

Supporting Information for:

Synthesis of Bicyclo[3.1.0]hexane Derivatives as Conformationally-Restricted Analogues of β -Arabinofuranosyl and α -Galactofuranosyl Rings

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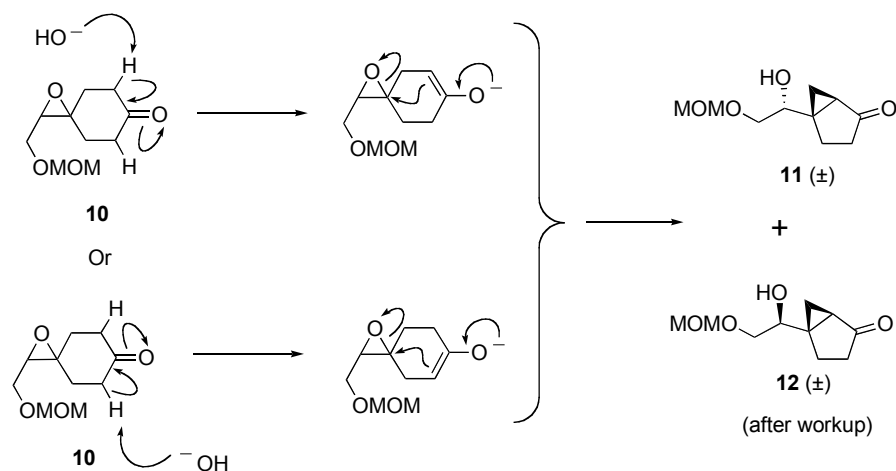


Figure S1. Proposed mechanism for the formation of (±)-**11** and (±)-**12** from **10** upon treatment with sodium hydroxide in ethanol.

General Methods

All reagents used were purchased from commercial sources and were used without further purification. Solvents used in reactions were purified by PURESOLV-400 System from Innovative Technology Inc. Unless stated otherwise, all reactions were monitored by TLC on silica gel G-25 UV₂₅₄ (0.25 mm, Macherey-Nagel). Spots were detected under UV light and/or by charring with acidified ethanolic anisaldehyde. Solvents were evaporated under reduced pressure and below 50 °C (water bath). Column chromatography was performed on silica gel 60 (40–60 μ m). The ratio between silica gel and crude product ranged from 100:1 to 20:1 (w/w). Iatrobeads refers to a beaded silica gel 6RS-8060, which was manufactured by Iatron Laboratories (Tokyo). ¹H NMR spectra were recorded on VARIAN INOVA-NMR spectrometers at 400, 500 MHz, and chemical shifts are referenced to TMS (0.0 ppm, CDCl₃) or CD₃OD (4.78 ppm, CD₃OD). ¹³C NMR one-dimensional and APT spectra¹ were recorded at 100 or 125 MHz, and chemical shifts are referenced to CDCl₃ (77.23 ppm, CDCl₃) or CD₃OD (48.9 ppm, CD₃OD). ¹H NMR data are reported as though they are first order, and the peak assignments are made by 2D-NMR spectroscopy (¹H–¹H COSY and HMQC). ESI-MS spectra were recorded on samples suspended in THF or CH₃OH and added NaCl. Optical rotations were measured on Perkin-Elmer 241 Polarimeter with sodium D line (589 nm) and are in units of deg·mL (dm·g)⁻¹.

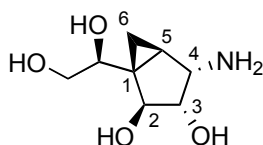
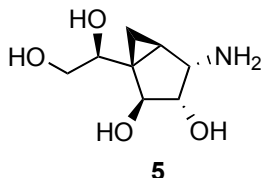
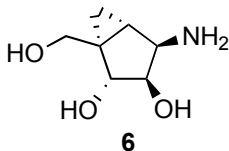


Figure S2. Numbering system used for NMR assignments, unless otherwise indicated.



(1*S*,2*S*,3*S*,4*S*,5*R*)-4-amino-1-[(1*S*)-1,2-dihydroxyethyl]bicyclo[3.1.0]hexane-2,3-diol (5).

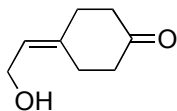
To a solution of compound **27** (0.013 g, 0.06 mmol) in THF (1 mL) was added 10% Pd/C (0.3 mg) and the reaction mixture was stirred under a hydrogen atmosphere for 12 h. The mixture was then filtered through Celite and concentrated. The resulting residue was purified by chromatography on Iatrobeds (16:5:1 CH₂Cl₂–CH₃OH–NH₄OH then 6:1 CH₂Cl₂–NH₄OH) to give **5** (0.011 g, 97%) as a foam. *R_f* 0.47 (6:1 CH₃OH–NH₄OH); ¹H NMR (400 MHz, CD₃OD, δ_H) 4.20 (dd, 1 H, *J* = 1.0, 7.2 Hz, H-2), 3.78 (dd, 1 H, *J* = 6.2, 6.2 Hz, CHOH), 3.64 (dd, 1 H, *J* = 6.2, 11.1 Hz, CH₂OH), 3.55–3.49 (m, 2 H, CH₂OH, H-3), 3.12 (d, 1 H, *J* = 5.4 Hz, H-4), 1.44 (dd, 1 H, *J* = 4.2, 8.4 Hz, H-5), 0.75–0.67 (m, 2 H, H-6a, H-6b); ¹³C NMR (100 MHz, CD₃OD, δ_C) 79.2 (C-2), 78.2 (C-3), 73.4 (CHOH), 66.0 (CH₂OH), 53.5 (C-4), 34.3 (C-1), 25.4 (C-5), 9.1 (C-6). HRMS (ESI) *m/z* Calcd for (M+H⁺) C₈H₁₅NO₄ 190.1074. Found: 190.1072.



(1*R*,2*R*,3*R*,4*R*,5*S*)-4-amino-1-(hydroxymethyl)bicyclo[3.1.0]hexane-2,3-diol (6).

To a solution of compound **29** (0.006 g, 0.032 mmol) in THF (2 mL) was added 10% Pd/C (0.5 mg) and the reaction mixture was stirred under a hydrogen atmosphere for 12 h. The mixture was filtered through Celite and concentrated. The resulting residue was purified by chromatography on Iatrobeds (16:5:1 CH₂Cl₂–CH₃OH–NH₄OH then 6:1 CH₃OH–NH₄OH) to yield **6** (0.005 g, 97%) as a foam. *R_f* 0.50 (6:1 CH₃OH–NH₄OH); ¹H NMR (400 MHz, CD₃OD, δ_H) 4.25 (d, 1 H, *J* = 7.0 Hz, H-2), 3.97 (d, 1 H, *J* = 11.6 Hz, CH₂OH), 3.57 (dd, 1 H, *J* = 6.2, 7.0 Hz, H-3), 3.21 (d, 1 H, *J* = 11.6 Hz, CH₂OH), 3.20 (d, 1 H, *J* = 6.2 Hz, H-4), 1.35 (dd, 1 H, *J* = 4.0, 8.4 Hz, H-5), 0.81 (dd, 1 H, *J* = 4.0, 5.8 Hz, H-6a), 0.54 (dd, 1 H, *J* = 5.8, 8.4 Hz,

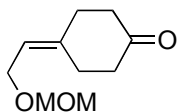
H-6b); ^{13}C NMR (125 MHz, CD_3OD , δ_{C}) 77.4 (C-2 or C-3), 77.3 (C-2 or C3), 64.4 (CH_2OH), 53.4 (C-4), 33.8 (C-1), 25.6 (C-5), 10.8 (C-6). HRMS (ESI) m/z Calcd for $(\text{M}+\text{H}^+)$ $\text{C}_7\text{H}_{13}\text{NO}_3$ 160.0968. Found: 160.0969.



8

4-(2-hydroxyethylidene)cyclohexanone (**8**).

8-(2-Hydroxyethylidene)-1,4-dioxaspiro[4.5] decane (**7**², 2.72 g, 14.76 mmol) was dissolved in 30 mL acetone and water (1:1) and oxalic acid dihydrate (3.75 g, 29.52 mmol) was added. The reaction mixture was stirred for 3 h at room temperature and then solid NaHCO_3 was added to consume the excess oxalic acid. The reaction mixture was filtered and the filtered solid was washed thoroughly with ether. The ether layer was dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography (1:3 hexane–EtOAc) to afford **8** (1.90 g, 92%) as a yellow oil. R_f 0.25 (1:3 hexane–EtOAc); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 5.62 (t, 1 H, $J = 6.9$ Hz, $\text{C}=\text{CH}$), 4.23 (d, 2 H, $J = 6.9$ Hz, CH_2OH), 2.59–2.52 (m, 4 H, cyclohexane CH_2), 2.46–2.42 (m, 4 H, cyclohexane CH_2); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 210.8 ($\text{C}=\text{O}$), 138.1 ($\text{C}=\text{CH}$), 124.1 ($\text{C}=\text{CH}$), 58.8 (CH_2OH), 41.3 (cyclohexane CH_2), 40.5 (cyclohexane CH_2), 34.0 (cyclohexane CH_2), 26.2 (cyclohexane CH_2). HRMS (ESI) m/z Calcd for $(\text{M}+\text{Na}^+)$ $\text{C}_8\text{H}_{12}\text{O}_2$: 163.0729. Found 163.0728.

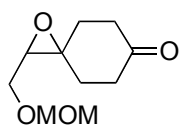


9

4-[2-(methoxymethoxy)ethylidene]cyclohexanone (**9**).

To a stirred solution of alcohol **8** (1.85 g, 13.20 mmol) in dimethoxymethane (30 mL) at room temperature, lithium bromide (0.23 g, 1.64 mmol) and *p*-toluenesulfonic acid monohydrate

(0.25 g, 1.32 mmol) were added. The mixture was stirred for 1 h, while being monitored by TLC. When the reaction was done, brine was added and the solution was then neutralized with Et₃N. The aqueous solution was extracted with ether, and the organic layers were combined, dried (Na₂SO₄) and concentrated. The resulting oil was purified by column chromatography (2:1 hexane–EtOAc) to afford the product **9** (1.74 g, 72%) as an oil. *R_f* 0.45 (2:1 hexane–EtOAc); ¹H NMR (400 MHz, CDCl₃, δ_H) 5.51 (t, 1 H, *J* = 7.1 Hz, C=CH), 4.58 (s, 2 H, OCH₂O), 4.05 (d, 2 H, *J* = 7.1 Hz, C=CHCH₂O), 3.31 (s, 3 H, OCH₃), 2.53–2.46 (m, 4 H, cyclohexane CH₂), 2.39–2.35 (m, 4 H, cyclohexane CH₂); ¹³C NMR (100 MHz, CDCl₃, δ_C) 210.6 (C=O), 139.2 (C=CH), 121.1 (C=CH), 95.5 (OCH₂O), 62.9 (=CHCH₂O), 55.2 (OCH₃), 41.2 (cyclohexane CH₂), 40.4 (cyclohexane CH₂), 33.9 (cyclohexane CH₂), 26.1 (cyclohexane CH₂). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₁₀H₁₆O₃: 207.0992. Found 207.0992.

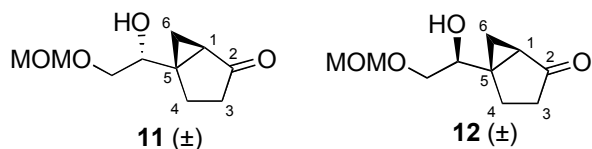


10

2-[(methoxymethoxy)methyl]-1-oxaspiro[2.5]octan-6-one (10).

A solution of *m*-CPBA (2.54 g, 11.34 mmol) in CH₂Cl₂ (10 mL) was added dropwise into an ice-cold CH₂Cl₂ (20 mL) solution of **9** (1.74 g, 9.45 mmol). The mixture was stirred for 2 h at room temperature before being diluted with CH₂Cl₂. The organic layer was then washed with 1 M NaOH and then water. After drying (Na₂SO₄) the organic extract was concentrated and the residue was purified by column chromatography (2:1 hexane–EtOAc) to afford compound **10** (1.32 g, 70%) as a light yellow oil. *R_f* 0.30 (2:1 hexane–EtOAc); ¹H NMR (400 MHz, CDCl₃, δ_H) 4.63 (d, 1 H, *J* = 6.6 Hz, OCH₂O), 4.60 (d, 1 H, *J* = 6.6 Hz, OCH₂O), 3.68 (d, 2 H, *J* = 5.4 Hz, CH₂O), 3.32 (s, 3 H, OCH₃), 3.16 (t, 1 H, *J* = 5.4 Hz, MOMOCH₂CH), 2.64–2.53 (m, 2 H, cyclohexane CH₂), 2.45–2.36 (m, 2 H, cyclohexane

CH₂), 2.11–2.00 (m, 2 H, cyclohexane CH₂), 1.88–1.82 (m, 1 H, cyclohexane CH₂), 1.79–1.72 (m, 1 H, cyclohexane CH₂); ¹³C NMR (125 MHz, CDCl₃, δ_C) 209.6 (C=O), 96.7 (OCH₂O), 66.0 (CH), 62.0 (CH₂O), 60.2 (quaternary C), 55.3 (OCH₃), 38.6 (cyclohexane CH₂), 38.5 (cyclohexane CH₂), 33.4 (cyclohexane CH₂), 27.8 (cyclohexane CH₂). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₁₀H₁₆O₄: 223.0941. Found 223.0942.



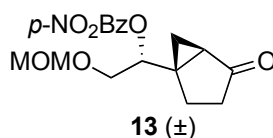
5-[1-hydroxy-2-(methoxymethoxy)ethyl]bicyclo[3.1.0]hexan-2-one (11/12).

To a solution of epoxide **10** (1.32 g, 6.60 mmol) in EtOH (50 mL) was added of 2 M NaOH (10 mL) and the solution was heated at reflux for 20 min. The EtOH was evaporated under reduced pressure and a satd aq NaCl solution was added to the residue, which was extracted with CH₂Cl₂. The CH₂Cl₂ solution was dried (Na₂SO₄) and concentrated to give a yellow oil, which was purified by chromatography (6:1 Et₂O–pentane) to afford **11** (0.53 g, 40%) and **12** (0.62 g, 47%).

Data for **11**: *R_f* 0.34 (1:20 CH₃OH–CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 4.67 (s, 2 H, OCH₂O), 3.76 (d, 1 H, *J* = 7.1 Hz, MOMOCH₂), 3.59–3.56 (m, 2 H, CHOH, MOMOCH₂), 3.39 (s, 3 H, OCH₃), 2.82 (d, 1 H, *J* = 2.6 Hz, OH), 2.34–2.27 (m, 1 H, H-3), 2.16–2.13 (m, 2 H, H-4), 1.96–1.91 (m, 1 H, H-3), 1.81 (dd, 1 H, *J* = 3.4, 9.3 Hz, H-1), 1.32 (ddd, 1 H, *J* = 1.4, 4.9, 9.3 Hz, H-6a), 1.12 (dd, 1 H, *J* = 3.4, 4.9 Hz, H-6b); ¹³C NMR (125 MHz, CDCl₃, δ_C) 213.5 (C-2), 97.1 (OCH₂O), 72.3 (CHOH), 71.0 (MOMOCH₂), 55.6 (OCH₃), 35.7 (C-5), 32.9 (C-3), 32.5 (C-1), 22.0 (C-4), 17.1 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₁₀H₁₆O₄: 223.0941. Found: 223.0940.

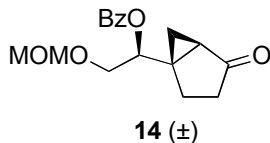
Data for **12**: *R_f* 0.35 (1:20 CH₃OH–CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 4.63 (s, 2 H, OCH₂O), 3.89 (dd, 1 H, *J* = 3.0, 7.7 Hz, CHOH), 3.74 (dd, 1 H, *J* = 3.0, 10.4 Hz, MOMOCH₂), 3.48 (dd, 1 H, *J* = 7.7, 10.4 Hz, MOMOCH₂), 3.36 (s, 3 H, OCH₃), 2.85 (br, 1

H, OH)2.15–2.09 (m, 2 H, H-3), 2.03–1.98 (m, 2 H, H-4), 1.86 (dd, 1 H, J = 3.2, 9.2 Hz, H-1), 1.45 (dd, 1 H, J = 4.7, 9.2 Hz, H-6a), 1.02 (dd, 1 H, J = 3.2, 4.7 Hz, H-6b); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 213.9 (C-2), 97.1 (OCH_2O), 71.2 (MOMOCH_2), 71.0 (CHOH), 55.5 (OCH_3), 35.4 (C-5), 33.0 (C-3), 31.1 (C-1), 24.5 (C-4), 16.0 (C-6). HRMS (ESI) m/z Calcd for $(\text{M}+\text{Na}^+)$ $\text{C}_{10}\text{H}_{16}\text{O}_4$: 223.0941. Found: 223.0941.



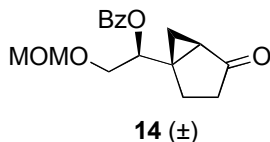
2-(methoxymethoxy)-1-[4-oxobicyclo[3.1.0]hex-1-yl]ethyl 4-nitrobenzoate (13).

To a stirred solution of 11 (1.23 g, 6.15 mmol) in CH_2Cl_2 –pyridine (10:1, 8.8 mL) was added *p*-nitrobenzoyl chloride (1.36 g, 7.38 mmol) at 0 °C. The mixture was then warmed to room temperature and stirred for 1 h. The reaction mixture was quenched by adding CH_3OH , and then diluted with CH_2Cl_2 . The solution was washed with 1 M HCl and water. The organic layer was dried (Na_2SO_4), filtered, concentrated, and the residue was purified by chromatography (1:1 EtOAc–hexane) to provide the product **13** as a light yellow solid (1.60 g, 76%). This material was recrystallized from CH_3OH to give a crystalline material (m.p. = 107–109 °C). R_f 0.36 (1:1 EtOAc–Hexane); ^1H NMR (500 MHz, CDCl_3 , δ_{H}) 8.32–8.30 (m, 2 H, Ar), 8.23–8.21 (m, 2 H, Ar), 5.11 (dd, 1 H, J = 4.7, 7.0 Hz, CHOBz-NO_2), 4.67–4.64 (m, 2 H, OCH_2O), 3.95–3.88 (m, 2 H, MOMOCH_2), 3.35 (s, 3 H, OCH_3), 2.40–2.32 (m, 1 H, H-3), 2.16–2.13 (m, 3 H, H-2, H-3), 2.00 (dd, 1 H, J = 3.6, 9.4 Hz, H-5), 1.47 (dd, 1 H, J = 5.2, 9.4 Hz, H-6a), 1.28 (dd, 1 H, J = 3.6, 5.2 Hz, H-6b); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 212.3 (C-4), 163.9 (O-C=O), 150.7 (Ar), 135.2 (Ar), 130.8 ($\text{Ar} \times 2$), 123.6 ($\text{Ar} \times 2$), 96.6 (OCH_2O), 76.2 (CHOBz-NO_2), 67.3 (MOMOCH_2), 55.5 (OCH_3), 34.3 (C-1), 32.8 (C-5), 32.6 (C-3), 22.7 (C-2), 17.9 (C-6). HRMS (ESI) m/z Calcd for $(\text{M}+\text{Na}^+)$ $\text{C}_{17}\text{H}_{19}\text{NO}_7$: 372.1054. Found: 372.1055.



2-(methoxymethoxy)-1-[4-oxobicyclo[3.1.0]hex-1-yl]ethyl benzoate (14).

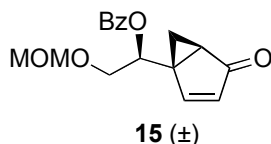
Benzoyl chloride (0.44 g, 3.12 mmol) was added, with stirring, to a solution of compound **12** (0.52 g, 2.60 mmol) in pyridine (25 mL) at 0 °C. The cooling bath was removed after 20 min and the mixture was stirred at room temperature for 2 h. The reaction was quenched by the addition of CH₃OH (1 mL) and diluted with EtOAc. The mixture was washed with water and 1 M HCl. The organic layer was dried (Na₂SO₄) and concentrated to afford a yellow oil, which was purified by chromatography (2:1 hexane–EtOAc) to give the product **14** (0.73 g, 93%) as a colorless oil. *R_f* 0.46 (2:1 hexane–EtOAc); ¹H NMR (500 MHz, CDCl₃, δ_H) 8.02–8.00 (m, 2 H, Ar), 7.58–7.53 (m, 1 H, Ar), 7.46–7.43 (m, 2 H, Ar), 5.37 (dd, 1 H, *J* = 5.6, 5.6 Hz, CHOBz), 4.61 (s, 2 H, OCH₂O), 3.83 (d, 2 H, *J* = 5.6 Hz, MOMOCH₂), 3.31 (s, 3 H, OCH₃), 2.23–2.13 (m, 4 H, H-2, H-3), 1.90 (dd, 1 H, *J* = 3.3, 9.3 Hz, H-5), 1.58 (dd, 1 H, *J* = 5.0, 9.3 Hz, H-6a), 1.16 (dd, 1 H, *J* = 3.3, 5.0 Hz, H-6b); ¹³C NMR (125 MHz, CDCl₃, δ_C) 212.7 (C-4), 165.6 (O–C=O), 133.3 (Ar), 129.8 (Ar), 129.6 (Ar × 2), 128.5 (Ar × 2), 96.5 (OCH₂O), 73.7 (CHOBz), 67.3 (MOMOCH₂), 55.4 (OCH₃), 33.9 (C-1), 32.8 (C-3), 31.8 (C-5), 24.1 (C-2), 17.3 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₁₇H₂₀O₅: 327.1203. Found: 327.1199.



2-(methoxymethoxy)-1-[4-oxobicyclo[3.1.0]hex-1-yl]ethyl benzoate (14).

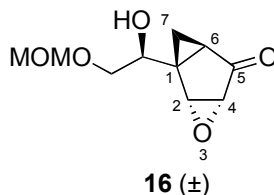
Compound **7** (0.15 g, 0.75 mmol), benzoic acid (0.93 g, 0.75 mmol) and triphenylphosphate (0.20 g, 0.76 mmol) was dissolved in THF (15 mL). The solution was cooled to 0 °C and treated with DIAD (0.15 g, 0.75 mmol) dropwise. The mixture was warmed to room temperature and stirred for 1 h. The reaction was then diluted with EtOAc and washed with

1 M NaOH and water. The organic layer was dried (Na₂SO₄) and concentrated and the residue was purified by chromatographic (4:1 hexane–EtOAc) to yield **8** (0.19 g, 84%). The spectral data for **14** produced in this manner was identical to that described above.



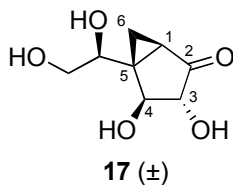
2-(methoxymethoxy)-1-[4-oxobicyclo[3.1.0]hex-2-en-1-yl]ethyl benzoate (15**).**

To a solution of compound **14** (0.65 g, 2.14 mmol) in dry EtOAc (20 mL), which had been saturated with HCl gas, was added PhSeCl (0.41 g, 2.14 mmol). After 2 h, the mixture was poured onto a saturated aqueous solution of NaHCO₃. The aqueous layer was extracted with EtOAc and the organic layers were combined, dried (Na₂SO₄) and concentrated. The residue was purified by chromatography (4:1 hexane–EtOAc) to afford the selenide isomers (0.45 g, 45%) as a yellow oil, *R_f* 0.68 (2:1 hexane–EtOAc). This mixture of compounds was dissolved in THF (10 mL) and NaIO₄ (0.42 g, 1.92 mmol) and H₂O (3 mL) were added. The mixture was stirred overnight, filtered and the filtrate was extracted with EtOAc. The organic layers were combined, dried (Na₂SO₄) and concentrated. The resulting oil was purified by column chromatography (3:1 hexane–EtOAc) to afford the enone **15** (0.28 g, 95% from mixture of selenides, 43% from **14**) as an oil. *R_f* 0.51 (2:1 hexane–EtOAc); ¹H NMR (400 MHz, CDCl₃, δ_H) 8.09–8.07 (m, 2 H, Ar), 7.78 (d, 1 H, *J* = 5.7 Hz, H-2), 7.62–7.58 (m, 1 H, Ar), 7.50–7.46 (m, 2 H, Ar), 5.68 (d, 1 H, *J* = 5.7 Hz, H-3), 5.35 (dd, 1 H, *J* = 5.3, 5.3 Hz, CHOBz), 4.61 (s, 2 H, OCH₂O), 3.86–3.79 (m, 2 H, MOMOCH₂), 3.31 (s, 3 H, OCH₃), 2.35 (dd, 1 H, *J* = 3.9, 8.7 Hz, H-5), 1.79 (dd, 1 H, *J* = 3.9, 8.7 Hz, H-6a), 1.58 (dd, 1 H, *J* = 3.9, 3.9 Hz, H-6b); ¹³C NMR (125 MHz, CDCl₃, δ_C) 204.8 (C-4), 165.6 (O–C=O), 161.4 (C-2), 133.4 (Ar), 129.8 (Ar), 129.7 (Ar × 2), 128.5 (Ar × 2), 128.4 (C-3), 96.5 (OCH₂O), 72.6 (CHOBz), 67.9 (MOMOCH₂), 55.4 (OCH₃), 40.1 (C-6), 36.6 (C-1), 28.9 (C-5). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₁₇H₁₈O₅: 325.1046. Found: 325.1042.



1-[1-hydroxy-2-(methoxymethoxy)ethyl]-3-oxatricyclo[4.1.0.^{2,4}]heptan-5-one (16).

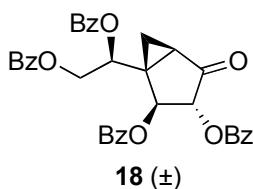
To an ice cold solution of enone **15** (3.07 g, 10.16 mmol) in CH₃OH (60 mL) and 30% hydrogen peroxide (20 mL) was slowly added 4 M NaOH (8 mL). After stirring for 1 h, the mixture was diluted with water and extracted repeatedly with Et₂O. The organic layers were combined, dried (Na₂SO₄) and concentrated. The resulting yellowish oil was purified by chromatography (9:1 CH₂Cl₂–CH₃OH) to afford the epoxide **16** (1.72 g, 79%) as an oil. *R_f* 0.33 (ethyl ether); ¹H NMR (500 MHz, CDCl₃, δ_H) 4.66 (s, 2 H, OCH₂O), 3.98 (dd, 1 H, *J* = 2.5, 2.5 Hz, H-2), 3.83–3.81 (m, 2 H, MOMOCH₂, CHOH), 3.72 (dd, 1 H, *J* = 8.6, 11.2 Hz, MOMOCH₂), 3.37 (s, 3 H, OCH₃), 3.19 (dd, 1 H, *J* = 1.2, 2.5 Hz, H-4), 3.13 (br, 1 H, OH), 1.76 (dddd, 1 H, *J* = 1.2, 2.5, 3.5, 8.5 Hz, H-6), 1.55 (dd, 1 H, *J* = 5.2, 8.5 Hz, H-7a), 1.22 (dd, 1 H, *J* = 3.5, 5.2 Hz, H-7b); ¹³C NMR (125 MHz, CDCl₃, δ_C) 202.5 (C-5), 97.3 (OCH₂O), 71.7 (MOMOCH₂), 69.8 (CHOH), 57.1 (C-2), 55.6 (OCH₃), 51.0 (C-4), 38.1 (C-1), 25.6 (C-6), 21.0 (C-7). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₁₀H₁₄O₅: 237.0733. Found: 237.0735.



5-(1,2-dihydroxyethyl)-3,4-dihydroxybicyclo[3.1.0]hexan-2-one (17).

A mixture of epoxide **16** (1.52 g, 7.10 mmol) and 3.5 M H₂SO₄ (10 mL) was heated with stirring at 50 °C for 12 h whereupon a homogenous solution resulted. The solution was neutralized with solid NaHCO₃ to pH 7 and concentrated. The residue was purified by chromatography on Iatrobeds (4:1 CH₂Cl₂–CH₃OH) to give the tetrol **17** (0.93 g, 70%) as a

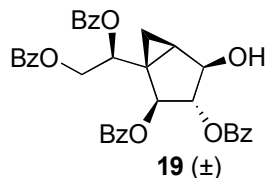
foam. R_f 0.29 (4:1 CH_2Cl_2 – CH_3OH); ^1H NMR (400 MHz, CD_3OD , δ_{H}) 4.12 (dd, 1 H, J = 1.0, 6.9 Hz, H-4), 3.96–3.92 (m, 2 H, H-3, CHOH), 3.71 (dd, 1 H, J = 5.4, 11.2 Hz, CH_2OH), 3.55 (dd, 1 H, J = 6.4, 11.2 Hz, CH_2OH), 2.01 (ddd, 1 H, J = 1.0, 4.8, 8.1 Hz, H-1), 1.59–1.52 (m, 2 H, H-6a, H-6b); ^{13}C NMR (100 MHz, CD_3OD , δ_{C}) 209.6 (C-2), 78.0 (C-3), 76.6 (C-4), 72.1 (CHOH), 66.0 (CH_2OH), 41.3 (C-5), 31.9 (C-1), 15.6 (C-6). HRMS (ESI) m/z Calcd for $(\text{M}+\text{Na}^+)$ $\text{C}_8\text{H}_{12}\text{O}_5$: 211.0577. Found: 211.0577.



1-[-1,2-bis(benzoyloxy)ethyl]-4-oxobicyclo[3.1.0]hexane-2,3-diyl dibenzoate(18).

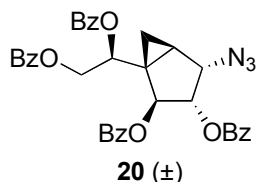
Benzoyl chloride (1.26 g, 9.00 mmol) was added slowly, with stirring, to a solution of **17** (0.38 g, 2.00 mmol) in pyridine (20 mL) at 0 °C. The cooling bath was removed after 20 min and the mixture was kept at 10 °C for 2 h. The reaction was quenched by the addition of CH_3OH and was then diluted with EtOAc. The mixture was washed with water and 1 M HCl. The organic layer was dried (Na_2SO_4) and concentrated to afford a yellow oil, which was purified by chromatography (3:1 hexane–EtOAc) to give **18** (1.08 g, 90%) as a colorless oil. R_f 0.52 (3:1 hexane–EtOAc); ^1H NMR (400 MHz, CDCl_3 , δ_{H}) 8.06–7.97 (m, 6 H, Ar), 7.81–7.79 (m, 2 H, Ar), 7.59–7.49 (m, 3 H, Ar), 7.45–7.32 (m, 7 H, Ar), 7.14–7.10 (m, 2 H, Ar), 6.54 (dd, 1 H, J = 1.3, 6.4 Hz, H-2), 5.57 (d, 1 H, J = 6.4 Hz, H-3), 5.40 (dd, 1 H, J = 5.3, 6.8 Hz, CHOBz), 4.94 (dd, 1 H, J = 5.3, 11.9 Hz, CH_2OBz), 4.84 (dd, 1 H, J = 6.8, 11.9 Hz, CH_2OBz), 2.48 (dd, 1 H, J = 4.0, 9.4 Hz, H-5), 2.03 (dd, 1 H, J = 4.0, 6.0 Hz, H-6a), 1.95–1.91 (m, 1 H, H-6b); ^{13}C NMR (125 MHz, CDCl_3 , δ_{C}) 198.6 (C-4), 166.0 ($\text{O}-\text{C}=\text{O}$), 165.6 ($\text{O}-\text{C}=\text{O}$), 166.5 ($\text{O}-\text{C}=\text{O}$), 165.4 ($\text{O}-\text{C}=\text{O}$), 133.6 (Ar), 133.4 (Ar), 133.3 (Ar), 133.2 (Ar), 130.2 (Ar \times 2), 129.9 (Ar \times 2), 129.8 (Ar \times 2), 129.7 (Ar \times 2), 129.3 (Ar), 129.1 (Ar), 128.8 (Ar), 128.7 (Ar), 128.5 (Ar \times 2), 128.4 (Ar \times 2), 128.3 (Ar \times 2), 128.2 (Ar \times 2), 76.7

(CHOBz), 72.9 (C-3), 72.4 (C-2), 63.5 (CH₂OBz), 34.9 (C-1), 33.4 (C-5), 18.2 (C-6).
 HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₃₆H₂₈O₉: 627.1625. Found: 627.1624.



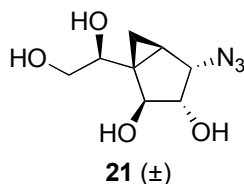
1-[1,2-bis(benzoyloxy)ethyl]-4-hydroxybicyclo[3.1.0]hexane-2,3-diyl dibenzoate (19).

Compound **18** (0.732 g, 1.21 mmol) was dissolved in CH₃OH at −30 °C and NaBH₄ (0.092 g, 2.42 mmol) was added in one portion. The mixture was stirred for 5 min, before being warmed to room temperature and stirred for 15 min. The reaction mixture was diluted with CH₂Cl₂ and washed 1 M HCl. The organic layer was dried (Na₂SO₄), concentrated and the residue was purified by chromatography (3:1 hexane–EtOAc) to provide the product **19** (0.607 g, 83%) as a foam. *R_f* 0.32 (1:2 hexane–EtOAc); ¹H NMR (400 MHz, CDCl₃, δ_H) 8.05–8.00 (m, 6 H, Ar), 7.78–7.76 (m, 2 H, Ar), 7.61–7.34 (m, 10 H, Ar), 7.10–7.06 (m, 2 H, Ar), 6.48 (d, 1 H, *J* = 6.0 Hz, H-2), 5.30 (dd, 1 H, *J* = 5.3, 7.2 Hz, CHOBz), 4.93–4.88 (m, 2 H, CH₂OBz, H-3), 4.76 (dd, 1 H, *J* = 7.2, 11.7 Hz, CH₂OBz), 4.50 (dd, 1 H, *J* = 5.0, 5.4 Hz, H-4), 3.90 (br, 1 H, OH), 2.06 (ddd, 1 H, *J* = 4.5, 5.0, 8.5 Hz, H-5), 1.56 (dd, 1 H, *J* = 4.5, 6.3 Hz, H-6a), 1.20 (dd, 1 H, *J* = 6.3, 8.5 Hz, H-6b); ¹³C NMR (125 MHz, CDCl₃, δ_C) 168.1 (O–C=O), 166.1 (O–C=O), 165.7 (O–C=O), 165.6 (O–C=O), 133.7 (Ar), 133.2 (Ar × 2), 133.0 (Ar), 130.1 (Ar × 2), 129.9 (Ar × 2), 129.7 (Ar × 4), 129.6 (Ar), 129.5 (Ar), 129.2 (Ar), 128.8 (Ar), 128.5 (Ar × 2), 128.4 (Ar × 2), 128.3 (Ar × 2), 128.1 (Ar × 2), 84.9 (C-3), 75.5 (C-2), 73.8 (2 C, CHOBz, C-4), 63.9 (CH₂OBz), 29.9 (C-1), 26.4 (C-5), 11.2 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₃₆H₃₀O₉: 629.1782. Found: 629.1776.



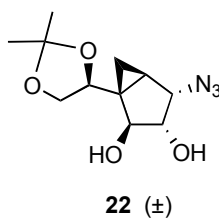
4-azido-1-[1,2-bis(benzoyloxy)ethyl]bicyclo[3.1.0]hexane-2,3-diyl dibenzoate (20**).**

To a solution of alcohol **19** (0.078 g, 0.13 mmol) and triphenylphosphine (0.034 g, 0.13 mmol) and molecular sieves in THF (5 mL) at room temperature was slowly added diisopropyl azodicarboxylate (0.023 g, 0.13 mmol) and the mixture was stirred for 5 min. Diphenylphosphoryl azide (0.036 g, 0.13 mmol) was added dropwise and the solution was stirred for another 10 min. The mixture was diluted with EtOAc and was washed with water. The organic layer was dried (Na₂SO₄), concentrated and the residue purified by chromatography (3:1 hexane–EtOAc) to give **20** (0.068 g, 84%) as a colorless oil. *R_f* 0.46 (3:1 hexane–EtOAc); IR 2100 cm⁻¹ (N₃); ¹H NMR (500 MHz, CDCl₃, δ_H) 8.09–7.97 (m, 6 H, Ar), 7.77–7.75 (m, 2 H, Ar), 7.60–7.32 (m, 10 H, Ar), 7.08–7.04 (m, 2 H, Ar), 6.52 (d, 1 H, *J* = 7.2 Hz, H-2), 5.28 (dd, 1 H, *J* = 4.7, 7.2 Hz, CHOBz), 5.21 (dd, 1 H, *J* = 5.3, 7.2 Hz, H-3), 4.96–4.88 (m, 2 H, CH₂OBz), 4.47 (d, 1 H, *J* = 5.3 Hz, H-4), 1.94 (dd, 1 H, *J* = 4.5, 8.9 Hz, H-5), 1.39 (dd, 1 H, *J* = 4.5, 6.6 Hz, H-6a), 1.27 (dd, 1 H, *J* = 6.6, 8.9 Hz, H-6b); ¹³C NMR (100 MHz, CDCl₃, δ_C) 166.2 (O–C=O), 166.0 (O–C=O), 165.7 (O–C=O), 165.6 (O–C=O), 133.6 (Ar), 133.1 (Ar), 133.0 (Ar), 132.9 (Ar), 130.1 (Ar × 2), 129.8 (Ar × 2), 129.7 (Ar × 2), 129.6 (Ar), 129.6 (Ar × 2), 129.5 (Ar), 129.1 (Ar), 128.5 (Ar × 3), 128.3 (Ar × 2), 128.2 (Ar × 2), 128.0 (Ar × 2), 77.3 (C-3) 75.4 (C-2), 74.2 (CHOBz), 64.3 (CH₂OBz), 60.5 (C-4), 29.6 (C-1), 25.7 (C-5), 13.4 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₃₆H₂₉N₃O₈: 654.1847. Found: 654.1842.



4-azido-1-[1,2-dihydroxyethyl]bicyclo[3.1.0]hexan-2,3-diol (21**).**

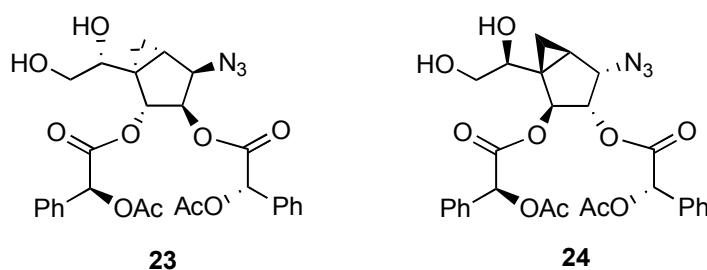
To a solution of compound **20** (0.063 g, 0.10 mmol) in CH₃OH (10 mL) was added 2 M NaOCH₃ (0.1 mL). The reaction mixture was stirred for 30 min, neutralized with HOAc and then concentrated. The resulting residue was purified by chromatography on Iatrobeds (9:1 CH₂Cl₂–CH₃OH) to give **21** (0.019 g, 91%) as a colorless oil. *R_f* 0.25 (5:1 CH₂Cl₂–CH₃OH); ¹H NMR (500 MHz, CD₃OD, δ_{H}) 4.14 (d, 1 H, *J* = 7.3 Hz, H-2), 3.81 (d, 1 H, *J* = 5.4, H-4), 3.78 (dd, 1 H, *J* = 5.5, 6.6 Hz, CHOH), 3.72 (dd, 1 H, *J* = 5.4, 7.3 Hz, H-3), 3.66 (dd, 1 H, *J* = 5.5, 11.1 Hz, CH₂OH), 3.52 (dd, 1 H, *J* = 6.6, 11.1 Hz, CH₂OH), 1.50 (dd, 1 H, *J* = 4.2, 8.6 Hz, H-5), 0.78 (dd, 1 H, *J* = 5.7, 8.6 Hz, H-6a), 0.78 (dd, 1 H, *J* = 4.2, 5.7 Hz, H-6b); ¹³C NMR (125 MHz, CD₃OD, δ_{C}) 79.3 (C-3), 79.2 (C-2), 73.2 (CHOH), 66.4 (CH₂OH), 64.8 (C-4), 34.7 (C-1), 22.8 (C-5), 8.7 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₈H₁₃N₃O₄: 238.0798. Found: 238.0798.



4-azido-1-[2,2-dimethyl-1,3-dioxolan-4-yl]bicyclo[3.1.0]hexane-2,3-diol (22**).**

To a solution of **21** (0.182 g, 0.85 mmol) and 2,2-dimethoxypropane (0.133 g, 1.27 mmol) in dry acetone (30 mL) was added *p*-toluenesulfonic acid monohydrate (0.015 g, 0.08 mmol), and the solution was stirred for 30 min at room temperature. Several drops of Et₃N were added to neutralize the acid and the solution was concentrated. The residue was purified by column chromatography (1:1 hexane–EtOAc) to give **22** (0.217 g, 86%). *R_f* 0.10 (1:1 hexane–EtOAc); ¹H NMR (500 MHz, CD₂Cl₂, δ_{H}) 4.22 (dd, 1 H, *J* = 3.3, 7.1 Hz, H-2),

4.07–4.01 (m, 2 H, $\underline{\text{CHO}}$, $\underline{\text{CH}_2\text{O}}$), 3.97 (d, 1 H, $J = 5.3$ Hz, H-4), 3.77 (dd, 1 H, $J = 6.0$, 7.2 Hz, $\underline{\text{CH}_2\text{O}}$), 3.67 (ddd, 1 H, $J = 5.3$, 7.1, 8.9 Hz, H-3), 2.28 (d, 1 H, $J = 3.3$ Hz, 2-OH), 2.18 (d, 1 H, $J = 8.9$ Hz, 3-OH), 1.50 (dd, 1 H, $J = 4.1$, 8.6 Hz, H-5), 1.40 (s, 3 H, $(\underline{\text{CH}_3})_2\text{C}$), 1.32 (s, 3 H, $(\underline{\text{CH}_3})_2\text{C}$), 0.90 (dd, 1 H, $J = 4.1$, 6.0 Hz, H-6a), 0.75 (dd, 1 H, $J = 6.0$, 8.6 Hz, H-6b); ^{13}C NMR (100 MHz, CD_2Cl_2 , δ_{C}) 109.4 ($(\underline{\text{CH}_3})_2\text{C}$), 78.2 (C-2), 77.9 ($\underline{\text{CHO}}$), 77.7 (C-3), 67.7 ($\underline{\text{CH}_2\text{O}}$), 63.8 (C-4), 31.9 (C-1), 26.6 ($(\underline{\text{CH}_3})_2\text{C}$), 25.2 ($(\underline{\text{CH}_3})_2\text{C}$), 21.8 (C-5), 10.7 (C-6). HRMS (ESI) m/z Calcd for $(\text{M}+\text{Na}^+)$ $\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}_4$: 278.1111. Found: 278.1110.

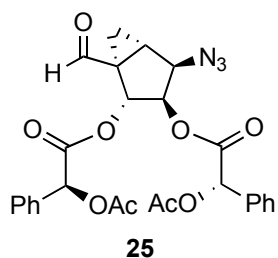


(1R,2R,3R,4R,5S)-4-azido-1-[(1R)-1,2-dihydroxyethyl]bicyclo[3.1.0]hexane-2,3-diyl (2S,2'S)bis[(acetyloxy)(phenyl)ethanoate] (23) and (1S,2S,3S,4S,5R)-4-azido-1-[(1S)-1,2-dihydroxyethyl]bicyclo[3.1.0]hexane-2,3-diyl (2S,2'S)bis[(acetyloxy)(phenyl)ethanoate] (24).

Compound **22** (0.255 g, 1.00 mmol), *O*-acetyl-(*S*)-(+)-mandelic acid (0.427 g, 2.20 mmol) and *N,N'*-dicyclohexylcarbodiimide (0.457 g, 2.20 mmol) were dissolved in CH_2Cl_2 and 4-(dimethylamino)pyridine (0.013 g, 0.11 mmol) was added. The reaction mixture was stirred for 30 min and then concentrated. The residue was purified by chromatography (4:1 hexane–EtOAc) to give an inseparable mixture of diastereomers (0.575 g, 95%) as a colorless oil. R_f 0.65 (2:1 hexane–EtOAc). HRMS (ESI) m/z Calcd for $(\text{M}+\text{Na}^+)$ $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_{10}$: 630.2058. Found: 630.2058. This mixture of diastereomers was dissolved in 5:3:2 HOAc– H_2O –THF (20 mL) and was stirred at 50 °C for 12 h. The mixture was concentrated and the residue was purified by chromatography (1:2 hexane–EtOAc) to give compounds **23** and **24** (0.488 g, 91% combined yield).

Data for **23**: R_f 0.47 (20:1 CH₂Cl₂–CH₃OH); $[\alpha]_D$ –32.3 (c 0.11, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.48–7.35 (m, 10 H, Ar), 5.99 (s, 1 H, CHPh), 5.95 (s, 1 H, CHPh), 5.76 (d, 1 H, J = 7.2 Hz, H-2), 4.82 (dd, 1 H, J = 5.4, 7.2 Hz, H-3), 4.02 (d, 1 H, J = 5.4 Hz, H-4), 3.47 (dd, 1 H, J = 4.0, 6.7 Hz, CHOH), 3.37 (dd, 1 H, J = 4.0, 11.4 Hz, CH₂OH), 3.26 (dd, 1 H, J = 6.7, 11.4 Hz, CH₂OH), 2.14 (s, 3 H, acetate CH₃), 2.02 (s, 3 H, acetate CH₃), 1.67 (dd, 1 H, J = 7.0, 7.3 Hz, H-5), 0.79–0.78 (m, 2 H, H-6a, H-6b), ¹³C NMR (125 MHz, CDCl₃, δ_C) 170.3 (O–C=O), 170.0 (O–C=O), 168.8 (O–C=O), 168.3 (O–C=O), 133.4 (Ar), 133.0 (Ar), 129.5 (Ar), 129.4 (Ar), 128.9 (Ar \times 2), 128.8 (Ar \times 2), 127.8 (Ar \times 4), 77.9 (2 C, CHPh, CHPh), 74.6 (C-3), 74.1 (C-2), 71.2 (CHOH), 63.8 (CH₂OH), 60.4 (C-4), 30.8 (C-1), 24.0 (C-5), 20.7 (acetate CH₃), 20.2 (acetate CH₃), 10.4 (C-6). HRMS (ESI) m/z Calcd for (M+Na⁺) C₂₈H₂₉N₃O₁₀: 590.1745. Found: 590.1748

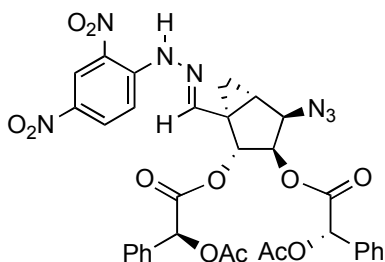
Data for **24**: R_f 0.46 (20:1 CH₂Cl₂–CH₃OH); $[\alpha]_D$ +160.3 (c 0.25, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H) 7.38–7.29 (m, 10 H, Ar), 5.91 (s, 1 H, CHPh), 5.81 (s, 1 H, CHPh), 5.77 (d, 1 H, J = 7.0 Hz, H-2), 4.73 (dd, 1 H, J = 5.5, 7.0 Hz, H-3), 4.11 (d, 1 H, J = 5.5 Hz, H-4), 3.69 (dd, 1 H, J = 4.0, 11.2 Hz, CH₂OH), 3.64 (dd, 1 H, J = 4.0, 6.4 Hz, CHOH), 3.50 (dd, 1 H, J = 6.4, 11.2 Hz, CH₂OH), 2.18 (s, 3 H, acetate CH₃), 2.14 (s, 3 H, acetate CH₃), 1.74 (dd, 1 H, J = 4.6, 8.7 Hz, H-5), 0.96 (dd, 1 H, J = 6.7, 8.7 Hz, H-6a), 0.92 (dd, 1 H, J = 4.6, 6.7 Hz, H-6b); ¹³C NMR (100 MHz, CDCl₃, δ_C) 170.6 (O–C=O), 169.9 (O–C=O), 168.5 (O–C=O), 167.8 (O–C=O), 133.0 (Ar), 132.7 (Ar), 129.3 (Ar), 129.2 (Ar), 128.8 (Ar \times 2), 128.7 (Ar \times 2), 127.5 (Ar \times 2), 127.4 (Ar \times 2), 77.8 (CHPh), 77.6 (CHPh), 74.6 (C-2), 73.9 (C-3), 71.5 (CHOH), 64.1 (CH₂OH), 60.7 (C-4), 31.3 (C-1), 24.1 (C-5), 20.6 (acetate CH₃), 20.5 (acetate CH₃), 10.6 (C-6). HRMS (ESI) m/z Calcd for (M+Na⁺) C₂₈H₂₉N₃O₁₀: 590.1745. Found: 590.1748.



(1*S*,2*R*,3*R*,4*R*,5*S*)-4-azido-1-formylbicyclo[3.1.0]hexane-2,3-diyl

(2*S*,2'*S*)bis[(acetyloxy)(phenyl)ethanoate] (25).

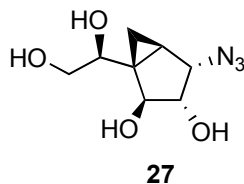
Compound **23** (0.026 g, 0.045 mmol) was dissolved in THF (4 mL) and NaIO₄ (0.020 g, 0.093 mmol) and a satd aq solution of NaHCO₃ (3 mL) was added. This reaction mixture was stirred for 2 h and EtOAc was added. The organic layer was dried (Na₂SO₄) and the residue was purified with chromatography (4:1 hexane–EtOAc) to give **25** (0.021 g, 90%) as a colorless oil. *R*_f 0.46 (2:1 hexane–EtOAc); [α]_D –16.8 (*c* 0.14, CHCl₃); ¹H NMR (500 MHz, CDCl₃, δ_H) 9.69 (s, 1 H, CHO), 7.52–7.37 (m, 10 H, Ar), 6.05 (s, 1 H, CHPh), 5.97 (s, 1 H, CHPh), 5.88 (dd, 1 H, *J* = 7.1 Hz, H-2), 4.79 (dd, 1 H, *J* = 5.6, 7.1 Hz, H-3), 4.07 (d, 1 H, *J* = 5.6 Hz, H-4), 2.23 (s, 3 H, acetate CH₃), 2.21 (s, 3 H, acetate CH₃), 1.96 (dd, 1 H, *J* = 5.6, 9.0 Hz, H-5), 1.53 (ddd, 1 H, *J* = 9.0, 11.4 Hz, H-6a), 0.90 (dd, 1 H, *J* = 5.6, 11.4 Hz, H-6b); ¹³C NMR (125 MHz, CDCl₃, δ_C) 196.6 (CHO), 170.1 (O–C=O), 170.1 (O–C=O), 168.9 (O–C=O), 168.2 (O–C=O), 133.3 (Ar), 132.9 (Ar), 129.5 (Ar), 129.5 (Ar), 128.9 (Ar × 2), 128.9 (Ar × 2), 127.8 (Ar × 4), 77.5 (C-3), 76.8 (C-2), 74.2 (CHPh), 74.1 (CHPh), 59.7 (C-4), 38.8 (C-1), 34.3 (C-5), 20.6 (2 C, acetate CH₃), 14.4 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₂₇H₂₅N₃O₉: 558.1483. Found: 558.1484.



26

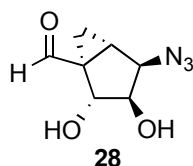
(1*R*,2*R*,3*R*,4*R*,5*S*)-4-azido-1-{(*E*)-[(2,4-dinitrophenyl)hydrazono]methyl}bicyclo[3.1.0]hexane-2,3-diyl (2*S*,2'*S*)bis[(acetyloxy)(phenyl)ethanoate] (26).

Compound **25** (5.8 mg, 0.011 mmol) was dissolved in CH₃OH (1 mL) and 1 M 2,4-dinitrophenylhydrazine (1 mL) was added. The mixture was swirled for 1 min and the solution was concentrated and the residue was purified by chromatography (3:1 hexane–EtOAc) to give **26** (4.2 mg, 53%) as yellow solid. This material was recrystallized from CH₂Cl₂ to provide a crystalline solid (m.p. 57–59 °C). *R_f* 0.21 (2:1 hexane–EtOAc); [α]_D 12.6 (*c* 0.27, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃, δ_H) 9.10 (d, 1 H, *J* = 2.3 Hz, N=CH), 8.27 (dd, 1 H, *J* = 2.3, 9.5 Hz, Ar), 7.64 (d, 1 H, *J* = 9.5 Hz, Ar), 7.52–7.51 (m, 2 H, Ar), 7.42–7.37 (m, 5 H, Ar), 7.21–7.18 (m, 4 H, Ar), 6.10 (d, 1 H, *J* = 7.7 Hz, H-2), 6.07 (s, 1 H, CHPh), 5.95 (s, 1 H, CHPh), 4.89 (dd, 1 H, *J* = 5.7, 7.7 Hz, H-2), 4.18 (d, 1 H, *J* = 5.7 Hz, H-4), 2.23 (s, 3 H, acetate CH₃), 2.22 (s, 3 H, acetate CH₃), 1.94 (dd, 1 H, *J* = 5.0, 8.2 Hz, H-5), 1.33–1.27 (m, 2 H, H-6a, H-6b); ¹³C NMR (125 MHz, CDCl₃, δ_C) 170.0 (O–C=O), 169.9 (O–C=O), 168.5 (O–C=O), 168.3 (O–C=O), 148.1 (Ar), 144.5 (Ar), 138.1 (Ar), 133.4 (Ar), 133.0 (Ar), 129.9 (Ar), 129.4 (Ar), 129.0 (Ar), 128.9 (Ar), 128.8 (Ar × 2), 128.5 (Ar × 2), 127.8 (Ar × 2), 127.4 (Ar × 2), 123.1 (N=CH), 116.7 (Ar), 76.8 (C-3), 76.3 (C-2), 74.1 (CHPh), 74.0 (CHPh), 60.1 (C-4), 31.3 (C-1), 30.2 (C-5), 20.6 (2 C, acetate CH₃), 14.3 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₃₃H₂₉N₇O₁₂: 738.1766. Found: 738.1763.



(1*S*,2*S*,3*S*,4*S*,5*R*)-4-azido-1-[(1*S*)-1,2-dihydroxyethyl]bicyclo[3.1.0]hexane-2,3-diol (27**).**

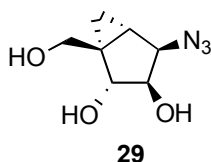
To a solution of **24** (0.034 g, 0.06 mmol) in CH₃OH (2 mL) was added 2 M NaOCH₃ (100 μL). The reaction mixture was stirred for 20 min, neutralized with HOAc and then concentrated. The resulting residue was purified by chromatography on Iatrobeds (9:1 CH₂Cl₂–CH₃OH) to give **27** (0.013 g, 100%) as a colorless oil. *R_f* 0.25 (5:1 CH₂Cl₂–CH₃OH); [α]_D +12.3 (*c* 0.11, CH₃OH); ¹H NMR (500 MHz, CD₃OD, δ_H) 4.14 (d, 1 H, *J* = 7.3 Hz, H-2), 3.81 (d, 1 H, *J* = 5.4 Hz, H-4), 3.78 (dd, 1 H, *J* = 5.5, 6.6 Hz, CHOH), 3.72 (dd, 1 H, *J* = 5.4, 7.3 Hz, H-3), 3.66 (dd, 1 H, *J* = 5.5, 11.1 Hz, CH₂OH), 3.52 (dd, 1 H, *J* = 6.6, 11.1 Hz, CH₂OH), 1.50 (dd, 1 H, *J* = 4.2, 8.6 Hz, H-5), 0.78 (dd, 1 H, *J* = 5.7, 8.6 Hz, H-6a), 0.78 (dd, 1 H, *J* = 4.2, 5.7 Hz, H-6b); ¹³C NMR (125 MHz, CD₃OD, δ_C) 79.3 (C-3), 79.2 (C-2), 73.2 (CHOH), 66.4 (CH₂OH), 64.8 (C-4), 34.6 (C-1), 22.8 (C-5), 8.7 (C-6). HRMS (ESI) *m/z* Calcd for (M+Na⁺) C₈H₁₃N₃O₄: 238.0798. Found: 238.0798.



(1*S*,2*R*,3*R*,4*R*,5*S*)-4-azido-2,3-dihydroxybicyclo[3.1.0]hexane-1-carbaldehyde (28**).**

To a solution of **25** (0.019 mg, 0.035 mmol), in CH₃OH (2 mL) was added 2 M NaOCH₃ (100 μL). This solution was stirred for 20 min and neutralized with HOAc. The mixture was concentrated and the resulting crude product was purified by chromatography (3:1 EtOAc–hexane), to give **28** (0.006 g, 96% yield) as an oil. *R_f* 0.42 (1:9 CH₃OH–CH₂Cl₂); [α]_D –35.3 (*c* 0.06, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 9.00 (s, 1 H, CHO), 4.70 (d, 1 H, *J* = 7.5 Hz, H-2), 4.11 (d, 1 H, *J* = 5.5 Hz, H-4), 3.79 (dd, 1 H, *J* = 5.5, 7.5 Hz, H-3), 2.51 (br s,

2 H, 2-OH, 3-OH), 2.15 (dd, 1 H, $J = 7.1$ Hz, H-5), 1.50 (d, 2 H, $J = 7.1$ Hz, H-6a, H-6b); ^{13}C NMR (100 MHz, CDCl_3 , δ_{C}) 198.1 (CHO), 76.4 (C-2), 74.3 (C-3), 61.9 (C-4), 41.8 (C-1), 27.8 (C-5), 14.1 (C-6). HRMS (ESI) m/z Calcd for ($\text{M}+\text{Na}^+$) $\text{C}_7\text{H}_9\text{N}_3\text{O}_3$: 206.0536. Found: 206.0538.



(1R,2R,3R,4R,5S)-4-azido-1-(hydroxymethyl)bicyclo[3.1.0]hexane-2,3-diol (29).

To a solution of **28** (0.006 g, 0.034 mmol) in CH_3OH (1 mL) was added NaBH_4 (0.003 g, 0.075 mmol) at -30°C . The mixture was stirred for 5 min and then warmed steadily to room temperature and stirred for another 5 min. The reaction mixture was neutralized with 1 M HCl to pH 7 and concentrated. The residue was purified by chromatography (1:9 $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$) to give **29** (0.006 g, 100%) as a foam. R_f 0.23 (1:9 $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$); $[\alpha]_{\text{D}} -15.0$ (c 0.06, CH_3OH); ^1H NMR (500 MHz, CD_3OD , δ_{H}) 4.24 (d, 1 H, $J = 7.0$ Hz, H-2), 3.83 (d, 1 H, $J = 11.8$ Hz, CH_2OH), 3.80 (d, 1 H, $J = 5.5$ Hz, H-4), 3.69 (dd, 1 H, $J = 5.5, 7.0$ Hz, H-3), 3.36 (d, 1 H, $J = 11.8$ Hz, CH_2OH), 1.39 (dd, 1 H, $J = 3.9, 8.5$ Hz, H-5), 0.80 (dd, 1 H, $J = 3.9, 5.9$ Hz, H-6a), 0.59 (dd, 1 H, $J = 5.9, 8.5$ Hz, H-6b); ^{13}C NMR (125 MHz, CD_3OD , δ_{C}) 78.9 (C-3), 77.7 (C-2), 64.7 (C-4), 64.2 (CH_2OH), 33.8 (C-1), 23.4 (C-5), 10.6 (C-6). HRMS (ESI) m/z Calcd for ($\text{M}+\text{Na}^+$) $\text{C}_7\text{H}_{11}\text{N}_3\text{O}_3$: 208.0693. Found: 208.0695.

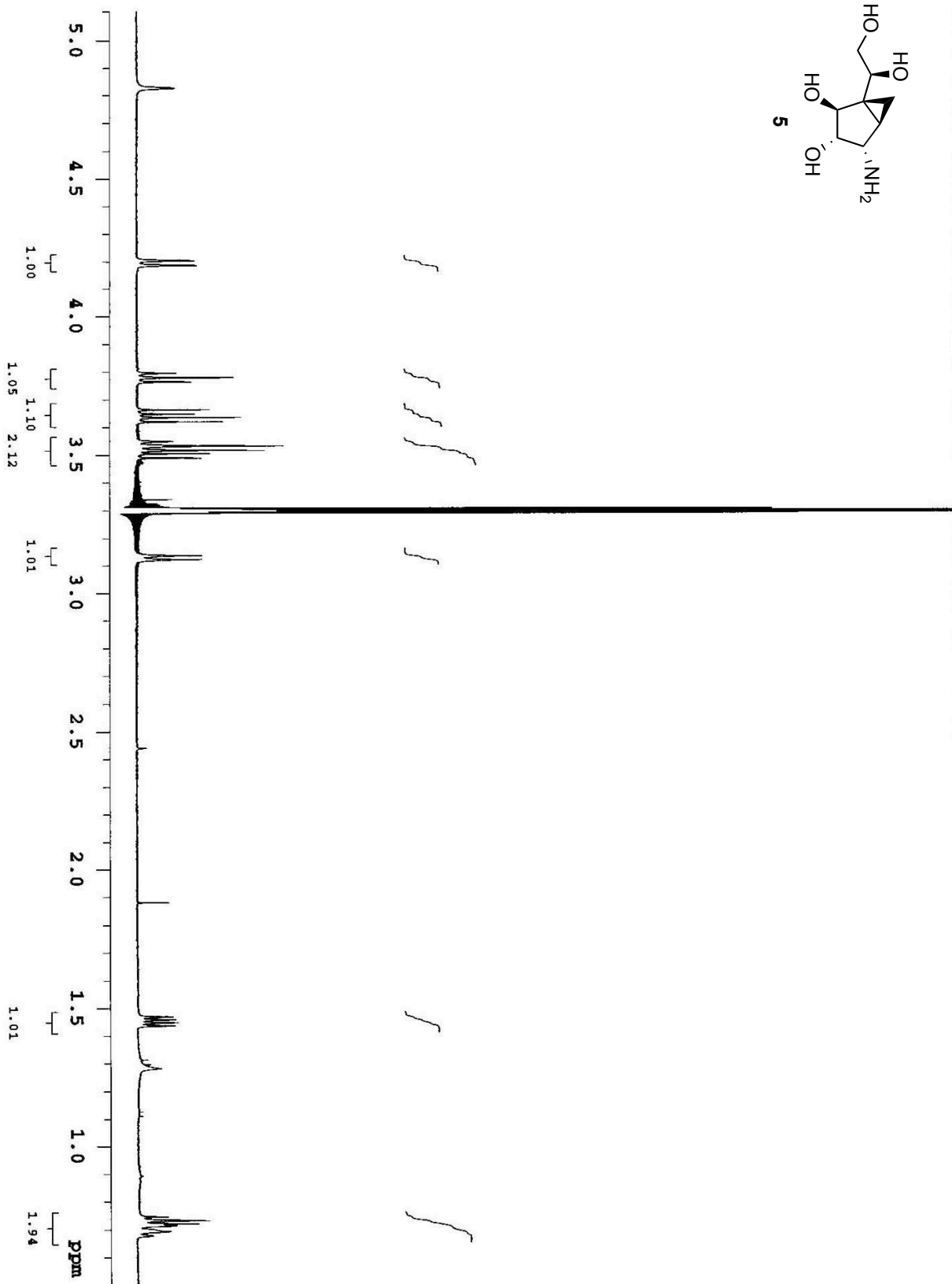
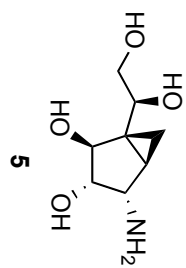
References

- (a) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535. (b) Torres, A. M.; Nakashima, T. T.; McClung, R. E. D. *J. Magn. Reson. Ser. A* **1993**, *101*, 285.
- Srikrishna, A.; Kumar, P. P. *Tetrahedron* **2000**, *56*, 8189.

Compound-5-E

Pulse Sequence: s2pul

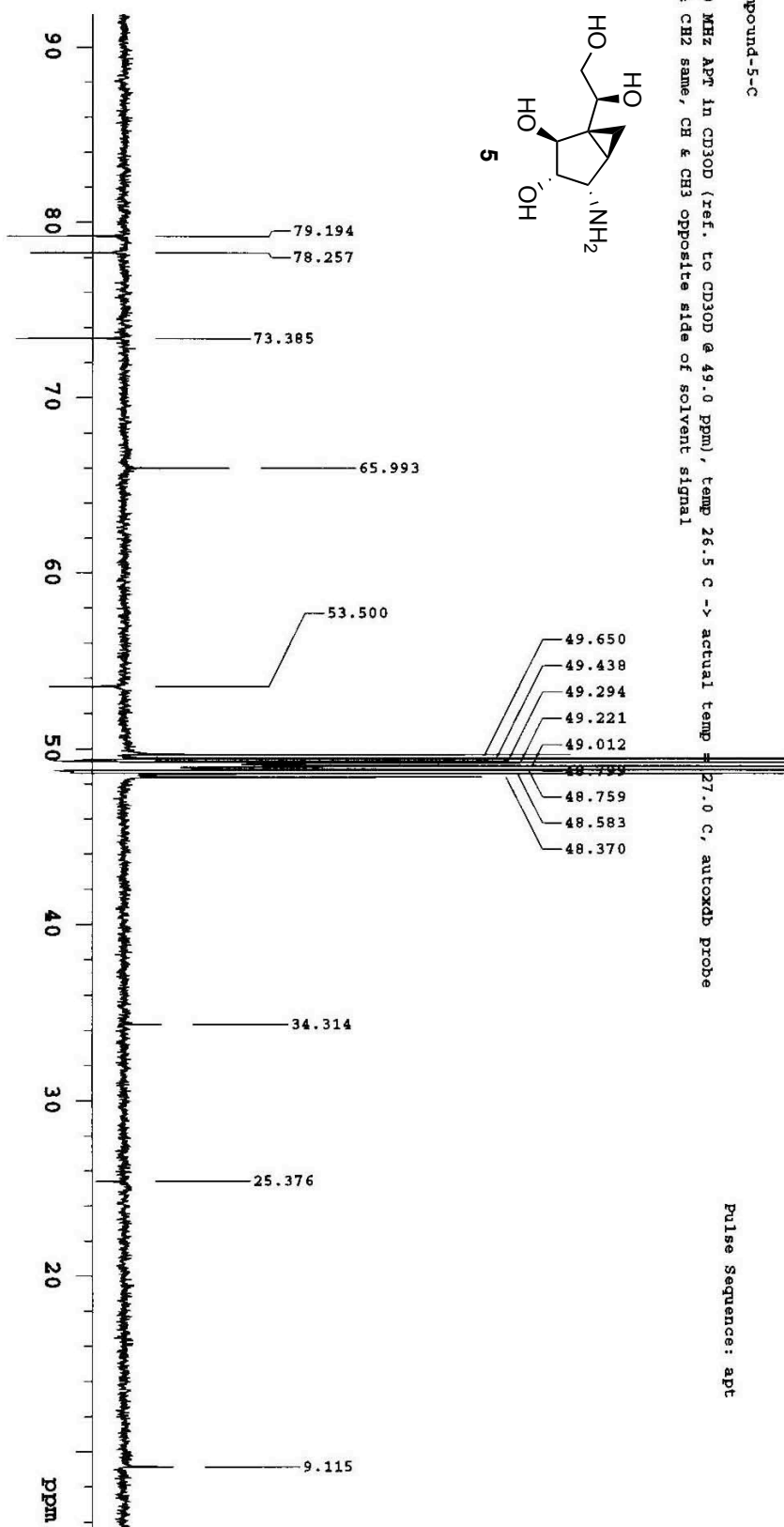
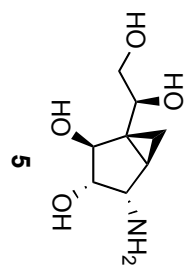
400 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autograd probe



Compound-5-C

100 MHz APF in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

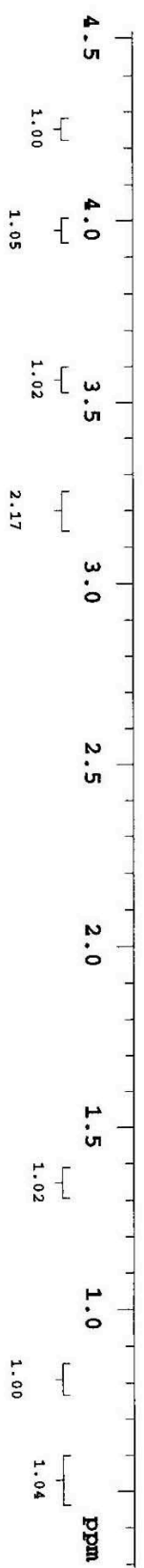
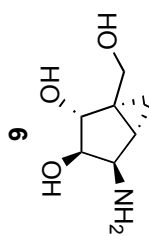
Pulse Sequence: apt



compound-6-H

Pulse Sequence: s2pul

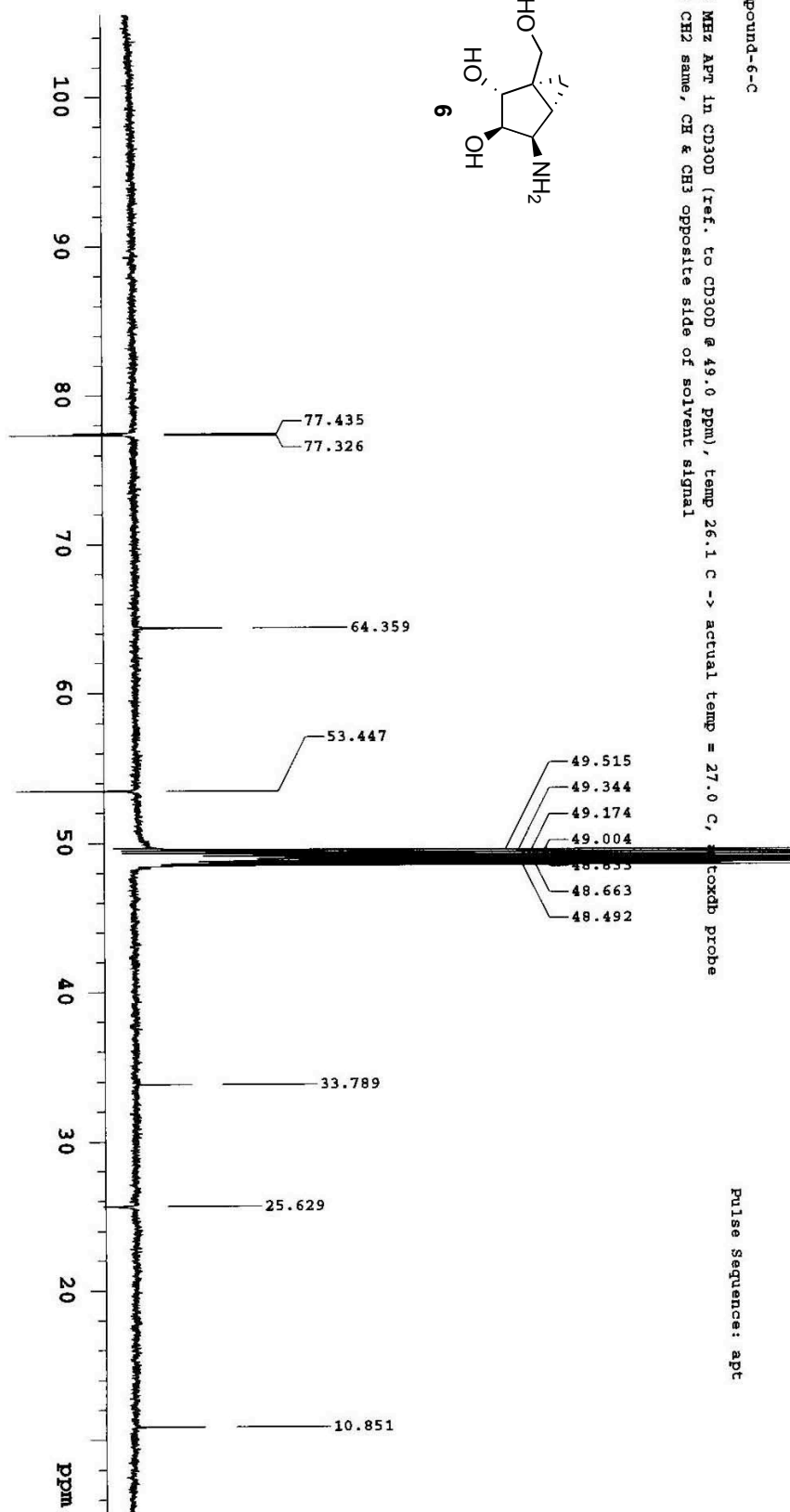
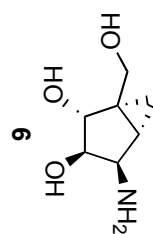
400 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxgb probe



compound-6-C

125 MHz APF in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 26.1 C -> actual temp = 27.0 C,
C & CH2 same, CH & CH3 opposite side of solvent signal

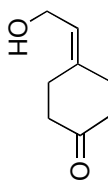
Pulse Sequence: apt



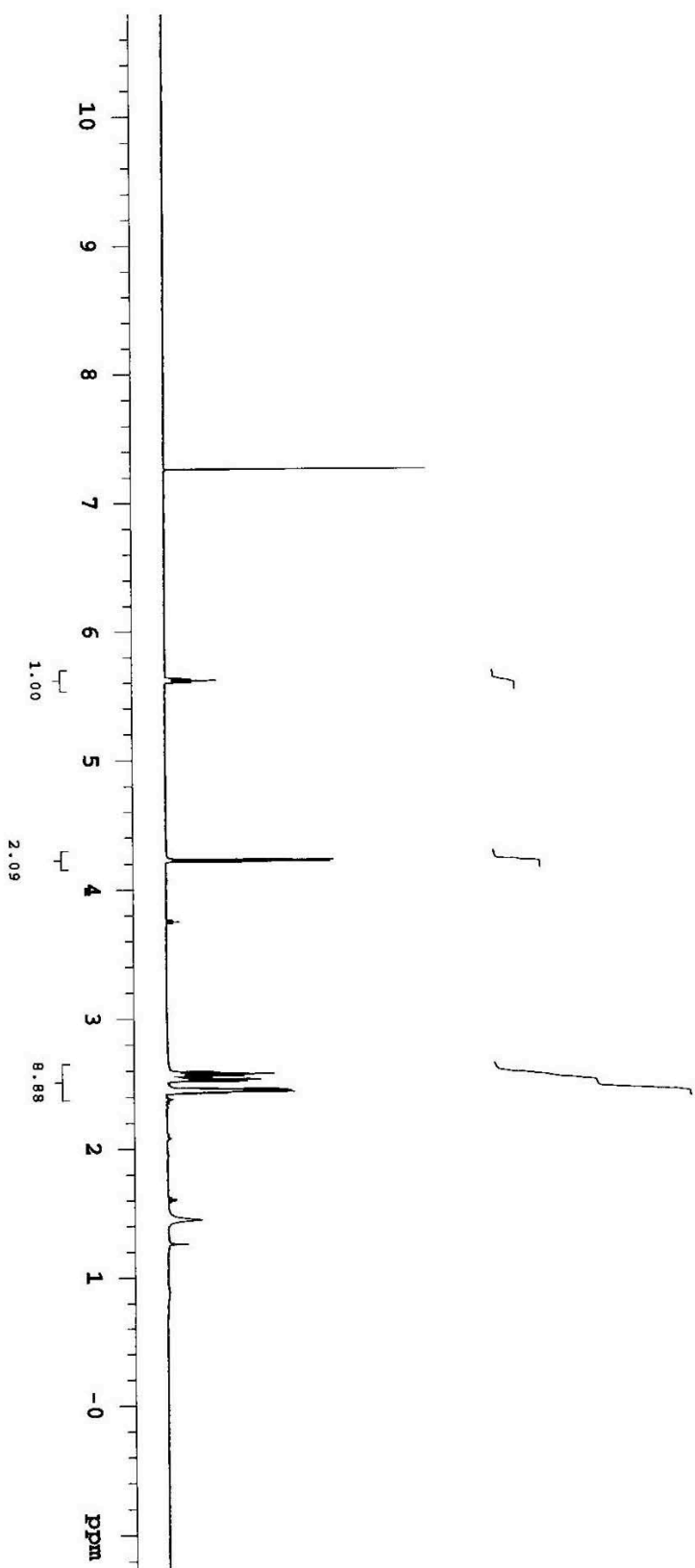
compound-8-B

Pulse Sequence: szpul

500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe



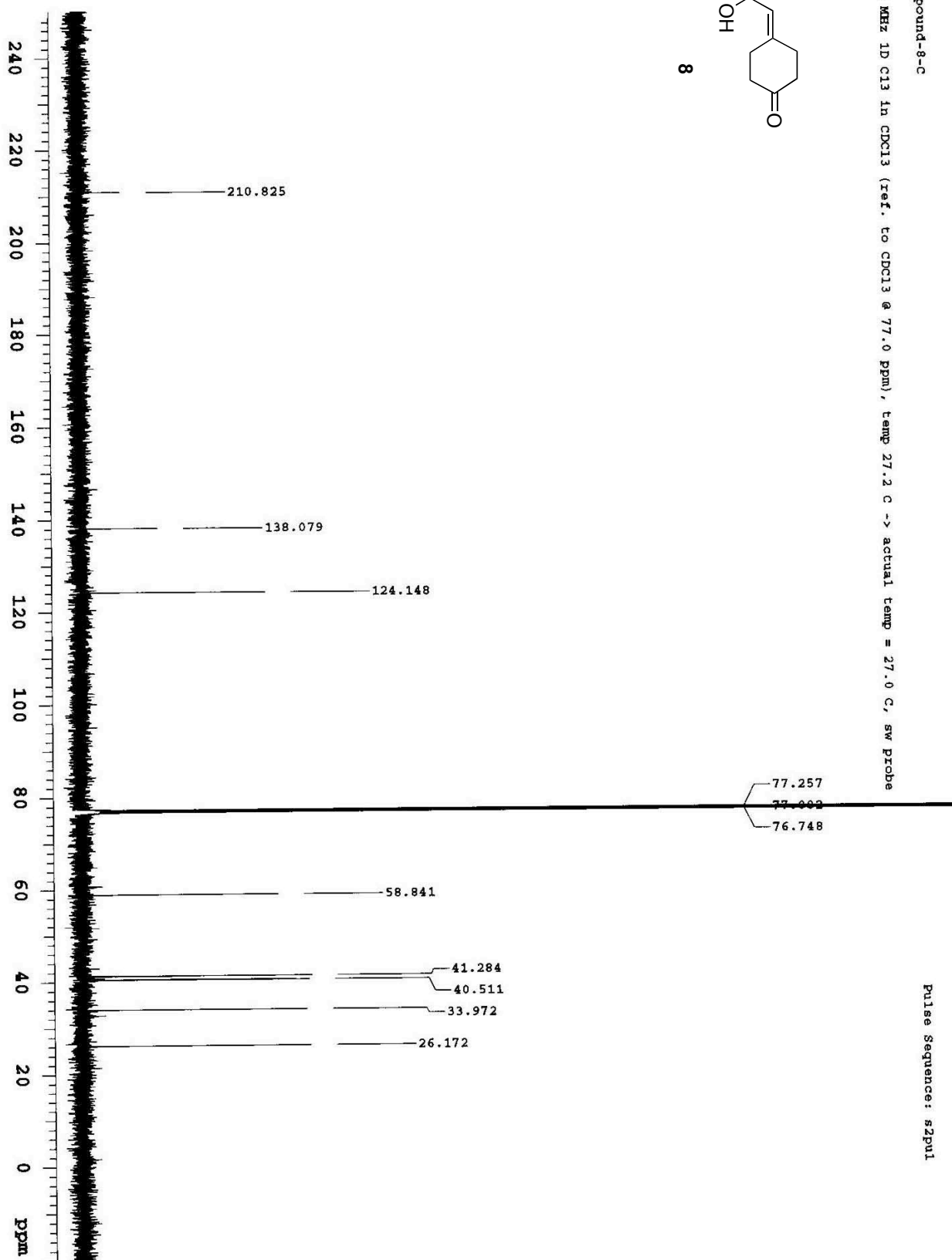
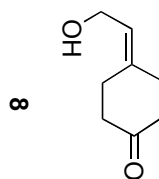
8



Compound-8-C

125 MHz 1D C13 In CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe

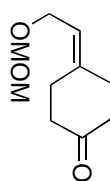
Pulse Sequence: szpul



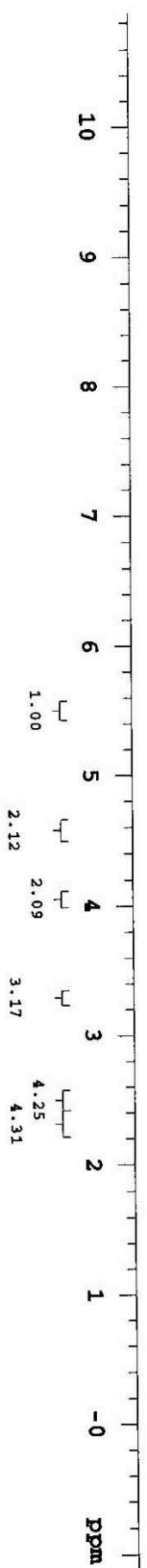
Compound-9-H

Pulse Sequence: szpul

400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe



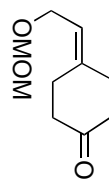
9



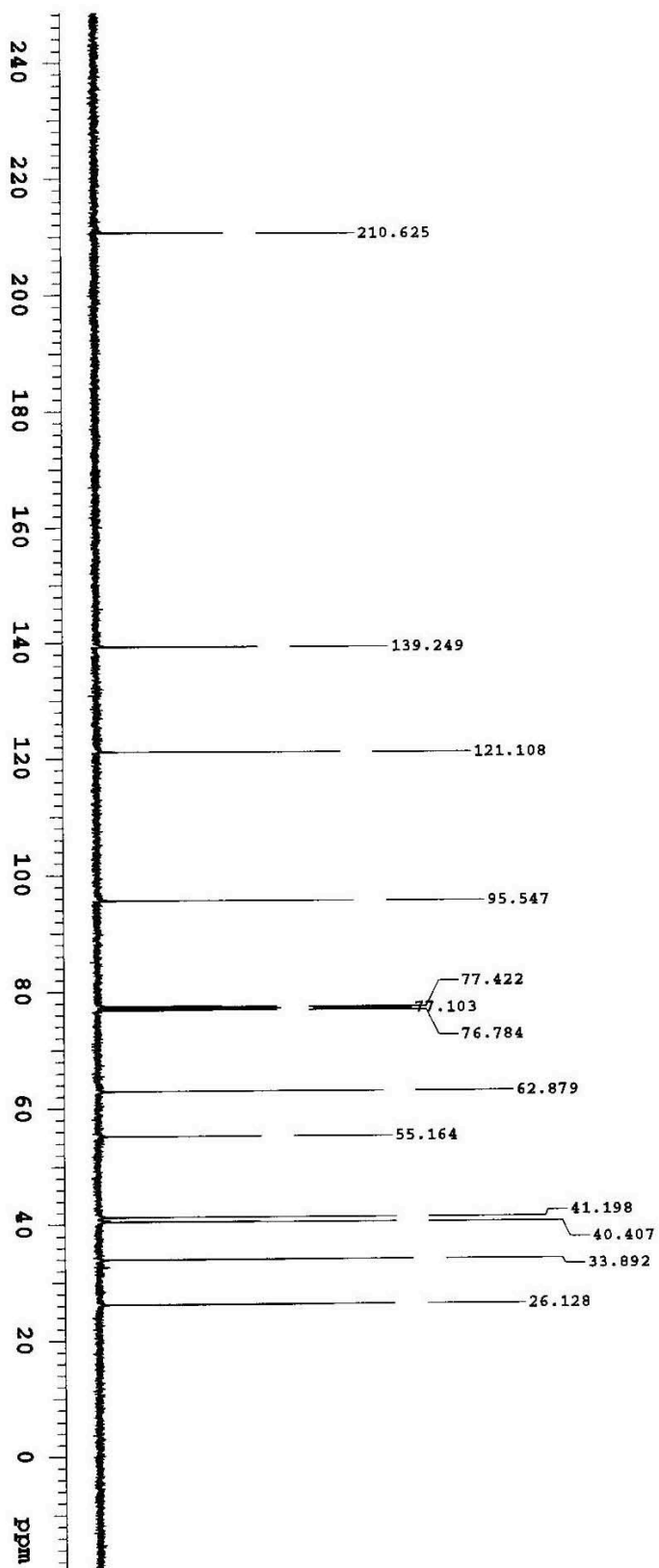
Compound-9-C

Pulse Sequence: szpul

100 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe



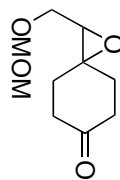
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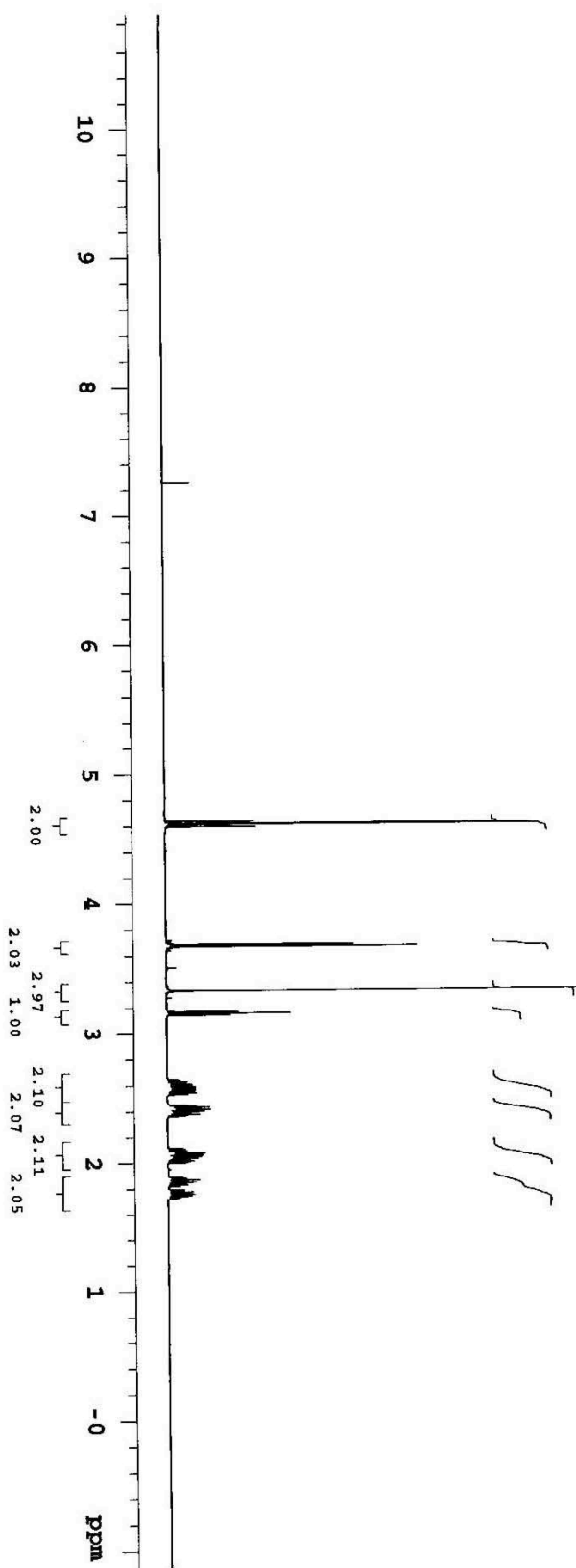
Compound-10-H

Pulse Sequence: szpu1

400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe



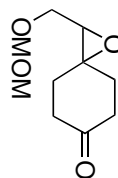
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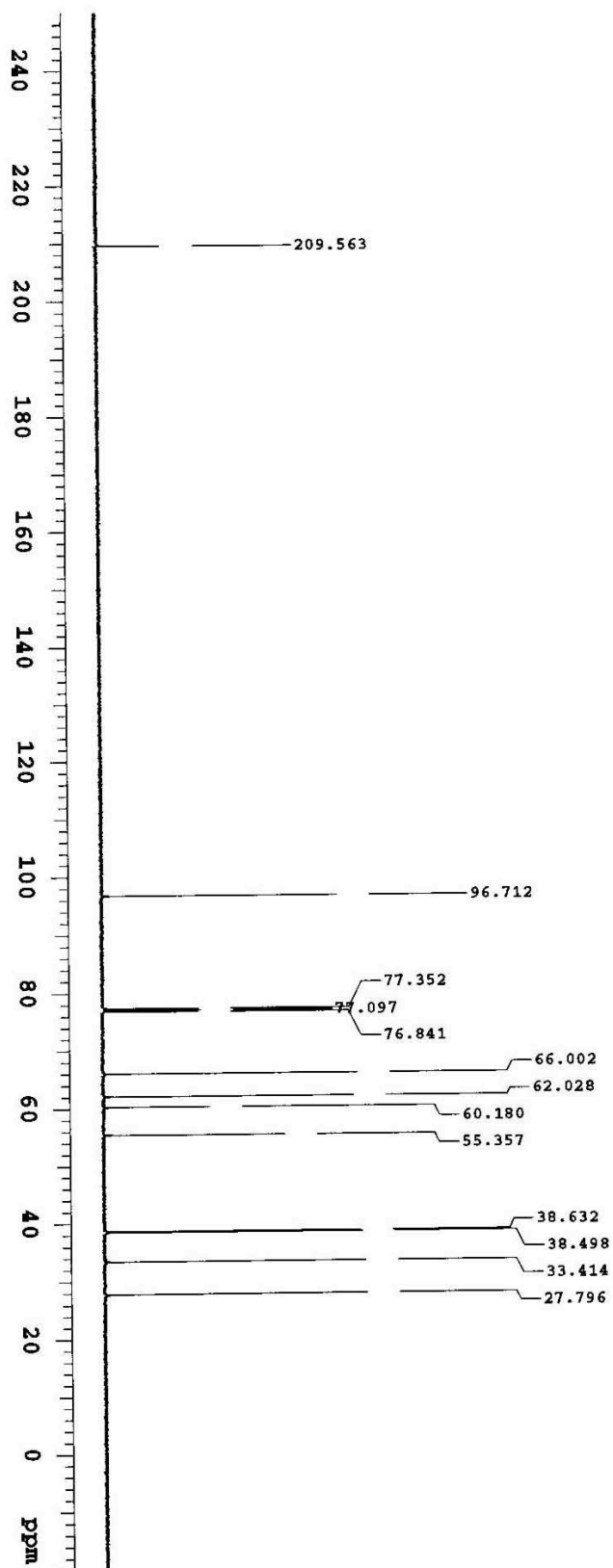
Compound-10-C

Pulse Sequence: szpul

125 MHz 1D C13 In CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe



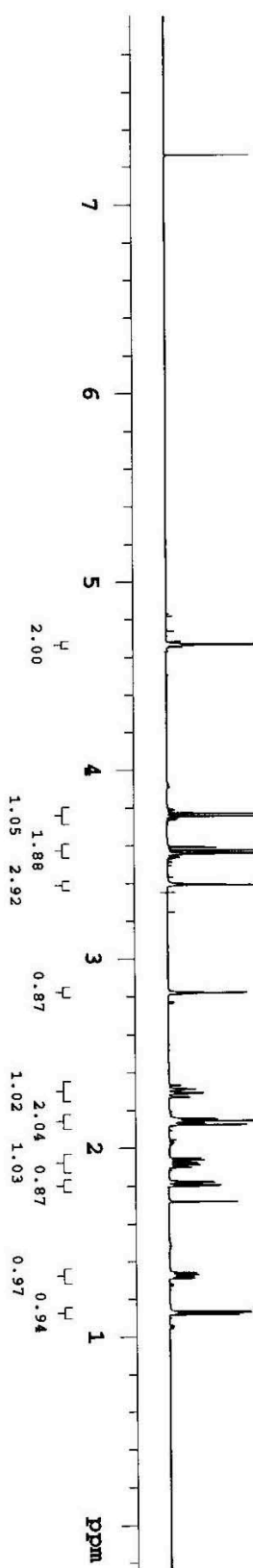
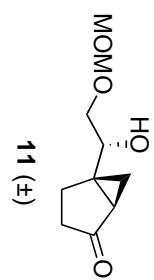
10



Compound-11-H

Pulse Sequence: s2pul

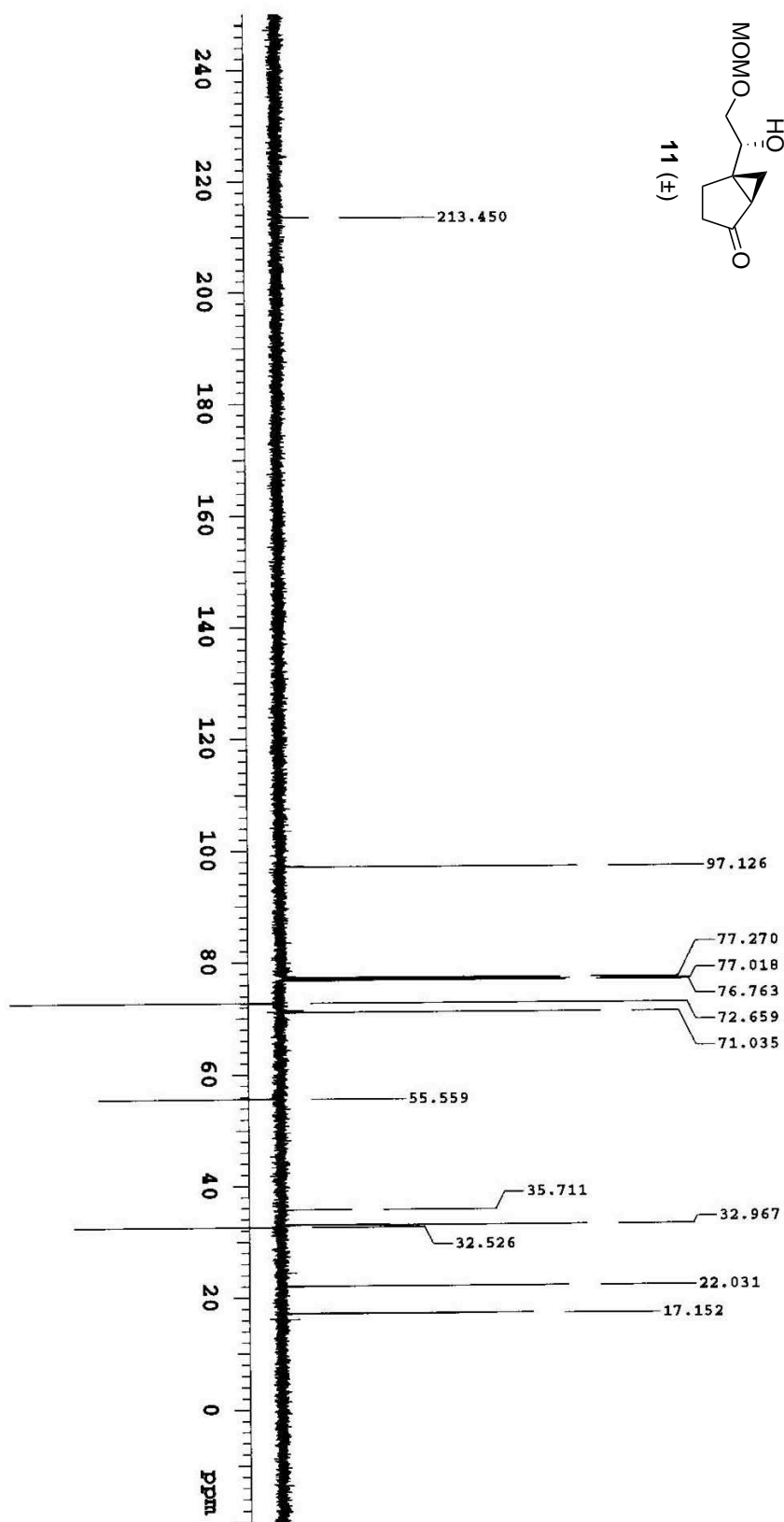
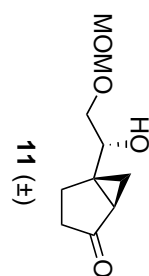
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe



Compound-11-C

125 MHz AP7 in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH₂ same, CH & CH₃ opposite side of solvent signal

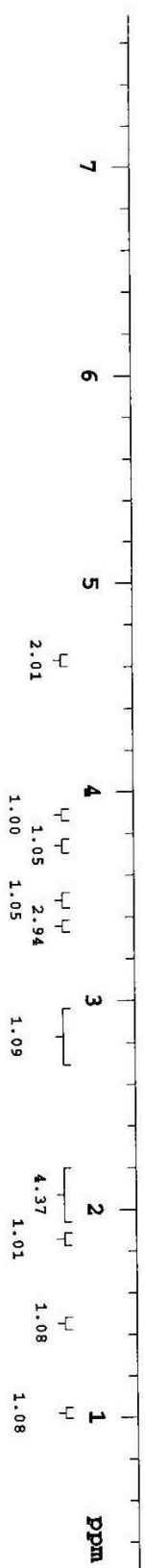
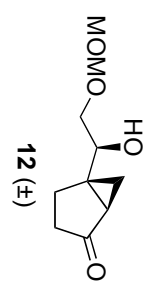
Pulse Sequence: apt



Compound-12-H

Pulse Sequence: s2pu1

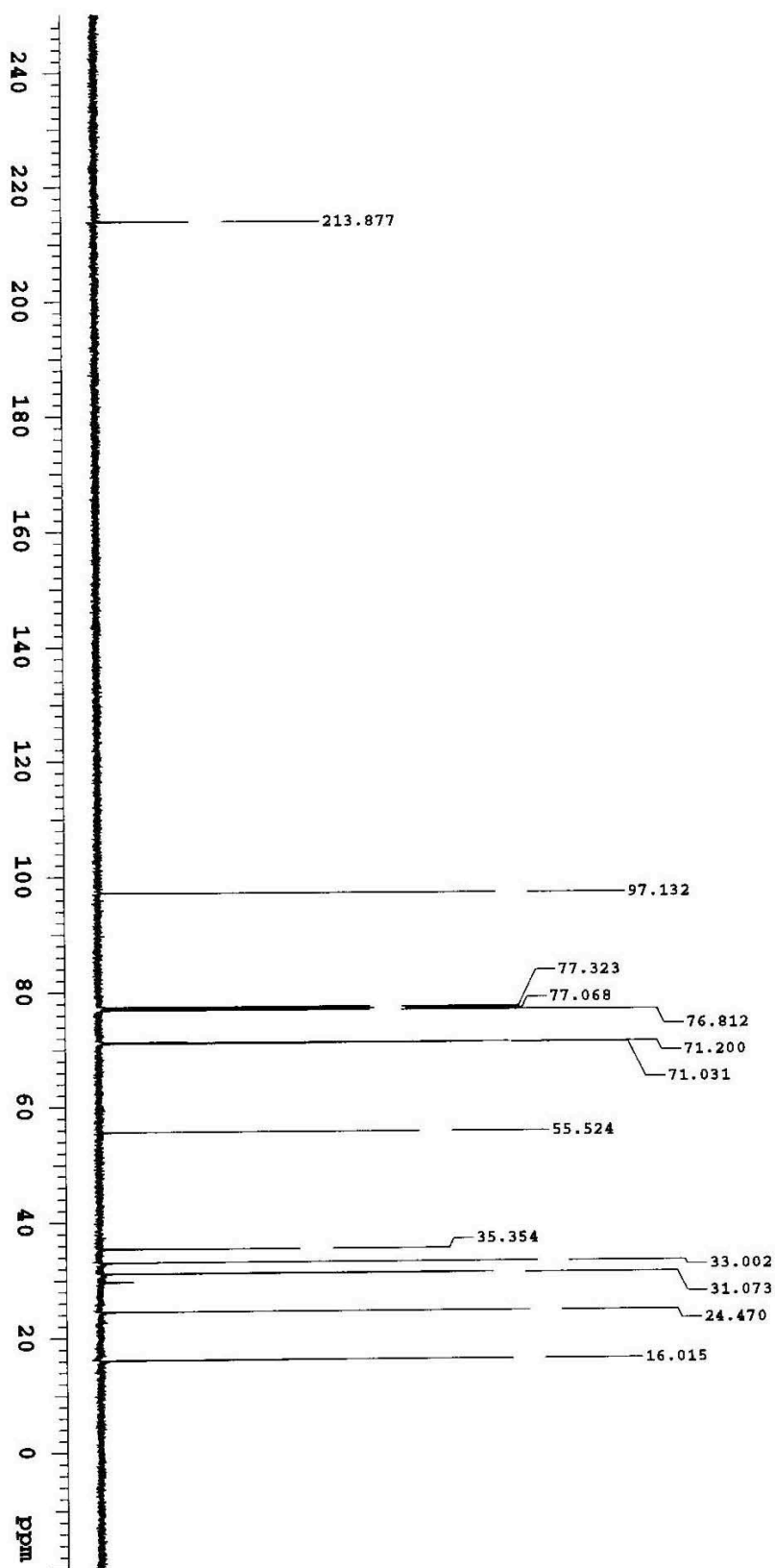
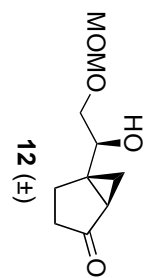
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe



Compound-12-C

Pulse Sequence: szpul

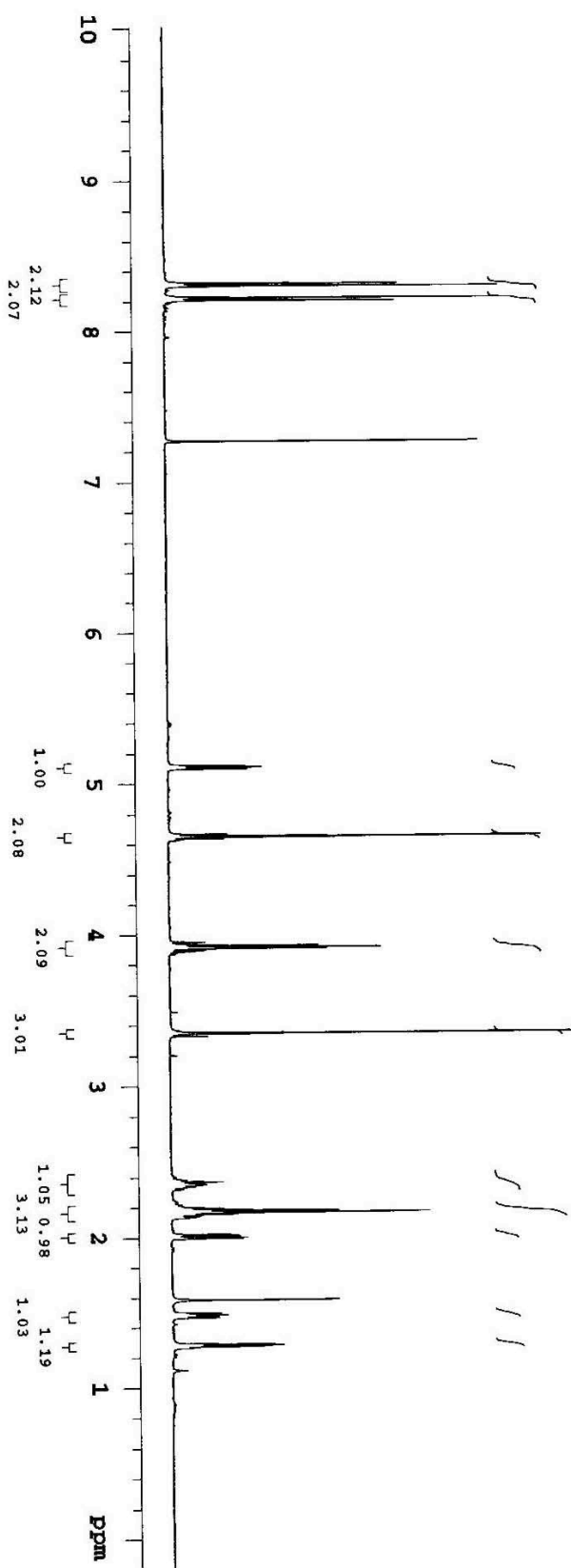
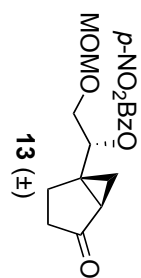
125 MHz 1D C13 in CDCl3 (ref. to CDCl3 @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe



Compound-13-H

Pulse Sequence: szpul

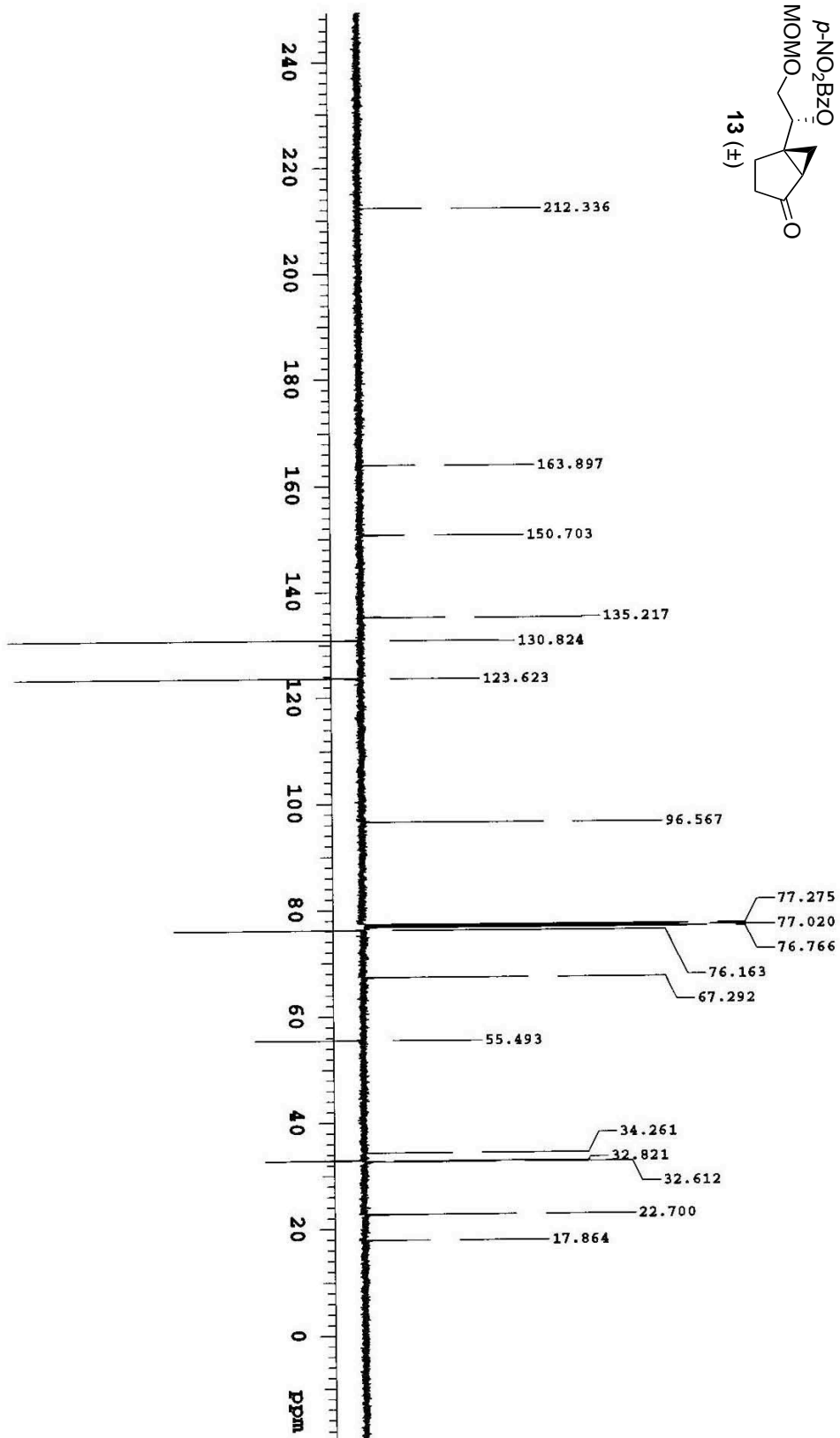
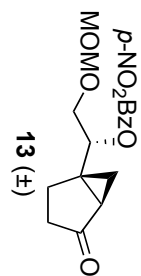
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdp probe



Compound-13-C

125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoexd probe
C & CH2 same, CH & CH3 opposite side of solvent signal

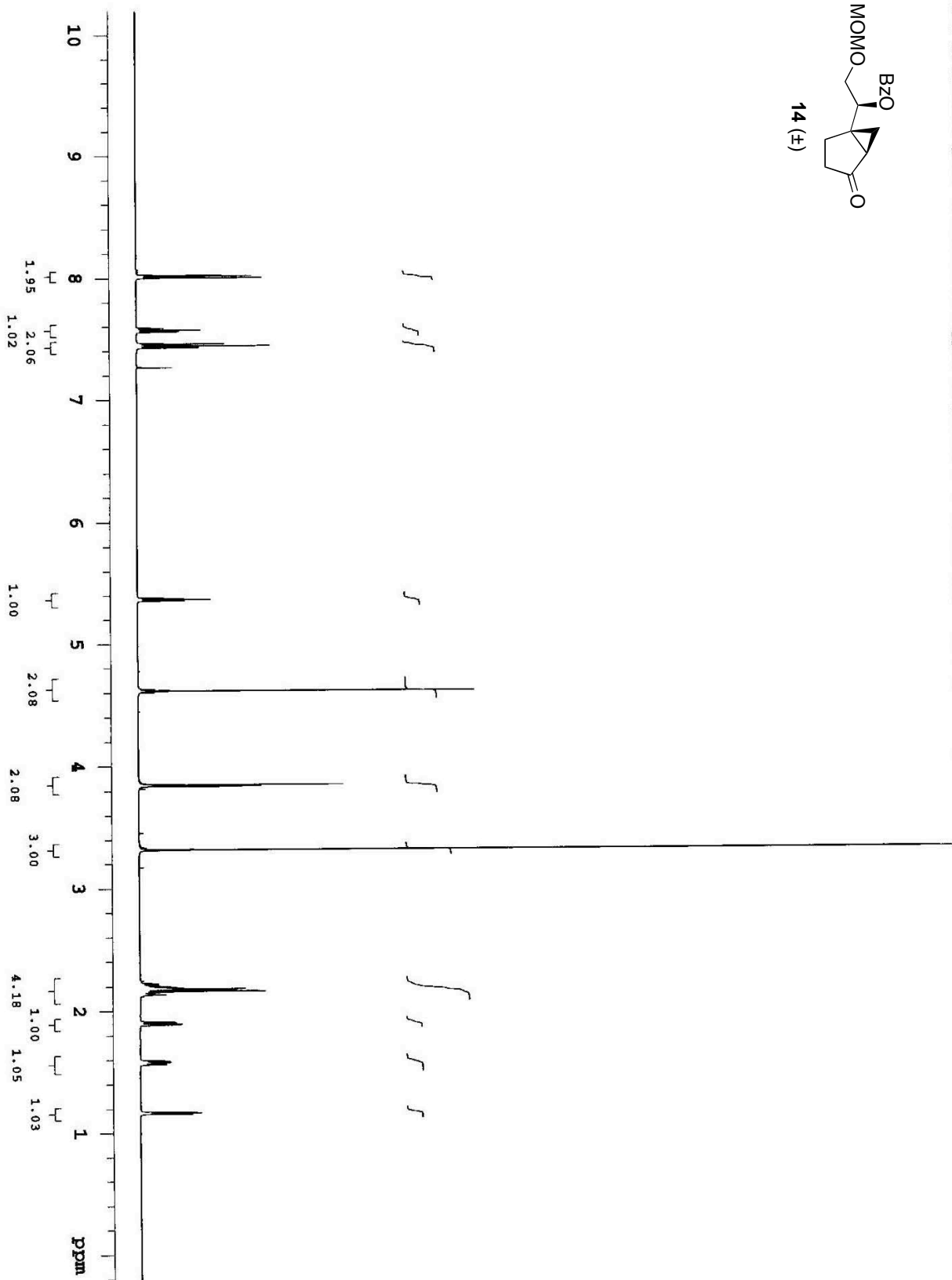
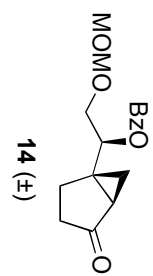
Pulse Sequence: apt



compound-14-H

Pulse Sequence: szpul

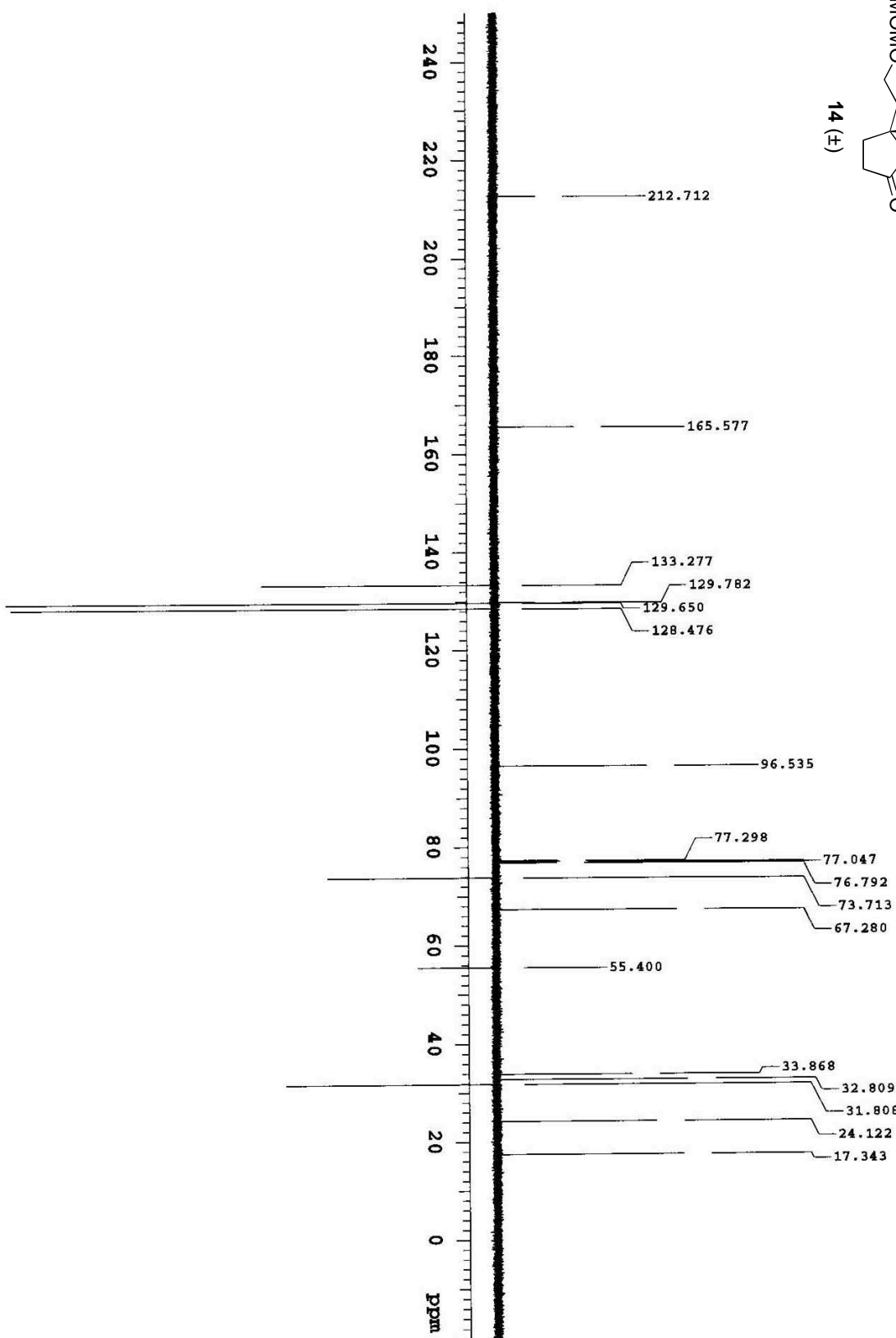
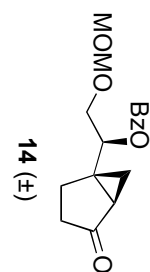
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe



Compound-14-C

125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe C & CH2 same, CH & CH3 opposite side of solvent signal

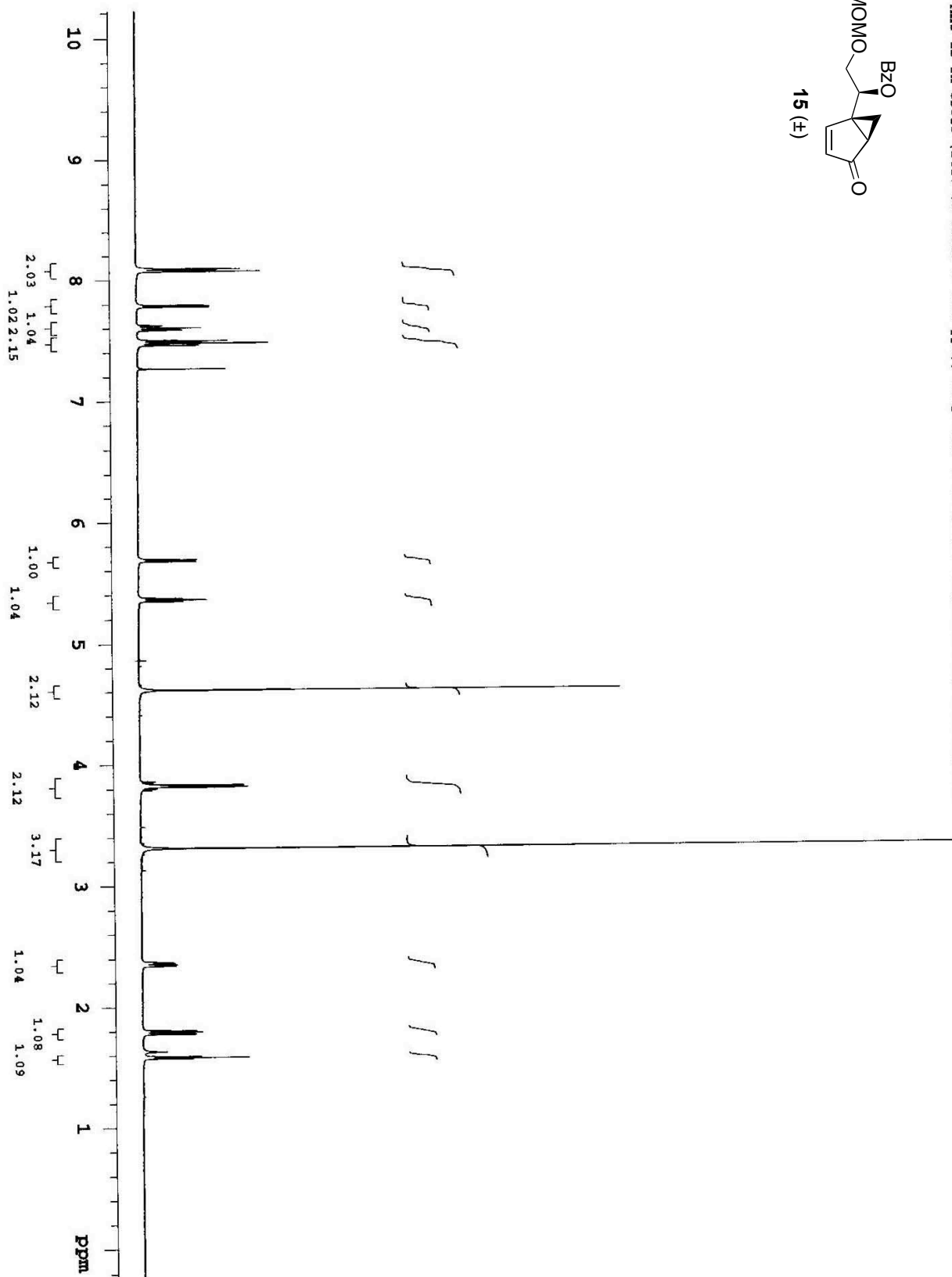
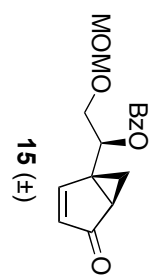
Pulse Sequence: apt



Compound-15-H

Pulse Sequence: szpul

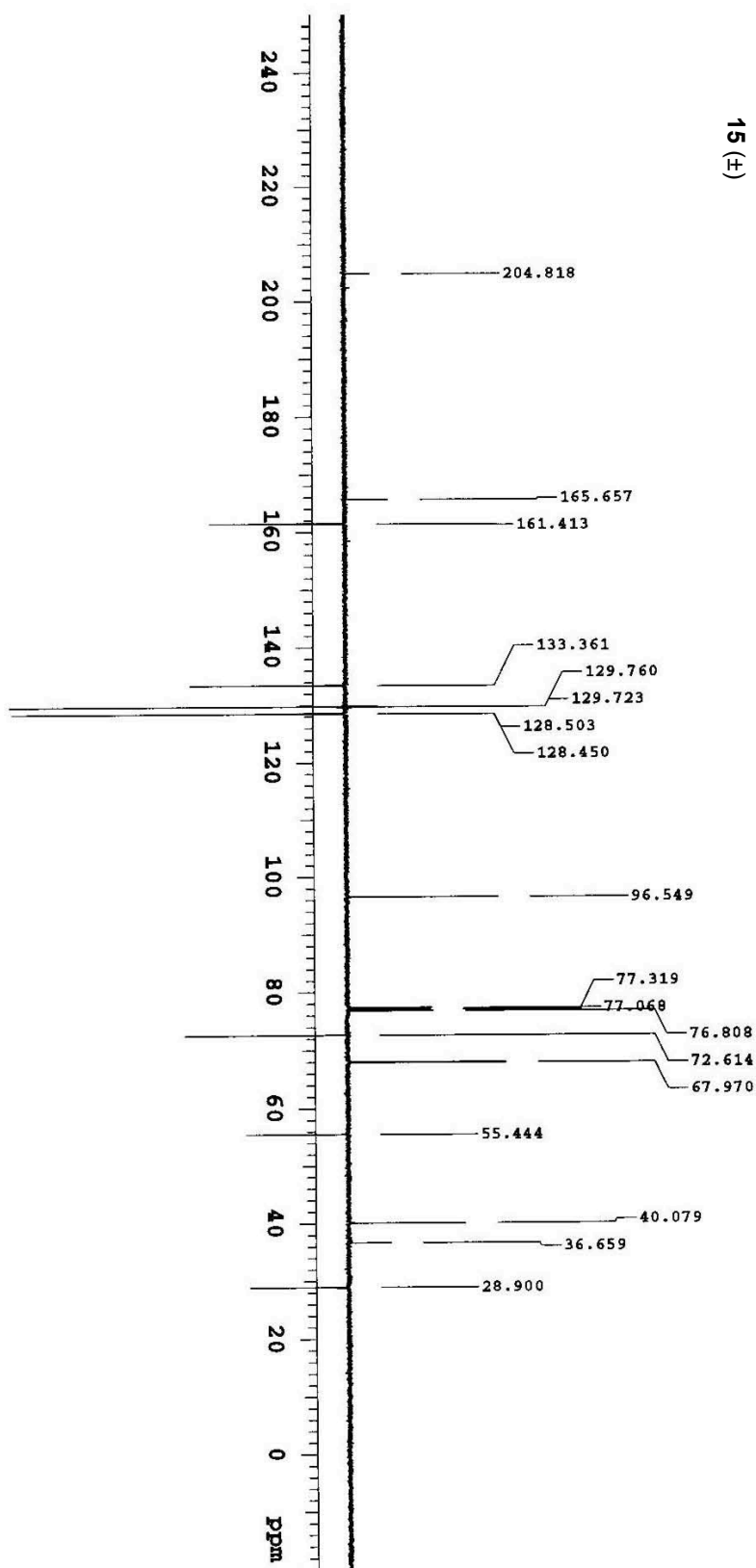
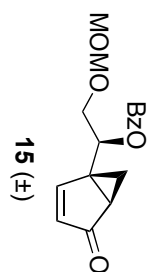
400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe



Compound-15-C

Pulse Sequence: apt

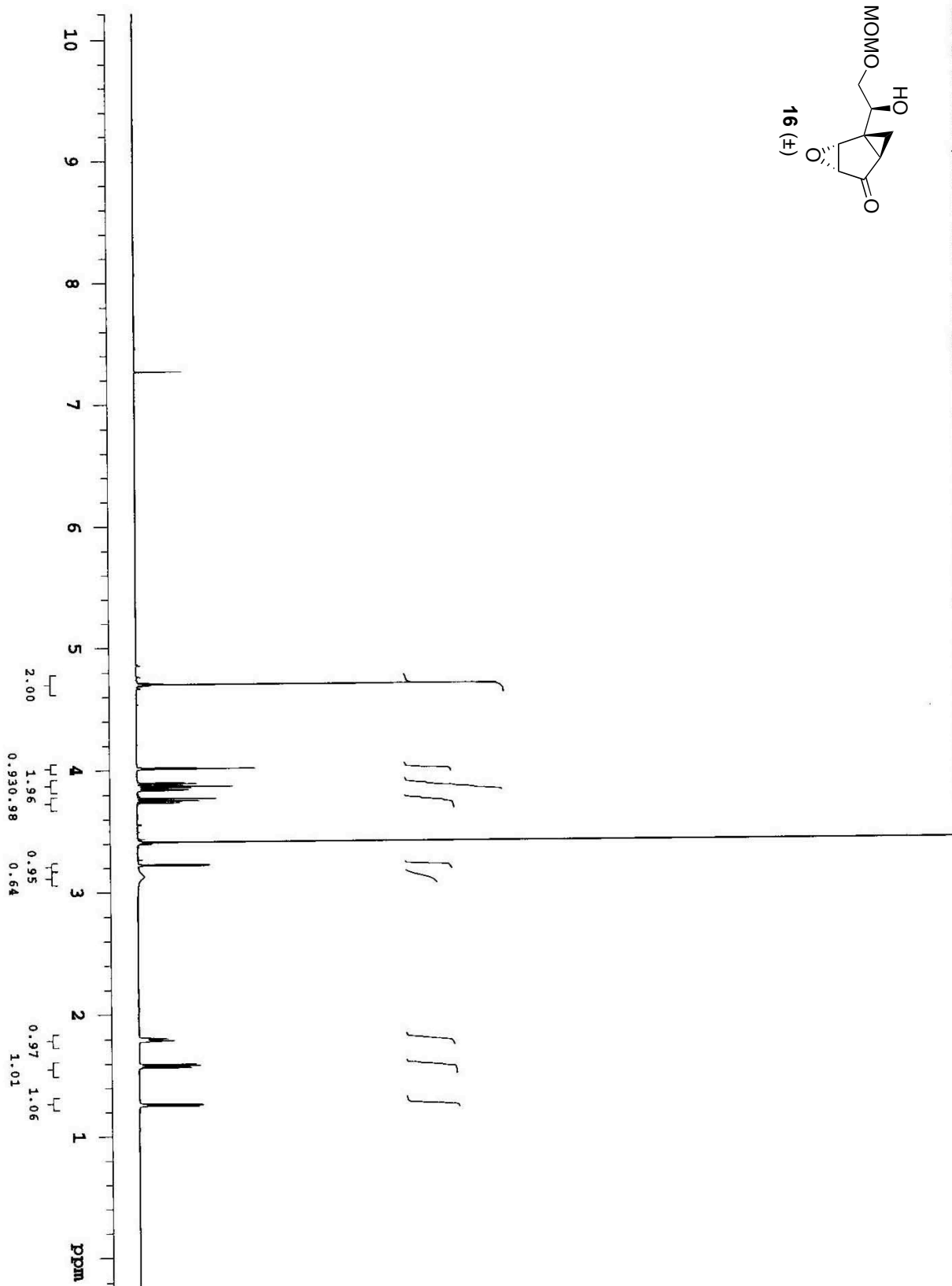
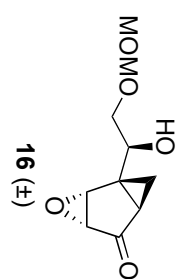
125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe C & CH2 same, CH & CH3 opposite side of solvent signal



Compound-16-H

Pulse Sequence: szpu1

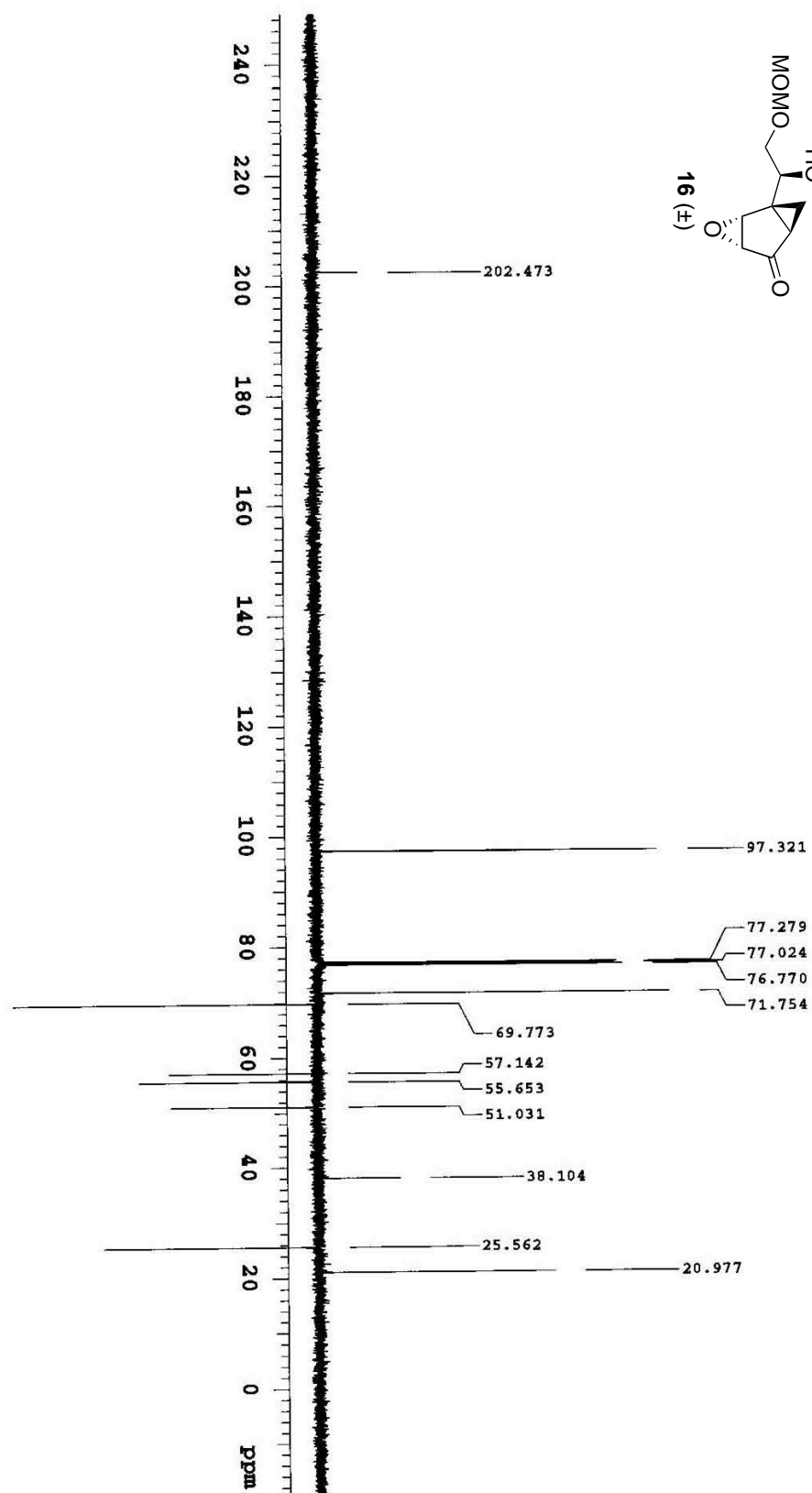
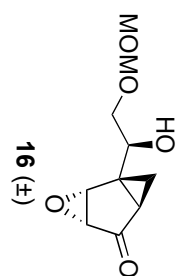
500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxgb probe



Compound-16-C

Pulse Sequence: apc

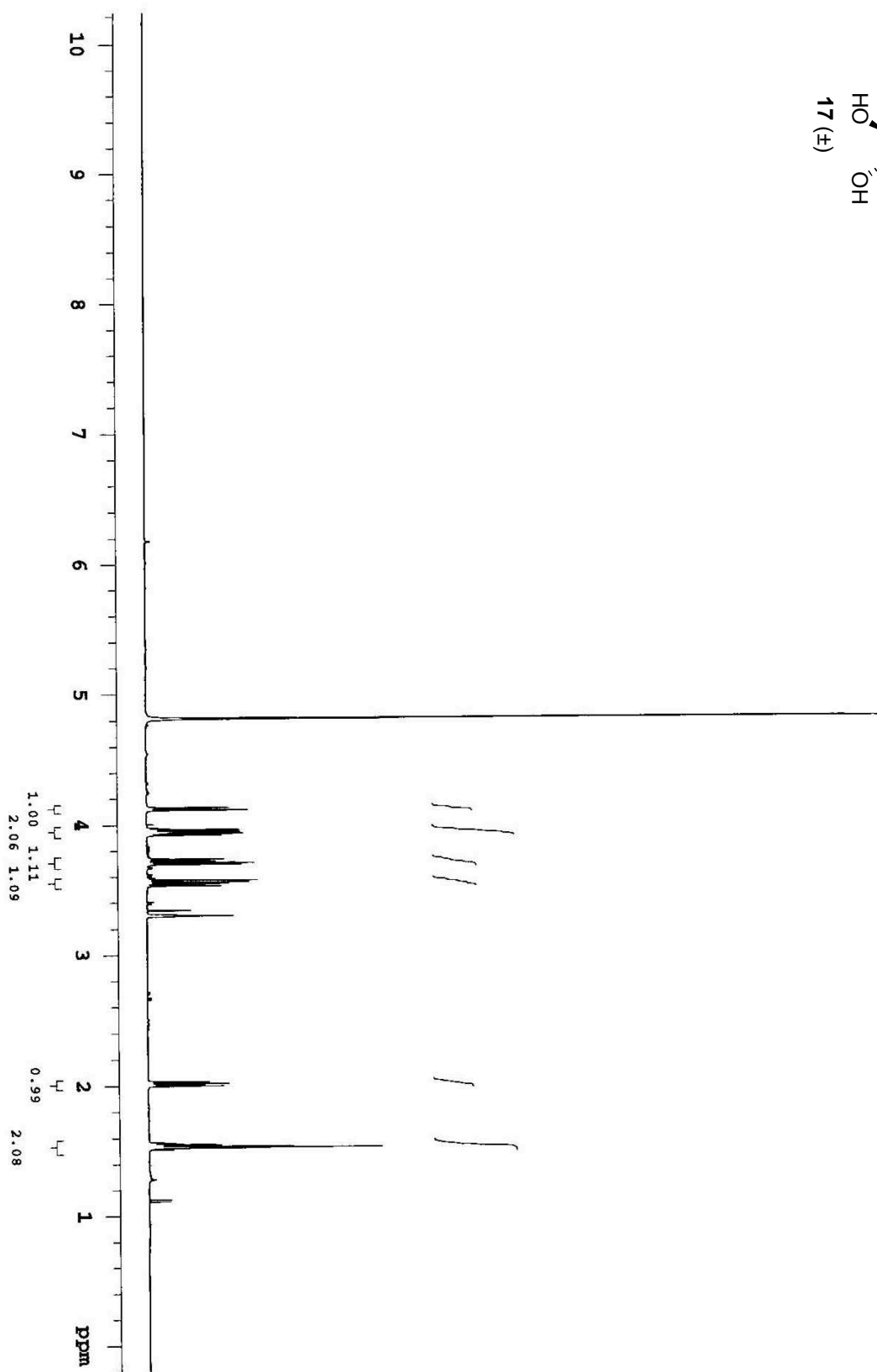
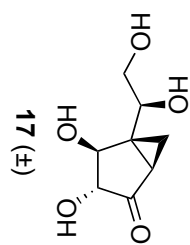
125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxkb probe
C & CH₂ same, CH & CH₃ opposite side of solvent signal



Compound-17-H

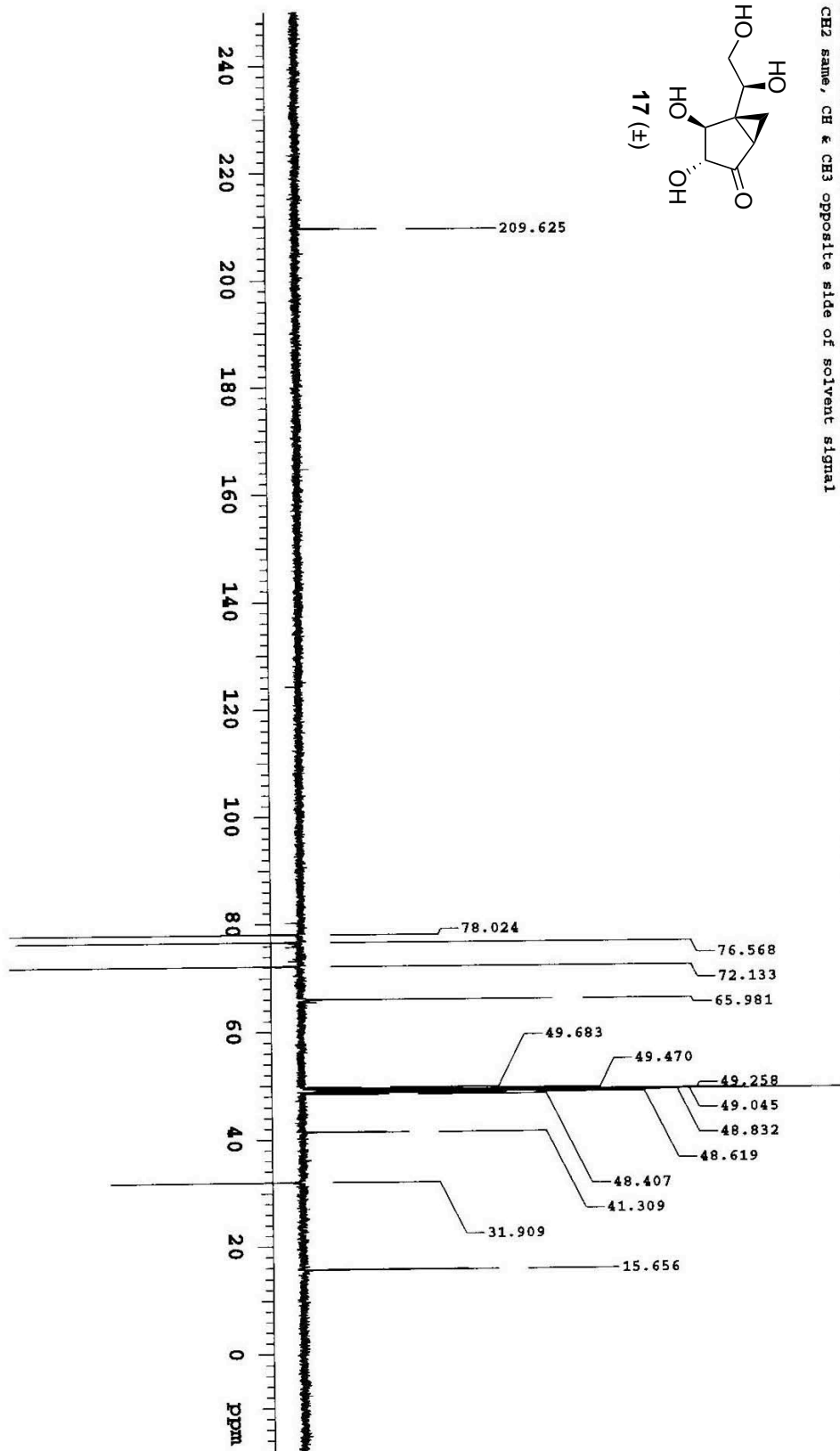
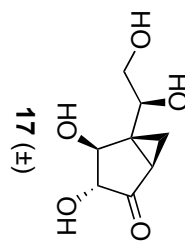
Pulse Sequence: s2pu1

400 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe



Compound-17-C

100 MHz APF In CD3OD (ref. to CD3OD @ 49.0 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
C & CH2 same, CH & CH3 opposite side of solvent signal

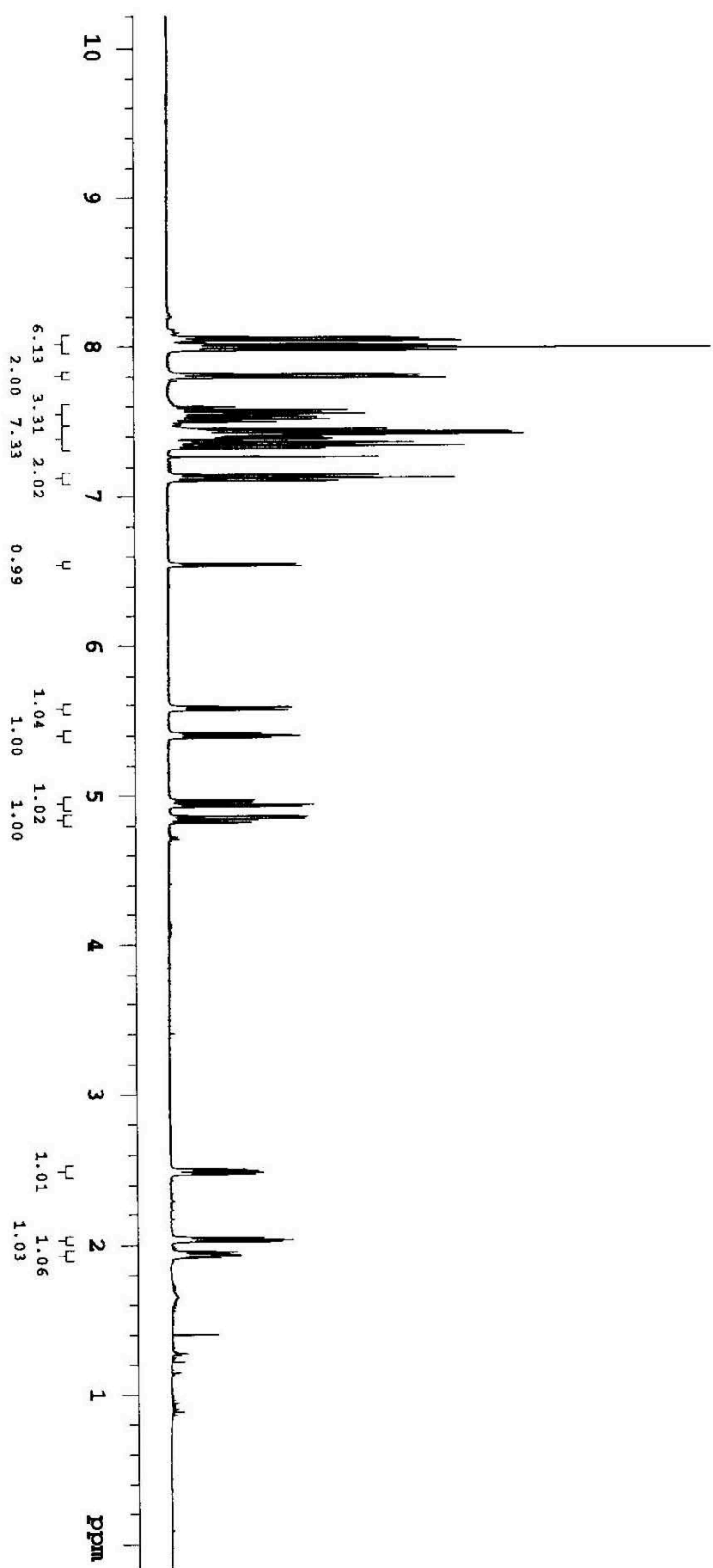
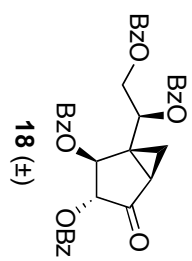


Pulse Sequence: apc

Compound-18-H

Pulse Sequence: s2pul1

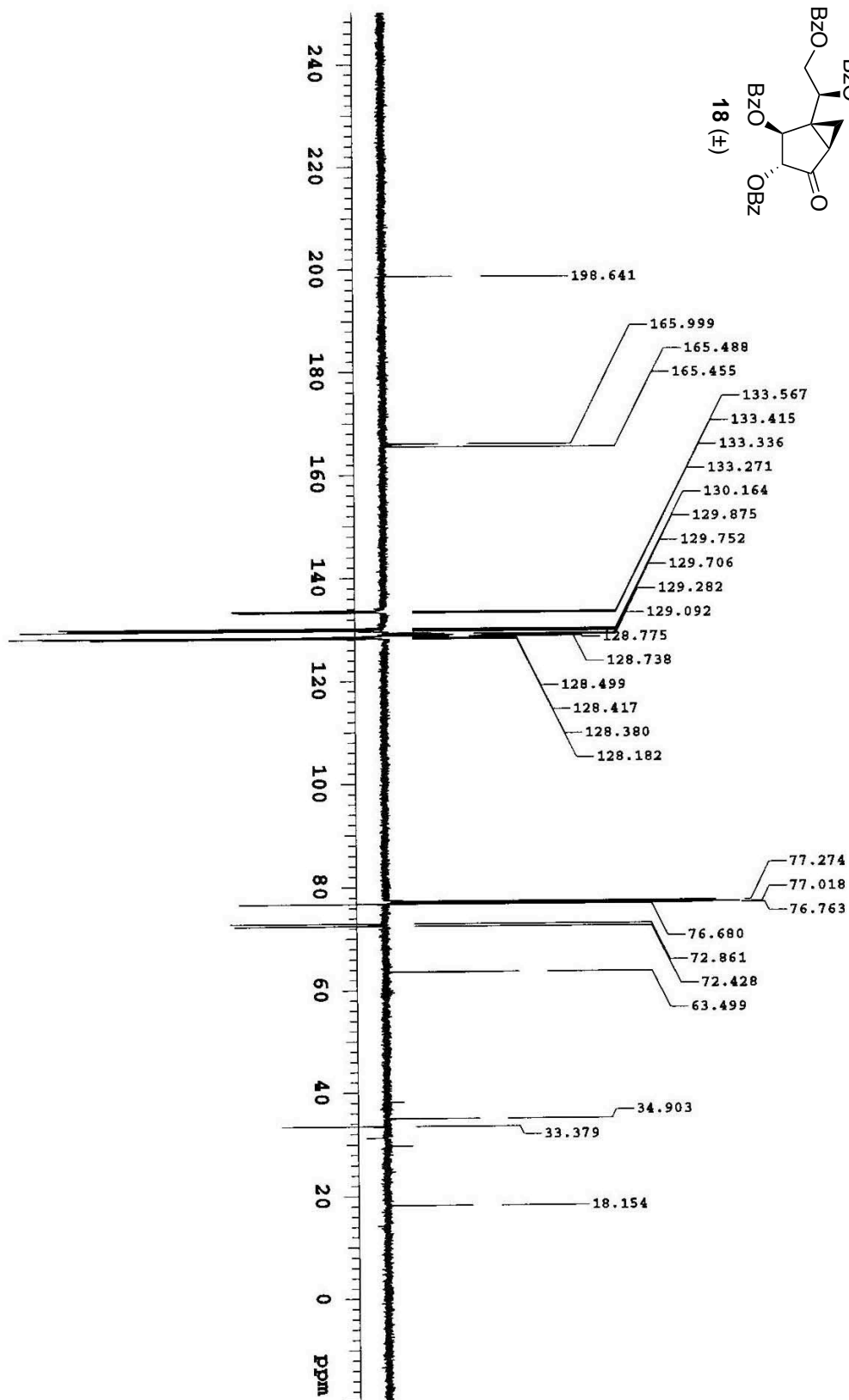
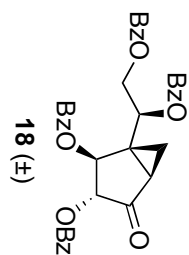
400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, aw400 probe



Compound-18-c

125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe C & CH2 same, CH & CH3 opposite side of solvent signal

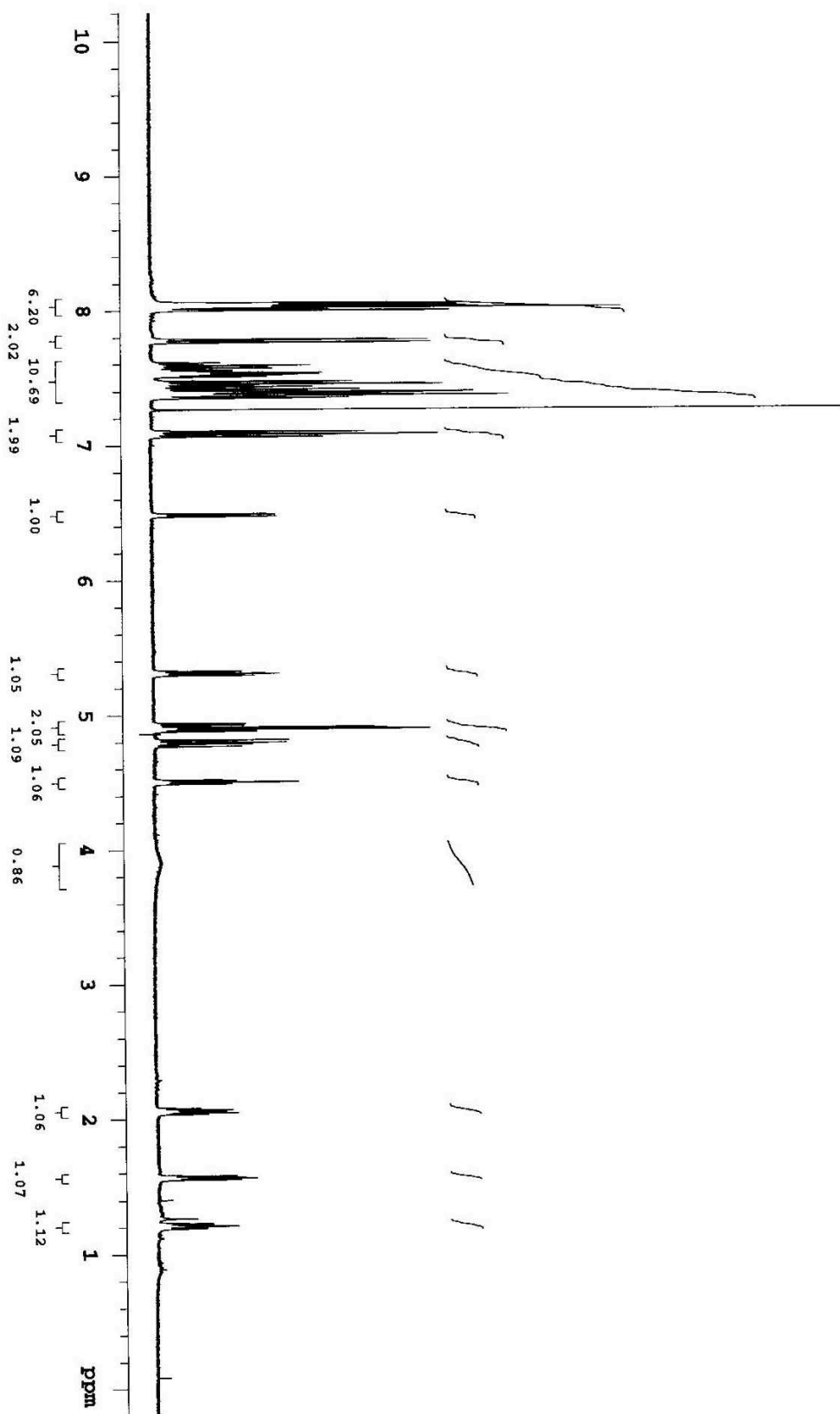
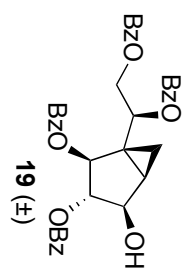
Pulse Sequence: apt



Compound-19-H

Pulse Sequence: szpul

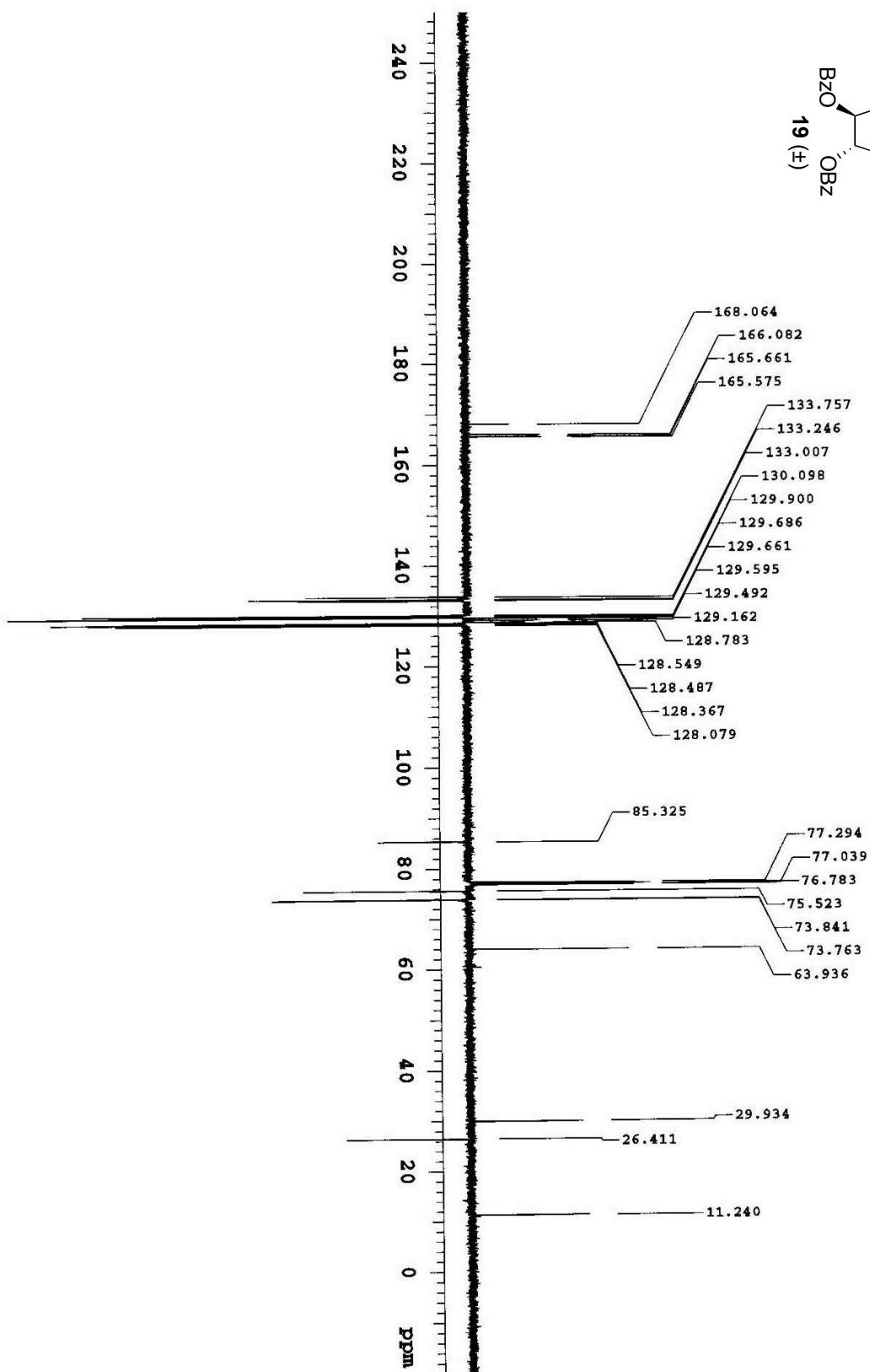
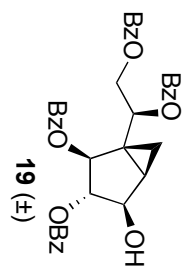
400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe



Compound-19-**c**

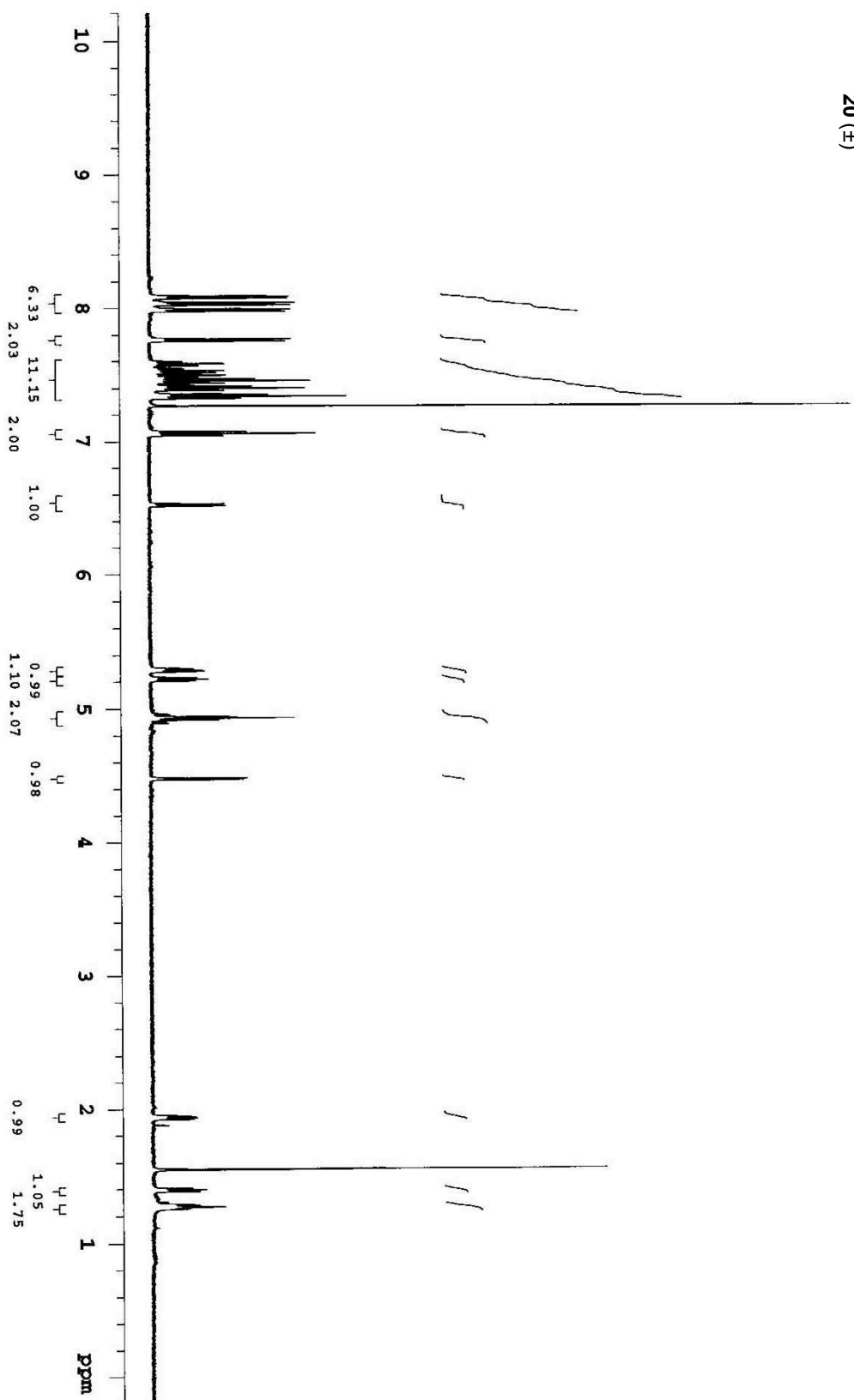
125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH₂ same, CH & CH₃ opposite side of solvent signal

Pulse Sequence: apf



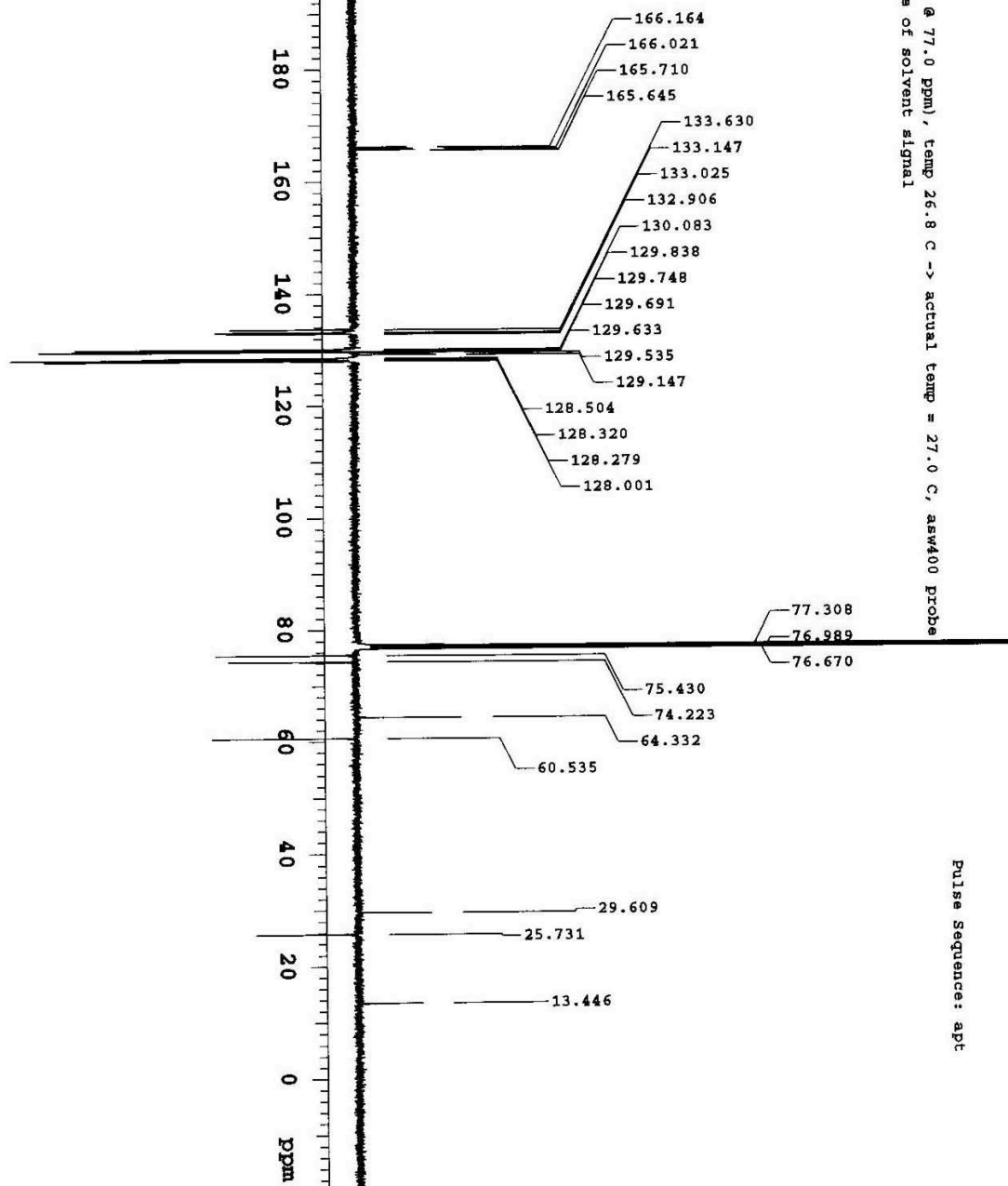
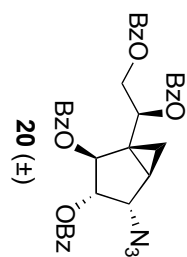
Pulse Sequence: s2pul

20 (±)



Compound-20-C

100 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 26.8 C -> actual temp = 27.0 C, asw400 probe
C & CH₂ same, CH & CH₃ opposite side of solvent signal

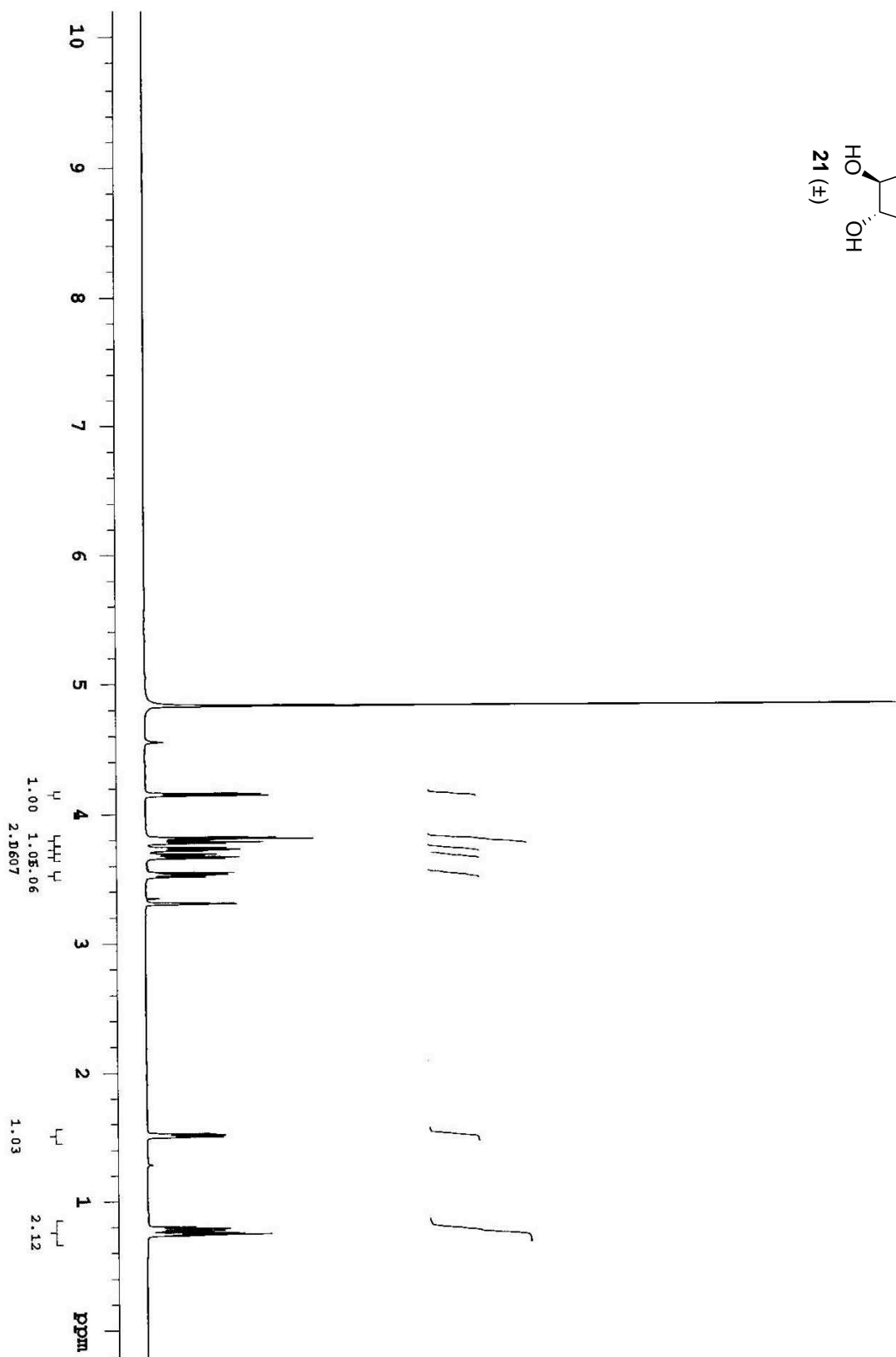
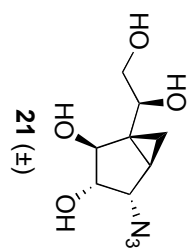


Pulse Sequence: apf

Compound-21-H

Pulse Sequence: presat

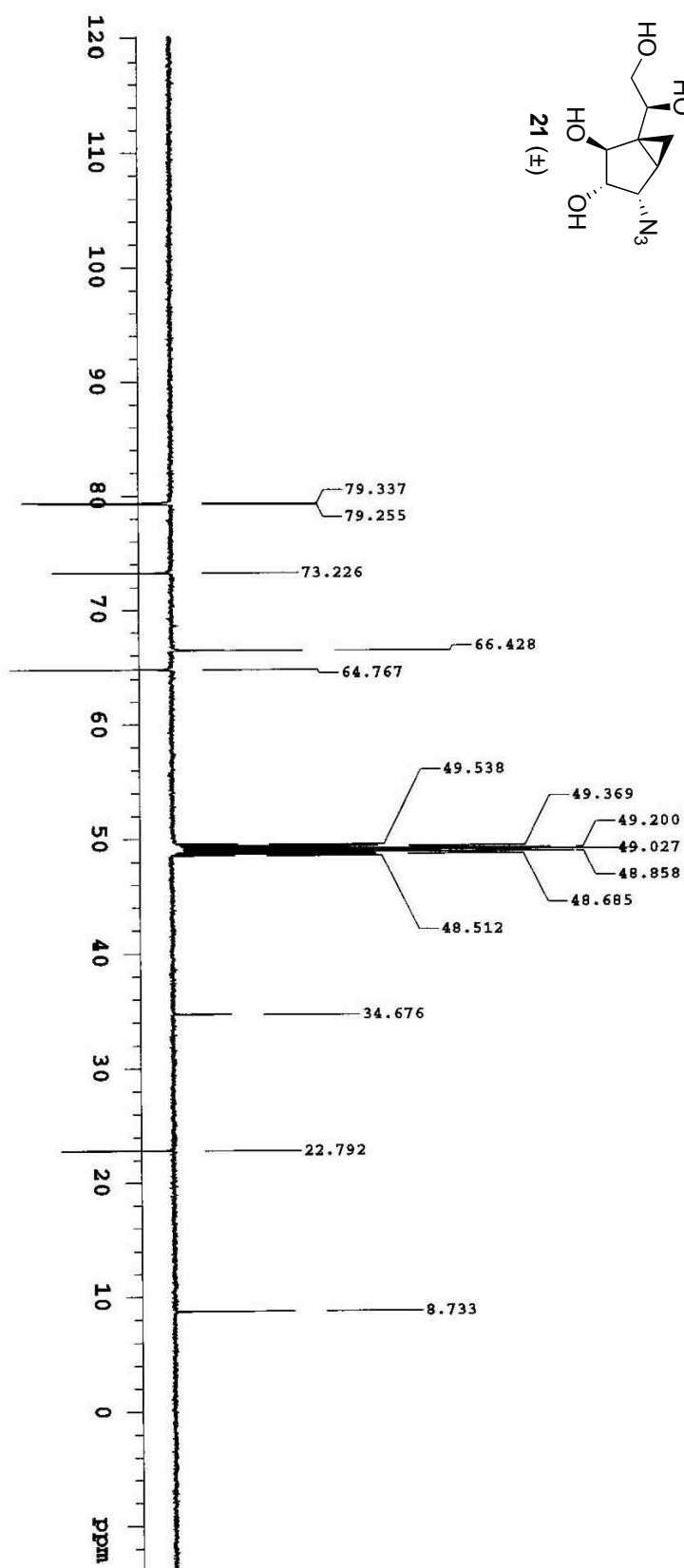
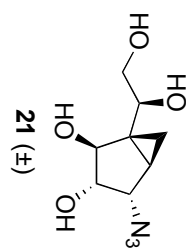
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxgb probe



Compound-21-C

Pulse Sequence: apt

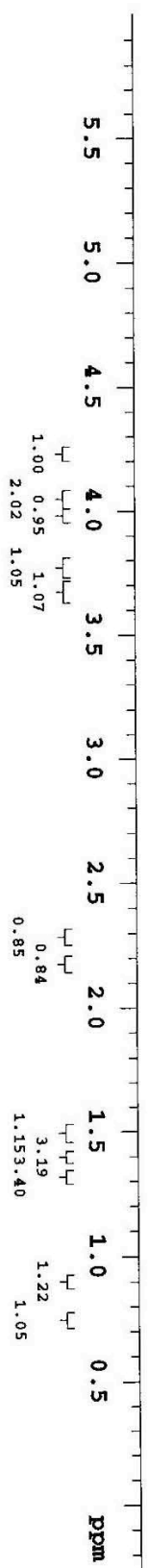
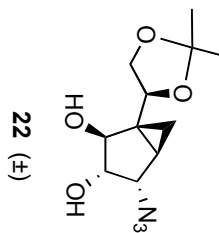
125 MHz APF in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal



Compound-22-B

Pulse Sequence: szpul

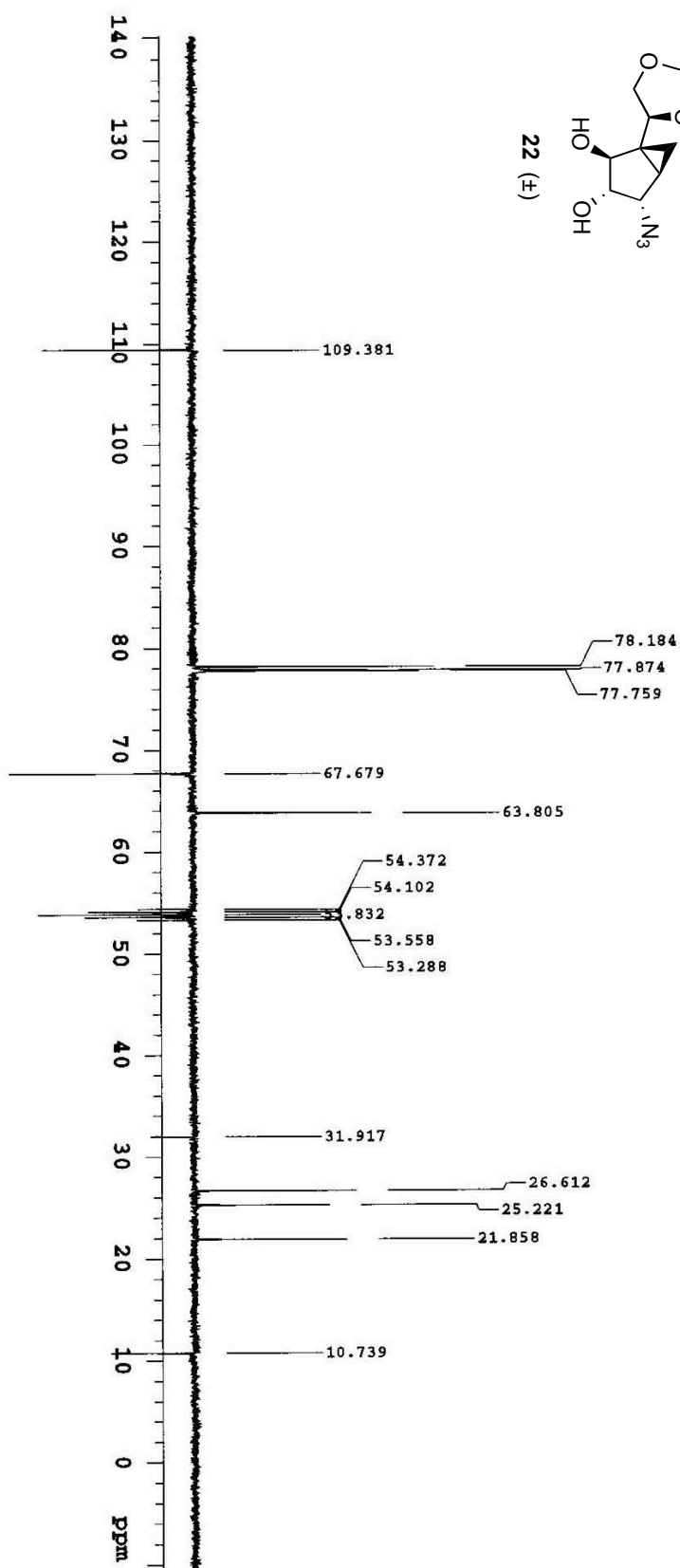
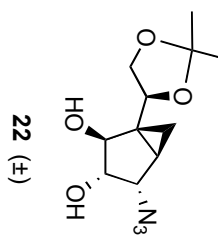
500 MHz ID in CD₂Cl₂ (ref. to CD₂Cl₂ @ 5.32 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe



Compound-22-C

Pulse Sequence: apt

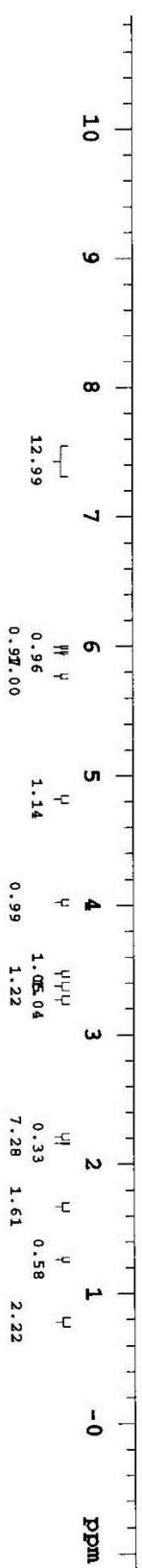
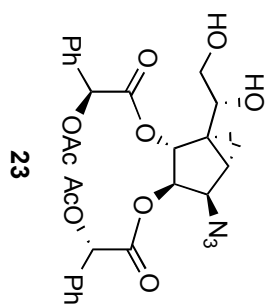
100 MHz APT in CD₂Cl₂ (ref. to CD₂Cl₂ @ 53.8 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxarb probe
C & CH₂ same, CH & CH₃ opposite side of solvent signal



Compound-23-H

Pulse Sequence: szpul

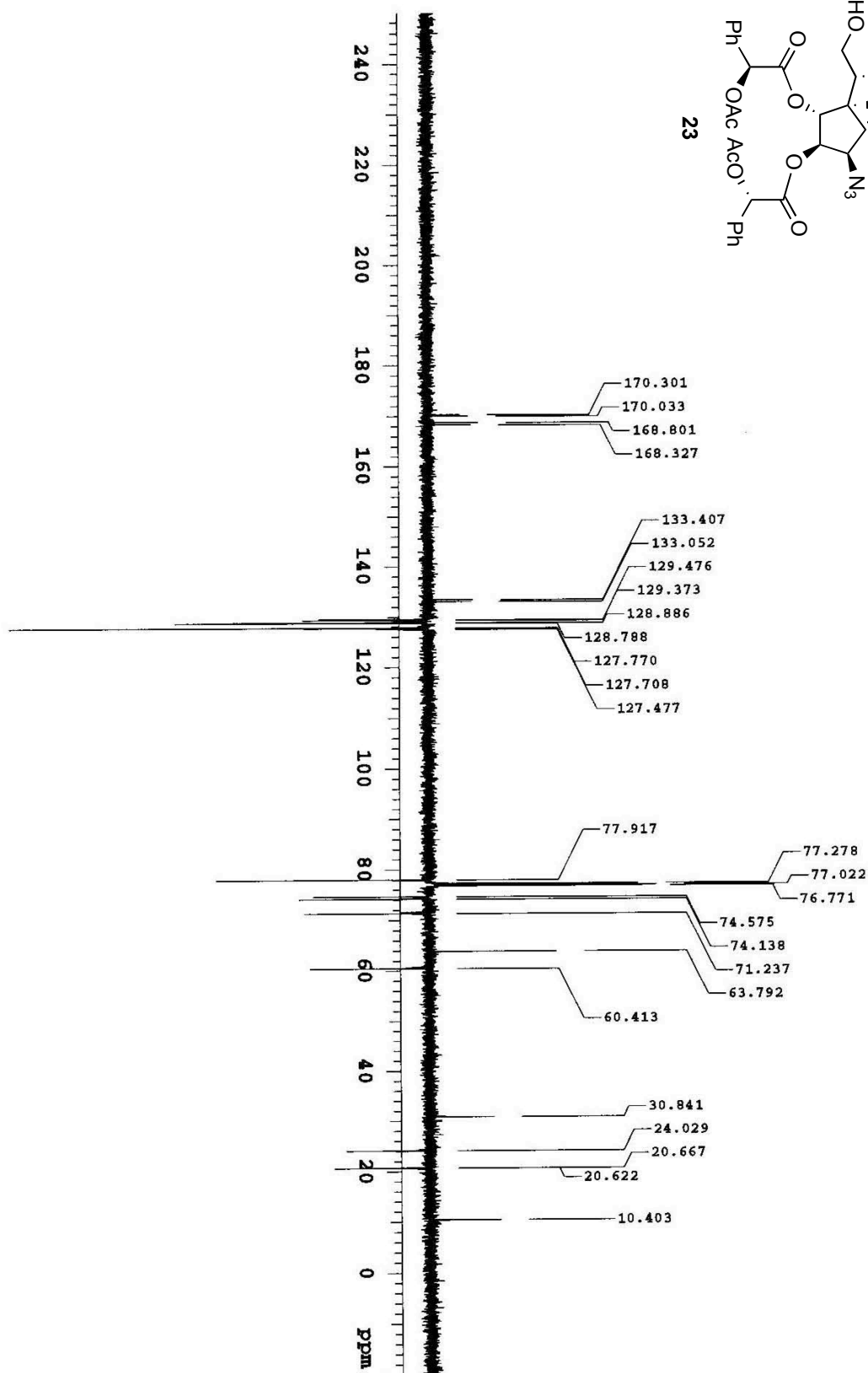
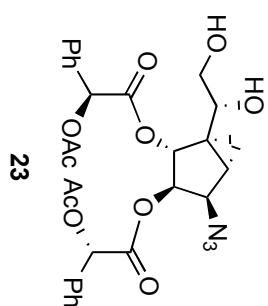
400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxdrb probe



Compound-23-C

125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH₂ same, CH & CH₃ opposite side of solvent signal

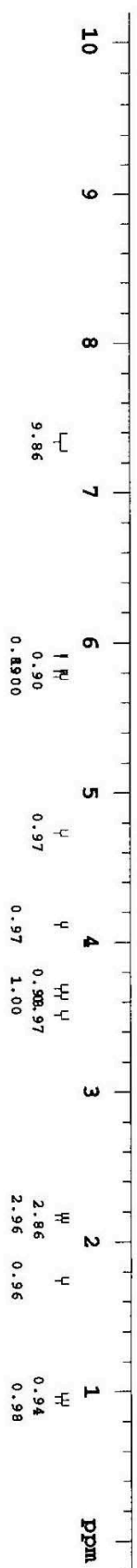
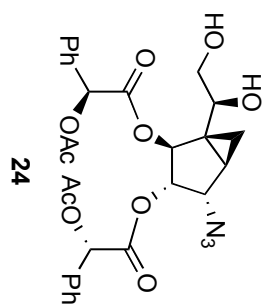
Pulse Sequence: apt



Compound-24-B

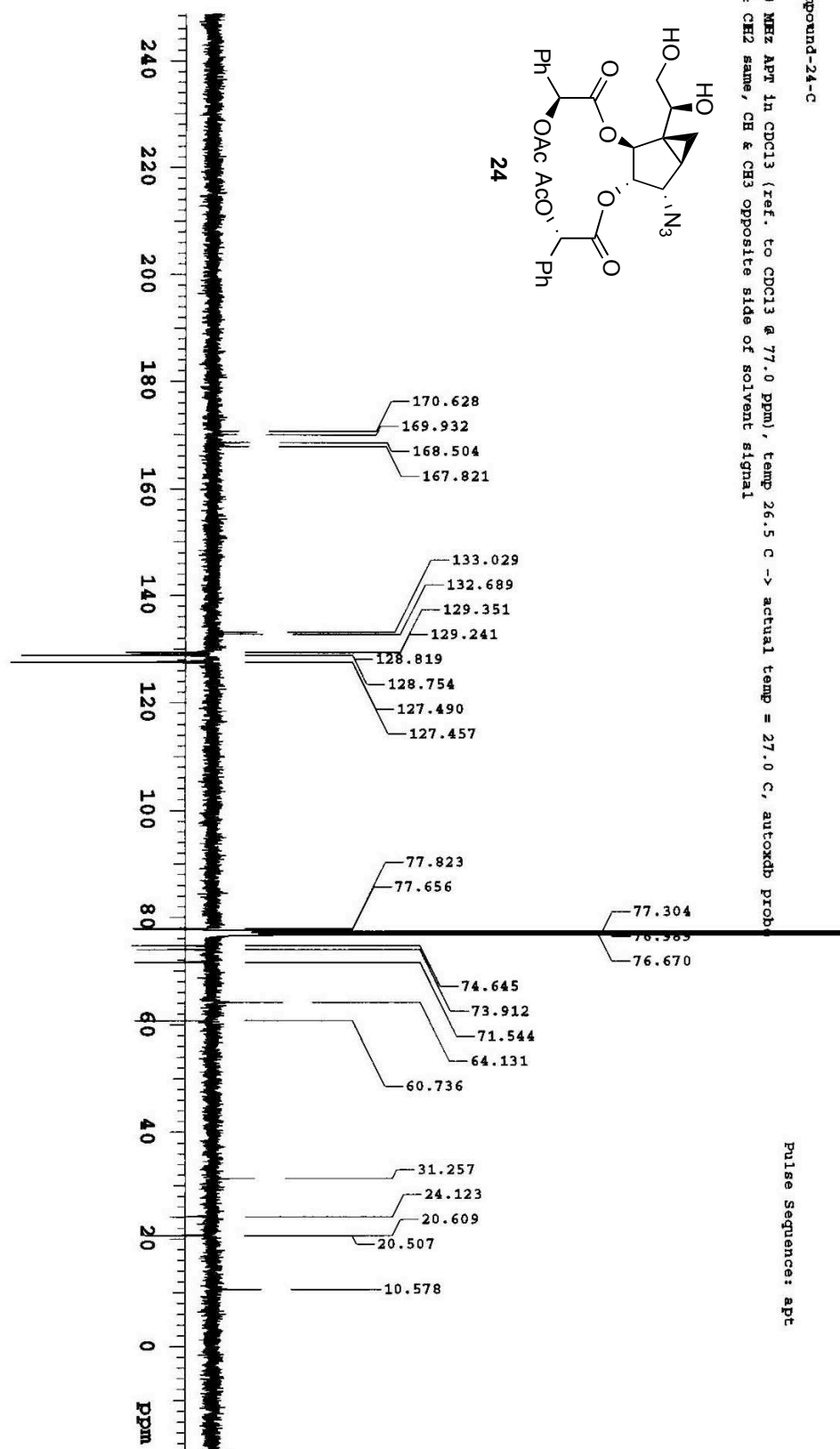
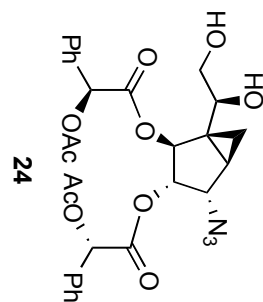
Pulse Sequence: szpul

500 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdr probe



Compound-24-C

100 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autotxdr prob
C & CH2 same, CH & CH3 opposite side of solvent signal

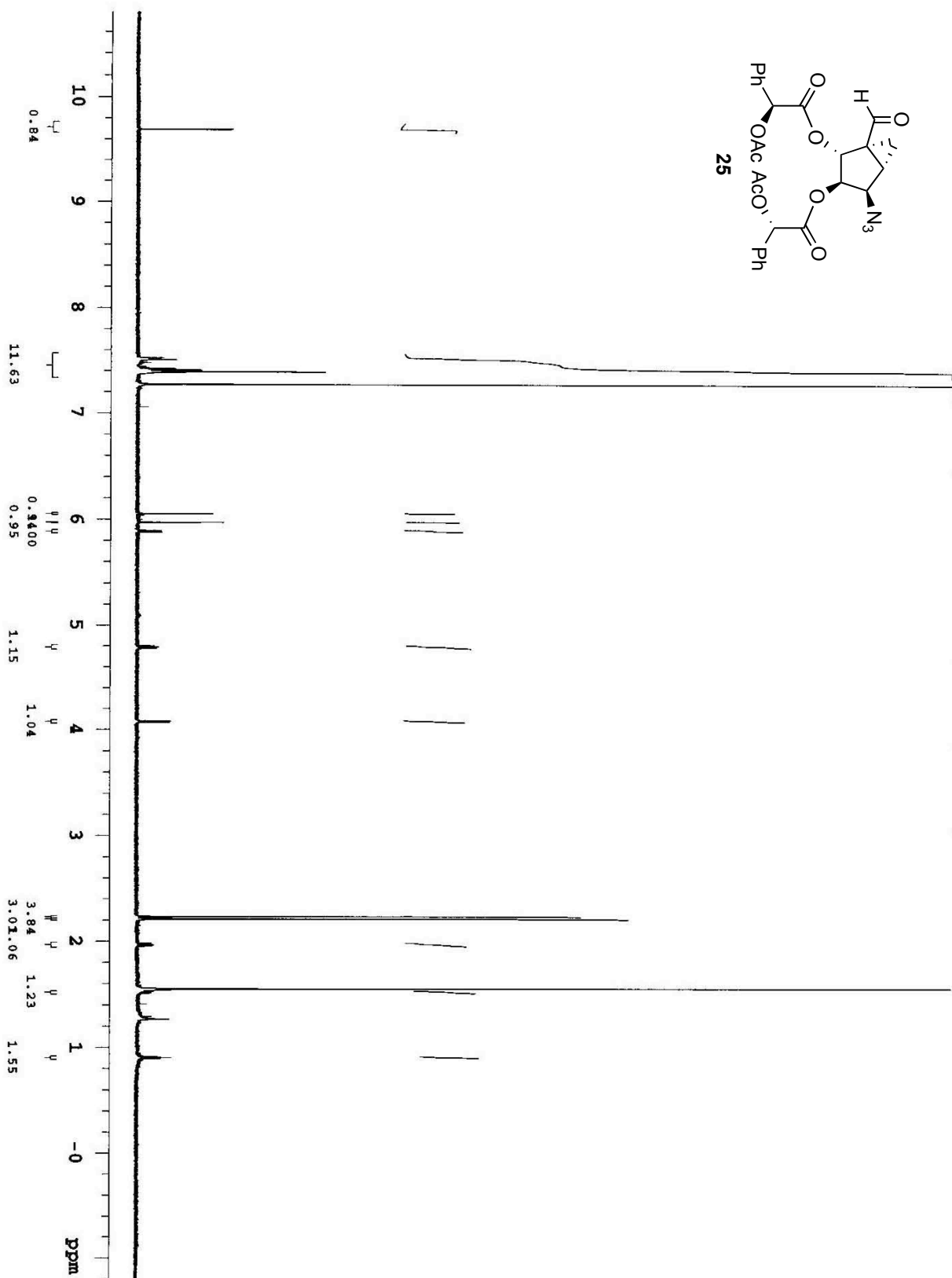
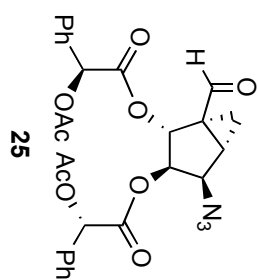


Pulse Sequence: apc

Compound-25-H

Pulse Sequence: szpui

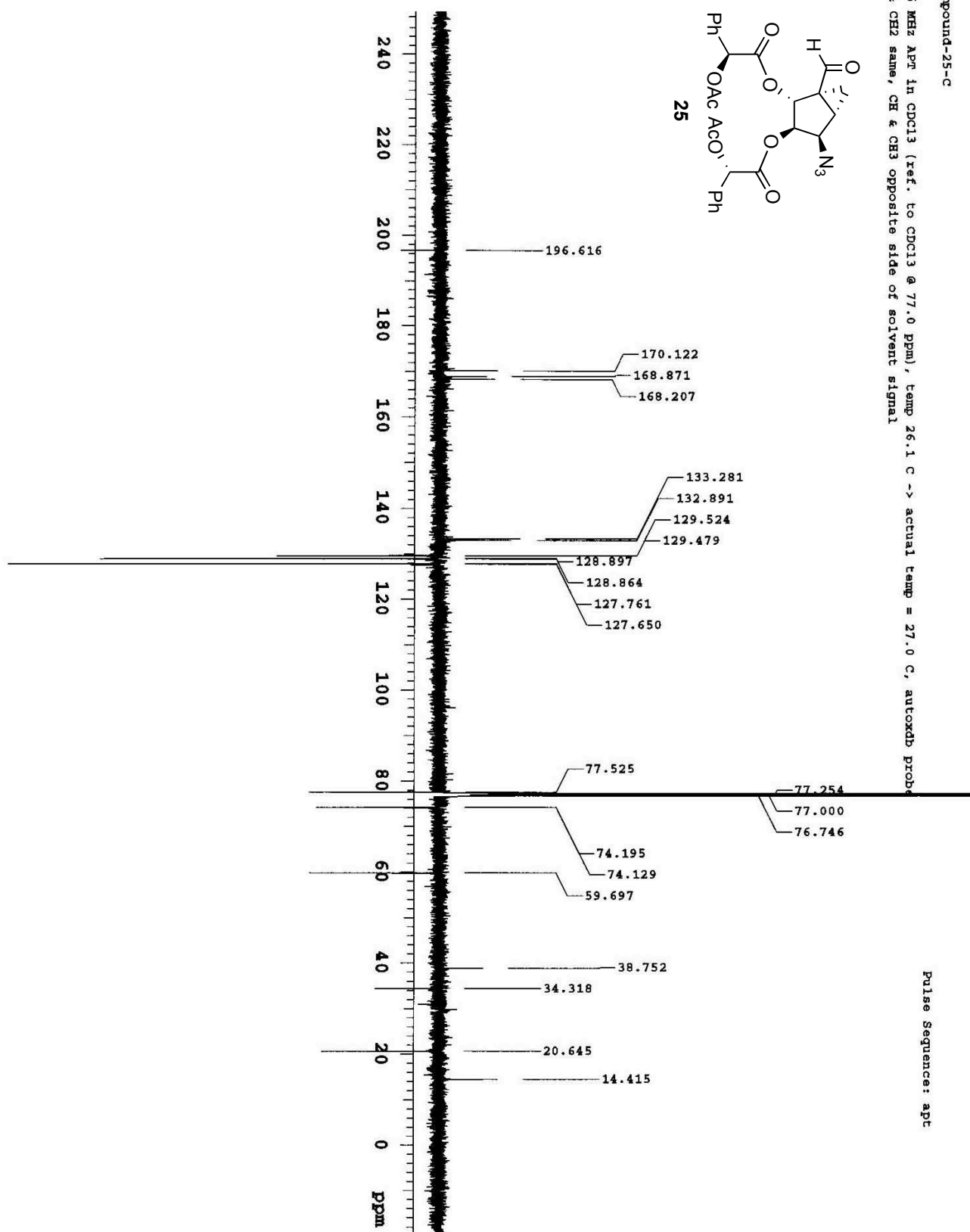
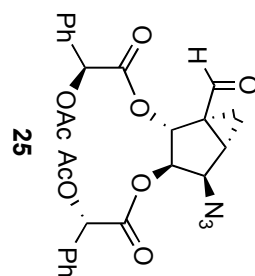
500 MHz 1D 1n CDC13 (ref. to CDC13 @ 7.26 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe



Compound-25-C

125 MHz APF in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxdb probe
C & CH2 same, CH & CH3 opposite side of solvent signal

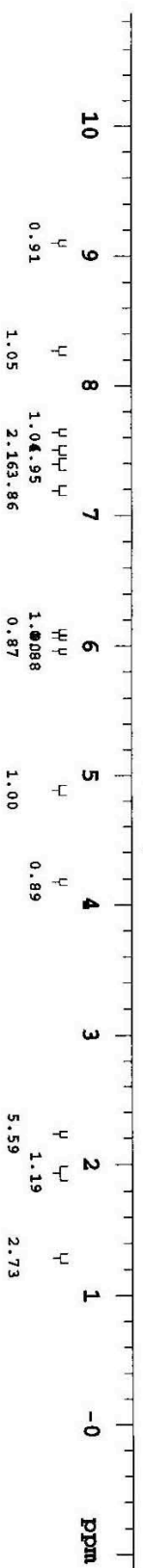
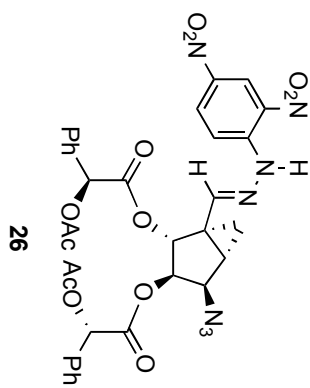
Pulse Sequence: apc



Compound-26-B

Pulse Sequence: s2pul

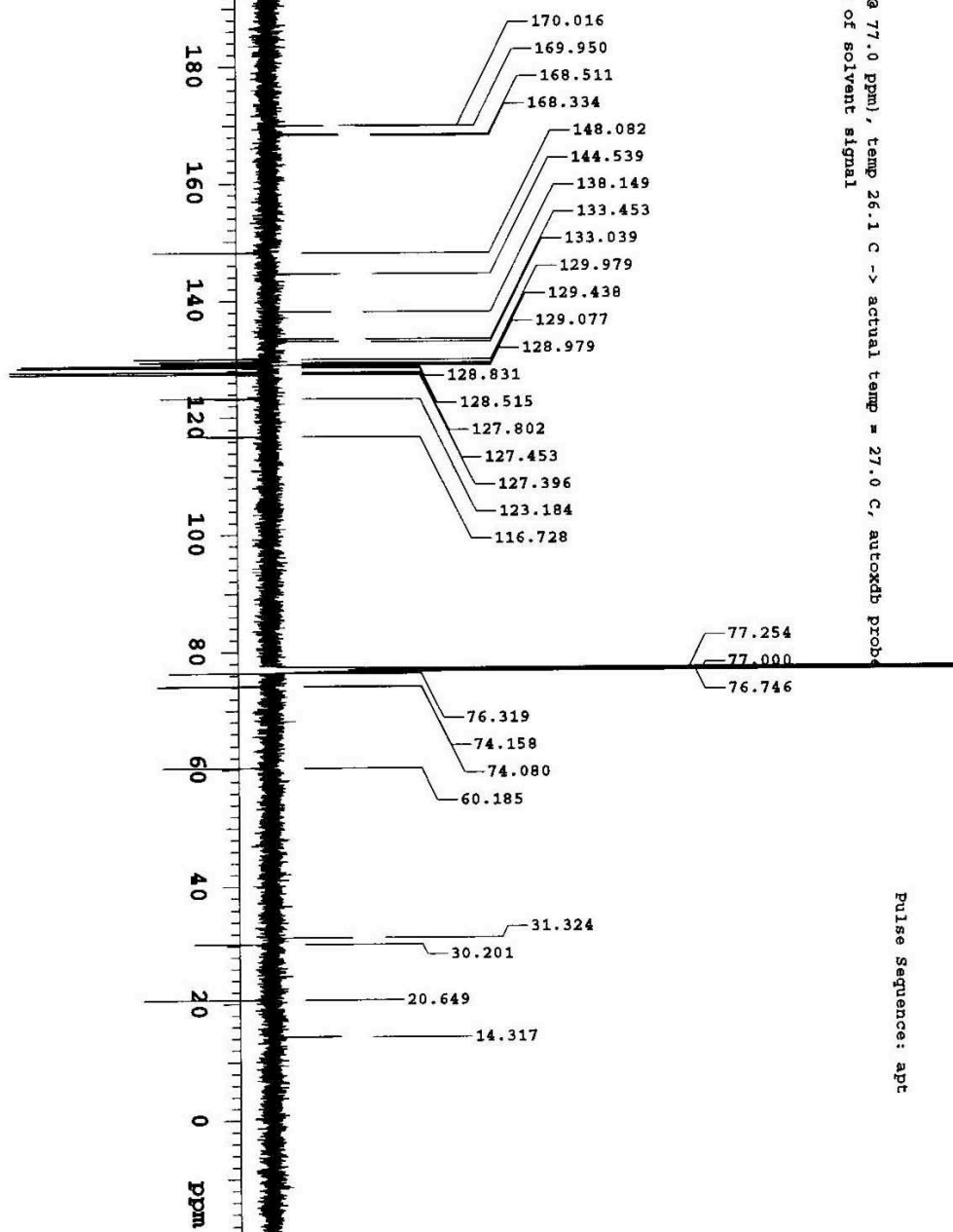
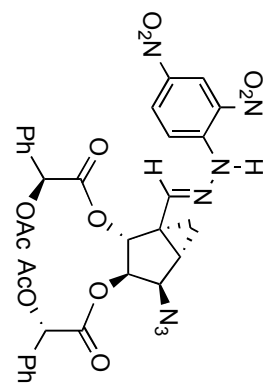
400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxgb probe



Compound-26-c

125 MHz APT in CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 26.1 C -> actual temp = 27.0 C, autoloxdb prob
C & CH2 same, CH & CH3 opposite side of solvent signal

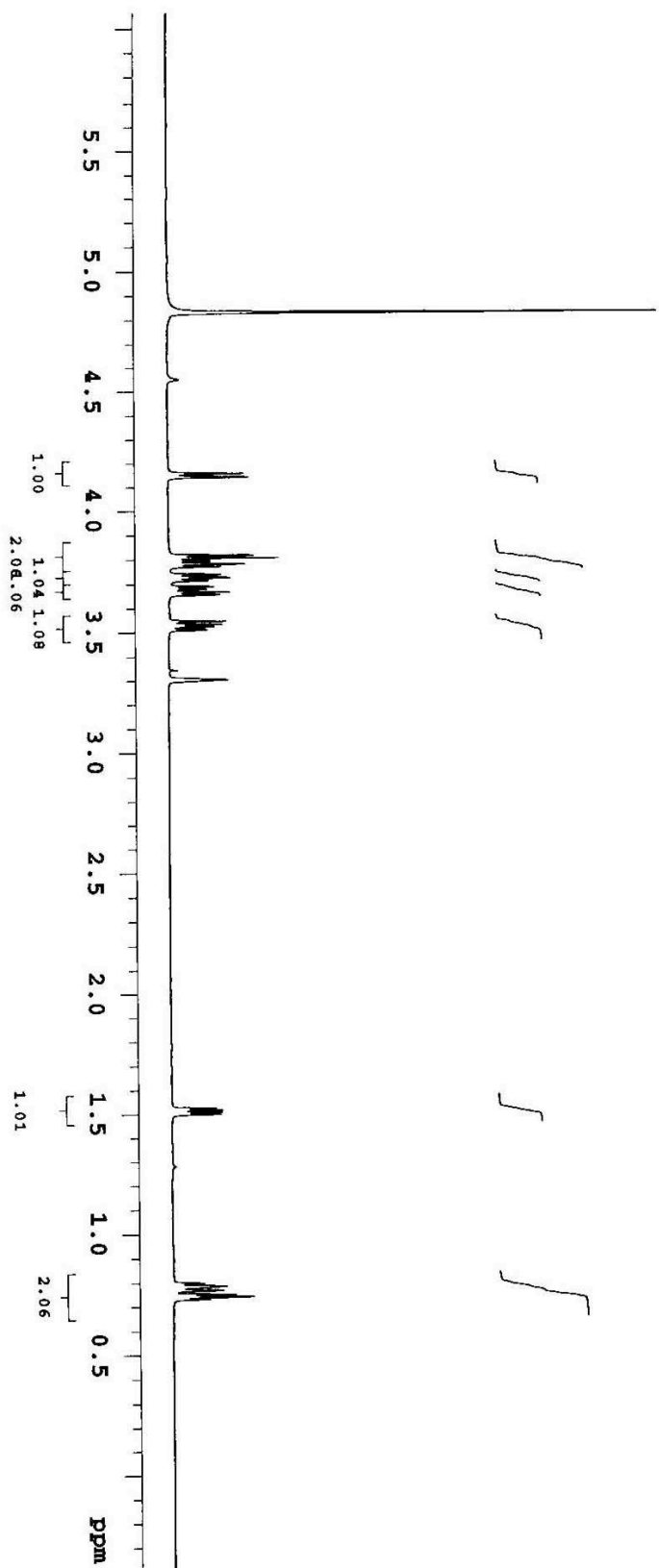
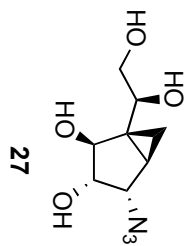
Pulse Sequence: apt



Compound-27-R

Pulse Sequence: Presat

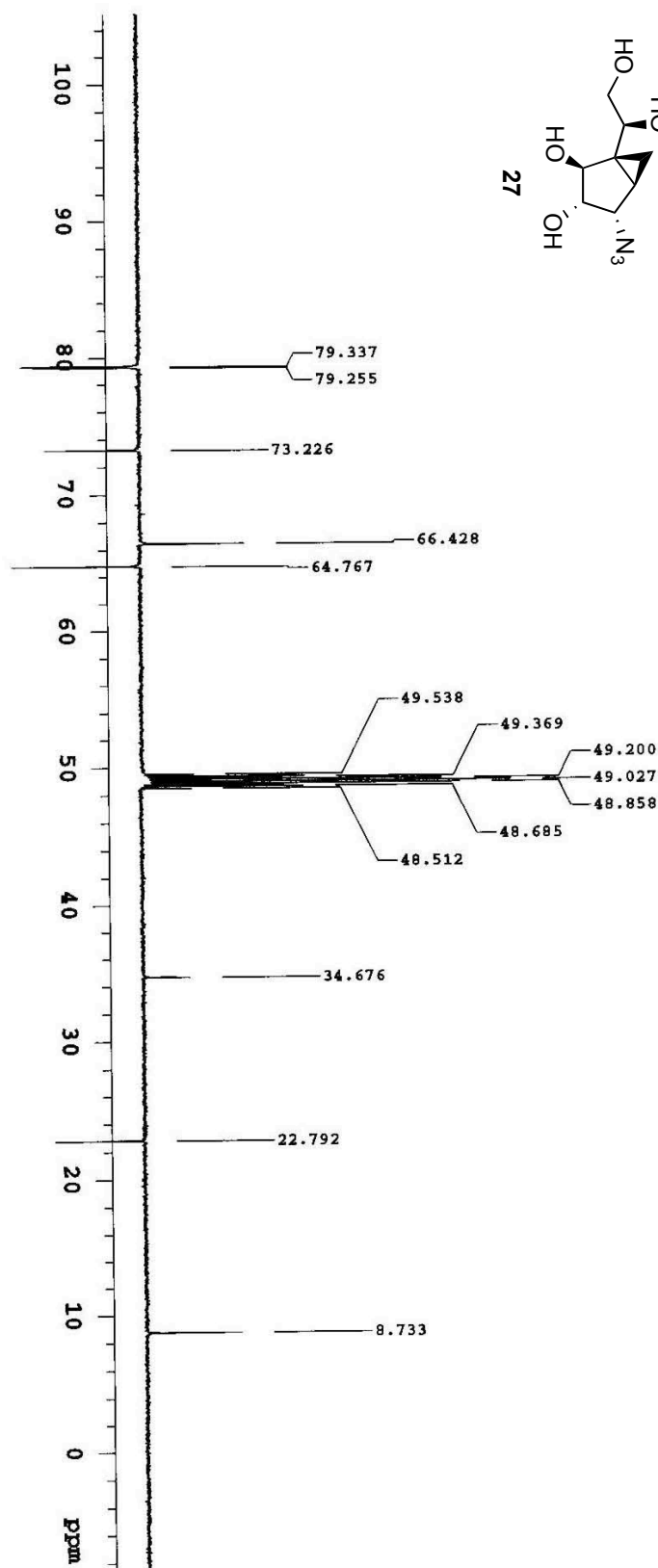
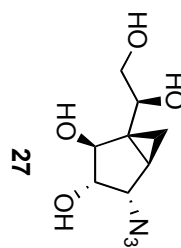
500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 26.1 C -> actual temp = 27.0 C, autoxgb probe



Compound-27-C

Pulse Sequence: apt

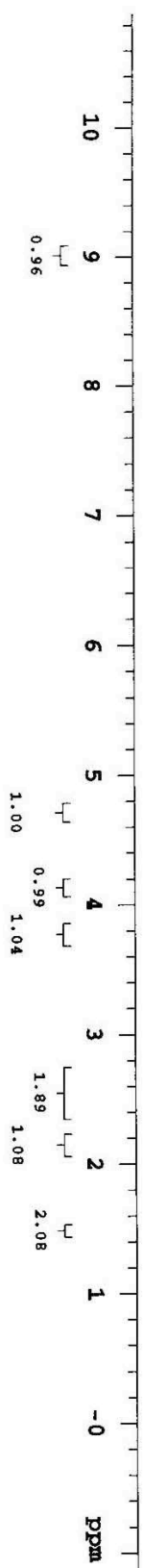
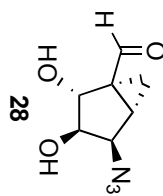
125 MHz AP1 in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, sw probe
C & CH2 same, CH & CH3 opposite side of solvent signal



Compound-28-H

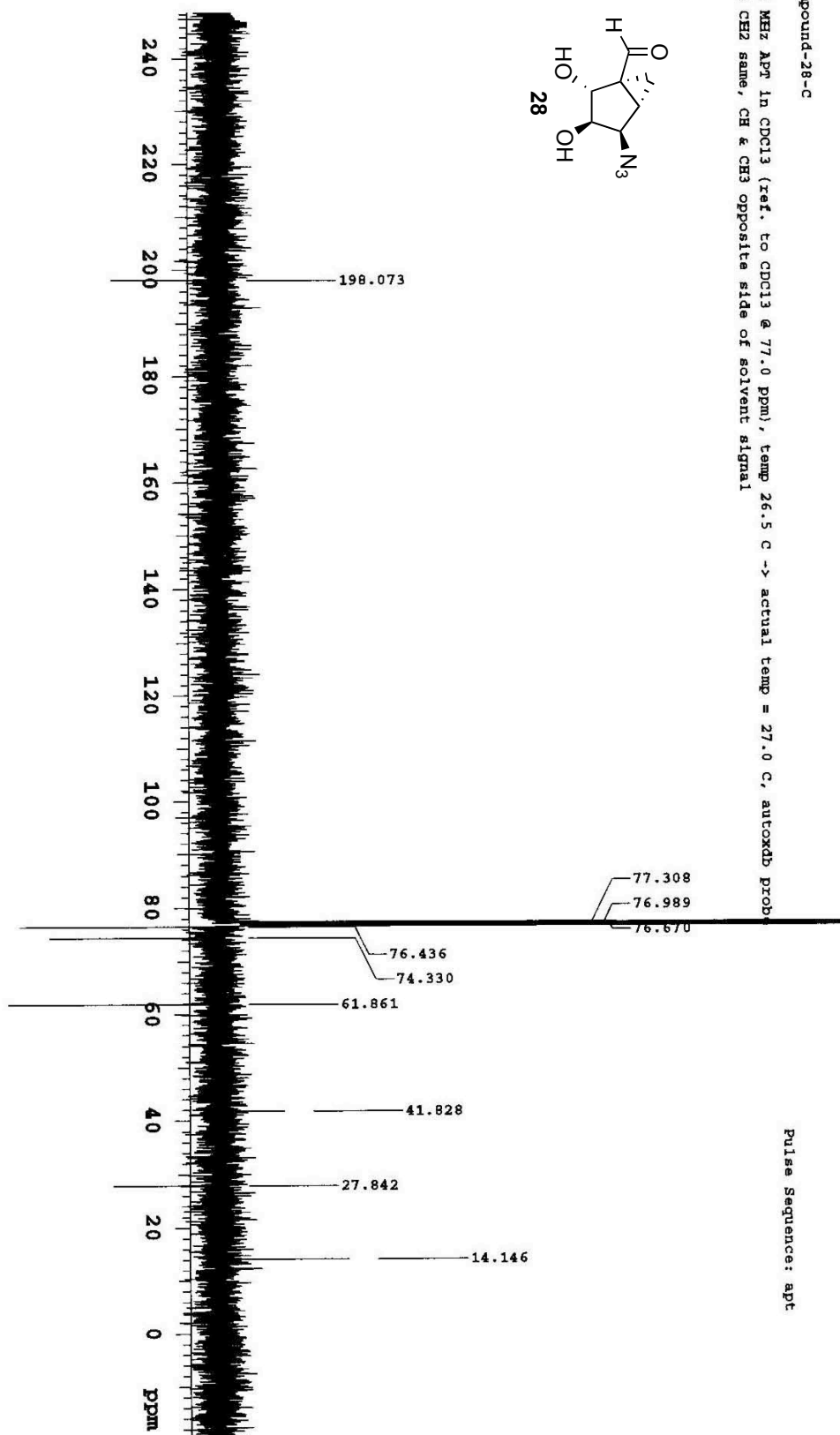
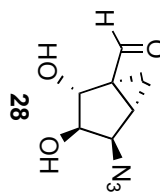
Pulse Sequence: szpu1

400 MHz 1D in CDCl₃ (ref. to CDCl₃ @ 7.26 ppm), temp 26.5 C -> actual temp = 27.0 C, autordb probe



Compound-28-C

100 MHz AP7 In CDCl₃ (ref. to CDCl₃ @ 77.0 ppm), temp 26.5 C -> actual temp = 27.0 C, autoxap prob
C & CH2 same, CH & CH3 opposite side of solvent signal

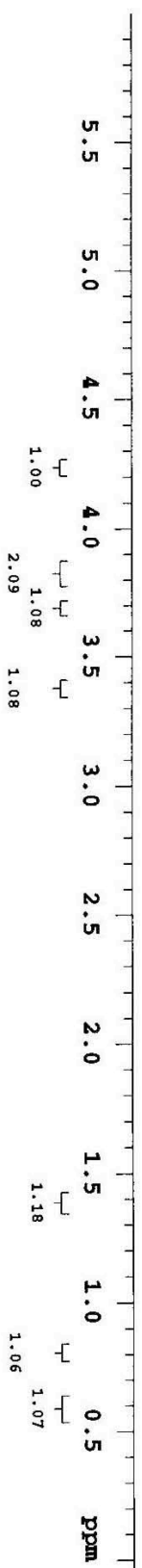
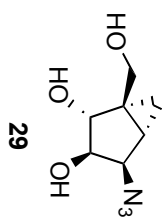


Pulse Sequence: apt

Compound-29-B

Pulse Sequence: szpul

500 MHz 1D in CD3OD (ref. to CD3OD @ 3.30 ppm), temp 27.2 C -> actual temp = 27.0 C, sw500 probe



Compound-29-C

125 MHz APT in CD3OD (ref. to CD3OD @ 49.0 ppm), temp 27.2 C -> actual temp = 27.0 C, w probe C & CH2 same, CH & CH3 opposite side of solvent signal

Pulse Sequence: apt

