

New sustainable synthetic routes to cyclic oxyterpenes using the Ecocatalyst toolbox - Supporting informations.

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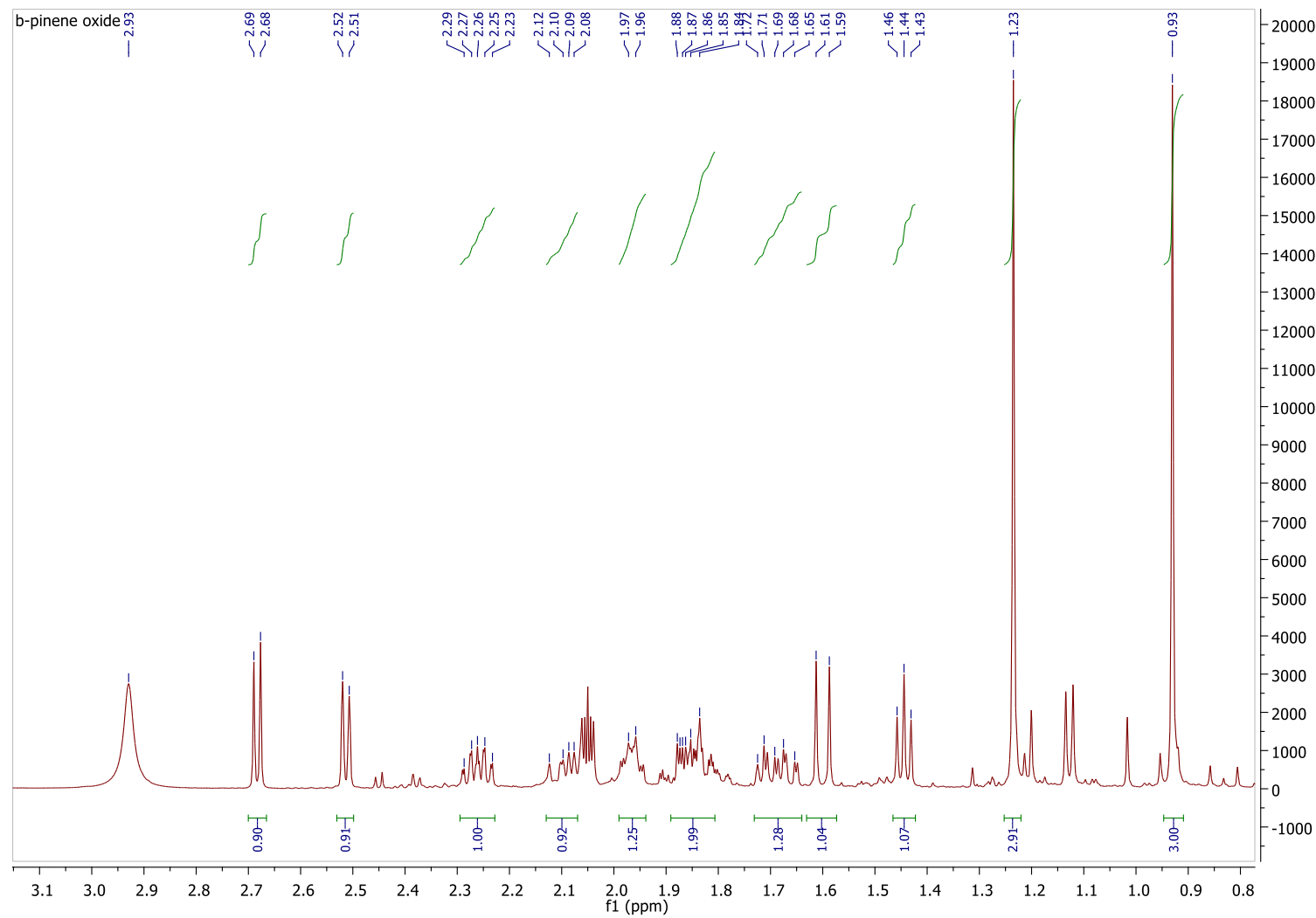
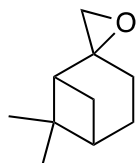
† These authors contributed equally to this work.

Table des matières

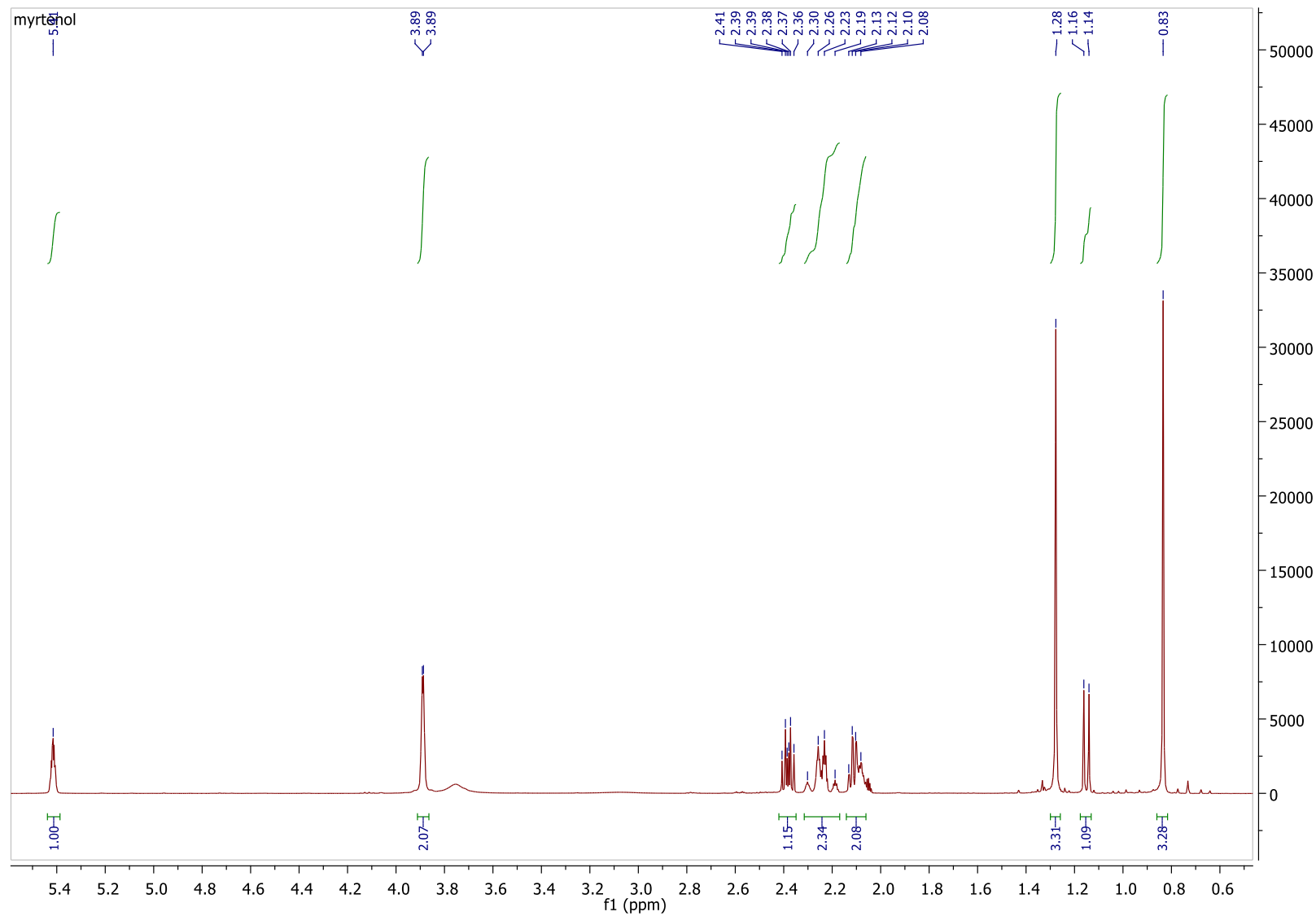
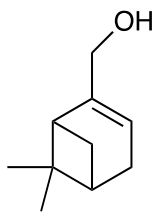
I.	¹ H NMR spectra.....	2
II.	Scale-up procedures.....	3

I. ¹H NMR Spectra

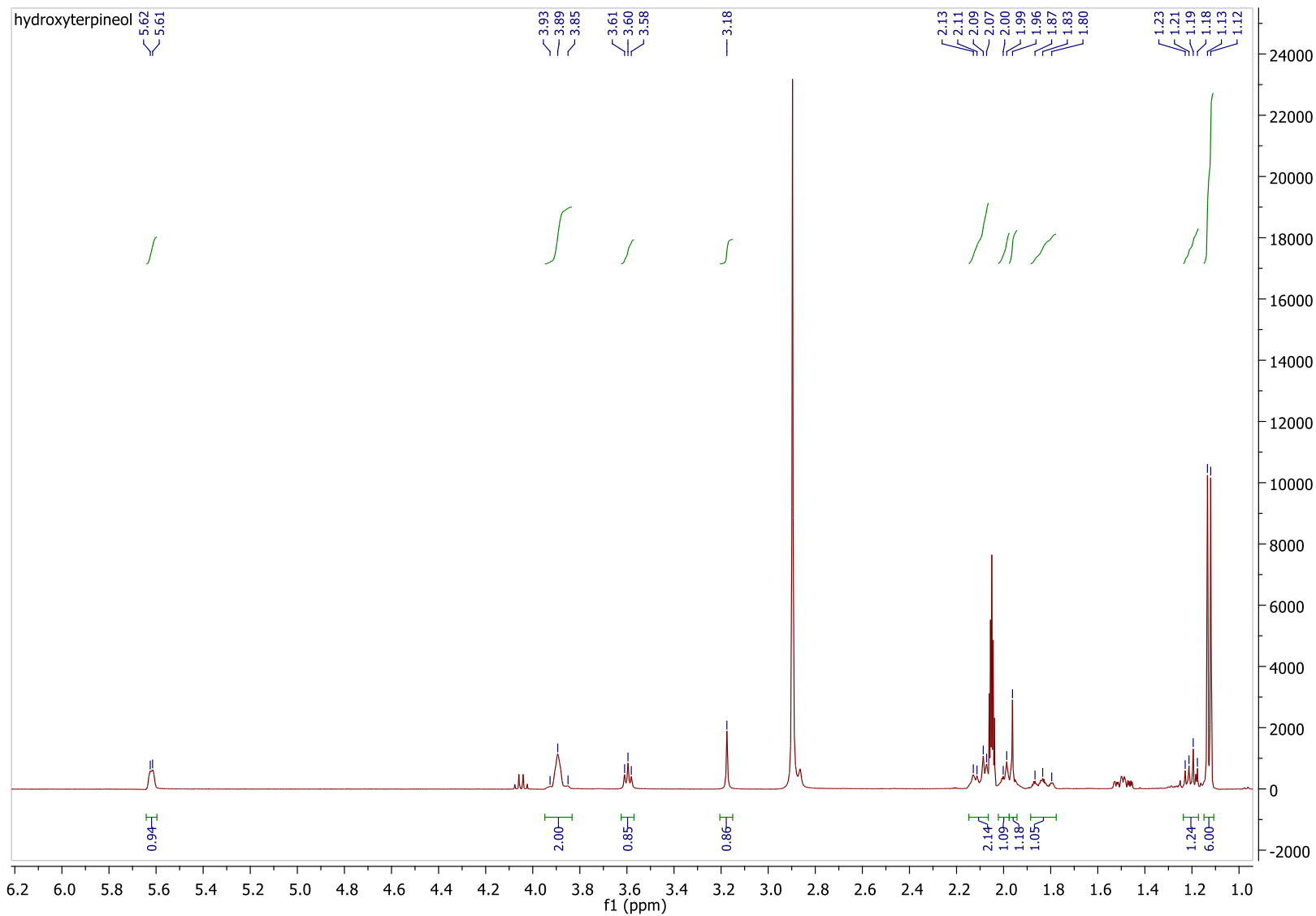
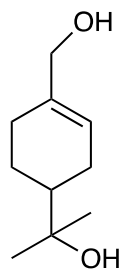
β-pinene oxide in acetone-d₆



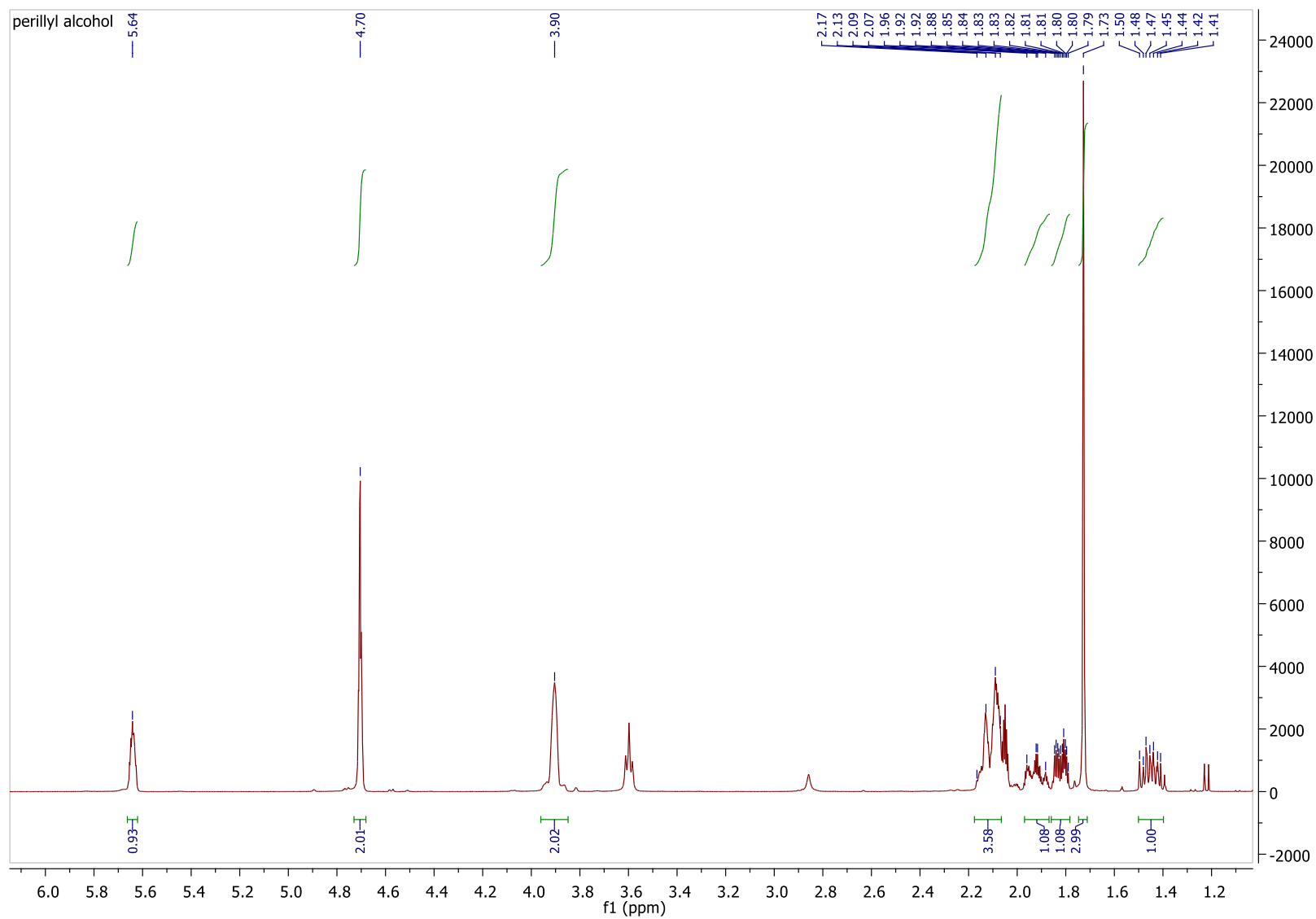
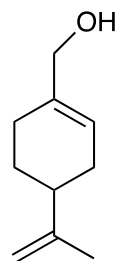
Myrtenol in acetone-d₆



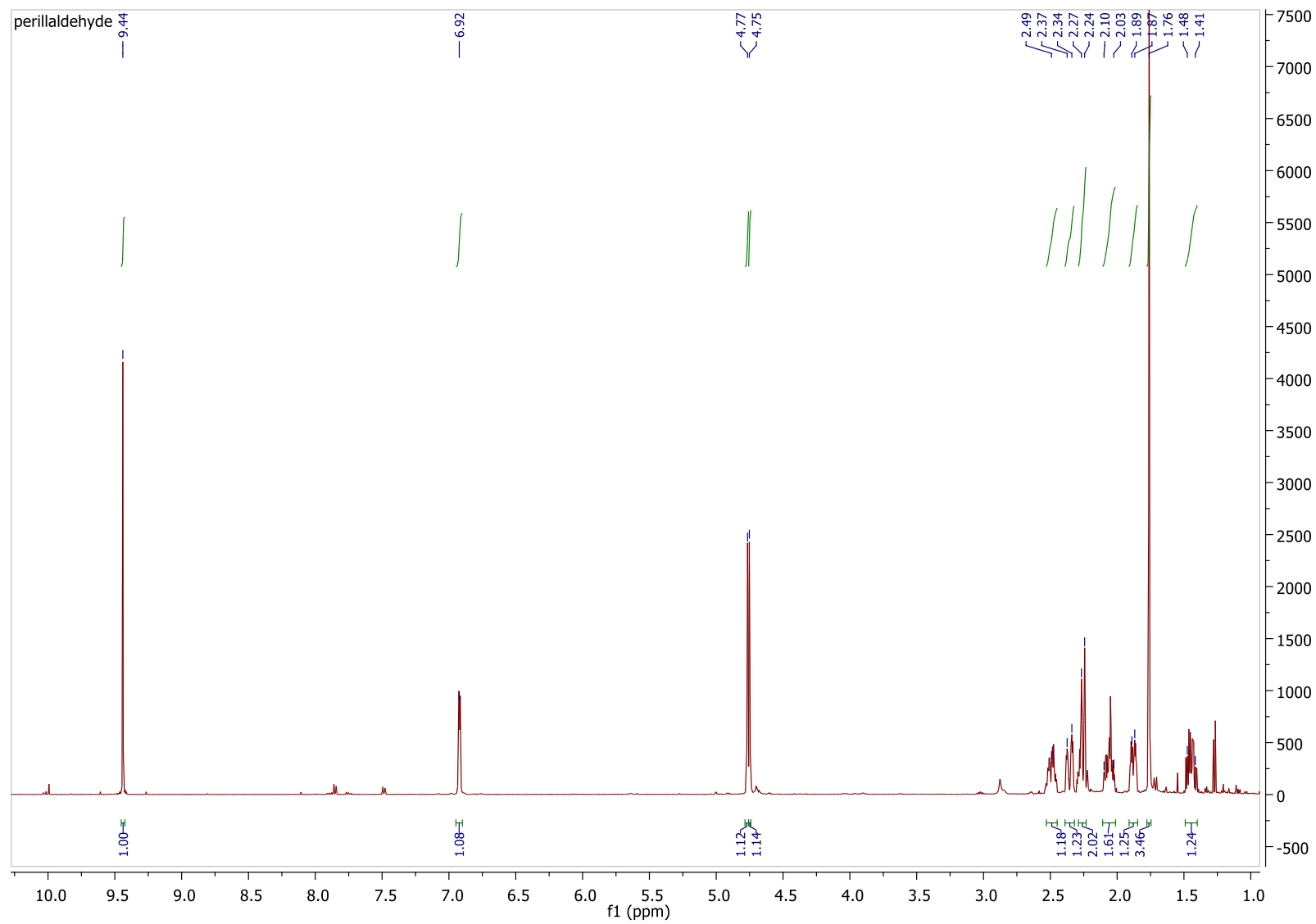
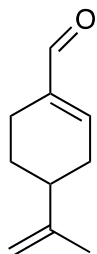
7-Hydroxyterpineol in acetone-d₆



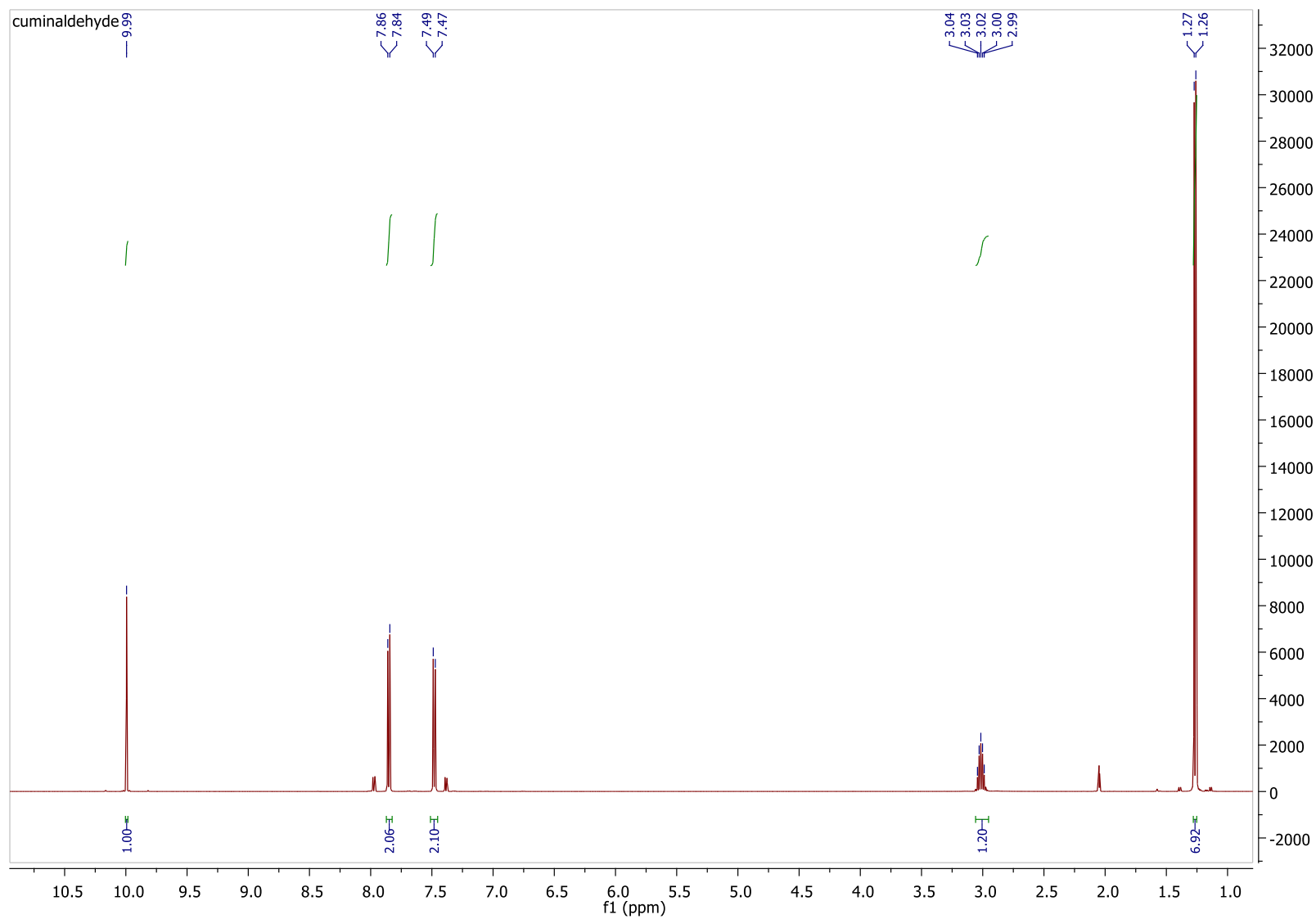
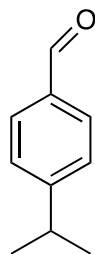
Perillyl alcohol in acetone-d₆



Perillaldehyde in acetone-d₆



Cuminaldehyde in acetone-d₆



II. Scale up procedures

Scale-up for the synthesis of β -pinene oxide **2**.

β -pinene **1** (38 mmol, 1 eq.), ecocatalyst (200 μ mol, 0.005 eq. of Mn) and NaHCO_3 (aq) (200 mmol, 5 eq.) were introduced in a flask containing distilled water (120 mL) and acetone (120 mL) at 30 °C for 10 minutes. H_2O_2 (aq) (40 % w/w in H_2O ; 200 mmol, 5 eq.) was added dropwise for 2 h. After 2 h, the suspension was filtered and extracted three times with ethyl acetate. The organic layers were collected together and dried using anhydrous MgSO_4 . The solvent was then evaporated. The crude was distilled under vacuum with a cooled trap.

Scale-up for the one pot synthesis of 7-hydroxyterpineol **4** from β -pinene **1**.

For the one-pot synthesis, β -pinene **1** (38 mmol, 1 eq.), ecocatalyst (200 μ mol, 0.005 eq. of Mn) and NaHCO_3 (s) (200 mmol, 5 eq.) were placed in a mixture of distilled water (120 mL) and acetone (120 mL) at 30 °C for 10 minutes while stirring. H_2O_2 (aq) (40 % w/w in H_2O ; 200 mmol, 5 eq.) was added dropwise for 2 h using a syringe-pushing device. After 2 h, oxalic acid (304 mmol, 8 eq.) was added into the mixture. It was stirred for 1 more hour at 30 °C. It was then filtered and extracted three times with ethyl acetate. The organic layers were collected together and extracted with a saturated solution of NaHCO_3 , then with brine before being dried using anhydrous MgSO_4 . The solvent was evaporated.