New Sesquiterpenoids from *Bontia daphnoides*: Antioxidant and Antidiabetic Evaluation

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Supplementary material:

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Experimental section

General instruments and chemicals

For chromatographic separation, silica gel 60 (Sigma-Aldrich Chemicals, Darmstadt, Germany), and sephadex LH-20 (0.25-0.1 mm, GE Healthcare Bio-Sciences AB SE 75184 Uppsala, Sweden) were used for column chromatography (CC). TLC plates (Fluka precoated silica gel F254) were used for column monitoring. Deuterated solvents were used for NMR analysis includedfor NMR analysis were MeOH-d_4 (CD_3OD), dimethyl sulphoxide-d_6 (DMSO-d_6), and chloroform-d ($CDCl_3$) were purchased from (Sigma-Aldrich, Germany). Brucker NMR spectrometer was used to acquire NMR data running at 400 MHz for ^1H, and 100 MHz for ^{13}C NMR and DEPTQ.

Exploration of the ethyl alcohol extract of *Bontia daphnoides* aerial parts

The dried aerial parts of *B. daphnoides* (1.6 kg) were exhaustively extracted by cold maceration (6×8 L, each 48 h) with aqueous ethanol (80%). The evaporated extract was suspended in distilled water and successively partitioned with *n*-hexane (5×1 L), then methylene chloride (DCM) (6×1 L), followed by ethyl acetate (EtOAc) (6×1 L) and finally *n*-butanol (5×1 L). The different extractives evaporated to dryness to yield 10, 6, 5 and 67 g, respectively.

The *n*-hexane fraction (10 g) was subjected to silica gel CC and *n*-hexane as a mobile phase with gradual increase in polarity using EtOAc 2.5% till 10%, then 5% increments in polarity till 30%, then 100% EtOAc and finally 100% MeOH. Thin layer chromatography (TLC) and the universal spray reagent *p*-anisaldehyde were used for monitoring the collected fractions similarity. Similar fractions were combined together and evaporated separately under reduced pressure till dryness to yield three main subfractions (**HA-HC**).

Sub-fraction H**A** (0.2 gm) eluted with *n*-hexane:EtOAc (86%) was subjected to further purification on silica gel CC using 100% DCM, then 100% MeOH. Similar fractions were collected and evaporated to dryness yielding sub-fraction H$\mathbf{A_1}$. Sub-fraction H$\mathbf{A_1}$ (25 mg) was found to contain one major spot and was subjected to further purification using a CC of Sephadex LH-20 and 100% MeOH as a mobile phase to afford **compound 1** (20 mg).

Sub-fraction HB (2 g) eluted with *n*-hexane:EtOAc (85%) was re-crystalized from *n*-Hexane using methanol to afford **compound 2** (48.9 mg). The soluble part of sub-fraction HB was subjected to further purification on silica gel CC (60 g) using *n*-Hexane:EtOAc mixture with 10% increments in polarity till 50% EtOAc, then 100% EtOAc. Thin layer chromatography

(TLC) and the universal spray reagent *p*-anisaldehyde were used for monitoring the collected fractions similarity. Similar fractions were combined together and evaporated separately under reduced pressure till dryness to yield **Sub-fraction HB_1** that was obtained at *n*-hexane-EtOAc (90:10%). Sub-fraction B_1 was subjected to preparative TLC using solvent system Hexane: ethyl acetate (8.5:1.5) to afford **compound 3** (3.3 mg).

Sub-fraction HC (1 g) eluted with *n*-hexane:EtOAc (10%) was precipitation from MeOH to afford **compound 4** (10 mg).

The methylene chloride fraction (6 gm) was subjected to silica gel CC (180 gm) using *n*-Hexane-EtOAc mixture with 10% increments in polarity till 25% EtOA, then 5% increments in polarity till 50% EtOAc, then 100% EtOAc and finally 100% MeOH. Thin layer chromatography (TLC) and the universal spray reagent *p*-anisaldehyde were used for monitoring the collected fractions similarity. Similar fractions were combined together and evaporated separately under reduced pressure till dryness to yield **Sub-fraction MA** that was obtained at *n*- hexane:EtOAc (65%).

Sub-fraction MA (0.6 g) was subjected to silica gel CC (40gm) using *n*-Hexane- EtOAc mixture with 5% increments in polarity till 30% EtOAc, then 100% EtOAc and finally 100% MeOH. Thin layer chromatography (TLC) and the universal spray reagent *p*-anisaldehyde were used for monitoring the collected fractions similarity. Similar fractions were combined and evaporated separately under reduced pressure till dryness to yield **Sub-fraction MA_1** which was obtained at *n*-hexane:EtOAc (85%). **Sub-fraction MA_1** was further purified using Sephadex LH-20 CC using (80-20%) MeOH-DCM to afford mixture of **compound 5 and 6** (5 mg).

The *n*-butanol fraction (15 g) was subjected to polyamide CC using Distilled H_2O-methanol mixture with 10% increments in polarity till 100% MeOH. Thin layer chromatography (TLC) and the universal spray reagent *p*-anisaldehyde were used for monitoring the collected fractions similarity. Similar fractions were combined and evaporated separately under reduced pressure till dryness to yield four main subfractions **(BA-BD)** were obtained.

Sub-fraction BA (6 g) eluted with H_2O:MeOH (90%) was subjected to further purification on silica gel CC (210 g) using DCM:MeOH mixture with 10% increments in polarity till 50%, then 5% increments in polarity till 100% MeOH. Thin-layer chromatography (TLC), in combination with the universal detection reagent *p*-anisaldehyde, was employed to monitor and evaluate the similarity among collected fractions. Fractions displaying comparable chromatographic profiles

were subsequently pooled and concentrated individually under reduced pressure to dryness, affording one main **sub-fraction BA_1** was obtained.

Sub-fraction BA_1 (2.5 gm) eluted with DCM:MeOH (75%) and (70%) were subjected to further purification on silica gel CC (75 g) using DCM:MeOH mixture with10% increments in polarity till 10% (isocratic) then 5% increments in polarity till 30% then 100% MeOH. Thin-layer chromatography (TLC), together with the universal spray reagent *p*-anisaldehyde, was utilized to assess the similarity of the collected fractions. Fractions exhibiting analogous chromatographic patterns were subsequently combined and concentrated separately under reduced pressure to dryness, yielding one main **sub-fraction BA_{1a}**.

Sub-fraction BA_{1a} (1.2 gm) eluted with DCM:MeOH (90%) isocratic was subjected to further purification on silica gel column (36 g) using DCM-MeOH mixture with 1% increments in polarity till 10% then 2% increments in polarity till 20% then 100% MeOH. Thin layer chromatography (TLC) and the universal spray reagent *p*-anisaldehyde were used for monitoring the collected fractions similarity. Similar fractions were combined and evaporated separately under reduced pressure till dryness to afford one main **sub-fraction BA_{1a1}**.

Sub-fraction BA_{1a1} eluted with DCM:MeOH (82%) was subjected to further purification using preparative TLC and solvent system DCM:MeOH (8:2) to afford **compound 7** (10.3 mg).

Sub-fraction BB (1.5 g) eluted with H_2O:MeOH (20%) was subjected to further purification on silica gel CC (45 g) using DCM:MeOH mixture with 1% increments in polarity till 10%, then 5% increment in polarity till 20% MeOH and finally 100% MeOH. Thin-layer chromatography (TLC), in conjunction with the universal detection reagent *p*-anisaldehyde, was applied to monitor and compare the collected fractions. Fractions exhibiting similar chromatographic characteristics were subsequently pooled and concentrated individually under reduced pressure to dryness, affording one main **sub-fraction BB_1**.

Sub-fraction BB_1 (0.8 gm) was subject to further purification using Sephadex LH-20 CC using 100% MeOH to afford **compound 8** (37.7 mg).

Sub-fraction C (1.5 g) eluted with H_2O:MeOH (40%) was subjected to further purification on silica gel CC (45 g) using DCM:MeOH mixture with 10% increments in polarity till isocratic, then 5% increments in polarity till 20% MeOH and finally 100% MeOH. Thin-layer chromatography (TLC) coupled with the universal visualization reagent *p*-anisaldehyde was employed to evaluate and monitor the collected fractions. Fractions displaying comparable

chromatographic profiles were subsequently combined and concentrated separately under reduced pressure to dryness, yielding one main **sub-fraction BC_1**.

Sub-fraction BC_1 (0.4 gm) was subject to further purification using Sephadex LH-20 CC using 100% MeOH to afford **compound 9** (3 mg).

Sub-fraction BD (0.2 g) eluted with H_2O:MeOH (10%) was subjected to further purification using Sephadex LH-20 CC using 100% MeOH to afford **compound 10** (3 mg).

Spectral data of the isolated compounds

Dehydromyoporone (1): White powder (20 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ_H 8.01 (1H, s, H-15), 7.41 (1H, s, H-1), 6.73 (1H, s, H-2), 6.04 (1H, s, H-10), 2.66~2.78 (2H, m, H-5a,b), 2.40 (1H, dd, *J*=16, 8 Hz, H-8a), 2.25 (1H, dd, *J*=16, 8 Hz, H-8b), 2.11 (3H, s, H-13), 2.02~2.07 (1H, m, H-7), 1.85 (3H, s, H-12), 1.67~1.76 (1H, m, H-6a), 1.52~1.61 (1H, m, H-6b), 0.925 (3H, d, *J*= 6.8 Hz, H-14) Figure S_1. DEPTQ ($CDCl_3$,100 MHz): δ_C 200.5 (C, C-9), 195.2 (C, C-4), 155.4 (C, C-11), 147.2 (CH, C-15), 144.2 (CH, C-1), 127.7 (C, C-3), 124.2 (CH, C-10), 108.8 (CH, C-2), 51.5 (CH_2, C-8), 38.3 (CH_2, C-5), 31.4 (CH_2, C-6), 29.5 (CH, C-7), 27.7 (CH_3, C-12), 20.8 (CH_3, C-13), 19.9 (CH_3, C-14) Figure S_2 [1].

***β*-sitosterol (2):** White powder (48.9 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): showed six methyl groups at: δ_H 0.68, 0.80, 0.83, 0.84, 0.91, 1.01 (H-28, H-27, H-26, H-24, H-19, H-29), δ_H: 3.52 (1H, m, H-3), 5.34 (1H, d, *J*=4, H-6) Figure S_3. DEPT-Q ($CDCl_3$,100 MHz) δ_C: 37.2 (C-1), 31.6 (C-2), 71.9 (C-3), 42.2 (C-4), 140.8 (C-5), 122.1 (C-6), 31.9 (C-7), 31.8 (C-8), 50.1 (C-9), 36.4 (C-10), 21.0 (C-11), 39.7 (C-12), 42.2 (C-13), 56.7 (C-14), 26.0 (C-15), 28.2 (C-16), 56.0 (C-17), 36.1 (C-18), 19.0 (C-19), 33.9 (C-20), 26.0 (C-21), 45.8 (C-22), 23.0 (C-23), 11.9 (C-24), 29.1 (C-25), 19.8 (C-26), 19.4 (C-27), 18.7 (C-28), 11.8 (C-29) Figure S_4 [2, 3].

***α*- amyrin (3):** White powder (3.3 mg), ^{1}H NMR (DMSO, 400 MHz): δ_H 5.135 (1H, m, H-12), 2.99 (1H, m, H-3), 1.23, 0.90, 0.87, 0.86, 0.80 and 0.74 (3H, s, 6 x CH_3), 1.459 (3H, d, 2 x CH_3). Figure S_5. DEPTQ (DMSO, 400 MHz): δ_C 138.2 (C, C-13), 124.6 (CH, C-12), 76.9 (CH, C-3), 54.8 (CH, C-18), 52.4 (CH, C-5), 47.0 (CH, C-9), 42.11 (C, C-14), 41.7 (CH_2, C-22), 40.58 (C, C-8), 38.5 (CH, C-19 & 20), 38.4 (CH_2, C-1), 38.2 (C, C-4), 36.5 (C, C-10), 32.7 (CH_2, C-7), 32.7 (C, C-17), 30.2 (CH_2, C-21)), 28.3 (CH_3, C-28), 28 (CH_3, C-23), 27.6 (CH_2, C-15), 27.0 (CH_2, C-2), 23.8 (CH_2, C-16), 23.3 (CH_3, C-27), 22.9 (CH_2, C-11), 21.1 (CH_3, C-30), 18.0 (CH_2, C-6), 17.0 (CH_3, C-26), 16.1 (CH_3, C-29), 15.2 (CH_3, C-24 & 25) Figure S_6 [4, 5].

***β*- Sitosterol glycoside (4):** White needle crystals (10 mg), ^{1}H NMR (C_5D_5N, 400 MHz): δ_H 5.37 (1H, s, H-6), 5.07 (1H, d, *J*= 7.6, 1.6Hz, H- Glc-1'), 0.69, 0.88, 0.90, 0.92, 0.96, 1.02 (6 CH_3, H-18, 19, 21, 26, 27 & 29), Figure S_7. DEPT-Q (C_5D_5N, 100 MHz): δ_C 141.4 (C, C-5), 122.4 (CH, C-6), 103.11 (CH, C- Glc-1'), 79.1 (CH, C-3), 78.9 (CH, C- Glc-3'), 78.7 (CH, C- Glc-5'), 75.8 (CH, C- Glc-2'), 72.2 (CH, C- Glc-4'), 63.3 (CH_2, C- Glc-6'), 57.3 (CH, C-14), 56.8 (CH, C-17), 50.9 (CH, C-9), 46.6 (CH, C-24), 43.0 (C, C-13), 40.5 (CH_2, C-4), 39.8 (CH_2, C-12), 38.0 (CH_2, C-1), 37.4 (C, C-10), 36.9 (CH, CH-20), 34.7 (CH_2, C-22), 32.7 (CH_2, C-7), 32.6 (CH, C-8), 30.8 (CH_2, C-16), 30.5 (CH_2, C-2), 30.0 (CH, C-25), 29.1 (CH_2, C-16), 26.9 (CH_2, C-23), 25.0 (CH_2, C-15), 23.9 (CH_2, C-28), 21.8 (CH_2, C-11), 20.5 (CH_3, C-27), 19.9 (CH_3, C-19), 19.7 (CH_3, C-26), 19.5 (CH_3, C-21), 12.7 (CH_3, C-29), 12.5 (CH_3, C-18) Figure S_8 [6, 7].

8-acetyl harpagide (7): White powder (10.3 mg), ^{1}H NMR (CD_3OD, 400 MHz): δ_H 6.42 (1H, d, *J*= 6.4 Hz, H-3), 6.11 (1H, br s, H-1), 4.95 (1H, dd, *J*= 6.4, 1.6Hz, H-4), 4.63 (1H, d, *J*= 8 Hz, H-1`), 3.93 ((1H, d, *J*= 12 Hz, H-6`), 3.75 (2H, m, H-3`& 6`), 3.72 (1H, d, *J*= 5.2 Hz, H-6), 3.35-3.34 (2H, m, H-4` & 5`), 3.24 (1H, t, *J*= 16.8, 8 Hz, H-2`), 2.89 (1H, s, H-9), 2.21 (1H, d, *J*= 15.2 Hz, H-7), 2.05 (3H, s, $CH_3CO$), 1.98 (1H, dd, *J*= 15.2, 4.8 Hz, H-7), 1.49 (3H, s, H-10) Figure $S_{14}$. DEPTQ ($CD_3OD$, 100 MHz): $\delta_C$ 173.4 (C, CO), 143.8 (CH, C-3), 106.9 (CH, C-4), 99.9 (CH, C-1`), 94.5 (CH, C-1), 88.6 (C, C-8), 78.1 (CH, C-3`), 77.6 (CH, C-6 & 5`), 74.5 (CH, C-2`), 73.3 (C, C-5), 71.6 (CH, C-4`), 62.8 (CH_2, C-6`), 55.4 (CH, C-9), 46.0 (CH_2, C-7), 22.5 (CH_3, C-14), 22.2 (CH_3, C-10) Figure S_{15} [8, 9].

Verbascoside (8): Pale yellow powder (37.7 mg), ^{1}H NMR (CD_3OD, 400 MHz): δ_H 7.62 (1H, d, *J*= 16 Hz, H-7``), 7.09 (1H, s, H-2``), 6.98 (1H, d, *J*= 8 Hz, H-6``), 6.81 (1H, d, *J*= 8 Hz, H-5``), 6.72 (2H, m, H-2 & H-5), 6.59 (1H, d, *J*= 8 Hz, H-6), 6.30 (1H, d, *J*= 16 Hz, H-8``), 5.22 (1H, s, H-1```), 4.99 (1H, m, H-4`), 4.40 (1H, d, *J*= 8 Hz, H-1`), 4.05 (1H, m, H-8), 3.96 (1H, s, H-**2**```), 3.84 (1H, m, H-**3**`), 3.74 (1H, m, H-**3**```), 3.54-3.67 (6H, m, H-8, **2`, 5`, 6` & 5**```), 3.43 (1H, m, H-4```), 2.81 (2H, m, H-7), 1.1195 (3H, d, *J*= 6 Hz, H- 6```) Figure S_{16}. DEPTQ (CD_3OD, 100 MHz): δ_C 168.3 (C, C- **9**``), 146.8 (C, C-**4**``), 148.0 (CH, C-**7**``), 149.8 (C, C-**3**``), 146.1 (C, C-3), 144.7 (C, C-4), 131.5 (C, C-1), 127.6 (C, C-**1**``), 123.2 (CH, C-**6**``), 121.3 (CH, C-6), 117.1 (CH, C-2), 116.3 (CH, C-**5**``), 116.3 (CH, C-5), 115.2 (CH, C-**2**``), 114.7 (CH, C-**8**``), 103.0 (CH, C-**1**```), 104.2 (CH, C-**1**`), 81.7 (CH, C-**3**`), 76.3 (CH, C-**2**`), 76.0 (CH, C-**5**`), 73.8 (CH, C-**4**```), 72.3 (CH_2, C-**8**), 72.3 (CH, C-**2**```), 72.1 (CH, C-**3**```), 70.4 (CH, C-**4**`), 70.6 (CH, C-**5**```), 62.4 (CH_2, C-**6**`), 18.4 (CH_3, C-**6**```) Figure S_{17} [10].

Crenatoside (9): Amorphous powder (3 mg), ^{1}H NMR (CD_3OD, 400 MHz): δ_H 7.64 (1H, d, *J*= 16 Hz, H-7‟), 7.09 (1H, d, *J*= 2 Hz, H-2‟), 6.99 (1H, dd, *J*= 2, 8.4 Hz, H-6‟), 6.85 (1H, d, *J*= 2 Hz, H-2), 6.81 (1H, d, *J*= 8 Hz, H-5‟), 6.76 (1H, d, *J*= 8 Hz, H-5), 6.71 (1H, dd, *J*= 1.6, 8 Hz, H-6), 6.30 (1H, d, *J*= 16 Hz, H-8‟), 5.19 (1H, d, *J*= 1.6 Hz, H-1‟‟‟), 5.12 (1H, t, *J*= 9.6, 19.2 Hz, H-4`), 4.92 (1H, dd, *J*= 2.4, 10.8 Hz, H-7), 4.57 (1H, d, *J*= 7.6 Hz, H-1`), 4.15 (1H, t, *J*= 9.6, 18.8 Hz, H-3`), 4.01 (1H, dd, *J*= 2.8, 12 Hz H-8), 3.80 (2H, m, H-5` & 2‟‟‟), 3.68 (1H, m, H-6`), 3.62 (1H, m, H-8), 3.57 (1H, m, H- 6`), 3.54 (1H, dd, *J*= 3.2, 9.6 Hz, H-3`), 3.47 (1H, m, H-2`), 1.25 (3H, d, *J*= 6.4 Hz, H-6‟‟‟) Figure S_{18}. DEPTQ (CD_3OD, 100 MHz): δ_C 168.1 (C, C- **9**‟), 148.3 (CH, C-**7**‟), 146.8 (C, C-**3 & 4**), 146.4 (C, C-**3**‟ **& 4**‟), 129.8 (C, C-1), 127.6 (C, C-**1**‟), 123.3 (CH, C-**6**‟), 118.9 (CH, C-**6**), 116.5 (CH, C-**5**‟), 116.3 (CH, C-5), 115.3 (CH, C-**2**‟), 114.5 (CH, C-**2**), 114.4 (CH, C-**8**‟), 102.2 (CH, C-**1**‟‟‟), 99.1 (CH, C-**1**`), 81.9 (CH, C-**2**`), 78.4 (CH, C-**7**), 77.8 (CH, C-**5**`), 77.4 (CH, C-**3**`), 73.6 (CH, C-**4**‟‟‟), 73.0 (CH_2, C-**8**), 72.1 (CH, C-**2**‟‟‟), 72.0 (CH, C-**3**‟‟‟), 70.4 (CH, C-**4**`), 70.2 (CH, C-**5**‟‟‟) , 62.1 ($CH_2$, C-**6**`), 18.3 (CH_3, C-**6**‟‟‟) Figure S_{19} [11, 12].

Apigenin-7-*O* glucuronide (10): Yellow amorphous powder (3 mg), ^{1}H NMR (CD_3OD, 400 MHz): δ_H 7.92 (2H, d, *J*= 8.8 Hz, H-2` & 6`), 6.96 (2H, d, *J*= 8.7 Hz, H-3` & 5`), 6.88 (1H, d, *J*= 2 Hz, H-8), 6.68 (1H, s, H-3), 6.54 (1H, d, *J*= 2 Hz, H-6), 5.13 (1H, d, *J*=6.4, H-1‟), 3.90 (1H, d, *J*= 8.6 Hz, H-5‟), 3.58 (3H, m, H-2‟ & 3‟& 4‟) Figure S_{20}. DEPTQ (CD_3OD, 100 MHz): δ_C 184.1 (C, C-4), 176.3 (C, C-6‟), 166.9 (C, C-2), 164.9 (C, C-7), 162.8 (C, C-5), 159.0 (C, C-4`), 129.6 (CH, C-2` & 6`), 123.0 (C, C-1`), 117.0 (CH, C-3` & 5`), 107.1 (C, C-10), 104.0 (CH, C-3), 101.6 (CH, C-6), 101.4 (CH, C-1‟), 96.1 (CH, C-8), 77.6 (CH, C-5‟), 76.5 (CH, C-3‟) , 74.5 (CH, C-2‟) , 73.4 (CH, C-4‟) Figure S_{21} [13, 14].

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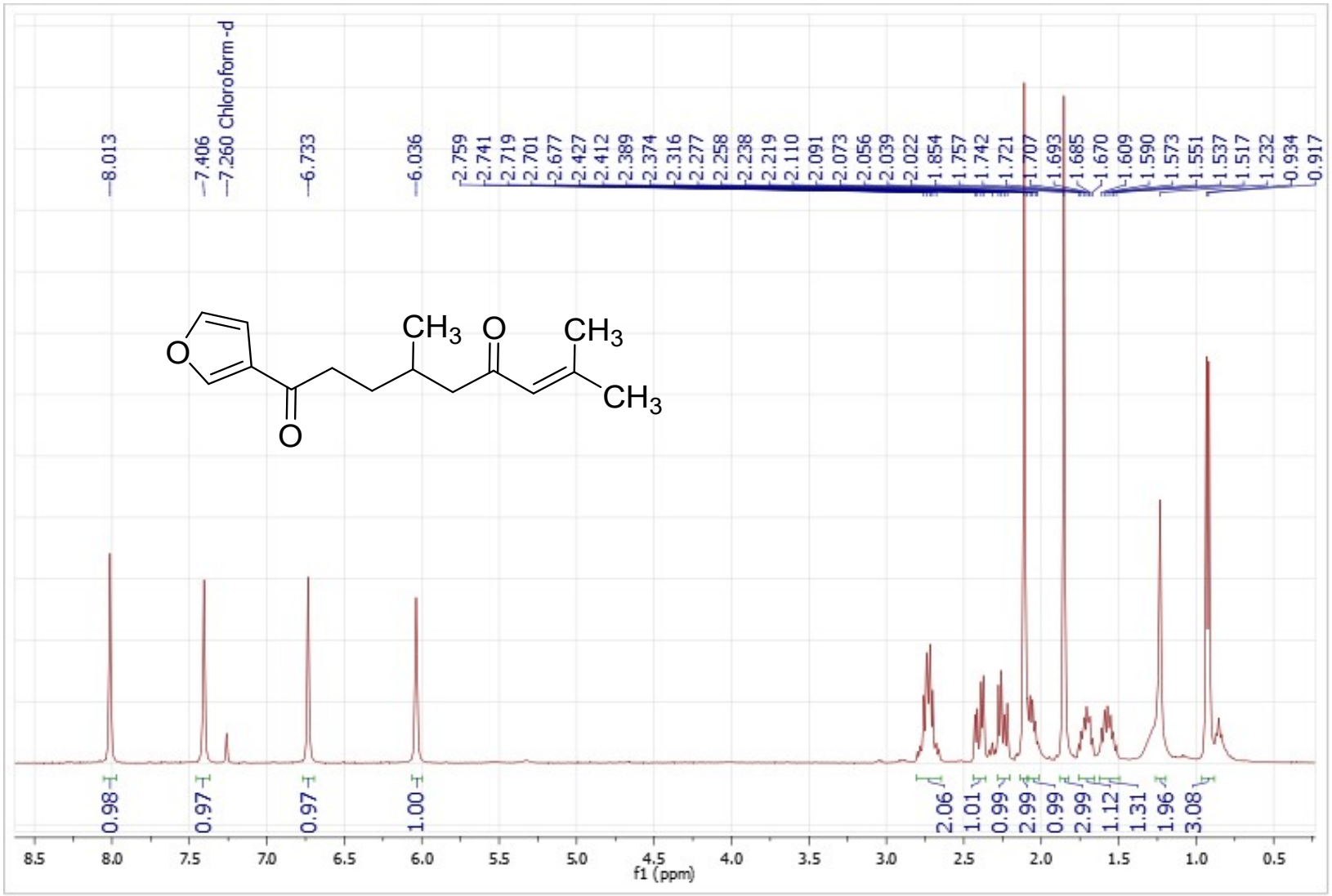


Figure S_1: ^{1}H NMR spectrum of compound (1) Dehydromyoporone ($CDCl_3$, 400 MHz)

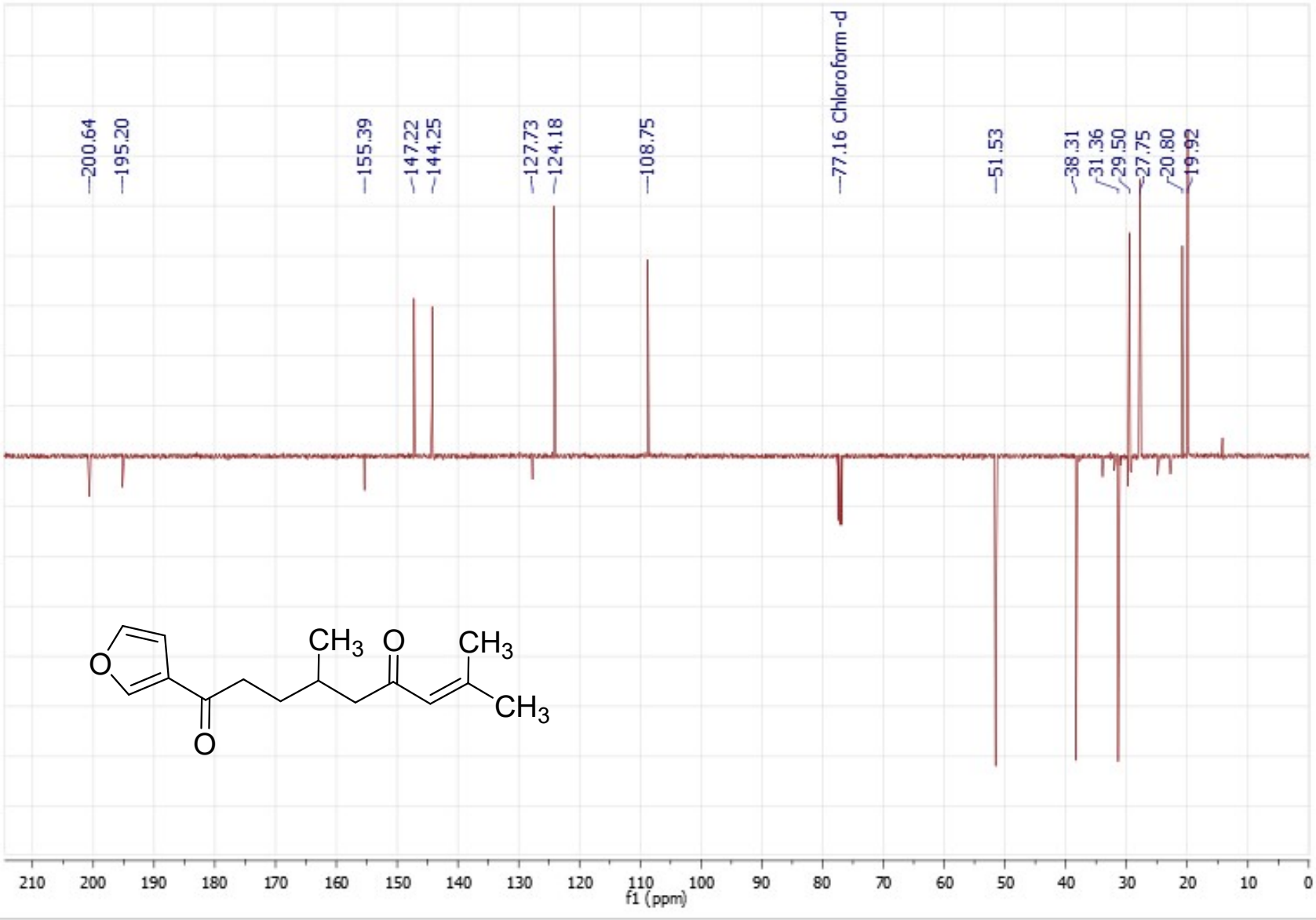


Figure S_2: DEPT-Q spectrum of compound (1) Dehydromyoporone ($CDCl_3$, 100 MHz)

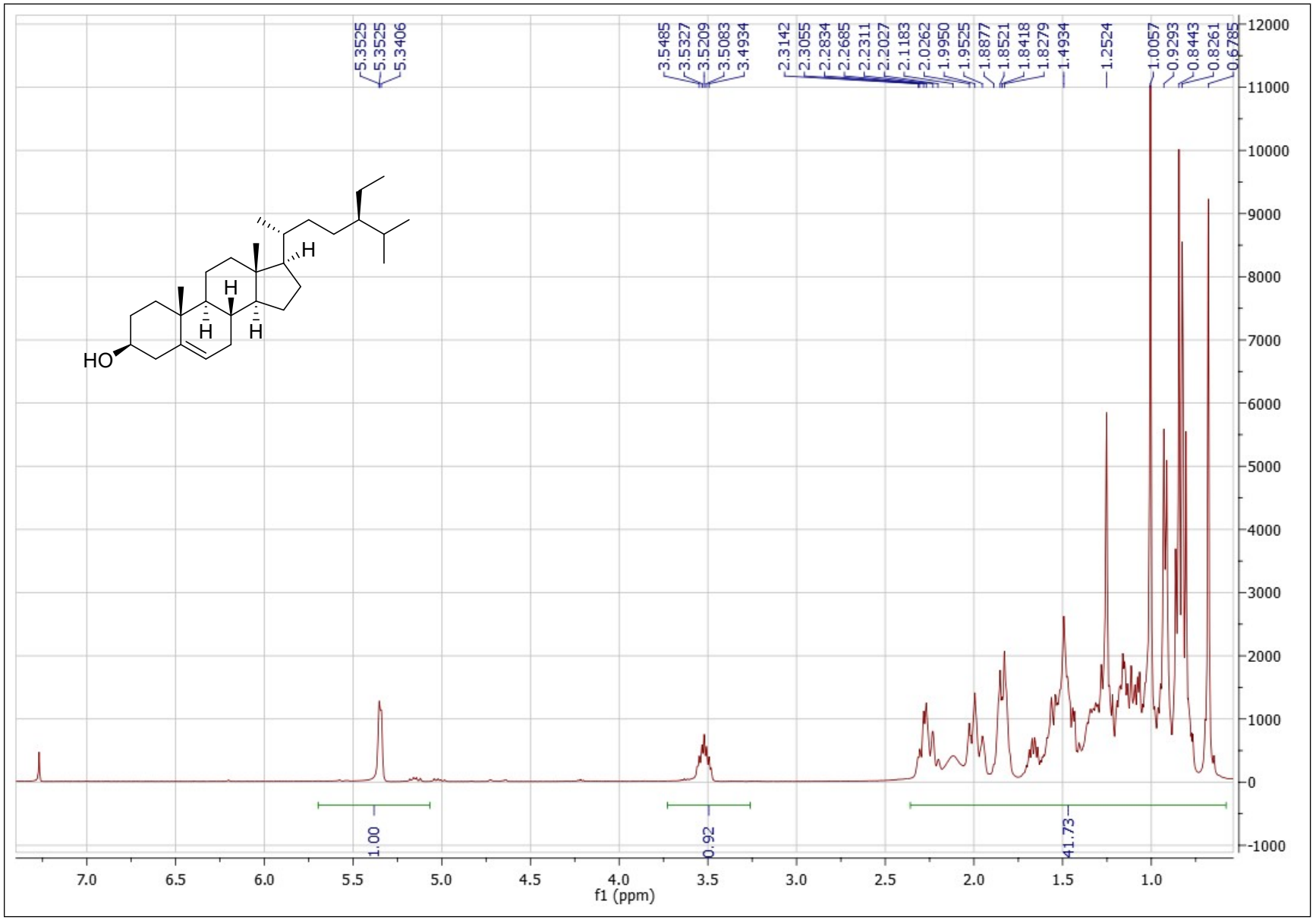


Figure S_3: ^{1}H NMR spectrum of compound (2) *β*-sitosterol ($CDCl_3$, 400 MHz)

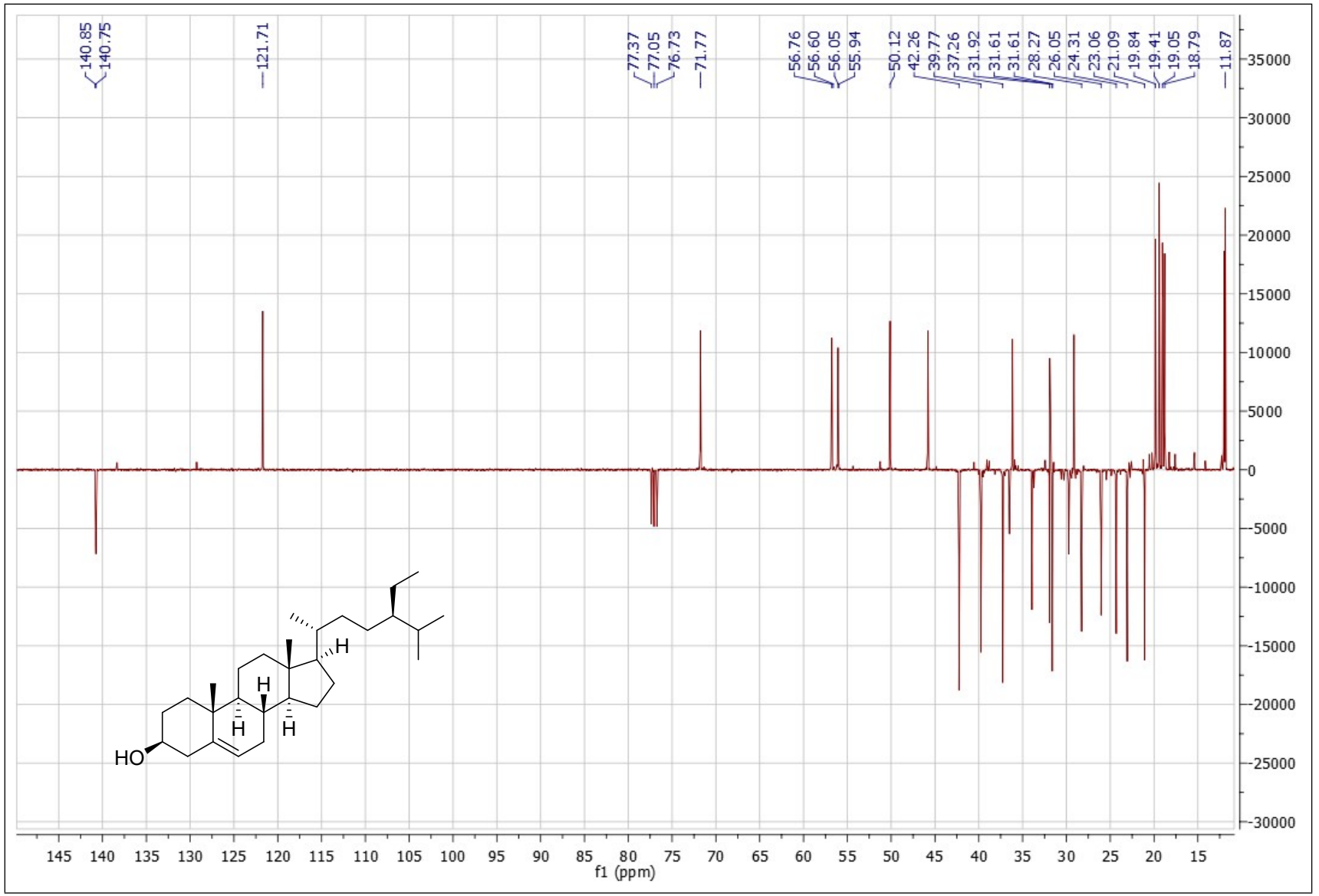


Figure S_4: DEPT-Q spectrum of compound (2) *β*-sitosterol ($CDCl_3$, 100 Hz)

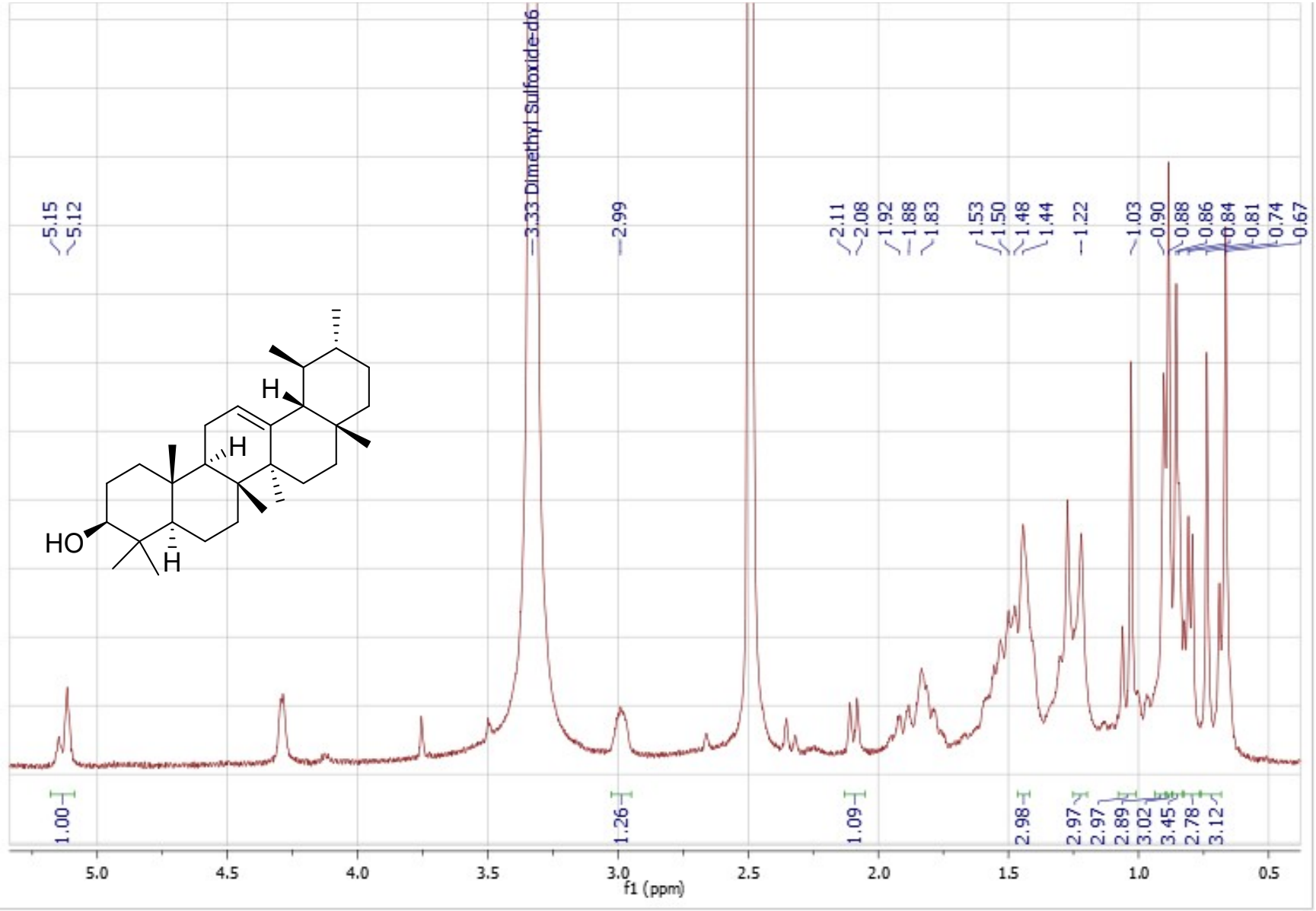


Figure S_5: ^{1}H NMR spectrum of compound (3) α-amyrin (DMSO, 400 MHz)

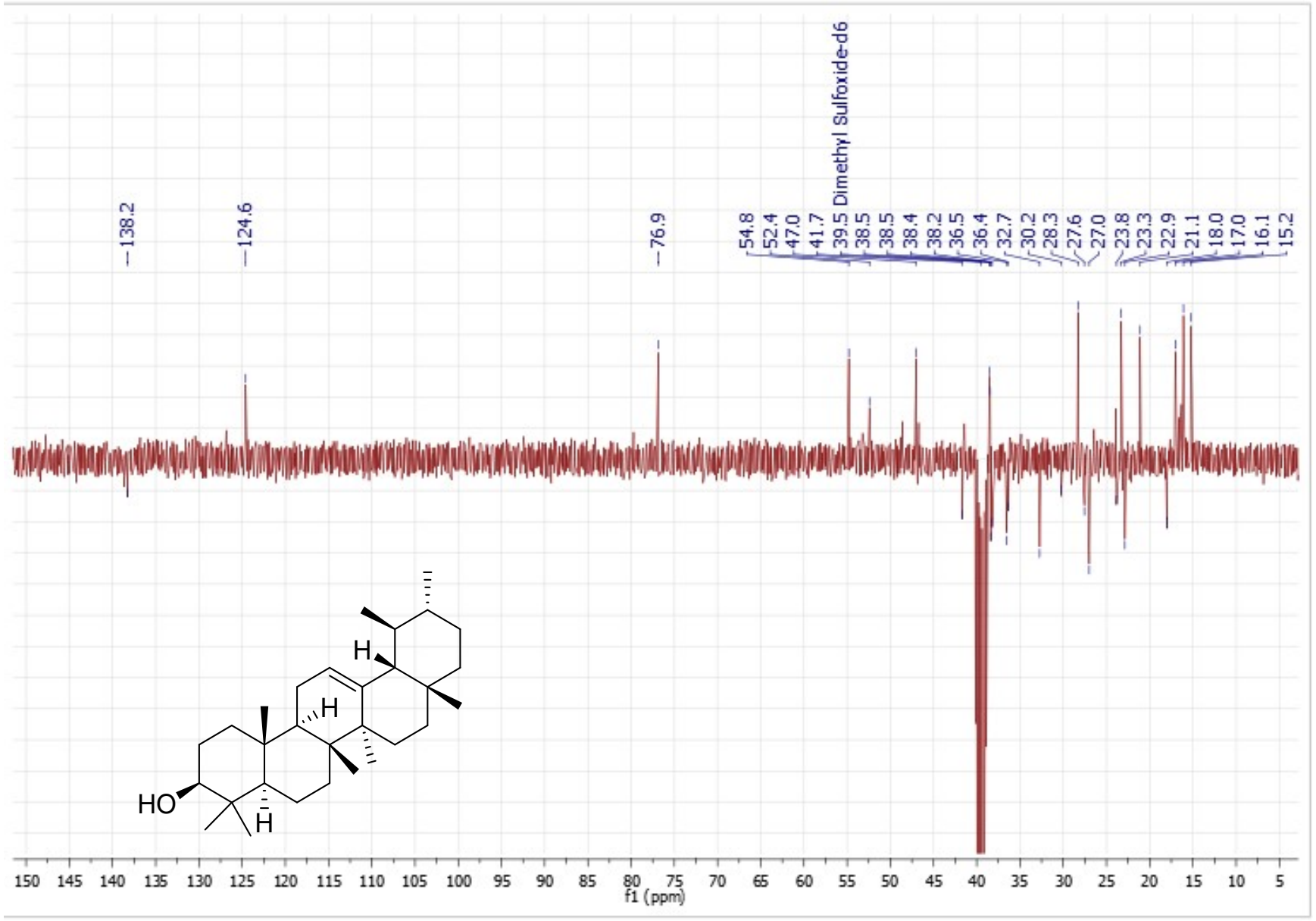


Figure S_6: DEPT-Q spectrum of compound (3) *α*-amyrin (DMSO, 100 MHz)

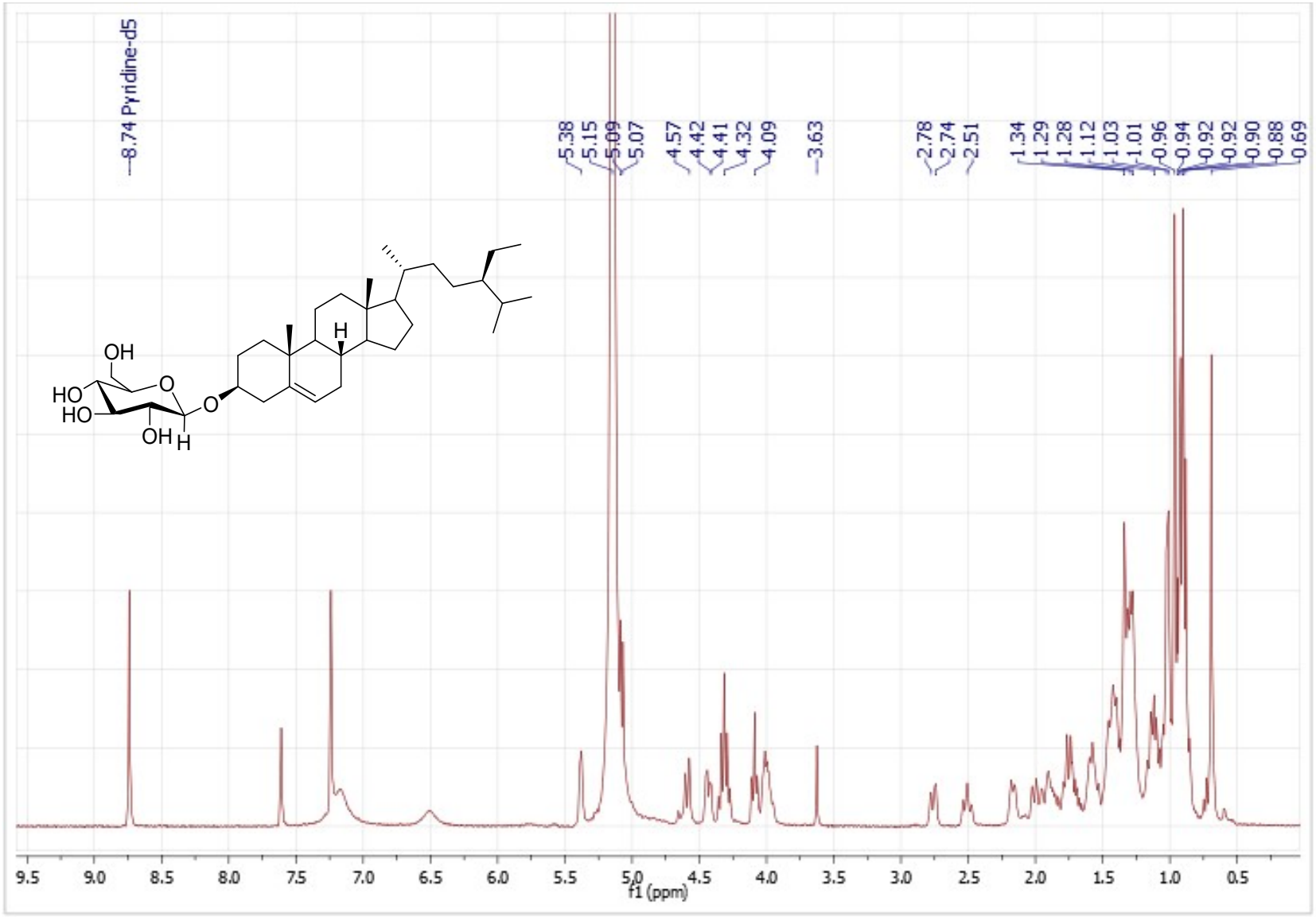


Figure S_7: ^{1}H NMR spectrum of compound (4) *β*-sitosterol glycoside (Pyridine, 400 MHz)

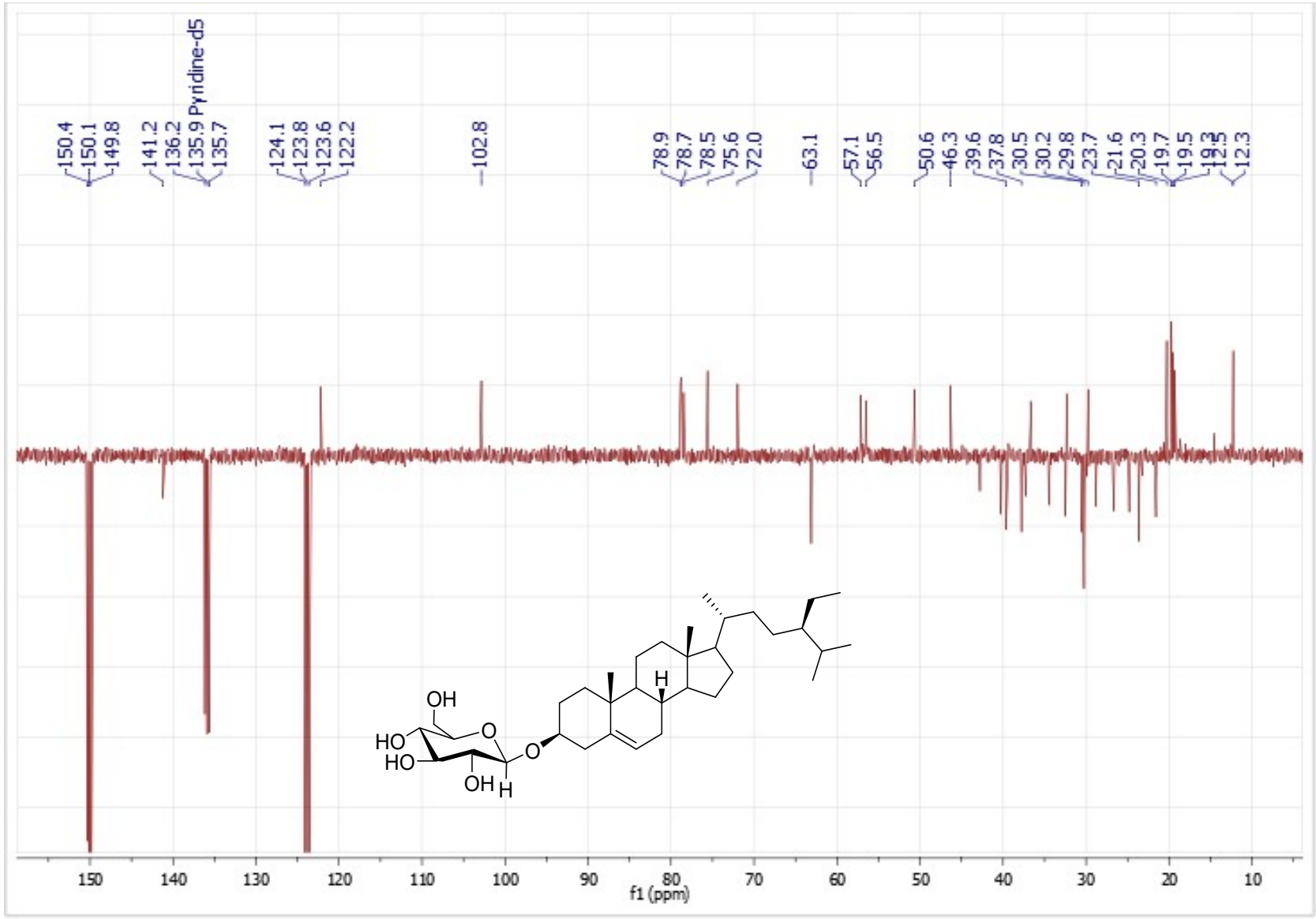


Figure S_8: DEPT-Q spectrum of compound (4) *β*-sitosterol glycoside (Pyridine, 100 MHz)

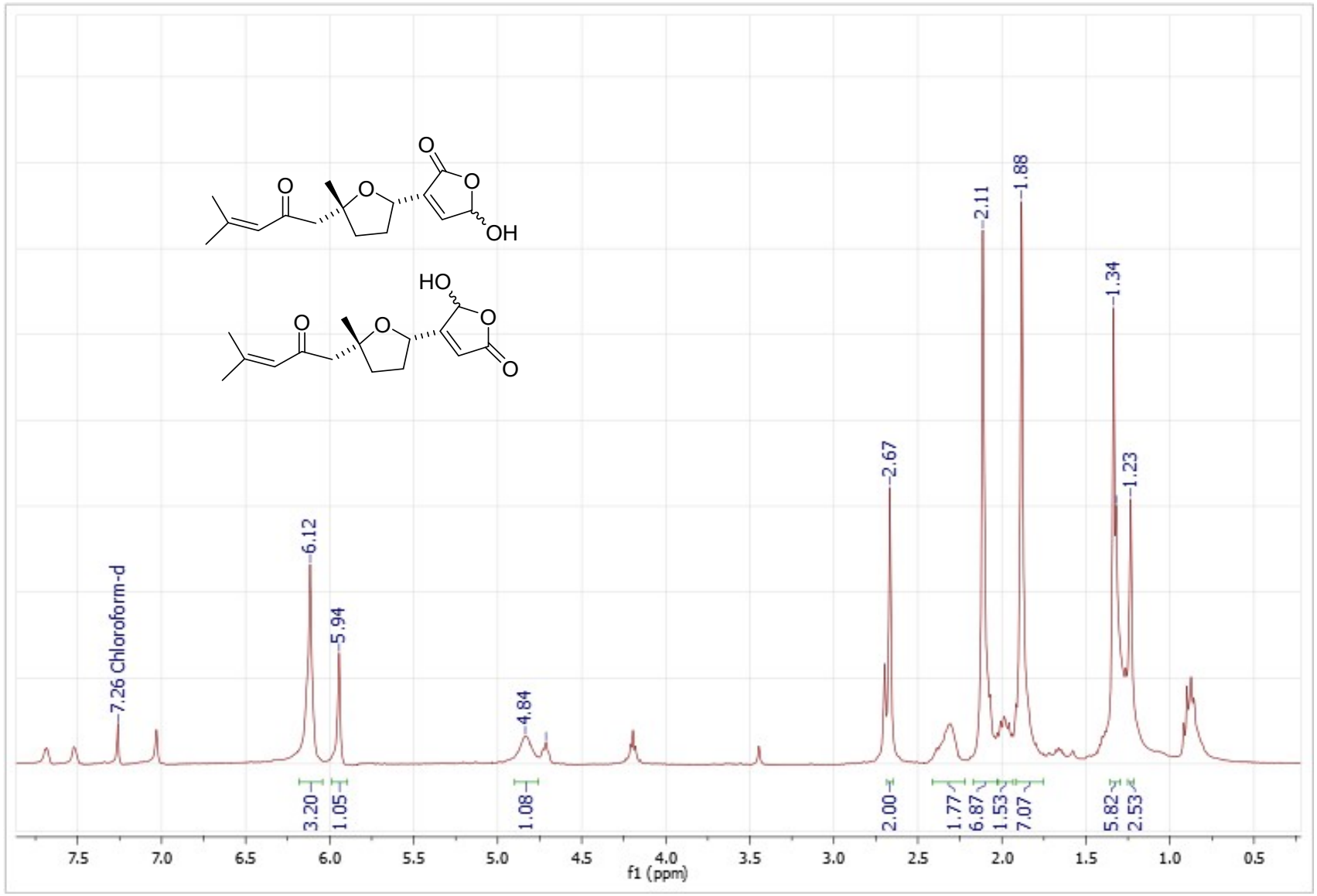


Figure S_9: ^{1}H NMR spectrum of compounds (5 and 6) ($CDCl_3$, 400 MHz)

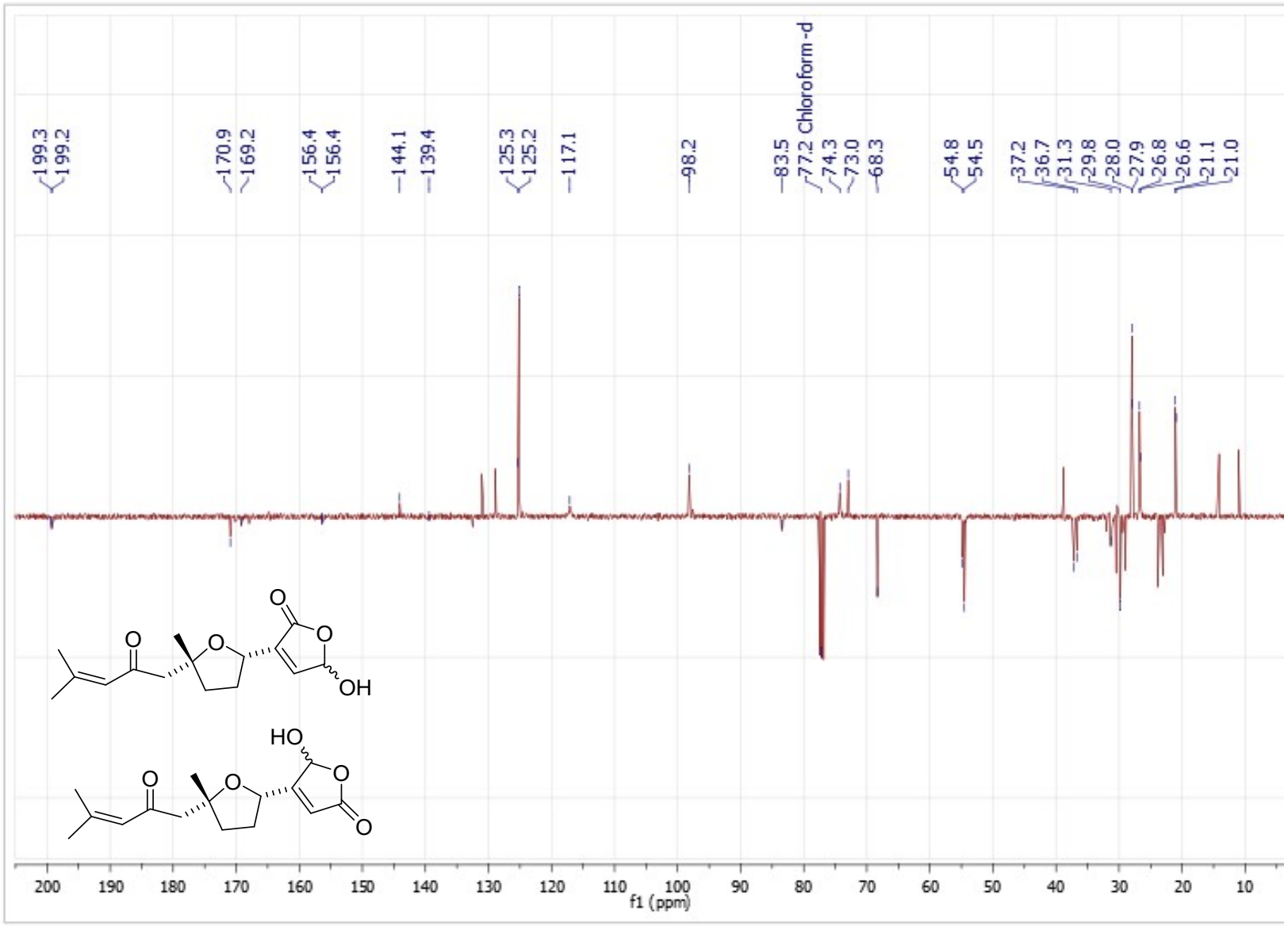


Figure S_{10}: DEPT-Q spectrum of compound (5 and 6) ($CDCl_3$, 100 MHz)

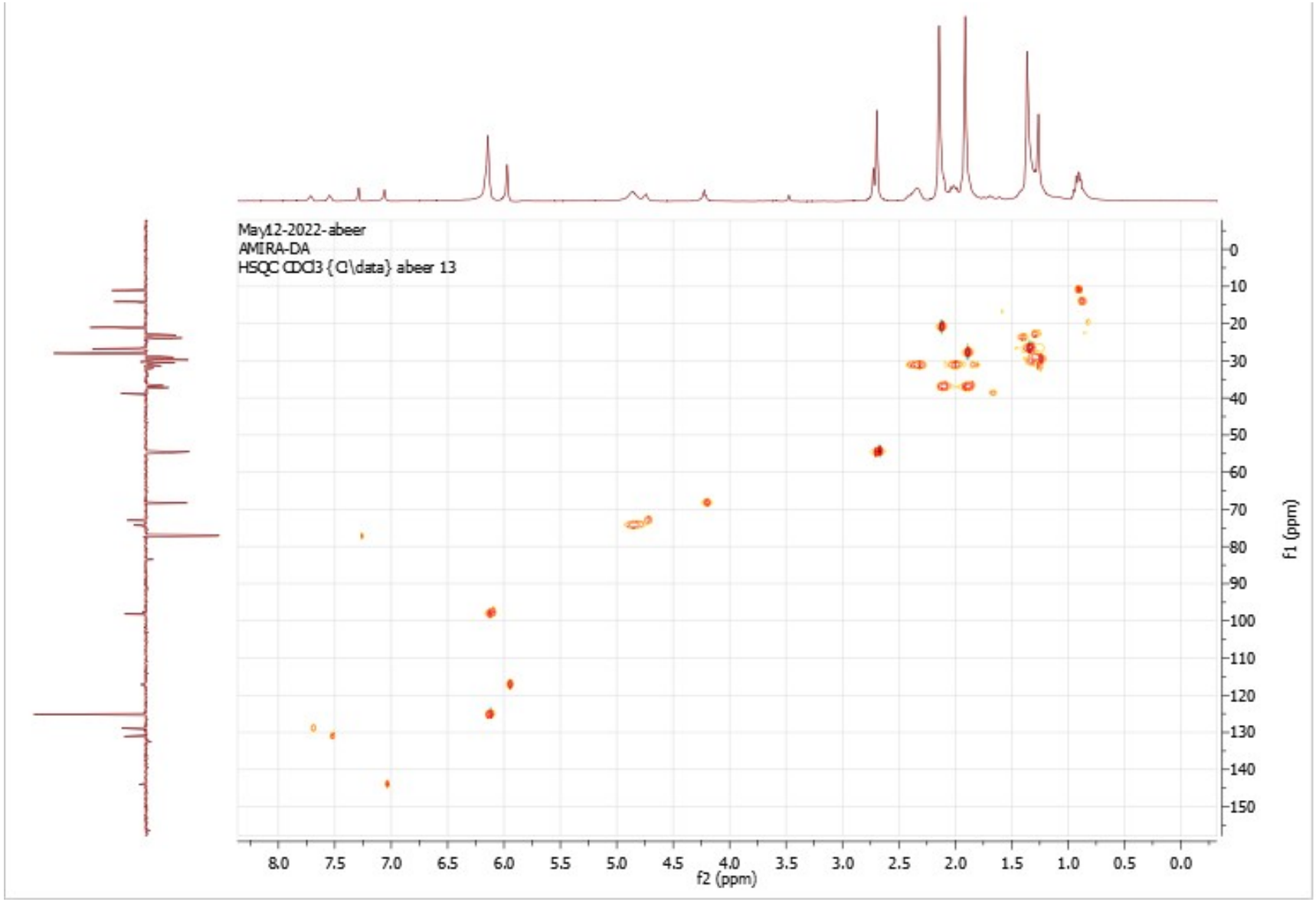


Figure S_{11}: HSQC spectrum of compound (5 and 6) ($CDCl_3$, 100 MHz)

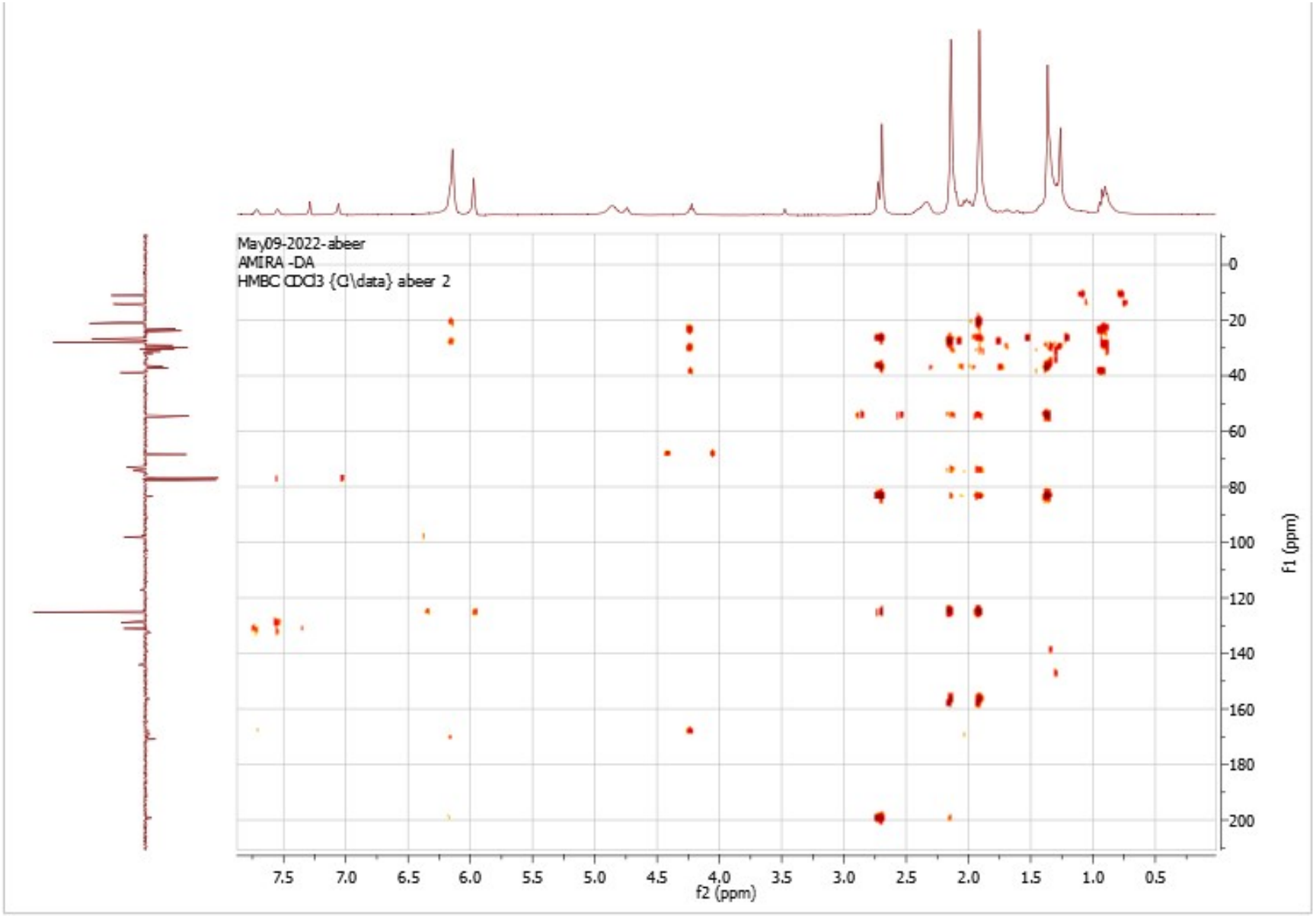
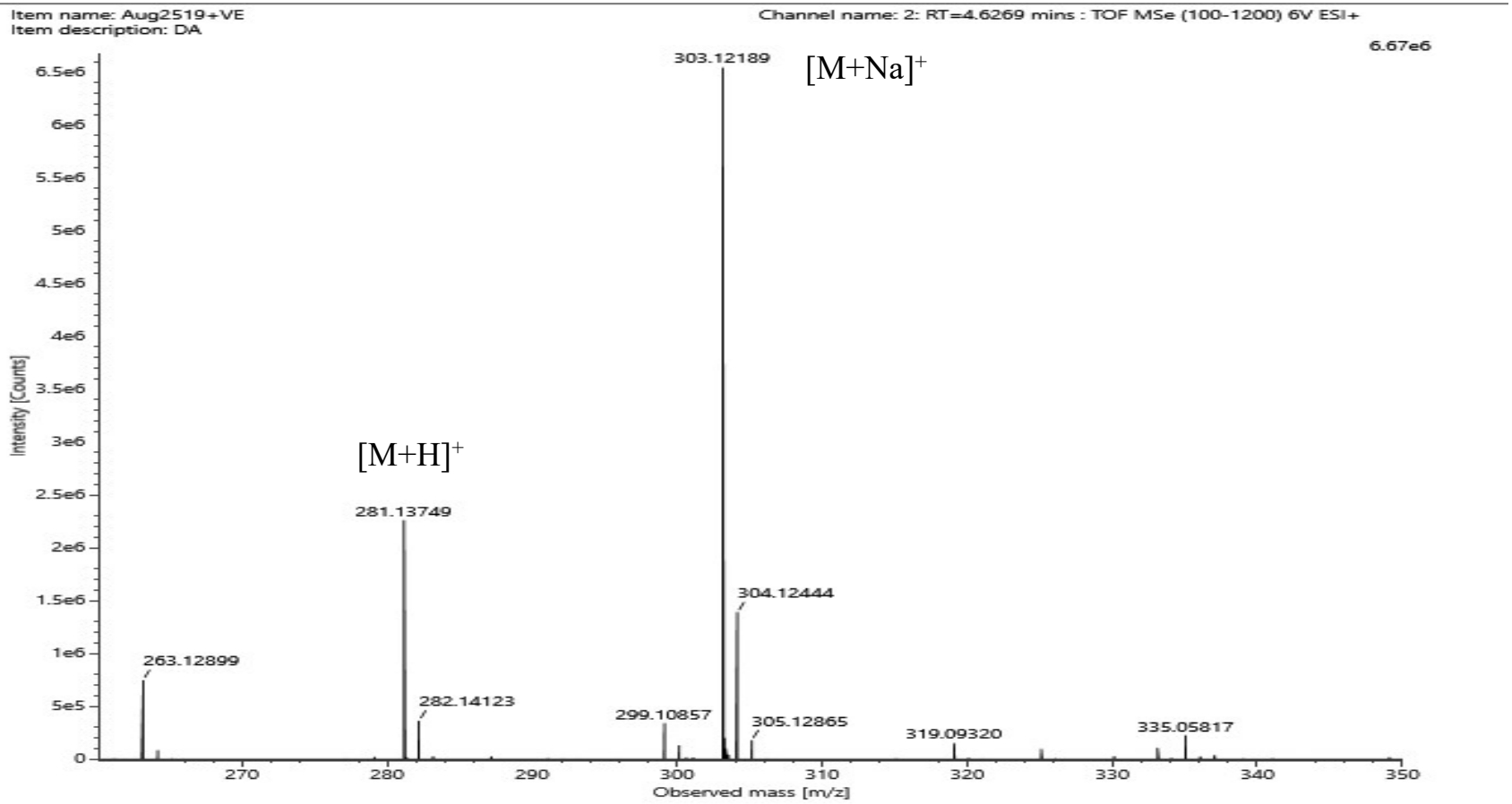


Figure S_{12}: HMBC spectrum of compound (5 and 6) ($CDCl_3$, 100 MHz)



Composition	i-FIT Confidence (%)	m/z RMS (ppm)	Intensity RMS (%)	Predicted m/z	m/z Error (ppm)
C15H20O5	98.873041	0.608481	17.341696	281.138350	0.499047
C3H17N10NaO4	0.939500	6.879311	61.876886	281.140470	-7.068893
C16H15N4NaO	50.370716	3.923565	53.511264	303.121632	-4.310447
C15H19NaO5	48.459181	0.799309	44.474352	303.120295	0.116415

Figure S_{13}: HR-ESI-MS spectrum of compounds (5 and 6)

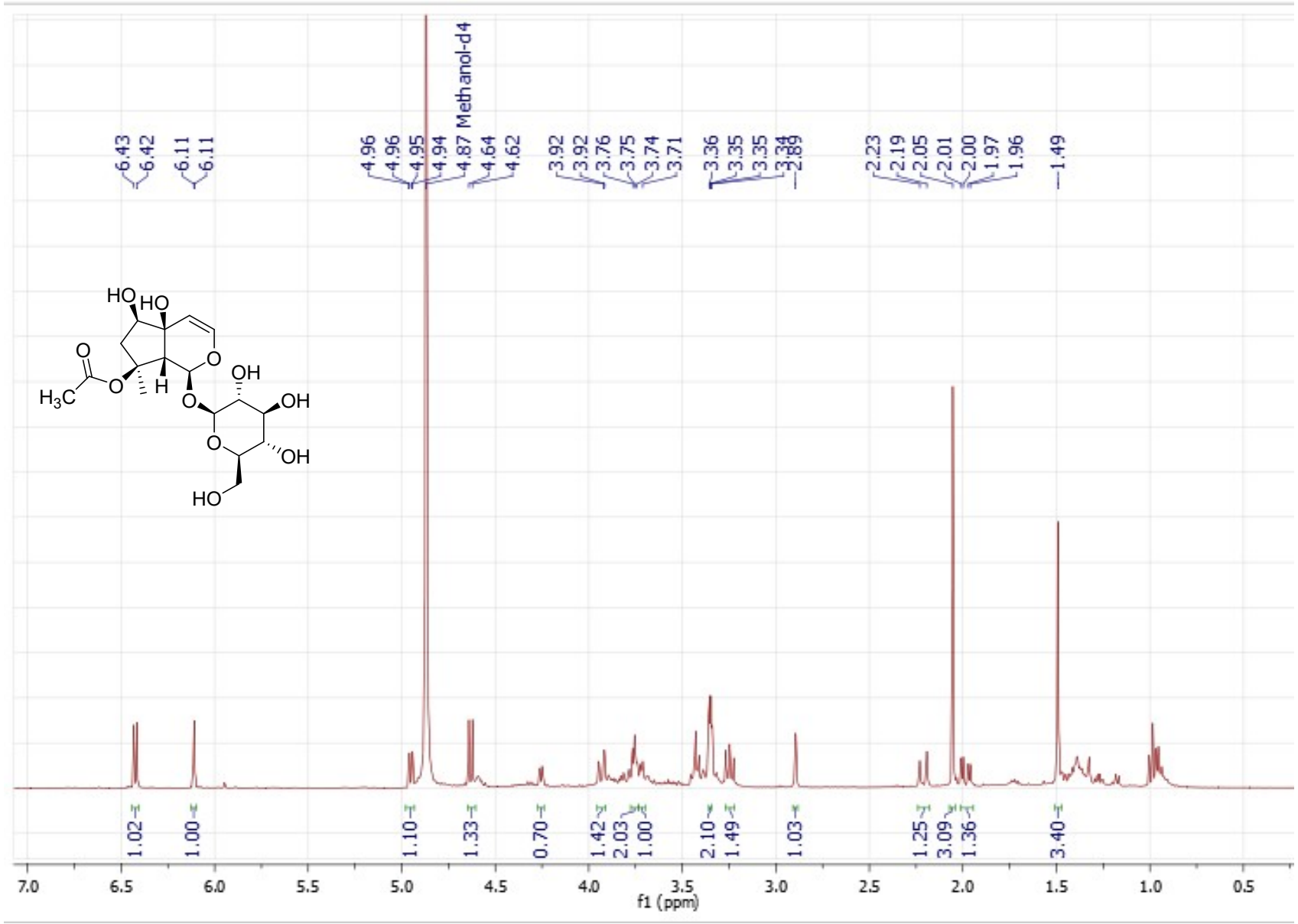


Figure S_{14}: ^{1}H NMR spectrum of compound (7) 8-acetyl harpagide (CD_3OD, 400 MHz)

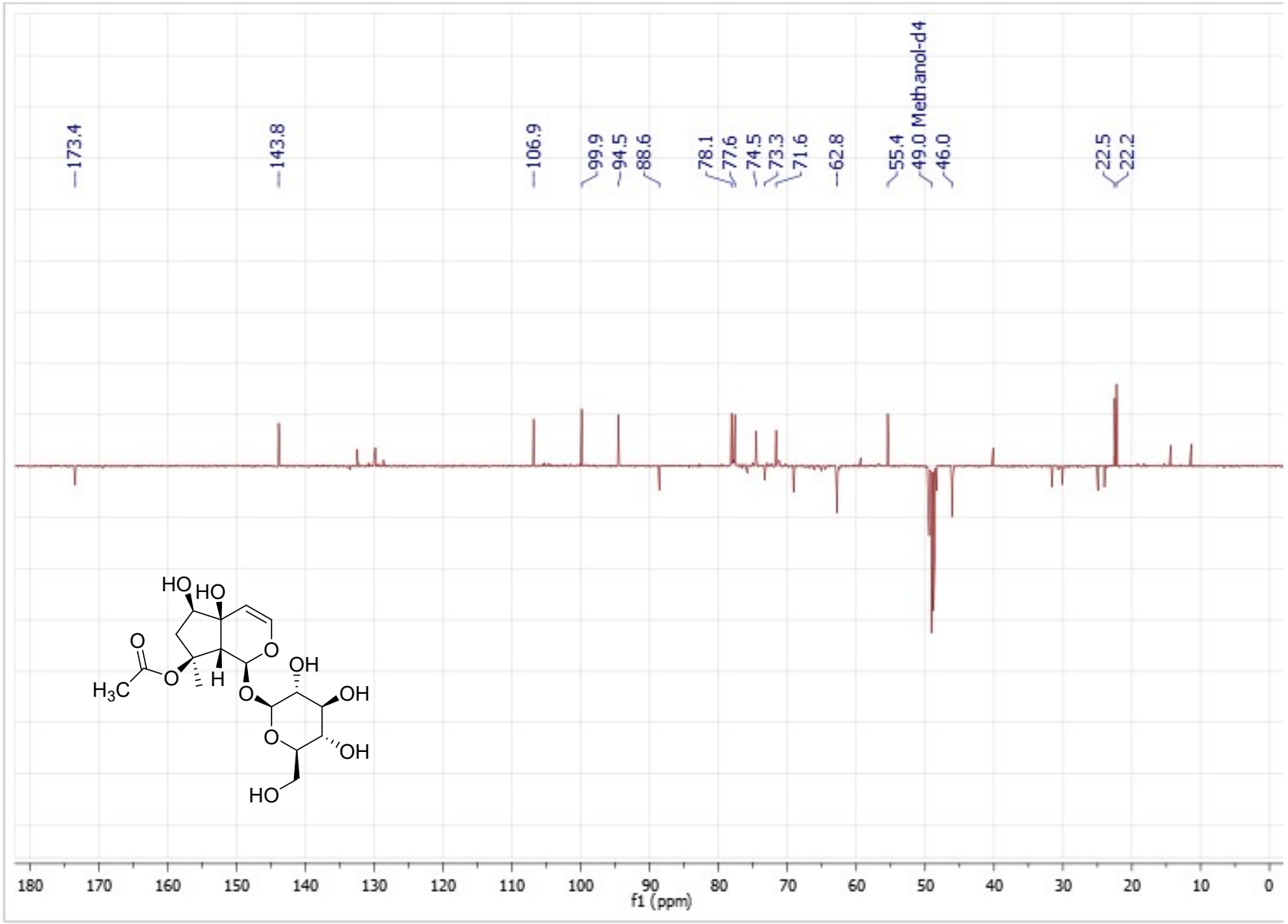


Figure S_{15}: DEPT-Q spectrum of compound (7) 8-acetyl harpagide (CD_3OD, 100 MHz)

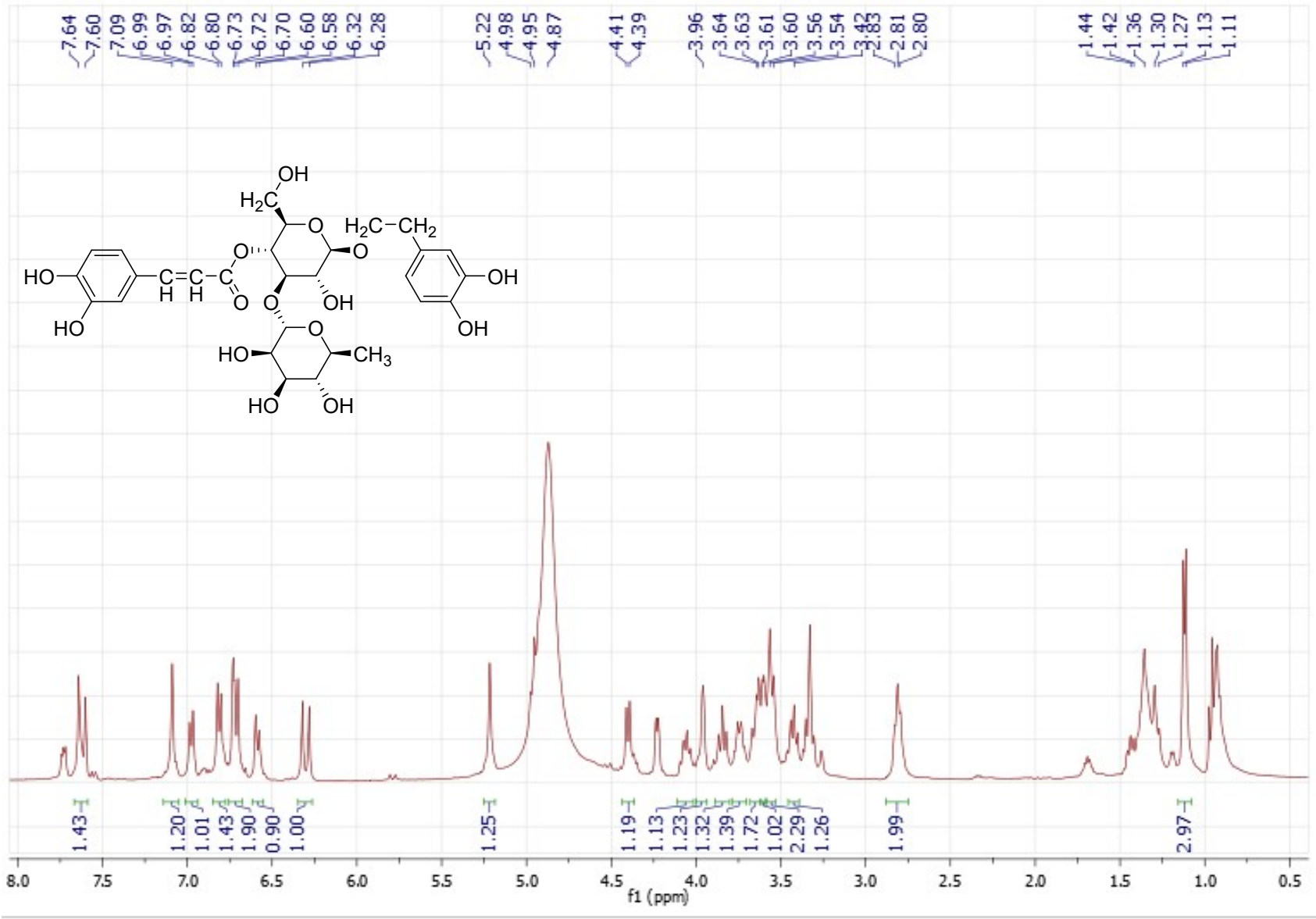


Figure S_{16}: ^{1}H NMR spectrum of compound (8) Verbascoside (CD_3OD, 400 MHz)

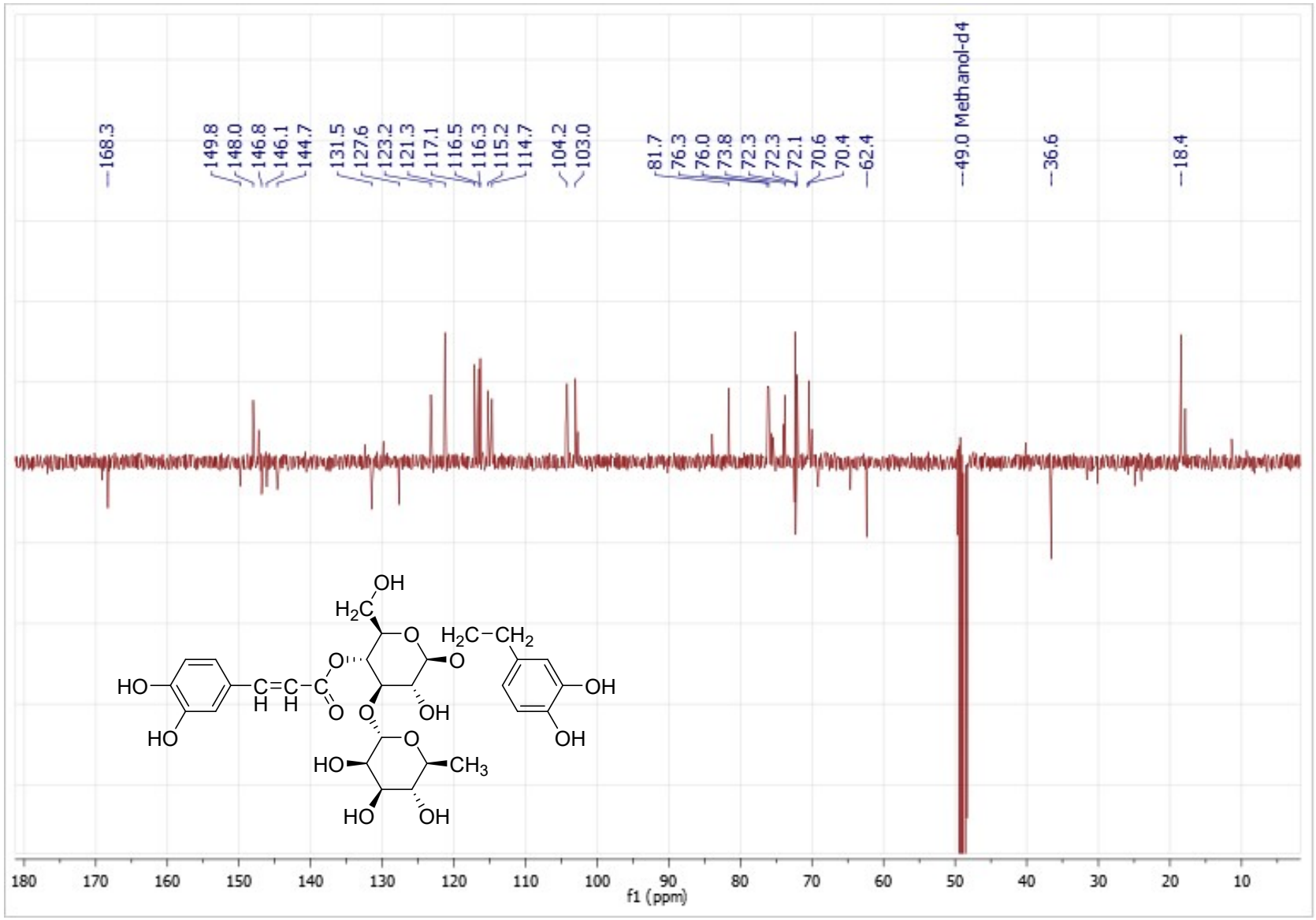


Figure S_{17}: DEPT-Q spectrum of compound (8) Verbascoside (CD_3OD, 100 MHz)

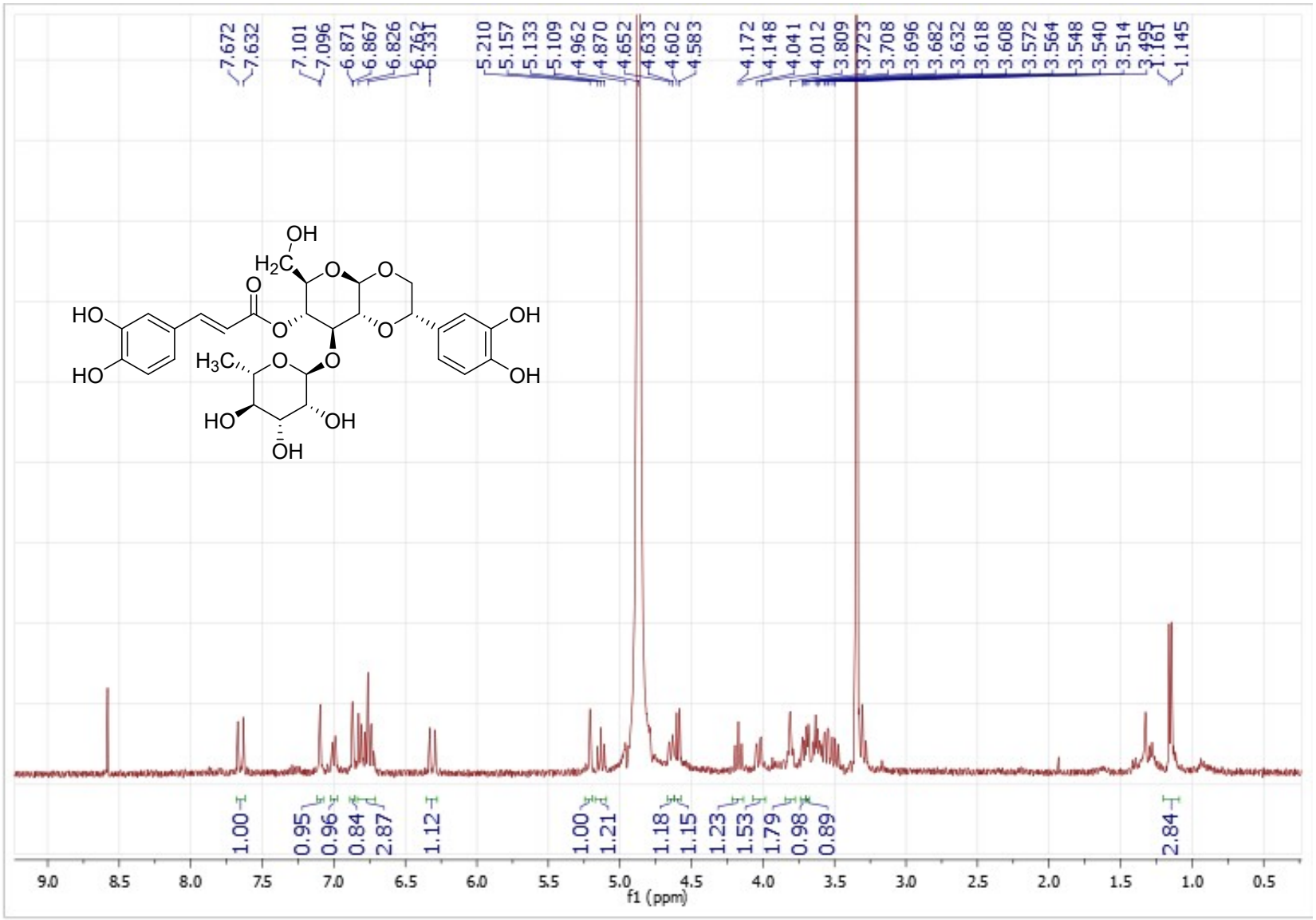


Figure S_{18}: ^{1}H NMR spectrum of compound (9) Crenatoside (CD_3OD, 400 MHz)

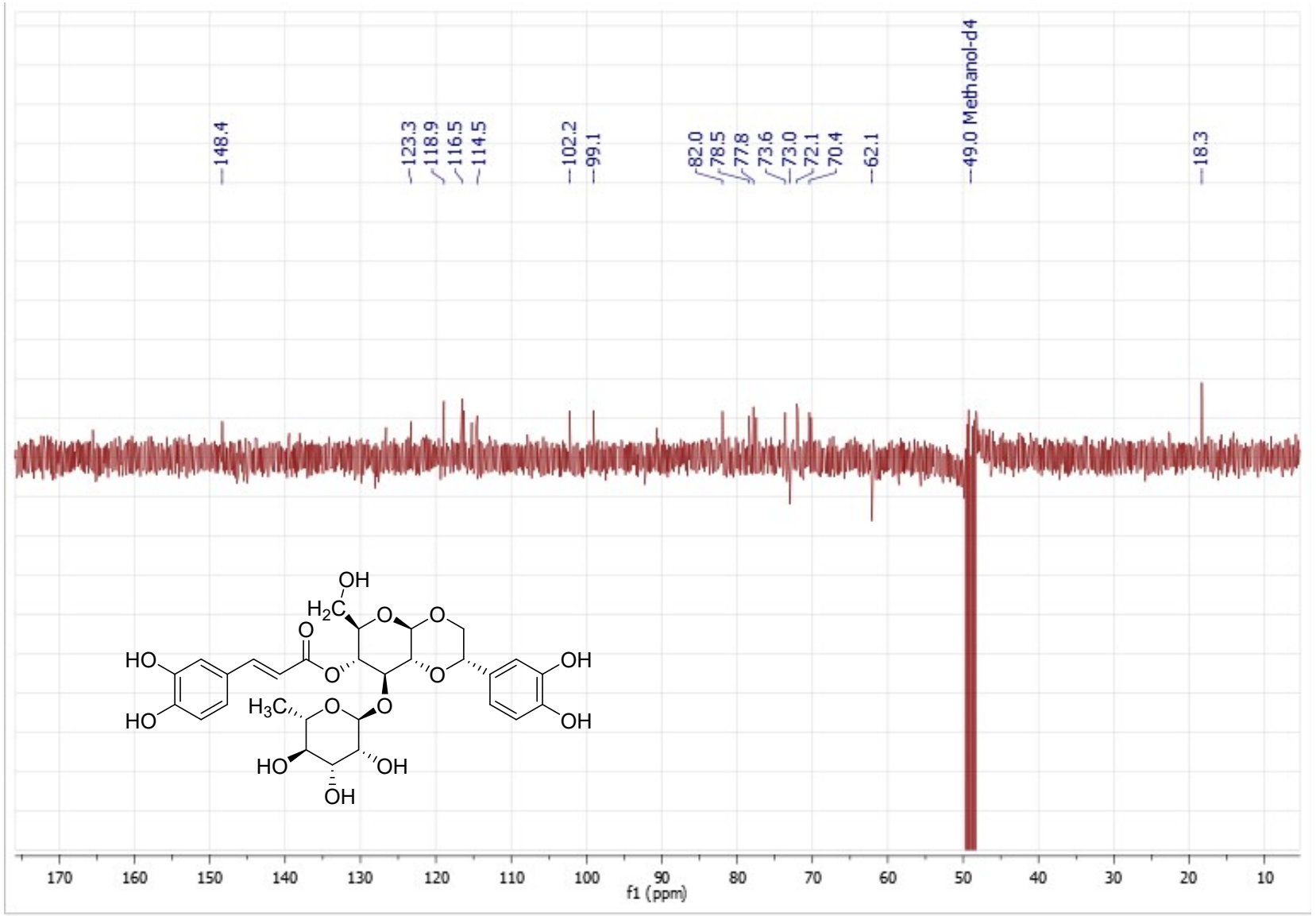


Figure S_{19}: DEPT-Q spectrum of compound (9) Crenatoside (CD_3OD, 100 MHz)

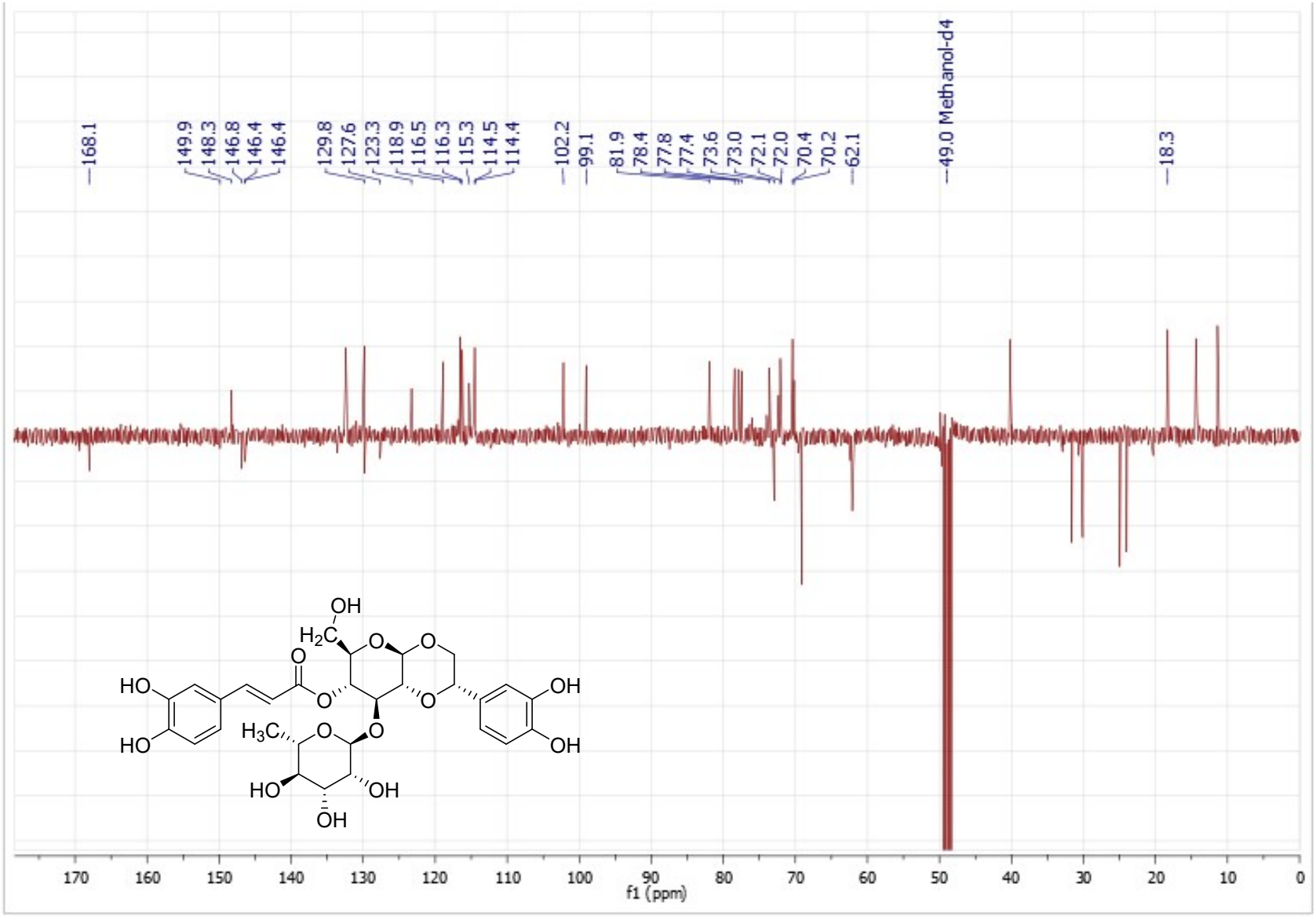


Figure S_{20}: DEPT-Q spectrum of compound (9) Crenatoside (CD_3OD, 100 MHz)

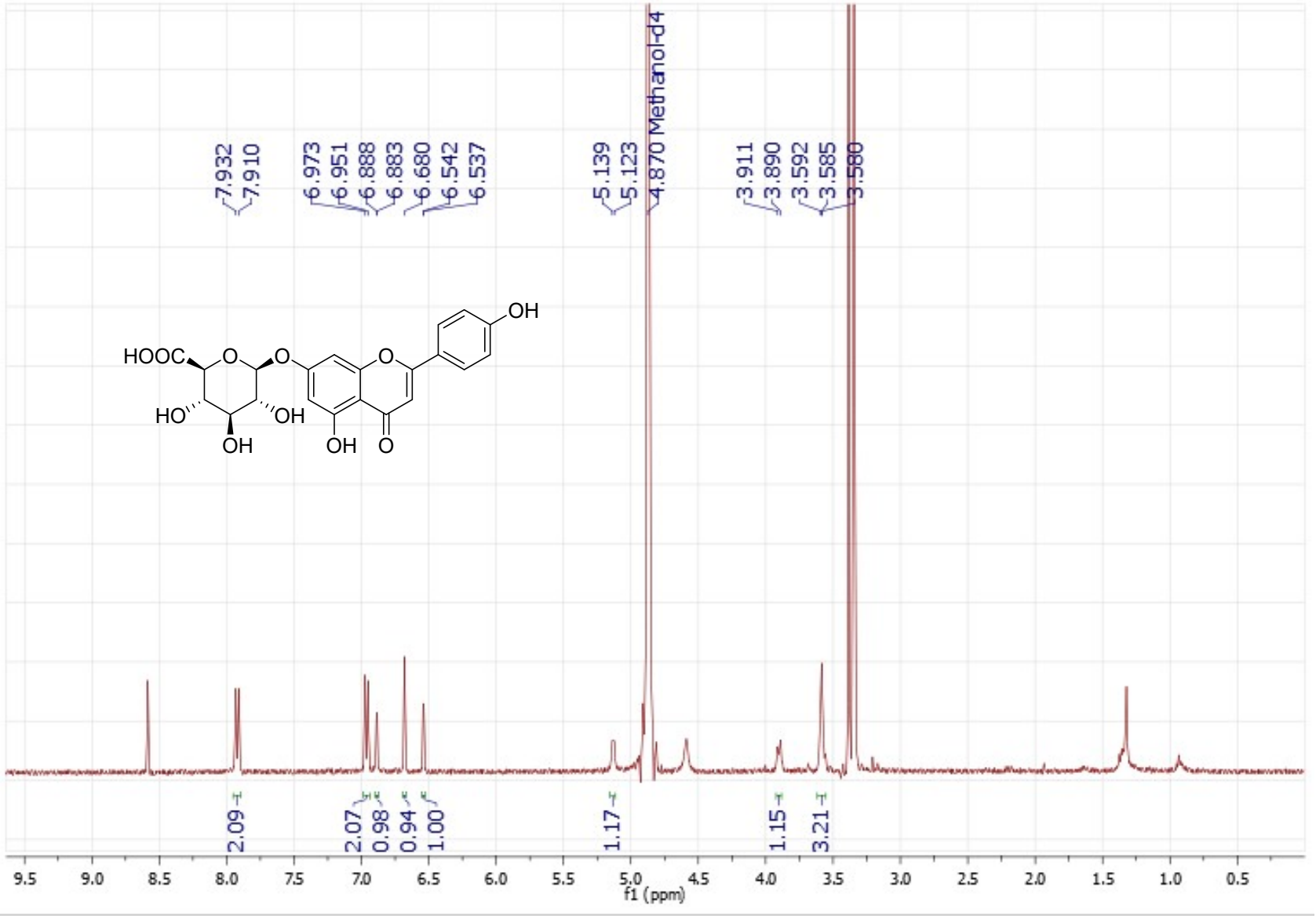


Figure S_{21}: ^{1}H NMR spectrum of compound (10) Apigenin-7-*O* glucuronide (CD_3OD, 400 MHz)

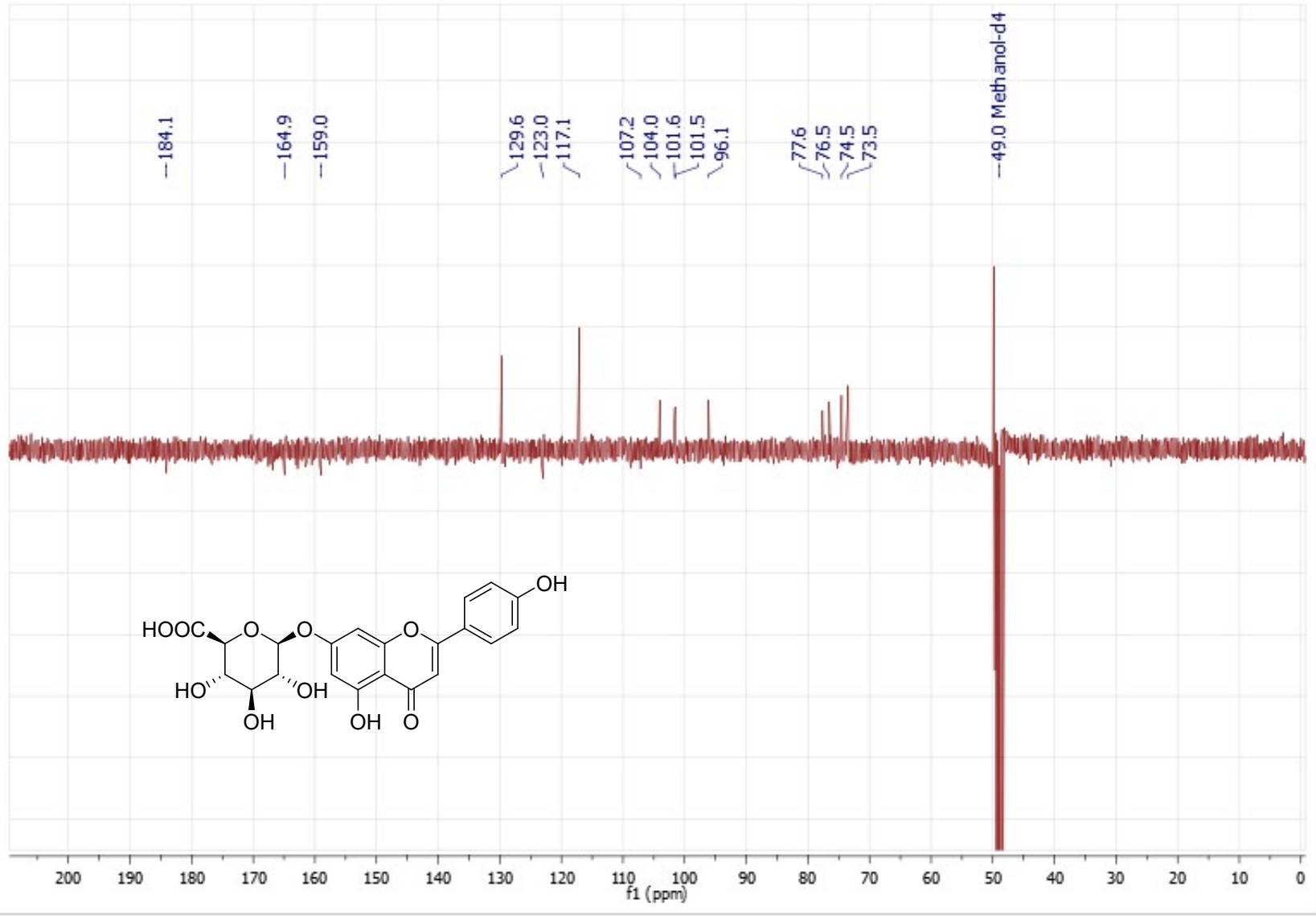


Figure S_{22}: DEPT-Q spectrum of compound (10) Apigenin-7-*O* glucuronide (CD_3OD, 100 MHz)

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