Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Electronic Supplementary Information

Triterpenoids functionalized at C-2 as diagenetic transformation products of 2,3-dioxygenated triterpenoids from higher plants in buried wood

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1. Extraction, fractionation of the organic extract of the buried oak wood sample and isolation of compounds 5a, 7a-12

1.1 Isolation of compounds 5a, 7a-10a

Wood chips (26 g) were extracted by sonication (1 h, x 2) with a mixture of CH_2Cl_2/CH_3OH (1:1, v/v; 600 ml, x 2). The solvent extract was filtered through a cotton plug and the solvent removed under reduced pressure yielding 490 mg of crude extract. An aliquot of the extract (340 mg) was acetylated overnight at room temperature (Ac_2O/Pyridine 1:1 v/v, 4 ml). After removal of the solvent and excess reagent under reduced pressure, the acetylated extract was dissolved in CH_2Cl_2 and esterified using an ethereal solution of diazomethane. The derivatized extract was further fractionated by liquid chromatography on silica gel eluting with a mixture of CH_2Cl_2/AcOEt (92:8 v/v) into 21 fractions (F1 - F21) which were analyzed by GC and GC-MS. The fractions F10 (5.4 mg) and F11 (3.6 mg) were fractionated by reversed phase HPLC (Dupont, Zorbax ODS 5 μm; 250 x 4.6 mm; CH_3OH/H_20, 9:1 v/v; 1 ml min^{-1}), yielding *ca.* 2 mg of each compound **7a** and **8a** with a purity > 90% (GC).

Similarly, the fractions F15 (4.0 mg), F16 (4.2 mg) and F17 (4.2 mg) where further fractionated by reversed phase HPLC (Dupont, Zorbax ODS 5 mm; 250 x 4.6 mm;

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CH_3OH/H_20, 85:15 v/v; 0.8 ml min^{-1}), yielding compound **9a** and **10a** (*ca.* 1.5 mg of each) with a purity > 90% (GC) and < 1 mg of compound **5a**.

1.2 Isolation of compounds 11-12

Wood chips (43 g) were extracted by sonication (90 min) with a mixture of CH_2Cl_2/CH_3OH (1:1, v/v; 300 ml). The solvent extract was filtered through a cotton plug, and the solvent removed under reduced pressure, yielding 702 mg of crude extract. An aliquot of the extract (564 mg) was acetylated overnight at room temperature (Ac_2O/Pyridine 1:1 v/v, 4 ml). After removal of the solvent and excess reagent under reduced pressure, the acetylated extract was dissolved in CH_2Cl_2 and esterified using an ethereal solution of diazomethane. The derivatized extract was further fractionated by liquid chromatography on silica gel eluting with a mixture of CH_2Cl_2/AcOEt (92:8 v/v) into 15 fractions (F1 – F15) which were analyzed by GC and GC-MS. The fractions F5-F10 (26 mg) which contained compounds **11** and **12** were combined and further fractionated by reversed phase HPLC (Dupont, Zorbax ODS 5 μm; 250 x 4.6 mm; CH_3OH/H_20, 85:15 v/v; 0.8 ml min^{-1}), yielding < 1 mg of each compound **11** and **12** with a purity > 90% (GC).

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2. NMR Data

2.1 Compound 8a

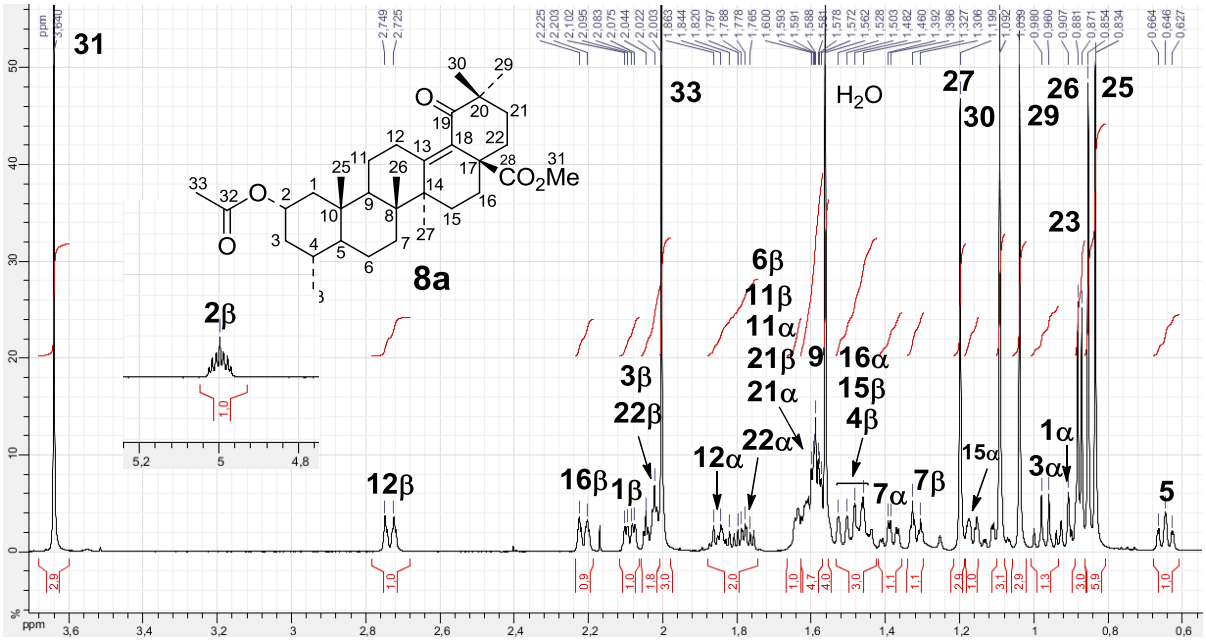

Figure 1: ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of compound **8a**.

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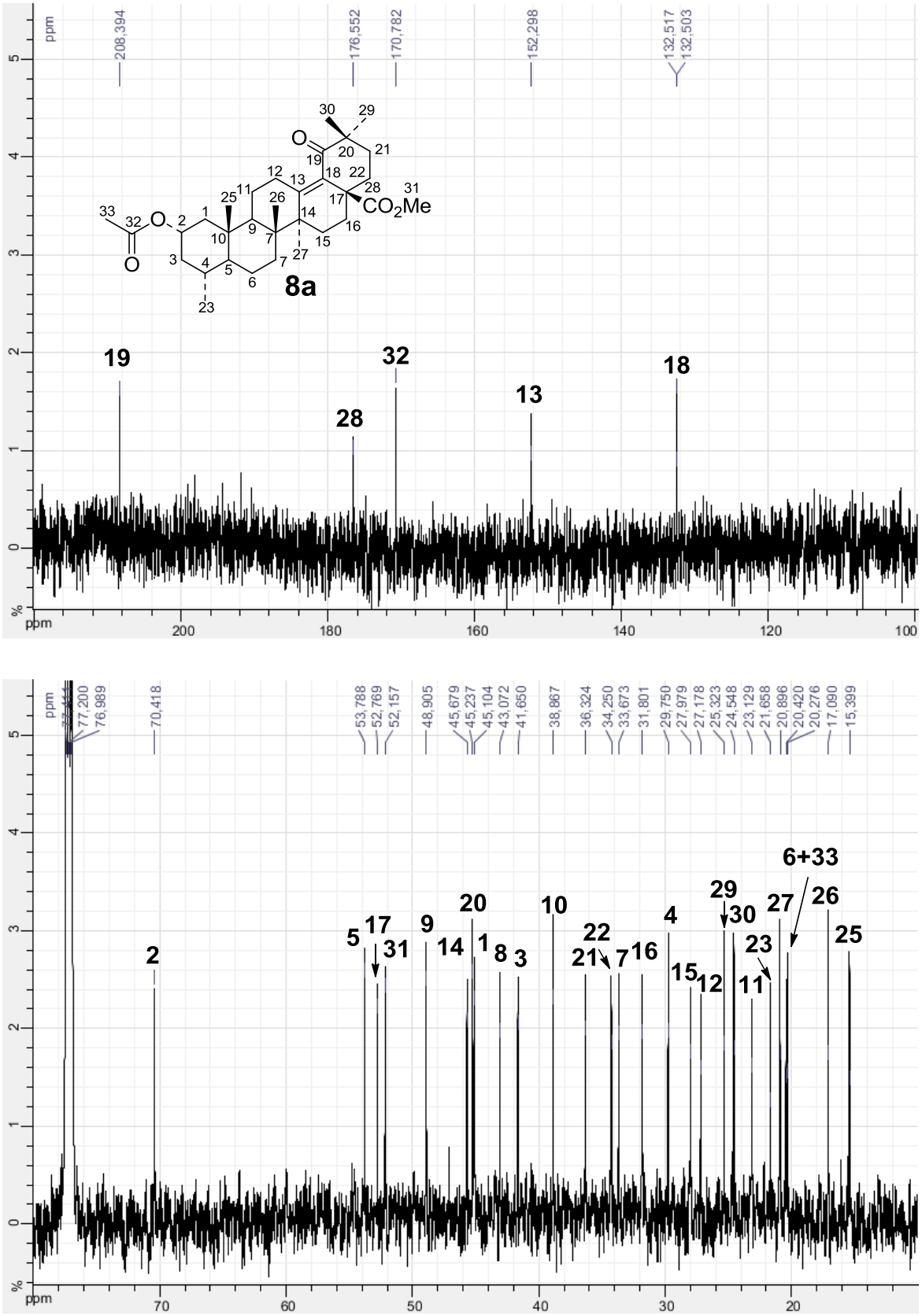

Figure 2: ^{13}C-NMR spectrum (600 MHz, $CDCl_3$) of compound **8a**

2.2 Compound 9a

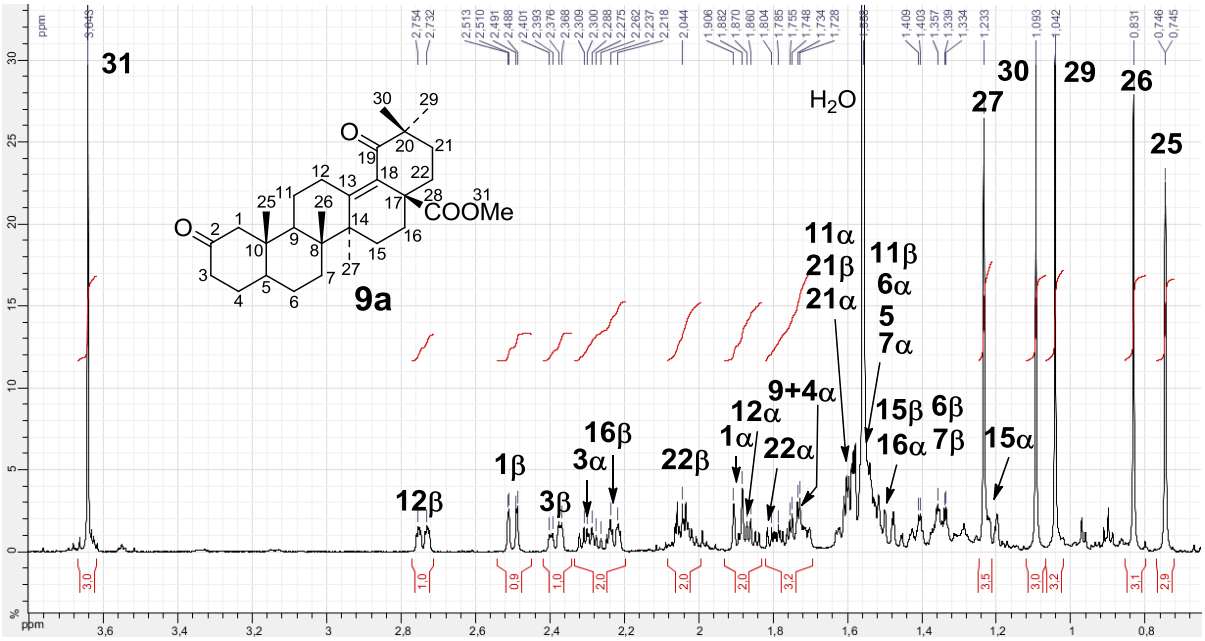

Figure 3: ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of compound **9a**

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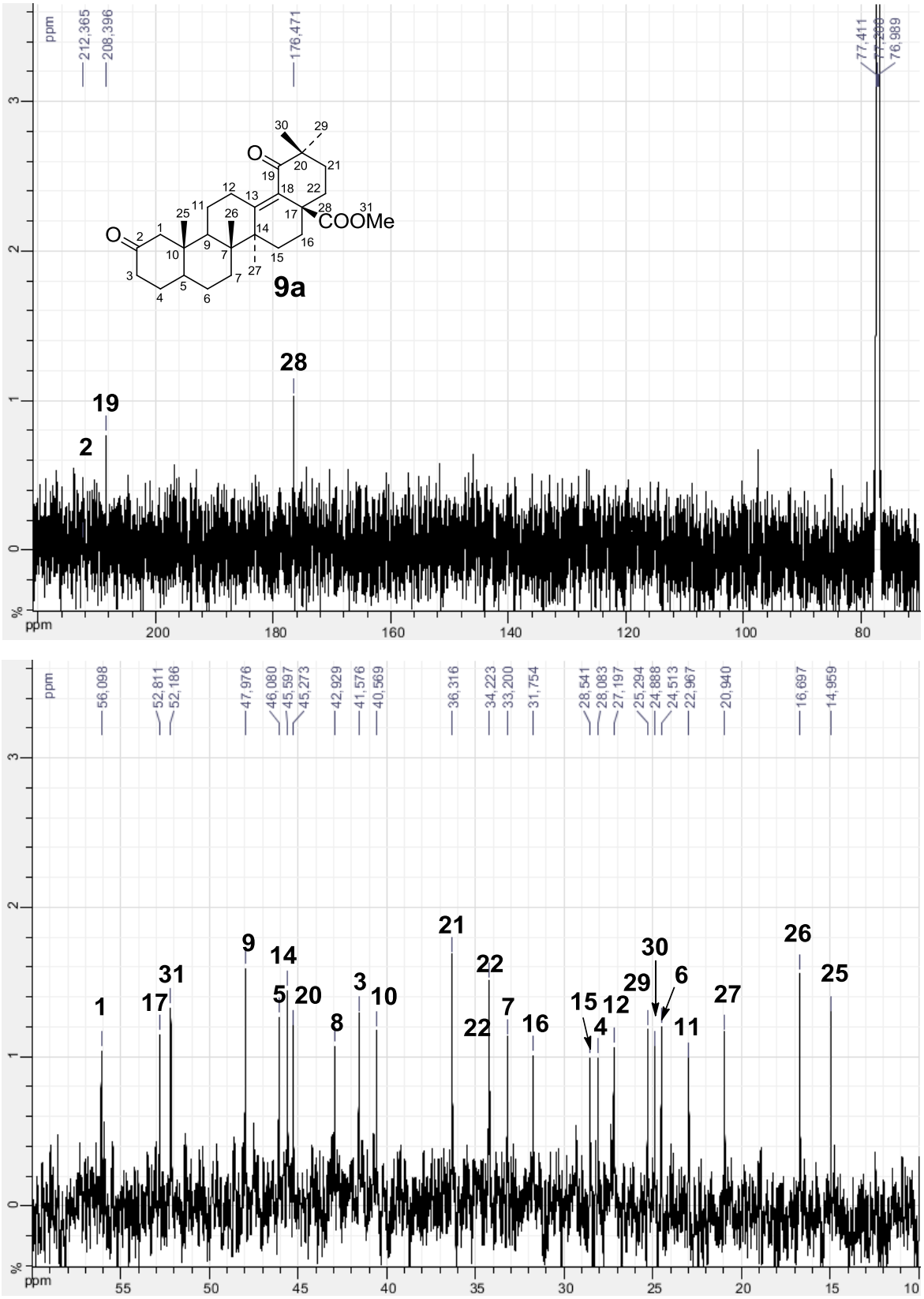

Figure 4: ^{13}C-NMR spectrum (600 MHz, $CDCl_3$) of compound **9a**. C-13 and C-18 could not be seen due to the low amounts of compound **9a** available. ^{13}C chemical shifts of C-13 and C-18 were deduced from the HMBC experiment.

2.3 Compound 11

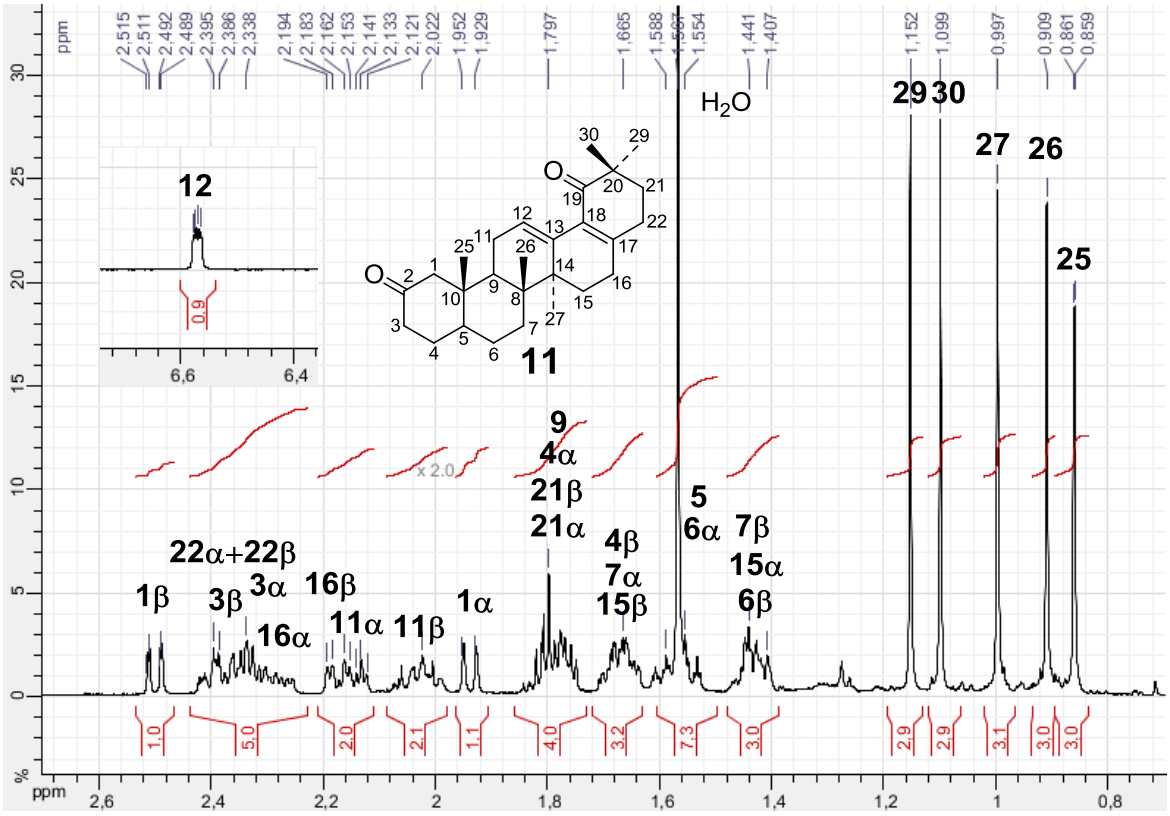

Figure 5: ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of compound **11**

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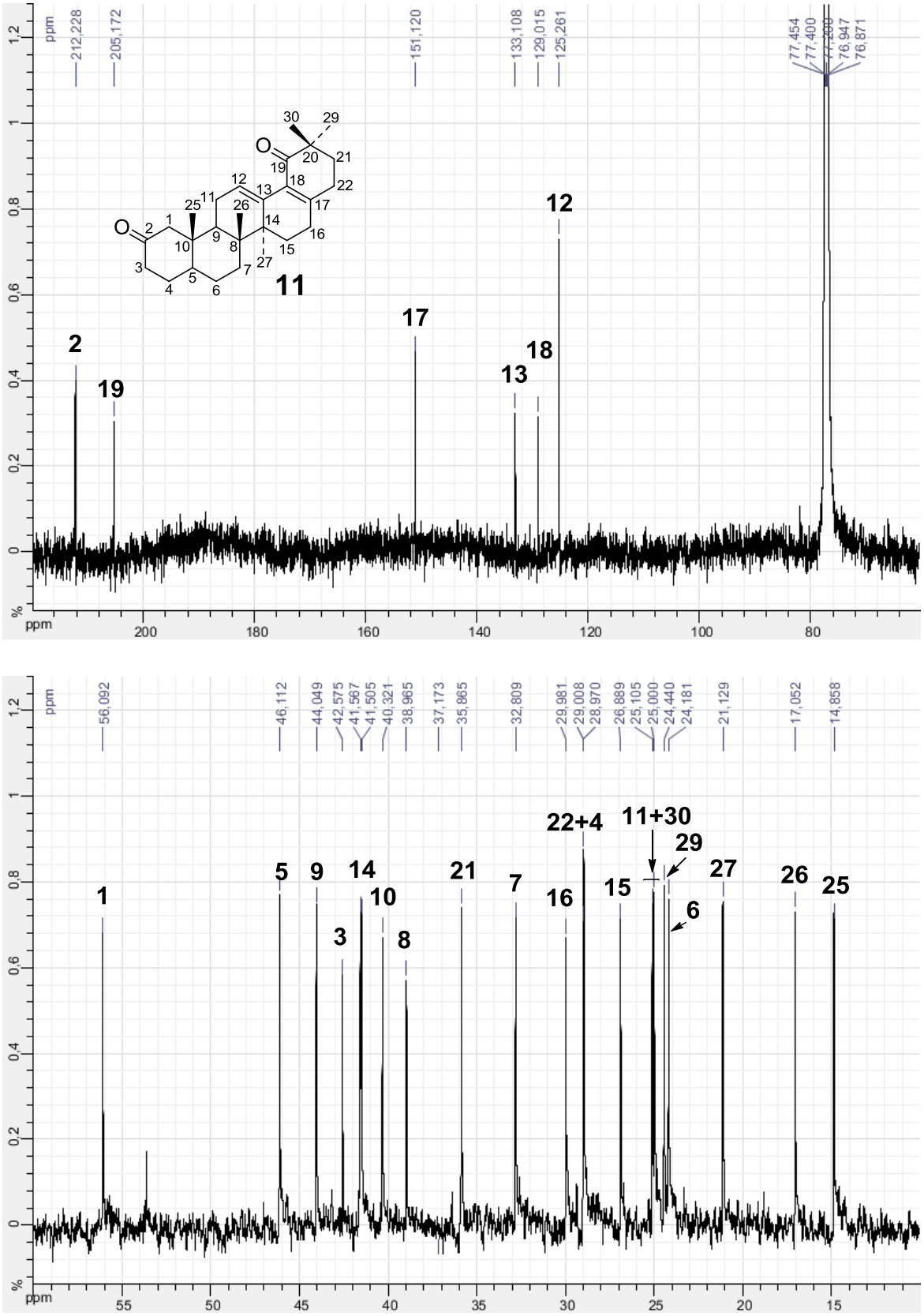

Figure 6: ^{13}C-NMR spectrum (500 MHz, $CDCl_3$) of compound **11**

2.4 Compound 5a

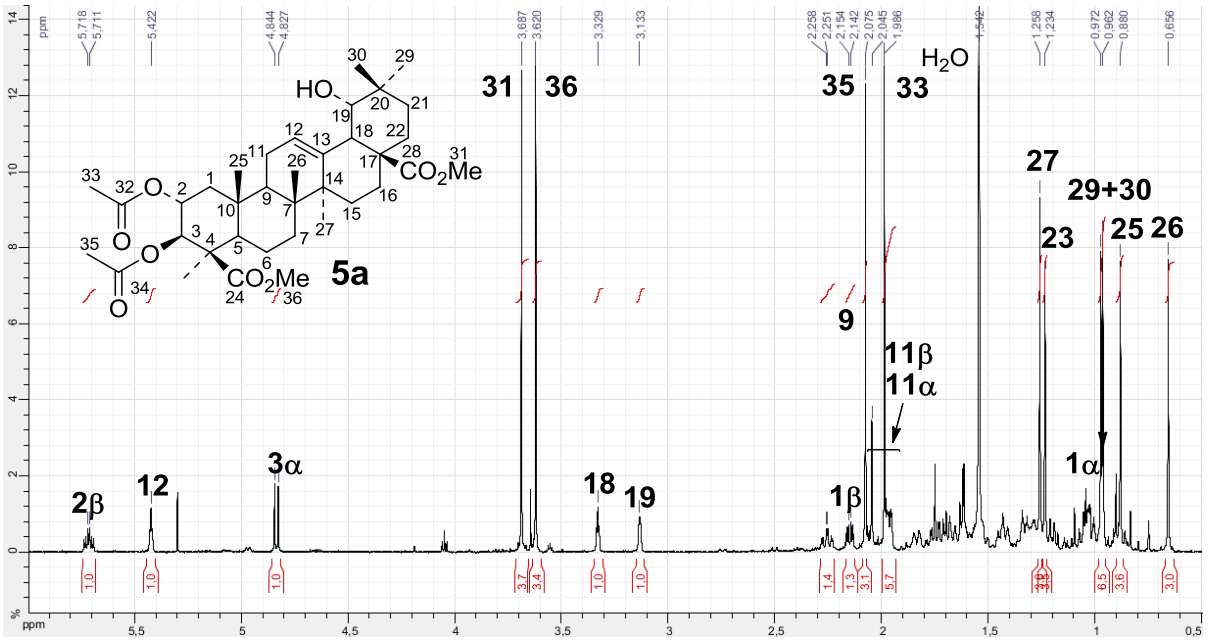

Figure 7: ^{1}H-NMR spectrum (600 MHz, $CDCl_3$) of compound **5a**

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