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Supporting Information

β-Mannosylation through *O*-Alkylation of Anomeric Cesium Alkoxides: Mechanistic Studies and Synthesis of the Hexasaccharide Core of Complex Fucosylated N-Linked Glycans

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Supporting Information

General information

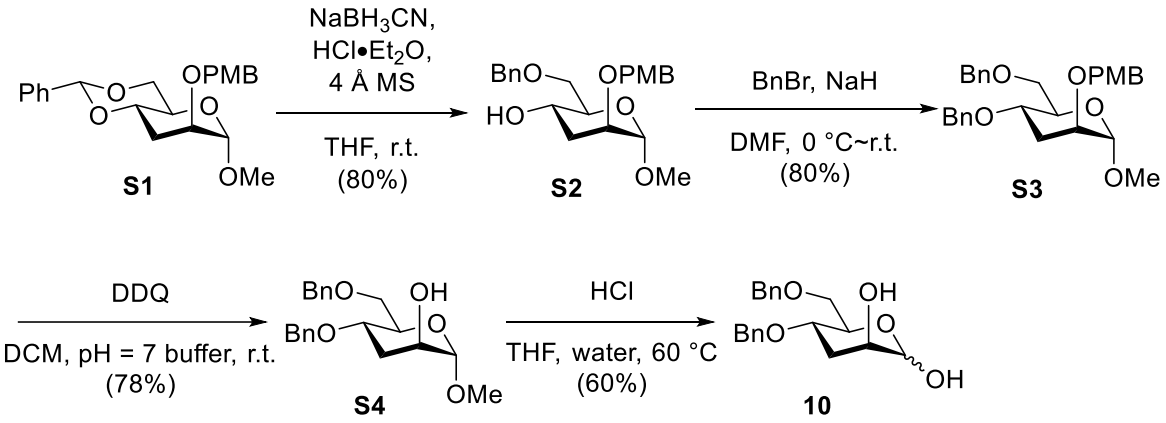
All reagents and chemicals were purchased from Acros Organics, Sigma-Aldrich, Fisher Scientific, Alfa Aesar, and Strem Chemicals and used without further purification. THF, methylene chloride, toluene, and diethyl ether were purified by passing through two packed columns of neutral alumina (Innovative Technology). Anhydrous DMF and benzene were purchased from Acros Organics and Sigma-Aldrich and used without further drying. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash column chromatography was performed using 200-400 mesh silica gel (Scientific Absorbents, Inc.). Yields refer to chromatographically and spectroscopically pure materials, unless otherwise stated.

Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on Bruker Advance-600 (^{1}H NMR-600 MHz; ^{13}C NMR-150 MHz) at ambient temperature with $CDCl_3$ as the solvent unless otherwise stated. Chemical shifts are reported in parts per million relative to residual protic solvent internal standard $CDCl_3$: ^{1}H NMR at δ 7.26, ^{13}C NMR at δ 77.16. Data for ^{1}H NMR are reported as follows: chemical shift, integration, multiplicity (app = apparent, par obsc = partially obscure, ovrlp = overlapping, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constants in Hertz. All ^{13}C NMR spectra were recorded with complete proton decoupling. High resolution mass spectra (HRMS)

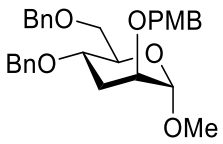
were acquired on a Waters Acuity Premiere XE TOF LC-MS by electrospray ionization. Optical rotations were measured with Autopol-IV digital polarimeter; concentrations are expressed as g/100 mL. Infrared spectra were recorded on a PerkinElmer FT-IR spectrophotometer.

Synthesis of lactol donor 10, 14, 17, 19, 20 and 21.

Synthesis of lactol donor 10.



Methyl 2-*O*-(4-methoxybenzyl)-4,6-di-*O*-benzyl-3-deoxy-*α*-D-mannopyranoside (S3)

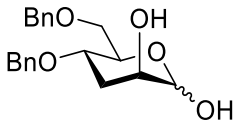


To a solution of known compound **S1**[1] (772 mg, 2.0 mmol) in THF (20 mL) was added freshly dried 4 Å molecular sieves (2 g) and $NaBH_3CN$ (375 mg, 6 mmol). The resulting mixture was cooled to 0 °C and 1 N HCl in Et_2O (8 mL) was added. The mixture was warmed up to room temperature and stirred for 20 min. The resulting

mixture was quenched with saturated $NaHCO_3$ solution (2 mL) and filtered through a pad of celite. THF was removed under reduced pressure and extracted with EtOAc (20 mL × 3), washed with water (50 mL × 3) and brine (50 mL), dried over Na_2SO_4 and filtered. The concentrated residue was purified by flash column chromatography (Hexanes/EtOAc =5/1 to 3/1 with 1% MeOH) to afford compound **S2** (621 mg, 80%). **S2** (970 mg, 2.5 mmol) was dissolved in DMF (5 mL) and cooled to 0 °C before NaH (200 mg, 5 mmol, 60% in mineral oil) was added portion wise. The resulting mixture was stirred at 0 °C for 1 h before BnBr (0.44 mL, 3.75 mmol) was added. The resulting mixture was warmed up and stirred at room temperature for 40 minutes and quenched with water (5 mL). The resulting mixture was extracted with EtOAc (20 mL × 3), washed with water (50 mL × 3) and brine (50 mL), dried over anhydrous Na_2SO_4 and filtered. The concentrated residue was purified by flash column chromatography (Hexanes/EtOAc= 5/1 to 3/1) to afford compound **S3** (1.10 g, 80%) as light yellow syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +64 .5 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 2906, 1611, 1512, 1453, 1366, 1301, 1246, 1173, 1059, 821, 736, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.19 (m, 12H, H_{Ar}), 6.91 – 6.82 (m, 2H, H_{Ar}), 4.70 – 4.64 (m, 2H, -OCH_2Ar, *H*-1), 4.58 (d, *J* = 12.2 Hz, 1H, -OCH_2Ar), 4.55 – 4.50 (m, 2H, -OCH_2Ar), 4.46 (d, *J* = 11.9 Hz, 1H, -OCH_2Ar), 4.39 (d, *J* = 11.5 Hz, 1H, -OCH_2Ar), 3.84 – 3.71 (m, 7H, -OCH_3, *H*-4, *H*-5, *H*-6a, *H*-6b), 3.58 (td, *J* = 3.3, 1.5 Hz, 1H, *H*-2), 3.39 (s, 3H, -OCH_3), 2.24 (m, 1H, *H*-3a), 1.78 (m, 1H, *H*-3b); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 159.29, 138.68, 138.53, 130.48, 129.33, 128.45, 128.38, 127.82, 127.70, 127.52, 113.89, 98.31, 74.41, 73.48, 71.81, 71.17, 70.73, 70.04, 69.77, 55.40, 54.74, 29.72; **HRMS (ESI)** calculated for

$C_{29}H_{34}NaO_6$ $[M+Na]^+$ 501.2248, found 501.2254.

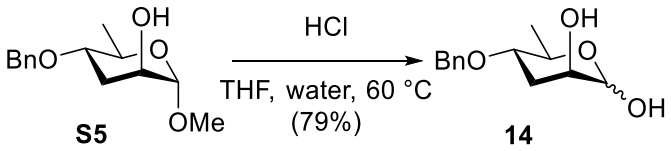
4,6-Di-*O*-benzyl-3-deoxy-*α*/*β*-D-mannopyranose (10)



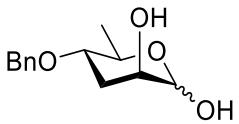
DDQ (660 mg, 2.91 mmol) was added to a solution of **S3** (927 mg, 1.94 mmol) in CH_2Cl_2 (19.4 mL) and pH 7.0 buffer (3.2 mL). The reaction mixture was stirred at ambient temperature for 4 h and then quenched with saturated $NaHCO_3$ solution (5 mL). The resulting mixture was extracted with EtOAc (25 mL × 3). The organic layer was washed with water (50 mL × 2), brine (20 mL), dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by flash column chromatography (Hexanes/EtOAc = 5/1 to 2/1 with 1% MeOH) to furnish **S4** (594 mg, 78%). Compound **S4** (179 mg, 0.5 mmol) was dissolved in THF (125 μL) followed by the addition of 2 M HCl (10 mL). The resulting mixture was stirred at 60 °C for 36 h before saturated $NaHCO_3$ solution (1 mL) was added. THF was removed under reduced pressure and the aqueous mixture was extracted with EtOAc (10 mL × 3). The combined organic layer was washed with water (20 mL × 3), brine (20 mL), dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by silica gel column chromatography (Hexanes/EtOAc = 2/1 to 1/2 with 1% MeOH) to furnish the title compound **10** (*α*/*β* = 1/1 mixture, 105 mg, 60%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +36.7 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3384, 3257, 2919, 1731, 1454, 1360, 1310, 1253, 1134, 1087, 1020, 946, 902, 836, 731, 695 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.36 – 7.26 (m, 16H, H_{Ar}), 7.24 – 7.19 (m, 4H, H_{Ar}), 5.06 (s, 1H, *H*-1 *α*), 4.74 (s, 1H, *H*-1 *β*), 4.63

– 4.46 (m, 6H, -OCH_2Ar), 4.44 – 4.35 (m, 3H, C1-O*H* β, -OCH_2Ar × 2), 4.07 (ddd, *J* = 9.5, 5.4, 2.4 Hz, 1H, *H*-5 α), 3.82 (m, 1H, *H*-2 α), 3.79 – 3.60 (m, 7H, *H*-6 α, *H*-6 β, *H*-4 α, *H*-4 β, *H*-2 β), 3.57 (ddd, *J* = 9.4, 4.0, 3.0 Hz, 1H, *H*-5 β), 3.28 (s, 2H, C1-O*H* α, C2-O*H*), 2.45 (ddd, *J* = 13.6, 4.8, 3.6 Hz, 1H, *H*-3a β), 2.30 (s, 1H, C2-O*H*), 2.20 (m, 1H, *H*-3a α), 1.91 (ddd, *J* = 13.5, 10.9, 3.0 Hz, 1H, *H*-3b α), 1.56 (ddd, *J* = 13.8, 11.0, 3.1 Hz, 1H, *H*-3b β); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.29, 138.20, 138.03, 137.75, 128.54, 128.52, 128.51, 128.28, 128.16, 127.98, 127.88, 127.84, 127.81, 95.72, 93.84, 78.11, 73.74, 73.64, 71.61, 71.45, 71.02, 69.66, 69.62, 69.43, 69.06, 68.46, 68.31, 34.66, 31.12. **HRMS (ESI)** calculated for $C_{20}H_{24}NaO_5$ $[M+Na]^+$ 367.1516, found 367.1533.

Synthesis of lactol donor 14.



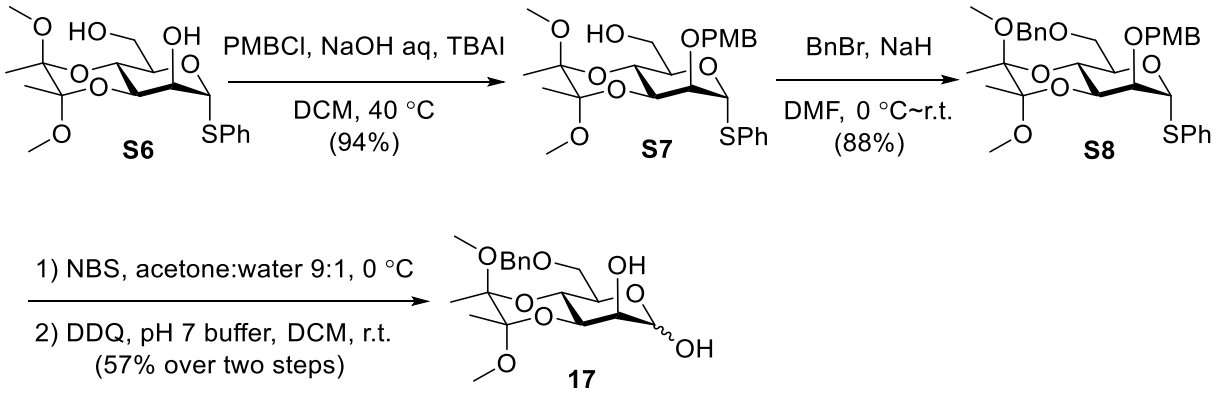
4-*O*-Benzyl-3,6-dideoxy-α/β-D-mannopyranose (14)



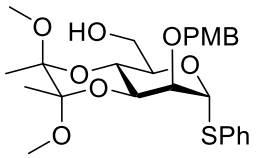
Known compound **S5**[2] (100 mg, 0.39 mmol) was dissolved in THF (98 µL) followed by the addition of 2 M HCl (7.8 mL). The resulting mixture was stirred at 60 °C for 12 h before saturated $NaHCO_3$ solution (1 mL) was added. THF was removed under reduced pressure and the aqueous mixture was extracted with EtOAc (10 mL × 3). Combined extracts were washed with water (20 mL × 3), brine (20 mL), dried over Na_2SO_4, filtered and concentrated. The crude residue was purified by silica

gel column chromatography (Hexanes/EtOAc = 2/1 to 1/1 with 1% MeOH) to furnish compound **14** (α/β = 0.8/1.0 mixture, 74 mg, 79%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +126.3 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3374, 2929, 1717, 1452, 1361, 1270, 1068, 1027, 737, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 – 7.27 (m, 9H, H_{Ar}), 4.98 (s, 0.8H, *H*-1 α), 4.78 (d, *J* = 7.4 Hz, 1H, *H*-1 β), 4.64 – 4.59 (m, 1.8H, -OCH_2Ar), 4.50 – 4.46 (m, 1.8H, -OCH_2Ar), 4.07 – 3.99 (m, 1.8H, *H*-5 α, C1-O*H* β), 3.92 – 3.86 (m, 1.8H, *H*-2 α, *H*-2 β), 3.51 (dq, *J* = 9.0, 6.1 Hz, 1H, *H*-5 β), 3.44 – 3.37 (m, 1.8H, *H*-4 α, *H*-4 β), 3.34 (s, 0.8H, C1-O*H* α), 2.58 (s, 1H, C2-O*H* β), 2.46 (m, 1H, *H*-3a β), 2.27 – 2.11 (m, 1.6H, C2-O*H* α, *H*-3a α), 1.93 (ddd, *J* = 13.4, 10.3, 3.2 Hz, 1H, *H*-3b α), 1.58 (ddd, *J* = 13.9, 11.0, 3.0 Hz, 1H, *H*-3b β), 1.34 (d, *J* = 6.1 Hz, 3H, *H*-6 β), 1.28 (d, *J* = 6.3 Hz, 2.4H, *H*-6 α); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.35, 138.21, 128.57, 128.54, 127.93, 127.89, 127.88, 127.86, 94.94, 93.82, 75.23, 75.14, 74.56, 71.68, 71.12, 68.74, 68.65, 68.41, 34.68, 31.12, 18.37, 18.13; **HRMS (ESI)** calculated for $C_{13}H_{18}NaO_4$ $[M+Na]^+$ 261.1097, found 261.1104.

Synthesis of lactol donor 17.

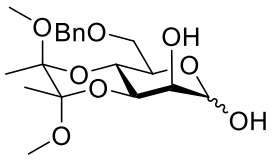


Phenyl 2-*O*-(*para*-methoxyphenyl)-3,4-*O*-[(1′*S*,2′*S*)-1′,2′-dimethoxy-1′,2′-dimethyl-1′,2′-ethylene]-1-thio-*α*-D-mannopyranoside (S7)



To a solution of **S6**[3] (2.34 g, 6.05 mmol) in CH_2Cl_2 (30 mL) were added PMBCl (1.0 mL, 7.4 mmol) and TBAI (447 mg, 1.21 mmol). Then a solution of NaOH (726 mg, 18.15 mmol) in water (30 mL) was added. The mixture was stirred vigorously at 40 °C for 8 h before being transferred into a separating funnel. The organic layer was washed with brine (30 mL), dried over Na_2SO_4 and then filtered. The concentrated residue was purified by flash column chromatography (Hexanes/EtOAc = 3/1), which gave compound **S7** (2.87 g, 5.66 mmol, 94%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +322.2 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3059, 2930, 1732, 1657, 1445, 1210, 1035, 744, 689 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43 – 7.39 (m, 2H, H_{Ar}), 7.38 – 7.35 (m, 2H, H_{Ar}), 7.32 – 7.25 (m, 3H, H_{Ar}), 6.88 (d, *J* = 8.6 Hz, 2H, H_{Ar}), 5.44 (d, *J* = 1.3 Hz, 1H, *H*-1), 4.88 (d, *J* = 11.5 Hz, 1H, C2-OCH_2Ar), 4.62 (d, *J* = 11.5 Hz, 1H, C2-OCH_2Ar), 4.35 – 4.18 (m, 2H, *H*-4, *H*-5), 4.07 (dd, *J* = 10.0, 2.9 Hz, 1H, *H*-3), 3.98 (dd, *J* = 2.9, 1.4 Hz, 1H, *H*-2), 3.87 – 3.76 (m, 5H, *H*-6a/6b, -OCH_3), 3.34 (s, 3H, -OCH_3), 3.31 (s, 3H, -OCH_3), 1.88 (dd, *J* = 7.5, 5.7 Hz, 1H, C6-O*H*), 1.38 (s, 3H, -CH_3), 1.35 (s, 3H, -CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 159.32, 134.09, 131.86, 130.54, 129.75, 129.17, 127.69, 113.79, 100.11, 99.71, 87.74, 77.12, 72.95, 72.04, 69.52, 64.00, 61.62, 55.38, 48.16, 48.03, 17.93; **HRMS (ESI)** calculated for $C_{26}H_{35}O_8S$ $[M+H]^+$ 507.2047, found 507.2051.

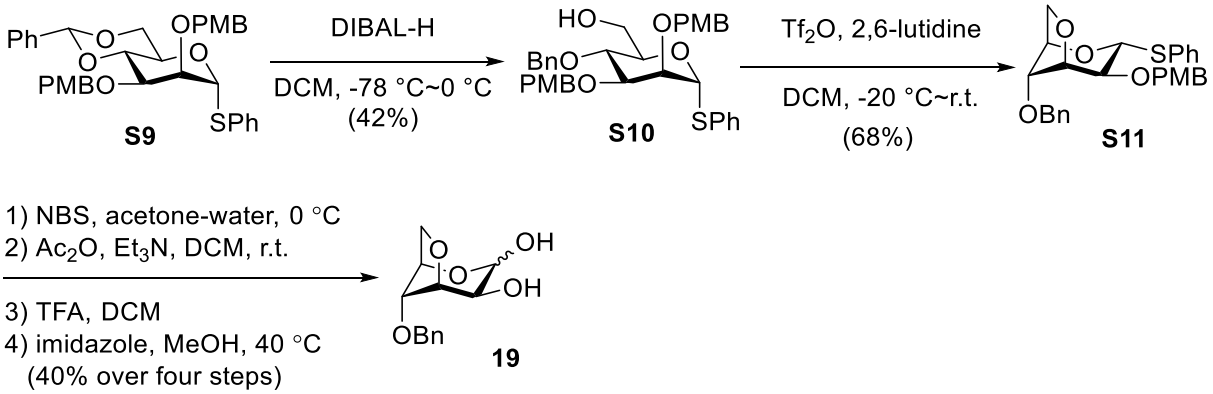
3,4-*O*-[(1′*S*,2′*S*)-1′,2′-dimethoxy-1′,2′-dimethyl-1′,2′-ethylene]-6-*O*-benzyl-*α*/*β*-D-mannopyranose (17)



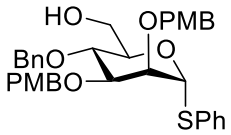
Compound **S7** (3.51 g, 6.93 mmol) was dissolved in dry DMF (15 mL). NaH (333 mg, 8.32 mmol, 60% in mineral oil) was added at 0 ℃. The mixture was stirred for 30 min and then BnBr (1.0 mL, 8.32 mmol) was added dropwise. The mixture was stirred for another 30 min at 0 ℃ and then warmed to room temperature. After being stirred at room temperature for 4 h, methanol (1.0 mL) was added to quench the reaction and CH_2Cl_2 (100 mL) was used to dilute the solution. The organic layer was washed by water (50 mL × 2) and brine (50 mL), then dried over Na_2SO_4 and filtered. The concentrated residue was purified by flash column chromatography (Hexanes/EtOAc = 4/1), which gave compound **S8** (3.64 g, 6.10 mmol, 88%) as colorless syrup. **S8** (3.64 g, 6.10 mmol) was dissolved in acetone (36 mL) and water (4 mL), followed by the addition of NBS (3.26 g, 18.3 mmol) at 0 ℃. The reaction mixture was quenched by 40% $Na_2S_2O_3$ aqueous solution (5 mL) after 2 h. The acetone was removed under vacuum. CH_2Cl_2 (100 mL) was used to extract the water phase. The organic layer was washed by saturated $NaHCO_3$ aqueous solution (50 mL × 2) and brine (50 mL), then dried over Na_2SO_4. To the filtrate was added DDQ (2.18 g, 9.6 mmol). The mixture was stirred for 6 h at room temperature. Then saturated $NaHCO_3$ aqueous solution was added until the solids were all dissolved. The organic layer was separated out, washed by brine (50 mL), dried over Na_2SO_4 and filtered. The concentrated residue was purified by flash column chromatography (Hexanes/EtOAc = 1/2), which gave the

title compound **17** (α/β = 3/1 mixture, 1.33 g, 3.46 mmol, 57%) as white solids. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +205.2 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3417, 2938, 1451, 1376, 1114, 1032, 743, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.19 (m, 6.8H), 5.23 (dd, *J* = 3.4, 1.5 Hz, 1H, *H*-1 *α*), 4.74 (dd, *J* = 9.9, 1.3 Hz, 0.32H, *H*-1 *β*), 4.62 – 4.56 (m, 3H, C6-OC*H*$_2$Ph *α*/*β*, C1-O*H β*), 4.17 (ddd, *J* = 10.2, 6.7, 1.9 Hz, 1H, *H*-5 *α*), 4.07 (dd, *J* = 10.2, 3.0 Hz, 1H, *H*-3 *α*), 4.02 – 3.94 (m, 2.33H, C1-O*H α*, *H*-4 *α*/*β*), 3.92 (m, 1H, *H*-2 *α*), 3.86 (m, 0.33H, *H*-2 *β*), 3.79 – 3.62 (m, 3H, *H*-6a/6b *α*/*β*, *H*-3 *β*), 3.58 (ddd, *J* = 9.9, 5.4, 2.0 Hz, 0.33H, *H*-5 *β*), 3.29 – 3.24 (m, 4H, -OC*H*$_3$ *α*/*β*), 3.19 – 3.14 (m, 4H, -OC*H*$_3$ *α*/*β*), 3.11 (d, *J* = 3.6 Hz, 0.33H, C2-O*H β*), 2.77 (d, *J* = 2.8 Hz, 1H, C2-O*H α*), 1.34 – 1.30 (m, 4H, -C*H*$_3$ *α*/*β*), 1.28 – 1.25 (m, 4H, -C*H*$_3$ *α*/*β*); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.08, 128.36, 127.87, 127.64, 100.32, 100.25, 99.89, 99.83, 94.88, 94.56, 73.96, 73.66, 73.49, 70.49, 69.99, 69.86, 69.78, 69.00, 68.48, 67.94, 63.68, 62.76, 48.17, 48.03, 47.94, 17.84, 17.77, 17.70; **HRMS (ESI)** calculated for $C_{19}H_{32}NO_8$ $[M+NH_4]^+$ 402.2122, found 402.2136.

Synthesis of lactol donor 19.

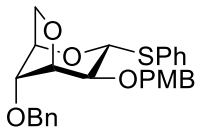


Phenyl 2,3-di-*O*-(*para*-methoxyphenyl)-4-*O*-benzyl-1-thio-*α*-D-mannopyranoside (S10)



Compound **S9**[4] (2.0 g, 3.33 mmol) was dissolved in dry CH_2Cl_2 (100 mL). The solution was stirred at -78 ℃ for 1 h and then DIBAL-H (1.0 M in hexane) was added. The mixture was stirred at -78 ℃ for 1 h and then slowly warmed to 0 ℃. The reaction was quenched by methanol (10 mL) after being stirred at 0 ℃ for 2 h. To the mixture was added saturated potassium sodium tartrate solution and it was stirred vigorously at room temperature until all the solids were dissolved. The organic layer was separated out, washed with brine and dried over Na_2SO_4. After filtration and concentration, the crude product was purified by flash column chromatography (Toluene/CH_2Cl_2/EtOAc = 5/4/1), which gave **S10** (836 mg, 1.39 mmol, 42%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +78.0 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3443, 2868, 1610, 1511, 1245, 1085, 820, 742, 696 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.43 – 7.16 (m, 14H, H_{Ar}), 6.94 – 6.79 (m, 4H, H_{Ar}), 5.45 (d, *J* = 1.5 Hz, 1H, *H*-1), 4.95 (d, *J* = 10.9 Hz, 1H, -OCH_2Ar), 4.69 – 4.60 (m, 3H, -OCH_2Ar), 4.58 – 4.49 (m, 2H, -OCH_2Ar), 4.10 (m, 1H, *H*-5), 3.98 (t, *J* = 9.5 Hz, 1H, *H*-4), 3.94 (dd, *J* = 3.1, 1.8 Hz, 1H, *H*-2), 3.85 (dd, *J* = 9.3, 3.1 Hz, 1H), 3.84 – 3.75 (m, 8H, -OCH_3 × 2, *H*-6a/6b), 1.81 (dd, *J* = 7.4, 5.8 Hz, 1H, C6-O*H*); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 159.47, 159.39, 138.48, 134.12, 131.99, 130.35, 129.99, 129.76, 129.62, 129.22, 128.57, 128.18, 127.91, 127.75, 113.95, 86.21, 79.80, 75.96, 75.40, 74.92, 73.32, 72.07, 71.97, 62.41, 55.43, 55.41; **HRMS (ESI)** calculated for $C_{35}H_{39}O_7S$ $[M+H]^+$ 603.2411, found 603.2426.

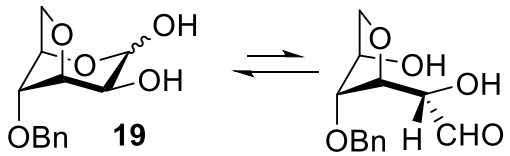
Phenyl 2-*O*-(4-methoxyphenyl)-4-*O*-benzyl-3,6-anhydro-1-thio-*α*-D-mannopyranoside (S11)



S10 (640 mg, 1.06 mmol) and 2,6-lutidine (370 μL, 3.20 mmol) were dissolved in dry CH_2Cl_2 (20 mL). The mixture was cooled at -20 ℃ for 30 min and then Tf_2O (268 μL, 1.59 mmol) was added. The mixture was stirred at -20 ℃ for 30 min and then warmed to room temperature. The reaction was quenched by saturated $NaHCO_3$ solution (5 mL) when the TLC (Hexanes/EtOAc = 2/1) showed the complete consumption of triflate intermediate. The mixture was diluted by CH_2Cl_2 (100 mL) and washed by 1 M HCl (50 mL × 2), saturated $NaHCO_3$ aqueous solution (50 mL) and brine (50 mL), then dried over Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography (Hexanes/EtOAc = 3/1), which gave the title compound **S11** (335 mg, 0.72 mmol, 68%) as light yellow syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +39.0 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 2880, 1610, 1511, 1246, 1100, 1057, 741, 695 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.68 – 7.53 (m, 2H, H_{Ar}), 7.43 – 7.29 (m, 3H, H_{Ar}), 7.29 – 7.05 (m, 7H, H_{Ar}), 6.84 (d, *J* = 8.6 Hz, 2H, H_{Ar}), 5.08 (d, *J* = 8.8 Hz, 1H, *H*-1), 4.63 – 4.56 (m, 2H, -OCH_2Ar), 4.50 – 4.41 (m, 2H, -OCH_2Ar, *H*-5), 4.37 (d, *J* = 11.8 Hz, 1H, -OCH_2Ar), 4.18 (dd, *J* = 6.0, 1.4 Hz, 1H, *H*-3), 4.14 (d, *J* = 10.8 Hz, 1H, *H*-6a), 4.00 – 3.86 (m, 2H, *H*-4, *H*-6b,), 3.79 (s, 3H, -OCH_3), 3.71 (dd, *J* = 8.8, 1.5 Hz, 1H, *H*-2); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 159.44, 137.38, 133.70, 132.19, 130.18, 130.06, 128.85, 128.62, 128.12, 127.96, 127.42, 113.84, 83.72, 77.64, 75.55, 74.38, 73.84, 72.56, 71.91,

69.30, 55.40; **HRMS (ESI)** calculated for $C_{27}H_{29}O_5S$ $[M+H]^+$ 465.1730, found 465.1739.

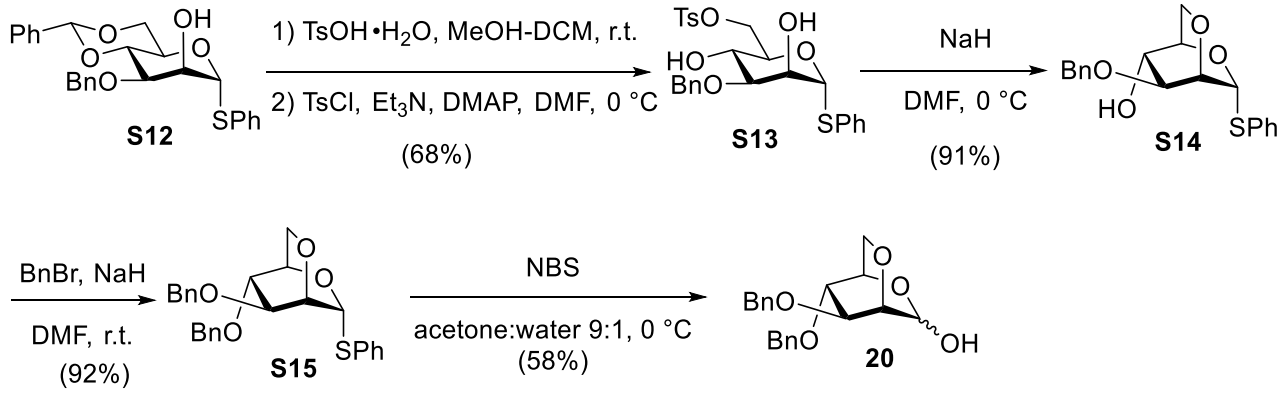
4-*O*-Benzyl-3,6-anhydro-*α*/*β*-D-mannopyranose (19)



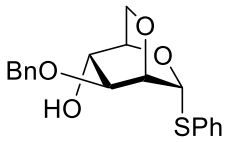
S11 (378 mg, 0.814 mmol) was dissolved in acetone (9 mL) and water (1 mL). To the mixture cooled at 0 ℃ was added NBS (434 mg, 2.44 mmol). The reaction was quenched by saturated $NaHCO_3$ aqueous solution after 2 h and acetone was removed under reduced pressure. The residue was extracted by CH_2Cl_2 (10 mL × 2). The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was dissolved in pyridine (1 mL) and acetic anhydride (0.5 mL) was added at 0 ℃. The mixture was stirred at room temperature for 2 h and quenched by methanol (1 mL), which was then diluted by CH_2Cl_2 (10 mL) and washed by 1 M HCl solution (5 mL × 2). The organic layer was separated and TFA (0.1 mL) was added at room temperature. The mixture was stirred at ambient temperature for 4 h before being washed with saturated $NaHCO_3$ aqueous solution (20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was dissolved in methanol (5 mL) and imidazole (55.0 mg, 0.814 mmol) was added to the solution. The mixture was stirred at 40 ℃ for 5 h, which was then concentrated and purified by silica gel column chromatography (CH_2Cl_2/MeOH = 20/1) to furnish the title compound **19** (partially converted to aldehyde, *α*/*β*/aldehyde = 0.5/1/1.5 mixture, 82.1 mg, 40%) as colorless

syrup. $[\alpha]_D^{29}$ = +33.0 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3127, 2928, 1588, 1326, 1104, 745, 616 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.77 (s, 1.5H, *H*-1 aldehyde **19a**), 7.45 – 7.28 (m, 15H, H_{Ar}), 5.44 (t, *J* = 5.4 Hz, 0.5H, *H*-1 *α*), 5.00 (t, *J* = 6.9 Hz, 1H, *H*-1 *β*), 4.79 (d, *J* = 11.3 Hz, 0.5H, -OCH_2Ar *α*), 4.76 – 4.65 (m, 4H), 4.65 – 4.54 (m, 2.5H), 4.43 (t, *J* = 2.8 Hz, 1H), 4.42 – 4.37 (m, 2H), 4.36 – 4.30 (m, 1H), 4.28 – 4.18 (m, 4H), 4.09 (d, *J* = 10.7 Hz, 1H), 4.04 (m, 1H), 4.02 – 3.94 (m, 3H), 3.91 – 3.72 (m, 5H), 3.49 – 3.45 (m, 1H), 3.36 (m, 1H), 3.08 (d, *J* = 8.3 Hz, 1H), 2.67 (d, *J* = 8.0 Hz, 0.5H), 2.46 (s, 0.5H), 2.21 (d, *J* = 7.8 Hz, 1H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 201.68, 137.25, 137.21, 136.90, 128.84, 128.77, 128.74, 128.51, 128.35, 128.31, 128.17, 128.04, 127.98, 97.18, 92.81, 80.32, 79.29, 78.18, 76.80, 76.66, 76.08, 74.00, 73.70, 73.42, 72.24, 72.15, 72.01, 71.01, 70.08, 69.47, 66.39, 51.06; **HRMS (ESI)** calculated for $C_{13}H_{16}NaO_5$ $[M+Na]^+$ 275.0890, found 275.0893.

Synthesis of lactol donor 20.



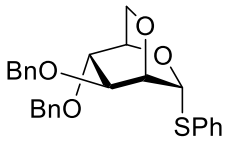
Phenyl 3-*O*-benzyl-2,6-anhydro-1-thio-*α*-D-mannopyranoside (S14)



S12[5] (1.07 g, 2.37 mmol) was dissolved in CH_2Cl_2 (10 mL) and MeOH (10 mL). To this solution was added *p*-toluenesulfonic acid monohydrate (0.1 g). The mixture was stirred at room temperature for 4 h and then neutralized by 0.1 mL Et_3N. To the concentrated residue was added dry CH_2Cl_2 (100 mL), followed by the addition of Et_3N (0.6 mL, 4.3 mmol) and DMAP (26 mg, 0.21 mmol) at 0 °C. The mixture was stirred in ice bath for 30 min and then tosyl chloride (480 mg, 2.52 mmol) was added. After 5 h, the organic solution was washed by water and dried over Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography (Hexanes/EtOAc = 3/2), which gave compound **S13** (835 mg, 1.62 mmol, 68%) as colorless syrup. To a solution of **S13** (446 mg, 0.863 mmol) in dry DMF (17 mL) was added sodium hydride at 0 °C. The mixture was stirred at 0 °C for 2 h and then quenched by methanol (0.5 mL). CH_2Cl_2 (100 mL) was used to dilute the mixture and the organic layer was washed with water. After general drying procedure, the concentrated crude product was purified by flash column chromatography (Hexanes/EtOAc = 2/1), which gave the title compound **S14** (270 mg, 0.784 mmol, 91%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +129.3 (*c* 0.05, $CHCl_3$); **FT-IR (thin film)** 2878, 1439, 1099, 856, 739, 694 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.53 – 7.28 (m, 10H, H_{Ar}), 5.72 (d, *J* = 2.7 Hz, 1H, *H*-1), 4.73 (d, *J* = 11.9 Hz, 1H, -OCH_2Ar), 4.70 (d, *J* = 11.9 Hz, 1H, -OCH_2Ar), 4.21 – 4.15 (m, 2H, *H*-2, *H*-6a), 4.01 (m, 1H, *H*-5), 3.93 (dd, *J* = 10.1, 0.8 Hz, 1H, *H*-6b), 3.89 – 3.83 (m, 2H, *H*-4, *H*-3), 2.90 (d, *J* = 11.4 Hz, 1H, C4-O*H*);

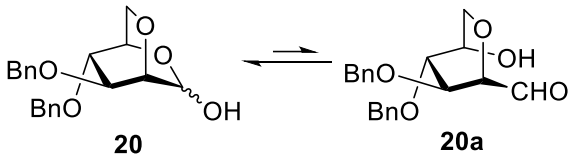
^{13}C NMR (150 MHz, $CDCl_3$) δ 137.50, 133.22, 131.88, 129.43, 128.67, 128.16, 128.12, 128.10, 86.15, 80.11, 73.67, 71.80, 70.85, 69.20, 65.72; **HRMS (ESI)** calculated for $C_{19}H_{21}O_4S$ $[M+H]^+$ 345.1155, found 345.1158.

Phenyl 3,4-di-*O*-benzyl-2,6-anhydro-1-thio-*α*-D-mannopyranoside (S15)



To **S14** (270 mg, 0.783 mmol) was added dry DMF (5 mL). BnBr (112 μL, 0.94 mmol) and NaH (38 mg, 0.94 mmol) were added at 0 ℃. The reaction was quenched by methanol (0.1 mL) after 3 h and then diluted by CH_2Cl_2 (50 mL). The organic layer was washed by brine (50 mL) and dried over Na_2SO_4. After filtration, the concentrated residue was purified by flash column chromatography (Hexanes/EtOAc = 4/1), which gave compound **S15** (312 mg, 0.718 mmol, 92%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +56.7 (*c* 0.05, $CHCl_3$); **FT-IR (thin film)** 2874, 1454, 1104, 855, 739, 693 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.52 – 7.46 (m, 2H, H_{Ar}), 7.43 – 7.27 (m, 13H, H_{Ar}), 5.68 (d, *J* = 2.4 Hz, 1H, *H*-1), 4.69 – 4.65 (m, 2H, -OCH_2Ar), 4.60 (d, *J* = 12.3 Hz, 1H, -OCH_2Ar), 4.56 (d, *J* = 11.7 Hz, 1H, -OCH_2Ar), 4.20 – 4.15 (m, 2H, *H*-2, *H*-6a), 4.14 – 4.10 (m, 2H, *H*-3, *H*-5), 3.87 (dd, *J* = 10.1, 1.1 Hz, 1H, *H*-6b), 3.69 (m, 1H, *H*-4); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 137.85, 137.64, 134.31, 132.07, 129.27, 128.64, 128.55, 128.26, 128.13, 128.10, 127.93, 127.80, 87.00, 80.57, 78.81, 71.04, 70.46, 70.04, 69.74, 66.92; **HRMS (ESI)** calculated for $C_{26}H_{27}O_4S$ $[M+H]^+$ 435.1625, found 435.1649.

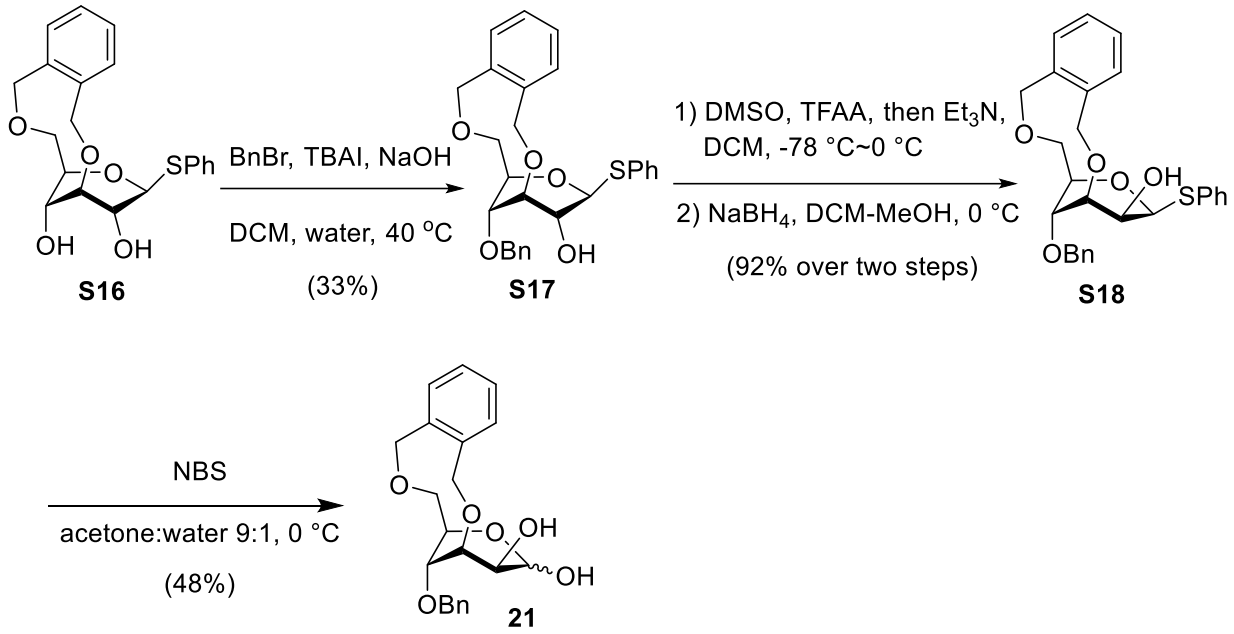
3,4-Di-*O*-benzyl-2,6-anhydro-*α*/*β*-D-mannopyranose (20)



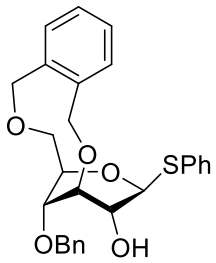
S15 (312 mg, 0.718 mmol) was dissolved in acetone (9 mL) and water (1 mL), followed by the addition of NBS (383 mg, 2.15 mmol) at 0 ℃. The mixture was quenched by 40% $Na_2S_2O_3$ aqueous solution (10 mL) after 1 h. The acetone was removed under reduced pressure and CH_2Cl_2 (50 mL) was used to extract the water phase. The organic layer was washed by saturated $NaHCO_3$ aqueous solution (50 mL) and brine (50 mL), then dried over Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography (CH_2Cl_2/Acetone = 3/1), which gave the title compound **20** (partially converted to aldehyde, *α*/*β*/aldehyde = 1/0.4/0.4 mixture, 142 mg, 0.415 mmol, 58%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = -19.5 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3404, 2872, 1722, 1453, 1087, 1021, 857, 736, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.74 (d, *J* = 0.8 Hz, 0.4H, *H*-1 aldehyde **20a**), 7.43 – 7.28 (m, 18H, H_{Ar}), 5.42 (dd, *J* = 7.4, 3.0 Hz, 0.4H, *H*-1 *β*), 5.09 (d, *J* = 9.6 Hz, 1H, *H*-1 *α*), 4.76 – 4.61 (m, 4H, -OCH_2Ar), 4.60 – 4.48 (m, 3.2H, -OCH_2Ar), 4.26 (dd, *J* = 10.1, 3.0 Hz, 1H, *H*-6a *α*), 4.19 (m, 0.4H), 4.08 (m, 1H, *H*-5 *α*), 4.07 – 3.97 (m, 2.2H), 3.92 (s, 1H, *H*-2 *α*), 3.89 (d, *J* = 6.6, 0.4H), 3.84 – 3.78 (m, 2.2H), 3.77 – 3.72 (m, 0.8H), 3.71 – 3.64 (m, 2.4H), 3.38 (m, 0.4H), 3.43 (d, *J* = 7.8 Hz, 0.4H), 2.37 (d, *J* = 5.7 Hz, 0.4H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 198.89, 137.65, 137.50, 137.42, 137.17, 128.79, 128.69, 128.67, 128.62, 128.59, 128.39, 128.22, 128.18, 128.13, 128.12, 128.09, 128.07, 128.03, 93.68, 92.95, 80.63, 80.53, 79.36, 79.32, 78.76, 76.12, 74.05, 74.03, 72.13, 70.94, 70.78, 70.65, 70.51, 70.23, 68.19, 68.08,

67.47, 67.00, 66.96, 65.00, 64.40; **HRMS (ESI)** calculated for $C_{20}H_{23}O_5$ $[M+H]^+$ 343.1540, found 343.1545.

Synthesis of lactol donor 21.



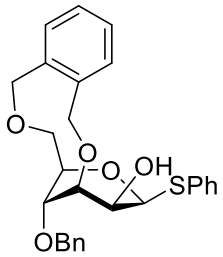
Phenyl 3,6-*O*-(*o*-xylylene)-4-*O*-benzyl-1-thio-*β*-D-glucopyranoside (S17)



To a solution of compound **S16**[6] (670 mg, 1.79 mmol) in CH_2Cl_2 (15 mL) were added BnBr (234 μL, 1.97 mmol) and TBAI (115 mg, 0.358 mmol). Then a solution of NaOH (215 mg, 5.37 mmol) in water (15 mL) was added. The mixture was stirred vigorously at 40 °C for 8 h and then transferred into a separating funnel. The organic layer was washed with brine (20 mL), dried over Na_2SO_4 and then filtered. The concentrated residue was purified by flash column chromatography (Hexanes/EtOAc = 4/1), which gave compound **S17** (277 mg,

0.60 mmol, 33%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = -42.5 (*c* 0.04, $CHCl_3$); **FT-IR (thin film)** 2886, 1457, 1010, 1025, 744, 690 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.52 – 7.45 (m, 2H, H_{Ar}), 7.39 – 7.29 (m, 5H, H_{Ar}), 7.28 – 7.18 (m, 5H, H_{Ar}), 7.16 – 7.12 (m, 2H, H_{Ar}), 5.62 (d, *J* = 10.0 Hz, 1H, -OCH_2Ar), 5.12 (d, *J* = 10.2 Hz, 1H, -OCH_2Ar), 4.74 (d, *J* = 8.1 Hz, 1H, *H*-1), 4.63 (d, *J* = 11.8 Hz, 1H, -OCH_2Ar), 4.60 (d, *J* = 11.8 Hz, 1H, -OCH_2Ar), 4.52 (m, 1H, *H*-3), 4.41 (d, *J* = 10.2 Hz, 1H, -OCH_2Ar), 4.35 (d, *J* = 10.0 Hz, 1H, -OCH_2Ar), 4.18 (d, *J* = 3.3 Hz, 1H, *H*-5), 3.95 (d, *J* = 3.3 Hz, 1H, *H*-4), 3.91 (dd, *J* = 13.6, 1.0 Hz, 1H, *H*-6a), 3.82 (m, 1H, *H*-2), 3.75 (dd, *J* = 13.6, 3.3 Hz, 1H, *H*-6b), 2.62 (d, *J* = 10.8 Hz, 1H, C2-O*H*); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 136.97, 136.96, 136.23, 134.99, 130.81, 129.47, 128.94, 128.92, 128.74, 128.54, 128.07, 127.94, 127.86, 127.22, 87.86, 84.18, 77.15, 75.07, 74.23, 72.79, 71.78, 71.08, 70.89; **HRMS (ESI)** calculated for $C_{27}H_{28}NaO_5S$ $[M+Na]^+$ 487.1550, found 487.1541.

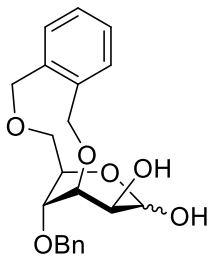
Phenyl 3,6-*O*-(*o*-xylylene)-4-*O*-benzyl-1-thio-*β*-D-mannopyranoside (S18)



To dry CH_2Cl_2 (10 mL) was added DMSO (149 μL, 2.1 mmol). The solution was stirred at -78 °C for 10 min and then TFAA (209 μL, 1.5 mmol) was added over a 5 min period. After 15 min, **S17** (277 mg, 0.60 mmol) in dry CH_2Cl_2 (10 mL) was added to this solution. The mixture was stirred at -78 °C for another 3 h and then Et_3N (291 μL, 2.1 mmol) was added. The mixture was warmed to -20 °C over 2 h and then warmed to room temperature quickly, quenched by water. The organic layer was washed by brine (20 mL), dried over

anhydrous Na_2SO_4, filtered and concentrated. The residue was dissolved in CH_2Cl_2 (5 mL) and MeOH (5 mL). $NaBH_4$ (39 mg, 1.03 mmol) was added at 0 ℃. The mixture was warmed to room temperature after 1 h and stirred for 30 min. After being quenched with saturated NH_4Cl solution, the mixture was concentrated and then purified by flash column chromatography (Hexanes/EtOAc = 8/1), which gave compound **S18** (123 mg, 0.265 mmol, 52%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = -13.8 (*c* 0.04, $CHCl_3$); **FT-IR (thin film)** 2920, 2850, 1454, 1114, 1032, 742, 694 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 – 7.43 (m, 2H, H_{Ar}), 7.38 – 7.27 (m, 7H, H_{Ar}), 7.25 – 7.14 (m, 5H, H_{Ar}), 5.61 (d, *J* = 10.2 Hz, 1H, -OCH_2Ar), 5.28 – 5.12 (m, 2H, *H*-1, -OCH_2Ar), 4.59 (d, *J* = 12.0 Hz, 1H, -OCH_2Ar), 4.55 (d, *J* = 12.0 Hz, 1H, -OCH_2Ar), 4.44 – 4.37 (m, 3H, -OCH_2Ar × 2, *H*-4), 4.33 (ddd, *J* = 10.7, 6.2, 4.4 Hz, 1H, *H*-2), 4.09 – 4.05 (m, 2H, *H*-3, *H*-5), 3.94 (dd, *J* = 13.5, 1.4 Hz, 1H, *H*-6a), 3.77 (dd, *J* = 13.5, 3.5 Hz, 1H, *H*-6b), 3.70 (d, *J* = 10.7 Hz, 1H, C2-O*H*); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 137.49, 137.14, 136.27, 135.70, 130.15, 129.62, 128.92, 128.84, 128.79, 128.31, 128.21, 127.89, 127.82, 126.75, 88.26, 83.89, 75.19, 72.64, 72.55, 71.70, 70.99, 70.70, 66.58; **HRMS (ESI)** calculated for $C_{27}H_{28}NaO_5S$ $[M+Na]^+$ 487.1550, found 487.1559.

3,6-*O*-(*o*-Xylylene)-4-*O*-benzyl-*α*/*β*-D-mannopyranose (21)



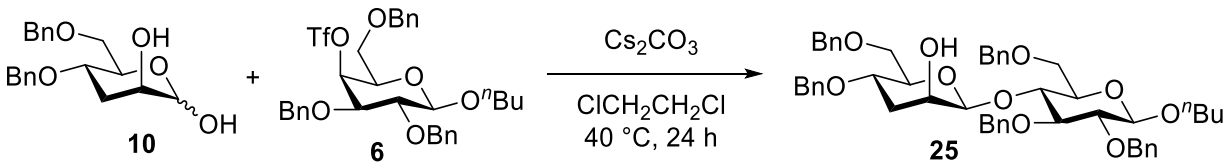
S18 (123 mg, 0.265 mmol) was dissolved in acetone (10 mL) and water (1 ml). To this solution was added NBS (141 mg, 0.792 mmol) at 0 ℃. After 1.5 h, the reaction was quenched by 40% $Na_2S_2O_3$ aqueous

solution (1 mL). The acetone was removed under vacuum and CH_2Cl_2 (10 mL × 3) was used to extract the water phase. The organic layer was washed by saturated $NaHCO_3$ aqueous solution (10 mL) and brine (10 mL), then dried over Na_2SO_4. After filtration and concentration, the residue was purified by flash column chromatography (Hexanes/EtOAc = 1/3), which gave the title compound **21** (α/β = 3/1 mixture, 47 mg, 0.126 mmol, 48%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +37.0 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3384, 2920, 2873, 1453, 1071, 1036, 734, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.15 (m, 36H, H_{Ar}), 5.24 (d, *J* = 10.4 Hz, 1H, -OCH_2Ar *β*), 5.00 (dd, *J* = 7.8, 4.8 Hz, 3H, *H*-1 *α*), 4.99 – 4.89 (m, 8H, -OCH_2Ar *β*, *H*-1 *β*, -OCH_2Ar ×2 *α*), 4.77 (d, *J* = 11.3 Hz, 1H, C1-O*H β*), 4.70 (d, *J* = 11.8 Hz, 3H, -OCH_2Ar *α*), 4.62 – 4.50 (m, 8H, -OCH_2Ar ×2 *α*, -OCH_2Ar ×2 *β*), 4.48 – 4.44 (m, 4H, -OCH_2Ar *α*, -OCH_2Ar *β*), 4.40 (d, *J* = 10.5 Hz, 1H, -OCH_2Ar *β*), 4.26 (t, *J* = 5.9 Hz, 3H, *H*-5 *α*), 4.15 (s, 1H, *H*-4 *β*), 4.12 – 4.07 (m, 4H, *H*-5 *β*, *H*-4 *α*), 4.06 – 3.98 (m, 5H, *H*-2 *β*, *H*-3 *α*, *H*-3 *β*), 3.98 – 3.90 (m, 4H, *H*-6a *α*, *H*-6a *β*), 3.87 – 3.82 (m, 6H, *H*-2 *α*, *H*-6b *α*), 3.63 (dd, *J* = 13.3, 3.3 Hz, 1H, *H*-6b *β*), 3.30 (d, *J* = 8.7 Hz, 3H, C1-O*H α*), 3.25 (d, *J* = 10.0 Hz, 1H, C2-O*H β*), 2.88 (d, *J* = 9.6 Hz, 3H, C2-O*H α*); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 137.45, 137.42, 137.36, 136.96, 136.36, 135.71, 130.38, 130.11, 130.08, 129.44, 128.93, 128.77, 128.73, 128.59, 128.42, 128.30, 128.24, 127.92, 127.84, 95.12, 92.42, 79.23, 75.10, 74.91, 74.60, 73.57, 72.66, 72.43, 71.77, 71.57, 71.40, 71.35, 71.27, 70.24, 69.73, 65.07; **HRMS (ESI)** calculated for $C_{21}H_{24}NaO_6$ $[M+Na]^+$ 395.1465, found 395.1486.

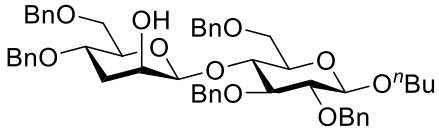
General procedure for Cs_2CO_3 mediated *O*-alkylation.

To a mixture of lactol donor (~0.1 mmol, 1.0 eq.), sugar derived triflate acceptor **6** (2.0 eq.), and Cs_2CO_3 (2.5 eq.) was added 1,2-dichloroethane (1.0 mL). The reaction mixture was stirred at 40 ℃ for 24 hours. The crude reaction mixture was purified by preparative TLC. The *β*-configuration of the new formed mannosidic linkage was unambiguously assigned by measuring the $^1J_{C\text{-}H}$ for the anomeric carbon.

Synthesis of compound 25, 27, 29, 32, 33, S19, 37, 39*α*, 39*β* and 40.

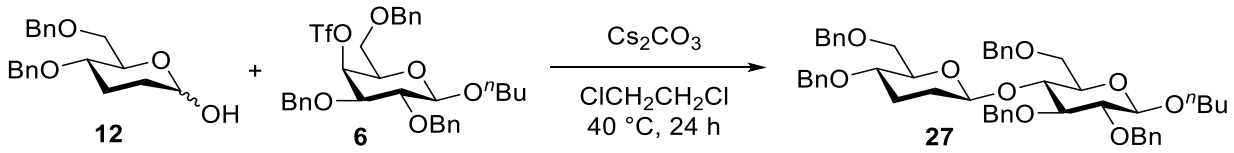


Butyl *O*-4,6-di-*O*-benzyl-3-deoxy-*β*-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (25)

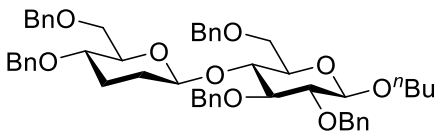


Disaccharide **25** was prepared from lactol donor **10** (34.4 mg, 0.1 mmol) and triflate acceptor **6** (128 mg, 0.2 mmol) following the general procedure. The crude reaction mixture was purified by preparative TLC (Hexanes/EtOAc/MeOH = 2/1/1%) to afford compound **25** (33.2 mg, 40%) as colorless syrup. The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon was determined to be 158.1 Hz. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +44.80 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 2926, 1730, 1453, 1362, 1056, 734, 696 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.35 – 7.19 (m, 25H, H_{Ar}), 4.95 – 4.89 (m, 2H, -

OCH_2Ar), 4.84 (d, J = 11.2 Hz, 1H, -OCH_2Ar), 4.73 (s, 1H, H-1′), 4.70 – 4.62 (m, 2H, -OCH_2Ar), 4.57 – 4.41 (m, 4H, -OCH_2Ar), 4.40 – 4.33 (m, 2H, -OCH_2Ar, H-1), 3.97 – 3.90 (m, 2H, -OCH_2CH$_2$CH$_2$CH$_3$, H-4), 3.78 – 3.69 (m, 4H, H-2′, H-6, H-4′), 3.69 – 3.61 (m, 2H, H-3, H-6′a), 3.56 (dd, J = 10.7, 5.1 Hz, 1H, H-6′b), 3.52 (dt, J = 9.5, 6.8 Hz, 1H, -OCH_2CH$_2$CH$_2$CH$_3$), 3.46 (dt, J = 9.7, 3.3 Hz, 1H, H-5), 3.45 – 3.38 (m, 2H, H-2, H-5′), 2.66 (br, 1H, C2′-OH), 2.35 (dt, J = 13.5, 4.3 Hz, 1H, H-3′a), 1.69 – 1.58 (m, 2H, -OCH$_2$CH_2CH$_2$CH$_3$), 1.50 – 1.32 (m, 3H, -OCH$_2$CH$_2$CH_2CH$_3$, H-3′b), 0.93 (t, J = 7.4 Hz, 3H, -OCH$_2$CH$_2$CH$_2$CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 138.92, 138.61, 138.49, 138.35, 137.97, 128.54, 128.49, 128.48, 128.38, 128.36, 128.34, 128.01, 127.90, 127.88, 127.84, 127.80, 127.53, 103.80, 100.57, 83.00, 82.28, 78.78, 75.93, 75.14, 74.97, 74.47, 73.67, 73.44, 71.56, 69.91, 69.66, 69.54, 69.20, 67.22, 34.15, 31.96, 19.45, 14.02; **HRMS (ESI)** calculated for $C_{51}H_{60}NaO_{10}$ $[M+Na]^+$ 855.4079, found 855.4120.

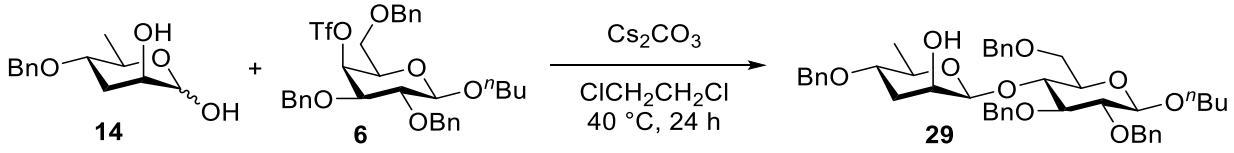


Butyl *O*-4,6-di-*O*-benzyl-2,3-dideoxy-*β*-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (27)

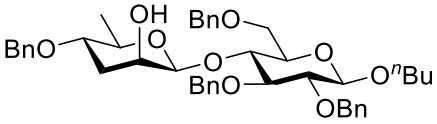


Disaccharide **27** was prepared from lactol donor **12**[7] (32.8 mg, 0.1 mmol) and triflate acceptor **6** (128 mg, 0.2 mmol) following the general procedure. The crude reaction mixture was purified by preparative TLC

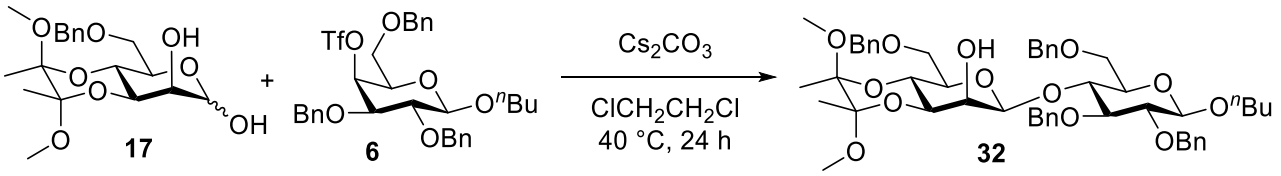
(Hexanes/EtOAc = 5/1) to afford compound **27** (21.5 mg, 26%) as colorless syrup. The $^{1}J_{C\text{-}H}$ of mannosidic anomeric carbon was determined to be 158.8 Hz. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +47.50 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3030, 2926, 1732, 1656, 1605, 1573, 1496, 1445, 1370, 1240, 1153, 1046, 745 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.19 (m, 25H, H_{Ar}), 5.02 (d, *J* = 11.2 Hz, 1H, -OCH_2Ar), 4.89 (d, *J* = 10.8 Hz, 1H, -OCH_2Ar), 4.79 (d, *J* = 11.2 Hz, 1H, -OCH_2Ar), 4.70 – 4.60 (m, 3H, -OCH_2Ar × 2, *H*-1′), 4.58 – 4.50 (m, 2H, -OCH_2Ar), 4.49 – 4.34 (m, 4H, -OCH_2Ar × 3, *H*-1), 3.94 (dt, *J* = 9.5, 6.5 Hz, 1H, -OC$H_2$$CH_2CH_2CH_3$), 3.83 (t, *J* = 9.4 Hz, 1H, *H*-4), 3.73 (dd, *J* = 10.8, 2.1 Hz, 1H, *H*-6a), 3.68 – 3.55 (m, 4H, *H*-6b, *H*-6′a, *H*-3, *H*-6′b), 3.52 (dt, *J* = 9.5, 6.8 Hz, 1H, -OC$H_2$$CH_2CH_2CH_3$), 3.47 – 3.35 (m, 4H, *H*-5, *H*-4′, *H*-2, *H*-5′), 2.13 (m, 1H, *H*-3′a), 1.75 (m, 1H, *H*-2′a), 1.70 – 1.57 (m, 2H, -OCH_2C$H_2CH_2CH_3$), 1.50 – 1.29 (m, 4H, -OCH_2CH_2CH_2CH_3, *H*-2′b, *H*-3′b), 0.93 (t, *J* = 7.4 Hz, 3H, -$OCH_2CH_2CH_2$CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 139.43, 138.78, 138.66, 138.47, 138.30, 128.48, 128.41, 128.34, 128.24, 127.88, 127.83, 127.79, 127.76, 127.73, 127.70, 127.44, 127.29, 103.75, 101.98, 83.38, 82.09, 78.80, 76.38, 75.24, 75.05, 74.86, 73.62, 73.43, 72.75, 71.36, 69.86, 69.70, 69.00, 31.98, 30.47, 27.70, 19.45, 14.03; **HRMS (ESI)** calculated for $C_{51}H_{60}NaO_9$ $[M+Na]^+$ 839.4130, found 839.4177.



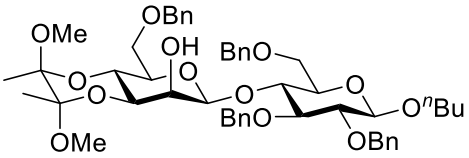
Butyl *O*-4-*O*-benzyl-3,6-dideoxy-*β*-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (29)



Disaccharide **29** was prepared from lactol donor **14** (23.8 mg, 0.1 mmol) and triflate acceptor **6** (128 mg, 0.2 mmol) following the general procedure. The crude reaction mixture was purified by preparative TLC (Hexanes/EtOAc/MeOH= 2/1/1%) to afford compound **29** (2.2 mg, 3%) as colorless syrup. The $^{1}J_{C\text{-}H}$ of mannosidic anomeric carbon was determined to be 159.0 Hz. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +45.71 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 2918, 1731, 1453, 1364, 1060, 731, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 – 7.00 (m, 20H, H_{Ar}), 4.94 – 4.82 (m, 3H, -OCH_2Ar), 4.72 – 4.63 (m, 3H, *H*-1′, -OCH_2Ar × 2), 4.59 – 4.53 (m, 2H, -OCH_2Ar), 4.43 (d, *J* = 11.4 Hz, 1H, -OCH_2Ar), 4.38 (d, *J* = 7.8 Hz, 1H, *H*-1), 3.97 – 3.88 (m, 2H, -OCH_2CH$_2$CH$_2$CH$_3$, *H*-4), 3.76 – 3.70 (m, 3H, *H*-2′, *H*-6), 3.64 (t, *J* = 9.0 Hz, 1H, *H*-3), 3.54 (dt, *J* = 9.5, 6.8 Hz, 1H, -OCH_2CH$_2$CH$_2$CH$_3$), 3.47 – 3.41 (m, 2H, *H*-5, *H*-2), 3.38 (ddd, *J* = 10.8, 9.1, 4.5 Hz, 1H, *H*-4′), 3.29 (dq, *J* = 9.1, 6.1 Hz, 1H, *H*-5′), 2.64 (s, 1H, C2′-O*H*), 2.36 (dt, *J* = 13.5, 4.0 Hz, 1H, *H*-3′a), 1.70 – 1.58 (m, 2H, -OCH$_2$CH_2CH$_2$CH$_3$), 1.49 – 1.37 (m, 2H, -OCH$_2$CH$_2$CH_2CH$_3$), 1.33 (ddd, *J* = 13.7, 10.9, 2.9 Hz, 1H, *H*-3′b), 1.23 (d, *J* = 6.1 Hz, 3H, *H*-6′), 0.93 (t, *J* = 7.4 Hz, 3H, -OCH$_2$CH$_2$CH$_2$CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.81, 138.51, 138.43, 137.90, 128.54, 128.49, 128.37, 128.33, 127.99, 127.93, 127.89, 127.84, 127.82, 127.62, 103.83, 100.67, 83.39, 82.22, 75.88, 75.41, 75.00, 74.88, 74.50, 73.71, 71.67, 69.94, 69.19, 67.43, 34.26, 31.95, 19.44, 18.40, 14.02; **HRMS (ESI)** calculated for $C_{44}H_{54}NaO_9$ $[M+Na]^+$ 749.3660, found 749.3701.

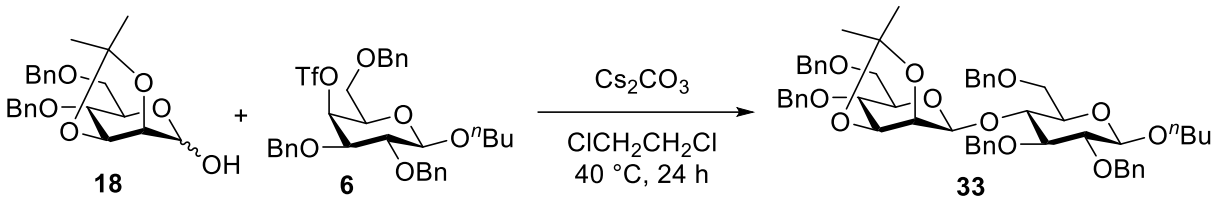


Butyl *O*-3,4-*O*-[(1′*S*,2′*S*)-1′,2′-dimethoxy-1′,2′-dimethyl-1′,2′-ethylene]-6-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (32)

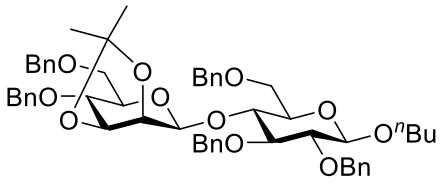


Disaccharide **32** was prepared from lactol donor **17** (42.0 mg, 0.109 mmol) and triflate acceptor **6** (139 mg, 0.218 mmol) following the general procedure. The crude reaction mixture was purified by preparative TLC (Hexanes/EtOAc = 1/1) to afford compound **32** (23.7 mg, 0.0271 mmol, 25%) as colorless syrup. The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon was determined to be 160.1 Hz. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +111.4 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 2928, 1732, 1453, 1086, 1041, 734, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.24 (m, 20H, H_{Ar}), 5.00 (d, *J* = 11.1 Hz, 1H, -OCH_2Ar), 4.97 (d, *J* = 10.9 Hz, 1H, -OCH_2Ar), 4.91 (d, *J* = 11.1 Hz, 1H, -OCH_2Ar), 4.83 (d, *J* = 1.1 Hz, 1H, *H*-1′), 4.74 (d, *J* = 10.9 Hz, 1H, -OCH_2Ar), 4.68 (d, *J* = 12.1 Hz, 1H, -OCH_2Ar), 4.61 (d, *J* = 12.1 Hz, 1H, -OCH_2Ar), 4.54 (d, *J* = 12.1 Hz, 1H, -OCH_2Ar), 4.49 (d, *J* = 12.1 Hz, 1H, -OCH_2Ar), 4.42 (d, *J* = 7.8 Hz, 1H, *H*-1), 4.07 (t, *J* = 10.0 Hz, 1H, *H*-4′), 4.02 – 3.92 (m, 3H, -OCH_2C$_3$H$_7$, *H*-4, *H*-2′), 3.84 (dd, *J* = 11.2, 4.0 Hz, 1H, *H*-6a), 3.80 (dd, *J* = 11.2, 2.4 Hz, 1H, *H*-6b), 3.75 (t, *J* = 9.1 Hz, 1H, *H*-3), 3.69 (dd, *J* = 11.0, 1.8 Hz, 1H, *H*-6′a), 3.62 – 3.53 (m, 4H, *H*-3′, *H*-6′a, *H*-5, -OCH_2C$_3$H$_7$), 3.50 (ddd, *J* = 10.0, 5.6, 1.8 Hz, 1H, *H*-5′), 3.46 (dd, *J* = 9.1, 7.8 Hz, 1H, *H*-2), 3.25 (s, 3H, -OCH_3), 3.21 (s, 3H, -OCH_3), 2.60 (d, *J* = 2.6 Hz, 1H, C2-O*H*), 1.74 – 1.62 (m, 2H, -OCH$_2$CH_2C$_2$H$_5$), 1.53 – 1.42 (m, 2H, -

$OC_2H_4CH_2CH_3$), 1.38 (s, 3H, -CH_3), 1.29 (s, 3H, -CH_3), 0.98 (t, J = 7.4 Hz, 3H, -$OC_3H_6CH_3$); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.85, 138.53, 138.40, 138.04, 128.38, 128.28, 128.22, 128.18, 127.77, 127.74, 127.70, 127.66, 127.52, 127.38, 127.30, 103.71, 100.38, 100.18, 99.68, 83.08, 82.12, 76.01, 75.20, 74.90, 74.88, 74.25, 73.47, 73.45, 70.16, 69.81, 69.03, 68.80, 68.59, 62.80, 48.07, 47.94, 31.86, 19.35, 17.81, 17.78, 13.93; **HRMS (ESI)** calculated for $C_{50}H_{65}O_{13}$ $[M+H]^+$ 873.4420, found 873.4390.

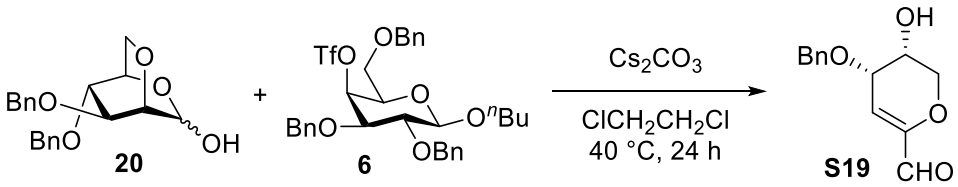


Butyl *O*-2,3-*O*-isopropylidene-4,6-di-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (33)

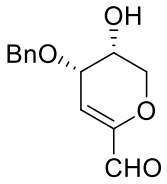


Disaccharide **33** was prepared from lactol donor **18**[8] (41.7 mg, 0.104 mmol) and triflate acceptor **6** (129 mg, 0.202 mmol) following the general procedure. The crude reaction mixture was purified by preparative TLC (Toluene/EtOAc = 8/1) to afford compound **33** (30.5 mg, 0.0343 mmol, 35%) as colorless syrup. The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon was determined to be 160.4 Hz. $[\alpha]_D^{29}$ = +23.0 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3386, 2930, 1453, 1370, 1217, 1065, 863, 735, 697 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.18 (m, 25H, H_{Ar}), 5.06 (d, J = 11.1 Hz, 1H, -OCH_2Ar), 4.91 (d, J = 1.9 Hz, 1H, *H*-1′), 4.88 (d, J = 10.9 Hz, 1H, -OCH_2Ar), 4.80 (d, J = 11.1 Hz, 1H, -OCH_2Ar), 4.72 – 4.60 (m, 3H, -OCH_2Ar), 4.55 – 4.42 (m, 3H, -OCH_2Ar), 4.40 – 4.32 (m, 2H, *H*-1, -

OCH_2Ar), 4.20 (t, J = 5.9 Hz, 1H, H-3′), 4.04 (dd, J = 6.2, 1.9 Hz, 1H, H-2′), 3.99 – 3.90 (m, 2H, -OCH_2C$_3$H$_7$, H-4), 3.75 (d, J = 3.1 Hz, 2H, H-6), 3.70 (t, J = 9.1 Hz, 1H, H-3), 3.62 – 3.56 (m, 2H, H-6′a, H-4′), 3.55 – 3.48 (m, 3H, -OCH_2C$_3$H$_7$, H-5′, H-5), 3.44 (dd, J = 10.4, 5.2 Hz, 1H, H-6′b), 3.39 (dd, J = 9.2, 7.8 Hz, 1H, H-2), 1.69 – 1.61 (m, 2H, -OCH$_2$CH_2C$_2$H$_5$), 1.50 – 1.36 (m, 5H, -CH_3, -OC$_2$H$_4$CH_2CH$_3$), 1.34 (s, 3H, -CH_3), 0.94 (t, J = 7.4 Hz, 3H, -OC$_3$H$_6$CH_3); **^{13}C NMR (150 MHz, CDCl$_3$)** δ 139.48, 138.76, 138.71, 138.20, 138.11, 128.49, 128.42, 128.39, 128.34, 128.30, 128.12, 128.10, 127.96, 127.94, 127.80, 127.78, 127.68, 127.63, 127.43, 127.23, 110.47, 103.79, 98.78, 82.66, 82.07, 79.27, 77.80, 75.83, 75.21, 75.12, 74.71, 74.53, 74.07, 73.59, 73.39, 72.34, 69.88, 69.83, 68.64, 31.98, 27.58, 26.03, 19.44, 14.03; **HRMS (ESI)** calculated for C$_{54}$H$_{65}$O$_{11}$ [M+H]$^+$ 889.4521, found 889.4579.

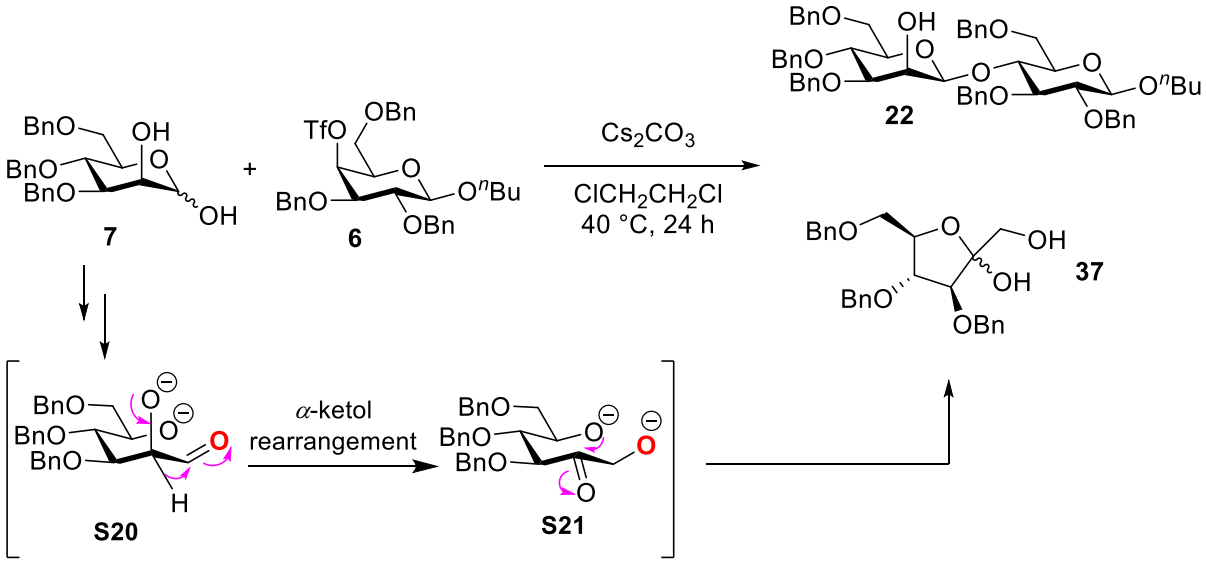


4-*O*-Benzyl-2,6-anhydro-3-deoxy-D-*erythro*-hex-2-enose (S19)

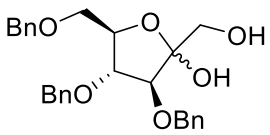


Aldohexose derived compound **S19** was obtained from lactol donor **20** (33.6 mg, 0.098 mmol) and galactoside derived triflate **6** (128 mg, 0.200 mmol) following the general procedure. The crude reaction mixture was purified by preparative TLC (Hexanes/EtOAc = 1/1) to afford enal **S19** (12.8 mg, 0.055 mmol, 56%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ = +25.0 (*c* 0.04, CHCl$_3$); **FT-IR (thin film)** 2919, 1696, 1074, 667 cm^{-1}; **^{1}H NMR (600 MHz, CDCl$_3$)** δ 9.21 (s, 1H, H-1 aldehyde), 7.46 – 7.30 (m,

5H, H_{Ar}), 5.80 (dd, J = 3.8, 0.8 Hz, 1H, H-3), 4.76 (d, J = 11.6 Hz, 1H, -OCH_2Ar), 4.70 (d, J = 11.6 Hz, 1H, -OCH_2Ar), 4.26 (td, J = 3.9, 1.2 Hz, 1H, H-4), 4.14 (dd, J = 11.3, 7.2 Hz, 1H, H-6a), 4.09 – 4.01 (m, 2H, H-6a, H-5), 2.59 (d, J = 6.1 Hz, 1H, C5-OH); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 186.65, 152.83, 137.26, 128.99, 128.66, 128.24, 115.95, 71.66, 69.27, 67.07, 63.96; **HRMS (ESI)** calculated for $C_{13}H_{14}NaO_4$ $[M+Na]^+$ 257.0784, found 257.0787.

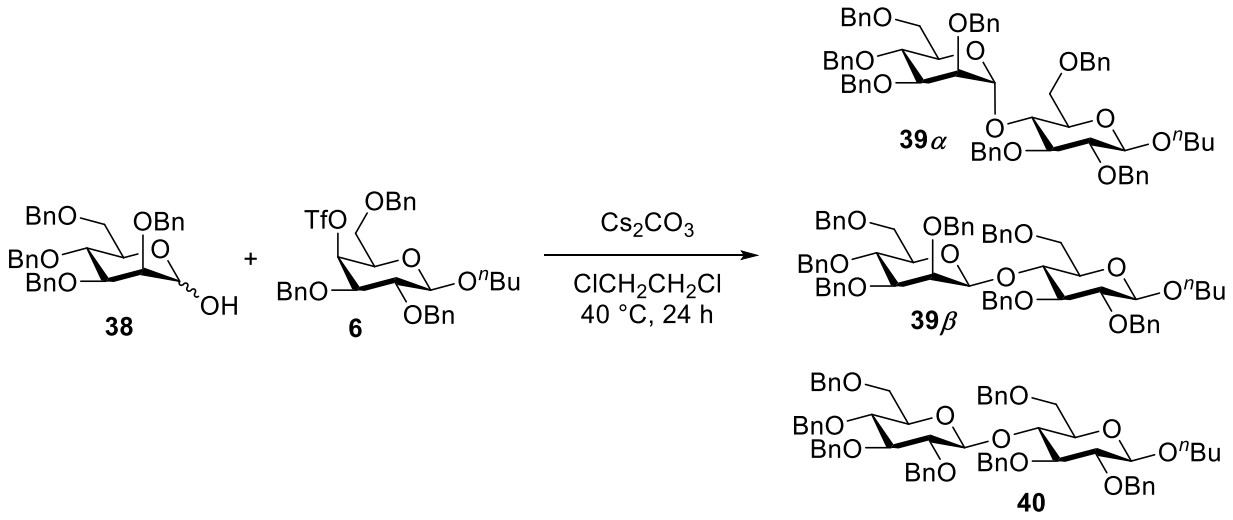


3,4,6-Tri-O-benzyl-α/β-D-fructofuranose (37)



A small amount of side product was always detected in all of the previous anomeric *O*-alkylation reactions involving 3,4,6-tri-*O*-benzyl-D-mannose **7** as the lactol donor. This side product shares the same molecular mass and has similar polarity as 3,4,6-tri-*O*-benzyl-D-mannopyranose **7**. In order to determine the structure of this side product, we re-carried out the reaction between **7** and D-galactose-derived C4 secondary triflate **6** under standard conditions. Beside desired *β*-disaccharide **22** was

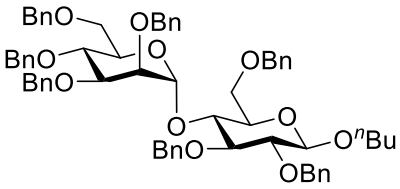
isolated in 67% yield, the side product **37** was also isolated in 8% yield. The structure of **37** was determined to be 3,4,6-tri-*O*-benzyl-D-fructose. **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 – 7.23 (m, 22.5H), 4.69 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.58 – 4.47 (m, 7H), 4.37 (m, 0.5H), 4.25 (s, 1H), 4.18 – 4.14 (m, 2H), 4.12 (m, 1H), 4.04 (m, 1H), 3.79 (d, *J* = 11.7 Hz, 0.5H), 3.70 (d, *J* = 11.7 Hz, 0.5H), 3.66 – 3.48 (m, 6H), 2.23 – 1.96 (b, 1H). **^{13}C NMR (150 MHz, $CDCl_3$)** δ 137.91, 137.73, 137.54, 137.43, 137.36, 128.65, 128.63, 128.60, 128.57, 128.53, 128.24, 128.12, 128.11, 128.01, 127.99, 127.96, 127.94, 127.92, 105.66, 103.23, 86.46, 83.62, 83.42, 82.20, 81.19, 80.72, 73.68, 73.45, 73.00, 72.35, 72.21, 72.18, 70.80, 69.76, 65.29, 64.39. The NMR data agree with the reported ones.[9] Mechanistically, it is believed that dianion **S20** was produced via deprotonation of **7** followed by ring opening. Subsequently, **S20** underwent an *α*-keto rearrangement[10] to afford **S21** which cyclizes to give rise to 3,4,6-tri-*O*-benzyl-D-fructose **37**.



Disaccharides **39*α*/*β*** and **40** were obtained from 2,3,4,6-tetra-*O*-benzyl-D-mannose

donor **38** (54 mg, 0.1 mmol) and galactoside derived triflate acceptor **6** (128 mg, 0.2 mmol) following the general procedure. The crude reaction mixture was purified by preparative TLC (Hexanes/ EtOAc/CH_2Cl_2/Toluene = 10/1/1/1) to furnish **39*α*** (3.1 mg, 3%), **39*β*** (42.3 mg, 46%) and **40** (5.1 mg, 5%) as colorless syrup.

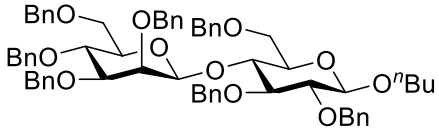
Butyl *O*-2,3,4,6-tetra-*O*-benzyl-*α*-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (39*α*)



The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon for **39*α*** was determined to be 170.3 Hz. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{23}}$ = +5.2 (*c* 0.5, $CHCl_3$); **FT-IR (thin film)**: 3067, 3033, 2929, 2869, 1721, 1692, 1454, 1292, 1098, 1056, 735, 698 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.34 – 7.27 (m, 22H, H_{Ar}), 7.25 – 7.23 (m, 6H, H_{Ar}), 7.21 – 7.17 (m, 5H, H_{Ar}), 7.15 – 7.12 (m, 2H, H_{Ar}), 5.32 (d, *J* = 2.0 Hz, 1H, *H*-1′), 5.05 (d, *J* = 11.6 Hz, 1H, -OCH_2Ar), 4.94 (d, *J* = 10.8 Hz, 1H, -OCH_2Ar), 4.84 (d, *J* = 10.8 Hz, 1H, -OCH_2Ar), 4.65 – 4.45 (m, 9H, -OCH_2Ar), 4.41 (d, *J* = 7.7 Hz, 1H, *H*-1), 4.27 (d, *J* = 12.1 Hz, 1H, -OCH_2Ar), 4.19 (d, *J* = 12.1 Hz, 1H, -OCH_2Ar), 4.01 – 3.95 (m, 2H, -OCH_2C$_3$H$_7$, *H*-4′), 3.89 – 3.82 (m, 2H, *H*-6′a, *H*-3′), 3.81 (m, 1H, *H*-5′), 3.72 – 3.64 (m, 4H, *H*-6′b, *H*-2′, *H*-6a, *H*-4), 3.61 – 3.54 (m, 2H, -OCH_2C$_3$H$_7$, *H*-6b), 3.52 (t, *J* = 9.0 Hz, 1H, *H*-3), 3.48 – 3.43 (m, 2H, *H*-5, *H*-2), 1.70 – 1.63 (m, 2H, -OCH$_2$CH_2C$_2$H$_5$), 1.51 – 1.39 (m, 2H, -OC$_2$H$_4$CH_2CH$_3$), 0.96 (t, *J* = 7.4 Hz, 3H, -OC$_3$H$_6$CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 138.72, 138.61, 138.56, 138.33, 128.49, 128.45, 128.42, 128.38, 128.17, 128.14, 127.85, 127.83, 127.73, 127.72, 127.66,

127.53, 127.22, 127.82, 103.53, 100.36, 84.52, 82.21, 79.76, 77.64, 76.33, 75.13, 74.93, 74.75, 74.72, 73.49, 73.46, 73.06, 72.24, 72.17, 70.05, 69.93, 69.36, 31.98, 19.46, 14.02.; **HRMS (ESI)** calculated for $C_{65}H_{73}O_{11}$ $[M+H]^+$ 1029.5153, found 1029.5115.

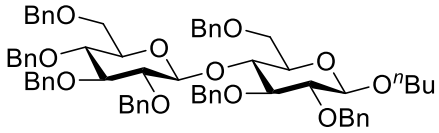
Butyl *O*-2,3,4,6-tetra-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (39*β*)



The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon for **39*β*** was determined to be 154.5 Hz. $[\alpha]_D^{23}$ = + 2.0 (*c* 1.0, $CHCl_3$); **FT-IR (thin film)**: 3065, 3030, 2925, 2865, 1730, 1496, 1453, 1362, 1093, 1060, 734, 696 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.49 – 7.11 (m, 35H, H_{Ar}), 5.15 (d, *J* = 11.5 Hz, 1H, -OCH_2Ar), 4.93 (d, *J* = 10.8 Hz, 1H, -OCH_2Ar), 4.90 – 4.85 (m, 3H, -OCH_2Ar), 4.79 (d, *J* = 11.5 Hz, 1H, -OCH_2Ar), 4.73 (d, *J* = 10.8 Hz, 1H, -OCH_2Ar), 4.61 (d, *J* = 12.1 Hz, 1H, -OCH_2Ar), 4.58 – 4.53 (m, 2H, -OCH_2Ar, *H*-1′), 4.53 – 4.39 (m, 6H, -OCH_2Ar × 5, *H*-1), 4.00 – 3.88 (m, 3H, -OCH_2C$_3$H$_7$, *H*-4, *H*-4′), 3.80 (d, *J* = 2.9 Hz, 1H, *H*-2′), 3.75 – 3.62 (m, 4H, *H*-6a, *H*-6′a, *H*-3, *H*-6b), 3.60 (dd, *J* = 11.1, 5.3 Hz, 1H, *H*-6′b), 3.55 (dt, *J* = 9.5, 6.8 Hz, 1H, -OCH_2C$_3$H$_7$), 3.50 (ddd, *J* = 9.9, 4.2, 2.4 Hz, 1H, *H*-5), 3.44 (dd, *J* = 9.1, 7.8 Hz, 1H, *H*-2), 3.36 (dd, *J* = 9.4, 2.9 Hz, 1H, *H*-3′), 3.32 (ddd, *J* = 9.7, 5.3, 1.9 Hz, 1H, *H*-5′), 1.76 – 1.60 (m, 2H, -OCH$_2$CH_2C$_2$H$_5$), 1.54 – 1.40 (m, 2H, -OC$_2$H$_4$CH_2CH$_3$), 0.97 (t, *J* = 7.4 Hz, 3H, -OC$_3$H$_6$CH_3); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 139.52, 139.03, 138.82, 138.61, 138.58, 138.41, 138.20, 128.54, 128.48, 128.40, 128.29, 128.20, 128.14, 128.08, 127.98, 127.79, 127.73, 127.69, 127.68, 127.60,

127.40, 127.28, 127.14, 103.75, 100.95, 82.74, 82.01, 77.49, 76.10, 75.14, 75.02, 74.97, 74.95, 74.87, 74.69, 74.11, 73.55, 73.47, 71.74, 69.84, 69.62, 69.18, 31.95, 19.42, 14.01; **HRMS (ESI)** calculated for $C_{65}H_{73}O_{11}$ $[M+H]^+$ 1029.5153, found 1029.5112.

Butyl *O*-2,3,4,6-tetra-*O*-benzyl-*β*-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (40)

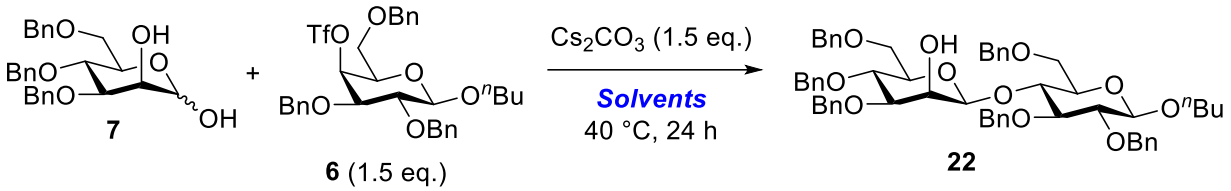


$[\alpha]_D^{24}$ = +47.0 (*c* 0.1, $CHCl_3$) ; **FT-IR (thin film)** 2917, 2867, 1453, 1093, 1067, 733, 695 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.38 – 7.34 (m, 2H, H_{Ar}), 7.32 – 7.20 (m, 28H, H_{Ar}), 7.20 – 7.15 (m, 5H, H_{Ar}), 5.06 (d, *J* = 11.4 Hz, 1H, -OCH_2Ar), 4.88 (d, *J* = 10.9 Hz, 2H, -OCH_2Ar × 2), 4.83 – 4.77 (m, 3H, -OCH_2Ar), 4.76 – 4.71 (m, 2H, -OCH_2Ar), 4.68 (d, *J* = 10.8 Hz, 1H, -OCH_2Ar), 4.56 (m, 2H, -OCH_2Ar), 4.59 – 4.53 (d, *J* = 7.8 Hz, 1H, *H*-1′), 4.45 (d, *J* = 12.2 Hz, 1H, -OCH_2Ar), 4.39 (s, 2H, -OCH_2Ar), 4.36 (d, *J* = 7.8 Hz, 1H, *H*-1), 3.99 (dd, *J* = 9.8, 8.9 Hz, 1H, *H*-4), 3.93 (dt, *J* = 9.5, 6.5 Hz, 1H, -OC$H_2$$C_3H_7$), 3.81 (dd, *J* = 10.9, 4.3 Hz, 1H, *H*-6a), 3.71 (dd, *J* = 10.9, 1.9 Hz, 1H, *H*-6b), 3.68 (dd, *J* = 10.9, 1.9 Hz, 1H, *H*-6′a), 3.63 (t, *J* = 9.4 Hz, 1H, *H*-4′), 3.60 – 3.48 (m, 4H, *H*-3, *H*-6′b, *H*-3′, -OC$H_2$$C_3H_7$), 3.43 – 3.33 (m, 3H, *H*-2, *H*-2′, *H*-5), 3.30 (ddd, *J* = 9.9, 4.4, 1.9 Hz, 1H, *H*-5′), 1.68 – 1.58 (m, 2H, -$OCH_2CH_2C_2H_5$), 1.49 – 1.36 (m, 2H, -$OC_2H_4CH_2CH_3$), 0.93 (t, *J* = 7.4 Hz, 3H, -$OC_3H_6CH_3$); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 139.51, 138.75, 138.73, 138.59, 138.41, 138.37, 128.51, 128.50, 128.48, 128.45, 128.38, 128.28, 128.15, 127.99, 127.95, 127.91, 127.90, 127.84, 127.80, 127.73, 127.68, 127.66, 127.47, 127.21, 103.75, 102.60, 85.05,

83.00, 82.85, 81.84, 78.13, 75.77, 75.18, 75.14, 75.12, 75.07, 75.03, 74.96, 73.40, 73.35, 69.80, 69.00, 68.32, 31.96, 19.44, 14.03; **HRMS (ESI)** calculated for $C_{65}H_{72}NaO_{11}$ $[M+Na]^+$ 1051.4967, found 1051.4961.

Comprehensive studies of various conditions for *β*-mannosylation.

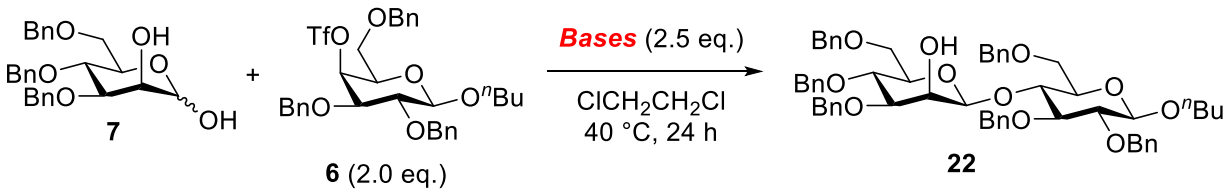
Table S1. Screening solvents for *β*-mannosylation *via O*-alkylation.[a]



Entry	***Solvents***	Yield[b], *α*/*β* ratio
1	CH_3CN	25%, *β* only
2	DMF	trace
3	1,4-Dioxane	24%, *β* only
4	THF	30%, *β* only
5	$ClCH_2CH_2Cl$	48%, *β* only
6	Toluene	21%, *β* only
7	$ClCH_2CH_2Cl$/DMF (10/1, *v*/*v*)	23%, *β* only
8	$CHCl_3$	48%, *β* only
9	*α*,*α*,*α*-Trifluorotoluene	34%, *β* only

[a] All reactions were performed using 0.1 mmol of 3,4,6-tri-*O*-benzyl-D-mannopyranose **7**, 1.5 eq. of triflate acceptor **6** and 1.5 eq. of cesium carbonate in 1 mL solvent at 40 °C for 24 hours.
[b] Isolated yield based on the lactol donor **7**.

Table S2. Screening bases for *β*-mannosylation *via O*-alkylation.[a]



Entry	***Bases***	Yield[b], α/β ratio
1	MgO	No reaction
2	$Ba(OH)_2$	trace
3	Na_2CO_3	trace
4	NaOH	5%, β only
5	K_2CO_3	10%, β only
6	KOH	5.7%, β only
7	Rb_2CO_3	50%, β only
8	$RbOH \cdot H_2O$	13%, β only
9	Cs_2CO_3	67% (73% BRSM), β only
10	$CsOH \cdot H_2O$	52%, β only
11	$CsHCO_3$	trace
12	CsF	3%, β only
13	CsOAc	trace
14	Cs_3PO_4	59% (63% BRSM), β only
15[c]	NaH (2.5 or 3 eq.), 15-C-5 (1.5 eq.)	trace
16[d]	NaH (2.5 or 3 eq.), 15-C-5 (1.5 eq.)	trace
17[e]	2-Aminoethyl diphenylborinate (0.1 eq.), K_2CO_3 or DIPEA	no desired product

[a] All reactions were performed using 0.1 mmol of 3,4,6-tri-*O*-benzyl-D-mannopyranose **7**, 2.0 eq. of triflate acceptor **6** and 2.5 eq. of base in 1 mL 1,2-dichloroethane at 40 °C for 24 hours except for entry 15~17.

[b] Isolated yield based on the lactol donor **7**. Yield calculated based on recovered lactol donor **7** is reported in the parenthesis. BRSM = based on recovered starting material (donor **7**).

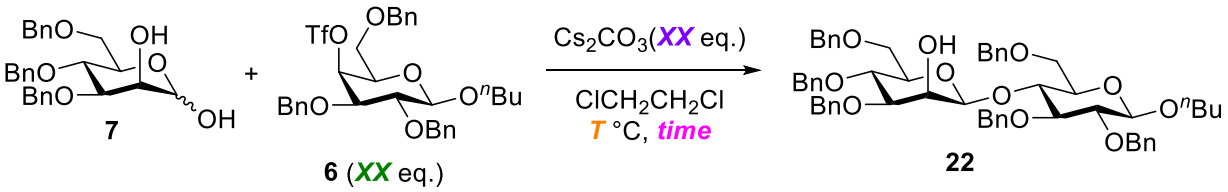
[c] This reaction was performed using 0.1 mmol of donor **7** and 2.0 eq. of triflate acceptor **6** in 1 mL 1,4-

dioxane at room temperature for 24 hours.

[d] This reaction was carried out under the same condition with entry 15 except for using dichloromethane as the solvent.

[e] This reaction was carried out using 0.1 mmol of donor **7** and 2.0 eq. of triflate acceptor **6** in 1 mL acetonitrile in the presence of base and borinate catalyst at 40 ℃ for 24 hours.

Table S3. The effect of reaction time, temperature and the equivalent of acceptor and cesium carbonate in the *β*-mannosylation *via O*-alkylation.[a]

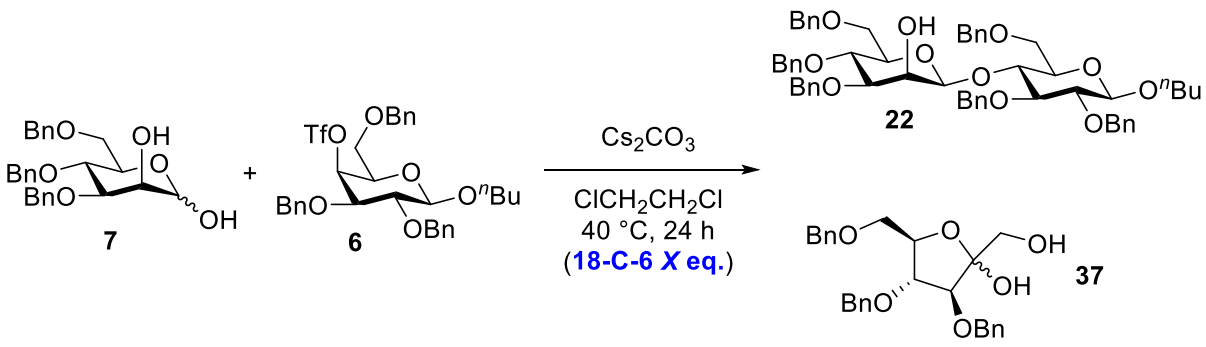


Entry	*Donor 6*	*Cs_2CO_3*	*T*/℃	*time*/h	Yield[b], *α*/*β* ratio
1	1.5 eq.	1.5 eq.	40	24	48%, *β* only
2	1.5 eq.	2.0 eq.	40	24	52%, *β* only
3	1.5 eq.	2.5 eq.	40	24	54%, *β* only
4	2.0 eq.	2.0 eq.	40	24	58%, *β* only
5	2.0 eq.	2.5 eq.	40	24	67%, *β* only
6	2.0 eq.	2.5 eq.	**50**	24	64%, *β* only
7	2.5 eq.	3.0 eq.	40	24	75%, *β* only
8	2.5 eq.	3.0 eq.	40	**40**	75%, *β* only

[a] All reactions were performed using 0.1 mmol of 3,4,6-tri-*O*-benzyl-D-mannopyranose **7** in 1 mL 1,2-dichloroethane.

[b] Isolated yield based on the lactol donor **7**.

Table S4. 18-Crown-6 titration studies.



Entry[a]	Eq. of 18-C-6 added	Yield of **22** / **37** / **7**(recovered)
1	0	67% (β only) / 8% (α/β = 1/2) / trace
2	0.5	36% (β only) / trace / 34%
3	1	26% (β only) / trace / 52%
4	1.5	22% (β only) / trace / 50%
5	2	20% (β only) / trace / 49%
6	3	16% (β only) / trace / 54%
7	4	13% (β only) / trace / 58%

[a] General conditions: lactol **7** (0.1 mmol, 1.0 eq.), triflate **6** (2.0 eq.), Cs_2CO_3 (2.5 eq.), $ClCH_2CH_2Cl$, 40 °C, 24 h.

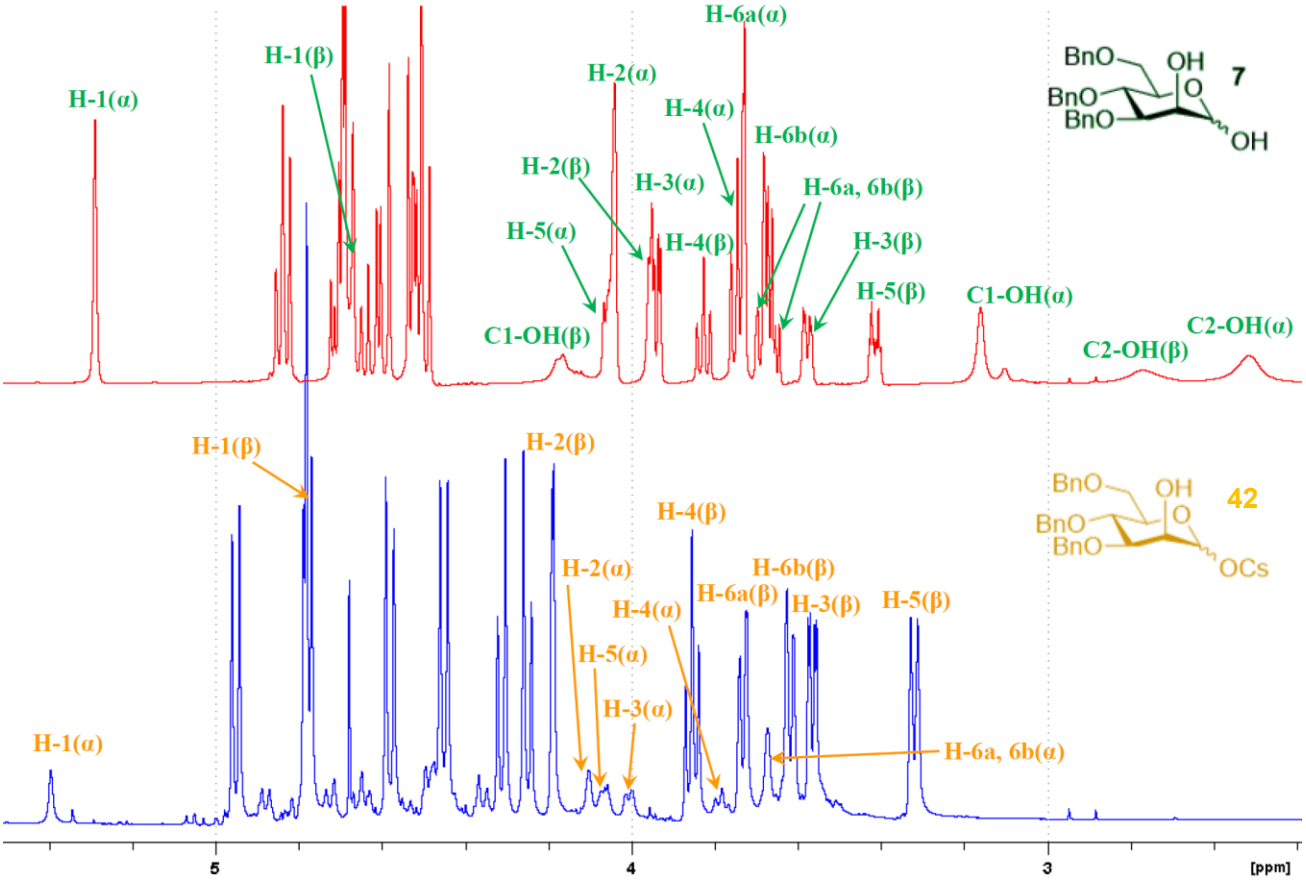
In order to study possible chelation effect of cesium ion with sugar oxygen atoms, we explored the effect of 18-crown-6 to this anomeric *O*-alkylation reaction. As shown in the table, addition of crown ether 18-C-6 to the reaction mixture dramatically disturbed the reaction and caused the formation of desired β-mannoside **22** in much lower yields. The more crown ether was added, the worse the reaction outcome. In addition, a significant amount of starting lactol **7** was always recovered from the reaction mixtures

in the presence of 18-C-6. These results were found to be complete contrast to our previously reported synthesis of 2-deoxy-*β*-glycosides involving the use of sodium hydride as base which requires the addition of 15-crown-5 to increase the nucleophilicity of the anomeric alkoxides.[11] We reason that, in the absence of 18-C-6, cesium ion may chelate with oxygen atoms at C1 and other carbons in mannose substrates, increase the acidity of the anomeric hydroxyl group, and facilitate the deprotonation. Once added, 18-C-6 may compete with the oxygen atoms of the sugar substrates in chelating with cesium ion and then slow down the deprotonation, which may account for the recovery of significant amounts of the starting lactol **7**.

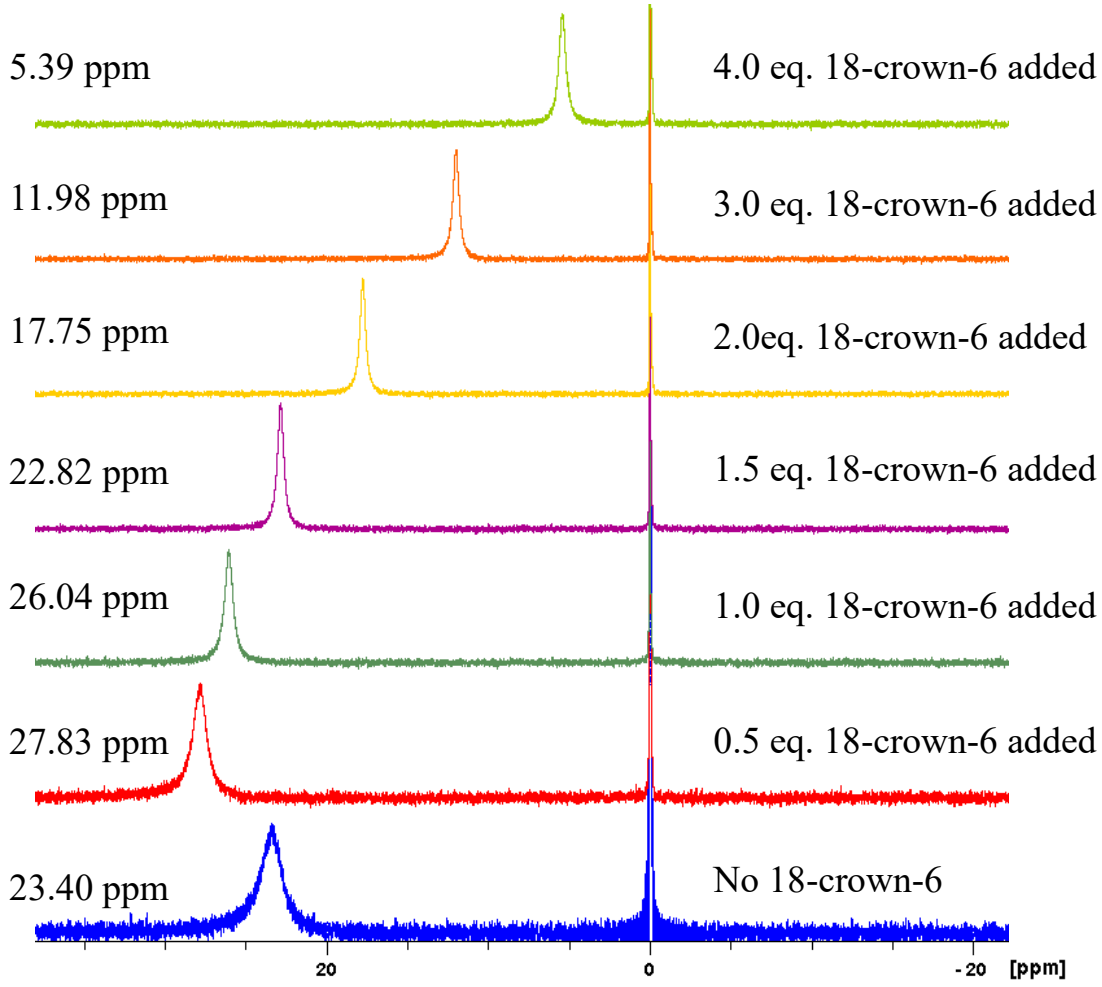
NMR study for cesium alkoxide.

Preparation of cesium alkoxide 42 from donor 7 and extensive NMR studies (including ^{133}Cs NMR).

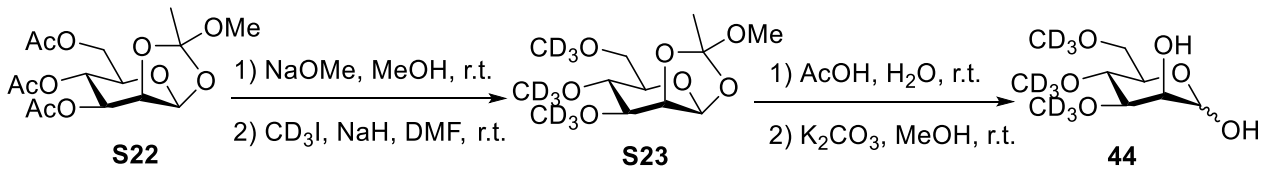
To a 0.1 M solution of 3,4,6-tri-*O*-benzyl-D-mannopyranose **7** in $CDCl_3$ was added 3.0 eq. of Cs_2CO_3 and the reaction mixture was stirred at 40 °C for 1 h. The resulting mixture was allowed to stand for 0.5 h at room temperature and the supernatant, presumably containing cesium alkoxide **42** was taken out and subjected to NMR study. The comparison of ^{1}H NMR spectra of **7** and **42** is shown below.



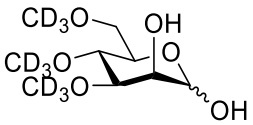
Previously, Popov and co-workers demonstrated that ^{133}Cs NMR was an effective tool to study ion pairing involving cesium ion.[12] Therefore, we carried out extensive ^{133}Cs NMR experiments in order to examine the interaction of cesium ion with the sugar substrate. In the event, to a 0.1 M solution of 3,4,6-tri-*O*-benzyl-D-mannose (**7**, α/β = 3.0/1) in $CDCl_3$[13] was added 3 eq. of Cs_2CO_3 and the reaction mixture was stirred at 40 °C for 1 hour. The resulting mixture was allowed to stand for 0.5 hour and the supernatant, presumably containing cesium alkoxide **42** in $CDCl_3$, was taken out. Various amounts of 18-C-6 was added to the supernatant and the mixture was stirred for another 0.5 before being subjected to ^{133}Cs NMR studies (use of a 1 M solution of CsCl in D_2O as the reference). Before 18-C-6 was added, the chemical shift of ^{133}Cs in cesium alkoxide **42** (α/β = 1/3.0) in $CDCl_3$ was 23.40 ppm. Addition of 0.5 eq. of 18-C-6 increased the ^{133}Cs chemical shift to a maximum (27.83 ppm) which dropped to 26.04 ppm when a total amount of 1.0 eq. of 18-C-6 was added. The ^{133}Cs chemical shift kept decreasing as more 18-C-6 was added. Not surprisingly, this observed trend of ^{133}Cs chemical shift change with the addition of various amounts of 18-C-6 suggests that cesium alkoxide **42** is not dissociated in free ions or solvent separated ion pairs in chloroform. In addition, according to those observations reported by Popov, the ^{133}Cs chemical shift reaches a maximum or minimum at a 1:1 ratio of crown ether to the cesium ion. However, in this experiment the chemical shift of ^{133}Cs reached a maximum when 0.5 eq. of 18-C-6 was added, which may suggest that the cesium ion may also interact with other oxygen atoms on the sugar, besides the anomeric oxygen. The ^{133}Cs NMR spectra are shown here.



Synthesis of perdeuteriomethyl protected lactol donor 44.



3,4,6-Tri-*O*-perdeuteriomethyl-*α*/*β*-D-mannopyranose (44)



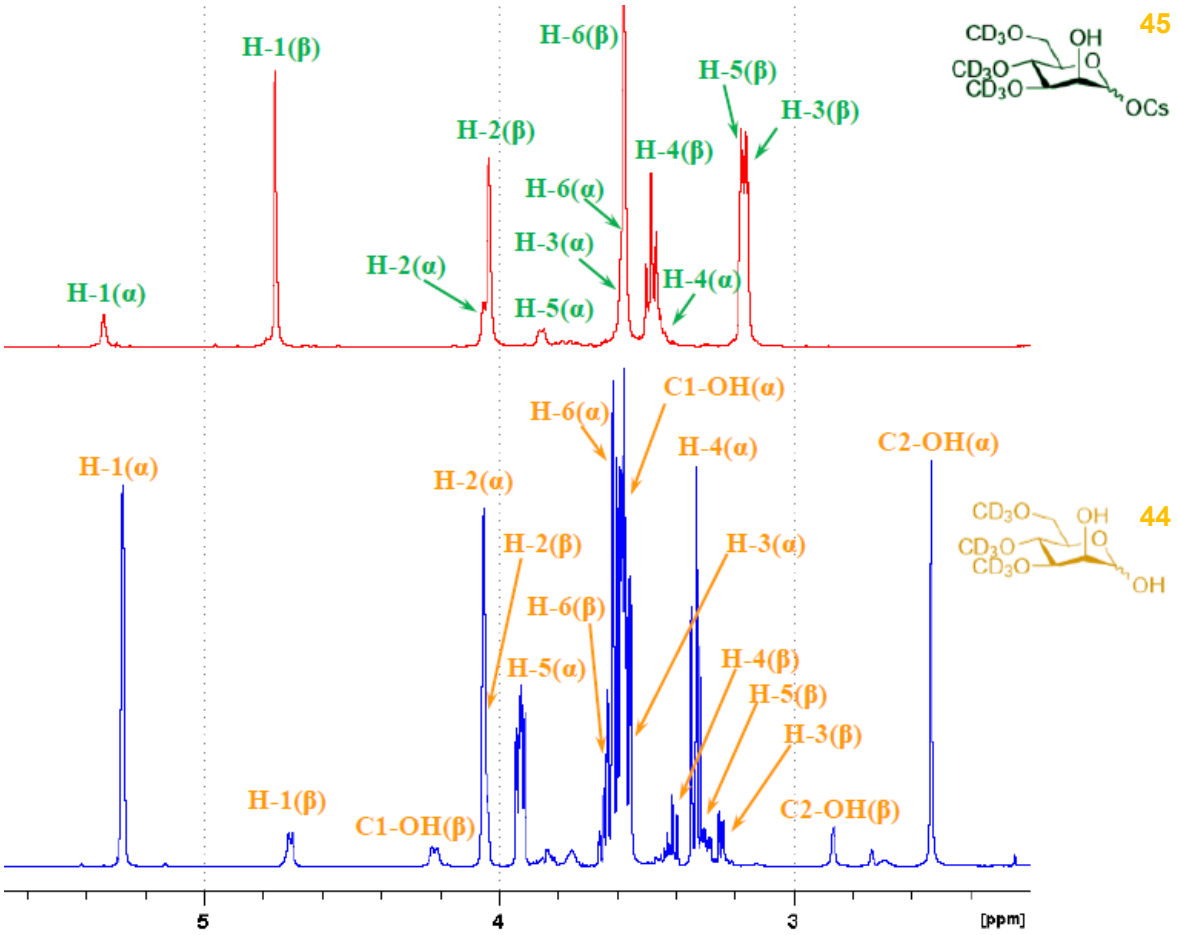
To a solution of triol (0.93 g, 4.0 mmol) obtained from global deacetylation of known compound **S22**[14] in DMF (13.3 mL) cooled at 0 °C was added NaH (0.96 g, 24 mmol, 60% in mineral oil) portion wise. The resulting

mixture was stirred at 0 °C for 30 min before deuterated methyl iodide (1.52 mL, 24 mmol) was added. The reaction mixture was warmed up and stirred at ambient temperature for 3 h. The resulting mixture was diluted with CH_2Cl_2 (50 mL), washed with water (50 mL × 4), brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography (Hexanes/EtOAc = 3/1 to 1/2) to give desired product **S23**. Orthoester **S23** (820 mg, 2.85 mmol) was suspended in 60% acetic acid aqueous solution (28.5 mL) and stirred at room temperature for 1 h. The resulting mixture was concentrated and the residue azeotroped with toluene. The crude product was dissolved in MeOH (29 mL) and 5.4 M sodium methoxide solution in methanol (0.5 mL, 2.85 mmol) was added. The mixture was stirred at room temperature for 2 h before being neutralized with Amberlyst IR-120 (H^+). After filtration and concentration, the residue was recrystallized with hexanes and EtOAc to give the title compound **44** (461 mg, 70%, α/β = 5/1) as a white solid. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{29}}$ **=** +25.00 (*c* 0.1, $CHCl_3$); **FT-IR (thin film)** 3333, 2950, 2227, 2059, 1732, 1658, 1264, 1107, 1049, 979, 781, 695, 563 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 5.27 (s, 1H, *H*-1 *α*), 4.70 (d, *J* = 8.6 Hz, 0.2H, *H*-1 *β*), 4.21 (d, *J* = 10.3 Hz, 0.2H, C1-O*H β*), 4.07 – 4.0 (m, 1.2H, *H*-2 *α*, *H*-2 *β*), 3.92 (ddd, *J* = 10.2, 6.1, 2.2 Hz, 1H, *H*-5 *α*), 3.67 – 3.51 (m, 4.4H, *H*-6 *β*, *H*-6 *α*, C1-O*H α*, *H*-3 *α*), 3.41 (t, *J* = 9.5 Hz, 0.2H, *H*-4 *β*), 3.33 (t, *J* = 9.6 Hz, 1H, *H*-4 *α*), 3.29 (ddd, *J* = 9.8, 4.5, 2.1 Hz, 0.2H, *H*-5 *β*), 3.24 (dd, *J* = 9.2, 3.3 Hz, 0.2H, *H*-3 *β*), 2.86 (s, 0.2H, C2-O*H β*), 2.53 (s, 1H, C2-O*H α*); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 94.29, 94.08, 83.64, 81.00, 76.33, 75.37, 74.57, 72.03, 71.29, 70.57, 68.39, 68.00, 59.88 (m), 58.38 (m), 56.66 (m); **HRMS (ESI)** calculated for $C_9H_9D_9NaO_6$

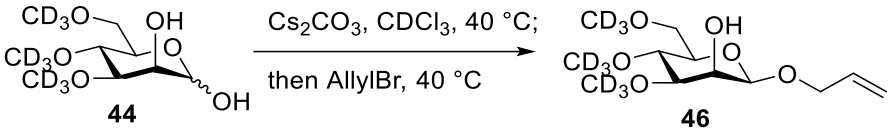
$[M+Na]^+$ 254.1561, found 254.1577.

Preparation of cesium alkoxide 45 from donor 44 and extensive NMR studies.

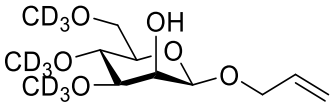
To a 0.1 M solution of 3,4,6-tri-*O*-perdeuteriomethyl-D-mannopyranose **44** in $CDCl_3$ was added 3.0 eq. of Cs_2CO_3 and the reaction mixture was stirred at 40 °C for 1 h. The resulting mixture was allowed to stand for 0.5 h at room temperature and the supernatant, presumably containing cesium alkoxide **45** was taken out and subjected to NMR study. The comparison of ^1H NMR spectra of **44** and **45** is shown below.



Synthesis of perdeuteriomethyl protected *β*-mannoside 46.

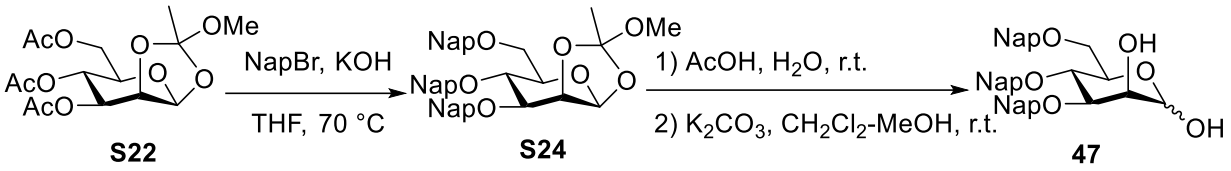


Allyl 3,4,6-tri-*O*-perdeuteriomethyl-*β*-D-mannopyranoside (46)



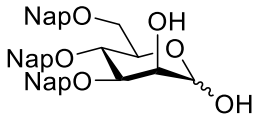
To a 0.1 M solution of lactol **44** (23.1 mg, 0.10 mmol) in $CDCl_3$ (1.0 mL) was added Cs_2CO_3 (97.7 mg, 0.3 mmol). The resulting mixture was stirred at 40 ℃ for 1 h and then cooled to ambient temperature. The mixture was allowed to stand at ambient temperature for 0.5 h and the supernatant (0.5 mL, presumably containing 0.0455 mmol corresponding alkoxide) was taken out. Allyl bromide (6 μL) was added to this supernatant and the resulting mixture was stirred at 40 ℃ for 24 h. The crude mixture was purified by silica gel column chromatography (Hexanes/ EtOAc = 2/1) to give compound **46** (2.7 mg, 0.010 mmol, 22%) as colorless syrup. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{24}}$ = -31.0 (*c* 0.1, $CHCl_3$) ; **FT-IR (thin film)** 3471, 2865, 2206, 2061, 1380, 1317, 1118, 1054, 992, 781 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 5.90 (m, 1H, -OCH_2CH=CH_2), 5.28 (m, 1H, -OCH_2CH=CH_2), 5.19 (dd, *J* = 10.4, 1.4 Hz, 1H, -OCH_2CH=CH_2), 4.45 (d, *J* = 1.0 Hz, 1H, *H*-1), 4.40 (dd, *J* = 12.8, 5.1 Hz, 1H, -OCH_2CH=CH_2), 4.14 – 4.05 (m, 2H, *H*-2, -OCH_2CH=CH_2), 3.66 (dd, *J* = 10.7, 2.0 Hz, 1H, *H*-6a), 3.59 (dd, *J* = 10.6, 5.2 Hz, 1H, *H*-6b), 3.46 (t, *J* = 9.4 Hz, 1H, *H*-4), 3.27 (ddd, *J* = 9.7, 5.2, 2.0 Hz, 1H, *H*-5), 3.21 (dd, *J* = 9.1, 3.2 Hz, 1H, *H*-3), 2.36 (s, 1H, C2-O*H*); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 133.78, 118.01, 98.59, 83.61, 75.75, 75.24, 71.59, 69.89, 67.77, 59.96 (m), 58.60 (m), 56.34 (m); **HRMS (ESI)** calculated for $C_{12}H_{13}D_9NaO_6$ $[M+Na]^+$ 294.1874, found 294.1891.

Synthesis of lactol 47.



S22 S24 47

3,4,6-Tri-*O*-(2-naphthalenyl)methyl-*α*/*β*-D-mannopyranose (47)



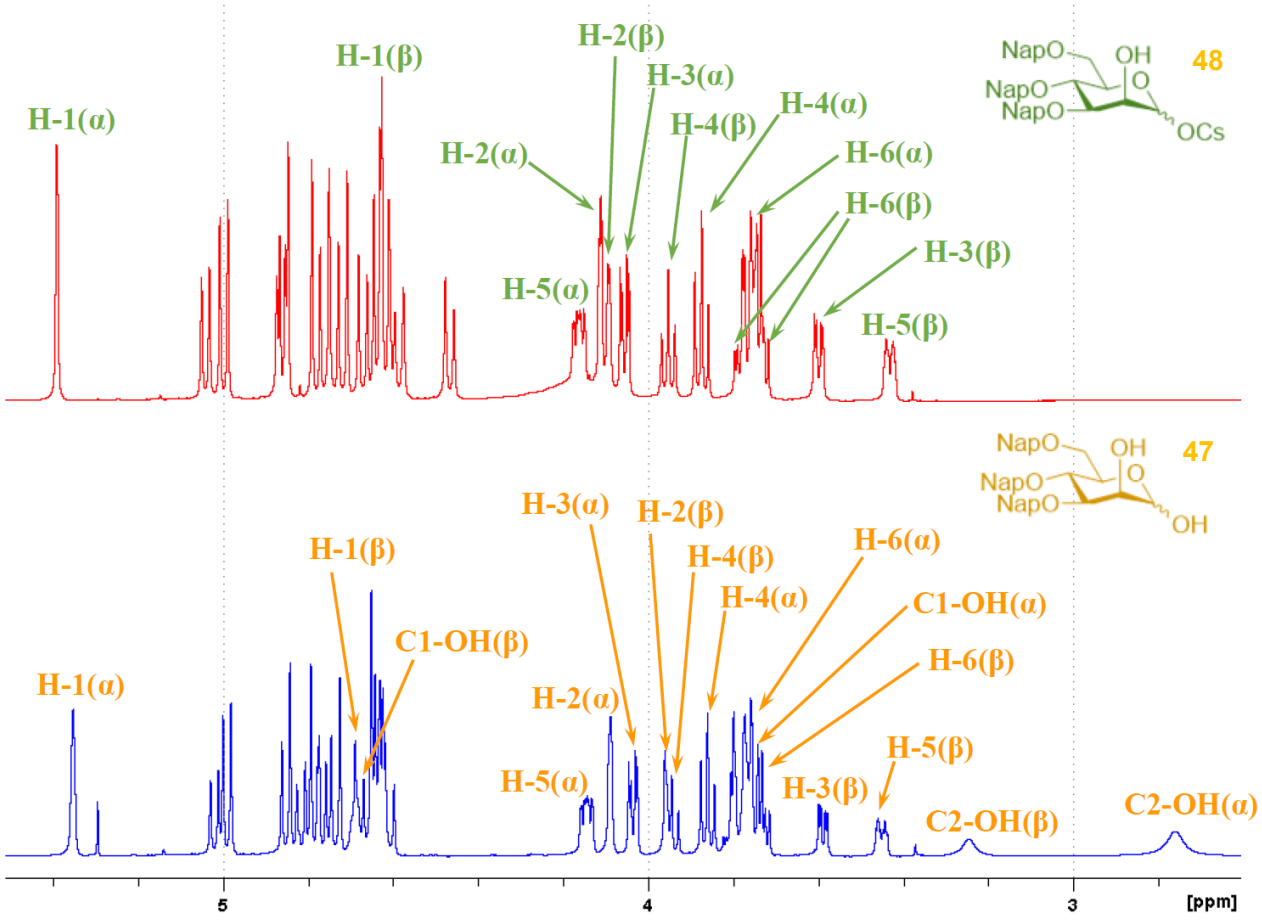
To a solution of compound **S22** (1.32 g, 3.65 mmol) in dry THF (50 mL) were added (2-naphthalenyl)methyl bromide (2.66 g, 12.0 mmol) and KOH (2.44 g, 43.64 mmol). The mixture was stirred at room temperature for 30 min and then warmed to 70 °C. After being stirred at 70 °C for 6 h, the mixture was cooled to ambient temperature and diluted by CH_2Cl_2 (200 mL), which was then washed by water (100 mL × 2) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (Hexanes/EtOAc = 5/1) on silica gel to afford **S24** (1.29 g, 54%) as light yellow solids. **S24** was suspended in 80% acetic acid aqueous solution (20 mL) and stirred vigorously at room temperature overnight. The mixture was diluted by CH_2Cl_2 (150 mL) and the organic layer was washed by saturated $NaHCO_3$ aqueous solution (100 mL × 3) and brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was dissolved in CH_2Cl_2 (20 mL) and MeOH (20 mL). To this solution was added K_2CO_3 (27 mg, 0.20 mmol). The mixture was stirred at room temperature for 6 h and neutralized by Amberlyst IR-120 (H^+). The filtrate was concentrated and purified by flash column chromatography

(Hexanes/EtOAc = 3/2) on silica gel to furnish the title compound **47** (α/β = 2/1 mixture, 756 mg, 64%) as white solids. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{24}}$ = +5.5 (*c* 1.0, $CHCl_3$) ; **FT-IR (thin film)** 3404, 3050, 2855, 1094, 1051, 809, 746, 473 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 – 7.69 (m, 14H, H_{Ar}), 7.60 – 7.40 (m, 16H, H_{Ar}), 7.17 – 7.13 (m, 1.5H, H_{Ar}), 5.35 (d, *J* = 2.7 Hz, 1H, *H*-1 α), 5.04 – 4.97 (m, 1.5H, -OCH_2Ar), 4.88 – 4.58 (m, 8.5H, -OCH_2Ar × 7.5, *H*-1 β, C1-O*H* β), 4.14 (ddd, *J* = 10.0, 5.8, 2.1 Hz, 1H, *H*-5 α), 4.09 (m, 1H, *H*-2 α), 4.03 (dd, *J* = 9.2, 3.2 Hz, 1H, *H*-3 α), 3.97 – 3.91 (m, 1H, *H*-2 β, *H*-4 β), 3.86 (t, *J* = 9.6 Hz, 1H, *H*-4 α), 3.83 – 3.70 (m, 4H, *H*-6 β, *H*-6 α, C1-O*H* α), 3.59 (dd, *J* = 9.2, 3.2 Hz, 1H, *H*-3 β), 3.45 (ddd, *J* = 9.9, 4.0, 2.5 Hz, 0.5H, *H*-5 β), 3.24 (br, 0.5H, C2-O*H* β), 2.76 (br, 0.5H, C2-O*H* α); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 135.74, 135.68, 135.44, 135.37, 135.24, 133.34, 133.30, 133.26, 133.14, 133.00, 132.98, 128.47, 128.44, 128.39, 128.36, 128.11, 128.06, 128.02, 127.83, 127.81, 127.71, 127.13, 127.02, 126.81, 126.79, 126.57, 126.55, 126.32, 126.29, 126.26, 126.23, 126.19, 126.17, 126.13, 126.08, 126.04, 125.95, 125.93, 125.91, 94.52, 94.10, 81.66, 79.84, 75.21, 75.19, 74.73, 74.64, 73.79, 73.77, 73.62, 72.08, 71.59, 70.92, 69.39, 69.03, 68.83, 68.68; **HRMS (ESI)** calculated for $C_{39}H_{36}NaO_6$ $[M+Na]^+$ 623.2410, found 623.2397.

Preparation of cesium alkoxide 48 from donor 47 and extensive NMR studies.

To a 0.1 M solution of 3,4,6-tri-*O*-(2-naphthalenyl)methyl-D-mannopyranose **47** in $CDCl_3$ was added 3.0 eq. of Cs_2CO_3 and the reaction mixture was stirred at 40 ℃ for 1 h. The resulting mixture was allowed to stand for 0.5 h at room temperature and the

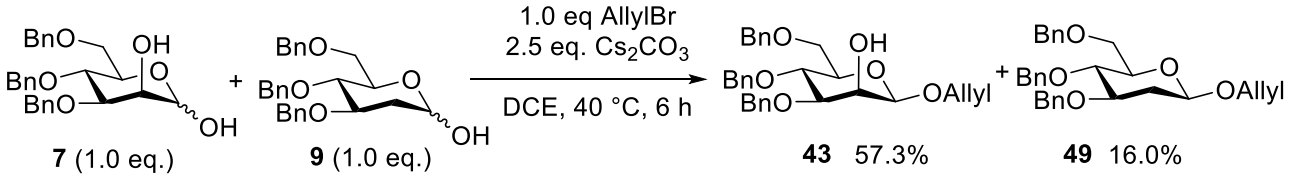
supernatant, presumably containing cesium alkoxide **48** was taken out and then subjected to NMR study. The comparison of ^{1}H NMR spectra of **47** and **48** is shown below.



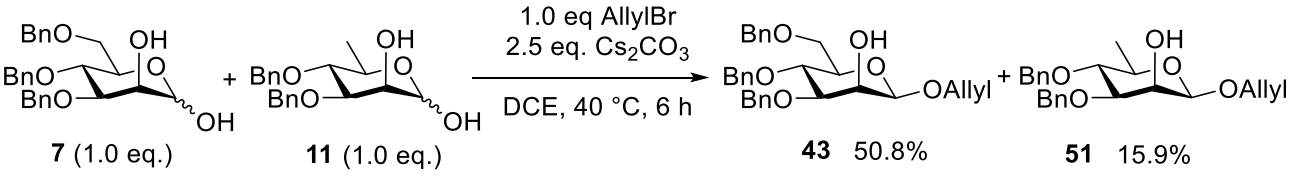
Competing experiments between different mannose-derived lactols.

General procedure for competition using different deoxy-mannose donors in the anomeric *O*-alkylation with allyl bromide.

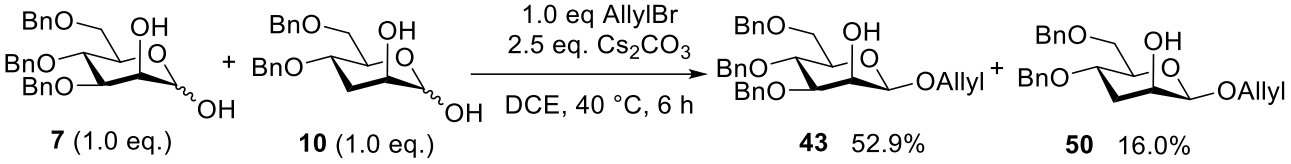
Two kinds of mannose derived donors (**7**, **9**, **10**, or **11**, 0.1 mmol + 0.1 mmol) were treated with allyl bromide (0.1 mmol) and cesium carbonate (0.25 mmol) in DCE (1.0 mL) at 40 ℃ for 6 h. After filtration, the corresponding allyl mannosides were isolated by preparative TLC.



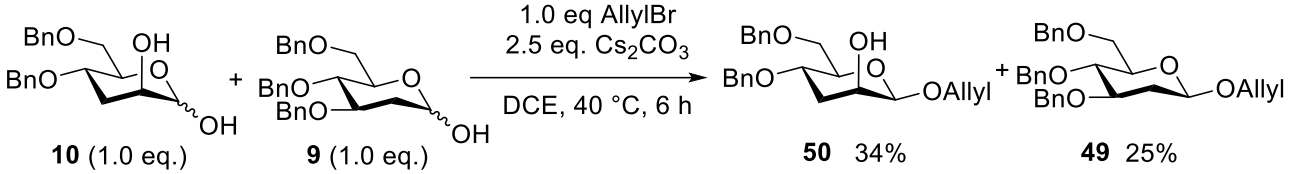
Mannoside **43** (28.1 mg) and 2-deoxy mannoside **49** (7.6 mg) were produced by donor **7** (45 mg) and **9** (43 mg) following the general procedure in the yield of 57% and 16%, respectively.



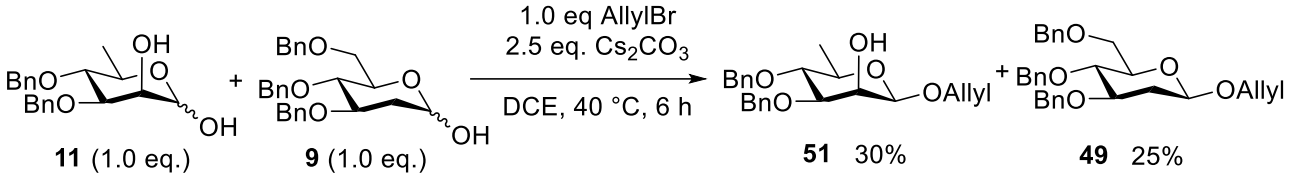
Mannoside **43** (24.9 mg) and 6-deoxy mannoside **51** (6.1 mg) were produced by donor **7** (45 mg) and **11** (34 mg) following the general procedure in the yield of 51% and 16%, respectively.



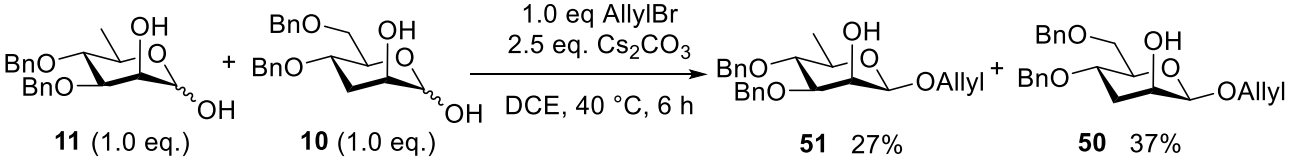
Mannoside **43** (26.2 mg) and 3-deoxy mannoside **50** (6.2 mg) were produced by donor **7** (45 mg) and **10** (43 mg) following the general procedure in the yield of 53% and 16%, respectively.



2-deoxy mannoside **49** (12.0 mg) and 3-deoxy mannoside **50** (13.1 mg) were produced by donor **9** (43 mg) and **10** (34 mg) following the general procedure in the yield of 25% and 34%, respectively.

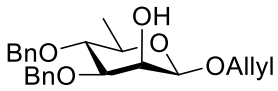


2-deoxy mannoside **49** (12.1 mg) and 6-deoxy mannoside **51** (11.6 mg) were produced by donor **9** (43 mg) and **11** (34 mg) following the general procedure in the yield of 25% and 30%, respectively.



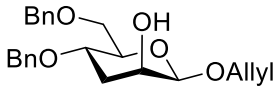
3-deoxy mannoside **50** (14.3 mg) and 6-deoxy mannoside **51** (10.2 mg) were produced by donor **10** (34 mg) and **11** (34 mg) following the general procedure in the yield of 37% and 27%, respectively.

Allyl 3,4-di-*O*-benzyl-6-deoxy-*β*-D-mannopyranoside (51)



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 10H, H_{Ar}), 5.93 (dddd, *J* = 17.2, 10.6, 6.5, 5.1 Hz, 1H, -OCH_2CH=CH_2), 5.29 (dd, *J* = 17.3, 1.7 Hz, 1H, -OCH_2CH=CH_2), 5.21 (dd, *J* = 10.3, 1.5 Hz, 1H, -OCH_2CH=CH_2), 4.95 (d, *J* = 10.8 Hz, 1H, -OCH_2Ph), 4.77 (d, *J* = 11.9 Hz, 1H, -OCH_2Ph), 4.70 – 4.64 (m, 2H, -OCH_2Ph), 4.46 – 4.34 (m, 2H, *H*-1, -OCH_2CH=CH_2), 4.16 – 4.05 (m, 2H, *H*-2, -OCH_2CH=CH_2), 3.60 – 3.48 (m, 2H, *H*-3, *H*-4), 3.32 (dq, *J* = 8.7, 6.2 Hz, 1H, *H*-5), 1.36 (d, *J* = 6.1 Hz, *H*-6); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.41, 137.92, 133.83, 128.59, 128.50, 128.23, 128.01, 127.97, 127.88, 118.01, 98.46, 81.46, 79.73, 75.60, 71.54, 71.48, 69.95, 68.61, 17.98; The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon was determined to be 156.3 Hz; **LRMS (ESI)** calculated for $C_{23}H_{28}NaO_5$ $[M+Na]^+$ 407.2, found 407.6.

Allyl 4,6-di-*O*-benzyl-3-deoxy-*β*-D-mannopyranoside (50)

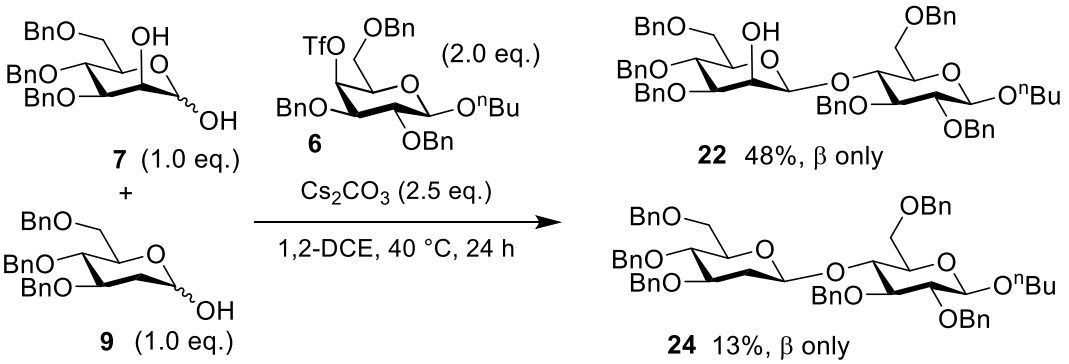


^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.19 (m, 10H, H_{Ar}), 5.92 (dddd, *J* = 16.9, 10.4, 6.3, 5.1 Hz, 1H, -OCH_2CH=CH_2), 5.35 – 5.25 (m, 1H, -OCH_2CH=CH_2), 5.21 (dd, *J* = 10.5, 1.5 Hz, 1H, -OCH_2CH=CH_2), 4.67 – 4.53 (m, 4H,

-OCH_2Ph × 3, *H*-1), 4.46 – 4.36 (m, 2H, -OCH_2Ph, -OCH_2CH=CH_2), 4.13 (ddt, *J* = 12.8, 6.4, 1.3 Hz, 1H, -OCH_2CH=CH_2), 3.95 (ddd, *J* = 4.7, 3.3, 1.4 Hz, 1H, *H*-2), 3.81 – 3.77 (m, 2H, *H*-6a, *H*-4), 3.68 (dd, *J* = 10.6, 5.6 Hz, 1H, *H*-6b), 3.61 (ddd, *J* = 8.5, 5.6, 2.9 Hz, 1H, *H*-5), 2.43 (dt, *J* = 13.6, 4.5 Hz, 1H, *H*-3a), 2.32 (s, 1H, C2-O*H*), 1.62 (ddd, *J* = 13.4, 10.1, 3.2 Hz, 1H, *H*-3b); The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon was determined to be 159.0 Hz; **LRMS (ESI)** calculated for $C_{23}H_{28}NaO_5$ $[M+Na]^+$ 407.2, found 407.6.

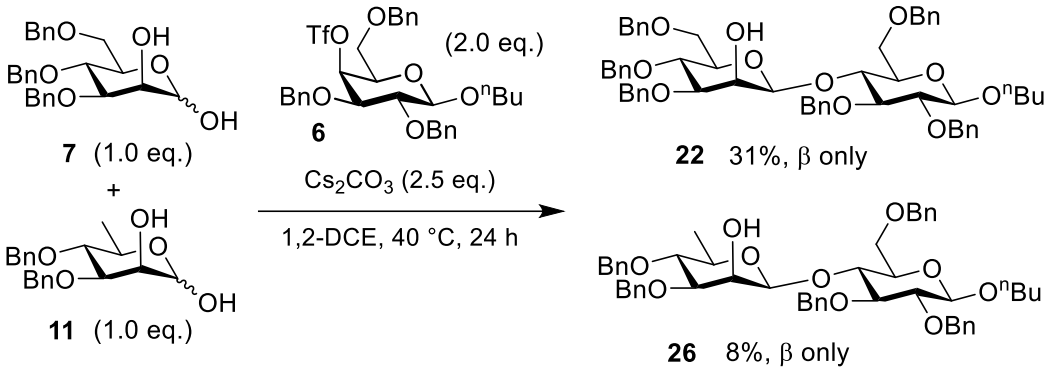
General procedure for competition using different deoxy-mannose donors in the anomeric *O*-alkylation with triflate 6.

Two kinds of mannose derived donors (**7**, **9**, **10**, or **11**, 0.1 mmol + 0.1 mmol) were treated with triflate acceptor **6** (0.1 mmol) and cesium carbonate (0.25 mmol) in DCE (1.0 mL) at 40 ℃ for 24 h. After filtration, the corresponding disaccharides were isolated by preparative TLC.

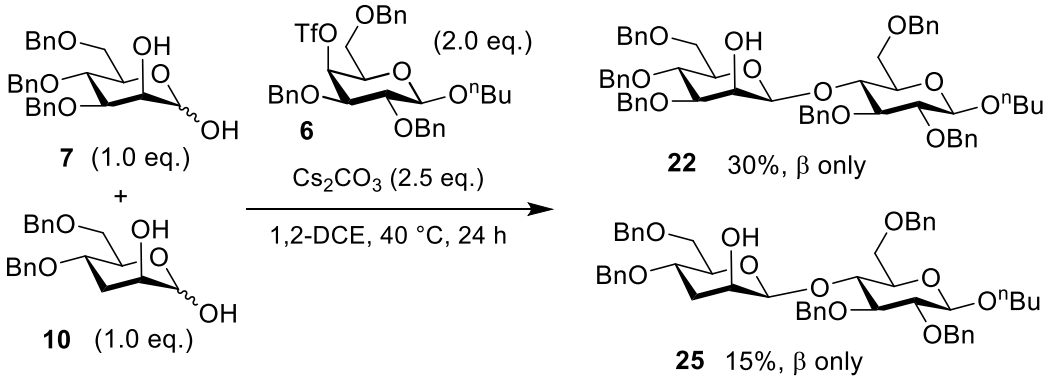


Mannose derived disaccharide **22** (45.2 mg) and 2-deoxy mannose derived disaccharide **24** (12.1 mg) were produced by mannose donor **7** (45 mg) and 2-deoxy mannose donor

9 (43 mg) following the general procedure in the yield of 48% and 12%, respectively.



Mannose derived disaccharide **22** (28.5 mg) and 6-deoxy mannose derived disaccharide **26** (6.8 mg) were produced by mannose donor **7** (45 mg) and 6-deoxy mannose donor **11** (34 mg) following the general procedure in the yield of 31% and 8%, respectively.



Mannose derived disaccharide **22** (28.3 mg) and 3-deoxy mannose derived disaccharide **25** (12.6 mg) were produced by mannose donor **7** (45 mg) and 3-deoxy mannose donor **10** (34 mg) following the general procedure in the yield of 30% and 15%, respectively.

Kinetic studies

The kinetic study was performed with a HPLC instrument equipped with a CHIRALPAK® AD-H column (5 μm, 4.6 mm ϕ × 250 mmL) and a UV-vis detector. A representative procedure (using 0.201 mmol of 3,4,6-tri-*O*-benzyl-D-mannose, 0.603 mmol of Cs_2CO_3, and 0.402 mmol of allyl bromide) was conducted as follows. To a solution of mannose lactol in 1,2-dichloroethane (2.0 mL) was added allyl bromide, followed by the addition of 1,4,6,7-tetramethylnaphthalene (19.9 mg, 0.108 mmol) as the internal standard. The resulting solution was stirred at 40 °C for 30 min. The reaction was initiated by the addition of cesium carbonate. The reaction was followed by monitoring the concentration of mannose lactol and the corresponding allyl mannoside. 10 μL of reaction solution was taken out by micro syringe every 15 min within 1 hour after the reaction began and every 20 min after 1 hour. The solvent was evaporated under vacuum and dissolved in 2-propanol (1 mL). The resulting solution was subjected to HPLC analysis (n-hexane/2-propanol 90/10, 0.1 mL/min). The concentration was calculated based on the area. The graph of the negative natural logarithm of [mannose] versus time was found to linear.

Table S5. Data of the reaction with the initial concentration of mannose as 0.1005 M.

time (hours)	[mannose] (M)	[allyl mannoside] (M)	- ln ([mannose]/M)
0	0.1005	0	2.297597551

0.25	0.096247392	0.007441148	2.340833406
0.5	0.08649566	0.012243623	2.447661042
0.75	0.08129823	0.016286536	2.509631032
1	0.075439833	0.020969195	2.58441986
$1\frac{1}{3}$	0.067355466	0.027163303	2.69777122
$1\frac{2}{3}$	0.06003926	0.034161479	2.812756594
2	0.052698657	0.041845293	2.943165298
$2\frac{1}{3}$	0.044305967	0.049163232	3.116635925
$2\frac{2}{3}$	0.035567293	0.054879129	3.336328813
3	0.030381289	0.06095279	3.493928342
$3\frac{1}{3}$	0.026675363	0.064536711	3.624014887
$3\frac{2}{3}$	0.022596235	0.067417141	3.789971983

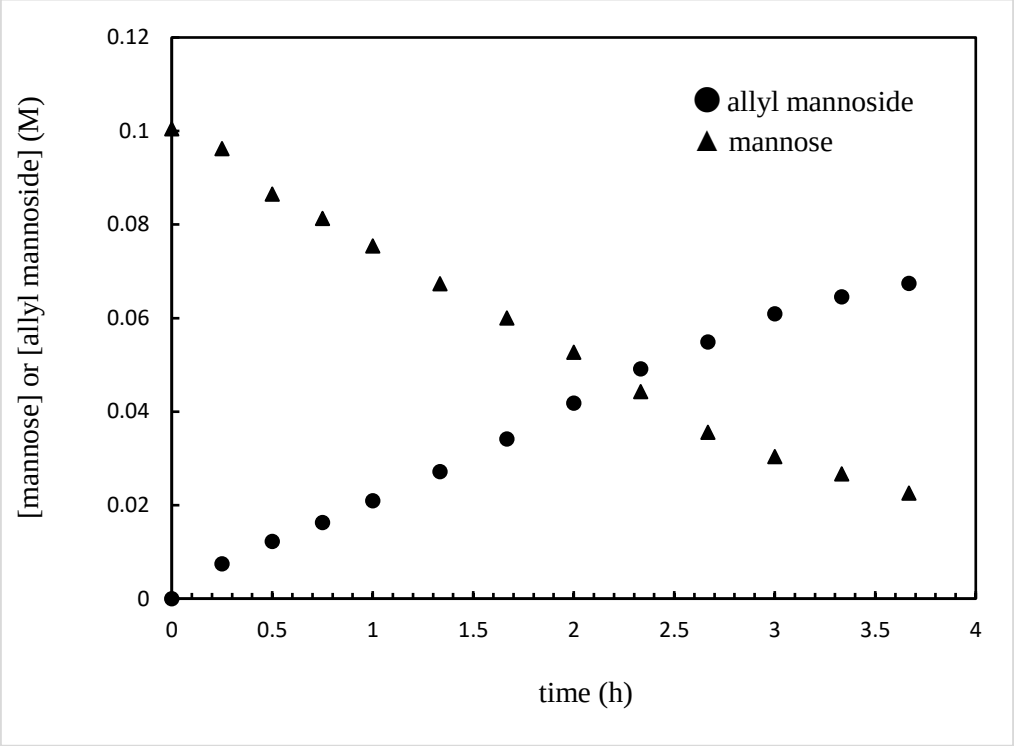


Figure S1. [mannose] and [allyl mannoside]

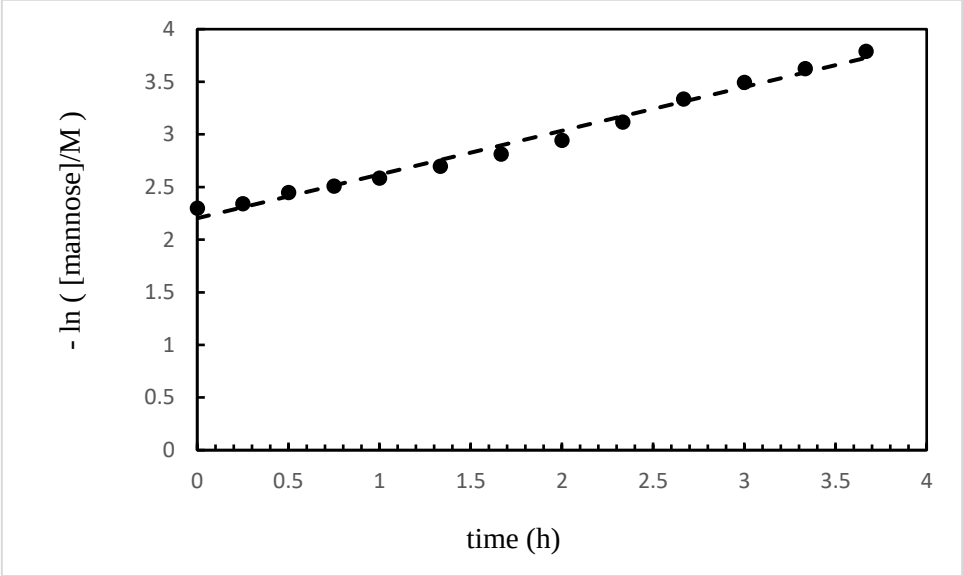


Figure S2. The linear relationship of negative natural logarithm of [mannose] versus time.

Table S6. Data of the reaction with the initial concentration of mannose as 0.2015 M.

time (hours)	[mannose] (M)	[allyl mannoside] (M)	- ln ([mannose]/M)
0	0.2015	0	1.601965898
0.25	0.178575006	0.016845652	1.722746563
0.5	0.172425148	0.026221723	1.757792064
0.75	0.157473659	0.034634933	1.848497078
1	0.151679266	0.045958032	1.885987082
$1\frac{1}{3}$	0.133820301	0.059034496	2.01125742
$1\frac{2}{3}$	0.121586277	0.078025137	2.107131171
2	0.108556463	0.086351397	2.220484849
$2\frac{1}{3}$	0.096722369	0.094662191	2.33591058
$2\frac{2}{3}$	0.088707165	0.10224475	2.422414612
3	0.083391357	0.109851803	2.484210609
$3\frac{1}{3}$	0.081093243	0.118845292	2.512155639
$3\frac{2}{3}$	0.073212813	0.120541381	2.614384836

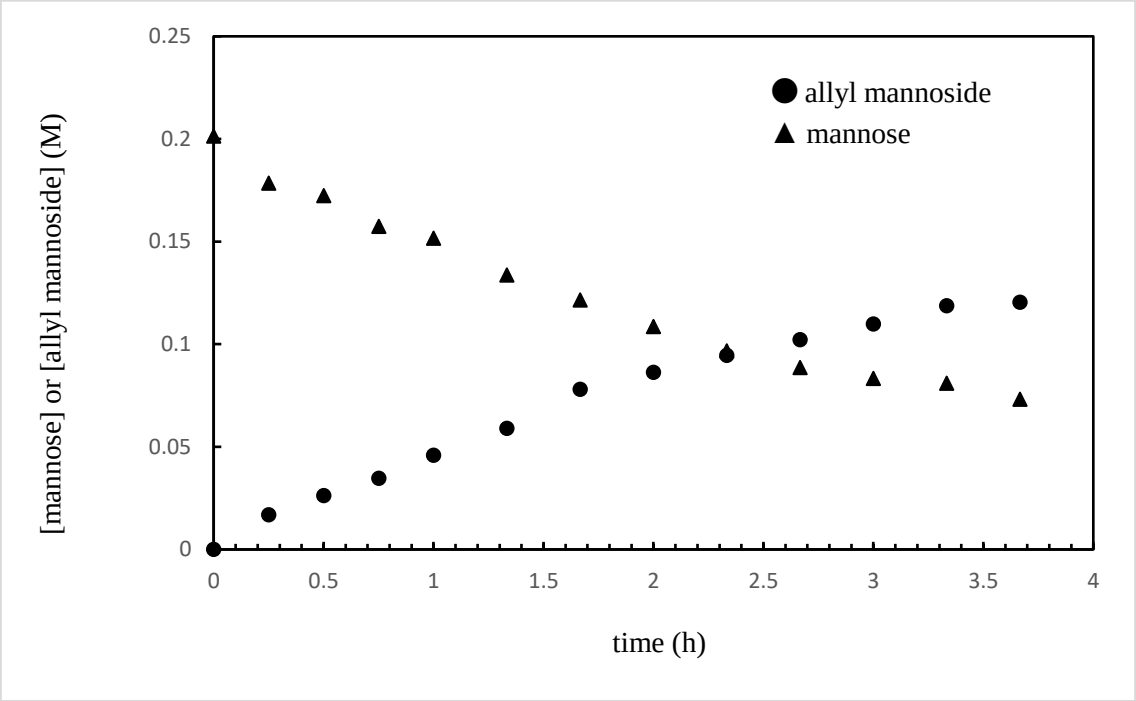


Figure S3. [mannose] and [allyl mannoside]

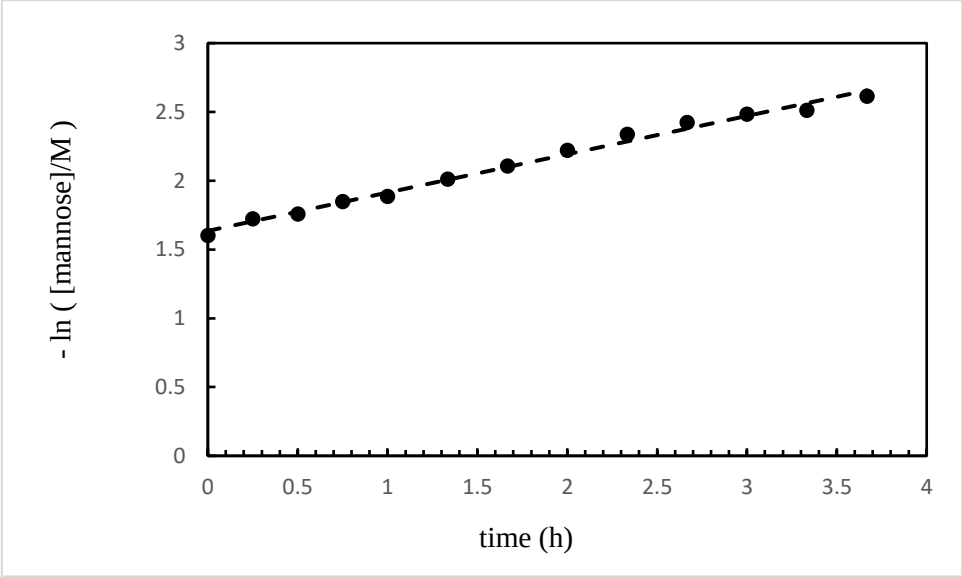


Figure S4. The linear relationship of negative natural logarithm of [mannose] versus time.

Computational studies on the *O*-allylation of D-mannose 7 and deoxy-D-mannoses 9, 10, and 11 with allyl bromide

Computational methods

All density functional theory (DFT) calculations were performed using the Gaussian 09 software package.[15] Geometries were optimized in the gas phase using the M06-2X[16] functional and a mixed basis set of SDD[17] for Cs and 6-31G(d)[18] for other atoms. Vibrational frequency calculations were performed for all the stationary points to confirm if each optimized structure is a local minimum or a transition state structure. Single point energies were calculated using M06-2X and the def2-QZVP[19] basis set in dichloroethane using the SMD solvation model.[20] Reported Gibbs free energies and enthalpies in solution include thermal corrections computed at 298K.

Additional computational results

Different conformers of the anomeric cesium alkoxides were considered to identify the most stable conformer. The lowest-energy conformers of anomeric cesium alkoxides derived from D-mannose **7** and deoxy-D-mannose **9** are shown in Figure S1. Besides the $^{4}\boldsymbol{C}_{1}$ conformer as in **7-Cs**, a $^{1}\boldsymbol{C}_{4}$ (flipped chair) conformer of **7-Cs** is also located. In this conformer (**7b-Cs**, Figure S1a), the C3-OH is coordinated with cesium instead of C2-OH. The relative free energy of **7b-Cs** is 6.4 kcal/mol higher than that of **7-Cs**. Moreover, the corresponding activation free energy of the *O*-allylation transition state

7b-TS from this $^{1}\boldsymbol{C}_{4}$ conformer is higher than that of **7-TS** by 6.3 kcal/mol.

A higher energy boat conformation ($\boldsymbol{B}^{1,4}$) was also located for the cesium alkoxide derived from deoxy-D-mannose **9** (Figure S1b). Compared to the $^{4}\boldsymbol{C}_{1}$ conformer **9-Cs**, this conformer (**9b-Cs**) has an additional chelating Cs–O interaction with O4. However, the free energy of **9b-Cs** is 3.2 kcal/mol higher than that of **9-Cs**, and the activation free energy of the *O*-allylation transition state **9b-TS** is higher than that of **9-TS** by 1.4 kcal/mol. Therefore, conformers that adopt $\boldsymbol{B}^{1,4}$ and $^{1}\boldsymbol{C}_{4}$ conformations are less stable than the $^{4}\boldsymbol{C}_{1}$ conformer and are less likely to contribute to the subsequent anomeric *O*-allylation reaction.

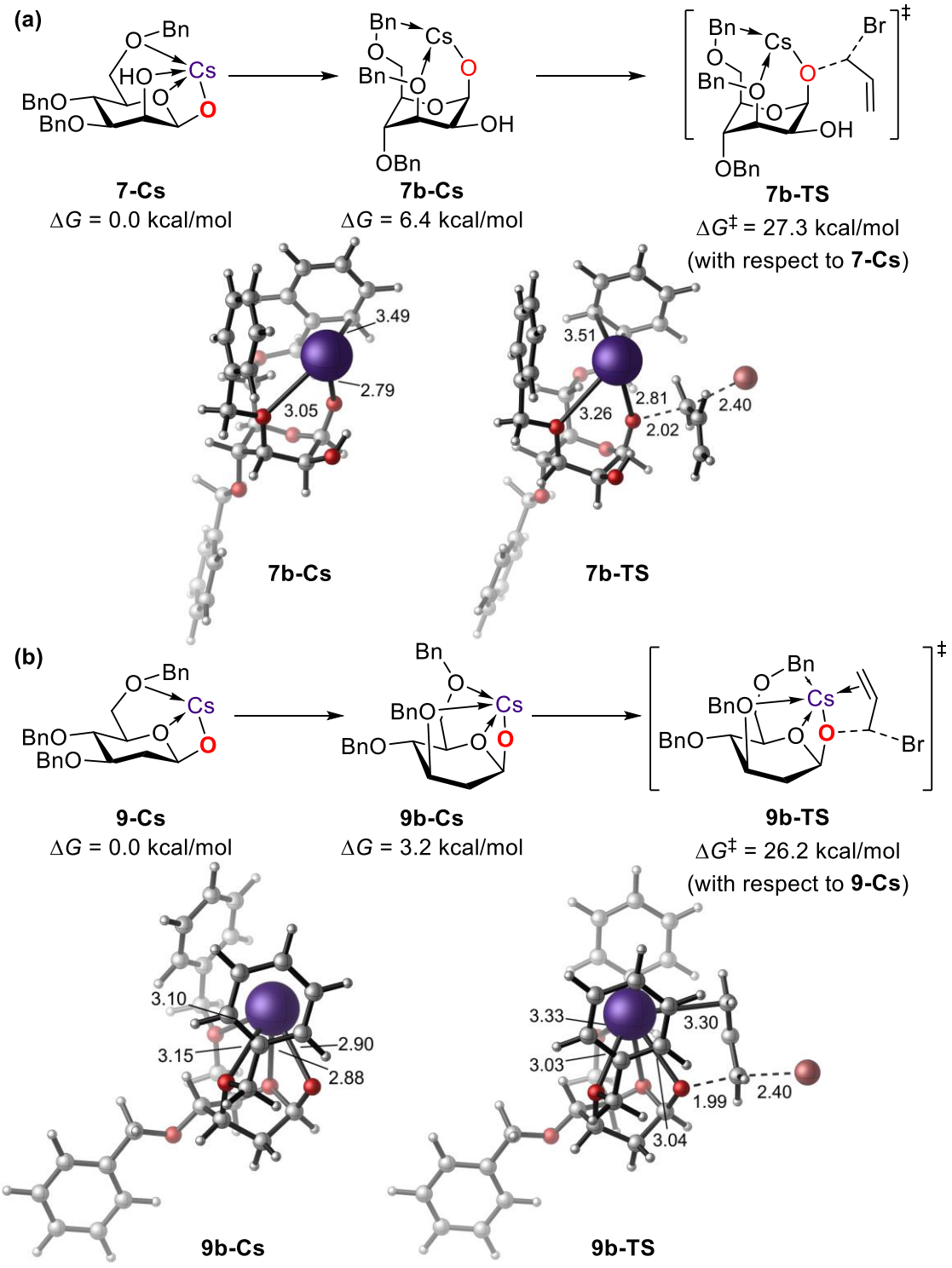


Figure S1. Optimized low-energy conformers of anomeric cesium alkoxides derived from D-mannose **7** and deoxy-D-mannose **9** and the corresponding *O*-allylation transition states.

Cartesian coordinates (Å) and energies of optimized structures

7

M06-2X SCF energy: -1497.59980715 a.u.

M06-2X enthalpy: -1497.035779 a.u.

M06-2X free energy: -1497.126152 a.u.

M06-2X SCF energy in solution: -1498.37279823 a.u.

M06-2X enthalpy in solution: -1497.808770 a.u.

M06-2X free energy in solution: -1497.899143 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.842475	-3.844619	-0.337282
C	-2.597767	-2.537599	-0.055894
C	-1.972016	-1.331683	-0.767173
C	-0.467639	-1.324329	-0.566956
C	0.099499	-2.686436	-0.969834
H	-3.640789	-2.679144	-0.380942
H	-2.025032	-4.168334	-1.374041
H	-2.183410	-1.364916	-1.847307
H	-0.252658	-1.187152	0.498602
H	-0.165090	-2.896842	-2.022426
O	-0.452526	-3.681580	-0.135351

O	-2.294942	-4.843971	0.496300
O	0.143698	-0.322577	-1.343184
C	1.616995	-2.694428	-0.856409
H	1.964504	-3.730977	-0.736580
H	2.042254	-2.288831	-1.785465
O	2.005217	-1.891015	0.230551
O	-2.541364	-2.343901	1.340512
H	-2.706830	-1.399519	1.496685
C	0.602738	0.797010	-0.614892
H	-0.215516	1.517240	-0.470280
H	0.953375	0.471939	0.376022
C	3.380325	-1.569260	0.223233
H	3.974067	-2.467166	0.459475
H	3.683406	-1.219392	-0.775666
C	3.618148	-0.481949	1.236709
C	3.178017	-0.649118	2.552963
C	4.247798	0.705803	0.871539
C	3.376788	0.356422	3.491918
H	2.666978	-1.567717	2.827718
C	4.452026	1.712939	1.813702
H	4.560152	0.855568	-0.160219
C	4.019174	1.539320	3.124195

H	3.030573	0.220179	4.511993
H	4.936712	2.637323	1.513526
H	4.174294	2.323597	3.858874
C	1.761127	1.450413	-1.326621
C	2.418941	0.821957	-2.382143
C	2.229974	2.685586	-0.872904
C	3.541496	1.411296	-2.963708
H	2.036616	-0.124212	-2.749788
C	3.348997	3.274389	-1.450464
H	1.724778	3.178871	-0.045472
C	4.012994	2.635366	-2.497684
H	4.045326	0.913149	-3.786782
H	3.705434	4.232420	-1.083769
H	4.886464	3.093609	-2.951071
O	-2.490701	-0.134878	-0.207462
C	-3.699347	0.295567	-0.798352
H	-4.462190	-0.496461	-0.743737
H	-3.524609	0.506387	-1.864708
C	-4.208111	1.533714	-0.103380
C	-5.489721	1.997297	-0.407090
C	-3.427064	2.235048	0.812459
C	-5.983679	3.150695	0.190386

H	-6.104928	1.448502	-1.117053
C	-3.924955	3.389297	1.415517
H	-2.433978	1.871085	1.053076
C	-5.199974	3.851072	1.105964
H	-6.981671	3.500956	-0.054272
H	-3.310881	3.929127	2.129959
H	-5.584459	4.750903	1.575729
H	-2.301682	-4.459455	1.390191

9

M06-2X SCF energy: -1422.40820896 a.u.

M06-2X enthalpy: -1421.849170 a.u.

M06-2X free energy: -1421.941154 a.u.

M06-2X SCF energy in solution: -1423.13572553 a.u.

M06-2X enthalpy in solution: -1422.576687 a.u.

M06-2X free energy in solution: -1422.668671 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.715623	-4.045691	-0.181204

C	-2.492956	-2.805530	0.231294
C	-2.004305	-1.580279	-0.546195
C	-0.490626	-1.487202	-0.442838
C	0.147918	-2.810758	-0.870729
H	-3.561802	-2.985900	0.080079
H	-1.907297	-4.276796	-1.248402
H	-2.269497	-1.670402	-1.614340
H	-0.223493	-1.318522	0.607704
H	-0.137788	-3.027838	-1.915851
O	-0.321495	-3.849210	-0.031964
O	-2.096158	-5.094857	0.639000
O	-2.528652	-0.373098	-0.036858
O	0.026651	-0.466089	-1.260444
C	1.666229	-2.727549	-0.808968
H	2.083262	-3.741814	-0.721504
H	2.026158	-2.284359	-1.747962
O	2.050049	-1.917560	0.274107
H	-2.319082	-2.644063	1.300748
C	3.372403	-1.431071	0.169283
H	4.087505	-2.252703	0.338048
H	3.549719	-1.033227	-0.841514
C	3.559221	-0.334620	1.183594

C	3.236375	-0.561846	2.524399
C	4.028219	0.919005	0.796002
C	3.391010	0.450472	3.464496
H	2.851379	-1.534001	2.819614
C	4.185780	1.934026	1.738532
H	4.252502	1.111452	-0.251400
C	3.869631	1.701246	3.073128
H	3.137624	0.266252	4.504154
H	4.543240	2.908887	1.420509
H	3.989828	2.491076	3.808344
C	-3.859337	-0.120460	-0.417664
H	-4.529474	-0.898635	-0.018440
H	-3.949568	-0.148029	-1.515509
C	0.391774	0.714195	-0.574773
H	0.809787	0.450591	0.409201
H	-0.490888	1.347703	-0.411652
C	-4.296627	1.227827	0.097293
C	-5.415102	1.843098	-0.466768
C	-3.629865	1.855114	1.148605
C	-5.868087	3.066307	0.015246
H	-5.933094	1.361104	-1.293018
C	-4.080782	3.083437	1.628326

H	-2.757871	1.376668	1.581611
C	-5.200187	3.690652	1.066730
H	-6.738181	3.535397	-0.433752
H	-3.554655	3.566800	2.446022
H	-5.549759	4.646979	1.442978
C	1.455254	1.455804	-1.345823
C	1.827716	2.739155	-0.938805
C	2.126392	0.862970	-2.413467
C	2.867881	3.409698	-1.573223
H	1.310129	3.207948	-0.104853
C	3.169649	1.533755	-3.051787
H	1.816390	-0.122517	-2.743665
C	3.547780	2.805403	-2.630791
H	3.149892	4.405135	-1.243054
H	3.684292	1.060968	-3.883162
H	4.359861	3.327127	-3.127642
H	-1.510703	-5.841709	0.442631

10

M06-2X SCF energy: -1152.16906153 a.u.

M06-2X enthalpy: -1151.727285 a.u.

M06-2X free energy: -1151.803545 a.u.

M06-2X SCF energy in solution: -1152.77306755 a.u.

M06-2X enthalpy in solution: -1152.331291 a.u.

M06-2X free energy in solution: -1152.407551 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.512394	0.127461	-0.377824
C	-4.209485	0.430566	1.097304
C	-2.974626	1.317382	1.245164
C	-1.824990	0.728901	0.435398
C	-2.284337	0.541737	-1.011354
H	-5.097808	0.919030	1.522241
H	-4.850127	1.046698	-0.881658
H	-3.194143	2.326781	0.873284
H	-1.582099	-0.268250	0.818137
H	-2.619731	1.515606	-1.413106
O	-3.363151	-0.372423	-1.032985
O	-5.521961	-0.804329	-0.484291
O	-0.687695	1.565959	0.454248
C	-1.159344	0.032119	-1.898343

H	-1.590428	-0.477183	-2.772884
H	-0.572396	0.892117	-2.251634
O	-0.329497	-0.829540	-1.157641
O	-4.013621	-0.844660	1.695173
H	-4.029606	-0.741872	2.655949
H	-2.697155	1.414494	2.302310
C	0.405988	1.064875	1.191160
H	0.304217	1.323948	2.256831
H	0.439557	-0.031119	1.110615
C	0.897180	-1.102720	-1.800988
H	0.723669	-1.758510	-2.669846
H	1.347267	-0.168383	-2.171457
C	1.826515	-1.752130	-0.810622
C	1.406381	-2.869582	-0.082976
C	3.101411	-1.234559	-0.592426
C	2.257935	-3.465053	0.840744
H	0.403611	-3.257492	-0.239567
C	3.957963	-1.834067	0.329196
H	3.418530	-0.342263	-1.128689
C	3.538866	-2.950414	1.045278
H	1.925577	-4.332434	1.403194
H	4.945515	-1.413827	0.495106

H	4.203551	-3.416627	1.766354
C	1.704133	1.611908	0.650856
C	1.770879	2.224522	-0.598722
C	2.878083	1.438890	1.386739
C	2.997729	2.644138	-1.112619
H	0.852250	2.382294	-1.153707
C	4.102286	1.855469	0.876175
H	2.833017	0.954916	2.360055
C	4.166655	2.457858	-0.380028
H	3.038330	3.123995	-2.086189
H	5.008013	1.710649	1.457848
H	5.120841	2.787554	-0.779367
H	-5.284011	-1.513981	0.137473

11

M06-2X SCF energy: -1152.17461546 a.u.

M06-2X enthalpy: -1151.733167 a.u.

M06-2X free energy: -1151.811756 a.u.

M06-2X SCF energy in solution: -1152.77852863 a.u.

M06-2X enthalpy in solution: -1152.337080 a.u.

M06-2X free energy in solution: -1152.415669 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-4.046898	-0.433075	-0.460010
C	-3.026591	0.691053	-0.265402
C	-1.593737	0.219987	-0.516412
C	-1.296622	-1.097637	0.192097
C	-2.416120	-2.105552	-0.098220
H	-3.281224	1.511013	-0.956025
H	-4.125806	-0.696018	-1.526220
H	-1.422224	0.064513	-1.593136
H	-1.250604	-0.915513	1.278002
H	-2.410154	-2.303565	-1.185558
O	-3.664737	-1.567723	0.285184
O	-5.295302	-0.026819	-0.038581
O	-0.703759	1.210867	-0.016806
O	-0.099939	-1.681237	-0.269406
C	-2.227850	-3.403032	0.662239
H	-3.033049	-4.098620	0.415626
H	-1.266614	-3.855835	0.412232
H	-2.259344	-3.204101	1.737794

O	-3.159550	1.113626	1.074111
H	-2.349374	1.603035	1.290893
C	-0.327738	2.187657	-0.965729
H	0.083018	1.684503	-1.856020
H	-1.201144	2.770456	-1.295428
C	1.093800	-1.056720	0.148533
H	0.996038	-0.740792	1.200216
H	1.288131	-0.146013	-0.435265
C	2.259666	-2.003643	0.001761
C	3.552557	-1.499762	0.162328
C	2.085846	-3.357424	-0.273972
C	4.656302	-2.337972	0.059271
H	3.692279	-0.439663	0.366537
C	3.192905	-4.197500	-0.383241
H	1.082583	-3.744776	-0.412544
C	4.478560	-3.693307	-0.214896
H	5.655718	-1.933446	0.186974
H	3.047170	-5.251189	-0.601592
H	5.338762	-4.350147	-0.298948
C	0.712645	3.105730	-0.374882
C	0.976231	4.324837	-1.001558
C	1.446021	2.745795	0.755222

C	1.966145	5.170308	-0.513725
H	0.400816	4.613758	-1.878195
C	2.433878	3.596678	1.247782
H	1.231770	1.804852	1.251564
C	2.698837	4.807230	0.614768
H	2.160961	6.116252	-1.009288
H	2.996694	3.311583	2.131395
H	3.467987	5.468634	1.000755
H	-5.163106	0.359465	0.844499

7-Cs

M06-2X SCF energy: -1517.13322054 a.u.

M06-2X enthalpy: -1516.580667 a.u.

M06-2X free energy: -1516.683258 a.u.

M06-2X SCF energy in solution: -1517.93365013 a.u.

M06-2X enthalpy in solution: -1517.381097 a.u.

M06-2X free energy in solution: -1517.483688 a.u.

Cartesian coordinates

ATOM	X	Y	Z

C	1.003560	-1.868513	-2.401907
C	-0.122402	-2.172081	-1.374659
C	-1.218990	-1.115409	-1.353324
C	-0.648614	0.261918	-1.055134
C	0.508745	0.572243	-2.016642
H	-0.548389	-3.146711	-1.660298
H	0.491756	-1.720894	-3.394731
H	-1.735708	-1.070494	-2.324529
H	-0.275206	0.273246	-0.019530
H	0.055458	0.763047	-3.008722
O	1.458823	-0.437868	-2.057164
O	2.010625	-2.658921	-2.352216
O	-1.600760	1.291459	-1.241977
C	1.239455	1.835537	-1.577132
H	1.956088	2.135475	-2.355653
H	0.530649	2.656794	-1.398963
O	1.944017	1.517976	-0.387214
Cs	3.293417	-1.412519	-0.100192
O	0.427647	-2.258440	-0.060992
H	-0.342426	-2.287006	0.529722
C	-2.578288	1.433956	-0.240472
H	-3.408882	0.731404	-0.398742

H	-2.146771	1.187820	0.743751
C	2.729935	2.570518	0.120708
H	3.313464	3.043645	-0.684048
H	2.093607	3.345322	0.575697
C	3.651984	1.945897	1.137853
C	5.009794	1.769100	0.871755
C	3.113238	1.407096	2.310501
C	5.821175	1.063641	1.760989
H	5.433220	2.179245	-0.041787
C	3.917543	0.698536	3.198032
H	2.052989	1.535940	2.513232
C	5.274584	0.521907	2.922024
H	6.878298	0.938315	1.546906
H	3.490373	0.287396	4.107679
H	5.904307	-0.026572	3.615807
C	-3.103918	2.850529	-0.224349
C	-2.600167	3.832124	-1.074512
C	-4.123967	3.183345	0.670195
C	-3.105157	5.130733	-1.025294
H	-1.820941	3.566442	-1.780331
C	-4.626281	4.478352	0.721822
H	-4.527950	2.417441	1.329872

C	-4.115514	5.459206	-0.127687
H	-2.707412	5.886846	-1.695798
H	-5.419047	4.723219	1.422420
H	-4.507555	6.470876	-0.090341
O	-2.159741	-1.423495	-0.318865
C	-3.224615	-2.241358	-0.745610
H	-2.854062	-3.209641	-1.114408
H	-3.742269	-1.752737	-1.587470
C	-4.198879	-2.459179	0.385004
C	-5.137736	-3.487847	0.287212
C	-4.213154	-1.629357	1.505580
C	-6.084919	-3.679424	1.286995
H	-5.126085	-4.143085	-0.580874
C	-5.159082	-1.824413	2.510544
H	-3.473836	-0.839339	1.588275
C	-6.098384	-2.845545	2.403528
H	-6.810233	-4.482229	1.197198
H	-5.160399	-1.175465	3.381254
H	-6.835517	-2.994535	3.186265

7b-Cs

M06-2X SCF energy: -1517.14092625 a.u.

M06-2X enthalpy: -1516.586854 a.u.

M06-2X free energy: -1516.682649 a.u.

M06-2X SCF energy in solution: -1517.93171174 a.u.

M06-2X enthalpy in solution: -1517.377639 a.u.

M06-2X free energy in solution: -1517.473434 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-2.131935	-0.331845	0.574452
C	-1.369076	-1.086266	-0.520179
C	-1.347532	-0.232409	-1.799328
C	-0.901693	1.251584	-1.575103
C	-1.542698	1.072803	0.777067
H	-1.891766	-2.032642	-0.732097
H	-2.185326	1.618394	1.481939
H	-2.103448	-0.874396	1.536905
H	-1.367331	1.850879	-2.384342
H	-2.369007	-0.253763	-2.194364
O	0.428410	1.328397	-1.544774
O	-1.600056	1.806051	-0.416961

O	-0.447719	-0.770019	-2.745406
O	-0.041310	-1.393214	-0.105728
O	-3.462901	-0.309998	0.098428
C	-0.165606	1.043005	1.455299
H	-0.223376	0.391933	2.339831
H	0.587627	0.652787	0.772141
O	0.209907	2.320515	1.934840
Cs	2.623095	-0.339543	-1.140437
C	-4.360552	0.499066	0.815539
H	-4.181069	1.559738	0.591545
H	-4.212253	0.358738	1.900699
C	0.047330	-2.474143	0.801475
H	-0.467247	-2.247131	1.745978
H	-0.418853	-3.371279	0.367920
H	0.231050	-0.055626	-2.729976
C	0.836644	3.118147	0.949369
H	0.280580	3.094441	0.008367
H	0.835105	4.138094	1.350979
C	-5.779953	0.132123	0.453260
C	-6.076905	-1.037644	-0.242833
C	-6.821905	0.974668	0.845978
C	-7.399792	-1.360570	-0.539317

H	-5.263577	-1.682145	-0.556473
C	-8.142359	0.650292	0.555454
H	-6.594597	1.894661	1.380320
C	-8.435393	-0.521376	-0.140183
H	-7.620609	-2.271830	-1.087232
H	-8.943171	1.314786	0.865683
H	-9.465258	-0.774085	-0.373187
C	1.515366	-2.699783	1.055829
C	2.242086	-3.597543	0.271129
C	2.193538	-1.902844	1.982143
C	3.626356	-3.695842	0.404757
H	1.717707	-4.214207	-0.454891
C	3.576685	-1.997530	2.119076
H	1.632534	-1.193674	2.586498
C	4.296405	-2.891231	1.325604
H	4.181278	-4.403419	-0.203993
H	4.091609	-1.378775	2.847555
H	5.373593	-2.971037	1.435728
C	2.266716	2.699758	0.679148
C	2.885746	3.086643	-0.514183
C	2.995836	1.954745	1.607323
C	4.220271	2.769816	-0.755429

H	2.301286	3.615853	-1.261233
C	4.328960	1.620253	1.361083
H	2.503887	1.650346	2.527587
C	4.948825	2.033227	0.182449
H	4.694114	3.093389	-1.678374
H	4.890824	1.053869	2.098792
H	5.992662	1.794468	-0.000721

9-Cs

M06-2X SCF energy: -1441.93592889 a.u.

M06-2X enthalpy: -1441.389701 a.u.

M06-2X free energy: -1441.490811 a.u.

M06-2X SCF energy in solution: -1442.69325802 a.u.

M06-2X enthalpy in solution: -1442.147030 a.u.

M06-2X free energy in solution: -1442.248140 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	0.900824	-2.271997	-2.089789
C	-0.275866	-2.422864	-1.093246

C	-1.332606	-1.335772	-1.197062
C	-0.707688	0.032100	-0.981401
C	0.463467	0.225997	-1.956503
H	-0.714210	-3.414386	-1.251319
H	0.483153	-2.229675	-3.130669
H	-1.787835	-1.334533	-2.203195
H	-0.330803	0.091096	0.054383
H	0.020487	0.335481	-2.965274
O	1.384890	-0.809355	-1.892692
O	1.890563	-3.066587	-1.878179
O	-2.364038	-1.475908	-0.226733
O	-1.611136	1.089877	-1.229245
C	1.221127	1.510452	-1.637595
H	1.916374	1.746946	-2.456823
H	0.522690	2.347692	-1.500285
O	1.964303	1.281729	-0.448756
Cs	3.497112	-1.499642	-0.133250
H	0.149378	-2.414872	-0.079189
C	2.692869	2.401435	-0.000438
H	3.242239	2.868187	-0.832713
H	2.015556	3.159055	0.422349
C	3.656216	1.879309	1.036199

C	5.026291	1.807314	0.785080
C	3.151729	1.326551	2.218036
C	5.883729	1.191217	1.697803
H	5.424626	2.230158	-0.134047
C	4.002443	0.707382	3.128944
H	2.082665	1.373967	2.409511
C	5.372081	0.634890	2.867661
H	6.949632	1.148787	1.495194
H	3.601064	0.286987	4.046091
H	6.038240	0.159037	3.580700
C	-3.340862	-2.427327	-0.556900
H	-2.905936	-3.438696	-0.594469
H	-3.751665	-2.218124	-1.558624
C	-2.521102	1.397530	-0.199112
H	-2.055204	1.209317	0.781588
H	-3.404378	0.748586	-0.250985
C	-4.454527	-2.394505	0.461514
C	-5.644218	-3.075990	0.196385
C	-4.315785	-1.715177	1.670810
C	-6.678971	-3.082800	1.124561
H	-5.760246	-3.602182	-0.748780
C	-5.354197	-1.719193	2.600618

H	-3.390000	-1.187129	1.872448
C	-6.536489	-2.402018	2.332562
H	-7.599269	-3.615109	0.904014
H	-5.236826	-1.187132	3.540234
H	-7.344270	-2.403523	3.057977
C	-2.935051	2.847983	-0.290145
C	-3.825316	3.358118	0.658617
C	-2.461825	3.688404	-1.295324
C	-4.228796	4.687207	0.609850
H	-4.206148	2.702893	1.439699
C	-2.867753	5.021409	-1.346515
H	-1.784455	3.285648	-2.040254
C	-3.748478	5.525813	-0.395327
H	-4.920958	5.070188	1.353791
H	-2.495355	5.666909	-2.136663
H	-4.063816	6.563879	-0.436807

9b-Cs

M06-2X SCF energy: -1441.94823977 a.u.

M06-2X enthalpy: -1441.401010 a.u.

M06-2X free energy: -1441.499549 a.u.

M06-2X SCF energy in solution: -1442.69180321 a.u.

M06-2X enthalpy in solution: -1442.144573 a.u.

M06-2X free energy in solution: -1442.243112 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-1.743101	-0.233745	-0.510560
C	-1.376659	-1.714470	-0.312557
C	-1.249694	-2.385440	-1.677794
C	-0.025002	-1.848135	-2.468895
C	-1.296402	0.271597	-1.894152
H	-2.175838	-2.199170	0.275007
H	-2.121357	0.059373	-2.599138
H	-1.232232	0.345369	0.274881
H	-0.244060	-1.934799	-3.559293
H	-2.194386	-2.195663	-2.206032
O	1.132188	-2.277648	-2.079775
O	-0.091631	-0.295861	-2.289531
O	-0.176824	-1.713877	0.454315
O	-3.141114	-0.017074	-0.434503
C	-1.109288	1.781822	-1.860841

H	-0.892067	2.157444	-2.870858
H	-2.020139	2.270148	-1.480193
O	-0.012041	2.051850	-1.004877
Cs	2.249244	-0.028893	-0.630581
H	-1.152833	-3.472154	-1.603669
C	0.373413	-3.002507	0.671747
H	-0.241827	-3.546251	1.407376
H	0.417760	-3.558074	-0.266314
C	-3.617076	0.107719	0.881579
H	-3.291431	-0.749834	1.493082
H	-3.192348	1.011037	1.351409
C	0.290183	3.418132	-0.850342
H	0.468731	3.892530	-1.827517
H	-0.550599	3.943743	-0.370103
C	1.529908	3.476971	0.006396
C	2.755787	3.896787	-0.506977
C	1.472191	2.985060	1.314562
C	3.910381	3.831504	0.274243
H	2.809647	4.272163	-1.525850
C	2.621811	2.912471	2.094549
H	0.518197	2.644052	1.709574
C	3.845958	3.334734	1.573007

H	4.858499	4.168597	-0.133392
H	2.565010	2.530261	3.109248
H	4.743397	3.284885	2.181693
C	1.780113	-2.814294	1.175477
C	2.859409	-3.213205	0.383005
C	2.023710	-2.149231	2.379708
C	4.166128	-2.958267	0.797816
H	2.654469	-3.663275	-0.584744
C	3.328147	-1.881645	2.788934
H	1.180754	-1.831370	2.988612
C	4.403136	-2.287543	1.996989
H	5.000831	-3.273856	0.178446
H	3.508674	-1.366369	3.727977
H	5.421218	-2.088241	2.318629
C	-5.123868	0.184742	0.886378
C	-5.870750	-0.209739	-0.222215
C	-5.785532	0.631387	2.031637
C	-7.262594	-0.158189	-0.182498
H	-5.351145	-0.548200	-1.111756
C	-7.174664	0.678018	2.073399
H	-5.206722	0.945940	2.897640
C	-7.918422	0.282967	0.962956

H	-7.836268	-0.463456	-1.052492
H	-7.677363	1.027658	2.970184
H	-9.002954	0.322482	0.991198

10-Cs

M06-2X SCF energy: -1171.69974392 a.u.

M06-2X enthalpy: -1171.269823 a.u.

M06-2X free energy: -1171.354306 a.u.

M06-2X SCF energy in solution: -1172.33314316 a.u.

M06-2X enthalpy in solution: -1171.903222 a.u.

M06-2X free energy in solution: -1171.987705 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	-0.855295	-3.066543	0.700944
C	-0.083619	-3.112172	-0.648940
C	1.367708	-2.658164	-0.512728
C	1.423242	-1.228483	0.014381
C	0.661091	-1.138754	1.340513
H	-0.128003	-4.155828	-0.990269

H	-0.246965	-3.676706	1.425114
H	1.893139	-3.313272	0.195032
H	0.947604	-0.548861	-0.709975
H	1.258290	-1.693541	2.091028
O	-0.633312	-1.630404	1.228560
O	-2.113392	-3.295485	0.621439
O	2.744747	-0.785650	0.278008
C	0.537835	0.305553	1.810936
H	0.115320	0.323882	2.826395
H	1.518709	0.801845	1.815228
O	-0.351178	0.967040	0.922963
Cs	-2.896825	-0.673613	-0.220788
O	-0.770378	-2.276098	-1.590900
H	-0.354446	-2.419794	-2.451739
H	1.891059	-2.739071	-1.476668
C	3.515354	-0.533240	-0.864885
H	3.809592	-1.473210	-1.358573
H	2.925460	0.041805	-1.599740
C	-0.657699	2.290024	1.292824
H	-0.893374	2.349019	2.366686
H	0.198086	2.955760	1.099890
C	-1.859952	2.688980	0.473606

C	-3.114447	2.855206	1.060470
C	-1.744984	2.769431	-0.917808
C	-4.240318	3.098444	0.272836
H	-3.212546	2.786601	2.141141
C	-2.865679	3.007374	-1.707709
H	-0.769383	2.629735	-1.376313
C	-4.118392	3.169519	-1.112655
H	-5.210256	3.233080	0.741875
H	-2.764247	3.073049	-2.786923
H	-4.992306	3.363093	-1.727110
C	4.755017	0.247204	-0.495179
C	5.060231	0.545105	0.831076
C	5.618328	0.675049	-1.506140
C	6.214159	1.264072	1.139873
H	4.390014	0.205806	1.612917
C	6.768889	1.392193	-1.198749
H	5.385284	0.444476	-2.543884
C	7.070300	1.689911	0.129540
H	6.443802	1.490492	2.176926
H	7.430581	1.720462	-1.994684
H	7.967476	2.250404	0.373171

11-Cs

M06-2X SCF energy: -1171.70134882 a.u.

M06-2X enthalpy: -1171.271526 a.u.

M06-2X free energy: -1171.355932 a.u.

M06-2X SCF energy in solution: -1172.33518751 a.u.

M06-2X enthalpy in solution: -1171.905365 a.u.

M06-2X free energy in solution: -1171.989771 a.u.

Cartesian coordinates

ATOM	X	Y	Z
C	2.589040	-0.109675	1.712238
C	1.547415	0.905796	1.169653
C	0.134450	0.334871	1.100551
C	0.080795	-0.989239	0.345685
C	1.196103	-1.929329	0.829070
H	1.563902	1.776608	1.843412
H	2.169524	-0.525973	2.668888
H	-0.260047	0.161168	2.113473
H	0.225069	-0.782518	-0.729197
H	0.960791	-2.188199	1.878116

O	2.441193	-1.300349	0.751863
O	3.801371	0.320537	1.741352
O	-0.708560	1.261406	0.405305
O	-1.141243	-1.670096	0.550272
C	1.237600	-3.203886	0.000593
H	2.021357	-3.865584	0.378564
H	0.278293	-3.725457	0.033277
Cs	4.483479	0.009559	-0.898900
H	1.464062	-2.958785	-1.044114
O	1.922167	1.315588	-0.146318
H	1.132281	1.754660	-0.502094
C	-1.332319	2.218051	1.230731
H	-1.869013	1.702120	2.043865
H	-0.589510	2.878617	1.703335
C	-2.280488	-1.099097	-0.044129
H	-2.027306	-0.721083	-1.048836
H	-2.639844	-0.233661	0.531456
C	-3.385477	-2.122718	-0.147979
C	-4.652955	-1.703406	-0.559563
C	-3.175712	-3.468050	0.144233
C	-5.693520	-2.615979	-0.687370
H	-4.822805	-0.650283	-0.777358

C	-4.220220	-4.383026	0.021101
H	-2.194560	-3.787187	0.477490
C	-5.478950	-3.962720	-0.396522
H	-6.673713	-2.276884	-1.008733
H	-4.047341	-5.429421	0.254868
H	-6.290315	-4.677678	-0.491902
C	-2.308603	3.032857	0.417894
C	-2.794436	4.238370	0.927947
C	-2.768207	2.584067	-0.820028
C	-3.733263	4.979455	0.218306
H	-2.433383	4.599299	1.888405
C	-3.705186	3.328708	-1.533421
H	-2.378028	1.655506	-1.222885
C	-4.192593	4.525321	-1.016667
H	-4.103116	5.915104	0.626316
H	-4.054594	2.971106	-2.497385
H	-4.923300	5.103864	-1.573191

7-TS

M06-2X SCF energy: -4205.84340442 a.u.

M06-2X enthalpy: -4205.210424 a.u.

M06-2X free energy: -4205.327523 a.u.

M06-2X SCF energy in solution: -4209.48449969 a.u.

M06-2X enthalpy in solution: -4208.851519 a.u.

M06-2X free energy in solution: -4208.968618 a.u.

Imaginary frequency: -455.3980 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-1.101295	-1.778609	0.544633
C	0.210281	-2.078534	-0.200804
C	1.428701	-1.559997	0.562472
C	1.280555	-0.078759	0.881715
C	-0.059735	0.178538	1.580854
H	0.272282	-3.170344	-0.321974
H	-1.026875	-2.285875	1.540531
H	1.564544	-2.105202	1.508728
H	1.305995	0.490136	-0.060036
H	-0.002811	-0.268372	2.589514
O	-1.132290	-0.342462	0.847585
O	-2.176751	-2.083625	-0.159238
O	2.282718	0.378449	1.761296

C	-0.326702	1.668375	1.724100
H	-1.223431	1.821182	2.342020
H	0.531028	2.165722	2.197657
O	-0.554995	2.179333	0.422899
Cs	-2.142261	0.396101	-1.805678
O	0.199100	-1.449245	-1.476338
H	1.126361	-1.471398	-1.768910
C	-5.029178	-0.508606	-0.272378
H	-5.376921	-1.269585	-0.966953
H	-5.410590	0.500292	-0.407149
C	-4.257451	-0.826621	0.771006
H	-3.951381	-0.063906	1.483539
C	-3.763626	-2.187376	1.054499
H	-3.063318	-2.364190	1.853708
H	-4.099920	-3.020386	0.458267
Br	-5.464178	-2.598806	2.689426
C	-0.912823	3.545538	0.395770
H	-0.028765	4.177848	0.566495
H	-1.645844	3.765246	1.185997
C	3.544277	0.641418	1.188042
H	3.418859	1.037370	0.168717
H	4.125910	-0.285875	1.089951

C	-1.519852	3.793300	-0.961213
C	-2.902118	3.904042	-1.116701
C	-0.706388	3.772049	-2.098046
C	-3.468037	3.992112	-2.388637
H	-3.540507	3.913458	-0.236706
C	-1.266852	3.857126	-3.369931
H	0.370444	3.680275	-1.978312
C	-2.650855	3.963495	-3.517170
H	-4.544323	4.085826	-2.497005
H	-0.626377	3.849162	-4.246637
H	-3.088382	4.039481	-4.507831
C	4.300519	1.636494	2.035612
C	5.533979	2.108083	1.579215
C	3.813116	2.084945	3.261223
C	6.267328	3.017383	2.332067
H	5.920396	1.758837	0.623690
C	4.548724	2.996980	4.017078
H	2.860858	1.710746	3.620709
C	5.774744	3.466163	3.556756
H	7.222980	3.378050	1.963994
H	4.160677	3.339850	4.971560
H	6.345487	4.176122	4.147138

O	2.580811	-1.706664	-0.263887
C	3.290216	-2.919394	-0.052606
H	2.598552	-3.773001	-0.100686
H	3.744843	-2.907434	0.948773
C	4.345149	-3.036738	-1.117329
C	3.980710	-3.401354	-2.415103
C	5.679146	-2.742960	-0.841037
C	4.937129	-3.475350	-3.421545
H	2.939827	-3.634475	-2.630764
C	6.641306	-2.819085	-1.845709
H	5.965775	-2.456764	0.168088
C	6.270891	-3.185354	-3.136310
H	4.646420	-3.765644	-4.426339
H	7.679001	-2.594438	-1.619660
H	7.019883	-3.250188	-3.919432

7b-TS

M06-2X SCF energy: -4205.84654015 a.u.

M06-2X enthalpy: -4205.213113 a.u.

M06-2X free energy: -4205.324861 a.u.

M06-2X SCF energy in solution: -4209.48026850 a.u.

M06-2X enthalpy in solution: -4208.846841 a.u.

M06-2X free energy in solution: -4208.958589 a.u.

Imaginary frequency: -467.2594 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.775808	-0.538060	0.344220
C	-2.087910	-0.741968	-1.009379
C	-1.731330	0.624439	-1.599462
C	-0.918540	1.497740	-0.615600
C	-1.917708	0.334117	1.273670
H	-2.786298	-1.244033	-1.695114
H	-2.530533	0.619033	2.138242
H	-2.960084	-1.508211	0.841412
H	-1.000649	2.546889	-0.958410
H	-2.681108	1.122794	-1.818613
O	0.365188	1.071215	-0.582918
O	-1.570684	1.558679	0.664830
O	-0.996973	0.489198	-2.790476
O	-0.920220	-1.545927	-0.867834
O	-4.011487	0.060355	0.016386

C	-0.734421	-0.434423	1.873491
H	-1.094753	-1.413393	2.219005
H	0.041025	-0.590692	1.122062
O	-0.215786	0.217889	3.016154
Cs	2.287524	-0.969327	-0.772193
C	-4.856172	0.358449	1.103461
H	-4.537982	1.285500	1.599967
H	-4.798468	-0.452490	1.850302
C	-1.188607	-2.933523	-0.940989
H	-1.934241	-3.228106	-0.187763
H	-1.589088	-3.189543	-1.932180
H	-0.076148	0.630379	-2.499204
C	0.813932	1.139835	2.729444
H	0.553521	1.753069	1.858406
H	0.887492	1.795880	3.603201
C	-6.278386	0.504501	0.619072
C	-6.712179	-0.124753	-0.546657
C	-7.187172	1.251451	1.369489
C	-8.039090	-0.010045	-0.952932
H	-5.998588	-0.689168	-1.137056
C	-8.514831	1.360589	0.968366
H	-6.850755	1.756778	2.272065

C	-8.944587	0.728883	-0.196239
H	-8.366024	-0.497753	-1.866479
H	-9.210839	1.947340	1.560020
H	-9.978237	0.818045	-0.515781
C	0.114162	-3.645852	-0.690293
C	0.900815	-4.095834	-1.752360
C	0.604457	-3.758072	0.614120
C	2.161345	-4.646108	-1.517335
H	0.522959	-4.010343	-2.768326
C	1.860507	-4.309211	0.853999
H	-0.002862	-3.404944	1.443965
C	2.644731	-4.749507	-0.213532
H	2.760531	-5.001975	-2.350117
H	2.223555	-4.405048	1.872499
H	3.620987	-5.187019	-0.028671
C	2.153016	0.466713	2.491992
C	3.233667	1.221244	2.019851
C	2.338550	-0.895202	2.740933
C	4.461518	0.618404	1.755524
H	3.125133	2.290001	1.835780
C	3.574323	-1.497771	2.495406
H	1.507530	-1.471210	3.139057

C	4.635433	-0.747642	1.988715
H	5.275129	1.227817	1.372626
H	3.713688	-2.553605	2.710276
H	5.597407	-1.216940	1.803377
C	1.295461	2.601546	-3.191805
H	0.322899	3.055862	-3.025492
H	1.586506	2.426034	-4.222181
C	2.100452	2.284068	-2.176767
H	3.085535	1.862412	-2.374209
C	1.769782	2.510376	-0.755697
H	2.249353	1.947832	0.021526
H	1.020232	3.238081	-0.475019
Br	3.561045	4.057032	-0.373827

9-TS

M06-2X SCF energy: -4130.64632756 a.u.

M06-2X enthalpy: -4130.019844 a.u.

M06-2X free energy: -4130.136277 a.u.

M06-2X SCF energy in solution: -4134.24220735 a.u.

M06-2X enthalpy in solution: -4133.615724 a.u.

M06-2X free energy in solution: -4133.732157 a.u.

Imaginary frequency: -460.8448 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-0.918134	-1.956871	0.342283
C	0.394753	-2.182551	-0.417508
C	1.614488	-1.622139	0.305684
C	1.404444	-0.153751	0.651083
C	0.083286	0.015574	1.409891
H	0.501721	-3.255658	-0.605239
H	-0.876349	-2.485150	1.324856
H	1.785205	-2.161564	1.253833
H	1.360235	0.427610	-0.285680
H	0.200200	-0.474586	2.392447
O	-0.989107	-0.524653	0.691214
O	-1.986251	-2.243254	-0.392122
O	2.785307	-1.694459	-0.488298
O	2.409810	0.354881	1.496741
C	-0.249880	1.480805	1.647204
H	-1.079662	1.559583	2.364732
H	0.627543	2.005656	2.048168

O	-0.648548	2.039874	0.405906
Cs	-2.708974	0.388493	-1.465914
H	0.305663	-1.685078	-1.392541
C	-4.666832	-2.792724	-1.296527
H	-3.931623	-3.558981	-1.521715
H	-5.470934	-2.631826	-2.009009
C	-4.594756	-2.095527	-0.162093
H	-5.336355	-1.332803	0.067917
C	-3.555806	-2.318426	0.875934
H	-3.200916	-3.313783	1.089144
H	-3.117598	-1.488299	1.408649
Br	-5.135036	-2.468584	2.656969
C	-0.972366	3.413668	0.481876
H	-1.564557	3.620530	1.385569
H	-0.056066	4.020009	0.530644
C	3.371528	-2.970409	-0.558092
H	3.459607	-3.400528	0.452960
H	2.744398	-3.657083	-1.147454
C	3.646851	0.663776	0.890726
H	3.486071	0.956769	-0.158349
H	4.295923	-0.220987	0.869439
C	-1.780906	3.723535	-0.752167

C	-1.171304	3.662880	-2.009262
C	-3.158766	3.930180	-0.675314
C	-1.928605	3.800070	-3.169470
H	-0.098504	3.497288	-2.070658
C	-3.921164	4.072175	-1.835328
H	-3.639911	3.976992	0.298733
C	-3.307779	4.000470	-3.084180
H	-1.444647	3.758621	-4.140722
H	-4.991024	4.242013	-1.762042
H	-3.897485	4.115132	-3.988508
C	4.741177	-2.870286	-1.186075
C	5.211923	-1.674977	-1.726045
C	5.552910	-4.005986	-1.233894
C	6.480064	-1.616956	-2.301917
H	4.577681	-0.795807	-1.694192
C	6.816572	-3.948849	-1.809930
H	5.191322	-4.941918	-0.813122
C	7.285442	-2.750319	-2.345942
H	6.838868	-0.680281	-2.718359
H	7.438062	-4.838586	-1.837030
H	8.273213	-2.701861	-2.793515
C	4.323192	1.792144	1.632943

C	5.514770	2.313553	1.122596
C	3.800610	2.321135	2.810888
C	6.168589	3.353783	1.772486
H	5.931407	1.898045	0.206908
C	4.456466	3.364077	3.464154
H	2.884726	1.904932	3.216015
C	5.638002	3.885266	2.947341
H	7.092785	3.750900	1.363752
H	4.041823	3.767395	4.383231
H	6.146675	4.697584	3.456929

9b-TS

M06-2X SCF energy: -4130.65511132 a.u.

M06-2X enthalpy: -4130.027964 a.u.

M06-2X free energy: -4130.139089 a.u.

M06-2X SCF energy in solution: -4134.24077298 a.u.

M06-2X enthalpy in solution: -4133.613626 a.u.

M06-2X free energy in solution: -4133.724751 a.u.

Imaginary frequency: -455.5810 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	-2.399194	-0.349243	-0.285522
C	-1.964188	-1.293340	0.858045
C	-1.228639	-2.490521	0.261528
C	0.060537	-2.058482	-0.470093
C	-1.587959	-0.610589	-1.560986
H	-2.865607	-1.637235	1.391525
H	-2.038306	-1.485780	-2.057882
H	-2.233794	0.689956	0.048056
H	0.286371	-2.816704	-1.251860
H	-1.928534	-2.981195	-0.426265
O	1.088296	-1.819880	0.343296
O	-0.239130	-0.824274	-1.239240
O	-1.168565	-0.512608	1.740509
O	-3.752443	-0.534229	-0.638758
C	-1.677200	0.561350	-2.536708
H	-1.434560	0.225379	-3.552438
H	-2.703523	0.944278	-2.537026
O	-0.811100	1.623165	-2.163796
Cs	1.033973	1.214025	0.574283

H	-0.958993	-3.240900	1.007673
C	3.916903	-0.240757	-0.123250
H	4.186491	-0.482281	0.902883
H	4.261376	0.712391	-0.515720
C	3.267043	-1.122518	-0.887636
H	3.042840	-0.893692	-1.928652
C	2.811980	-2.444596	-0.421369
H	2.229409	-3.089291	-1.057852
H	3.083386	-2.787075	0.564870
Br	4.722700	-3.558781	-1.358065
C	0.407498	1.598566	-2.889304
H	0.889100	0.617977	-2.781097
H	0.197432	1.758401	-3.958736
C	-0.619071	-1.226543	2.840224
H	-0.151210	-2.152729	2.500911
H	-1.418982	-1.461955	3.559053
C	-4.655327	0.140954	0.207374
H	-4.437495	-0.095607	1.261642
H	-4.531171	1.229895	0.091994
C	1.319555	2.683434	-2.374278
C	2.702517	2.487839	-2.364669
C	0.795190	3.876081	-1.869335

C	3.552102	3.467965	-1.855088
H	3.116544	1.557157	-2.747173
C	1.643652	4.851967	-1.350584
H	-0.280702	4.021991	-1.873072
C	3.023265	4.649962	-1.340108
H	4.625342	3.302948	-1.854074
H	1.227747	5.775656	-0.959331
H	3.683618	5.411923	-0.938261
C	-6.071312	-0.259419	-0.122514
C	-6.346373	-1.453086	-0.787687
C	-7.127977	0.561639	0.273881
C	-7.664093	-1.819257	-1.052058
H	-5.522172	-2.083344	-1.103230
C	-8.443978	0.192796	0.016117
H	-6.918725	1.498861	0.785002
C	-8.715410	-1.000384	-0.649956
H	-7.868799	-2.748384	-1.575176
H	-9.257891	0.840180	0.327713
H	-9.741516	-1.286916	-0.858167
C	0.438037	-0.351352	3.459914
C	1.788197	-0.676818	3.311633
C	0.086700	0.847589	4.085559

C	2.775709	0.185063	3.787430
H	2.053636	-1.584001	2.775108
C	1.071599	1.715084	4.551710
H	-0.965036	1.100814	4.196842
C	2.419058	1.384314	4.402141
H	3.823308	-0.077071	3.672313
H	0.790837	2.642845	5.041344
H	3.187190	2.055908	4.773254

10-TS

M06-2X SCF energy: -3860.41115218 a.u.

M06-2X enthalpy: -3859.901245 a.u.

M06-2X free energy: -3860.001590 a.u.

M06-2X SCF energy in solution: -3863.88476731 a.u.

M06-2X enthalpy in solution: -3863.374860 a.u.

M06-2X free energy in solution: -3863.475205 a.u.

Imaginary frequency: -457.5178 cm-1

Cartesian coordinates

ATOM	X	Y	Z

C	0.938664	-1.694287	1.226056
C	-0.064578	-1.503604	2.378975
C	-1.483363	-1.855269	1.933766
C	-1.874813	-1.008952	0.724194
C	-0.841585	-1.194101	-0.390173
H	0.263978	-2.158625	3.196170
H	0.858888	-2.766906	0.916469
H	-1.534378	-2.914821	1.651605
H	-1.891864	0.055580	1.004731
H	-0.932456	-2.230978	-0.761182
O	0.454577	-0.925118	0.070711
O	2.159539	-1.283784	1.518217
O	-3.122856	-1.382179	0.175871
C	-1.083402	-0.241514	-1.549864
H	-0.393296	-0.484042	-2.371130
H	-2.118734	-0.328751	-1.906992
O	-0.820207	1.069842	-1.080919
Cs	1.640370	1.592585	0.963983
O	-0.008741	-0.138123	2.799524
H	-0.544262	-0.062909	3.601168
H	-2.189675	-1.707071	2.761566
C	4.359868	0.121912	-0.437639

H	5.040230	0.139410	0.410431
H	4.429940	0.939791	-1.150027
C	3.553297	-0.921739	-0.652738
H	2.907465	-0.948522	-1.527404
C	3.465475	-2.097420	0.233526
H	2.725440	-2.861859	0.066718
H	4.142941	-2.195495	1.066624
Br	4.891531	-3.418002	-1.160567
C	-0.906587	2.063955	-2.078981
H	-1.956956	2.233825	-2.361024
H	-0.360406	1.752668	-2.982020
C	-4.237340	-0.951037	0.913804
H	-4.142061	0.124162	1.142762
H	-4.297626	-1.480457	1.877755
C	-0.284532	3.306801	-1.495122
C	0.938802	3.789862	-1.960045
C	-0.880595	3.916728	-0.386632
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H	1.410792	3.316860	-2.817651
C	-0.260724	4.989217	0.247839
H	-1.830508	3.536285	-0.019591
C	0.965220	5.465133	-0.221614

H	2.508957	5.240792	-1.706101
H	-0.735282	5.461670	1.102601
H	1.445857	6.306420	0.267833
C	-5.504766	-1.192494	0.129376
C	-6.722505	-0.752345	0.652665
C	-5.487983	-1.847850	-1.099493
C	-7.907724	-0.961793	-0.042603
H	-6.741523	-0.239644	1.612429
C	-6.676711	-2.057981	-1.796717
H	-4.542195	-2.193750	-1.500905
C	-7.887462	-1.616912	-1.272937
H	-8.847758	-0.613070	0.373969
H	-6.653652	-2.571920	-2.752989
H	-8.811903	-1.782688	-1.817196

11-TS

M06-2X SCF energy: -3860.40999131 a.u.

M06-2X enthalpy: -3859.900347 a.u.

M06-2X free energy: -3860.000092 a.u.

M06-2X SCF energy in solution: -3863.88541842 a.u.

M06-2X enthalpy in solution: -3863.375774 a.u.

M06-2X free energy in solution: -3863.475519 a.u.

Imaginary frequency: -451.1589 cm-1

Cartesian coordinates

ATOM	X	Y	Z
C	1.544040	-0.303163	-0.681381
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C	-0.983861	-0.331812	-0.799637
C	-1.010317	0.811445	0.212200
C	0.328645	1.562958	0.219312
H	0.358164	-1.887806	-1.505107
H	1.507388	0.305309	-1.618696
H	-1.051750	0.106549	-1.806828
H	-1.189333	0.383215	1.213516
H	0.429655	2.058585	-0.761623
O	1.397316	0.663664	0.409995
O	2.663264	-0.996922	-0.528980
O	-2.115183	-1.162543	-0.547401
O	-1.997520	1.767533	-0.096370
C	0.382169	2.604601	1.321158
H	1.335282	3.138004	1.284482

H	-0.435832	3.319863	1.214092
Cs	2.595044	-1.376965	2.284260
H	0.290860	2.117258	2.298943
O	0.210718	-1.889414	0.564544
H	-0.709139	-2.200000	0.617599
C	5.461314	-0.198363	0.941655
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H	4.320015	1.499648	0.431363
C	4.205979	0.051731	-1.188960
H	3.505146	0.634368	-1.763334
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C	-3.334488	1.388712	0.136123
H	-3.398587	0.799585	1.065610
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C	-2.649073	-1.783269	-1.700838
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H	-2.928117	-1.004795	-2.429169
C	-3.862481	-2.594568	-1.322550
C	-4.613010	-2.276813	-0.190164

C	-4.269999	-3.652180	-2.136421
C	-5.758381	-3.006137	0.119227
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H	-3.683978	-3.911889	-3.014916
C	-6.165557	-4.054986	-0.700492
H	-6.334161	-2.753502	1.004368
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C	-6.414639	3.554226	0.571969
H	-5.990558	1.445919	0.540281
C	-4.526225	5.010083	0.242162
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C	-5.888933	4.841164	0.463156
H	-7.477704	3.411827	0.740802
H	-4.110363	6.008937	0.150580
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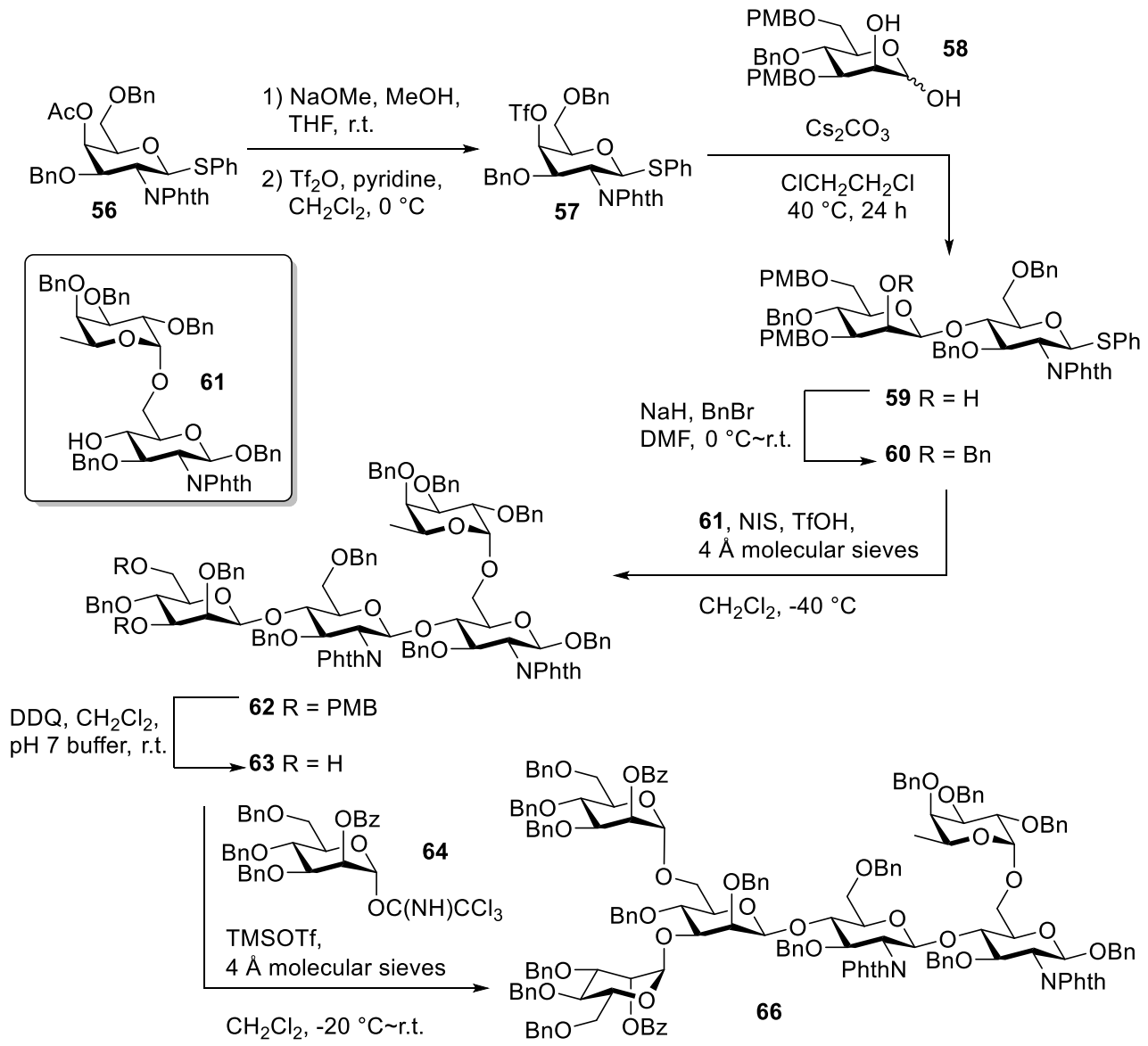
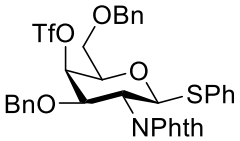
Synthesis of the hexasaccharide core of the fucosylated *N*-linked glycans.



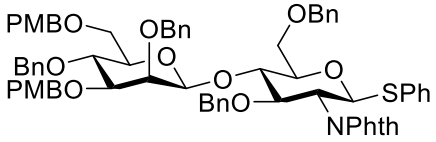
Phenyl 3,6-di-*O*-benzyl-4-*O*-trifluoromethylsulfonyl-2-deoxy-2-phthalimido-1-thio-*β*-D-galactopyranoside (57)



To a solution of known compound **56**[21] (2.67 g, 4.6 mmol) in MeOH (25 mL) and THF (25 mL) was added 0.5 M NaOMe solution in MeOH (6.4 mL, 3.22 mmol). The mixture was stirred at room temperature for 7 h. The

reaction mixture was neutralized by the addition of Amberlyst IR-120 (H^+), stirred for 30 min, filtered and concentrated. This residue was purified by silica gel column chromatography (Hexanes/EtOAc = 5/1 to 3/1) to give the corresponding alcohol (2.52 g, 94 %). To a solution of the obtained alcohol (0.67 g, 1.2 mmol) and pyridine (1.0 mL, 12 mmol) in CH_2Cl_2 (3.0 mL) cooled at 0 ℃ was added Tf_2O (0.35 mL, 2.0 mmol) dropwise. The resulting mixture was stirred at 0 ℃ for 2 h and then quenched with ice water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (50 mL × 3). The combined organic layer was washed sequentially with saturated $CuSO_4$ (50 mL × 3) and water (50 mL × 3), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel column chromatography with CH_2Cl_2 to afford the sugar derived triflate **57** (725 mg, 85%). **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.85 (m, 1H, H_{Ar}), 7.74 (m, 1H, H_{Ar}), 7.70 (m, 1H, H_{Ar}), 7.58 (dd, J = 7.3, 1.1 Hz, 1H, H_{Ar}), 7.42 – 7.32 (m, 7H, H_{Ar}), 7.25 – 7.18 (m, 3H, H_{Ar}), 6.98 – 6.93 (m, 3H, H_{Ar}), 6.90 – 6.83 (m, 2H, H_{Ar}), 5.54 (d, J = 2.9 Hz, 1H, *H*-4), 5.52 (d, J = 10.5 Hz, 1H, *H*-1), 4.70 (d, J = 12.6 Hz, 1H, -OCH_2Ar), 4.65 (d, J = 11.2 Hz, 1H, -OCH_2Ar), 4.52 – 4.45 (m, 2H, -OCH_2Ar, *H*-2), 4.38 (dd, J = 10.5, 2.9 Hz, 1H, *H*-3), 4.21 (d, J = 12.6 Hz, 1H, -OCH_2Ar), 4.01 (dd, J = 8.3, 5.6 Hz, 1H, *H*-5), 3.79 (dd, J = 9.2, 5.6 Hz, 1H, *H*-6a), 3.69 (dd, J = 9.2, 8.4 Hz, 1H, *H*-6b); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 168.05, 166.87, 137.36, 136.51, 134.26, 133.98, 132.81, 131.67, 131.62, 131.61, 129.01, 128.69, 128.44, 128.36, 128.34, 128.28, 128.24, 128.01, 123.80, 123.45, 118.68 (q, $^1J_{C\text{-}F}$ = 319.7 Hz), 84.21, 80.57, 75.14, 73.91, 72.97, 71.89, 67.20, 50.99.

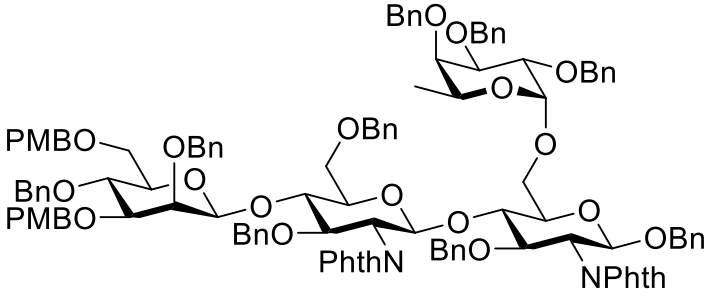
Phenyl *O*-2,4-di-*O*-benzyl-3,6-di-*O*-(*para*-methoxybenzyl)-*β*-D-mannopyranosyl-(1→4)-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-*β*-D-gluopyranoside (60)



To a mixture of mannopyranosyl donor **58**[22] (1.02 g, 2.0 mmol), sugar-derived triflate acceptor **57** (3.7 g, 5.0 mmol), and Cs_2CO_3 (2.0 g, 6.0 mmol) was added 1,2-dichloroethane (20 mL). The reaction mixture was stirred at 40 °C for 24 h. The crude reaction mixture was purified by silica gel column chromatography (Hexanes/EtOAc = 5/1 to 1/1) to give disaccharide **59** (1.73 g, 80%). To a solution of **59** (1.0 g, 0.93 mmol) in DMF (4.0 mL) cooled at 0 °C was added NaH (75 mg, 1.86 mmol, 60% in mineral oil) portion wise. The resulting mixture was stirred at 0 °C for 1 h before BnBr (0.17 mL, 1.4 mmol) was added. The reaction mixture was warmed up and stirred at ambient temperature for 3 h before being quenched with water. The resulting mixture was extracted with EtOAc three times, and combined organic extracts were washed with water and brine, dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography (Hexanes/EtOAc = 5/1 to 3/1) to give the title compound **60** (1.01 g, 94%). The $^1J_{C\text{-}H}$ of mannosidic anomeric carbon for **60** was determined to be 159.0 Hz. $[\boldsymbol{\alpha}]_{\mathbf{D}}^{\mathbf{23}}$ = +5.9 (*c* 1.0, $CHCl_3$); **FT-IR (thin film)**: 3064, 3032, 2938, 2863, 1777, 1714, 1678, 1512, 1455, 1388, 1250, 1174, 1102, 1070, 917, 807, 701 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.3 Hz, 1H, H_{Ar}), 7.70 (m, 1H, H_{Ar}), 7.65 (m, 1H, H_{Ar}), 7.58 (d, *J* = 7.3 Hz, 1H, H_{Ar}), 7.50 – 7.44 (m, 2H, H_{Ar}), 7.42 – 7.38 (m, 2H, H_{Ar}), 7.37 – 7.27 (m, 11H, H_{Ar}), 7.24 – 7.13 (m, 9H, H_{Ar}), 6.89 – 6.81 (m, 4H, H_{Ar}), 6.78 – 6.69 (m, 5H, H_{Ar}), 5.52 (d, *J* = 9.9

Hz, 1H, *H*-1), 4.96 (d, *J* = 13.0 Hz, 1H, -OCH_2Ar), 4.91 (s, 2H, -OCH_2Ar), 4.86 (d, *J* = 10.9 Hz, 1H, -OCH_2Ar), 4.60 (d, *J* = 12.0 Hz, 1H, -OCH_2Ar), 4.56 (s, 1H, H-1′), 4.55 – 4.49 (m, 2H, -OCH_2Ar), 4.49 – 4.41 (m, 4H, -OCH_2Ar), 4.38 (d, *J* = 11.6 Hz, 1H, -OCH_2Ar), 4.32 – 4.23 (m, 2H, *H*-3, *H*-2), 4.02 (dd, *J* = 9.8, 8.0 Hz, 1H, *H*-4), 3.90 (t, *J* = 9.6 Hz, 1H, *H*-4′), 3.81 – 3.78 (m, 4H, *H*-2′, -OCH_3), 3.77 – 3.70 (m, 5H, -OCH_3, *H*-6a, *H*-6′a), 3.66 – 3.59 (m, 3H, *H*-6b, *H*-6′b, *H*-5), 3.42 – 3.34 (m, 2H, *H*-3′, *H*-5′); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 168.08, 167.31, 159.25, 158.98, 139.03, 138.91, 138.63, 138.06, 133.86, 133.69, 132.82, 132.06, 131.80, 131.69, 130.74, 130.48, 129.33, 129.28, 128.87, 128.58, 128.38, 128.25, 128.06, 128.00, 127.94, 127.85, 127.78, 127.72, 127.66, 127.45, 126.82, 123.44, 123.33, 113.86, 113.73, 101.79, 83.37, 82.50, 79.26, 78.57, 76.04, 75.21, 75.11, 74.99, 74.81, 74.18, 73.59, 73.07, 71.61, 69.22, 68.91, 55.36, 55.31, 54.86; **LRMS (ESI)** calculated for $C_{70}H_{69}NNaO_{13}S$ $[M+Na]^+$ 1187.44, found 1187.30.

Benzyl *O*-2,4-di-*O*-benzyl-3,6-di-*O*-(*para*-methoxybenzyl)-*β*-D-mannopyranosyl-(1→4)-*O*-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-*β*-D-gluopyranosyl-(1→4)-*O*-[2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl-(1→6)]-3-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-gluopyranoside (62)

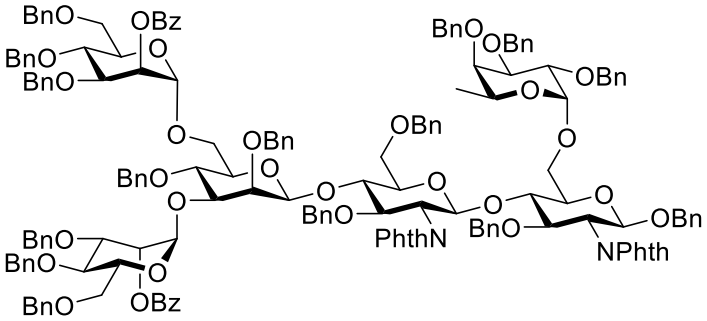


To a mixture of donor **60** (87 mg, 0.075 mmol), acceptor **61**[23] (45 mg, 0.05 mmol), activated 4 Å molecular sieves (300 mg), and NIS (84 mg) was added

CH_2Cl_2 (2.5 mL). The solution was cooled to -40 °C and TfOH (2.0 μL) was added. The resulting mixture was stirred at this temperature overnight and then filtered through celite. The filtrate was quenched and washed with saturated $Na_2S_2O_3$ aqueous solution. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude reaction mixture was purified by preparative TLC (EtOAc/ CH_2Cl_2/Toluene = 1/5/5) to furnish the title tetra-saccharide **62** (57 mg, 58%). $[\alpha]_D^{23}$ = -3.3 (*c* 1.0, $CHCl_3$); **FT-IR (thin film)**: 3065, 3033, 2934, 2867, 1777, 1716, 1614, 1514, 1454, 1388, 1249, 1091, 1038, 749, 724, 700 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 7.3 Hz, 1H, H_{Ar}), 7.82 (d, *J* = 7.2 Hz, 1H, H_{Ar}), 7.76 – 7.56 (m, 7H, H_{Ar}), 7.50 (d, *J* = 7.3 Hz, 1H, H_{Ar}), 7.46 – 7.11 (m, 32H, H_{Ar}), 7.07 (m, 1H, H_{Ar}), 7.04 – 6.91 (m, 6H, H_{Ar}), 6.87 – 6.69 (m, 12H, H_{Ar}), 5.59 (d, *J* = 8.4 Hz, 1H, H-1), 5.01 – 4.91 (m, 5H), 4.91 – 4.81 (m, 4H), 4.80 – 4.72 (m, 2H), 4.66 – 4.47 (m, 9H), 4.45 – 4.26 (m, 8H), 4.21 – 4.16 (m, 2H), 4.12 (dd, *J* = 10.7, 8.5 Hz, 1H), 4.07 – 4.01 (m, 2H), 3.99 (dd, *J* = 10.2, 2.8 Hz, 1H), 3.90 – 3.85 (m, 2H), 3.83 – 3.77 (m, 4H), 3.77 – 3.72 (m, 3H), 3.68 (s, 3H), 3.65 – 3.57 (m, 3H), 3.41 (dd, *J* = 10.8, 3.0 Hz, 1H), 3.38 (dd, *J* = 9.4, 3.0 Hz, 1H), 3.35 (ddd, *J* = 9.8, 5.1, 1.7 Hz, 1H), 3.28 (ddd, *J* = 9.9, 3.0, 1.6 Hz, 1H), 1.01 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 168.27, 167.89, 167.78, 167.67, 159.19, 158.91, 139.21, 139.17, 139.05, 138.96, 138.86, 138.73, 138.07, 137.16, 133.91, 133.73, 133.67, 133.58, 132.01, 131.79, 131.66, 130.87, 130.59, 129.28, 129.19, 128.62, 128.60, 128.51, 128.42, 128.34, 128.23, 128.19, 128.10, 128.07, 128.05, 127.91, 127.89, 127.74, 127.72, 127.62, 127.60, 127.57, 127.55, 127.47, 127.44, 127.37, 127.08, 126.95, 126.72, 123.55, 123.31, 123.20, 113.81, 113.68, 101.45, 96.90, 96.86, 96.70, 82.46, 79.57, 79.24, 77.71, 77.33, 76.09,

76.05, 75.82, 75.30, 75.09, 75.06, 74.84, 74.82, 74.69, 74.63, 74.43, 74.36, 73.79, 73.39, 73.20, 73.09, 72.52, 71.30, 69.96, 69.27, 68.51, 66.07, 63.94, 56.68, 55.95, 55.35, 55.25, 16.51; **LRMS (ESI)** calculated for $C_{119}H_{118}N_2Na_2O_{24}$ $[M+2Na]^{2+}$ 1002.89, found 1002.80.

Benzyl *O*-2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl-(1→3)-*O*-[2-*O*-benzoyl-3,4,6-tri-*O*-benzyl-*α*-D-mannopyranosyl-(1→6)]-*O*-2,4-di-*O*-benzyl-*β*-D-mannopyranosyl-(1→4)-*O*-3,6-di-*O*-benzyl-2-deoxy-2-phthalimido-1-thio-*β*-D-gluopyranosyl-(1→4)-*O*-[2,3,4-tri-*O*-benzyl-*α*-L-fucopyranosyl-(1→6)]-3-*O*-benzyl-2-deoxy-2-phthalimido-*β*-D-gluopyranoside (66)



To a solution of tetra-saccharide **62** (57 mg, 0.029 mmol) in CH_2Cl_2 (3.0 mL) was added a solution of pH 7 (1.0 mL) buffer and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (18 mg, 0.079 mmol). The resulting mixture was stirred at room temperature for 3 h before additional amount of DDQ (13 mg, 0.057 mmol) was added. The mixture was stirred for another 2 hours and another portion of DDQ (13 mg, 0.057 mmol) was added. After 2 hours, the mixture was quenched with saturated $NaHCO_3$ solution and extracted with ethyl acetate (10 mL × 3). The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude reaction mixture was purified by preparative TLC ($EtOAc/CH_2Cl_2$ = 1/10) to furnish the corresponding diol **63** (37 mg, 74%). The spectroscopic data was consistent

with the data reported in the literature.[23] To a mixture of diol acceptor **63** (74 mg, 0.043 mmol), donor **64**[24] (95 mg, 0.13 mmol), activated 4 Å molecular sieves (100 mg) was added CH_2Cl_2 (1.0 mL). The solution was cooled to -20 ℃ and TMSOTf (1.0 μL) was added. The resulting mixture was slowly warmed up to room temperature over 2 hours. The reaction was quenched with Et_3N (200 μL) and filtered through celite. The filtrate was washed with saturated $NaHCO_3$ aqueous solution and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by preparative TLC (EtOAc/Toluene = 1/10) to afford hexasaccharide **66** (115 mg, 95%). $[\alpha]_D^{23}$ = -7.0 (*c* 1.0, $CHCl_3$); **FT-IR (thin film)**: 3091, 3061, 3030, 2933, 2872, 1777, 1717, 1496, 1455, 1390, 1266, 1099, 1077, 737, 696 cm^{-1}; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.07 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.83 – 7.78 (m, 2H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.67 – 7.63 (m, 2H), 7.61 – 7.55 (m, 2H), 7.49 – 7.43 (m, 2H), 7.43 (m, 1H), 7.40 – 7.34 (m, 6H), 7.33 – 7.08 (m, 60H), 7.06 – 7.00 (m, 2H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.95 – 6.92 (m, 2H), 6.90 – 6.87 (m, 2H), 6.76 – 6.68 (m, 4H), 6.63 – 6.55 (m, 1H), 6.50 (t, *J* = 7.5 Hz, 2H), 5.72 (t, *J* = 2.5 Hz, 1H), 5.54 (t, *J* = 2.3 Hz, 1H), 5.46 (d, *J* = 8.3 Hz, 1H), 5.20 (d, *J* = 2.0 Hz, 1H), 4.95 – 4.78 (m, 12H), 4.74 – 4.56 (m, 8H), 4.55 – 4.37 (m, 11H), 4.34 (d, *J* = 11.3 Hz, 1H), 4.29 (d, *J* = 12.3 Hz, 1H), 4.27 – 4.18 (m, 4H), 4.17 – 4.10 (m, 3H), 4.09 – 4.04 (m, 2H), 4.00 – 3.91 (m, 7H), 3.90 – 3.83 (m, 2H), 3.80 (m, 1H), 3.76 – 3.69 (m, 5H), 3.64 (dd, *J* = 10.8, 1.5 Hz, 1H), 3.61 – 3.53 (m, 5H), 3.29 (dd, *J* = 10.8, 3.4 Hz, 1H), 3.24 – 3.19 (m, 2H), 0.95 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR (150 MHz, $CDCl_3$)** δ 168.05, 167.87, 167.64, 165.56, 165.07, 139.01, 138.91, 138.89, 138.78, 138.76, 138.70, 138.41, 138.20, 138.04, 138.01, 137.94, 137.18, 133.75, 133.55, 133.24, 132.76, 131.95, 131.80,

131.63, 130.10, 130.00, 129.97, 129.95, 128.74, 128.58, 128.57, 128.54, 128.52, 128.49, 128.46, 128.37, 128.33, 128.30, 128.24, 128.21, 128.18, 128.02, 128.01, 127.98, 127.89, 127.87, 127.85, 127.77, 127.67, 127.63, 127.61, 127.59, 127.57, 127.53, 127.46, 127.43, 127.38, 127.15, 126.91, 126.84, 126.78, 123.52, 123.25, 102.06, 99.60, 98.34, 96.91, 96.69, 82.21, 79.77, 79.46, 78.35, 78.23, 77.80, 76.51, 76.31, 75.54, 75.24, 75.20, 75.17, 75.06, 74.81, 74.78, 74.58, 74.54, 74.47, 74.43, 74.16, 74.13, 73.85, 73.55, 73.41, 73.36, 72.66, 72.48, 72.10, 71.60, 71.03, 69.94, 69.08, 69.04, 69.00, 68.48, 67.99, 66.55, 66.04, 63.93, 56.64, 55.92, 16.51. **LRMS (ESI)** calculated for $C_{171}H_{166}N_2Na_2O_{34}$ $[M+2Na]^{2+}$ 1419.56, found 1419.80.

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NMR spectra of the products

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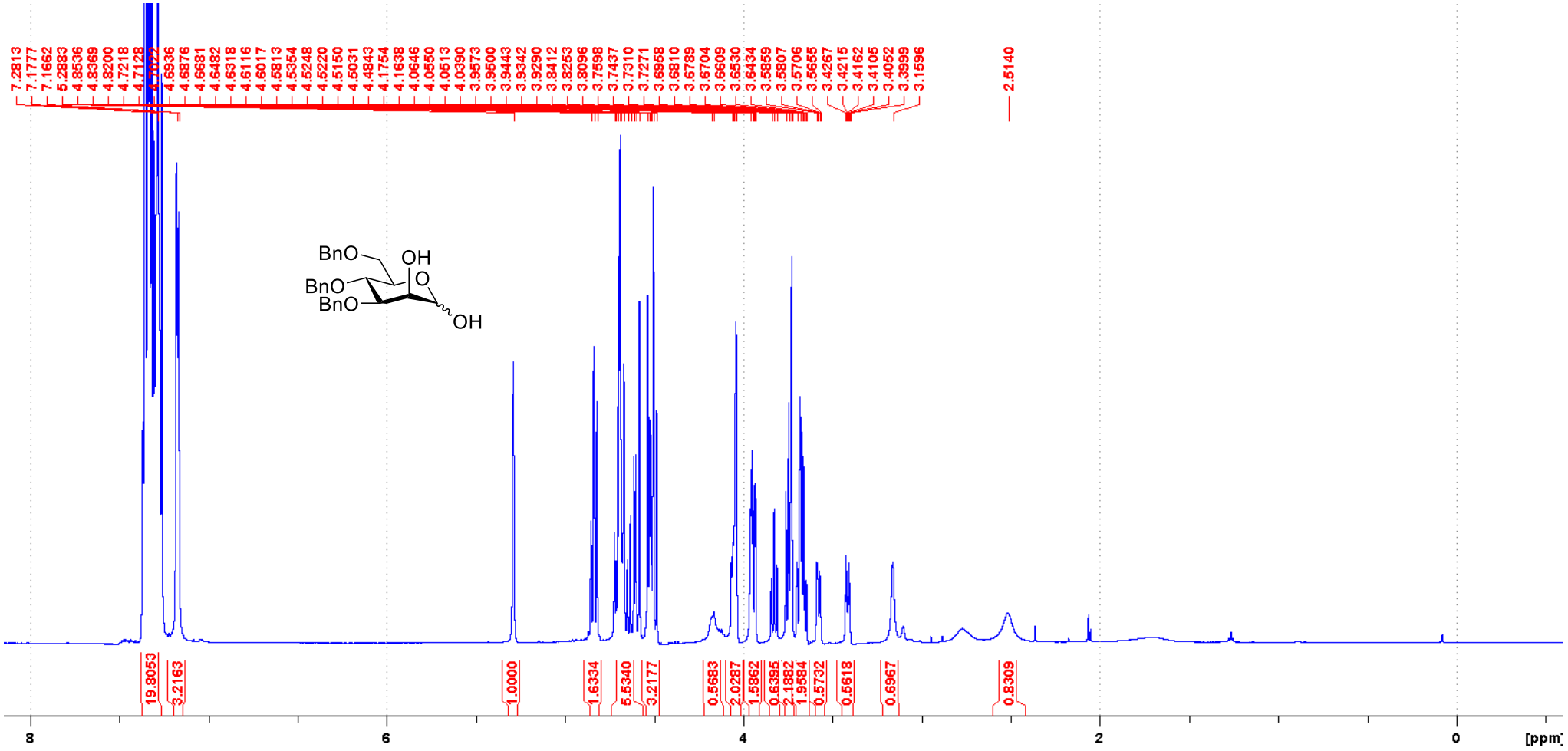

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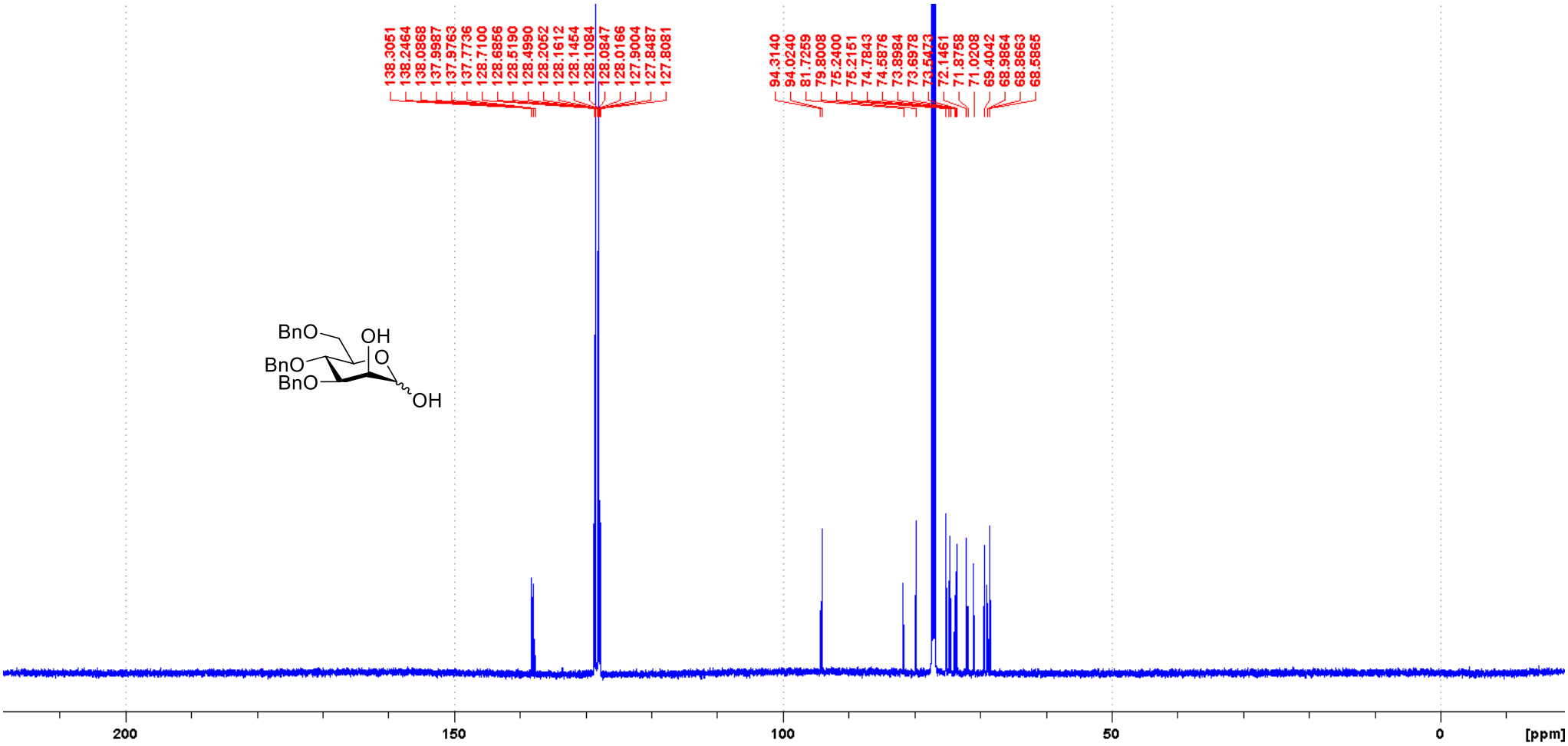

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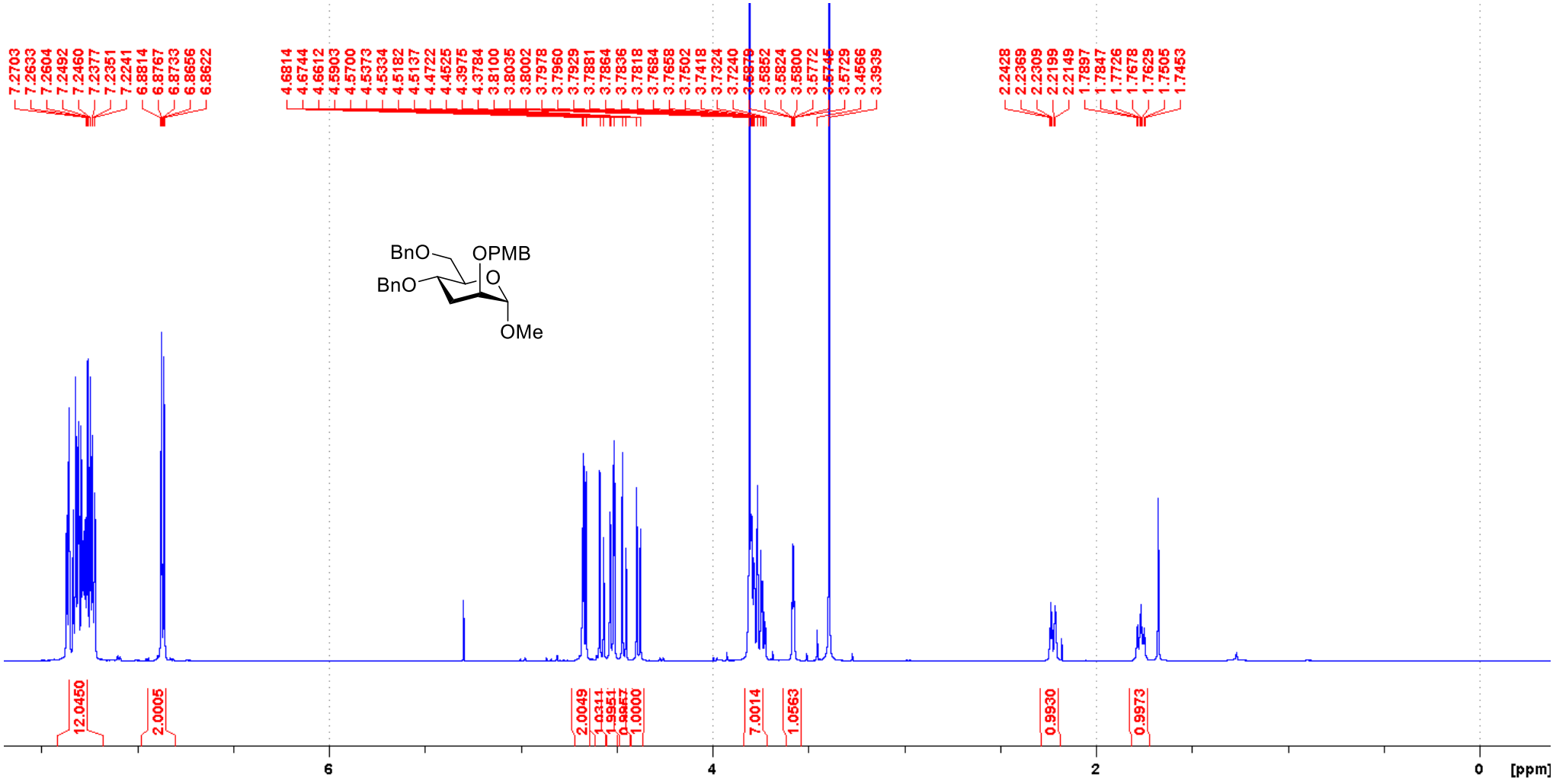

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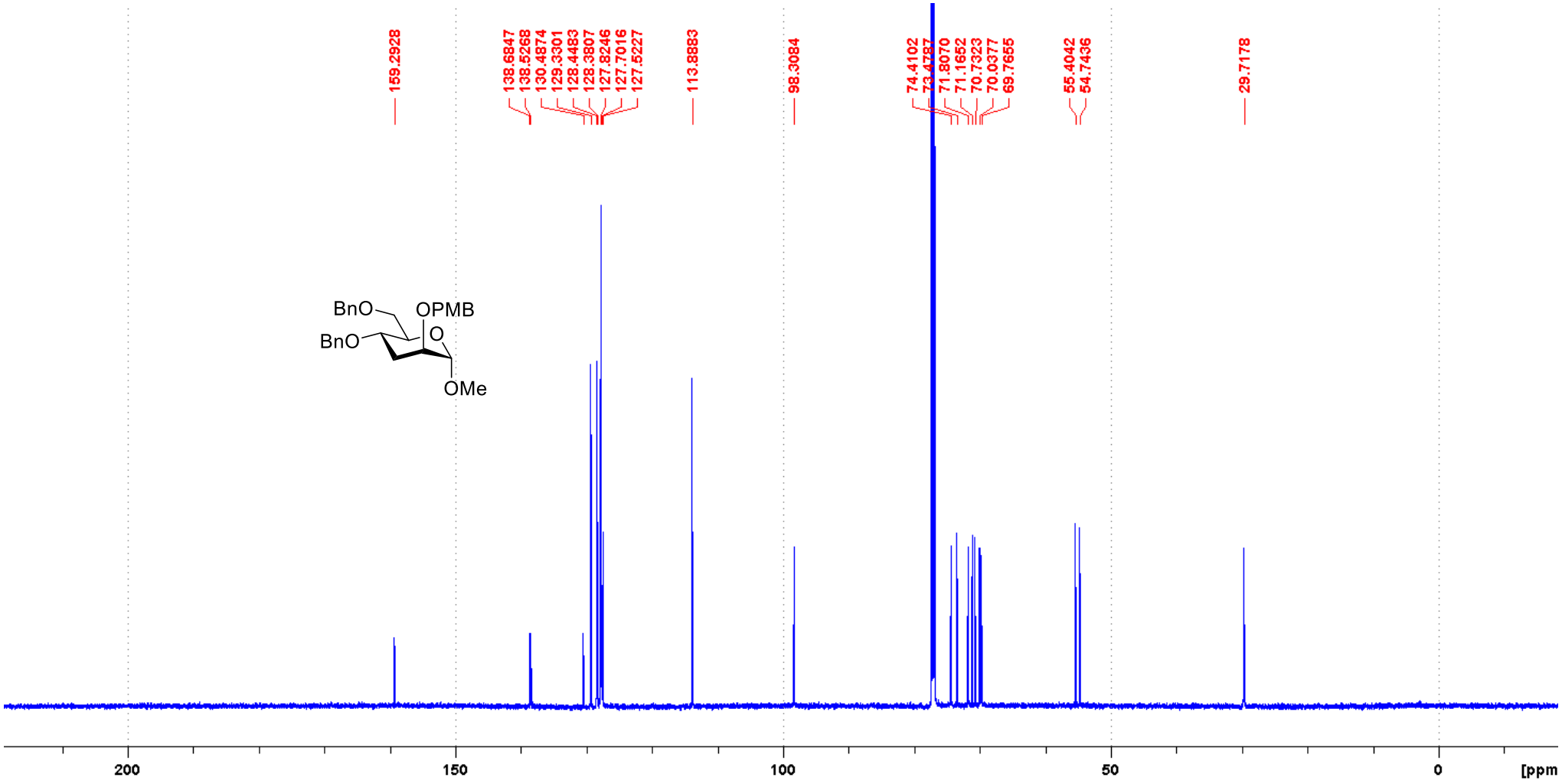

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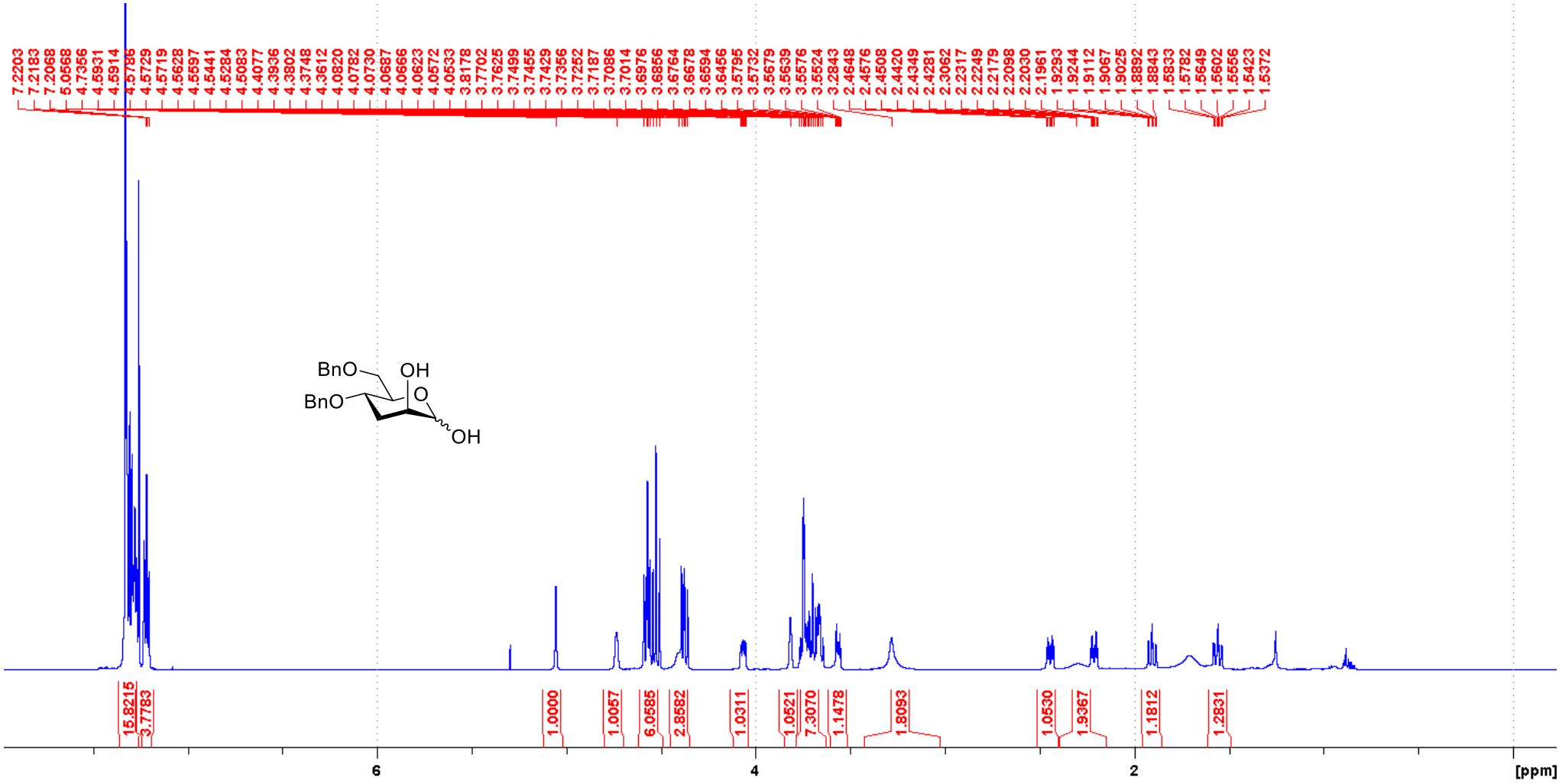

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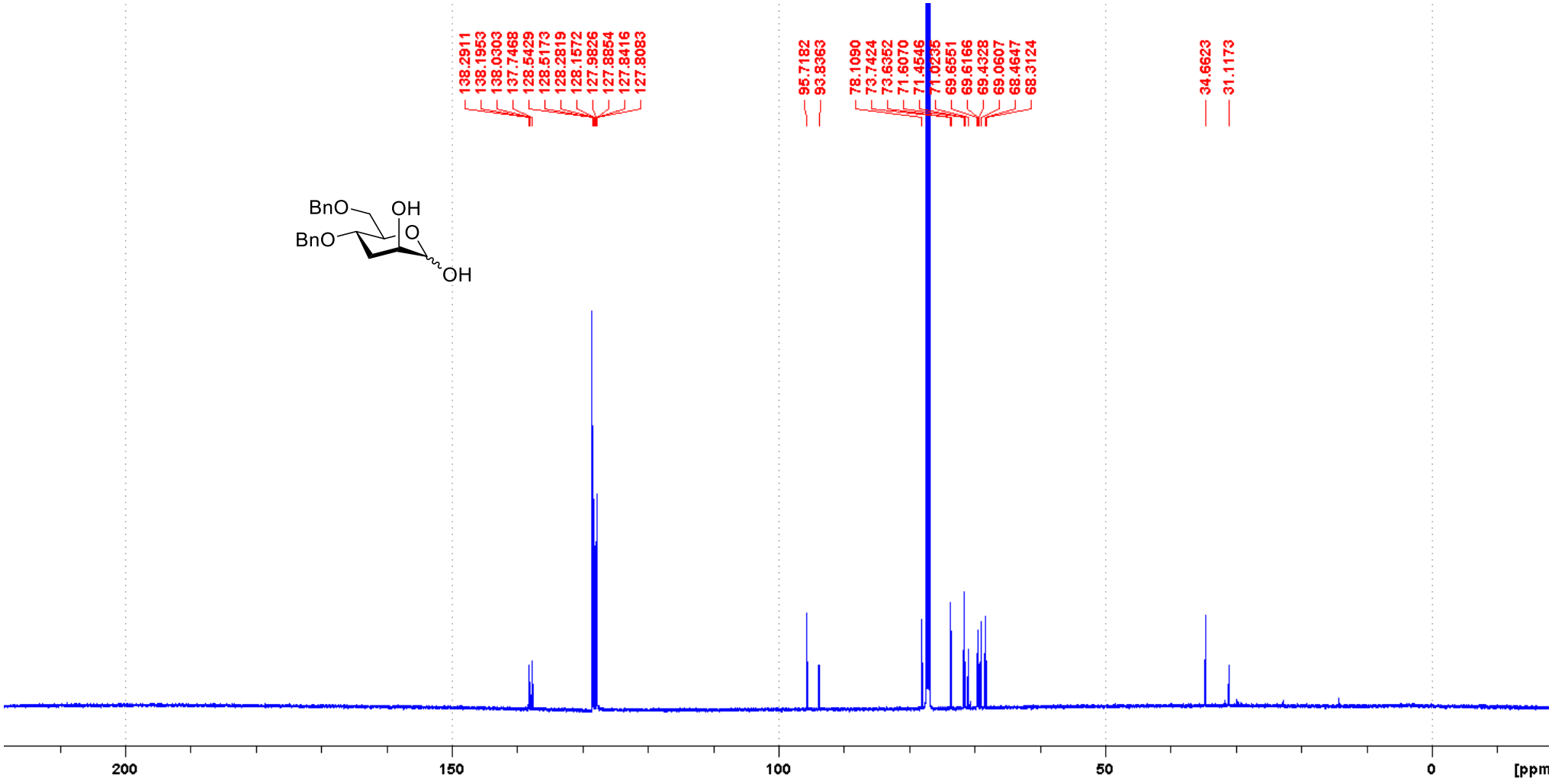

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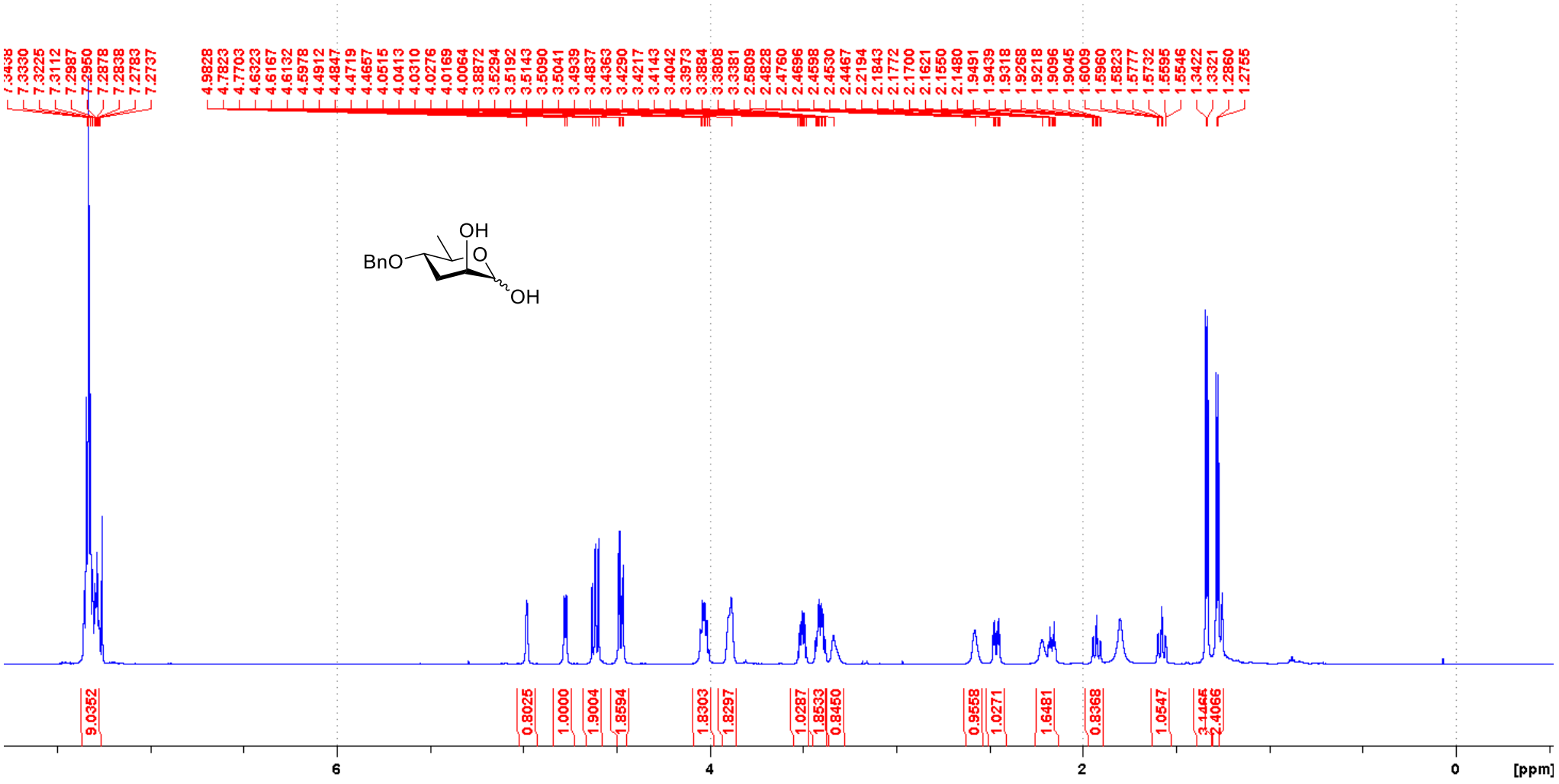

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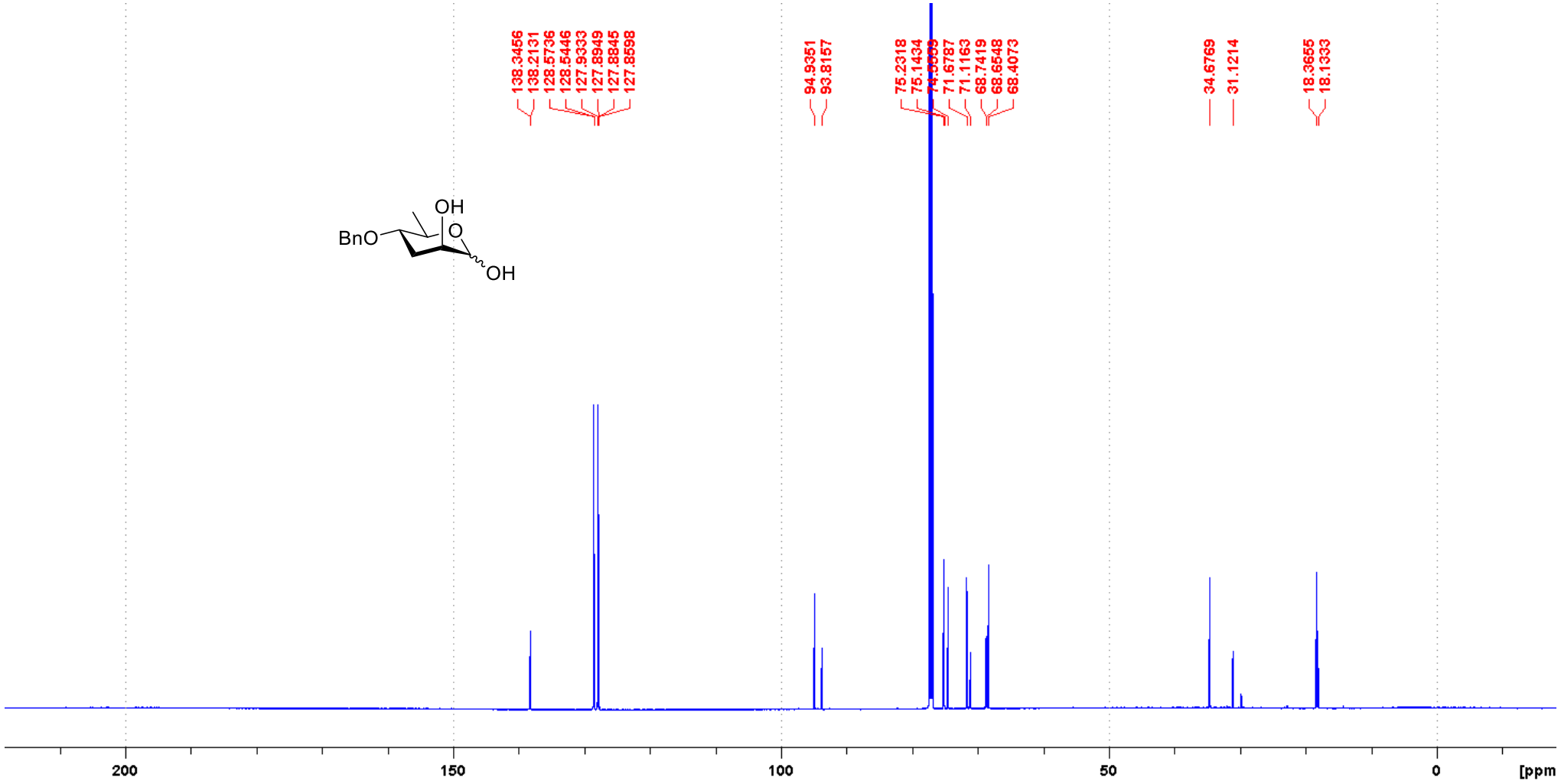

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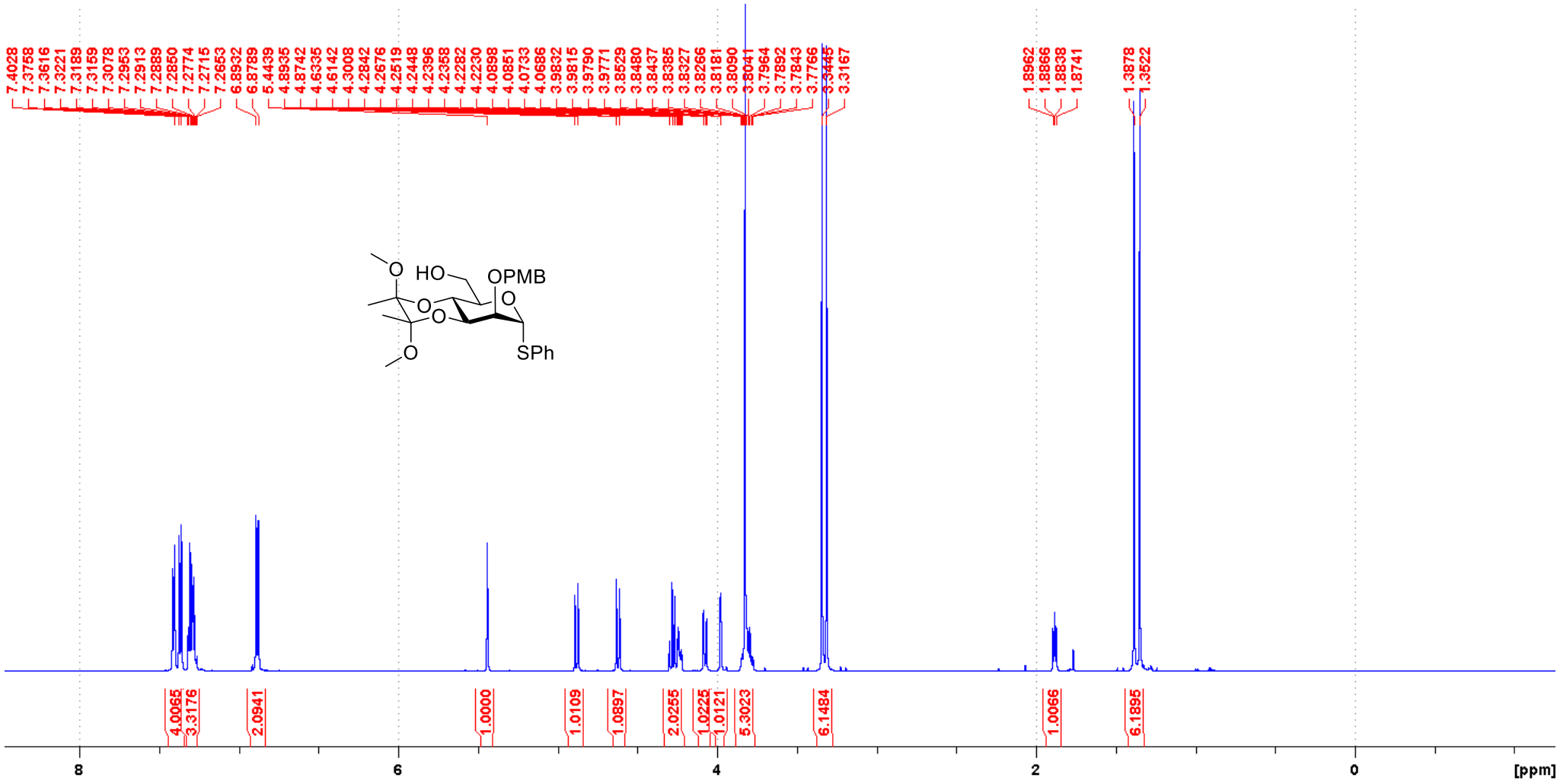

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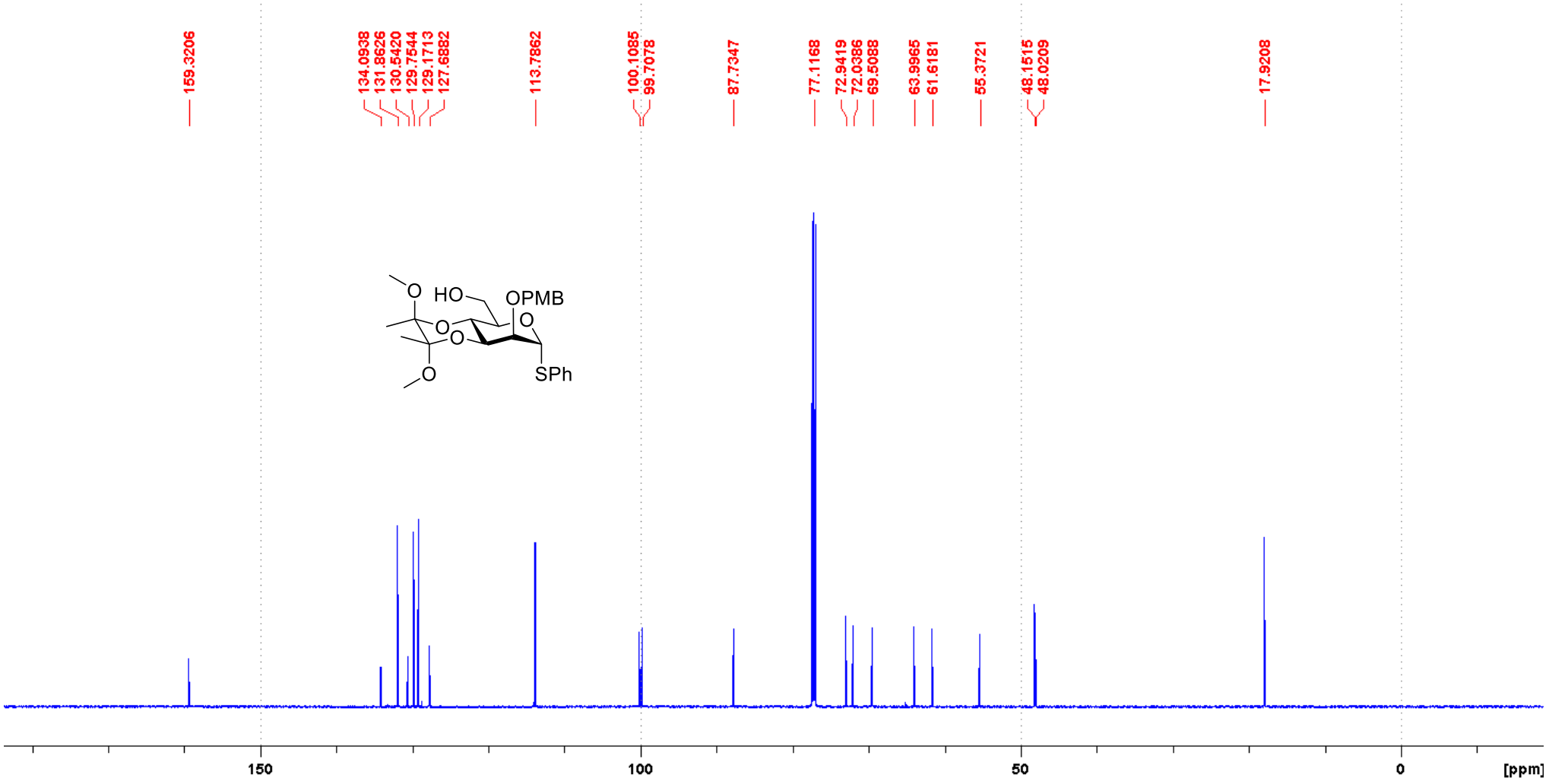

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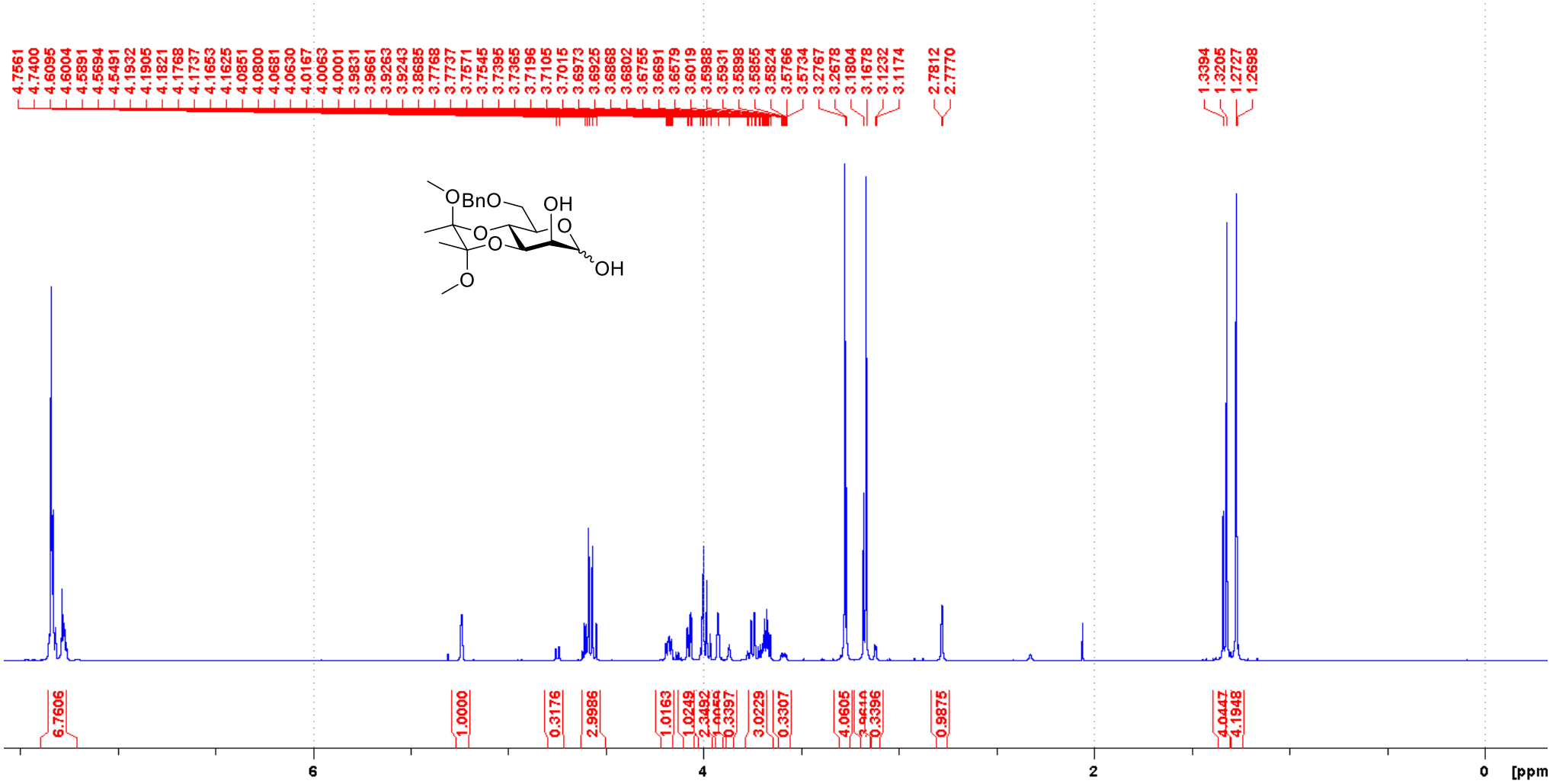

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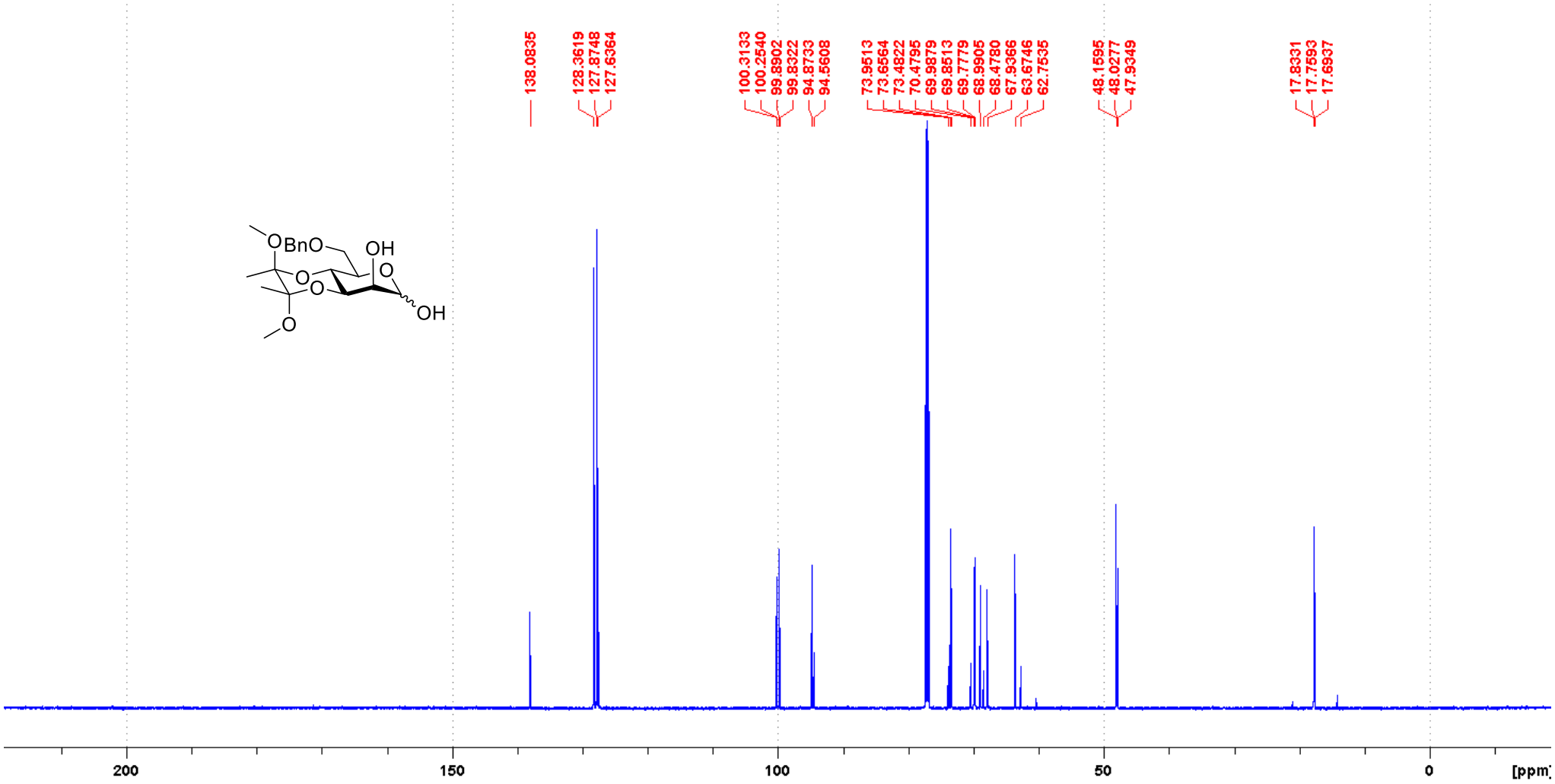

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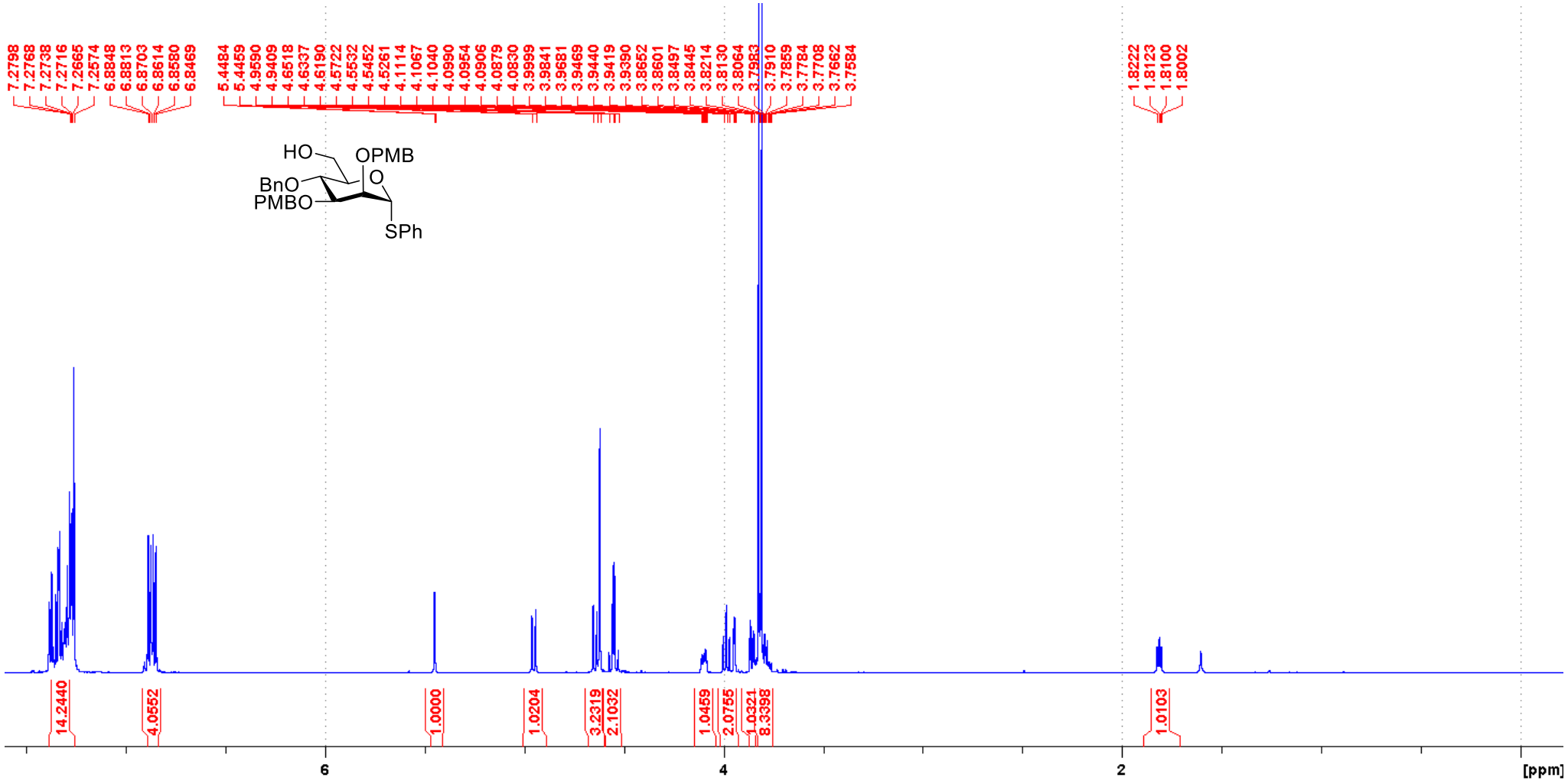

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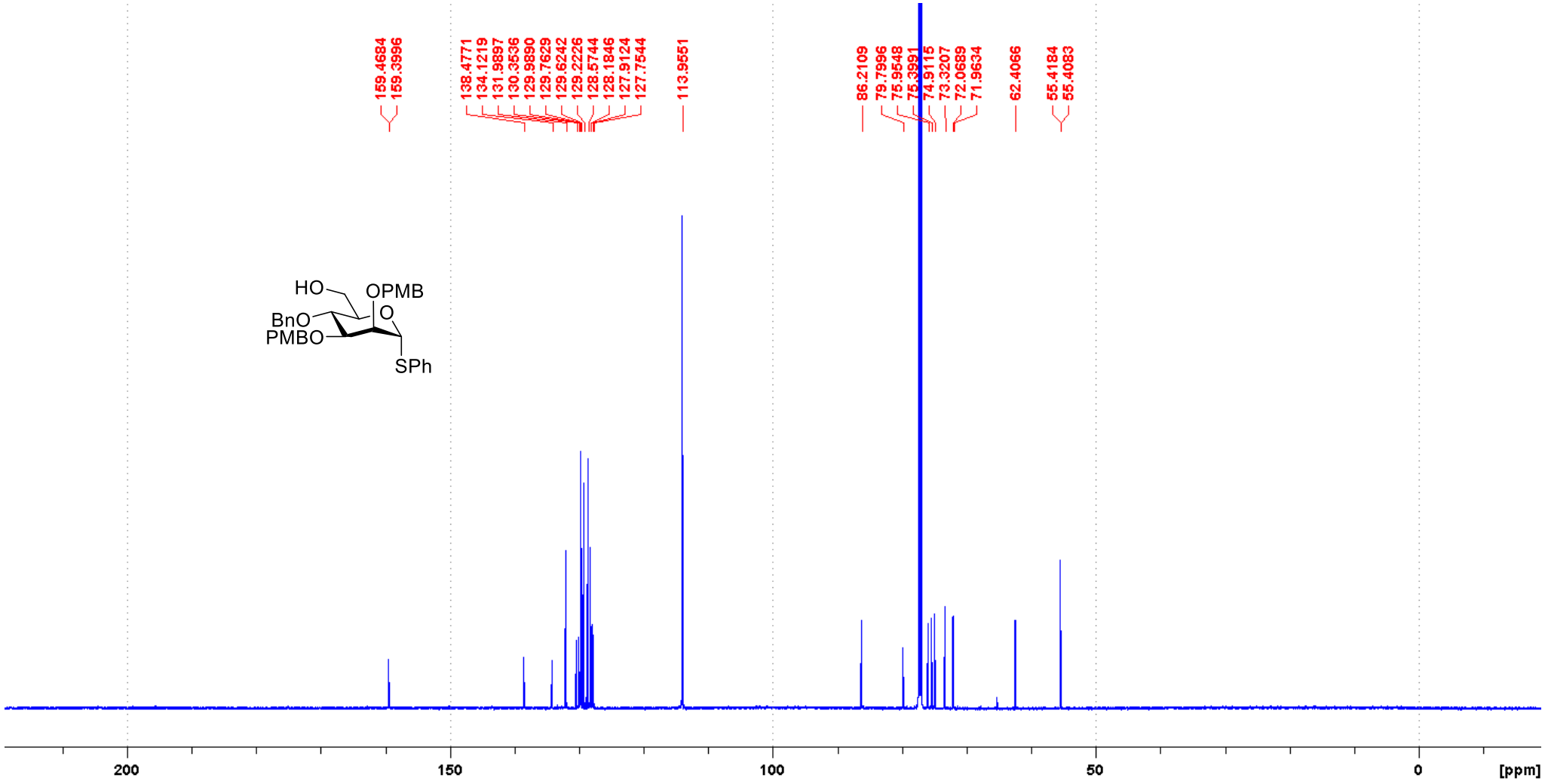

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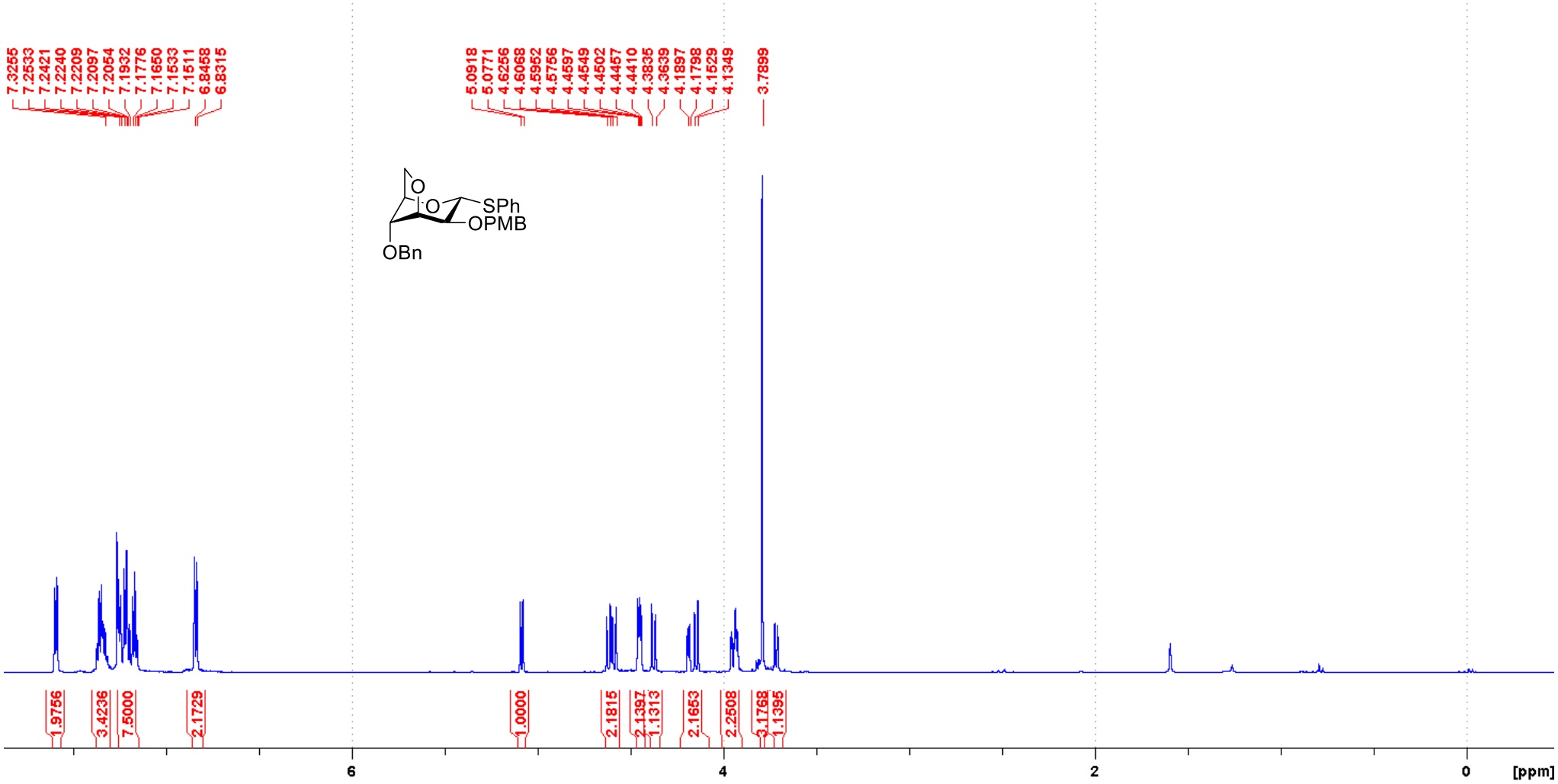

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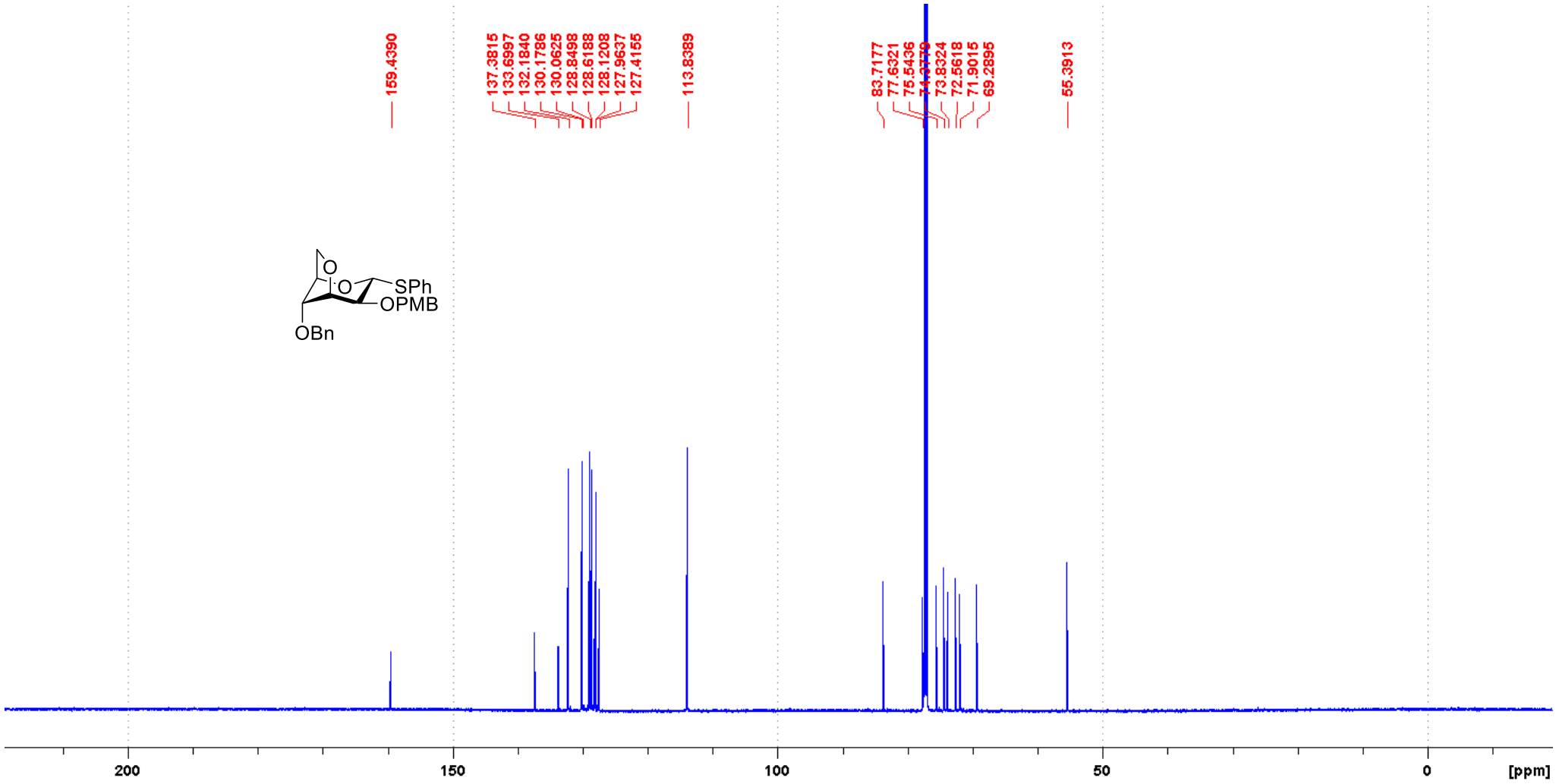

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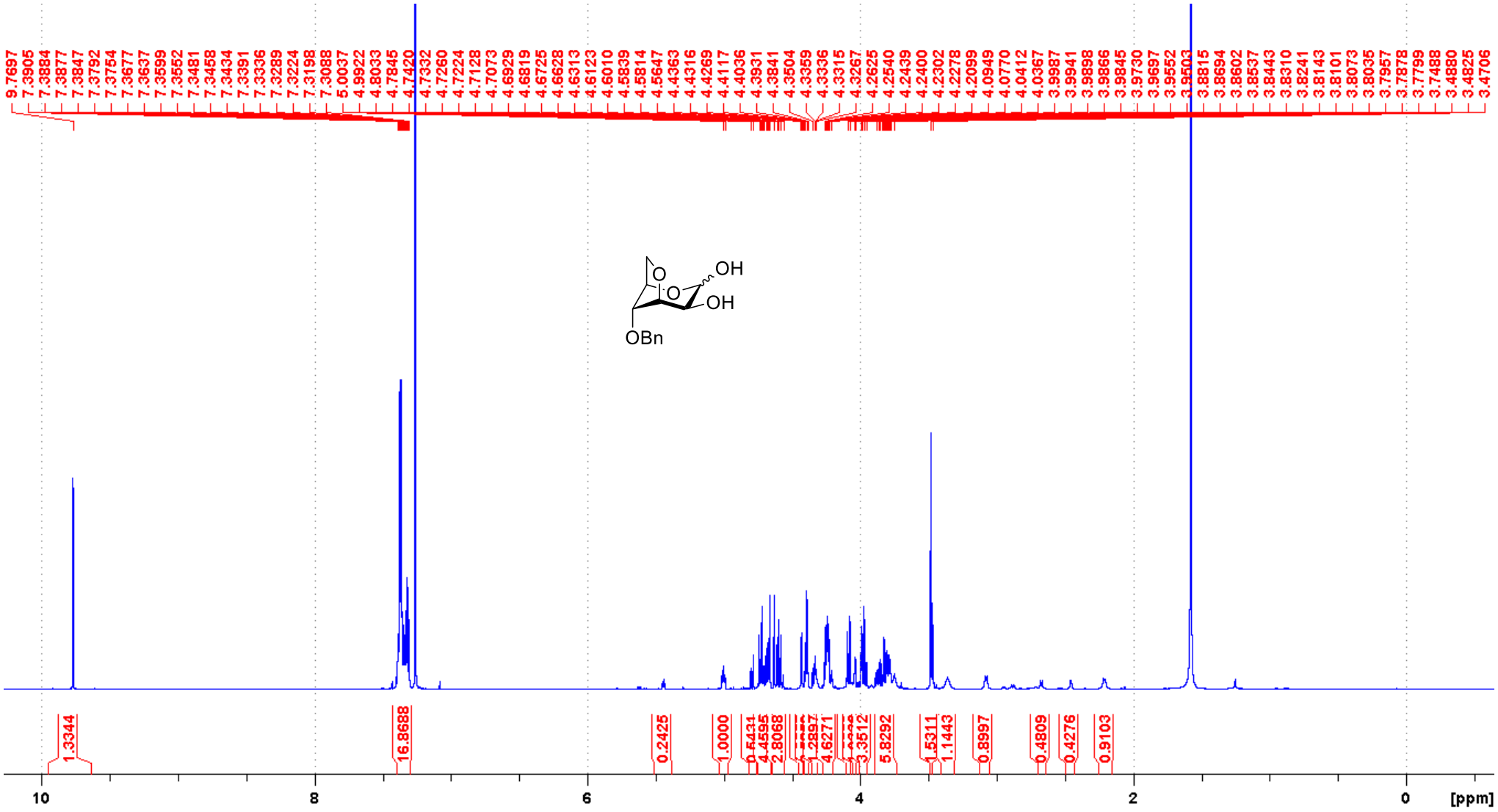

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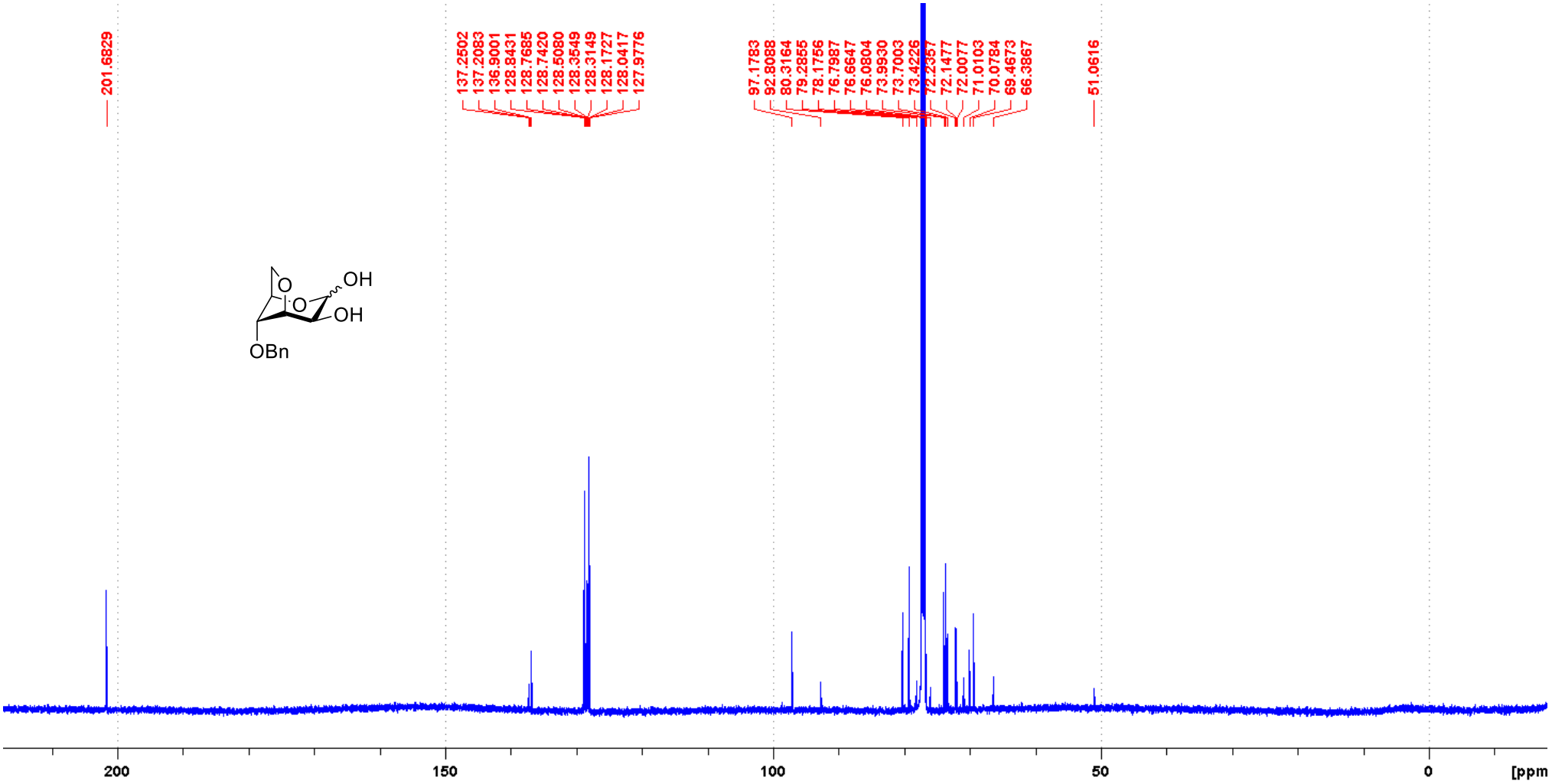

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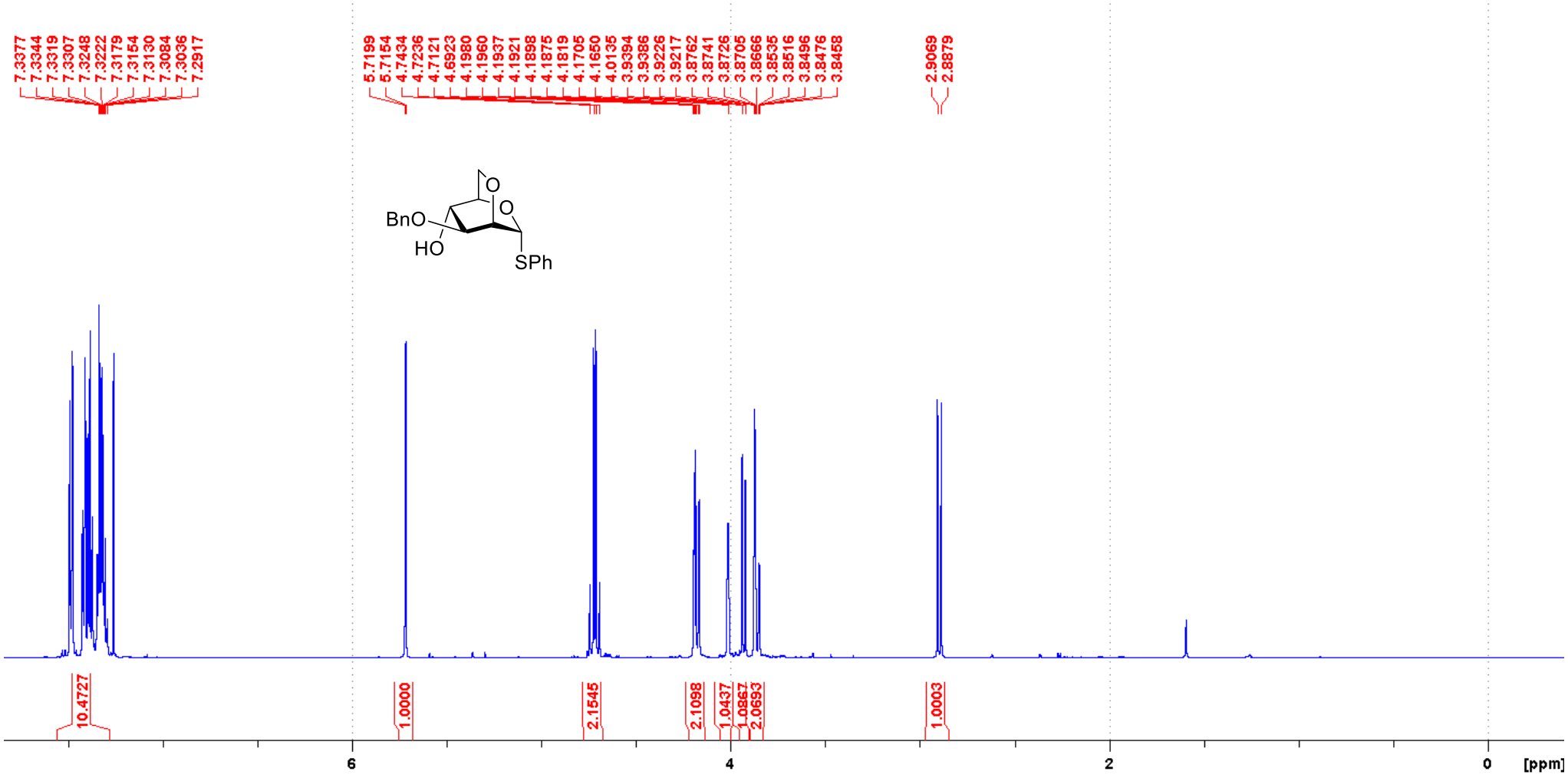

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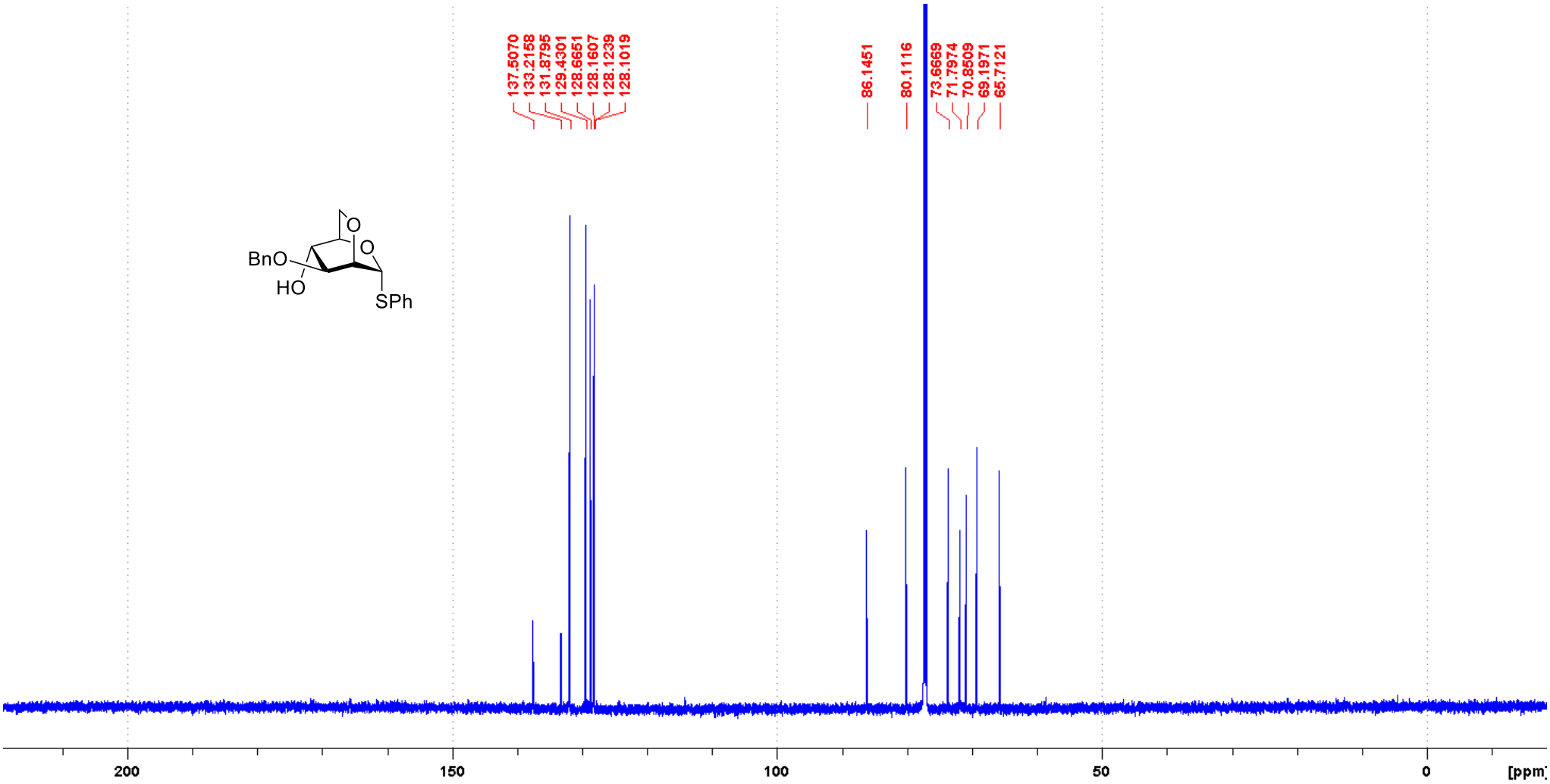

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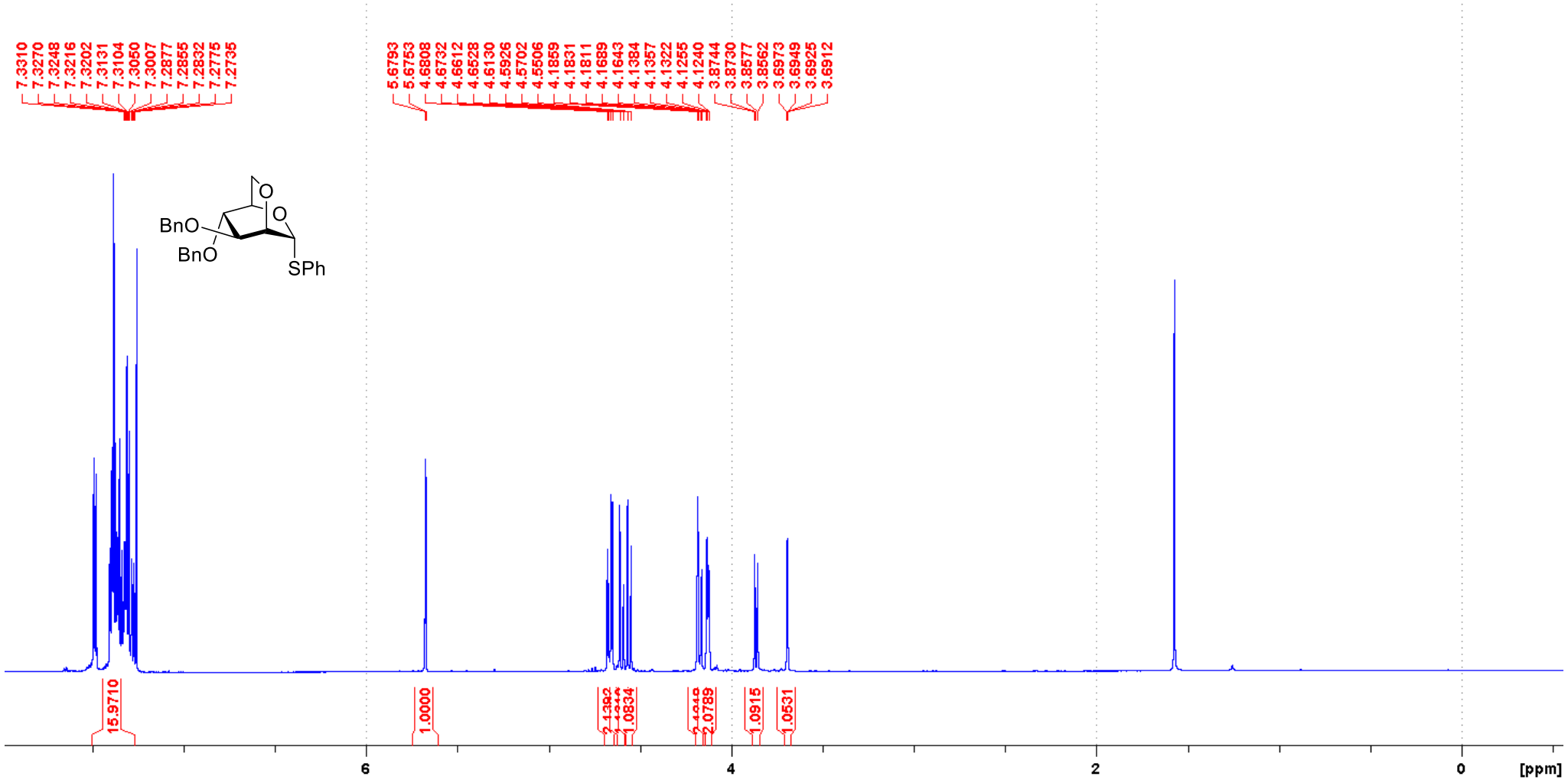

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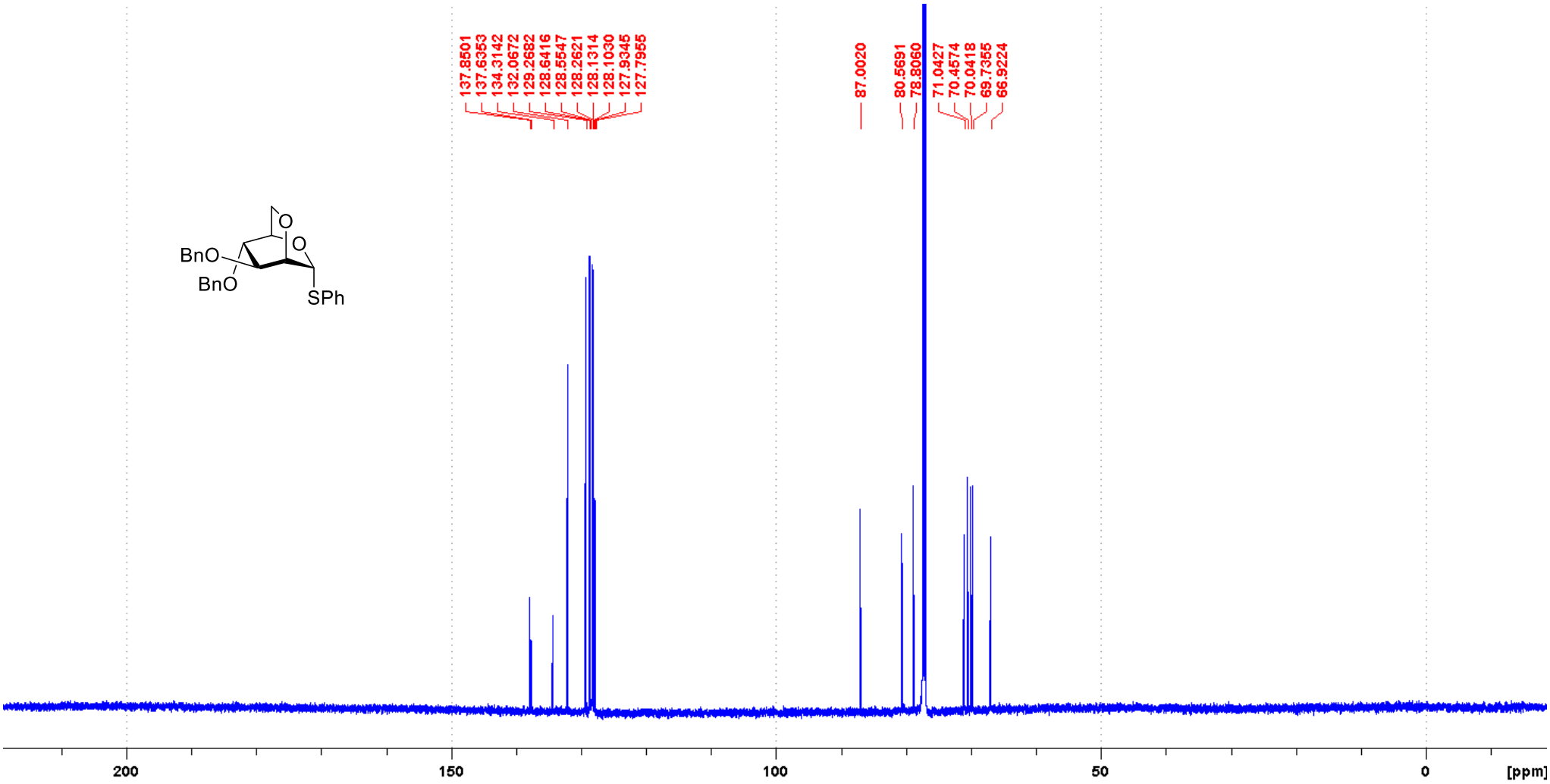

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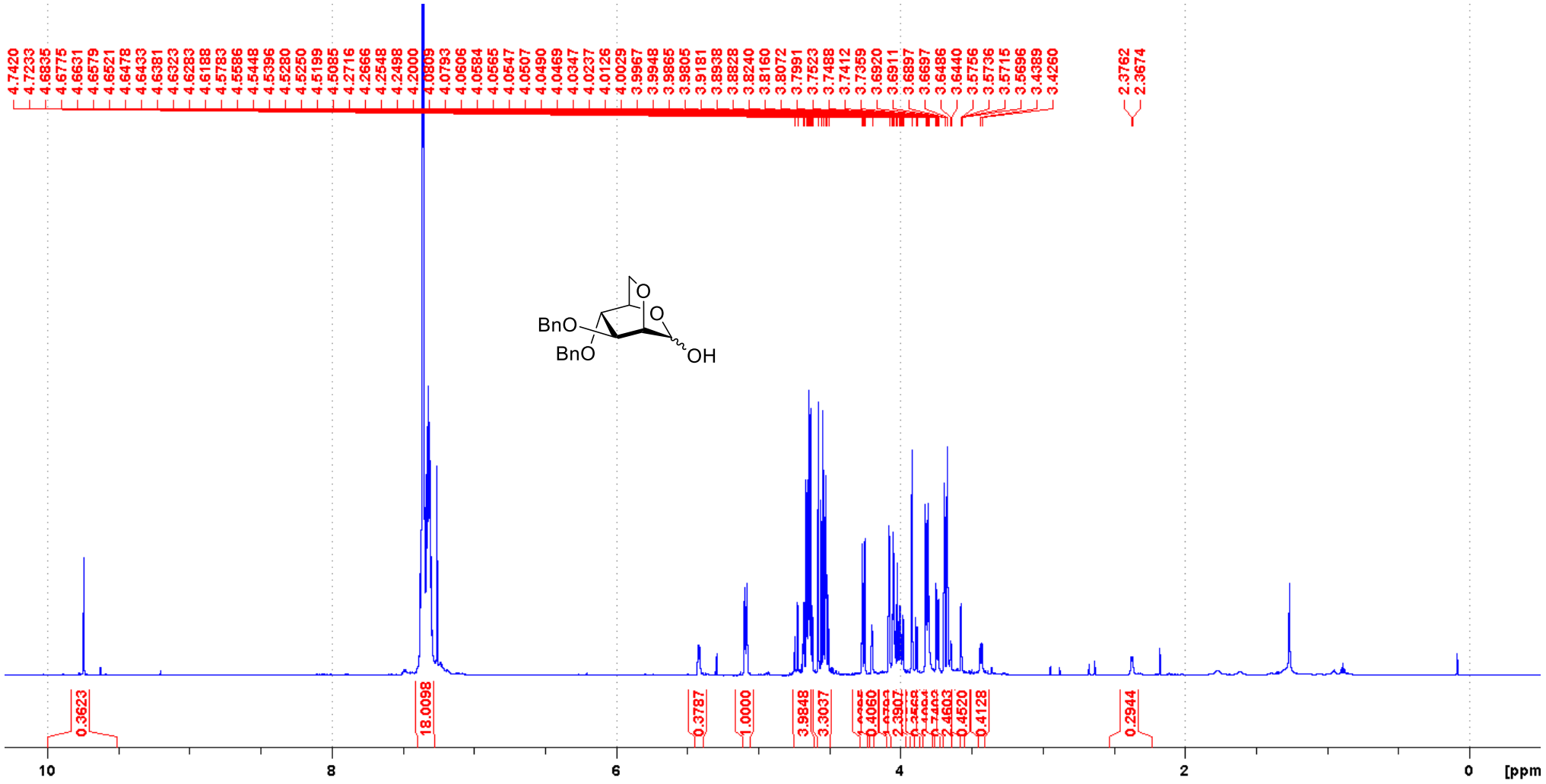

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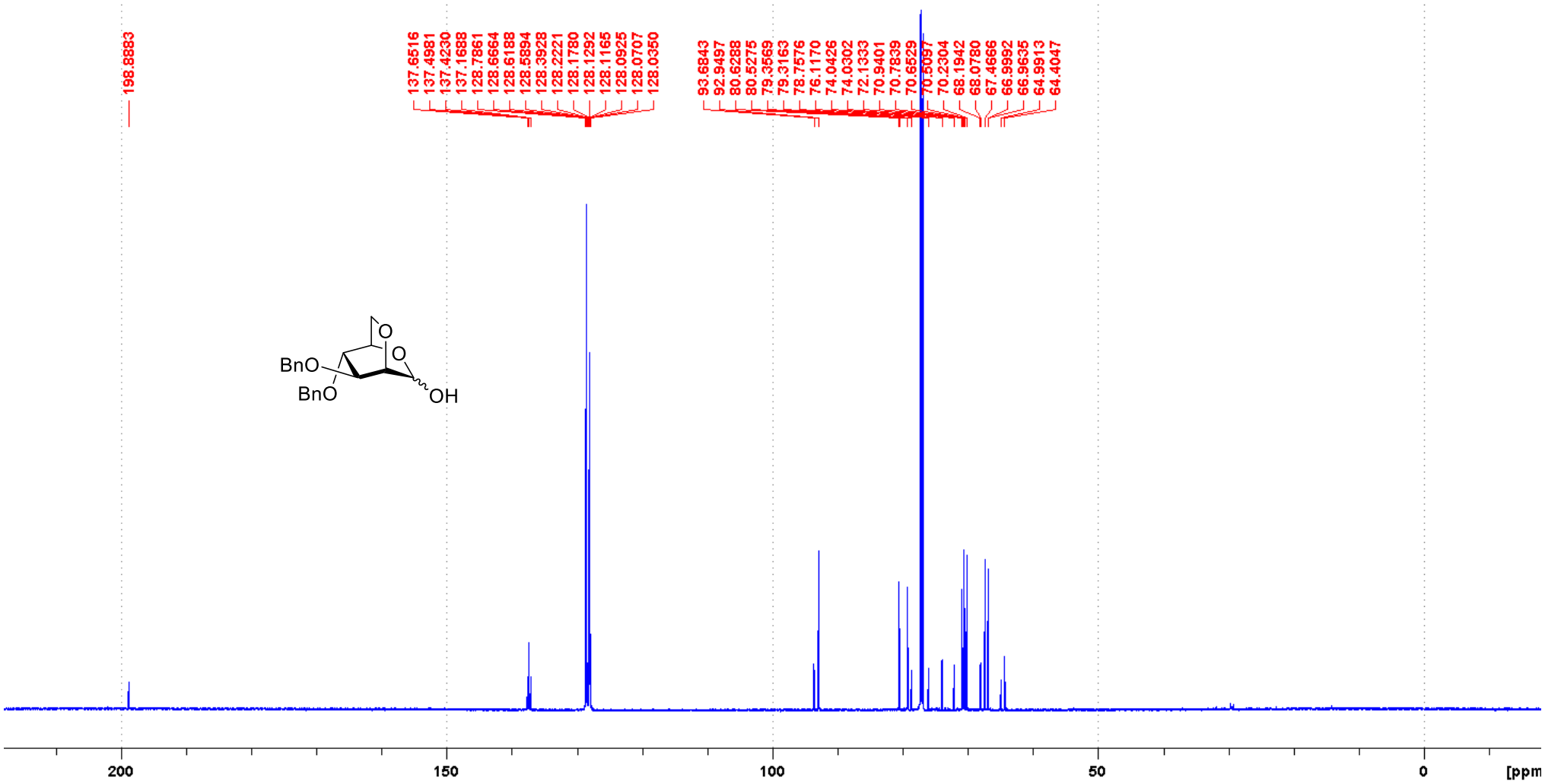

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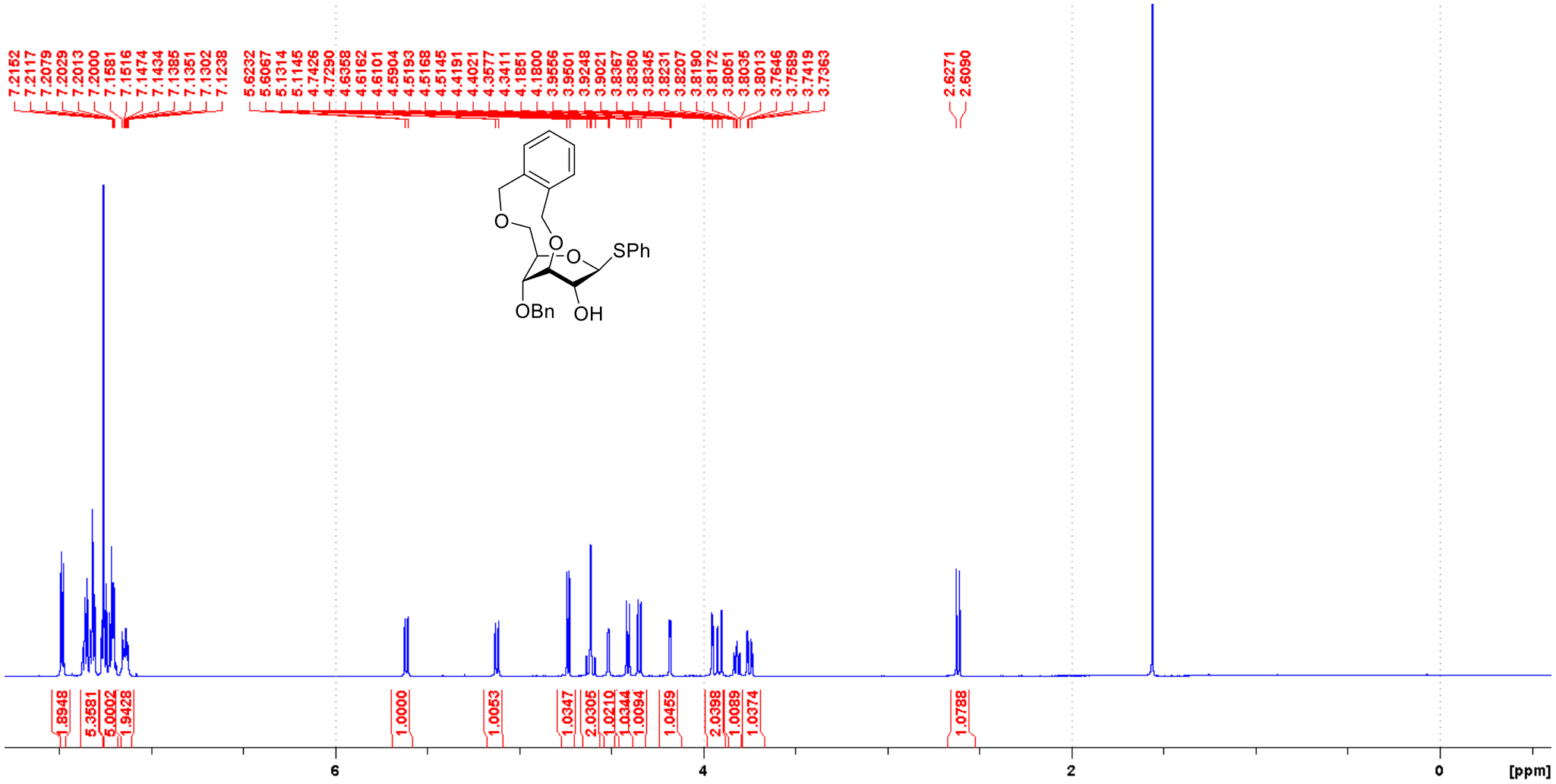

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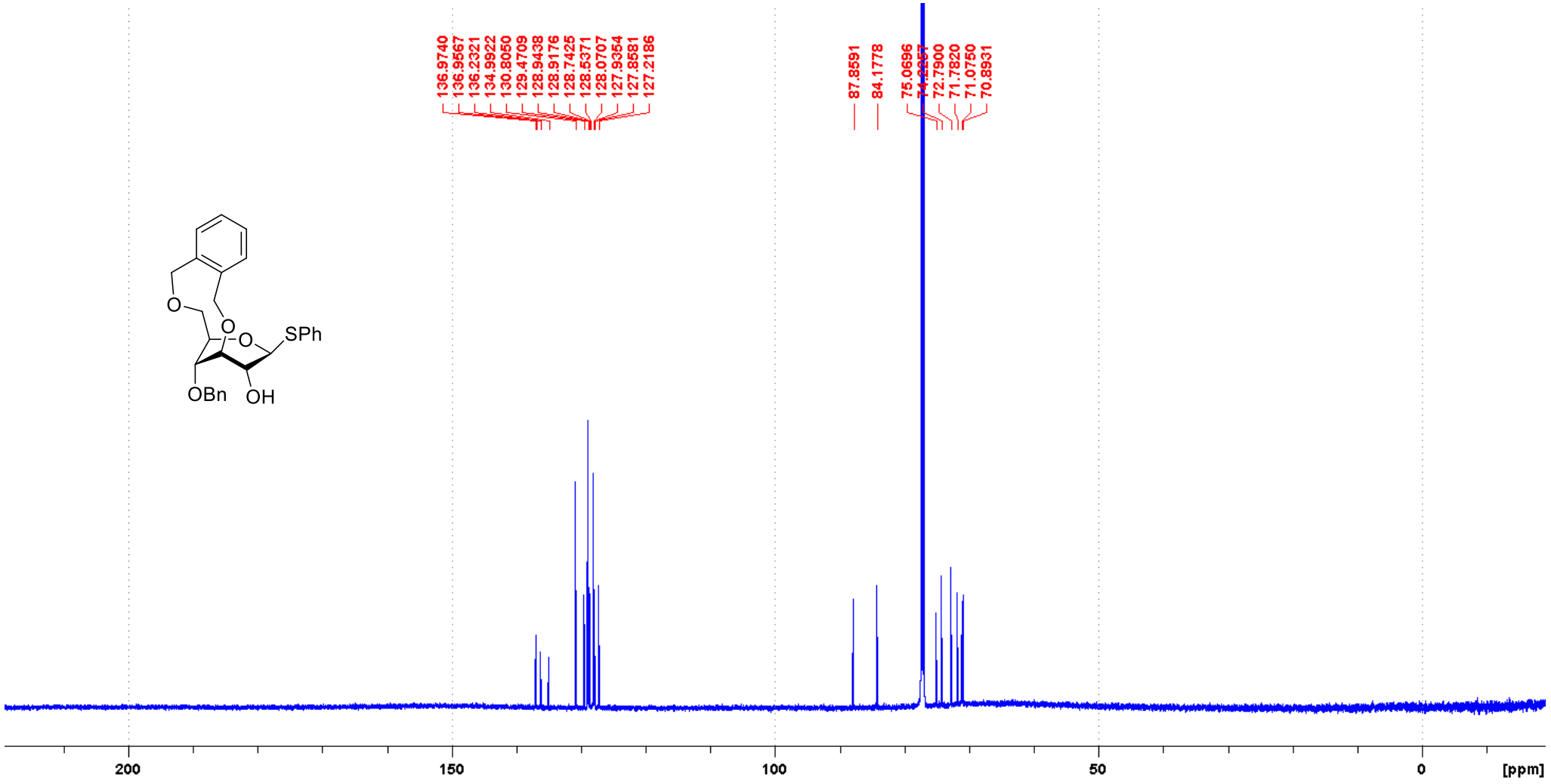
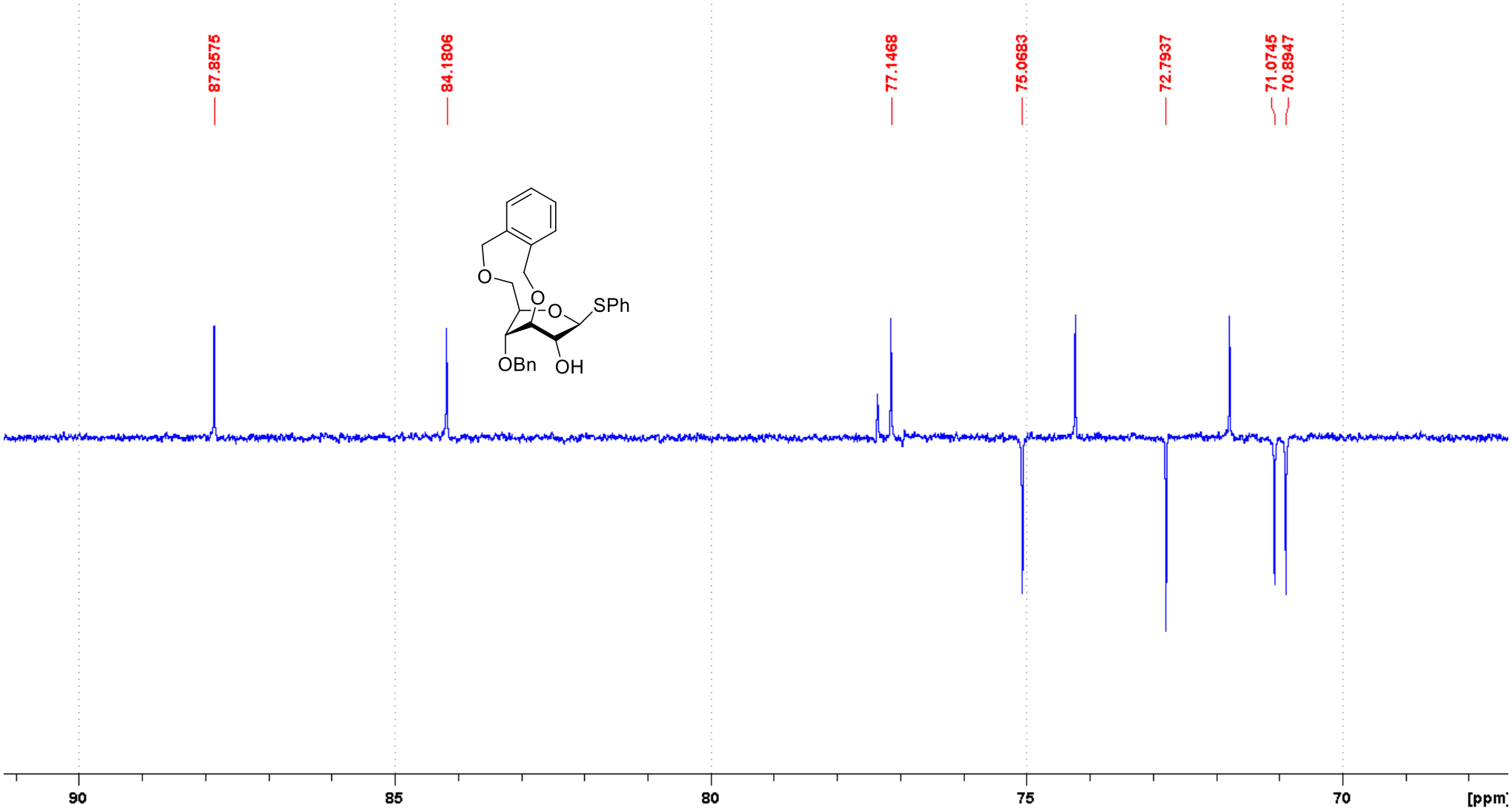


DEPT135 of compound **S17**



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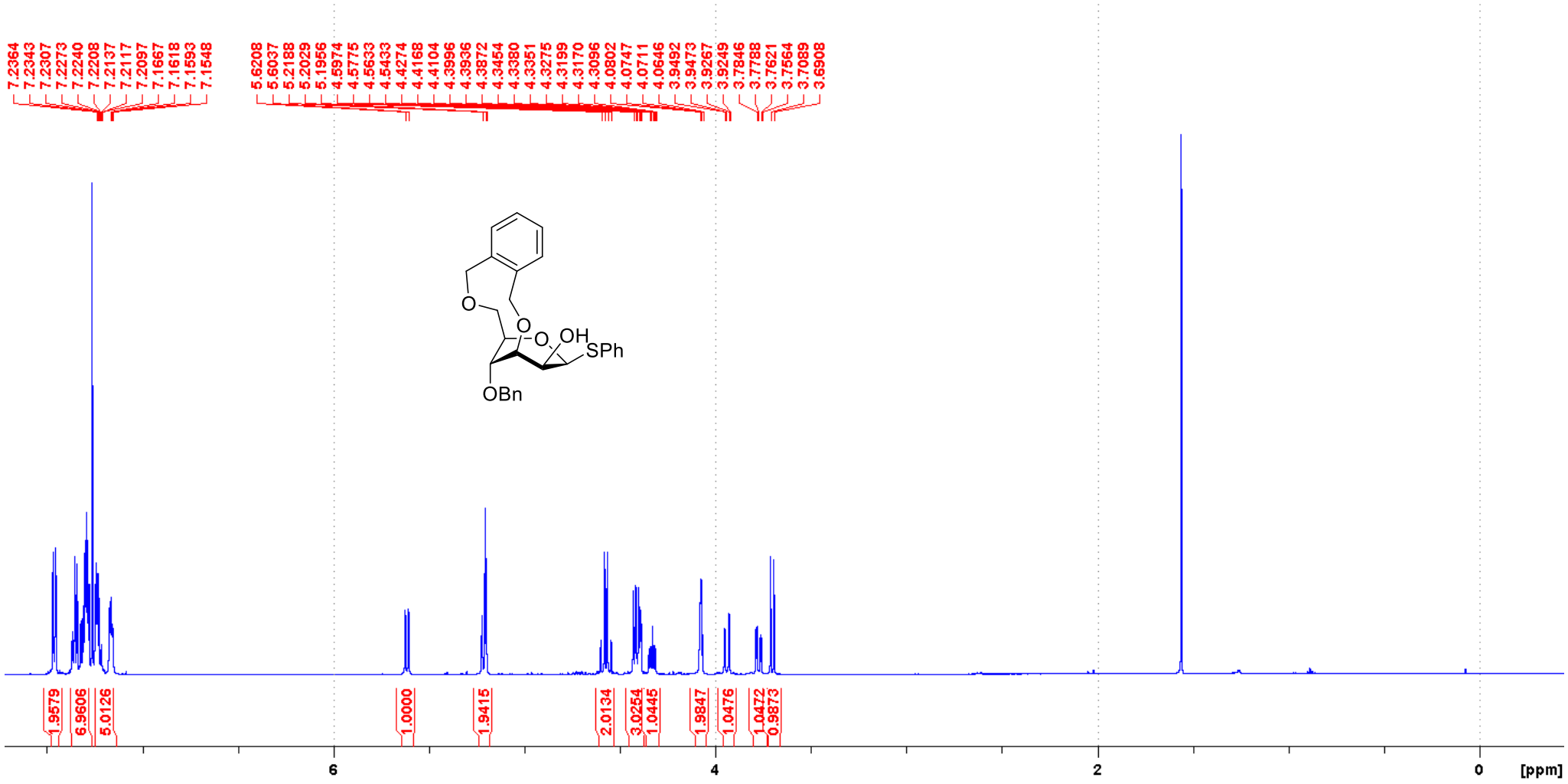

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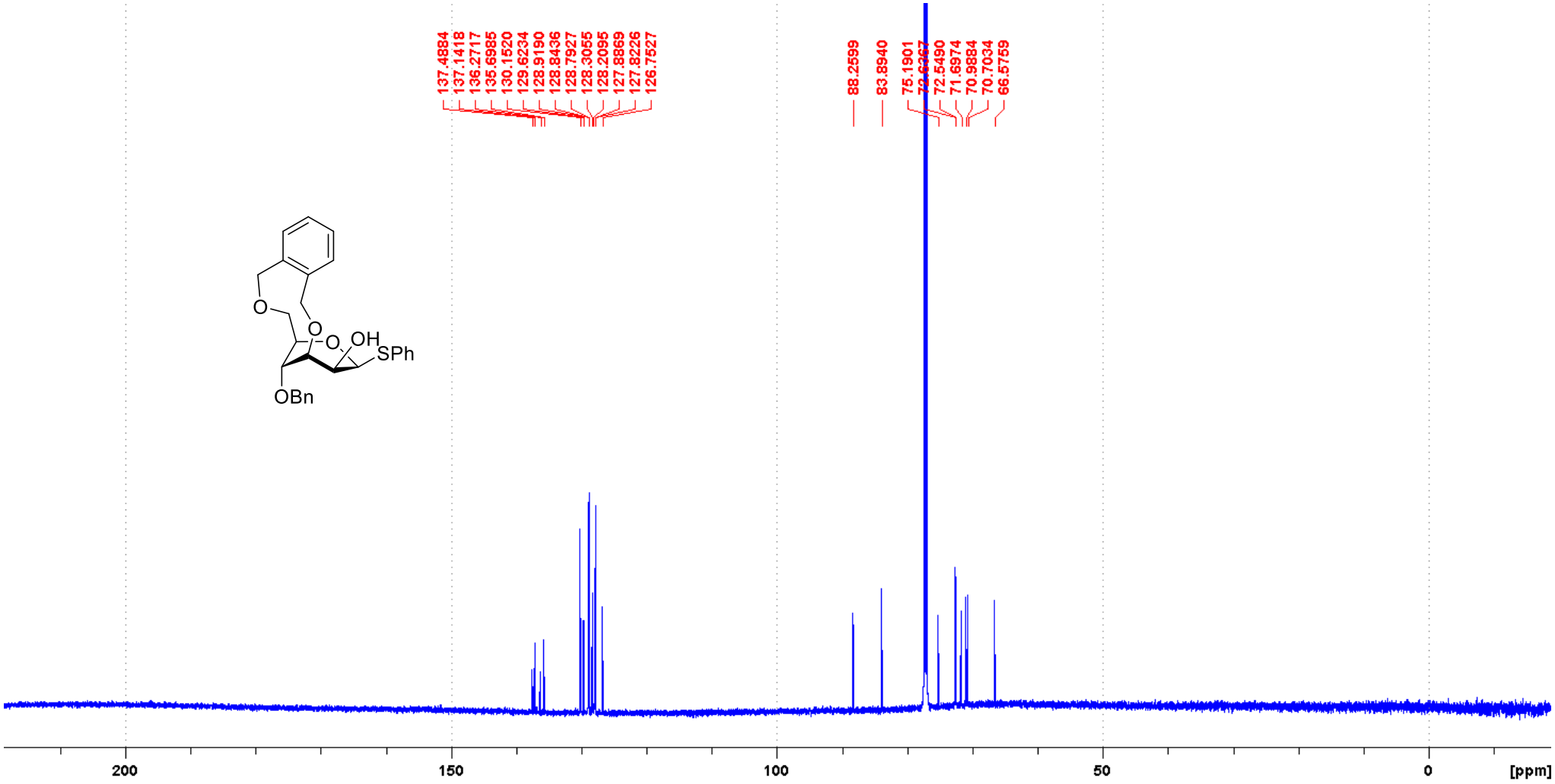

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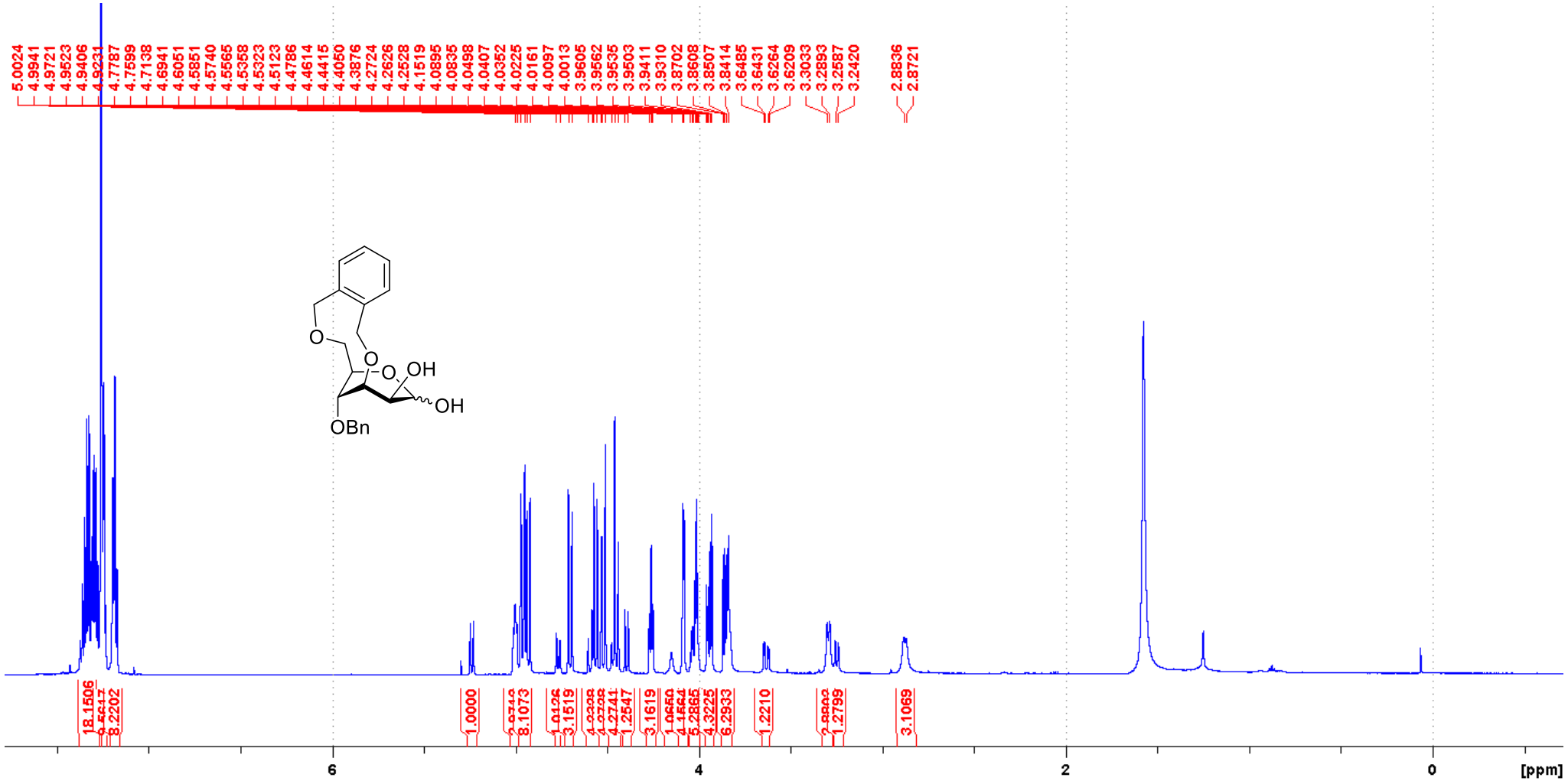
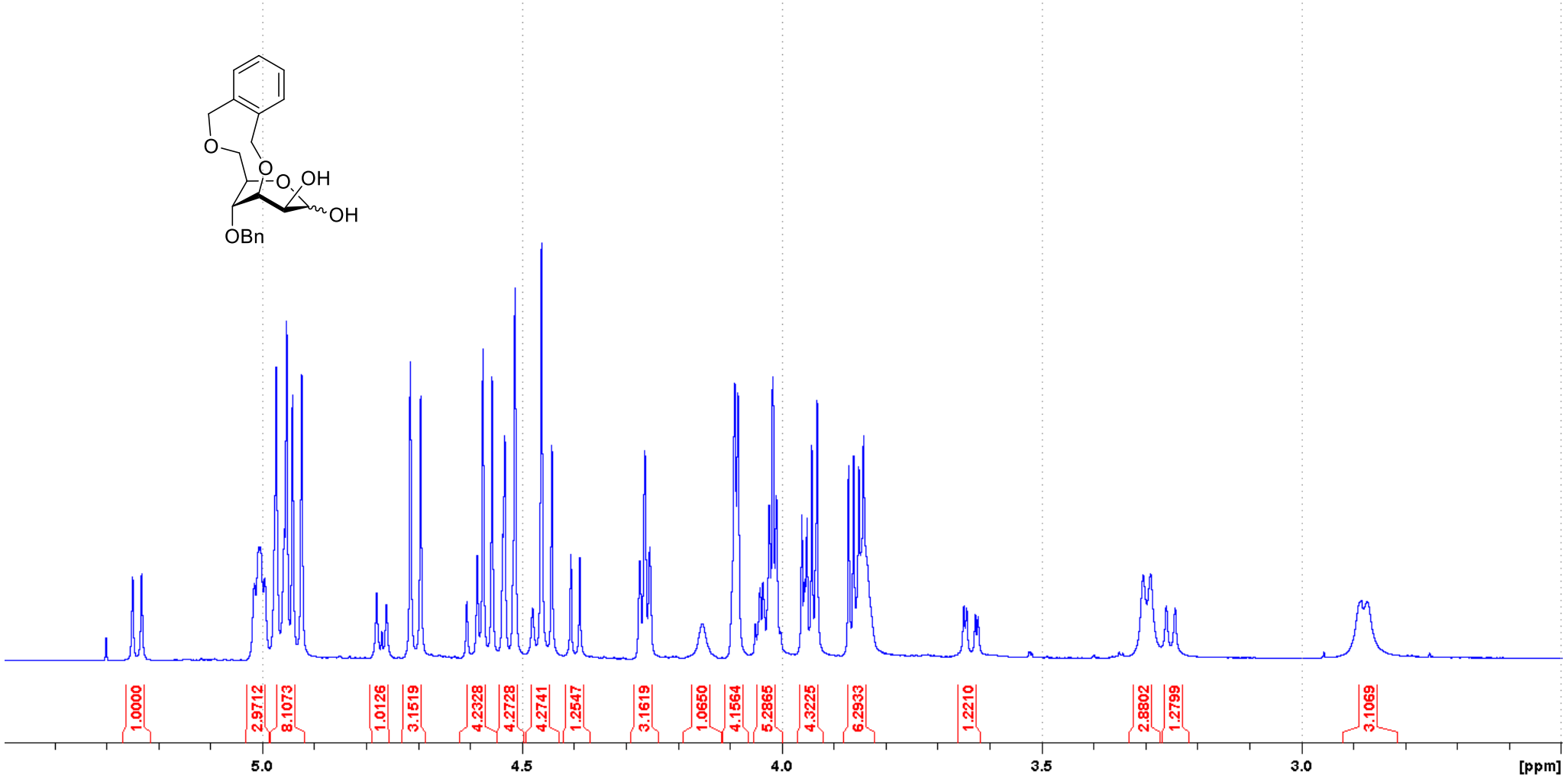


^{1}H NMR of compound **21** (5.50~2.50 ppm expanded)



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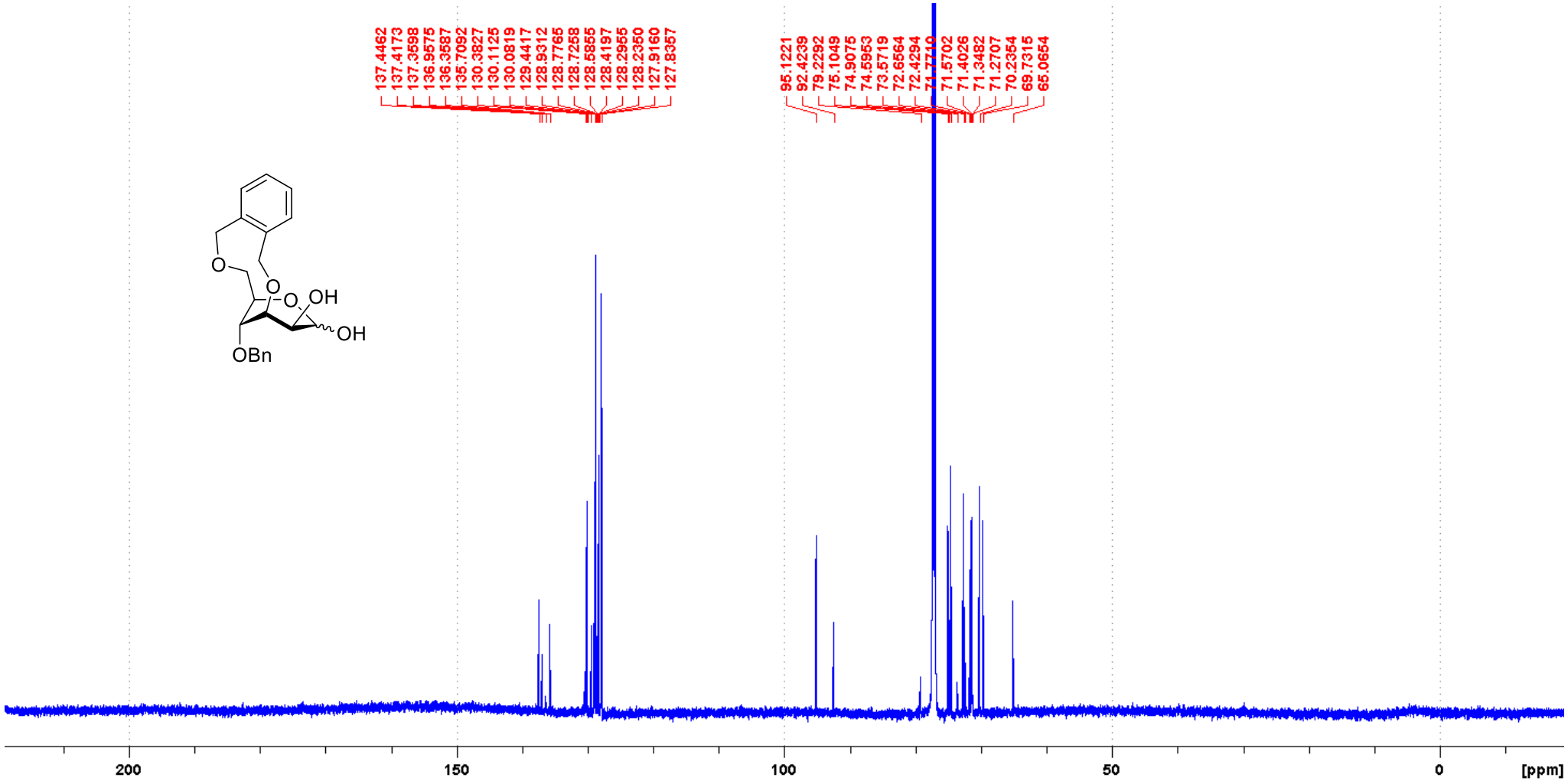
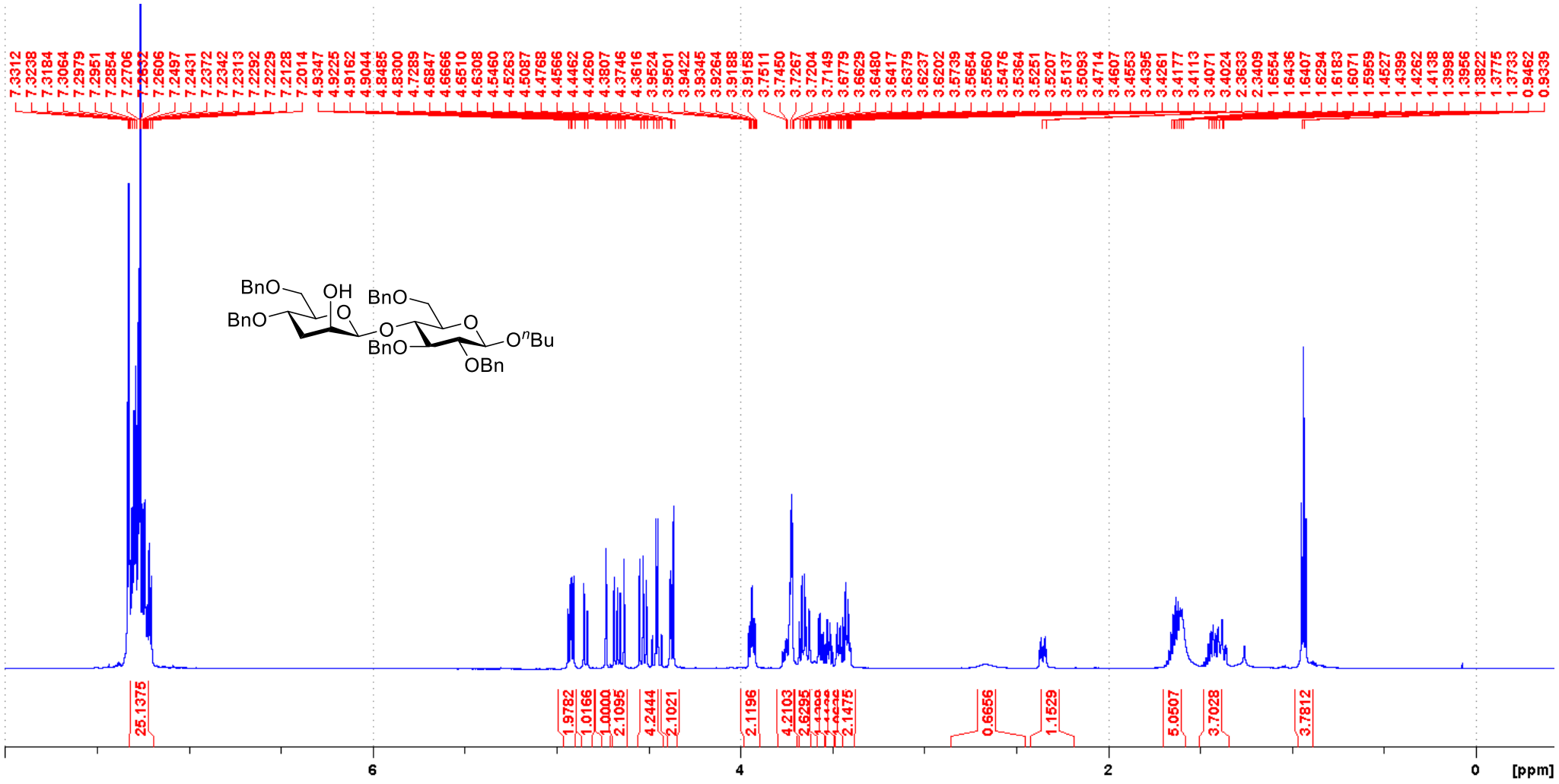
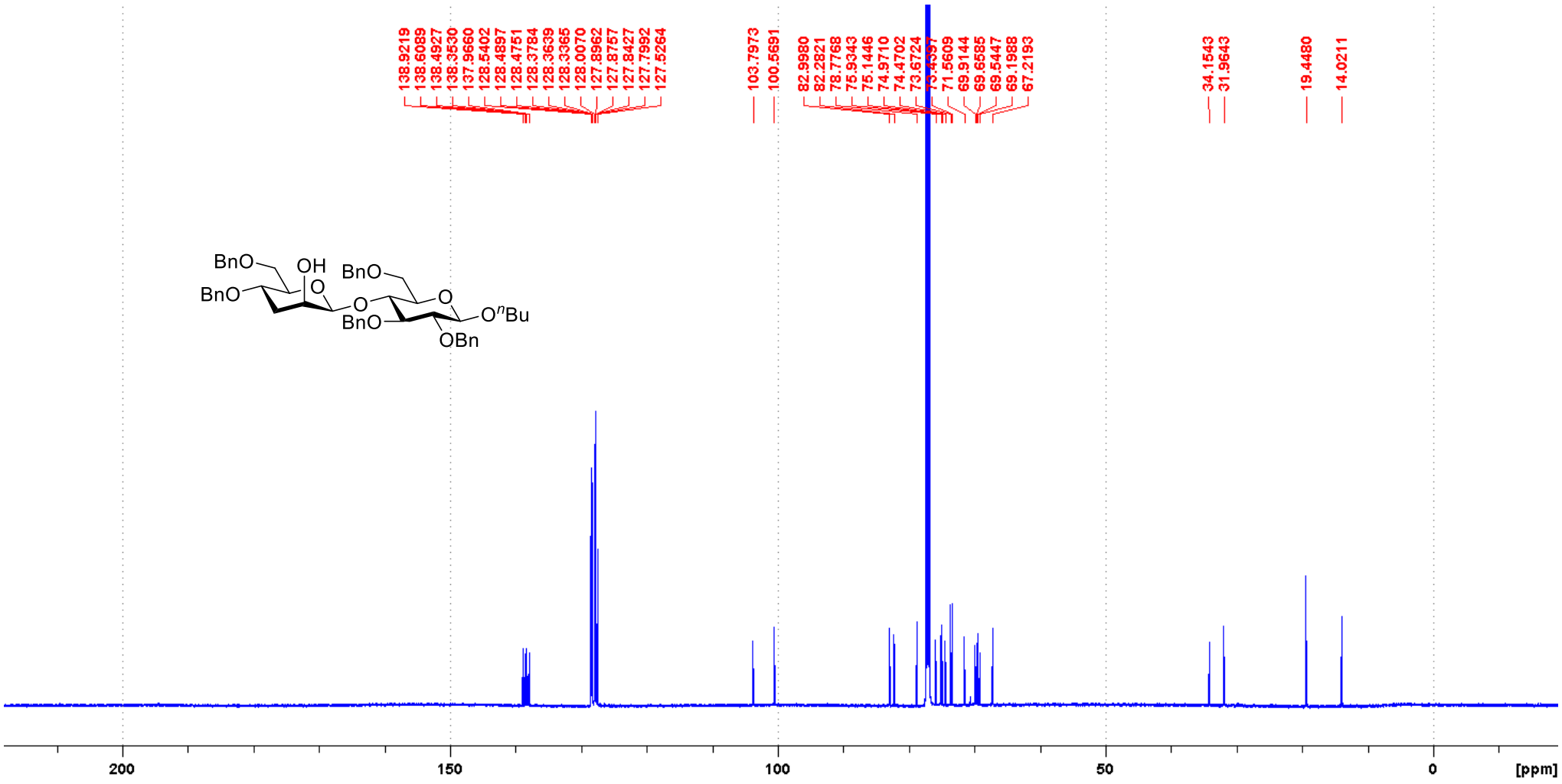


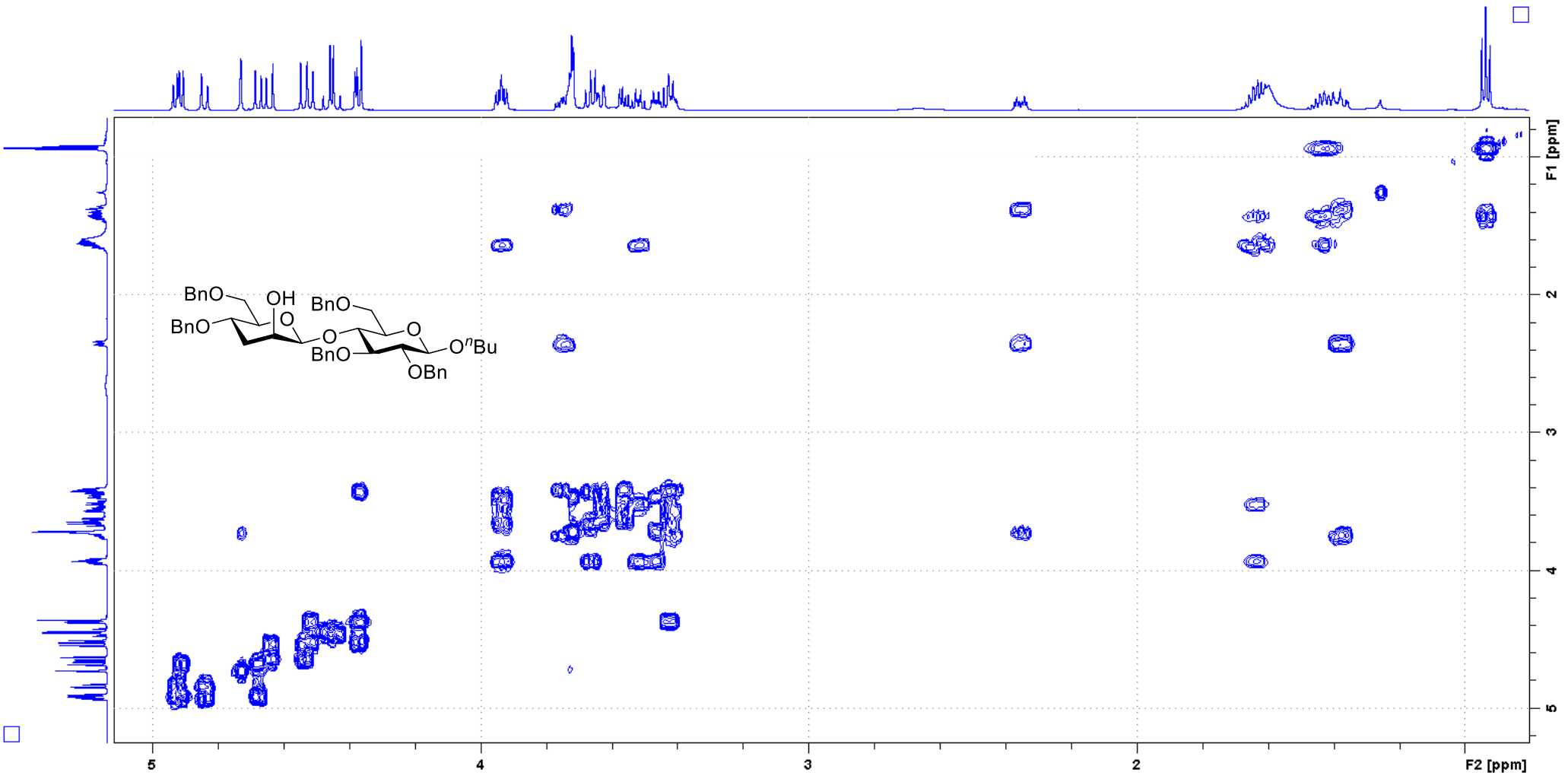
^{1}H NMR of compound **25**



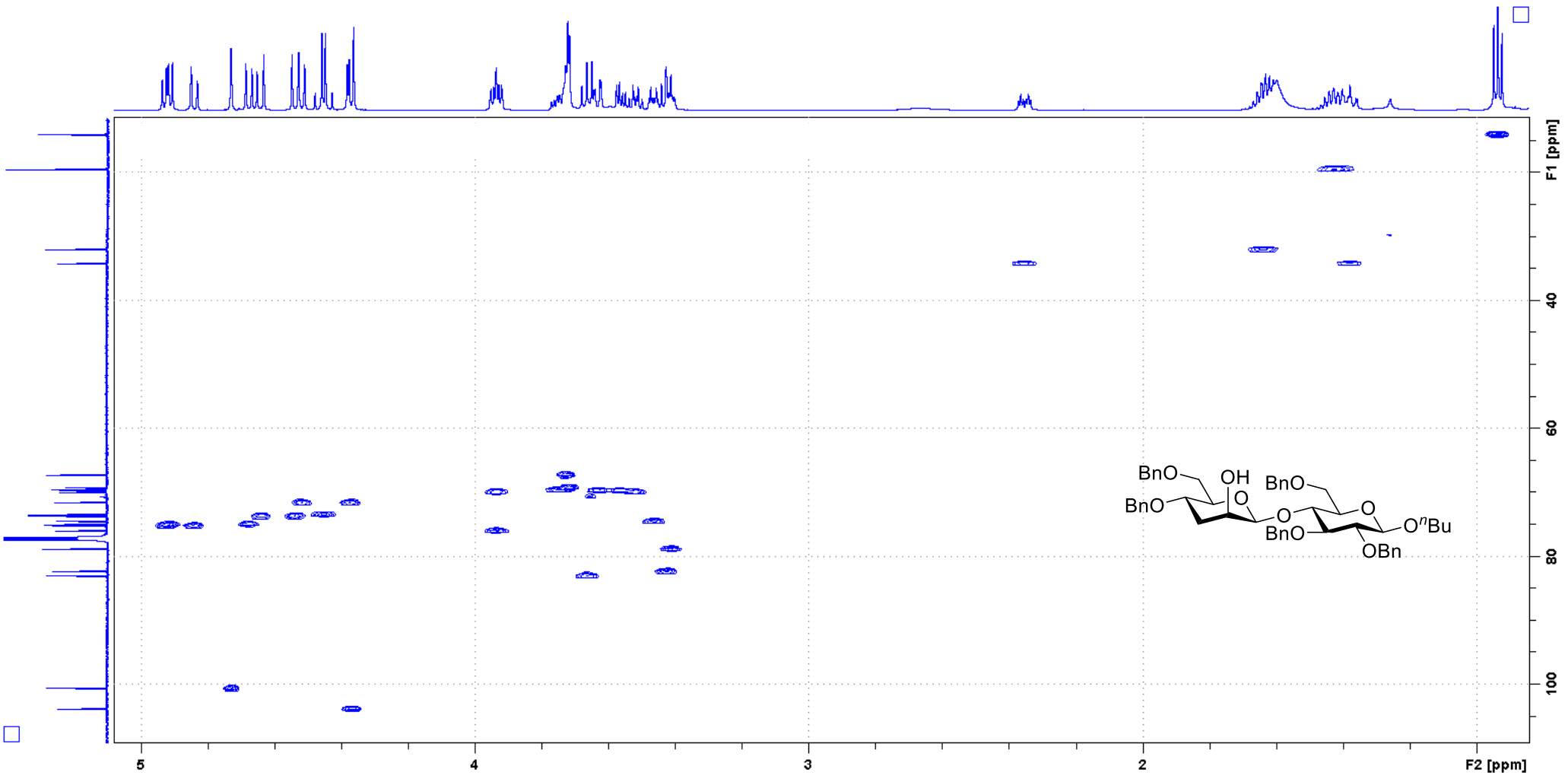
^{13}C NMR of compound **25**



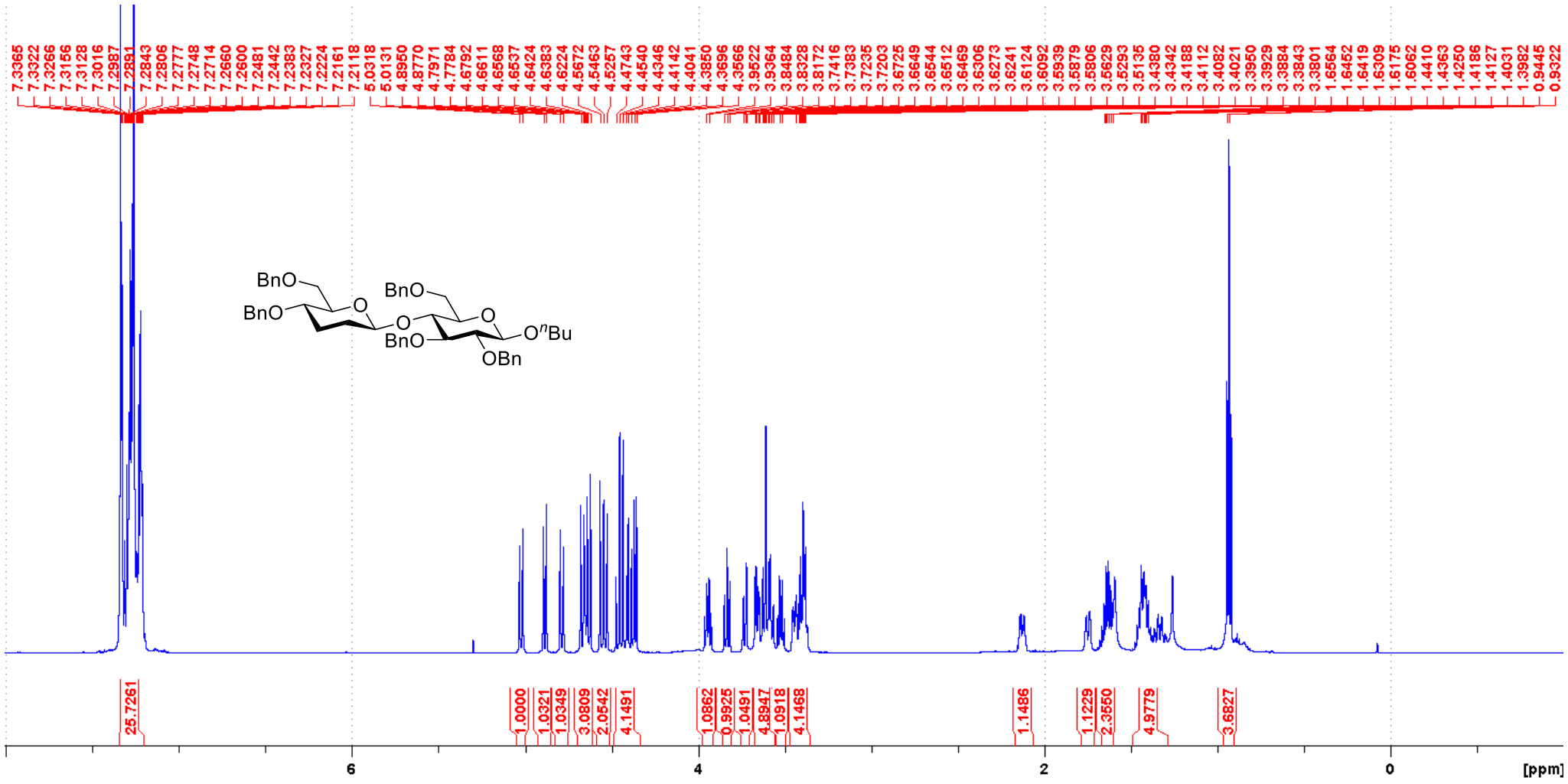
H-H COSY of compound **25**



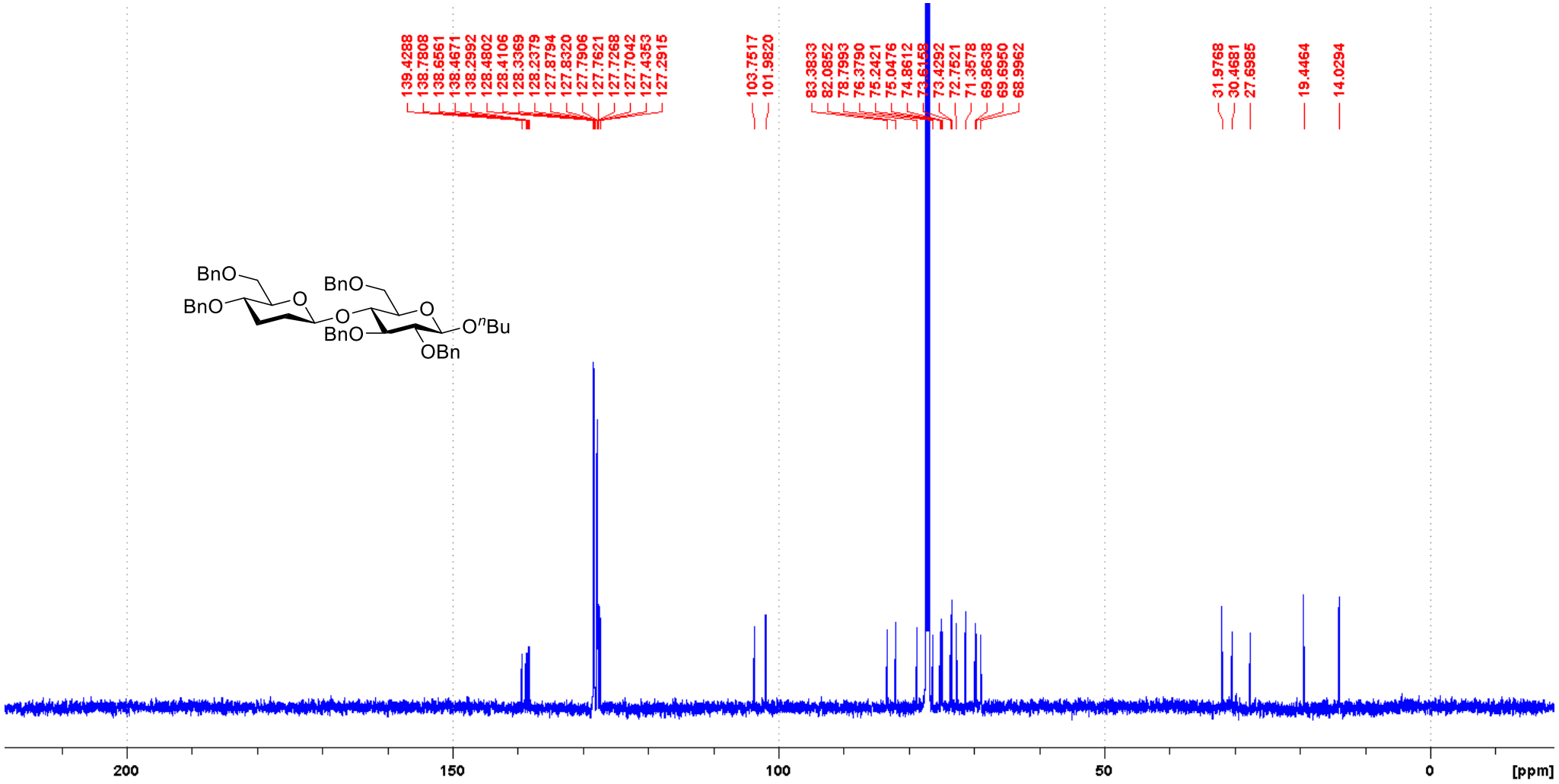
HSQC of compound **25**



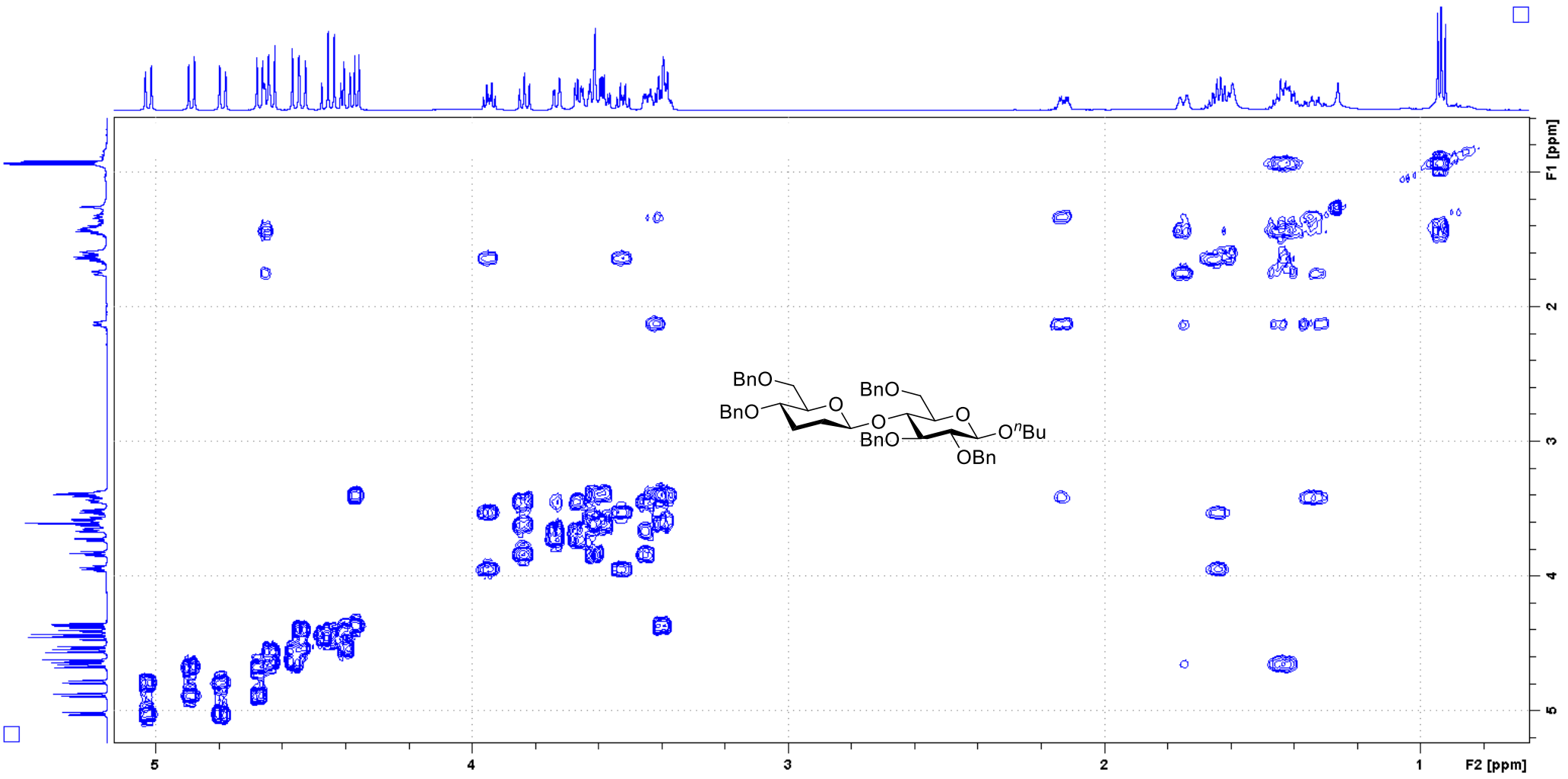
^{1}H NMR of compound **27**



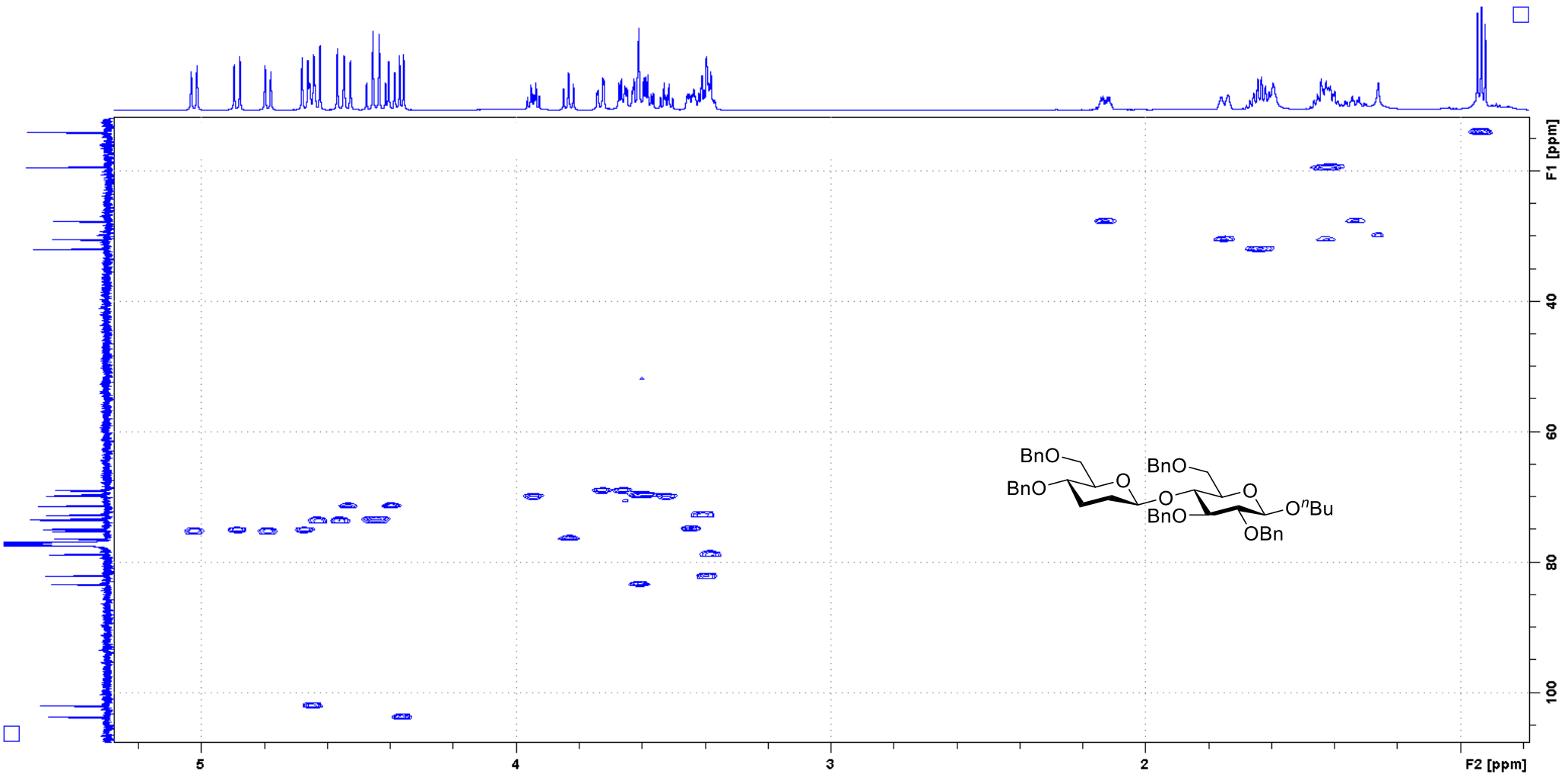
^{13}C NMR of compound **27**



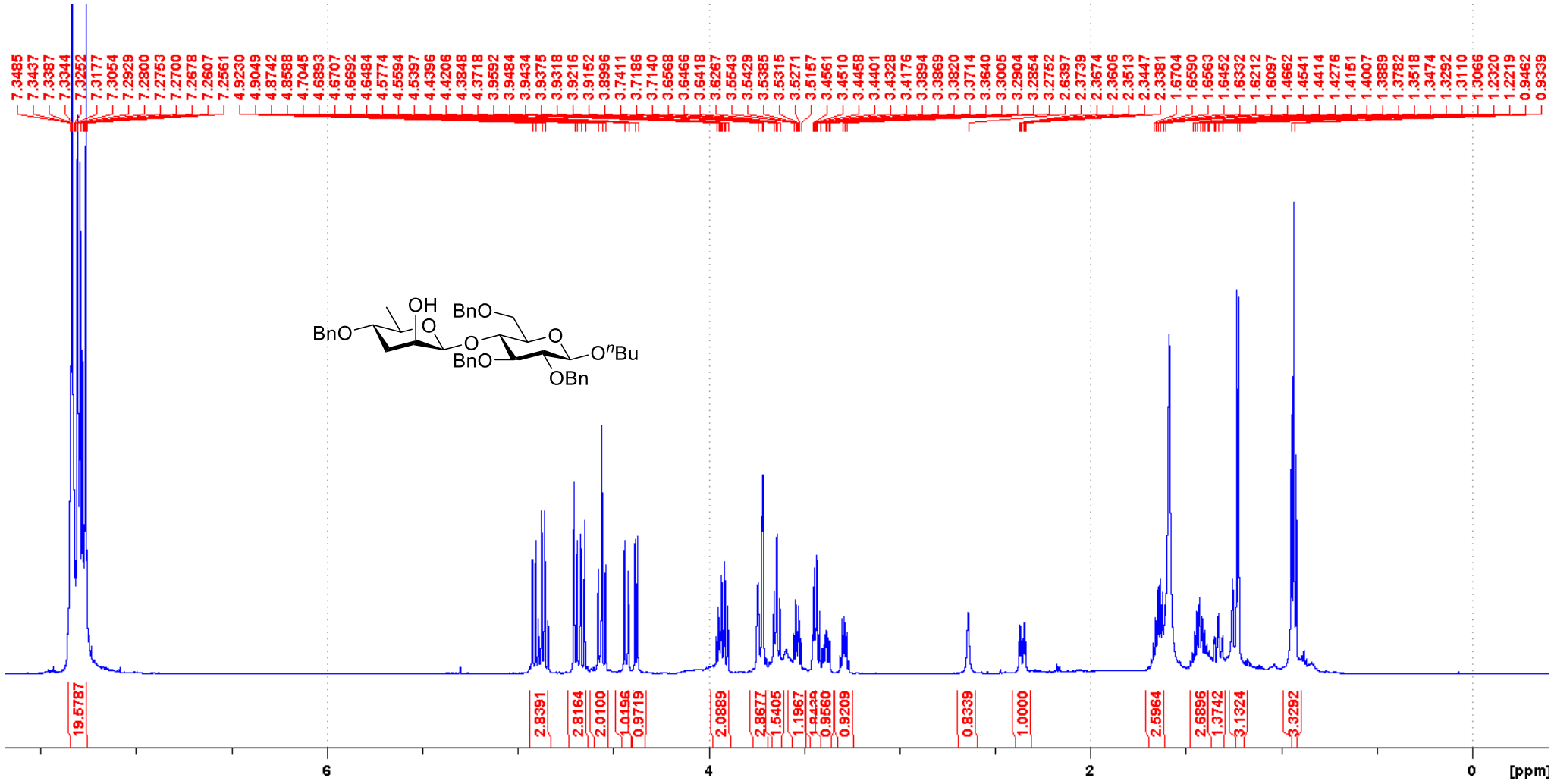
H-H COSY of compound **27**



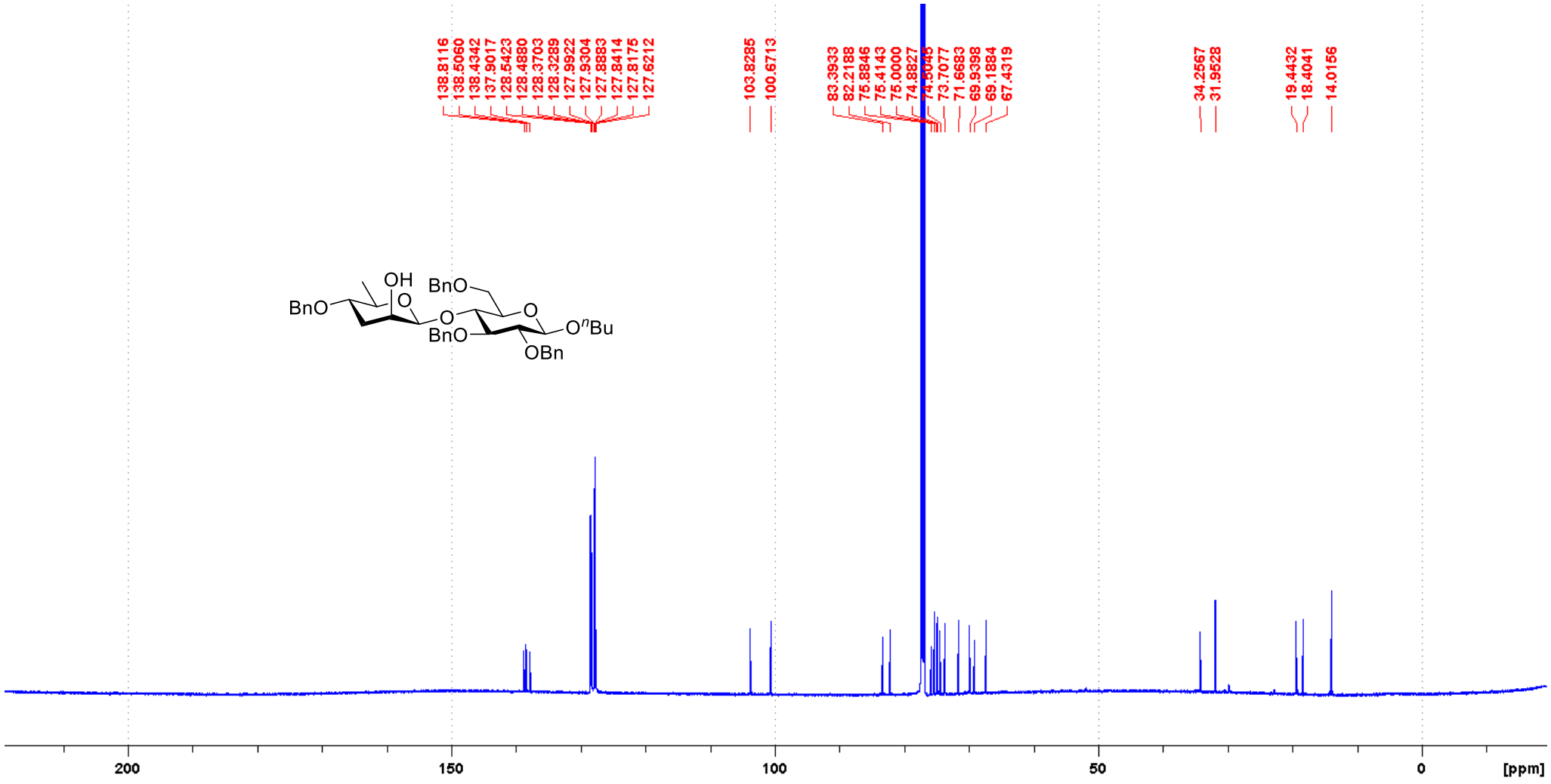
HSQC of compound **27**



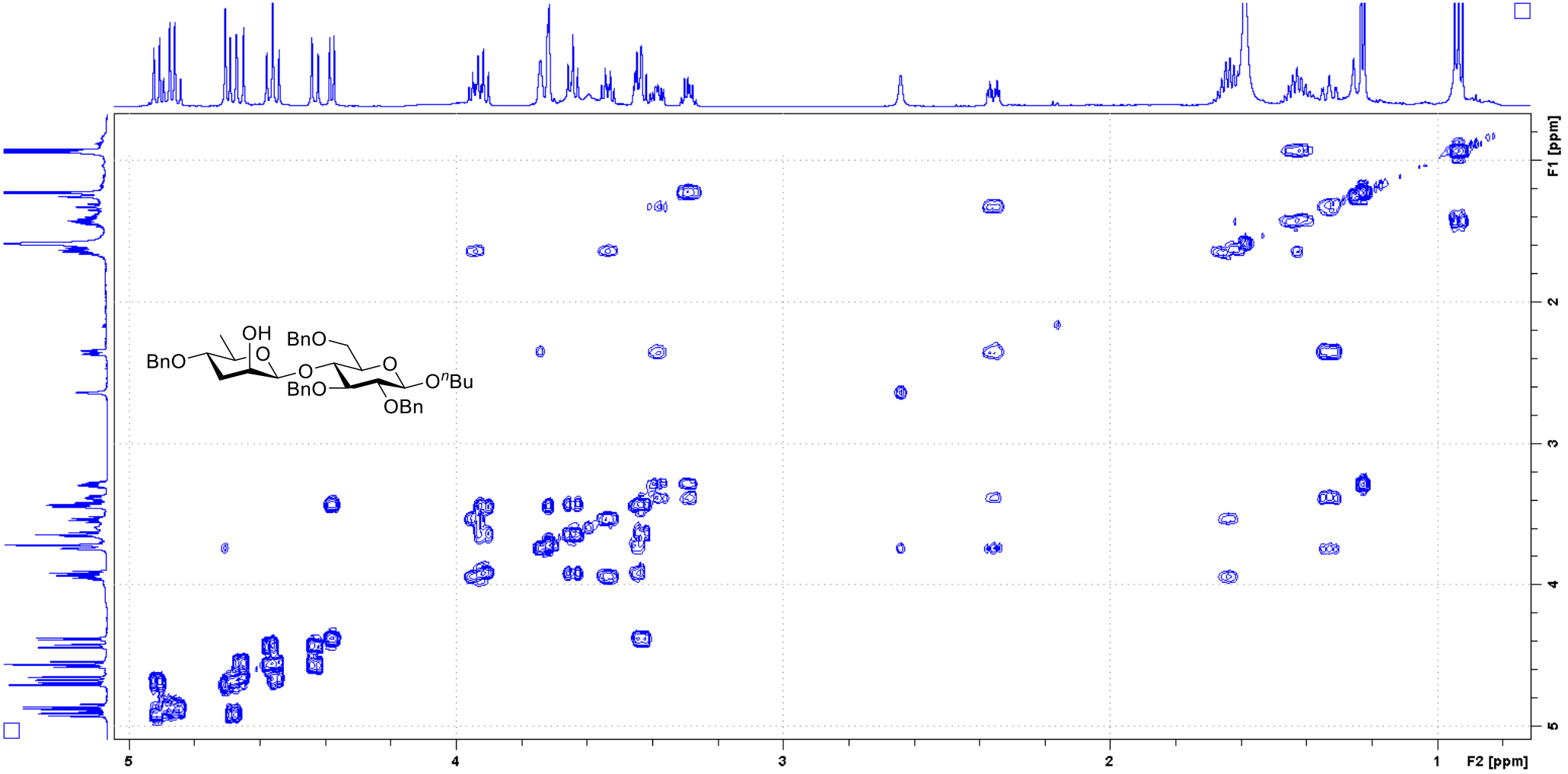
^{1}H NMR of compound **29**



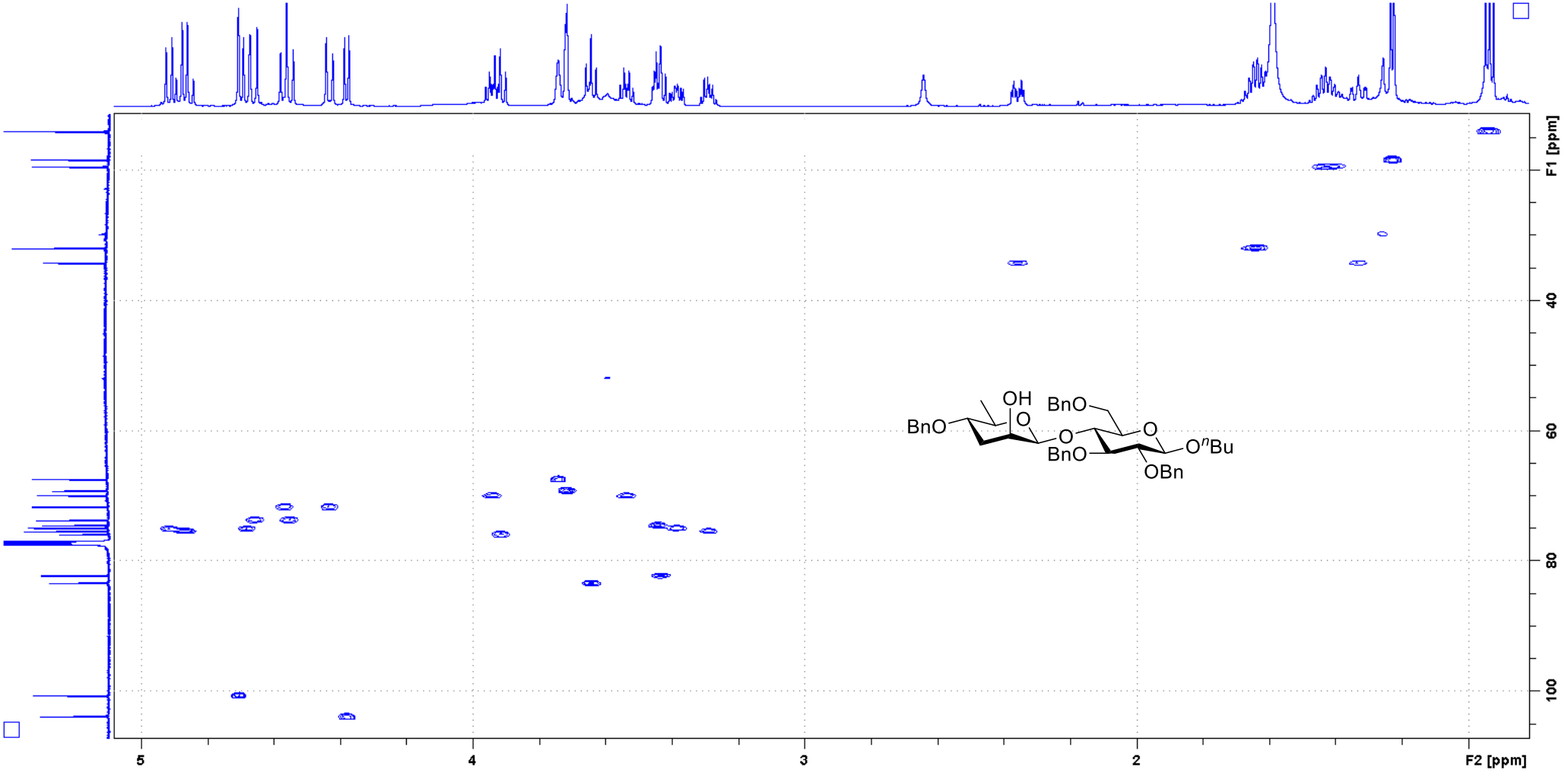
^{13}C NMR of compound **29**



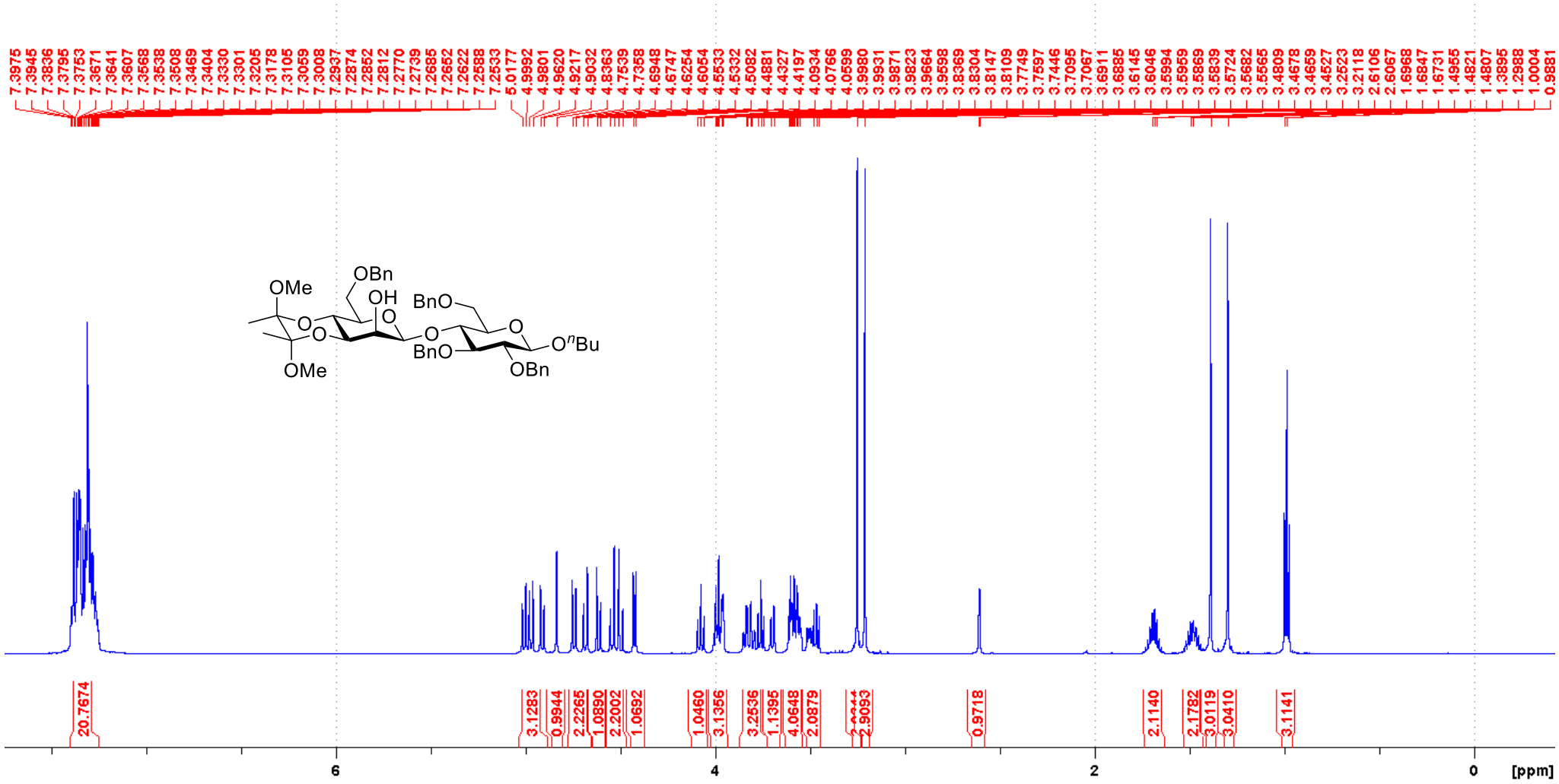
H-H COSY of compound **29**



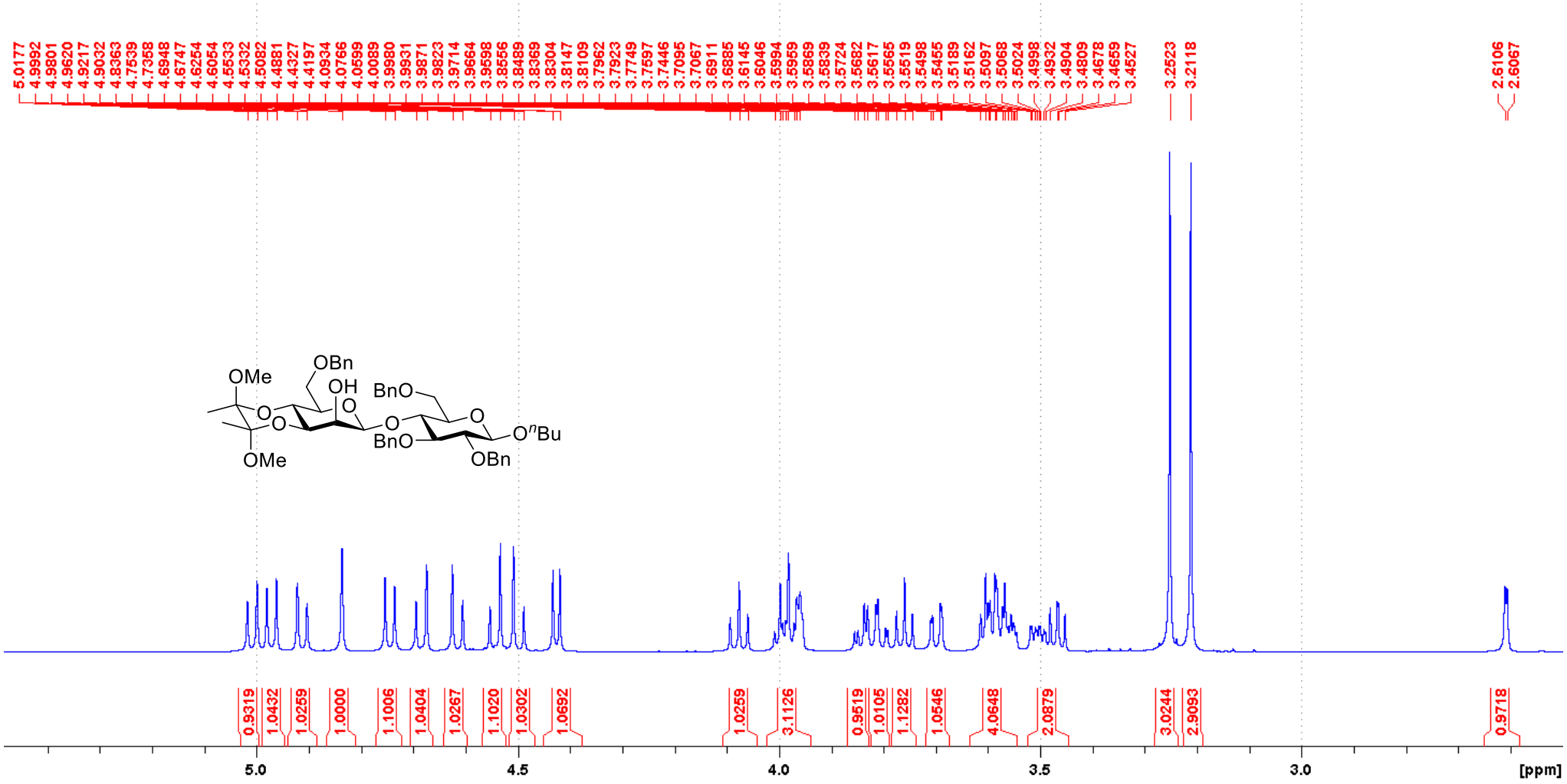
HSQC of compound **29**



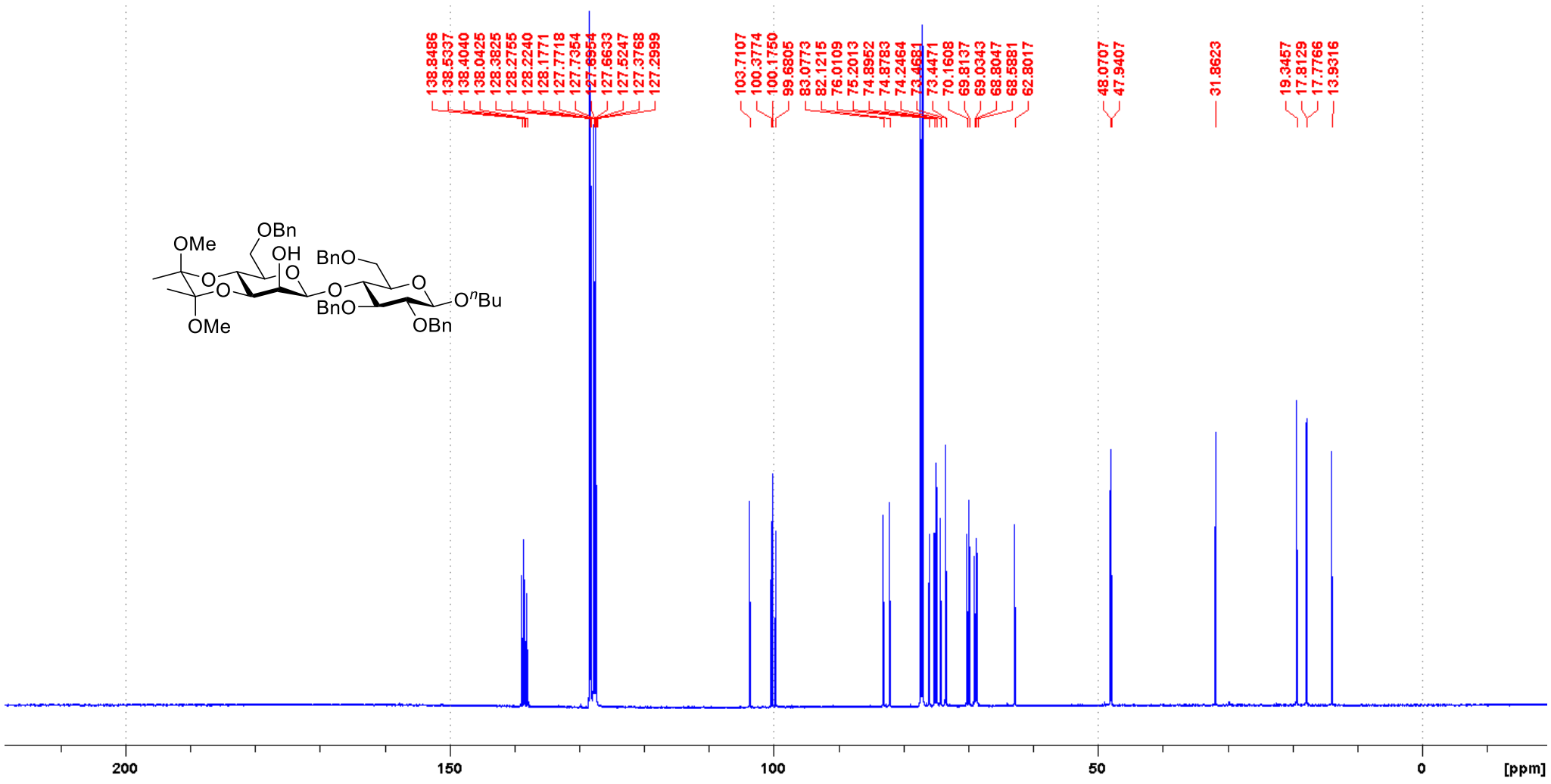
^{1}H NMR of compound **32**



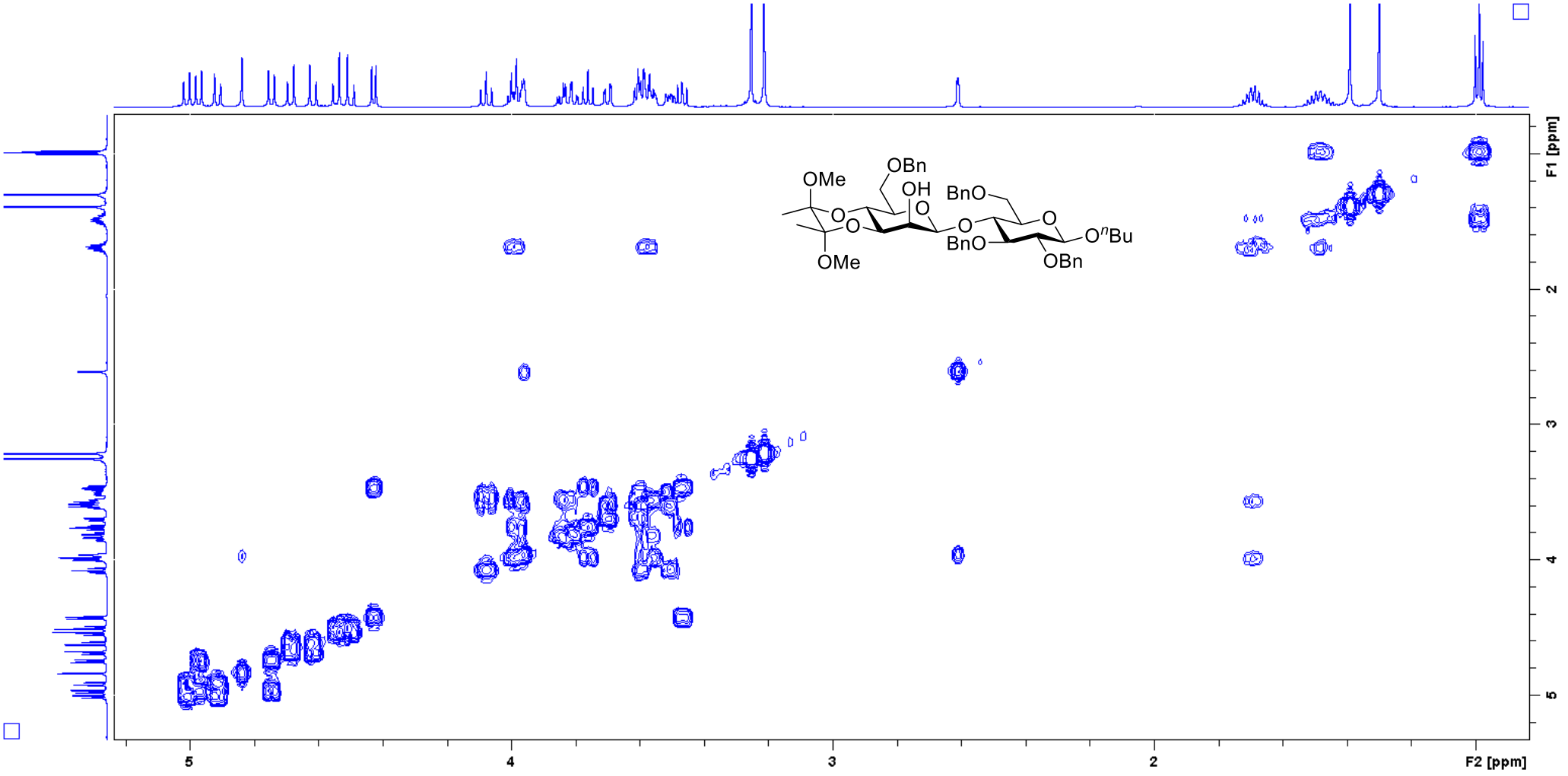
^{1}H NMR of compound **32** (5.50~2.50 ppm expanded)



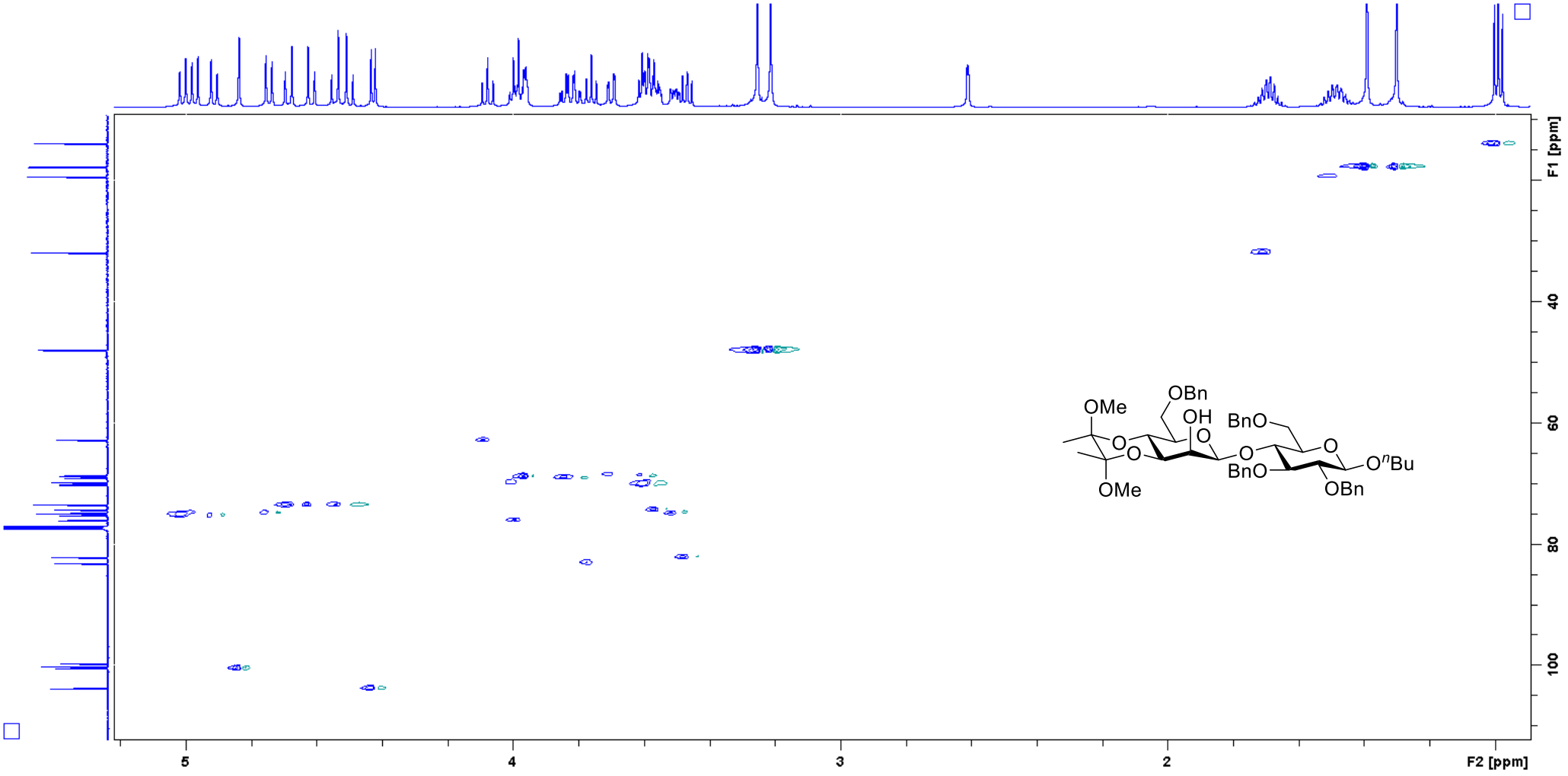
^{13}C NMR of compound **32**



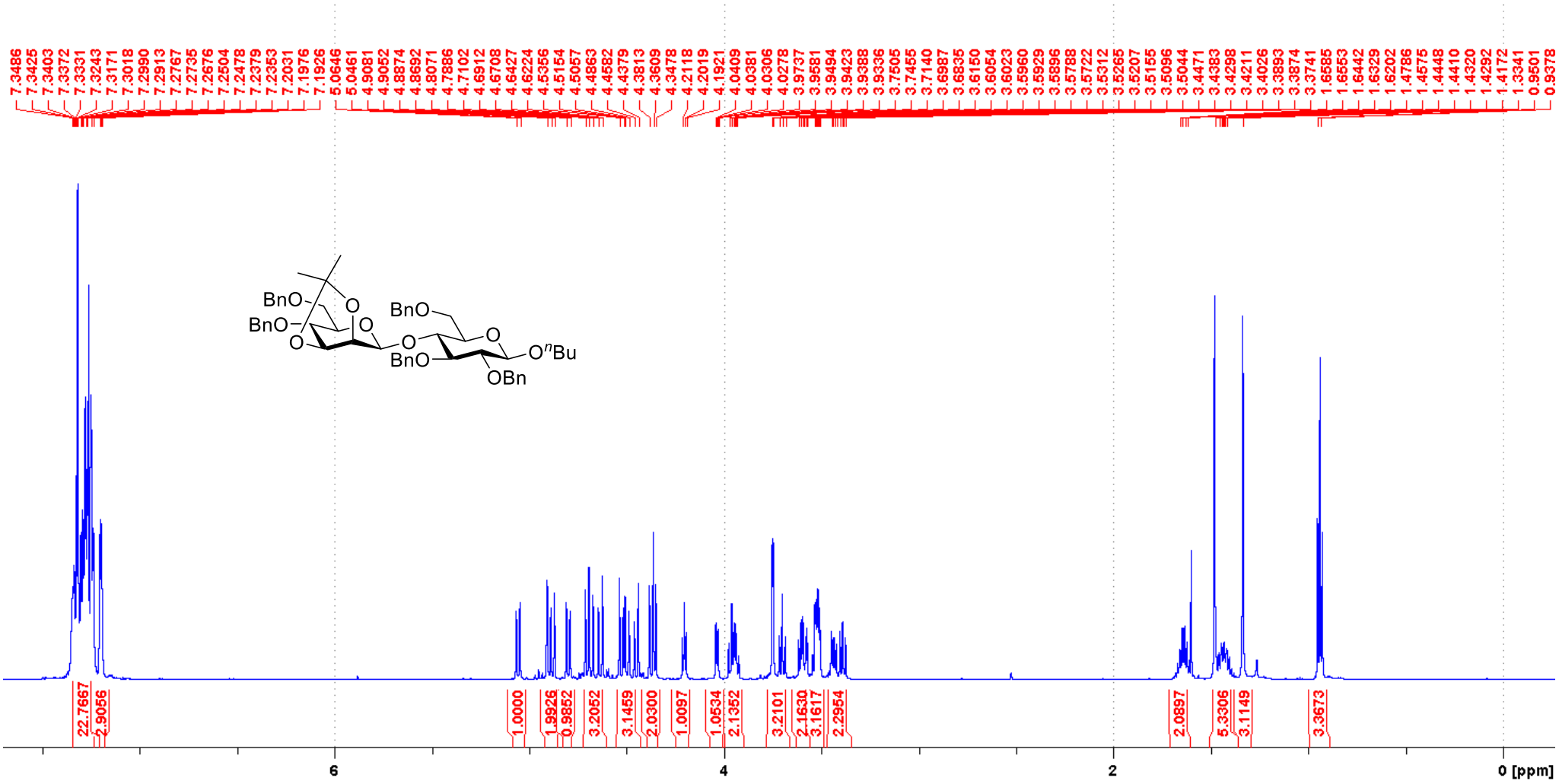
H-H COSY of compound **32**



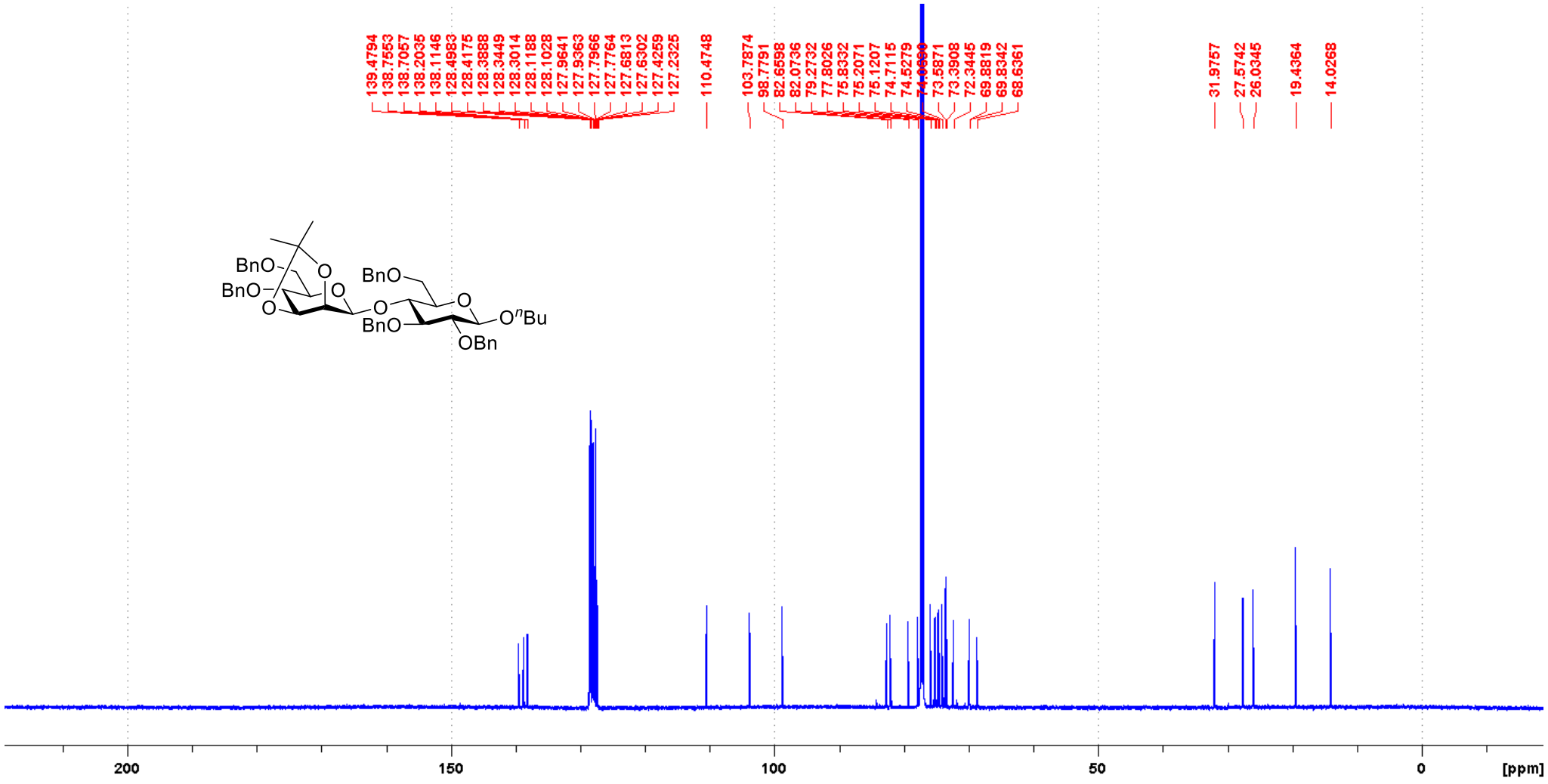
HSQC of compound **32**



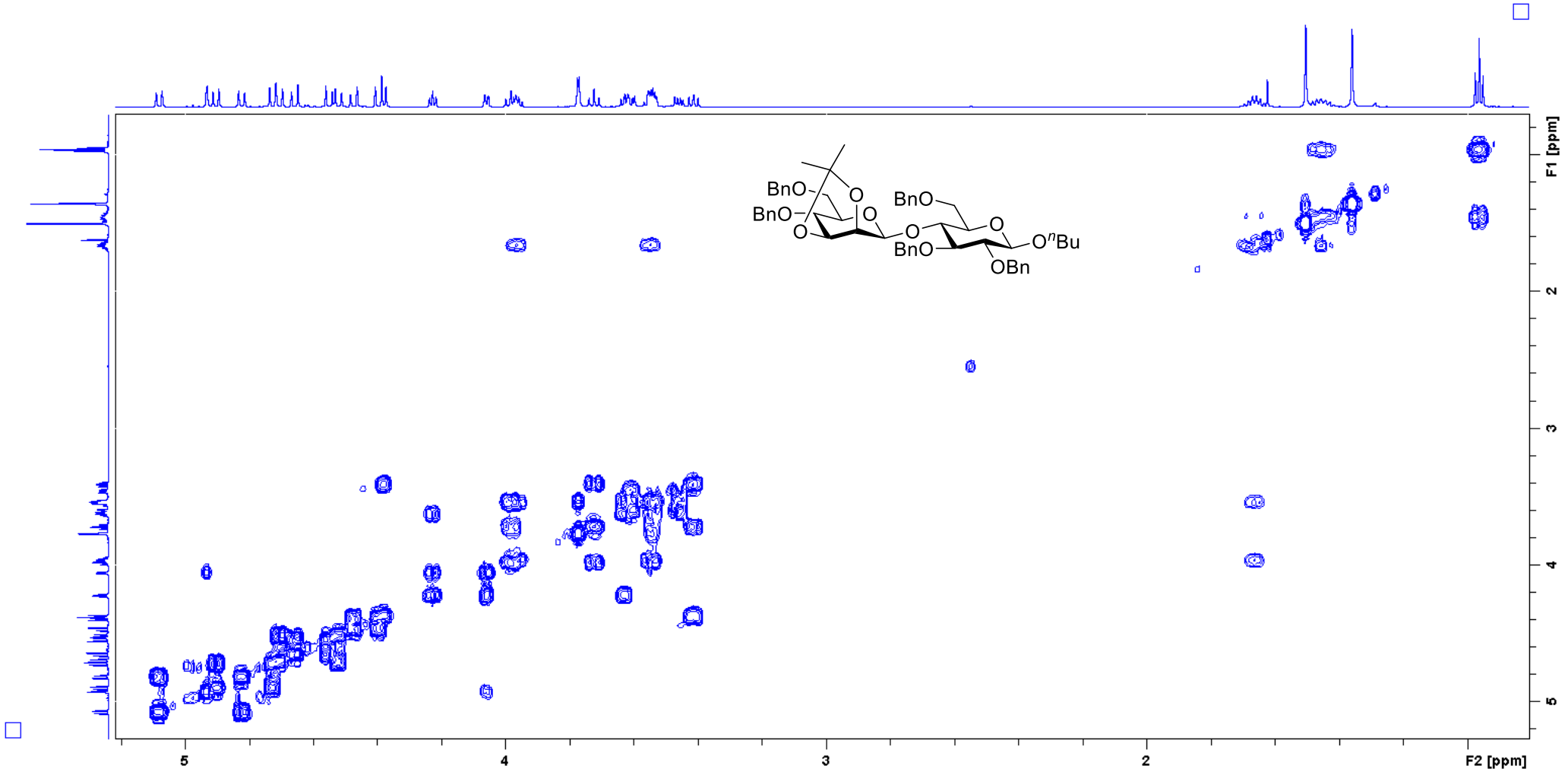
^{1}H NMR of compound **33**



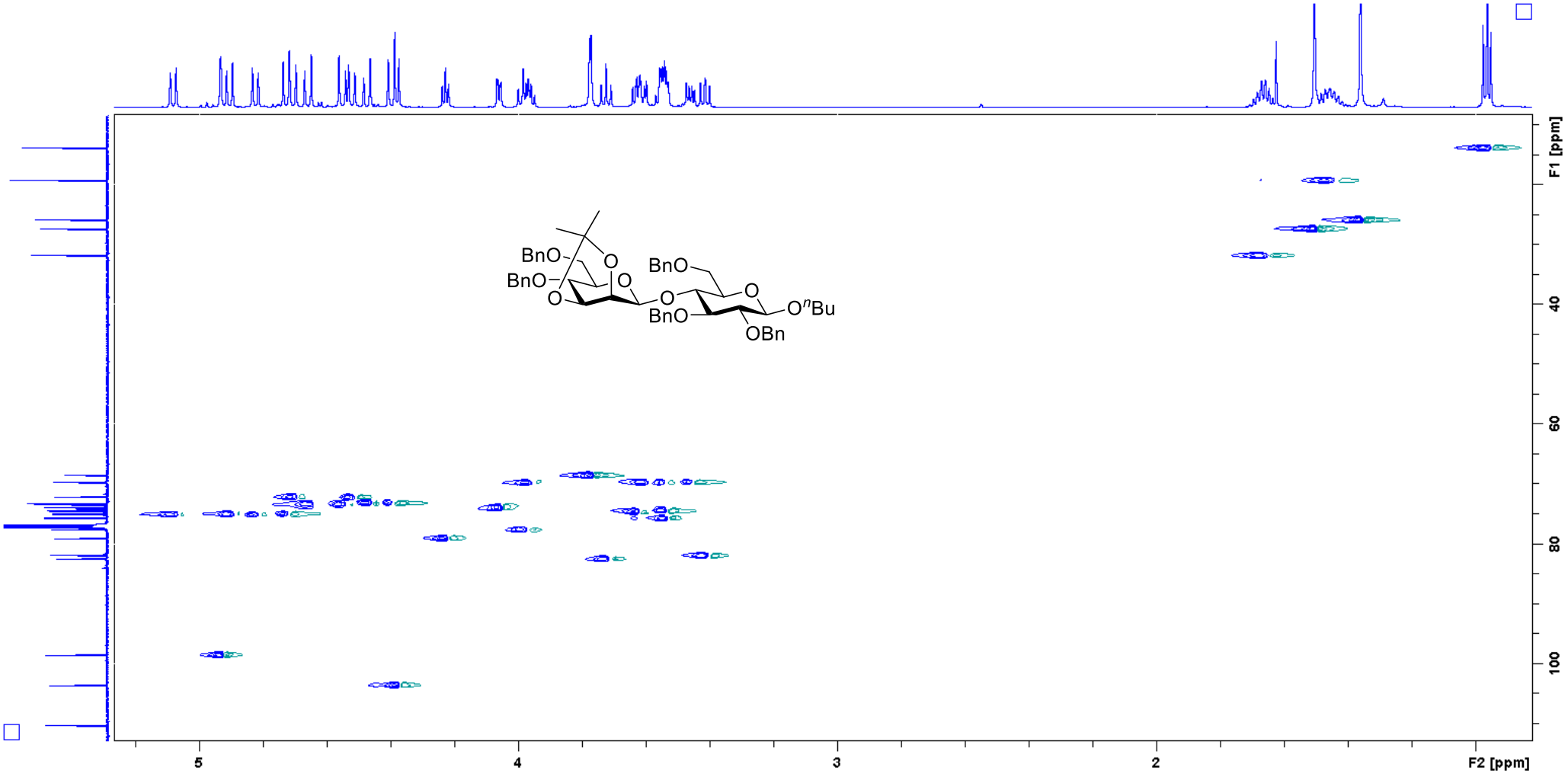
^{13}C NMR of compound **33**



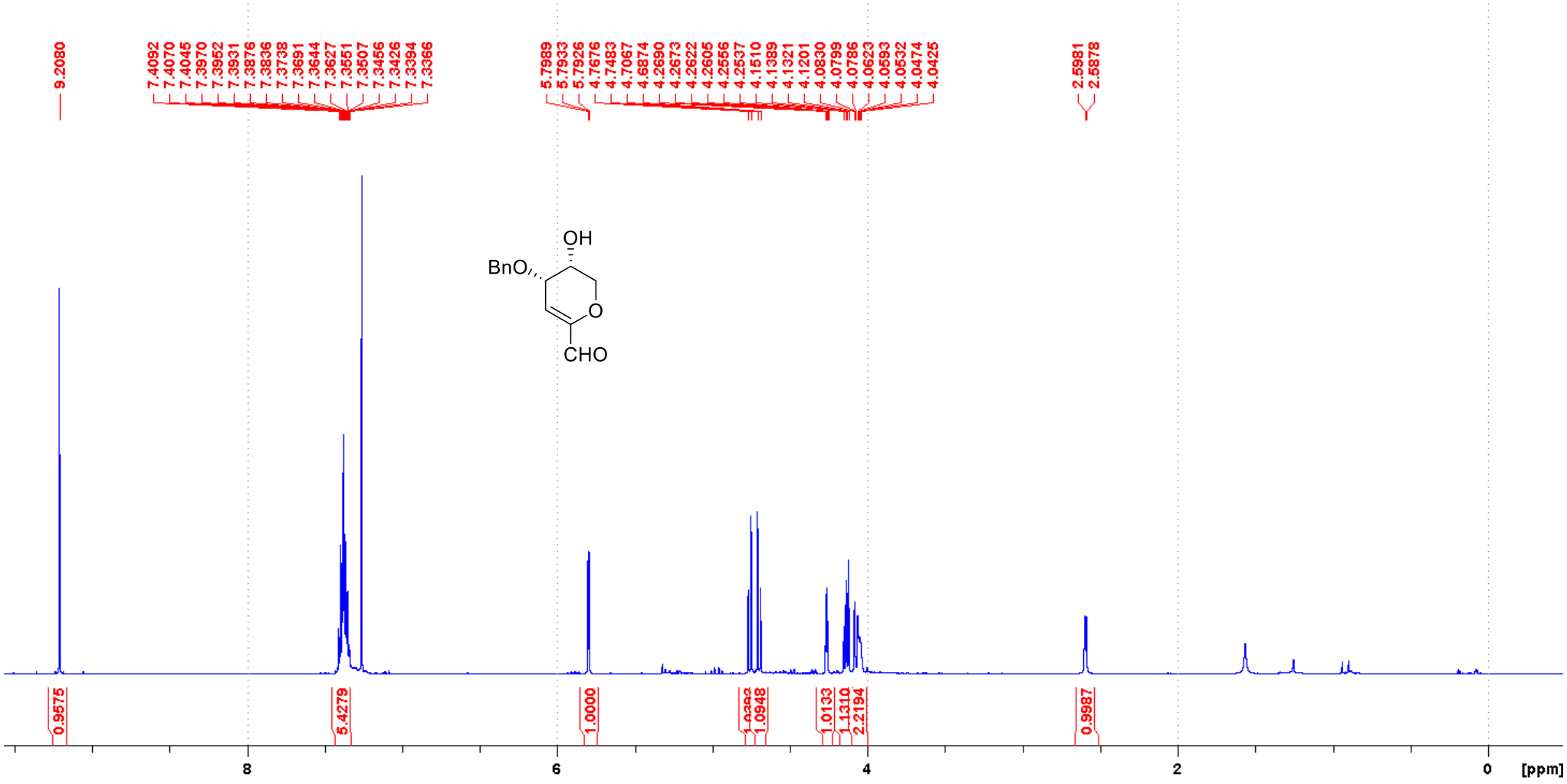
H-H COSY of compound **33**



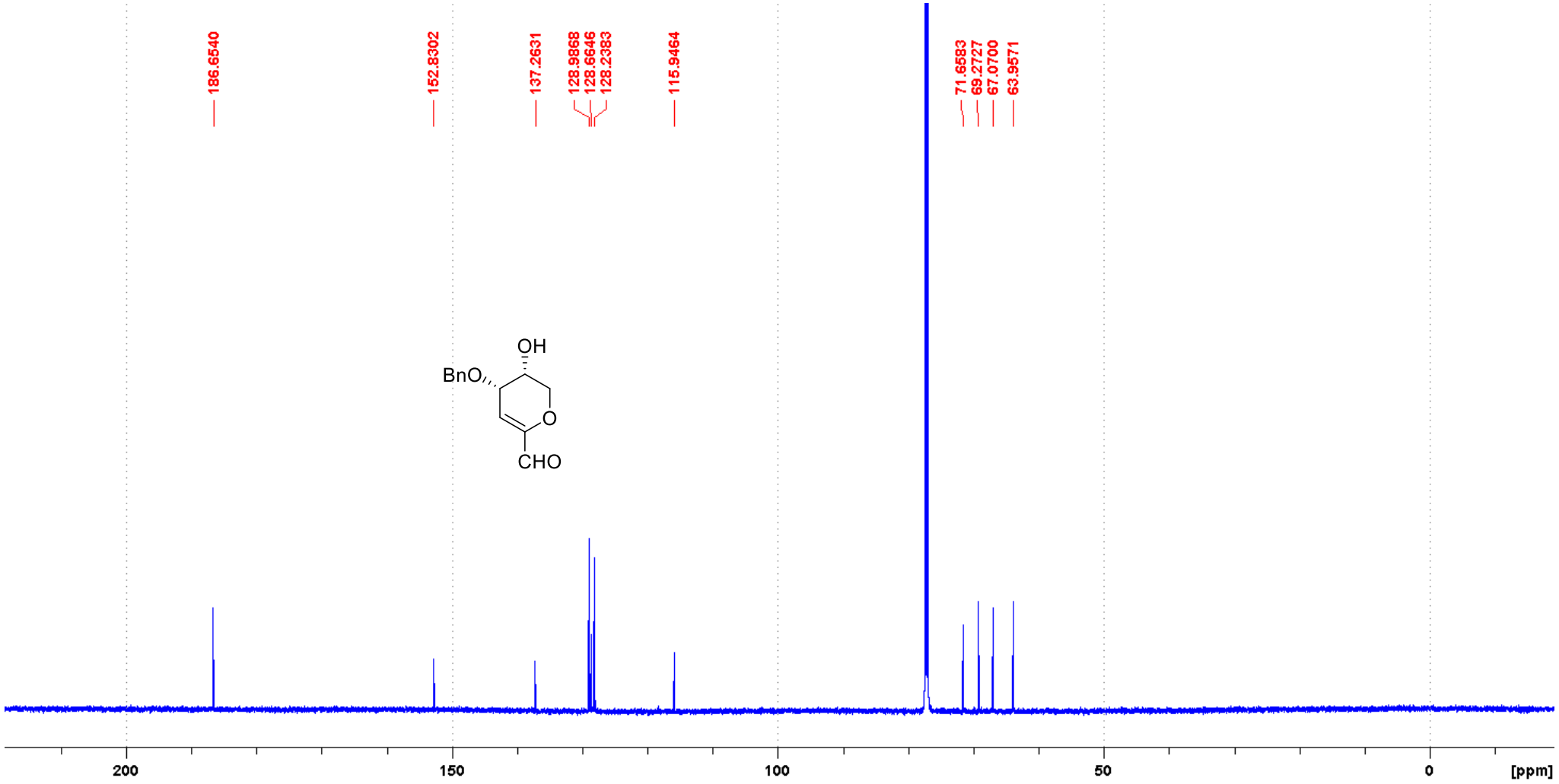
HSQC of compound **33**



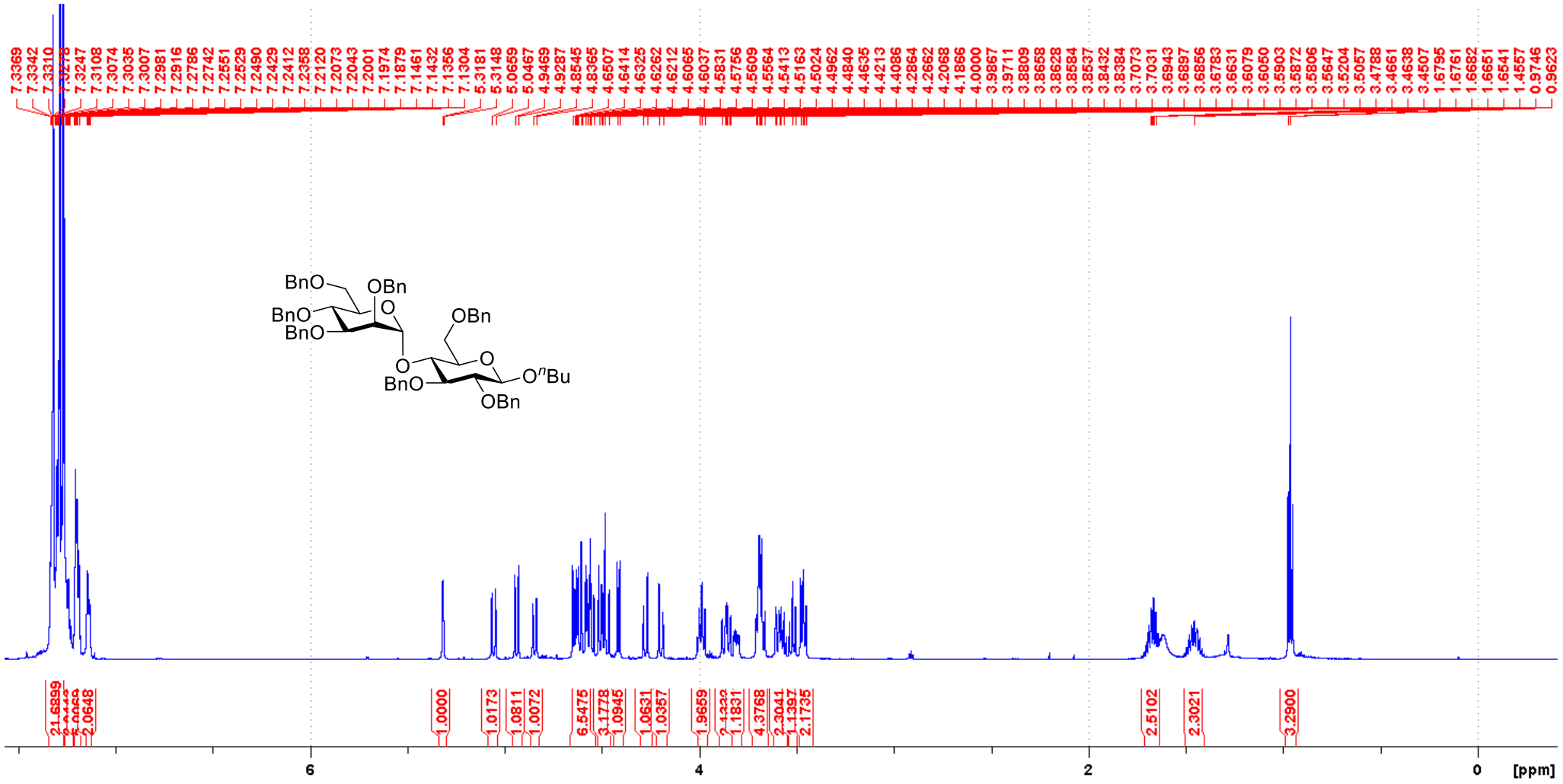
^{1}H NMR of compound **S19**



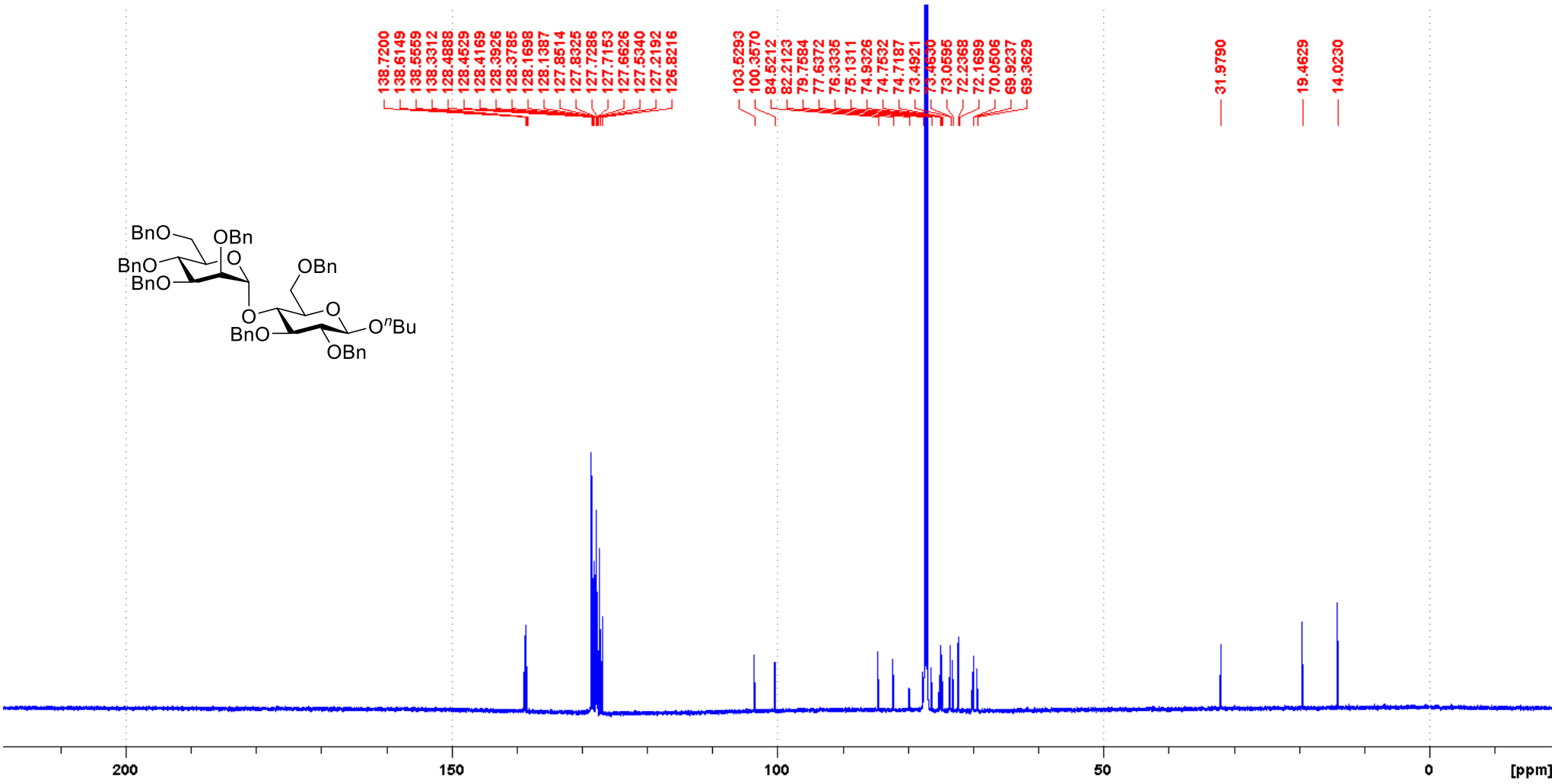
^{13}C NMR of compound **S19**



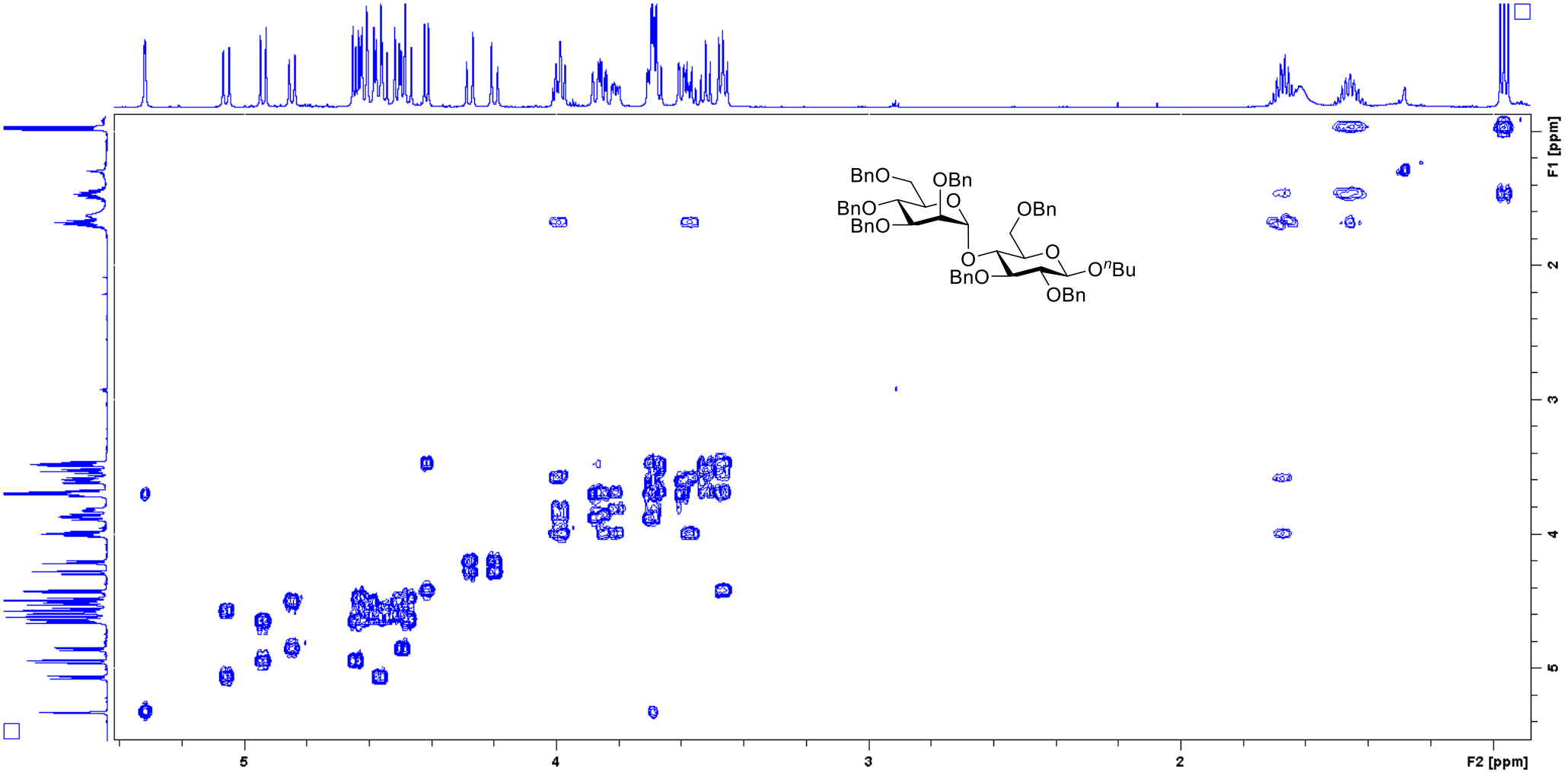
^{1}H NMR of compound **39*α***



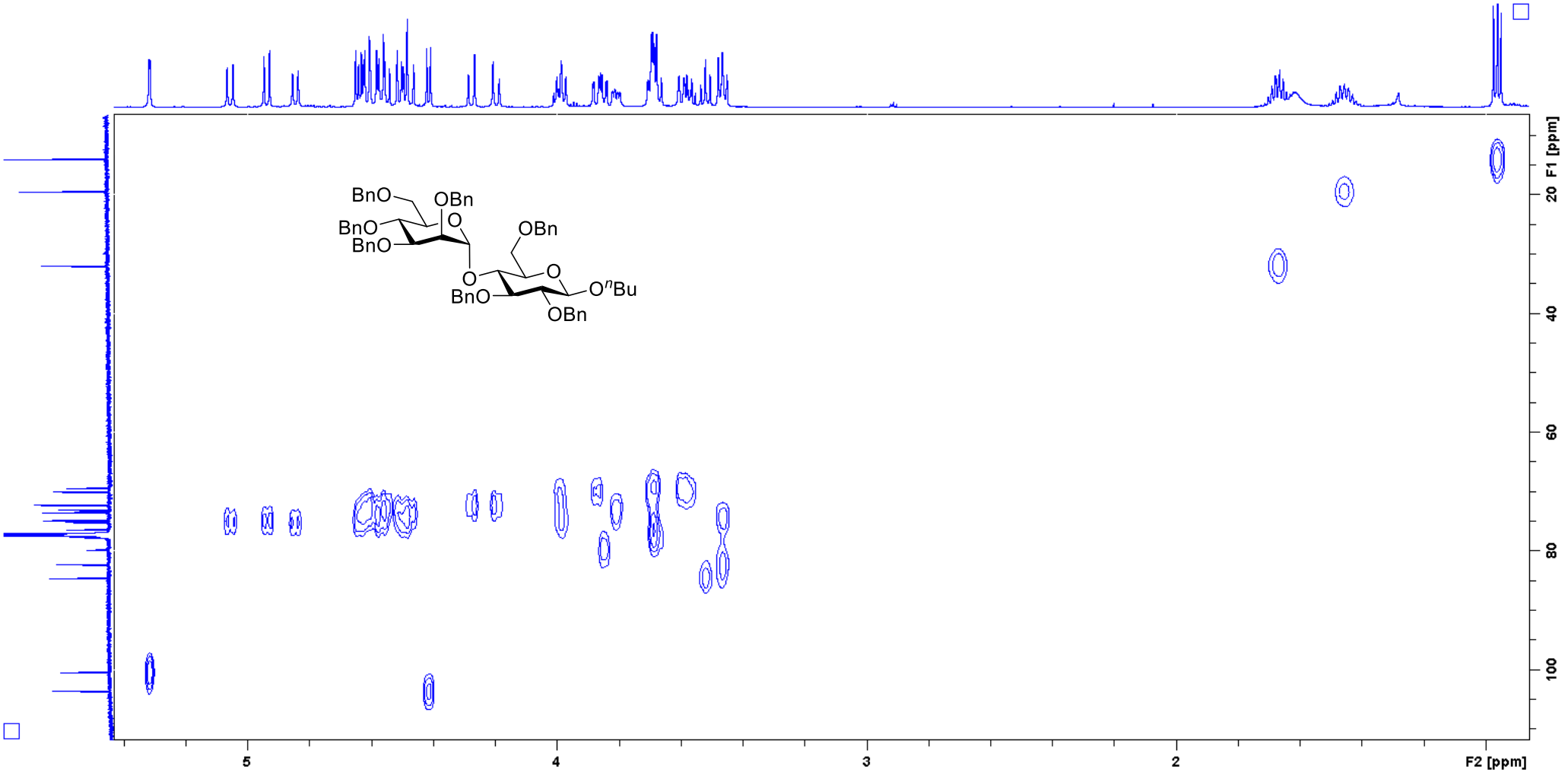
^{13}C NMR of compound **39*α***



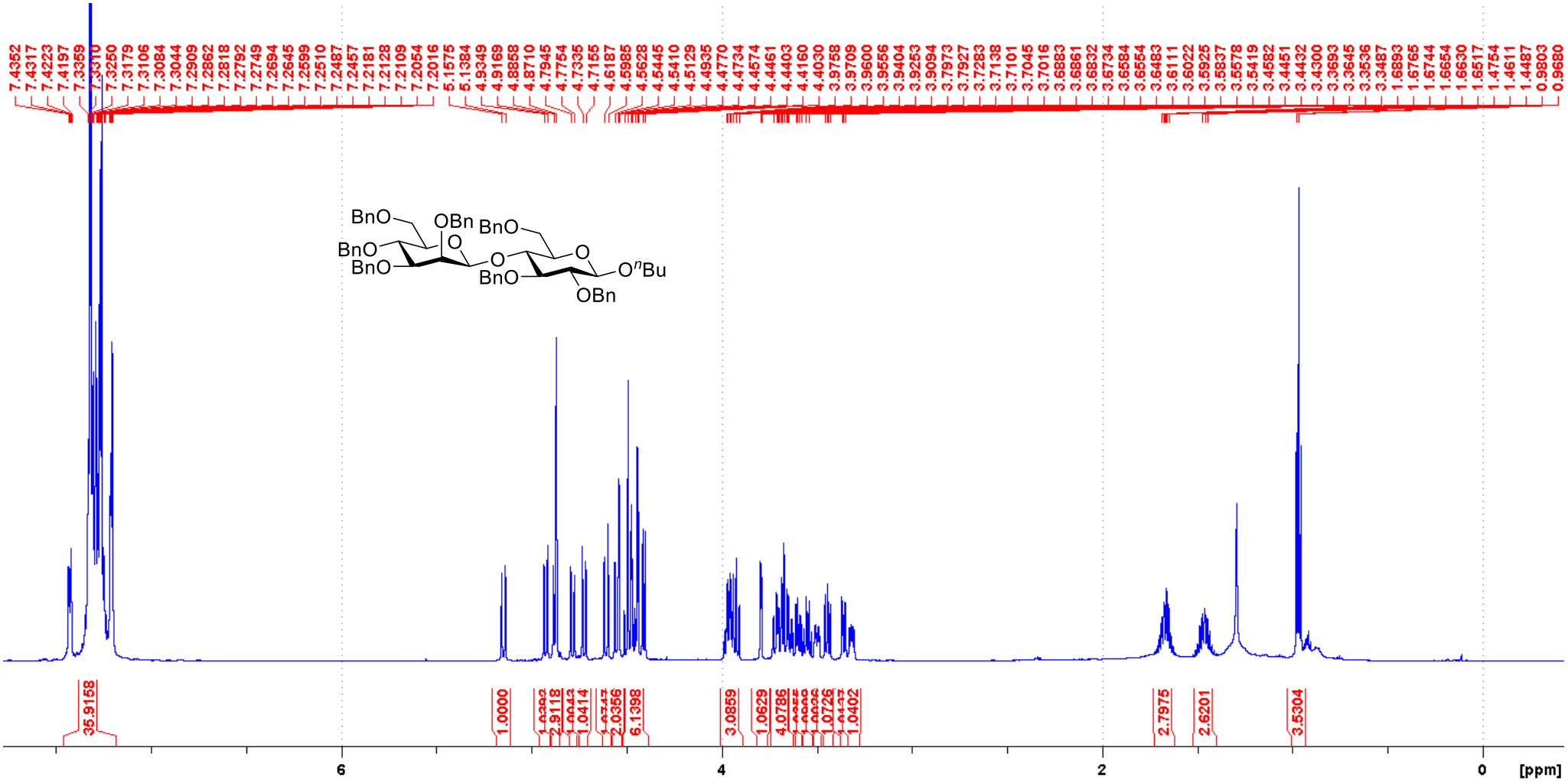
H-H COSY of compound **39*α***



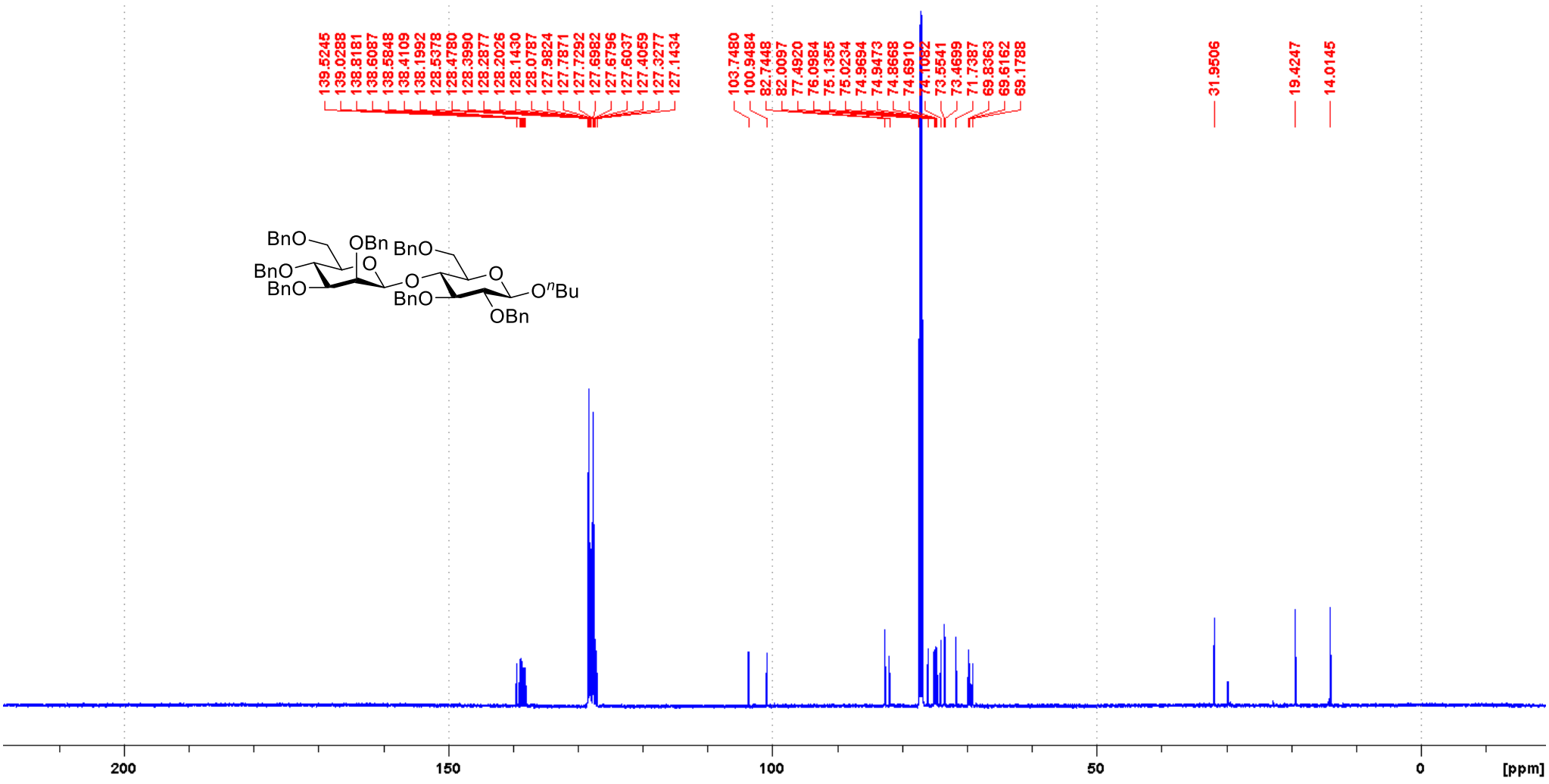
HSQC of compound **39*α***



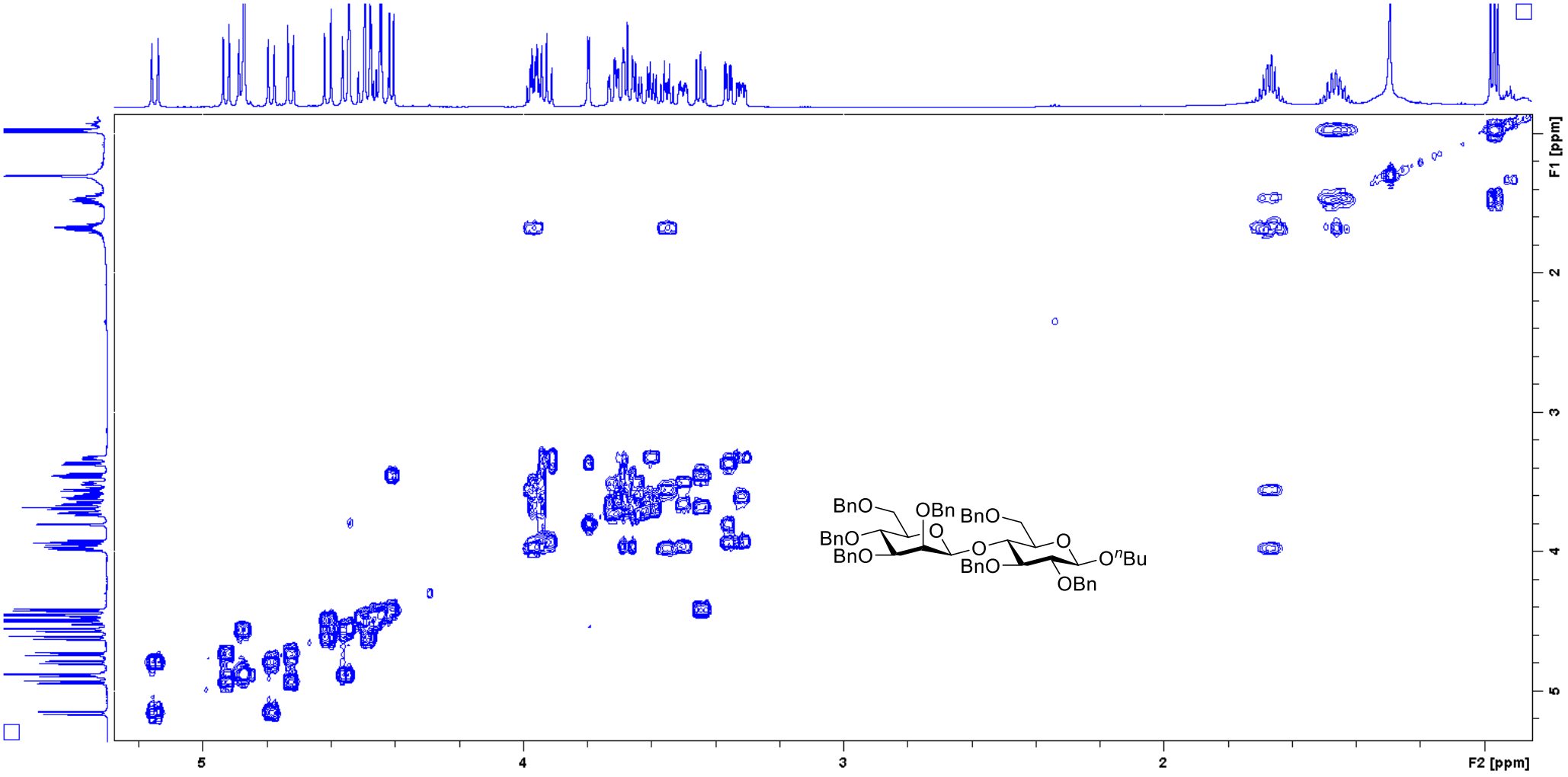
^{1}H NMR of compound **39*β***



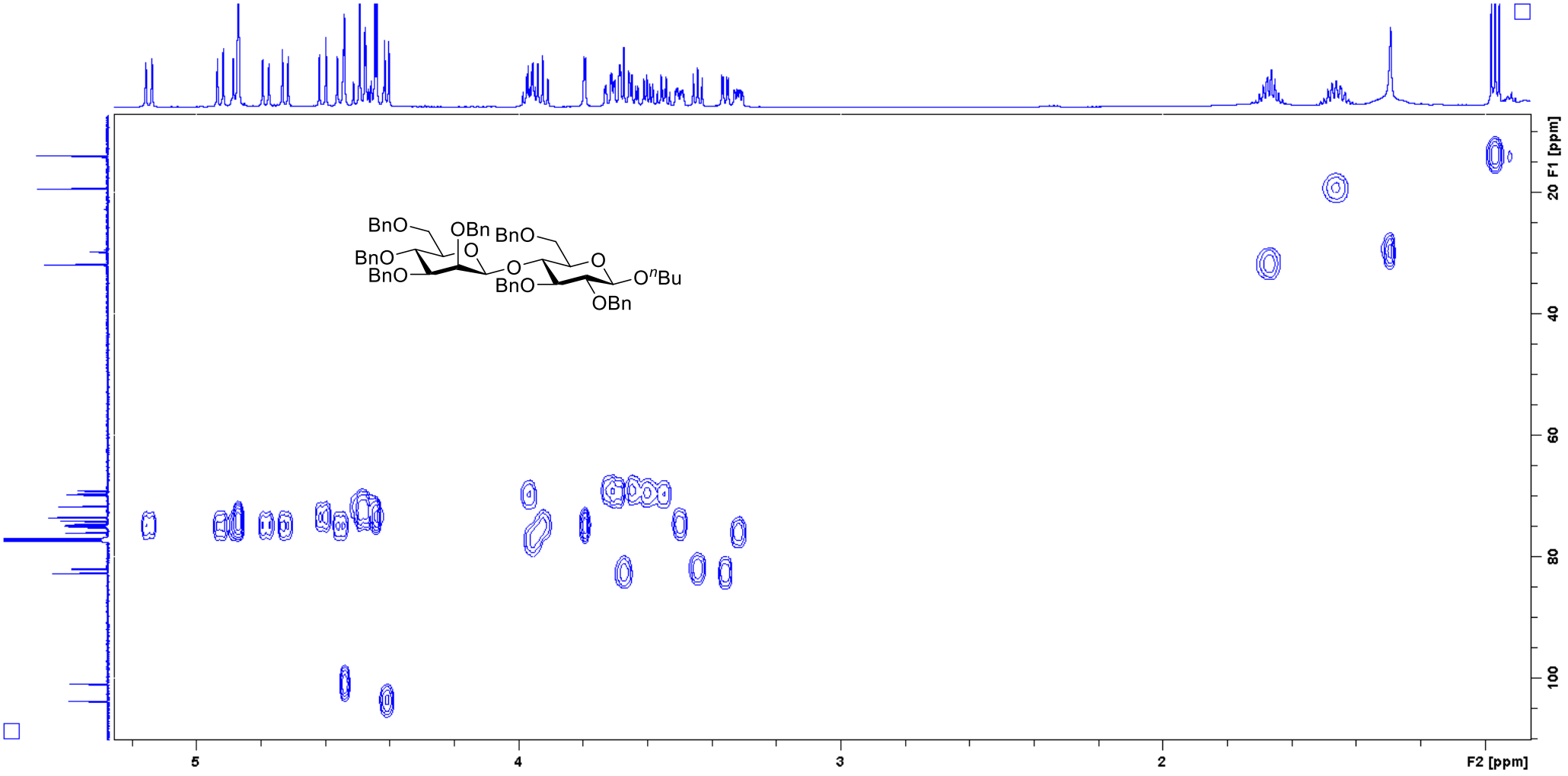
^{13}C NMR of compound ***39β***



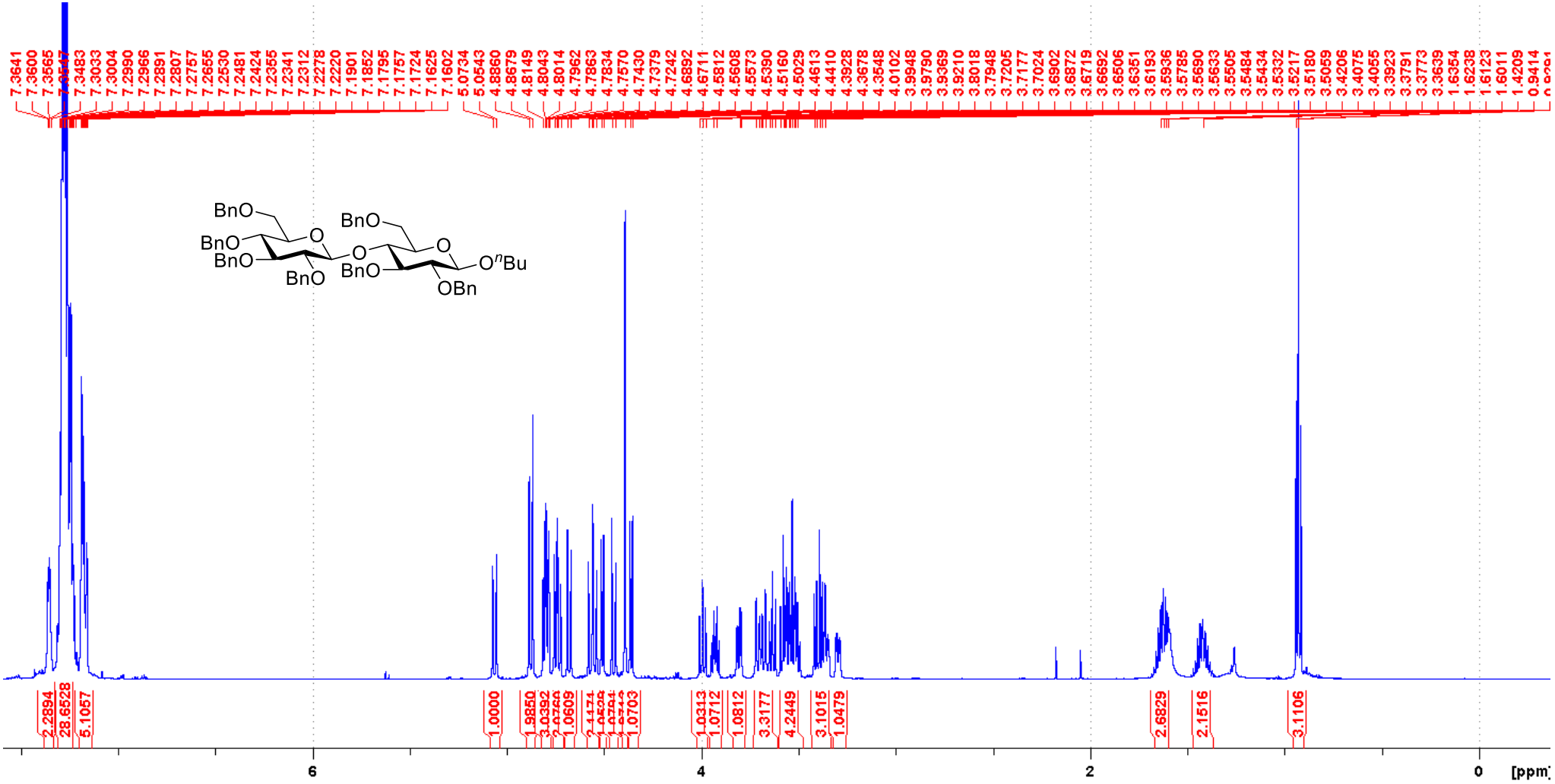
H-H COSY of compound **39*β***



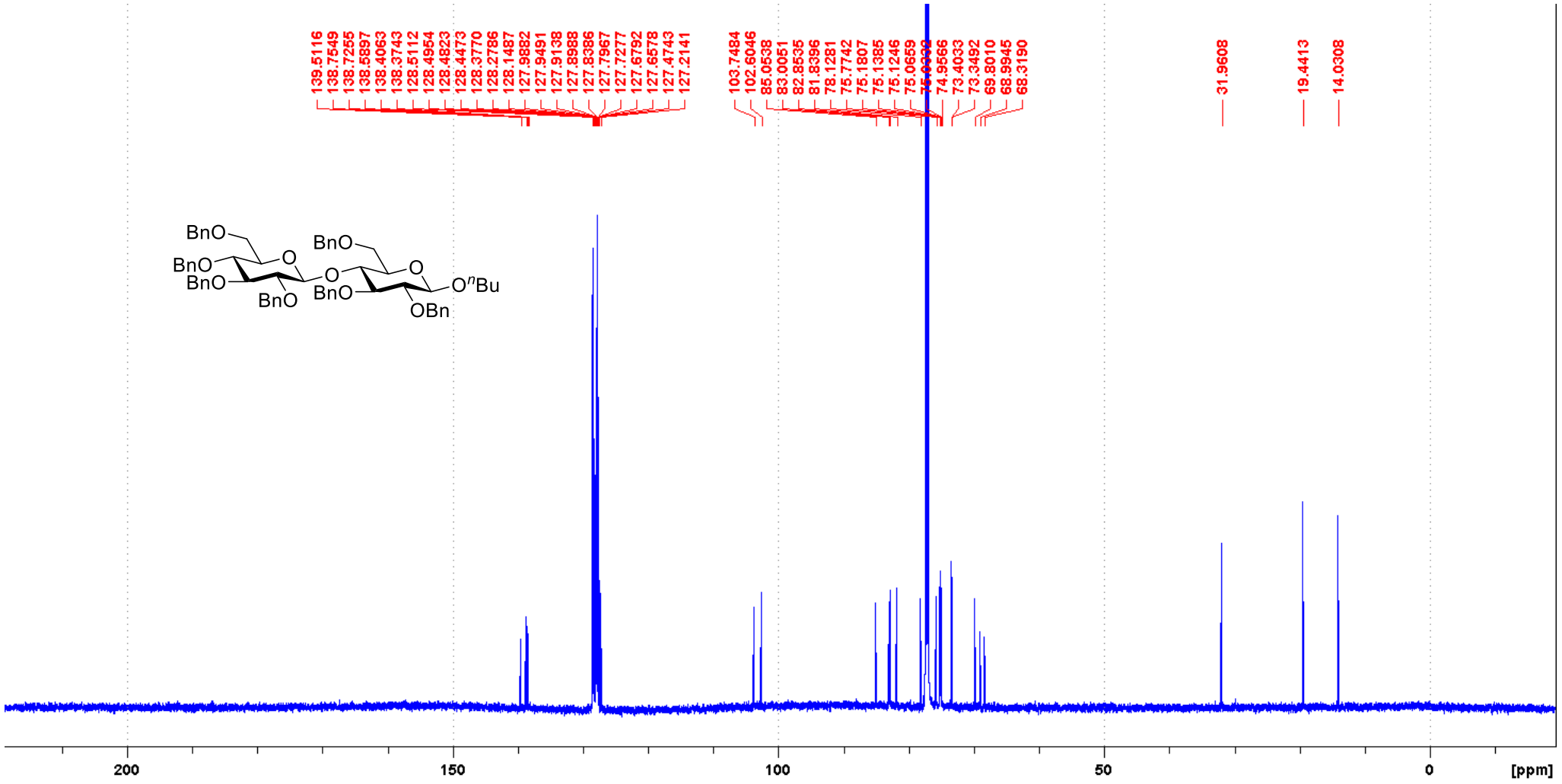
HSQC of compound **39*β***



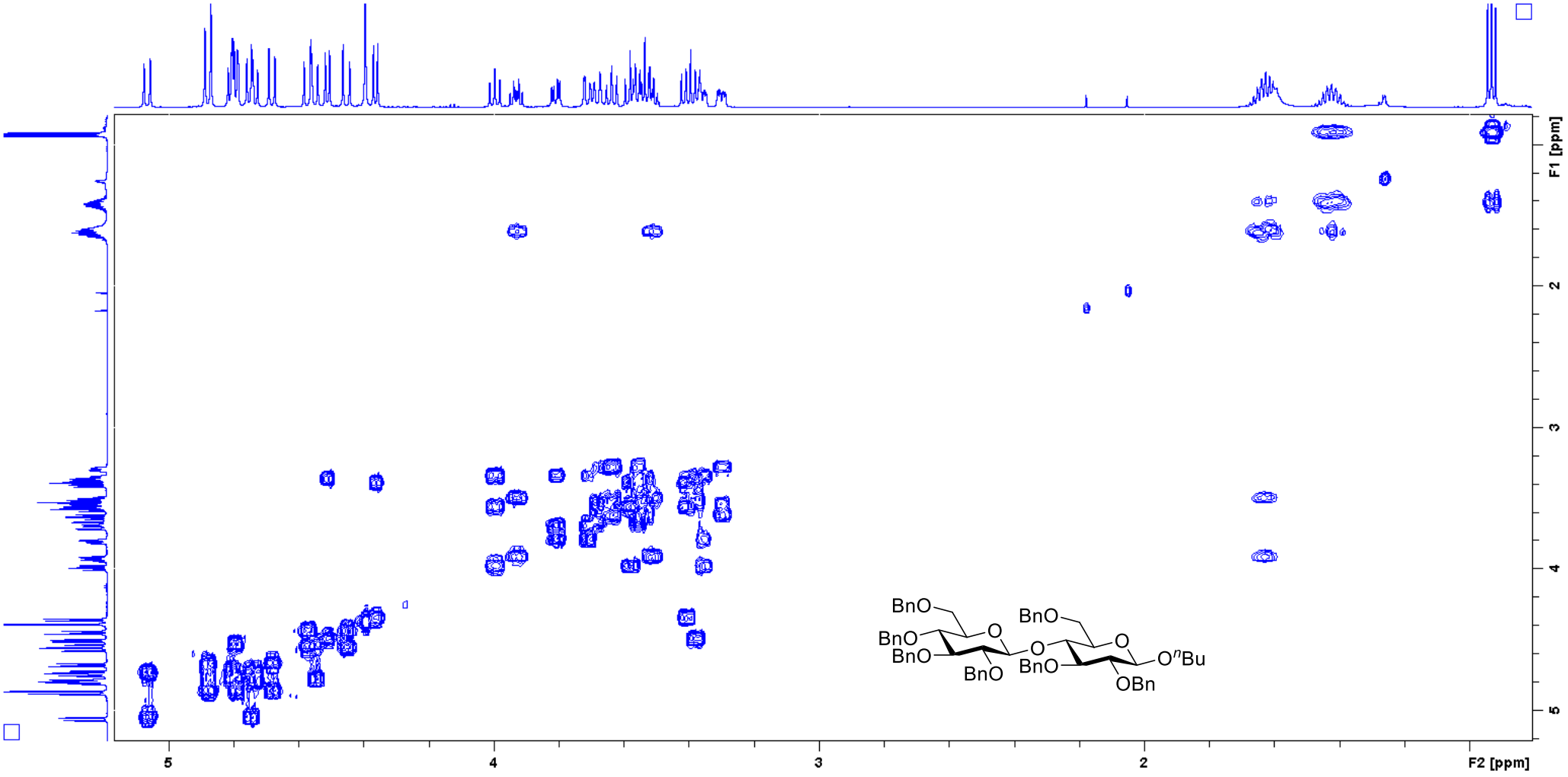
^{1}H NMR of compound **40**



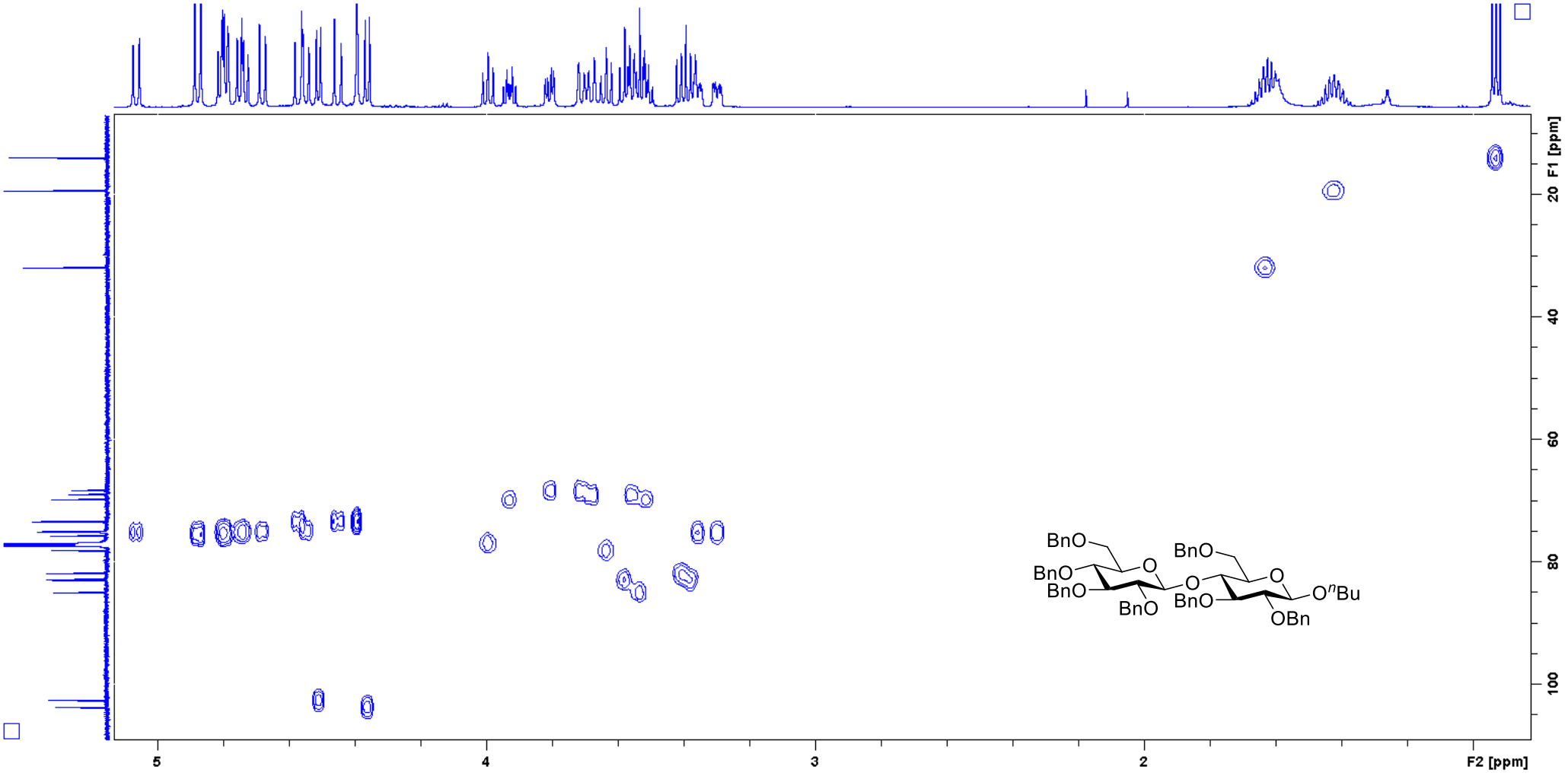
^{13}C NMR of compound **40**



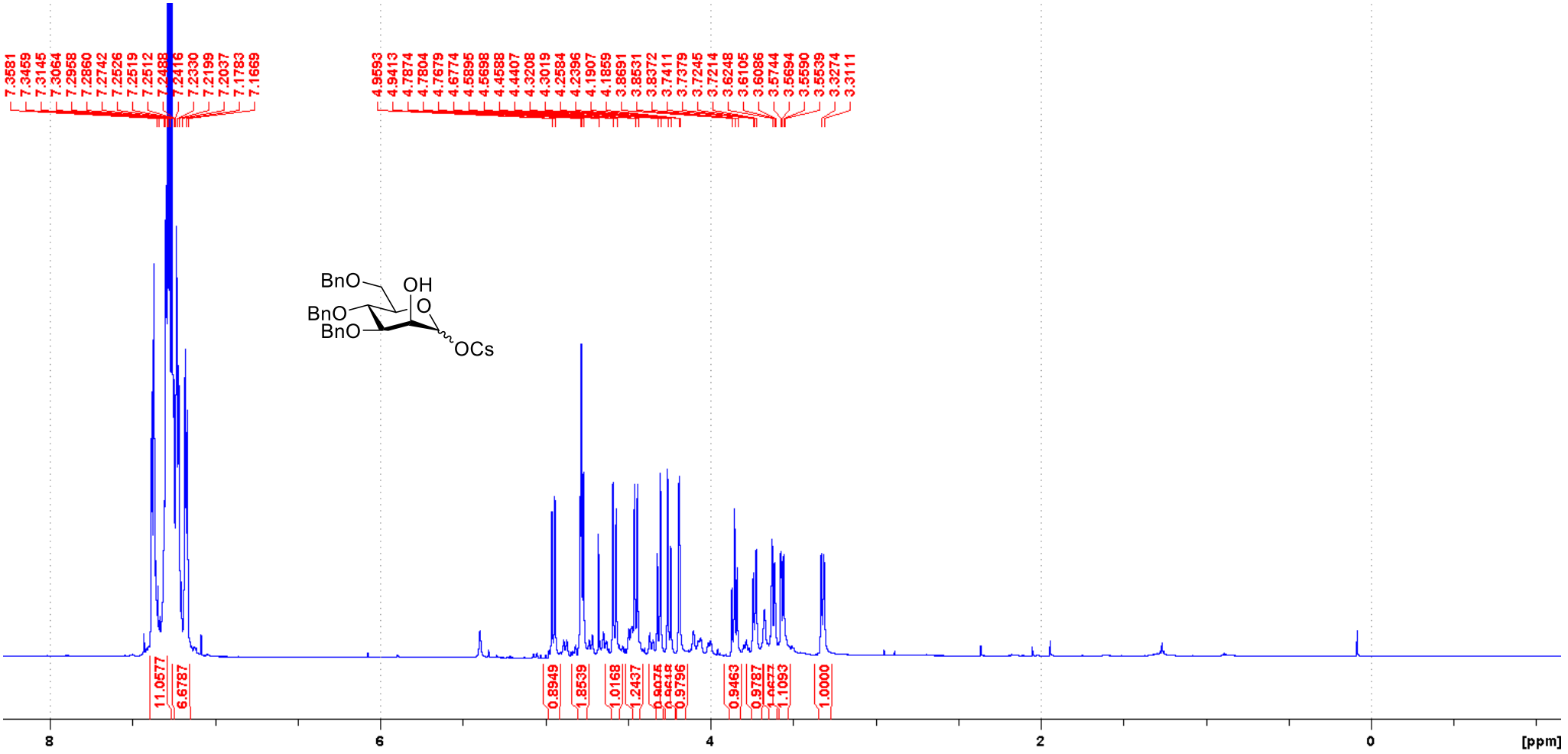
H-H COSY of compound **40**



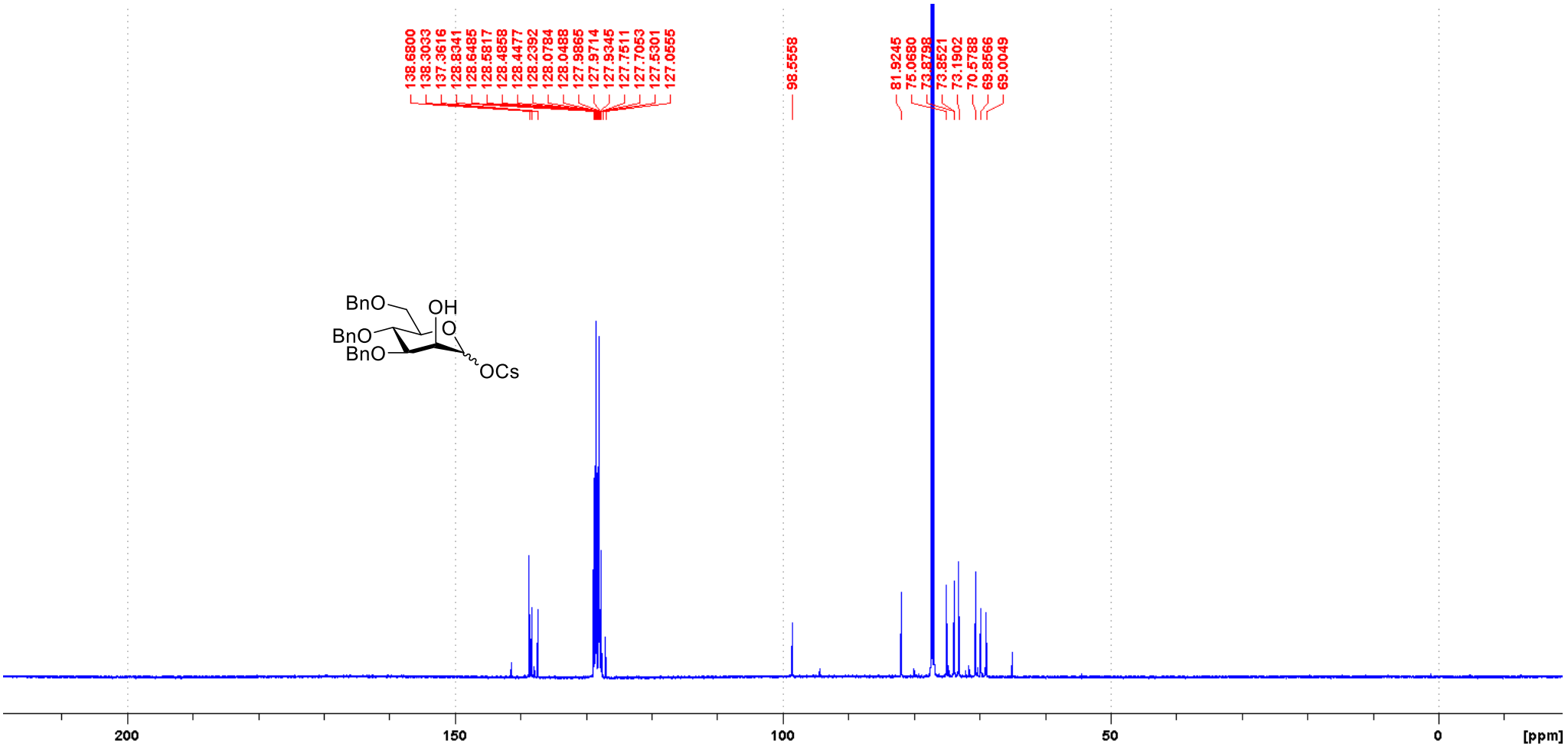
HSQC of compound **40**



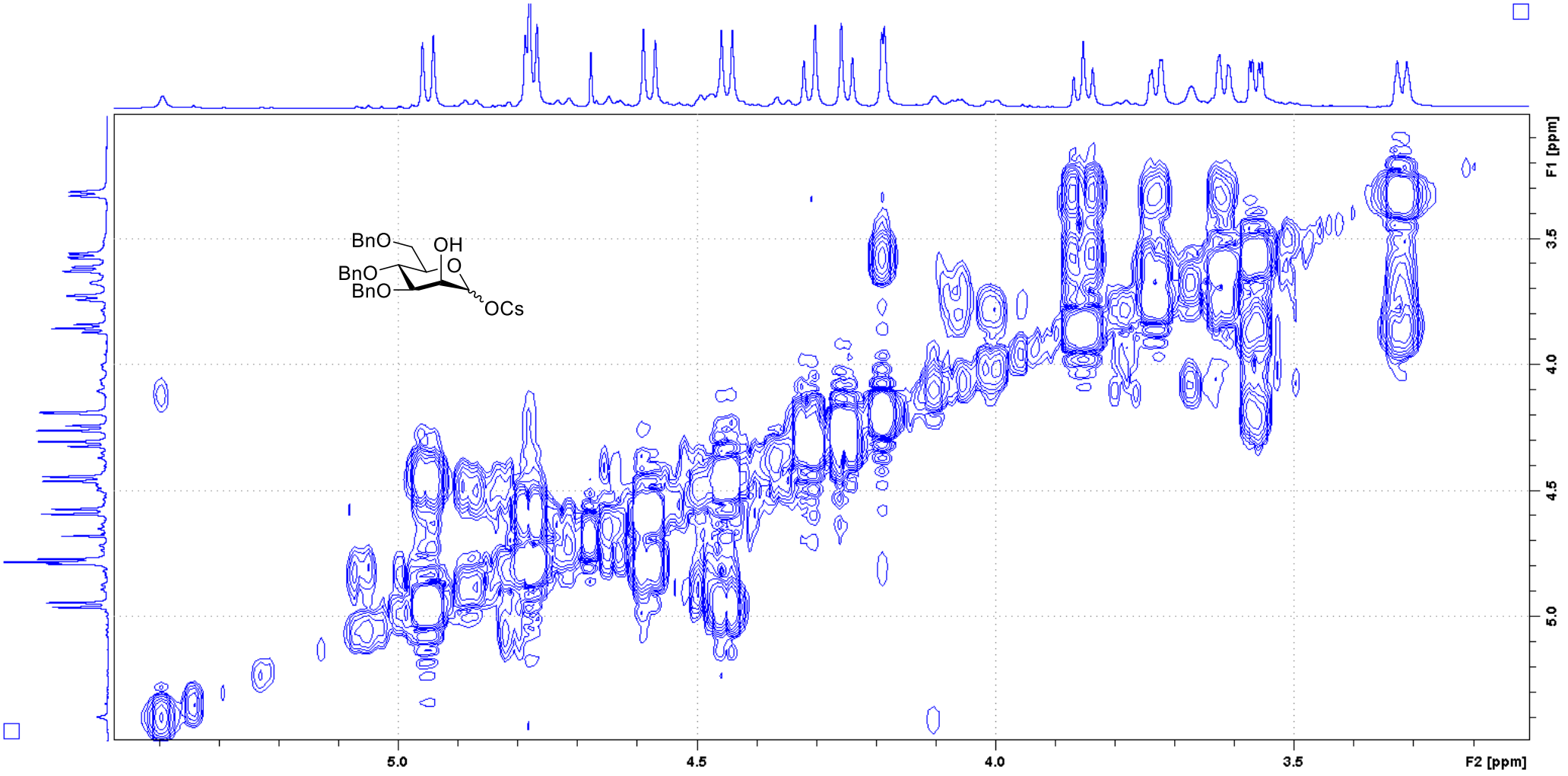
^{1}H NMR of compound **42**



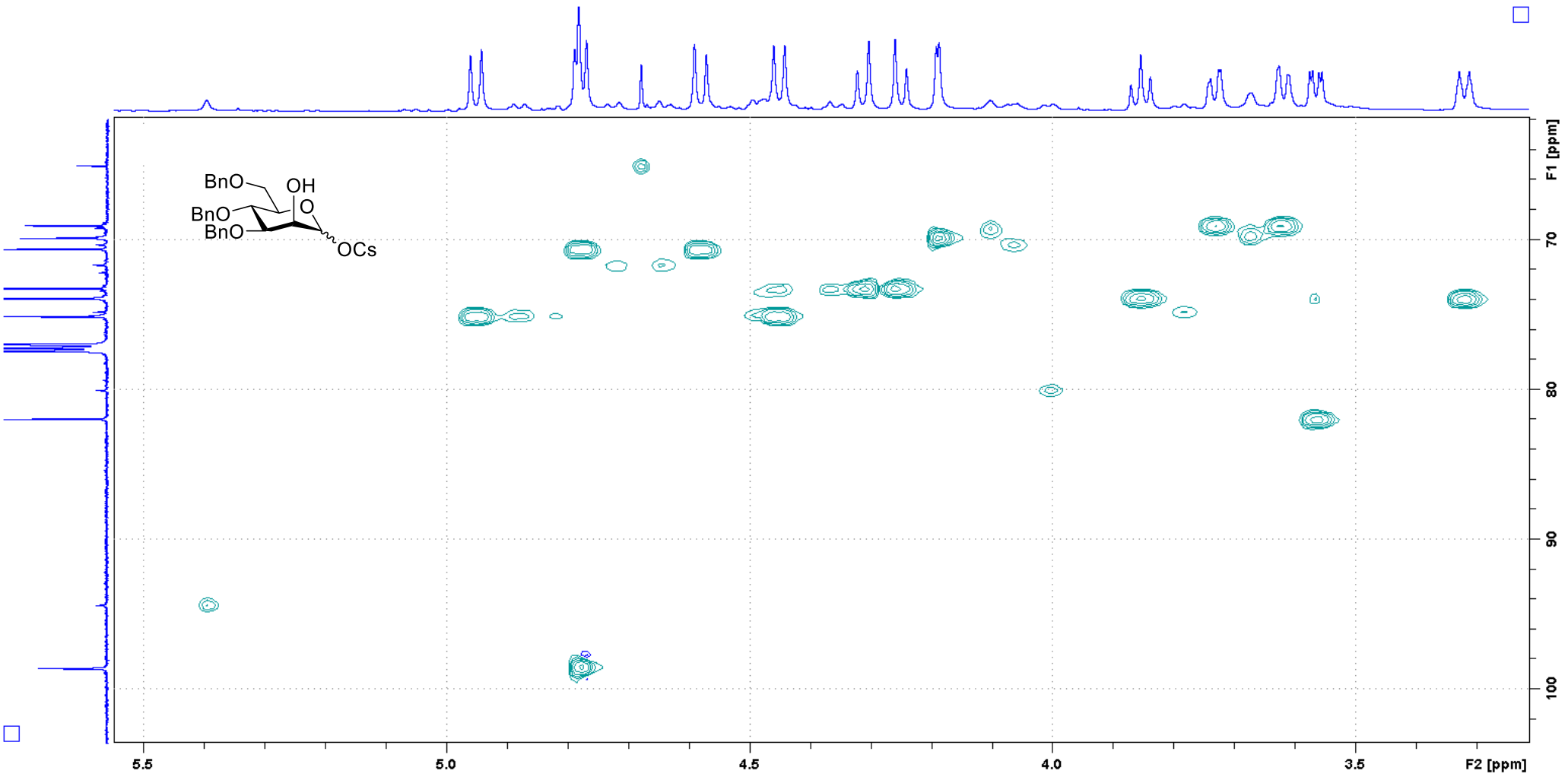
^{13}C NMR of compound **42**



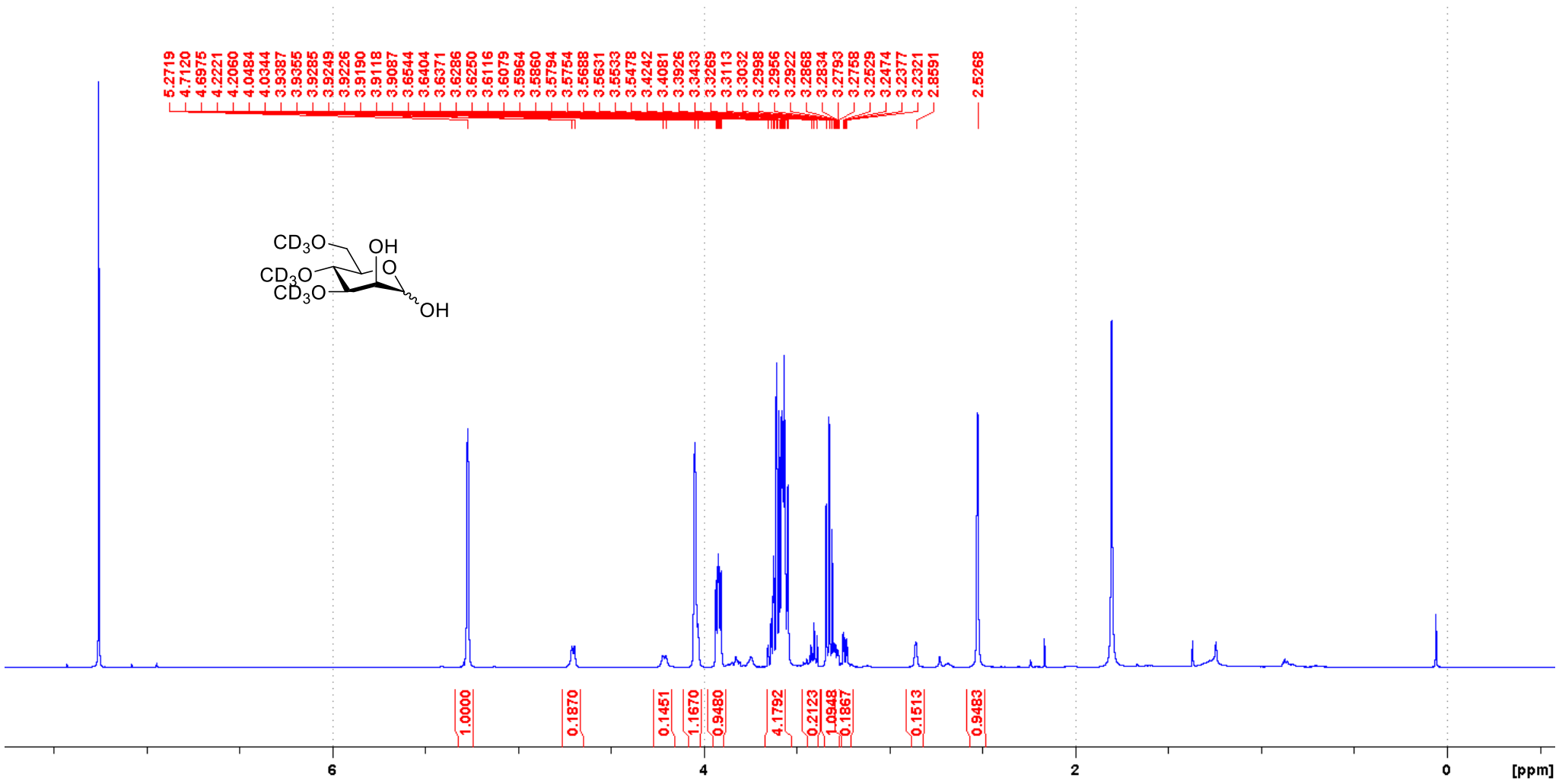
H-H COSY of compound **42**



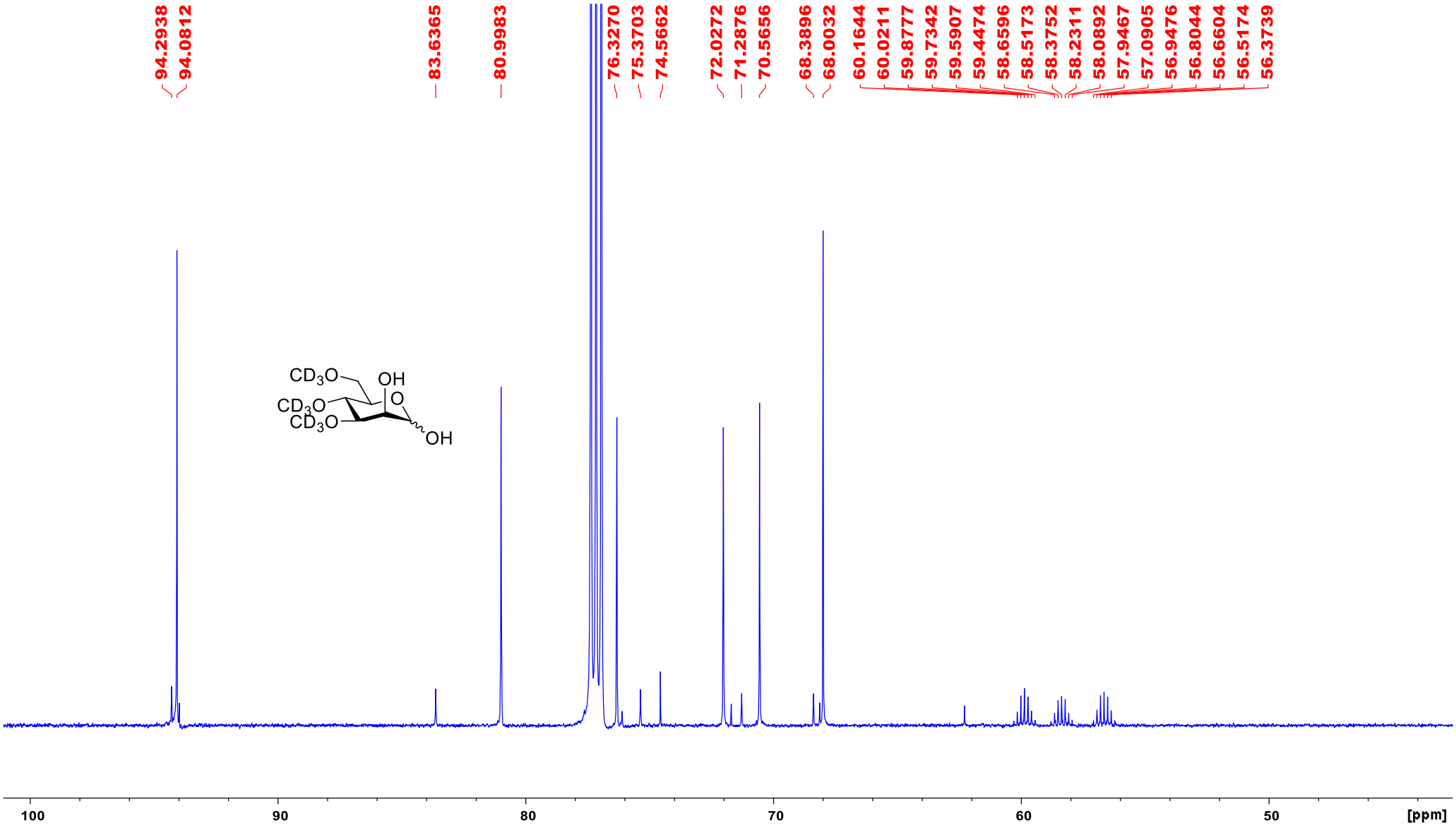
HSQC of compound **42**



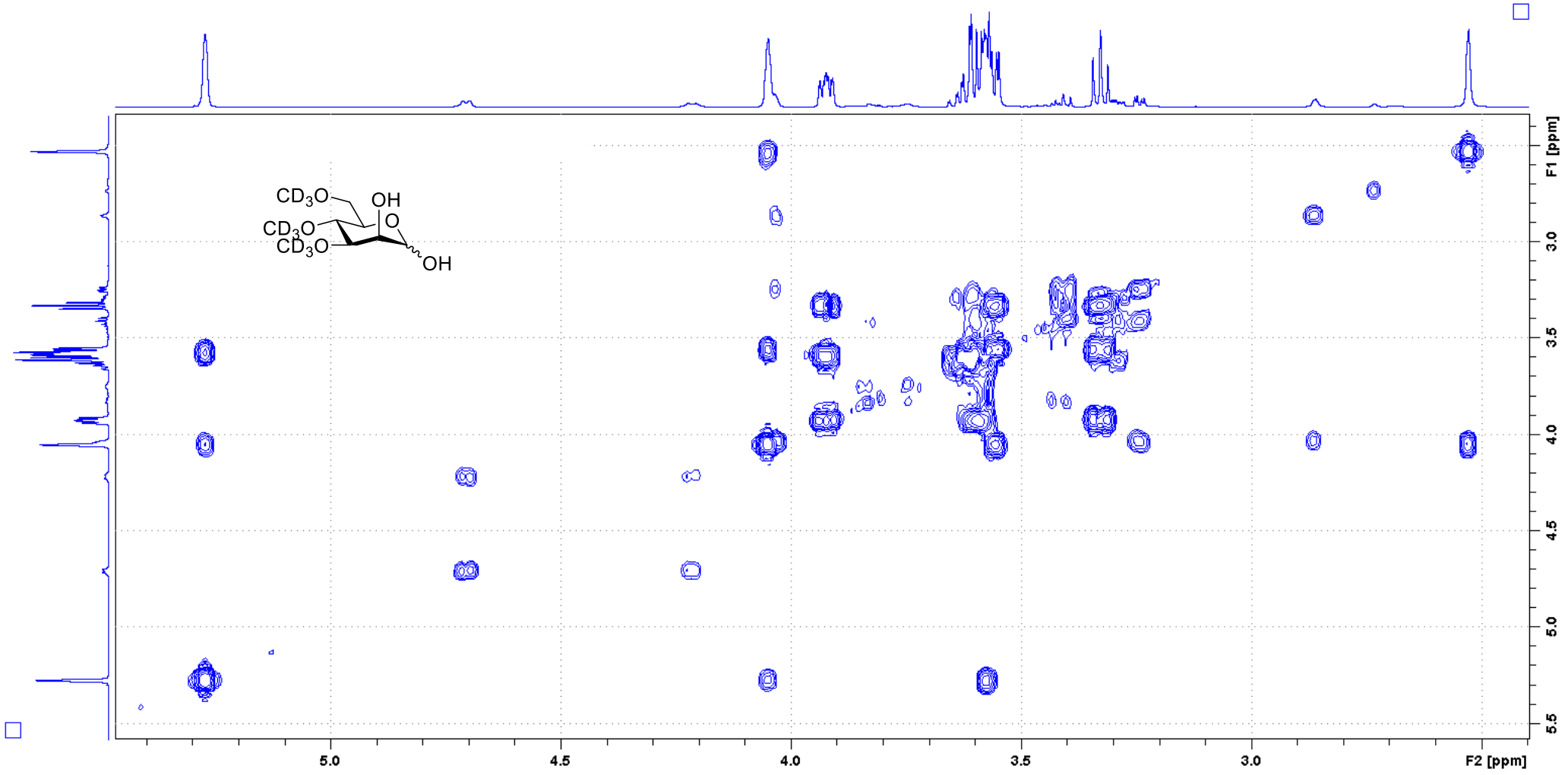
^{1}H NMR of compound **44**



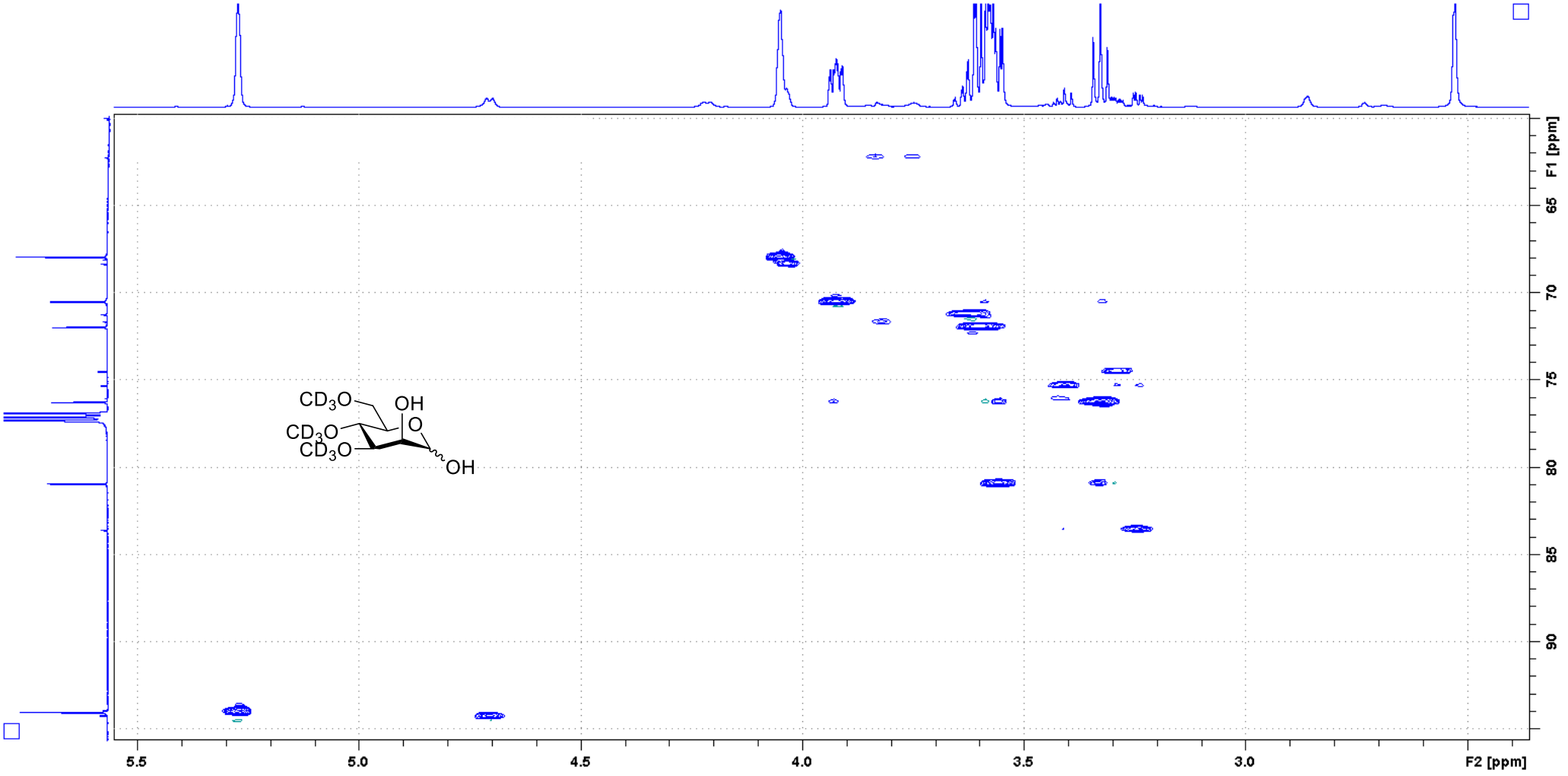
^{13}C NMR of compound **44**



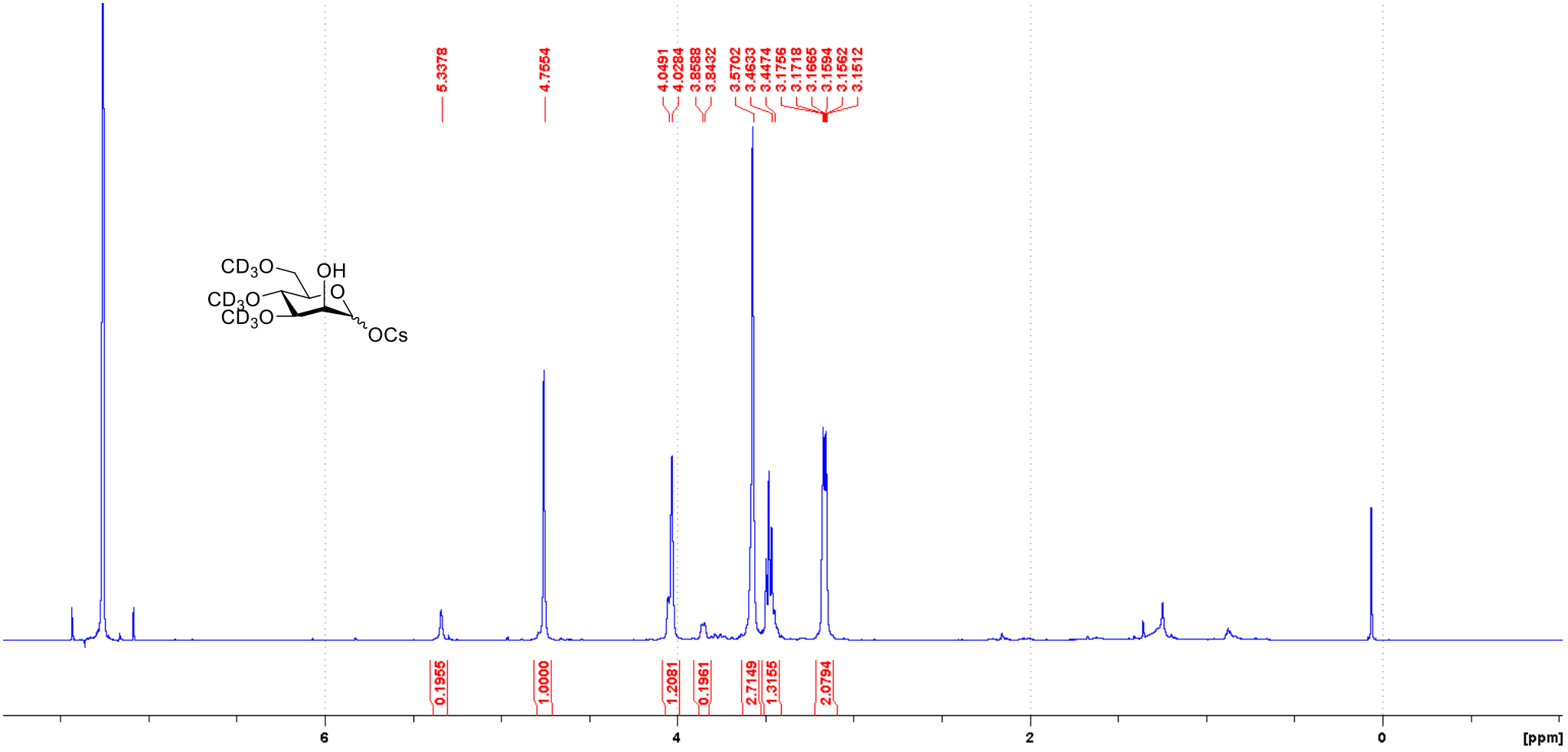
H-H COSY of compound **44**



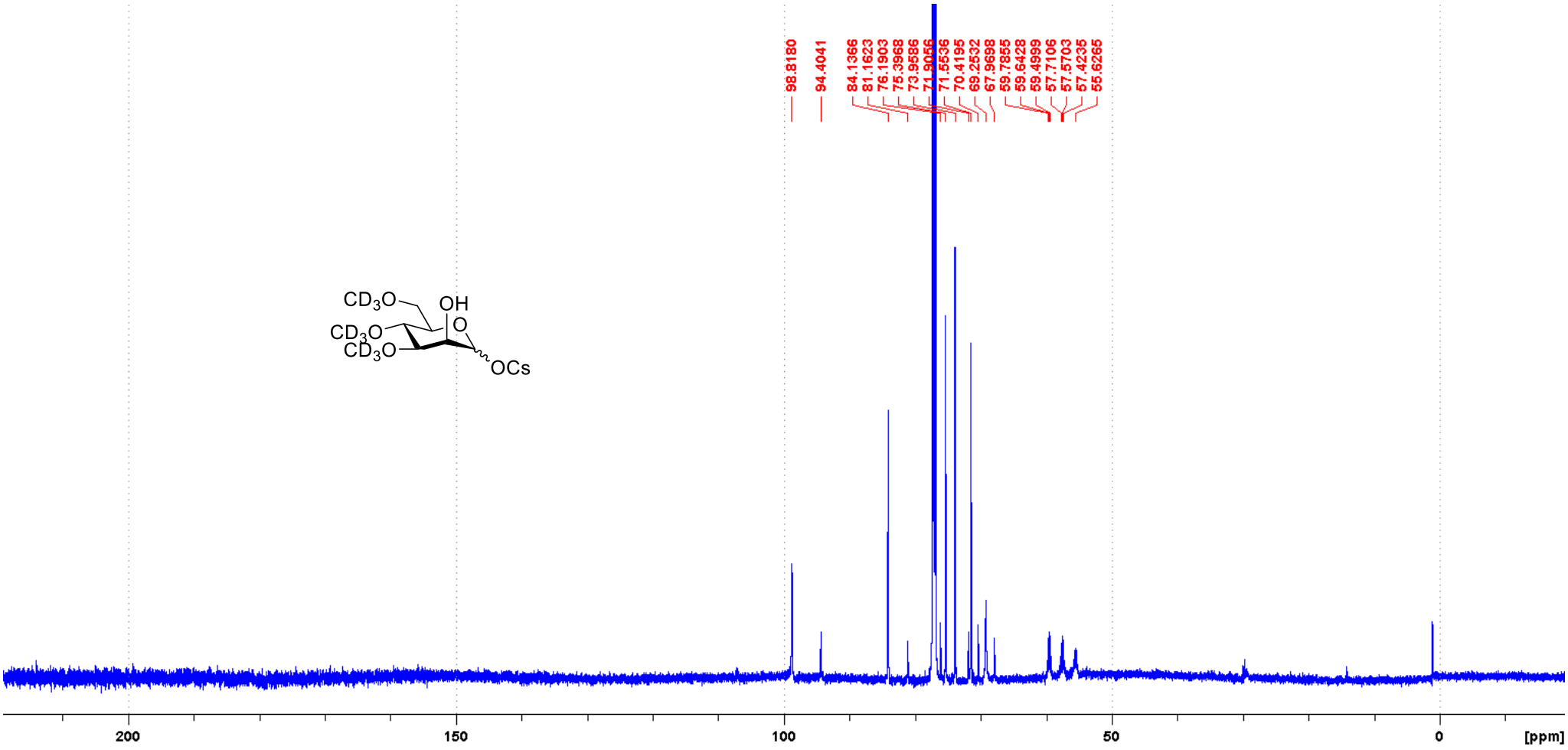
HSQC of compound **44**



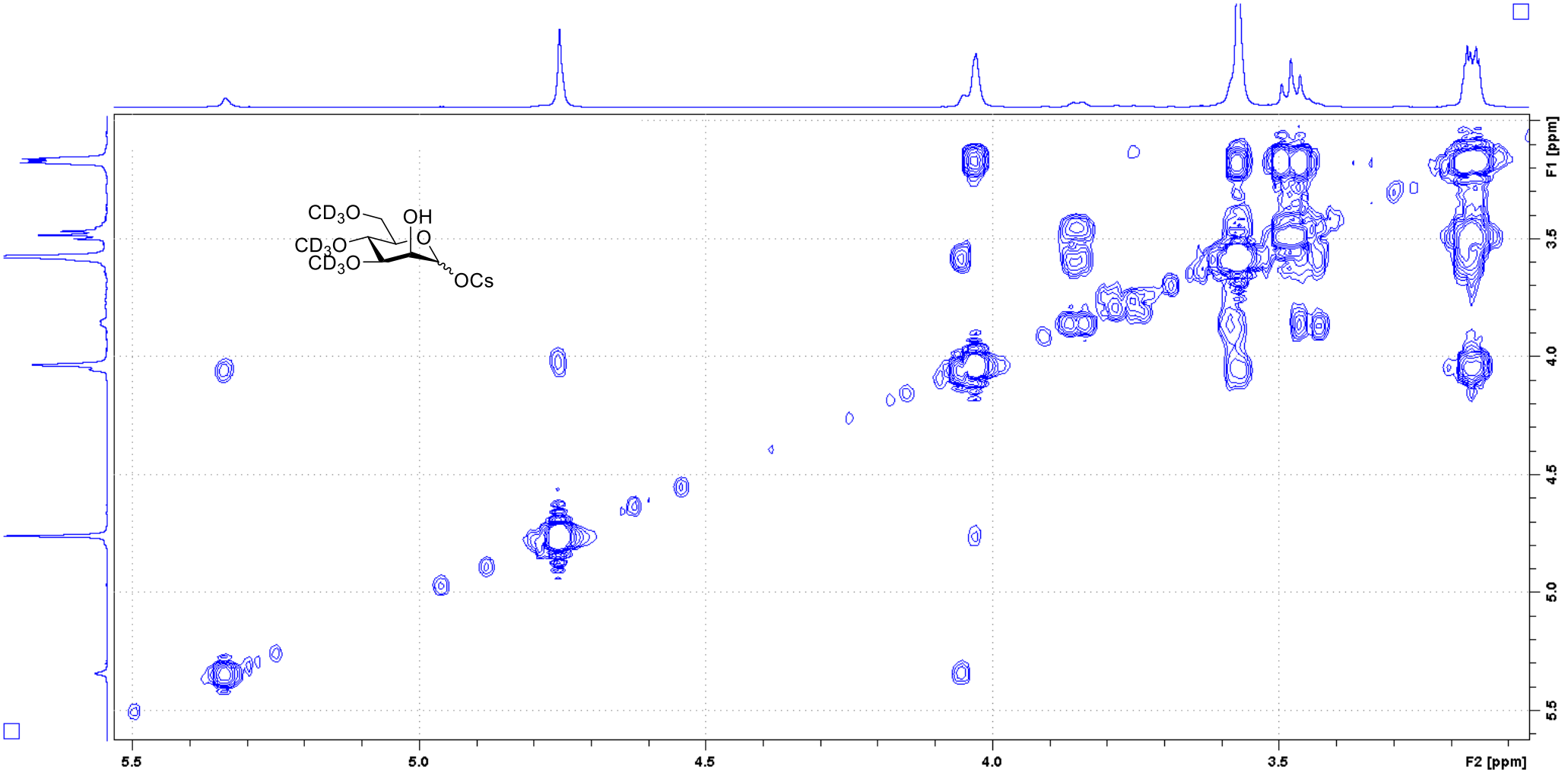
^{1}H NMR of compound **45**



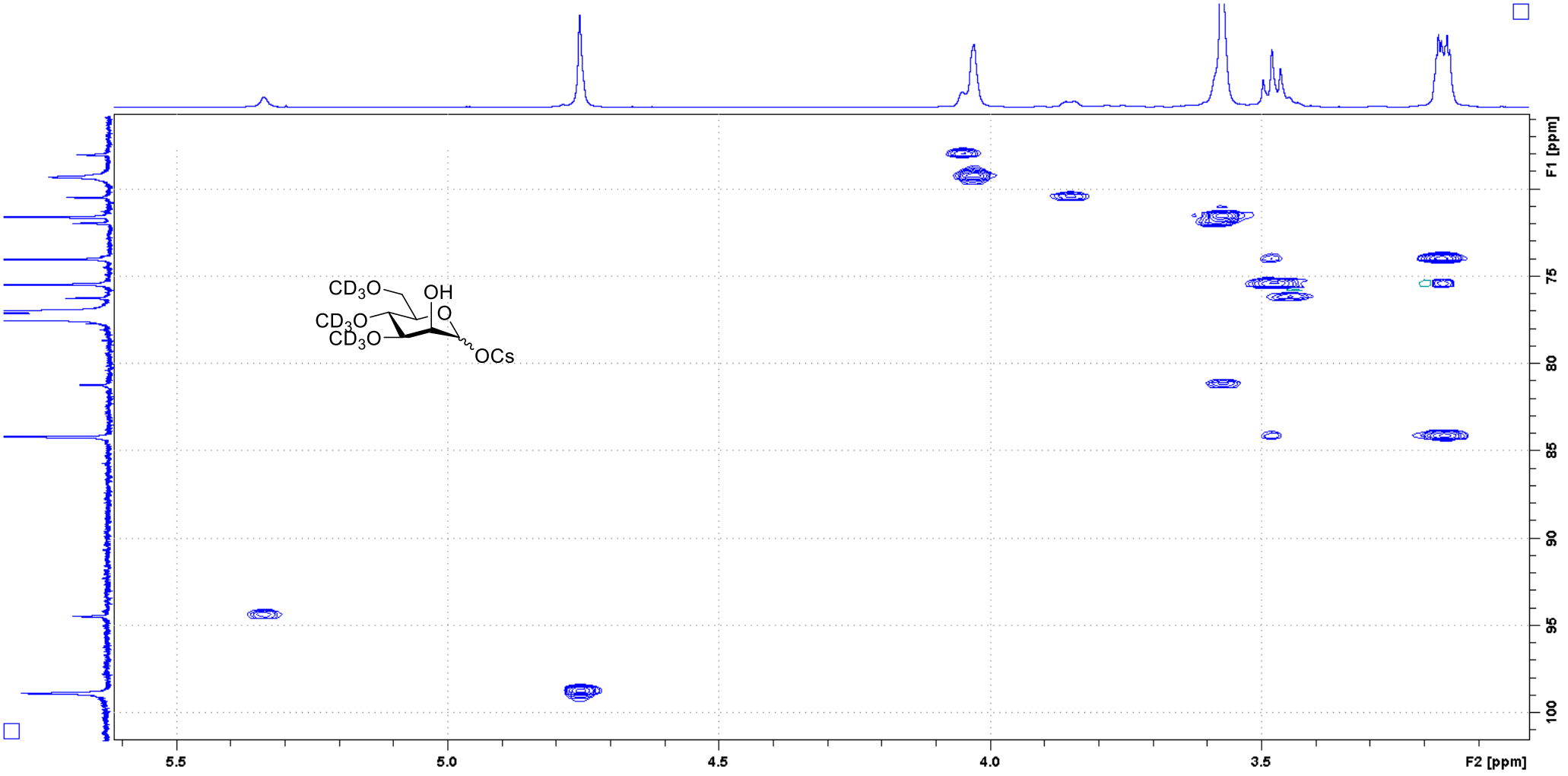
^{13}C NMR of compound **45**



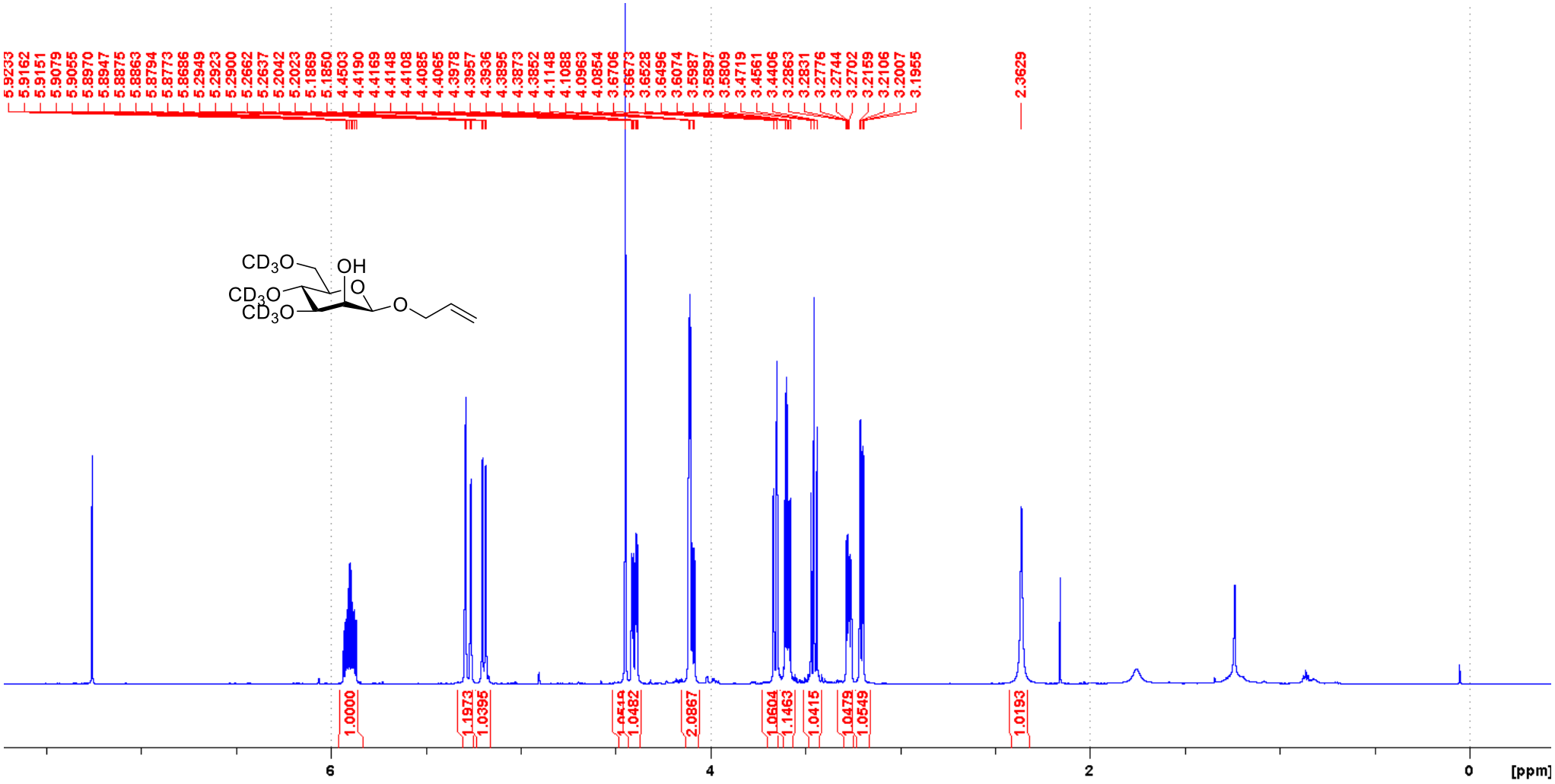
H-H COSY of compound **45**



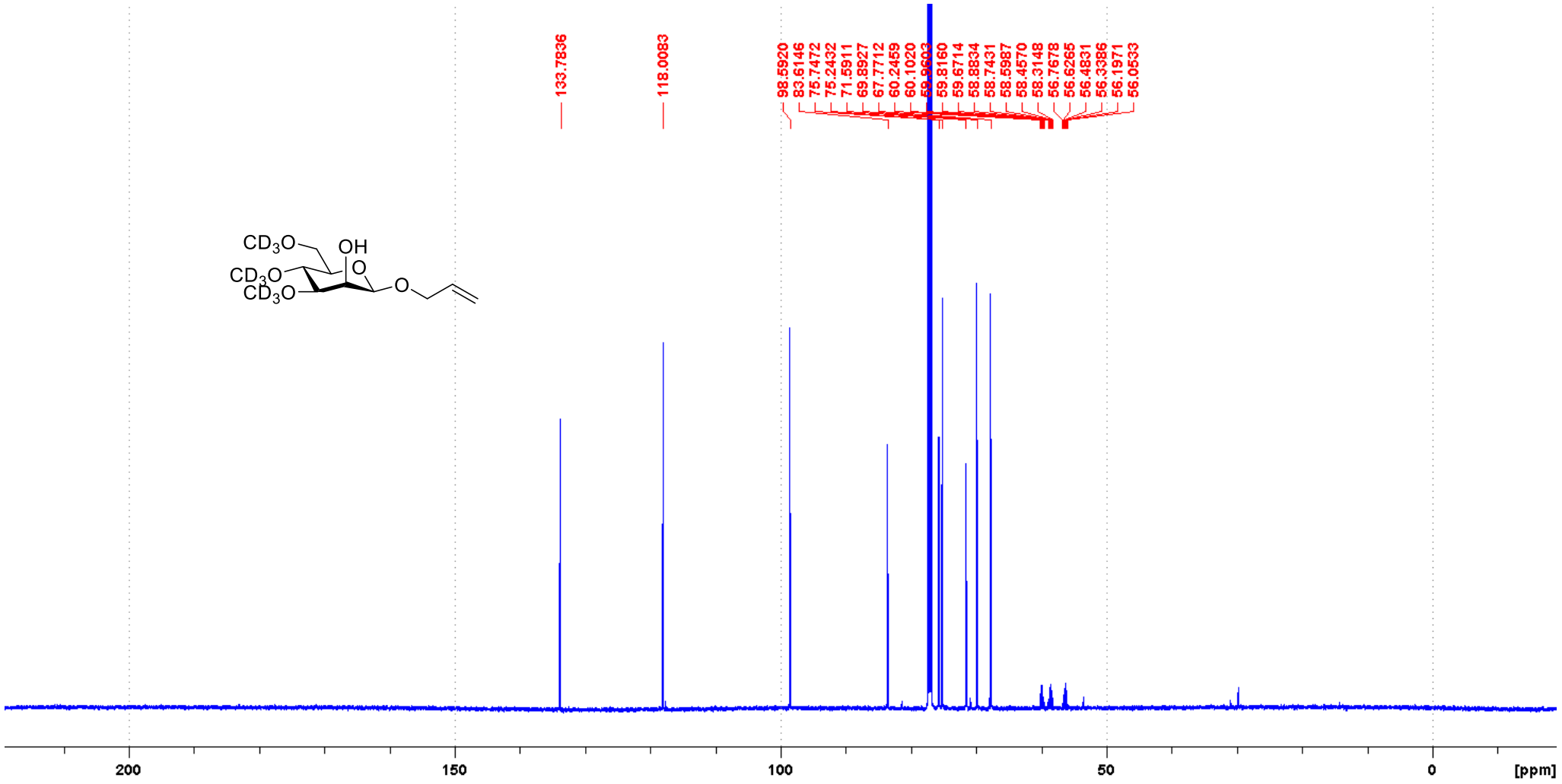
HSQC of compound **45**



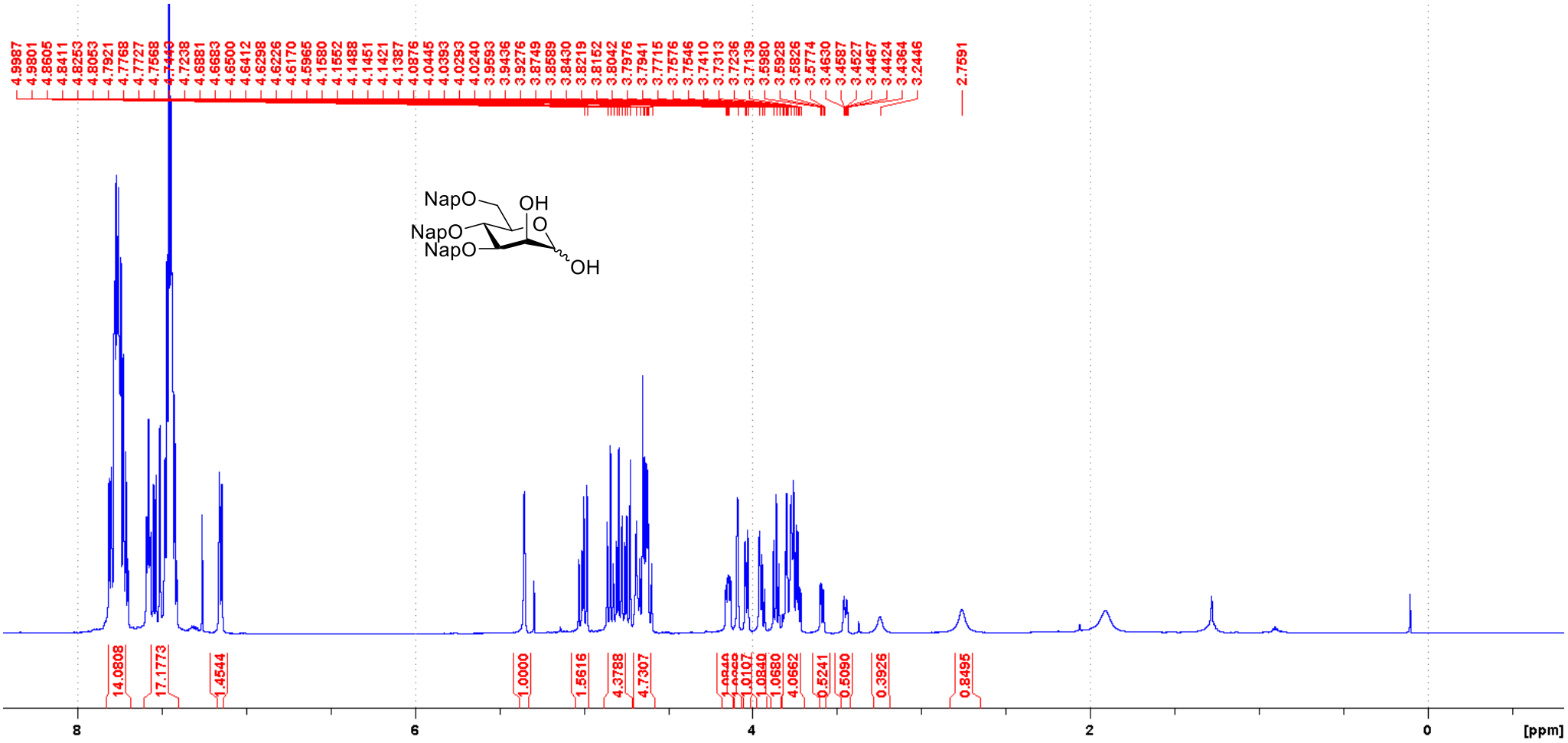
^{1}H NMR of compound **46**



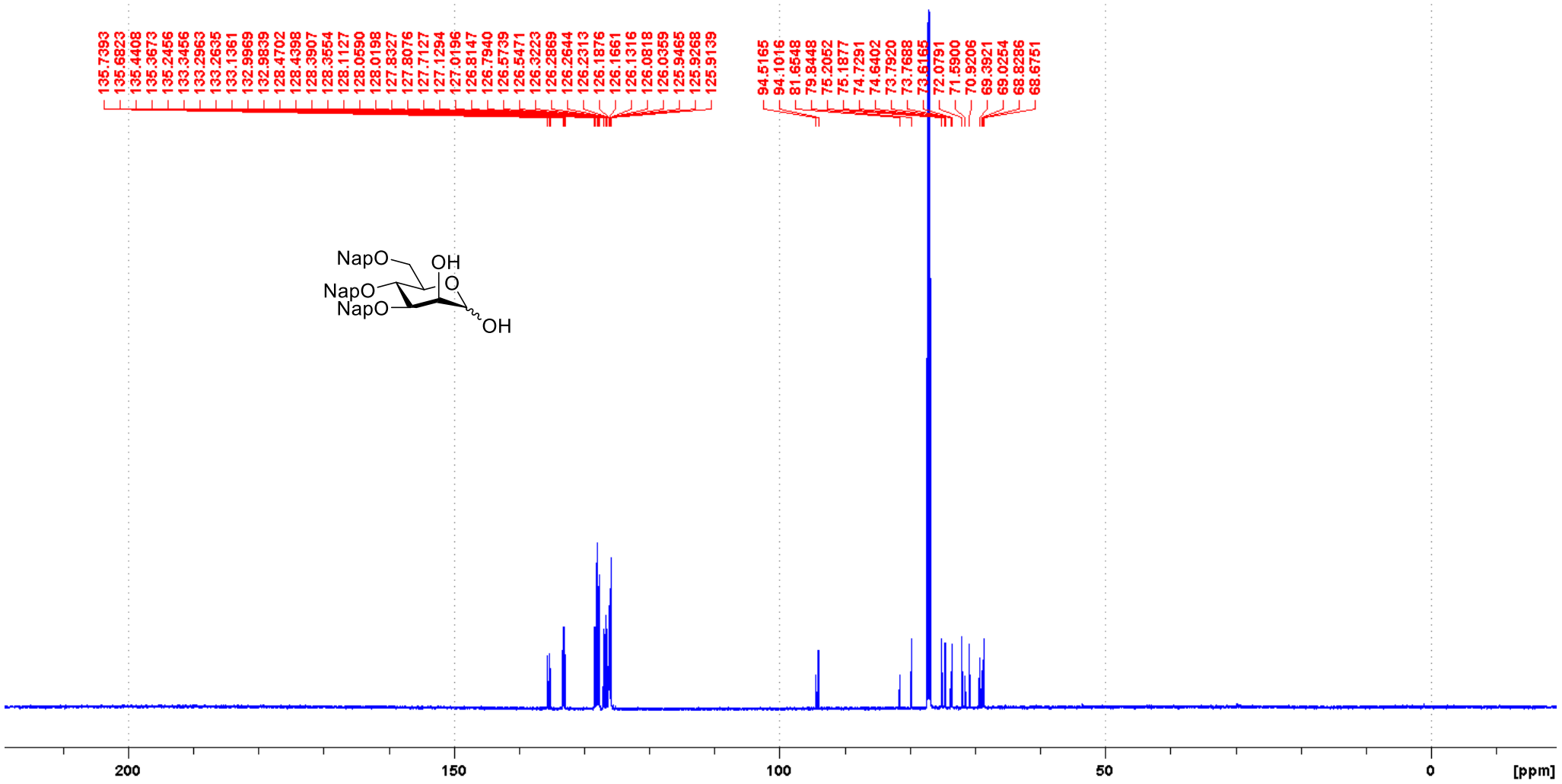
^{13}C NMR of compound **46**



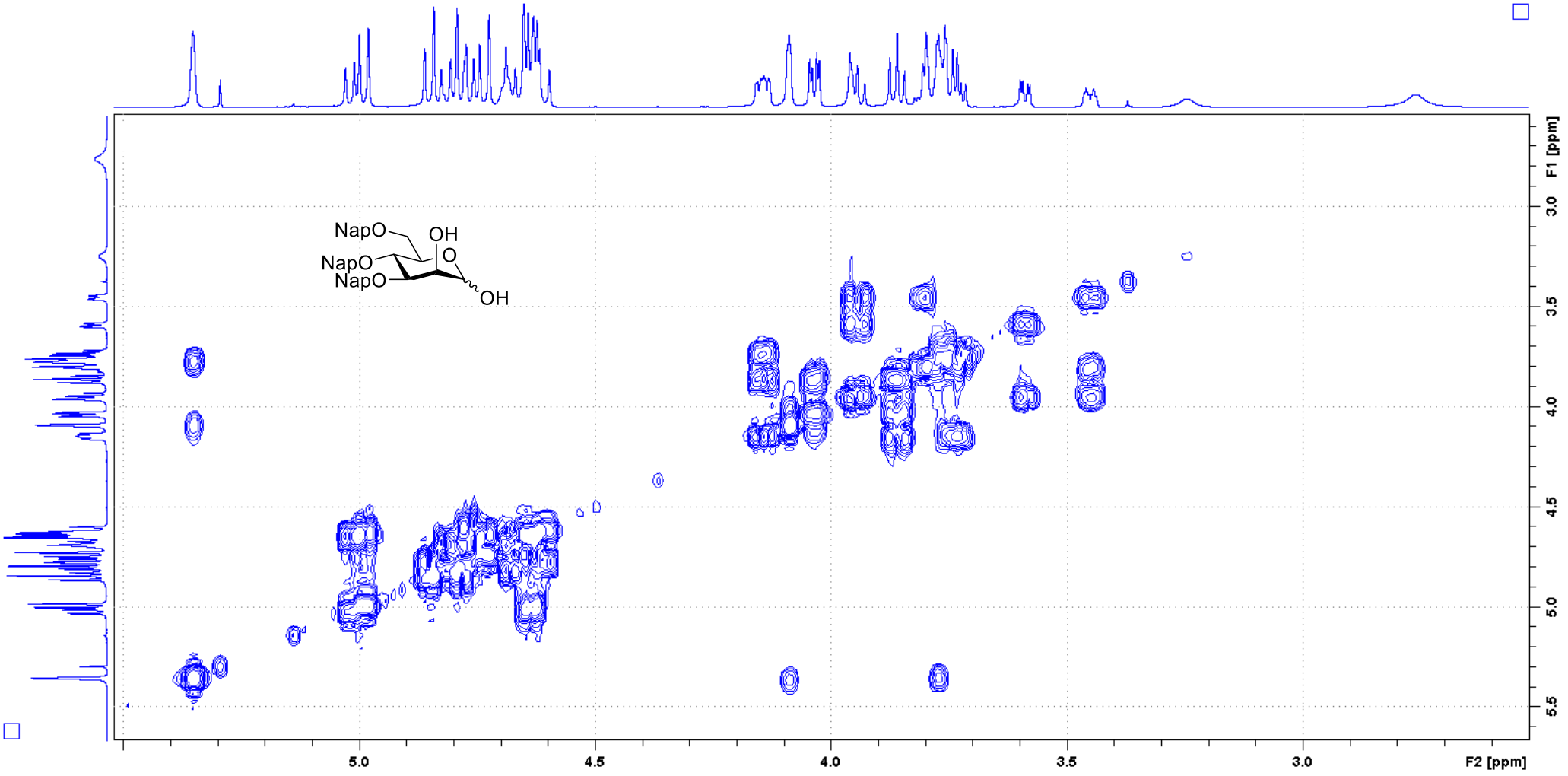
^{1}H NMR of compound **47**



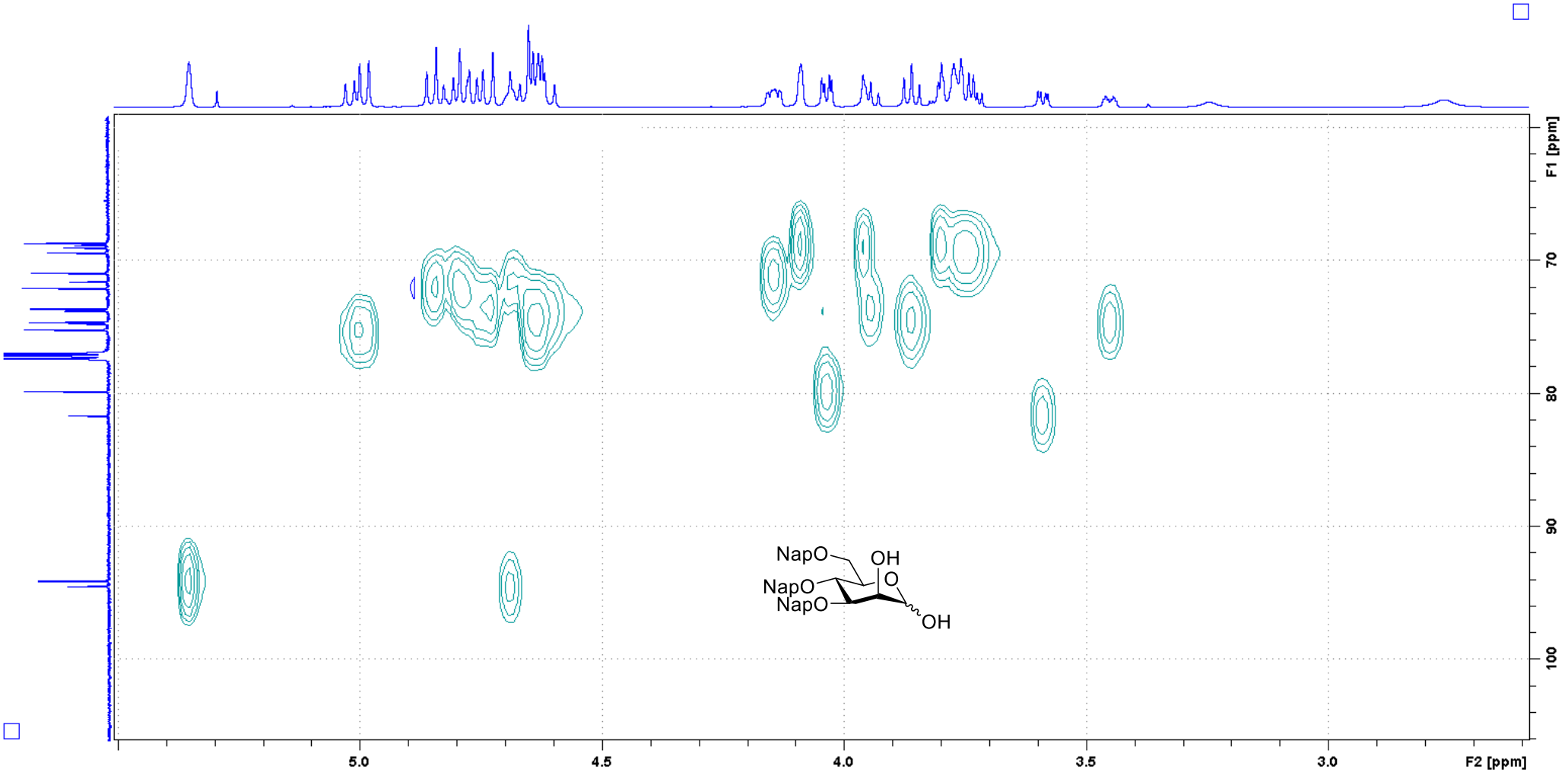
^{13}C NMR of compound **47**



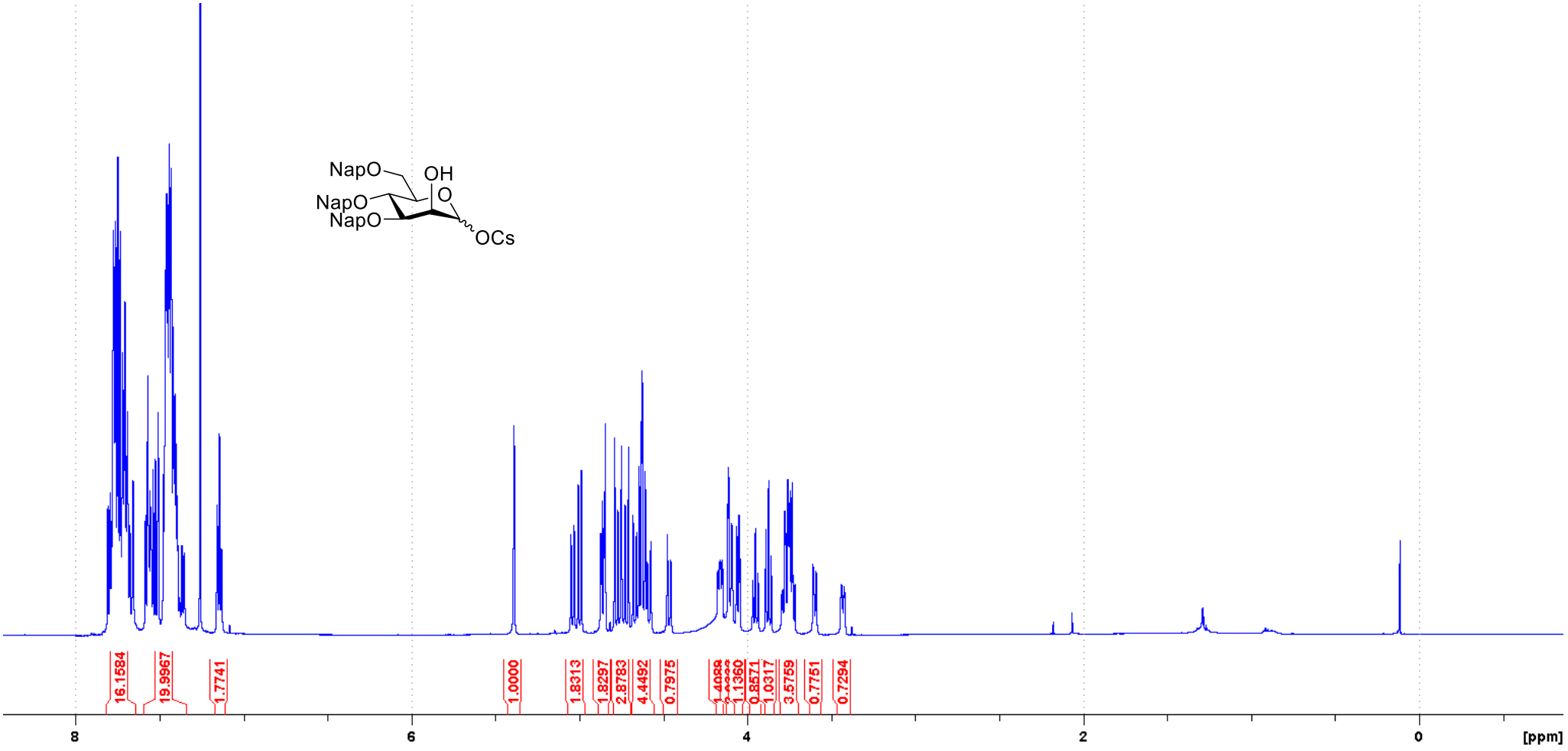
H-H COSY of compound **47**



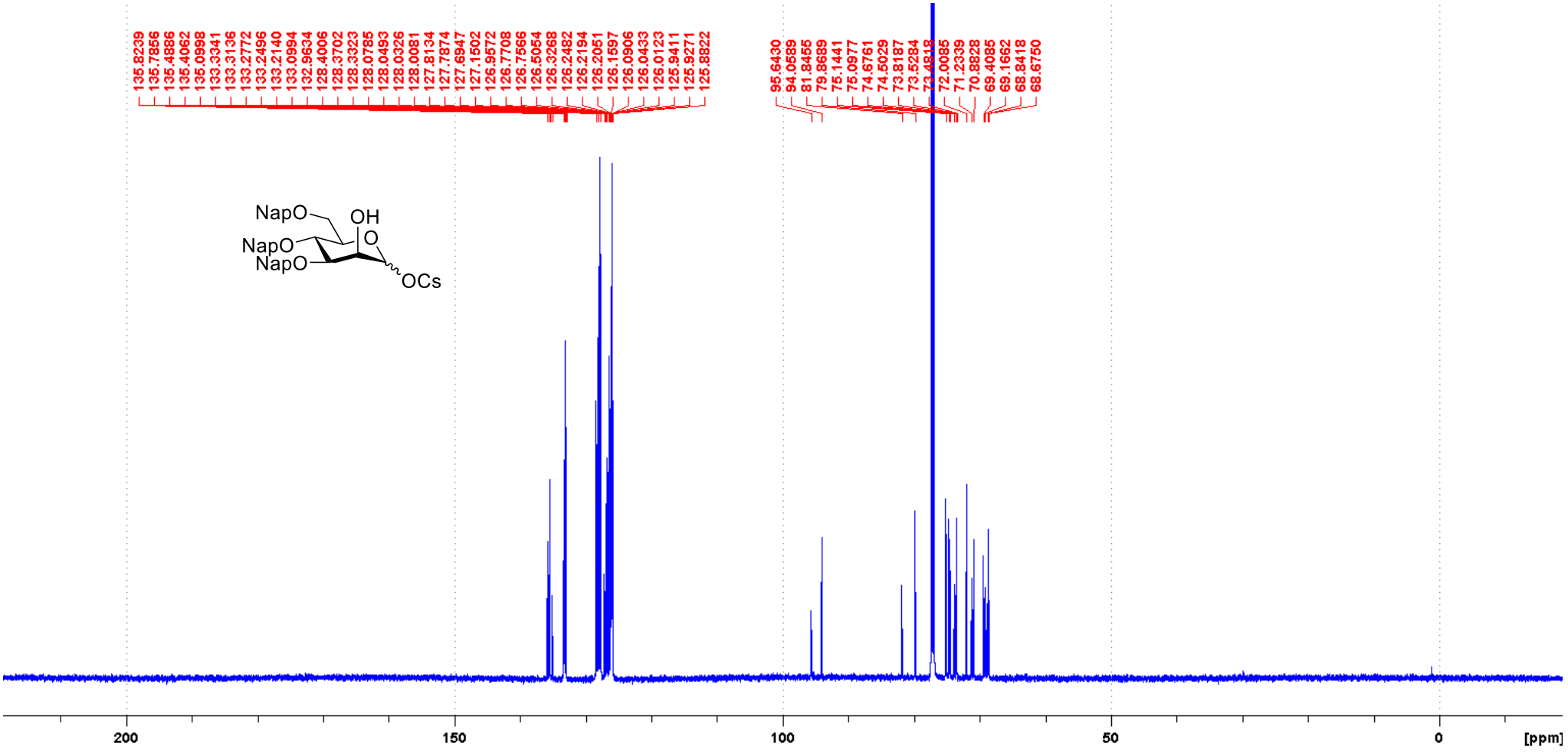
HSQC of compound **47**



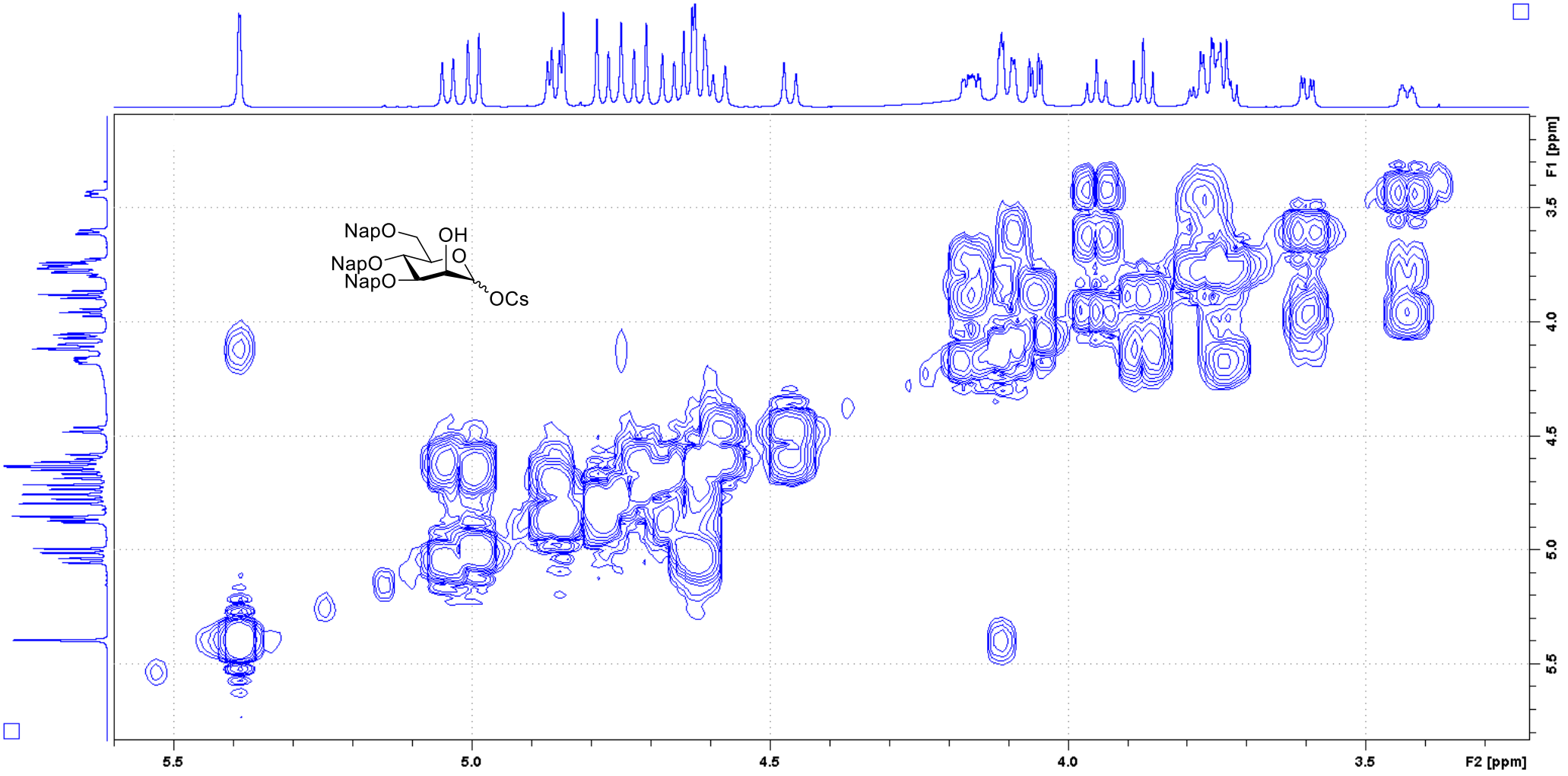
^{1}H NMR of compound **48**



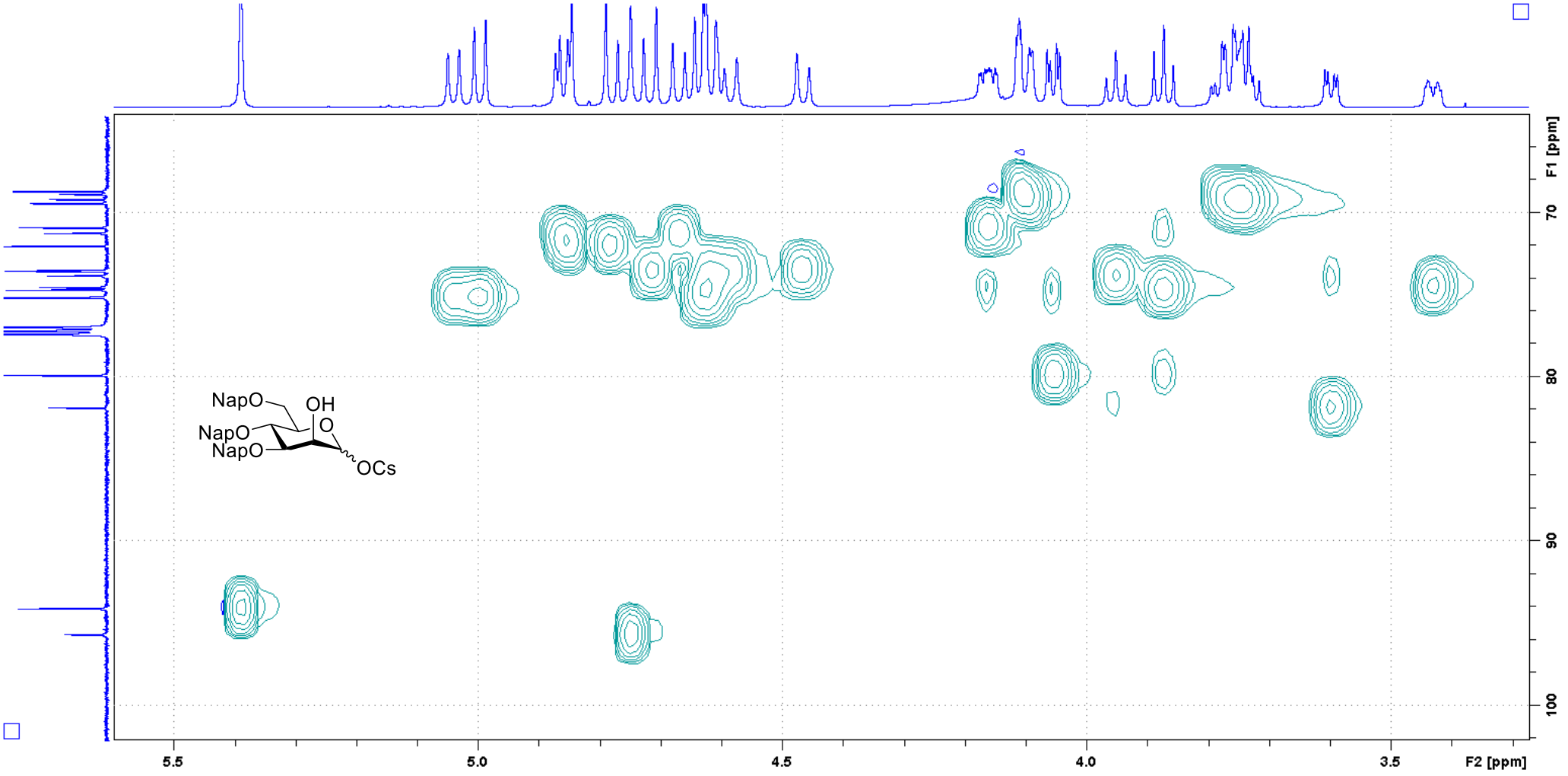
^{13}C NMR of compound **48**



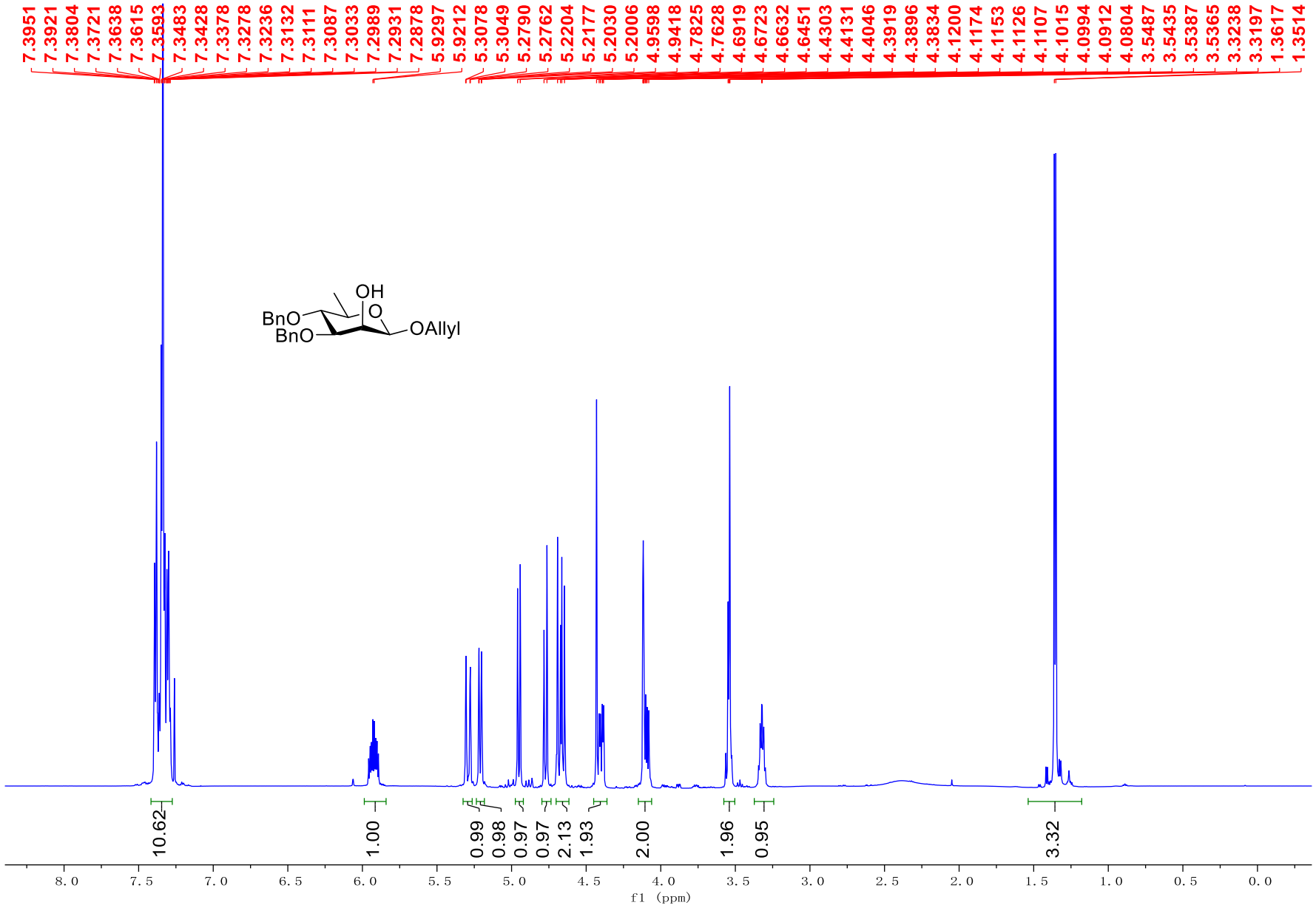
H-H COSY of compound **48**



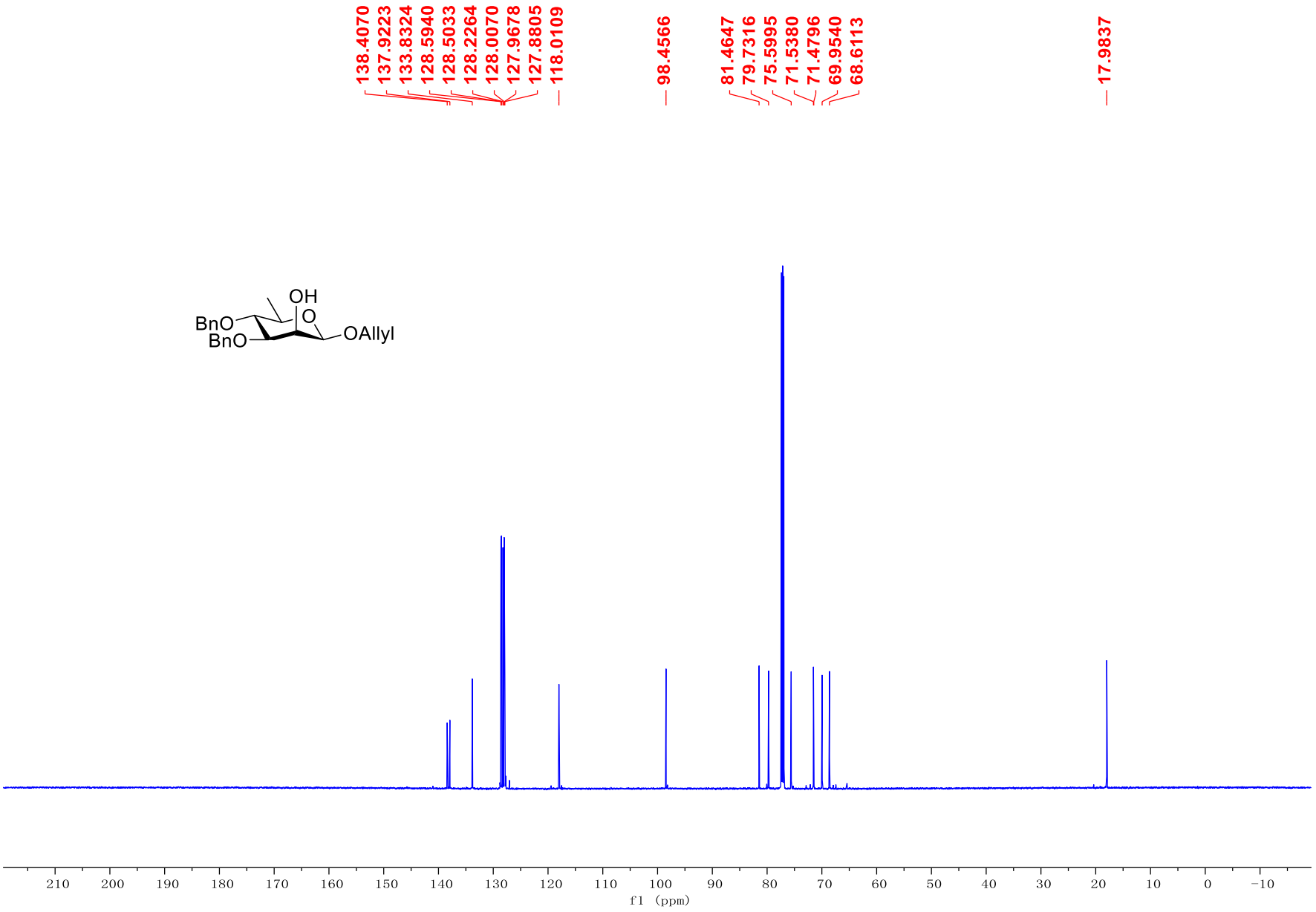
HSQC of compound **48**



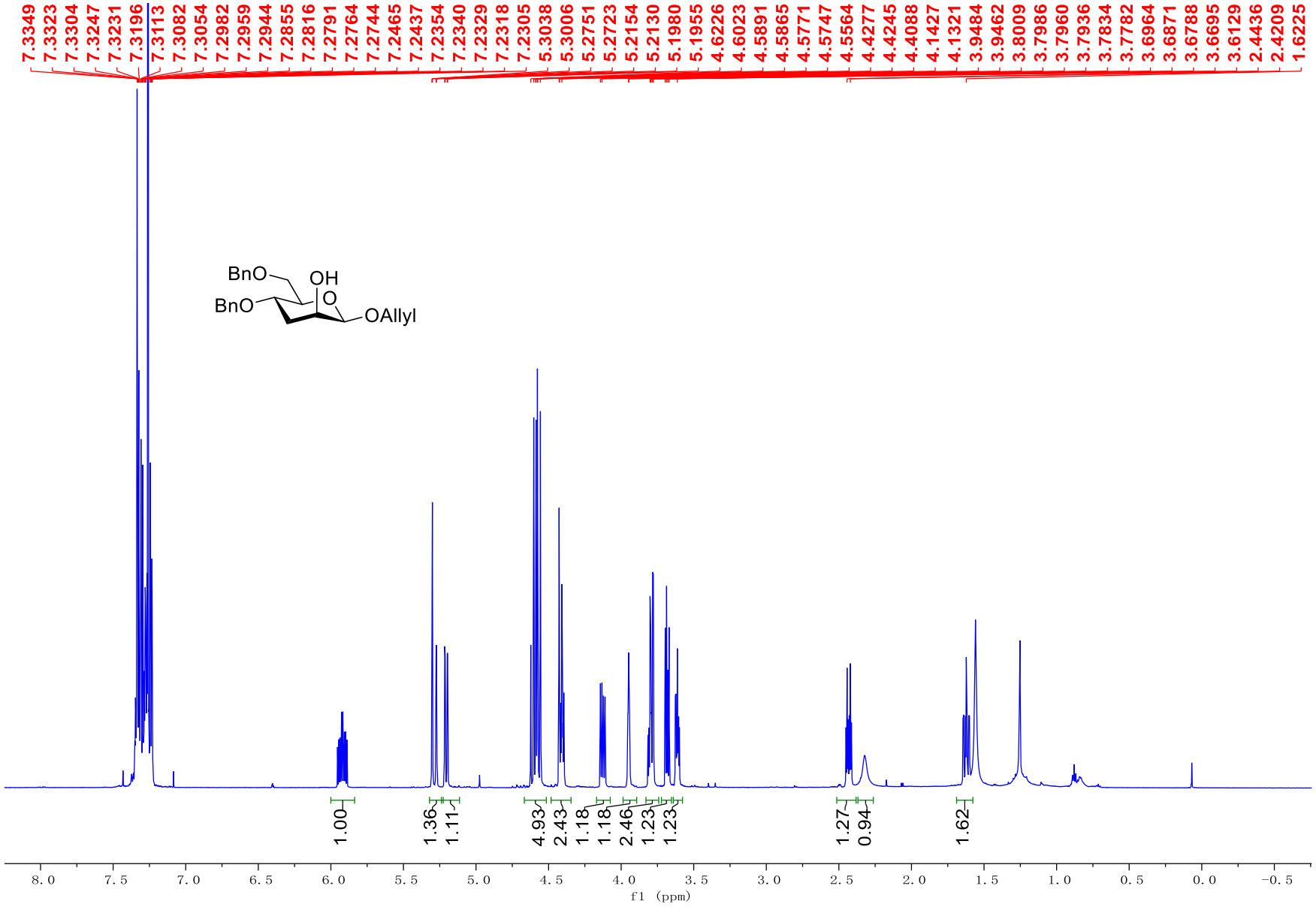
^{1}H NMR of compound **51**



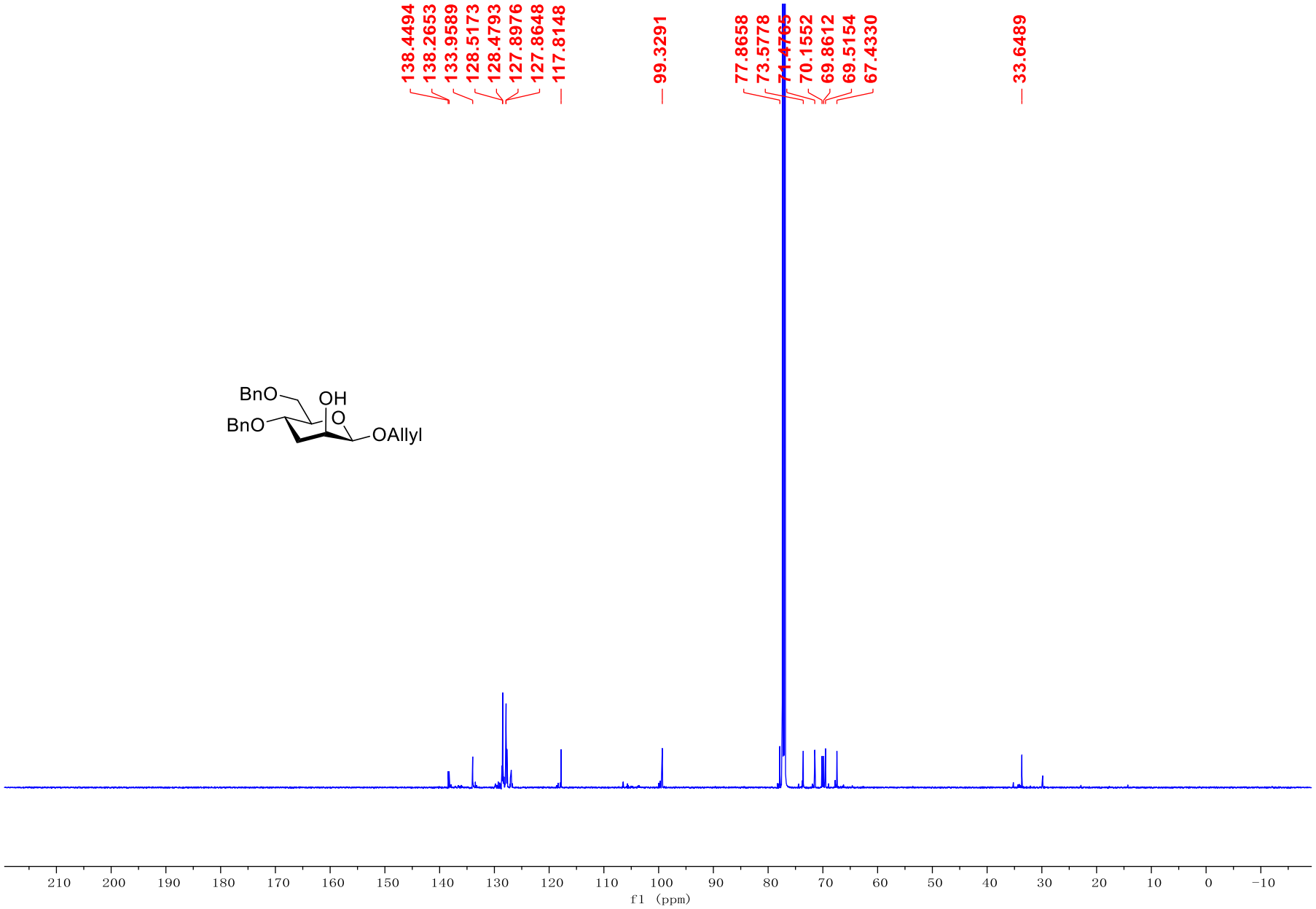
^{13}C NMR of compound **51**



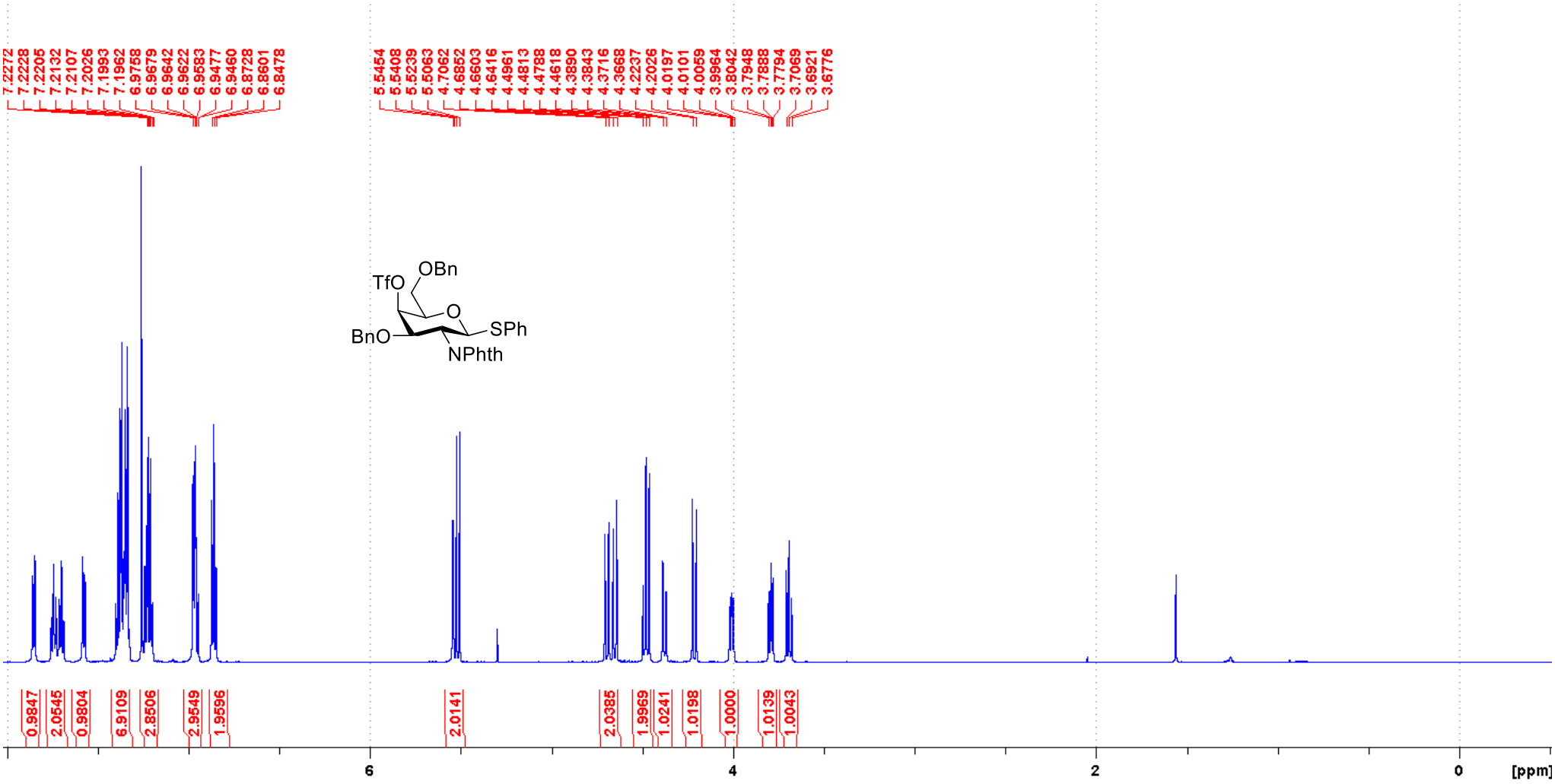
^{1}H NMR of compound **50**



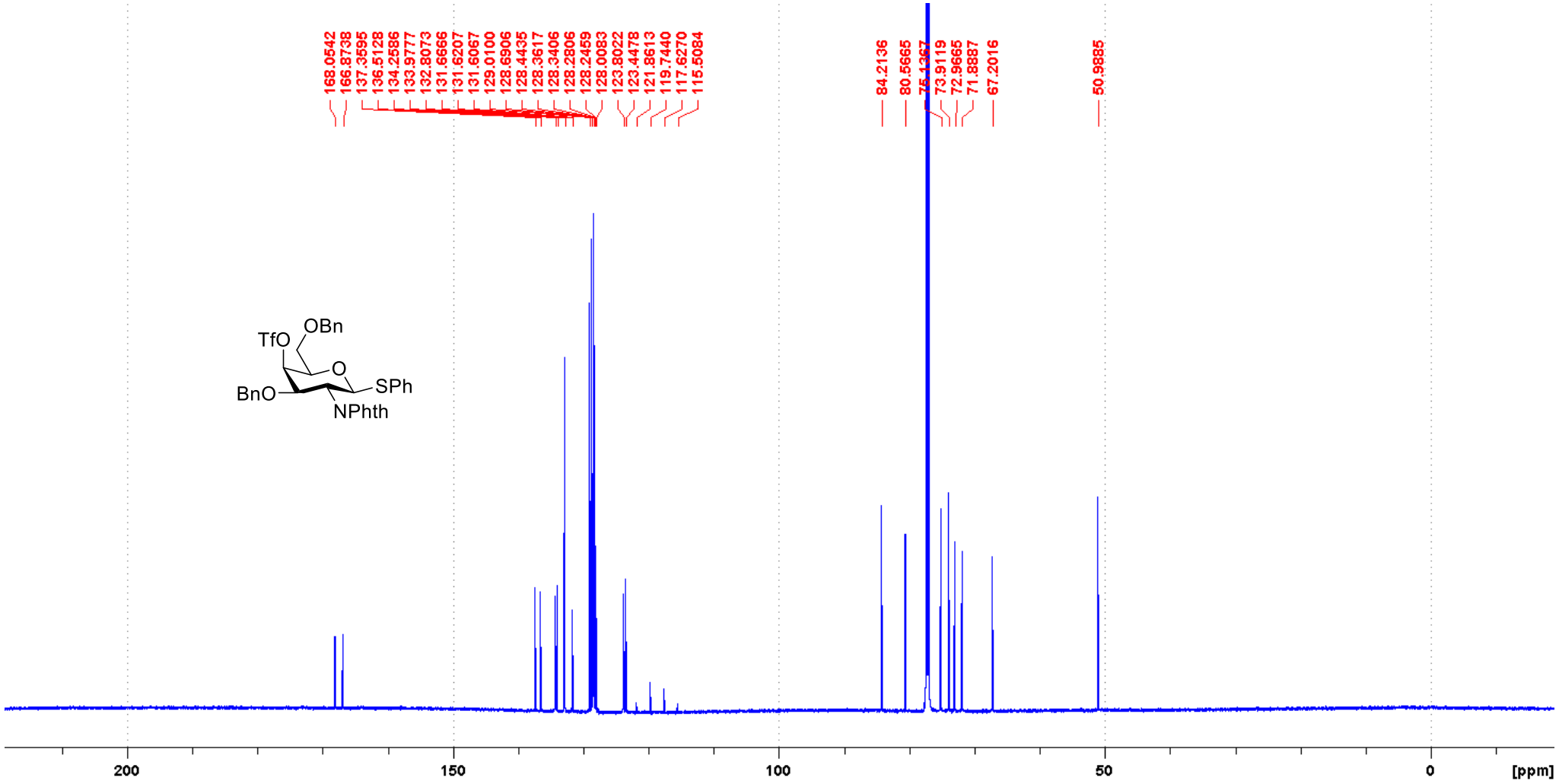
^{13}C NMR of compound **50**



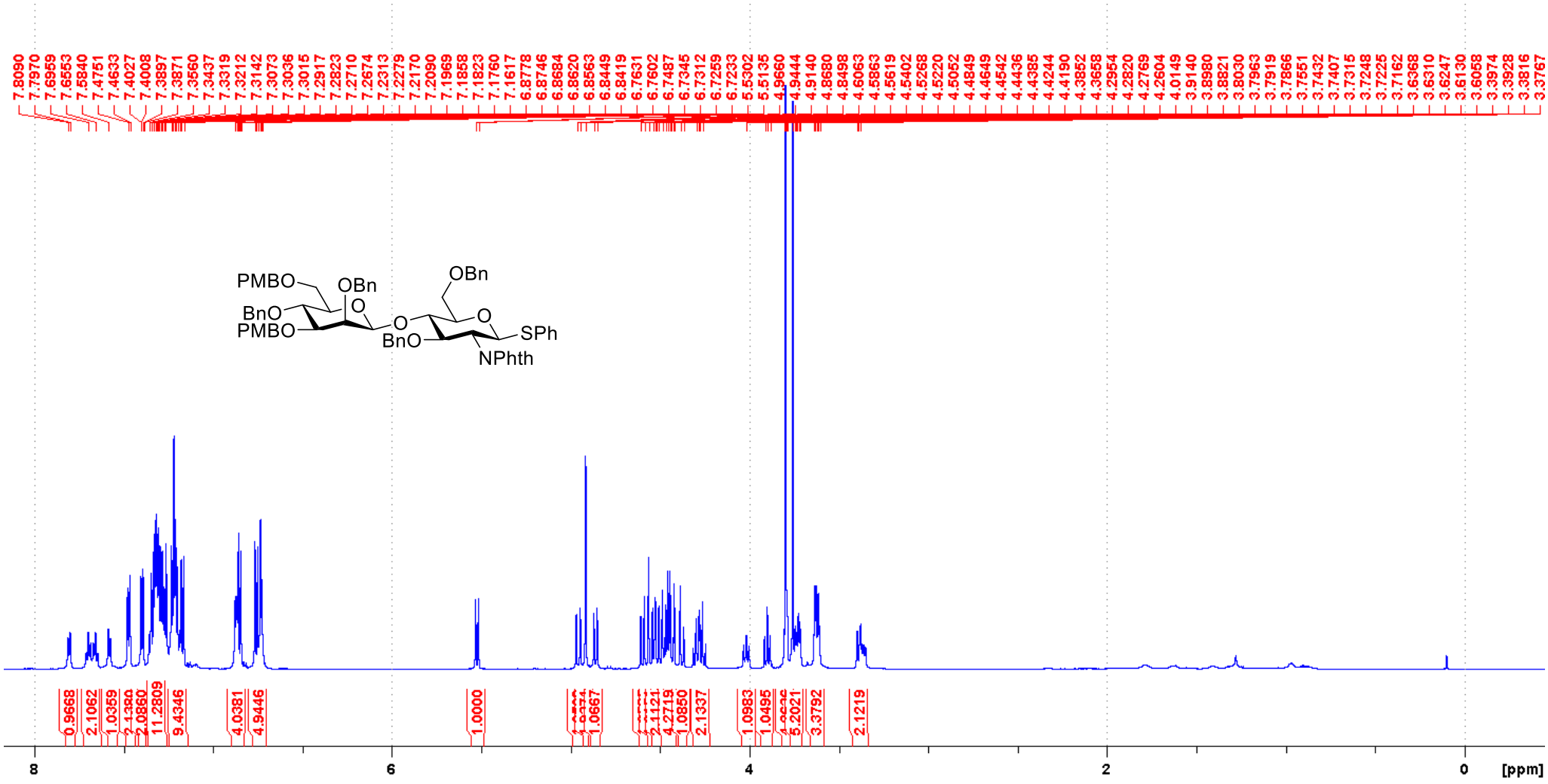
^{1}H NMR of compound **57**



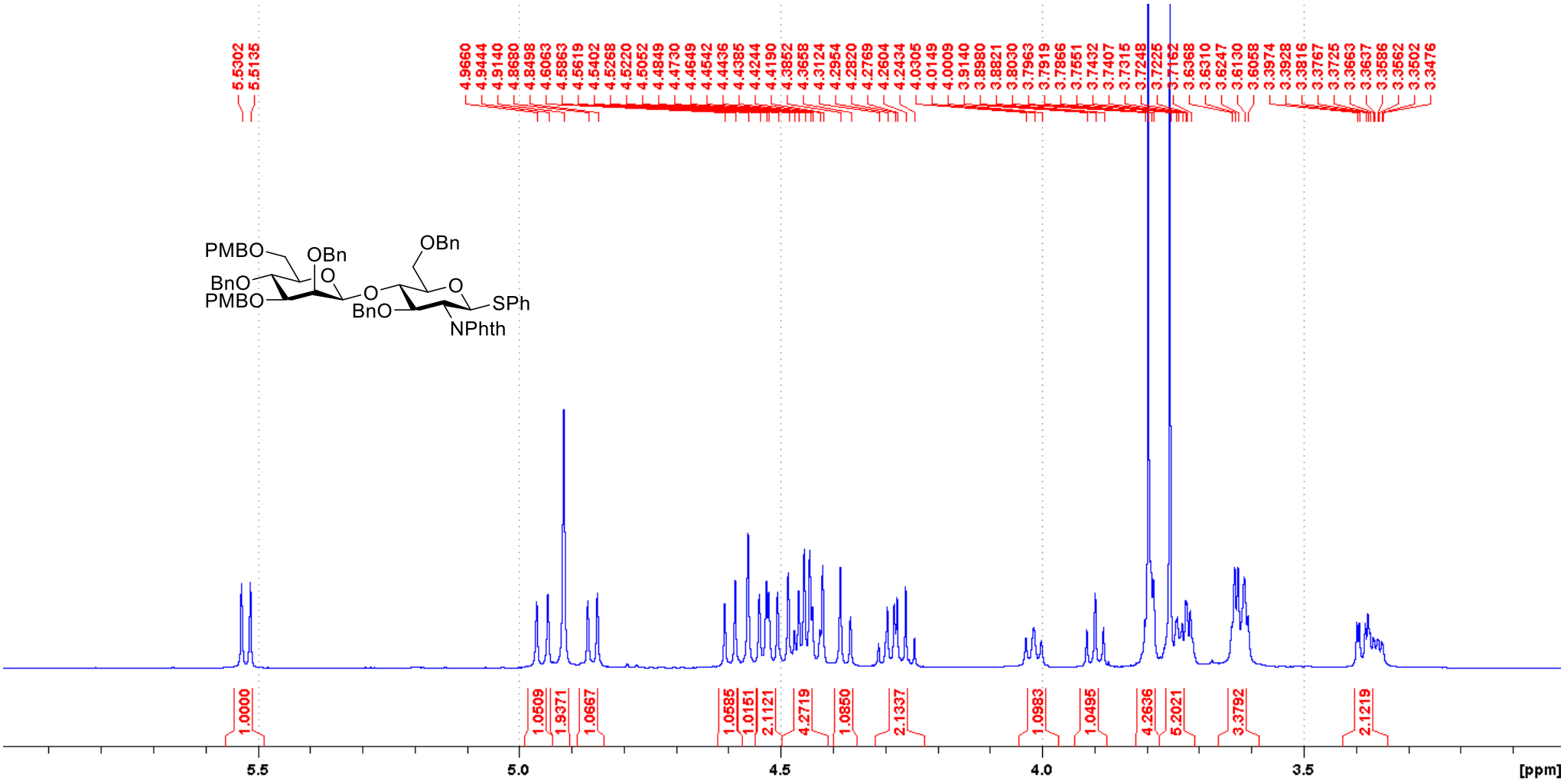
^{13}C NMR of compound **57**



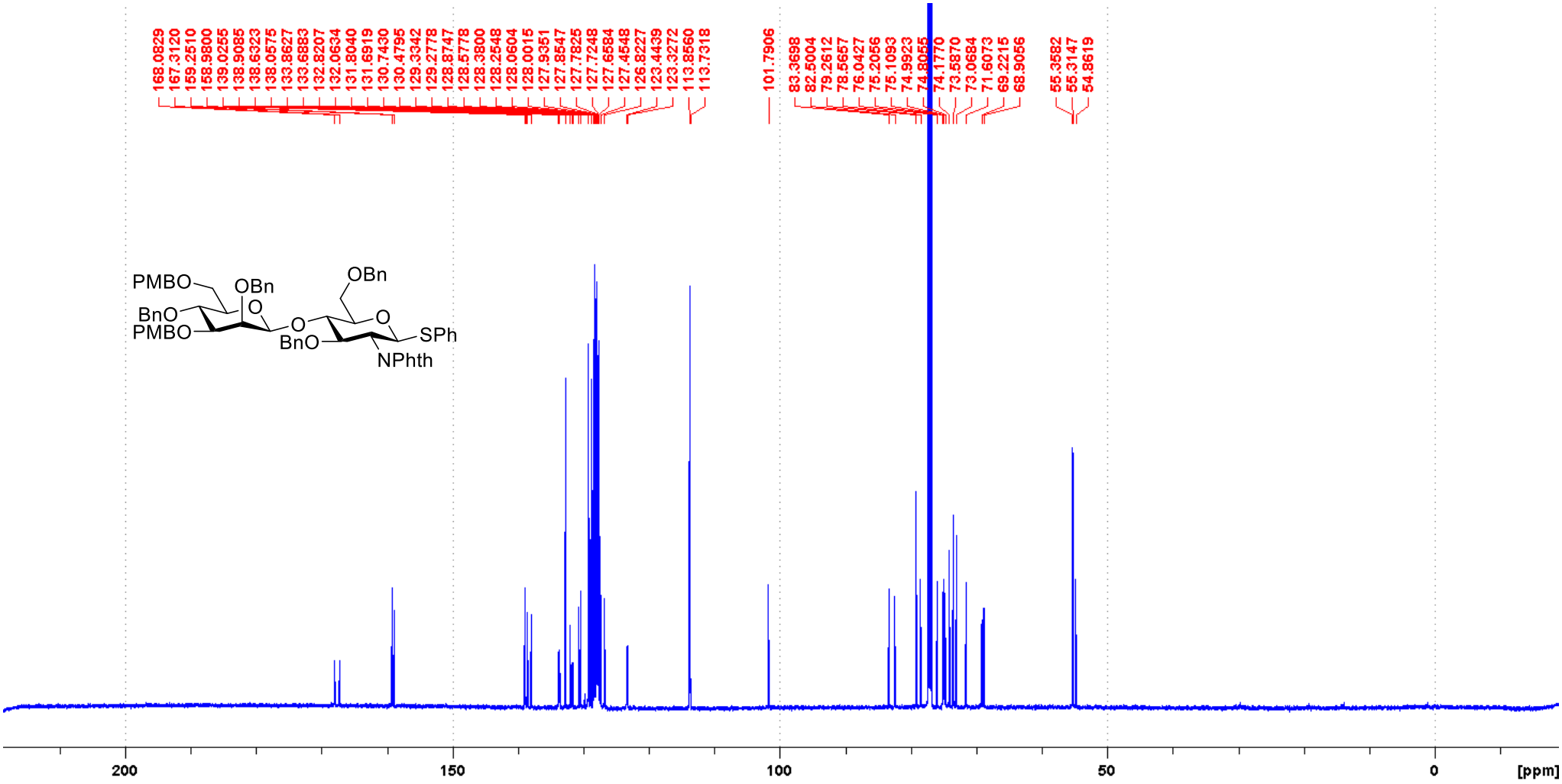
^{1}H NMR of compound **60**



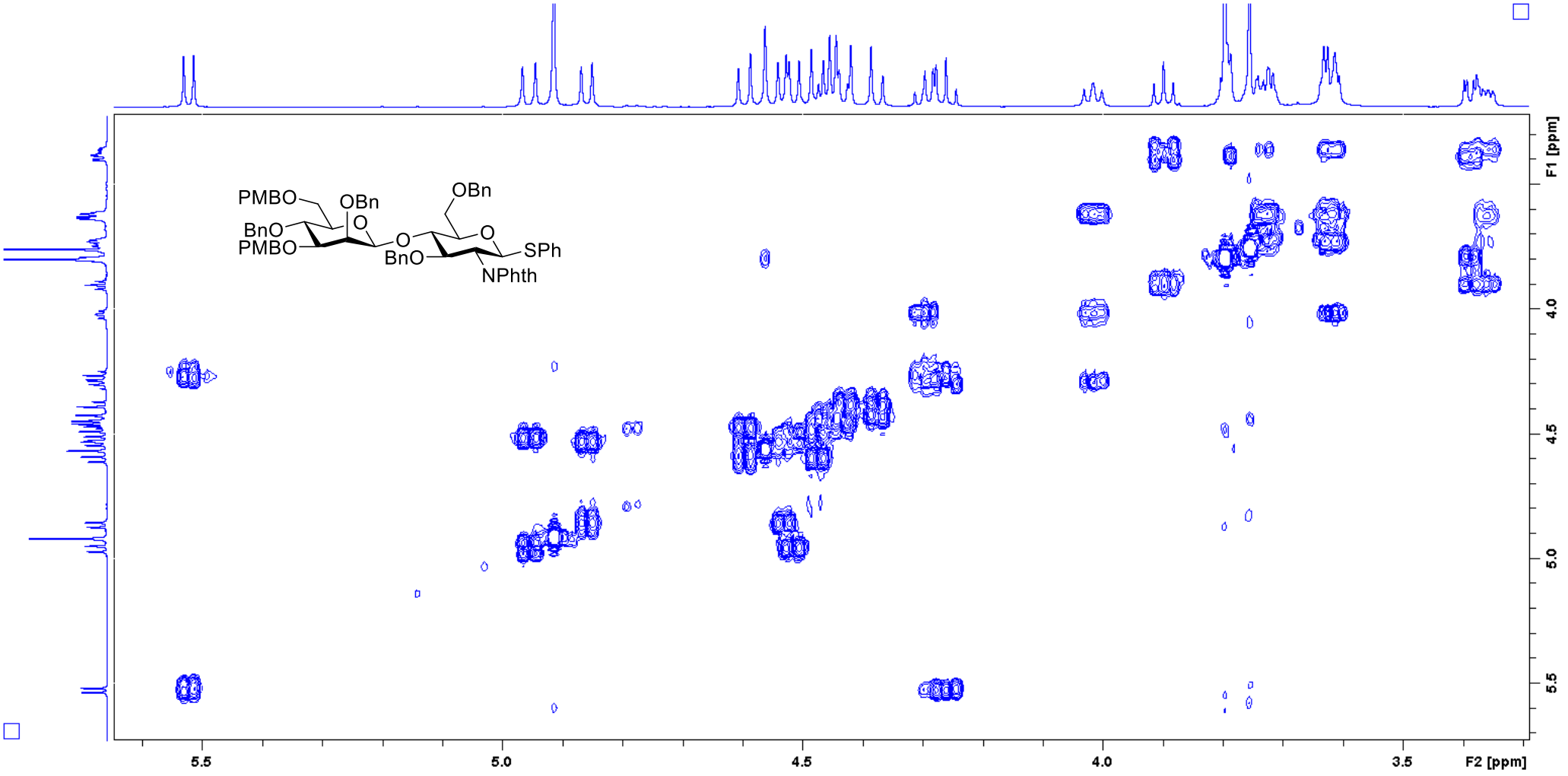
^{1}H NMR of compound **60** (6.00~3.00 ppm expanded)



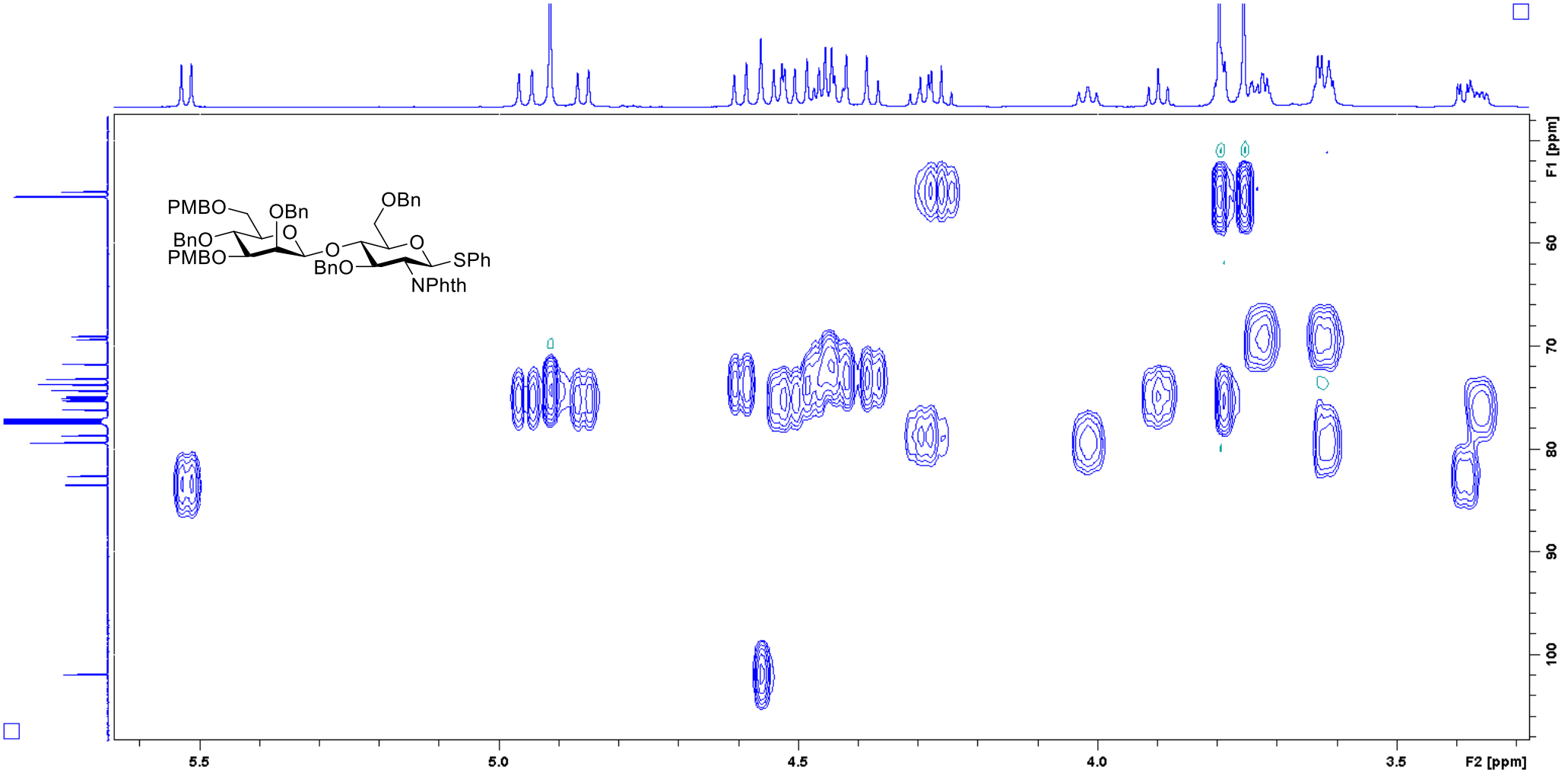
^{13}C NMR of compound **60**



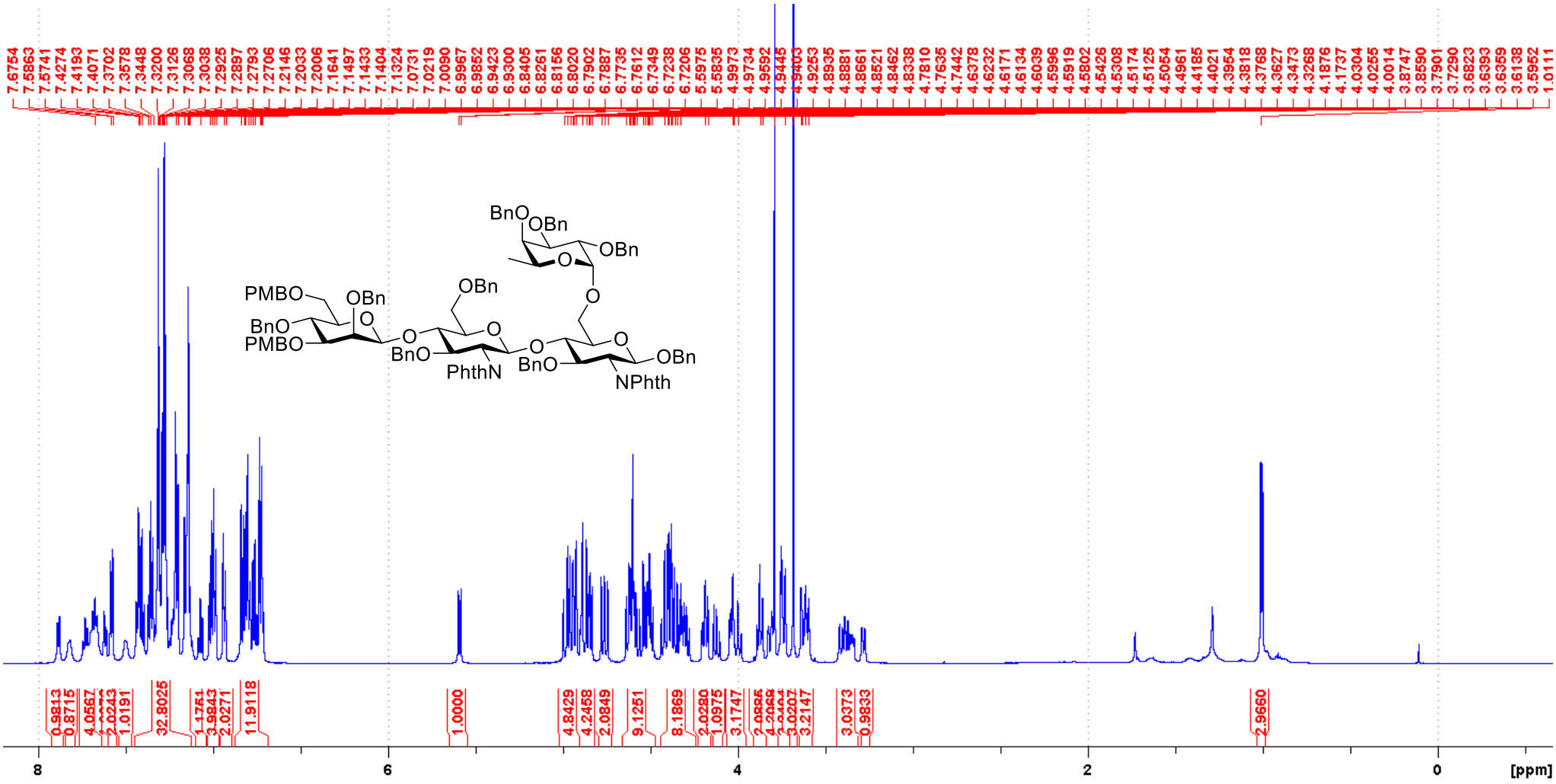
H-H COSY of compound **60**



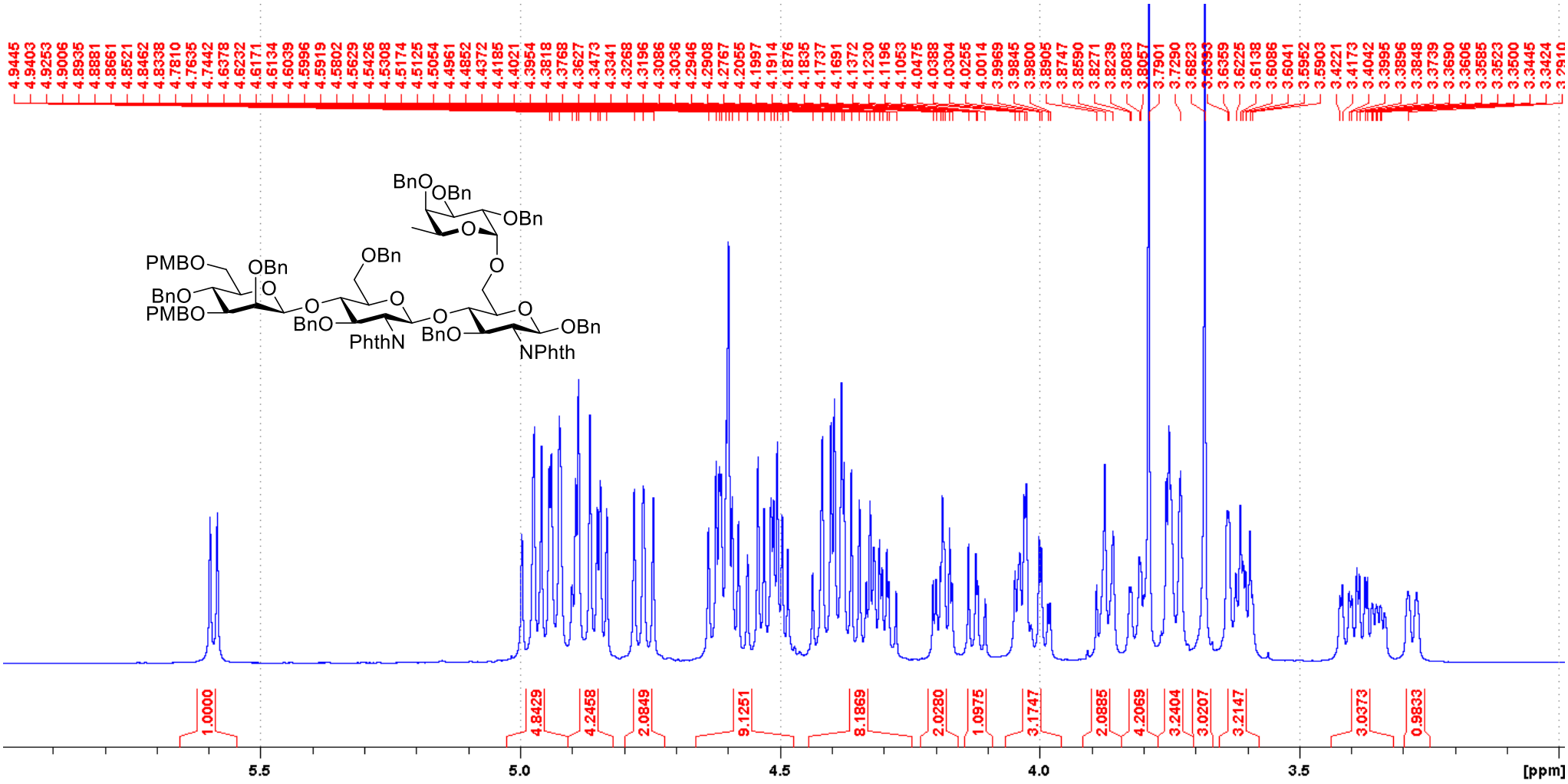
HSQC of compound **60**



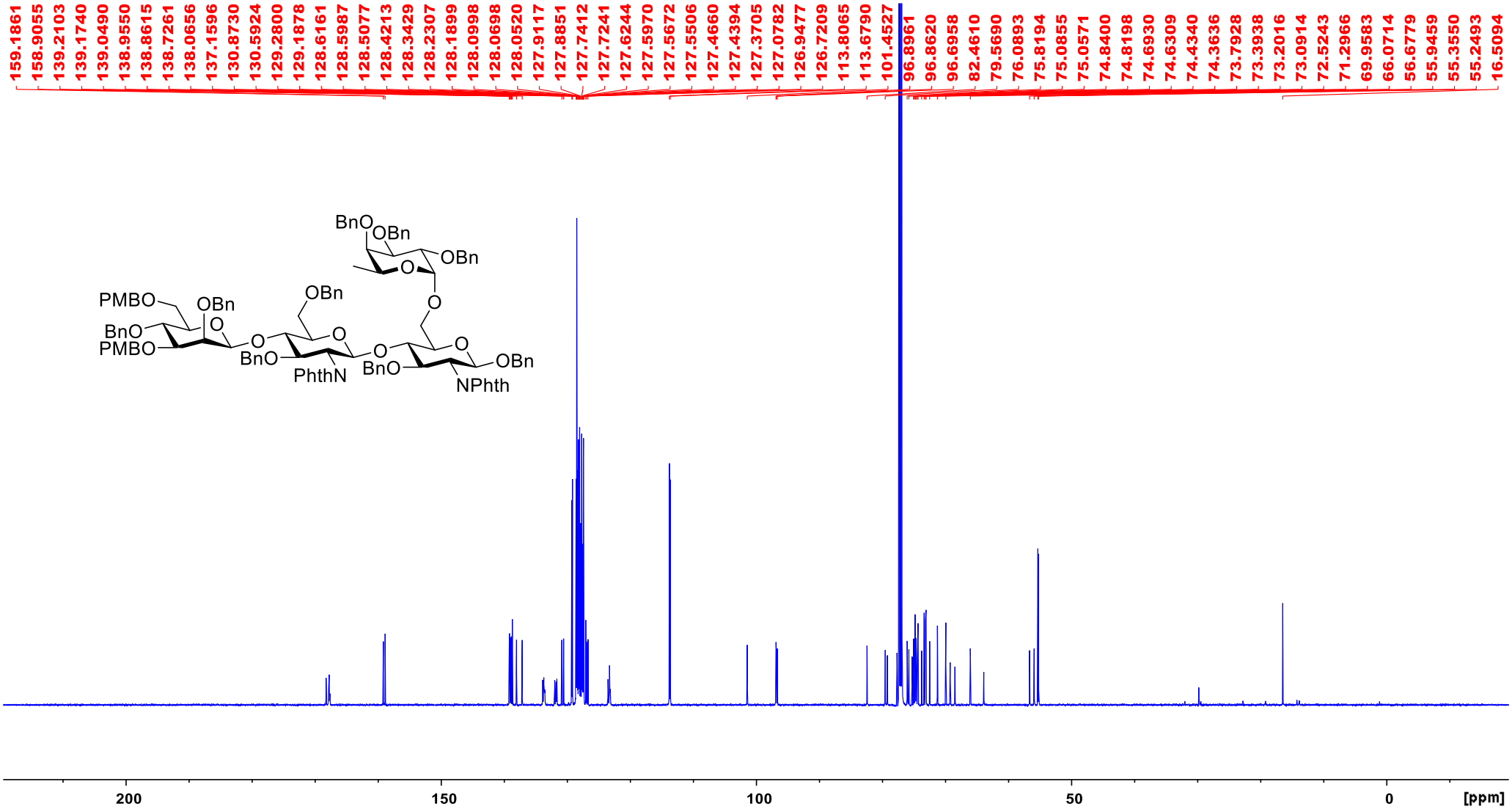
^{1}H NMR of compound **62**



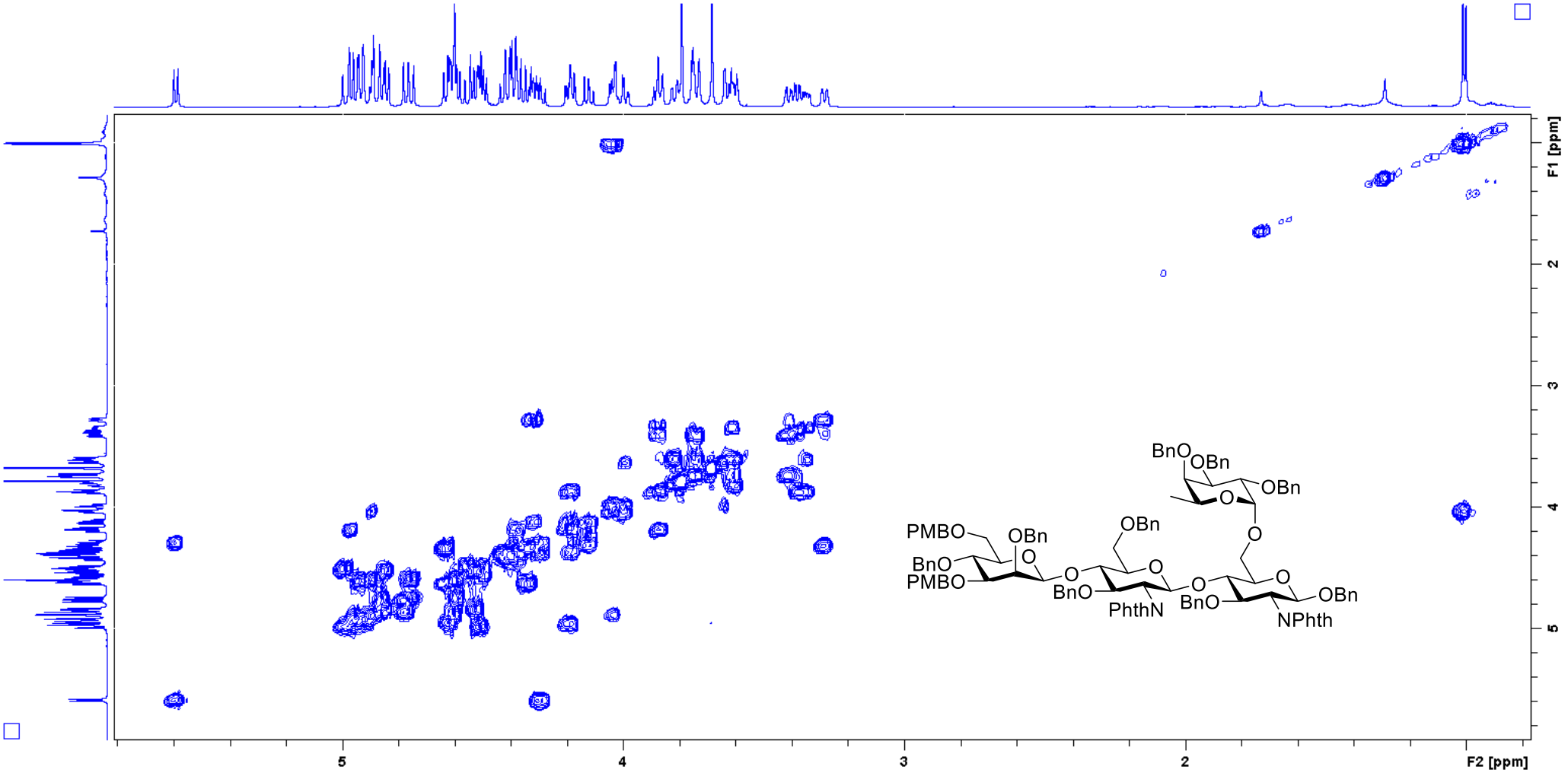
^{1}H NMR of compound **62** (6.00~3.00 ppm expanded)



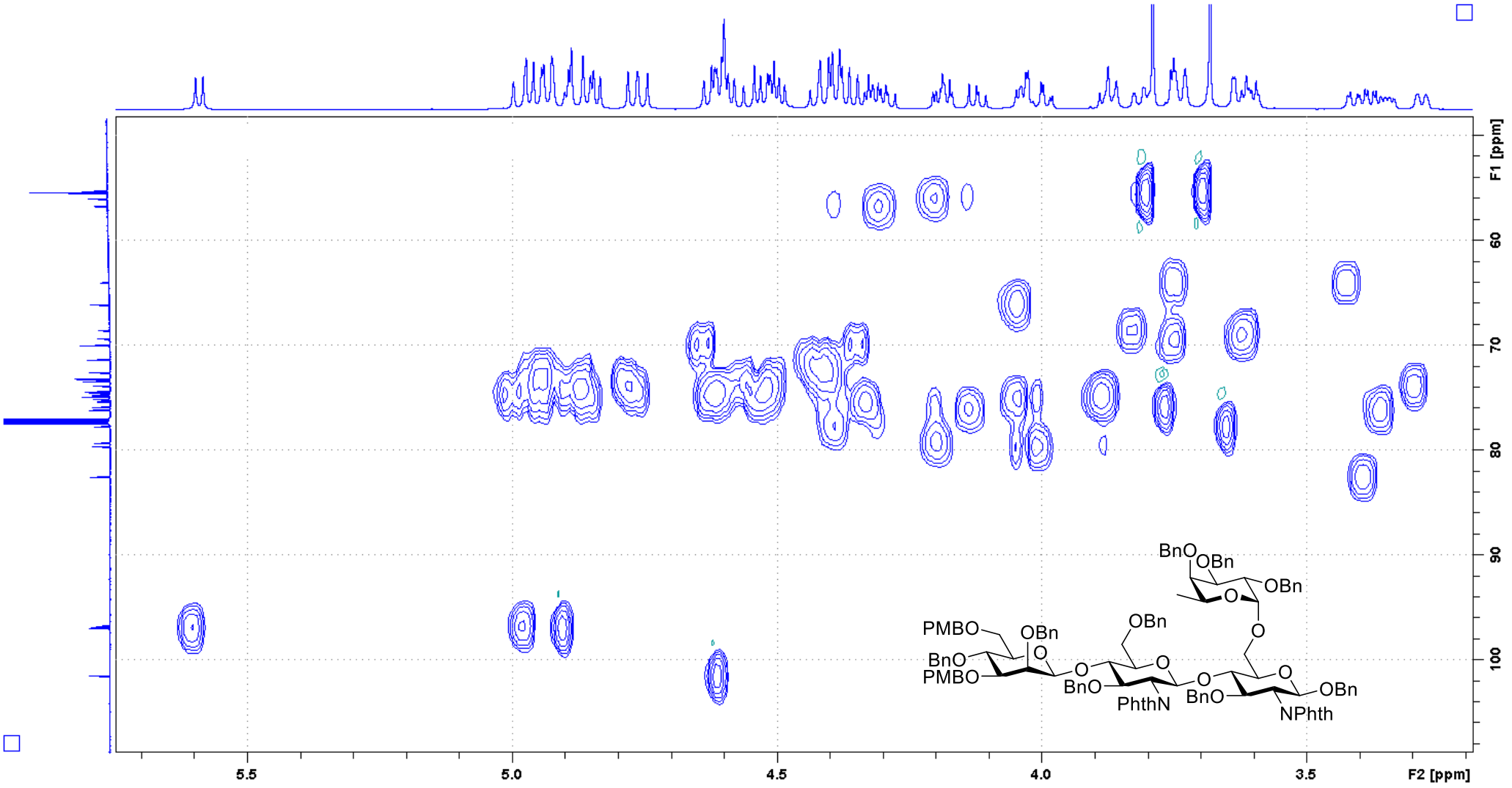
^{13}C NMR of compound **62**



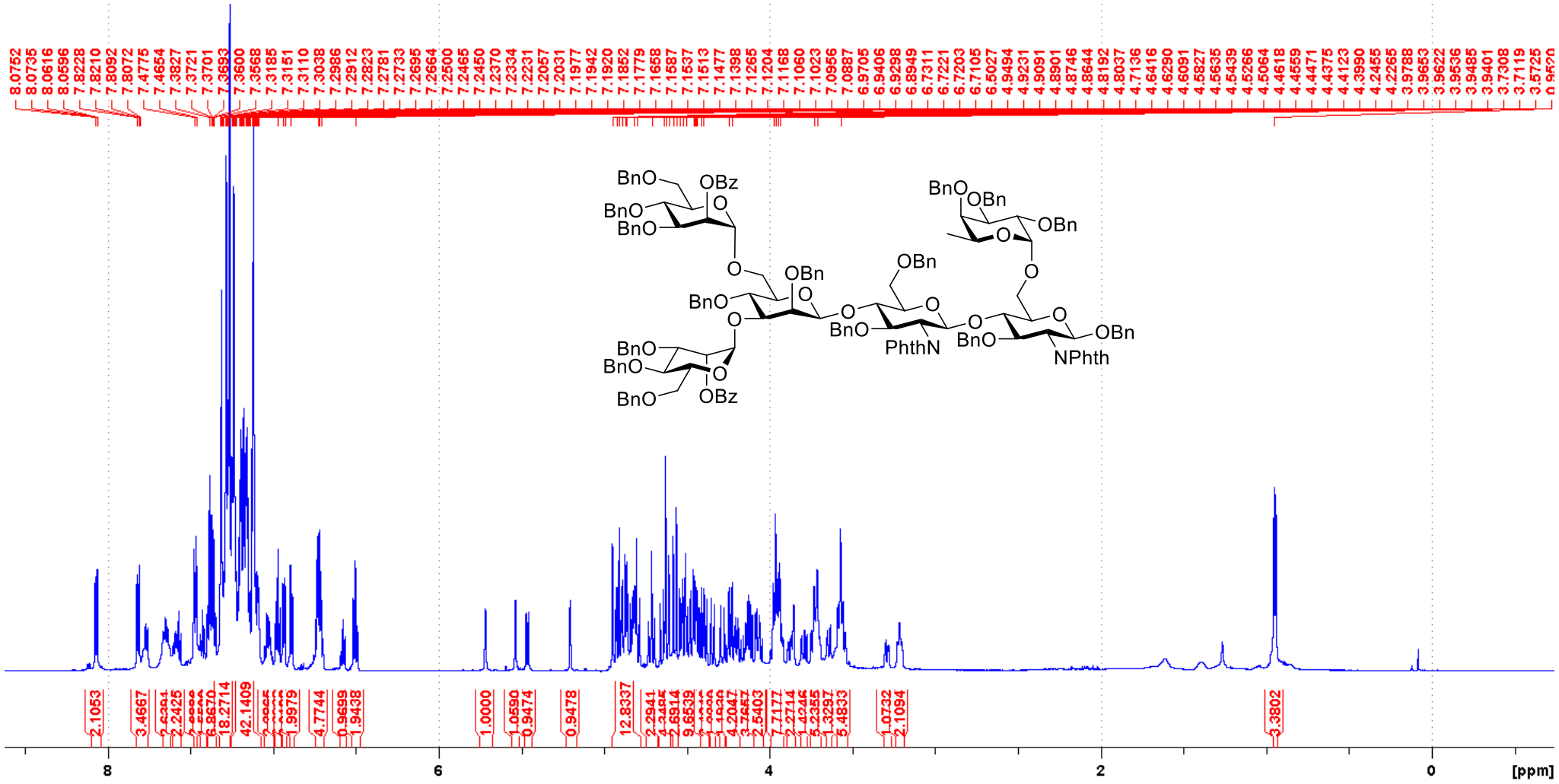
H-H COSY of compound **62**



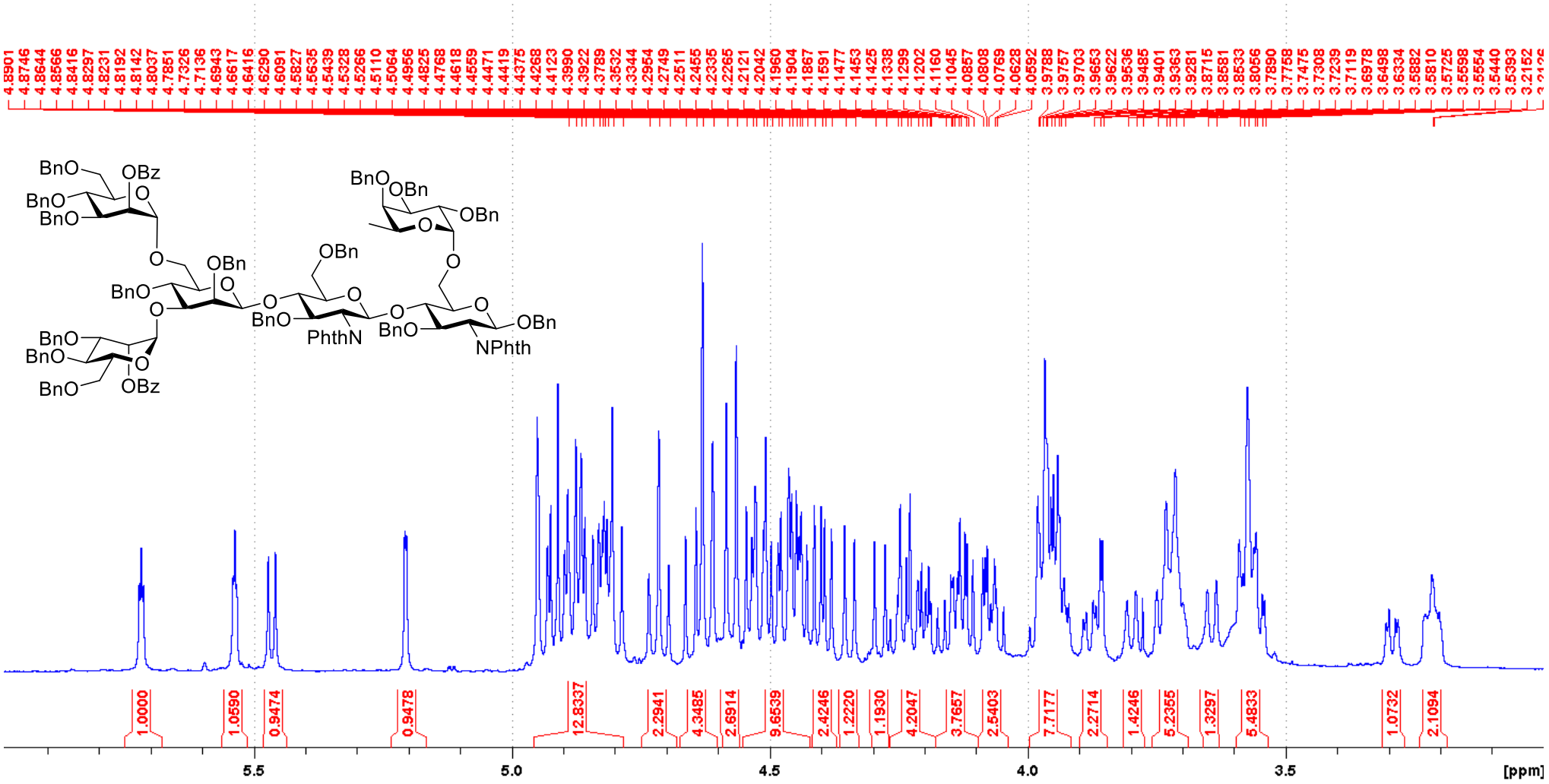
HSQC of compound **62**



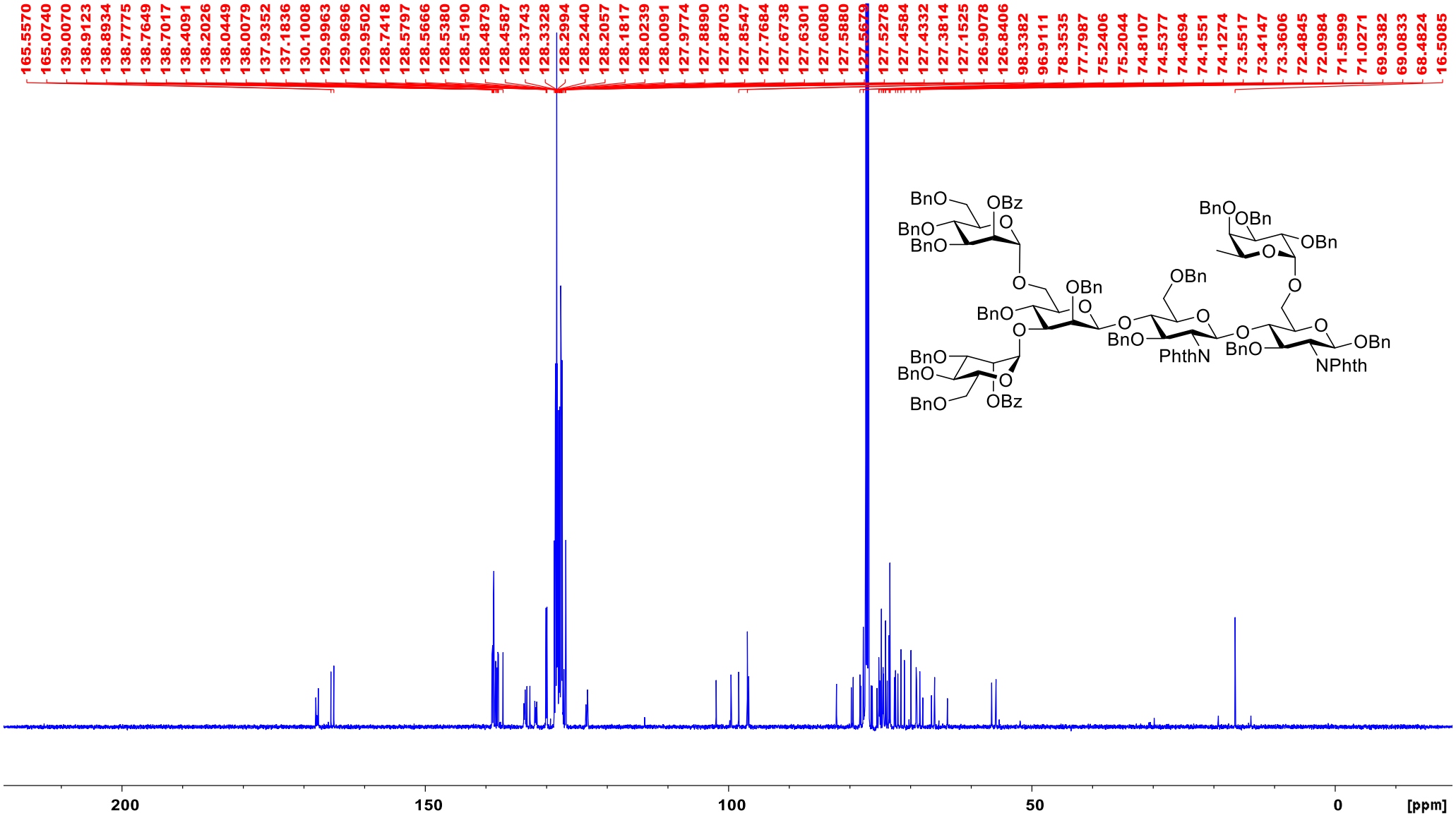
^{1}H NMR of compound **66**



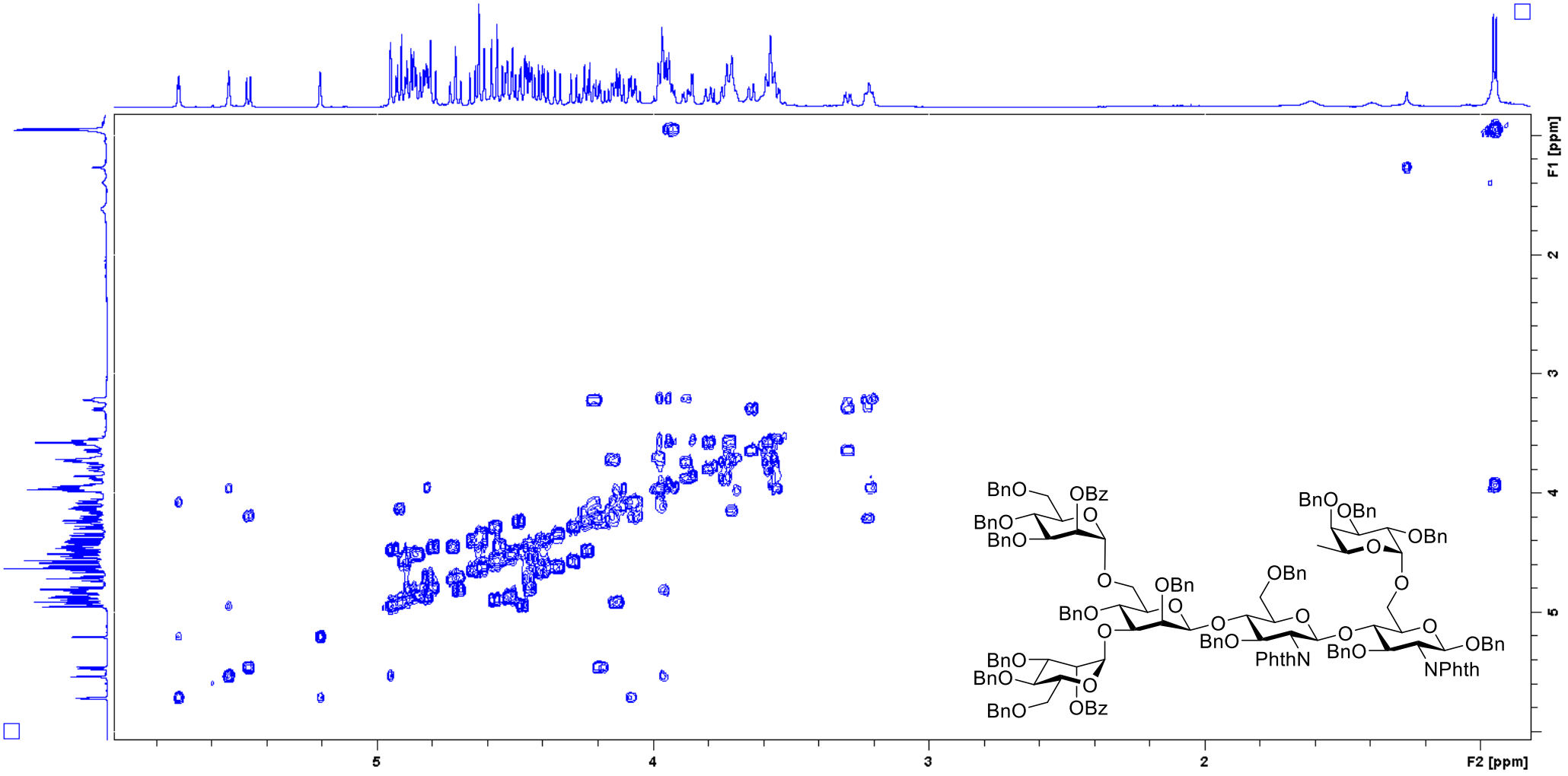
^{1}H NMR of compound **66** (6.00~2.00 ppm expanded)



^{13}C NMR of compound **66**



H-H COSY of compound **66**



HSQC of compound **66**