

A Ring Expansion-Glycosylation Strategy toward the Synthesis of Septano-oligosaccharides

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Supporting Information

Contents:

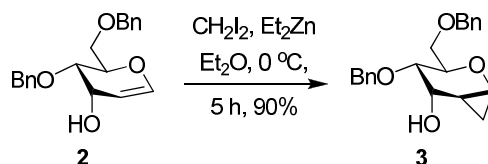
1. General	S2
2. Experimental procedures and spectral data	S3-S22
3. NMR Spectra	S23-S134

1. General:

All the reactions were carried out under nitrogen or argon atmosphere and monitored by thin layer chromatography (TLC) using silica gel GF₂₅₄ plates with detection by charring with 5% (v/v) H₂SO₄ in methanol or by phosphomolybdic acid (PMA) stain or by ultra violet (UV) detection. All the chemicals were purchased from local suppliers and Sigma-Aldrich Chemicals Company. Solvents used in the reactions were distilled over dehydrated agents. Silica-gel (100-200 mesh) was used for column chromatography. ¹H, ¹³C, DEPT, COSY, NOESY spectra were recorded on Bruker 400 MHz and 500 MHz spectrometer in CDCl₃. ¹H NMR chemical shifts were reported in ppm (δ) with TMS as internal standard (δ 0.00) and ¹³C NMR were reported in chemical shifts with solvent reference (CDCl₃, δ 77.00). High resolution mass spectra (HRMS) were obtained in the ESI mode.

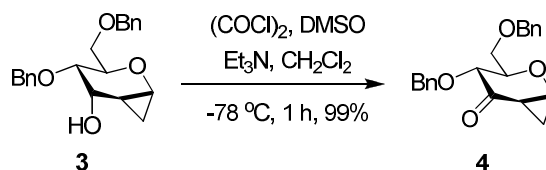
2. Experimental procedures and spectral data:

2.1. 4,6-di-*O*-benzyl-1,5-anhydro-2-deoxy- α -1,2-*C*-methylene-D-*allo*-pyranose 3:



To a solution of **2** (1.5 g, 4.6 mmol) in ether (15 mL) at $0\text{ }^\circ\text{C}$ was added 1 M Et_2Zn in hexane (13.7 mL, 13.7 mmol) and CH_2I_2 (1.2 mL, 13.7 mmol). The mixture was stirred for 5 h at same temperature, then quenched with saturated NH_4Cl solution (75 mL) and extracted with ether (75 mL x 2). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4 . Purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7) provided **3** (1.4 g, 90%) as a colorless solid. $R_f = 0.32$ (2:3 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3):** δ 7.22 - 7.32 (m, 10H), 4.69 (d, 1H, $J = 12.0$ Hz), 4.60 (d, 1H, $J = 12.0$ Hz), 4.58 (d, 1H, $J = 12.0$ Hz), 4.53 (d, 1H, $J = 12.0$ Hz), 4.26 (t, 1H, $J = 7.2$ Hz), 3.74 – 3.78 (m, 1H), 3.68 (dd, 1H, $J = 2.0$ Hz, $J = 10.8$ Hz), 3.56 (dd, 1H, $J = 4.8$ Hz, $J = 10.4$ Hz), 3.41 – 3.45 (m, 1H), 3.23 (dd, 1H, $J = 7.6$ Hz, $J = 9.2$ Hz), 1.34 – 1.42 (m, 1H), 0.66 – 0.76 (m, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 138.2, 137.9, 128.4, 128.2, 127.8, 127.7, 127.5, 79.7, 77.5, 74.0, 73.5, 71.3, 69.1, 53.9, 18.3, 11.4. **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{24}\text{O}_4 + \text{Na}$ 363.1573, found 363.1573.

2.2. Compound 4:



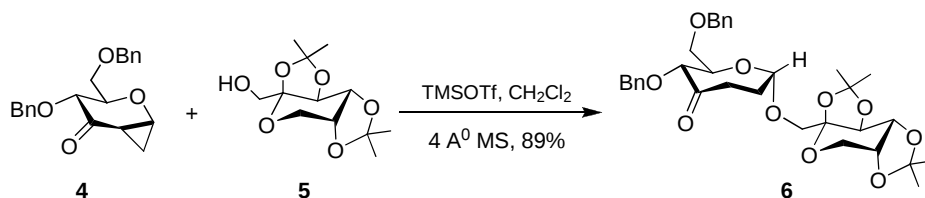
To a solution of $(\text{COCl})_2$ (380 μL , 4.4 mmol) in CH_2Cl_2 (12 mL) at $-78\text{ }^\circ\text{C}$ was added DMSO (520 μL , 7.3 mmol) dropwise. After 10 min of stirring at the same temperature, **3** (1 g, 2.9 mmol) in CH_2Cl_2 (12 mL) was added dropwise for a period of 15 min. After stirring for 30 min at $-78\text{ }^\circ\text{C}$, Et_3N (1.47 mL, 14.5 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH_2Cl_2 (75 mL), washed with water (50 mL x 2), brine (50 mL) and dried over anhydrous Na_2SO_4 . Removal of solvent gave the crude residue which

upon purification by silica-gel column chromatography with ethyl acetate/hexane (3:7) provided D-glucose-derived 1,2-cyclopropa-3-pyranone **4** (980 mg, 99%) as a colorless solid. R_f = 0.58 (2:3 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3):** δ 7.26 - 7.35 (m, 10H), 4.97 (d, 1H, J = 11.2 Hz), 4.59 (d, 1H, J = 12.0 Hz), 4.53 (d, 1H, J = 12.0 Hz), 4.50 (d, 1H, J = 11.2 Hz), 4.17 – 4.20 (m, 1H), 4.00 (ddd, 1H, J = 2.0 Hz, J = 4.4 Hz, J = 10.0 Hz), 3.91 (d, 1H, J = 10.0 Hz), 3.72 (dd, 1H, J = 2.0 Hz, J = 10.8 Hz), 3.62 (dd, 1H, J = 4.4 Hz, J = 10.8 Hz), 1.92 (dt, 1H, J = 6.0 Hz, J = 10.8 Hz), 1.27 – 1.37 (m, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 205.0, 137.8, 137.4, 128.3, 128.3, 128.1, 127.8, 127.7, 127.6, 81.5, 77.6, 74.1, 73.6, 68.8, 57.8, 25.7, 19.8. **HRMS (ESI)** calcd for $\text{C}_{21}\text{H}_{22}\text{O}_4 + \text{Na}$ 361.1416, found 361.1416.

2.3. General procedure for ring expansion-glycosylation reaction:

A suspension of 1,2-cyclopropanated sugar ketone (0.3 mmol), glycosyl acceptor (0.33 mmol) and 4 Å MS powder in dry CH_2Cl_2 (5 mL) was stirred at room temperature for 30 min under argon. After cooling the reaction mixture to $-78\text{ }^\circ\text{C}$, TMSOTf (0.06 mmol) was added dropwise and the solution was warmed slowly to $25\text{ }^\circ\text{C}$ for a period of 1 h and stirred for 3 h at the same temperature. After completion of reaction (by TLC), the reaction mixture was quenched with saturated NaHCO_3 solution (5 mL), filtered through celite and the filter cake was washed with CH_2Cl_2 (20 mL x 2). The organic phase was separated and washed with aq. NaHCO_3 (10 mL x 2), water (10 mL) and brine (5 mL). Removal of CH_2Cl_2 under reduced pressure provided the crude disaccharide which upon purification by silica-gel column chromatography (ethyl acetate/hexane) afforded pure septanosyl disaccharide.

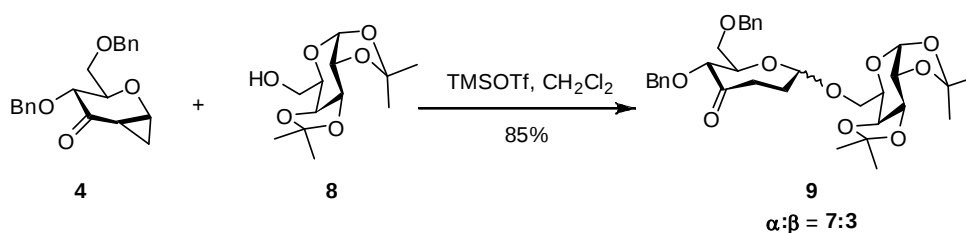
2.4. Compound 6:



Compound **6** was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone **4** (100 mg, 0.29 mmol), glycosyl acceptor **5** (84 mg, 0.32 mmol), TMSOTf (10 μL , 0.05 mmol) and 4 Å MS power in CH_2Cl_2 (5 mL) according to the general procedure for ring expansion-glycosylation

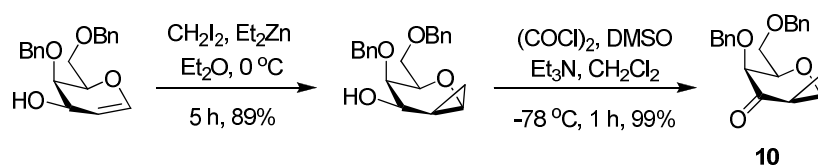
reaction (2.3). The reaction mixture was stirred at -78 °C for 1 h and at 25 °C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to afford septanosyl disaccharide **6** (156 mg, 89%) as a colorless oil. $R_f = 0.53$ (2:3 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3):** δ 7.26 - 7.31 (m, 10H), 4.96 (dd, 1H, $J = 4.4$ Hz, $J = 8.0$ Hz), 4.58-4.64 (m, 3H), 4.49 (d, 1H, $J = 12.0$ Hz), 4.41 (d, 1H, $J = 12.0$ Hz), 4.34 (d, 1H, $J = 2.8$ Hz), 4.22 – 4.27 (m, 2H), 4.01 (d, 1H, $J = 7.2$ Hz), 3.96 (d, 1H, $J = 10.4$ Hz), 3.90 (d, 1H, $J = 12.8$ Hz), 3.73 (d, 1H, $J = 12.8$ Hz), 3.67 (dd, 1H, $J = 4.0$ Hz, $J = 10.0$ Hz), 3.57 (dd, 1H, $J = 4.0$ Hz, $J = 10.0$ Hz), 3.52 (d, 1H, $J = 10.4$ Hz), 2.58 (ddd, 1H, $J = 2.8$ Hz, $J = 6.4$ Hz, $J = 14.4$ Hz), 2.44 (td, 1H, $J = 2.8$ Hz, $J = 14.4$ Hz), 2.25 – 2.32 (m, 1H), 2.05 – 2.10 (m, 1H), 1.52 (s, 3H), 1.46 (s, 3H), 1.38 (s, 3H), 1.34 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 208.4, 137.9, 137.3, 128.3, 128.1, 127.9, 127.8, 127.7, 127.6, 108.9, 108.5, 102.2, 100.5, 84.1, 73.4, 73.0, 70.9, 70.4, 70.1, 70.0, 69.1, 68.5, 61.0, 35.6, 28.0, 26.5, 25.9, 25.3, 24.0. **HRMS (ESI)** calcd for $\text{C}_{33}\text{H}_{42}\text{O}_{10} + \text{Na}$ 621.2676, found 621.2686.

2.5. Compounds **9 α** and **9 β** :



Compound **6** was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone **4** (120 mg, 0.35 mmol), sugar acceptor **8** (100 mg, 0.38 mmol), TMSOTf (12 μL , 0.07 mmol) and 4 Å MS power in CH_2Cl_2 (6 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78 °C for 1 h and room temperature for 2 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to afford septanosyl disaccharides **9 α** and **9 β** (180 mg, 85%) as an inseparable mixture.

2.6. 4,6-di-O-benzyl-1,5-anhydro-2-deoxy- α -1,2-C-methylene-D-galacto-pyranose:

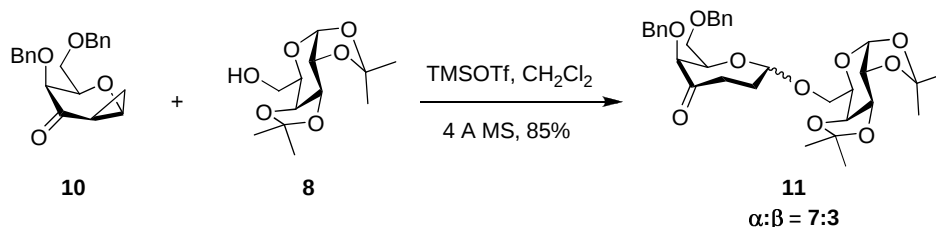


To a solution of 4,6-di-*O*-benzyl-D-galactal (1 g, 3.06 mmol) in ether (10 mL) at 0 °C was added 1 M Et₂Zn in hexane (9.2 mL, 9.2 mmol) and CH₂I₂ (0.74 mL, 9.19 mmol). The mixture was stirred for 5 h at same temperature, then quenched with saturated NH₄Cl solution (75 mL) and extracted with ether (50 mL x 2). The combined organic layers were washed with water (30 mL), brine (30 mL) and dried over anhydrous Na₂SO₄. Purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (2:3) provided 4,6-di-*O*-benzyl-1,5-anhydro-2-deoxy- α -1,2-C-methylene-D-galacto-pyranose (0.92 g, 89%) as a colorless oil. *R*_f = 0.32 (2:3 ethyl acetate/hexane). *R*_f = 0.32 (2:3 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.23 – 7.31 (m, 10H), 4.61 (d, 1H, *J* = 11.6 Hz), 4.53 (d, 1H, *J* = 11.6 Hz), 4.51 (d, 1H, *J* = 11.6 Hz), 4.40 (d, 1H, *J* = 11.6 Hz), 4.16 (t, 1H, *J* = 6.0 Hz), 3.73 – 3.79 (m, 2H), 3.50 – 3.56 (m, 2H), 3.38 – 3.41 (m, 1H), 1.19 -1.25 (m, 1H), 1.09 -1.10 (m, 1H), 0.58 – 0.61 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 138.0, 137.6, 128.3, 127.8, 127.6, 127.5, 76.4, 75.6, 75.5, 73.3, 68.8, 65.3, 54.0, 16.9, 11.1. **HRMS (ESI)** calcd for C₂₁H₂₄O₄+Na 363.1573, found 363.1573.

2.7. Compound 10:

To a solution of oxaloyl chloride (342 μ L, 3.96 mmol) in CH₂Cl₂ (10 mL) at -78 °C was added DMSO (468 μ L, 6.6 mmol) dropwise. After 10 min of stirring at the same temperature, 4,6-di-*O*-benzyl-1,5-anhydro-2-deoxy- α -1,2-C-methylene-D-galacto-pyranose (0.9 g, 2.64 mmol) in CH₂Cl₂ (10 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et₃N (1.8 mL, 13.0 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH₂Cl₂ (75 mL), washed with water (50 mL x 2), brine (50 mL) and dried over anhydrous Na₂SO₄. Removal of solvent gave the crude residue which upon purification by silica-gel column chromatography with ethyl acetate/hexane (3:7) provided D-galactose-derived 1,2-cyclopropa-3-pyranone 10 (885 mg, 99%) as a colorless liquid. *R*_f = 0.64 (2:3 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.23 – 7.32 (m, 10H), 4.61 (d, 1H, *J* = 11.6 Hz), 4.52 (d, 1H, *J* = 11.6 Hz), 4.40 (d, 1H, *J* = 12.0 Hz), 4.38 (d, 1H, *J* = 12.0 Hz), 4.16 – 4.19 (m, 1H), 4.03 (t, 1H, *J* = 6.0 Hz), 3.62 – 3.66 (m, 2H), 3.48 (dd, 1H, *J* = 6.0 Hz, *J* = 9.6 Hz), 1.83 – 1.87 (m, 1H), 1.72 – 1.78 (m, 1H), 1.23 – 1.28 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 201.9, 137.6, 136.8, 128.2, 128.0, 127.8, 127.6, 80.0, 79.5, 73.4, 71.5, 68.3, 58.0, 23.8, 19.0. **HRMS (ESI)** calcd for C₂₁H₂₂O₄+Na 361.1416, found 361.1416.

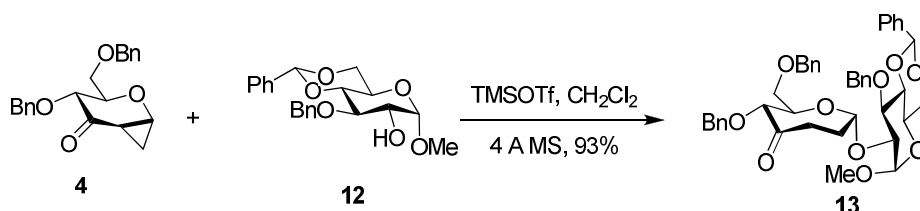
2.8. Compounds **11 α** and **11 β** :



Compound **11** was synthesized using D-galactose-derived 1,2-cyclopropa-3-pyranone **10** (150 mg, 0.44 mmol), sugar acceptor **8** (126 mg, 0.48 mmol), TMSOTf (15 μ L, 0.08 mmol) and 4 Å MS powder in CH_2Cl_2 (8 mL) according to the general procedure for ring expansion-glycosylation reaction (**2.3**). The reaction mixture was stirred at -78°C for 1 h and then at room temperature for 5 h. The obtained crude product was purified and separated by silica-gel column chromatography (ethyl acetate/hexane 3:7 to 2:3) to give septanosyl disaccharides **11 α** (156 mg) and **11 β** (66 mg) (85% combined yield). **11 β** : colorless oil. $R_f = 0.66$ (2:3 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3)**: δ 7.22 - 7.32 (m, 10H), 5.47 (d, 1H, $J = 5.2$ Hz), 5.02 (dd, 1H, $J = 4.4$ Hz, $J = 6.4$ Hz), 4.67 (d, 1H, $J = 11.6$ Hz), 4.59 (dd, 1H, $J = 2.4$ Hz, $J = 8.0$ Hz), 4.45 (d, 1H, $J = 12.0$ Hz), 4.40 (d, 1H, $J = 12.0$ Hz), 4.37 (d, 1H, $J = 12.0$ Hz), 4.29 (dd, 1H, $J = 2.4$ Hz, $J = 5.2$ Hz), 4.19 - 4.23 (m, 1H), 4.18 (dd, 1H, $J = 1.6$ Hz, $J = 8.0$ Hz), 3.95 (d, 1H, $J = 1.2$ Hz), 3.92 (dd, 1H, $J = 1.6$ Hz, $J = 6.4$ Hz), 3.86 (dd, 1H, $J = 6.4$ Hz, $J = 10.0$ Hz), 3.69 (dd, 1H, $J = 6.4$ Hz, $J = 10.0$ Hz), 3.58-3.64 (m, 2H), 2.66 (ddd, 1H, $J = 3.2$ Hz, $J = 9.6$ Hz, $J = 13.6$ Hz), 2.46 (ddd, 1H, $J = 2.4$ Hz, $J = 5.6$ Hz, $J = 13.6$ Hz), 2.19 - 2.27 (m, 1H), 1.73 - 1.81 (m, 1H), 1.51 (s, 3H), 1.41 (s, 3H), 1.32 (bs, 6H). **^{13}C NMR (100 MHz, CDCl_3)**: δ 209.3, 137.9, 137.1, 128.4, 128.3, 128.3, 127.9, 127.6, 127.5, 109.2, 108.5, 99.3, 96.2, 82.8, 73.1, 73.0, 70.9, 70.6, 70.5, 68.7, 66.2, 66.0, 65.9, 34.9, 28.6, 26.0, 25.9, 24.8, 24.5. **HRMS (ESI)** calcd for $\text{C}_{33}\text{H}_{42}\text{O}_{10} + \text{Na}$ 621.2676, found 621.2693. **11 α** : colorless oil. $R_f = 0.33$ (2:3 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3)**: δ 7.25 - 7.34 (m, 10H), 5.51 (d, 1H, $J = 5.2$ Hz), 4.74 (d, 1H, $J = 11.6$ Hz), 4.53 - 4.57 (m, 2H), 4.48 (d, 1H, $J = 11.6$ Hz), 4.45 (d, 1H, $J = 11.6$ Hz), 4.43 (d, 1H, $J = 11.6$ Hz), 4.27 (dd, 1H, $J = 2.4$ Hz, $J = 4.8$ Hz), 4.10 (dd, 1H, $J = 1.2$ Hz, $J = 8.0$ Hz), 4.03 (d, 1H, $J = 2.4$ Hz), 3.92 - 3.98 (m, 3H), 3.70 (dd, 1H, $J = 6.4$ Hz, $J = 8.8$ Hz), 3.62 (dd, 1H, $J = 8.8$ Hz, $J = 12.4$ Hz), 2.70 (dt, 1H, $J = 6.0$ Hz, $J = 13.2$ Hz), 2.39 (dt, 1H, $J = 7.2$ Hz, $J = 13.2$ Hz), 2.01 - 2.06 (m, 2H), 1.51 (s, 3H), 1.40 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H).

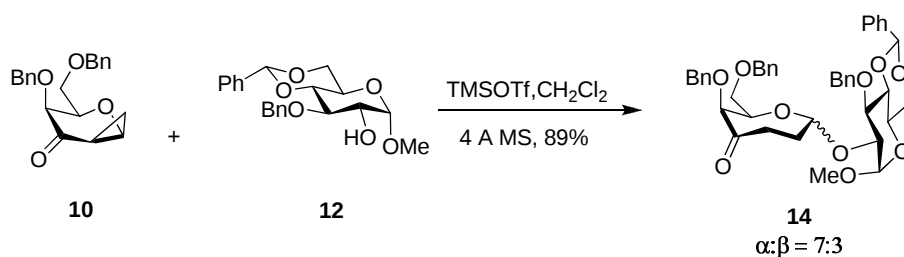
¹³C NMR (100 MHz, CDCl₃): δ 210.6, 137.9, 137.2, 128.3, 128.3, 128.1, 127.8, 127.6, 127.6, 109.2, 108.6, 106.2, 96.2, 85.3, 76.0, 73.4, 73.3, 71.4, 70.6, 70.4, 69.1, 67.8, 67.7, 34.8, 30.6, 26.0, 25.9, 24.9, 24.4. **HRMS (ESI)** calcd for C₃₃H₄₂O₁₀+Na 621.2676, found 621.2686.

2.9. Compound 13:



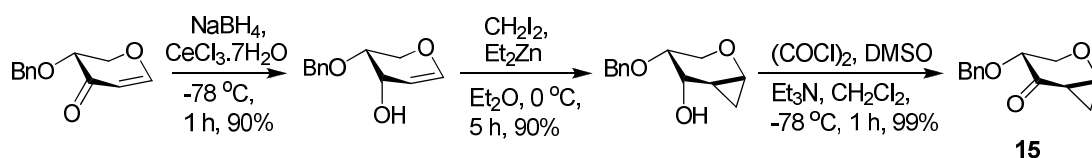
Compound **13** was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone **4** (100 mg, 0.29 mmol), sugar acceptor **12** (118 mg, 0.32 mmol), TMSOTf (10 μL, 0.05 mmol) and 4 Å MS power in CH₂Cl₂ (5 mL) according to the general procedure for ring expansion-glycosylation reaction (**2.3**). The reaction mixture was stirred at -78 °C for 5 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to afford septanosyl disaccharide **13** (195 mg, 93%) as a thick gum. *R_f* = 0.7 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.46 – 7.48 (m, 2H), 7.24 – 7.38 (m, 18H), 5.47 (s, 1H), 4.97 (dd, 1H, *J* = 2.8 Hz, *J* = 9.2 Hz), 4.87 (d, 1H, *J* = 11.6 Hz), 4.84 (d, 1H, *J* = 3.6 Hz), 4.67 (d, 1H, *J* = 11.6 Hz), 4.51 – 4.54 (m, 3H), 4.34 (d, 1H, *J* = 11.6 Hz), 4.24 (dd, 1H, *J* = 4.8 Hz, *J* = 10.4 Hz), 3.97 (t, 1H, *J* = 9.2 Hz), 3.75 – 3.87 (m, 3H), 3.61 – 3.65 (m, 2H), 3.52 – 3.59 (m, 2H), 3.43 (t, 1H, *J* = 9.2 Hz), 3.38 (s, 3H), 2.80 (td, 1H, *J* = 4.4 Hz, *J* = 12.4 Hz), 2.26 (dt, 1H, *J* = 4.8 Hz, *J* = 12.0 Hz), 2.02 – 2.07 (m, 1H), 1.85 – 1.95 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 208.7, 138.6, 137.8, 137.3, 136.7, 128.8, 128.4, 128.3, 128.2, 128.1, 128.1, 127.6, 127.5, 125.9, 108.2, 101.0, 100.1, 84.6, 82.2, 78.3, 77.9, 77.8, 75.1, 73.2, 72.3, 70.8, 68.9, 62.0, 55.1, 33.7, 33.0. **HRMS (ESI)** calcd for C₄₂H₄₆O₁₀+Na 733.2989, found 733.2989.

2.10. Compound 14α and 14β:



Compound **14** was synthesized using D-galactose-derived 1,2-cyclopropa-3-pyranone **10** (135 mg, 0.39 mmol), sugar acceptor **12** (163 mg, 0.43 mmol), TMSOTf (14 μ L, 0.07 mmol) and 4 Å MS powder in CH₂Cl₂ (7 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78 °C for 1 h and at room temperature for 3 h. The obtained crude product was purified and separated by silica-gel column chromatography (ethyl acetate/hexane 3:7 to 2:3) as clean septanosyl disaccharides **14a** (176 mg) and **14b** (75 mg) (89% combined yield). **14b**: colorless solid. R_f = 0.45 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃)**: δ 7.45 – 7.48 (m, 2H), 7.24 – 7.37 (m, 18H), 5.44 (s, 1H), 4.77 – 4.88 (m, 4H), 4.65 (d, 1H, J = 11.6 Hz), 4.52 (d, 1H, J = 11.6 Hz), 4.44 (d, 1H, J = 11.6 Hz), 4.42 (d, 1H, J = 11.6 Hz), 4.22 (dd, 1H, J = 4.8 Hz, J = 10.0 Hz), 4.01 – 4.05 (m, 2H), 3.96 (t, 1H, J = 9.2 Hz), 3.82 (dd, 1H, J = 3.6 Hz, J = 9.6 Hz), 3.71 – 3.79 (m, 2H), 3.56 – 3.61 (m, 2H), 3.39 – 3.41 (m, 4H), 2.55 – 2.60 (m, 1H), 2.33 – 2.40 (m, 1H), 1.98 – 2.03 (m, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ 209.5, 138.7, 138.0, 137.3, 137.0, 128.8, 128.3, 128.2, 128.1, 128.0, 127.6, 127.6, 127.9, 108.4, 101.0, 100.2, 85.3, 82.3, 78.4, 77.6, 75.1, 73.5, 73.3, 70.0, 68.9, 62.0, 55.1, 34.8, 31.6. **HRMS (ESI)** calcd for C₄₂H₄₆O₁₀+Na 733.2989, found 733.2989. **14a**: colorless oil. R_f = 0.3 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃)**: δ 7.17 – 7.46 (m, 20H), 5.49 (s, 1H), 5.11 – 5.12 (m, 1H), 4.89 (d, 1H, J = 3.6 Hz), 4.79 (d, 1H, J = 11.6 Hz), 4.72 (d, 1H, J = 11.6 Hz), 4.65 (1H, J = 12.0 Hz), 4.34 – 4.41 (m, 2H), 4.21 – 4.29 (m, 3H), 4.02 (dd, 1H, J = 3.6 Hz, J = 9.6 Hz), 3.87 – 3.92 (m, 2H), 3.73 – 3.78 (m, 1H), 3.61 – 3.69 (m, 2H), 3.52 (t, 1H, J = 8.4 Hz), 3.42 – 3.47 (m, 1H), 3.39 (s, 3H), 2.62 – 2.66 (m, 1H), 2.52 – 2.56 (m, 1H), 2.27 – 2.34 (m, 1H), 1.80 – 1.83 (m, 1H). **¹³C NMR (100 MHz, CDCl₃)**: δ 208.9, 138.7, 138.2, 137.3, 137.0, 128.8, 128.4, 128.3, 128.1, 128.0, 127.5, 127.3, 125.9, 123.9, 101.1, 97.1, 95.6, 82.7, 81.8, 75.2, 73.6, 73.1, 72.8, 68.8, 68.7, 66.1, 62.2, 55.1, 34.7, 31.4. **HRMS (ESI)** calcd for C₄₂H₄₆O₁₀+Na 733.2989, found 733.2989.

2.11. Compound 15:



4-O-benzyl-D-arabinal: To a solution of sugar enone (2 g, 9.8 mmol) and CeCl₃·7H₂O (5.47 g, 14.7 mmol) in MeOH (30 mL) at -78 °C was added cooled (-10 °C) solution of NaBH₄

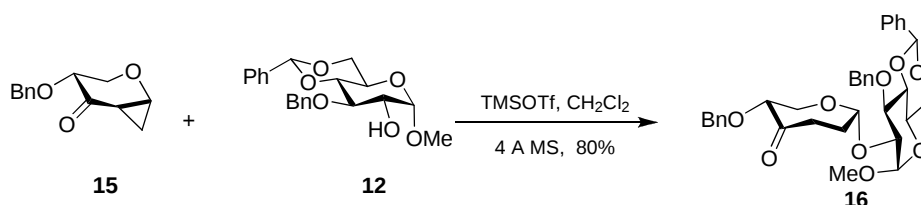
(556 mg, 14.7 mmol) in MeOH (12 mL) dropwise for a period of 10 min. The solution was stirred for 1 h at -78 °C, then quenched with saturated NH₄Cl and extracted twice with ethyl acetate (100 mL x 2). The combined organic layers were washed with water (75 mL), brine (75 mL) and dried (Na₂SO₄). Removal of solvent and purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (1:4) gave 4-*O*-benzyl-D-arabinal (1.8 g, 90%) as a colorless oil. *R*_f = 0.6 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.29 – 7.35 (m, 5H), 6.38 (d, 1H, *J* = 6.0 Hz), 4.86 (dd, 1H, *J* = 5.2 Hz, *J* = 6.0 Hz), 4.65 (s, 1H), 4.64 (s, 1H), 4.21 (t, 1H, *J* = 4.4 Hz), 3.92 (s, 1H), 3.90 (s, 1H), 3.70 (dd, 1H, *J* = 4.0 Hz, *J* = 6.0 Hz), 3.68 (dd, 1H, *J* = 4.0 Hz, *J* = 6.0 Hz), 2.59 (bs, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 146.2, 137.4, 128.4, 128.0, 127.7, 100.9, 73.1, 71.3, 62.3, 60.6. **HRMS (ESI)** calcd for C₂₁H₂₄O₄+Na 229.0841, found 229.0841.

4-*O*-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-D-arabino-pyranose: To a solution of 4-*O*-benzyl-D-arabinal (700 mg, 3.39 mmol) in ether (10 mL) at 0 °C was added 1 M Et₂Zn in hexane (10.2 mL, 10.2 mmol) and CH₂I₂ (0.81 mL, 10.18 mmol). The mixture was stirred for 5 h at same temperature, then quenched with saturated NH₄Cl solution (75 mL) and extracted with ether (50 mL x 2). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. Removal of solvent followed by purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7 to 2:3) provided 4-*O*-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-D-arabino-pyranose (672 mg, 90%) as a colorless liquid. *R*_f = 0.27 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.26 – 7.33 (m, 5H), 4.64 (d, 1H, *J* = 11.6 Hz), 4.37 (d, 1H, *J* = 11.6 Hz), 4.17 (bs, 1H), 3.83 (dd, 1H, *J* = 3.2 Hz, *J* = 12.4 Hz), 3.70 – 3.74 (m, 1H), 3.57 – 3.59 (m, 1H), 3.25 (d, 1H, *J* = 12.4 Hz), 2.79 (d, 1H, *J* = 9.6 Hz), 1.14 – 1.25 (m, 2H), 0.57 – 0.62 (m, 1H). **¹³C NMR (100 MHz, CDCl₃):** δ 137.6, 128.2, 127.6, 127.5, 74.9, 71.1, 64.1, 63.9, 53.9, 16.4, 10.8. **HRMS (ESI)** calcd for C₁₃H₁₆O₃+Na 243.0997, found 243.0997.

Compound 15: To a solution of (COCl)₂ (293 μL, 3.40 mmol) in CH₂Cl₂ (8 mL) at -78 °C was added DMSO (403 μL, 5.67 mmol) dropwise. After 10 min of stirring at the same temperature, the above 4-*O*-benzyl-1,5-anhydro-2-deoxy-α-1,2-C-methylene-D-arabino-pyranose (500 mg, 2.27 mmol) in CH₂Cl₂ (8 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et₃N (1.5 mL, 11.2 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH₂Cl₂ (50 mL), washed with water (25 mL x 2), brine

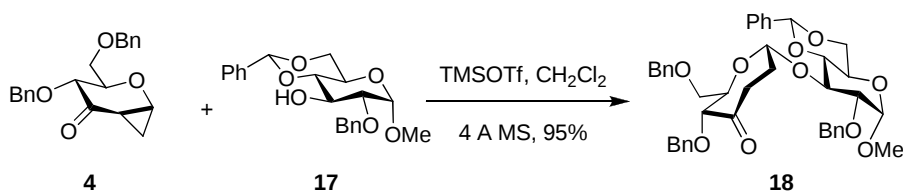
(25 mL) and dried over anhydrous Na₂SO₄. Removal of solvent gave the crude residue which upon purification by silica-gel column chromatography with ethyl acetate/hexane (1:4) provided compound **15** (490 mg, 99%) as a colorless oil. *R_f* = 0.48 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.26 – 7.34 (m, 5H), 4.90 (d, 1H, *J* = 12.0 Hz), 4.59 (d, 1H, *J* = 12.0 Hz), 4.13 (dd, 1H, *J* = 4.0 Hz, *J* = 9.6 Hz), 3.94 (dd, 1H, *J* = 5.2 Hz, *J* = 10.0 Hz), 3.85 (dd, 1H, *J* = 5.6 Hz, *J* = 10.4 Hz), 3.74 (t, 1H, *J* = 10.4 Hz), 1.85 – 1.91 (m, 1H), 1.25 – 1.29 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 204.0, 137.3, 128.3, 127.8, 127.7, 76.3, 73.0, 71.0, 59.1, 25.7, 19.5. **HRMS (ESI)** calcd for C₁₃H₁₄O₃+Na 241.0841, found 241.0841.

2.12. Compound 16:



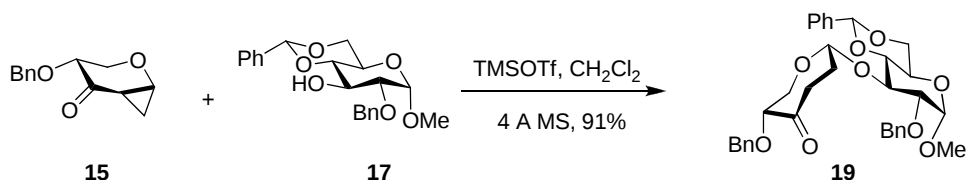
Compound **16** was synthesized using D-arabinose-derived 1,2-cyclopropa-3-pyranone **15** (100 mg, 0.45 mmol), sugar acceptor **12** (187 mg, 0.5 mmol), TMSOTf (16 μL, 0.09 mmol) and 4 Å MS powder in CH₂Cl₂ (5 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78 °C for 5 h. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septanosyl disaccharide **16** (216 mg, 80%) as a semi solid. *R_f* = 0.46 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.47 – 7.49 (m, 2H), 7.25 – 7.39 (m, 13H), 5.57 (s, 1H), 5.00 (dd, 1H, *J* = 4 Hz, 8.8 Hz), 4.88 (d, 1H, *J* = 11.6 Hz), 4.79 (d, 1H, *J* = 3.6 Hz), 4.72 (d, 1H, *J* = 12.0 Hz), 4.68 (d, 1H, *J* = 12.0 Hz), 4.37 (d, 1H, *J* = 12.0 Hz), 4.27 – 4.33 (m, 2H), 4.18 (dd, 1H, *J* = 4.8 Hz, *J* = 6.0 Hz), 3.95 (t, 1H, *J* = 9.6 Hz), 3.82 (td, 1H, *J* = 4.4 Hz, *J* = 9.6 Hz), 3.75 (dd, 1H, *J* = 9.6 Hz, *J* = 10.4 Hz), 3.69 (dd, 1H, *J* = 3.6 Hz, *J* = 9.6 Hz), 3.62 (dd, 1H, *J* = 9.2 Hz, *J* = 8.4 Hz), 3.58 (dd, 1H, *J* = 4.4 Hz, *J* = 13.2 Hz), 3.41 (s, 3H), 2.49 (dtd, 1H, *J* = 3.2 Hz, *J* = 12.4 Hz, *J* = 16.0 Hz), 2.34 (ddd, 1H, *J* = 3.6 Hz, *J* = 5.2 Hz, *J* = 16.0 Hz), 1.92 – 2.09 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 207.6, 138.6, 137.6, 137.2, 128.9, 128.5, 128.3, 128.2, 128.1, 127.7, 126.0, 103.7, 101.2, 99.9, 82.2, 82.2, 79.0, 78.1, 75.2, 72.2, 69.0, 62.1, 61.5, 55.3, 35.5, 28.3. **HRMS (ESI)** calcd for C₃₄H₃₈O₉+Na 613.2414, found 613.2414.

2.13. Compound 18:



Compound **18** was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone **4** (250 mg, 0.73 mmol), glycosyl acceptor **17** (302 mg, 0.81 mmol), TMSOTf (26 μL , 0.14 mmol) and 4 Å MS powder in CH_2Cl_2 (13 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78°C for 1 h and at 25°C for 3 h. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to afford septanosyl disaccharide **18** (498 mg, 95%) as a thick gum. $R_f = 0.6$ (2:3 ethyl acetate/hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.46 – 7.48 (m, 2H), 7.20 – 7.36 (m, 18H), 5.48 (s, 1H), 5.09 (dd, 1H, $J = 2.0\text{ Hz}$, 8.8 Hz), 4.72 (d, 1H, $J = 12.0\text{ Hz}$), 4.62 (d, 1H, $J = 12.0\text{ Hz}$), 4.55 (d, 1H, $J = 3.6\text{ Hz}$), 4.46 (d, 1H, $J = 12.0\text{ Hz}$), 4.33 (bs, 2H), 4.29 (d, 1H, $J = 12.0\text{ Hz}$), 4.20 (dd, 1H, $J = 4.4\text{ Hz}$, $J = 6.0\text{ Hz}$), 4.11 (t, 1H, $J = 9.6\text{ Hz}$), 3.78 – 3.84 (m, 2H), 3.73 (td, 1H, $J = 4.4\text{ Hz}$, $J = 10.0\text{ Hz}$), 3.65 (t, 1H, $J = 10.4\text{ Hz}$), 3.49 – 3.54 (m, 2H), 3.37 – 3.41 (m, 2H), 3.34 (s, 3H), 2.80 (td, 1H, $J = 4.8\text{ Hz}$, $J = 12.0\text{ Hz}$), 2.26 (dt, 1H, $J = 5.2\text{ Hz}$, $J = 12.0\text{ Hz}$), 2.02 – 2.06 (m, 1H), 1.83 – 1.92 (m, 1H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 209.5, 138.2, 137.8, 137.4, 137.0, 128.8, 128.5, 128.3, 128.1, 128.0, 127.9, 127.8, 127.6, 127.3, 126.3, 106.1, 101.3, 98.7, 85.4, 79.8, 79.6, 78.1, 76.7, 73.4, 73.2, 72.2, 70.3, 68.8, 62.5, 55.2, 33.9, 32.1. HRMS (ESI) calcd for $\text{C}_{42}\text{H}_{46}\text{O}_{10} + \text{Na}$ 733.2989, found 733.3007.

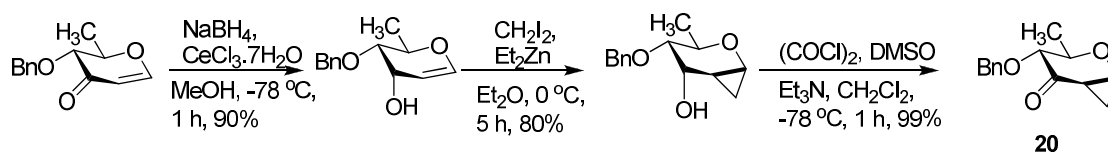
2.14. Compound 19:



Compound **19** was synthesized using D-arabinose-derived 1,2-cyclopropa-3-pyranone **15** (80 mg, 0.36 mmol), glycosyl acceptor **17** (150 mg, 0.4 mmol), TMSOTf (13 μL , 0.07 mmol) and 4 Å MS powder in CH_2Cl_2 (5 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78°C for 1 h and at 25°C for 3

h. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) to afford septanosyl disaccharide **19** (197 mg, 91%) as white solid. $R_f = 0.37$ (3:7 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3):** δ 7.17 – 7.45 (m, 15H), 5.49 (s, 1H), 5.20 (dd, 1H, $J = 4.0$ Hz, $J = 8.0$ Hz), 4.67 (d, 1H, $J = 12.4$ Hz), 4.59–4.63 (m, 2H), 4.55 (d, 1H, $J = 12.4$ Hz), 4.32 (d, 1H, $J = 12.4$ Hz), 4.27 (dd, 1H, $J = 5.6$ Hz, $J = 14.4$ Hz), 4.24 (dd, 1H, $J = 4.8$ Hz, $J = 10.0$ Hz), 4.21 (dd, 1H, $J = 9.6$ Hz, $J = 18.8$ Hz), 3.94 (dd, 1H, $J = 4.4$ Hz, $J = 5.6$ Hz), 3.81 (td, 1H, $J = 4.4$ Hz, $J = 9.6$ Hz), 3.68 (t, 1H, $J = 10.0$ Hz), 3.50 (dd, 1H, $J = 3.6$ Hz, $J = 9.6$ Hz), 3.45 (t, 1H, $J = 9.6$ Hz), 3.32 – 3.38 (m, 4H), 2.43 (dtd, 1H, $J = 3.6$ Hz, $J = 11.6$ Hz, $J = 16.4$ Hz), 2.33 (ddd, 1H, $J = 3.6$ Hz, $J = 6.8$ Hz, $J = 16.4$ Hz), 2.00 – 2.08 (m, 1H), 1.76 – 1.85 (m, 1H). **^{13}C NMR (100 MHz, CDCl_3):** δ 208.2, 137.7, 137.4, 137.2, 129.1, 128.5, 128.3, 128.2, 127.9, 127.6, 126.2, 101.7, 100.7, 98.5, 82.5, 80.3, 80.0, 74.1, 73.1, 71.4, 69.0, 62.5, 60.5, 55.3, 35.5, 28.2. **HRMS (ESI)** calcd for $\text{C}_{34}\text{H}_{38}\text{O}_9 + \text{Na}$ 613.2414, found 613.2414.

2.15. Compounds 20:

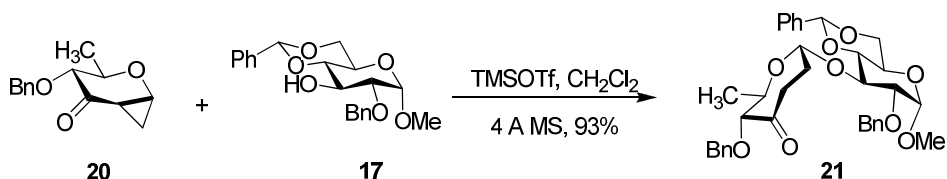


6-deoxy-4-O-benzyl-D-allal: To a solution of D-rhamnose derived enone (1 g, 4.58 mmol) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (2.56 g, 6.87 mmol) in MeOH (20 mL) at -78°C was added cooled (-10°C) solution of NaBH_4 (260 mg, 6.87 mmol) in MeOH (7 mL) dropwise for a period of 10 min. The solution was stirred for 1 h at -78°C , then quenched with saturated NH_4Cl solution (30 mL) and extracted twice with ethyl acetate (50 mL x 2). The combined organic layers were washed with water (25 mL), brine (25 mL) and dried (Na_2SO_4). Removal of solvent and purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7 to 2:3) provided 6-deoxy-4-O-benzyl-D-allal (0.9 g, 90%) as crystalline needles. $R_f = 0.61$ (3:7 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3):** δ 7.24 – 7.35 (m, 5H), 6.30 (dd, 1H, $J = 1.2$ Hz, $J = 6.0$ Hz), 4.83 (d, 1H, $J = 11.6$ Hz), 4.77 (d, 1H, $J = 11.6$ Hz), 4.68 (dd, 1H, $J = 2.4$ Hz, $J = 6.0$ Hz), 4.33 (bs, 1H), 3.86 – 3.93 (m, 1H), 3.26 (dd, 1H, $J = 6.8$ Hz, $J = 9.6$ Hz), 1.86 (d, 1H, $J = 5.2$ Hz), 1.39 (d, 3H, $J = 6.4$ Hz). **^{13}C NMR (100 MHz, CDCl_3):** δ 144.6, 138.2, 128.5, 127.9, 103.2, 82.4, 74.2, 74.1, 69.9, 17.6. **HRMS (ESI)** calcd for $\text{C}_{13}\text{H}_{16}\text{O}_3 + \text{Na}$ 243.0997, found 243.0997.

4-O-benzyl-1,5-anhydro-2,6-dideoxy- α -1,2-C-methylene-D-allo-pyranose: To a solution of 6-deoxy-4-O-benzyl-D-allal (800 mg, 3.63 mmol) in ether (15 mL) at 0 °C was added 1 M Et₂Zn in hexane (10.8 mL, 10.8 mmol) and CH₂I₂ (0.87 mL, 10.8 mmol). The mixture was stirred for 5 h at same temperature, then quenched with saturated NH₄Cl solution (75 mL) and extracted with ether (50 mL x 2). The combined organic layers were washed with water (50 mL), brine (50 mL) and dried over anhydrous Na₂SO₄. Removal of solvent followed by purification of the crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7 to 2:3) provided 4-O-benzyl-1,5-anhydro-2,6-dideoxy- α -1,2-C-methylene-D-allo-pyranose (680 mg, 80%) as a white solid. R_f = 0.38 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.26 – 7.34 (m, 5H), 4.75 (d, 1H, *J* = 12.0 Hz), 4.67 (d, 1H, *J* = 12.0 Hz), 4.21 (t, 1H, *J* = 7.6 Hz), 3.69 – 3.72 (m, 1H), 3.35 (dd, 1H, *J* = 6.4 Hz, *J* = 9.6 Hz), 2.84 (dd, 1H, *J* = 7.6 Hz, *J* = 9.2 Hz), 1.34 – 1.38 (m, 1H), 1.22 (d, 3H, *J* = 6.4 Hz), 0.64 – 0.69 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 138.2, 128.6, 127.7, 84.7, 74.4, 74.2, 71.5, 54.0, 18.7, 17.5, 11.6. **HRMS (ESI)** calcd for C₁₄H₁₈O₃+Na 257.1154, found 257.1154.

Compound 20: To a solution of (COCl)₂ (331 μ L, 3.84 mmol) in CH₂Cl₂ (8 mL) at -78 °C was added DMSO (454 μ L, 6.4 mmol) dropwise. After 10 min of stirring at the same temperature, the above 4-O-benzyl-1,5-anhydro-2,6-dideoxy- α -1,2-C-methylene-D-allo-pyranose (600 mg, 2.56 mmol) in CH₂Cl₂ (8 mL) was added dropwise for a period of 15 min. After stirring for 30 min at -78 °C, Et₃N (1.76 mL, 12.6 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH₂Cl₂ (50 mL), washed with water (25 mL x 2), brine (25 mL) and dried over anhydrous Na₂SO₄. Removal of solvent gave the crude residue which upon purification by silica-gel column chromatography with ethyl acetate/hexane (1:4) provided D-rhamnose-derived 1,2-cyclopropa-3-pyranone **20** (588 mg, 99%) as a colorless solid. R_f = 0.62 (3:7 ethyl acetate/hexane). **¹H NMR (400 MHz, CDCl₃):** δ 7.26 – 7.33 (m, 5H), 4.99 (d, 1H, *J* = 11.6 Hz), 4.53 (d, 1H, *J* = 11.6 Hz), 4.10 (dd, 1H, *J* = 4.4 Hz, *J* = 9.2 Hz), 3.89 – 3.96 (m, 1H), 3.45 (d, 1H, *J* = 9.6 Hz), 1.86 – 1.91 (m, 1H), 1.26 (d, 3H, *J* = 6.0 Hz), 1.25 – 1.28 (m, 2H). **¹³C NMR (100 MHz, CDCl₃):** δ 204.8, 137.4, 128.2, 128.1, 127.8, 82.0, 78.7, 73.8, 57.6, 25.8, 19.8, 18.1. **HRMS (ESI)** calcd for C₁₄H₁₆O₃+Na 255.0997, found 255.0997.

2.16. Compound 21:



Compound **21** was synthesized using D-rhamnose-derived 1,2-cyclopropa-3-pyranone **20** (85 mg, 0.36 mmol), glycosyl acceptor **17** (150 mg, 0.4 mmol), TMSOTf (13 μ L, 0.07 mmol) and 4 Å MS powder in CH_2Cl_2 (5 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78°C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septanosyl disaccharide **21** (205 mg, 93%) as a colorless solid. $R_f = 0.7$ (3:7 ethyl acetate/hexane). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.25 – 7.41 (m, 15H), 5.47 (s, 1H), 5.29 (dd, 1H, $J = 4.8$ Hz, $J = 8.4$ Hz), 4.77 (d, 1H, $J = 12.0$ Hz), 4.65 (d, 1H, $J = 11.6$ Hz), 4.59 (d, 1H, $J = 12.0$ Hz), 4.55 (d, 1H, $J = 3.6$ Hz), 4.39 (d, 1H, $J = 11.6$ Hz), 4.33 (t, 1H, $J = 9.6$ Hz), 4.26 (t, 1H, $J = 6.8$ Hz), 4.22 (dd, 1H, $J = 4.8$ Hz, $J = 10.4$ Hz), 3.78 (td, 1H, $J = 4.8$ Hz, $J = 10.4$ Hz), 3.66 (t, 1H, $J = 10.0$ Hz), 3.58 (d, 1H, $J = 10.8$ Hz), 3.52 (t, 1H, $J = 9.6$ Hz), 3.43 (dd, 1H, $J = 3.6$ Hz, $J = 9.6$ Hz), 3.36 (s, 3H), 2.49 (ddd, 1H, $J = 3.2$ Hz, $J = 6.4$ Hz, $J = 15.2$ Hz), 2.32 – 2.40 (m, 1H), 2.17 – 2.27 (m, 1H), 1.96 – 2.04 (m, 1H), 1.23 (d, 3H, $J = 6.4$ Hz). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 209.0, 138.0, 137.5, 137.3, 129.0, 128.4, 128.4, 128.3, 128.0, 127.9, 125.9, 101.4, 100.1, 99.0, 89.1, 83.0, 77.8, 73.7, 72.9, 72.9, 69.1, 66.1, 61.8, 55.3, 35.9, 28.1, 20.6. HRMS (ESI) calcd for $\text{C}_{35}\text{H}_{40}\text{O}_9 + \text{Na}$ 627.2570, found 627.2570.

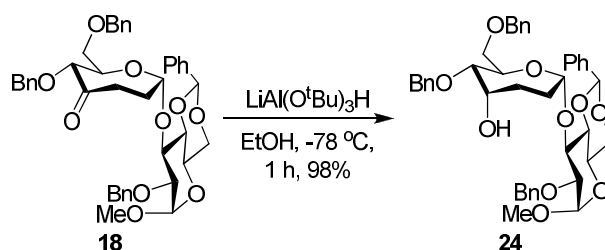
2.17. Compound 23:



Compound **23** was synthesized using D-rhamnose-derived 1,2-cyclopropa-3-pyranone **20** (70 mg, 0.3 mmol), glycosyl acceptor **22** (85 mg, 0.33 mmol), TMSOTf (10 μ L, 0.06 mmol) and 4 Å MS powder in CH_2Cl_2 (5 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78°C for 3 h. The crude

product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septanosyl disaccharide **23** (141 mg, 96%) as a colorless solid. $R_f = 0.67$ (3:7 ethyl acetate/hexane). **^1H NMR (400 MHz, CDCl_3):** δ 7.31 – 7.37 (m, 6H), 5.41 (dd, 1H, $J = 4.4$ Hz, $J = 8.4$ Hz), 5.35 (d, 1H, $J = 6.0$ Hz), 4.69 (d, 1H, $J = 11.2$ Hz), 4.44 (d, 1H, $J = 11.2$ Hz), 4.42 (d, 1H, $J = 11.6$ Hz), 4.31 (ddd, 1H, $J = 3.2$ Hz, $J = 4.4$ Hz, $J = 11.2$ Hz), 4.12 (t, 1H, $J = 6.4$ Hz), 3.00 (dd, 1H, $J = 3.2$ Hz, $J = 11.6$ Hz), 3.92 (dd, 1H, $J = 4.4$ Hz, $J = 11.6$ Hz), 3.65 (d, 1H, $J = 6.4$ Hz), 2.41 – 2.49 (m, 2H), 2.30 – 2.38 (m, 1H), 2.19 – 2.29 (m, 1H), 1.31 (d, 3H, $J = 6.4$ Hz), 0.97 (s, 9H), 0.10 (s, 6H). **^{13}C NMR (100 MHz, CDCl_3):** δ 208.4, 192.6, 162.3, 137.2, 128.4, 128.0, 128.0, 104.7, 100.6, 89.1, 82.0, 73.0, 70.2, 67.0, 61.6, 35.9, 27.1, 25.8, 20.8, 18.4, -5.2, -5.2. **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{38}\text{O}_7\text{Si}+\text{Na}$ 513.2285, found 513.2285.

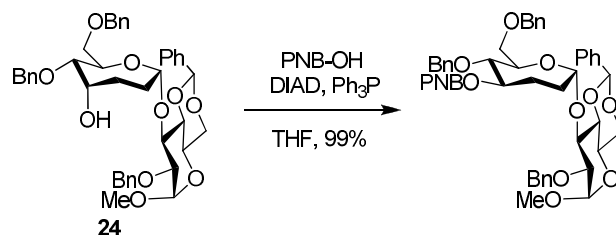
2.18. Compound 24:



A solution of ketone **18** (350 mg, 0.49 mmol) in EtOH (10 mL) was added dropwise to a solution of $\text{LiAlH}(\text{OC}(\text{CH}_3)_3)_3$ (250 mg, 0.98 mmol) in EtOH (10 mL) at $-78\text{ }^\circ\text{C}$. The mixture was stirred for 1 h at same temperature, then slowly quenched with saturated NH_4Cl solution (20 mL) and allowed to warm to room temperature. Ethanol was evaporated under reduced pressure and the obtained thick syrup was extracted twice with ethyl acetate (20 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (MgSO_4). Purification of crude residue by silica-gel column chromatography with ethyl acetate/hexane (3:7 to 2:3) provided septano-hexose disaccharide **24** (343 mg, 98%) as a colorless oil. $R_f = 0.38$ (3:7 ethyl acetate/hexane). **^1H NMR (500 MHz, CDCl_3):** δ 7.47 – 7.49 (m, 2H), 7.18 – 7.36 (m, 18H), 5.47 (s, 1H), 5.03 (dd, 1H, $J = 2.8$ Hz, $J = 8.0$ Hz), 4.75 (d, 1H, $J = 12.0$ Hz), 4.61 (d, 1H, $J = 12.0$ Hz), 4.55 (d, 1H, $J = 3.2$ Hz), 4.32 – 4.45 (m, 6H), 4.19 (dd, 1H, $J = 4.4$ Hz, $J = 10.0$ Hz), 4.08 (d, 1H, $J = 9.2$ Hz), 3.99 – 4.01 (m, 1H), 3.73 – 3.80 (m, 2H), 3.61 – 3.67 (m, 2H), 3.51 (dtd, 1H, $J = 2.8$ Hz, $J = 6.8$ Hz, $J = 9.2$ Hz), 3.38 – 3.45 (m, 2H), 3.34 (s, 3H), 1.92 – 2.07 (m, 3H),

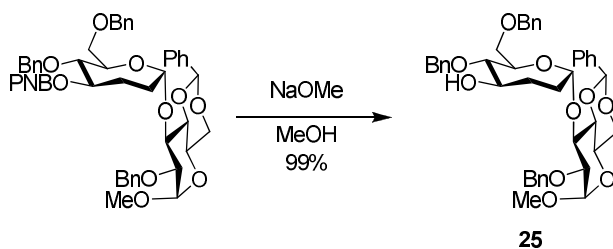
1.73 – 1.79 (m, 1H), 1.60 – 1.66 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 138.4, 138.2, 138.0, 137.5, 128.8, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.3, 126.4, 105.4, 101.5, 98.9, 82.6, 80.3, 79.4, 77.0, 76.4, 73.6, 73.3, 72.0, 71.2, 69.7, 68.9, 62.4, 55.2, 30.9, 25.4. HRMS (ESI) calcd for $\text{C}_{42}\text{H}_{48}\text{O}_{18}+\text{Na}$ 735.3145, found 735.3145.

2.19. *p*-Nitrobenzoate of diaccharide 24:



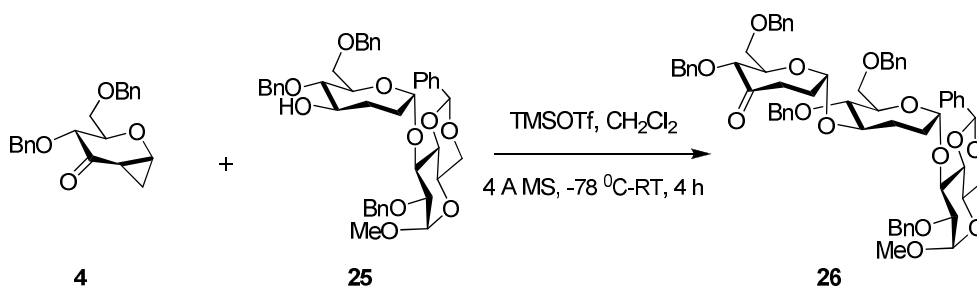
A solution of alcohol **24** (300 mg, 0.42 mmol), triphenylphosphine (441 mg, 1.68 mmol) and *p*-nitrobenzoic acid (281 mg, 1.68 mmol) in THF (10 mL) at 0 °C was added DIAD (330 μL , 1.68 mmol) dropwise. Upon completion of the addition, the solution was allowed to stir at room temperature for over night. Removal the solvent under reduced pressure followed by purification of crude mixture by silica-gel column chromatography with ethyl acetate/hexane (1:4) gave *p*-nitrobenzoate of diaccharide **24** (358 mg, 99% yield) as light yellow oil. R_f = 0.61 (3:7 ethyl acetate/hexane). ^1H NMR (400 MHz, CDCl_3): δ 8.10 (d, 2H, J = 9.2 Hz), 8.01 (d, 2H, J = 9.2 Hz), 7.16 – 7.35 (m, 20H), 5.53 (s, 1H), 5.35 (dd, 1H, J = 4.4 Hz, J = 7.2 Hz), 4.74 (d, 1H, J = 12.0 Hz), 4.65 (d, 1H, J = 12.0 Hz), 5.59 (d, 1H, J = 12.0 Hz), 4.58 (d, 1H, J = 4.0 Hz), 4.47 (d, 1H, J = 12.0 Hz), 4.36 (s, 2H), 4.21 – 4.27 (m, 2H), 3.74 – 3.79 (m, 2H), 3.65 – 3.72 (m, 2H), 3.54 – 3.59 (m, 2H), 3.43 – 3.50 (m, 2H), 3.36 (s, 3H), 2.03 – 2.09 (m, 1H), 1.89 – 1.99 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.8, 150.3, 138.3, 137.9, 137.7, 137.5, 135.6, 130.7, 128.8, 128.5, 128.3, 128.1, 128.0, 127.7, 127.7, 127.3, 126.3, 123.4, 106.2, 101.4, 98.8, 79.9, 79.8, 79.7, 78.0, 75.4, 74.8, 73.5, 73.3, 72.7, 71.1, 69.0, 62.6, 55.3, 30.3, 22.7. HRMS (ESI) calcd for $\text{C}_{49}\text{H}_{51}\text{NO}_{13}+\text{Na}$ 884.3258, found 884.3258.

2.20. Compound 25:



To a solution of above *p*-nitrobenzoate sugar derivative (250 mg, 0.29 mmol) in MeOH (2.3 mL) at room temperature was added methonolic solution of NaOMe (330 μ L) (freshly prepared from 100 mg of Na in 20 mL of MeOH) and stirred for 1 h. The solution was neutralised with amberlite IR120 (acetic resin) and filtered. Removal of solvent under reduced pressure followed by purification of the crude residue by silica-gel chromatography with ethyl acetate/hexane (2:3) gave disaccharide **25** (203 mg, 99%) as a colorless gum. R_f = 0.36 (3:7 ethyl acetate/hexane). **^1H NMR (500 MHz, CDCl_3):** δ 7.47 – 7.49 (m, 2H), 7.18 – 7.35 (m, 18H), 5.49 (s, 1H), 4.91 (dd, 1H, J = 3.0 Hz, J = 9.0 Hz), 4.74 (d, 1H, J = 12.0 Hz), 4.63 (d, 1H, J = 12.0 Hz), 4.55 (d, 1H, J = 3.5 Hz), 4.42 (d, 1H, J = 12.0 Hz), 4.39 (d, 1H, J = 12.0 Hz), 4.38 (d, 1H, J = 12.0 Hz), 4.34 (d, 1H, J = 12.0 Hz), 4.20 (dd, 1H, J = 4.5 Hz, J = 10.0 Hz), 4.13 (t, 1H, J = 9.5 Hz), 3.88 – 3.91 (m, 1H), 3.68 – 3.76 (m, 2H), 3.66 (t, 1H, J = 10.0 Hz), 3.55 (t, 1H, J = 5.5 Hz), 3.54 (dd 1H, J = 3.5 Hz, J = 9.5 Hz), 3.51 (t, 1H, J = 9.0 Hz), 3.38 – 3.44 (m, 2H), 3.34 (s, 3H), 1.93 – 2.01 (m, 1H), 1.80 – 1.91 (m, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 138.2, 138.0, 137.8, 137.4, 128.8, 128.4, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 127.2, 126.2, 107.1, 101.3, 98.6, 81.6, 80.1, 79.8, 79.6, 75.9, 73.4, 73.2, 72.1, 71.7, 70.7, 68.8, 62.4, 55.2, 29.7, 24.0. **HRMS (ESI)** calcd for $\text{C}_{42}\text{H}_{48}\text{O}_{18}+\text{Na}$ 735.3145, found 735.3145.

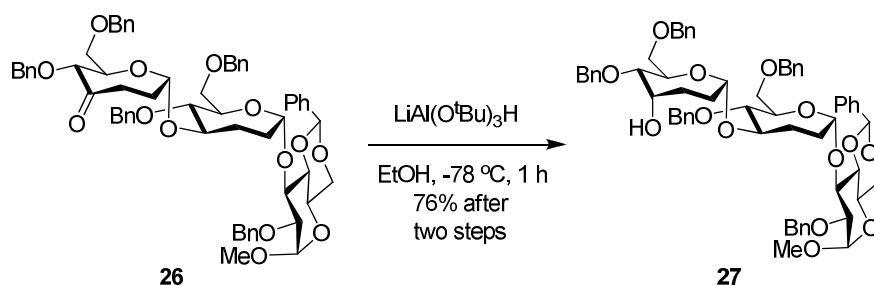
2.21. Compound 26:



Disepitano-hexose trisaccharide derivative **26** was synthesized using D-glucose-derived 1,2-cyclopropa-3-pyranone **4** (65 mg, 0.19 mmol), glycosyl acceptor **25** (150 mg, 0.21 mmol), TMSOTf (5.4 μ L, 0.03 mmol) and 4 Å MS powder in CH_2Cl_2 (5 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h and then at $25\text{ }^\circ\text{C}$ for 3 h. The crude product was purified by silica-gel column

chromatography (ethyl acetate/hexane 3:7) to give diseptano-hexose trisaccharide derivative **23** (160 mg, 79%) as colorless oil. $R_f = 0.77$ (2:3 ethyl acetate/hexane). **^1H NMR (500 MHz, CDCl_3):** δ 7.47 – 7.49 (m, 2H), 7.14 – 7.36 (m, 30H), 5.47 (s, 1H), 4.95 – 5.00 (m, 1H), 4.88 (dd, 1H, $J = 3.0$ Hz, $J = 7.5$ Hz), 4.77 (1H, $J = 12.0$ Hz), 4.75 (dd, 1H, $J = 2.5$ Hz, $J = 9.0$ Hz), 4.67 (d, 1H, $J = 12.5$ Hz), 4.52 – 4.54 (m, 3H), 4.38 – 4.40 (m, 2H), 4.35 (d, 1H, $J = 3.5$ Hz), 4.32 (d, 1H, $J = 12.0$ Hz), 4.28 (d, 1H, $J = 12.5$ Hz), 4.12 – 4.19 (m, 3H), 3.71 – 3.80 (m, 3H), m3.65 (d, 1H, $J = 9.0$ Hz), 3.61 (dd, 1H, $J = 3.0$ Hz, $J = 13.0$ Hz), 3.57 (dd, 1H, $J = 4.0$ Hz, $J = 5.5$ Hz), 3.51 – 3.53 (m, 2H), 3.47 – 3.50 (m, 2H), 3.43 – 3.46 (m, 1H), 3.33 – 3.36 (m, 4H), 2.84 (td, 1H, $J = 5.0$ Hz, $J = 11.5$ Hz), 2.29 – 2.35 (m, 1H), 2.03 – 2.06 (m, 1H), 1.81 – 1.91 (m, 3H), 1.67 – 1.71 (m, 2H). **^{13}C NMR (100 MHz, CDCl_3):** δ 209.3, 138.7, 138.5, 138.3, 137.9, 137.5, 136.8, 128.7, 128.4, 128.3, 128.3, 128.1, 128.1, 128.0, 128.0, 127.8, 127.8, 127.7, 127.6, 127.5, 127.3, 127.1, 126.3, 105.0, 103.0, 101.1, 99.2, 85.2, 81.1, 79.6, 78.9, 78.2, 77.3, 76.3, 76.1, 73.5, 73.2, 73.1, 72.4, 72.2, 71.6, 70.6, 68.9, 62.5, 55.2, 34.0, 32.9, 30.2, 21.3. **HRMS (ESI)** calcd for $\text{C}_{63}\text{H}_{70}\text{O}_{14} + \text{Na}$ 1073.4663, found 1073.4664.

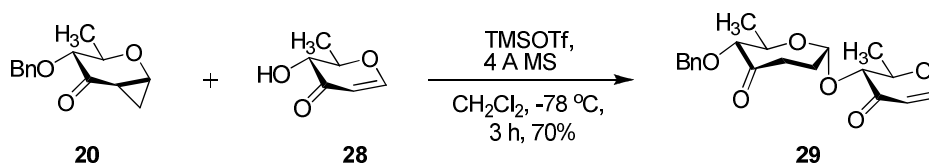
2.22. Compound 27:



A solution of ketone **26** (155 mg, 0.14 mmol) in EtOH (5 mL) was added dropwise to a solution of $\text{LiAlH}(\text{OC}(\text{CH}_3)_3)_3$ (71 mg, 0.28 mmol) in EtOH (5 mL) at -78°C . The mixture was stirred for 1 h at same temperature, then slowly quenched with saturated NH_4Cl solution (10 mL) and allowed to warm to room temperature. Ethanol was evaporated under reduced pressure and the obtained thick syrup was extracted twice with ethyl acetate (20 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (MgSO_4). Purification of crude residue by silica-gel column chromatography with ethyl acetate/hexane (2:3) provided diseptano-hexose trisaccharide **27** (153 mg, over all 76% for two steps) as a colorless oil. $R_f = 0.5$ (2:3 ethyl acetate/hexane). **^1H NMR (500 MHz, CDCl_3):** δ 7.48 – 7.50 (m, 2H), 7.18 – 7.38

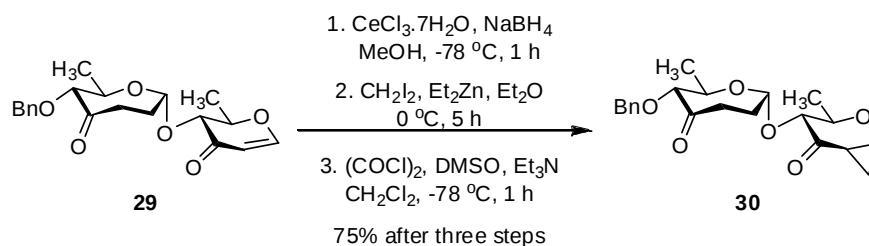
(m, 28H), 5.48 (s, 1H), 4.89 (dd, 1H, $J = 3.0\text{ Hz}$, $J = 8.0\text{ Hz}$), 4.78 (d, 1H, $J = 12.0\text{ Hz}$), 4.75 (dd, 1H, $J = 3.5\text{ Hz}$, $J = 7.0\text{ Hz}$), 4.69 (d, 1H, $J = 12.0\text{ Hz}$), 4.53 (d, 1H, $J = 12.0\text{ Hz}$), 4.52 (d, 1H, $J = 3.5\text{ Hz}$), 4.50 (d, 1H, $J = 12.0\text{ Hz}$), 4.45 (d, 1H, $J = 12.0\text{ Hz}$), 4.41 (d, 1H, $J = 12.0\text{ Hz}$), 4.37 (d, 1H, $J = 12.0\text{ Hz}$), 4.35 (d, 1H, $J = 12.0\text{ Hz}$), 4.29 (d, 1H, $J = 12.0\text{ Hz}$), 4.17 (dtd, 1H, $J = 2.0\text{ Hz}$, $J = 6.0\text{ Hz}$, $J = 10.0\text{ Hz}$), 4.07 – 4.11 (m, 2H), 3.74 (dd, 1H, $J = 4.5\text{ Hz}$, $J = 7.5\text{ Hz}$), 3.68 – 3.72 (m, 1H), 3.66 (t, 1H, $J = 7.5\text{ Hz}$), 3.60 (dd, 1H, $J = 4.5\text{ Hz}$, $J = 9.0\text{ Hz}$), 3.57 – 3.59 (m, 1H), 3.55 – 3.56 (m, 2), 3.53 – 3.54 (m, 2H), 3.49 – 3.50 (m, 1H), 3.45 – 2.46 (m, 1H), 3.36 – 3.91 (m, 1H), 3.34 (s, 3H), 1.92 – 2.06 (m, 2H), 1.82 – 1.87 (m, 1H), 1.64 – 1.75 (m, 6H). **^{13}C NMR (100 MHz, CDCl_3):** δ 138.7, 138.7, 138.4, 138.1, 137.9, 137.6, 128.7, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.3, 127.1, 126.3, 105.3, 101.8, 101.2, 82.3, 81.5, 79.5, 78.8, 77.5, 76.8, 76.2, 75.9, 73.5, 73.2, 73.1, 72.6, 72.2, 71.7, 71.2, 69.4, 68.9, 62.6, 55.3, 30.6, 30.3, 25.3, 21.6. **HRMS (ESI)** calcd for $\text{C}_{63}\text{H}_{72}\text{O}_{14} + \text{Na}$ 1075.4820, found 1075.4820.

2.23. Compound 29:



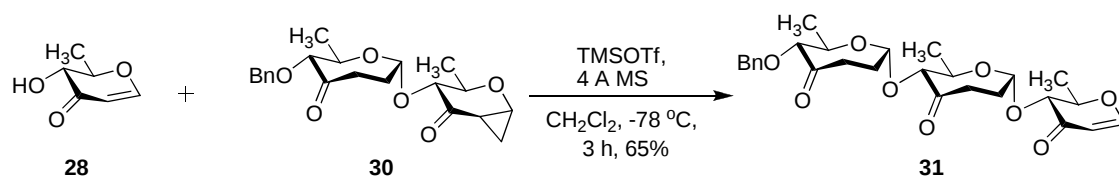
Septano-hexose disaccharide derivative **29** was synthesized using D-rhamnose-derived 1,2-cyclopropa-3-pyranone **20** (200 mg, 0.86 mmol), glycosyl acceptor **28** (120 mg, 0.94 mmol), TMSOTf (31 μL , 0.17 mmol) and 4 Å MS powder in CH_2Cl_2 (15 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at -78°C for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give septano-hexose disaccharide derivative **29** (217 mg, 70%) as a colorless solid. $R_f = 0.5$ (3:7 ethyl acetate/hexane). **^1H NMR (500 MHz, CDCl_3):** δ 7.28 – 7.38 (m, 6H), 5.35 – 5.38 (m, 2H), 4.69 (d, 1H, $J = 11.5\text{ Hz}$), 5.41 (4.42 (d, 1H, $J = 11.5\text{ Hz}$), 4.34 (dd, 1H, $J = 6.0\text{ Hz}$, $J = 11.5\text{ Hz}$), 4.12 – 4.18 (m, 2H), 3.65 (d, 1H, $J = 6.5\text{ Hz}$), 2.53 (ddd, 1H, $J = 3.6\text{ Hz}$, $J = 5.6\text{ Hz}$, $J = 15.6\text{ Hz}$), 2.41 – 2.49 (m, 1H), 2.31 – 2.39 (m, 1H), 2.22 – 2.27 (m, 1H), 1.50 (d, 3H, $J = 6.5\text{ Hz}$), 1.30 (d, 3H, $J = 6.5\text{ Hz}$). **^{13}C NMR (125 MHz, CDCl_3):** δ 208.3, 193.3, 162.6, 137.1, 128.4, 128.1, 128.0, 105.1, 100.8, 89.1, 78.2, 74.8, 73.0, 66.8, 35.8, 27.0, 20.9, 17.5. **HRMS (ESI)** calcd for $\text{C}_{20}\text{H}_{24}\text{O}_6 + \text{Na}$ 383.1471, found 383.1471.

2.24. Compound 30:

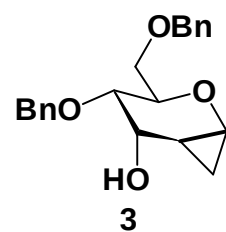


To a solution of septano-hexose disaccharide derivative **29** (150 mg, 0.41 mmol) and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (458 mg, 1.23 mmol) in MeOH (6 mL) at $-78\text{ }^\circ\text{C}$, was added cooled ($-10\text{ }^\circ\text{C}$) solution of NaBH_4 (46 mg, 1.23 mmol) in MeOH (2 mL) dropwise for a period of 10 min. The solution was stirred for 1 h at same temperature and slowly quenched with saturated NH_4Cl solution (15 mL). The mixture was extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (Na_2SO_4). Removal of solvent provided the crude diol (148 mg, 0.4 mmol) as colorless gum. This crude diol mixture was dissolved in ether (5 mL), and subsequently 1 M Et_2Zn in hexane (1.2 mL, 1.21 mmol) and CH_2I_2 (98 μL , 1.21 mmol) were added at $0\text{ }^\circ\text{C}$ and stirred for 5 h at the same temperature. After completion of reaction (TLC), saturated NH_4Cl (15 mL) was added and extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed with water (10 mL), brine (10 mL) and dried (Na_2SO_4). Removal of solvent gave crude 1,2-cyclopropanated disaccharide diol mixture (130 mg, 0.34 mmol) which was used for next step without purification. For oxidation of diol, DMSO (120 μL , 1.7 mmol) was added dropwise to a solution of $(\text{COCl})_2$ (88 μL , 1.02 mmol) in CH_2Cl_2 (3 mL) at $-78\text{ }^\circ\text{C}$. After stirring for 10 min at the same temperature, the above 1,2-cyclopropanated disaccharide diol mixture (130 mg, 0.34 mmol) in CH_2Cl_2 (3 mL) was added dropwise for a period of 15 min. After stirring for 30 min at $-78\text{ }^\circ\text{C}$, Et_3N (468 μL , 3.36 mmol) was added and allowed to warm to room temperature. The reaction mixture was diluted with CH_2Cl_2 (20 mL), washed with water (10 mL x 2), brine (10 mL) and dried over anhydrous Na_2SO_4 . The crude residue was purified by silica-gel column chromatography (ethyl acetate/hexane 3:7) provided 1,2-cyclopropanated-septanosyl disaccharide-derivative **30** (115 mg, 75% after three steps) as a mixture ($\alpha:\beta = 2:1$).

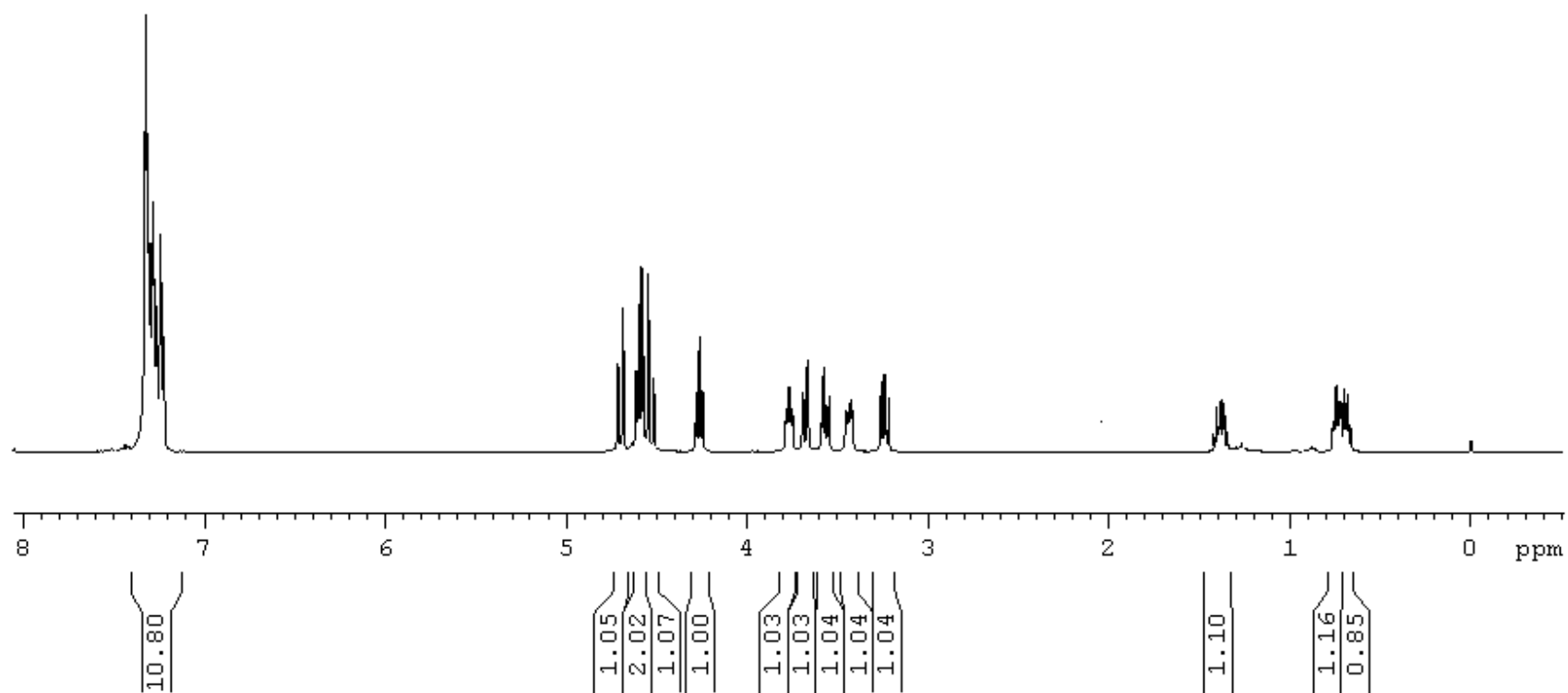
2.25. Compound 31:

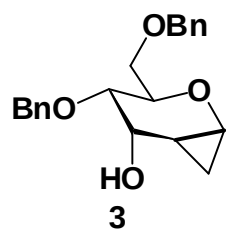


Diseptano-hexose trisaccharide derivative **31** was synthesized using glycosyl donor **30** (100 mg, 0.26 mmol), glycosyl acceptor **28** (37 mg, 0.29 mmol), TMSOTf (9.4 μL , 0.05 mmol) and 4 Å MS powder in CH_2Cl_2 (5 mL) according to the general procedure for ring expansion-glycosylation reaction (2.3). The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 3 h. The crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:4) to give diseptano-hexose trisaccharide derivative **31** (87 mg, 65%) as a colorless oil. $R_f = 0.32$ (3:7 ethyl acetate/hexane). **^1H NMR (500 MHz, CDCl_3):** δ 7.29 – 7.37 (m, 6H), 5.44 (dd, 1H, $J = 5.0\text{ Hz}$, $J = 8.5\text{ Hz}$), 5.36 (d, 1H, $J = 6.0\text{ Hz}$), 4.86 (dd, 1H, $J = 5.0\text{ Hz}$, $J = 8.5\text{ Hz}$), 4.67 (d, 1H, $J = 11.5\text{ Hz}$), 4.40 (d, 1H, $J = 11.5\text{ Hz}$), 4.36 (dd, 1H, $J = 6.5\text{ Hz}$, $J = 12.0\text{ Hz}$), 4.18 (d, 1H, $J = 12.0\text{ Hz}$), 4.13 (t, 1H, $J = 6.5\text{ Hz}$), 4.05 (d, 1H, $J = 8.5\text{ Hz}$), 4.03 (dd, 1H, $J = 5.5\text{ Hz}$, $J = 11.5\text{ Hz}$), 3.62 (d, 1H, $J = 7.0\text{ Hz}$), 2.51 – 2.55 (m, 1H), 2.44 – 2.50 (m, 2H), 2.38 – 2.43 (m, 1H), 2.28 – 2.37 (m, 2H), 2.15 – 2.20 (m, 1H), 1.90 – 1.97 (m, 1H), 1.49 (d, 3H, $J = 6.0\text{ Hz}$), 1.33 (d, 3H, $J = 5.5\text{ Hz}$), 1.29 (d, 3H, $J = 6.5\text{ Hz}$). **^{13}C NMR (100 MHz, CDCl_3):** δ 208.2, 207.6, 193.3, 162.7, 137.1, 128.5, 128.1, 128.1, 105.1, 100.3, 99.8, 89.1, 83.6, 78.2, 74.7, 73.1, 66.9, 65.3, 35.8, 35.7, 27.2, 27.0, 20.9, 20.2, 17.6. **HRMS (ESI)** calcd for $\text{C}_{27}\text{H}_{34}\text{O}_9 + \text{Na}$ 525.2101, found 525.2101.



^1H NMR, 400 MHz, CDCl_3



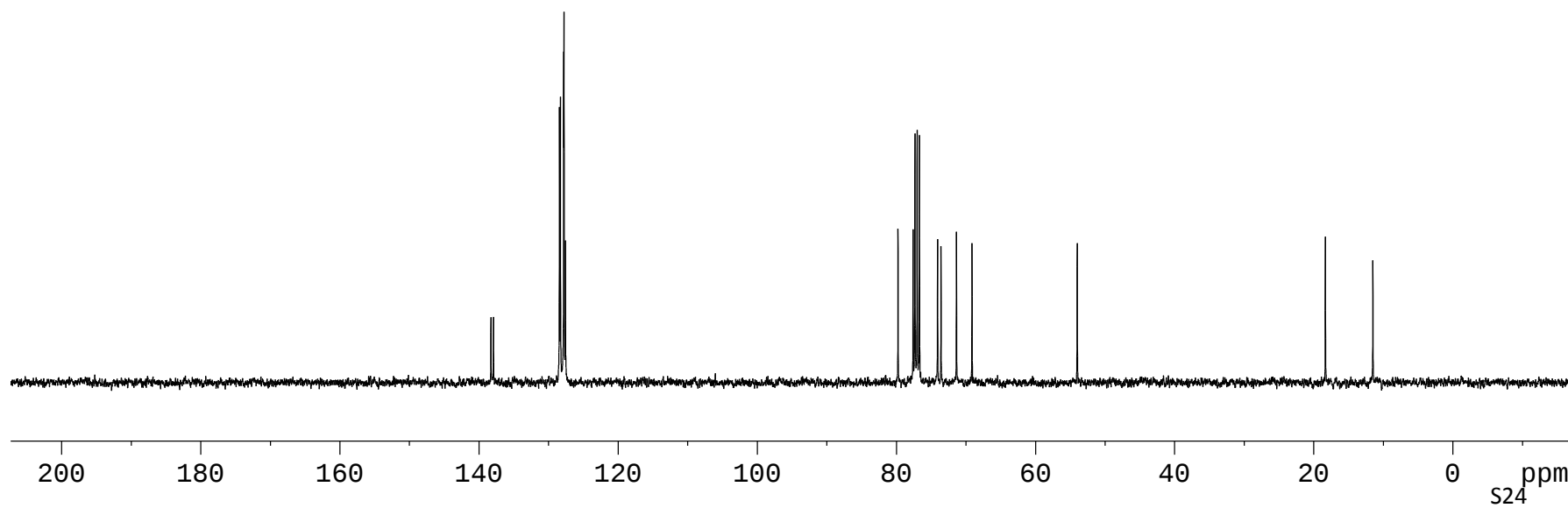


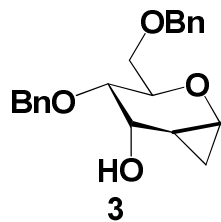
^{13}C NMR, 100 MHz, CDCl_3

138.26
137.91
128.42
128.28
127.81
127.77
127.56

79.75
77.58
77.32
77.00
76.68
74.06
73.57
71.34
69.11
53.99

18.31
11.48





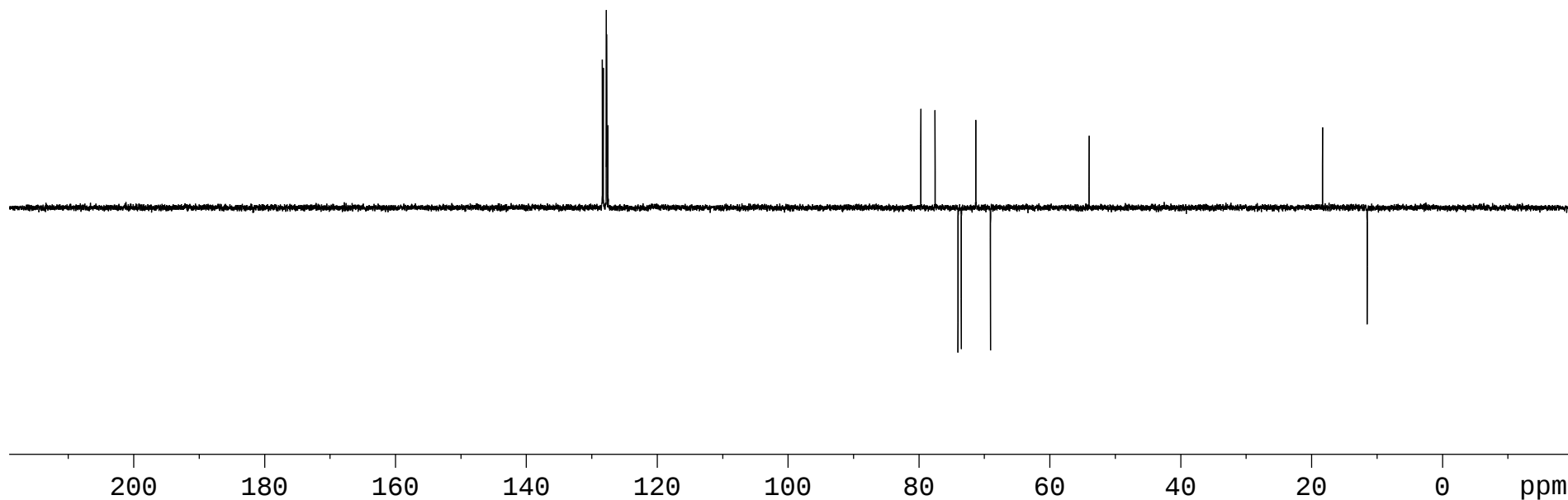
^{13}C DEPT NMR, 100 MHz, CDCl_3

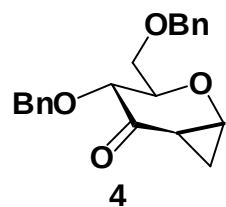
128.42
128.28
127.82
127.77
127.75
127.56

79.74
77.57
74.06
73.57
71.35
69.11

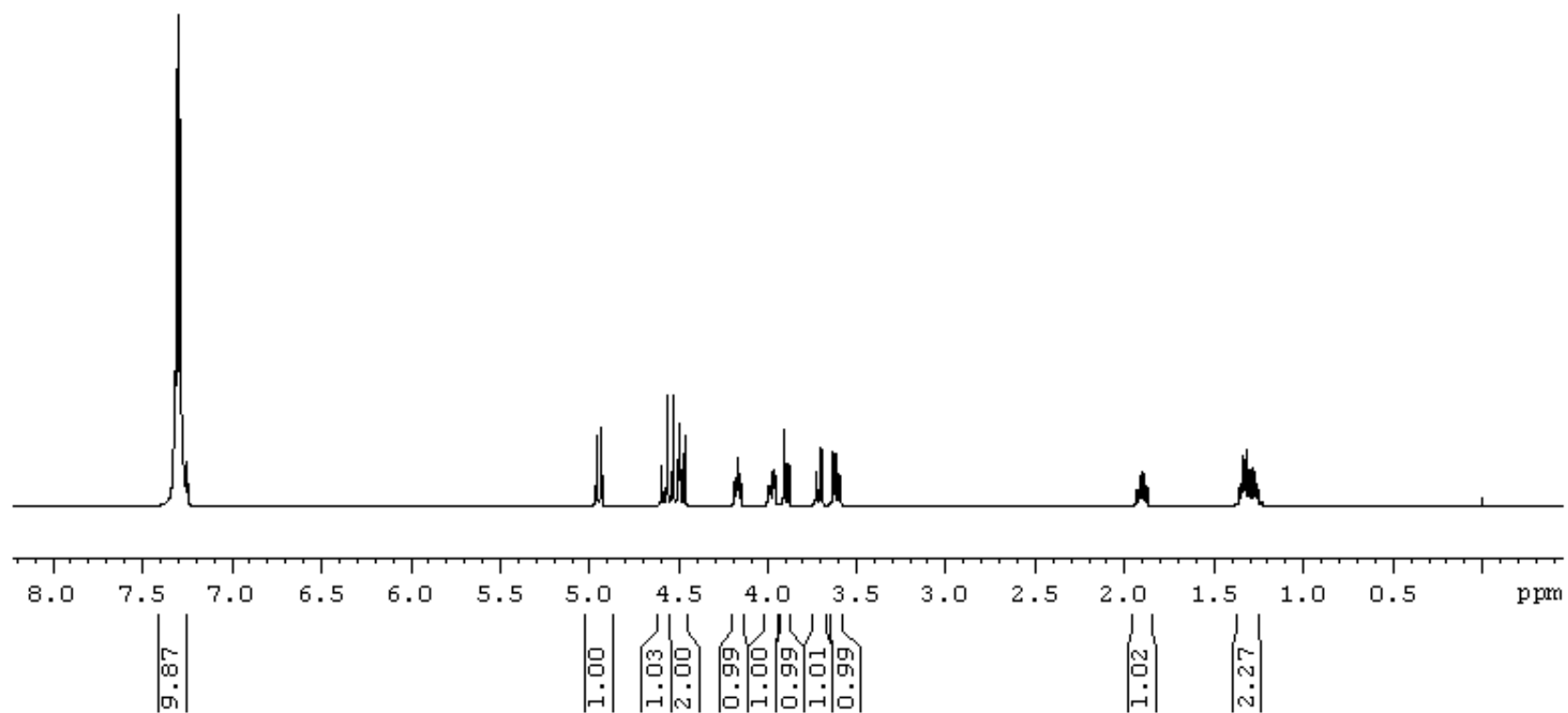
53.99

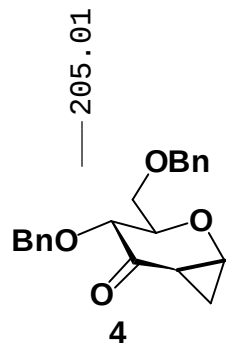
18.31
11.48



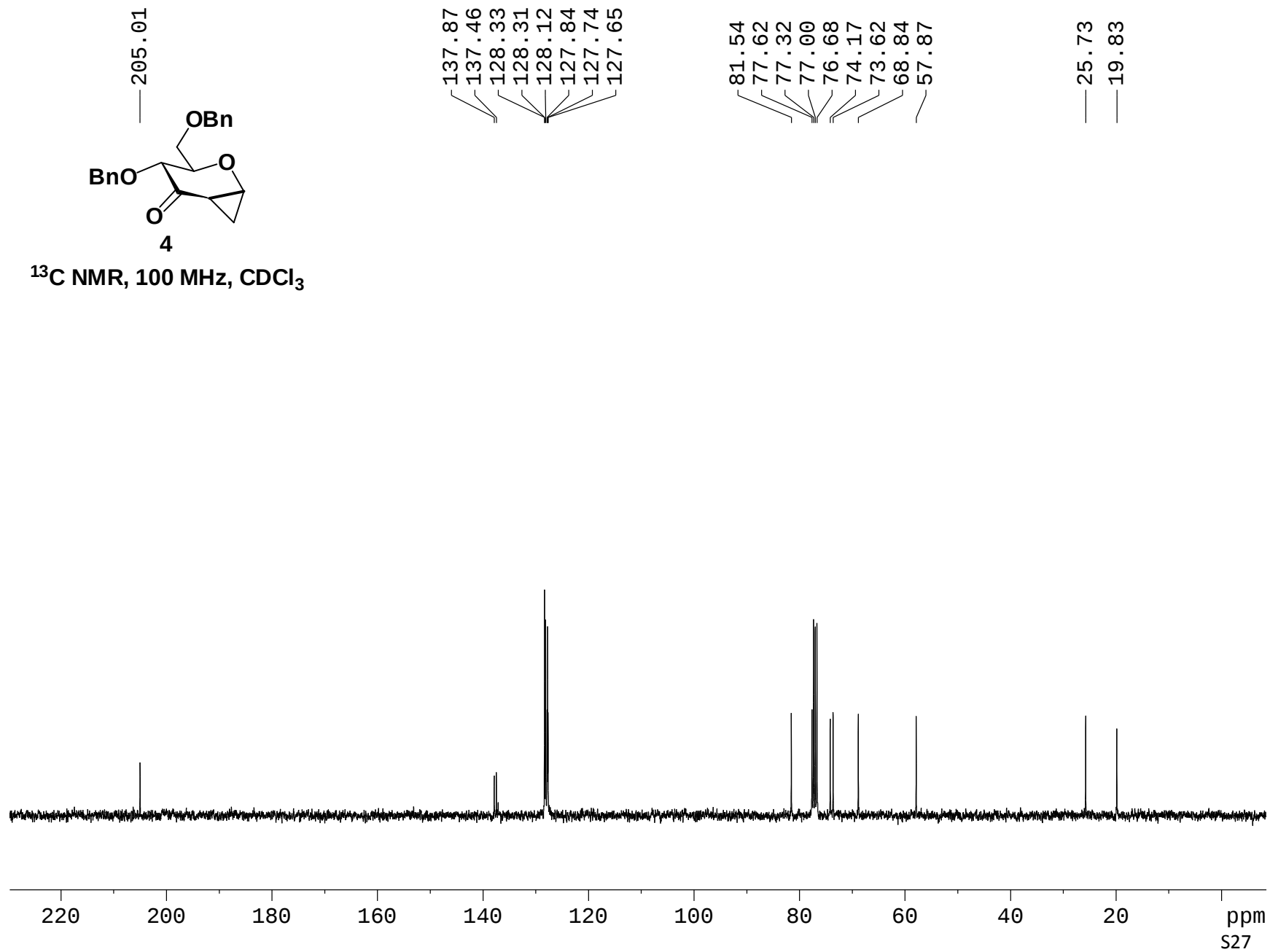


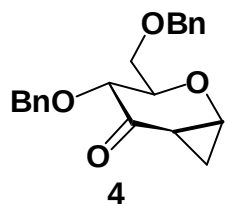
^1H NMR, 400 MHz, CDCl_3





^{13}C NMR, 100 MHz, CDCl_3



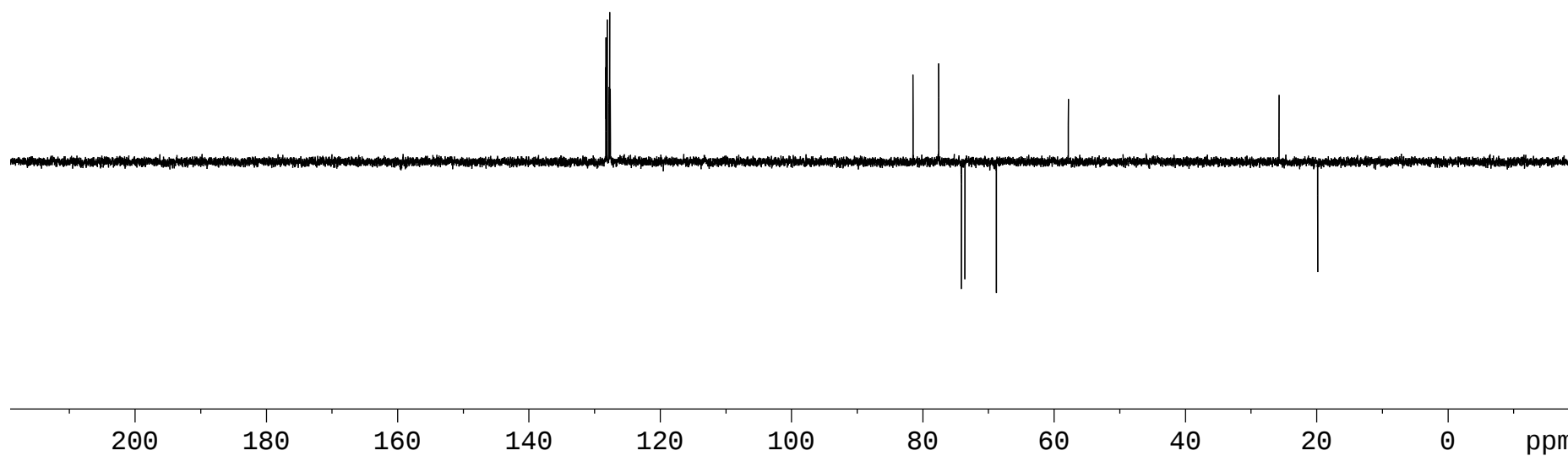


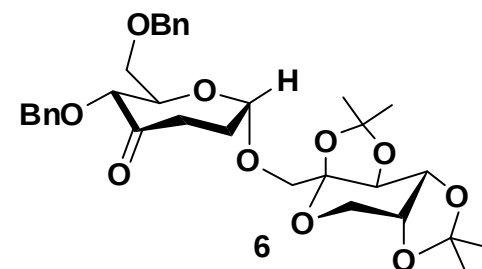
DEPT NMR, 100 MHz, CDCl₃

128.33
128.30
128.11
127.83
127.74
127.64

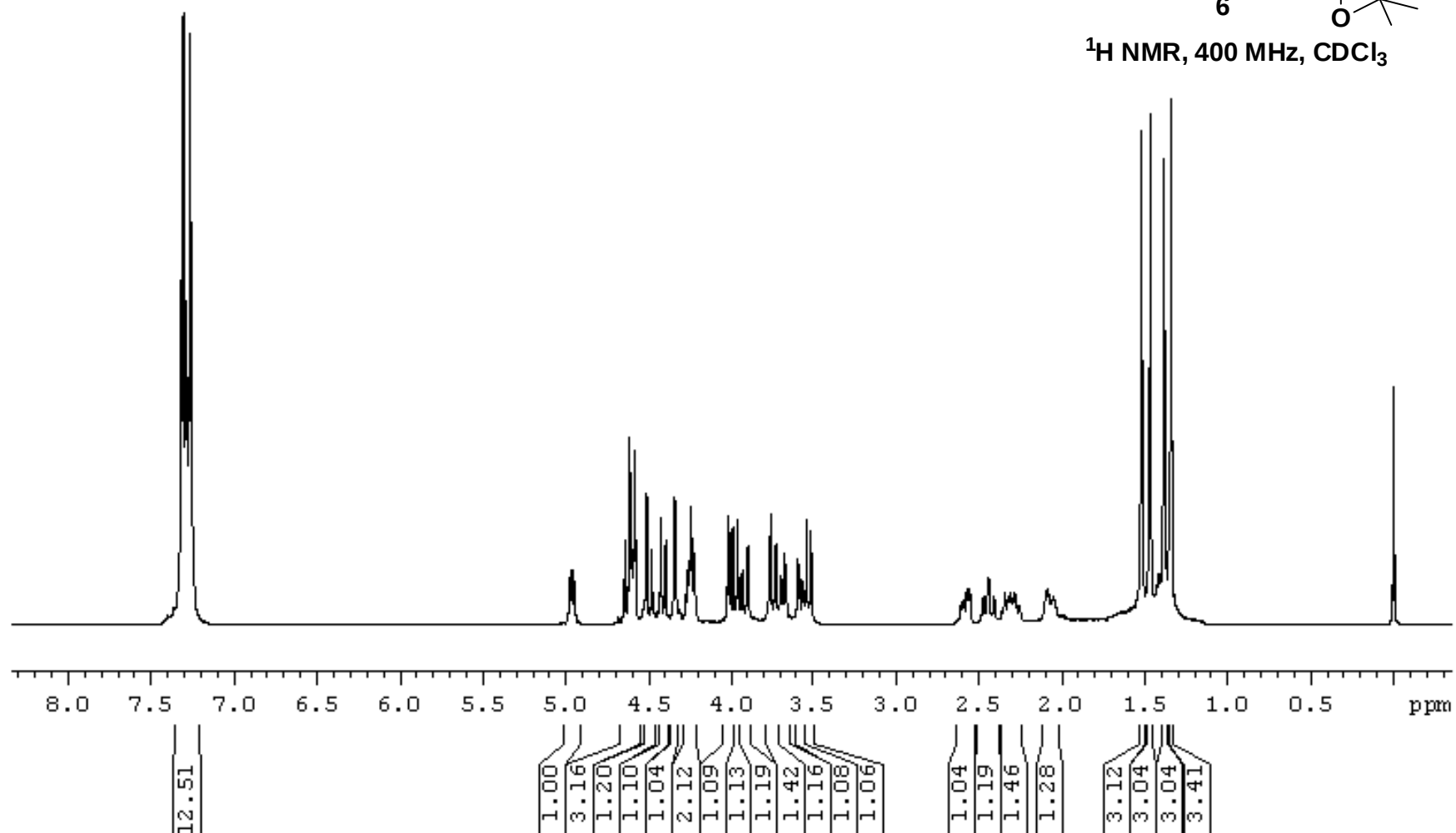
81.53
77.61
74.16
73.61
68.83
57.86

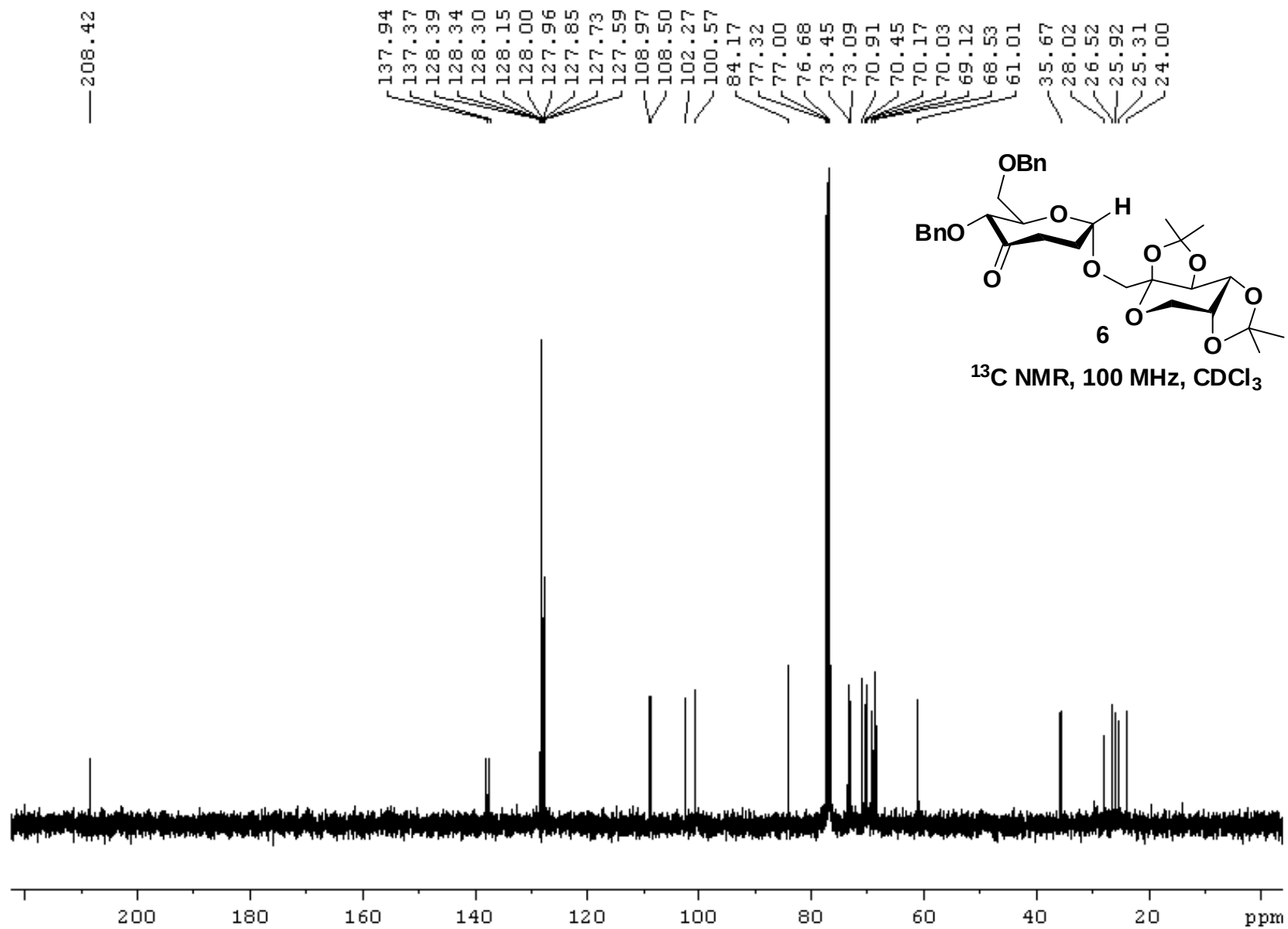
25.72
19.83

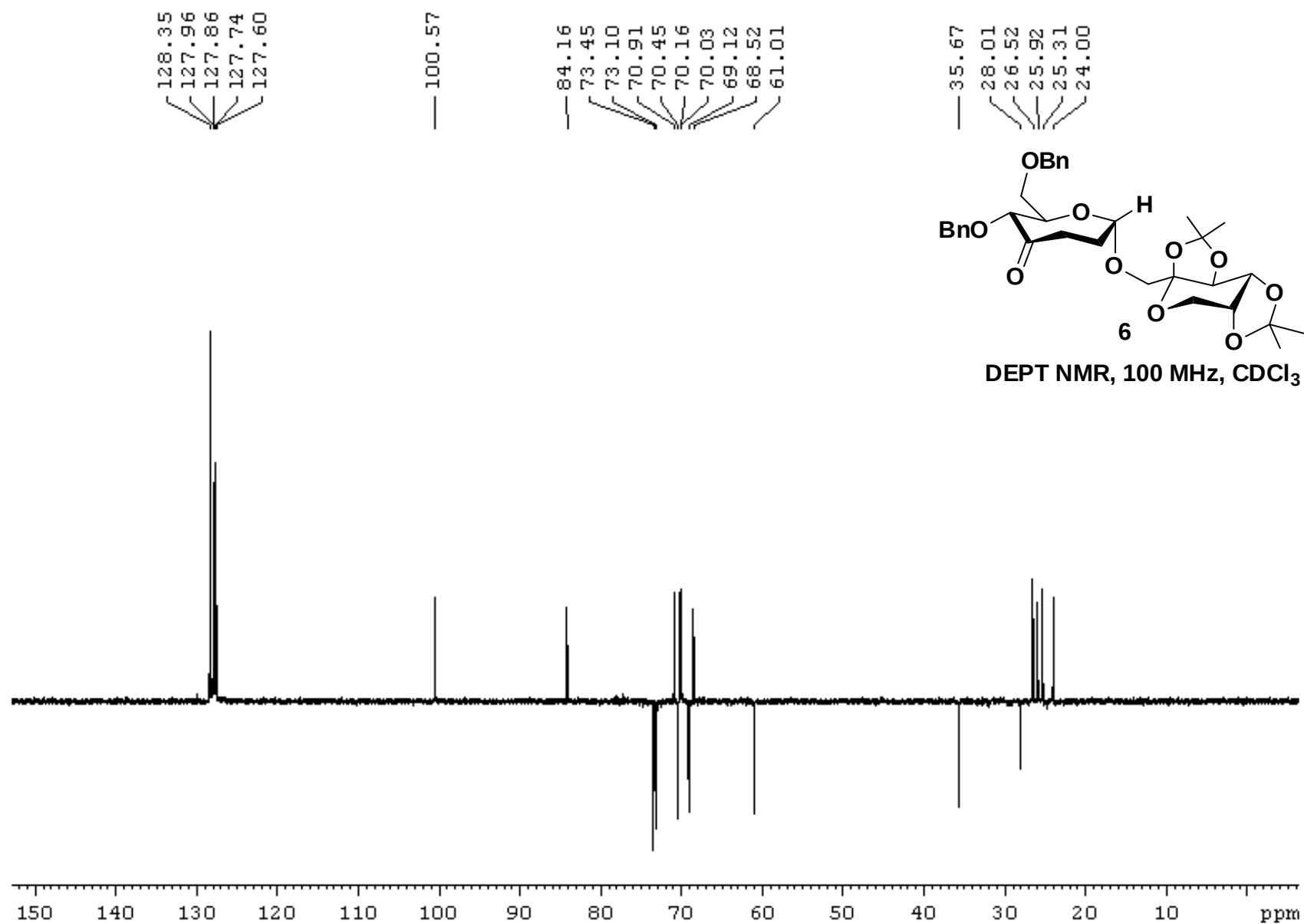


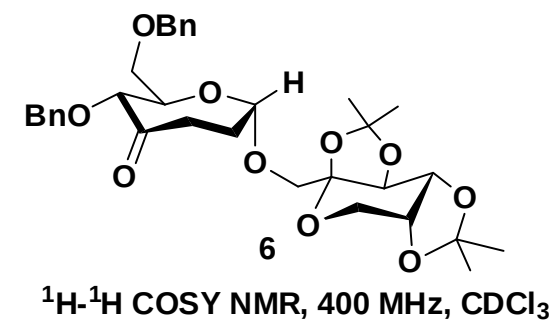
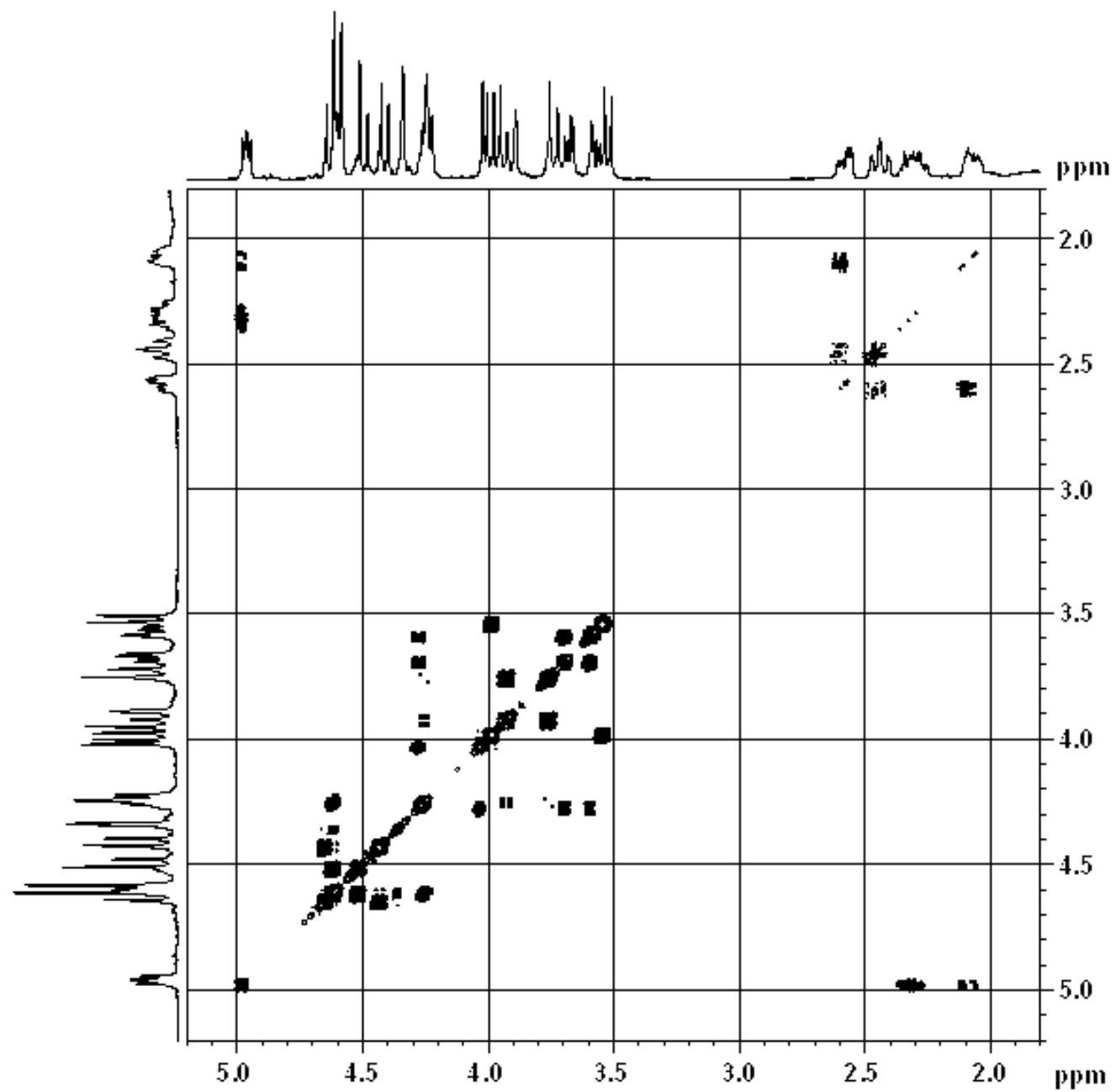


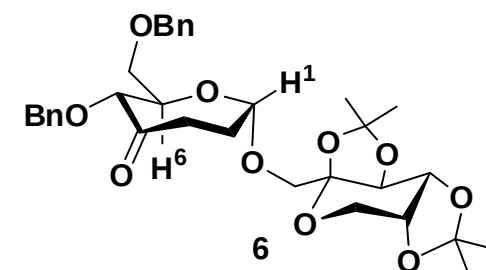
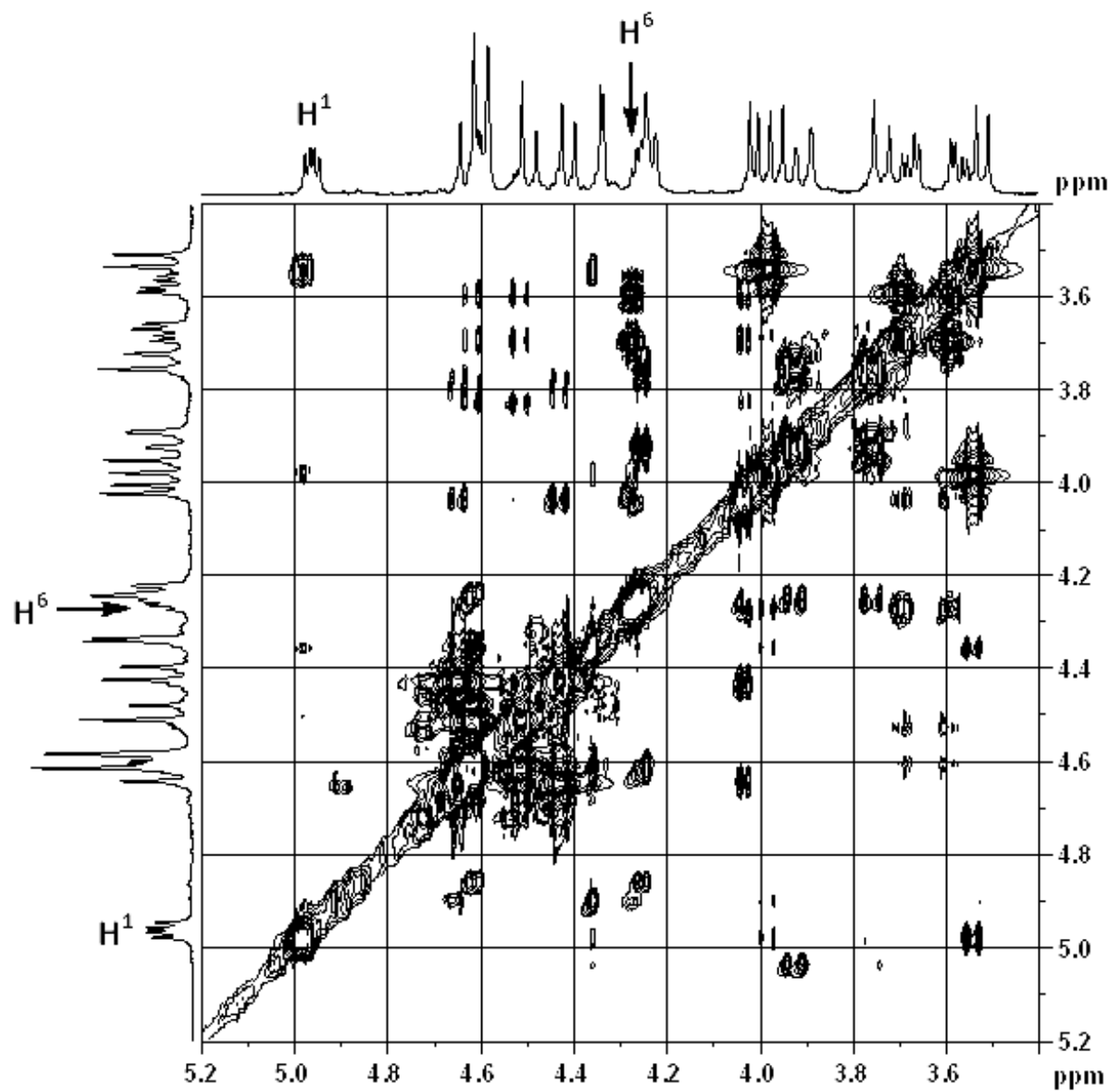
^1H NMR, 400 MHz, CDCl_3





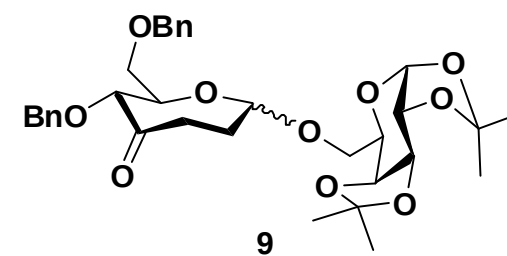




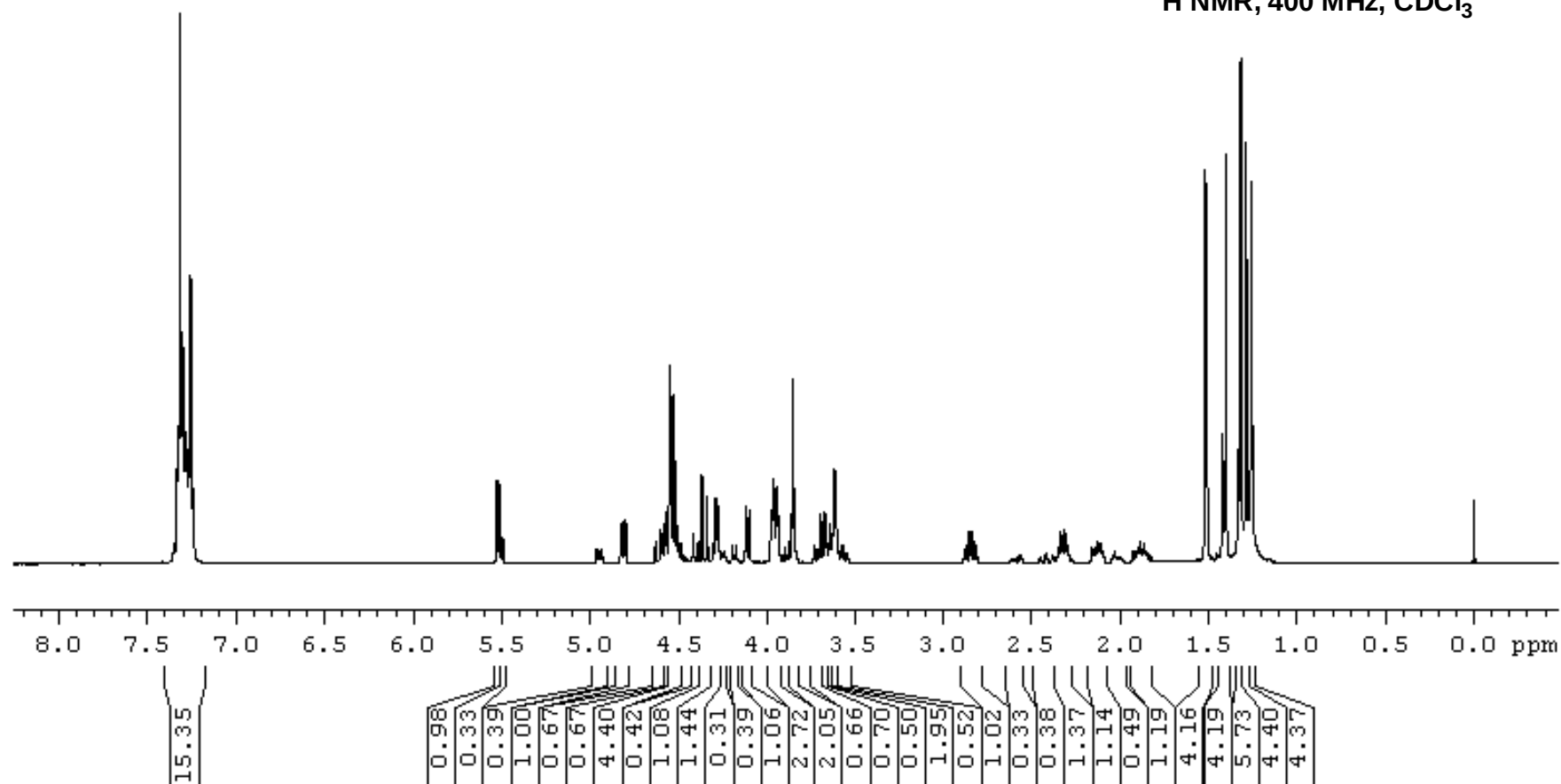


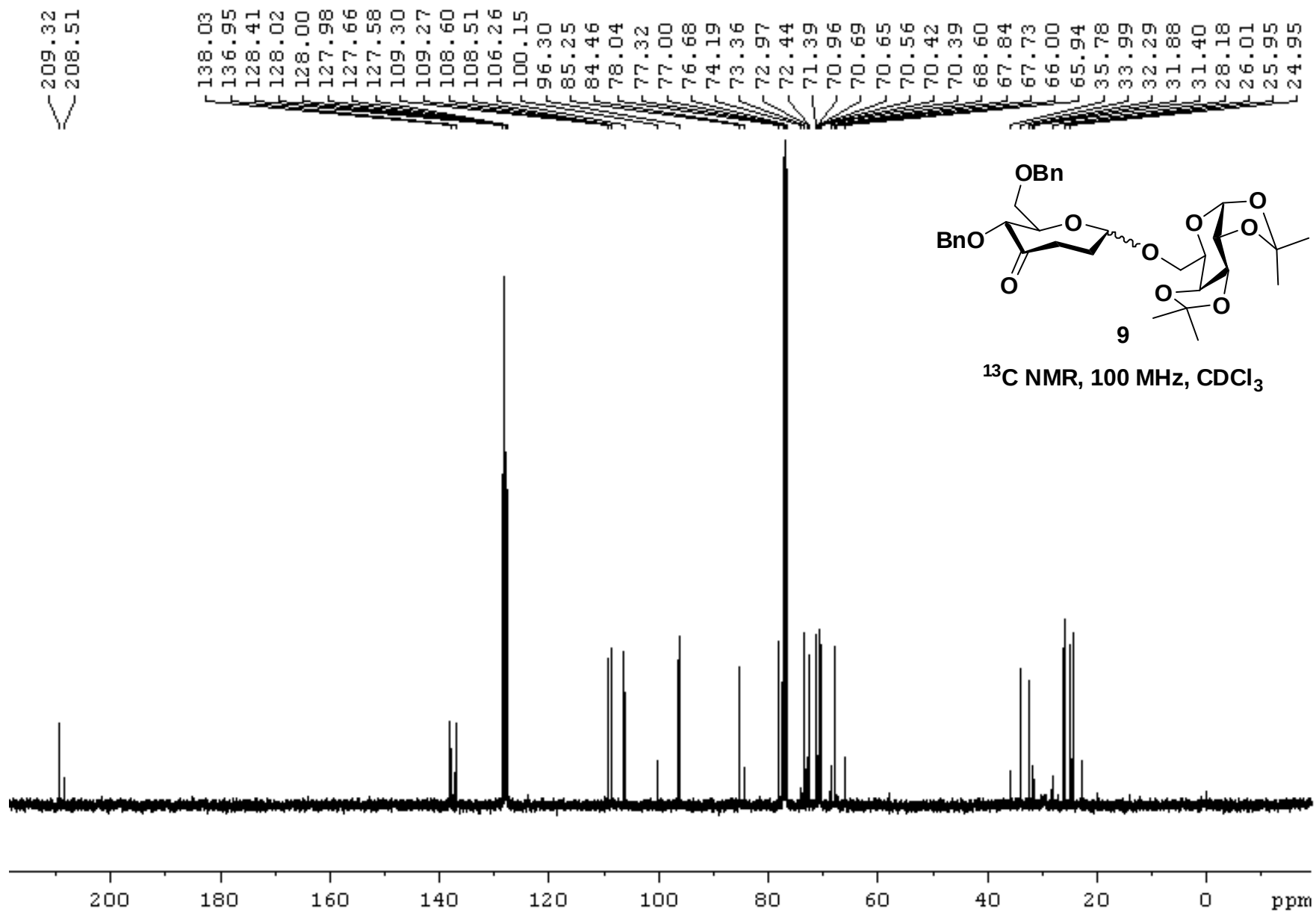
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

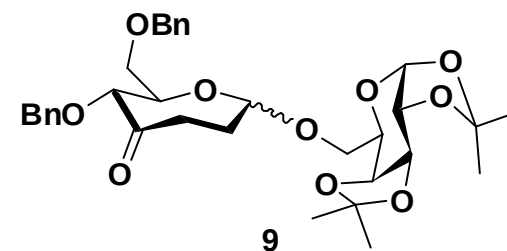
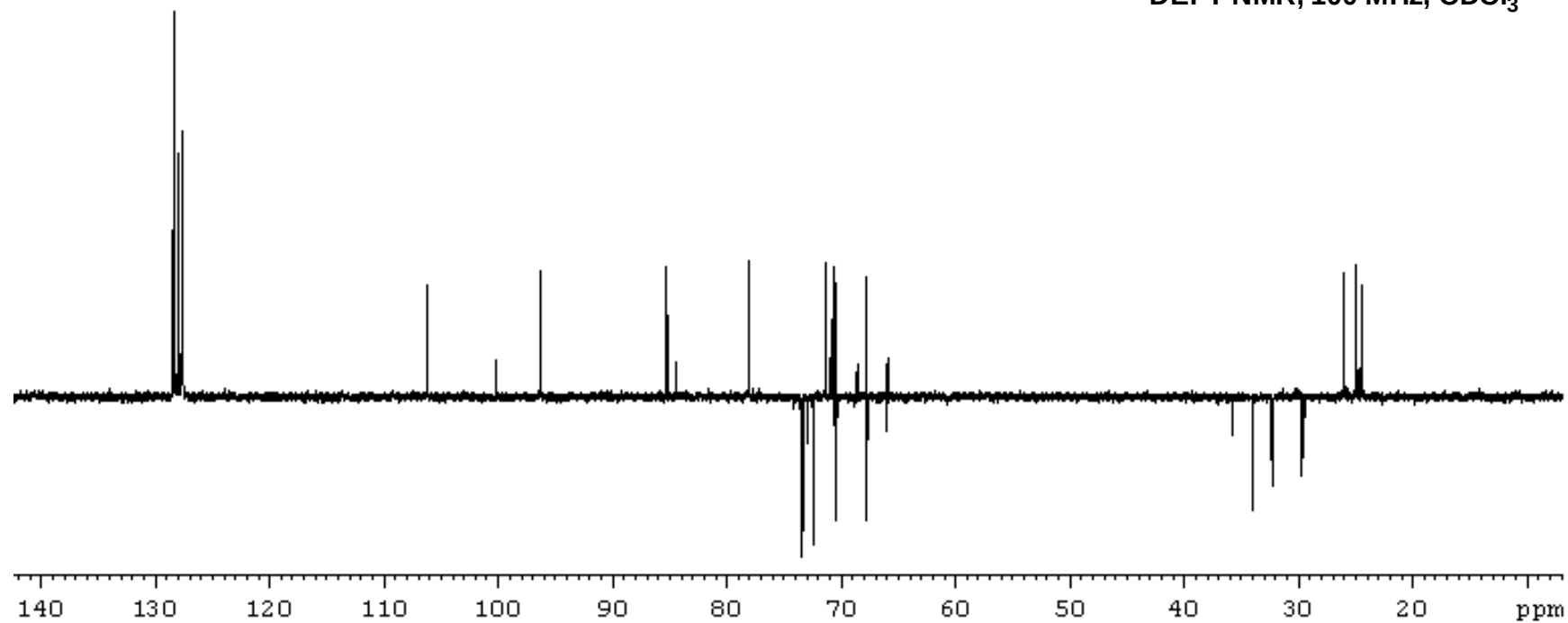
NOE not observed between H^1 and H^6



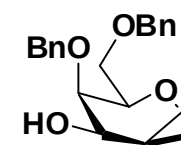
^1H NMR, 400 MHz, CDCl_3



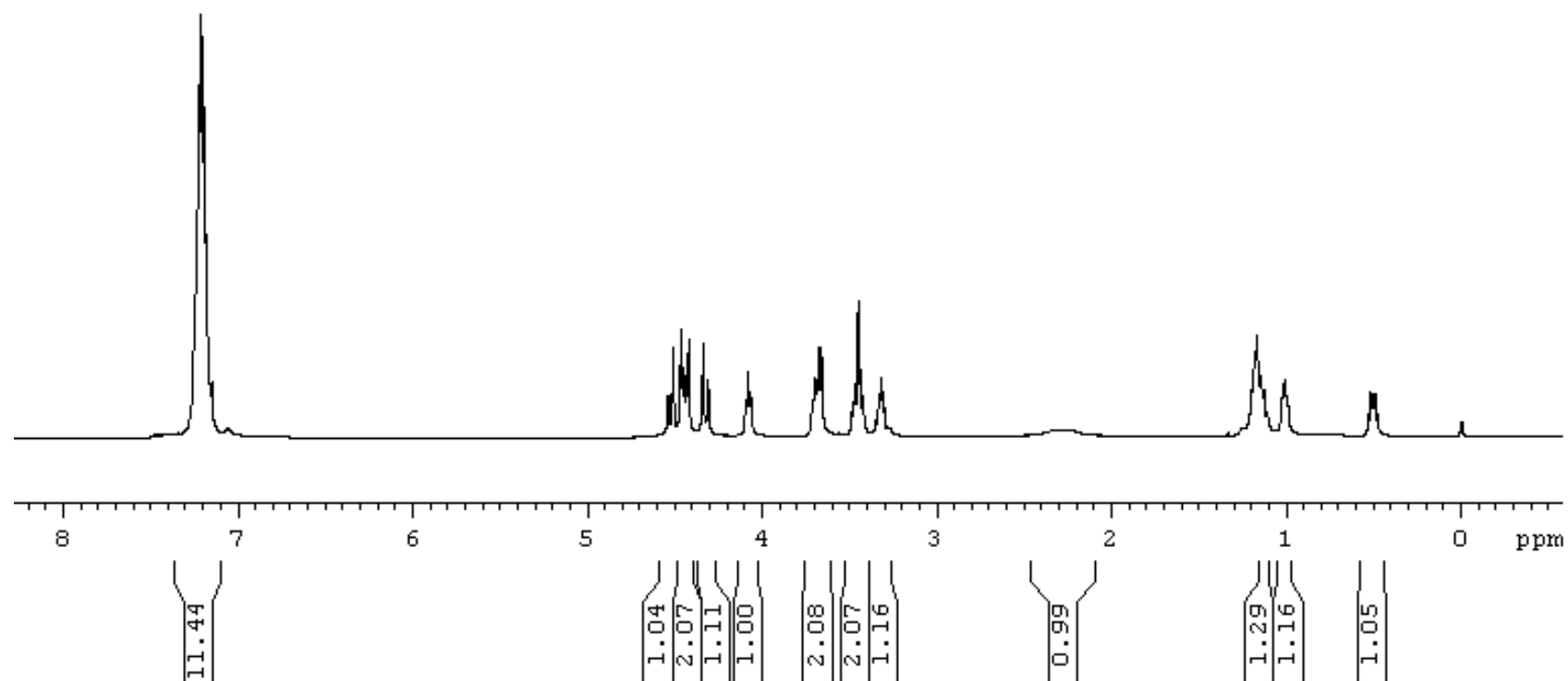




DEPT NMR, 100 MHz, CDCl₃



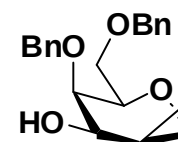
^1H NMR, 400 MHz, CDCl_3



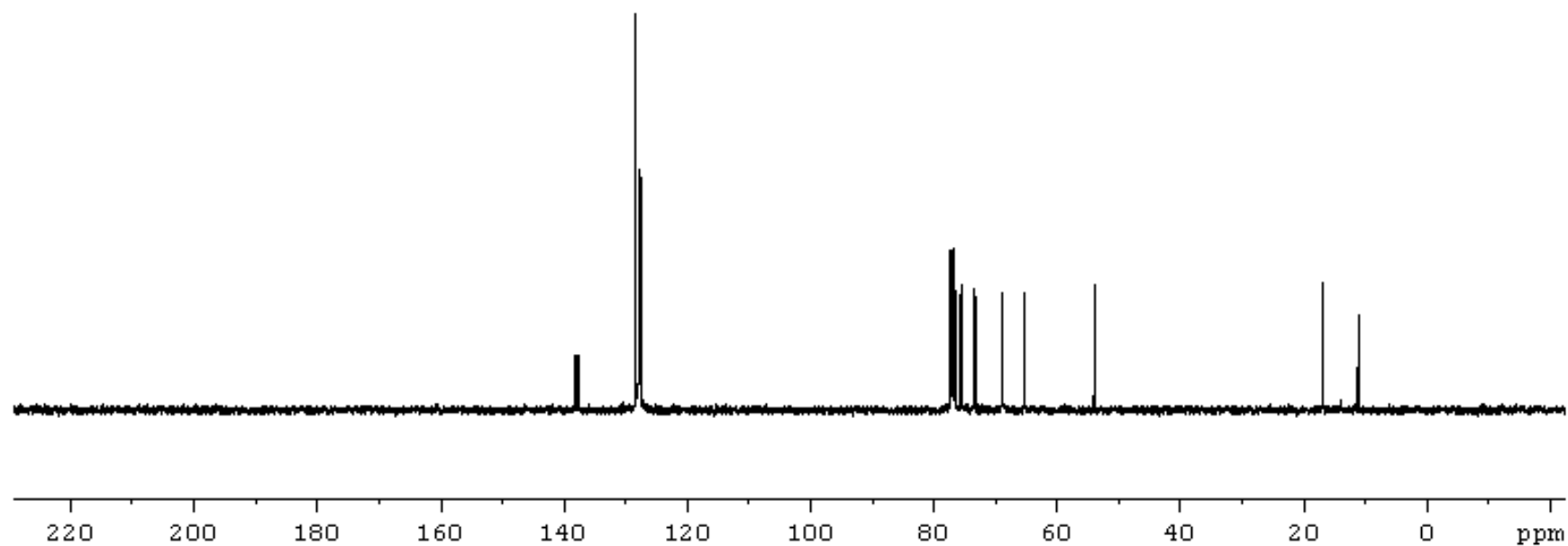
138.06
137.61
128.32
127.81
127.69
127.53

77.32
77.00
76.68
76.47
75.61
75.52
73.36
68.88
65.33
54.00

16.97
11.19



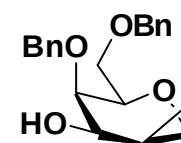
^{13}C NMR, 100 MHz, CDCl_3



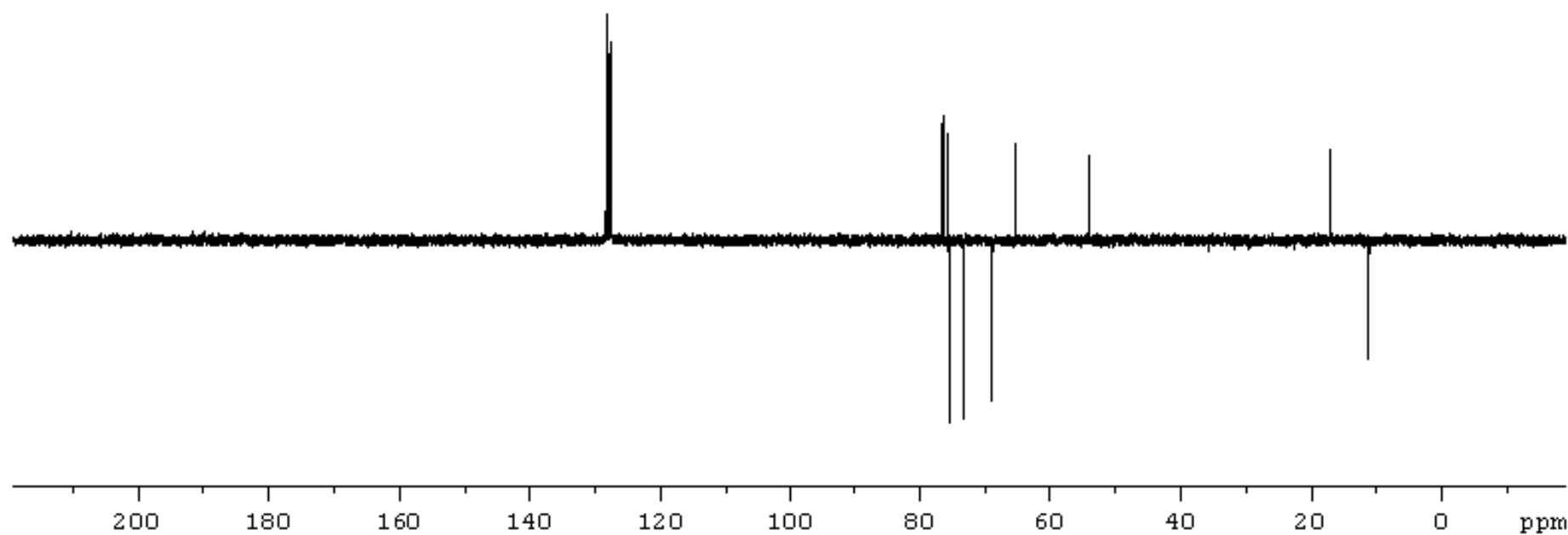
128.31
127.81
127.69
127.66
127.53

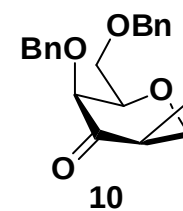
76.46
75.60
75.52
73.35
68.88
65.33
— 54.00

— 16.97
— 11.19

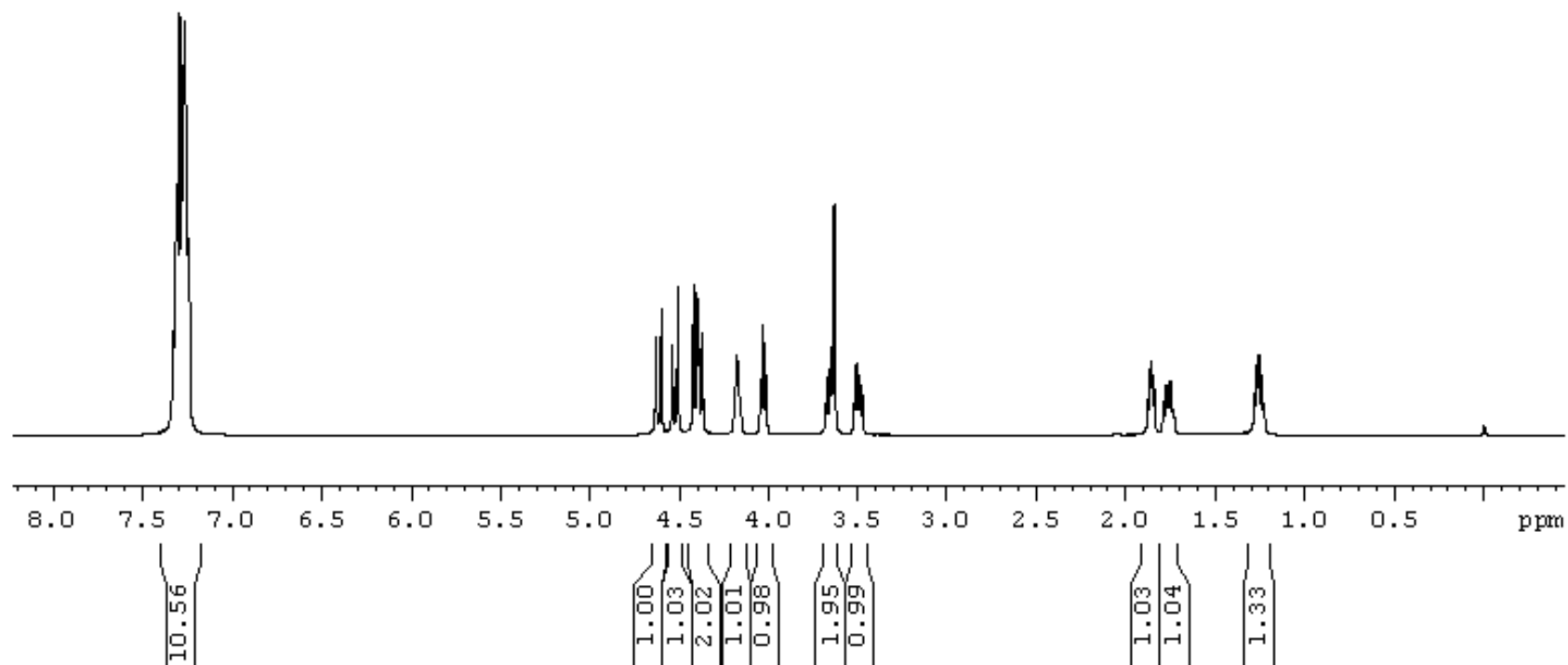


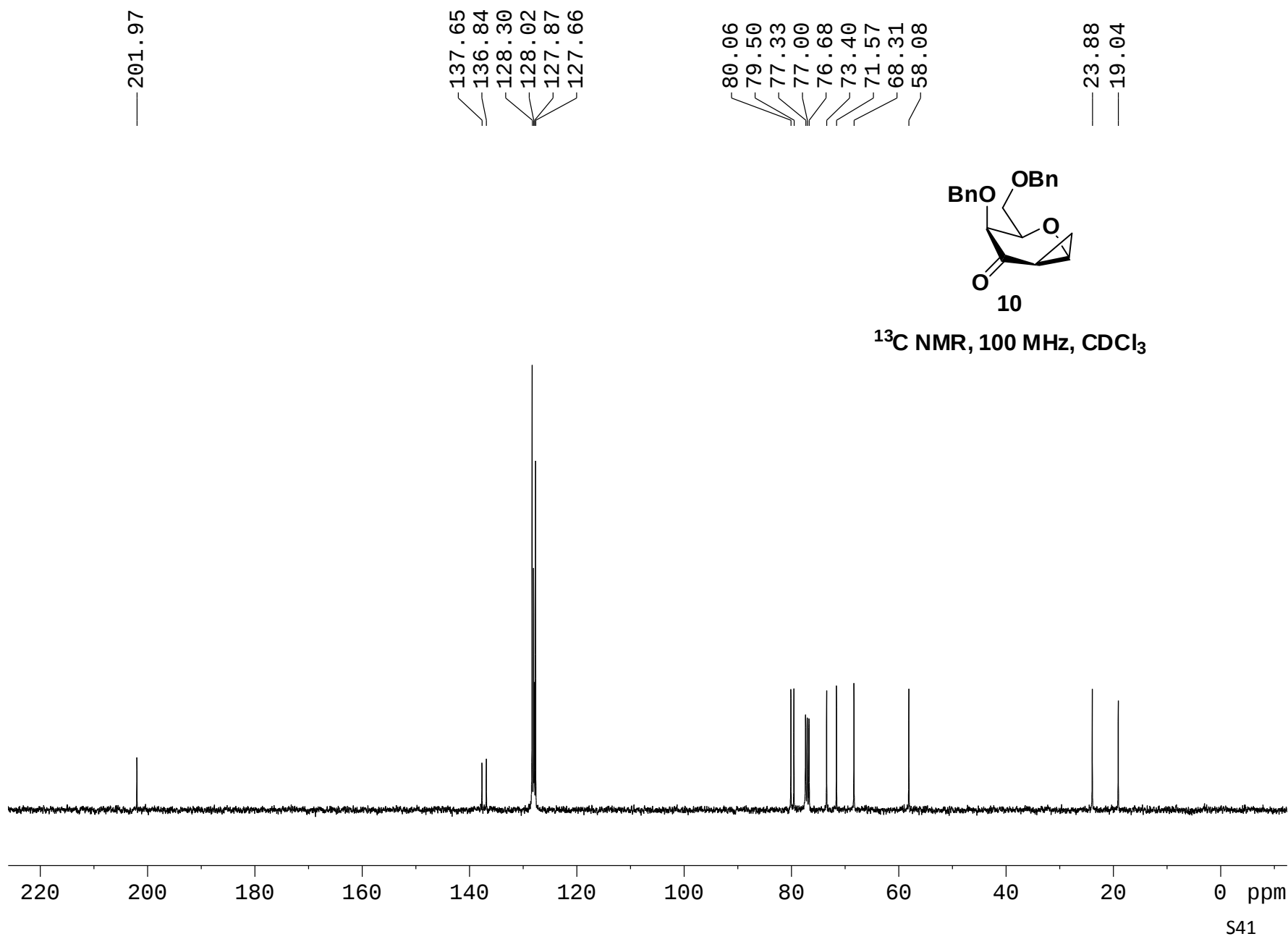
DEPT NMR, 100 MHz, CDCl_3





^1H NMR, 400 MHz, CDCl_3

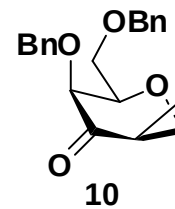




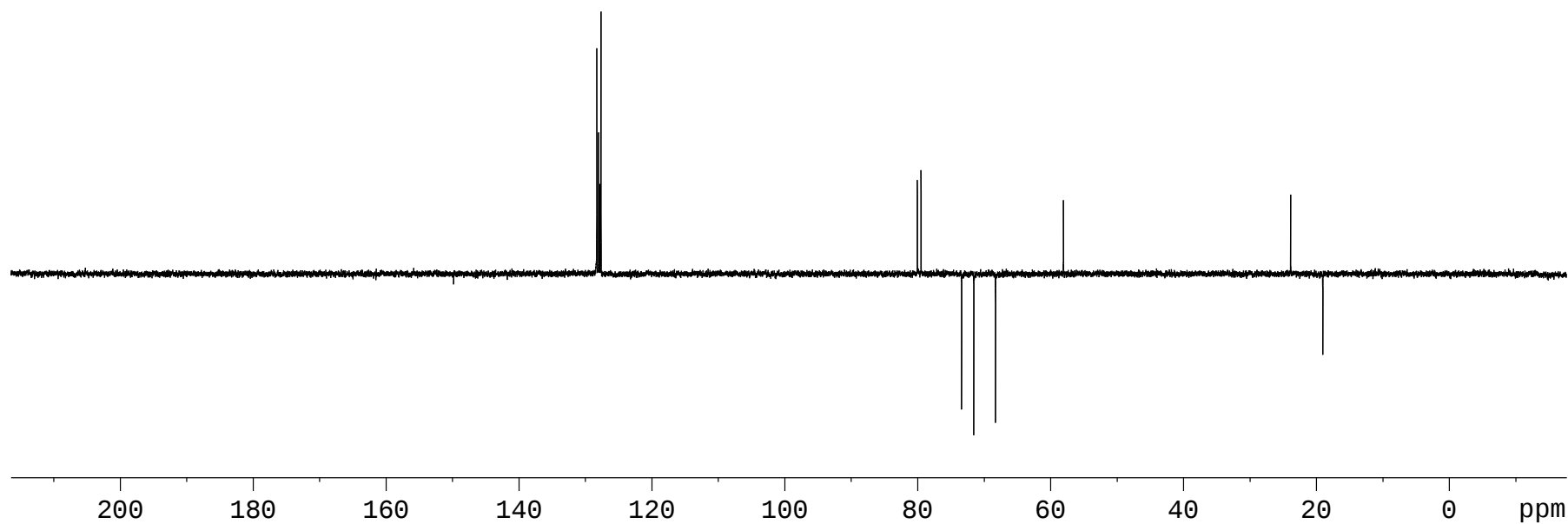
128.30
128.02
127.87
127.66

80.06
79.50
73.40
71.56
68.30
58.08

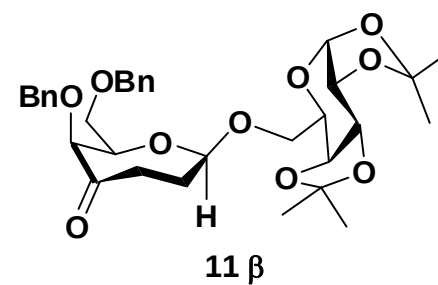
23.88
19.04



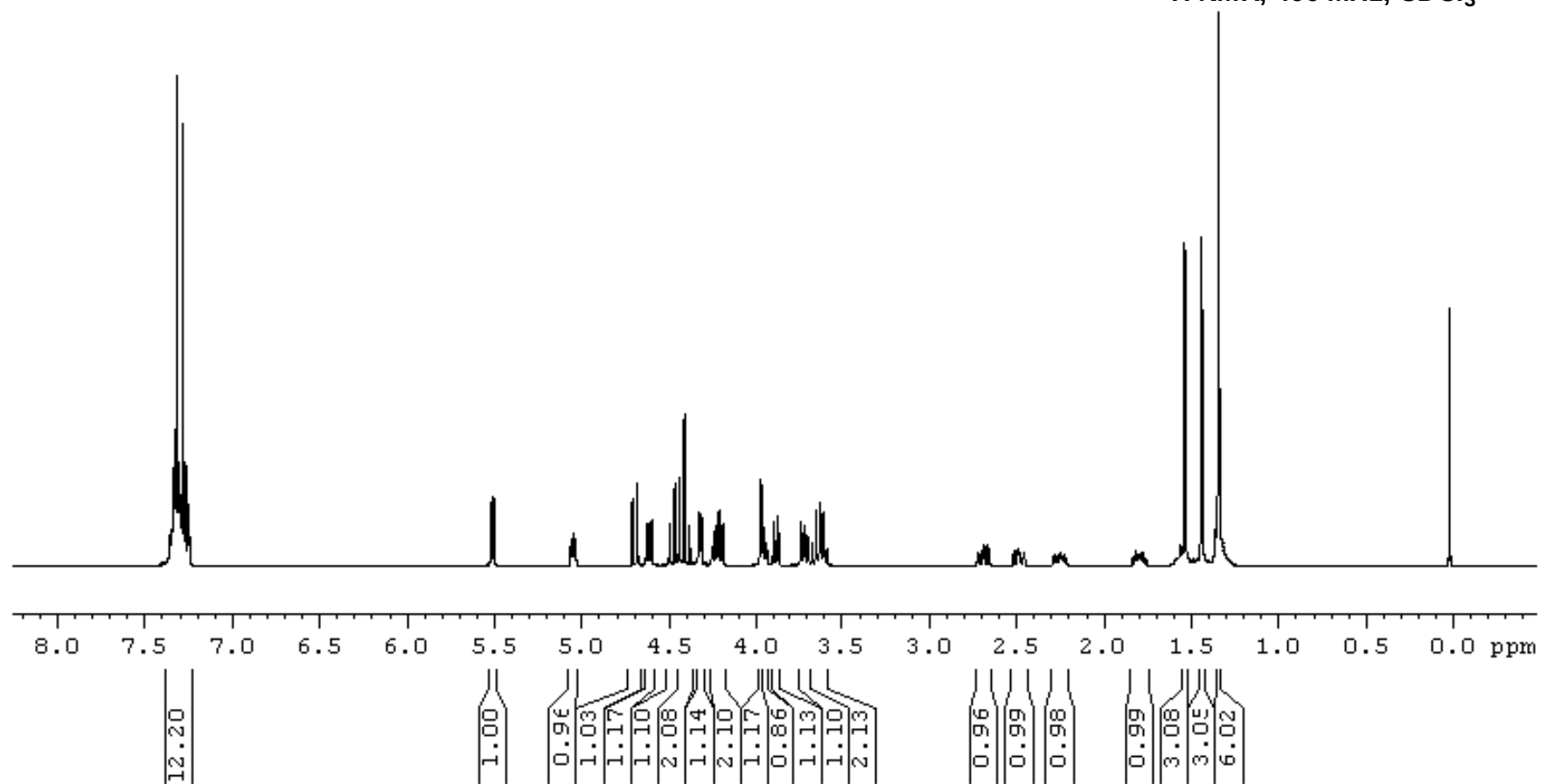
DEPT NMR, 100 MHz, CDCl_3



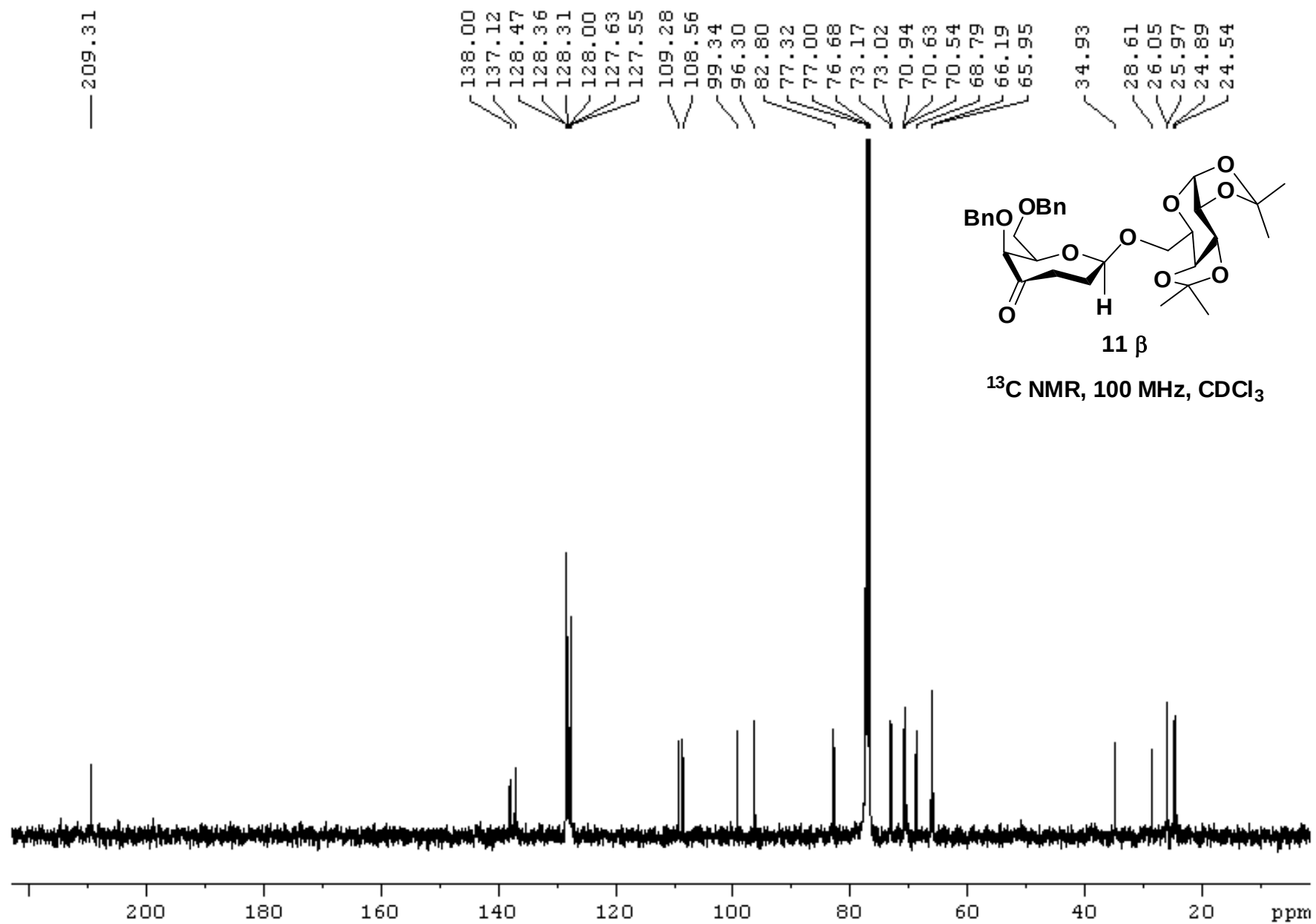
S42

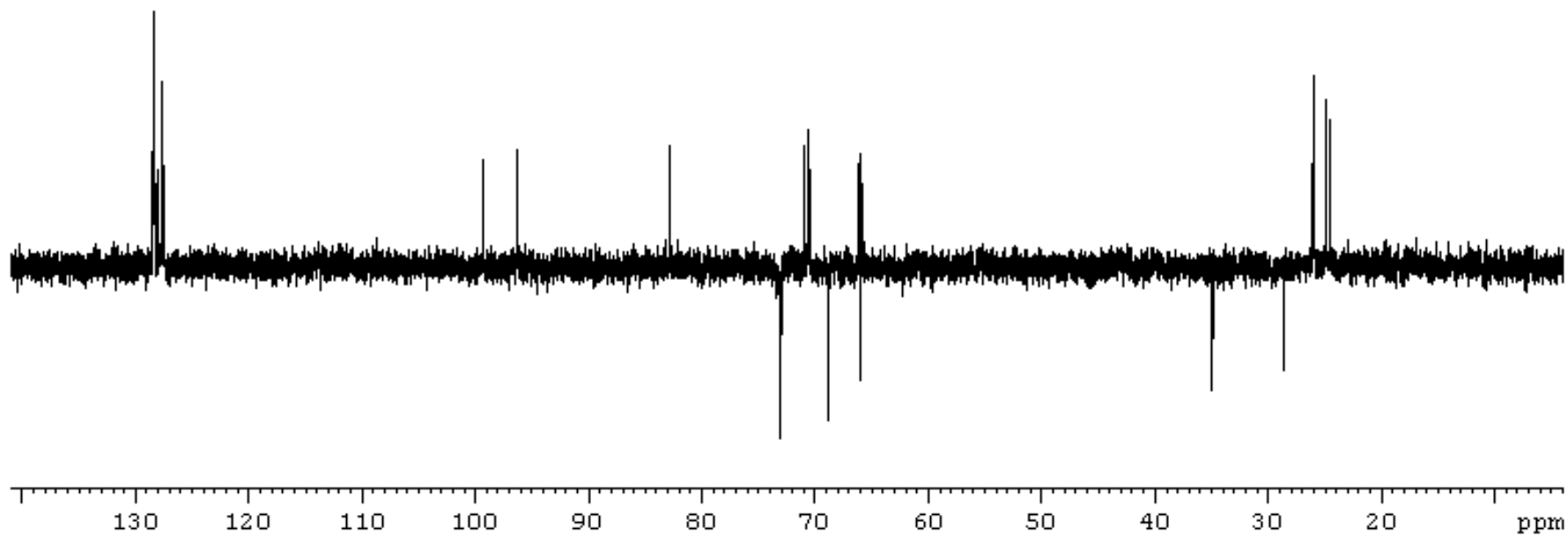


^1H NMR, 400 MHz, CDCl_3



— 209.31



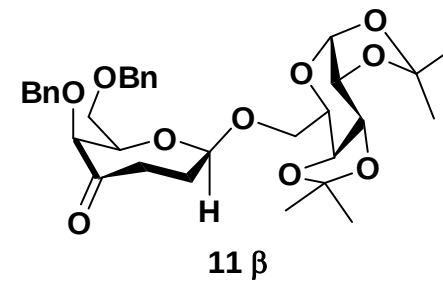


128.47
128.36
128.32
128.01
127.64
127.56

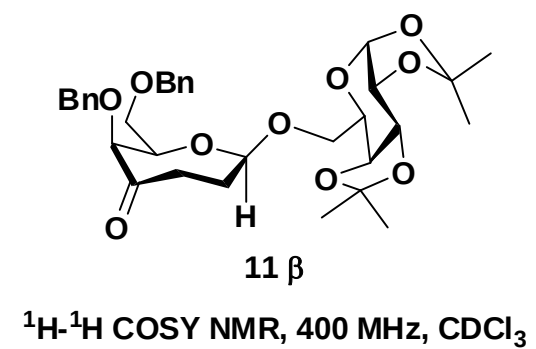
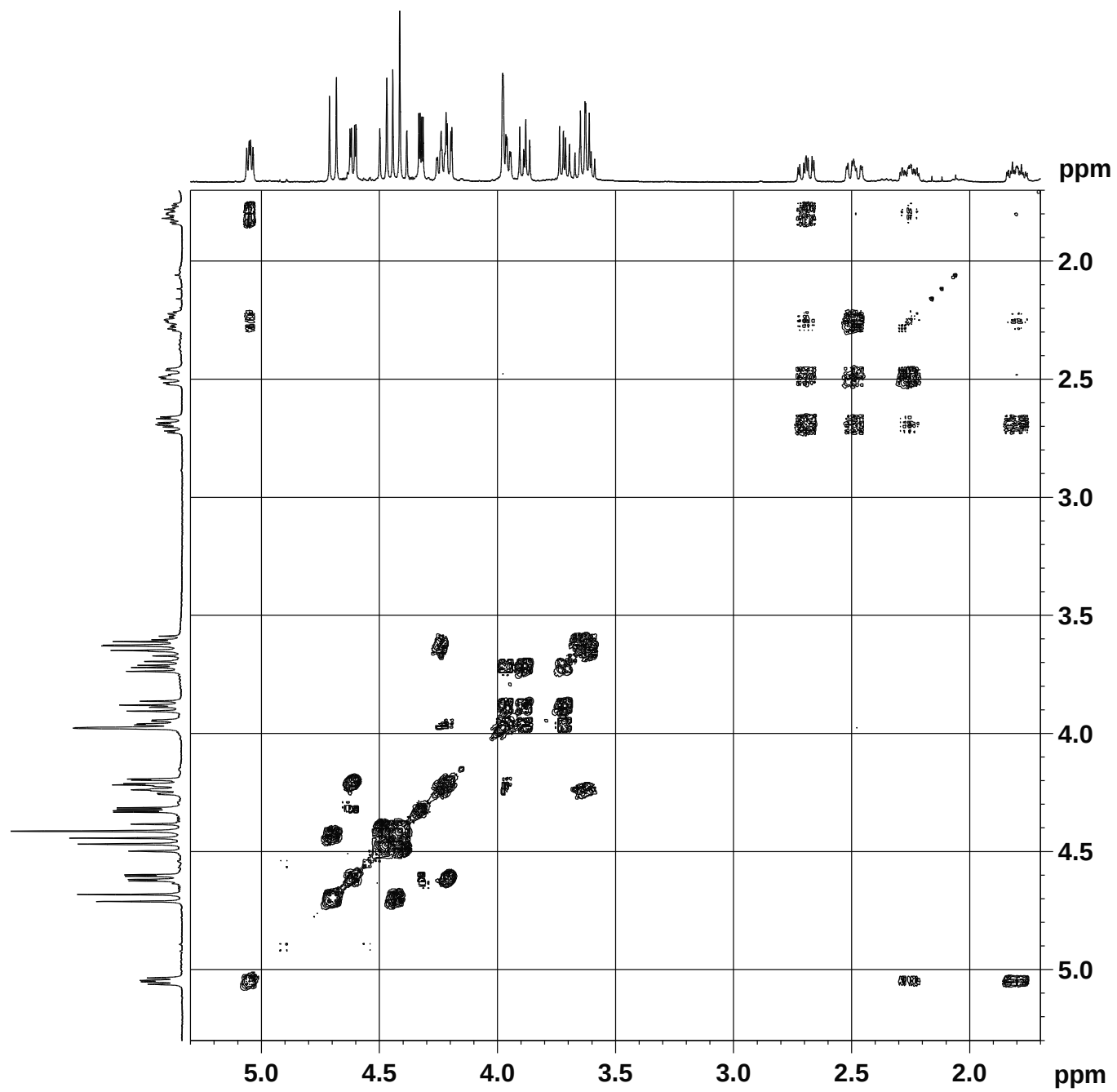
— 99.34
— 96.30

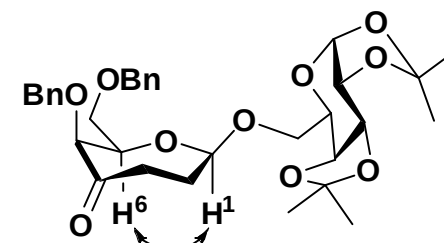
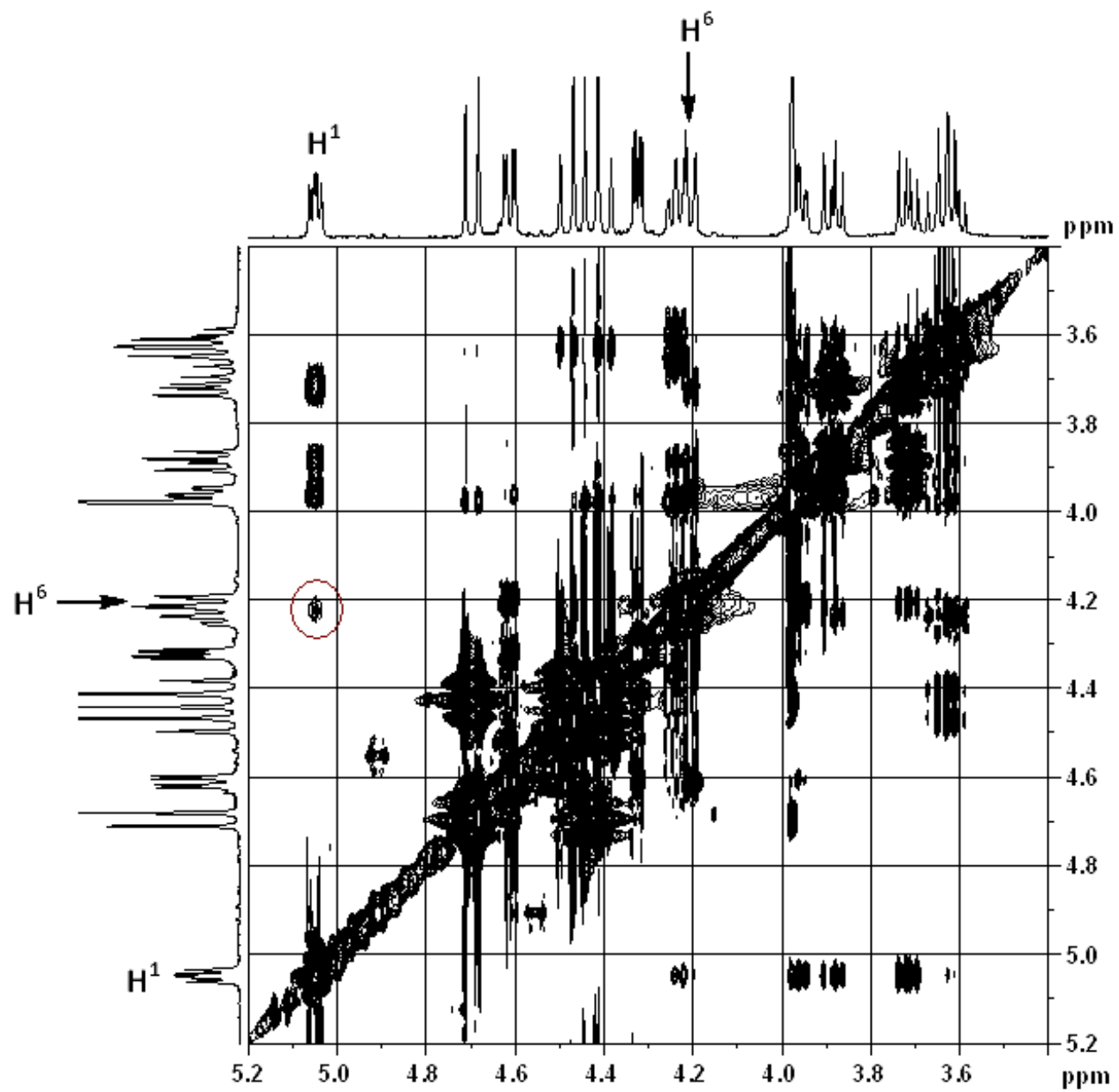
— 82.80
73.17
73.03
70.95
70.63
70.54
68.79
66.20
65.98
65.95

— 34.93
28.62
26.05
25.98
24.90
24.54



DEPT NMR, 100 MHz, CDCl₃

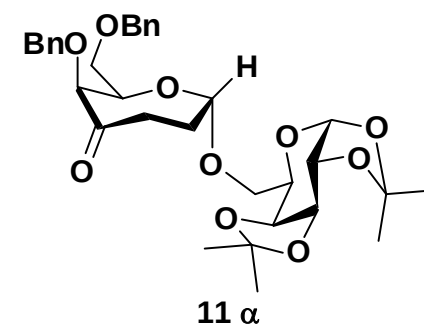




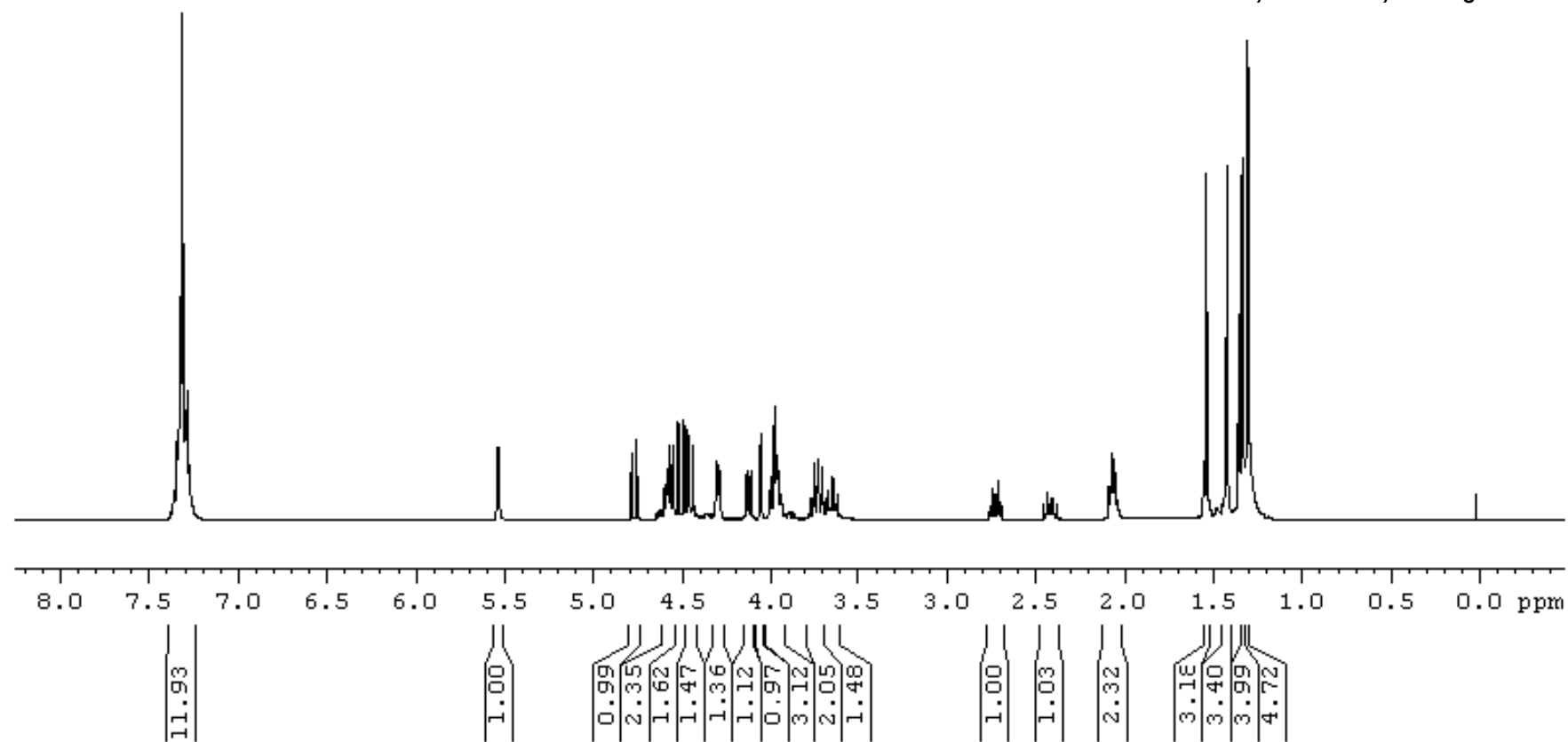
11 β

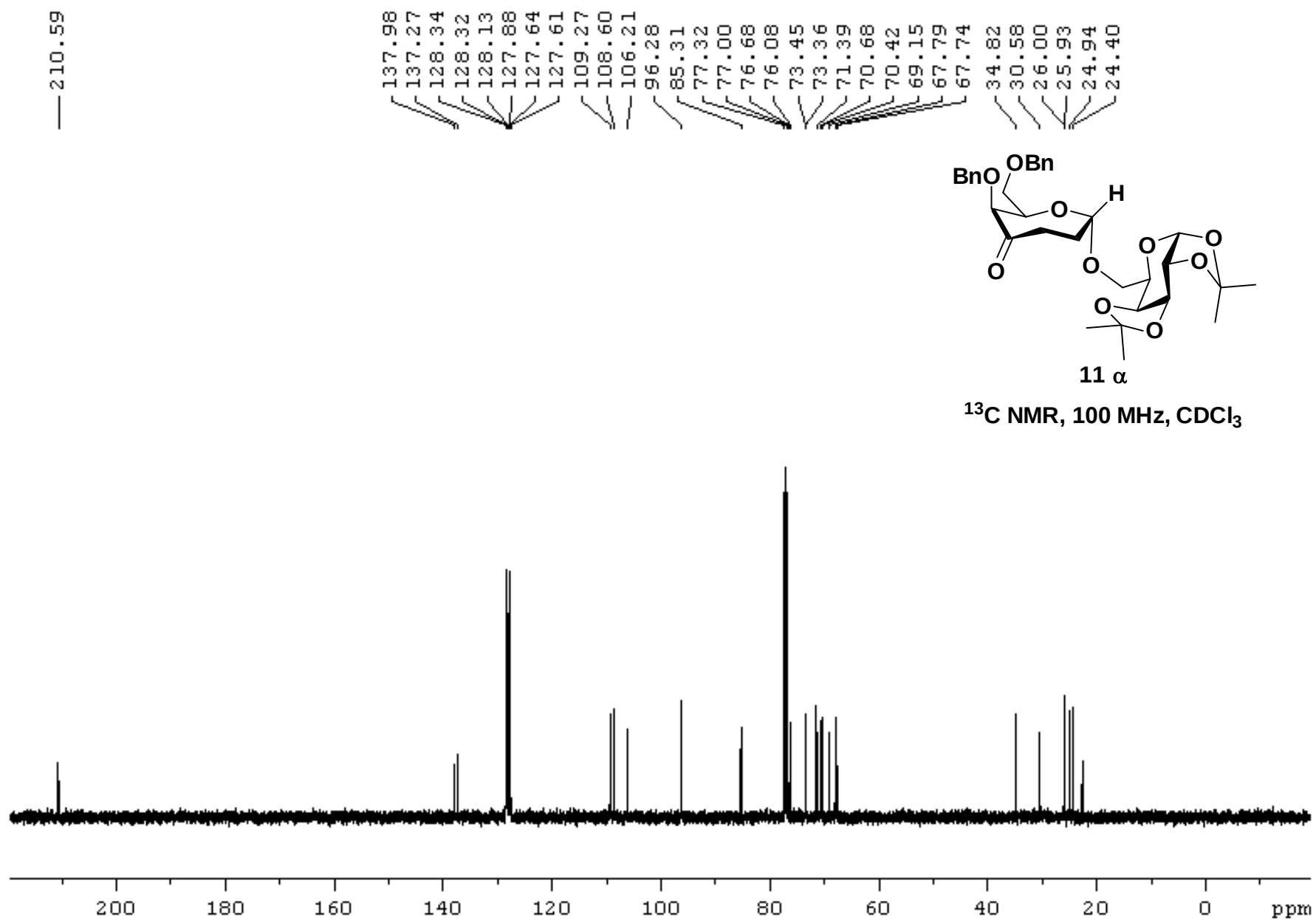
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

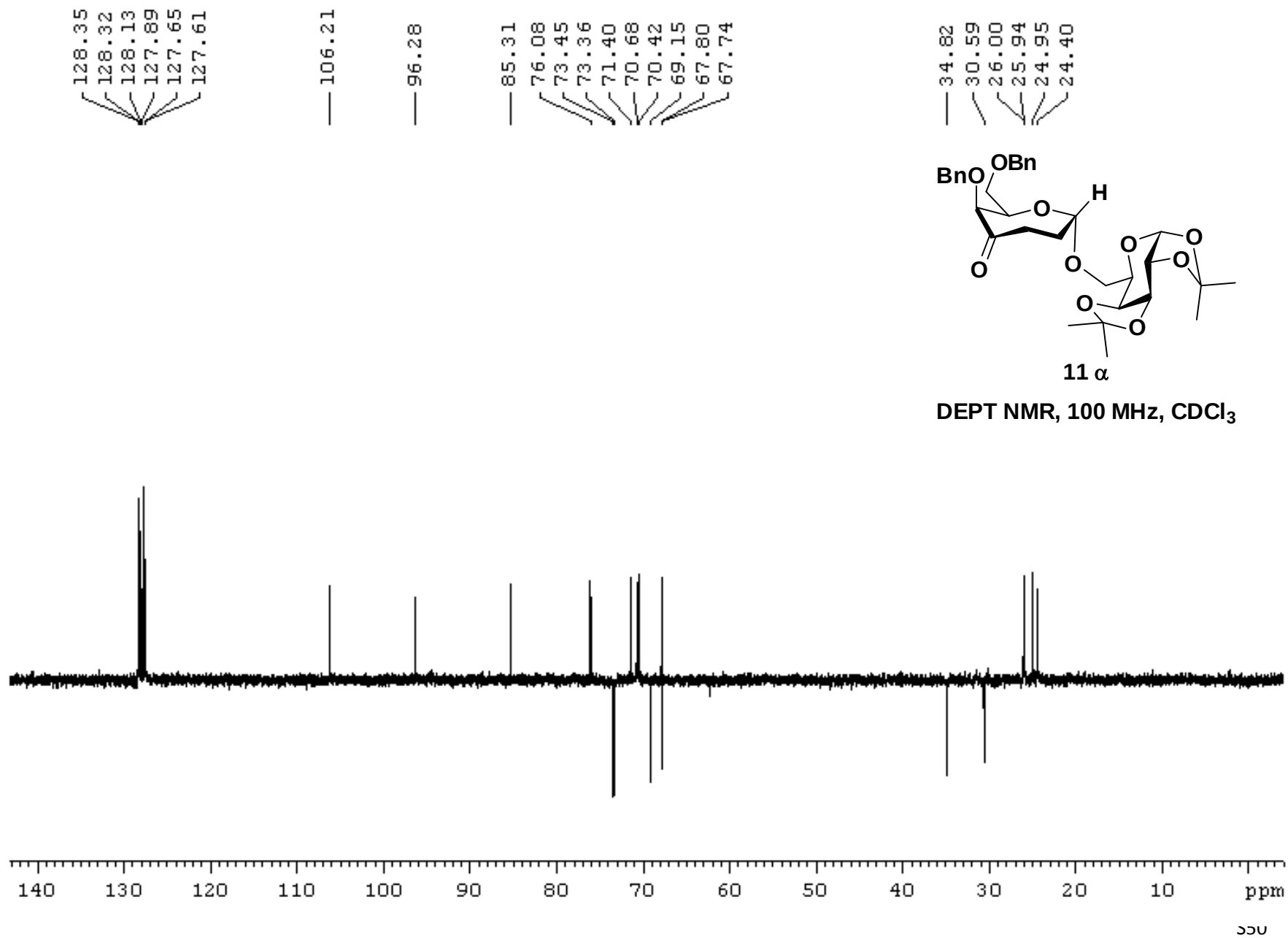
NOE observed between H^1 and H^6

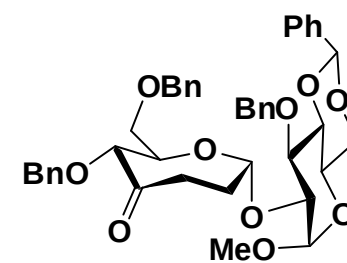


^1H NMR, 400 MHz, CDCl_3



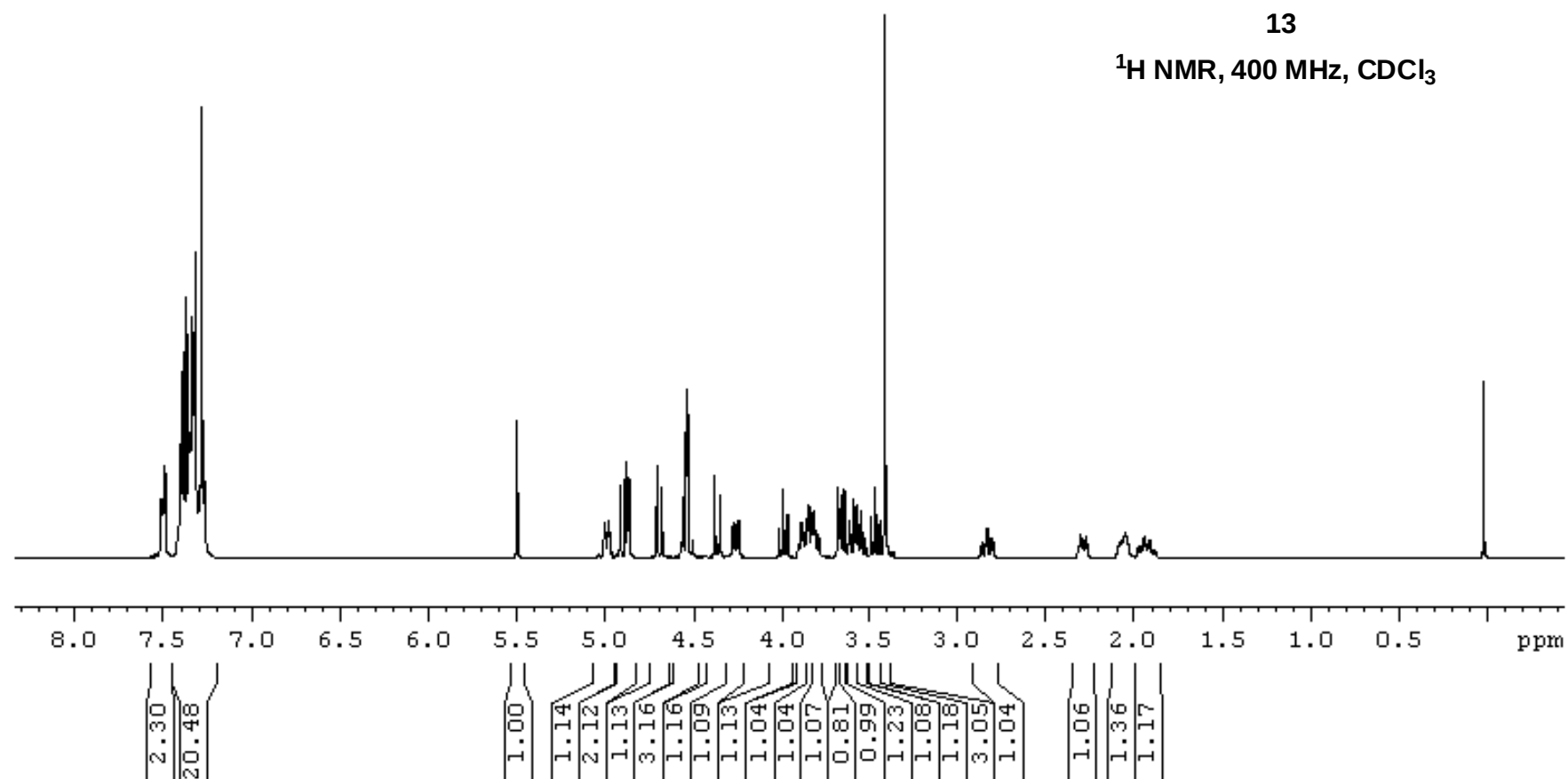


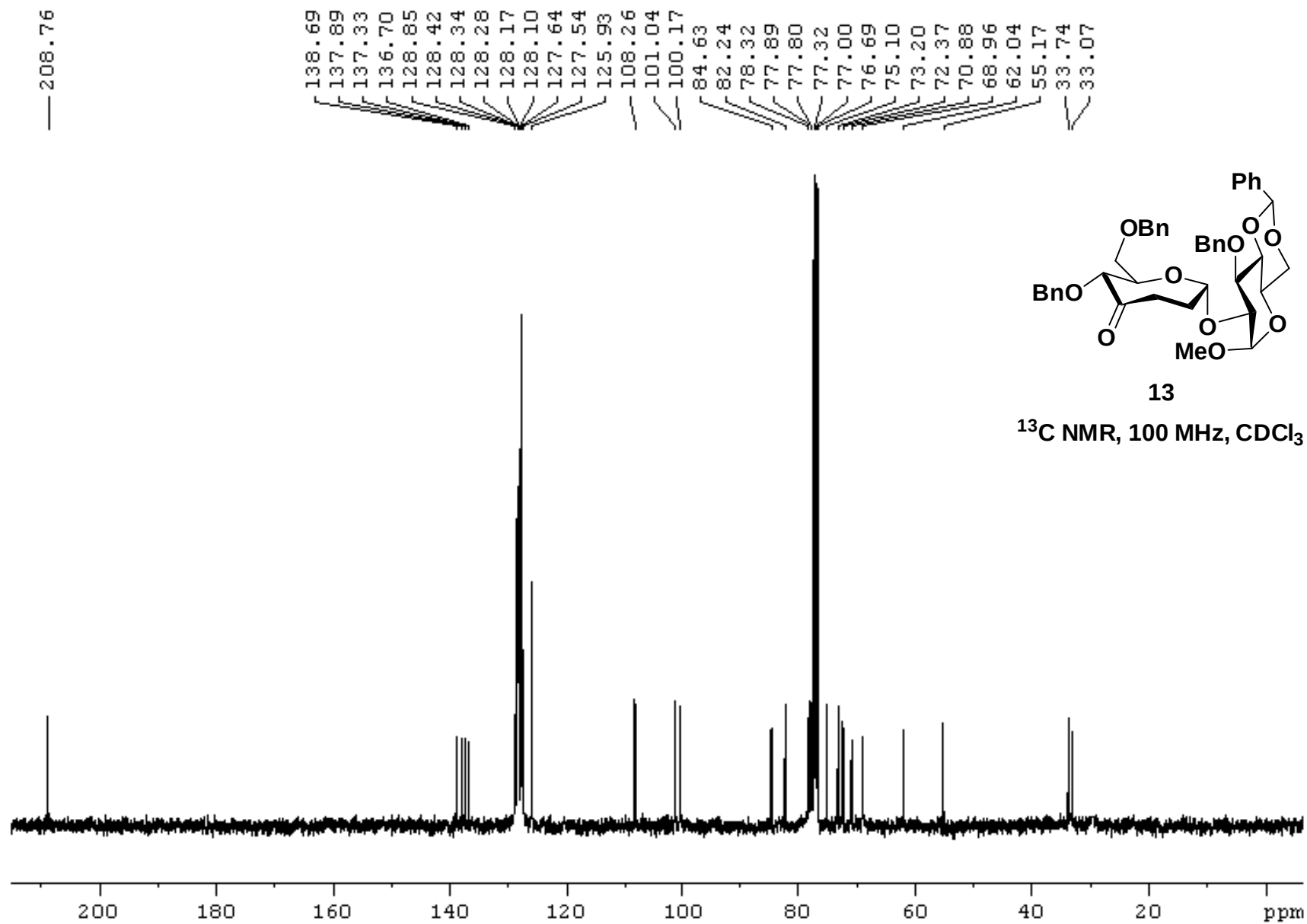


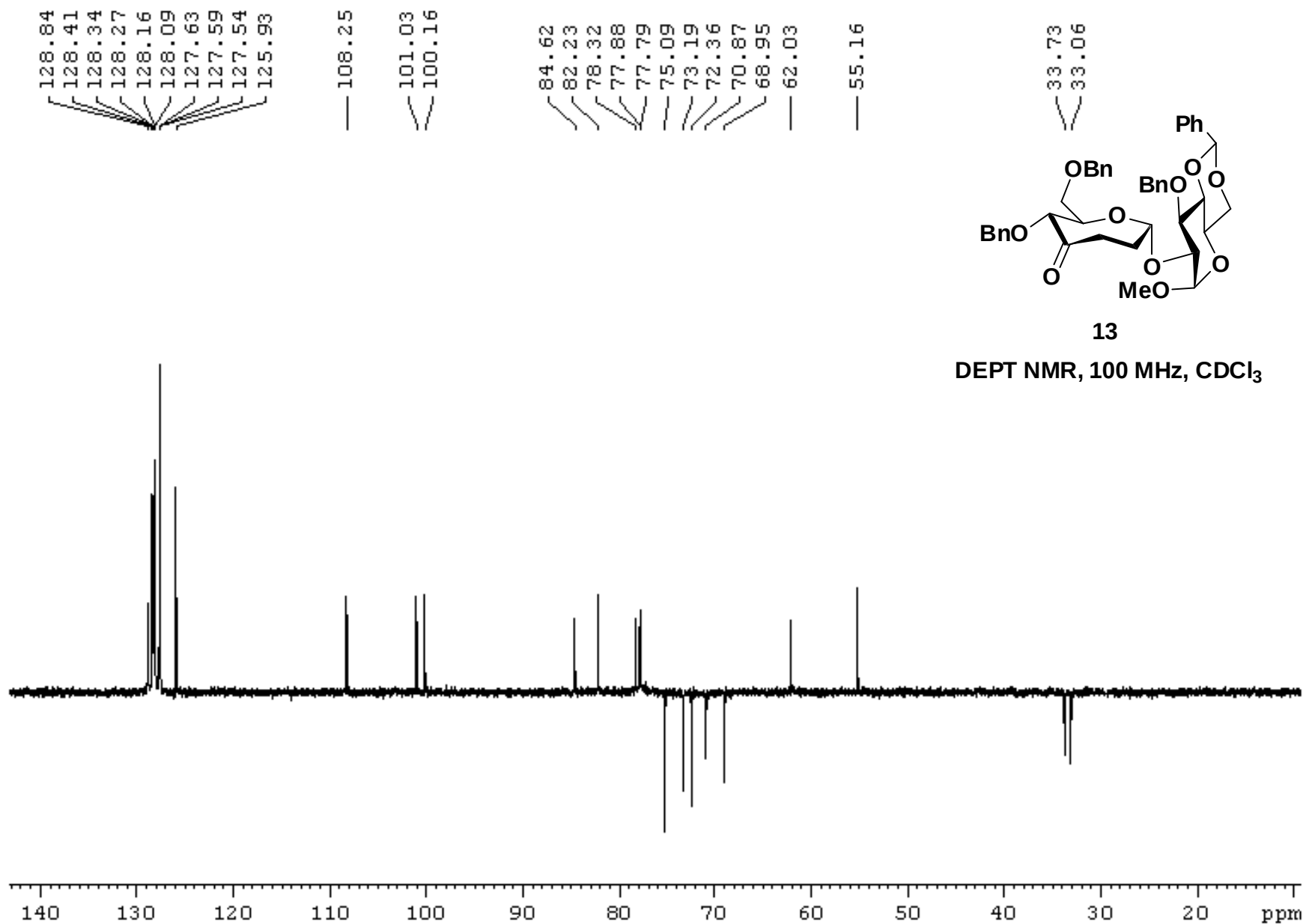


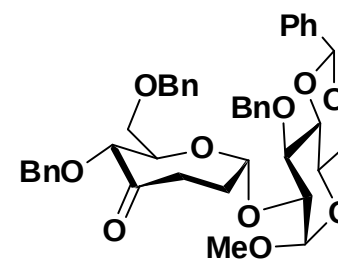
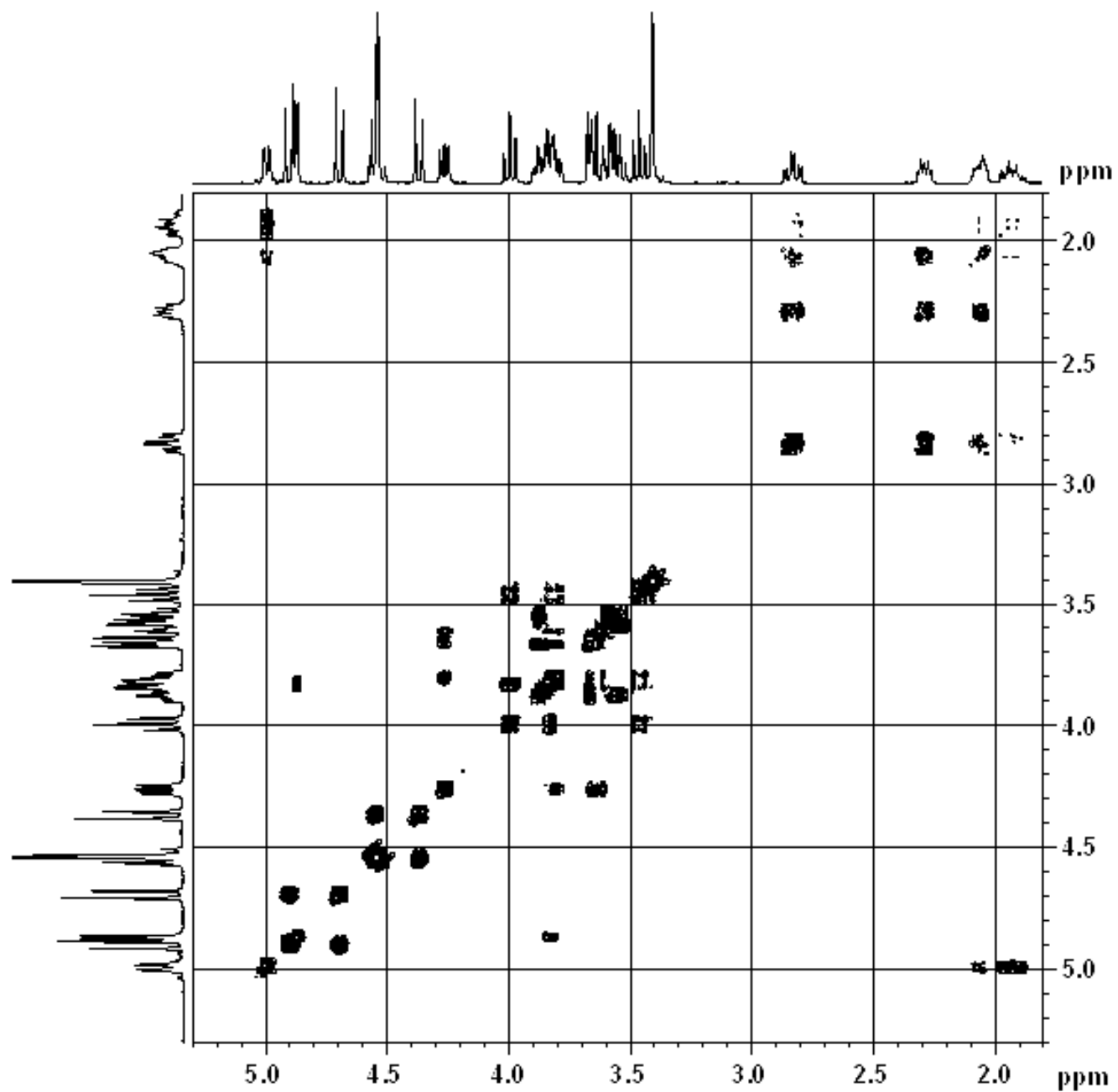
13

^1H NMR, 400 MHz, CDCl_3



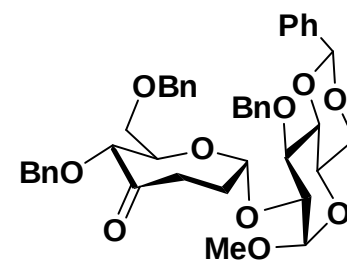
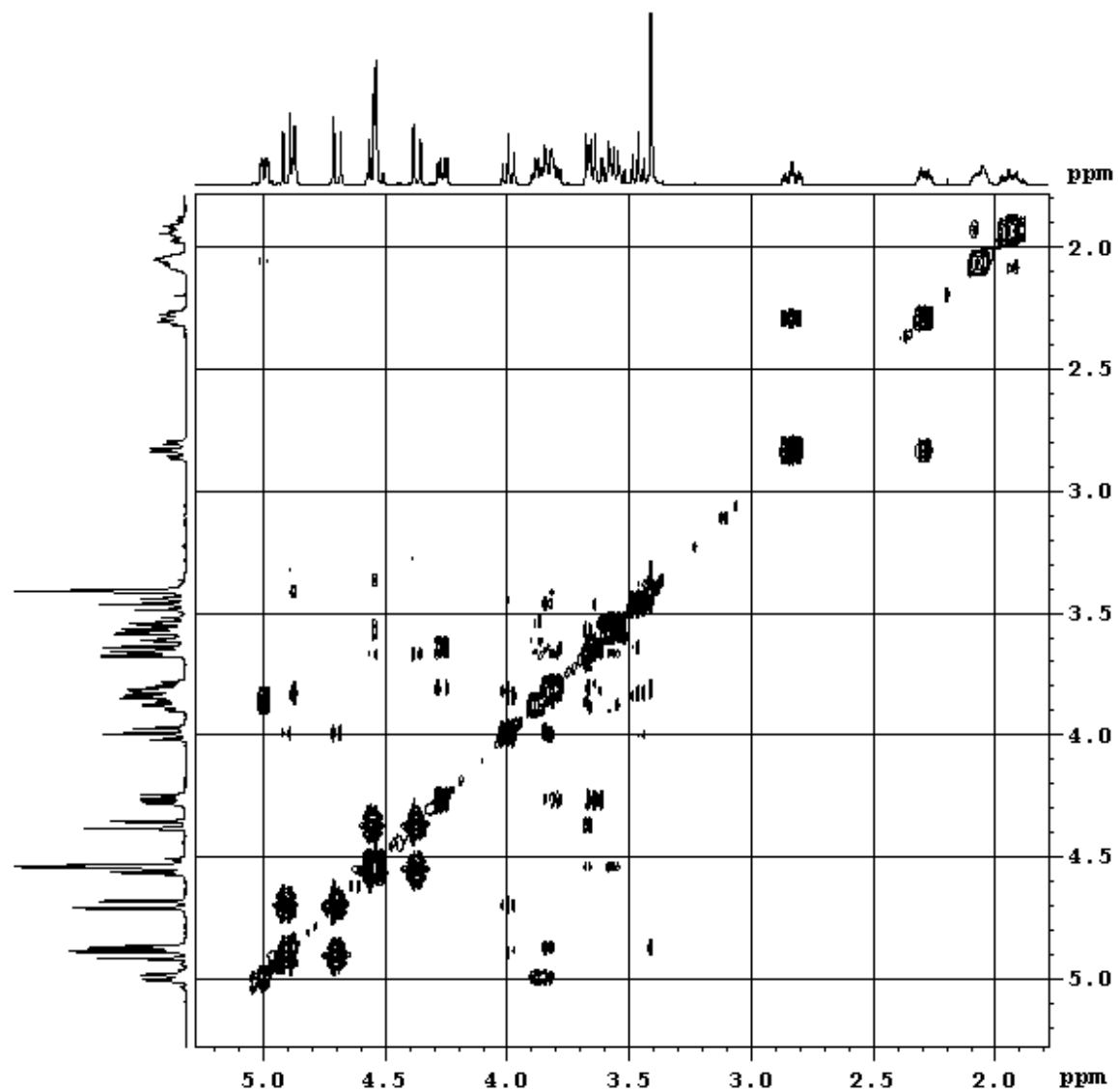






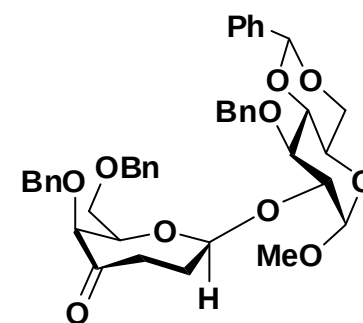
13

^1H - ^1H COSY NMR, 400 MHz, CDCl_3



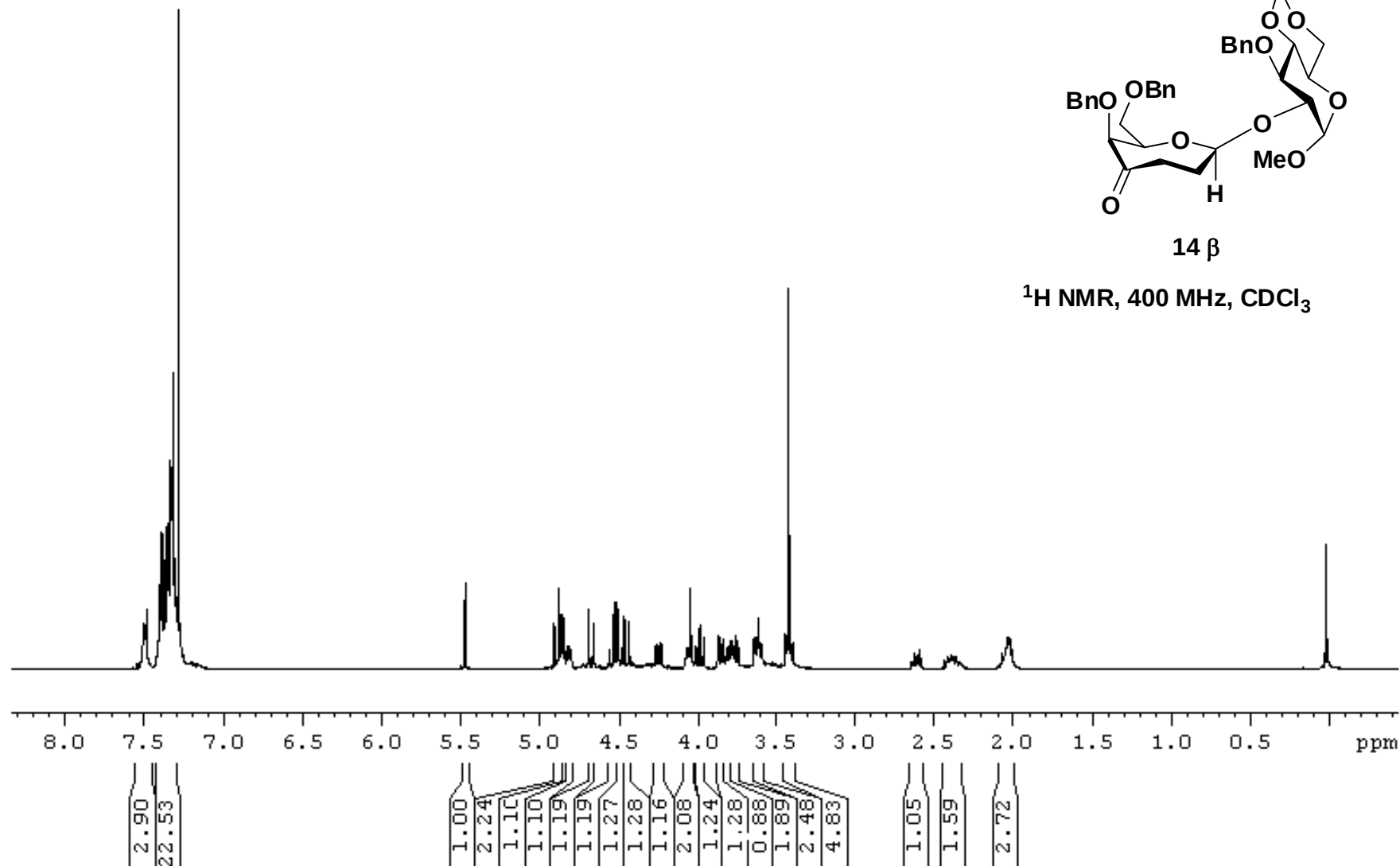
13

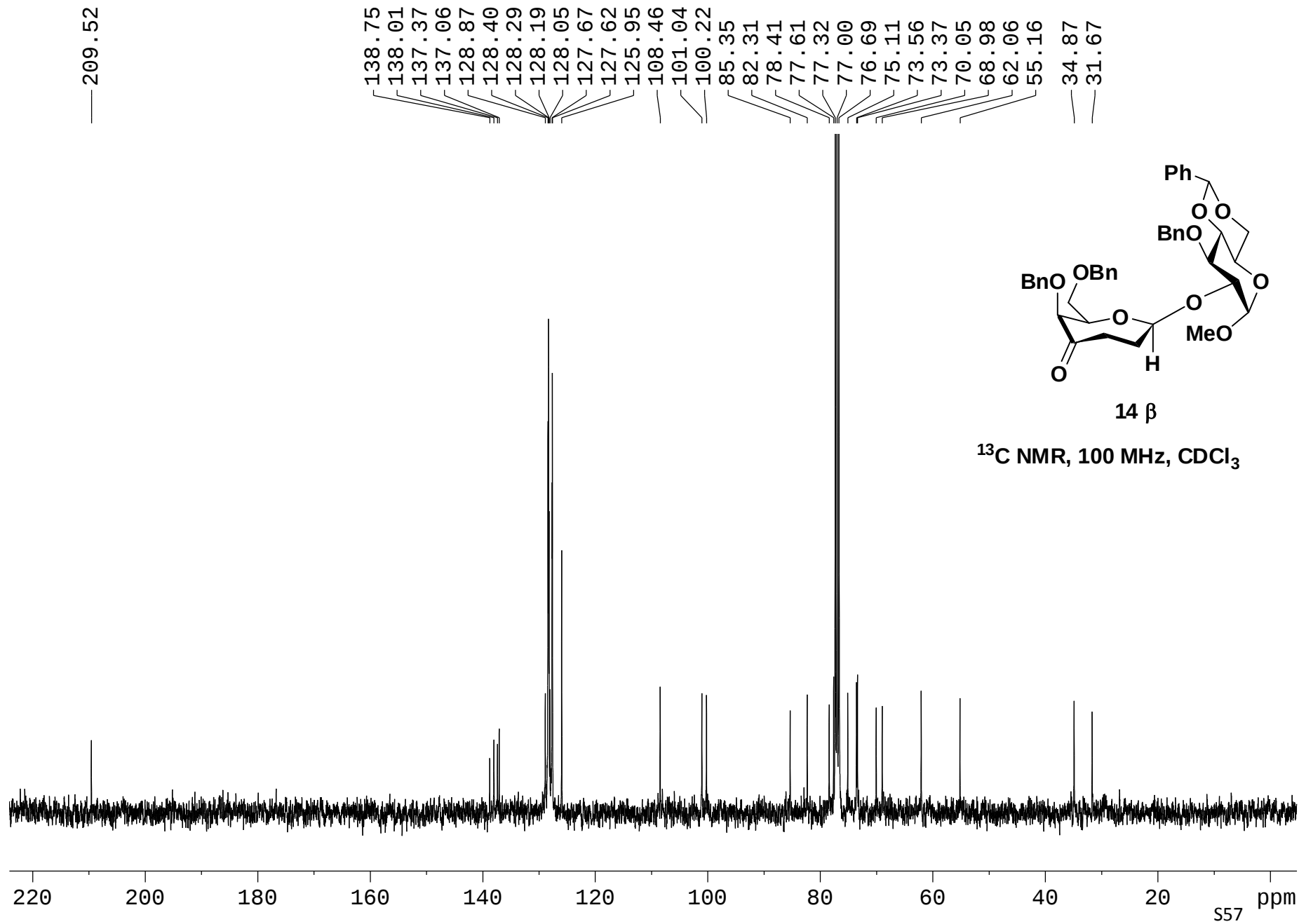
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

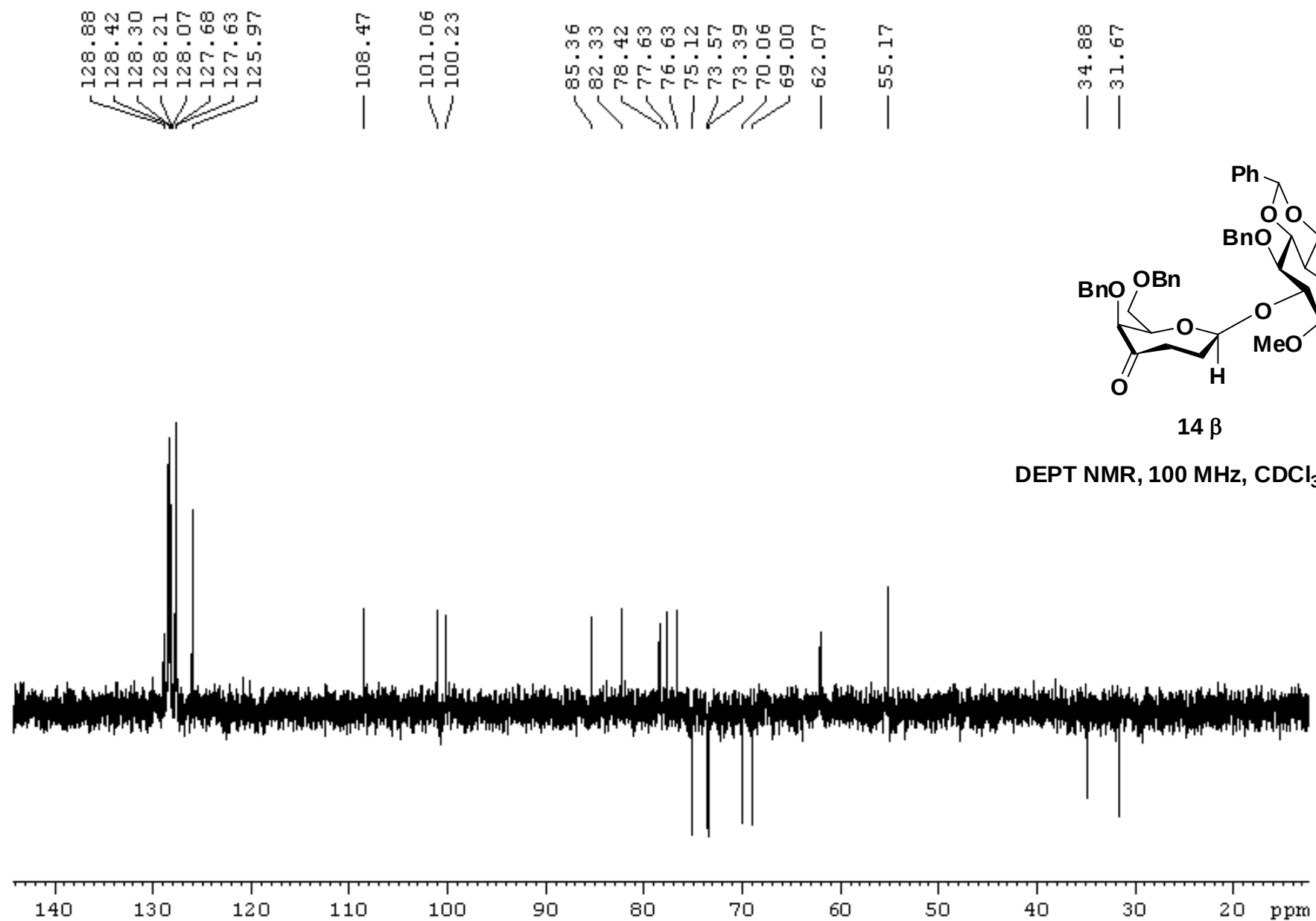


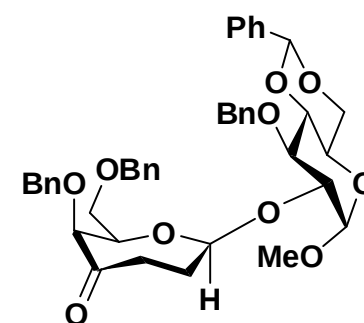
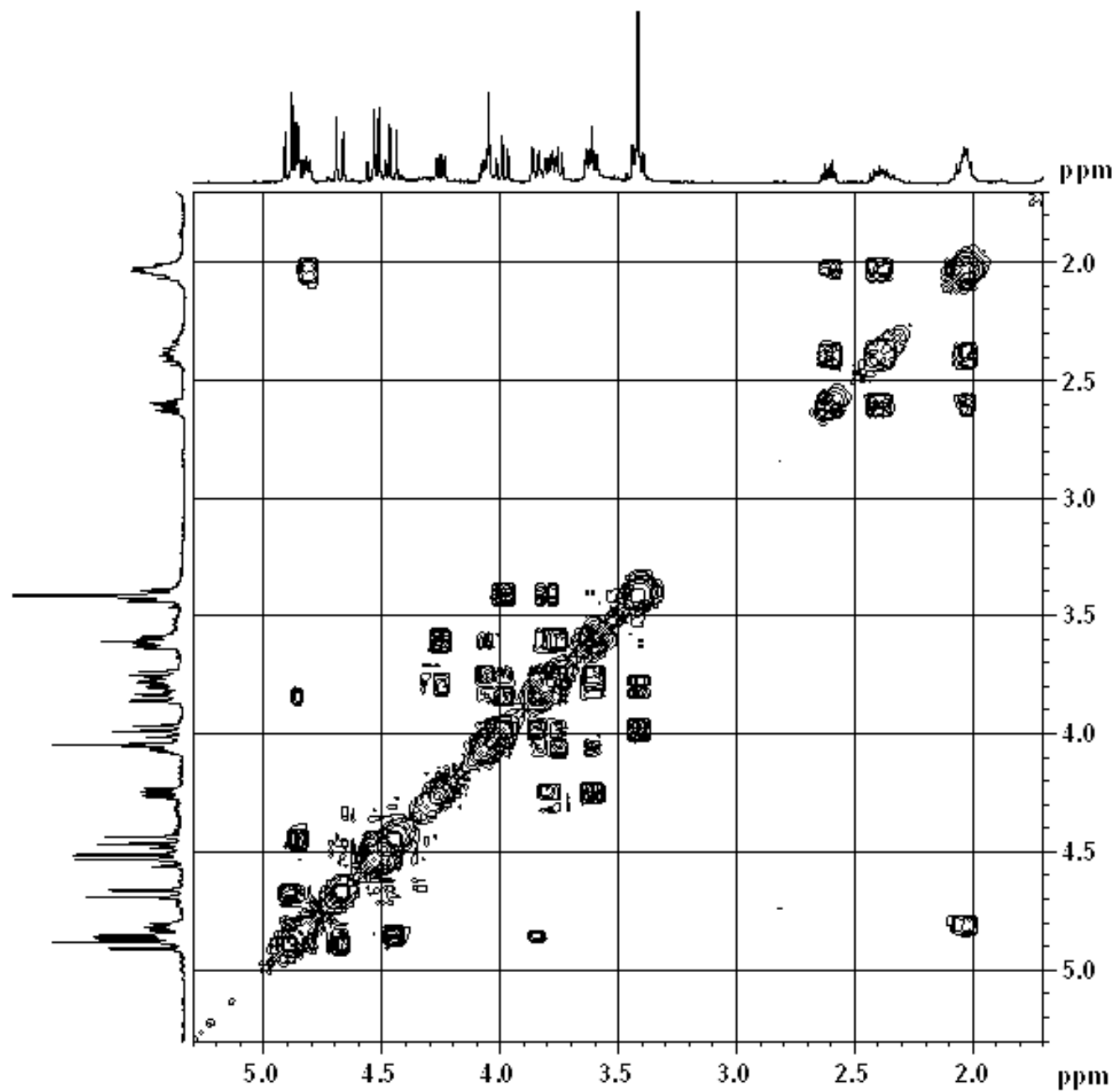
14 β

^1H NMR, 400 MHz, CDCl_3



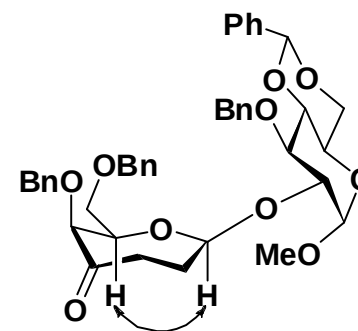
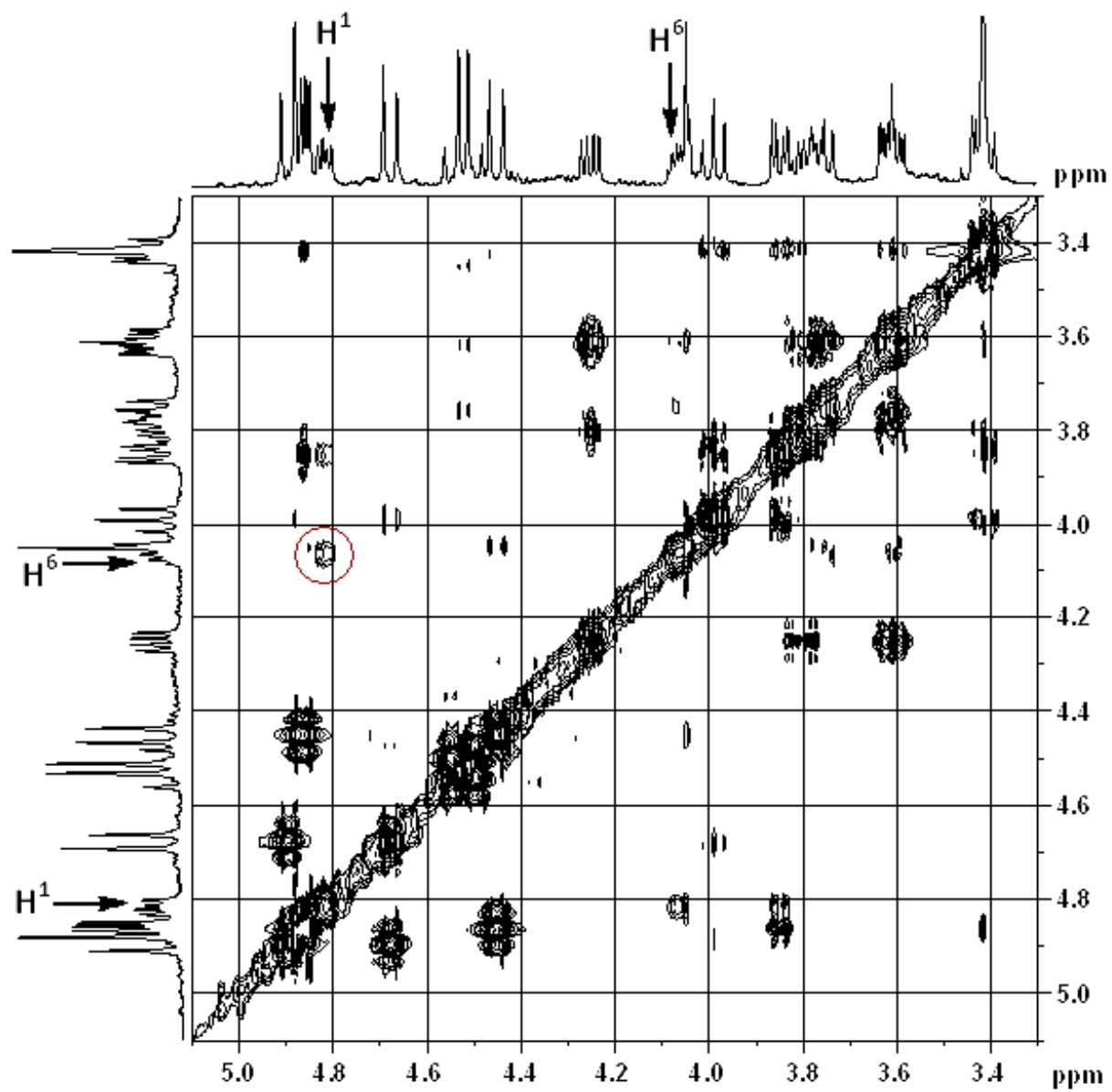






14 β

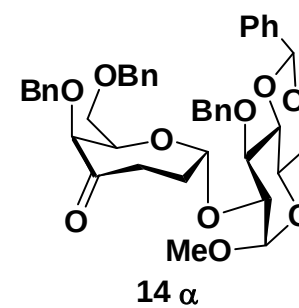
^1H - ^1H COSY NMR, 400 MHz, CDCl_3



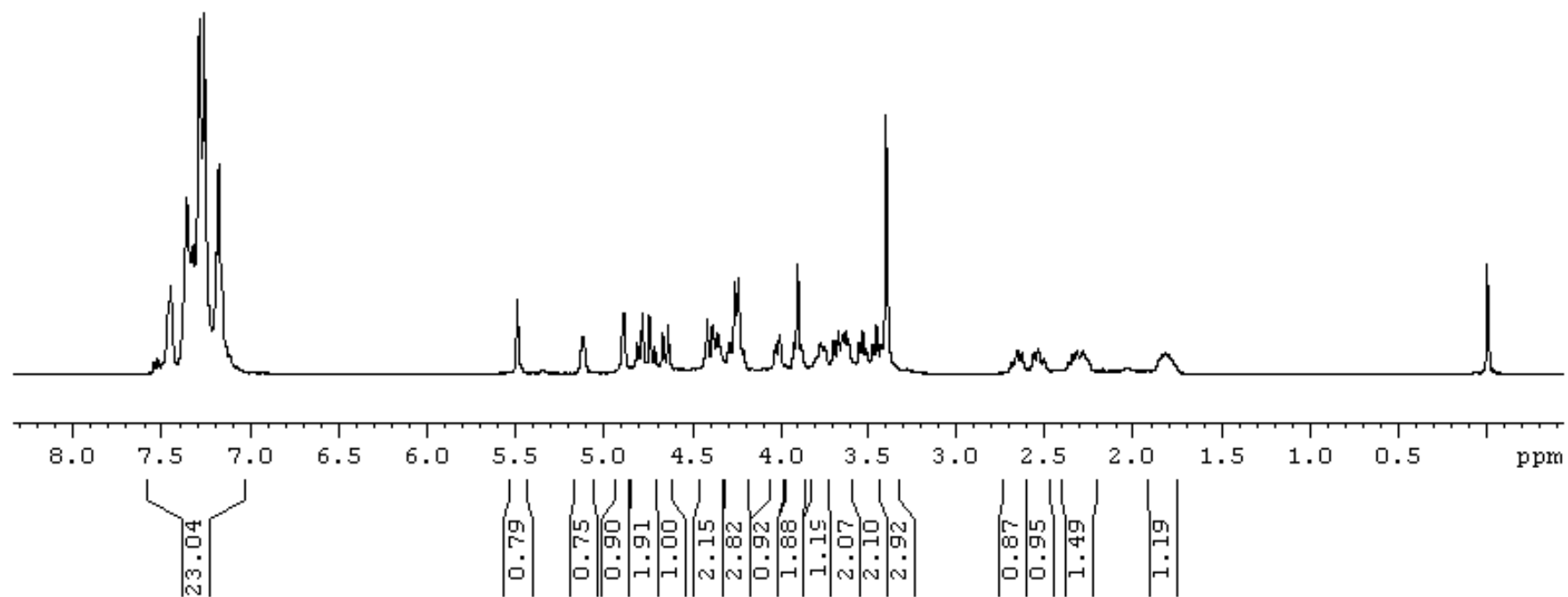
14 β

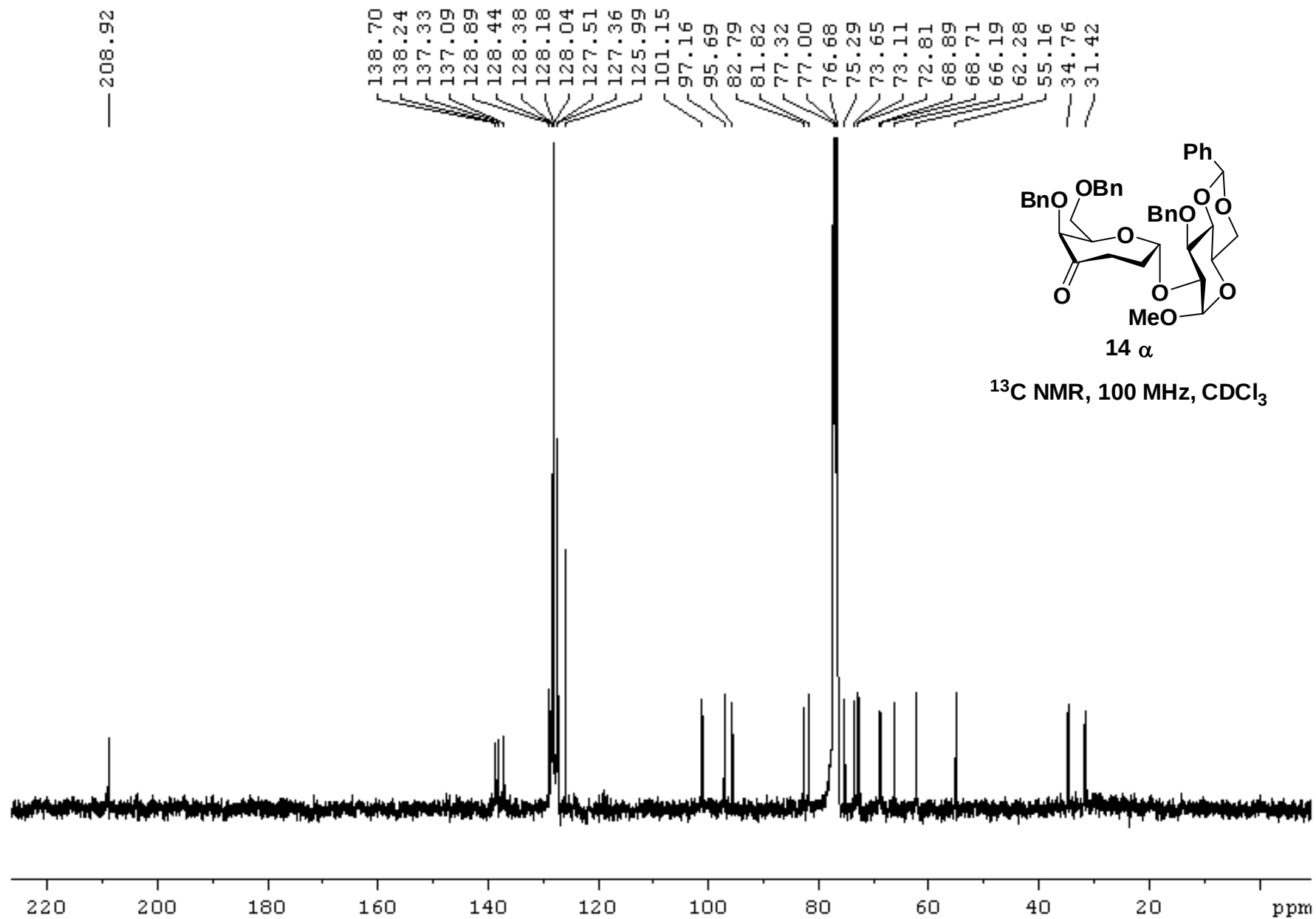
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

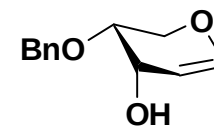
NOE observed between H^1 and H^6



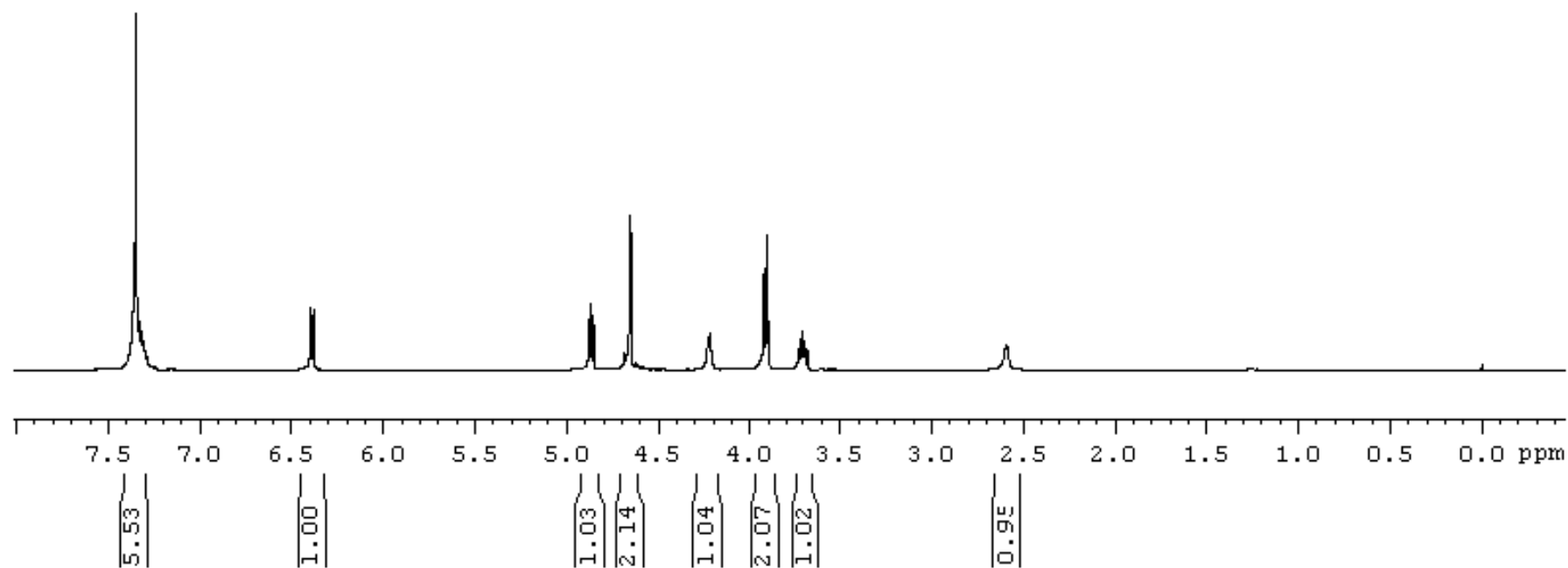
^1H NMR, 400 MHz, CDCl_3

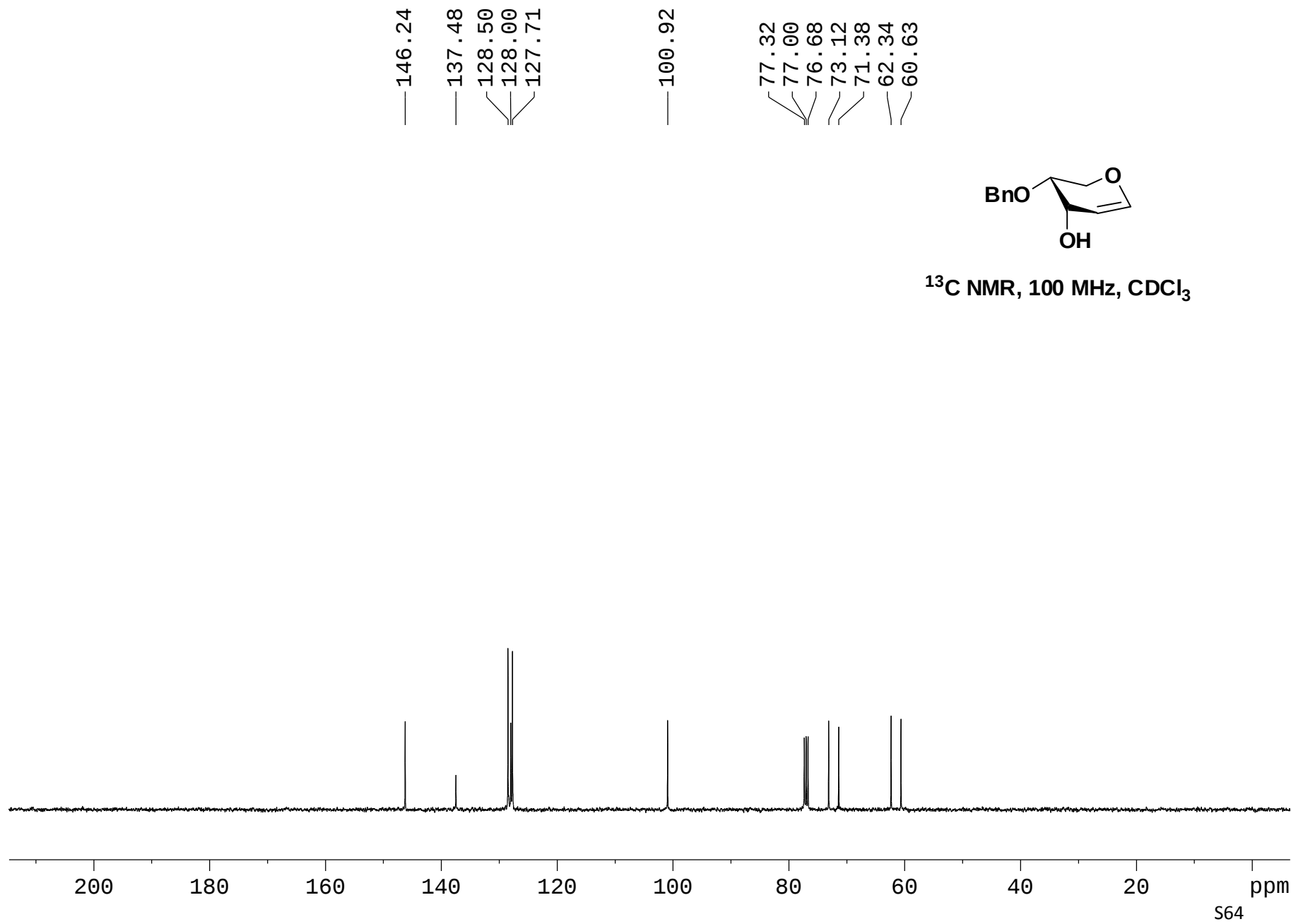


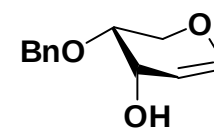




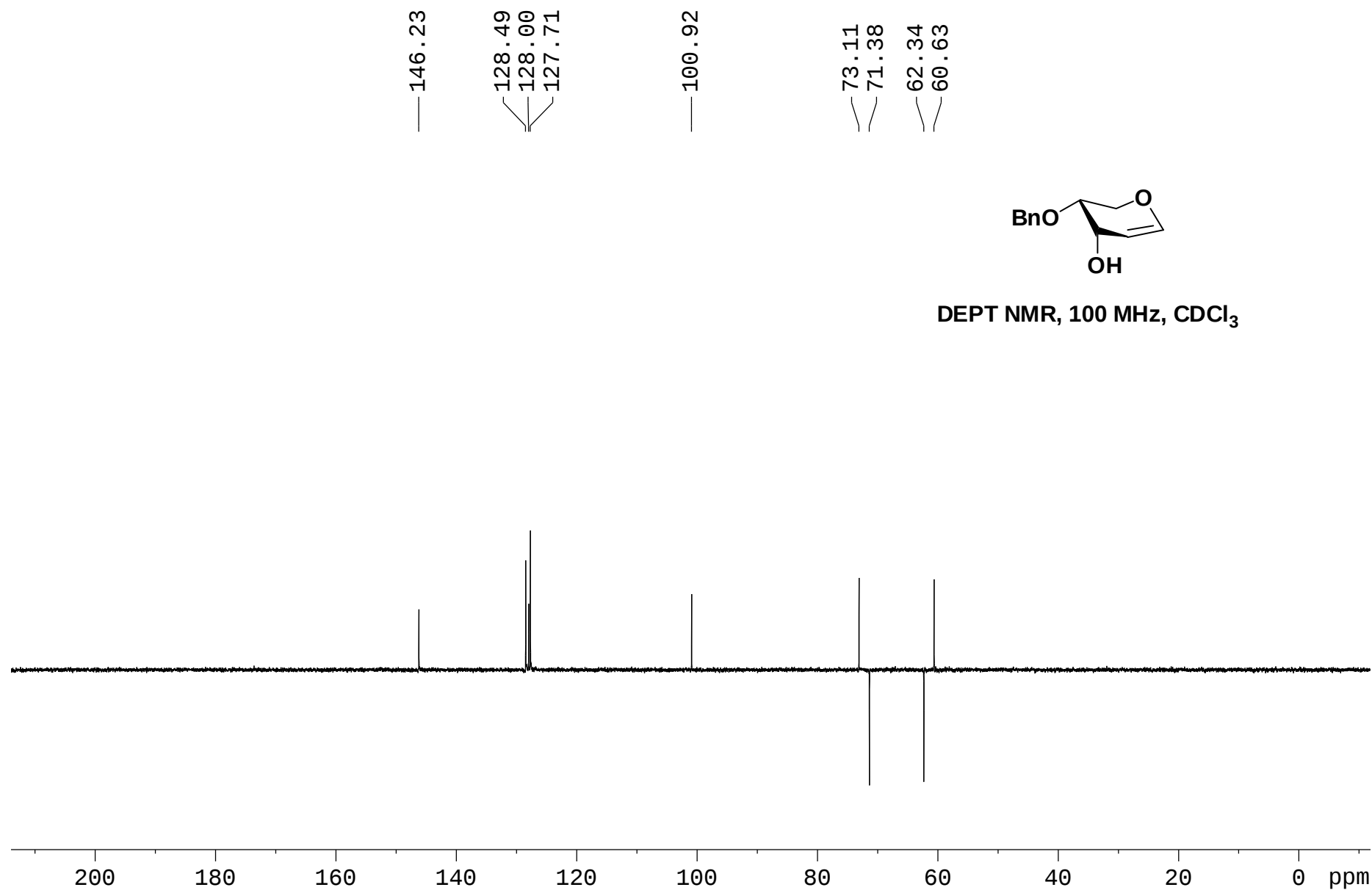
^1H NMR, 400 MHz, CDCl_3

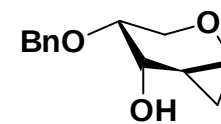




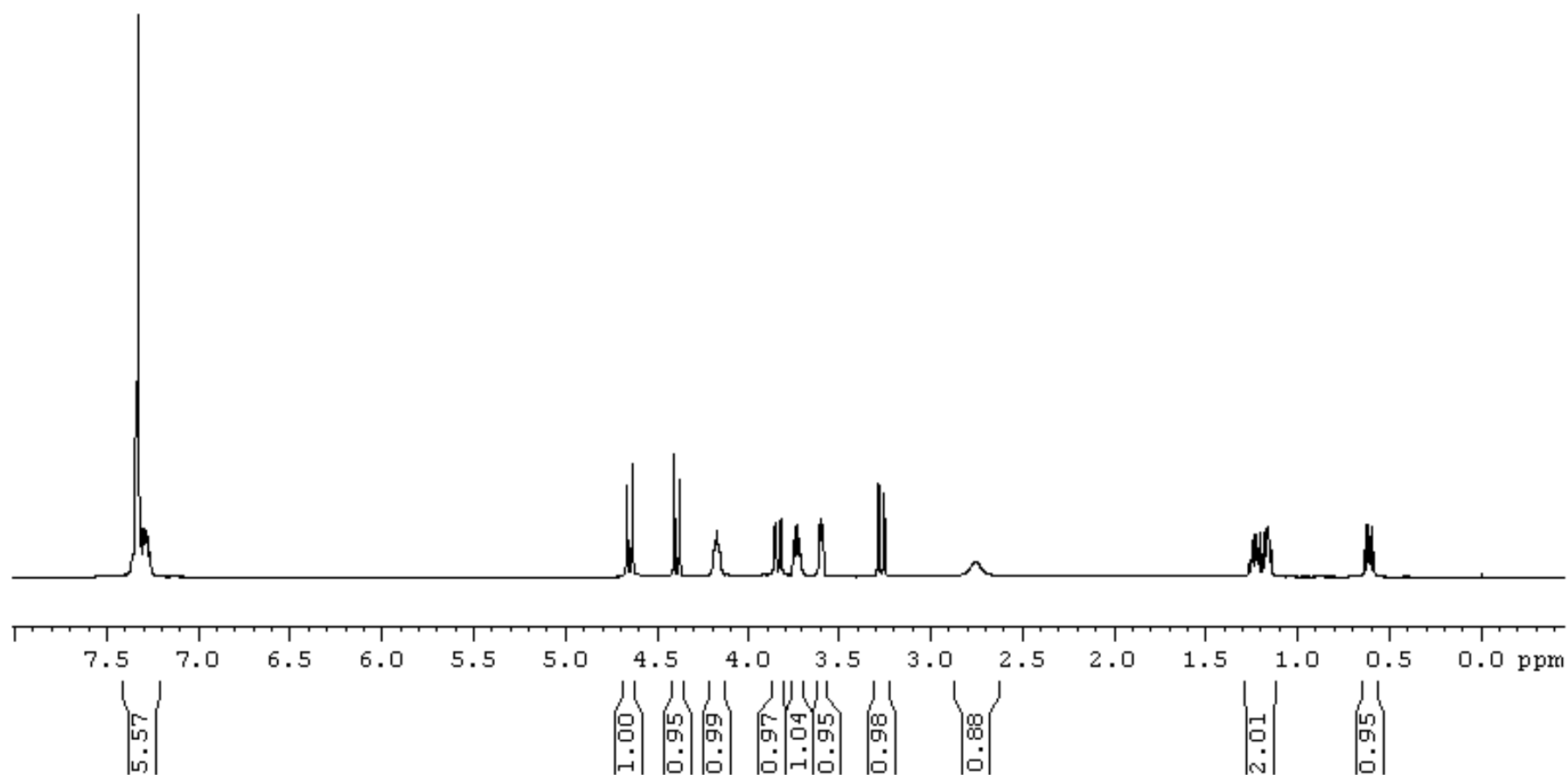


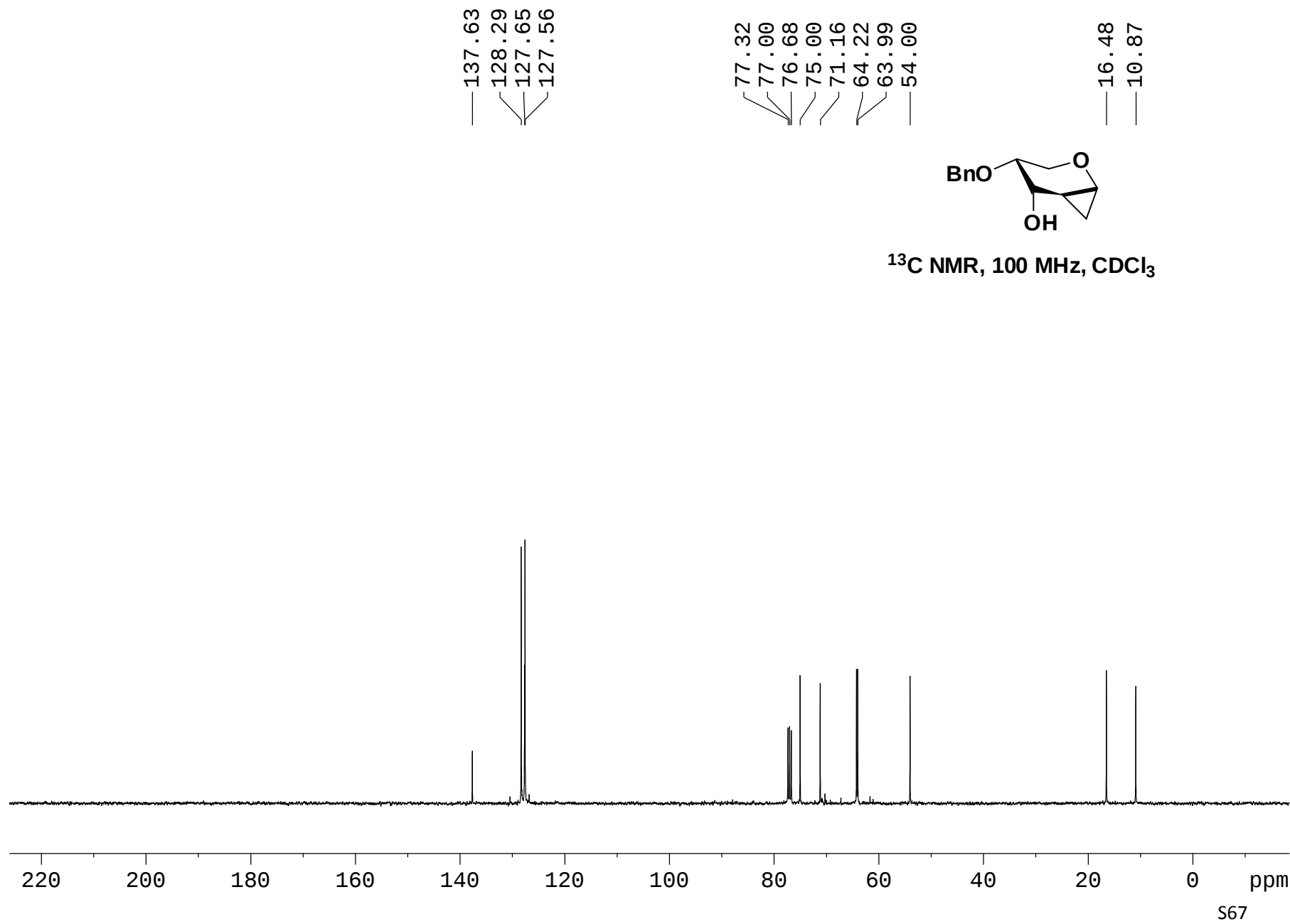
DEPT NMR, 100 MHz, CDCl₃





^1H NMR, 400 MHz, CDCl_3

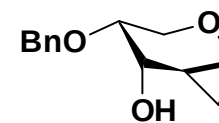




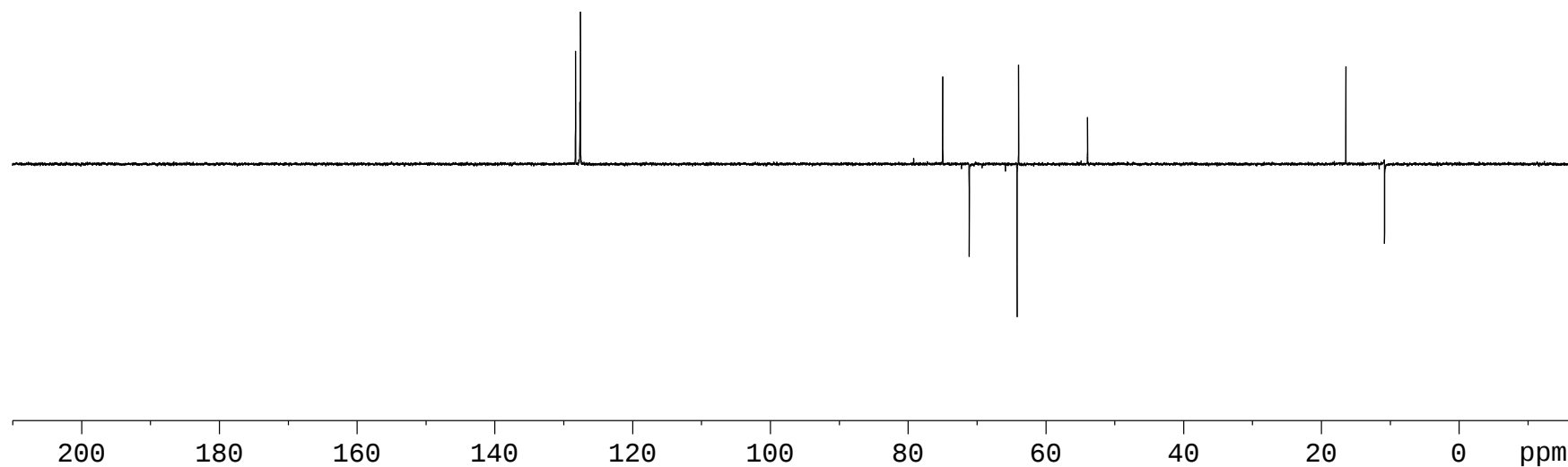
128.28
127.64
127.56

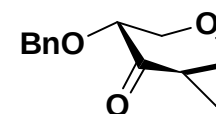
75.01
71.16
64.22
63.99
53.98

16.47
10.86



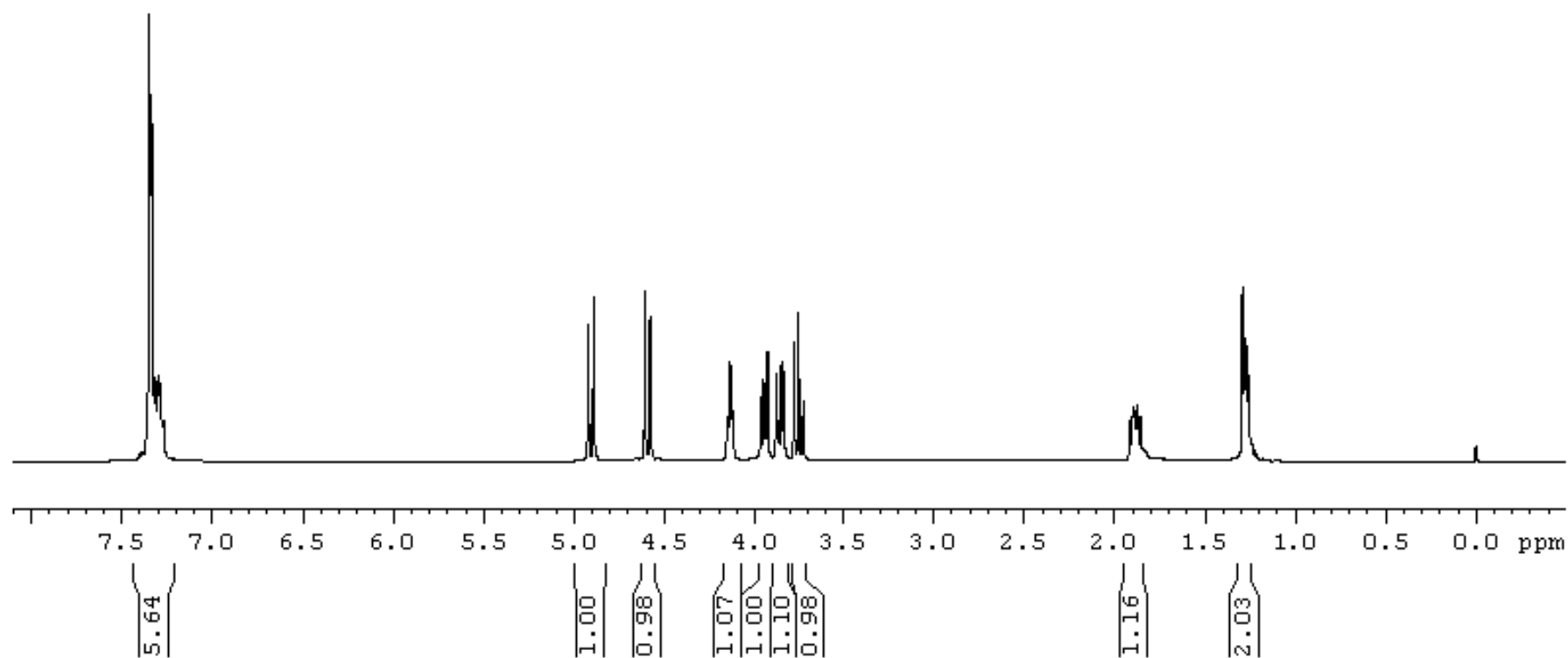
DEPT NMR, 100 MHz, CDCl₃

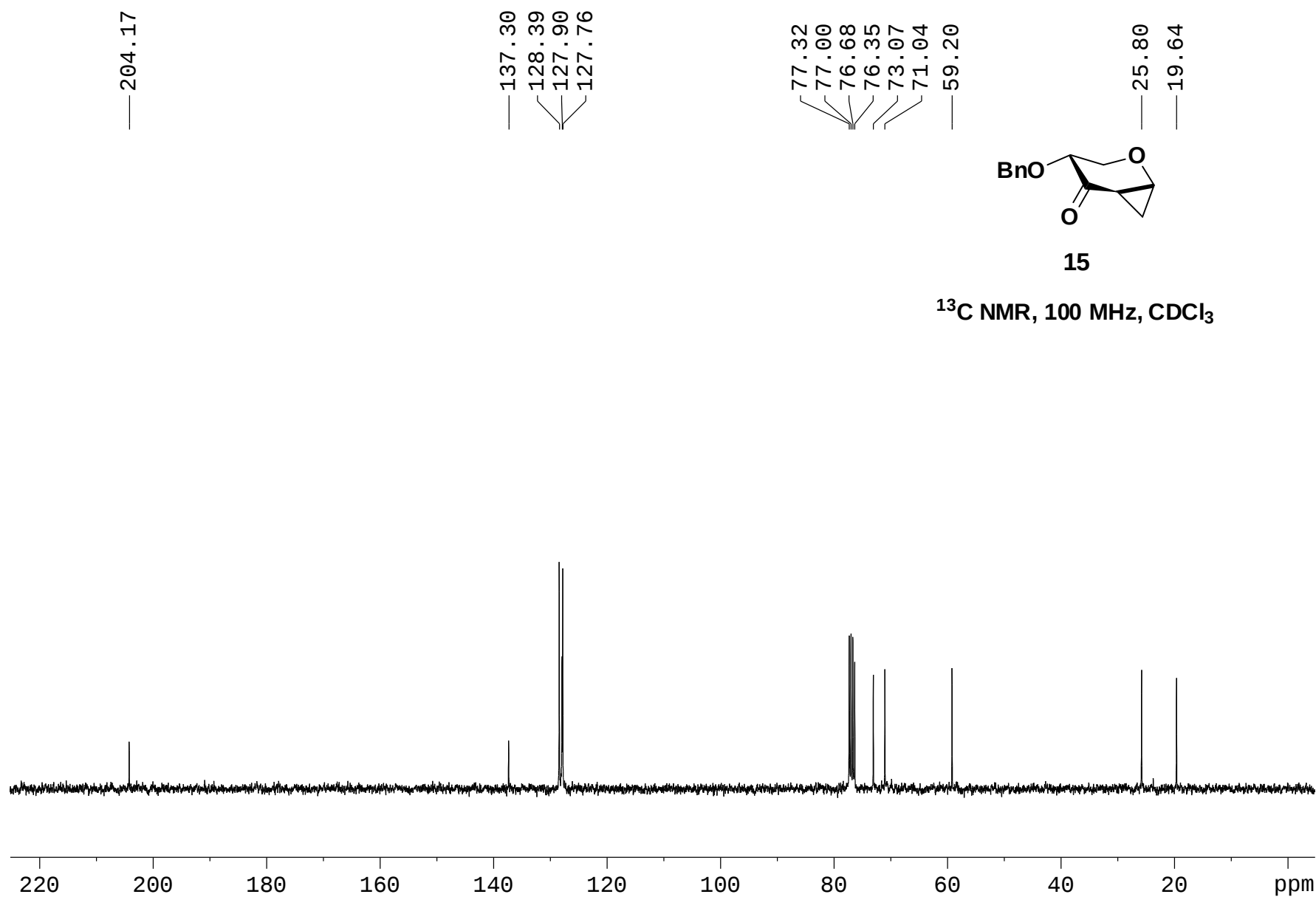




15

^1H NMR, 400 MHz, CDCl_3

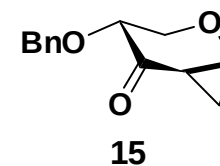




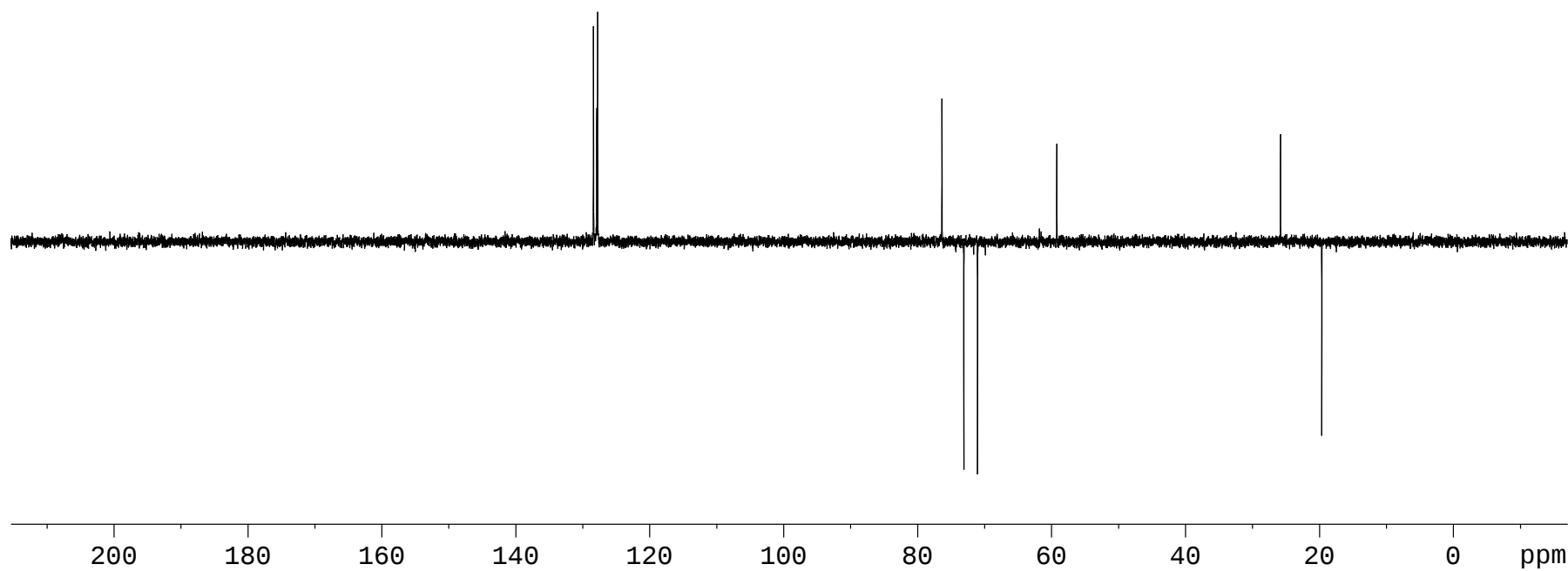
128.39
127.90
127.77

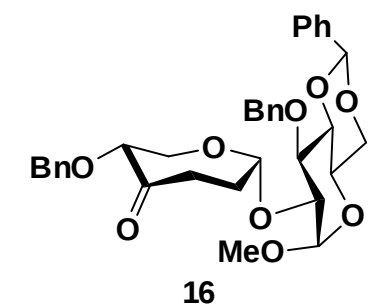
76.36
73.08
71.04
59.21

25.80
19.64

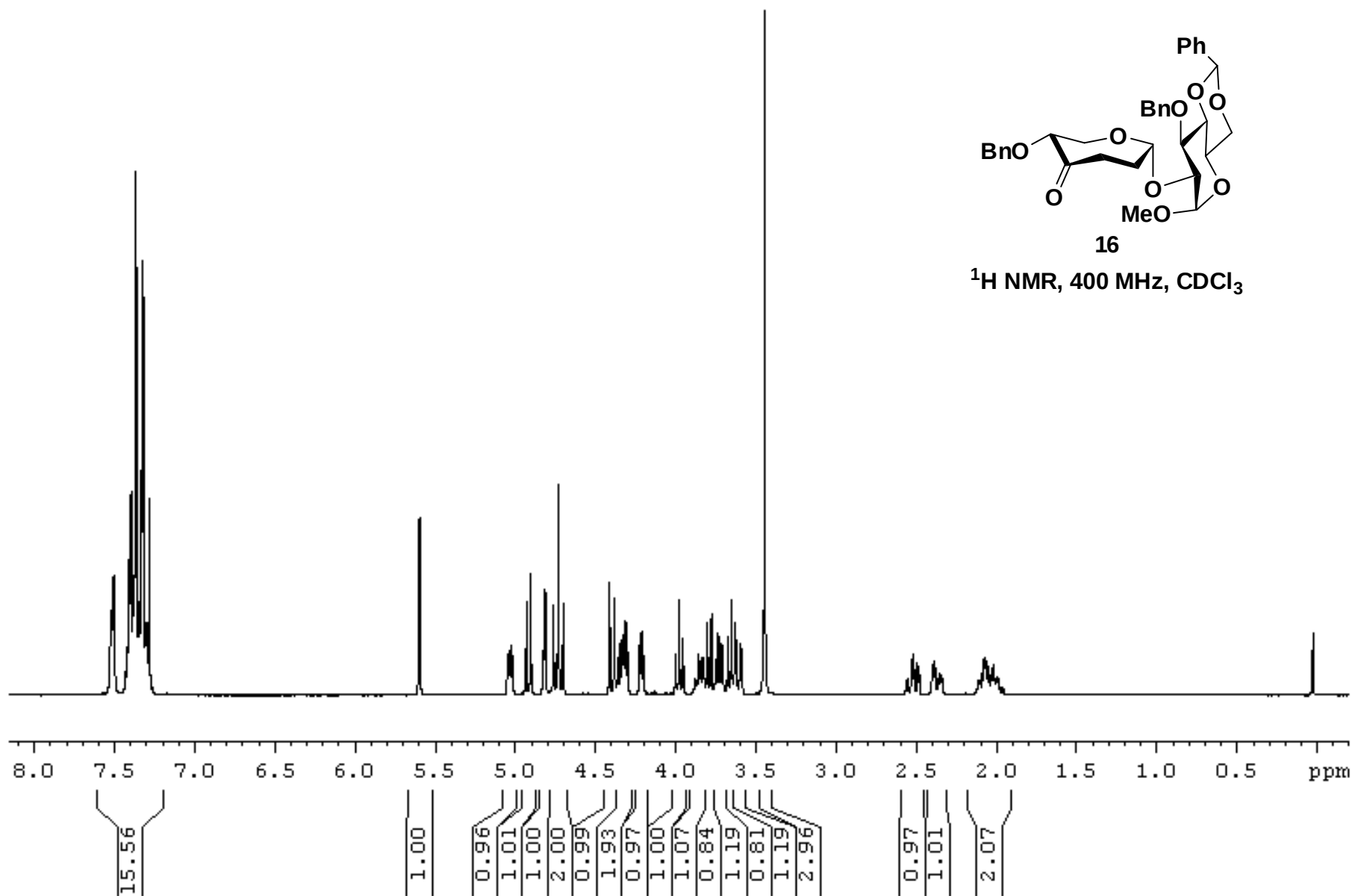


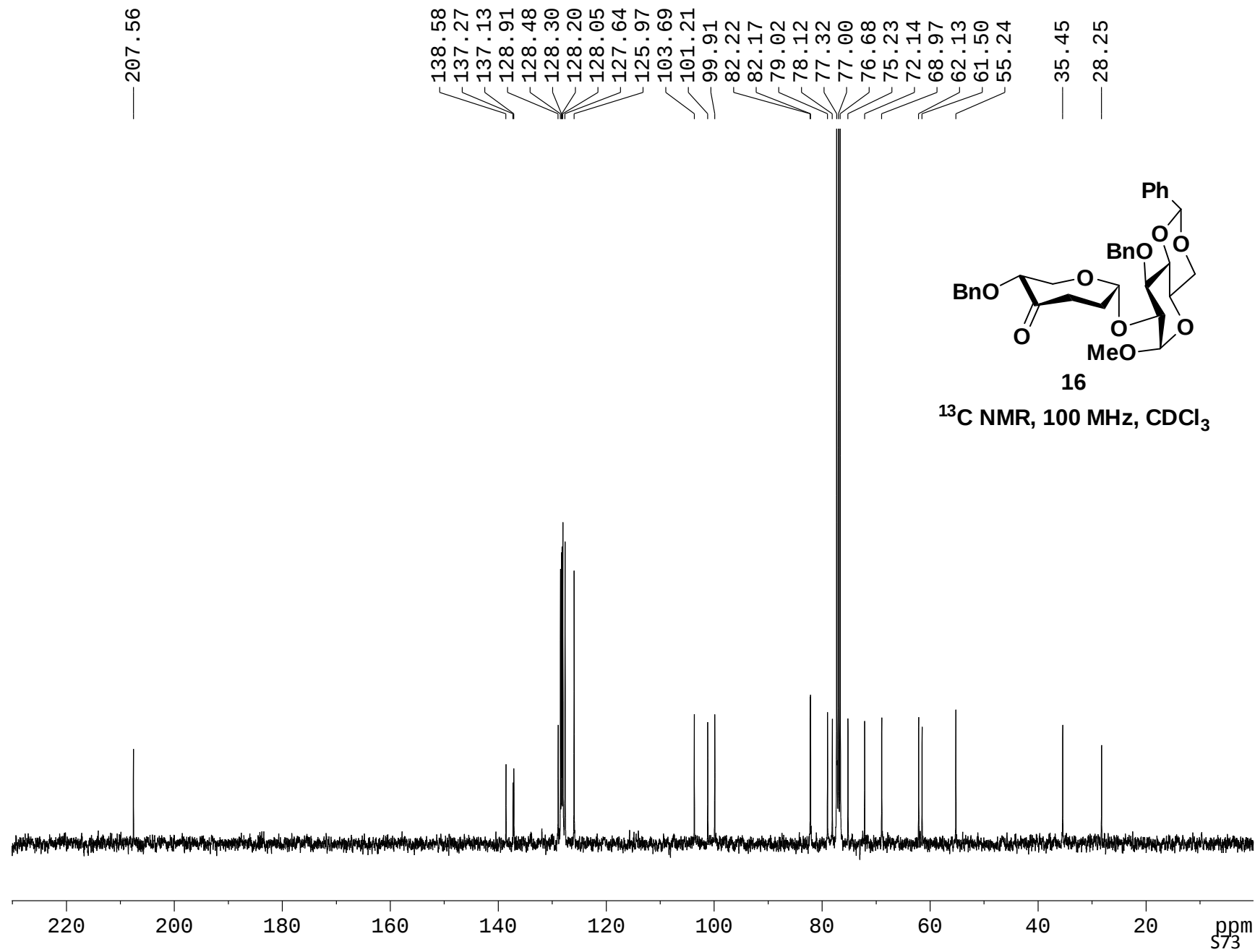
¹³C DEPT NMR, 100 MHz, CDCl₃

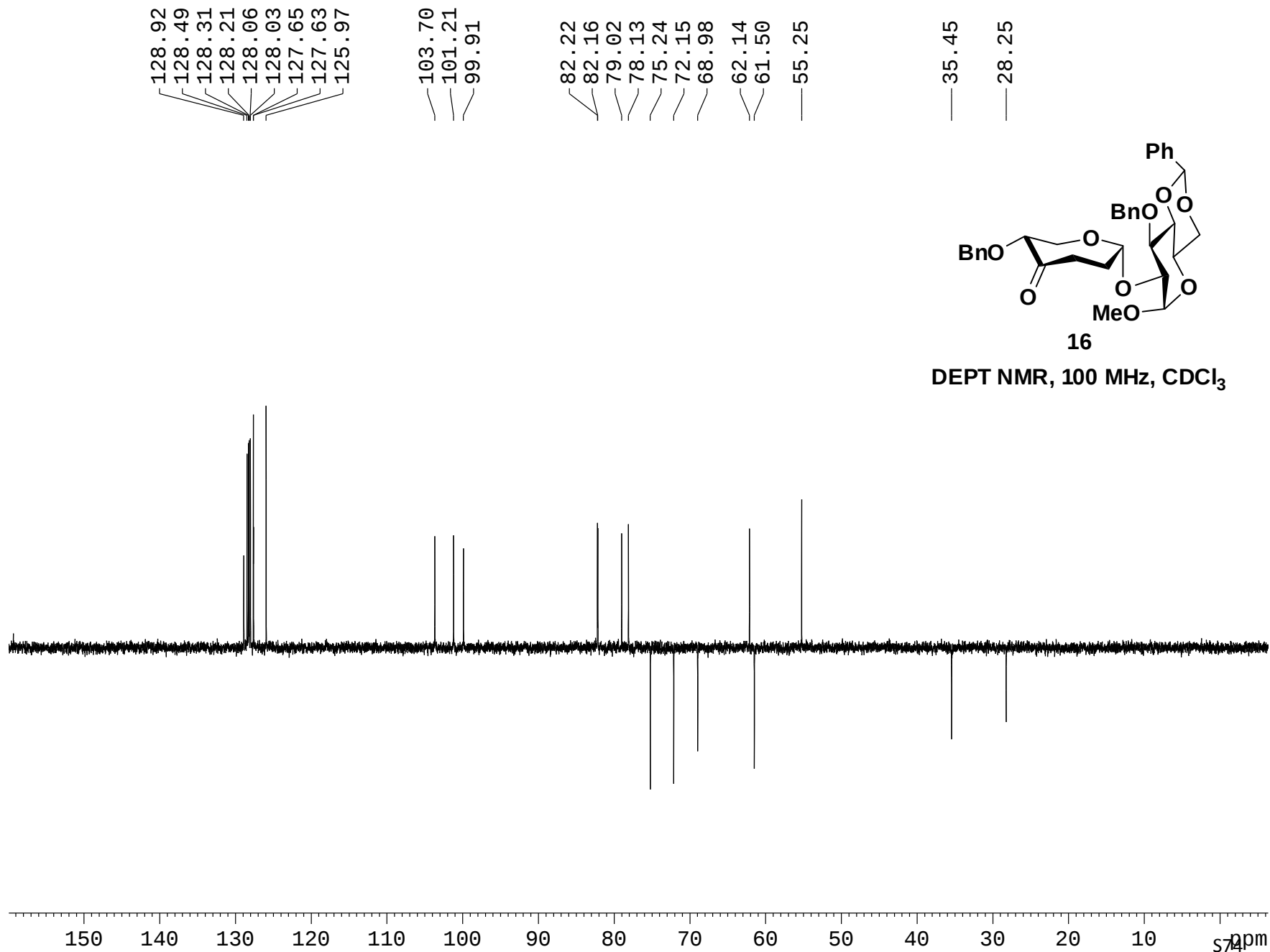


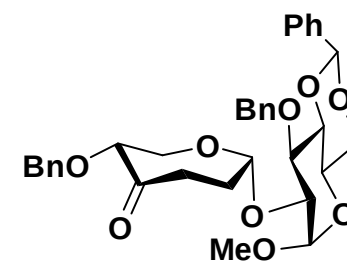
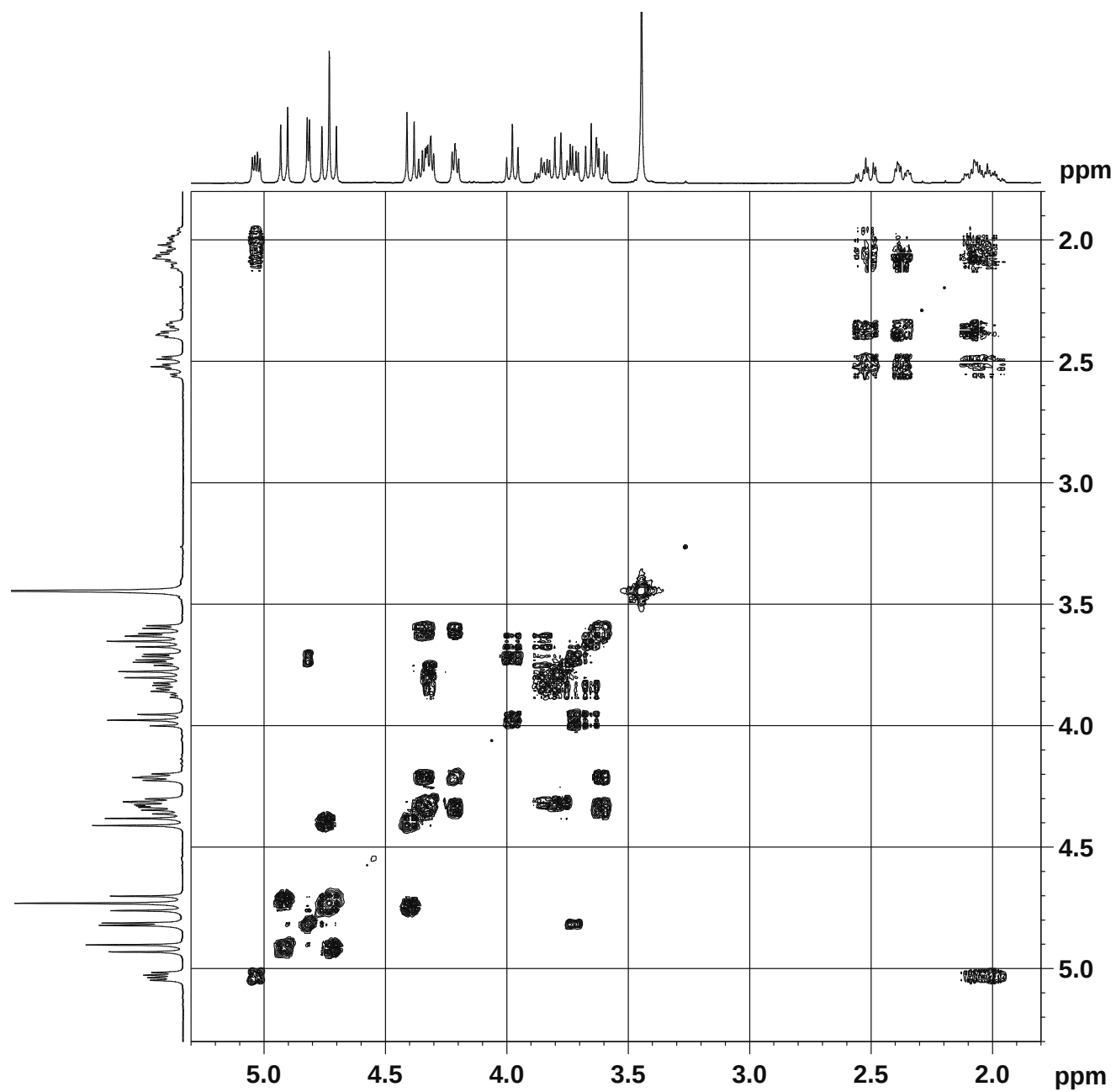


^1H NMR, 400 MHz, CDCl_3



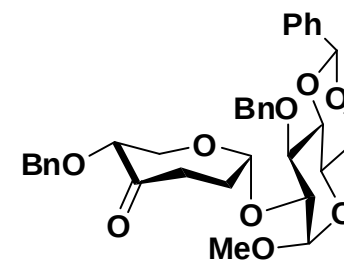
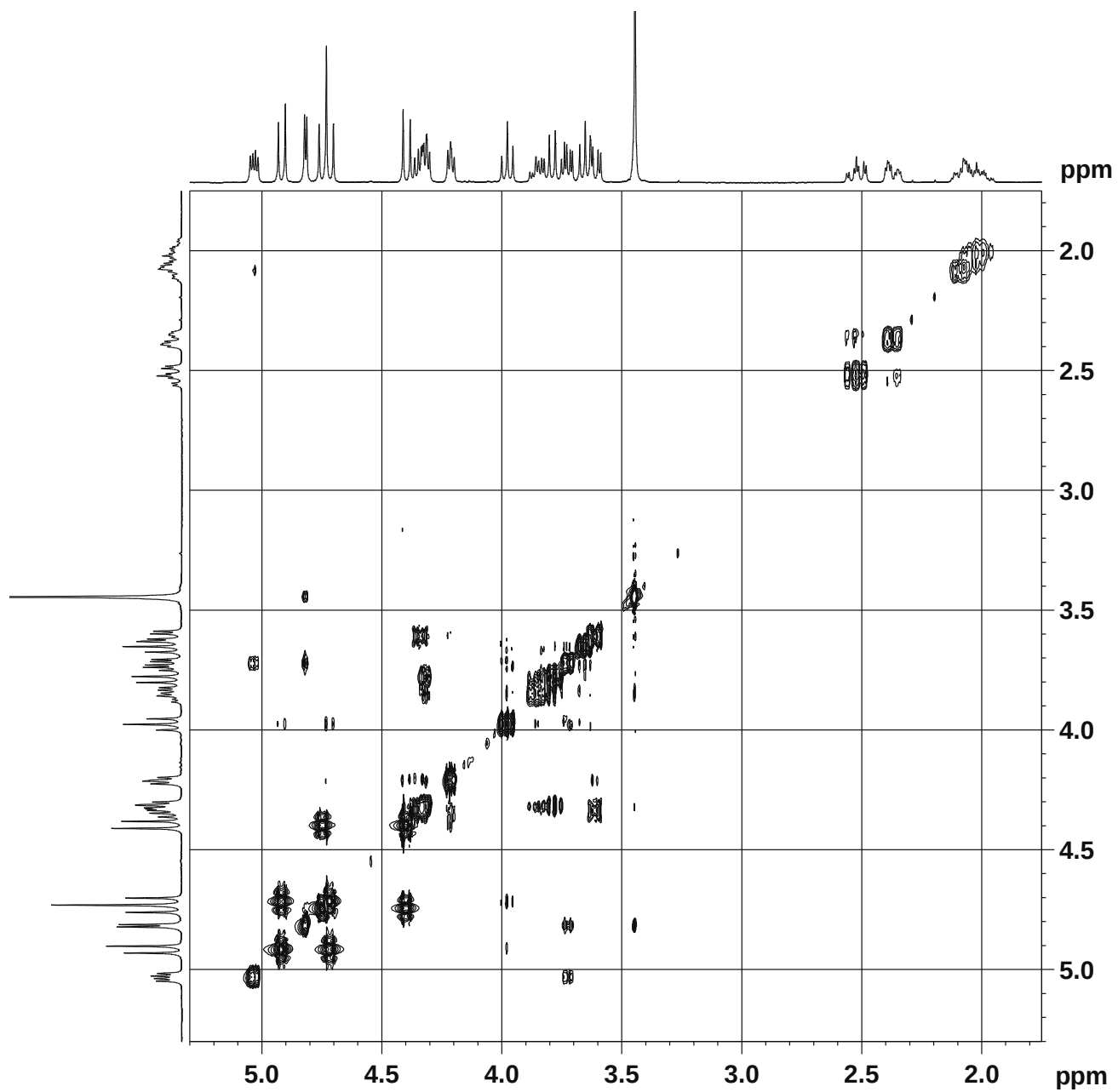






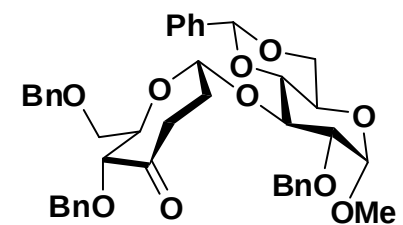
16

^1H - ^1H COSY NMR, 400 MHz, CDCl_3



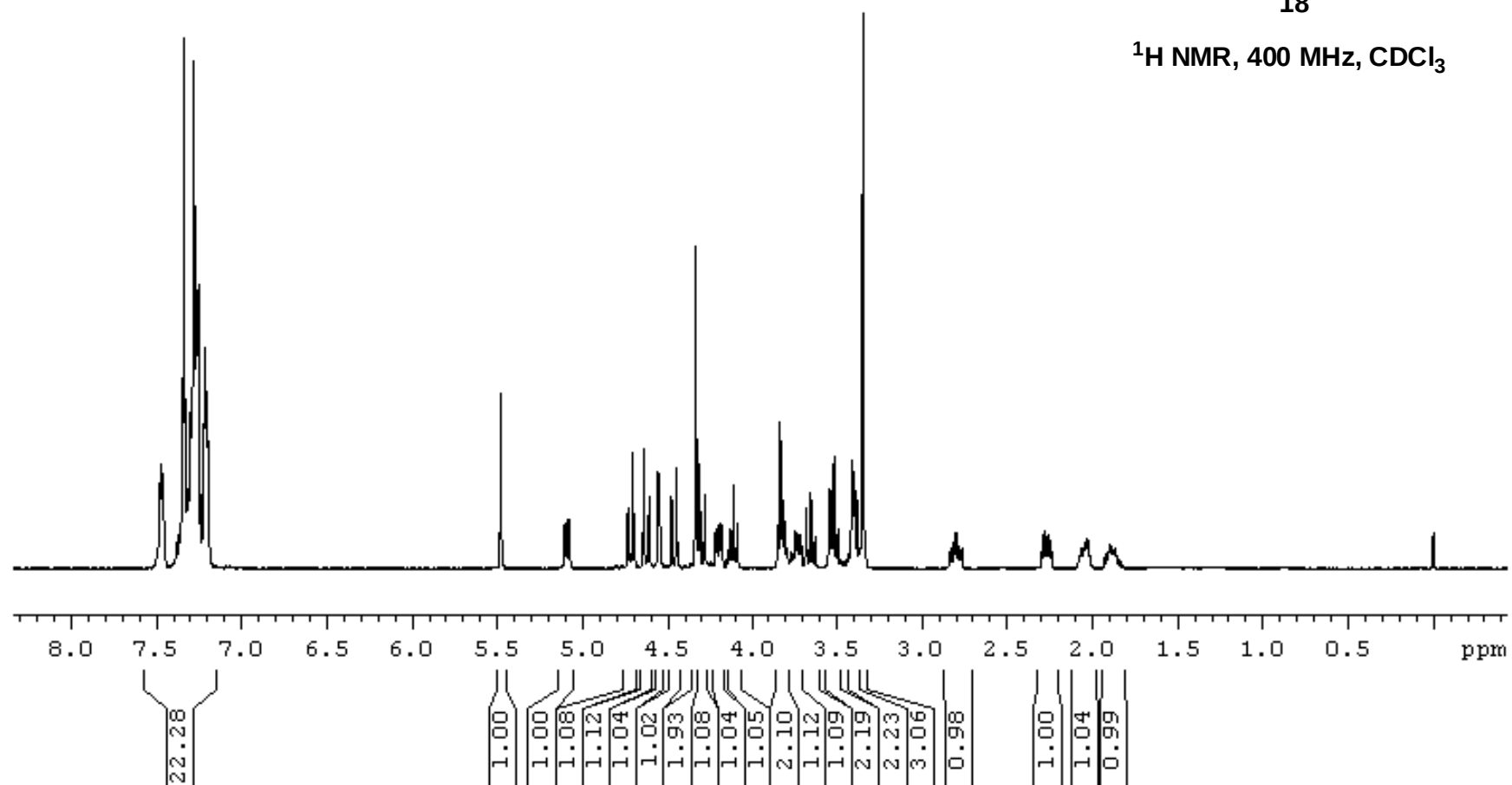
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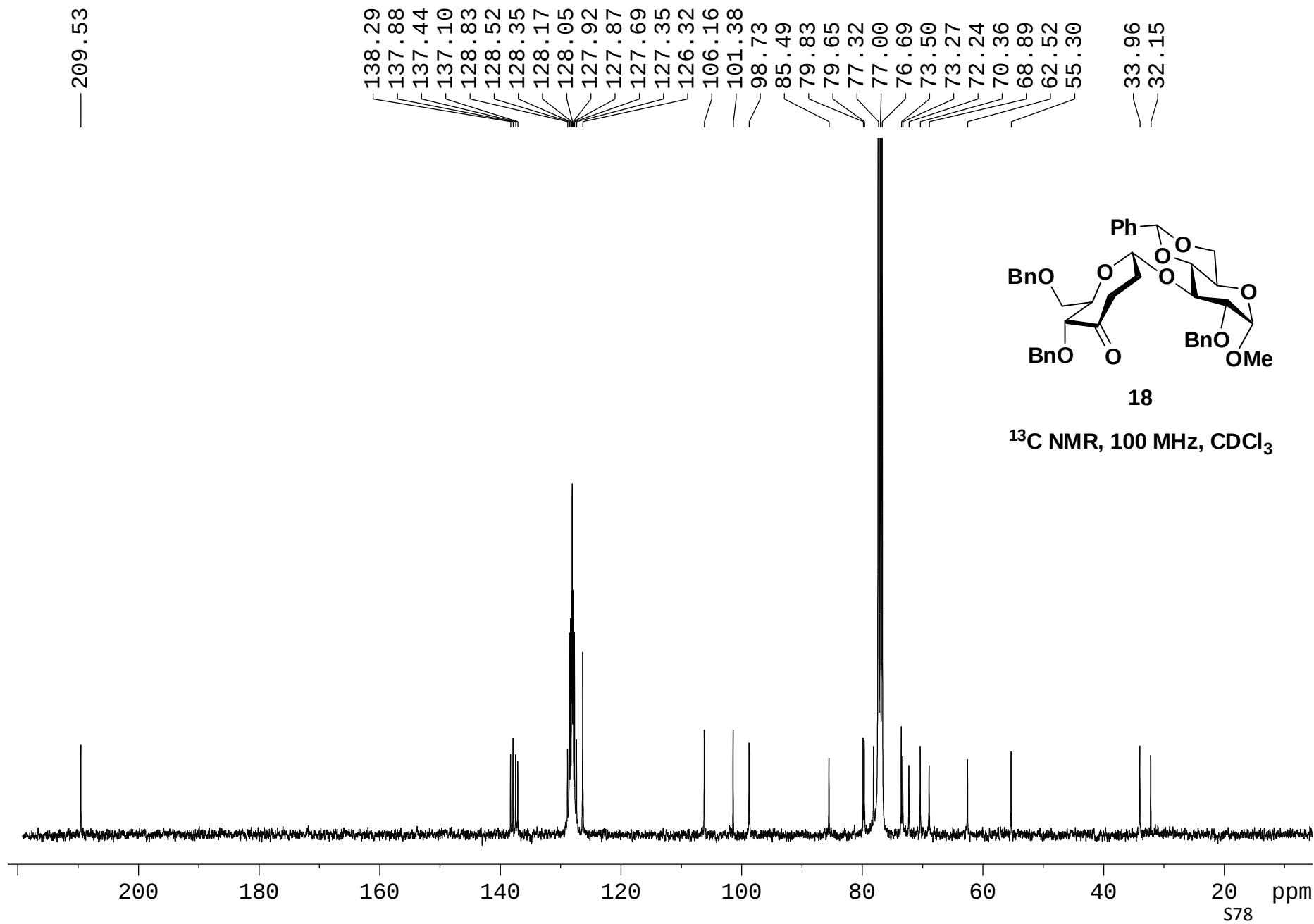
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

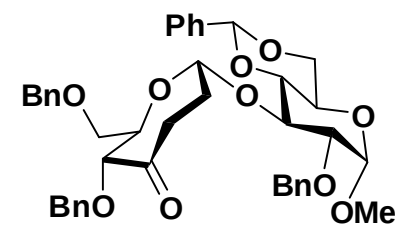
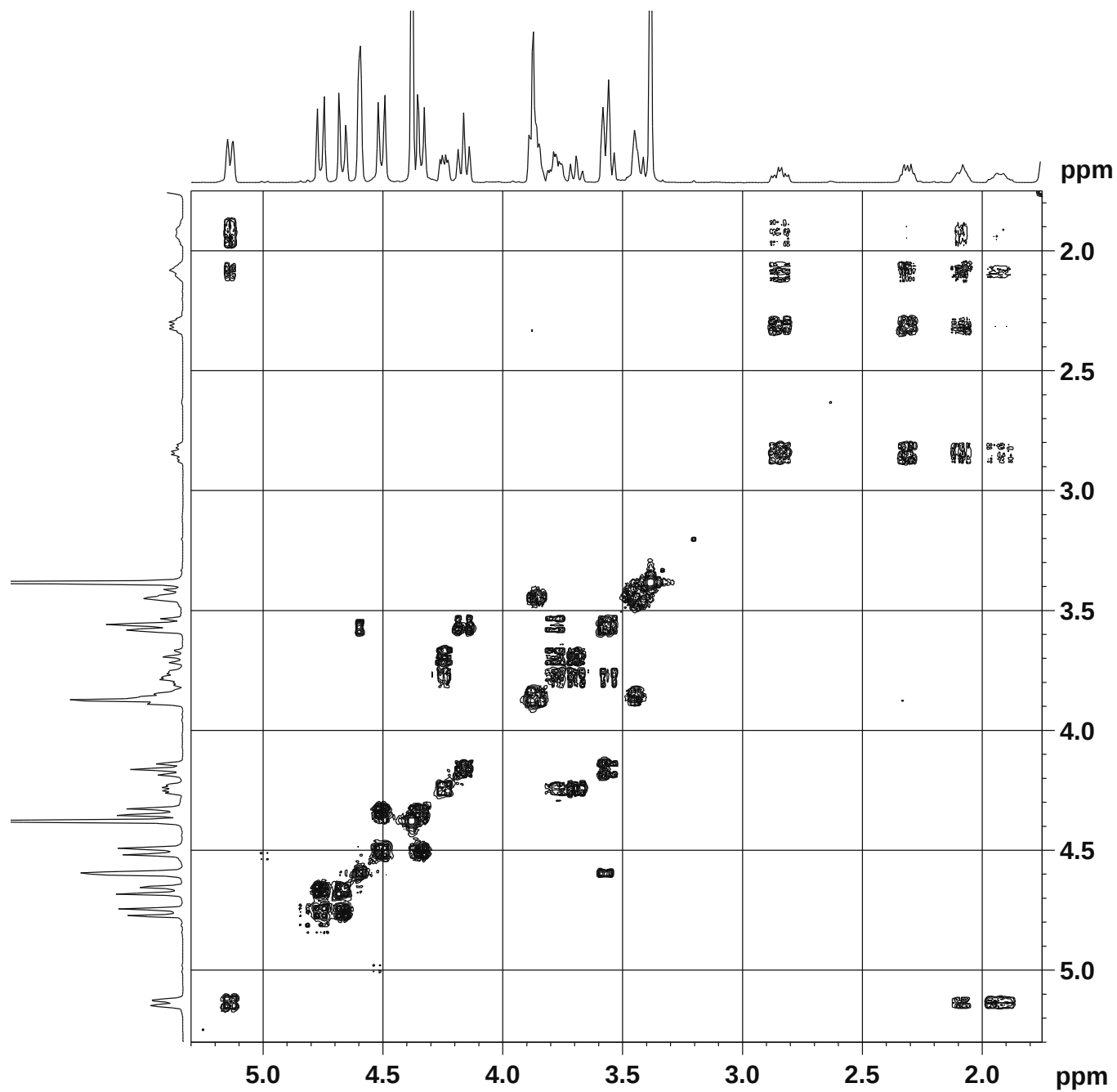


18

^1H NMR, 400 MHz, CDCl_3

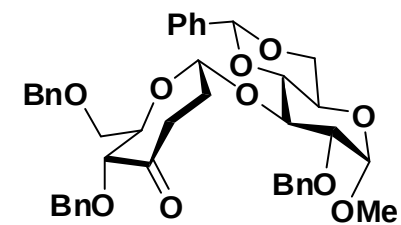
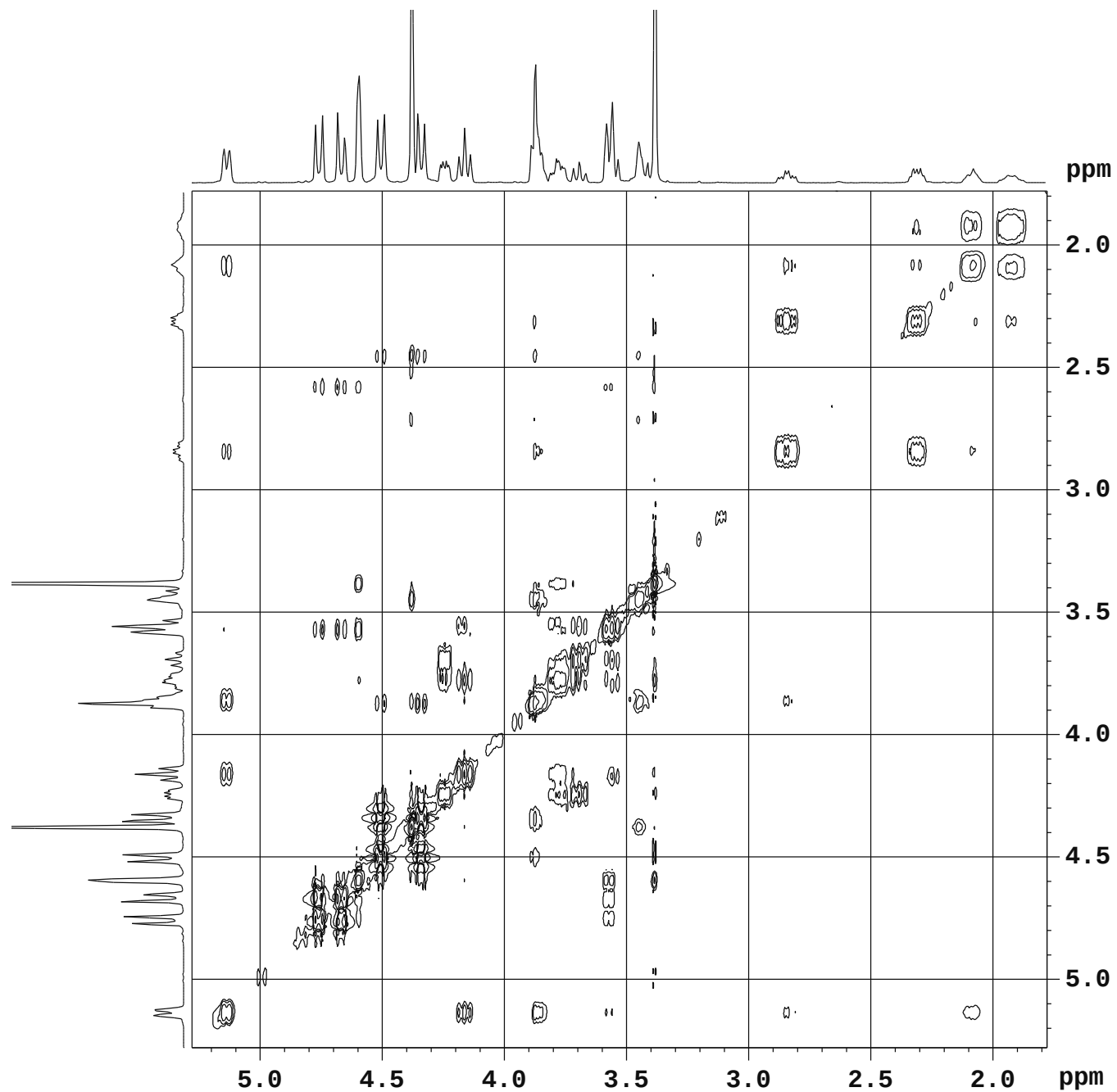






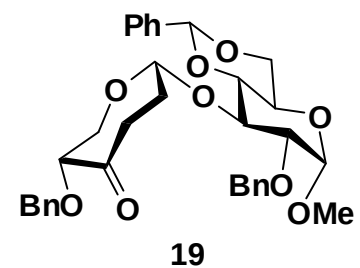
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^1H - ^1H COSY NMR, 400 MHz, CDCl_3

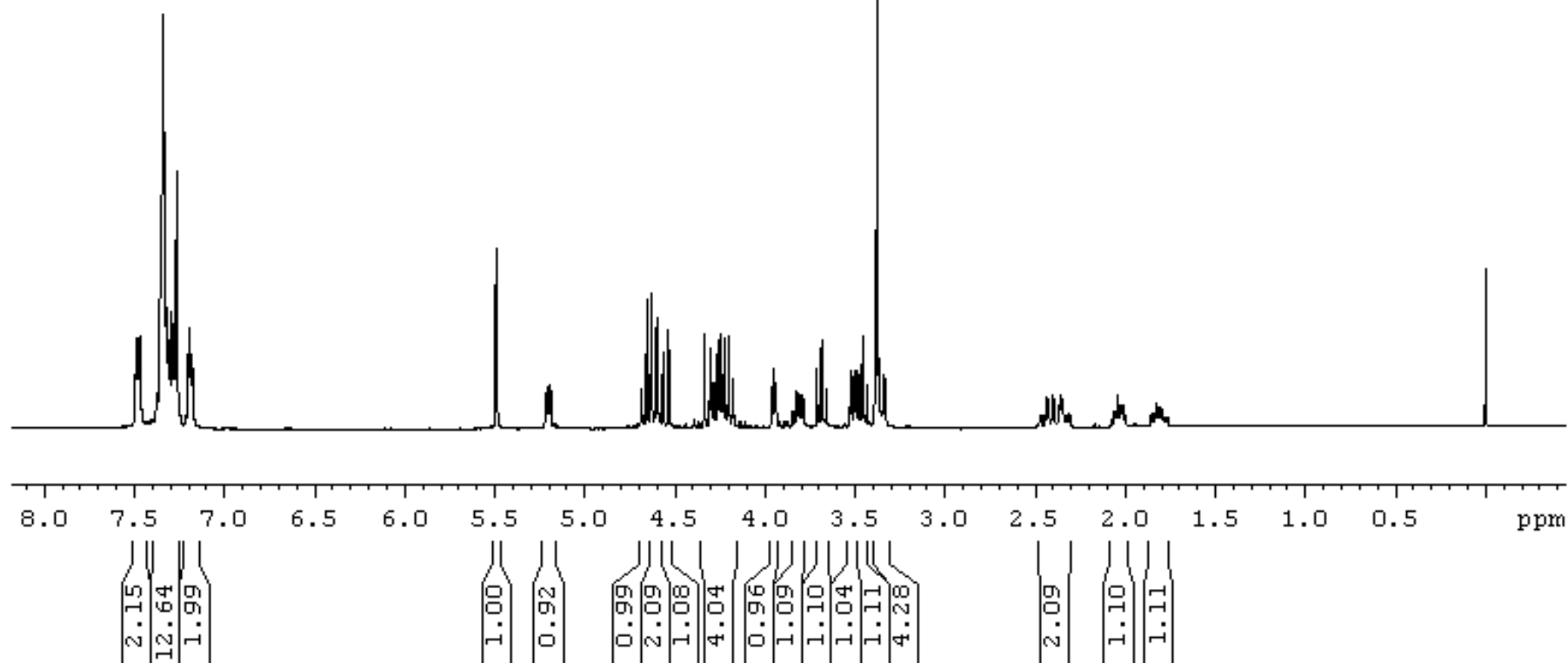


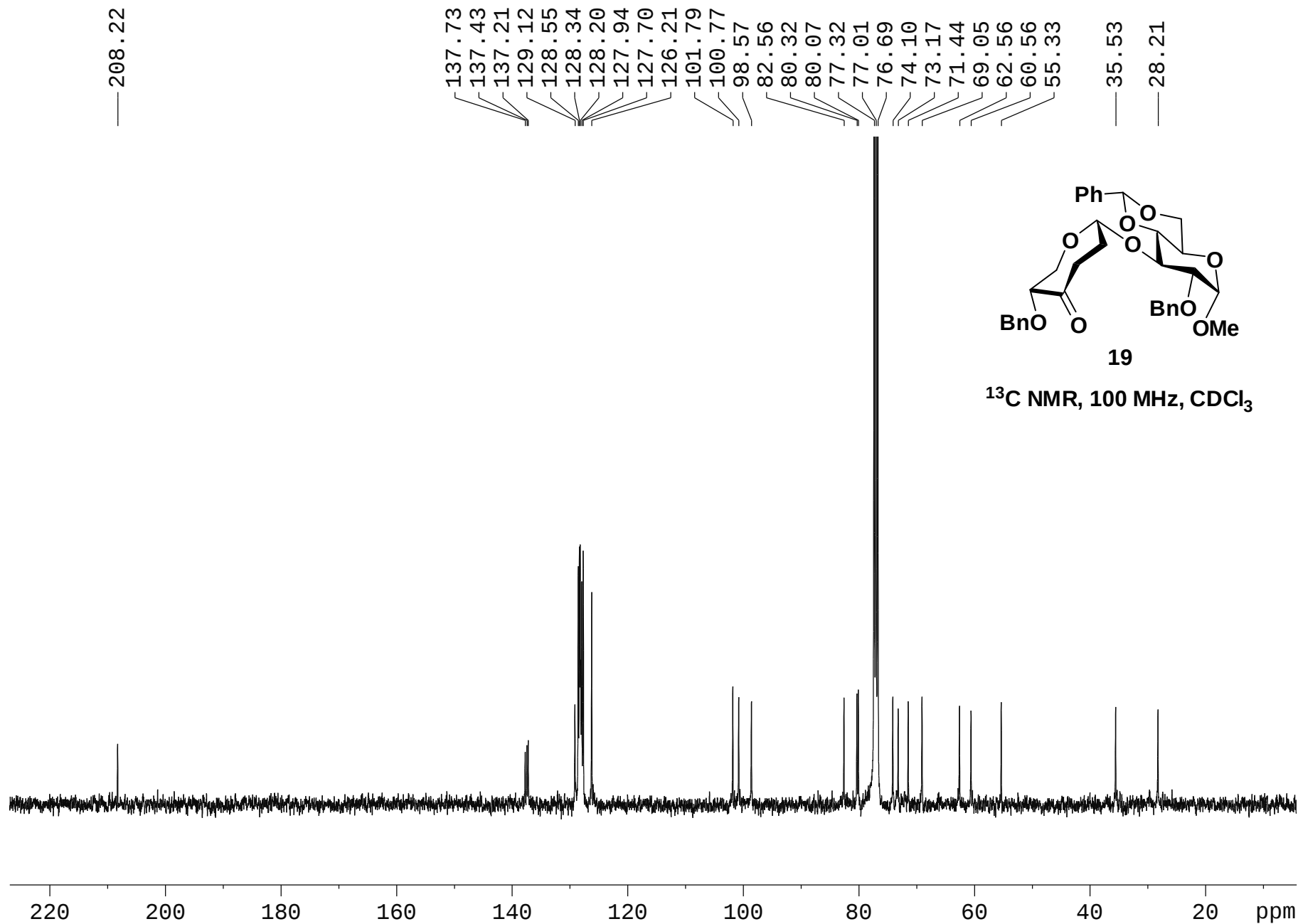
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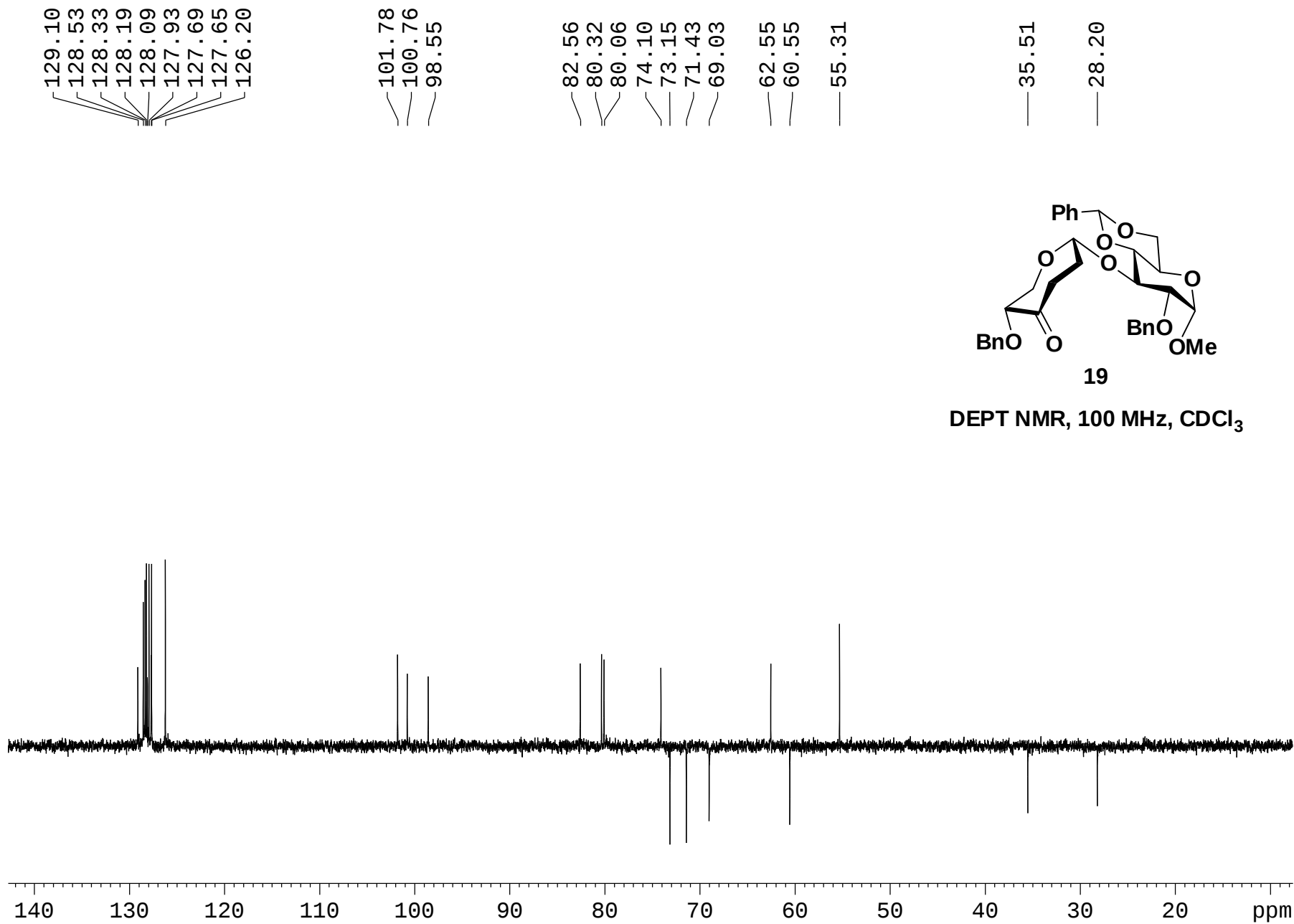
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

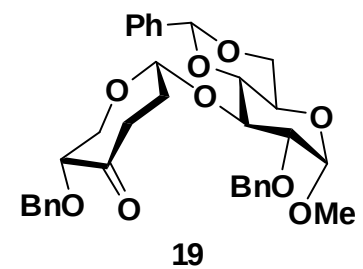
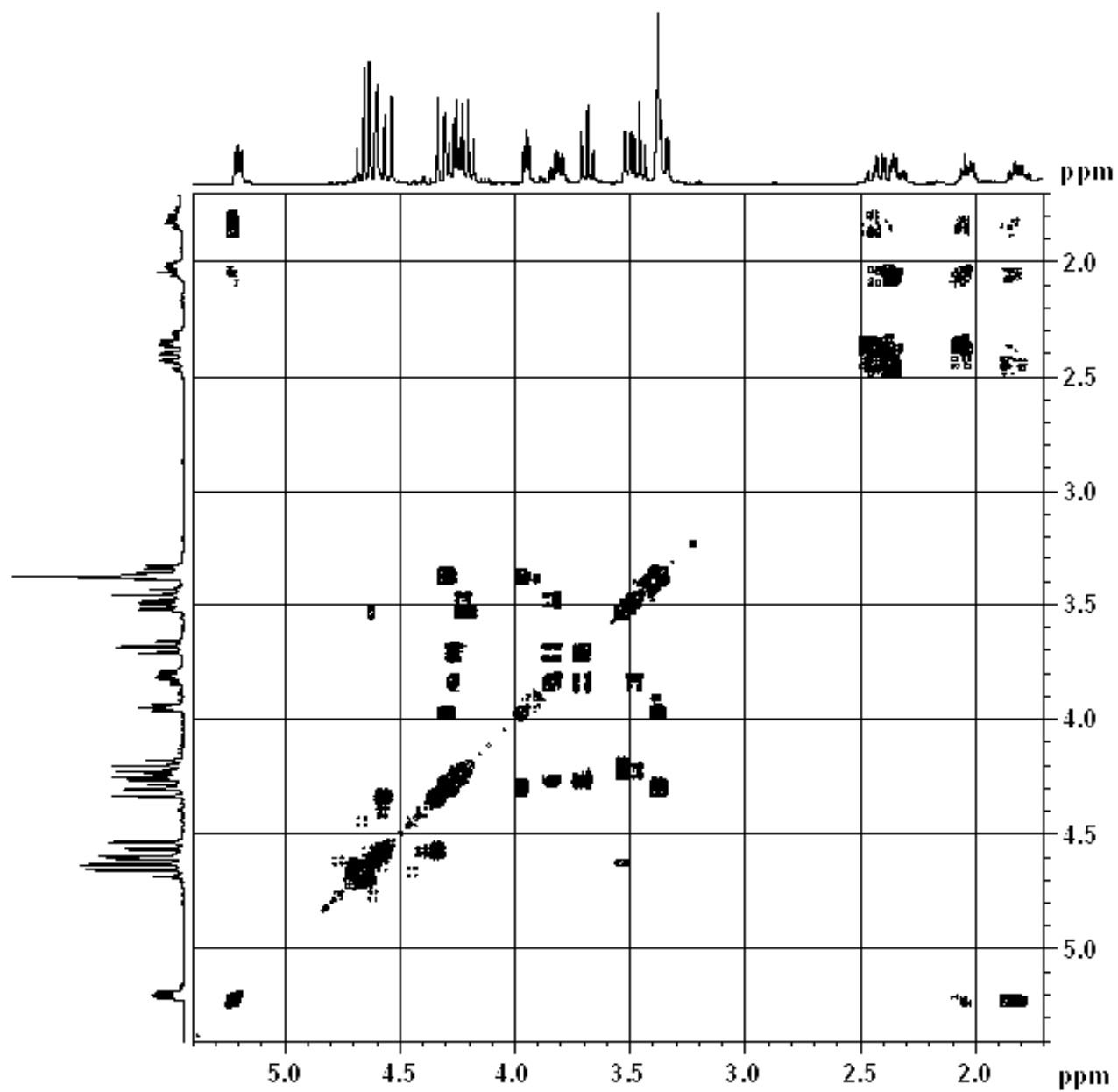


^1H NMR, 400 MHz, CDCl_3

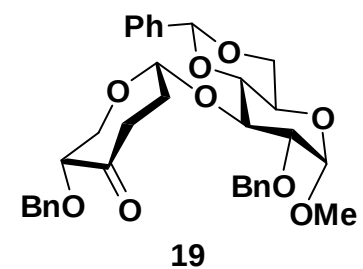
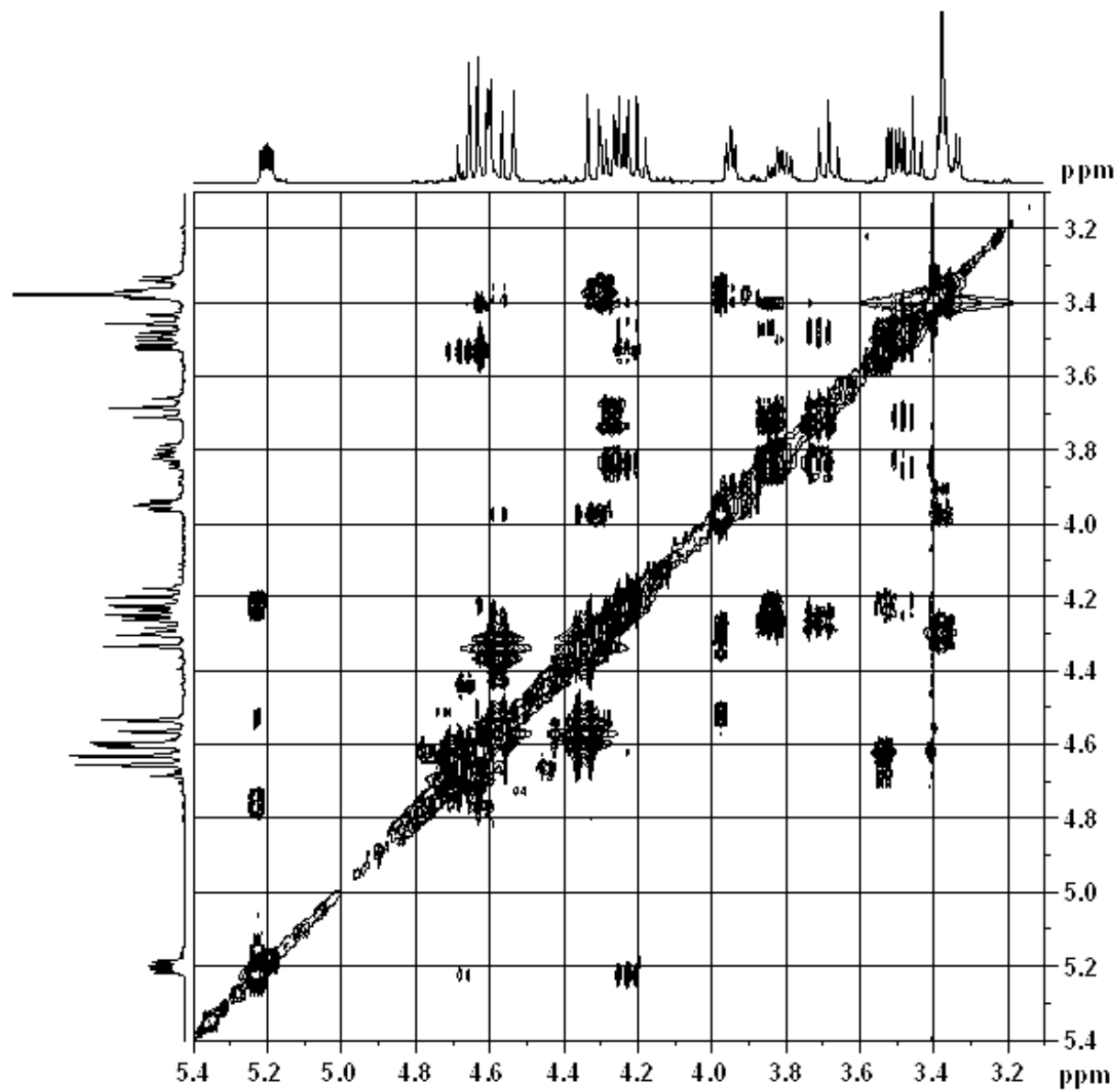




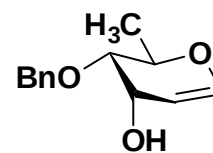




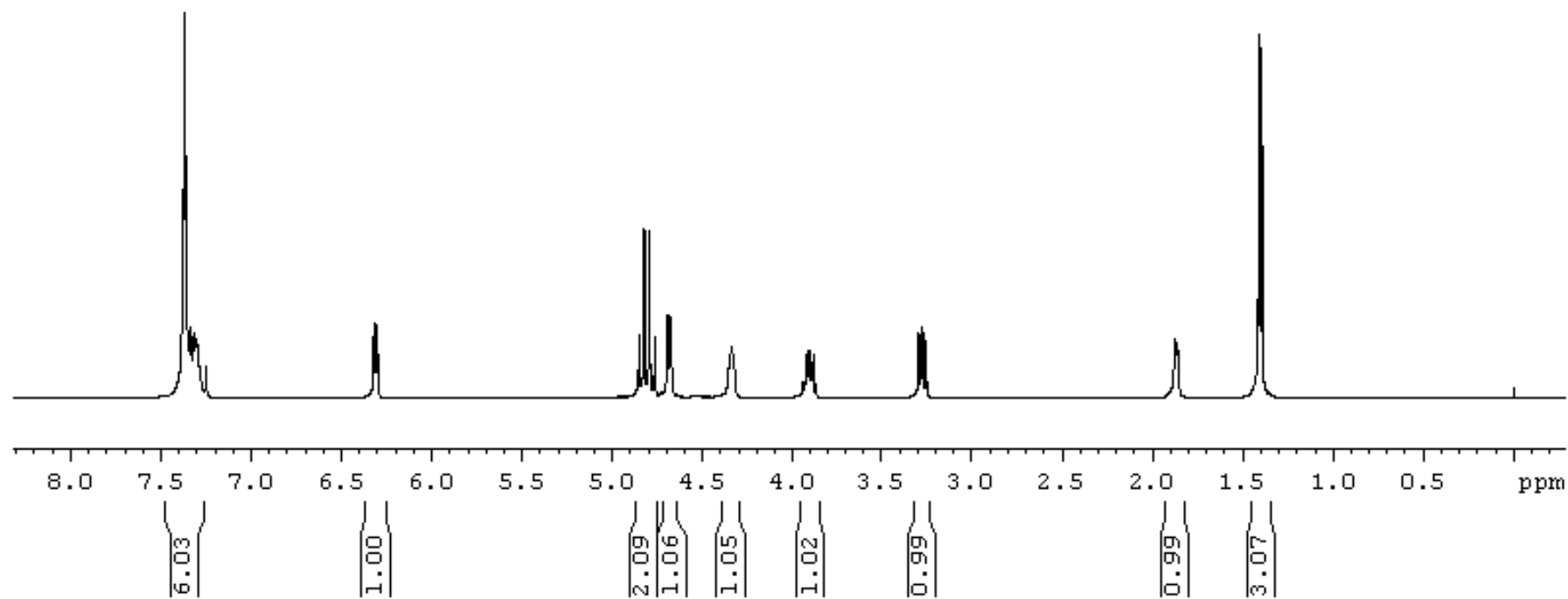
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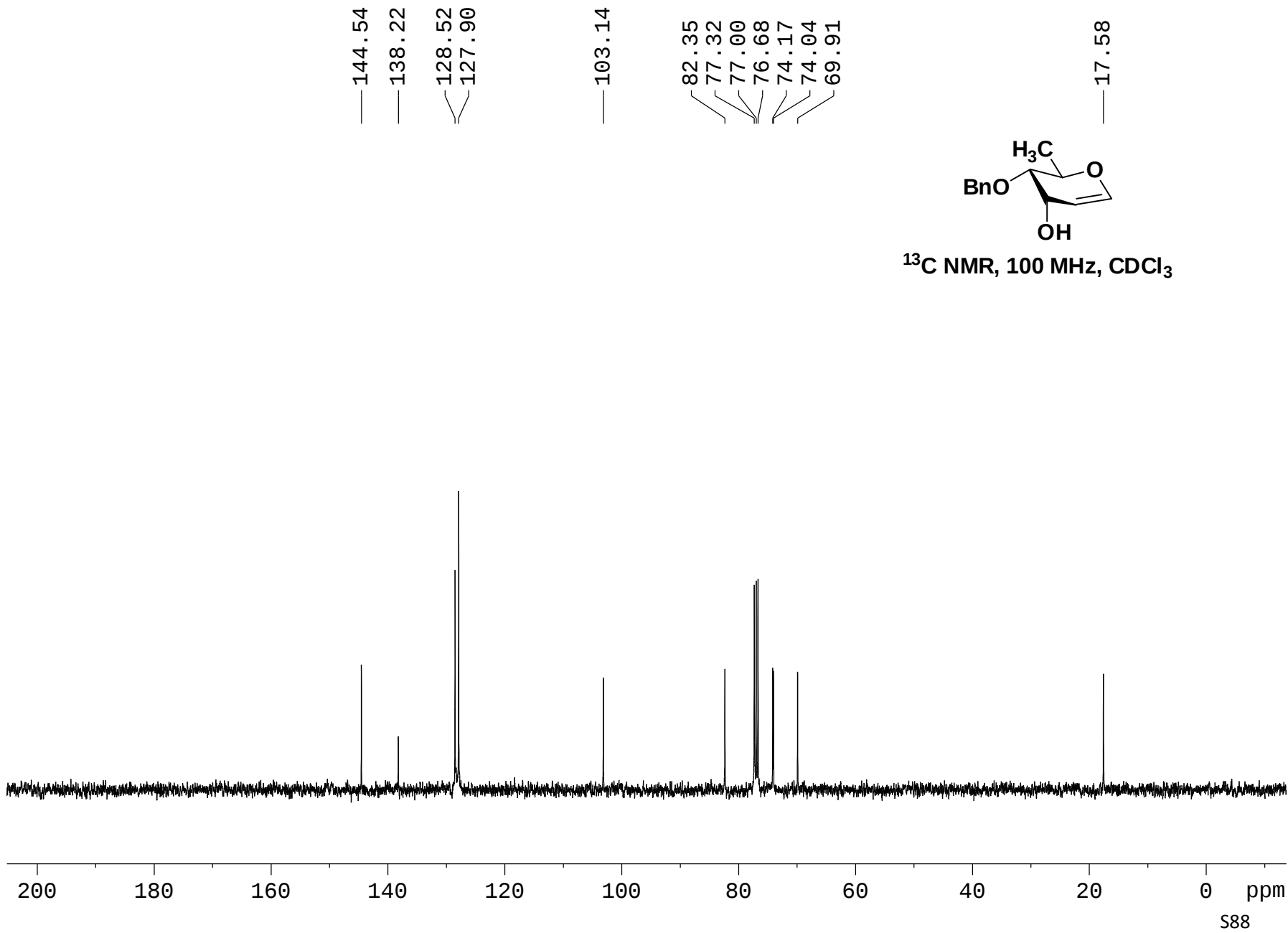


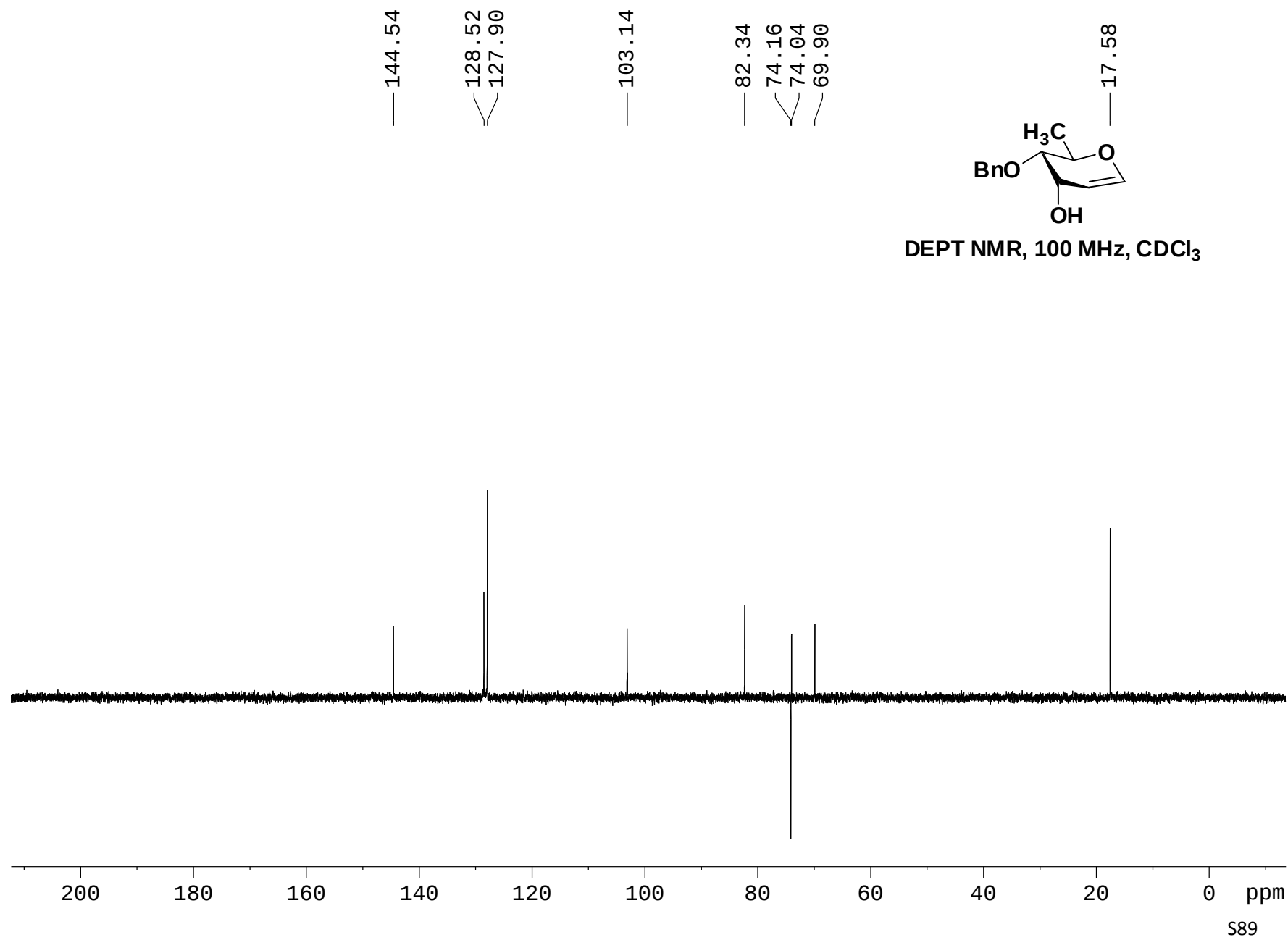
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

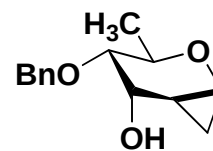


^1H NMR, 400 MHz, CDCl_3

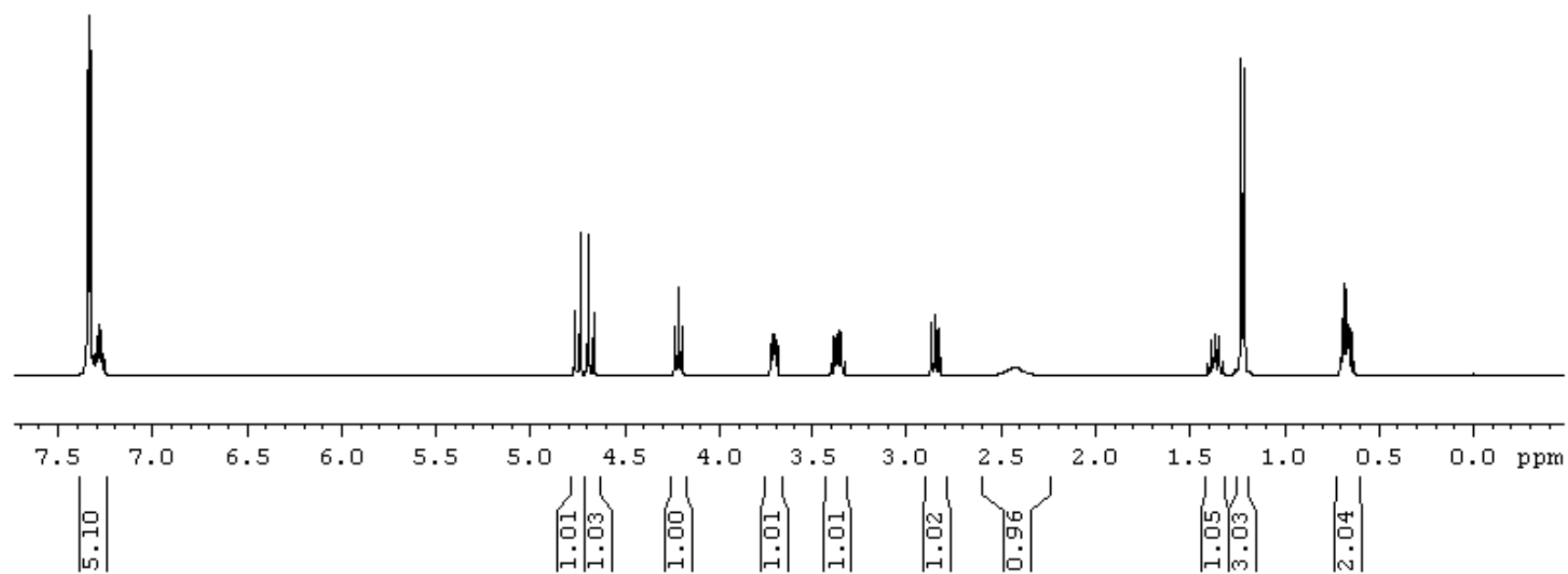


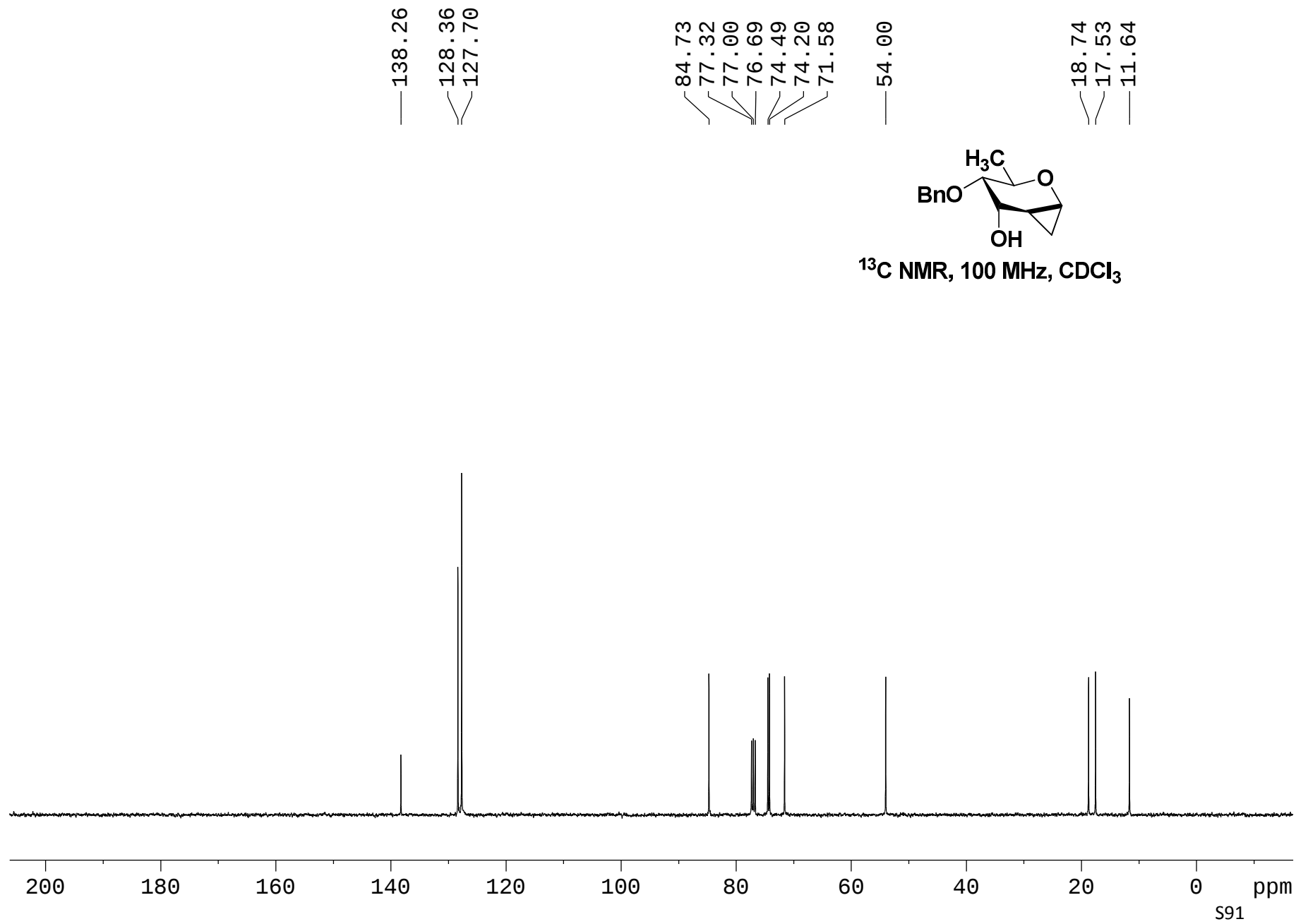


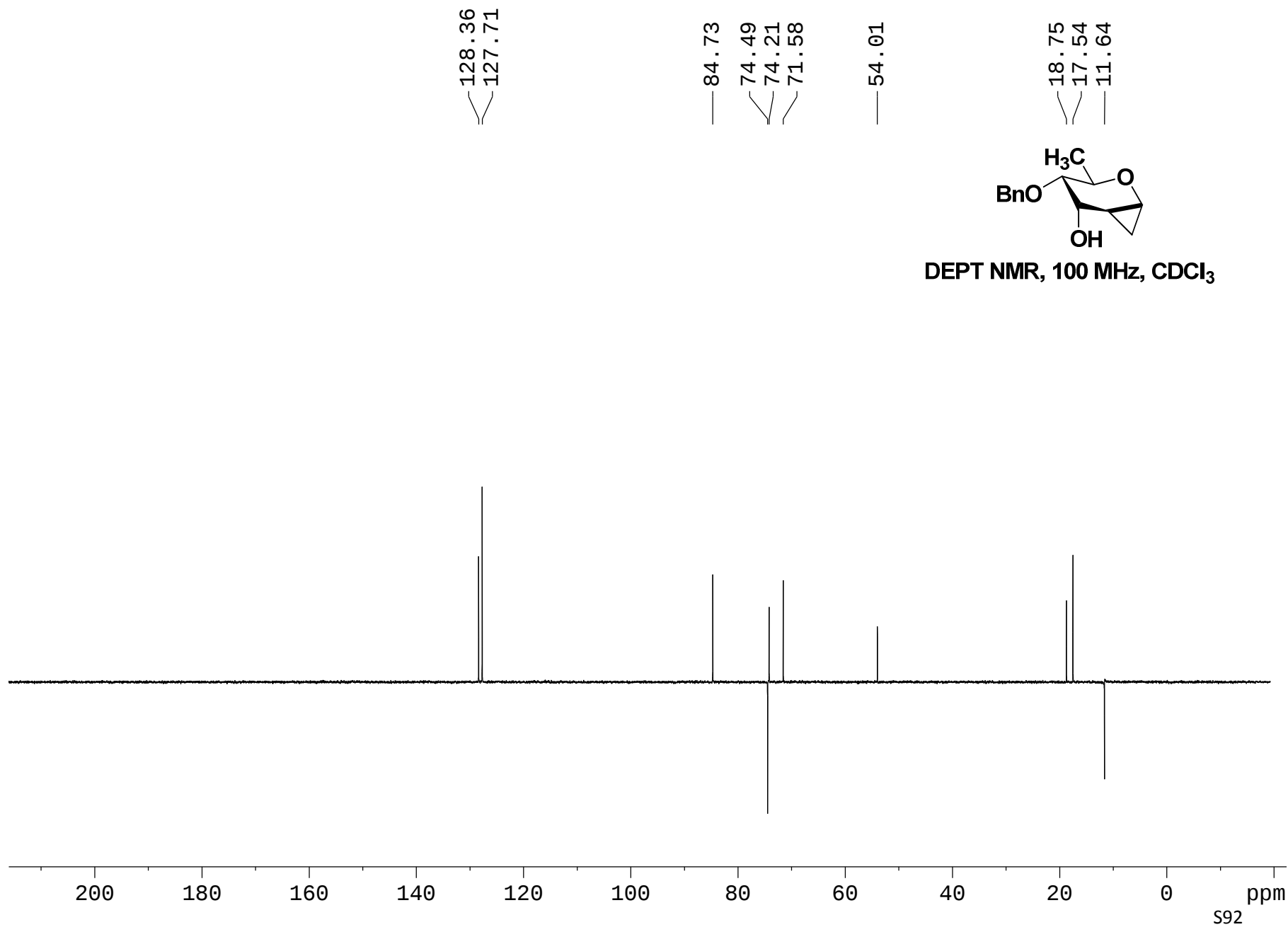


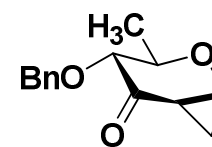


^1H NMR, 400 MHz, CDCl_3



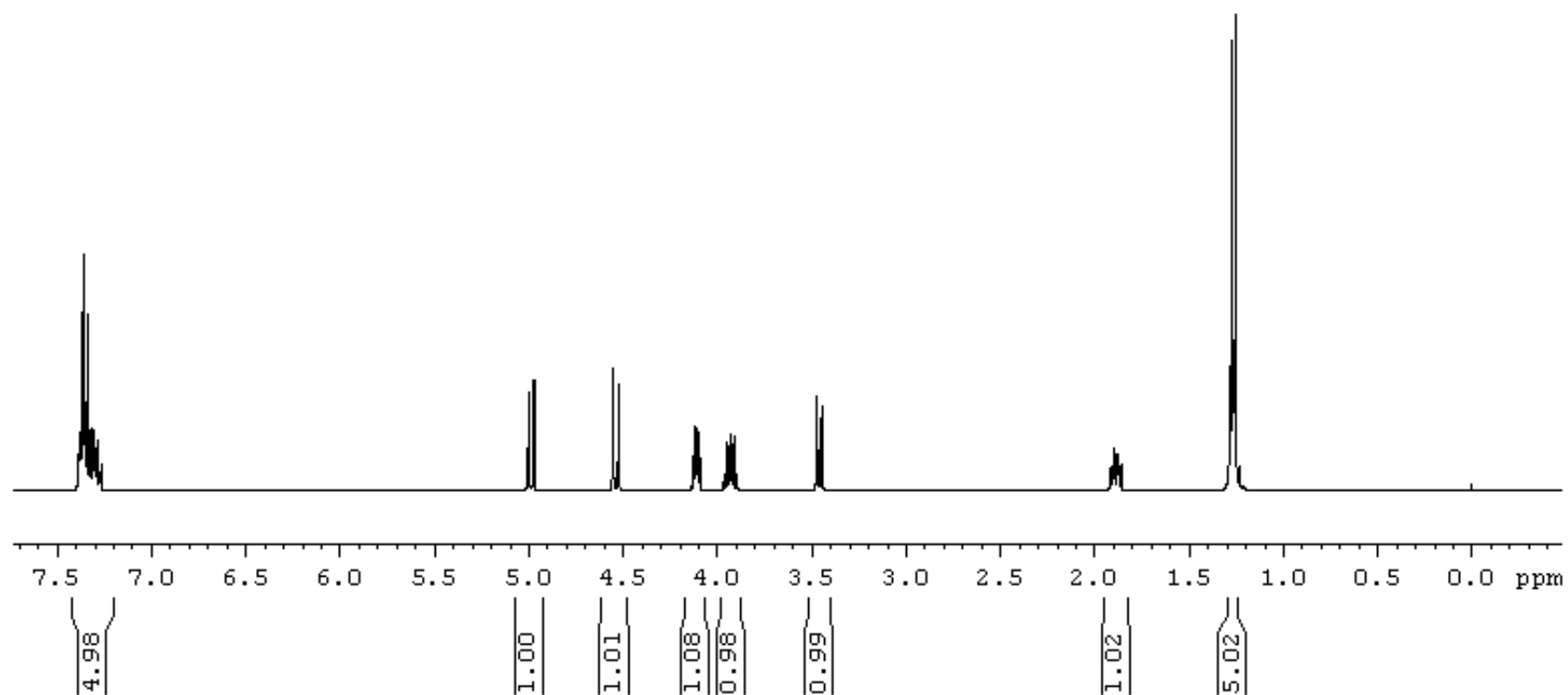


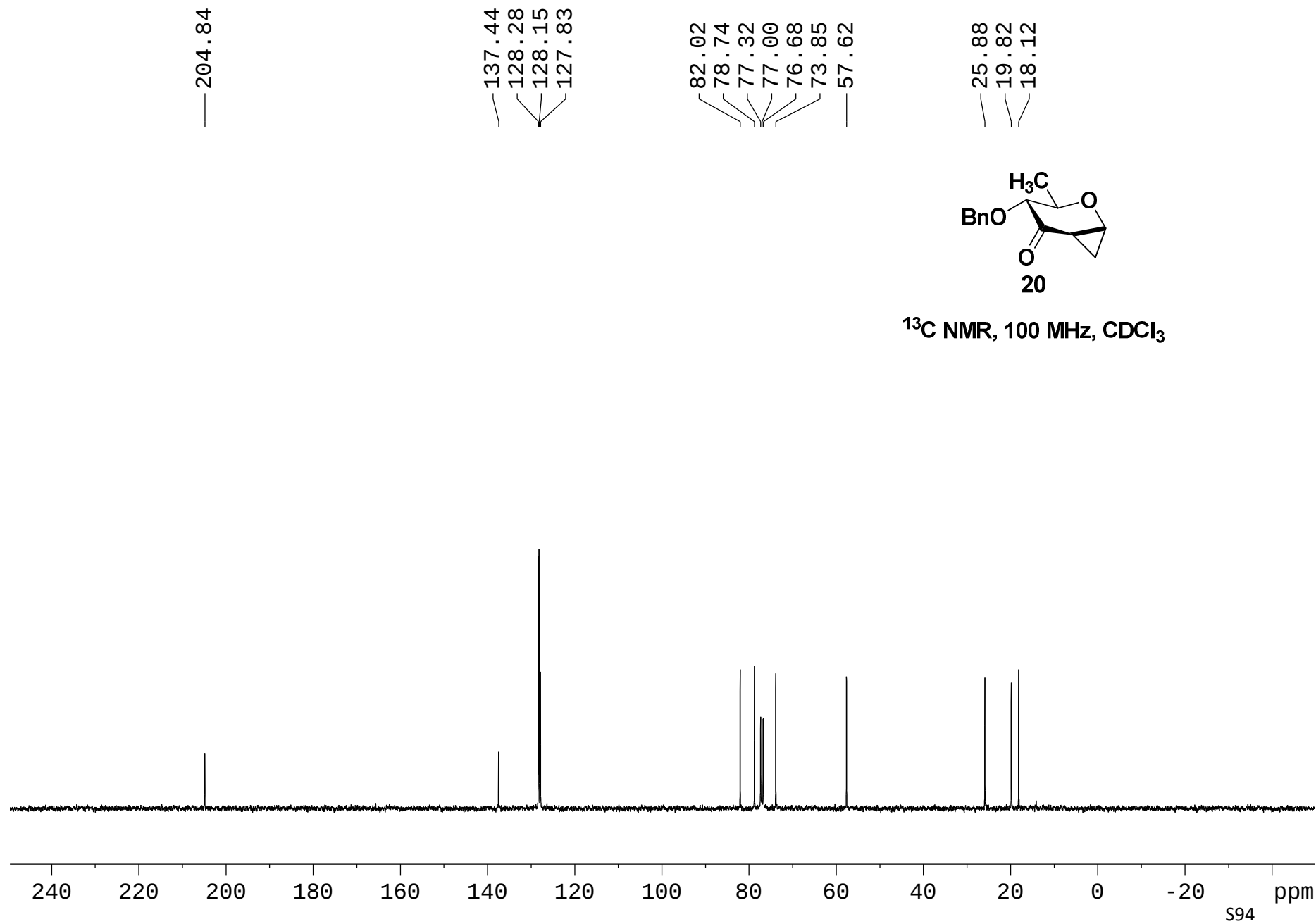


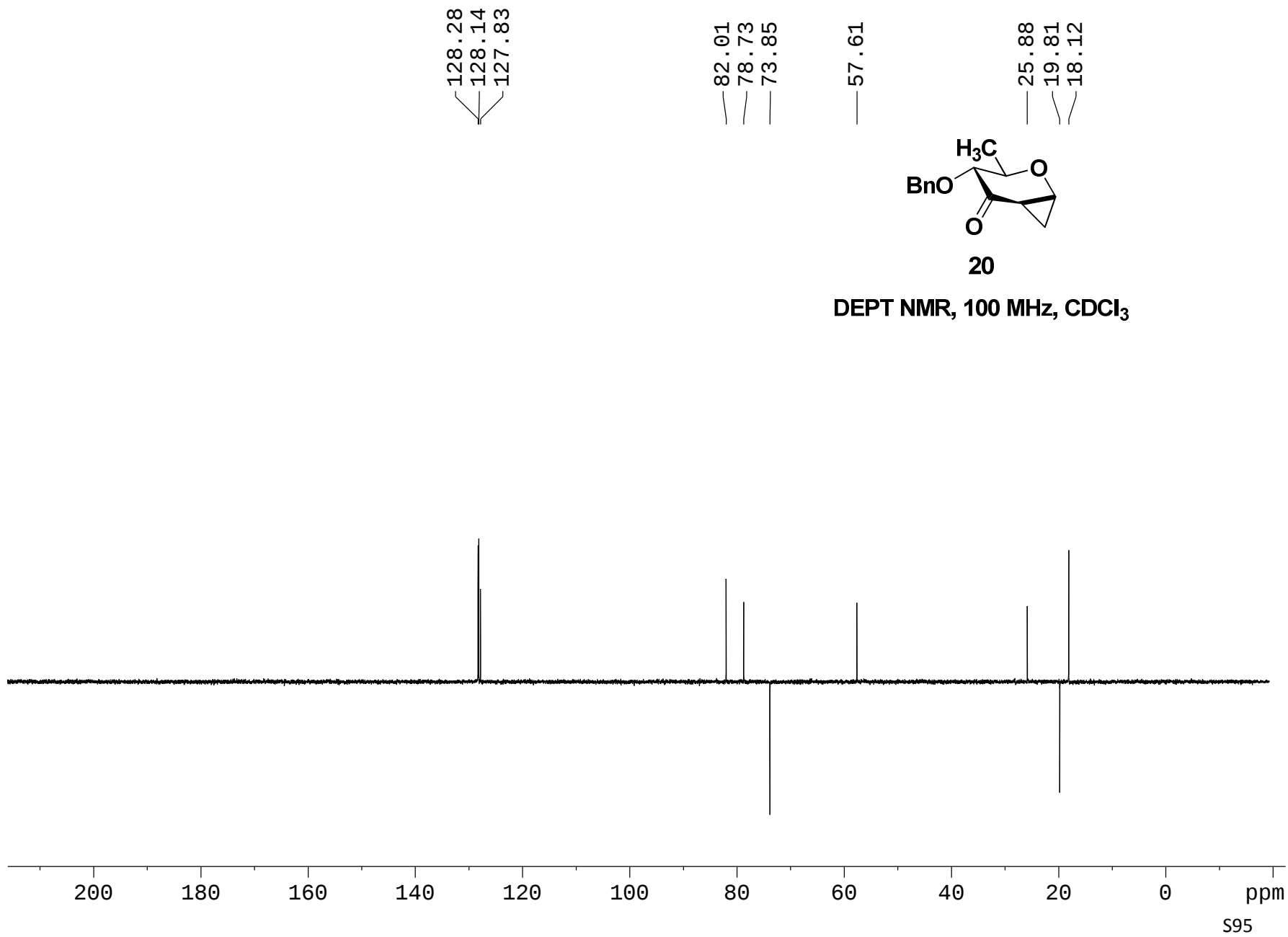


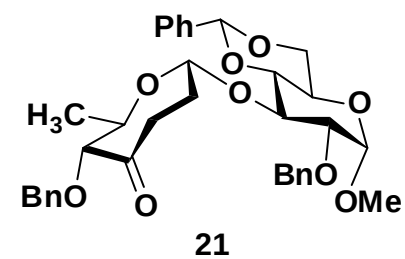
20

¹H NMR, 400 MHz, CDCl₃

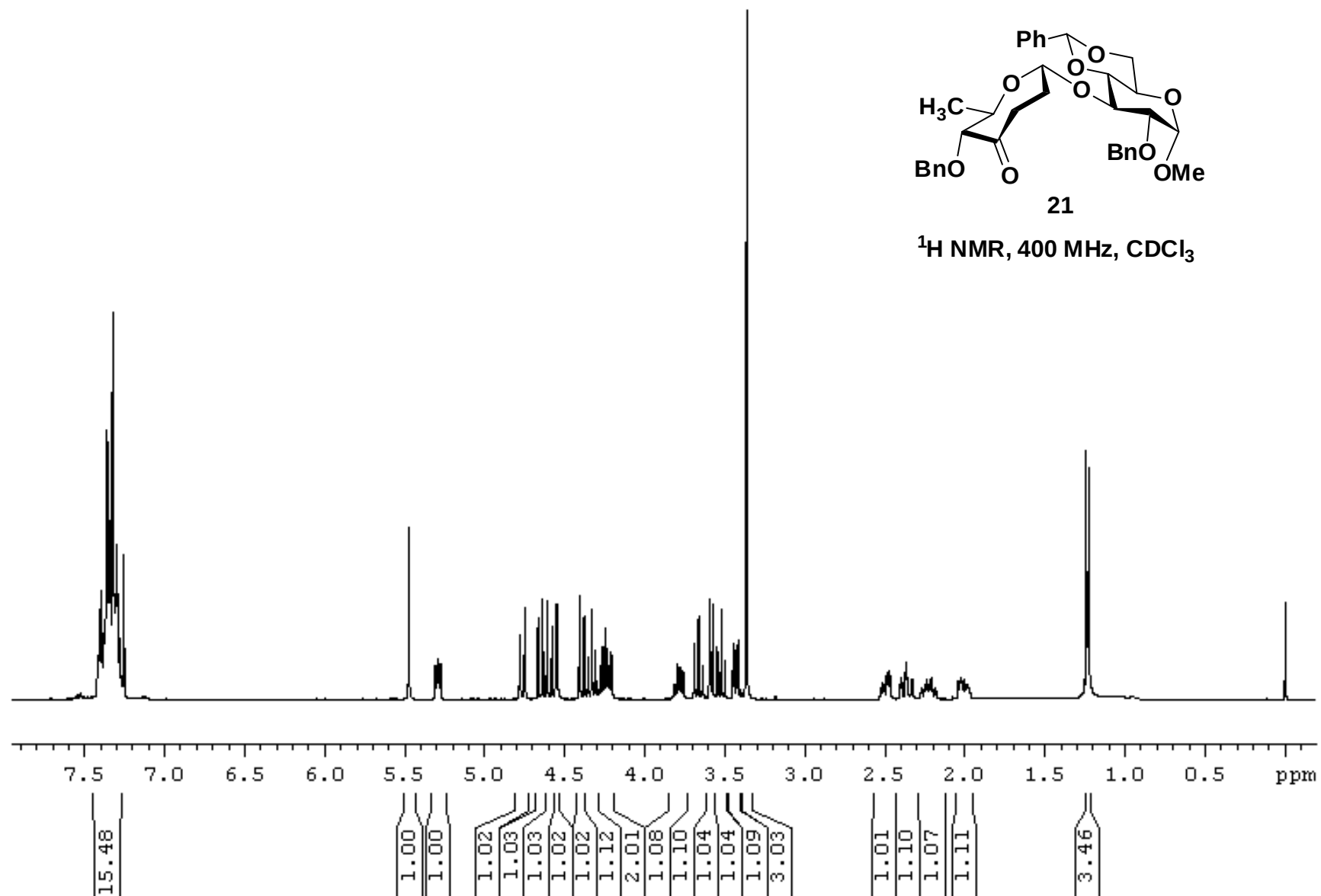








^1H NMR, 400 MHz, CDCl_3



129.02
128.42
128.36
128.29
128.28
127.97
127.95
127.86
125.94

101.41
100.11
98.99

89.06

83.00

77.75

73.66

72.92

72.89

69.05

66.14

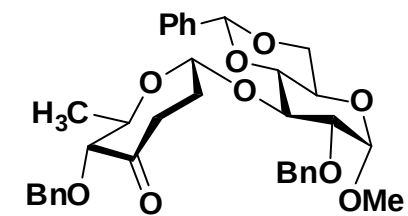
61.84

55.26

35.88

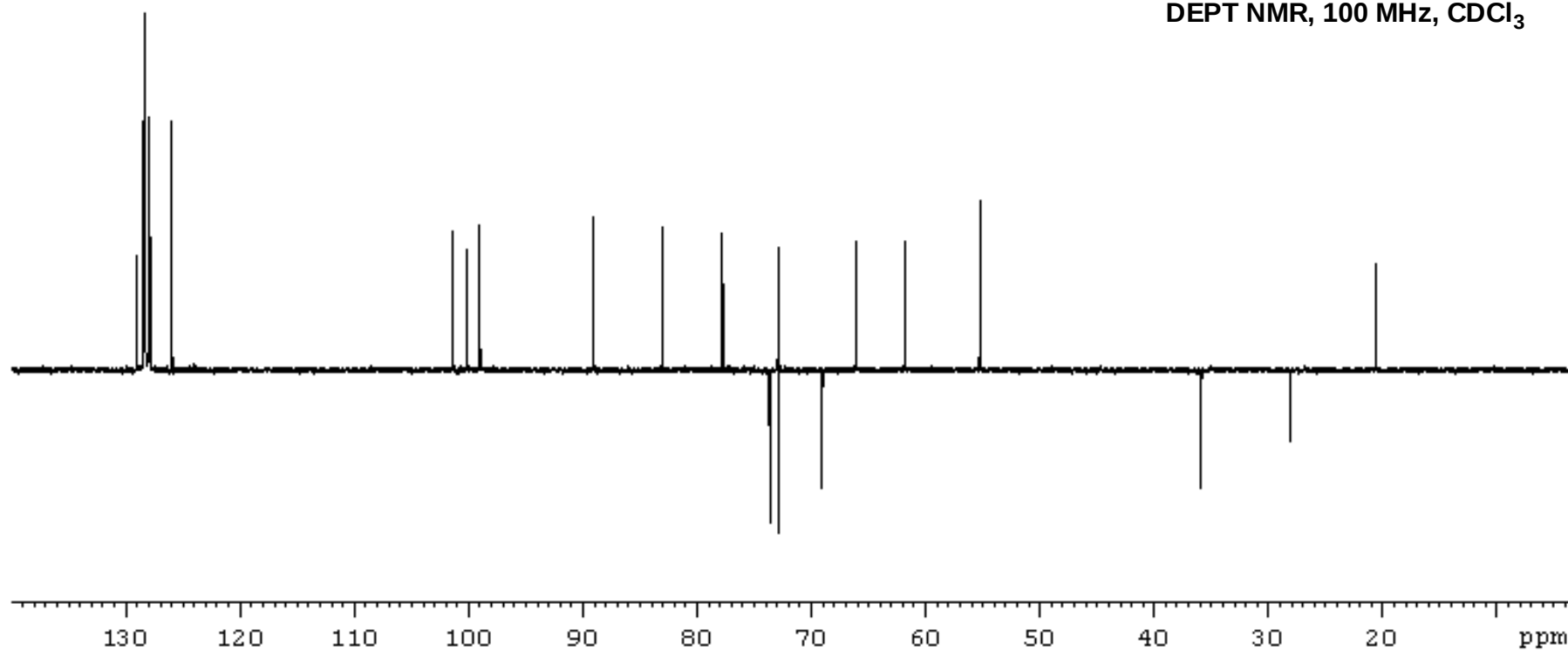
28.08

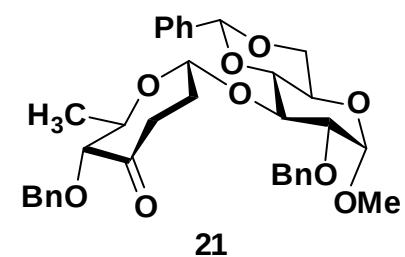
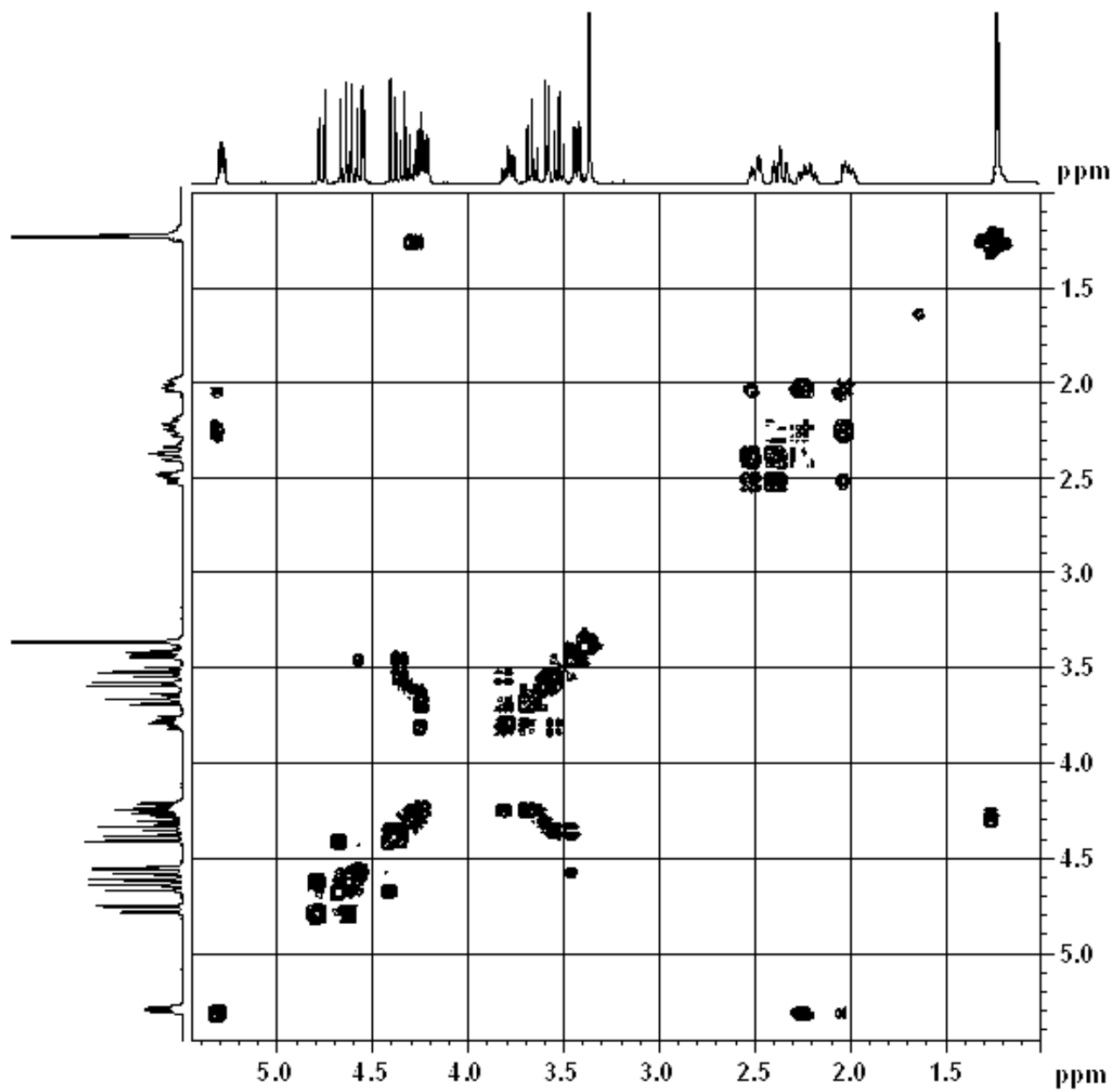
20.60



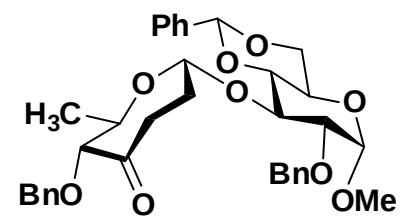
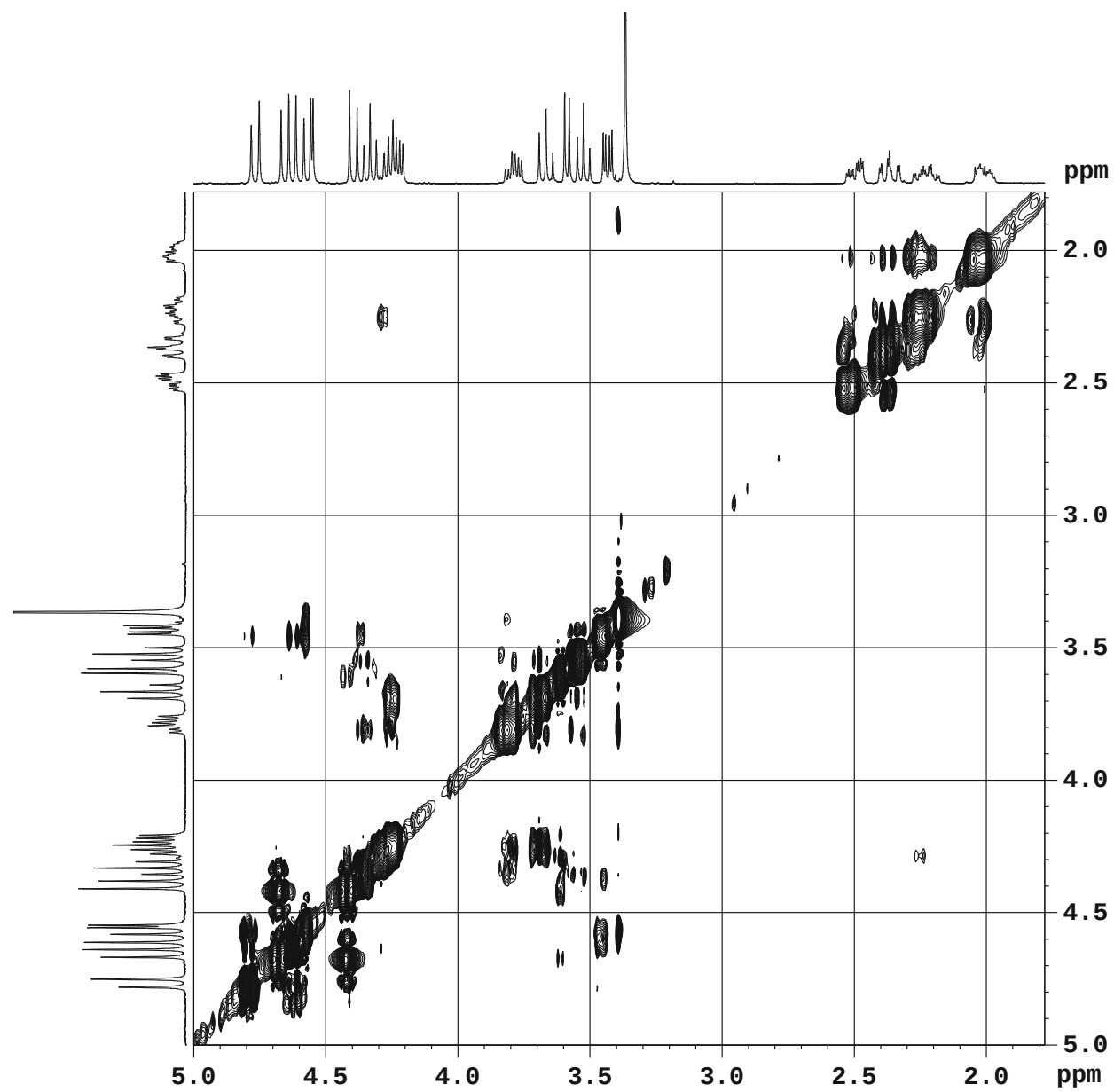
21

DEPT NMR, 100 MHz, CDCl₃



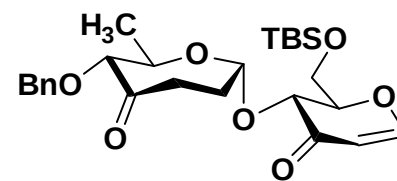


^1H - ^1H COSY NMR, 400 MHz, CDCl_3



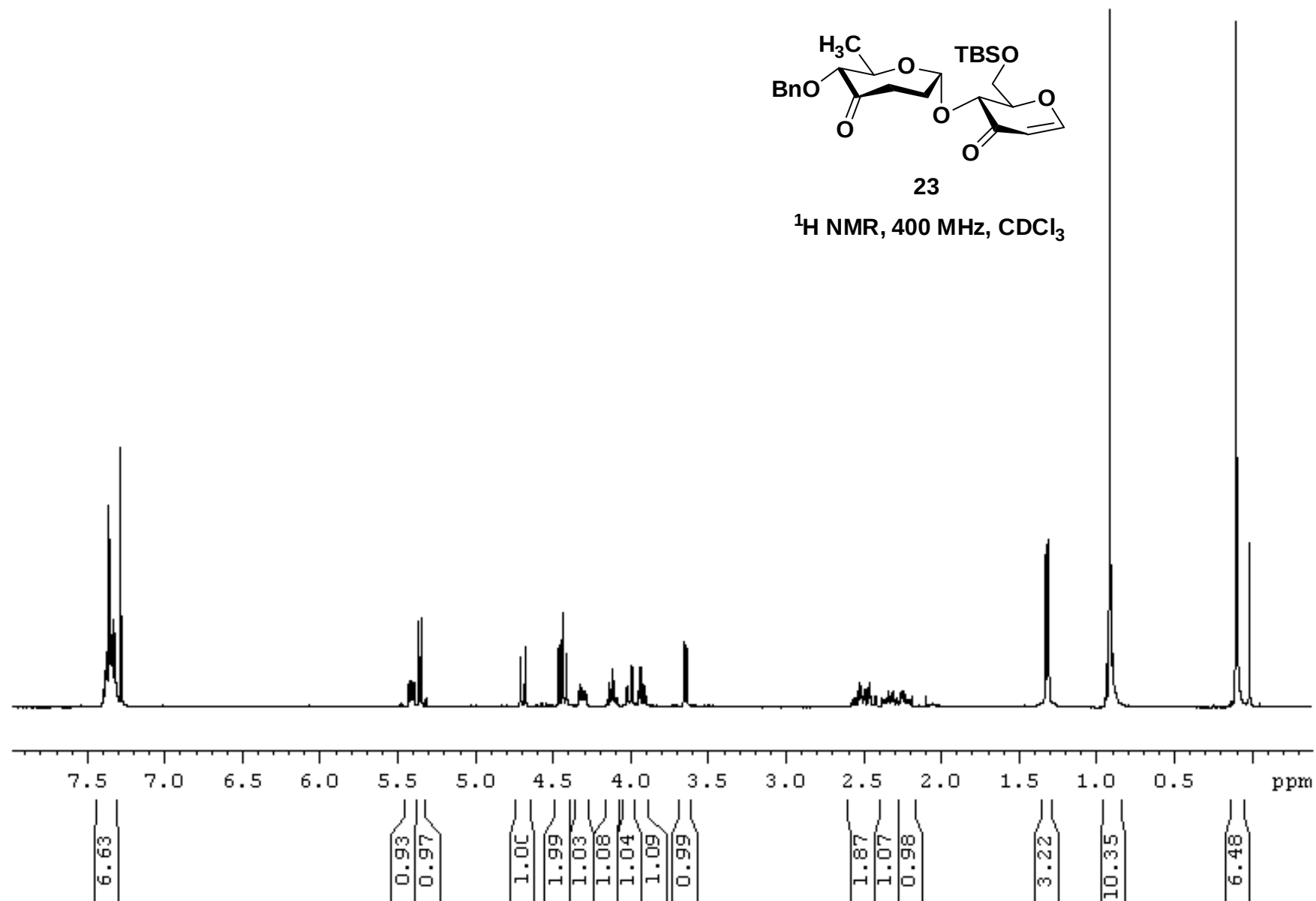
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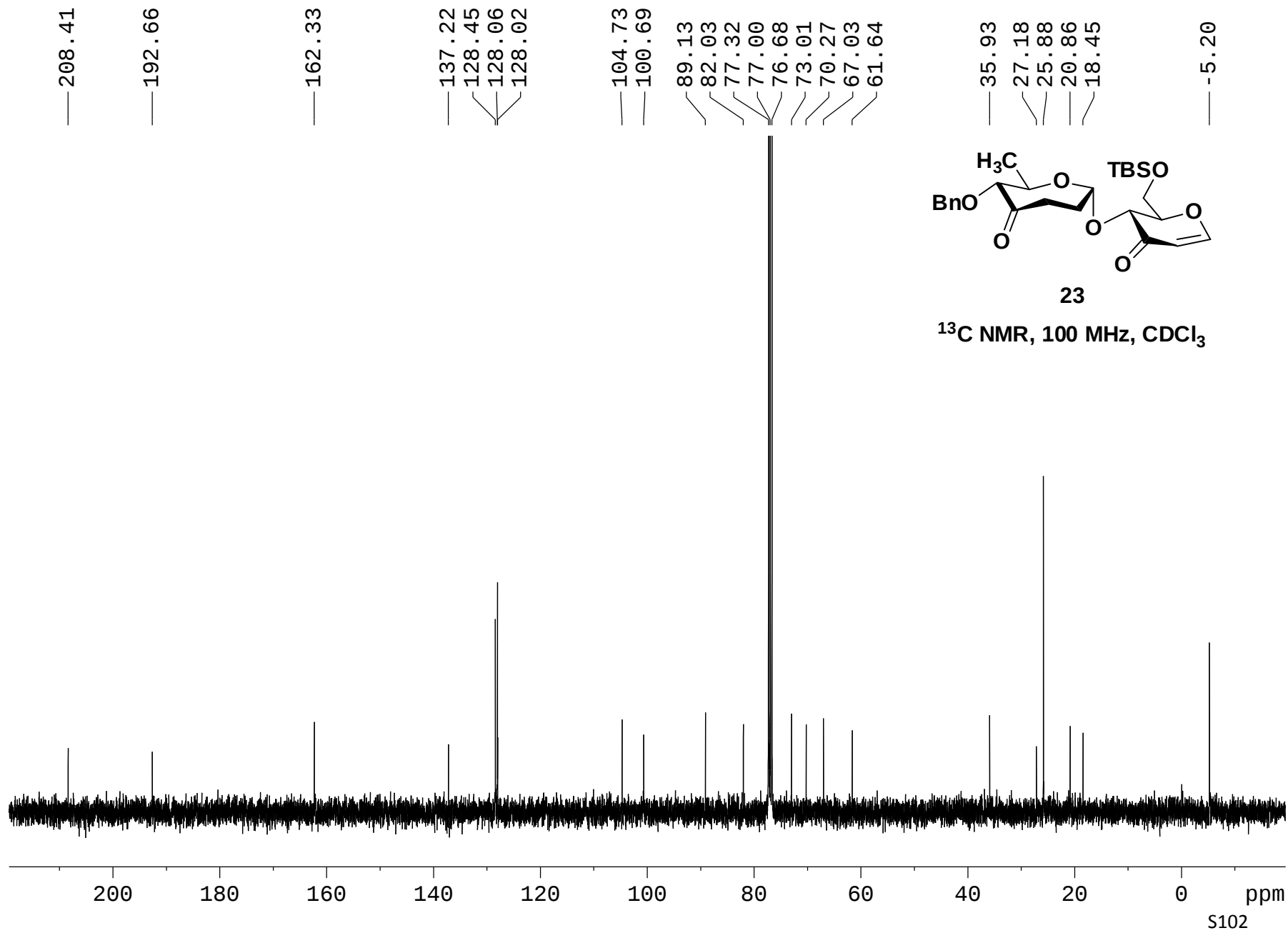
^1H - ^1H NOESY NMR, 400 MHz, CDCl_3

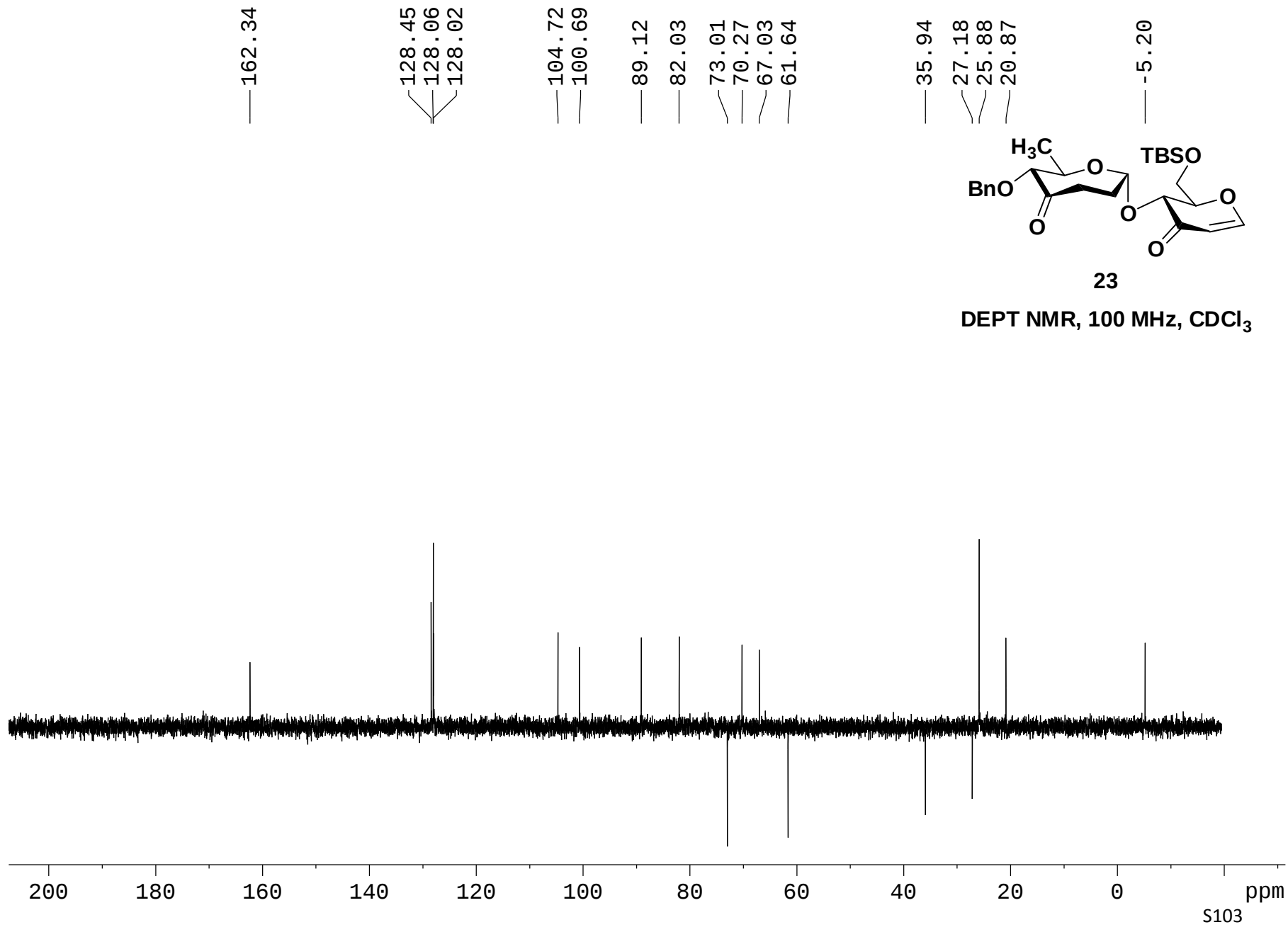


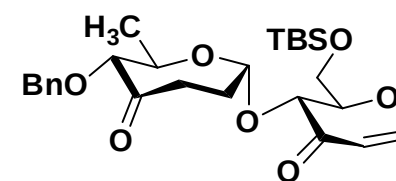
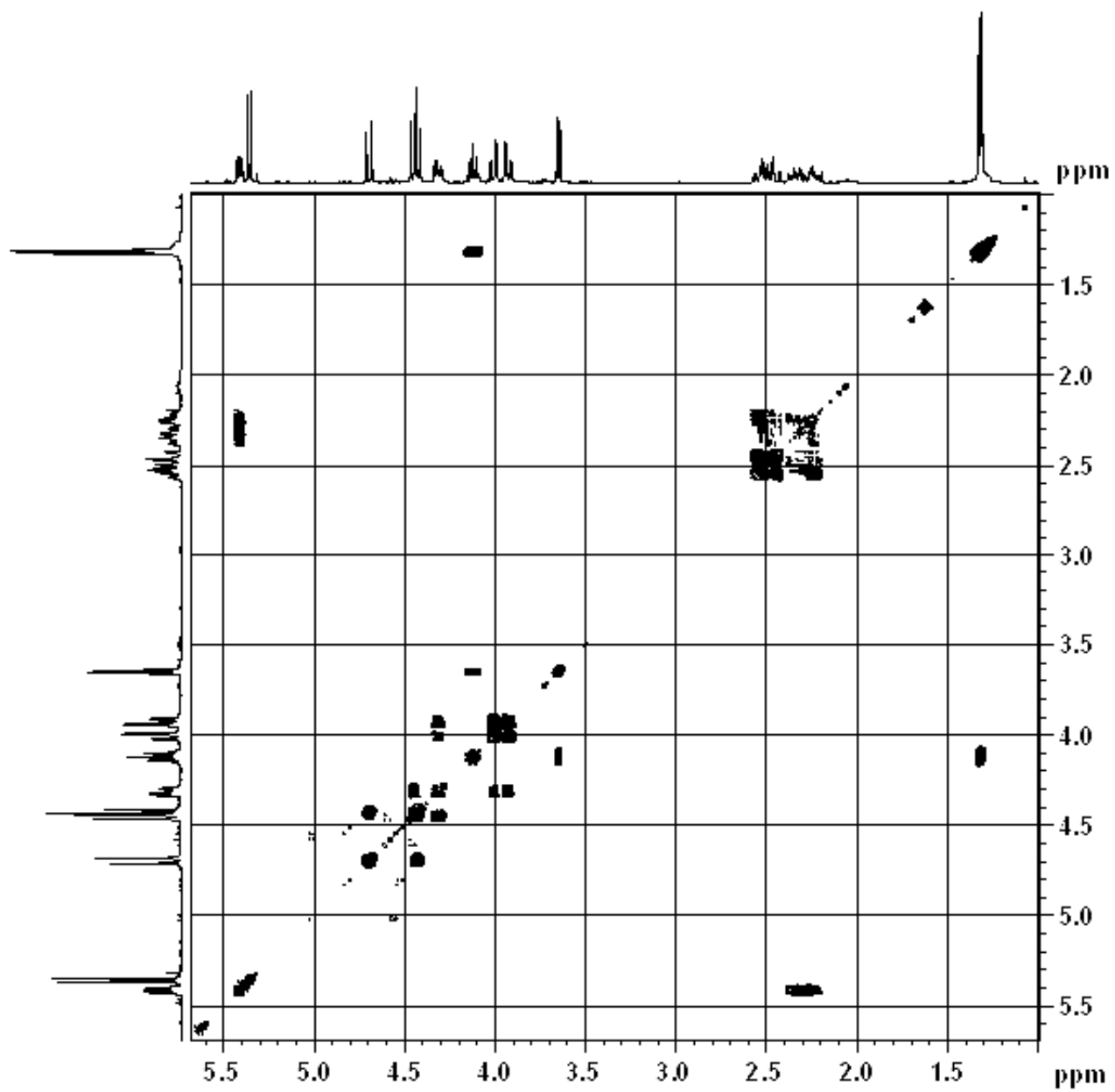
23

^1H NMR, 400 MHz, CDCl_3



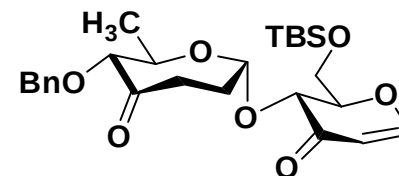
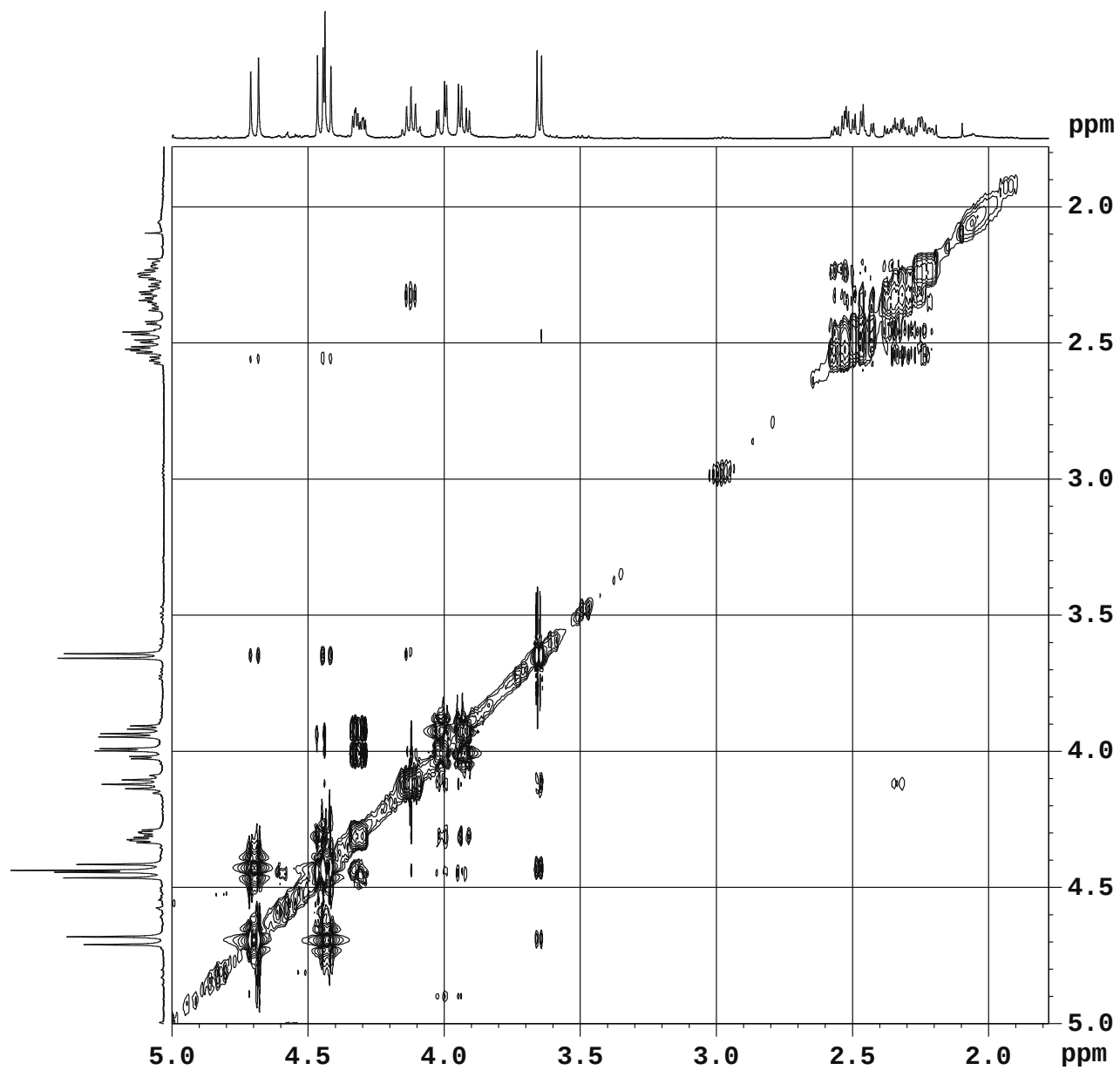






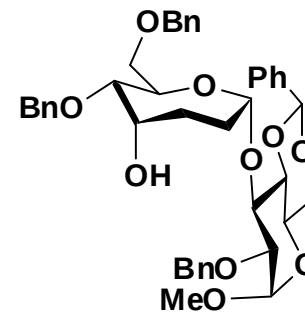
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^1H - ^1H COSY NMR, 100 MHz, CDCl_3



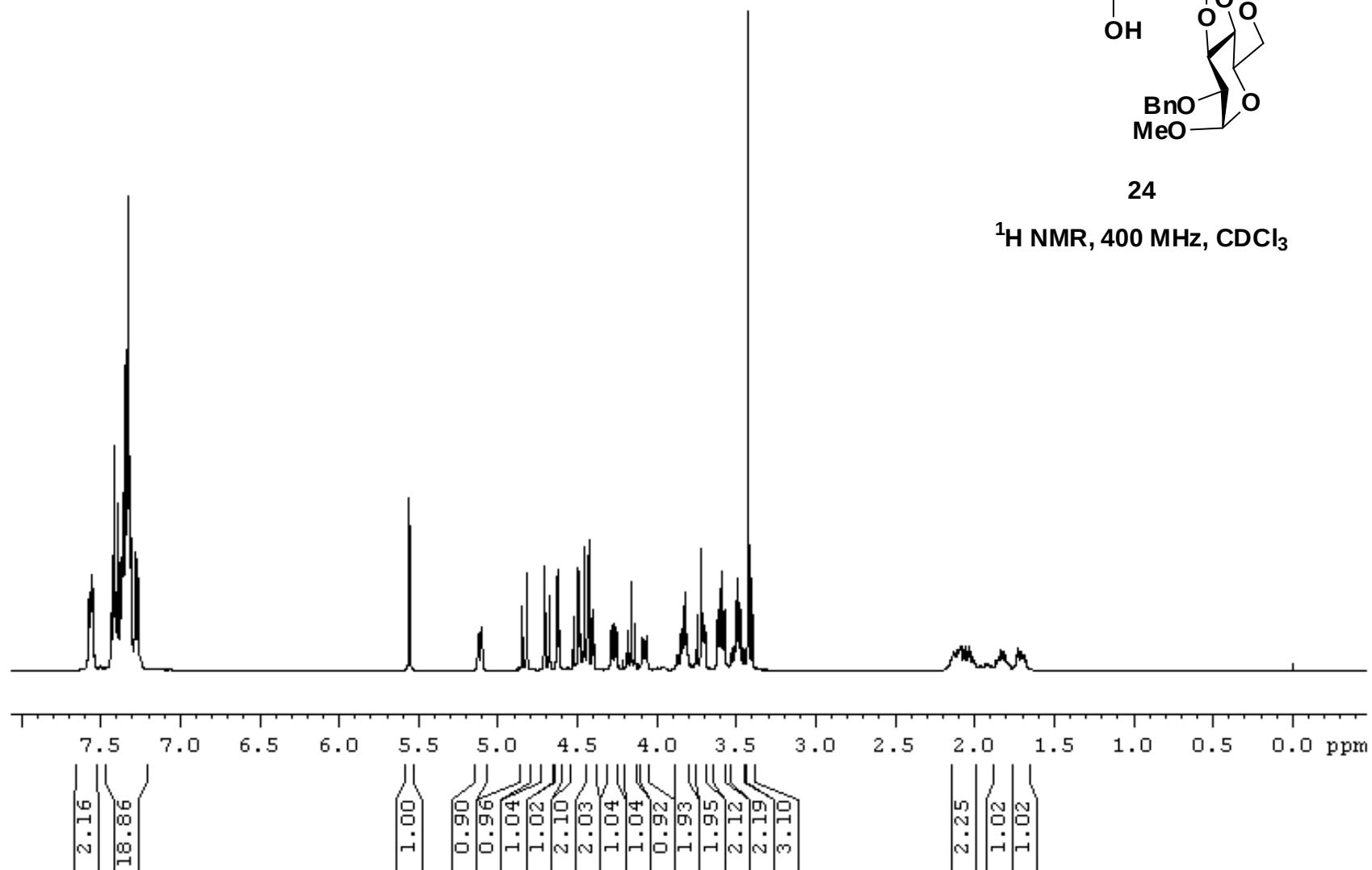
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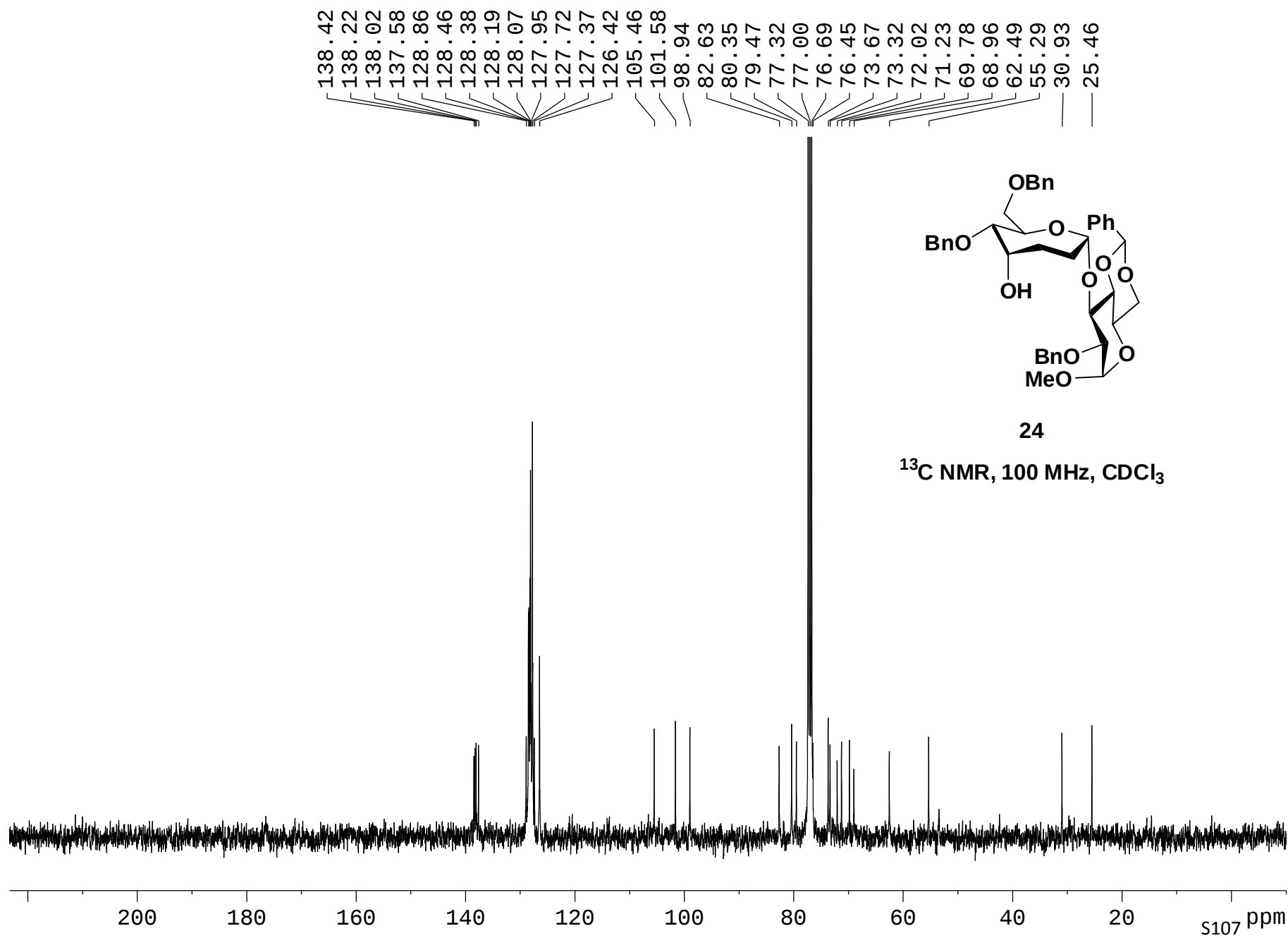
^1H - ^1H NOESY NMR, 100 MHz, CDCl_3



24

^1H NMR, 400 MHz, CDCl_3





128.46
128.38
128.20
128.08
128.06
127.95
127.72
127.66
127.60
127.38
126.42
126.34

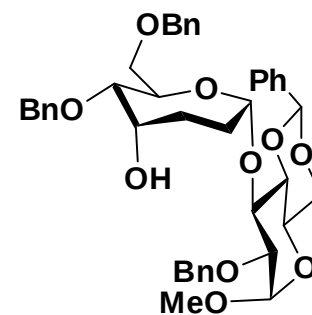
— 105.49
— 101.58
— 98.94

82.62
80.34
79.44
77.00
76.50
73.68
73.32
72.01
71.21
69.77
68.96
62.48

— 55.30

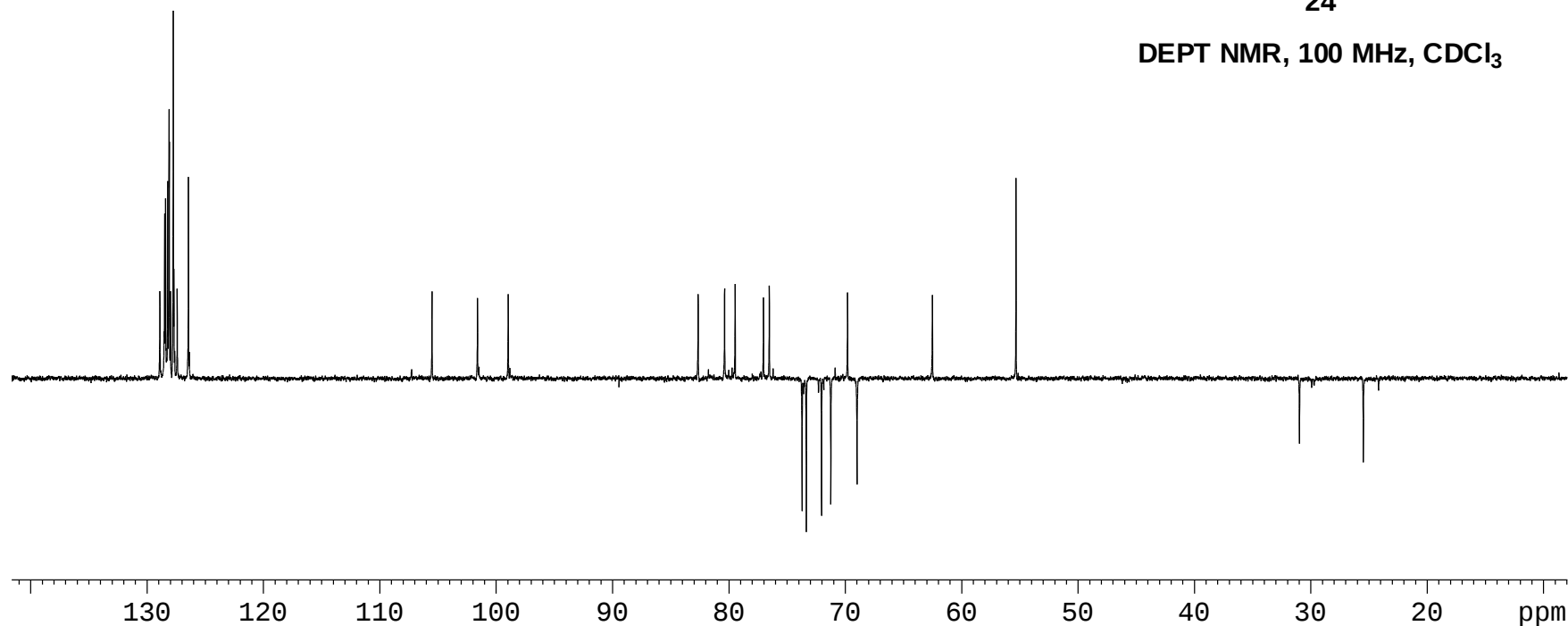
— 30.94

— 25.46

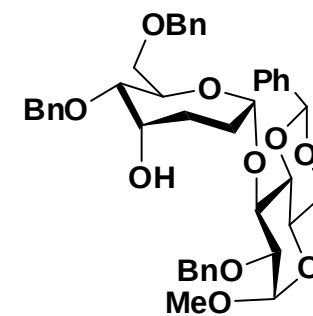
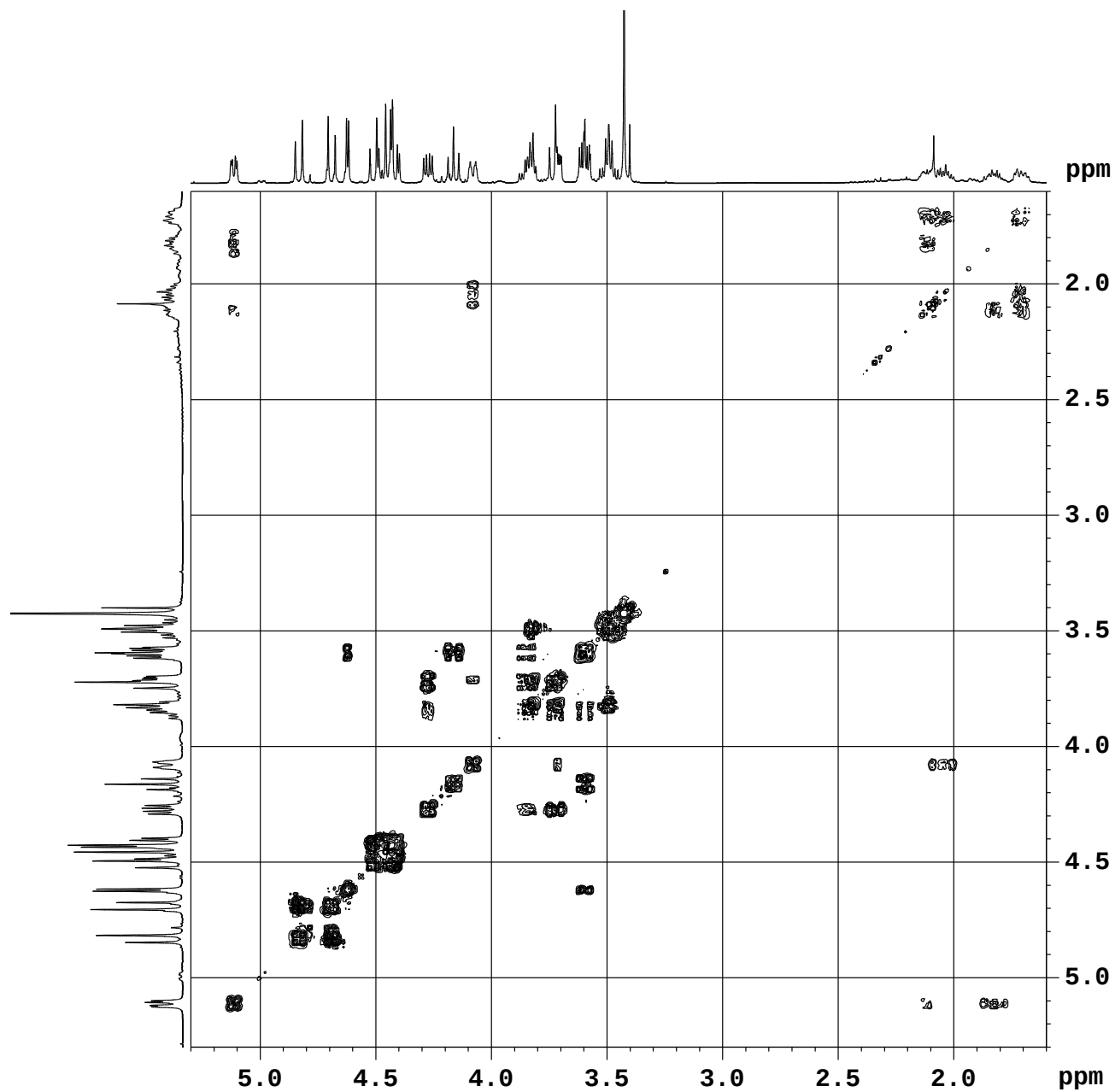


24

DEPT NMR, 100 MHz, CDCl₃

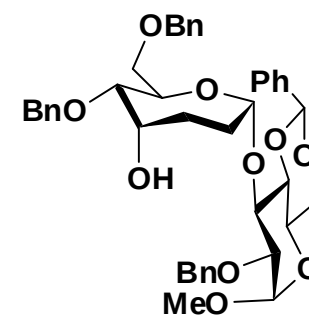
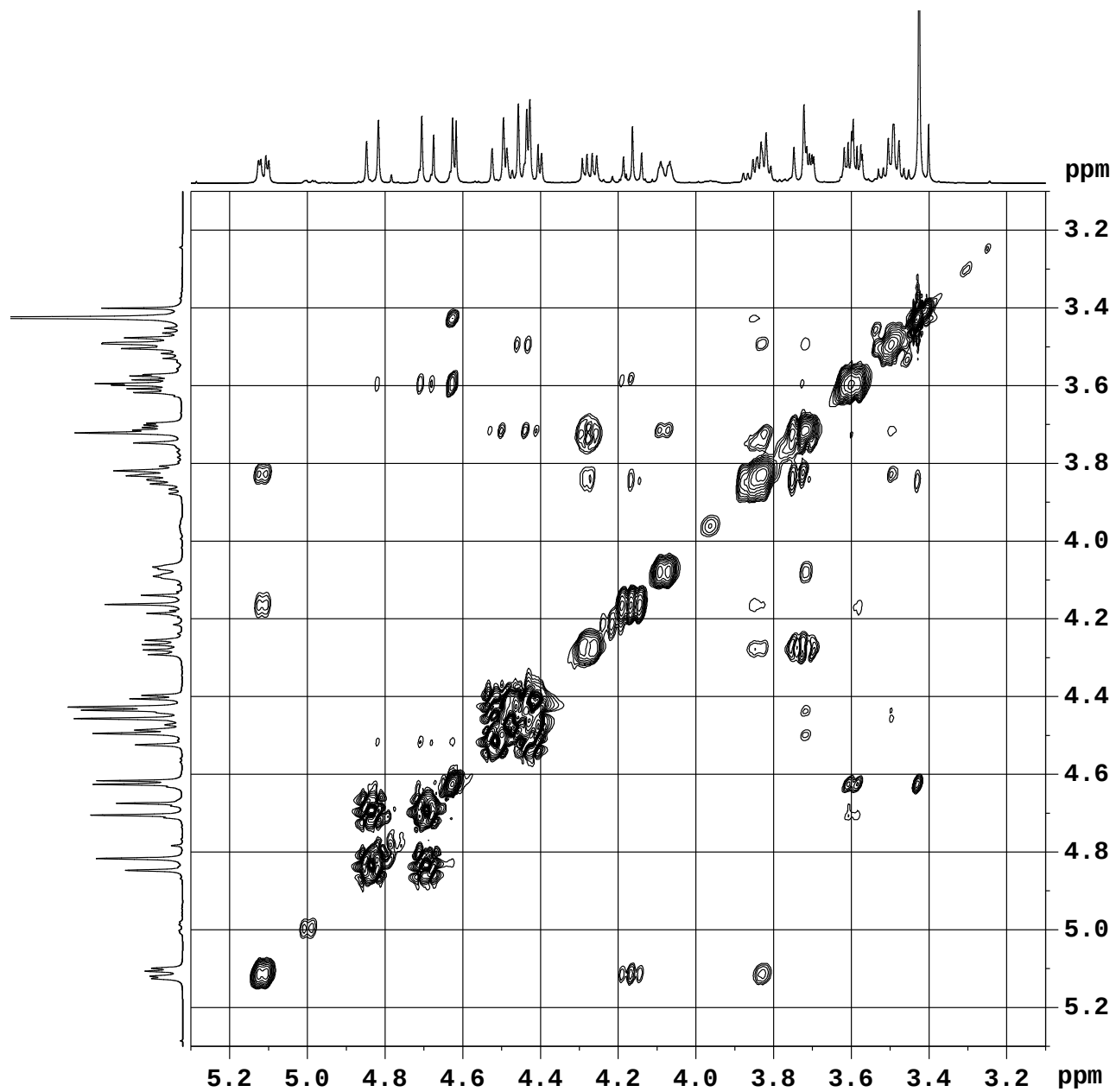


S108



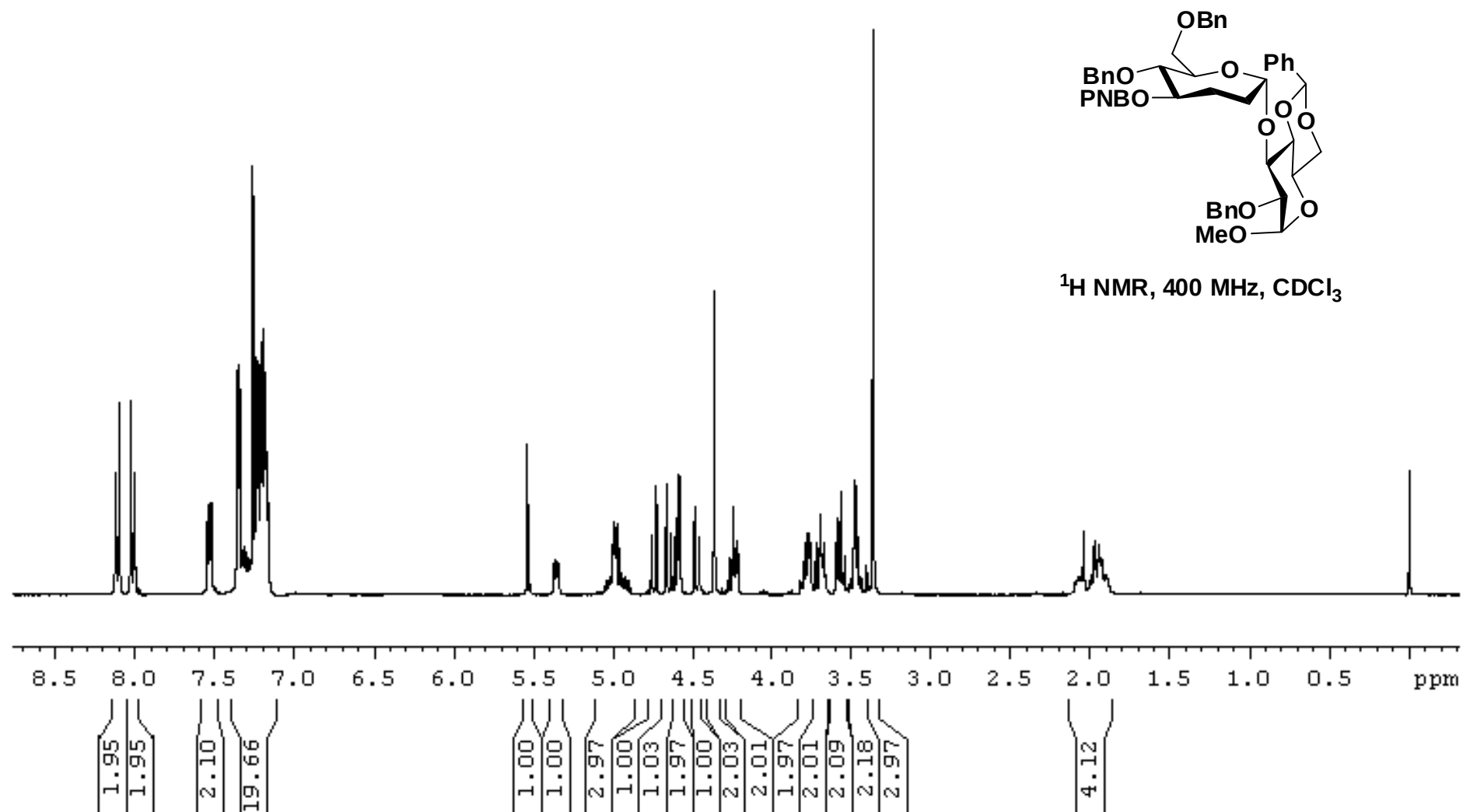
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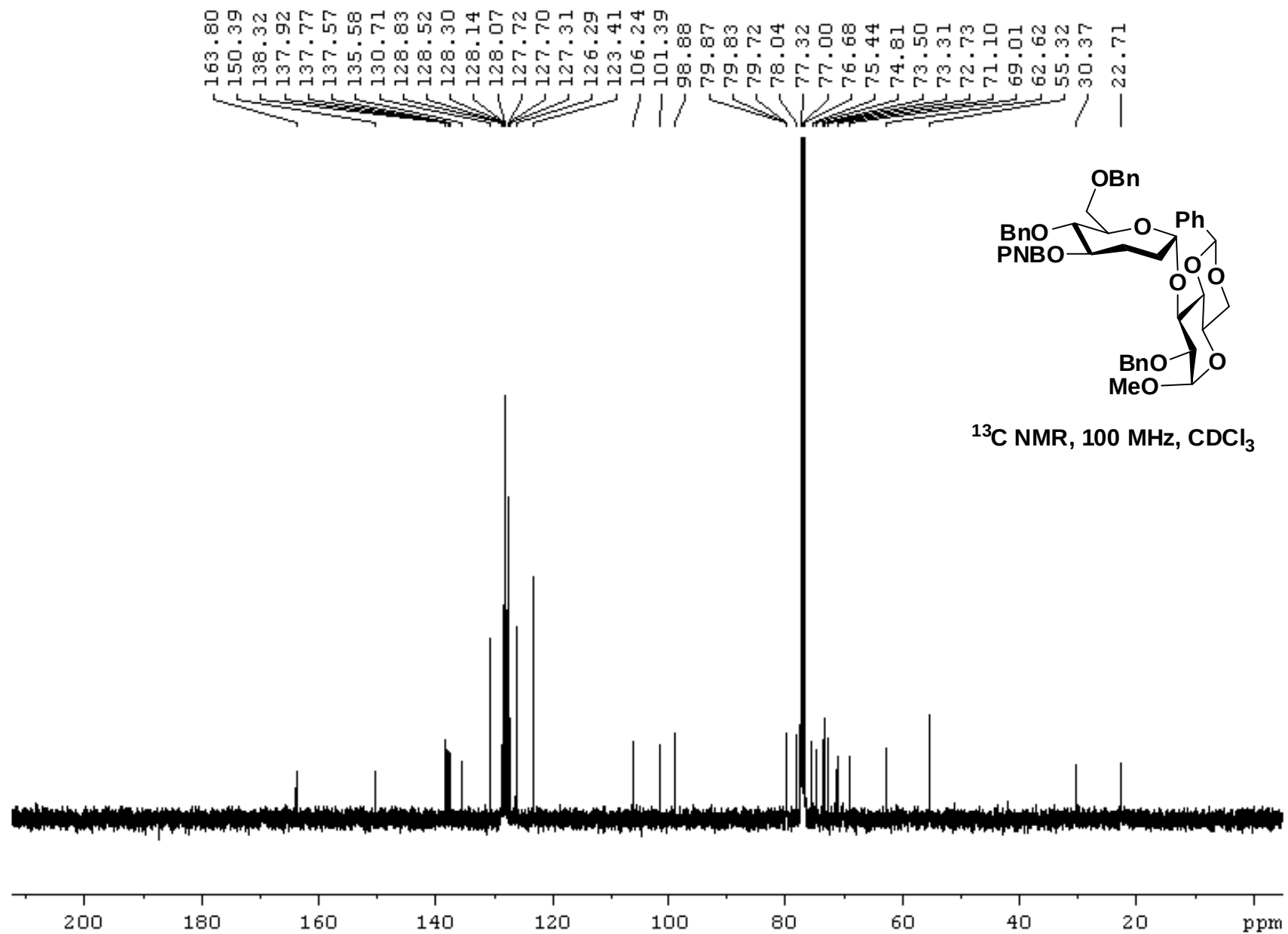
^1H - ^1H COSY NMR, 400 MHz, CDCl_3

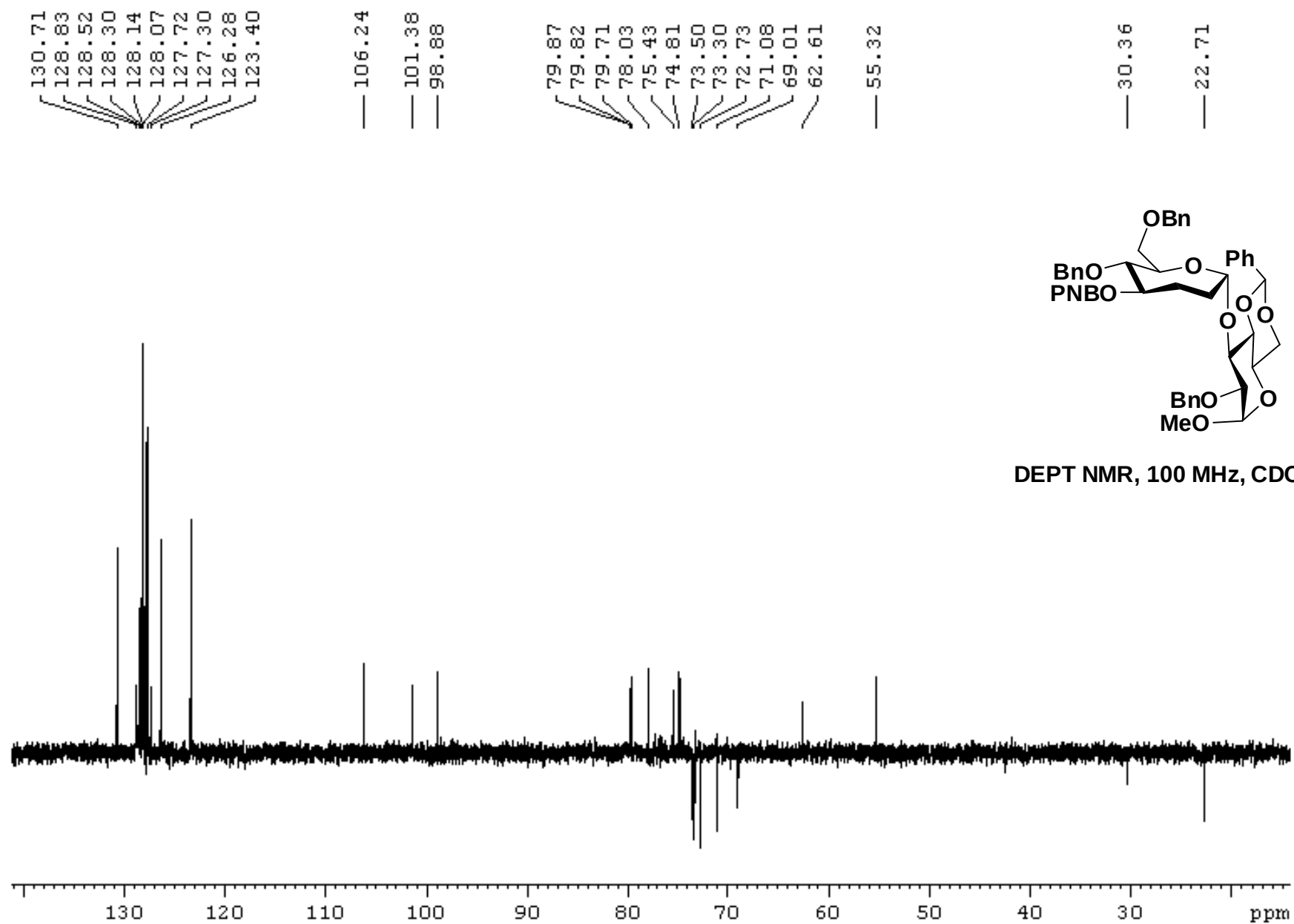


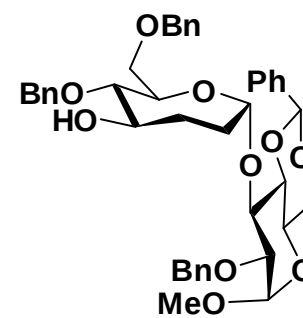
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^1H - ^1H NOESY NMR, 400 MHz, CDCl_3



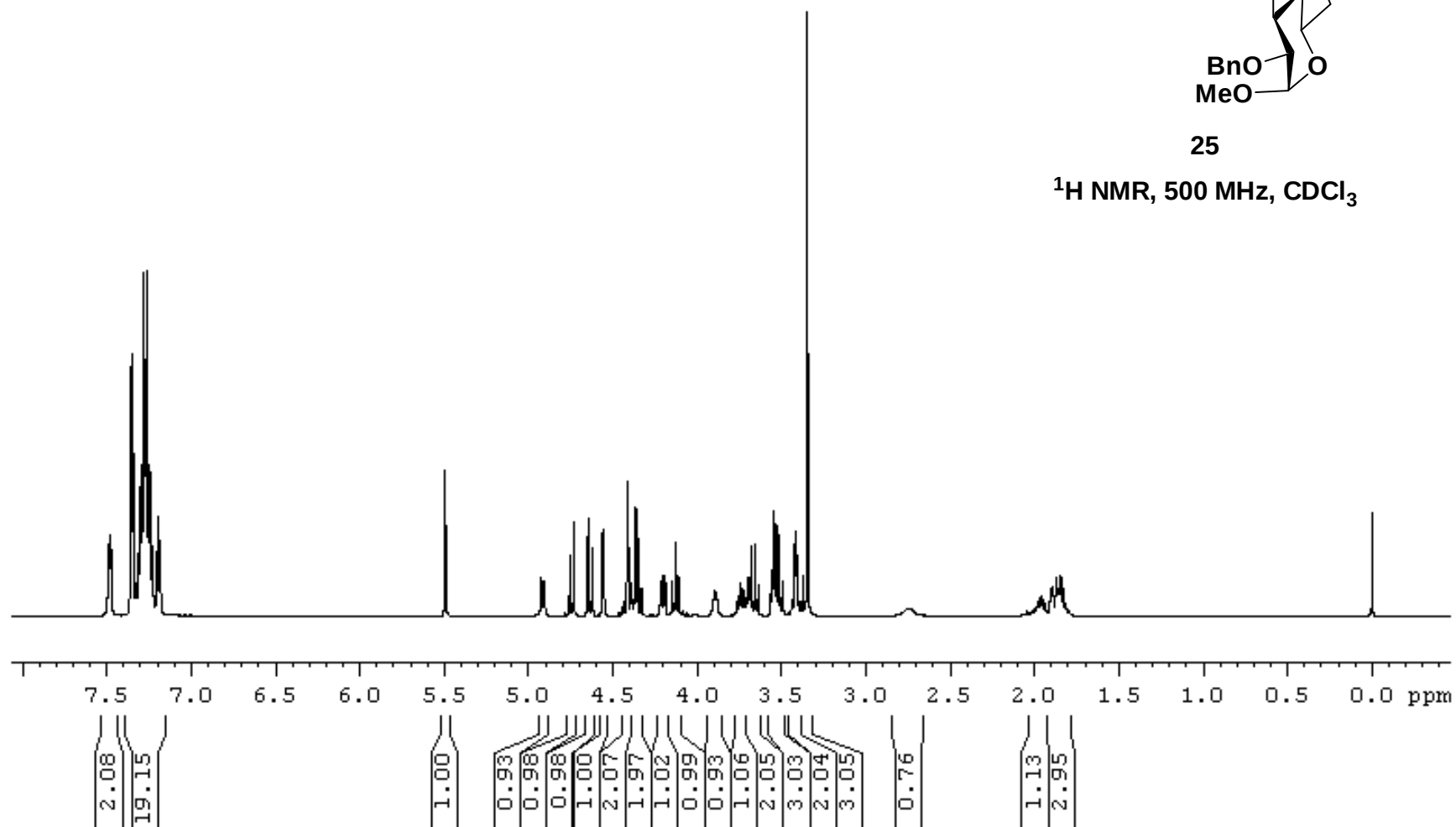


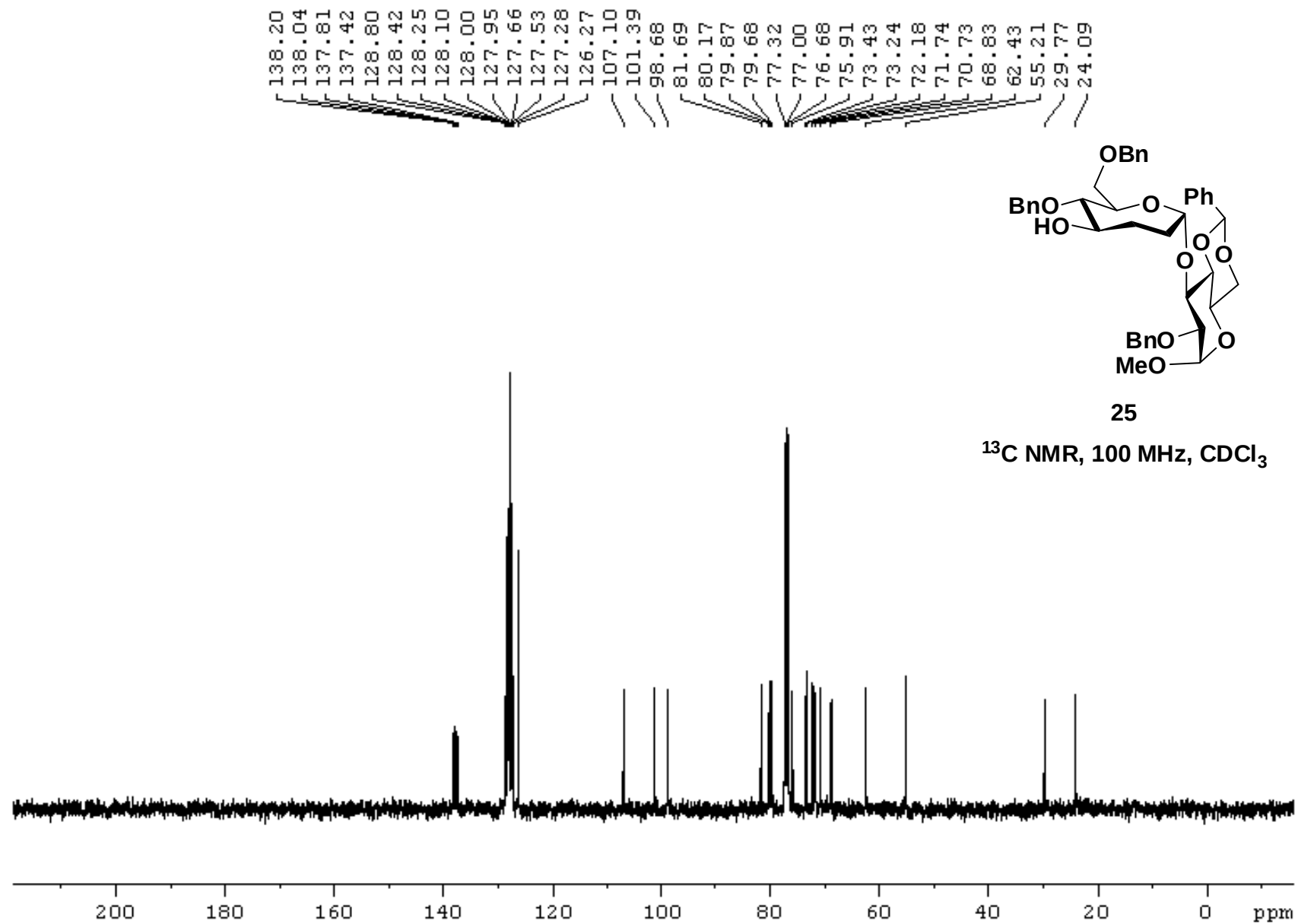


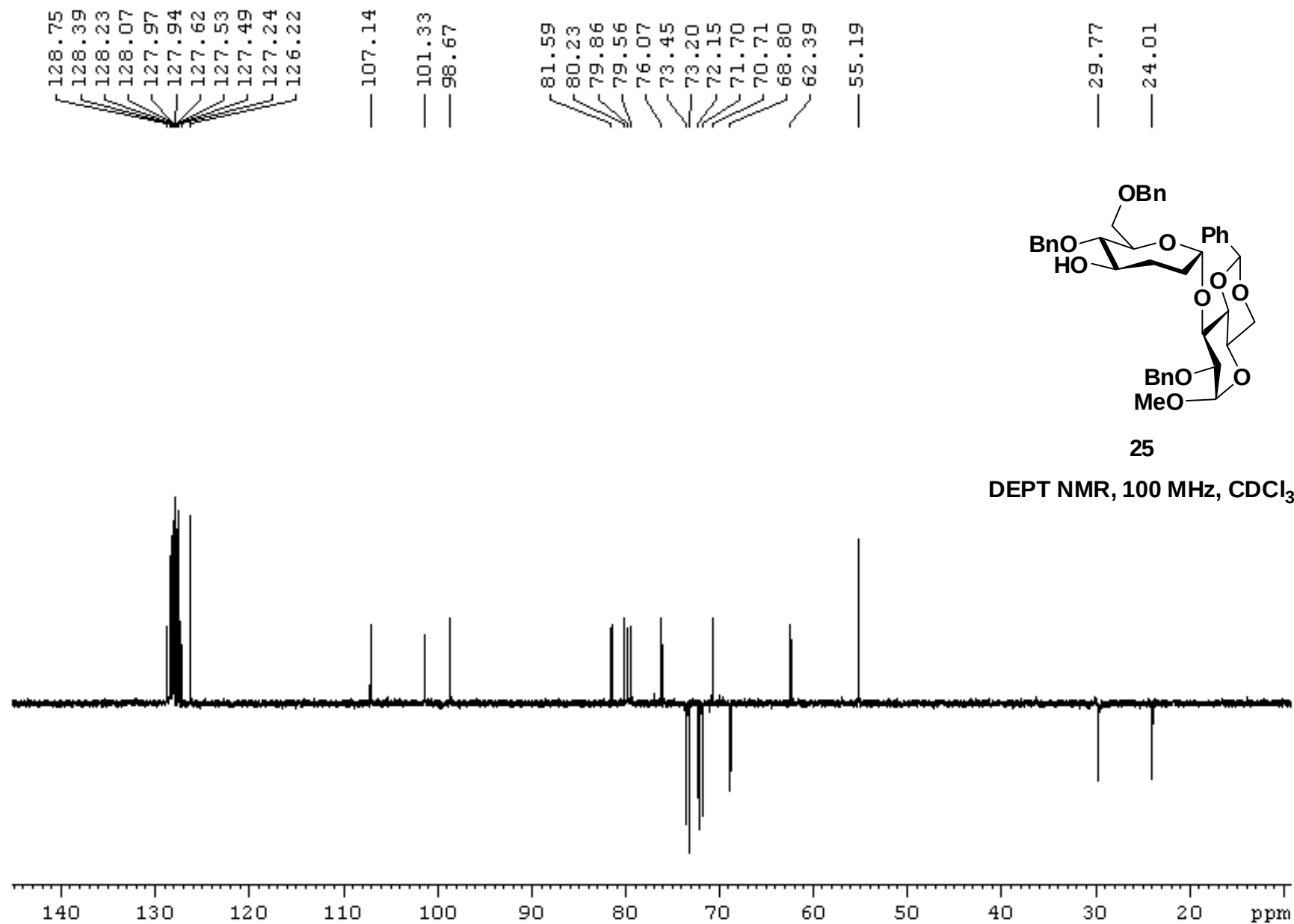


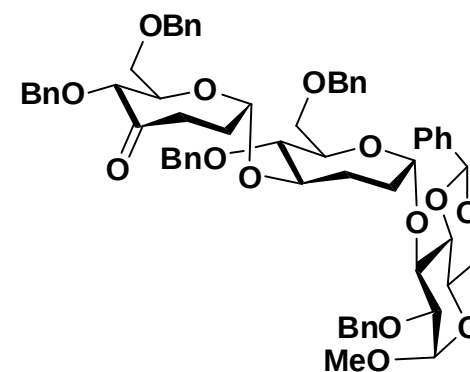
25

^1H NMR, 500 MHz, CDCl_3



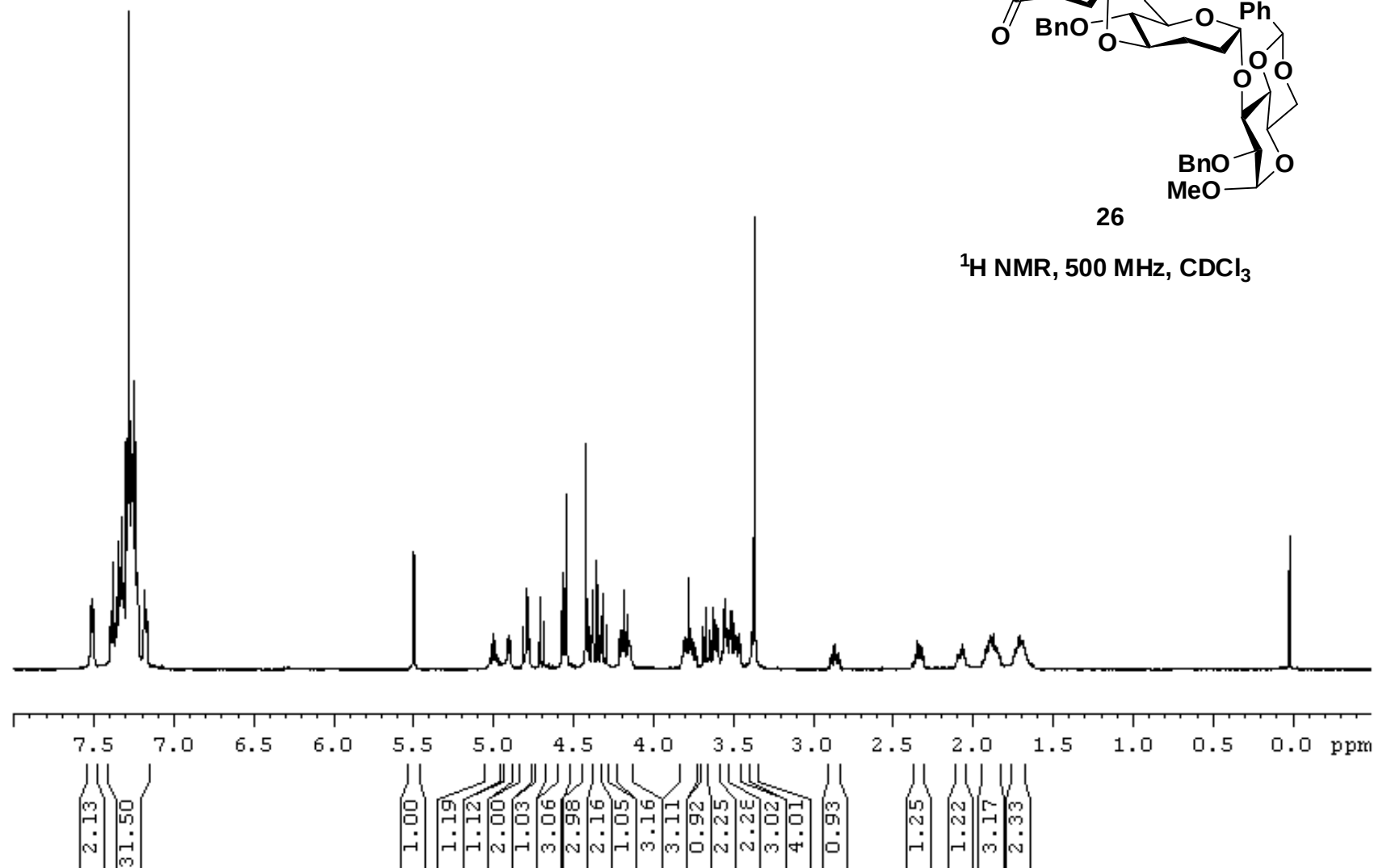


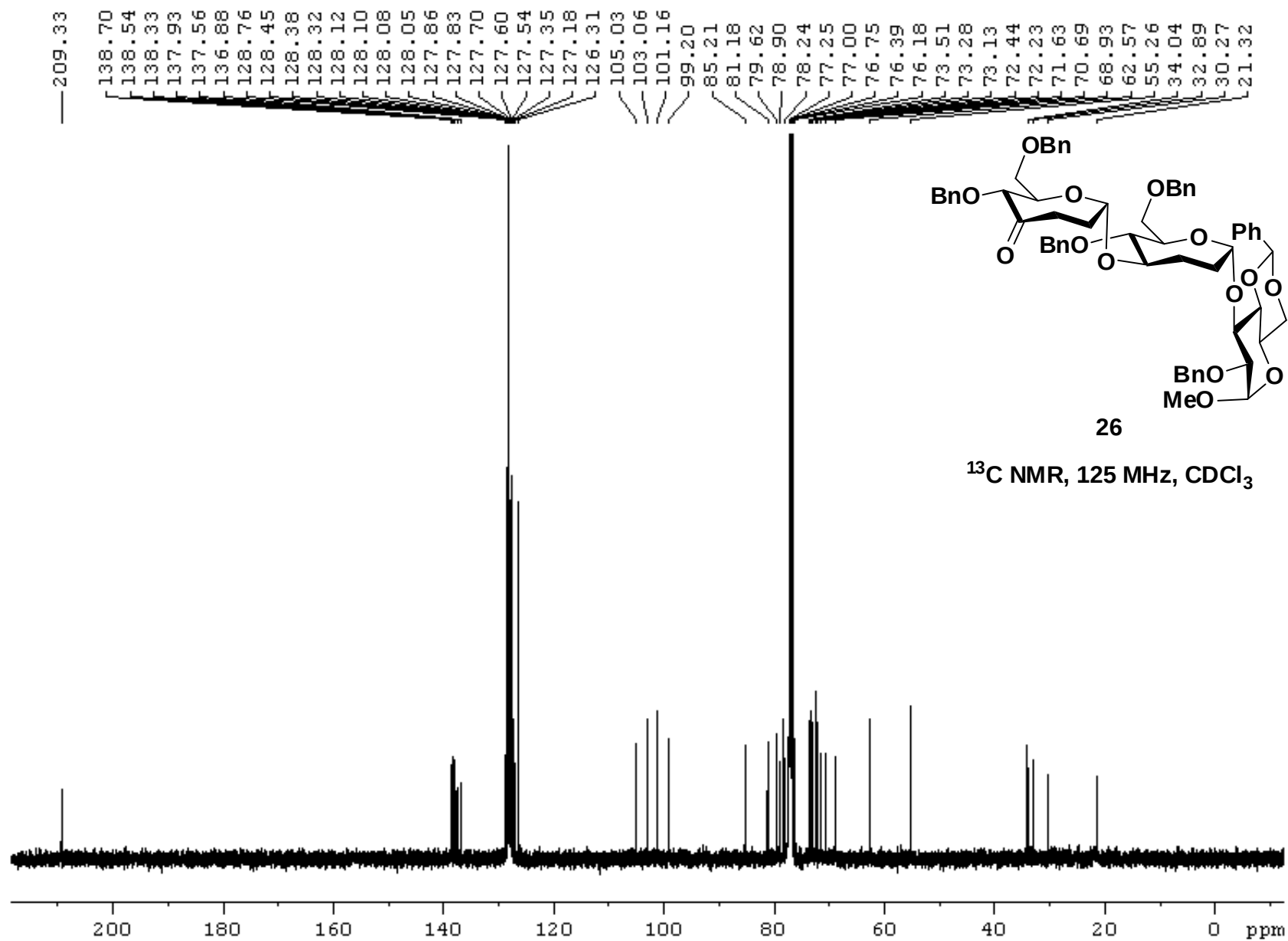


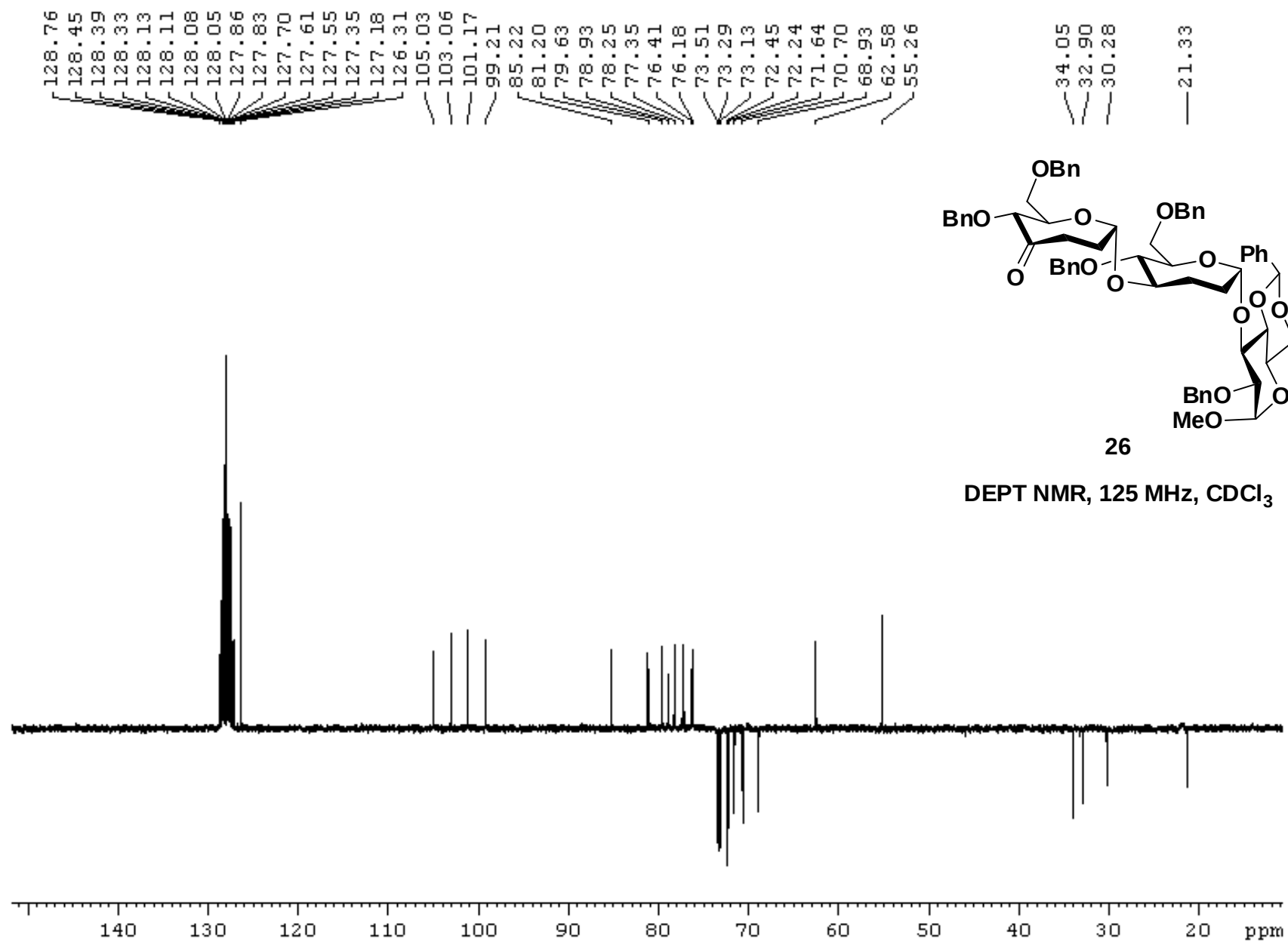


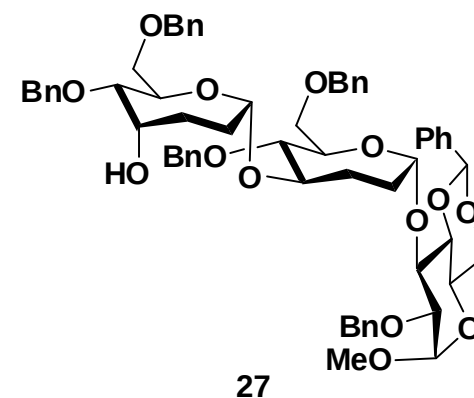
26

^1H NMR, 500 MHz, CDCl_3

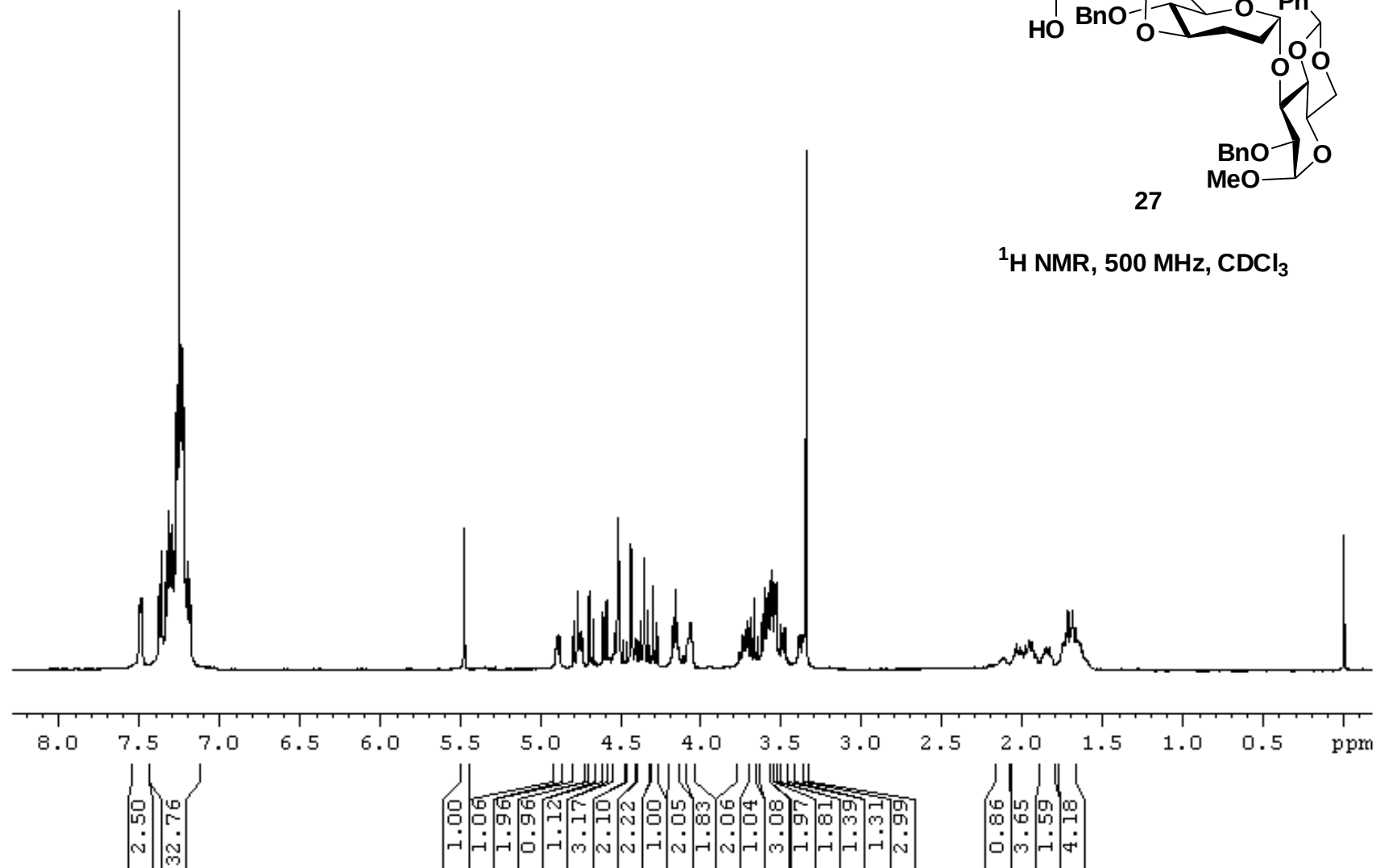


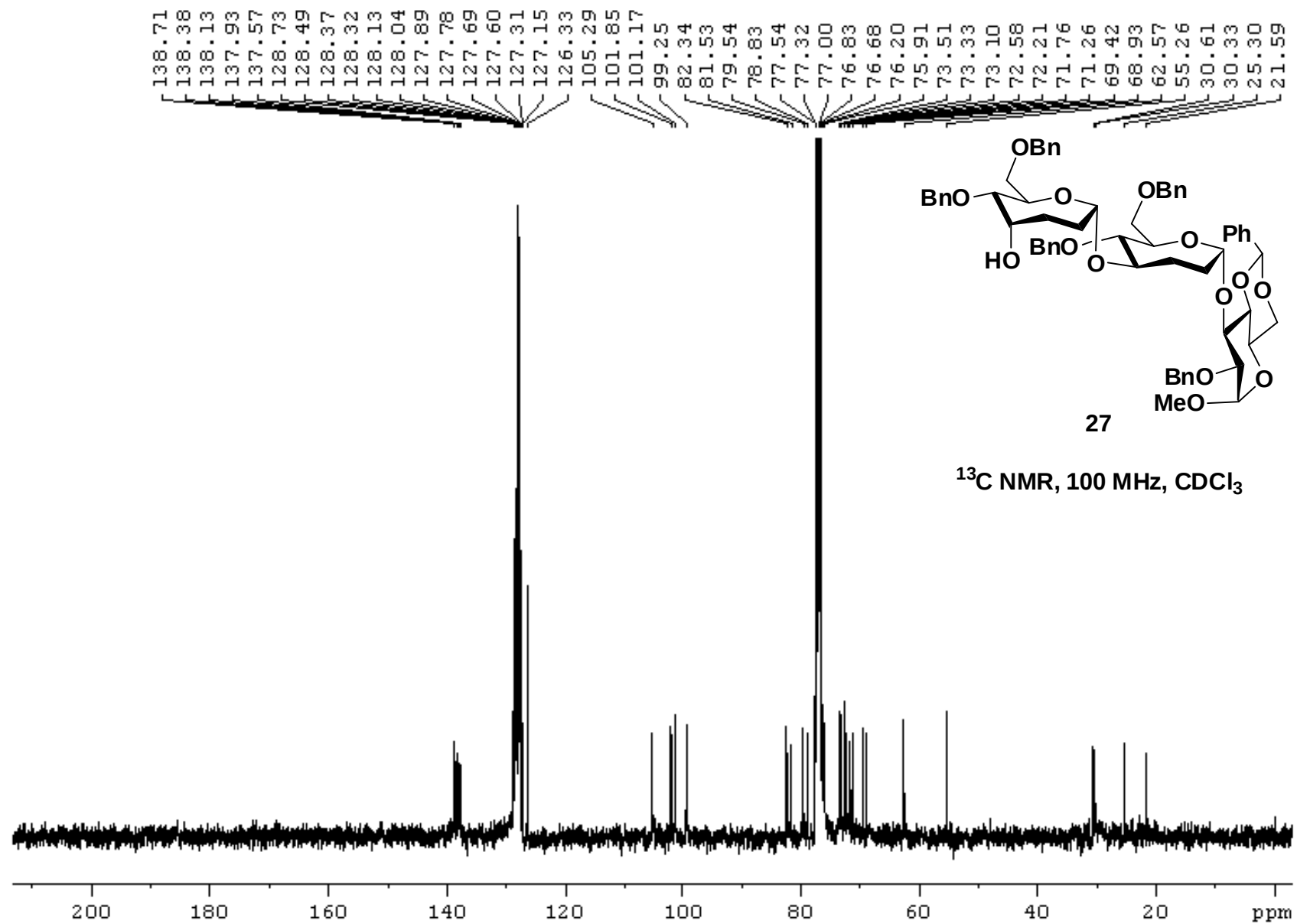


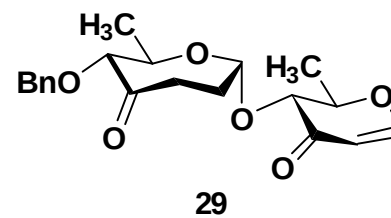




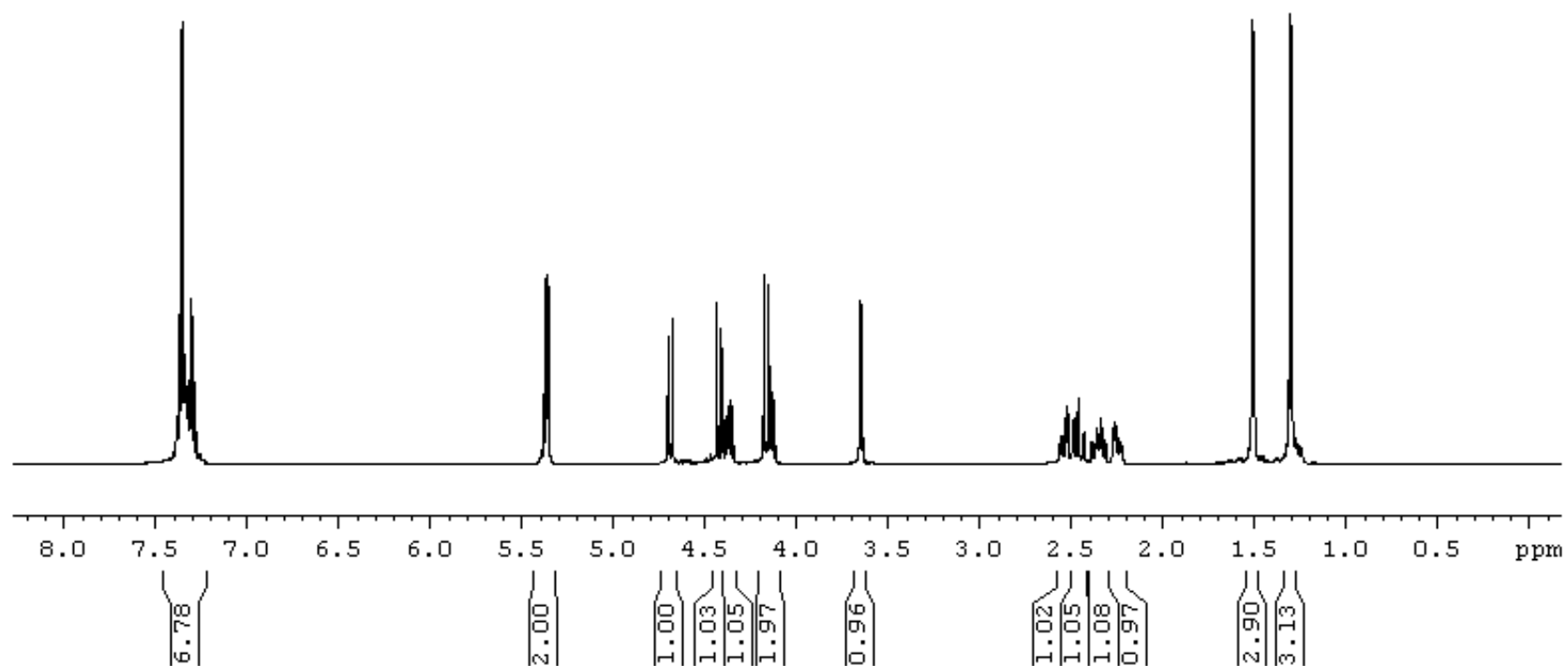
^1H NMR, 500 MHz, CDCl_3

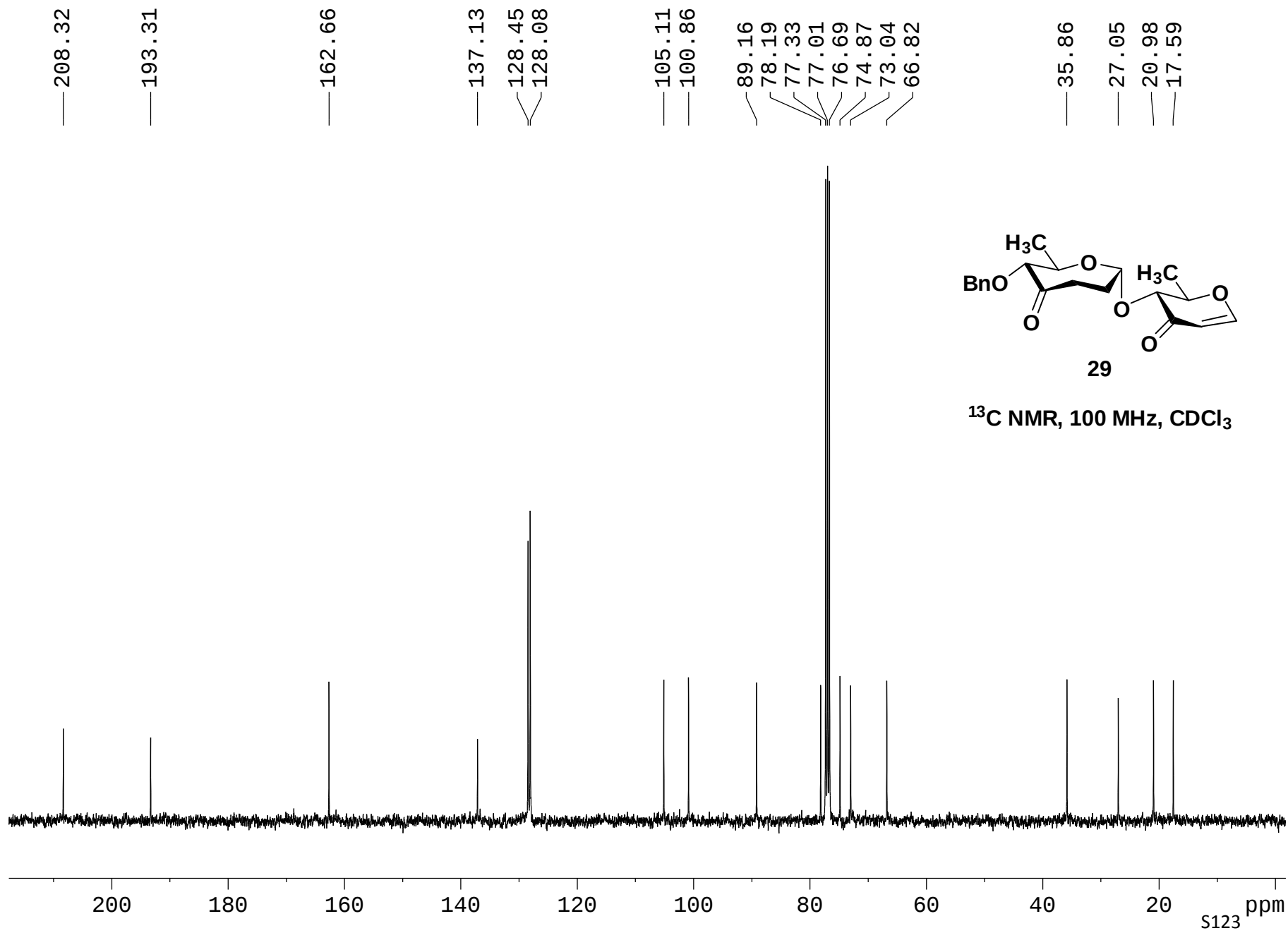


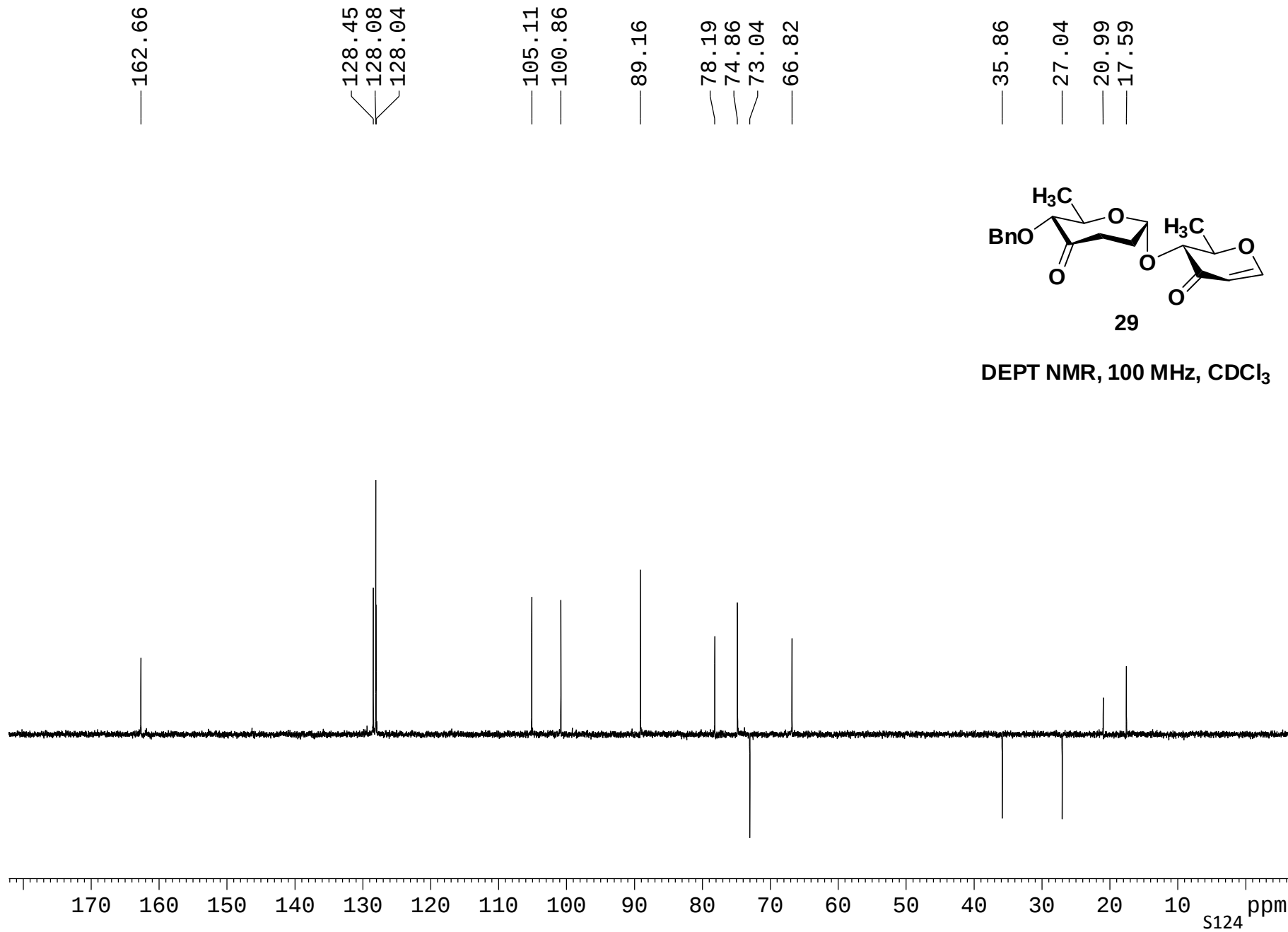


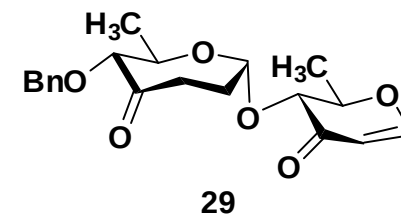
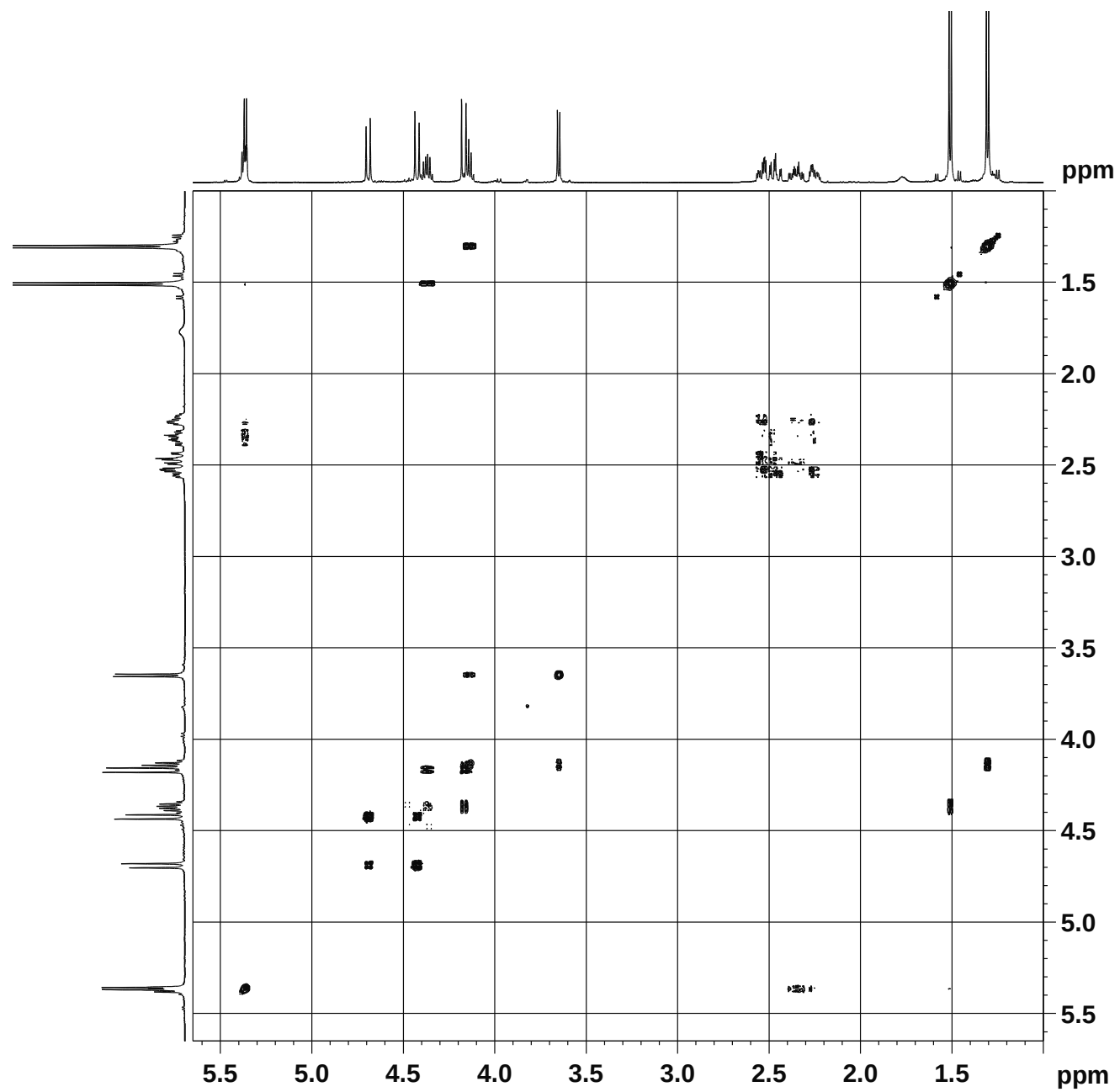


^1H NMR, 500 MHz, CDCl_3

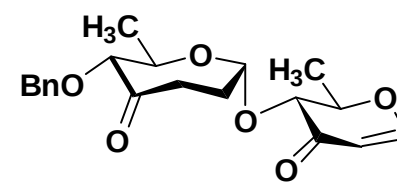
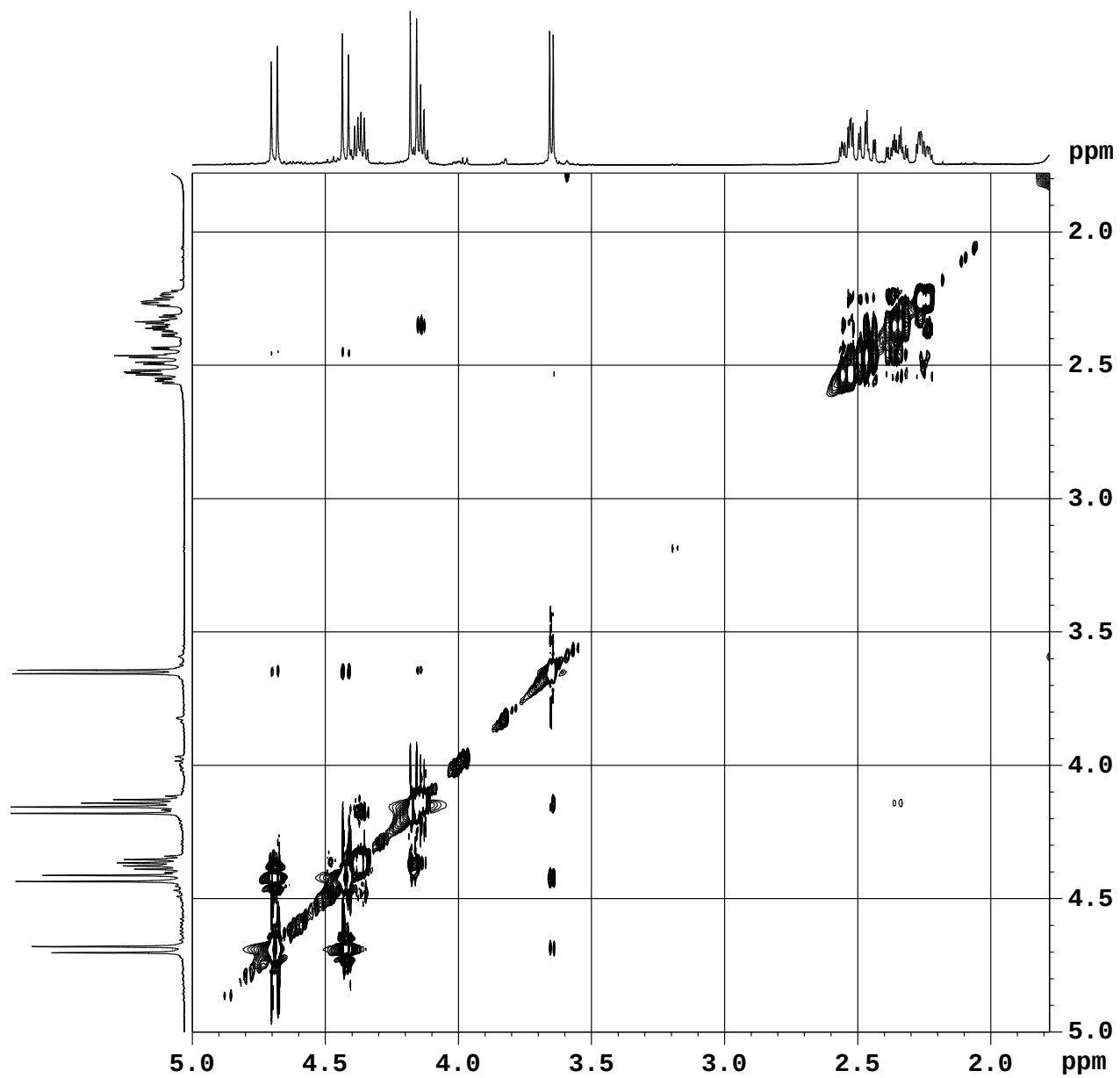






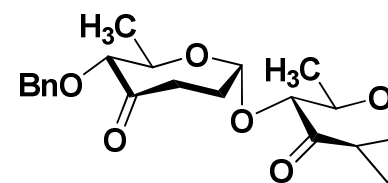


^1H - ^1H COSY NMR, 500 MHz, CDCl_3



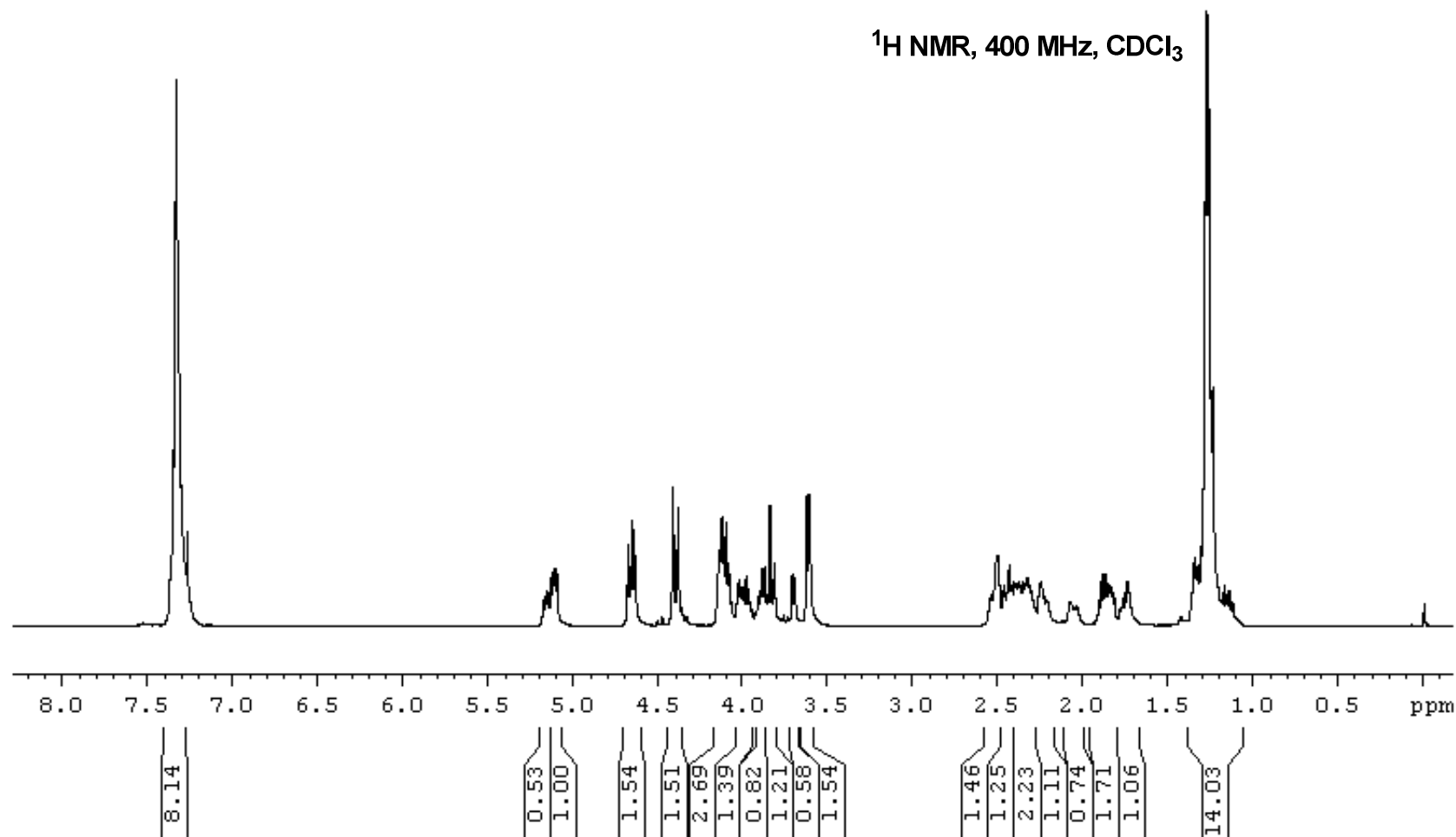
29

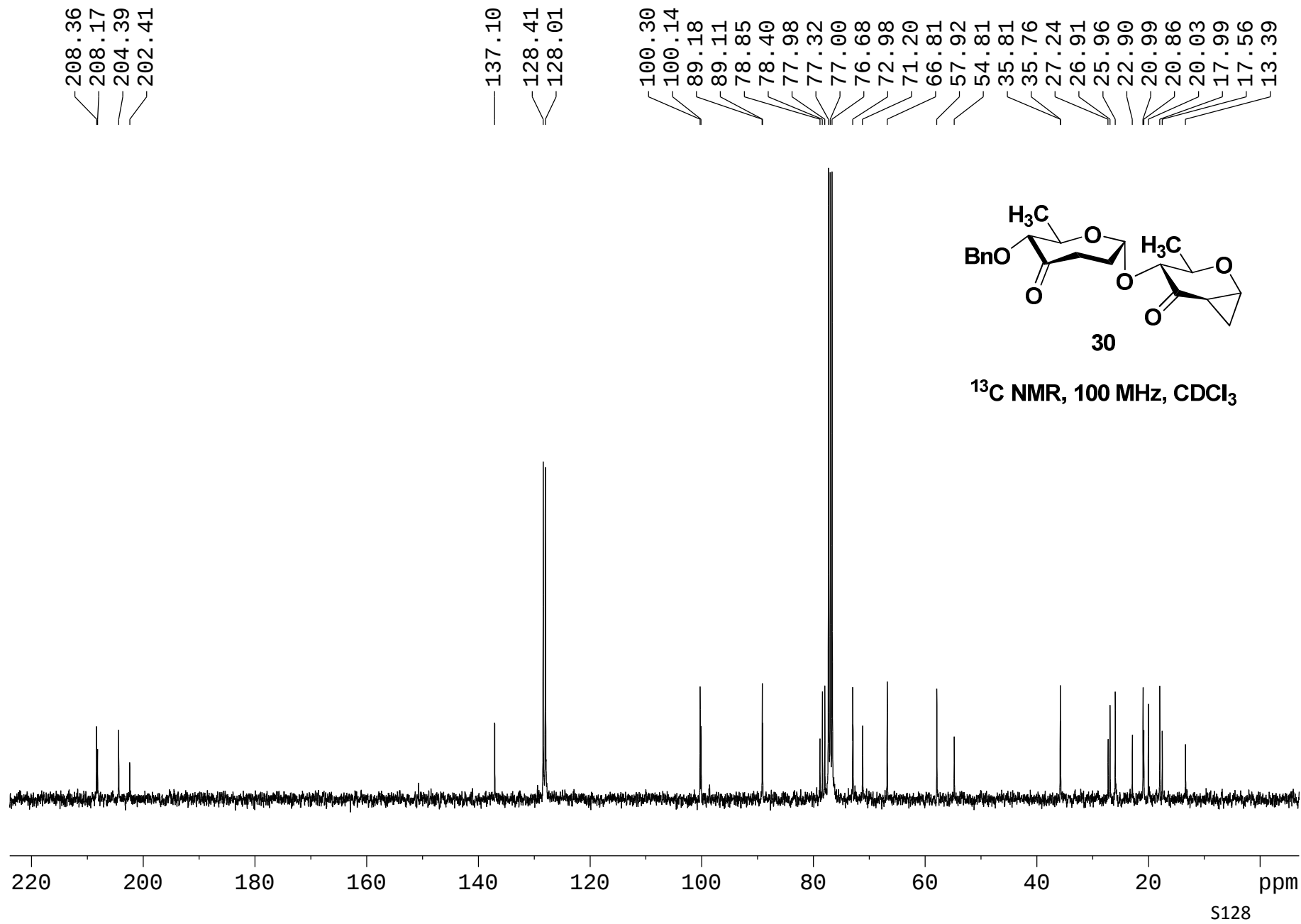
^1H - ^1H NOESY NMR, 500 MHz, CDCl_3

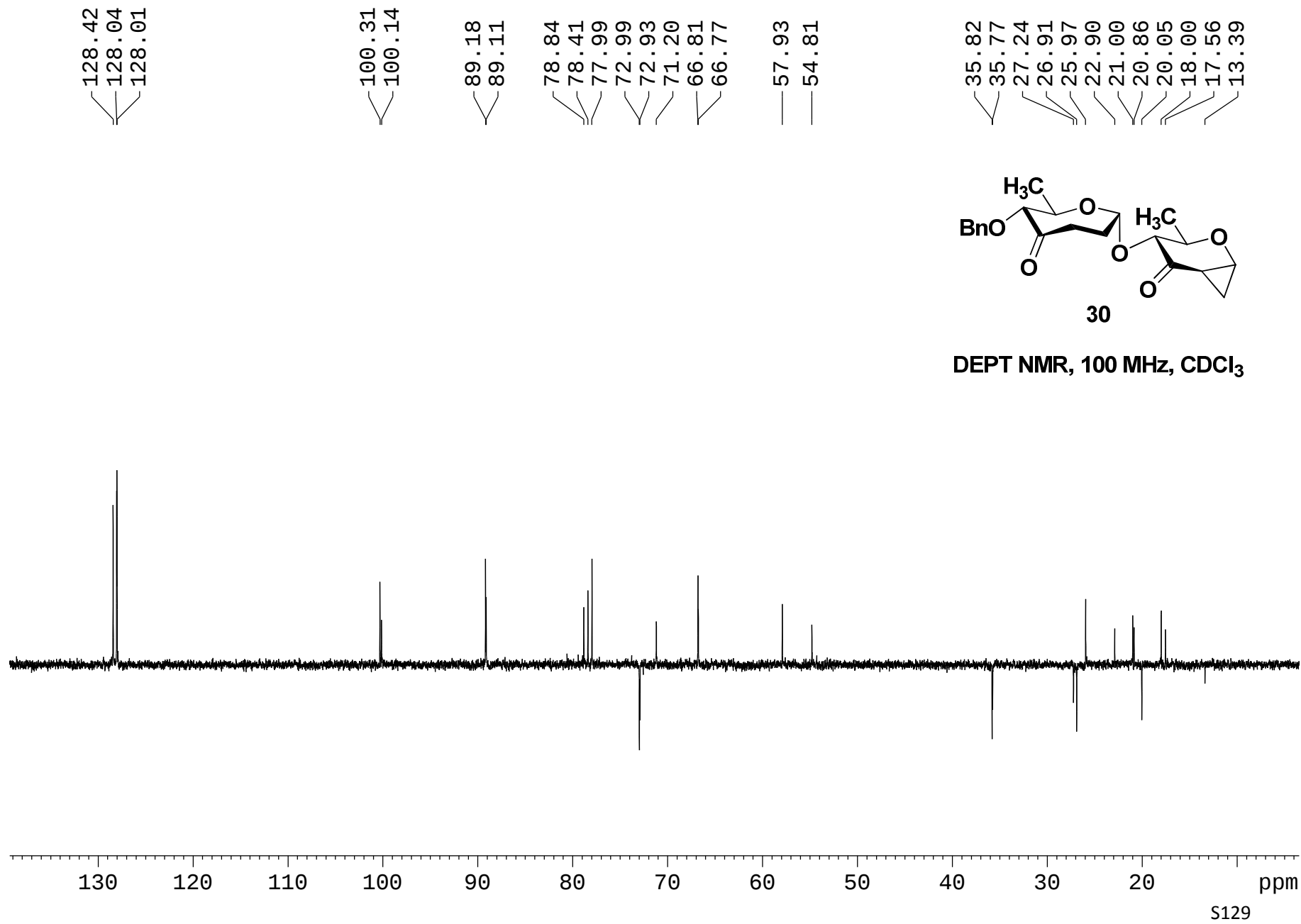


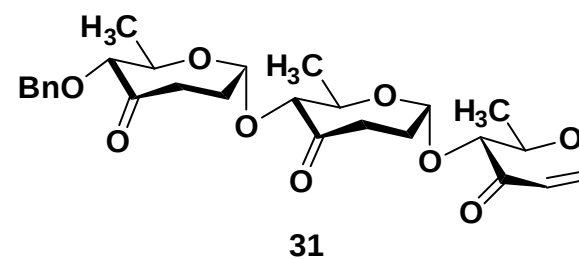
30

^1H NMR, 400 MHz, CDCl_3

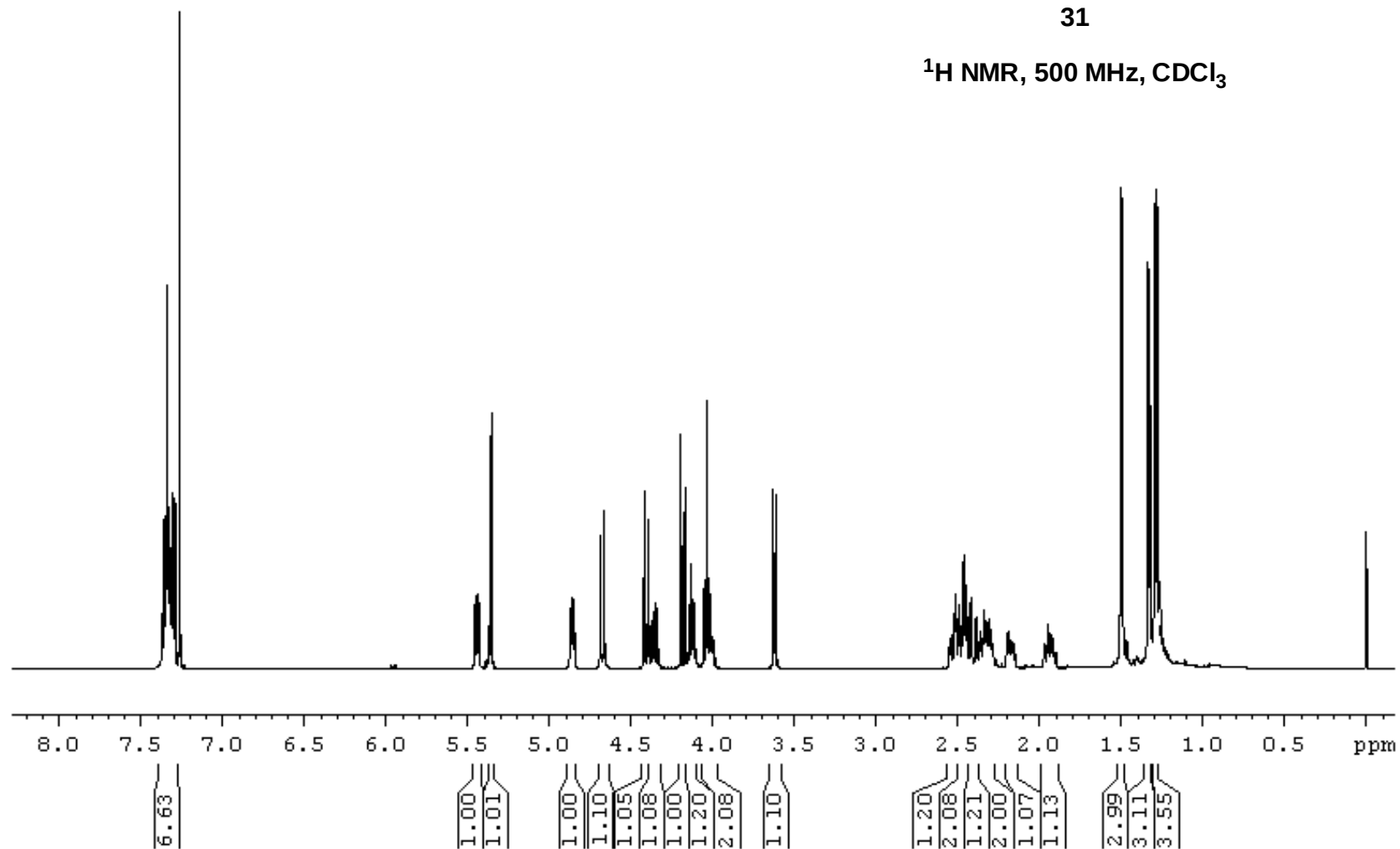


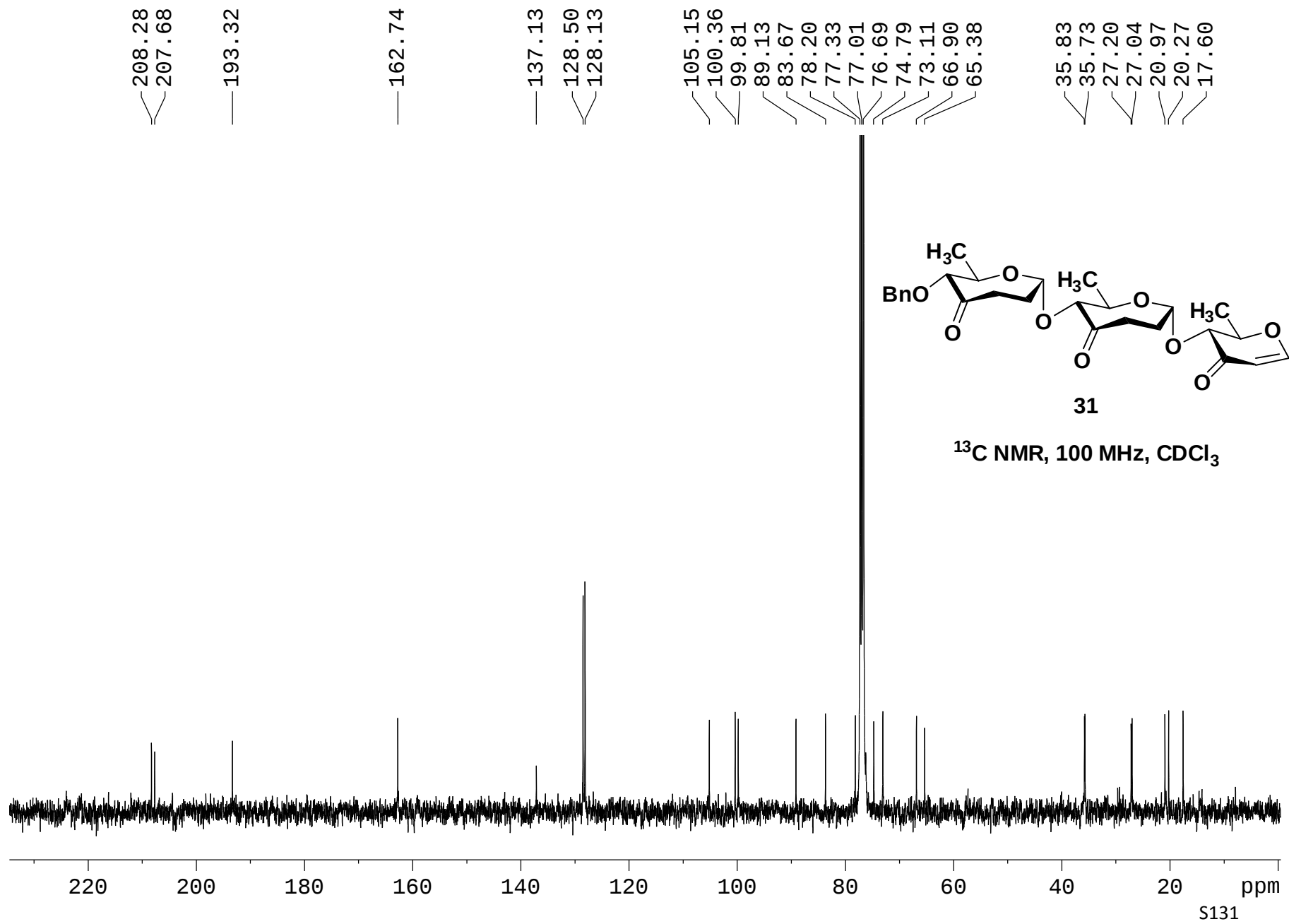


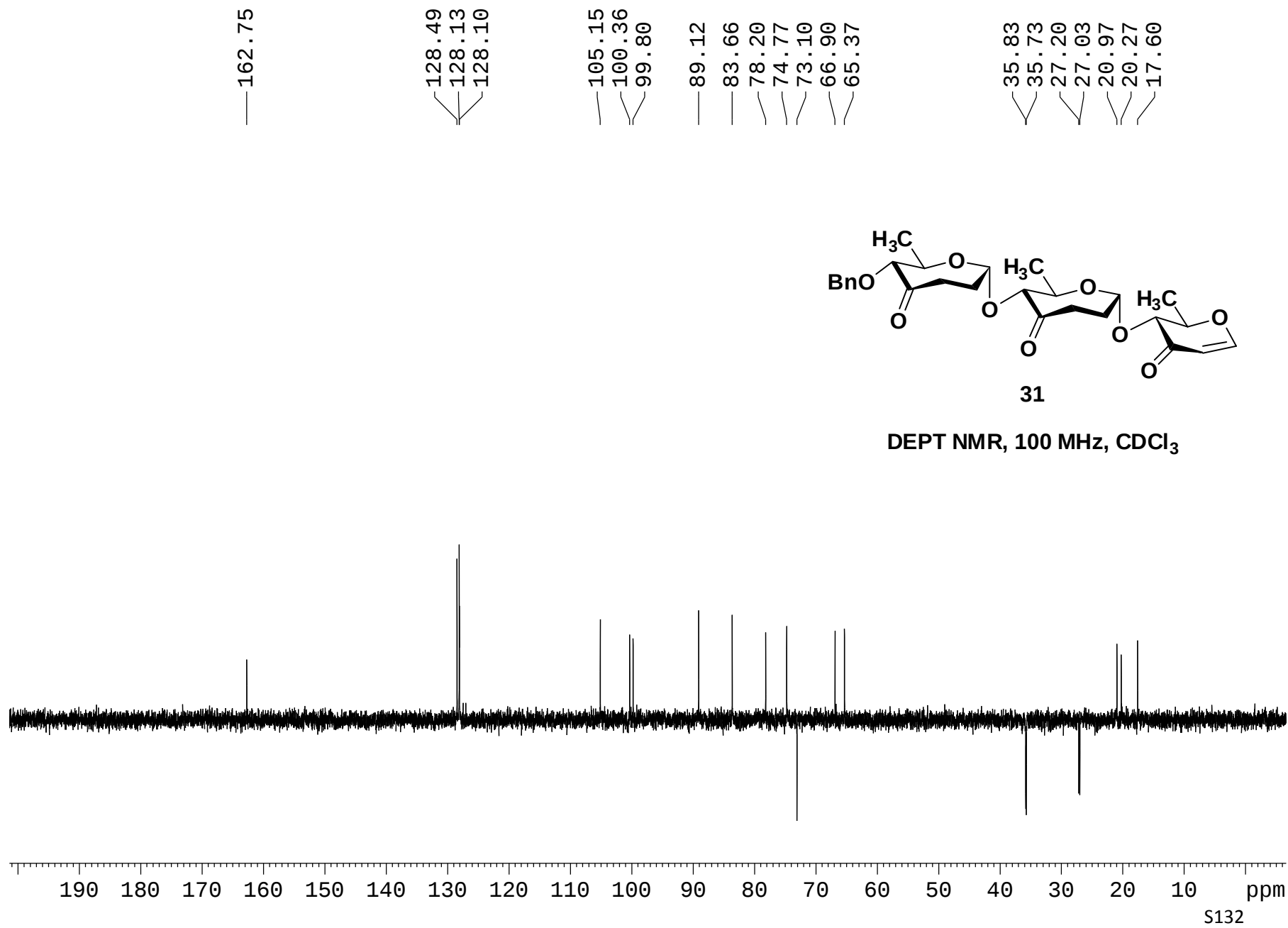


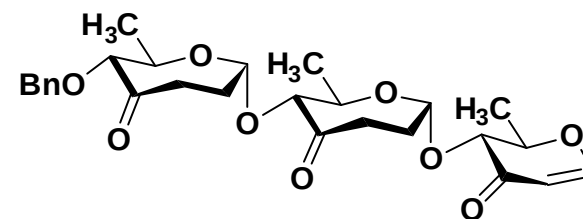
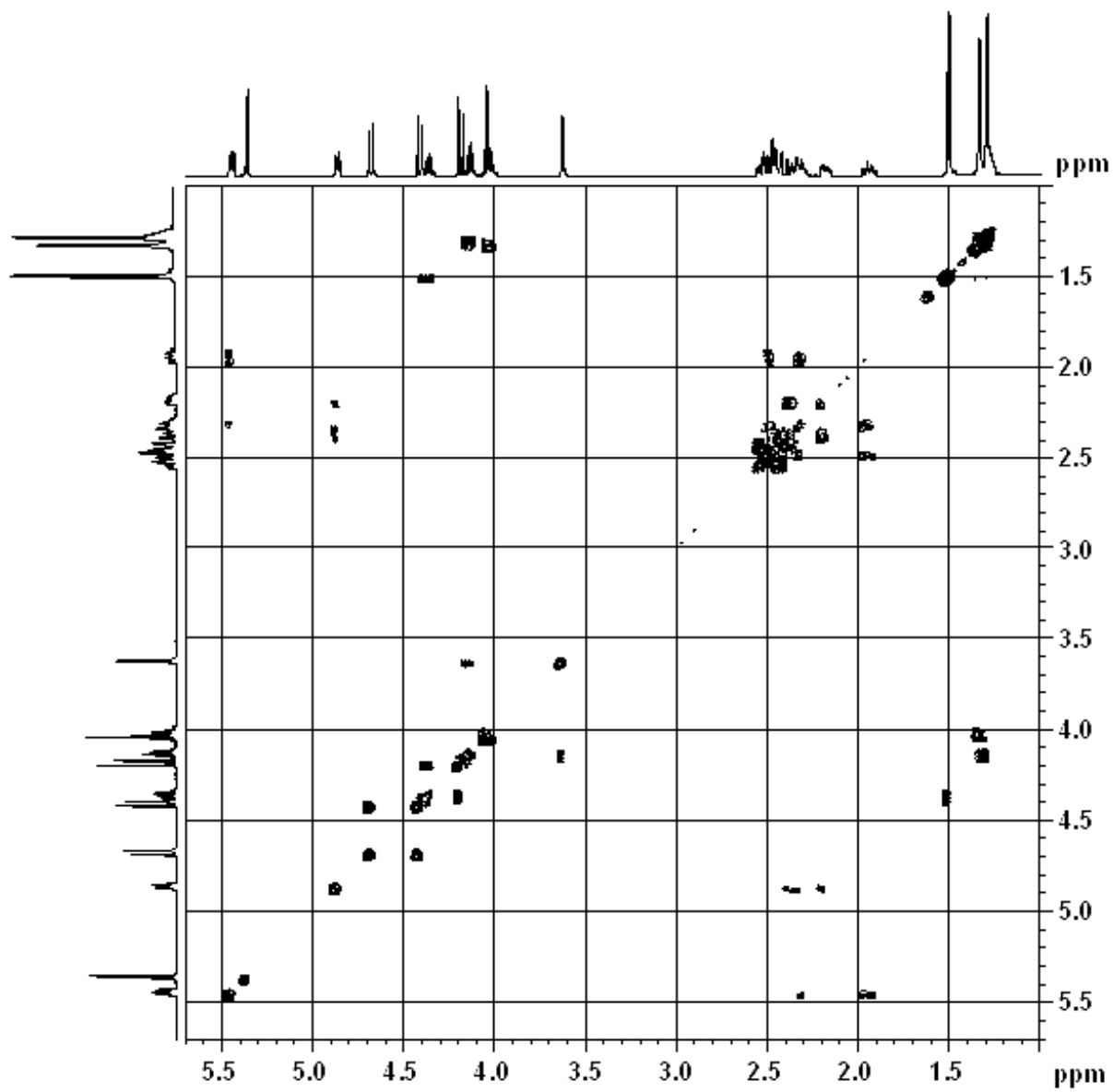


^1H NMR, 500 MHz, CDCl_3



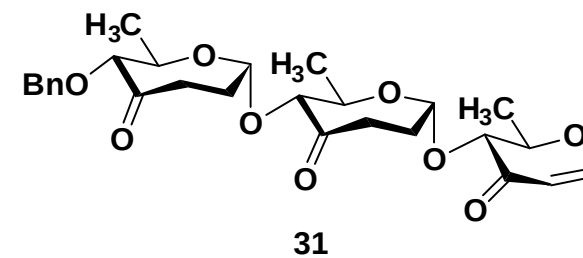
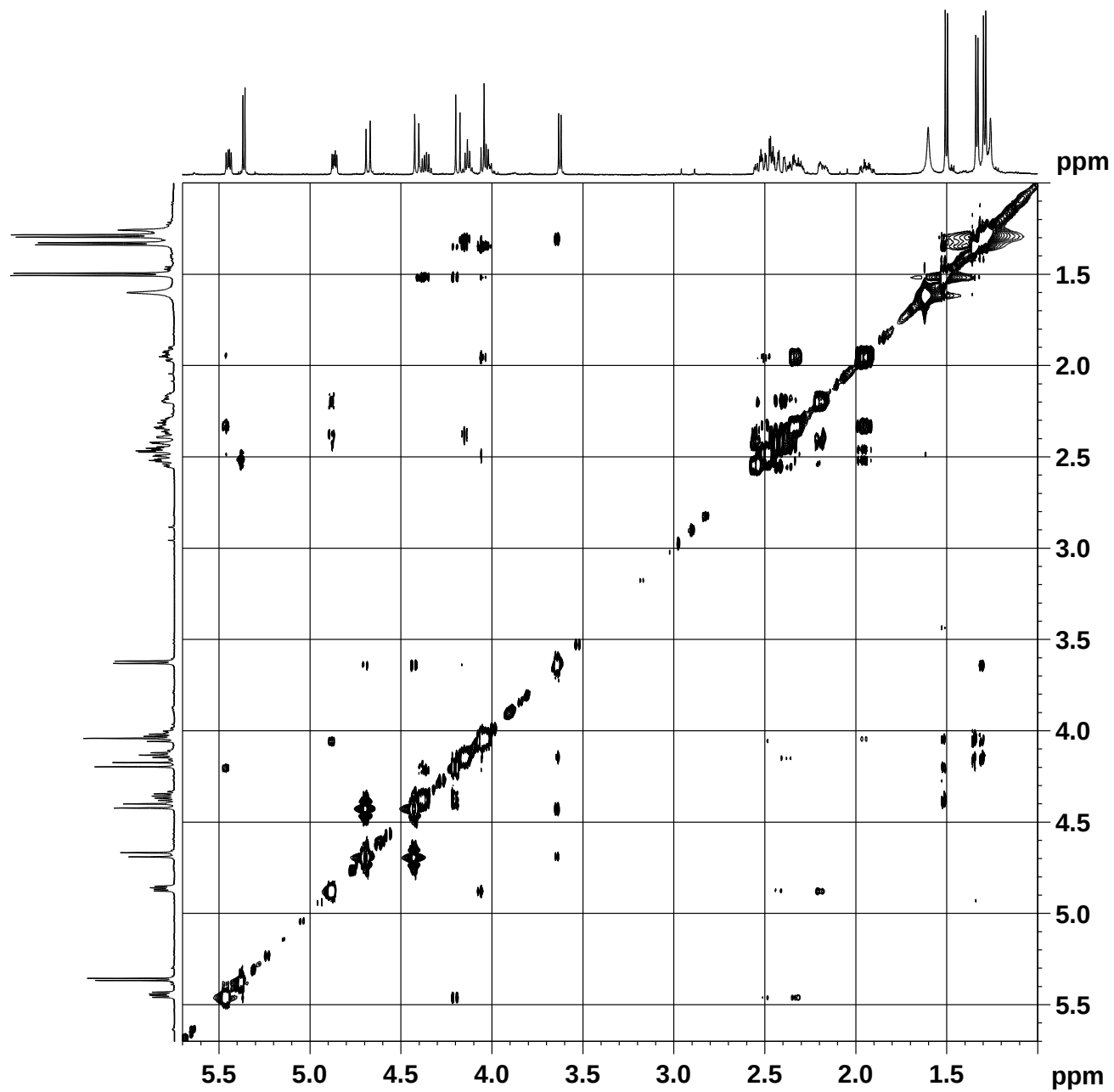






31

^1H - ^1H COSY NMR, 500 MHz, CDCl_3



^1H - ^1H NOESY NMR, 500 MHz, CDCl_3

