

## Sustainable access to fully biobased epoxidized vegetable oil thermoset materials prepared by thermal or UV-cationic processes.

### Supporting information

#### 1. <sup>1</sup>H NMR method for the determination of VOs composition

In <sup>1</sup>H NMR spectra, the signal area is equivalent to a molar quantity. By comparing the relative integration value (integration equivalent to 1 proton) of one characteristic signal of each fatty acid with other signals, we can thus reach the proportion of each fatty acid within the analysed VO. As a representative example, the fatty acid composition determination within hemp oil is described here after. The NMR labeled signal (**8**) in Figure 2 (see scientific article) corresponds to the 4 protons of the glycerol unit and an integration of 4 was thus attributed to this signal and considered in the following equations. The relative linolenic fatty acid fraction (**LNF**) can be easily deducted from equation (**ES1**) by measuring the area of the signal labeled (**2**) at 0.96 ppm in Figure 2 (see scientific article).

$$(ES1) \quad LNF = (2)/3$$

Signal labeled (**7**) at 2.79 ppm can be attributed to 2 protons of the linoleic fatty acid and 4 protons of linolenic fatty acid. Thus, the relative linoleic fatty acid fraction (**LF**) can be evaluated by substituting the linolenic fatty acid fraction based on this following equation (**ES2**):

$$(ES2) \quad LF = ((7) - (LNF*4))/2$$

Signal labeled (**10**) at 5.3 ppm combines the total ethylenic protons of linolenic, linoleic and oleic fatty acids. Thanks to signal labeled (**8**), which is equivalent to 4 protons of the glycerol unit, the overlapping issue of signal labeled (**10**) with signal labeled (**9**) (equivalent to 1 proton of the glycerol moiety) can be solved out. Therefore, the relative oleic fatty acid fraction (**OF**) is extracted with the equation (**ES3**):

$$(ES3) \quad OF = ((10) - (LF*4) - (LNF*6))/2$$

Signal labeled (**5**) at 2.0 ppm can also be used for the determination of **OF**. In this case, equation (**ES4**) is applied:

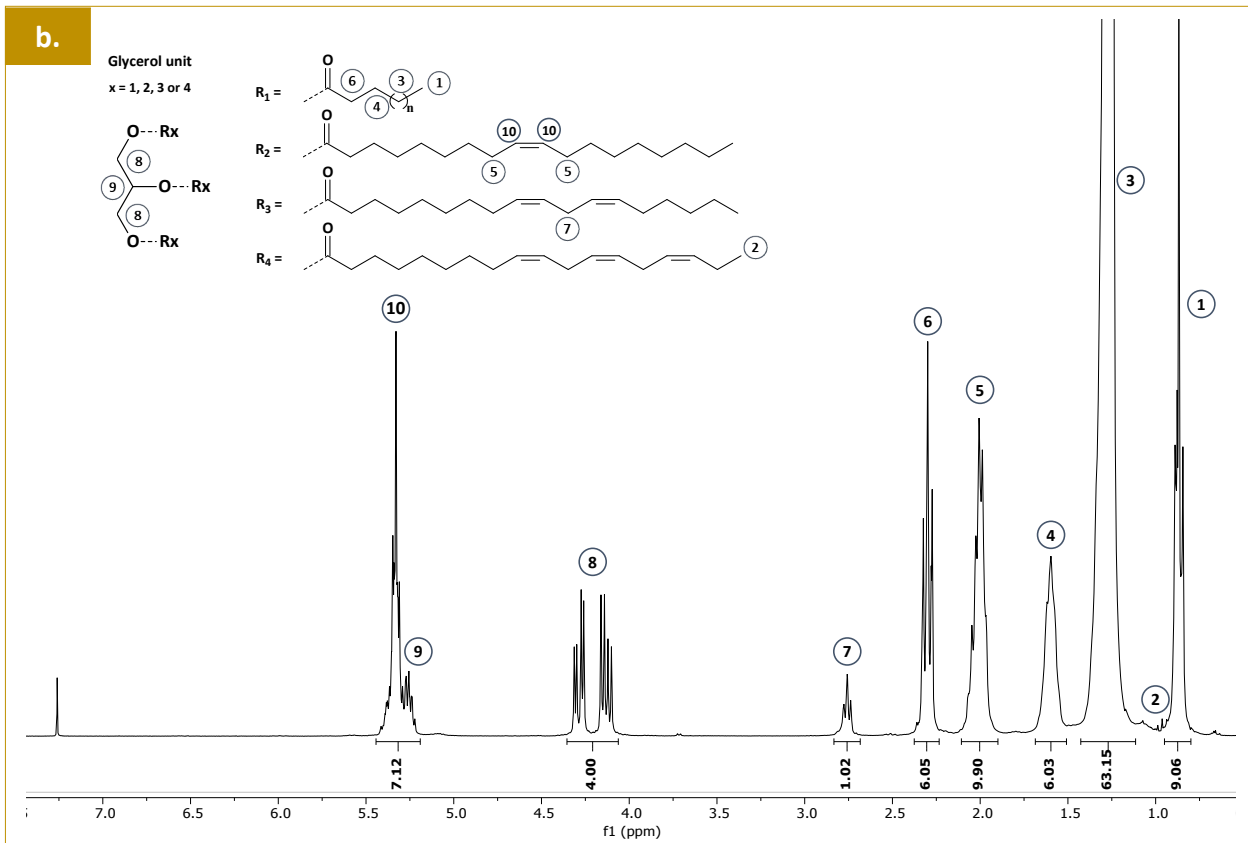
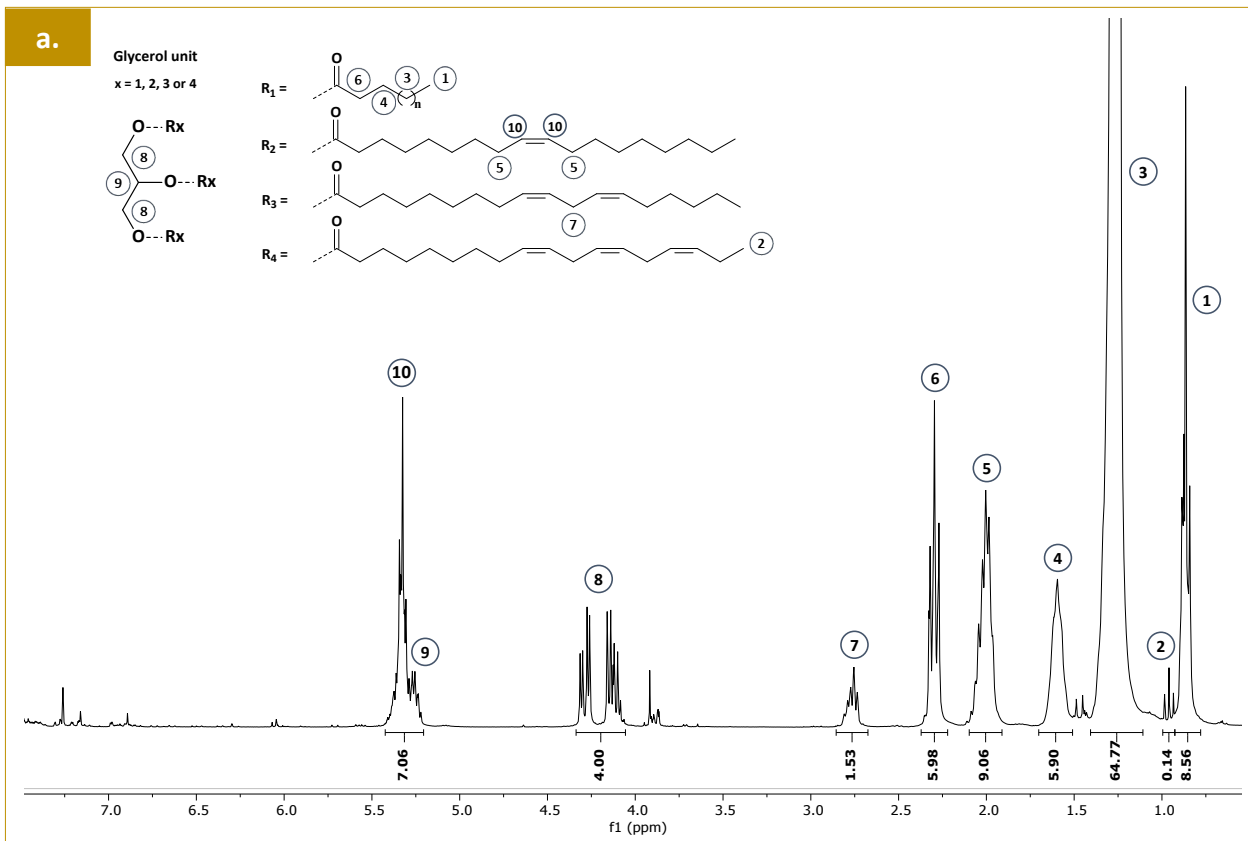
$$(ES4) \quad OF = ((5) - (LF*4) - (LNF*4))/4$$

Finally, the relative saturated fatty acid fraction (**SF**) is assessed by using signal (**1**) at 0.87 ppm which is attributed to the terminal methyl group of all the fatty acids apart from linolenic fatty acid (signal (**2**)). The SF is determined by equation (**ES5**):

$$(ES5) \quad SF = ((1) - (OF*3) - (LF*3))/3$$

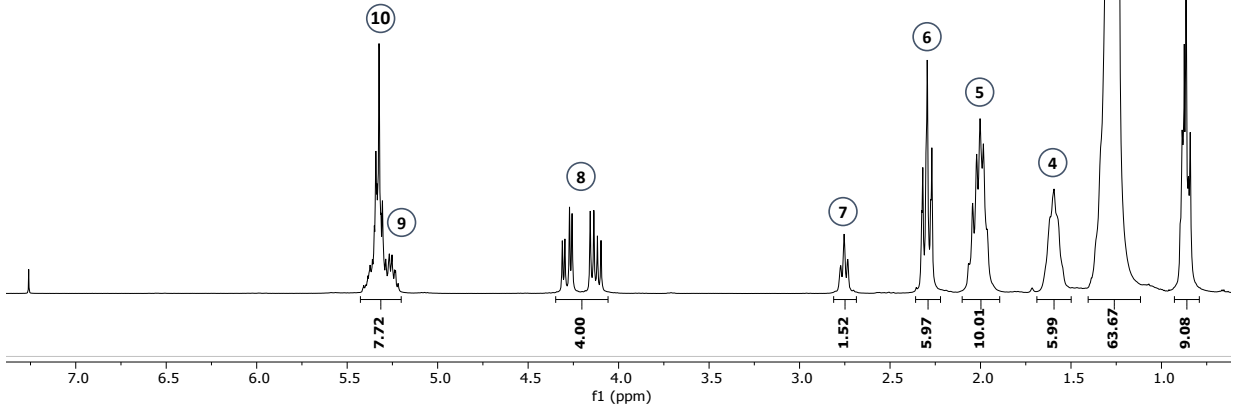
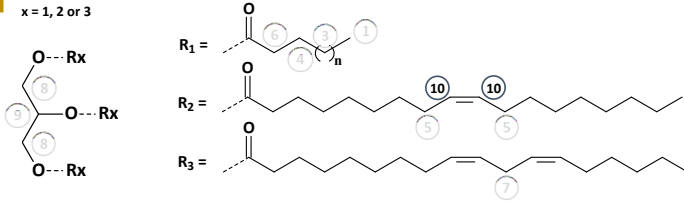
By combining these equations, the proportion of each fatty acids comprised within the selected VOs can be determined.

## 2. <sup>1</sup>H NMR analysis of VO raw materials



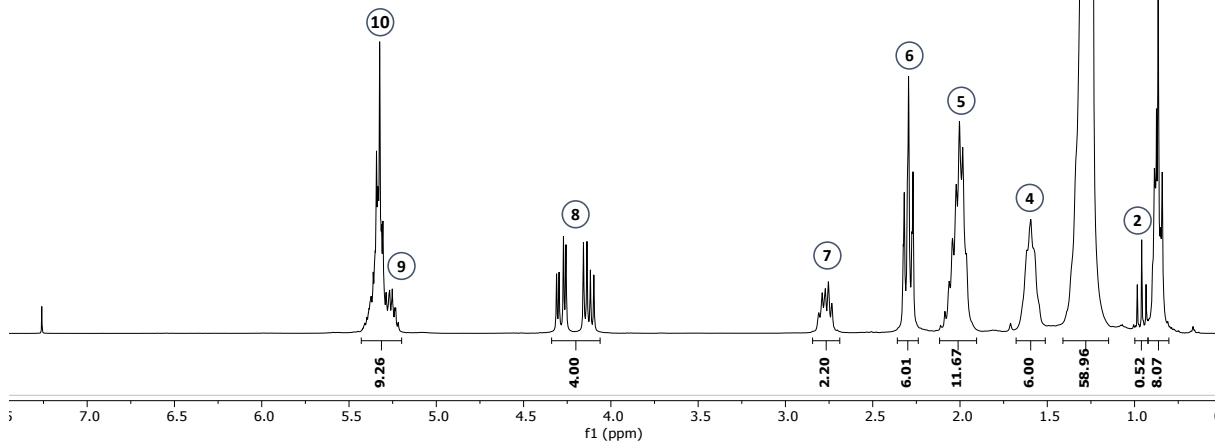
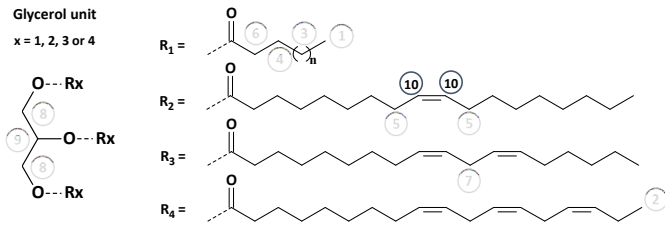
C.

Glycerol unit  
x = 1, 2 or 3



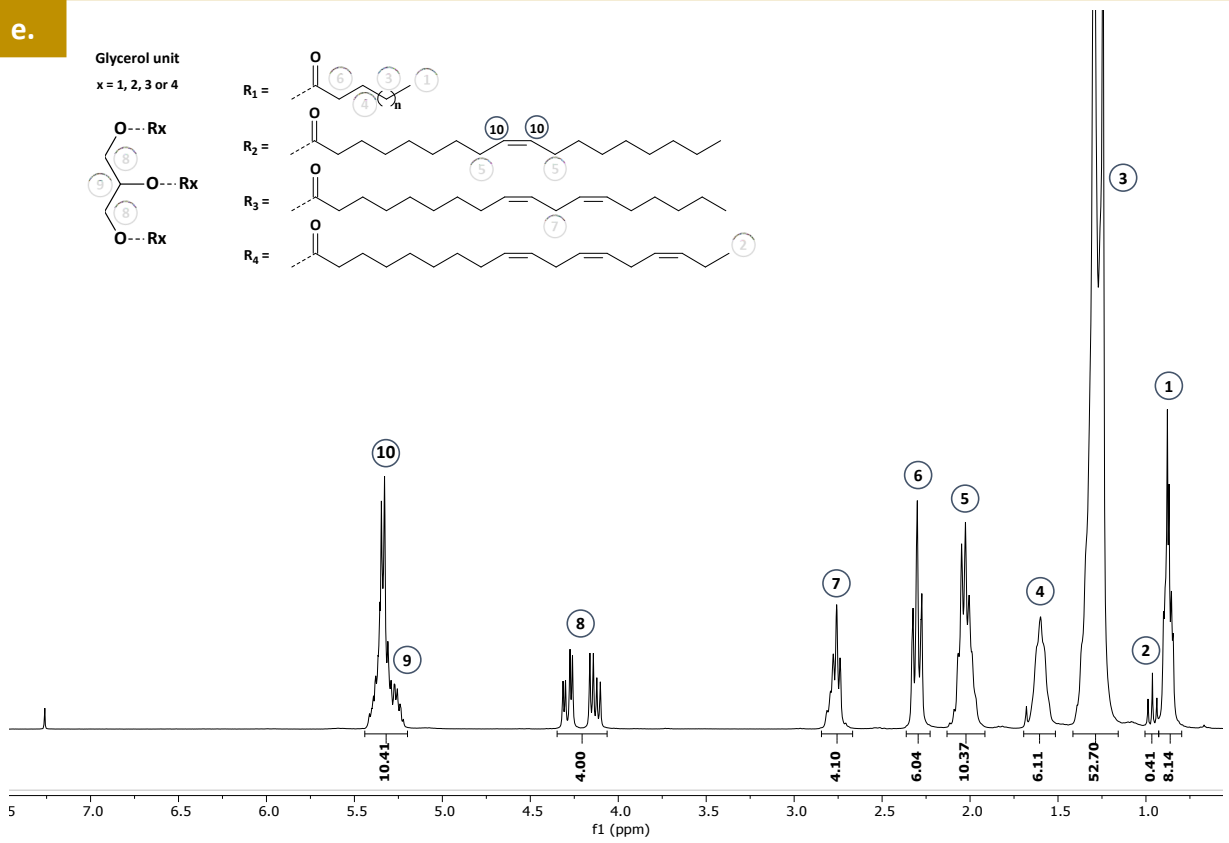
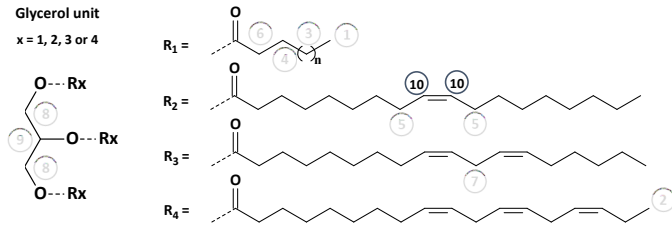
d.

Glycerol unit  
x = 1, 2, 3 or 4



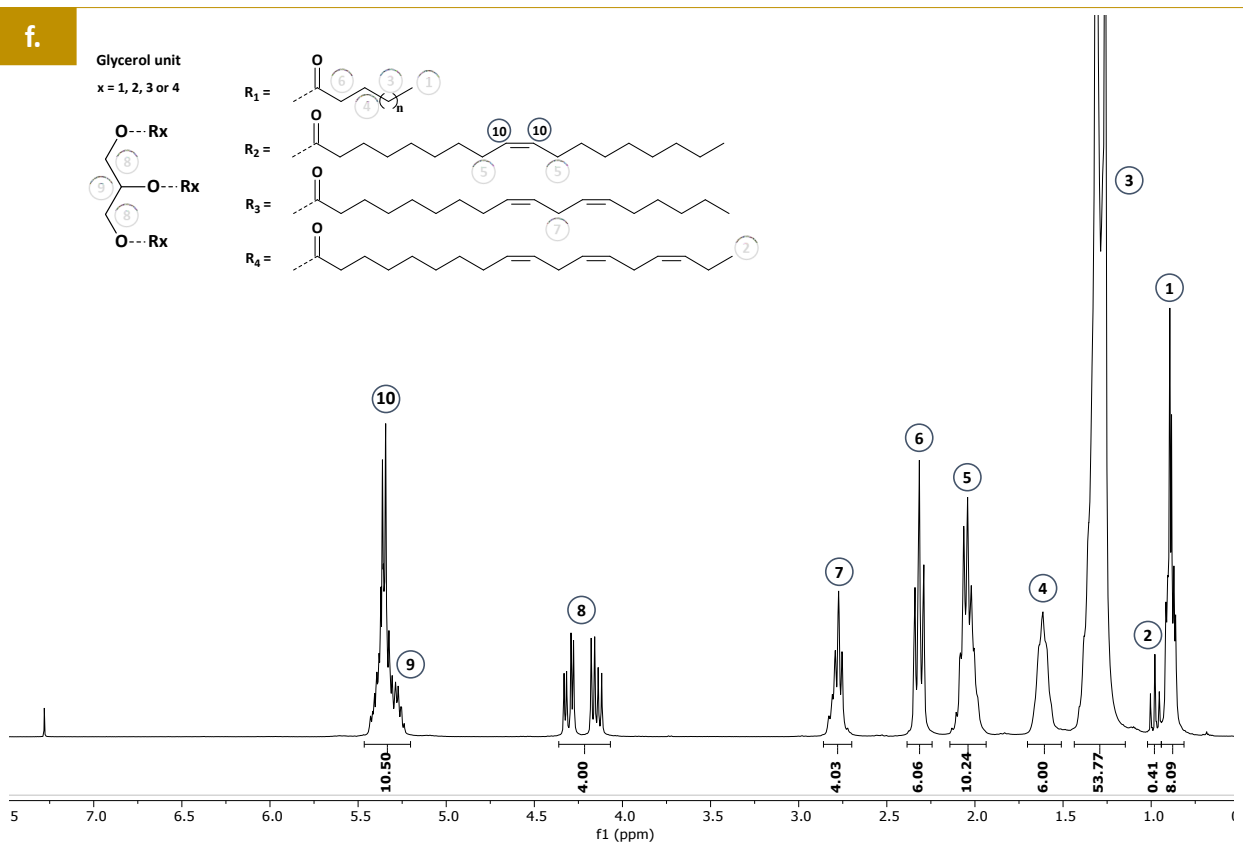
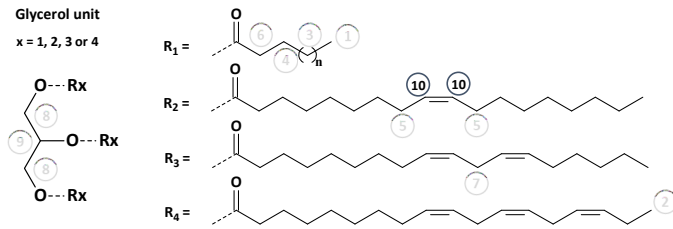
e.

Glycerol unit  
x = 1, 2, 3 or 4



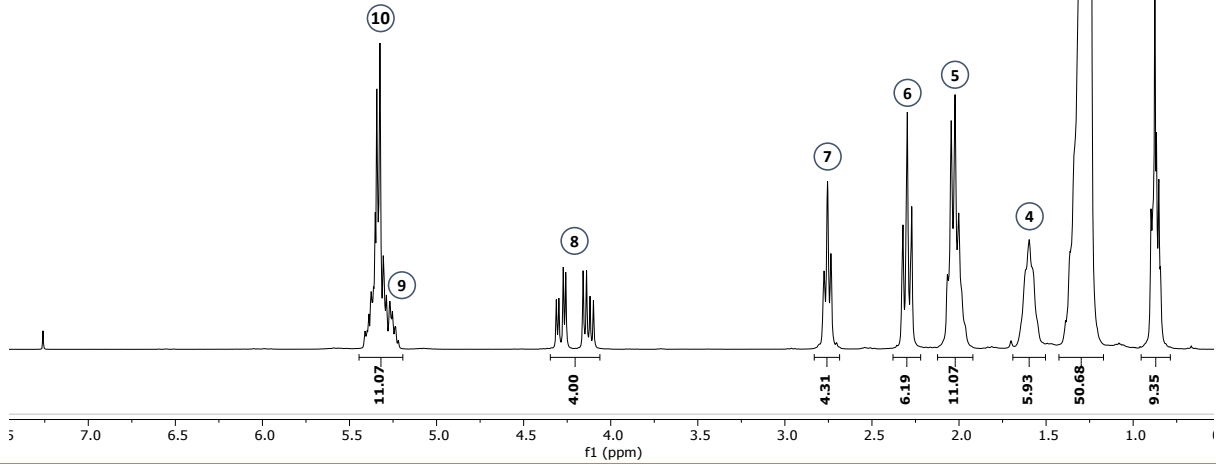
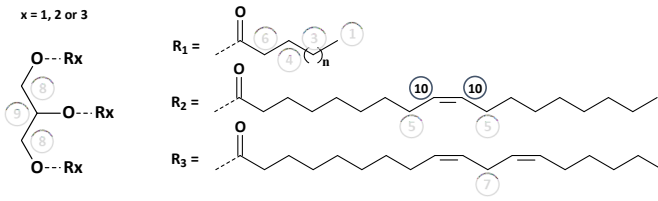
f.

Glycerol unit  
x = 1, 2, 3 or 4



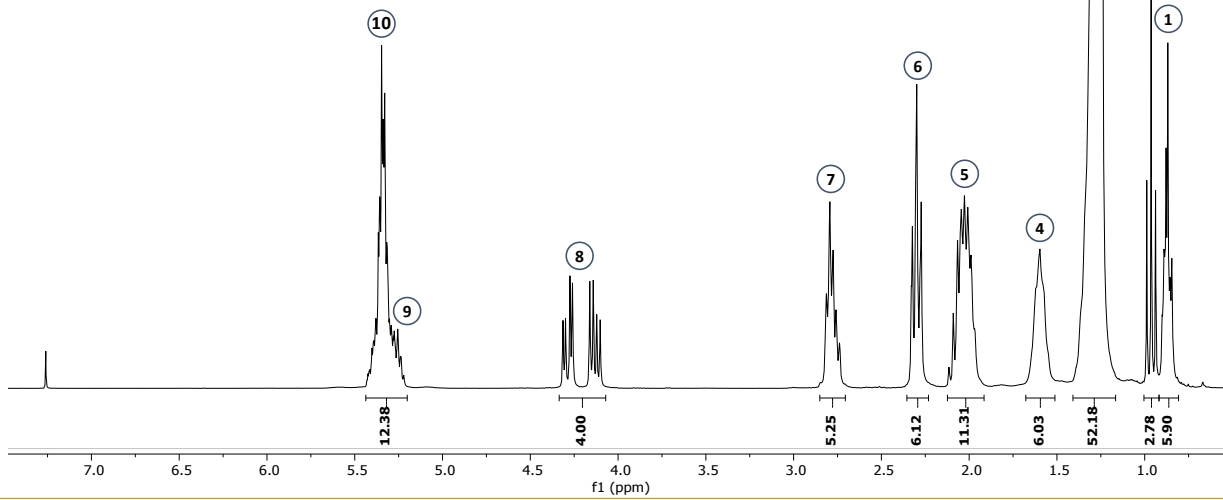
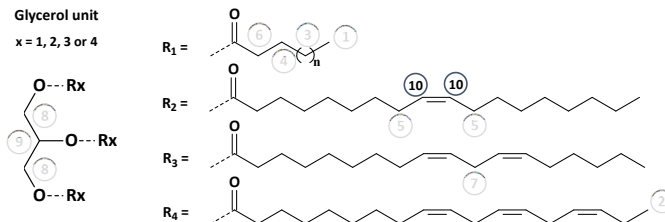
g.

Glycerol unit  
x = 1, 2 or 3



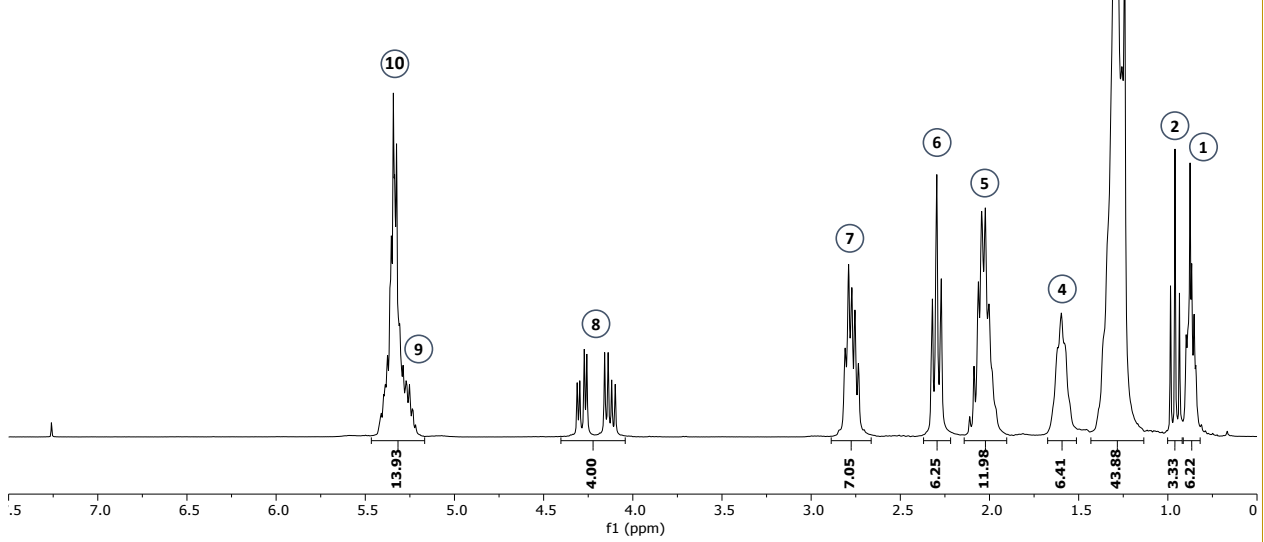
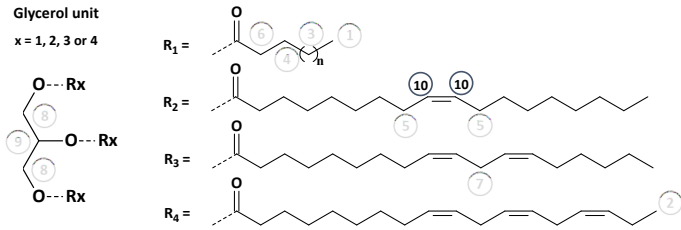
h.

Glycerol unit  
x = 1, 2, 3 or 4



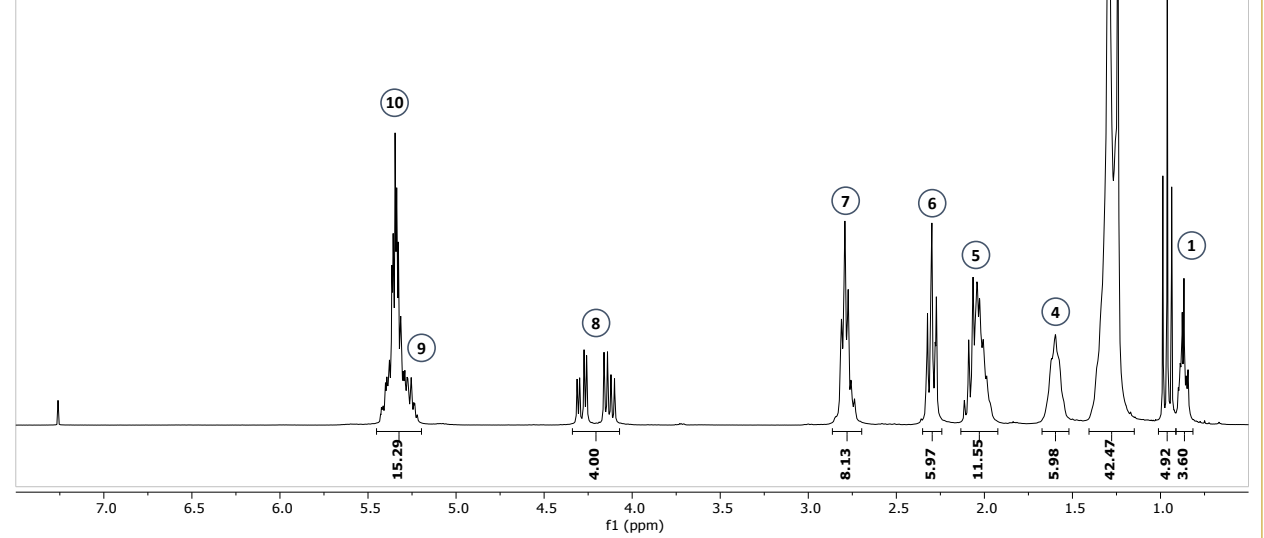
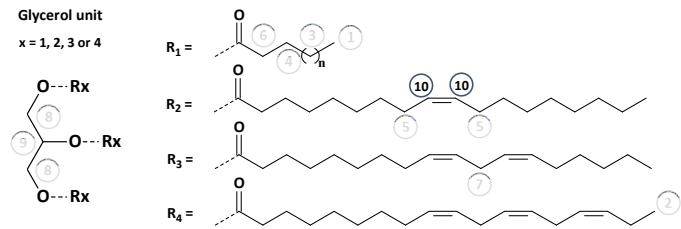
i.

Glycerol unit  
x = 1, 2, 3 or 4



j.

Glycerol unit  
x = 1, 2, 3 or 4



k.

Glycerol unit  
x = 1, 2, 3 or 4

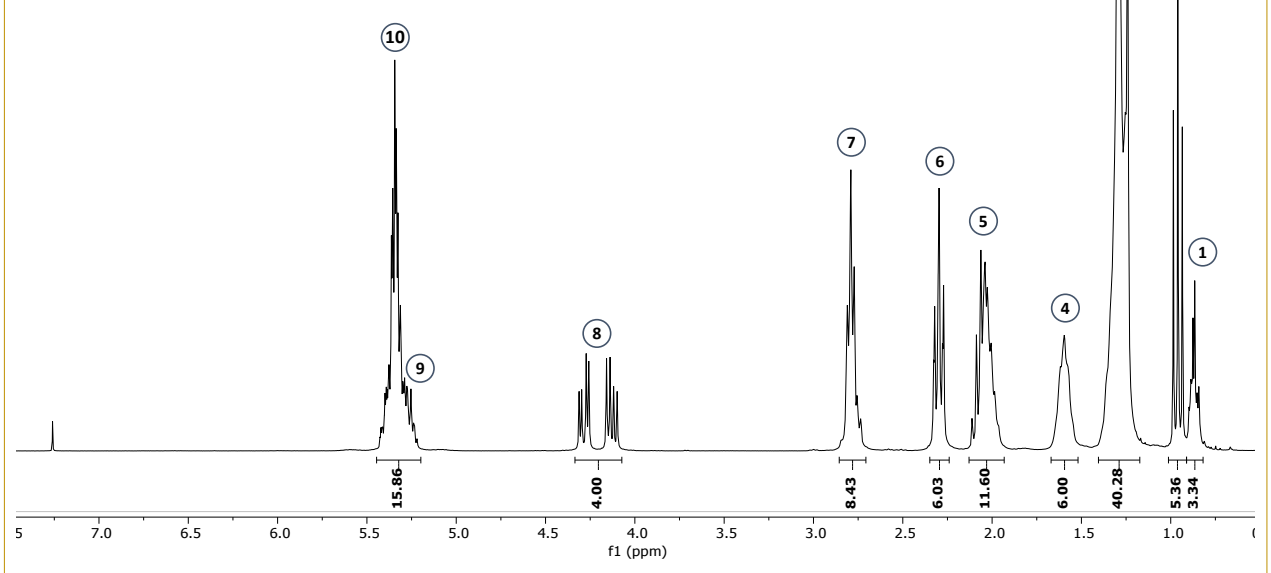
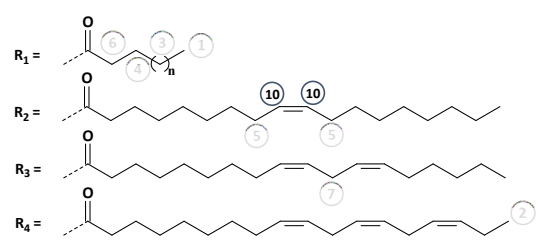
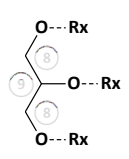
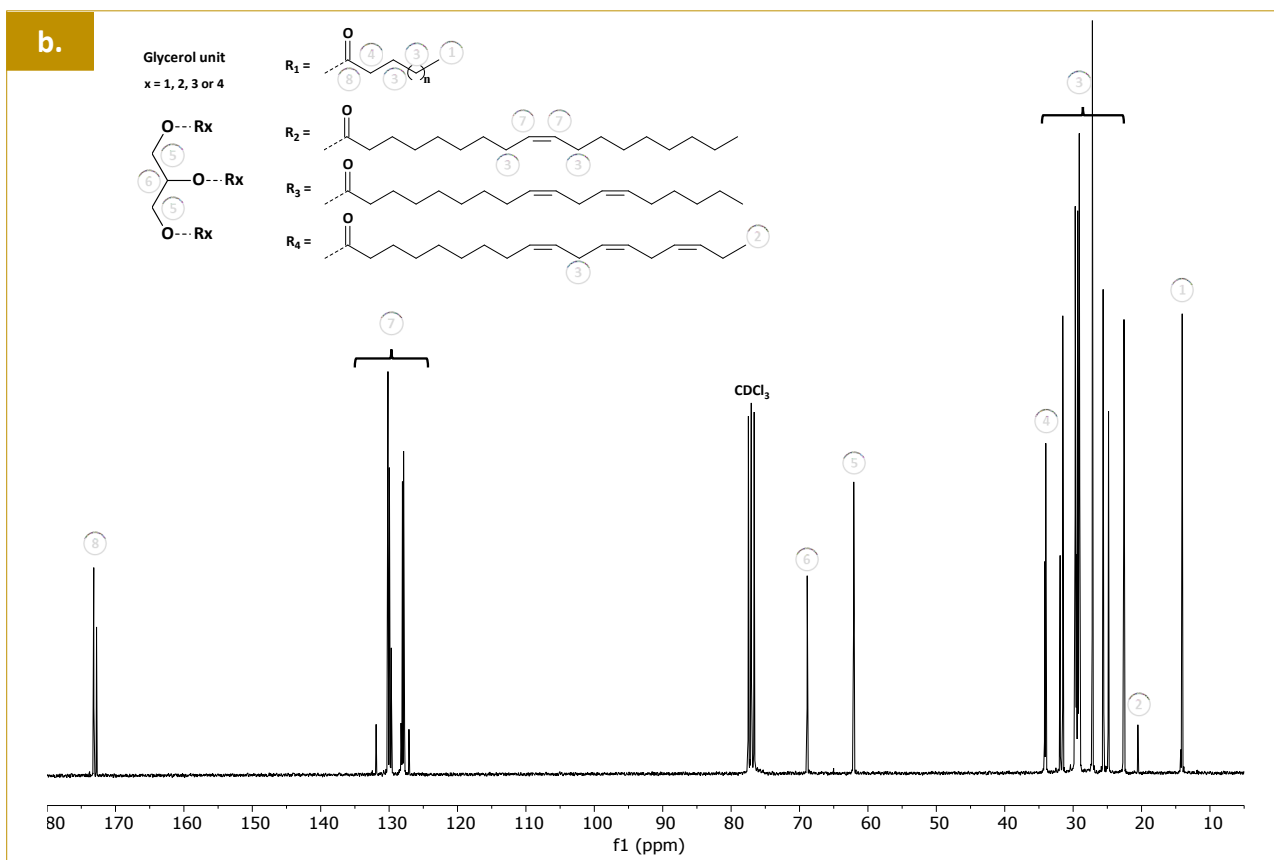
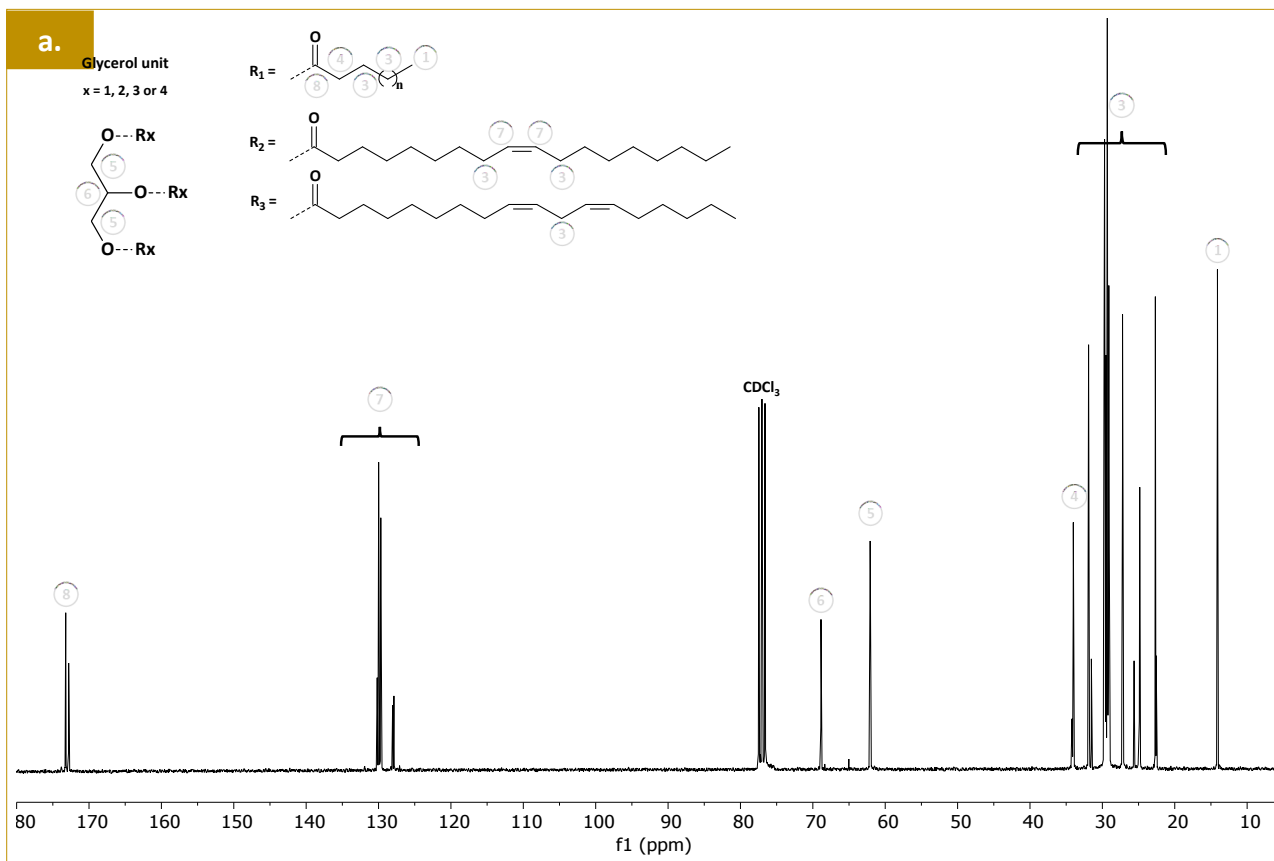


Figure S2. <sup>1</sup>H NMR of Karanja oil (VO 1) (a), St John's Wort oil (VO 2) (b), Peanut oil (VO 3) (c), Rapeseed oil (VO 4) (d), Soybean oil (VO 5) (e), Rose hip seed oil (VO 6) (f), Safflower oil (VO 7) (g), Camelina oil (VO 8) (h), Rose Hip seed oil (VO 10) (i), Linseed oil (VO 11) (j) and Perilla oil (VO 12) (k).

### 3. <sup>13</sup>C NMR analysis of VO raw materials





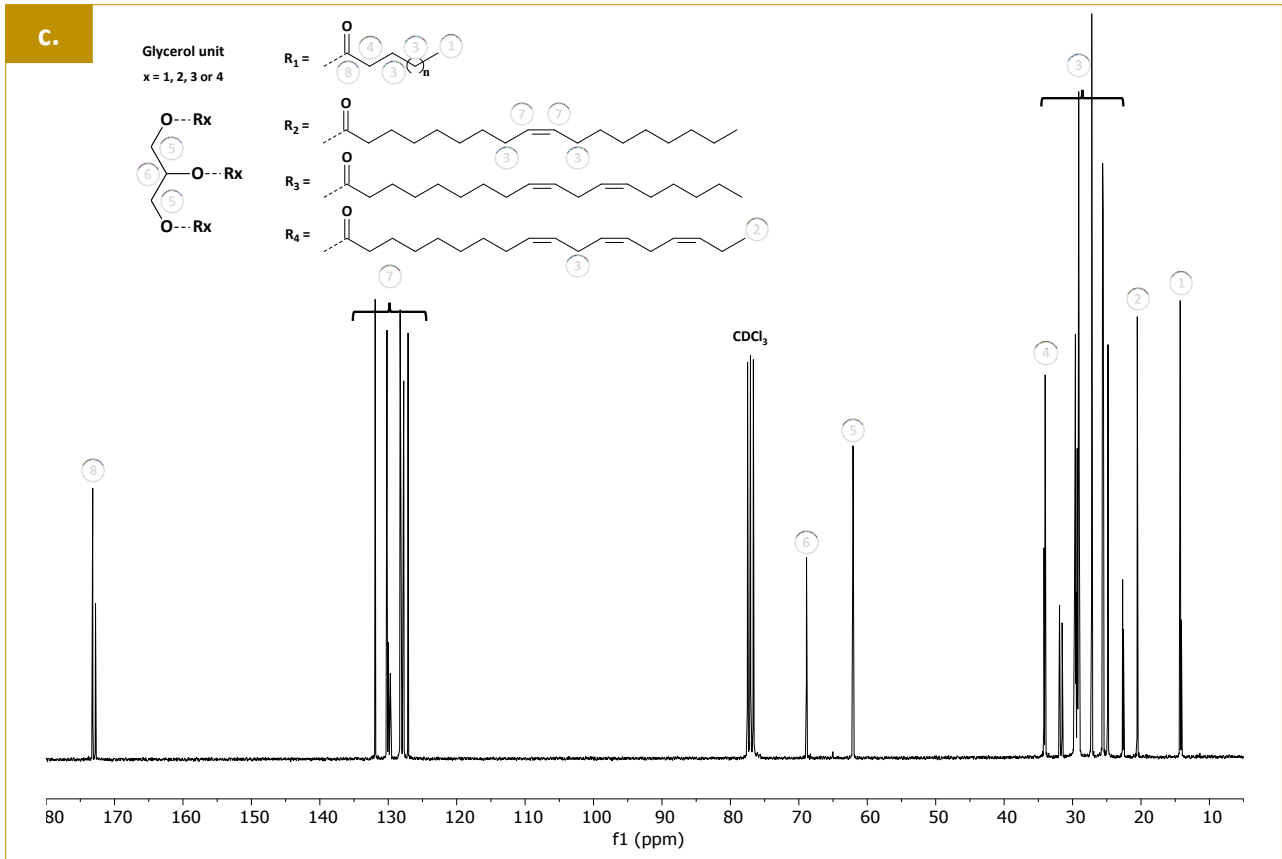
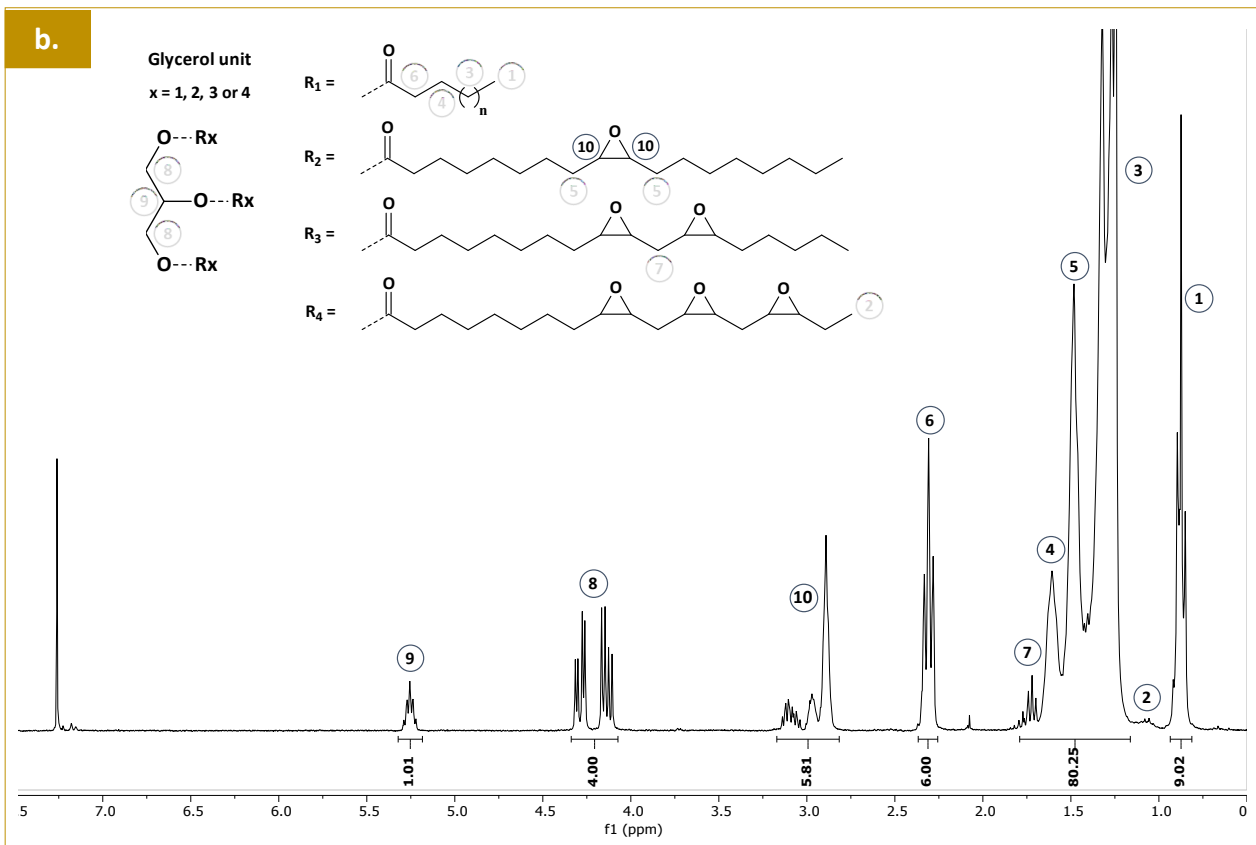
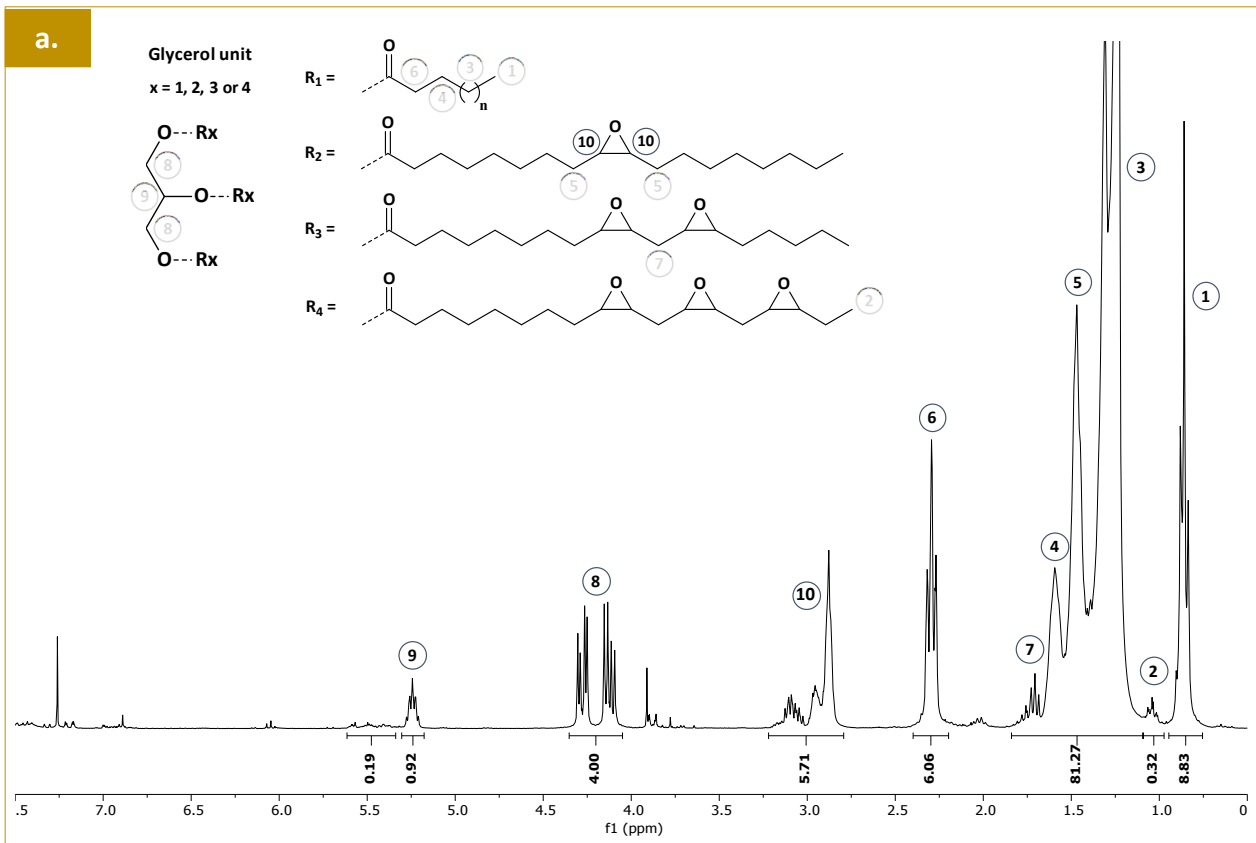


Figure S3. <sup>13</sup>C NMR of some vegetable oils: St John's Wort oil (VO 2) (a), Rose hip seed oil (VO 6) (b) and Perilla oil (VO 12) (c).

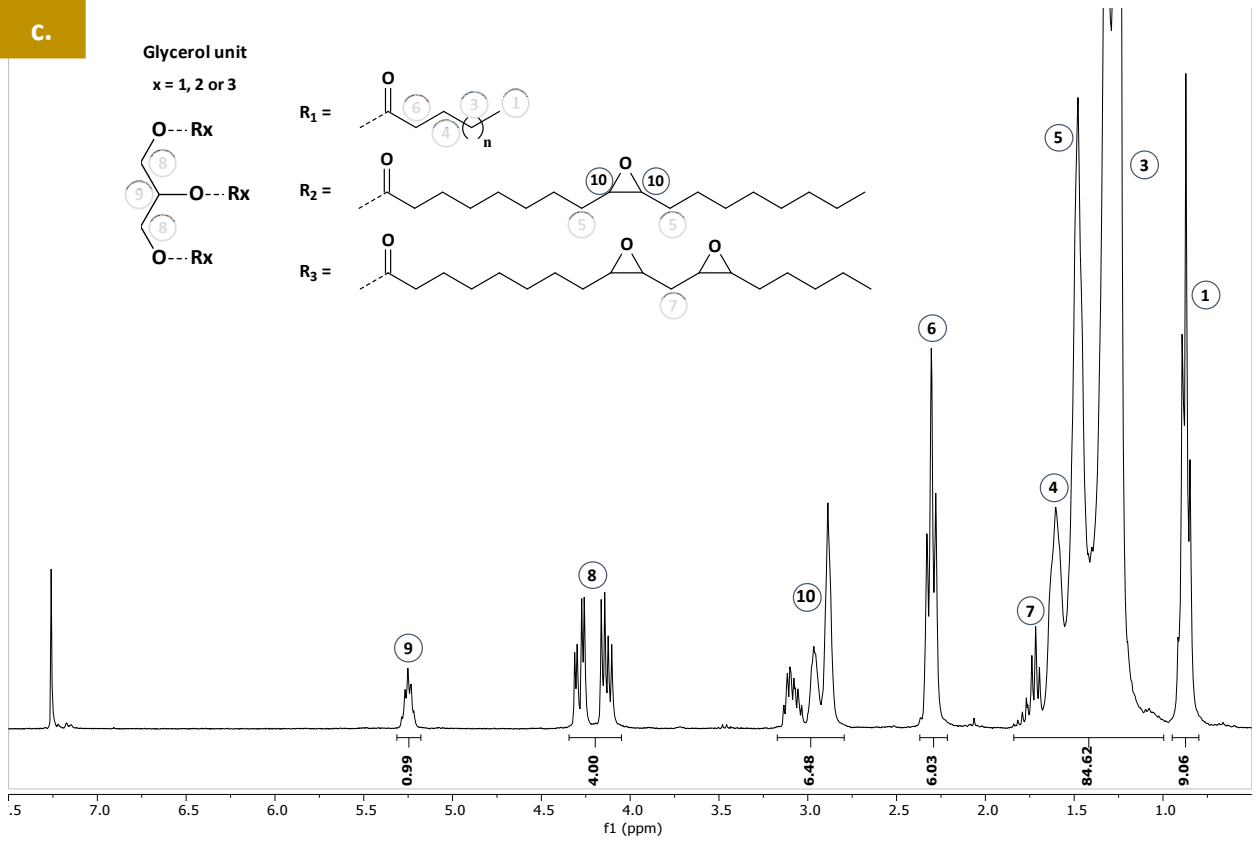
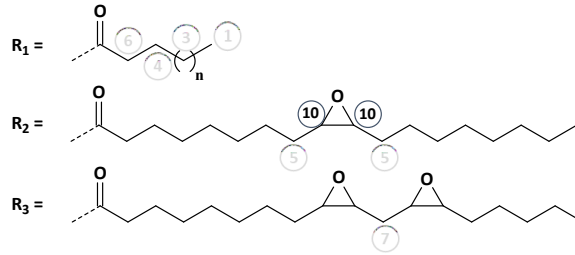
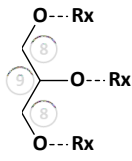
#### 4. $^1\text{H}$ NMR analysis of EVOs



c.

Glycerol unit

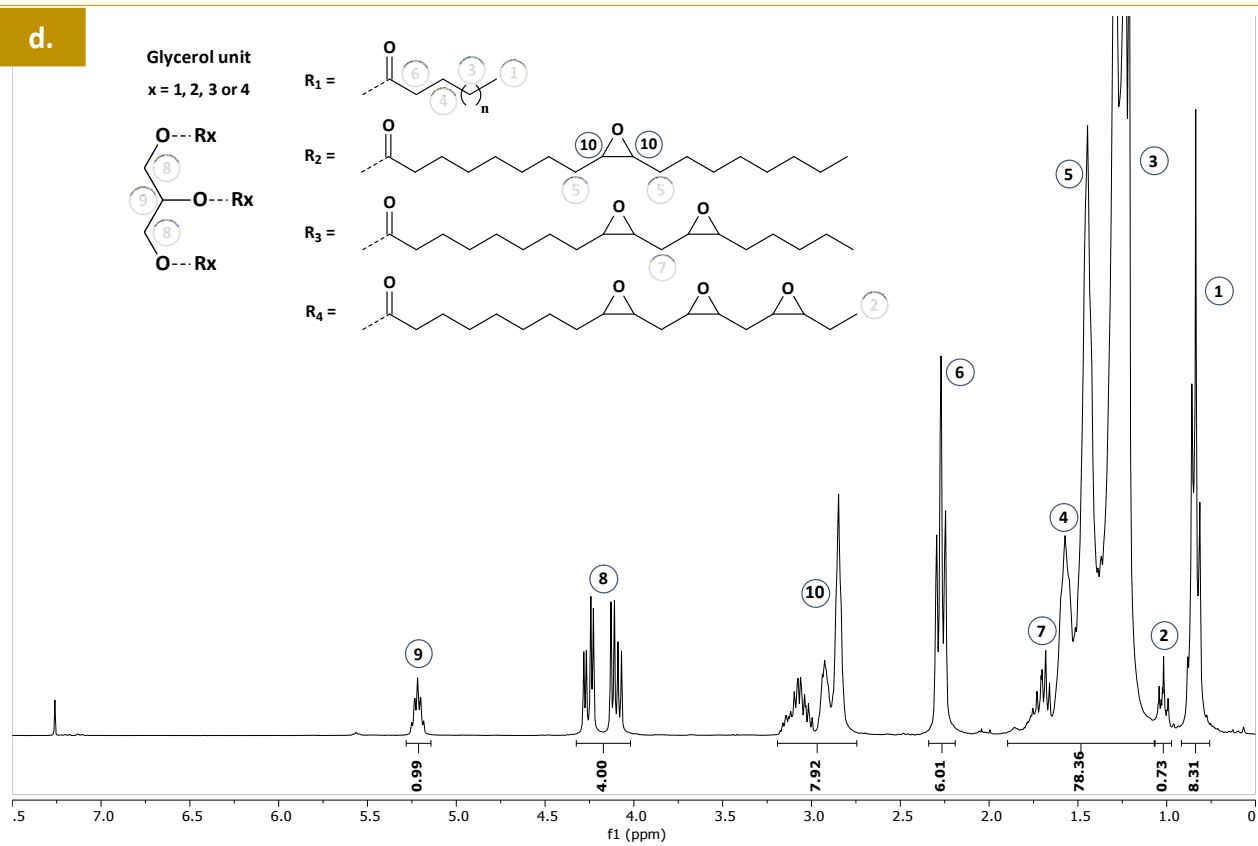
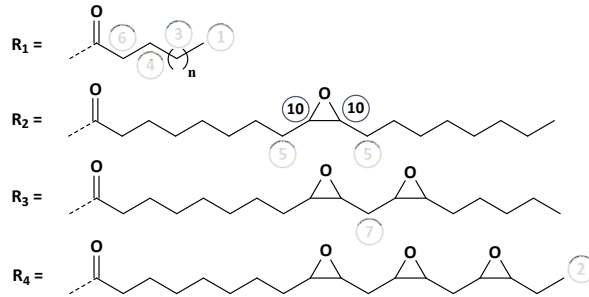
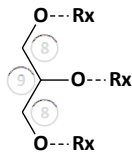
x = 1, 2 or 3



d.

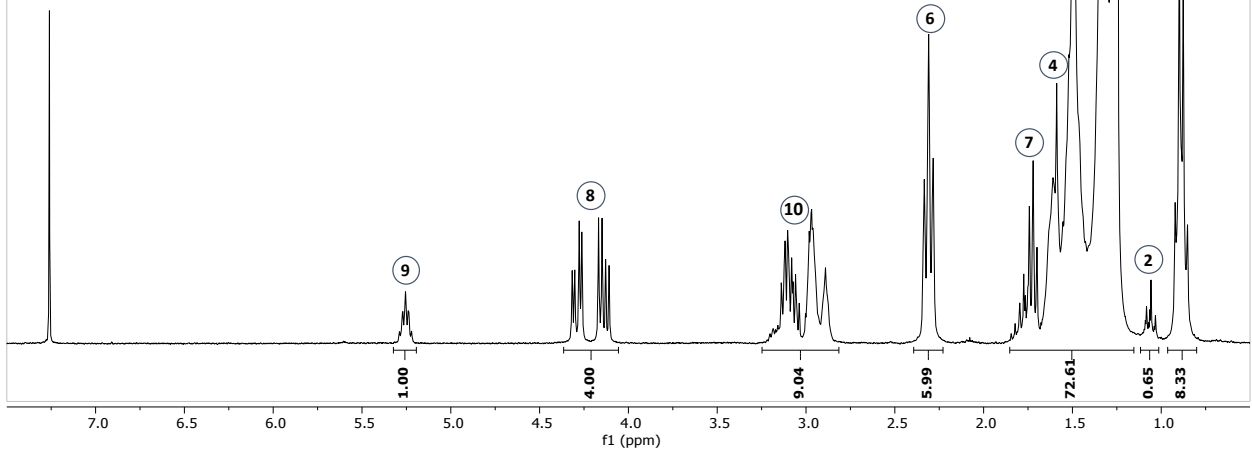
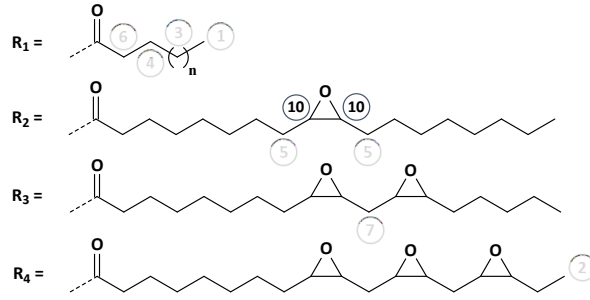
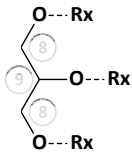
Glycerol unit

x = 1, 2, 3 or 4



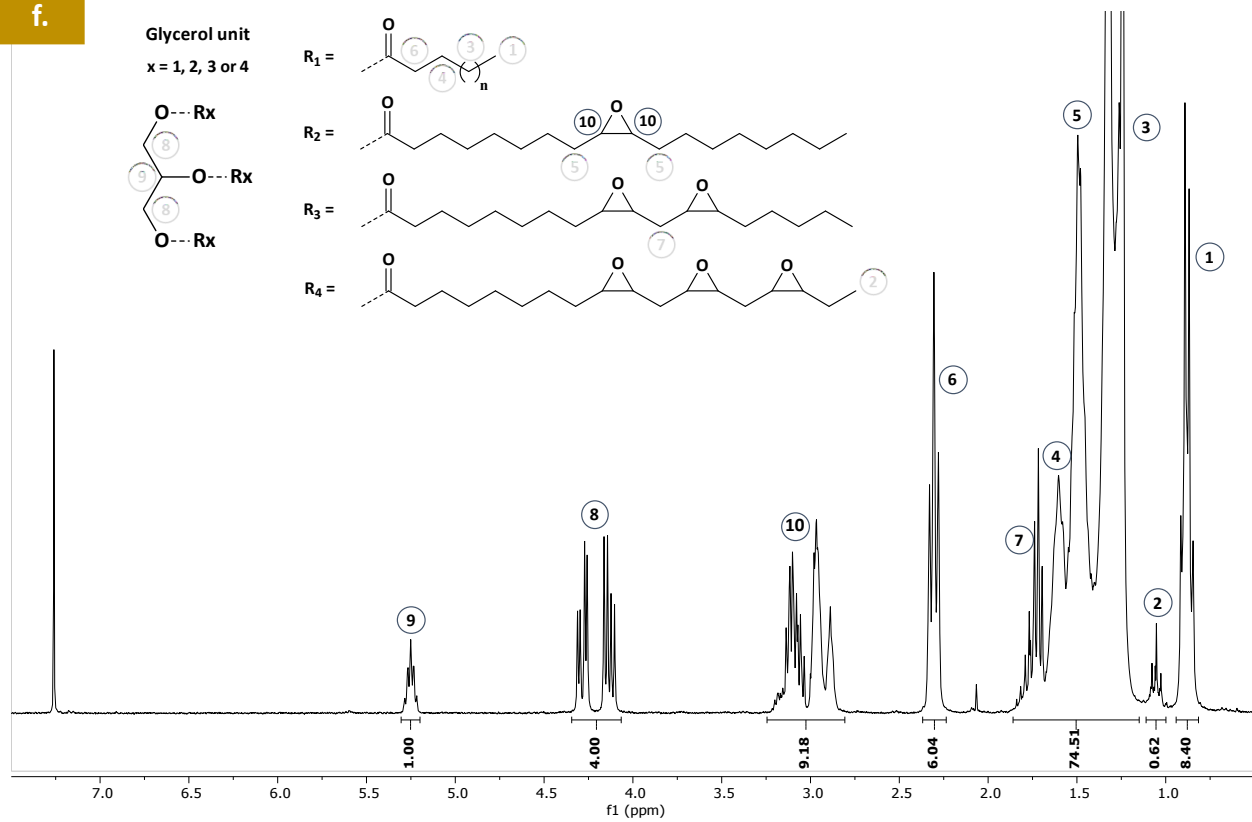
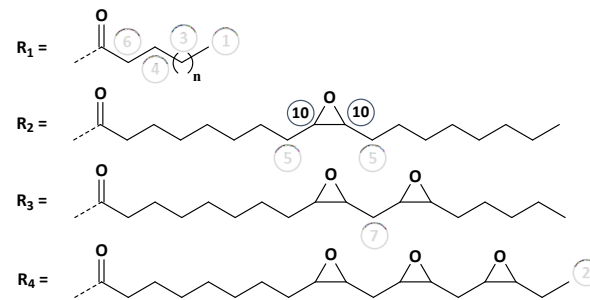
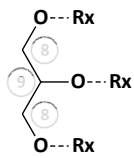
e.

Glycerol unit  
x = 1, 2, 3 or 4



f.

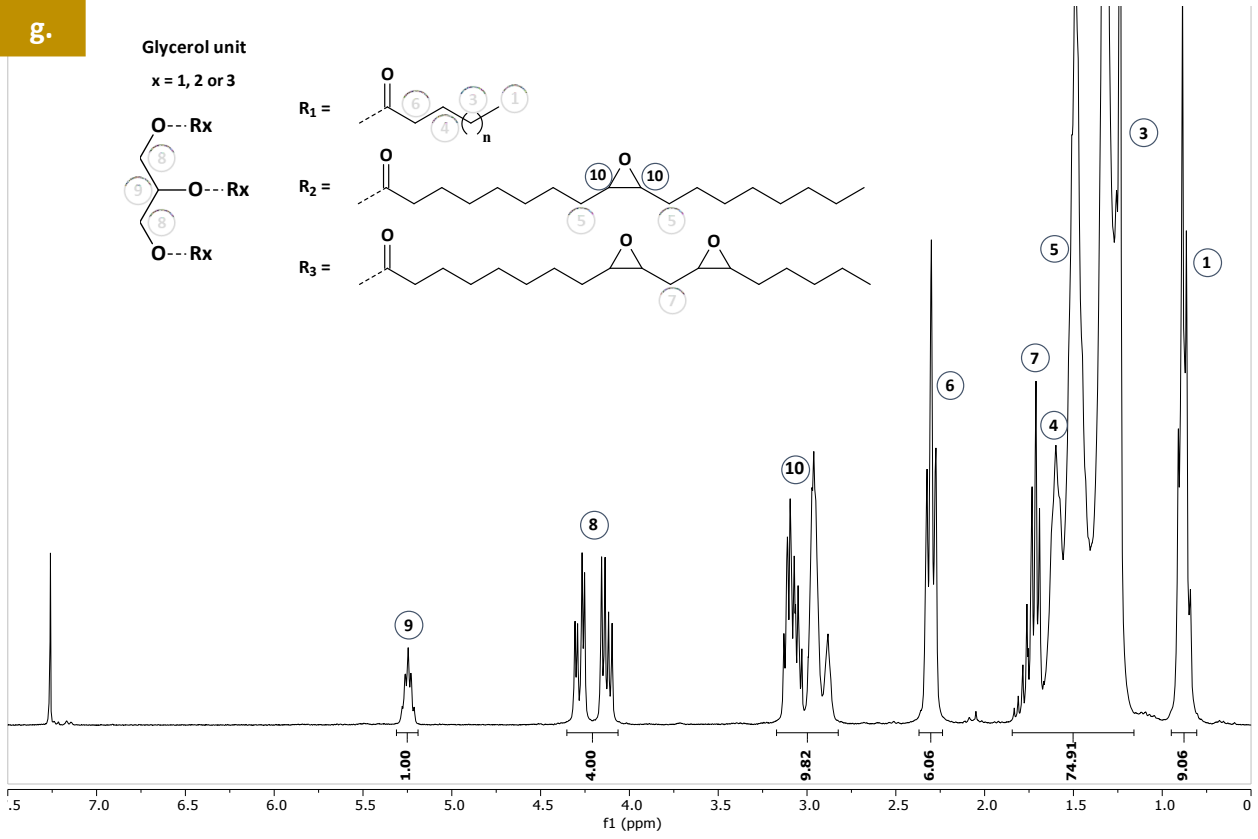
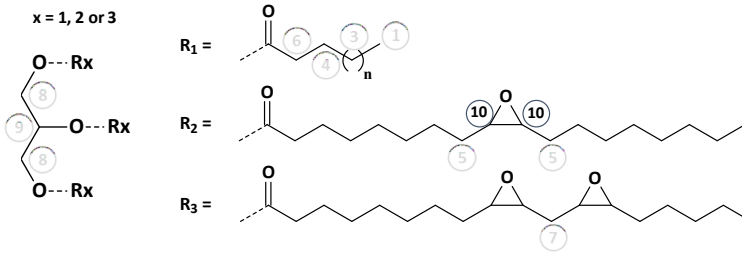
Glycerol unit  
x = 1, 2, 3 or 4



g.

Glycerol unit

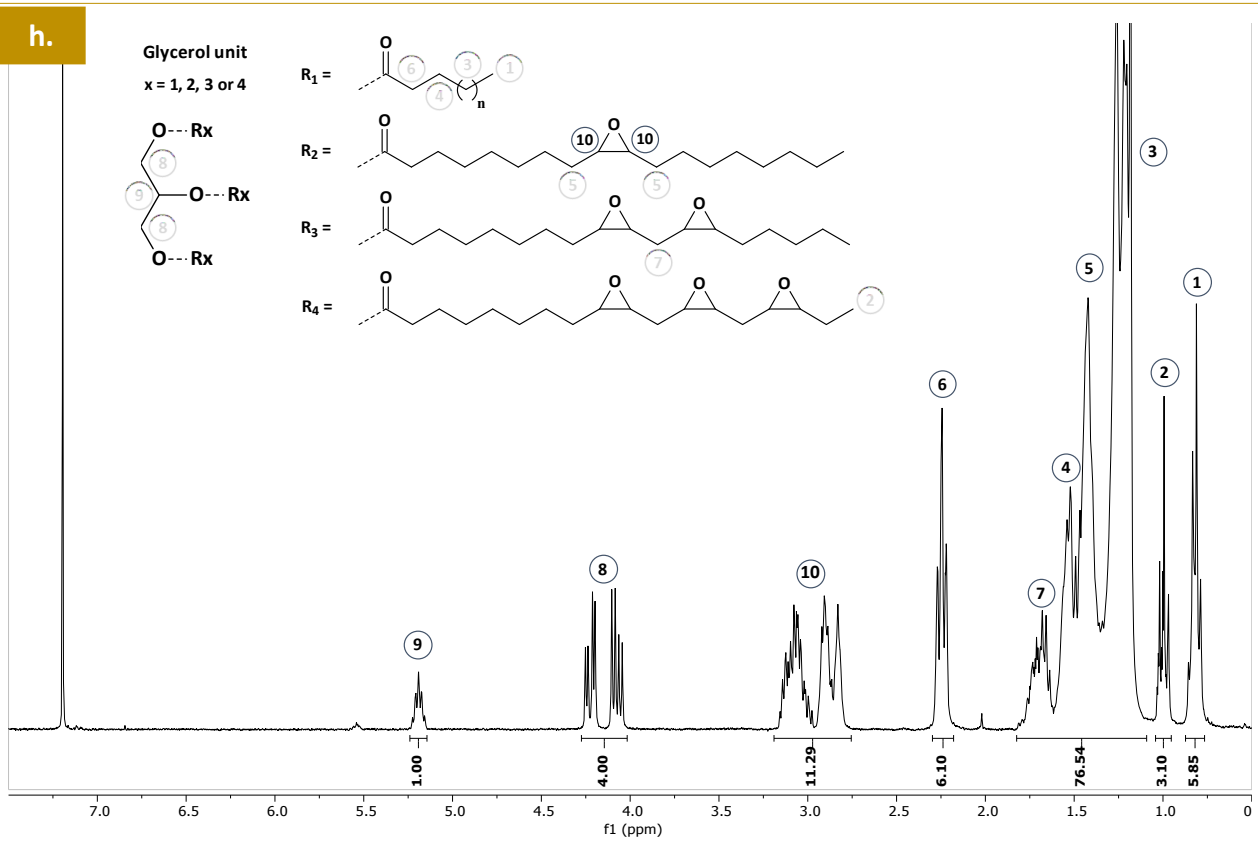
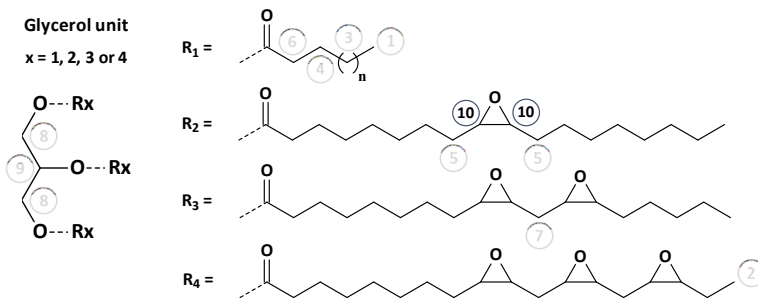
x = 1, 2 or 3



h.

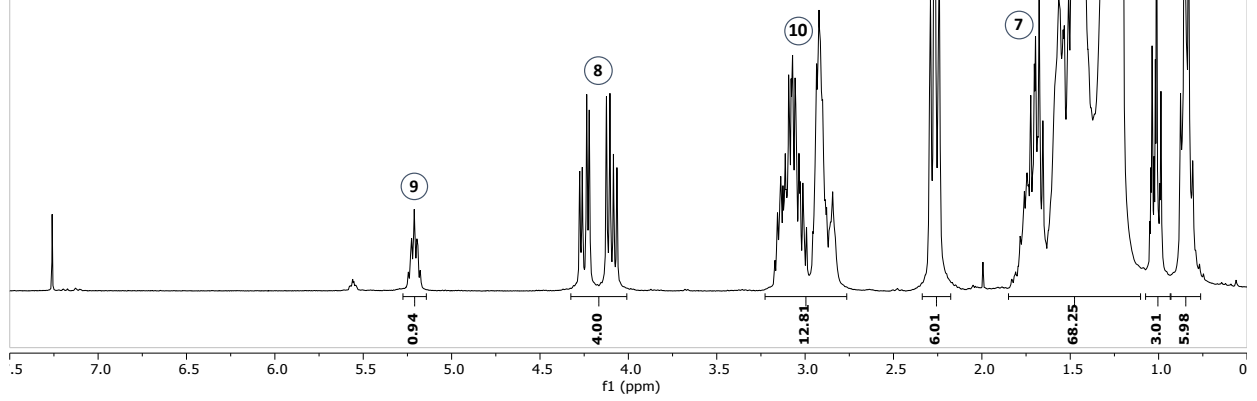
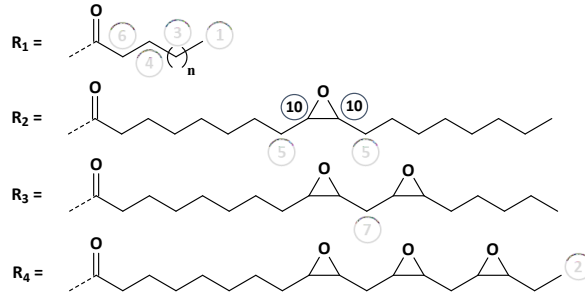
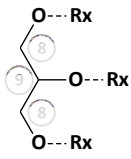
Glycerol unit

x = 1, 2, 3 or 4



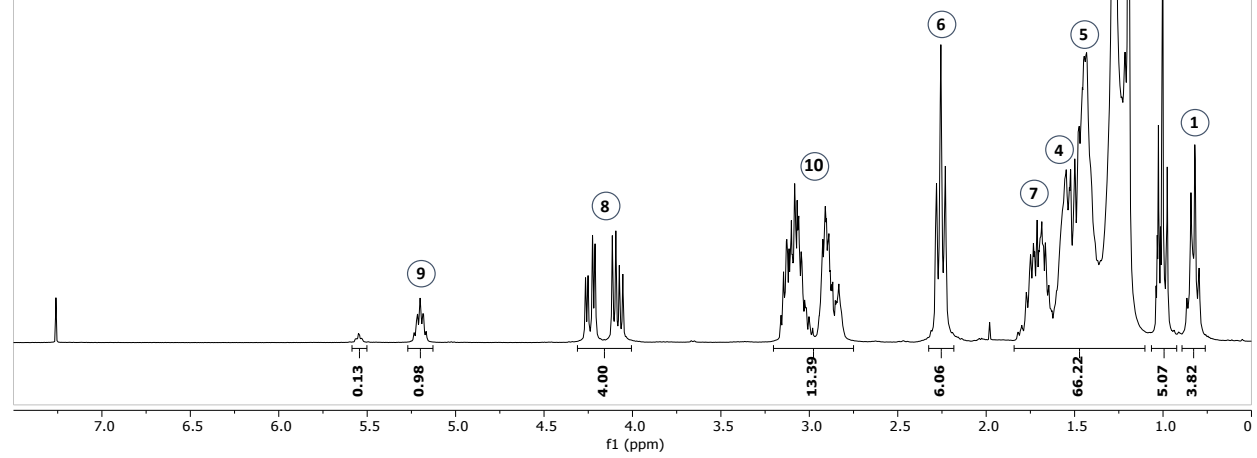
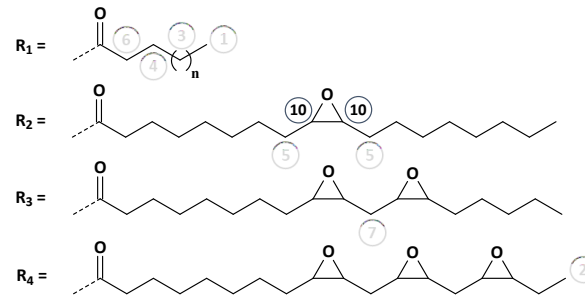
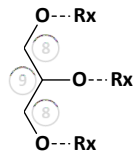
i.

Glycerol unit  
x = 1, 2, 3 or 4



j.

Glycerol unit  
x = 1, 2, 3 or 4



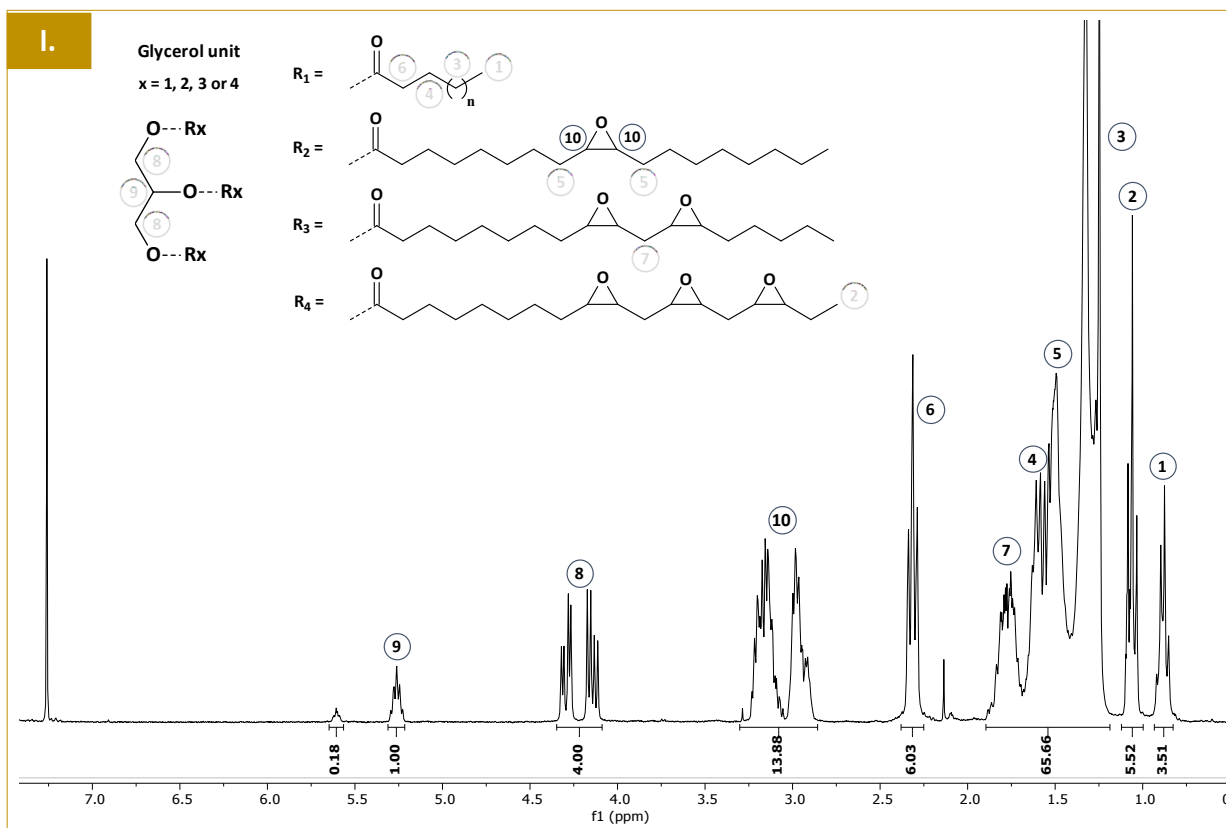
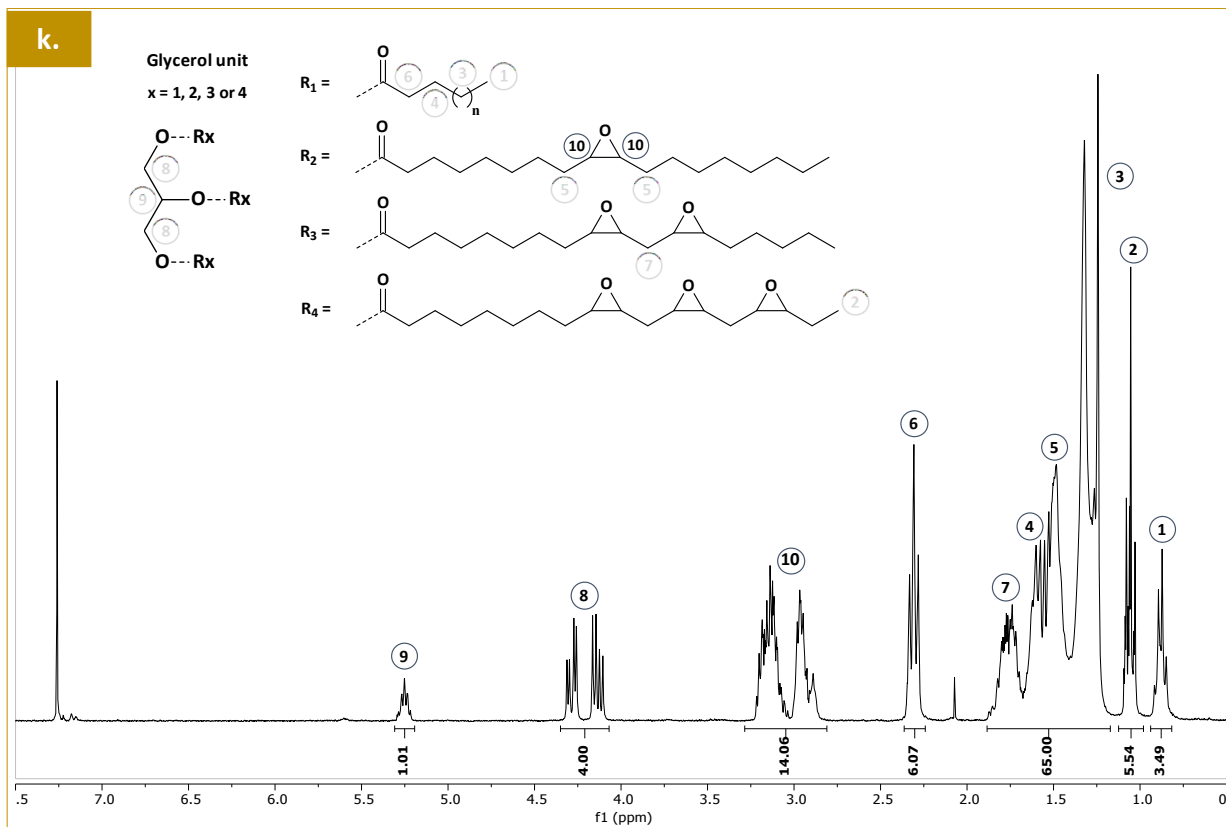
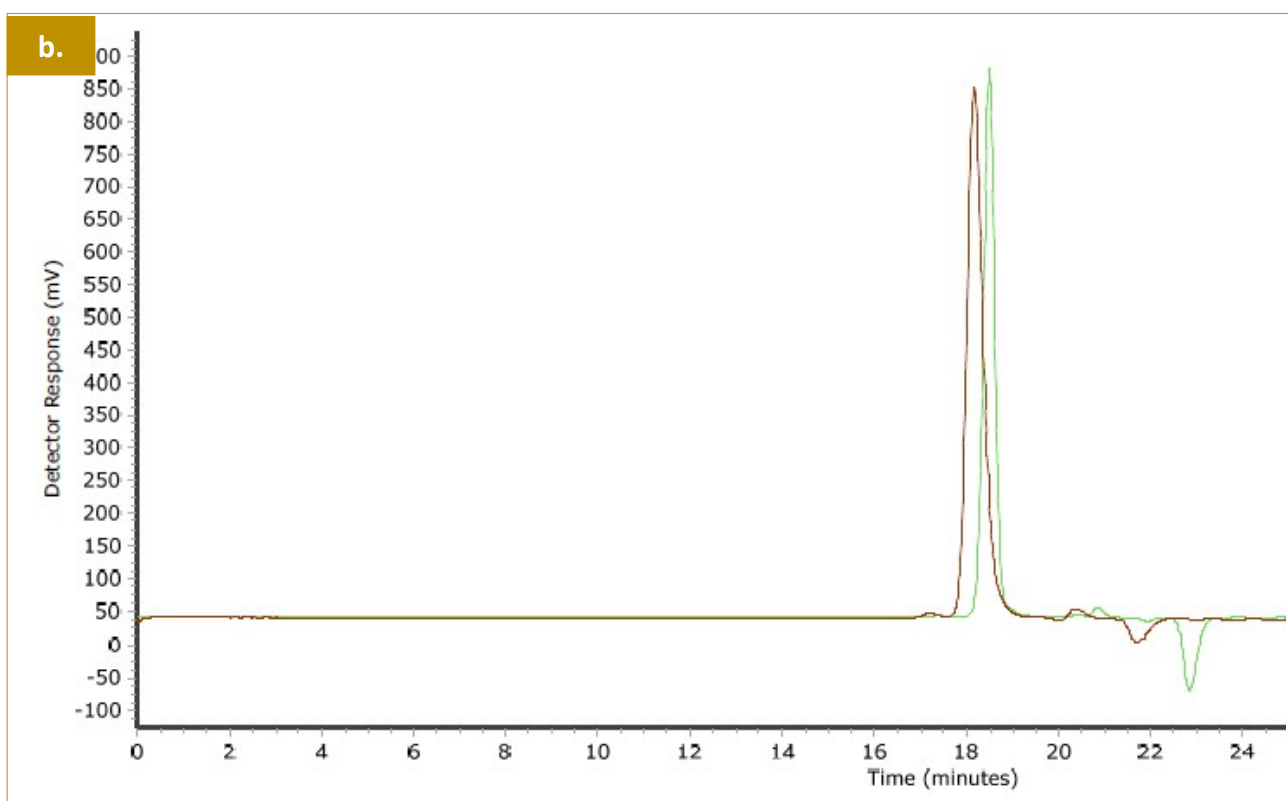
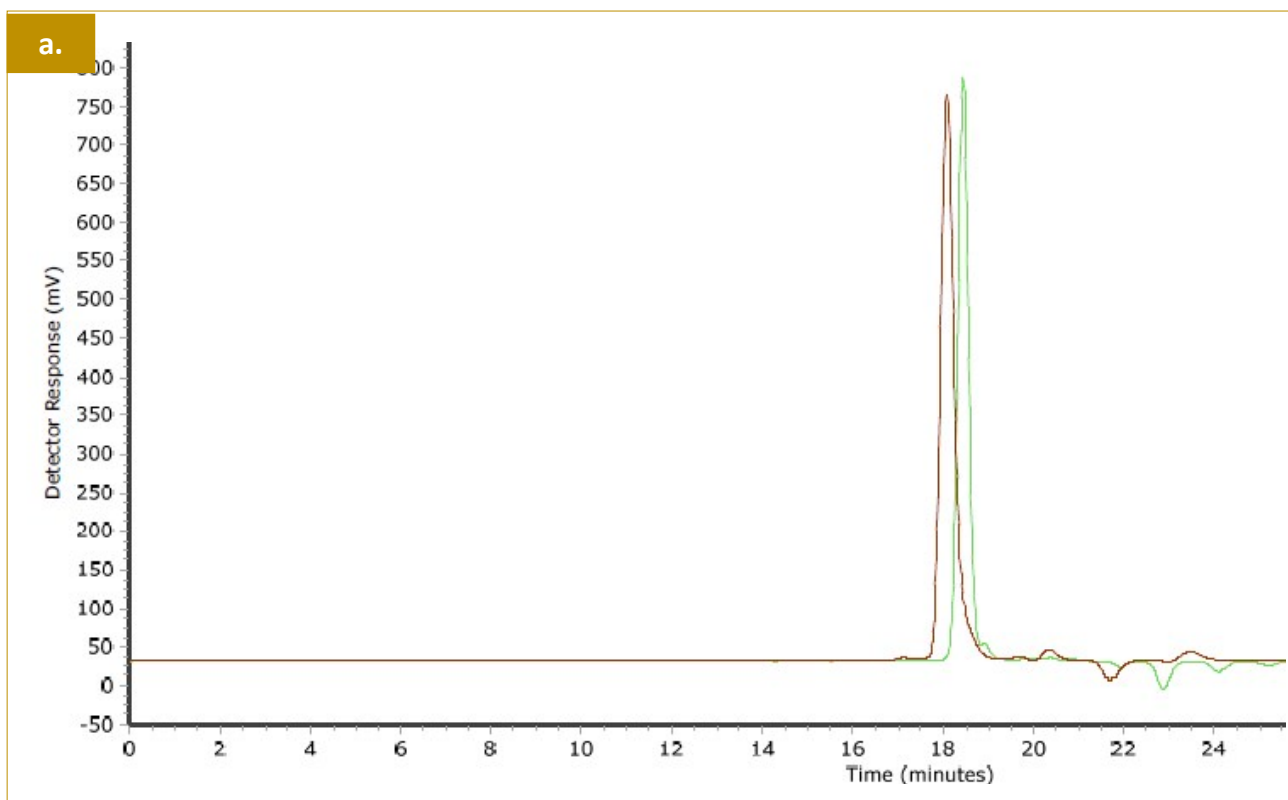


Figure S4.  $^1\text{H NMR}$  of epoxidized Karanja oil (EVO 1) (a), epoxidized St John's Wort oil (EVO 2) (b), epoxidized Peanut oil (EVO 3) (c), epoxidized Rapeseed oil (EVO 4) (d), epoxidized Soybean oil (EVO 5) (e), epoxidized Rose hip seed oil (EVO 6) (f), epoxidized Safflower oil (EVO 7) (g), epoxidized Camelina oil (EVO 8) (h), epoxidized Rose Hip seed oil (EVO 10) (i), epoxidized Linseed oil (EVO 11) (j) and epoxidized Perilla oil (EVO 12 and EVO 13) (k, l).

5. SEC analysis – evolution of the chain distribution before and after epoxidation





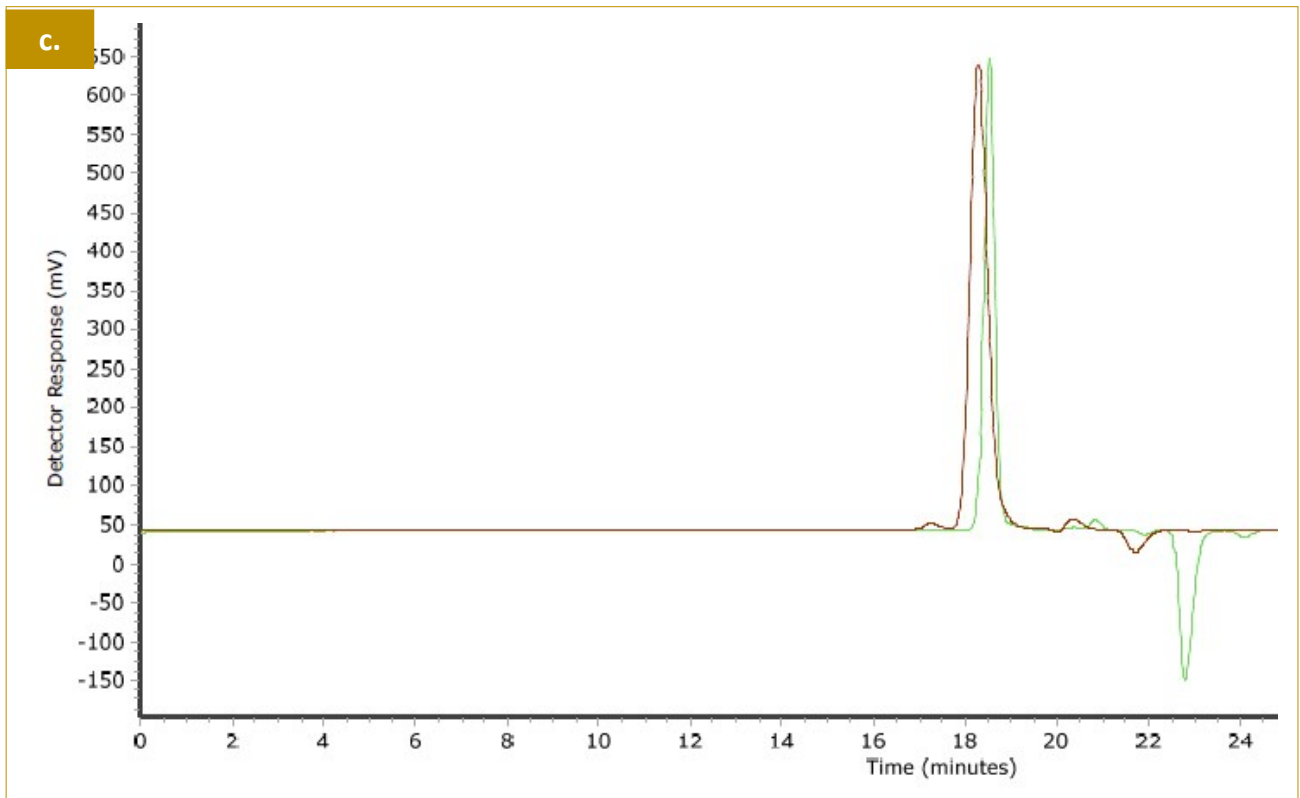
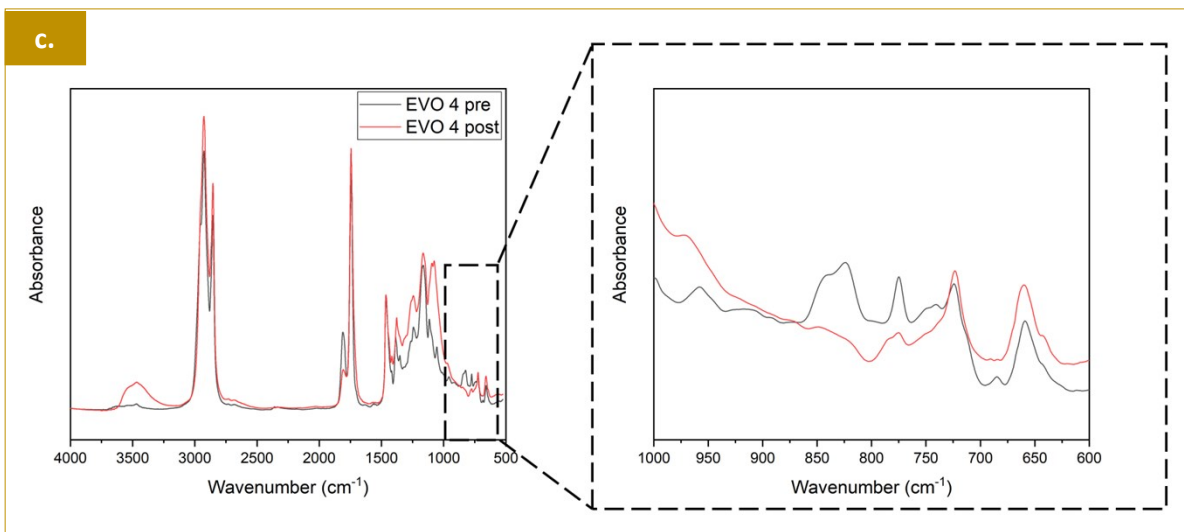
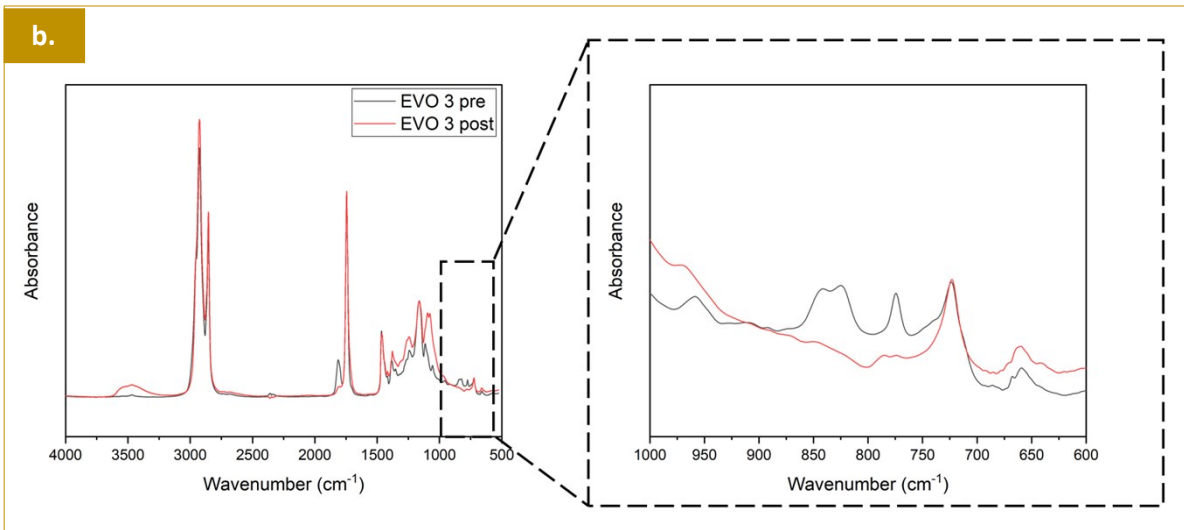
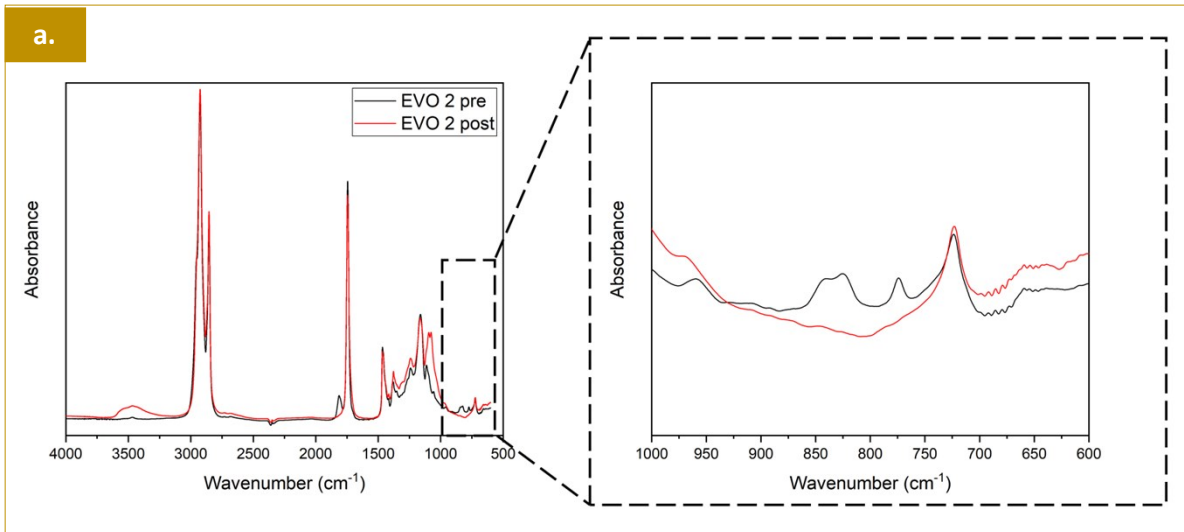
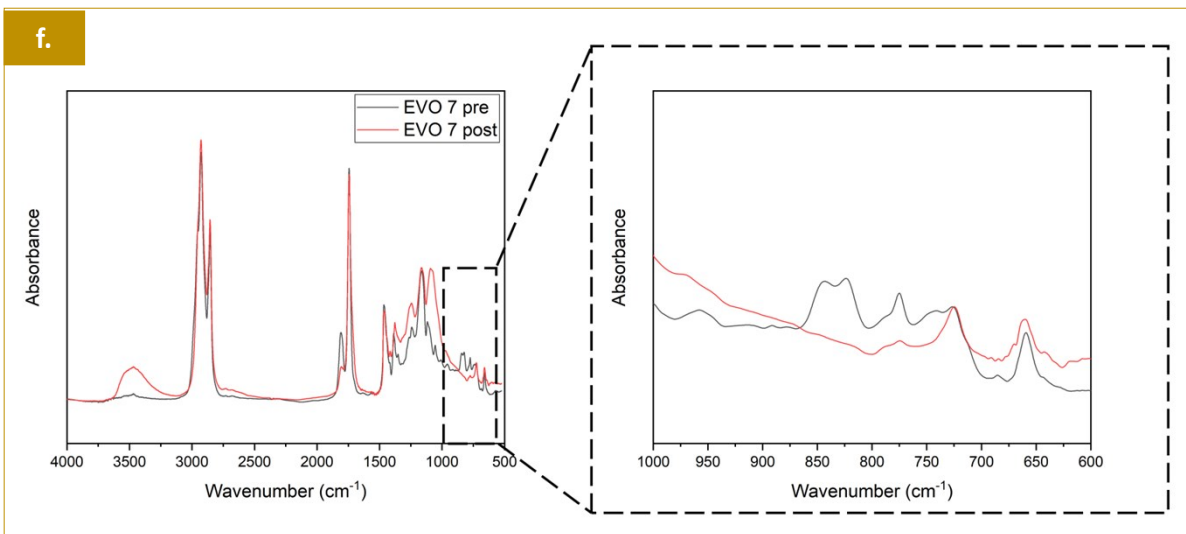
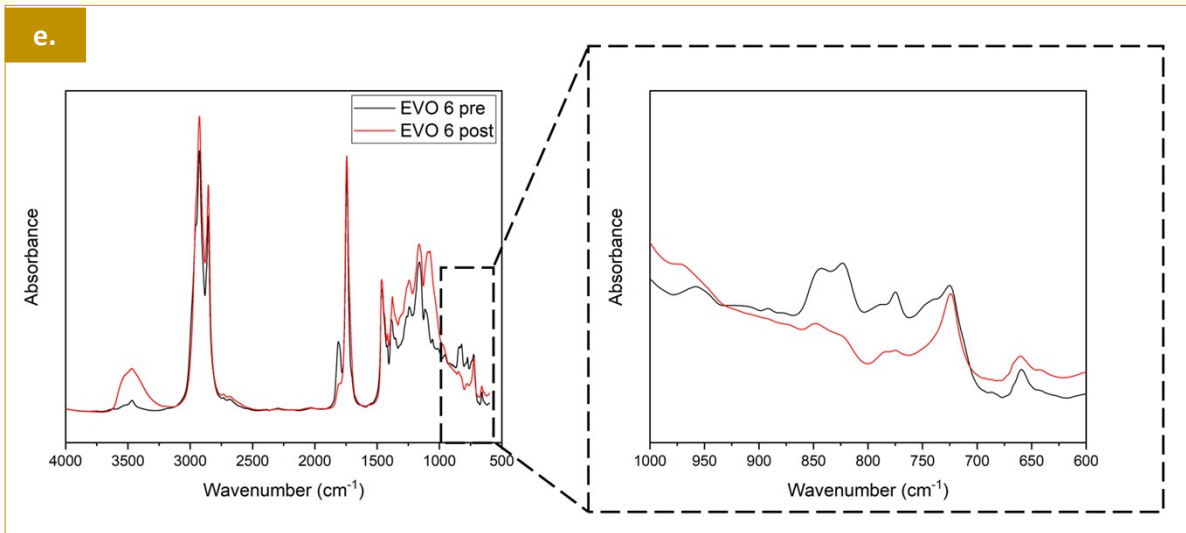
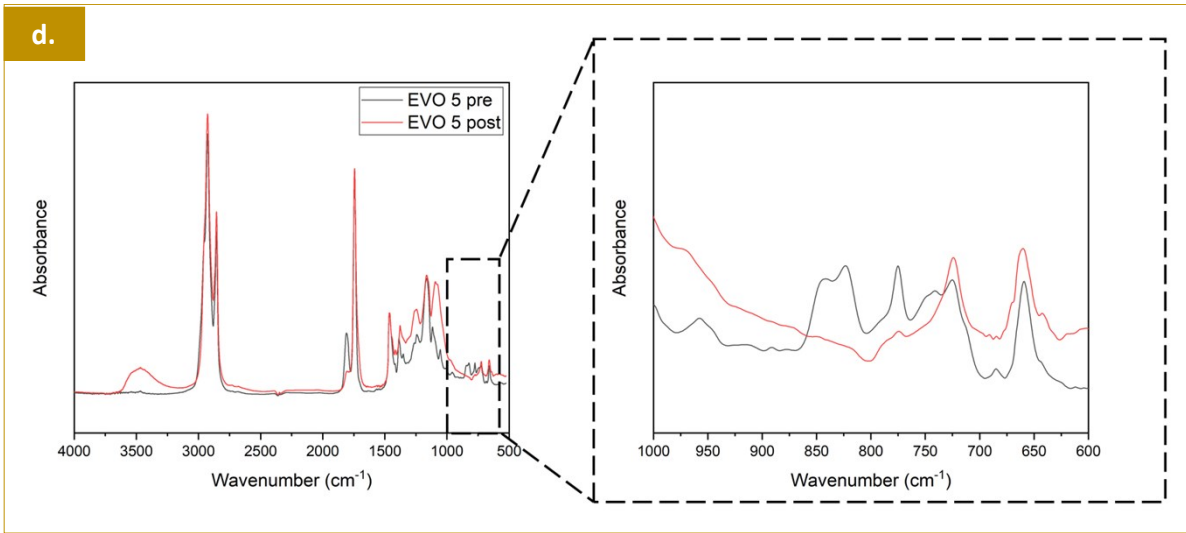
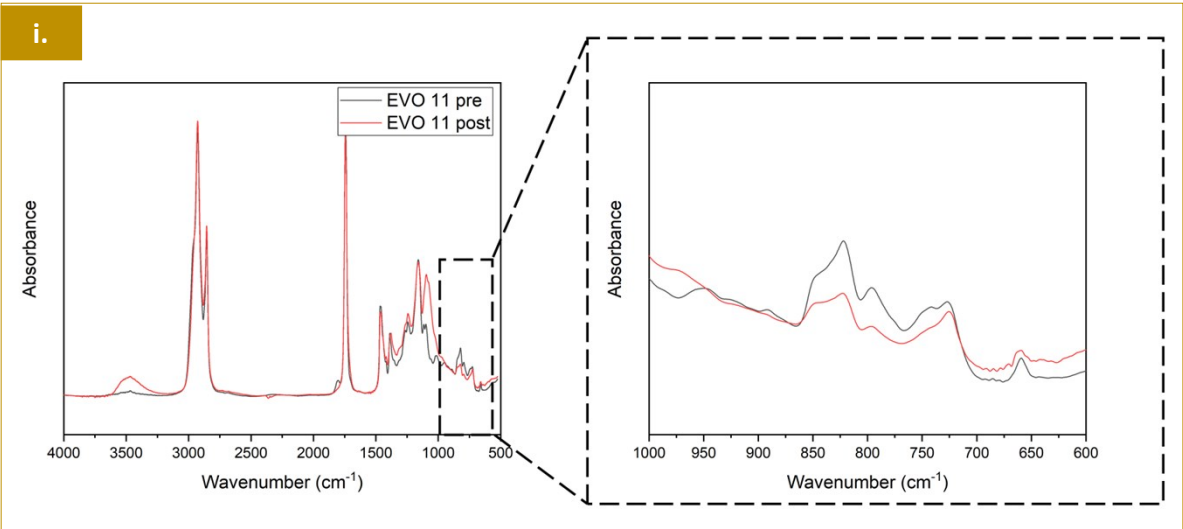
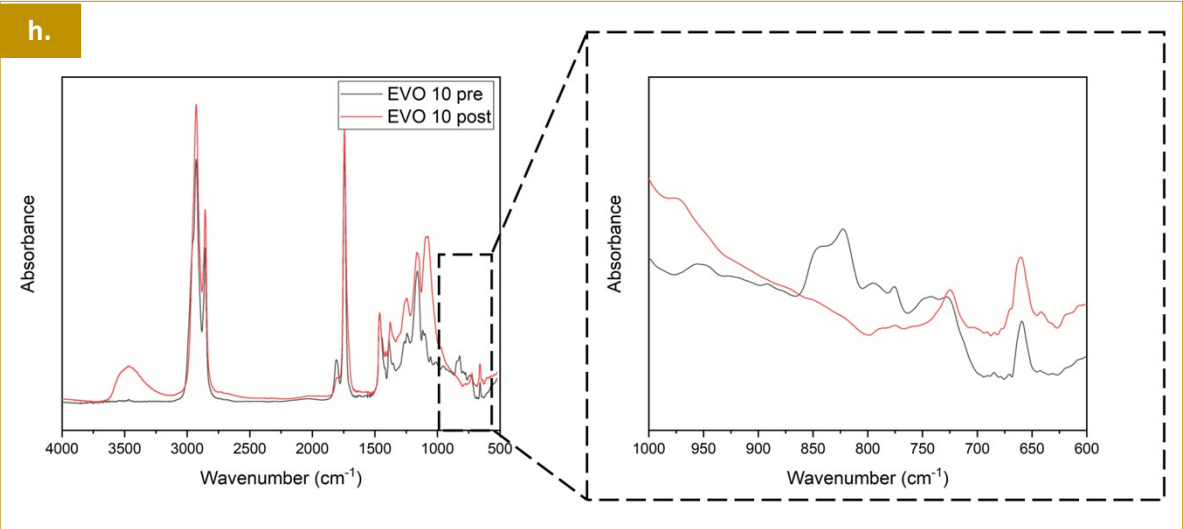
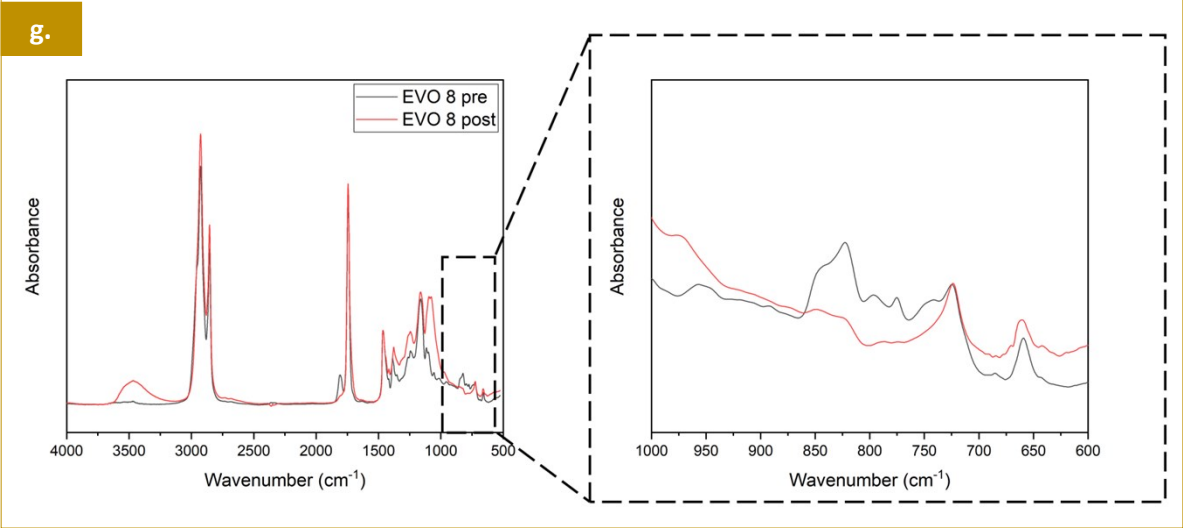


Figure S5. SEC analysis of some vegetable oils before (green curves) and after (red curves) epoxidation of St John's Wort oil (VO 2 and EVO 2) (a), Rose hip seed oil (VO 6 and EVO 6) (b) and Perilla oil (VO 12 and EVO 12) (c).

## 6. FT-IR analysis of UV-cured EVOs monomers and materials







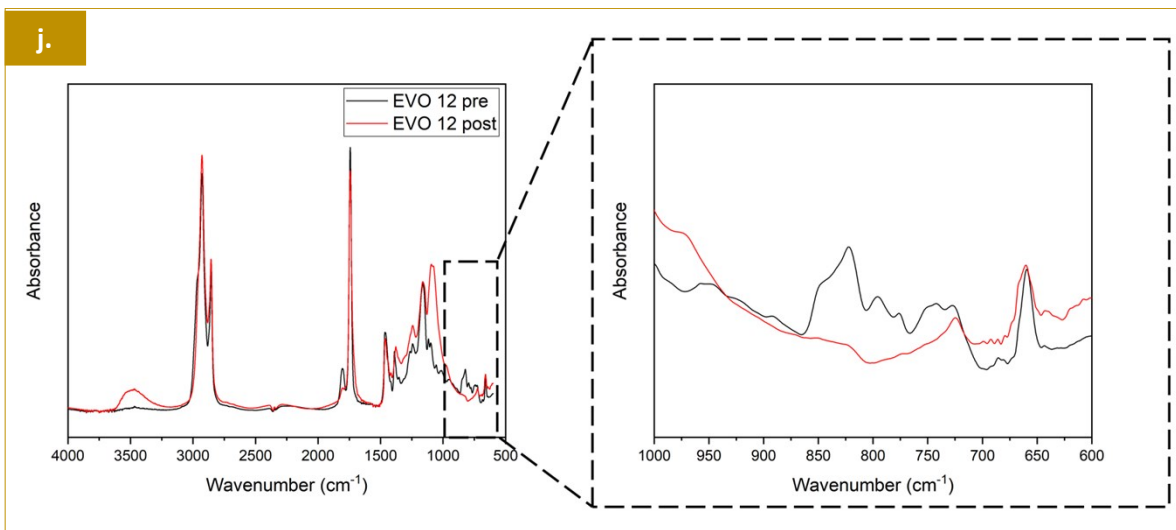


Figure S6. FT-IR analysis of epoxidized St John's Wort oil (EVO 2) (a), epoxidized Peanut oil (EVO 3) (b), epoxidized Rapeseed oil (EVO 4) (c), epoxidized Soybean oil (EVO 5) (d), epoxidized Rose hip seed oil (EVO 6) (e), epoxidized Safflower oil (EVO 7) (f), epoxidized Camelina oil (EVO 8) (g), epoxidized Rose Hip seed oil (EVO 10) (h), epoxidized Linseed oil (EVO 11) (i) and epoxidized Perilla oil (EVO 12) (j) monomers and thermoset materials.

## 7. DSC and DMA analyses of UV-cured EVOs materials

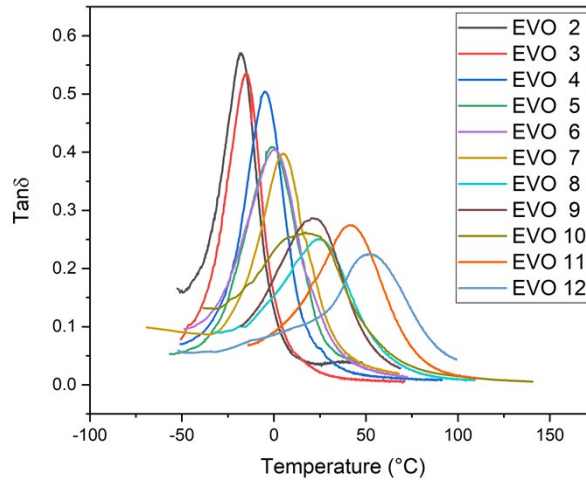
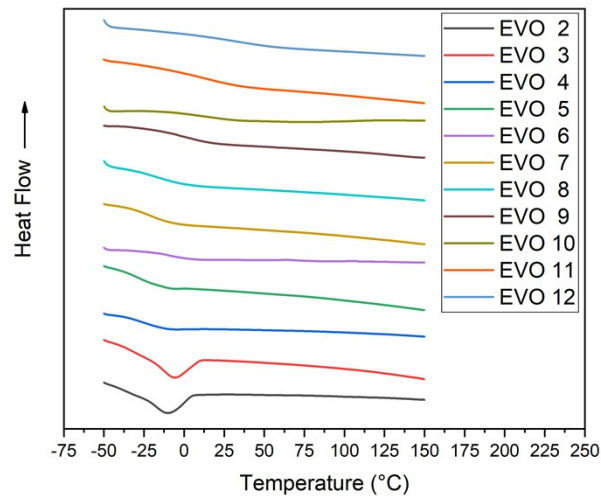


Figure S7.1. DSC thermograms of all UV-cured EVOs materials after the irradiation under the Fusion Lamp.

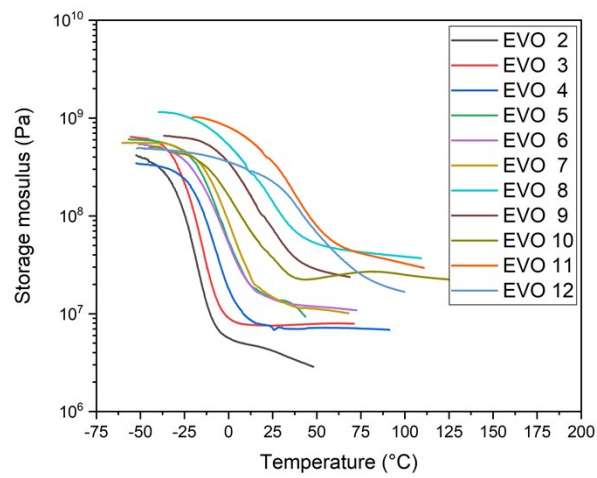


Figure S7.2. DMA results: Graphs of Tan  $\delta$  versus Temperature of all UV-cured EVOs materials determined by DMA analysis.

Figure S7.3. DMA results: Storage modulus of all UV-cured EVOs materials

---

## 8. Thermal behaviour of EVOs monomers

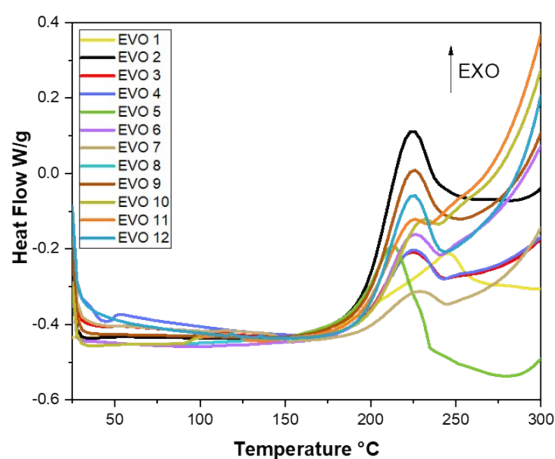
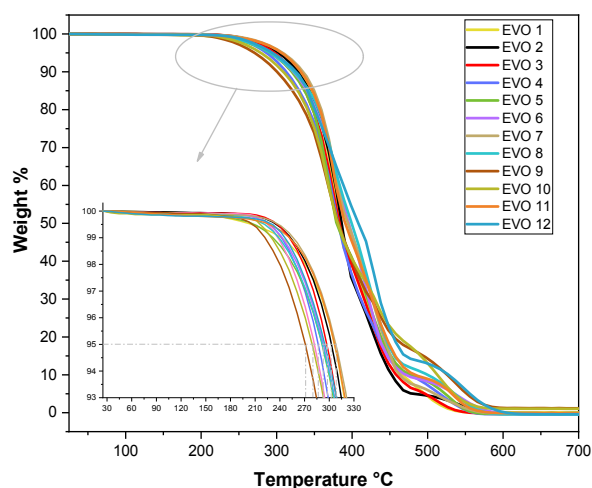


Figure S8.1. TGA analyses of the EVO monomers in air at 10 °C min<sup>-1</sup> heating rate

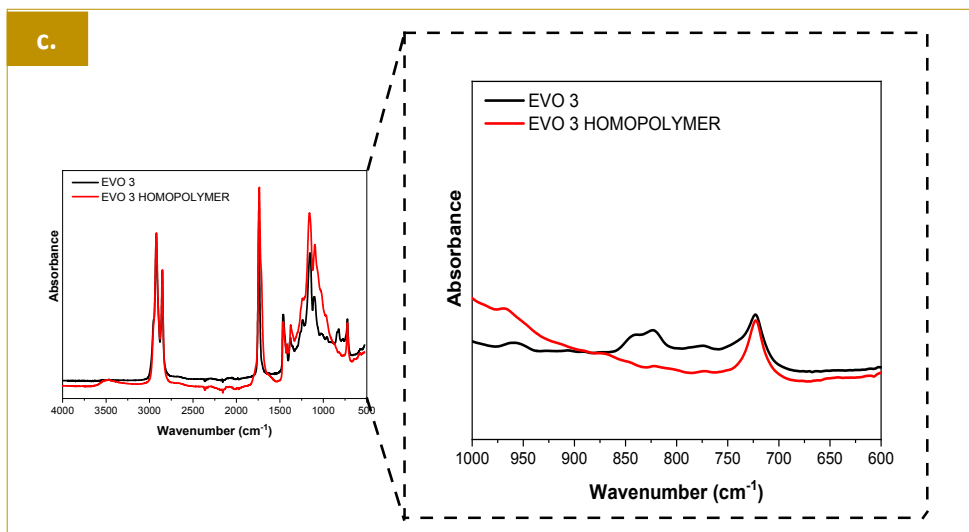
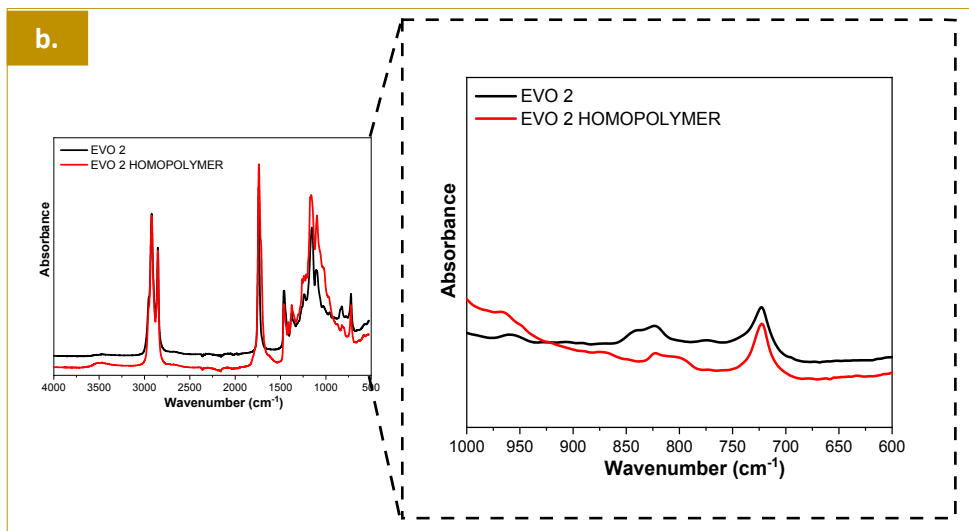
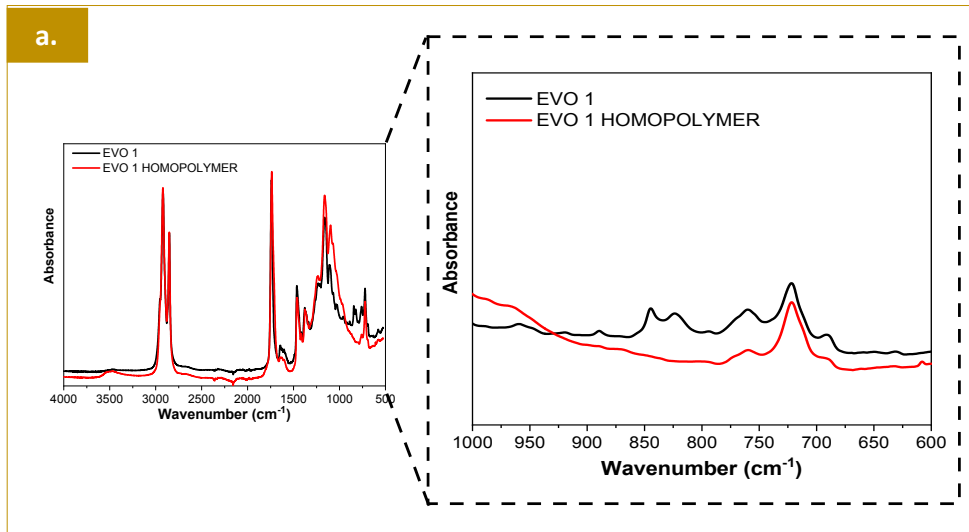
Figure S8.2. DSC dynamic analysis of EVOs homopolymerization reaction during heating from 25 to 300 °C at 10 °C.min<sup>-1</sup>.

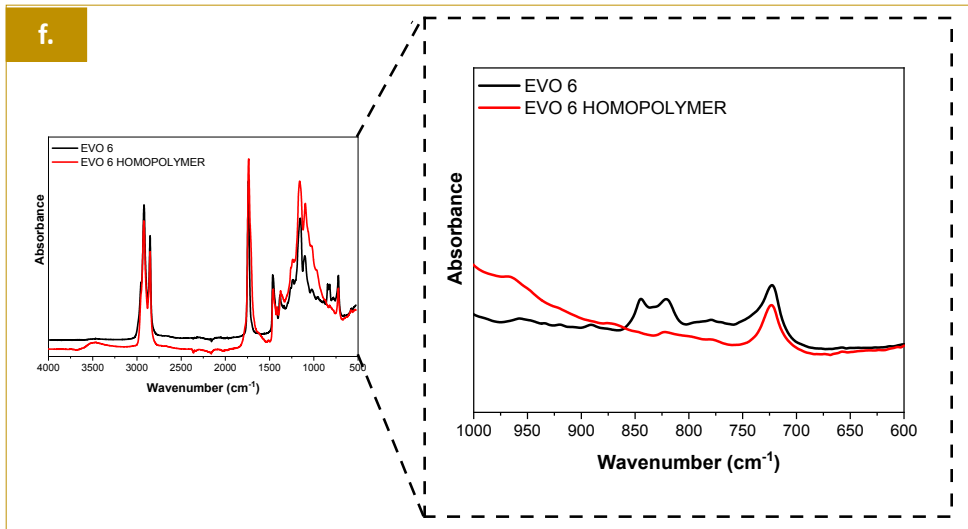
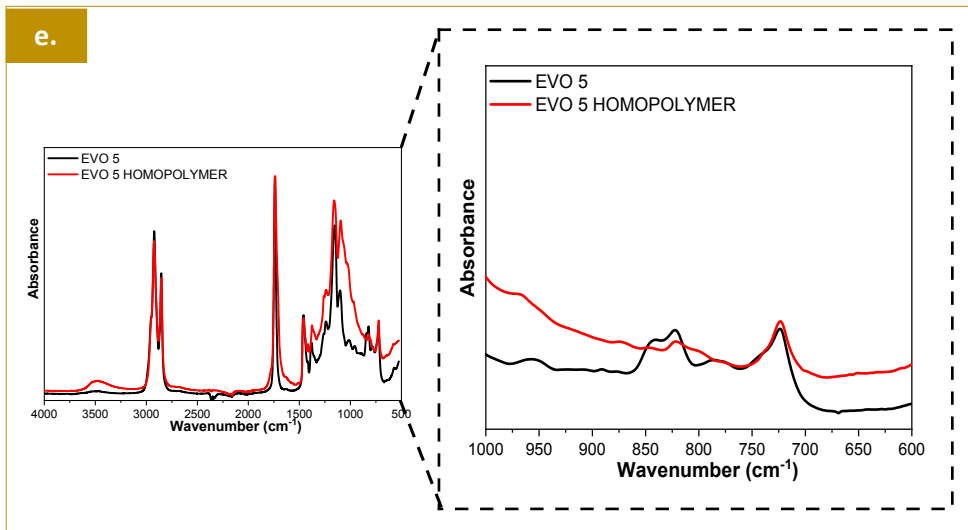
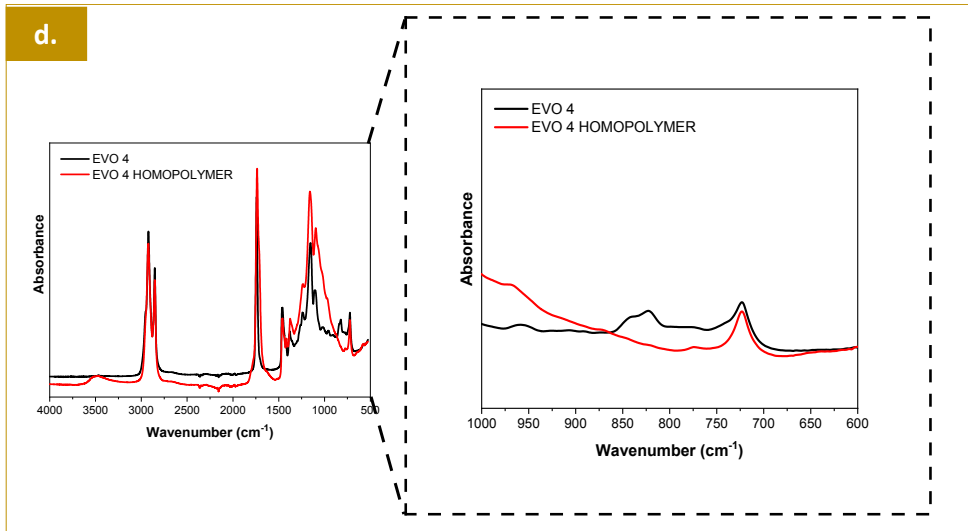
Table S8.1. T<sub>5%</sub> and T<sub>30%</sub> determined by TGA analysis for the starting EVO monomers. Determination of the reaction interval and temperature of the reaction peak (T<sub>peak</sub>) by DSC.

EVOs label	TGA T <sub>5%</sub> (°C)	TGA T <sub>30%</sub> (°C)	DSC T <sub>peak</sub> (°C)	DSC Reaction interval (°C)	ΔH (J/g)
EVO 1	305 ± 1	415 ± 1	245 ± 2	197 – 270	14
EVO 2	300 ± 1	410 ± 1	217 ± 1	176 – 247	12
EVO 3	300 ± 1	415 ± 1	219 ± 1	170 – 250	12
EVO 4	291 ± 1	415 ± 1	223 ± 2	174 – 246	21
EVO 5	300 ± 1	425 ± 1	213 ± 2	169 – 239	43
EVO 6	295 ± 1	415 ± 1	223 ± 1	172 – 244	19
EVO 7	305 ± 1	425 ± 1	225 ± 1	179 – 248	12
EVO 8	295 ± 1	430 ± 1	221 ± 1	175 – 261	17
EVO 9	271 ± 1	425 ± 1	221 ± 1	156 – 245	16
EVO 10	285 ± 1	430 ± 1	218 ± 2	163 – 236	35
EVO 11	300 ± 1	428 ± 1	221 ± 2	156 – 234	54
EVO 12	295 ± 1	430 ± 1	223 ± 1	161 – 236	29

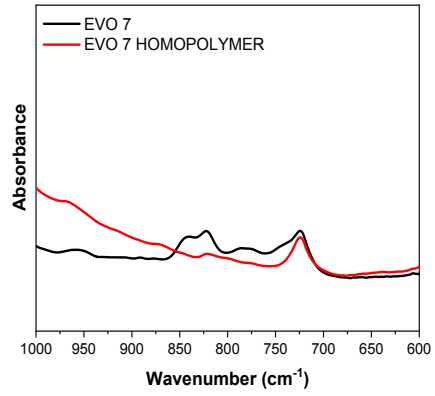
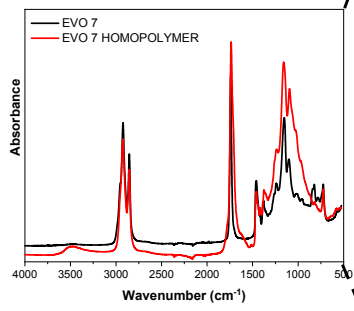


## 9. FT-IR analysis of thermally cured EVOs monomers and materials

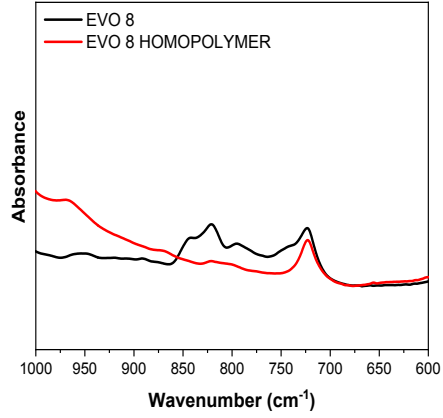
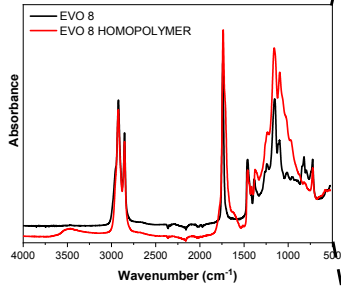




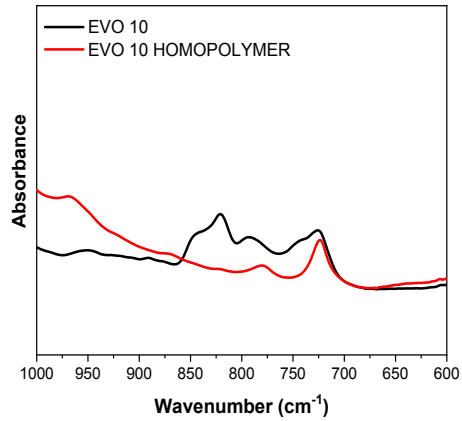
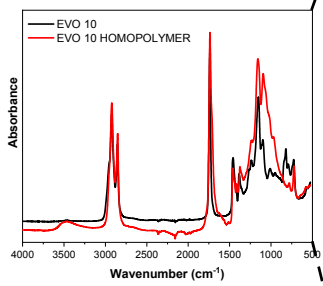
g.



h.



i.



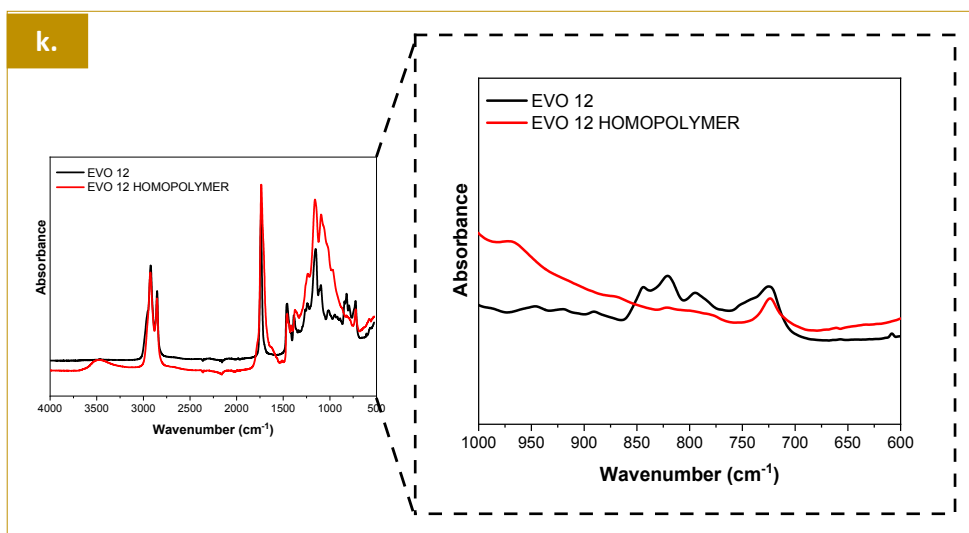
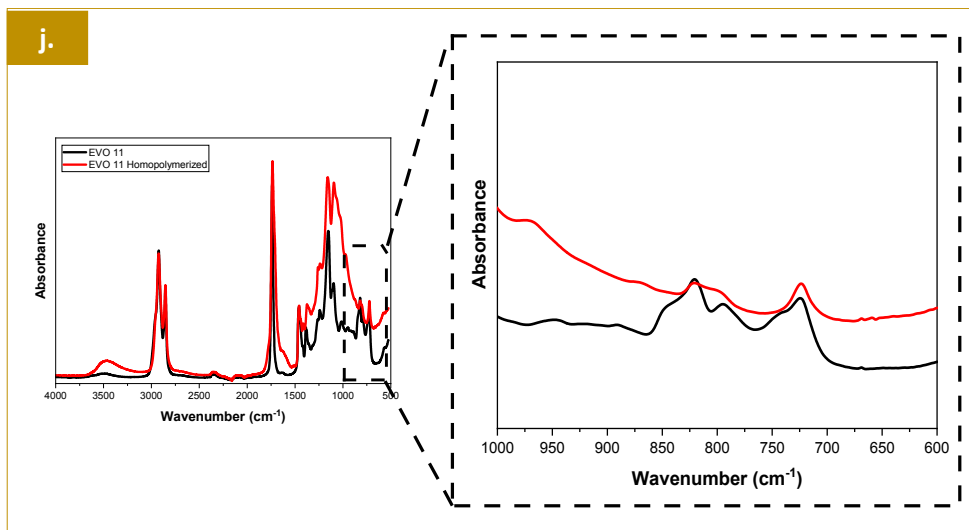


Figure S9. FT-IR analysis of epoxidized Karanja oil (EVO 1) (a), epoxidized St John's Wort oil (EVO 2) (b), epoxidized Peanut oil (EVO 3) (c), epoxidized Rapeseed oil (EVO 4) (d), epoxidized Soybean oil (EVO 5) (e), epoxidized Rose hip seed oil (EVO 6) (f), epoxidized Safflower oil (EVO 7) (g), epoxidized Camelina oil (EVO 8) (h), epoxidized Rose Hip seed oil (EVO 10) (i), epoxidized Linseed oil (EVO 11) (j) and epoxidized Perilla oil (EVO 12) (k) monomers and thermoset materials.

## 10. Solvent stability of thermally cured EVOs materials

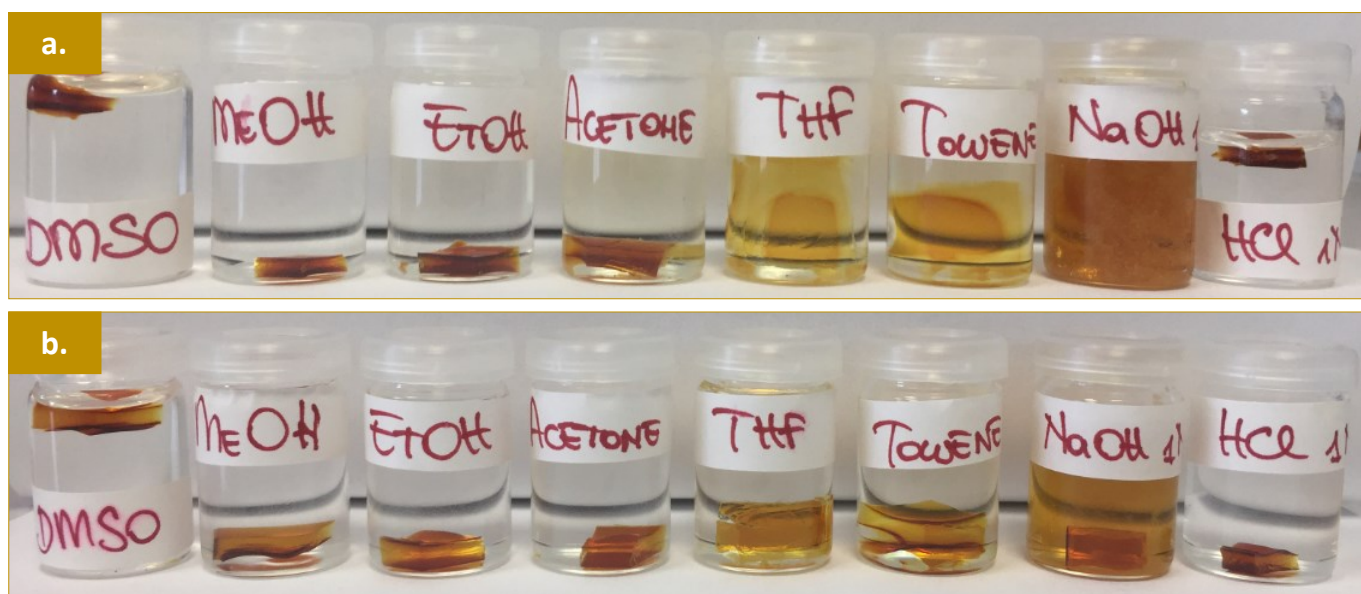


Figure S10. Solvent stability of epoxidized St John's Wort oil (EVO 2) (a) and epoxidized perilla oil (EVO 12) (b) thermoset materials in (from left to right) DMSO, methanol, ethanol, acetone, THF, toluene, NaOH solution (1M) and HCl solution (1M)

### 11. DSC and DMA analyses of thermally cured EVOs materials

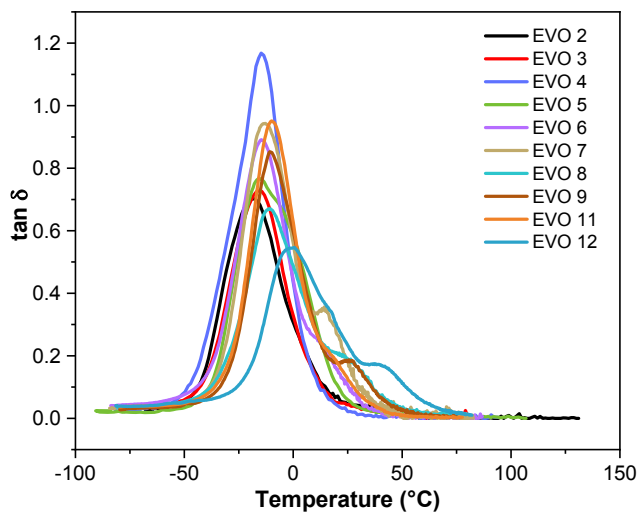
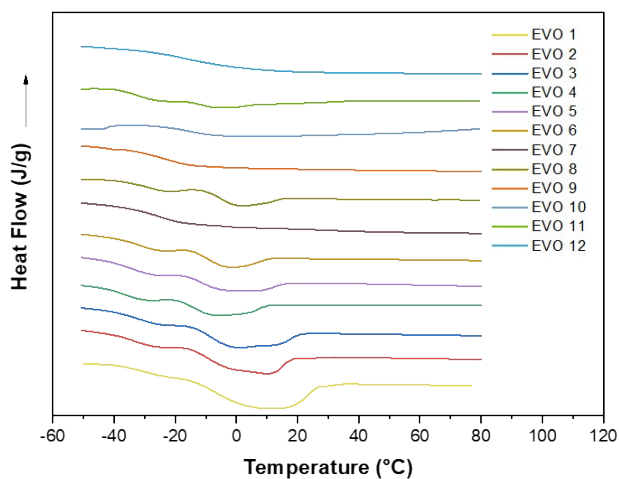


Figure S11.1. DSC thermograms of all EVOs materials after the thermal crosslinking

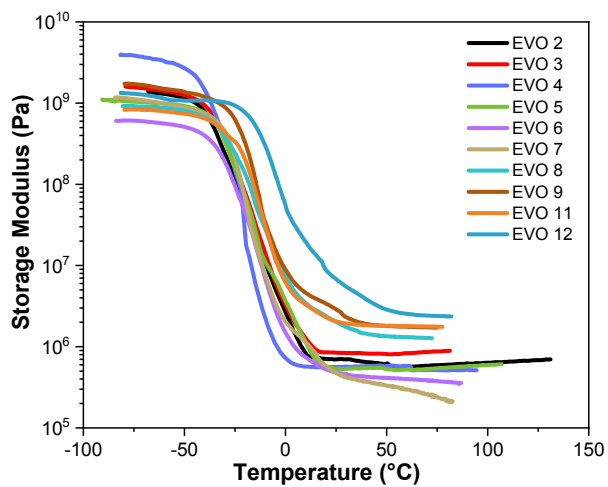


Figure S11.2. DMA results: evolution of tan  $\delta$  with temperature for all thermally crosslinked EVOs materials

Figure S11.3. DMA results: evolution of storage modulus with temperature for all thermally crosslinked EVOs materials

---