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Electronic Supplementary Information

Copper-mediated anomeric *O*-arylation with organoboron reagents

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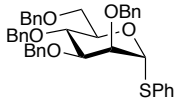
General methods

Screw cap tubes were purchased from Pyrex® (13 mm x 100 mm, mfr. no. = Corning, 9825-13). Schlenk flasks were dried at 140 °C for at least 24 hours prior to use. Acetonitrile and tetrahydrofuran were HPLC grade and purified using a solvent purification system equipped with columns of activated alumina under nitrogen. (Innovative Technology, Inc.). Acetonitrile was dried further over activated 4 Å molecular sieves prior to use. Anhydrous dimethylformamide and was purchased from Sigma Aldrich and used directly from the SureSeal bottle. Phenylboronic acid was purchased from Sigma Aldrich and recrystallized from water and dried under high vacuum prior to use. Other reagents and solvents were used without further purification. Flash column chromatography was carried out using neutral silica gel (60 Å, 230–400 mesh, Silicycle). Analytical thin layer chromatography was carried out using aluminum-backed silica gel 60 F_{254} plates (EMD), and compounds were visualized through the use of UV light and aqueous basic $KMnO_4$ stain. ^1H and ^{13}C NMR and 2D NMR spectra were recorded using a Varian Mercury 400 MHz, Bruker Avance III 400 MHz, Agilent DD2 600, or Agilent DD2-500 spectrometer equipped with a XSens cryoprobe. ^1H NMR are reported in parts per million (ppm) relative to tetramethylsilane and referenced to residual protium in the solvent. Spectral features are tabulated in the following order: chemical shift (δ, ppm); multiplicity (s-singlet, d-doublet, t-triplet, q-quartet, m-complex multiplet); number of protons; coupling constant(s) (*J*, Hz); assignment. Assignments were made on the basis of coupling constants and 2D NMR spectra. High-resolution mass spectra (HRMS) were obtained on a JEOL AccuTOF JMS- T1000LC mass spectrometer equipped with a DART (direct analysis in real time) ion source. Infrared (IR) spectra were obtained on a Perkin-Elmer Spectrum 100 instrument equipped with a single-bounce diamond/ZnSe ATR accessory as neat samples, or as thin film from CH_2Cl_2 as indicated. Spectral features are tabulated as follows: wavenumber (cm^{-1}); intensity (s-strong, m-medium, w-weak).

Synthesis of Carbohydrate Substrates

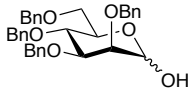
S1 – Thiophenyl-2,3,4,6-tetra-*O*-benzyl-α- D-mannopyranoside



Prepared from thiophenyl-α-D-mannopyranoside as previously reported.[1]

^1H NMR (400 MHz, $CDCl_2$): δ (ppm) = 7.52–7.45 (m, 2H), 7.43–7.20 (m, 23H), 5.67–5.63 (m, 1H), 4.94 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 12.3 Hz, 1H), 4.71–4.65 (m, 2H), 4.64 (d, *J* = 2.0 Hz, 2H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.35–4.29 (m, 1H), 4.13–4.07 (m, 1H), 4.04 (dd, *J* = 3.1, 1.8 Hz, 1H), 3.93–3.85 (m, 2H), 3.78 (dd, *J* = 10.9, 2.0 Hz, 1H).

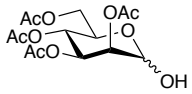
1a –2,3,4,6-Tetra-*O*-benzyl- D-mannopyranoside



Prepared from thiophenyl-2,3,4,6-tetra-*O*-benzyl-α- D-mannopyranoside as previously reported.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.26 (m, 18H), 7.16 (dd, *J* = 7.1, 2.6 Hz, 2H), 5.27 (dd, *J* = 3.5, 1.9 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.79–4.69 (m, 2H), 4.64 – 4.47 (m, 5H), 4.03 (ddd, *J* = 8.4, 5.7, 2.4 Hz, 1H), 3.96 (dd, *J* = 9.3, 3.0 Hz, 1H), 3.89 (d, *J* = 9.6 Hz, 1H), 3.81 (dd, *J* = 3.0, 2.0 Hz, 1H), 3.76–3.65 (m, 2H).

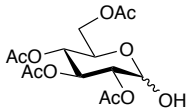
1c –2,3,4,6-Tetra-*O*-acetyl- D-mannopyranoside



Prepared from 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranoside as previously reported.[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.42 (dd, *J* = 10.0, 3.4 Hz, 1H), 5.34–5.23 (m, 3H), 4.29–4.19 (m, 2H), 4.17– 4.07 (m, 1H), 2.16 (s, 3H), 2.10 (d, *J* = 1.9 Hz, 3H), 2.05 (s, 3H), 2.00 (s, 3H).

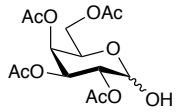
1d – 2,3,4,6-Tetra-*O*-acetyl- D-glucopyranoside



Prepared from 1,2,3,4,6-penta-*O*-acetyl-D-glucopyranoside as previously reported.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (dd, *J* = 10.2, 9.4 Hz, 1H), 5.45–5.39 (m, 1H), 5.22 (dd, *J* = 9.6 Hz, 0.26H), 5.10–5.01 (m, 1H), 4.88–4.84 (m, 1H), 4.73 (d, *J* = 8.0 Hz, 0.22H), 4.27–4.17 (m, 2H), 4.13–4.06 (m, 2H), 3.9–3.86 (m, 1H), 3.73 (ddd, *J* = 10.1, 4.8, 2.4 Hz, 0.19H), 2.07 (s, 4H), 2.06 (s, *J* = 0.7 Hz, 4H), 2.02 (d, *J* = 1.4 Hz, 1H), 2.01 (s, 3H), 2.00 (s, 1H), 1.99 (s, 3H).

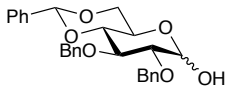
1e – 2,3,4,6-Tetra-*O*-acetyl- D-galactopyranoside



Prepared from 1,2,3,4,6-penta-*O*-acetyl- D-glucopyranoside as previously reported.[4]

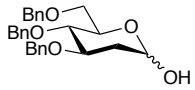
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.53 (dd, *J* = 3.6, 3.6 Hz, 1H), 5.48 (dd, *J* = 3.4, 1.3 Hz, 1H), 5.42 (dd, *J* = 10.8, 3.4 Hz, 1H), 5.17 (ddd, *J* = 10.8, 3.6, 1.2 Hz, 1H), 5.09 – 5.04 (m, 0.55H), 4.69 (ddd, *J* = 9.1, 4.6, 3.3 Hz, 0.25H), 4.50–4.44 (m, 1H), 4.18–4.03 (m, 3H), 3.96 (dd, *J* = 6.5, 1.2 Hz, 0.31H), 3.47 (dd, *J* = 9.1, 0.7 Hz, 0.25H), 2.86 (dd, *J* = 3.5, 1.3 Hz, 1H), 2.16 (d, *J* = 0.6 Hz, 0.84H), 2.15 (d, *J* = 0.6 Hz, 3H), 2.11 (d, *J* = 0.6 Hz, 0.88H), 2.10 (d, *J* = 0.5 Hz, 3H), 2.06 (s, 4H), 2.00 (s, 0.87H), 2.00 (s, 2H).

1f – 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene- D-glucopyranose



Prepared from 1,2,3,4,6-penta-*O*-acetyl-β- D-glucopyranoside as previously reported.[5]

1g – 3,4,6-Tri-*O*-benzyl-2-deoxy-D-glucopyranose

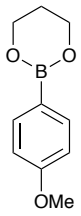


Prepared from 3,4,6-tri-*O*-benzyl-D-glucal as previously reported.[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.27 (m, 18H), 7.21 – 7.15 (m, 3H), 5.42 (s, 1H), 4.90 (d, *J* = 10.9 Hz, 1H), 4.70–4.57 (m, 4H), 4.53 (d, *J* = 11.0 Hz, 3H), 4.09 –3.98 (m, 2H), 3.75–3.62 (m, 3H), 3.53 (dd, *J* = 9.9, 8.9 Hz, 1H), 2.45 (d, *J* = 4.0 Hz, 1H), 2.30 (ddd, *J* = 13.1, 5.1, 1.5 Hz, 1H), 1.77–1.66 (m, 1H).

Synthesis of Boronic Esters and Boroxines

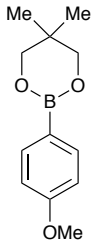
2b – 2-*(*4-methoxyphenyl)-1,3,2-dioxaborinane



4-methoxyphenylboronic acid (303.9 mg, 2 mmol), 1,3-propane diol (152.2 mg, 2 mmol) and dichloromethane (6mL) were combined in a long screw-cap tube and stirred at room temperature for 16 hours. Upon completion, the reaction was concentrated under reduced pressure and dried by azeotropic removal of water with toluene (0.5 mL x 3). The product was then dried under high-vacuum to afford a white solid. Spectral data were in agreement with previous reports.[7]

^{1}H NMR (400 MHz, $CDCl_2$): δ (ppm) = 7.77 – 7.70 (m, 2H), 6.91 – 6.85 (m, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 1.02 (s, 6H).

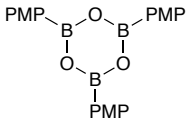
2c – 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane



4-methoxyphenylboronic acid (303.9 mg, 2 mmol), neopentyl glycol (208.3 mg, 2 mmol) and toluene (5mL) were combined in a long screw-cap tube and stirred at reflux for 16 hours. Upon completion, the reaction was concentrated under reduced pressure and dried by azeotropic removal of water with toluene (0.5 mL x 3). The product was then dried under high-vacuum prior to use to afford a white solid. Spectral data are in agreement with those previously reported.[8]

^{1}H NMR (400 MHz, $CDCl_2$): δ (ppm) 7.77–7.70 (m, 2H), 6.91–6.85 (m, 2H), 3.82 (s, 3H), 3.75 (s, 3H), 1.02 (s, 6H).

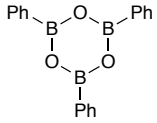
2d – Tri(4-methoxyphenyl)boroxine



4-methoxyphenylboronic acid was condensed through the use of the Kugelrohr Apparatus at 100 °C for 3 hours to afford the corresponding boroxine as a white solid.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.20–8.14 (m, 6H), 7.05–6.99 (m, 6H), 3.90 (s, 9H).

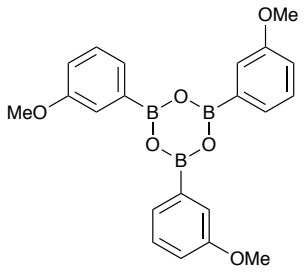
2e – Triphenylboroxine



Phenylboronic acid was condensed through the use of the Kugelrohr Apparatus at 100 °C for 2 hours to afford the corresponding boroxine as a white solid.[9]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27–8.23 (m, 6H), 7.64–7.58 (m, 3H), 7.54–7.49 (m, 6H).

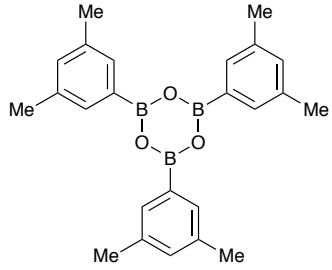
2l – Tri(3-methoxyphenyl)boroxine



3-methoxyphenylboronic acid was condensed through the use of the Kugelrohr Apparatus at 110 °C for 8 hours to afford the corresponding boroxine as a white solid.[9]

^{1}H NMR (400 MHz, CDCl3): δ 7.83 (d, *J* = 7.3 Hz, 3H), 7.79–7.71 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 3H), 7.20–7.10 (m, 3H), 3.92 (s, 9H).

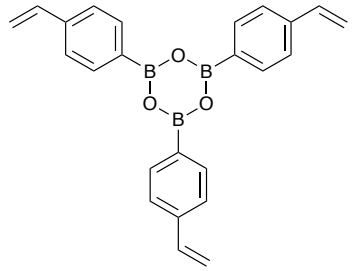
2m – Tri(3,5-dimethylphenyl)boroxine



3,5-dimethylphenylboronic acid was condensed through the use of the Kugelrohr Apparatus at 110 °C for 5 hours to afford the corresponding boroxine as a white solid.

^{1}H NMR (400 MHz, CDCl3): 7.85 (s, 6H), 7.24 (s, 3H), 2.45 (s, 18H).

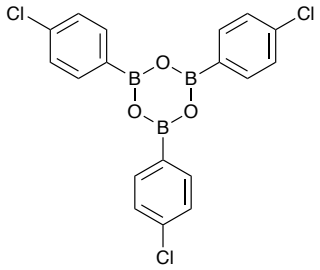
2n – Tri(4-vinylphenyl)boroxine



4-Vinylphenylboronic acid was condensed through the use of the Kugelrohr Apparatus at 100 °C for 4 hours to afford the corresponding boroxine as a white solid. Spectral data are in agreement with those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25–8.16 (m, 6H), 7.57–7.52 (m, 6H), 6.81 (dd, *J* = 17.6, 10.9 Hz, 3H), 5.91 (dd, *J* = 17.6, 0.9 Hz, 3H), 5.38 (dd, *J* = 10.9, 0.9 Hz, 3H).

2o – Tri(4-chlorophenyl)boroxine



4-Chlorophenylboronic acid was condensed through the use of the Kugelrohr Apparatus at 110 °C for 4 hours to afford the corresponding boroxine as a white solid. Spectral data are in agreement with those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.3 Hz, 6H), 7.53–7.43 (m, 6H).

Copper-Mediated O-Arylation

General procedure A: Optimization of reaction conditions for O-arylation of hemiacetals. Carbohydrate (0.2 mmol, 1 equiv.), $Cu(OAc)_2$ (72.7 mg, 0.4 mmol, 2 equiv.) and aryl boron reagent (1 mmol, 5 equiv. boron) were combined in an oven-dried long screw-cap tube charged with a magnetic stir bar. Anhydrous acetonitrile (2 mL) was then added, followed by triethylamine (0.11 mL, 0.8 mmol). The reaction tube was then capped and sealed with Teflon and parafilm and allowed to stir at 40 °C overnight. The crude mixture was then concentrated under reduced pressure, diluted with ethyl acetate and washed with a solution of 1M sorbitol/1M Na_2CO_3 (2x50mL). The aqueous phase was then backwashed with ethyl acetate three times. The organic layers were combined then dried over $MgSO_4$ before being concentrated under reduced pressure. 1,3,5-trimethoxybenzene was added to the crude mixture, which was then analyzed by ^{1}H NMR spectroscopy in $CDCl_3$.

General procedure B: Preparation of O-aryl glycosides, phase-switching workup with sorbitol/NaOH.[*]

Carbohydrate (0.2 mmol, 1 equiv.), $Cu(OAc)_2$ (72.7 mg, 0.4 mmol, 2 equiv.) and aryl boroxine (0.33 mmol, 1.67 equiv.) were combined in an oven-dried long screw-cap tube charged with a magnetic stir bar. Anhydrous acetonitrile (2 mL) was then added, followed by triethylamine (0.11 mL, 0.8 mmol). The reaction tube was then capped and sealed with Teflon and parafilm

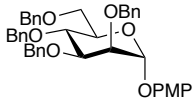
[*] A sorbitol/NaOH solution was used to remove an aryl alcohol byproduct from the crude reaction mixture in cases where it was difficult to separate this byproduct from the desired product by column chromatography.

and allowed to stir at 40 °C overnight. The crude mixture was then concentrated under reduced pressure, diluted with dichloromethane and and vigorously hand shaken with a solution of 1M sorbitol/1M NaOH (2x50mL). The aqueous phase was then backwashed with dichloromethane three times. The organic layers were combined then dried over $MgSO_4$ before being concentrated under reduced pressure. The crude reaction mixture was analyzed by crude ^{1}H NMR to obtain anomeric ratios and was then purified by flash column chromatography on silica gel.

General procedure C: Preparation of O-aryl glycosides, phase-switching workup with sorbitol/Na_2CO_3.

Carbohydrate (0.2 mmol, 1 equiv.), $Cu(OAc)_2$ (72.7 mg, 0.4 mmol, 2 equiv.) and aryl boroxine (0.33 mmol, 1.67 equiv.) were combined in an oven-dried long screw-cap tube charged with a magnetic stir bar. Anhydrous acetonitrile (2 mL) was then added, followed by triethylamine (0.11 mL, 0.8 mmol). The reaction tube was then capped and sealed with Teflon and parafilm and allowed to stir at 40 °C overnight. The crude mixture was then concentrated under reduced pressure, diluted with ethyl acetate and vigorously hand shaken with a solution of 1M sorbitol/1M Na_2CO_3 (50mL) for 5 minutes. The aqueous phase was then backwashed with ethyl acetate three times. The organic layers were combined then dried over $MgSO_4$ before being concentrated under reduced pressure. The crude reaction mixture was analyzed by crude ^{1}H NMR to obtain anomeric ratios and was then purified by flash column chromatography on silica gel.

3a – 4-Methoxyphenyl-2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside



Synthesized according to general procedure B from 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside (108.1 mg, 0.2 mmol) and tri(4-methoxyphenyl)boroxine (103.9 mg, 0.33 mmol). The α anomer was isolated as light yellow oil, and the β anomer was isolated as a white solid after flash chromatography on silica gel, eluting with 10% to 40% diethyl ether in hexanes (α: 58.4 mg, β: 13.5 mg, combined yield: 56%).

α: β= 8:1 (determined through analysis of the crude ^{1}H NMR spectrum)

α anomer:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.22 (m, 20H, ArH), 7.22–7.16 (m, 2H, ArH), 7.01–6.91 (m, 2H, ArH), 6.82–6.74 (m, 2H, ArH), 5.48 (d, *J* = 2.0 Hz, 1H, H-1), 4.91 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.79 (m, 2H, $PhCH_2$), 4.70 (m, 2H, $PhCH_2$), 4.64 (d, *J* = 11.9 Hz, 1H, , $PhCH_2$), 4.55 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.47 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.12–4.09 (m, 2H, H-3 and H-4), 3.97 (dd, *J* = 2.2, 2.2 Hz, 1H, H-2), 3.95–3.89 (m, 1H, H-5), 3.80 (dd, 11.0, 4.7 Hz, 1H, H-6a), 3.76 (s, 3H, OCH_3), 3.71 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) = 155.1, 150.4, 138.6, 138.6, 138.5, 138.4, 128.5, 128.5, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 118.0, 114.7, 97.31, 80.16, 75.3, 75.0, 74.8, 73.4, 72.9, 72.5, 72.5, 69.3, 55.8.

IR (thin film, cm^{-1}): 3031.1 (w), 2901 (w), 2873 (w), 2347 (w), 1598 (w), 1506 (s), 1454.00 (w), 1363 (w), 1291 (w), 1219 (m), 1132 (m), 1100 (m), 1033 (m), 1005 (m), 829(w), 801 (w), 739 (m).

HRMS ($DART^+$, m/z): calculated for $C_{41}H_{46}NO_7$ $[M+NH_4]^+$: 664.3274, found 664.32727.

β anomer:

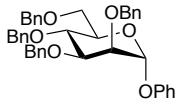
^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) = 7.55–7.51 (m, 2H, ArH), 7.35–7.21 (m, 20H, ArH), 7.01–6.97 (m, 2H, ArH), 6.80–6.76 (m, 2H, ArH), 5.08 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.99 (d, *J* = 12.4 Hz, 1H, $PhCH_2$), 4.93 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.87 (d, *J* = 0.8 Hz, 1H, H-1), 4.63–4.50 (m, 5H, $PhCH_2$), 4.09 (dd, *J* = 3.1, 0.8 Hz, 1H, H-2), 3.95 (dd, *J* = 9.4, 9.4 Hz, 1H, H-4), 3.87 (dd, *J* = 10.9, 2.0 Hz, 1H, H-6a), 3.78 (d, *J* = 6.4 Hz, 1H, H-6b), 3.76 (s, 3H, OCH_3), 3.58–3.50 (m, 2H, H-3 and H-5).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) = 155.2, 151.6, 138.8, 138.7, 138.4, 138.2, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.8, 127.8, 127.7, 127.6, 118.0, 114.6, 100.5, 82.4 76.3, 75.3, 75.0, 74.4, 74.3, 73.6, 71.9, 69.7, 55.8.

IR (thin film, cm^{-1}): 3063.62 (w), 3030 (w), 2915 (w), 2861 (w), 2346 (w), 1728 (w), 1601 (w), 1507 (s), 1454 (w), 1365 (w), 1312 (w), 1222 (m), 1177 (w), 1097 (s), 1065 (s), 1028 (m), 911 (w), 827 (w), 793 (w), 737 (m).

HRMS ($DART^+$, m/z): calculated for $C_{41}H_{46}NO_7$ $[M+NH_4]^+$: 664.32743, found 664.32695.

3b – Phenyl-2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside



Synthesized according to general procedure B from 2,3,4,6-tetra-*O*-benzyl-D-mannopyranoside (108.1 mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). Both anomers were isolated as light yellow solids after flash chromatography on silica gel, eluting with 10% to 30% ethyl acetate in hexanes (α: 60.2 mg, β: 9.6mg, combined yield: 57%).

α: β= 7:1 (determined through analysis of the crude ^{1}H NMR spectrum)

α anomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 – 7.27 (m, 20H, ArH), 7.25–7.18 (m, 2H, ArH), 7.09–6.99 (m, 3H, ArH), 5.64 (d, *J* = 2.0 Hz, 1H, H-1), 4.95 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.88–4.79 (m, 2H, $PhCH_2$), 4.79–4.71 (m, 2H, $PhCH_2$), 4.69 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.58 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.49 (d, *J* = 12.0 Hz, 1H, $PhCH_2$), 4.23–4.13 (m, 2H, H-3 and H-4), 4.01 (dd, *J* = 2.3, 2.3 Hz, 1H, H-2), 3.97–3.88 (m, 1H, H-5), 3.84 (dd, *J* = 11.0, 4.5 Hz, 1H, H-6a), 3.72 (dd, *J* = 11.0, 1.9 Hz, 1H, H-6b).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 156.4, 138.6, 138.6, 138.7, 138.3, 129.6, 128.5, 128.5, 128.4, 128.4, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 127.5, 122.4, 116.6, 96.46, 80.11, 75.3, 74.9, 74.7, 73.4, 72.9, 72.6, 72.5, 69.1.

IR (thin film, cm^{-1}): 3089 (w), 3063 (w), 3031 (w), 2908 (w), 2863 (w), 1598 (w), 1588 (w), 1495(m), 1454 (m), 1362 (w), 1290 (w), 1225 (m), 1130 (s), 1094 (s), 1050 (m), 1028 (s), 1008 (s), 989 (s), 908 (w), 846 (w), 740 (s).

HRMS (DART-TOF$^+$, m/z): calculated for $C_{40}H_{44}NO_6$ $[M+NH_4]^+$: 634.31686, found 634.31606.

β anomer:

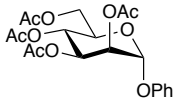
^{1}H NMR (600 MHz, $CDCl_3$) δ:7.55–7.52 (m, 2H, ArH), 7.36–7.22 (m, 20H, ArH), 7.06–7.00 (m, 3H, ArH), 5.10 (d, *J* = 12.3 Hz, 1H, ArH), 5.03–4.98 (m, 2H, H-1 and $PhCH_2$), 4.94 (d, *J* = 10.8 Hz, 1H, $PhCH_2$), 4.62–4.52 (m, 5H, $PhCH_2$), 4.10 (d, *J* = 2.9 Hz, 1H, H-2), 3.97 (dd, *J* = 9.5, 9.5 Hz, 1H, H-4), 3.88 (dd, *J* = 10.9, 1.9 Hz, 1H, H-6a), 3.77 (dd, *J* = 10.9, 6.3 Hz, 1H, H-6b), 3.65–3.59 (m, 2H, H-3 and H-5).

^{13}C NMR (151 MHz, $CDCl_3$) δ:157.3, 138.6, 138.4, 138.3, 138.0, 129.4, 128.4, 128.4, 128.4, 128.2, 128.2, 128.0, 127.7, 127.7, 127.6, 127.5, 127.4, 122.4, 116.4, 99.4, 82.2, 76.2, 75.2, 74.8, 74.2, 73.5, 71.8, 69.5, 65.9, 29.7.

IR (thin film, cm^{-1}): 3064(w), 3031 (w), 2912 (w), 2869 (w), 1602 (m), 1495 (m), 1454 (m), 1366 (w), 1316 (w), 1231 (m), 1098 (s), 1072 (s), 1027 (m) 909 (w), 840 (w), 752 (m), 737 (m).

HRMS (DART$^+$, m/z): calculated for $C_{40}H_{44}NO_6$ $[M+NH_4]^+$: 634.31686, found 634.31670.

3c – Phenyl-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside



Synthesized according to general procedure C from 2,3,4,6-tetra-*O*-acetyl-D-mannopyranoside (69.7 mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). Isolated as a light yellow solid after flash chromatography on silica gel, eluting with 10% to 30% ethyl acetate in hexanes (62.4 mg, 73% (isolated material contained 10% of the β anomer). Spectral data were in agreement with previous reports.[12]

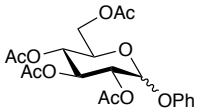
α: β= 10:1 (determined through analysis of the crude ^{1}H NMR spectrum)

^{1}H NMR (400 MHz, $CDCl_3$) δ:7.33–7.27 (m, 2H, ArH), 7.12–7.01 (m, 3H, ArH), 5.67 (dd, *J* = 3.3, 1.3 Hz, 0.1H, H-2 β), 5.57 (dd, *J* = 10.0, 3.5 Hz, 1H, H-3α), 5.52 (d, *J* = 1.9 Hz, 1H, H-1α), 5.44 (dd, *J* = 3.5, 1.9 Hz, 1H, H-2α), 5.36 (dd, *J* = 10.0, 10.0 Hz, 1H, H-4α), 5.22 (d, *J* = 1.3 Hz, 0.08H, H-1 β), 5.14 (dd, *J* = 9.9, 3.3 Hz, 0.1H H-3β), 4.33–4.22 (m, 1H, H-6aα), 4.15–4.03 (m, 2H, H-5, H-6bα), 2.19 (s, 3H, CH_3α), 2.05 (s, 3H, CH_3α), 2.03 (s, 3H, CH_3α), 2.02 (s, 3H, CH_3α).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.6, 170.1, 170.0, 169.8, 155.7, 129.7, 123.1, 116.6, 95.9, 77.5, 77.2, 76.8, 69.6, 69.3, 69.0, 66.1, 62.3, 29.8, 21.0, 20.8, 20.8, 20.8.

IR (neat, cm^{-1}): 2921 (w), 2867 (w), 1743 (s), 1590 (m), 1493 (m), 1434 (m), 1368 (s), 1209 (s), 1126 (m), 1035 (s), 979 (m), 757 (m), 691 (m).

3d – Phenyl-2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside



Synthesized according to general procedure C from 2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside (69.7 mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). The anomers ware isolated as light yellow solids after flash chromatography on silica gel, eluting with 10% to 30% ethyl acetate in hexanes (α: 30.5 mg, β: 16.8 mg, combined yield: 56%). Spectral data for both anomers were in agreement with previous reports.[11,12]

α: β= 1.2:1 (determined through analysis of the crude ^{1}H NMR spectrum)

α anomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ:7.36–7.28 (m, 2H, ArH), 7.10–7.04 (m, 3H, ArH), 5.73 (d, J=4.0 Hz, 1H, H-1), 5.70 (d, J=9.40 Hz, 1H, H-3), 5.15 (dd, J= 1.1, 10 Hz, 1H, H-4), 5.04 (dd, J= 10.2, 3.66 Hz, 1H, H-2), 4.24 (dd, J=12.0, 5.0 Hz, 1H, H-6a), 4.15–4.11 (m, 1H, H-5), 4.06 (dd, J= 12.0, 2.30 Hz, H-6b), 2.06 (s, 3H, CH_3), 2.05(s, 3H, CH_3), 2.04(s, 3H, CH_3), 2.03 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.7, 170.3, 169.7, 156.2, 129.8, 123.2, 116.8, 94.4, 77.5, 77.2, 76.8, 70.6, 70.3, 68.5, 68.1, 61.8, 20.87, 20.80, 20.78, 20.76.

IR (neat, cm^{-1}): 2920 (w), 2850 (w), 1736 (s), 1600 (w), 1494 (m), 1365 (m), 1218 (s), 1033 (s), 958 (w), 848 (s) 764 (m), 695 (m).

β anomer:

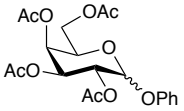
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31–7.27 (m, 2H, ArH), 7.09–7.05 (m, 1H, ArH), 7.01–6.98 (m, 2H, ArH), 5.30–5.27 (m, 2H, H-3, H-2), 5.17 (dd, J=9.8, 9.8 Hz, 1H, H-4), 5.08(d, J=7.4

Hz, 1H, H-1), 4.29 (dd, J=2.2, 5 Hz, 1H, H-6a), 4.18 (dd, J=2.4, 12.0 Hz, 1H,H-6b), 3.85 (ddd, J= 10.0, 5.4, 2.5 Hz, 1H, H-5), 2.07 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.03 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.7, 170.4, 169.5, 169.4, 157.0, 129.7, 123.5, 117.1, 99.3, 77.5, 77.4, 77.2, 76.8, 72.9, 72.2, 71.4, 68.5, 62.1, 20.82, 20.78, 20.77, 20.74.

IR (neat, cm^{-1}): 2924 (m), 2856 (m), 1756 (s), 1596 (w), 1493 (w), 1378 (m), 1223 (s), 1074 (m), 1047 (m), 913 (w), 766 (w), 698(w).

3e – Phenyl-2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside



Synthesized according to general procedure C from 2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (69.7 mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). The anomers ware isolated as light yellow solids after flash chromatography on silica gel, eluting with 20% to 60% diethyl ether in hexanes (α: 25.5 mg, β: 22.1 mg). The β anomer was inseparable from an acyl transfer compound derived from 2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (20% by mass). The combined yield of the anomers of 3e was therefore 51%. Spectral data for both anomers were in agreement with previous reports. [12, 13]

α: β= 1:1 (determined through analysis of the crude ^{1}H NMR spectrum)

α anomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.27 (m, 2H, ArH), 7.13–7.02 (m, 3H, ArH), 5.78 (d, J=3.5 Hz, 1H, H-1), 5.58 (dd, J=10.8, 3.4 Hz, 1H, H-3), 5.53 (dd, *J* = 3.4, 1.3 Hz, 1H, H-4), 5.29 (dd, J=10.3, 3.4 Hz, 1H, H-2), 4.38–4.33 (m, 1H, H-5), 4.15–4.02 (m, 2H, H-6a, H-6b), 2.17 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.93 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 170.5, 170.4, 170.3, 170.2, 156.4, 129.8, 123.1, 116.9, 95.0, 68.0, 67.9, 67.7, 67.3, 61.6, 20.9, 20.87, 20.82, 20.7.

IR (neat cm^{-1}) 2923 (w), 1737 (s), 1603 (m), 1497 (m), 1358 (s), 1210 (s), 1064 (s), 987 (m), 909(m), 848 (m).

β anomer:

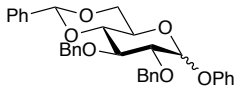
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35–7.27 (m, 2H, ArH), 7.10–7.04 (m, 1H, ArH), 7.02–6.98 (m, 2H, ArH), 5.52–5.47 (m, 1H, H-2), 5.45 (dd, *J* = 3.5, 1.1 Hz, 1H, H-4), 5.11 (dd, J= 10,4, 3.1 Hz, 1H, H-3), 5.04 (d, *J*=8.0 Hz, 1H, H-1), 4.23 (dd, *J* = 11.3, 7.0 Hz, 1H, H-6a), 4.16 (dd, *J* = 11.3, 6.3 Hz, 1H, H-6b), 4.08–4.01 (m, 1H, H-5), 2.18 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.01 (s, 3H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 170.4, 170.3, 169.5, 157.1, 129.7, 123.5, 117.1, 99.9, 71.2, 71.0, 68.8, 67.0, 61.5, 29.8, 20.88, 20.81, 20.79, 20.73.

Select peaks belonging to acyl transfer by-product: 6.38 (d, *J* = 1.7 Hz, 0.19H), 5.35–5.32 (m, 0.42H), 4.38–4.31 (m, 0.18H)

IR (neat cm^{-1}): 2926 (w), 1737 (s), 1603 (w), 1496 (w), 1431 (w), 1367 (m), 1238 (s), 1186 (s), 1042 (s), 987 (s), 847 (m).

3f – Phenyl-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranoside



Synthesized according to general procedure C from 2,3-Di-*O*-benzyl-4,6-*O*-benzylidene-D-glucopyranose (89.7 mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). A mixture of anomers was isolated as a white solid after flash chromatography on silica gel, eluting with 10% to 30% diethyl ether in hexanes (47.3 mg, 45%).

α: β= 1:1 (determined through analysis of the crude ^{1}H NMR spectrum)

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55–7.46 (m, 4H, ArH), 7.46–7.26 (m, 28H, ArH), 7.12–7.03 (m, 5H, ArH) 5.61 (s, 0.47H, CHPh), 5.58 (s, 1H, CHPh), 5.45 (d, J=5.5 Hz, 1H, H-1α), 5.15 (d, J= 7.4 Hz, 0.41H, H-1β), 5.01–4.83 (m, 6H, CH_2Ph), 4.73 (d, J=11.9 Hz, 1H CH_2Ph), 4.40 (dd, J= 10.5, 4.80 Hz, 0.26H, H-6β), 4.27 (dd, J= 9.3, 9.3, 1H, H-3α), 4.21 (dd, J= 10.3, 4.76 Hz, H-6α), 4.02 (dd, J=9.9, 4.6 Hz, 1H, H-5α), 3.92–3.64 (m, 5H, H-2β, H-3β, H-4β, H-6β, H-2α, H-4α, H-6α), 3.61–3.51 (m, 0.33H, H-5β).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.2, 156.7, 138.9, 138.2, 137.5, 137.4, 129.8, 129.7, 129.1, 129.1, 128.6, 128.5, 128.5, 128.4, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.8, 126.2, 126.2, 123.2, 122.8, 117.1, 117.1, 102.2, 101.5, 101.4, 96.6, 82.2, 81.9, 81.4, 81.0, 79.3, 78.6, 75.7, 75.5, 75.3, 73.8, 69.0, 68.9, 66.4, 63.3, 32.1, 30.3, 29.5, 26.9, 22.8, 14.3.

IR (neat, cm^{-1}): 2922 (m), 2860 (m), 1603 (w), 1455 (m), 1495 (m), 1382 (m), 1224(w), 1090 (s), 1030 (m), 908 (m), 734 (s), 697 (s).

HRMS (DART-TOF$^+$, m/z): Calculated for $C_{33}H_{36}NO_6[M+NH_4]^+$:525.22771, found 525.22776.

3g – Phenyl-3,4,6-tri-*O*-benzyl-2-deoxy-D-glucopyranoside

Synthesized according to general procedure C from 3,4,6-tri-O-benzyl-2-deoxy D-glucopyranoside (86.9 mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). A mixture of anomers was isolated as a light yellow oil after flash chromatography on silica gel, eluting with 10% to 30% diethyl ether in hexanes (49 mg, 48%).

α: β= 1:1.3 (determined through analysis of the crude ^{1}H NMR spectrum)

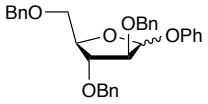
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.42–7.26 (m, 31H), 7.26–7.17 (m, 2H), 7.10–6.97 (m, 7H), 5.72 (dd, *J* = 2.0, 1.3 Hz, 1H, H-1α), 5.09 (dd, *J* = 9.7, 2.1 Hz, 1H, H-1β), 4.94 (dd, *J* = 10.9, 2.8 Hz, 2H), 4.79–4.69 (m, 3H), 4.69–4.52 (m, 7H), 4.45 (d, *J* = 12.1 Hz, 1H), 4.21 (ddd, *J* = 11.4, 8.7, 5.0 Hz, 1H), 3.91–3.69 (m, 7H), 3.65–3.56 (m, 4H), 2.57– 2.45 (m, 2H, H-2a), 2.02–1.86 (m, 2H, H-2b).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 157.3, 156.6, 138.7, 138.6, 138.43, 138.42, 138.3, 138.2, 129.54, 129.53, 128.6, 128.55, 128.51, 128.45, 128.44 128.42, 128.1, 128.02, 128.01, 127.89, 127.87, 127.86, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 122.4, 122.0, 116.7, 116.6, 97.8, 95.9, 79.3, 78.1, 78.0, 77.6, 75.6, 75.2, 75.1, 73.6, 73.5, 72.1, 71.7, 71.6, 69.4, 68.8, 36.7, 35.6.

IR (thin film, cm^{-1}): 3071 (w), 3031 (w), 2884 (w), 2864 (w), 1594 (m), 1495 (s), 1454 (m), 1364 (s), 1193 (w), 1089 (s), 1074 (s), 1027 (s), 974 (s), 908 (w), 850 (w), 751 (s), 732 (s), 693 (s).

HRMS (DART-TOF$^+$, m/z): Calculated for $C_{33}H_{38}NO_5$ $[M+NH_4]^+$:528.27500, found 528.27475.

3h – Phenyl 2,3,5-*O*-benzyl- D-arabinofuranoside



Synthesized according to general procedure C from 2,3,5-*O*-benzyl- D-arabinofuranoside (84.1mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). The anomers ware isolated as colourless oils after flash chromatography on silica gel, eluting with 10% to 40% diethyl ether in hexanes (56.8 mg combined yield: 57%).

α: β= 3:1 (determined through analysis of the crude ^{1}H NMR spectrum)

α anomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.25 (m, 17H, ArH), 7.12–7.06 (m, 2H, ArH), 7.06–7.00 (m, 1H, ArH), 5.74 (d, *J* = 1.5 Hz, 1H, H-1), 4.66–4.52 (m, 6H, CH_2Ph), 4.40–4.32 (m, 2H, H-2 and H-4), 4.13 (dd, *J* = 6.8, 3.3 Hz, 1H, H-3), 3.73–3.62 (m, 2H, H-5).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.75, 138.2, 138.0, 137.5, 129.6, 128.6, 128.5, 128.5, 128.1, 128.8, 127.96, 127.91, 127.8, 122.2, 116.9, 104.7, 88.6, 83.3, 81.7, 73.5, 72.4, 72.3, 69.4.

IR (thin film, cm^{-1}): 2925 (w), 2860 (w), 1599 (w), 1496 (m), 1455 (m), 1265 (m), 1226 (m), 1079 (s), 909 (m), 735 (s), 697 (m).

HRMS (DART-TOF^{+}, m/z): Calculated for $C_{32}H_{32}O_5[M+NH4]^+$:514.25935, found 514.25895.

β anomer:

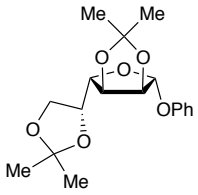
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.11 (m, 17H, Ar-H), 7.06–6.92 (m, 3H, ArH), 5.50 (d, *J* = 4.2 Hz, 1H, H-1), 4.70–4.53 (m, 4H, CH_2Ph), 4.44–4.33 (m, 2H, CH_2Ph), 4.29–4.11 (m, 3H, H-2, H-3, H-4), 3.50 (d, *J* = 6.0 Hz, 2H, H5).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.2, 138.27, 138.20, 137.6, 129.6, 128.60, 128.52, 128.41, 128.19, 128.10, 127.88, 127.82, 127.7, 127.6, 122.4, 117.1, 99.2, 84.2, 83.2, 81.4, 73.5, 72.8, 72.6, 72.4.

IR (thin film, cm^{-1}): 2925 (s), 2860 (m), 1598 (m), 1495 (s), 1455 (m), 1225 (s), 1028 (s), 737 (s), 697 (s).

HRMS (DART-TOF^{+}, m/z): Calculated for $C_{32}H_{32}O_5[M+NH4]^+$:514.25935, found 514.25895.

3i – Phenyl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside

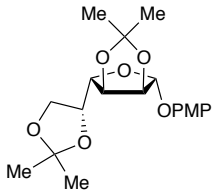


Synthesized according to general procedure C from 2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (52.1 mg, 0.2 mmol) and triphenylboroxine (103.9 mg, 0.33 mmol). Isolated as a white solid after flash chromatography on silica gel, eluting with 10% diethyl ether in hexanes (39.1 mg, 58%). Spectral data were in agreement with previous reports.[14]

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31–7.26 (m, 2H), 7.04–6.98 (m, 3H), 5.64 (s, 1H), 4.92 (dd, *J* = 5.9, 3.5 Hz, 1H), 4.87 (d, *J* = 5.9 Hz, 1H), 4.43 (ddd, *J* = 8.0, 6.2, 4.2 Hz, 1H), 4.12–4.06 (m, 2H), 3.99 (dd, *J* = 8.8, 4.2 Hz, 1H), 1.52 (s, 3H), 1.43 (s, 3H), 1.38 (d, *J* = 1.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.4, 129.6, 122.4, 116.8, 113.1, 109.5, 105.0, 85.6, 81.3, 79.7, 73.1, 67.1, 27.1, 26.1, 25.4, 24.8.

3k – 4-Methoxyphenyl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside



Synthesized according to general procedure C from 2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (52.1 mg, 0.2 mmol) and tri(4-methoxyphenyl)boroxine (132.6 mg, 0.33 mmol). Isolated as a white solid after flash chromatography on silica gel, eluting with 2.5% acetone in dichloromethane (45.5 mg, 62%).

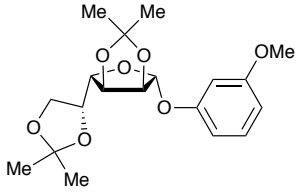
^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.98–6.89 (m, 2H, ArH), 6.84–6.78 (m, 2H, ArH), 5.51 (s, 1H, H-1), 4.90 (dd, *J* = 5.9, 3.5 Hz, 1H, H-3), 4.84 (d, *J* = 5.9 Hz, 1H, H-2), 4.42 (ddd, *J* = 8.0, 6.3, 4.2 Hz, 1H, H-5), 4.12 – 4.04 (m, 2H, H-6a, H-4), 3.98 (dd, *J* = 8.8, 4.3 Hz, 1H, H-6b), 3.76 (s, 3H, OMe), 1.50 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.37 (d, *J* = 4.1 Hz, 6H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 155.1, 150.3, 118.2, 114.7, 113.0, 109.5, 105.9, 85.5, 81.1, 79.7, 73.1, 67.1, 55.7, 27.0, 26.1, 25.3, 24.7.

IR (neat, cm^{-1}): 2989 (w), 2943 (m), 2885 (w), 2842 (w), 1510 (s), 1463 (m), 1382 (m), 1370 (s), 1242 (s), 1214 (s), 1181 (m), 1163 (m), 980 (s), 1066 (s), 1033 (s), 1007 (s), 980 (s), 953 (s), 893 (m), 859 (m), 821 (s), 776 (m), 763 (m), 673 (m).

HRMS (DART-TOF$^+$, m/z): Calculated for $C_{19}H_{27}O_7$ [$(M + H)^+$]: 367.17568. Found: 367.17615.

3l – 3-Methoxyphenyl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside



Synthesized according to general procedure C from 2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (52.1 mg, 0.2 mmol) and tri(3-methoxyphenyl)boroxine (132.6 mg, 0.33 mmol). Isolated as a colourless oil after flash chromatography on silica gel, eluting with 2.5% acetone in dichloromethane (39.6 mg, 54%).

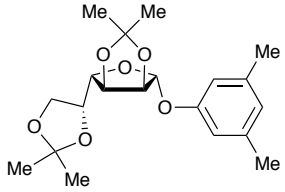
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.19–7.15 (m, 1H, Ar-H), 6.62–6.55 (m, 3H, Ar-H), 5.62 (s, 1H, H-1), 4.91 (dd, *J* = 5.9, 3.5 Hz, 1H, H-3), 4.86 (d, *J* = 5.9 Hz, 1H, H-2), 4.42 (ddd, *J* = 8.0, 6.2, 4.2 Hz, 1H, H-5), 4.12–4.05 (m, 2H, H-4, H-6a), 3.99 (dd, *J* = 8.8, 4.3 Hz, 1H, H-6b), 3.78 (s, 3H, OMe), 1.51 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.37 (s, 6H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 160.86, 157.58, 130.04, 113.11, 109.51, 108.86, 108.07, 105.00, 103.02, 85.60, 81.30, 79.70, 73.11, 67.07, 55.44, 27.08, 26.10, 25.37, 24.75.

IR (thin film, cm^{-1}): 2993 (w), 2942 (w), 1598 (m), 1492 (m), 1455 (w), 1374 (m), 1261 (m), 1202 (m), 1150 (s), 1114 (m), 1066 (s), 1050 (s), 1006 (s), 986 (a), 889 (w), 846 (s), 766 (m), 733 (m), 686 (m), 650 (w).

HRMS (DART-TOF$^+$, m/z): Calculated for $C_{19}H_{27}O_7$ [$(M + H)^+$]: 367.17568. Found: 367.17505.

3m – 3,5-Dimethylphenyl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside



Synthesized according to general procedure C from 2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (52.1 mg, 0.2 mmol) and tri(3,5-dimethylphenyl)boroxine (130.6 mg, 0.33 mmol). Isolated as a colourless oil after flash chromatography on silica gel, eluting with 2.5% acetone in dichloromethane (46 mg, 63%).

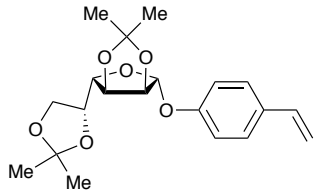
^{1}H NMR (500 MHz, $CDCl_3$) δ: 6.67 (s, 1H, ArH), 6.64 (s, 2H, ArH), 5.62 (s, 1H, H-1), 4.91 (dd, *J* = 5.9, 3.5 Hz, 1H, H-3), 4.84 (d, *J* = 5.9 Hz, 1H, H-2), 4.43 (ddd, *J* = 8.0, 6.3, 4.2 Hz, 1H, H-5), 4.14–4.05 (m, 2H, H-4 and H-6a), 4.01 (dd, *J* = 8.8, 4.2 Hz, 1H, H-6b), 2.28 (s, 6H Ar-Me), 1.52 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.37 (s, 3H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.4, 139.4, 124.1, 114.4, 113.0, 109.5, 104.9, 85.6, 81.2, 79.7, 77.4, 77.2, 76.9, 73.1, 67.0, 27.0, 26.1, 25.4, 24.7, 21.5.

IR (thin film, cm^{-1}): 2989 (w), 2946 (w), 1618 (w), 1596 (m), 1465 (w) 1375 (m), 1297 (m), 1261 (m), 1210 (m), 1153 (s), 1114 (m), 1088 (s), 1064 (s), 1025 (s), 1004 (s), 994 (s), 981 (s), 953 (m), 890 (m)< 843 (s), 733 (s), 687 (m), 650 (w).

HRMS (DART-TOF$^+$, m/z): Calculated for $C_{20}H_{29}O_6$ [$(M + H)^+$]: 365.19641. Found: 365.19643.

3n – 4-Vinylphenyl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside



Synthesized according to general procedure C from 2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (52.1 mg, 0.2 mmol) and tri(4-vinylphenyl)boroxine (128.7 mg, 0.33 mmol). Isolated as a white solid after flash chromatography on silica gel, eluting with 10% ether in hexane (41.5 mg, 57%).

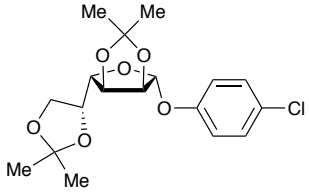
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.36–7.31 (m, 2H, ArH), 6.98–6.94 (m, 2H, ArH), 6.66 (dd, *J* = 17.6, 10.9 Hz, 1H, C**H**CH_2), 5.66–5.60 (m, 2H, H-1, CHC**H**$_2$), 5.16 (dd, *J* = 10.9, 0.9 Hz, 1H, CHC**H**$_2$), 4.91 (dd, *J* = 5.9, 3.5 Hz, 1H, H-3), 4.86 (d, *J* = 5.9 Hz, 1H, H-2), 4.43 (ddd, *J* = 8.0, 6.3, 4.2 Hz, 1H, H-5), 4.12 – 4.05 (m, 2H, H-4, H-6a), 3.98 (dd, *J* = 8.8, 4.2 Hz, 1H, H-6b), 1.52 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.37 (s, 6H,CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 156.1, 136.2, 132.0, 127.5, 116.7, 113.1, 112.5, 109.5, 105.0, 85.6, 81.3, 79.7, 73.1, 67.0, 27.1, 26.1, 25.3, 24.7.

IR (neat, cm^{-1}): 2988 (m), 2951 (w), 2902 (w), 1630 (w) 1606 (m), 1510 (s), 1455 (q), 1376 (m), 1367 (m), 1283 (w), 1238 (m), 1206 (s), 1177 (w), 1159 (s), 1109 (s), 1078 (s), 1049 (s), 994 (s), 981 (s), 920 (s), 896 (w), 863 (s), 842 (s), 819 (s), 775 (w), 737 (w), 692 (w).

HRMS (DART-TOF$^+$, m/z): Calculated for $C_{20}H_{27}O_6$ [$(M + H)^+$]: 363.18076. Found: 363.18048.

3o – 4-Chlorophenyl-2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside



Synthesized according to general procedure C from 2,3:5,6-di-O-isopropylidene-α-D-mannofuranoside (52.1 mg, 0.2 mmol) and tri(4-chlorophenyl)boroxine (137 mg, 0.33 mmol). Isolated as a light yellow oil after flash chromatography on silica gel, eluting with 2.5% acetone in dichloromethane (26 mg, 35%).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.25–7.20 (m, 2H, ArH), 6.95–6.90 (m, 2H, ArH), 5.57 (s, 1H, H-1), 4.90 (dd, *J* = 5.9, 3.5 Hz, 1H, H-3), 4.85 (d, *J* = 5.8 Hz, 1H, H-2), 4.42 (ddd, *J* = 7.8, 6.2, 4.2 Hz, 1H, H-5), 4.11–4.03 (m, 2H, H-4, H-6a), 3.96 (dd, *J* = 8.8, 4.2 Hz, 1H, H-6b), 1.50 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.37 (s, 6H, CH_3).

^{13}C NMR (126 MHz, $CDCl_3$) δ: 154.9, 129.5, 127.4, 118.1, 113.2, 109.5, 105.2, 85.5, 81.4, 79.7, 73.1, 67.0, 27.0, 26.1, 25.3, 24.7.

IR (thin film, cm^{-1}): 2993 (w), 2939 (w), 1596 (w), 1490 (s), 1457 (w), 1375 (m), 1229 (s), 1208 (s), 1161 (m), 1115 (m), 1088 (s), 1067 (s), 998 (s), 981 (s), 891 (w), 845 (s), 825 (s), 732 (m), 643 (m).

HRMS (DART-TOF$^+$, m/z): Calculated for $C_{18}H_{24}ClO_6$[$(M + H)^+$]: 371.12614 Found: 371.12633.

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^{1}H, ^{13}C and 2D NMR Spectra

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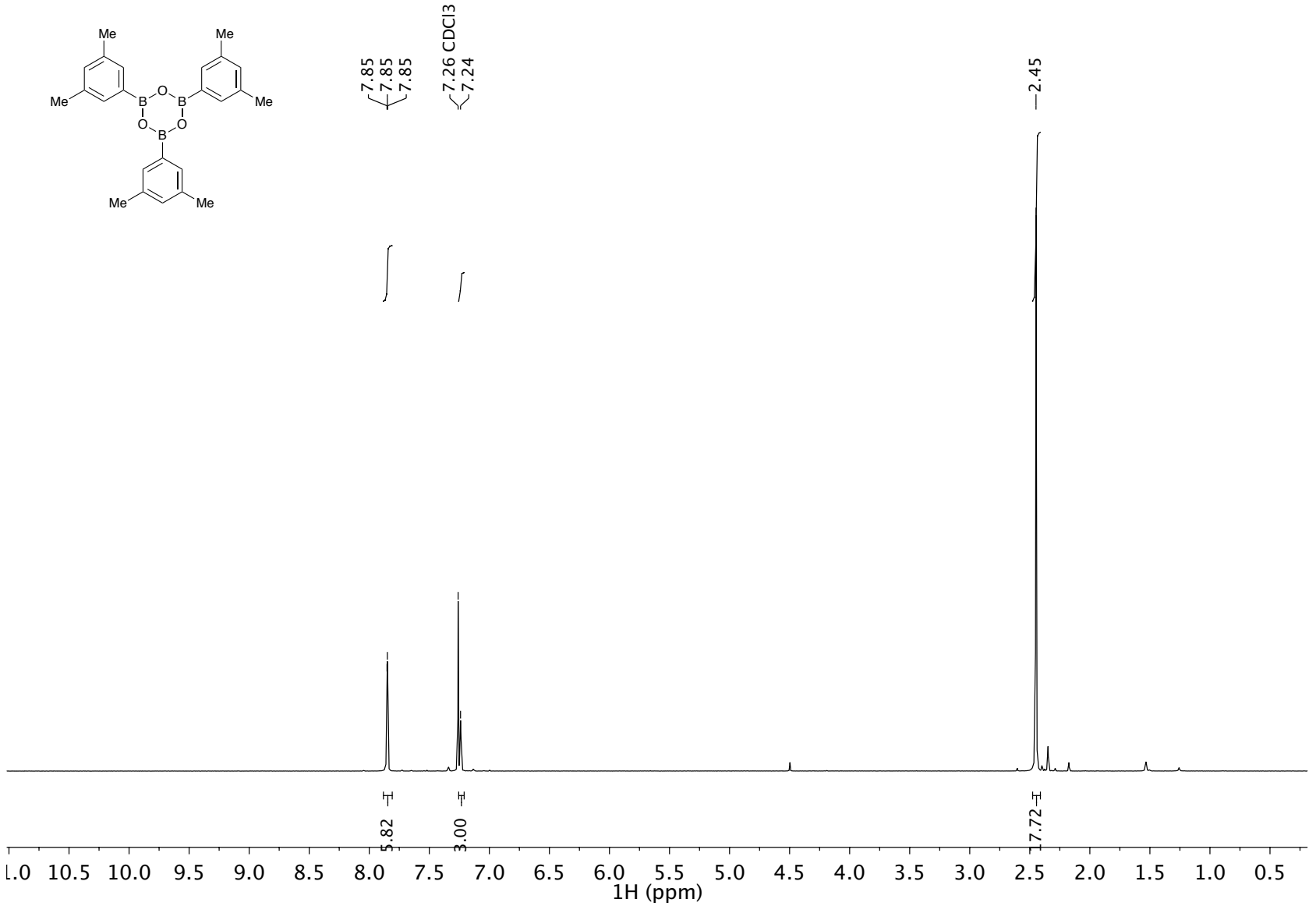
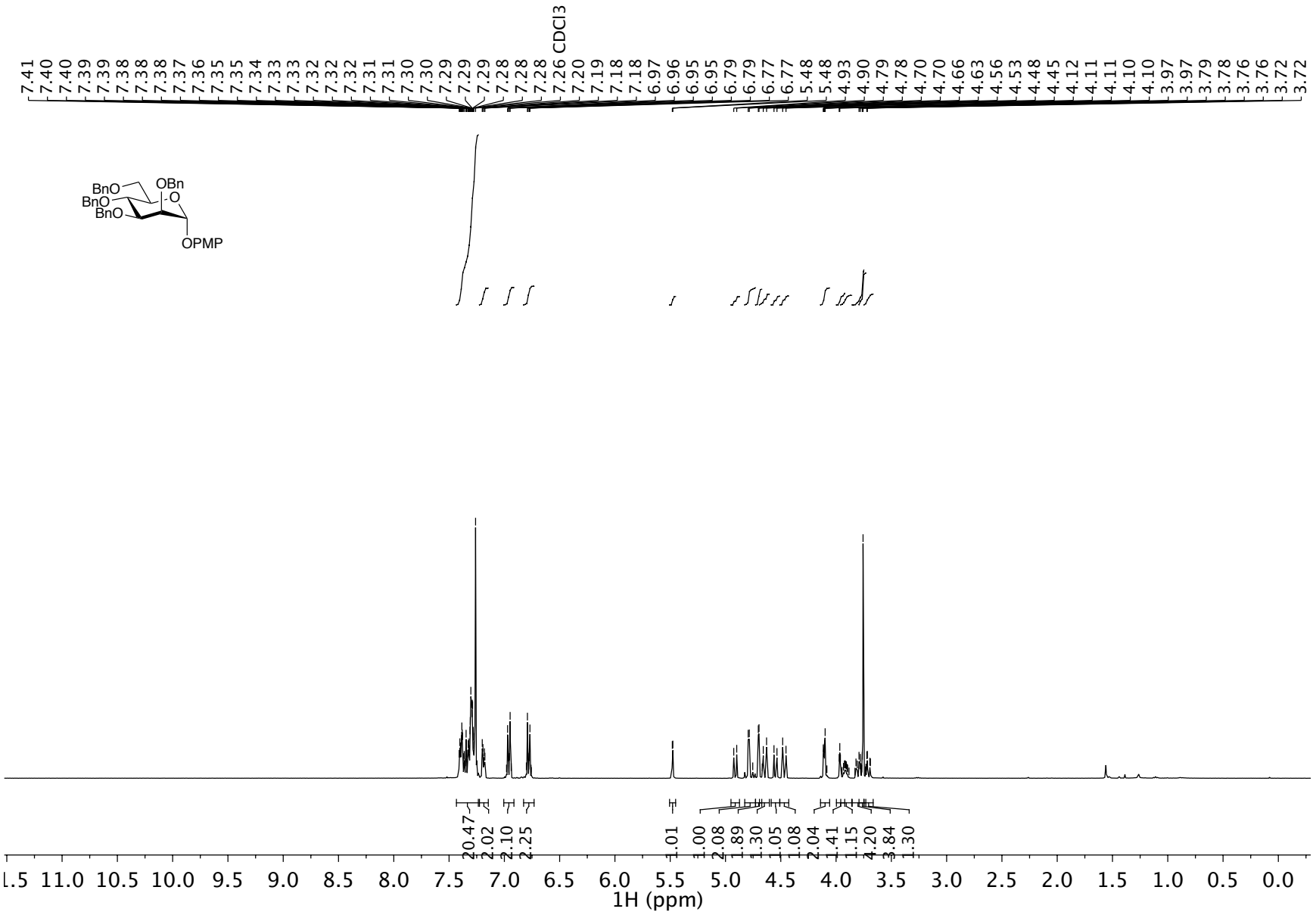
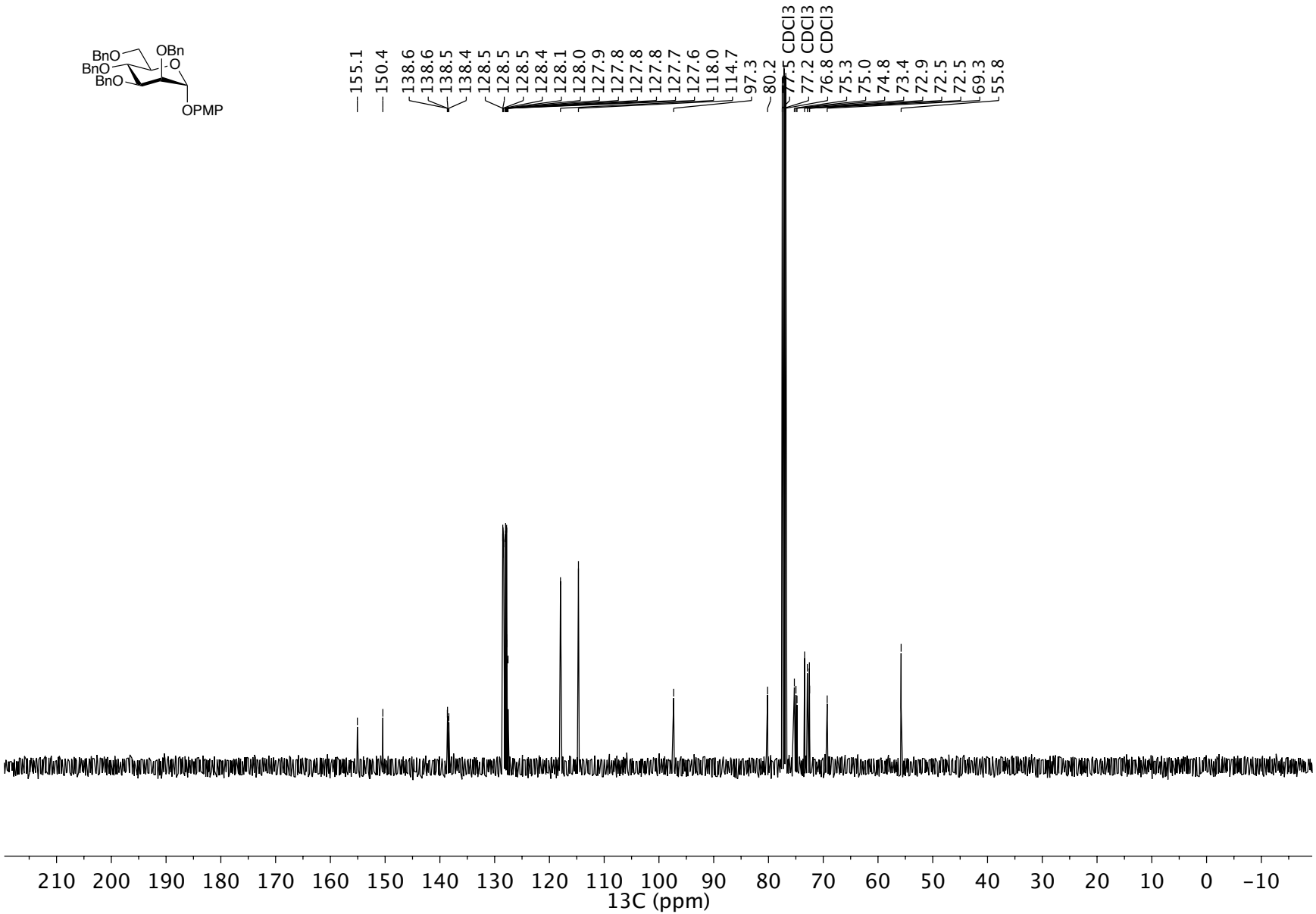
2m – ^{1}H NMR (400 MHz, $CDCl_3$)



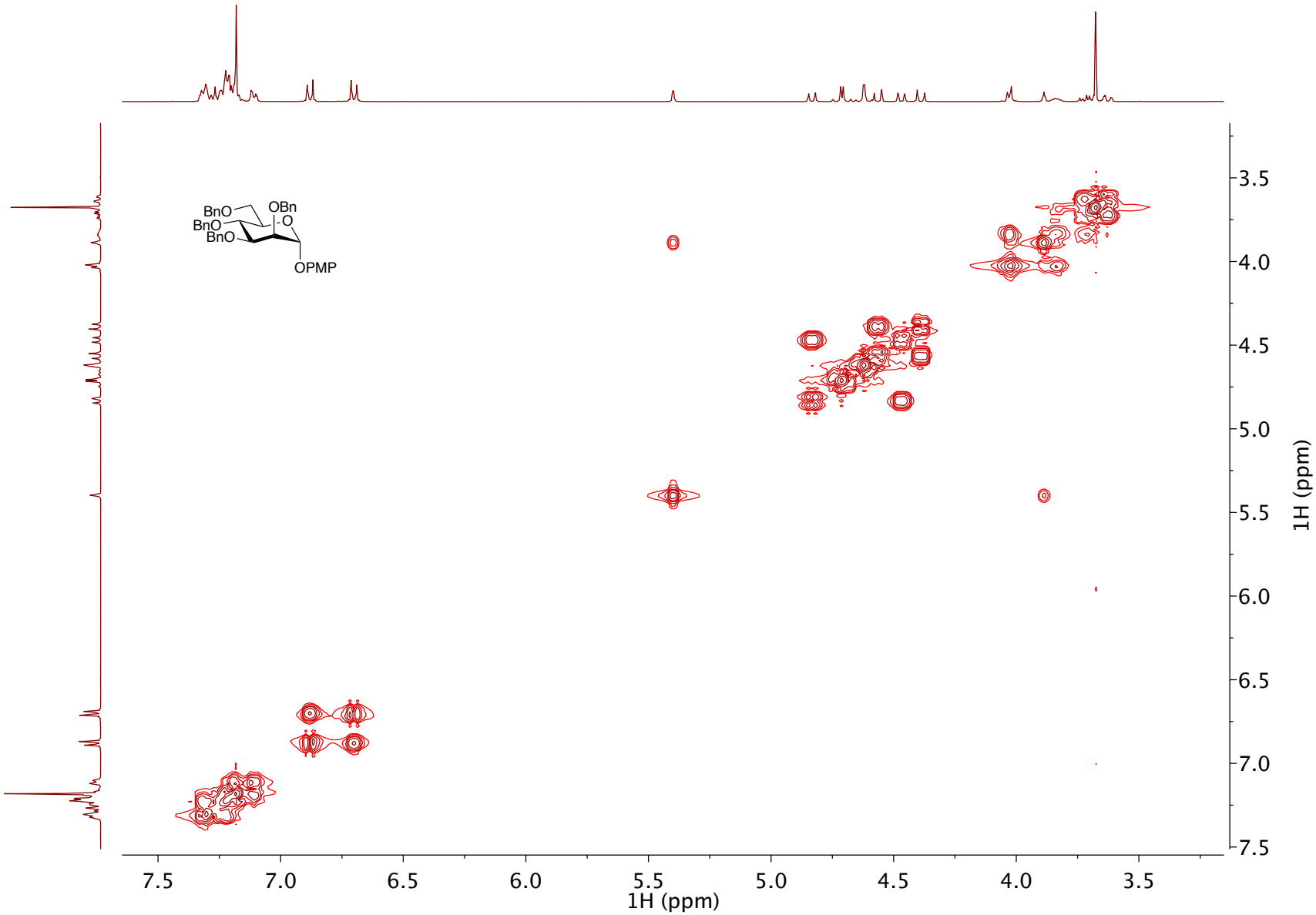
3aα – ^{1}H NMR (400 MHz, $CDCl_3$)



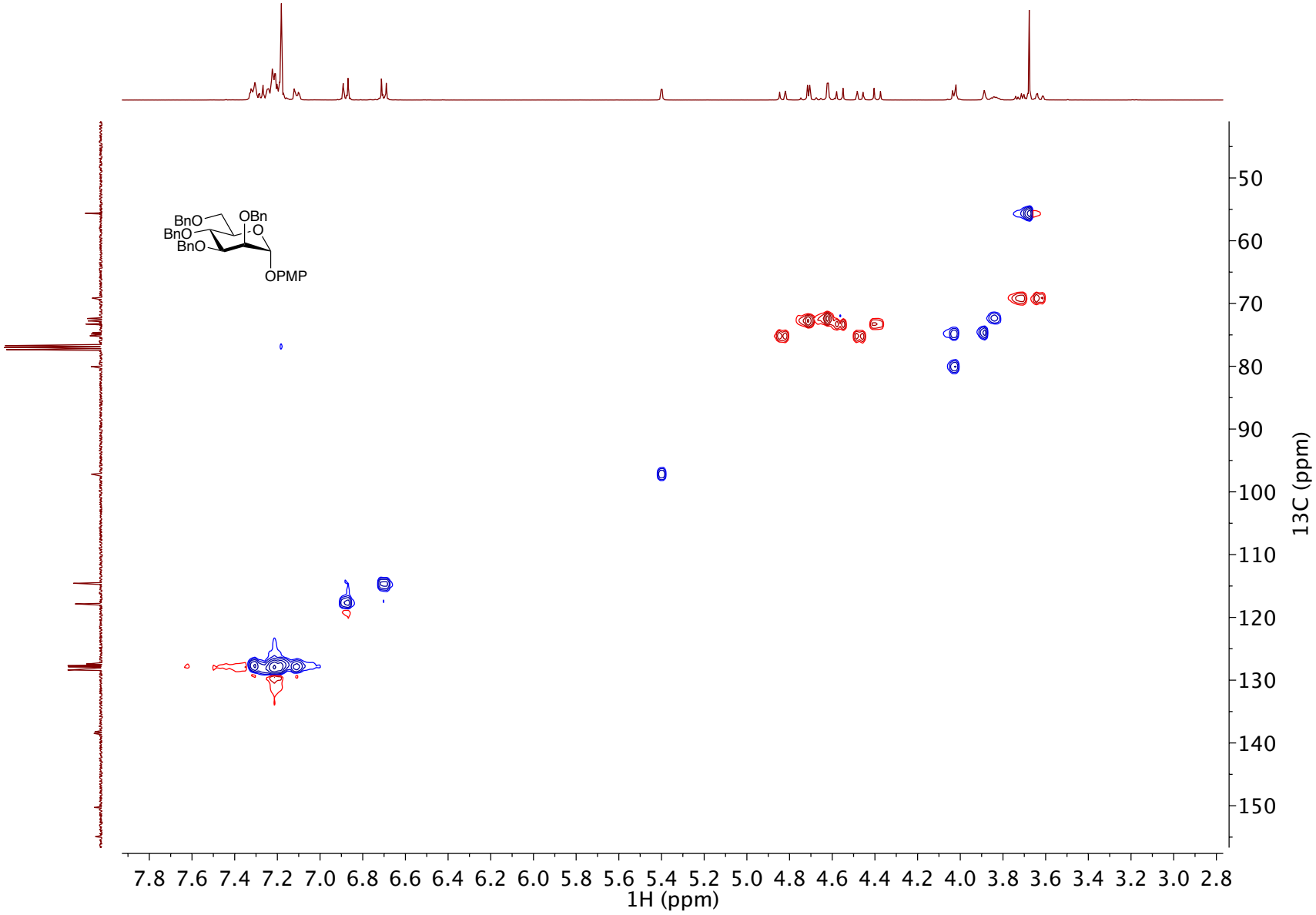
3aα – ^{13}C NMR (101 MHz, $CDCl_3$)



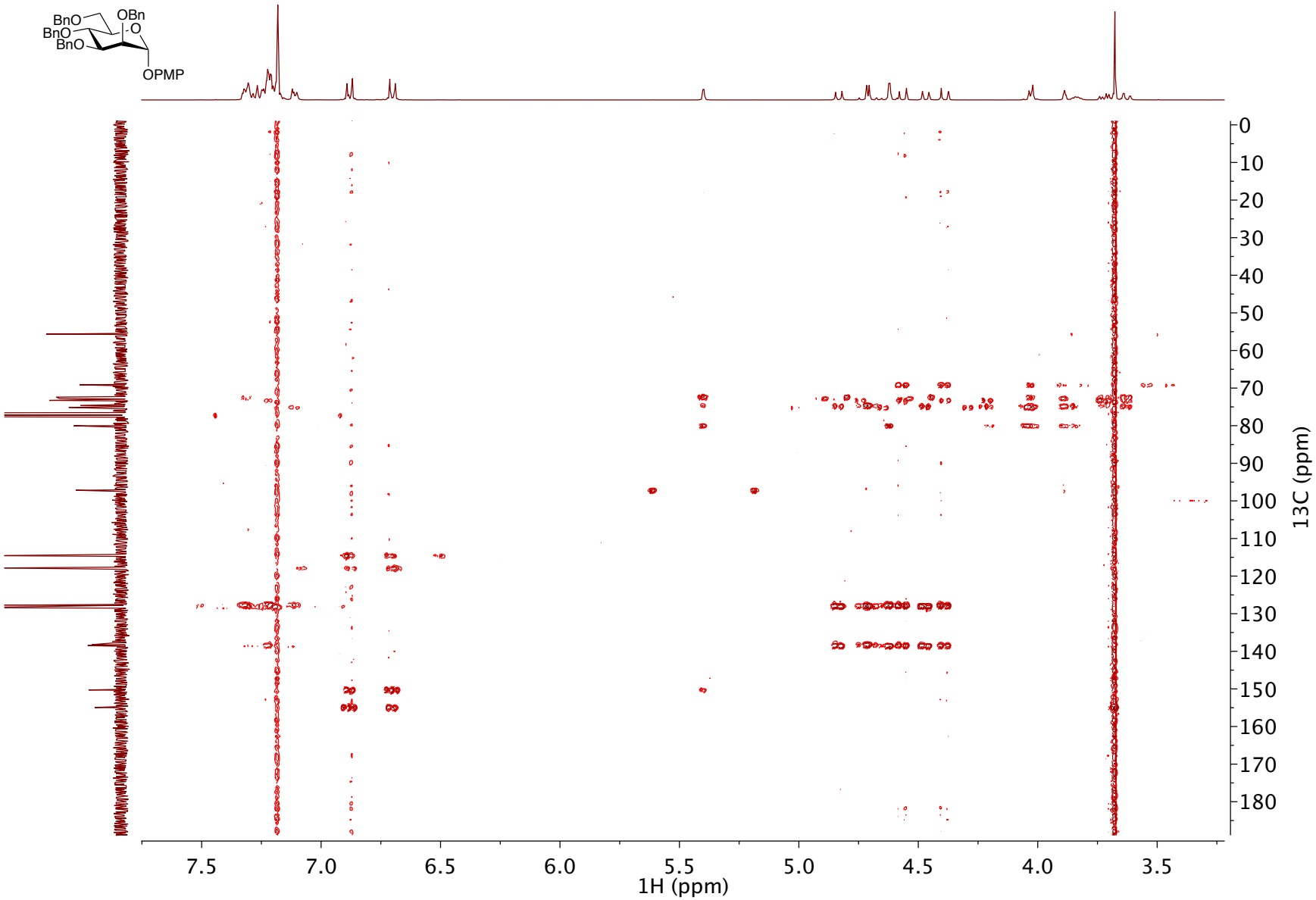
3aα – COSY (400 MHz, $CDCl_3$)



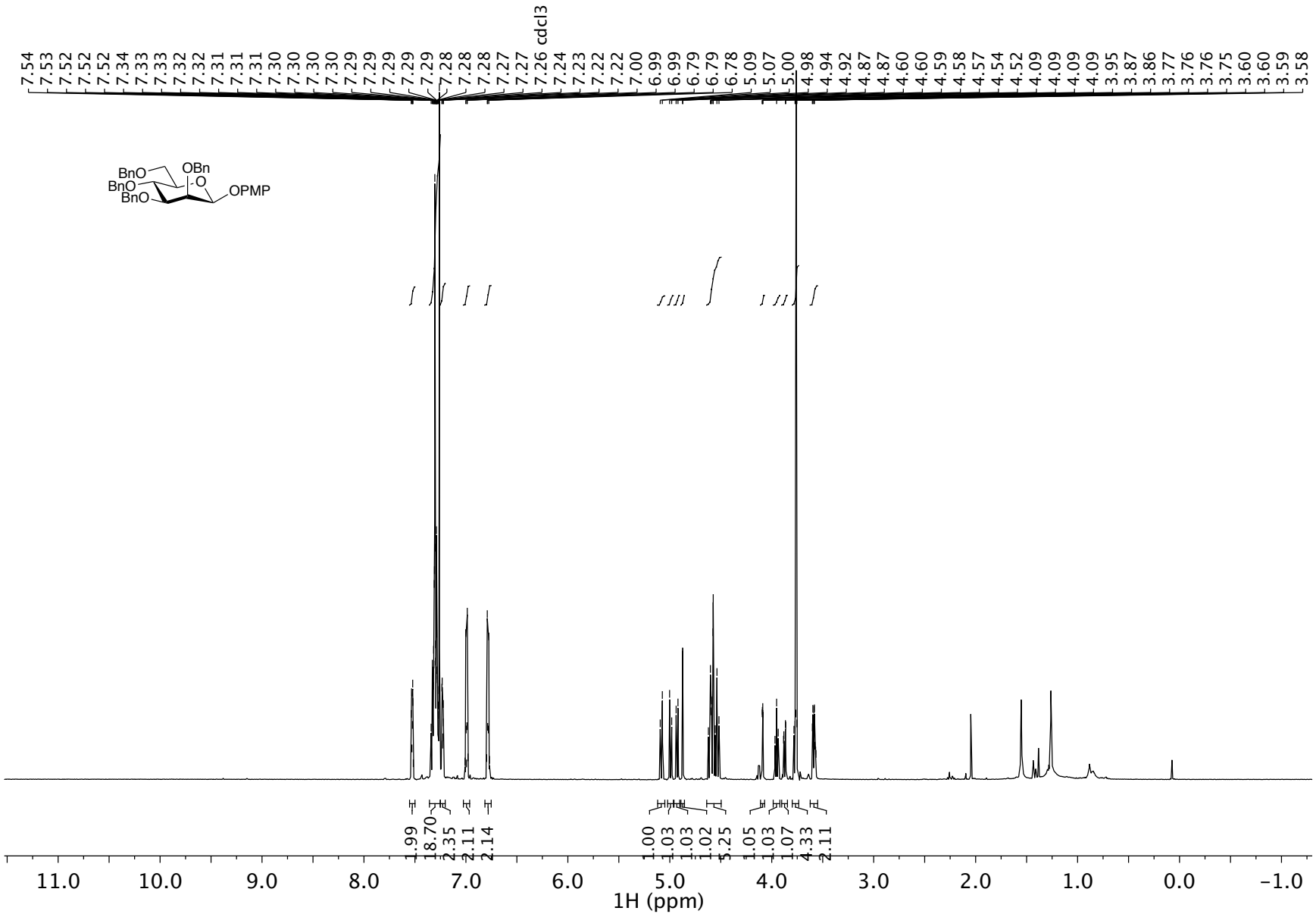
3aα – HSQC (400 MHz, $CDCl_3$)



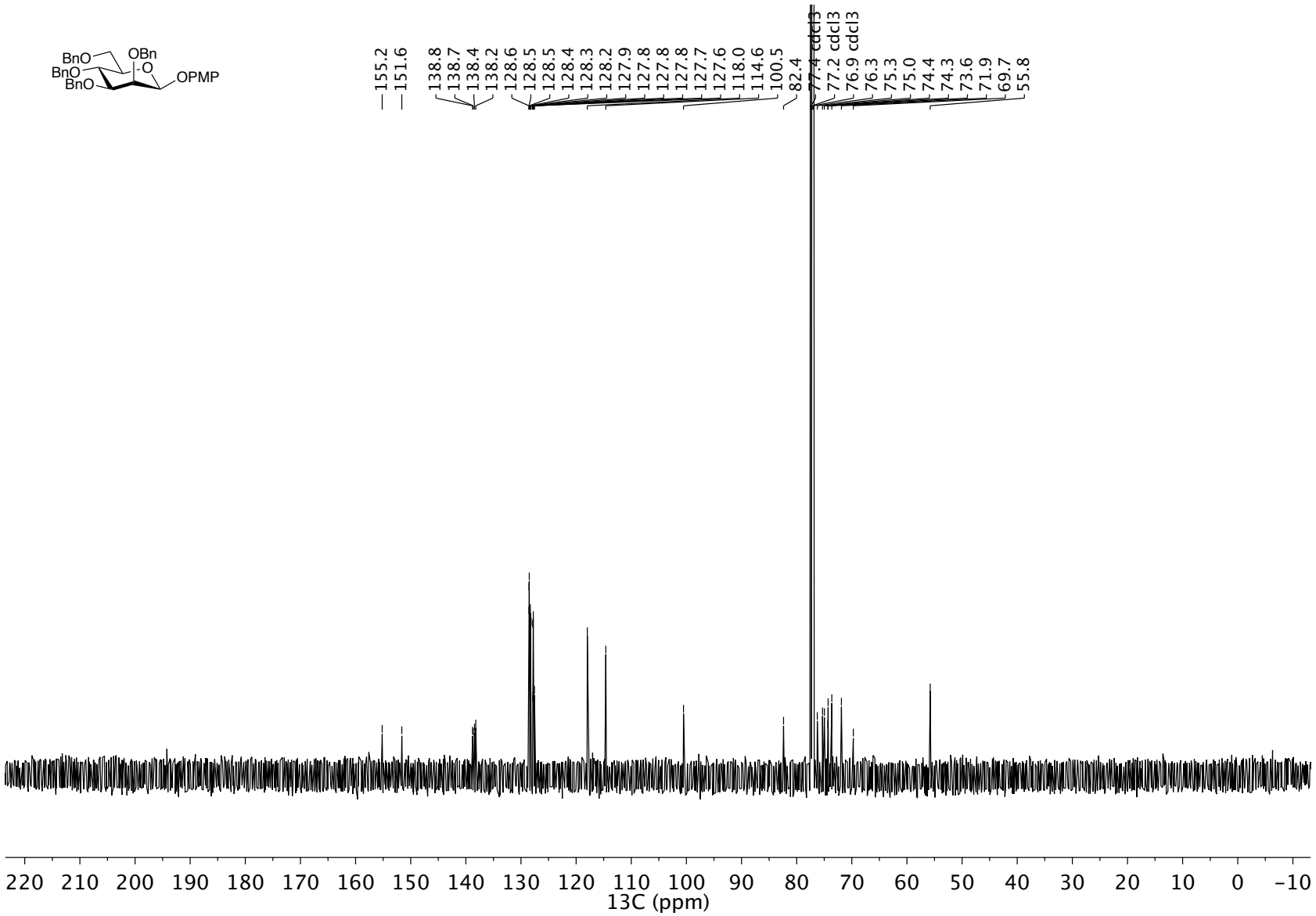
3aα – HMBC (400 MHz, $CDCl_3$)



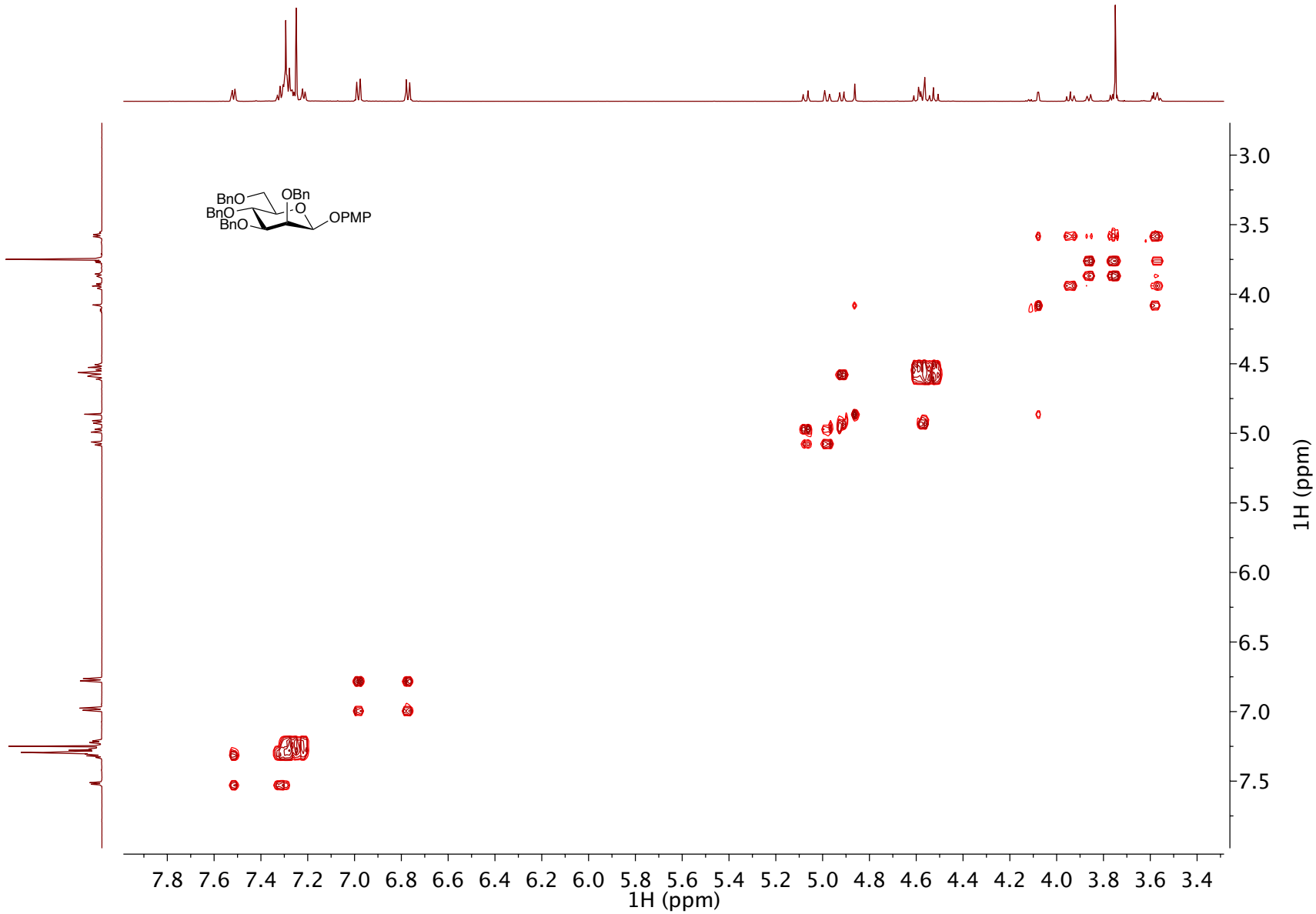
3aβ – ^{1}H NMR (600 MHz, $CDCl_3$)



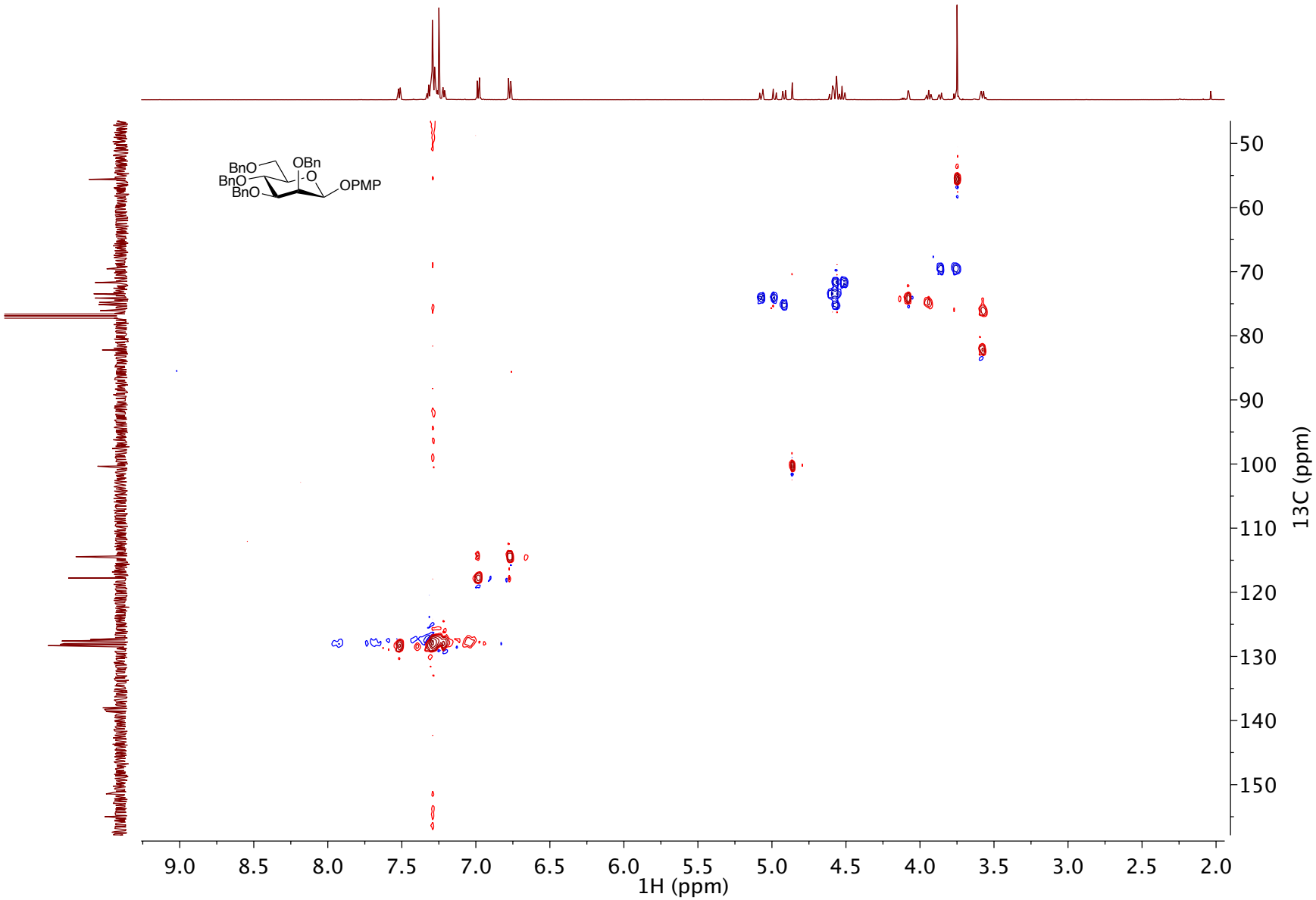
3aβ – ^{13}C NMR (151 MHz, $CDCl_3$)



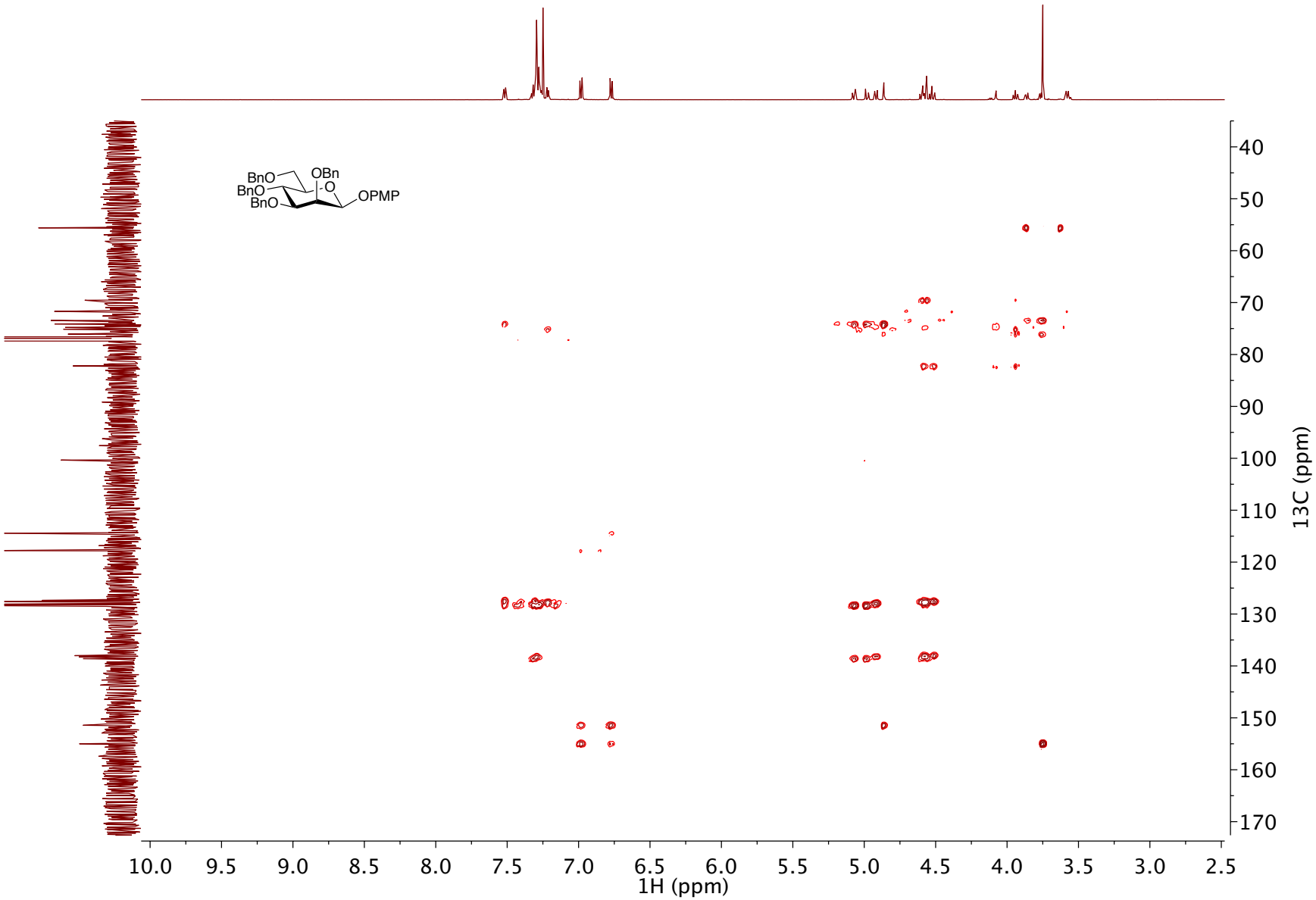
3aβ – COSY (600 MHz, $CDCl_3$)



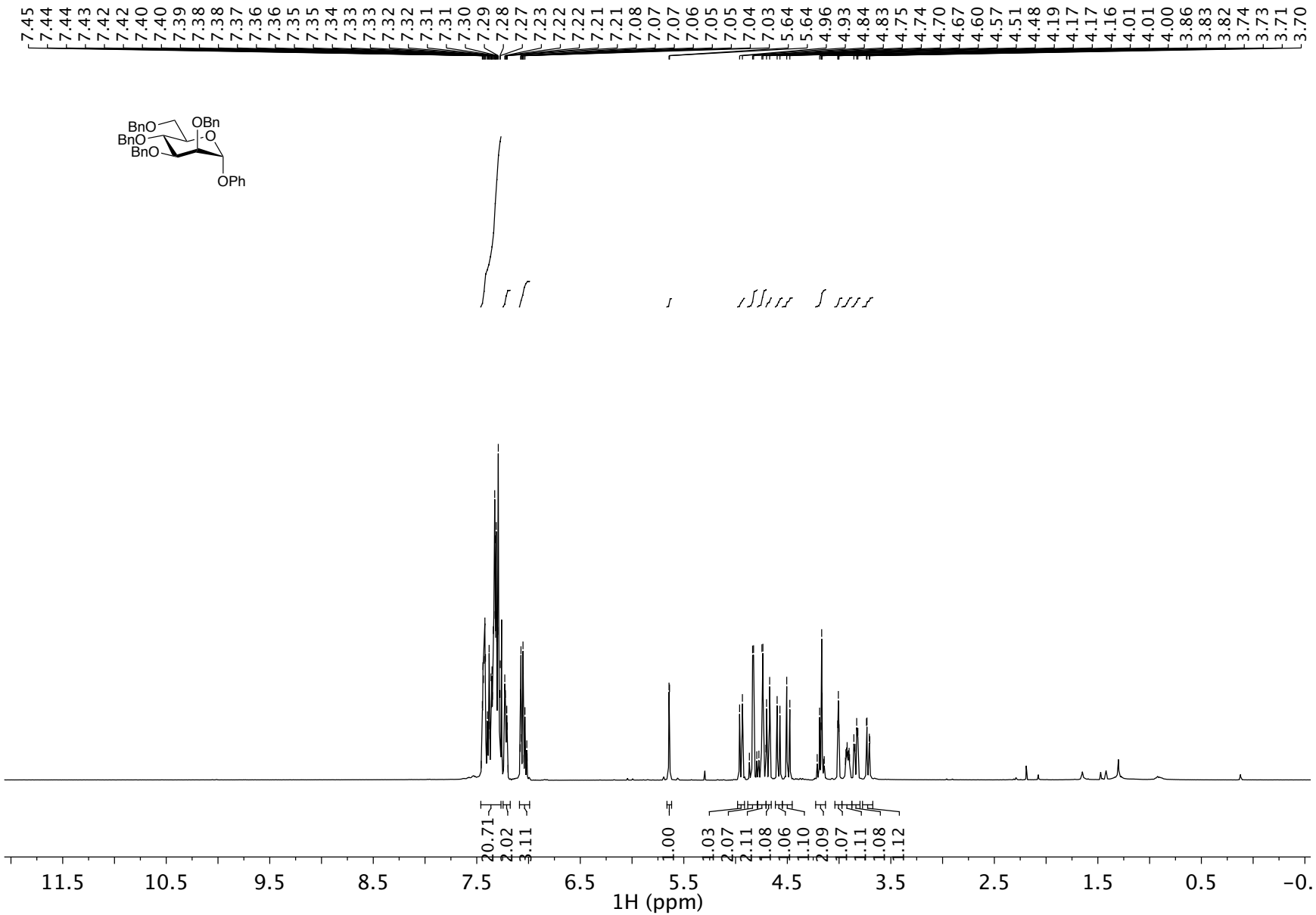
3aβ – HSQC (600 MHz, $CDCl_3$)



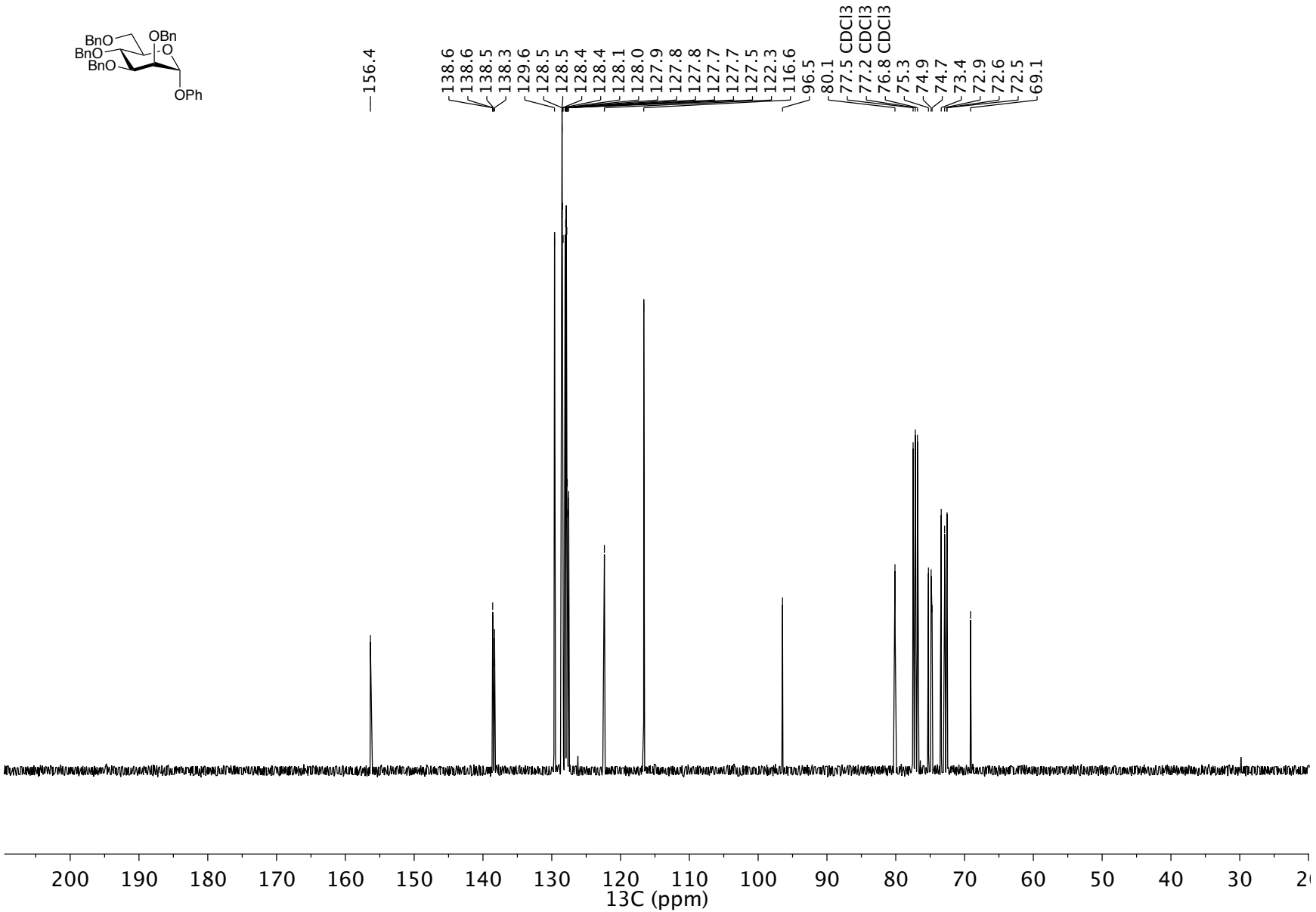
3aβ – HMBC (600 MHz, $CDCl_3$)



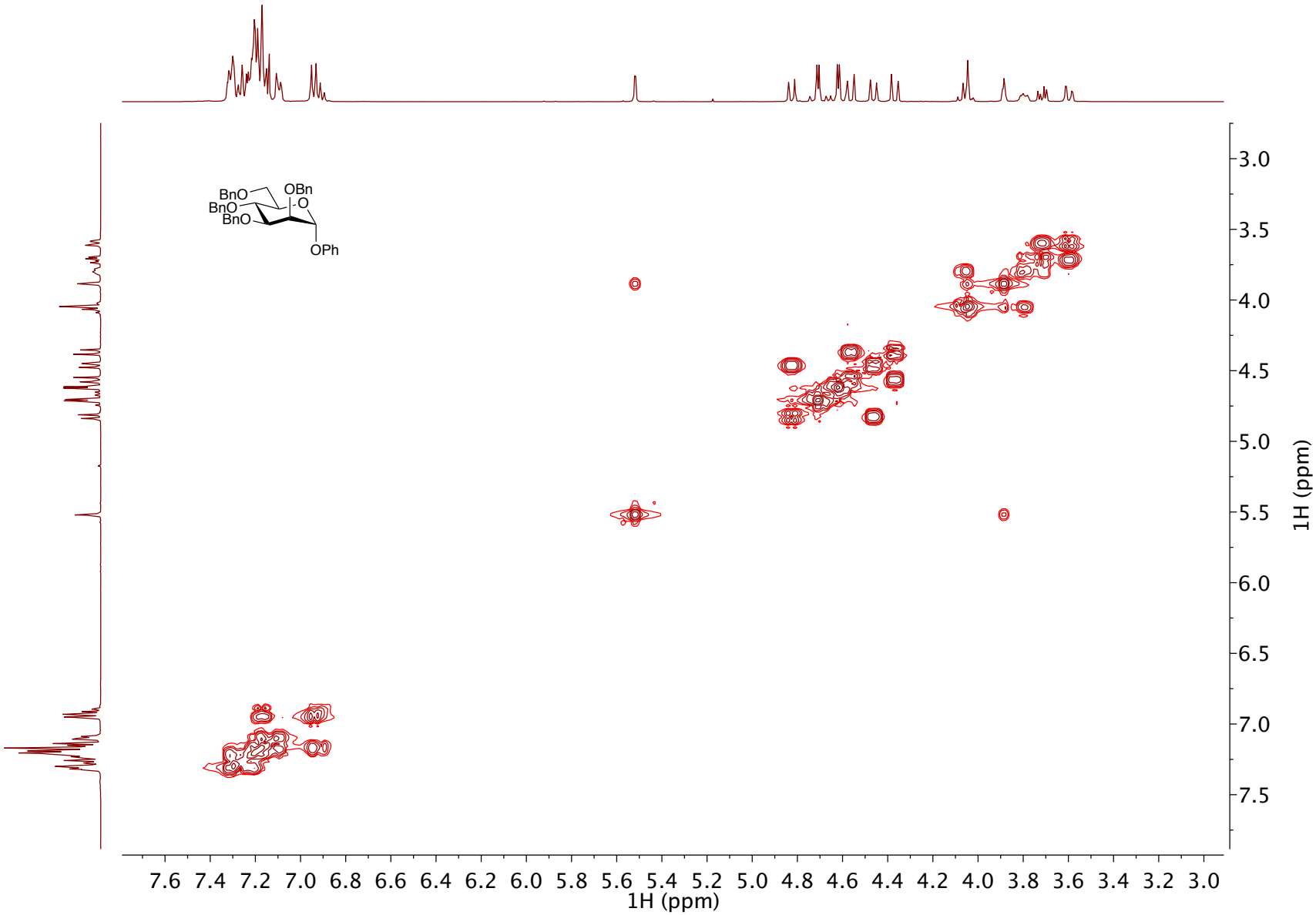
3bα – ^{1}H NMR (400 MHz, $CDCl_3$)



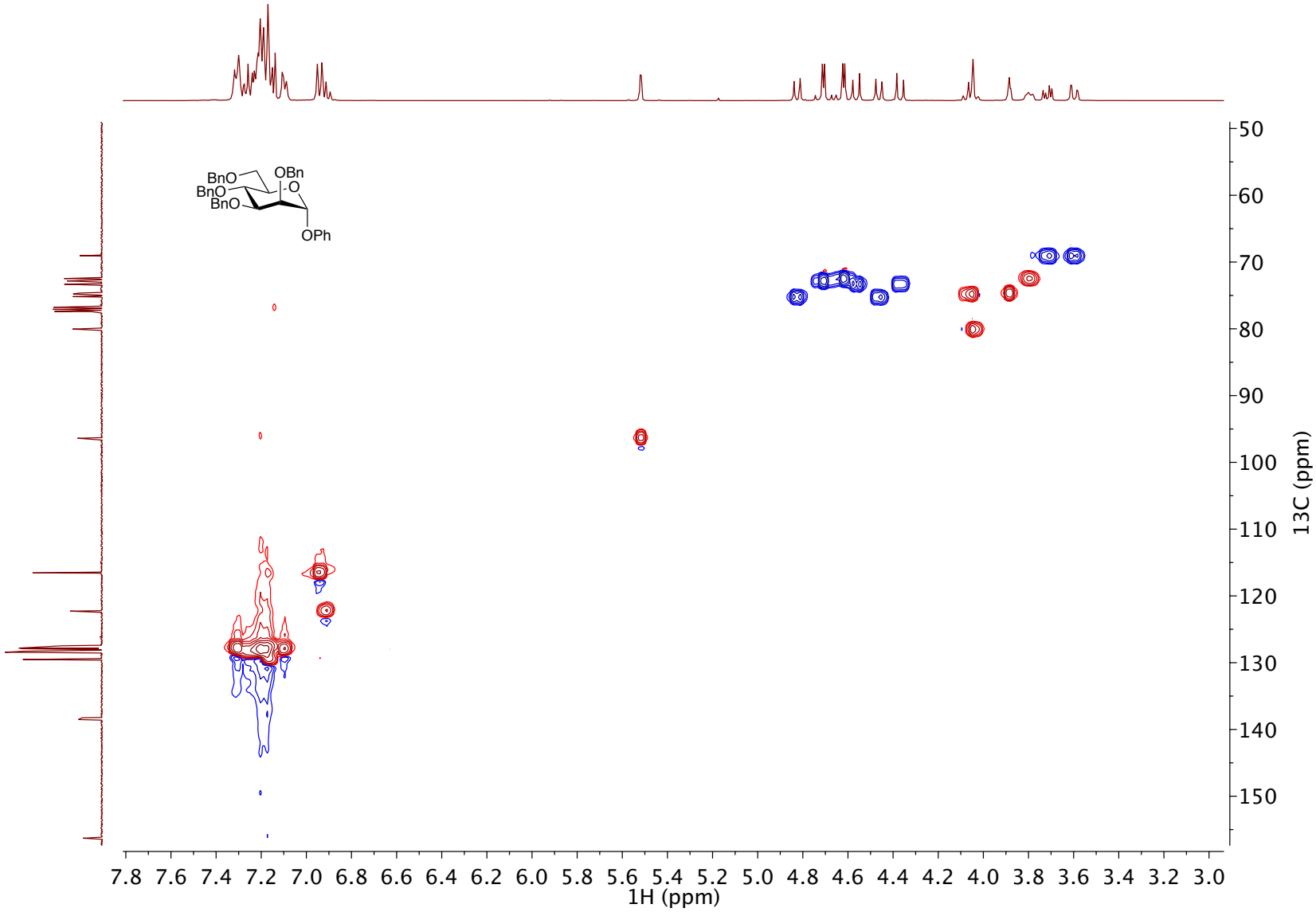
3bα – ^{13}C NMR (101 MHz, $CDCl_3$)



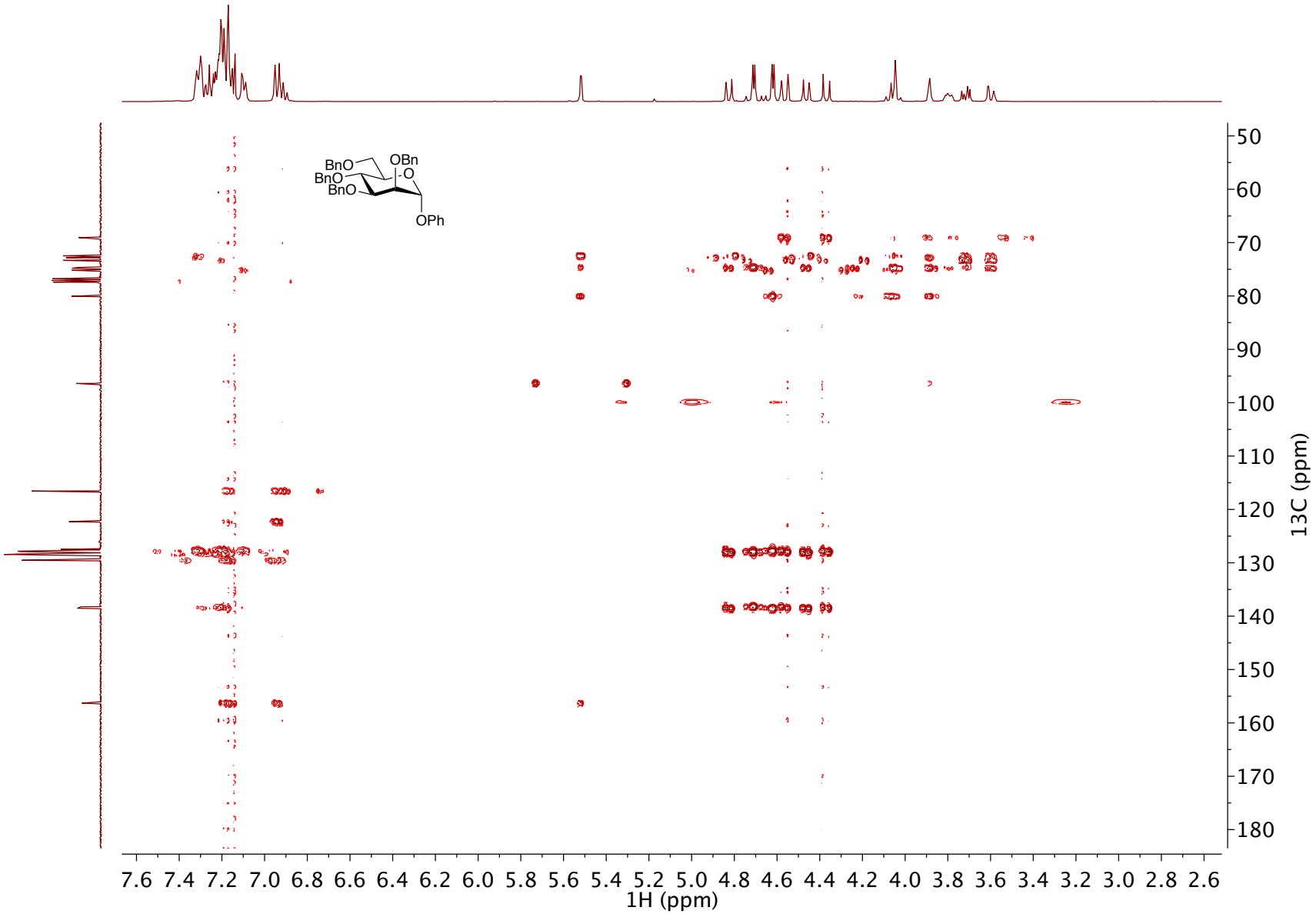
3bα – COSY (400 MHz, $CDCl_3$)



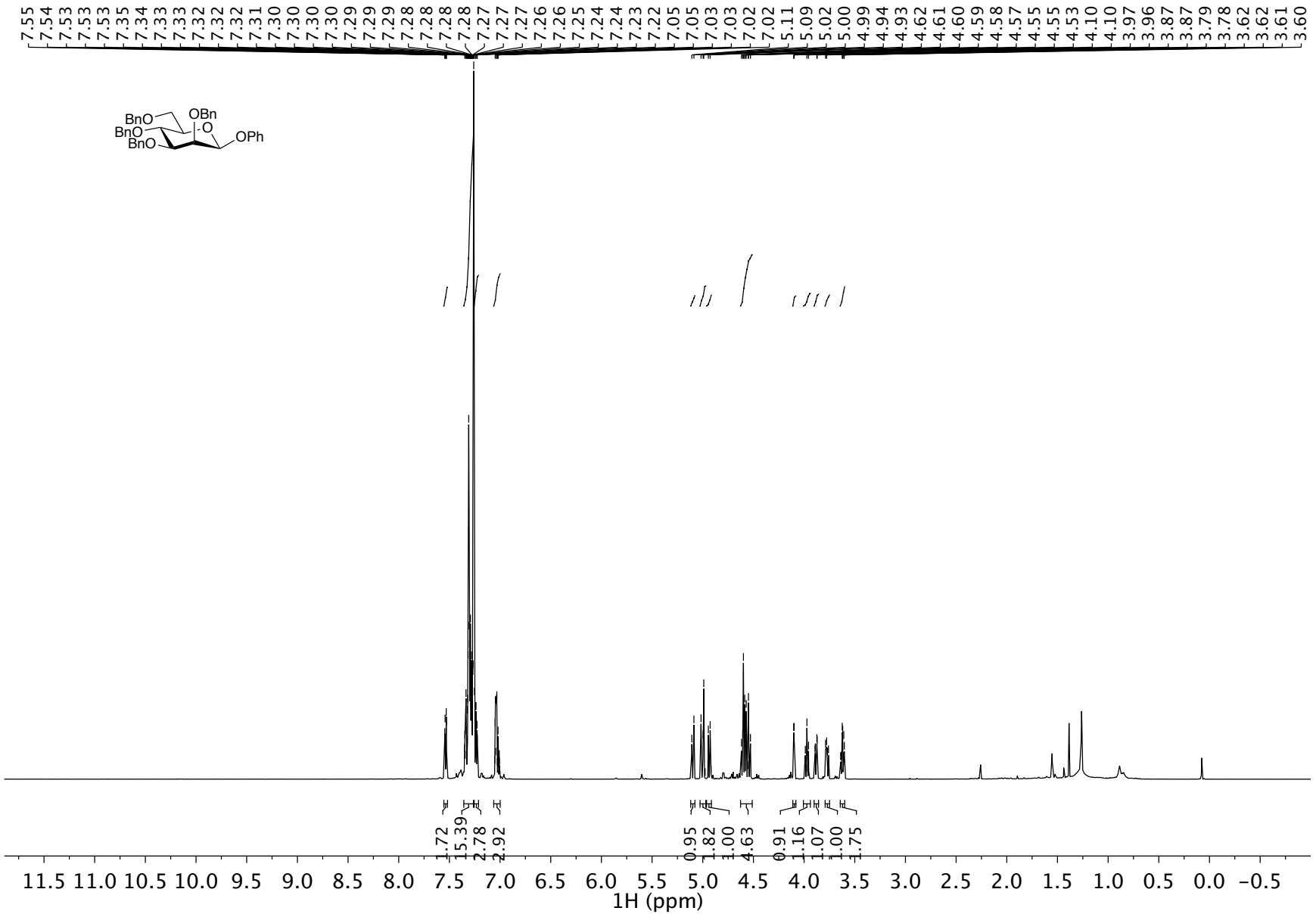
3bα – HSQC (400 MHz, $CDCl_3$)



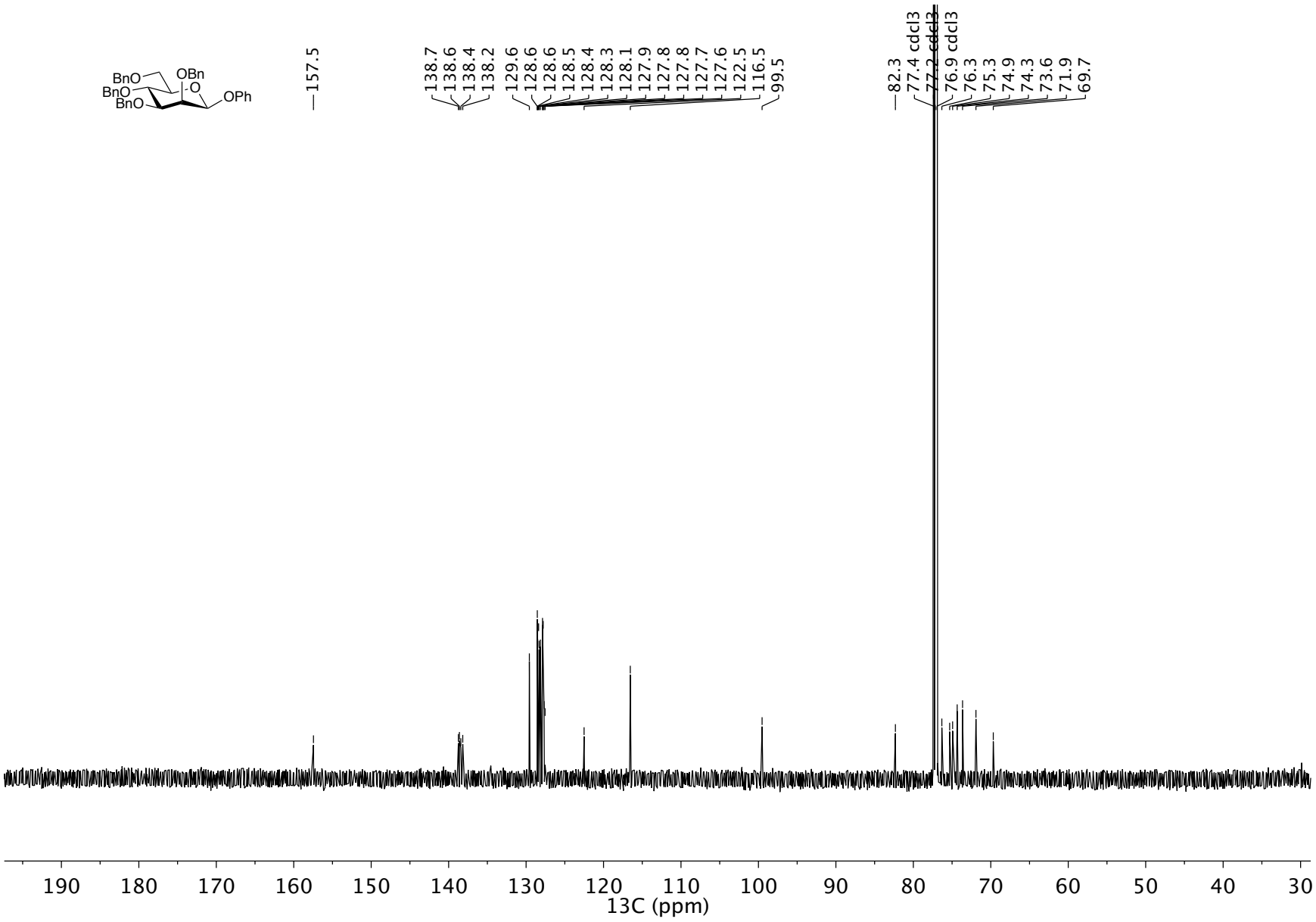
3bα – HSQC (400 MHz, $CDCl_3$)



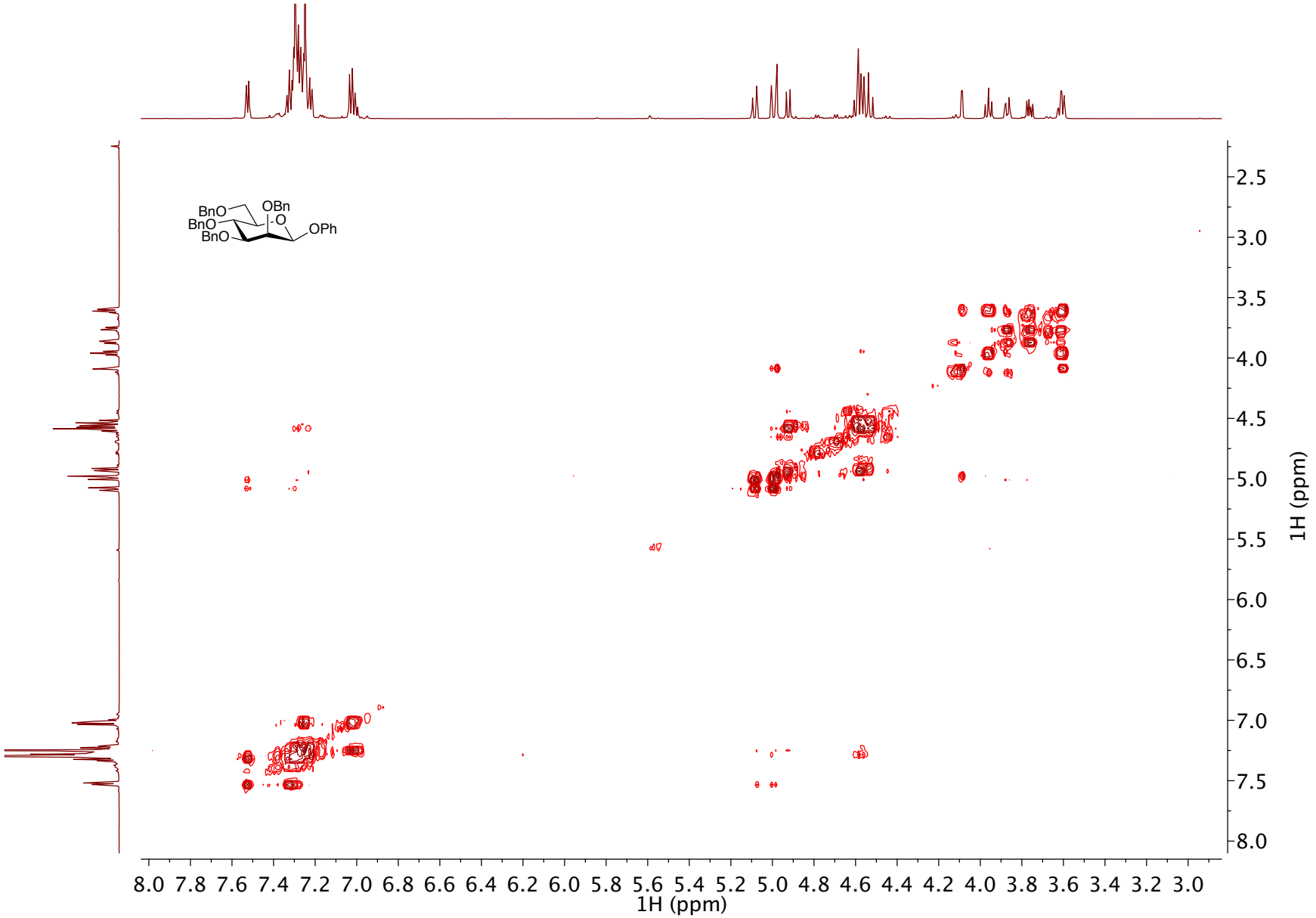
3bβ – ^{1}H NMR (600 MHz, $CDCl_3$)



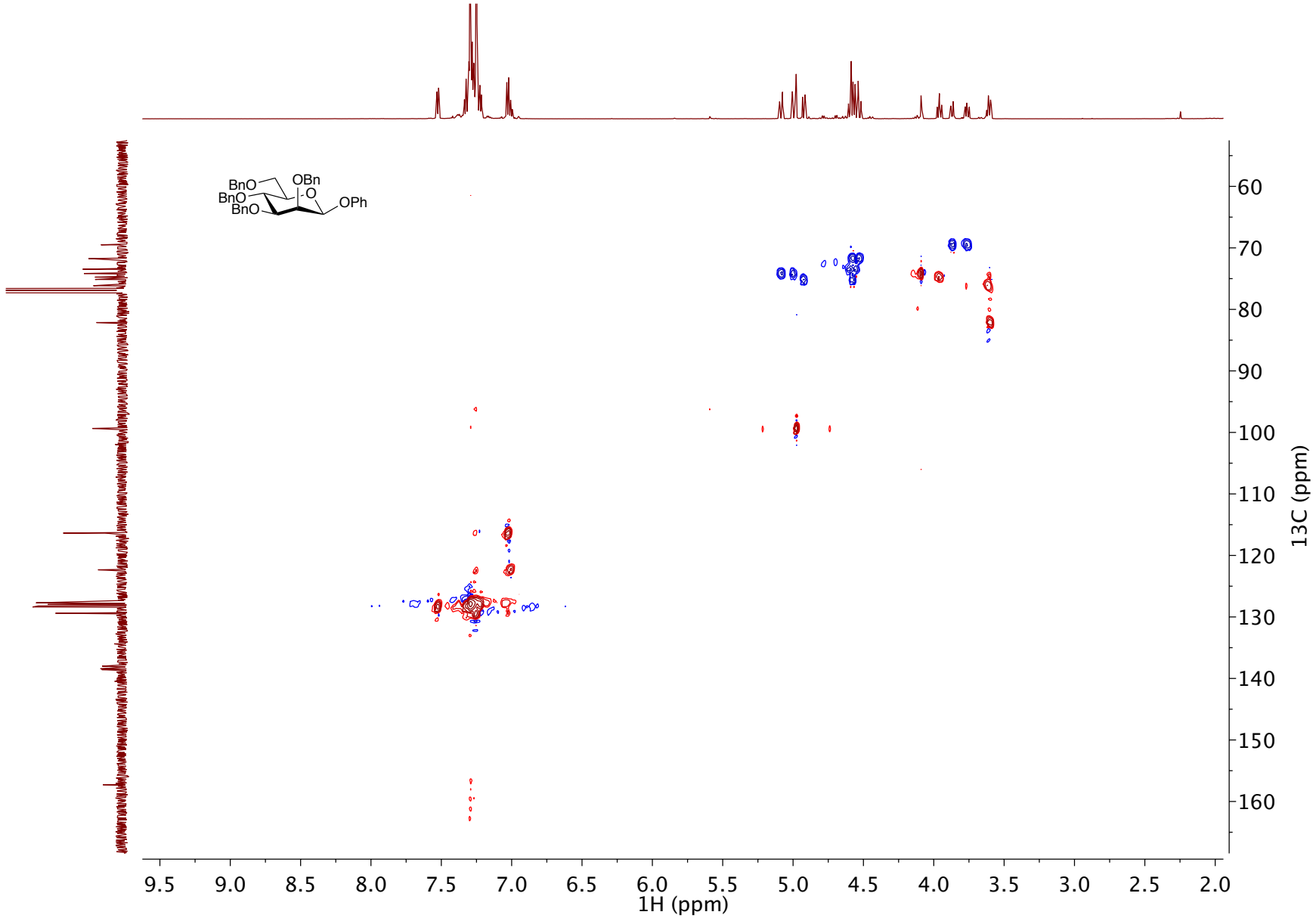
3bβ – ^{13}C NMR (151 MHz, $CDCl_3$)



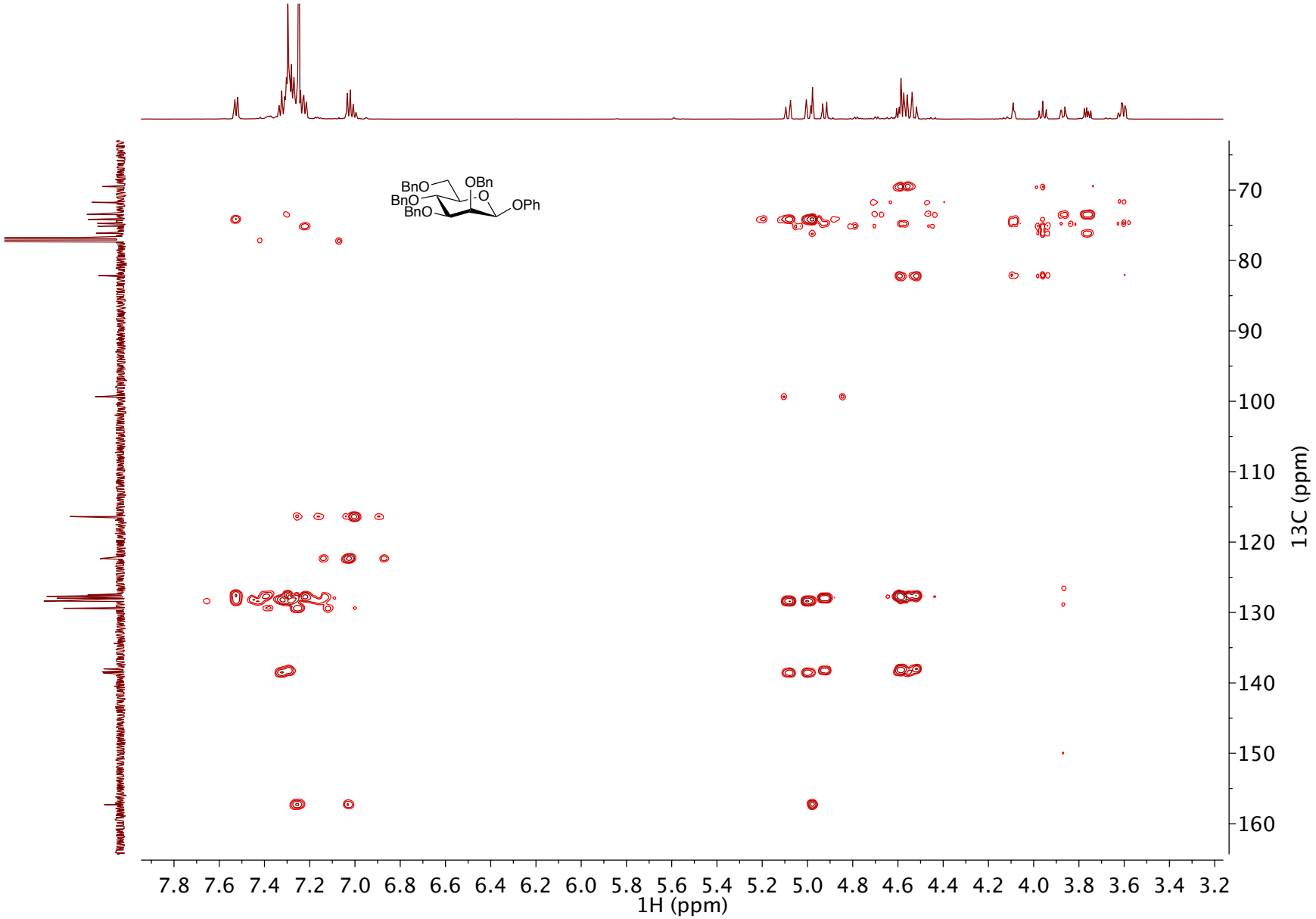
3bβ – COSY (600 MHz, $CDCl_3$)



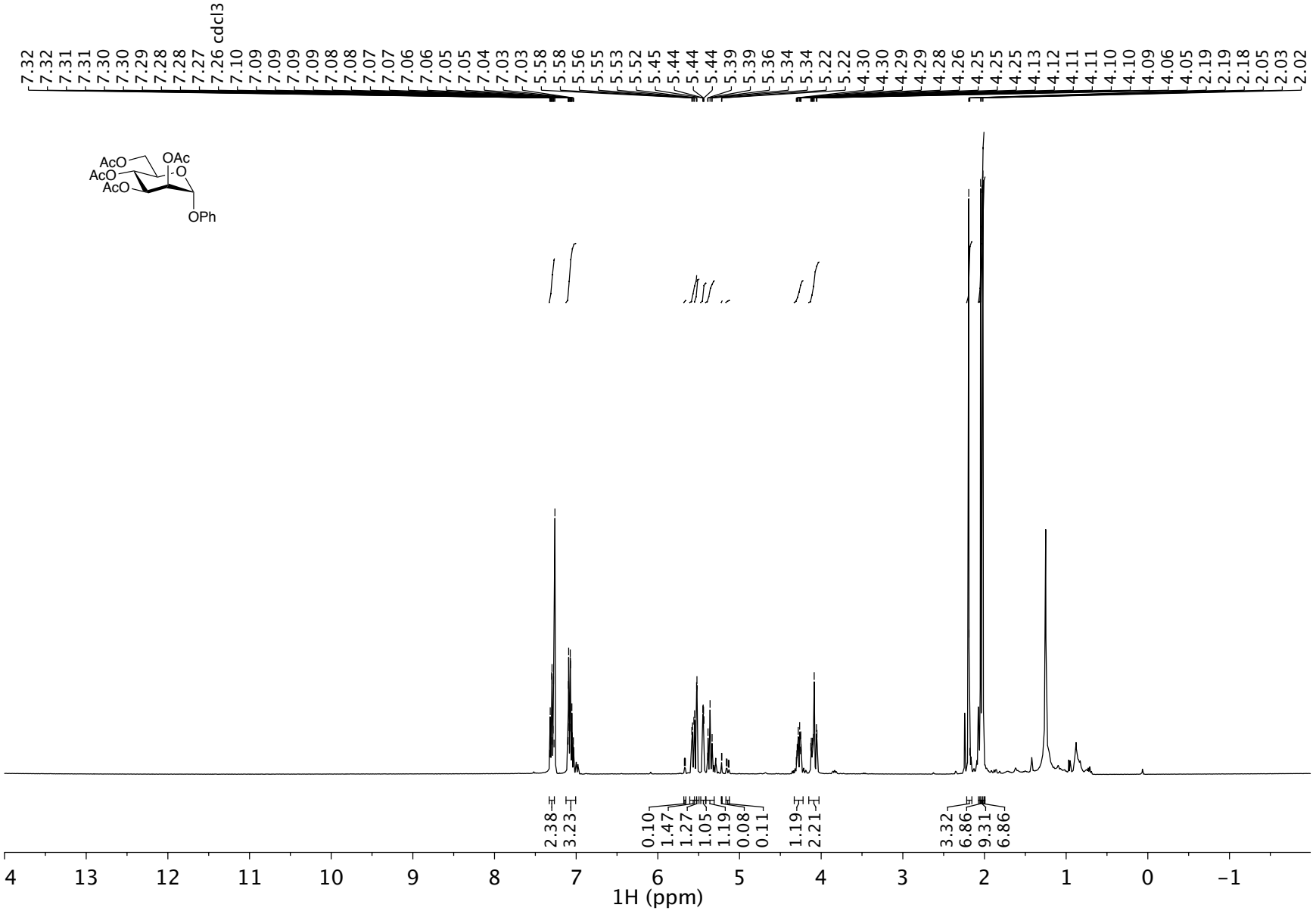
3bβ – HSQC (600 MHz, $CDCl_3$)



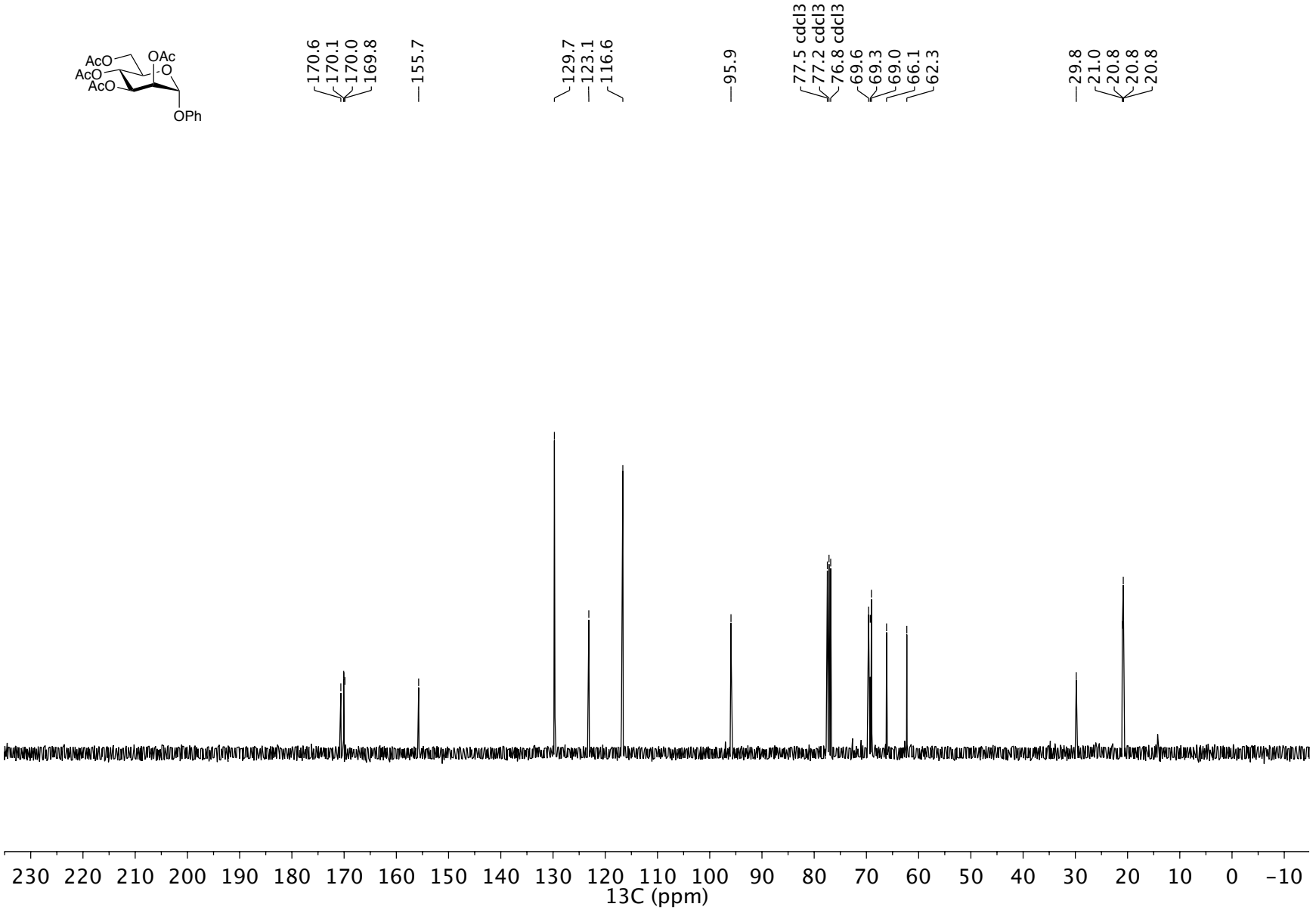
3bβ – HMBC (600 MHz, $CDCl_3$)



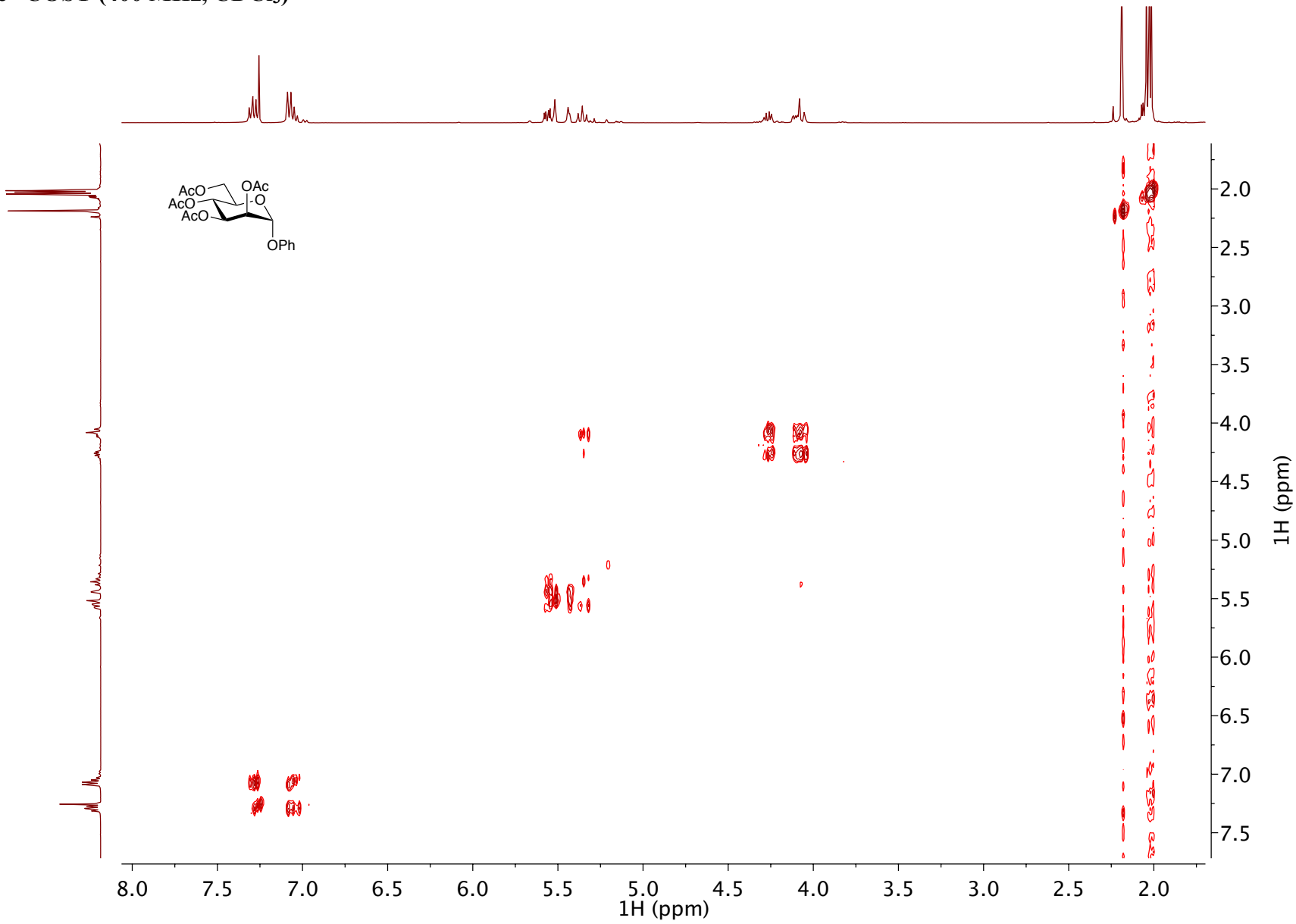
3c – ^{1}H NMR (400 MHz, $CDCl_3$)



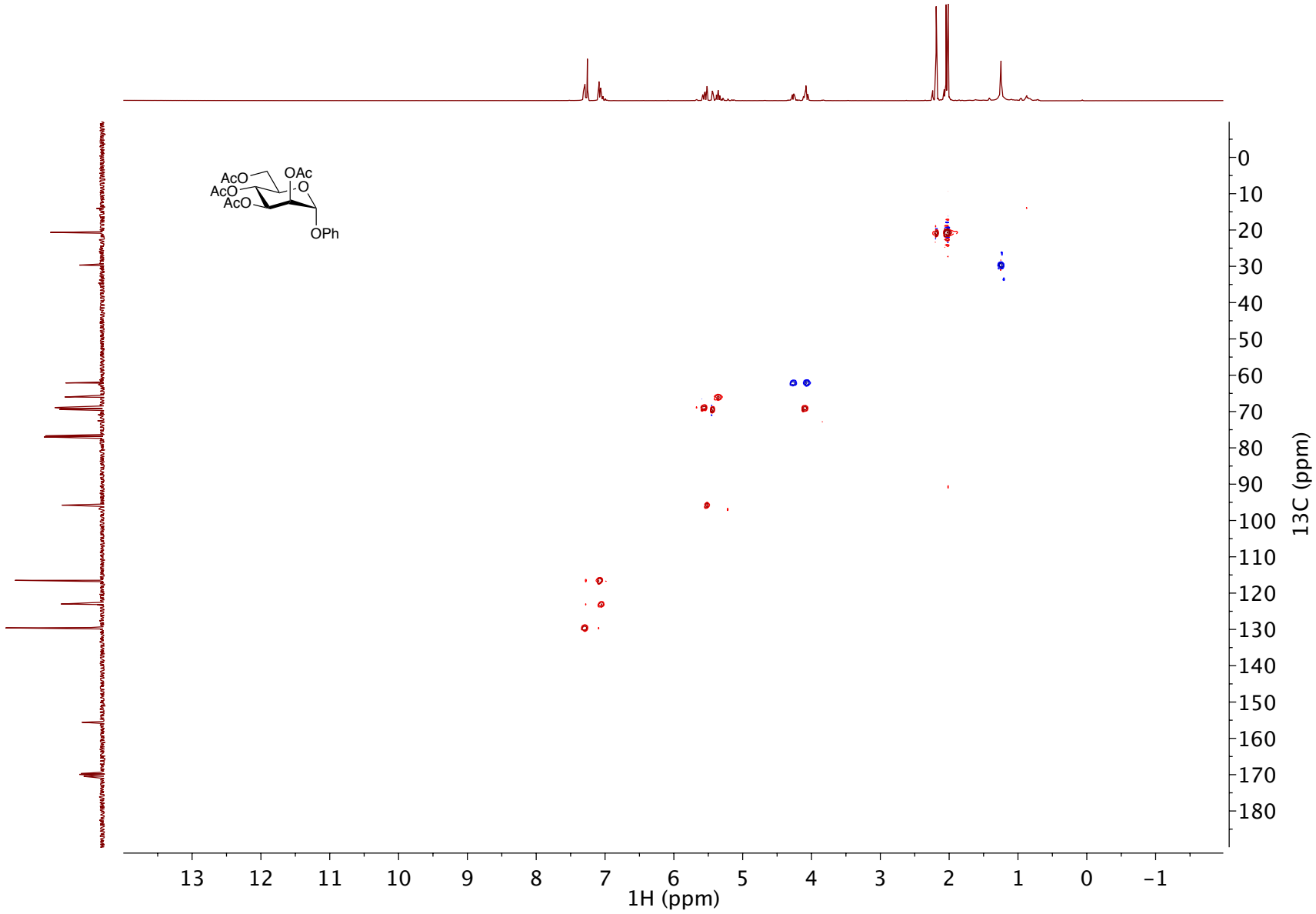
3c – ^{13}C NMR (100 MHz, $CDCl_3$)



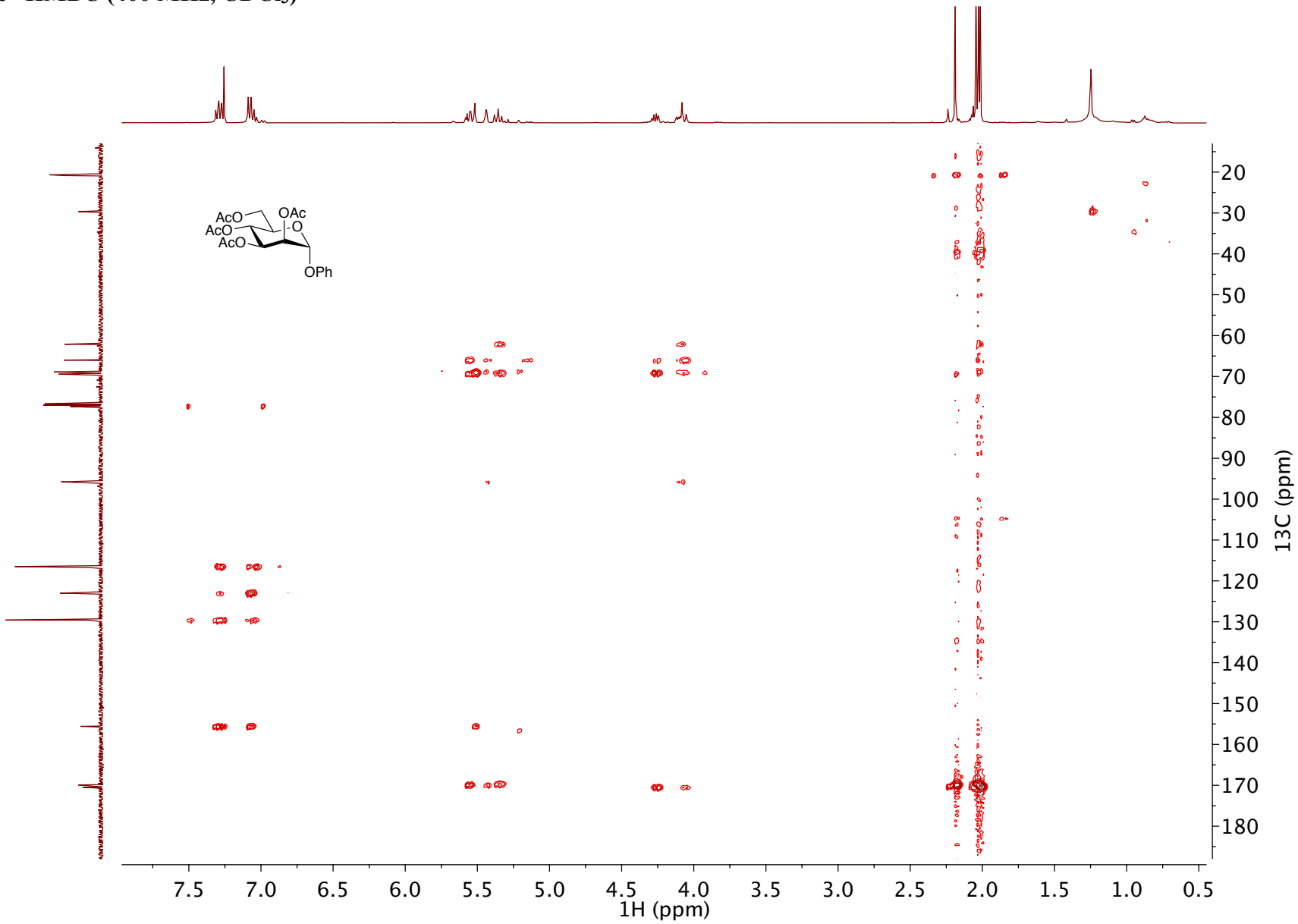
3c– COSY (400 MHz, $CDCl_3$)



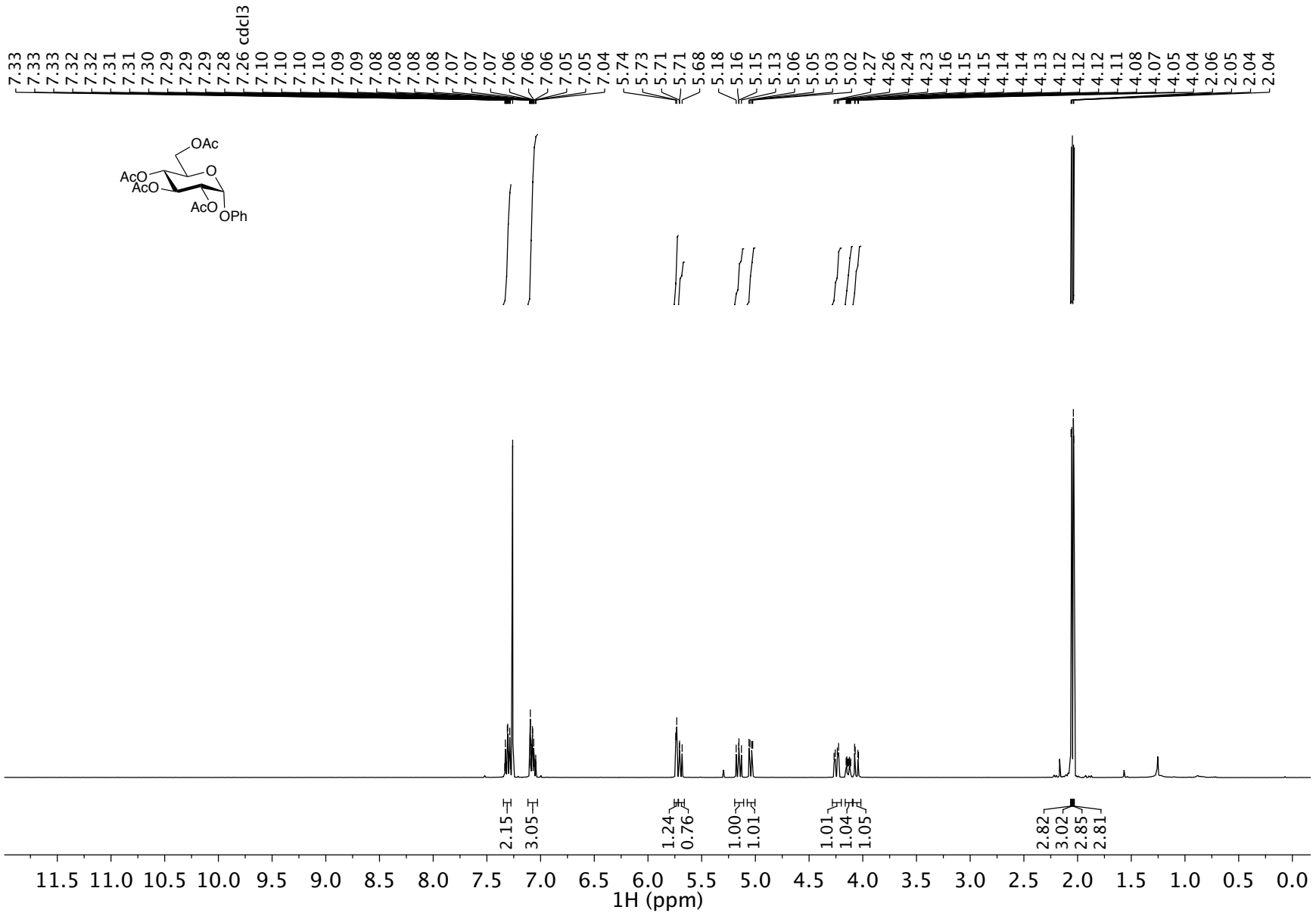
3c– HSQC (400 MHz, $CDCl_3$)



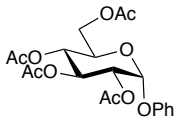
3c– HMBC (400 MHz, $CDCl_3$)



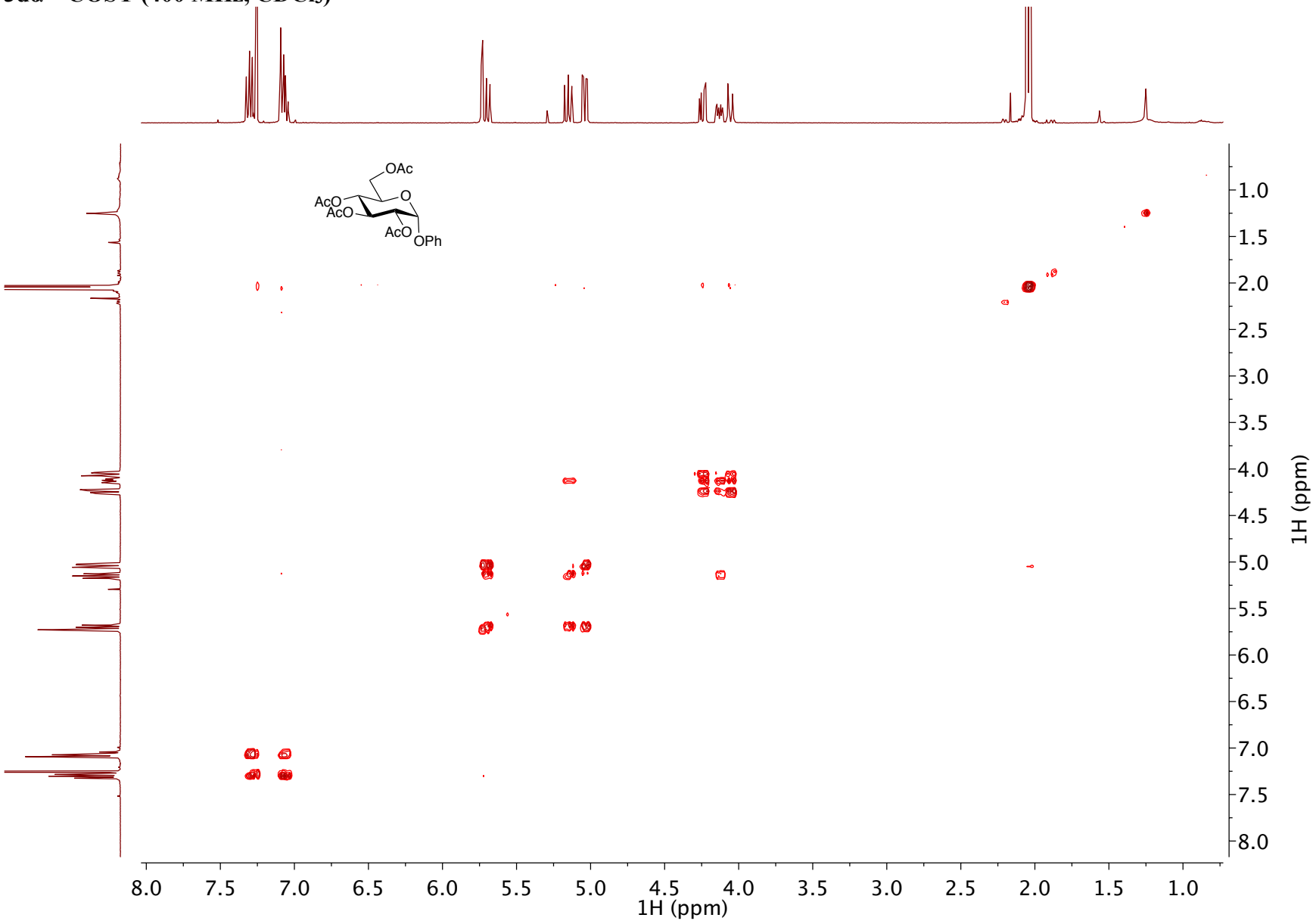
3dα – ^{1}H NMR (400 MHz, $CDCl_3$)



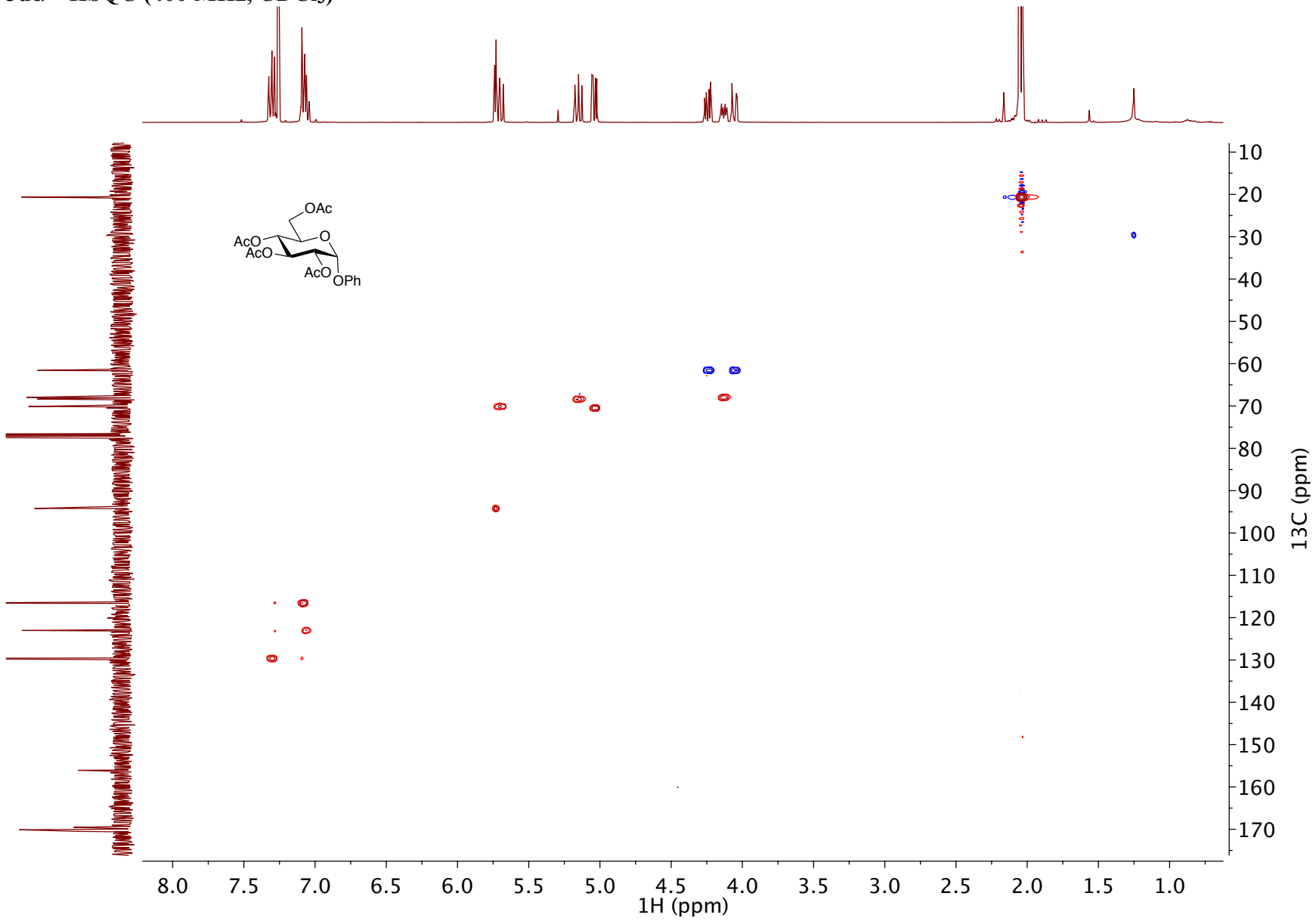
3dα – ^{13}C NMR (100 MHz, $CDCl_3$)



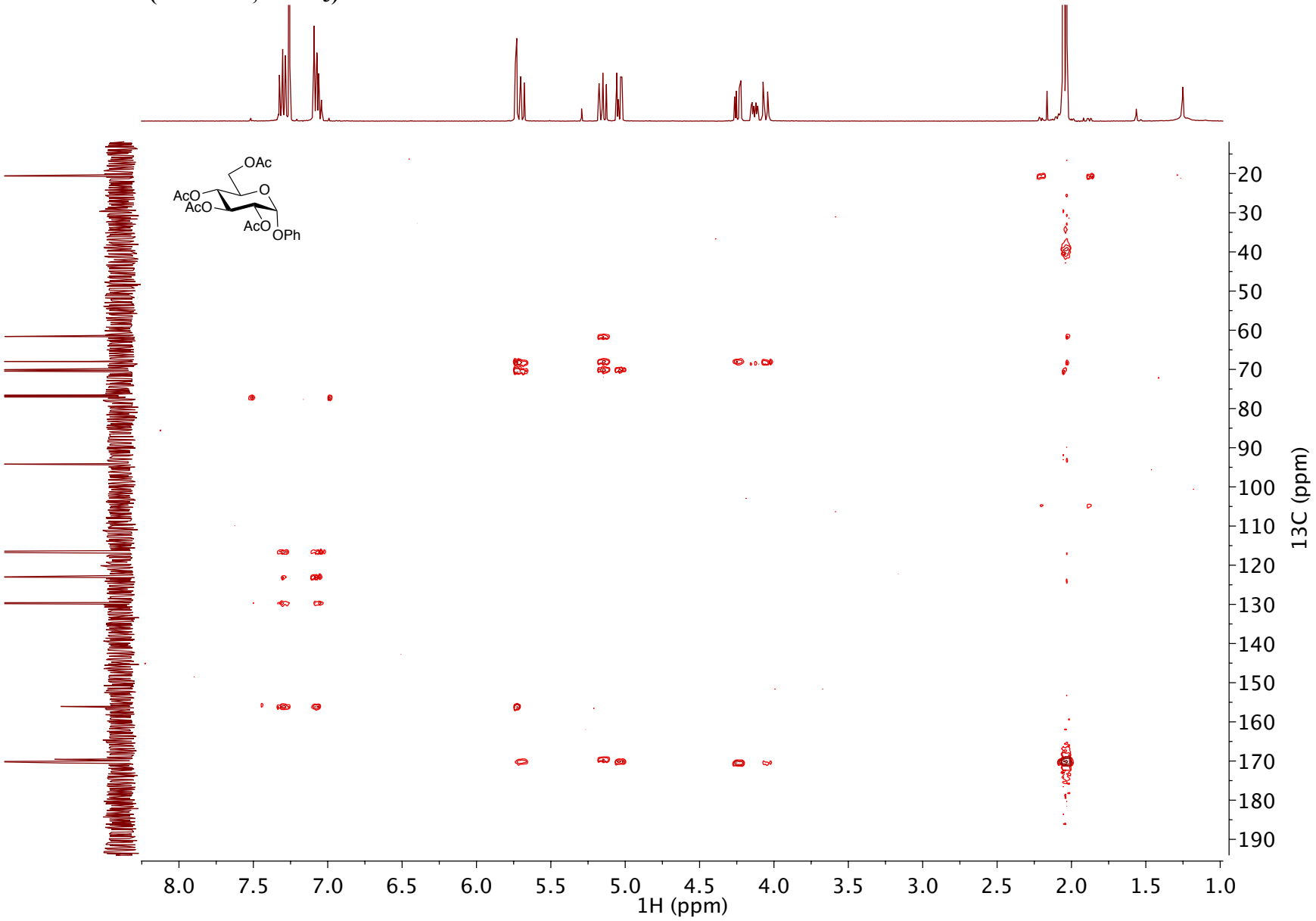
3dα – COSY (400 MHz, $CDCl_3$)



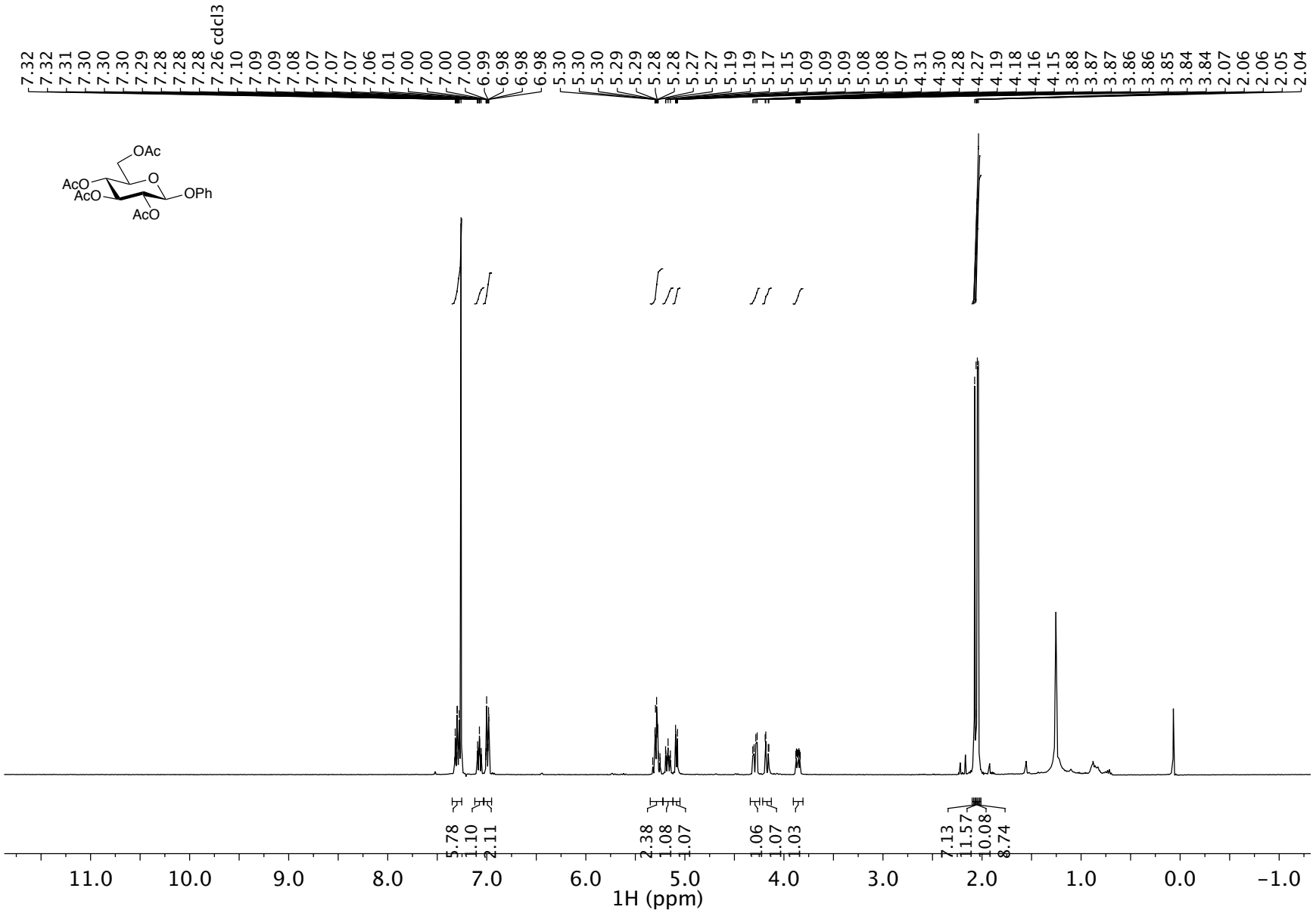
3dα – HSQC (400 MHz, $CDCl_3$)



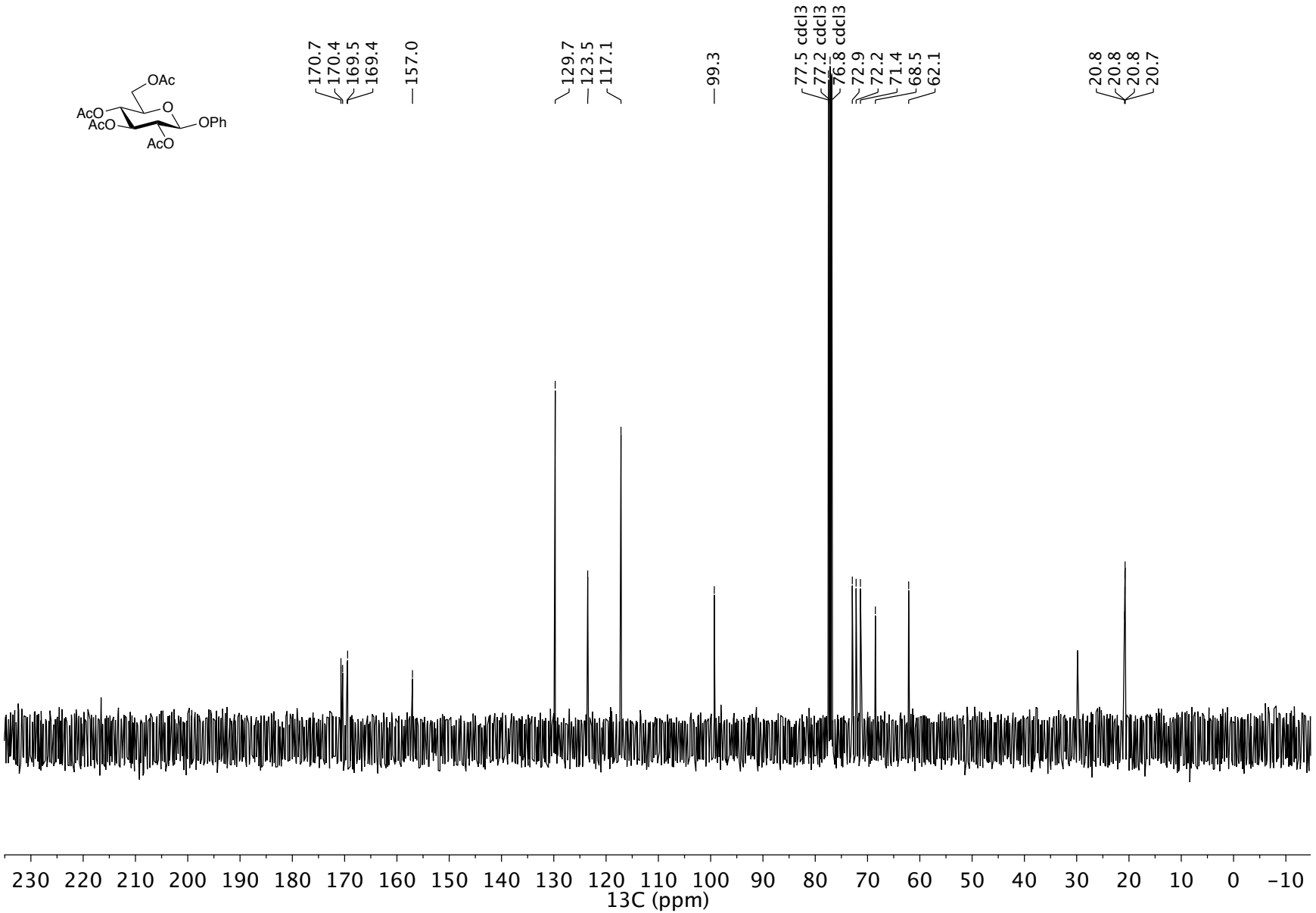
3dα – HMBC (400 MHz, $CDCl_3$)



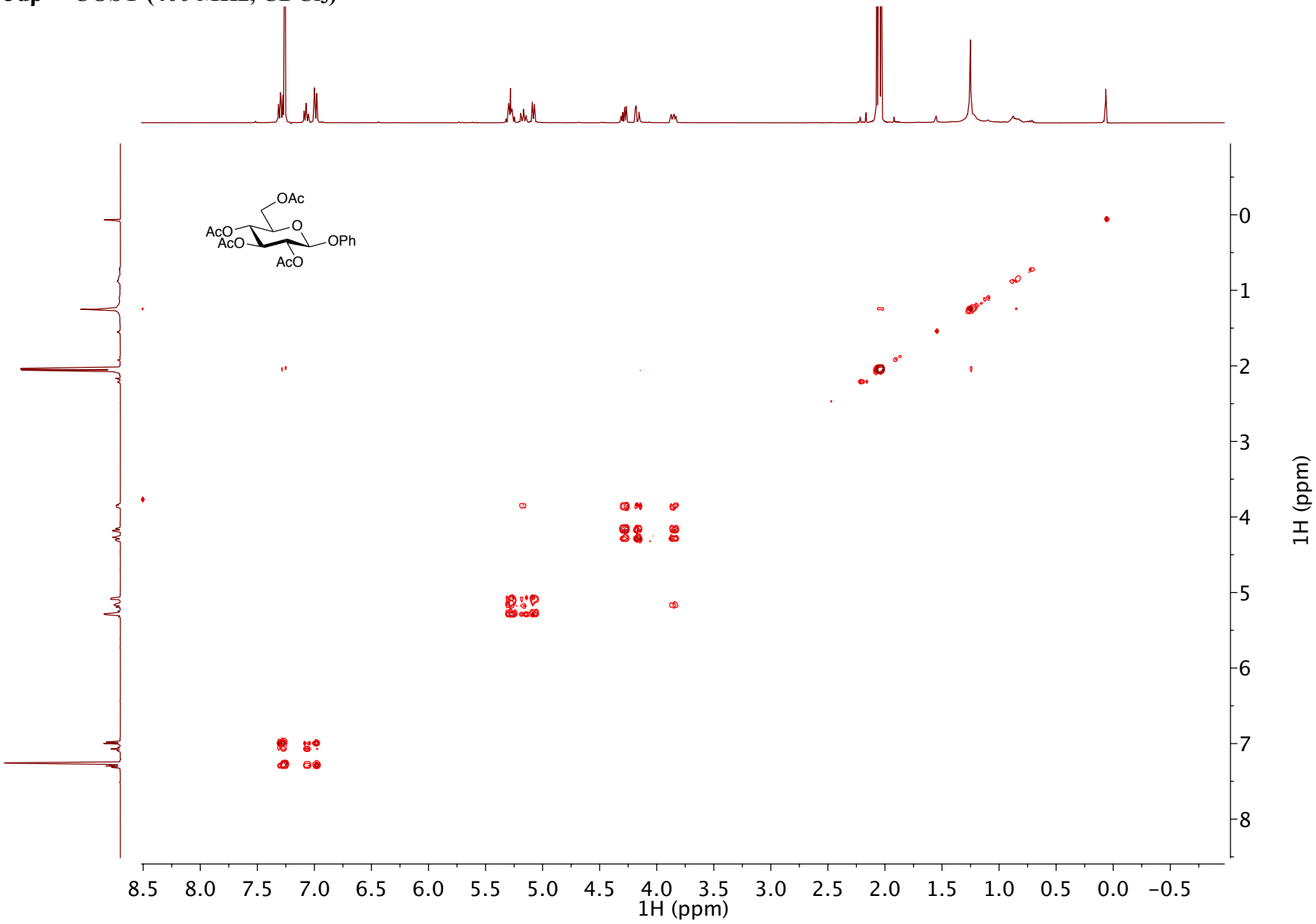
3dβ – ^{1}H NMR (400 MHz, $CDCl_3$)



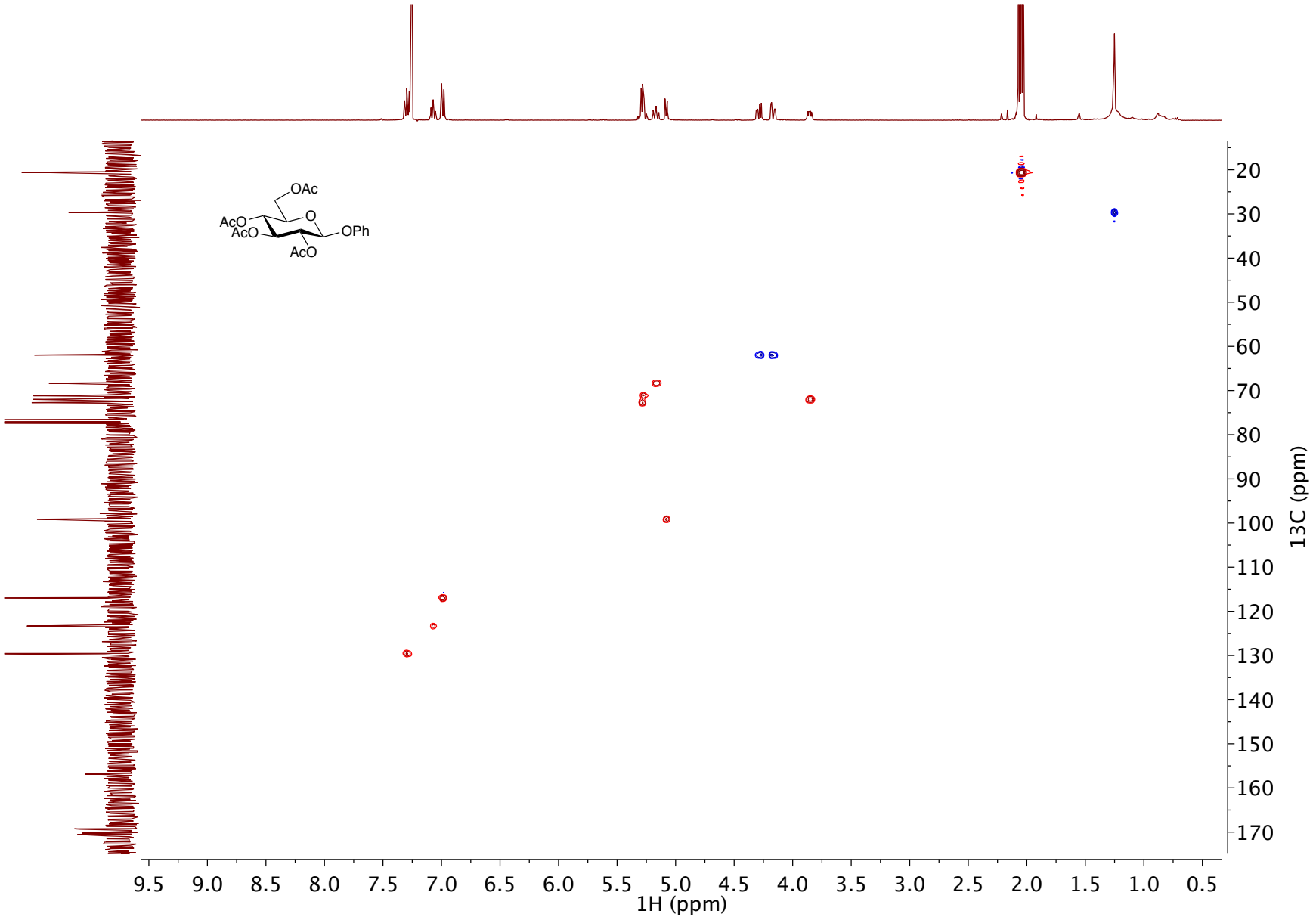
3dβ – ^{13}C NMR (100 MHz, $CDCl_3$)



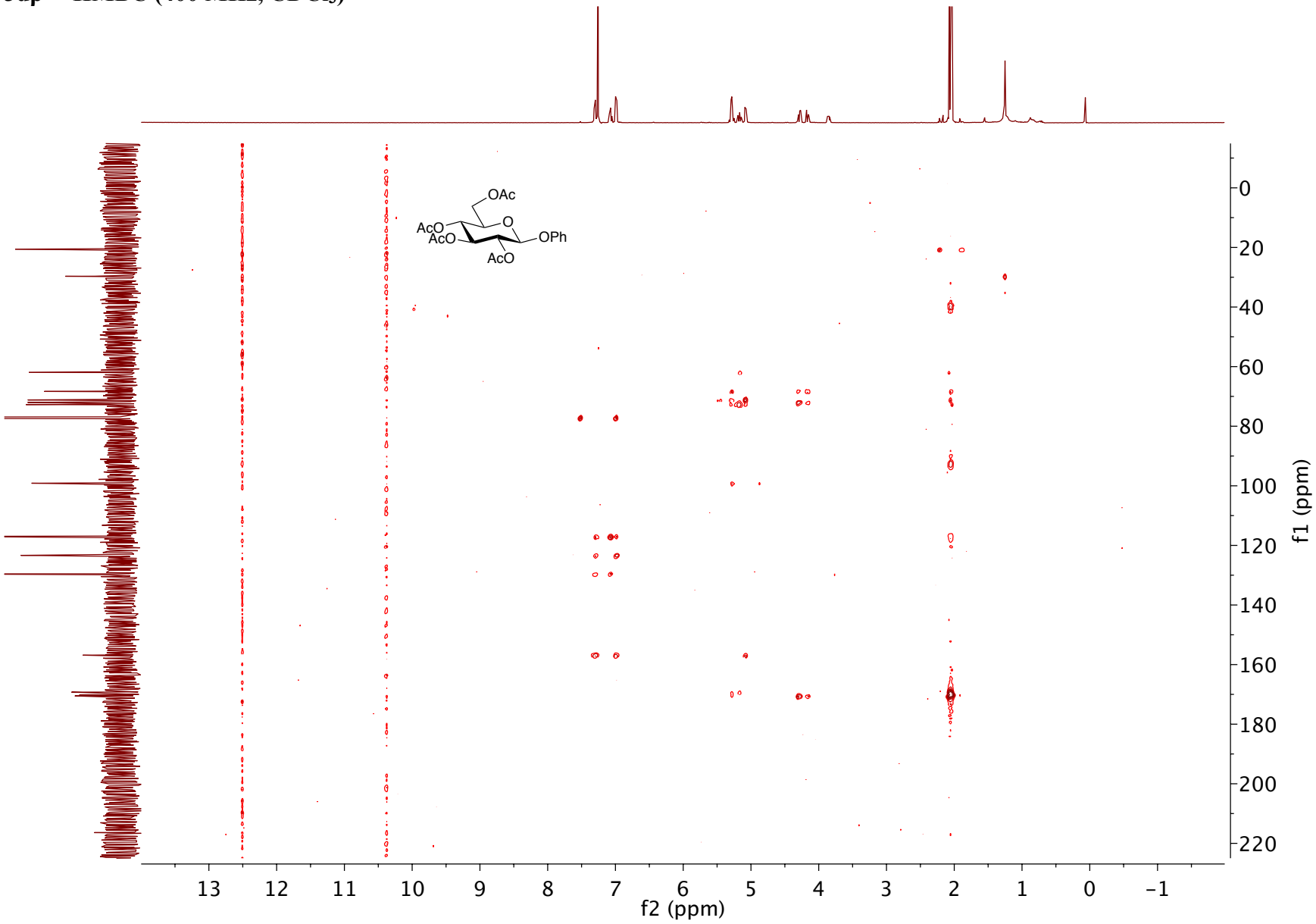
3dβ – COSY (400 MHz, $CDCl_3$)



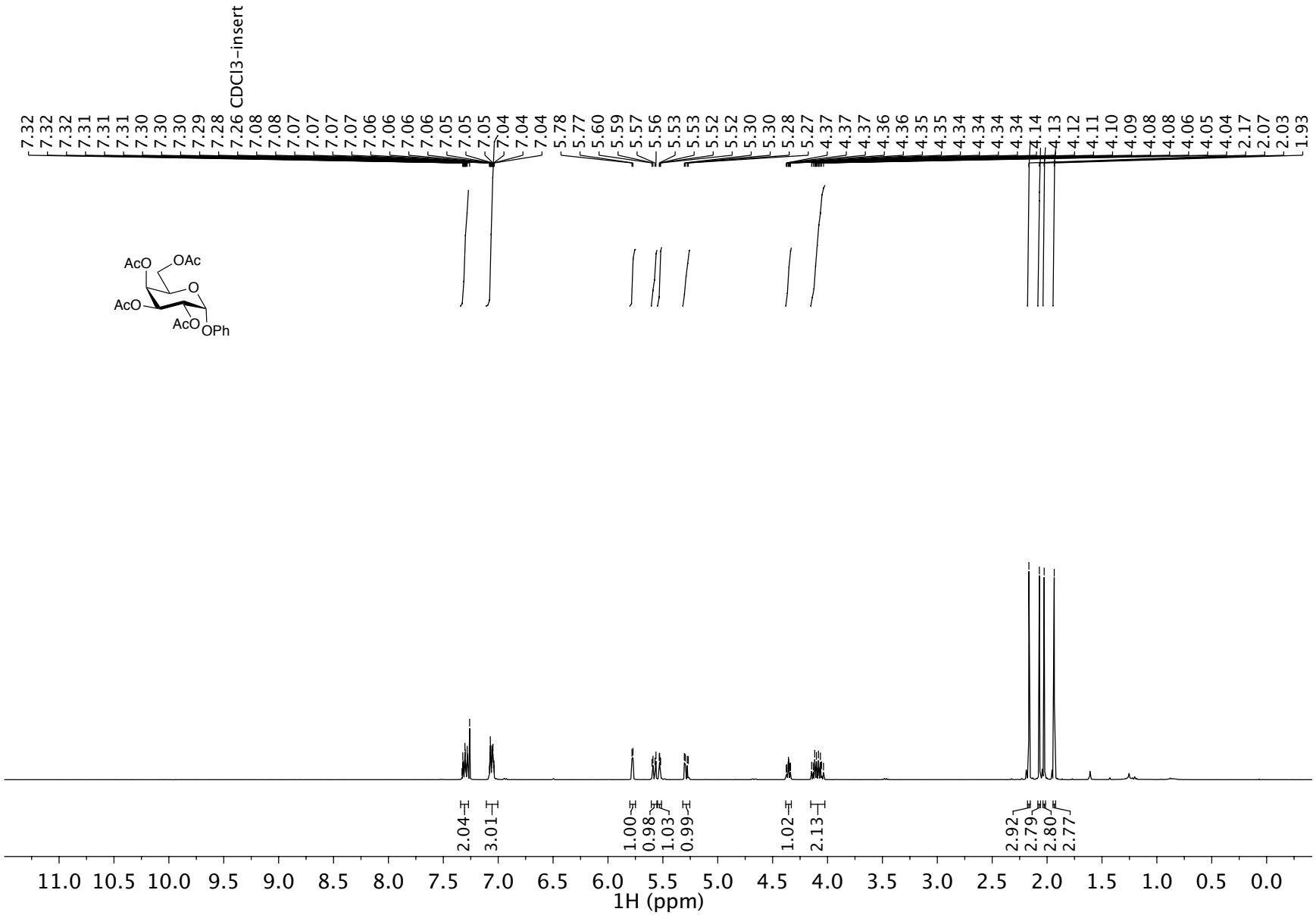
3dβ – HSQC (400 MHz, $CDCl_3$)



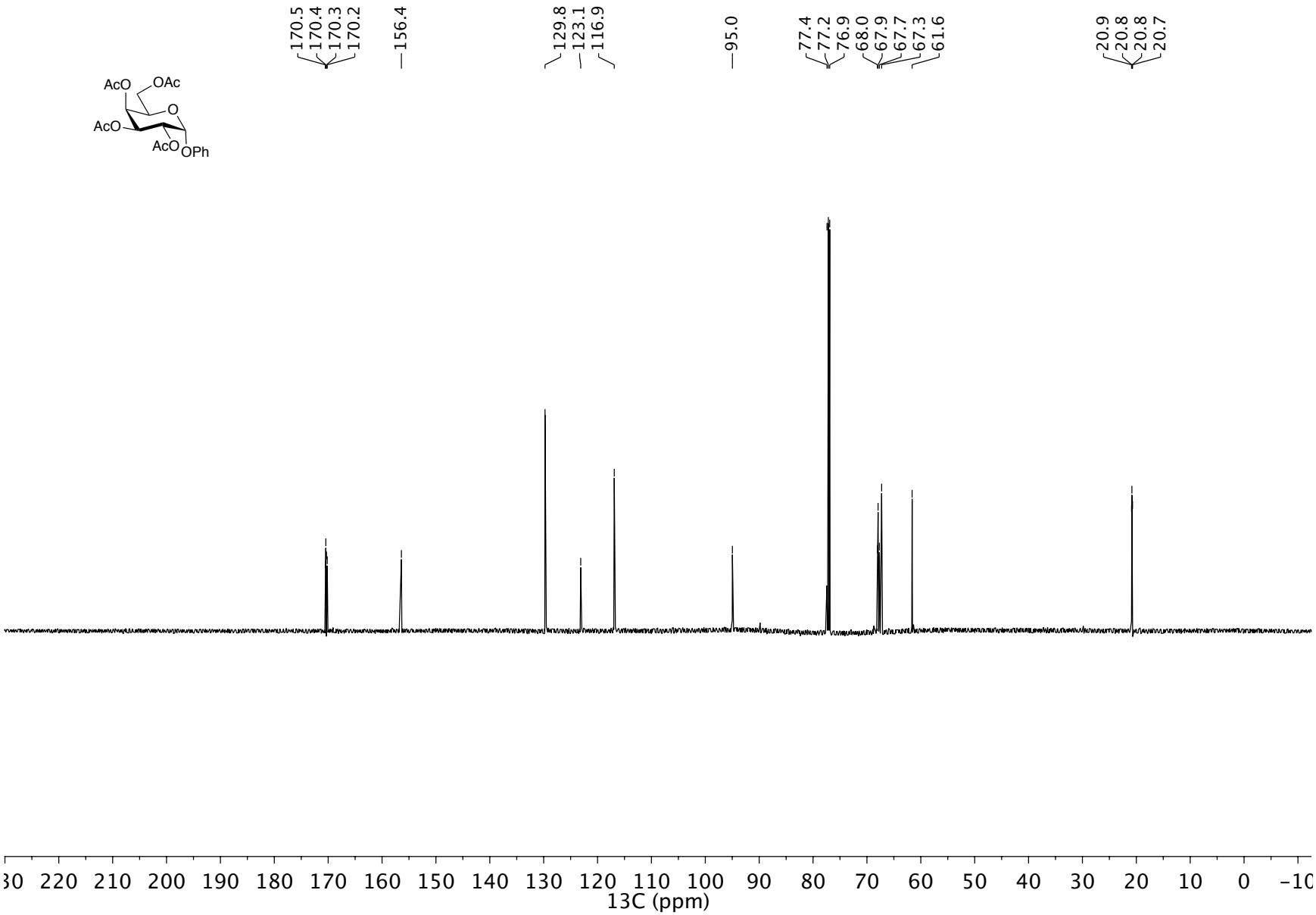
3dβ – HMBC (400 MHz, $CDCl_3$)



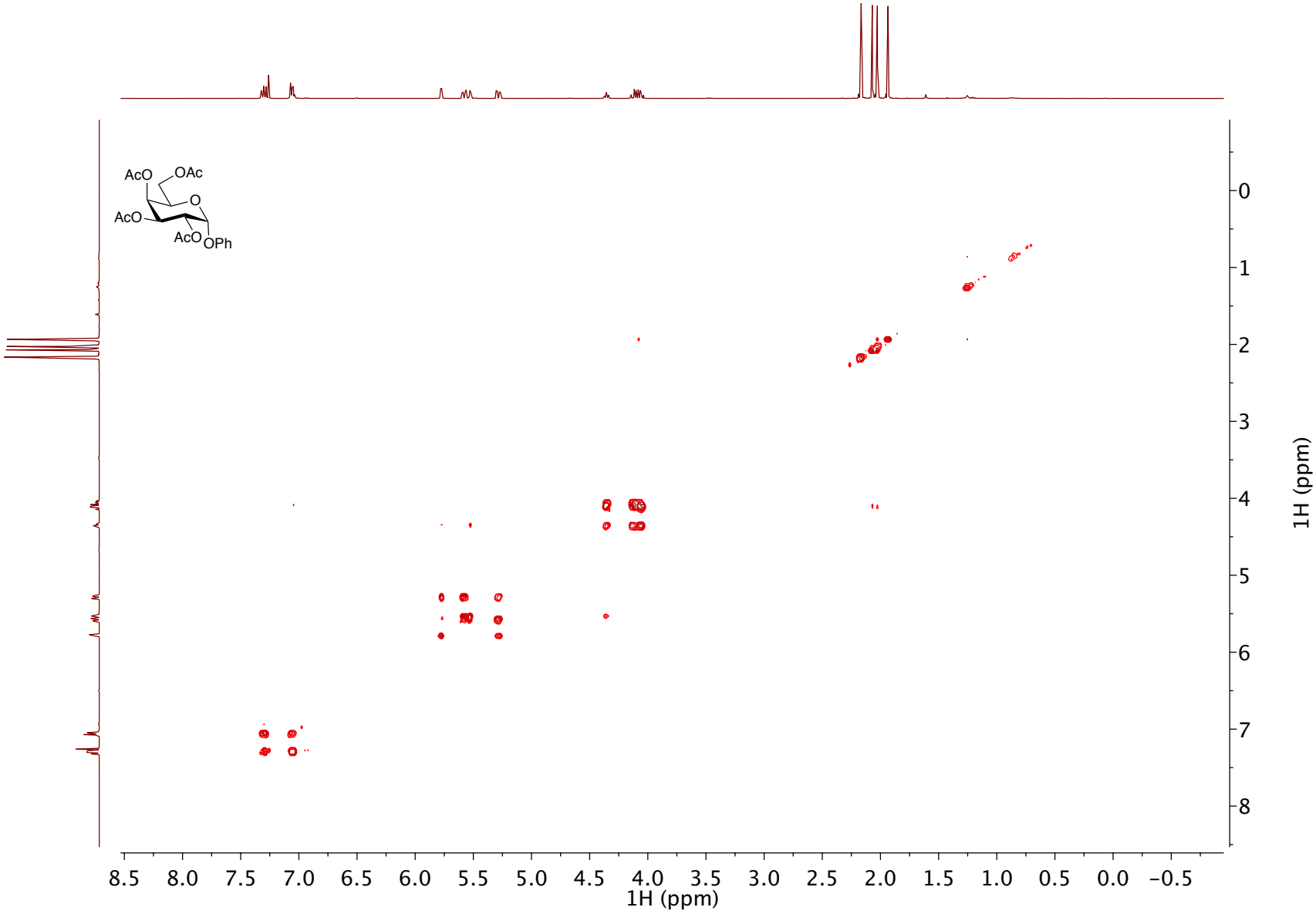
3eα – ^{1}H NMR (400 MHz, $CDCl_3$)



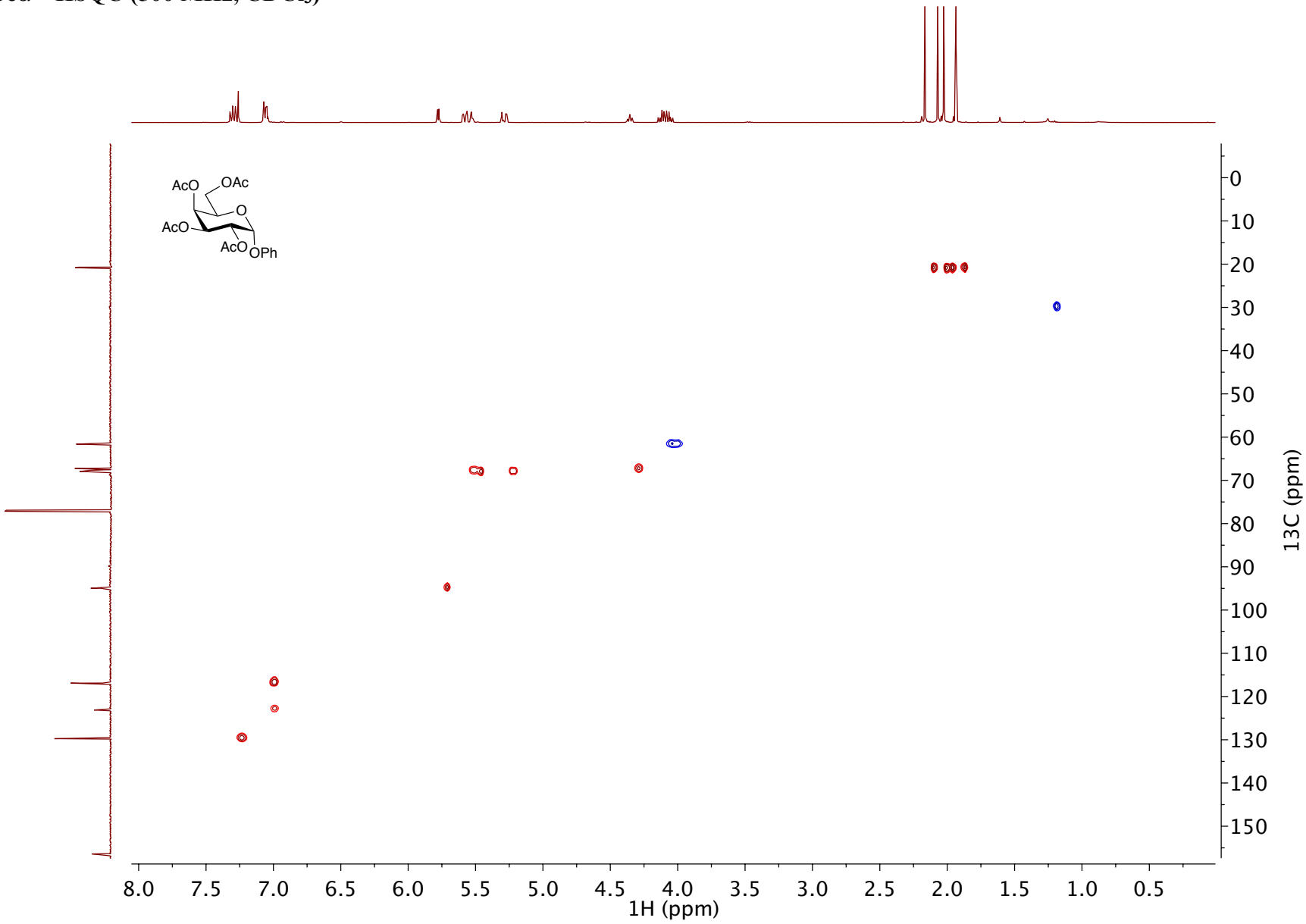
3eα – ^{13}C NMR (126 MHz, $CDCl_3$)



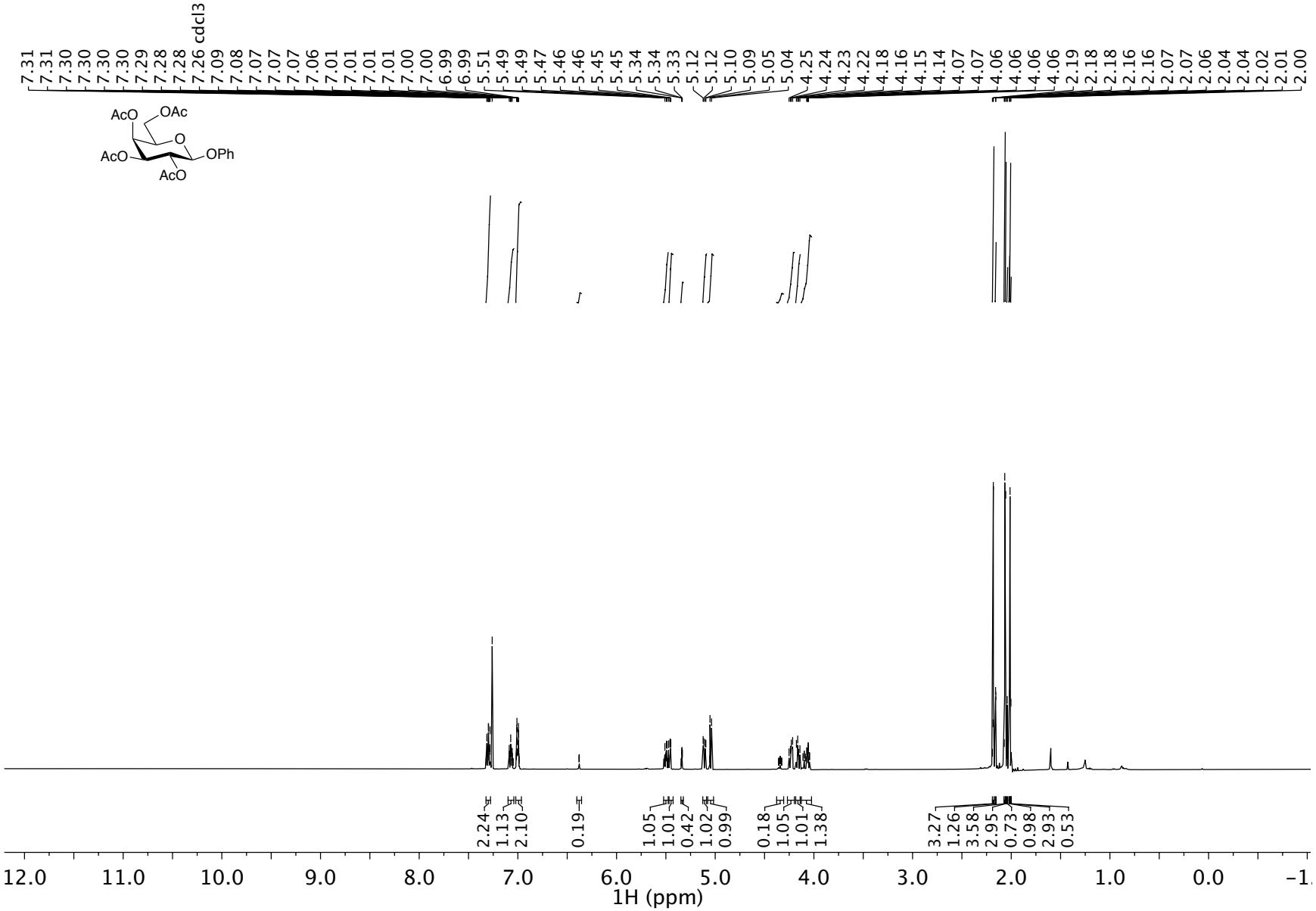
3eα – COSY (400 MHz, $CDCl_3$)



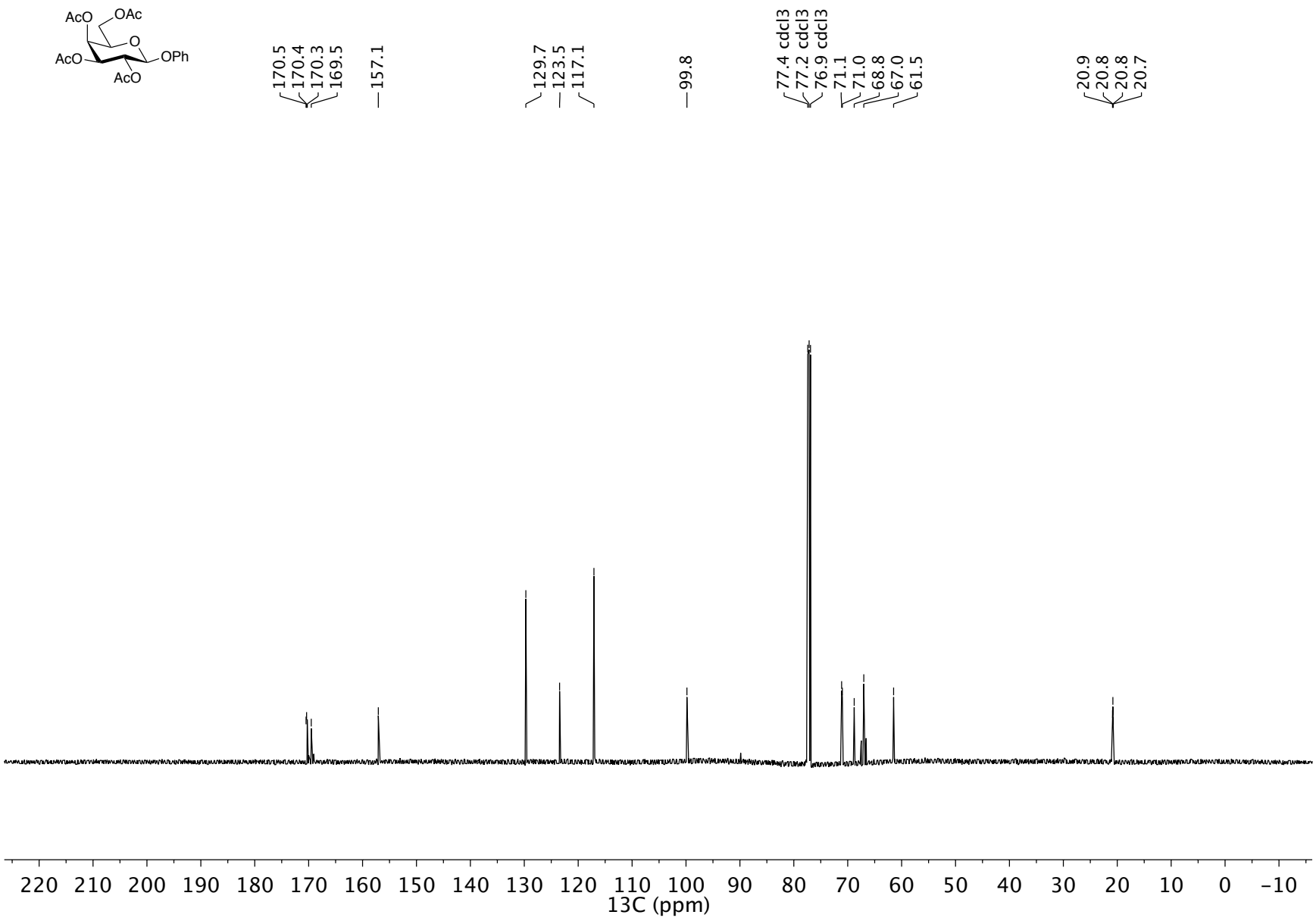
3eα – HSQC (500 MHz, $CDCl_3$)



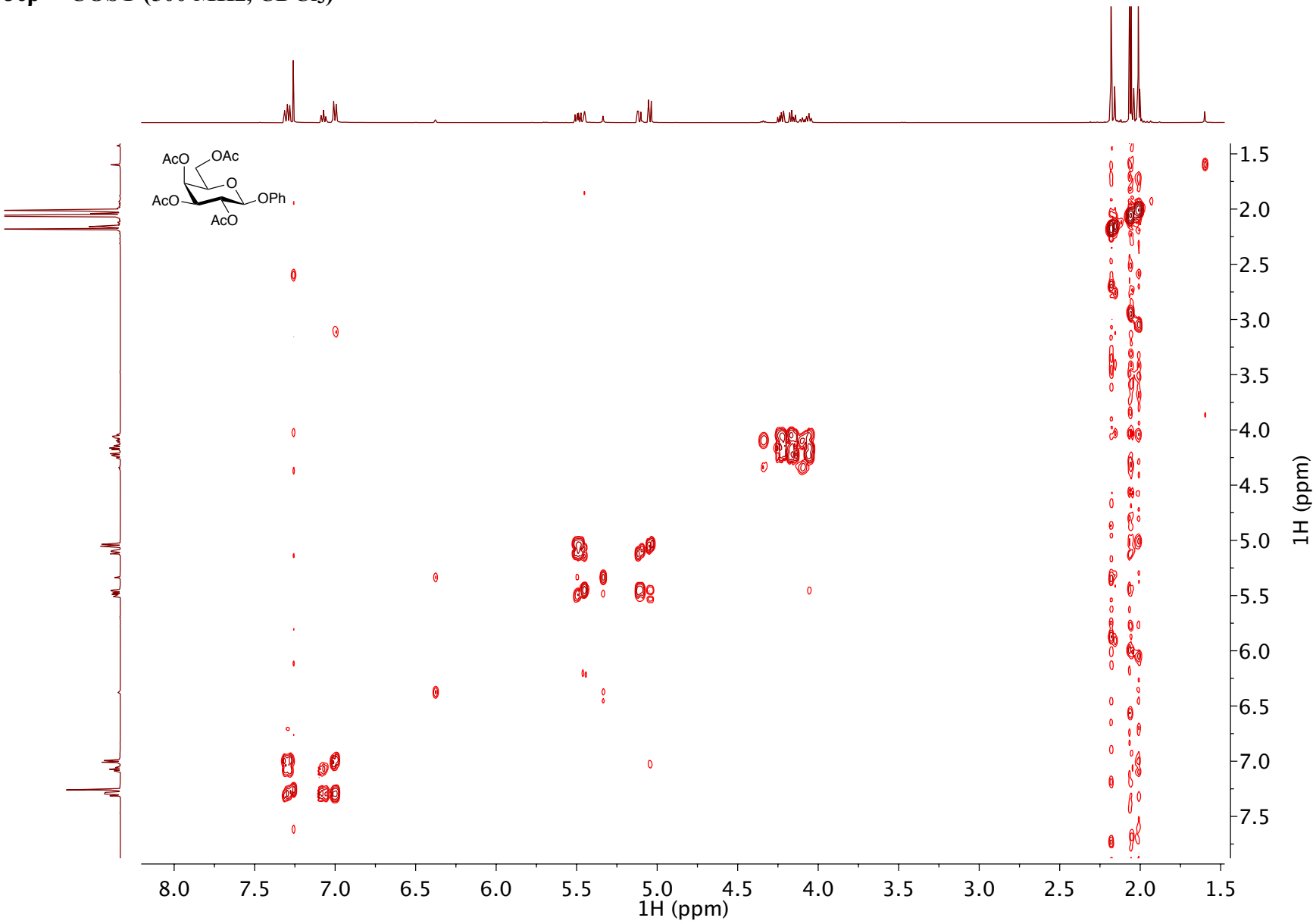
3eβ – ^{1}H NMR (500 MHz, $CDCl_3$)



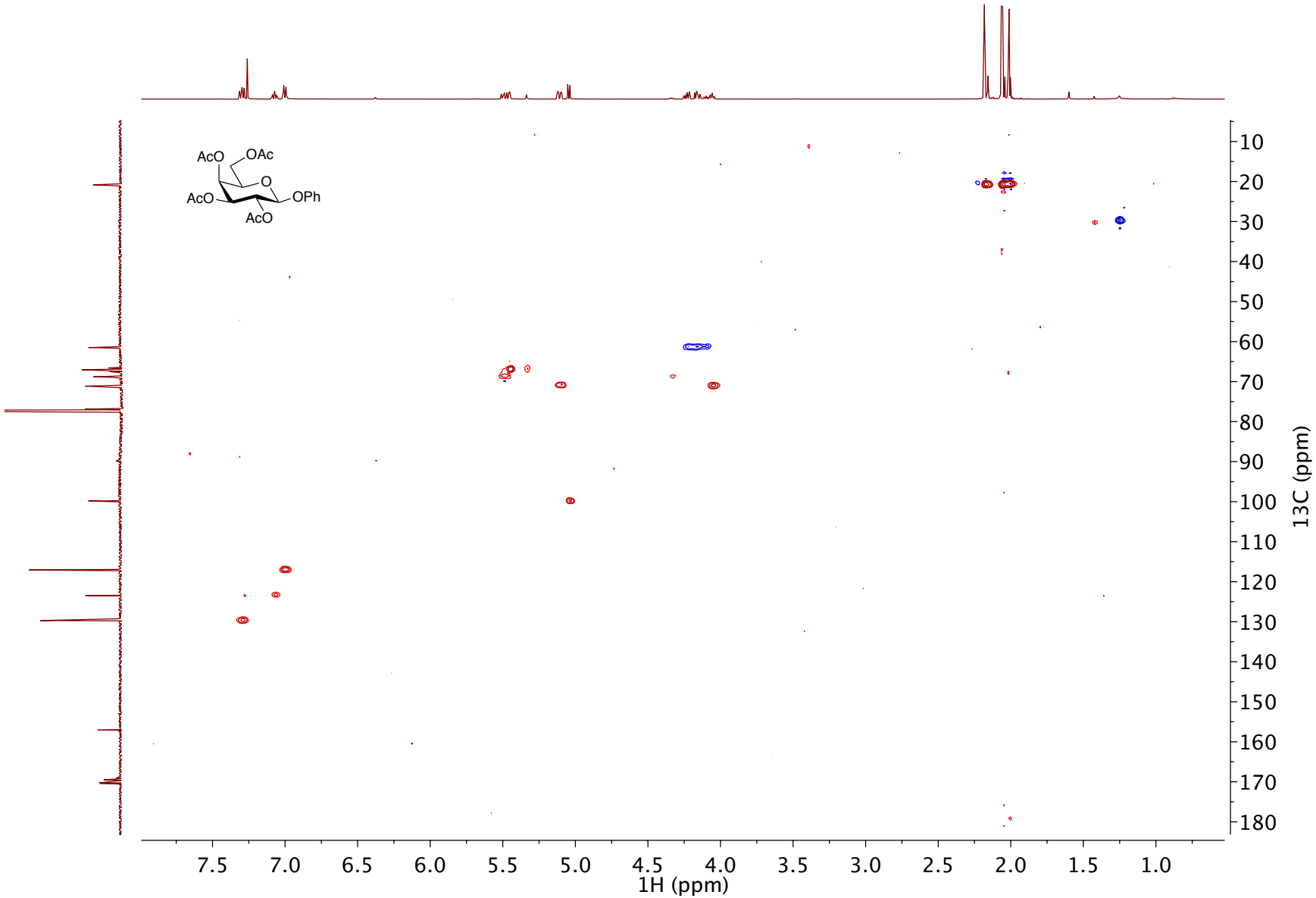
3eβ – ^{13}C NMR (126 MHz, $CDCl_3$)



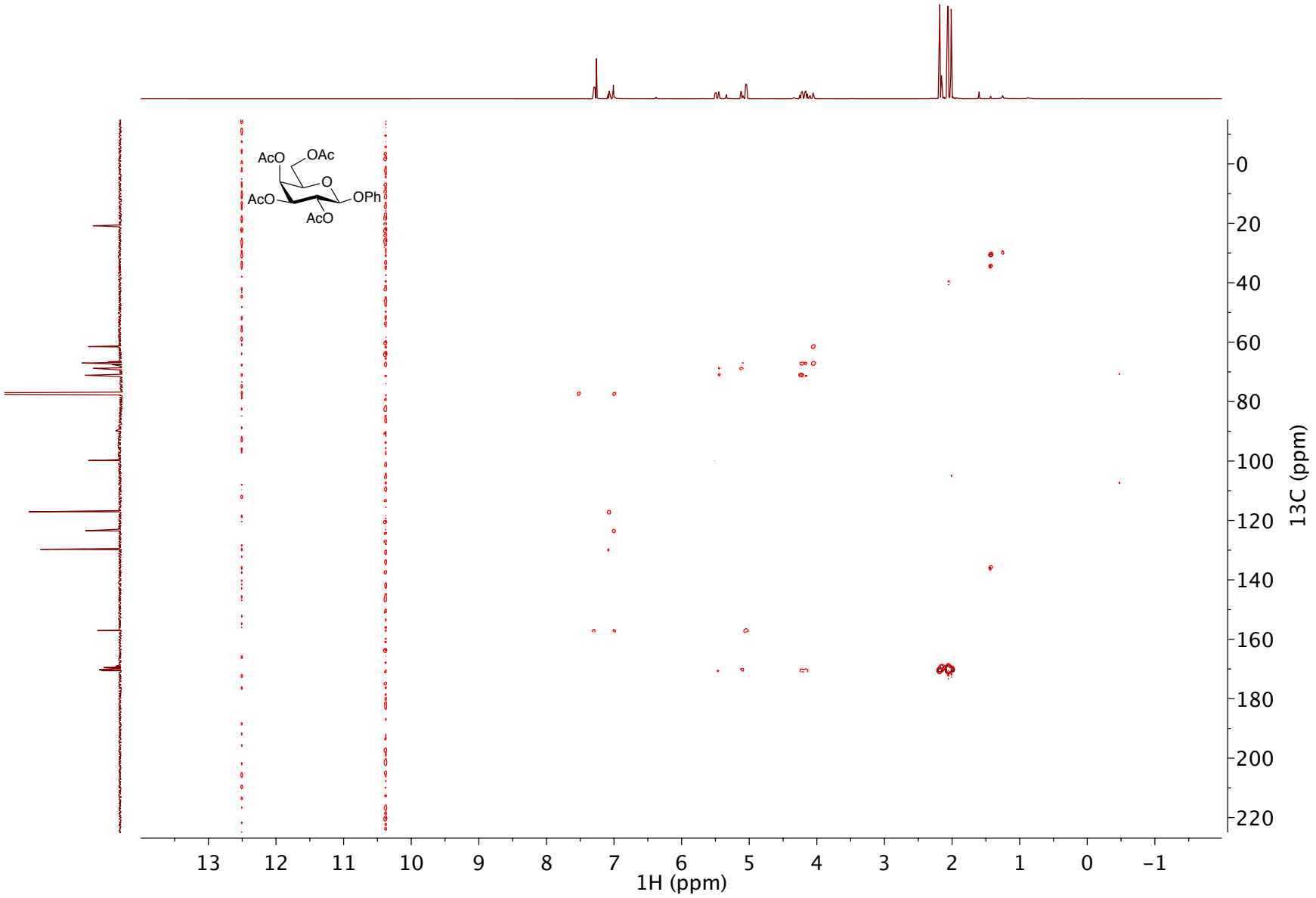
3eβ – COSY (500 MHz, $CDCl_3$)



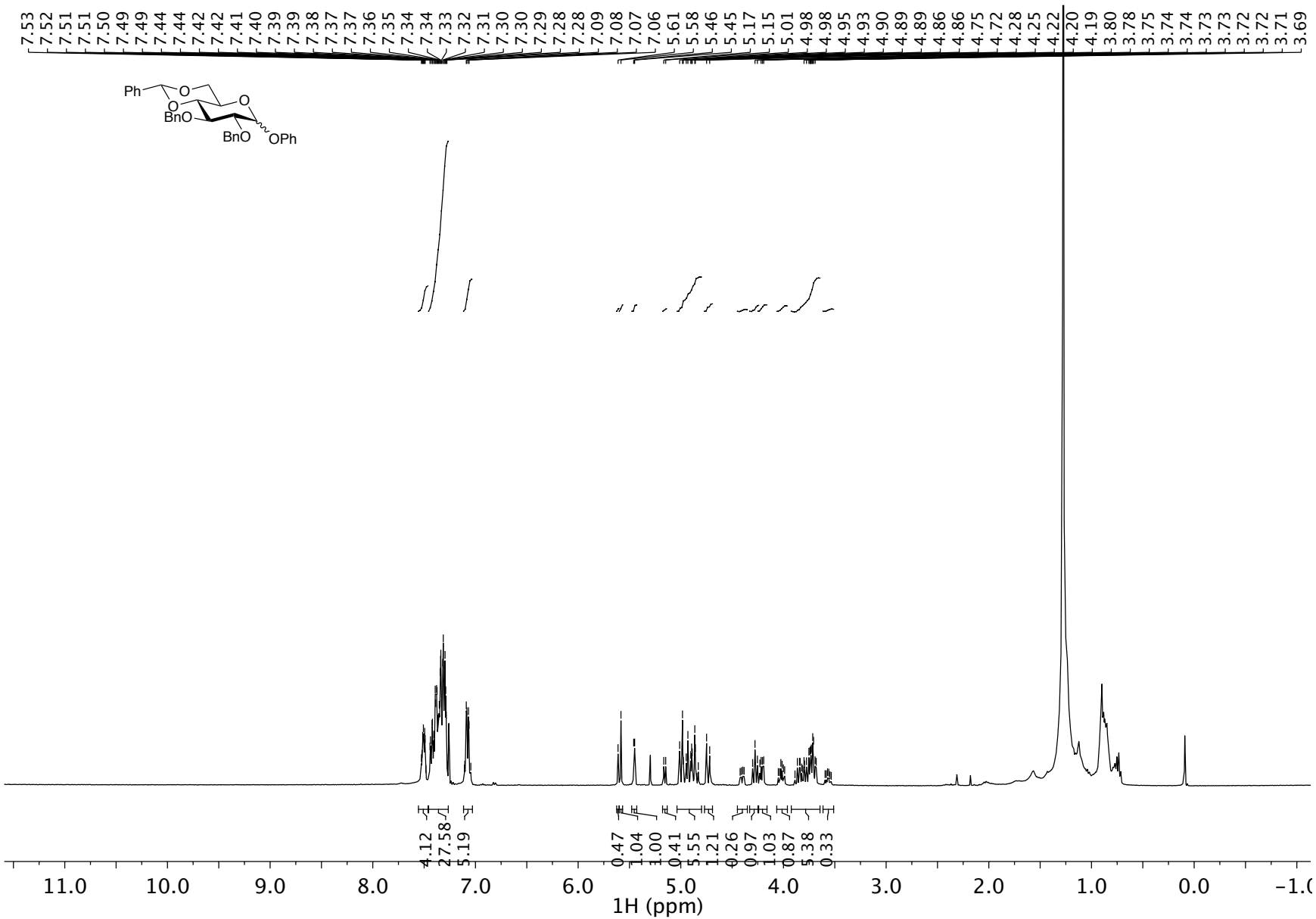
3eβ – HSQC (400 MHz, $CDCl_3$)



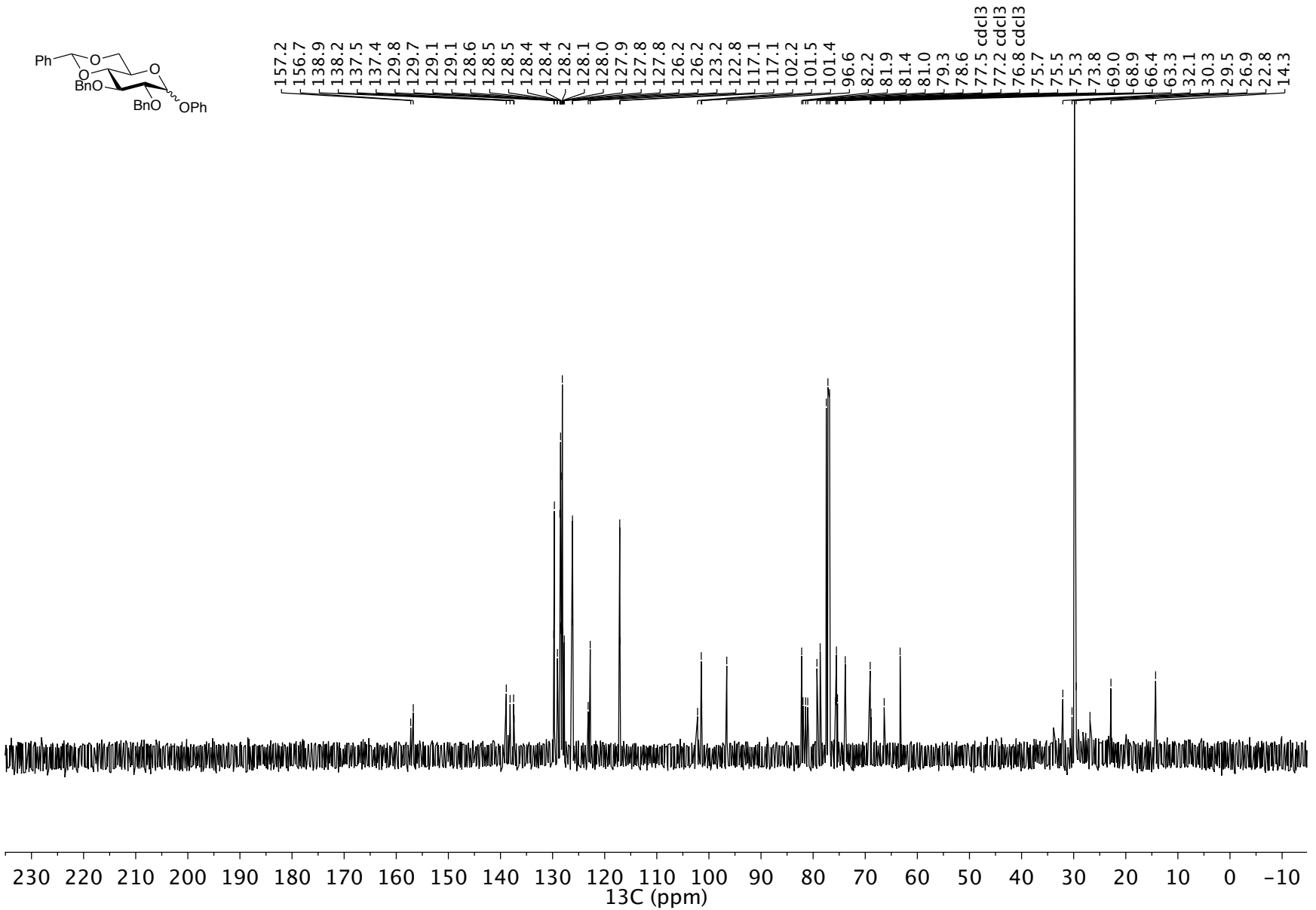
3eβ – HMBC (400 MHz, $CDCl_3$)



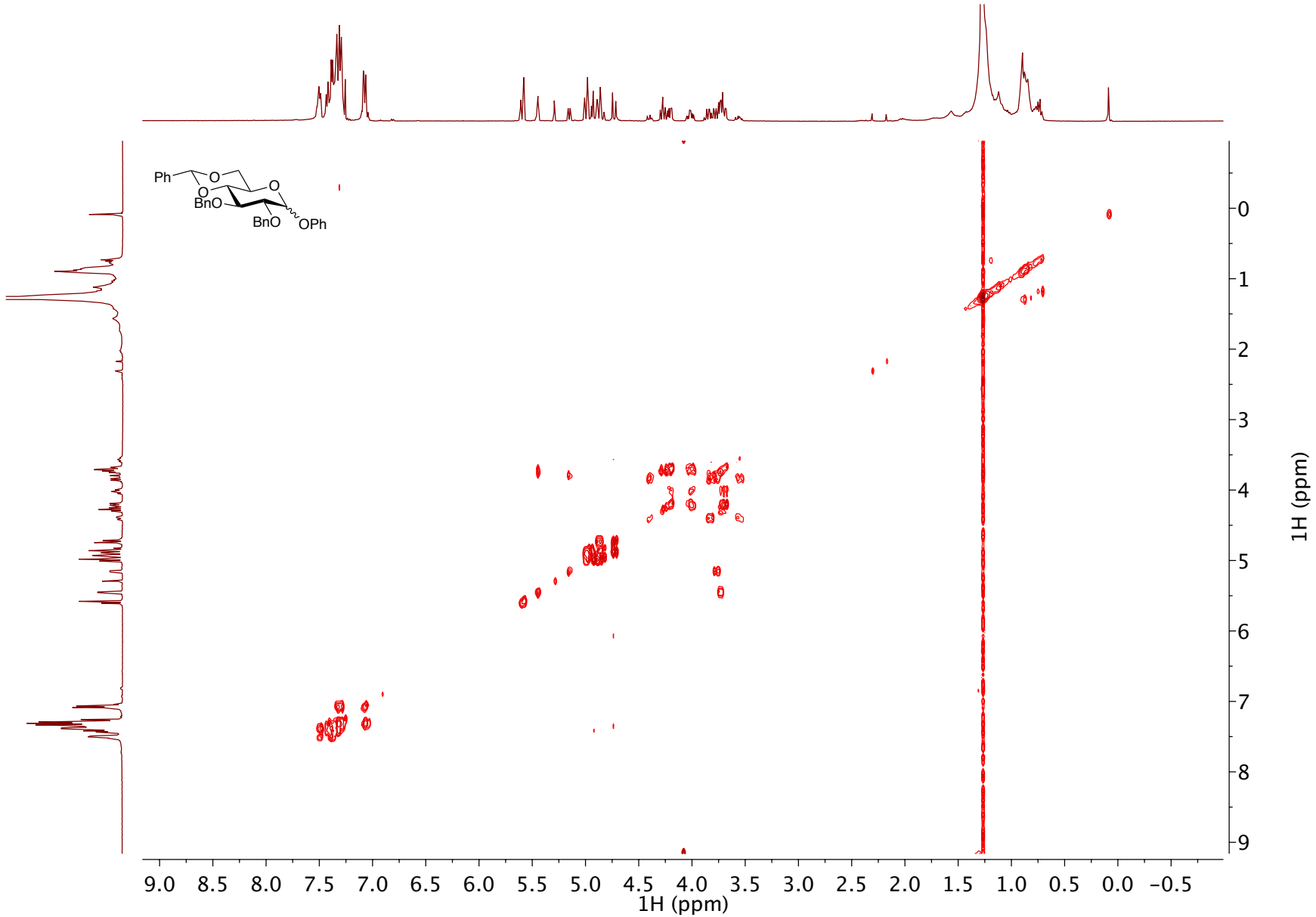
3f – ^{1}H NMR (400 MHz, $CDCl_3$)



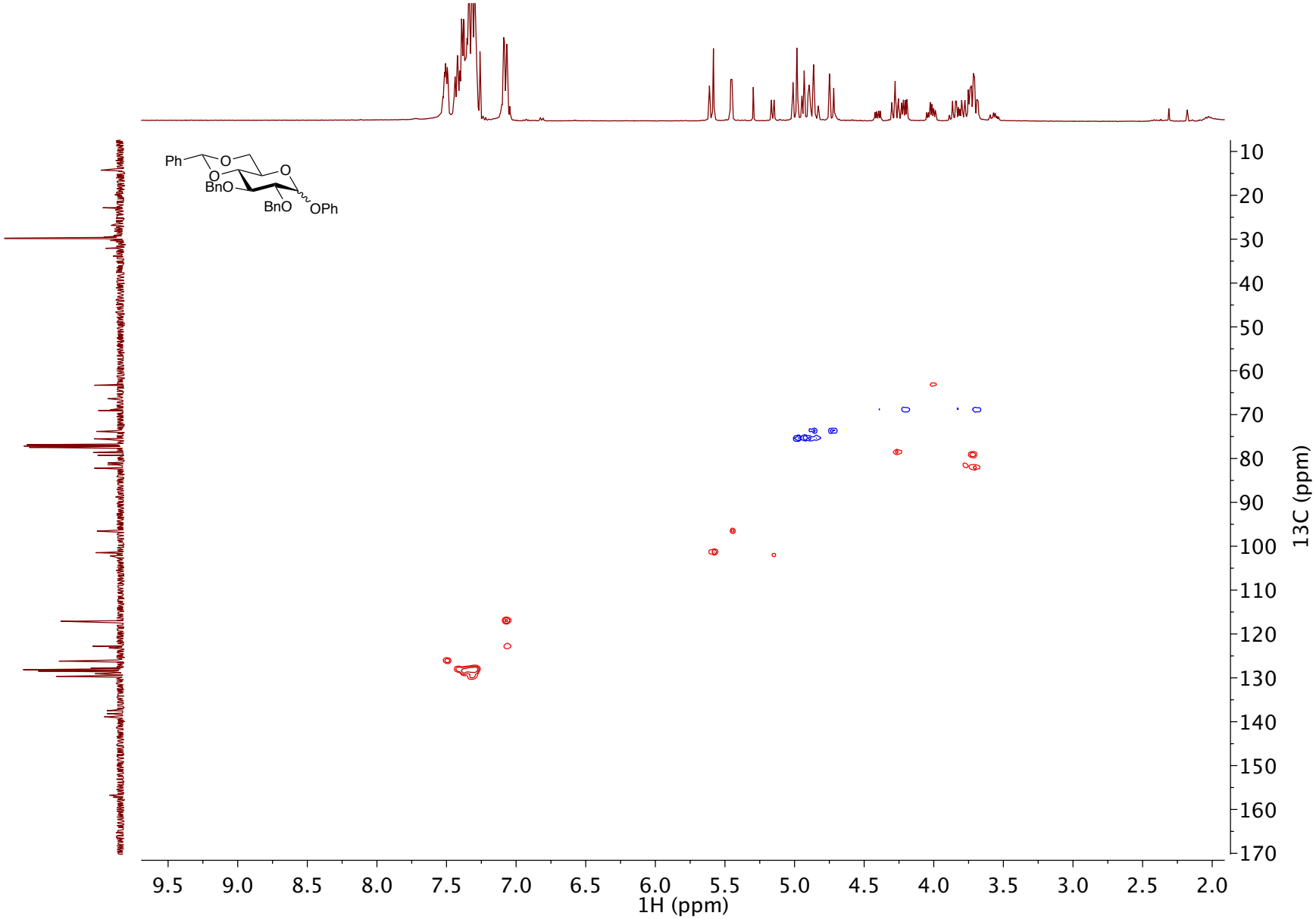
3f – ^{13}C NMR (100 MHz, $CDCl_3$)



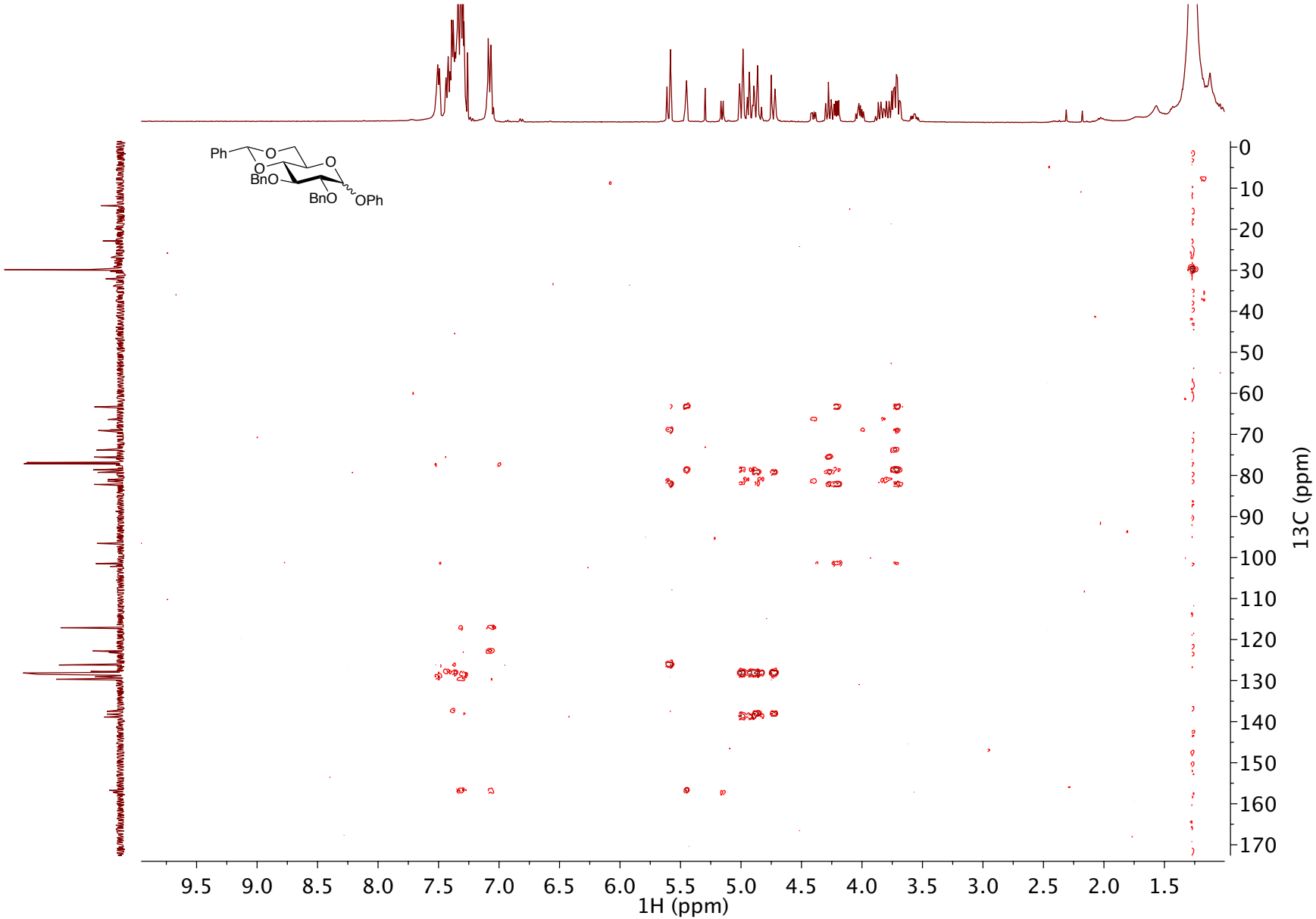
3f – COSY (400 MHz, $CDCl_3$)



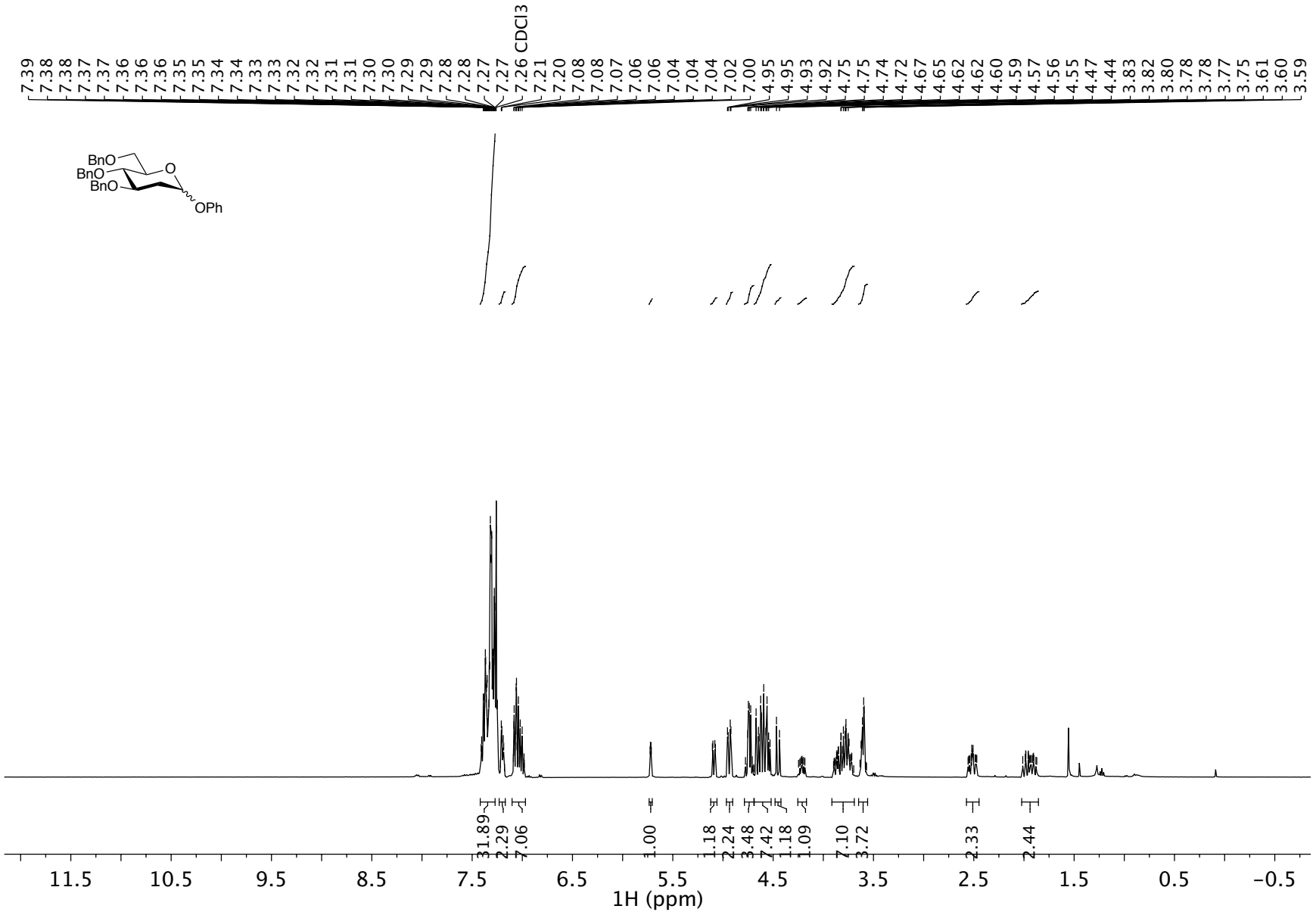
3f – HSQC (400 MHz, $CDCl_3$)



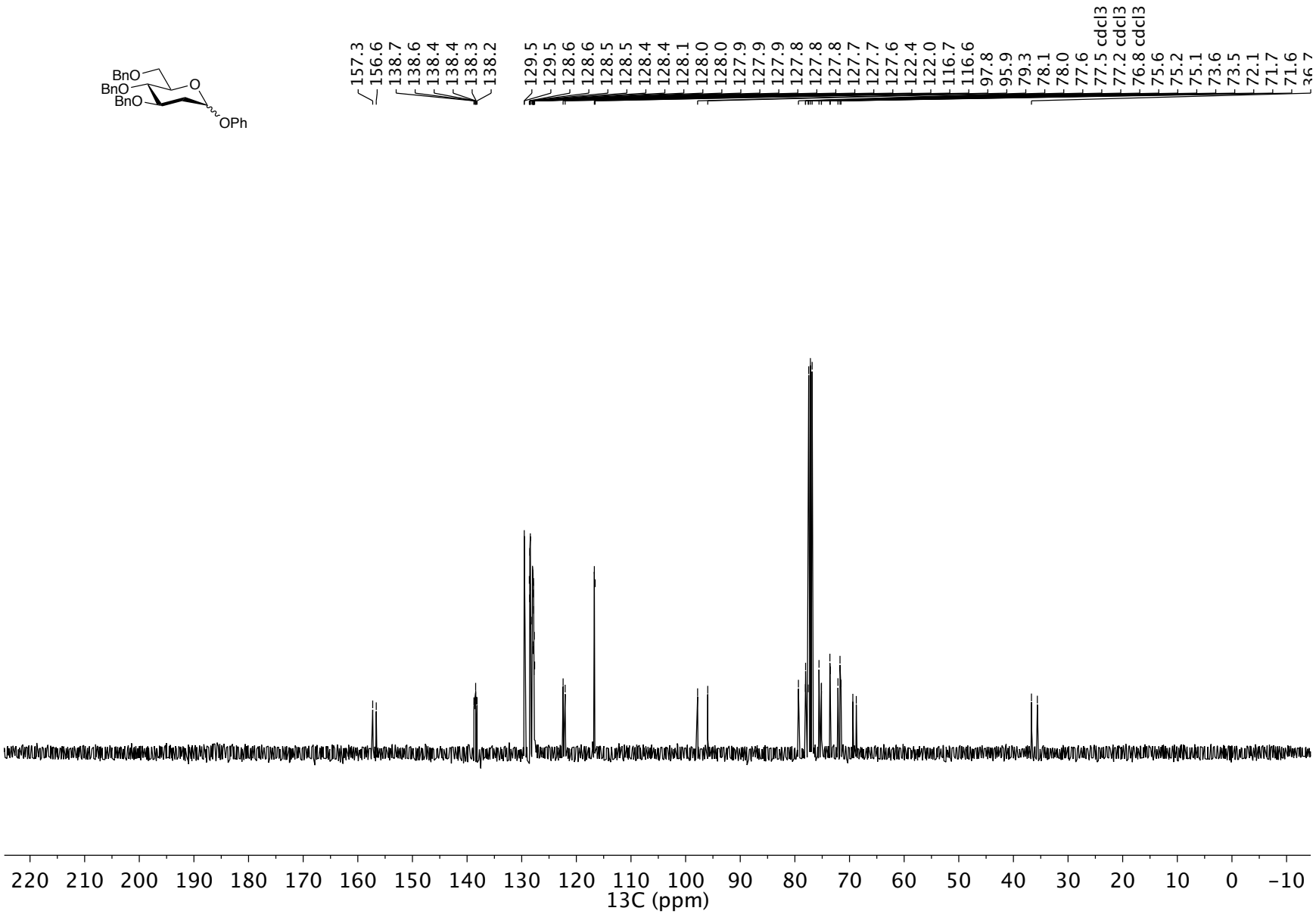
3f – HMBC (400 MHz, $CDCl_3$)



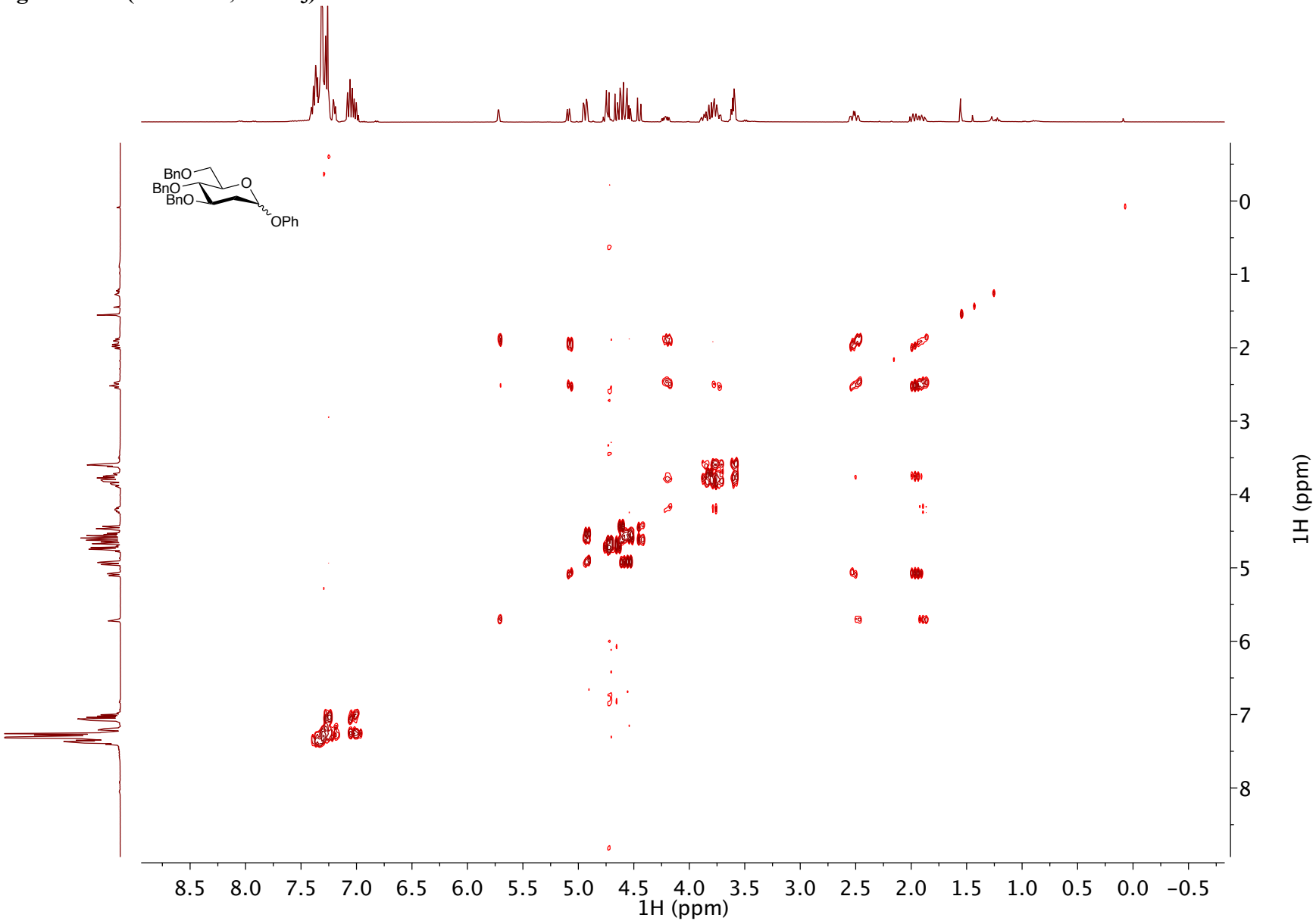
3g –^{1}H NMR (400 MHz, $CDCl_3$)



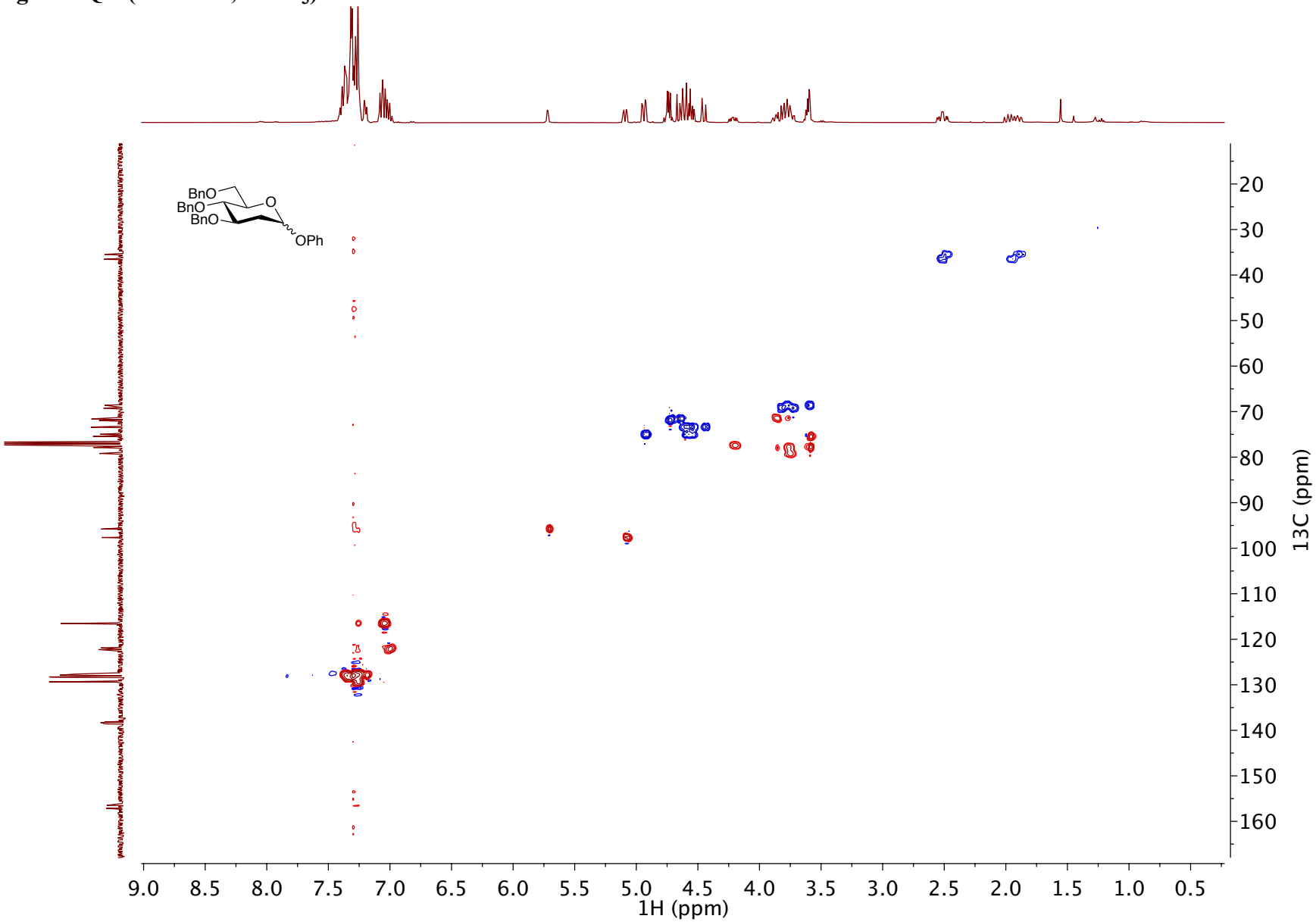
3g –^{13}C-NMR (101 MHz, $CDCl_3$)



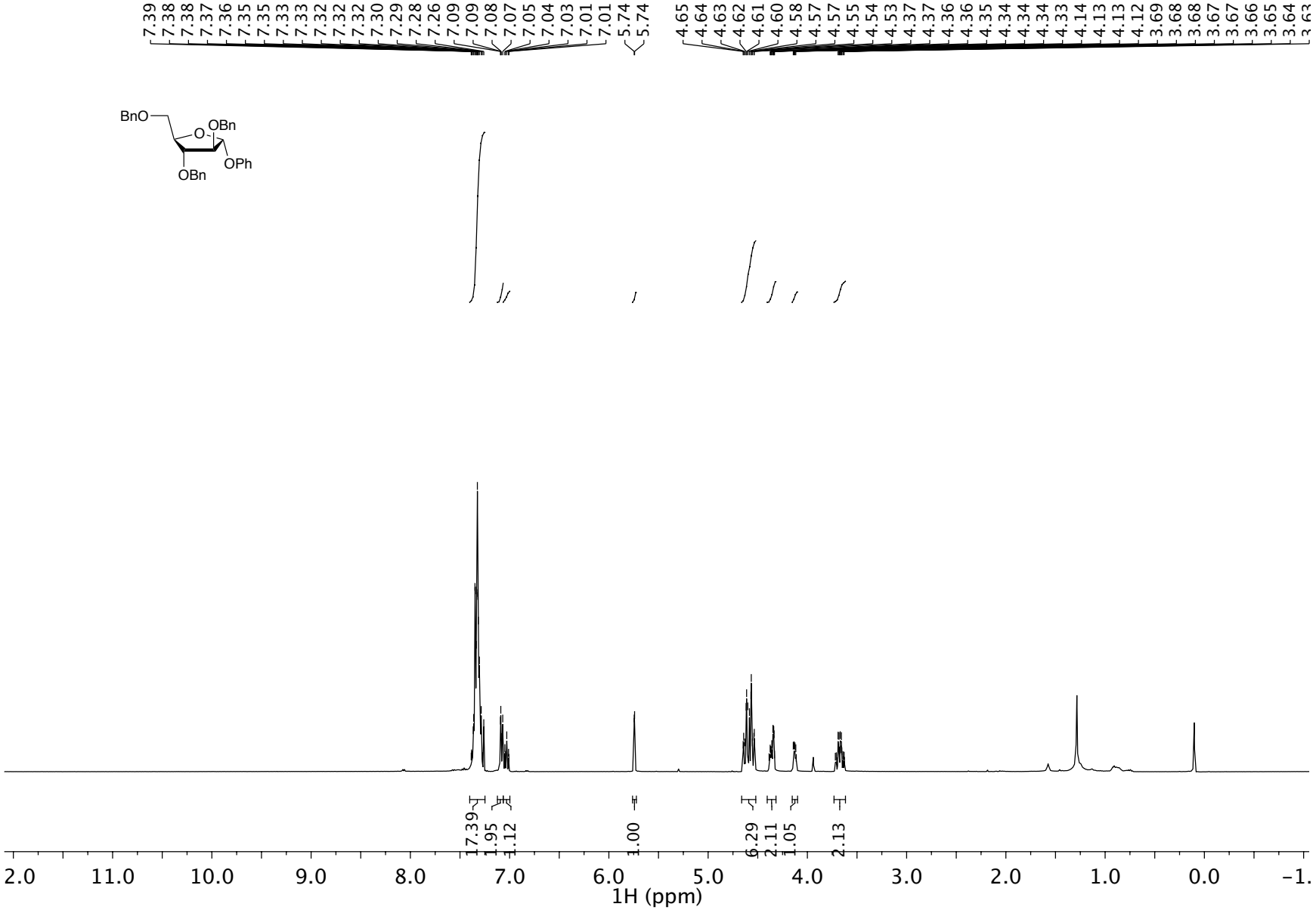
3g – COSY (400 MHz, $CDCl_3$)



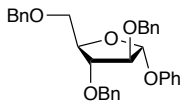
3g – HSQC (400 MHz, $CDCl_3$)

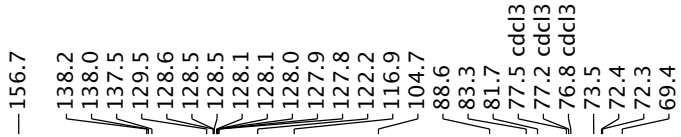


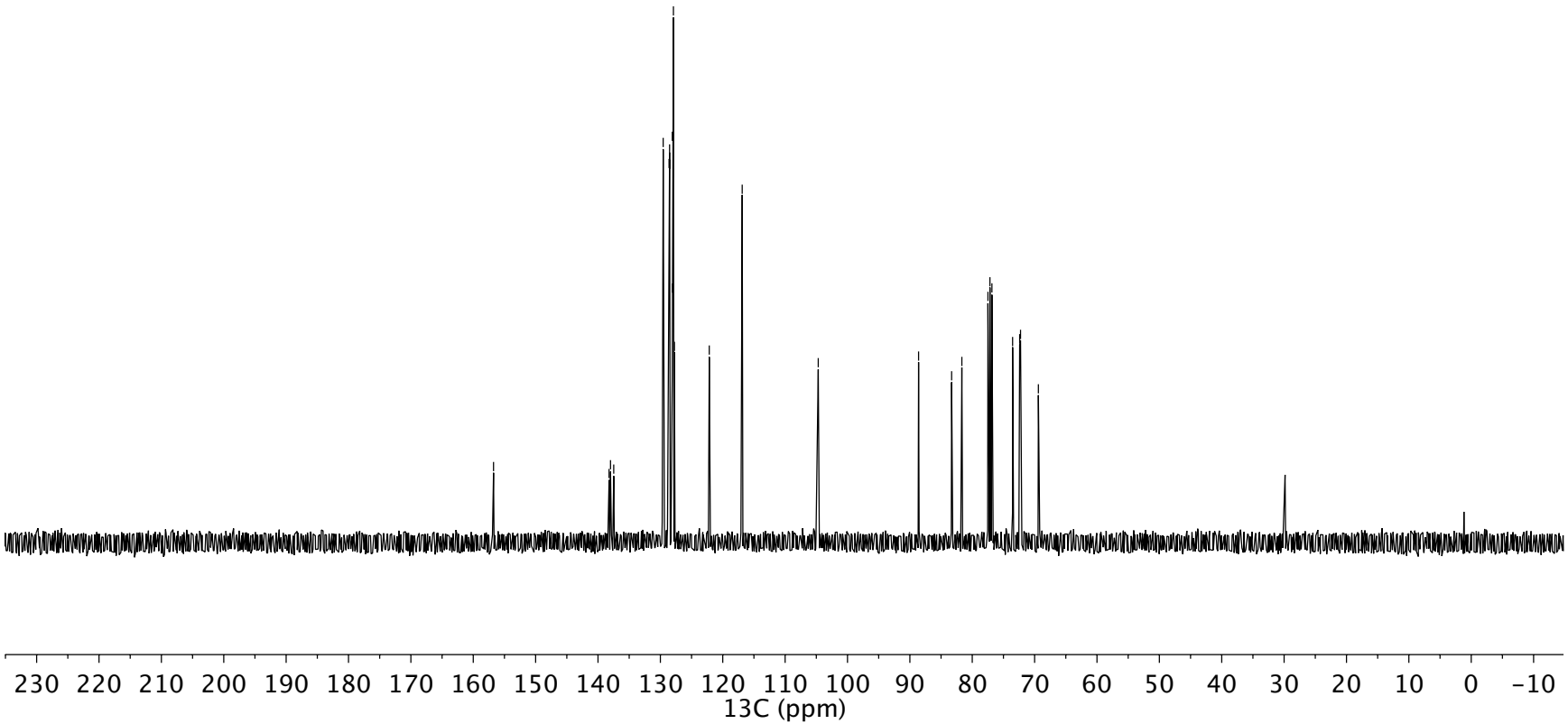
3hα – ^{1}H NMR (400 MHz, $CDCl_3$)



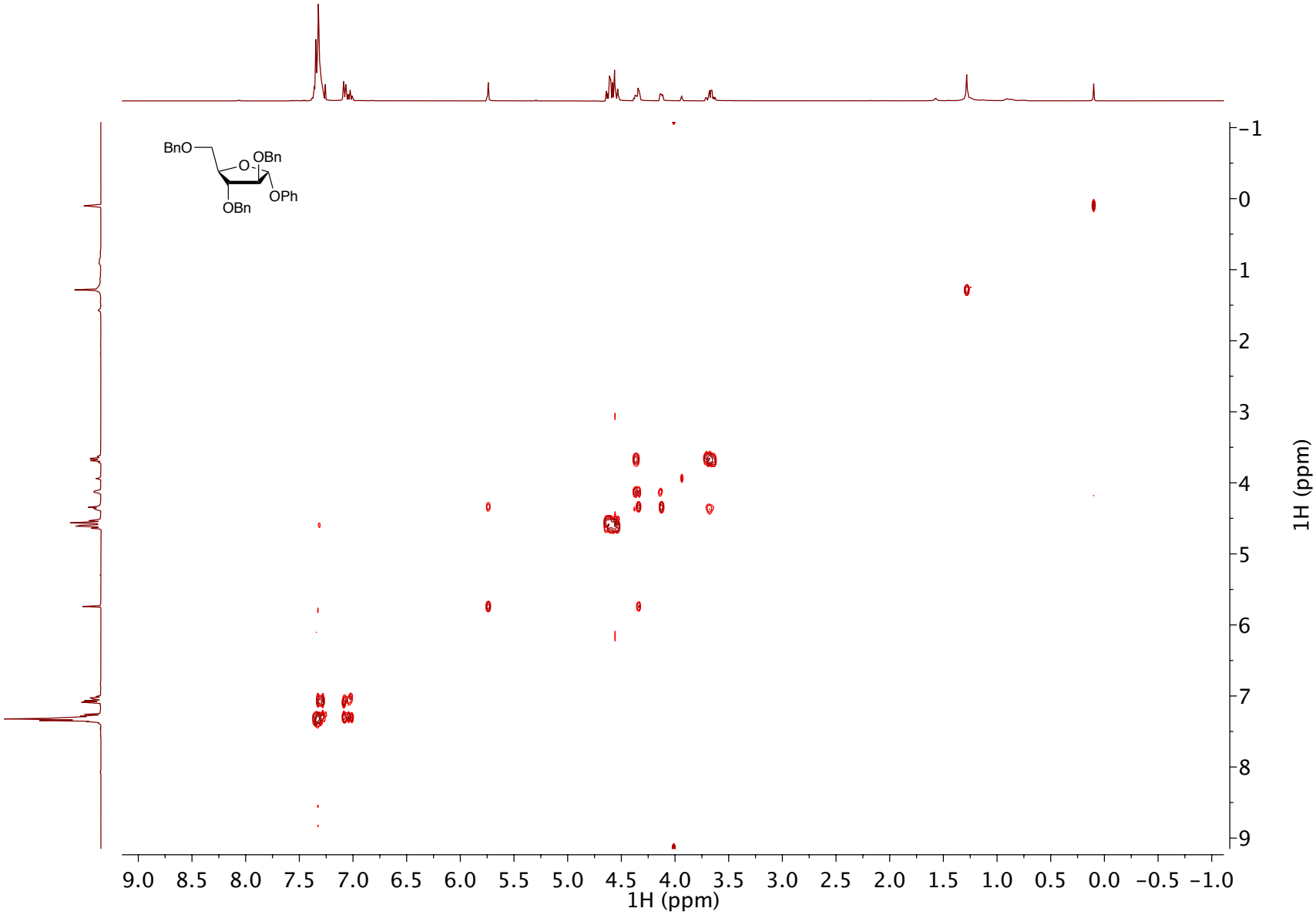
3hα – ^{13}C NMR (100 MHz, $CDCl_3$)



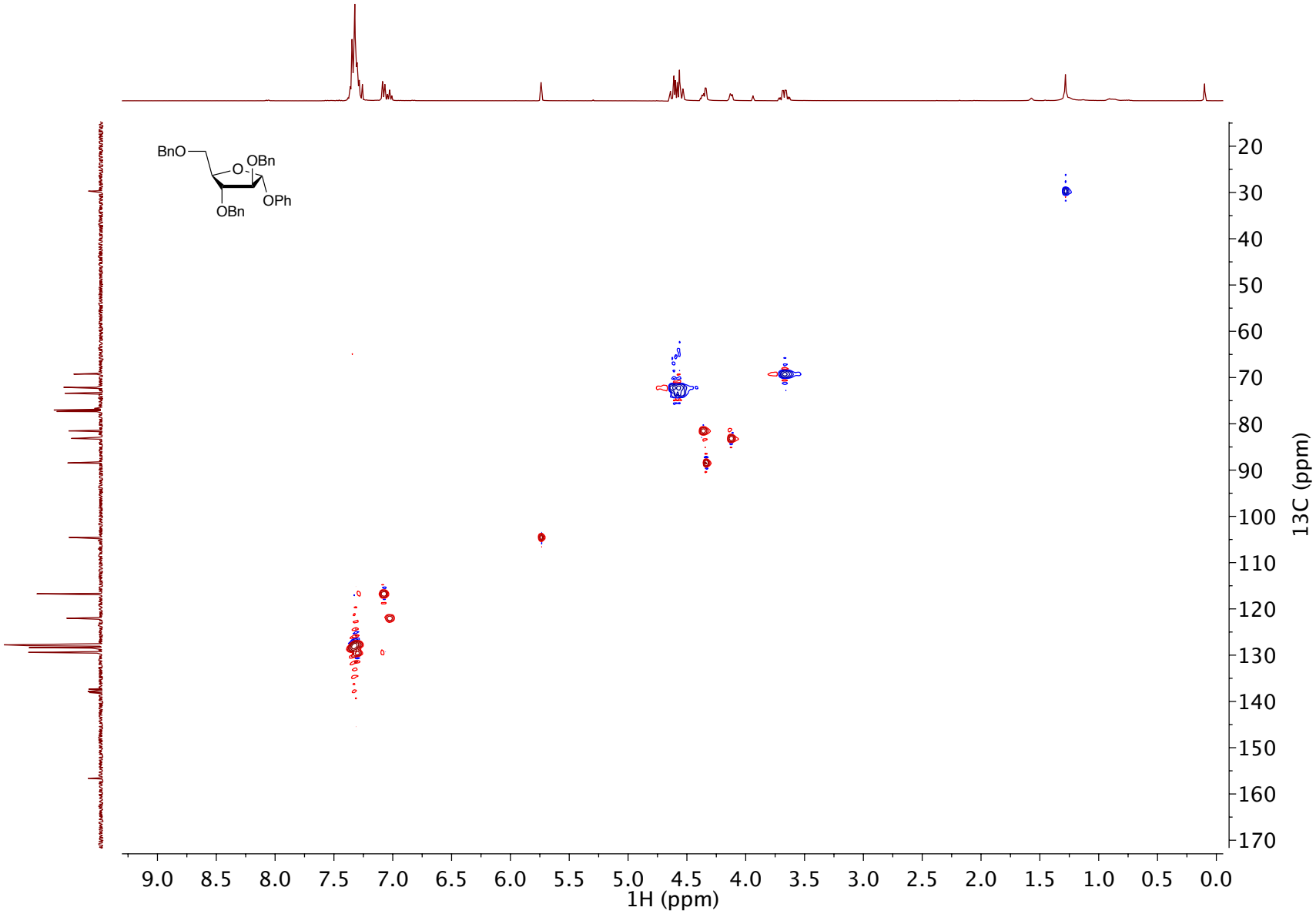




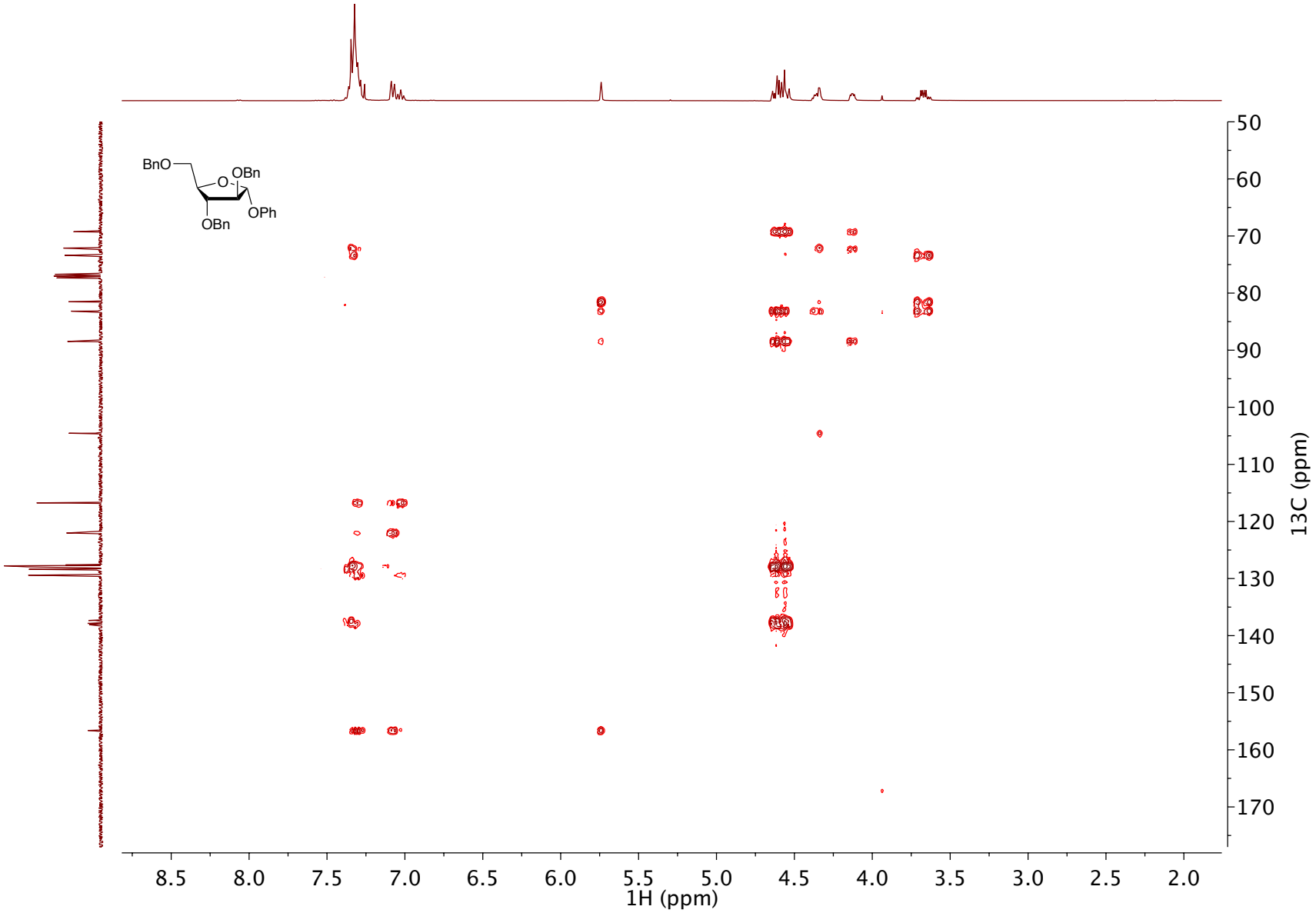
3hα – COSY (400 MHz, $CDCl_3$)



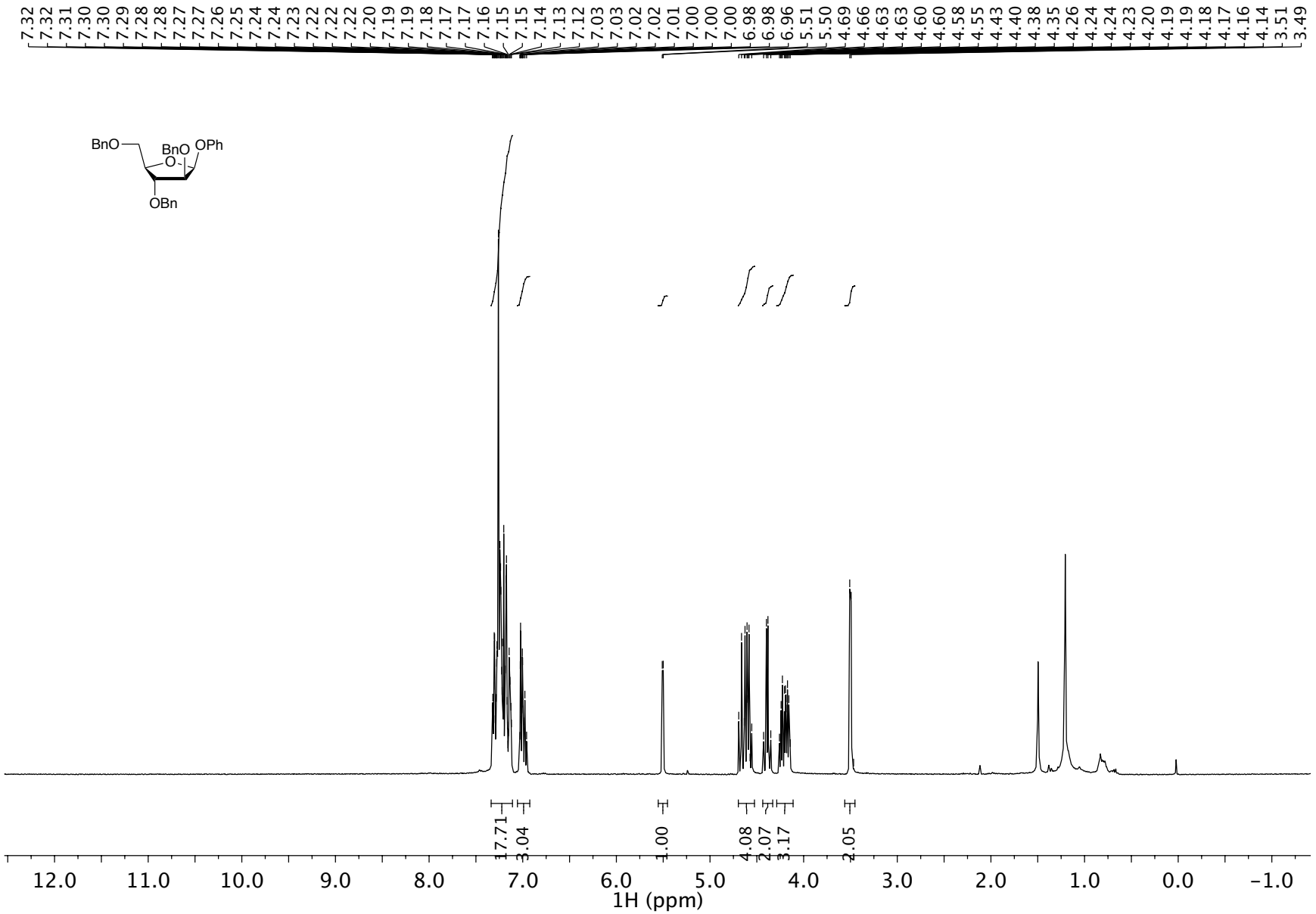
3hα – HSQC (400 MHz, $CDCl_3$)



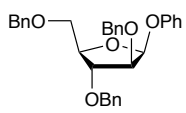
3hα – HMBC (400 MHz, $CDCl_3$)

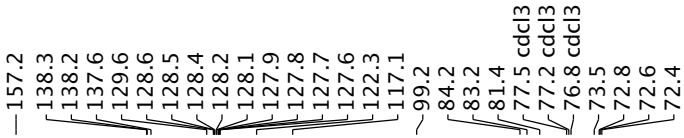


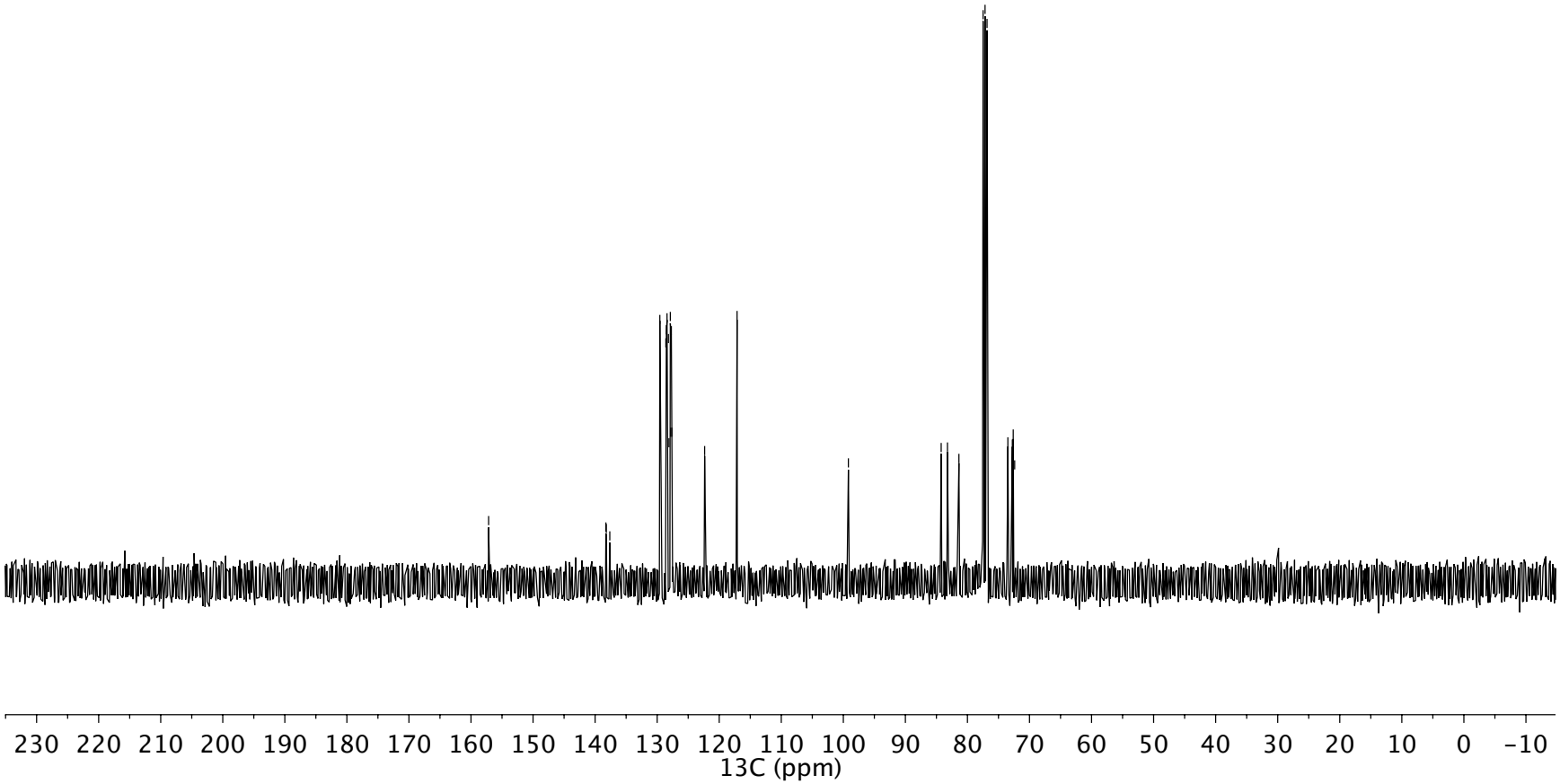
3hβ – ^{1}H NMR (400 MHz, $CDCl_3$)



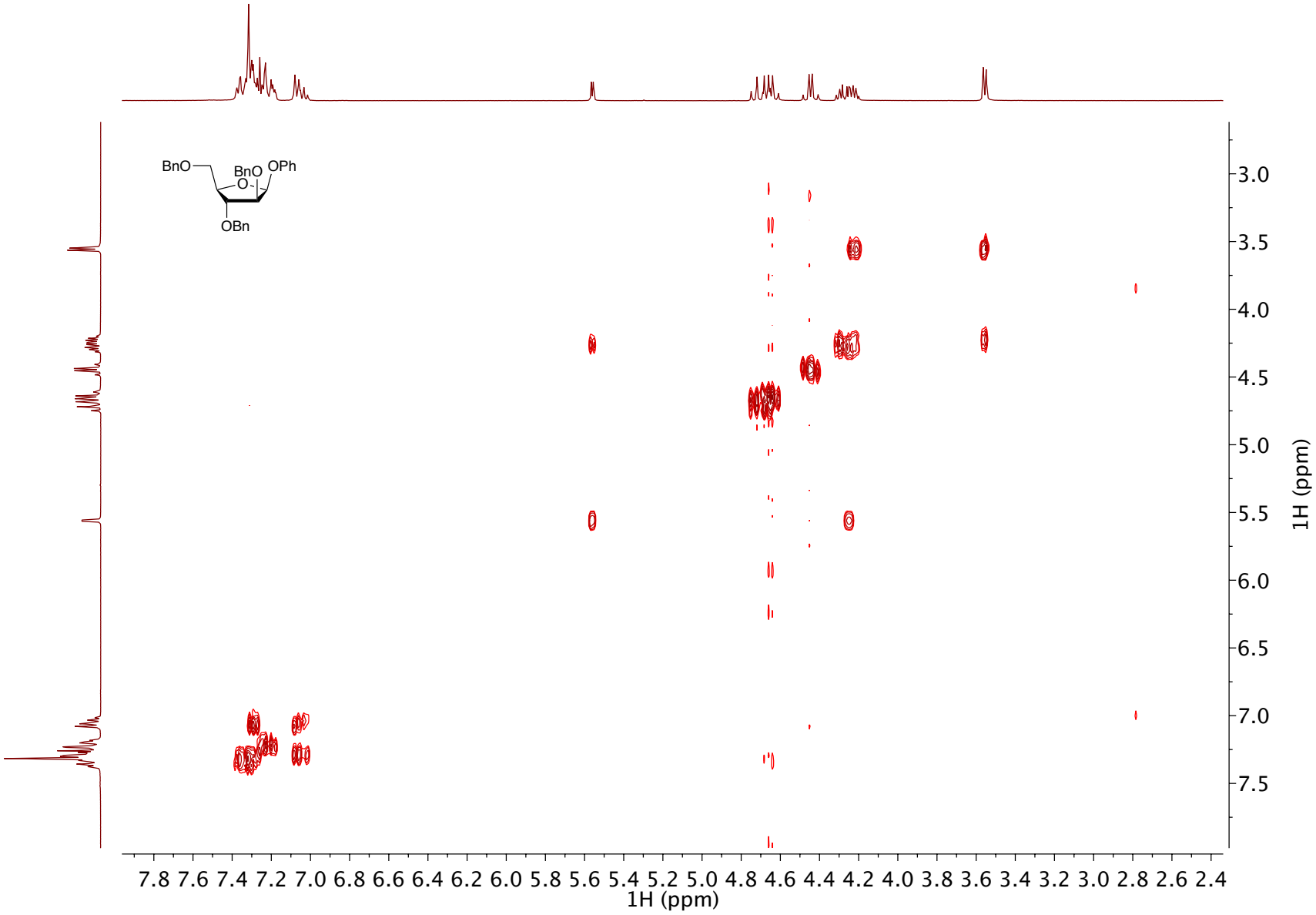
3hβ – ^{13}C NMR (100 MHz, $CDCl_3$)



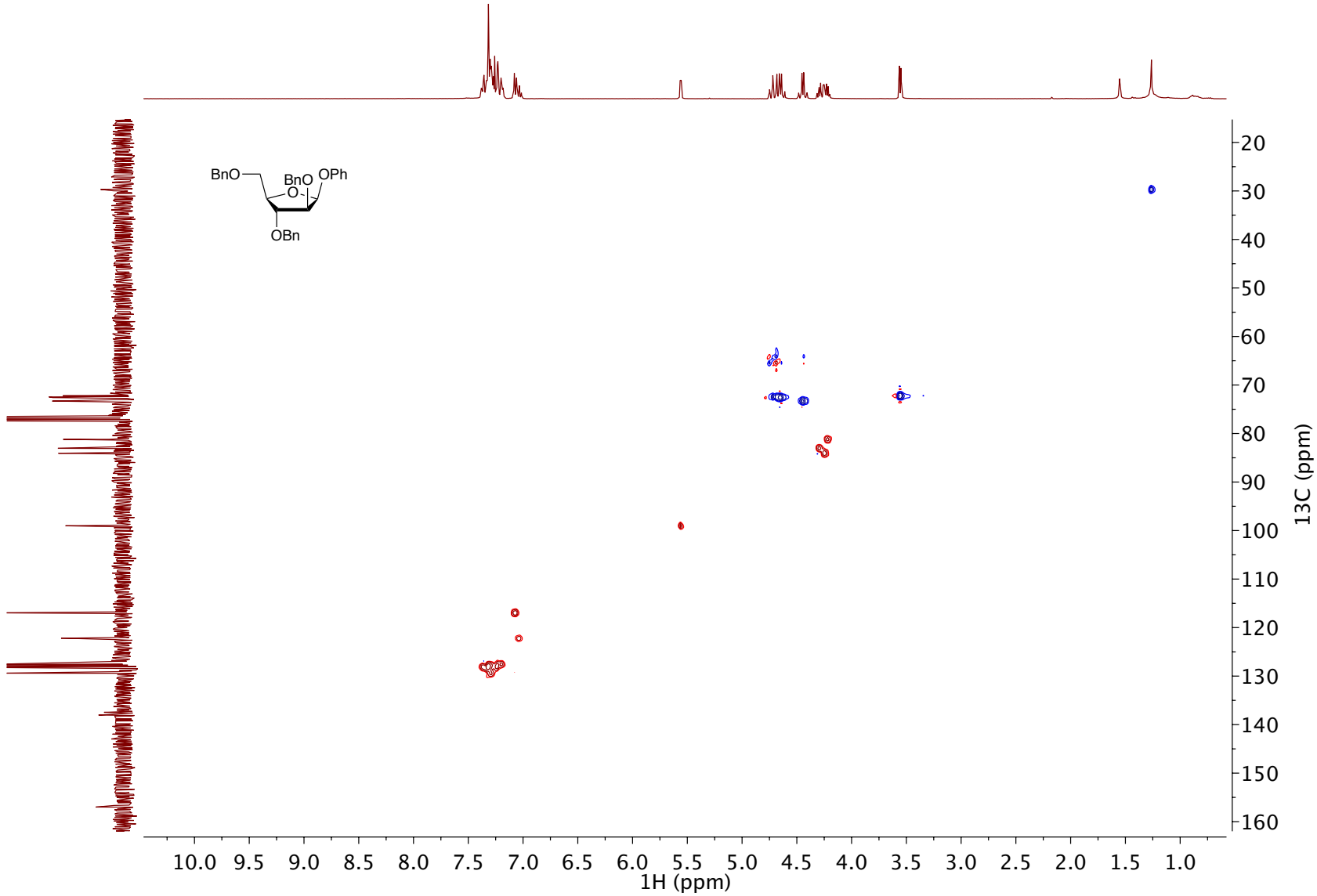




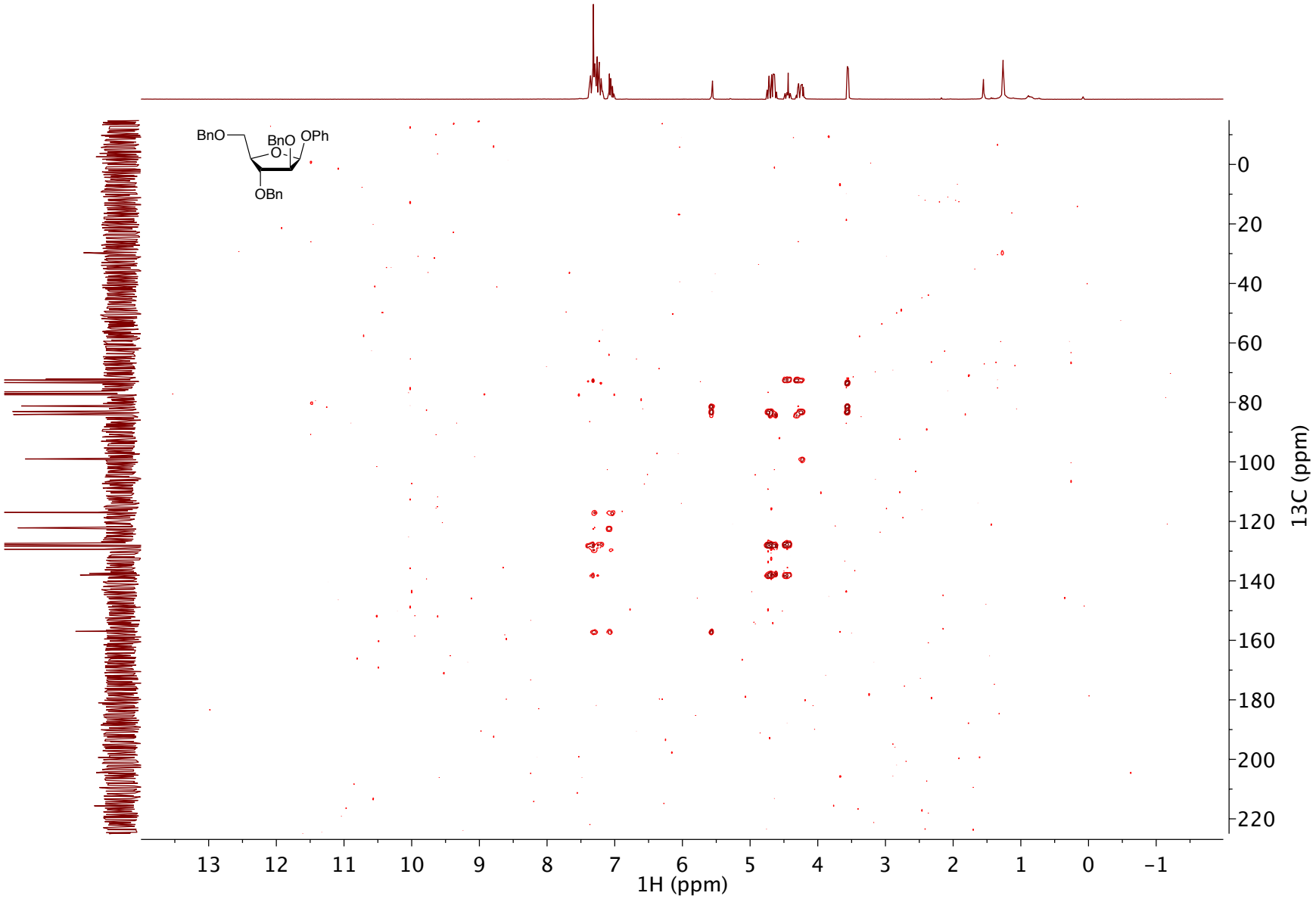
3hβ – COSY (400 MHz, $CDCl_3$)



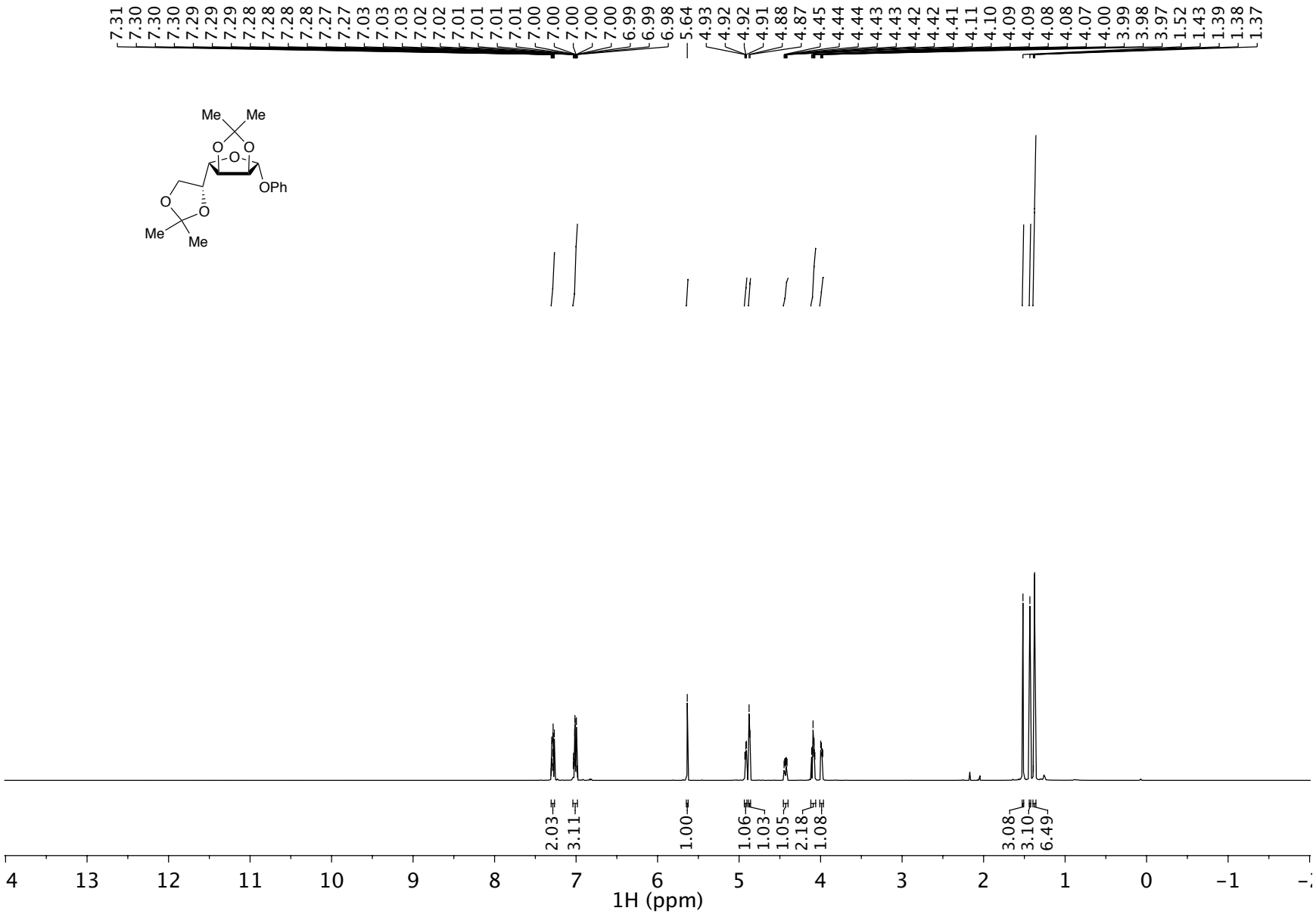
3hβ – HSQC (400 MHz, $CDCl_3$)



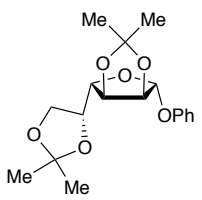
3hβ – HMBC (400 MHz, $CDCl_3$)



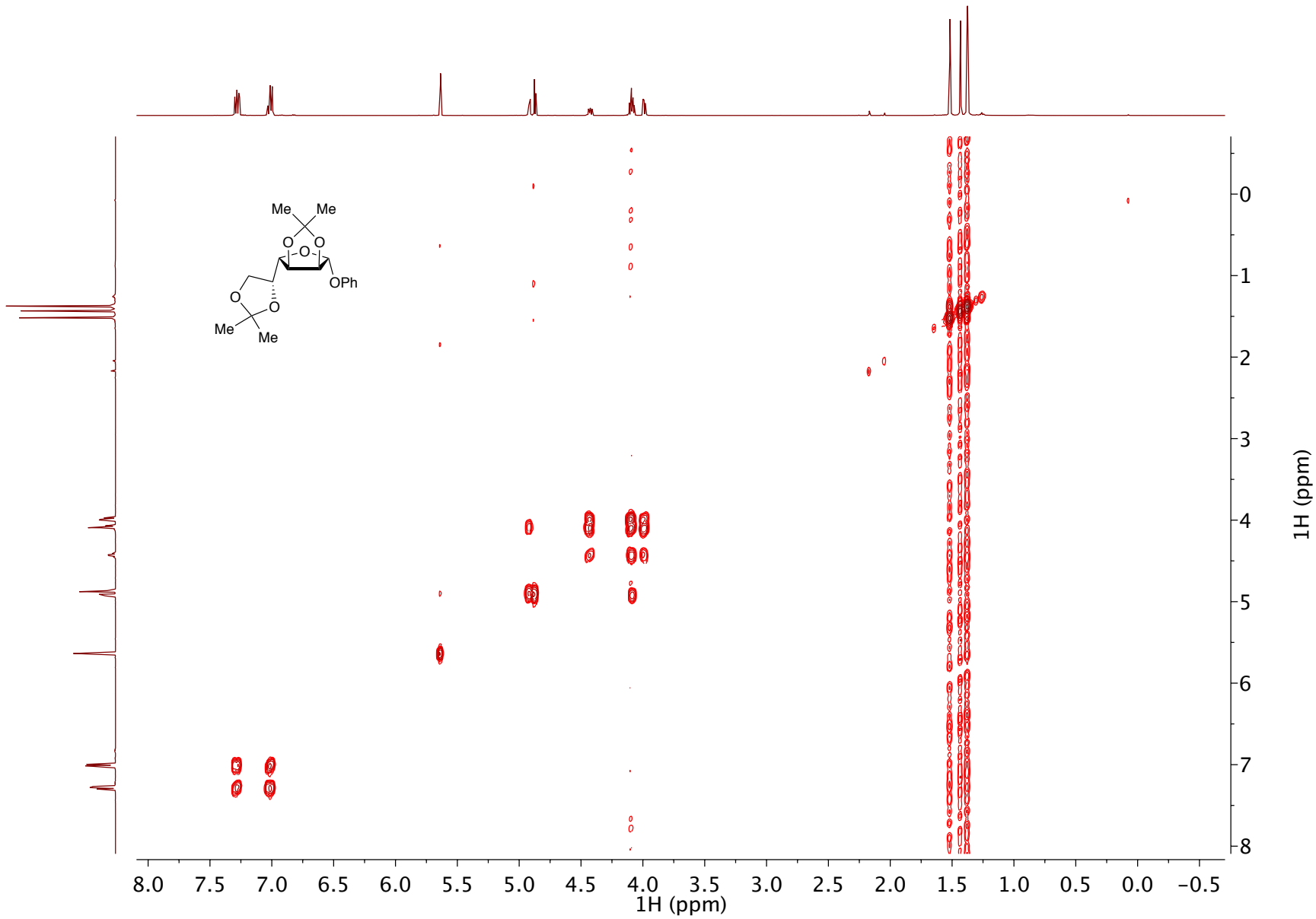
3i – ^{1}H NMR (500 MHz, $CDCl_3$)



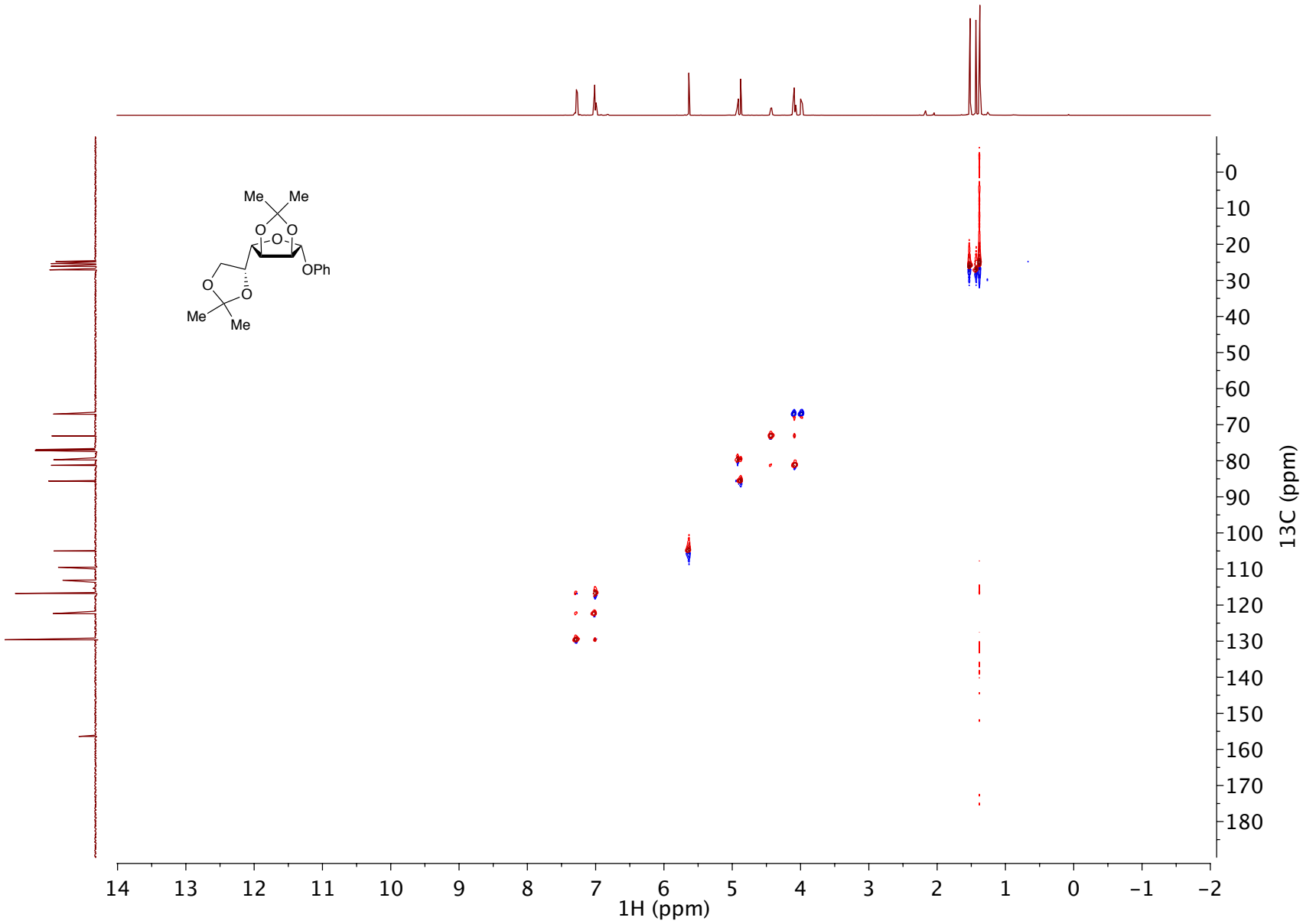
3i – ^{13}C NMR (126 MHz, $CDCl_3$)



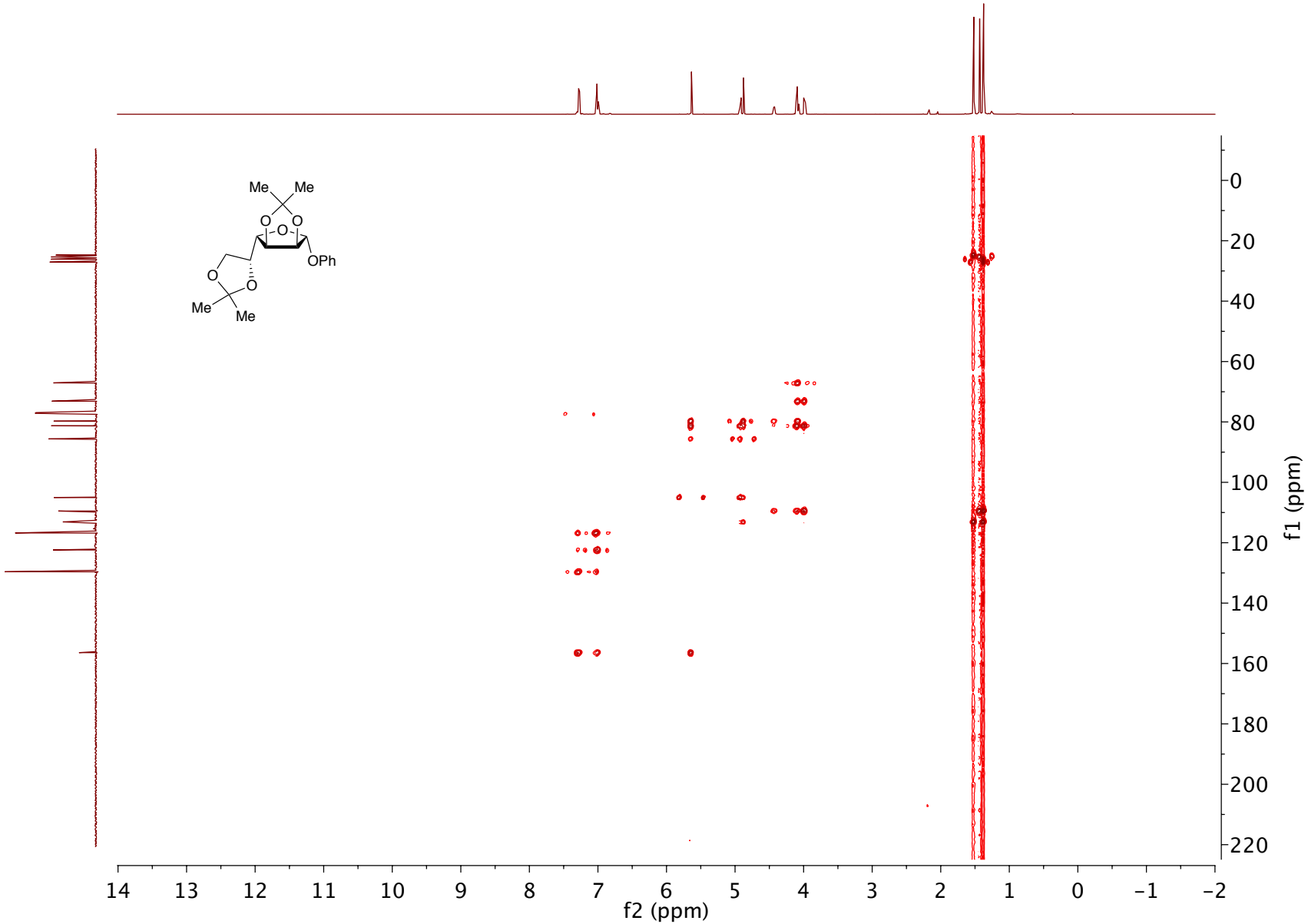
3i – COSY (500 MHz, $CDCl_3$)



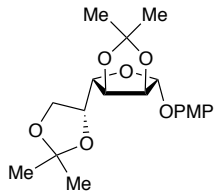
3i – HSQC (500 MHz, $CDCl_3$)



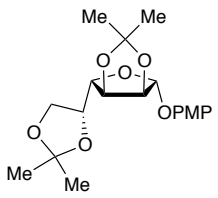
3i – HMBC (500 MHz, $CDCl_3$)



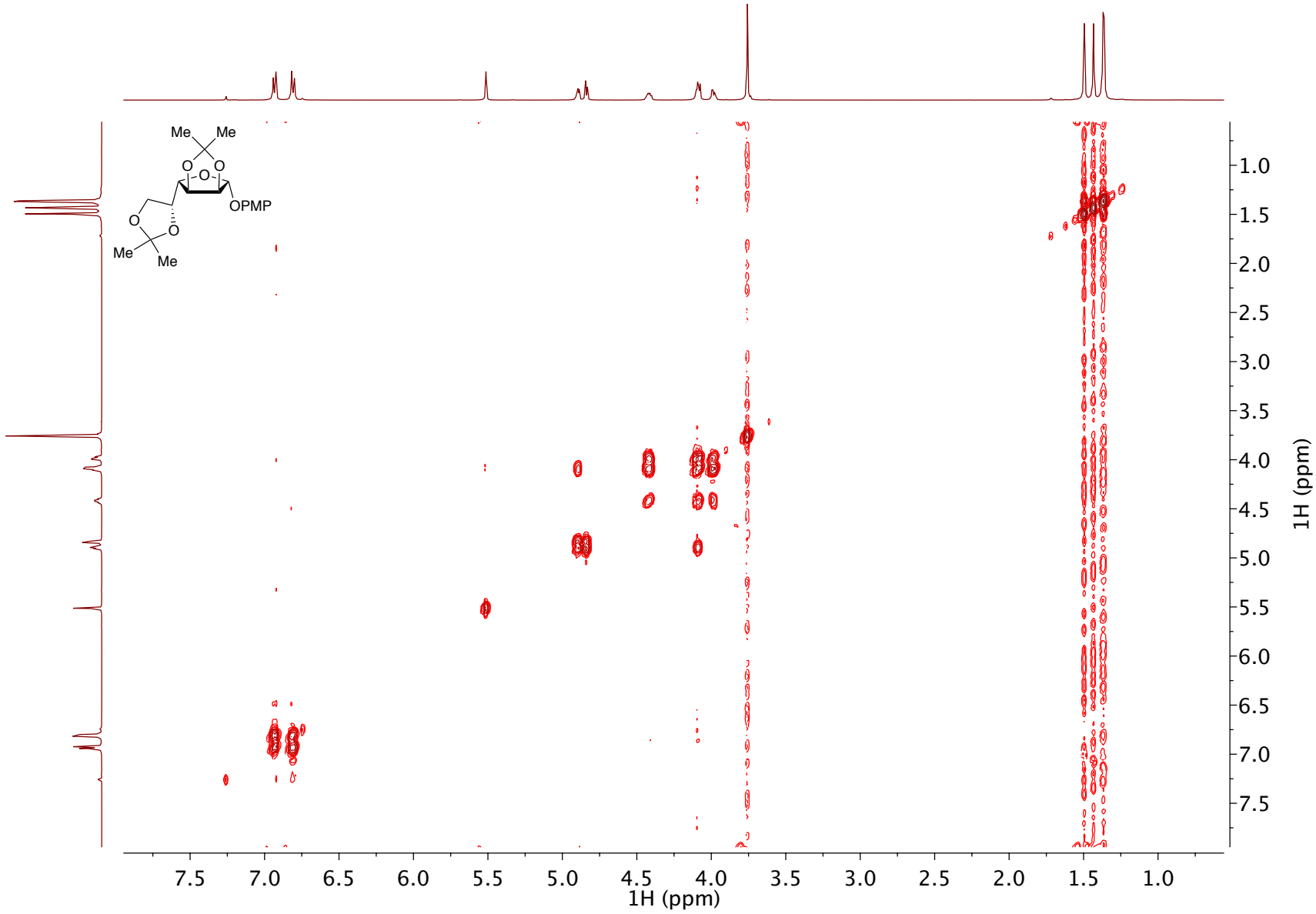
3k – ^{1}H NMR (500 MHz, $CDCl_3$)



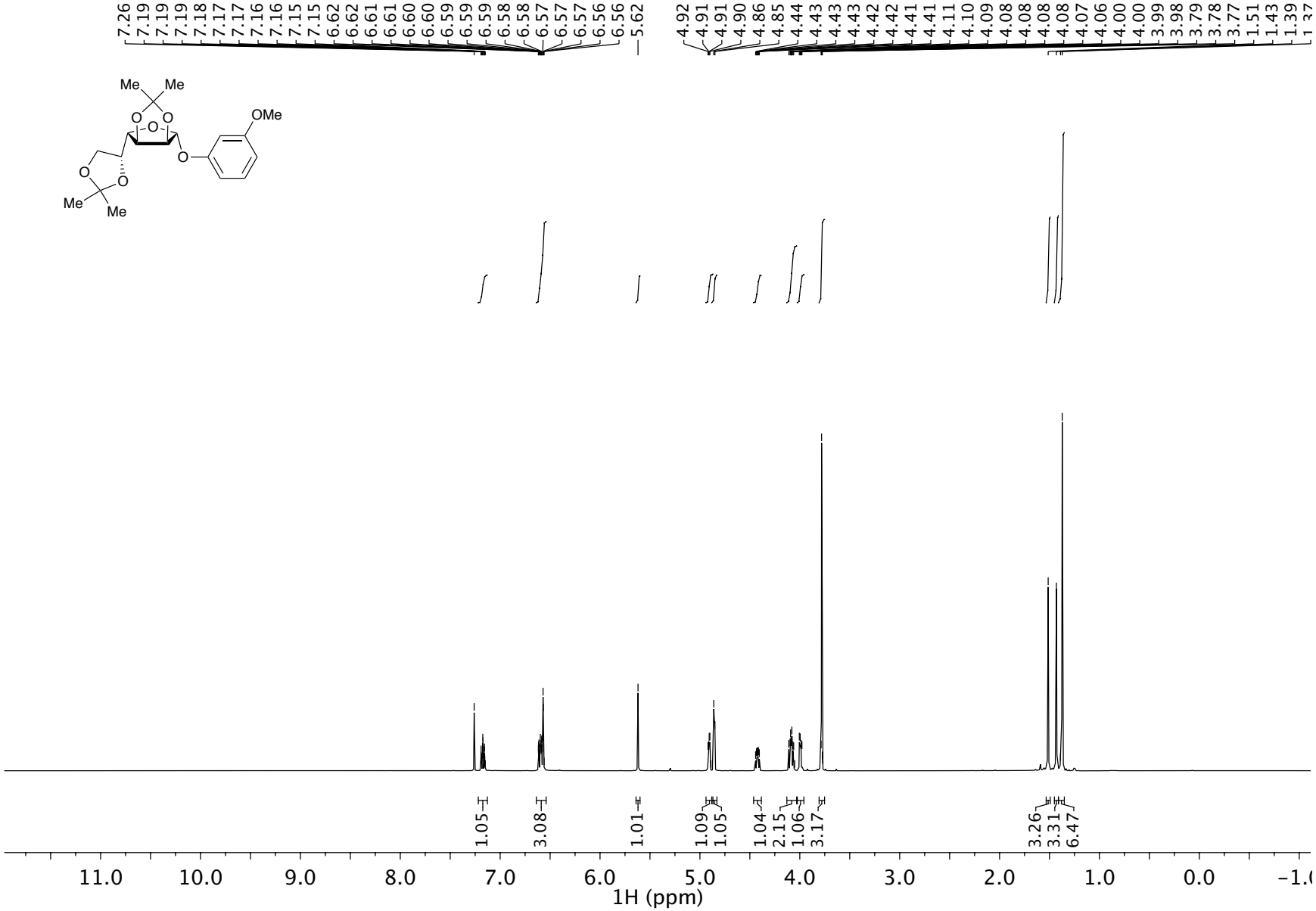
3k – ^{13}C NMR (126 MHz, $CDCl_3$)



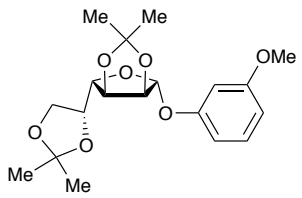
3k – COSY (500 MHz, $CDCl_3$)



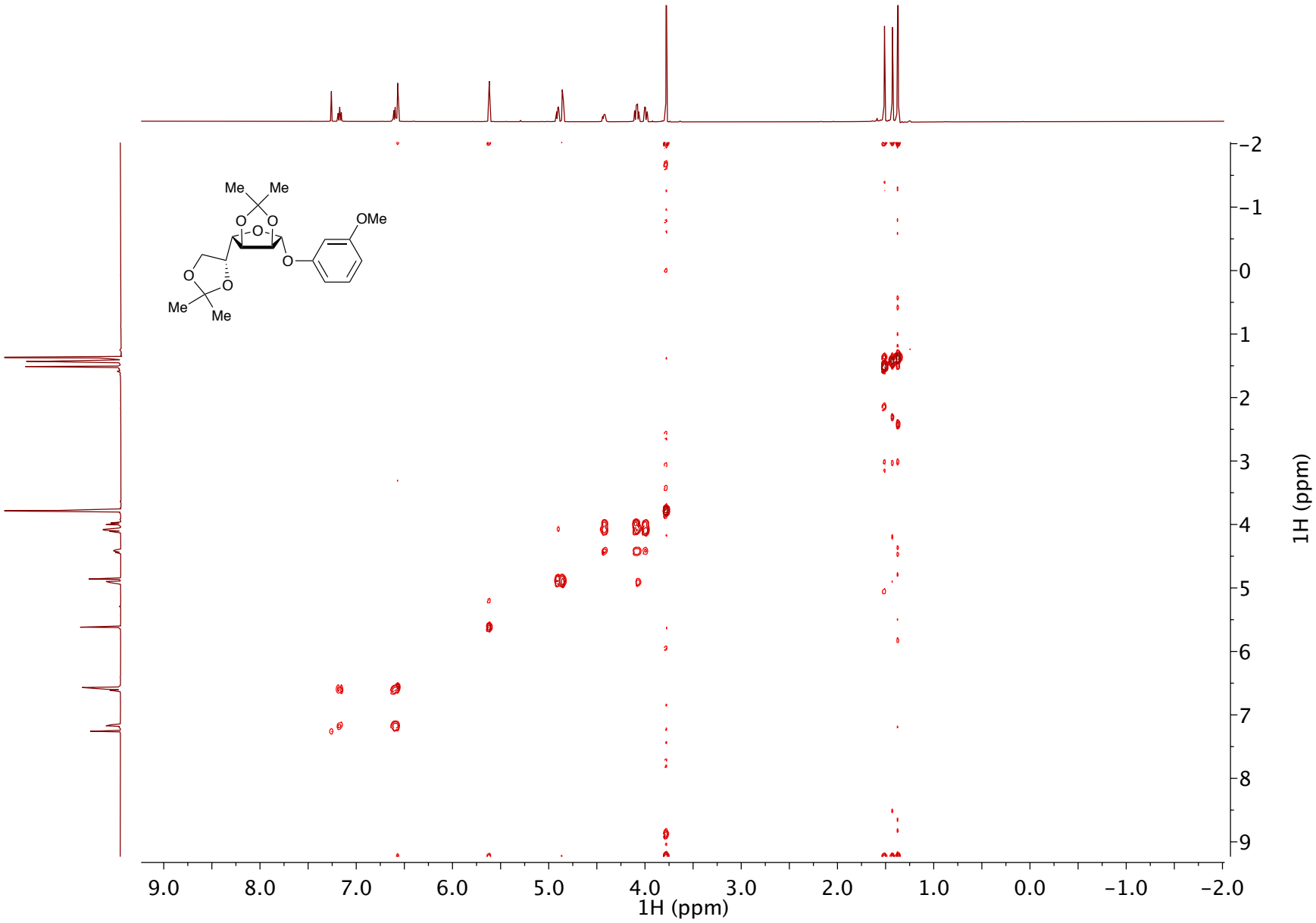
3l – ^{1}H NMR (500 MHz, $CDCl_3$)



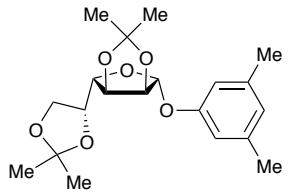
3l – ^{13}C NMR (126 MHz, $CDCl_3$)



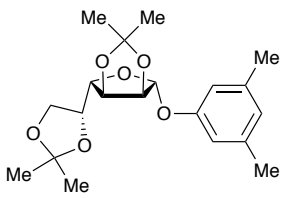
3l – COSY (500 MHz, $CDCl_3$)



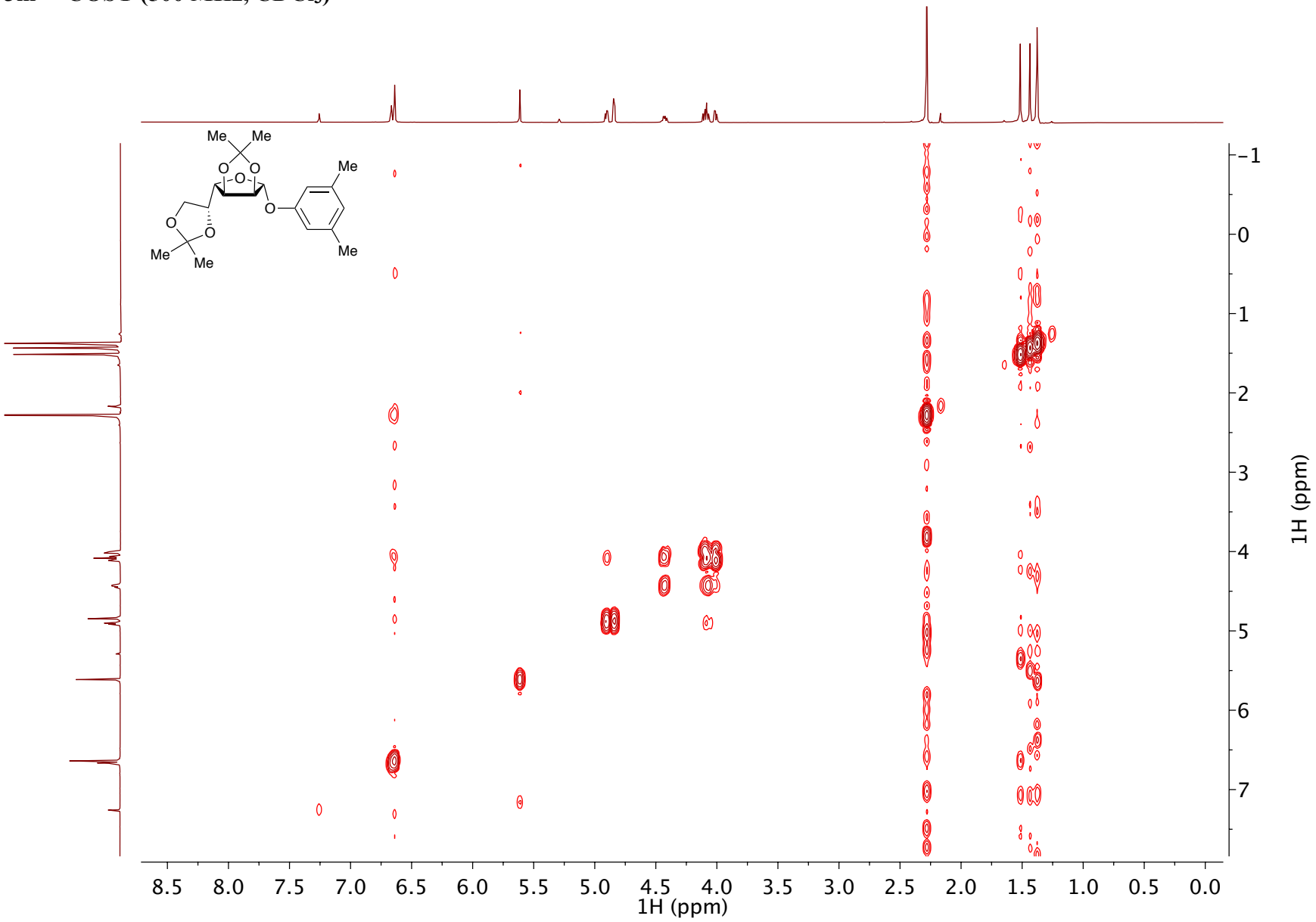
3m – ^{1}H NMR (500 MHz, $CDCl_3$)



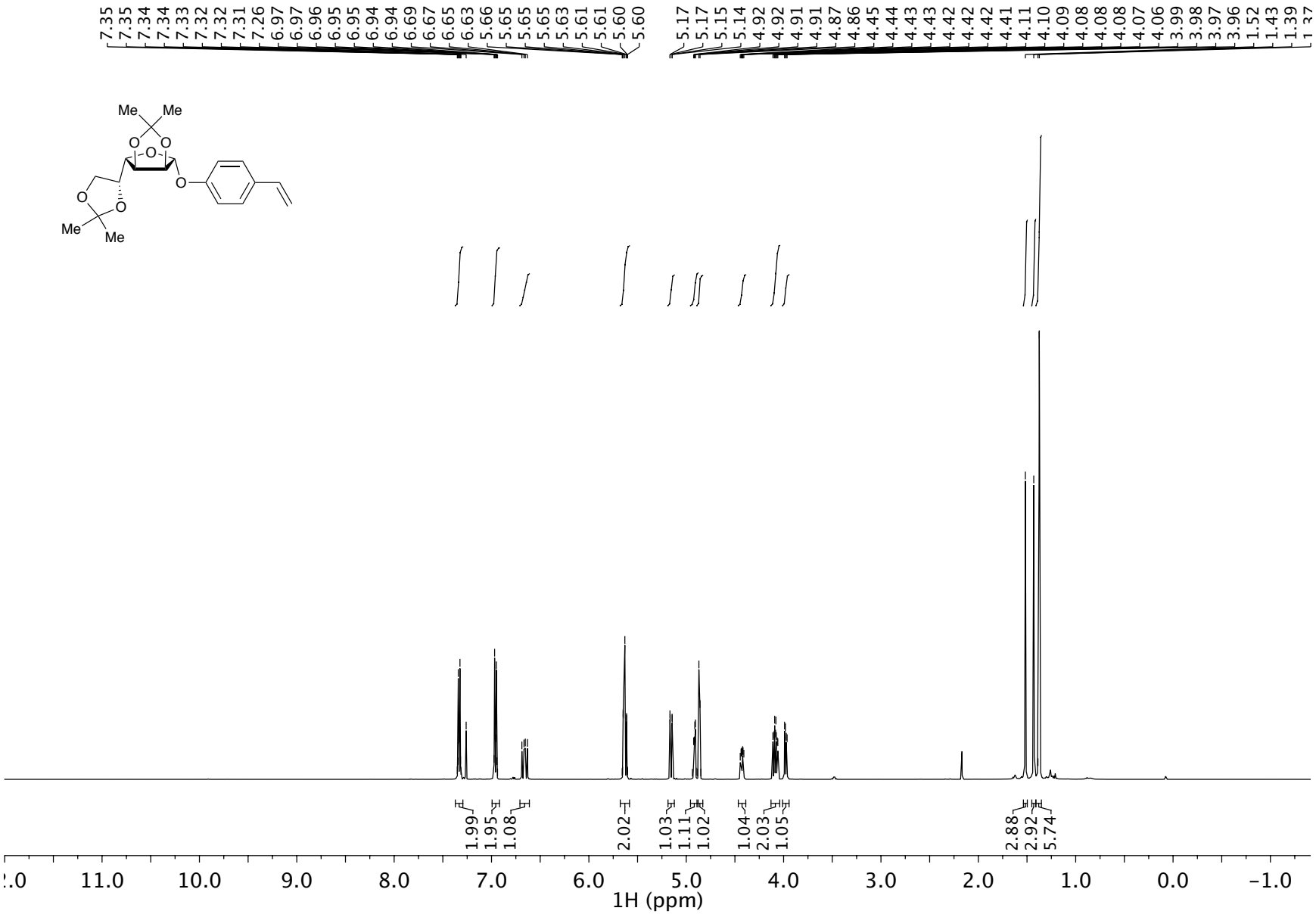
3m – ^{13}C NMR (126 MHz, $CDCl_3$)



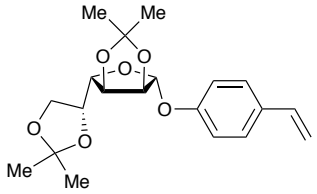
3m – COSY (500 MHz, $CDCl_3$)



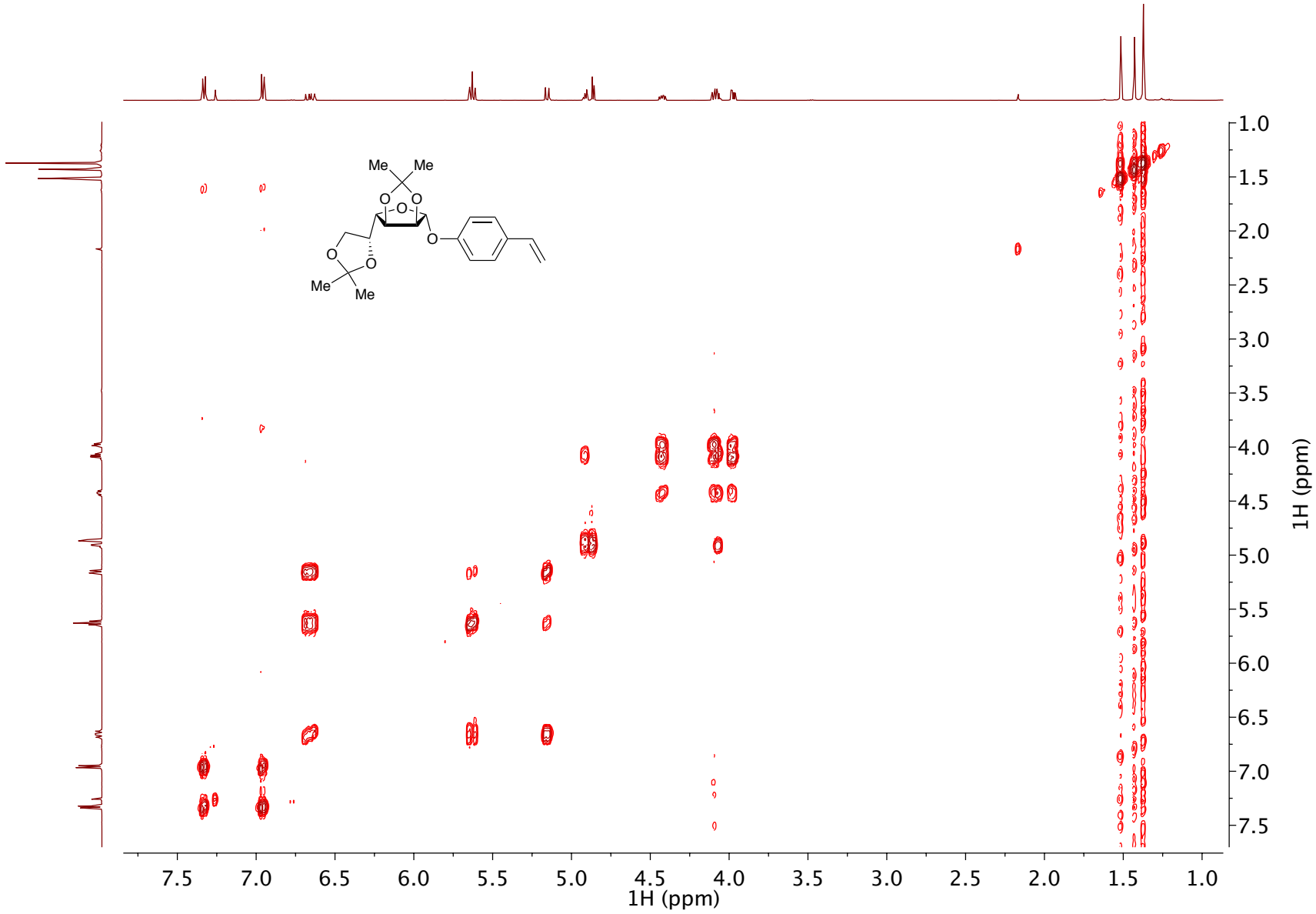
3n – ^{1}H NMR (500 MHz, $CDCl_3$)



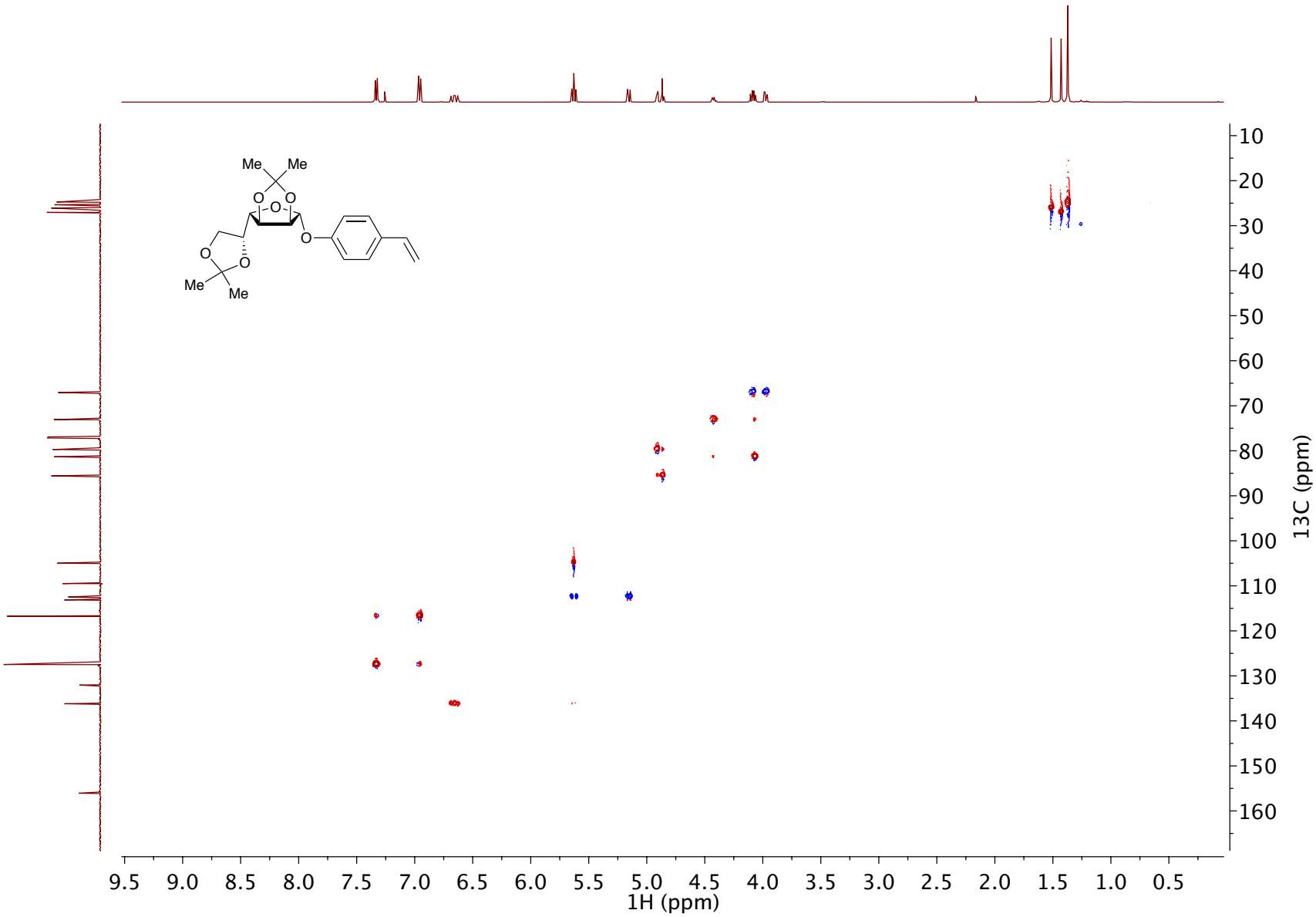
3n – ^{13}C NMR (126 MHz, $CDCl_3$)



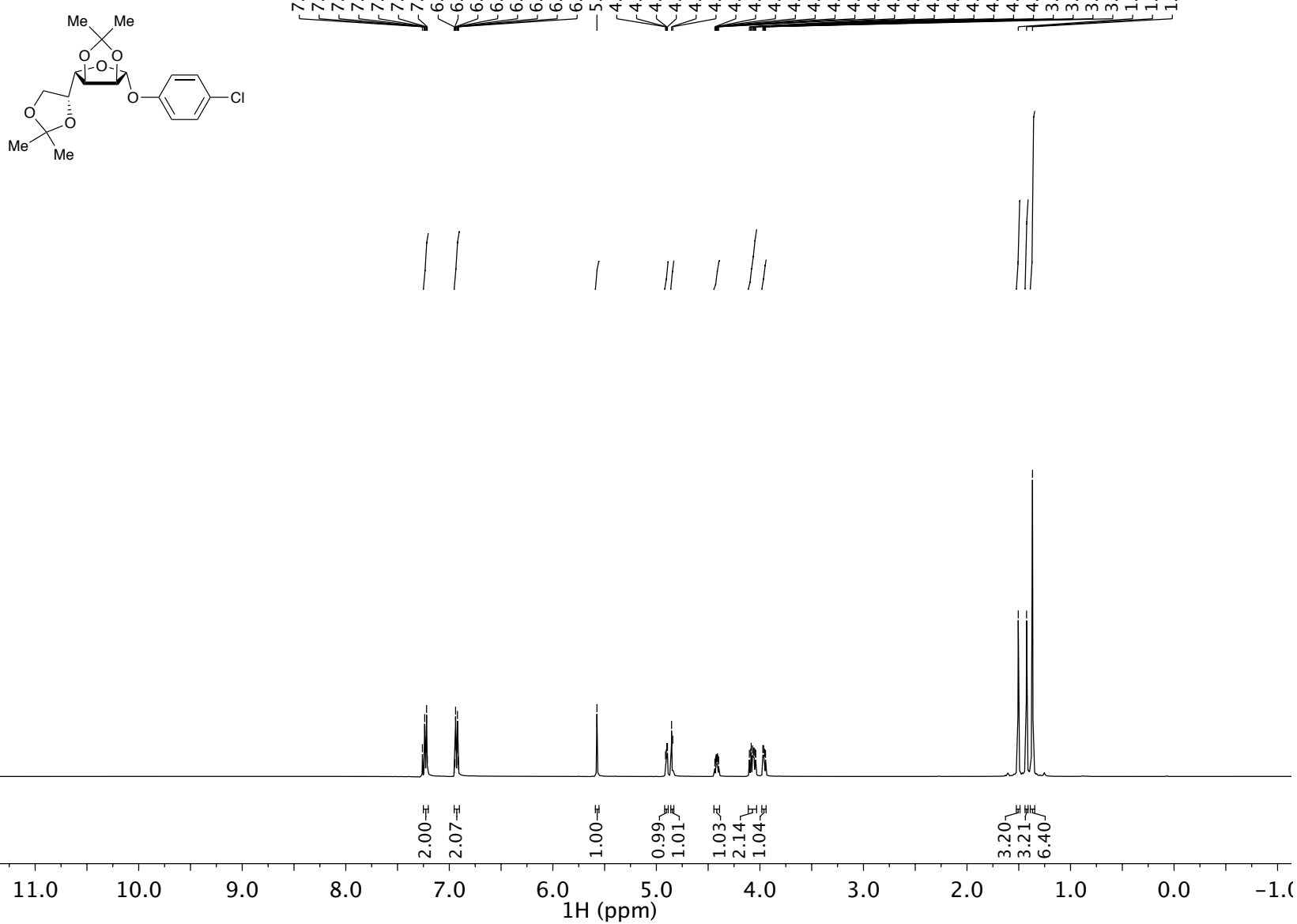
3n – COSY (500 MHz, $CDCl_3$)



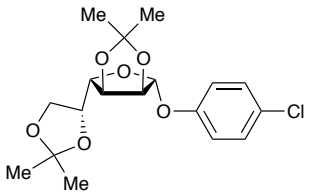
3n – HSQC (500 MHz, $CDCl_3$)



3o –^{1}H NMR (500 MHz, $CDCl_3$)



3o –^{13}C NMR (126 MHz, $CDCl_3$)



3o – COSY (500 MHz, $CDCl_3$)