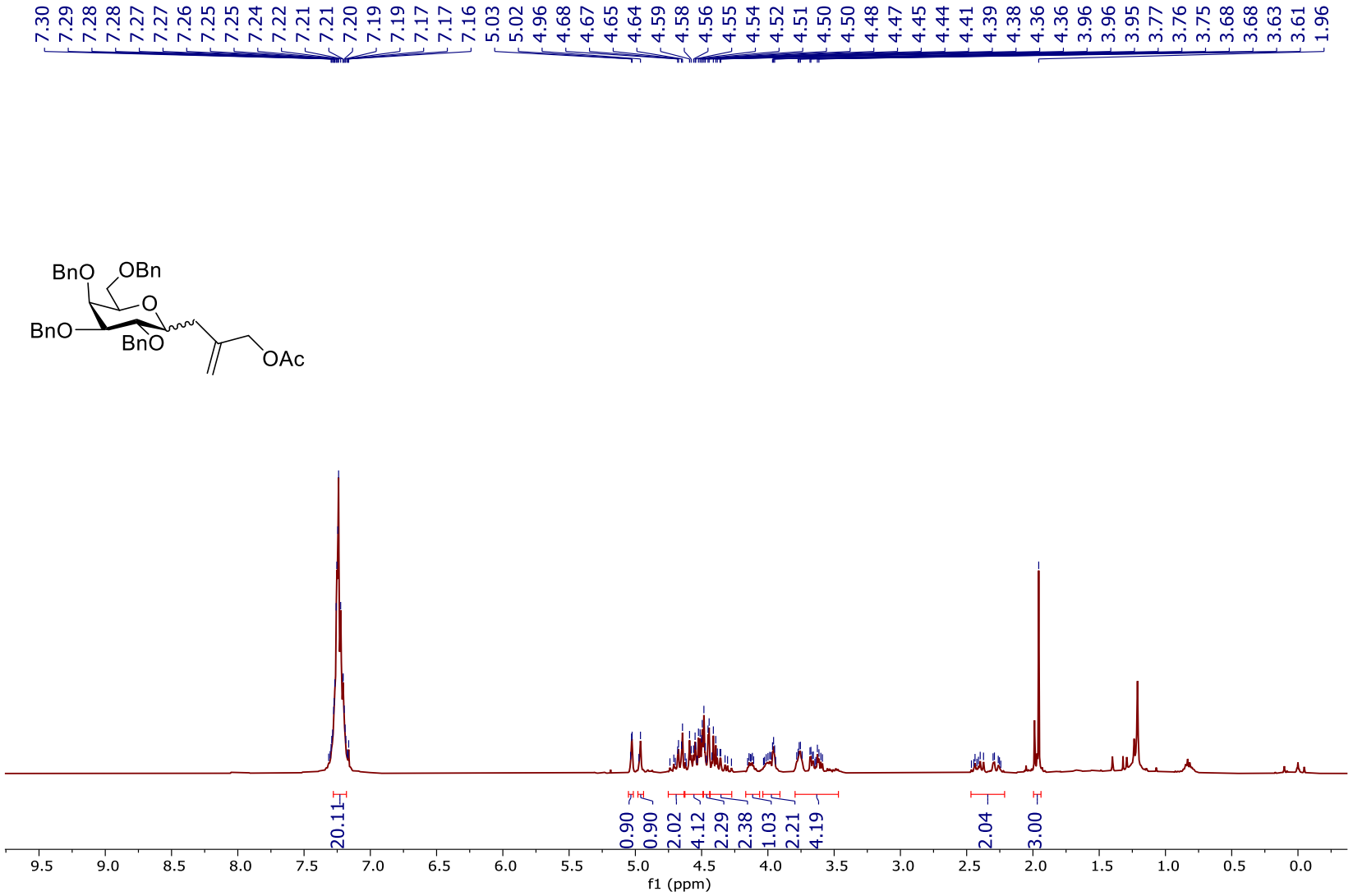
HSQC coupled Spectrum (600 MHz) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D- glucopyranoside **(12c):**



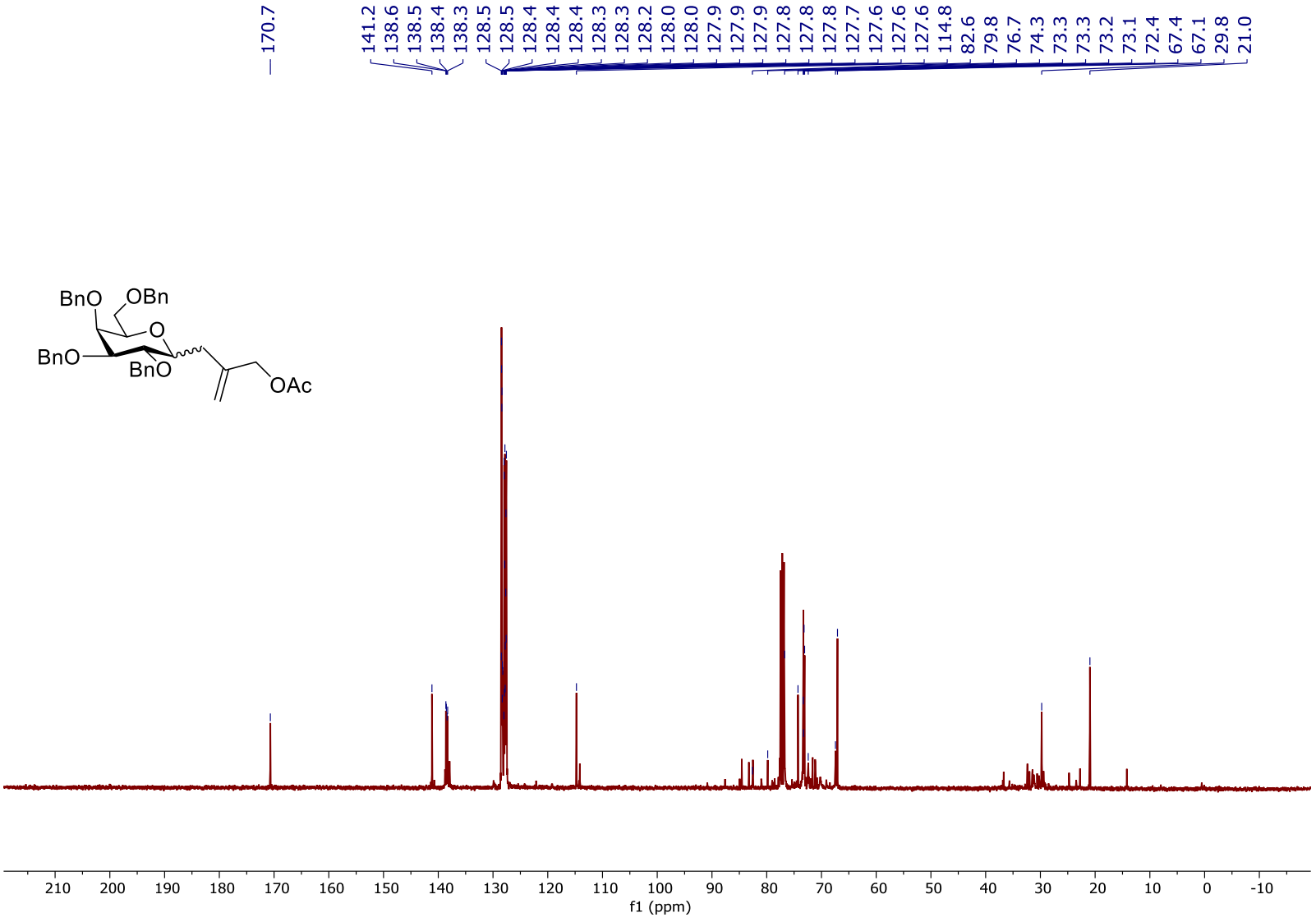
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α-D- glucopyranoside **(12c):**



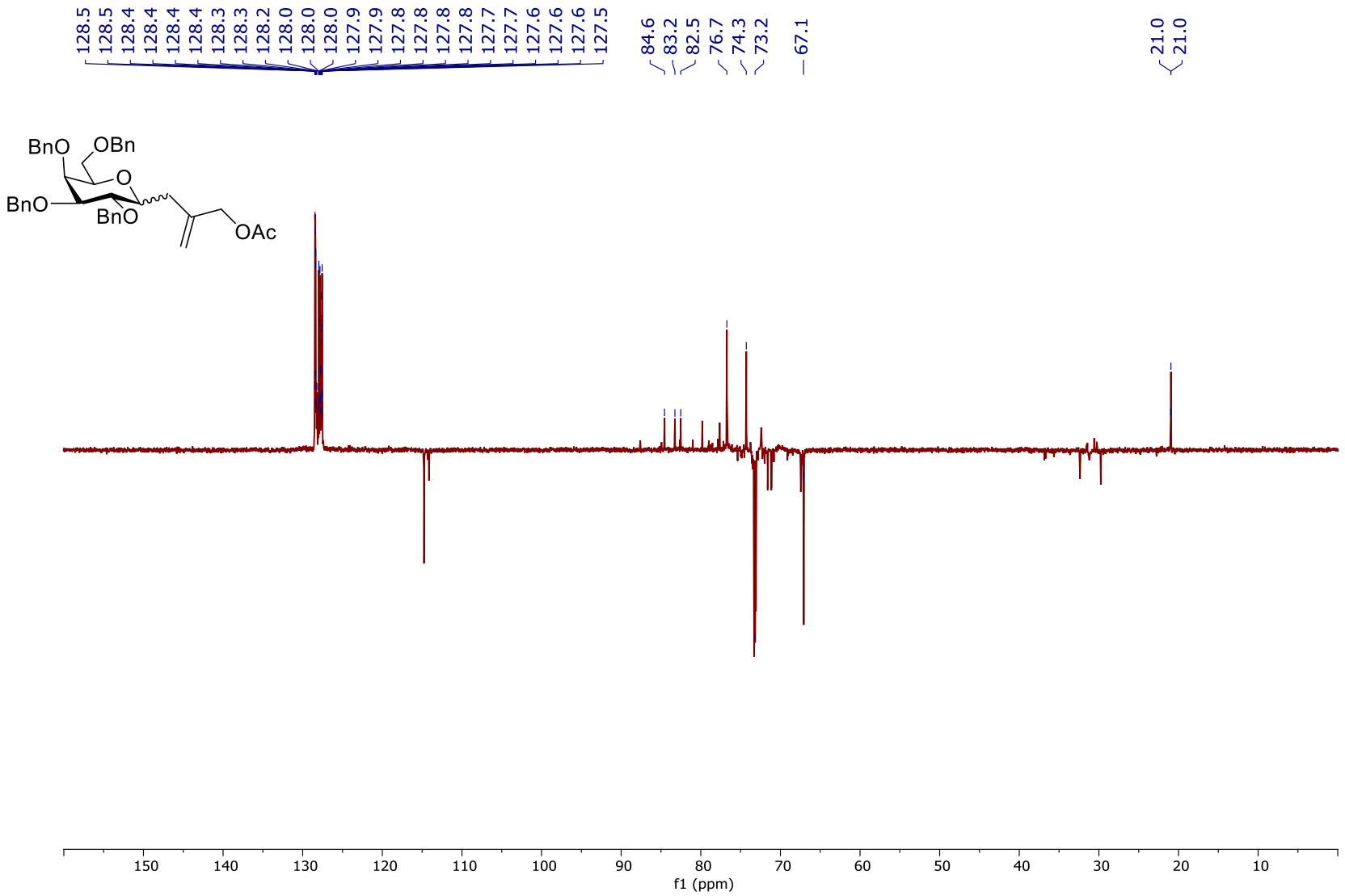
^{1}H Spectrum (400 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranoside **(12d):**



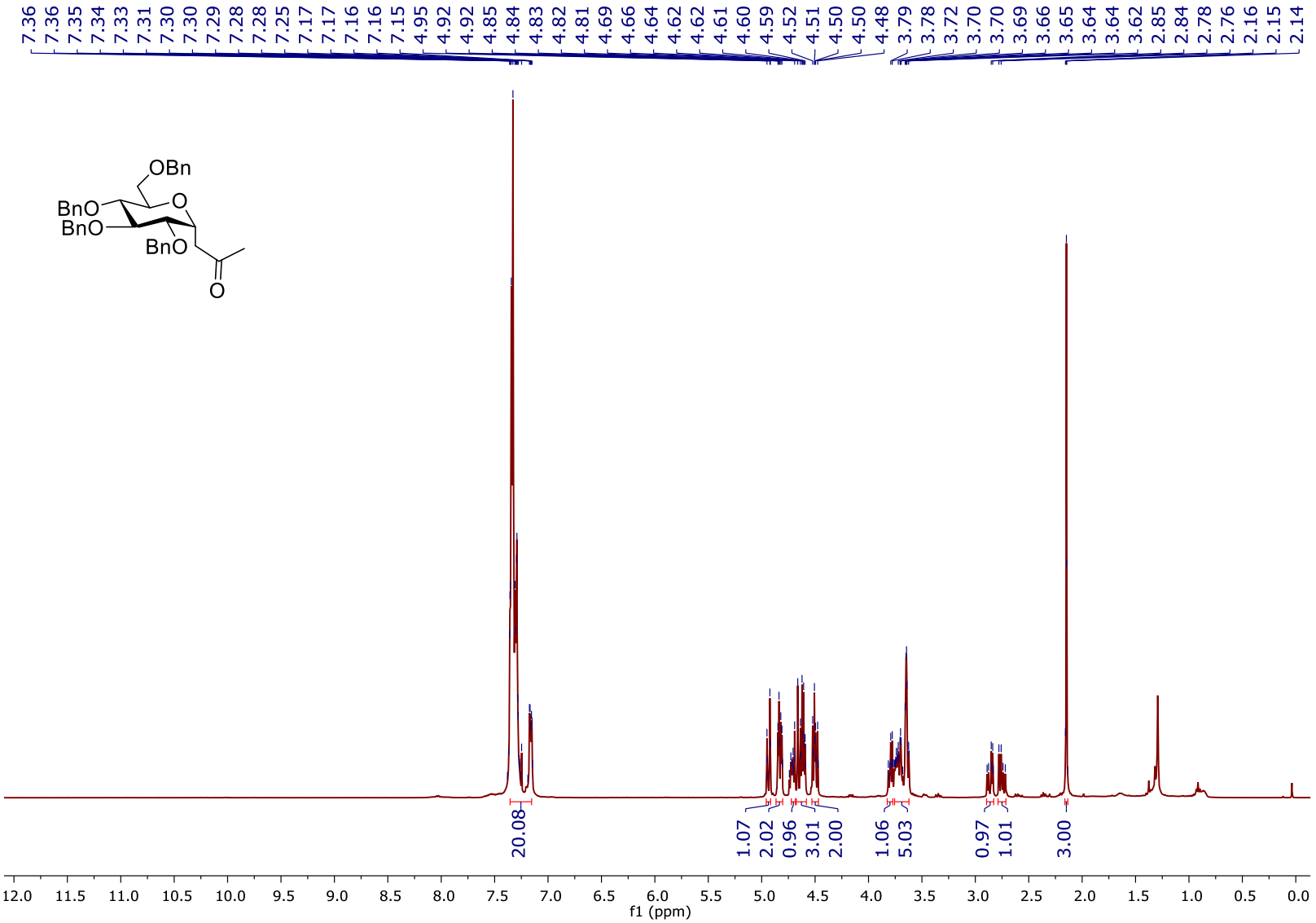
^{13}C Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranoside **(12d):**



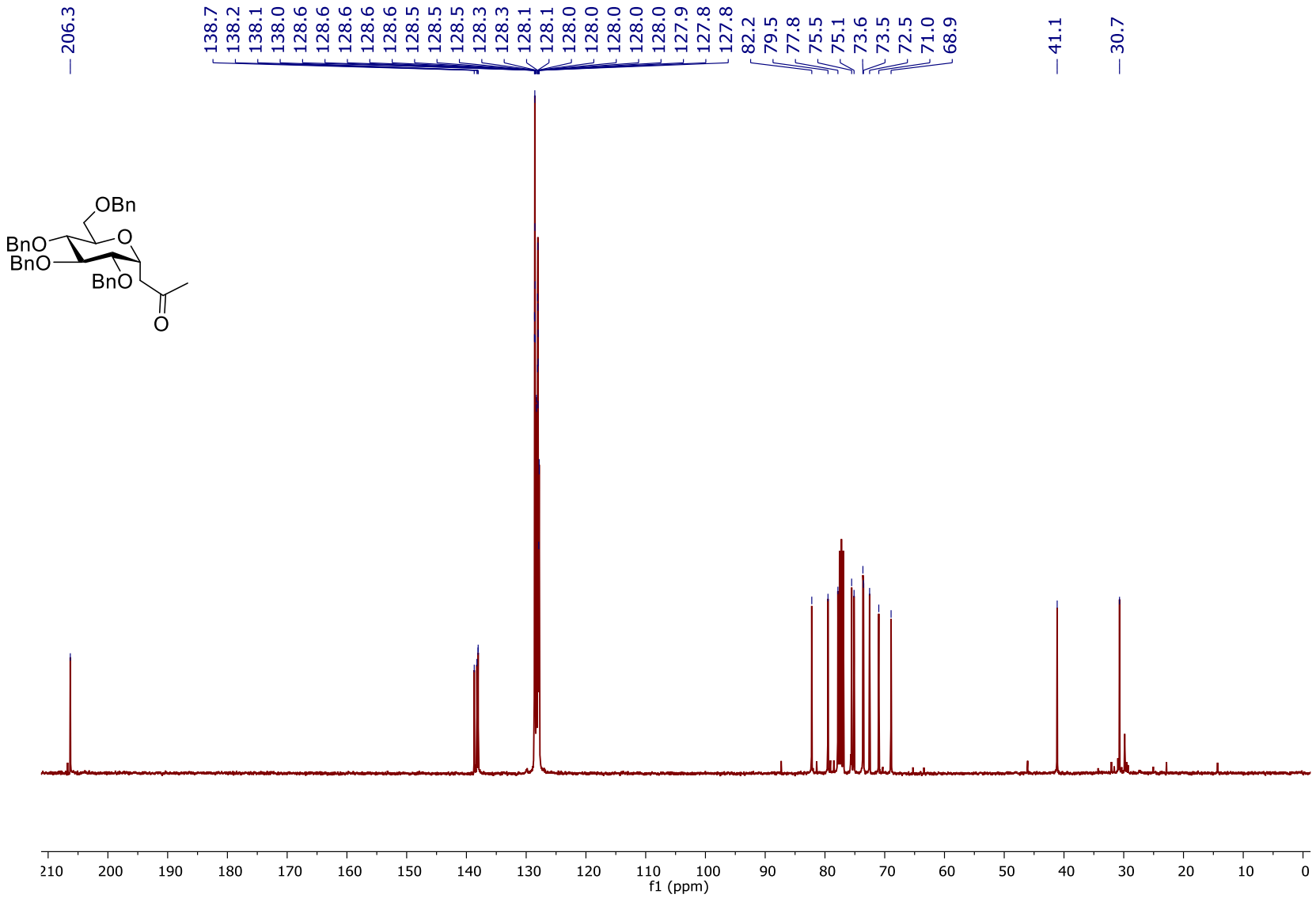
DEPT Spectrum (101 MHz, $CDCl_3$) of 1-(2-acetoxymethyl allyl)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl α/β-D-galactopyranoside **(12d):**



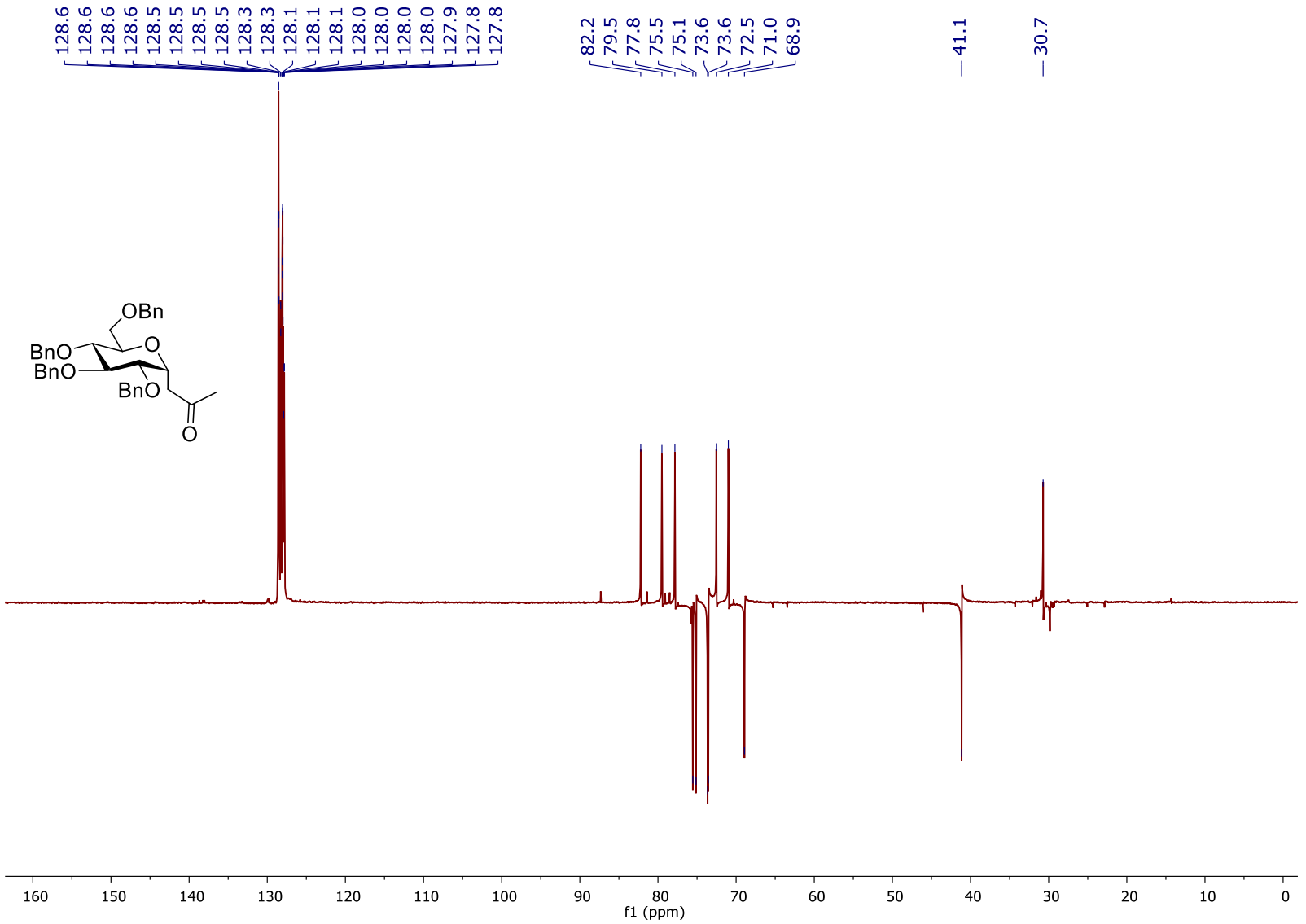
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside **(13a):**



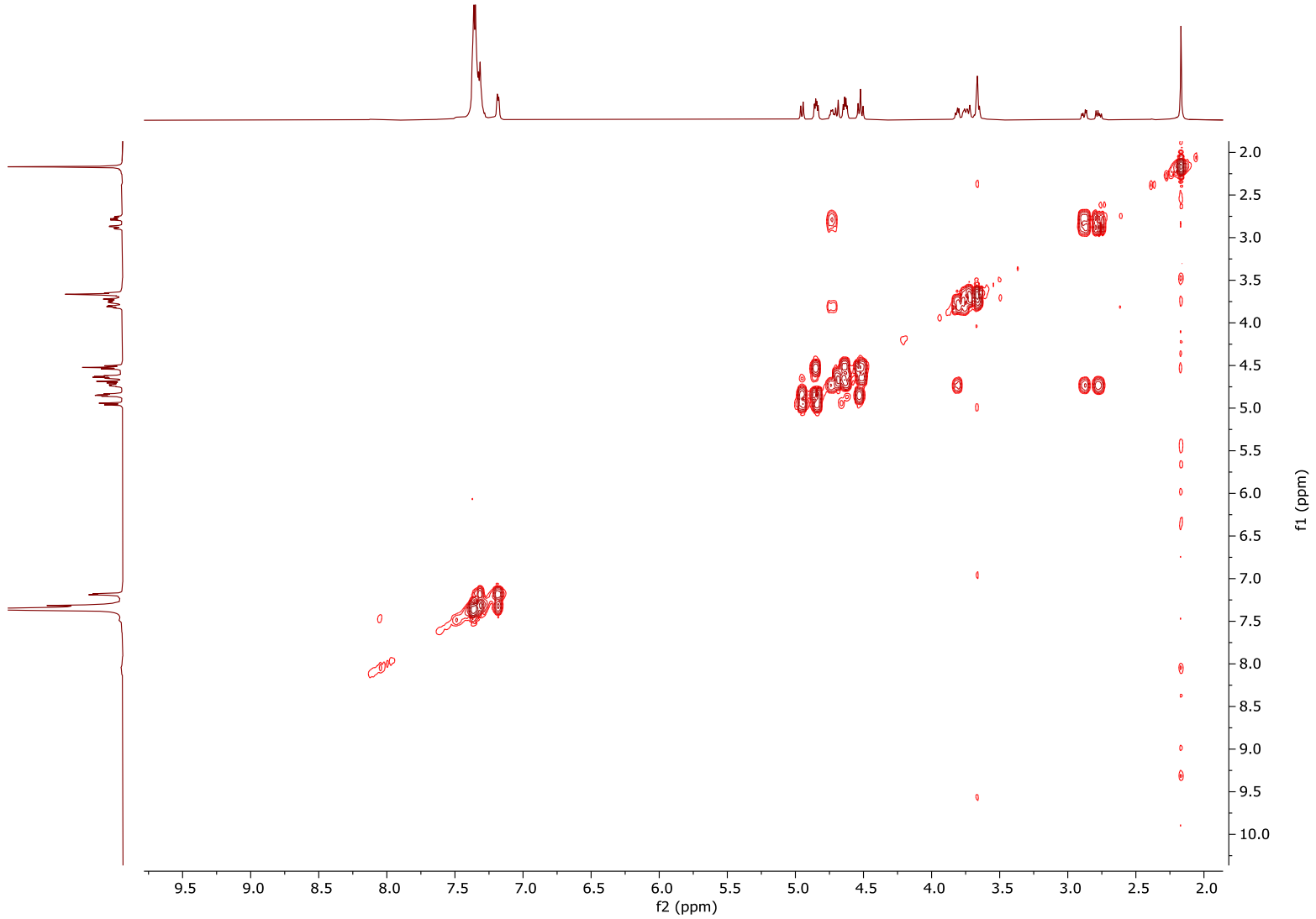
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside **(13a):**



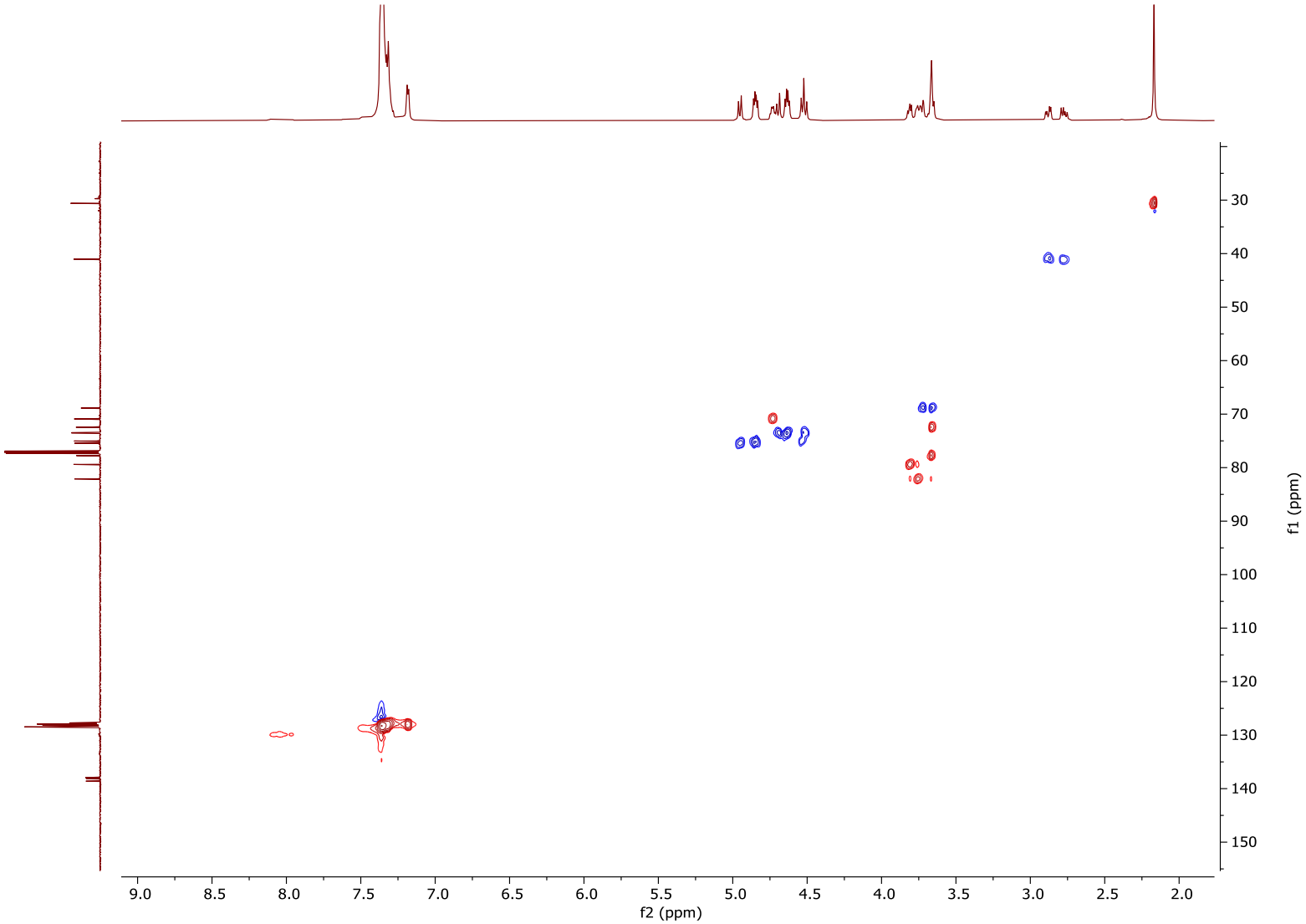
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside **(13a):**



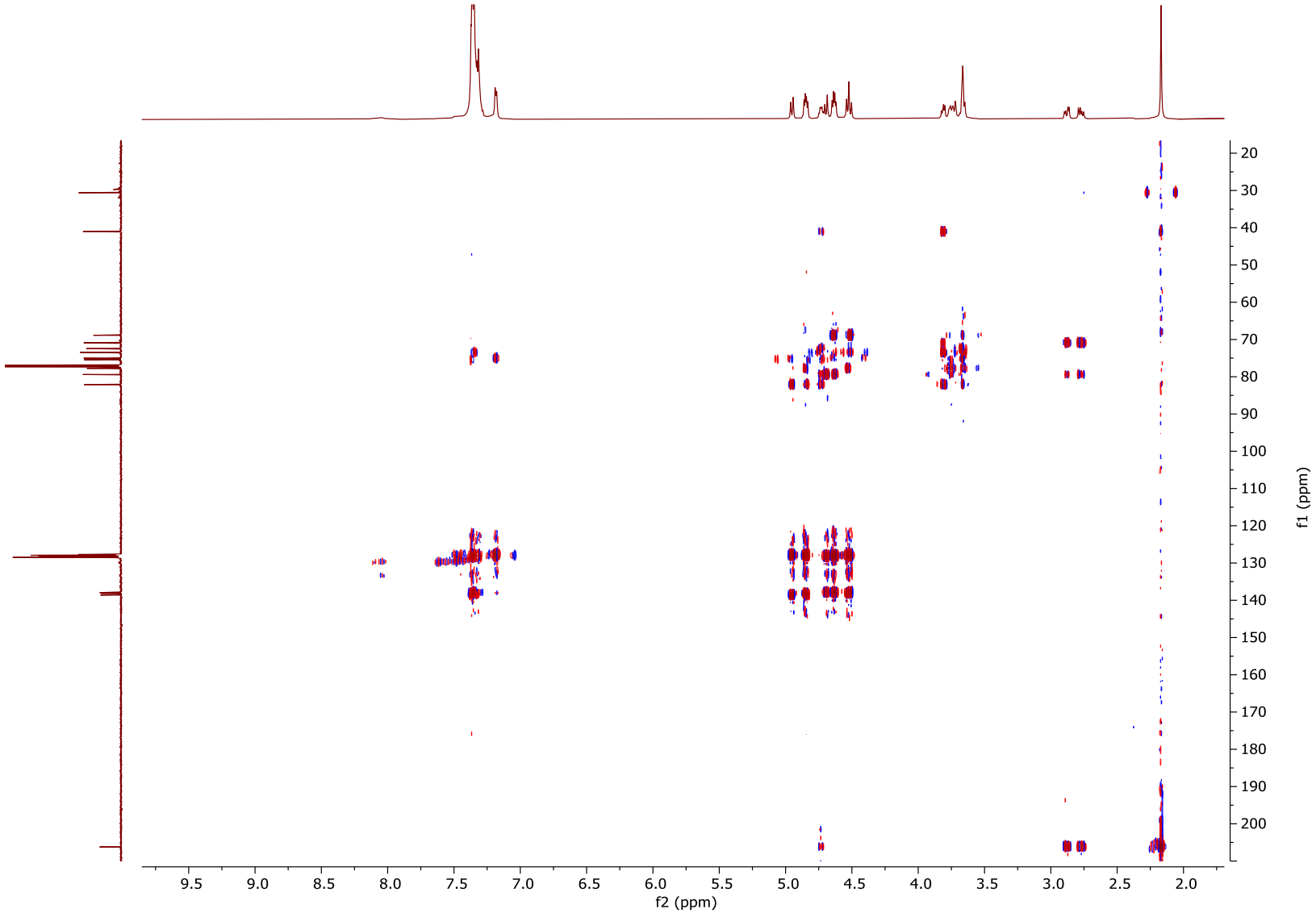
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside **(13a):**



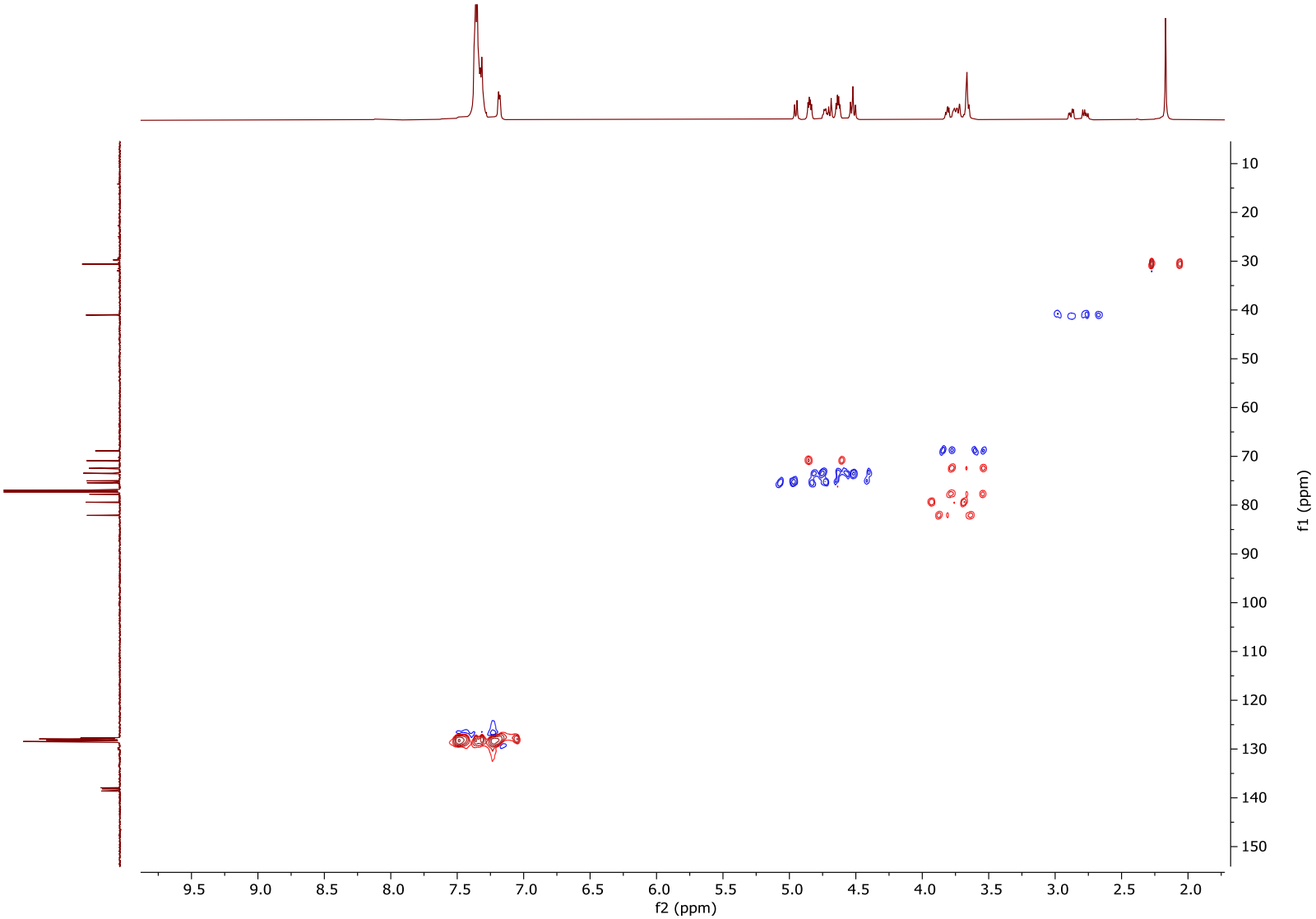
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside **(13a):**



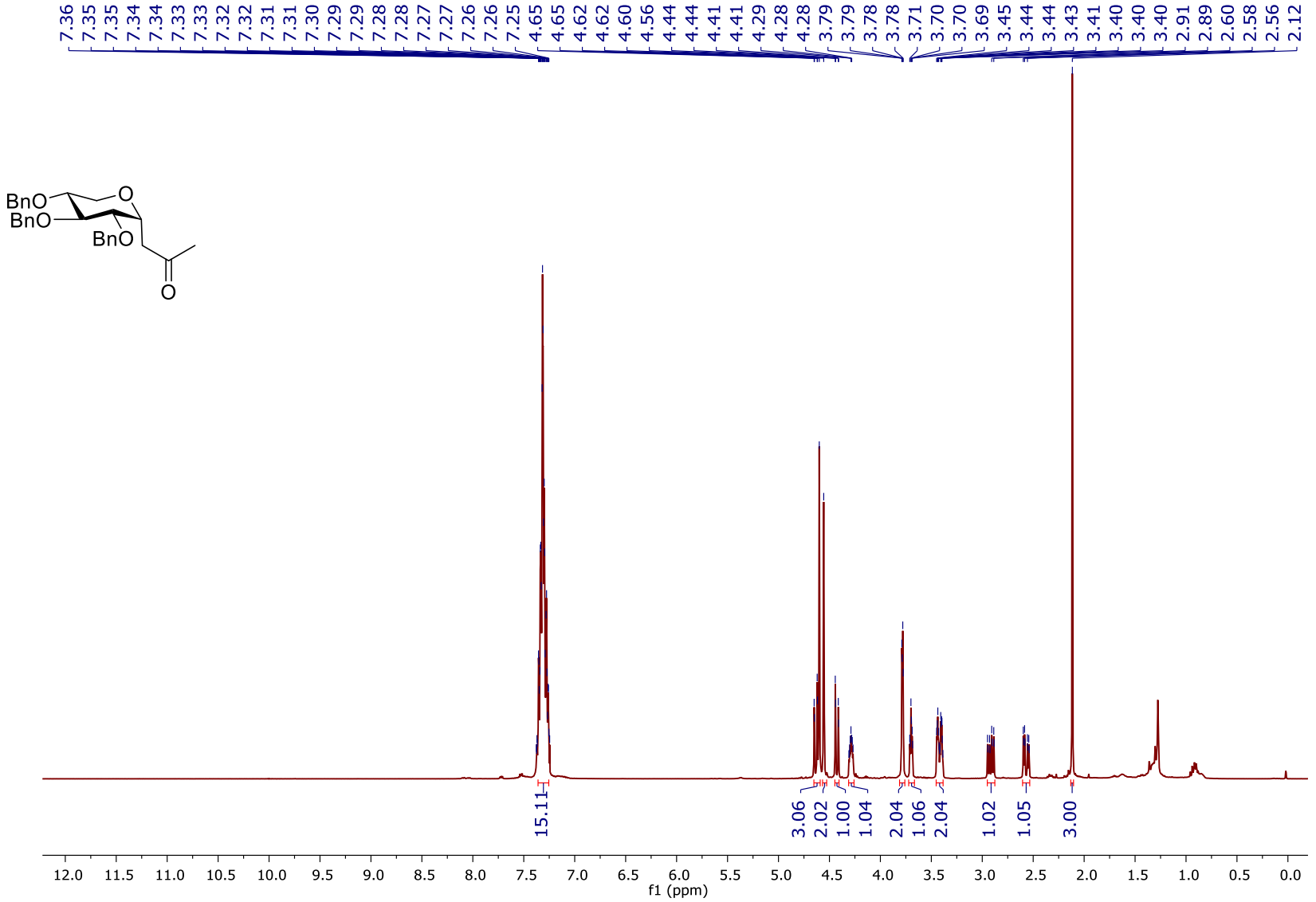
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside **(13a):**



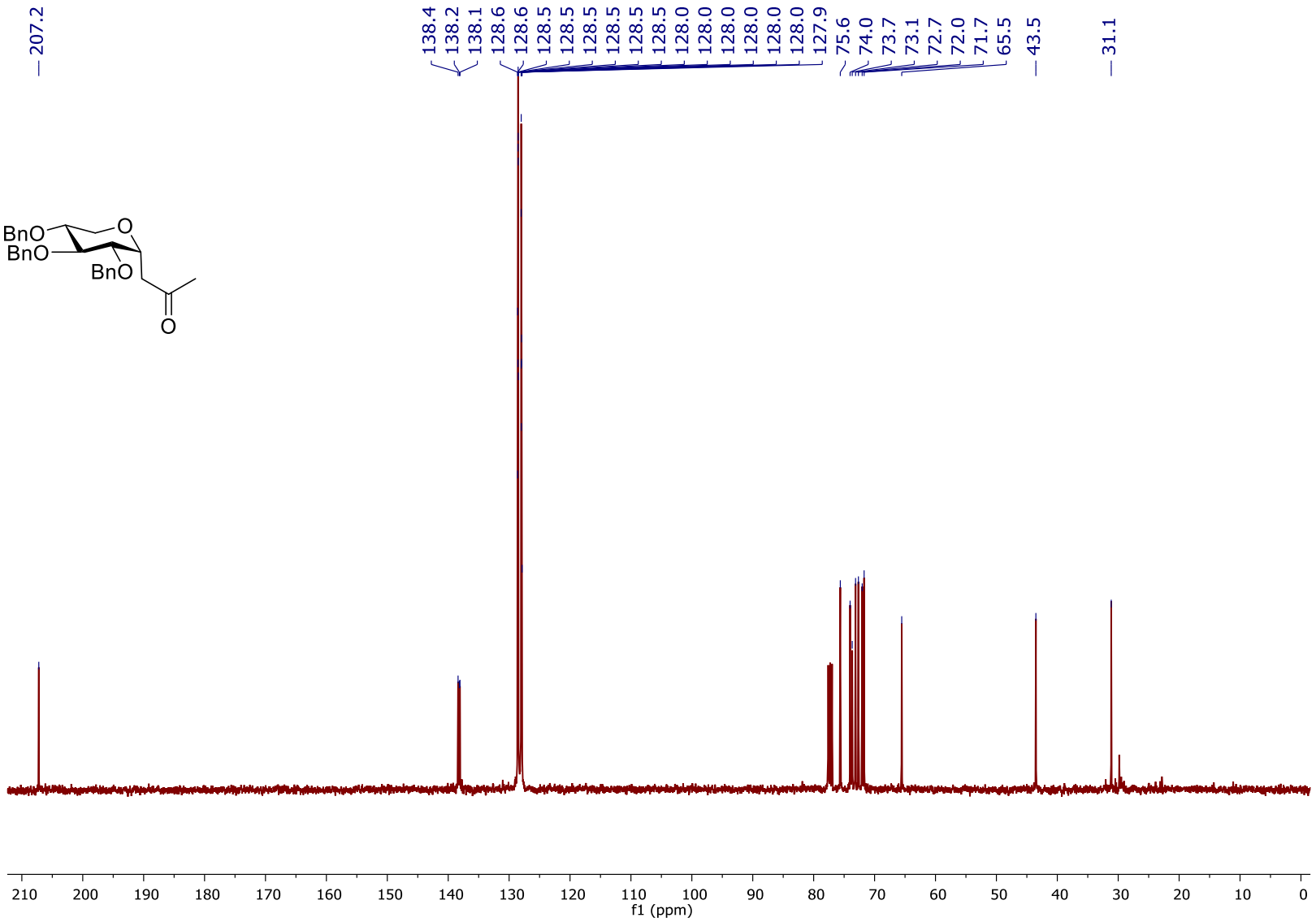
HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4,6-tetra-*O*-benzyl glucopyranoside **(13a):**



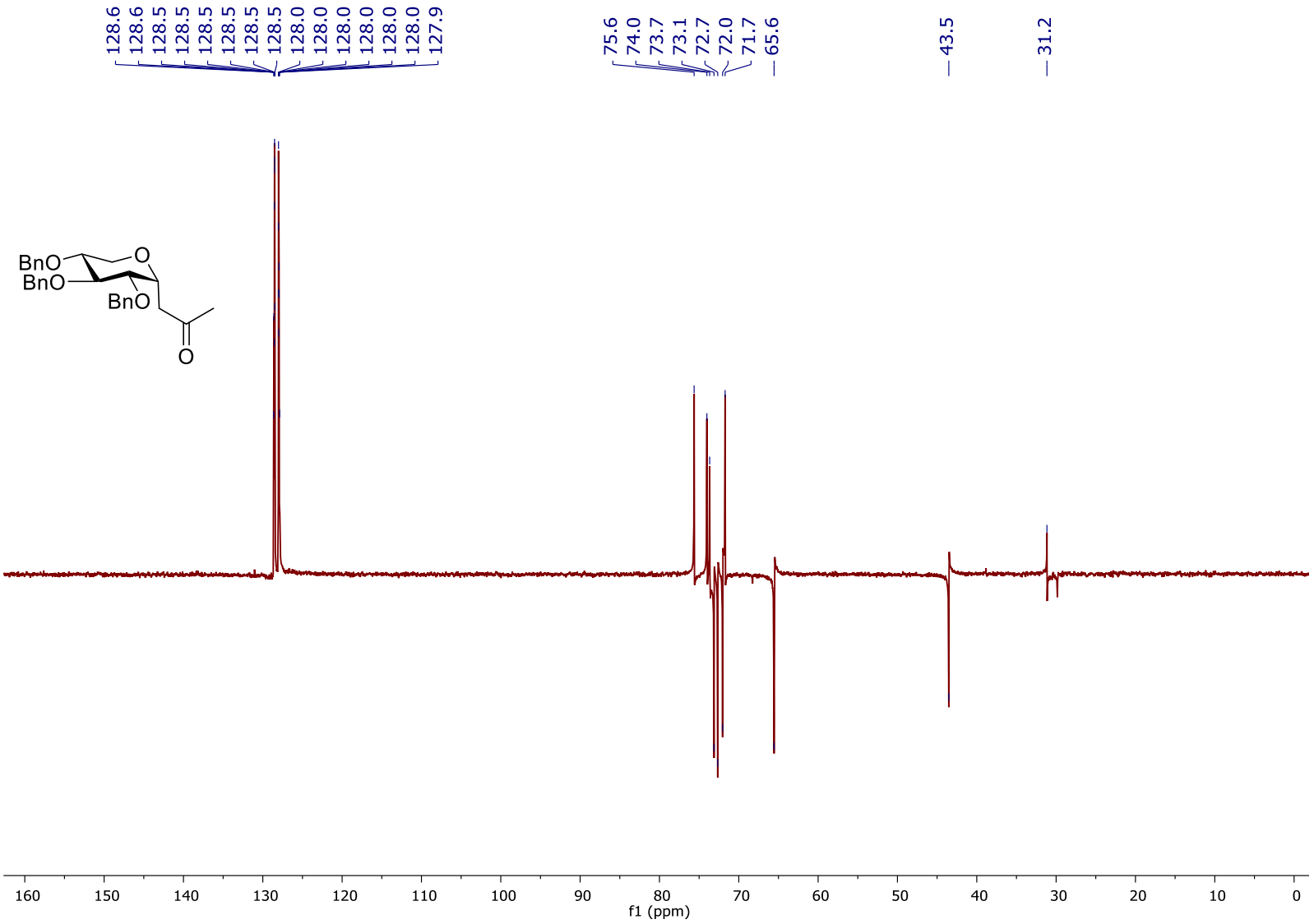
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside **(13b):**



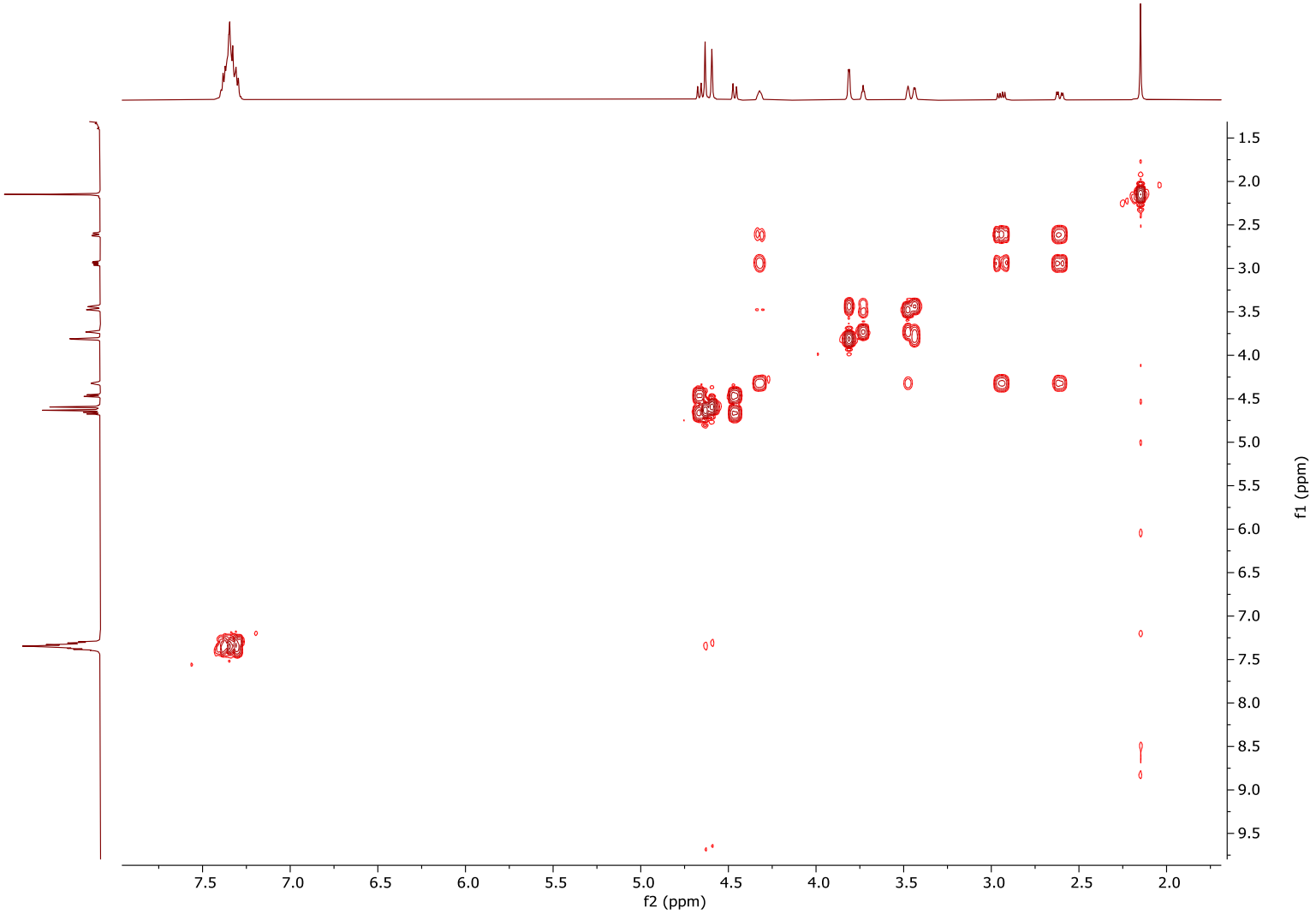
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside **(13b):**



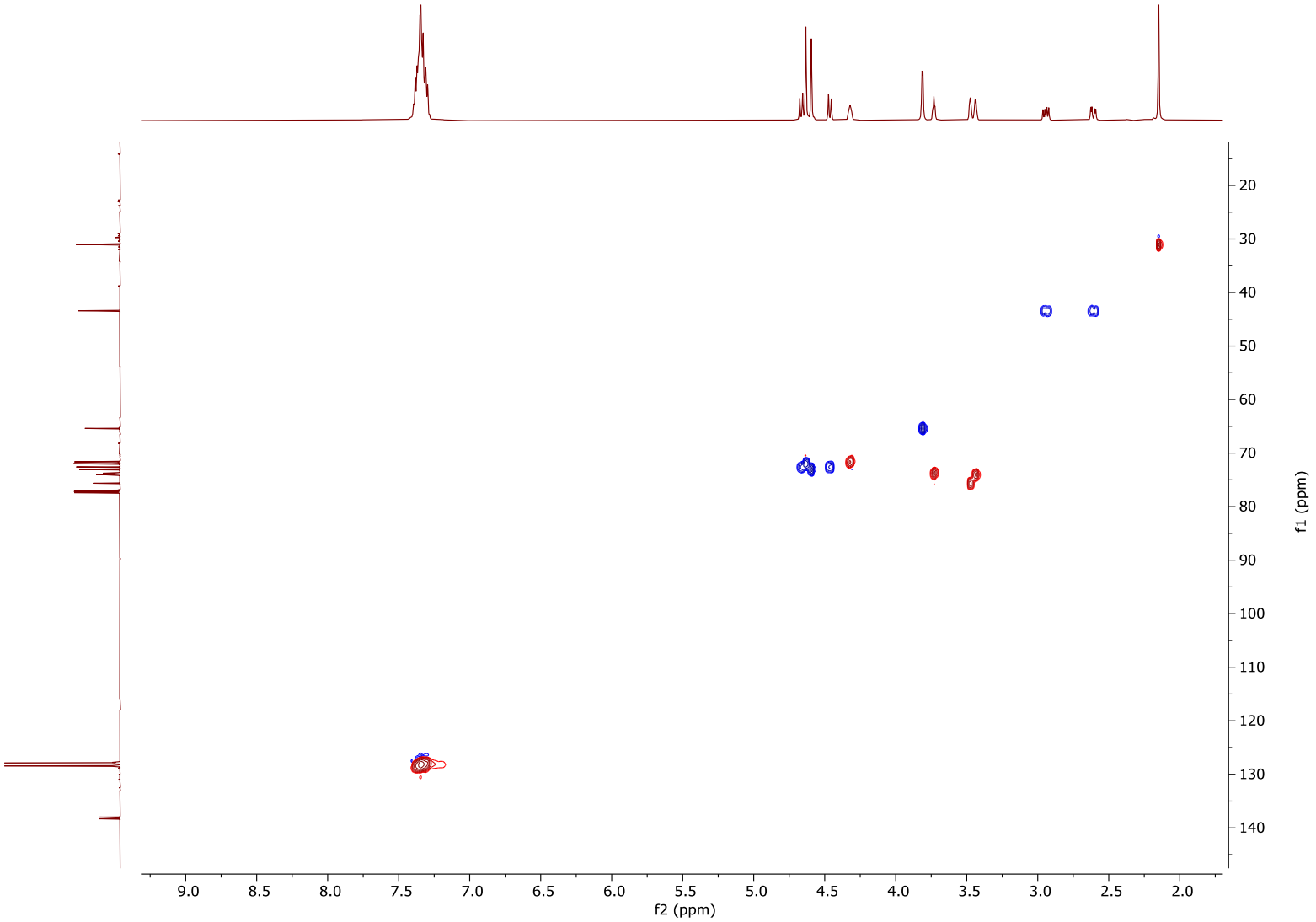
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside **(13b):**



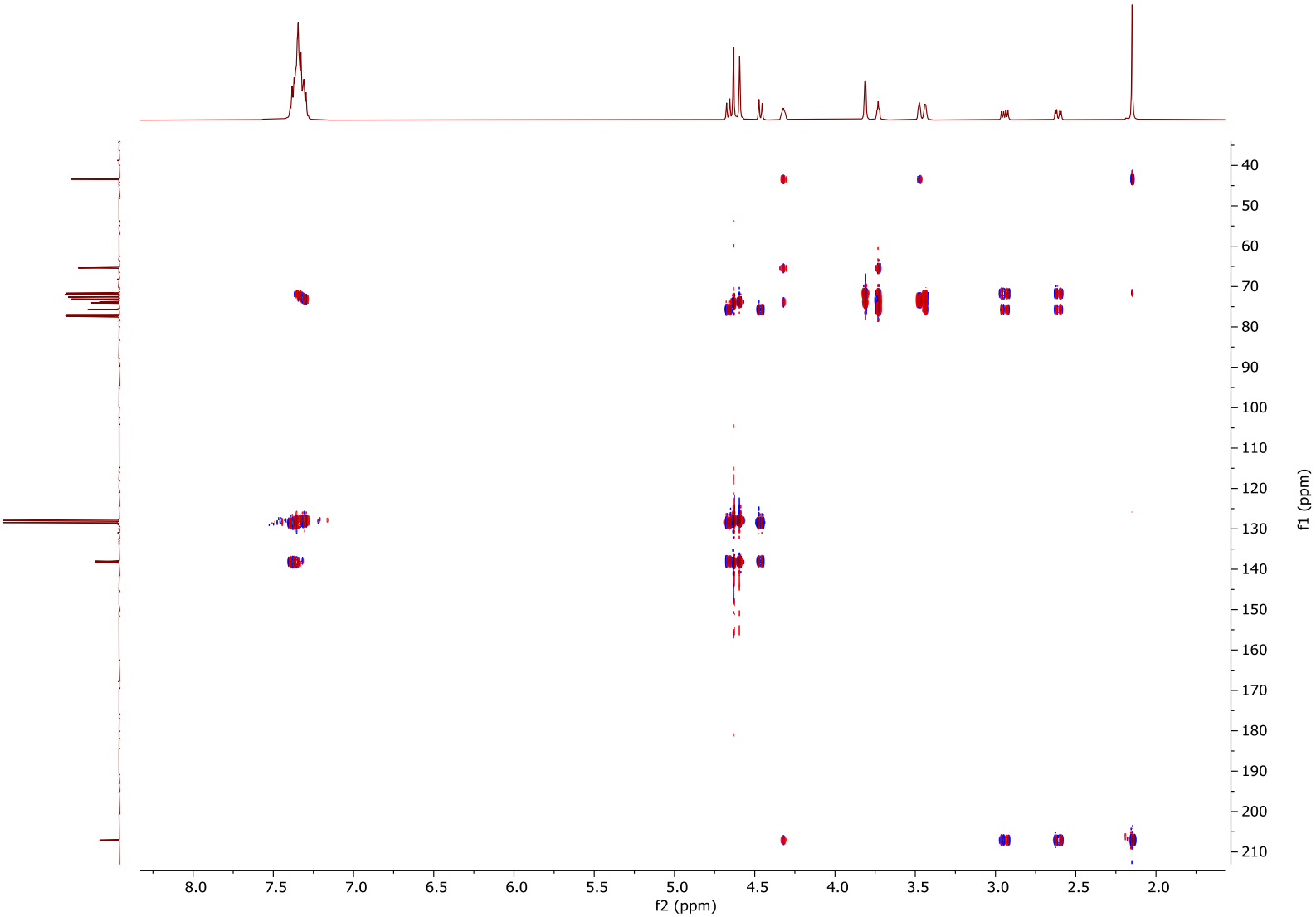
gCOSY Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside **(13b):**



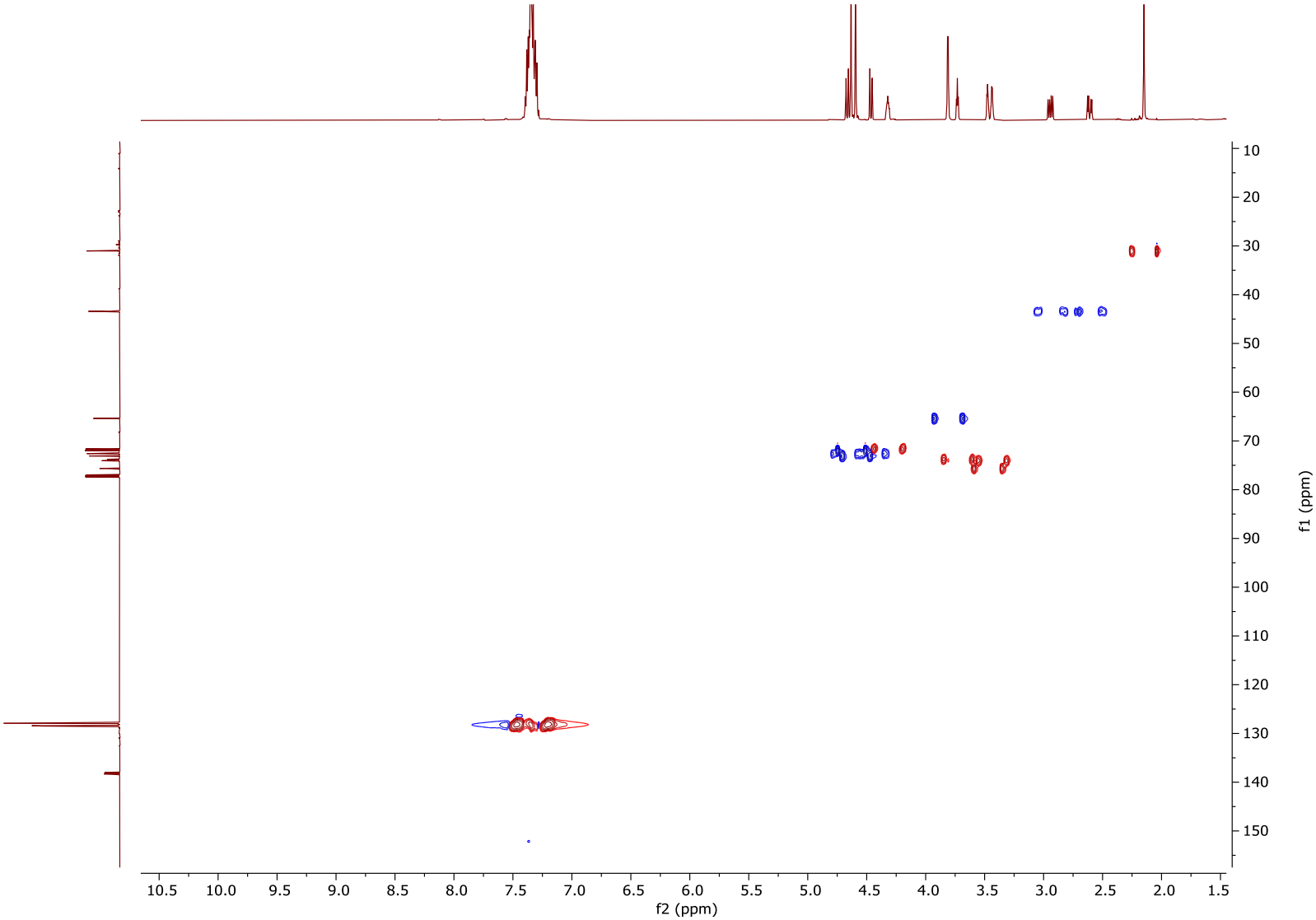
gHSQC Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside **(13b):**



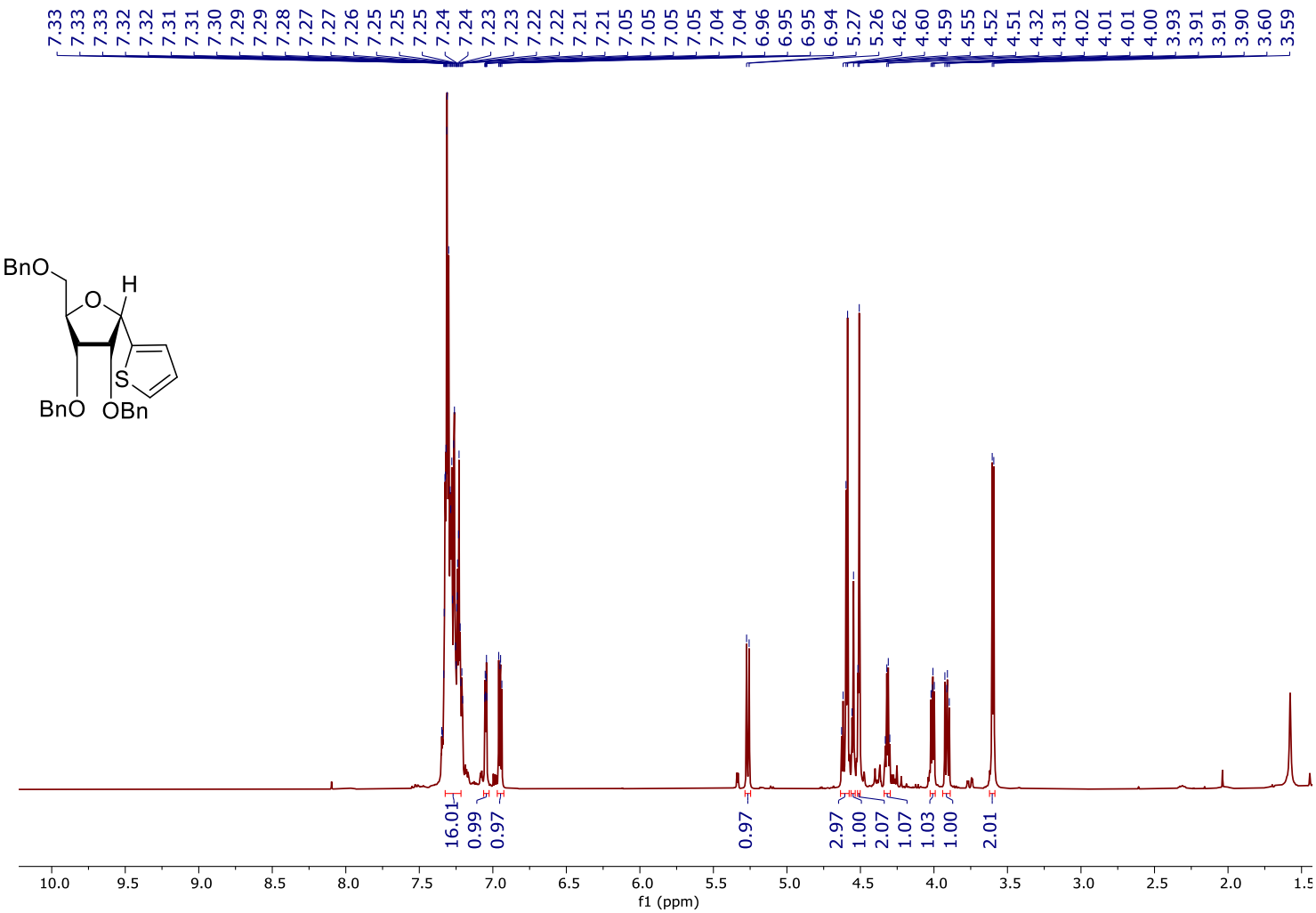
gHMBC Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside **(13b):**



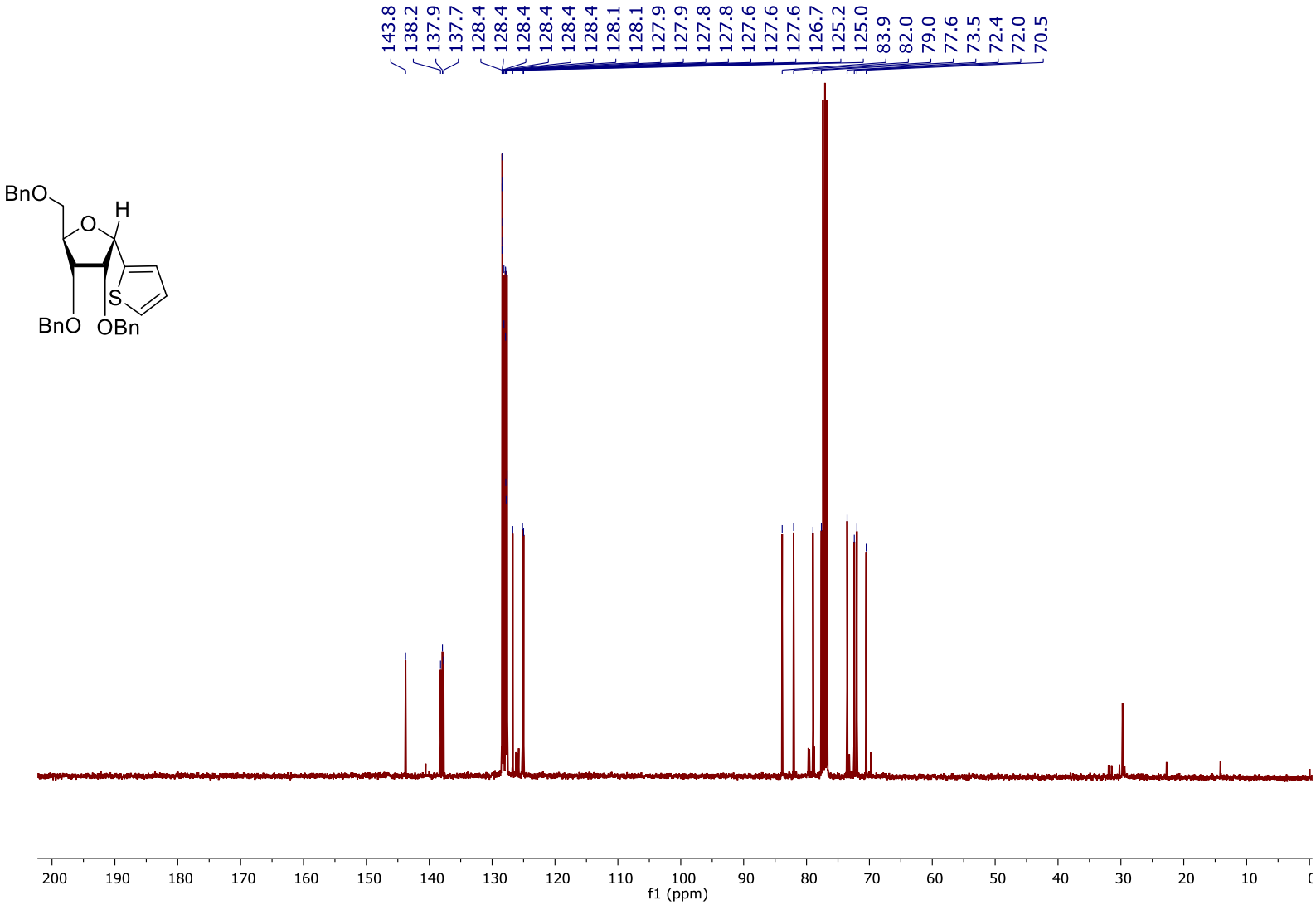
HSQC coupled Spectrum (600 MHz, $CDCl_3$) of 1-(2-propanone)-1-*deoxy* 2,3,4-tri-*O*-benzyl xylopyranoside **(13b):**



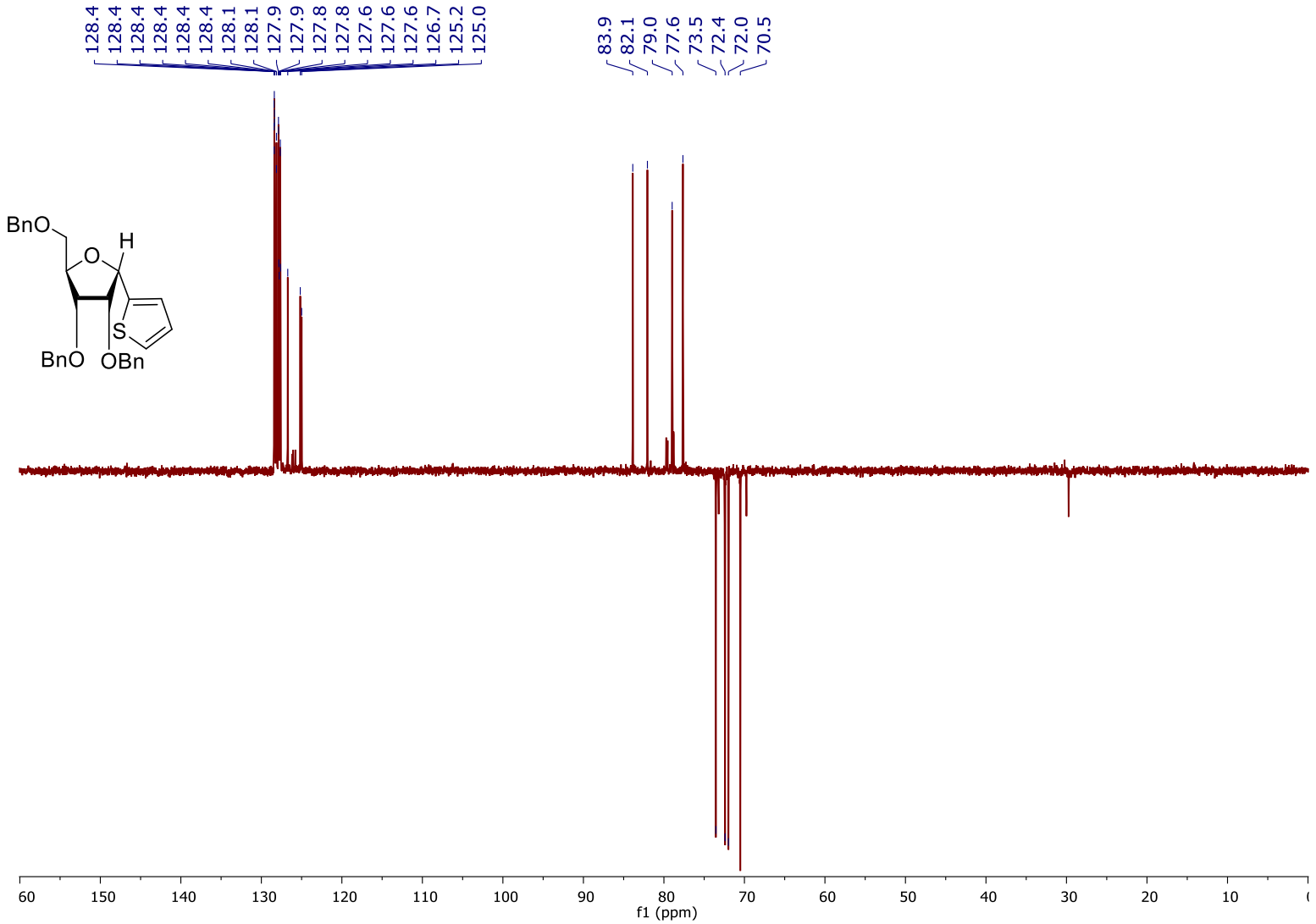
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(16a):**



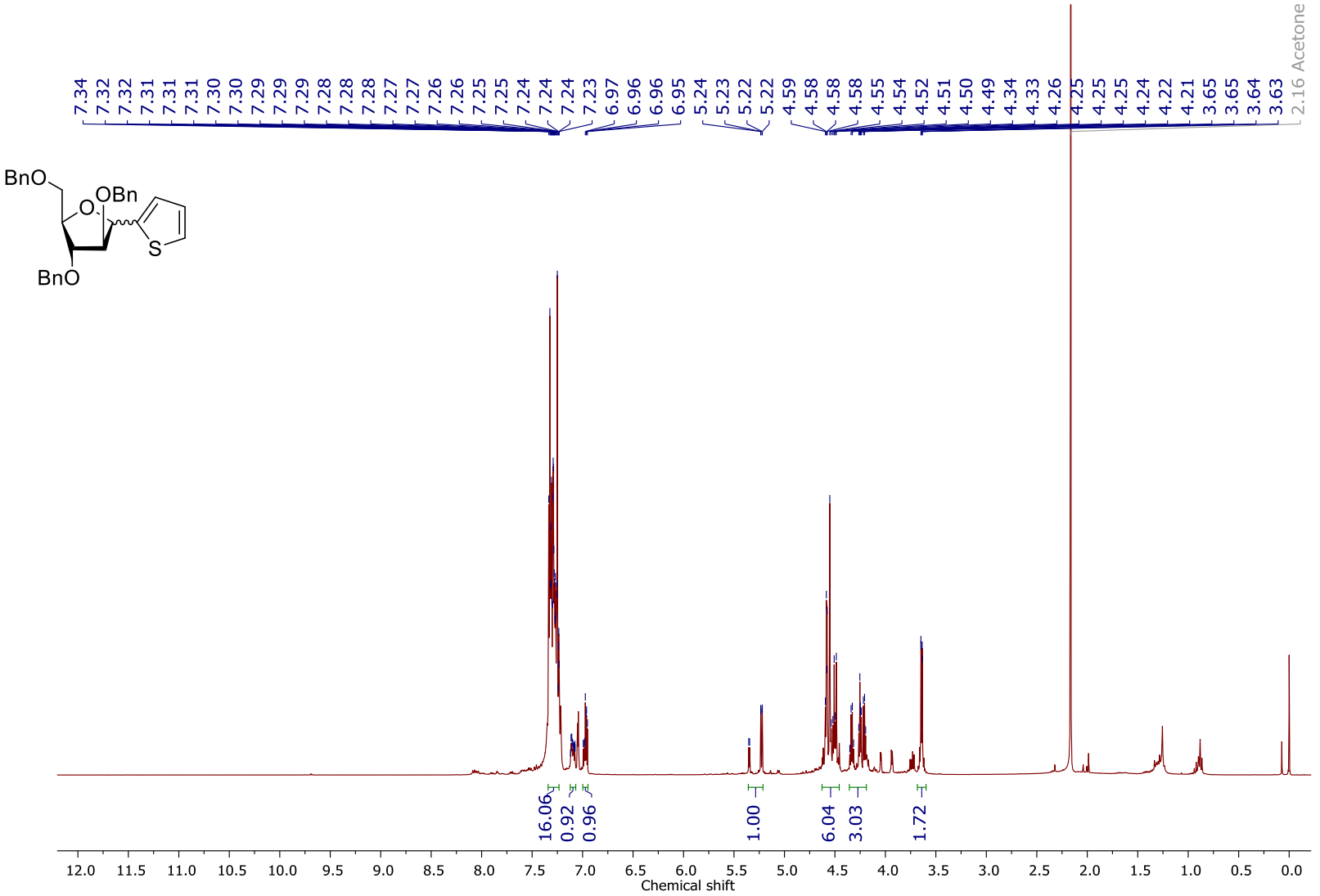
^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(16a):**



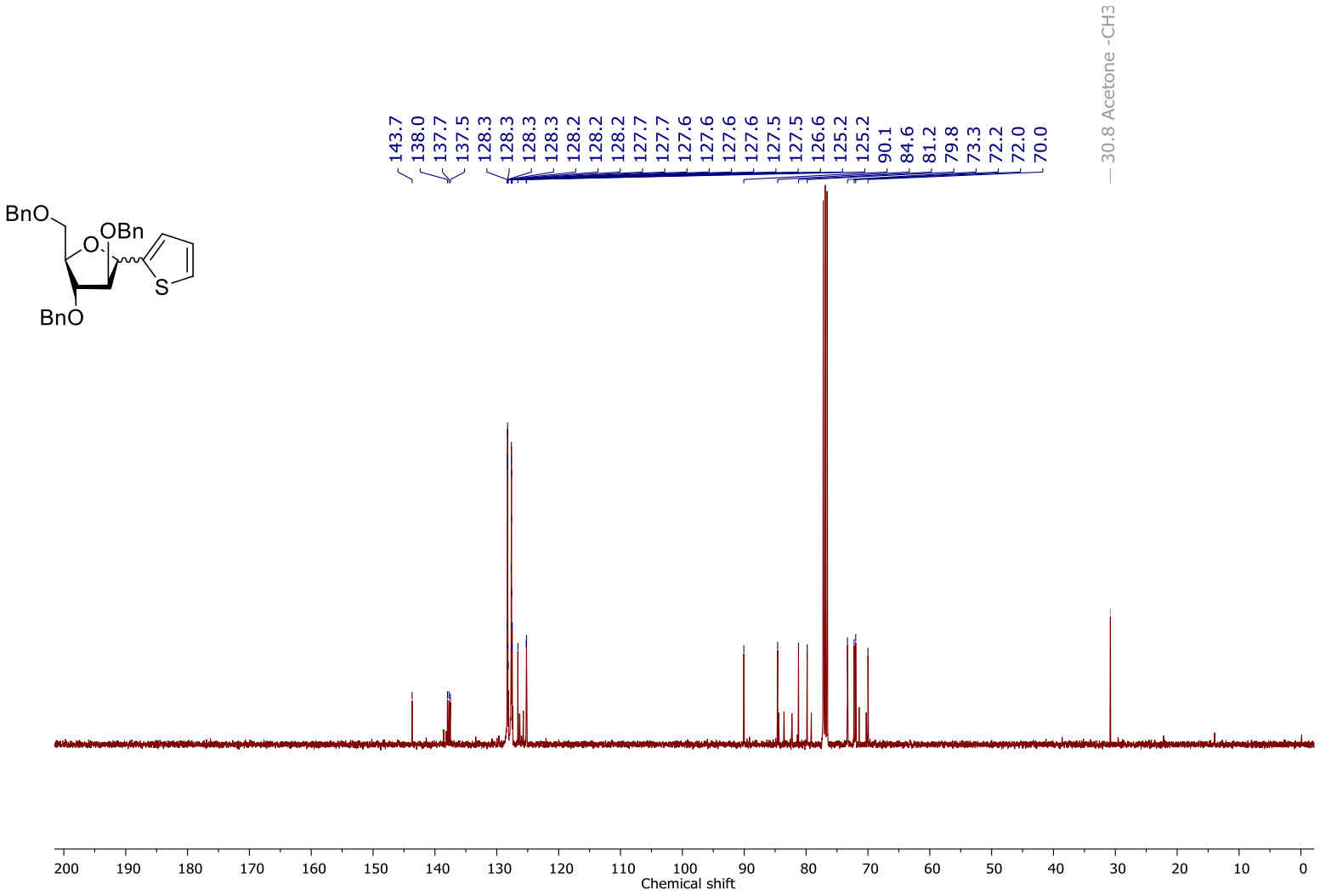
DEPT NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl α-D-ribofuranoside **(16a):**



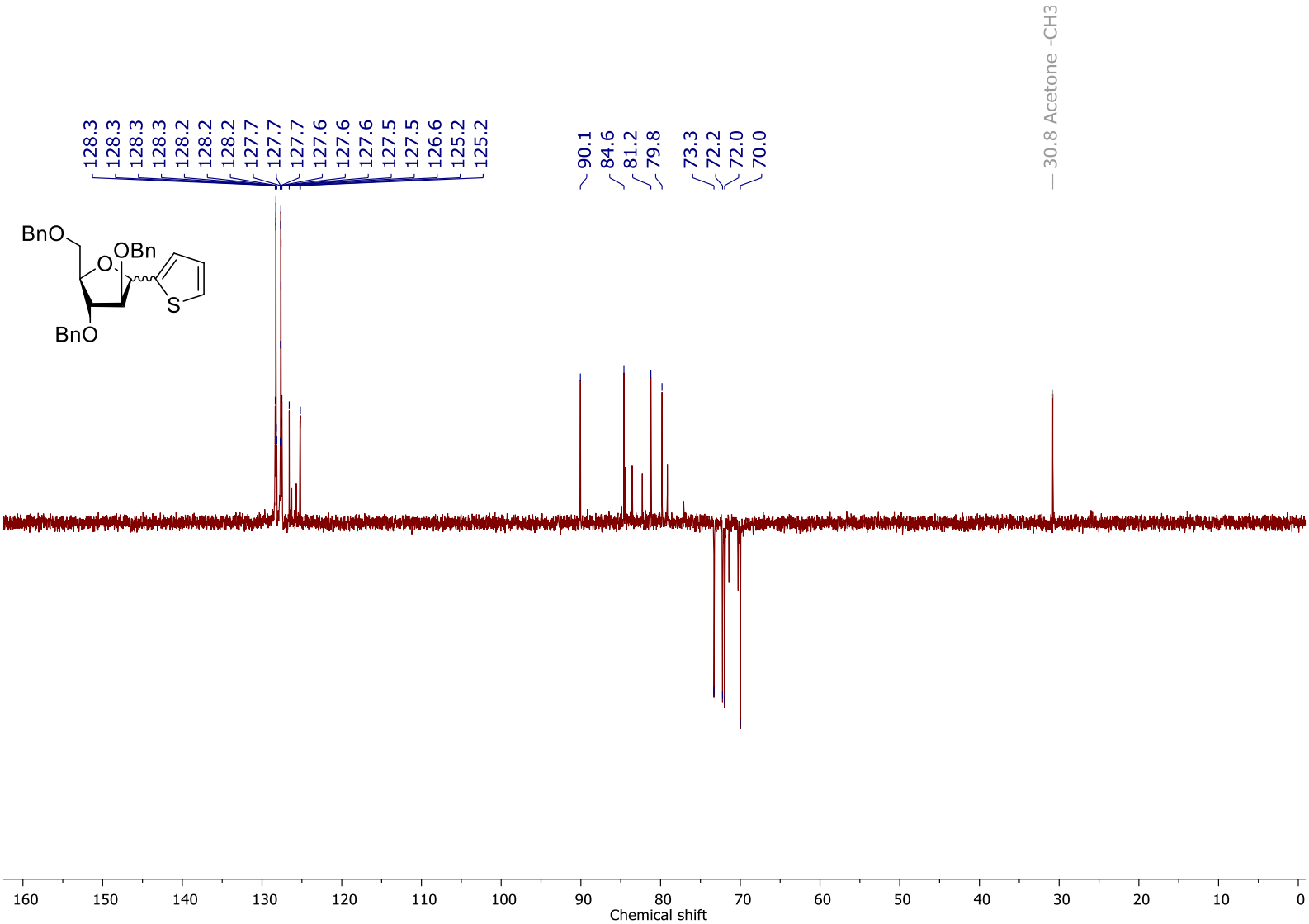
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of 1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside **(16b):**



^{13}C NMR Spectrum (101 MHz, $CDCl_3$) of 1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside **(16b):**



DEPT NMR Spectrum (101 MHz, $CDCl_3$) of **1-*deoxy*-2-thiophene-2,3,5-tri-*O*-benzyl α/β-D-arabinofuranoside (16b):**



Stability of TMS-nucleophile through NMR analysis:

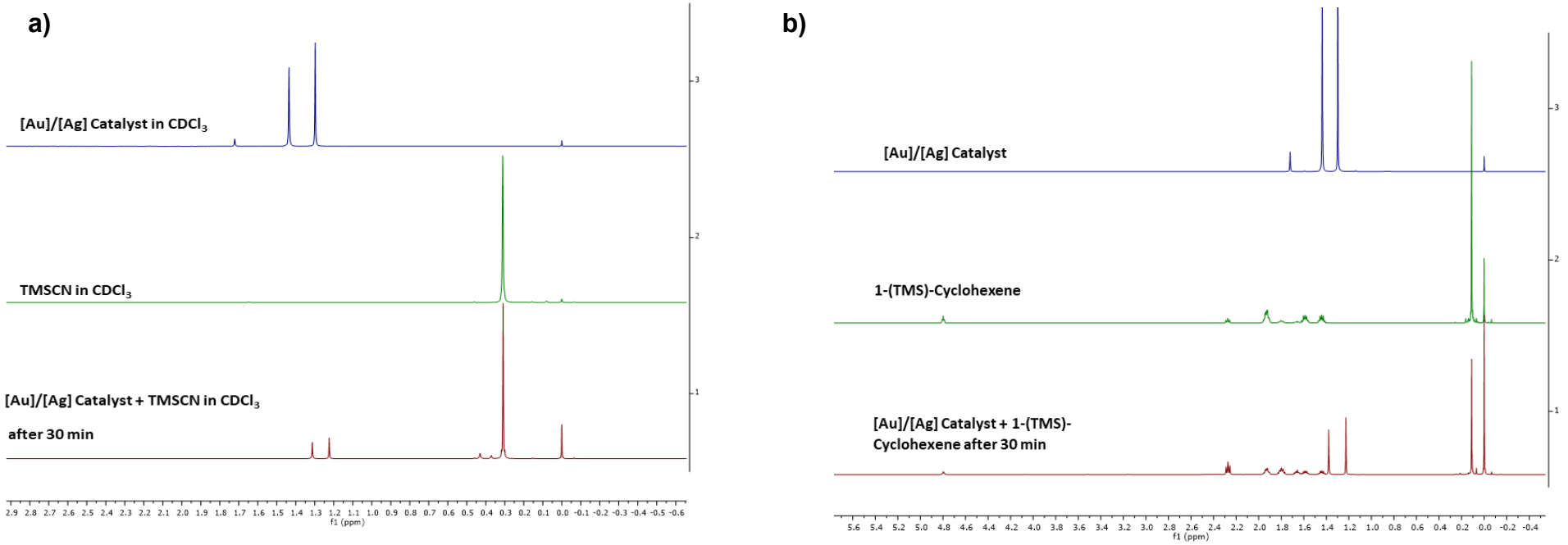


Fig. SI 1: a) Stability of TMSCN with Au-Phosphite and AgOTf **b)** Stability of 1-TMS-Cyclohexene with Au-Phosphite and AgOTf

To an NMR tube was added 10 mol% gold (I) Phosphite **6** and AgOTf in $CDCl_3$, followed by the addition of an amount of Trimethylsilyl cyanide (**5b**) and 1-Trimethylsiloxy-cyclohexene (**5d**) and 1-(acetoxymethyl) allyl trimethyl silane (**5e**) that is required for a 100mg scale glycosylation reaction. The tube was vortexed and subjected to ^{1}H NMR analysis after 30 minutes at room temperature. The 1H NMR signals of **5b** and **5d** remained after 30 minutes (**Fig. S1**) but decomposition of **5e** was prominent in the ^{1}H NMR spectra (**Fig S2**).

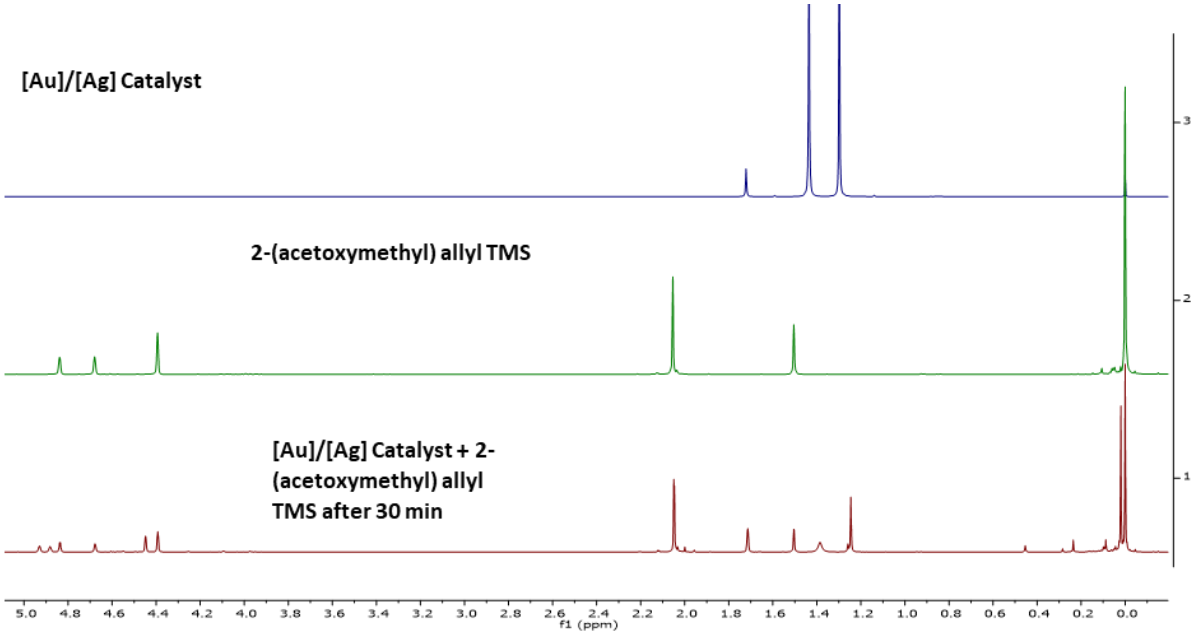


Fig. S2: Stability of 1-acetoxymethyl allyl TMS with Au-Phosphite and AgOTf

Quantifying percentage yield using qNMR analysis with 1,3,5-Trimethoxybenzene as Internal Standard:

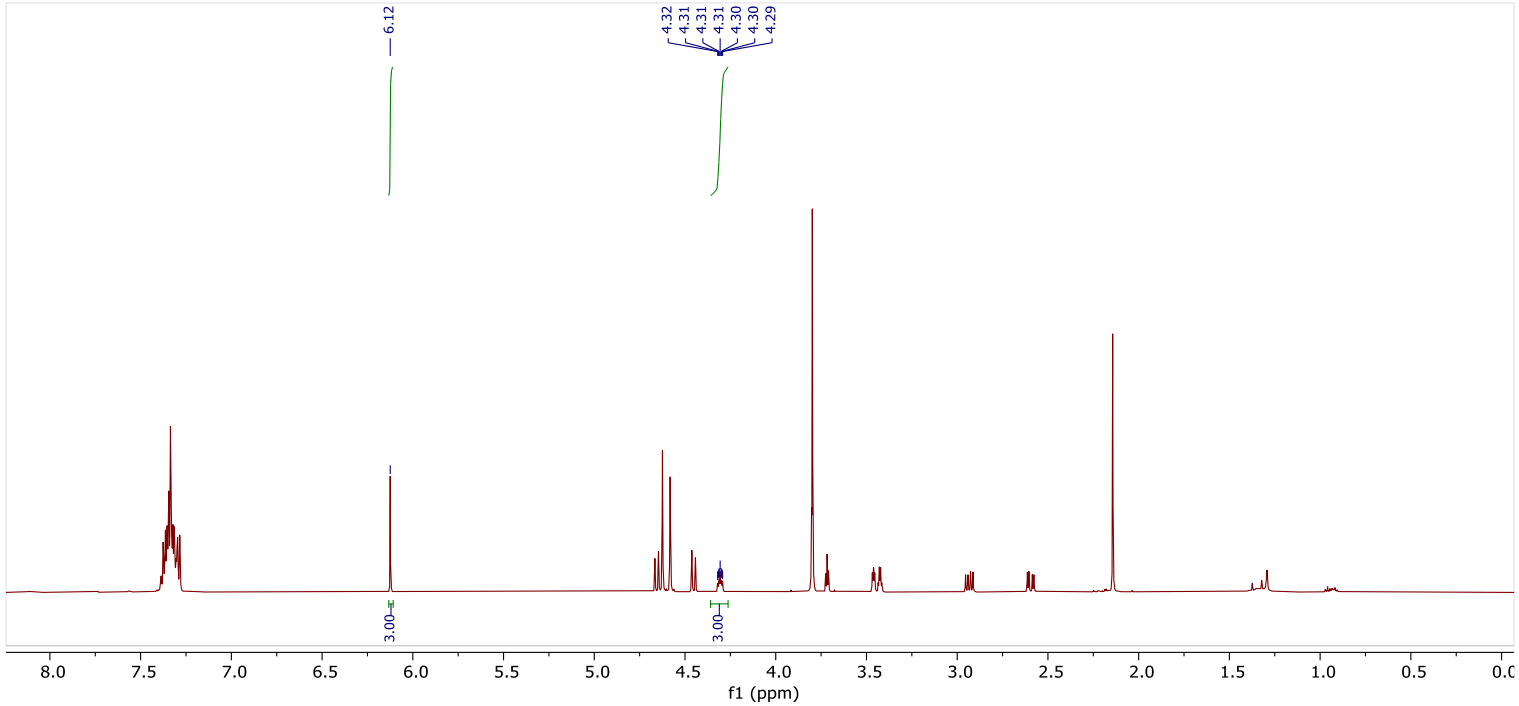


Fig S3: qNMR analysis of 13b

We calculated the actual percentage yield for compounds that we observed aliphatic impurities by analyzing ^{1}H NMR with qNMR Internal Standard 1,3,5-Trimethoxybenzene. The singlet peak at 6.1 ppm representing three symmetric aromatic protons of Phloroglucinol trimethyl ether does not overlap with any of the C-glycosidic compound's peaks along with its high solubility in $CDCl_3$ makes it an ideal internal standard for qNMR experiments. The aforementioned singlet peak (3H) was compared to well-resolved and characterized single protons (1H) from respective compounds to check percentage purity. For example, the isolated crude yield for

compounds **10b** and **13b** were 102.5 mg and 80.5 mg. To evaluate the actual percentage yield, 2.5 mg of NMR standard 1,3,5-Trimethoxybenzene (0.015 mmol) was dissolved in 400 µL of $CDCl_3$ along with 23.5 mg of **13b,** and ^1H NMR was recorded. Comparing the integration value of the aromatic protons (6.1 ppm) to H4 of **13b** at 4.31 (m) (Fig **S3**), we understood that the amount of the pure compound present is 0.045 mmol or 21.55 mg, suggesting 92% purity. The actual percentage yield was reported as 74 mg instead of 80.5 mg in the characteristic data. Similarly, 12mg of **10b** and 2.5 mg of 1,3,5-Trimethoxybenzene was dissolved in 400 µL of $CDCl_3$ and qNMR analysis was performed (Fig **S4**). Comparing the integration value of H3 (**10b**) at 4.04 (d) to aromatic protons (6.1 ppm) revealed 80% purity (9.6mg, 82 mg reported in the characteristic data).

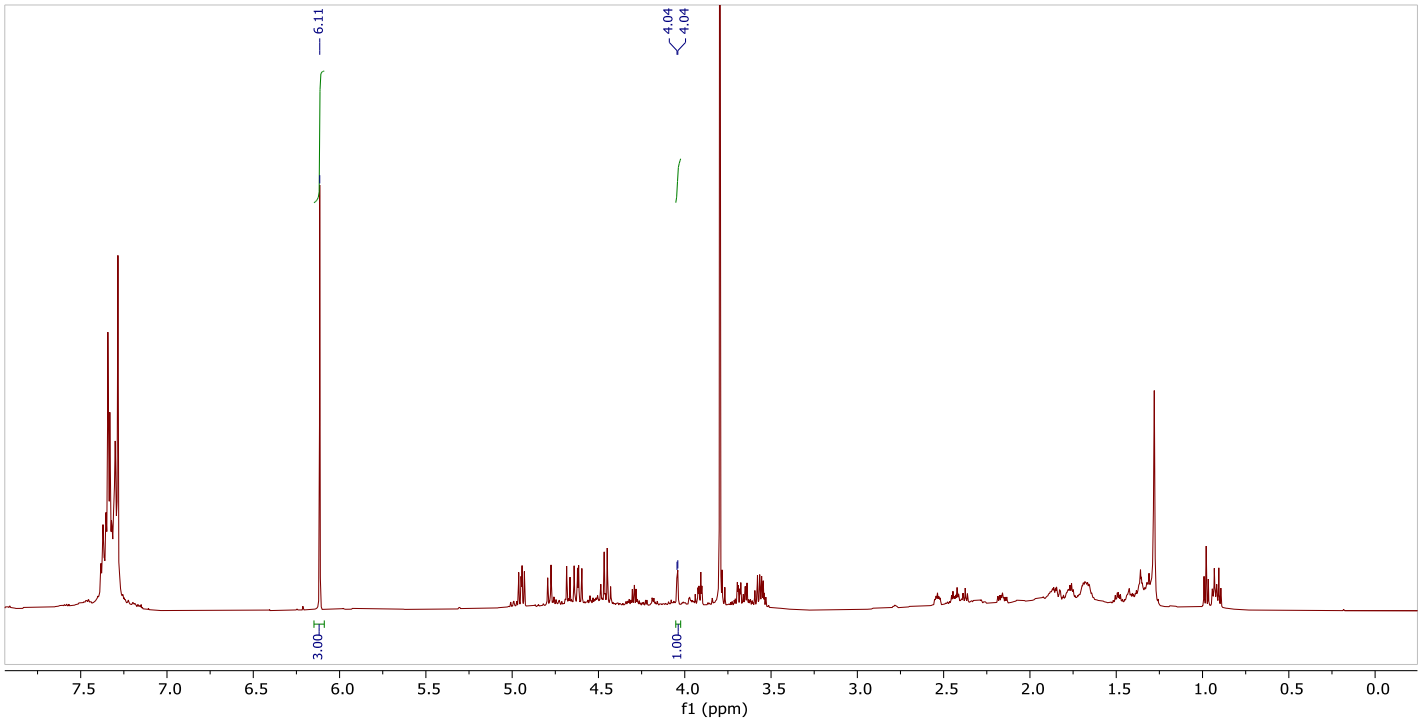


Fig S4: qNMR analysis of 10b