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SUPPORTING INFORMATION

Synthesis of the Aglycon of Aspafiliosides E and F Based on Cascade Reactions

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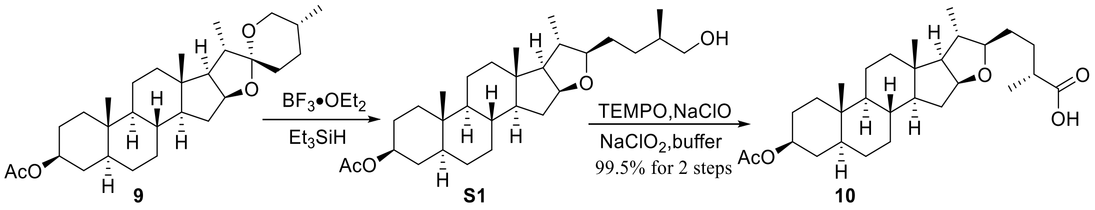
Experimental Procedures and Characterization Data

General Methods: All reactions sensitive to air or moisture were performed in flame-dried round bottom flasks with rubber septum under a positive pressure of argon or nitrogen atmosphere, unless otherwise noted. Air and moisture-sensitive liquids and solutions were transferred via syringe and stainless steel cannula. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium/benzophenone, methylene chloride (DCM), toluene, and 2,6-lutidine from calcium hydride, *N,N*-dimethylformamide (DMF) and dimethylsulfoxide from calcium hydride under reduced pressure, acetone from K_2CO_3 onto activated 3Å molecular sieves, others according to the standard procedures described in *Purification of Laboratory Chemicals* (2009). Yields refer to chromatographically and spectroscopically (^1H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates using UV light as visualizing agent and an ethanolic solution of phosphomolybic acid, and heat as developing agents. NMR spectra were recorded on Bruker DRX-400 instrument and calibrated using residual undeuterated solvent as an internal reference [^1H NMR: $CHCl_3$ (7.26), C_6HD_5 (7.16), DMSO-d_6 (2.50); ^{13}C NMR: $CDCl_3$ (77.16), C_6D_6 (128.06)]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad.

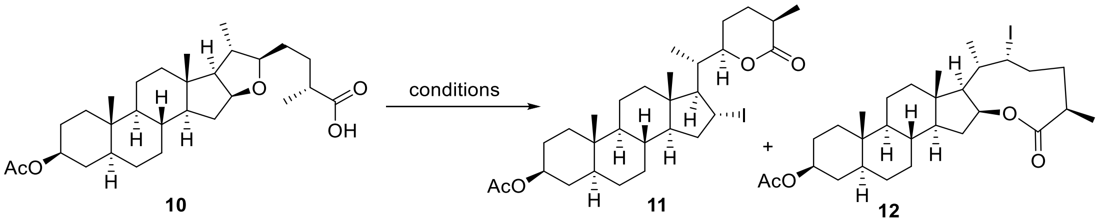


Under a positive pressure of nitrogen, to a solution of tigogenin acetate **9** (2.75 g, 6 mmol) and Et_3SiH (1.9 mL, 12 mmol) in dried CH_2Cl_2 (40 mL) was added boron trifluoride diethyl etherate (1.25 mL, 12 mmol) dropwise at 0 °C. The resulting mixture was warmed to room temperature, stirred for 12 h, quenched with saturated aqueous $NaHCO_3$, diluted with water, and extracted with CH_2Cl_2 (50 + 30 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude **S1** was used in next step without purification.

To a mixture of crude **S1**, TEMPO (46 mg, 0.30 mmol), MeCN (30 mL), and solium phosphate buffer (25 mL) were added an aqueous solution of $NaClO_2$ (1.02 g, 12 mmol, in 5 mL water) and dilute bleach (0.5 mL in 5 mL water) separately.[1] The orange solution was stirred at ambient temperature for 3 h, quenched with cold Na_2SO_3 solution, and extracted with $CHCl_3$ (60 + 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated to afford **10** (2.88 g , 99.5% from **9**) as white solid. The crude **10** does not need purification for further use.

S1 (Known compound)[2]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.73 – 4.62 (m, 1H), 4.28 (dd, *J* = 13.0, 7.4 Hz, 1H), 3.47 (dd, *J* = 10.4, 6.2 Hz, 1H), 3.40 (dd, *J* = 10.5, 6.2 Hz, 1H), 3.32 (td, *J* = 7.8, 4.2 Hz, 1H), 2.99 (s, 1H), 2.01 (s, 3H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.84 (s, 3H), 0.79 (s, 3H), 0.66 (td, *J* = 15.6, 6.6 Hz, 1H).

10 (Known compound): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75 – 4.60 (m, 1H), 4.31 (dd, *J* = 13.1, 7.4 Hz, 1H), 3.34 (t, *J* = 7.7 Hz, 1H), 2.52 (s, 1H), 2.01 (s, 3H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.83 (s, 3H), 0.76 (s, 3H).



Entries	Conditions	Yields
1	TFAA, TBAI (2 eq), CH_2Cl_2, 0 ℃ to rt, 23 h	**11**, 78%; **12**, 6.5%
2	TFAA, LiI (4 eq), TBAI (0.5 eq), CH_2Cl_2/MeCN (4/1), 0 ℃ to rt, 8 h	**11**, 89%; **12**, 3.8%
3	TFAA, LiI (3 eq), CH_2Cl_2/MeCN (4/1), 0 ℃ to rt, 2.5 h	**11**, 88%; **12**, 7.8%
4	TFAA, NaI (3 eq), CH_2Cl_2/MeCN (4/1), 0 ℃ to rt, 6 h	**11**, 87%; **12**, 11.6%
5	TFAA, LiBr (3 eq), CH_2Cl_2/MeCN (4/1), 0 ℃ to rt, 6 h	C16-Br-**11**, 86%; C22-Br-**12**, 8.7%

Under a positive pressure of nitrogen, to a solution of **10** (238 mg 0.5 mmol) and sodium iodide (225 mg, 1.5 mmol) in CH_2Cl_2/MeCN (4 mL/1 mL) was added $(CF_3CO)_2O$

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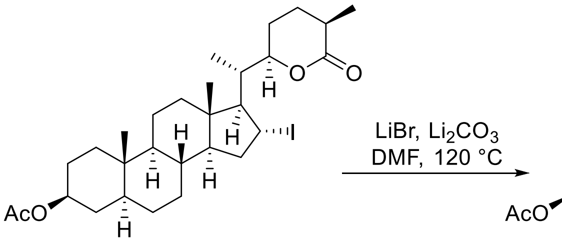
[1] Zhao, M.; Li, J.; Mano, E.; Song, Z.; Tschaen, D. M.; Grabowski, E. J. J.; Reider, P. J., Oxidation of Primary Alcohols to Carboxylic Acids with Sodium Chlorite Catalyzed by TEMPO and Bleach. *J. Org. Chem.* **1999,** *64* (7), 2564-2566.

[2] Seo, S.; Uomori, A.; Takeda, K. I., Direct observation of the reverse 1,5-hydride shift: the mechanism of acid-catalyzed isomerization at C-25 of spirostanols. *J. Org. Chem.* **1986,** *51* (20), 3823-3827.

(TFAA, 0.15 mL, 1.0 mmol) at 0 ℃. The resulting mixture was vigorously stirred at ambient temperature for 2.5 h, quenched with saturated aqueous $NaHCO_3$ and saturated aqueous Na_2SO_3, diluted with water, and extracted with CH_2Cl_2 (30 + 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and purified by silica gel column chromatography (PE/EA=7:1 to 6:1 to 3:1) to give **11** (253 mg, 87%) as white solid and **12** (34mg, 12%) as foam.

11: mp 165.5-166.4 ℃; $[\alpha]_D^{24}$ -2.13 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.76 – 4.64 (m, 2H), 4.08 (t, *J* = 7.6 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.27 (dd, *J* = 14.4, 6.1 Hz, 1H), 2.02 (s, 3H), 1.23 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.81 (s, 3H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 170.8, 79.7, 73.7, 65.0, 53.9, 53.1, 45.6, 44.6, 41.8, 39.9, 39.5, 36.8, 35.6, 34.3, 34.0, 33.2, 31.9, 28.9, 28.4, 27.5, 25.2, 21.6, 21.1, 20.8, 16.5, 13.9, 12.7, 12.3; IR 2968.6, 2929.6, 2868.4, 2849.5, 1742.1, 1731.1, 1449.2, 1363.0, 1042.6 cm^{-1}; ESI-MS: 457.2 $[M-I^-]^+$; HRMS (MADAI) $(M-I+Na)^+$ calculated for $C_{29}H_{44}O_4$ 479.3131, found 479.3145.

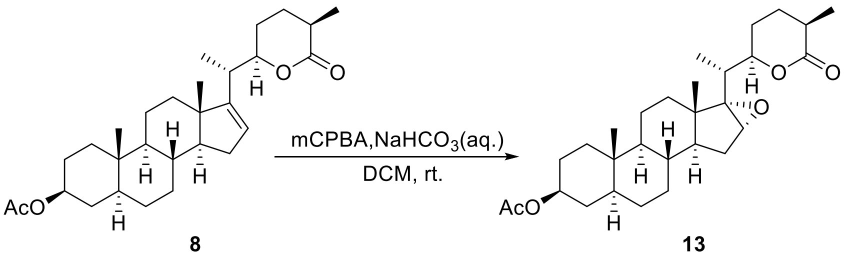
12: ^1H NMR (400 MHz, $CDCl_3$) δ 5.31 (dd, *J* = 14.4, 8.2 Hz, 1H), 4.75 – 4.63 (m, 1H), 4.34 – 4.21 (m, 1H), 2.55 – 2.39 (m, 1H), 2.02 (s, 3H), 1.19 (d, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 6.5 Hz, 3H), 0.91 (s, 4H), 0.83 (s, 3H), 0.67 (td, *J* = 11.9, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 170.8, 76.3, 73.7, 58.6, 54.0, 53.8, 44.6, 42.8, 42.2, 41.6, 39.6, 39.4, 36.8, 35.6, 34.9, 34.1, 34.1, 32.9, 32.0, 30.7, 28.5, 27.5, 24.1, 21.6, 20.9, 18.6, 13.5, 12.3; ESI-MS: 457.2, $[M-I]^+$.



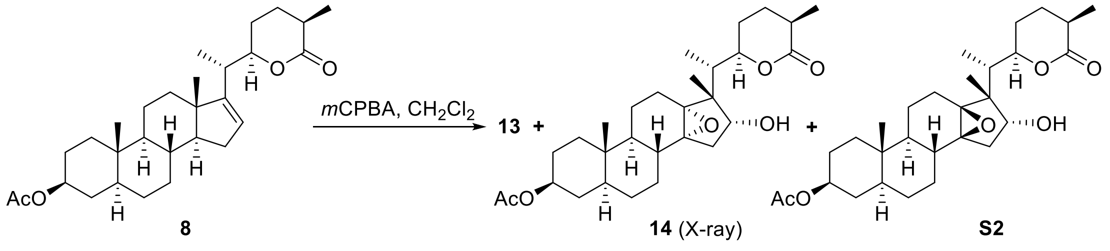
11 **8**

Under nitrogen, to a solution of **11** 3.5 g (6 mmol) in DMF (50 mL) were added lithium carbonate (1.45 g, 18 mmol) and lithium bromide (1.3 g, 12 mmol). The mixture was stirred at 120 ℃ for 8 h and concentrated under reduced pressure to remove the solvent. The residue was diluted with water and extracted with CH_2Cl_2 (100 + 80 mL); the combined oganic layers were washed with brine, dried over sodium sulfate, filtered, concentrated in vacuo, and purified through silica gel chromatography (PE/EA: 8/1) to give **8** (2.63 g, 96.3%) as white solid.

mp 144.3-145.5 ℃; $[\alpha]_D^{24}$ -13.85(*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 1H), 4.74 – 4.63 (m, 1H), 4.42 – 4.31 (m, 1H), 2.66 – 2.53 (m, 1H), 2.52 – 2.41 (m, 1H), 2.02 (s, 3H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.85 (s, 3H), 0.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 170.8, 155.9, 124.2, 80.6, 73.8, 57.4, 54.9, 47.3, 45.0, 36.7, 36.4, 35.8, 34.9, 34.2, 34.1, 33.2, 31.9, 31.3, 28.6, 27.6, 25.7, 22.9, 21.6, 21.1, 16.6, 16.6, 16.4, 12.3; IR: 2926.7, 2851.2, 1737.3, 1456.2, 1376.7, 1245.9, 1026.6 cm^{-1}; ESI-MS: 457.3 $[M+H]^+$; HRMS (MALDI) $(M+Na)^+$ calculated for $C_{29}H_{44}O_4$ 479.3155, found 479.3149.



To a solution of **8** (913 mg, 2 mmol) in DCM (20 mL) were added saturated aqueous $NaHCO_3$ (8 mL) and *m*CPBA (863 mg, 4 mmol). The mixture was stirred at room temperature for 6 h, quenched with saturated aqueous Na_2SO_3, and extracted with CH_2Cl_2 (40 + 20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA: 4/1) to give **13** (723 mg, 76.5%). mp 191.8-192.6 ℃; $[\alpha]_D^{25}$ -40.67 (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.73 – 4.62 (m, 1H), 3.92 – 3.82 (m, 1H), 3.35 (s, 1H), 2.54 (dd, *J* = 16.8, 7.3 Hz, 1H), 2.39 – 2.28 (m, 1H), 2.02 (s, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 4H), 0.86 (s, 4H), 0.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 170.8, 77.8, 73.8, 71.5, 61.9, 54.7, 44.9, 44.9, 42.8, 36.8, 35.7, 34.8, 34.1, 34.0, 33.5, 33.2, 31.7, 28.6, 27.6, 25.6, 24.3, 21.6, 21.1, 16.3, 16.3, 12.5, 12.3; IR: 2921.8, 2851.7, 1750.2, 1732.4, 1456.0, 1378.9, 1260.5, 1197.9, 1025.9 cm^{-1}; ESI-MS: 473.1 $[M+H]^+$; HRMS (MALDI) $(M+Na)^+$ calculated for $C_{29}H_{44}O_5$ 495.3081, found 495.3089.



To a solution of **8** (645 mg, 1.41 mmol) in DCM (20 mL) was added *m*-CPBA (763 mg, 3.5 mmol). The mixture was stirred at room temperature for 24 h, quenched with saturated aqueous Na$_2$SO$_3$, and extracted with CH$_2$Cl$_2$ (40 + 20 mL). The combined organic layers were washed with brine, dried over a$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA: 4/1 to 2/1) to give **13** (238 mg, 35.7%), **14** (301 mg, 43.7%), and **S2** (40 mg, 5.8%)

14: mp = 173.1-174.6 ˚C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.76 (t, *J* = 8.4 Hz, 1H), 4.72 – 4.63 (m, 1H), 3.83 (dd, *J* = 11.7, 4.9 Hz, 1H), 2.67 (d, *J* = 11.7 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.02 (s, 3H), 1.20 (d, *J* = 6.7 Hz, 3H), 1.14 (d, *J* = 7.3 Hz, 3H), 1.07 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 176.5, 170.8, 80.6, 77.5, 74.5, 73.5, 69.8, 51.7, 46.1, 43.9, 43.3, 38.5, 38.3, 36.9, 35.2, 33.9, 33.0, 28.6, 28.4, 27.4, 25.8, 25.3, 24.5, 23.7, 23.2, 21.6, 16.2, 14.9, 11.5; IR: 3520.9, 2928.7, 2870.5, 1738.1, 1732.0, 1244.1, 1051.8, 1020.7 cm^{-1}; ESI-MS: 511.1 [M+Na]$^+$; HRMS (MALDI) (M+Na)$^+$ calculated for C$_{29}$H$_{44}$O$_6$ 511.3030, found 511.3035.

S2: ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.87 (dd, *J* = 10.5, 4.5 Hz, 1H), 4.74 – 4.63 (m, 1H), 3.82 (t, *J* = 7.9 Hz, 1H), 2.65 – 2.53 (m, 1H), 2.33 (dd, *J* = 13.7, 8.0 Hz, 1H), 2.02 (s, 3H), 1.23 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 7.5 Hz, 3H), 0.74 (s, 3H), 0.66 (t, *J* = 11.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 177.0, 170.9, 80.2, 79.9, 73.6, 72.7, 70.5, 51.2, 47.55, 44.57, 42.38, 38.79, 36.88, 36.33, 35.93, 33.69, 32.89, 30.17, 29.07, 27.31, 25.69, 24.77, 23.13, 21.54, 20.82, 18.38, 16.15, 12.37, 11.69; IR: 3466.2, 2932.0, 2855.1, 1731.7, 1377.7, 1244.9, 1066.7, 1027.7 cm^{-1}; ESI-MS: 511.5 [M+Na]$^+$; HRMS (MALDI) (M+Na)$^+$ calculated for C$_{29}$H$_{44}$O$_6$ 511.3030, found 511.3022.

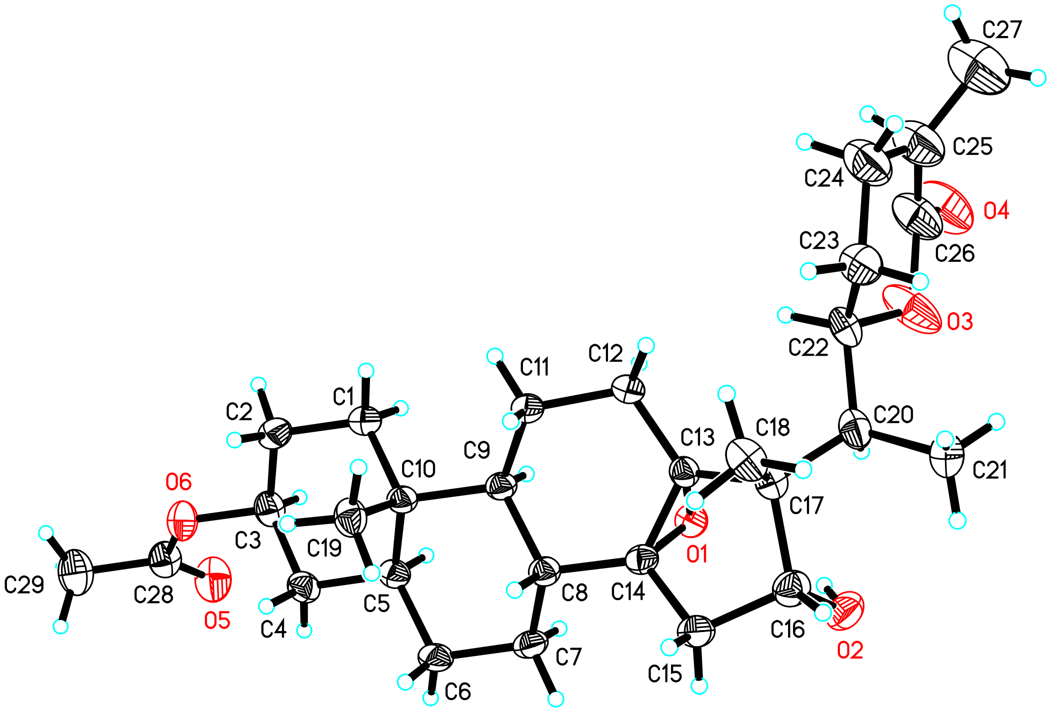
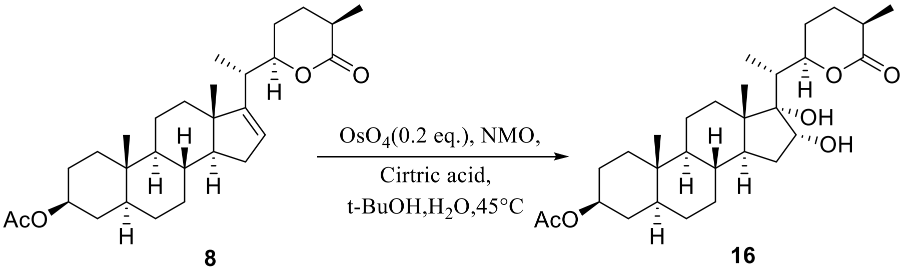

C27
C25
C24
O4
C23
C26
O3
C22
C12
C11
C1
C20
C2
C18
C13
C21
C10
C9
C17
O6
C3
C19
O1
C29
C28
C5
C8
C14
O5
C4
C16
C7
O2
C6
C15

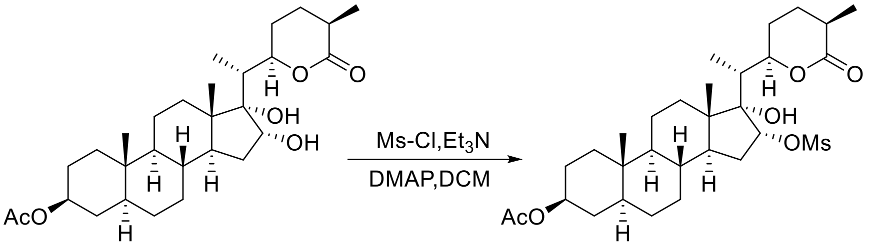
Table 1. Crystal Data and Structure Refinement for **14**

Empirical formula	$C_{29}H_{44}O_6$
Formula weight	488.64
Temperature (K)	293(2)
wavelength	0.71073 A
Crystal system , Space group	Monoclinic , *P*2(1)
Unit cell dimensions	*a* (Å) = 9.9607 (10), α (deg) = 90
	b (Å) = 7.2910 (8), β (deg) = 91.928(2)
	c (Å) = 18.5284 (19),γ (deg) = 90
Volume (Å^3)	1339.9 (2)
Z, Calculated density (g/cm^3)	2, 1.211
Absorption coefficient (mm^-1)	0.071
F(000)	532
Crystal size (mm)	0.211* 0.154 * 0.117
The Range for data collection (deg)	2.05 - 25.99
Limiting indices	$-11\leq h\leq 12$, $-8\leq k\leq 8$, $-22\leq l\leq 21$
Reflections collected/ unique	8136/ 4367 [R(int) = 0.0290]
Completeness to theta = 27.00	99.9%
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.68398
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/ parameter	4763/ 55 /368
Goodness-of-fit on F^2	1.035
Final R ($I > 2\sigma(I)$)	R_1= 0.0583, wR_2= 0.1516
R indices (all data)	R_1= 0.0638, wR_2= 0.1574
Absolute structure parameter	-1.8 (14)
Largest diff. peak and hole (e.Å^{-3})	0.215 and -0.242



To a solution of cirtric acid (2.52 g, 13 mmol) and **8** (2.0 g, 4.38 mmol) in *t*-BuOH/water (30 mL/10 mL) were added OsO_4 (11.2 mL, 2.5 wt% in *t*-BuOH, 0.90 mmol) and NMO (5.5 mL, 50% aqueous solution, 26.2 mmol). The mixture was stirred at 45 ℃ for 48 h, quenched with saturated aqueous Na_2SO_3, and extracted with $CHCl_3$ (150 + 50 mL). The combined organic layers were washed with brine, dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The crude product (2.10 g) was purified through flash column chromatography on silica gel (PE/EA: 2/1 to 1/1) to give **16** (1.78 g, 83%) as white solid.

mp 213.7–214.6 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ 4.73 – 4.63 (m, 1H), 4.57 (dd, *J* = 10.1, 4.5 Hz, 1H), 4.28 (d, *J* = 6.8 Hz, 1H), 2.80 (s, 2H), 2.62 (dd, *J* = 15.1, 8.0 Hz, 1H), 2.13 (dd, *J* = 12.9, 6.7 Hz, 1H), 2.02 (s, 5H), 1.21 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.81 (s, 3H), 0.79 (s, 3H), 0.72 – 0.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 170.9, 82.9, 80.0, 76.0, 73.8, 53.6, 49.2, 48.5, 44.7, 43.5, 36.7, 35.9, 35.5, 35.3, 34.1, 33.3, 33.2, 32.0, 28.6, 27.5, 25.9, 23.8, 21.6, 20.7, 16.3, 14.8, 12.3, 10.3; IR: 3449.6, 2933.8, 2868.9, 1732.3, 1462.0, 1378.5, 1247.4, 1029.6 cm^{-1}; ESI-MS: 513.3 $[M+Na]^+$; HRMS (MALDI) $(M+Na)^+$ calculated for $C_{29}H_{46}O_6$ 513.3186, found 513.3192.

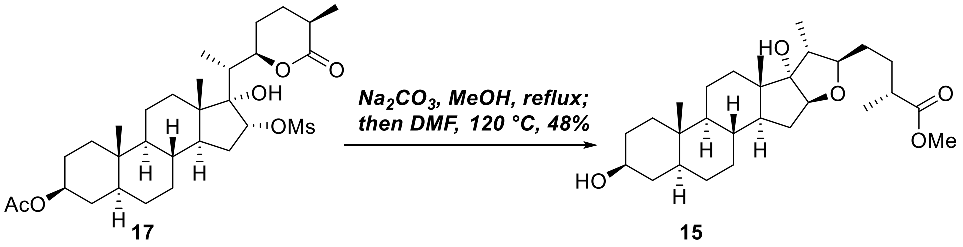


16 **17**

To a solution of **16** (596 mg, 1.2 mmol), DMAP (15 mg, 0.12 mmol) and Et_3N (0.85 mL, 6 mmol) in DCM (15 mL) was added MsCl (160 μL, 1.6 mmol) at 0 ℃. The mixture was stirred at ambient temperature for 5 h, quenched with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (40 + 20 mL). The combined organic layers were washed with brine, dried over $NaSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA: 5/1) to give **17** (648 mg, 95%).

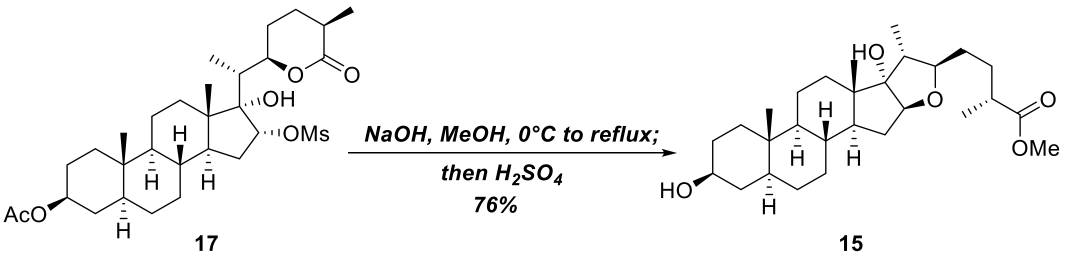
^1H NMR (400 MHz, $CDCl_3$) δ 5.16 (d, *J* = 6.4 Hz, 1H), 4.74 (dt, *J* = 11.8, 3.2 Hz, 1H), 4.70– 4.63 (m, 1H), 3.08 (s, 3H), 2.74 – 2.64 (m, 1H), 2.41 – 2.32 (m, 1H), 2.11 (dt, *J* = 16.0, 8.3 Hz, 1H), 2.02 (s, 3H), 1.18 (d, *J* = 6.7 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 0.82 (s, 3H), 0.80 (s, 3H), 0.70 (td, *J* = 12.6, 3.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 177.1, 170.8, 85.4, 84.2, 78.2, 73.6, 53.6, 48.8, 48.6, 44.7, 42.1, 39.8, 36.7, 35.5, 35.3, 34.0, 32.9, 32.9, 32.4, 32.0, 28.4, 27.5, 25.7, 22.9, 21.6, 20.6, 16.1, 15.4, 12.3, 8.8; IR: 3519.0, 2926.3, 2865.9, 2853.9, 1732.3, 1462.6, 1349.2, 1248.7, 1175.2 cm^{-1}; ESI-MS: 591.0, [M+Na]$^+$; HRMS (MALDI) (M+Na)$^+$ calculated for $C_{30}H_{48}O_8S$ 591.2962, found 591.2964.

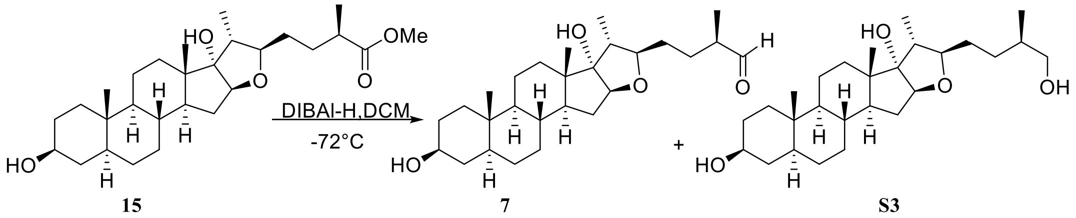


To a solution of **17** (142 mg, 0.25 mmol) in CH_3OH (5 mL), sodium carbonate (106 mg, 1 mmol) was added, the mixture was heated to reflux for 12 h. Then CH_3OH was removed in vacuo, and DMF (4 mL) was added, the resulting solution was heated to 120 ˚C for 12 h, then DMF was removed under reduced pressure, the residue was diluted with water, and extracted with CH_2Cl_2 (30 + 10 mL), washed with brine, dried over sodium sulfate. After removal of the organic solvents under reduced pressure, the residue was subjected to silica gel chromatography (PE/EA = 3:1 to 2:1) to give desired **15** (55 mg, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.85 (t, *J* = 6.8 Hz, 1H), 3.67 (s, 3H), 3.64 – 3.54 (m, 1H), 3.49 (td, *J* = 9.0, 2.8 Hz, 1H), 2.46 (dd, *J* = 13.9, 7.0 Hz, 1H), 2.11 – 2.02 (m, 1H), 1.90 (td, *J* = 14.0, 6.9 Hz, 1H), 1.16 (d, *J* = 7.0 Hz, 4H), 0.86 (d, *J* = 6.9 Hz, 4H), 0.82 (s, 3H), 0.80 (s, 3H), 0.64 (td, *J* = 11.0, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 91.6, 91.2, 88.9, 71.4, 54.0, 52.5, 51.7, 45.0, 44.9, 41.1, 39.8, 38.3, 37.1, 35.7, 35.7, 32.2, 32.0, 31.6, 31.2, 31.2, 30.7, 28.7, 20.7, 17.4, 17.3, 12.5, 11.4; IR: 3406.1, 2954.8, 2923.7, 2852.3, 1738.1, 1462.9, 1377.1, 1186.4, 1155.3 cm^{-1}; ESI-MS: 463.3 [M+H]$^+$, 485.4 [M+Na]$^+$; HRMS (MALDI) (M+Na)$^+$ calculated for $C_{28}H_{46}O_5$ 485.3237, found 485.3257.



To a solution of **17** (142 mg, 0.25 mmol) in CH_3OH (8 mL) was added NaOH (200 mg, 5 mmol) at 0 ℃. The mixture was stirred at 0 ℃, and after TLC indicated complete conversion of the starting material, was heated to reflux for 5 h. Then the mixture was cooled to 0 ℃ and was added concentrated sulfuric acid (0.35 mL, 6.4 mmol) dropwise, and stirred at ambient temperature for 2 h and quenched with saturated aqueous Na_2CO_3 and extracted with $CHCl_3$ (30 + 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated at reduced pressure. Purification of the residue by flash column chromatography on silica gel (PE/EA: 2/1) provided **15** (87 mg, 75%). This method may caused slight isomerization of C25, which would be restalled in the following steps.

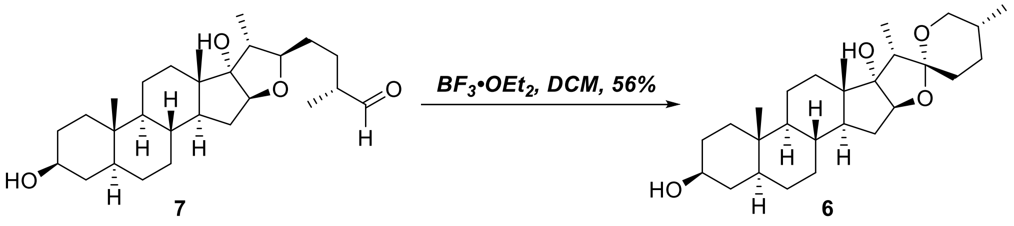


Under argon, to a solution of **15** (87 mg, 0.188 mmol) in DCM (5 mL) was added DIBAL-H (0.6 mL, 1 M in hexane, 0.6 mmol) dropwise at -72 ℃. The mixture was stirred at -72 ℃ for 40 min, quenched with CH_3OH (2 mL), warmed to ambient temperature. After its pH value was adjusted with HCl (1.2 N) to 2, the mixture was extracted with $CHCl_3$ (30 + 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the residue by flash column chromatography on silica gel (PE/EA: 3/1 to 1/1) gave **7** (68 mg, 83.7%) and over reduced product **S3** (12 mg, 14.7%).

7： ^1H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 3.86 (t, J = 6.8 Hz, 1H), 3.63 – 3.55 (m, 1H), 3.51 (t, J = 8.2 Hz, 1H), 2.38 (dd, J = 12.9, 6.4 Hz, 1H), 1.10 (d, J = 6.9 Hz, 3H), 0.87 (d, J = 6.9 Hz, 3H), 0.82 (s, 3H), 0.80 (s, 3H), 0.69 – 0.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3, 91.6, 91.2, 88.7, 88.6, 71.3, 54.1, 52.5, 46.4, 46.4, 45.0, 44.9, 41.0, 41.0, 38.2, 37.2, 35.6, 32.2, 32.0, 31.5, 31.2, 30.6, 28.6, 27.3, 20.7, 17.3, 13.5, 12.5, 11.3; IR: 3458.5, 3339.1, 2953.9, 2923.8, 2851.4, 1733.4, 1717.6, 1457.8, 1376.8 cm^{-1}; ESI-MS: 455.2 $[M+Na]^+$; HRMS (MALDI) $(M+Na)^+$ calculated for $C_{27}H_{44}O_4$ 455.3131, found 455.3133.

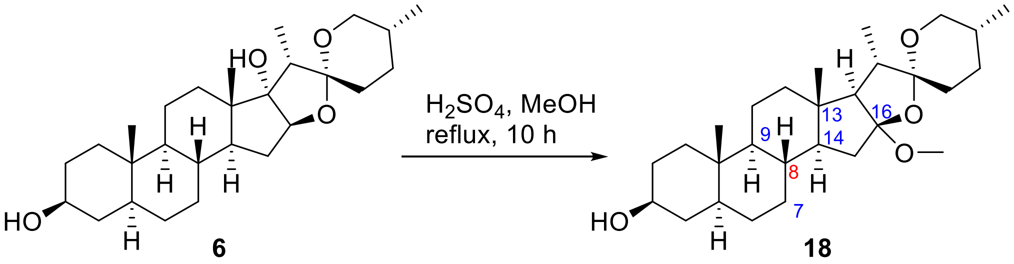
S3: ^1H NMR (400 MHz, $CDCl_3$) δ 3.86 (t, J = 6.8 Hz, 1H), 3.59 (td, J = 10.7, 5.2 Hz, 1H), 3.54 – 3.41 (m, 3H), 2.11 – 2.02 (m, 1H), 1.98 – 1.88 (m, 1H), 0.92 (d, J = 6.7 Hz, 3H), 0.87 (d, J = 6.8 Hz, 4H), 0.82 (s, 3H), 0.81 (s, 3H), 0.66 (td, J = 10.9, 3.6 Hz, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 91.6, 91.6, 91.2, 89.5, 89.3, 71.4, 68.2, 68.1, 54.0, 52.5, 45.0, 44.9, 41.1, 38.3, 37.1, 36.1, 35.9, 35.7, 35.7, 32.2, 32.0, 31.6, 31.2, 30.7, 30.5, 29.8, 29.7, 28.7, 20.7, 17.4, 16.9, 16.7, 12.5, 11.4, 11.4; IR: 3397.5, 2923.9, 2851.5, 1458.4, 1377.3 cm^{-1}; ESI-MS: 435.3 [M+H]$^+$; HRMS (MALDI) (M+H)$^+$calculated for $C_{27}H_{47}O_4$ 435.3469, found 435.3463.



(sapogenin of aspafilioside E, F)

To a solution of **7** (34 mg, 0.078 mmol) in dried CH_2Cl_2 (2 mL) was added $BF_3 \cdot OEt_2$ (50 µL, 0.4 mmol) at ambient temperature. The mixture was stirred 6 h, quenched with water, added HCl (1.2 N, 0.1 mL), stirred for 1 h, and extracted with $CHCl_3$ (25 + 15 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography on silica gel (PE/EA: 3/1) afforded **6** (19 mg, 56%). $[\alpha]_D^{24.8}$ -57.08 (*c* 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (t, J = 7.6 Hz, 1H), 3.62 – 3.55 (m, 1H), 3.50 (dd, J = 10.4, 2.6 Hz, 1H), 3.37 (t, J = 10.8 Hz, 1H), 2.04 (dq, J = 21.0, 7.1 Hz, 2H), 0.89 (d, J = 7.1 Hz, 3H), 0.82 (s, 3H), 0.80 (d, J = 4.8 Hz, 3H), 0.79 (s, 3H), 0.69 (td, J = 11.6, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 110.2, 91.1, 90.2, 71.4, 67.0, 54.1, 52.8, 44.9, 44.8, 44.2, 38.3, 37.1, 35.7, 35.3, 32.3, 32.0, 31.6, 31.2, 30.9, 30.2, 28.7, 28.2, 21.0, 17.4, 17.2, 12.5, 8.2; IR: 3366.9, 2954.8, 2924.5, 2853.3, 1457.6, 1376.8, 1154.6 cm^{-1}; ESI-MS: 455.3, [M+Na]$^+$; HRMS (MALDI) (M+Na)$^+$ calculated for $C_{27}H_{44}O_4$ 455.3131, found 455.3122.



A solution of **6** (42 mg, 0.098 mmol) in MeOH (5 mL) was treated with 1M H_2SO_4 (10 mL), and the mixture was heated to reflux for 10 h. The reaction mixture was neutralized with a saturated aqueous solution of Na_2SO_4 and extracted with $CHCl_3$ (20 mL*3). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the crude product by flash column chromatography on silica gel (PE/EA: 6/1 to 3/1, 5% CH_2Cl_2) afforded **18** (20 mg, 46%) as white powder. $[\alpha]_D^{25}$ -21.8 (*c* 0.10, MeOH/$CHCl_3$, ref.[3] -23 (*c* 0.10, MeOH/$CHCl_3$)); ^1H NMR (400 MHz, pyridine-d5) δ 3.82-3.92 (m, 1H), 3.72-3.78 (m, 1H), 3.63-3.70 (m, 1H), 2.20-2.26 (m, 1H), 1.21 (d, *J* = 6.6 Hz, 3H), 0.84 (s, 3H), 0.82 (s, 3H); ^{13}C NMR (100 MHz, pyridine-d5, the biggest chemical shift (119.66 ppm) was set as 119.3 ppm for comparison) δ 119.3, 111.0, 70.5, 70.2, 68.8, 55.3, 54.5, 50.6, 45.1, 42.7, 41.2, 40.1, 39.3, 37.4, 35.9, **34.8**[4], 34.5, 34.0, 32.5, 32.4, 30.6, 29.5, 29.0, 21.3, 17.4, 15.8, 15.7, 12.5; IR: 2926, 1448, 1385, 1247, 1045, 977, 890, 878 cm^{-1};ESI-MS: 469.3 $[M+Na]^+$.

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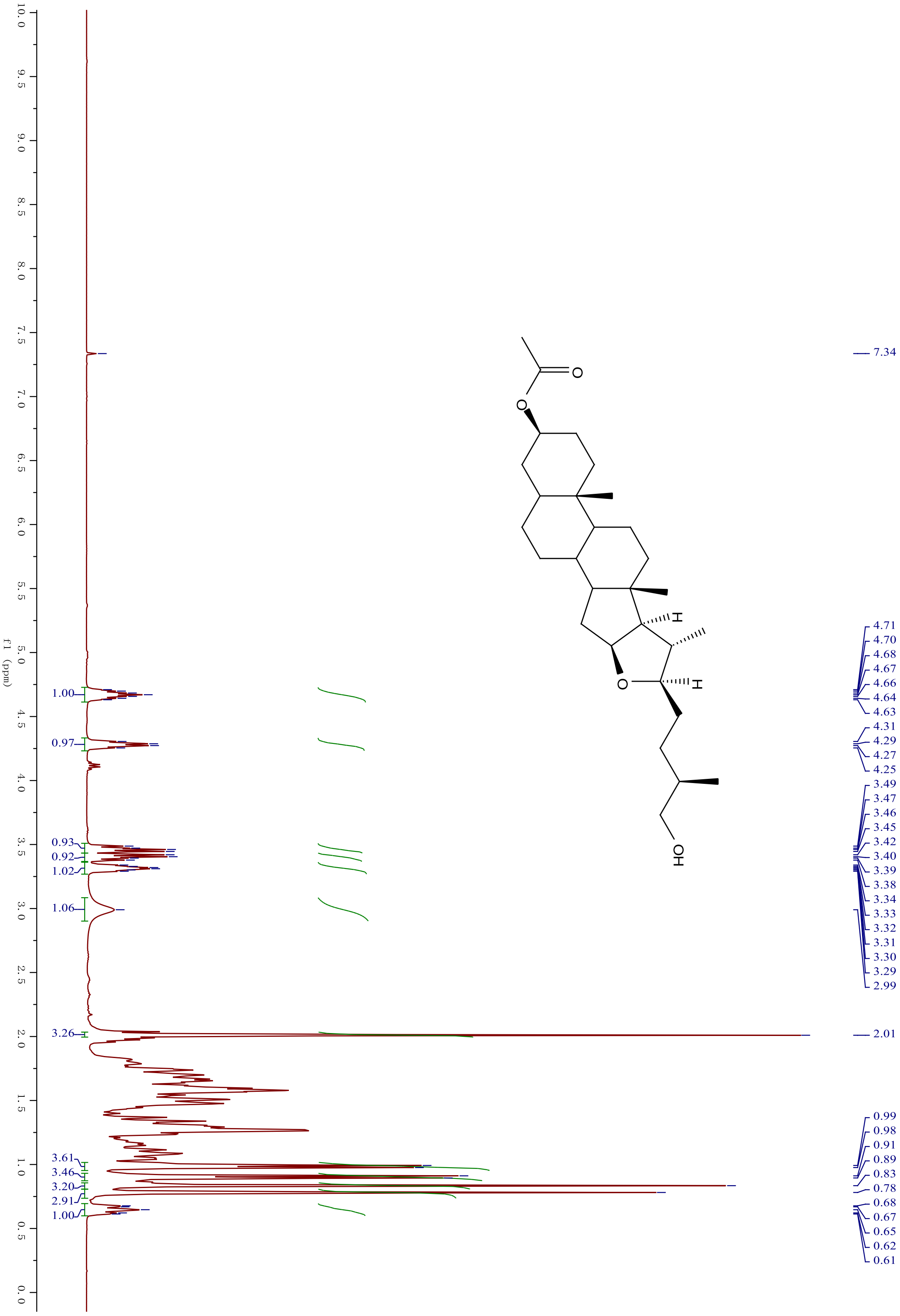
[3] Zhou, L.-B.; Chen, D.-F. Steroidal saponins from the roots of Asparagus filicinus. *Steroids* **2008,** *73, (1),* 83-87

[4] All the NMR data matched those reported except the ^{13}C NMR chemical shift of C8. The reason was unknown.

	^{1}H NMR reported **18**	^{13}C NMR reported **18**	^{1}H NMR synthesized **18**	^{13}C NMR synthesized **18**
1	0.94 m, 1.70 m	37.4		37.4
2	1.70 m, 2.08 m	32.5		32.5
3	3.87 m	70.5	3.87 m (3.82-3.92)	70.5
4	1.61 m, 1.83 m	39.3		39.3
5	1.14 m	45.1		45.1
6	1.27 m	29.0		29.0
7	0.89 m, 1.63 m	32.4		32.4
8	**1.34 m**	**30.0**		**34.8**
9	0.61 m	54.8	0.61 m	54.5
10	--	35.9		35.9
11	1.30 m, 1.52 m	21.3		21.3
12	1.23 m, 1.72 m	40.1		40.1
13	--	41.2		41.2
14	1.50 m	55.4		55.3
15	1.40 m, 2.23 m	34.0	2.23 m (2.20-2.26)	34.0
16	--	119.3		119.3
17	2.10 m	70.2		70.2
18	0.84 s	15.8	0.84 s	15.8
19	0.82 s	12.5	0.82 s	12.5
20	2.11 m	42.7		42.7
21	1.21 d (6.6)	15.7	1.21 d (6.6)	15.7
22	--	111.0		111.0
23	1.70 m, 1.78 m	34.5		34.5
24	1.63 m	29.5		29.5
25	1.63 m	30.6		30.6
26	3.69 m, 3.75 m	68.8	3.72-3.78 m 3.63-3.70 m	68.8
27	0.75 d (5.6)	17.4	0.75 d (5.6)	17.4
OMe	3.48 s	50.6	3.48 s	50.6



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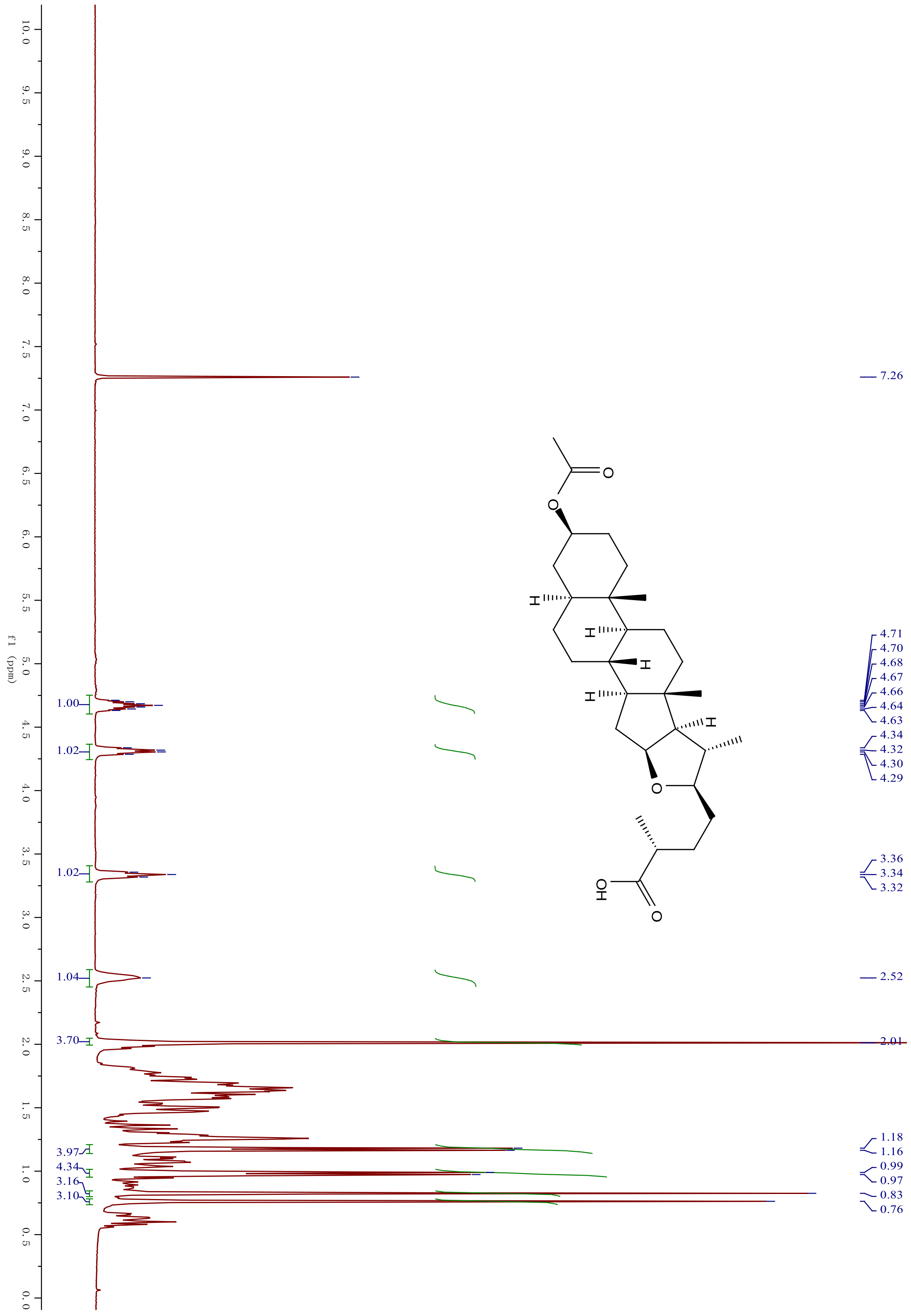
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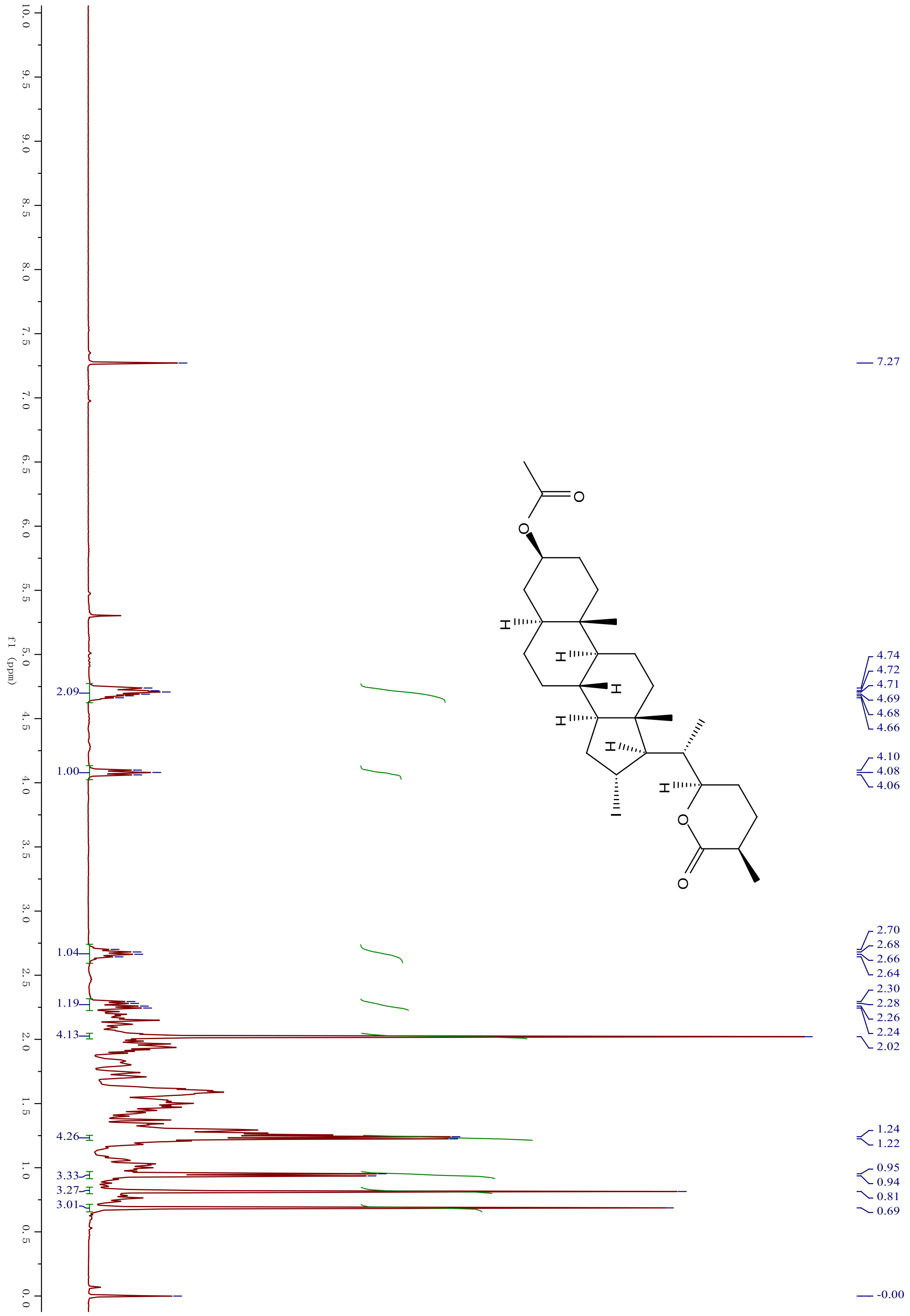

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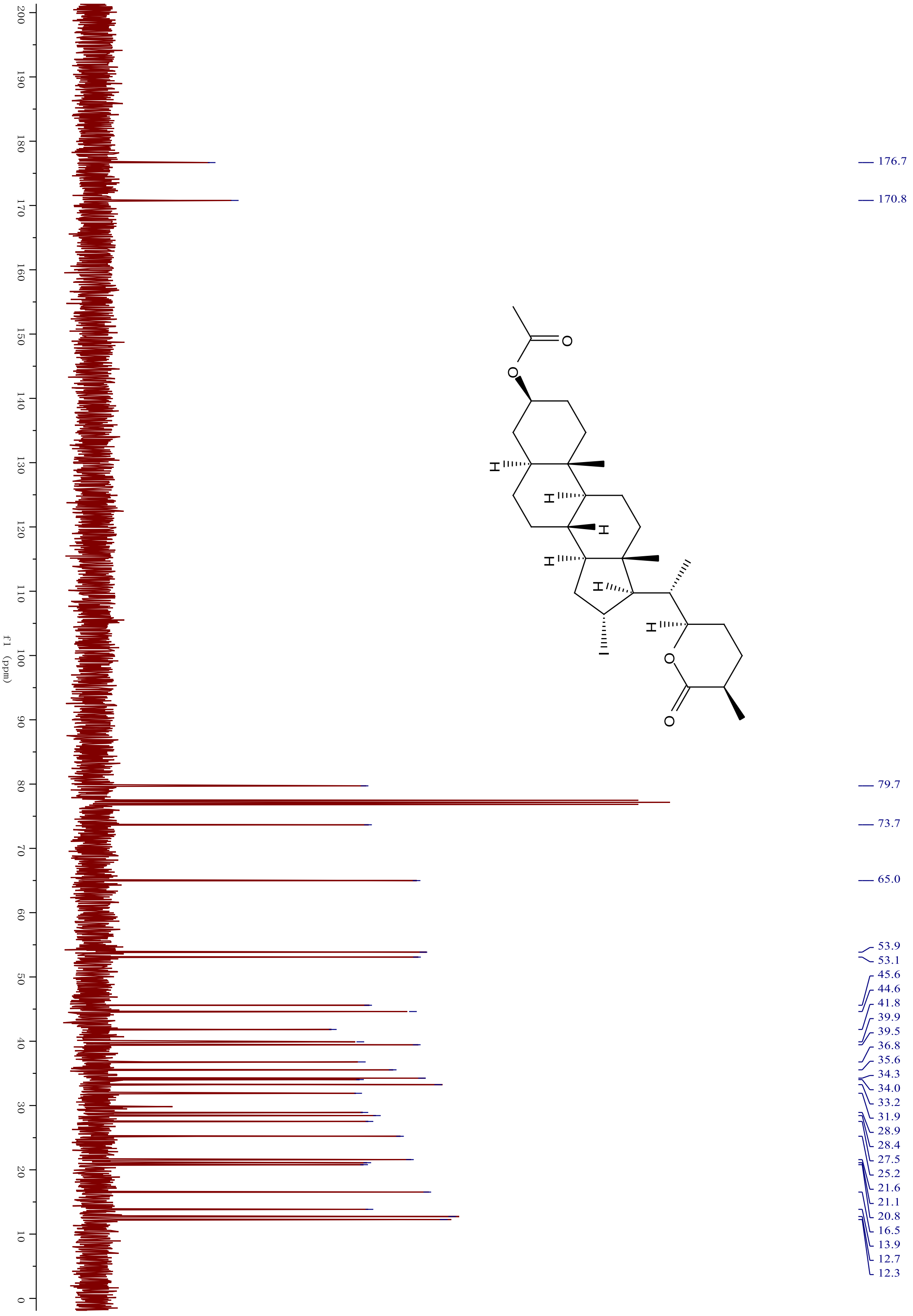
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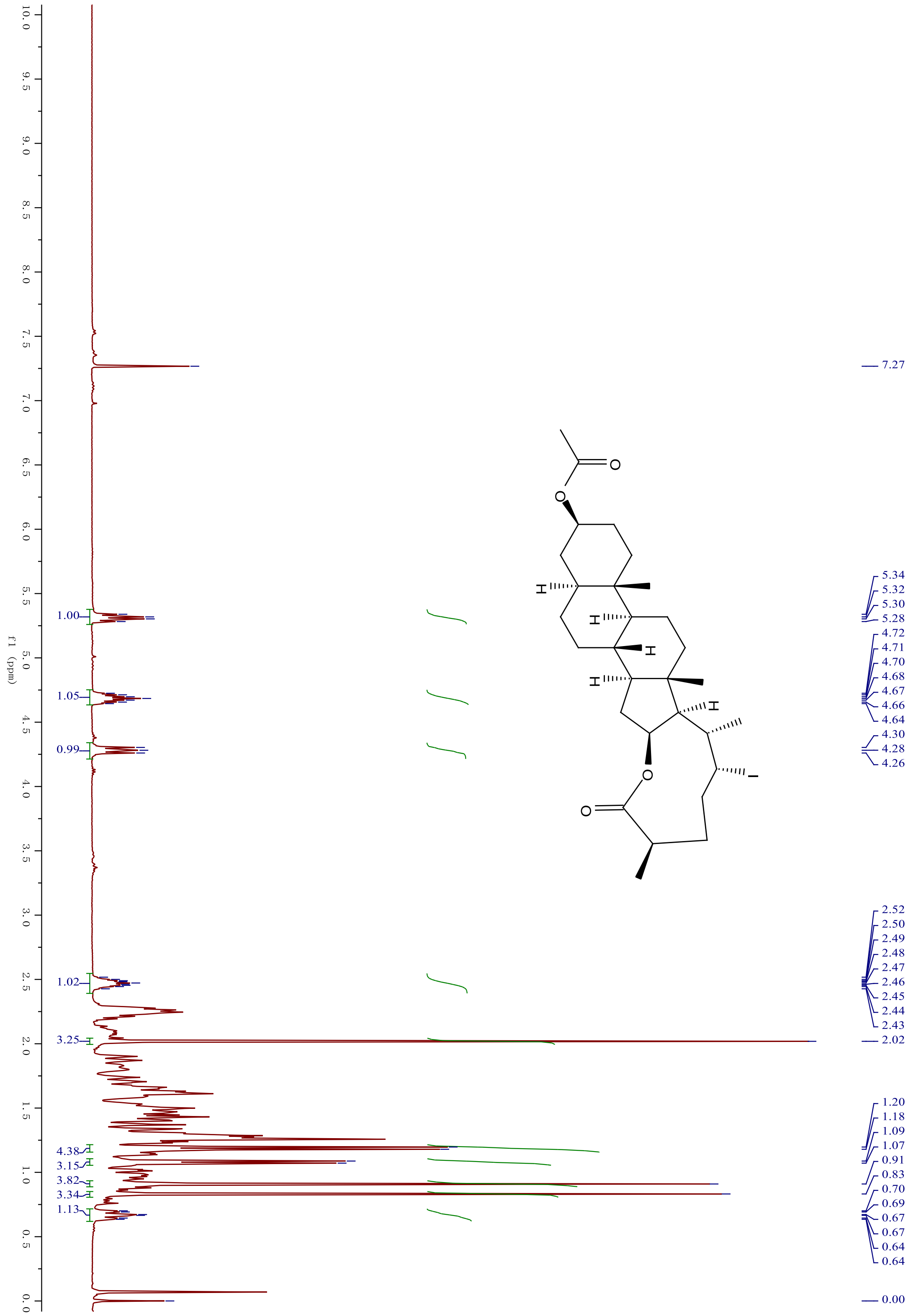

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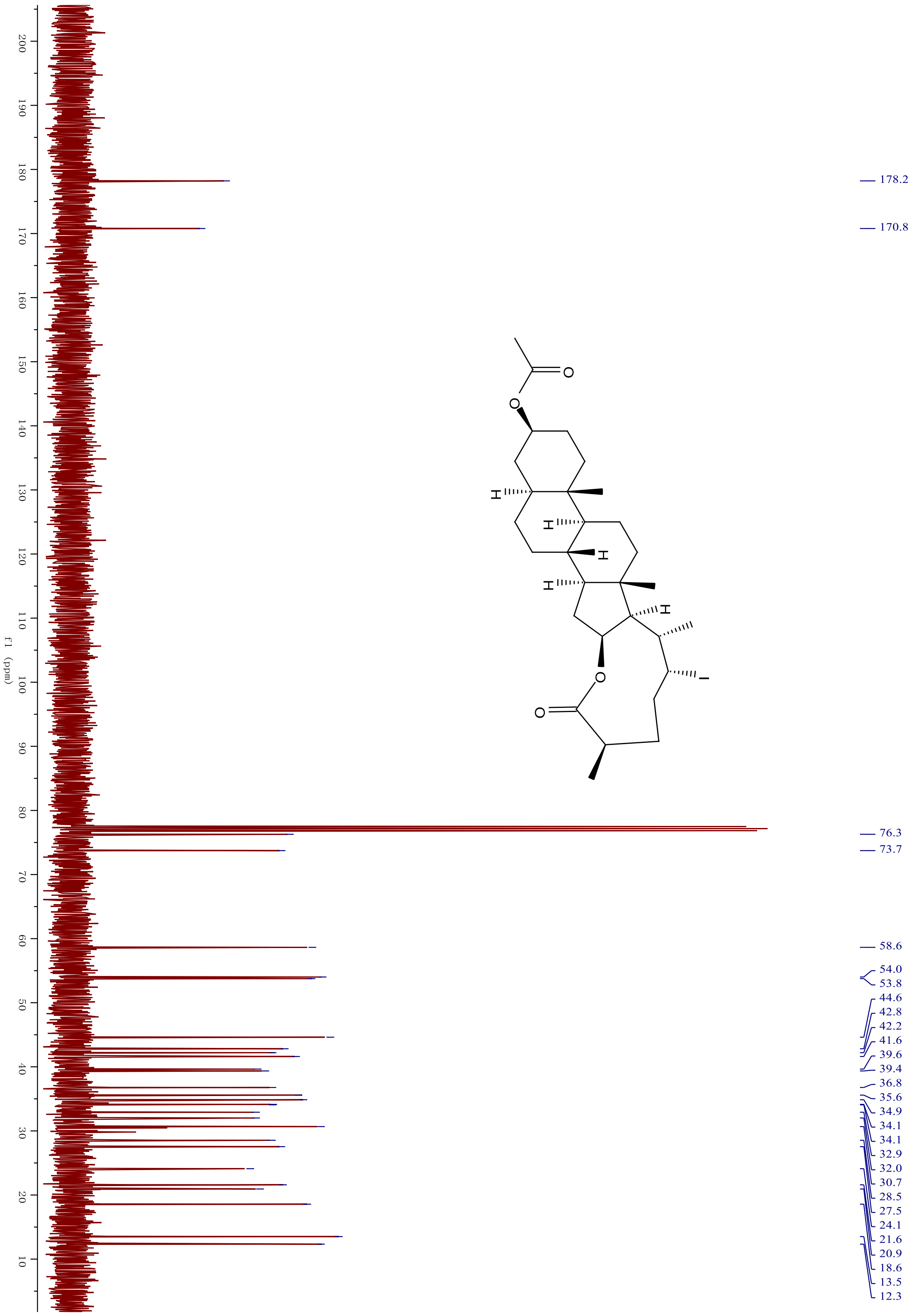
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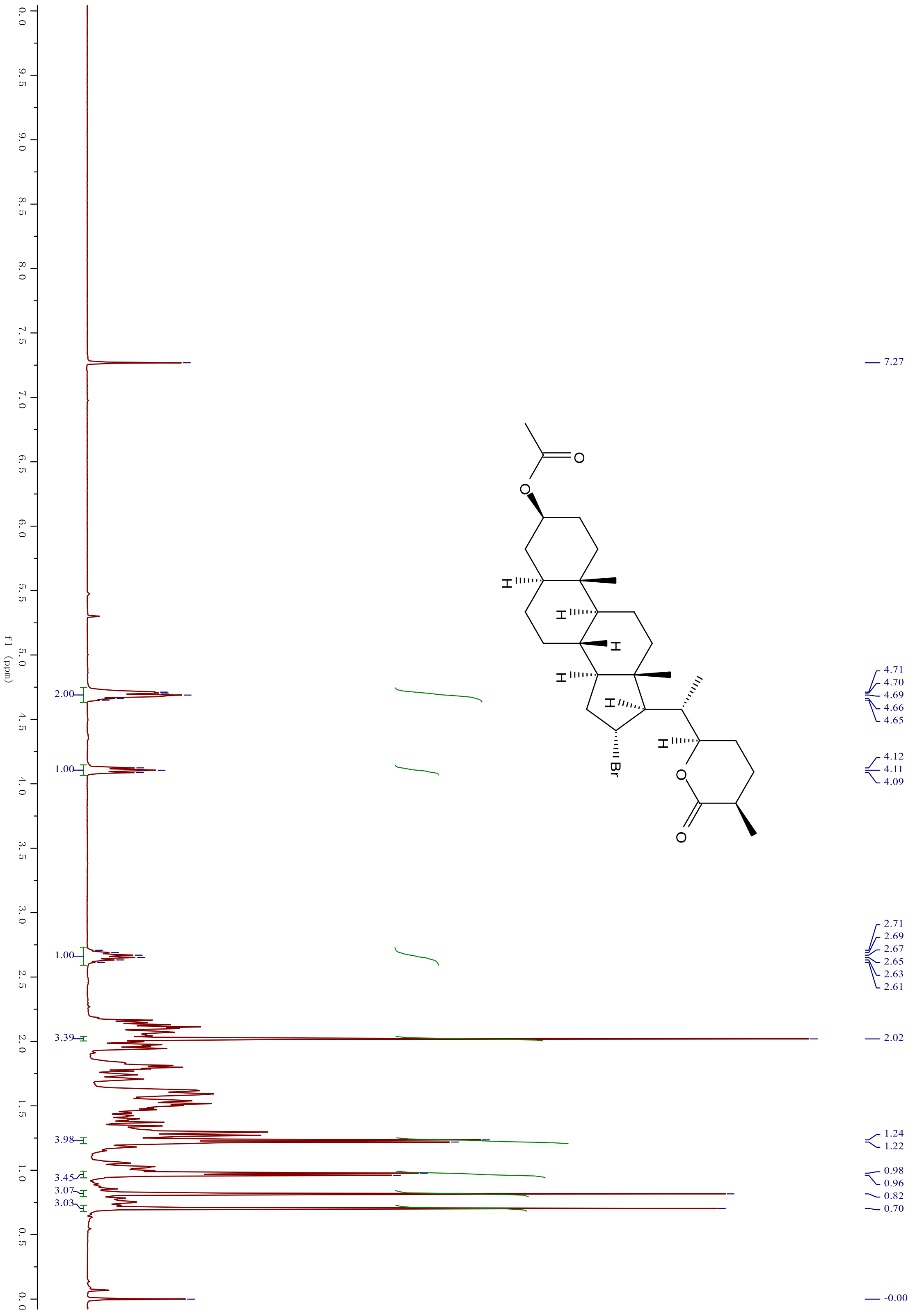

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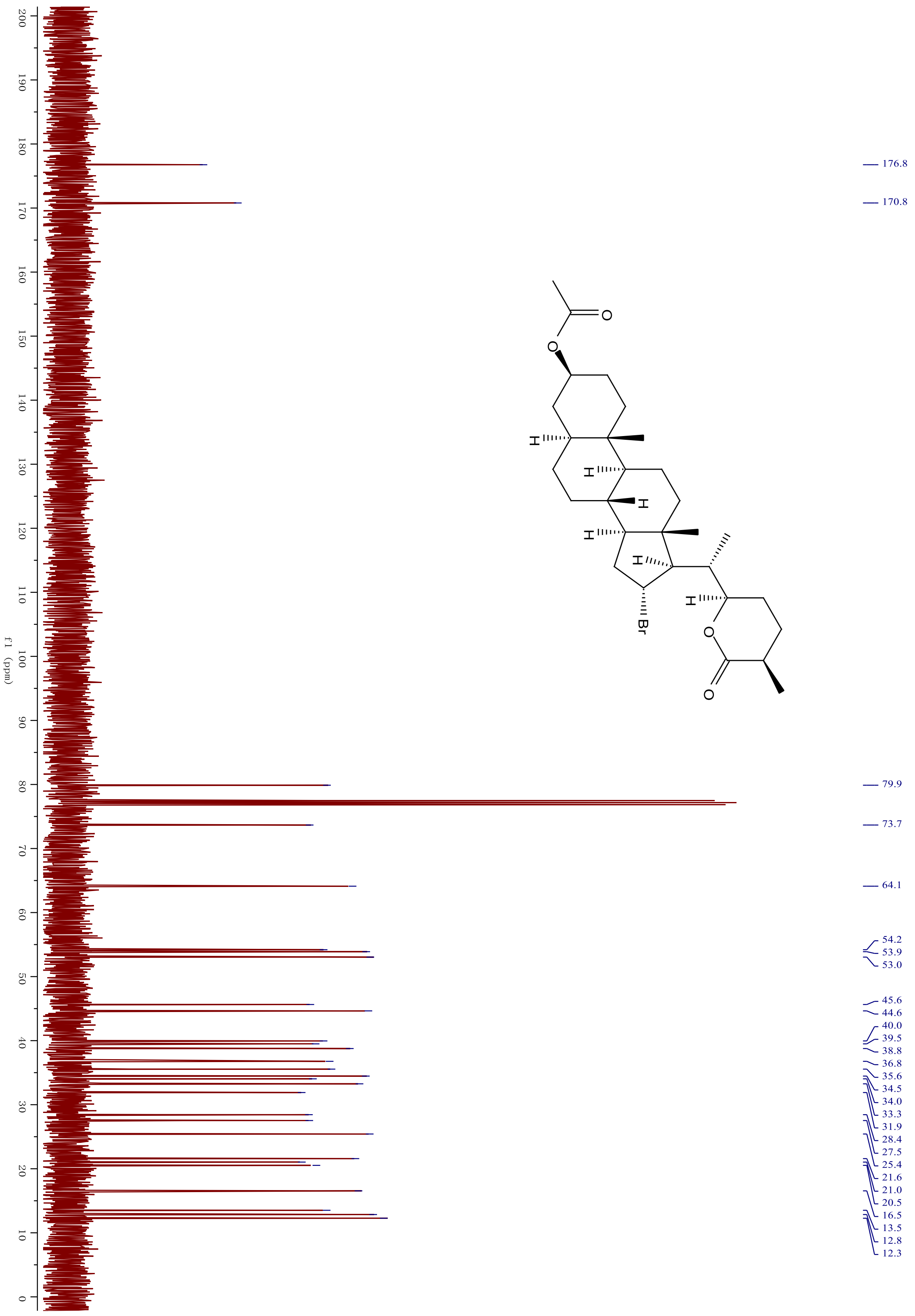
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12.3
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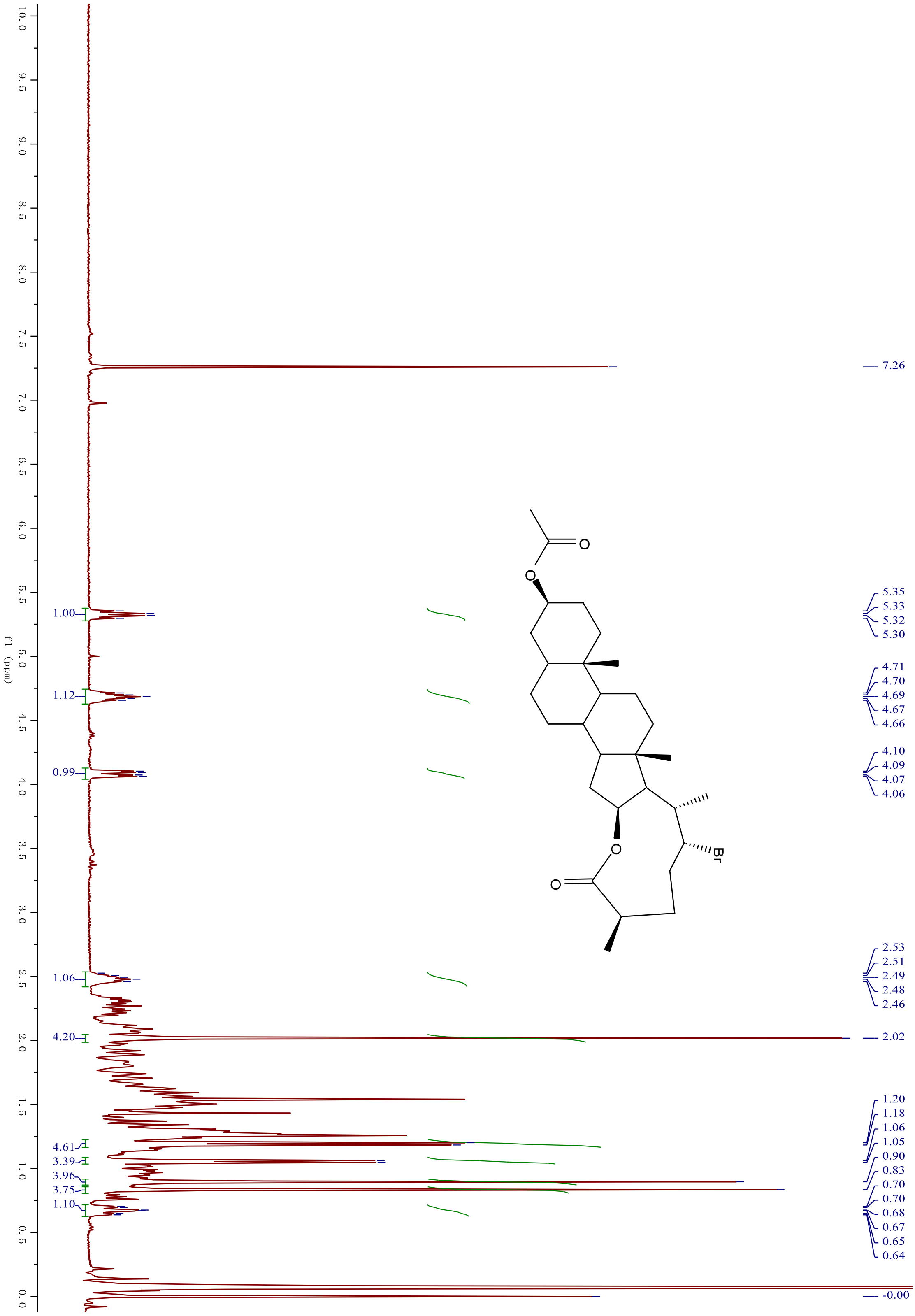

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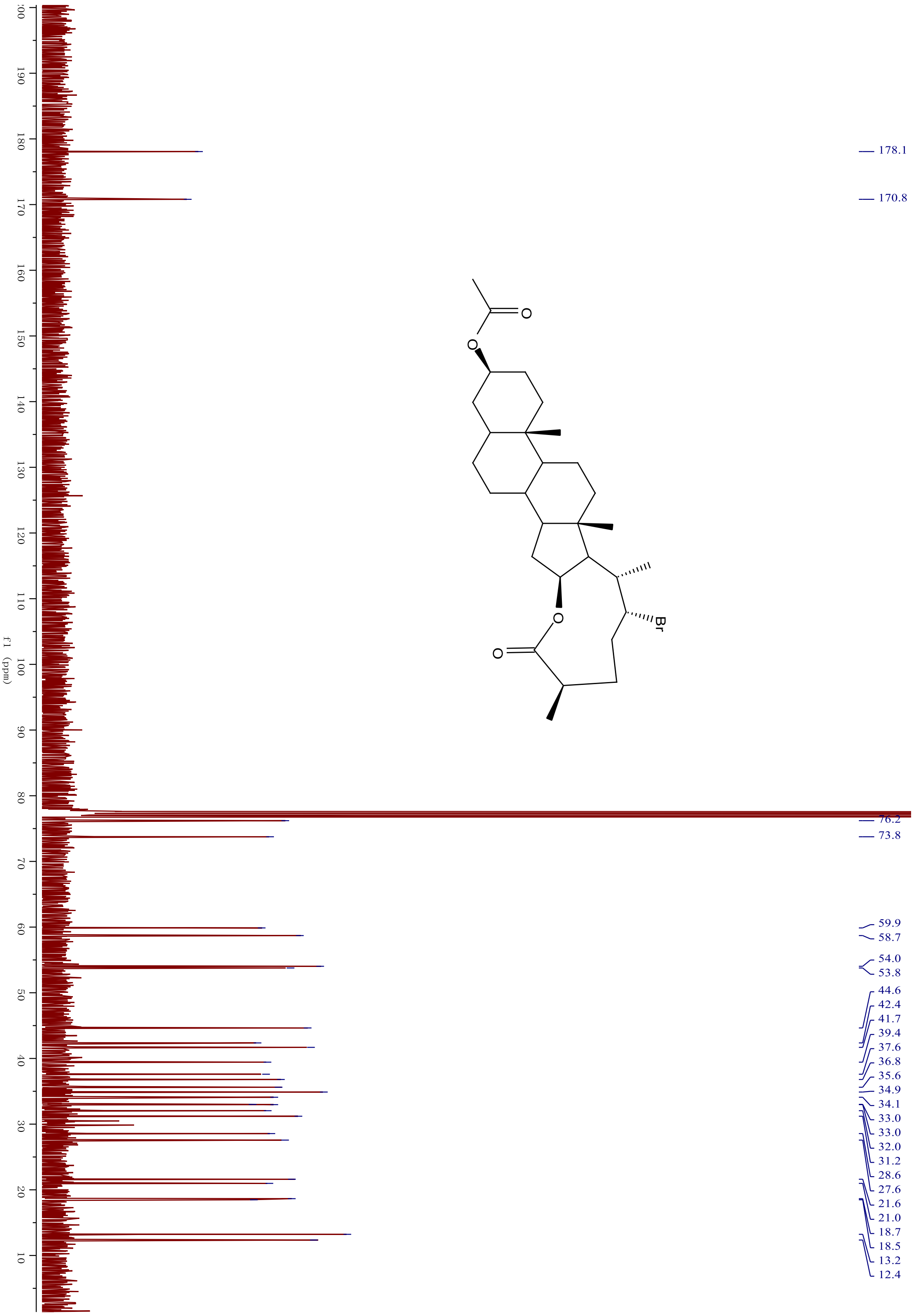

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18.7
18.5
13.2
12.4
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O
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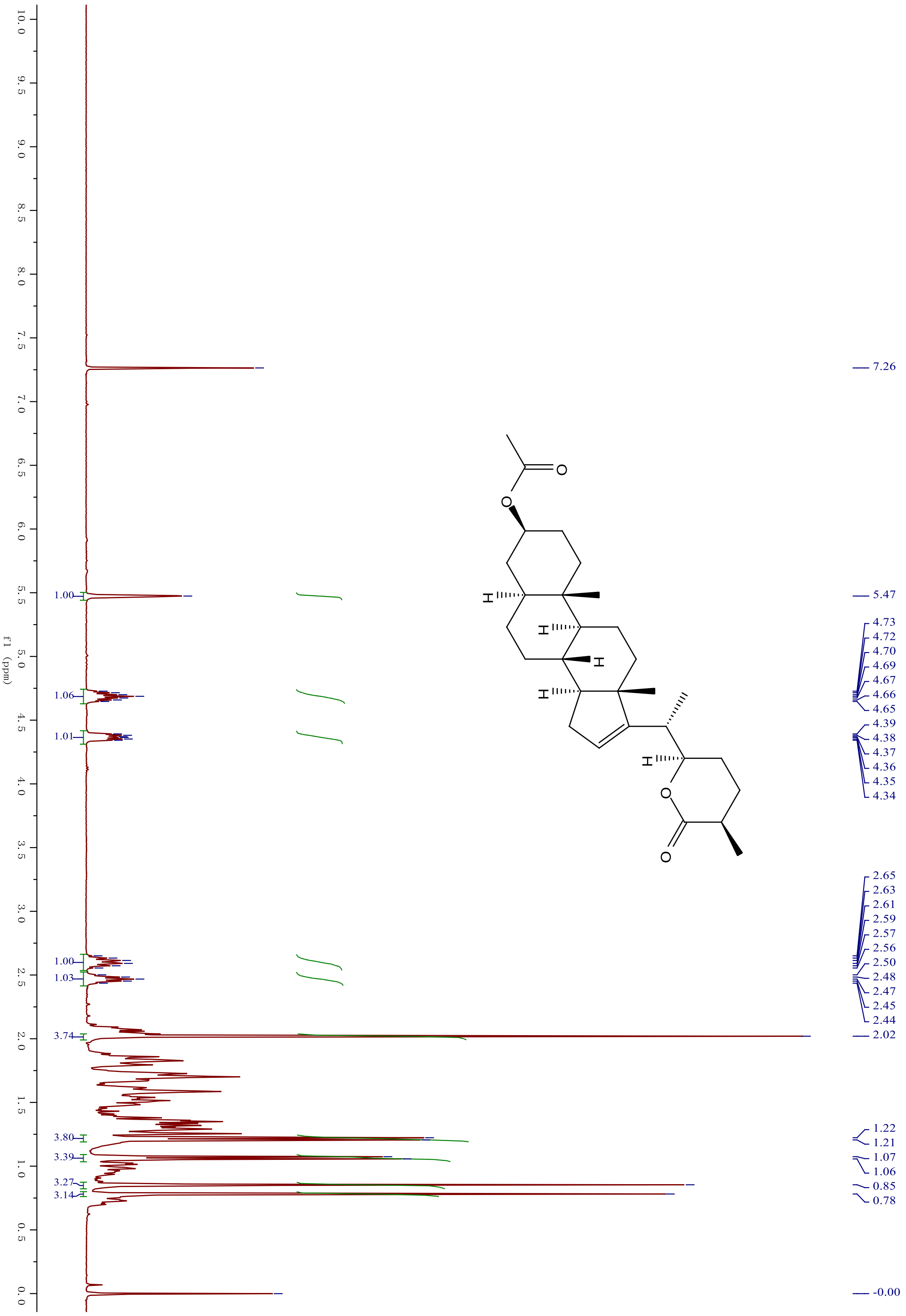
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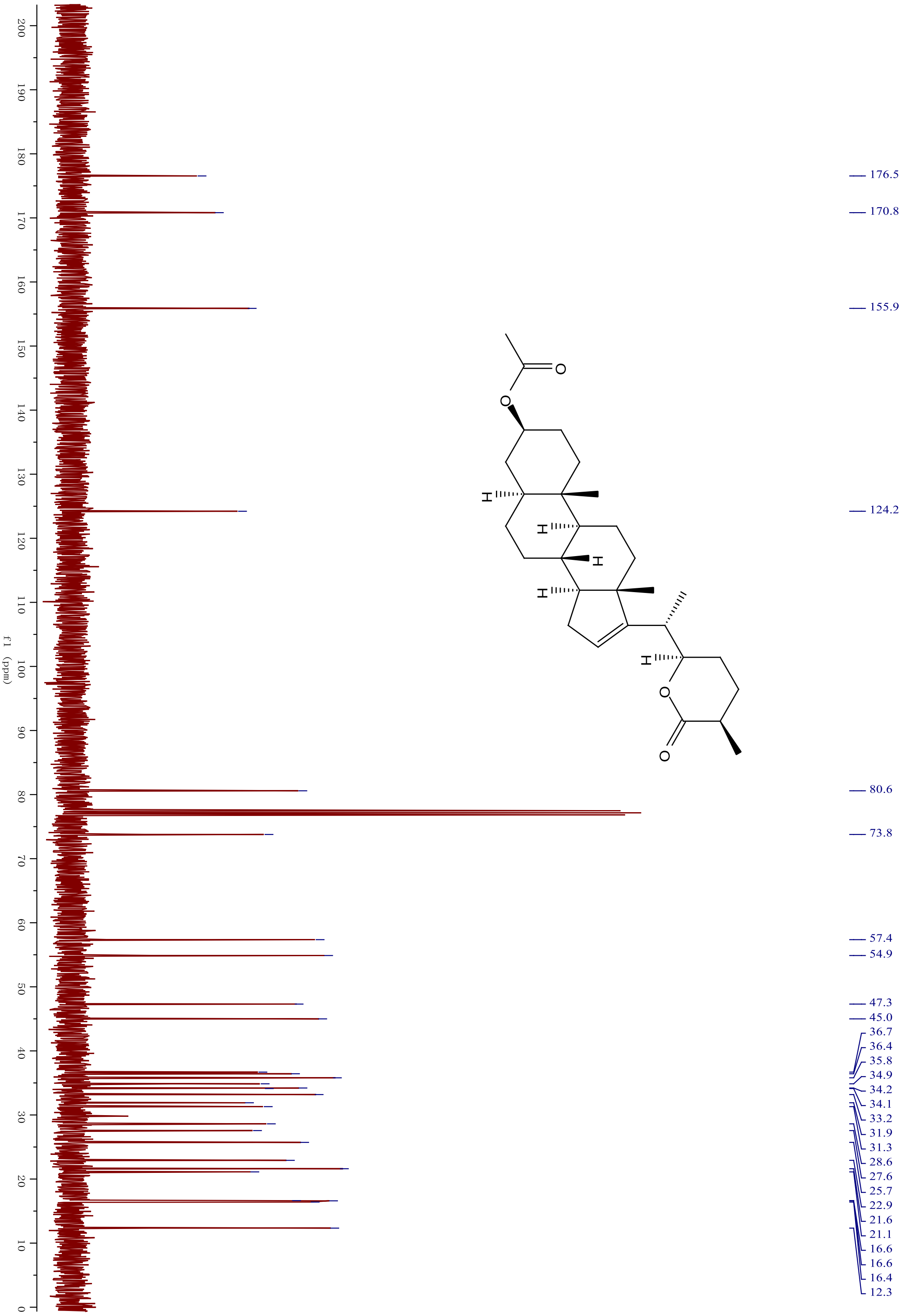
4.38
4.37
4.36
4.35
4.34
2.65
2.63
2.61
2.59
2.57
2.56
2.50
2.48
2.47
2.45
2.44
2.02
1.22
1.21
1.07
1.06
0.85
0.78
-0.00
1.00
1.06
1.01
1.00
1.03
3.74
3.80
3.39
3.27
3.14
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
H
H
H
H
H
O
O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180
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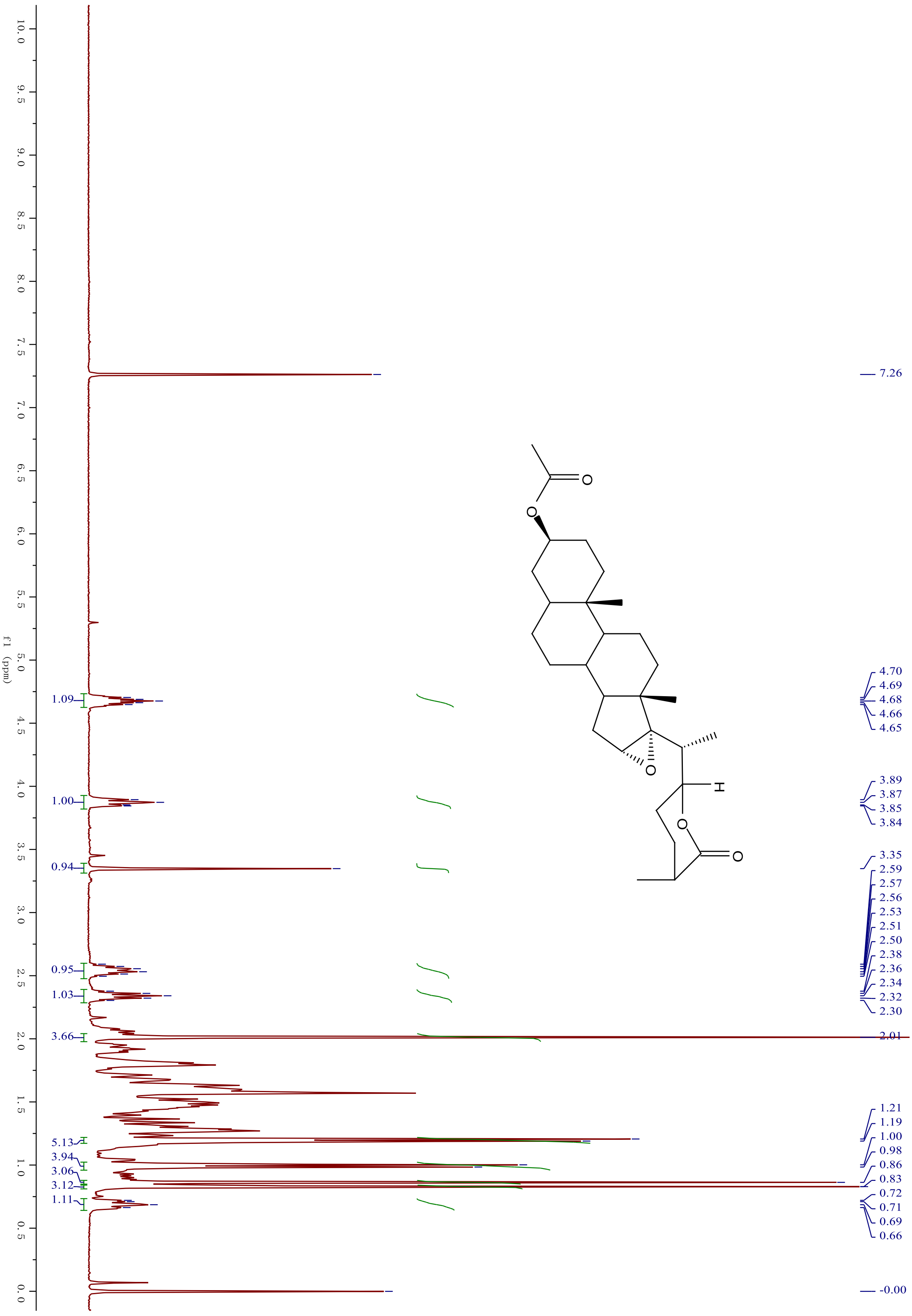
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
O
O
H
H
H
H
H
176.5
170.8
155.9
124.2
80.6
73.8
57.4
54.9
47.3
45.0
36.7
36.4
35.8
34.9
34.2
34.1
33.2
31.9
31.3
28.6
27.6
25.7
22.9
21.6
21.1
16.6
16.6
16.4
12.3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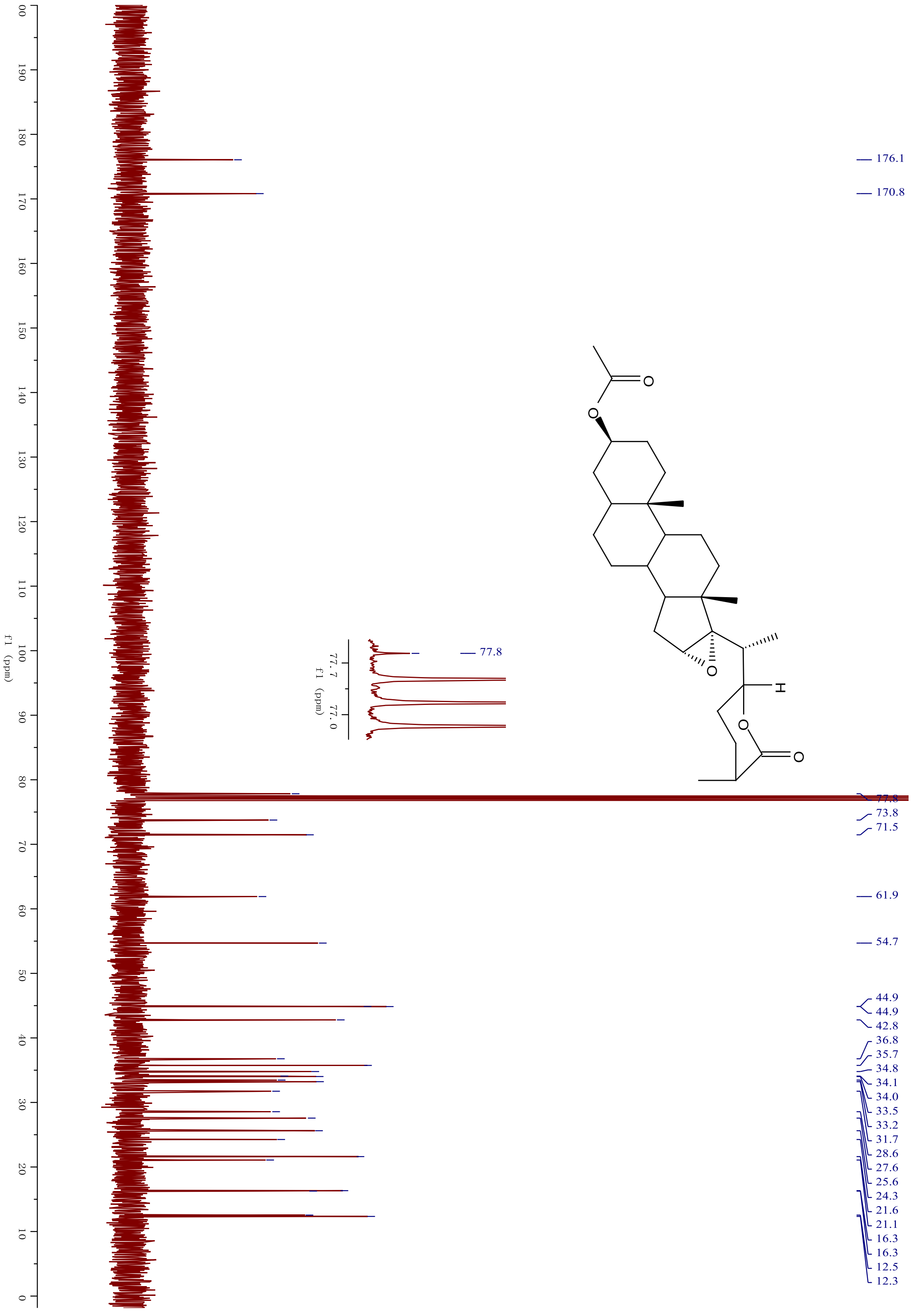
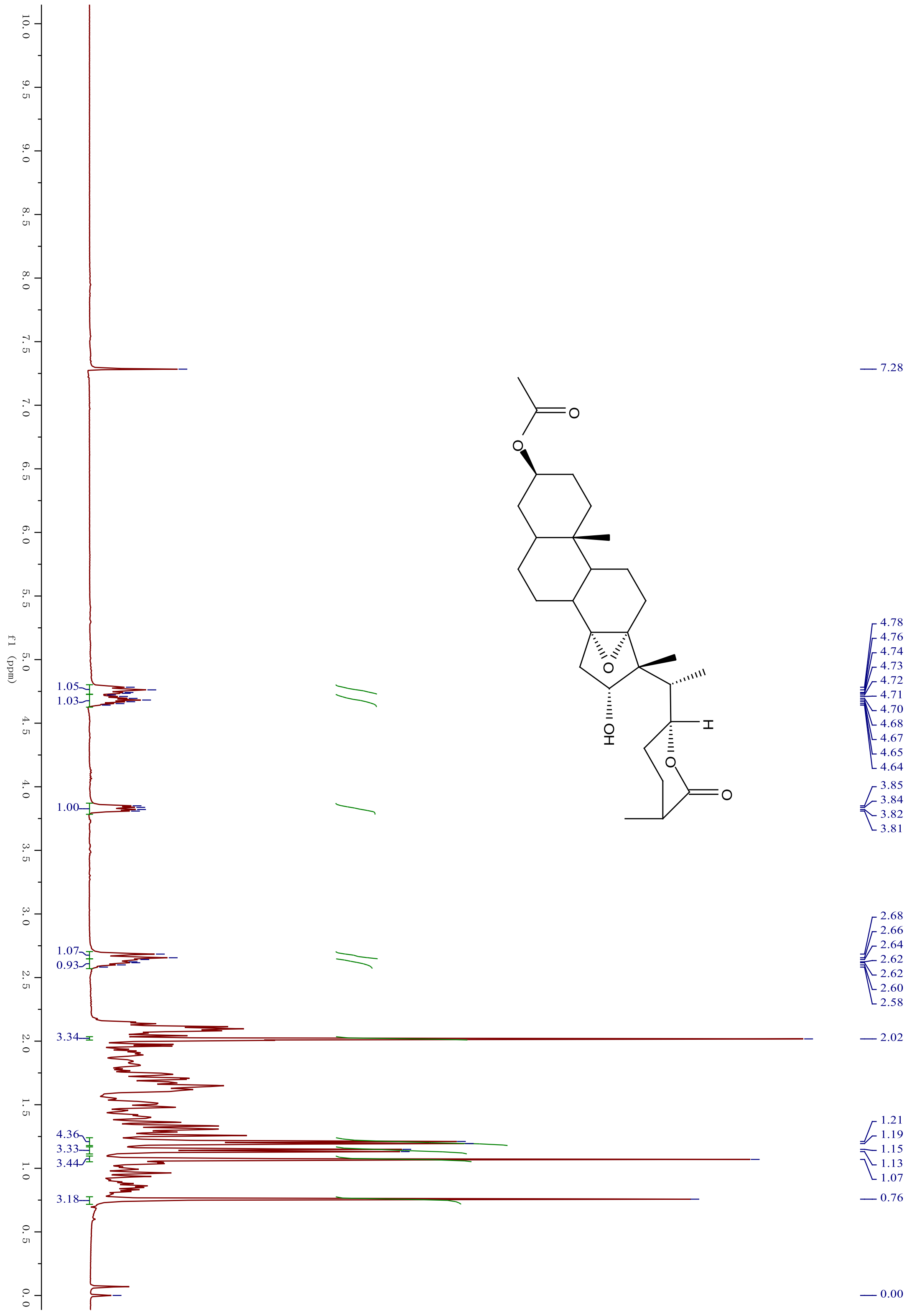
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.09
1.00
0.94
0.95
1.03
3.66
5.13
3.94
3.06
3.12
1.11
7.26
4.70
4.69
4.68
4.66
4.65
3.89
3.87
3.85
3.84
3.35
2.59
2.57
2.56
2.53
2.51
2.50
2.38
2.36
2.34
2.32
2.30
2.01
1.21
1.19
1.00
0.98
0.86
0.83
0.72
0.71
0.69
0.66
-0.00
O
O
O
O
O
H



00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
77.8
77.7
77.0
f1 (ppm)
176.1
170.8
77.8
73.8
71.5
61.9
54.7
44.9
44.9
42.8
36.8
35.7
34.8
34.1
34.0
33.5
33.2
31.7
28.6
27.6
25.6
24.3
21.6
21.1
16.3
16.3
12.5
12.3
O
O
O
O
O
H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9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.05
1.03
1.00
1.07
0.93
3.34
4.36
3.33
3.44
3.18
7.28
4.78
4.76
4.74
4.73
4.72
4.71
4.70
4.68
4.67
4.65
4.64
3.85
3.84
3.82
3.81
2.68
2.66
2.64
2.62
2.62
2.60
2.58
2.02
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1.19
1.15
1.13
1.07
0.76
0.00
O
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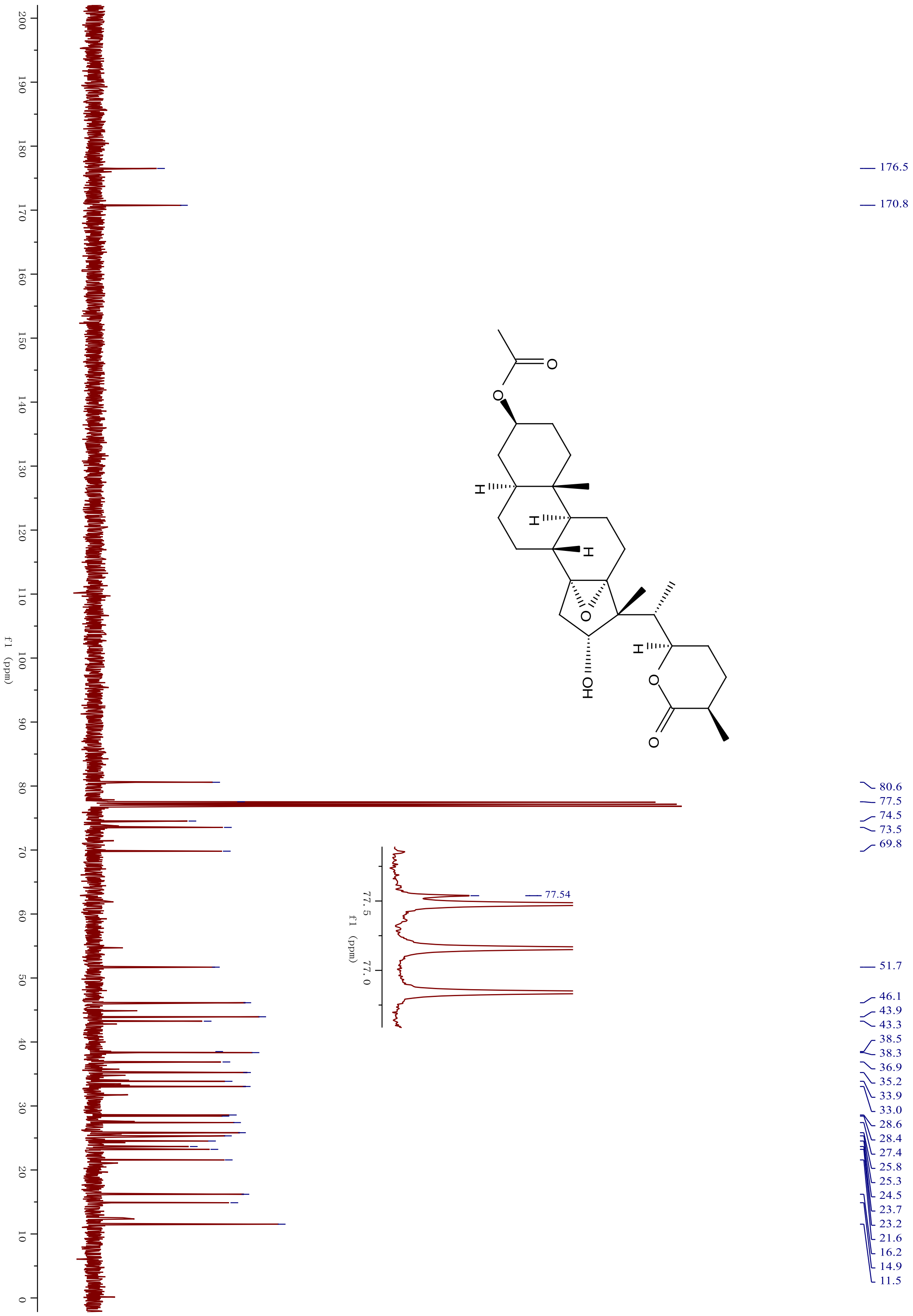
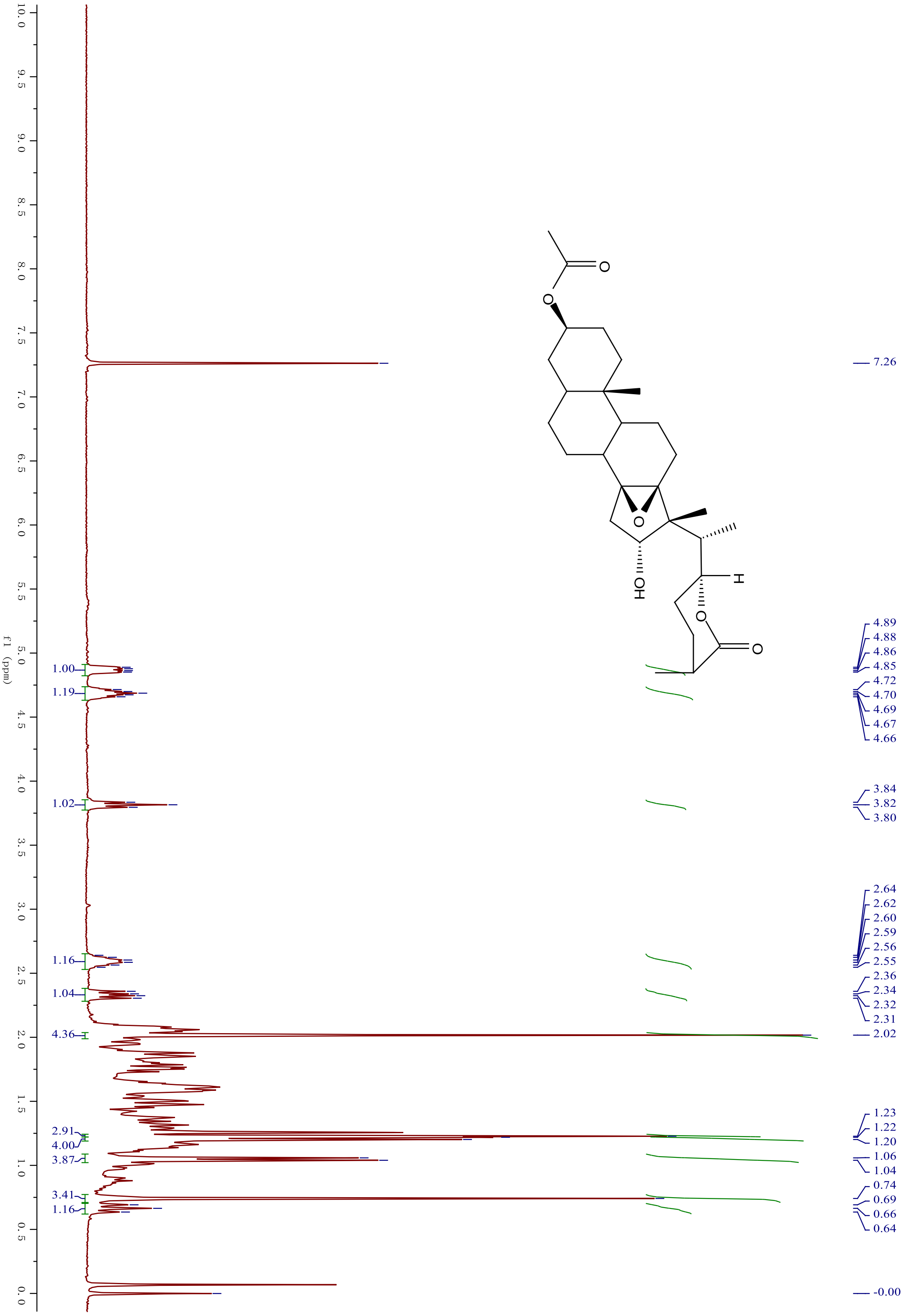
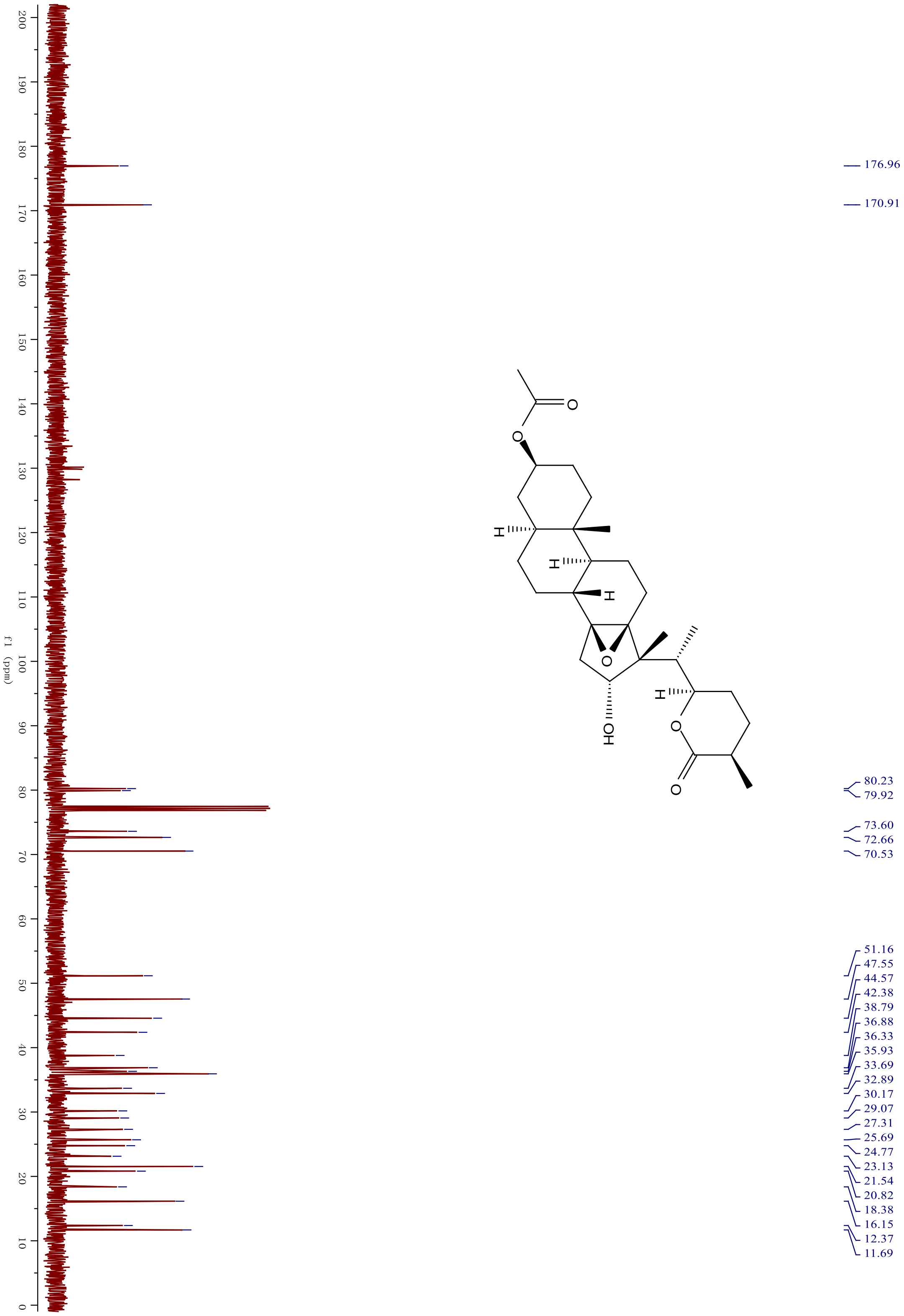
O
OH
H
O
O

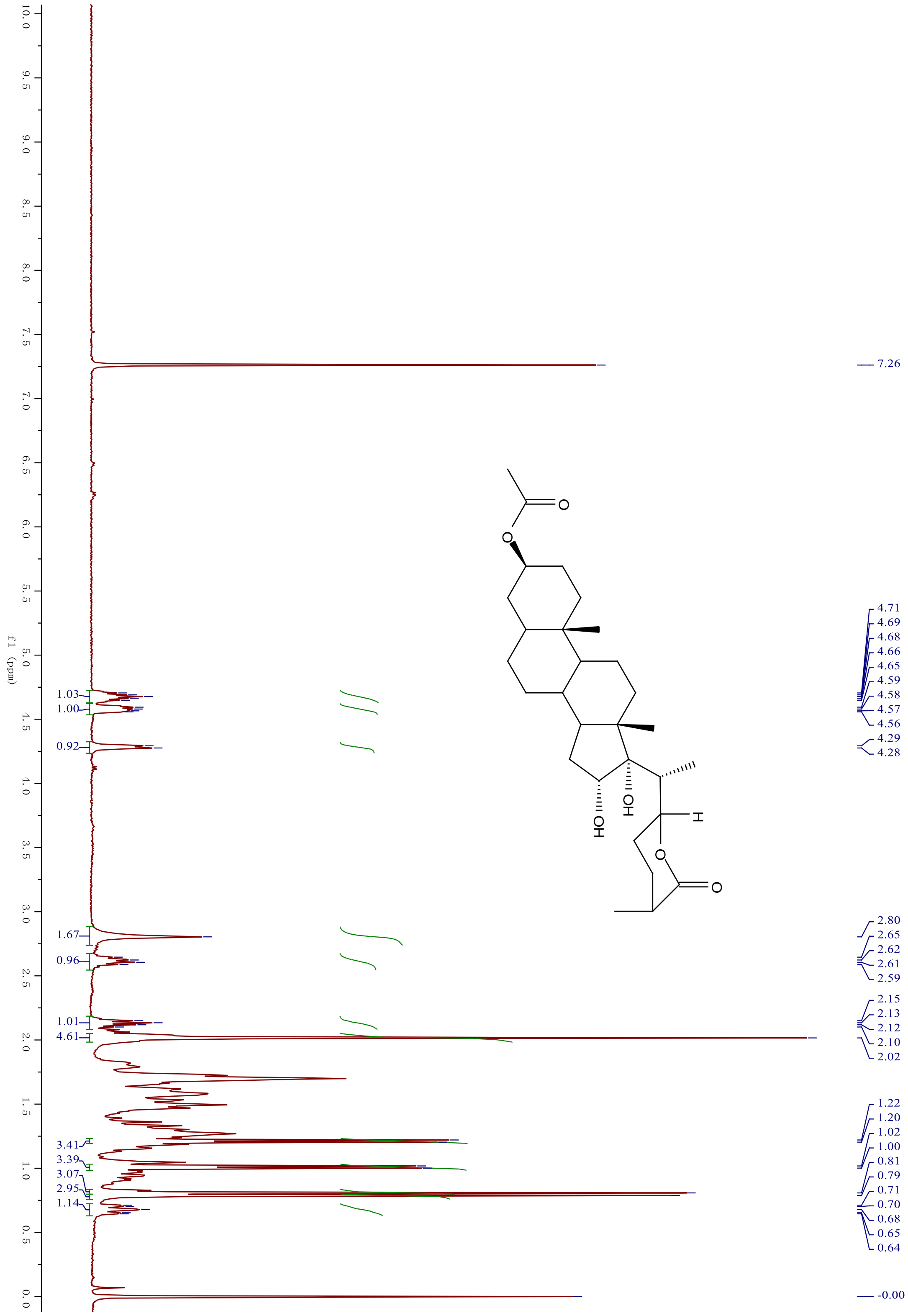


176.5
170.8
80.6
77.5
74.5
73.5
69.8
51.7
46.1
43.9
43.3
38.5
38.3
36.9
35.2
33.9
33.0
28.6
28.4
27.4
25.8
25.3
24.5
23.7
23.2
21.6
16.2
14.9
11.5
77.54
77.5
77.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
H
H
H
O
OH
H
O
O


7.26
4.89
4.88
4.86
4.85
4.72
4.70
4.69
4.67
4.66
3.84
3.82
3.80
2.64
2.62
2.60
2.59
2.56
2.55
2.36
2.34
2.32
2.31
2.02
1.23
1.22
1.20
1.06
1.04
0.74
0.69
0.66
0.64
-0.00
1.00
1.19
1.02
1.16
1.04
4.36
2.91
4.00
3.87
3.41
1.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
O
O
O
O
HO
H
O



176.96
170.91
80.23
79.92
73.60
72.66
70.53
51.16
47.55
44.57
42.38
38.79
36.88
36.33
35.93
33.69
32.89
30.17
29.07
27.31
25.69
24.77
23.13
21.54
20.82
18.38
16.15
12.37
11.69
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
H
H
H
O
OH
H
O
O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9.0
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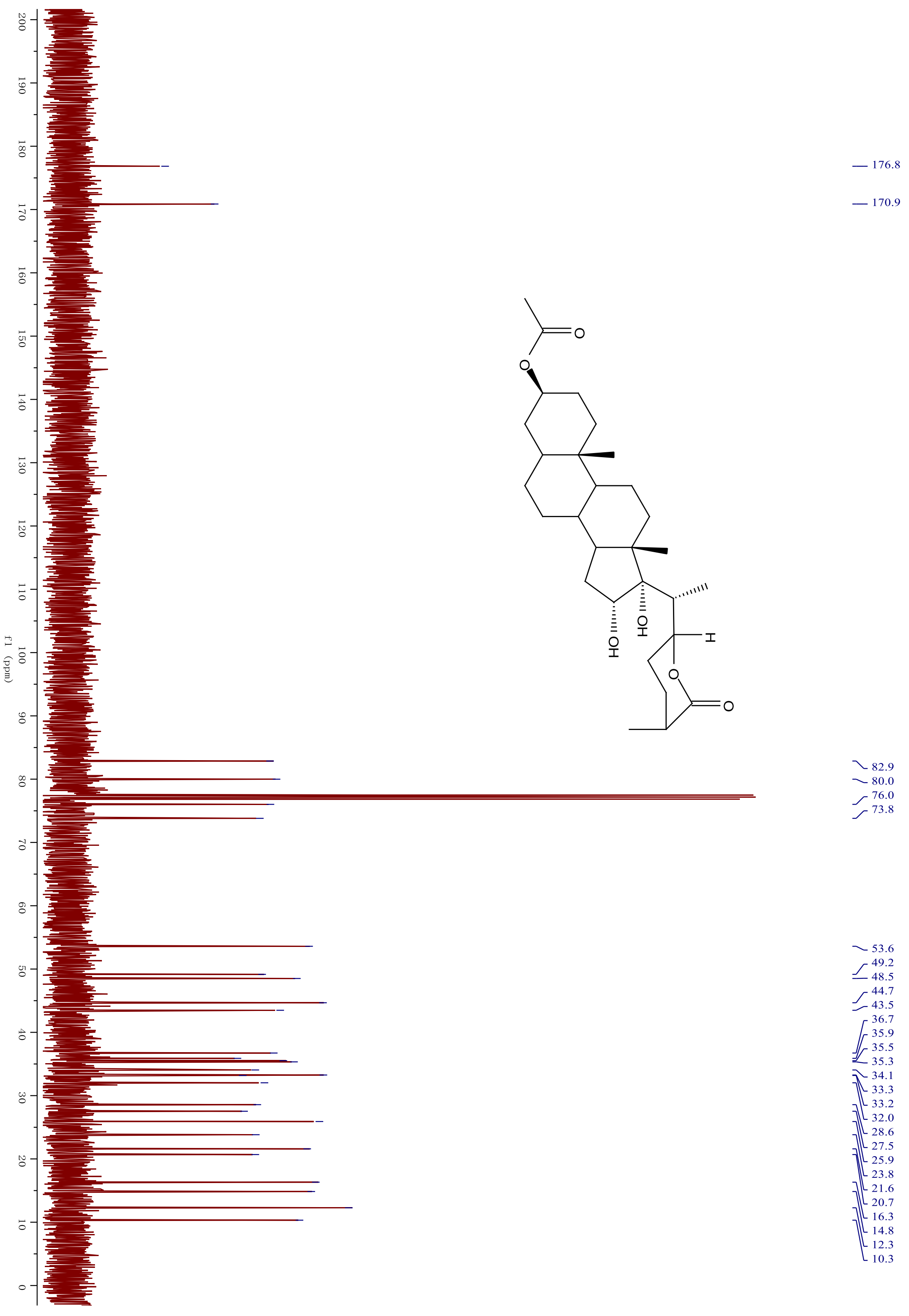
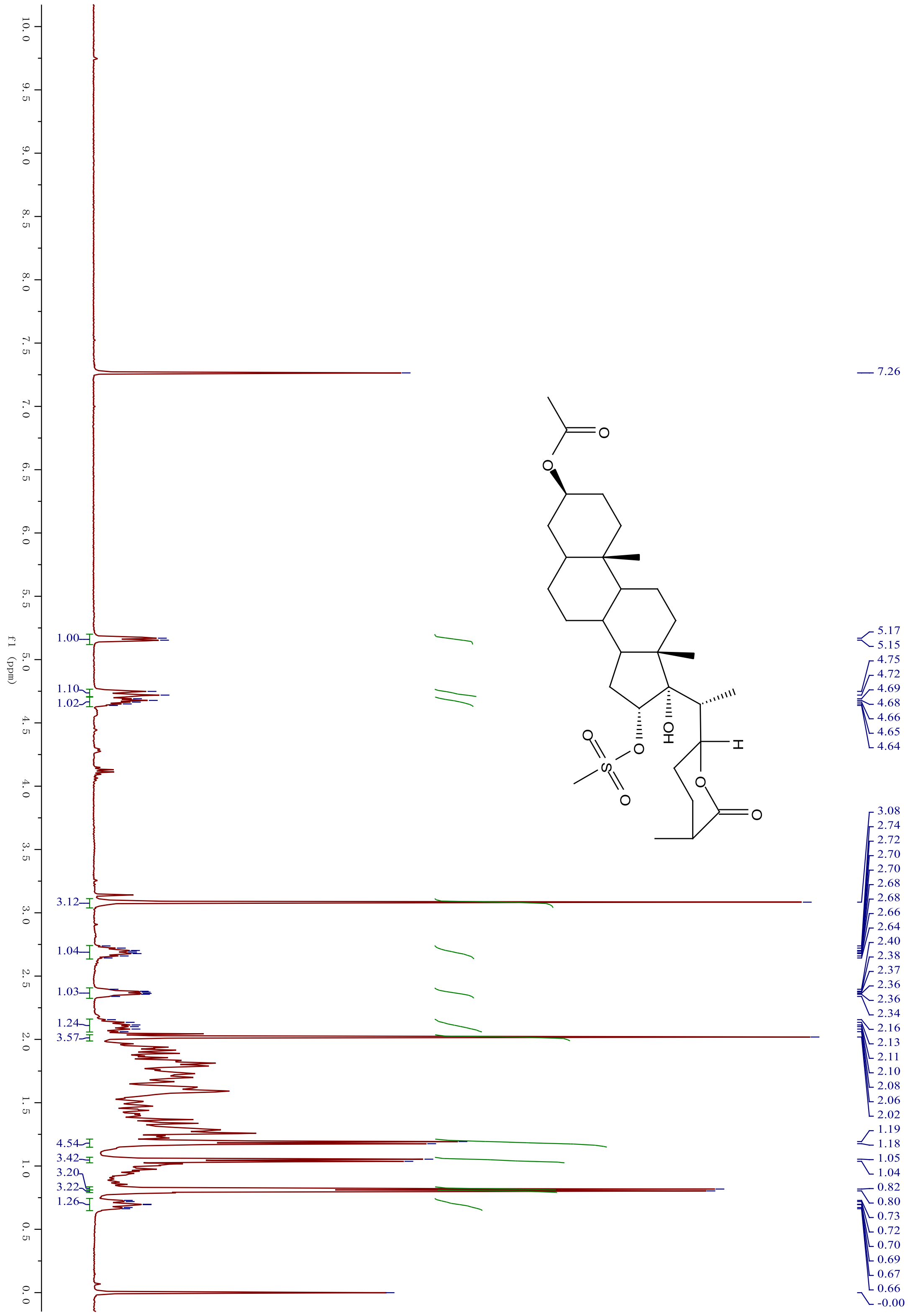
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.03
1.00
0.92
1.67
0.96
1.01
4.61
3.41
3.39
3.07
2.95
1.14
7.26
4.71
4.69
4.68
4.66
4.65
4.59
4.58
4.57
4.56
4.29
4.28
2.80
2.65
2.62
2.61
2.59
2.15
2.13
2.12
2.10
2.02
1.22
1.20
1.02
1.00
0.81
0.79
0.71
0.70
0.68
0.65
0.64
-0.00
O
O
HO
HO
H
O
O


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
176.8
170.9
82.9
80.0
76.0
73.8
53.6
49.2
48.5
44.7
43.5
36.7
35.9
35.5
35.3
34.1
33.3
33.2
32.0
28.6
27.5
25.9
23.8
21.6
20.7
16.3
14.8
12.3
10.3
O
O
HO
HO
H
O
O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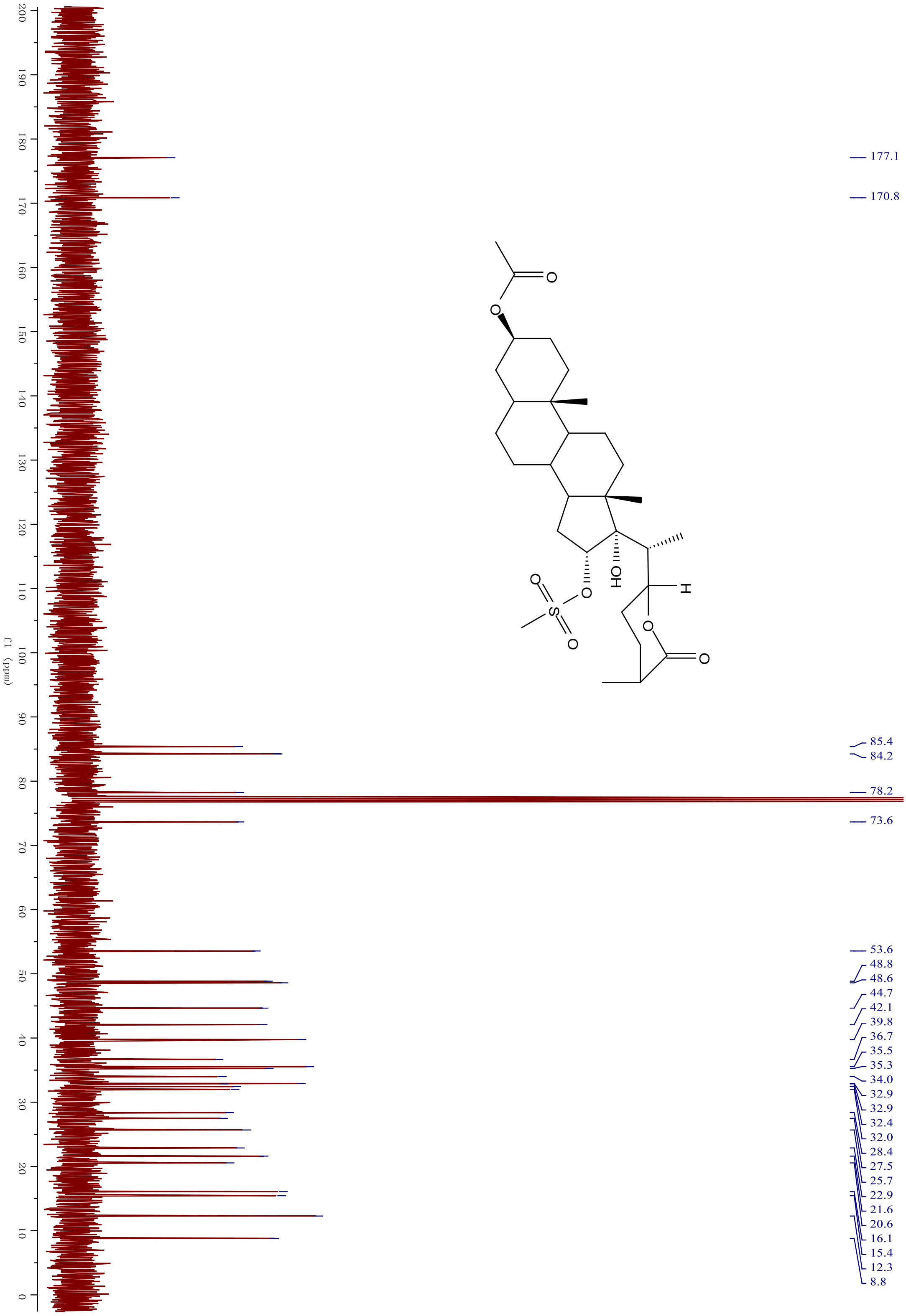
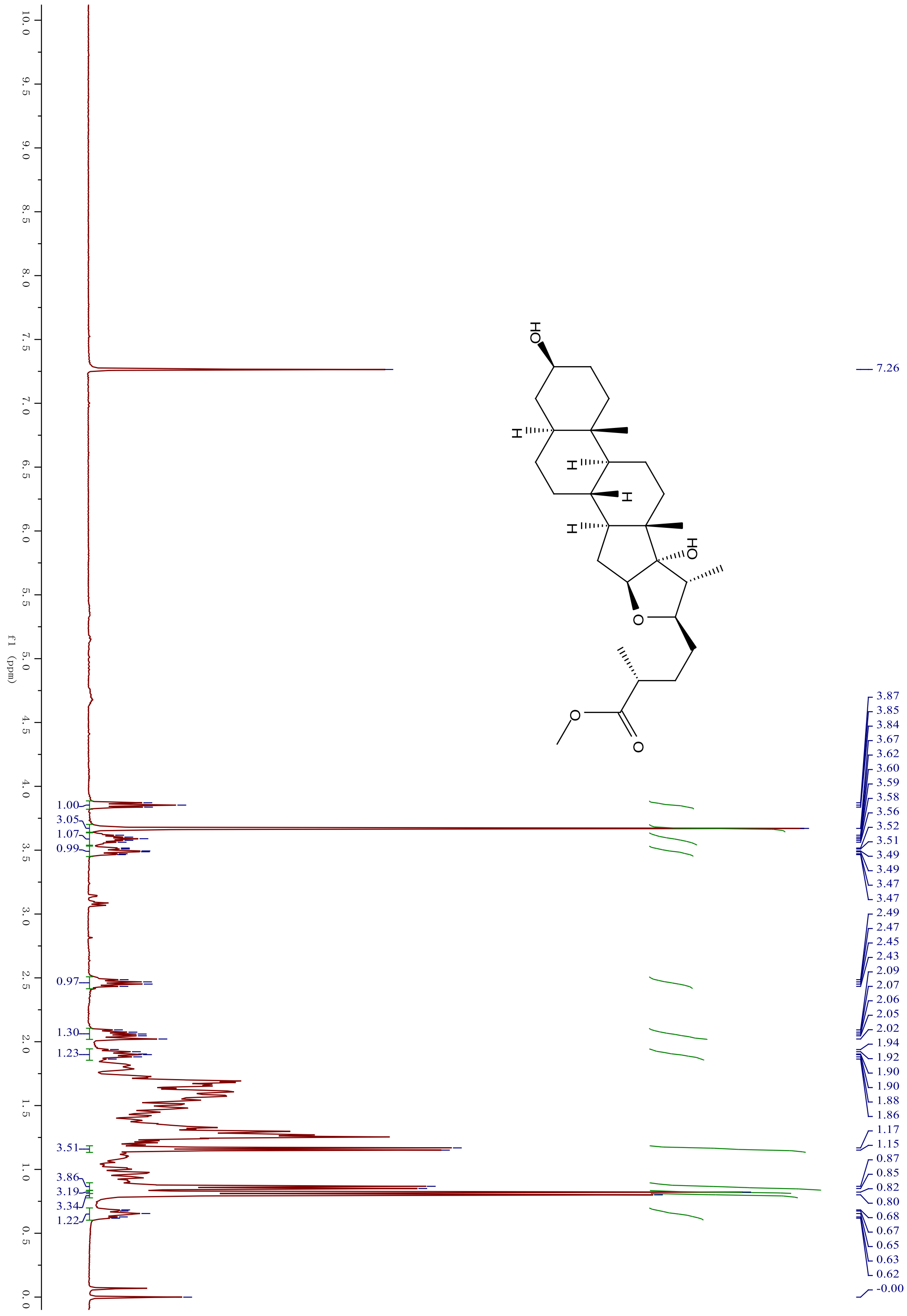
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
1.10
1.02
3.12
1.04
1.03
1.24
3.57
4.54
3.42
3.20
3.22
1.26
7.26
5.17
5.15
4.75
4.72
4.69
4.68
4.66
4.65
4.64
3.08
2.74
2.72
2.70
2.70
2.68
2.68
2.66
2.64
2.40
2.38
2.37
2.36
2.36
2.34
2.16
2.13
2.11
2.10
2.08
2.06
2.02
1.19
1.18
1.05
1.04
0.82
0.80
0.73
0.72
0.70
0.69
0.67
0.66
-0.00
O
O
O
O
S
O
HO
H
O
O



177.1
170.8
85.4
84.2
78.2
73.6
53.6
48.8
48.6
44.7
42.1
39.8
36.7
35.5
35.3
34.0
32.9
32.9
32.4
32.0
28.4
27.5
25.7
22.9
21.6
20.6
16.1
15.4
12.3
8.8
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
O
O
O
O
O
S
OH
H
O
O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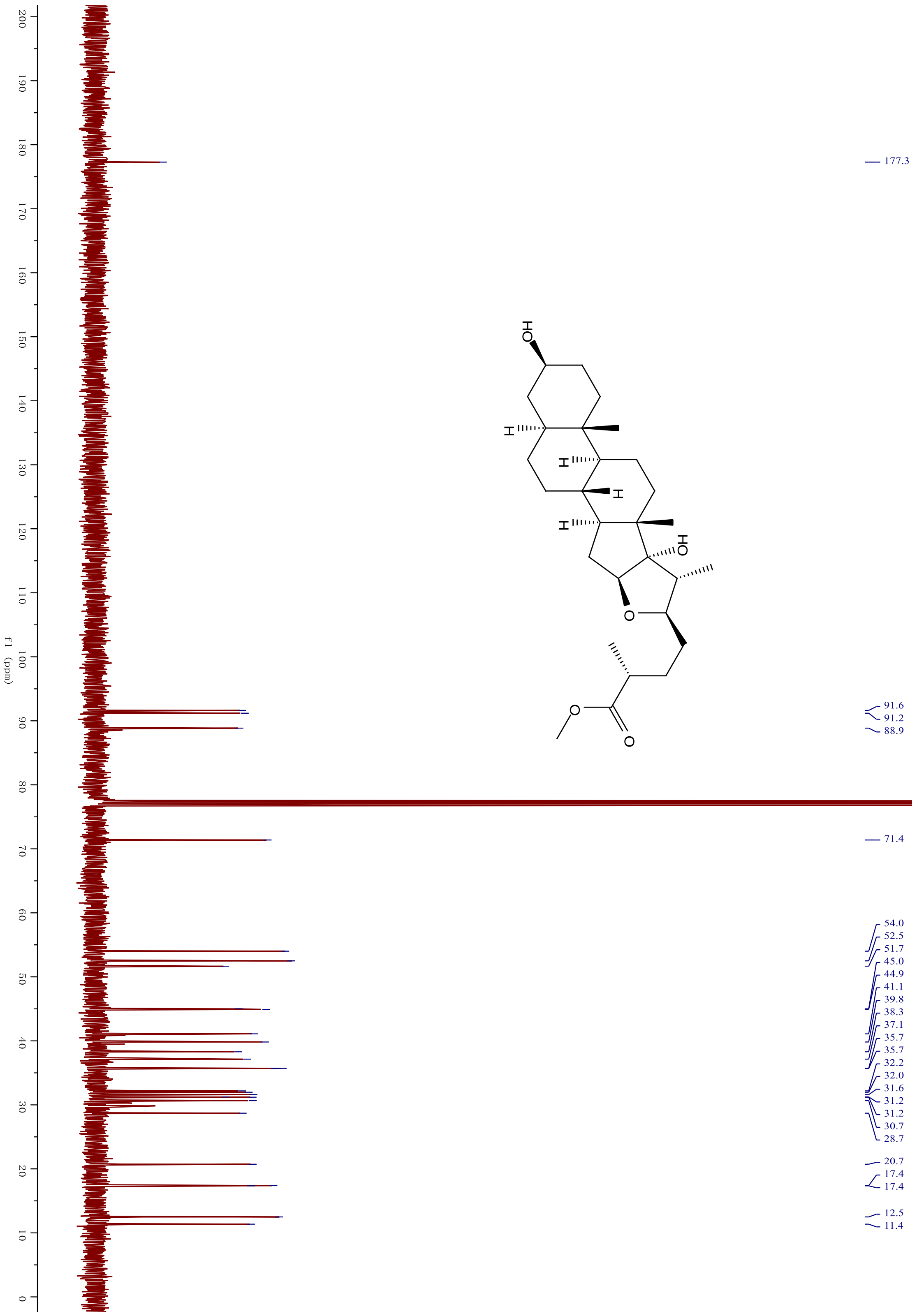
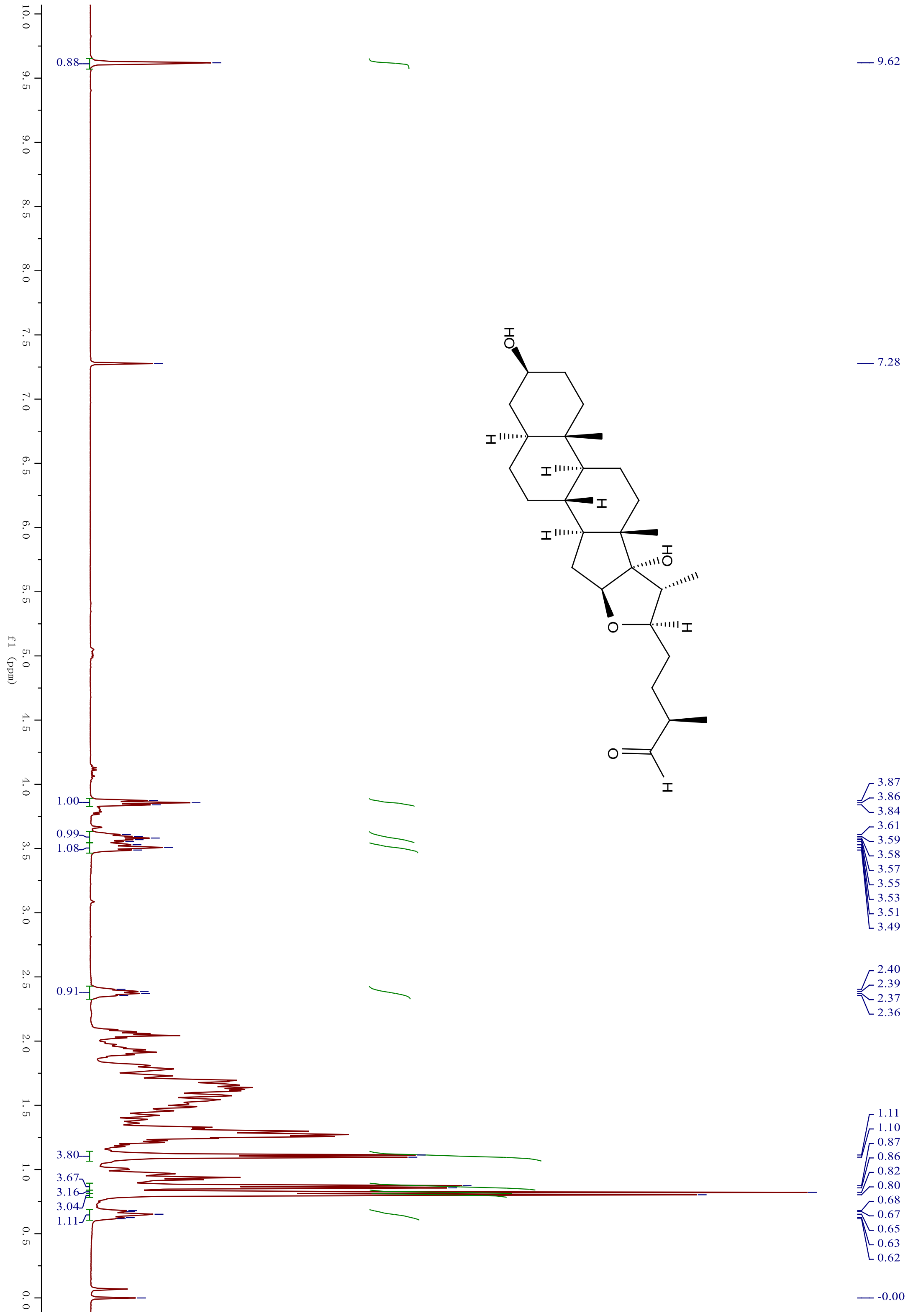
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
3.05
1.07
0.99
0.97
1.30
1.23
3.51
3.86
3.19
3.34
1.22
7.26
3.87
3.85
3.84
3.67
3.62
3.60
3.59
3.58
3.56
3.52
3.51
3.49
3.49
3.47
3.47
2.49
2.47
2.45
2.43
2.09
2.07
2.06
2.05
2.02
1.94
1.92
1.90
1.90
1.88
1.86
1.17
1.15
0.87
0.85
0.82
0.80
0.68
0.67
0.65
0.63
0.62
-0.00
HO
H
H
H
H
HO
O
O
O


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
177.3
91.6
91.2
88.9
71.4
54.0
52.5
51.7
45.0
44.9
41.1
39.8
38.3
37.1
35.7
35.7
32.2
32.0
31.6
31.2
31.2
30.7
28.7
20.7
17.4
17.4
12.5
11.4
HO
H
H
H
H
HO
O
O
O



f1 (ppm)
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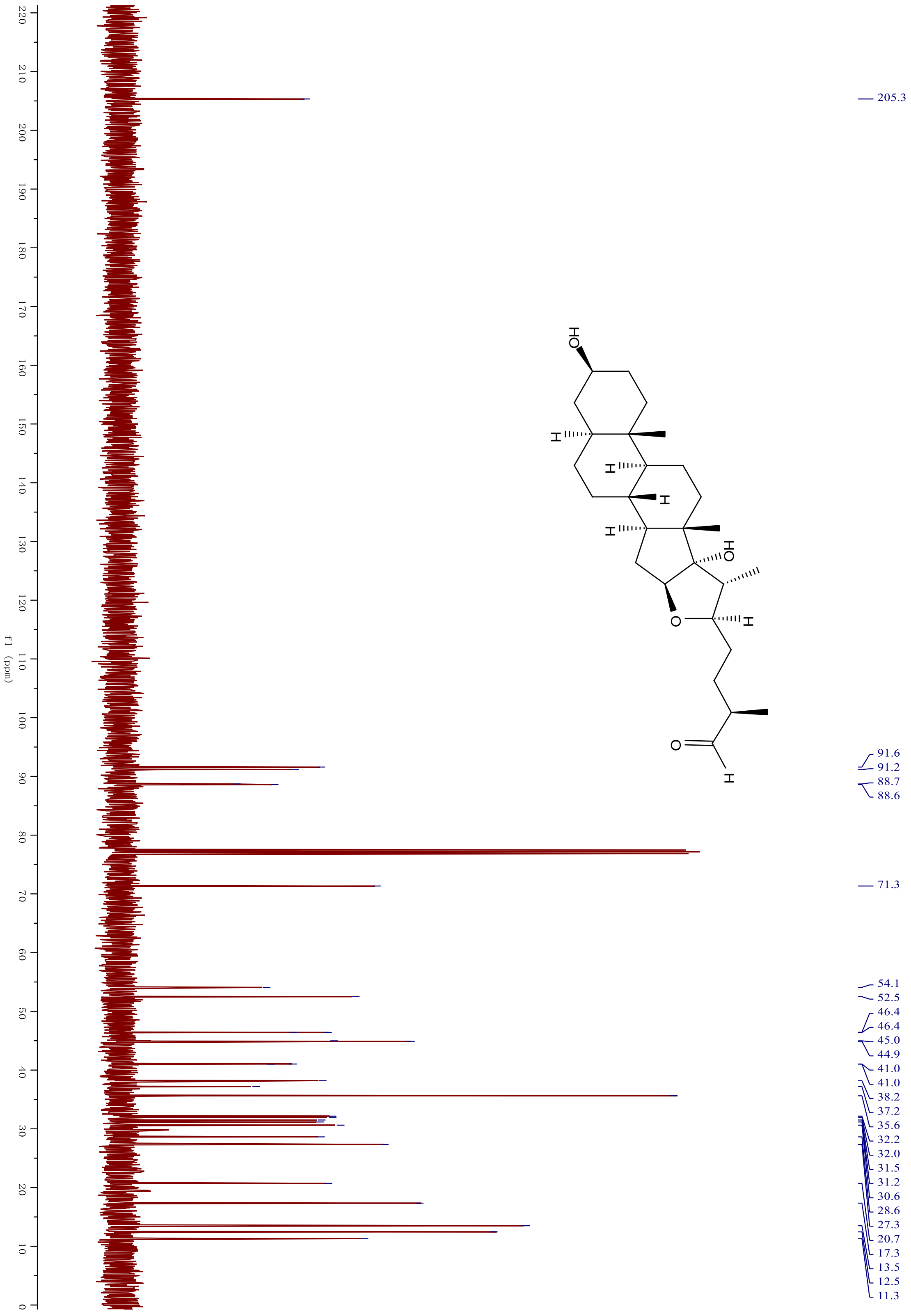
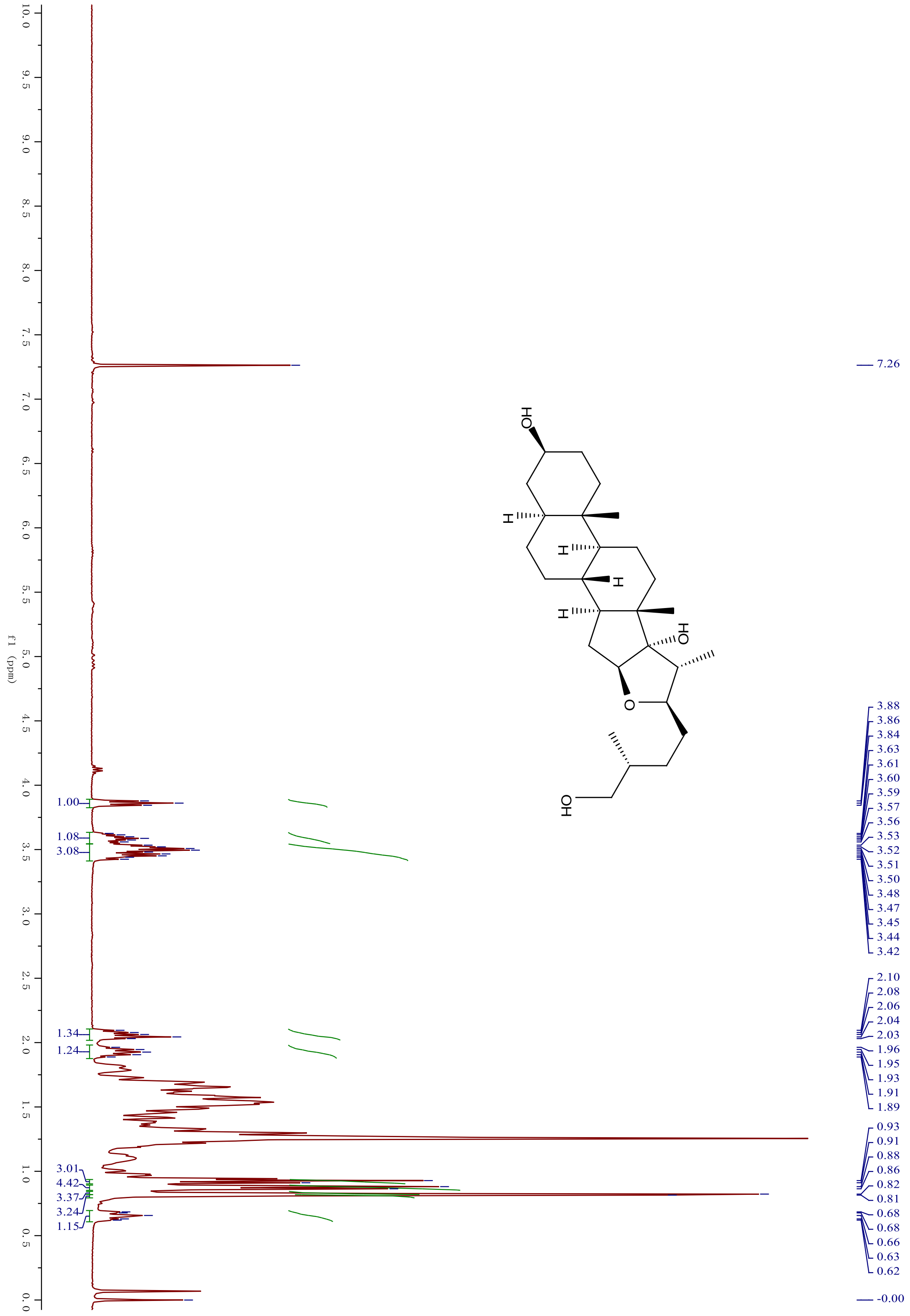
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.88
1.00
0.99
1.08
0.91
3.80
3.67
3.16
3.04
1.11
9.62
7.28
3.87
3.86
3.84
3.61
3.59
3.58
3.57
3.55
3.53
3.51
3.49
2.40
2.39
2.37
2.36
1.11
1.10
0.87
0.86
0.82
0.80
0.68
0.67
0.65
0.63
0.62
-0.00
HO
H
H
H
H
HO
H
O
O
H



220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
205.3
91.6
91.2
88.7
88.6
71.3
54.1
52.5
46.4
46.4
45.0
44.9
41.0
41.0
38.2
37.2
35.6
32.2
32.0
31.5
31.2
30.6
28.6
27.3
20.7
17.3
13.5
12.5
11.3
HO
H
H
H
H
HO
O
H
O
H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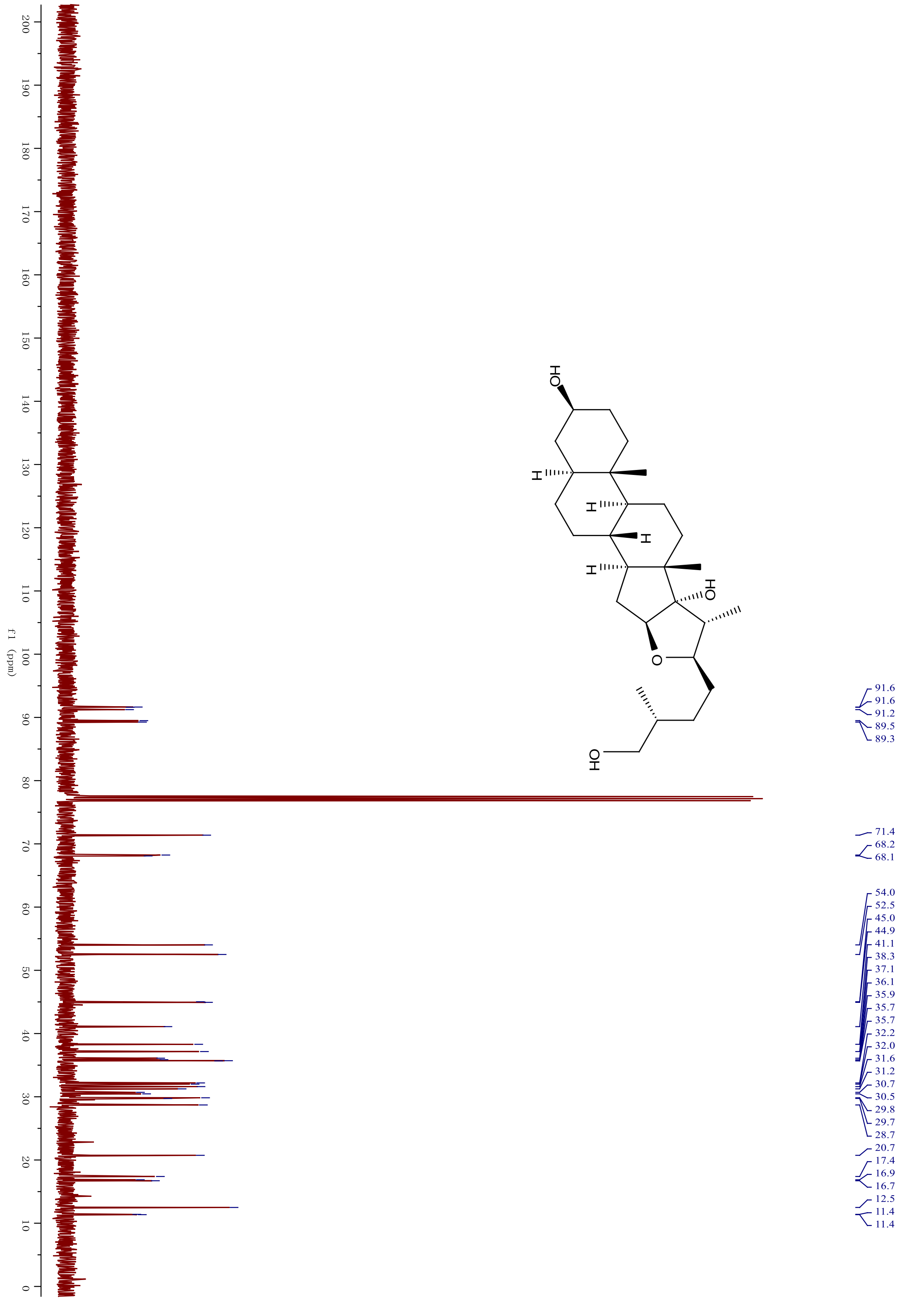
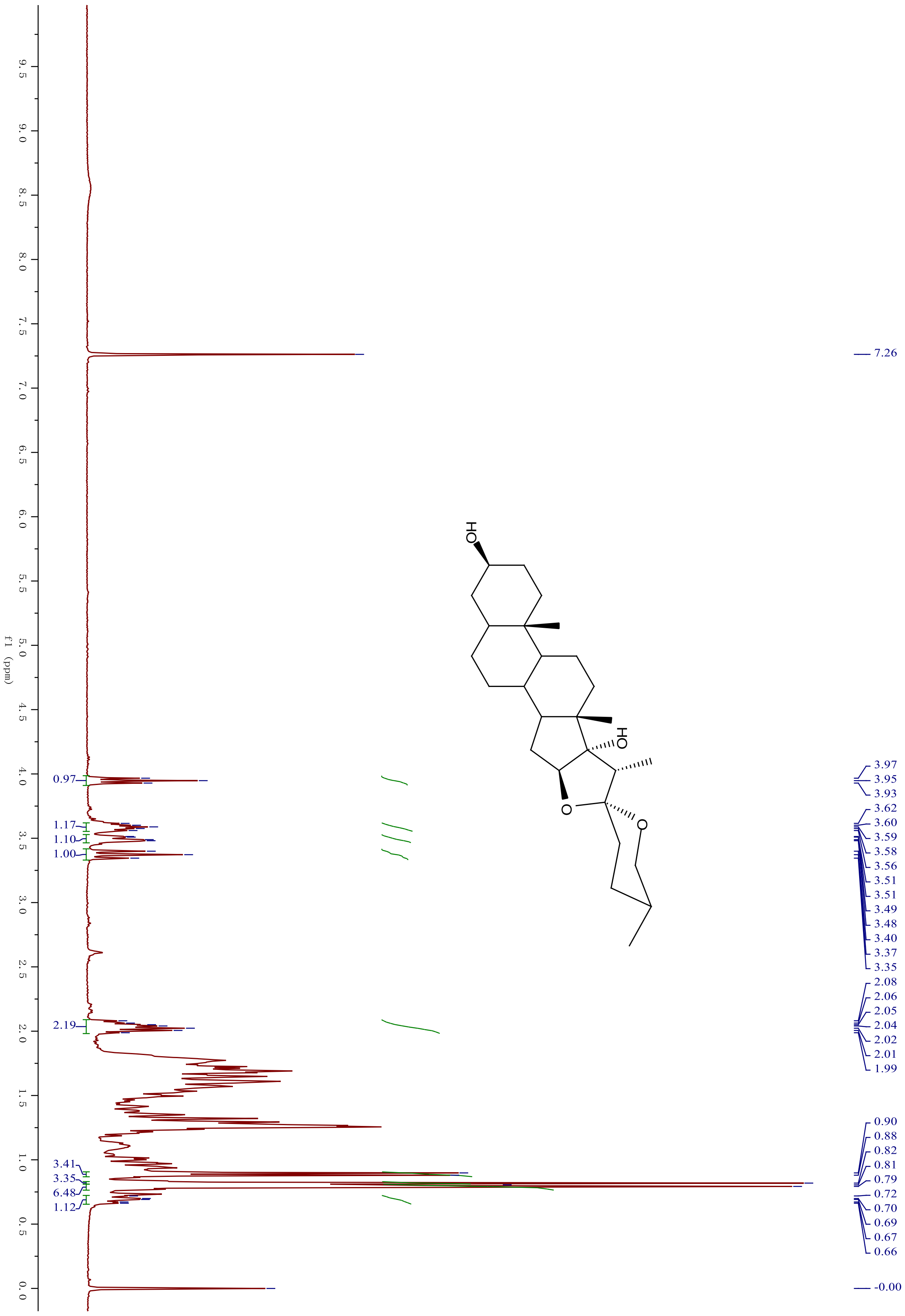
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1.00
1.08
3.08
1.34
1.24
3.01
4.42
3.37
3.24
1.15
7.26
3.88
3.86
3.84
3.63
3.61
3.60
3.59
3.57
3.56
3.53
3.52
3.51
3.50
3.48
3.47
3.45
3.44
3.42
2.10
2.08
2.06
2.04
2.03
1.96
1.95
1.93
1.91
1.89
0.93
0.91
0.88
0.86
0.82
0.81
0.68
0.68
0.66
0.63
0.62
-0.00
HO
H
H
H
H
HO
O
OH


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
HO
H
H
H
H
HO
O
OH
91.6
91.6
91.2
89.5
89.3
71.4
68.2
68.1
54.0
52.5
45.0
44.9
41.1
38.3
37.1
36.1
35.9
35.7
35.7
32.2
32.0
31.6
31.2
30.7
30.5
29.8
29.7
28.7
20.7
17.4
16.9
16.7
12.5
11.4
11.4


9.5
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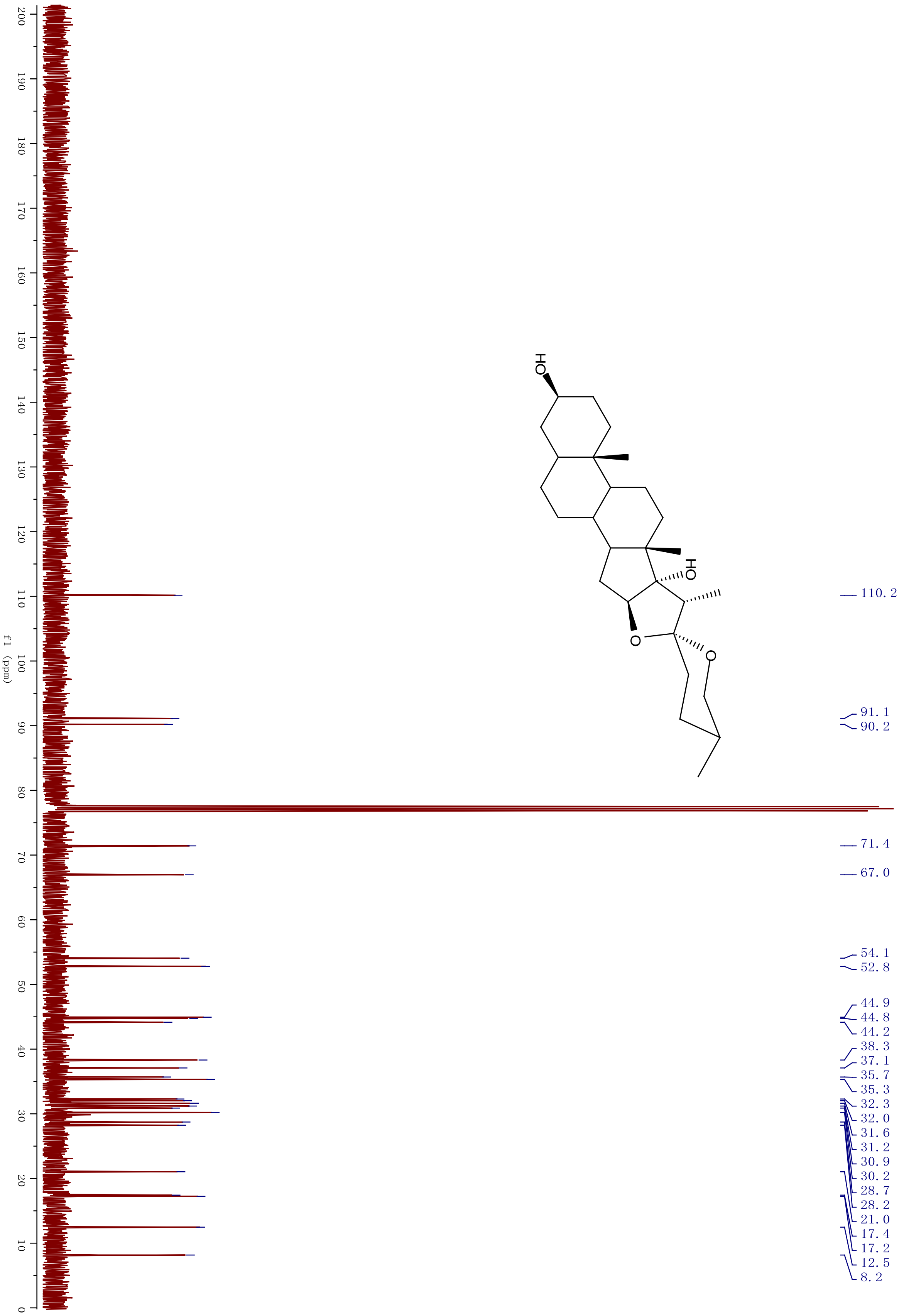
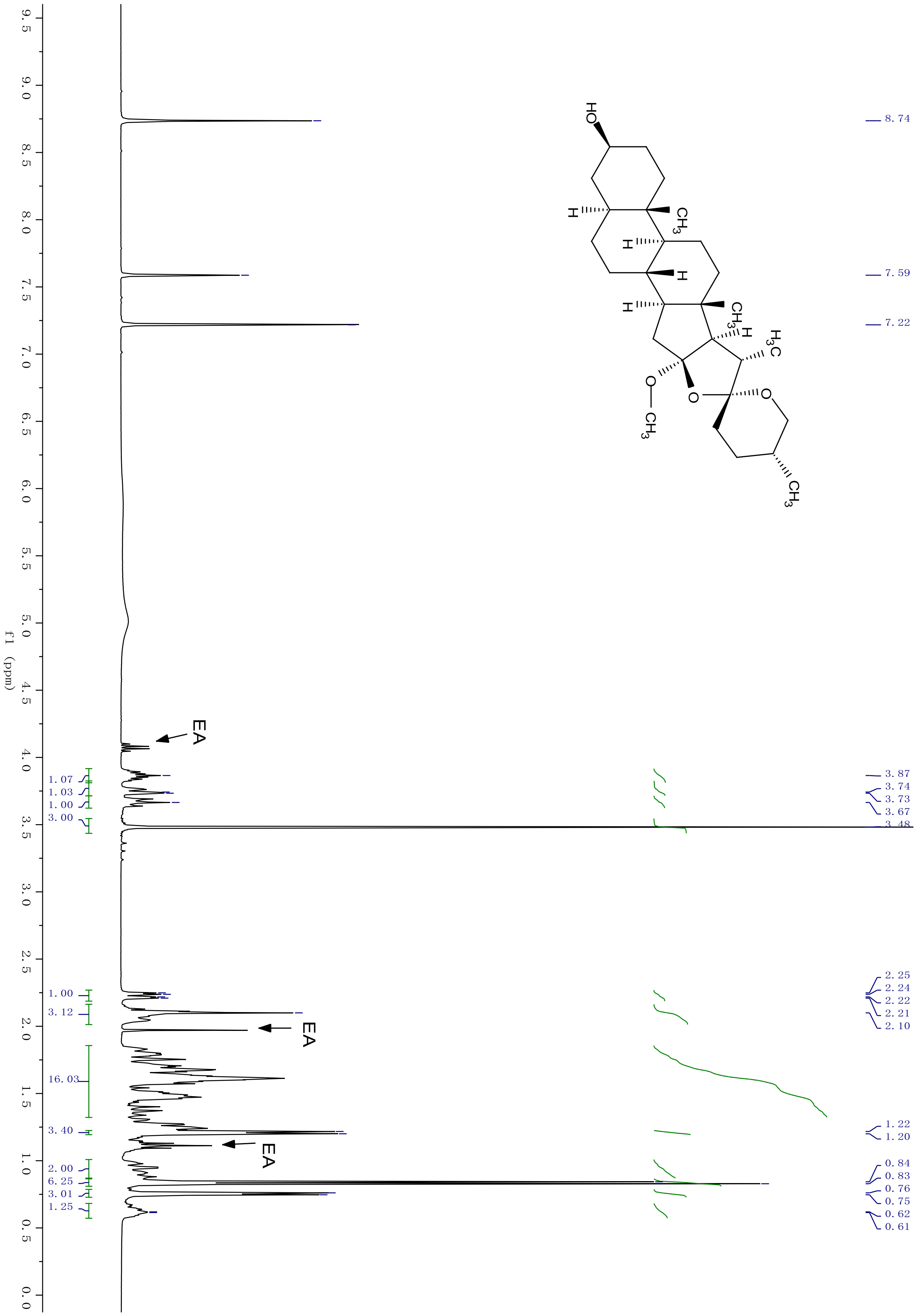
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.97
1.17
1.10
1.00
2.19
3.41
3.35
6.48
1.12
7.26
3.97
3.95
3.93
3.62
3.60
3.59
3.58
3.56
3.51
3.51
3.49
3.48
3.40
3.37
3.35
2.08
2.06
2.05
2.04
2.02
2.01
1.99
0.90
0.88
0.82
0.81
0.79
0.72
0.70
0.69
0.67
0.66
-0.00
HO
HO
O
O


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
HO
HO
O
O
110. 2
91. 1
90. 2
71. 4
67. 0
54. 1
52. 8
44. 9
44. 8
44. 2
38. 3
37. 1
35. 7
35. 3
32. 3
32. 0
31. 6
31. 2
30. 9
30. 2
28. 7
28. 2
21. 0
17. 4
17. 2
12. 5
8. 2

400 MHz ^1H NMR of compound **18** in pyridine-d5.



100 MHz ^{13}C NMR of compound **18** in pyridine-d5