Chemo- and Regio-selective Enzymatic Lipophilisation of Rutin, and Physicochemical and Antioxidant Properties of Rutin Ester Derivatives

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Supporting Information

NMR Spectra

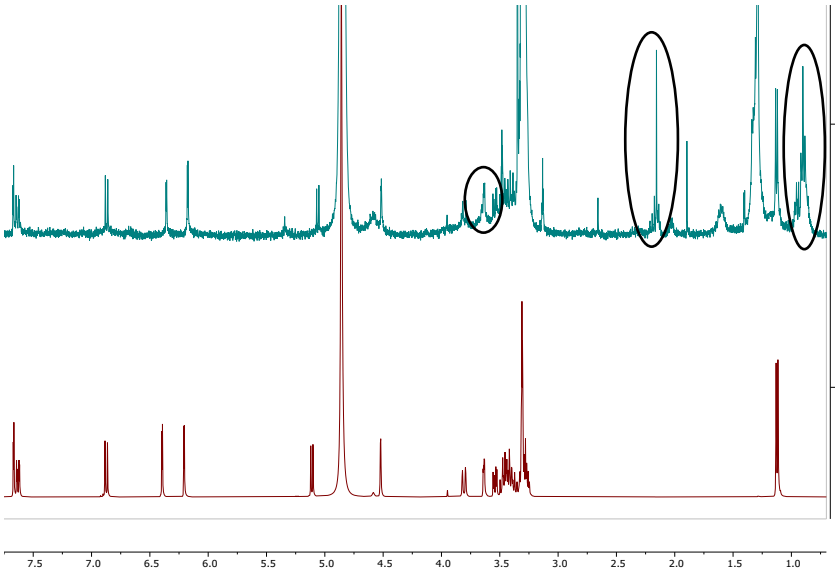
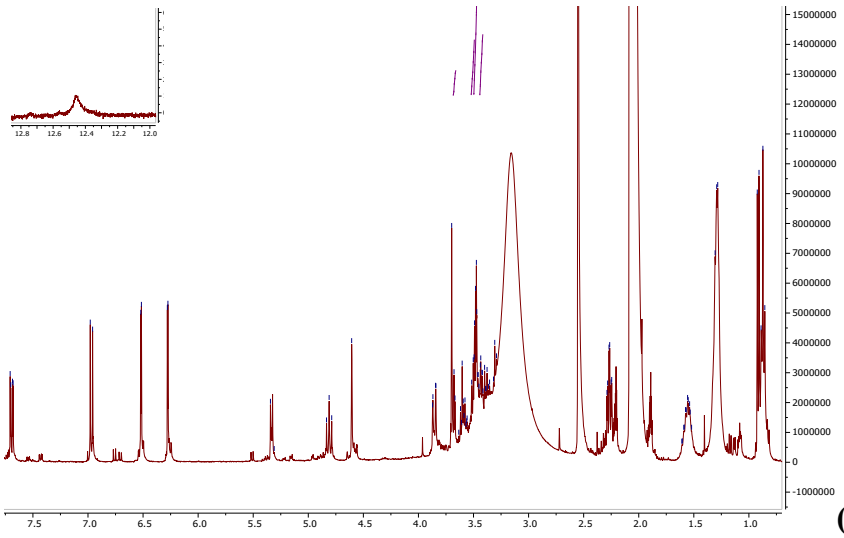
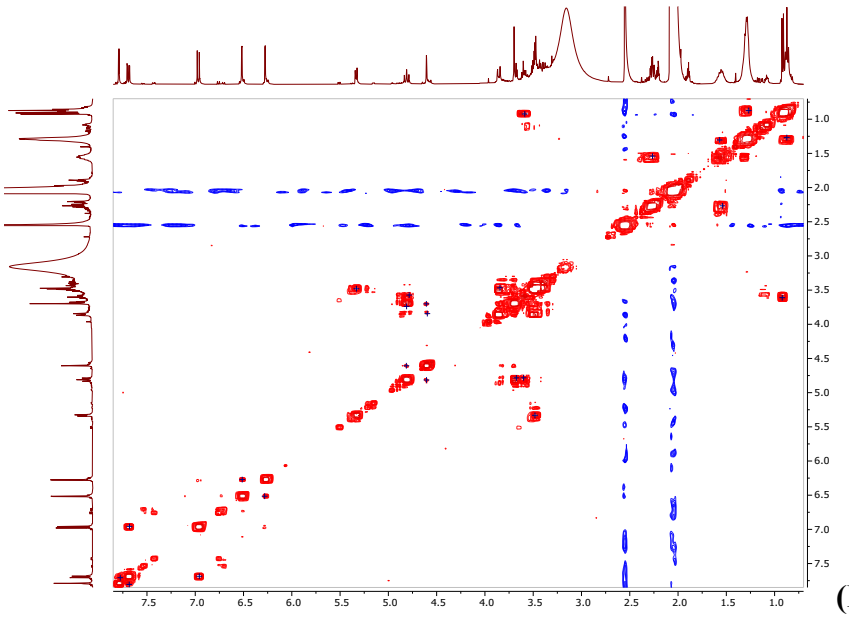


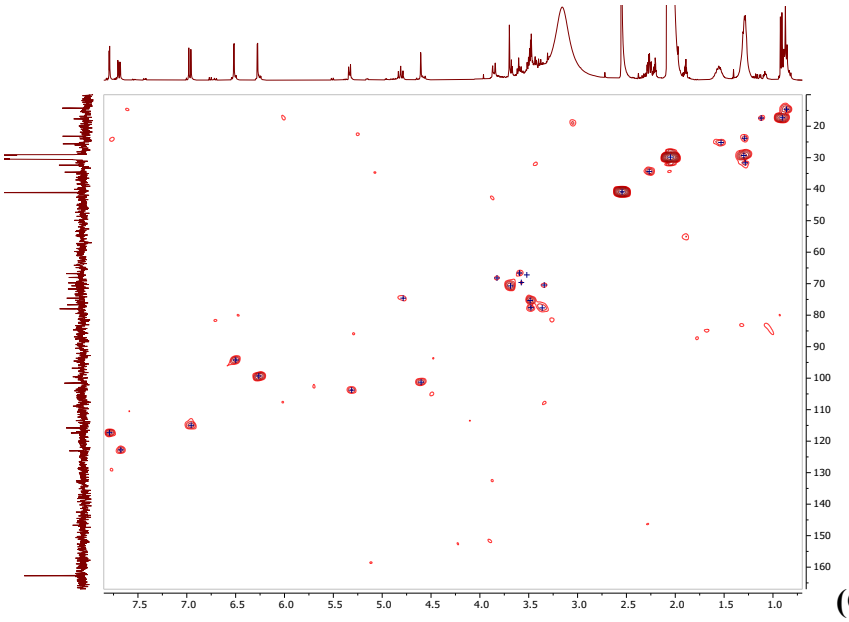
Figure S.1. ^{1}H-NMR of rutin (**2**; Red) and rutin butyrate (**3a**; Green) in MeOD with some significant differences marked.



(A)



(B)



(C)

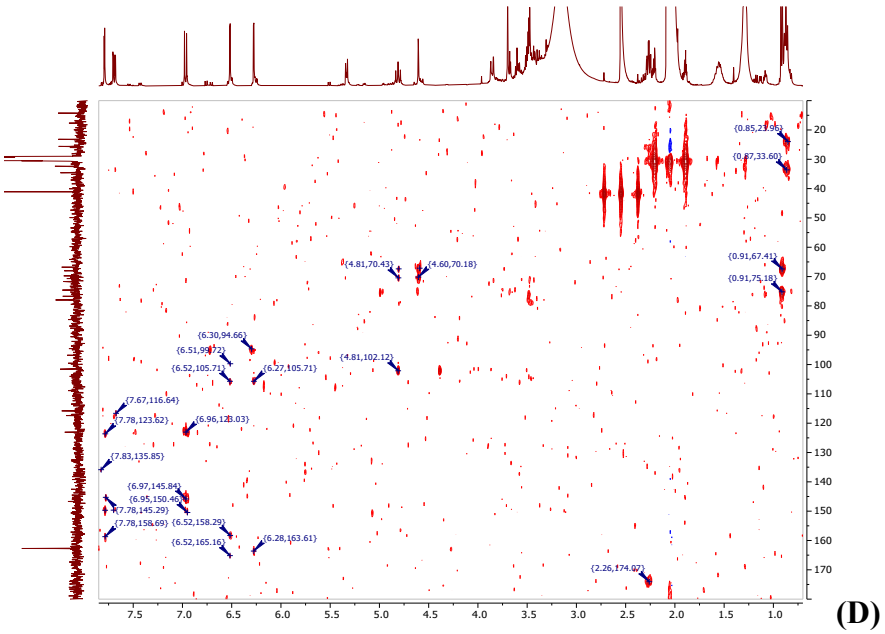
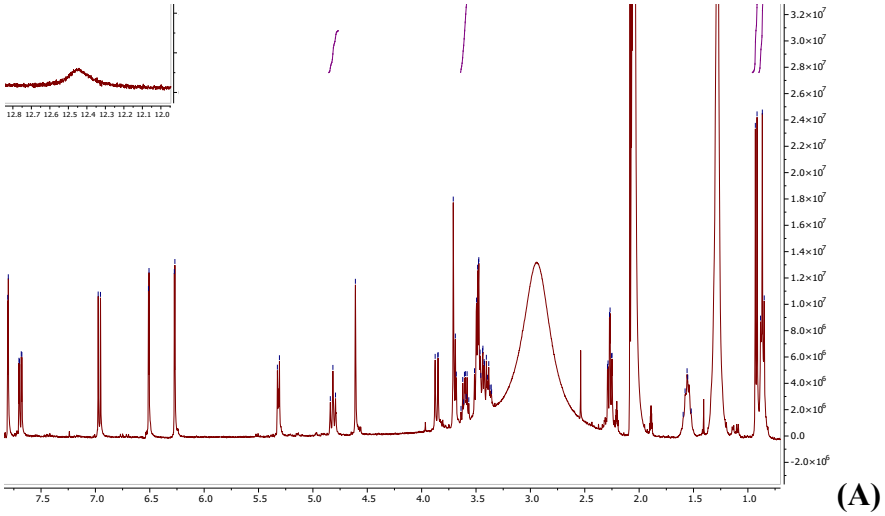
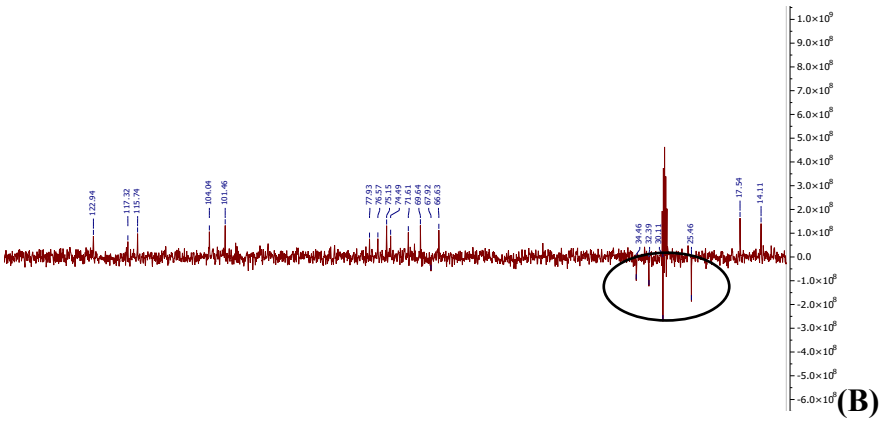


Figure S.2. Full NMR spectra of rutin octanoate (**3b**) in acetone-d_6 **(A)** ^{1}H-NMR with expansion for the 12-12.8ppm area; **(B)** COSY; **(C)** HMQC; **(D)** HMBC.





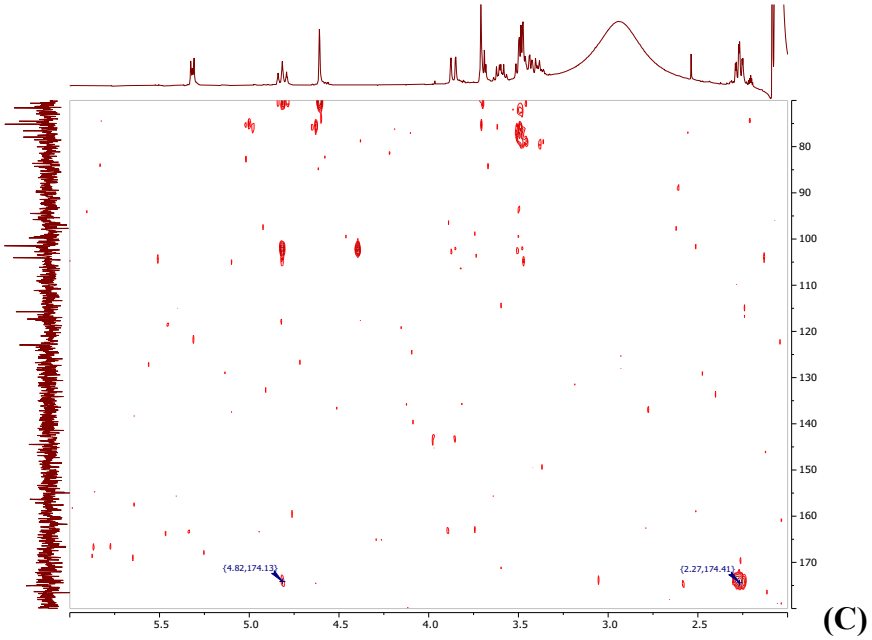
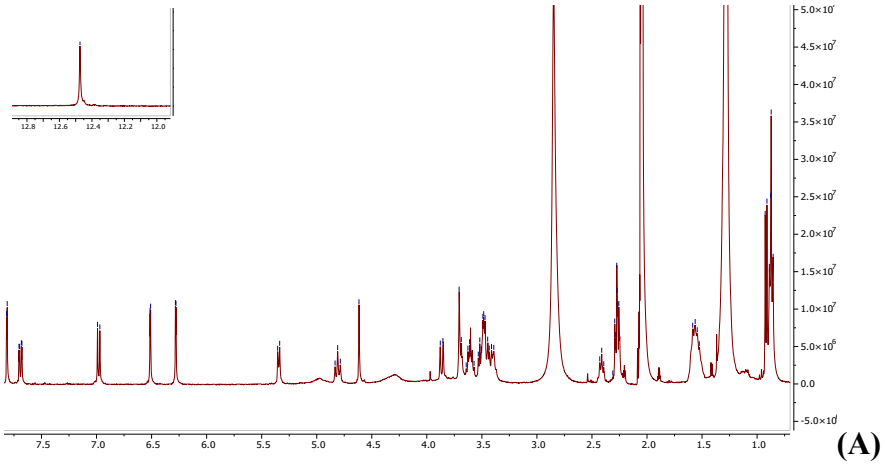


Figure S.3. Indicative NMR spectra of rutin laureate (**3c**) in acetone-d_6 **(A)** ^{1}H-NMR with expansion for the 12-12.8ppm area; **(B)** ^{13}C-DEPT (marked are the -CH_2- groups); **(C)** HMBC (marked are the signals relating H-4''' and -CH_2aC=O with the same carbonyl group, indicating the coupling between rutin and the fatty acid chain).



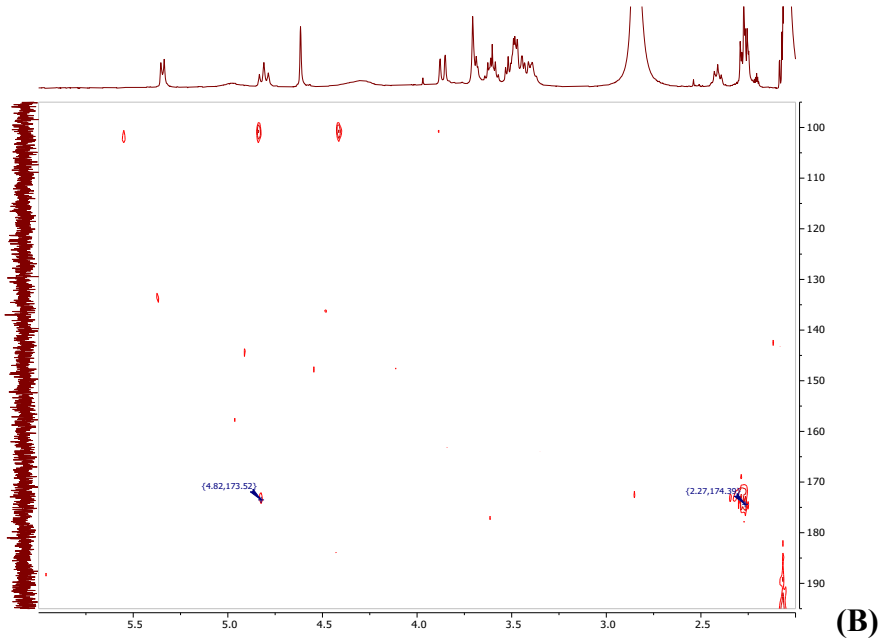


Figure S.4. Indicative NMR spectra of rutin palmitate (**3d**) in acetone-d_6 **(A)** ^{1}H-NMR with expansion for the 12-12.8ppm area; **(B)** HMBC (marked are the signals relating H-4''' and -CH_2aC=O with the same carbonyl group, indicating the coupling between rutin and the fatty acid chain).

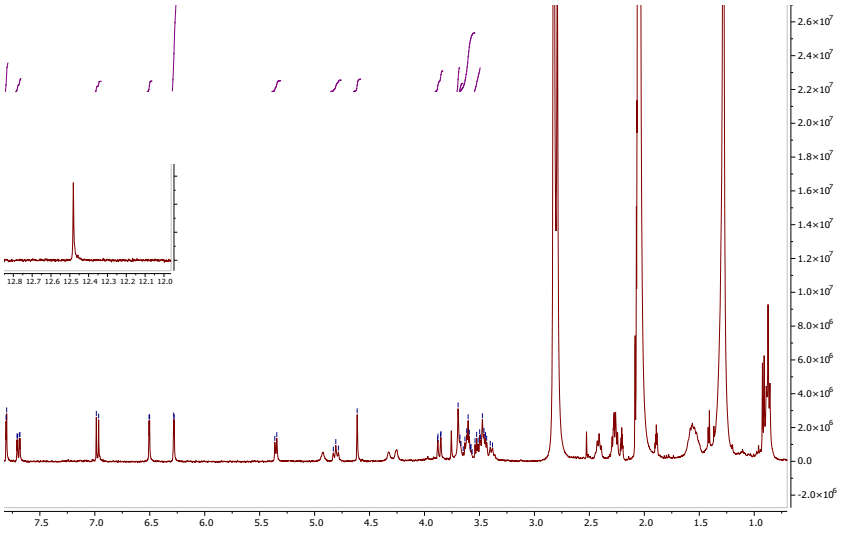
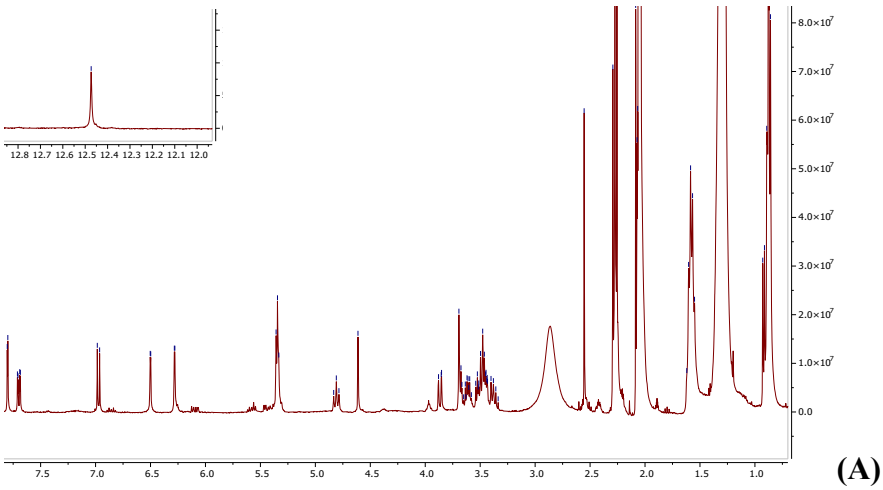
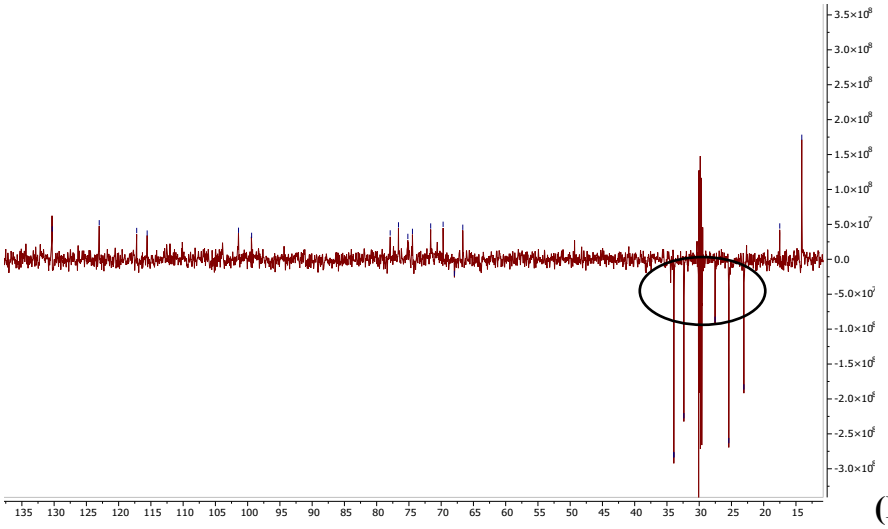


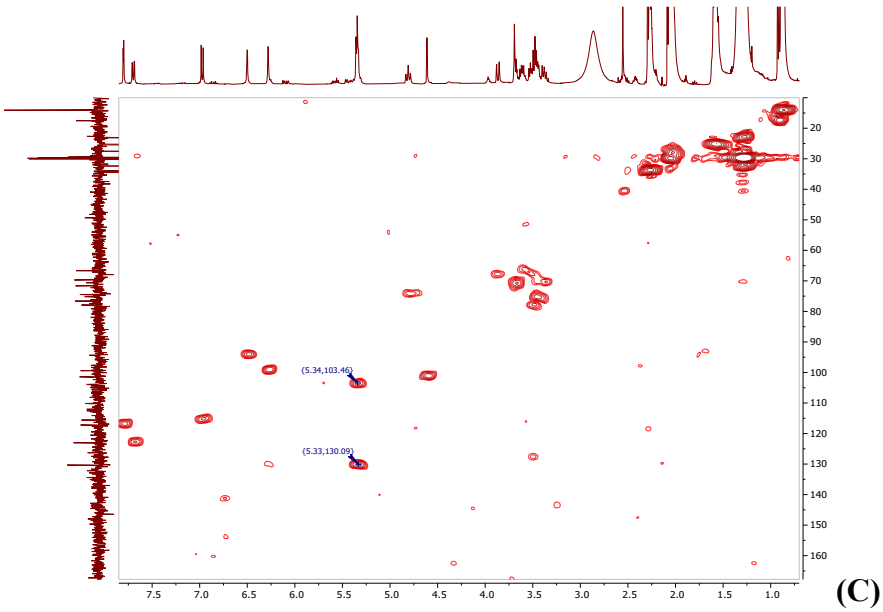
Figure S.5. ^{1}H-NMR spectra of rutin stearate (**3e**) in acetone-d_6 with expansion for the 12-12.8ppm area.



(A)



(B)



(C)

Figure S.6. Indicative NMR spectra of rutin oleate (**3f**) in acetone-d_6 **(A)** ^{1}H-NMR with expansion for the 12-12.8ppm area; **(B)** ^{13}C-DEPT (marked are the -CH_2- groups); **(C)** HMQC-DEPT (marked are the carbons corresponding to the –CH- groups forming the double bond).

Mass Spectra

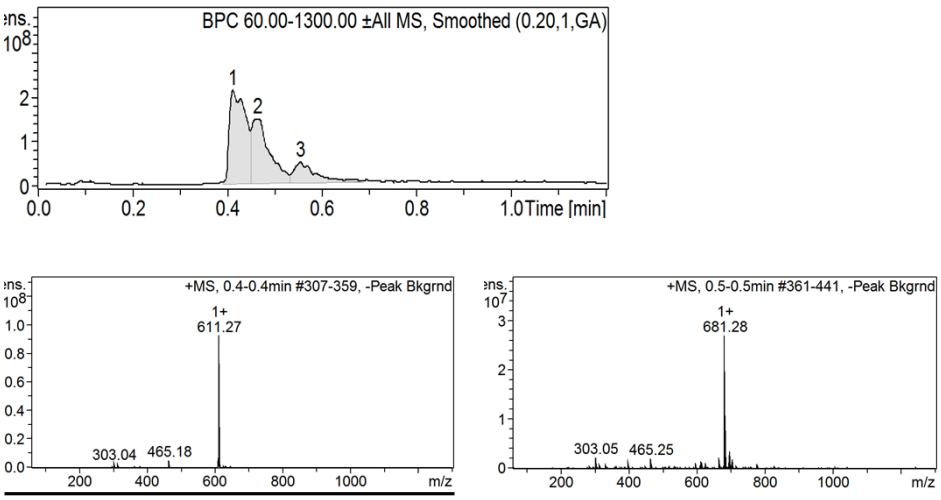


Figure S.7. Mass spectra in methanol of rutin (**2**; peak 1) and rutin butyrate (**3a**; peaks 2-3).

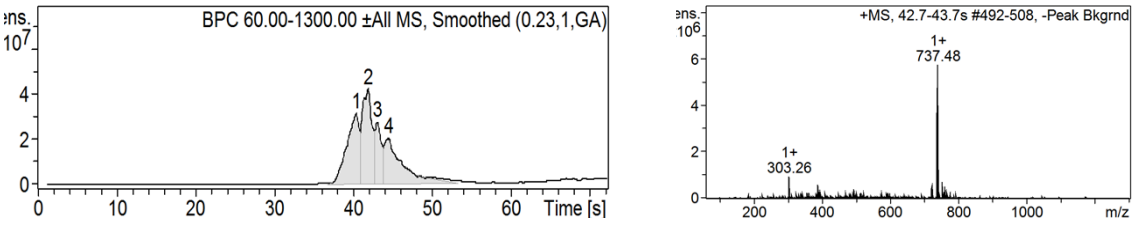


Figure S.8. Mass spectra in methanol of rutin octanoate (**3b**).

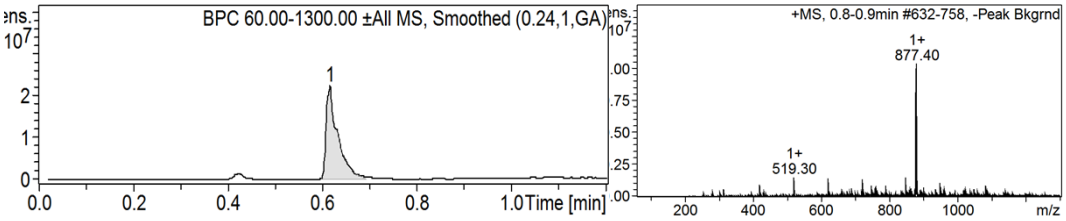


Figure S.9. Mass spectra in methanol of rutin laureate (**3c**).

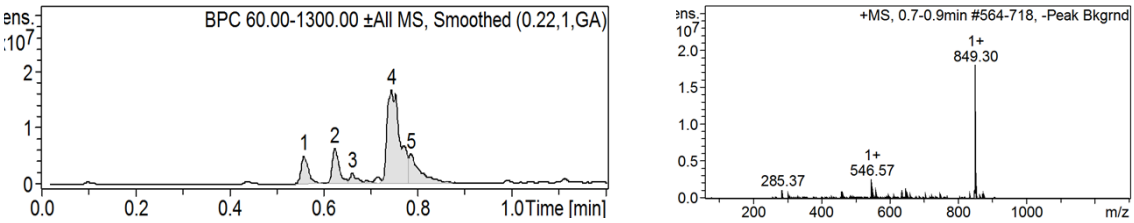


Figure S.10. Mass spectra in methanol of rutin palmitate (**3d** ;peaks 4&5).

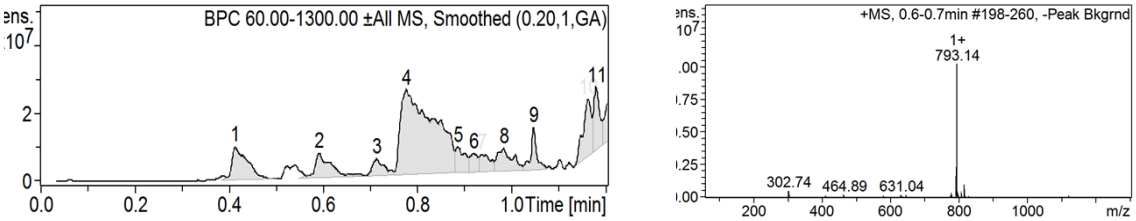


Figure S.11. Mass spectra in methanol of rutin stearate (**3e** ;peaks 3-6).

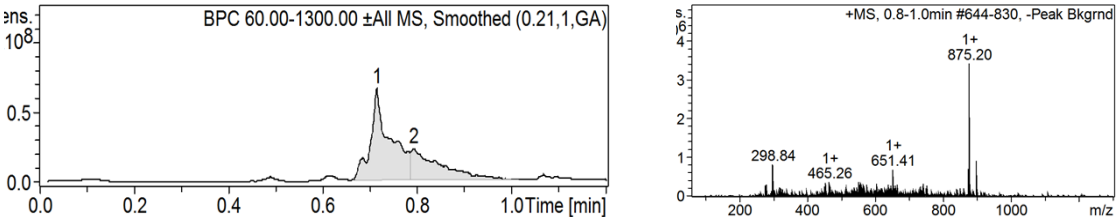


Figure S.12. Mass spectra in methanol of rutin oleate (**3f**).

UV-Vis Spectra

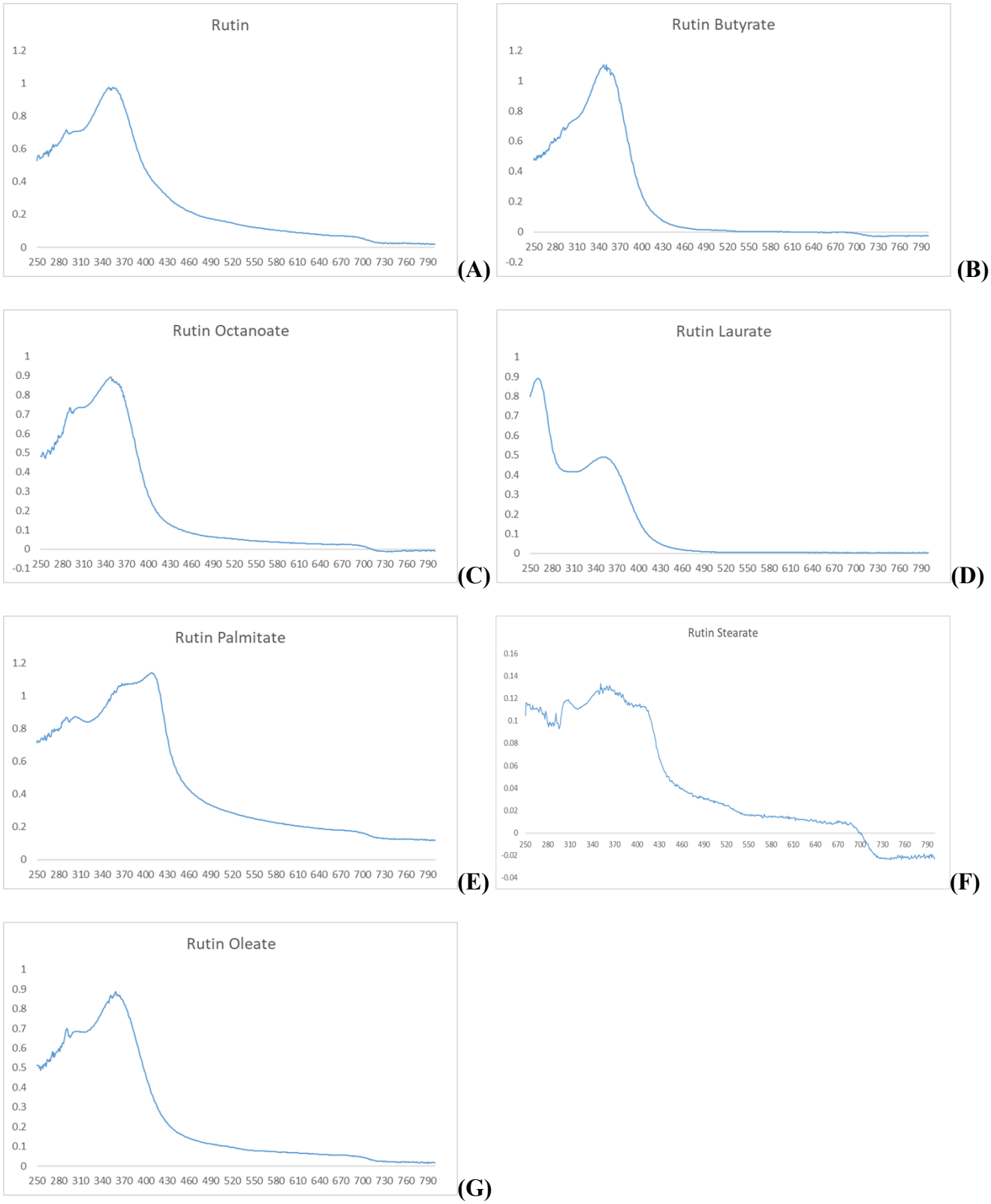


Figure S.13. UV-Vis spectra in 1:1 *v*/*v* methanol:water of: **(A)** rutin (**2**); **(B)** rutin butyrate (**3a**); **(C)** rutin octanoate (**3b**); **(D)** rutin laureate (**3c**); **(E)** rutin palmitate (**3d**); **(F)** rutin stearate (**3e**); **(G)**.rutin oleate (**3f**).

LC-MS Chromatograms for Kinetic Study

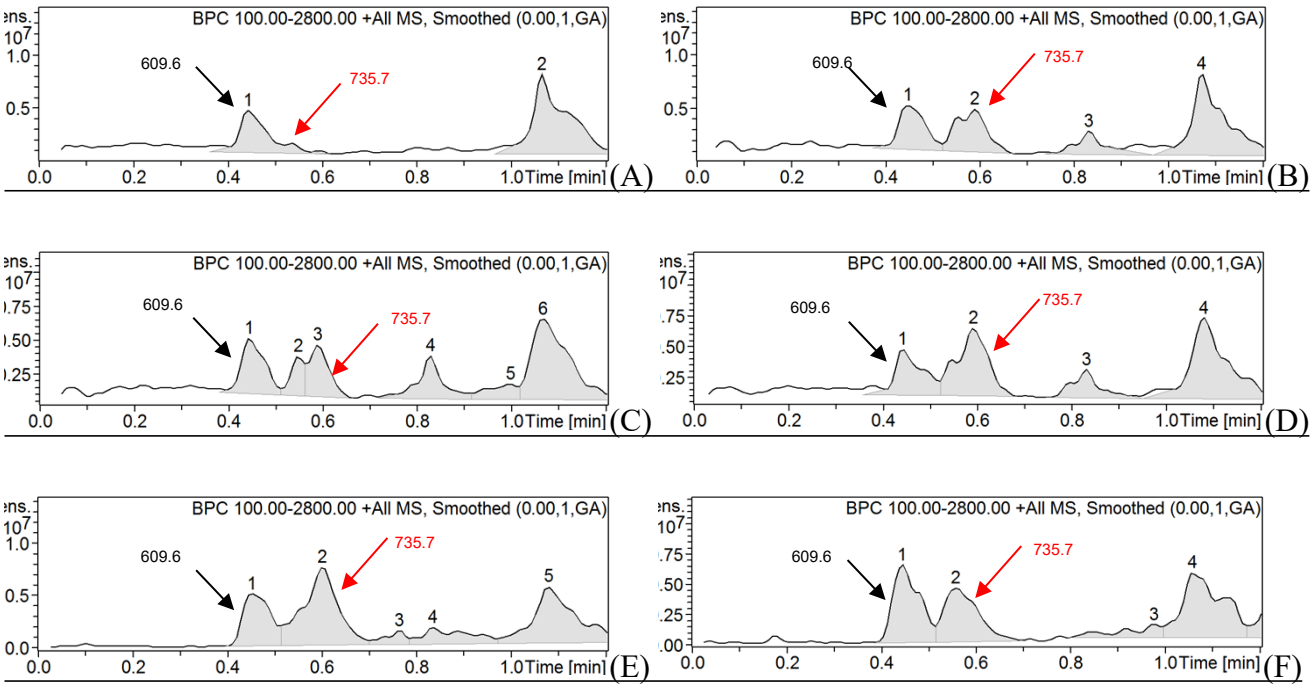


Figure S.14. LC-MS chromatograms for Experiment 45: rutin (4.4 mM) acylation by *Ca*lB on acrylic resin with 100 equivalents of octanoic acid in 10:1 acetonitrile:DMSO, at 55 °C with no mechanical stirring after (A) 2 h; (B) 18 h; (C) 24 h; (D) 48 h; (E) 72 h; (F) 96 h. Black arrow indicates peak for rutin (**2**) and red arrow indicates peak for rutin octanoate (**3b**).

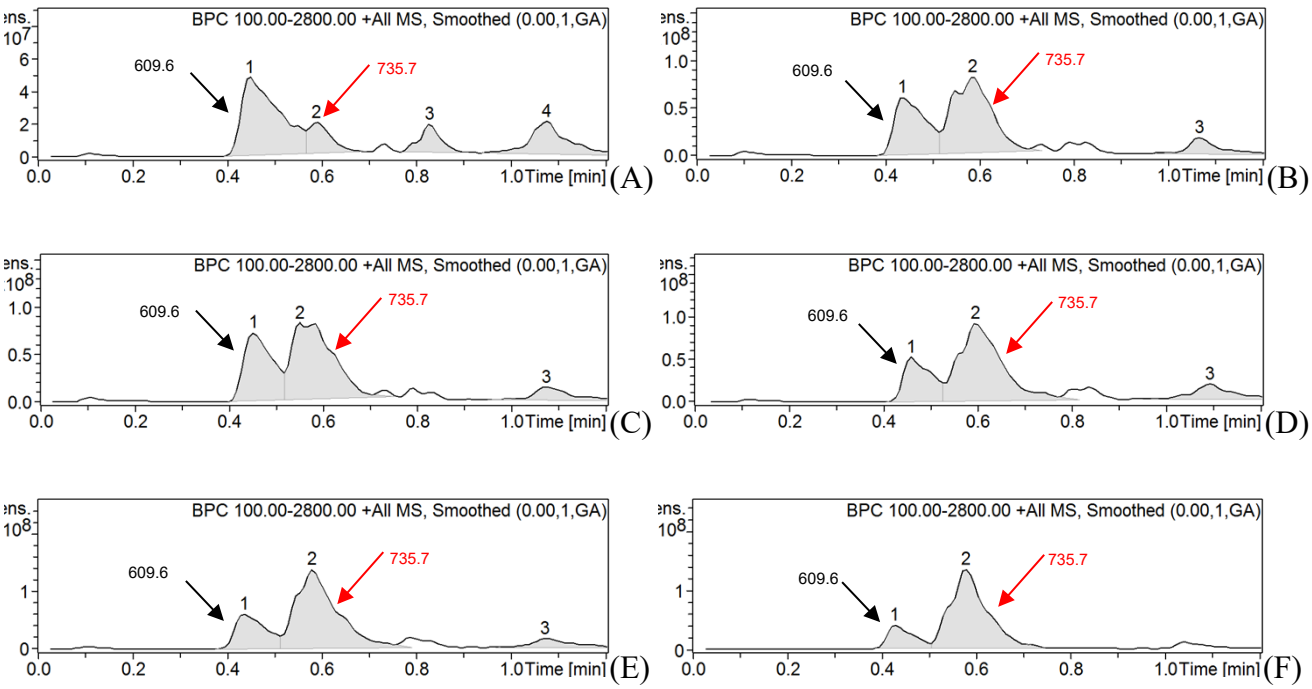


Figure S.15. LC-MS chromatograms for Experiment 46: rutin (13.3 mM) acylation by *Ca*lB on acrylic resin with 100 equivalents of octanoic acid in 10:1 acetonitrile:DMSO, at 55 °C with no mechanical stirring after (A) 2 h; (B) 18 h; (C) 24 h; (D) 48 h; (E) 72 h; (F) 96 h. Black arrow indicates peak for rutin (**2**) and red arrow indicates peak for rutin octanoate (**3b**).

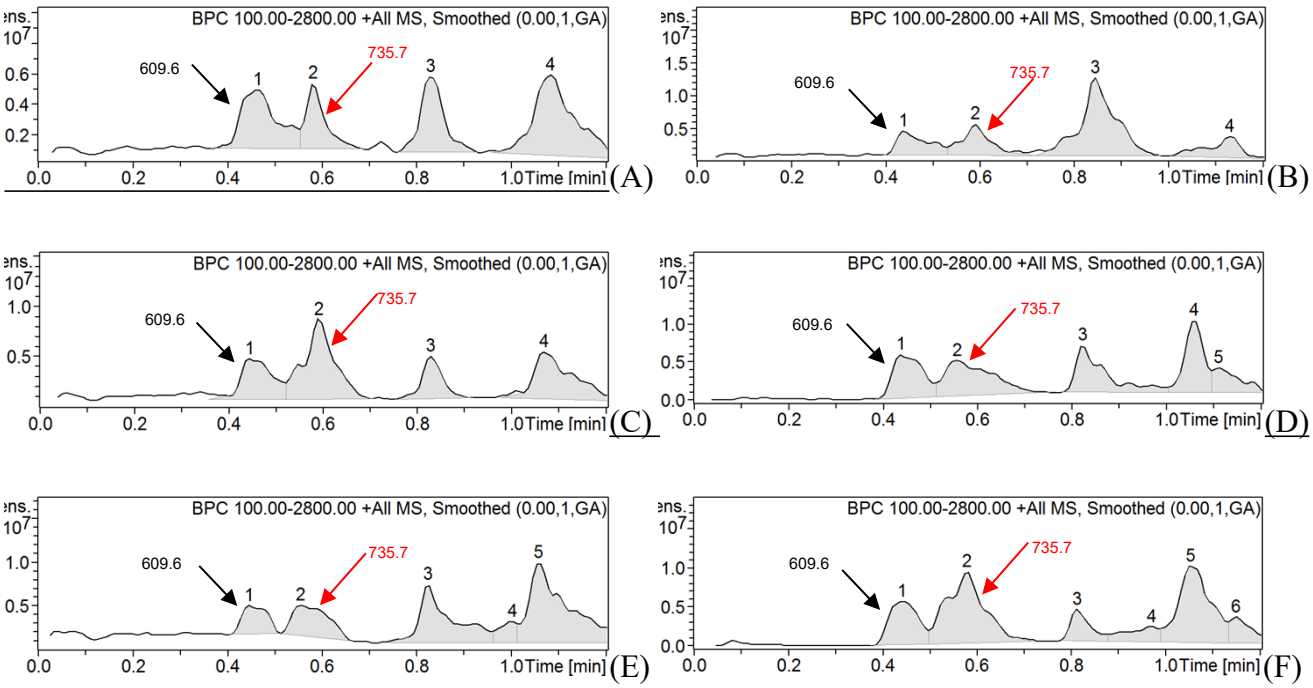


Figure S.16. LC-MS chromatograms for Experiment 47: rutin (22.2 mM) acylation by *Ca*lB on acrylic resin with 100 equivalents of octanoic acid in 10:1 acetonitrile:DMSO, at 55 °C with no mechanical stirring after (A) 2 h; (B) 18 h; (C) 24 h; (D) 48 h; (E) 72 h; (F) 96 h. Black arrow indicates peak for rutin (**2**) and red arrow indicates peak for rutin octanoate (**3b**).