Electronic Supplementary Material (ESI) for ChemComm.

Stereoselective synthesis of glycosides using (salen)Co catalysts as promoters.

Sandra Medina, Alexander S. Henderson,[a] John F. Bower[a] and M. Carmen Galan[a*]

Table of contents

Experimental Procedures

General.

Chemicals were purchased and used without further purification. Anhydrous solvents were obtained by passage through a column of anhydrous alumina using equipment from Anhydrous Engineering (University of Bristol) based on the Grubbs' design. Reactions requiring anhydrous conditions were performed under N_2; glassware and needles were either flame dried immediately prior to use or placed in an oven (150 °C) for at least 2 h and allowed to cool either in desiccators or under reduced pressure; liquid reagents, solutions or solvents were added via syringe through rubber septa. Reactions were monitored by TLC on Kieselgel 60 F254 (Merck). Detection was by examination under UV light (254 nm) and by charring with 10% H_2SO_4 in EtOH. Flash column chromatography (FFC) was performed using silica gel [Merck, 230−400 mesh (40−63 μm)]. Extracts were concentrated *in vacuo* using both a rotary evaporator (bath temperatures up to 40 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature. ^{1}H and ^{13}C NMR spectra were measured in the solvent stated at 400 or 500 MHz and 101 or 126 MHz respectively. ^{1}H and ^{13}C NMR chemical shifts are quoted in parts per million (ppm) and referenced to the residual solvent peak ($CDCl_3$: ^{1}H = 7.26 ppm and ^{13}C = 77.2 ppm), coupling constants (*J*) are given in Hertz (Hz). Multiplicities are abbreviated as: br (broad), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) or combinations thereof. Assignments were made, where necessary, with the aid of COSY, HSQC and HMBC NMR experiments. For α/β mixtures only peaks that can clearly be assigned have been reported.

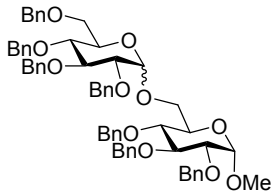
Synthesis and activation of Catalysts.

Catalysts **1a-c** were activated following the reported procedure by Jacobsen *et al*.[1] Catalysts **2a-2d** were prepared following the reported synthesis the same group.[2]

General glycosylation procedure.

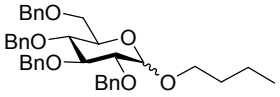
Trichloroacetimidate glycosyl donor (1.2 eq.), acceptor (1.0 eq.) and catalyst (0.1 eq.) were weighed into a round bottom flask and then put under vacuum for 1 h. The flask was then filled with N_2, followed by the addition of anhydrous solvent (0.1 M). The solution was then stirred at room temperature for the times stated in tables 1, 2 and 3. Once the TLC showed complete consumption of starting materials, the reaction mixture was quenched by filtering through a pad of Celite®, washed with additional solvent (5 mL) and concentrated *in vacuo*. All reactions were purified by FCC.

Methyl (2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)-(1->6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 5a:



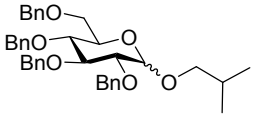
Following the general glycosylation procedure, trichloroacetimidate donor **3** (50 mg, 73 μmol) and monosaccharide acceptor **4a** (28 mg, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 1 hour to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/9:1), the desired glycosylated product **5a** (55 mg, 56 μmol) in 92% yield as a mixture of anomers (α:β = 1:4), as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[3]

Butyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside 5b:



Following the general glycosylation procedure, trichloroacetimidate donor **3** (50 mg, 0.073 mmol) and acceptor **4b** (5.6 μl, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 1 hour to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/20:1), the desired glycosylated product **5b** (32 mg, 0.054 mmol) as a pale yellow solid in 88% yield as a mixture of anomers (α:β = 1:4.9), as determined by ^{1}H NMR and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[4]

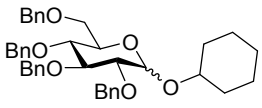
Isobutyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside 5c:



Following the general glycosylation procedure, trichloroacetimidate donor **3** (50 mg, 73 μmol) and acceptor **4c** (5.6 μl, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 1 hour to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/20:1) the desired glycosylated product **5c** (29 mg, 0.048 mmol) as a pale yellow oil in 78% yield as a mixture of anomers (α:β = 1:5.3), as determined by ^{1}H NMR and ^{13}C NMR. **α:β mixture**: ^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 – 7.22 (m, 25H, Ar), 7.17-7.13 (m, , 3H, Ar), 5.01 – 4.92 (m, 3H, C$\underline{H_2}$Ph), 4.85 – 4.71 (m, 5H, C$\underline{H_2}$Ph), 4.75 (d, *J* = 3.3 Hz, 1H, H-1α), 4.67 – 4.46 (m, 5H, C$\underline{H_2}$Ph), 4.39 (d, *J* = 7.8 Hz, 1H, H-1β), 3.99 (t, *J* = 9.3 Hz, 1H, H3α), 3.81 – 3.60 (m, 7H, H-6aβ, -OC$\underline{H_2}$CH(CH$_3$)$_2$, H-3β, H-4β), 3.49 – 3.44 (m, 2H, H-2β and H-5β), 3.39 (dd, J = 9.5, 7.3 Hz, 1H, H-6aα), 3.28 (dd, J_1 = 9.3 Hz, J_2 = 7.1 Hz, 1H, H-6bβ), 3.18 (dd, J_1 = 9.5 Hz, J_2 = 6.3 Hz, 1H, H-6bα), 2.08 – 1.92 (m, 2H, -OCH$_2$C$\underline{H}$(CH$_3$)$_2$), 1.00 – 0.93 (m, 8H, -OCH$_2$CH(C$\underline{H_3}$)$_2$). ^{13}C NMR (101 MHz, Chloroform-d) δ 138.9, 138.6, 138.5, 138.4, 138.3, 138.2, 138.1, 138.0, 128.4, 128.3, 128.3 128.2, 128.0, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 103.8 (C-1β anomer), 97.1 (C-1α anomer),

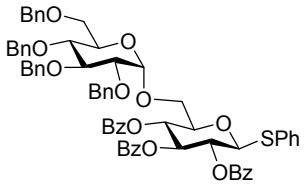
84.7, 82.3, 82.1, 80.2, 78.0, 78.0, 76.7, 75.7, 75.0, 75.0, 75.0, 74.8, 73.4, 73.0, 70.1, 69.0, 28.6, 28.2, 19.6, 19.6, 19.4, 19.4. IR (film) ν_{max}/cm^{-1} 3675, 2987, 2901, 1406, 1394, 1250, 1066, 1057, 892. ESI-HRMS for $C_{38}H_{44}NaO_6^+$ (M+Na$^+$) calculated: 619.3030; found: 619.3028.

Cyclohexyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranoside 5d:



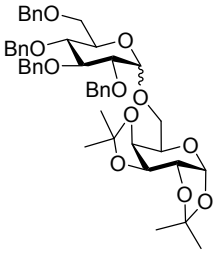
Following the general glycosylation procedure, trichloroacetimidate donor **3** (50 mg, 73 μmol) and acceptor **4d** (6.4 μL, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 1 hour to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/20:1) the desired glycosylated product **5d** (30 mg, 48 μmol) as a white solid in 78% yield as a mixture of anomers (α:β = 1:5.3), as determined by ^{1}H NMR and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[5]

Phenyl *O*-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-(1->6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside 5e:



Following the general glycosylation procedure, trichloroacetimidate donor **3** (50 mg, 73 μmol) and monosaccharide acceptor **4e** (36 mg, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 2 hours to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/4:1) the desired glycosylated product **5e** (50 mg, 0.049 mmol) as a colourless oil in 74% yield as the α product only, as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[6]

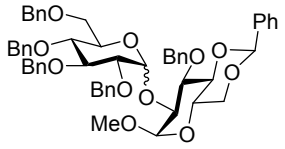
2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl-(1->6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside 5f:



Following the general glycosylation procedure, trichloroacetimidate donor **3** (50 mg, 73 μmol) and monosaccharide acceptor **4f** (16 mg, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6

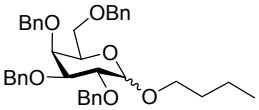
μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 2 hours to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/9:1) the desired glycosylated product **5f** (45 mg, 58 μmol) as a pale yellow syrup in 94% yield as a mixture of anomers (α:β = 1:4.3), as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[3]

Methyl 3-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α/β-D-glucopyranosyl)(1->2)-4,6-*O*-benzylidene-α-D-glucopyranoside 5g:



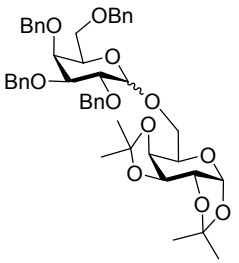
Following the general glycosylation procedure, trichloroacetimidate donor **3** (50 mg, 73 μmol) and monosaccharide acceptor **4g** (23 mg, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous dichloromethane at room temperature for 2.5 hours to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/9:1)the desired glycosylated product **5g** (47 mg, 52 μmol) as a pale yellow oil in 85% yield as a mixture of anomers (α:β = 9:1), as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[7]

Butyl 2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranoside 7:



Following the general glycosylation procedure, trichloroacetimidate donor **6a** (50 mg, 73 μmol) and acceptor **4b** (5.6 μl, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 30 minutes to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/20:1) the desired glycosylated product **7** (30 mg, 50 μmol) as a pale yellow oil in 82% yield as mixture of anomers (α:β = 1:6) as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[8]

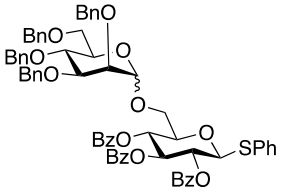
2,3,4,6-tetra-*O*-benzyl-α/β-D-galactopyranosyl-(1->6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside 8:



Following the general glycosylation procedure, trichloroacetimidate donor **7a** (50 mg, 73 μmol) and monosaccharide acceptor **4f** (16 mg, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 30 minutes to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/15:1 to 6:1) the desired glycosylated product **8** (30

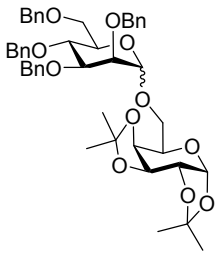
mg, 38 μmol) as a pale yellow oil in 62% yield as mixture of anomers (α:β = 4:1), as determined by ^{1}H NMR and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[9]

Phenyl *O*-(2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranosyl)-(1->6)-2,3,4-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside 9:



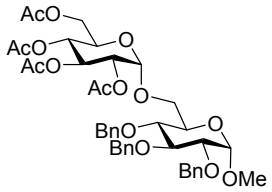
Following the general glycosylation procedure, trichloroacetimidate donor **6b** (50 mg, 73 μmol) and monosaccharide acceptor **4e** (42 mg, 61 μmol) were reacted in presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 2 hours to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/15:1 to 9:1) the desired glycosylated product **9** as a mixture of anomers (α:β = 7.2:1), (40 mg, 36 μmol, 60%) as a pale yellow oil as determined by ^{1}H and ^{13}C NMR. **α anomer.** ^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 – 7.94 (m, 2H, Ar), 7.85 (dd, J = 8.3, 1.4 Hz, 2H, Ar), 7.81 – 7.76 (m, 2H, Ar), 7.55 – 7.20 (m, 34H, Ar), 7.18-7.13 (m, 2H, Ar), 5.84 (t, *J* = 9.6 Hz, 1H), 5.53-5.48 (m, 1H), 4.96 (d, *J* = 10.0 Hz, 1H, H-1β), 4.91 (d, *J* = 1.8 Hz, 1H, H-1'α), 4.84 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.68 (d, *J* = 2.2 Hz, 2H, C*H*$_2$Ph), 4.57 (d, *J* = 12.1 Hz, 1H, C*H*$_2$Ph), 4.49 – 4.37 (m, 4H, C*H*$_2$Ph), 3.98 – 3.88 (m, 3H), 3.81 (dd, *J* = 9.4, 3.1 Hz, 1H), 3.72 – 3.56 (m, 5H). ^{13}C NMR (126 MHz, Chloroform-d) δ 165.8, 165.1, 165.0, 138.7, 138.6, 138.4, 138.4, 133.3, 133.2, 133.1, 131.9, 129.9, 129.9, 129.8, 129.7, 129.2, 129.1, 129.0, 129.0, 128.9, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.3, 128.3, 128.2, 128.2, 127.9, 127.7, 127.7, 127.5, 127.4, 127.4, 98.4 (C1-α anomer), 86.5 (C1'-β anomer), 80.1, 76.9, 74.9, 74.7, 74.7, 74.2 73.2, 72.5, 72.1, 71.9, 70.6, 69.8, 69.1, 66.8. IR (film) ν_{max}/cm^{-1} 1733, 1601, 1449, 1279, 1260, 1090, 1066, 1023, 711. ESI-HRMS for $C_{67}H_{62}NaO_{13}S^{+}$ (MNa^{+}) calculated: 1129.3803; found: 1129.3825. $[\propto]_D^{23}$ = 42 (*c* 0.012, Dichloromethane).

2,3,4,6-tetra-*O*-benzyl-α/β-D-mannopyranosyl-(1->6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside 10:



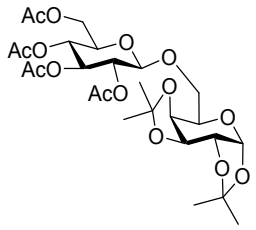
Following the general glycosylation procedure, trichloroacetimidate donor **6b** (50 mg, 73 μmol) and monosaccharide acceptor **4f** (28 mg, 61 μmol) were reacted in the presence of catalyst **2d** (8 mg, 6 μmol) in 0.6 mL of anhydrous acetonitrile at room temperature for 30 minutes to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/9:1) the desired glycosylated product **10** (26 mg, 56 μmol, 92% yield) as a mixture of anomers (α:β = 1:4) as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[3]

Methyl *O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-(1->6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 11:



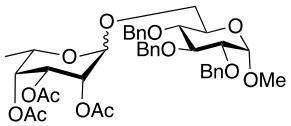
Following the general glycosylation procedure, trichloroacetimidate donor **6c** (100 mg, 204 μmol) and monosaccharide acceptor **4a** (39 mg, 85 μmol) were reacted in presence of catalyst **2d** (12 mg, 9 μmol) in 1.0 mL of anhydrous dichloromethane at room temperature for 24 hours (an extra aliquot of 50 mg of trichloroacetimidate was added after 8 hours stirring) to afford, after FCC on silica gel (Toluene:Acetone/20:1), the desired glycosylated product **11** (33 mg, 42 μmol, 50% yield) as a β only as a pale yellow oil as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[10]

2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1->6)-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranoside 12:



Following the general glycosylation procedure, trichloroacetimidate donor **6c** (100 mg, 204 μmol) and monosaccharide acceptor **4f** (44 mg, 169 μmol) were reacted in presence of catalyst **2d** (22 mg, 17 μmol) in 1.7 mL of anhydrous dichloromethane at room temperature for 24 hours to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/4:1) the desired glycosylated product **12** (52 mg, 87 μmol, 52% yield) as a β only as a pale yellow oil as determined by ^{1}H and ^{13}C NMR. The spectroscopic data was in agreement with previously reported data.[11]

Methyl *O*-(2,3,4-tri-*O*-acetyl-α/β-L-fucopyranosyl)-(1->6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside 13:



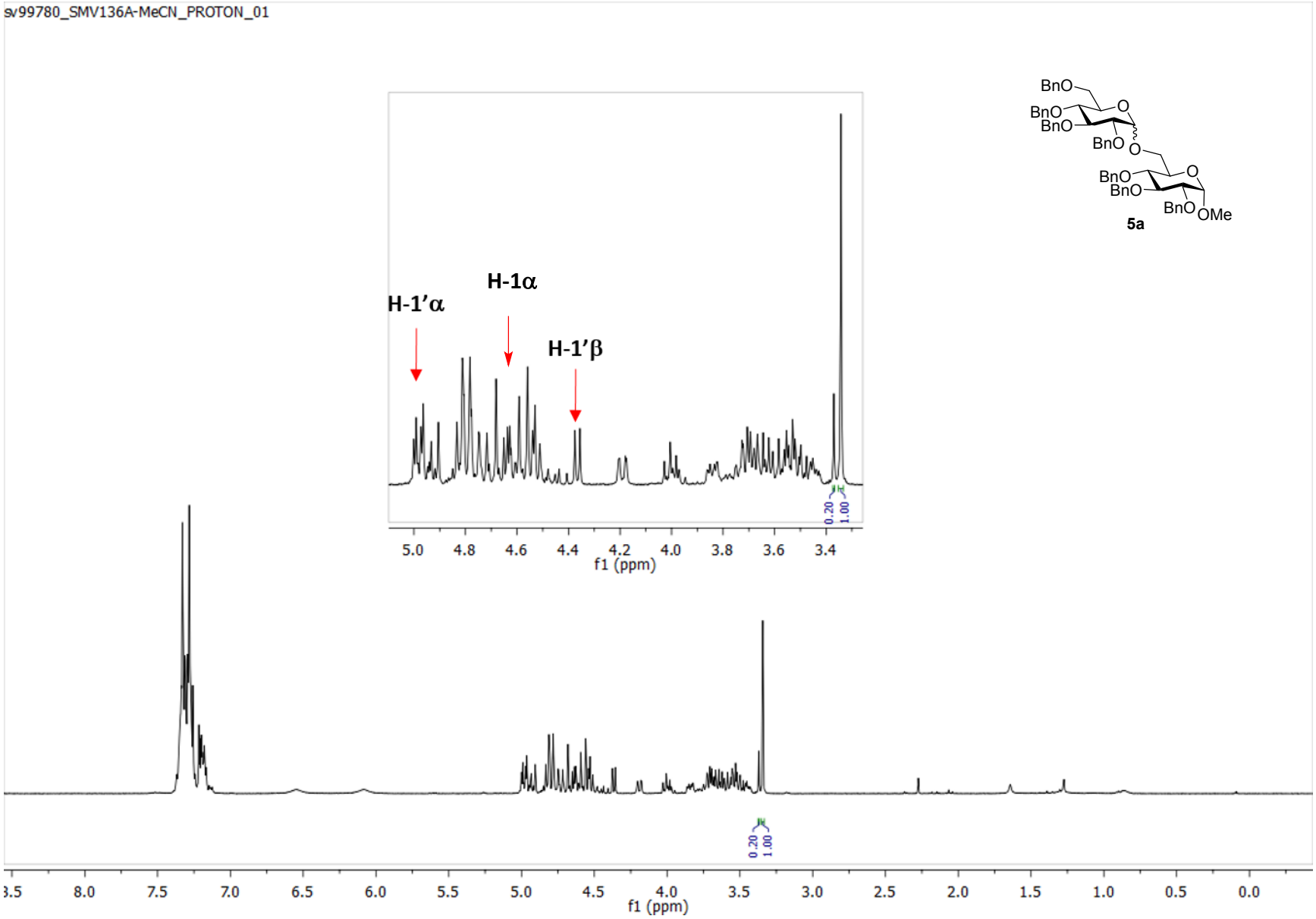
Following the general glycosylation procedure, trichloroacetimidate donor **6e** (100 mg, 344 μmol) and monosaccharide acceptor **4a** (67 mg, 143 μmol) were reacted in presence of catalyst **2d** (18 mg, 14 μmol) in 1.5 mL of anhydrous dichloromethane at room temperature for 3 hours (3 aliquots of 50 mg of trichloroacetimidate were added until not more acceptor was left) to give, after purification on FCC on silica gel (*n*-Hexane:EtOAc/5:1 to 3:1) the desired glycosylated product **13** (87 mg, 118 μmol, 83% yield) as a separable mixture of anomers (α:β = 1:4.9) as determined by ^{1}H and ^{13}C NMR.

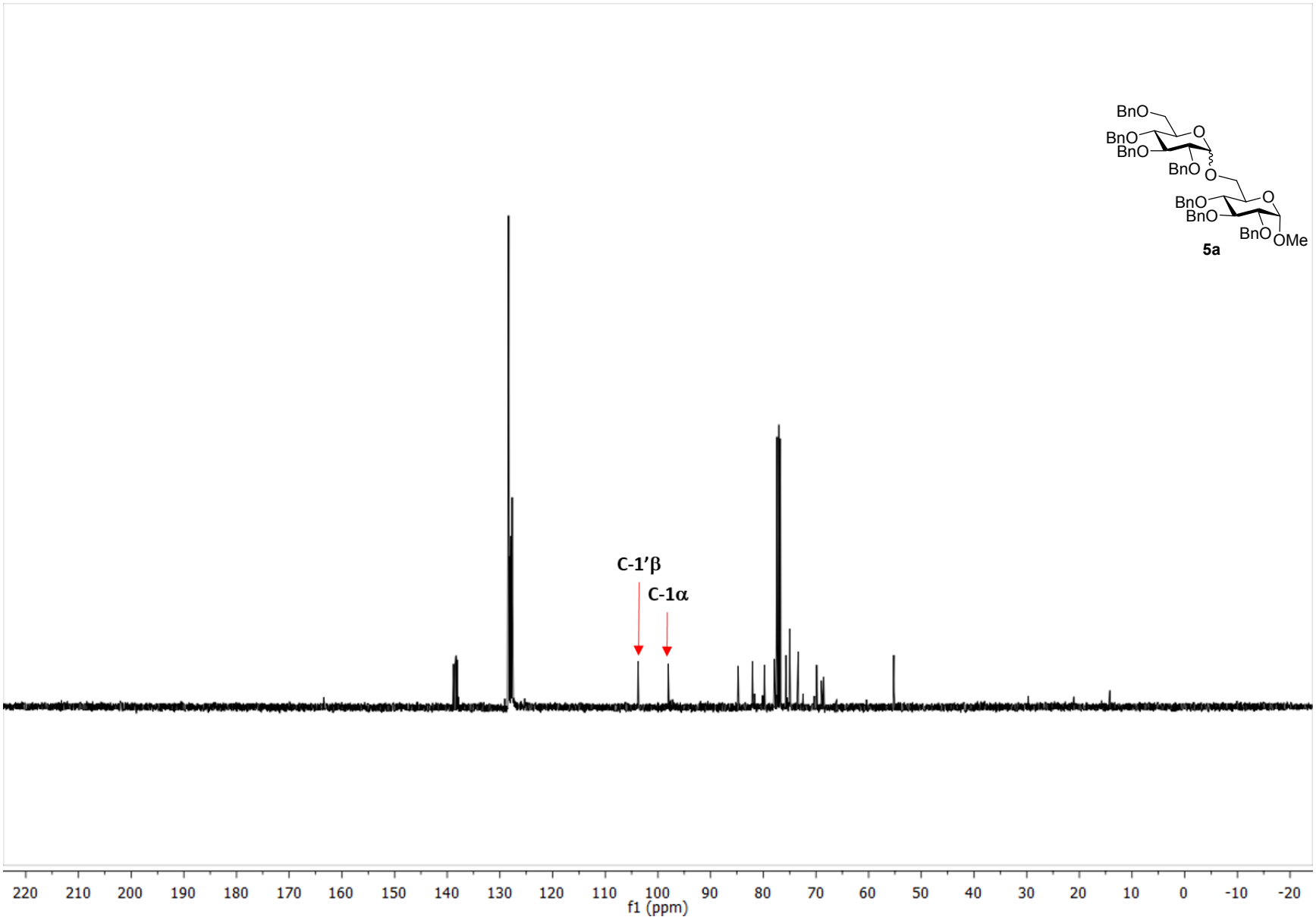
α anomer. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.35 – 7.25 (m, 15H, Ar), 5.74 (d, *J* = 5.0 Hz, 1H, H-1'), 5.23 (dd, *J* = 3.4, 1.9 Hz, 1H, H-2), 5.00 (dd, *J* = 7.2, 3.4 Hz, 1H, H-3'), 4.98 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.88 (d, *J* = 10.9 Hz, 1H, C*H*$_2$Ph), 4.81 (d, *J* = 11.0 Hz, 1H, C*H*$_2$Ph), 4.77 (d, *J* = 12.7 Hz, 1H, C*H*$_2$Ph), 4.66 – 4.59 (m, 2H, 2x C*H*$_2$Ph), 4.60 (d, *J* = 3.64 Hz, 1H, H-1), 4.22 – 4.19 (m, 2H, H-2'), 3.97 (t, *J* = 9.2 Hz, 1H, H-4), 3.73 – 3.67 (m, 3H, H-6a, H-6b and H-3), 3.55 – 3.48 (m, 2H, H-5 and H-5'), 3.35 (s, 3H, OMe), 2.12 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.65 (s, 3H, OAc), 1.17 (d, *J* = 6.6 Hz, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, Chloroform-d) δ 13C NMR (126 MHz, cdcl3) δ 170.2, 170.1, 138.7, 138.4, 138.1, 128.5, 128.5, 128.5, 128.4, 128.4, 128.4, 128.1, 128.1, 128.1, 128.0, 127.9, 127.9, 127.7, 127.6, 98.0 (C-1), 97.8 (C-1'), 82.1 (C-4), 79.9, 77.6, 75.8, 74.9, 73.4, 73.4, 72.1 (C-3'), 69.4 (C-3), 68.9 (C-2), 67.3, 61.4 (C-6), 55.1, 29.7, 24.3, 20.8, 20.6, 16.1. IR (film) ν_{max}/cm^{-1} 2928, 1747, 1369, 1220, 1072, 1021, 911, 736, 698. ESI-HRMS for $C_{40}H_{48}NaO_{13}^{+}$ (MNa^{+}) calculated: 759.2987; found: 759.2987. $[\propto]_D^{23}$ = -4 (*c* 0.007, Dichloromethane).

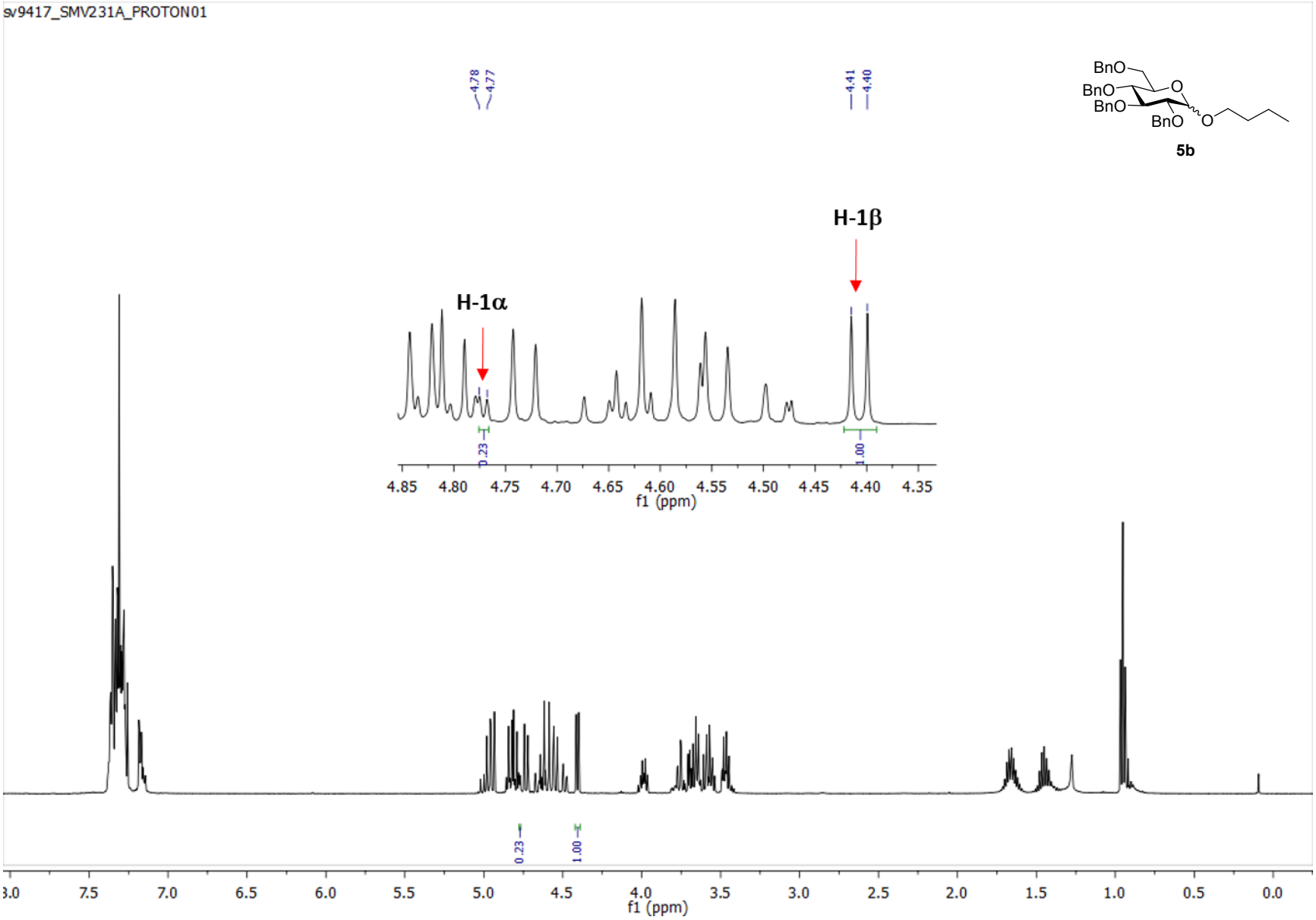
β anomer. ^{1}H NMR (400 MHz, Chloroform-d) δ δ 7.35 – 7.24 (m, 15H, Ar), 5.21 – 5.16 (m, 2H, H-2 and H-2'), 5.00 (dd, *J* = 10.6, 3.5 Hz, 1H, H-3'), 4.96 (d, *J* = 11.1 Hz, 1H, C*H*$_2$Ph), 4.84 – 4.75 (m, 3H, C*H*$_2$Ph), 4.68 – 4.55 (m, 4H, C*H*$_2$Ph, H-1 and H-1'), 4.11 – 4.05 (m, 1H, H-6a), 3.95 (t, *J* = 9.3 Hz, 1H, H-4), 3.68 – 3.66 (m, 3H, H-5, H-5' and H-6b), 3.49 (t, *J* = 9.4 Hz, 1H, H-3), 3.43 (dd, *J* = 9.6, 3.5 Hz, 1H, H-4'), 3.35 (s, 3H, OMe), 2.13 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.94 (s, 3H, OAc), 1.19 (d, *J* = 6.4 Hz, 3H, C*H*$_3$). ^{13}C NMR (126 MHz, Chloroform-d) δ 170.7, 170.3, 169.4, 138.91, 38.3, 138.1, 128.5, 128.4, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.9, 127.9, 127.7, 127.7, 127.5, 101.1 (C-1'), 98.0 (C-1), 81.8 (C-4), 79.8 (C-4'), 77.6 (C-3), 75.6, 75.1, 73.2, 71.3 (C-3'), 70.3, 70.3, 69.1, 69.0, 67.3 (C-6), 55.1, 20.8, 20.7, 20.6. IR (film) ν_{max}/cm^{-1} 2928, 1747, 1369, 1220, 1072, 1021, 911, 736, 698. IR (film) ν_{max}/cm^{-1} 2936, 2251, 1747, 1368, 1219, 1054, 1027, 909, 729, 697. ESI-HRMS for $C_{40}H_{48}NaO_{13}^{+}$ (MNa^{+}) calculated: 759.2987; found: 759.2987. $[\propto]_D^{23}$ = 7 (*c* 0.029, Dichloromethane).

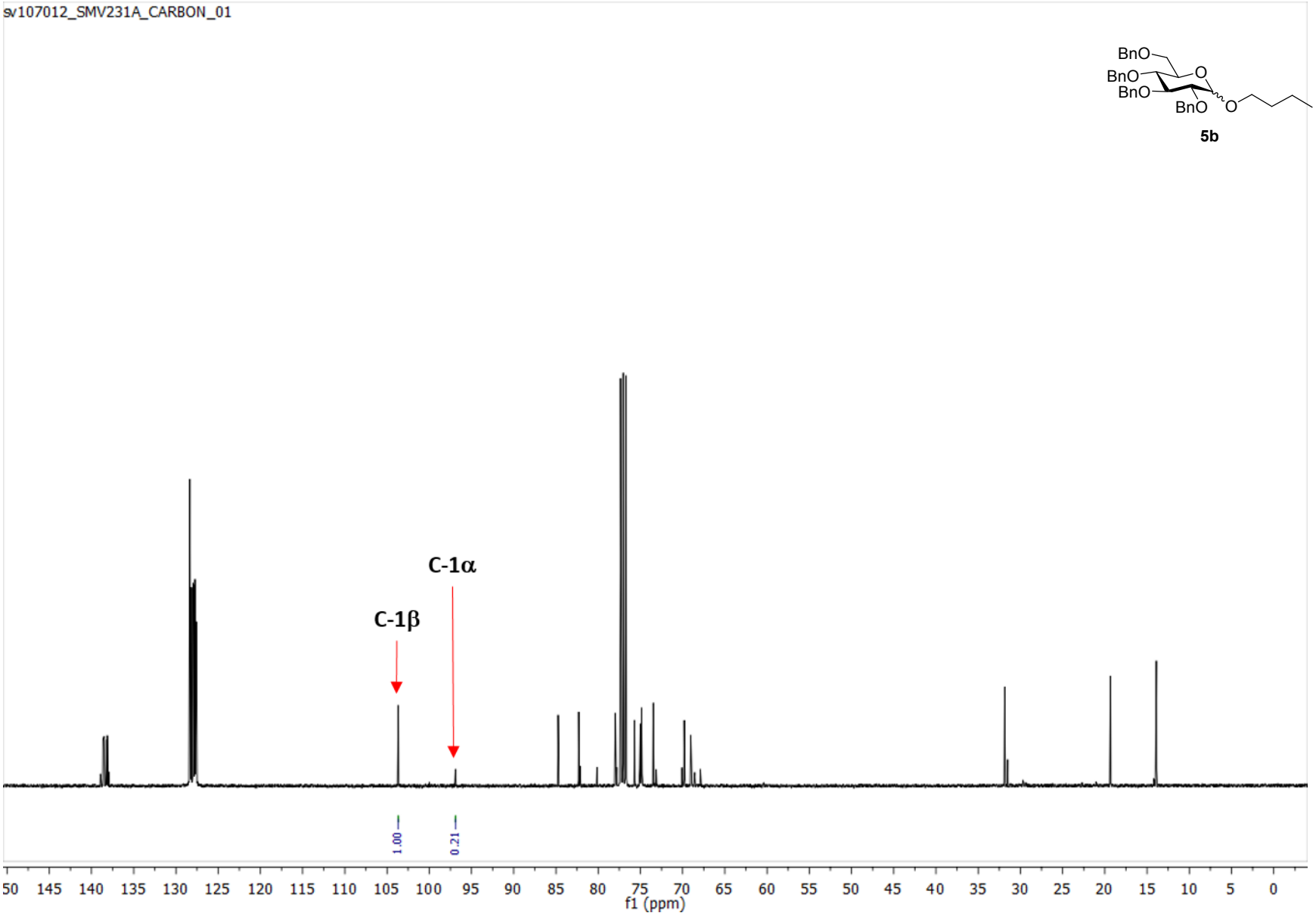
References

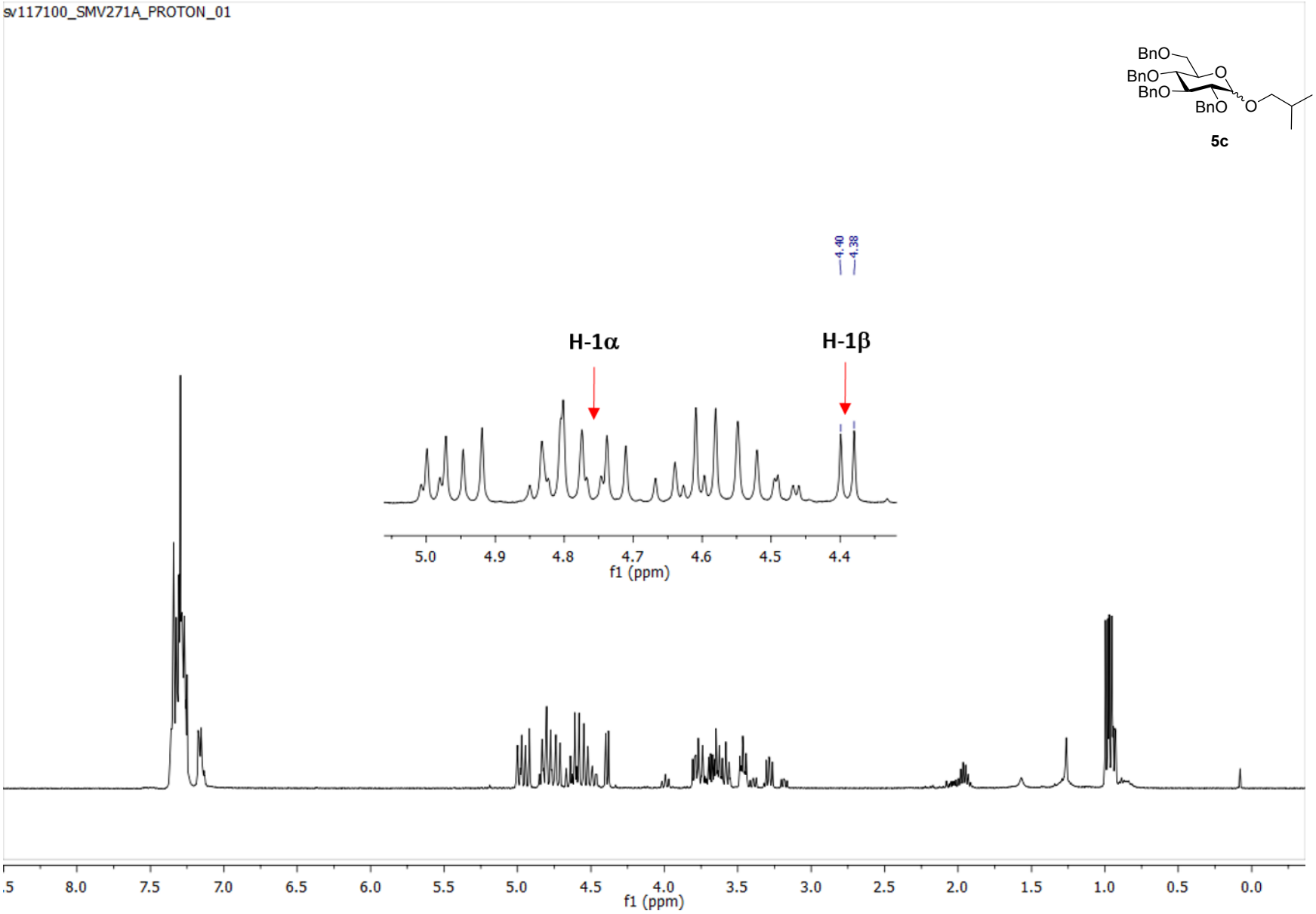
(1) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936.
(2) White, D. E.; Jacobsen, E. N. *Tetrahedron-Asymmetr* **2003**, *14*, 3633.
(3) Kim, K. S.; Fulse, D. B.; Baek, J. Y.; Lee, B. Y.; Jeon, H. B. *J Am Chem Soc* **2008**, *130*, 8537.
(4) Hoang, K. L. M.; Bai, Y.; Ge, X.; Liu, X. W. *J Org Chem* **2013**, *78*, 5196.
(5) Imagawa, H.; Kinoshita, A.; Fukuyama, T.; Yamamoto, H.; Nishizawa, M. *Tetrahedron Lett* **2006**, *47*, 4729.
(6) He, H. W.; Zhu, X. M. *Org Lett* **2014**, *16*, 3102.
(7) Nagai, H.; Sasaki, K.; Matsumura, S.; Toshima, K. *Carbohydr Res* **2005**, *340*, 337.
(8) Mattson, A. L.; Michel, A. K.; Cloninger, M. J. *Carbohydr Res* **2012**, *347*, 142.
(9) Kumar, V.; Taxak, N.; Jangir, R.; Bharatam, P. V.; Kartha, K. P. R. *J Org Chem* **2014**, *79*, 3427.
(10) Xiong, D. C.; Yang, A. Q.; Yu, Y.; Ye, X. S. *Tetrahedron Lett* **2015**, *56*, 211.
(11) Mukherjee, D.; Ray, P. K.; Chowdhury, U. S. *Tetrahedron* **2001**, *57*, 7701.

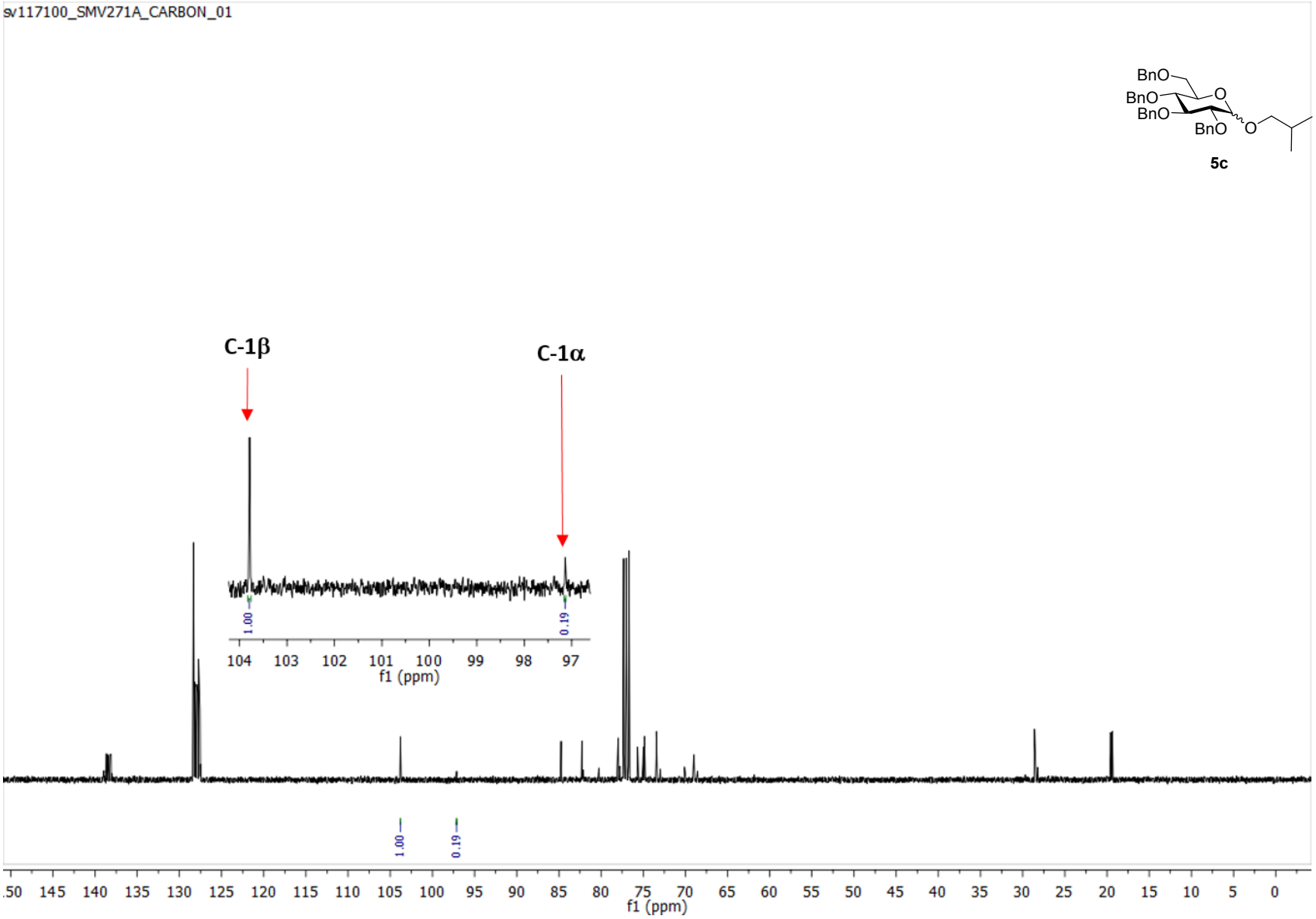

sv99780_SMV136A-MeCN_PROTON_01
H-1'α
H-1α
H-1'β
BnO
BnO
BnO
BnO
O
BnO
BnO
BnO
OMe
5a
0.20
1.00
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
f1 (ppm)
0.20
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

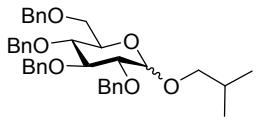

BnO
BnO
BnO
BnO
O
O
BnO
BnO
BnO
BnO
OMe
5a
C-1'β
C-1α
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


sv9417_SMV231A_PROTON01
4.78
4.77
4.41
4.40
BnO
BnO
BnO
BnO
O
O
5b
H-1β
H-1α
0.23
1.00
4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35
f1 (ppm)
0.23
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

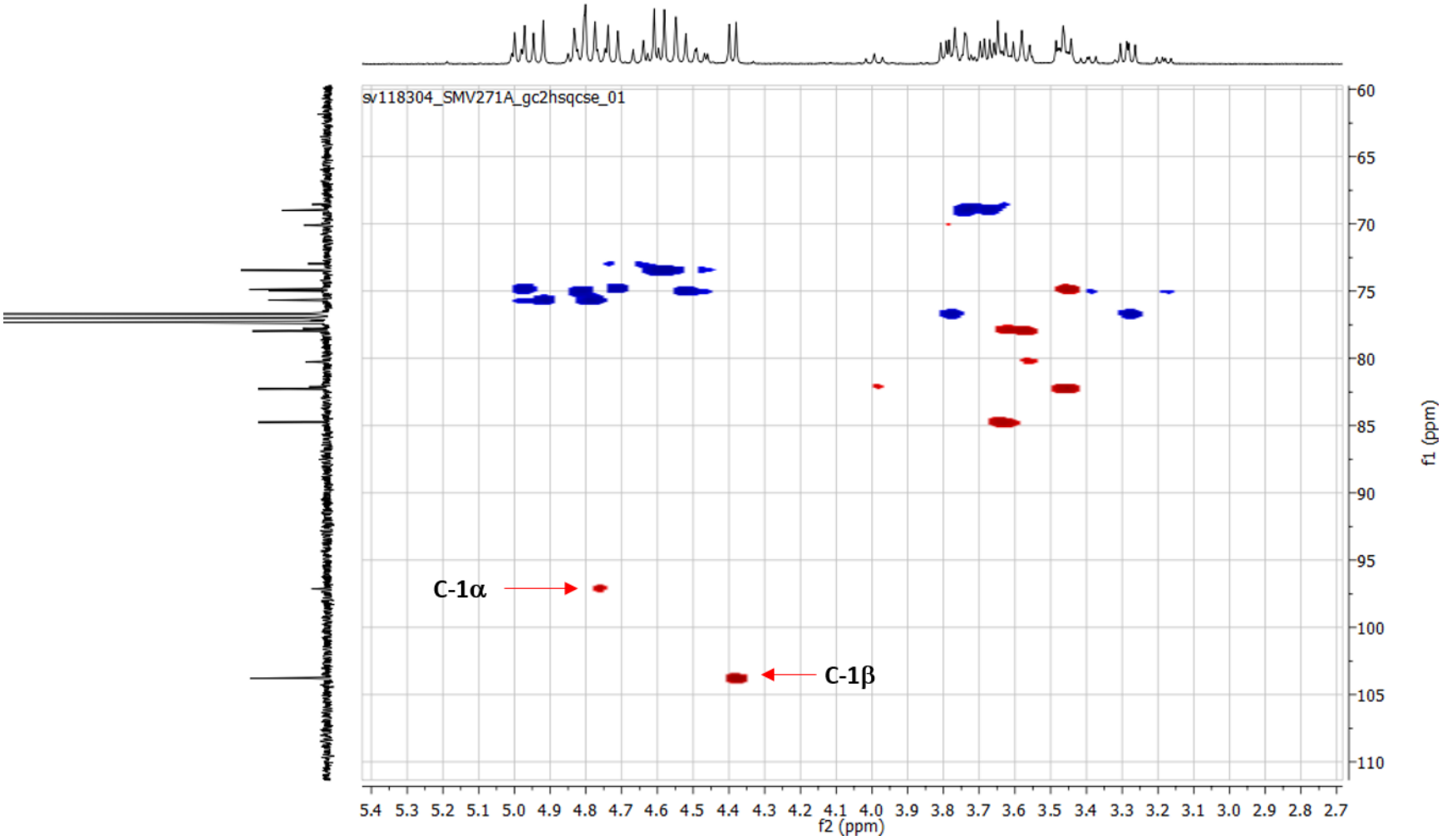

sv107012_SMV231A_CARBON_01
BnO
BnO
BnO
BnO
O
O
5b
C-1α
C-1β
1.00
0.21
50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

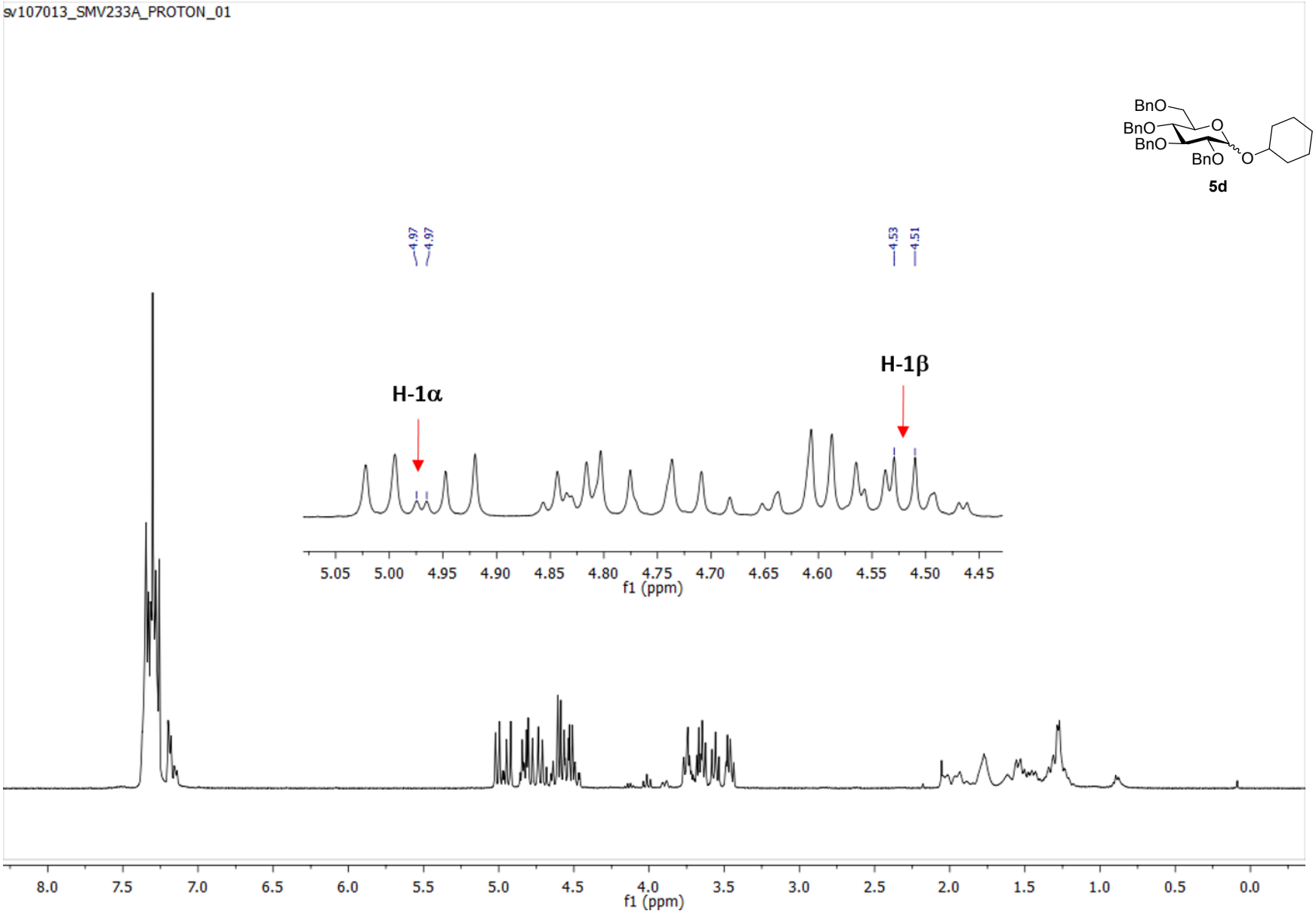

sv117100_SMV271A_PROTON_01
BnO
BnO
BnO
BnO
O
O
5c
4.40
4.38
H-1α
H-1β
5.0
4.9
4.8
4.7
4.6
4.5
4.4
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

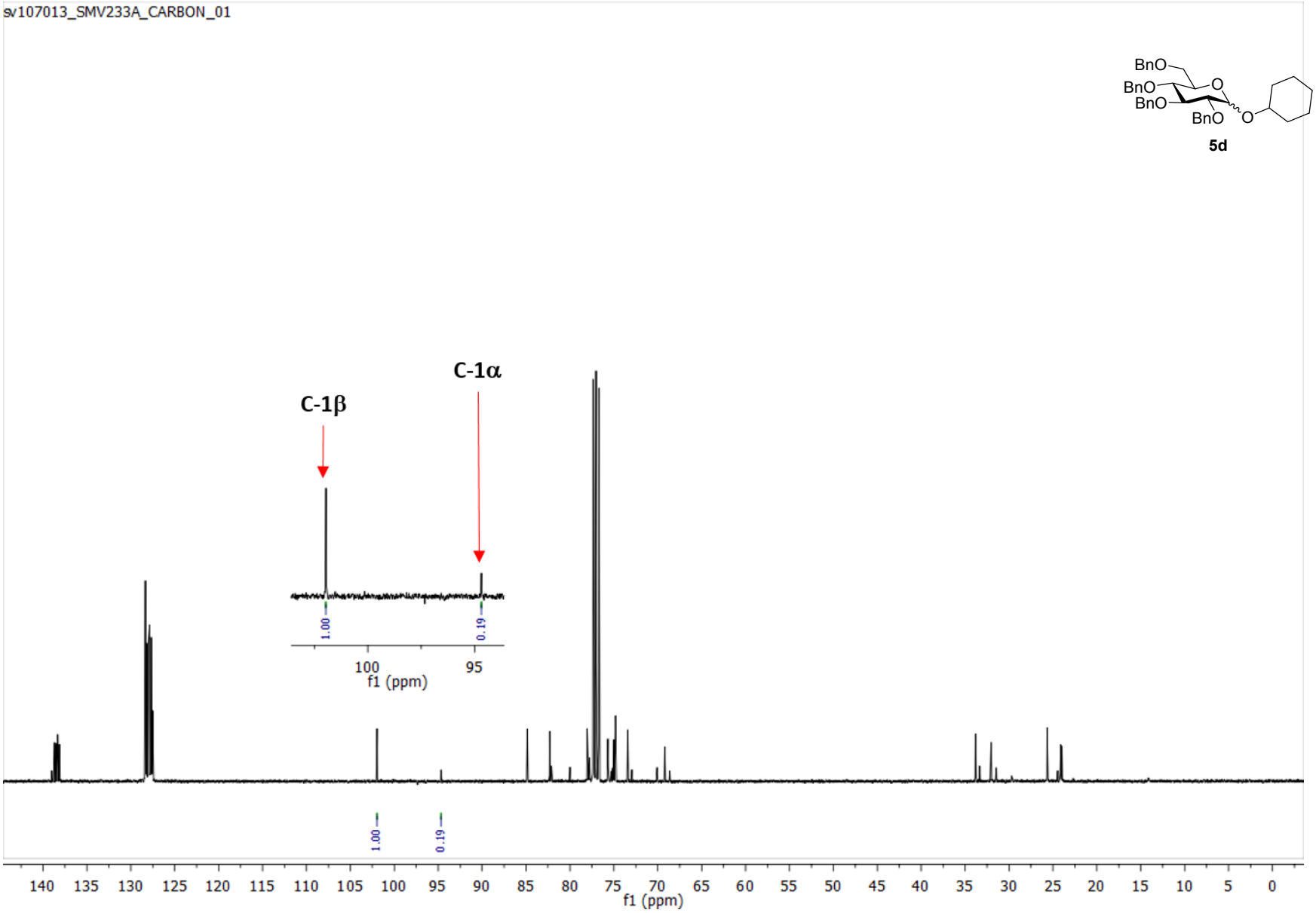

sv117100_SMV271A_CARBON_01
BnO
BnO
BnO
BnO
O
O
5c
C-1β
C-1α
1.00
0.19
104 103 102 101 100 99 98 97
f1 (ppm)
1.00
0.19
.50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

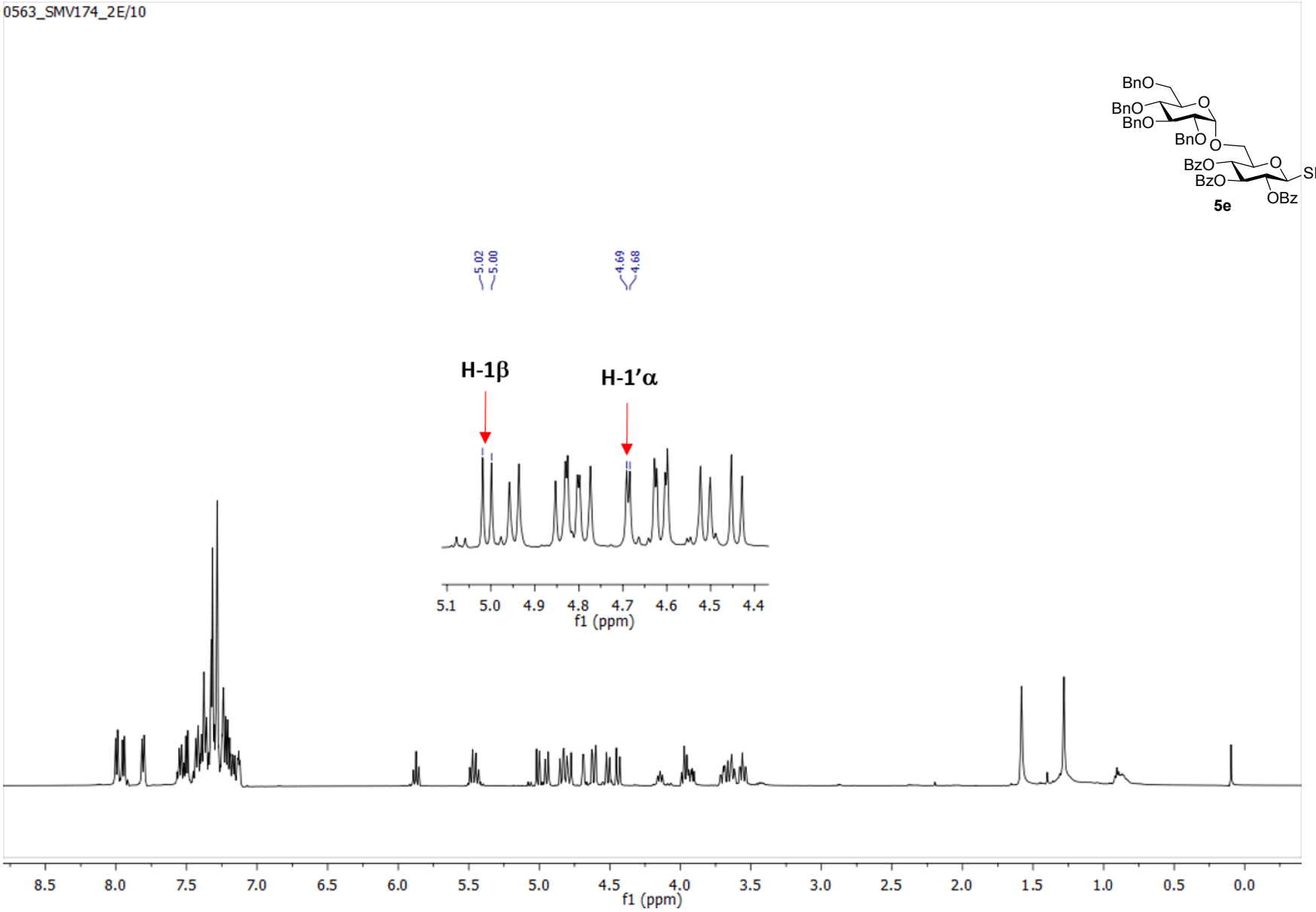

BnO
BnO
BnO
BnO
O
O

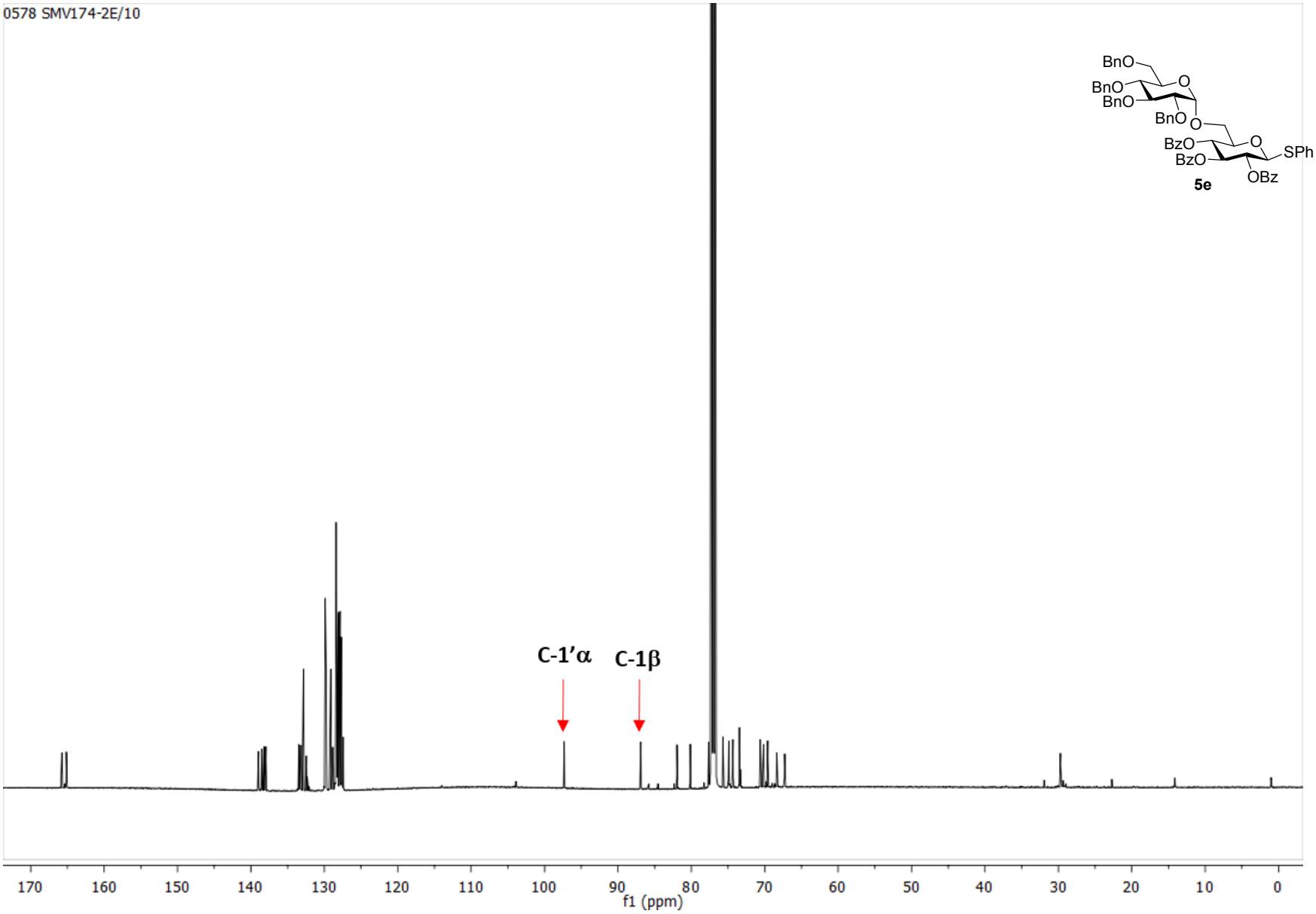
5c

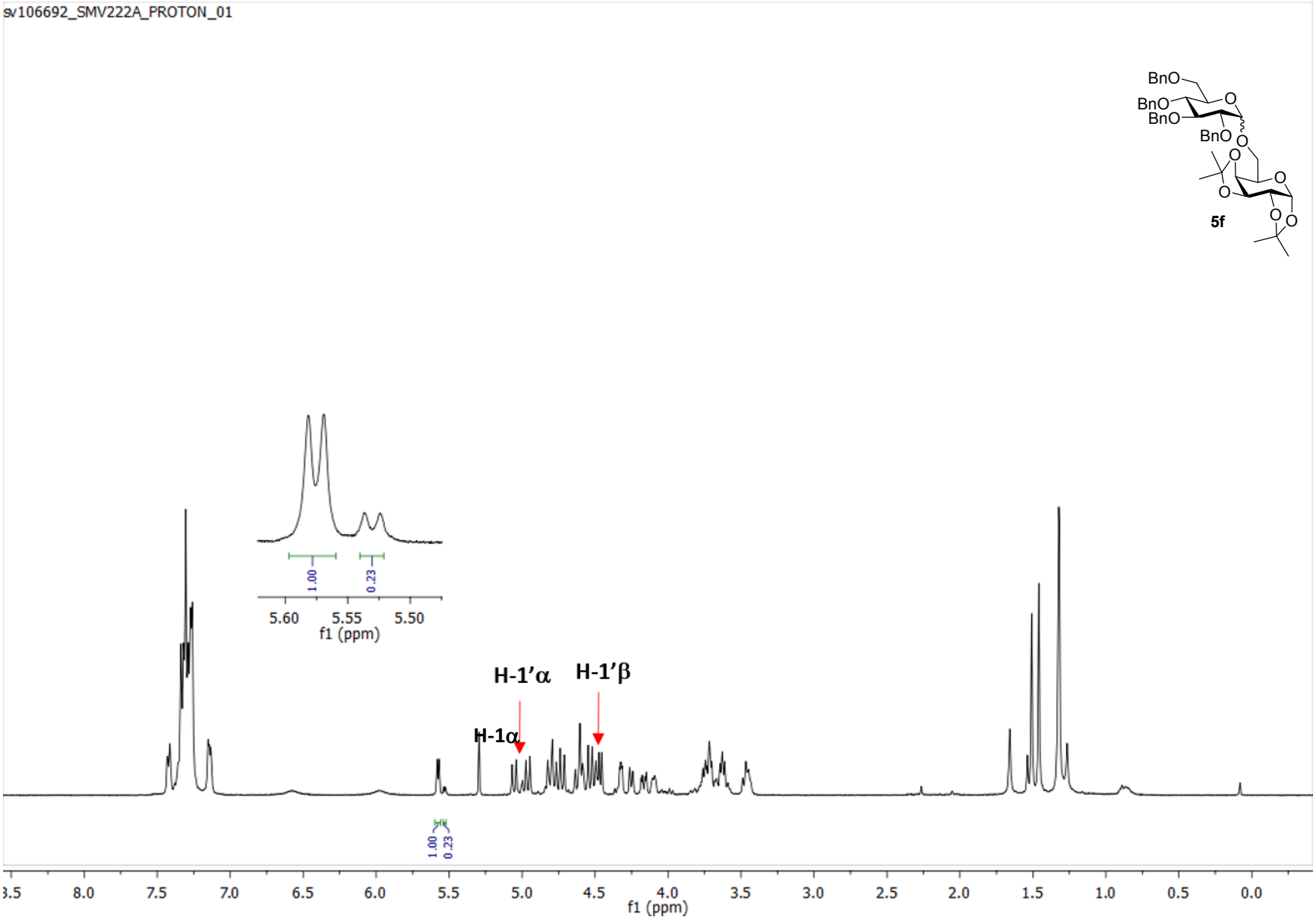

sv118304_SMV271A_gc2hsqcse_01
C-1α
C-1β
f2 (ppm)
f1 (ppm)

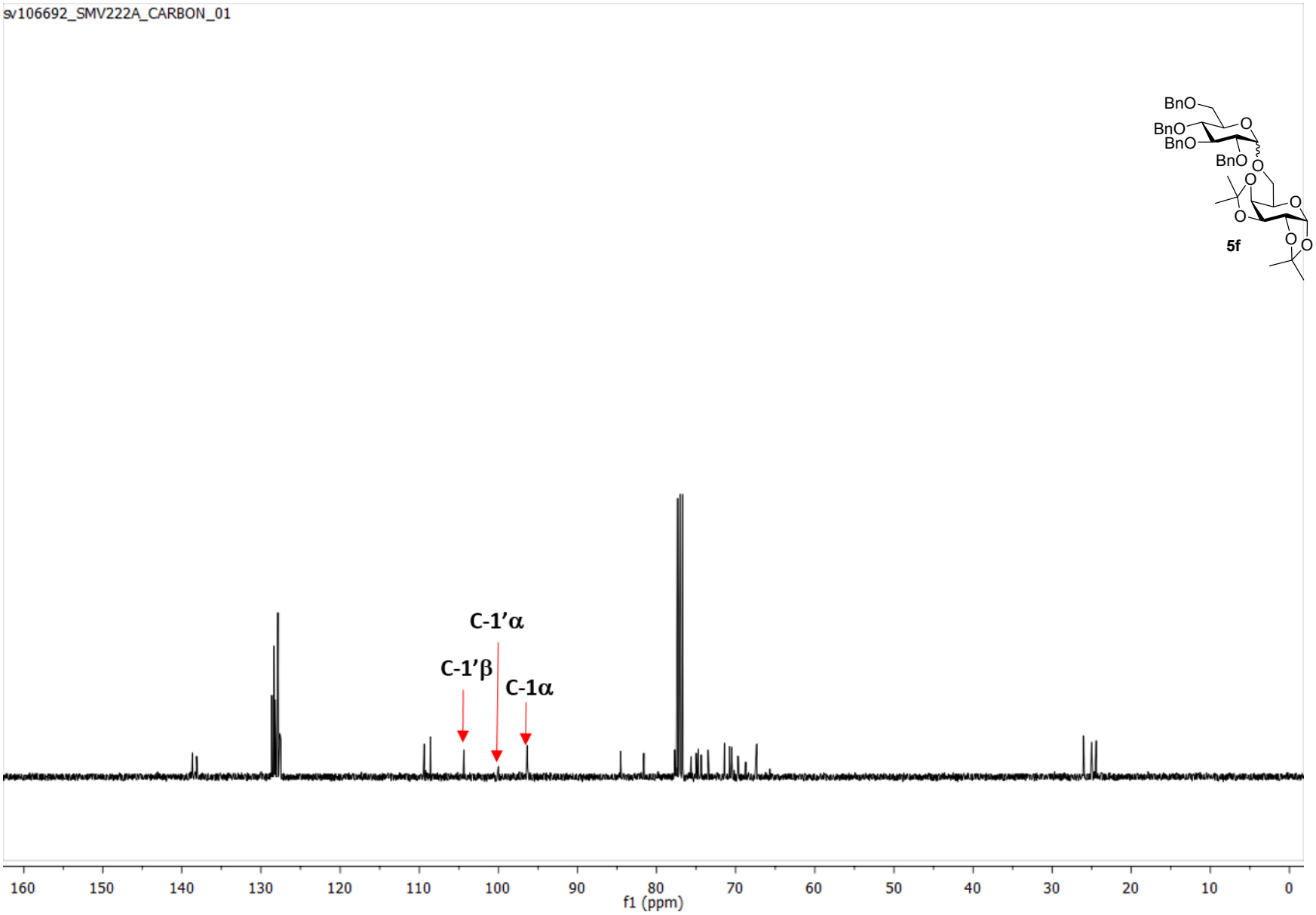

sv107013_SMV233A_PROTON_01
BnO
BnO
BnO
BnO
O
O
5d
4.97
4.97
4.53
4.51
H-1α
H-1β
5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45
f1 (ppm)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

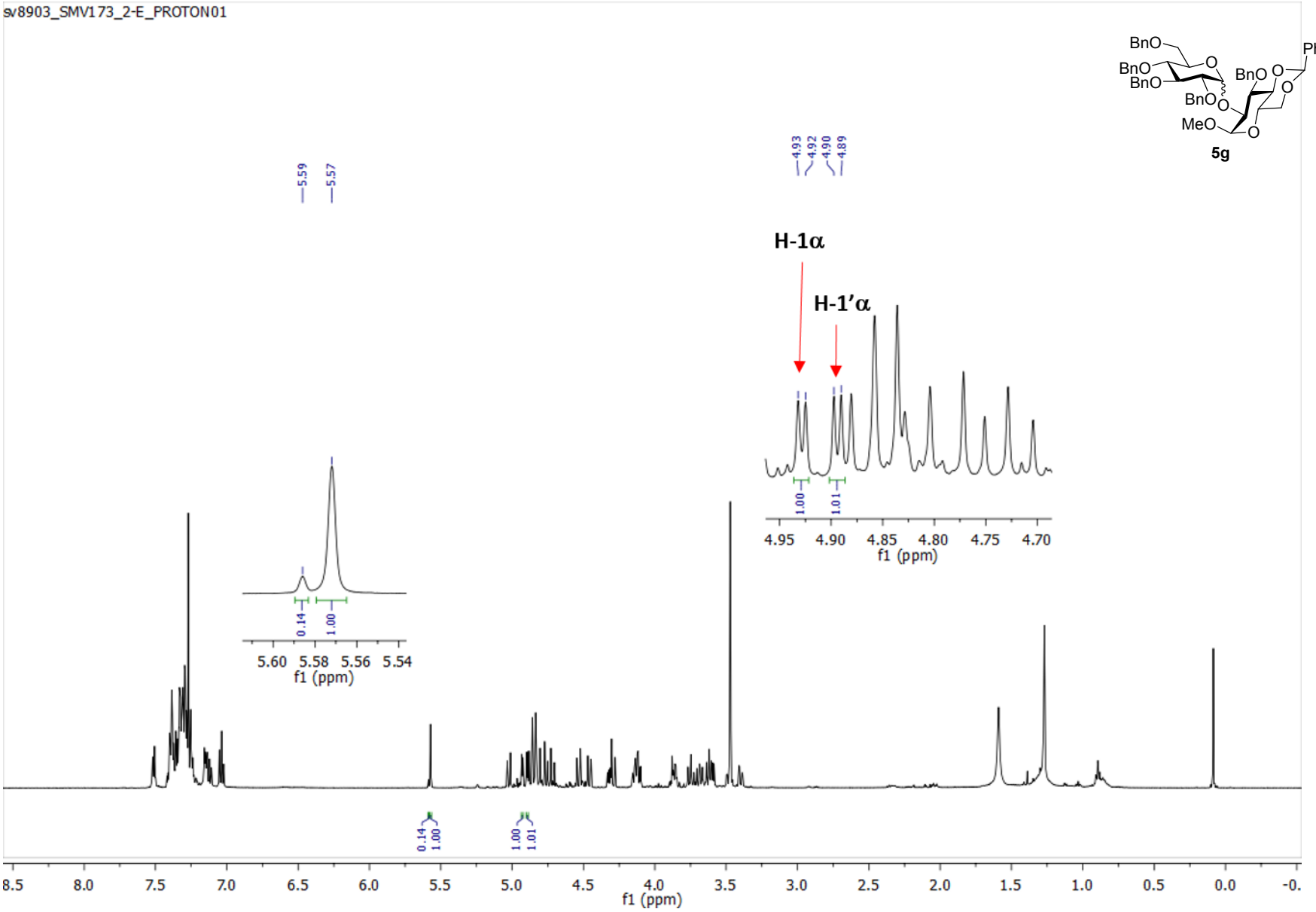

sv107013_SMV233A_CARBON_01
BnO
BnO
BnO
BnO
O
O
5d
C-1α
C-1β
1.00
0.19
100
95
f1 (ppm)
1.00
0.19
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

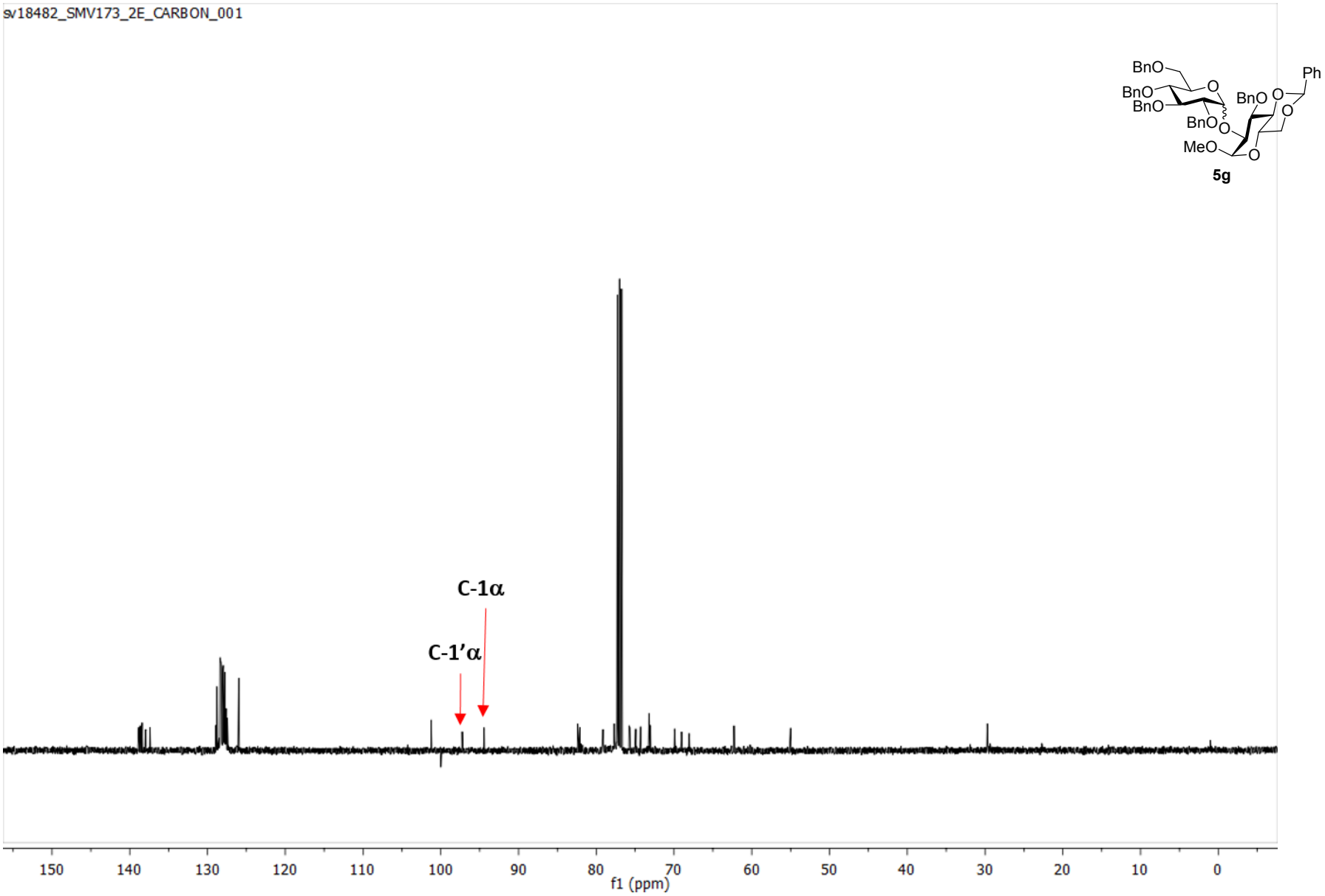

0563_SMV174_2E/10
BnO
BnO
BnO
BnO
O
O
BzO
BzO
O
SPh
OBz
5e
5.02
5.00
4.69
4.68
H-1β
H-1'α
5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

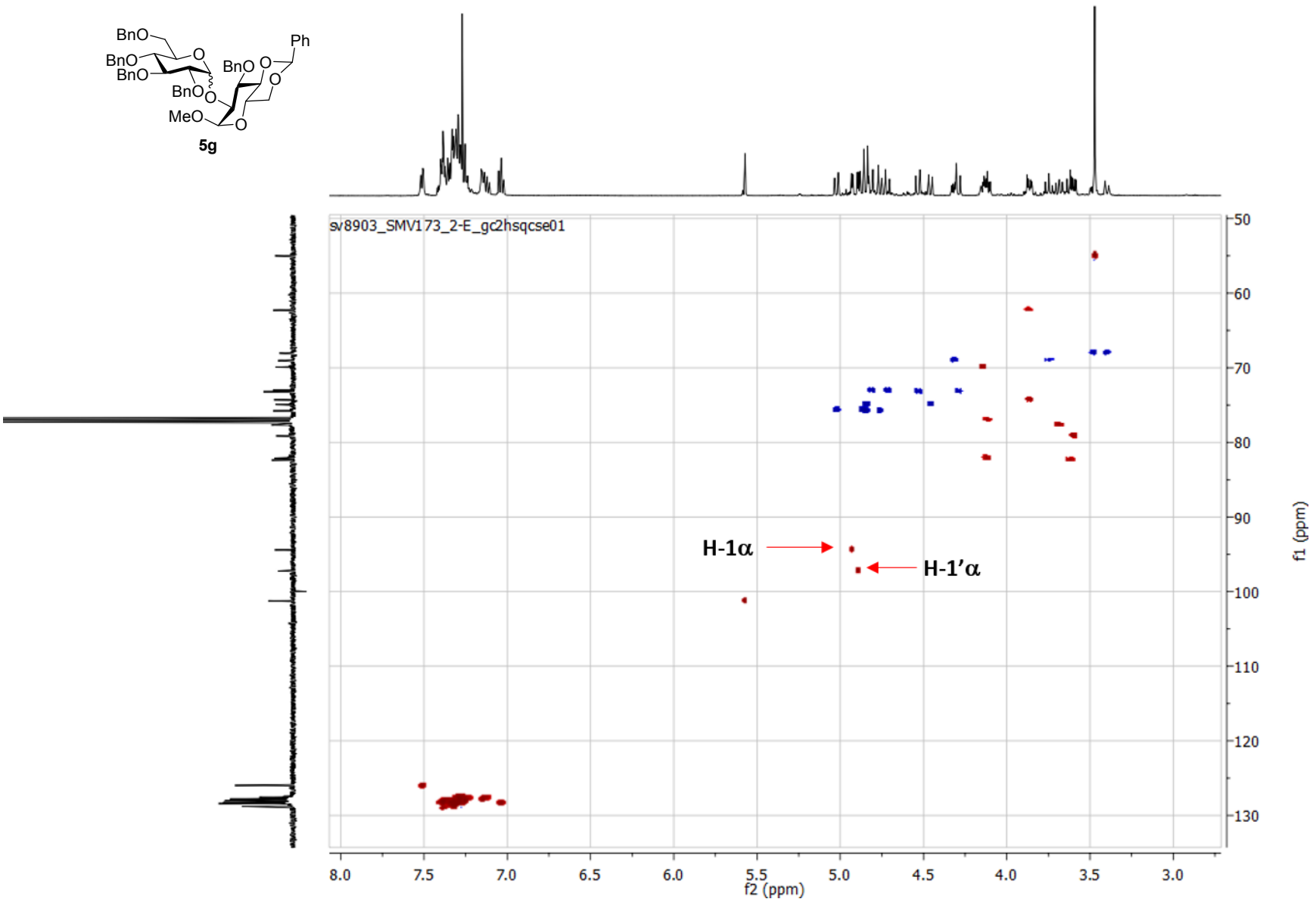

0578 SMV174-2E/10
BnO
BnO
BnO
BnO
O
O
BzO
BzO
O
SPh
OBz
5e
C-1'α
C-1β
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

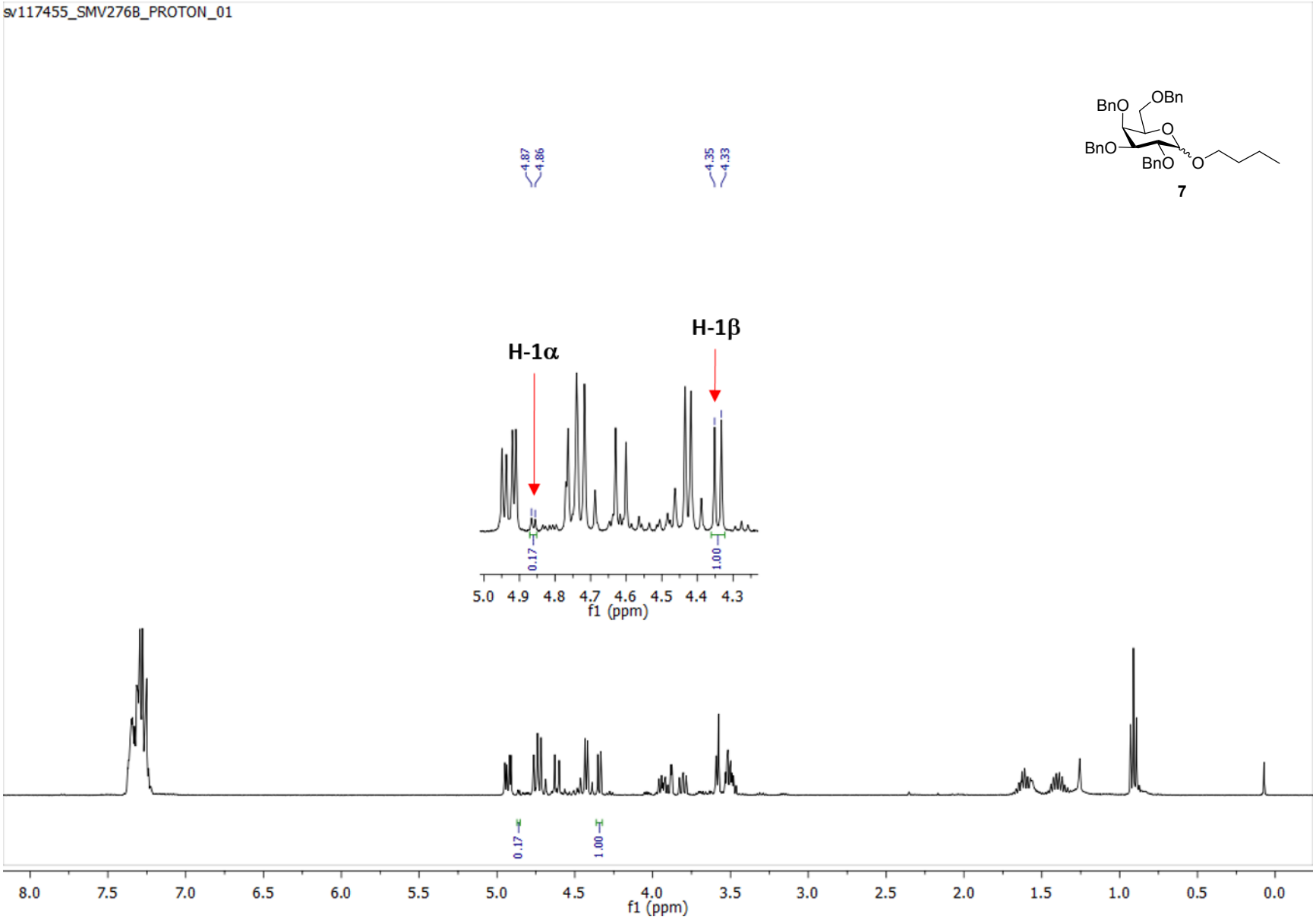

sv106692_SMV222A_PROTON_01
BnO
BnO
BnO
BnO
O
O
O
O
O
O
O
5f
1.00
0.23
5.60
5.55
5.50
f1 (ppm)
H-1'α
H-1'β
H-1α
1.00
0.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

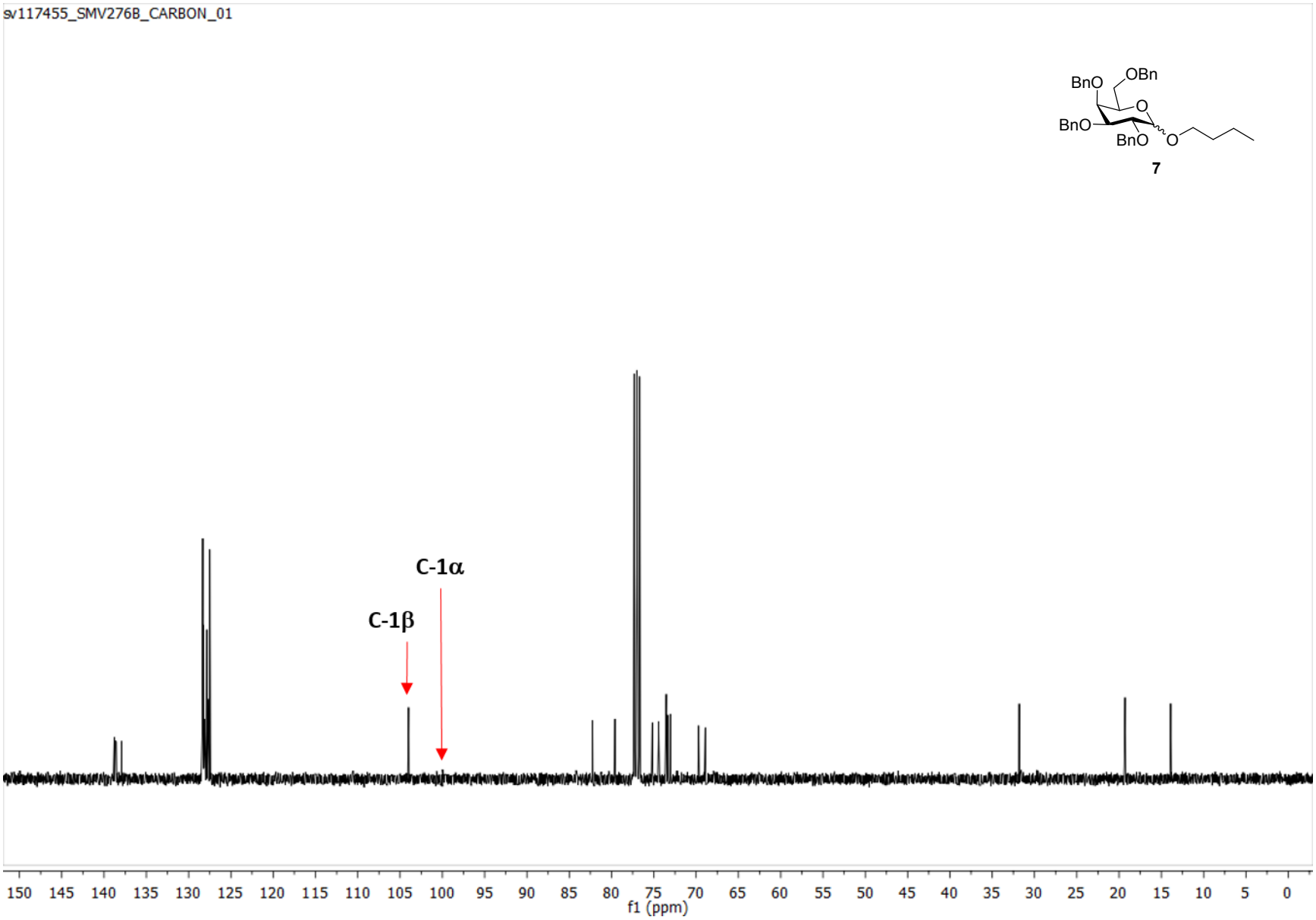

sv106692_SMV222A_CARBON_01
BnO
BnO
BnO
BnO
O
O
O
O
O
O
O
O
5f
C-1'α
C-1'β
C-1α
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

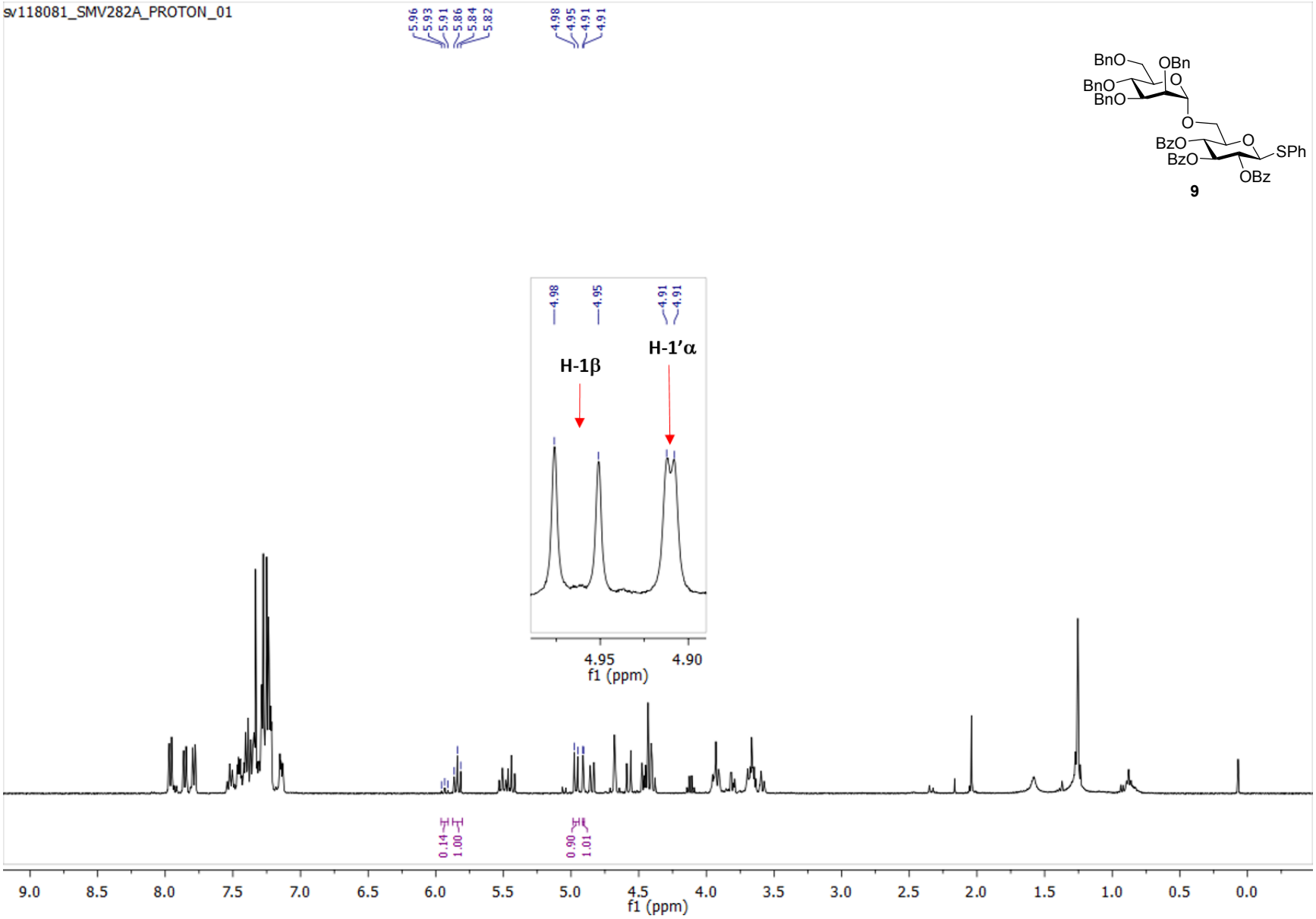

sv8903_SMV173_2-E_PROTON01
BnO
BnO
BnO
BnO
BnO
O
O
O
O
MeO
Ph
5g
5.59
5.57
4.93
4.92
4.90
4.89
H-1α
H-1'α
1.00
1.01
4.95 4.90 4.85 4.80 4.75 4.70
f1 (ppm)
0.14
1.00
5.60 5.58 5.56 5.54
f1 (ppm)
0.14
1.00
1.00
1.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

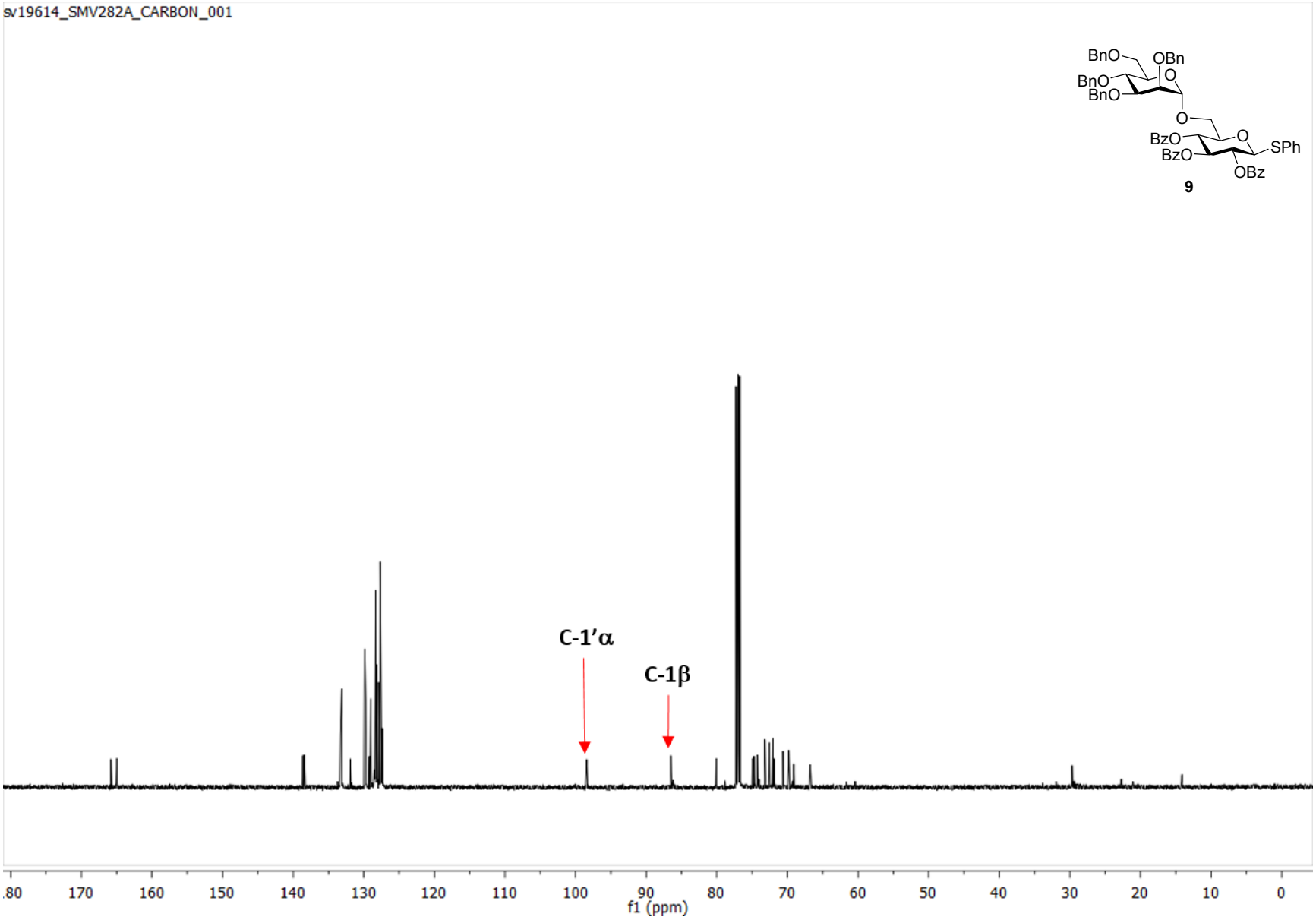

sv18482_SMV173_2E_CARBON_001
BnO
BnO
BnO
O
BnO
O
BnO
O
O
Ph
MeO
O
5g
C-1α
C-1'α
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

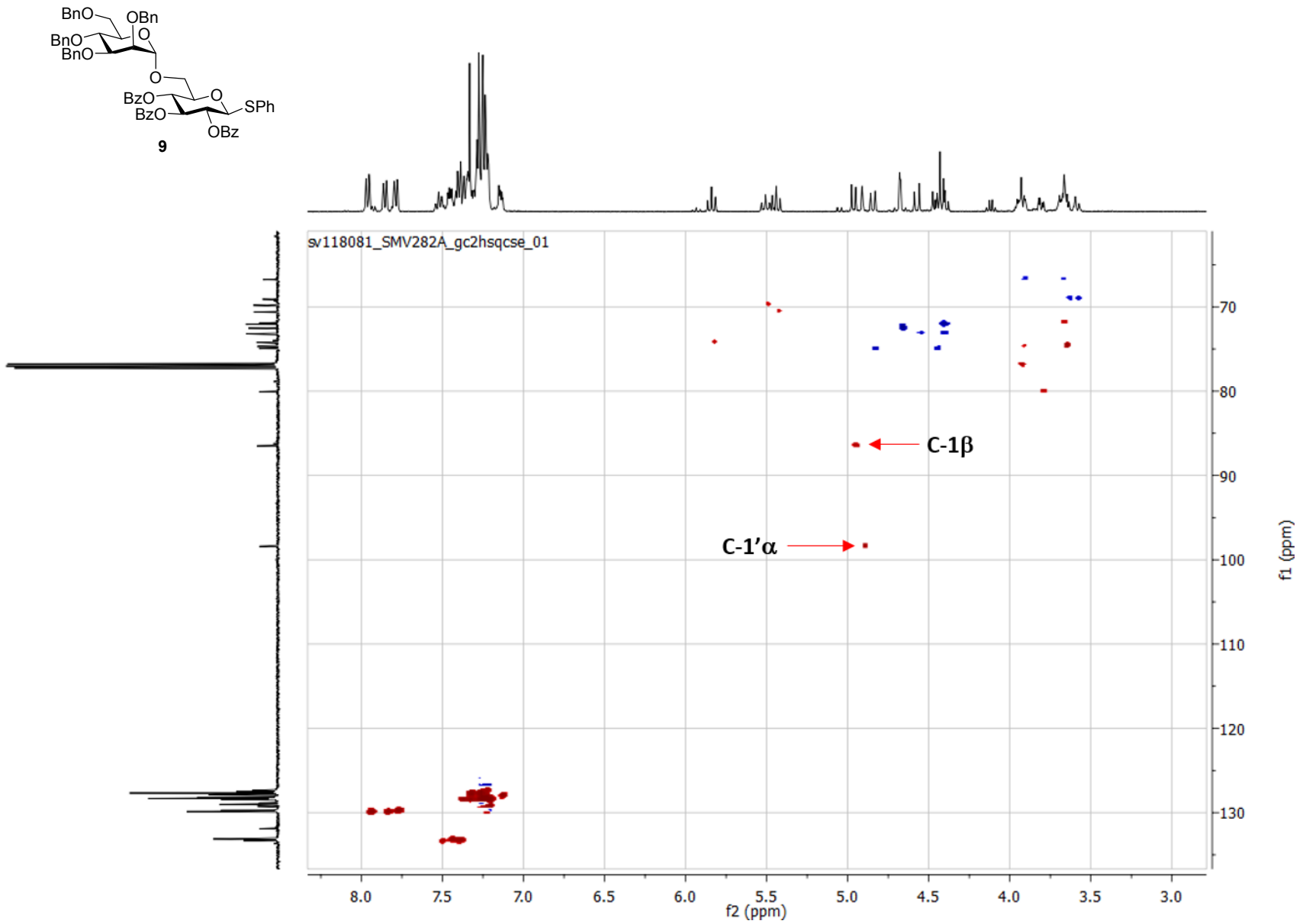

BnO
BnO
BnO
BnO
O
BnO
O
Ph
O
O
MeO
O
5g
sv8903_SMV173_2-E_gc2hsqcse01
H-1α
H-1'α
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)
50
60
70
80
90
100
110
120
130
f1 (ppm)

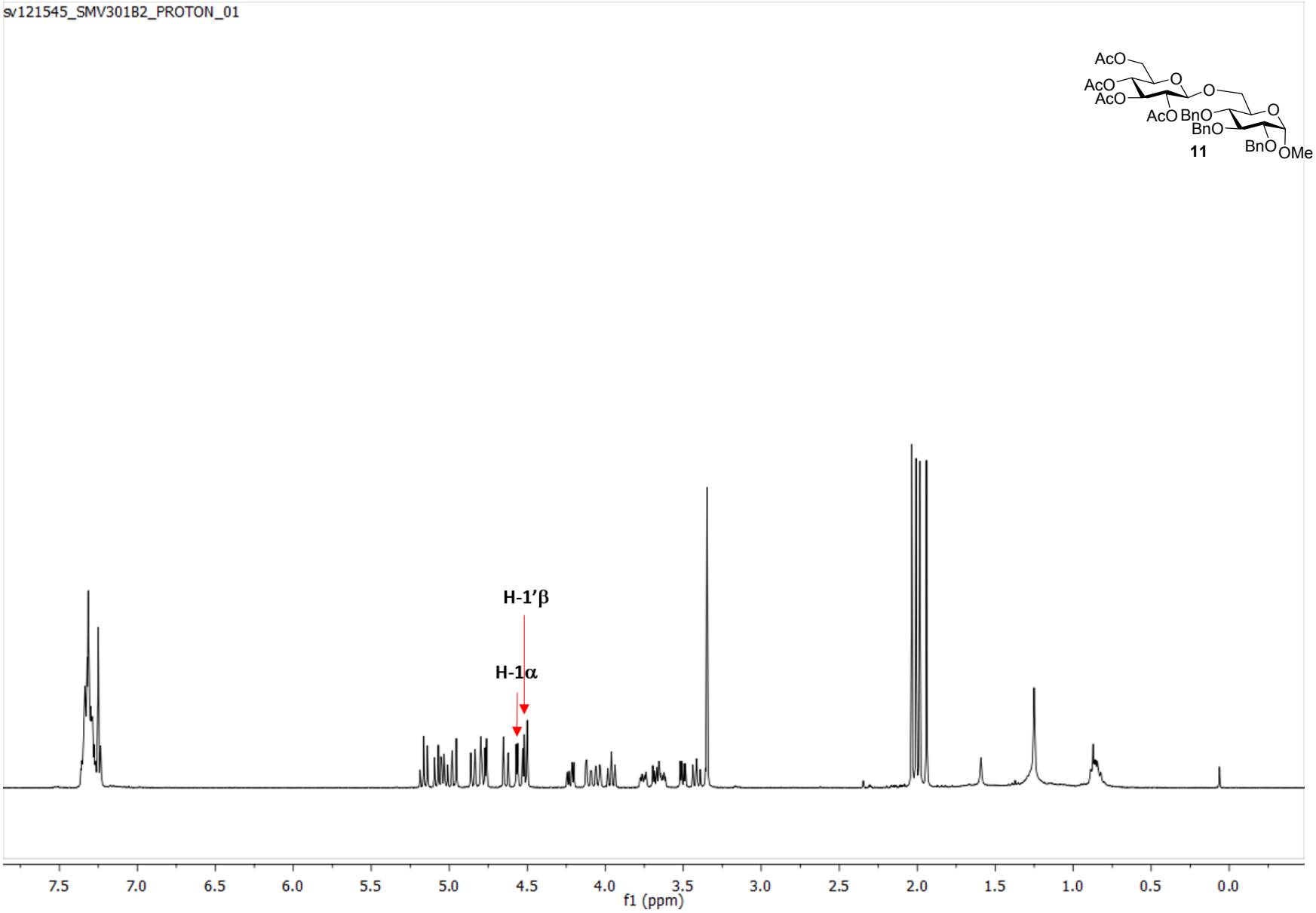

sv117455_SMV276B_PROTON_01
BnO
OBn
O
BnO
BnO
O
7
4.87
4.86
4.35
4.33
H-1α
H-1β
0.17
1.00
5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3
f1 (ppm)
0.17
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

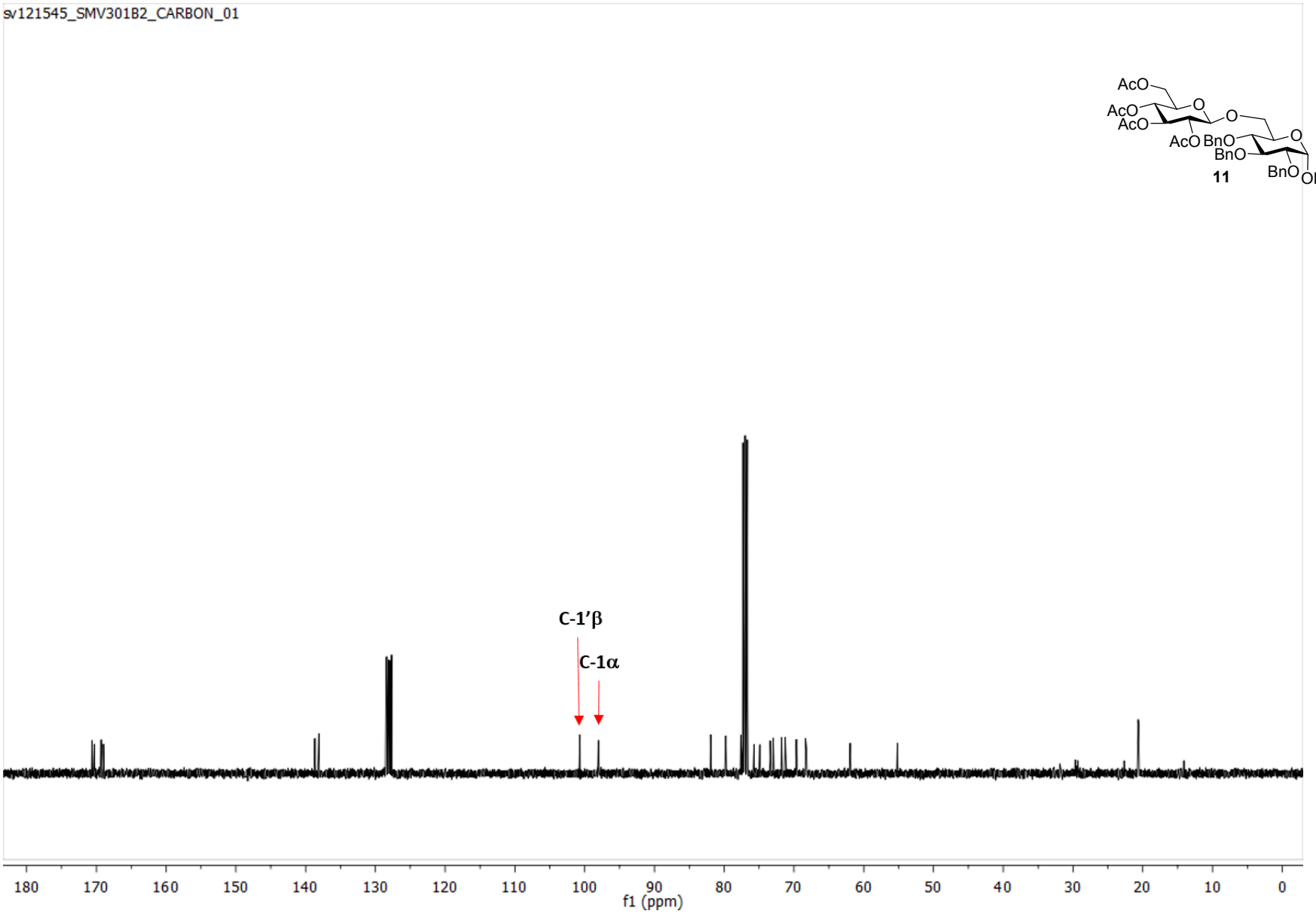

sv117455_SMV276B_CARBON_01
BnO
OBn
O
BnO
BnO
O
7
C-1α
C-1β
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

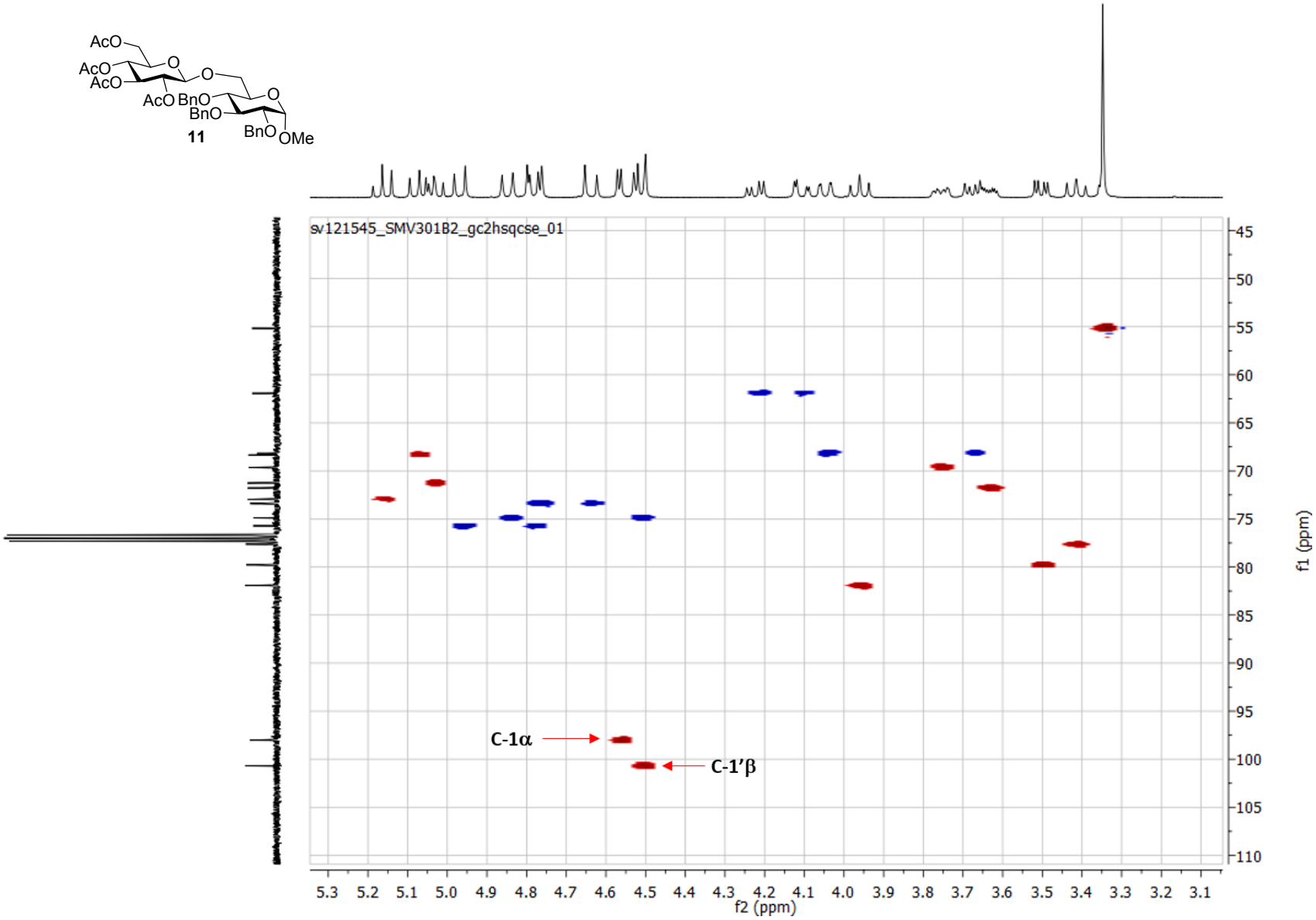

sv118081_SMV282A_PROTON_01
5.96
5.93
5.91
5.86
5.84
5.82
4.98
4.95
4.91
4.91
BnO
OBn
BnO
BnO
O
O
BzO
BzO
SPh
OBz
9
H-1β
H-1'α
4.95
4.90
f1 (ppm)
0.14
1.00
0.90
1.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

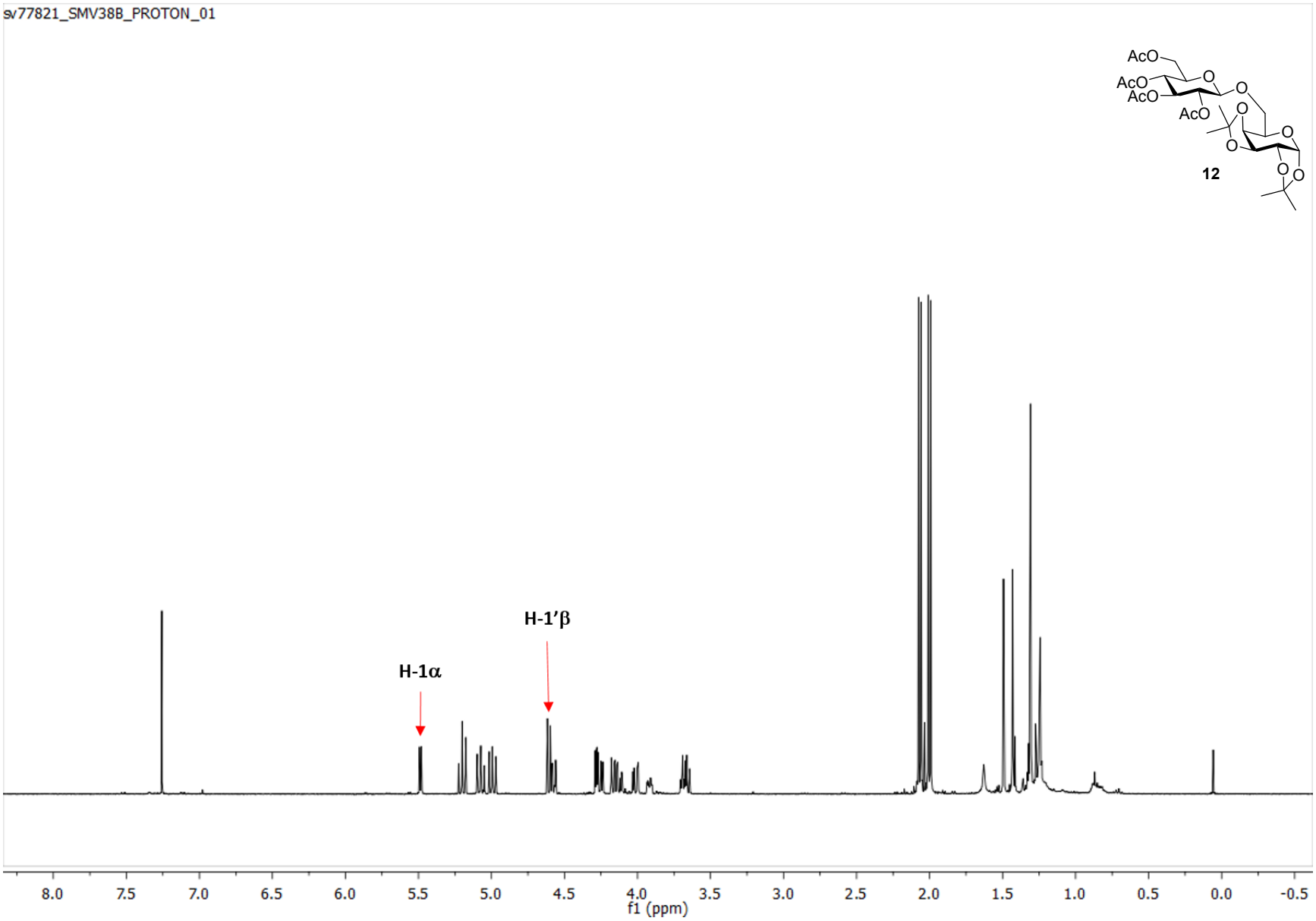

sv19614_SMV282A_CARBON_001
BnO
OBn
BnO
BnO
O
O
BzO
BzO
O
SPh
OBz
9
C-1'α
C-1β
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

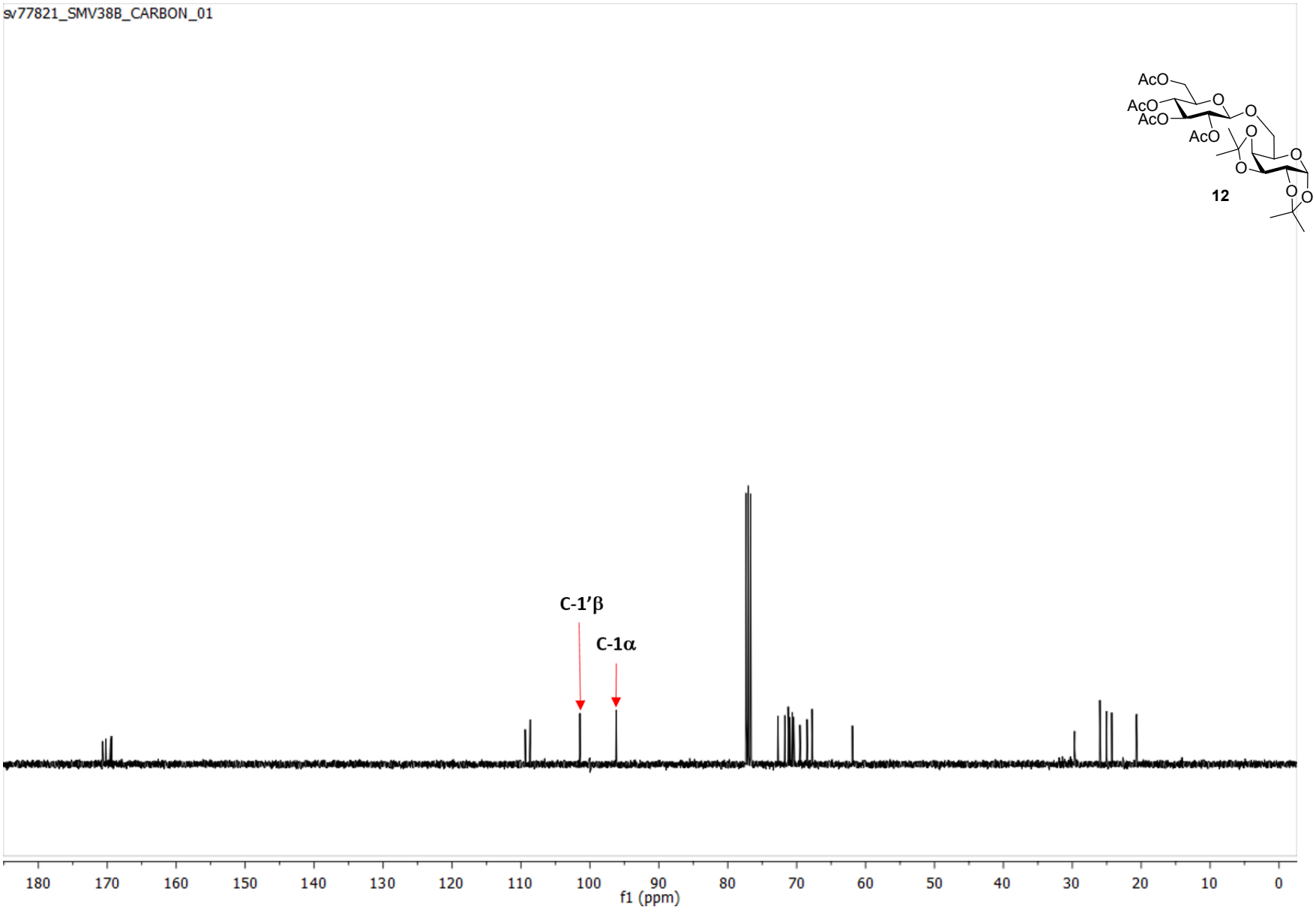

BnO
OBn
BnO
O
BnO
O
BzO
O
SPh
BzO
OBz
9
sv118081_SMV282A_gc2hsqcse_01
C-1β
C-1'α
70
80
90
100
110
120
130
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
f2 (ppm)

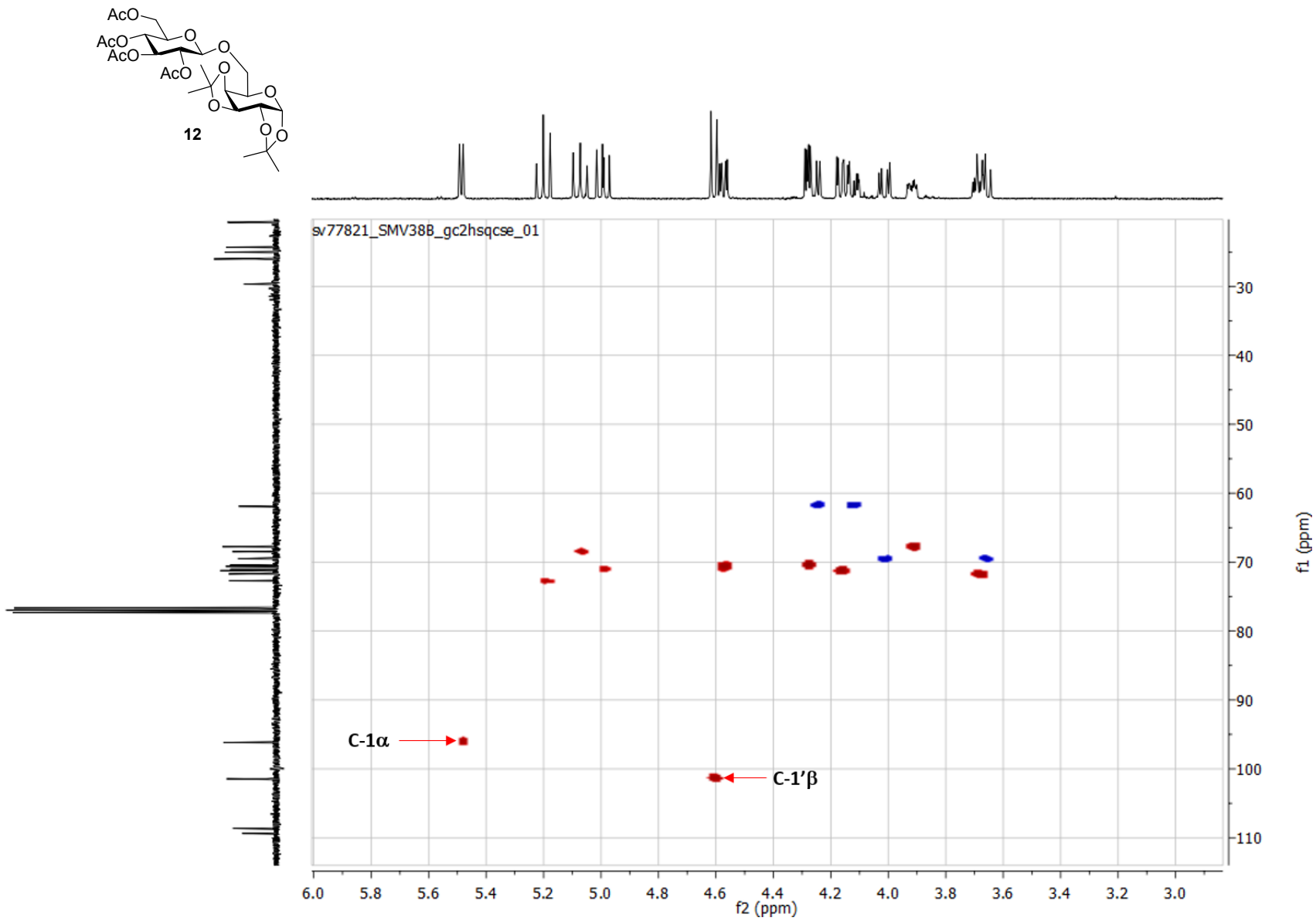

sv121545_SMV301B2_PROTON_01
AcO
AcO
AcO
AcO
BnO
BnO
BnO
OMe
11
H-1'β
H-1α
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

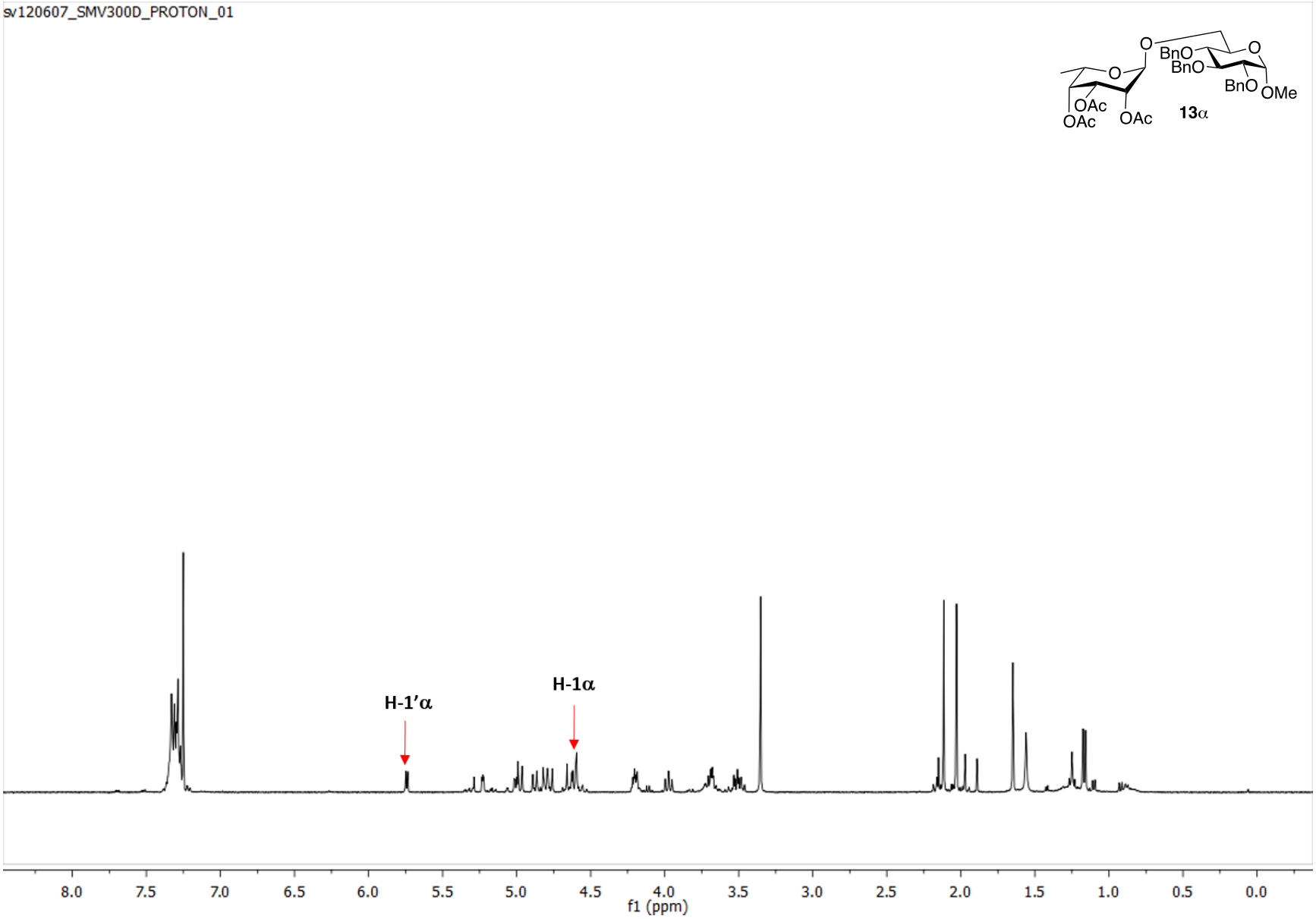

sv121545_SMV301B2_CARBON_01
AcO
AcO
AcO
AcO
O
O
BnO
BnO
BnO
O
OMe
11
C-1'β
C-1α
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

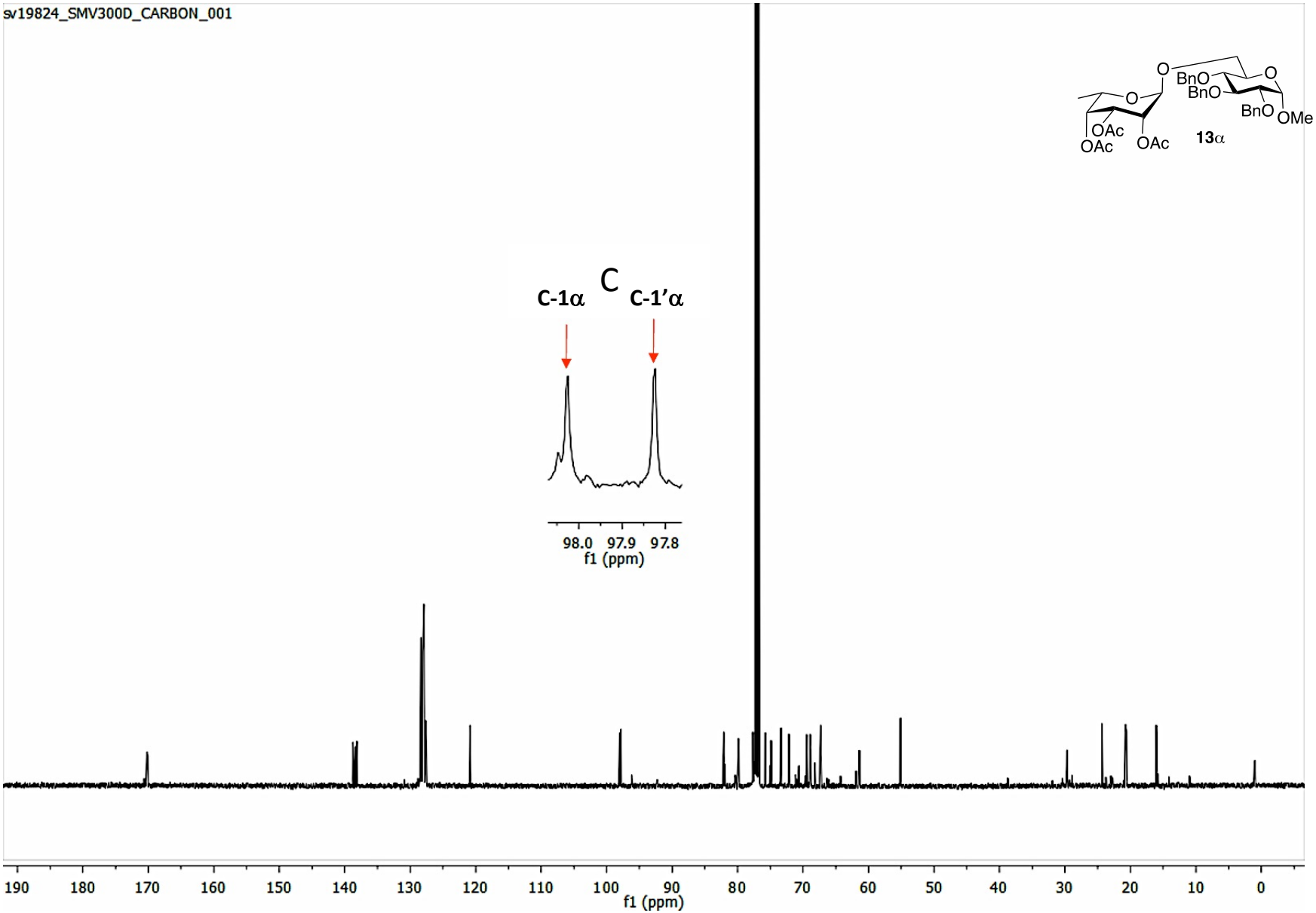

AcO
AcO
AcO
AcO
BnO
BnO
BnO
OMe
11
sv121545_SMV301B2_gc2hsqcse_01
C-1α
C-1'β
f2 (ppm)
f1 (ppm)

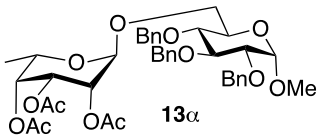

sv77821_SMV38B_PROTON_01
AcO
AcO
AcO
AcO
O
O
O
O
O
O
O
O
12
H-1α
H-1'β
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


sv77821_SMV38B_CARBON_01
AcO
AcO
AcO
AcO
O
O
O
O
O
O
O
O
12
C-1'β
C-1α
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

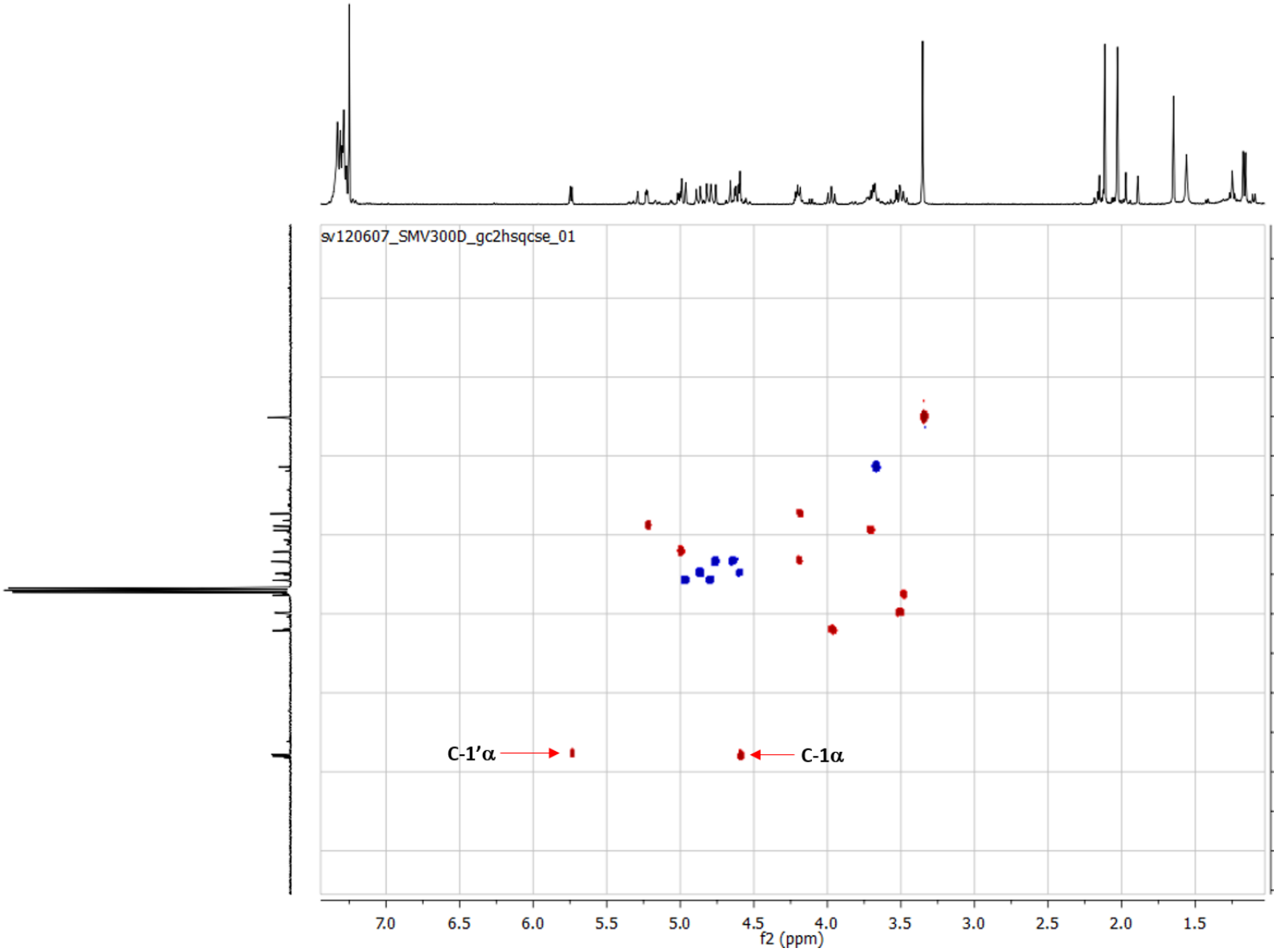

AcO
AcO
AcO
AcO
O
O
O
O
O
O
O
12
sv77821_SMV38B_gc2hsqcse_01
C-1α
C-1'β
f2 (ppm)
f1 (ppm)
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
30
40
50
60
70
80
90
100
110

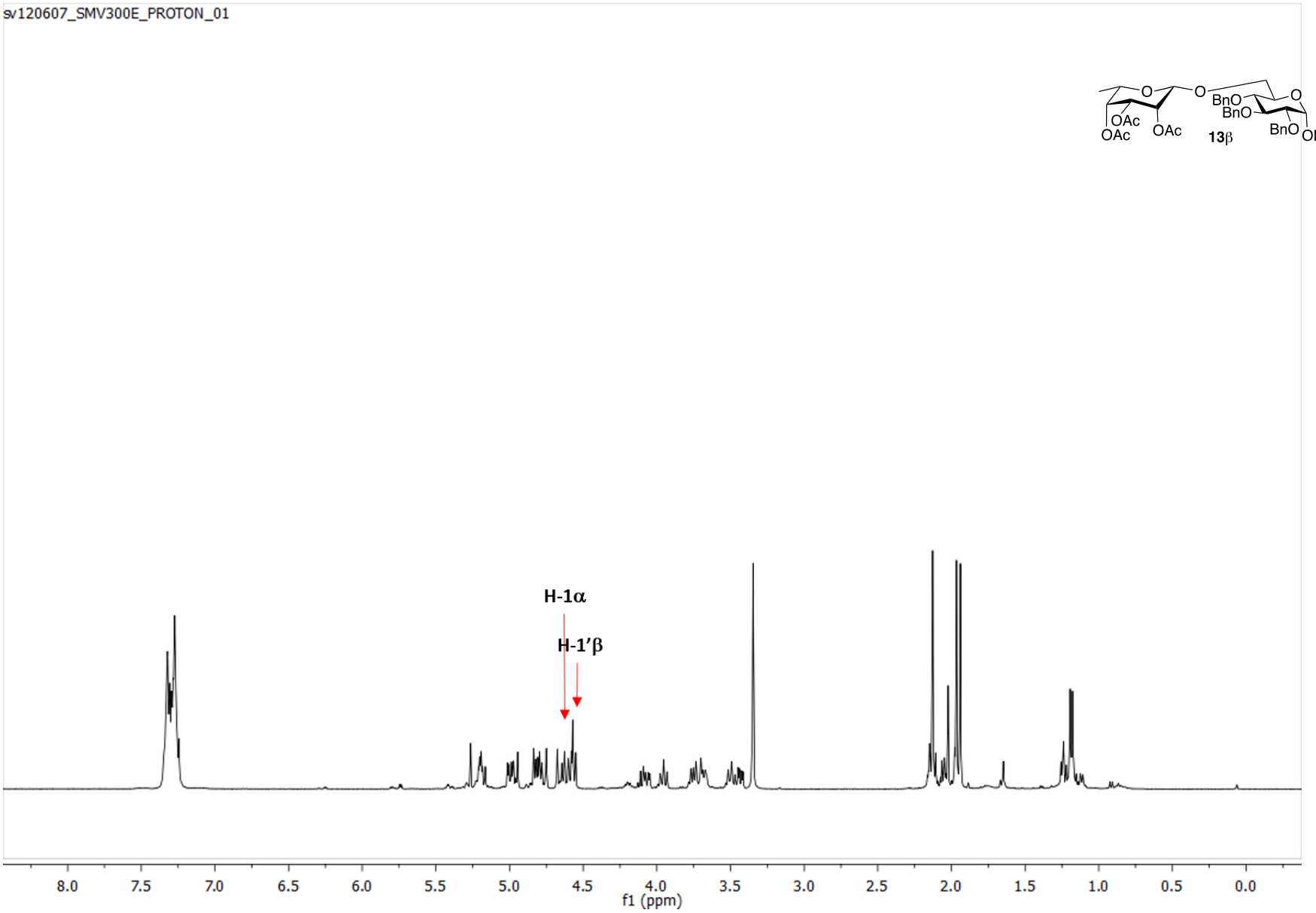

sv120607_SMV300D_PROTON_01
O
BnO
BnO
O
BnO
OMe
O
OAc
OAc
OAc
13α
H-1'α
H-1α
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

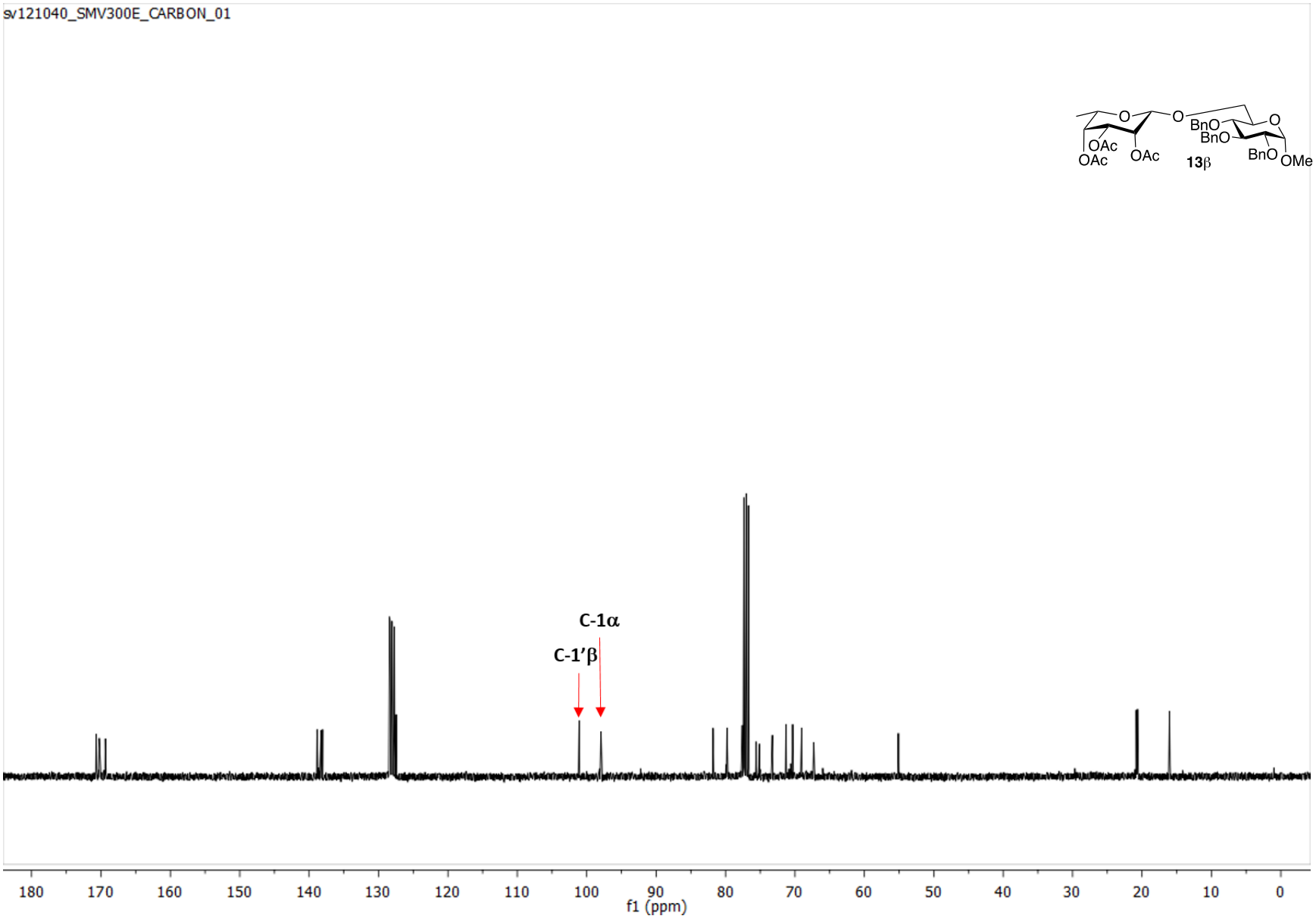

sv19824_SMV300D_CARBON_001
C
C-1α
C-1'α
98.0
97.9
97.8
f1 (ppm)
BnO
BnO
BnO
OMe
OAc
OAc
OAc
13α
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

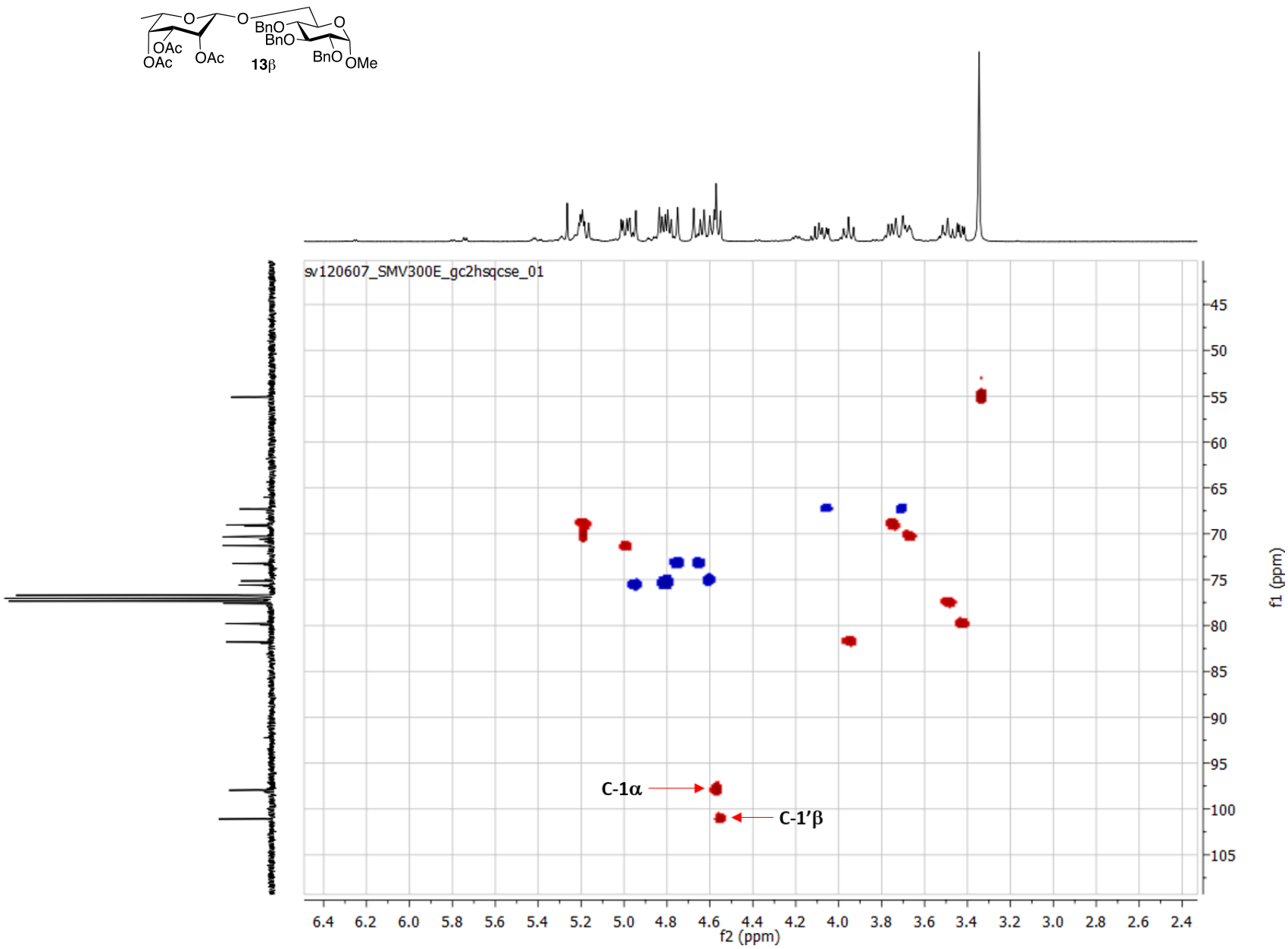

O
BnO
BnO
O
BnO
OMe
O
OAc
OAc
OAc

13α


sv120607_SMV300D_gc2hsqcse_01
C-1'α
C-1α
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f2 (ppm)


sv120607_SMV300E_PROTON_01
OAc
OAc
OAc
BnO
BnO
BnO
OMe
13β
H-1α
H-1'β
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


sv121040_SMV300E_CARBON_01
OAc
OAc
OAc
BnO
BnO
BnO
OMe
13β
C-1α
C-1'β
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OAc
OAc
OAc
O
O
BnO
BnO
BnO
O
OMe
13β
sv120607_SMV300E_gc2hsqcse_01
C-1α
C-1'β
f2 (ppm)
f1 (ppm)