SUPPORTING INFORMATION

Cyclisations and Hydrolysis of Geranyl and Farnesyl Halides in water Facilitated by Ultrasound-Induced Emulsification

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1. Materials and methods

1.1 General information

The synthetic chemical procedures listed below were performed in the absence of oxygen and water by using pre-dried glassware and an argon atmosphere. Unless stated otherwise, dry solvents were used for each reaction setup that required a pre-dried round-bottom flask. Dry solvents were drawn directly into the pre-marked reaction flask using a Braun solvent purification system. Deuterated solvents, used for the preparation of NMR samples, were obtained from Deutero GmbH. Unless stated otherwise, all reactants mentioned in the synthetic chemical procedures were bought from commercial suppliers and used without further purification.

Temperatures mentioned in these procedures refer to the temperature that was set for the bath vessel. Any temperature below 0 °C was achieved using a cryostat and acetone as coolant. The only exception was the usage of a dry ice and acetone mixture as a coolant for −78 °C.

Analytical thin-layer chromatography (TLC) was performed to observe the reaction progress. This was done, using precoated silica gel plates with fluorescent indicator UV_{254} (Macherey-Nagel, Düren). The spots were visualised, either by staining with a vanillin or by exposing the TLC plates to UV light (254 nm/ 366 nm). Purification through column chromatography was performed with silica gel obtained from Macherey-Nagel (particle size of 40-63 µm). Elution was supported by the usage of compressed air. The solvent ratios used are described in each procedure.

^{1}H-, ^{13}C-, ^{31}P- and 2D-NMR experiments were performed on the following spectrometers: Bruker AVANCE I ($\nu_L(^1H)$= 400 MHz) equipped with a DUL probe or Bruker AVANCE III HD ($\nu_L(^1H)$400 MHz) equipped with either a PRODIGY BBFO or BBO probe. All probes are equipped with z-Gradient coils. Data analysis was performed using the Mestrelab Mestrenova software. The residual solvent signal of the deuterated solvents was used to calibrate the chemical shift scale of the NMR spectra. Chemical shifts δ are given in ppm, J coupling constants are given in Hz and were determined manually. The abbreviations used for multiplicities are s (singlet), d (doublet), t (triplet), q (quartet), qi (quintet), and m (multiplet). Structure elucidations of novel compounds were supported by the usage of 2D-NMR experiments (namely: ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H COSY and ^{1}H-^{1}H NOESY).

GC/MS analyses were carried out with an Agilent 7890B GC with 5977B GC/MSD and Gerstel MPS Robotic XL with KAS 4C injector. Samples were analysed on an Optima 5HT column, 30 m x 250 µm i.d. x film thickness 0.25 µm). Carrier gas, He; injector temp.: 60 °C to 300 °C at 12°C/s, splitless or split ratio 1:40; temp. program: 50 °C (isothermal 1 min) to 300 °C, at 20 °C/min and held isothermal for 6.5 min at 300°C; FID: 300°C, H_2: 30 mL/min, N_2: 25 mL/min, MSD: ion source: EI 70 eV, 230 °C; detector: quadrupole, EI mass spectra were acquired over the mass range of 30 –650 amu. Further GC/MS analyses were carried out with an Agilent GC 7890B chromatograph with Gerstel CIS4 Cold Injector.

HR-GC/MS analyses were carried out on a Waters GCT Premier mass spectrometer coupled with an Agilent 6890n GC with CTC CombiPAL sampler. Samples were analysed on an Optima 5HT column, 30 m x 250 µm i.d. x film thickness 0.25 µm). Carrier gas, He; injector temp. 300°C,

split ratio 1:40; temp. program: 50°C (isothermal 1 min) to 300°C, at 20 °C/min and held isothermal for 6.5 min at 300°C; FID: 300°C, H_2: 30 mL/min, N_2: 25 mL/min, GCT-Premier: ion source: EI 70 eV, 250 °C; detector-voltage: 2500 V, EI mass spectra were acquired over the mass range of 20 –800 amu. HRCI-MS was performed with a HP 6890 Series GC-system by Hewlett Packard.

Ultrasound sonication was generated using a Branson Sonifier 250. The probe (tip diameter: 3 mm) was immersed directly into the reaction mixture and positioned 0.5 mm above the bottom surface of the vial. The output power was 200 W, the power control was set to 4 (effective energy input of 32 W according to the device's power meter), and the duty cycle was set to 90% (0.9 seconds of constant ultrasonic treatment, 0.1 seconds of pause).

The phosphate buffer was generated by mixing 3.57 g of sodium phosphate dibasic heptahydrate with 0.92 g of sodium phosphate monobasic monohydrate in 200 mL of water. Afterwards, the pH was adjusted to 7.2 using aqueous solutions of HCl (1 M) and NaOH (1 M).

Monoterpenes **3**, **8**, **15**, **16**, **19** and **24** were purchased from TCI GmbH, Eschborn, Germany)

1.2 General procedures

1.2.1 Preparation of volatile NMR samples

The product containing fractions derived from the column chromatography were combined and concentrated to a volume of 50 μL using a light stream of argon gas. To avoid evaporation of the product, deuterated benzene (1 mL) was added to the vial. The mixture was again concentrated to a total volume of 50 μL using a light stream of argon gas. The solvent evaporation cools the mixture, which lowers evaporation of the product to a minimum. The co-evaporation of deuterated benzene and hexane/diethylether allows the removal of non-deuterated solvents. Subsequently, deuterated benzene (1 mL) was again added to the vial. This time, the mixture was concentrated to approximately 650 μL and transferred to an NMR tube.

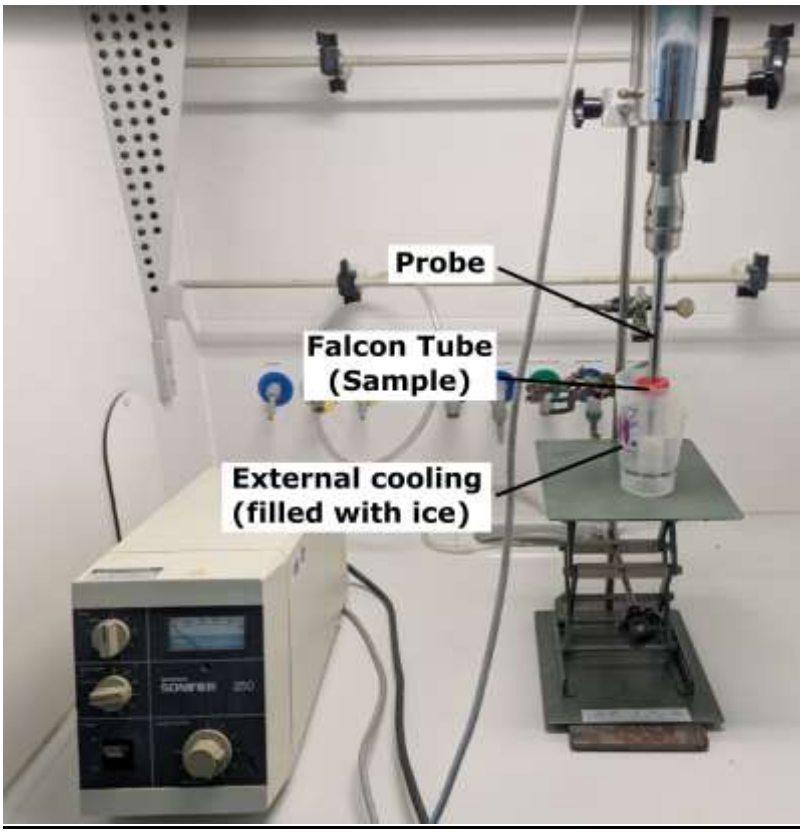
1.2.2 Decomposition of bromides in water

To a microwave tube was added the desired bromide (20 mg/mL) and distilled water. The tube was sealed and the emulsion was stirred vigorously at 70 °C over night. Subsequently, the tube was opened and the aqueous phase was extracted with *n*-hexane. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated to a volume of 1 mL under reduced pressure (750 mbar, 40 °C). The samples were then submitted to GC-MS analysis. Isolated spots on the TLC's were isolated through silica column chromatography.

1.2.3 Ultrasound-assisted decomposition of bromides in water

To a falcon tube was added the desired bromide (20 mg/mL) and distilled water or phosphate buffer (pH 7.2). The tube was sealed with a perforated cap. The hole in the lid was used to insert the ultrasound probe. During the hydrolysis, the falcon tube was constantly cooled externally with ice (exemplary reaction setup is shown below). The sonifier was set up with an output control of 4 and the duty cycle was set to 90%. After 20 minutes of sonication, the milky emulsion was extracted with *n*-hexane. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated to a volume of 1 mL under reduced

pressure (750 mbar, 40 °C). The samples were then submitted to GC-MS analysis. Isolated spots on the TLC's were isolated through silica column chromatography.



1.2.4 Generation of bromides

(*E*,*E*)-Farnesol, Geraniol and Nerol were purchased from commercial suppliers. The remaining alcohols were synthesised according to literature.[S1]

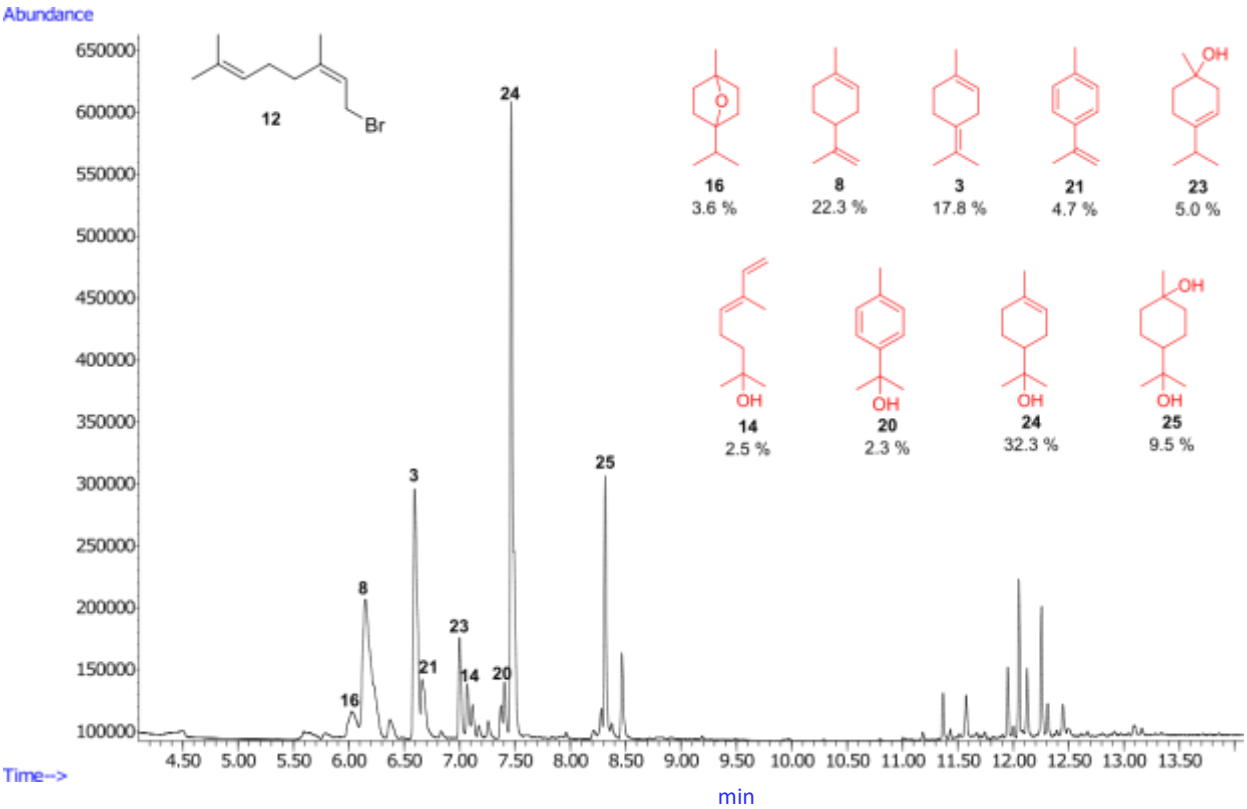
To a solution of the respective alcohol (1.0 eq) in Et_2O (0.2 M) was added PBr_3 (0.4 eq) at 0 °C. The mixture was stirred for 1 h. After full conversion (TLC), the reaction was terminated by addition of water (20 mL). The layers were separated and the aqueous phase was extracted with Et_2O. The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude bromide, which was used for hydrolysis without further purification.

2. GC Data

The analysed structures were identified through NIST Webbook comparison (see below). The relative quantification is derived from the GC integrals. Only peaks that could be assigned to a known structure were taken into account.

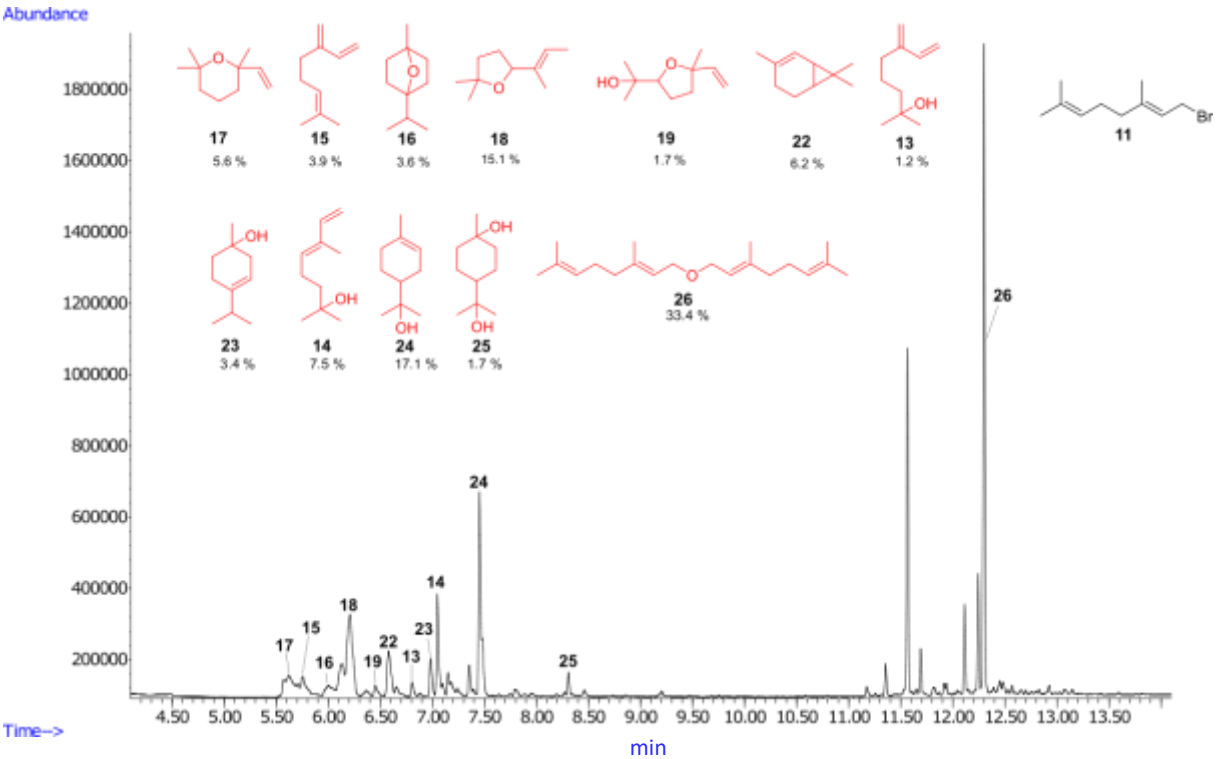
2.1 Hydrolysis of neryl bromide (12)

Hydrolysis of neryl bromide (**12**) was performed according to general procedure 1.2.2.



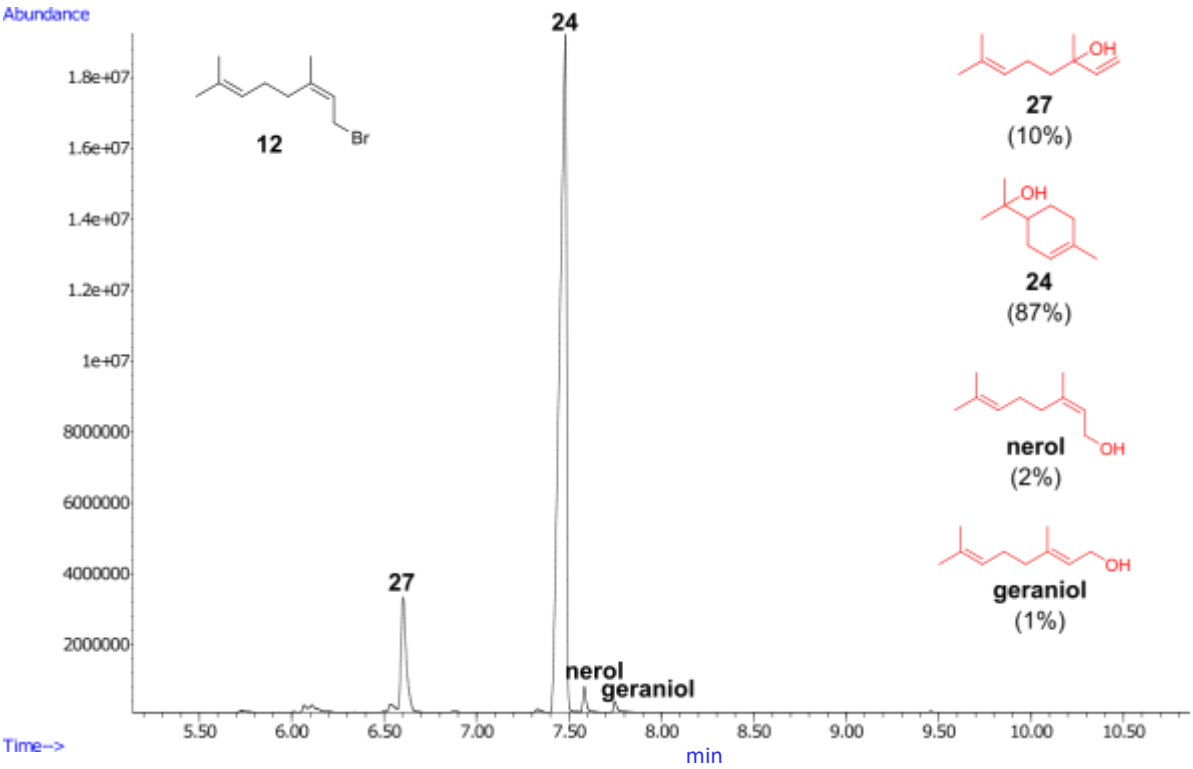
2.2 Hydrolysis of geranyl bromide (11)

Hydrolysis of geranyl bromide (**11**) was performed according to general procedure 1.2.2.

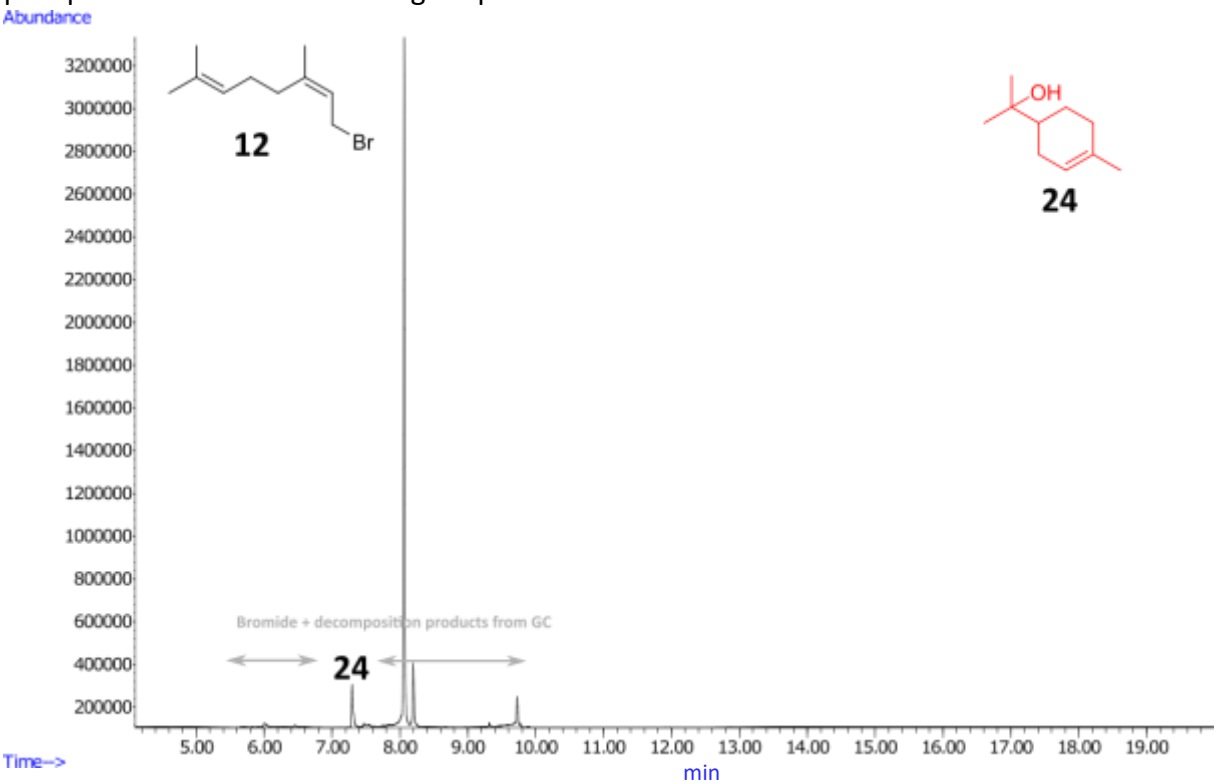


2.3 Ultrasound-assisted hydrolysis of neryl bromide (12)

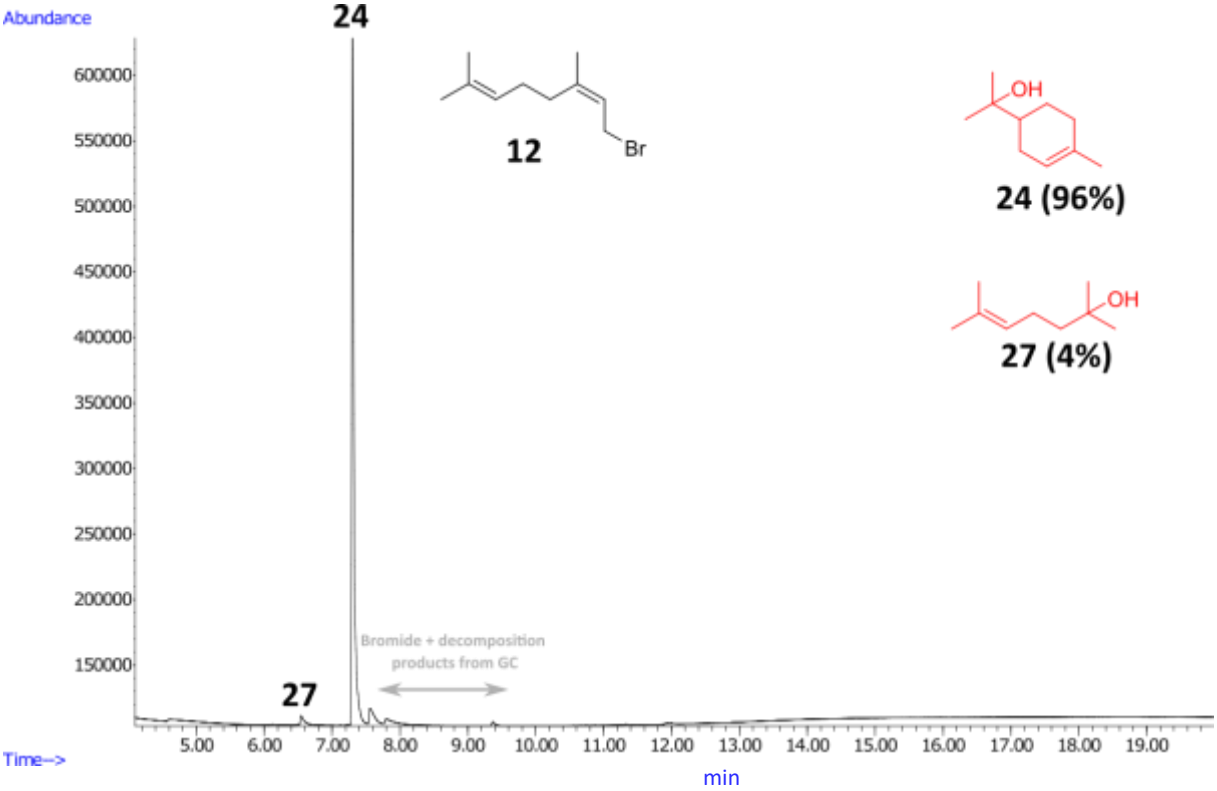
Hydrolysis of neryl bromide (**12**) was performed according to general procedure 1.2.3 using phosphate buffer.



Hydrolysis of neryl bromide (**12**) was performed according to general procedure 1.2.3 using phosphate buffer but the analog output control was set to 1 instead of 4.

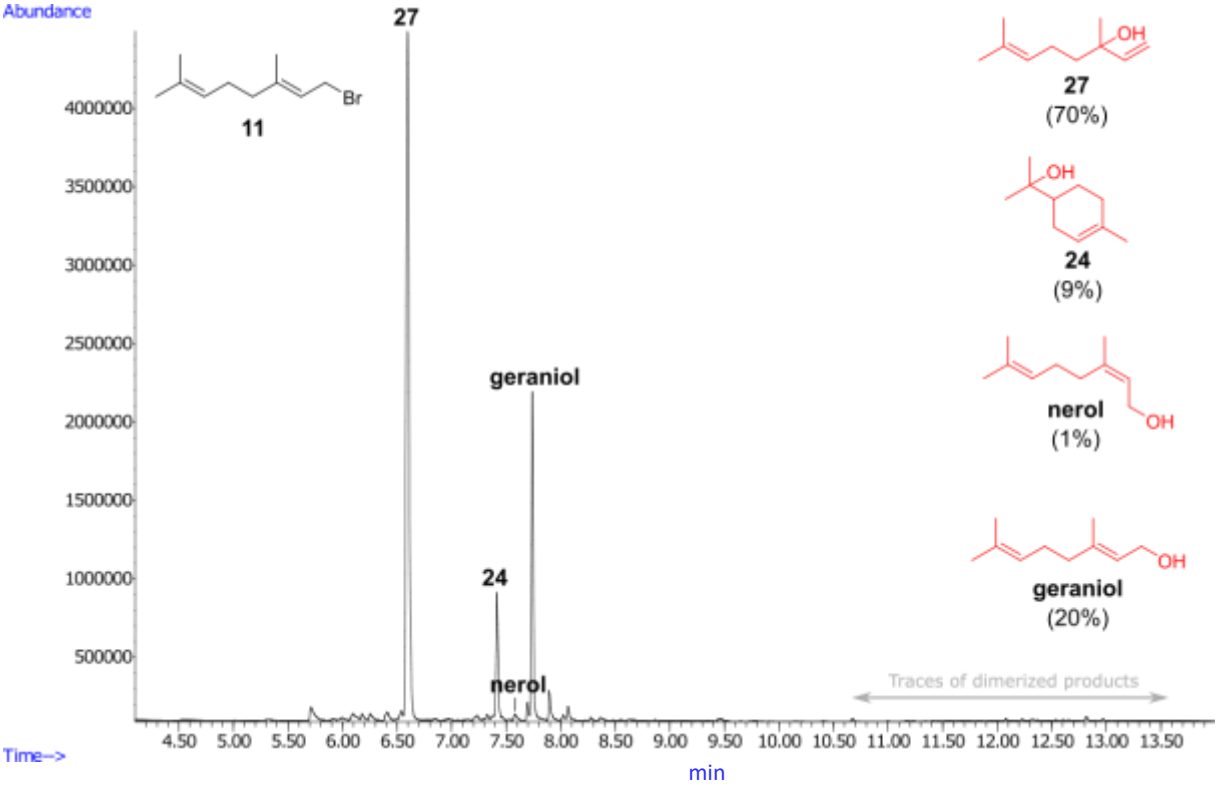


Hydrolysis of neryl bromide (**12**) was performed according to general procedure 1.2.3 using phosphate buffer but the analog output control was set to 2.5 instead of 4.



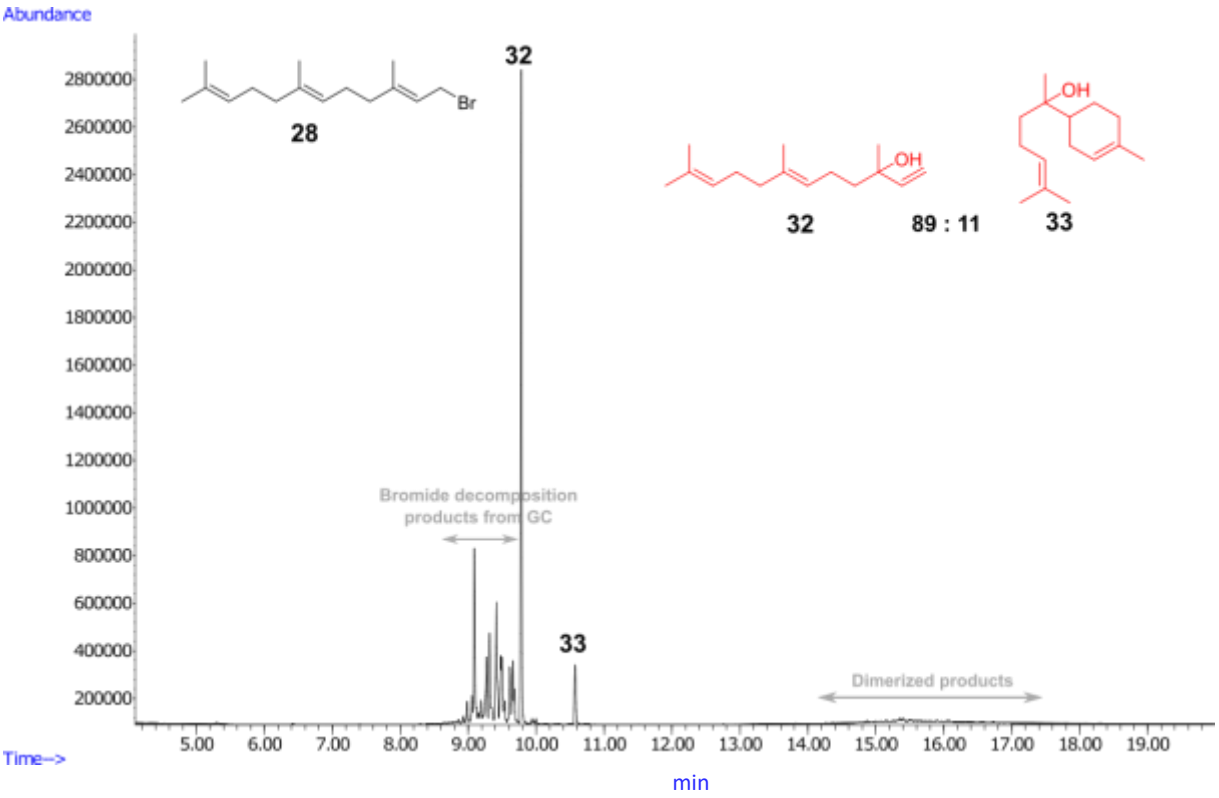
2.4 Ultrasound-assisted hydrolysis of geranyl bromide (11)

Hydrolysis of geranyl bromide (**11**) was performed according to general procedure 1.2.3 using phosphate buffer.

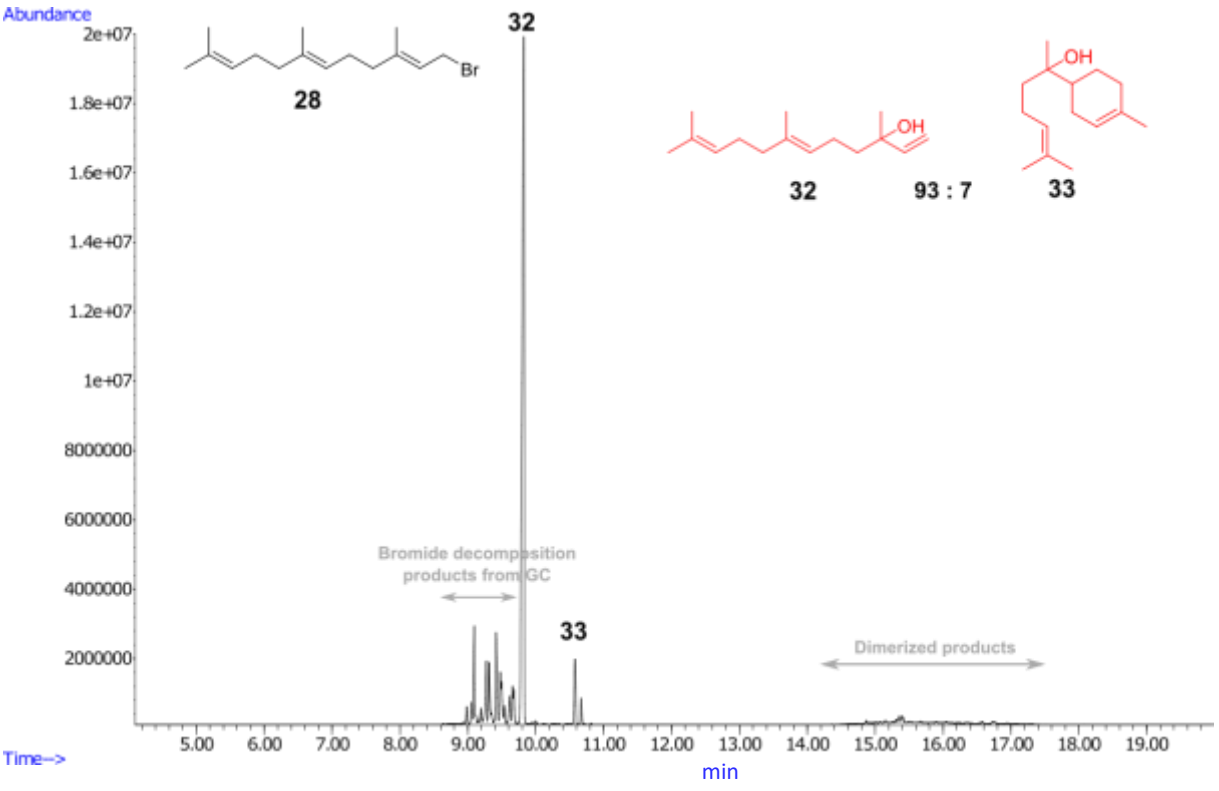


2.5 Ultrasound-assisted hydrolysis of (*E*,*E*)-farnesyl bromide (28)

Hydrolysis of (*E*,*E*)-farnesyl bromide (**28**) was performed according to general procedure 1.2.3 using phosphate buffer.

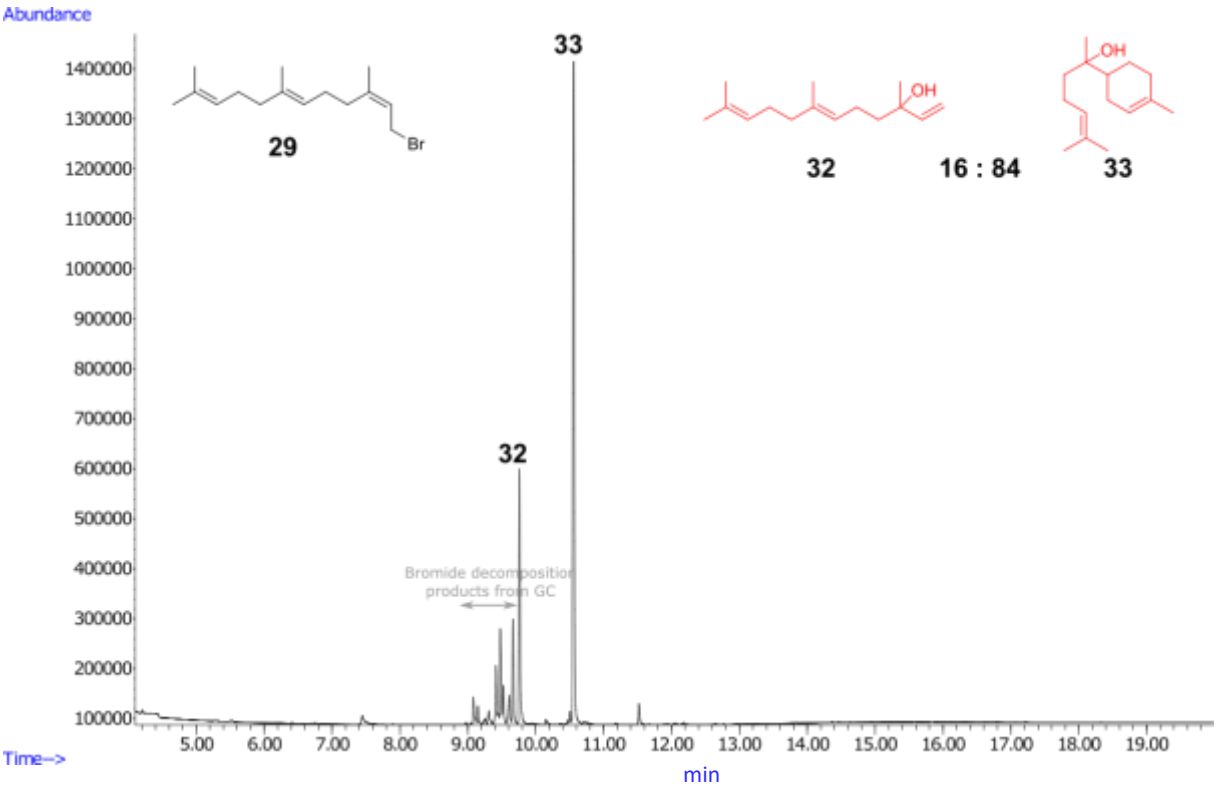


Hydrolysis of (*E*,*E*)-farnesyl bromide (**28**) was performed according to general procedure 1.2.3 using solely distilled water.



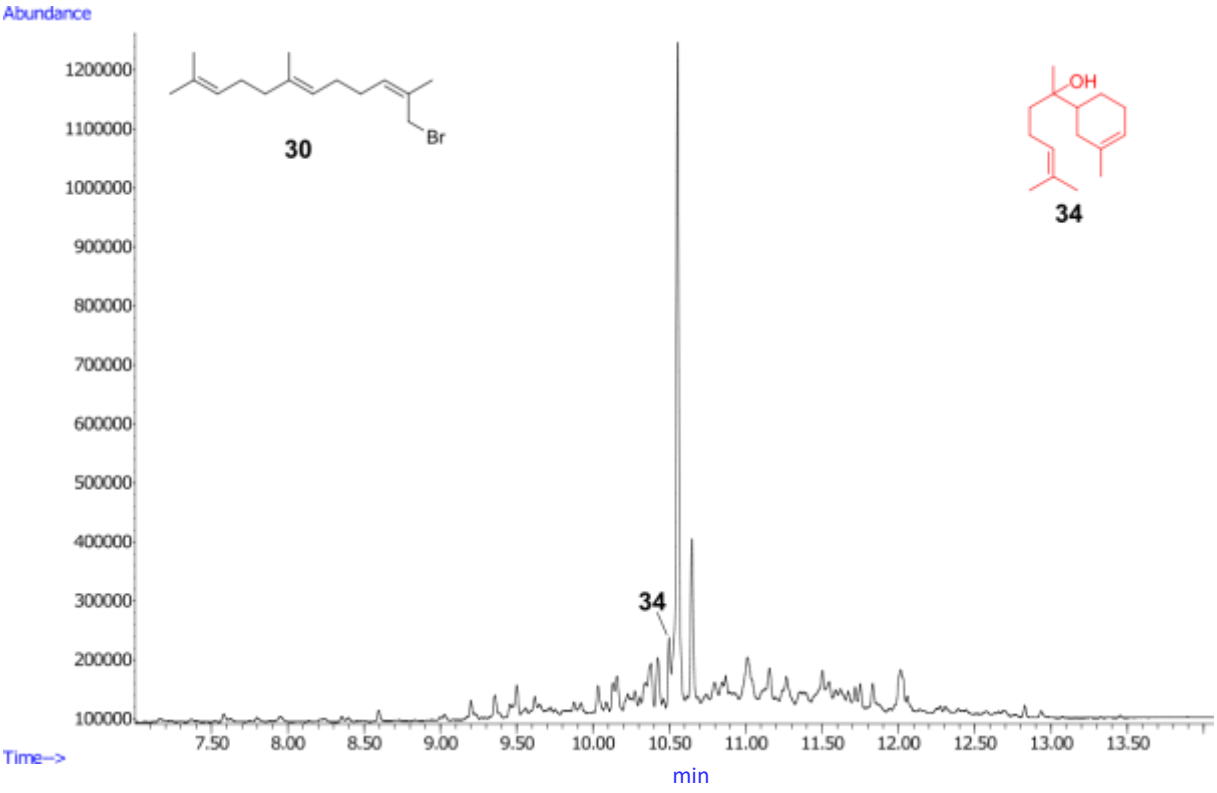
2.6 Ultrasound-assisted hydrolysis of (*Z*,*E*)-farnesyl bromide (29)

Hydrolysis of (*Z*,*E*)-farnesyl bromide (**29**) was performed according to general procedure 1.2.3 using phosphate buffer.



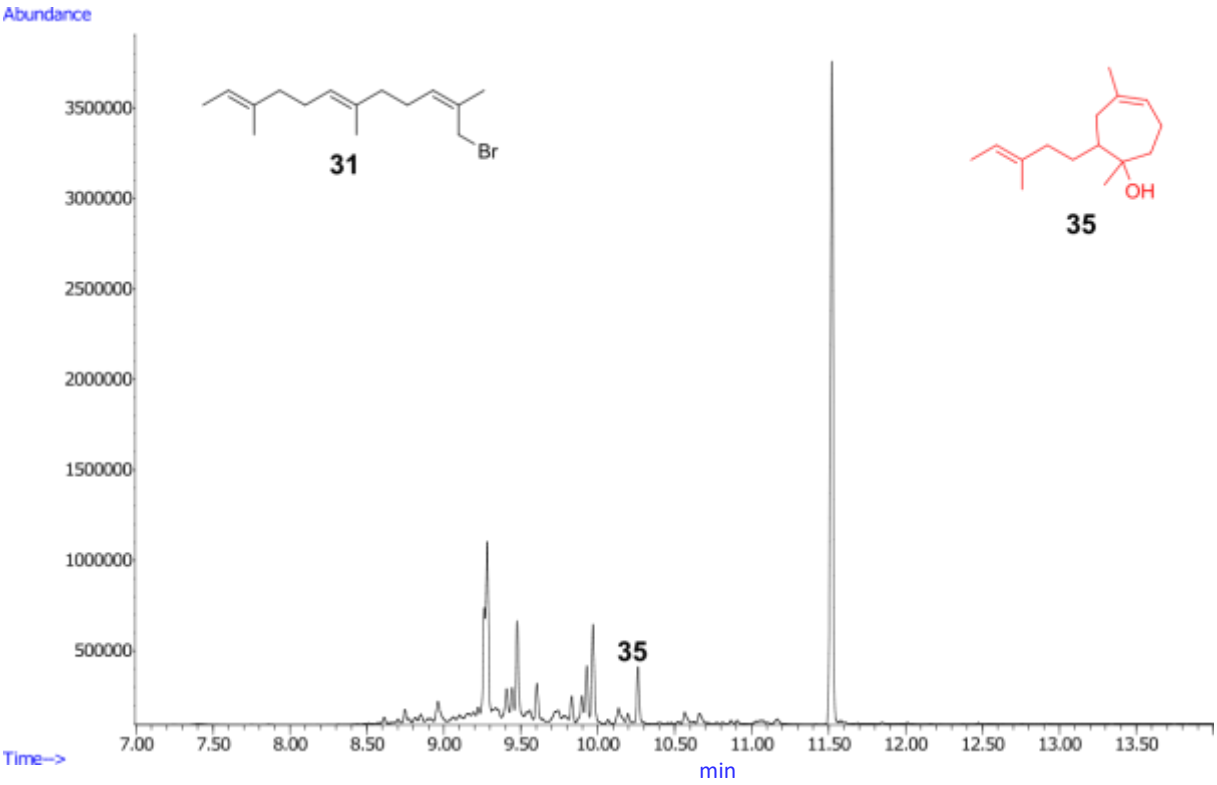
2.7 Ultrasound-assisted hydrolysis of unnatural bromide 30

Hydrolysis of unnatural bromide **30** was performed according to general procedure 1.2.3 using phosphate buffer.

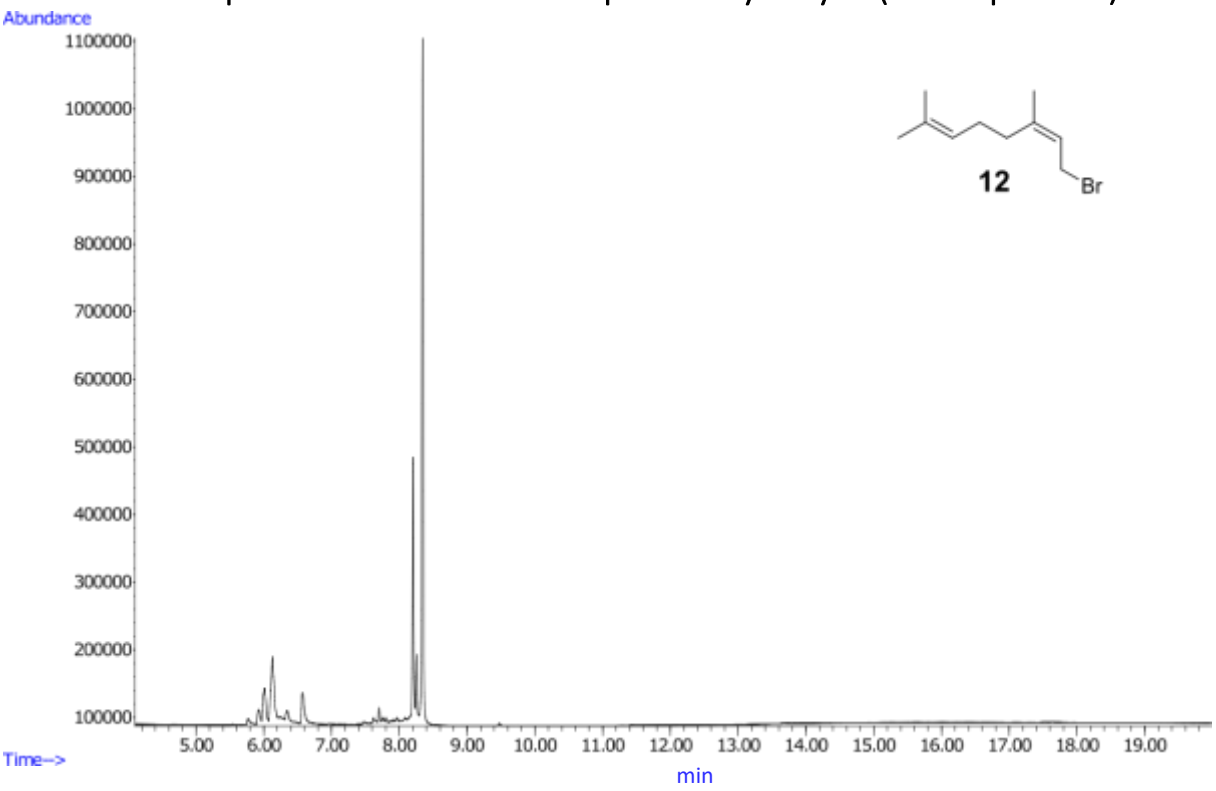


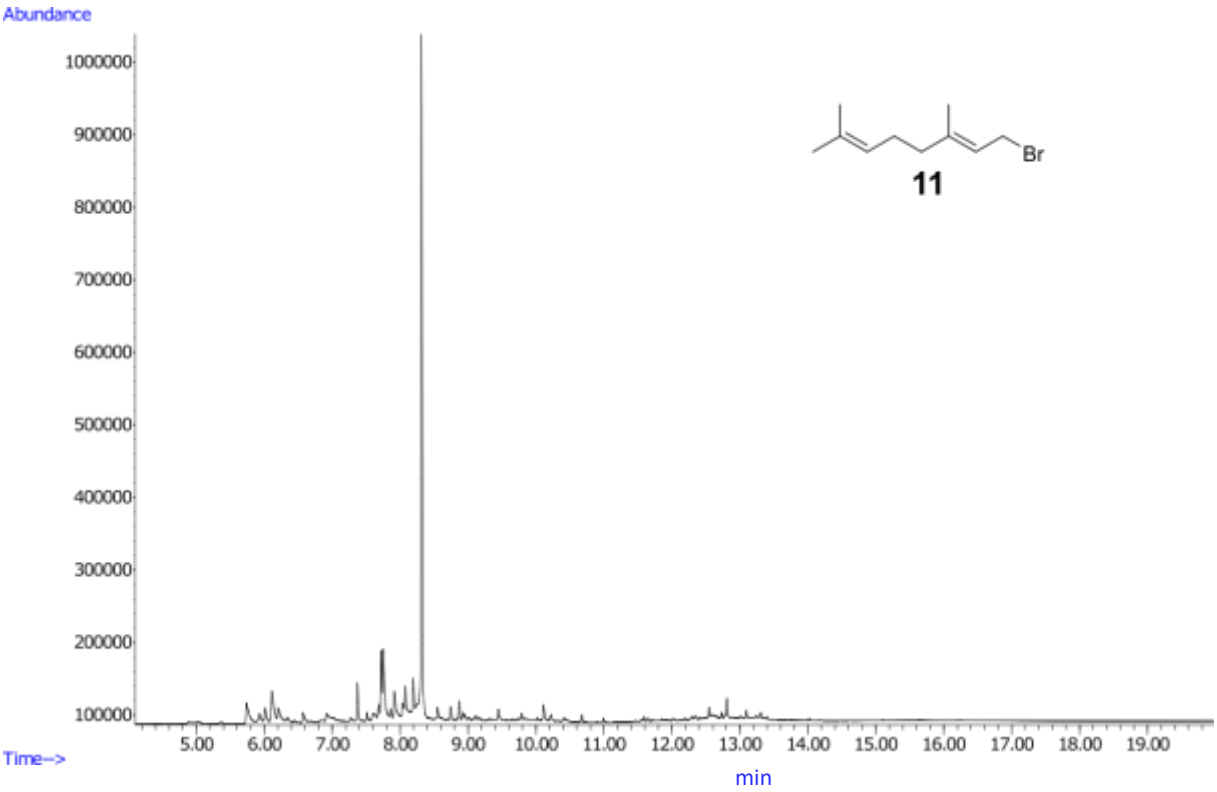
2.8 Ultrasound-assisted hydrolysis of unnatural bromide 31

Hydrolysis of unnatural bromide **31** was performed according to general procedure 1.2.3 using phosphate buffer.



2.9 GC Data of pure bromide derivatives prior to hydrolysis (decomposition)




Abundance
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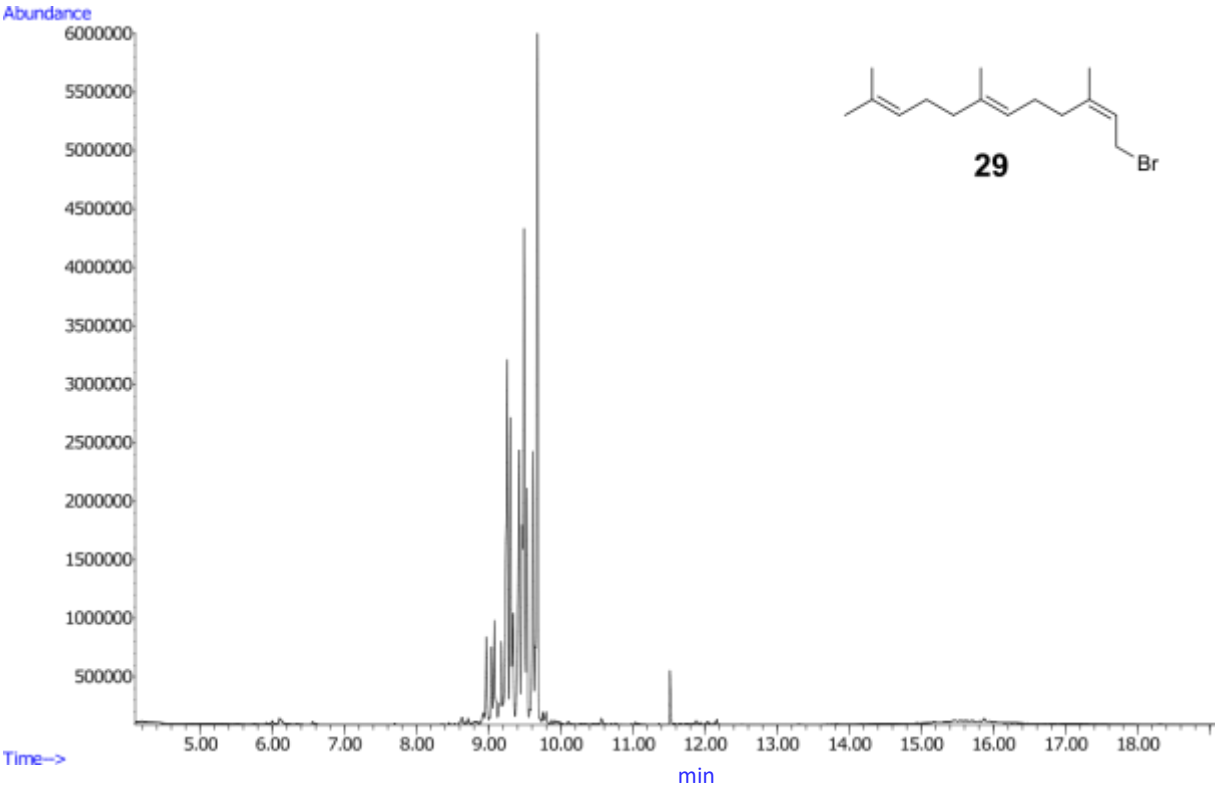
900000
800000
700000
600000
500000
400000
300000
200000
100000
5.00
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
Time-->
min
Br
11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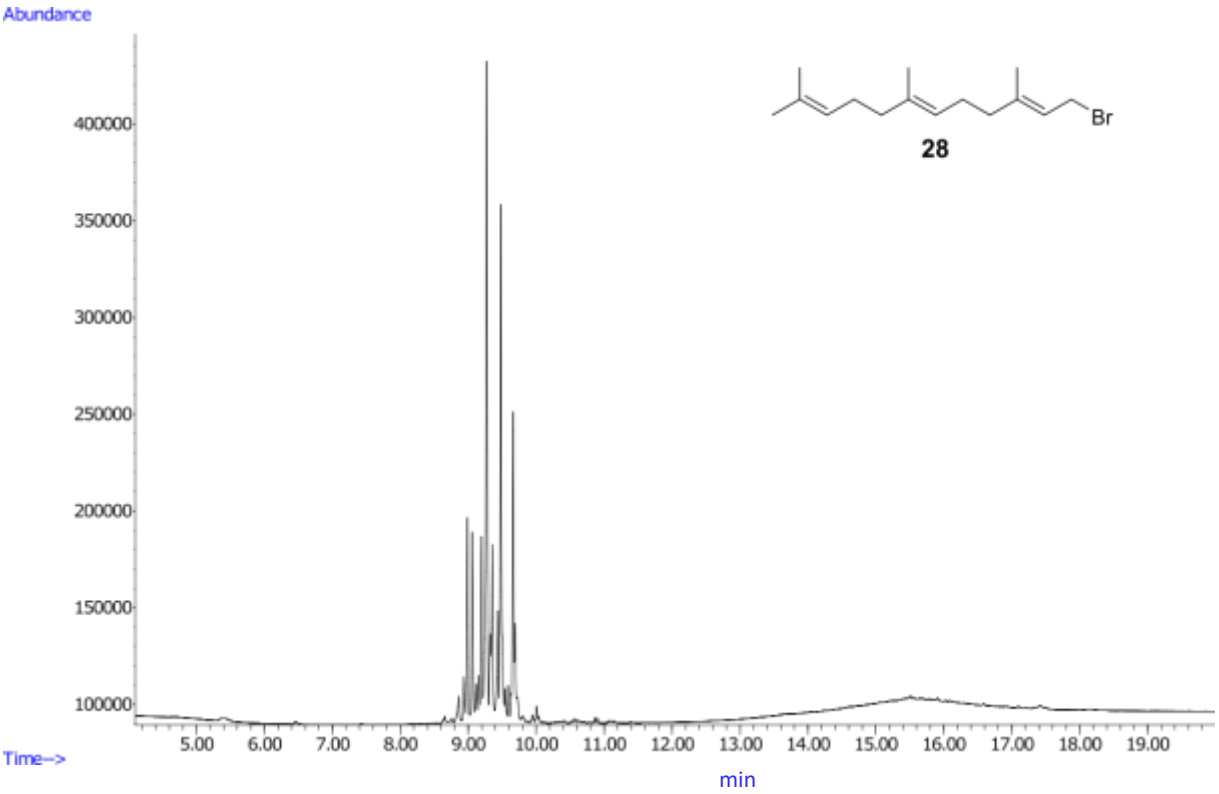
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
Time-->
min
Br
29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200000
150000
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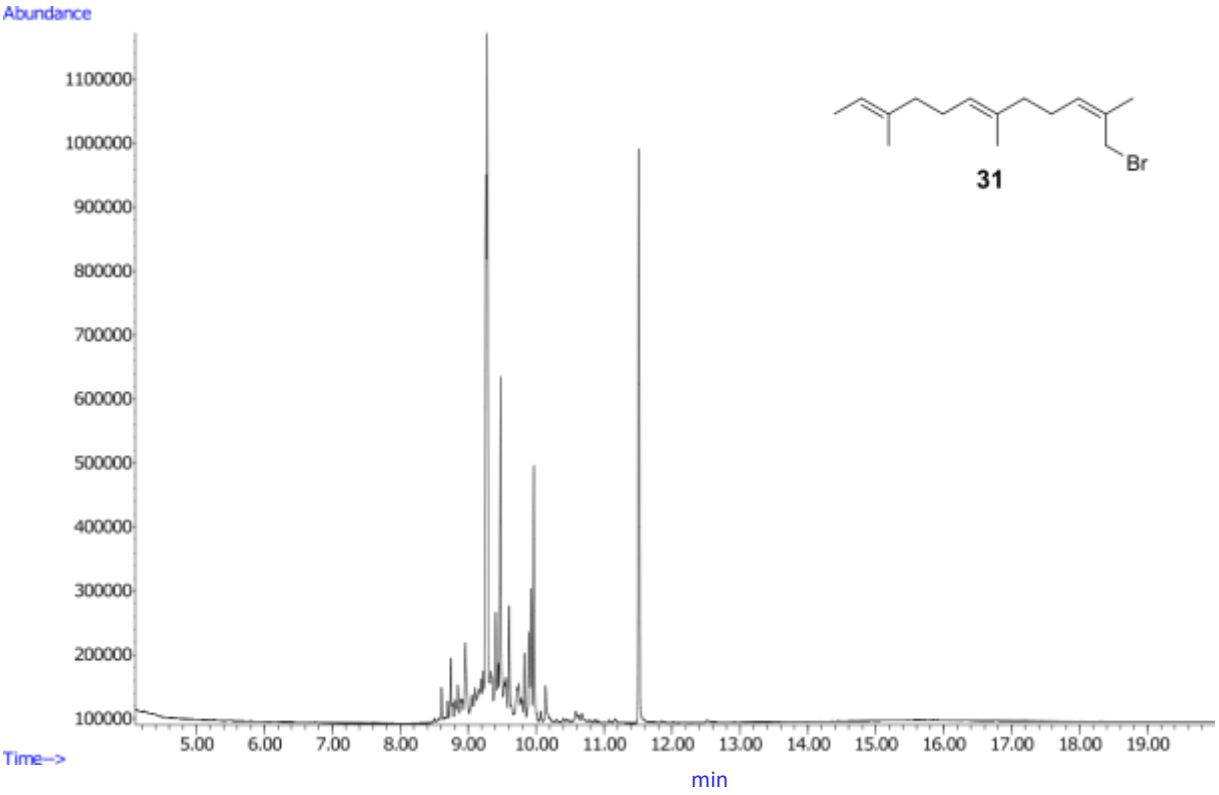
6.00
7.00
8.00
9.00
10.00
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
Time-->
min
Br
28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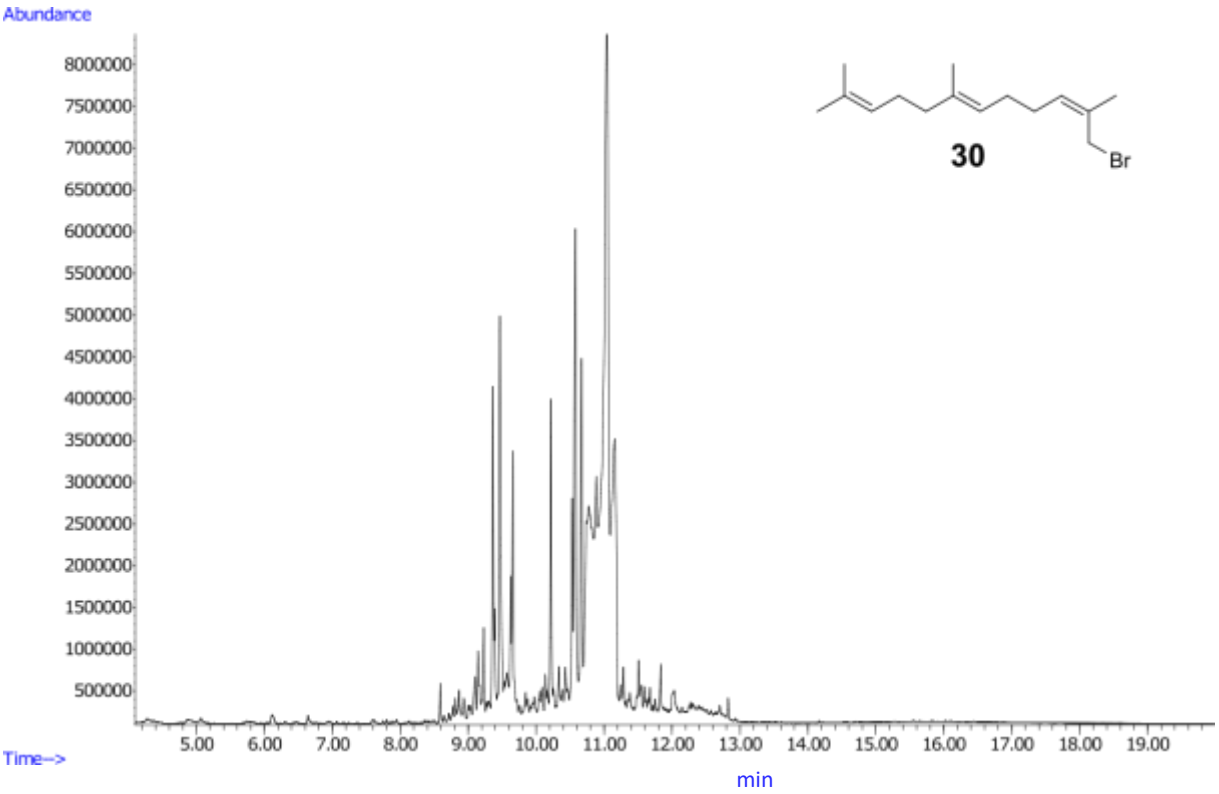
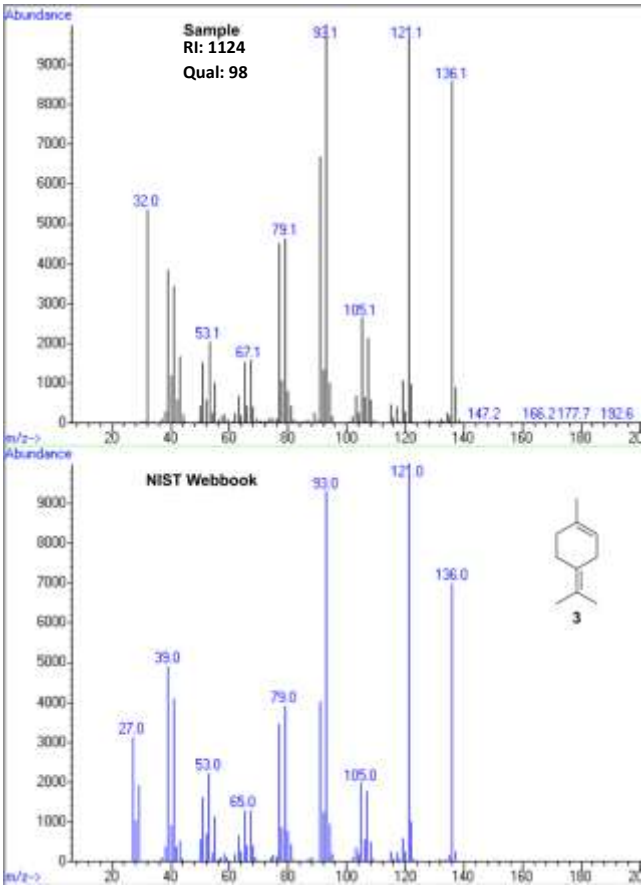
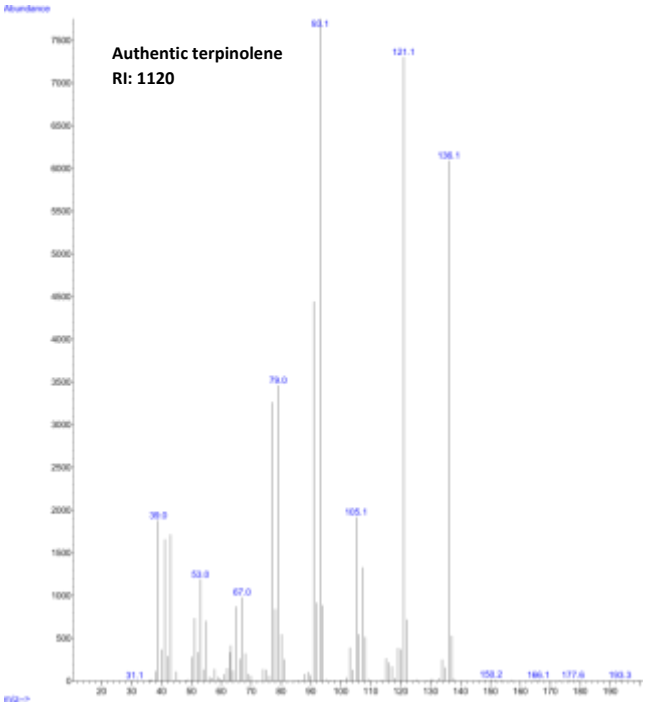
17.00
18.00
19.00
Time-->
min
Br
31

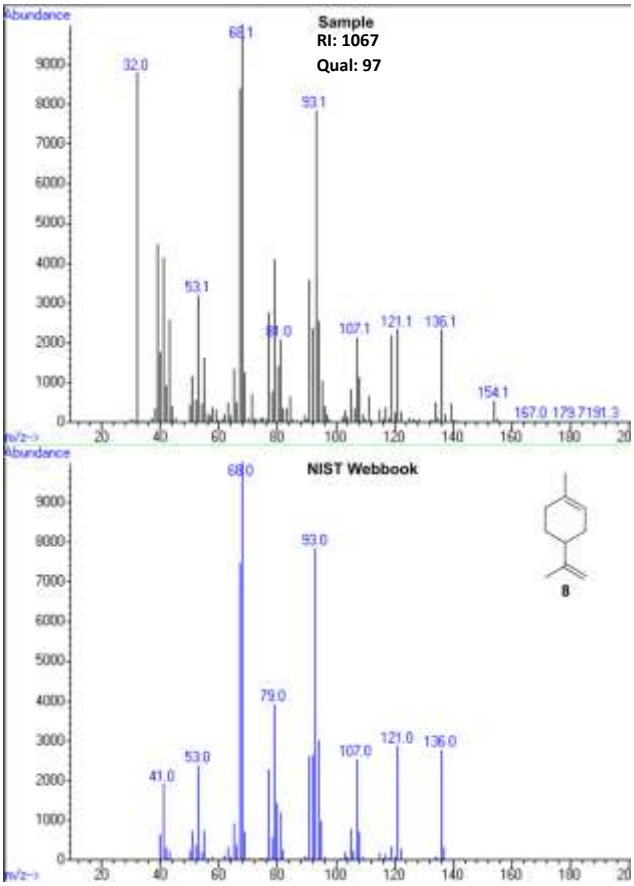


3. MS Data

The following spectra shown in black (marked as „sample“) present the mass spectra obtained from GC measurements of the hydrolysis experiments (retention indices are displayed). The reference spectrum shown in blue (marked as „NIST Webbook“) was retrieved from the open-access NIST Webbook and served as the basis for comparison. Mass spectra for the unnatural terpene products were obtained from the literature quoted. For commercially available monoterpenes (purchased from TCI) an additional authentic sample was measured and the respective mass spectra as well as the observed retention index are displayed.


Abundance
Sample
RI: 1124
Qual: 98
93.1
121.1
136.1
32.0
79.1
105.1
53.1
67.1
147.2
168.2
177.7
192.6
m/z-->
Abundance
NIST Webbook
93.0
121.0
136.0
39.0
27.0
79.0
53.0
105.0
65.0
3
m/z-->


Authentic terpinolene
RI: 1120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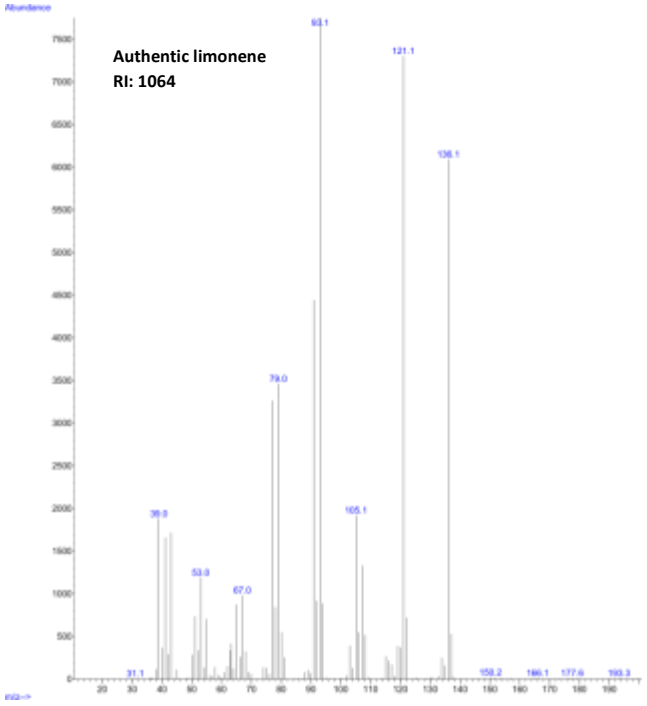
32.0
93.1
53.1
88.0
107.1
121.1
136.1
154.1
157.0
179.7
191.3
m/z-->
Abundance
NIST Webbook
68.0
93.0
79.0
53.0
41.0
107.0
121.0
136.0
8
m/z-->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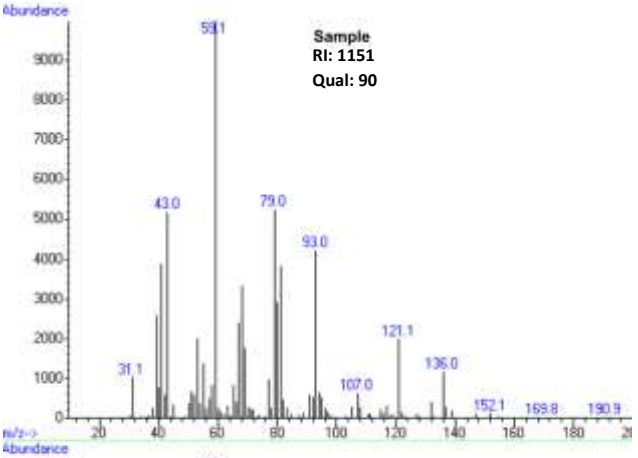
RI: 1064


Abundance
Sample
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Qual: 90
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79.0
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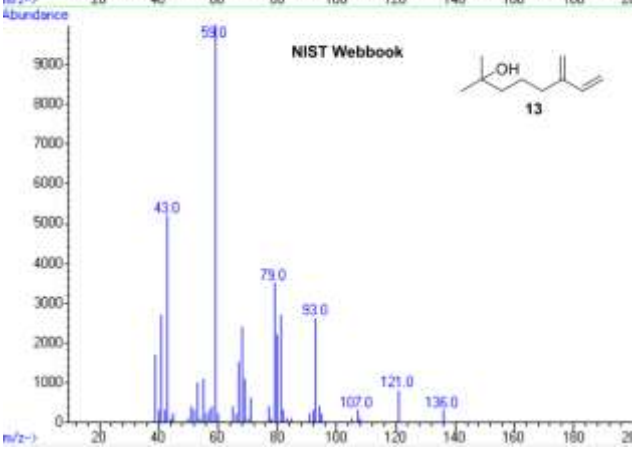
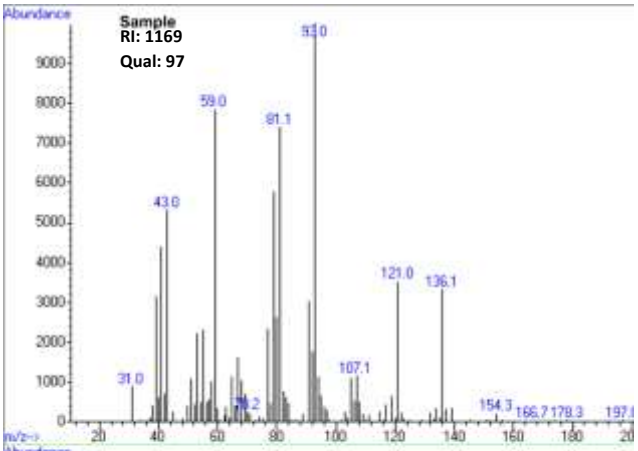
136.0
31.1
107.0
152.1
169.8
190.9
m/z-->


Abundance
NIST Webbook
OH
13
59.0
43.0
79.0
93.0
121.0
107.0
136.0
m/z-->


Abundance
Sample
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Qual: 97
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31.0
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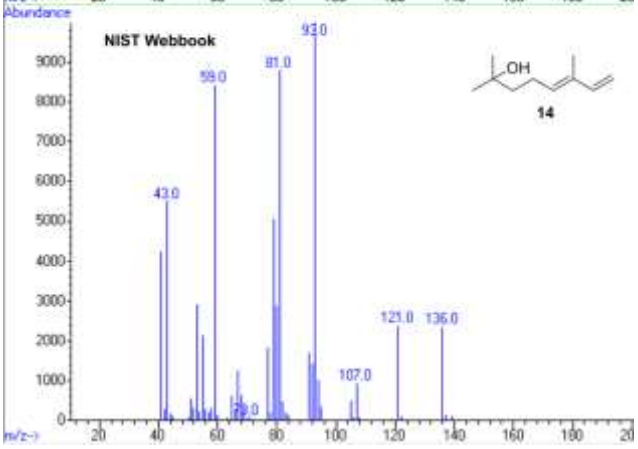
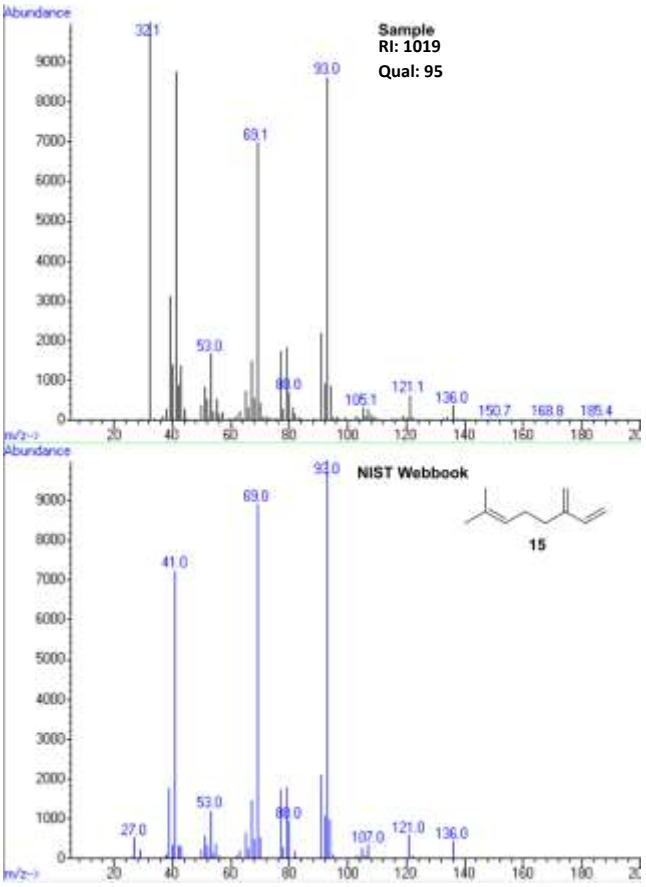
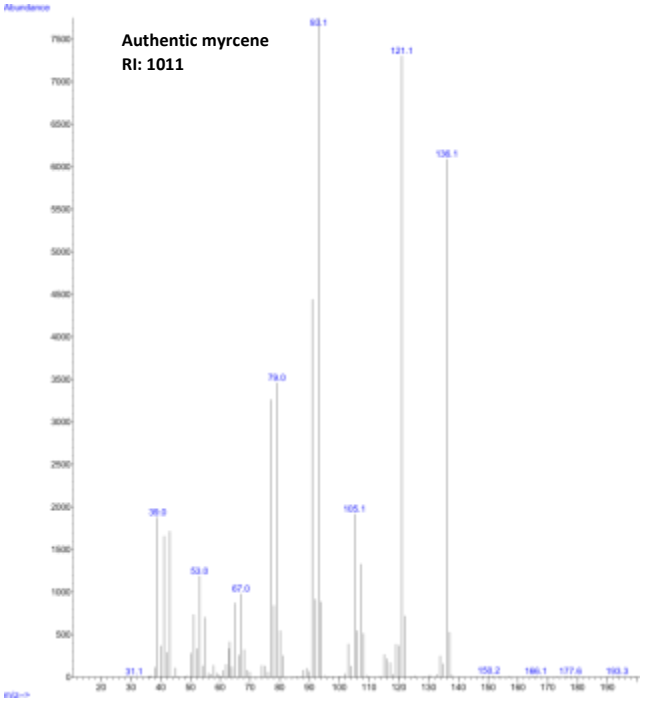
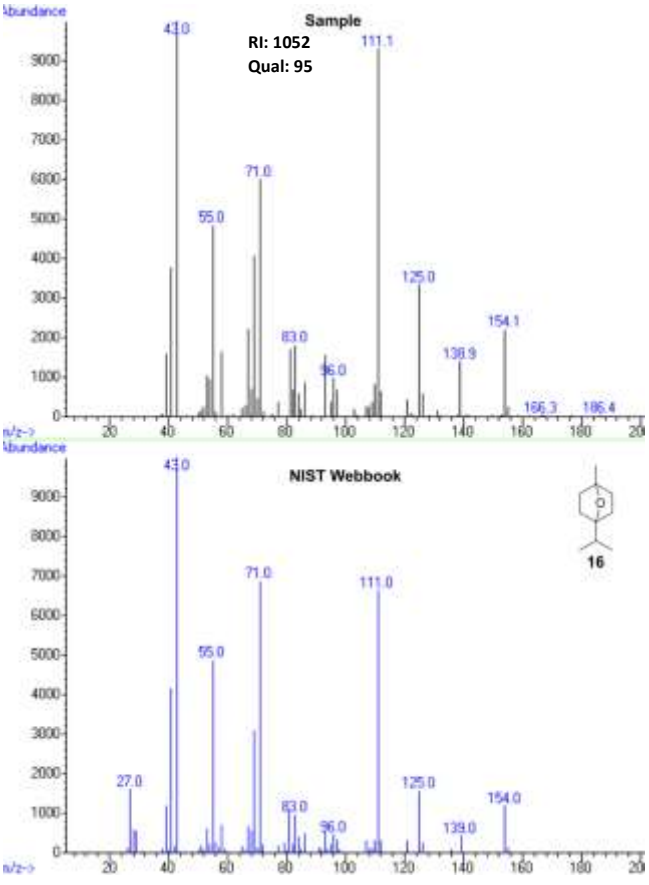
154.3
166.7
179.3
m/z-->


Abundance
NIST Webbook
OH
14
93.0
81.0
59.0
43.0
121.0
136.0
107.0
m/z-->


Abundance
Sample
RI: 1019
Qual: 95
NIST Webbook
15
m/z-->


Authentic myrcene
RI: 1011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Qual: 95
NIST Webbook
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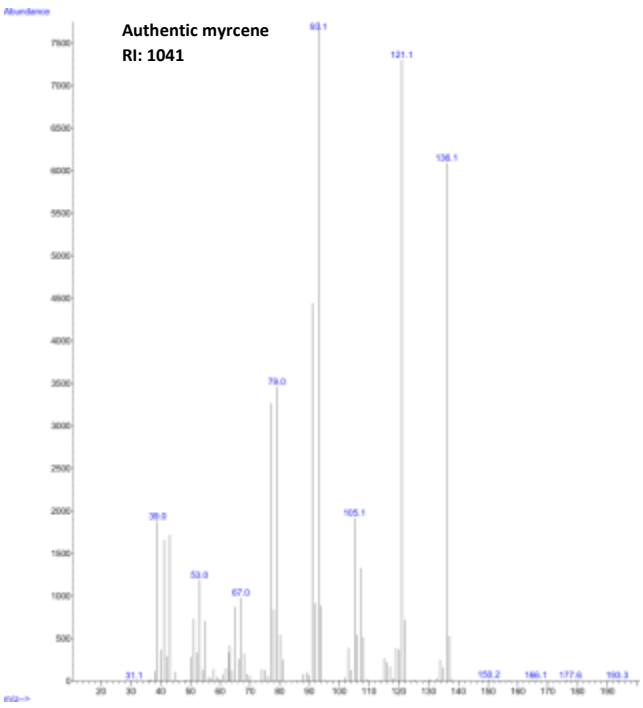
m/z-->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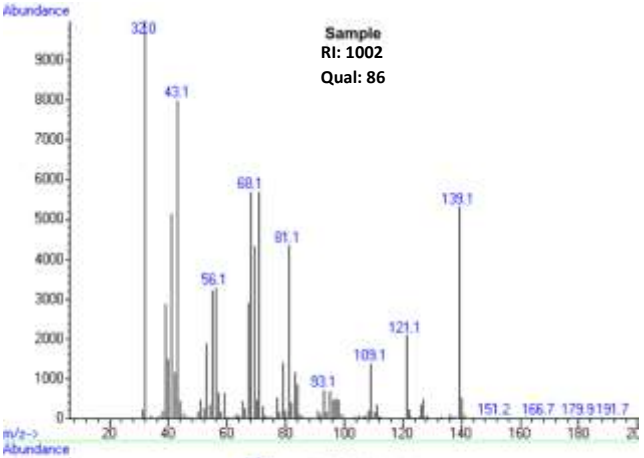
Abundance
Sample
RI: 1002
Qual: 86
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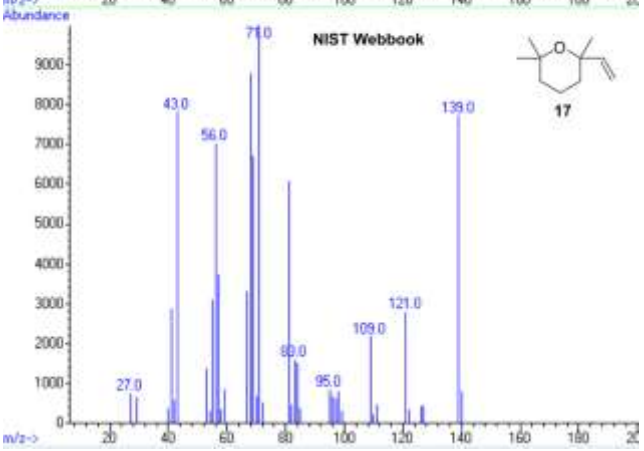
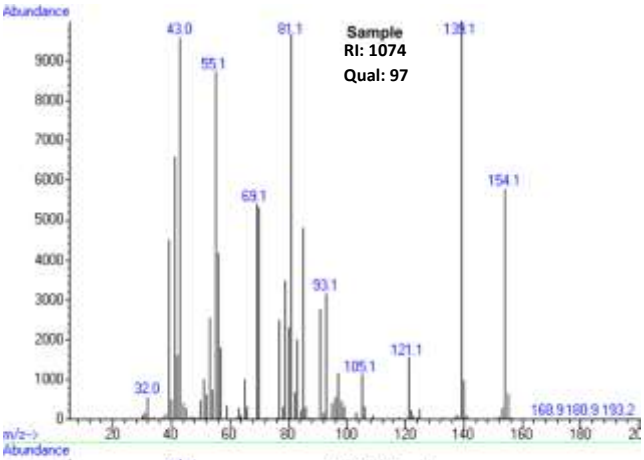
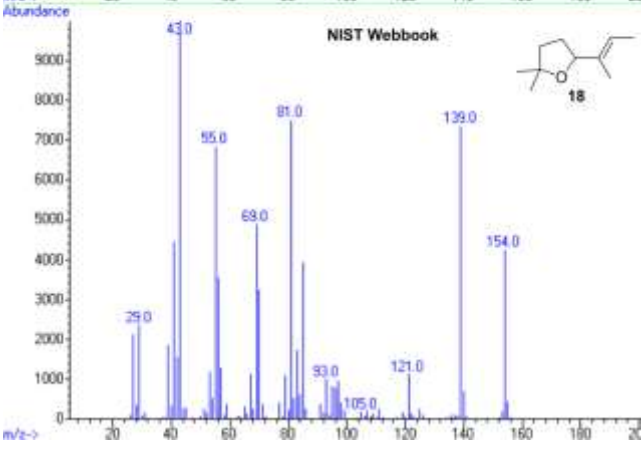
43.1
68.1
81.1
56.1
139.1
121.1
109.1
93.1
151.2 166.7 179.9 191.7
m/z->

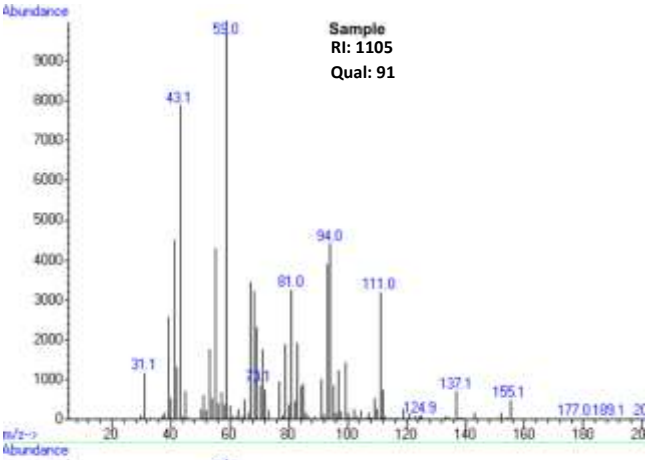

Abundance
NIST Webbook
71.0
43.0
56.0
139.0
121.0
109.0
95.0
27.0
m/z->

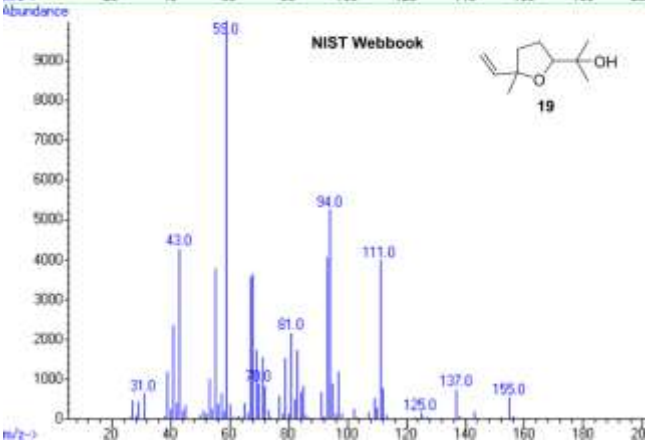
17

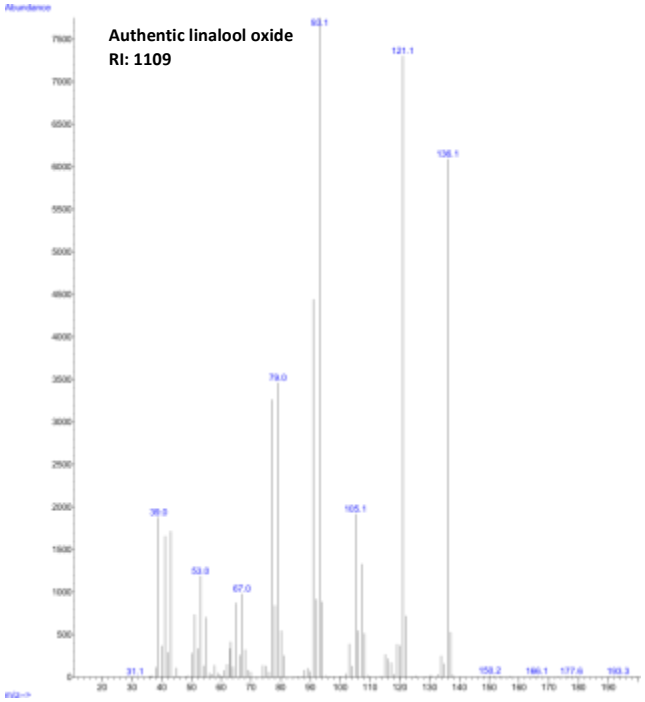

Abundance
Sample
RI: 1074
Qual: 97
43.0
55.1
81.1
139.1
69.1
154.1
93.1
121.1
105.1
32.0
168.9 180.9 193.2
m/z->

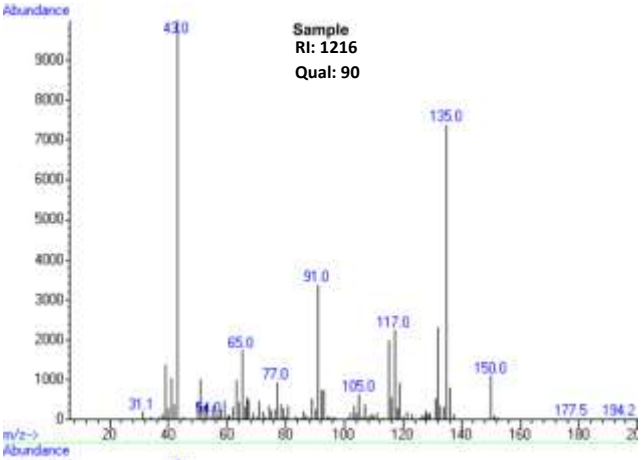

Abundance
NIST Webbook
43.0
81.0
55.0
139.0
69.0
154.0
29.0
93.0
121.0
105.0
m/z->

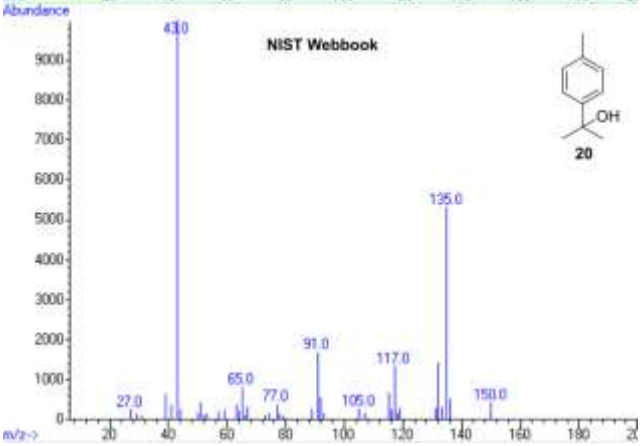
18

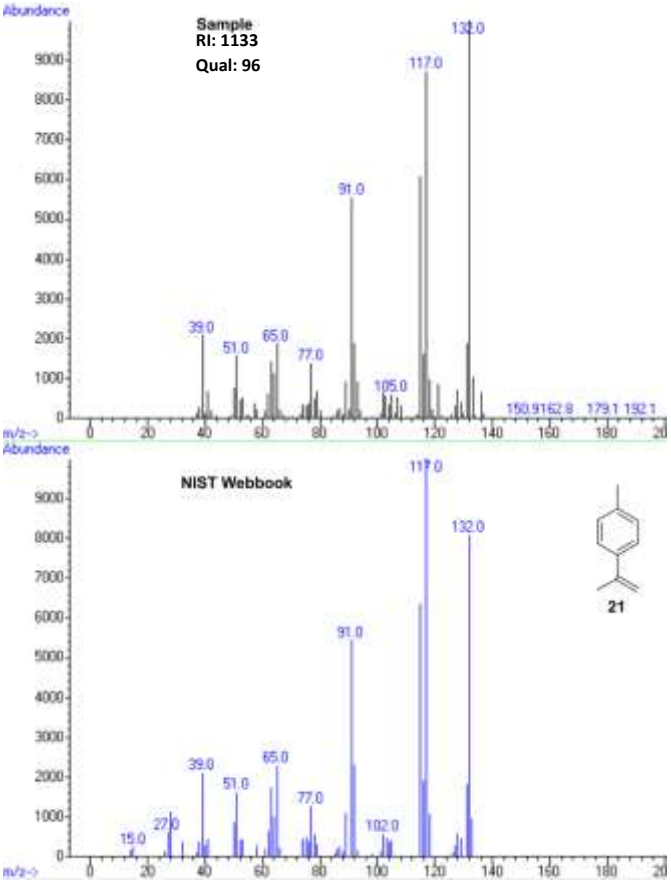

Abundance
Sample
RI: 1105
Qual: 91
59.0
43.1
94.0
81.0
111.0
31.1
137.1
155.1
124.9
177.0 189.1
m/z-->


Abundance
NIST Webbook
59.0
OH
19
94.0
43.0
111.0
81.0
31.0
137.0
155.0
125.0
m/z-->

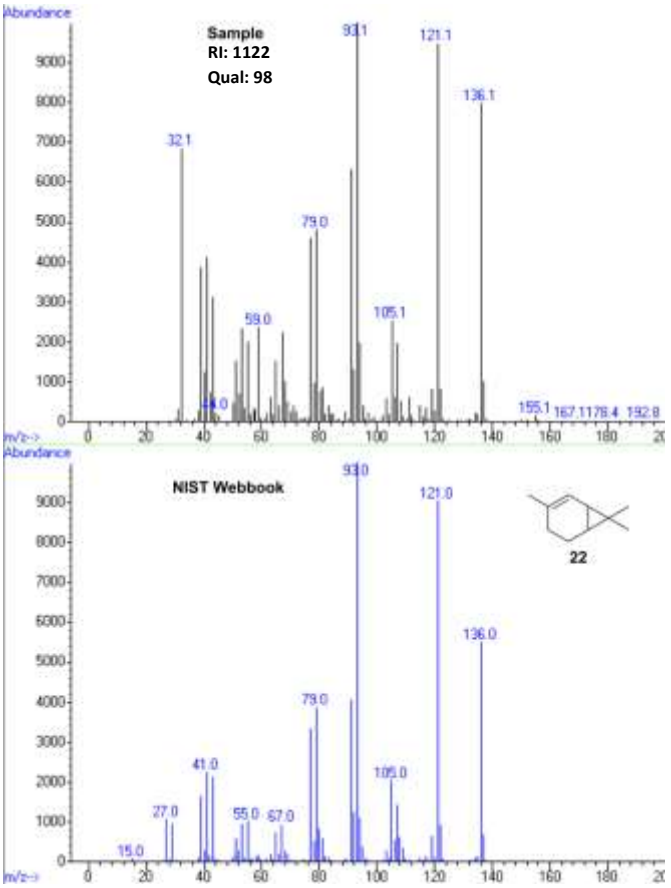

Authentic linalool oxide
RI: 1109
93.1
121.1
136.1
79.0
105.1
39.0
53.0
67.0


Abundance
Sample
RI: 1216
Qual: 90
43.0
135.0
91.0
117.0
65.0
77.0
105.0
150.0
31.1
177.5
194.2
m/z-->

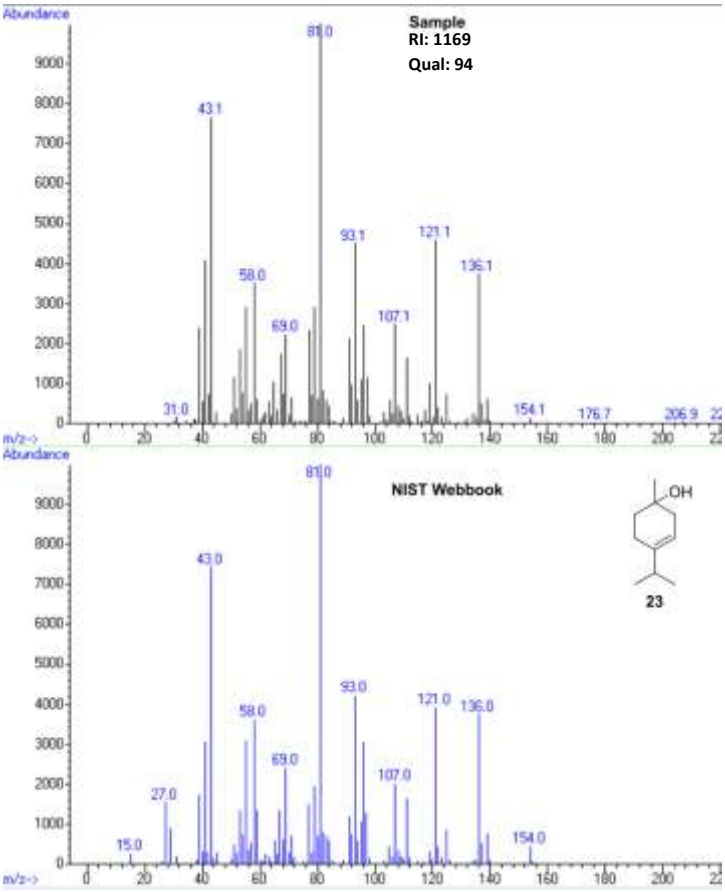

Abundance
NIST Webbook
43.0
OH
20
135.0
91.0
117.0
65.0
27.0
77.0
105.0
150.0
m/z-->


Abundance
Sample
RI: 1133
Qual: 96
132.0
117.0
91.0
39.0
51.0
65.0
77.0
105.0
150.9162.8
179.1
192.1
m/z-->
Abundance
NIST Webbook
117.0
132.0
91.0
39.0
65.0
51.0
77.0
27.0
15.0
102.0
m/z-->

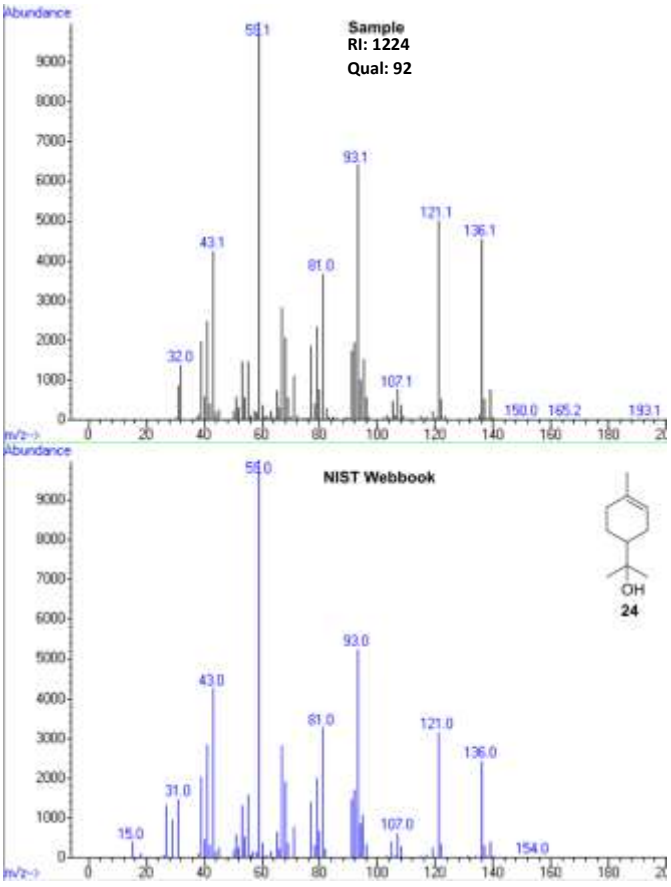
21


Abundance
Sample
RI: 1122
Qual: 98
93.1
121.1
136.1
32.1
79.0
59.0
105.1
155.1
167.1178.4
192.8
m/z-->
Abundance
NIST Webbook
93.0
121.0
136.0
79.0
41.0
105.0
27.0
55.0
67.0
15.0
m/z-->

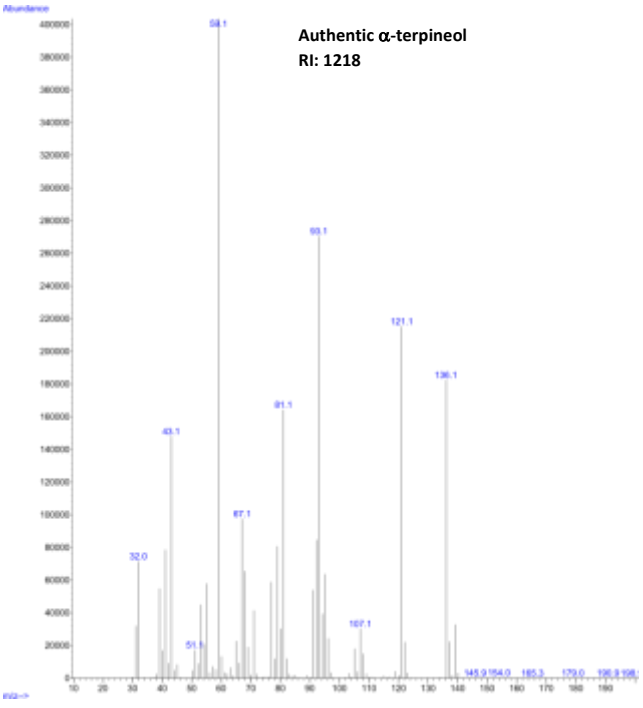
22



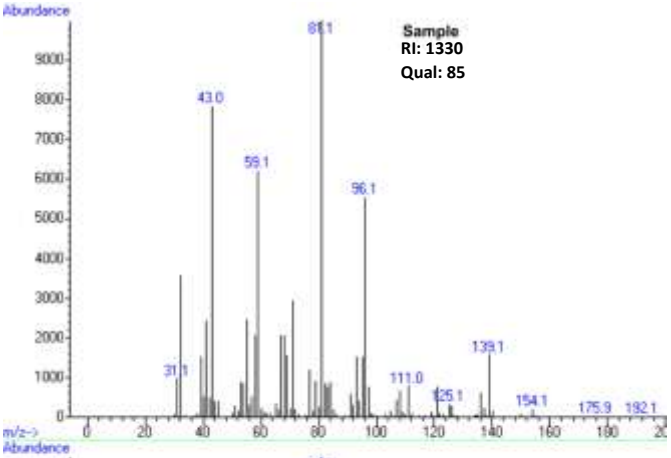
23

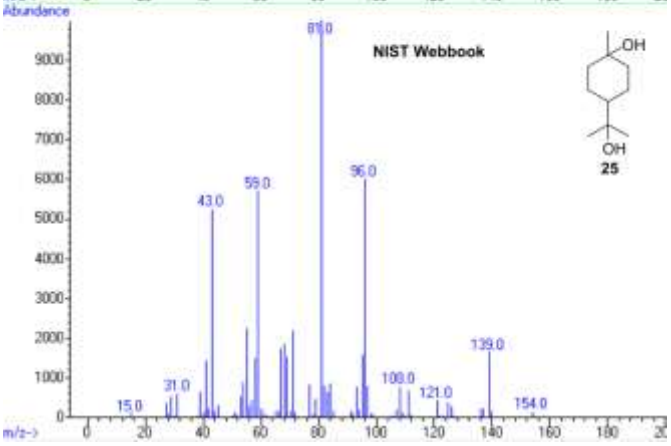


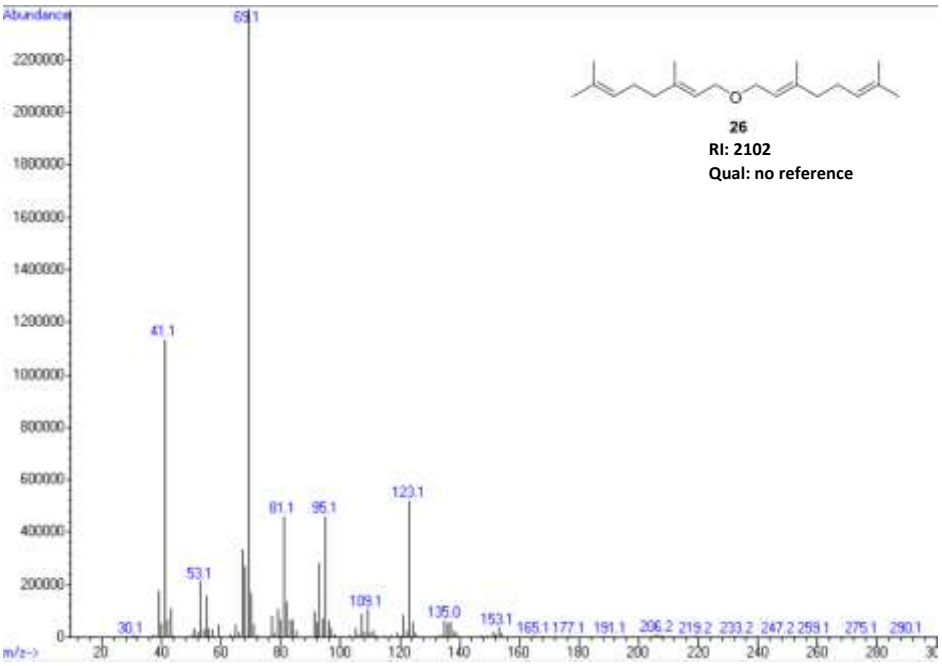
24



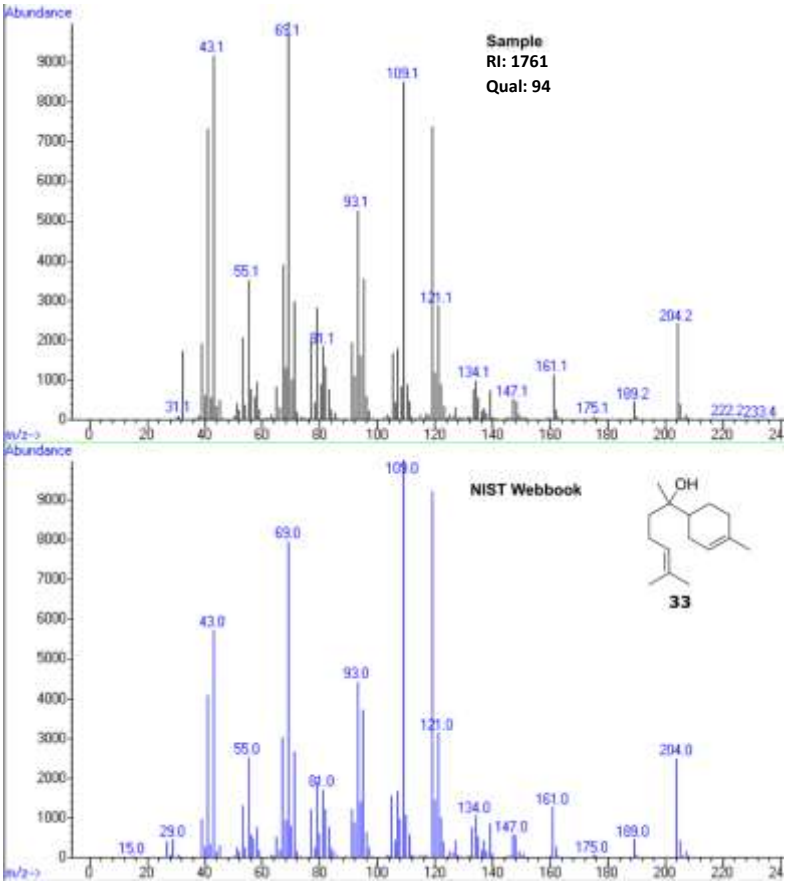
Authentic α-terpineol
RI: 1218

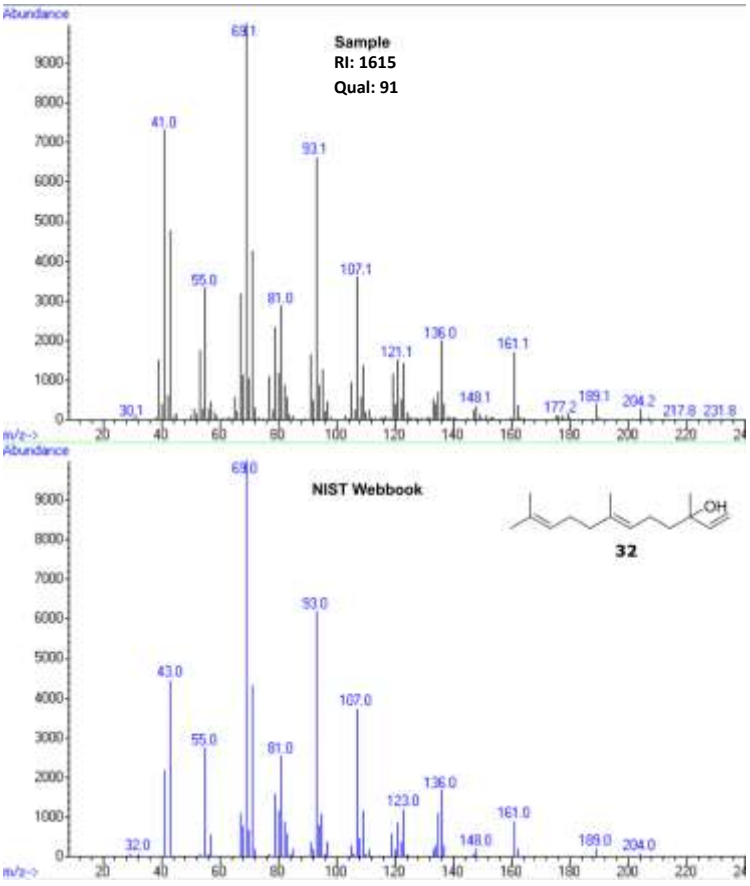


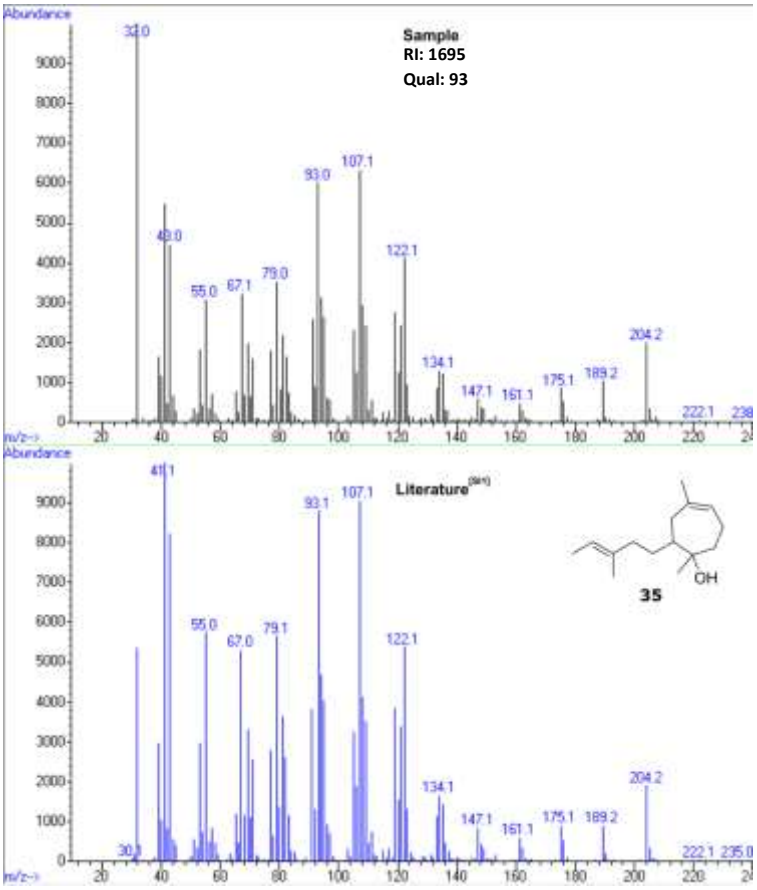


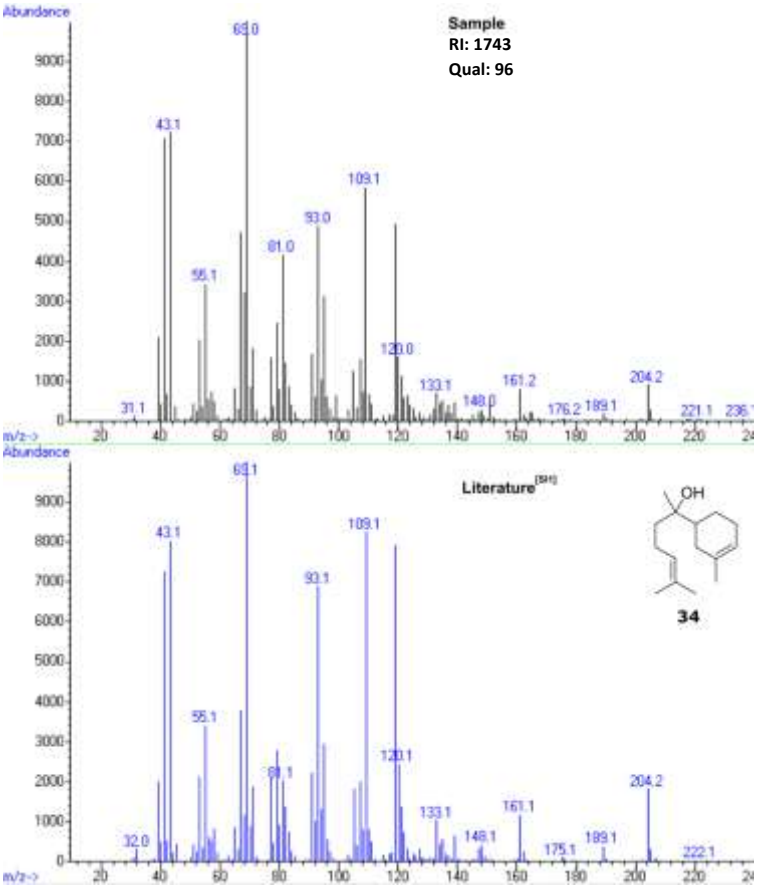


26
RI: 2102
Qual: no reference


Abundance
Sample
RI: 1761
Qual: 94
43.1
69.1
109.1
93.1
55.1
121.1
81.1
204.2
134.1
161.1
147.1
189.2
175.1
31.1
222.2233.4
m/z->
Abundance
NIST Webbook
OH
109.0
69.0
43.0
93.0
121.0
55.0
204.0
81.0
134.0
161.0
147.0
189.0
175.0
29.0
15.0
m/z->
33

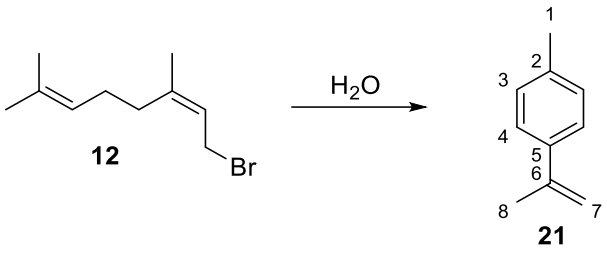

Abundance
Sample
RI: 1615
Qual: 91
69.1
41.0
93.1
55.0
107.1
81.0
136.0
121.1
161.1
148.1
30.1
177.2
189.1
204.2
217.8
231.8
m/z->
Abundance
NIST Webbook
OH
69.0
93.0
43.0
107.0
55.0
81.0
136.0
123.0
161.0
148.0
189.0
204.0
32.0
m/z->
32


Abundance
Sample
RI: 1695
Qual: 93
Abundance
Literature[SH1]
OH
35
m/z-->


Abundance
Sample
RI: 1743
Qual: 96
Abundance
Literature[SH1]
OH
34
m/z-->

4. NMR Data

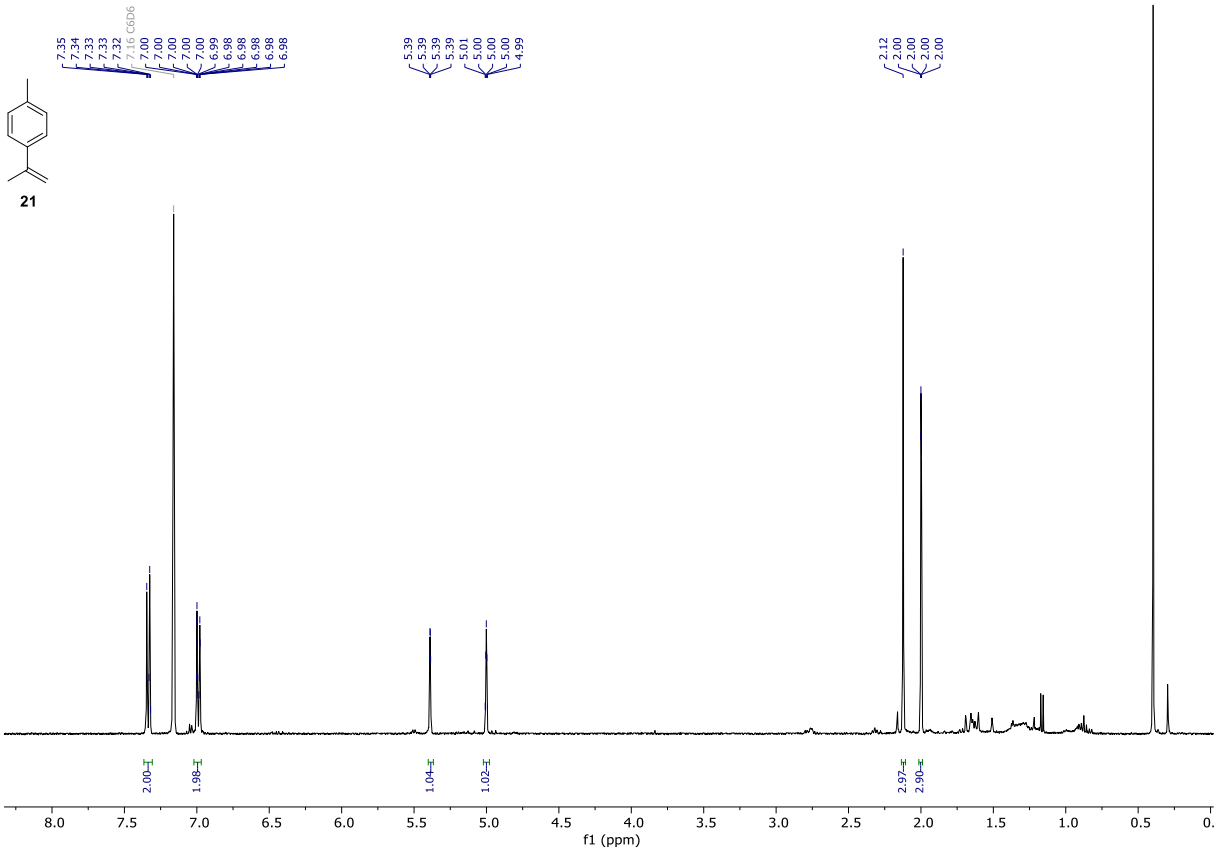
4.1 NMR validation of *p*-cymenene (21)



Neryl bromide (**12**, 200 mg) was hydrolysed according to general procedure 1.2.2. *P*-cymenene (**21**, 3.3 mg, 2.7 %) could be isolated through silica column chromatography (SiO_2, *n*-pentane/Et_2O 100:1) . Because of volatility issues, the NMR sample was prepared according to general procedure 1.2.1. After recording the NMR data, the solvent was removed with a gentle stream of argon until the mass was nearly constant, allowing the yield to be determined.

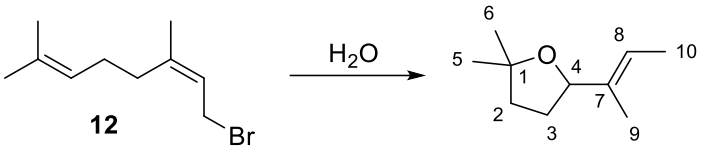
The ^{1}H-NMR data match those reported in literature.[SI2]

R_f = 0.66 (*n*-pentane/Et_2O 100:1), **^{1}H-NMR** (400 MHz, C_6D_6): δ = 7.33 (m, 2H, H-4), 6.99 (m, 2H, H-3), 5.39 (m, 1H, H-7), 5.00 (m, 1H, H-7), 2.12 (m, 3H, H-1), 1.99 (m, 3H, H-8) ppm.



Spectrum 1: ^{1}H-NMR of **21**

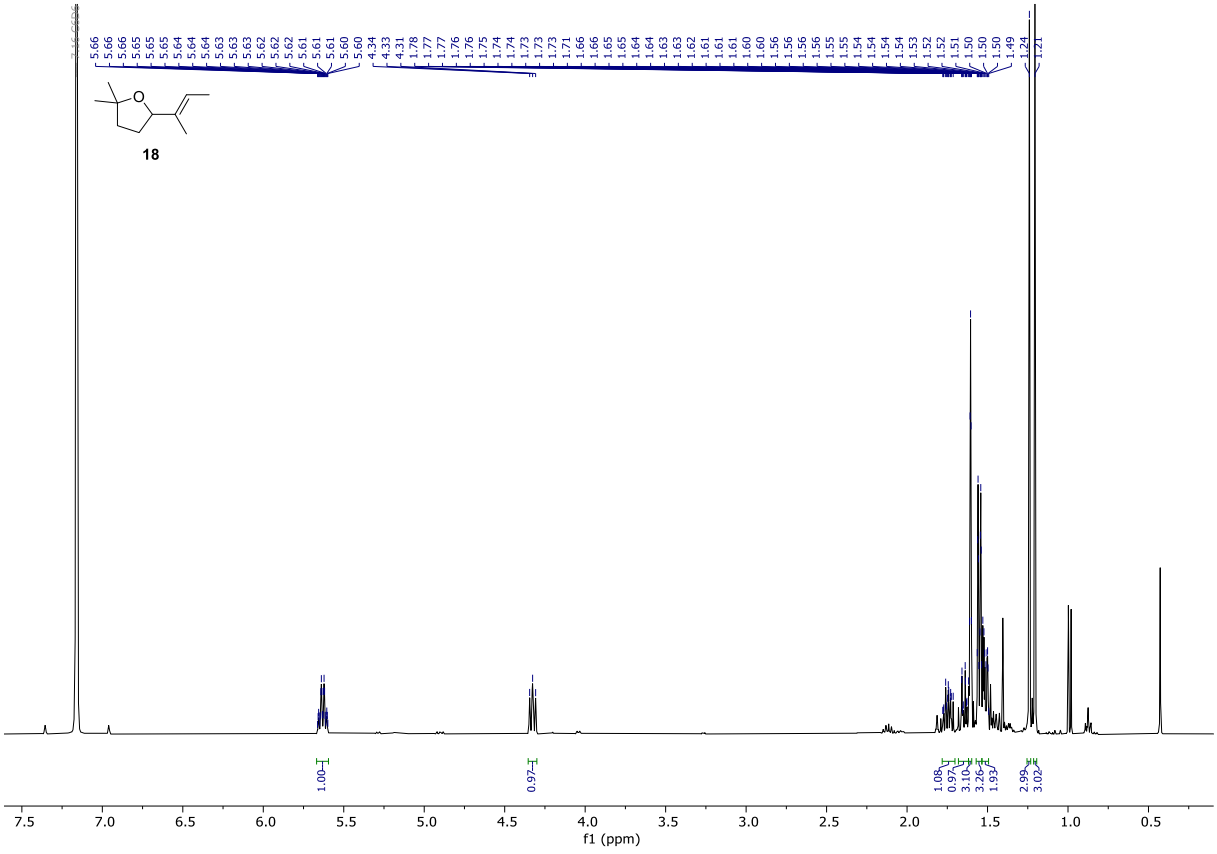
4.2 NMR validation of ocimenoyl oxide (18)



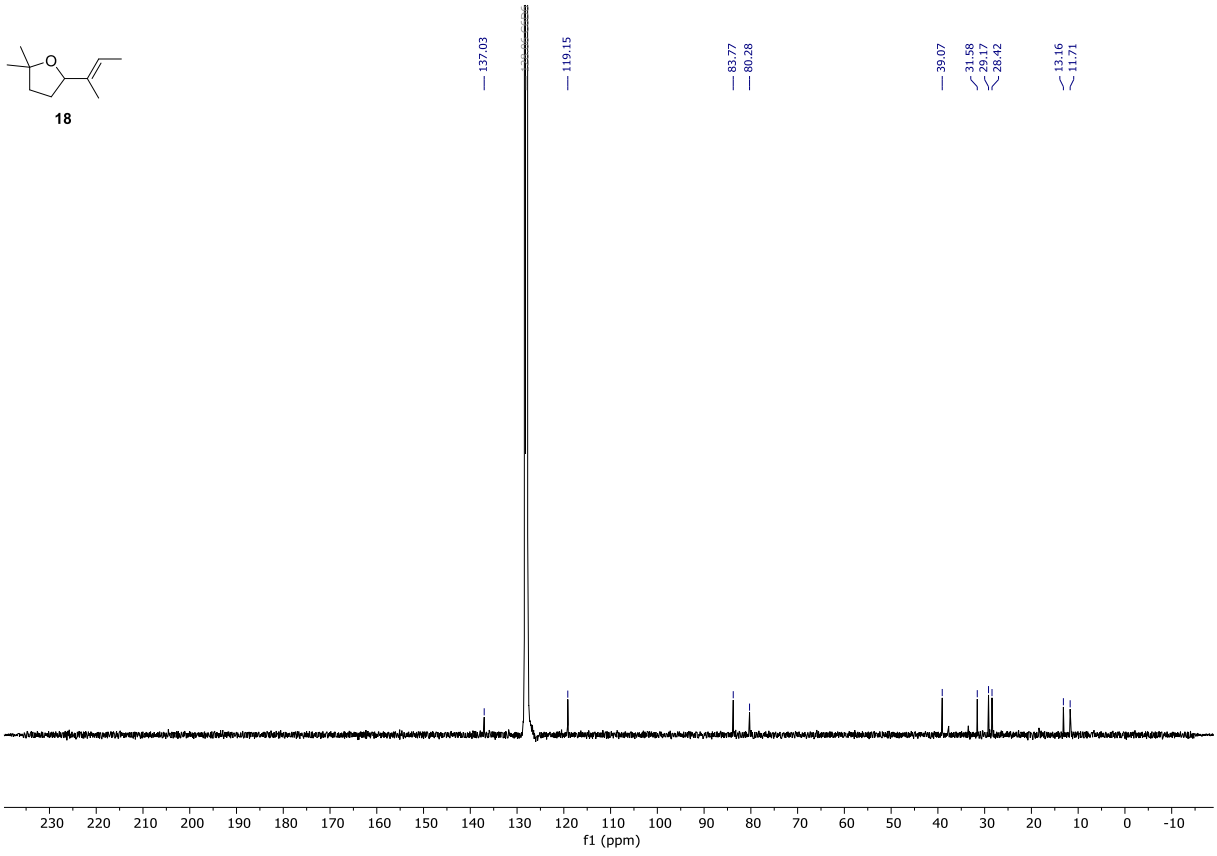
18

Neryl bromide (**12**, 200 mg) was hydrolysed according to general procedure 1.2.2. Ocimenoyl oxide (**18,** 2.6 mg, 1.8 %) could be isolated through silica column chromatography (SiO_2, *n*-pentane/Et_2O 50:1). Because of volatility issues, the NMR sample was prepared according to general procedure 1.2.1. After recording the NMR data, the solvent was removed with a gentle stream of argon until the mass was nearly constant, allowing the yield to be determined.

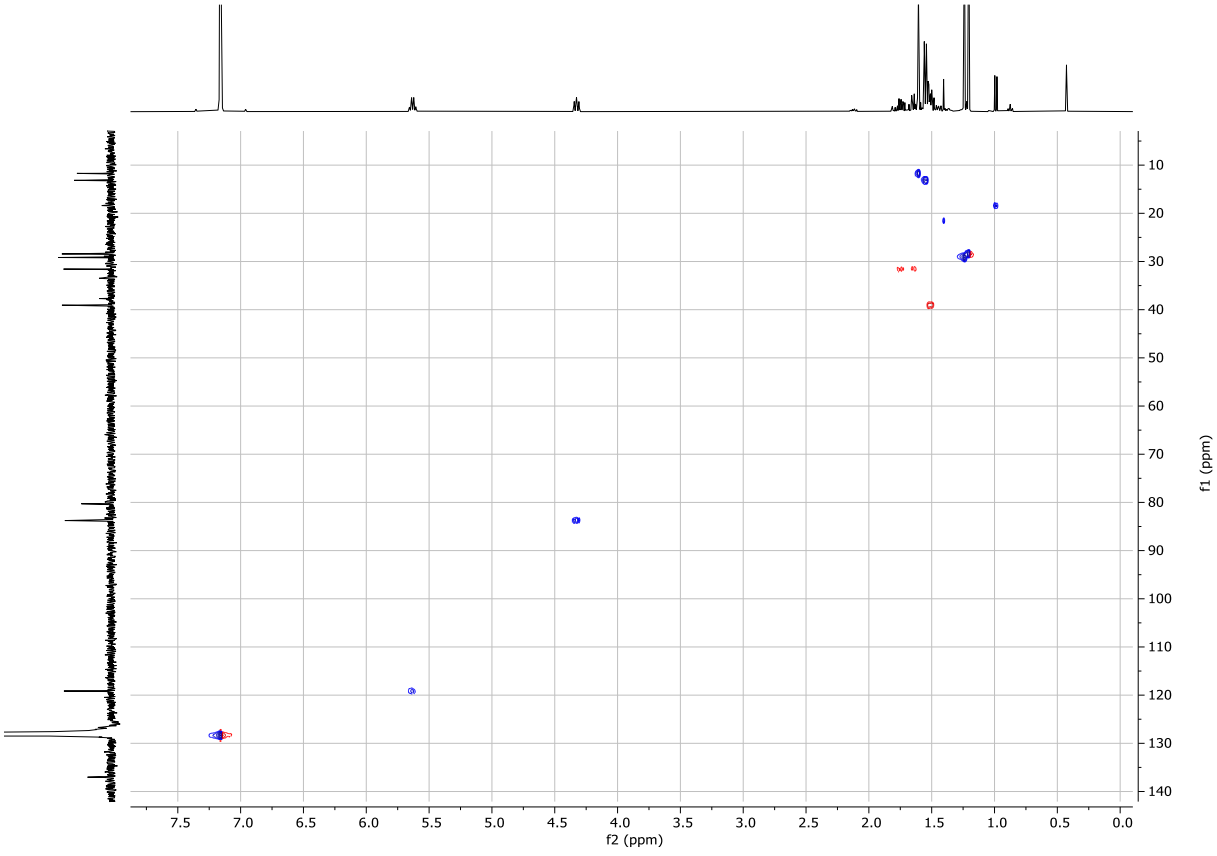
R_f = 0.36 (*n*-pentane/Et_2O 50:1), **^{1}H-NMR** (400 MHz, C_6D_6): δ = 5.63 (m, 1H, H-8), 4.33 (dd, J = 8.9, 5.9 Hz, 1H, H-4), 1.75 (m, 1H, H-3), 1.64 (m, 1H, H-3), 1.61 (p, J = 1.1 Hz, 3H, H-9), 1.55 (dp, J = 6.8, 1.0 Hz, 3H, H-10), 1.51 (m, 2H, H-2), 1.24 (s, 3H, H-5/H-6), 1.21 (s, 3H, H-5/H-6) ppm. **^{13}C-NMR** (101 MHz, C_6D_6): δ = 137.0 (C-7), 119.2 (C-8), 83.8 (C-4), 80.3 (C-1), 39.1 (C-2), 31.6 (C-3), 29.2 (C-5/C-6), 28.4 (C-5/C-6), 13.2 (C-10), 11.7 (C-9) ppm. **HRMS** [CI]: m/z calc for $C_{10}H_{18}O$ [M^+] 154.1358, found: 154.1365.



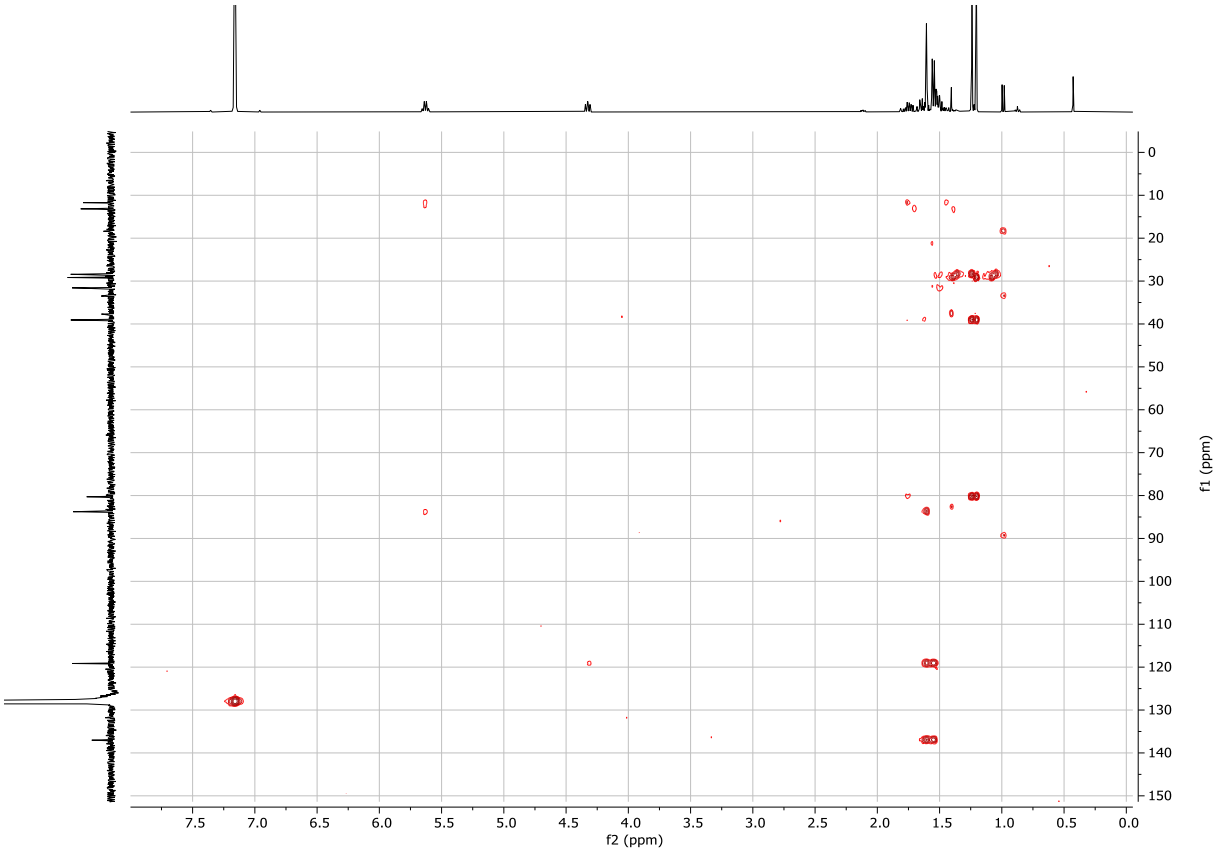
Spectrum 2: ^{1}H-NMR of **18**



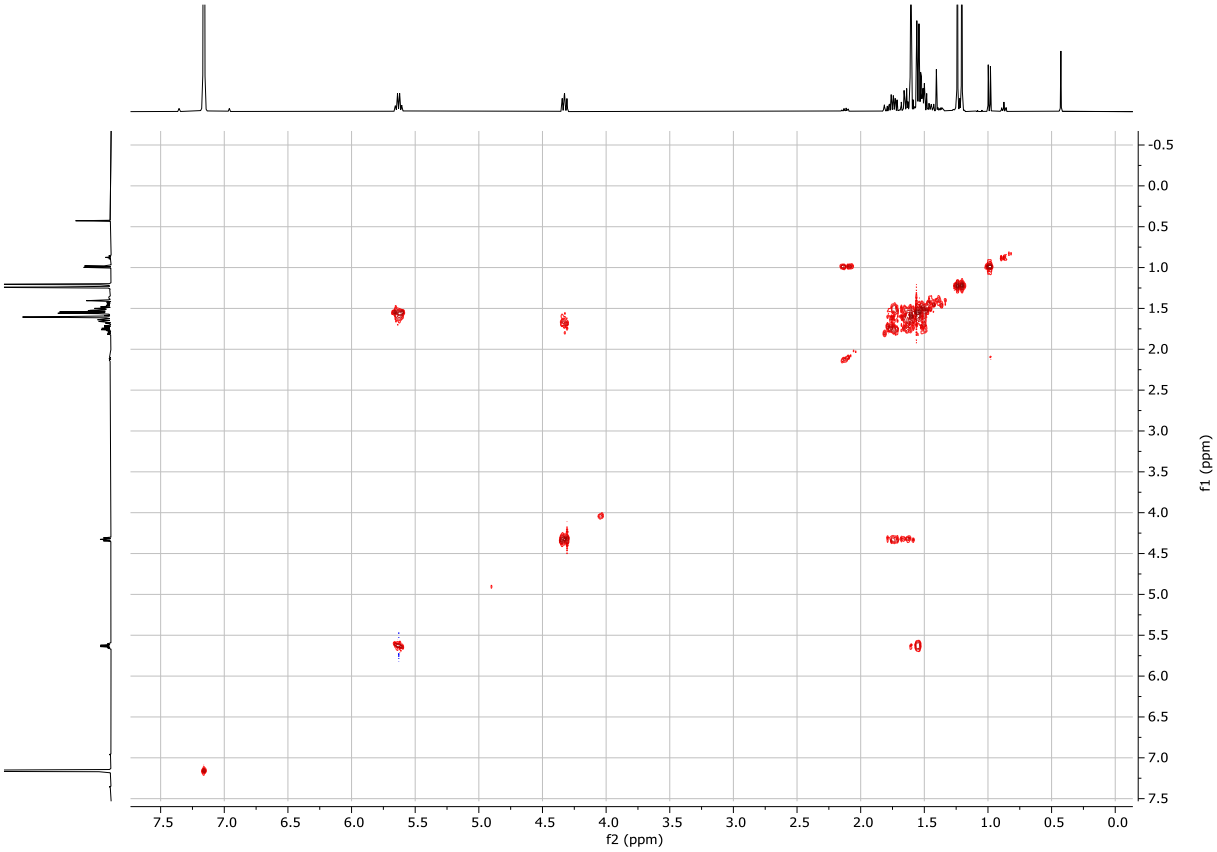
Spectrum 3: ^{13}C-NMR of **18**



Spectrum 4: HSQC of **18**

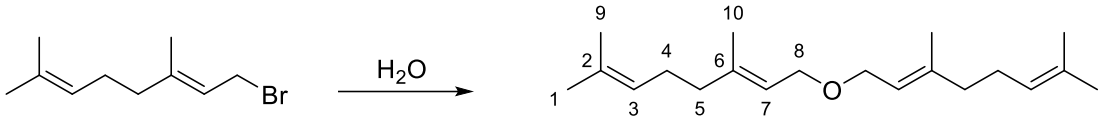


Spectrum 5: HMBC of **18**



Spectrum 6: COSY of **18**

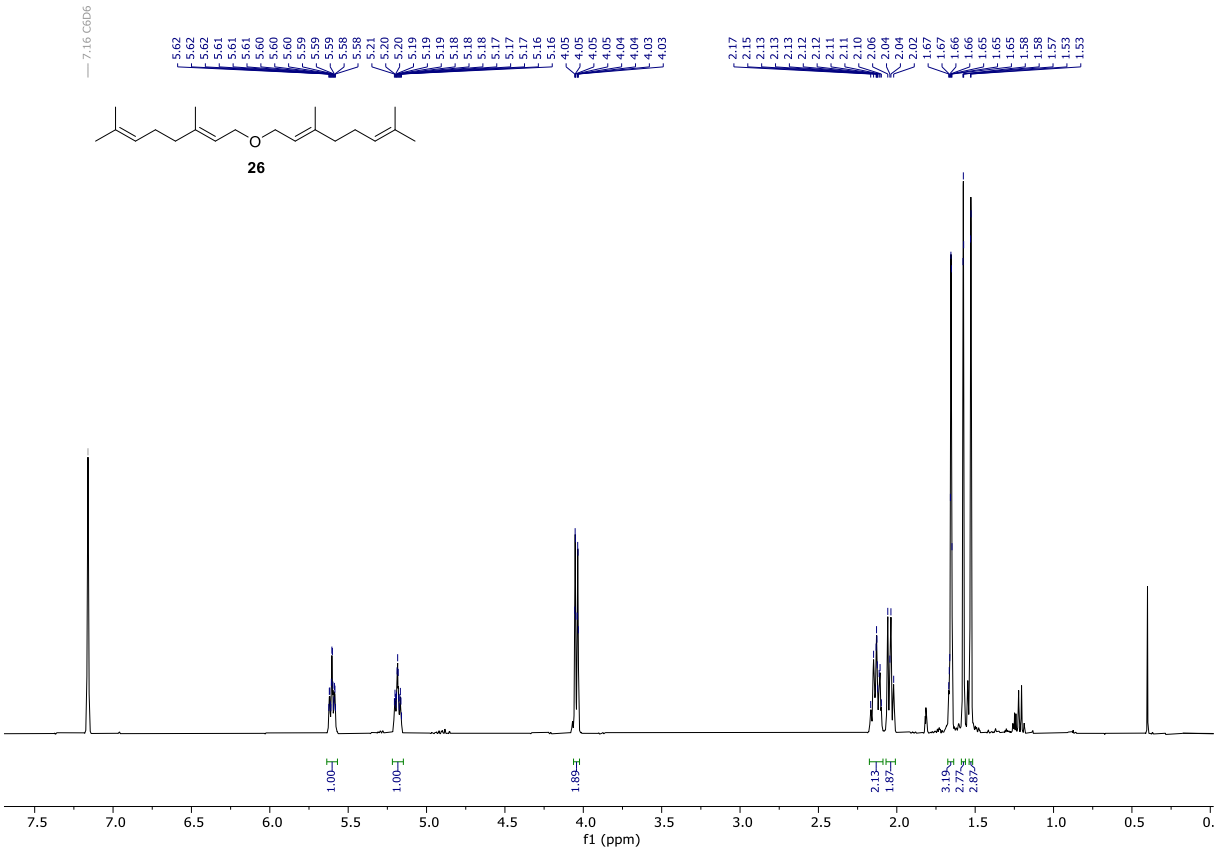
4.3 NMR validation of ether 26



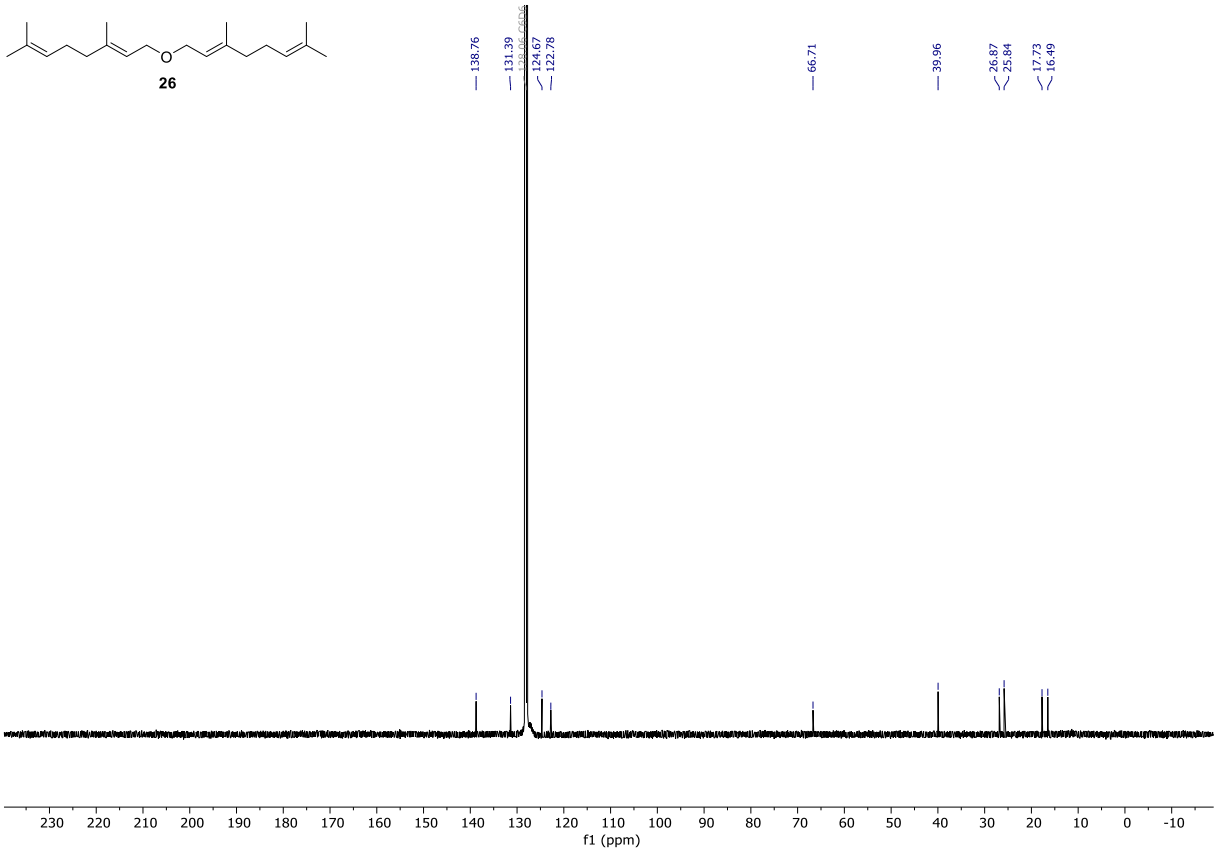
11 **26**

Geranyl bromide (**11**, 200 mg) was hydrolysed according to general procedure 1.2.2. Ether (**26**, 8.1 mg, 3.1 %) could be isolated through silica column chromatography (SiO_2, *n*-pentane/Et_2O 50:1). The NMR sample was prepared according to general procedure 1.2.1. After recording the NMR data, the solvent was removed with a gentle stream of argon until the mass was nearly constant, allowing the yield to be determined.

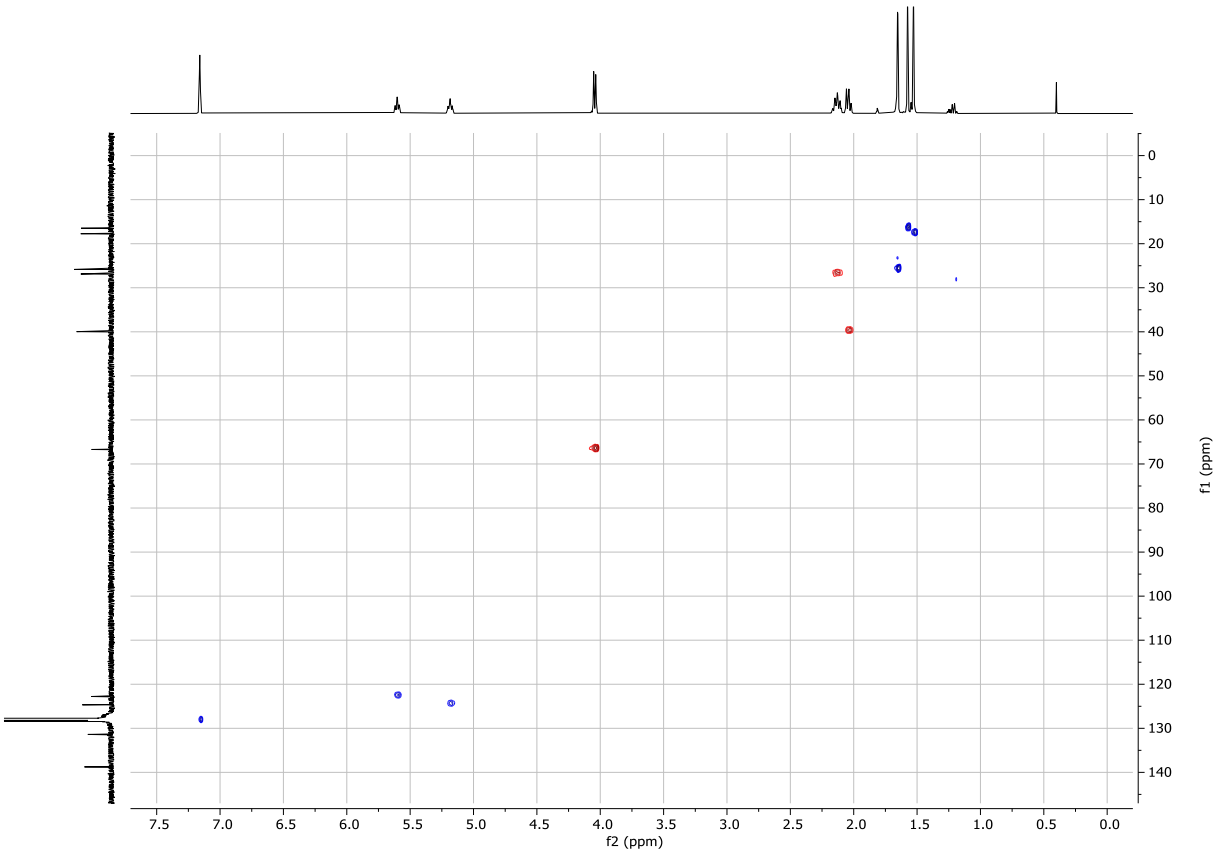
R_f = 0.41 (*n*-pentane/Et_2O 50:1), **^{1}H-NMR** (400 MHz, C_6D_6): δ = 5.60 (m, 1H, H-7), 5.18 (m, 1H, H-3), 4.04 (dq, J = 6.6, 0.9 Hz, 2H, H-8), 2.13 (m, 2H, H-4), 2.04 (m, 2H, H-5), 1.65 (s, 3H, H-1), 1.58 (m, 3H, H-10), 1.53 (s, 3H, H-9) ppm. **^{13}C-NMR** (101 MHz, C_6D_6): δ = 138.8 (C-6), 131.4 (C-2), 124.7 (C-3), 122.8 (C-7), 66.7 (C-8), 40.0 (C-5), 26.9 (C-4), 25.8 (C-1), 17.7 (C-9), 16.5 (C-10) ppm. **HRMS** [CI]: m/z calc for $C_{20}H_{34}O$ [M^+] 290.2610, found: 290.2611.



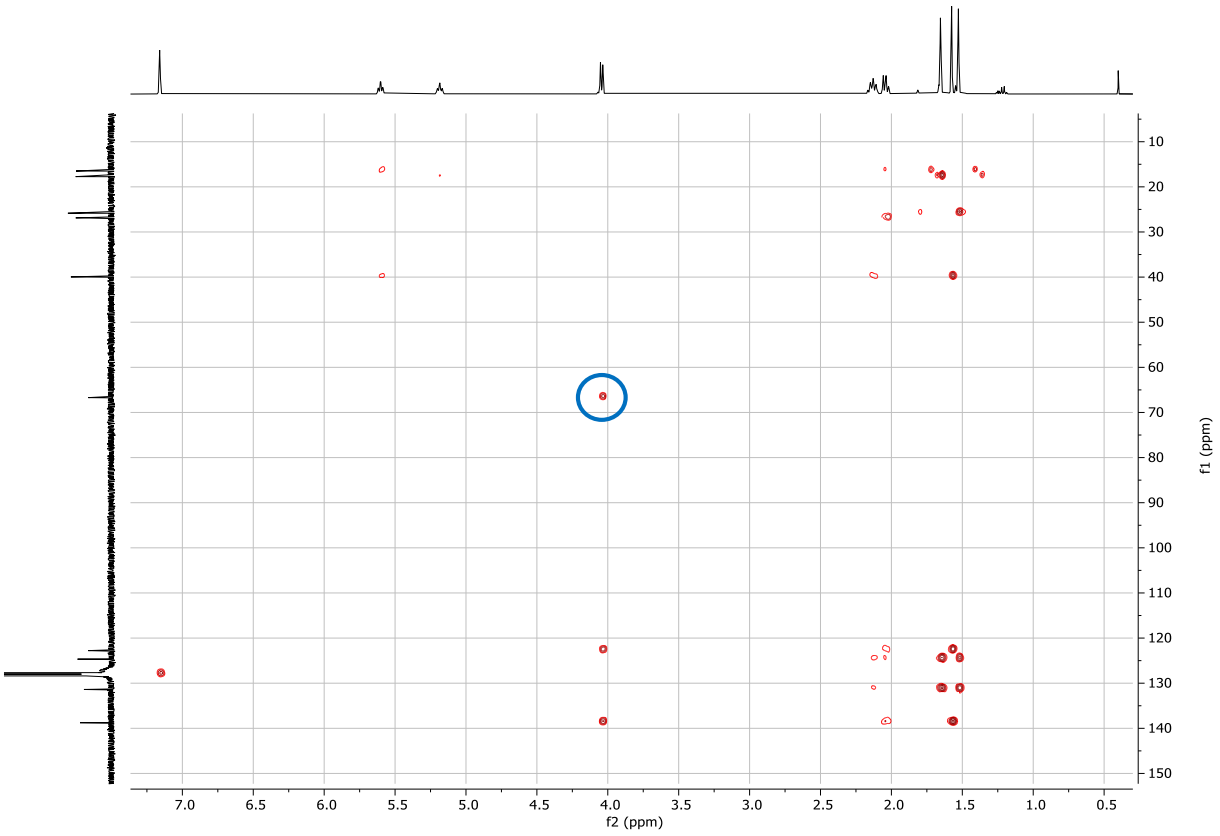
Spectrum 7: ^{1}H-NMR of **26**



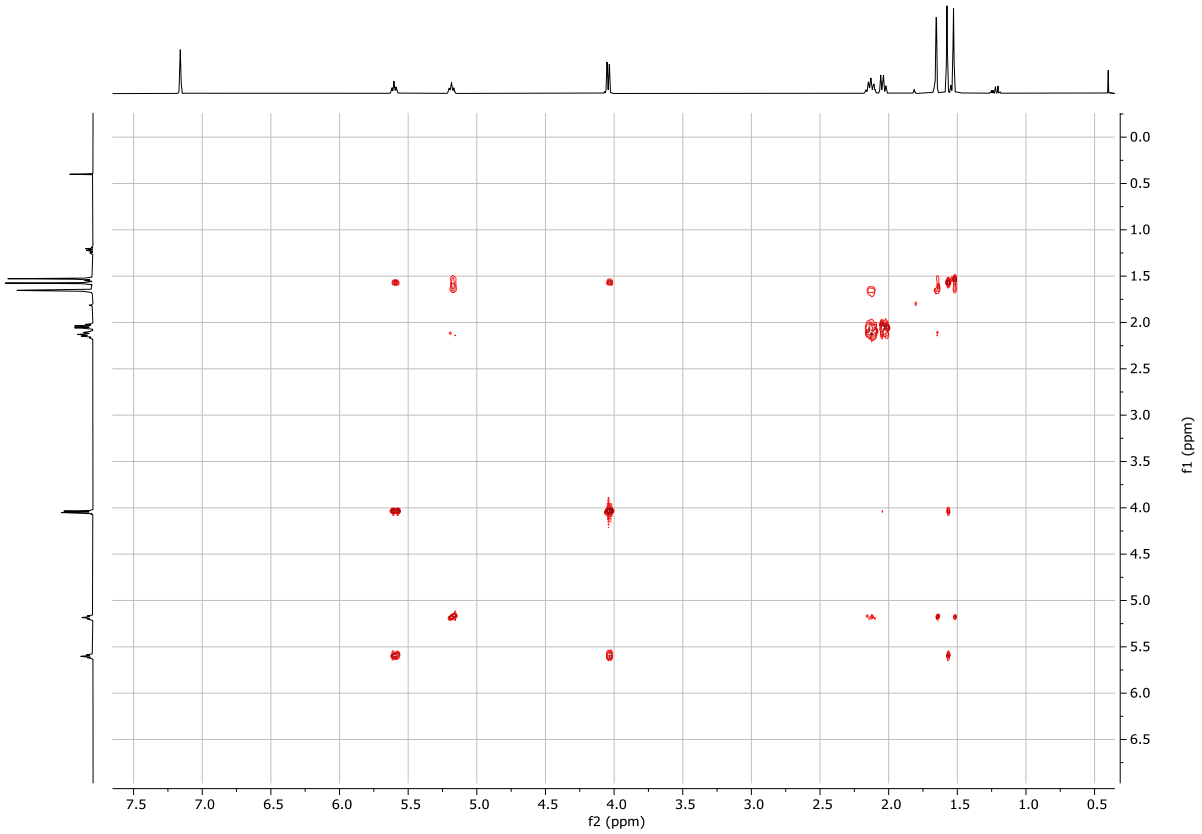
Spectrum 8: ^{13}C-NMR of **26**



Spectrum 9: HSQC of **26**

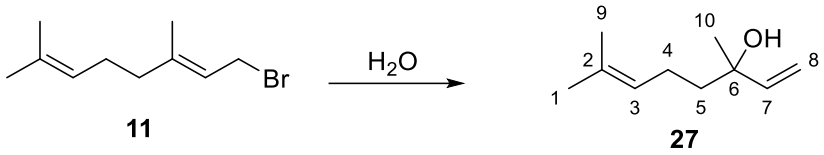


Spectrum 10: HMBC of **26** (crosspeak highlighted showcases the dimer-symmetry)



Spectrum 11: COSY of **26**

4.4 NMR validation of linalool (27)

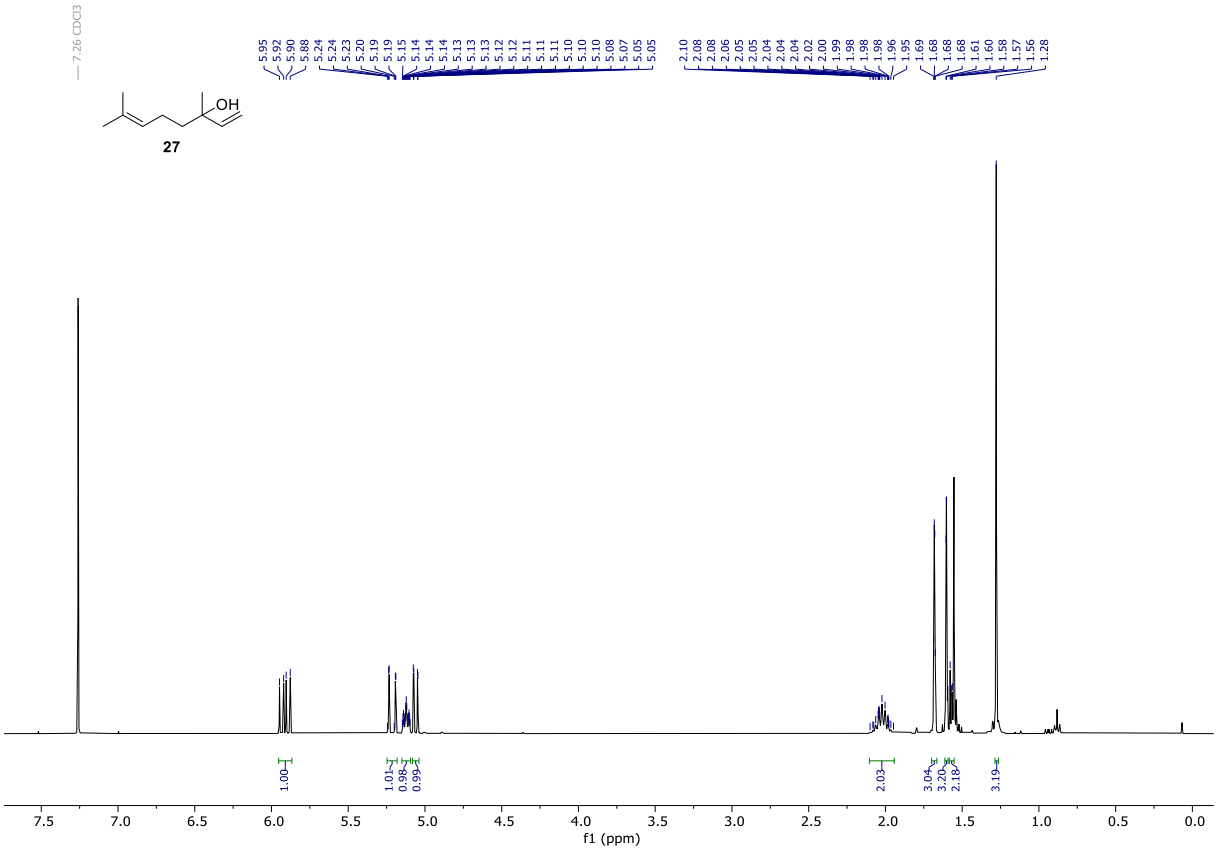


11 **27**

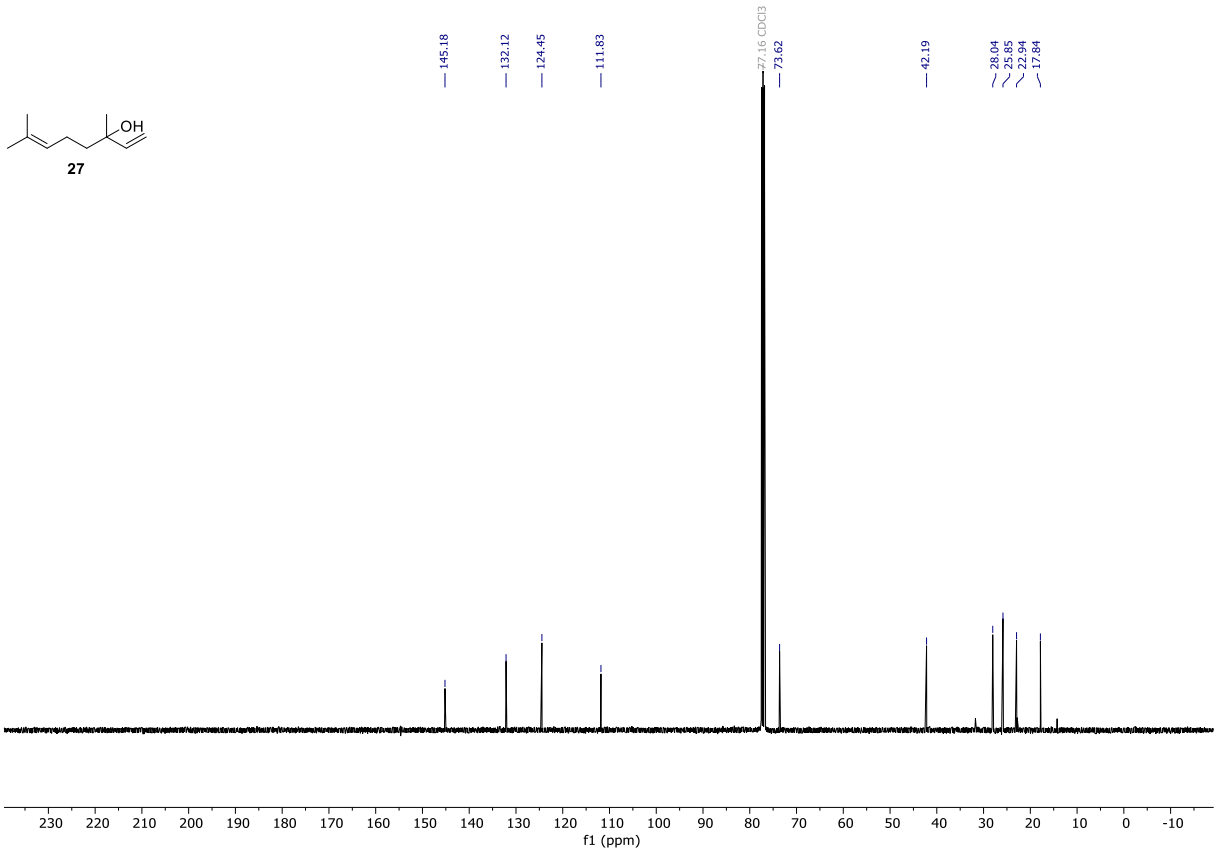
Geranyl bromide (**11**, 100 mg) was hydrolysed using ultrasound sonication according to general procedure 1.2.3. Linalool (**27**, 41.8 mg, 59%) could be isolated through silica column chromatography (SiO_2, *n*-pentane/Et_2O 10:1).

The analytical data match those reported in literature.[SI3]

R_f = 0.25 (*n*-pentane/Et_2O 10:1), **^{1}H-NMR** (400 MHz, C_6D_6): δ = 5.91 (dd, J = 17.3, 10.7 Hz, 1H, H-7), 5.21 (dd, J = 17.3, 1.3 Hz, 1H, H-8), 5.12 (m, 1H, H-3), 5.06 (dd, J = 10.7, 1.3 Hz, 1H, H-8), 2.02 (m, 2H, H-4), 1.68 (q, J = 1.3 Hz, 3H, H-1), 1.60 (s, 3H, H-9), 1.57 (m, 2H, H-5), 1.28 (s, 3H, H-10) ppm. **^{13}C-NMR** (101 MHz, C_6D_6): δ = 145.2 (C-7), 132.1 (C-2), 124.5 (C-3), 111.8 (C-8), 73.6 (C-6), 42.2 (C-5), 28.0 (C-10), 25.8 (C-1), 22.9 (C-4), 17.8 (C-9) ppm.

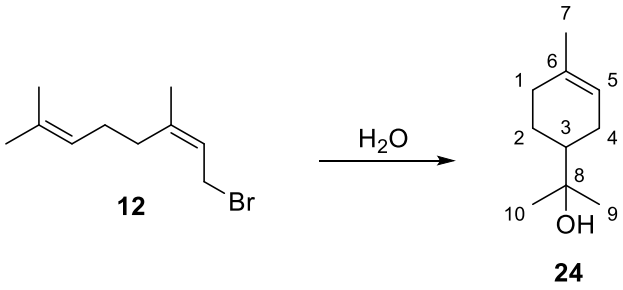


Spectrum 12: ^{1}H-NMR of **27**



Spectrum 13: ^{13}C-NMR of **27**

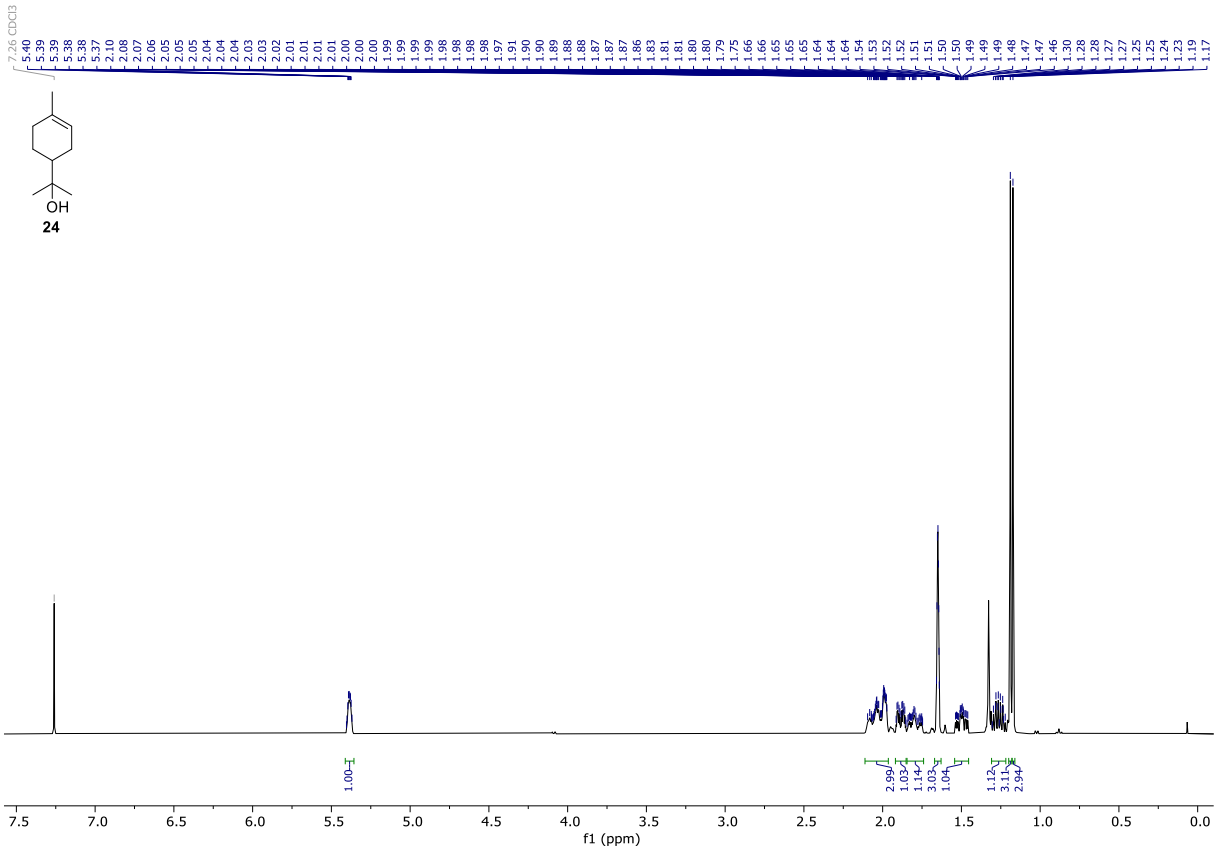
4.5 NMR validation of α-terpineol (24)



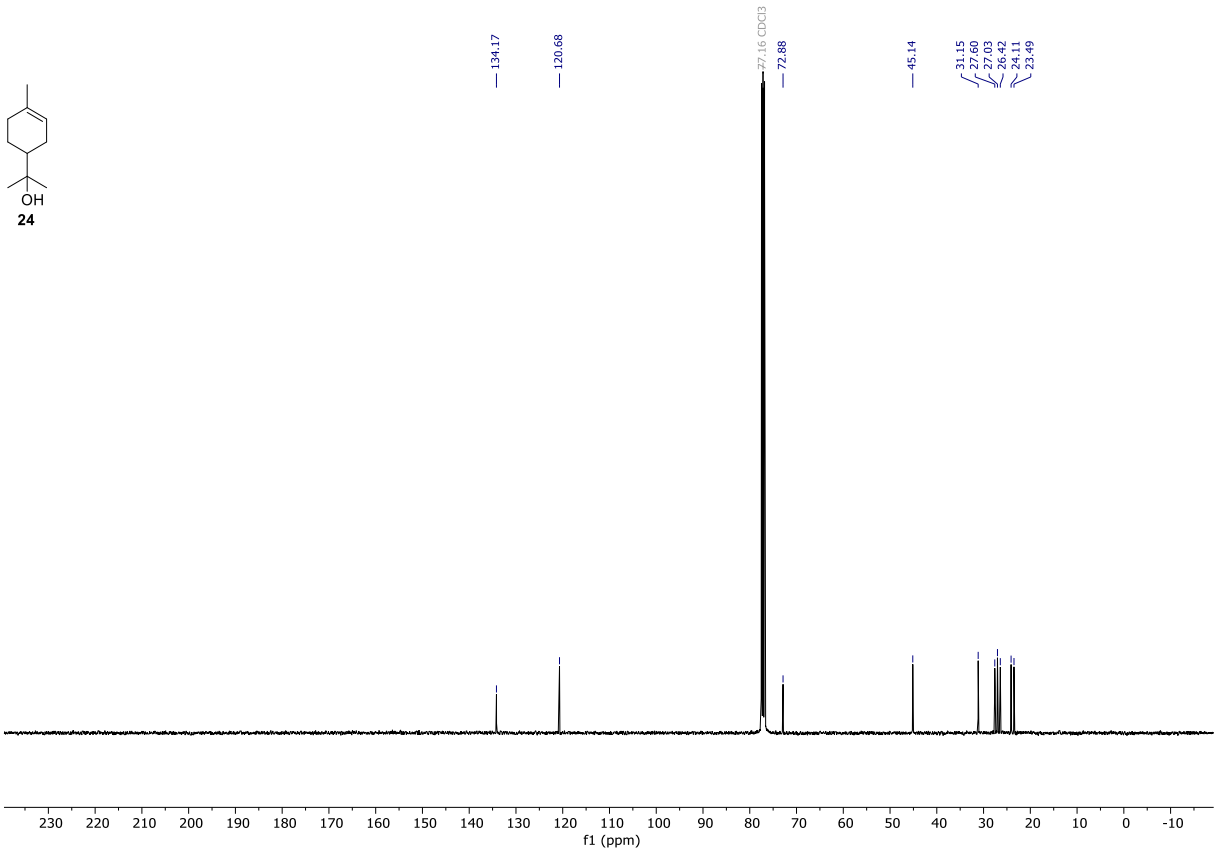
Neryl bromide (**12**, 100 mg) was hydrolysed using ultrasound sonication according to general procedure 1.2.3. α-Terpineol (**24**, 46.0 mg, 65%) could be isolated through silica column chromatography (SiO_2, *n*-pentane/Et_2O 10:1).

The analytical data match those reported in literature.[SI3]

R_f = 0.32 (*n*-pentane/Et_2O 10:1), **^{1}H-NMR** (400 MHz, $CDCl_3$): δ = 5.39 (m, 1H, H-5), 2.02 (m, 3H, H-1, H-4), 1.88 (m, 1H, H-2), 1.79 (m, 1H, H-4), 1.65 (s, 3H, H-7), 1.50 (m, 1H, H-3), 1.26 (m, 1H, H-2), 1.19 (s, 3H, H-9 / H-10), 1.17 (s, 3H, H-9 / H-10) ppm. **^{13}C-NMR** (101 MHz, $CDCl_3$): δ = 134.2 (C-6), 120.7 (C-5), 72.9 (C-8), 45.1 (C-3), 31.1 (C-1), 27.6 (C-9 / C-10), 27.0 (C-4), 26.4 (C-9 / C-10), 24.1 (C-2), 23.5 (C-7) ppm.



Spectrum 14: ^{1}H-NMR of **24**



Spectrum 15: ^{13}C-NMR of **24**

5. References

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SI2. C. Faverio, M. F. Boselli, T. Ruggiero, L. Raimondi, M. Benaglia, Hydrogen bond-mediated organocatalytic enantioselective reduction of nitroalkenes in deep eutectic solvents, *Tetrahedron Chem.* **2023**, *6*, 100038.

SI3. H. Yang, S. Liu, H. Dong, H. Huang, Y. Wang, W. Hao, Y. Lan, Q. Liu, Amplifying the Reactivity of Anionic Mn (I)-H Catalysts via the Cation Effect: Mechanistic Investigation and Application to the Hydrogenation of α-Trisubstituted Carboxylic Esters, *J. Am. Chem. Soc.* **2025**, *147*, 13491-13501.