

Supporting Information

Synthesis and self-assemblies of amphiphilic polymers based on polyoxazoline and vegetable oil derivatives

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A- Characterization of MO and GSO (p. 2-6)

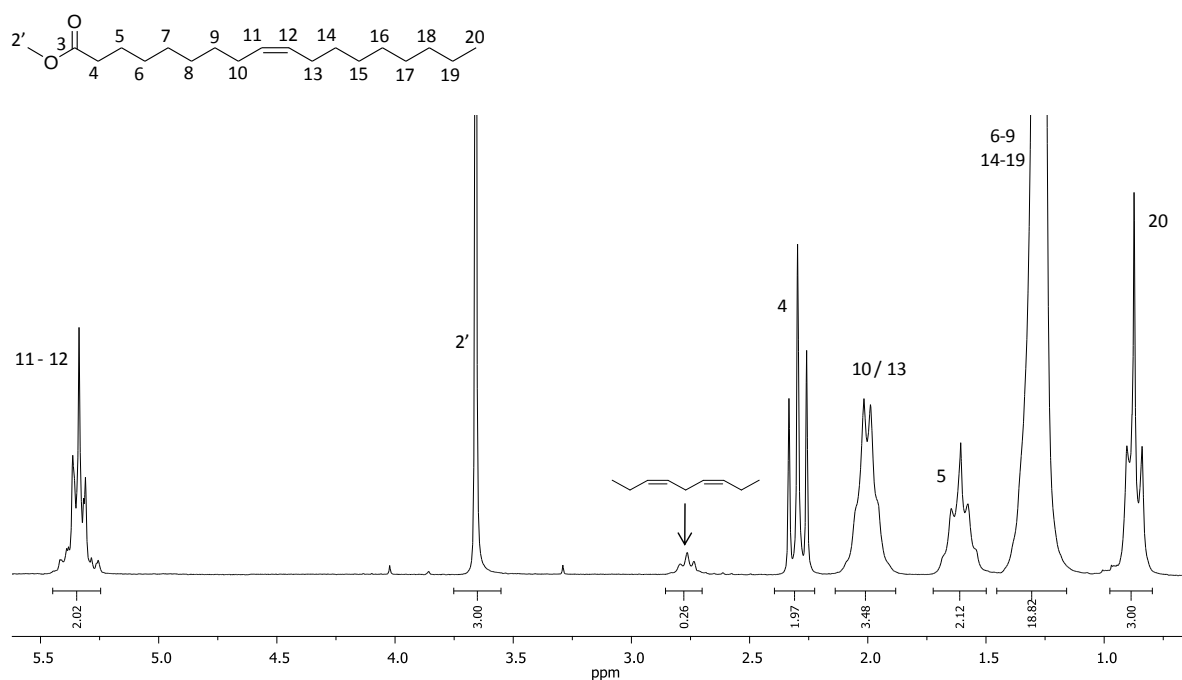
B- Characterization of HMO and HGSO (p. 6-11)

C- Characterization of macroinitiators (p. 11-17)

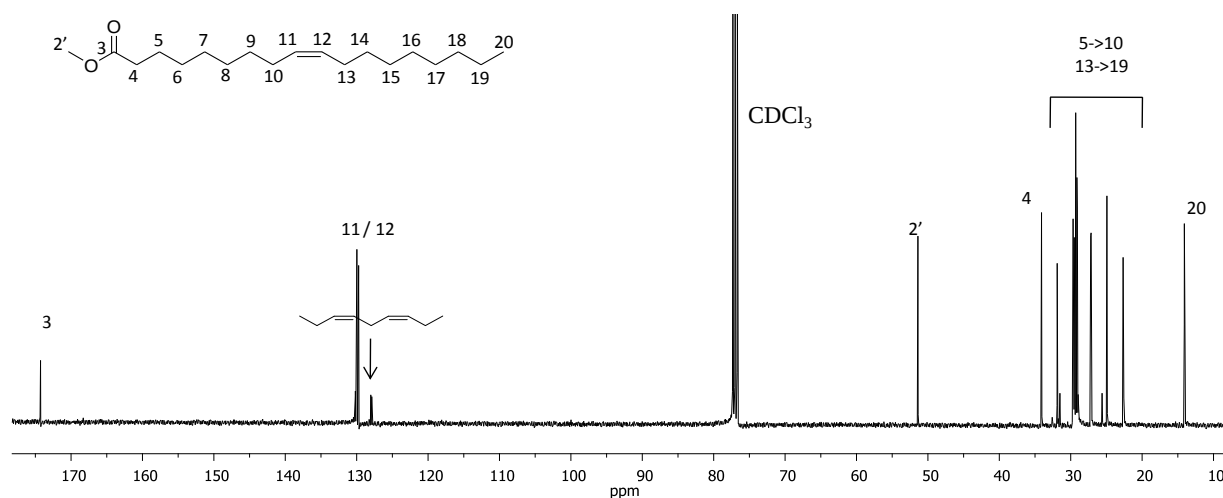
D- Characterization of LipoPOx (p. 17-19)

A- Characterization of MO and GSO

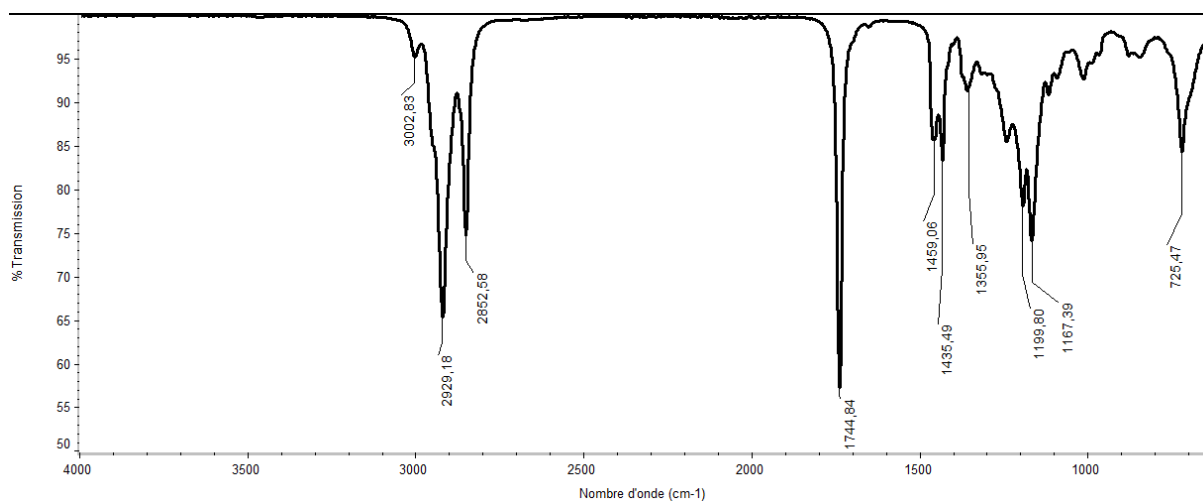
Methyl oleate: MO



^1H NMR (300 MHz, CDCl_3), δ = 0.79-0.88 (t, J = 7.0 Hz, 3H, $\text{CH}_2\text{-CH}_3$, H-20), 1.16-1.30 (m, 19H, CH_2 , H-6 to H-9 and H-14 to H-19), 1.6 (t, J = 7.0 Hz, 2H, $\text{CH}_2\text{-CH}_2\text{-C=O}$, H-5), 1.92-2.07 (m, 4H, $\text{-CH}_2\text{-CH=CH-}$, H-10 and H-13), 2.24-2.37 (t, J = 7.5 Hz, 2H, $\text{CH}_2\text{-CH}_2\text{-C=O}$, H-4), 2.74-2.78 (t, 0.26H, negligible), 3.66 (s, 3H, $\text{CH}_3\text{-O-(C=O)-}$, H-2'), 5.21-5.42 (m, 2H, CH=CH , H-11 and H-12).

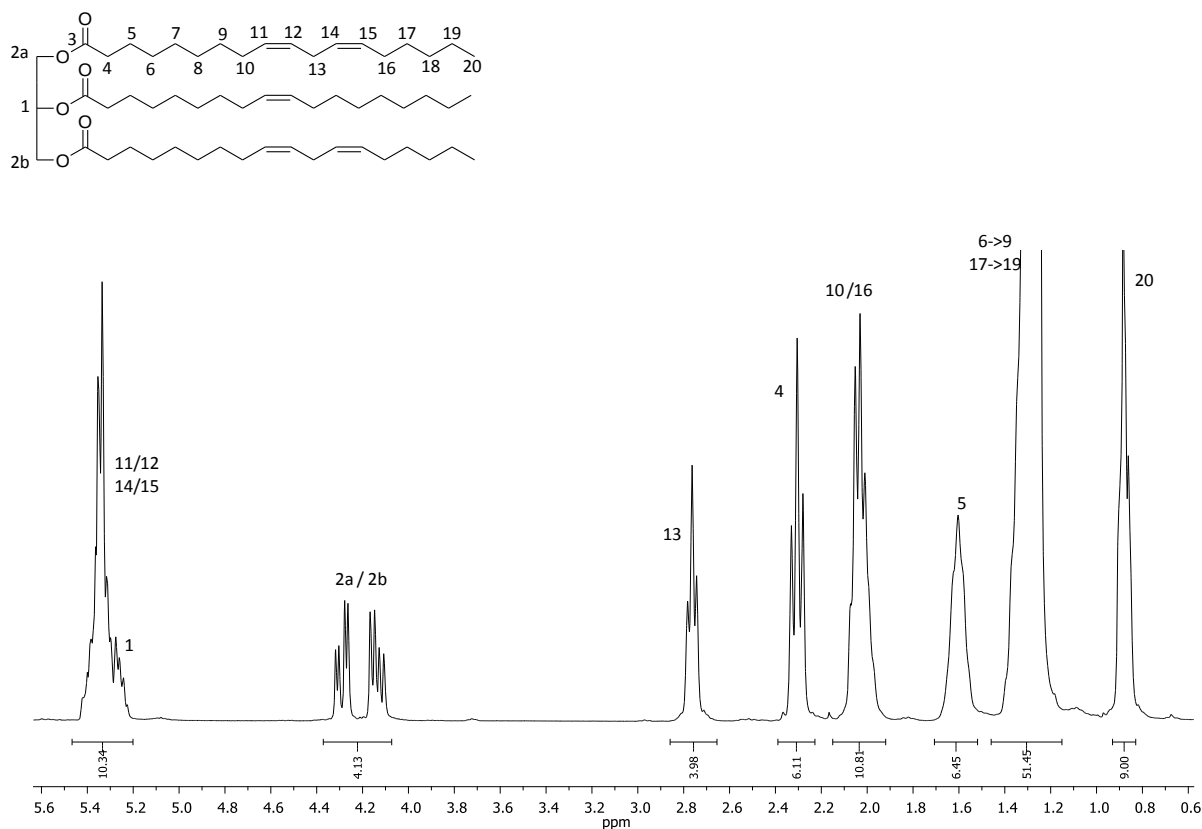


^{13}C NMR (75.47 MHz, CDCl_3), δ = 13.04 ($\text{CH}_2\text{-CH}_3$, C-20), 22.66-31.8 (CH_2 , C-5 to C-10 and C-13 to C-19), 34.9 ($\text{CH}_2\text{-(C=O)-}$, C-4), 51.4 ($\text{CH}_3\text{-O-(C=O)-}$, C-2'), 127.9 (negligible), 129.7 (CH=CH , C-11, C-12), 174.3 (C=O , C-3).

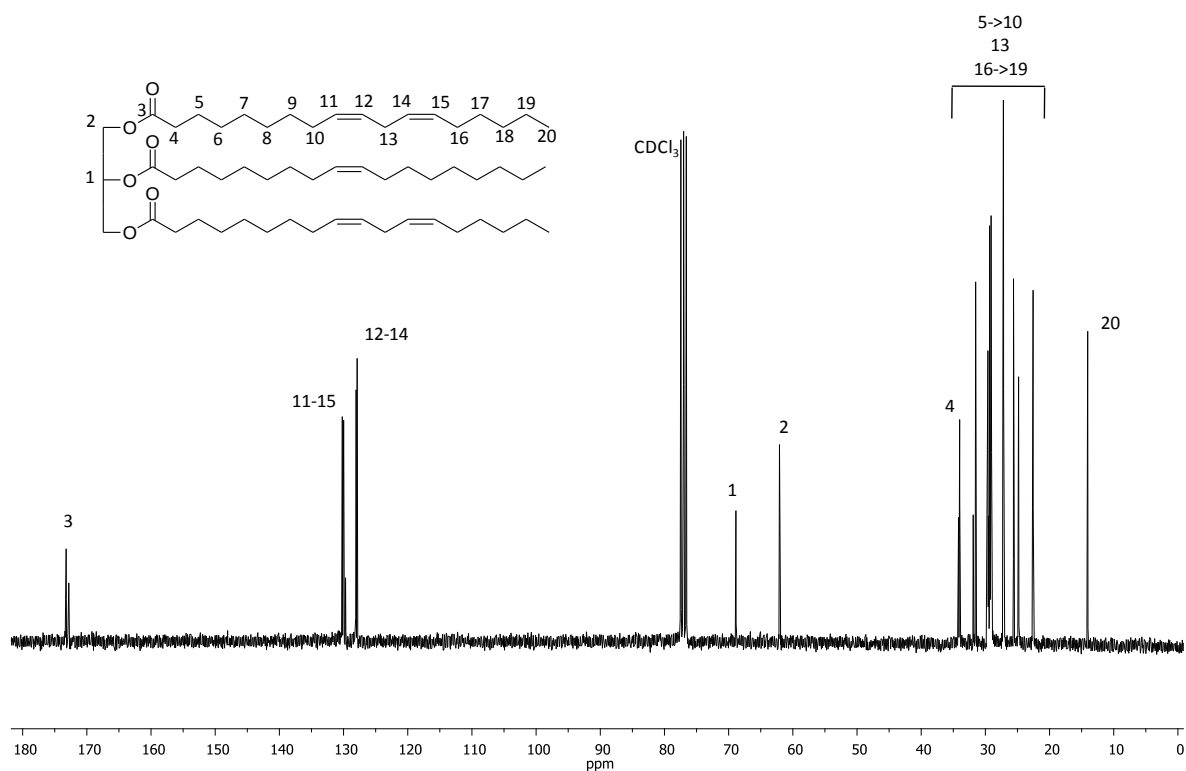


FTIR (cm^{-1}): 3003 (C=C-H (cis), asymmetrical elongation), 2929 (C-H , asymmetrical elongation), 2853 (C-H , symmetrical elongation), 1745 ($\text{C=O}_{\text{ester}}$, elongation), 1459-1436 (CH_2 scissoring), 1355 (CH_3 symmetrical deformation), 1167 ($\text{C-O}_{\text{ester}}$ elongation), 725 (CH_2 rocking).

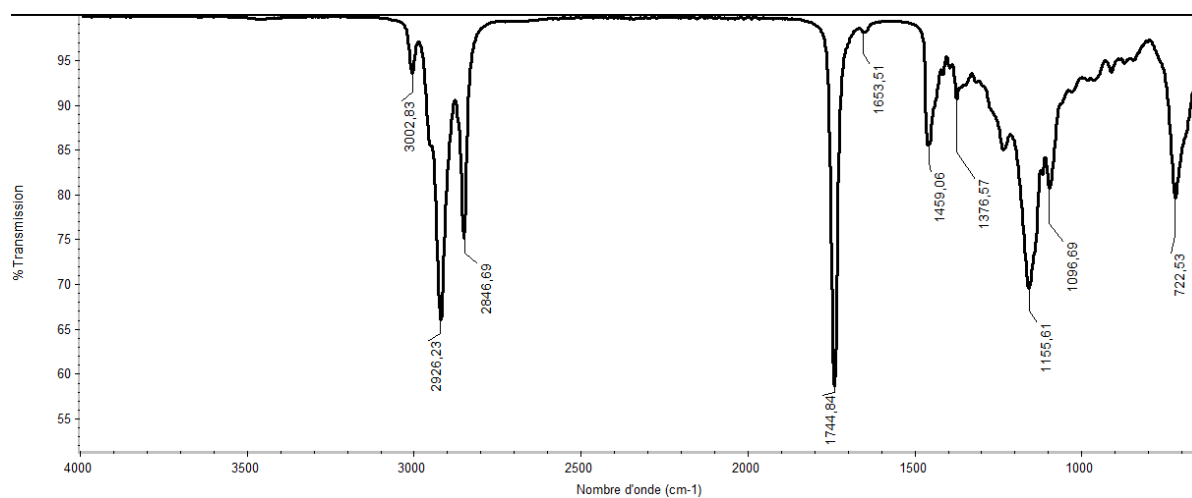
Grape seed oil: GSO



^1H NMR (300 MHz, CDCl_3), δ = 0.79-0.88 (m, 9 H, $\text{CH}_2\text{-CH}_3$, H-20), 1.16-1.43 (m, 51.5 H, CH_2 , H-6 to H-9, H-17 to H-19), 1.6 (m, 6.5 H, $\text{CH}_2\text{-CH}_2\text{-(C=O)-}$, H-5), 1.92-2.07 (m, 10.8 H, $\text{-CH}_2\text{-CH=CH-}$, H-10 and H-16), 2.24-2.37 (t, J = 7.5 Hz, 6.1H, $\text{CH}_2\text{-(C=O)-}$, H-4), 2.74-2.78 (t, J = 5.9 Hz, 4 H, $\text{CH=CH-CH}_2\text{-CH=CH}$, H-13), 4.11-4.17 (dd, 2 H, 2J = 11.7 Hz, 3J = 5.7 Hz, 3J = 6 Hz, $\text{CH}_2\text{-O}$, H-2a), 4.26-4.32 (dd, 2 H, 2J = 12 Hz, 3J = 4.2 Hz, $\text{CH}_2\text{-O}$, H-2b), 5.21-5.42 (m, 10.49 H, CH-O and CH=CH , H-1, H-11, H-12, H-14 and H-15).



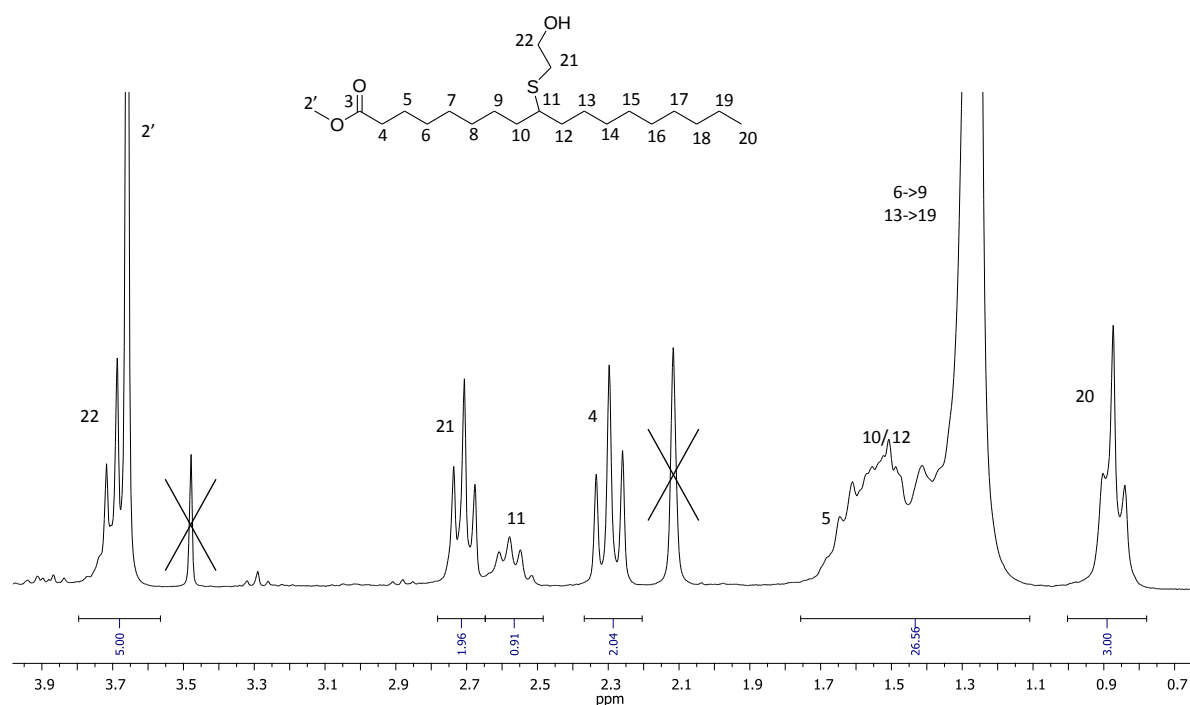
^{13}C NMR (75.47 MHz, CDCl_3), δ = 13.98 ($\text{CH}_3\text{-CH}_2$, C-20), 22.49-31.8 (CH_2 , C-5 to C-10, C-13 and C-16 to C-19), 33.9-34.07 ($\text{CH}_2\text{-C=O}$, C-4), 61.9 ($\text{CH}_2\text{-O}$, C-2), 68.8 ($\text{CH}_2\text{-CH-O}$, C-1), 127.8 ($\text{CH}_2\text{-CH=CH-CH}_2\text{-CH=CH}$, C-12 and C-14), 130.05 ($\text{CH}_2\text{-CH=CH-CH}_2\text{-CH=CH}$, C-11, C15), 172.64-173.04 (C=O , C-3).



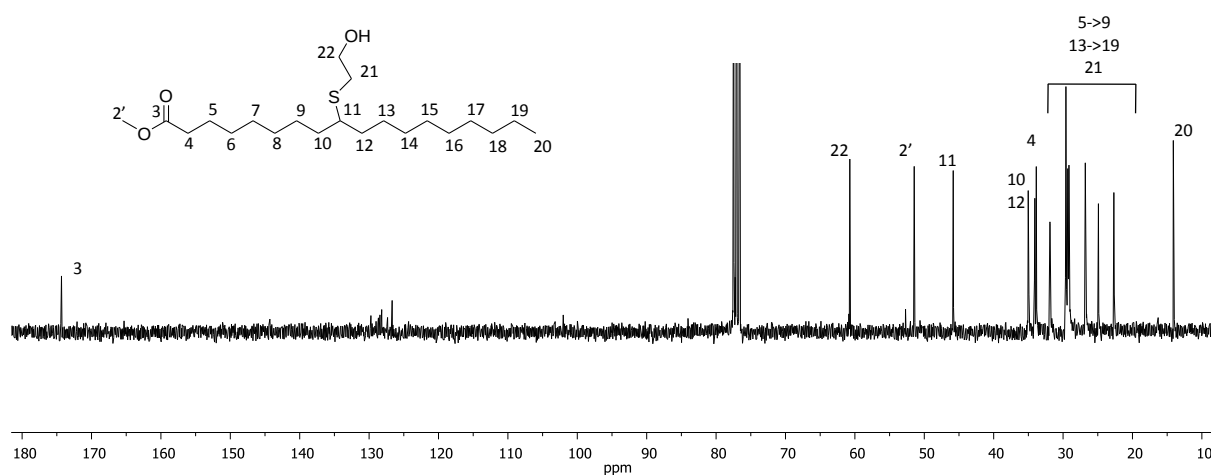
FTIR (cm^{-1}): 3003 (C=C-H (cis), asymmetrical elongation), 2920 (C-H, asymmetrical elongation), 2850 (C-H, symmetrical elongation), 1742 ($\text{C}=\text{O}_{\text{ester}}$, elongation), 1459 (CH_2 scissoring), 1377 (CH_3 symmetrical deformation), 1157 ($\text{C}-\text{O}_{\text{ester}}$ elongation), 725 (CH_2 rocking).

B- Characterization of HMO and HGSO

Hydroxylated methyloleate: HMO

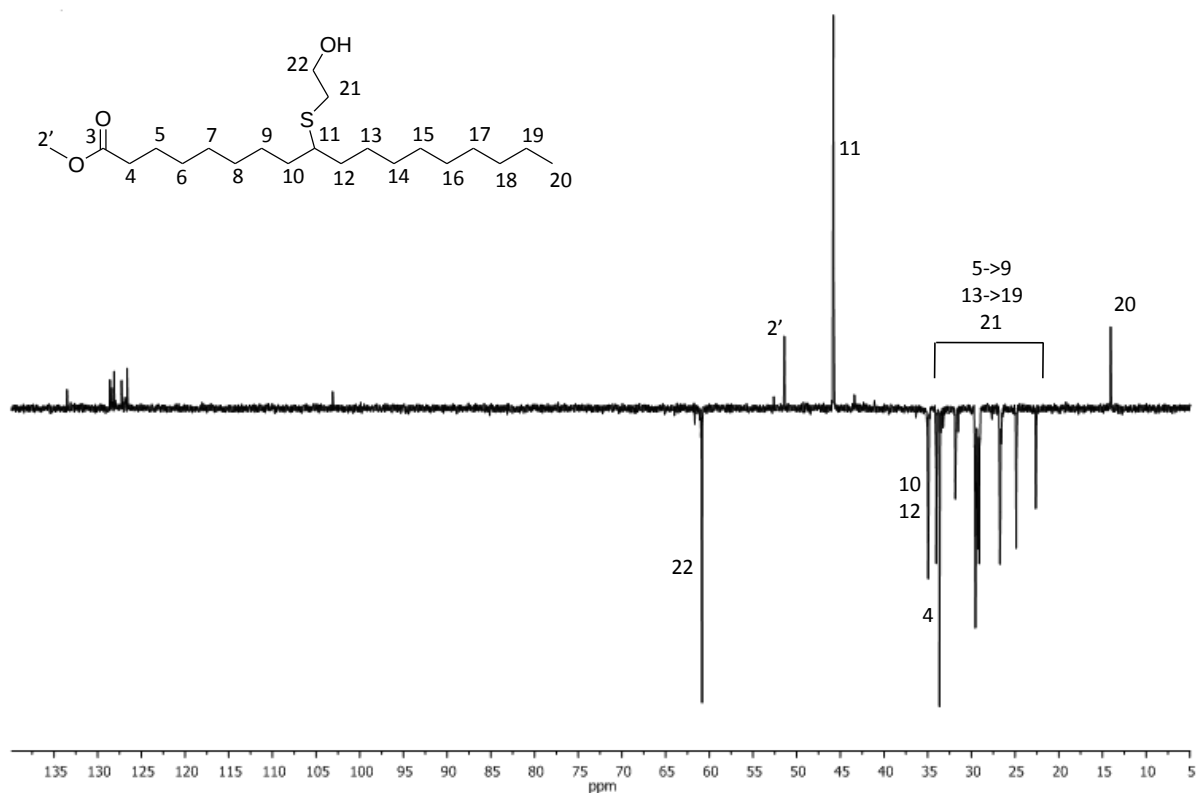


^1H NMR (300 MHz, CDCl_3), δ = 0.79-0.88 (t, J = 7.0 Hz, 3H, CH_2-CH_3 , H-20), 1.16-1.7 (m, 27H, CH_2 , H-5 to H-10 and H-12 to H-19), 2.24-2.37 (t, J = 7.5 Hz, 2 H, $\text{CH}_2-(\text{C}=\text{O})$, H-4), 2.56 (q, 1H, J = 12.4, 6.3 Hz, $\text{CH}-\text{S}$, H-11), 2.71 (t, 2H, J = 6.0 Hz, $\text{S}-\text{CH}_2$, H-21), 3.66 (s, 3H $\text{CH}_3-\text{O}-(\text{C}=\text{O})$, H-2'), 3.66-3.76 (t, 2H, CH_2-OH , H-22).

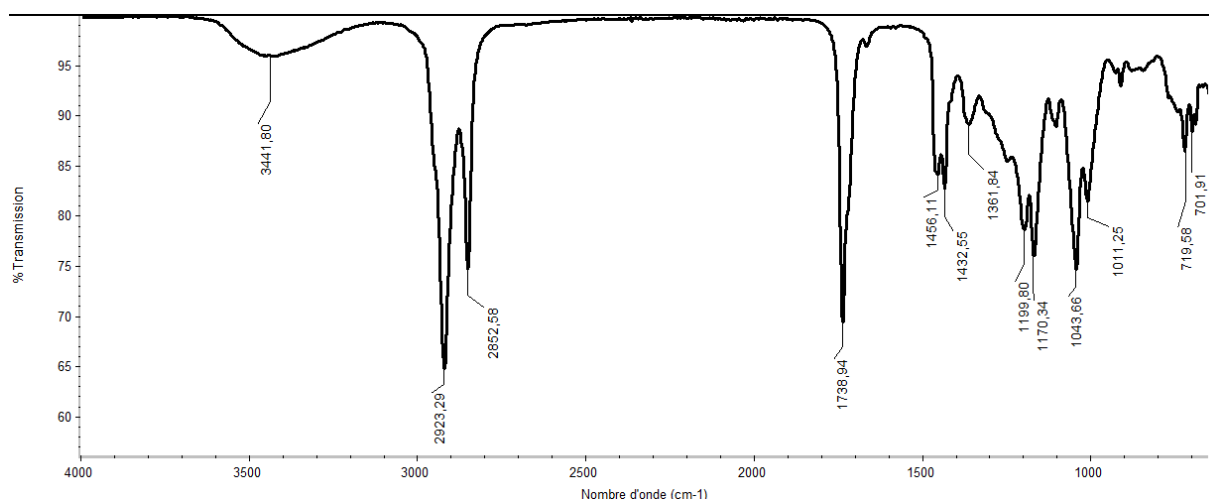


^{13}C NMR (75.47 MHz, CDCl_3), δ = 14.2 ($\text{CH}_2\text{-CH}_3$, C-20), 22.7-31.9 (CH_2 , C5 to C-9, C-13 to C-19 and C-21), 34.1 ($\text{CH}_2\text{-(C=O)-}$, C-4), 35.0 ($\text{CH}_2\text{-CH-S}$, C-10 and C-12), 45.1 (CH-S-CH_2 , C-11), 51.6 ($\text{CH}_3\text{-O-(C=O)-}$, C-2'), 60.9 ($\text{CH}_2\text{-OH}$), 127.9- 129.7 (negligible, residual double bonds), 174.4 (C=O , C-3).

DEPT 135

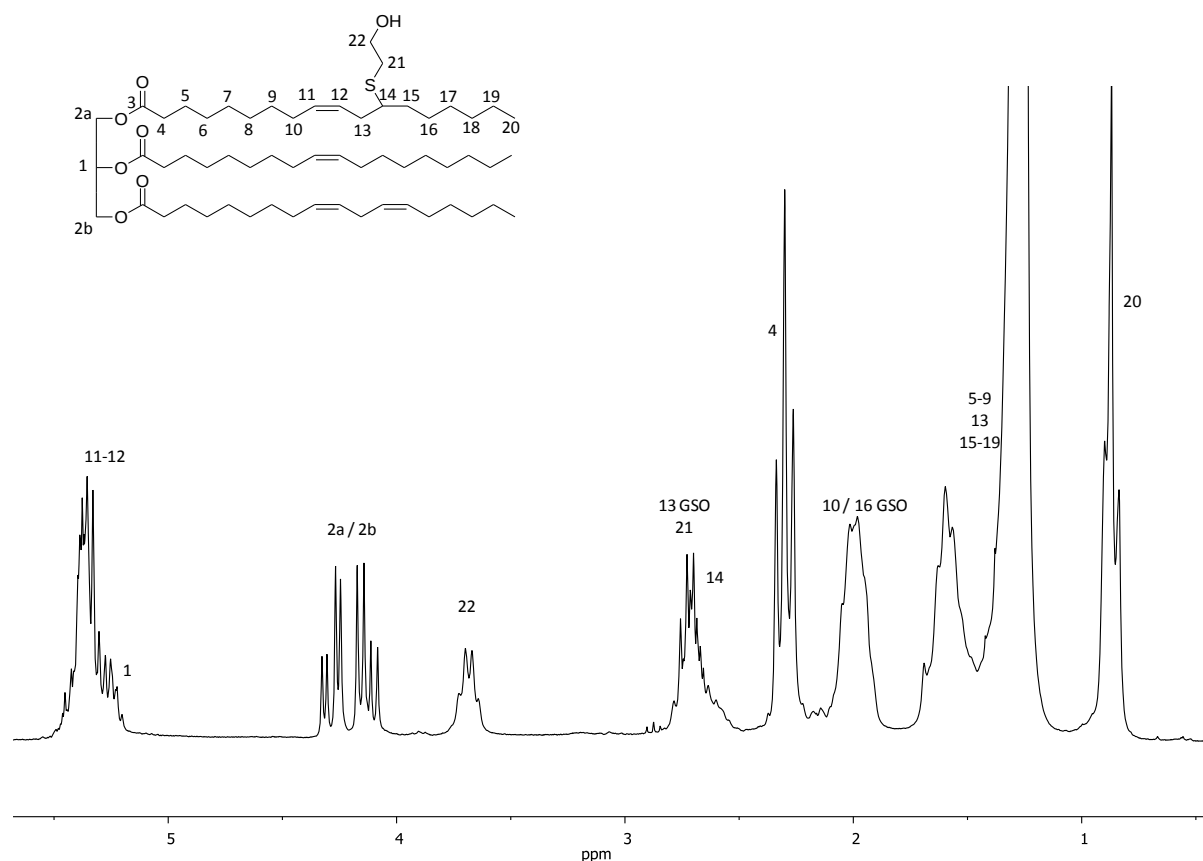


^{13}C NMR (75.47 MHz, CDCl_3), δ = 14.2 ($\text{CH}_2\text{-CH}_3$, C-20), 22.7-31.9 (CH_2 , C5 to C-9, C-13 to C-19 and C-21), 34.1 ($\text{CH}_2\text{-(C=O)-}$, C-4), 35 ($\text{CH}_2\text{-CH-S}$, C-10 and C-12), 45.1 (CH-S-CH_2 , C-11), 51.6 ($\text{CH}_3\text{-O-(C=O)-}$, C-2'), 60.9 ($\text{CH}_2\text{-OH}$), 127.9- 129.7 (negligible, residual double bonds).

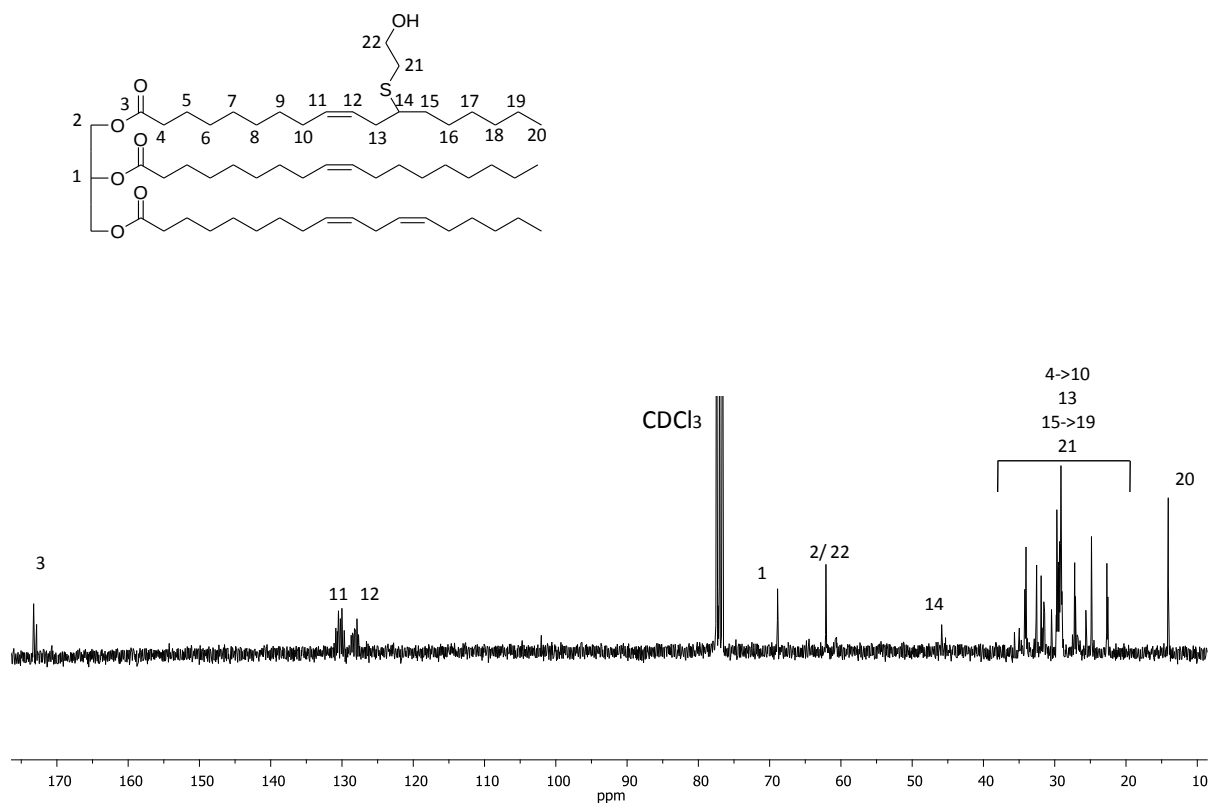


FTIR (cm^{-1}): 3440 (OH , stretching), 2923 (C-H , asymmetrical elongation), 2854 (C-H , symmetrical elongation), 1739 ($\text{C=O}_{\text{ester}}$, elongation), 1456-1433 (CH_2 scissoring), 1362 (CH_3 symmetrical deformation), 1170 ($\text{C-O}_{\text{ester}}$ elongation), 1043-1012 ($\text{C-C-OH}_{\text{mercaptoethanol}}$), 725 (CH_2 rocking).

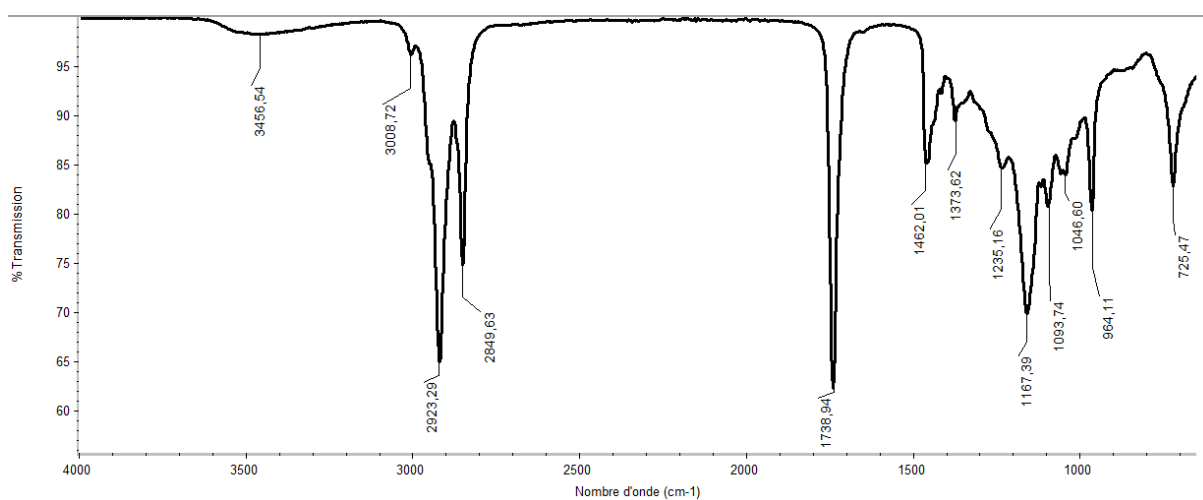
Hydroxylated grapeseed oil: HGSO



^1H NMR (300 MHz, CDCl_3), δ = 0.79-0.88 (9 H, $\text{CH}_2\text{-CH}_3$, H-20), 1.16-1.50 (49H, CH_2 , H-6 to H-9 and H-16 to H-19), 1.5-1.7 (9.5H, $\text{CH}_2\text{-CH-S}$ and $\text{CH}_2\text{-CH}_2\text{-C=O}$, H-13, H-15 and H-5), 1.92-2.07 (8.35H, $\text{CH}_2\text{-CH=CH-}$, H-10 and H-16 GSO), 2.24-2.37 (t, 7H, ^3J = 7.5 Hz, $\text{CH}_2\text{-(C=O)-}$, H-4), 2.5-2.8 (m, 5.1H, $\text{CH=CH-CH}_2\text{-CH=CH}$, CH-S and S-CH_2 , H-13 GSO, H-14 and H-21), 3.6-3.8 (dd, $\text{CH}_2\text{-OH}$, H-22), 4.11-4.17 (dd, 2H, ^2J = 11.7 Hz, ^3J = 5.7 Hz, ^3J = 6 Hz, $\text{CH}_2\text{-O}$, H-2a), 4.26-4.32 (dd, 2 H, ^2J = 12 Hz, ^3J = 4.2 Hz, $\text{CH}_2\text{-O}$, H-2b), 5.21-5.42 (m, 7.56H, CH-O and CH=CH , H-1 and H-11, H-12).



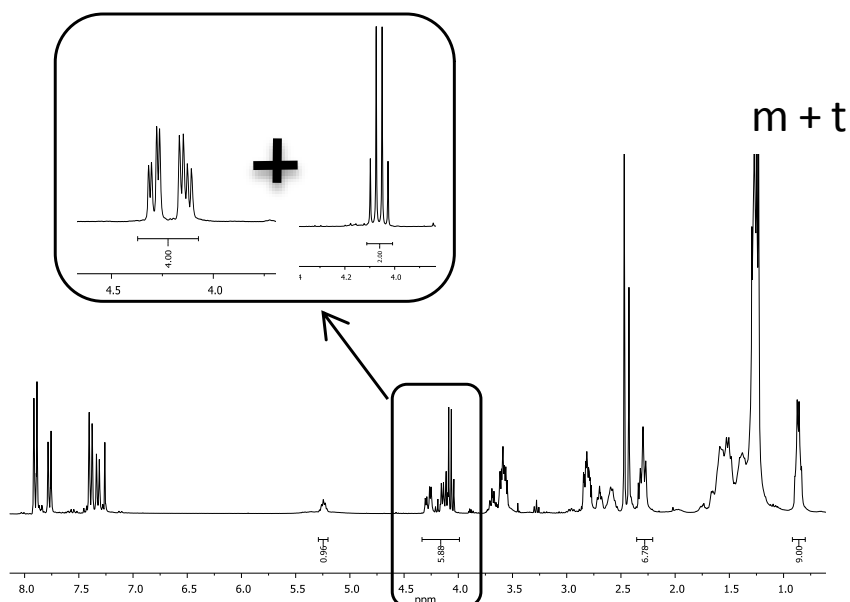
^{13}C NMR (75.47 MHz, CDCl_3), δ = 14.1 ($\text{CH}_2\text{-CH}_3$, C-20), 22.49-35 (CH_2 , C-4 to C-10, C-13, C-15 to C-19 and C-21), 45.1 (CH-S-CH_2 , C-14), 61.9 ($\text{CH}_2\text{-O}$ and $\text{CH}_2\text{-OH}$, C-2 and C-22), 68.8 (CH-O , C-1), 127.8-130.05 ($\text{CH}_2\text{-CH=CH-CH}_2\text{-CH=CH}$, C-11 and C-12), 172.9-173.3 (C=O , C-3).



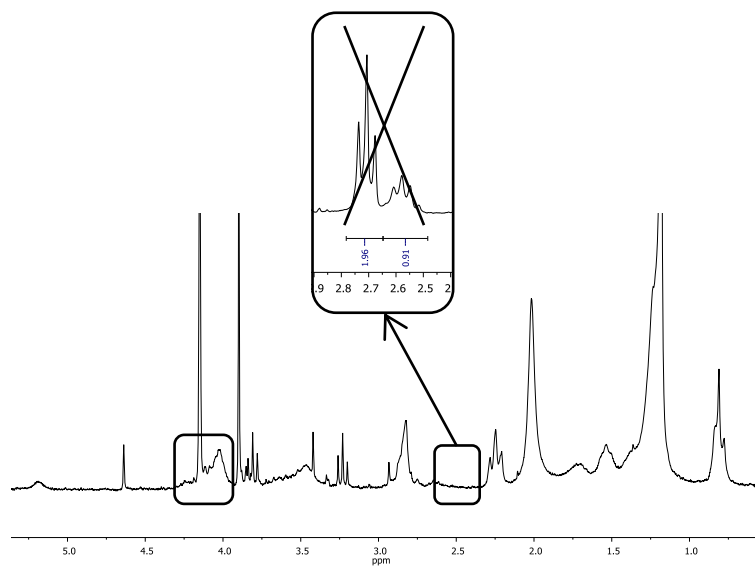
FTIR (cm^{-1}): 3457 (OH, stretching), 3009 (C=C-H (cis), asymmetrical elongation), 2923 (C-H, asymmetrical elongation), 2850 (C-H, symmetrical elongation), 1739 ($\text{C}=\text{O}_{\text{ester}}$, elongation), 1462 (CH_2 scissoring), 1374 (CH_3 symmetrical deformation), 1167 ($\text{C}-\text{O}_{\text{ester}}$ elongation), 1043-964 ($\text{C}-\text{C}-\text{OH}_{\text{mercaptoethanol}}$), 725 (CH_2 rocking).

C- Characterization of macroinitiators

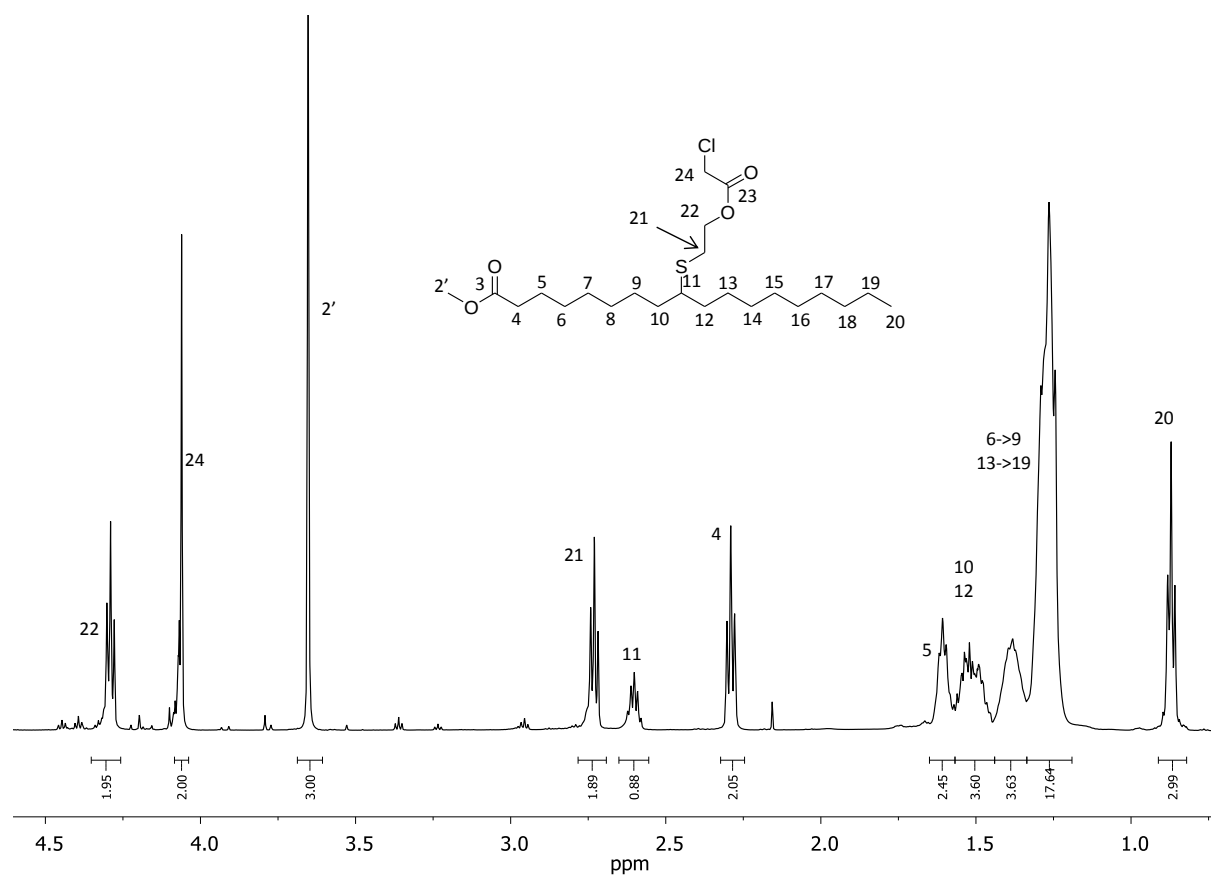
^1H NMR of reaction product of HGSO and *p*-toluenesulfonyl chloride



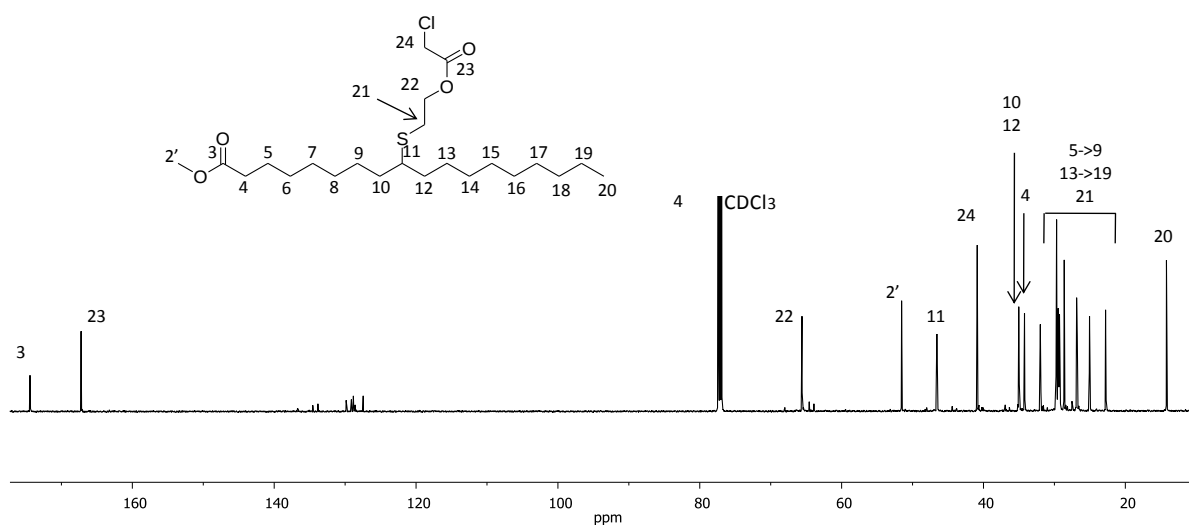
¹H NMR of reaction product of HGSO and trifluoromethanesulfonic anhydride



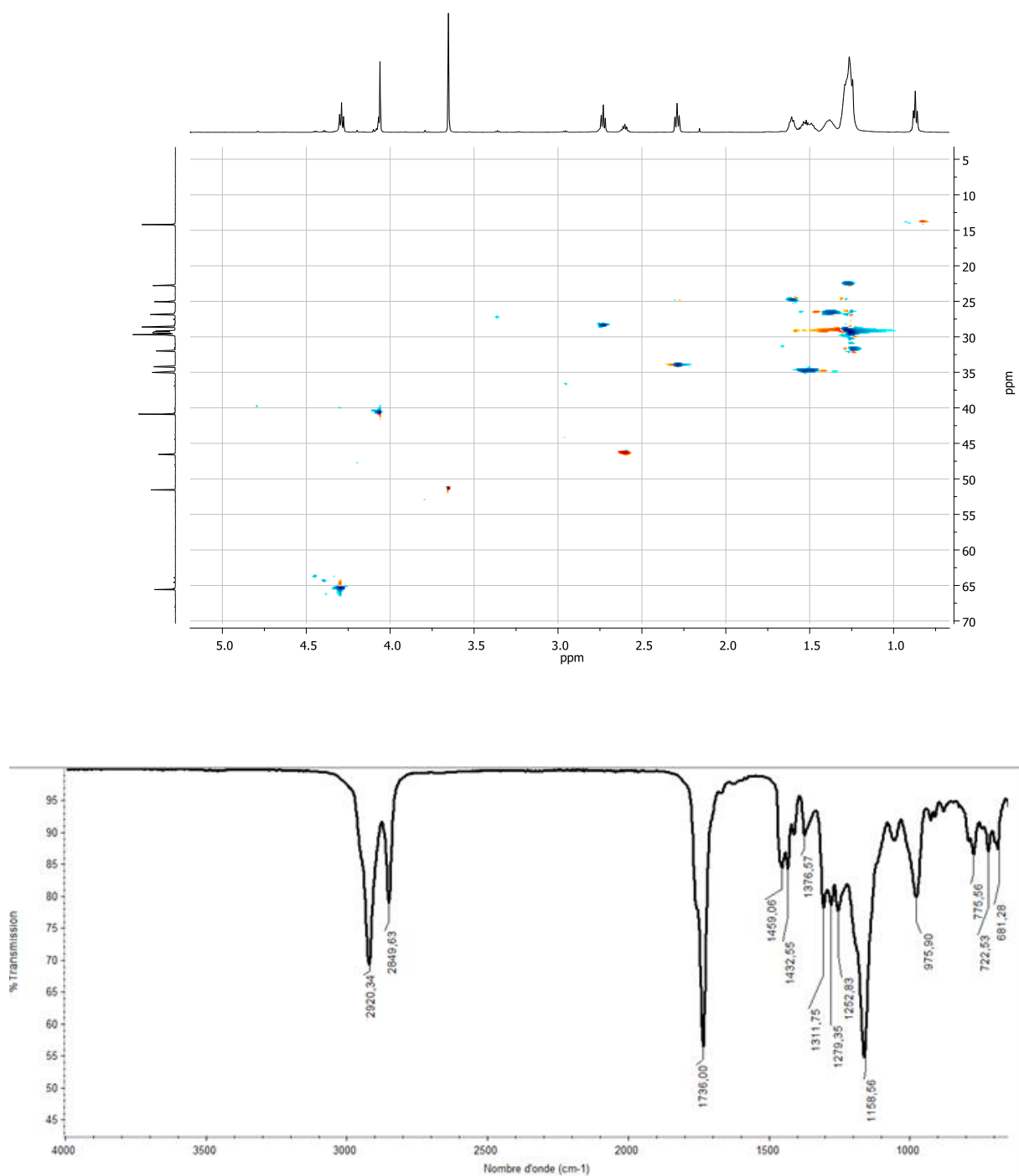
Chloro-methyloleate: Cl-MO



^1H NMR (300 MHz, CDCl_3), δ = 0.79-0.88 (t, J = 7.0 Hz, 3H, $\text{CH}_2\text{-CH}_3$, H-20), 1.16-1.7 (m, 27H, CH_2 , H-5 to H-10 and H-12 to H-19), 2.24-2.33 (t, J = 7.5 Hz, 2 H, $\text{CH}_2\text{-C=O}$, H-4), 2.6 (q, 1H, J = 12.4, 6.3 Hz, CH-S , H-11), 2.73 (t, J = 7.2 Hz, 2H, S-CH_2 , H-21), 3.65 (s, 3H, $\text{CH}_3\text{-O-C=O}$, H-2'), 4.06 (s, 2H, $\text{CH}_2\text{-Cl}$, H-24), 4.27-4.34 (t, J = 7.1 Hz, 2H, $\text{CH}_2\text{-O-(C=O)-CH}_2\text{-Cl}$, H-22).

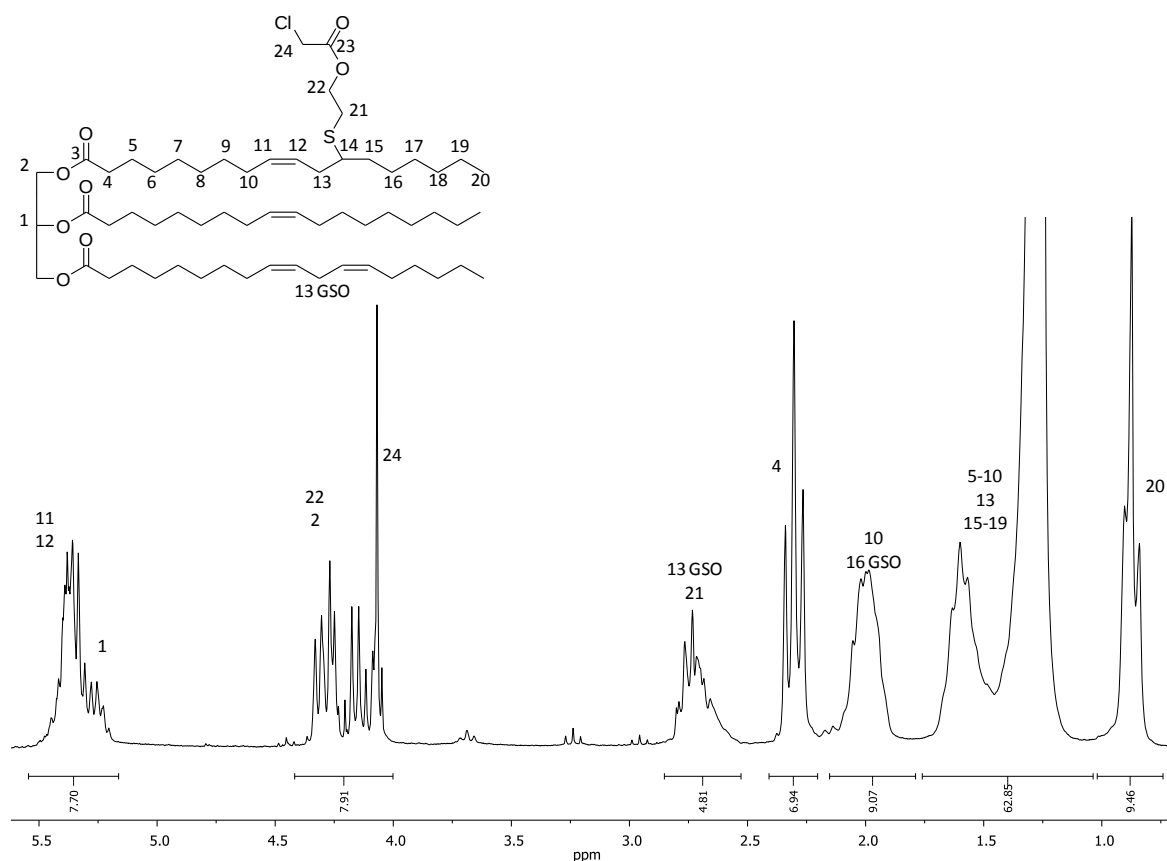


^{13}C NMR (75.47 MHz, CDCl_3), δ = 14.2 ($\text{CH}_2\text{-CH}_3$, C-20), 22.7-31.9 (CH_2 , C5 to C-9, C-13 to C-19 and C-21), 34.2 ($\text{CH}_2\text{-(C=O)-}$, C-4), 35 ($\text{CH}_2\text{-CH-S}$, C-10 and C12), 40.9 ($\text{CH}_2\text{-Cl}$, C-24), 46,6 (CH-S-CH_2 , C-11), 51.5 ($\text{CH}_3\text{-O-(C=O)-}$, C-2'), 65,6 ($\text{CH}_2\text{-O-(C=O)-CH}_2\text{-Cl}$, C-22), 127.9- 129,7 (negligible, residual double bonds), 167,2 ($\text{O-C=O-CH}_2\text{-Cl}$, C-23), 174.4 (C=O).

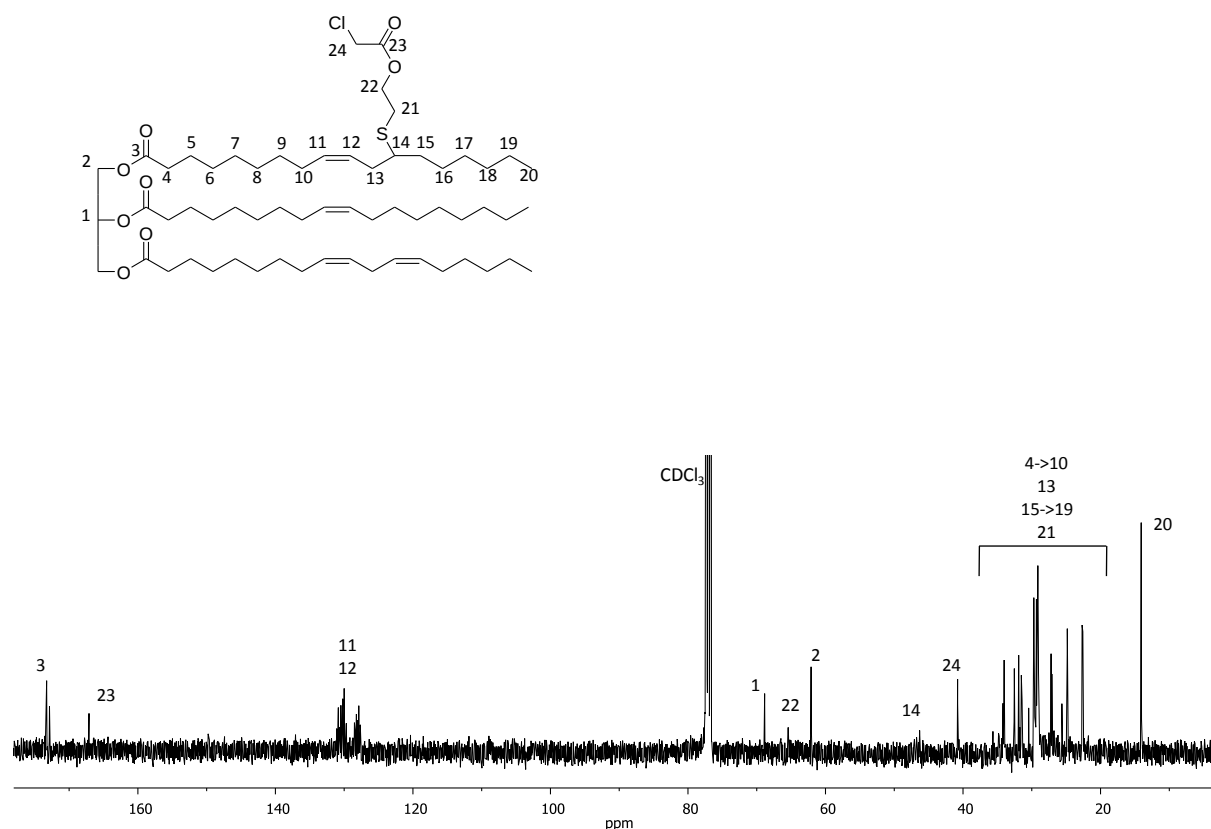


FTIR (cm⁻¹): 2920 (C-H, asymmetrical elongation), 2850 (C-H, symmetrical elongation), 1736 (C=O_{ester}, elongation), 1459-1432 (CH₂ scissoring), 1377 (CH₃ symmetrical deformation), 1159 (C-O_{ester} elongation), 776 (C-Cl stretching), 725 (CH₂ rocking).

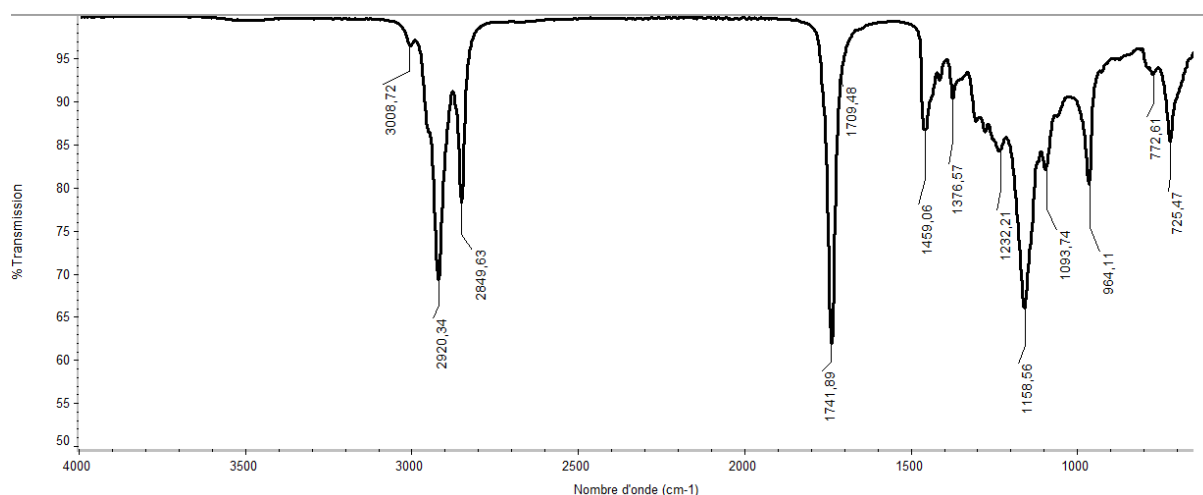
Chloro-grapeseed oil: Cl-GSO



^1H NMR (300 MHz, CDCl_3), δ = 0.79-0.88 (9 H, $\text{CH}_2\text{-CH}_3$, H-20), 1.16-1.70 (63H, CH_2 , $\text{CH}_2\text{-CH-S}$ and $\text{CH}_2\text{-CH}_2\text{-(C=O)-}$, H-6 to H-9, H-16 to H-19, H-13, H-15 and H-5), 1.92-2.07 (9H, $\text{-CH}_2\text{-CH=CH-}$, H-10 and H-16 GSO), 2.24-2.37 (t, 7H, 3J = 7.5 Hz, $\text{CH}_2\text{-(C=O)-}$, H-4), 2.5-2.8 (m, 5H, $\text{CH=CH-CH}_2\text{-CH=CH}$, CH-S and S-CH_2 , H-13 GSO, H-14 and H-21), 4.11-4.32 (m, 8H, $\text{CH}_2\text{-O}$, $\text{CH}_2\text{-O-(C=O)-CH}_2\text{-Cl}$, $\text{CH}_2\text{-Cl}$, H-2, H-22 and H-24), 5.21-5.42 (m, 7.7H, CH-O and CH=CH , H-1 and H-11, H-12).



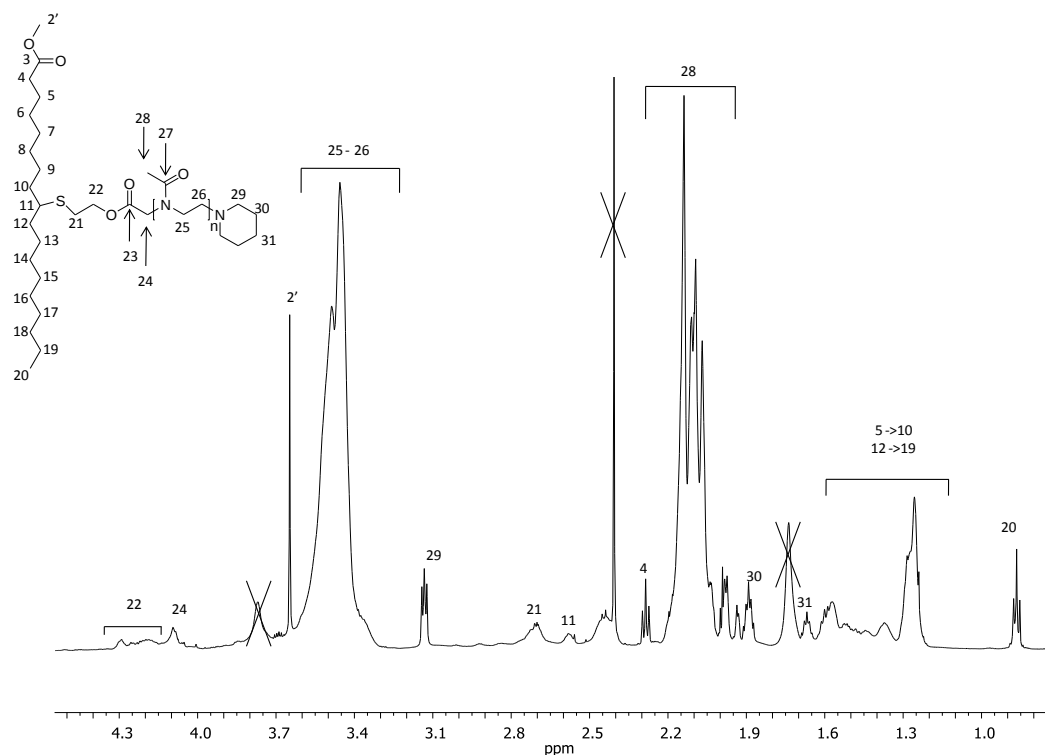
^{13}C NMR (75.47 MHz, CDCl_3), δ = 14.1 ($\text{CH}_2\text{-CH}_3$, C-20), 22.49-35.7 (CH_2 and S- CH_2 , C-4 to C-10, C-13, C-15 to C-19 and C-21), 40.8 ($\text{CH}_2\text{-Cl}$, C-24), 46.3 (CH-S , C-14), 62.1 ($\text{CH}_2\text{-O}$, C-2), 65.3 ($\text{CH}_2\text{-O-(C=O)-CH}_2\text{-Cl}$, C-22), 69.1 (CH-O , C-1), 127.8-130.05 ($\text{CH}_2\text{-CH=CH-CH}_2\text{-CH=CH}$, C-11 and C-12), 167.2 ($\text{-(C=O)-CH}_2\text{-Cl}$, C-23), 172.9-173.3 (C=O , C-3).



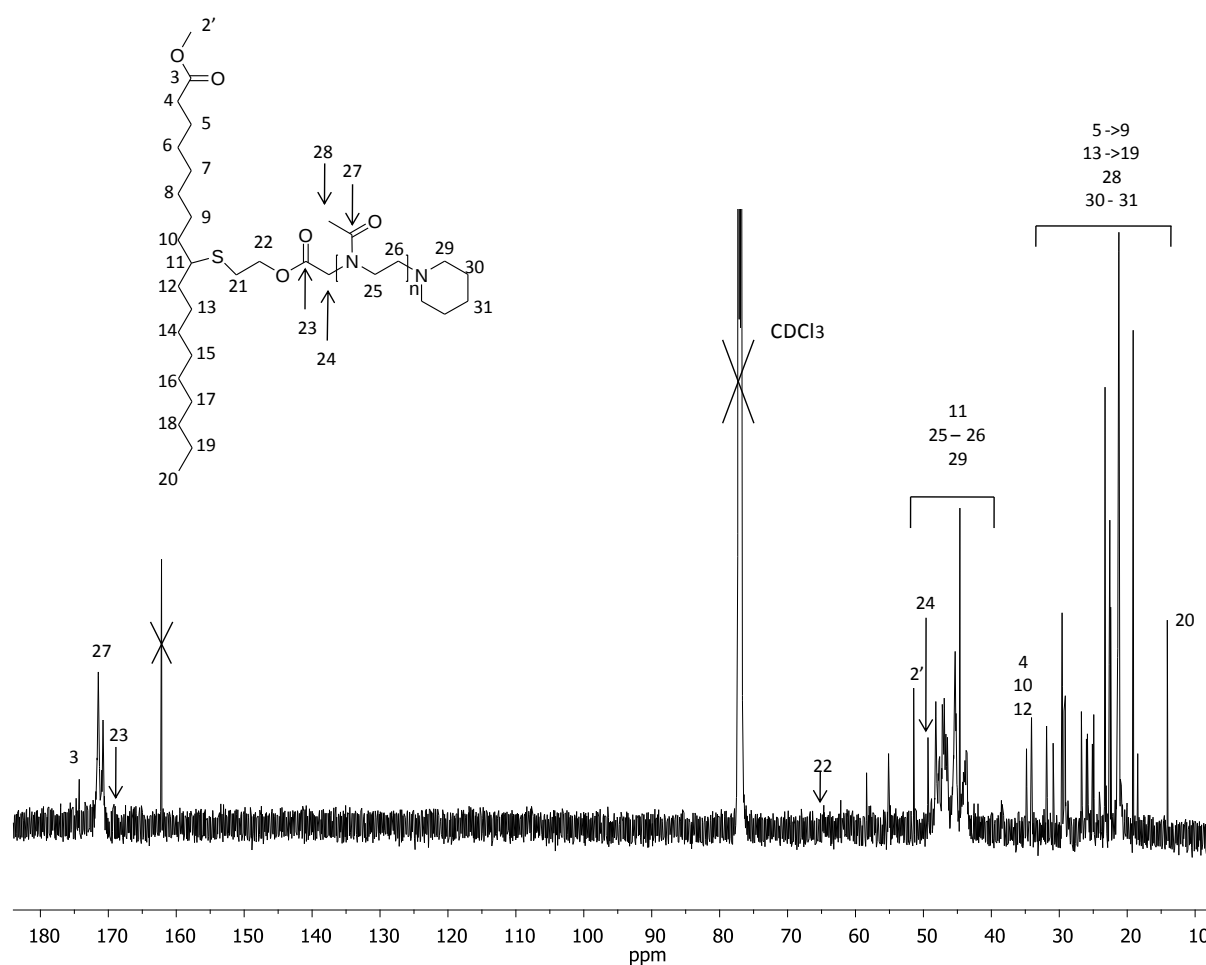
FTIR (cm^{-1}): 3009 (C=C-H (cis), asymmetrical elongation), 2920 (C-H, asymmetrical elongation), 2850 (C-H, symmetrical elongation), 1742 ($\text{C}=\text{O}_{\text{ester}}$, elongation), 1459 (CH_2 scissoring), 1377 (CH_3 symmetrical deformation), 1159 ($\text{C}-\text{O}_{\text{ester}}$ elongation), 772 (C-Cl stretching), 725 (CH_2 rocking).

D- Characterization of LipoPOx

Copolymer based on MO

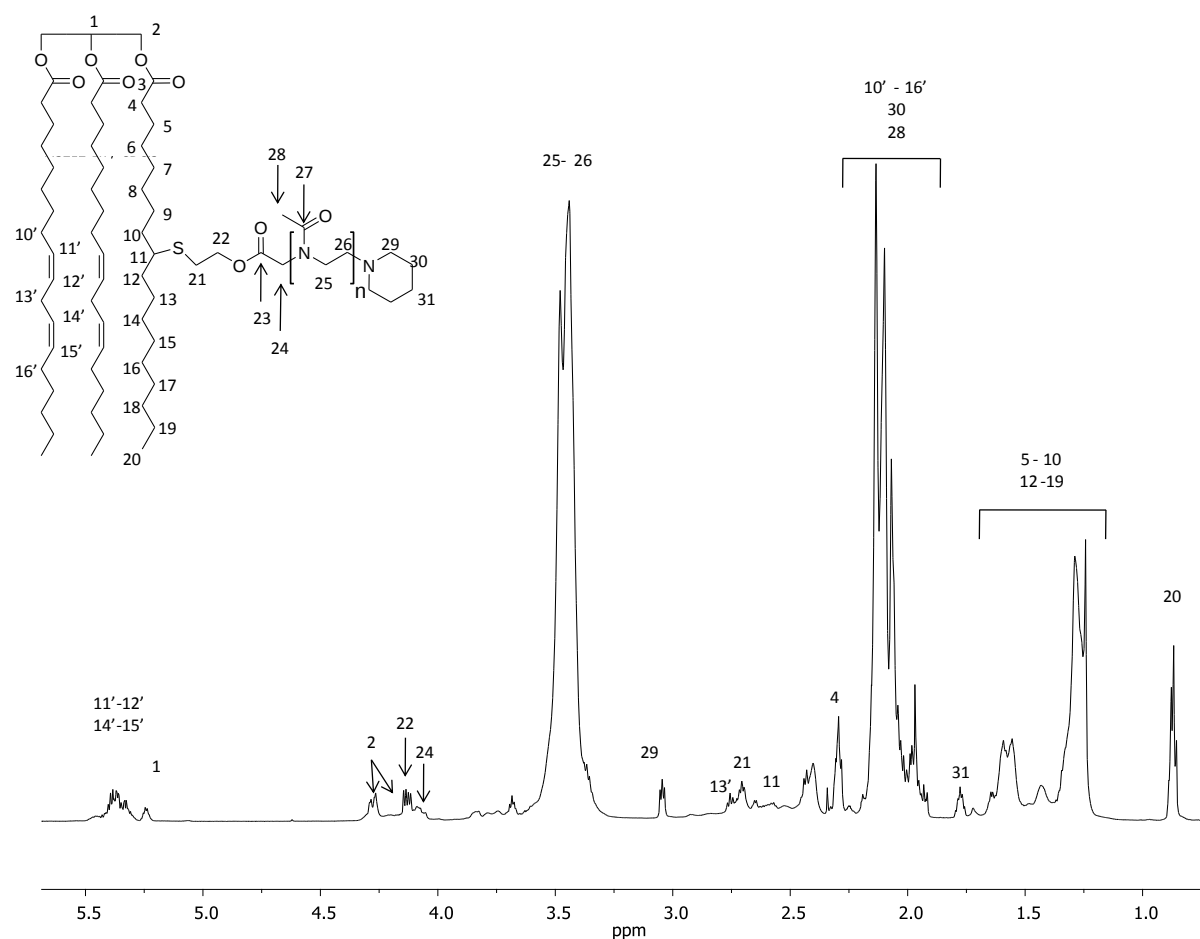


^1H NMR (300 MHz, CDCl_3), δ = 0.79-0.88 (t, $\text{CH}_2\text{-CH}_3$, H-20), 1.16-1.65 (m, CH_2 , H-5 to H-10 and H-12 to H-19), 1.67 ($\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$, H-31), 1.88 ($\text{CH}_2\text{-CH}_2\text{-N}$, H-30), 1.9-2.2 ($\text{CH}_3\text{-(C=O)-N}$, H-28), 2.27-2.31 (t, 2 H, $\text{CH}_2\text{-(C=O)-}$, H-4), 2.6 (m, CH-S , H-11), 2.73 (m, S-CH_2 , H-21), 3.1-3.15 (t, $\text{CH}_2\text{-N}$, H-29), 3.3-3.6 (m, $\text{CH}_2\text{-CH}_2\text{-N-(C=O)-}$, H-25, H-26), 3.65 (s, $\text{CH}_3\text{-O-(C=O)-}$, H-2'), 4.1 (m, $\text{-(C=O)-CH}_2\text{-N-(C=O)-}$, H-24), 4.1-4.3 (m, $\text{S-CH}_2\text{-CH}_2$, H-22).



^{13}C NMR (75.47 MHz, CDCl_3), δ = 14.2 ($\text{CH}_2\text{-CH}_3$, C-20), 22.7-31.9 (CH_2 , C5 to C-9, C-13 to C-19, C-28, C-30 and C-31), 34.1 ($\text{CH}_2\text{-(C=O)-}$, C-4), 34.9 ($\text{CH}_2\text{-CH-S}$, C-10 and C-12), 43- 50 (CH-S-CH_2 , $\text{CH}_2\text{-CH}_2\text{-N-(C=O)-}$, $\text{CH}_2\text{-N}$, C-11, C-25, C-26 and C-29), 49.6 ($\text{-(C=O)-CH}_2\text{-N-(C=O)-}$, C-24) 51.5 ($\text{CH}_3\text{-O-(C=O)-}$, C-2'), 64 ($\text{S-CH}_2\text{-CH}_2$, C-22), 169.2 ($\text{-(C=O)-CH}_2\text{-N}$, C-23), 170.9-171.6 (N-(C=O)-CH_3 , C-27), 174.4 ($\text{CH}_3\text{-(C=O)-}$, C-3).

Copolymer based on GSO



¹H NMR (300 MHz, CDCl₃), δ = 0.79-0.88 (t, CH₂-CH₃, H-20), 1.16-1.65 (m, CH₂, H-5 to H-10 and H-12 to H-19), 1.67 (CH₂-CH₂-CH₂-N, H-31), 1.88-2.2 (CH₂-CH=CH, CH₃-(C=O)-N, CH₂-CH₂-N, H-10', H16', H-28 and H-30), 2.27-2.31 (t, 2 H, CH₂-(C=O)-, H-4), 2.6 (m, CH-S, H-11), 2.73 (m, S-CH₂, H-21), 2.77 (CH=CH-CH₂-CH=CH, H-13'), 3.1-3.15 (t, CH₂-N, H-29), 3.3-3.6 (m, CH₂-CH₂-N-(C=O)-, H-25, H-26), 4.1 (m, -(C=O)-CH₂-N-(C=O)-, H-24), 4.1-4.3 (CH₂-CH₂-S, H-22), 4.11-4.32 (dd, CH₂-O, H-2), 5.25 (CH-O, H-1), 5.3-5.42 (m, CH=CH, H-11', H-12', H-14' and H-15').