

Supporting Information

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1. Acylation of perillyl alcohol

- Chromatograms

Transesterification between perillyl alcohol and vinyl acetate

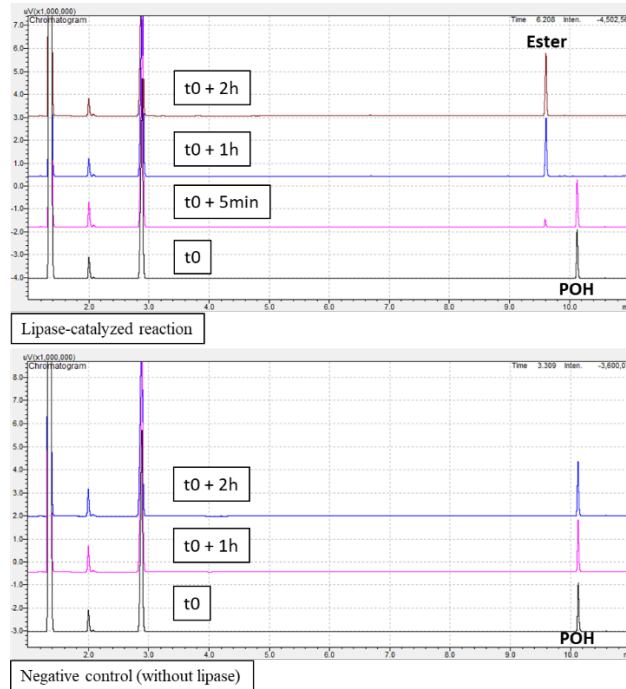


Figure S1. GC-FID of the transesterification of perillyl alcohol (POH, 100 mM) with vinyl acetate (300 mM) with 10 mg of N435 and the negative control without lipase

Esterification between perillyl alcohol and acetic acid

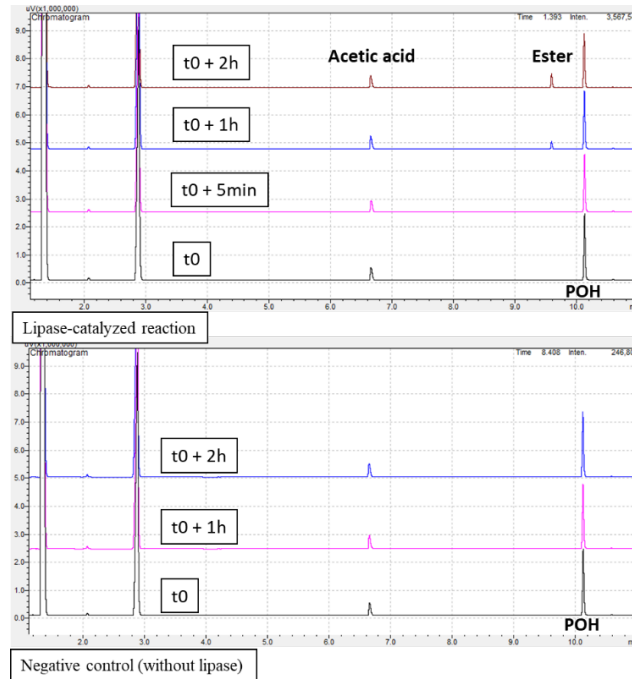


Figure S2. GC-FID chromatogram of the esterification of perillyl alcohol (POH, 100 mM) with acetic acid (300 mM) with 10 mg of N435 and the negative control without lipase

NMR Spectra :

(S)-perillyl alcohol

- ^1H NMR (300 MHz, $\text{DMSO-}D_6$) δ 5.58 (s, 1H), 4.70 (s, 2H), 4.59 (t, 1H, 11), 3.78 (d, 2H), 2.16 – 1.97 (m, 2H), 2.02 – 1.94 (m, 2H), 1.94 – 1.83 (m, 1H), 1.83 – 1.70 (m, 1H), 1.71 (s, 3H), 1.45 – 1.30 (m, 1H).
- ^{13}C NMR (75 MHz, $\text{DMSO-}D_6$) δ 119.37 (C2), 108.49 (C9), 64.57 (C7), 40.49 (C4), 29.48 (C3), 26.81 (C6), 25.32 (C5), 20.35 (C10).

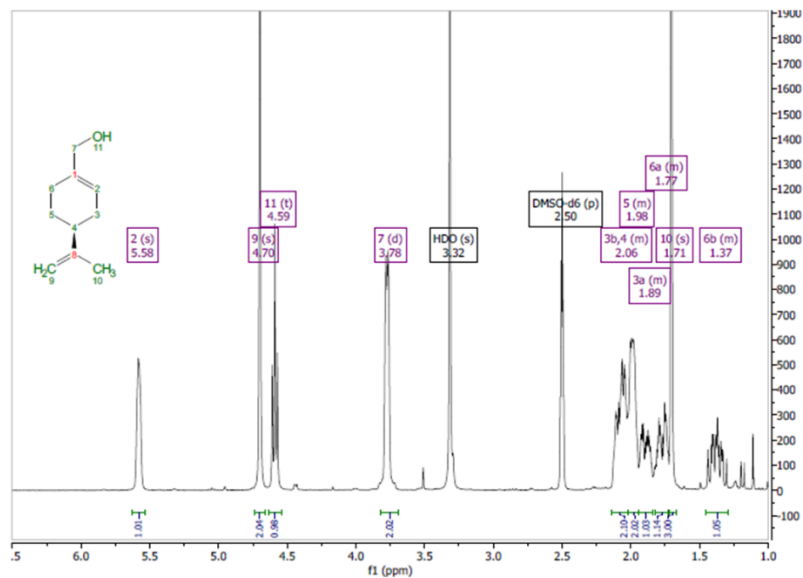
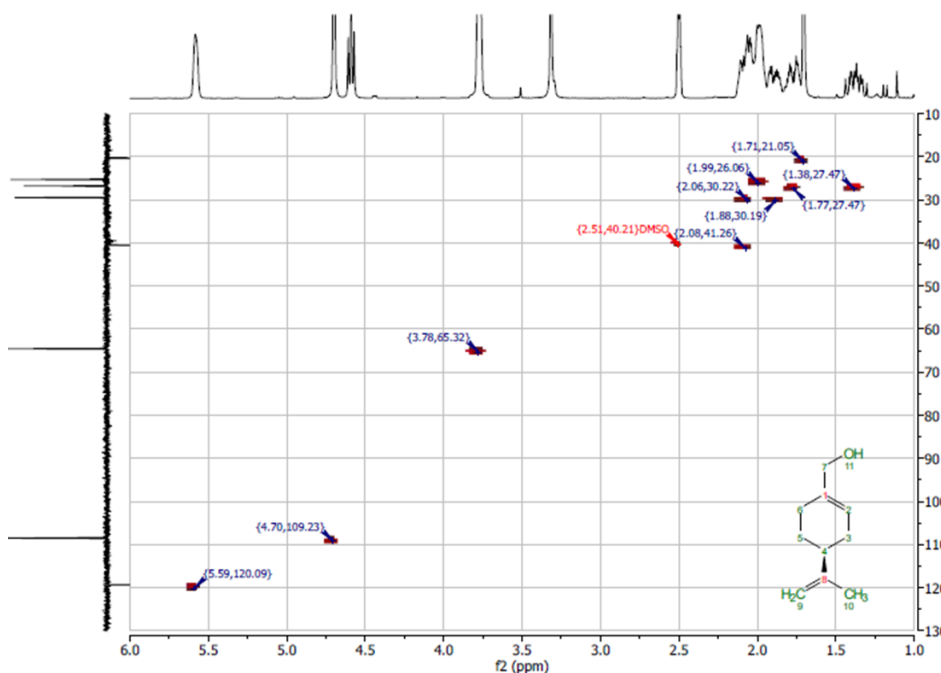
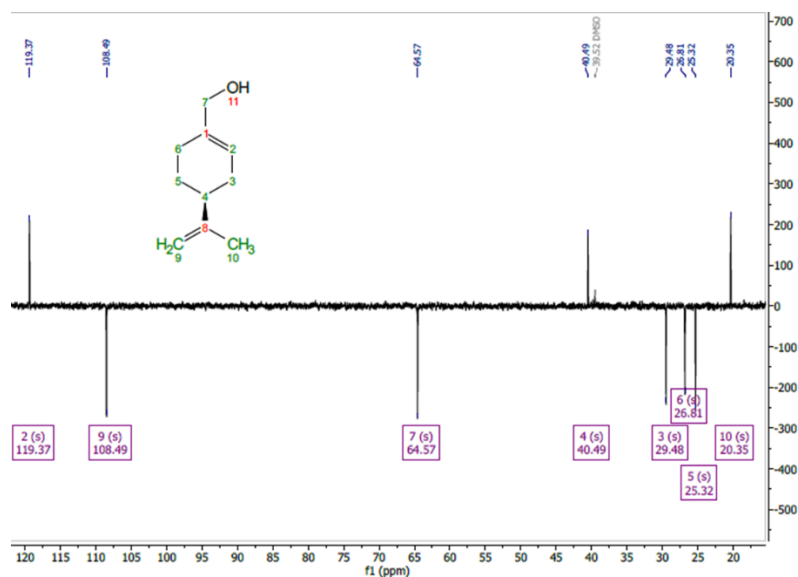


Figure S3. ^1H NMR (300 MHz, $\text{DMSO-}D_6$) spectra of perillyl alcohol 100 mM (reference)



(S)-perillyl acetate

- ¹H NMR (300 MHz, DMSO-D₆) δ 5.72 (s, 1H), 4.71 (s, 2H), 4.40 (s, 2H), 2.16 – 2.06 (m, 2H), 2.06 – 1.98 (m, 2H), 2.00 (s, 3H), 1.97 – 1.86 (m, 1H), 1.83 – 1.73 (m, 1H), 1.70 (s, 3H), 1.49 – 1.30 (m, 1H).
- ¹³C NMR, DEPT135 (75 MHz, DMSO-D₆) δ 125 (C2), 109.28 (C9), 67.68 (C7), 40.49 (C13), 30.06 (C3), 27.10 (C6), 26.06 (C5), 20.97 (C10), 20.89(C4).

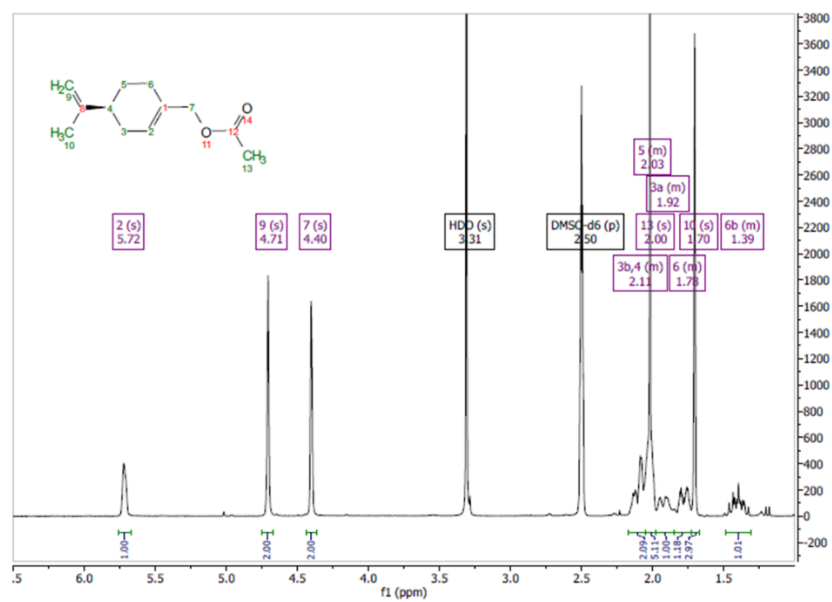


Figure S6. ^1H NMR (300 MHz, DMSO-d_6) spectra of perillyl acetate obtained via the transesterification with vinyl acetate

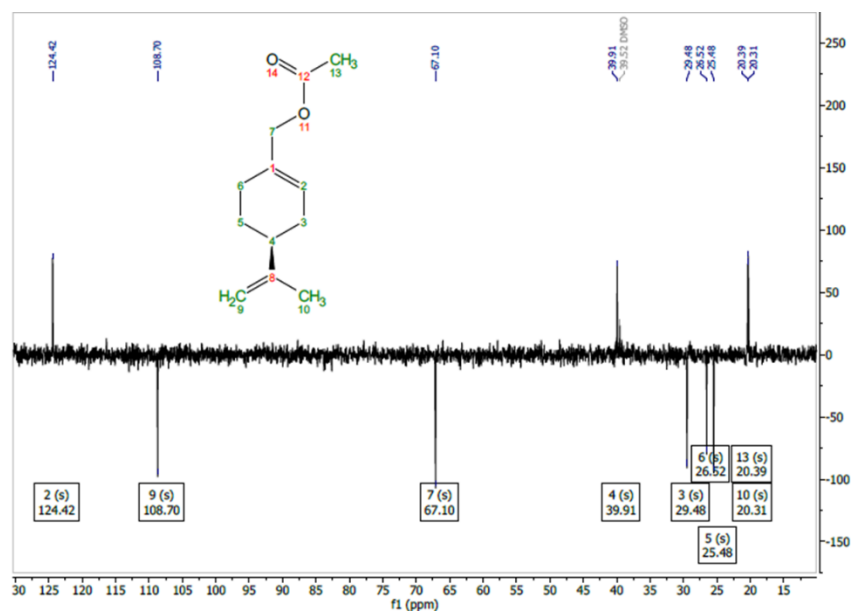


Figure S7. ^{13}C NMR DEPT135 (300 MHz, DMSO-d_6) spectra of perillyl acetate obtained via the transesterification with vinyl acetate

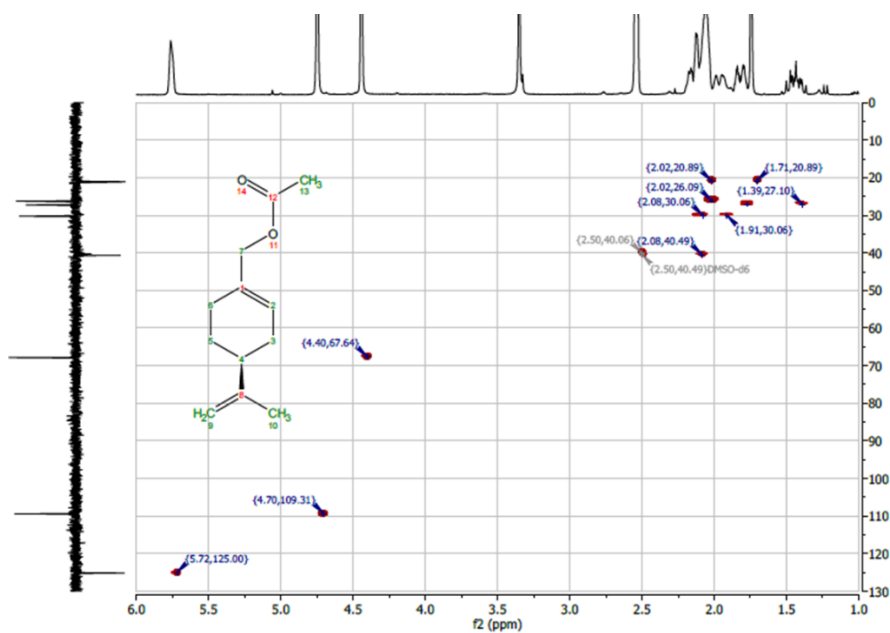


Figure S8. ^{13}C NMR HSQC (75 MHz, $\text{DMSO-}D_6$, $ns=128$) spectra of perillyl acetate

Reaction with Acetic acid:

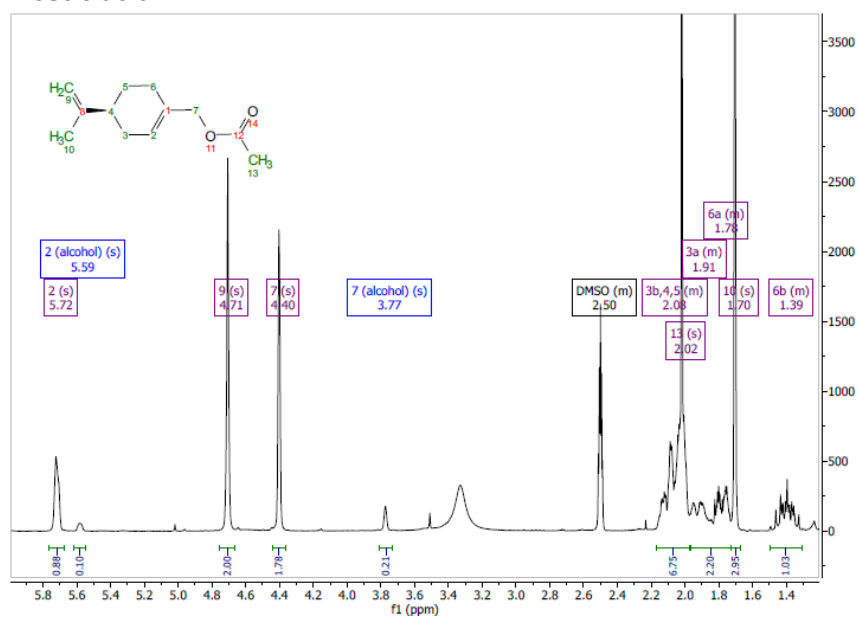


Figure S9. ^1H NMR (300 MHz, $\text{DMSO-}D_6$) spectra of the esterification of perillyl alcohol with acetic acid after 5 days (37°C)

Negative control

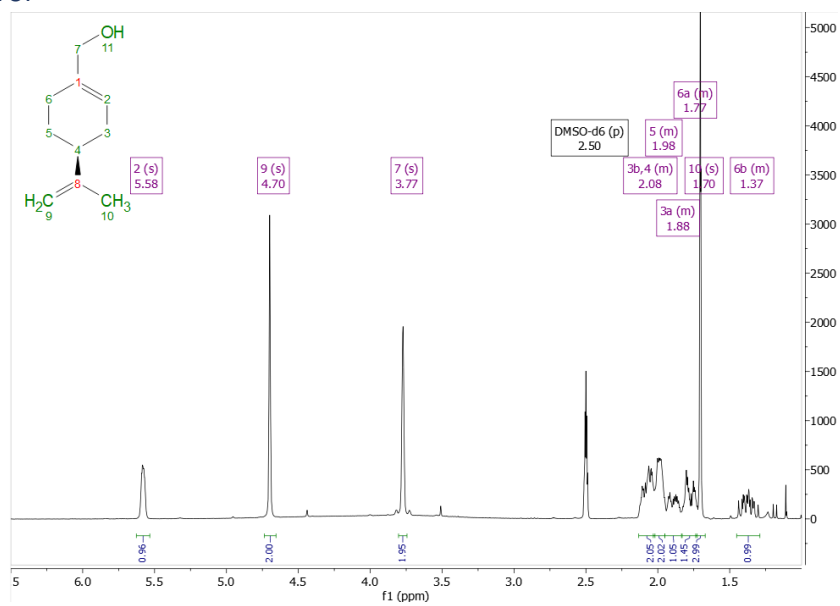


Figure S10. ¹H NMR (300 MHz, DMSO-D₆) of the negative control (reaction mixture) from the esterification with acetic acid after 5 days

2. Acylation of Sesquiterpene Lactones from chicory root

- Chromatograms and Mass Spectra

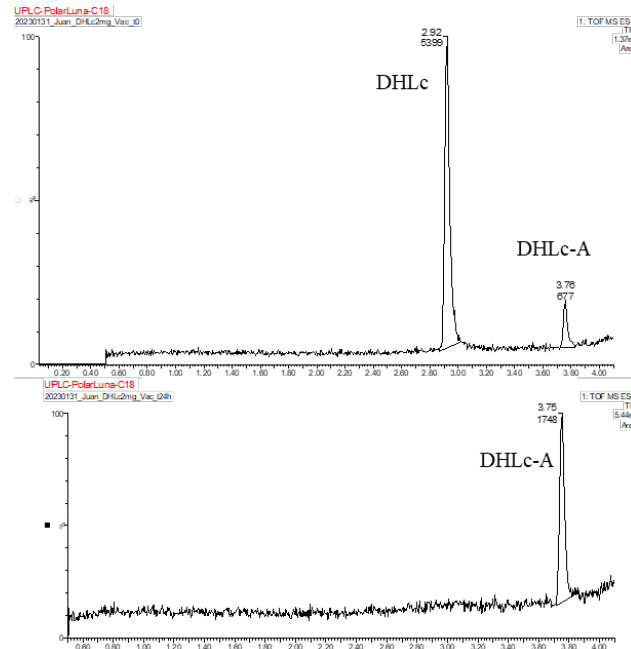


Figure S11. UPLC-MS analysis of the transesterification between 10 mM of DHLc and 100 mM of Vinyl acetate with 2 mg of N435 in 1 mL of MTBE-ACN in the presence of 5 A molecular sieves at 37 °C. Samples (25 μ L) diluted in 200 μ L ACN at t0+5 min and t0+24 h

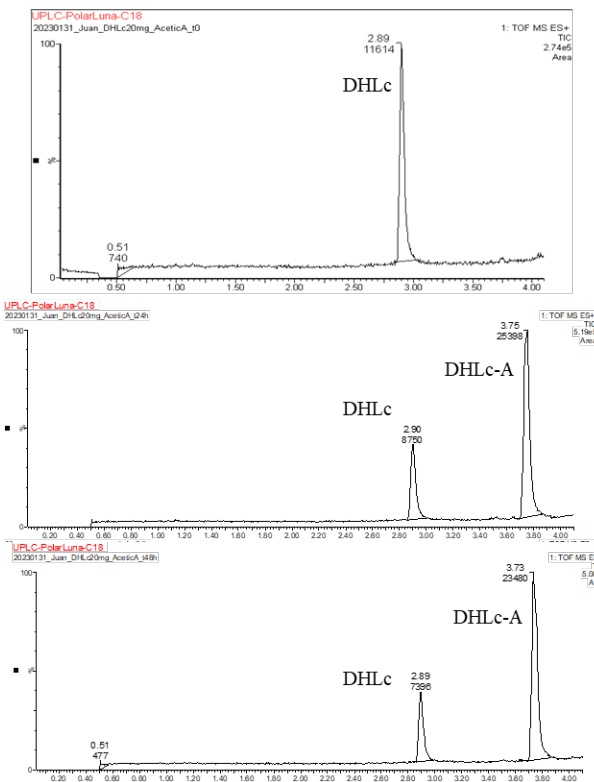


Figure S12. UPLC-MS analysis of the esterification between 10 mM of DHLc and 100 mM of acetic acid with 20 mg of N435 in 1 mL of MTBE-ACN in the presence of 5 Å molecular sieves at 37 °C. Samples (25 µL) diluted in 200 µL ACN at t0+5 min and t0+24 h

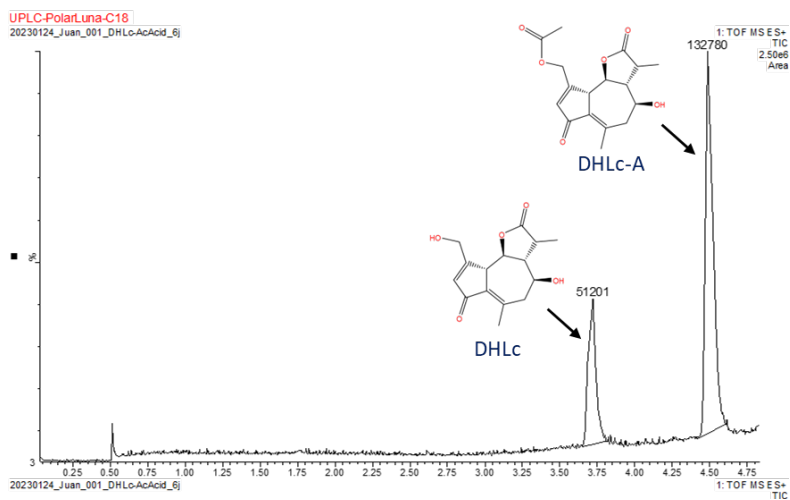


Figure S13. UPLC-MS of the esterification reaction between DHLc and acetic acid after 6 days at 30 °C. Luna Omega Polar C18

- Dihydrolactucin
 - Exact Mass: 278.1154 Da

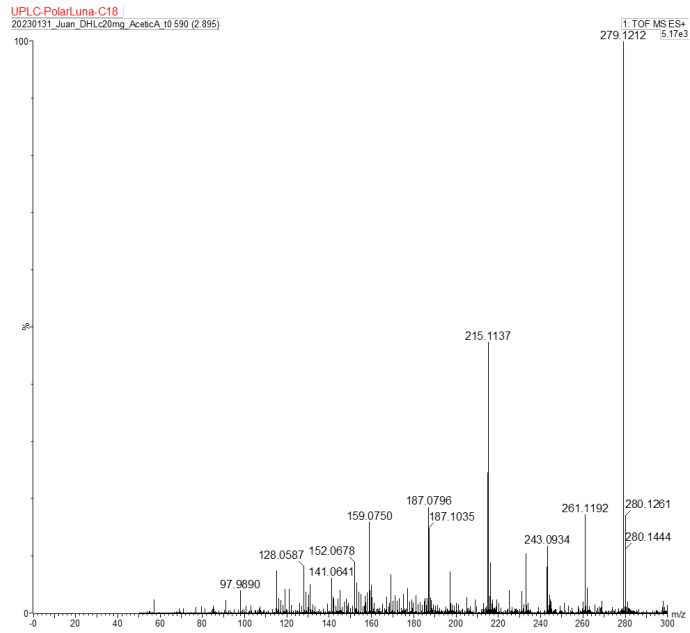


Figure S14. TOFMS-ES+ spectra of dihydrolactucin

- Dihydrolactucin acetate
 - Exact Mass : 320.1260 Da

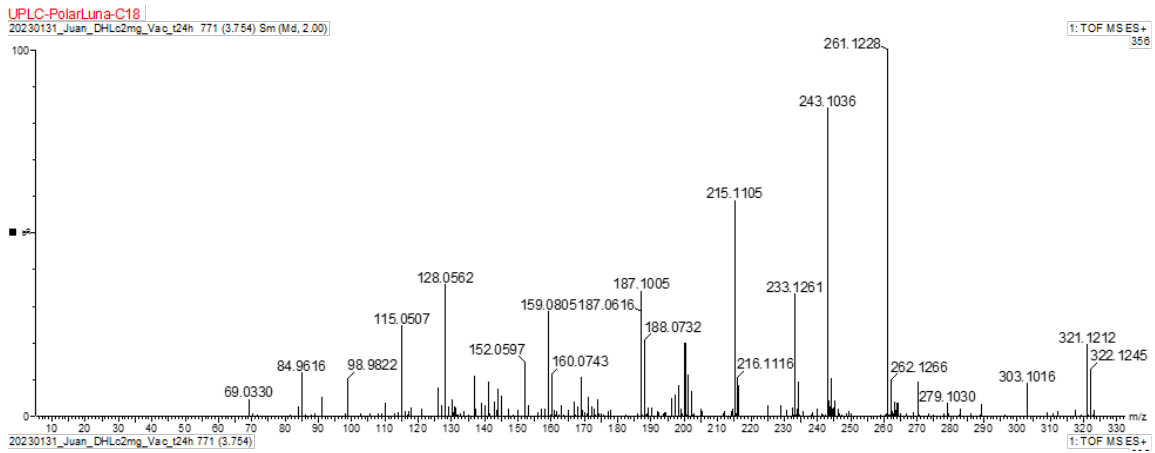


Figure S15. TOFMS-ES+ spectra of dihydrolactucin acetate

- Lactucin acetate
 - Exact Mass : 318.1103 Da

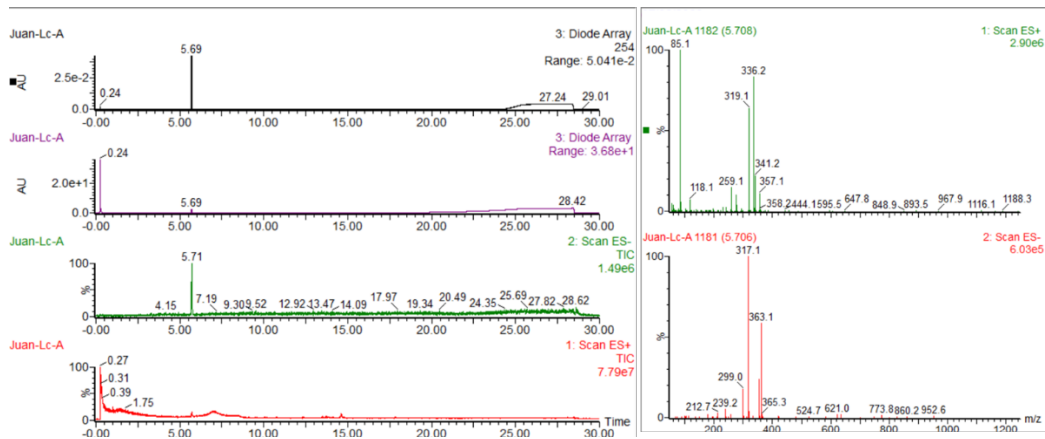


Figure S16. LC-MS analysis of the reaction between lactucin and vinyl acetate; UV at 254 nm, full diode array, TIC ESI⁺, TIC ESI⁻; mass spectra of lactucin acetate in ESI⁺ and ESI⁻

■ Lactucopicrin acetate

- Exact Mass : 452.1471 Da

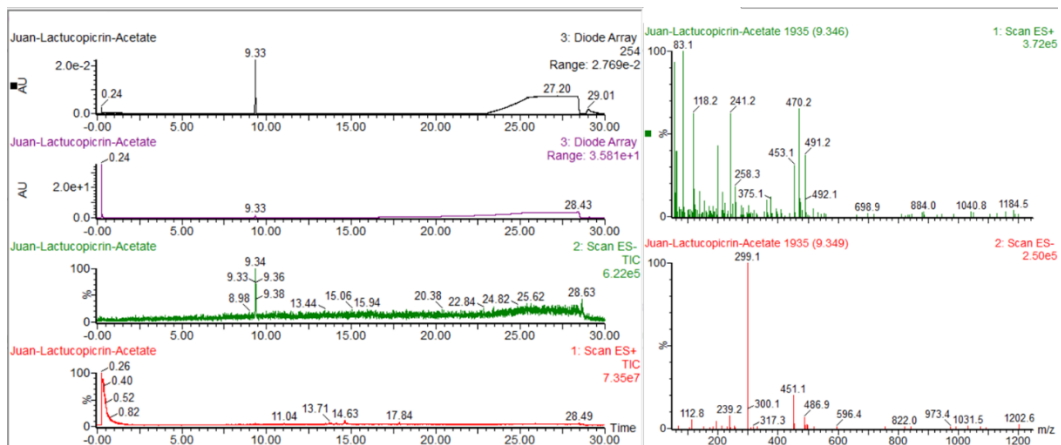


Figure S17. LC-MS analysis of the reaction between lactucopicrin and vinyl acetate; UV at 254 nm, full diode array, TIC ESI⁺, TIC ESI⁻; mass spectra of lactucopicrin acetate in ESI⁺ and ESI⁻

■ Dihydrolactucopicrin acetate

- Exact Mass : 454.1628 Da

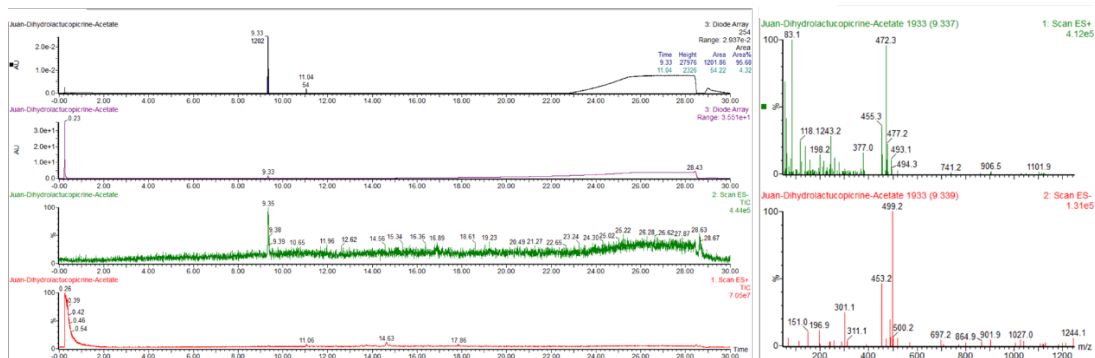


Figure S18. LC-MS analysis of the reaction between dihydrolactucopicrin and vinyl acetate; UV at 254 nm, full diode array, TIC ESI⁺, TIC ESI⁻; mass spectra of dihydrolactucopicrin acetate in ESI⁺ and ESI⁻

- DHLc chloroacetate
- Exact Mass: 354.09 Da

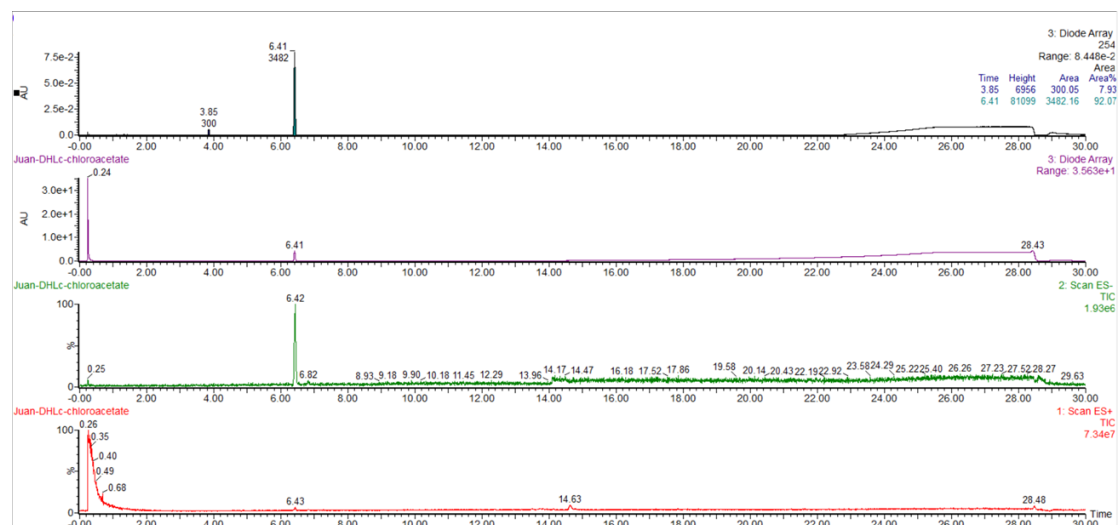


Figure S19. LC-MS analysis of the reaction between DHLc and vinyl chloroacetate; UV at 254 nm, full diode array, TIC ESI⁺, TIC ESI⁻

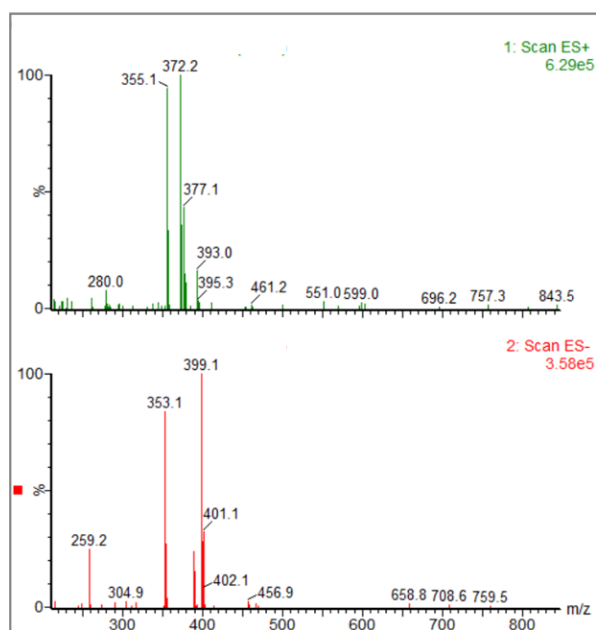


Figure S20. Mass spectra of DHLc chloroacetate in ESI⁺ and ESI⁻

- DHLc propionate

- Exact Mass: 334.14 Da

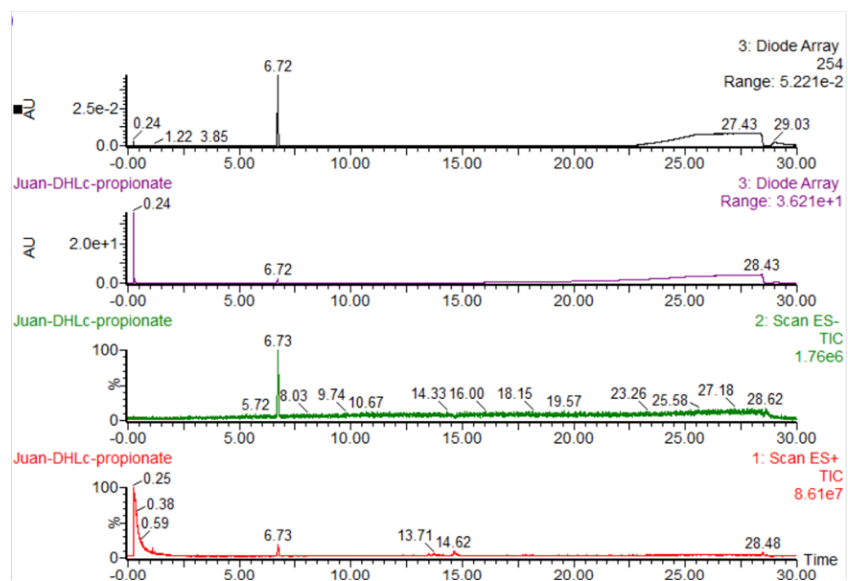


Figure S21. LC-MS analysis of the reaction between DHLc and vinyl propionate; UV at 254 nm, full diode array, TIC ES⁺, TIC ES⁻

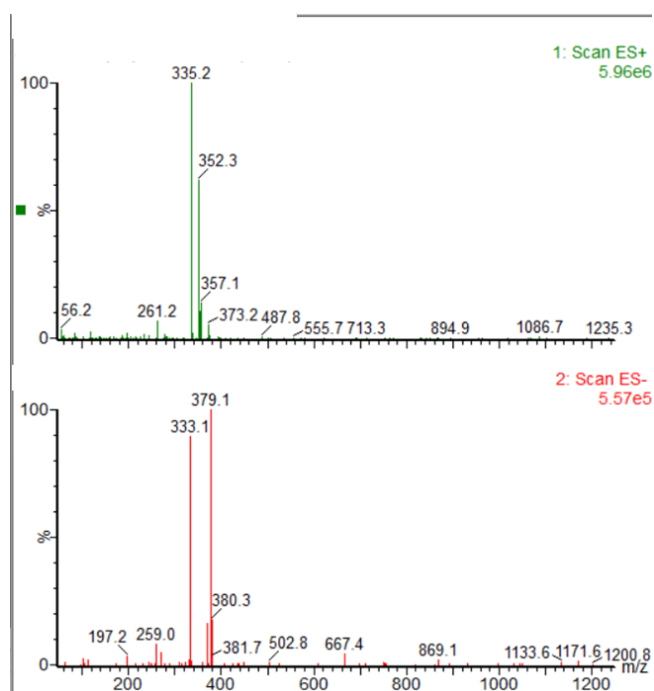


Figure S22. Mass spectra of DHLc propionate in ES⁺ and ES⁻

- DHLc hexanoate

- Exact Mass: 376.19 Da

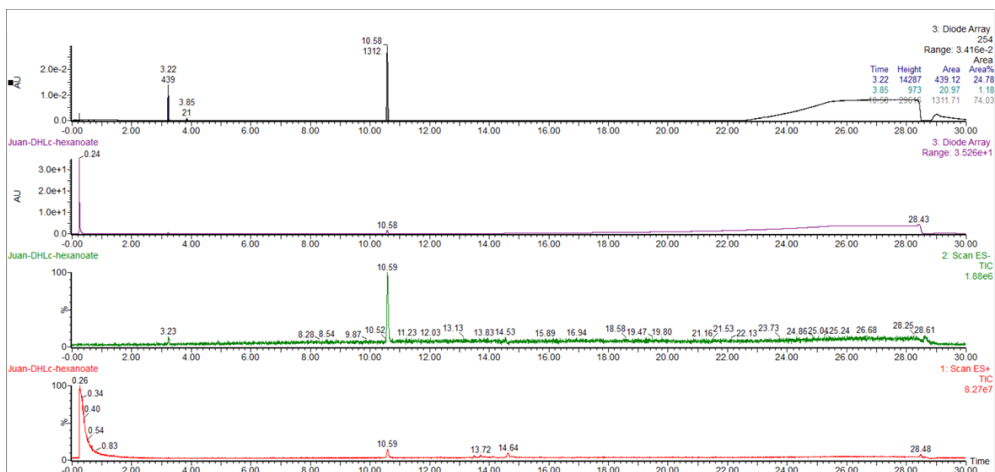


Figure S23. LC-MS analysis of the reaction between DHLc and vinyl hexanoate; UV at 254 nm, full diode array, TIC ES⁺, TIC ES⁻

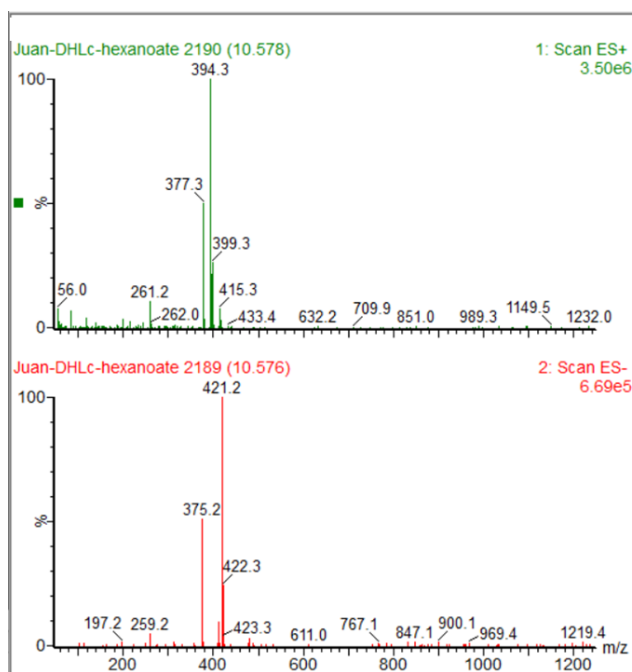


Figure S24. Mass spectra of DHLc hexanoate in ES⁺ and ES⁻

- DHLc octanoate
 - Exact Mass: 404.22 Da

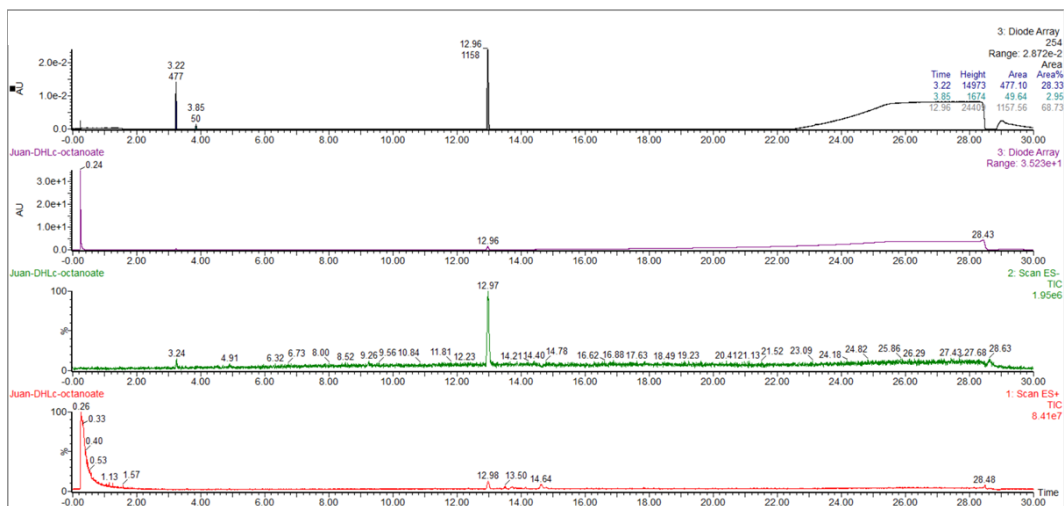


Figure S25. LC-MS analysis of the reaction between DHLc and vinyl octanoate; UV at 254 nm, full diode array, TIC ESI⁺, TIC ESI⁻

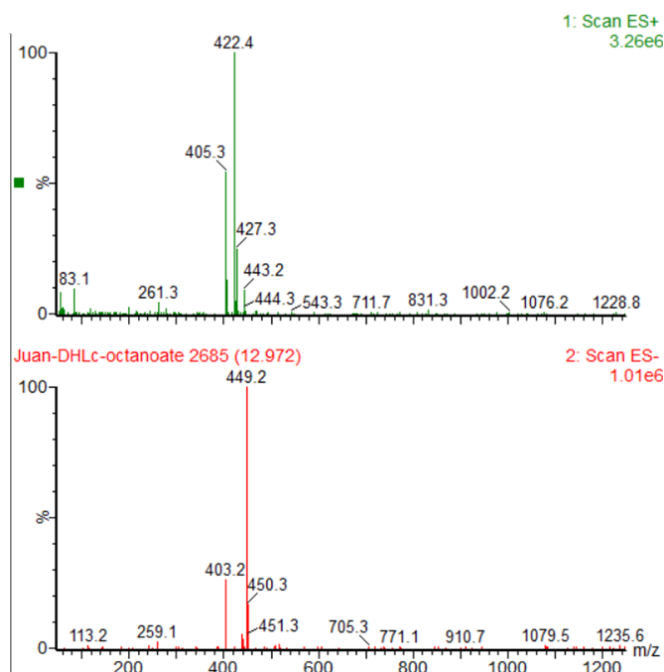


Figure S26. Mass spectra of DHLc octanoate in ESI⁺ and ESI⁻

Compound	Molecular weight	ESI+ major ions (m/z)
DHLc acetate	320.12	321.12 [M+H] ⁺
DHLc chloroacetate	354.09	355.1 [M+H] ⁺ 372.2 [M+NH ₄] ⁺ 377.1 [M+Na] ⁺
DHLc propionate	334.14	335.2 [M+H] ⁺ 352.3 [M+NH ₄] ⁺ 357.1 [M+Na] ⁺
DHLc hexanoate	376.19	377.3 [M+H] ⁺ 394.3 [M+NH ₄] ⁺ 399.3 [M+Na] ⁺
DHLc octanoate	404.22	405.3 [M+H] ⁺ 422.4 [M+NH ₄] ⁺ 427.3 [M+Na] ⁺

Figure 27 Molecular weight and main ion fragments detected in ESI+ of DHLc esters

■ NMR spectra of STLs

■ DHLc

¹H NMR (300 MHz, DMSO-*D*₆) δ 6.28 (s, 1H, 3), 5.29 (t, 1H, A), 5.21 (d, 1H, B), 4.65 (dd, 1H, 15a), 4.23 (dd, 1H, 15b), 3.71 (m, 2H, 5-6), 3.56 (m, 1H, 8), 2.66 (m, 2H, 9a-11), 2.35 (s, 3H, 14), 2.25 (dd, 2H, 7-9b), 2.13 (ddd, 1H, 7), 1.26 (d, 3H, 13).

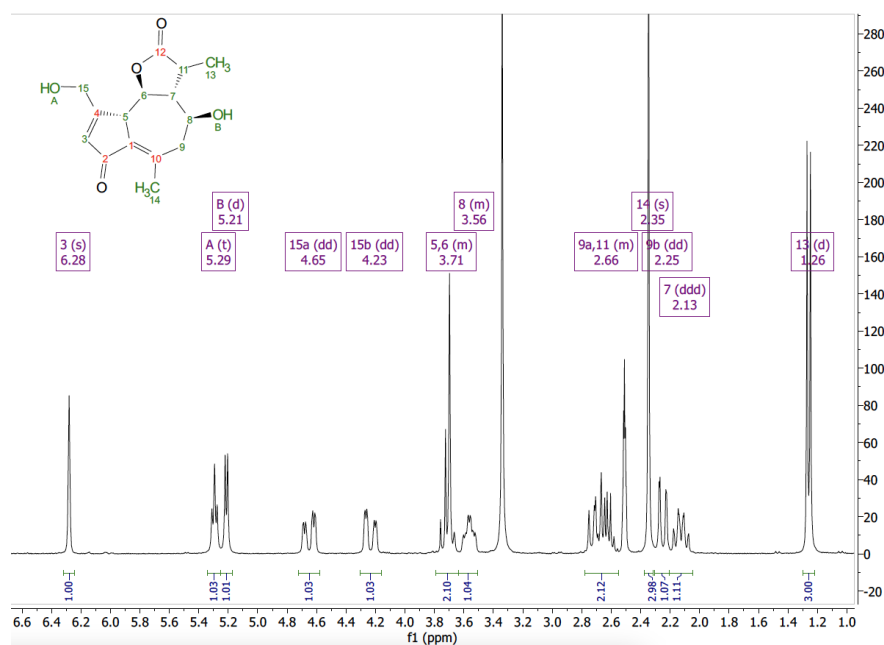


Figure S28. ¹H NMR (300 MHz, DMSO-*D*₆) of DHLc extracted from chicory root

■ DHLc acetate

^1H NMR (300 MHz, $\text{DMSO-}d_6$) 6.28 (s, 1H, 3), 5.30 – 5.18 (m, 2H, 15a-B), 4.83 (dd, 1H, 15b), 3.76 (m, 2H, 5-6), 3.57 (m, 1H, 8), 2.68 (m, 2H, 9a-11), 2.35 (s, 3H, 14), 2.32 – 2.13 (m, 2H, 7-9b), 2.12 (s, 3H, 17), 1.26 (d, 3H, 13).

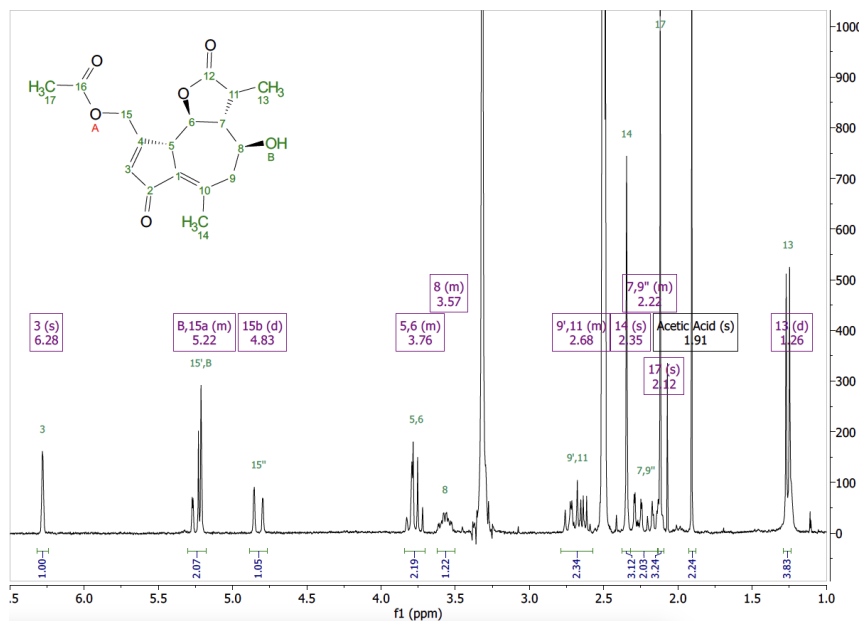


Figure S29. ^1H NMR (300 MHz, $\text{DMSO-}d_6$) spectra of DHLc-A

^{13}C APT NMR (75 MHz, $\text{DMSO-}d_6$) δ 194.49 (C2), 178.10 (C12), 170.44 (C16), 168.07 (C4), 148.64 (C10), 132.72 (C3), 131.84 (C1), 80.67 (C6), 68.29 (C8), 63.35 (C15), 60.40 (C7), 48.83 (C9), 48.65 (C5), 40.96 (C11), 21.65 (C17), 20.98 (C14), 15.67 (C13).

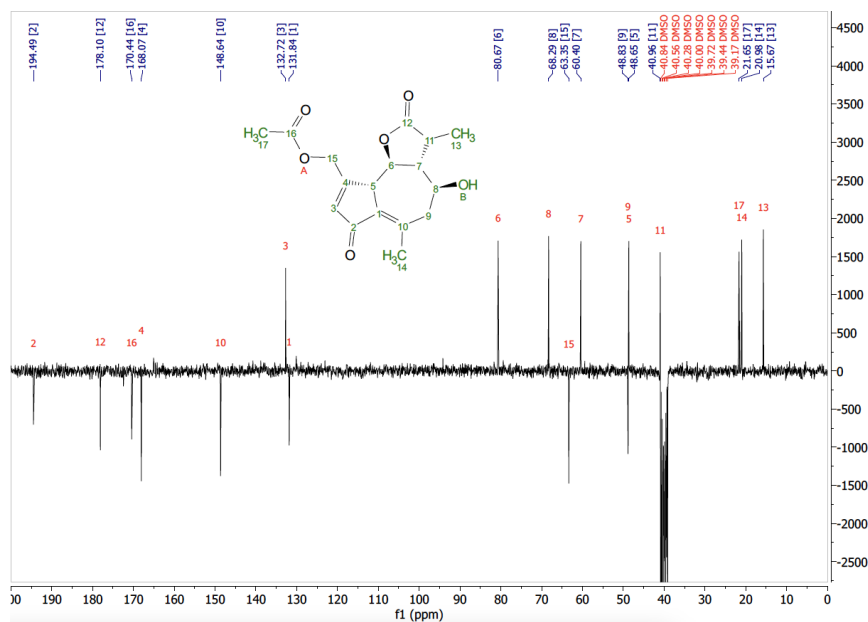


Figure S30. ^{13}C NMR APT (75 MHz, $\text{DMSO-}d_6$) spectra of DHLc-A

- Reaction between DHLc and acetic acid

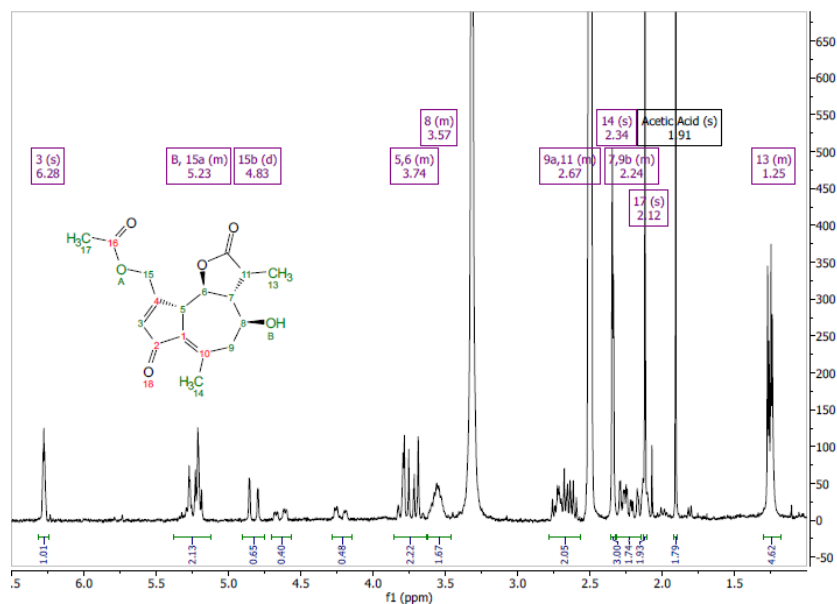


Figure S31. ^1H NMR (300 MHz, $\text{DMSO-}D_6$) spectra of the acylation of DHLc with 10 mM of DHLc, 100 mM of acetic acid, 20 mg N435 after 6 days at 37°C and 35 rpm in 1 mL of MTBE:ACN (3 :1)

- Controls

- Negative Control (without lipase and with DHLc and vinyl acetate)

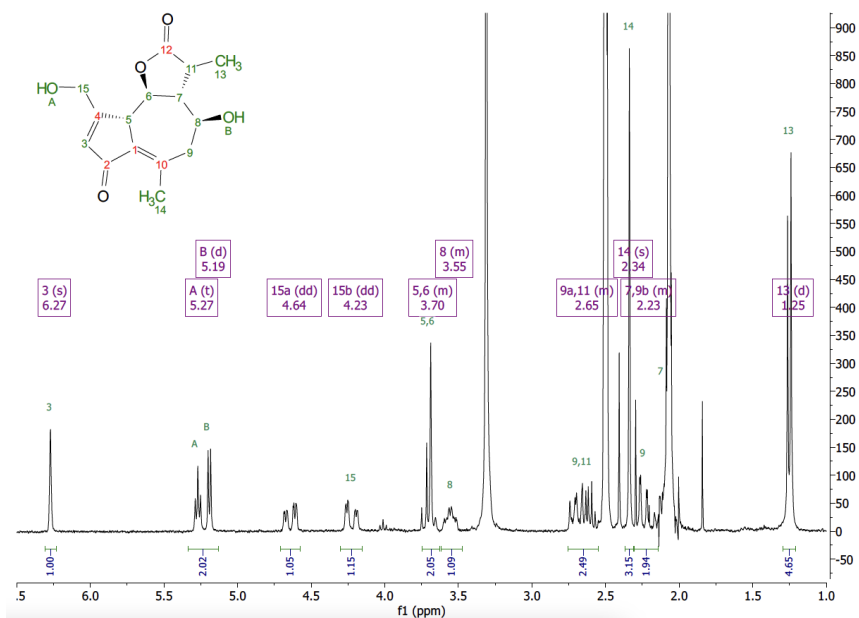


Figure S32. ^1H NMR (300 MHz, $\text{DMSO-}D_6$) spectra of the reaction mixture for the negative control without lipase (with DHLc and Vinyl Acetate) after 48 h at 37 °C

- Negative control without DHLc ; with 20 mg Novozym 435 and 100 mL of vinyl acetate in 1 mL MTBE:ACN (3:1)

Remark : after concentration at 8mbar for 2h no vinyl acetate or acetic acid were detected

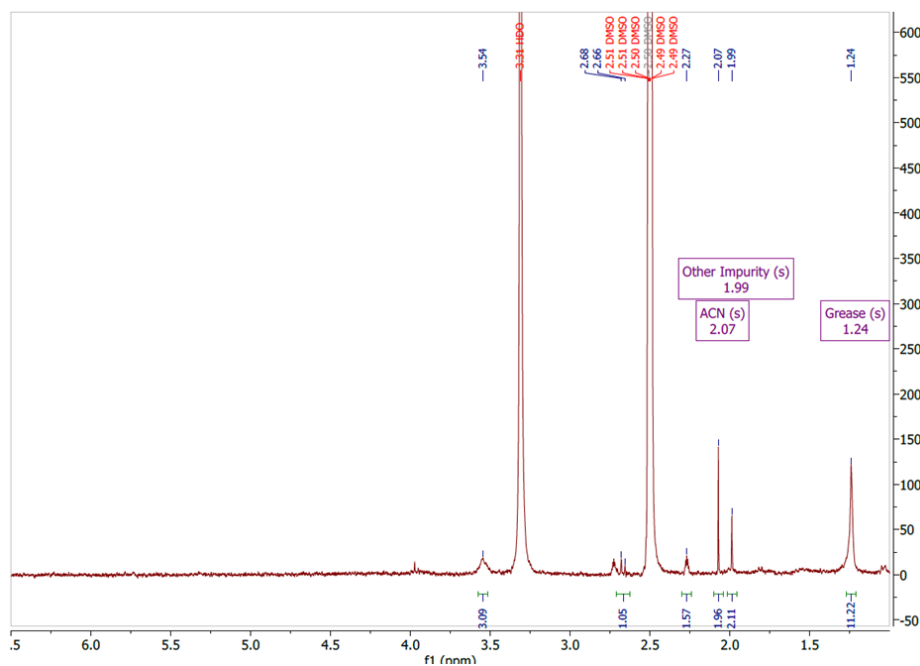


Figure S33. ^1H NMR (300 MHz, $\text{DMSO-}D_6$) spectra of the reaction mixture for the negative control without DHLc (with N435 and Vinyl Acetate) after 48 h at 37 °C

■ Lactucin

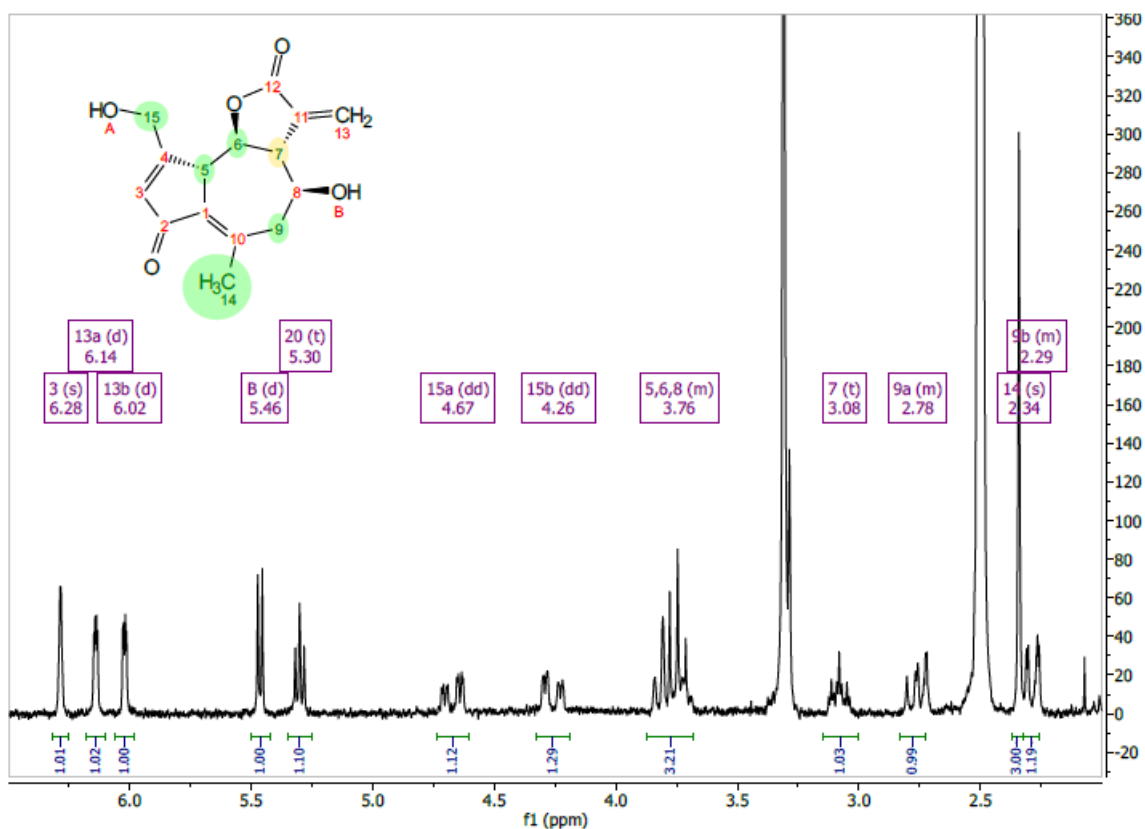


Figure S34. ^1H NMR (300 MHz, $\text{DMSO-}D_6$) spectra of the reaction mixture for the negative control without lipase (with Lc and Vinyl Acetate) after 48 h at 37 °C

■ Lactucin acetate

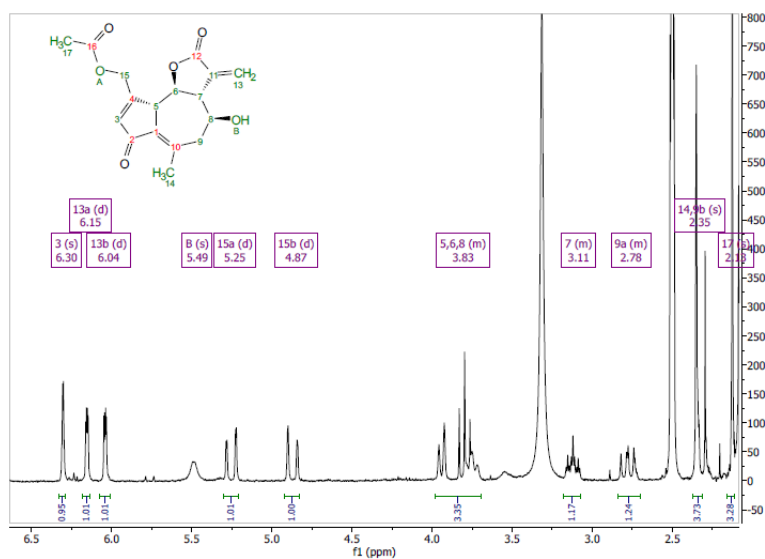


Figure S35. ^1H NMR ($\text{DMSO-}D_6$) spectra of lactucin acetate obtained via the lipase-catalyzed transesterification between lactucin and vinyl acetate (48 h at 37 °C)

- Lactucopicrin acetate

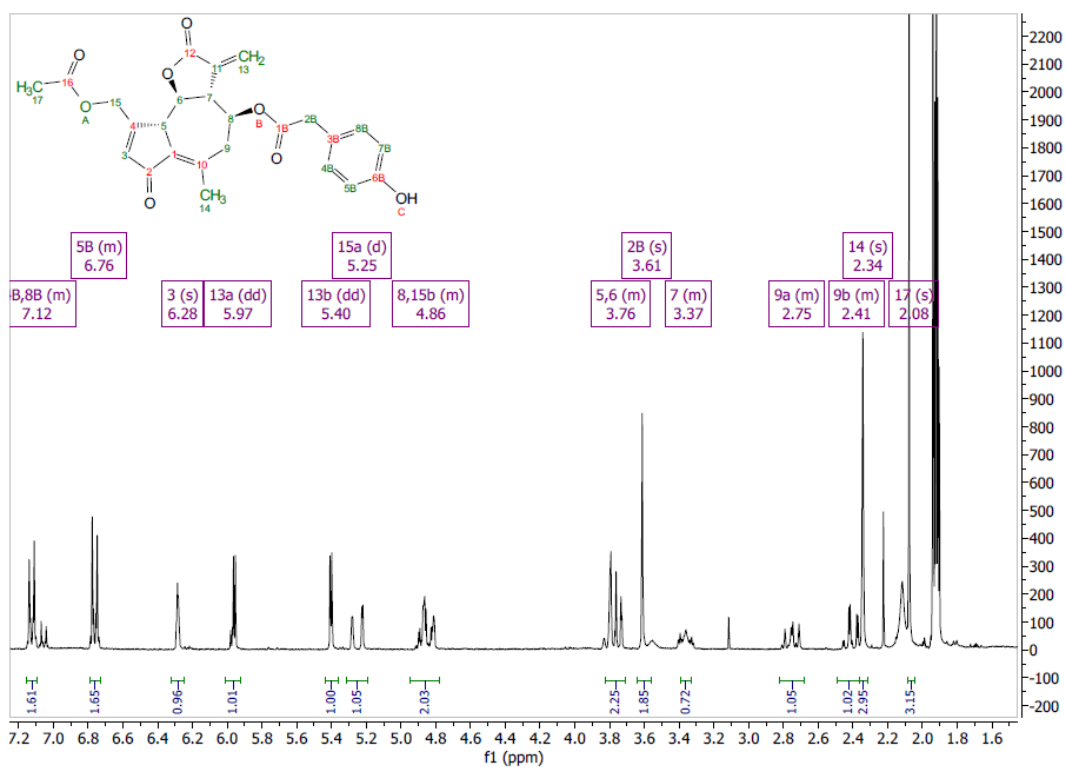


Figure S36. ^1H NMR ($\text{ACN-}D_3$) spectra of lactucopicrin acetate obtained via the lipase-catalyzed transesterification between lactucopicrin and vinyl acetate (48 h at 37 °C)

- Dihydrolactucopicrin

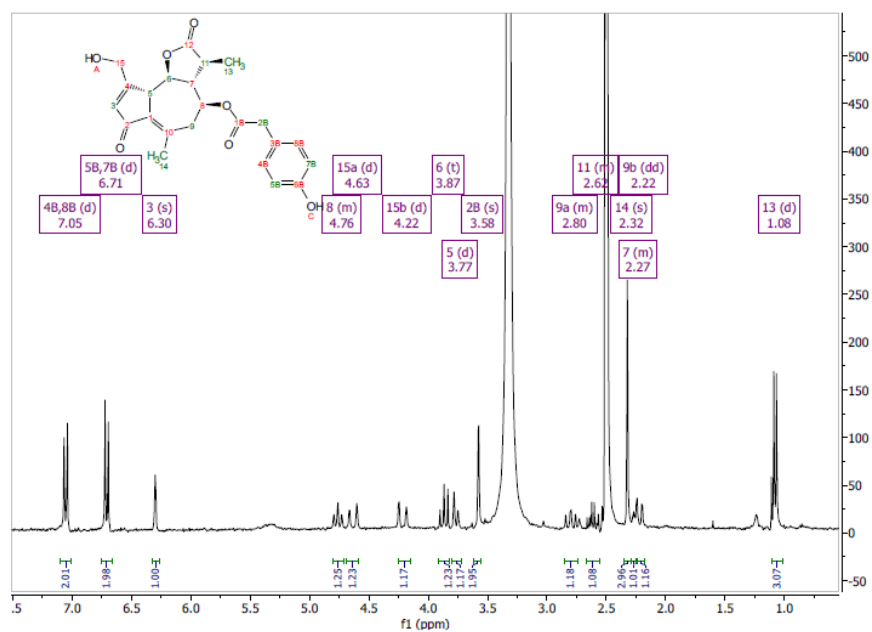


Figure 37. ^1H NMR (300MHz, $\text{DMSO-}d_6$) spectra of the reaction mixture for the negative control without lipase (with DHLp and vinyl acetate) after 48h at 37°C

- Dihydrolactucopiricin acetate

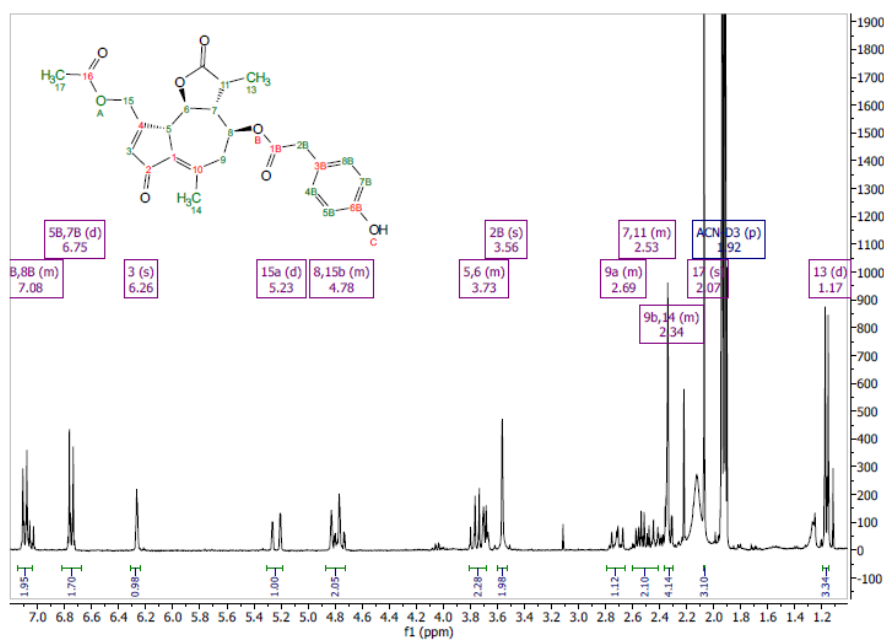


Figure S38. ^1H NMR ($\text{ACN-}d_3$) spectra of DHLp acetate obtained via the lipase-catalyzed transesterification between DHLp and vinyl acetate (48 h at 37°C)

- DHLc chloroacetate

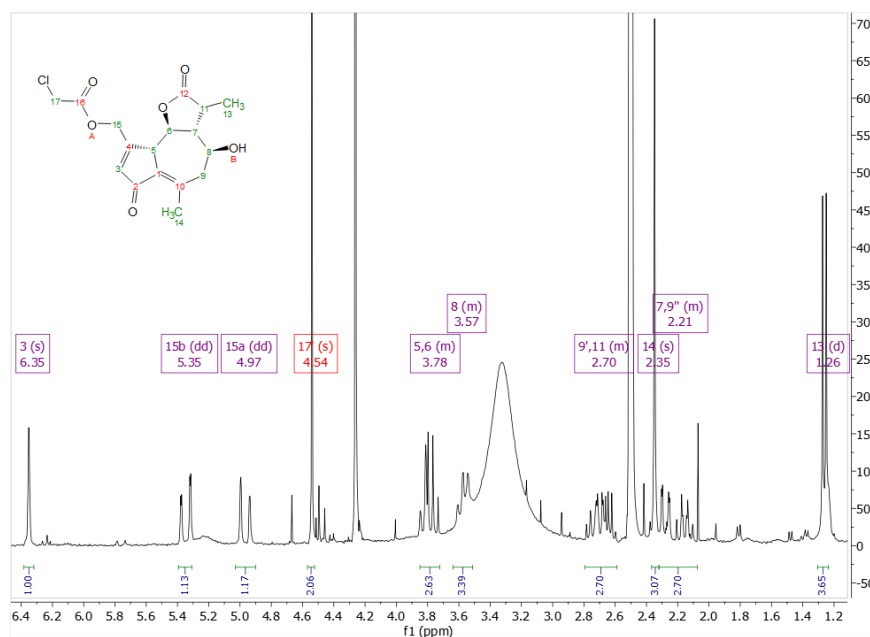


Figure S39. ^1H NMR ($\text{DMSO-}D_6$) spectra of DHLc chloroacetate obtained via the lipase-catalyzed transesterification between DHLc and vinyl chloroacetate (48 h at 37 °C)

- DHLc propionate

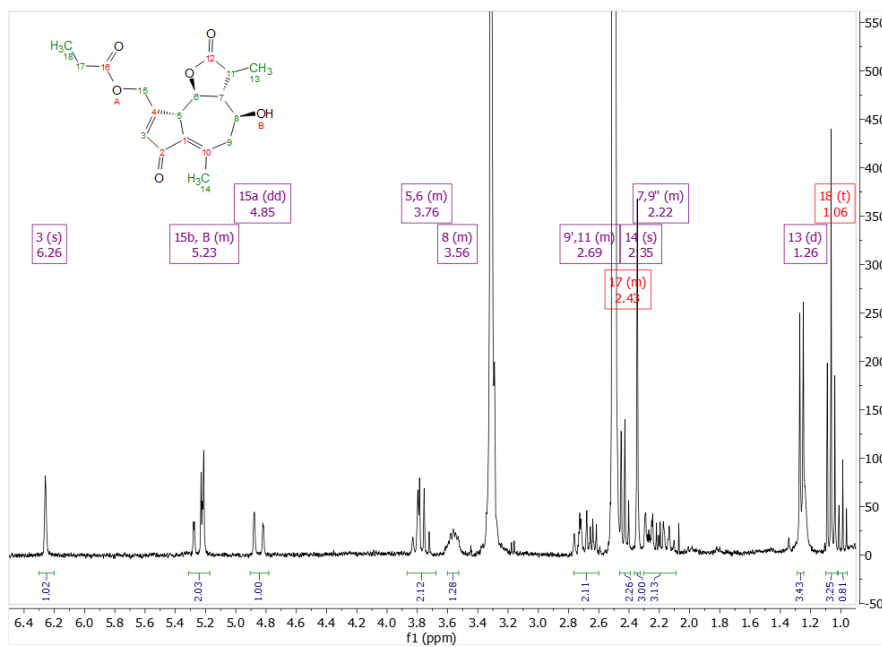


Figure S40. ^1H NMR ($\text{DMSO-}D_6$) spectra of DHLc propionate obtained via the lipase-catalyzed transesterification between DHLc and vinyl propionate (48 h at 37 °C)

- DHLc hexanoate

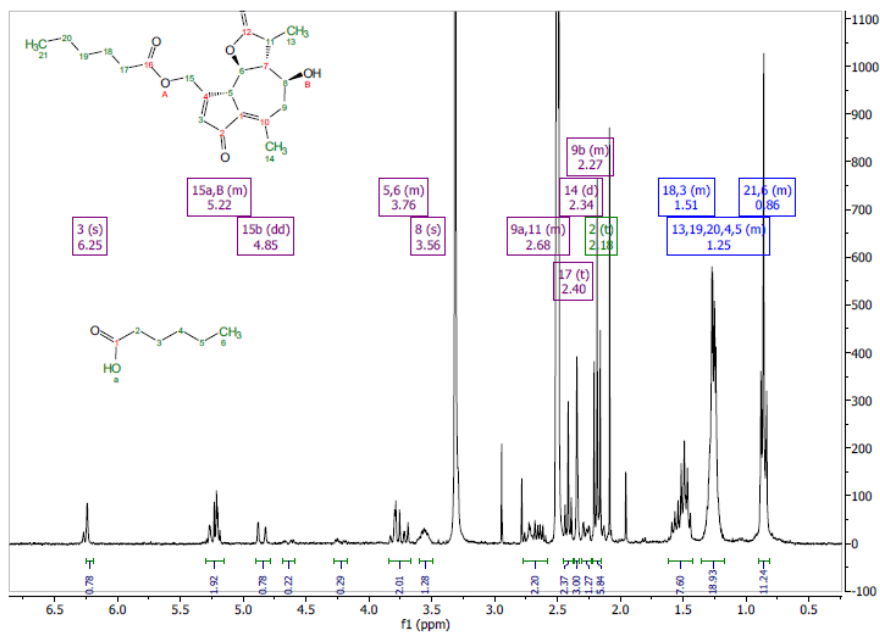


Figure S41. ^1H NMR ($\text{DMSO-}D_6$) spectra of DHLc hexanoate obtained via the lipase-catalyzed transesterification between DHLc and vinyl hexanoate (48 h at 37 °C). Purple : protons of DHLc-P ; Blue : protons of both DHLc-P and vinyl hexanoate/hexanoic acid ; Green : protons of vinyl hexanoate/hexanoic acid

- DHLc octanoate

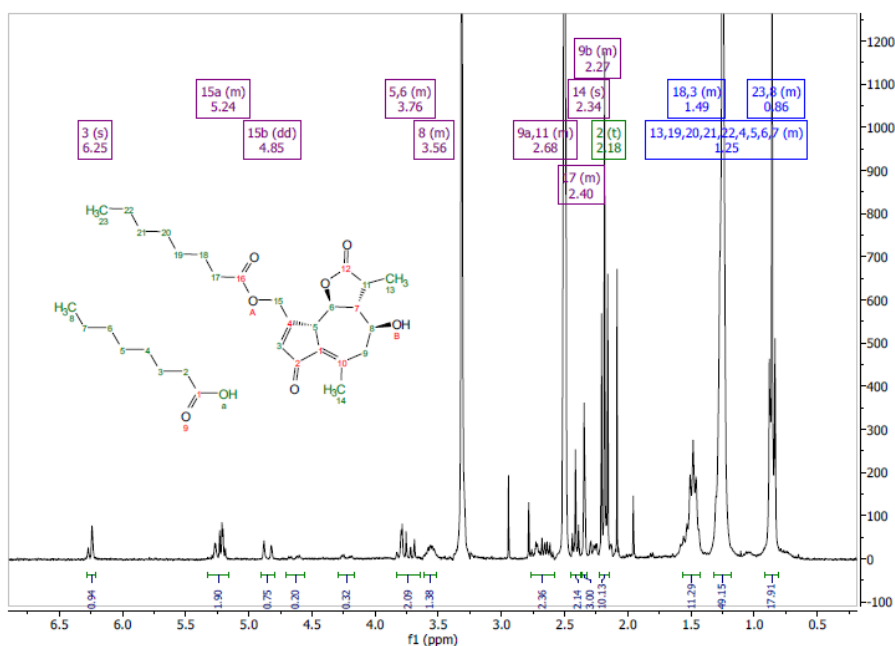


Figure S42. ^1H NMR ($\text{DMSO-}D_6$) spectra of DHLc octanoate obtained via the lipase-catalysed transesterification between DHLc and vinyl octanoate (48 h at 37 °C). Purple : protons of DHLc-P ; Blue : protons of both DHLc-P and vinyl octanoate/octanoic acid ; Green : protons of vinyl octanoate/octanoic acid

3. Synthesis of vinyl esters as acyl donors

- Pd-catalyzed esterification.

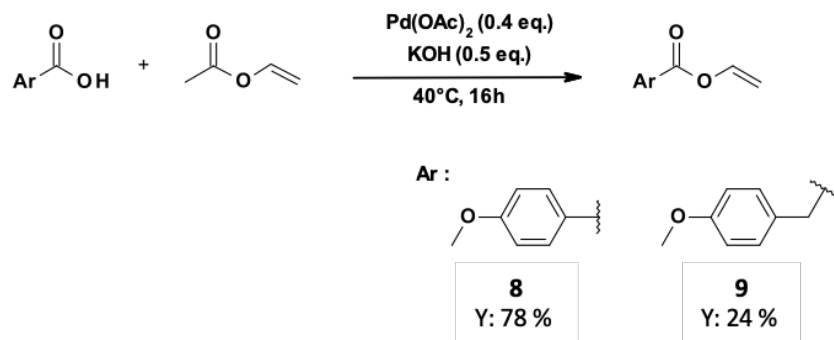


Figure S43. Synthesis of compounds 8 and 9

- Chan-Lam-Evans (CLE)-type esterification.

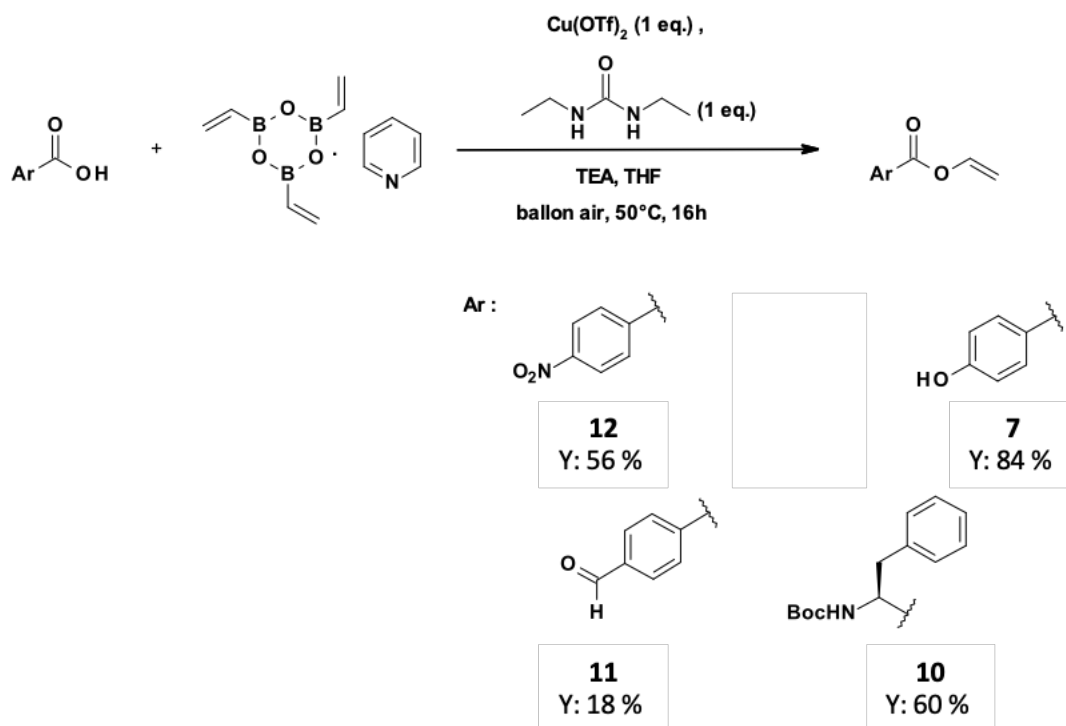


Figure S44. Synthesis of compounds 7,10,11,12.