SUPPLEMENTARY INFORMATION

for

First total synthesis of asperilactone B. Revision of absolute stereochemistry of asperilactones B and C.

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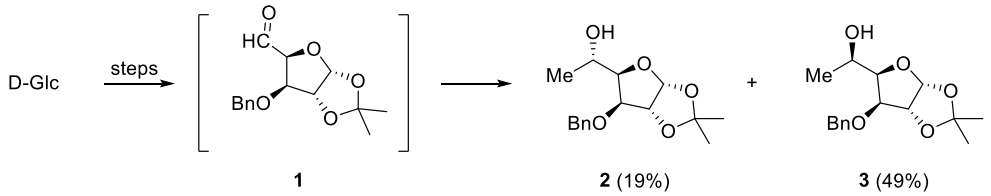
Experimental procedures

General experimental procedures

Melting points were determined on a hot stage microscope Nagema PHMK 05 and were not corrected. Optical rotations were measured on an Autopol IV (Rudolph Research) polarimeter at room temperature. NMR spectra were recorded on a Bruker Avance III instrument or a Bruker Ultrashield Avance III spectrometer, and chemical shifts are expressed in ppm downfield from TMS. IR spectra were recorded with Thermo Nicolet iS20 FTIR spectrophotometer (Thermo-Fisher SCIENTIFIC). High-resolution mass spectra (ESI) were acquired on a Thermo LTQ Orbitrap XL, and the purity of tested compounds was more than 95% (errors were less than 5 ppm). Flash column chromatography was performed using Kieselgel 60 (0.040–0.063, E. Merck). All organic extracts were dried with anhydrous Na_2SO_4. Organic solutions were concentrated in a rotary evaporator under diminished pressure at a bath temperature below 35 °C.

3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-β-L-*ido*-hexofuranose (2) and 3-*O*-Benzyl-6-deoxy-1,2-*O*-isopropylidene-α-D-*gluco*-hexofuranose (3)



Procedure for preparation of the crude aldehyde **1** is published in our previous article.[1] To a cooled solution (0 °C) of crude aldehyde **1** (1.836 g) in a dry THF (40 mL) was added commercial 3.0 M MeMgBr in diethyl ether (5.0 mL, 15.00 mmol) and LiCl (0.642 g, 15.14 mmol). The reaction mixture was stirred at 0 °C for 4.5 h (nitrogen atmosphere), then quenched with cold 10% NH_4Cl solution (100 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The collected extracts were washed with brine solution (100 mL), the organic layers were dried and evaporated, and the residue was purified by flash column chromatography (3:2 PE/Et_2O). Firstly, the major product **3** (0.823 g, 49%) is isolated as a colourless oil, $[\alpha]_D = -19.4$ (*c* 1.00, MeOH), lit.[2] $[\alpha]_D = -16.2$ (*c* 0.98, MeOH), $[\alpha]_D = -72.6$ (*c* 4.00, $CHCl_3$), lit.[3] $[\alpha]_D = -67.5$ (*c* 4.00, $CHCl_3$), $[\alpha]_D = -74.1$ (*c* 1.30, $CHCl_3$), lit.[4] $[\alpha]_D = -64.3$ (*c* 1.30, $CHCl_3$), $R_f = 0.55$ (1:1 PE/Et_2O). IR (film): ν_{max} 3493 (OH). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 1.29 (d, 3 H, $J_{5,6}$= 6.4 Hz, CH_3, H-6), 1.36 and 1.52 (2 × s, 2 × 3 H, C(CH_3)$_2$), 2.19 (bs, 1 H, OH), 3.96 (dd, 1 H, $J_{4,5}$= 7.0, $J_{3,4}$= 3.4 Hz, H-4), 4.11 (m, 2 H, $J_{3,4}$= 3.4, $J_{5,6}$= 6.3 Hz, H-3 and H-5), 4.53 (d, 1 H, J_{gem}= 11.8 Hz, CH_2Ph), 4.67 (d, 1 H, $J_{1,2}$= 3.9 Hz, H-2), 4.77 (d, 1 H, J_{gem}= 11.8 Hz, CH_2Ph), 6.00 (d, 1 H, $J_{1,2}$= 3.9 Hz, H-1), 7.33 – 7.43 (m, 5 H, CH_2Ph). ^{13}C NMR spectrum (100 MHz, $CDCl_3$): δ 20.5 (C-6, CH_3), 26.3 and 26.8 (C(CH_3)$_2$), 65.8 (C-5), 71.9 (CH_2Ph), 82.0 (C-2), 82.0 (C-3), 83.4 (C-4), 105.2 (C-1), 111.6 (C(CH_3)$_2$), 128.0, 128.4, 128.8 (5 C from CH_2Ph), 136.9 (C_q from CH_2Ph). HRMS (ESI): *m/z* 317.1349 (M^+ + Na), calcd for $C_{16}H_{22}NaO_5$: 317.1359.

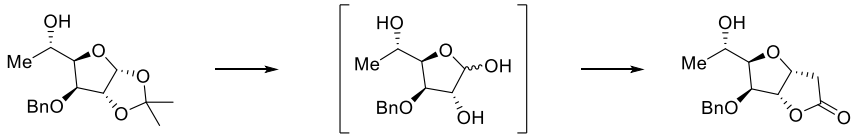
Minor product **2** (0.325 g, 19%) was secondly eluted and was isolated as a white powder. After recrystallization from the CH_2Cl_2/*n*-hexane system, pure product **2** was obtained in the form

of long transparent needles, mp 107–108 °C, $[\alpha]_D = -62.5$ (*c* 1.30, $CHCl_3$), lit.[5] $[\alpha]_D = -63.5$ (*c* 1.30, $CHCl_3$), R_f = 0.33 (1:1 PE/Et_2O). IR (KBr): ν_{max} 3462(OH). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 1.16 (dd, 3 H, $J_{5,6}$= 6.4, $J_{4,6}$= 1.0 Hz, CH_3, H-6), 1.35 and 1.51 (2 × s, 2 × 3 H, C(CH_3)$_2$), 2.66 (bs, 1 H, OH), 3.95 (bd, 1 H, $J_{3,4}$= 3.3 Hz, H-3), 3.99 (bdd, 1 H, $J_{4,5}$= 6.3, $J_{3,4}$= 3.4 Hz, H-4), 4.15 (pd, 1 H, $J_{4,5}$= 6.3, $J_{5,6}$= 6.4, $J_{3,5}$= 0.7 Hz, H-5), 4.47 (d, 1 H, J_{gem}=11.8 Hz, CH_2Ph), 4.67 (d, 1 H, $J_{1,2}$= 3.8 Hz, H-2), 4.72 (d, 1 H, J_{gem}=11.8 Hz, CH_2Ph), 5.99 (d, 1 H, $J_{1,2}$= 3.7 Hz, H-1), 7.30 – 7.40 (m, 5 H, CH_2*Ph*). ^{13}C NMR spectrum (100 MHz, $CDCl_3$): δ 18.5 (C-6, *C*H_3), 26.3 and 26.8 (C(*C*H_3)$_2$), 66.2 (C-5), 71.9 (*C*H_2Ph), 82.3 (C-2), 82.4 (C-3), 84.3 (C-4), 105.0 (C-1), 111.8 (*C*(CH$_3$)$_2$), 127.9, 128.2, 128.6 (5 C from CH_2*Ph*), 136.9 (C_q from CH_2*Ph*). HRMS (ESI): *m/z* 317.1350 (M^+ + Na), calcd for $C_{16}H_{22}NaO_5$: 317.1359.

General procedure for the preparation of compounds 6 and 7

Cooled (0 °C) starting compounds **2** and **3** (1 eq) were dissolved in 90% TFA (0.3 M) and the resulting solutions were stirred at room temperature until the starting materials were consumed (TLC, 1.5 h). The mixture was concentrated by co-distillation with toluene and the residue was purified by flash column chromatography (9:1 Et_2O/PE→Et_2O) to afford desired lactols **4** (80%) or **5** (85%). To a stirred solution of lactols **4** and **5** (1 eq) in dry DMF (0.3 M) was added Meldrum's acid (3 eq) and dry Et_3N (3 eq). The mixture was stirred at 46–48 °C until the starting materials were consumed (TLC, 72 h). The residue was evaporated and purified by flash column chromatography (7:3 CH_2Cl_2/EtOAc for **6** and 4:1 CH_2Cl_2/EtOAc for **7**).

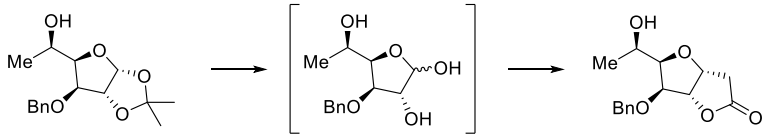
3,6-Anhydro-5-*O*-benzyl-2,8-dideoxy-L-*glycero*-D-*ido*-octono-1,4-lactone (6)



2 **4** (80%) **6** (35%)

Yield: 35%. Long colourless needles, mp 118–119 °C (CH_2Cl_2/*n*-hexane), $[\alpha]_D$ = + 2.8 (*c* 0.50, $CHCl_3$), R_f = 0.30 (7:3 CH_2Cl_2/EtOAc). IR (KBr): ν_{max} 3484 (OH), 1775 (C=O). ^{1}H NMR spectrum (400 MHz, $CDCl_3$ + D_2O): δ 1.17 (d, 3 H, $J_{7,8}$ = 6.4 Hz, CH_3, H-8), 2.68 (bd, 1 H, $J_{2a,2b}$ = 18.3 Hz, H-2a), 2.75 (dd, 1 H, $J_{2b,3}$ = 5.6, $J_{2a,2b}$ = 18.8 Hz, H-2b), 3.89 (t, 1 H, $J_{5,6}$ = 4.9, $J_{6,7}$= 5.0 Hz, H-6), 4.11 (p, 1 H, $J_{7,8}$ = 6.3, $J_{6,7}$ = 5.9 Hz, H-7), 4.22 (d, 1 H, $J_{5,6}$ = 4.4 Hz, H-5), 4.57 and 4.74 (2 × d, 2 ×1 H, J_{gem} = 11.7 Hz, CH_2Ph), 4.98 (d, 1 H, $J_{3,4}$ = 4.6 Hz, H-4), 5.03 (t, 1 H, $J_{3,4}$ = 4.5, $J_{2b,3}$ = 4.5 Hz, H-3), 7.32 – 7.41 (m, 5 H, CH_2*Ph*). ^{13}C NMR spectrum (100 MHz, $CDCl_3$): δ 18.6 (C-8, *C*H_3), 36.0 (C-2), 66.6 (C-7), 72.8 (*C*H_2Ph), 77.0 (C-3), 82.2 (C-5), 84.4 (C-6), 85.7 (C-4), 128.0, 128.5, 128.8 (5 C from CH_2*Ph*), 136.5 (C_q from CH_2*Ph*), 175.2 (C-1). HRMS (ESI): *m/z* 301.1041 (M^+ + Na), calcd for $C_{15}H_{18}NaO_5$: 301.1046.

3,6-Anhydro-5-*O*-benzyl-2,8-dideoxy-D-*glycero*-D-*ido*-octono-1,4-lactone (7)



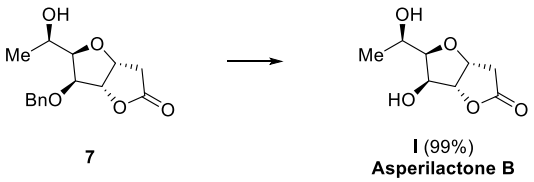
Yield: 31%. Long colourless prisms, mp 82–85 °C (CH_2Cl_2/*n*-hexane), $[\alpha]_D$ = – 16.0 (*c* 0.50, $CHCl_3$), R_f = 0.55 (7:3 CH_2Cl_2/EtOAc). IR (KBr): ν_{max} 3490 (OH), 1777 (C=O). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 1.27 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.24 (bs, 1 H, OH), 2.67 (d, 1 H, $J_{2a,2b}$ = 18.7 Hz, H-2a), 2.75 (m, 1 H, $J_{2a,2b}$ = 18.7, $J_{2b,3}$ = 5.4 Hz, H-2b) 3.82 (dd, 1 H, $J_{5,6}$ = 4.1, $J_{6,7}$ = 7.3 Hz, H-6), 4.07 (p, 1 H, $J_{7,8}$ = 6.4, $J_{6,7}$ = 6.7 Hz, H-7), 4.36 (d, 1 H, $J_{5,6}$ = 4.0 Hz, H-5), 4.63 and 4.77 (2 × d, 2 × 1 H, J_{gem} = 11.7 Hz, C*H*$_2$Ph), 4.96 – 4.99 (m, 2 H, H-3 and H-4), 7.34 – 7.44 (m, 5 H, *Ph*). ^{13}C NMR spectrum (100 MHz, $CDCl_3$): δ 20.5 (C-8), 36.0 (C-2), 65.9 (C-7), 72.9 (*C*H$_2$Ph), 76.9 (C-3), 81.7 (C-5), 84.1 (C-6), 85.2 (C-4), 128.1, 128.6, 128.9 (5C from Ph), 136.6 (C_q from Ph), 175.2 (C-1). HRMS (ESI): *m/z* 301.1043 (M^+ + Na), calcd for $C_{15}H_{18}NaO_5$: 301.1046.

General procedure for the preparation of asperilactone B (I) and 7-*epi*-asperilactone B (8)

A solution of **6** or **7** (1 eq) in MeOH (0.04 M) was hydrogenated over 10% Pd/C (0.04–0.06 g; the catalyst contained 50% of water) for 18 h at room temperature. The mixture was filtered and the catalyst was washed with EtOAc. The combined organic solutions were evaporated and the residue was purified by flash column chromatography (9:1 EtOAc/CH_2Cl_2 for **I**, 7:3 EtOAc/CH_2Cl_2 for **8**), to afford pure **I** or **8**.

NOTE: After repeating reactions, it was found that pure products **I** and **8** could be obtained without purification by flash chromatography. After filtration, organic solutions were evaporated and then purified by crystallization (EtOAc/*n*-hexane) to afford pure **I** and **8**.

3,6-Anhydro-2,8-dideoxy-D-*glycero*-D-*ido*-octono-1,4-lactone (Asperilactone B, I)

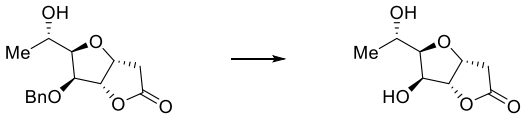


Yield: 99%. Transparent needles, mp 92–94 °C (EtOAc/*n*-hexane), $[\alpha]_D$ = + 43.6 (*c* 0.50, Me_2CO), $[\alpha]_D$ = + 24.0 (*c* 0.10, MeOH), lit.[6] $[\alpha]_D$ = + 22.0 (*c* 0.10, MeOH), R_f = 0.39 (EtOAc). IR (KBr): ν_{max} 3479, 3429 (OH), 1780 (C=O). ^{1}H NMR spectrum (400 MHz, CD_3COCD_3): δ 1.27 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.48 (d, 1 H, $J_{2a,2b}$ = 18.5 Hz, H-2a), 2.87 (dd, 1 H, $J_{2a,2b}$ = 18.5, $J_{2b,3}$ = 6.1 Hz, H-2b), 3.67 (dd, 1 H, $J_{5,6}$ = 3.1, $J_{6,7}$ = 7.0 Hz, H-6), 4.07 (m, 1 H, $J_{7,OH}$ = 5.3, $J_{7,8}$ = 6.4, $J_{6,7}$ = 6.6 Hz, H-7), 4.21 (d, 1 H, $J_{7,OH}$ = 5.2 Hz, C_7-O*H*), 4.47 (t, $J_{5,OH}$ = 3.5, $J_{5,6}$ = 3.5 Hz, H-5), 4.86 (d,

$J_{5,OH}$ = 4.3 Hz, C_5-O*H*), 4.89 (d, 1 H, $J_{3,4}$= 4.3 Hz, H-4), 4.94 – 4.99 (m, 1 H, $J_{3,4}$= 4.3, $J_{2b,3}$ = 6.1 Hz, H-3). ^{13}C NMR spectrum (100 MHz, CD_3COCD_3): δ 20.0 (C-8), 35.8 (C-2), 65.2 (C-7), 73.8 (C-5), 77.0 (C-3), 84.6 (C-6), 88.0 (C-4), 175.5 (C-1).

^{1}H NMR spectrum (500 MHz, CD_3OD): δ 1.26 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.52 (d, 1 H, $J_{2a,2b}$ = 18.7 Hz, H-2a), 2.86 (dd, 1 H, $J_{2a,2b}$ = 18.7, $J_{2b,3}$ = 6.2 Hz, H-2b), 3.60 (dd, 1 H, $J_{5,6}$ = 2.9, $J_{6,7}$ = 7.8 Hz, H-6), 3.98 (dq, 1 H, $J_{6,7}$ = 7.7, $J_{7,8}$ = 6.4 Hz, H-7), 4.41 (d, 1 H, $J_{5,6}$ = 2.9 Hz, H-5), 4.88 (d, 1 H, $J_{3,4}$= 4.4 Hz, H-4), 4.92 (dd, 1 H, $J_{2b,3}$ = 6.1, $J_{3,4}$ = 4.4 Hz, H-3). ^{13}C NMR spectrum (125 MHz, CD_3OD): δ 19.6 (C-8), 35.5 (C-2), 64.5 (C-7), 73.1 (C-5), 76.9 (C-3), 84.7 (C-6), 88.3 (C-4), 176.8 (C-1). HRMS (ESI): *m/z* 211.0586 (M^+ + Na), calcd for $C_8H_{12}NaO_5$: 211.0577.

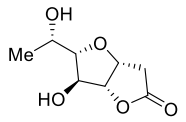
3,6-Anhydro-2,8-dideoxy-L-*glycero*-D-*ido*-octono-1,4-lactone (8)



6 **8** (96%)
7-*epi*-Asperilactone B

Yield: 96%. Colourless needles, mp 128–130 °C (EtOAc/*n*-hexane), $[\alpha]_D$ = + 38.4 (*c* 0.50, Me_2CO), $[\alpha]_D$ = + 16.0 (*c* 0.10, MeOH), R_f = 0.26 (EtOAc). IR (KBr): ν_{max} 3333 (OH), 1789 (C=O). ^{1}H NMR spectrum (400 MHz, CD_3COCD_3): δ 1.23 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.49 (dd, 1 H, $J_{2a,2b}$ = 18.5, $J_{2a,5}$ = 0.3 Hz, H-2a), 2.87 (dd, 1 H, $J_{2a,2b}$ = 18.4, $J_{2b,3}$ = 6.2 Hz, H-2b), 3.75 (dd, 1 H, $J_{5,6}$ = 3.4, $J_{6,7}$ = 5.5 Hz, H-6), 3.86 (d, 1 H, $J_{7,OH}$ = 4.6 Hz, C_7-O*H*), 4.09 (qdd, 1 H, $J_{6,7}$ = 5.5, $J_{7,8}$ = 6.4, $J_{7,OH}$ = 4.6 Hz, H-7), 4.37 (bt, 1 H, *J* = 4.0 Hz, H-5), 4.90 (dd, 1 H, $J_{3,4}$= 4.3, $J_{4,5}$ = 0.8 Hz, H-4), 4.93 (d, 1 H, $J_{5,OH}$ = 4.8 Hz, C_5-O*H*), 4.99 (dd, 1 H, $J_{3,4}$= 4.3, $J_{2b,3}$ = 6.2 Hz, H-3). ^{13}C NMR spectrum (100 MHz, CD_3COCD_3): δ 19.1 (C-8), 35.7 (C-2), 66.5 (C-7), 74.8 (C-5), 76.8 (C-3), 84.6 (C-6), 88.5 (C-4), 175.3 (C-1).
^{1}H NMR spectrum (500 MHz, CD_3OD): δ 1.21 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.57 (d, 1 H, $J_{2a,2b}$ = 18.6 Hz, H-2a), 2.86 (dd, 1 H, $J_{2a,2b}$ = 18.6, $J_{2b,3}$ = 6.3 Hz, H-2b), 3.68 (dd, 1 H, $J_{5,6}$ = 3.2, $J_{6,7}$ = 7.2 Hz, H-6), 3.99 (pseudo p, 1 H, $J_{6,7}$ = 6.9, $J_{7,8}$ = 6.4 Hz, H-7), 4.28 (d, 1 H, $J_{5,6}$ = 3.0 Hz, H-5), 4.88 (bd, 1 H, $J_{3,4}$= 4.3 Hz, H-4), 4.97 (dd, 1 H, $J_{2b,3}$ = 6.2, $J_{3,4}$ = 4.4 Hz, H-3). ^{13}C NMR spectrum (125 MHz, CD_3OD): δ 18.1 (C-8), 35.5 (C-2), 66.4 (C-7), 73.8 (C-5), 76.8 (C-3), 85.2 (C-6), 88.7 (C-4), 176.8 (C-1). HRMS (ESI): *m/z* 189.0760 (M^+ + H^+), calcd for $C_8H_{13}O_5$: 189.0758.

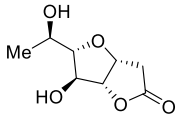
3,6-Anhydro-2,8-dideoxy-L-*glycero*-L-*gluco*-octono-1,4-lactone (Asperilactone C, II)



II
Asperilactone C

Colourless prisms, mp 123–124 °C (EtOAc/n-hexane), $[\alpha]_D$= + 63.8 (*c* 0.50, Me_2CO), $[\alpha]_D$= + 54.0 (*c* 0.50, MeOH). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): *δ* 1.30 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.00 (bs, 1 H, OH), 2.53 (d, *J* = 3.2 Hz, OH), 2.71 (dd, 1 H, $J_{2a,2b}$ = 18.5, $J_{2a,3}$ = 1.4 Hz, H-2a), 2.77 (dd, 1 H, $J_{2a,2b}$ = 18.5, $J_{2b,3}$ = 4.8 Hz, H-2b), 3.64 (t, 1 H, $J_{5,6}$ = 5.7, $J_{6,7}$ = 5.7 Hz, H-6), 3.98 (p, 1 H, $J_{6,7}$ = 6.1, $J_{7,8}$ = 6.2 Hz, H-7), 4.51 (bdd, 1 H, $J_{5,6}$ = 5.4, $J_{4,5}$ = 1.7 Hz, H-5), 4.83 (td, 1 H, $J_{2b,3}$= 4.7, $J_{2a,3}$ = 1.4, $J_{3,4}$ = 4.6 Hz, H-3), 4.88 (dd, 1 H, $J_{4,5}$= 1.1, $J_{3,4}$ = 4.5 Hz, H-4). ^{13}C NMR spectrum (100 MHz, $CDCl_3$): *δ* 19.7 (C-8), 35.9 (C-2), 67.8 (C-7), 77.1 (C-5), 77.4 (C-3), 89.6 (C-6), 90.6 (C-4), 175.0 (C-1).
^{1}H NMR spectrum (500 MHz, CD_3OD): *δ* 1.18 (d, 3 H, $J_{7,8}$= 6.5 Hz, H-8, C*H*$_3$), 2.58 (d, 1 H, $J_{2a,2b}$ = 18.4 Hz, H-2a), 2.83 (dd, 1 H, $J_{2a,2b}$ = 18.2, $J_{2b,3}$ = 4.7 Hz, H-2b), 3.62 (t, 1 H, $J_{5,6}$ = 5.0, $J_{6,7}$ = 5.0 Hz, H-6), 3.78 (qd, 1 H, $J_{6,7}$ = 5.3, $J_{7,8}$ = 6.5 Hz, H-7), 4.36 (d, 1 H, $J_{5,6}$ = 4.7 Hz, H-5), 4.79 (overlap, 1 H, $J_{3,4}$= 4.2, H-3), 4.81 (overlap, 1 H, $J_{3,4}$ = 4.2 Hz, H-4). ^{13}C NMR spectrum (125 MHz, CD_3OD): *δ* 18.0 (C-8), 35.7 (C-2), 66.6 (C-7), 75.3 (C-5), 77.6 (C-3), 90.7 (C-6), 91.2 (C-4), 176.5 (C-1). HRMS (ESI): *m/z* 211.0583 (M^+ + Na), calcd for $C_8H_{12}NaO_5$: 211.0577.

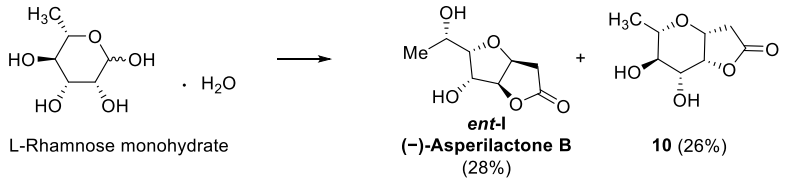
3,6-Anhydro-2,8-dideoxy-D-*glycero*-L-*gluco*-octono-1,4-lactone (9)



9
7-*epi*-Asperilactone C

Thin transparent needles, mp 124–126 °C (EtOAc/n-hexane), $[\alpha]_D$= + 42.8 (*c* 0.50, Me_2CO), $[\alpha]_D$= + 29.0 (*c* 0.50, MeOH). ^{1}H NMR spectrum (500 MHz, CD_3OD): *δ* 1.22 (d, 3 H, $J_{7,8}$= 6.5 Hz, H-8, C*H*$_3$), 2.63 (d, 1 H, $J_{2a,2b}$ = 18.3 Hz, H-2a), 2.84 (dd, 1 H, $J_{2a,2b}$ = 18.3, $J_{2b,3}$ = 5.6 Hz, H-2b), 3.56 (t, 1 H, $J_{5,6}$ = 5.7, $J_{6,7}$ = 5.7 Hz, H-6), 3.77 (p, 1 H, $J_{7,8}$ = 6.4, $J_{6,7}$ = 6.0 Hz, H-7), 4.15 (d, 1 H, $J_{5,6}$ = 5.8 Hz, H-5), 4.77 (t, 1 H, $J_{3,4}$= 4.8, $J_{2b,3}$= 5.1, H-3), 4.81 (dd overlap, 1 H, H-4). ^{13}C NMR spectrum (125 MHz, CD_3OD): *δ* 18.2 (C-8), 35.4 (C-2), 67.0 (C-7), 76.4 (C-5), 77.3 (C-3), 90.2 (C-6), 91.3 (C-4), 176.5 (C-1). HRMS (ESI): *m/z* 211.0583 (M^+ + Na), calcd for $C_8H_{12}NaO_5$: 211.0577.

3,6-Anhydro-2,8-dideoxy-L-*glycero*-L-*ido*-octono-1,4-lactone (*ent*-I) and 3,7-anhydro-2,8-dideoxy-L-*glycero*-L-*galacto*-octono-1,4-lactone (10)



To a stirred mixture of L-rhamnose monohydrate (2.028 g, 11.13 mmol) in dry DMF (15.50 mL) were added Meldrum's acid (3.383 g, 23.47 mmol) and *t*-$BuNH_2$ (1.17 mL, 11.12 mmol). The reaction mixture was stirred at 45–50 ºC for 6 days and then evaporated. The residue was purified by flash column chromatography (19:1 $CHCl_3$/EtOH → 9:1 $CHCl_3$/EtOH) to afford pure *ent*-**I** (0.588 g, 28%) and **10** (0.550 g, 26%).

Major compound *ent*-**I**: Transparent plates, mp 92–94 °C (EtOAc/*n*-hexane), $[\alpha]_D$ = – 41.4 (*c* 0.5, Me_2CO), $[\alpha]_D$ = – 28.0 (*c* 0.10, MeOH), R_f = 0.44 (9:1 $CHCl_3$/EtOH). IR (KBr): ν_{max} 3417 (OH). ^{1}H NMR (400 MHz, CD_3COCD_3): δ 1.27 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.48 (d, 1 H, $J_{2a,2b}$ = 18.5 Hz, H-2a), 2.87 (dd, 1 H, $J_{2a,2b}$ = 18.5, $J_{2b,3}$ = 6.1 Hz, H-2b), 3.67 (dd, 1 H, $J_{5,6}$ = 3.0, $J_{6,7}$ = 6.9 Hz, H-6), 4.07 (m, 1 H, $J_{7,OH}$ = 5.3, $J_{7,8}$ = 6.4, $J_{6,7}$ = 6.5 Hz, H-7), 4.19 (d, 1 H, $J_{7,OH}$ = 5.2 Hz, C_7-O*H*), 4.47 (t, $J_{5,OH}$ = 3.5, $J_{5,6}$ = 3.5 Hz, H-5), 4.82 (d, $J_{5,OH}$ = 4.3 Hz, C_5-O*H*), 4.89 (d, 1 H, $J_{3,4}$= 4.3 Hz, H-4), 4.96 (dd, 1 H, $J_{3,4}$= 4.3, $J_{2b,3}$ = 6.1 Hz, H-3). ^{13}C NMR (100 MHz, CD_3COCD_3): δ 20.0 (C-8), 35.8 (C-2), 65.2 (C-7), 73.8 (C-5), 77.0 (C-3), 84.6 (C-6), 88.0 (C-4), 175.4 (C-1).

^{1}H NMR (500 MHz, CD_3OD): δ 1.27 (d, 3 H, $J_{7,8}$= 6.4 Hz, H-8, C*H*$_3$), 2.53 (d, 1 H, $J_{2a,2b}$ = 18.7 Hz, H-2a), 2.86 (dd, 1 H, $J_{2a,2b}$ = 18.7, $J_{2b,3}$ = 6.2 Hz, H-2b), 3.61 (dd, 1 H, $J_{5,6}$ = 3.0, $J_{6,7}$ = 7.8 Hz, H-6), 3.99 (dq, 1 H, $J_{6,7}$ = 7.7, $J_{7,8}$ = 6.4 Hz, H-7), 4.41 (d, 1 H, $J_{5,6}$ = 2.9 Hz, H-5), 4.88 (d, 1 H, $J_{3,4}$= 4.3 Hz, H-4), 4.93 (dd, 1 H, $J_{2b,3}$ = 5.9, $J_{3,4}$ = 4.7 Hz, H-3). ^{13}C NMR (125 MHz, CD_3OD): δ 19.6 (C-8), 35.6 (C-2), 64.6 (C-7), 73.2 (C-5), 76.9 (C-3), 84.7 (C-6), 88.4 (C-4), 176.9 (C-1). HRMS (ESI): *m/z* 211.0574 (M^+ + Na), calcd for $C_8H_{12}NaO_5$: 211.0577.

Compound **10**: Colourless plates, mp 171–173 °C (EtOH), $[\alpha]_D$ = + 134.2 (*c* 0.50, H_2O), $[\alpha]_D$ = + 143.0 (*c* 0.50, Me_2CO), R_f = 0.19 (9:1 $CHCl_3$/EtOH). IR (KBr): ν_{max} 3488 (OH). ^{1}H NMR (400 MHz, D_2O): δ 1.30 (d, 3 H, $J_{7,8}$= 6.1 Hz, H-8, C*H*$_3$), 2.60 (d, 1 H, $J_{2a,2b}$ = 17.8 Hz, H-2a), 3.05 (dd, 1 H, $J_{2a,2b}$ = 17.8, $J_{2b,3}$ = 4.1 Hz, H-2b), 3.43 (t, 1 H, $J_{5,6}$ = 9.5, $J_{6,7}$ = 9.5 Hz, H-6), 3.53 (dq, 1 H, $J_{7,8}$= 6.1, $J_{6,7}$ = 9.5 Hz, H-7), 3.93 (dd, 1 H, $J_{5,6}$ = 9.6, $J_{4,5}$ = 4.1 Hz, H-5), 4.62 (dd, 1 H, $J_{2b,3}$ = 4.1, $J_{3,4}$= 2.0 Hz, H-3), 4.87 (dd, 1 H, $J_{4,5}$ = 4.1, $J_{3,4}$ = 2.0 Hz, H-4). ^{13}C NMR (100 MHz, D_2O): δ 19.4 (C-8), 40.8 (C-2), 73.8 (C-5), 74.4 (C-6), 76.4 (C-3), 77.3 (C-7), 85.5 (C-4), 181.8 (C-1). HRMS (ESI): *m/z* 211.0583 (M^+ + Na), calcd for $C_8H_{12}NaO_6$: 211.0577.

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3. M. L. Wolfrom and S. Hanessian, *J. Org. Chem.* 1962, **27**, 2107–2109.
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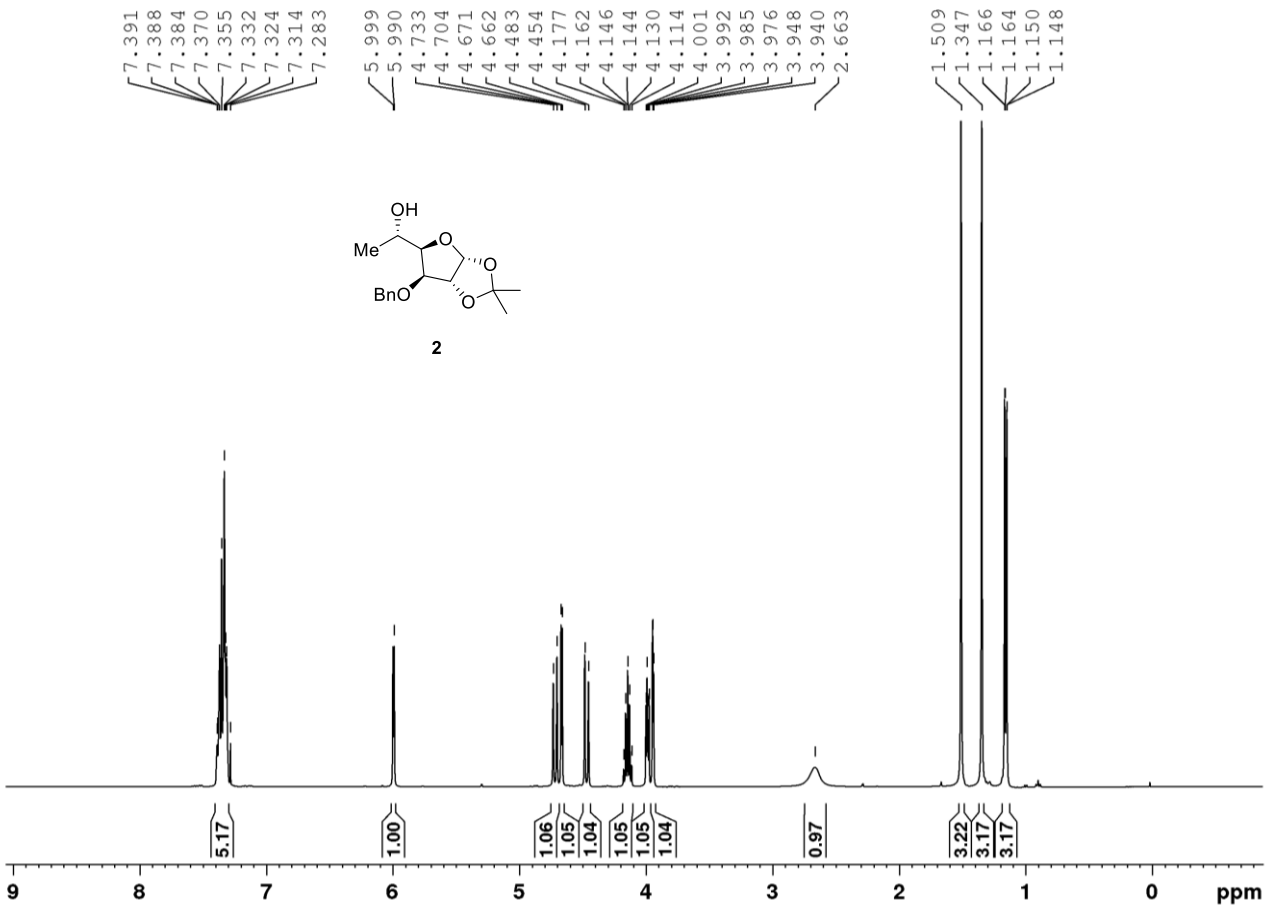
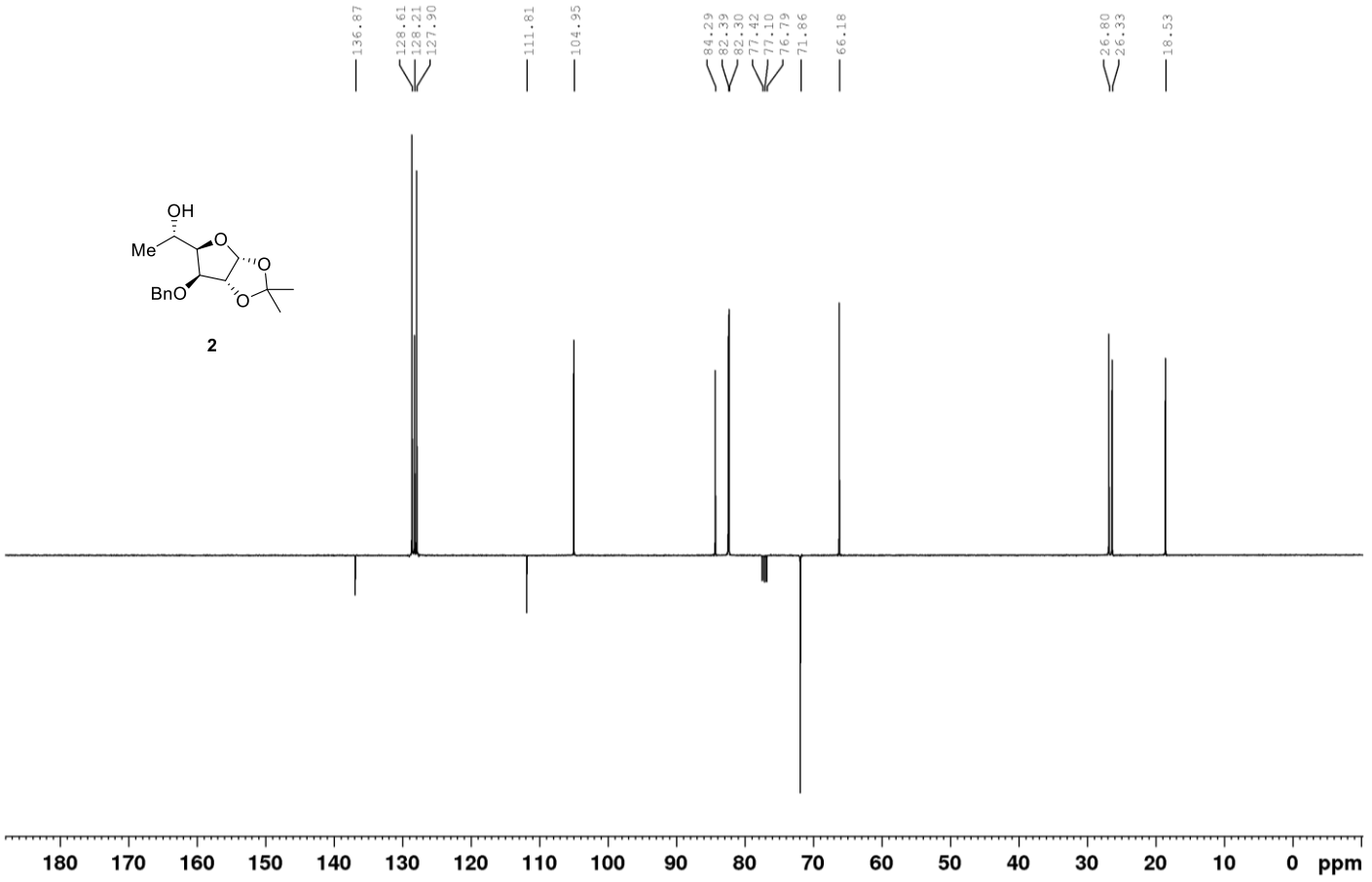
Selected Spectral Data of Key Intermediates and Final Products

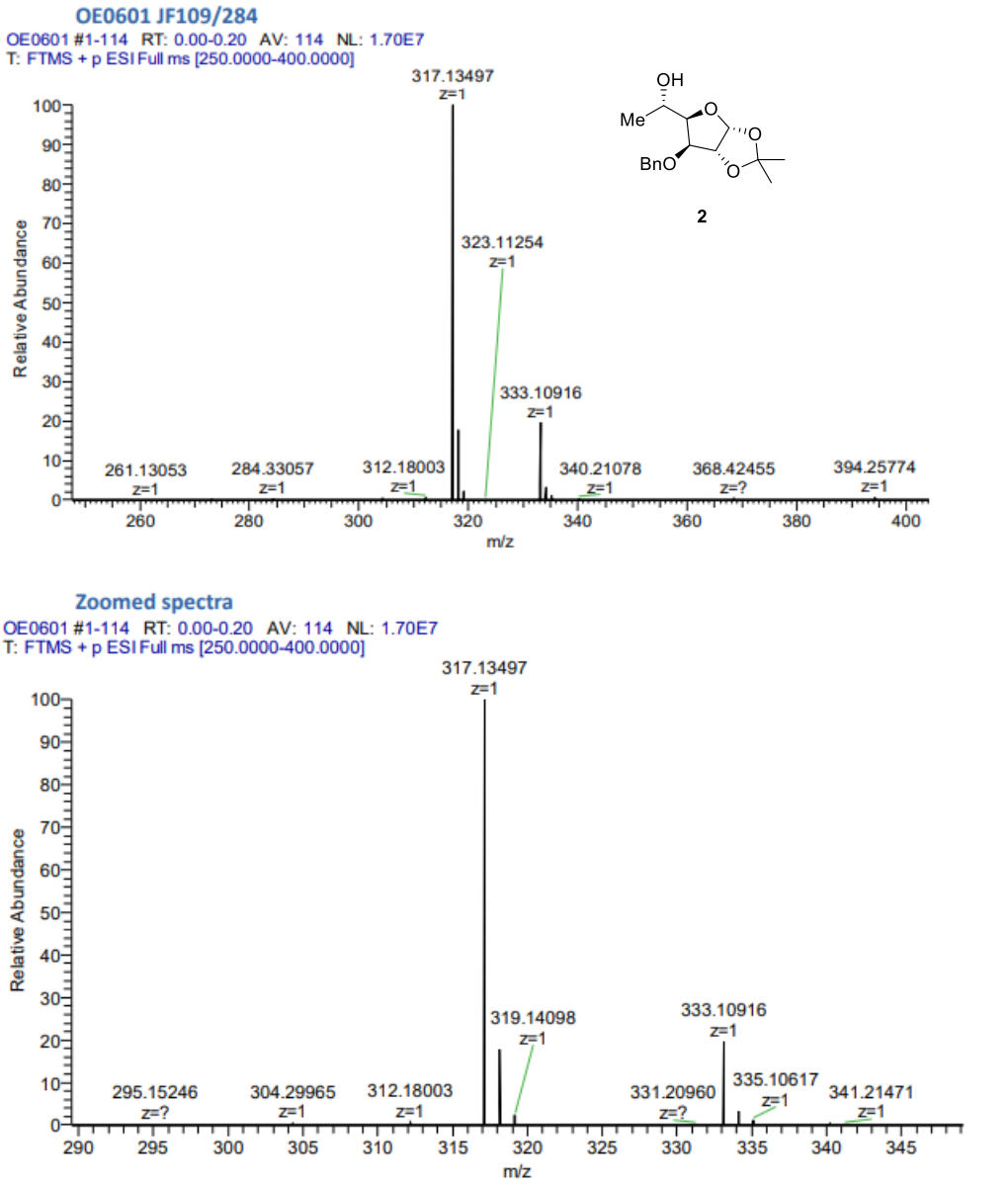
400 MHz ^{1}H NMR Spectrum of Compound **2** ($CDCl_3$)



100 MHz ^{13}C NMR Spectrum of Compound **2** ($CDCl_3$)

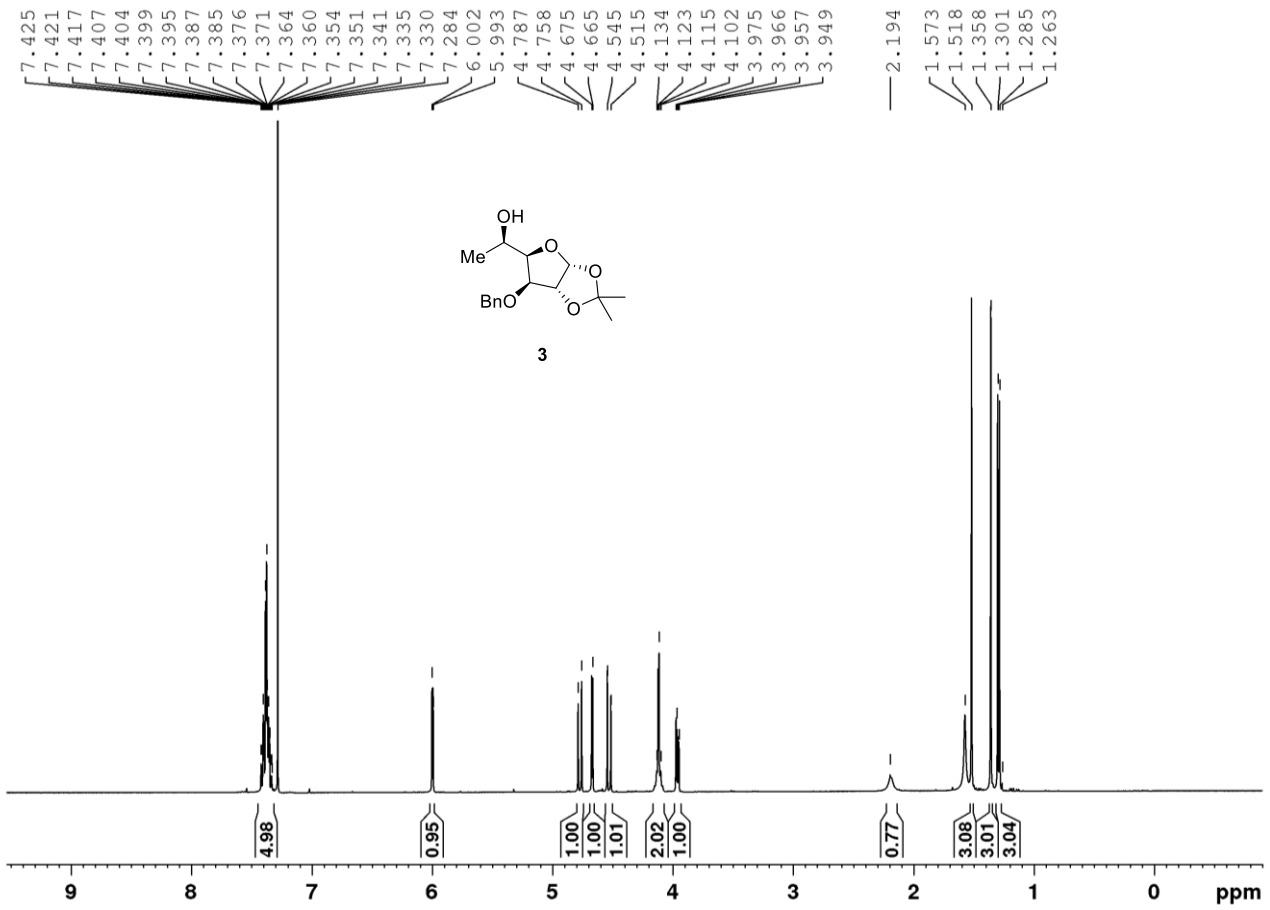


HRMS of compound **2**

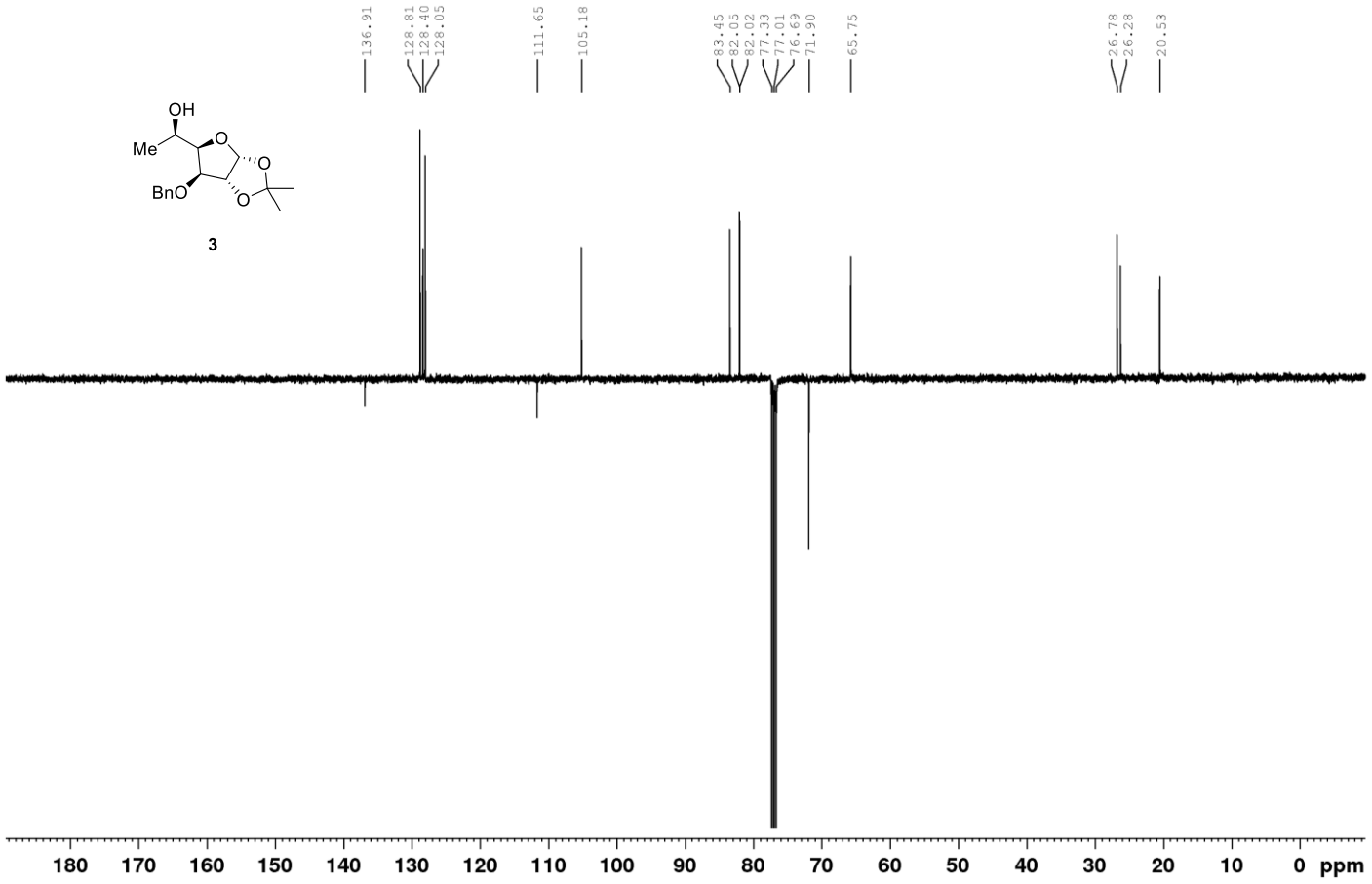


Exact mass	Observed mass	Observed ion type	Error (ppm)
317.13594	317.13497	$[M+Na]^+$	3.06

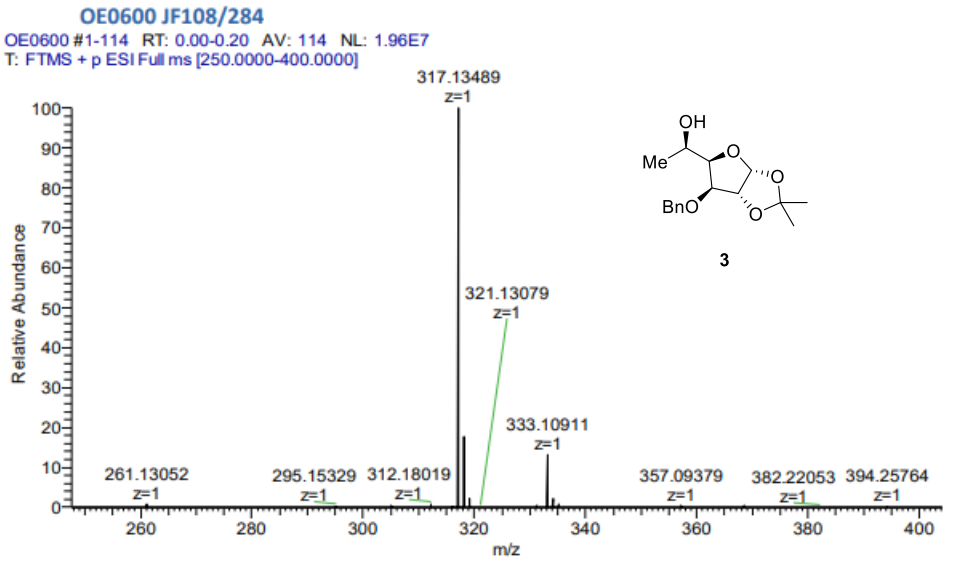
400 MHz ^{1}H NMR Spectrum of Compound **3** ($CDCl_3$)

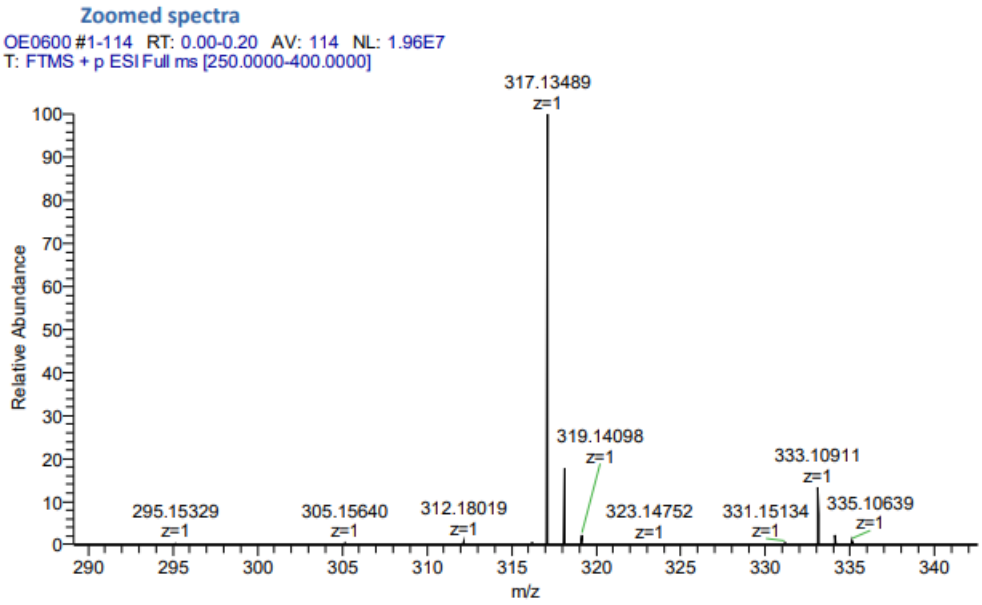


100 MHz ^{13}C NMR Spectrum of Compound **3** ($CDCl_3$)



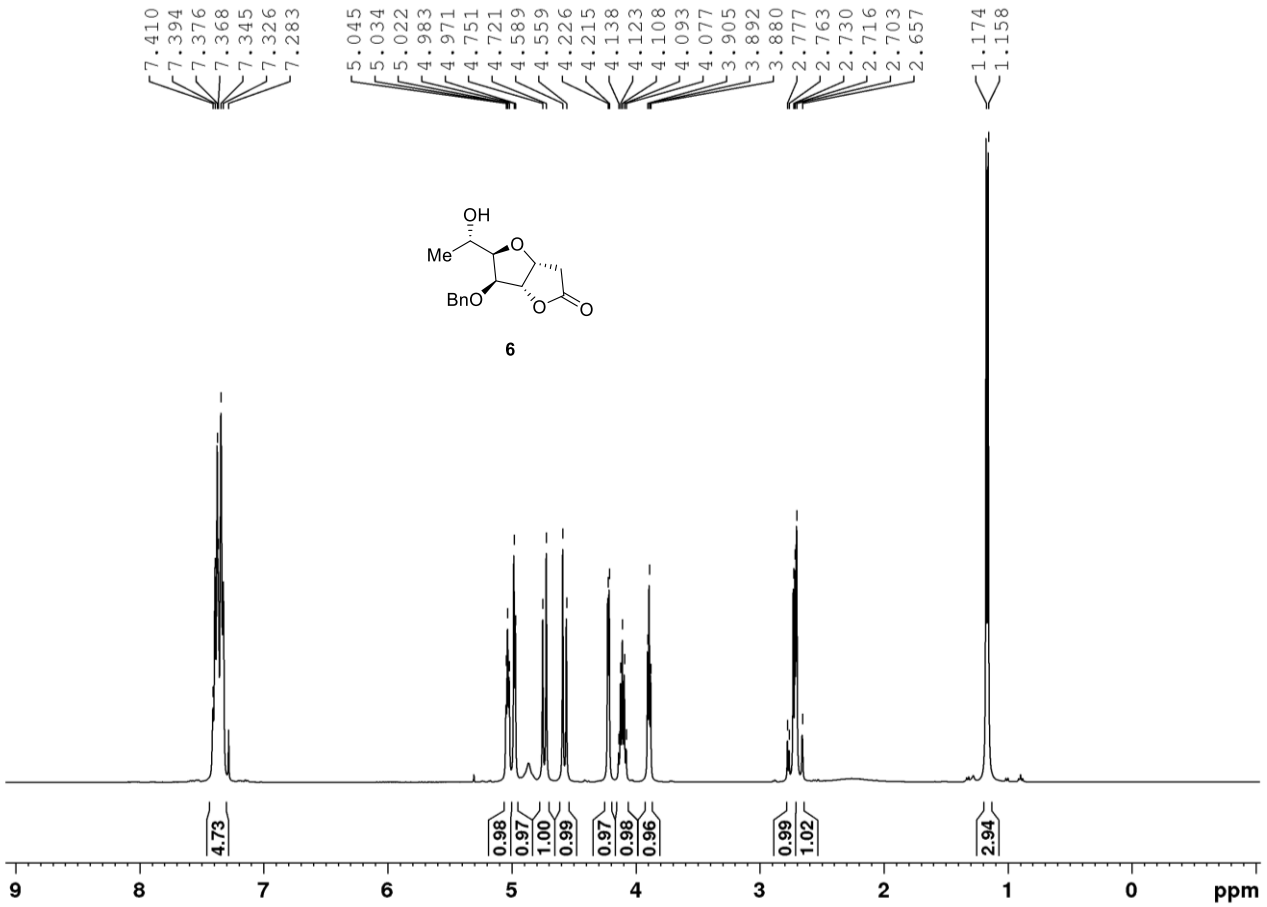
HRMS of compound **3**



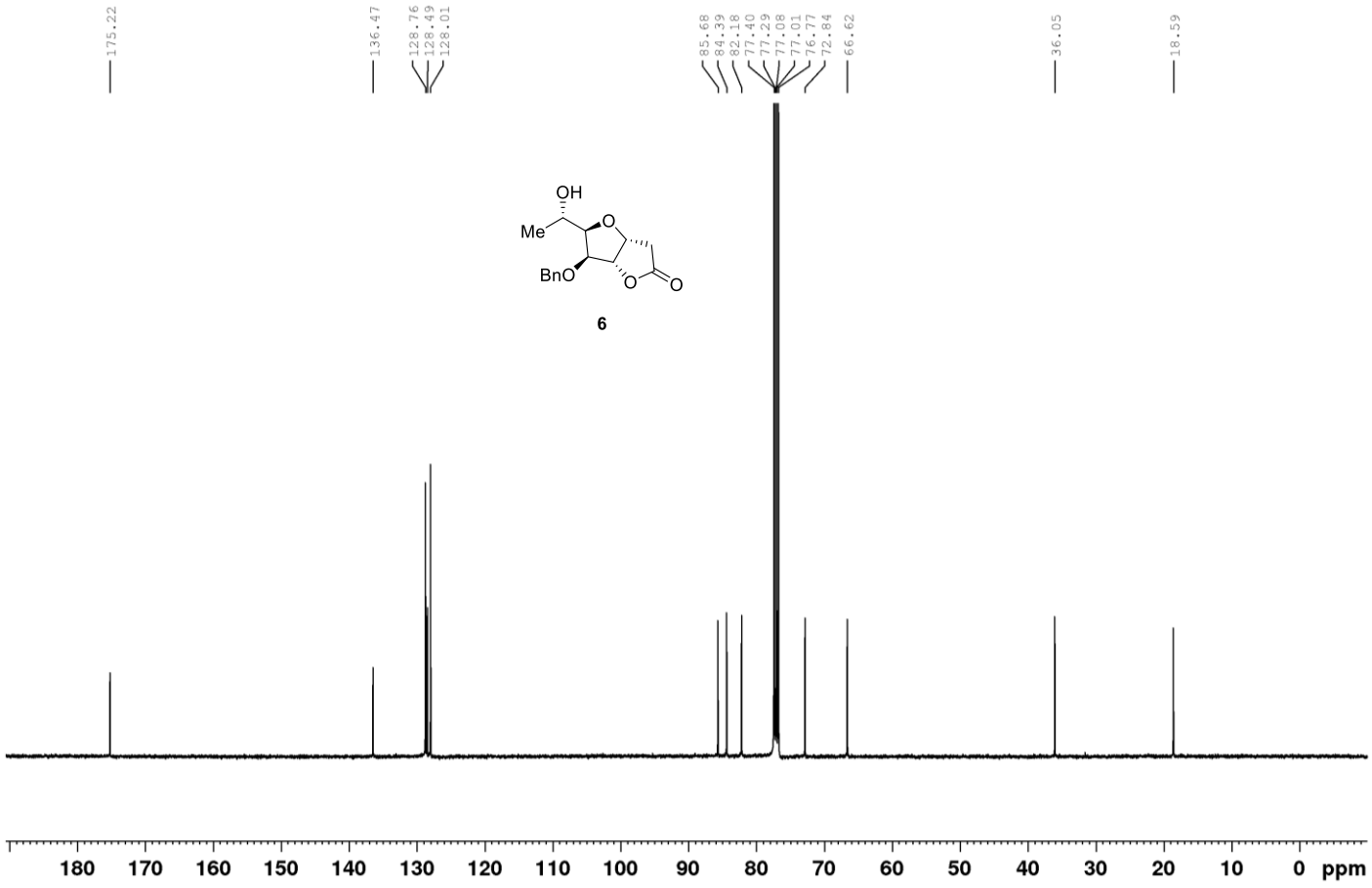


Exact mass	Observed mass	Observed ion type	Error (ppm)
317.13594	317.13489	$[M+Na]^+$	3.31

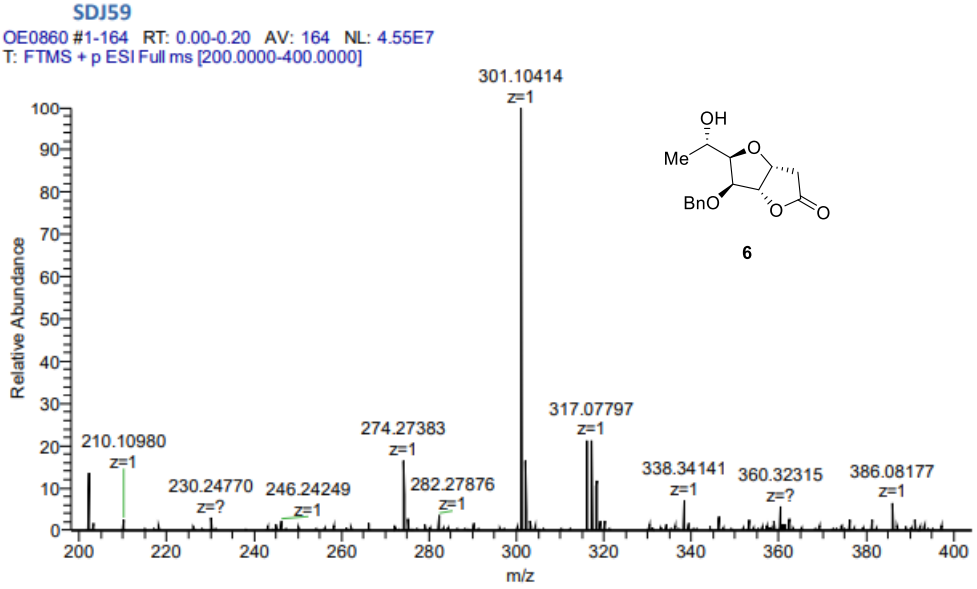
400 MHz ^{1}H NMR Spectrum of Compound **6** ($CDCl_3$ + D_2O)

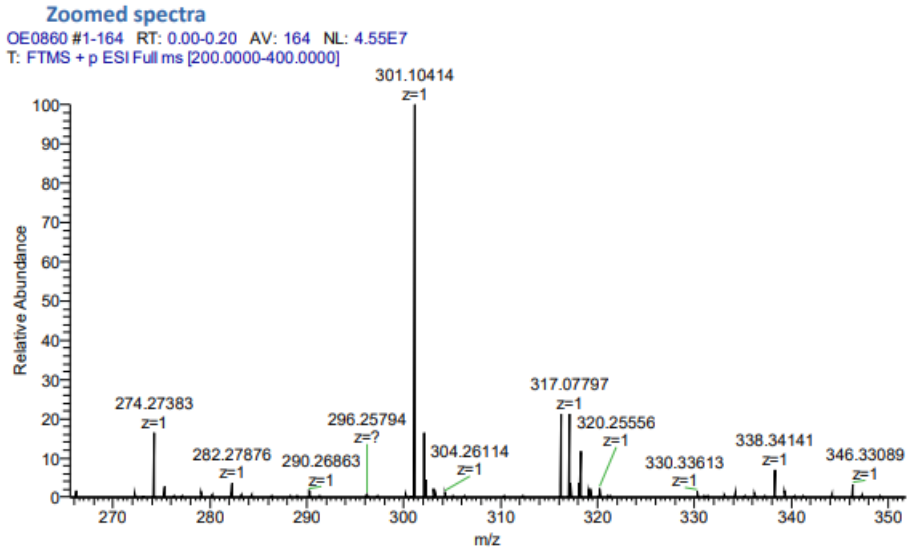


100 MHz ^{13}C NMR Spectrum of Compound **6** ($CDCl_3$)



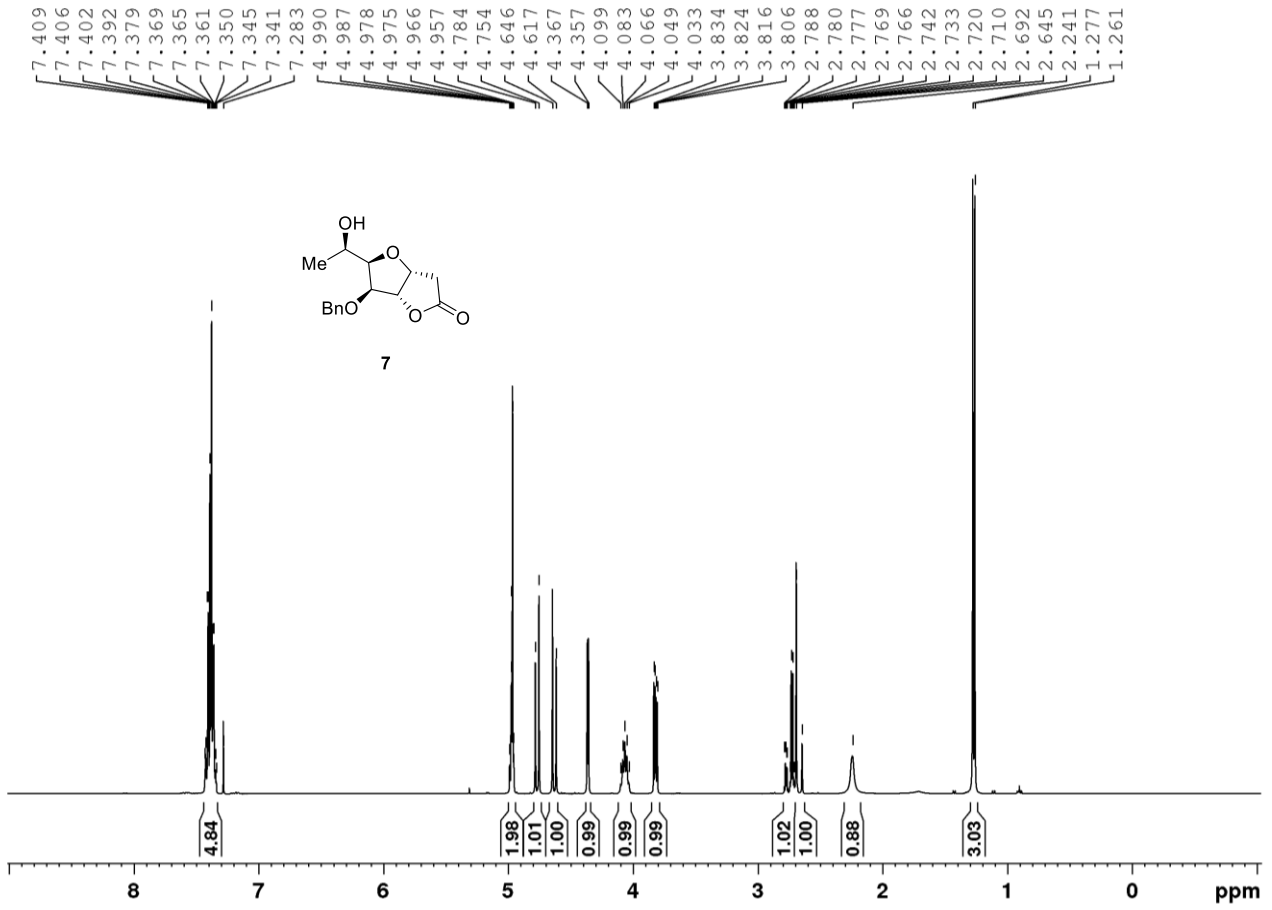
HRMS of compound **6**



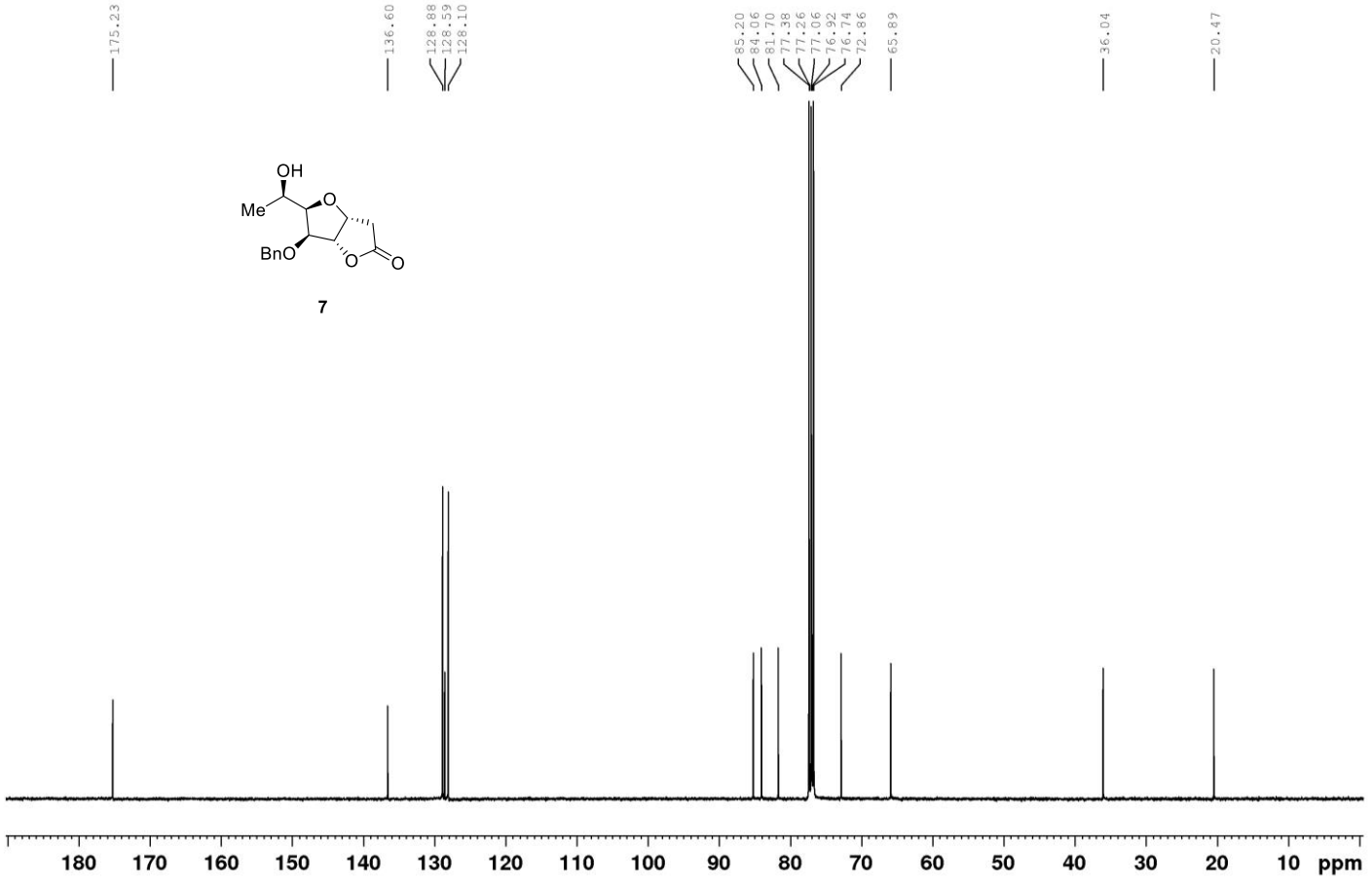


Exact mass	Observed mass	Observed ion type	Error (ppm)
301.10464	301.10414	$[M+Na]^+$	1.60

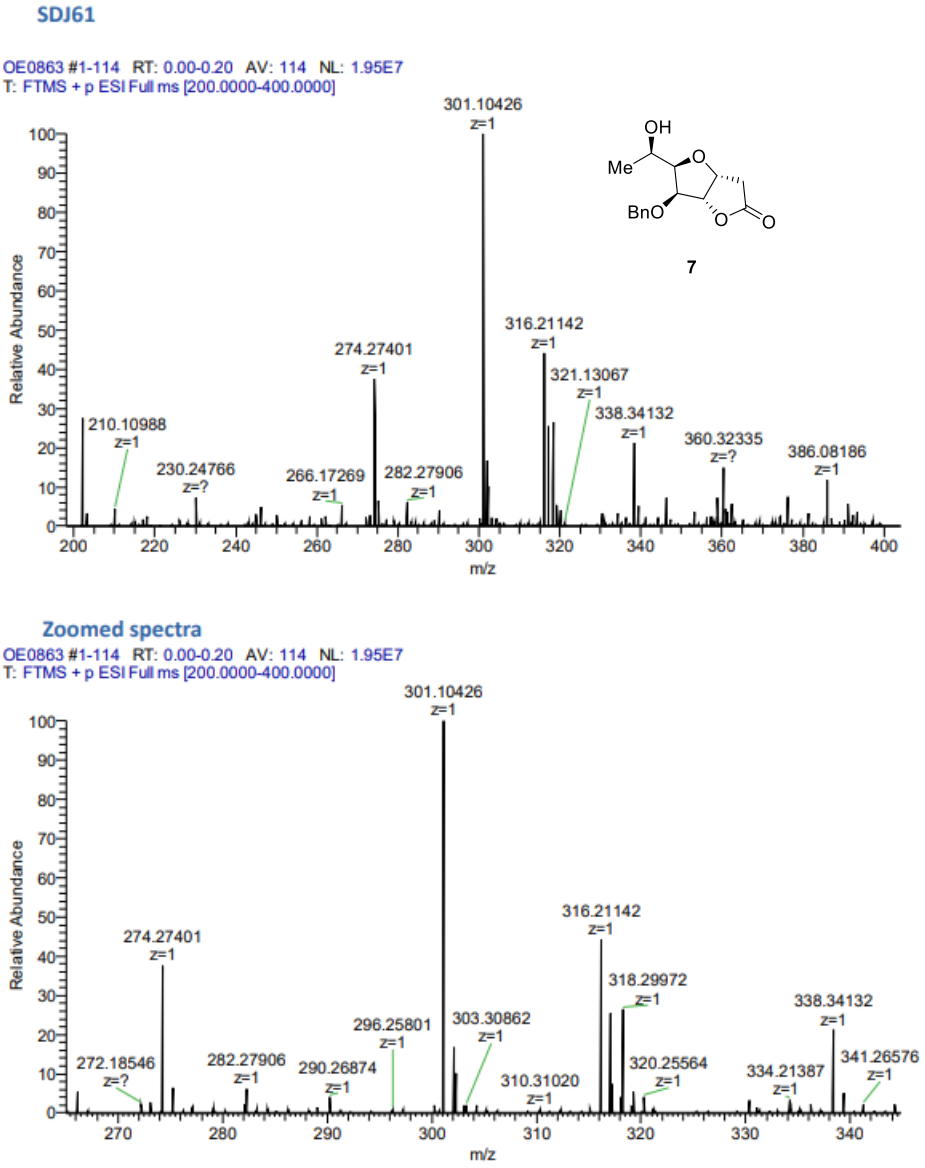
400 MHz ^{1}H NMR Spectrum of Compound **7** ($CDCl_3$)



100 MHz ^{13}C NMR Spectrum of Compound **7** ($CDCl_3$)

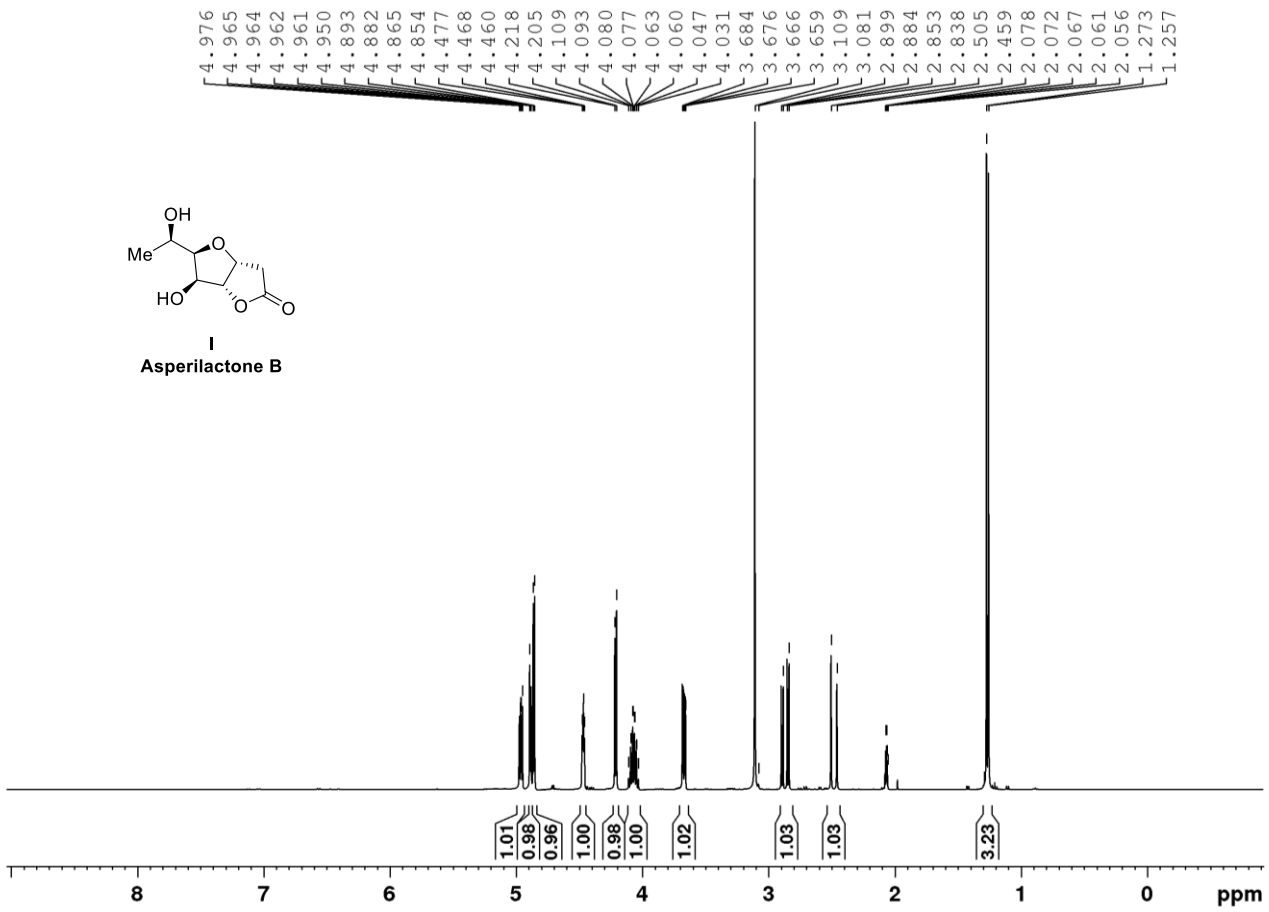


HRMS of compound **7**

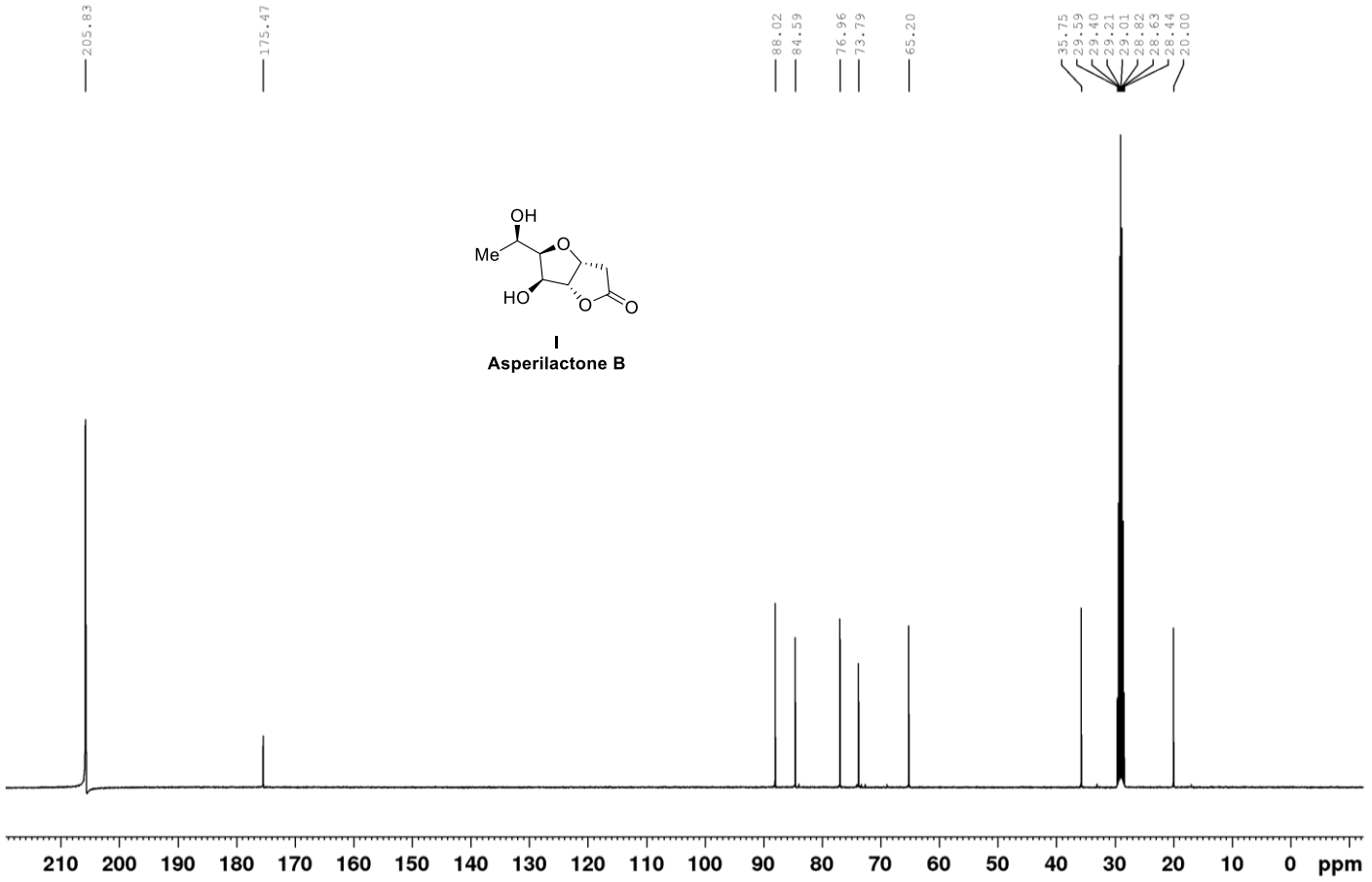


Exact mass	Observed mass	Observed ion type	Error (ppm)
301.10464	301.10426	$[M+Na]^+$	1.26

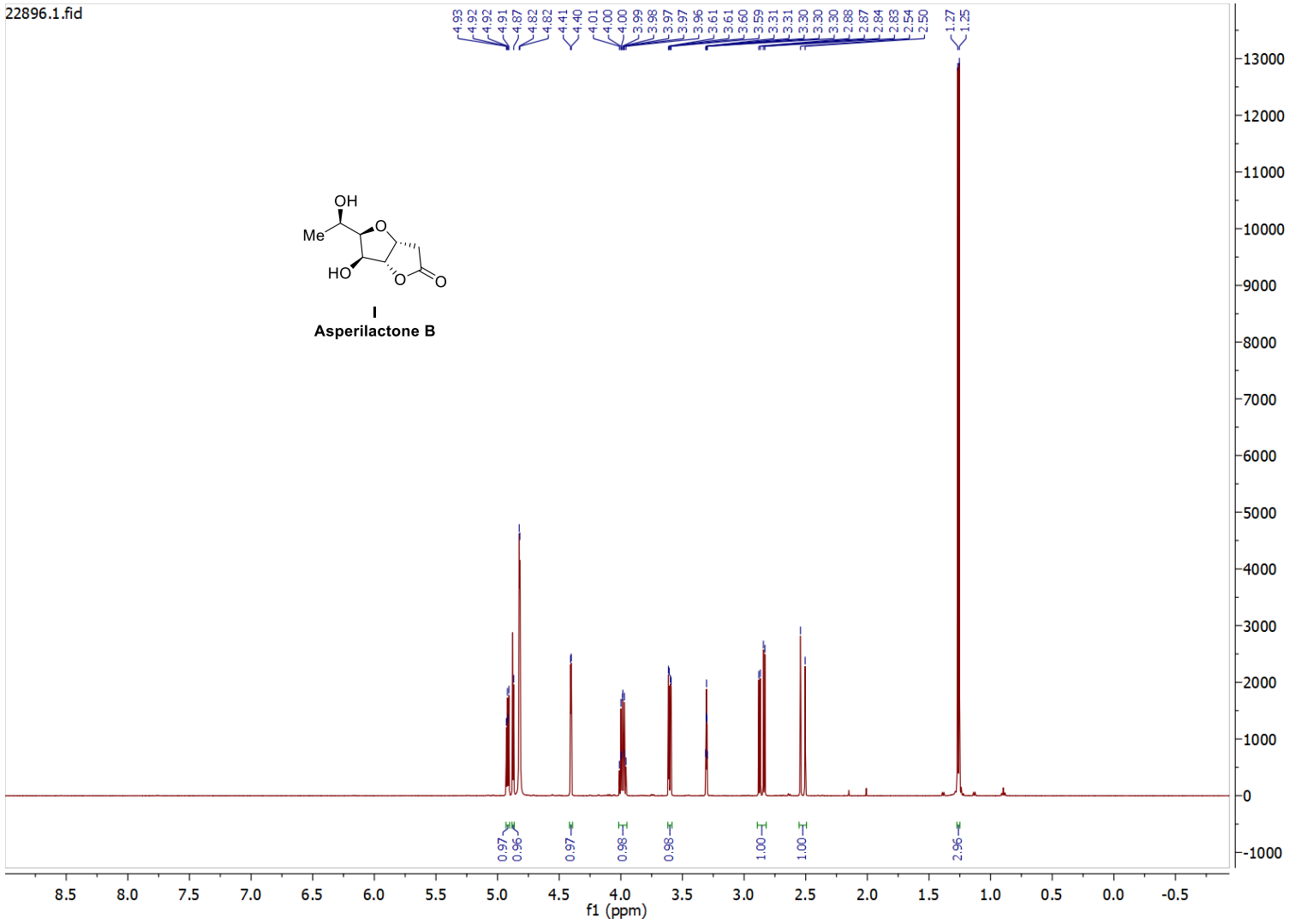
400 MHz ^{1}H NMR Spectrum of Compound **I** (Asperilactone B) (CD_3COCD_3)



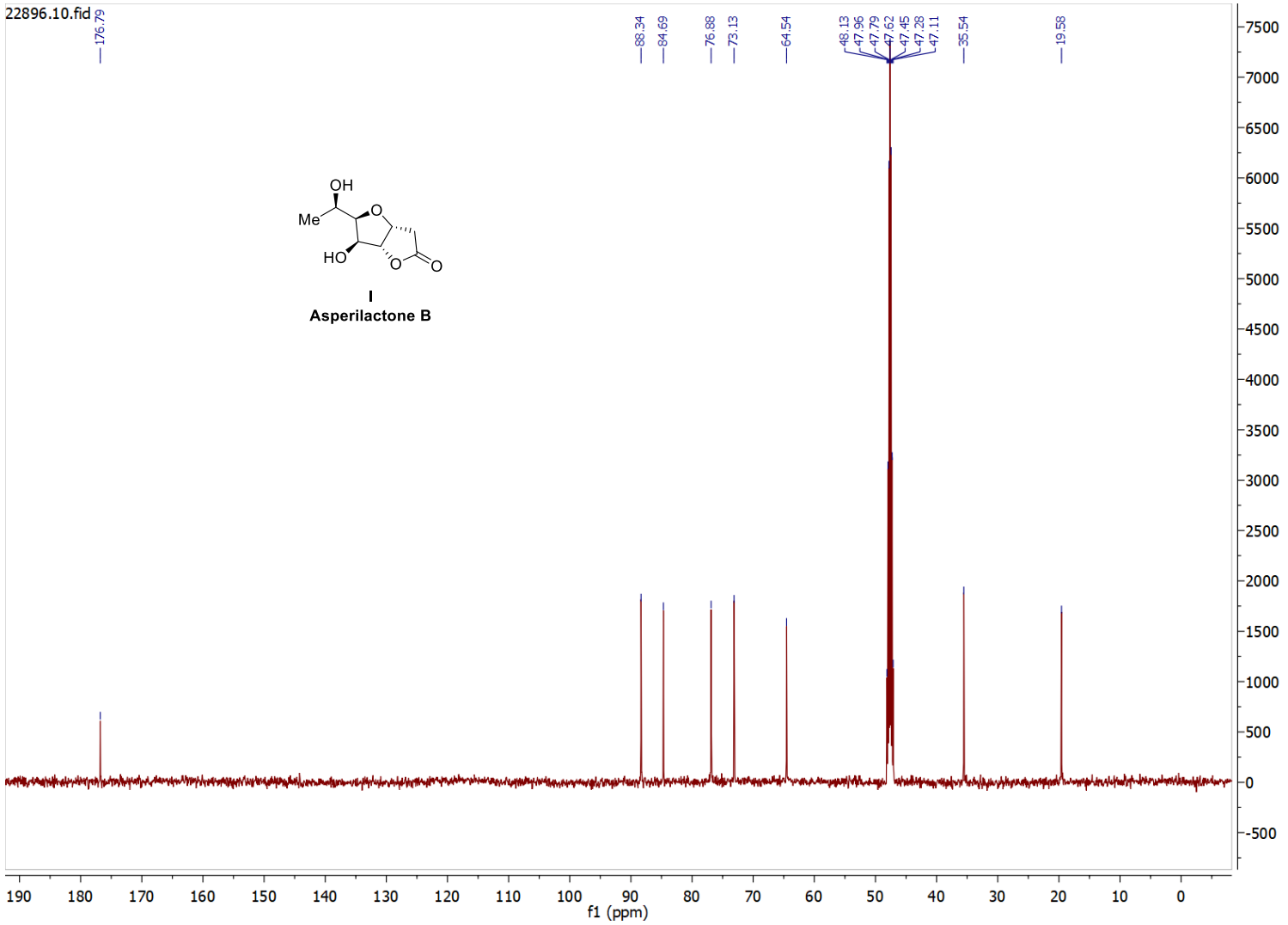
100 MHz ^{13}C NMR Spectrum of Compound **I** (Asperilactone B) (CD_3COCD_3)



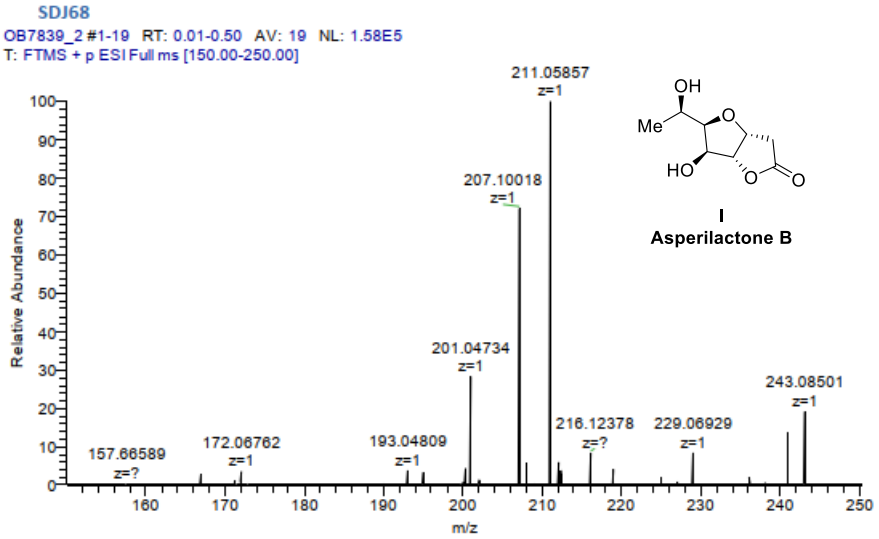
500 MHz ^{1}H NMR Spectrum of Compound **I** (Asperilactone B) (CD_3OD)

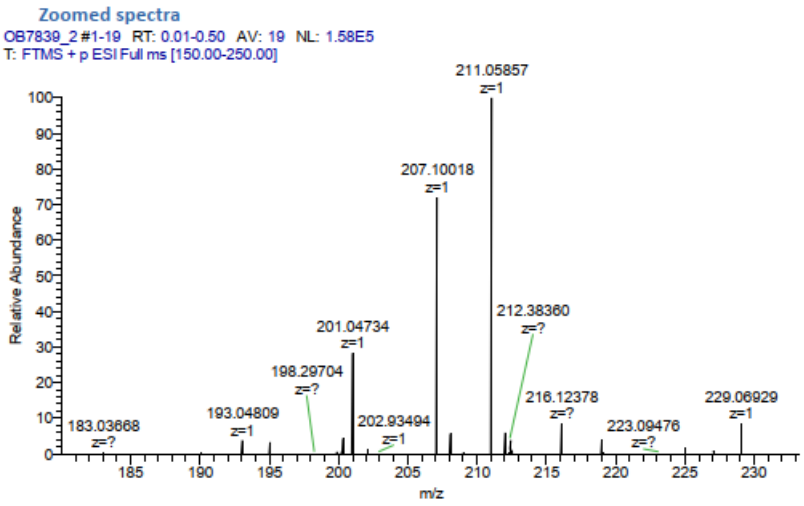


125 MHz ^{13}C NMR Spectrum of Compound **I** (Asperilactone B) (CD_3OD)



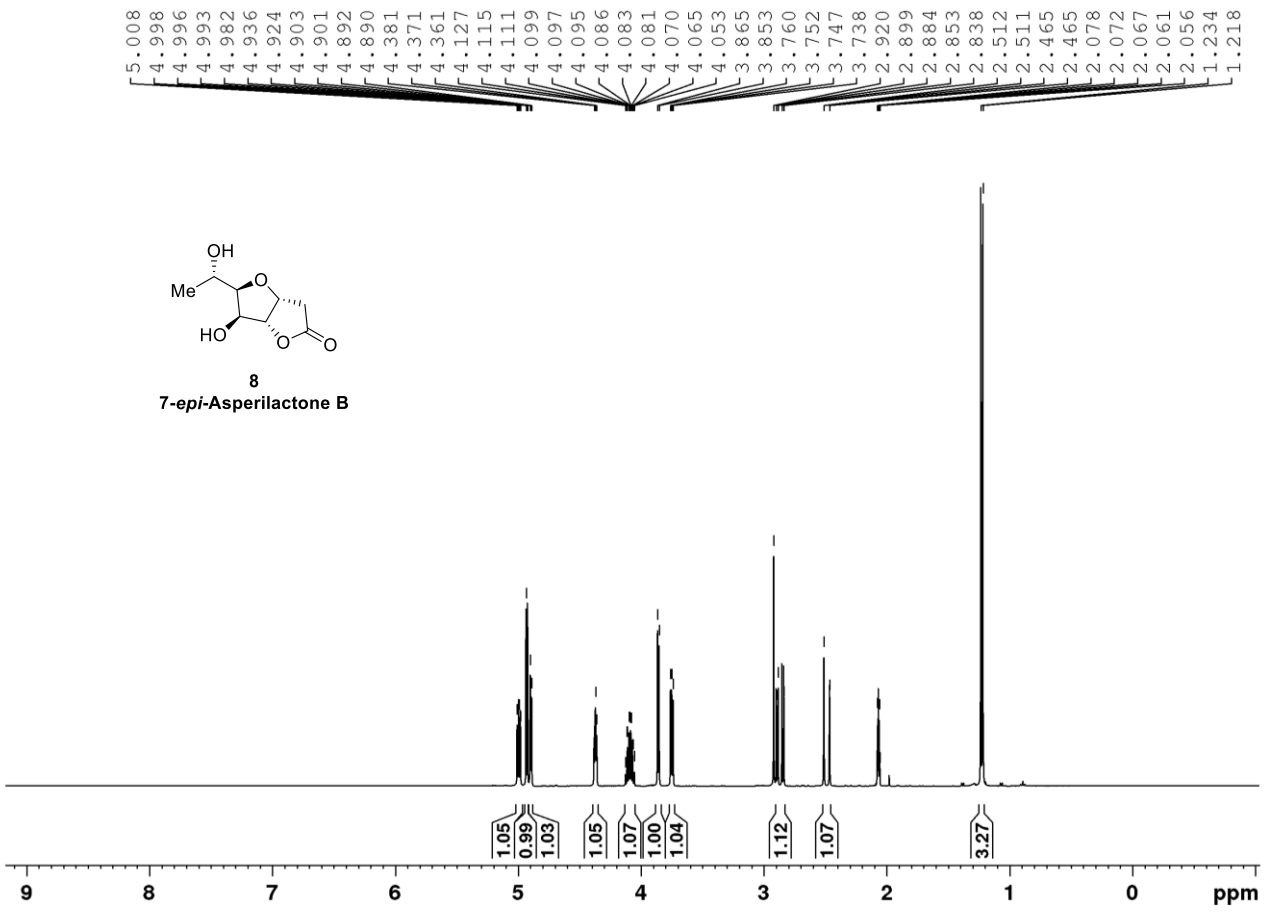
HRMS of compound **I** (Asperilactone B)



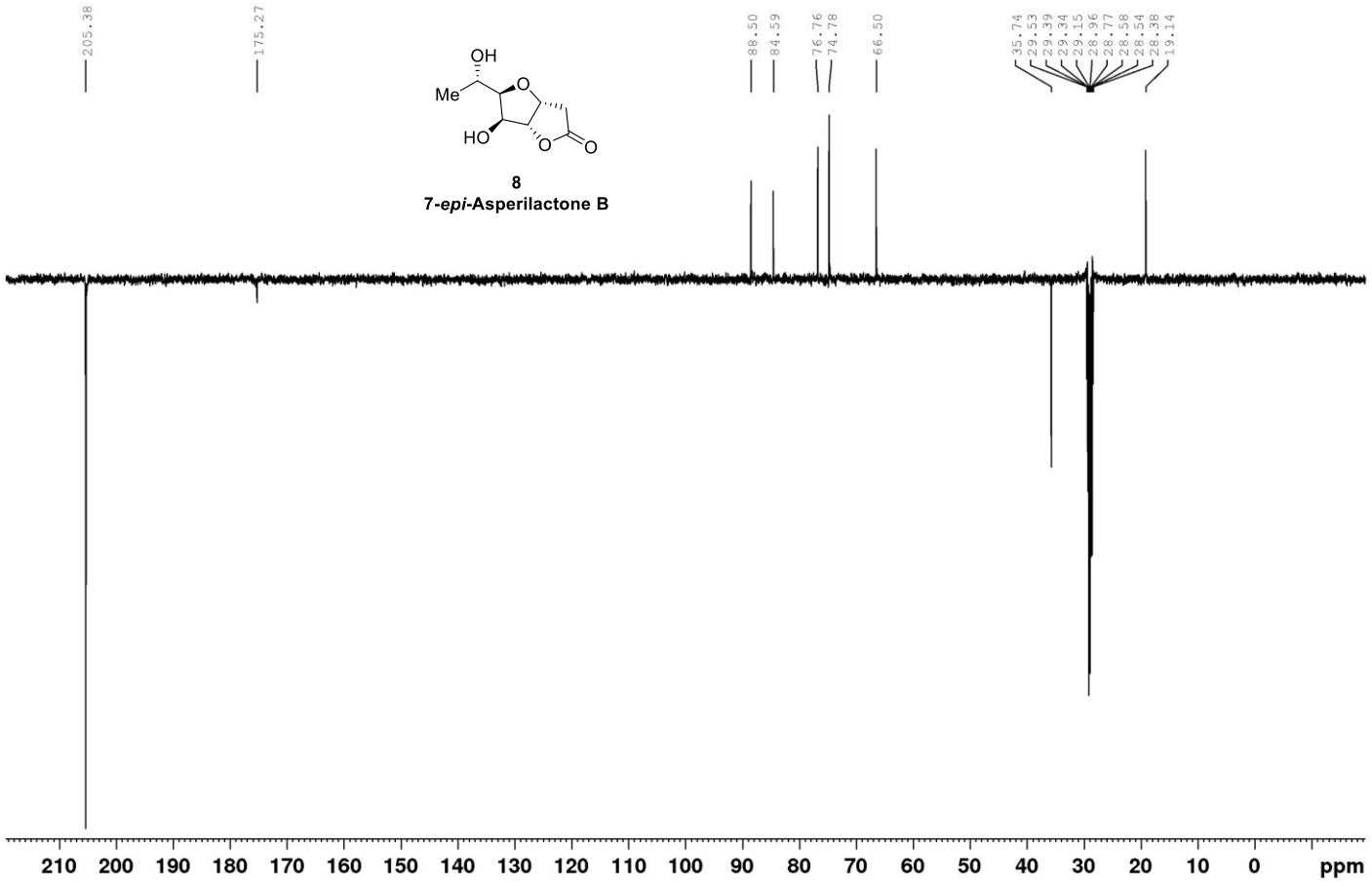


Exact mass	Observed mass	Observed ion type	Error (ppm)
211.05769	211.05857	$[M+Na]^+$	4.17

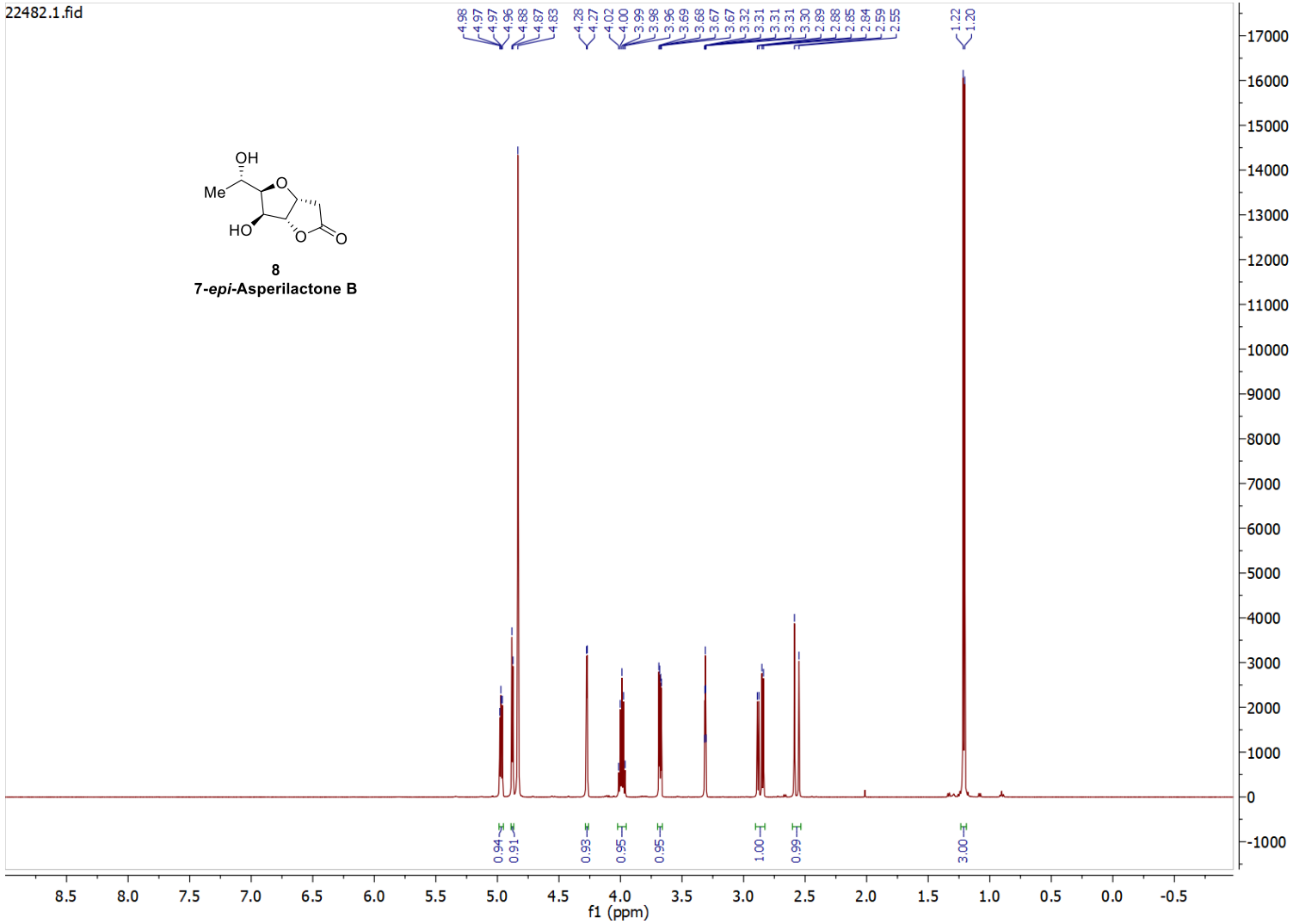
400 MHz ^{1}H NMR Spectrum of Compound **8** (7-*epi*-asperilactone B) (CD_3COCD_3)



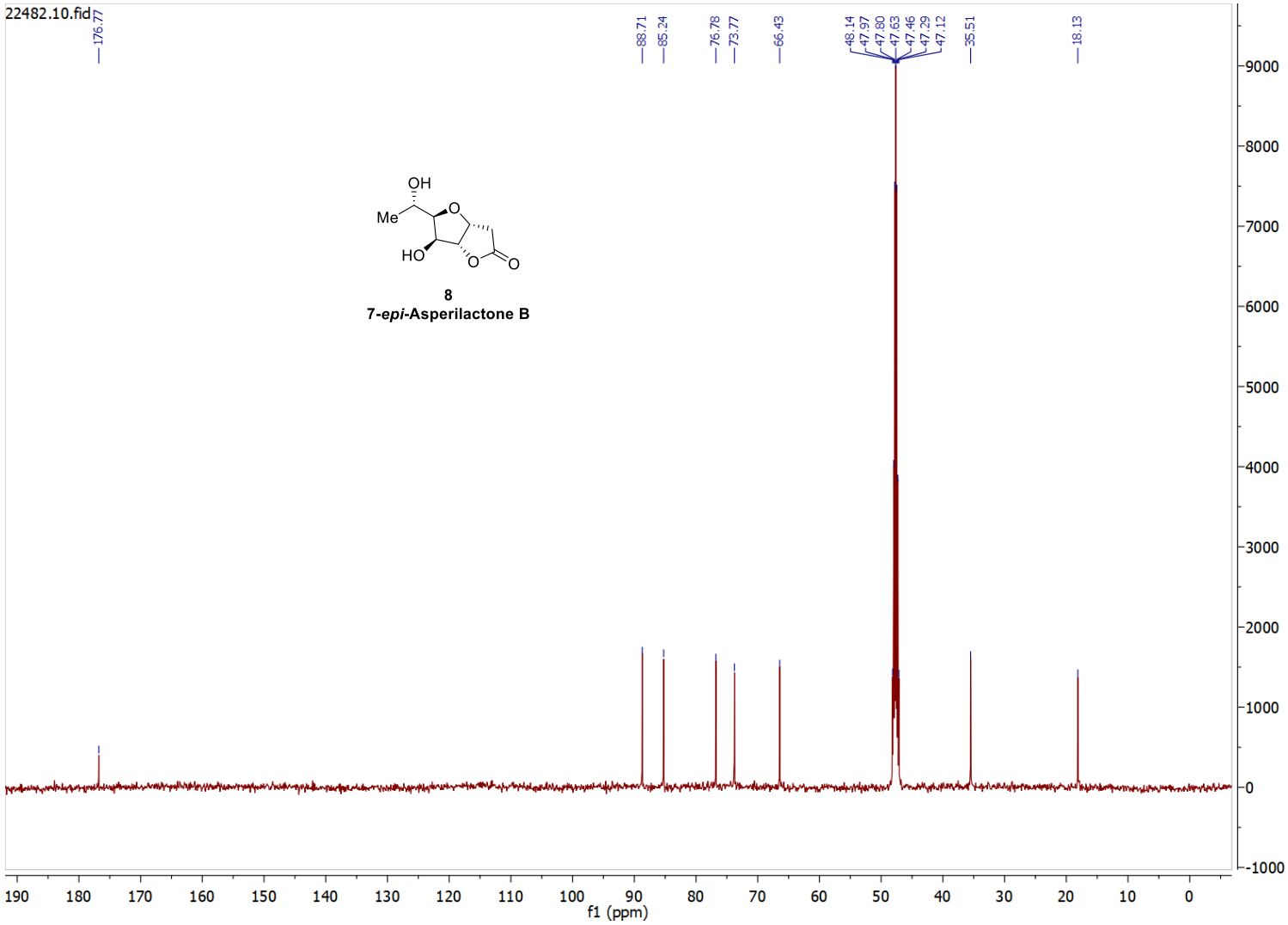
100 MHz ^{13}C NMR Spectrum of Compound **8** (7-*epi*-asperilactone B) (CD_3COCD_3)



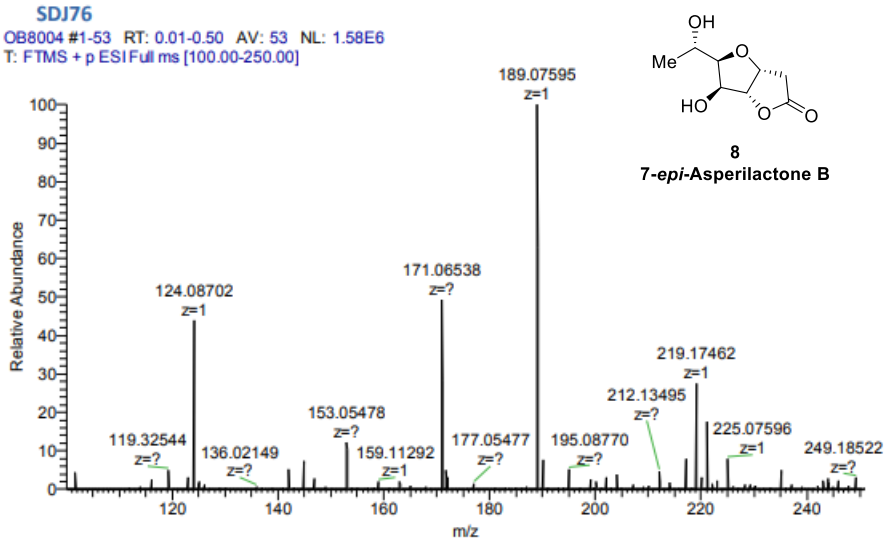
500 MHz ^{1}H NMR Spectrum of Compound **8** (7-*epi*-asperilactone B) (CD_3OD)

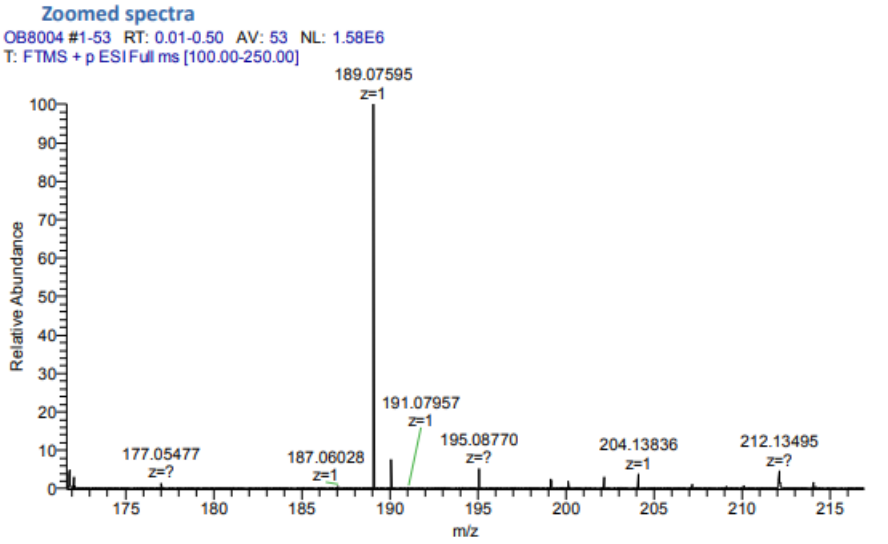


125 MHz ^{13}C NMR Spectrum of Compound **8** (7-*epi*-asperilactone B) (CD_3OD)



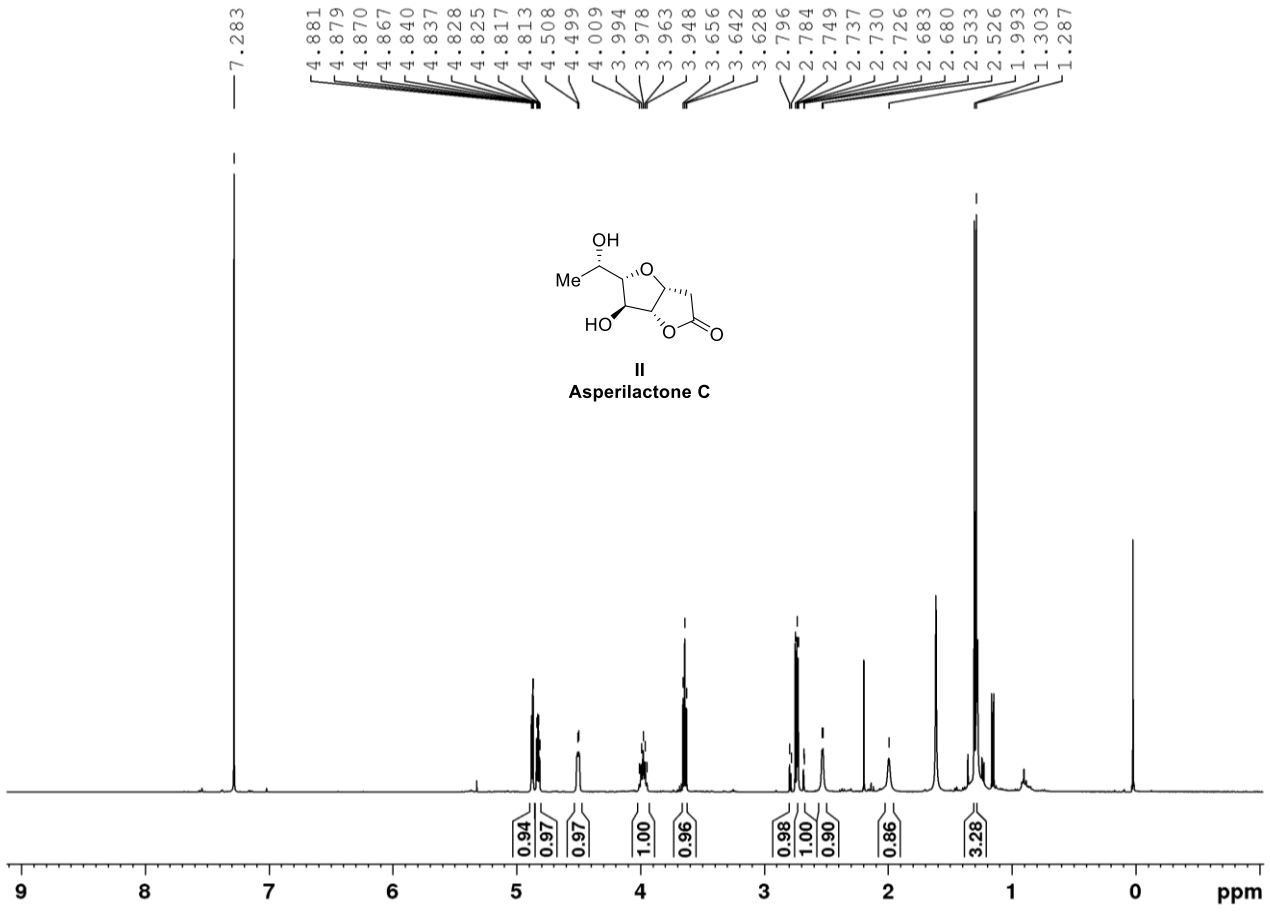
HRMS of compound **8** (7-*epi*-asperilactone B)



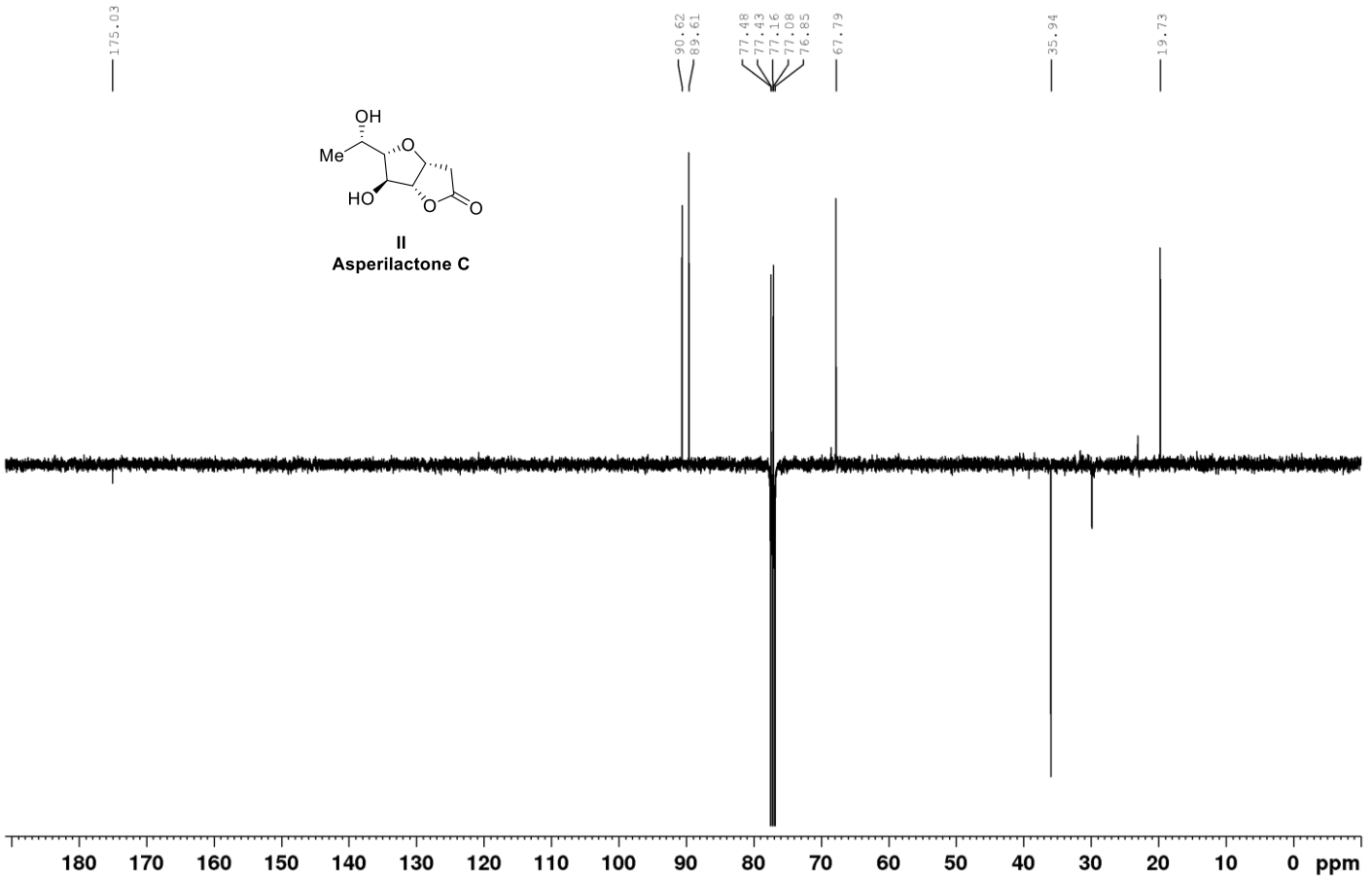


Exact mass	Observed mass	Observed ion type	Error (ppm)
189.07575	189.07595	$[M+H]^+$	1.06

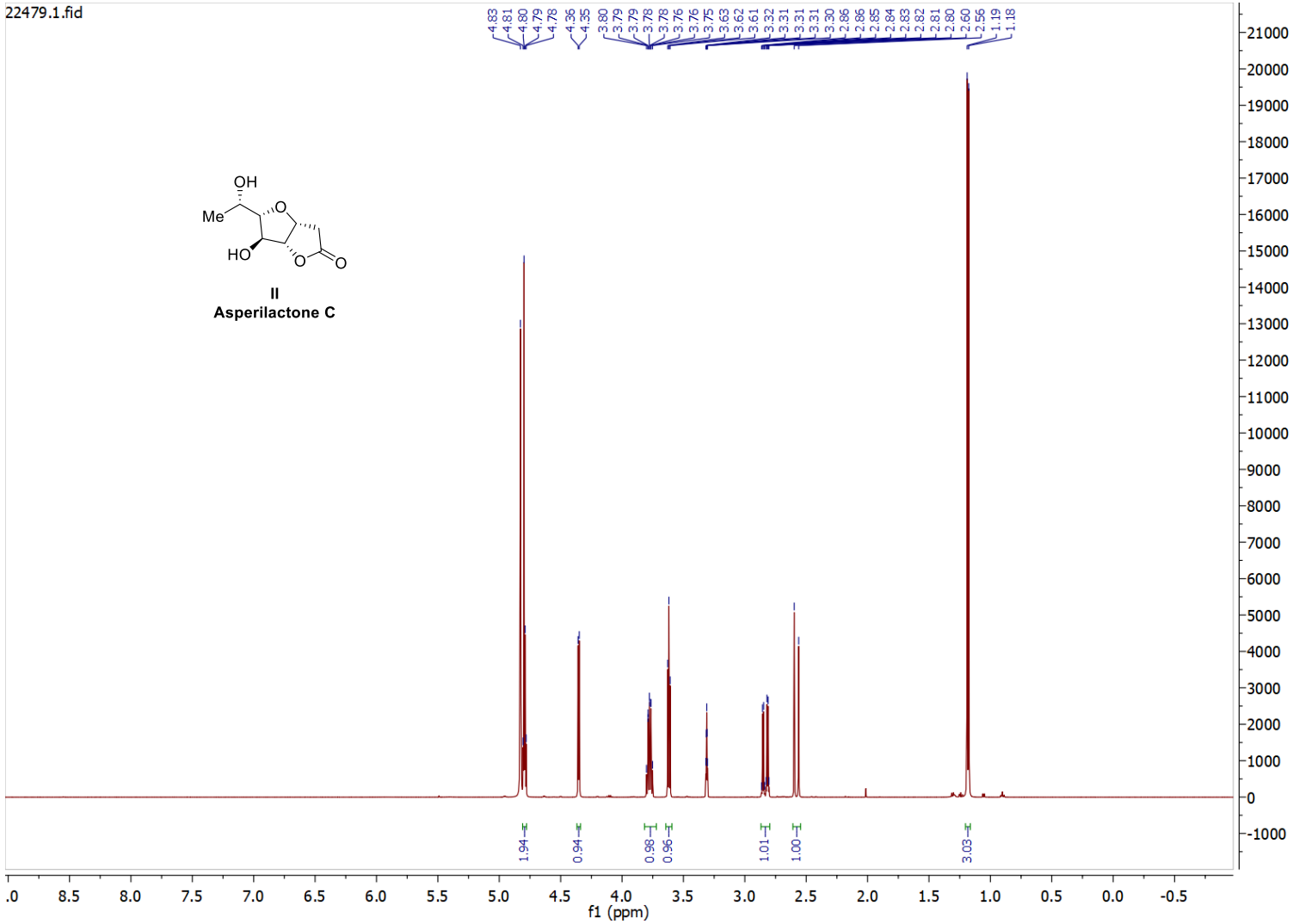
400 MHz ^{1}H NMR Spectrum of Compound **II** (Asperilactone C) ($CDCl_3$)



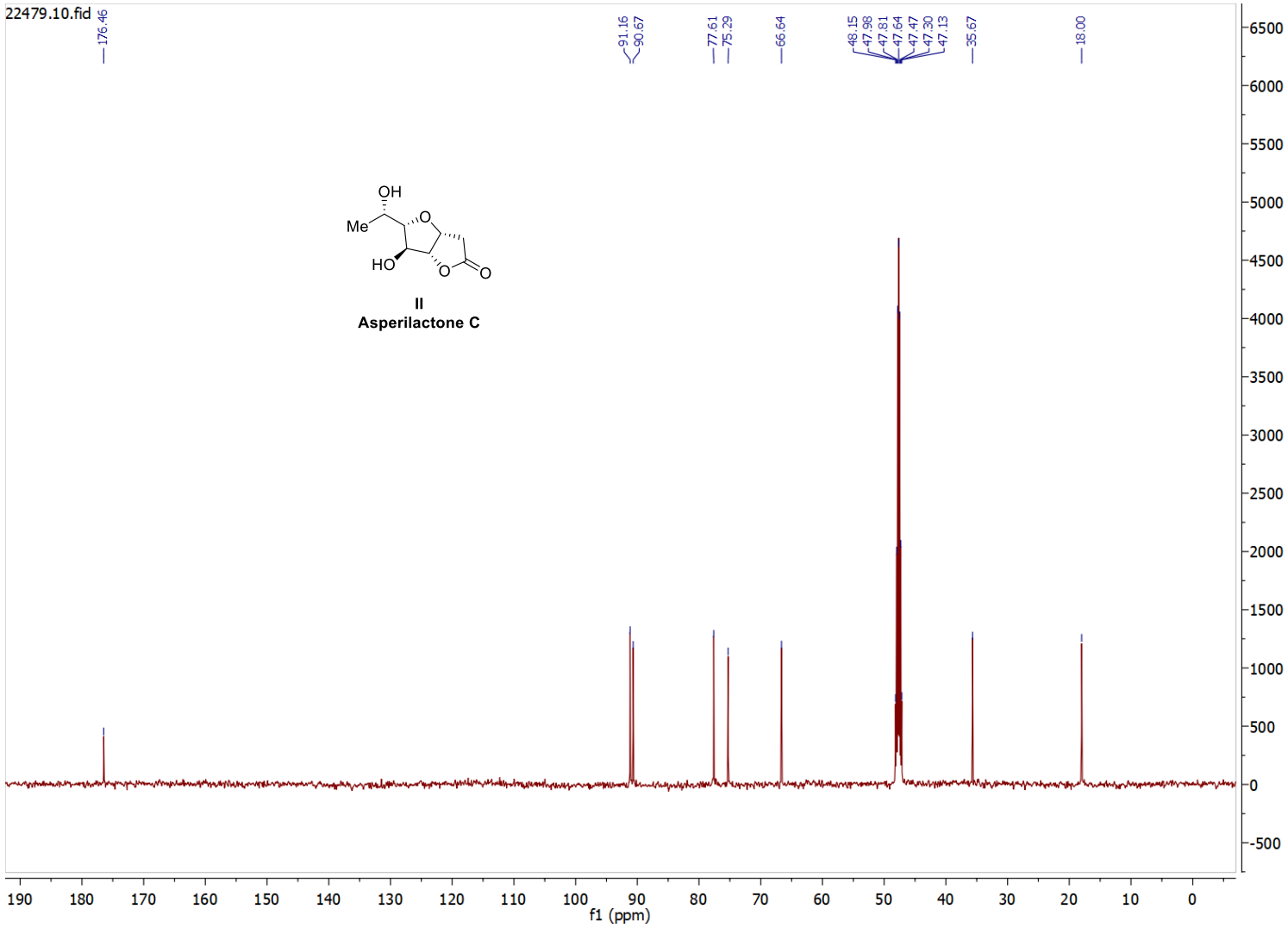
100 MHz ^{13}C NMR Spectrum of Compound **II** (Asperilactone C) ($CDCl_3$)



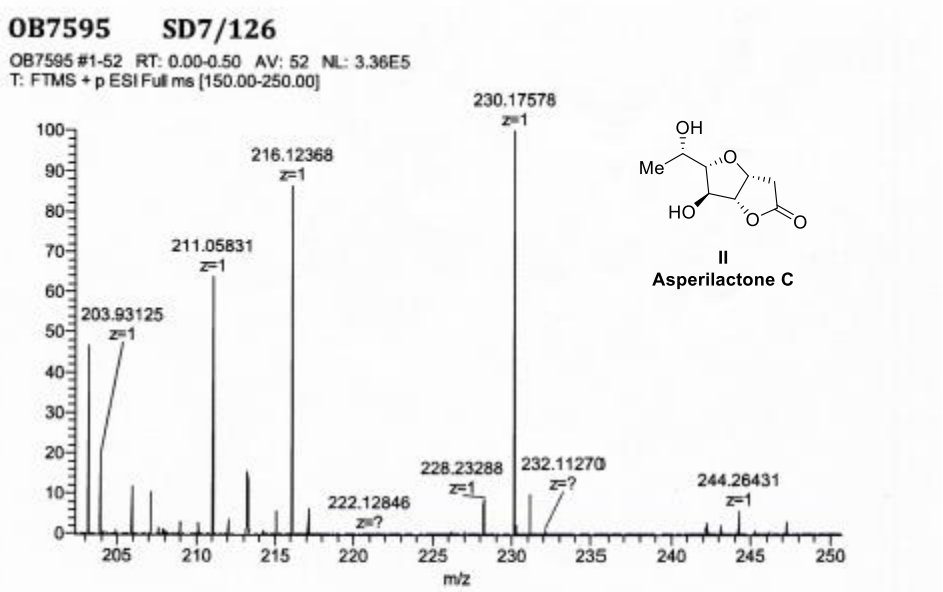
500 MHz ^{1}H NMR Spectrum of Compound **II** (Asperilactone C) (CD_3OD)



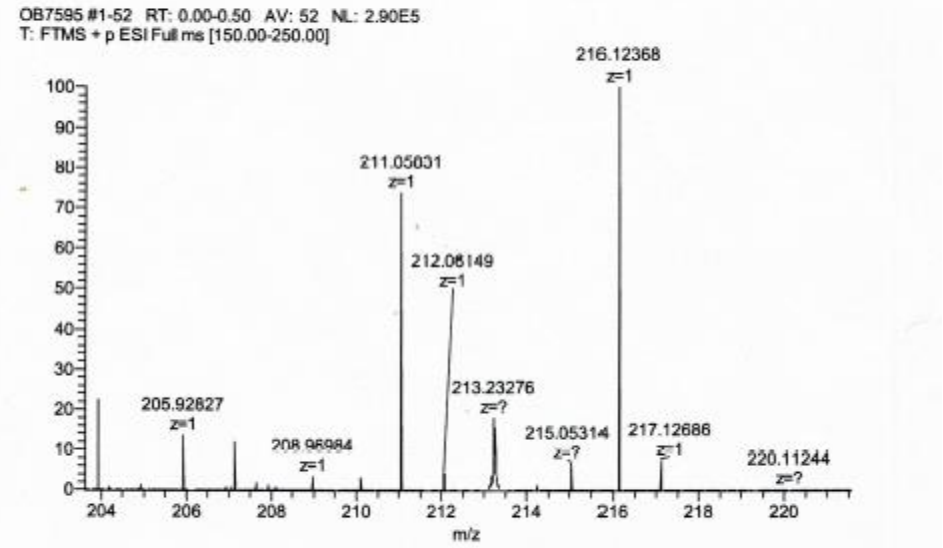
125 MHz ^{13}C NMR Spectrum of Compound **II** (Asperilactone C) (CD_3OD)



HRMS of compound **II** (Asperilactone C)



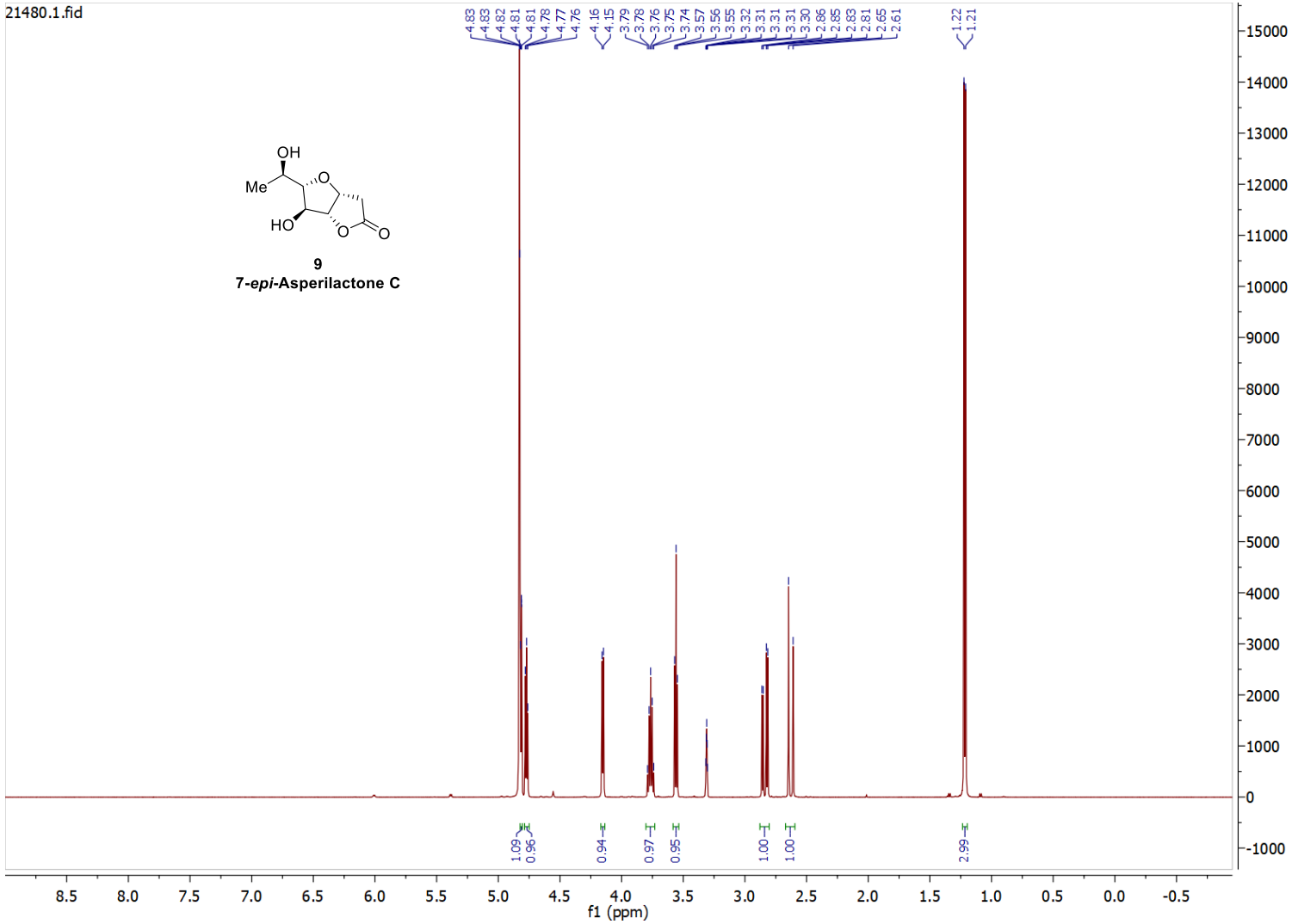
Zoomed spectra



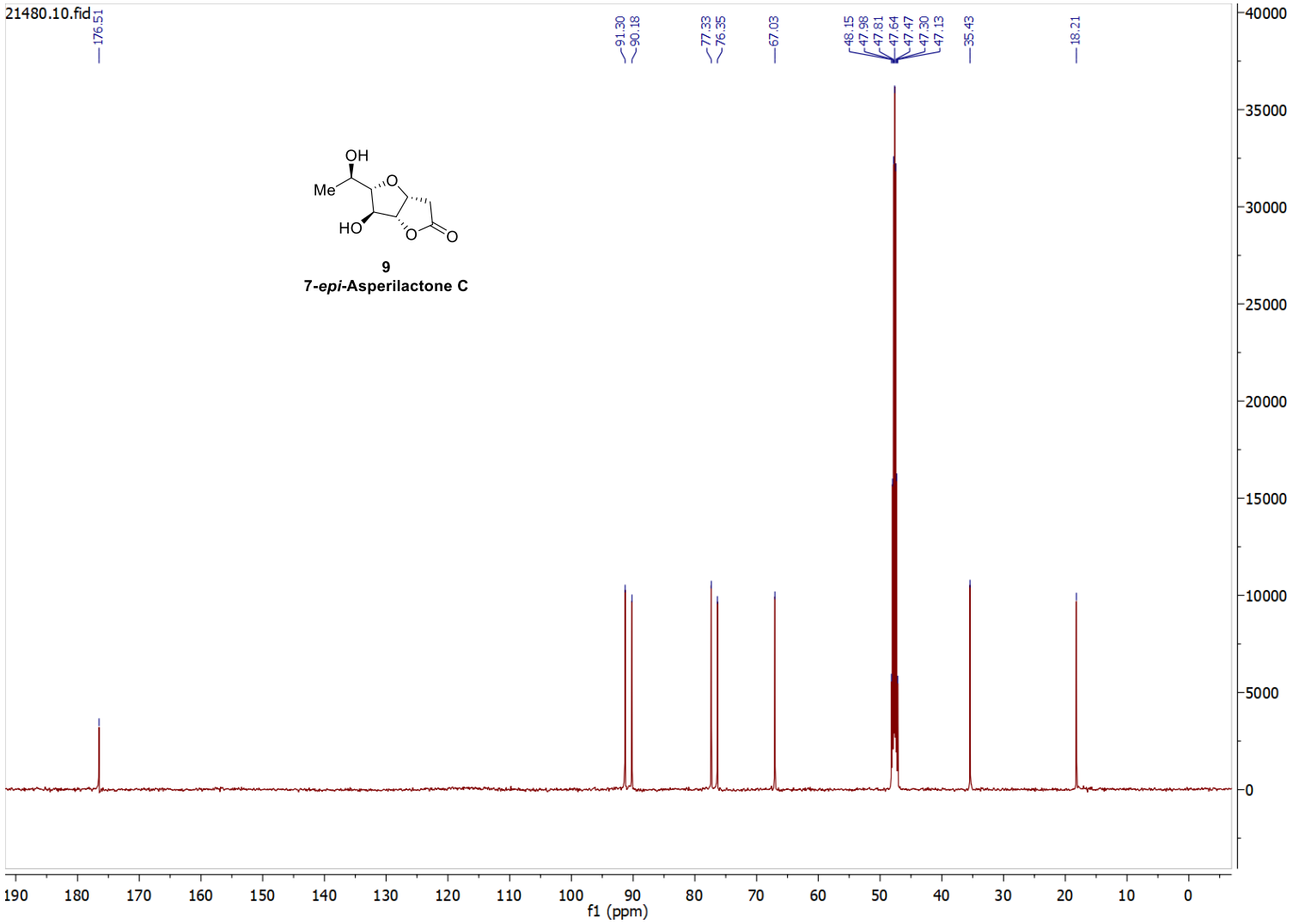
Exact mass	Observed mass	Observed ion type	Error (ppm)
211.05769	211.05831	$[M-Na]^+$	2.94

*NMR spectrum of compound **II** in CD_3COCD_3.[7]

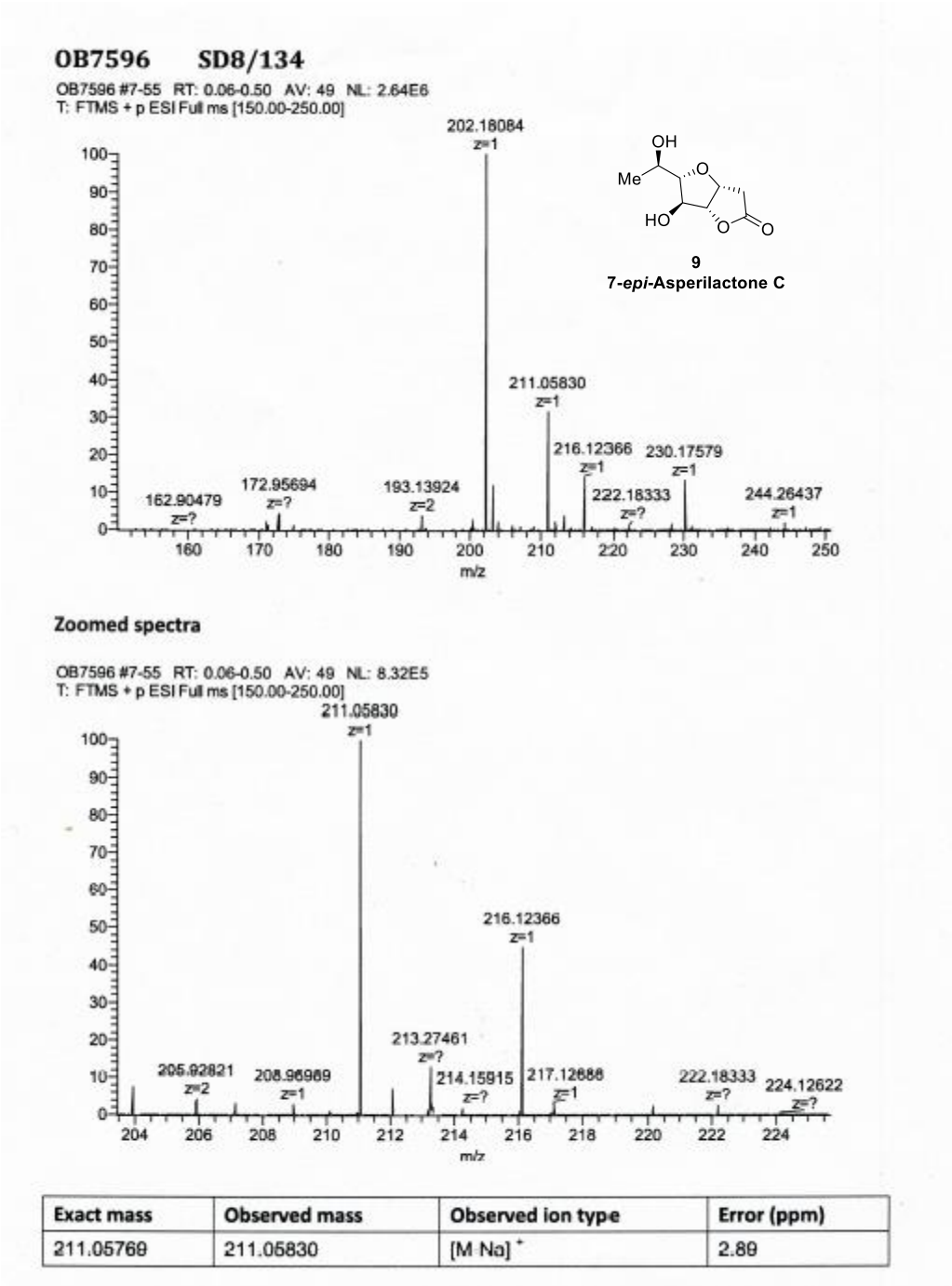
500 MHz ^{1}H NMR Spectrum of Compound **9** (7-*epi*-asperilactone C) (CD_3OD)



125 MHz ^{13}C NMR Spectrum of Compound **9** (7-*epi*-asperilactone C) (CD_3OD)



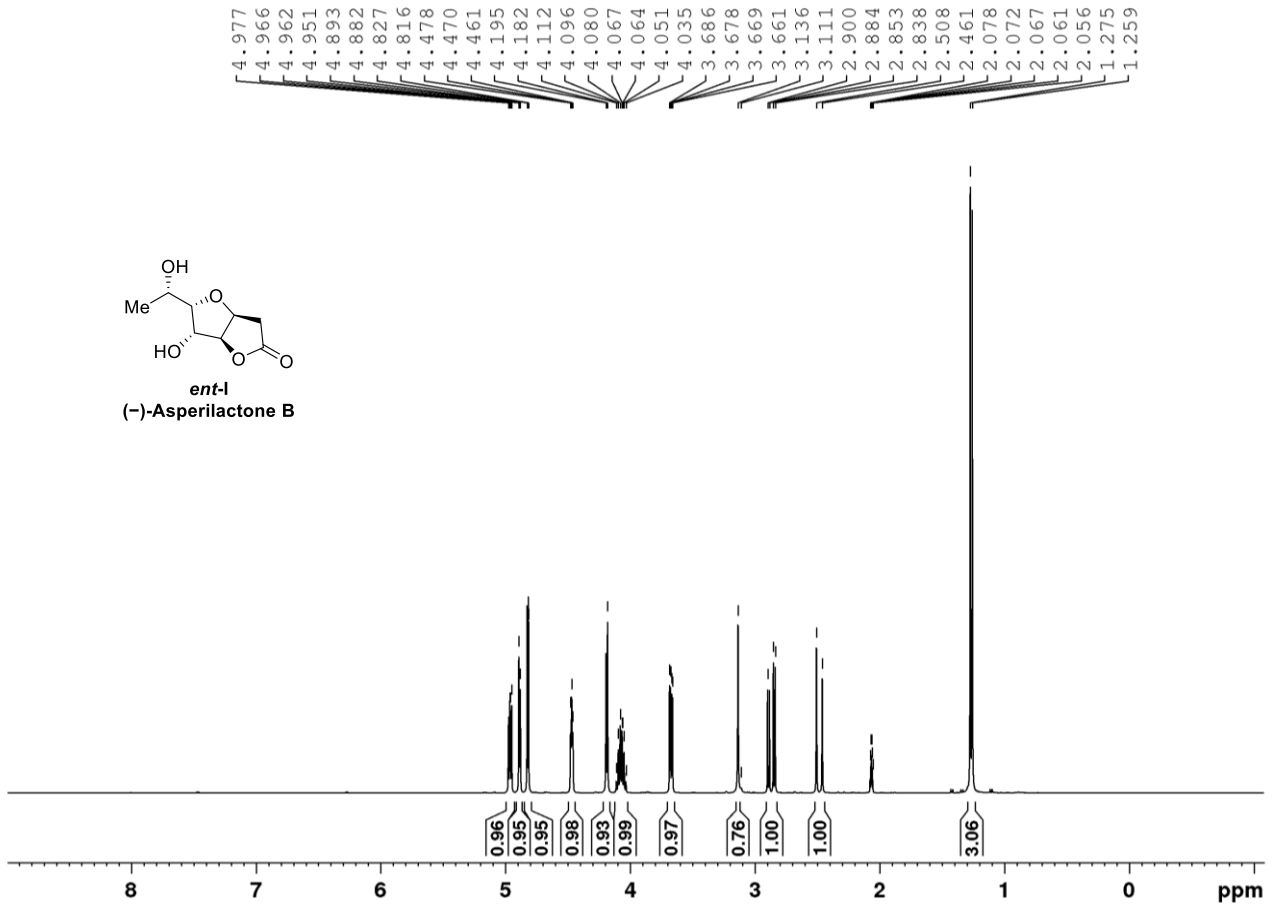
HRMS of compound **9** (7-*epi*-asperilactone C)



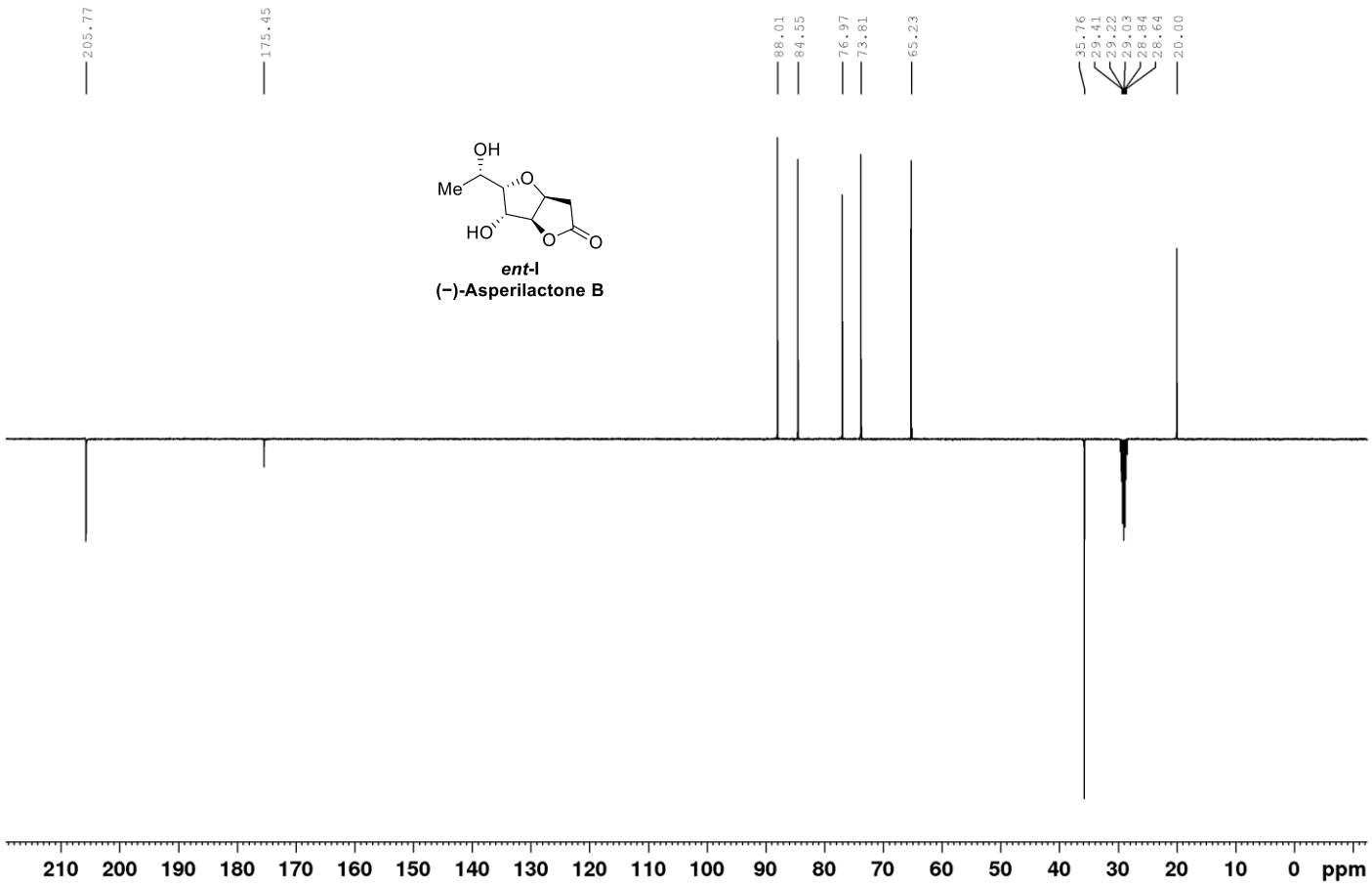
Exact mass	Observed mass	Observed ion type	Error (ppm)
211.05769	211.05830	$[M+Na]^+$	2.89

*NMR spectrum of compound **9** in CD_3COCD_3.[7]

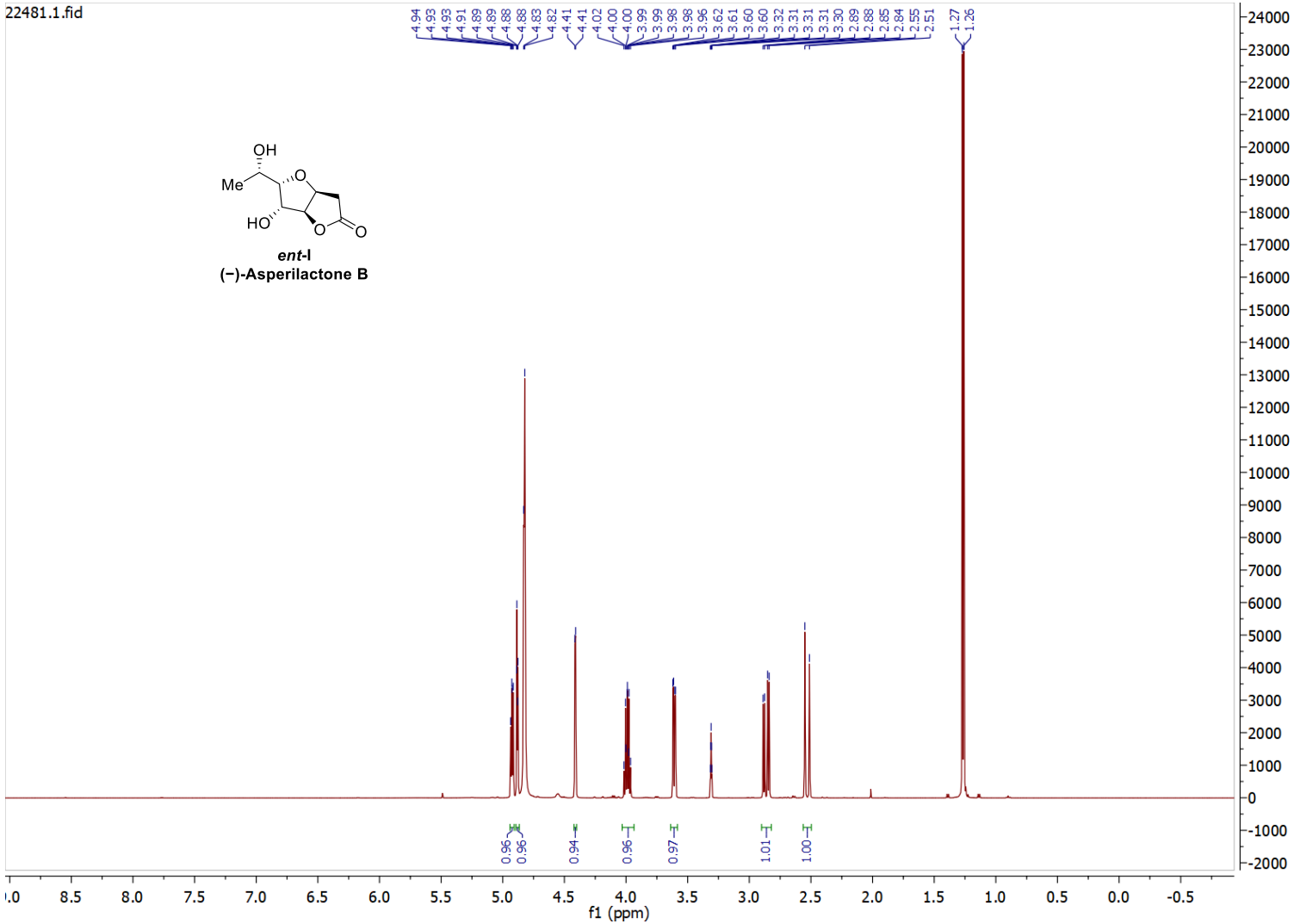
400 MHz ^{1}H NMR Spectrum of Compound ***ent*-I** (CD_3COCD_3)



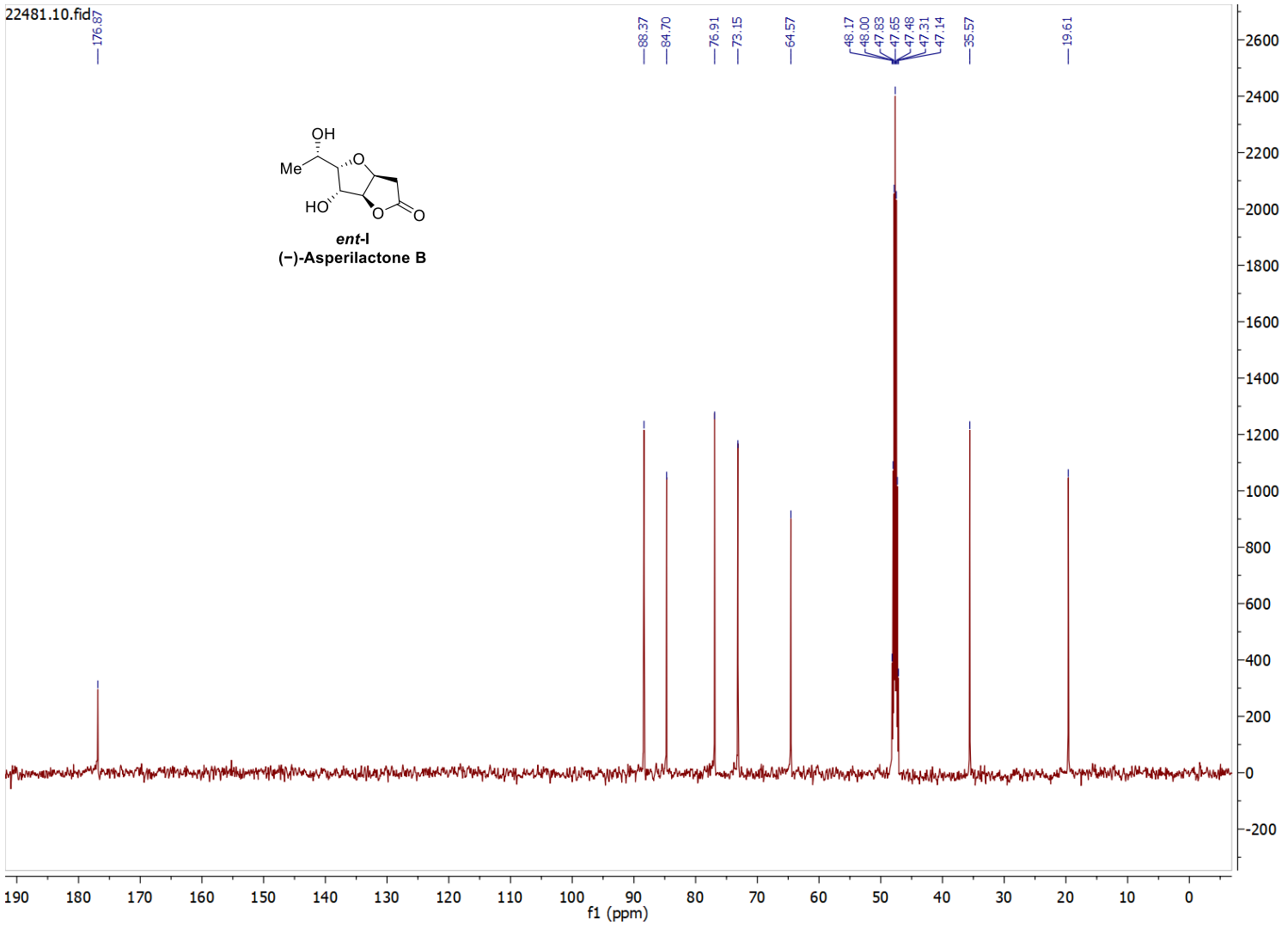
100 MHz ^{13}C NMR Spectrum of Compound ***ent*-I** (CD_3COCD_3)



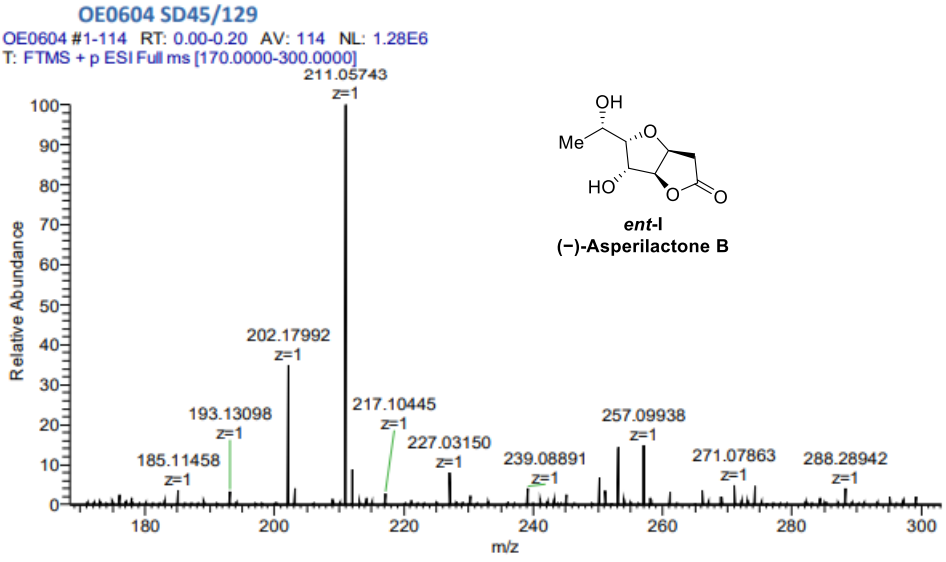
500 MHz ^{1}H NMR Spectrum of Compound ***ent*-I** (CD_3OD)

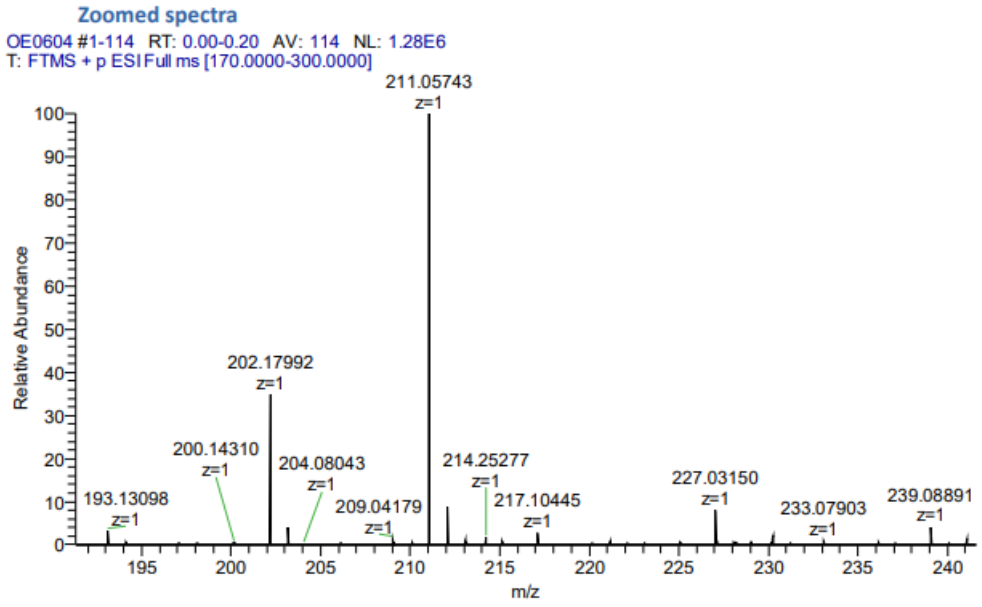


125 MHz ^{13}C NMR Spectrum of Compound ***ent*-I** (CD_3OD)



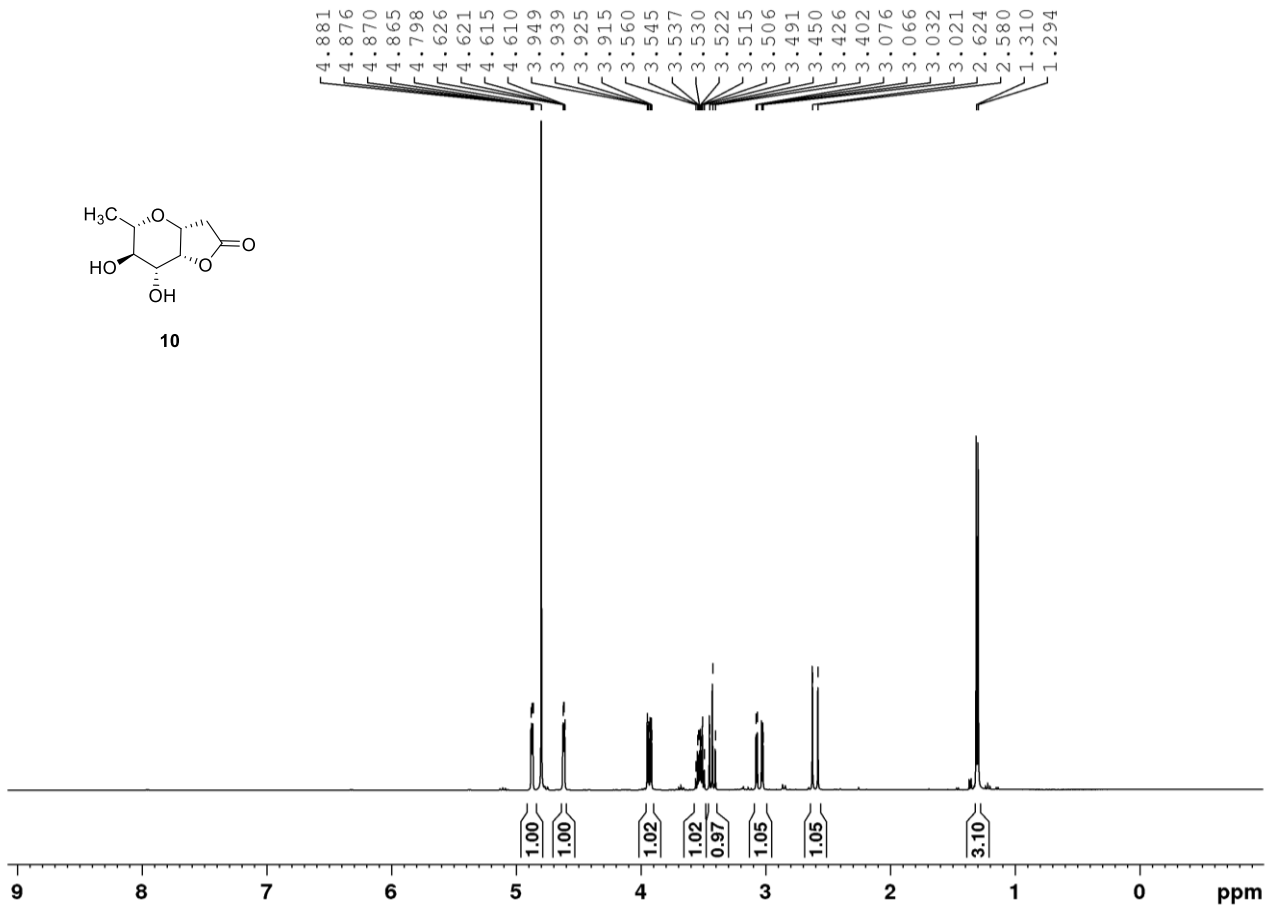
HRMS of compound ***ent*-I**



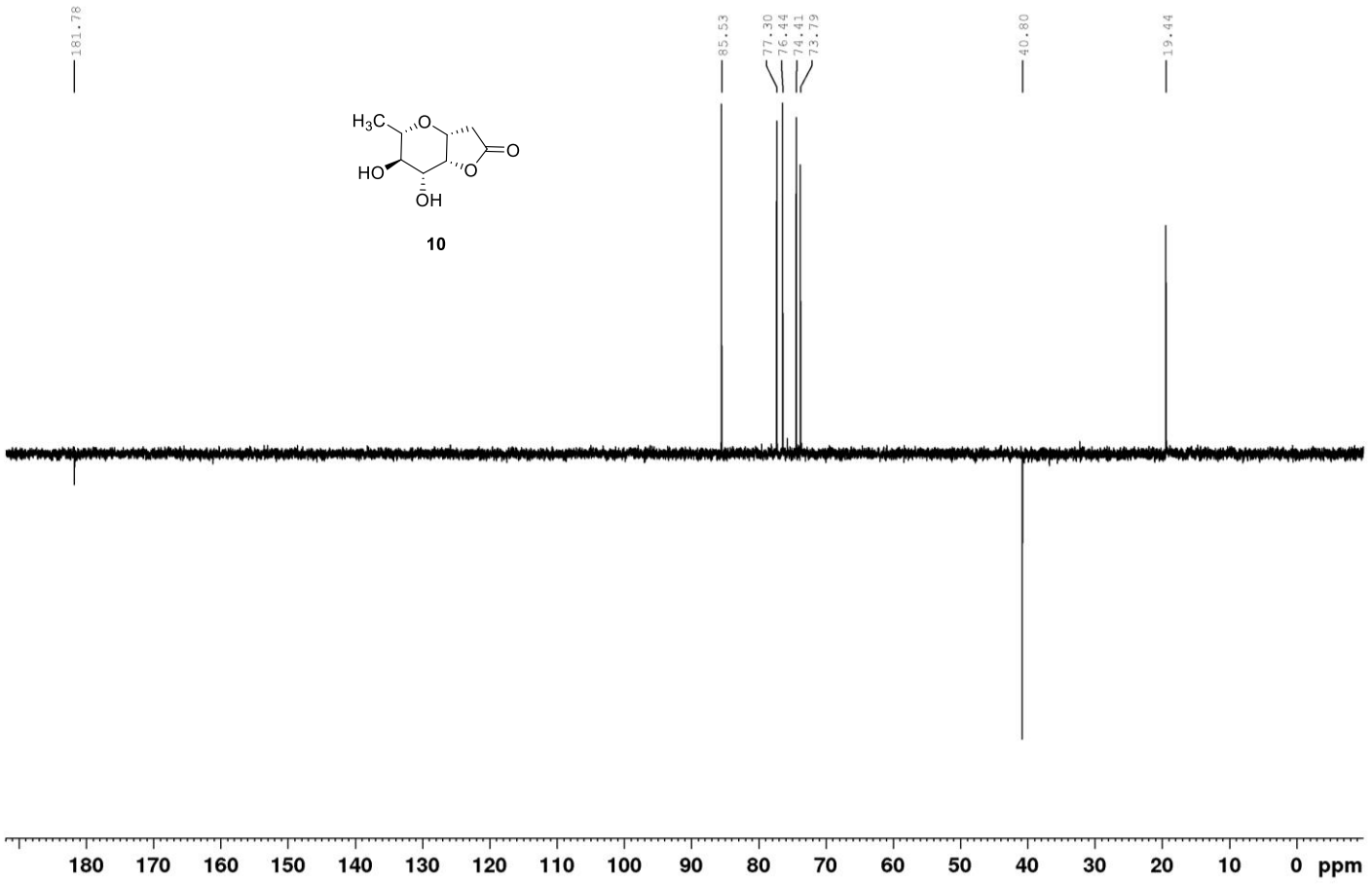


Exact mass	Observed mass	Observed ion type	Error (ppm)
211.05769	211.05743	$[M+Na]^+$	1.23

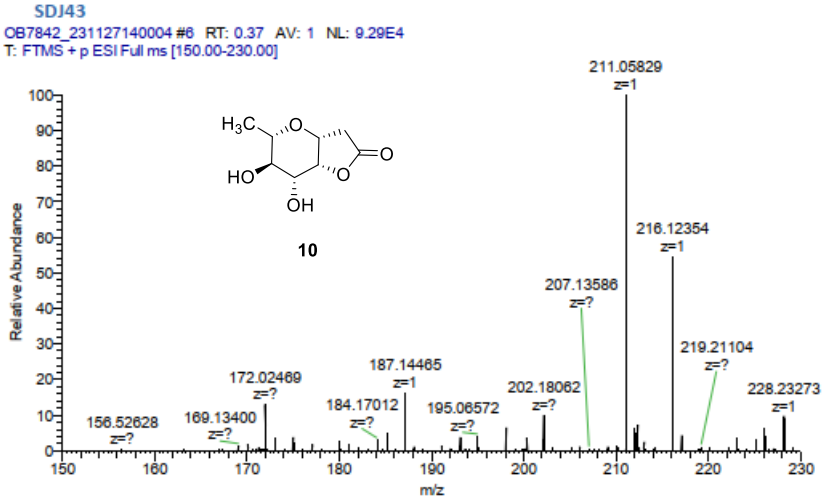
400 MHz ^{1}H NMR Spectrum of Compound **10** (D_2O)

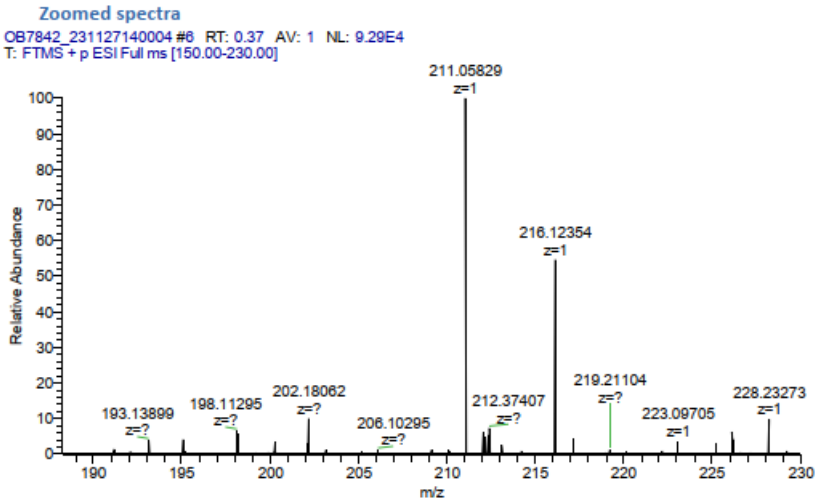


100 MHz ^{13}C NMR Spectrum of Compound **10** (D_2O)



HRMS of compound **10**





Exact mass	Observed mass	Observed ion type	Error (ppm)
211.05769	211.05829	$[M+Na]^+$	2.84

Crystal structures analysis

The diffraction analysis was conducted utilizing the Oxford Diffraction Gemini S diffractometer, which was outfitted with a Sapphire CCD detector. Data collection took place under standard room temperature conditions. Instrument control and data reduction were facilitated by the *CrysAlisPro*[1] software package. Crystal structures were solved with the utilization of *SHELXT*[2] followed by refinement procedures using *SHELXL*.[3] The *ShelXle*[4] facilitated these procedures, serving as the graphical user interface. Anisotropic refinement was applied to all non-hydrogen atoms, while hydrogen atoms were positioned in idealized coordinates and refined using a riding model. Water molecule in **I** and ***ent*-I** has one hydrogen atom disordered over two positions. Positions of water hydrogen atoms are modeled with the help of distance restraints. All details are included in the CIF files. Pertinent crystallographic and refinement data are listed in Table S1 and S2.

Crystallographic data associated with this publication are deposited with the Cambridge Crystallographic Data Centre under the CCDC Numbers 2333775–2333779. They are available for free at https://www.ccdc.cam.ac.uk/structures.

References

1. Rigaku Oxford Diffraction. *CrysAlisPro Software System*; Rigaku Corporation, Wroclaw, Poland, 2023.
2. G. M. Sheldrick, *Acta Cryst. A* 2015, **71**, 3–8.
3. G. M. Sheldrick, *Acta Cryst. C* 2015, **71**, 3–8.
4. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.* 2011, **44**, 1281–1284.

Table S1. Crystallographic and refinement details for **I** and ***ent*-I**.

	I	***ent*-I**
Crystal data		
CCDC No.	2333775	2333776
Chemical formula	$C_8H_{12}O_5 \cdot H_2O$	$C_8H_{12}O_5 \cdot H_2O$
M_r	206.19	206.19
Crystal system	Monoclinic	Monoclinic
Space group	*C*2	*C*2
a / Å	16.4932 (6)	16.5089 (3)
b / Å	6.85772 (19)	6.85830 (11)
c / Å	8.9304 (3)	8.93440 (19)
α / °	90	90
β / °	104.860 (3)	104.846 (2)
γ / °	90	90
V / Å^3	976.30 (6)	977.81 (3)
Z	4	4
Radiation type	Cu *Kα*	Cu *Kα*
μ / mm^{-1}	1.05	1.04
Crystal size, mm	0.70 × 0.24 × 0.06	0.77 × 0.40 × 0.12
Data collection		
Absorption correction	Multi-scan	Multi-scan
T_{min}	0.724	0.698
T_{max}	1.000	1.000
No. of measured reflections	6007	4973
No. of independent reflections	1874	1874
No. of observed reflections ($I > 2\sigma(I)$)	1769	1847
R_{int}	0.032	0.029
$(\sin \vartheta/\lambda)_{max}$ / Å^{-1}	0.617	0.616
Refinement		
$R[F^2 > \sigma(F^2)]$	0.034	0.035
$wR(F^2)$	0.092	0.092
S	1.05	1.06
No. of reflections	1874	1874
No. of parameters	141	142
No. of restraints	6	6
$\Delta\rho_{max}$ / e Å^{-3}	0.12	0.18
$\Delta\rho_{min}$ / e Å^{-3}	−0.13	−0.14
No. of quotients $[I^+ - I^-]/[I^+ + I^-]$	747	812
Parsons' *z*	−0.07 (12)	−0.01 (8)

Table S2. Crystallographic and refinement details for **8**–**10**.

	8	**9**	**10**
Crystal data			
CCDC No.	2333777	2333778	2333779
Chemical formula	$C_8H_{12}O_5$	$C_8H_{12}O_5$	$C_8H_{12}O_5$
M_r	188.18	188.18	188.18
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a / Å	5.37102 (6)	5.48541 (5)	8.5474 (5)
b / Å	12.47818 (12)	10.62294 (8)	5.4514 (3)
c / Å	26.7627 (3)	15.21442 (14)	9.7185 (6)
α / °	90	90	90
β / °	90	90	109.269 (7)
γ / °	90	90	90
V / Å^3	1793.65 (3)	886.56 (1)	427.47 (5)
Z	8	4	2
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ / mm^{-1}	1.00	1.01	0.12
Crystal size, mm	0.62 × 0.21 × 0.09	0.74 × 0.38 × 0.17	0.80 × 0.14 × 0.07
Data collection			
Absorption correction	Multi-scan	Analytical	Multi-scan
T_{min}	0.501	0.555	0.916
T_{max}	1.000	0.850	1.000
No. of measured reflections	19203	13317	10436
No. of independent reflections	3176	1726	2091
No. of observed reflections ($I > 2\sigma(I)$)	3032	1716	1835
R_{int}	0.026	0.035	0.039
$(\sin \vartheta/\lambda)_{max}$ / Å^{-1}	0.595	0.617	0.691
Refinement			
$R[F^2 > \sigma(F^2)]$	0.029	0.032	0.036
$wR(F^2)$	0.075	0.087	0.084
S	1.06	1.09	1.07
No. of reflections	3176	1726	2091
No. of parameters	245	128	123
No. of restraints	0	0	1
$\Delta\rho_{max}$ / e Å^{-3}	0.15	0.16	0.19
$\Delta\rho_{min}$ / e Å^{-3}	−0.11	−0.14	−0.16
No. of quotients $[I^+-I^-]/[I^++I^-]$	1195	683	703
Parsons' z	0.02 (6)	0.02 (4)	Meaningless

Figure S1. Molecular structure of **I** ((+)-Asperilactone B).

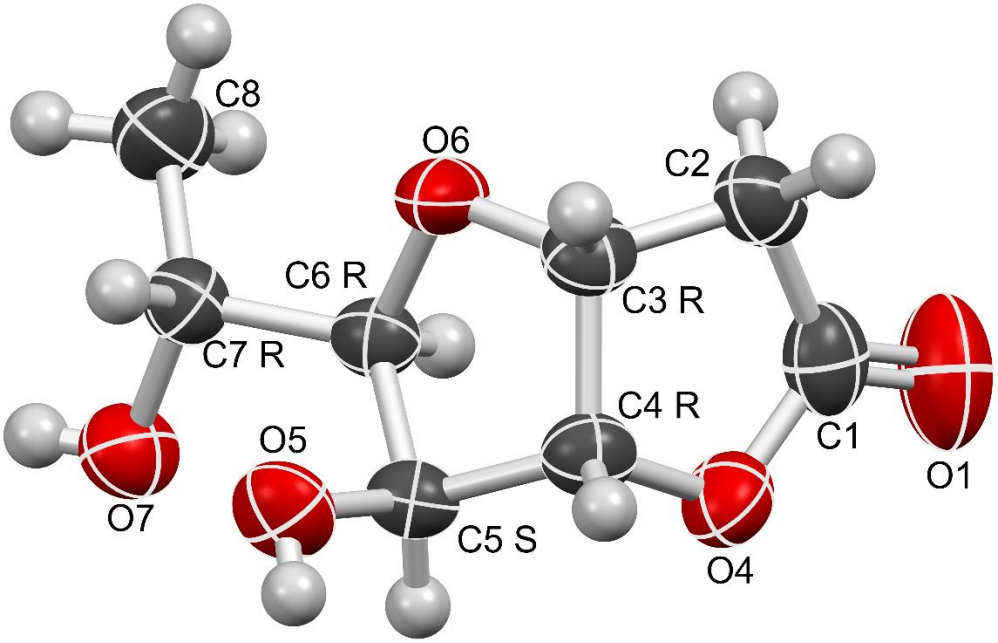


Figure S2. Molecular structure of ***ent*-I** ((−)-Asperilactone B).

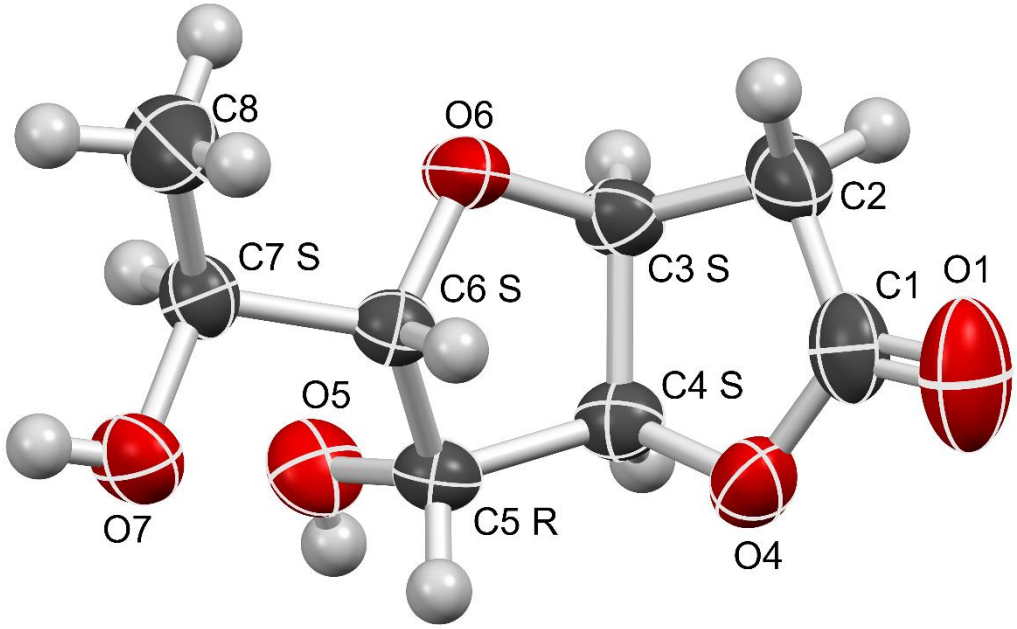


Figure S3. Molecular structure of **8**.

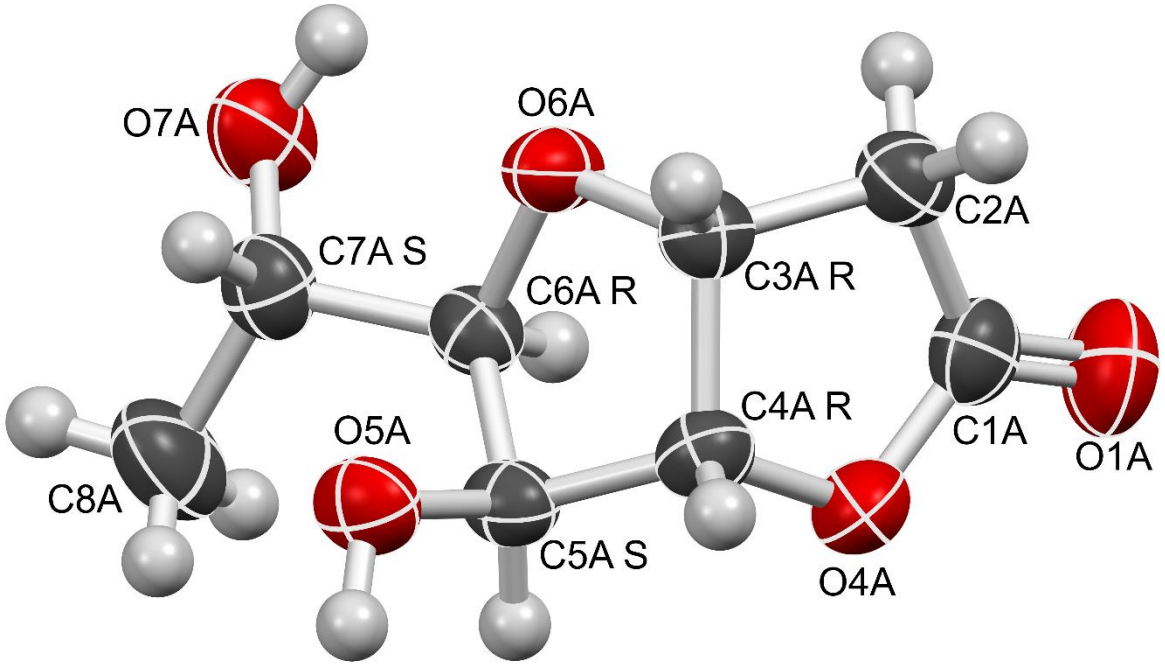


Figure S4. Molecular structure of **9**.

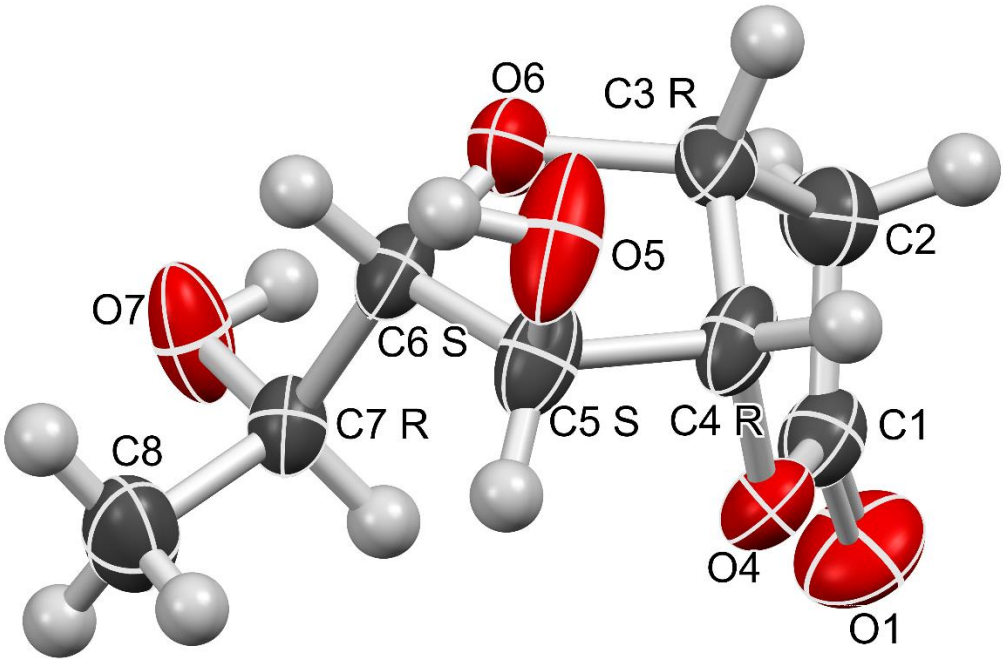
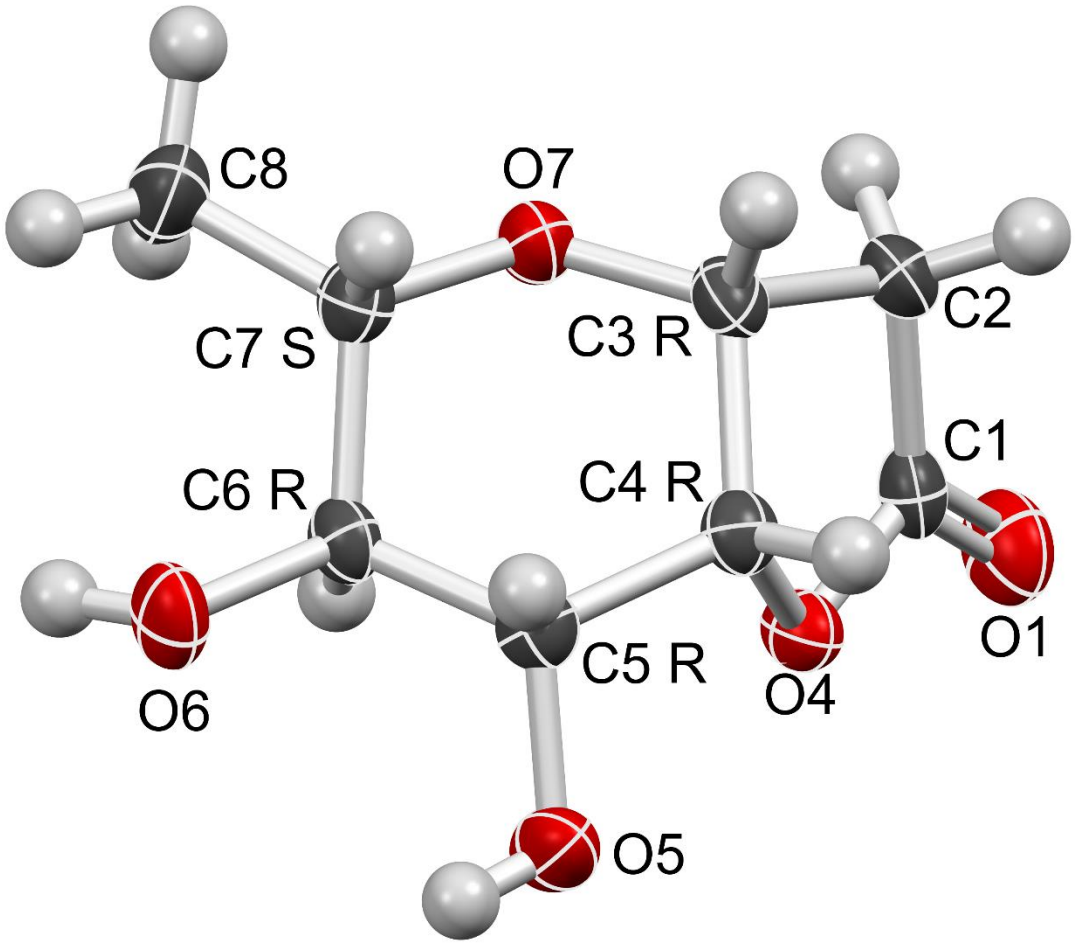
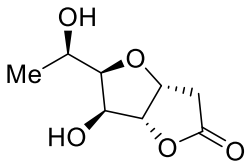


Figure S5. Molecular structure of **10**.



Comparison of NMR Spectra of Asperilactones B and C with Reported Data



I

Asperilactone B

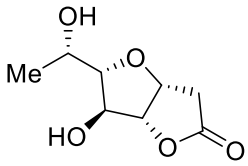
Table S3. Comparison of NMR spectra Asperilactone B (**I**) with reported data (CD_3OD).[a]

C/H	Observed δ_H (*J*)	Reported[a] δ_H (*J*)	Observed δ_C	Reported[a] δ_C
1			176.8	178.2
2a	2.52 d (18.7)	2.53 d (18.6)	35.5	36.9
2b	2.86 dd (18.7, 6.2)	2.86 dd (18.6, 6.2)		
3	4.92 dd (6.1, 4.4)	4.92 dd (6.2, 4.3)	76.9	78.3
4	4.88 d (4.4)	4.88 d (4.3)	88.3	89.7
5	4.41 d (2.9)	4.41 d (2.9)	73.1	74.5
6	3.60 dd (7.8, 2.9)	3.61 dd (7.8, 2.9)	84.7	86.1
7	3.98 dq (7.7, 6.4)	3.99 dq (7.8, 6.3)	64.5	65.9
8	1.26 d (6.4)	1.27 d (6.3)	19.6	21.0

[a] Q. Li, A. Fu, J. Dong, Y. Xiao, B. Dai, M. Wei, Z. Huang, J. Liu, C. Chen, H. Zhu, Y. Lu, D. Li and Y. Zhang, *Fitoterapia* 2024, **173**, 105790.

Table S4. Selected structural parameters relevant for absolute structure assignment and correlation with NMR data have been extracted from the crystallographic model (Asperilactone B, **I**), after normalizing C–H bonds to distances established by neutron diffraction measurements.

Atoms	Distance, Å	*J*	Atoms	Torsion angle, °
H3···H4	2.34	4.4	H3–C3–C4–H4	−12
H4···H5	2.74	0	H4–C4–C5–H5	−90
H5···H6	2.39	2.9	H5–C5–C6–H6	−41
H6···H7	3.03	7.8 (7.7)	H6–C6–C7–H7	−179



II
Asperilactone C

Table S5. Comparison of NMR spectra Asperilactone C (**II**) with reported data ($CDCl_3$).[a]

C/H	Observed δ_H (*J*)	Reported[a] δ_H (*J*)	Observed δ_C	Reported[a] δ_C
1	-	-	175.0	176.1
2a	2.71 dd (18.5, 1.4)	2.68 d (18.5)	35.9	36.2
2b	2.77 dd (18.5, 4.8)	2.75 dd (18.5, 4.8)		
3	4.83 td (4.7, 4.6, 1.4)	4.80 t (4.6)	77.4	77.5
4	4.88 dd (4.5, 1.1)	4.85 d (4.3)	90.6	91.2
5	4.51 bdd (5.4, 1.7)	4.46 d (5.4)	77.1	76.0
6	3.64 t (5.7, 5.7)	3.63 t (5.4)	89.6	90.0
7	3.98 p (6.2, 6.1)	3.91 p (6.2)	67.8	67.5
2×OH	2.00 bs, 2.53 d (3.2)	-	-	-
8	1.30 d (6.4)	1.23 d (6.4)	19.7	19.4

[a] Q. Li, A. Fu, J. Dong, Y. Xiao, B. Dai, M. Wei, Z. Huang, J. Liu, C. Chen, H. Zhu, Y. Lu, D. Li and Y. Zhang, *Fitoterapia* 2024, **173**, 105790.

Table S6. Comparison of NMR spectra Asperilactone C (**II**) with reported data (CD_3OD).[a]

C/H	Observed δ_H (*J*)	Reported[a] δ_H (*J*)	Observed δ_C	Reported[a] δ_C
1			176.5	177.9
2a	2.58 d (18.4)	2.58 d (18.6)	35.7	37.0
2b	2.83 dd (18.2, 4.7)	2.84 dd (18.6, 4.6)		
3	4.79 overlap (4.2)	4.80 overlap	77.6	79.0
4	4.81 overlap (4.2)	4.81 overlap	91.2	92.5
5	4.36 d (4.7)	4.35 d (4.7)	75.3	76.6
6	3.62 t (5.0, 5.0)	3.62 t (5.0)	90.7	92.0
7	3.78 qd (6.5, 5.3)	3.78 qd (6.5, 5.2)	66.6	68.0
8	1.18 d (6.5)	1.18 d (6.5)	18.0	19.3

[a] Q. Li, A. Fu, J. Dong, Y. Xiao, B. Dai, M. Wei, Z. Huang, J. Liu, C. Chen, H. Zhu, Y. Lu, D. Li and Y. Zhang, *Fitoterapia* 2024, **173**, 105790.