

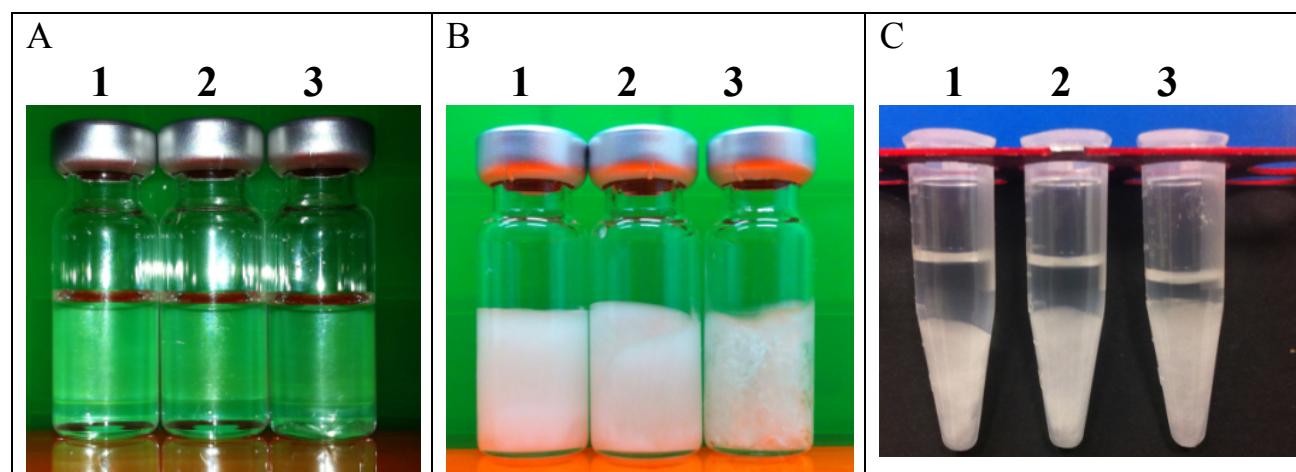
## SUPPLEMENTARY ELECTRONIC INFORMATION.

### Clean enzymatic process for producing flavour esters by direct esterification in switchable ionic liquid/solid phases.

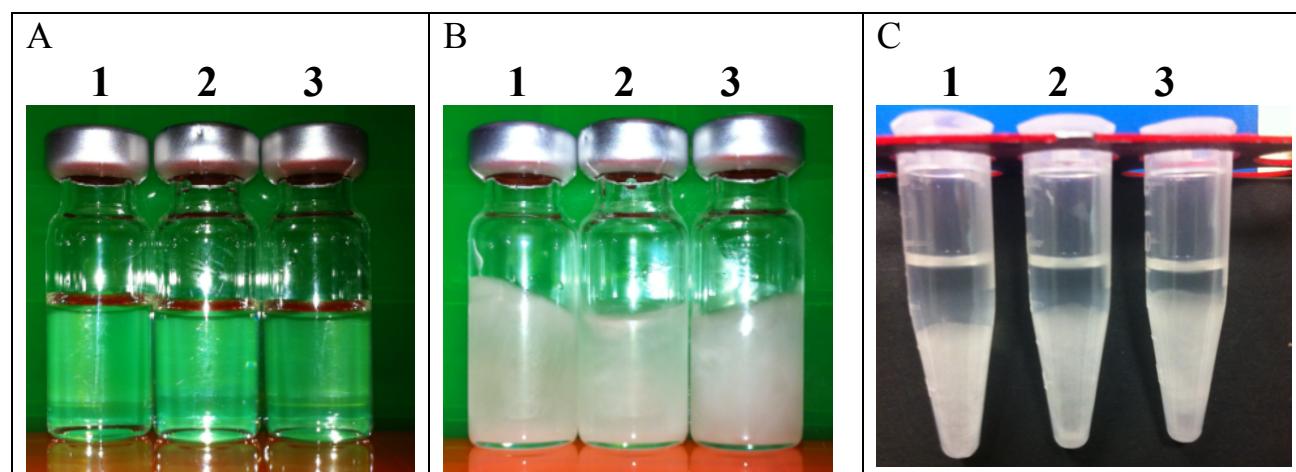
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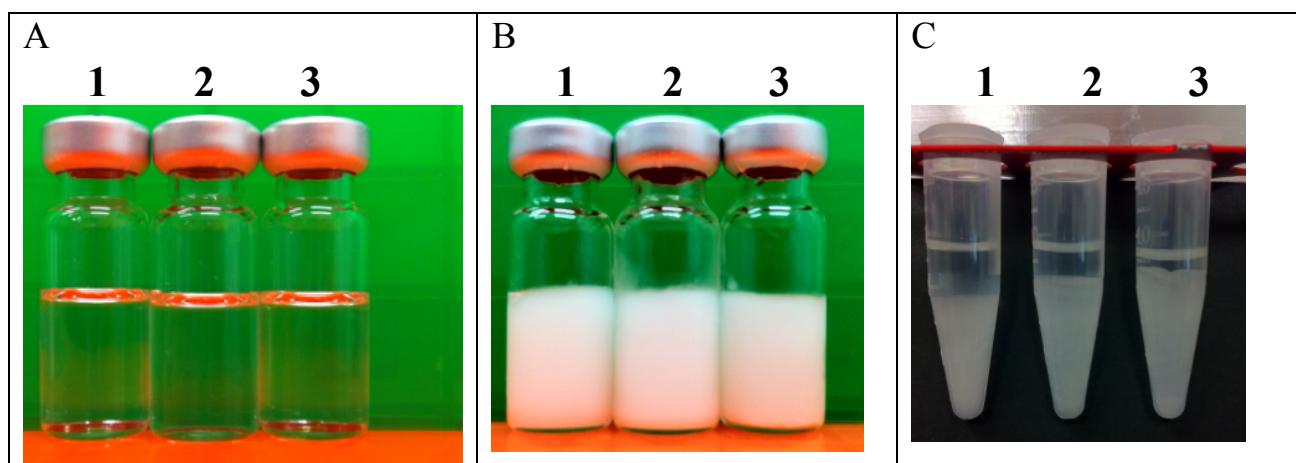
**Table 1** Phase behaviour of 50/50 (1), 60/40 (2) and 70/30 (3) (w/w) [ $\text{C}_{16}\text{tma}$ ][ $\text{NTf}_2$ ]/citronellyl acetate mixtures at 50°C (A), 25°C (B), and after four consecutive centrifugation steps at 14,000 rpm (15 min) and at room temperature, 21, 10 and 4 °C (C), respectively.



**Table 2** Phase behaviour of 50/50 (1), 60/40 (2) and 70/30 (3) (w/w) [ $\text{C}_{16}\text{tma}$ ][ $\text{NTf}_2$ ]/neryl acetate mixtures at 50°C (A), 25°C (B), and after four consecutive centrifugation steps at 14,000 rpm (15 min) and at room temperature, 21, 10 and 4 °C (C), respectively.



**Table 3** Phase behaviour of 50/50 (1), 60/40 (2) and 70/30 (3) (w/w)  $[C_{16}tma][NTf_2]$ /isoamyl acetate mixtures at 50°C (A), 25°C (B), and after four consecutive centrifugation steps at 14,000 rpm (15 min) and at room temperature, 21, 10 and 4 °C (C), respectively.



## NMR analyses

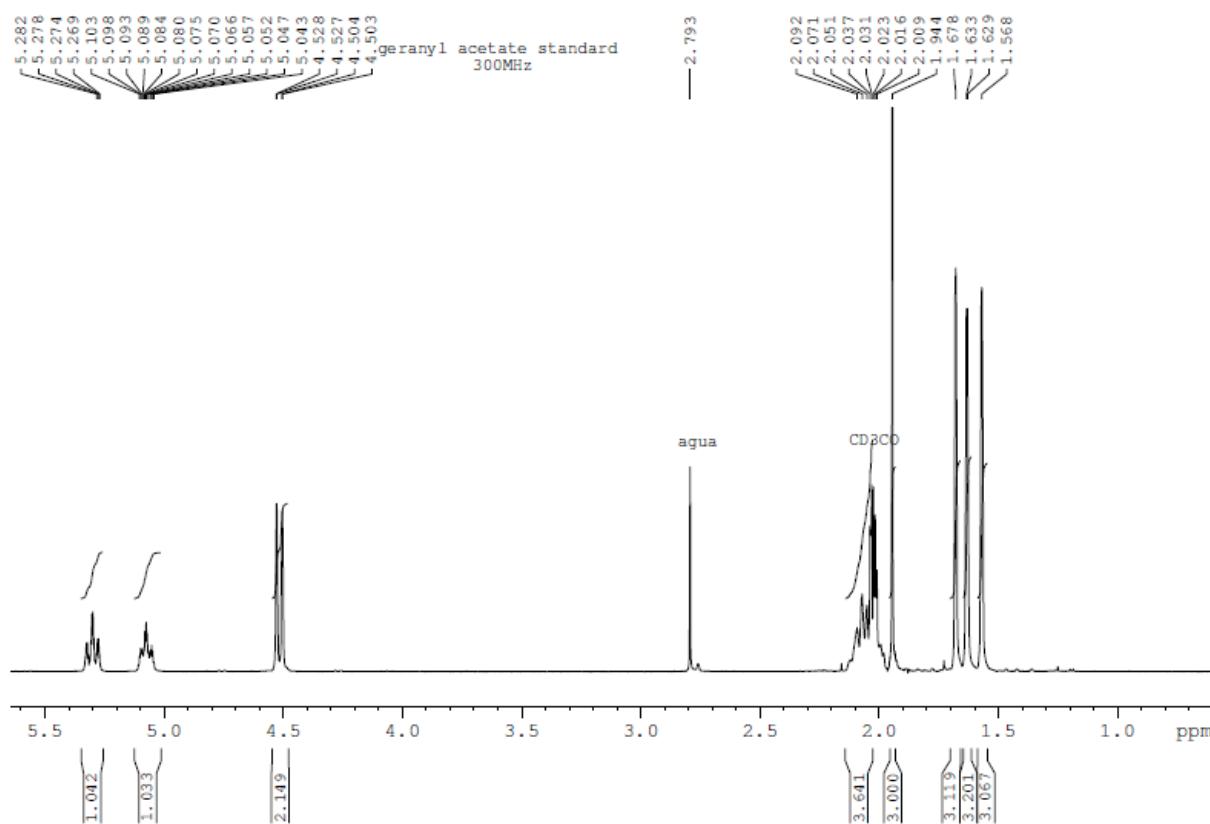
**Samples preparation** In four 1, 0.5 g of, geranyl acetate mixed with 0.5 g of  $[C_{16}tma][NTf_2]$  in four different 1.5-mL eppendorff vials. All IL/flavour ester mixtures were incubated under shaking (300 rpm) for 10 min at 50 °C, which produced fully clear monophasic systems. Then, each vials was treated as follows:

- Sample 1: Centrifugation at 14,000 rpm (15 min) and at room temperature
- Sample 2: A first centrifugation step at 14,000 rpm for 15 min at room temperature, followed to second centrifugation step at 14,000 rpm for 15 min at 21°C.
- Sample 3: A first centrifugation step at 14,000 rpm for 15 min at room temperature, followed to second centrifugation step at 14,000 rpm for 15 min at 21°C, followed to third centrifugation step at 14,000 rpm for 15 min at 10°C,
- Sample 4: A first centrifugation step at 14,000 rpm for 15 min at room temperature, followed to second centrifugation step at 14,000 rpm for 15 min at 21°C, followed to third centrifugation step at 14,000 rpm for 15 min at 10°C, followed to fourth centrifugation step at 14,000 rpm for 15 min at 4°C

For each sample, an aliquot (10  $\mu$ L) was taken from the resulting top flavour ester phase, being dissolved in 1 mL acetone- $d_6$ , then analyzed by 300 MHz  $^1H$  NMR and 282 MHz  $^{19}F$  NMR, respectively in a Brucker AC 300E spectrometer.

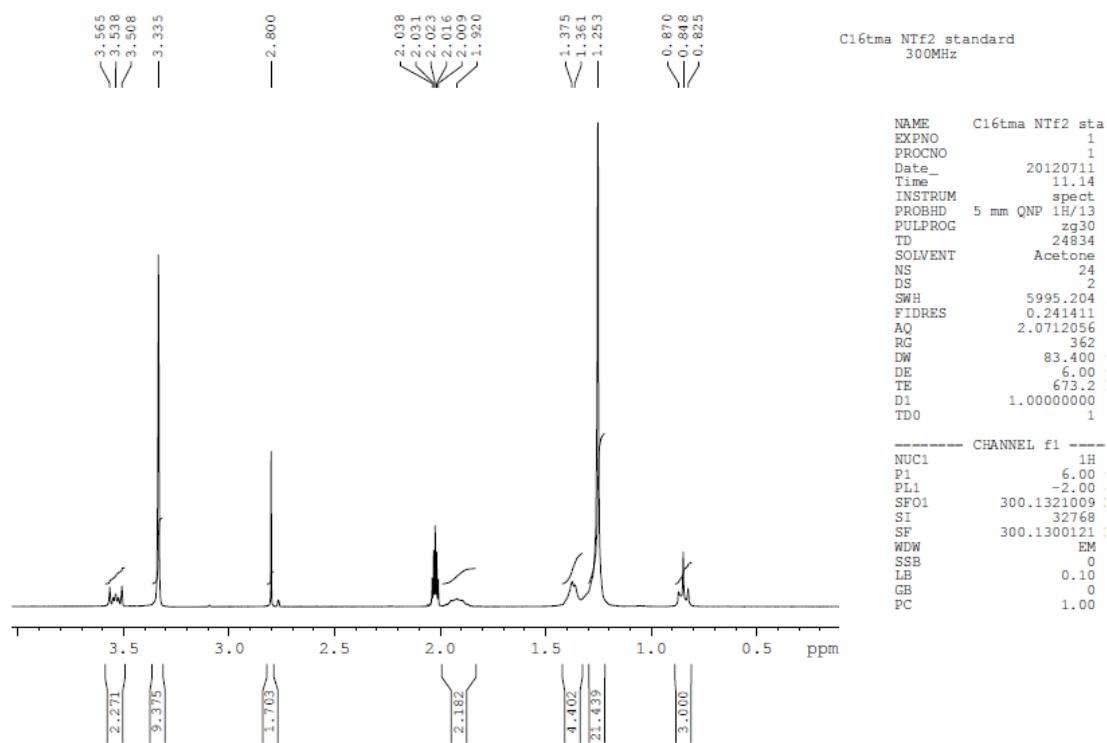
### 1. Standard Geranyl acetate

$^1H$ -NMR spectrum

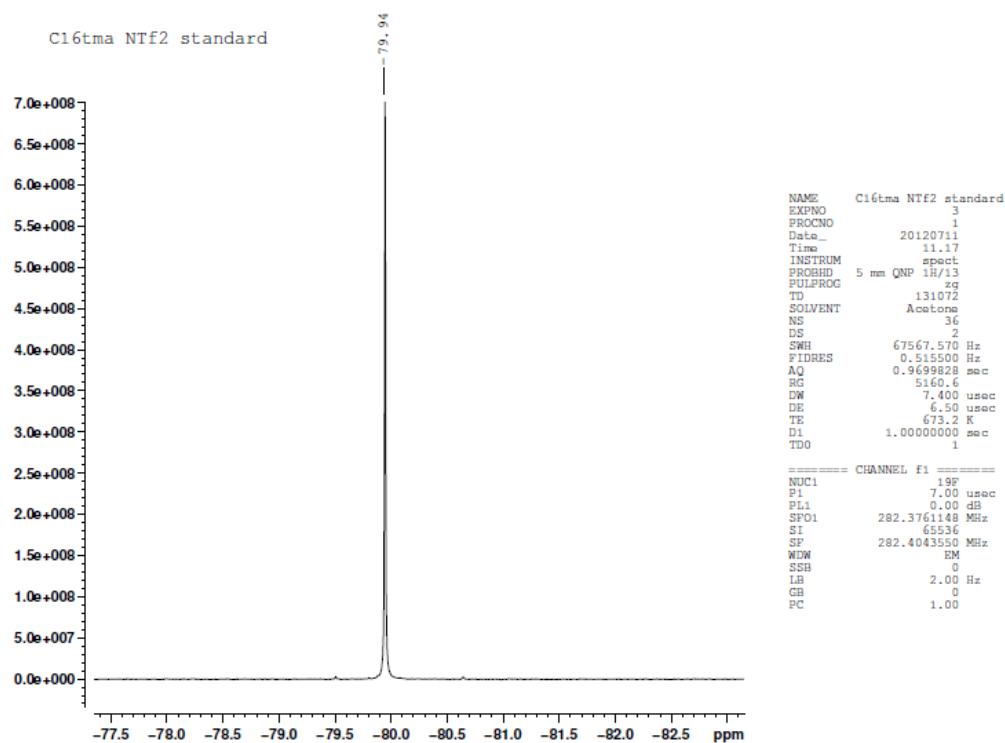


## 2. Standard [ $C_{16}tma]/[NTf_2]$

$^1\text{H}$ -NMR spectrum

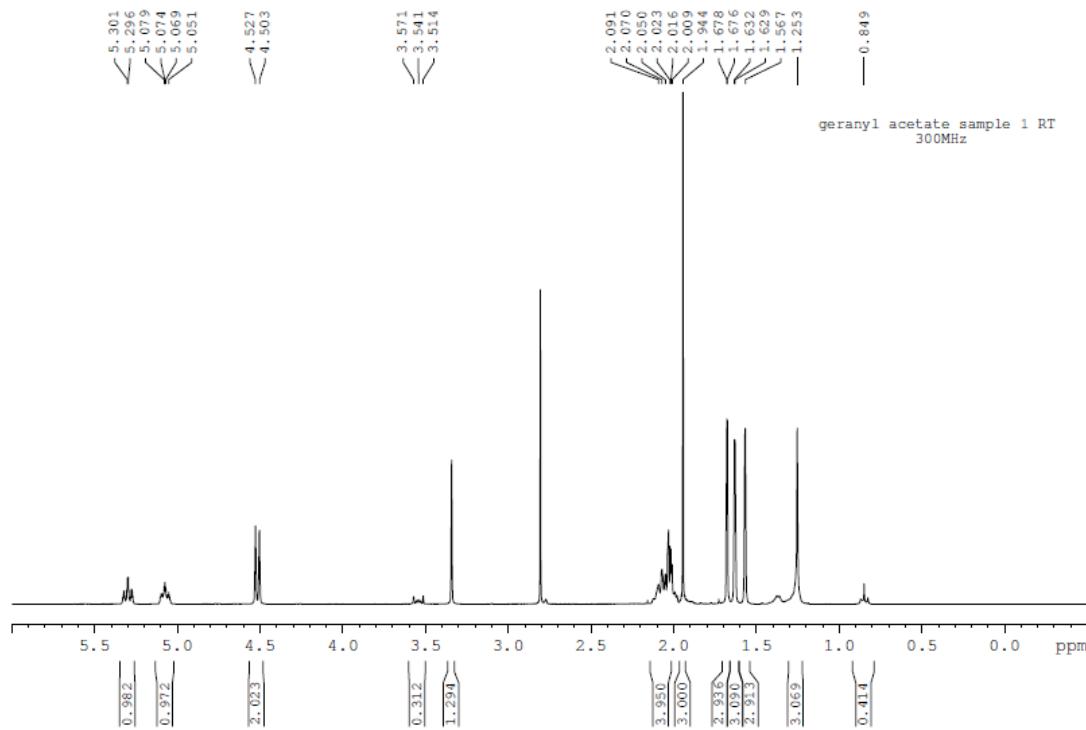


$^{19}\text{F}$ -NMR spectrum

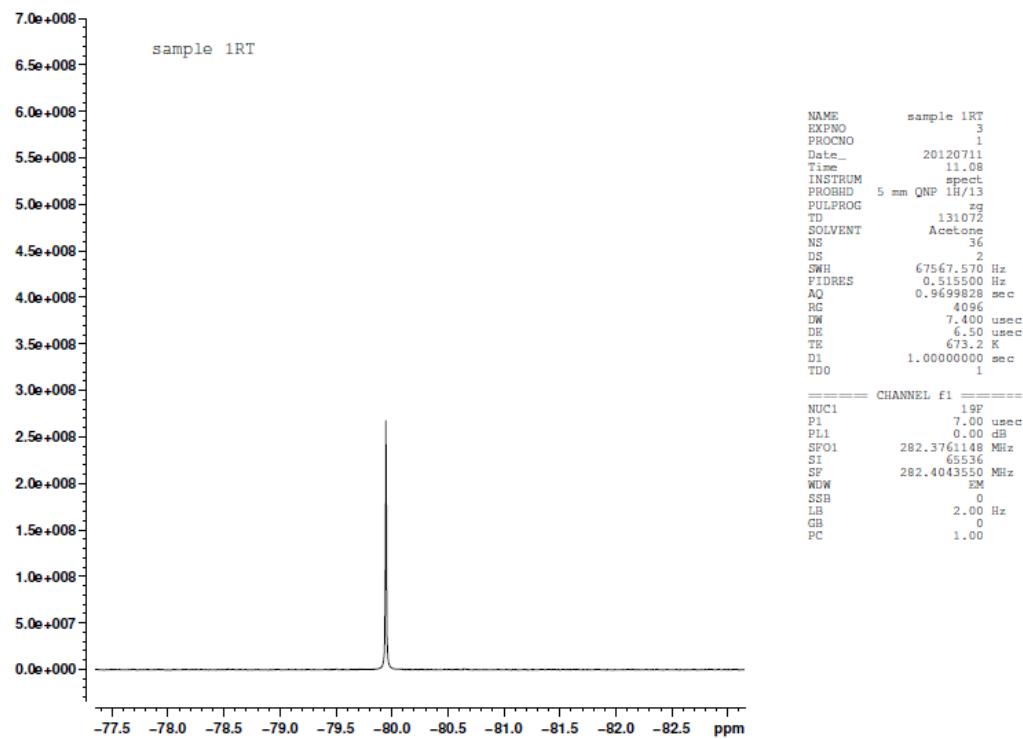


**Sample 1.** Top phase of 50/50 (w/w) [ $C_{16}tma$ ]/[NTf<sub>2</sub>]/geranyl acetate mixture after centrifugation at 14,000 rpm for 15 min at room temperature

### <sup>1</sup>H-NMR spectrum

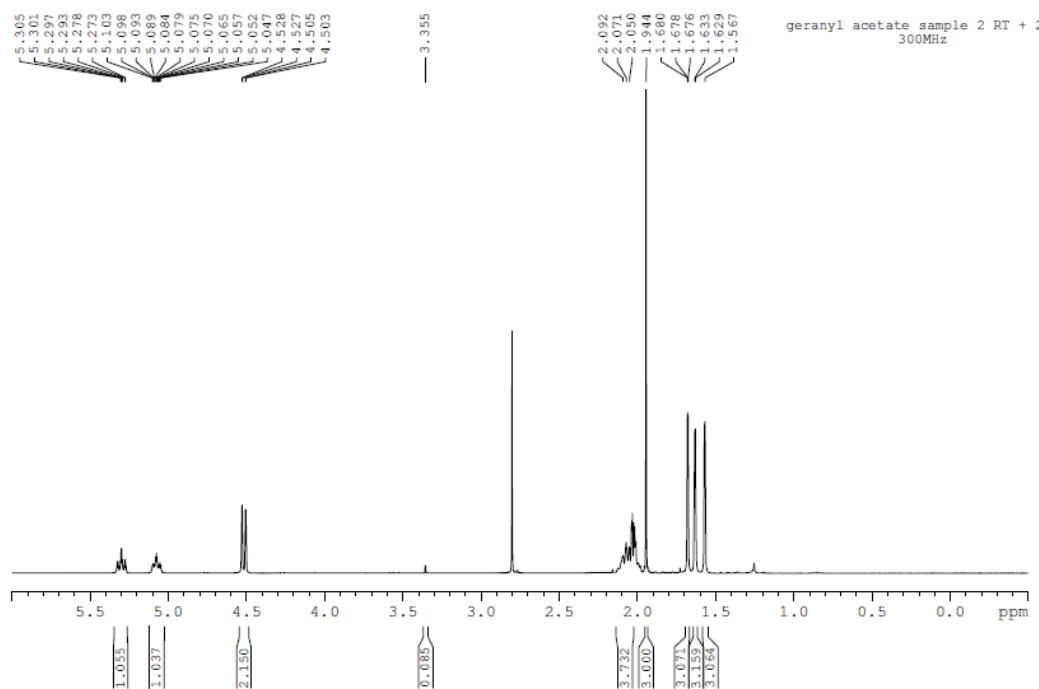


### <sup>19</sup>F-NMR spectrum

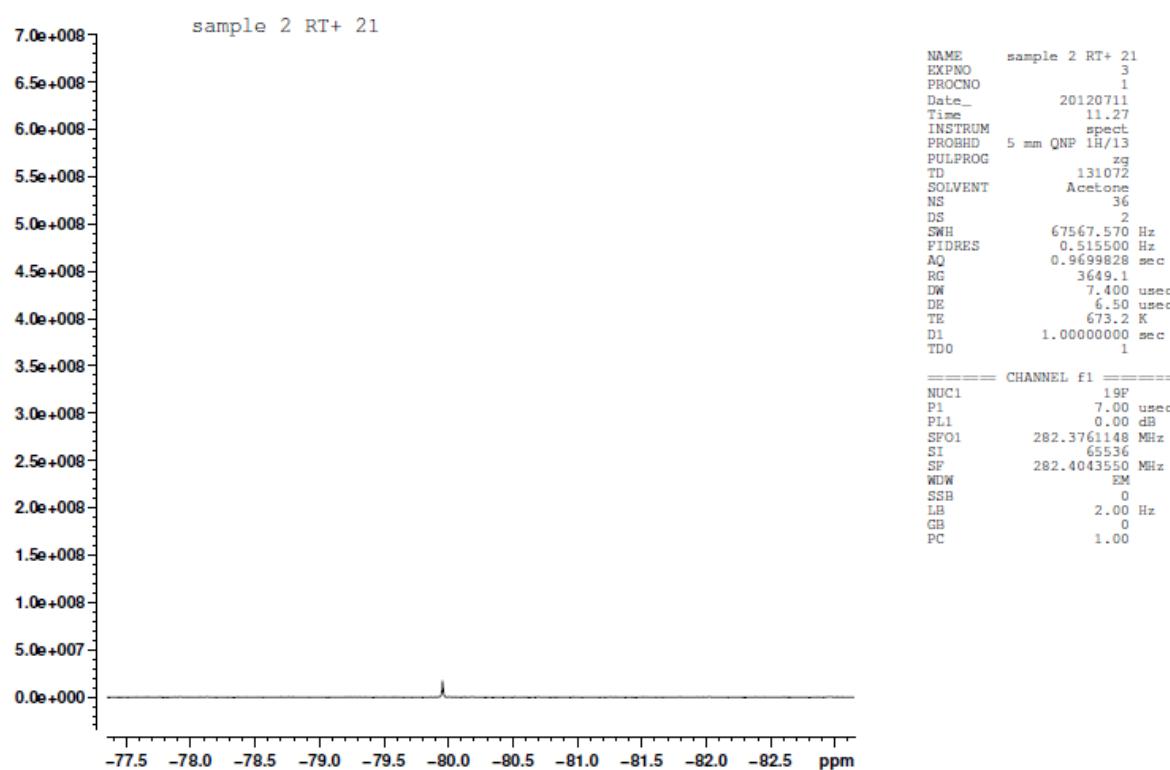


**Sample 2.** Top phase of 50/50 (w/w) [ $C_{16}tma$ ]/[ $NTf_2$ ]/geranyl acetate mixture after a first centrifugation step at 14,000 rpm for 15 min at room temperature, followed to second centrifugation step at 14,000 rpm for 15 min at 21°C

$^1\text{H}$ -NMR spectrum

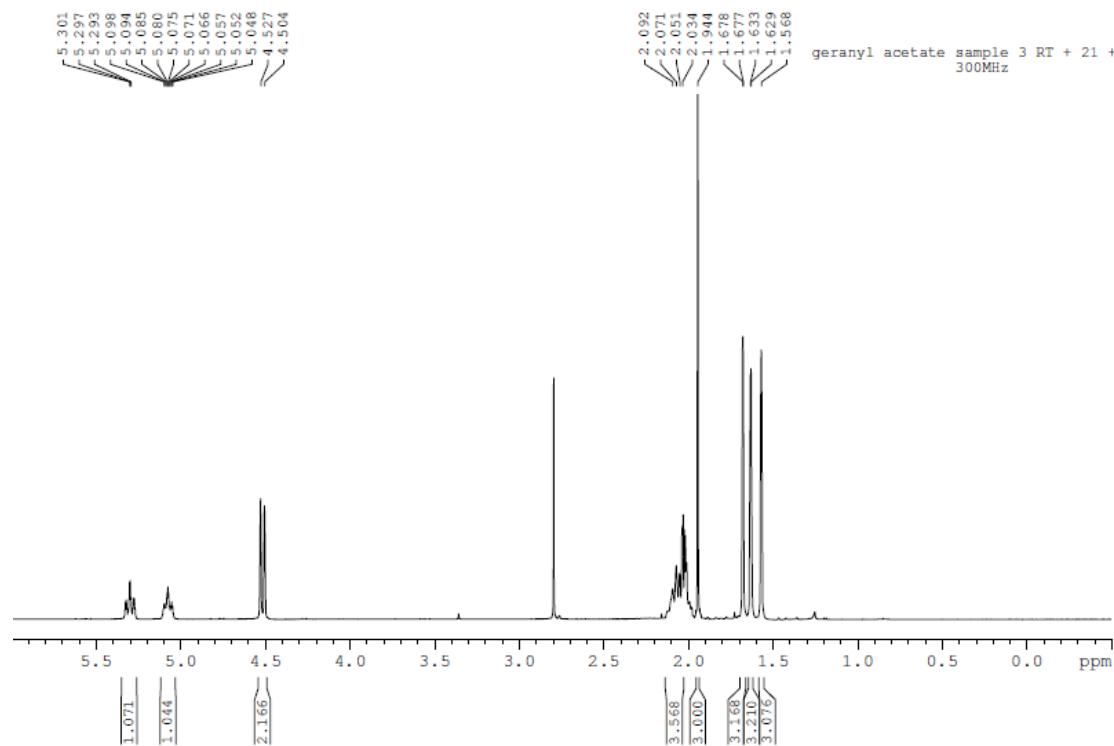


$^{19}\text{F}$ -NMR spectrum

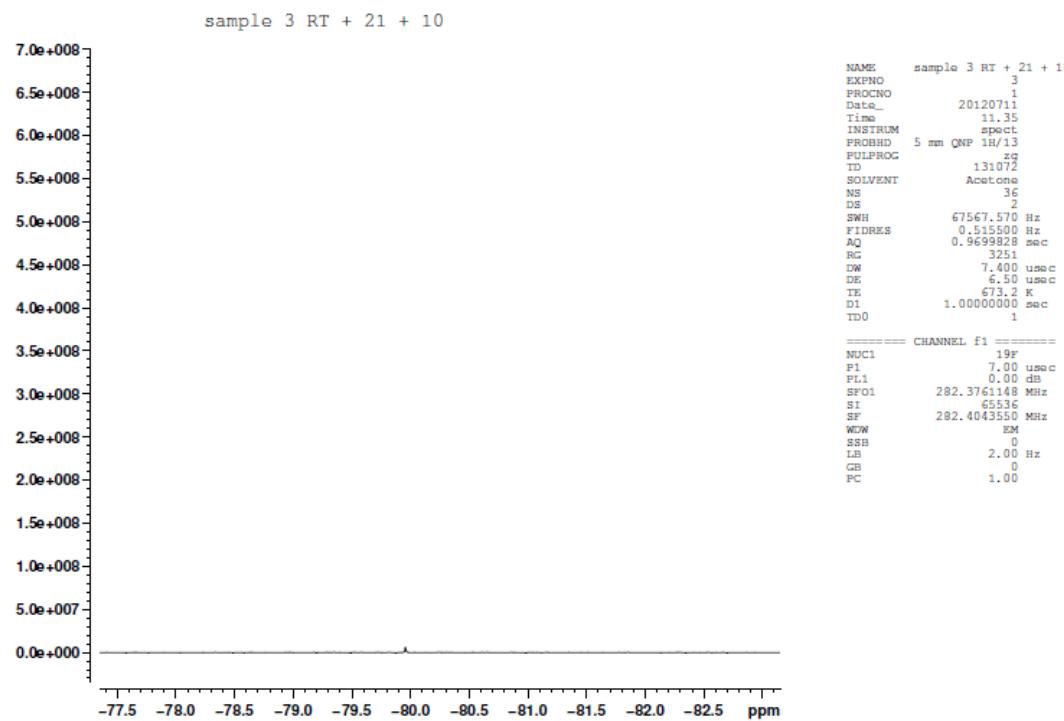


**Sample 3.** Top phase of 50/50 (w/w) [ $C_{16}tma$ ]/[NTf<sub>2</sub>]/geranyl acetate mixture after a first centrifugation step at 14,000 rpm for 15 min at room temperature, followed to second centrifugation step at 14,000 rpm for 15 min at 21°C, followed to third centrifugation step at 14,000 rpm for 15 min at 10°C

### <sup>1</sup>H-NMR spectrum

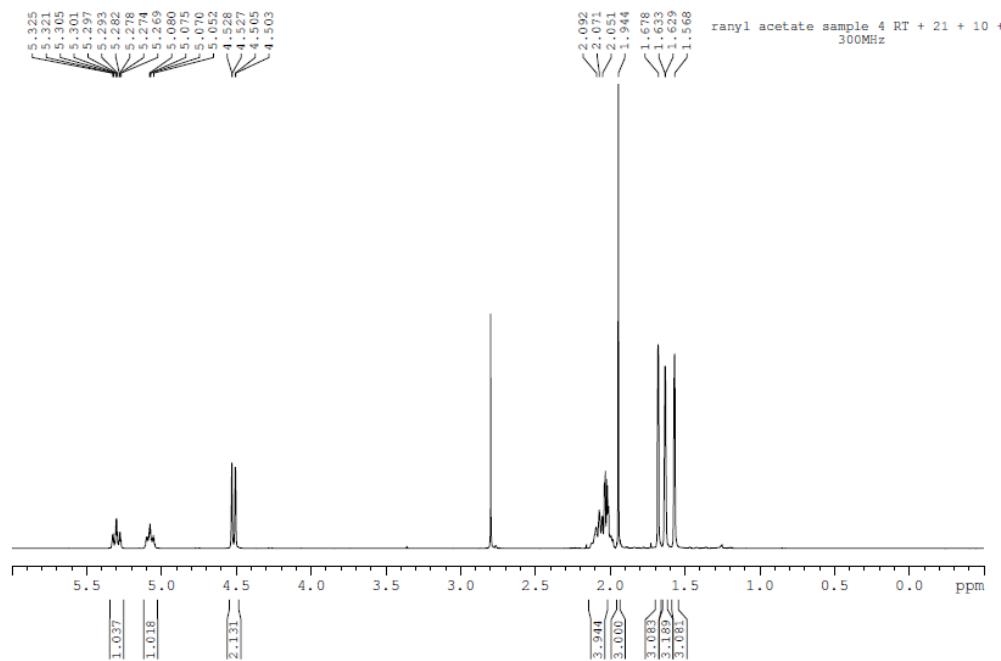


### <sup>19</sup>F-NMR spectrum

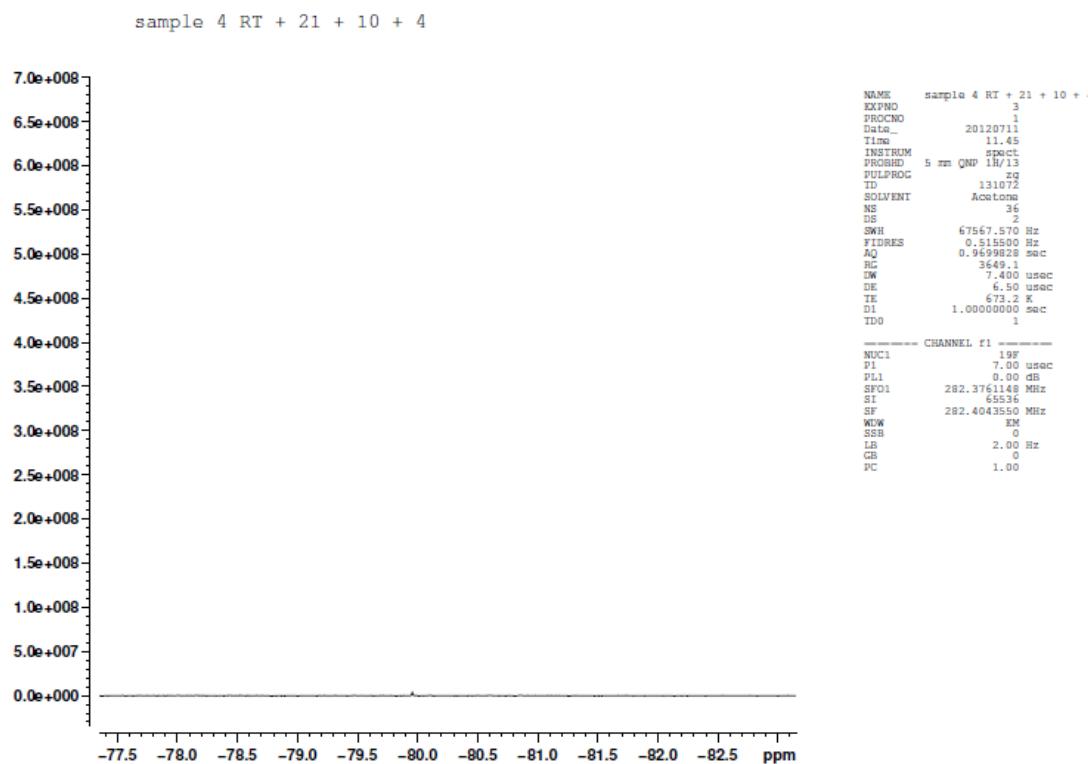


**Sample 4.** Top phase of 50/50 (w/w) [ $C_{16}tma$ ]/[NTf<sub>2</sub>]/geranyl acetate mixture after first centrifugation step at 14,000 rpm for 15 min at room temperature, followed to second centrifugation step at 14,000 rpm for 15 min at 21°C, followed to third centrifugation step at 14,000 rpm for 15 min at 10°C, followed to fourth centrifugation step at 14,000 rpm for 15 min at 4°C

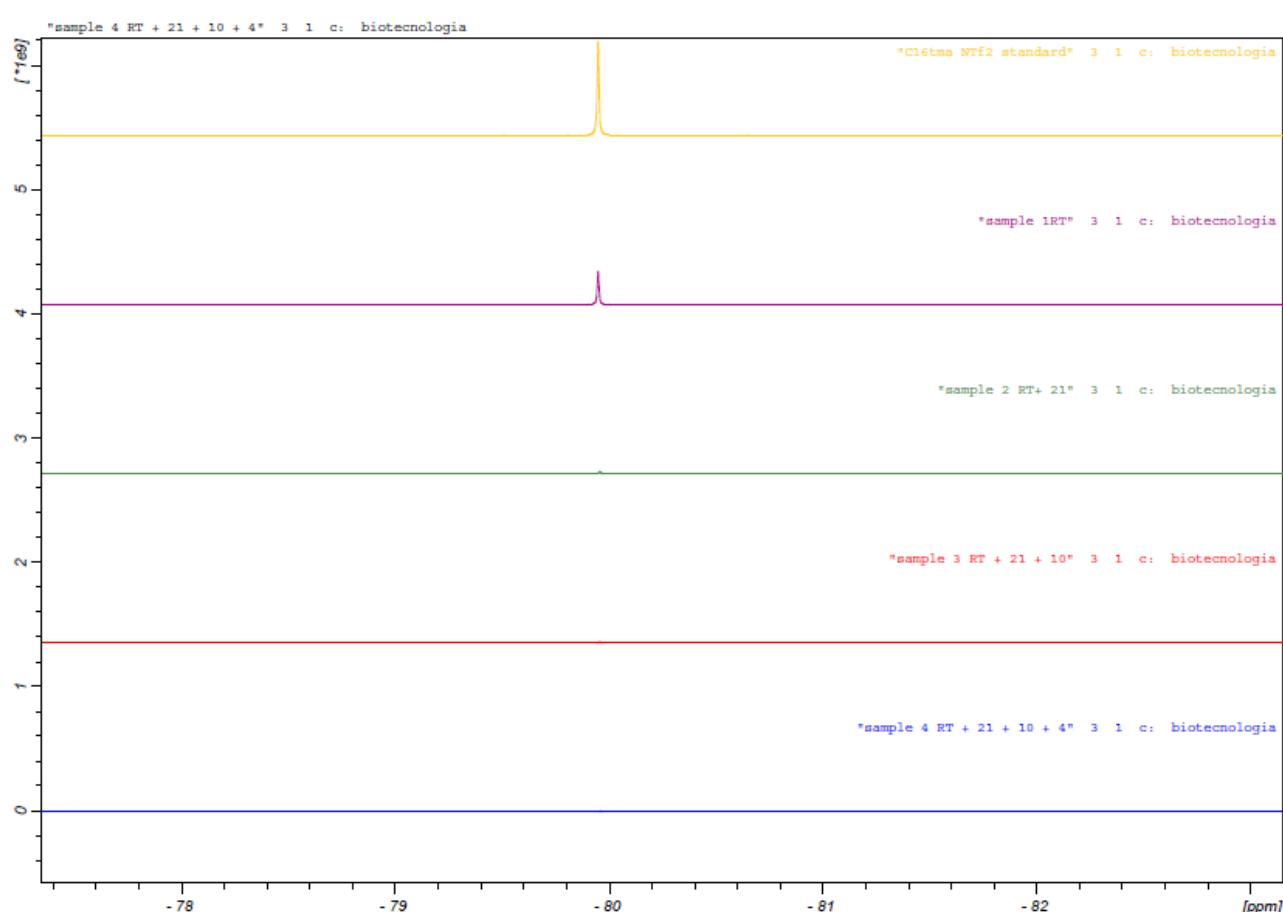
### <sup>1</sup>H-NMR spectrum



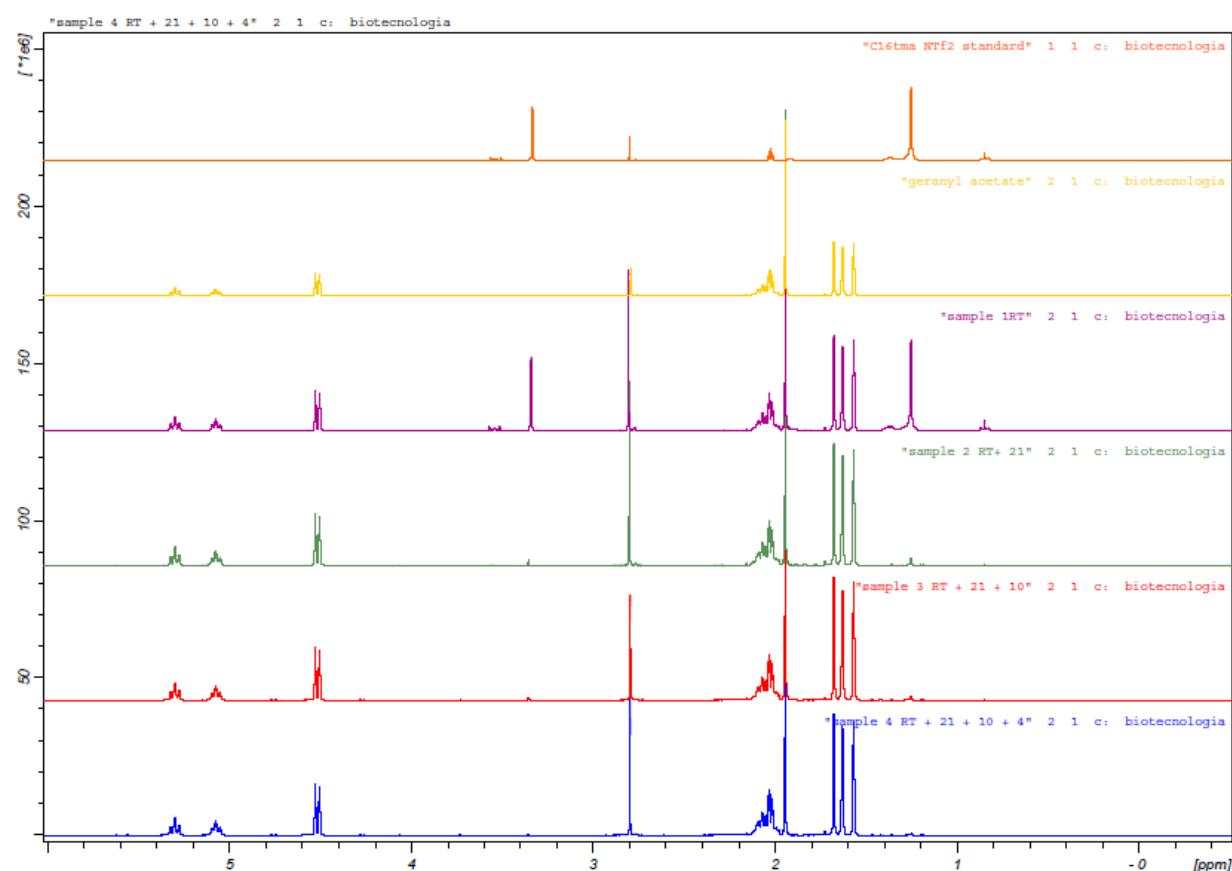
### <sup>19</sup>F-NMR spectrum



## Comparative $^{19}\text{F}$ -NMR spectra



## Comparative $^1\text{H}$ -NMR spectra

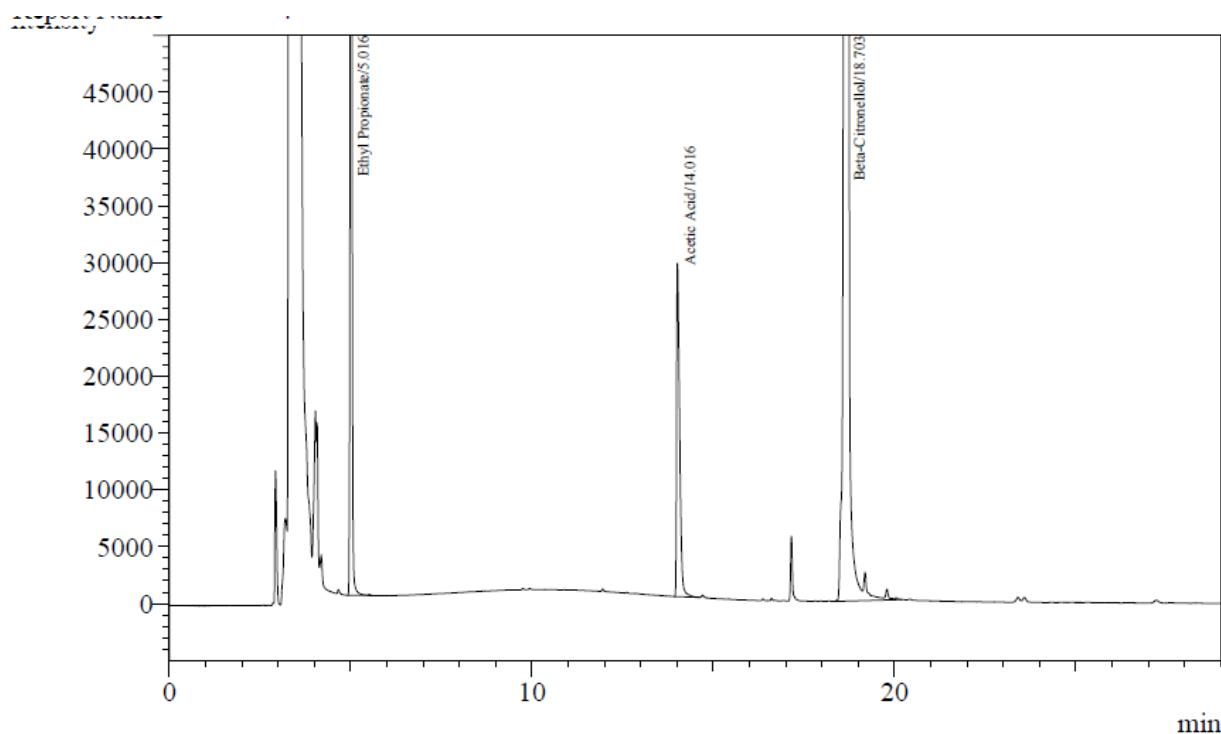


### Representative examples of GC chromatograms from reaction mixtures

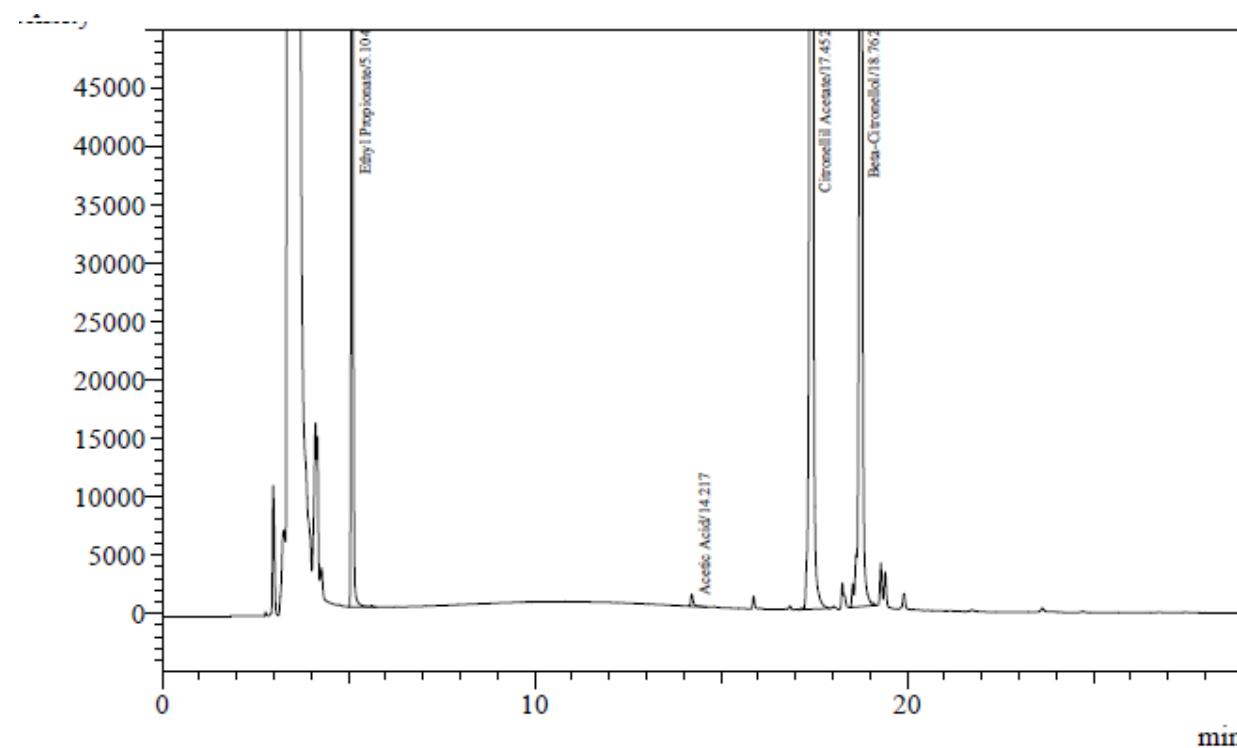
GC chromatograms of flavour esters samples obtained from Novozym 435-catalyzed esterification between a aliphatic carboxylic acid (acetic, propionic, butyric or valeric) with a flavour alcohol (isoamyl alcohol, nerol, geraniol or citronellol) in 60 % (w/w)  $[C_{16}tma][NTf_2]$ , at time zero and after 4 h reaction at 50°C. (see Table 1, column B)

#### 1. Citronellyl acetate synthesis

Time = 0 h

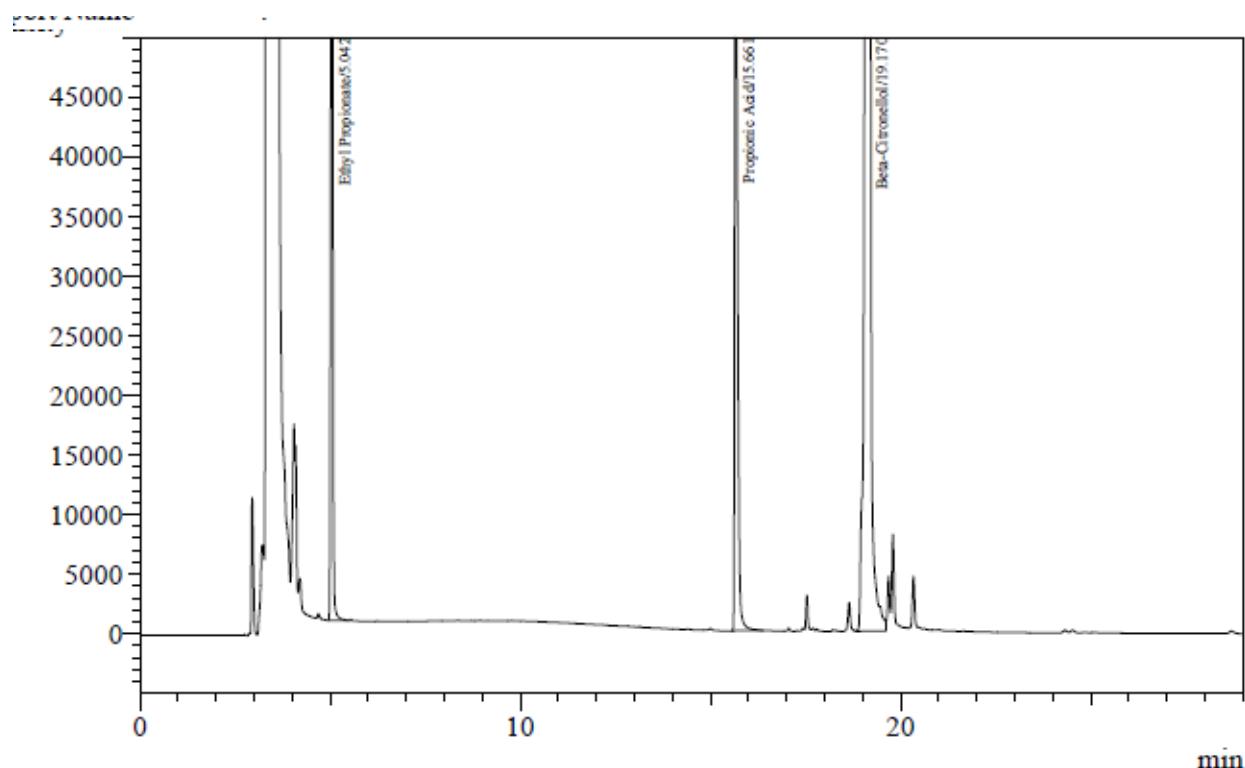


Time = 4 h

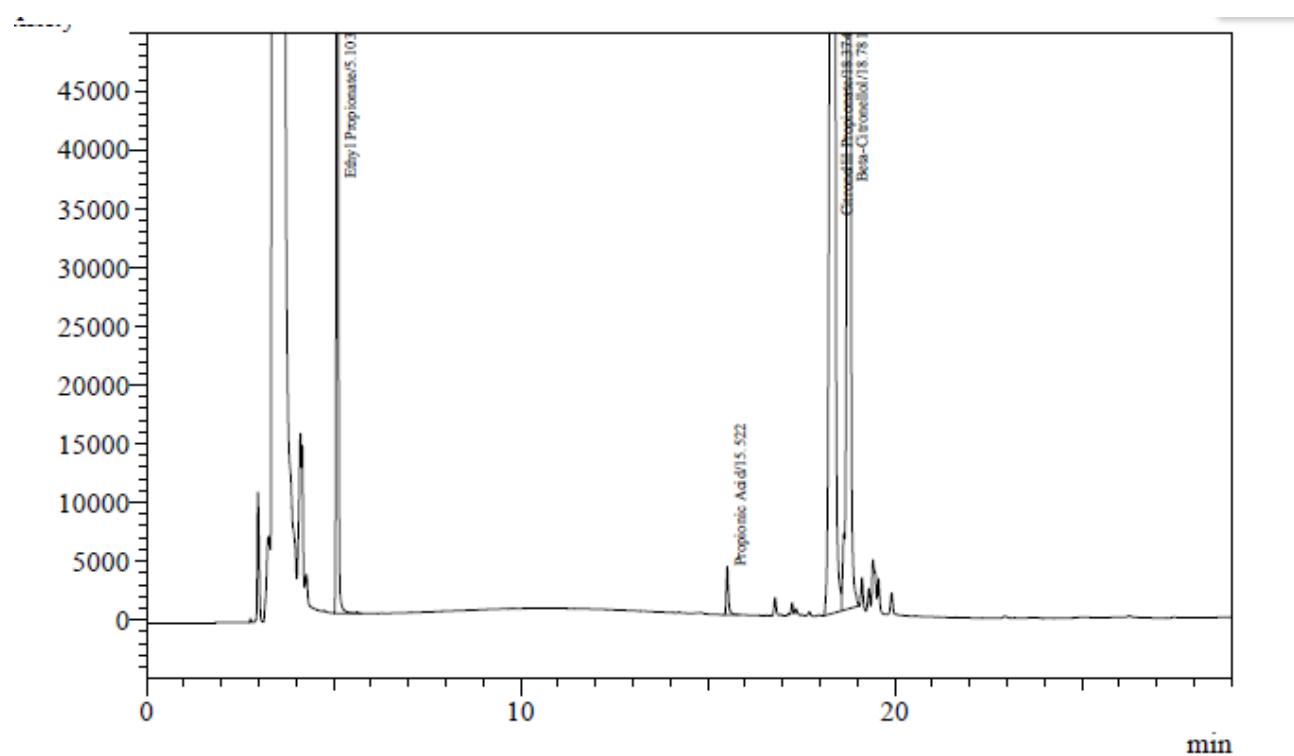


## 2. Citronellyl propionate synthesis

Time = 0 h

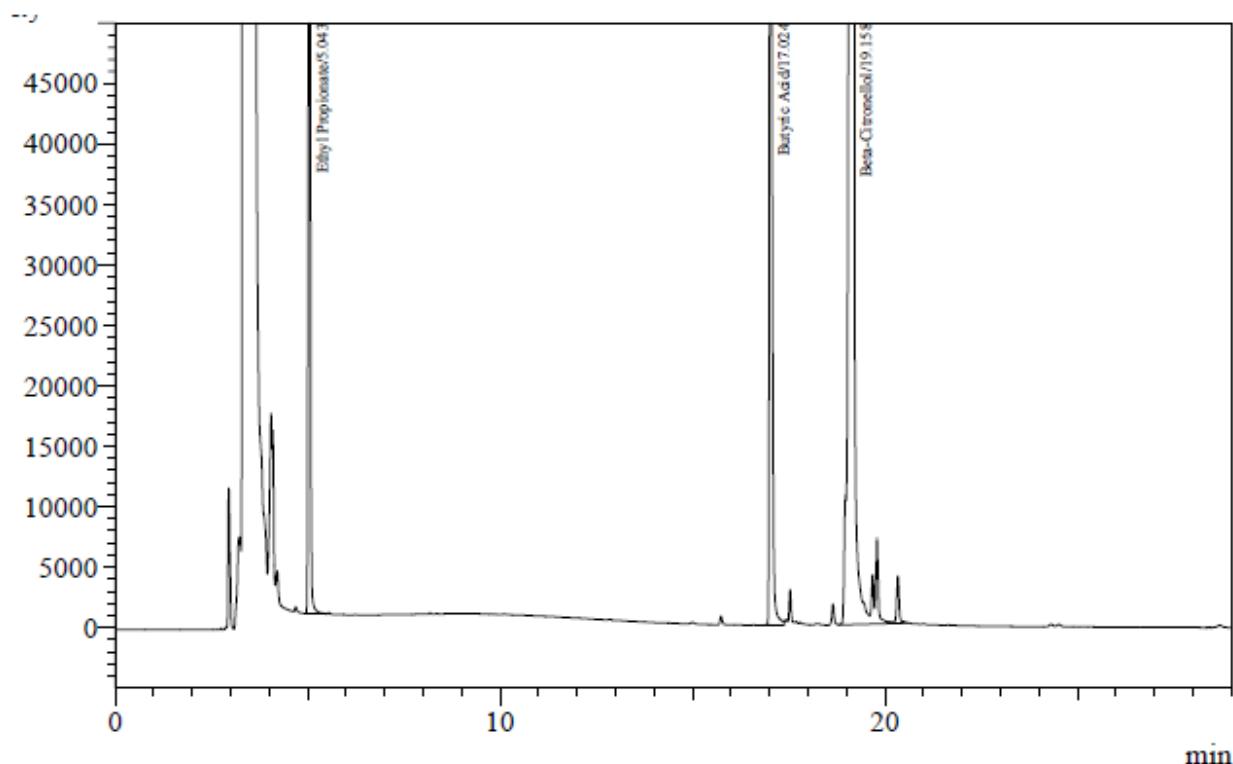


Time = 4 h

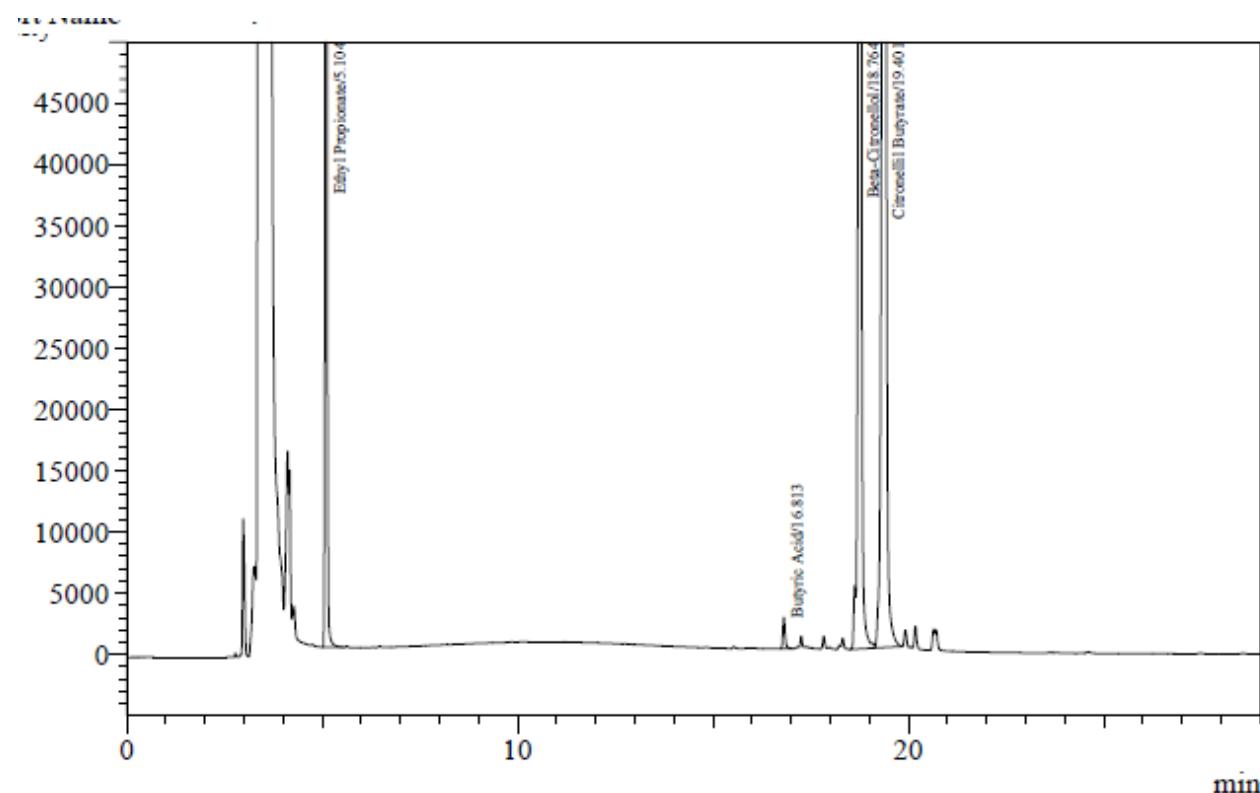


### 3. Citronellyl butyrate synthesis

Time = 0 h

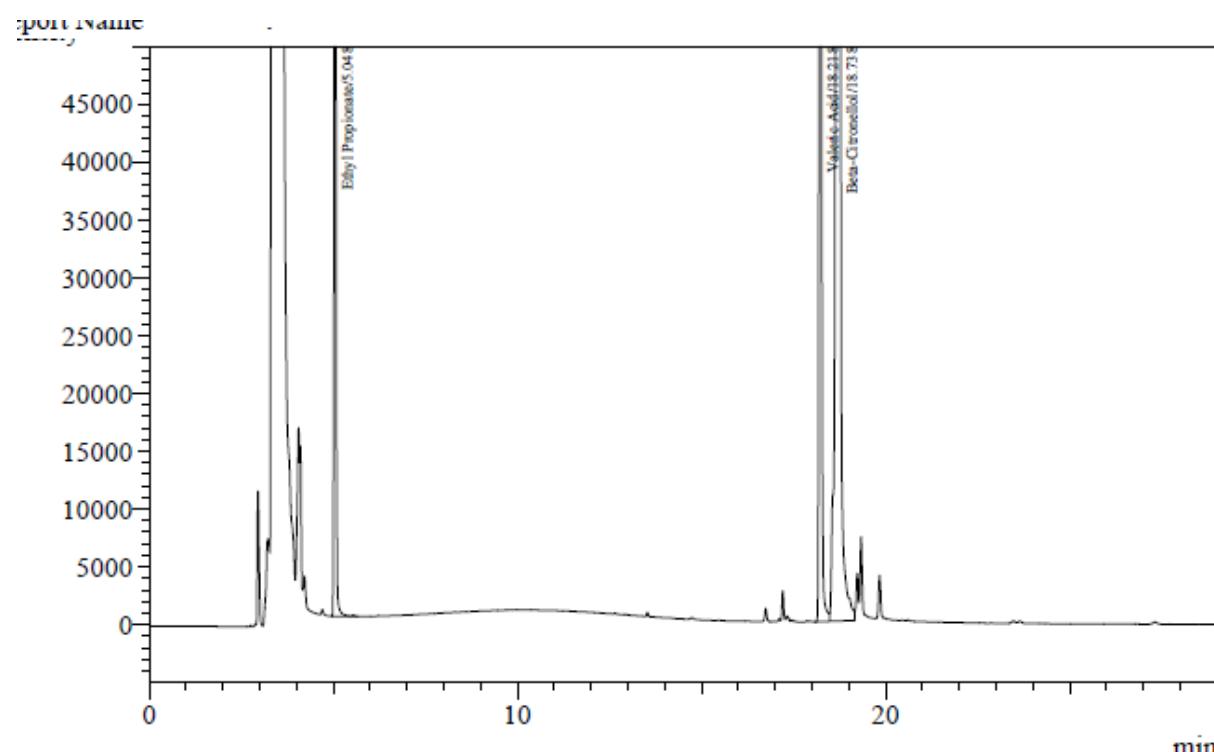


Time = 4 h

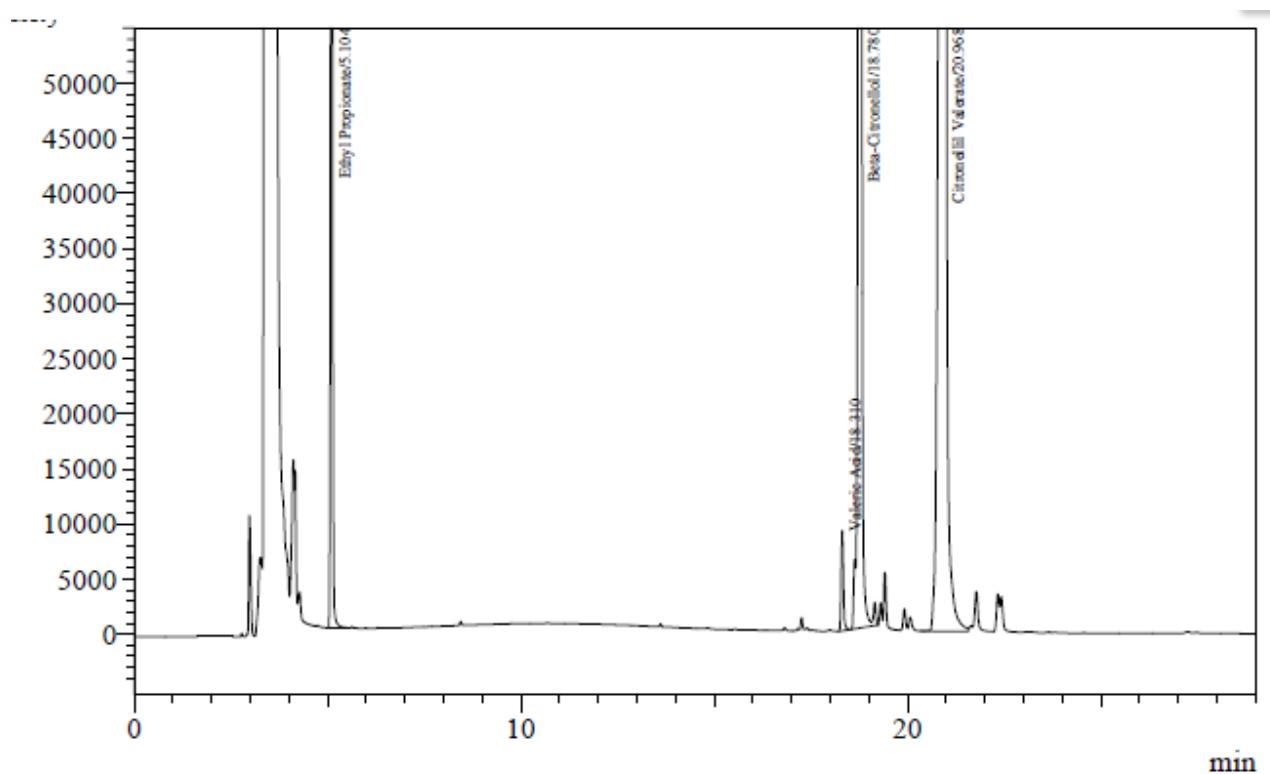


#### 4. Citronellyl valerate synthesis

Time = 0 h

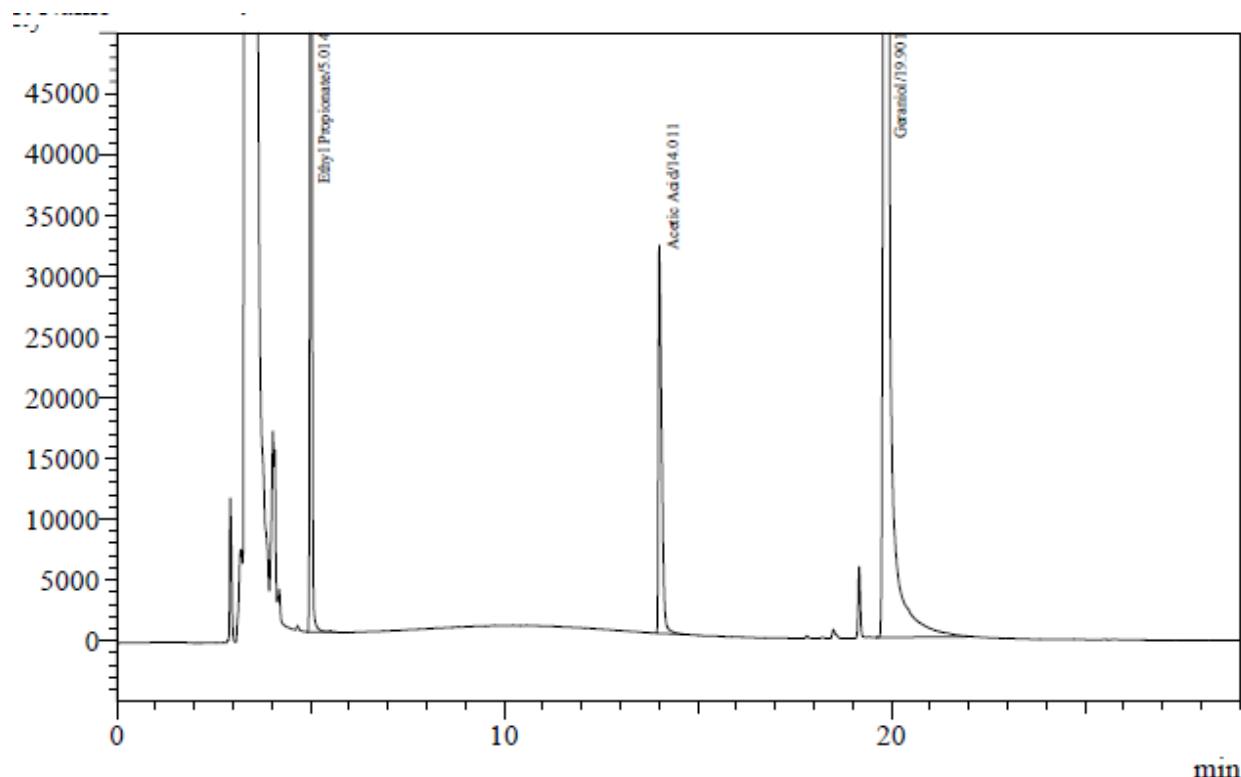


Time = 4 h

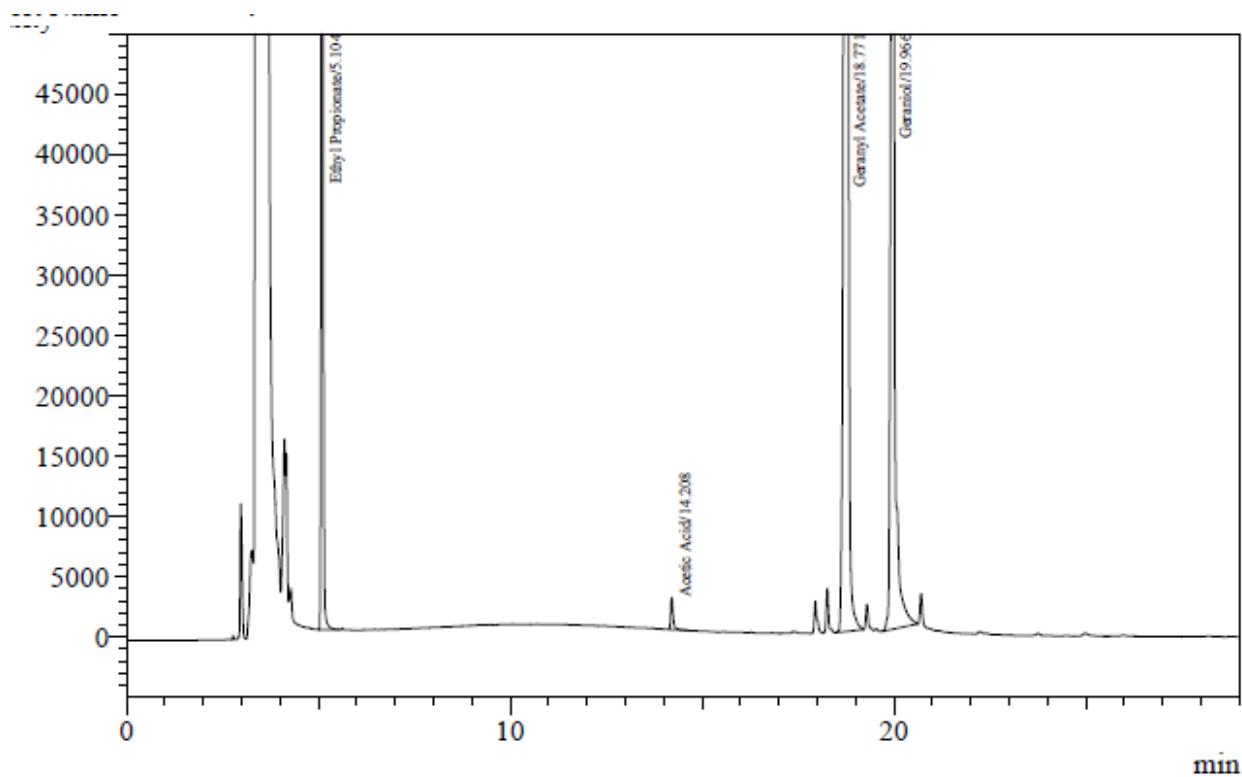


## 5. Geranyl acetate synthesis

Time = 0 h

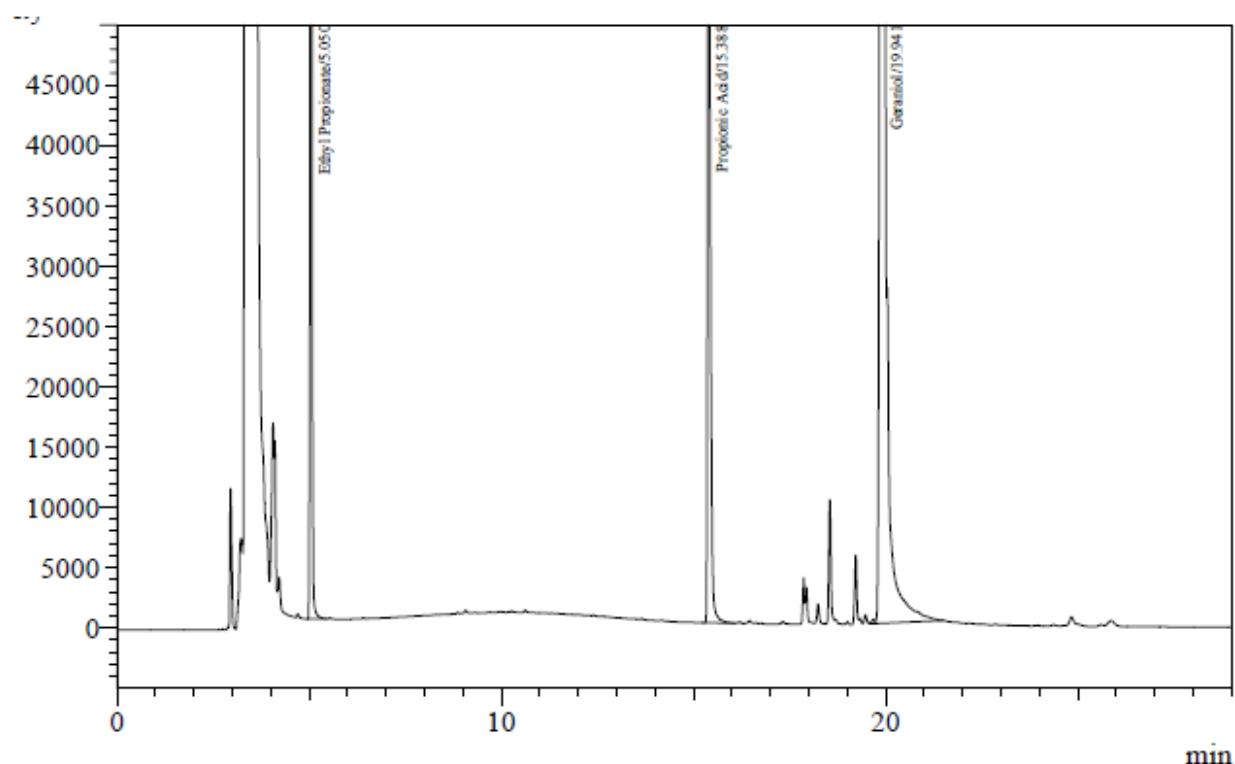


Time = 4 h

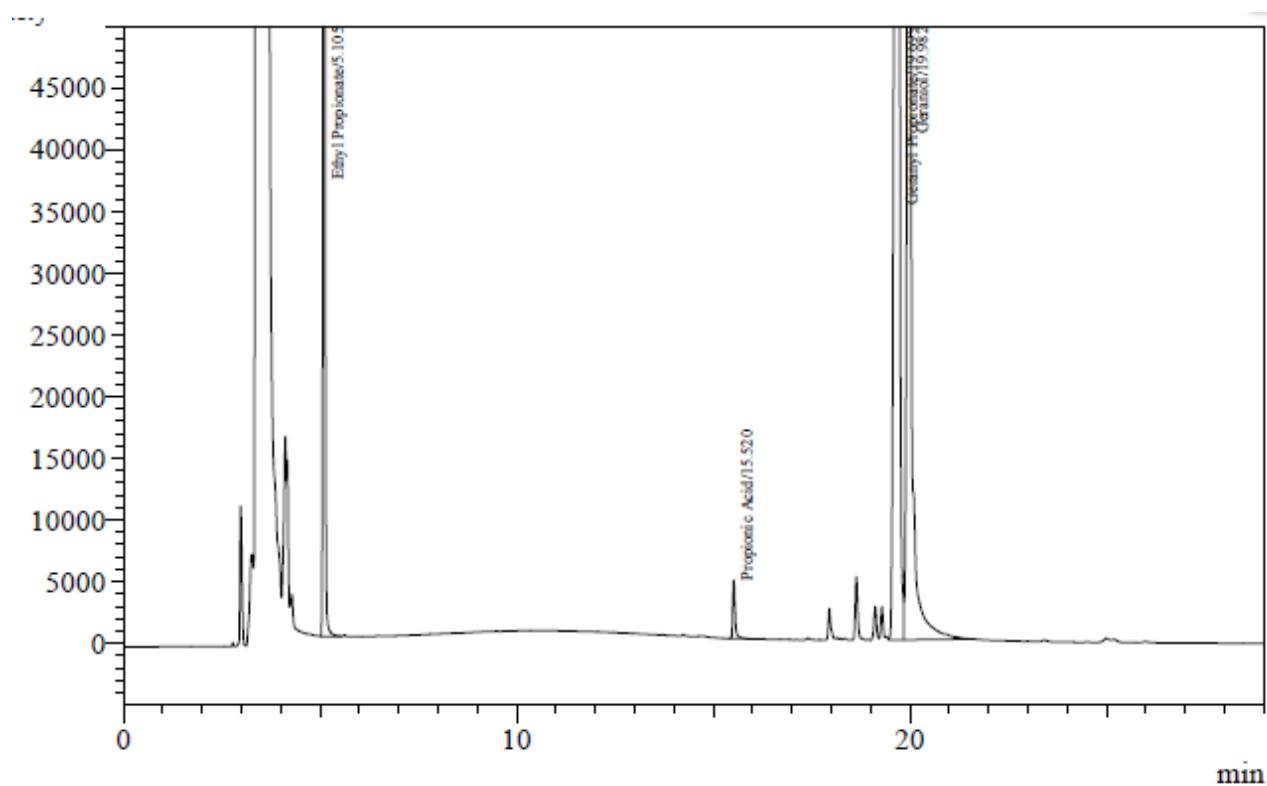


## 6. Geranyl propionate synthesis

Time = 0 h

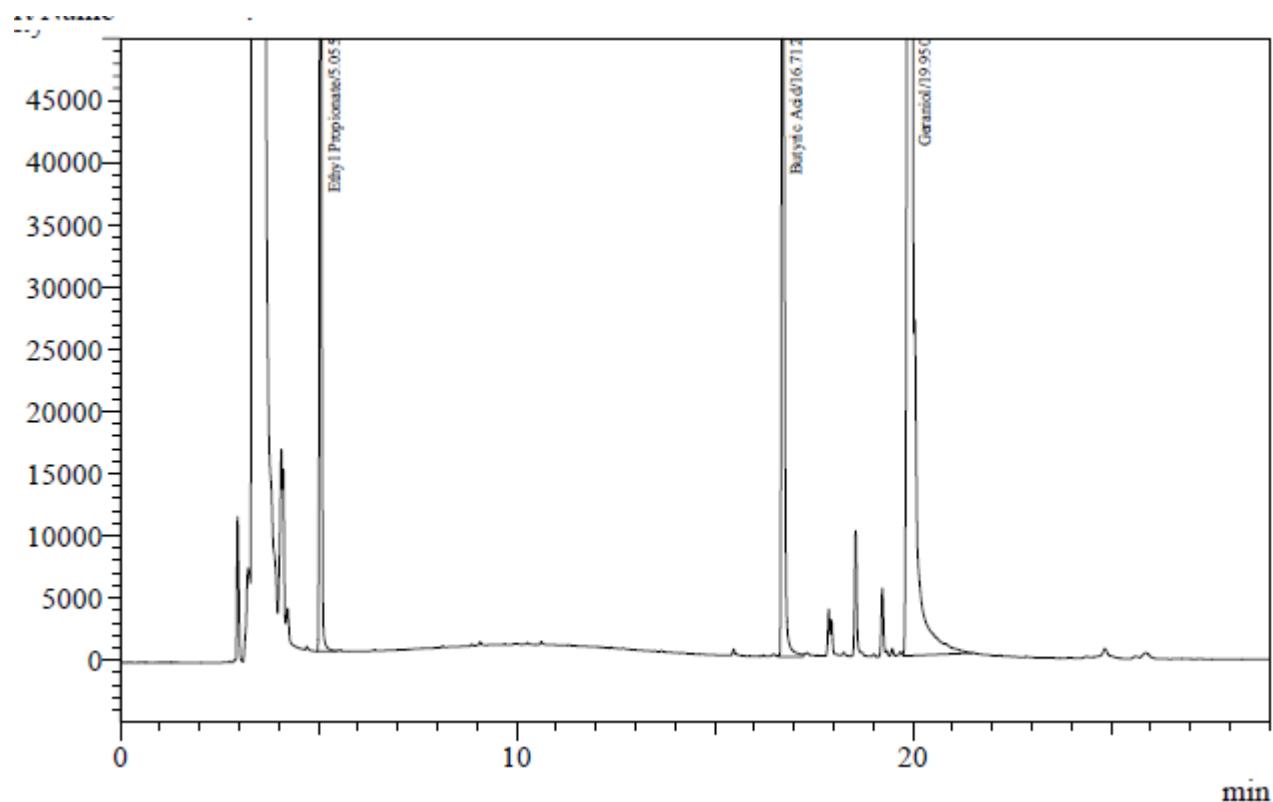


Time = 4 h

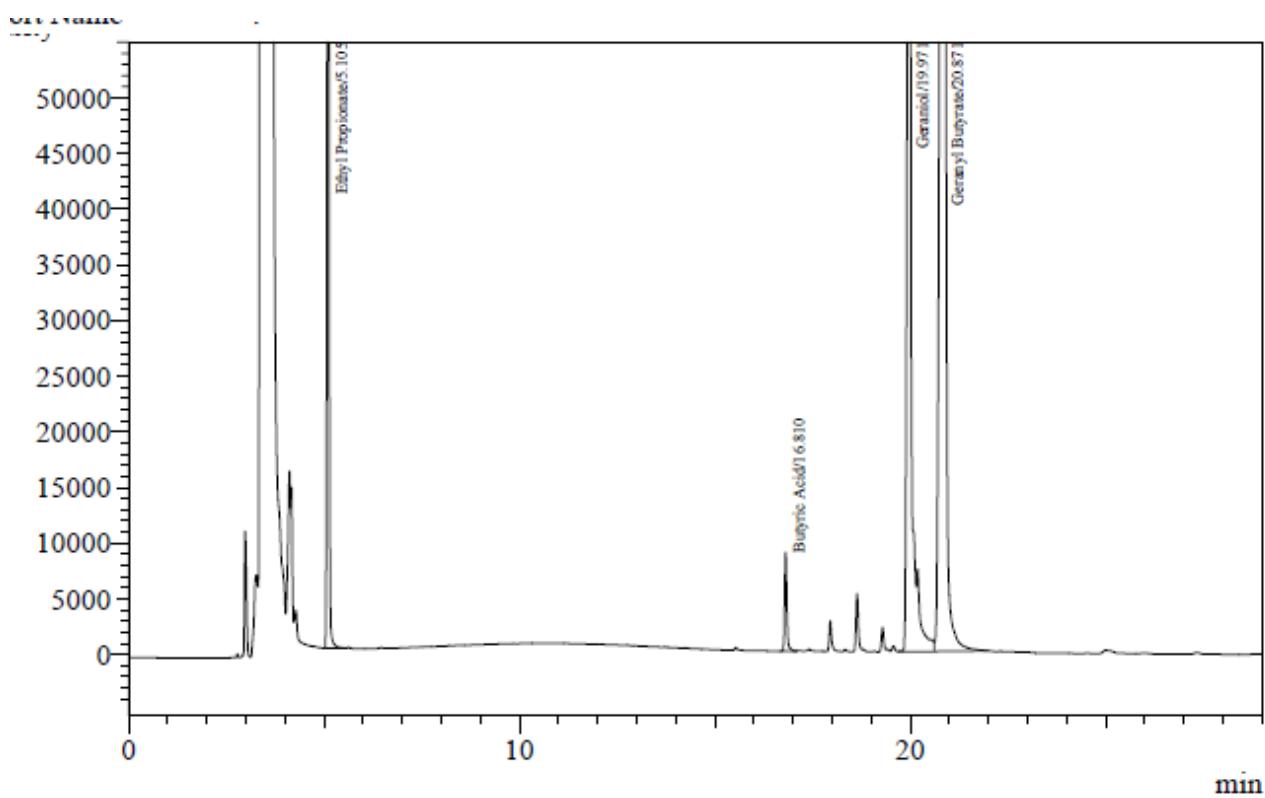


## 7. Geranyl butyrate synthesis

Time = 0 h

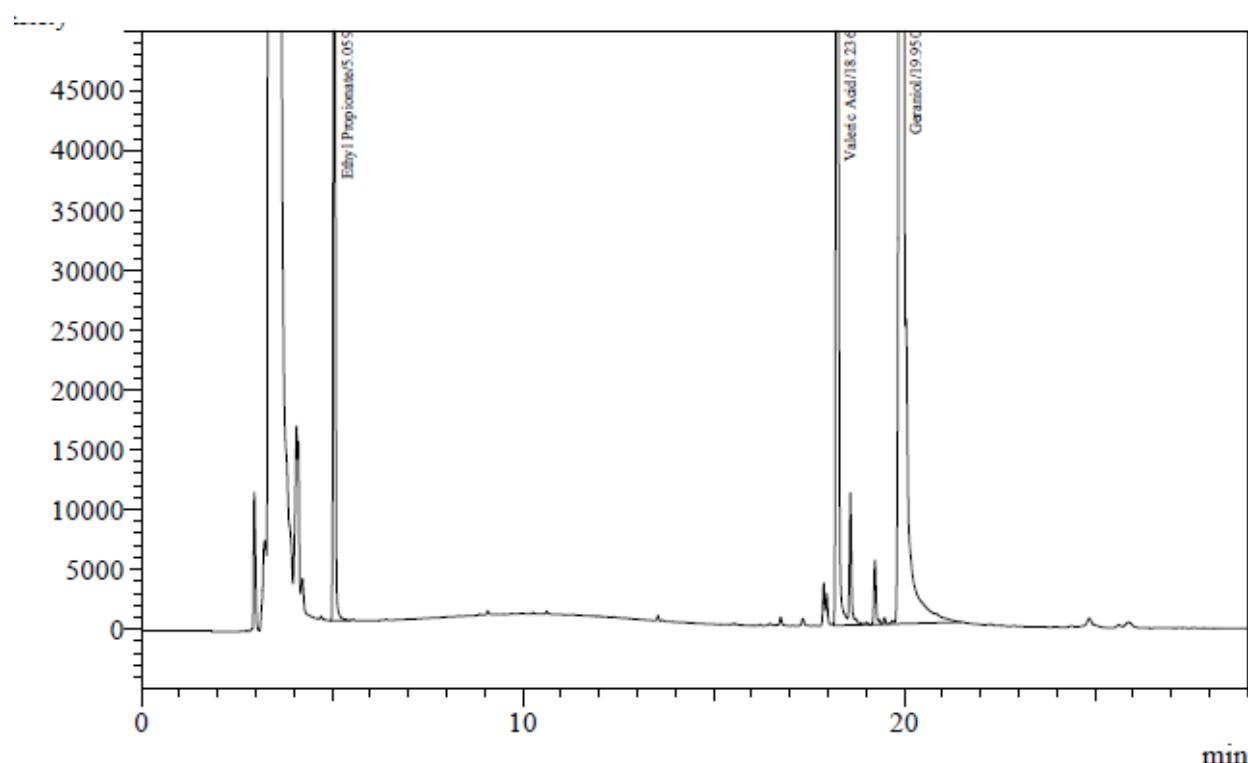


Time = 4 h

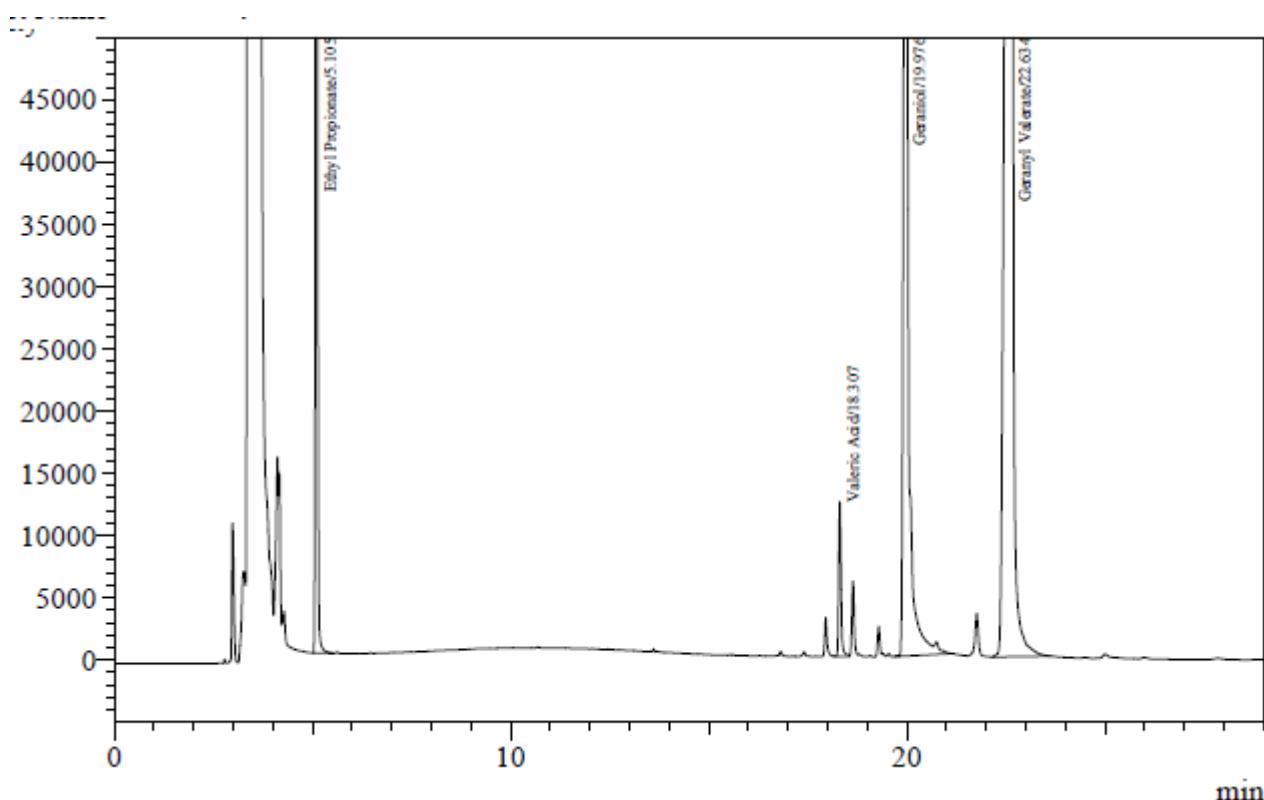


## 8. Geranyl valerate synthesis

Time = 0 h

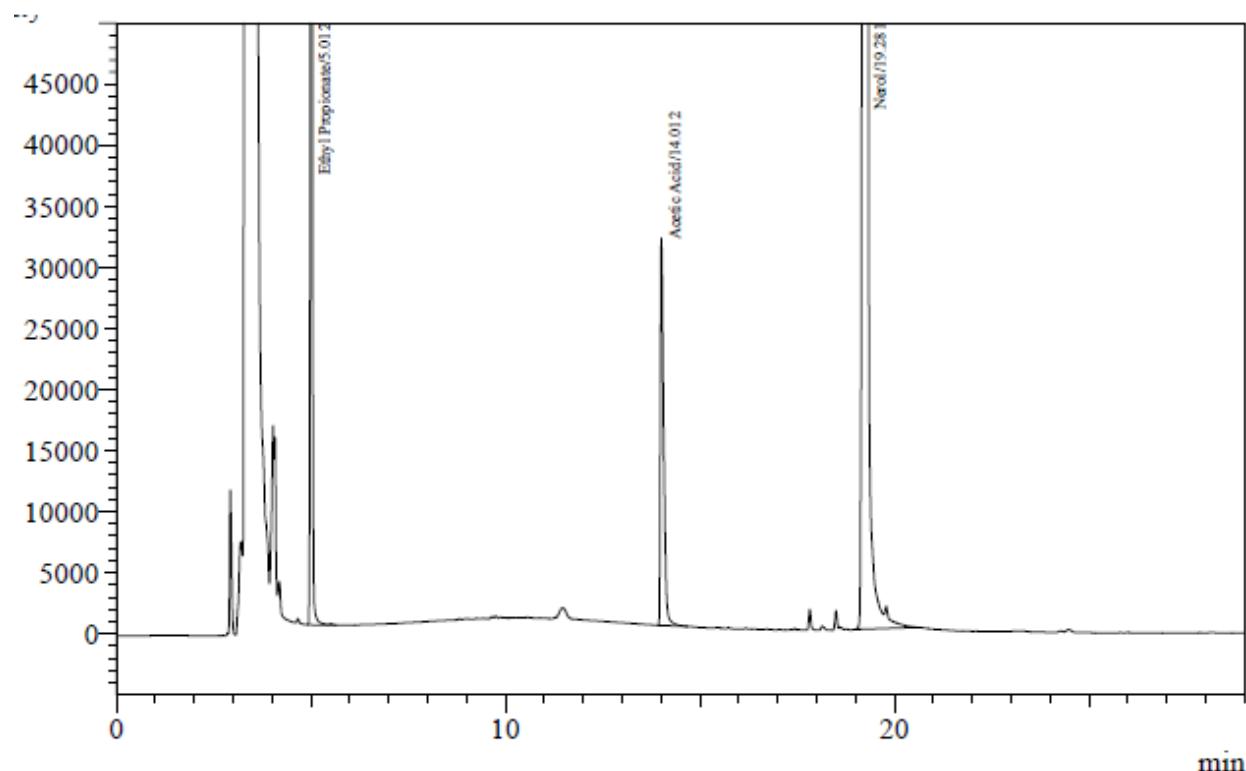


Time = 4 h

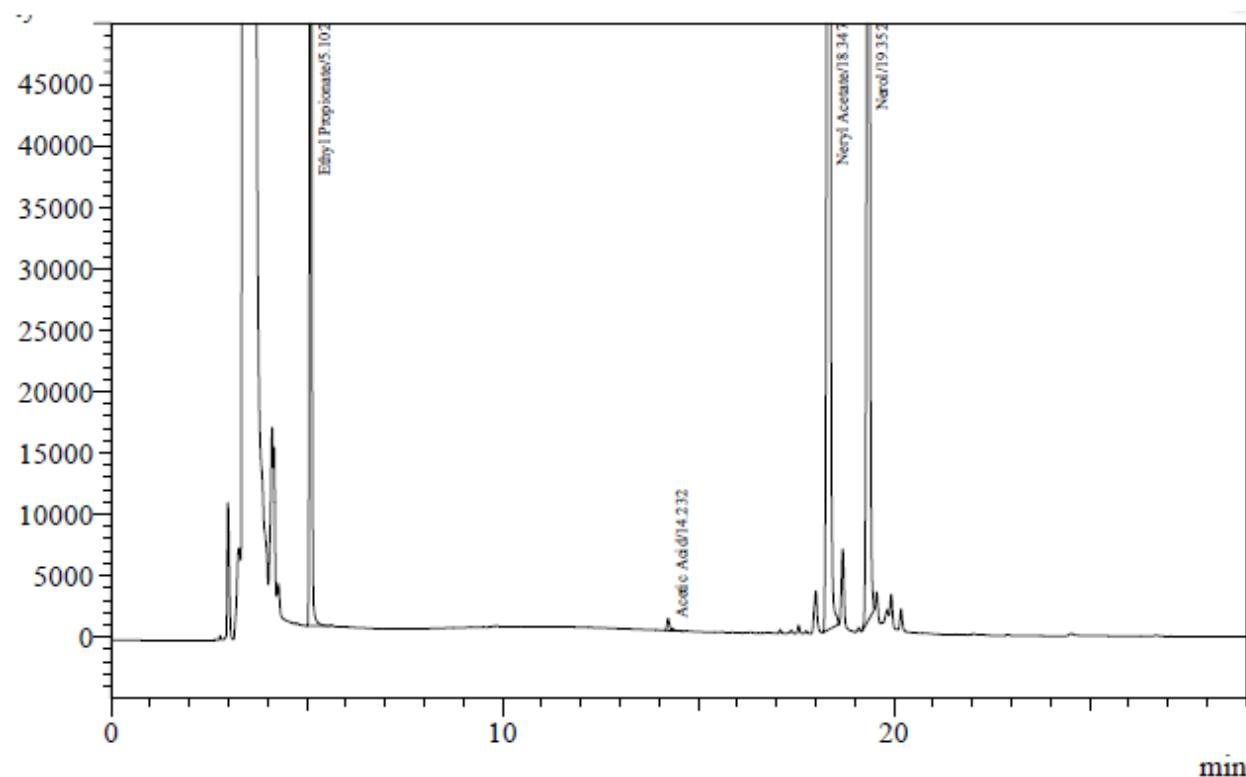


## 9. Neryl acetate synthesis

Time = 0 h

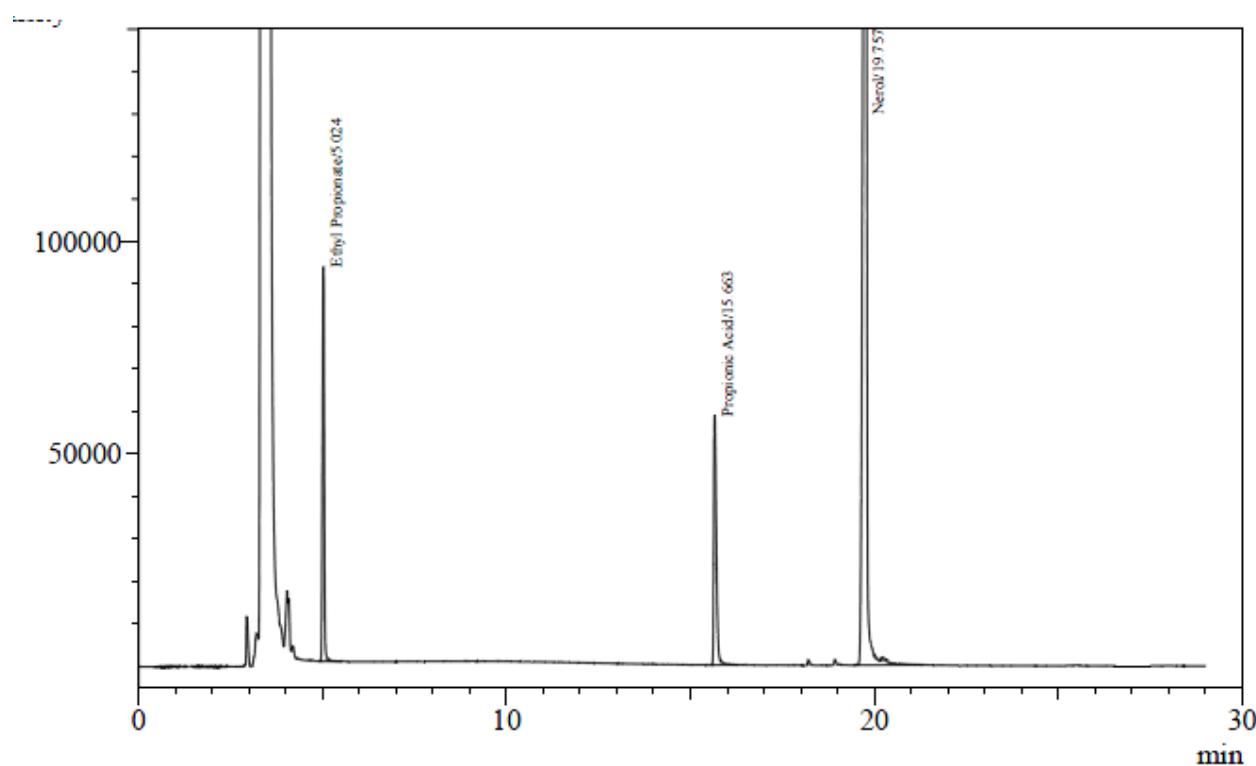


Time = 4 h

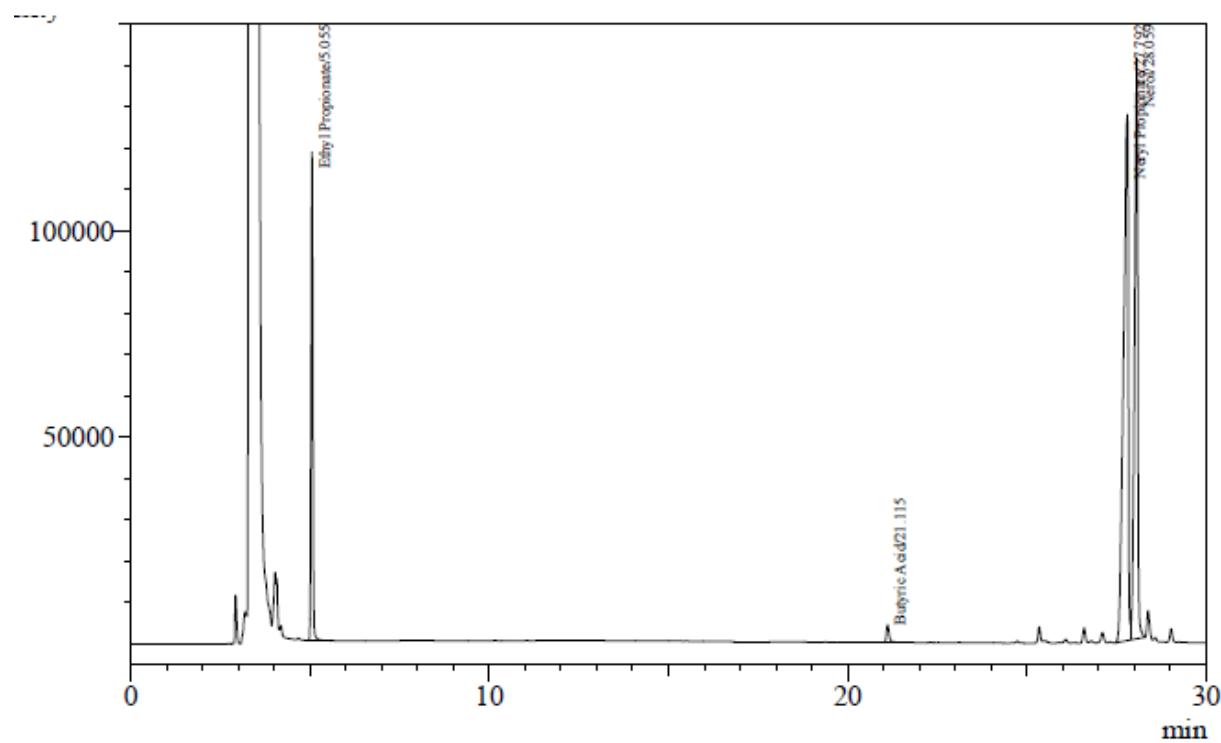


## 10. Neryl propionate synthesis

Time = 0 h

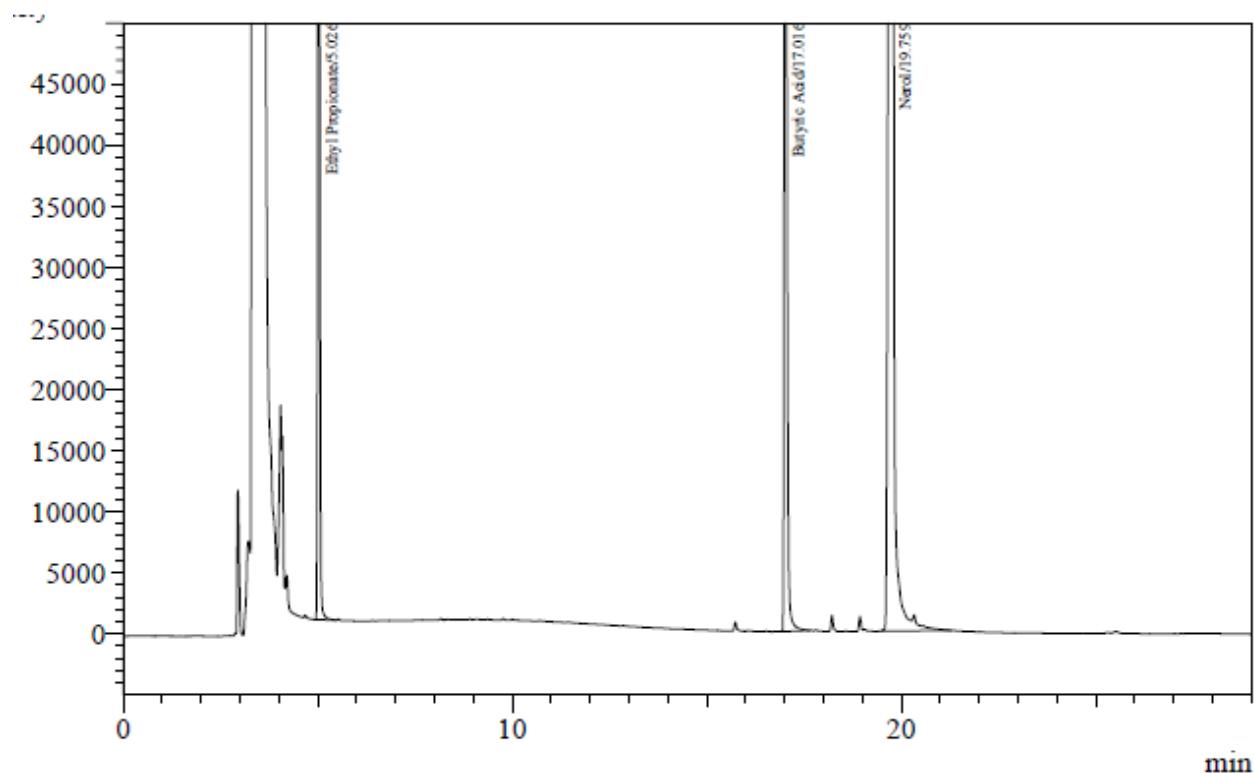


Time = 4 h

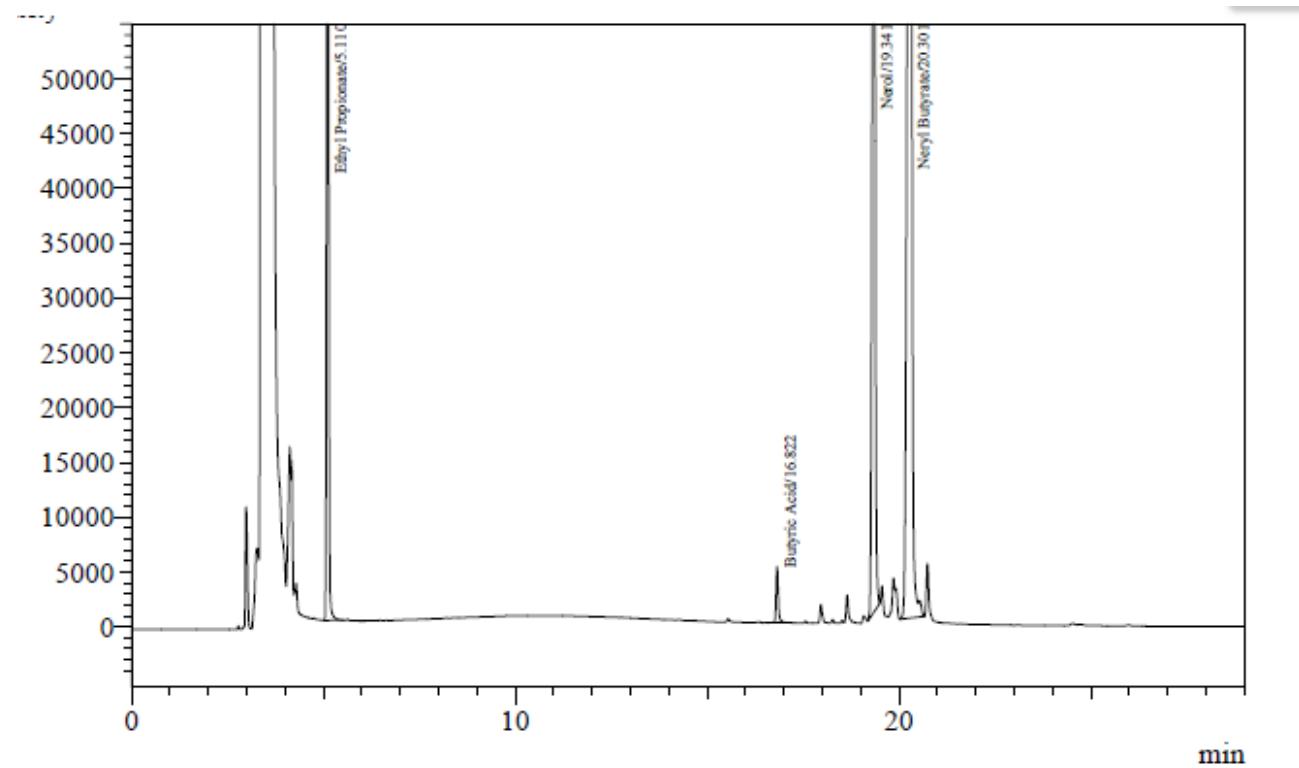


## 11. Neryl butyrate synthesis

Time = 0 h

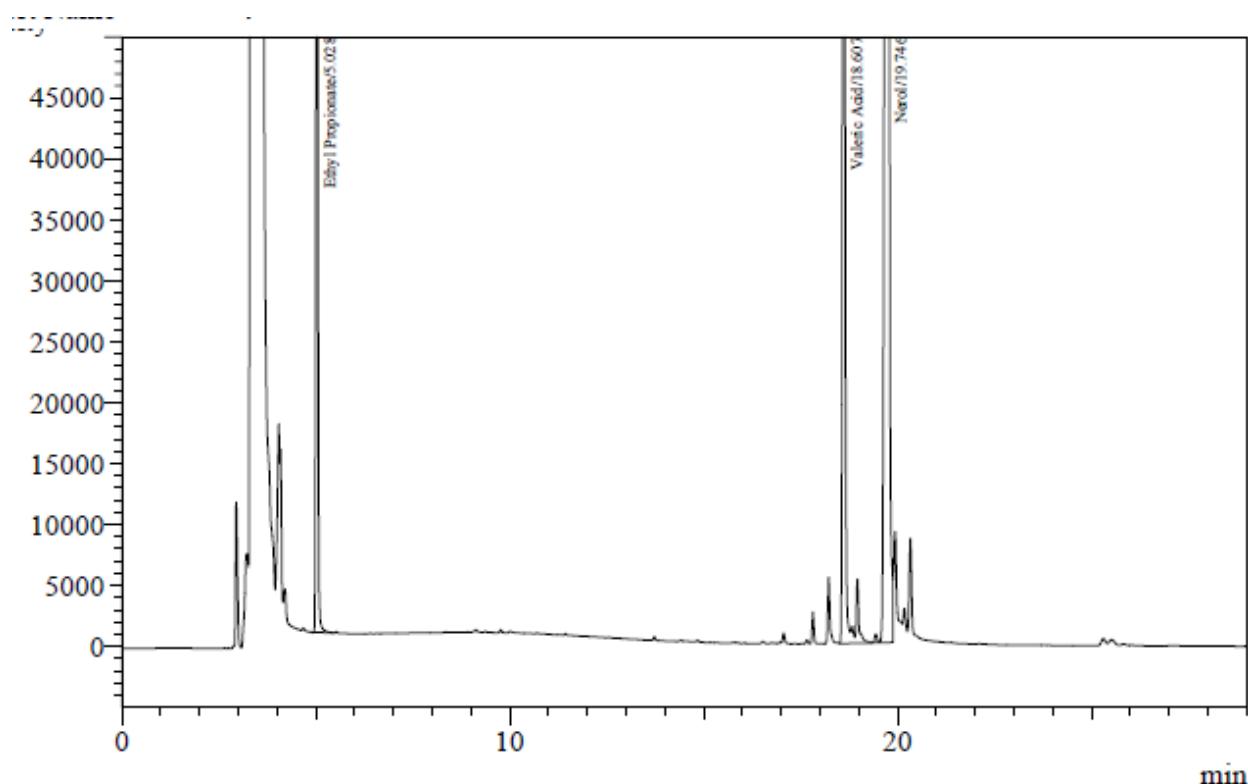


Time = 4 h

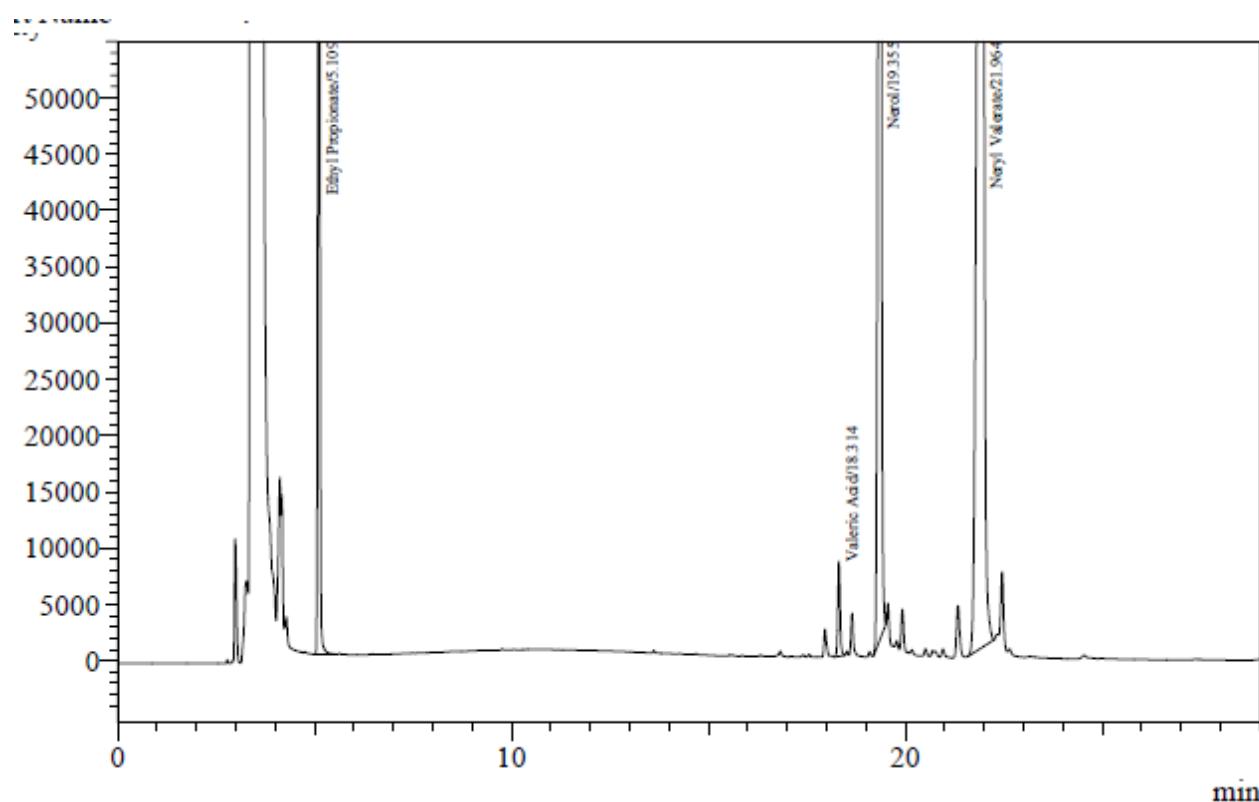


## 12. Neryl valerate synthesis

Time = 0 h

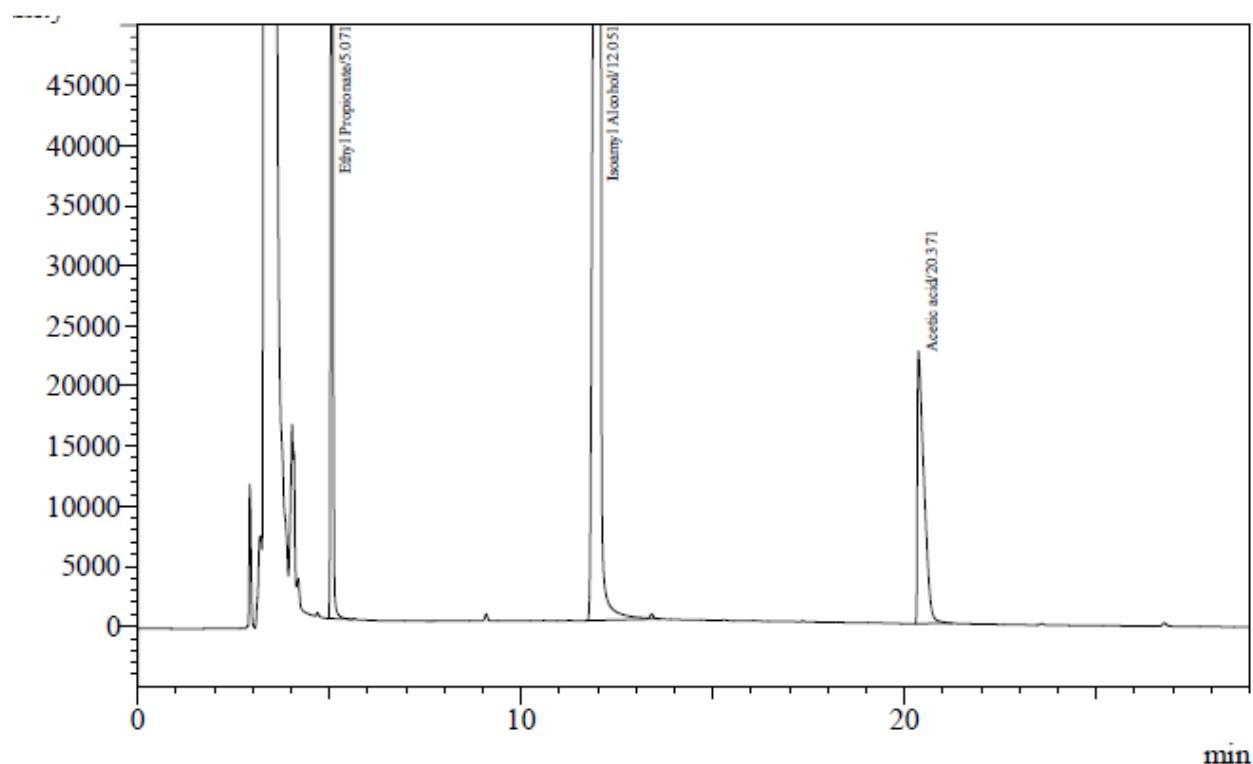


Time = 4 h

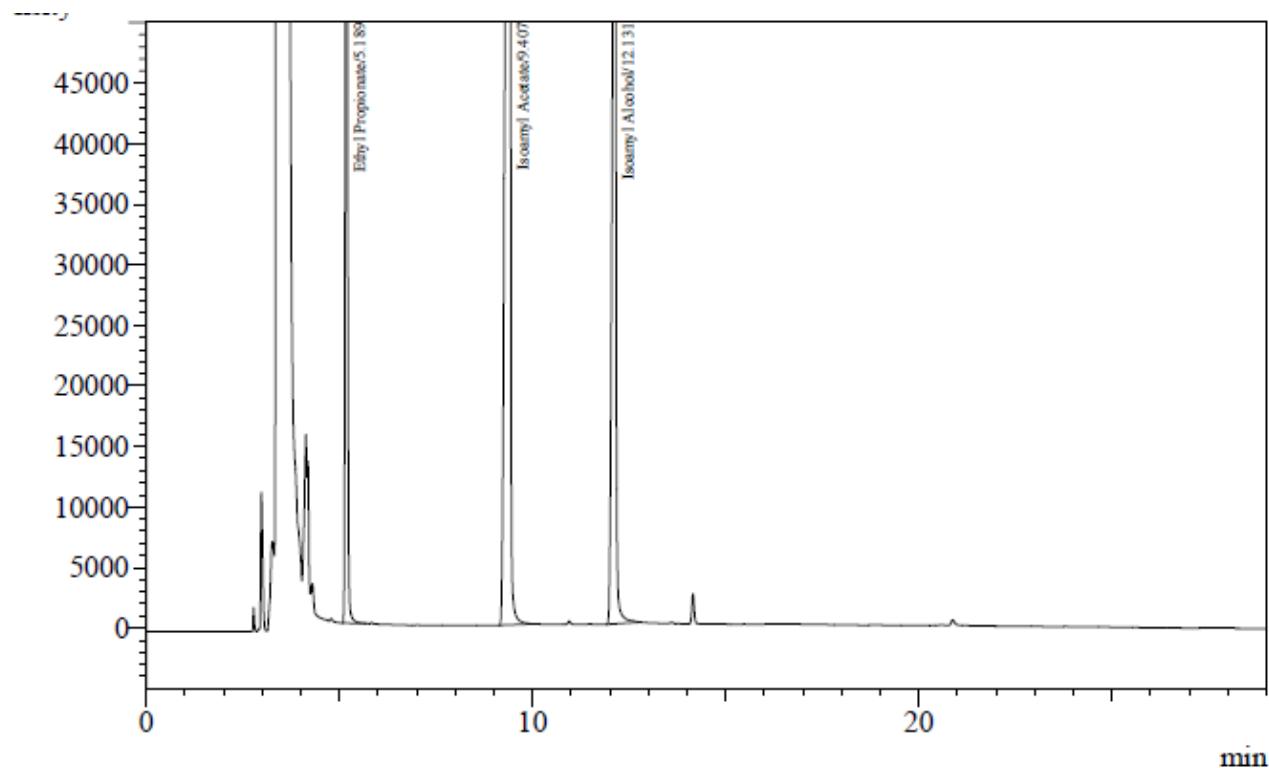


### 13. Isoamyl acetate synthesis

Time = 0 h

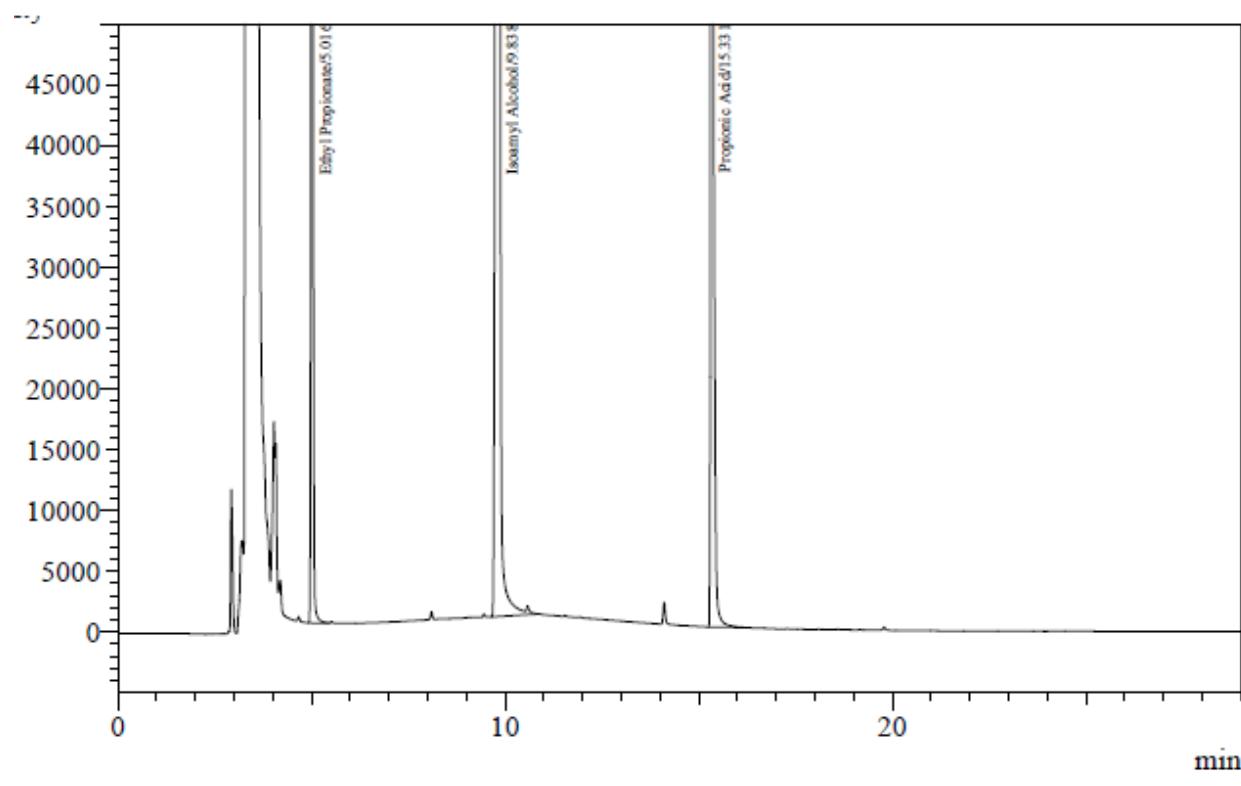


Time = 4 h

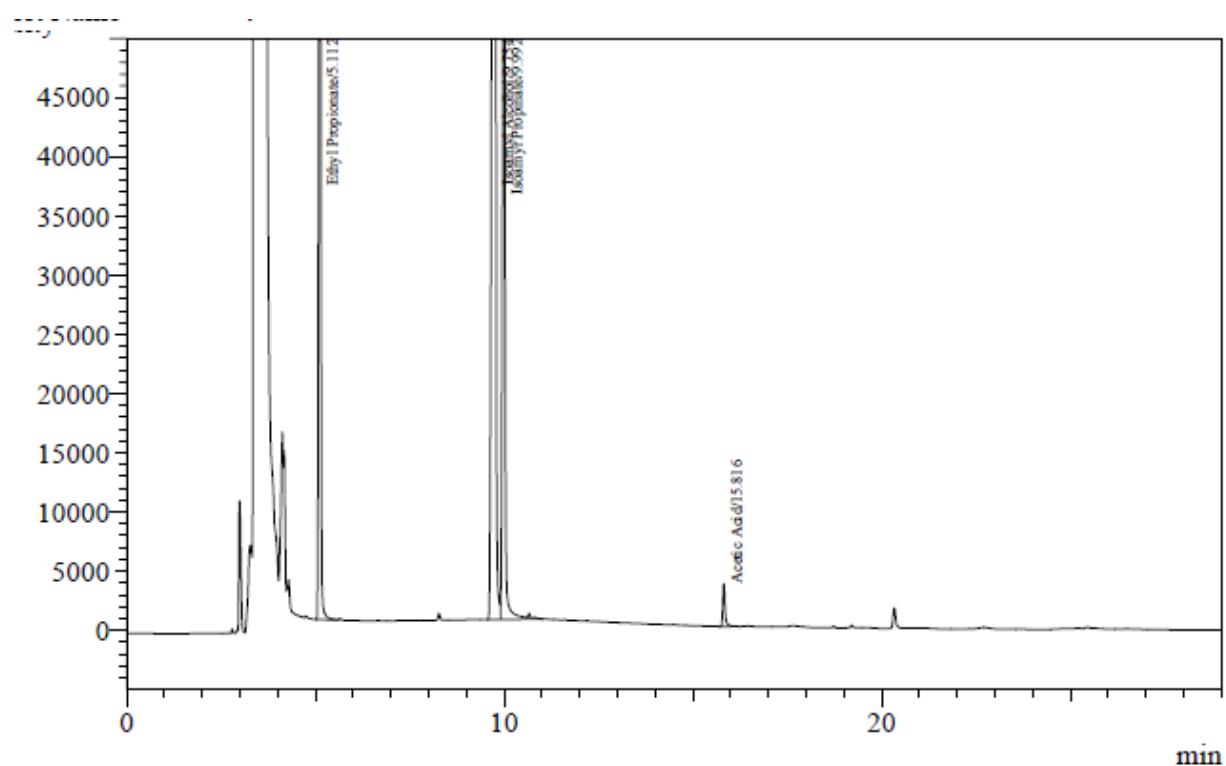


#### 14. Isoamyl propionate synthesis

Time = 0 h

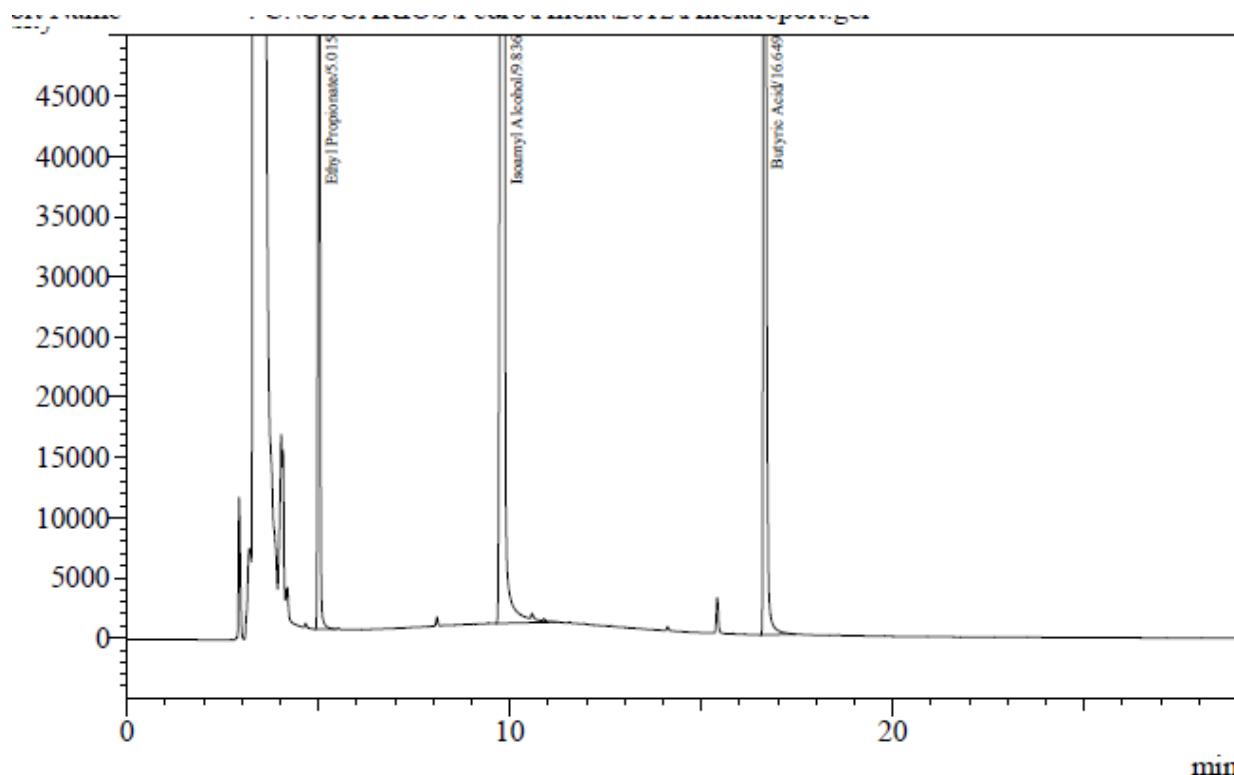


Time = 4 h

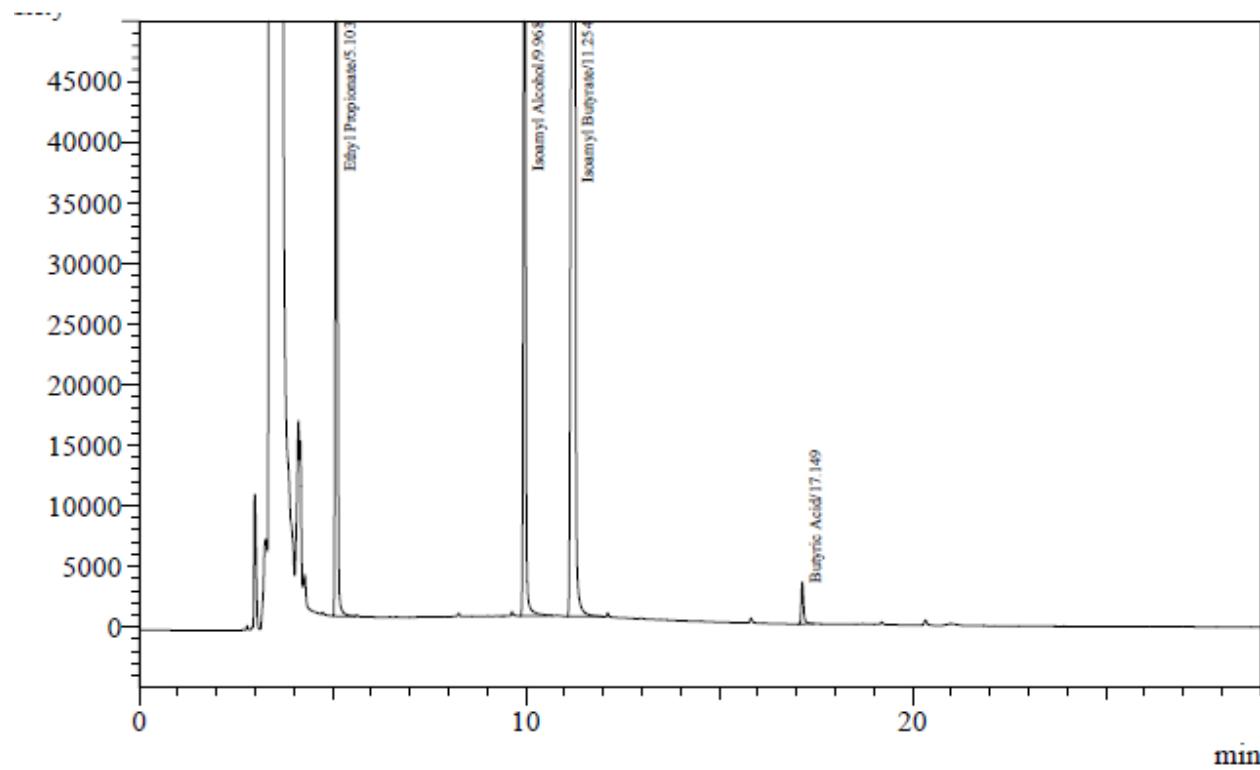


## 15. Isoamyl butyrate synthesis

Time = 0 h

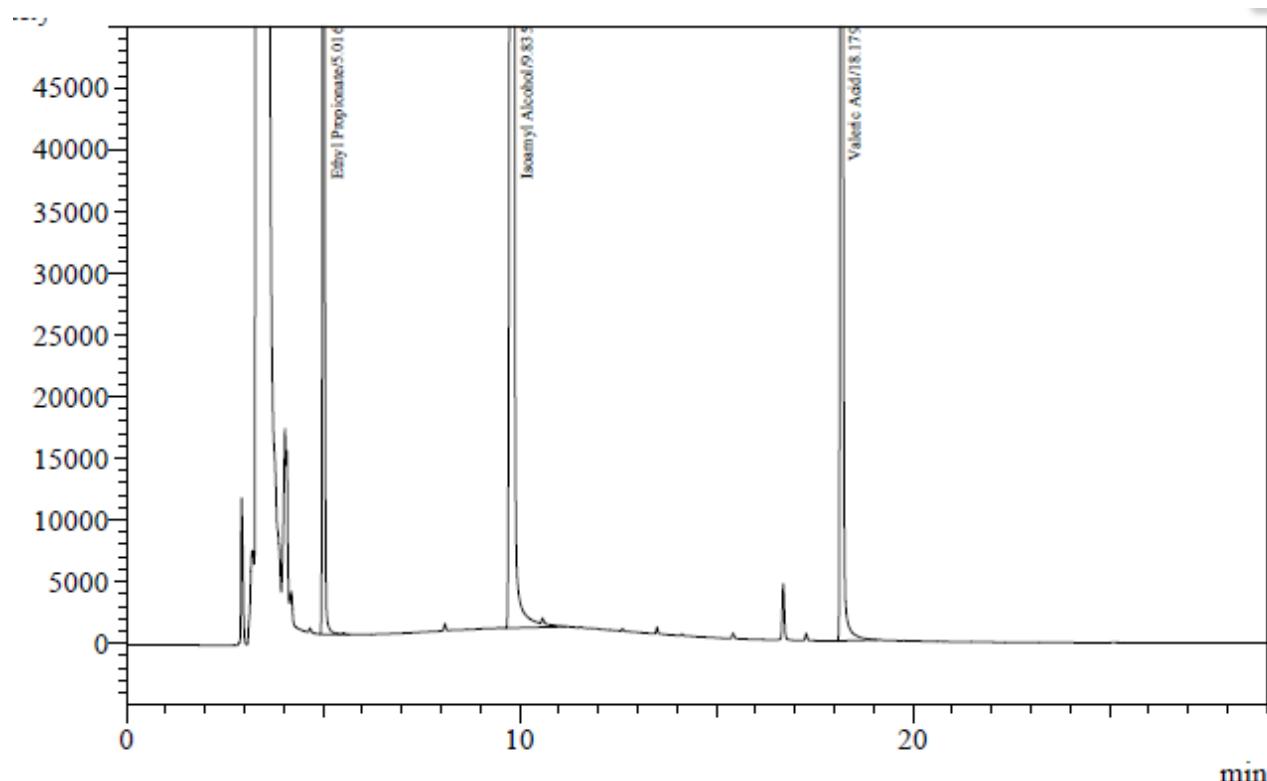


Time = 4 h



## 16. Isoamyl valerate synthesis

Time = 0 h



Time = 4 h

