Electronic Supplementary Material (ESI) for Chemical Communications

A one-pot septanoside formation and glycosylation of acyclic dithioacetals derived from 1,2-cyclopropanated sugars

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1. General materials and methods

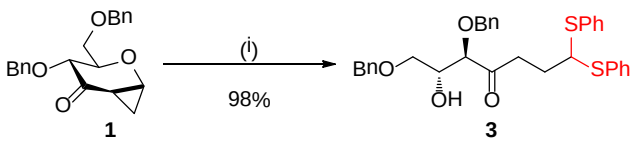
Chemicals and solvents were purchased from the local suppliers and Sigma-Aldrich® chemical company. Solvents were used in the reactions after distilled over the dehydrated agents. 4 Å Molecular sieves were used in the reactions after crushed and activated at 400 ^{o}C for 1 h. All the reactions were carried out under N_2 or Ar conditions and monitored by the thin layer chromatography (TLC) using silica-gel on aluminum plates (GF_{254}) by charring with 5% (v/v) H_2SO_4 in methanol or by phosphomolybdic acid (PMA) stain or by ultra violet (UV) detection. Silica-gel (100-200 mesh) was used for column chromatography to purify the all the compounds. ^{1}H, ^{13}C, DEPT spectra were recorded on Bruker® 400 MHz and 500 MHz spectrometers in $CDCl_3$. ^{1}H NMR chemical shifts were reported in parts per million (ppm) (δ) with TMS as internal standard (δ 0.00) and ^{13}C NMR were reported in chemical shifts with solvent reference ($CDCl_3$, δ 77.00). High resolution mass spectra (HRMS) were recorded on Bruker® maXis spectrometer.

2. Experimental Procedures and Spectral data

(2.1) General procedure (A): Synthesis of dithio-acetal derivatives from sugar-derived 1,2-cyclopropa-3-nones:

Thioalcohol (RSH) (0.66 mmol) and trimethylsilyl trifluoromethanesulfonate (TMSOTf) (0.06 mmol) were added to the stirred solution of sugar-derived 1,2-cyclopropa-3-pyranone (0.3 mmol) in CH_2Cl_2 (5 mL) at –10 ^{o}C. The reaction mixture was stirred for 30 min and quenched with the saturated $NaHCO_3$ solution (15 mL) at same temperature. Then, the solution was warmed to room temperature and extracted with CH_2Cl_2 (15 mL X 2). The combined organic layers were washed with water (10 mL), brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulted crude product was purified by silica-gel column chromatography (ethyl acetate/hexane) to afford pure dithio-acetal derivative.

(2.2) (5*R*,6*R*)-5,7-bis(benzyloxy)-6-hydroxy-1,1-bis(phenylthio)heptan-4-one (3):

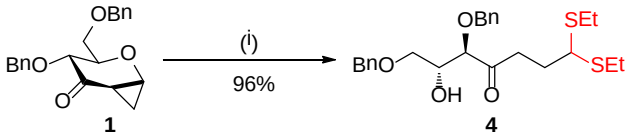


1 **3**

Reagents and Conditions: (i) PhSH, TMSOTf, CH_2Cl_2, -10 ^{o}C, 30 min.

The compound **3** was synthesized by following the general procedure **(A)** with D-glucose-derived 1,2-cyclopropa-3-pyranone **1** (100 mg, 0.295 mmol), PhSH (66.7 µL, 0.649 mmol) and TMSOTf (10.6 µL, 0.059 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min at –10 ^oC. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:3) to give the compound **3** (161 mg, 98% yield) as a thick gum. R_f = 0.67 (3:7 ethyl acetate/hexane). **IR (neat):** ν_{max}/cm^{-1} 3463, 3057, 3030, 2915, 2854, 1715, 1578, 1473, 1435, 1358, 1090, 1030, 739, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si)**: 7.42 – 7.46 (4H, m), 7.22 – 7.34 (16H, m), 4.54 – 4.57 (1H, d, *J* = 11.6 Hz), 4.41 – 4.50 (4H, m), 4.04 (1H, s), 3.87 – 3.89 (1H, d, *J* = 6.4 Hz), 3.55 – 3.59 (2H, dd, *J* = 10 Hz, *J* = 5.6 Hz), 2.90 – 2.95 (2H, m), 2.57 (1H, s), 2.07 – 2.13 (2H, m). **δ_C(100 MHz, $CDCl_3$):** 210.2, 137.5, 136.9, 133.7, 132.6, 132.5, 128.8, 128.4, 128.3, 128.0, 127.7, 127.6, 84.1, 73.3, 73.1, 71.0, 69.9, 57.1, 36.4, 28.9. **HRMS (ESI)** calcd for $C_{33}H_{34}O_4S_2$+H 559.1977, found 559.1976.

(2.3) (5*R*,6*R*)-5,7-bis(benzyloxy)-1,1-bis(ethylthio)-6-hydroxyheptan-4-one (4):

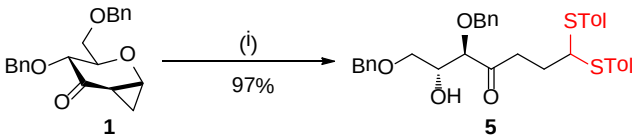


Reagents and Conditions: (i) EtSH, TMSOTf, CH_2Cl_2, -10 ^oC, 30 min.

The compound **4** was synthesized by following the general procedure **(A)** with D-glucose-derived 1,2-cyclopropa-3-pyranone **1** (110 mg, 0.325 mmol), EtSH (51.6 µL, 0.715 mmol) and TMSOTf (11.7 µL, 0.065 mmol) in CH_2Cl_2 (6 mL). The reaction mixture was stirred for 30 min at –10 ^oC. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:3) to provide compound **4** (144 mg, 96% yield) as a thick gum. R_f = 0.58 (3:7 ethyl acetate/hexane). **IR (neat):** ν_{max}/cm^{-1} 3446, 3090, 3057, 3024, 2969, 2926, 2860, 1715, 1495, 1452, 1402, 1364, 1265, 1210, 1095, 1030, 734, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si)**: 7.18 – 7.26 (10H, m), 4.53 – 4.56 (1H, d, *J* = 11.6 Hz), 4.44 – 4.47 (1H, d, *J* = 11.6 Hz), 4.37 – 4.41 (2H, dd, *J* = 11.6 Hz, *J* = 5.2 Hz), 3.97 – 4.01 (1H, dd, *J* = 10 Hz, *J* = 5.2 Hz), 3.84 – 3.86 (1H, d, *J* = 6.4 Hz), 3.71 – 3.75 (1H, dd, *J* = 7.2 Hz, *J* = 6.8 Hz), 3.48 – 3.55 (2H, m), 2.70 – 2.86 (2H, m), 2.44 – 2.63 (4H, m), 2.29 (1H, s), 1.95 – 2.00 (2H, dd, *J* = 13.6 Hz, *J* = 7.2 Hz), 1.14 – 1.18 (6H, m). **δ_C(100 MHz, $CDCl_3$):** 210.4, 137.6, 137.0, 128.5, 128.4, 128.1, 127.8, 84.1, 73.3,

73.1, 71.0, 70.0, 50.3, 36.8, 28.8, 24.1, 14.4. **HRMS (ESI)** calcd for $C_{25}H_{34}O_4S_2$+H 463.1977, found 463.1979.

(2.4) (5*R*,6*R*)-5,7-bis(benzyloxy)-6-hydroxy-1,1-bis(*p*-tolylthio)heptan-4-one (5):

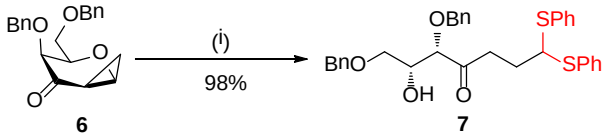


1 5

Reagents and Conditions: (i) EtSH, TMSOTf, CH_2Cl_2, -10 °C, 30 min.

The compound **5** was synthesized by following the general procedure **(A)** with D-glucose-derived 1,2-cyclopropa-3-pyranone **1** (92 mg, 0.271 mmol), toluene-4-thiol (74 mg, 0.598 mmol) and TMSOTf (9.8 µL, 0.054 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min at –10 °C. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:3) to provide compound **5** (154 mg, 97% yield) as thick gum. R_f = 0.63 (3:7 ethyl acetate/hexane). **IR (neat)**: ν_{max}/cm^{-1} 3463, 3063, 3030, 2915, 2854, 1715, 1495, 1452, 1391, 1364, 1210, 1084, 805, 745, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si)**: 7.26 – 7.35 (14H, m), 7.07 – 7.09 (4H, d, *J* = 7.6 Hz), 4.55 – 4.58 (1H, d, *J* = 11.2 Hz), 4.40 – 4.50 (3H, m), 4.33 – 4.36 (1H, t, *J* = 6.8 Hz), 4.02 – 4.06 (1H, dd, *J* = 10.8 Hz, *J* = 5.2 Hz), 3.87 – 3.89 (1H, d, *J* = 6.4 Hz), 3.55 – 3.57 (2H, dd, *J* = 5.2 Hz, *J* = 4.0 Hz), 2.84 – 2.99 (2H, m), 2.30 (6H, s), 2.02 – 2.08 (2H, m). **δ_C(100 MHz, $CDCl_3$):** 210.2, 137.9, 137.5, 136.9, 133.2, 129.9, 129.6, 128.4, 128.3, 128.0, 127.7, 84.1, 73.3, 73.1, 71.0, 70.0, 57.9, 36.5, 28.7, 21.1. **HRMS (ESI)** calcd for $C_{35}H_{38}O_4S_2$+H 587.2290, found 587.2289.

(2.5) (5*S*,6*R*)-5,7-bis(benzyloxy)-6-hydroxy-1,1-bis(phenylthio)heptan-4-one (7):



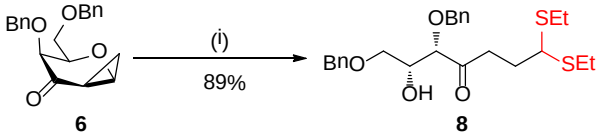
6 7

Reagents and Conditions: (i) PhSH, TMSOTf, CH_2Cl_2, -10 °C, 30 min.

The compound **7** was synthesized by following the general procedure **(A)** with D-galactose-derived 1,2-cyclopropa-3-pyranone **6** (98 mg, 0.289 mmol), PhSH (65.4 µL, 0.637 mmol) and TMSOTf (10.4 µL, 0.057 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min

at –10 °C. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:3) to give the compound **7** (158 mg, 98% yield) as a colorless oil. R_f = 0.30 (1:4 ethyl acetate/hexane). **IR (neat):** ν_{max}/cm^{-1} 3435, 3090, 3068, 3030, 2953, 2926, 2860, 1715, 1578, 1473, 1463, 1446, 1364, 1265, 1205, 1090, 1019, 734, 695. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.42 – 7.43 (4H, d, *J* = 0.8 Hz), 7.20 – 7.28 (16H, m), 4.61 – 4.64 (1H, d, *J* = 11.6 Hz), 4.38 – 4.49 (4H, m), 4.05 – 4.08 (1H, d, *J* = 10.4 Hz), 3.94 (1H, s), 3.50 – 3.54 (1H, dd, *J* = 9.6 Hz, *J* = 5.6 Hz), 3.43 – 3.47 (1H, dd, *J* = 9.2 Hz, *J* = 6.4 Hz), 2.83 – 2.99 (2H, m), 2.60 – 2.62 (1H, d, *J* = 7.2 Hz), 2.04 – 2.17 (2H, m). **δ_C(100 MHz, $CDCl_3$):** 210.7, 137.5, 136.7, 133.7, 133.6, 132.5, 132.4, 128.8, 128.4, 128.3, 128.2, 128.1, 127.7, 127.6, 83.8, 73.4, 73.2, 71.1, 70.2, 57.1, 36.8, 28.9. **HRMS (ESI)** calcd for $C_{33}H_{34}O_4S_2$+Na 581.1796, found 581.1831.

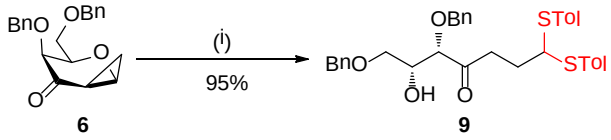
(2.6) (5*R*,6*R*)-5,7-bis(benzyloxy)-1,1-bis(ethylthio)-6-hydroxyheptan-4-one (8):



Reagents and Conditions: (i) EtSH, TMSOTf, CH_2Cl_2, -10 °C, 30 min.

The compound **8** was synthesized by following the general procedure **(A)** with D-galactose-derived 1,2-cyclopropa-3-pyranone **6** (92 mg, 0.271 mmol), EtSH (43.1 µL, 0.598 mmol) and TMSOTf (9.8 µL, 0.054 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min at –10 °C. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:3) to give compound **8** (111 mg, 89% yield) as a colorless oil. R_f = 0.31 (1:4 ethyl acetate/hexane). **IR (neat):** ν_{max}/cm^{-1} 3463, 3063, 3030, 2958, 2920, 2860, 1715, 1457, 1391, 1358, 1265, 1210, 1084, 734, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.25 – 7.32 (10H, m), 4.68 – 4.71 (1H, d, *J* = 11.2 Hz), 4.43 – 4.52 (3H, m), 4.09 (1H, s), 3.99 – 4.00 (1H, d, *J* = 3.2 Hz), 3.78 – 3.81 (1H, t, *J* = 6.8 Hz), 3.54 – 3.58 (1H, dd, *J* = 9.6 Hz, *J* = 6.0 Hz), 3.47 – 3.51 (1H, dd, *J* = 8.8 Hz, *J* = 6.0 Hz), 2.75 – 2.92 (2H, m), 2.51 – 2.69 (5H, m), 1.99 – 2.12 (2H, m), 1.21 – 1.25 (6H, m). **δ_C(100 MHz, $CDCl_3$):** 210.8, 137.6, 136.9, 128.4, 128.3, 128.2, 128.1, 127.7, 83.8, 73.4, 73.3, 71.1, 70.3, 50.3, 37.1, 28.8, 24.2, 24.1, 14.4. **HRMS (ESI)** calcd for $C_{25}H_{34}O_4S_2$+Na 485.1796, found 485.1795.

(2.7) (5*S*,6*R*)-5,7-bis(benzyloxy)-6-hydroxy-1,1-bis(p-tolylthio)heptan-4-one (9):



Reagents and Conditions: (i) TolSH, TMSOTf, CH_2Cl_2, -10 ^oC, 30 min.

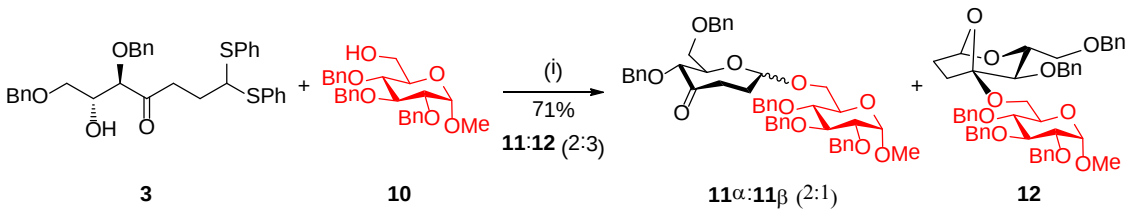
The compound **9** was synthesized by following the general procedure **(A)** with D-galactose-derived 1,2-cyclopropa-3-pyranone **6** (100 mg, 0.295 mmol), toluene-4-thiol (80.7 mg, 0.650 mmol) and TMSOTf (10.6 µL, 0.059 mmol) in CH_2Cl_2 (5 mL). The reaction mixture was stirred for 30 min at –10 ^oC. The obtained crude product was purified by silica-gel column chromatography (ethyl acetate/hexane 1:3) to provide compound **9** (164 mg, 95% yield) as a colorless oil. R_f = 0.31 (1:4 ethyl acetate/hexane). **IR (neat)**: ν_{max}/cm^{-1} 3457, 3062, 3024, 2920, 2859, 1709, 1489, 1451, 1391 1358, 1210, 1095, 815, 733, 700. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.26 – 7.34 (14H, m), 7.07 – 7.09 (4H, d, *J* = 7.6 Hz), 4.62 – 4.65 (1H, d, *J* = 11.2 Hz), 4.38 – 4.47 (3H, m), 4.33 – 4.36 (1H, t, *J* = 6.4 Hz), 4.05 (s, 1H), 3.95 (1H, s), 3.51 – 3.54 (1H, dd, *J* = 9.6 Hz, *J* = 4.8 Hz), 3.44 – 3.47 (1H, dd, *J* = 8.4 Hz, *J* = 6.0 Hz), 2.82 – 2.98 (2H, m), 2.64 (1H, s), 2.30 (6H, s), 2.02 – 2.09 (2H, m). **δ_C(100 MHz, $CDCl_3$):** 210.7, 137.8, 137.5, 136.8, 133.2, 133.1, 130.0, 129.9, 129.5, 128.4, 128.3, 128.2, 128.1, 127.7, 83.8, 73.4, 73.2, 71.0, 70.2, 57.9, 36.8, 28.7, 21.0. **HRMS (ESI)** calcd for $C_{35}H_{38}O_4S_2$+Na 609.2109, found 609.2110.

(2.8) General procedure (B): The one-pot septanoside formation and glycosylation of acyclic dithioacetals as glycosyl donors with various glycosyl acceptors

The suspension of sugar-derived dithioacetal (0.2 mmol), glycosyl acceptor (0.22 mmol) and 4 Å molecular sieves powder (approx. 100 mg) in dry CH_2Cl_2 (10 mL) was stirred under N_2 condition for 30 min at room temperature. After cooling the solution to –45 ^oC, NIS (67.4 mg, 0.3 mmol) and AgOTf (10.2 mg, 0.04 mmol) were added sequentially. Then, the reaction mixture was warmed –25 ^oC and stirred for 1 h at the same temperature. After completion of the reaction (by check the TLC), quenched with saturated $NaHCO_3$ solution (20 mL) at –25 ^0C, warmed to room temperature and extracted with CH_2Cl_2 (20 mL X 2). The combined organic layers were washed with saturated $Na_2S_2O_3$ solution (20 mL), water (20 mL), brine (15 mL) and dried over anhydrous Na_2SO_4. The resulted crude solution was concentrated under *vacuo* and

purified by silica-gel column chromatography (ethyl acetate/hexane or ethyl acetate/toluene) to give the pure septano-hexose derivatives.

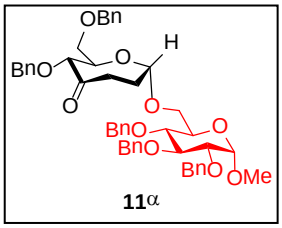
(2.9) Compounds 11 and 12:



3 **10** **11**α:**11**β (2:1) **12**

Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 °C to -25 °C, 1 h.

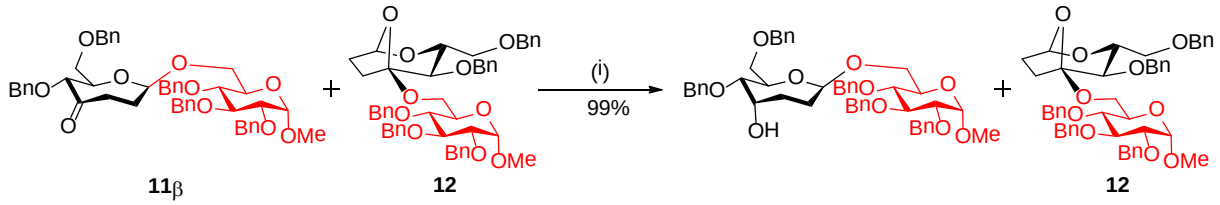
Following the general procedure **(B)**, the compounds **11** and **12** were synthesized using D-glucose-derived dithioacetal **3** (80 mg, 0.143 mmol), methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside **10** (73 mg, 0.157 mmol), NIS (40.2 mg, 0.178 mmol) and AgOTf (7.3 mg, 0.028 mmol) in CH_2Cl_2 (7 mL). The reaction mixture was warmed to –45 °C to –25 °C and stirred for 1 h at –25 °C. The silica-gel column chromatography of obtained crude product with ethyl acetate in hexane (1:3) gave the compounds **11***β* and **12** (61 mg, 53% yield) as inseparable mixture and **11**α (20 mg, 18% yield) as a pure septano-hexose derivative. R_f = 0.48 (11*β* &12), 0.42 (11α) [ethyl acetate/hexane 1:3].



11α

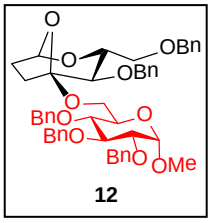
Compound 11α: Thick colorless gum. **IR (neat):** ν_{max}/cm^{-1} 2958, 2920, 2854, 1731, 1490, 1463, 1364, 1271, 1200, 1117, 1079, 958, 734, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.25 – 7.35 (25H, m), 4.95 – 4.98 (2H, m), 4.85 – 4.88 (1H, d, *J* = 11.2 Hz), 4.80 (1H, d, *J* = 3.2 Hz), 4.76 – 4.78 (1H, d, *J* = 4.8 Hz), 4.65 – 4.68 (1H, d, *J* = 12.4 Hz), 4.60 – 4.63 (1H, d, *J* = 11.2 Hz), 4.55 – 4.58 (2H, m), 4.46 – 4.49 (1H, d, *J* = 12.4 Hz), 4.36 – 4.41 (2H, dd, *J* = 12 Hz, *J* = 6.4 Hz), 4.15 – 4.19 (2H, m), 3.94 – 3.99 (1H, t, *J* = 9.2 Hz), 3.92 (1H, d, *J* = 7.2 Hz), 3.85 – 3.90 (1H, dd, *J* = 12 Hz, *J* = 5.2 Hz), 3.68 – 3.71 (2H, d, *J* = 10.4 Hz), 3.48 – 3.51 (2H, m), 3.42 – 3.47 (2H, m), 3.35 (3H, s), 2.54 – 2.60 (1H, m), 2.37 – 2.43 (1H, m), 2.21 – 2.29 (1H, m), 1.96 – 2.02 (1H, m). **δ_C(100 MHz, $CDCl_3$):** 208.5, 138.6, 138.2, 138.1, 137.9, 137.2, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 100.6, 97.8, 84.2, 82.0, 79.9, 77.7, 75.7, 74.8, 73.2, 73.0, 70.6, 69.9, 68.5, 66.4, 55.0, 35.6, 28.2 **HRMS (ESI)** calcd for $C_{49}H_{54}O_{10}$+Na 825.3615, found 825.3609.

(2.10) Compounds 12 and Reduced product of 11*β*:

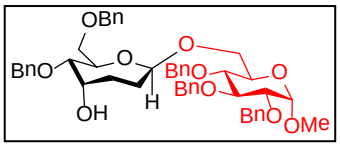


Reagents and Conditions: (i) $LiAl(O^tBu)_3H$, EtOH, -78 ^oC, 1 h.

To the cold (–78 ^oC) solution of $LiAl(O^tBu)_3H$ (31 mg, 0.124 mmol) in ethanol (2 mL) (*note: excess of the $LiAl(O^tBu)_3H$ (upto 6 eq) will not affect the selectivity of the reduction process*), was added mixture of compounds **11***β* and **12** (50 mg, 0.062 mmol) in ethanol (1.5 mL) in dropwise fashion. The reaction mixture was stirred for 1 h at –78 ^oC. TLC showed that 11*β* was completely consumed while the compound **12** was intact under these conditions. Then, the reaction was slowly quenched with the saturated NH_4Cl solution (15 mL), warmed to room temperature and extracted with ethyl acetate (15 mL x 2). The combined organic layers were washed brine (10 mL) and dried (Na_2SO_4). The crude solution was concentrated under reduced pressure and purified by the silica-gel column chromatography with ethyl acetate in hexane (3:7 to 2:3) to give the pure compounds **12** (40 mg) and septanosyl disaccharide alcohol (9 mg).

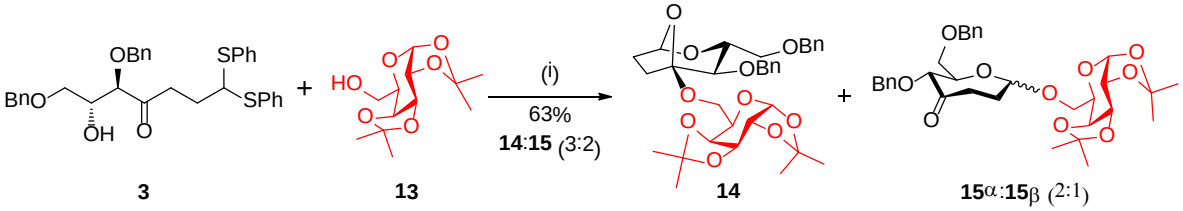


Compound 12: colorless semi solid. R_f = 0.70 (ethyl acetate/hexane 3:7). **IR (neat):** ν_{max}/cm^{-1} 3062, 3029, 2920, 1714, 1495, 1456, 1358, 1210, 1150, 1084 908, 739, 700. **δ_H(500 MHz, $CDCl_3$, Me_4Si):** δ 7.21 – 7.36 (23H, m), 7.14 – 7.15 (2H, m), 5.46 – 5.47 (1H, d, *J* = 4.5 Hz), 4.96 – 4.98 (1H, d, *J* = 10.5 Hz), 4.80 – 4.85 (3H, m), 4.77 – 4.79 (1H, d, *J* = 12.0 Hz), 4.64 – 4.66 1H, (d, *J* = 12.0 Hz), 4.59 – 4.61 (2H, m), 4.54 – 4.56 (1H, d, *J* = 12.5 Hz), 4.49 – 4.51 (1H, d, *J* = 12.5 Hz), 4.42 – 4.44 (1H, d, *J* = 11.0 Hz), 3.98 – 4.02 (1H, t, *J* = 9.2 Hz), 3.89 – 3.92 (1H, m), 3.79 – 3.83 (2H, m), 3.61 – 3.64 (1H, m), 3.50 – 3.58 (5H, m), 3.34 (3H, s), 2.06 – 2.17 (2H, m), 1.90 – 1.96 (1H, m), 1.77 – 1.83 (1H, m). **δ_C(125 MHz, $CDCl_3$):** 138.7, 138.3, 138.2, 138.1, 138.0, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 109.3, 98.3, 97.9, 82.1, 79.8, 77.9, 75.7, 74.9, 74.3, 73.9, 73.4, 73.3, 72.9, 69.6, 69.4, 61.1, 55.0, 29.1, 23.4. **HRMS (ESI)** calcd for $C_{49}H_{54}O_{10}$+Na 825.3615, found 825.3614.



Reduced product of 11*β*: colorless oil. R_f = 0.30 (ethyl acetate/hexane 3:7). **IR (neat)**: ν_{max}/cm^{-1} 3473, 3095, 3068, 3024, 2926, 2871, 1720, 1495, 1452, 1358, 1276, 1216, 1073, 909, 739, 695. **δ_H(500 MHz, $CDCl_3$, Me_4Si):** δ 7.23 – 7.35 (25H, m), 4.95 – 4.98 (1H, d, *J* = 11.0 Hz), 4.82 – 4.84 (1H, d, *J* = 11.0 Hz), 4.76 – 4.81 (2H, dd, *J* = 13.5 Hz, *J* = 11.5 Hz), 4.63 – 4.65 (1H, d, *J* = 12.0 Hz), 4.58 – 4.59 (1H, d, *J* = 3.5 Hz), 4.49 – 4.56 (6H, m), 4.07 – 4.09 (1H, d, *J* = 8.5 Hz), 4.01 – 4.03 (1H, dd, *J* = 10.5 Hz, *J* = 1.5 Hz), 3.94 – 3.98 (1H, t, *J* = 9.5 Hz), 3.69 – 3.72 (2H, m), 3.56 – 3.61 (2H, m), 3.48 – 3.55 (3H, m), 3.31 (3H, s), 2.09 (1H, s), 1.94 – 2.00 (2H, m), 1.63 – 1.74 (2H, m). **δ_C(125 MHz, $CDCl_3$):** 138.7, 138.3, 138.2, 138.1, 137.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 105.3, 97.9, 82.3, 82.1, 79.7, 77.6, 77.2, 75.7, 74.9, 73.4, 73.3, 72.5, 71.2, 69.7, 69.5, 66.6, 55.0, 30.5, 25.3. **HRMS (ESI)** calcd for $C_{49}H_{56}O_{10}$+Na 827.3771, found 827.3772.

(2.11) Compound 14 and 15:



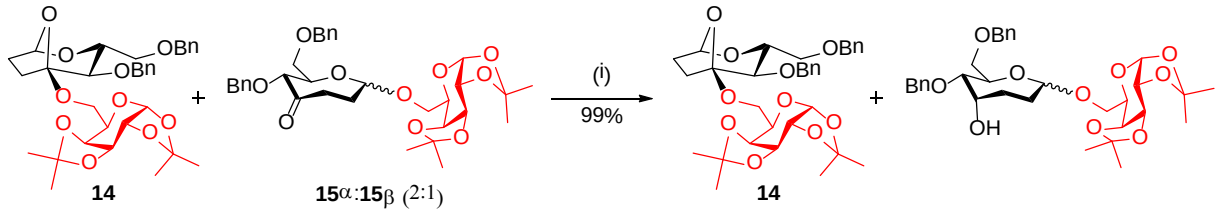
Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 °C to -25 °C, 1 h.

Followed the general procedure **(B)** to get the compounds **14** and **15** with D-glucose-derived dithioacetal **3** (110 mg, 0.196 mmol), 1,2;3,4-di-*O*-isopropylidine-α-D-galactose **13** (56.1 mg, 0.215 mmol), NIS (55.1 mg, 0.245 mmol) and AgOTf (10.0 mg, 0.039 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was warmed –45 °C to –25 °C and stirred for 1 h at –25 °C. The silica-gel column chromatography of crude product with ethyl acetate in hexane (1:3) gave inseparable mixture of **14** and **15** (74 mg, 63% yield).

(2.12) Compound 14 and Reduced products of 15:

To the cold (–78 °C) solution of $LiAl(O^tBu)_3H$ (42 mg, 0.166 mmol) in ethanol (2.5 mL), was added mixture of compounds **14** and **15** (70 mg, 0.083 mmol) in ethanol (2 mL) in dropwise

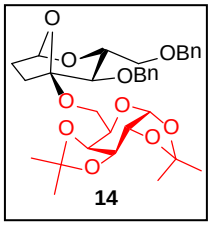
fashion. The reaction mixture was stirred for 1 h at –78 °C. TLC showed that compound **15** was completely consumed while the compound **14** was not changed in the reaction. Then the reaction



14 **15**α:**15**β (2:1) **14**

Reagents and Conditions: (i) $LiAl(O^tBu)_3H$, EtOH, -78 °C, 1 h.

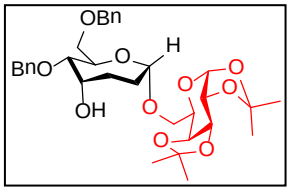
was slowly quenched with the saturated NH_4Cl solution (15 mL), warmed to room temperature and extracted with ethyl acetate (15 mL X 2). The combined organic layers were washed brine (10 mL) and dried (Na_2SO_4). The crude solution was concentrated under reduced pressure and purified by the silica-gel column chromatography with ethyl acetate in hexane (3:7 to 2:3) to give the **14** (43 mg) and reduced products of **15*α*** (17 mg) and **15*β*** (9 mg) as a single compounds.



14

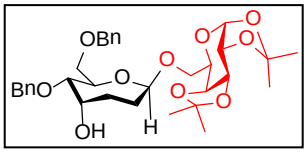
Compound 14: Colorless oil. R_f = 0.36 (ethyl acetate/hexane 3:7).

IR (neat): ν_{max}/cm^{-1} 3063, 3024, 2986, 2909, 2849, 1720, 1490, 1457, 1380, 1254, 1380, 1254, 1216, 1167, 1068, 997, 898, 734, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.24 – 7.31 (10H, m), 5.55 – 5.56 (1H, d, *J* = 4.8 Hz), 5.44 – 5.45 (1H, d, *J* = 4.4 Hz), 4.86 – 4.89 (1H, d, *J* = 11.2 Hz), 4.59 – 4.61 (1H, dd, *J* = 8.0 Hz, *J* = 2.0 Hz), 4.47 – 4.51 (4H, m), 4.30 – 4.32 (1H, d, *J* = 4.8 Hz, *J* = 2.0 Hz), 4.25 – 4.27 (1H, d, *J* = 8.0 Hz), 4.02 – 4.05 (1H, t, *J* = 5.6 Hz), 3.85 – 3.89 (1H, dd, *J* = 10.4 Hz, *J* = 4.8 Hz), 3.79 – 3.83 (1H, m), 3.61 – 3.64 (1H, m), 3.56 – 3.58 (1H, d, *J* = 10.4 Hz), 3.46 – 3.50 (1H, dd, *J* = 10.4 Hz, *J* = 5.6 Hz), 2.07 – 2.17 (2H, m), 1.88 – 1.97 (2H, m), 1.51 (3H, s), 1.45 (3H, s), 1.32 (6H, bs). **δ_C(100 MHz, $CDCl_3$):** 138.2, 138.0, 128.4, 128.2, 128.1, 127.9, 127.5, 109.5, 109.3, 108.5, 98.1, 96.3, 74.4, 73.6, 73.3, 72.7, 71.2, 70.6, 70.5, 69.4, 67.4, 61.4, 29.1, 26.0, 25.9, 25.0, 24.2, 22.6. **HRMS (ESI)** calcd for $C_{33}H_{42}O_{10}$+Na 621.2676, found 621.2675.



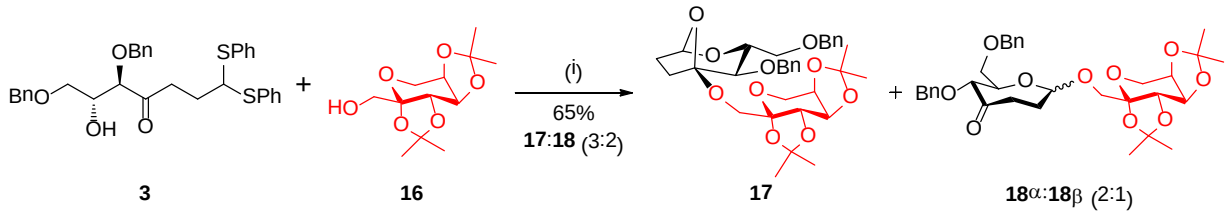
Reduced product of 15*α*: Thick syrup. R_f = 0.23 (ethyl acetate/hexane 3:7). **^{1}H NMR (500 MHz, $CDCl_3$)**: δ 7.22 – 7.34 (m, 10H), 5.51 – 5.52 (d, 1H, *J* = 5.0 Hz), 4.79 – 4.82 (dd, 1H, *J* = 9.5 Hz, *J* = 5.5 Hz), 4.66 – 4.69 (d, 1H, *J* = 9.6 Hz), 4.55 – 4.61 (m, 3H), 4.51 – 4.53 (d, 1H, *J* = 12.5 Hz), 4.30 – 4.31 (dd, 1H, *J* = 5.0 Hz, *J* = 2.5 Hz), 4.22 – 4.24 (dd, 1H, *J* = 8.0 Hz, *J* = 2.0 Hz), 4.14 – 4.15 (t, 1H, *J* = 3.5 Hz), 4.09 – 4.12 (dt, 1H, *J* = 9.5 Hz, *J* = 2.5 Hz), 3.91 – 3.94 (td,

1H, *J* = 6.5 Hz, *J* = 1.5 Hz), 3.86 – 3.90 (dd, 1H, *J* = 10.0 Hz, *J* = 6.5 Hz), 3.77 – 3.79 (dd, 1H, *J* = 10.0 Hz, *J* = 3.0 Hz), 3.67 – 3.70 (dd, 1H, *J* = 10.0 Hz, *J* = 6.5 Hz), 3.62 – 3.65 (dd, 1H, *J* = 10.0 Hz, *J* = 2.5 Hz), 3.59 – 3.61 (dd, 1H, *J* = 10.0 Hz, *J* = 4.0 Hz), 2.65 (s, 1H), 2.19 – 2.25 (m, 1H), 1.83 – 1.89 (m, 1H), 1.68 – 1.72 (m, 2H), 1.51 (s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H). **^{13}C NMR (125 MHz, CDCl$_3$):** 138.2, 137.9, 128.4, 128.3, 127.8, 127.7, 127.4, 109.1, 108.4, 100.8, 96.3, 79.5, 73.7, 72.3, 71.0, 70.7, 70.6, 70.5, 66.3, 66.2, 66.0, 65.6, 26.1, 26.0, 24.9, 24.7, 24.5, 24.2. **HRMS (ESI)** calcd for $C_{33}H_{44}O_{10}$+Na 623.2832, found 623.2832.



Reduced product of 15*β*: **L**ight yellow gum. R_f = 0.20 (ethyl acetate/hexane 3:7). **IR (neat)**: ν_{max}/cm^{-1} 3523, 3029, 2985, 2931, 1456, 1385, 1265, 1221, 1078, 1007, 744, 695. **^{1}H δ_H(500 MHz, CDCl$_3$, Me$_4$Si):** 7.24 – 7.35 (10H, m), 5.53 – 5.54 (1H, d, *J* = 5.5 Hz), 4.73 – 4.76 (1H, dd, *J* = 7.5 Hz, *J* = 3.0 Hz), 4.59 – 4.61 (1H, d, *J* = 12.0 Hz), 4.53 – 4.57 (4H, m), 4.28 – 4.30 (1H, dd, *J* = 5.5 Hz, *J* = 2.5 Hz), 4.15 – 4.16 (1H, dd, *J* = 8.0 Hz, *J* = 1.5 Hz), 4.09 – 4.11 (1H, dd, *J* = 7.0 Hz, *J* = 3.5 Hz), 3.93 – 3.99 (2H, m), 3.76 – 3.79 (1H, dd, *J* = 11.0 Hz, *J* = 5.5 Hz), 3.58 – 3.65 (4H, m), 2.06 – 2.12 (2H, m), 1.97 – 2.01 (1H, m), 1.65 – 1.76 (2H, m), 1.52 (3H, s), 1.42 (3H, s), 1.32 (3H, s), 1.31 (3H, s). **δ_C(125 MHz, CDCl$_3$):** 138.2, 137.9, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 109.2, 108.6, 105.2, 96.3, 82.3, 76.7, 73.4, 72.5, 71.4, 71.1, 70.7, 70.4, 69.5, 67.6, 67.2, 30.4, 26.0, 25.9, 25.3, 24.9, 24.4. **HRMS (ESI)** calcd for $C_{33}H_{44}O_{10}$+Na 623.2832, found 623.2832.

(2.13) Compound 17 and 18:

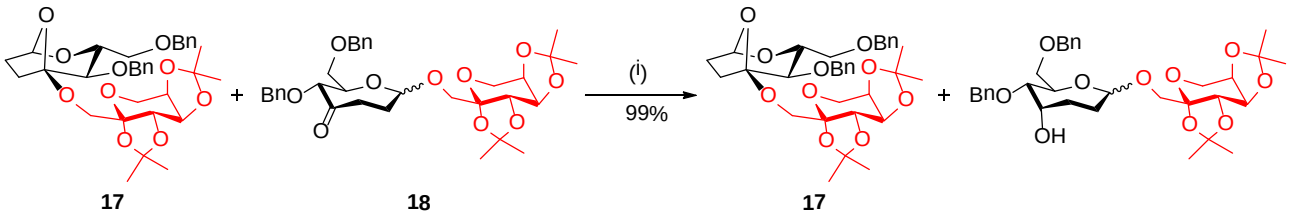


Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 ^{o}C to -25 ^{o}C, 1 h.

Followed the general procedure **(B)** to get the compounds **17** and **18** with D-glucose-derived dithioacetal **3** (160 mg, 0.286 mmol), 2,3;4,5-di-*O*-isopropylidene-α- D-fructopyranose **16** (82 mg, 0.314 mmol), NIS (80.4 mg, 0.357 mmol) and AgOTf (14.6 mg, 0.057 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was warmed –45 ^{o}C to –25 ^{o}C and stirred for 1 h at –25 ^{o}C. The

silica-gel column chromatography of crude product with ethyl acetate in toluene (1:4) gave the compounds **17** and **18** (111 mg, 65% yield) as inseparable mixture.

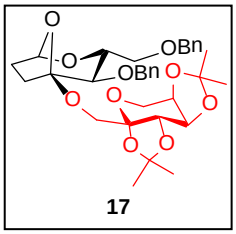
(2.14) Compound 17 and Reduced products of 18:



17 **18** **17**

Reagents and Conditions: (i) $LiAl(O^tBu)_3H$, EtOH, -78 ^oC, 1 h.

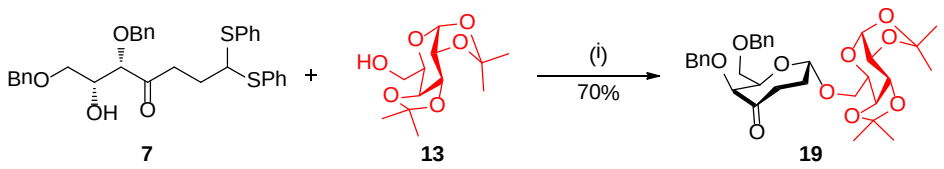
To the cold (–78 ^oC) solution of $LiAl(O^tBu)_3H$ (94.2 mg, 0.370 mmol) in ethanol (4 mL), was added mixture of **17** and **18** (111 mg, 0.185 mmol) in ethanol (3.5 mL) in dropwise fashion. The reaction mixture was stirred for 1 h at –78 ^oC. TLC showed that compound **18** was completely consumed while the compound **17** was not changed in the reaction. Then, the reaction was slowly quenched with saturated NH_4Cl solution (25 mL), warmed to room temperature and extracted with ethyl acetate (25 mL X 2). The combined organic layers were washed brine (15 mL) and dried (Na_2SO_4). The crude solution was concentrated under reduced pressure and purified by the silica-gel column chromatography with ethyl acetate in toluene (1:4 to 1:3) to give the pure compound **17** (66 mg) and inseparable mixture of **18** (43 mg (α:β = 2:1)).



17

Compound 17: Thick gum. R_f = 0.74 (ethyl acetate/hexane 2:3). **IR (neat)**: ν_{max}/cm^{-1} 3084, 3057, 3035, 2986, 2931, 1720, 1501, 1457, 1380, 1249, 1210, 1150, 1090, 1073, 991, 915, 882, 745, 706. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.17 – 7.33 (10H, m), 5.48 – 5.50 (1H, d, *J* = 4.8 Hz), 4.87 – 4.90 (1H, d, *J* = 11.2 Hz), 4.56 – 4.62 (2H, m), 4.49 – 4.52 (2H, m), 4.38 – 4.40 (1H, d, *J* = 11.2 Hz), 4.22 – 4.24 (1H, d, *J* = 8.0 Hz), 3.88 – 3.95 (2H, dd, *J* = 13.6 Hz, *J* = 10.8 Hz), 3.77 – 3.80 (1H, d, *J* = 10.8 Hz), 3.73 – 3.76 (1H, d, *J* = 13.2 Hz), 3.63 – 3.66 (1H, m), 3.55 – 3.61 (3H, m), 2.09 – 2.21 (2H, m), 1.88 – 1.97 (2H, m), 1.52 (3H, s), 1.45 (3H, s), 1.39 (3H, s), 1.33 (3H, s). **δ_C(100 MHz, $CDCl_3$):** 138.1, 138.0, 128.3, 128.2, 127.9, 127.7, 127.6, 109.3, 108.9, 108.5, 102.2, 98.3, 75.2, 74.3, 73.3, 73.0, 71.0, 70.2, 69.8, 69.2, 63.7, 61.1, 29.1, 26.6, 25.9, 25.8, 24.1, 24.0. **HRMS (ESI)** calcd for $C_{33}H_{42}O_{10}$+Na 621.2676, found 621.2675.

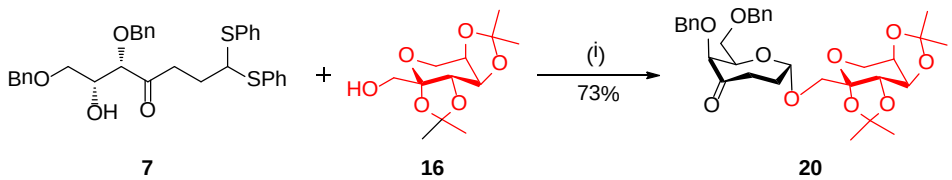
(2.15) Compound 19:



Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 ^oC to -25 ^oC, 1 h.

Followed the general procedure **(B)** to get the compound **19** with D-galactose-derived dithioacetal **7** (120 mg, 0.214 mmol), 1,2;3,4-di-*O*-isopropylidine-α-D-galactose **13** (61 mg, 0.236 mmol), NIS (60.3 mg, 0.267 mmol) and AgOTf (10.9 mg, 0.042 mmol) in CH_2Cl_2 (11 mL). The reaction mixture was warmed –45 ^oC to –25 ^oC and stirred for 1 h at –25 ^oC. The obtained crude product was purified by the silica-gel column chromatography (ethyl acetate/toluene 1:3) to afford the pure diastereomer **19** (90 mg, 70% yield) as a colorless oil. R_f = 0.46 (ethyl acetate/hexane 1:3). **IR (neat)**: ν_{max}/cm^{-1} 3057, 3024, 2986, 2926, 2871, 1715, 1490, 1452, 1386, 1304, 1254, 1210, 1112, 1068, 1002, 887, 865, 734, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.22 – 7.33 (10H, m), 5.47 – 5.49 (1H, d, *J* = 4.8 Hz), 5.00 – 5.03 (1H, dd, *J* = 4.4 Hz, *J* = 4.0 Hz), 4.65 – 4.68 (1H, d, *J* = 11.6 Hz), 4.57 – 4.59 (1H, dd, *J* = 8.0 Hz, *J* = 2.0 Hz), 4.44 – 4.47 (1H, d, *J* = 12.0 Hz), 4.36 – 4.41 (2H, t, *J* = 11.2 Hz), 4.29 – 4.30 (1H, dd, *J* = 4.8 Hz, *J* = 2.4 Hz), 4.16 – 4.23 (2H, m), 3.92 – 3.95 (2H, m), 3.84 – 3.88 (1H, dd, *J* = 10.0 Hz, *J* = 6.8 Hz), 3.66 – 3.71 (1H, dd, *J* = 10.0 Hz, *J* = 6.4 Hz), 3.56 – 3.64 (2H, m), 2.63 – 2.69 (1H, m), 2.44 – 2.49 (1H, m), 2.19 – 2.27 (1H, m), 1.68 – 1.81 (1H, m), 1.51 (3H, s), 1.41 (3H, s), 1.31 (6H, bs). **δ_C(100 MHz, $CDCl_3$):** 209.2, 137.9, 137.1, 128.4, 128.3, 128.2, 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 $C_{33}H_{42}O_{10}$+Na 621.2676, found 621.2675.

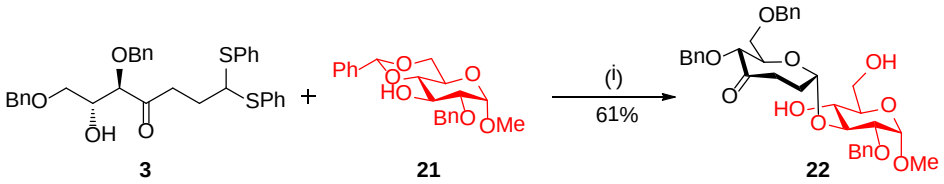
(2.16) Compound 20:



Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 ^oC to -25 ^oC, 1 h.

Followed the general procedure **(B)** to get the compound **20** with D-galactose-derived dithioacetal **7** (145 mg, 0.259 mmol), 2,3;4,5-di-*O*-isopropylidene-α-D-fructopyranose **16** (74.3 mg, 0.285 mmol), NIS (72.9 mg, 0.324 mmol) and AgOTf (13.3 mg, 0.051 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was warmed –45 ^oC to –25 ^oC and stirred for 1 h at –25 ^oC. The obtained crude product was purified by the silica-gel column chromatography (ethyl acetate/toluene 1:3) to afford the pure diastereomer **20** (93.8 mg, 73% yield) as a colorless oil. R_f = 0.62 (ethyl acetate/hexane 3:7). **IR (neat)**: ν_{max}/cm^{-1} 3380, 3068, 3035, 2991, 2936, 1720, 1501, 1457, 1375, 1315, 1254, 1216, 1112, 1073, 909, 887, 745, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.21 – 7.32 (10H, m), 5.00 – 5.02 (1H, dd, *J* = 4.4 Hz, *J* = 6.0 Hz), 4.64 – 4.67 (1H, d, *J* = 12.0 Hz), 4.57 – 4.60 (1H, dd, *J* = 2.0 Hz, *J* = 8.0 Hz), 4.43 – 4.46 (1H, d, *J* = 11.6 Hz), 4.39 – 4.42 (1H, d, *J* = 12.0 Hz), 4.31 – 4.36 (2H, m), 4.19 – 4.23 (2H, t, *J* = 7.6 Hz), 3.89 – 3.96 (3H, m), 3.71 – 3.74 (1H, d, *J* = 12.8 Hz), 3.58 – 3.66 (2H, m), 3.50 – 3.52 (1H, d, *J* = 10.4 Hz), 2.67 – 2.73 (1H, m), 2.40 – 2.45 (1H, m), 2.24 – 2.30 (1H, m), 1.74 – 1.82 (1H, m), 1.50 (3H, s), 1.45 (3H, s), 1.36 (3H, s), 1.33 (3H, s). **δ_C(100 MHz, $CDCl_3$):** 209.0, 137.9, 137.0, 128.5, 128.3, 128.2, 128.0, 127.5, 108.9, 108.5, 102.1, 100.0, 82.4, 73.1, 73.0, 70.9, 70.1, 69.9, 69.1, 68.4, 66.0, 61.0, 34.8, 28.4, 26.5, 25.9, 25.2, 23.9. **HRMS (ESI)** calcd for $C_{33}H_{42}O_{10}$+Na 621.2676, found 621.2678.

(2.17) Compound 22:

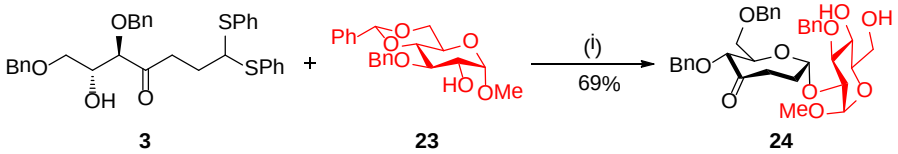


Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 ^oC to -25 ^oC, 1 h.

Followed the general procedure **(B)** to get the compound **22** with D-glucose-derived dithioacetal **3** (120 mg, 0.214 mmol), methyl 2-*O*-benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside **21** (87.9 mg, 0.235 mmol), NIS (60 mg, 0.267 mmol) and AgOTf (10.9 mg, 0.042 mmol) in CH_2Cl_2 (12 mL). The reaction mixture was warmed –45 ^oC to –25 ^oC and stirred for 1 h at –25 ^oC. The obtained crude product was purified by the silica-gel column chromatography (ethyl acetate/hexane 1:1) to afford the pure compound **22** (81.5 mg, 61% yield) as a light yellow semi solid. R_f = 0.38 (ethyl acetate/hexane 1:1). **IR (neat)**: ν_{max}/cm^{-1} 3463, 3068, 3024, 2909, 2860,

1715, 1495, 1452, 1364, 1205, 1095, 1073, 1052, 920, 734, 695. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.25 – 7.37 (15H, m), 4.86 – 4.89 (1H, d, *J* = 11.6 Hz), 4.70 – 4.74 (2H, m), 4.56 – 4.59 (2H, dd, *J* = 5.2 Hz, *J* = 6.0 Hz), 4.40 – 4.52 (3H, m), 4.05 – 4.09 (1H, dd, *J* = 4.8 Hz, *J* = 10 Hz), 4.03 (1H, m), 3.89 – 3.91 (1H, d, *J* = 6.4 Hz), 3.53 – 3.70 (5H, m), 3.44 – 3.49 (1H, t, *J* = 10 Hz), 3.44 (3H, s), 3.33 – 3.38 (1H, t, *J* = 9.2 Hz), 2.71 – 2.75 (2H, td, *J* = 3.2 Hz, *J* = 7.2 Hz), 2.56 – 2.58 (1H, d, *J* = 5.6 Hz), 2.32 – 2.34 (1H, d, *J* = 6.0 Hz), 1.91 – 1.95 (2H, m). **δ_C(100 MHz, $CDCl_3$):** 210.3, 138.4, 137.6, 137.0, 128.5, 128.4, 128.3, 128.1, 128.0, 127.8, 127.6, 101.0, 99.7, 84.1, 81.4, 78.6, 74.5, 73.3, 73.0, 72.2, 71.0, 70.0, 68.4, 62.5, 55.3, 33.7, 27.4. **HRMS (ESI)** calcd for $C_{35}H_{42}O_{10}$+Na 645.2676, found 645.2699.

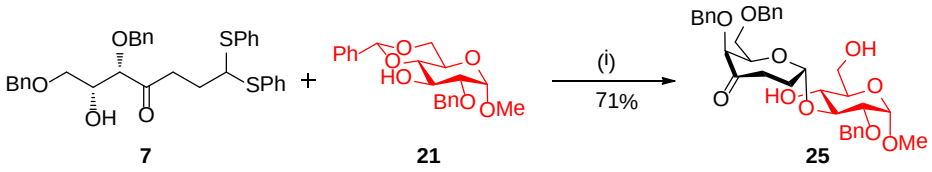
(2.18) Compound 24:



Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 °C to -25 °C, 1 h.

Followed the general procedure **(B)** to get the compound **24** with D-glucose-derived dithioacetal **3** (135 mg, 0.241 mmol), methyl 3-*O*-benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside **23** (99 mg, 0.265 mmol), NIS (67.7 mg, 0.301 mmol) and AgOTf (12.3 mg, 0.048 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was warmed –45 °C to –25 °C and stirred for 1 h at –25 °C. The obtained crude product was purified by the silica-gel column chromatography (ethyl acetate/hexane 1:1) to afford the pure compound **24** (103.8 mg, 69% yield) as a light yellow gum. R_f = 0.37 (ethyl acetate/hexane 1:1). **IR (neat)**: ν_{max}/cm^{-1} 3457, 3063, 3024, 2920, 2854, 1720, 1501, 1452, 1369, 1276, 1095, 1068, 739, 695. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.26 – 7.36 (15H, m), 4.74 – 4.77 (1H, d, *J* = 12.4 Hz), 4.65 – 4.68 (1H, d, *J* = 12.4 Hz), 4.46 – 4.60 (5H, m), 4.40 – 4.43 (1H, d, *J* = 11.6 Hz), 3.99 – 4.06 (3H, m), 3.93 – 3.95 (1H, d, *J* = 6.8 Hz), 3.57 – 3.63 (3H, m), 3.40 – 3.45 (1H, t, *J* = 10 Hz), 3.36 – 3.39 (1H, dd, *J* = 3.6 Hz, *J* = 9.6 Hz), 3.33 (3H, s), 3.17 – 3.22 (1H, t, *J* = 9.6 Hz), 2.64 – 2.85 (4H, m), 1.93 – 1.99 (2H, dd, *J* = 6.8 Hz, *J* = 12 Hz). **δ_C(100 MHz, $CDCl_3$):** 210.4, 137.8, 137.6, 137.0, 128.6, 128.5, 128.4, 128.0, 127.8, 101.1, 98.4, 83.7, 80.7, 79.5, 73.3, 73.2, 73.0, 70.9, 70.1, 70.0, 68.3, 61.9, 55.2, 33.8, 27.1. **HRMS (ESI)** calcd for $C_{35}H_{42}O_{10}$+Na 645.2676, found 645.2676.

(2.19) Compound 25:

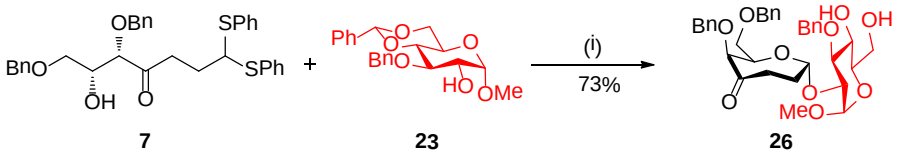


7 21 25

Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 °C to -25 °C, 1 h.

Followed the general procedure **(B)** to get the compound **25** with D-galactose-derived dithio-acetal **7** (110 mg, 0.196 mmol), methyl 2-*O*-benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside **21** (80.6 mg, 0.216 mmol), NIS (55.1 mg, 0.245 mmol) and AgOTf (10.0 mg, 0.039 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was warmed –45 °C to –25 °C and stirred for 1 h at –25 °C. The obtained crude product was purified by the silica-gel column chromatography (ethyl acetate/hexane 3:2) to afford the pure compound **25** (87 mg, 71% yield) as a thick syrup. R_f = 0.30 (ethyl acetate/hexane 1:1). **IR (neat)**: ν_{max}/cm^{-1} 3452, 3084, 3068, 3024, 2920, 2854, 1715, 1501, 1457, 1364, 1210, 1106, 1073, 1041, 739, 701. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.26 – 7.37 (15H, m), 4.74 – 4.78 (1H, d, *J* = 12.4 Hz), 4.66 – 4.68 (2H, d, *J* = 10.4 Hz), 4.60 – 4.62 (1H, t, *J* = 5.2 Hz), 4.55 (1H, d, *J* = 3.2 Hz), 4.43 – 4.52 (2H, dd, *J* = 11.6 Hz, *J* = 19.6 Hz), 4.42 (1H, d, *J* = 11.2 Hz), 3.99 – 4.06 (4H, m), 3.47 – 3.62 (3H, m), 3.41 – 3.46 (1H, t, *J* = 10.0 Hz), 3.36 – 3.39 (1H, dd, *J* = 3.6 Hz, *J* = 9.2 Hz), 3.32 (3H, s), 3.16 – 3.20 (1H, t, *J* = 9.6 Hz), 2.76 – 2.84 (2H, m), 2.65 – 2.73 (2H, m), 1.93 – 1.98 (2H, dd, *J* = 6.4 Hz, *J* = 12 Hz). **δ_C(100 MHz, $CDCl_3$):** 211.0, 137.9, 137.7, 137.0, 128.5, 128.4, 128.2, 128.1, 127.8, 100.8, 98.5, 83.7, 80.7, 79.5, 73.4, 73.3, 73.2, 71.1, 70.3, 70.0, 68.4, 62.0, 55.2, 34.0, 27.2. **HRMS (ESI)** calcd for $C_{35}H_{42}O_{10}$+Na 645.2676, found 645.2676.

(2.20) Compound 26:



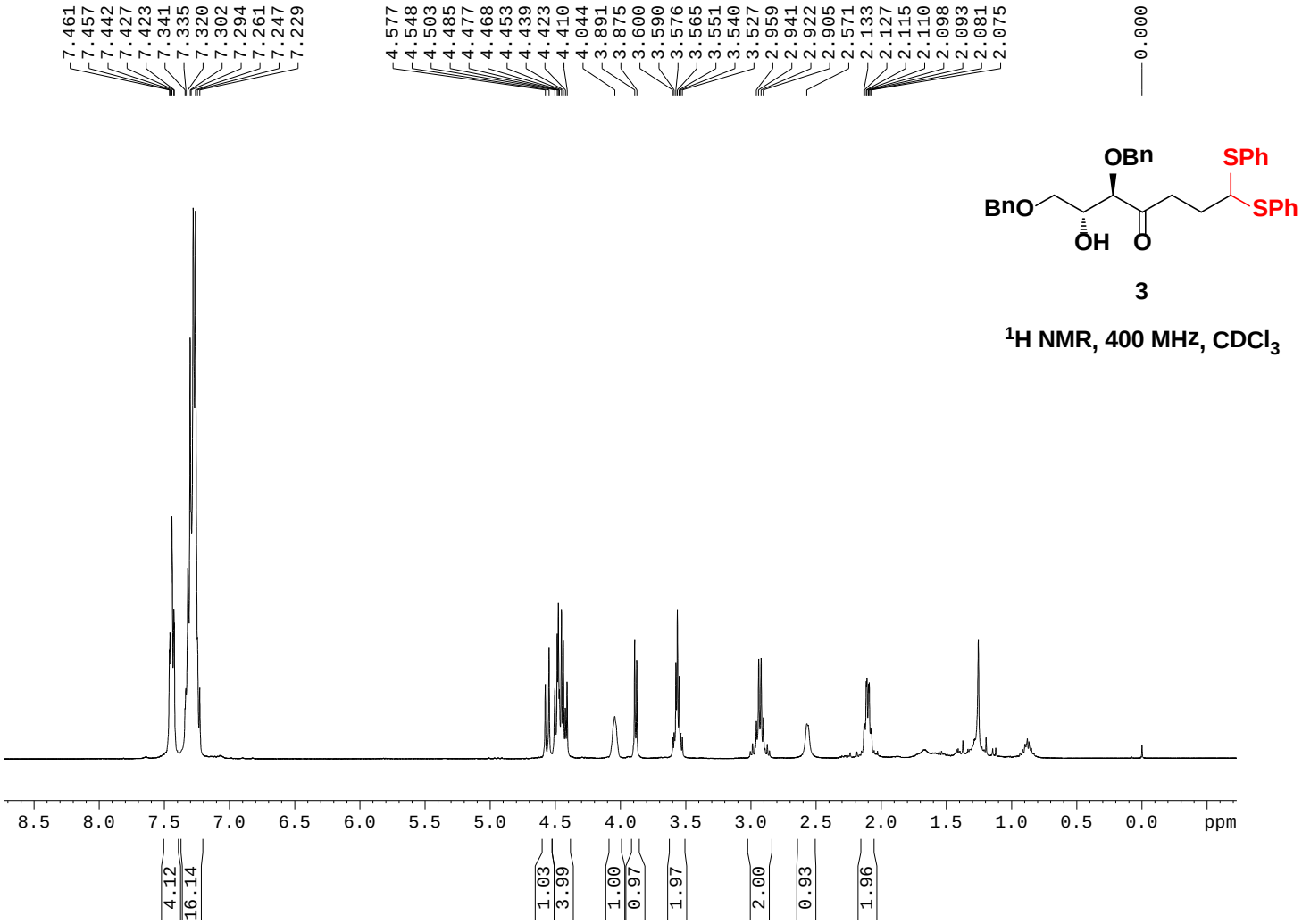
7 23 26

Reagents and Conditions: (i) NIS, AgOTf, CH_2Cl_2, 4 Å MS, -45 °C to -25 °C, 1 h.

Followed the general procedure **(B)** to get the compound **26** with D-galactose-derived dithio-acetal **7** (150 mg, 0.268 mmol), methyl 3-*O*-benzyl 4,6-*O*-benzylidene-α-D-glucopyranoside **23**

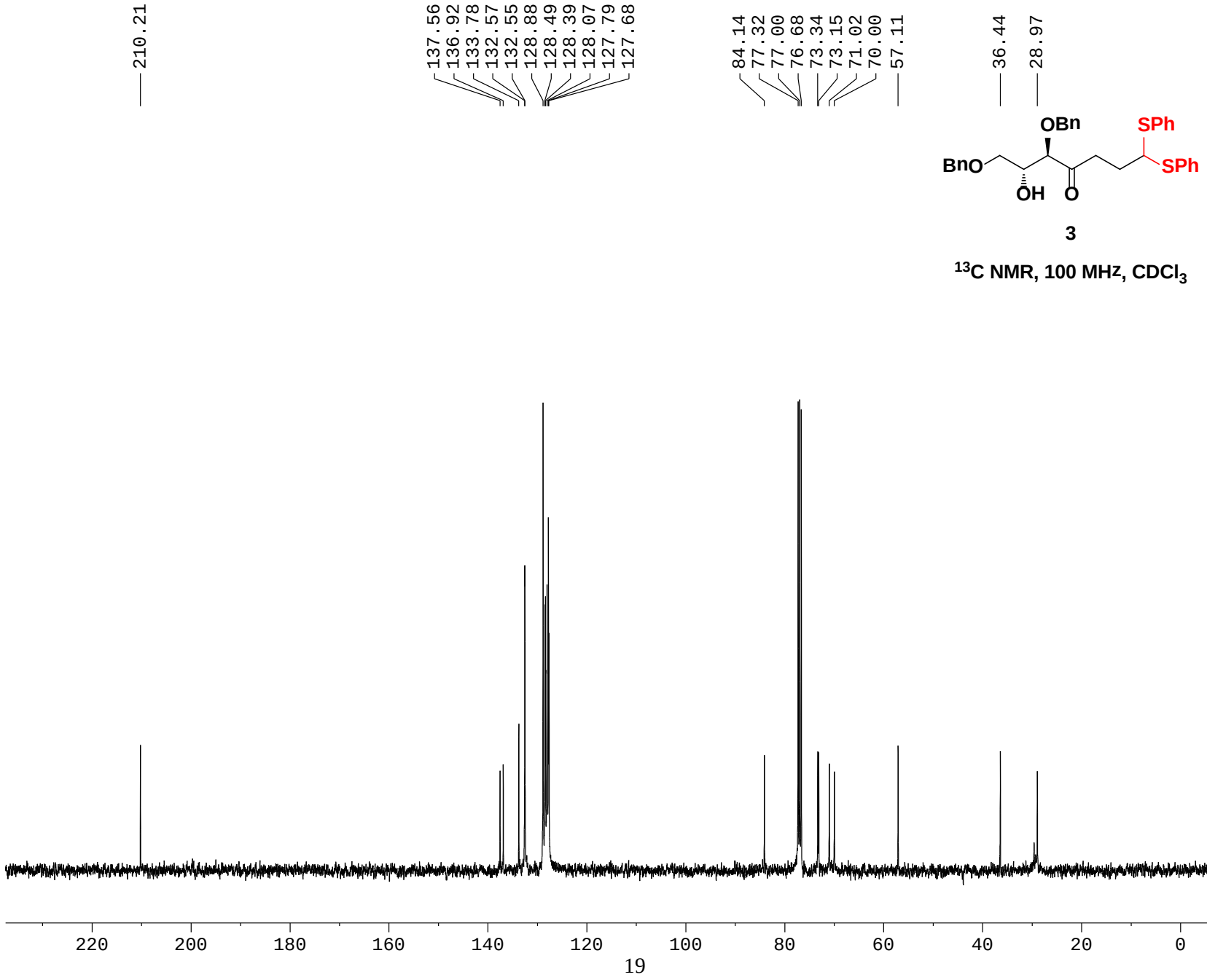
(110 mg, 0.295 mmol), NIS (75.4 mg, 0.335 mmol) and AgOTf (13.7 mg, 0.053 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was warmed –45 ^oC to –25 ^oC and stirred for 1 h at –25 ^oC. The obtained crude product was purified by the silica-gel column chromatography (ethyl acetate/hexane 1:1) to afford the pure compound **26** (122 mg, 73% yield) as a colorless oil. R_f = 0.32 (ethyl acetate/hexane 1:1). **IR (neat)**: ν_{max}/cm^{-1} 3457, 3068, 3030, 2920, 2865, 1720, 1501, 1452, 1364, 1128, 1090, 1052, 1030, 734, 695. **δ_H(400 MHz, $CDCl_3$, Me_4Si):** 7.23 – 7.36 (15H, m), 4.85 – 4.88 (1H, d, *J* = 11.6 Hz), 4.70 – 4.73 (2H, m), 4.62 – 4.65 (1H, d, *J* = 11.6 Hz) 4.54 – 4.56 (1H, t, *J* = 5.2 Hz), 4.40 – 4.48 (2H, dd, *J* = 12.0 Hz, *J* = 19.6 Hz), 4.38 (1H, d, *J* = 11.6 Hz), 4.04 – 4.08 (2H, dd, *J* = 4.4 Hz, *J* = 10.4 Hz), 3.95 (1H, d, *J* = 3.2 Hz), 3.59 – 3.70 (3H, m), 3.49 – 3.53 (1H, dd, *J* = 5.6 Hz, *J* = 9.6 Hz), 3.43 – 3.48 (2H, m), 3.38 (3H, s), 3.30 – 3.35 (1H, t, *J* = 9.2 Hz), 2.70 – 2.74 (2H, m), 2.63 (1H, d, *J* = 6.8 Hz), 2.43 (1H, d, *J* = 6.0 Hz), 1.90 – 1.95 (2H, dd, *J* = 6.8 Hz, *J* = 12.4 Hz). **δ_C(100 MHz, $CDCl_3$):** 210.9, 138.4, 137.6, 136.9, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 127.5, 100.9, 99.7, 83.9, 81.3, 78.6, 74.4, 73.3, 73.2, 72.1, 71.1, 70.2, 68.3, 62.4, 55.2, 33.8, 27.3. **HRMS (ESI)** calcd for $C_{35}H_{42}O_{10}$+Na 645.2676, found 645.2677.

3. NMR Spectra



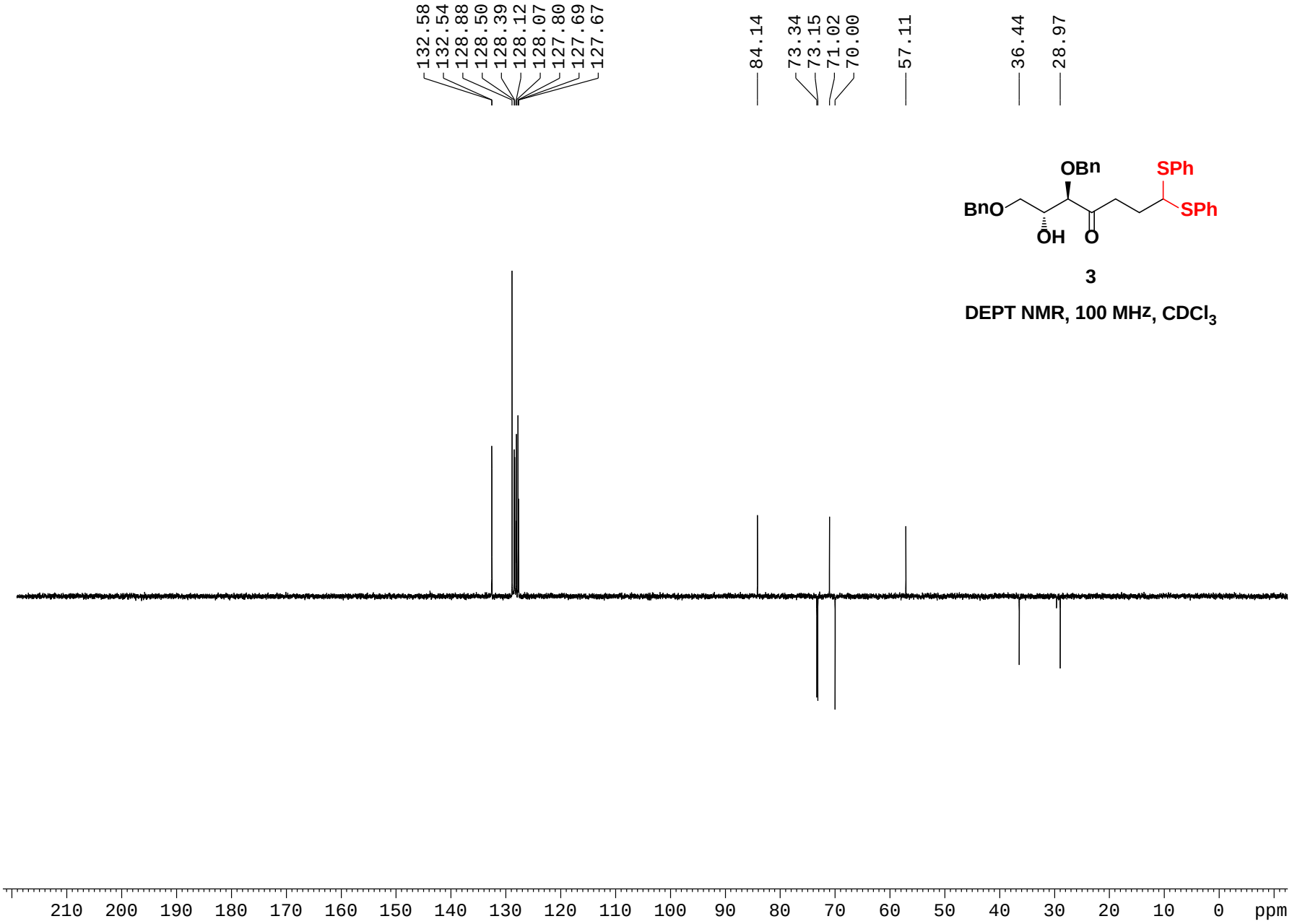
3

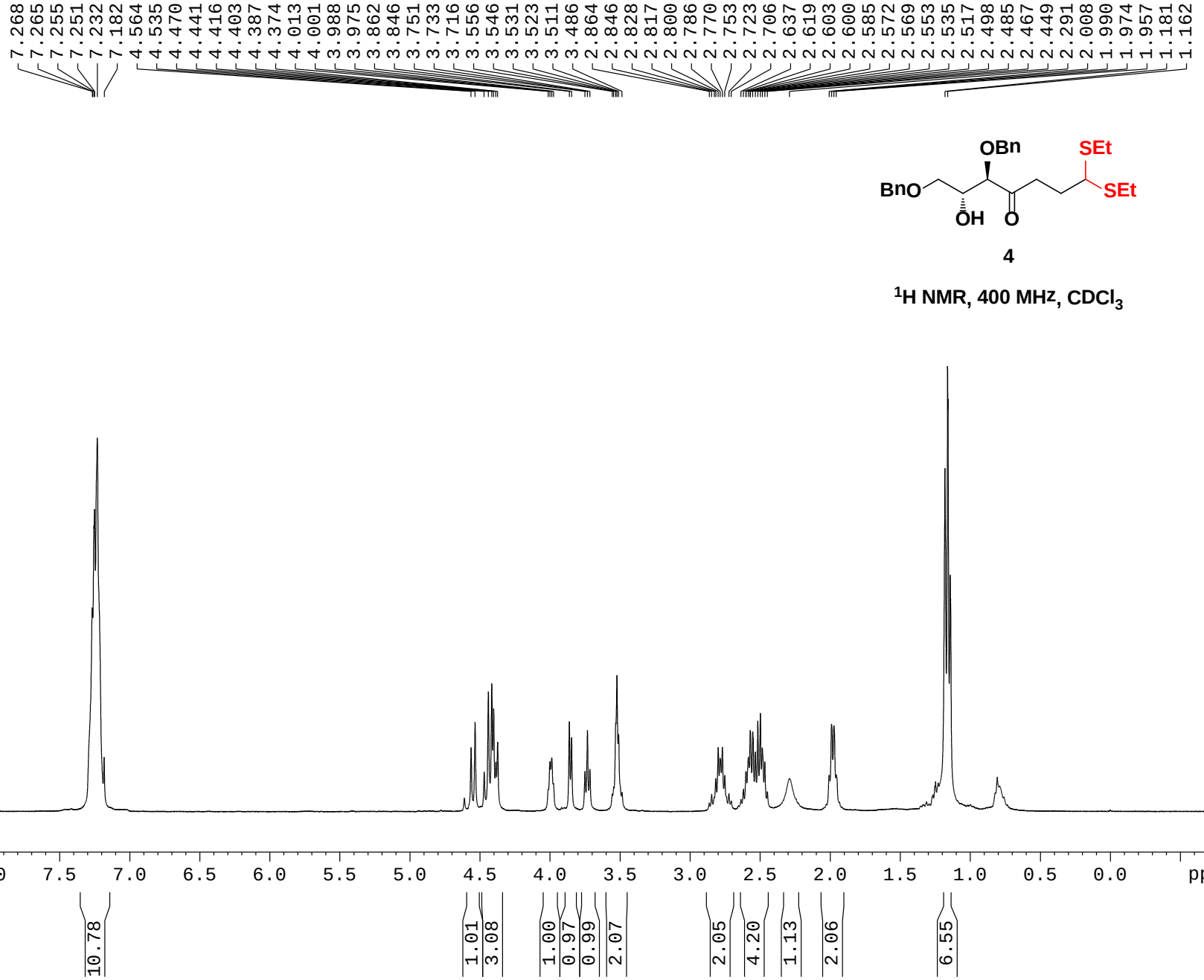
^{1}H NMR, 400 MHz, $CDCl_3$

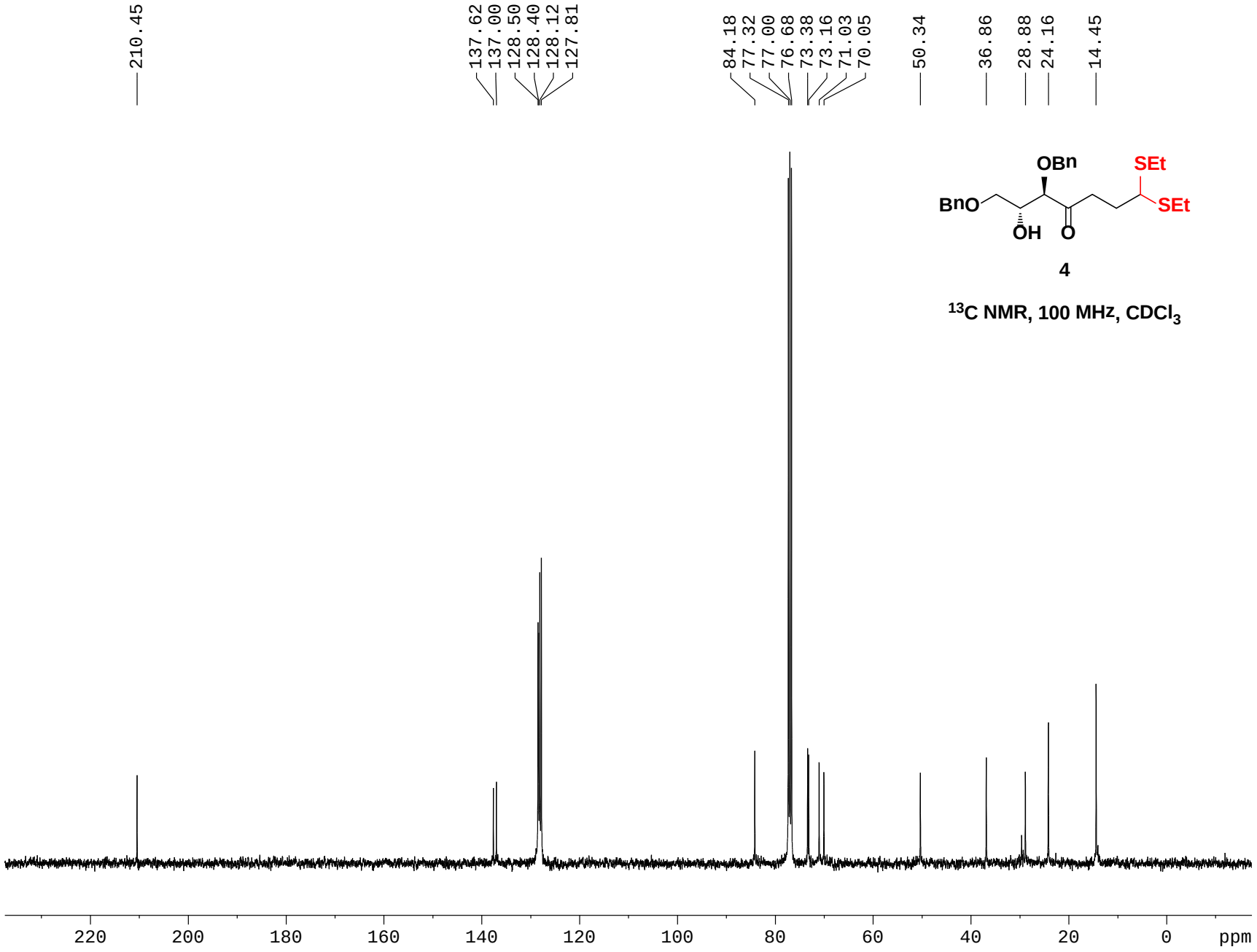


3

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






210.45
137.62
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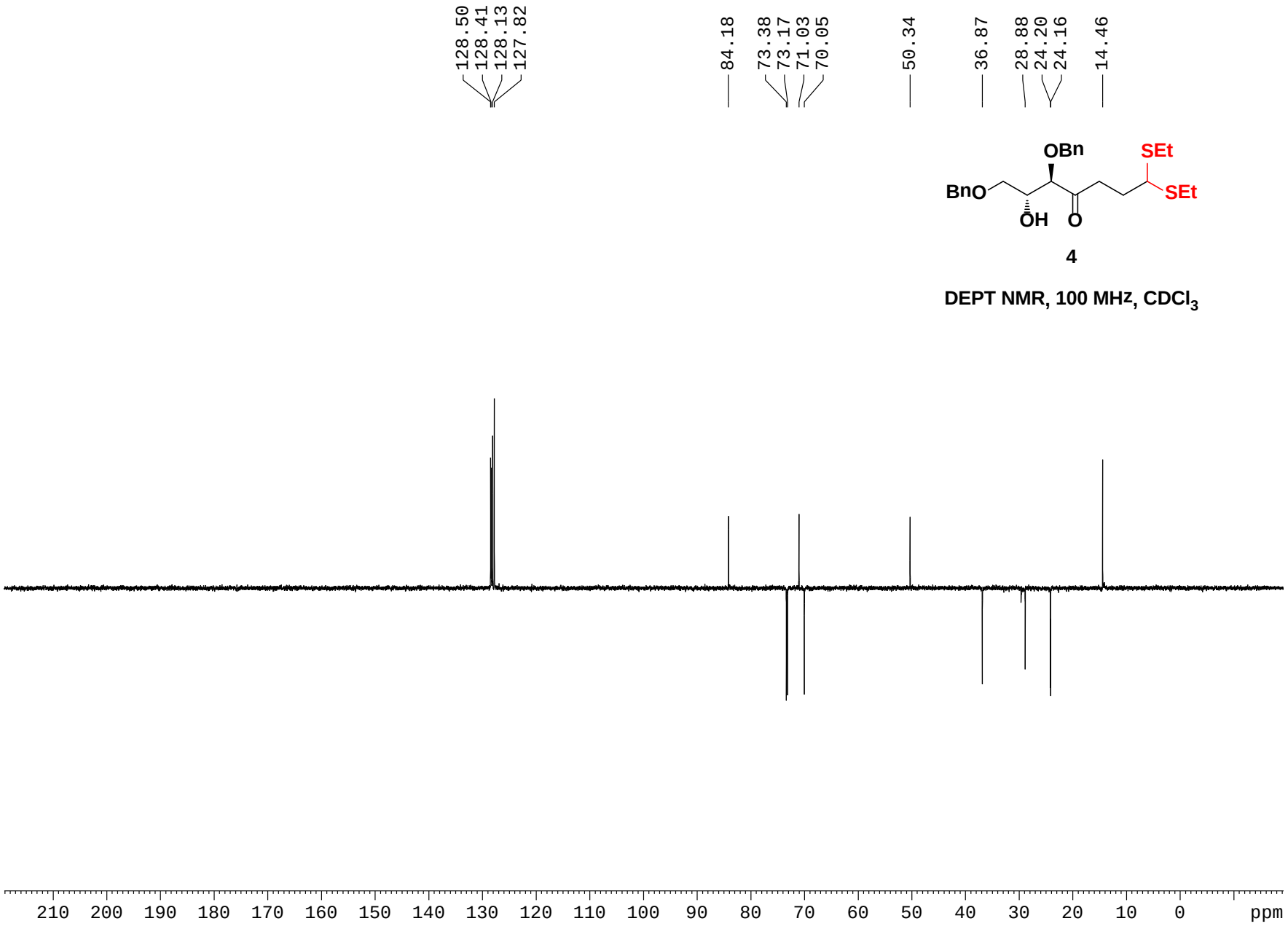
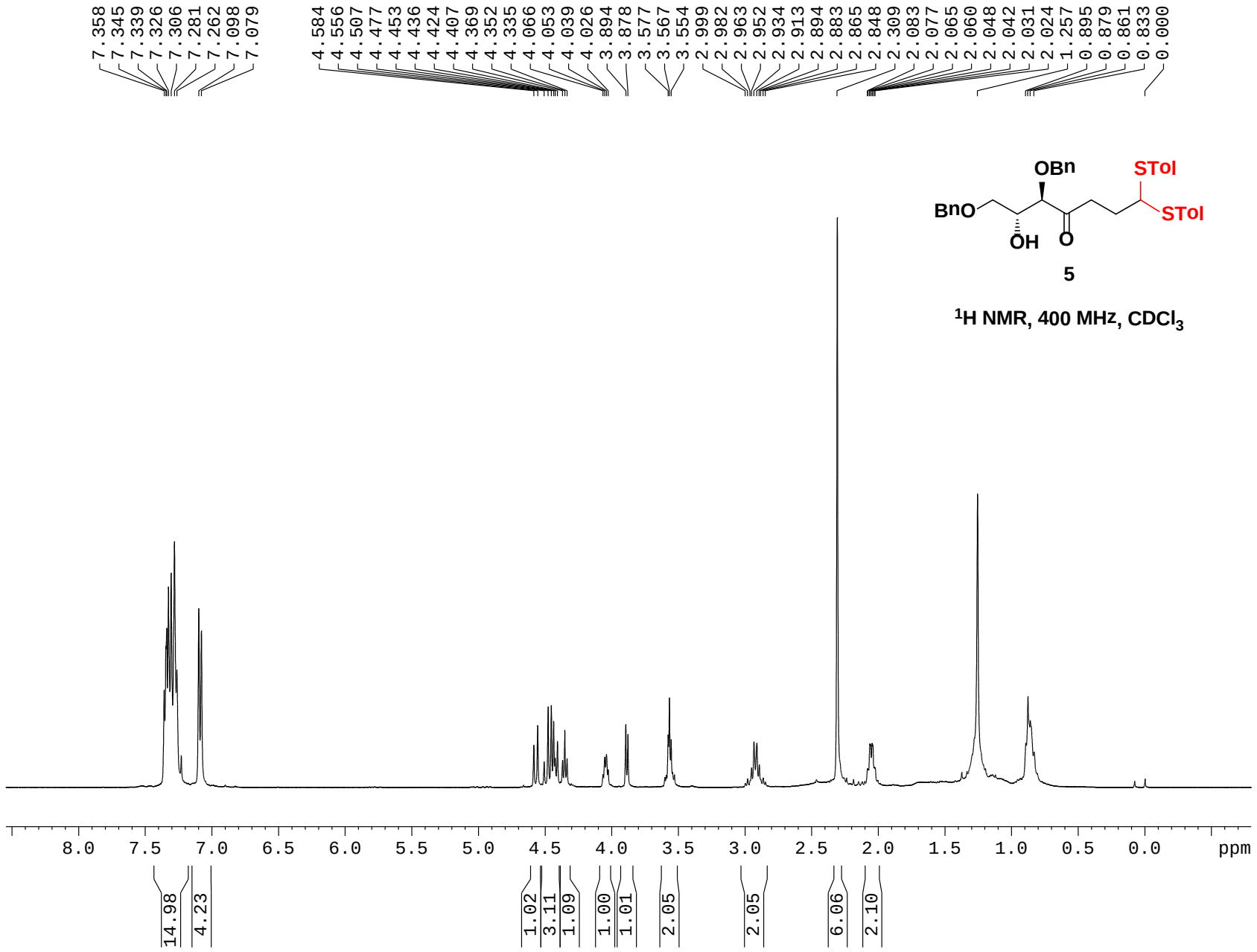
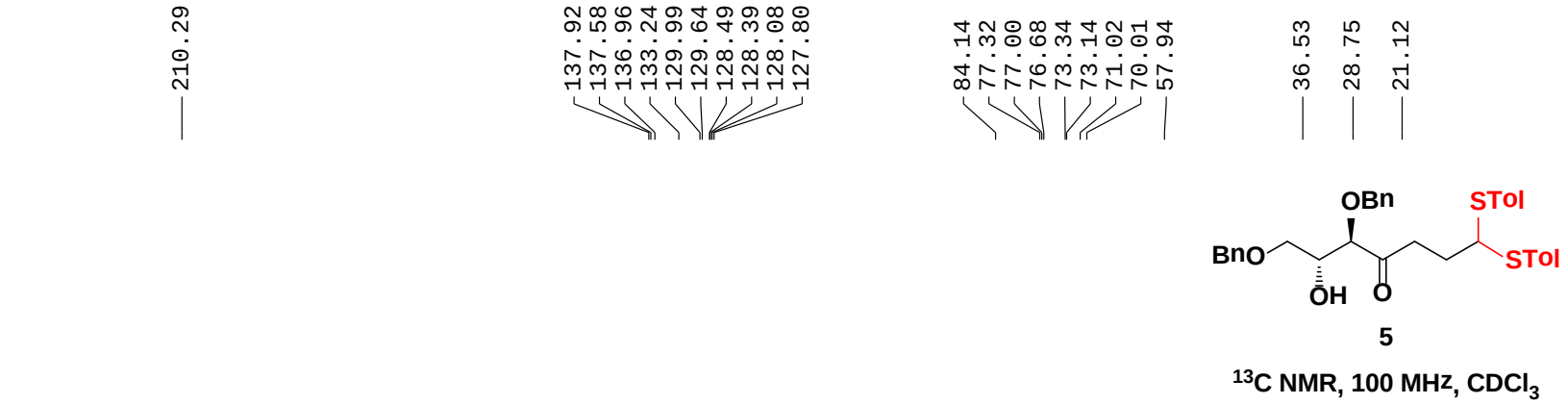
128.50
128.40
128.12
127.81
84.18
77.32
77.00
76.68
73.38
73.16
71.03
70.05
50.34
36.86
28.88
24.16
14.45
OBn
SEt
BnO
SEt
OH
O
4
13C NMR, 100 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm



4

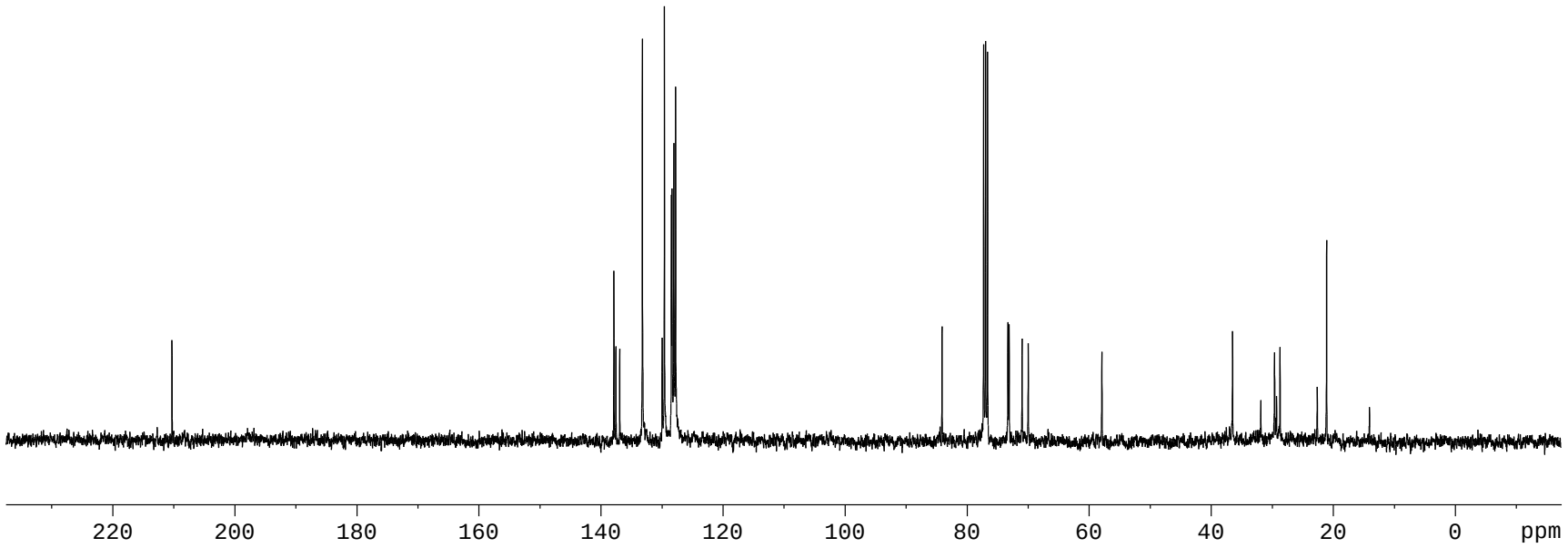
DEPT NMR, 100 MHz, $CDCl_3$

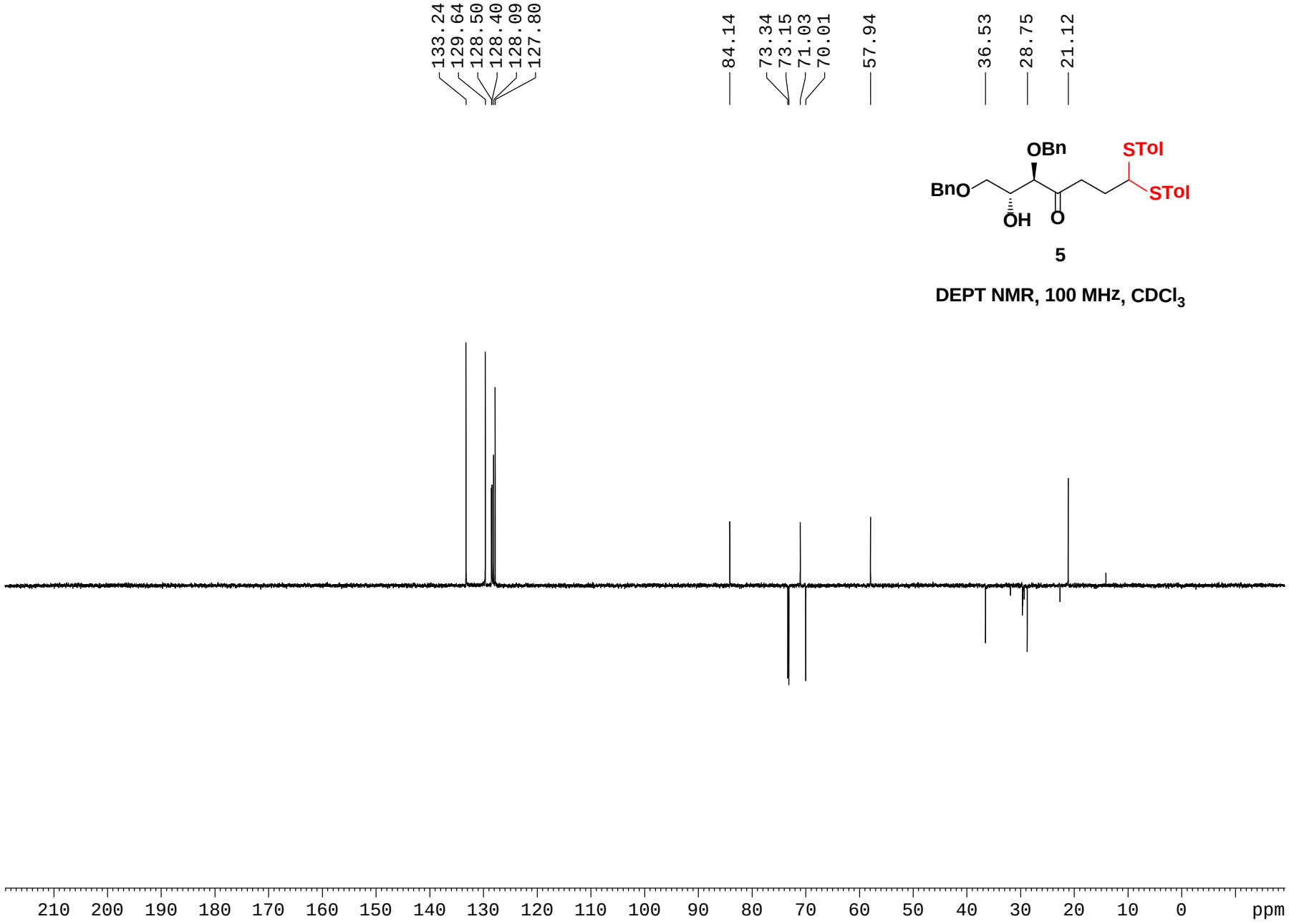




5

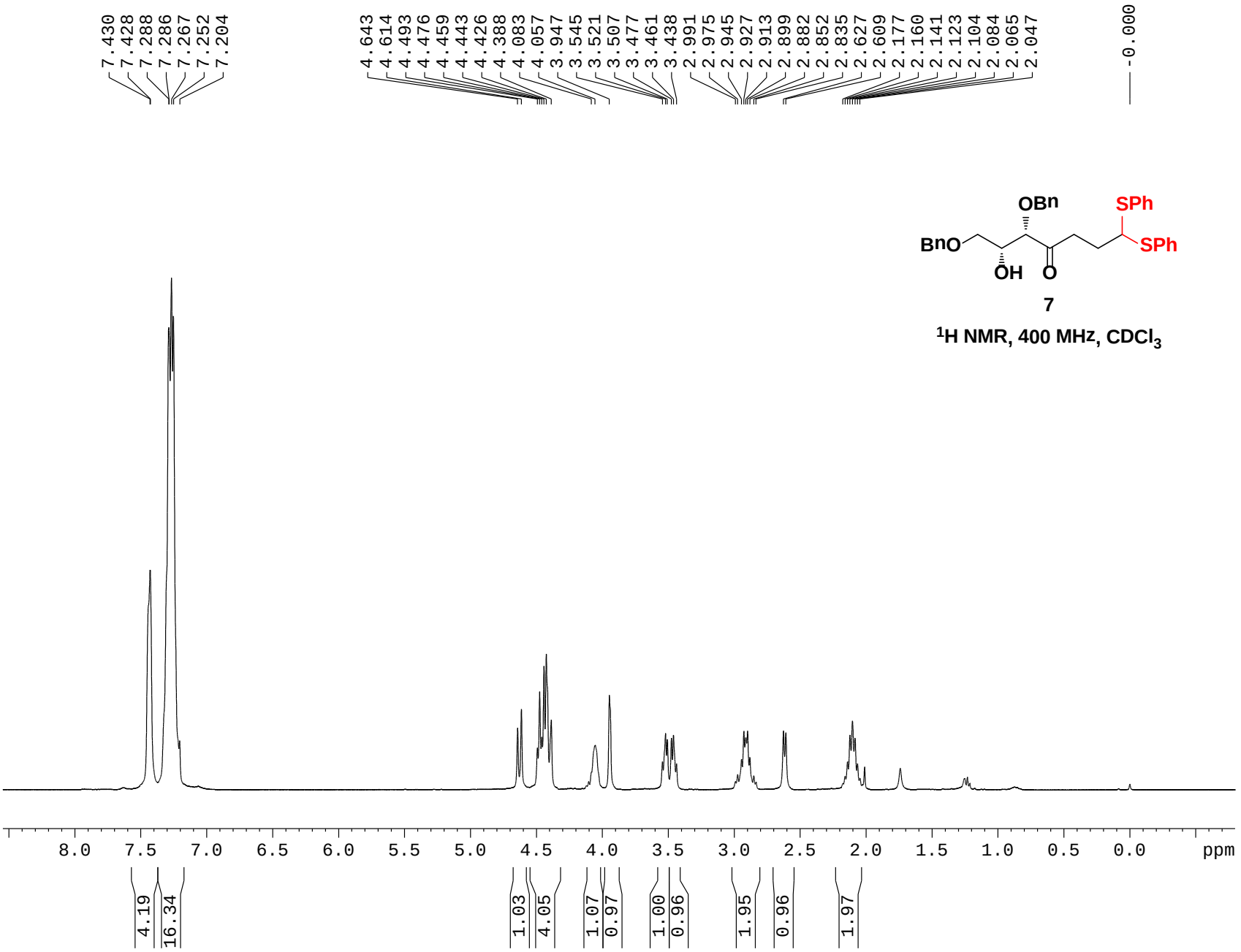
^{13}C NMR, 100 MHz, $CDCl_3$





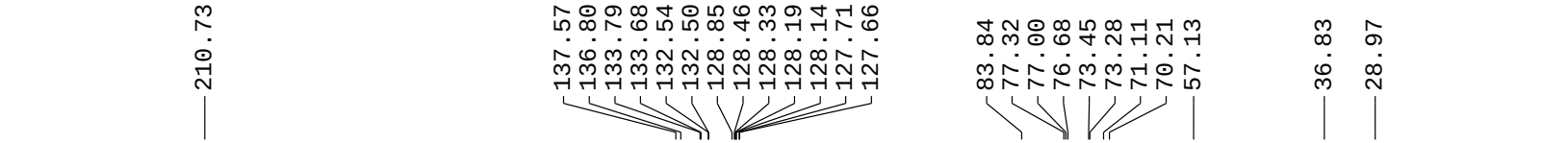
5

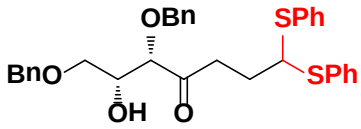
DEPT NMR, 100 MHz, $CDCl_3$



7

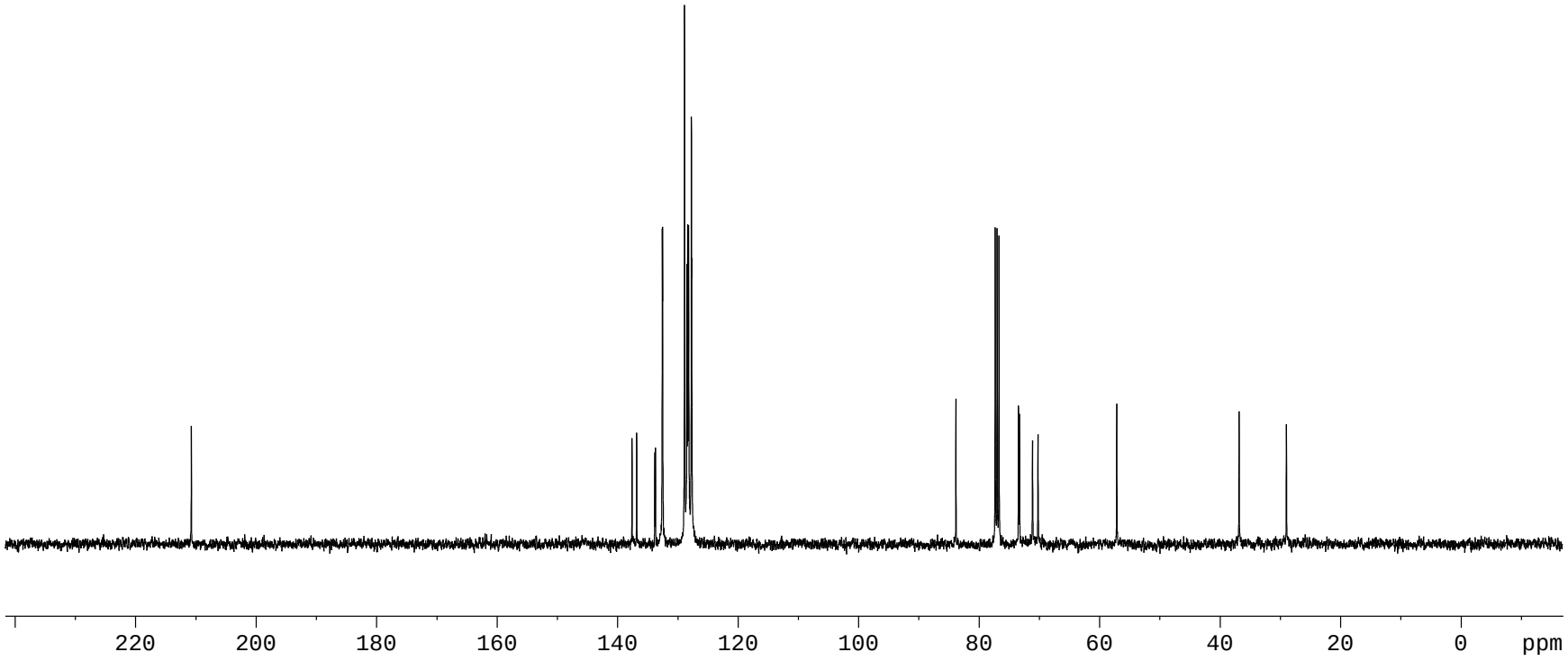
^{1}H NMR, 400 MHz, $CDCl_3$

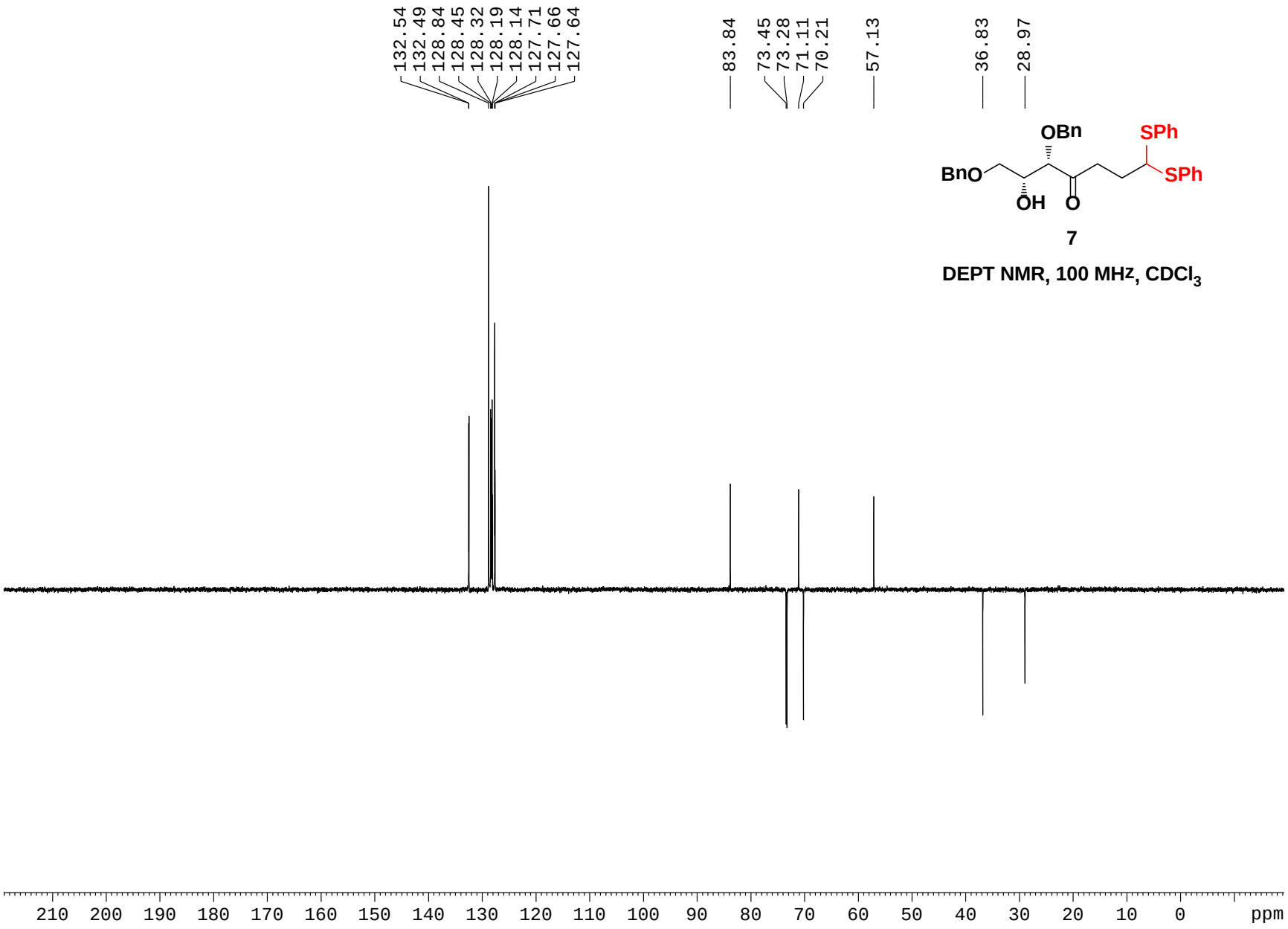




7

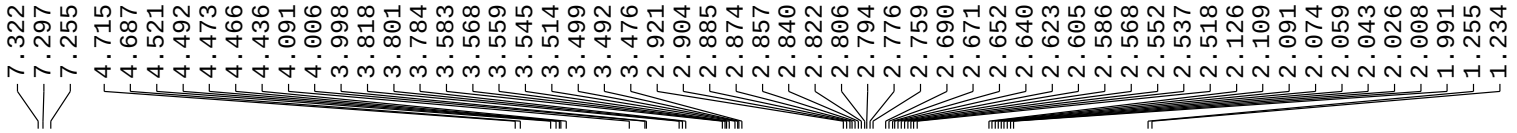
^{13}C NMR, 100 MHz, $CDCl_3$

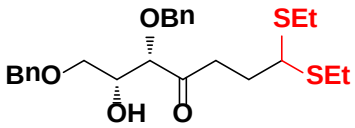




7

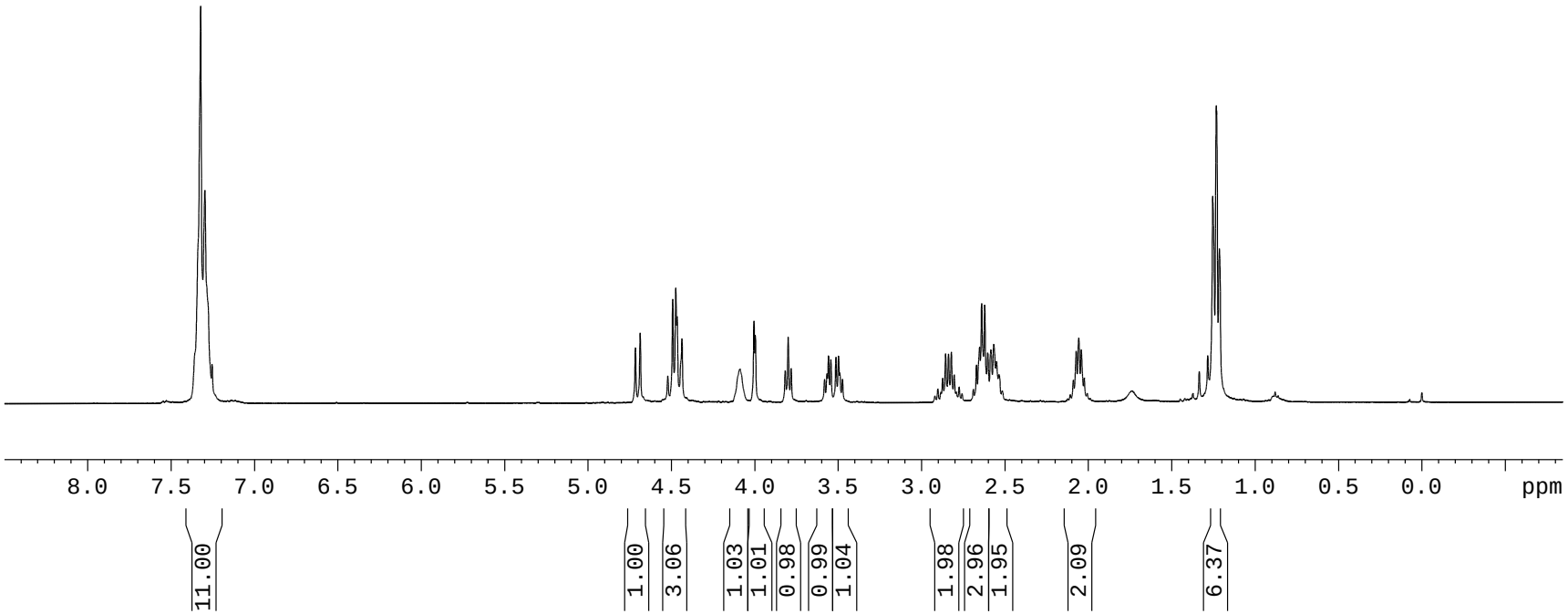
DEPT NMR, 100 MHz, $CDCl_3$

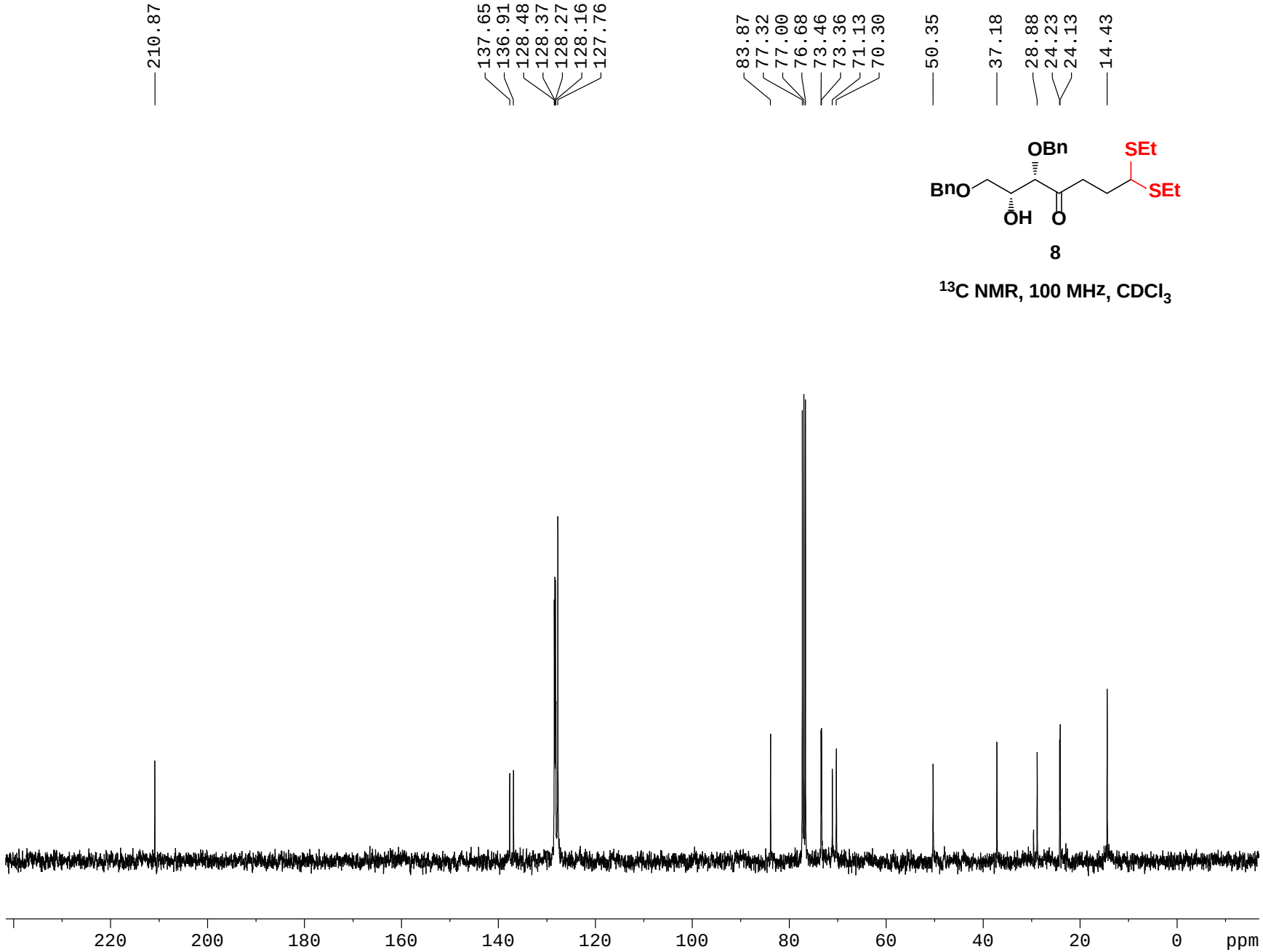




8

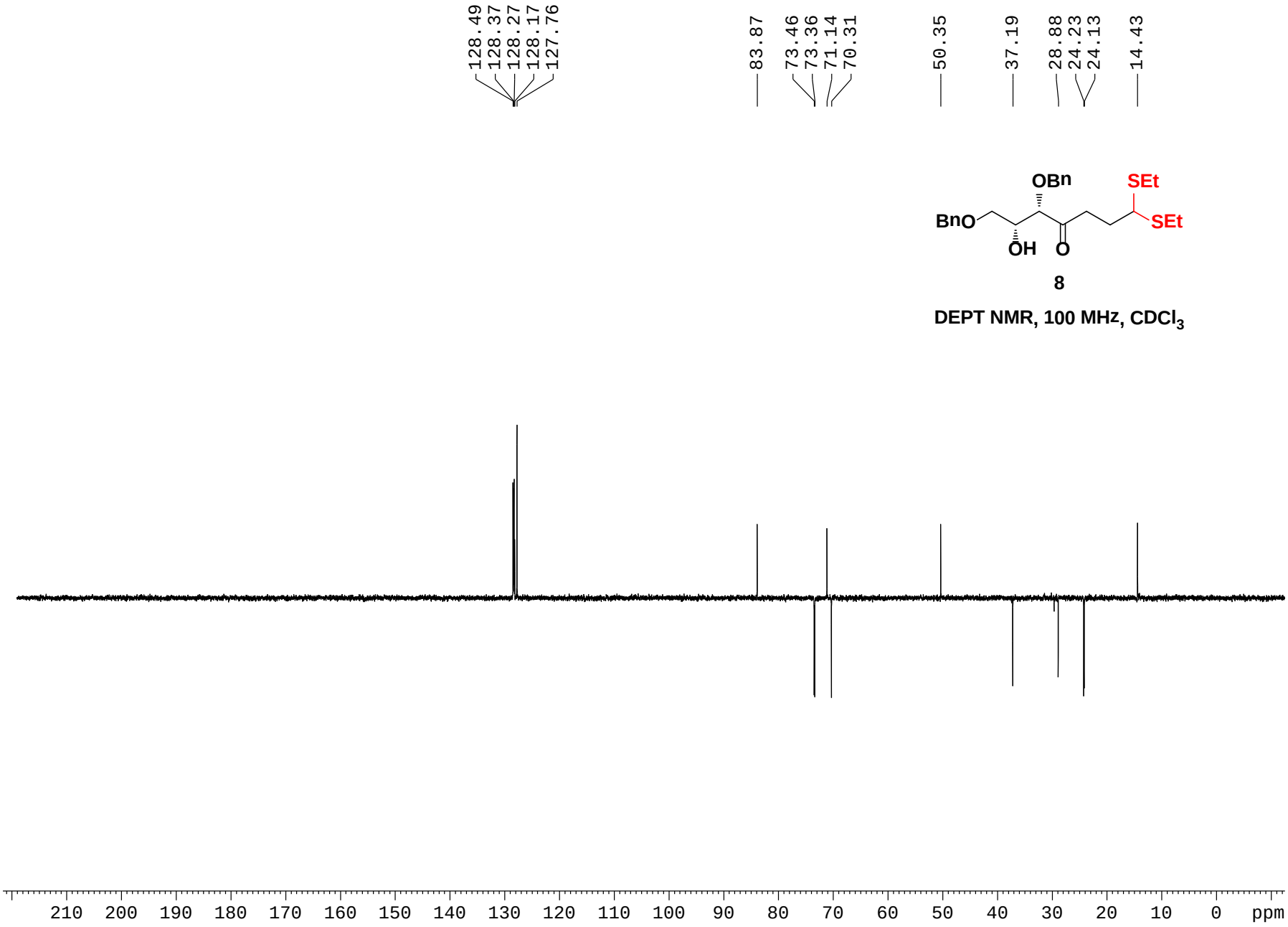
^{1}H NMR, 400 MHz, $CDCl_3$





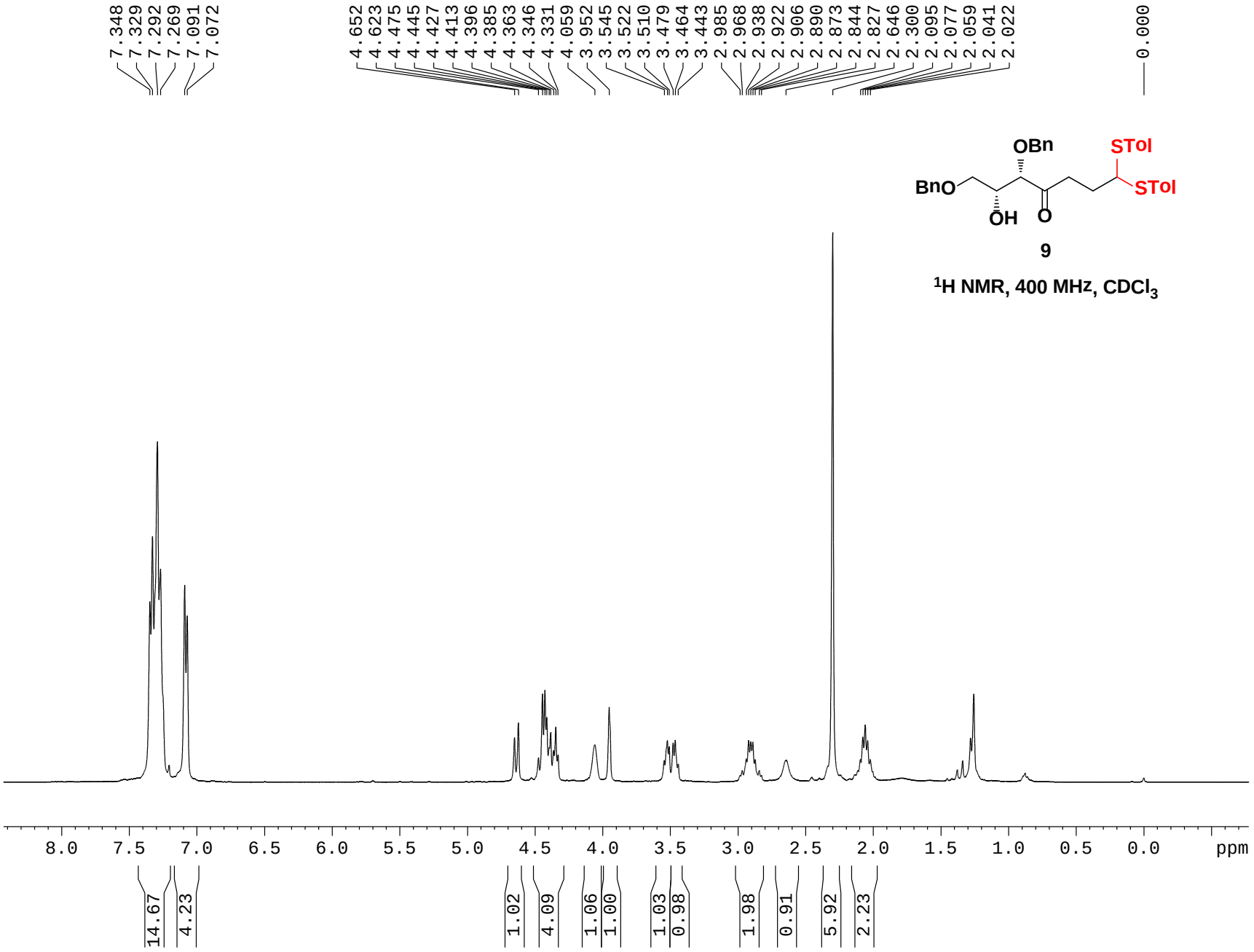
8

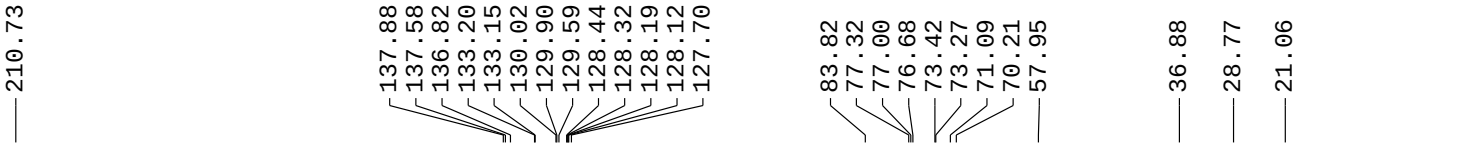
^{13}C NMR, 100 MHz, $CDCl_3$

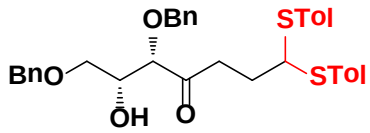


8

DEPT NMR, 100 MHz, $CDCl_3$

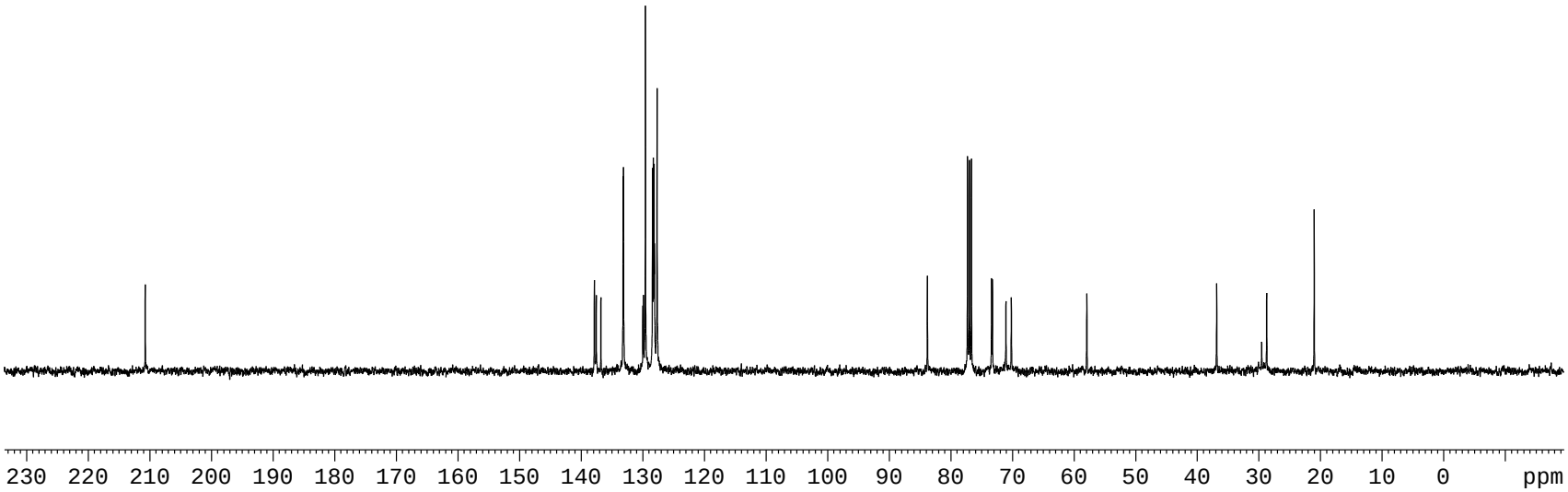


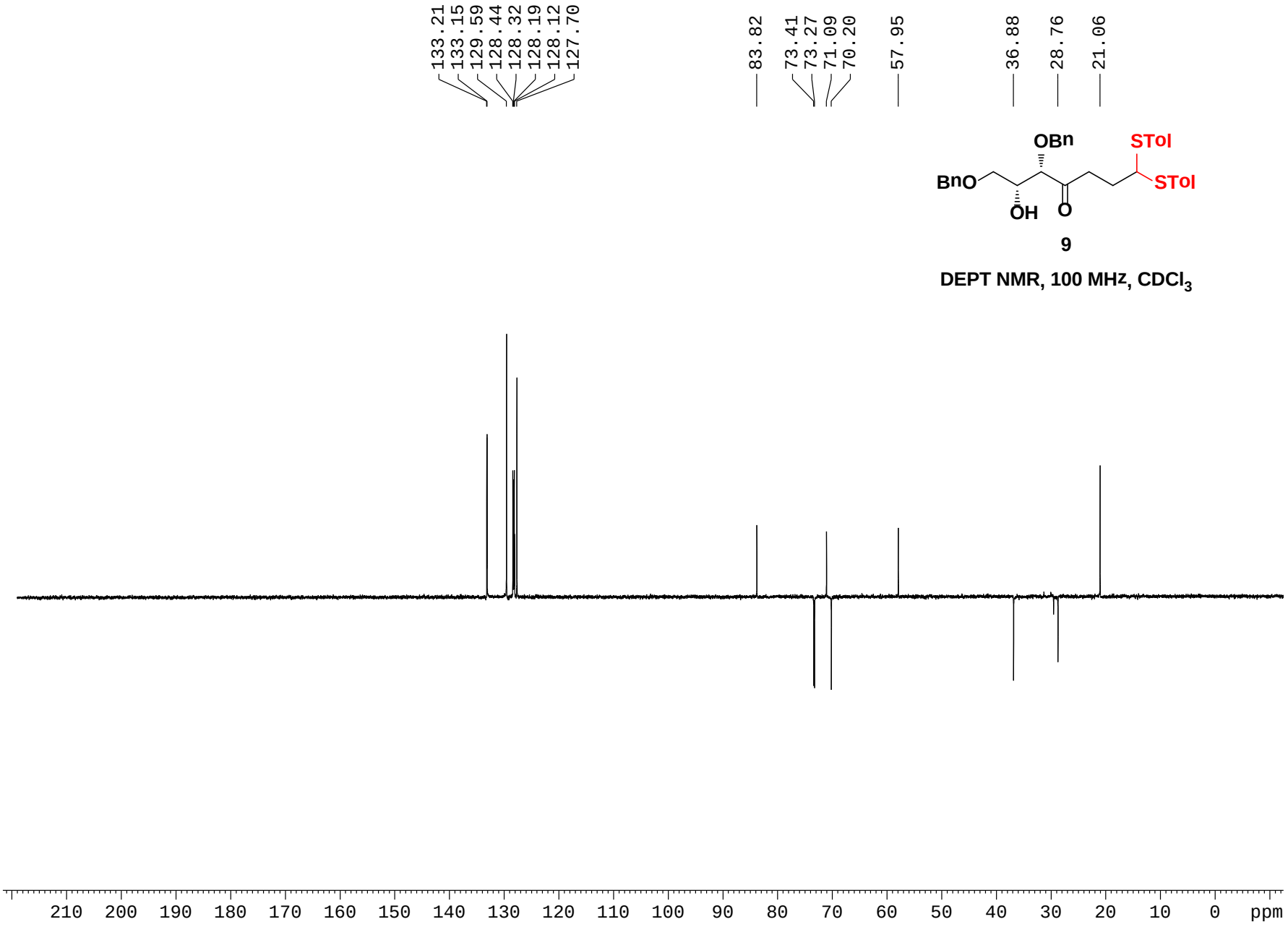




9

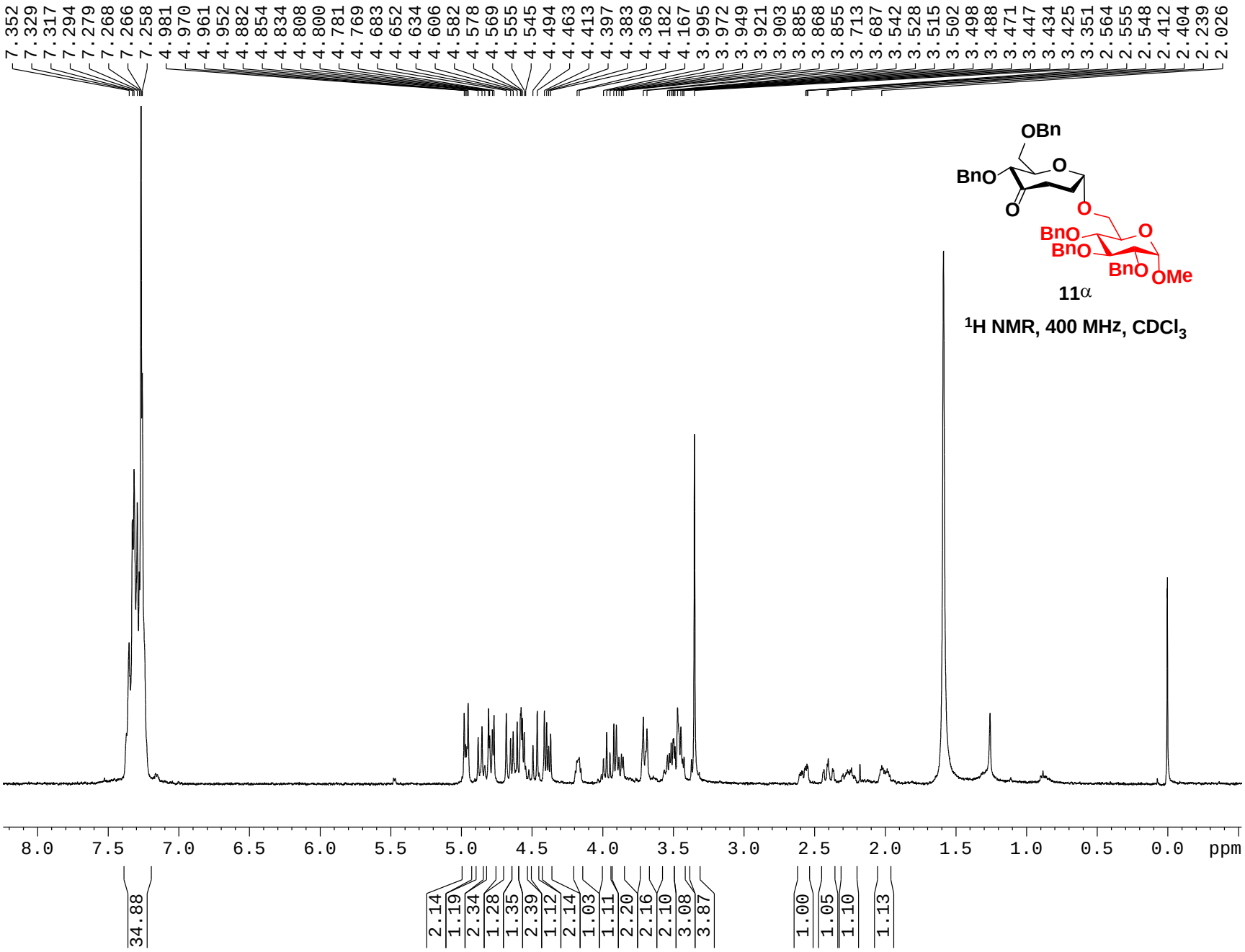
^{13}C NMR, 100 MHz, $CDCl_3$

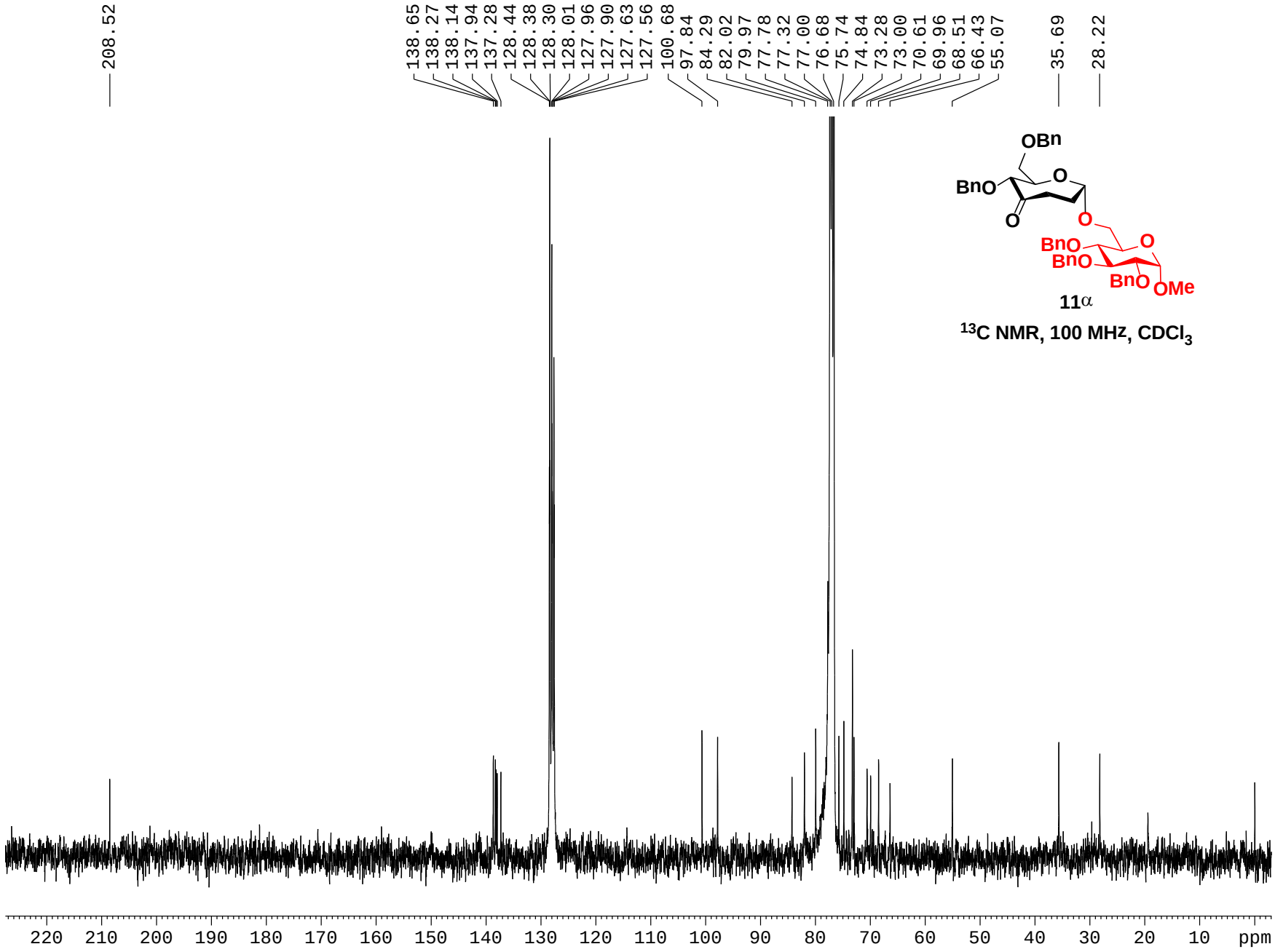


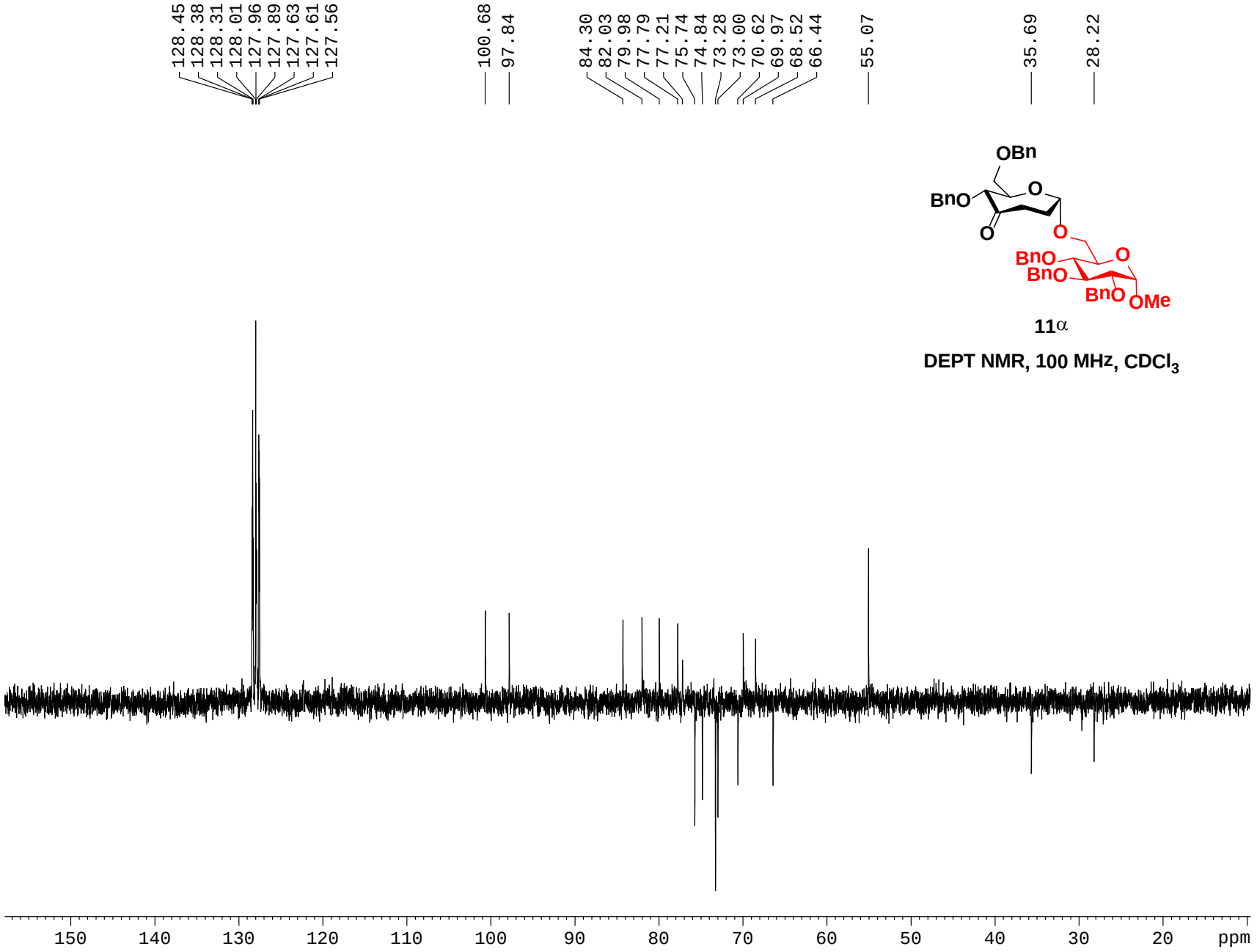


9

DEPT NMR, 100 MHz, $CDCl_3$

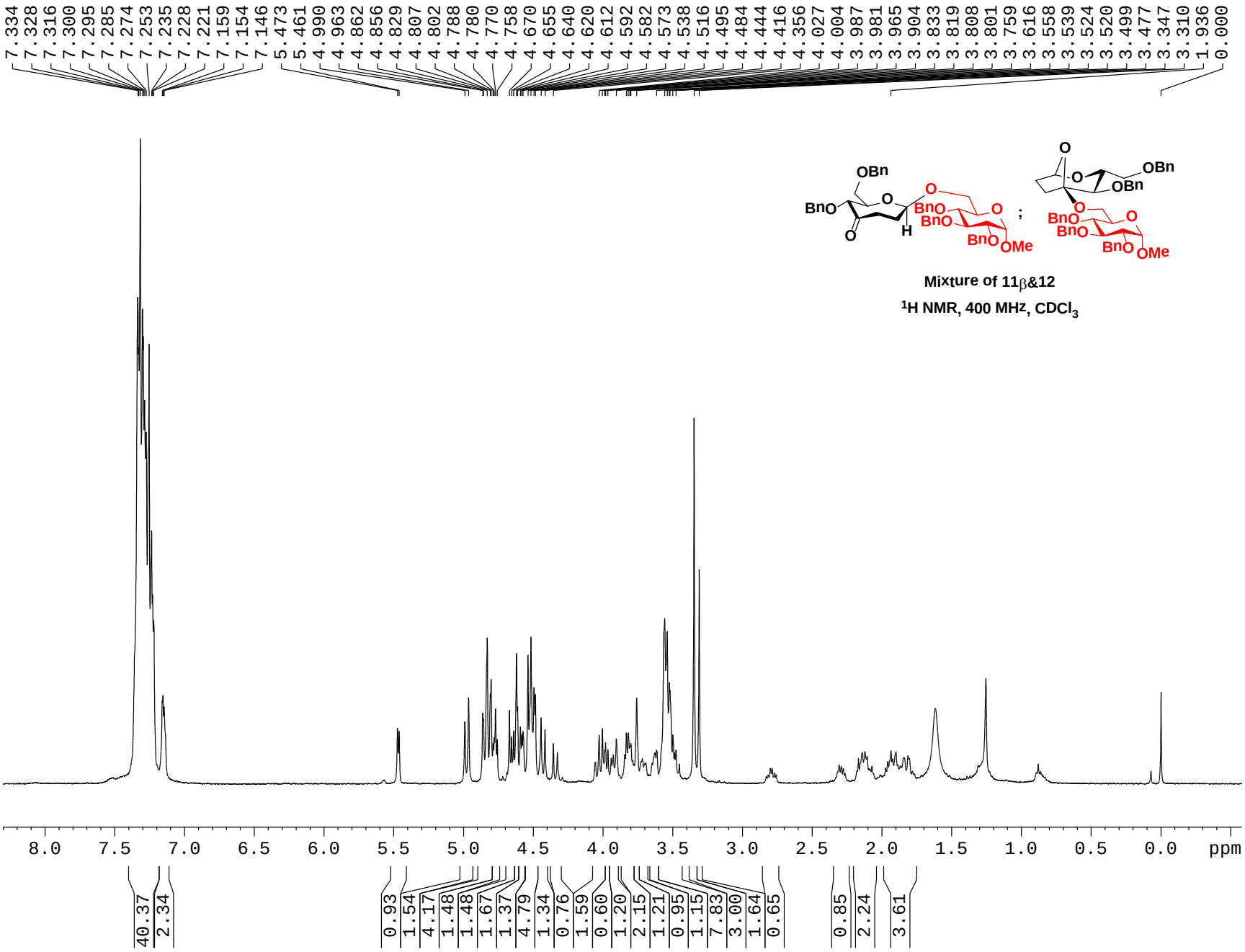


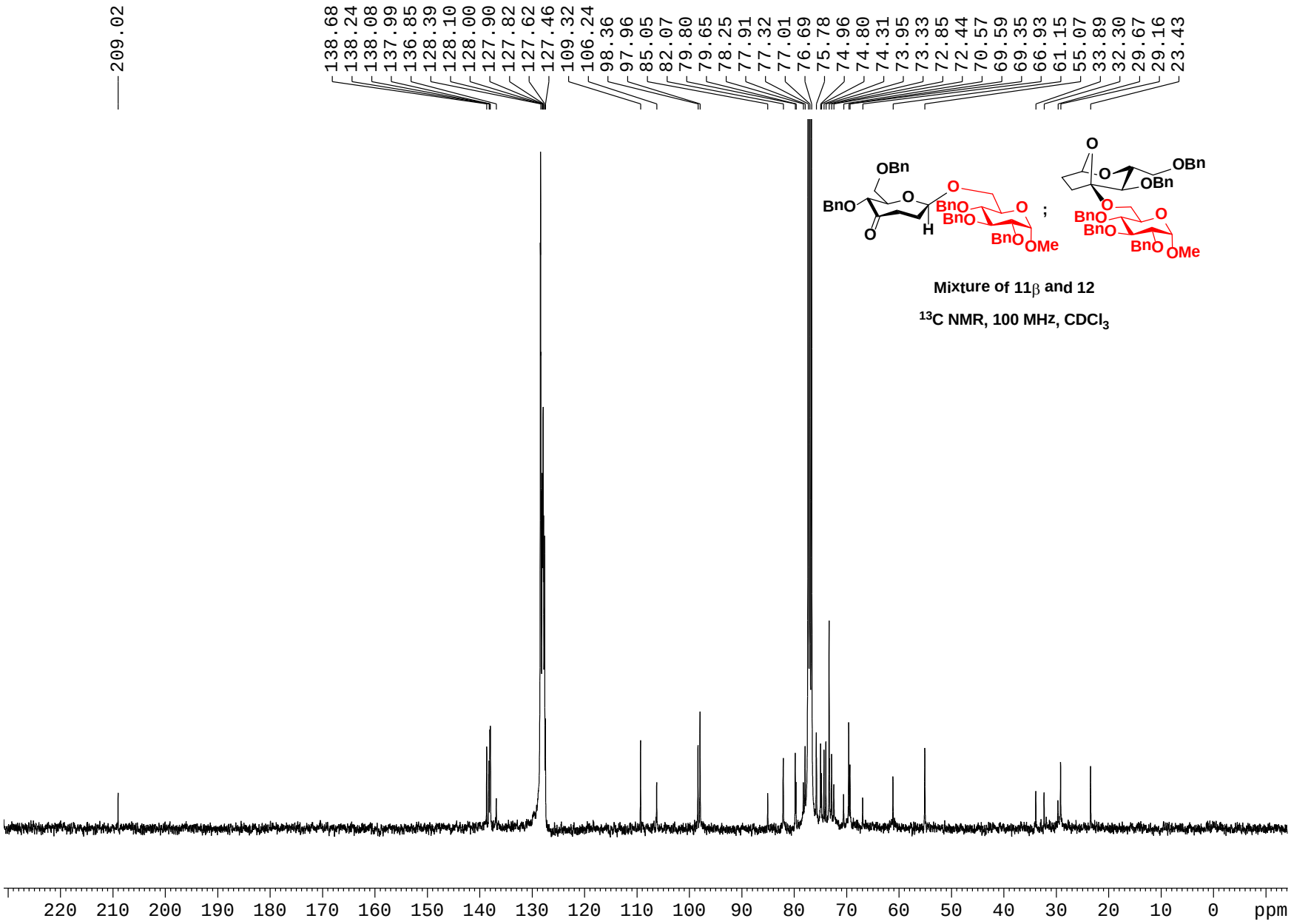




11α

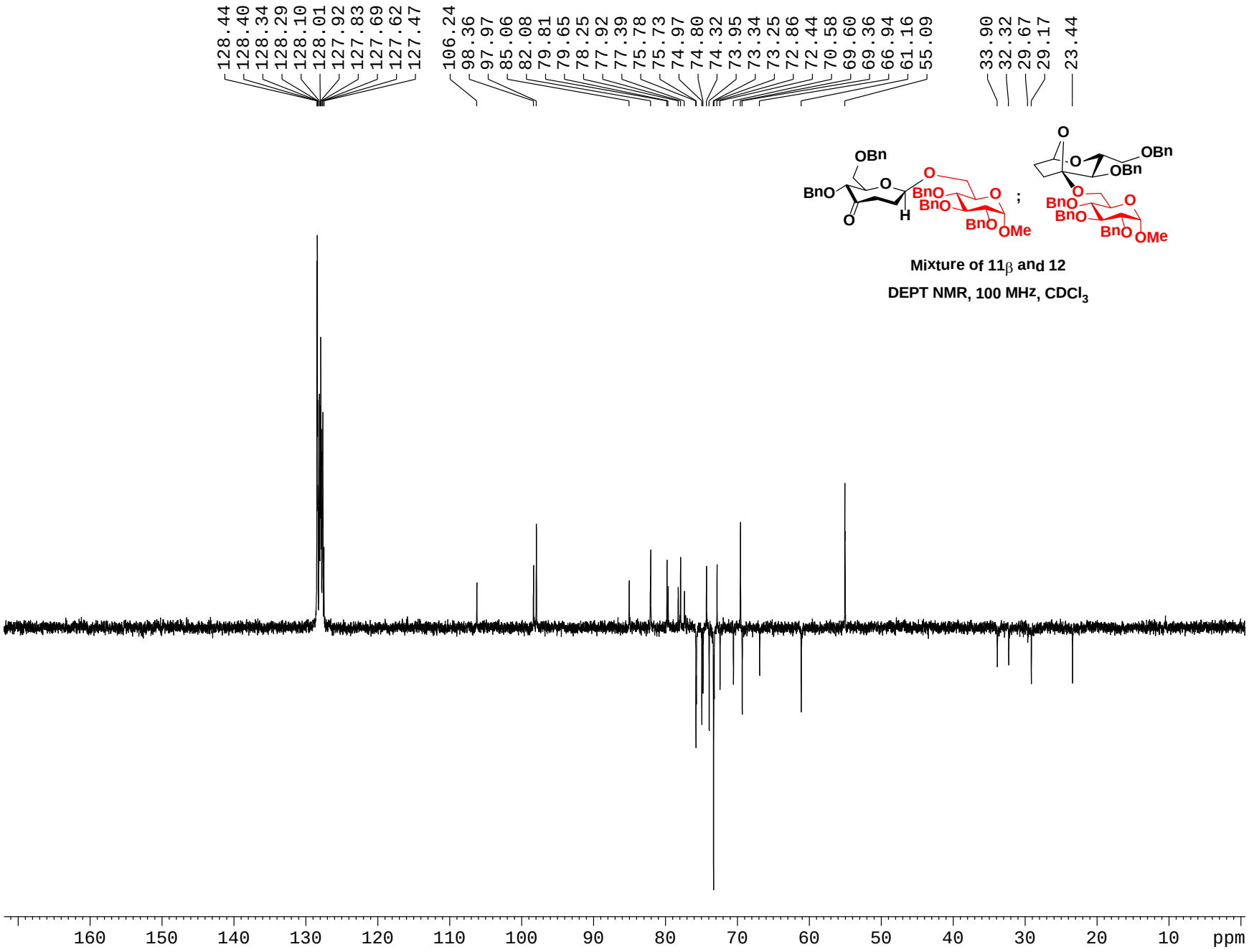
DEPT NMR, 100 MHz, $CDCl_3$

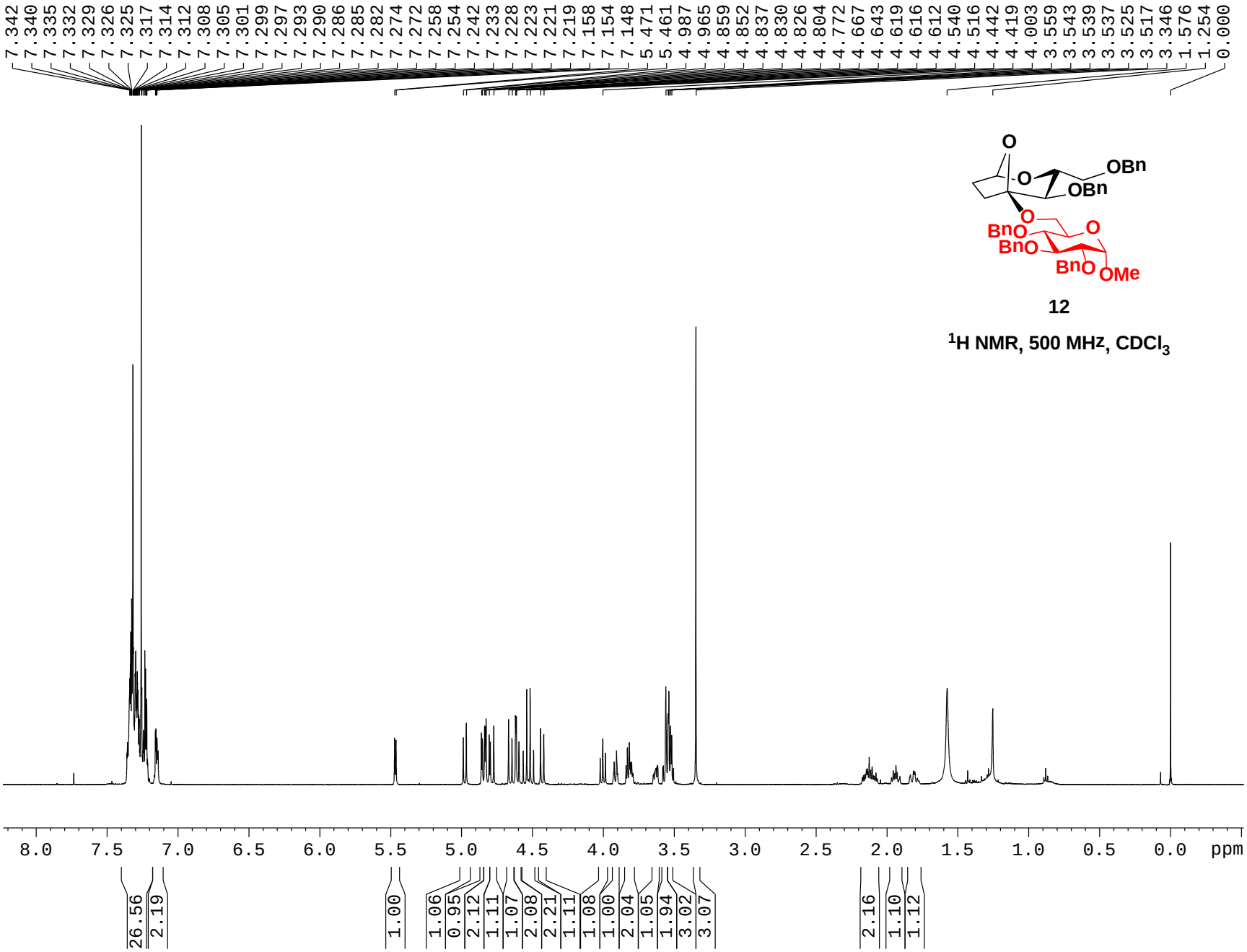




Mixture of 11β and 12

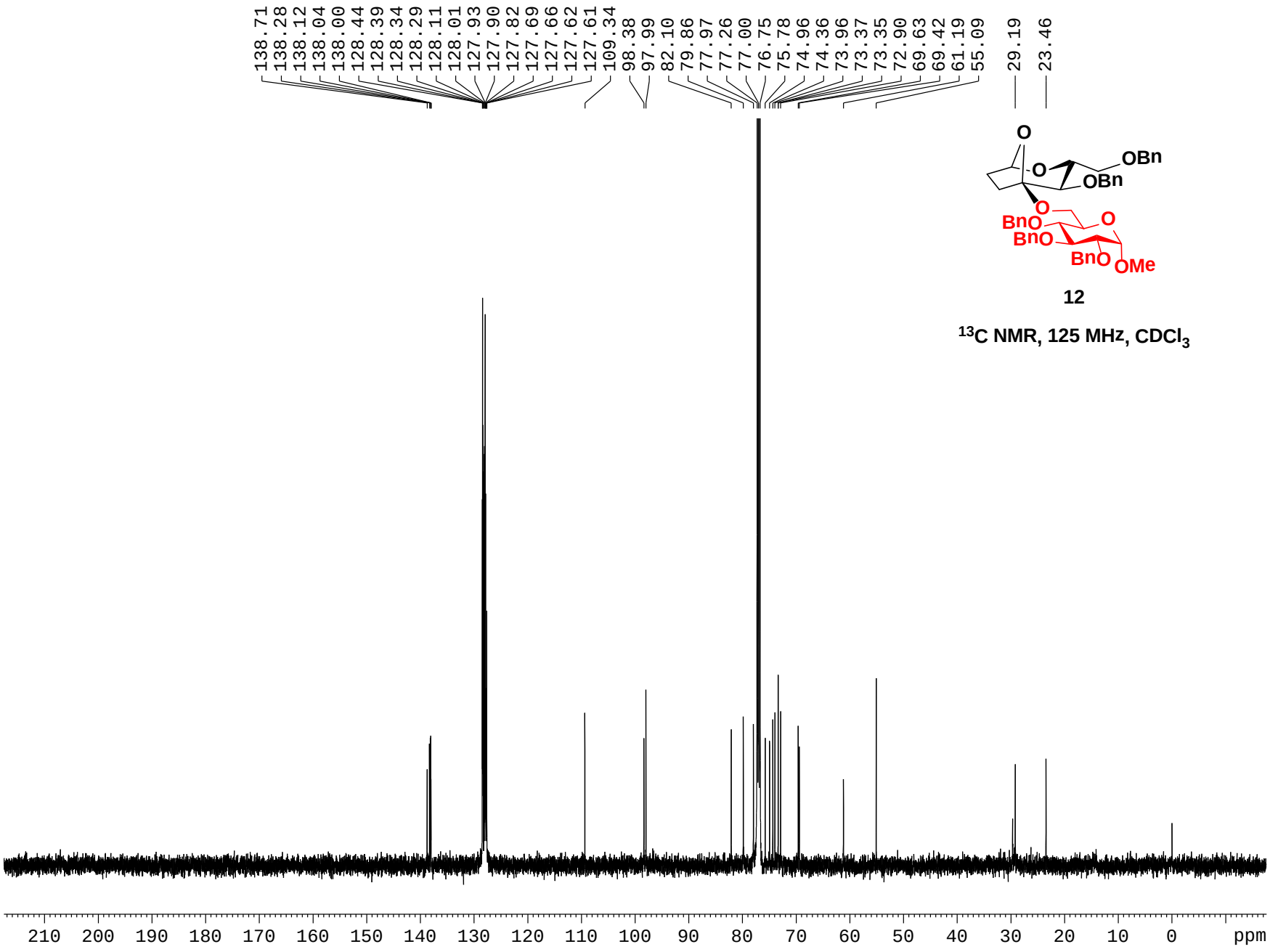
^{13}C NMR, 100 MHz, $CDCl_3$





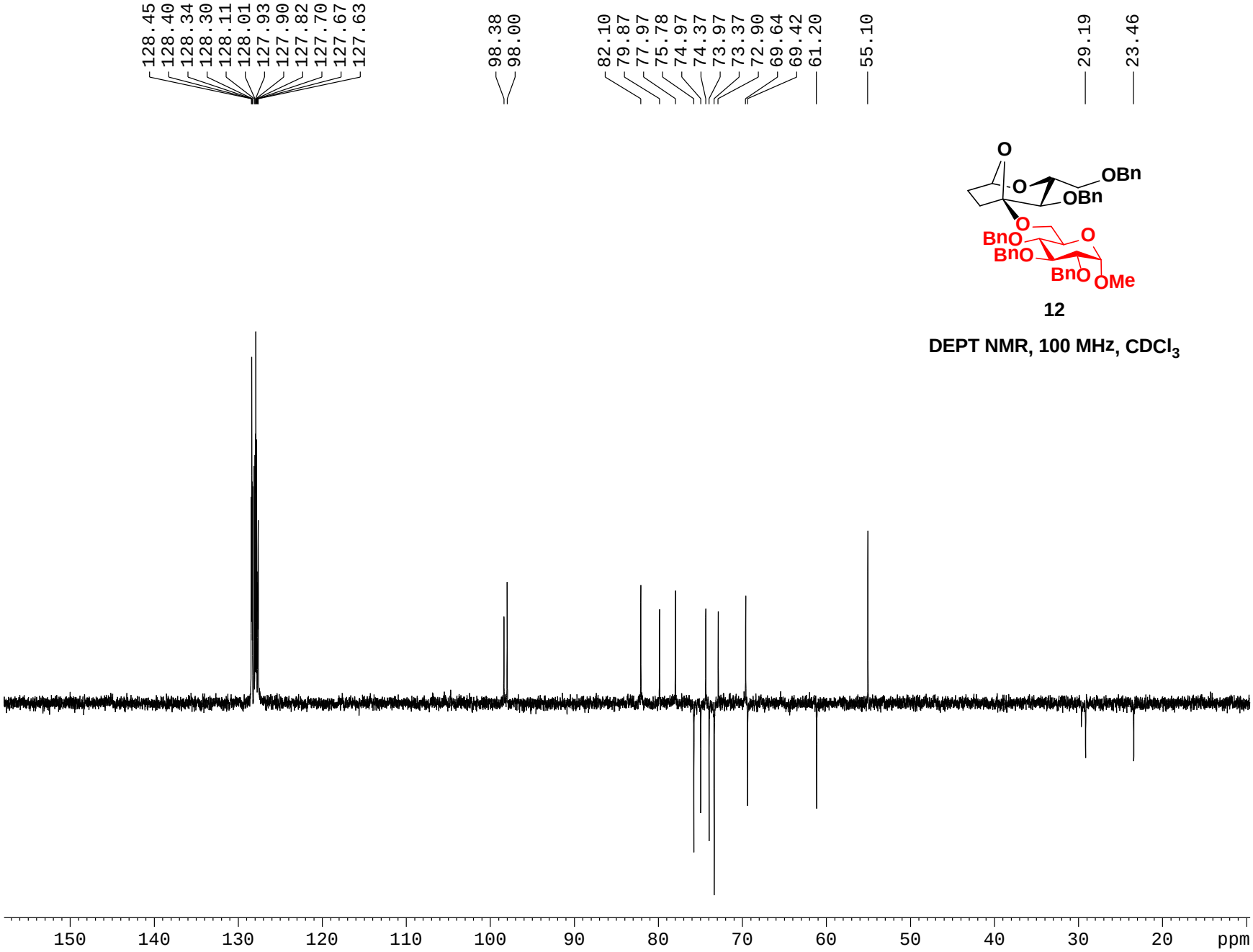
12

^{1}H NMR, 500 MHz, $CDCl_3$



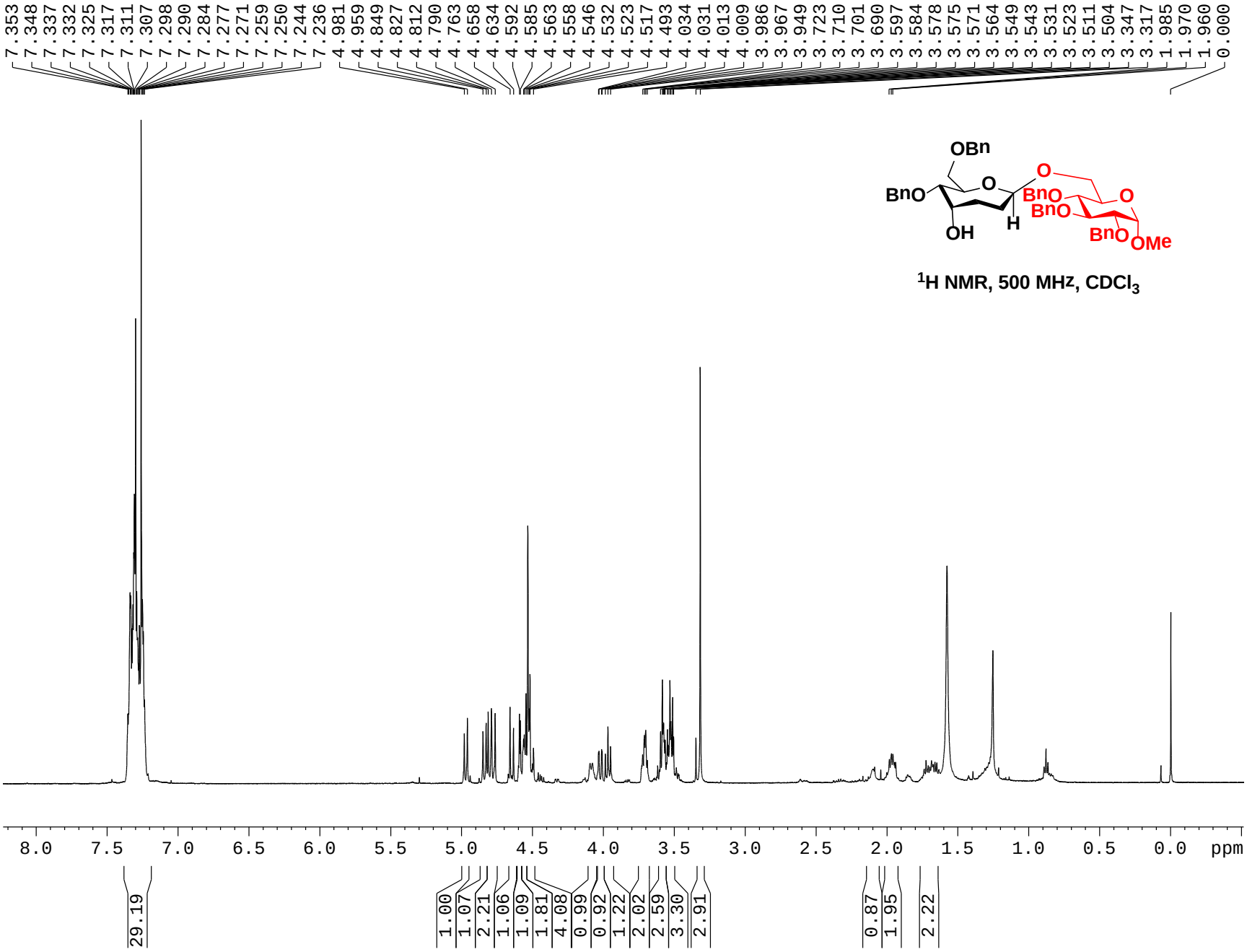
12

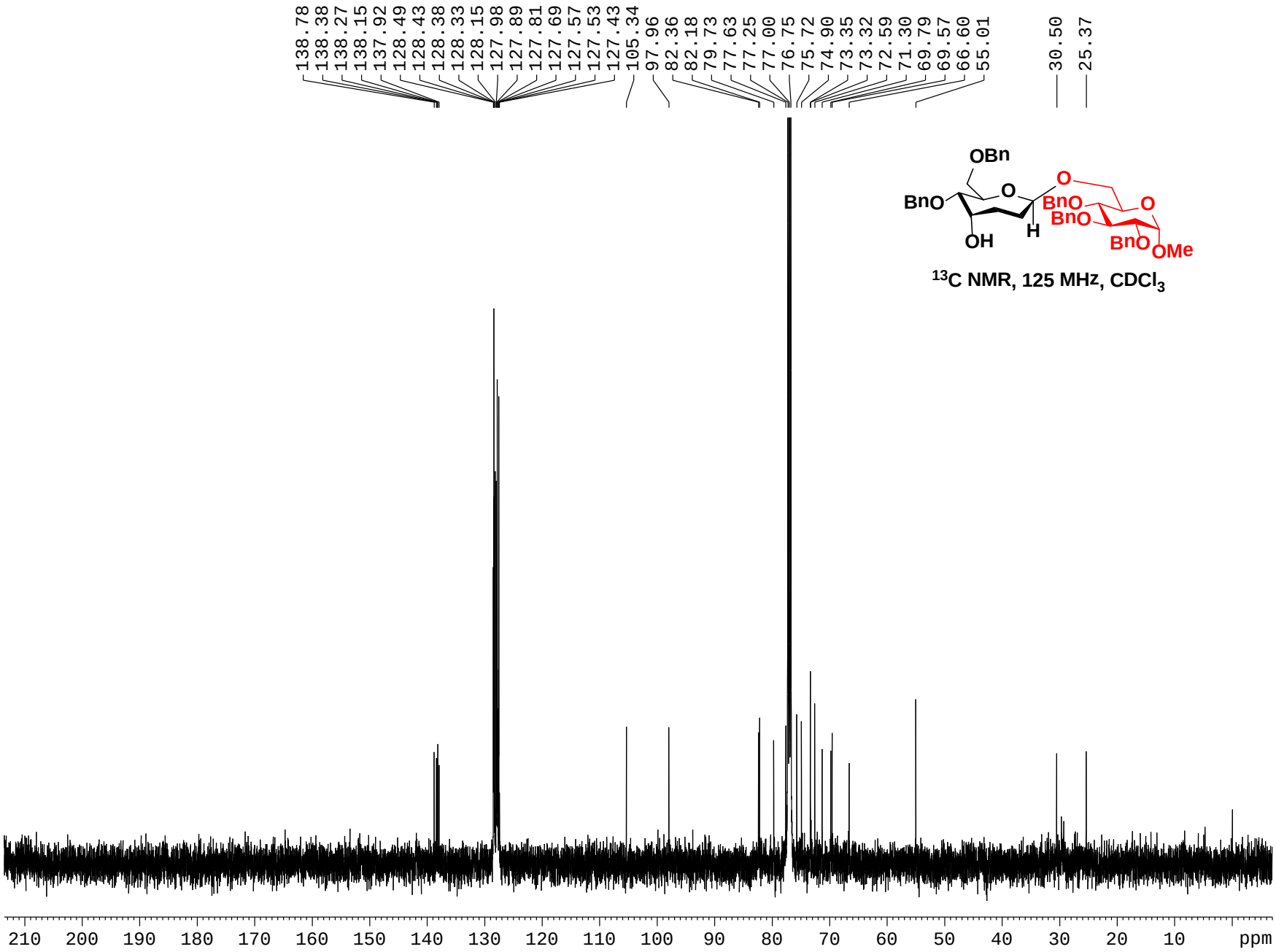
^{13}C NMR, 125 MHz, $CDCl_3$



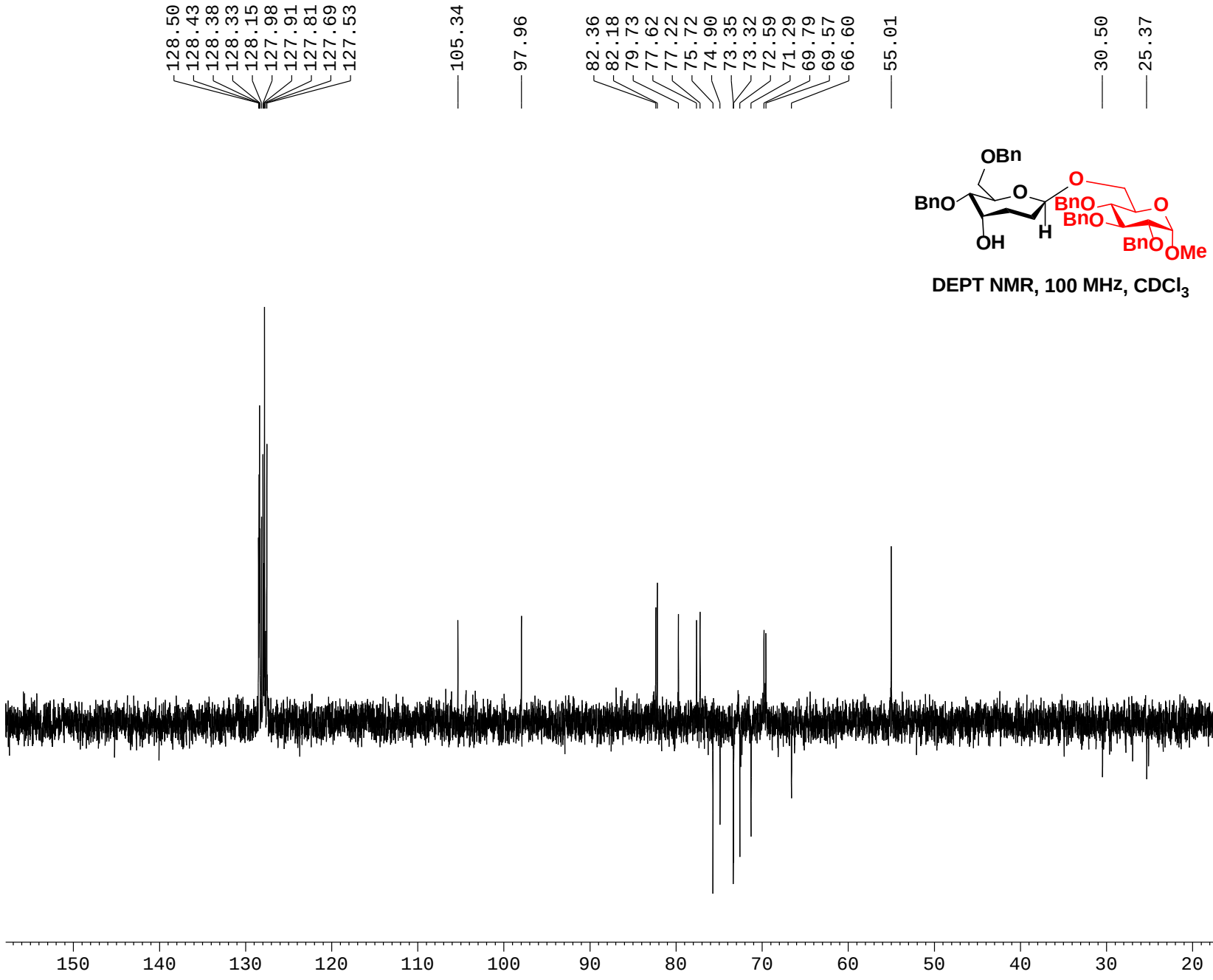
12

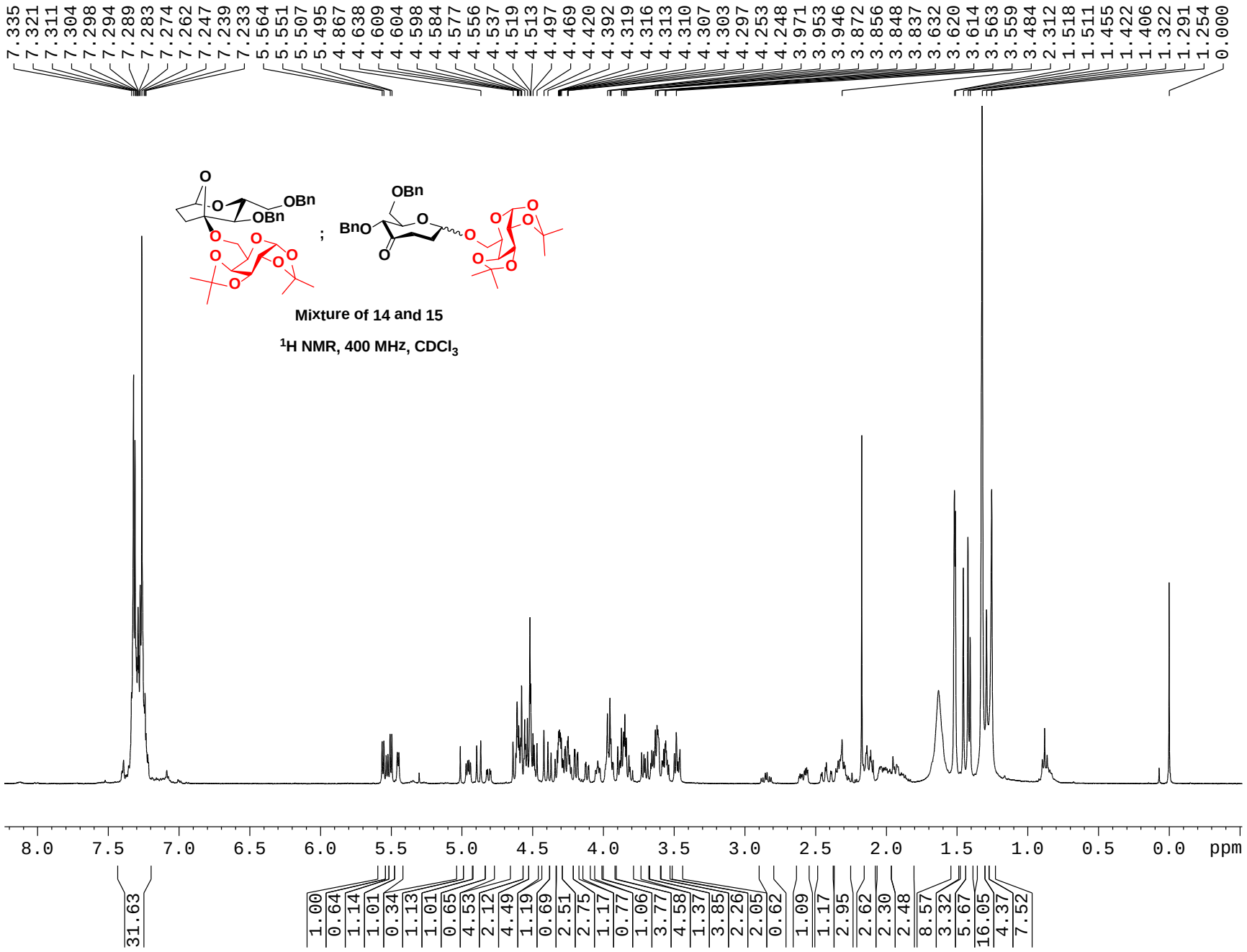
DEPT NMR, 100 MHz, $CDCl_3$





^{13}C NMR, 125 MHz, $CDCl_3$




7.335
7.321
7.311
7.304
7.298
7.294
7.289
7.283
7.274
7.262
7.247
7.239
7.233
5.564
5.551
5.507
5.495
4.867
4.638
4.609
4.604
4.598
4.584
4.577
4.556
4.537
4.519
4.513
4.497
4.469
4.420
4.392
4.319
4.316
4.313
4.310
4.307
4.303
4.297
4.253
4.248
3.971
3.953
3.946
3.872
3.856
3.848
3.837
3.632
3.620
3.614
3.563
3.559
3.484
2.312
1.518
1.511
1.455
1.422
1.406
1.322
1.291
1.254
0.000
OBn
OBn
O
O
O
O
O
O
O
O
;
OBn
BnO
O
O
O
O
O
O
O
Mixture of 14 and 15
1H NMR, 400 MHz, CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
31.63
1.00
0.64
1.14
1.01
0.34
1.13
1.01
0.65
4.53
2.12
4.49
1.19
0.69
2.51
2.75
1.17
0.77
1.06
3.77
4.58
1.37
3.85
2.26
2.05
0.62
1.09
1.17
2.95
2.62
2.30
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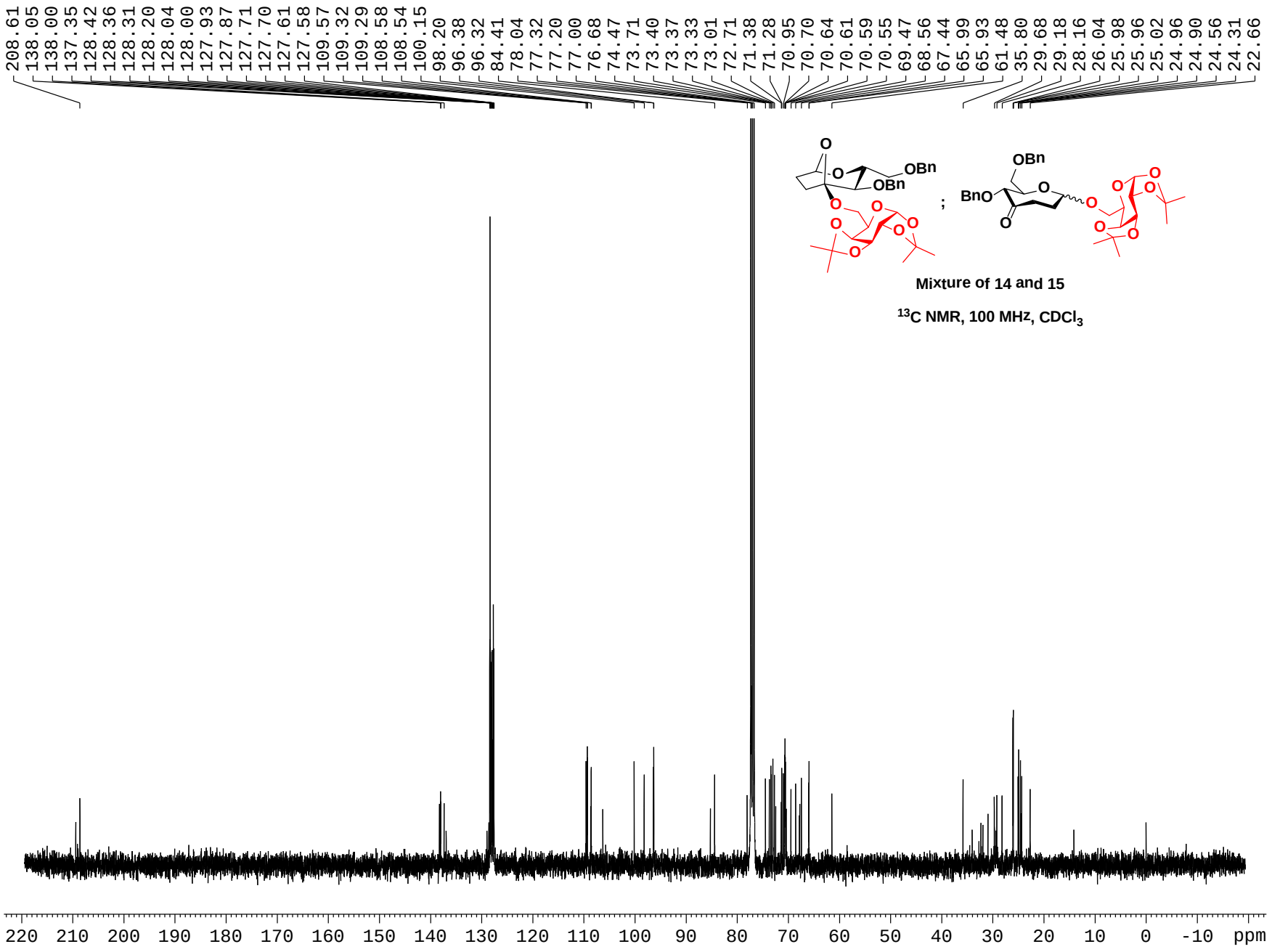
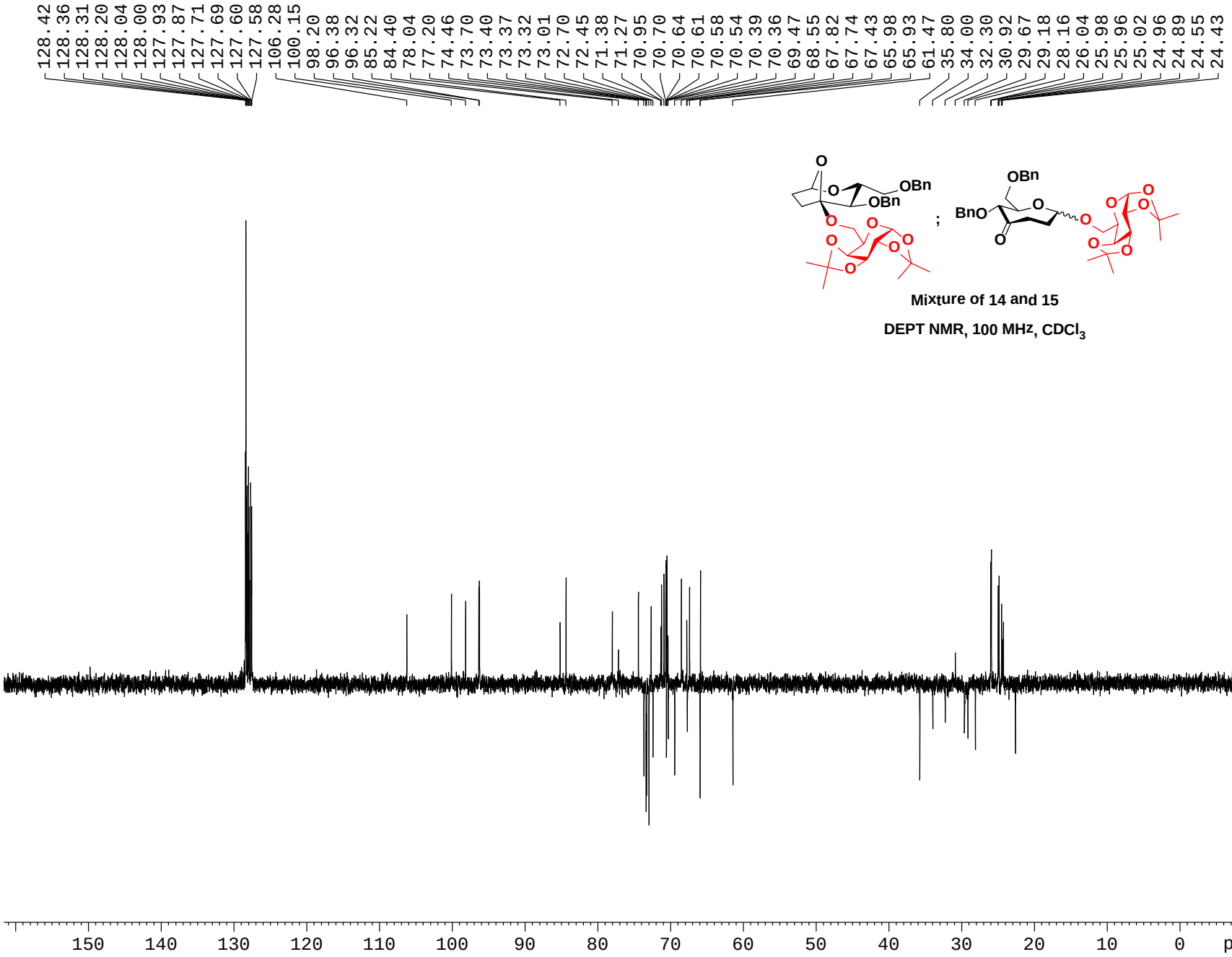
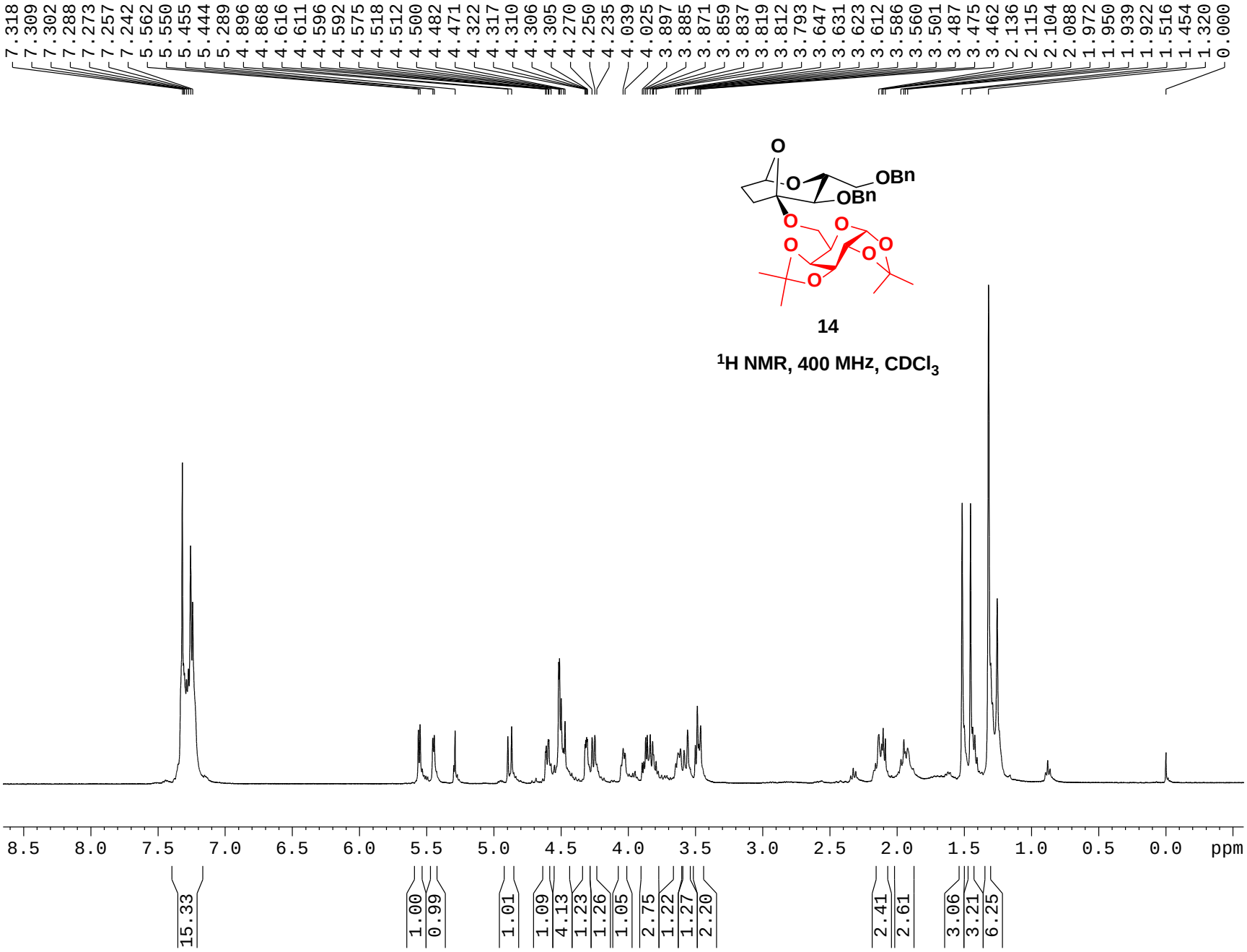
8.57
3.32
5.67
16.05
4.37
7.52

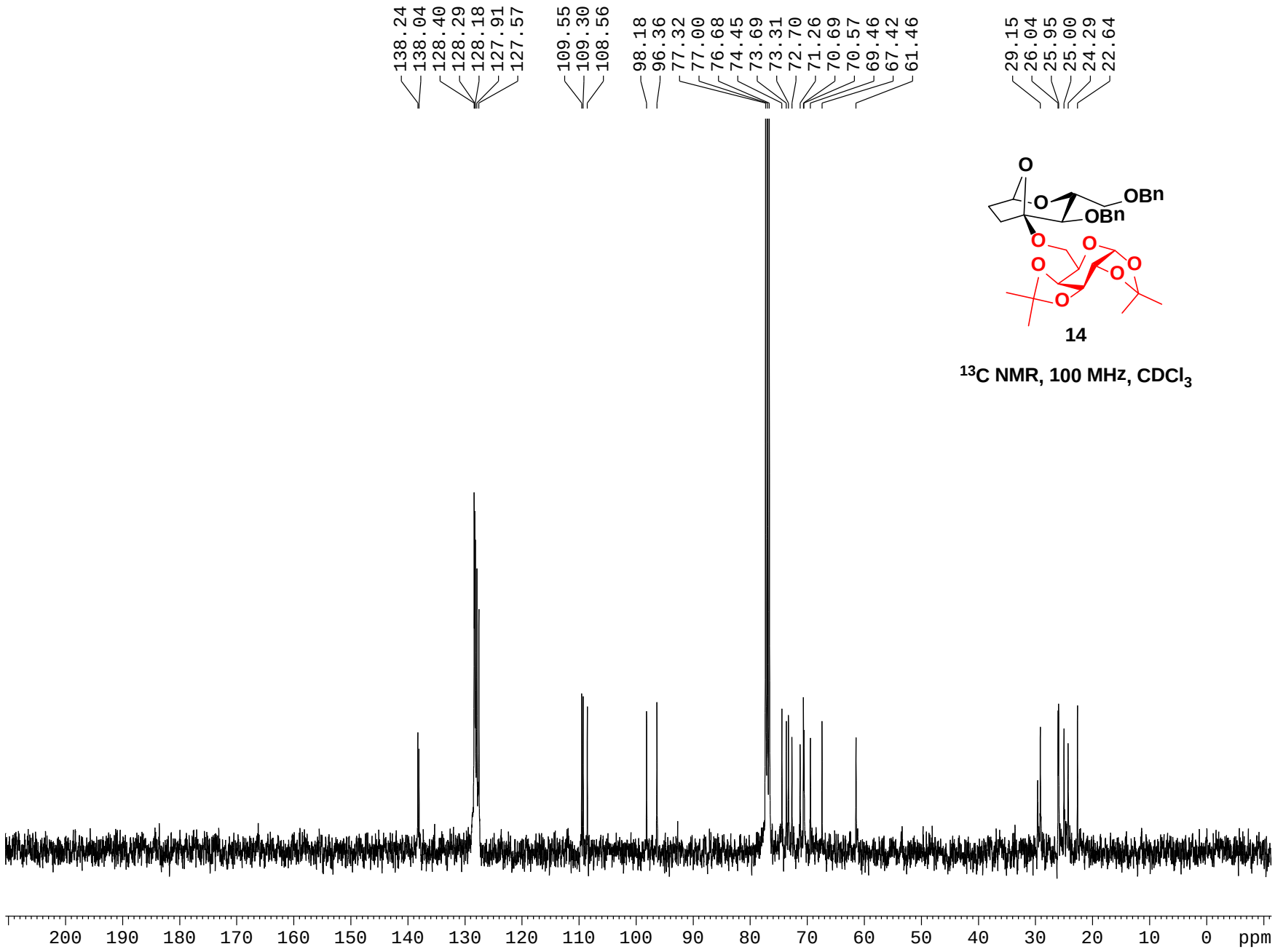




Mixture of 14 and 15

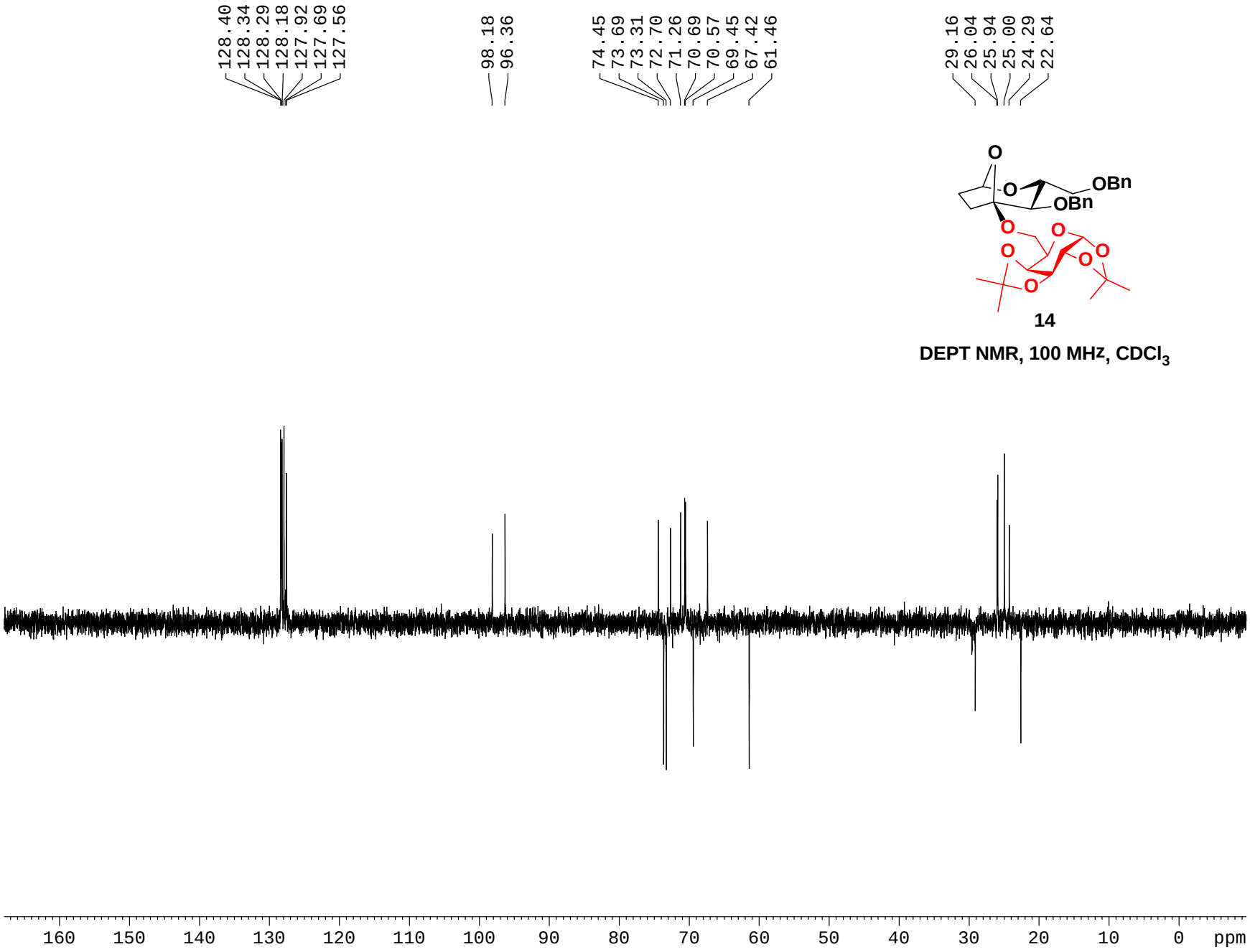
DEPT NMR, 100 MHz, $CDCl_3$





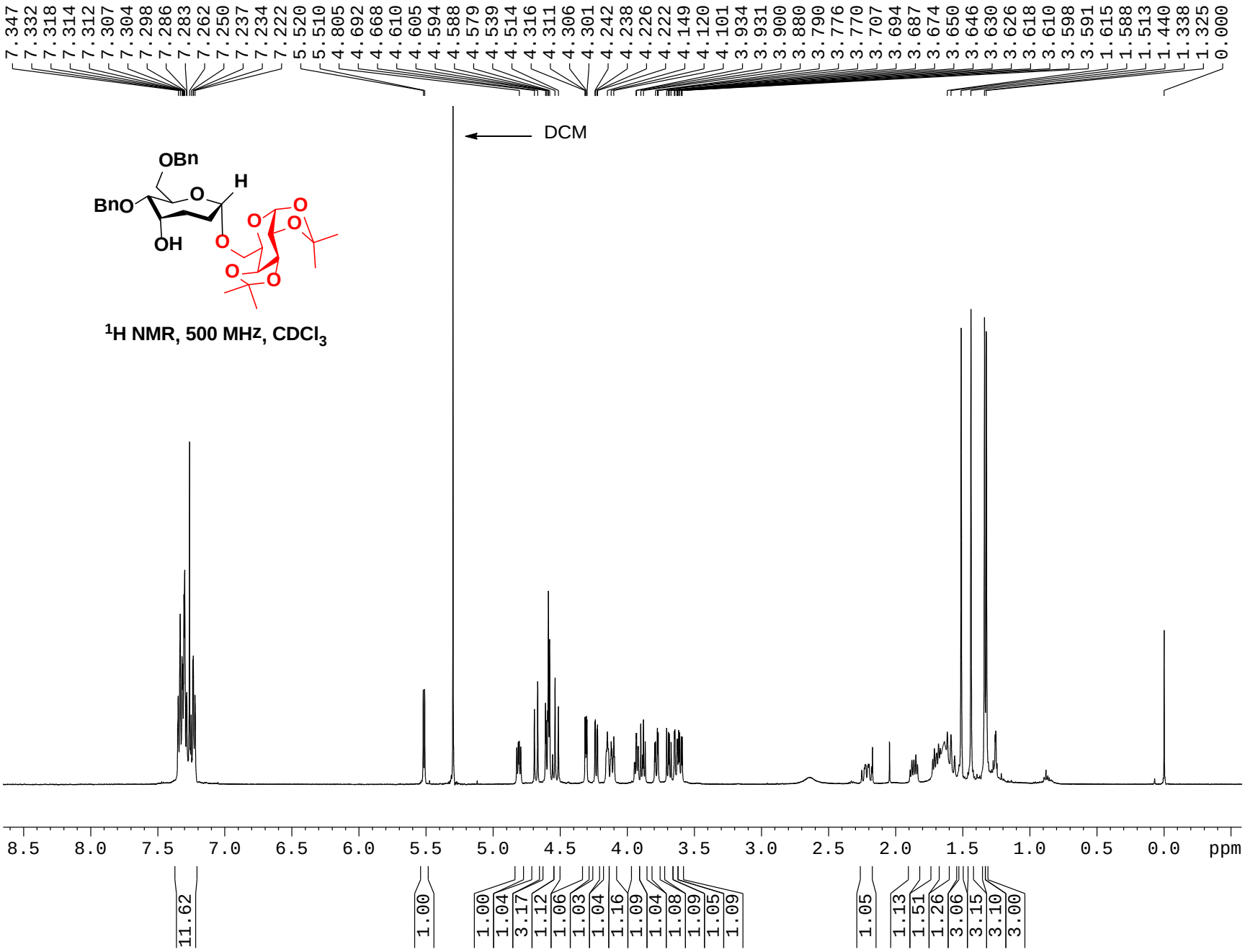
14

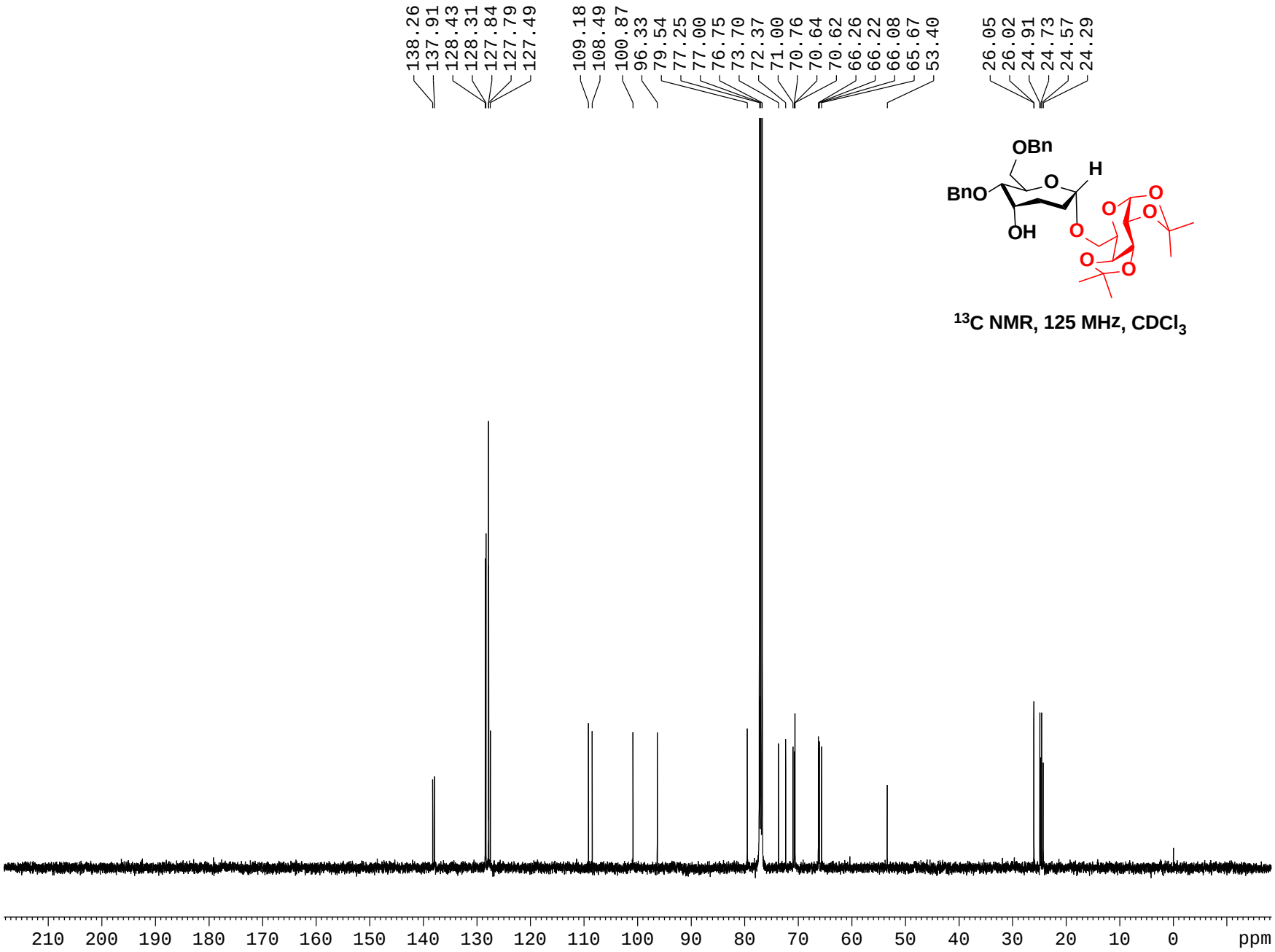
^{13}C NMR, 100 MHz, $CDCl_3$



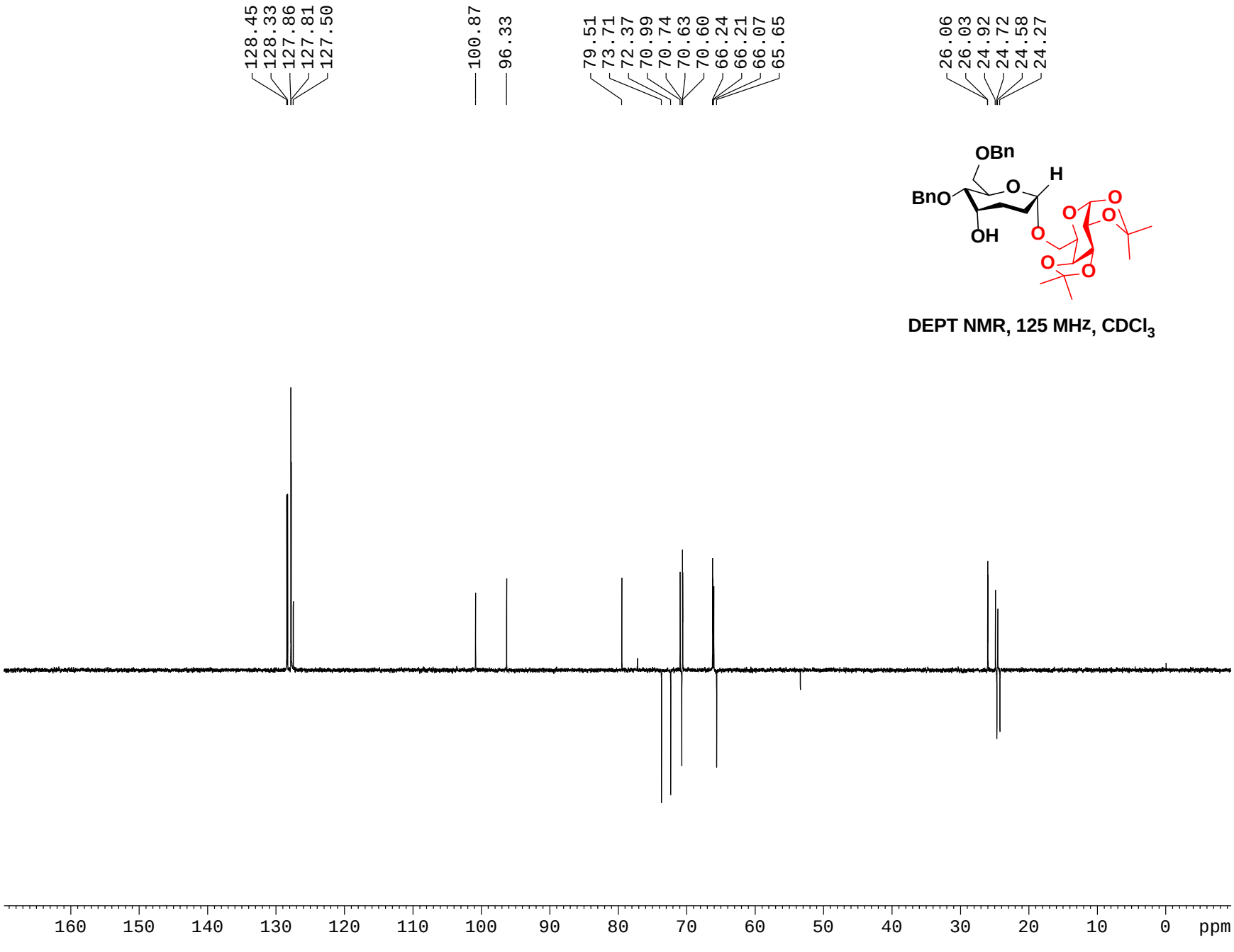
14

DEPT NMR, 100 MHz, $CDCl_3$

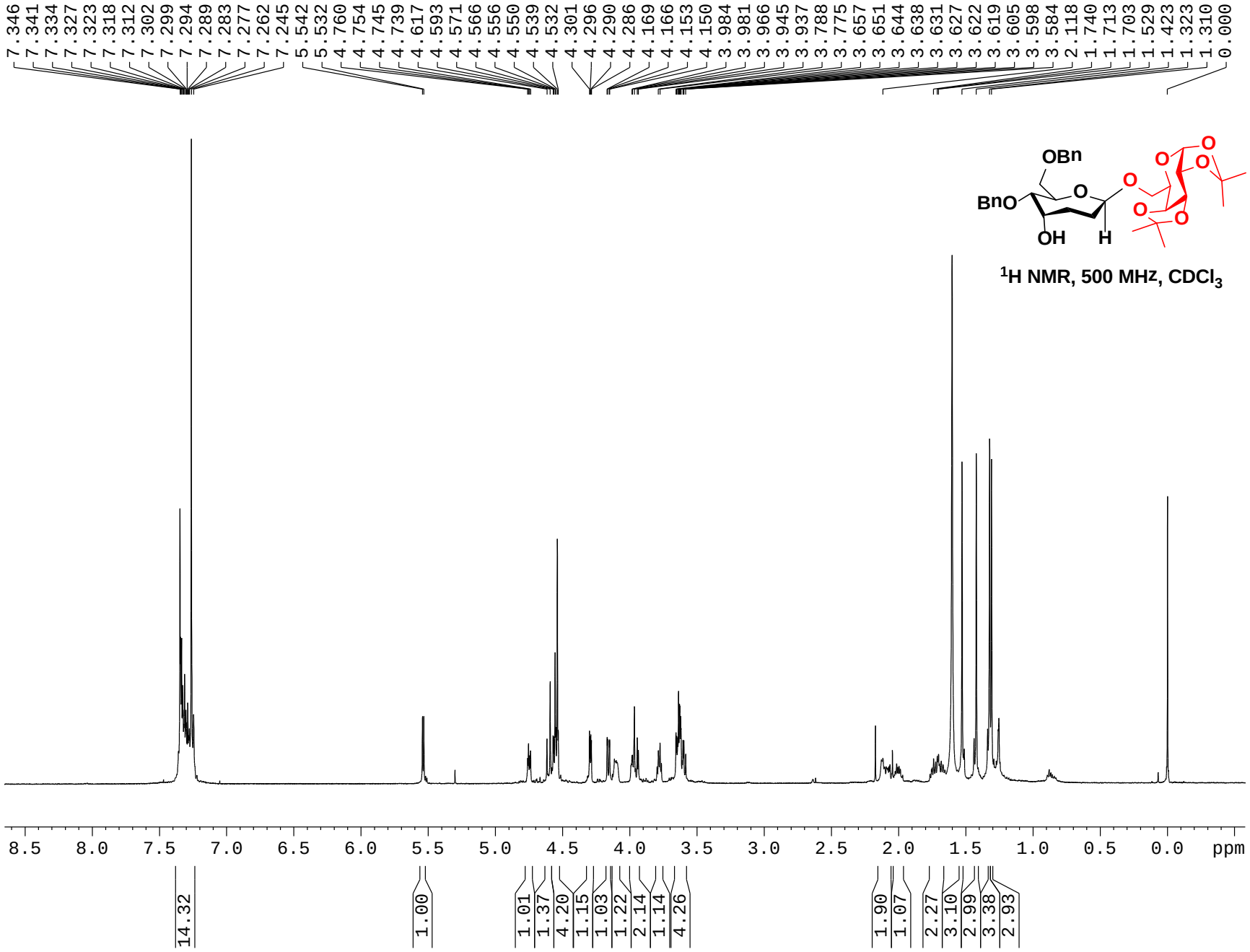


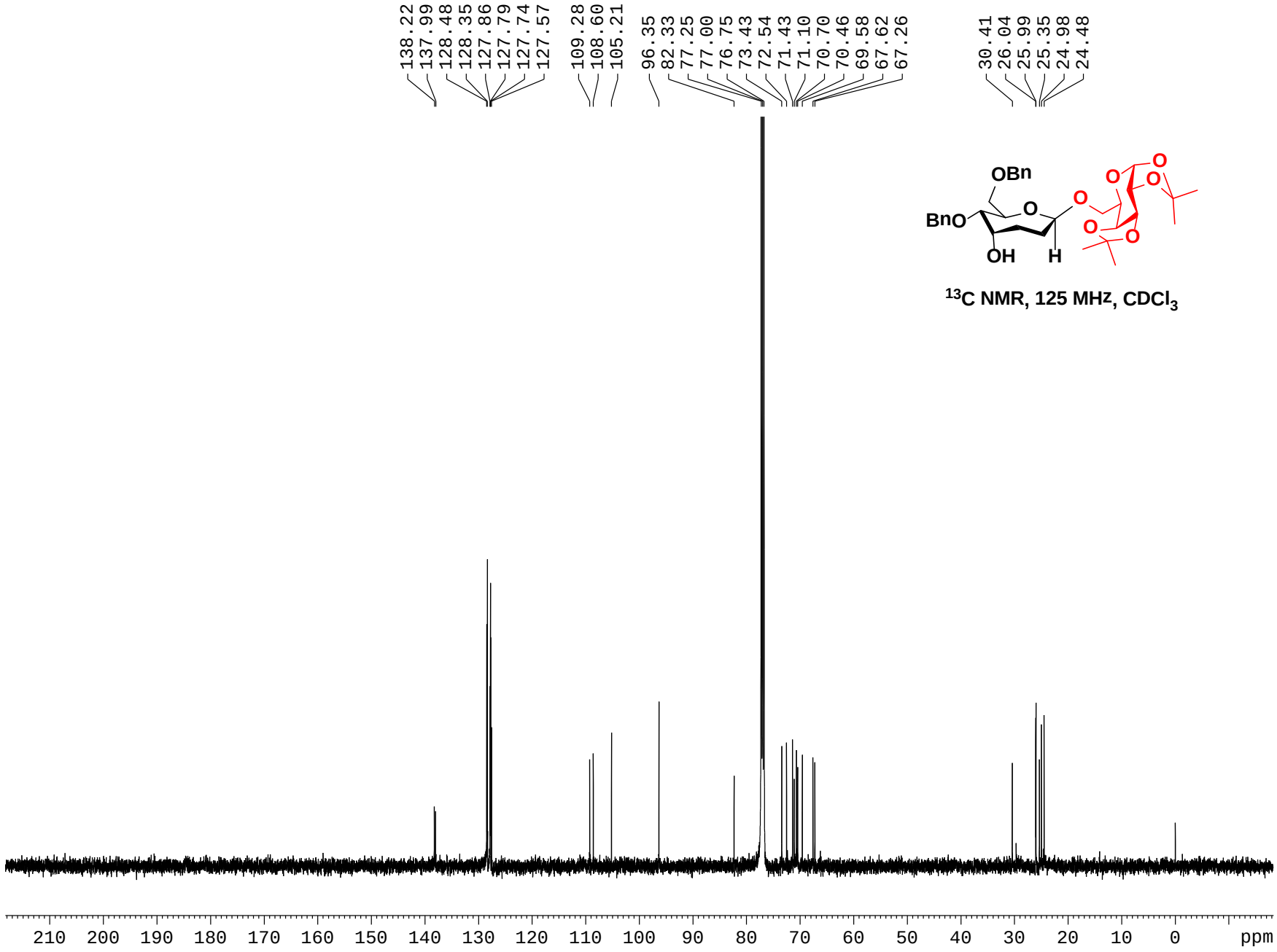


^{13}C NMR, 125 MHz, $CDCl_3$

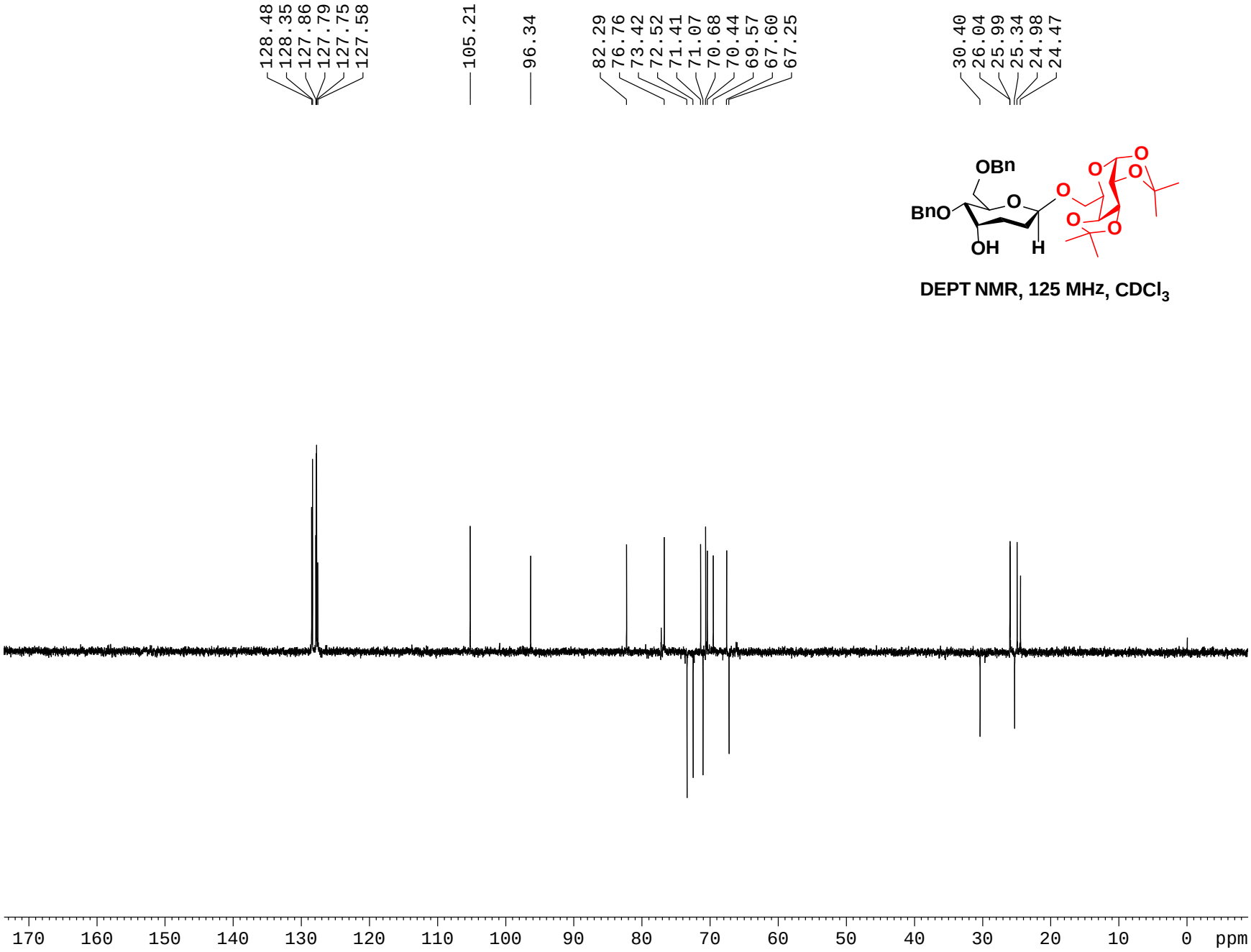


DEPT NMR, 125 MHz, $CDCl_3$

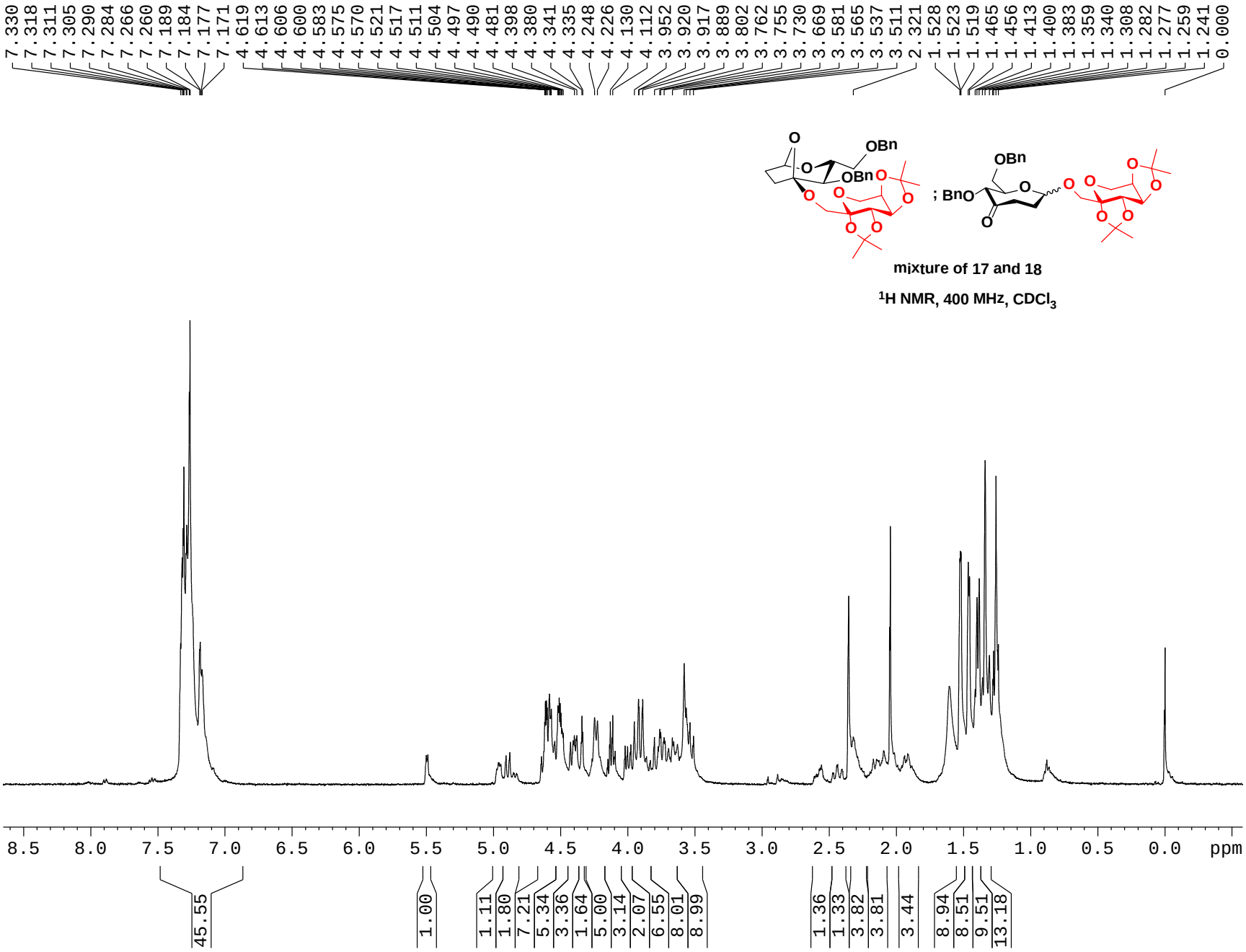


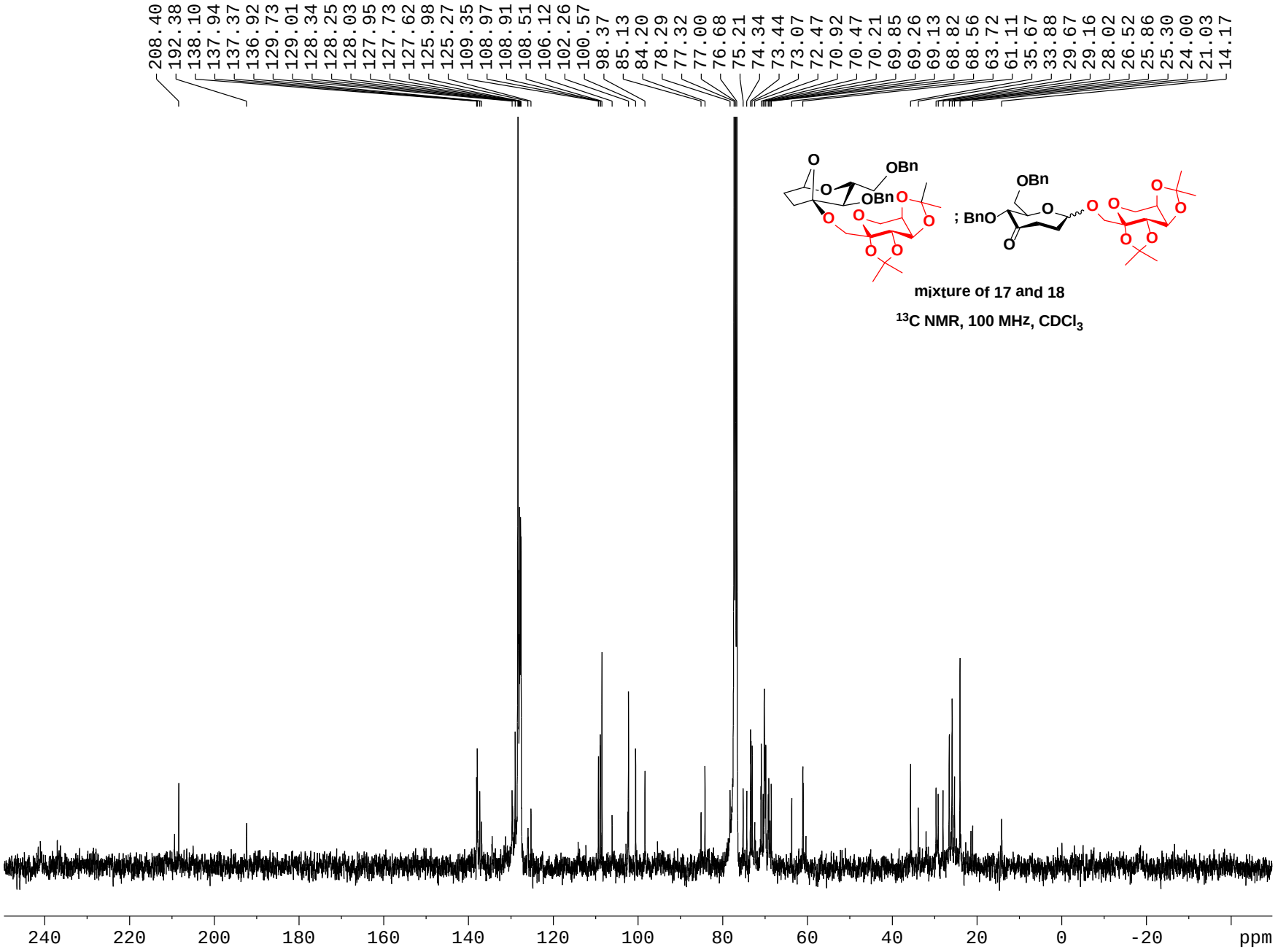


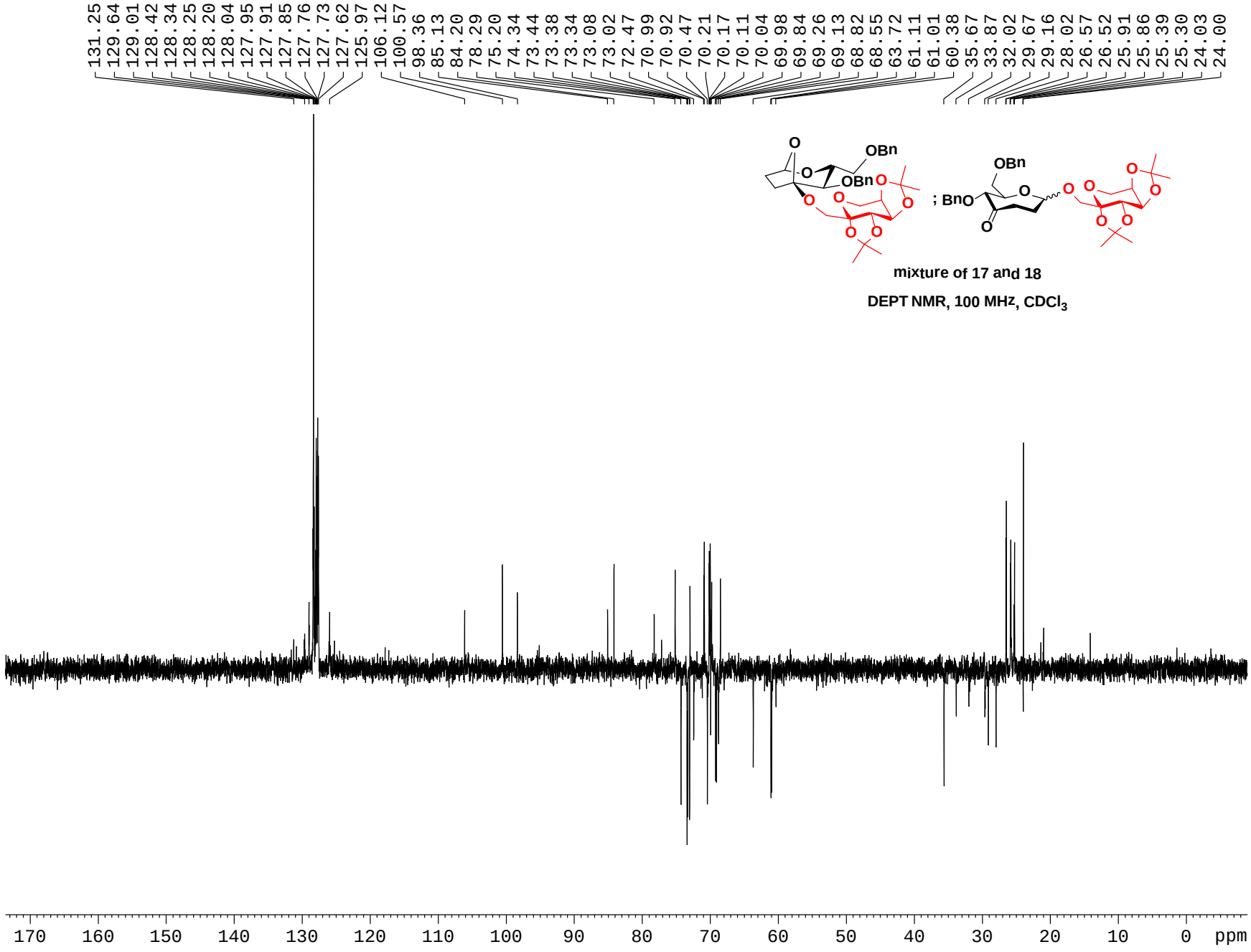
^{13}C NMR, 125 MHz, $CDCl_3$



DEPT NMR, 125 MHz, $CDCl_3$

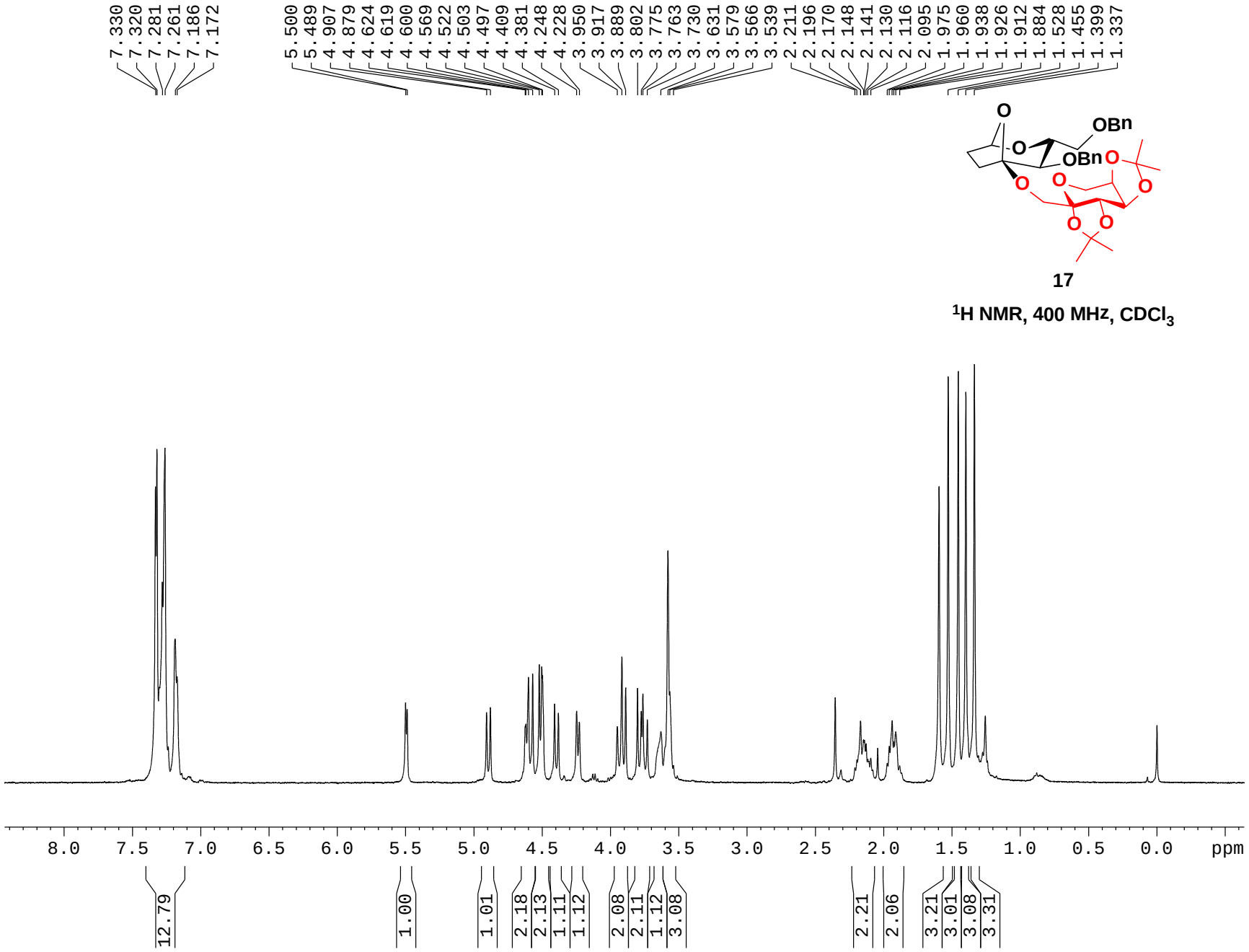


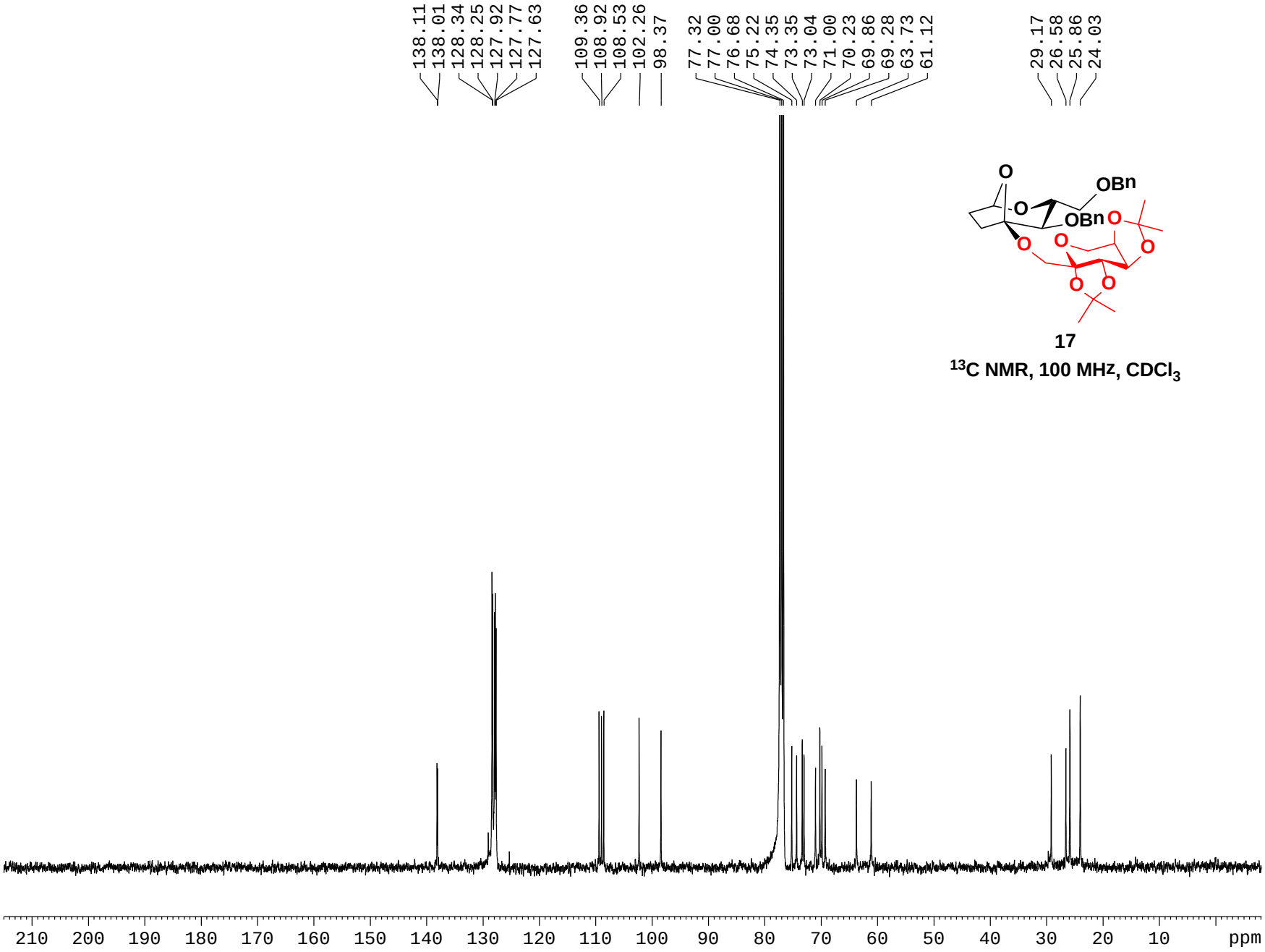




mixture of 17 and 18

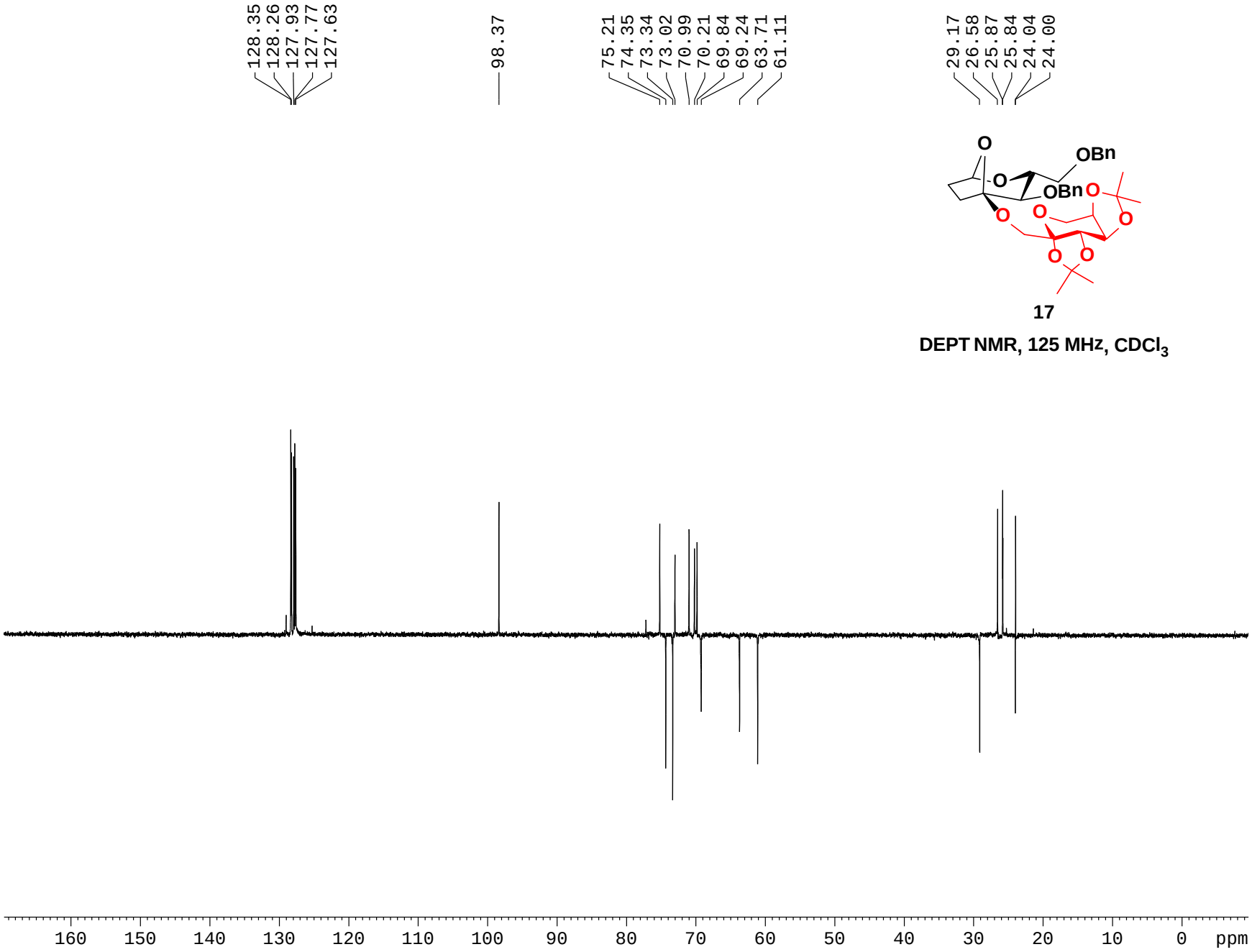
DEPT NMR, 100 MHz, $CDCl_3$





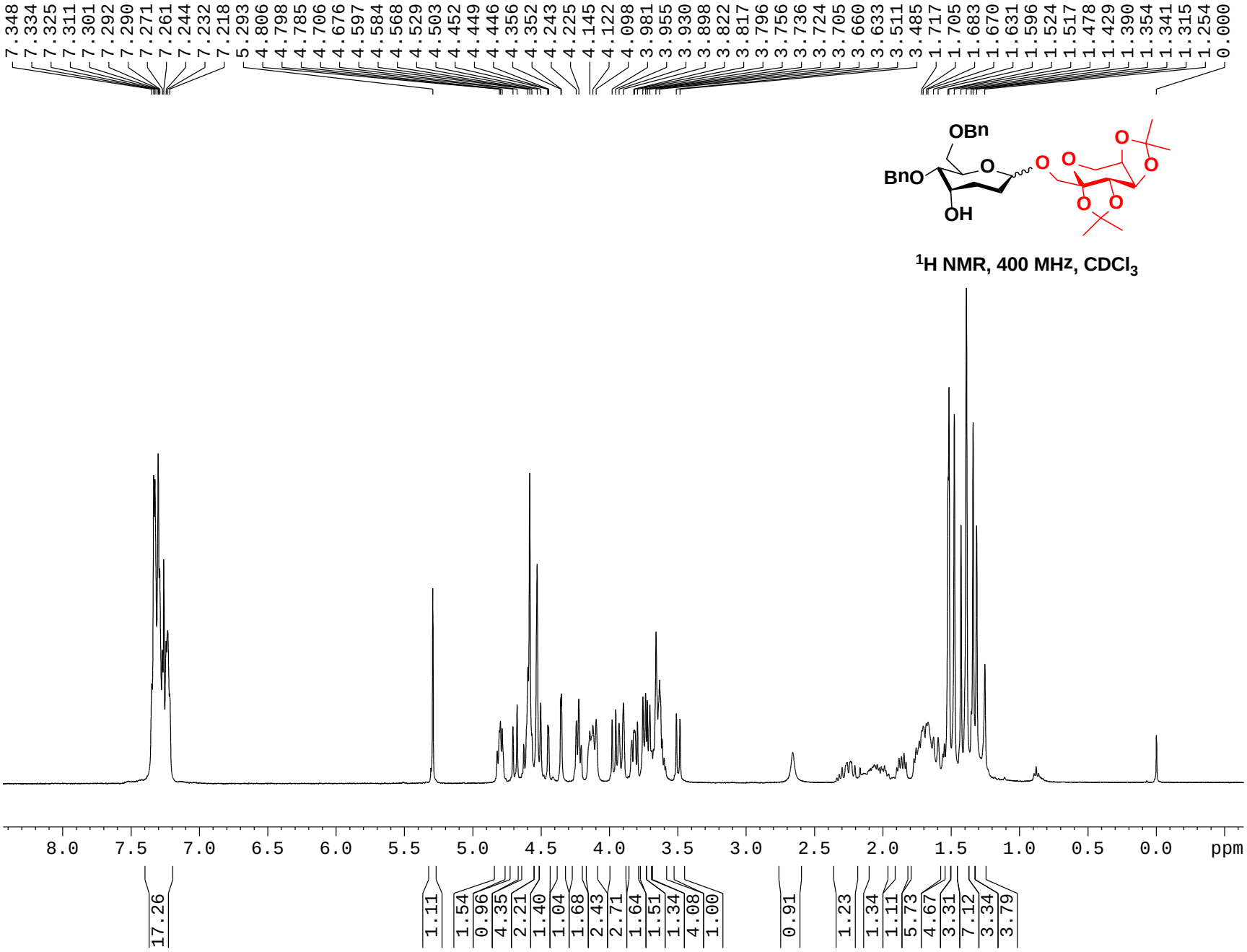
17

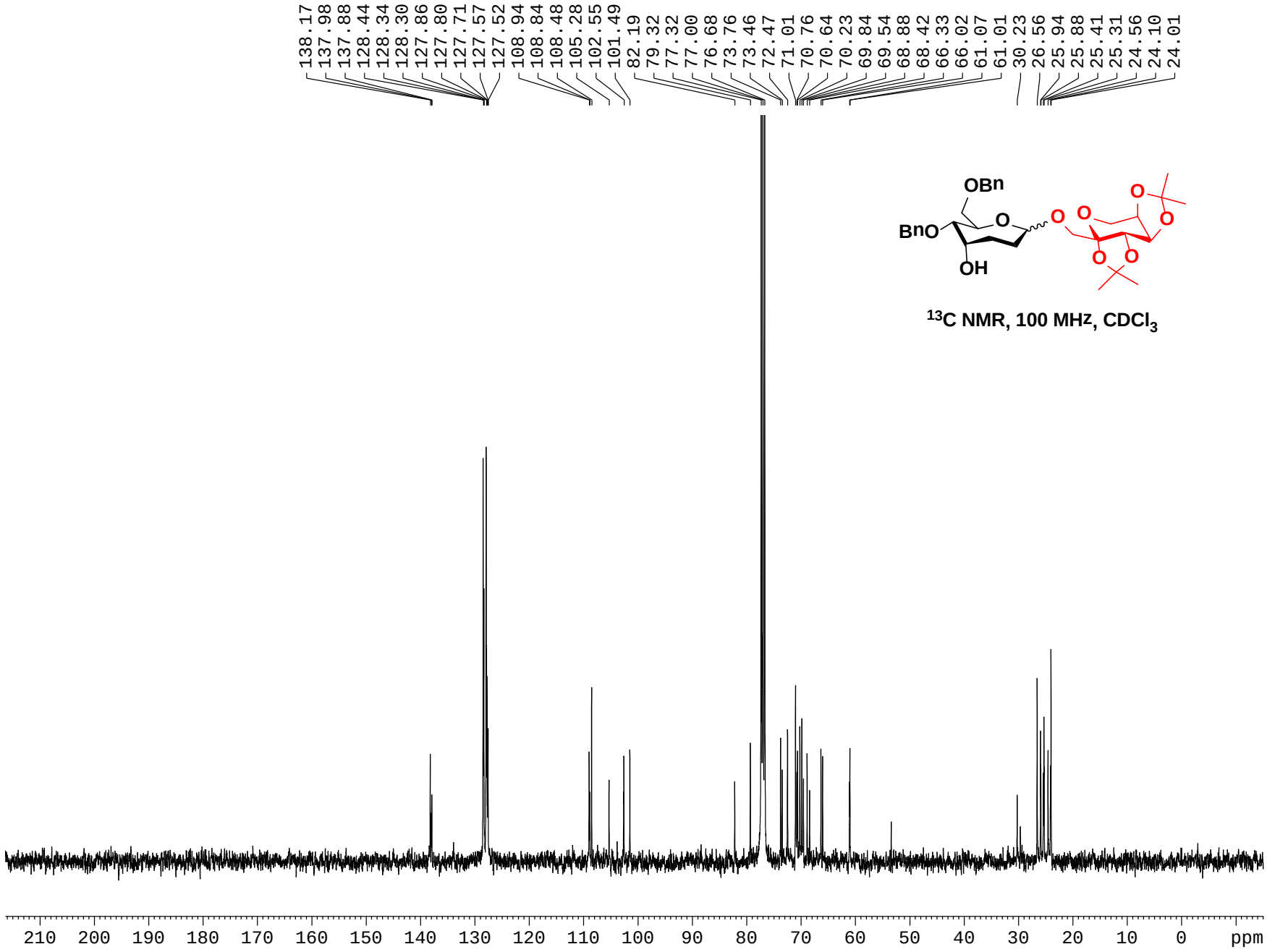
^{13}C NMR, 100 MHz, $CDCl_3$



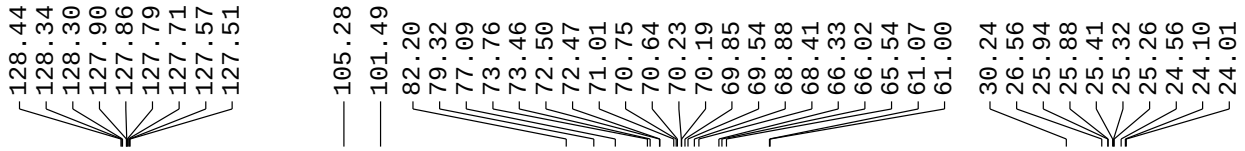
17

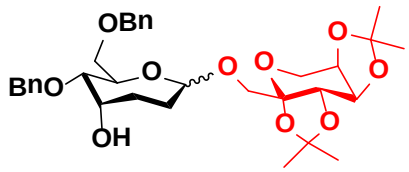
DEPT NMR, 125 MHz, $CDCl_3$



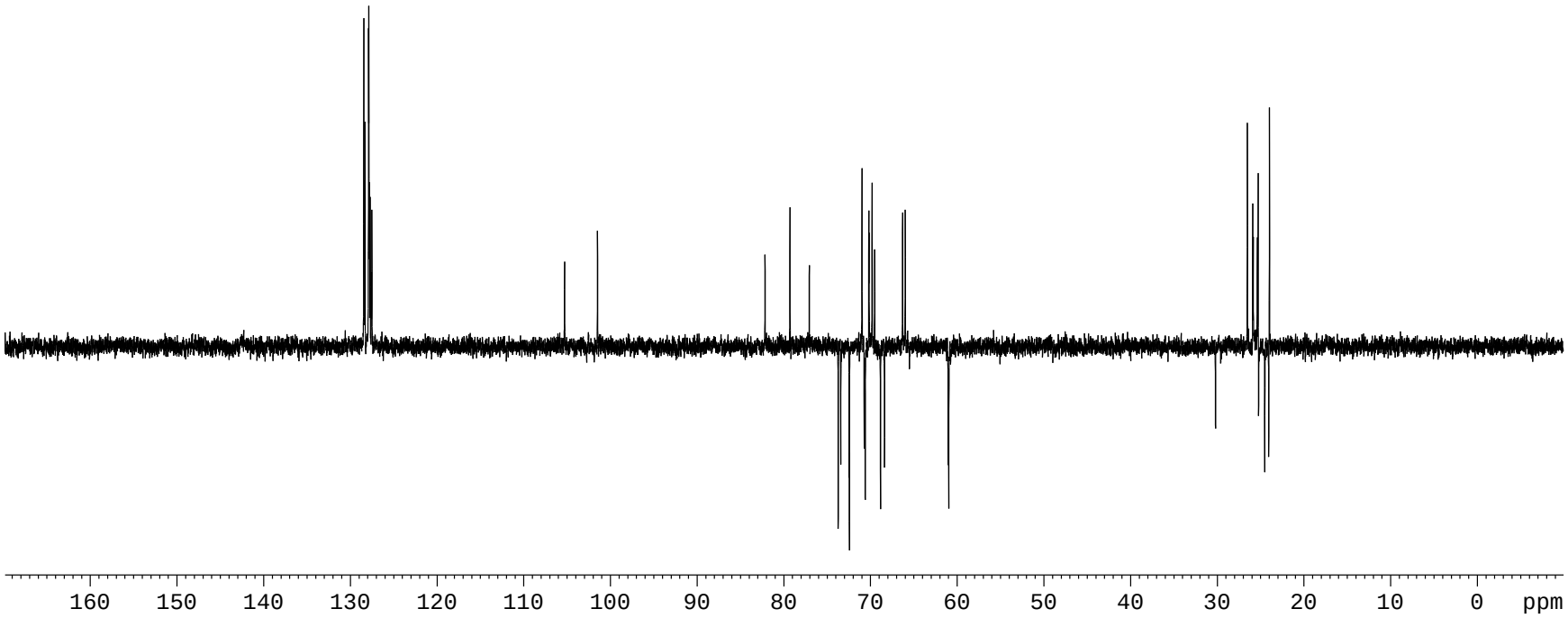


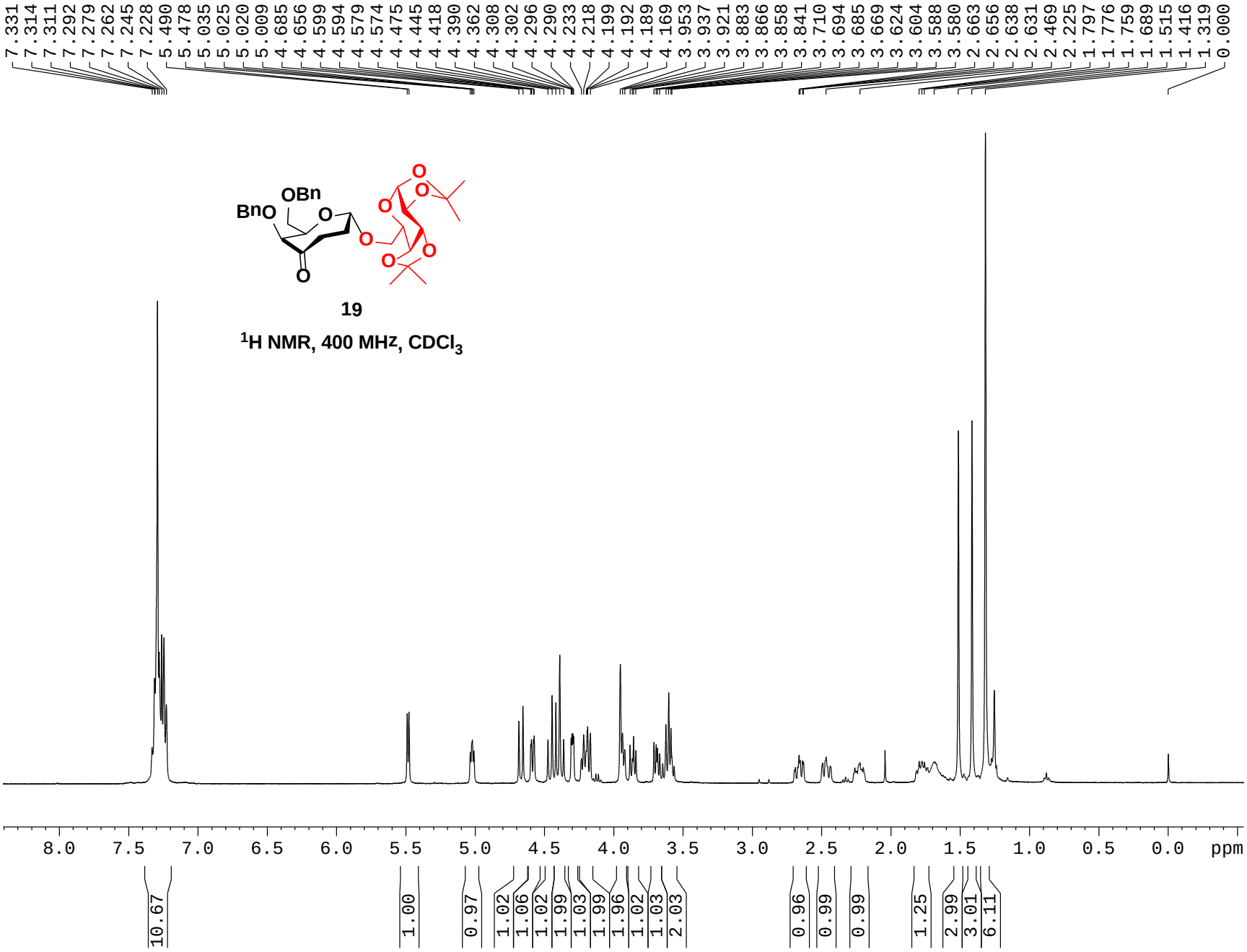
^{13}C NMR, 100 MHz, $CDCl_3$

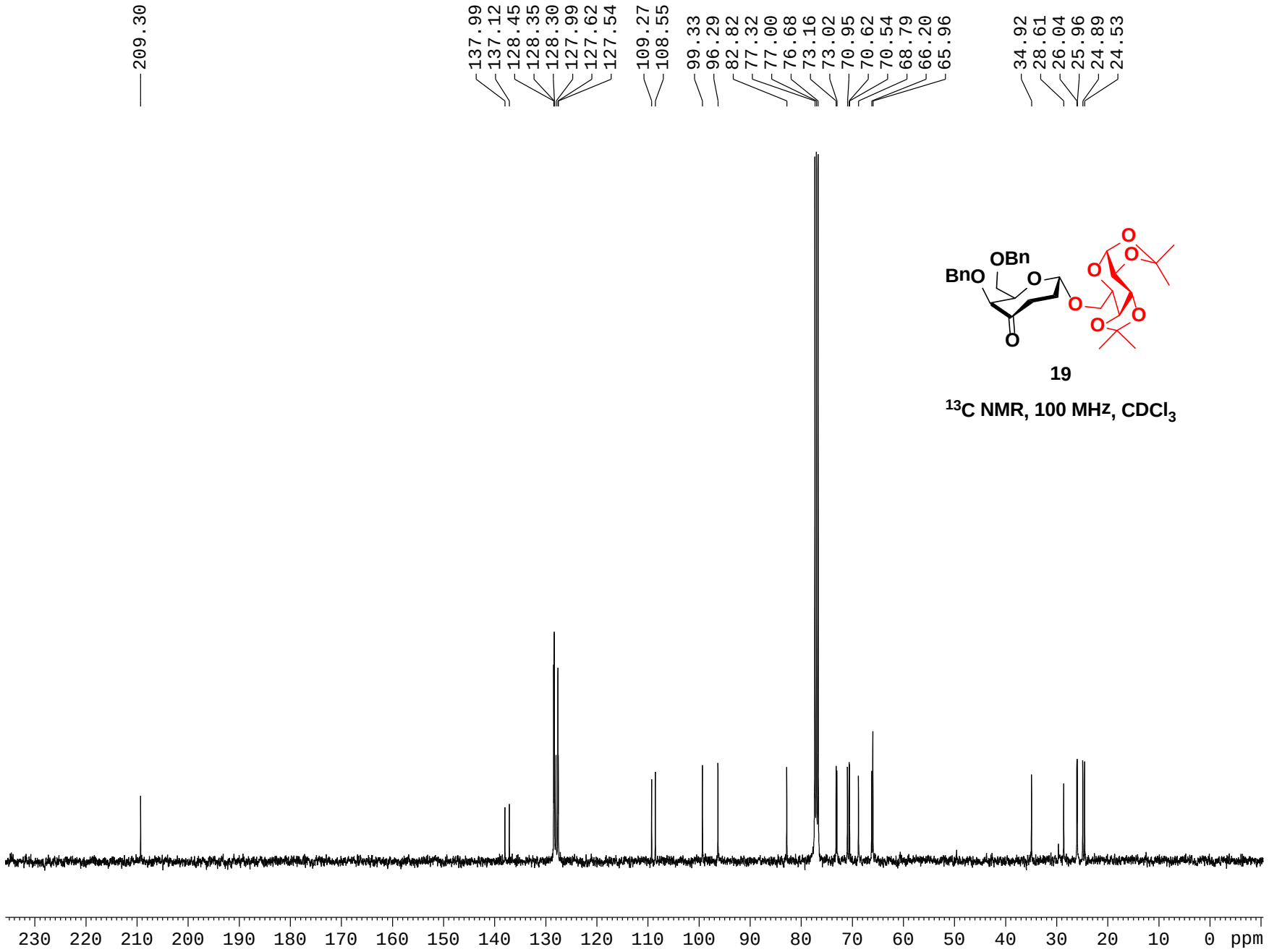


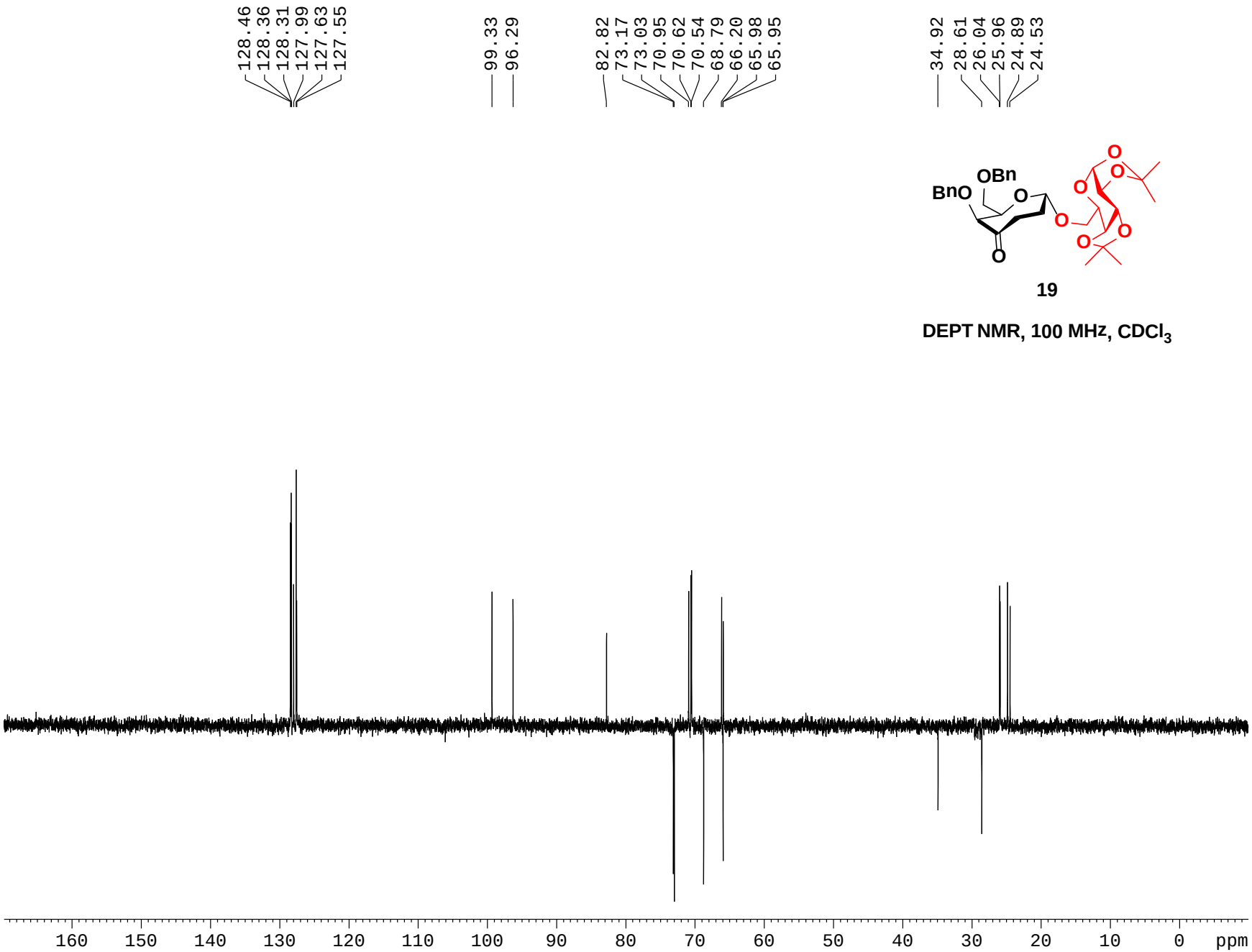


DEPT NMR, 100 MHz, $CDCl_3$



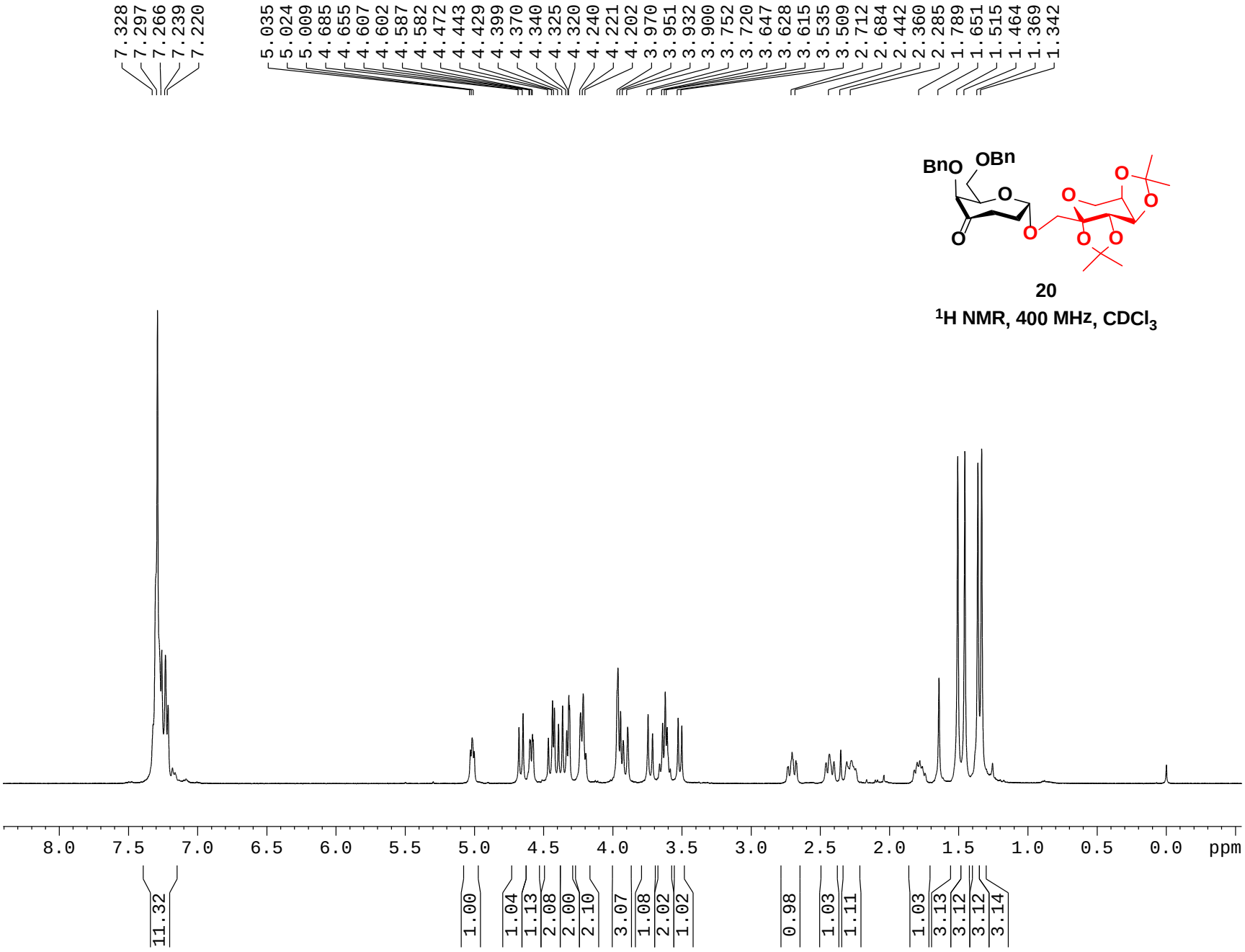


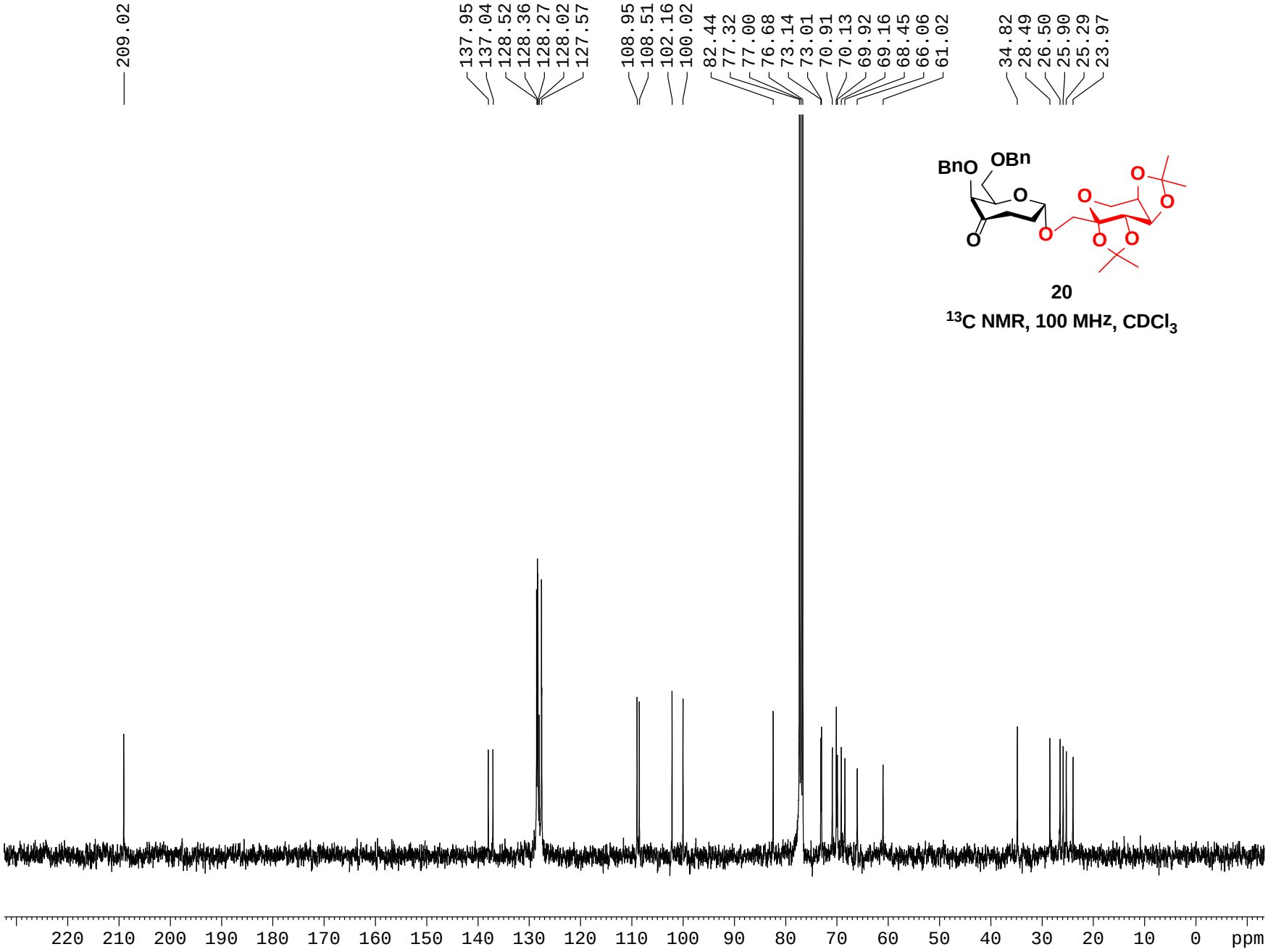




19

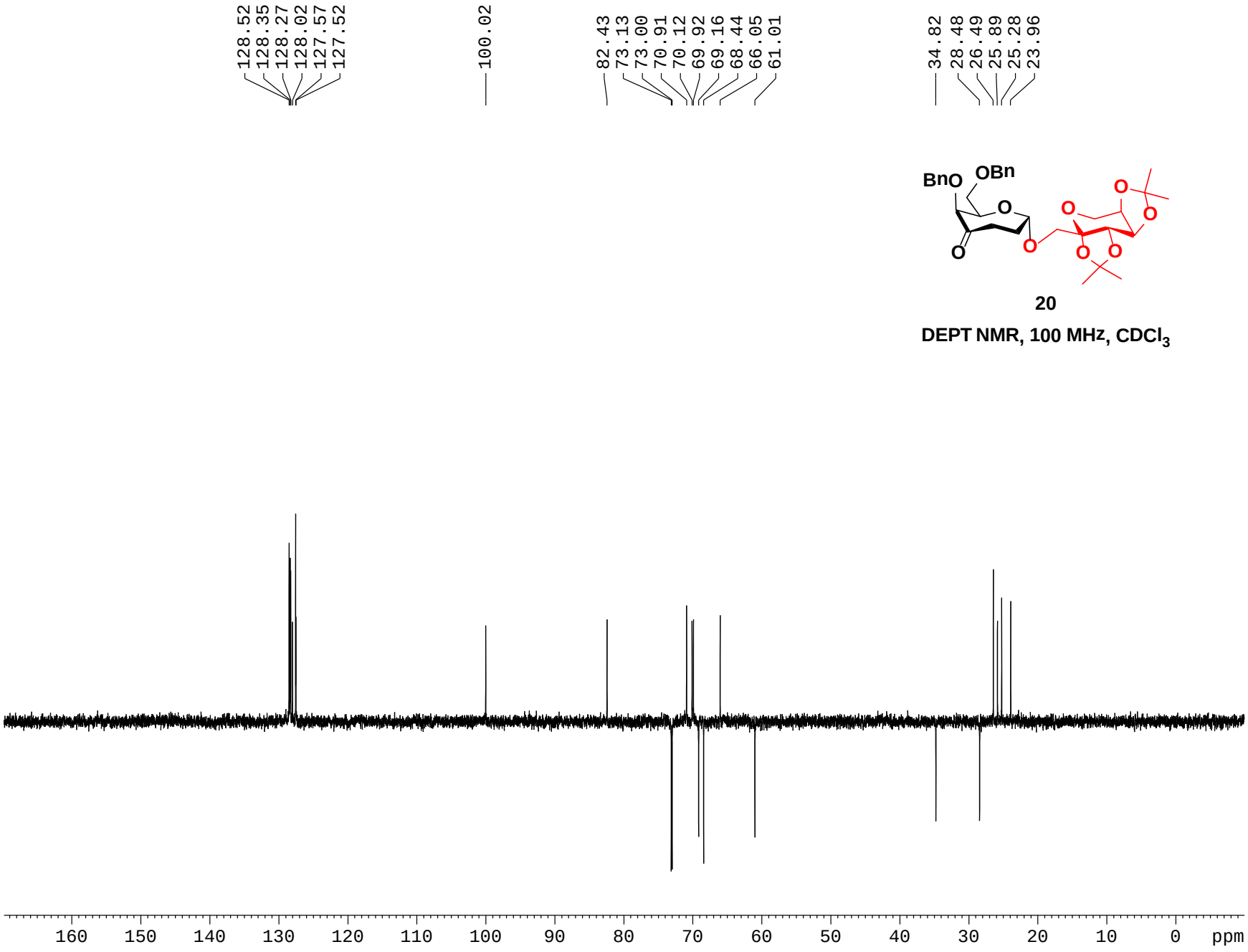
DEPT NMR, 100 MHz, $CDCl_3$





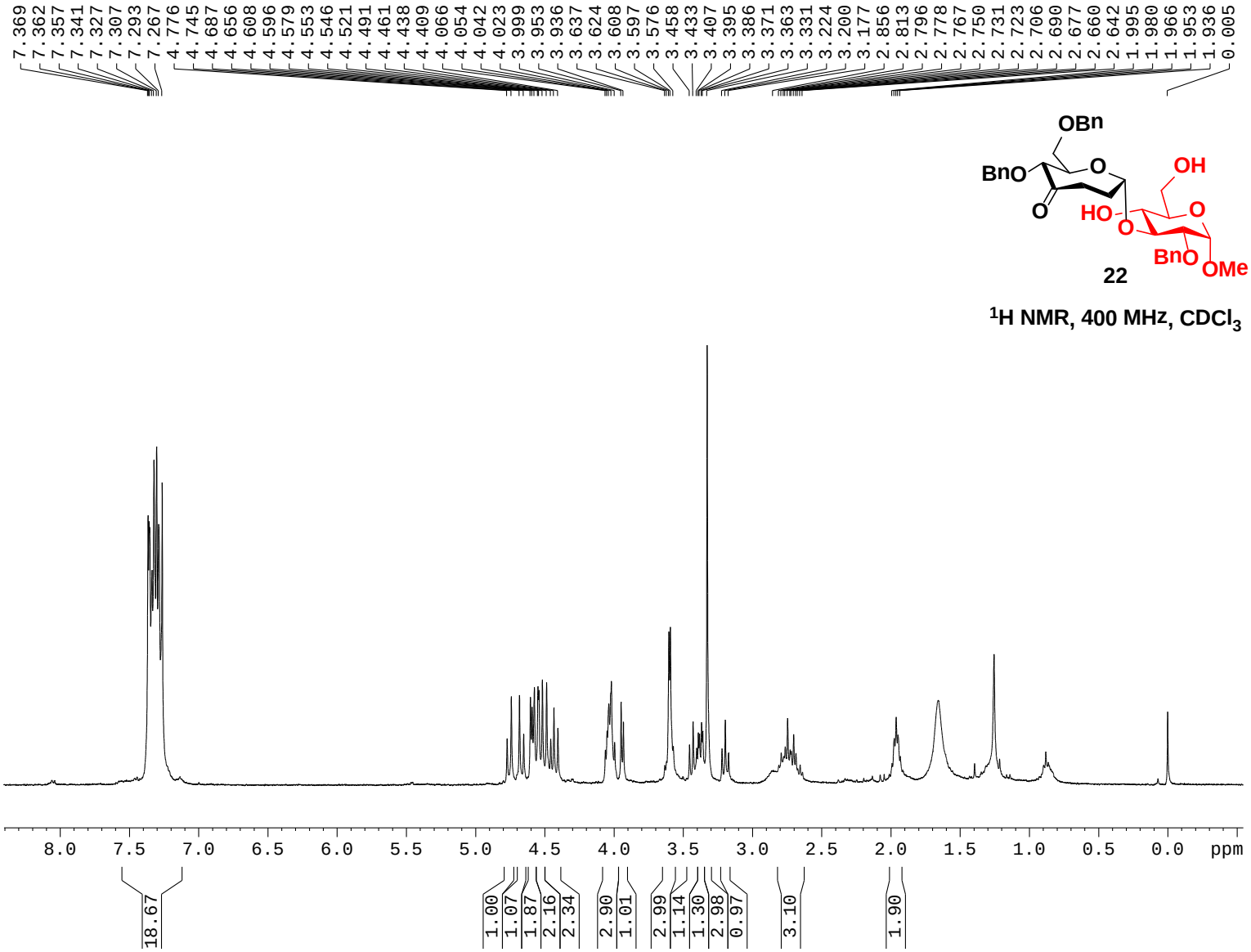
20

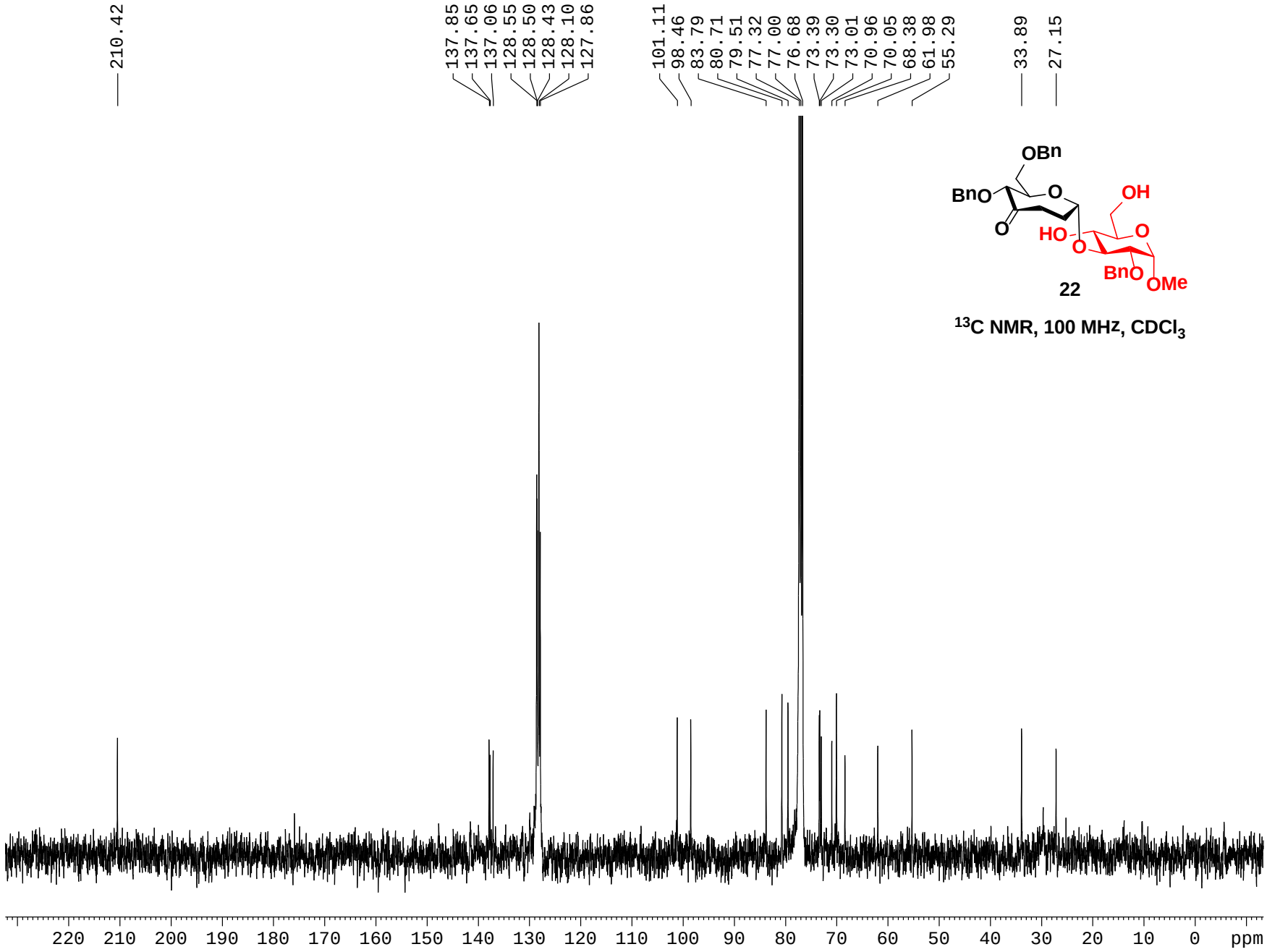
^{13}C NMR, 100 MHz, $CDCl_3$

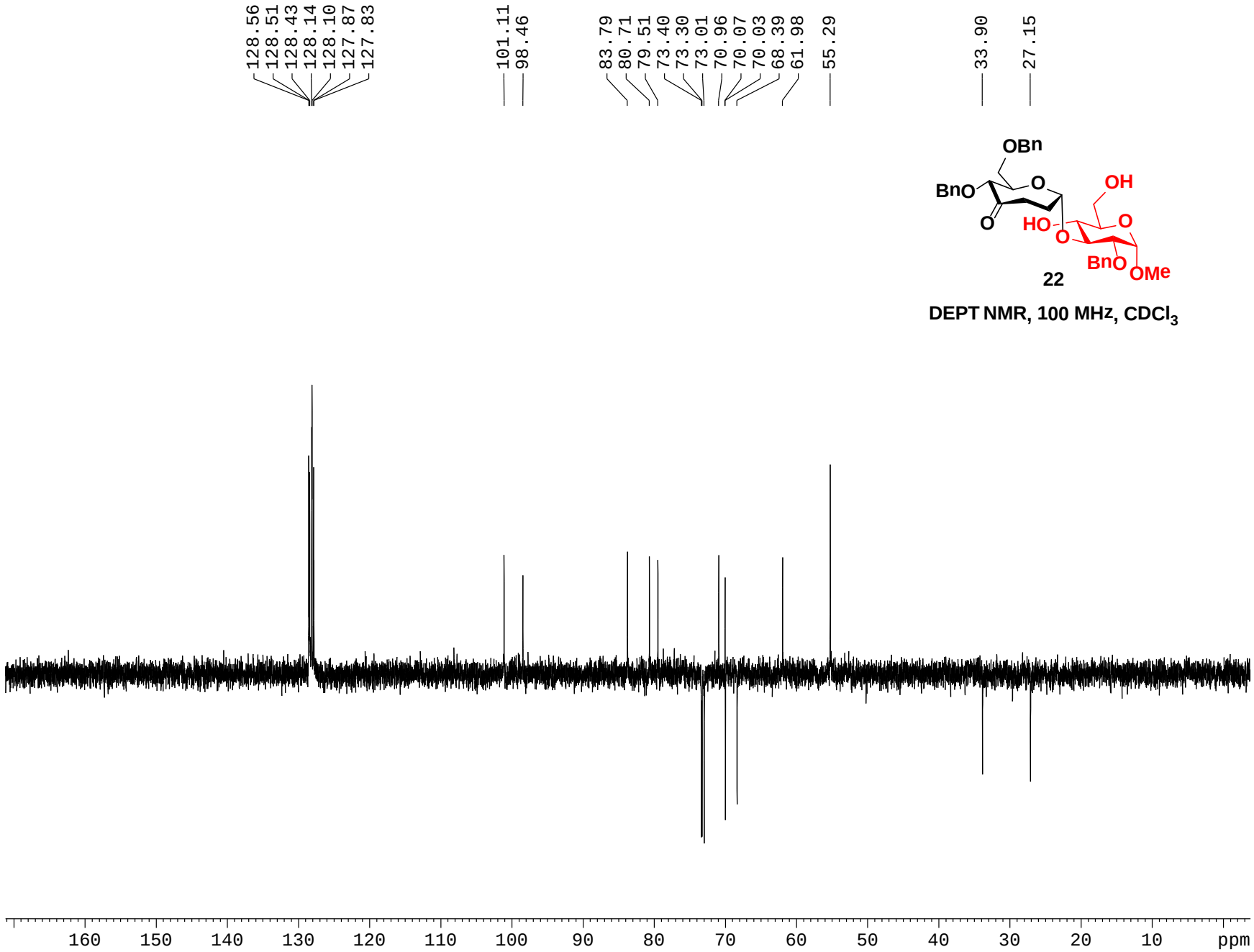


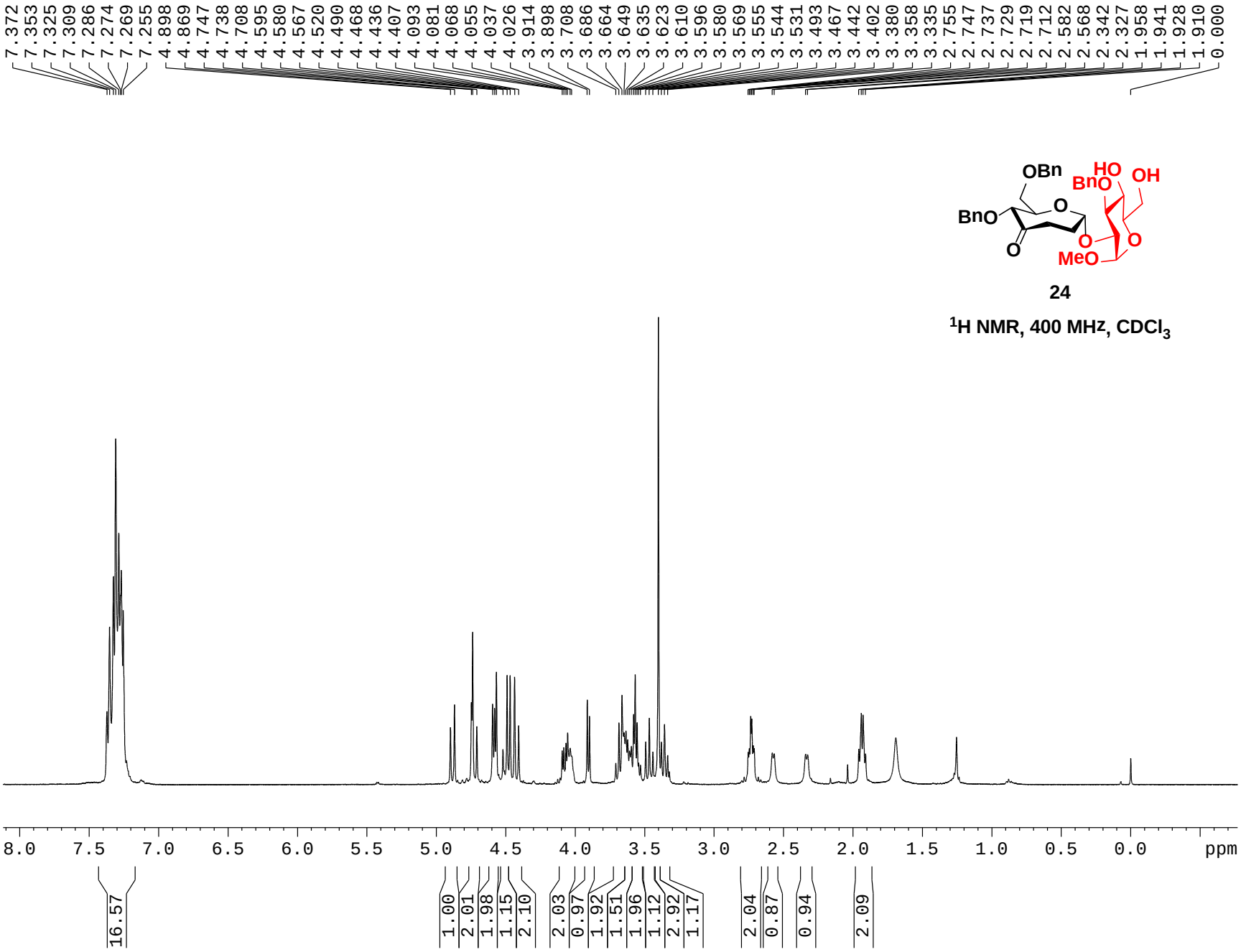
20

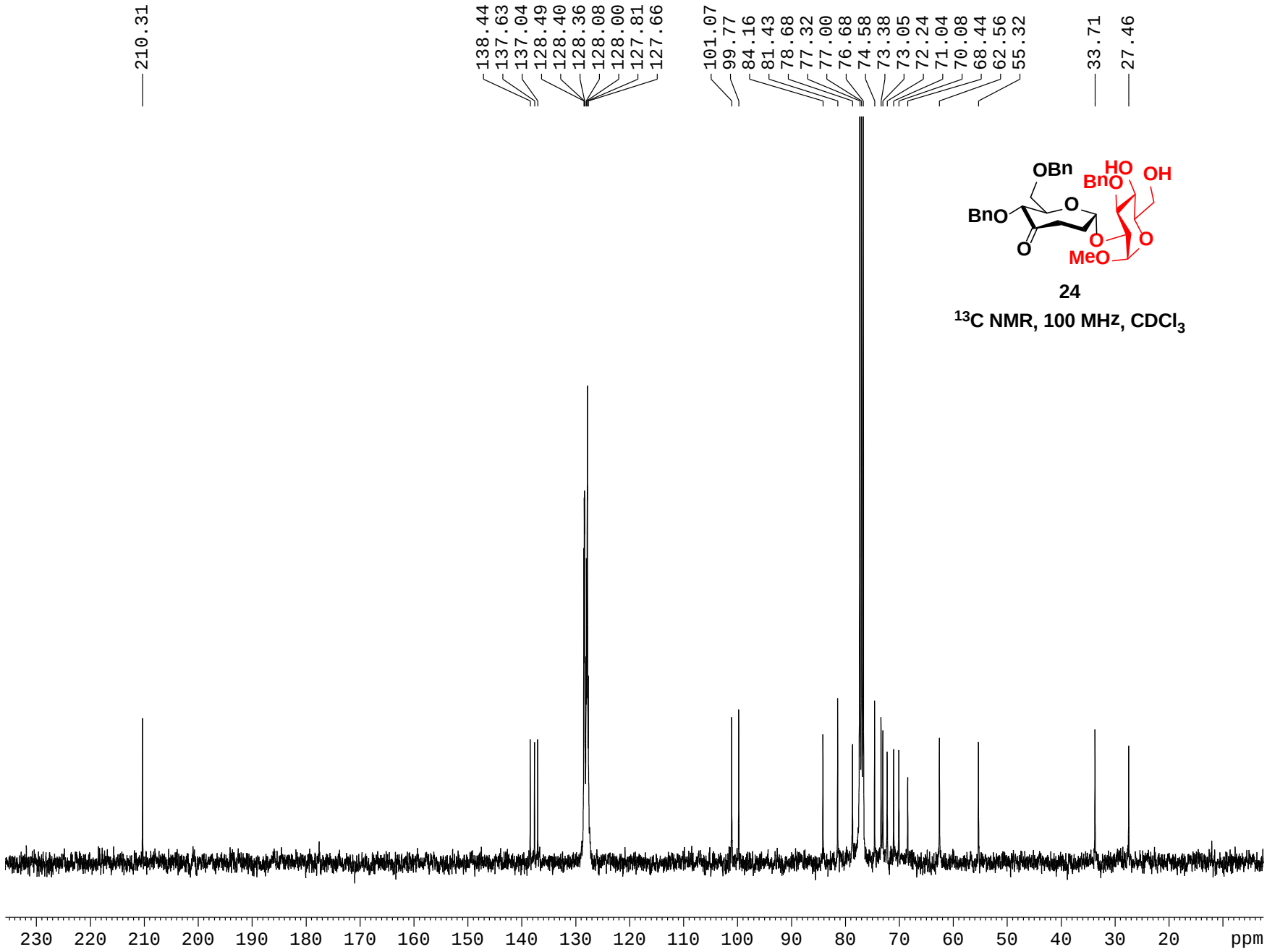
DEPT NMR, 100 MHz, $CDCl_3$





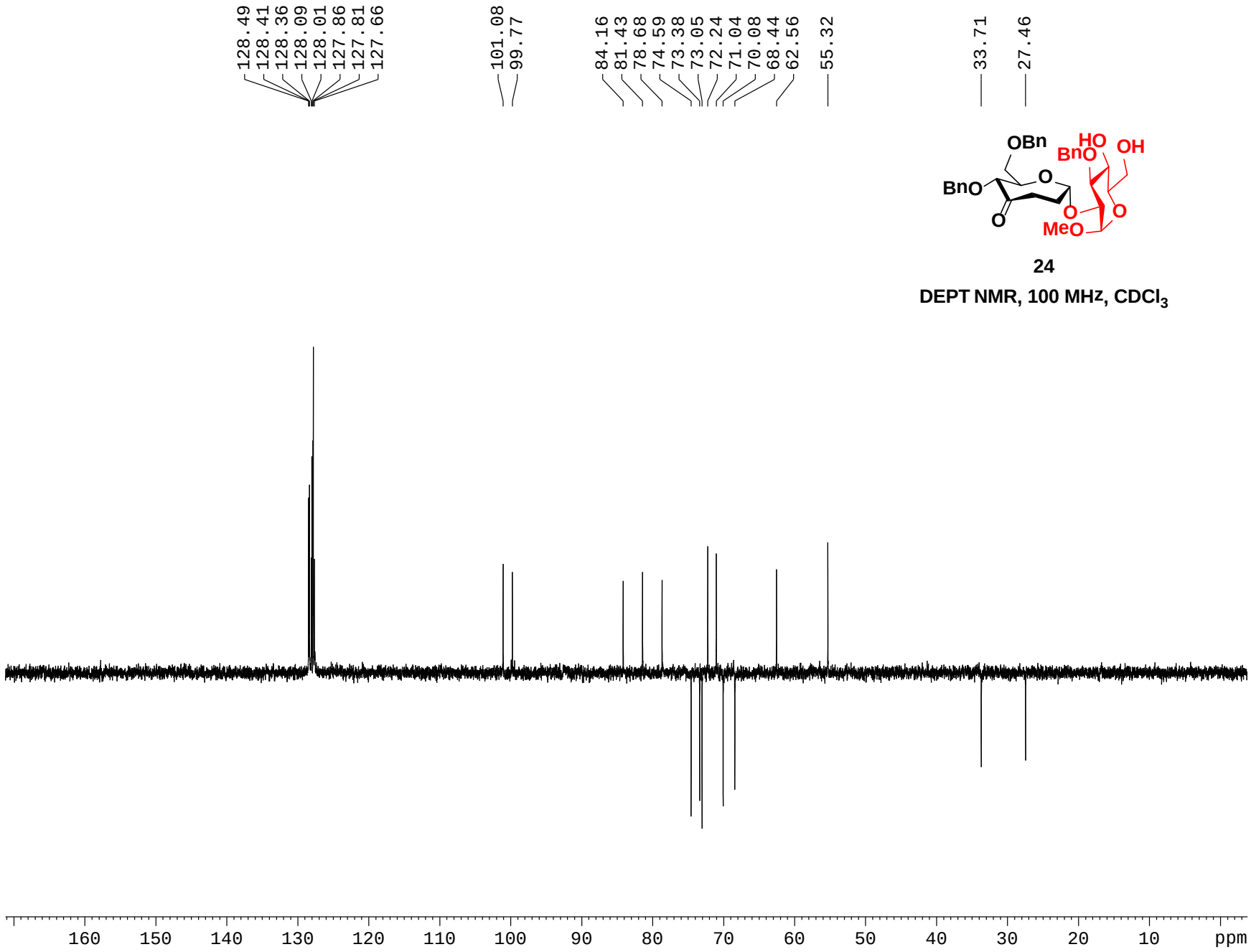






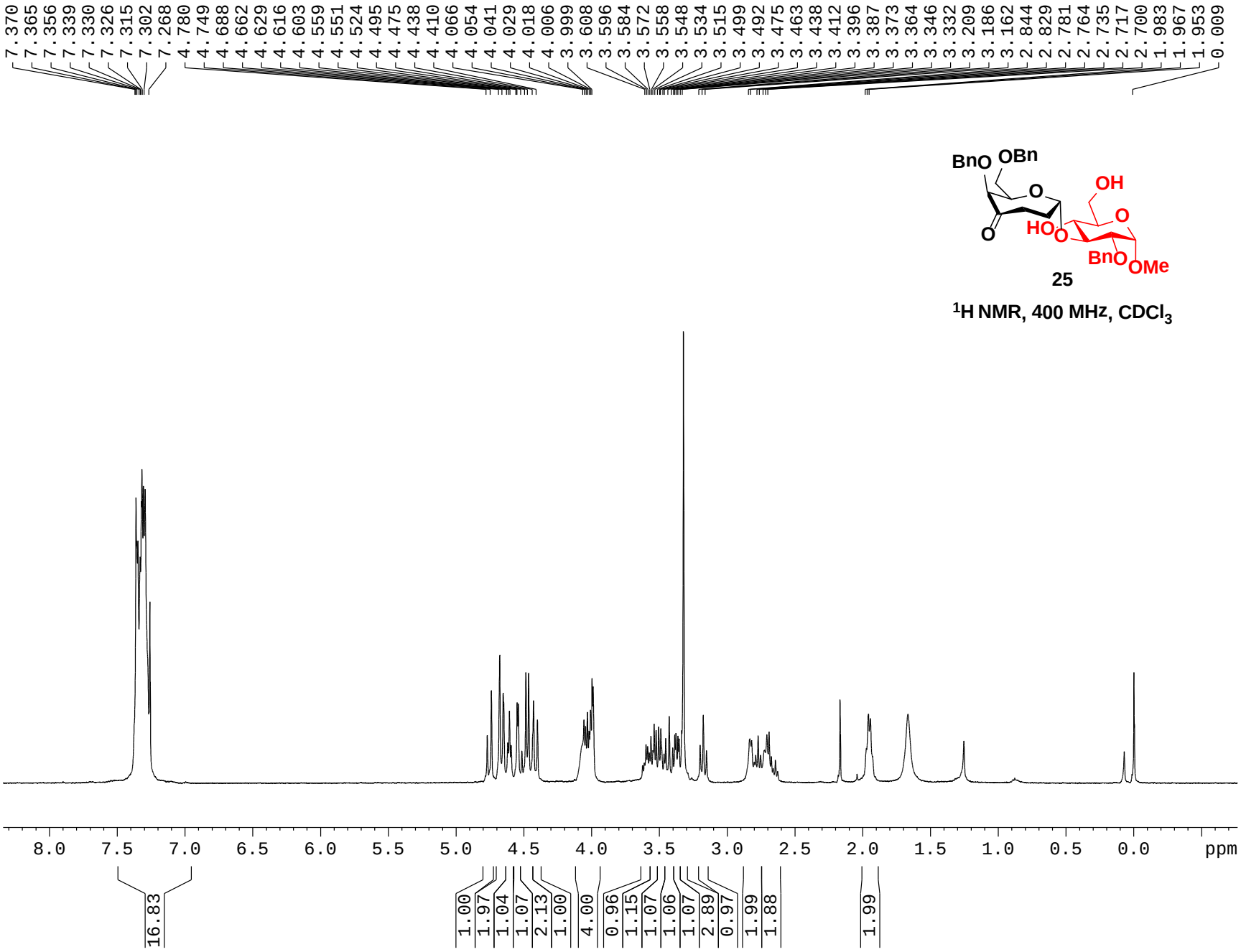
24

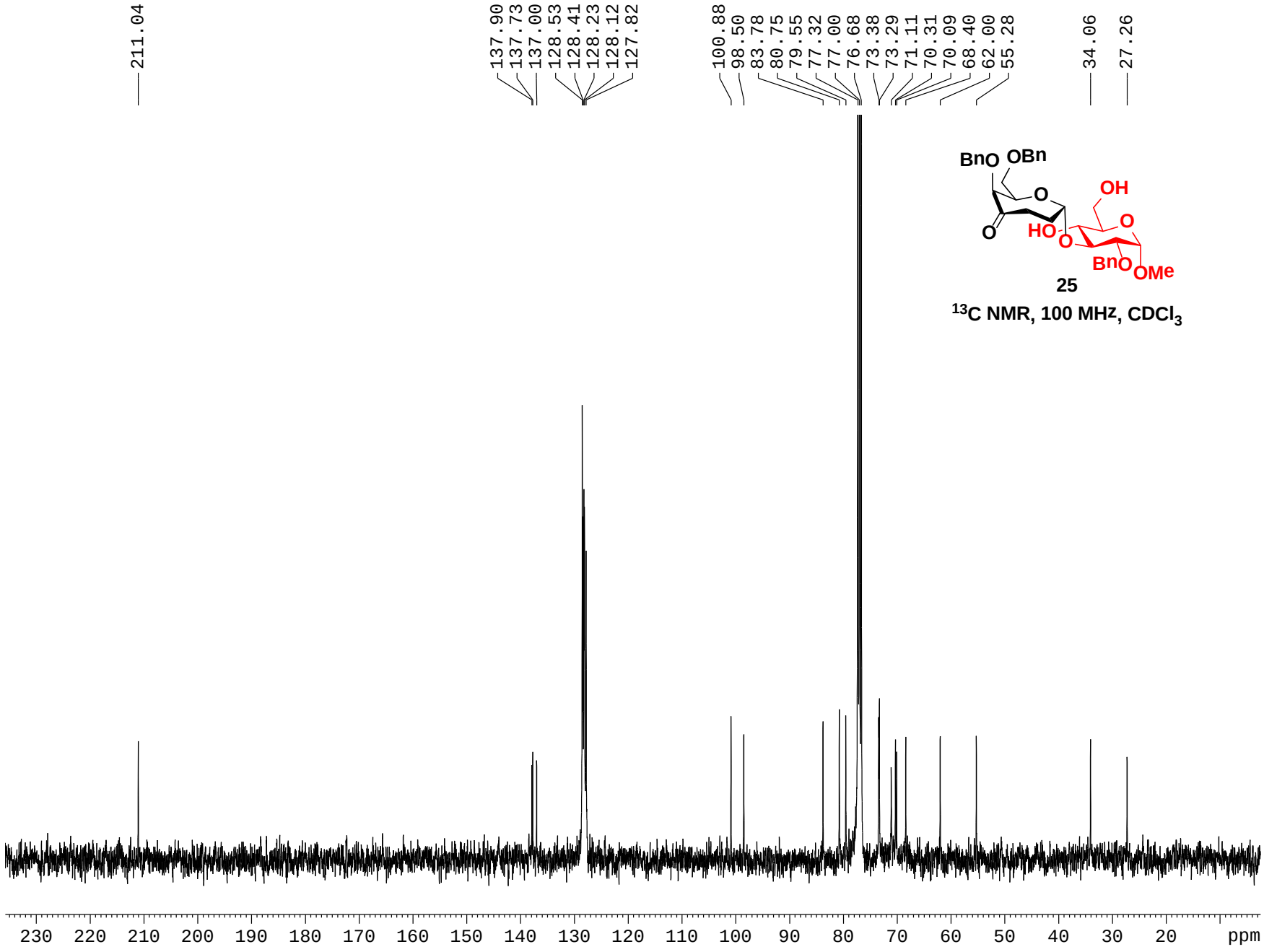
^{13}C NMR, 100 MHz, $CDCl_3$

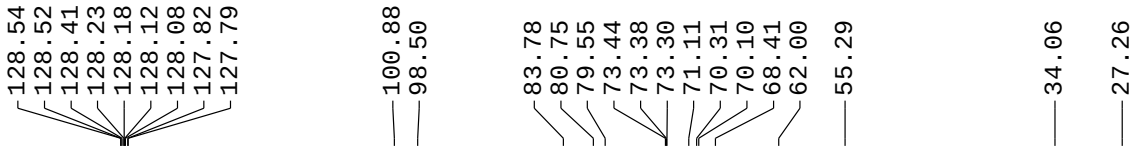


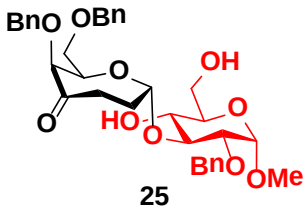
24

DEPT NMR, 100 MHz, $CDCl_3$



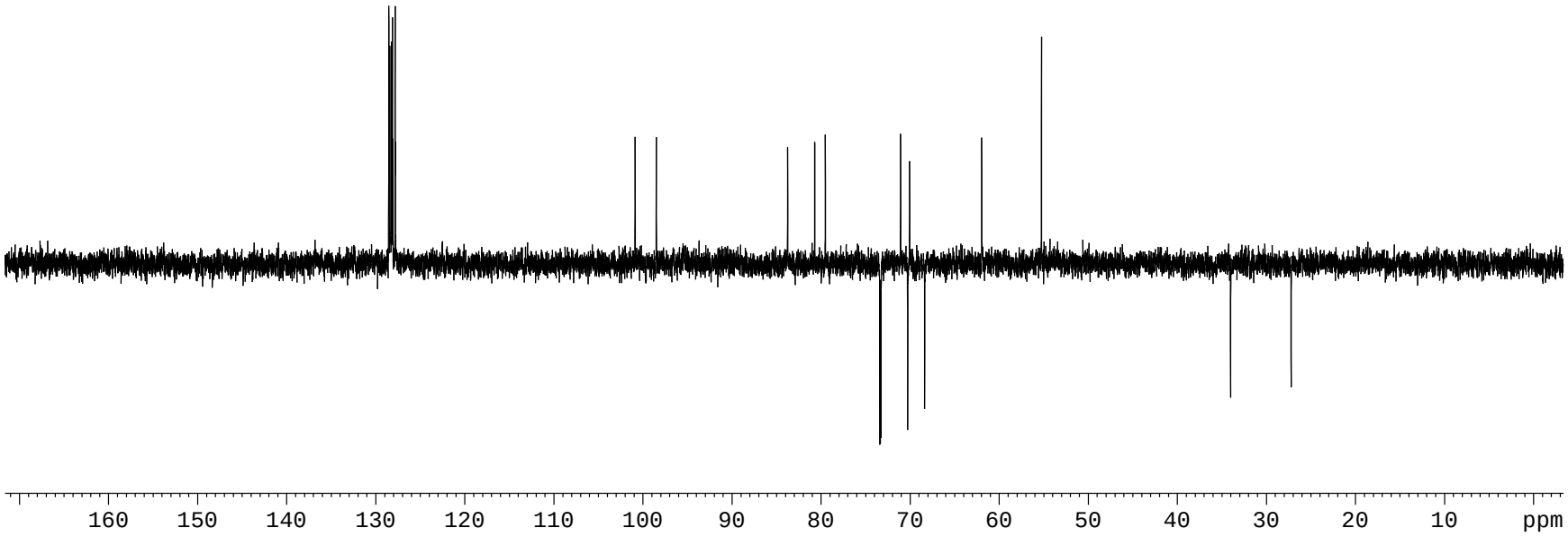


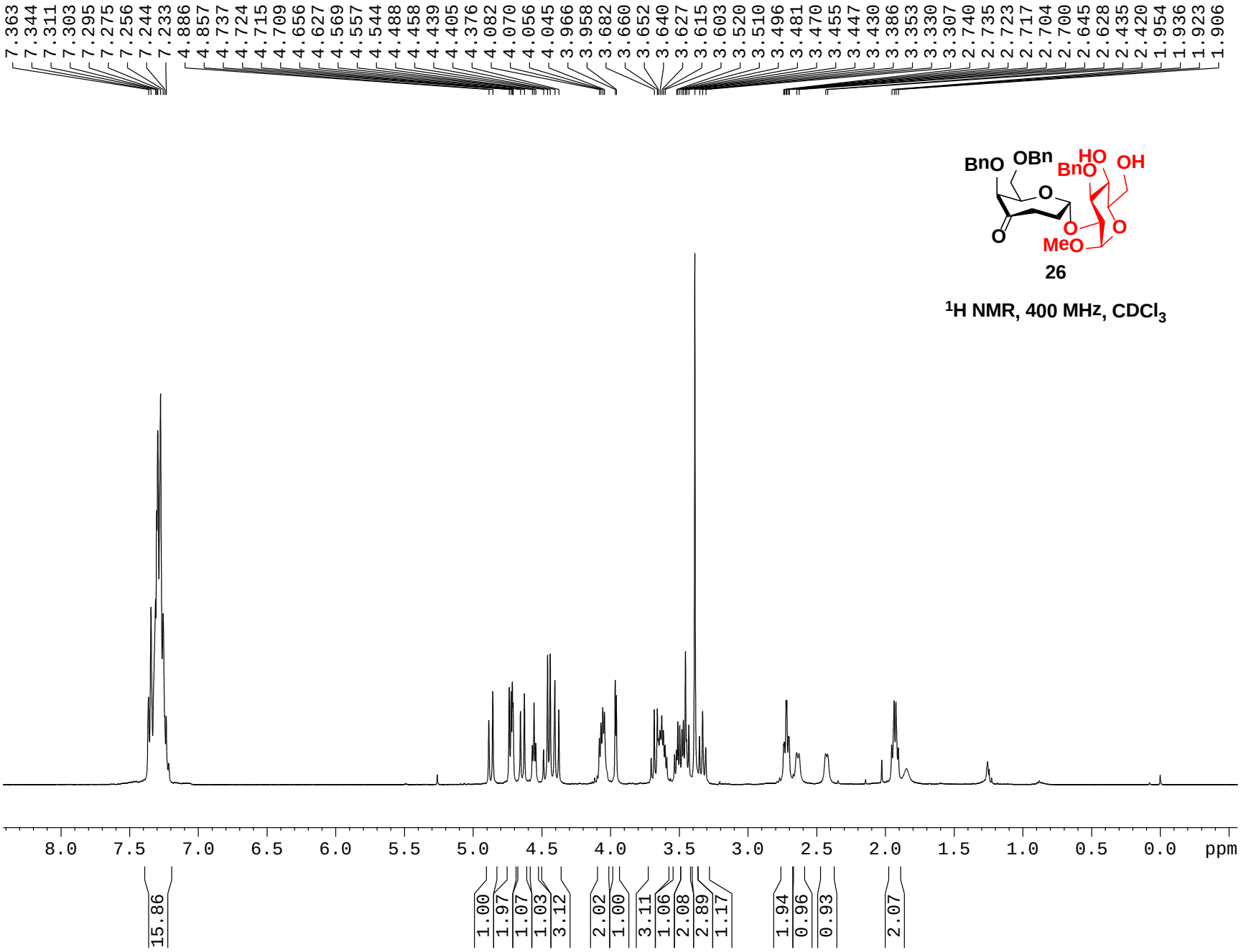


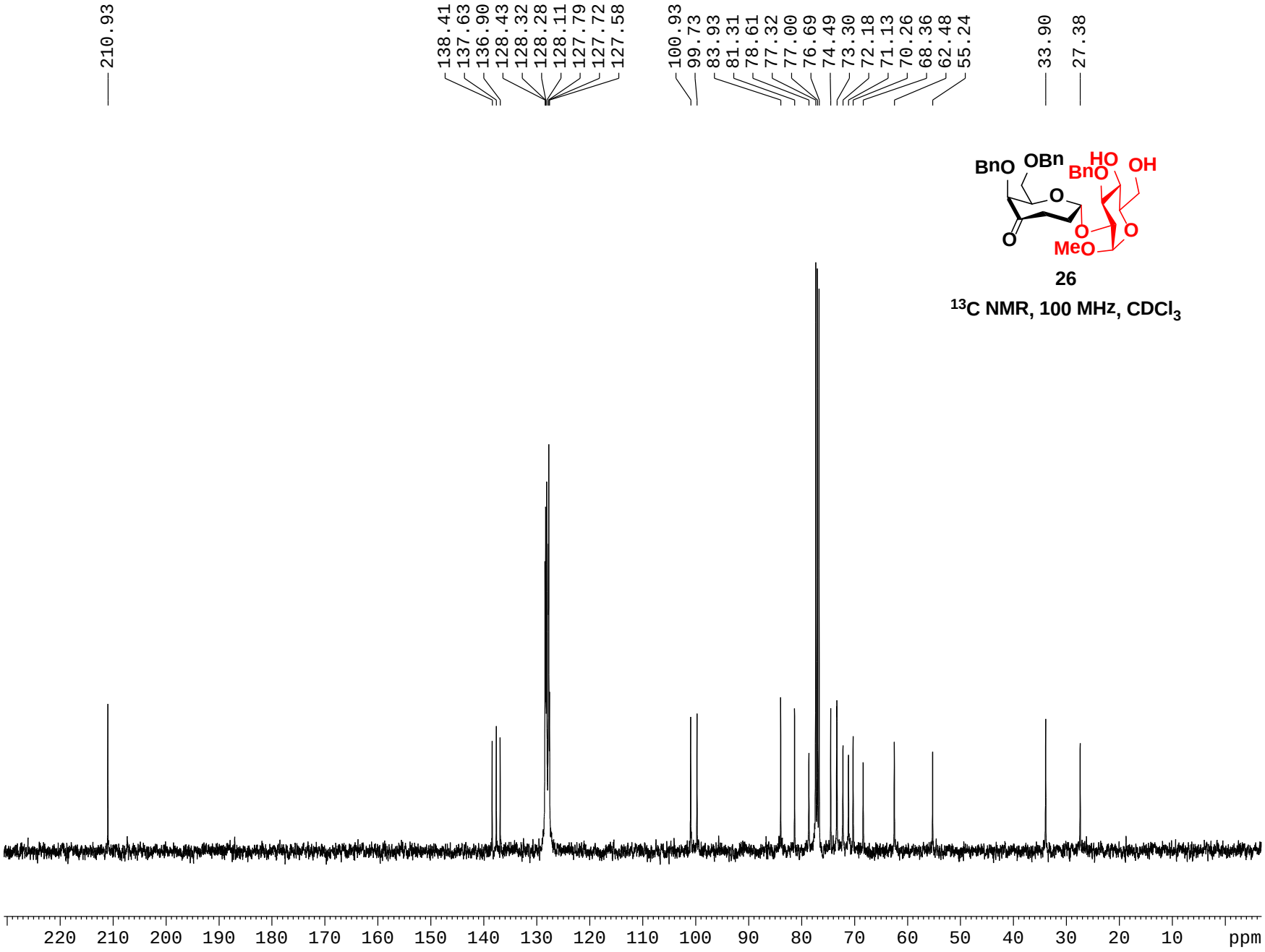


25

DEPT NMR, 100 MHz, $CDCl_3$







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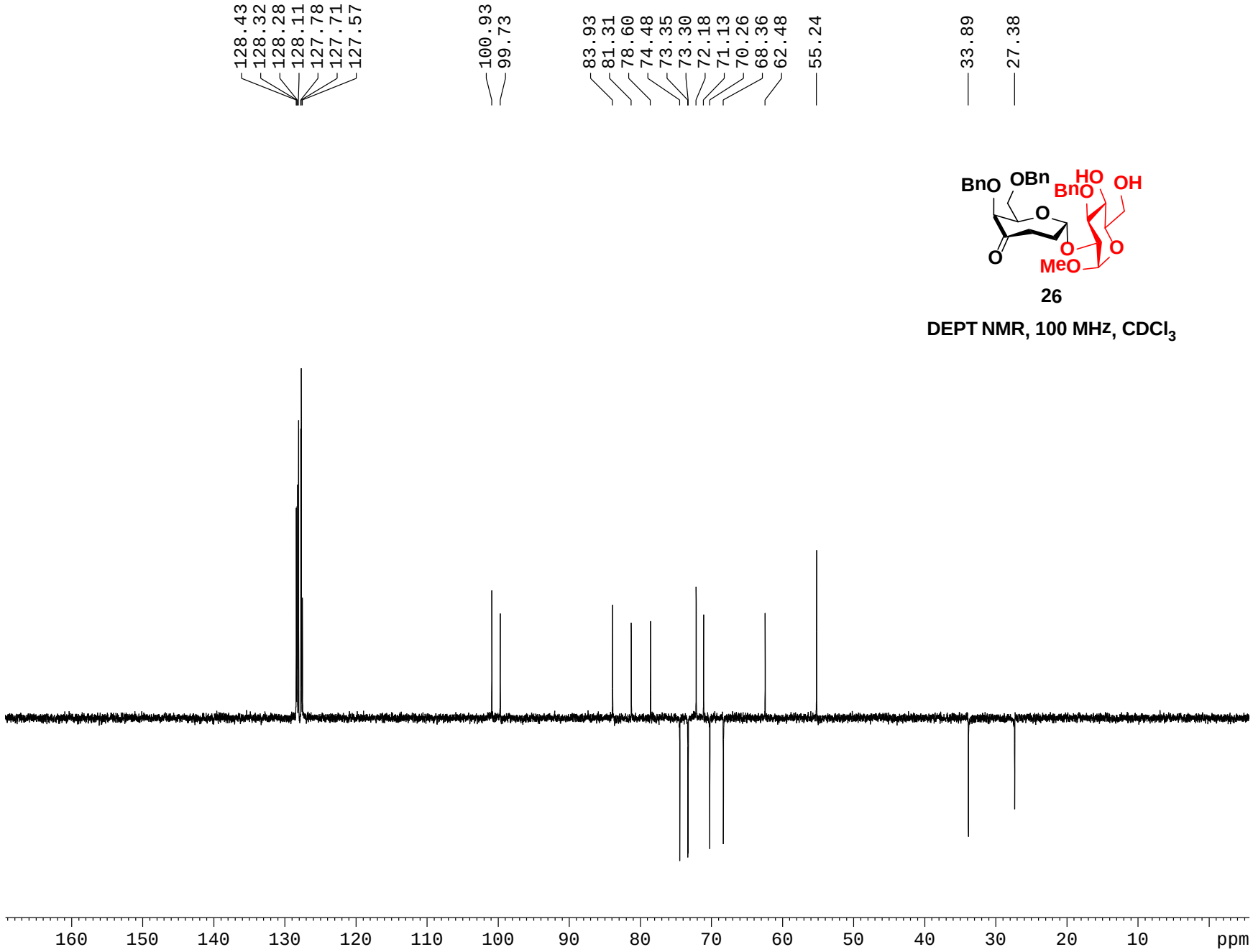
^{13}C NMR, 100 MHz, $CDCl_3$



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DEPT NMR, 100 MHz, $CDCl_3$