SUPPLEMENTARY INFORMATION – Part 1
Experimental Procedures and Characterization Data

Regiocontrolled syntheses of FAHFAs and LC-MS differentiation of regioisomers

Laurence Balas*[a], Justine Bertrand-Michel[b,c,d], Fanny Viars[b,c,d], Julien Faugere[b,c,d], Corinne Lefort[b,c], Sylvie Caspar-Bauguil [b,d,e], Dominique Langin[b, d, e], Thierry Durand[a]

[a] Institut des Biomolécules Max Mousseron (IBMM), UMR 5247, CNRS, Université Montpellier, ENSCM, Faculté de Pharmacie, 15 av. Charles Flahault, 34093 Montpellier Cedex 5, France.
[b]INSERM, UMR 1048, Institute of Metabolic and Cardiovascular Diseases, Toulouse, France
[c]Metatoul-Lipidomic Facility, MetaboHUB, France
[d]University of Toulouse, Paul Sabatier University, France
[e]Toulouse University Hospitals, Laboratory of Clinical Biochemistry, Toulouse, France

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A) General information

All reactions were performed under an atmosphere of argon. Excepted for the Jones oxidation, reactions were conducted in oven-dried glassware (120 °C, minimum 12 hours). Inert gas was dried by passing it through solid anhydrous calcium sulphate (Drierite). Anhydrous tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were obtained from a PureSolv™ PS-400 solvent purification system. Anhydrous DMF was purchased from Acros. Ethylenediamine and pyridine were freshly distilled over potassium hydroxide under an argon atmosphere. Acetone was distilled over CrO_3 (hazardous distillation). All reagents purchased commercially were used without further purification. Thin-layer chromatography (TLC) was performed on aluminium pre-coated silica gel plates from Merck, and developed plates were visualized by UV light (254 nm) and p-anisaldehyde solution. Column chromatography was performed using flash chromatography with the indicated eluent on Davisil 40-63 µm silica gel.

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Bruker AV300 or Bruker AV500 spectrometers. Chemical shifts are reported relative to chloroform at δ 7.24 ppm for ^{1}H NMR spectra and δ 77.16 ppm for ^{13}C spectra. The ^{1}H NMR spectra data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, q = quartet, quint. = quintet, m = multiplet, br. = broad), coupling constant(s) in Hertz (Hz), integration and assignment). All the NMR spectra were assigned with the help of 2D NMR techniques (COSY 1H-1H, HMQC or HSQC, and HMBC).

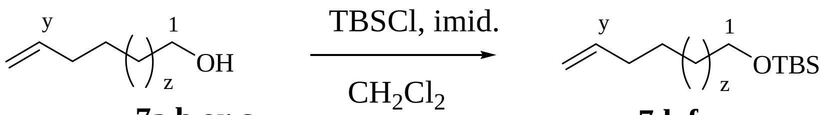
Infrared spectra were obtained using a Perkin-Elmer Spectrum One spectrophotometer. They were reported as wavenumber (cm^{-1}) of significant peaks.

For the chemical synthesis of the FAHFAs and their precursors, mass spectra (ESI) and high-resolution mass spectra (HRMS) were measured at the University of Montpellier on a Waters SYNAPT G2-S High Definition mass spectrometer equipped with a ESI source. Spectra were recorded in positive or negative mode from 100 to 1500 Da. The capillary voltage was adjusted to 1000V and the cone voltage was set at 30V. Source and desolvatation temperature was respectively set at 102°C and 250°C.

For the LC-MS/MS analysis, commercially available FAHFAs [9-PAHSA, 9-PAHSA-d_{31} (ISTD), 9-POHSA, 9-OAHSA and 13-OAHSA] were purchased from Cayman Chemicals (Ann Arbor, MI, USA). Hexane, absolute ethanol, acetic acid, citric acid, methanol (HPLC gradient Grade), ammonium formate and formic acid were purchased from Sigma Aldrich (Saint Quentin Fallavier, France). Ammonium hydroxide solution 30% (NH_4OH) was purchased from Carlo Erba Reagenti (Cornaredo, Italy). Water used in this study was purified on a milliQ system (Millipore). The SPE cartridges (3 mL, 500 mg, cartridge Chromabond) were purchased from Macherey Nagel (Duren, Germany).

B) Synthesis of branched FAHFAs

B1.1) General procedure for silylation of alcohols 7a-c and 8



7a,b or c **7d, f, or e**

The procedure for silylation of primary alcohols is exemplified with the silylation of 5-hexen-1-ol **7a** to TBS-ether **7d**.

A solution of 5-hexen-1-ol **7a** (1 g, 9.98 mmol, 1 equiv) in CH_2Cl_2 (15 mL) was added by cannulation to a solution of DMAP (0.120 g, 0.99 mmol, 0.1 equiv) and imidazole (0.81 g, 11.98 mmol, 1.2 equiv) in CH_2Cl_2 (10 mL). The mixture was cooled to 0°C on ice bath. Then, a solution of TBSCl (1.58 g, 10.5 mmol, 1.05 equiv) in CH_2Cl_2 (15 mL) was added by cannulation dropwise. The mixture was stirred at rt overnight. After cooling at 0°C, the reaction was quenched with addition of an aqueous saturated NH_4Cl (10 mL). The organic phase was washed with water (5 mL x 2). The aqueous phases were extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under vacuum. The oily crude product (2.4 g) was dry loaded with celite® on a flash chromatography column (silica gel, ~30 g) and eluted with cyclohexane. The appropriated fractions were combined and evaporated to dryness to give the desired product **7d** (1.9 g, 8.86 mmol, 99% yield) as a colorless oil.

B1.2) Chararacterization of silyl ethers 7d-f and 11

Compound 7d (colorless oil, 99% yield)

Rf: 0.73 (cyclohexane/AcOEt: 9/1); 0.95 (cyclohexane/AcOEt: 7/3) – Anisaldehyde – No UV

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 304 K): 5.79 (ddt, J = 17.1 Hz, 10.2 Hz and 6.7 Hz, 1H, H_{olefin}), 5.02-4.88 (m, 2H, H_{olefin}), 3.59 (t, J = 6.3 Hz, 2H, CH2OSi), 2.10-1.99 (m, 2H, $CH2_{allylic}$), 1.57-1.35 (m, 4H, CH2C), 0.88 (s, 9H, tBu), 0.03 (s, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 304 K): 139.10 (CH_{olefin}), 114.50 ($CH2_{olefin}$), 63.23 (CH2O), 33.69 ($CH2_{allylic}$), 32.47 (CH2), 26.13 (tBU), 25.33 (CH2), 18.5 (C_{quat} tBu), -5.13 (CH3).

IR (υcm^{-1}): 2953, 2930, 2858, 1642, 1463, 1472, 1387, 1361, 1254, 1099.

MS: (ESI) m/z: in our hands, No ionization.

Compound 7e (colorless oil, 99% yield)

Rf: 0.92 (pentane/Et_2O: 94/6) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 292 K): 5.79 (tdd, J = 17.0 Hz, 10.2 Hz and 6.7 Hz, 1H, CH_{olefin}), 5.02-4.87 (m, 2H, $CH2_{olefin}$), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.02 (q, J = 6.8 H, 1H, $CH2_{allylic}$), 1.56-1.43 (m, 2H, CH2), 1.43-1.20 (m, 10H, CH2), 0.87 (s, 9H, tBu), 0.03 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 139.39 (CH_{olefin}), 114.25 ($CH2_{olefin}$), 63.48 (CH2O), 33.96 (CH2), 33.02 (CH2), 29.62 (CH2), 29.53 (CH2), 29.23 (CH2), 29.07 (CH2), 26.14 (tBu), 25.93 (CH2), 18.53 (Cquat tBu), -5.11 (CH3Si).

IR (υcm^{-1}): 2927, 2856, 1642, 1463, 1388, 1361, 1254, 1097.

MS: (ESI) m/z: in our hands, no ionisation using positive or negative ESI.

Compound 7f (colorless oil, 97% yield)

Rf: 0.73 (cyclohexane/AcOEt: 9/1); 0.95 (cyclohexane/AcOEt: 7/3) – Anisaldehyde – No UV

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 301 K): 5.80 (ddt, J = 17.1 Hz, 10.2 Hz and 6.7 Hz, 1H, H$_{\text{olefin}}$), 5.02-4.87 (m, 2H, H$_{\text{olefin}}$), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.08-1.97 (m, 2H, CH2$_{\text{allylic}}$), 1.57-1.43 (m, 2H, CH2), 1.39-1.19 (m, 12H, CH2), 0.88 (s, 9H, tBu), 0.03 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 301 K): 139.40 (CH$_{\text{olefin}}$), 114.23 (CH2$_{\text{olefin}}$), 63.49 (CH2O), 33.96 (CH2), 33.06 (CH2), 29.74 (CH2), 29.59 (CH2), 29.29 (CH2), 29.11 (CH2), 26.15 (tBu), 25.97 (CH2), 18.21 (C$_{\text{quat}}$ tBu), -5.09 (CH3).

IR (υcm^{-1}): 2928, 2856, 1641, 1471, 1463, 1388, 1361, 1255, 1099.

MS: (ESI) m/z: in our hand, no ionization was found.

<u>**Compound 11**</u> (colorless oil, 93% yield)

Rf: 0.89 (Pentane/Et$_2$O: 94/6) –Anisaldehyde – No UV.

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 300 K): 3.67 (t, J = 6.0 Hz, 2H, CH2O), 2.25 (dt, J = 2.6 Hz and 7.0 Hz, 2H, CH2, CH2$_{\text{propargylic}}$), 1.90 (t, J = 2.7 Hz, 1H, **C**≡C-H), 1.77-1.65 (m, 2H, CH2, CH2), 087 (s, 9H, tBu), 0.03 (s, 6H, CH3Si).

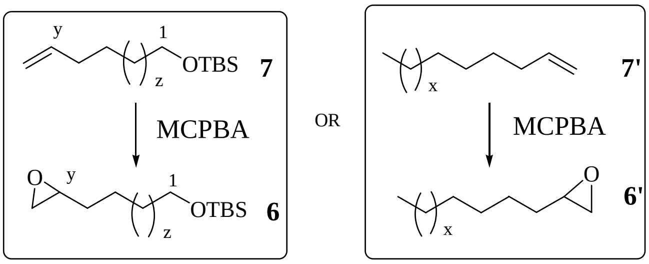
^{13}C NMR (75 MHz, CDCl$_3$, δppm, 300 K): 84.39 (C$_{\text{quat alkyne}}$), 68.36 (C≡C-H), 61.59 (CH2O), 31.70 (CH2), 26.08 (tBu), 18.46 (Cquat tBu), 14.99 (CH2), -5.21 (CH3Si).

IR (υcm^{-1}): 3314 (C≡C-H), 2954, 2930, 2858, 2120 (C≡C), 1472, 1434, 1389, 1361, 1254, 1103, 1072.

MS: (ESI) m/z: 199.15 (M+H)$^+$.

HRMS calcd for C$_{11}$H$_{23}$OSi, [M+H$^+$] 199.1518, found 199.1521.

B2.1) General procedure for epoxidation of alkenes 7d-f and 7'a-b



The epoxidation reactions were conducted according to a modified procedure from Paterson et al., OrgLett, **2009**, 3, 693-696. The synthesis of epoxide **6b** is taken as an example.

To a stirred solution of alkene **7d** (1.60 g, 5.917 mmol) in CH$_2$Cl$_2$ (21 mL) at - 2ºC was added mCPBA (70% purity, 1.75 g, 7.100 mmol) in several portions over 30 min. The reaction mixture turned cloudy after 10 min. It was allowed to warm to 27°C and stirred for 16 hr. It was then directly poured into a flash chromatography colonne (45g silica gel, cyclohexane/AcOEt: 100/1 to 98/2). Evaporation of the appropriate fractions afforded epoxide **6b** (1.6 g, 95% yield) as a colorless liquid.

B2.2) Chararacterization of epoxides 6 and 6'

Compound 6a (colorless oil, 88% yield)

Rf: 0.43 (cyclohexane/AcOEt: 9/1); 0.84 (cyclohexane/AcOEt: 7/3) – No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 304 K): 3.60 (t, J = 6.0 Hz, 2H, CH2O), 2.95-2.85 (m, 1H, $CHO_{epoxide}$), 2.73 (dd, J = 4.0 Hz and 5.0 Hz, 1H, $CHO_{epoxide}$), 2.45 (dd, J = 2.7 Hz and 5.0 Hz, 1H, $CHO_{epoxide}$), 1.66-1.38 (m, 6 H, CH2C), 0.87 (s, 9H, tBu), 0.03 (s, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 304 K): 63.09 (CH2O), 52.45 ($CHO_{epoxide}$), 47.22 ($CH2O_{epoxide}$), 32.71 (CH2), 32.41(CH2), 26.11(tBu), 22.48 (CH2), 18.51(C_{quat} tBu), -5.15 (CH3).

IR (υcm^{-1}): 2949, 2930, 2858, 1472, 1463, 1388, 1361, 1255, 1097.

MS: (ESI) m/z: 231.18 $(M+H)^+$.

HRMS calcd for $C_{12}H_{27}O_2Si$, $[M+H^+]$ 231.1780, found 231.1782.

Compound 6b (colorless oil, 95% yield)

Rf: 0.41 (cyclohexane/AcOEt: 9/1) –Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 292 K): 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.93-2.82 (m, 1H, $CHO_{epoxide}$), 2.72 (dd, J = 4.1 Hz and 5.0 Hz, 1H, $CH2O_{epoxide}$), 2.43 (dd, J = 2.7 Hz and 5.0 Hz, 1H, $CH2O_{epoxide}$), 1.57-1.36 (m, 6H, CH2), 1.36-1.18 (m, 8H, CH2), 0.86 (s, 9H, tBu), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 292 K): 63.42 (CH2O), 52.54 ($CHO_{epoxide}$), 47.28 ($CH2O_{epoxide}$), 32.98 (CH2), 32.62 (CH2), 29.66 (CH2), 29.51 (CH2), 29.46 (CH2), 26.11 (tBu), 25.89 (CH2), 18.51 (Cquat tBu), -5.13 (CH3Si).

IR (υcm^{-1}): 2928, 2856, 1469, 1463, 1409, 1388, 1361, 1254, 1097.

MS: (ESI) m/z: 287.24 $(M+H)^+$, 155.14 $(M-OTBS)^+$.

HRMS calcd for $C_{16}H_{35}O_2$ Si, $[M+H^+]$ 287.2406, found 287.2405; calcd for $C_{10}H_{19}O$, [M-OTBS] 155.1436, found 155.1435.

Compound 6c (colorless oil, 78% yield)

Rf: 0.43 (cyclohexane/AcOEt: 9/1); 0.84 (cyclohexane/AcOEt: 7/3) – No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 301 K): 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.91-2.83 (m, 1H, $CHO_{epoxide}$), 2.71 (dd, J = 4.0 Hz and 5.0 Hz, 1H, $CHO_{epoxide}$), 2.43 (dd, J = 5.0 and 2.73 Hz, 1H, $CH2O_{epoxide}$), 1.56-1.37 (m, 6H, CH2), 1.36-1.21 (m, 10H, CH2), 0.87 (s, 9H, tBu), 0.02 (s, 6H, CH3).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 301 K): 63.43 (CH2O), 52.49 (CHO$_{epoxide}$), 47.21 (CH2O$_{epoxide}$), 33.02 (CH2), 32.63 (CH2), 29.65 (CH2), 29.62 (CH2), 29.56 (CH2), 29.53 (CH2), 26.12 (tBu), 26.09 (CH2), 25.93 (CH2), 18.50 (C$_{quat}$ tBu), -5.13 (CH3Si).

IR (υcm^{-1}): 2928, 2856, 1467, 1463, 1410, 1388, 1361, 1254, 1097, 1006.

MS: (ESI) m/z: 301.26 (M+H)$^+$.

HRMS calcd for $C_{17}H_{36}O_2Si$, [M+H$^+$] 301.2563, found 301.2566.

Compound 6d (colorless oil, 73% yield)

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 304 K): 3.61 (t, J = 6.2 Hz, 2H, CH2O), 2.93-2.84 (m, 1H, CHO$_{epoxide}$), 2.71 (dd, J = 4.0 Hz and 4.9 Hz, 1H, CH2O$_{epoxide}$), 2.44 (dd, J = 2.7 Hz and 4.9 Hz, 1H, CH2O$_{epoxide}$), 1.96 (br s, 1H, OH), 1.66-1.44 (m, 6H, CH2).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 304 K): 62.68 (CH2OH), 52.39 (CHO$_{epoxide}$), 47.14 (CH2O$_{epoxide}$), 32.46 (CH2), 32.23 (CH2), 22.36 (CH2).

IR (υcm^{-1}): 3683-3082 (OH), 2936, 2865, 1480, 1458, 1411, 1260, 1072, 1053, 1043.

The ^{1}H and ^{13}C NMR data are in good agreement with previous reported data in *J. Org. Chem.* **2012**, 77, 6409-6413, Epoxidation of olefins with silica-supported peracid. R. Mello, A. Alcalde-Aragonès, M. E. Gonzalez Nunez and G. Asensio.

Compound 6e (colorless oil)

Rf: 0.31 (cyclohexane/AcOEt: 7/3) - Anisaldehyde – No UV.

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 304 K): 3.59 (t, J = 6.6 Hz, 2H, CH2O), 2.91-2.82 (m, 1H, CHO$_{epoxide}$), 2.70 (dd, J = 4.0 Hz and 5.0 Hz, 1H, CH2O$_{epoxide}$), 2.42 (dd, J = 2.7 Hz and 5.0 Hz, 1H, CH2O$_{epoxide}$), 1.72 (br s, 1H, OH), 1.59-1.37 (m, 6H, CH2), 1.37-1.23 (m, 8H, CH2).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 304 K): 63.08 (CH2OH), 52.51 (CHO$_{epoxide}$), 47.21 (CH2O$_{epoxide}$), 32.87 (CH2), 32.56 (CH2), 29.58 (CH2), 29.45 (CH2), 29.41 (CH2), 26.04 (CH2), 25.82 (CH2).

IR (υcm-1): 3644-3109 (OH), 2927, 2855, 1465, 1410, 1056.

The ^{1}H and ^{13}C NMR data are in good agreement with previous reported data in Chai et al., TL 1992, 33, 5, 585-588

Compound 6'a (colorless oil, 95% yield)

Rf: 0.59 (cyclohexane/ Et_2O: 9/1); No UV – Anisaldehyde

^{1}H NMR (500 MHz, CDCl$_3$, δppm, 293 K): 2.90-2.85 (m, 1H, CHO$_{epoxide}$), 2.72 (dd, J = 4.0 Hz and 5.0 Hz, 1H, CH2O$_{epoxide}$), 2.72 (dd, J = 5.0 Hz and J = 2.7 Hz, 1H, CH2O$_{epoxide}$), 1.53-1.46 (m, 2H, CH2), 1.46-1.35 (m, 2H, CH2), 1.34-1.18 (m, 12H, CH2), 0.85 (t, J = 7.0 Hz, 3H, CH3).

^{13}C NMR (125 MHz, $CDCl_3$, δppm, 293 K): 52.56 (CHO), 47.29 (CH2O), 32.64 (CH2), 32.02 (CH2), 29.70 (CH2), 29.65 (CH2), 29.58 (CH2), 29.44 (CH2), 26.11 (CH2), 22.81 (CH2), 14.25 (CH3).

IR (υcm^{-1}): 2924, 2855, 1466, 1410, 1378, 1258, 1131.

MS: (ESI) m/z: in our hands, no ionization.

Compound 6'b (colorless oil, 99% yield)

Rf: 0.88 (pentane/Et_2O: 9/1); 0.67 (pentane/ CH_2Cl_2: 1/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 2.92-2.84 (m, 1H, CHO), 2.72 (dd, J = 4.1 and 5.0 Hz, 1H, CH2O), 2.43 (dd, J = 5.0 and 2.7 Hz, 1H, CH2O), 1.55-1.36 (m, 4H, CH2), 1.36-1.15 (m, 16H, CH2), 0.85 (t, J = 6.9 Hz, 3H, CH3).

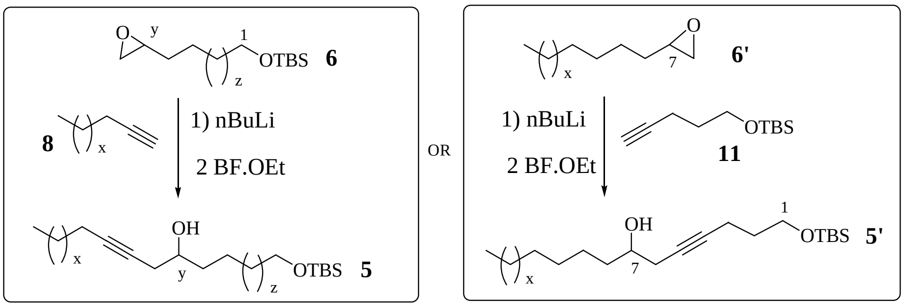
^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 52.56 (CHO), 47.27 (CH2O), 32.63 (CH2), 32.05 (CH2), 29.77 (CH2), 29.69 (CH2), 29.59 (CH2), 29.48 (CH2), 26.11 (CH2), 22.82 (CH2), 14.25 (CH3).

IR (υcm^{-1}): 2922, 2854, 1466. 1410, 1378, 1259, 1129.

MS: (ESI) m/z: 199.21 $(M+H)^+$, 240.23 $(M+MeCN)^+$.

HRMS calcd for $C_{13}H_{27}O$, $[M+H^+]$ 199.2062, found 199.2059.

B3.1) General procedure for epoxide ring opening



The synthesis of propargylic alcohol **5b** (y = 9, z = 5, x = 2) is given as an example.
To a solution of 1-heptyne (458 mg, 5.580 mmol, 4.0 equiv) in anhydrous THF (4.4 mL) at -78 °C was added n-BuLi (1.6 M solution in hexanes, 3.05 mL, 4.880 mmol, 3.5 equiv) over 10 min .The reaction mixture was stirred at -78 °C for 25 min. Freshly distilled (over CaH_2) $BF_3.OEt_2$ (527 µL, 4.170 mmol, 3.0 equiv) was added dropwise to the reaction mixture, followed by a solution of epoxide **6b** (400 mg, 1.39 mmol, 1.0 equiv) in anhydrous THF (4 mL). The reaction mixture was stirred at -78 °C for 1 h, then quenched with a saturated aqueous $NaHCO_3$ (2.5 mL) and diluted with Et_2O (10 mL). The organic layer is washed twice with water (3mL) and the combined aqueous phase are extracted with Et_2O (2 x 10 mL), then dried over $MgSO_4$, and evaporated to dryness. The crude residue was purified by flash column chromatography (silica gel,

cyclohexanes/AcOEt: 99/1 to 95/5) to give the expected propargylic alcohol **6** (523 mg, 95%) as a colorless oil.

B3.2) Chararacterization of alkynes 5 and 5'

Compound 5a (colorless oil, 95% yield)

Rf: 0.77 (cyclohexane/AcOEt: 9/1); 0.6 (cyclohexane/ Et_2O: 9/1) – No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 3.73-3.62 (m, 1H, CHO), 3.59 (t, J = 6.1 Hz, 2H, CH2O), 2.36 (dq, J = 16.4 Hz and 2.3 Hz, 1H, $CH2_{propargylic}$), 2.24 (tdd, J = 16.4 Hz, 2.3 Hz and 6.9 Hz, 1H, $CH2_{propargylic}$), 2.18-2.08 (m, 2H, $CH2_{propargylic}$), 1.89 (s br, 1H, OH), 1.59 - 1.18 (m, 18H, CH2C), 0.86 (s, 9 H, tBu), 0.85 (t, J = 7.02 Hz, 3H, CH3C), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 83.49 ($C_{quat\ alkyne}$), 76.16 ($C_{quat\ alkyne}$), 70.31 (CHO), 63.21 (CH2O), 36.09 (CH2), 32.83 (CH2), 31.99 (CH2), 29.35 (CH2), 29.25 (CH2), 29.15 (CH2), 29.06 (CH2), 27.90 (CH2), 26.11 (tBu), 22.80 (CH2), 22.11 (CH2), 18.89 (CH2), 18.51 (C_{quat} tBu), 14.25 (CH3), -5.14 (CH3).

IR (υcm^{-1}): 2953, 2928, 2856, 1469, 1463, 1388, 1361, 1255, 1100.

MS: (ESI) m/z : 369.32 $(M+H)^+$, 351.31 $(M-H_2O)^+$, 237.22 $(M-OTBS)^+$.

HRMS calcd for $C_{22}H_{45}O_2Si$, [M+H$^+$] 369.3189, found 369.3187; calcd for $C_{16}H_{29}O$, [M-OTBS] 237.2218, found 237.2220; calcd for $C_{22}H_{43}OSi$, [M-H_2O] 351.3083, found 351.3083.

Compound 5b (colorless oil, 95% yield)

Rf: 0.51 (cyclohexane/AcOEt: 9/1); – 0.63 (cyclohexane/Et_2O: 9/1) – No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 293 K): 3.71-3.60 (m, 1H, CHO), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.37 (dq, J = 16.4 Hz, and 2.4 Hz, 1H, $CH2_{propargylic}$), 2.23 (tdd, J = 16.4 Hz, 6.9 Hz and 2.4 Hz, 1H, $CH2_{propargylic}$), 2.20-2.10 (m, 2H, $CH2_{propargylic}$), 1.85 (s br,1H, OH), 1.54 - 1.32 (m, 10H, CH2C), 1.32 -1.21 (m, 8H, CH2C), 0.88 (t, J = 7.06 Hz, 3H, CH3) 0.87 (s, 9H, tBu), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 293 K): 83.39 ($C_{quat\ alkyne}$), 76.20 ($C_{quat\ alkyne}$), 70.35 (CHO), 63.46 (CH2O), 36.36 (CH2), 33.01 (CH2), 31.22 (CH2), 29.69 (CH2), 29.52 (CH2), 27.91 (CH2), 26.13 (tBu), 25.93 (CH2), 25.79 (CH2), 22.10 (CH2), 18.57 (C_{quat} tBu), 13.75 (CH3C), -5.11 (CH3Si).

IR (υcm$_{-1}$): 3661-3136 (OH), 2953, 2928, 2856, 1464, 1388, 1361, 1254, 1097.

MS: (ESI) m/z: 369.32 $(M+H)^+$, 351.31 $(M-H_2O)^+$, 237.22 $(M-OTBS)^+$, 219.21 $(M-OTBS-H_2O)^+$.

HRMS calcd for $C_{22}H_{45}O_2Si$, [M+H$^+$] 369.3189, found 369.3187 ; calcd for $C_{16}H_{27}$, [M-OTBS-H_2O] 219.2113, found 219.2112 ; calcd for $C_{22}H_{43}OSi$, [M-H_2O] 351.3083, found 351.3082.

Compound 5c (colorless oil, 88% yield)

Rf: 0.53 (cyclohexane/AcOEt: 9/1); No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 301 K): 3.72-3.59 (m, 1H, CHO), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.38 (d, J = 16.4 Hz, and 2.3 Hz, 1H, $CH2_{propargylic}$), 2.24 (tdd, J = 16.4 Hz, 6.9 Hz and 2.3 Hz, 1H, $CH2_{propargylic}$), 2.18-2.10 (m, 2H, $CH2_{propargylic}$), 1.71 (s br,1H, OH), 1.56-1.40 (m, 6H, CH2C), 1.40 -1.19 (m, 12H, CH2C), 0.92-0.80 (m, 3H, CH3), 0.88 (s, 9H, tBu), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 301 K): 83.48 ($C_{quat\ alkyne}$), 76.23 ($C_{quat\ alkyne}$), 70.38 (CHO), 63.48 (CH2O), 36.40 (CH2), 33.04 (CH2), 31.24 (CH2), 29.73 (CH2), 29.68 (CH2), 29.58 (CH2), 28.85 (CH2), 27.93 (CH2), 26.14 (tBu), 25.95 (CH2), 25.81 (CH2), 22.35 (CH2), 18.87 (C_{quat} tBu), 14.14 (CH3), -5.10 (CH3Si).

IR (υcm_{-1}): 3639-3113 (OH), 2928, 2856, 1464, 1388, 1361, 1255.

MS: (ESI) m/z: 397.36 $(M+H)^+$, 419.33 $(M+Na)^+$.

HRMS calcd for $C_{24}H_{49}O_2Si$, [M+H$^+$] 397.3502, found 397.3503 ; calcd for $C_{24}H_{48O2NaSi}$, [M+Na] 419.3321, found 419.3319.

Compound 5’a (colorless oil, 75% yield)

Rf: 0.80 (cyclohexane/AcOEt: 9/1); No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 3.72-3.60 (m, 1H, CHO), 3.66 (t, J = 6.1 Hz, 3H, CH2O), 2.43-2.31 (m, 1H, $CH2_{propargylic}$), 2.30-2.17 (m, 3H, $CH2_{propargylic}$), 1.87-1.60 (m, 3H, CH2 and OH), 1.55-1.36 (m, 2H, CH2), 1.36-1.16 (m, 14H, CH2), 0.87 (s, 9H, tBu), 0.86 (t, J= 6.9 Hz, 3H, CH3), 0.03 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 82.88 ($C_{quat\ alkyne}$), 76.45 ($C_{quat\ alkyne}$), 70.40 (CHO), 61.83 (CH2O), 36.44 (CH2), 32.20 (CH2), 32.05 (CH2), 29.75 (CH2), 29.47 (CH2), 27.94 ($CH2_{propargylic}$), 26.09 (tBu), 25.82, 22.83, 18.49 (Cquat tBu), 15.34 ($CH2_{propargylic}$), 14.25 (CH3), -5.18 (CH3Si).

IR (υcm^{-1}): 3617-3167 (OH), 2953, 2927, 2856, 1464, 1255, 1105.

MS: (ESI) m/z: 369.32 $(M+H)^+$, 237.22 $(M-TBSOH)^+$, 391.30 $(M+Na)^+$.

HRMS calcd for $C_{22}H_{45}O_2Si$, [M+H$^+$] 369.3189, found 369.3188.

Compound 5’b (colorless oil, 97% yield)

Rf: 0.30 (cyclohexane/AcOEt : 9/1) –Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 3.71-3.60 (m, 1H, CHO), 3.66 (t, J = 6.1 Hz, 2H, CH2O), 2.37 (ddt, J = 2.4 Hz, 4.6 Hz and 17.0 Hz, 1H, $H_{propargylic}$), 2.30-2.18 (m, 3H, $H_{propargylic}$), 1.82 (br s, 1H, OH), 1.67 (quint, J = 6.6 Hz, 2H, CH2), 1.55-1.36 (m, 3H, CH2), 1.36-1.17 (m, 17H, CH2), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 3H, CH3), 0.03 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 294 K): 82.86 (C≡C, C4), 76.43 (C≡C, C5), 70.36 (CHO), 61.79 (CH2O), 36.40 (CH2), 32.14 (CH2), 32.07 (CH2), 29.75 (CH2), 29.50 (CH2), 27.90 (CH2 $_{\text{propargylic}}$ C3), 26.08 (tBu), 25.82 (CH2), 22.84 (CH2), 18.49 (C$_{\text{quat}}$ tBu), 15.31 (CH2$_{\text{propargylic}}$ C6), 14.27 (CH3), -5.19 (CH3Si).

IR (υcm^{-1}): 3590-3149 (OH), 2953, 2925, 2855, 1464, 1388, 1361, 1254, 1103, 1071.

MS: (ESI) m/z: 397.35 (M+H)$^+$, 265.25 (M-OTBS)$^+$.

HRMS calcd for $C_{24}H_{49}O_2Si$, [M+H$^+$] 397.3502, found 397.3502; $C_{18}H_{33}O$, [M-OTBS]$^+$ 265.2331, found 265.2533.

B4.1) General procedure for hydrogenation of propargylic alcohols 5 and 5’ to alcohols 4 and 4’ respectively

The reduction of alkyne **5a** into its corresponding alkane **4a** (y=5, z= 1, x =6) is given as an example.

The alkyne **5a** (198 mg, 0.536 mmol) is added to a suspension of Rosenmund’s catalyst (5% Pd on BaSO$_4$, (10% weight, 19.8 mg) in AcOEt (6.8 mL). The reaction vessel was evacuated and back-filled with hydrogen gas (3 times, 1 atm.). The reaction mixture was stirred under hydrogen atmostphere at rt for 3h, then filtered through a short pad of Celite®. After evaporation to dryness, the resulting crude product was purified by flash chromatography on silica gel (~6.8 g, cyclohexane/AcOEt from 100:0 to 95:5) to give the desired saturated fatty chain **4a** (188 mg, 0.534 mmol, 95% yield)) as colorless oil.

B4.2) Chararacterization of alcohols 4a-c and 4’a-b

Compound 4a (colorless liquid, 95 % yield)

Rf: 0.34 (cyclohexane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 293 K): 3.65-3.51 (m, 1H, CHO), 3.59 (t, J = 6.3 Hz, 2H, CH2O), 1.58-1.32 (m, 10H, CH2), 1.32-1.16 (m, 16H, CH2), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 3H), 0.03 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 293 K): 72.06 (CHO), 63.29 (CH2O), 37.61 (CH2), 37.30 (CH2), 32.91 (CH2), 32.07 (CH2), 29.80 (CH2), 29.78 (CH2), 29.50 (CH2), 26.12 (tBu), 25.79 (CH2), 22.84 (CH2), 22.06 (CH2), 18.52 (Cquat tBu), 14.27 (CH3), -5.13 (CH3Si).

IR (υcm^{-1}): 3599-3105 (OH), 2949, 2925, 2855, 1462, 1388, 1361,1254, 1098, 1006.

MS: (ESI) m/z: 373.35 (M+H)$^+$, 355.34 (M–H$_2$O+H)$^+$.

HRMS calcd for $C_{22}H_{49}O_2Si$, $[M+H]^+$ 373.3502, found 373.3500.**;** calcd for $C_{22}H_{47}OSi$, $[M–H_2O+H]^+$ 355.3396, found 355.3394.

Compound 4b (93% yield) as colorless oil)

Rf: 0.26 (cyclohexane/AcOEt: 9/1); 0.33 (cyclohexane/ Et_2O: 9/1) – No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 3.58-3.50 (m, 1H, CHO), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 1.54-1.2 (m, 26H), 0.87 (s, 9H, tBu), 0.86 (t, J = 7.0 Hz, 3H, CH3), 0.02 (s, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 72.19 (CHO), 63.47 (CH2O), 37.67 (CH2), 33.04 (CH2), 31.99 (CH2), 29.82 (CH2), 29.76 (CH2), 29.55 (CH2), 29.45 (CH2), 26.15 (tBu), 25.96 (CH2), 25.81 (CH2), 22.81 (CH2), 18.53 (C_{quat} tBu), 14.23 (CH3), -5.10 (CH3Si).

IR (υcm^{-1}): 3554-3095 (OH), 2928, 2856, 1464, 1255, 1101.

MS: (ESI) m/z: 373.35 $(M+H)^+$, 395.33 $(M+Na)^+$, 355.34 $(M-H_2O)^+$

HRMS calcd for $C_{22}H_{49}O_2Si$, $[M+H^+]$ 373.3502, found 373.3500 ; calcd for $C_{22}H_{48}O_2SiNa$, $[M+Na^+]$ 395.3321, found 395.3320, calcd for $C_{22}H_{47}OSi$, $[M-H_2O^+]$ 355.3396, found 355.3395.

Compound 4c (colorless liquid, 72 % yield)

Rf: 0.60 (cyclohexane/AcOEt: 9/1); 0.20 (cyclohexane/AcOEt: 96/4) - Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 303 K): 3.62-3.51 (m, 1H, CHO), 3.58 (t, J = 6.6 Hz, 2H, CH2O), 1.56-1.33 (m, 10H, CH2), 1.33-1.18 (m, 20H, CH2), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 3H), 0.03 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 303 K): 72.20 (CHOH), 63.49 (CH2O), 37.68 (CH2), 33.06 (CH2), 32.04 (CH2), 29.87 (CH2), 29.74 (CH2), 29.58 (CH2), 29.43 (CH2), 26.15 (tBu), 25.96 (CH2), 25.81 (CH2), 22.82 (CH2), 18.48 (Cquat tBu), 14.24 (CH3), -5.09 (CH3Si).

IR (υcm^{-1}): 3577-3127 (OH), 2926, 2855, 1463, 1361, 1255, 1100.

MS: (ESI) m/z: 401.38 $(M+H)^+$, 423.36 $(M+Na)^+$, 383.37 $(M–H_2O+H)^+$.

HRMS calcd for $C_{24}H_{53}O_2Si$, $[M+H]^+$ 401.3815, found 401.3815.

Compound 4’a (colorless oil, 97% yield)

Rf: 0.81 ((cyclohexane/Et_2O: 9/1); 0.86 (CH_2Cl_2) – No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 3.62-3.50 (m, 1H, CHO), 3.58 (t, J = 6.5 Hz, 3H, CH2O), 1.57-1.15 (m, 26H), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 3H, CH3), 0.02 (s, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 179.51 (COOR), 72.17 (CHO), 63.42 (CH2O), 37.68 (CH2), 37.61 (CH2), 32.99 (CH2), 32.06 (CH2), 29.87 (CH2), 29.79 (CH2), 29.73 (CH2), 29.67

(CH2), 29.47 (CH2), 26.14 (tBu), 25.97 (CH2), 25.81 (CH2), 22.83 (CH2),18.53 (C_{quat} tBu), -5.10 (CH3Si).

IR (υcm^{-1}): 3563-31.27 (OH), 2926, 2855, 1463, 1255, 1175, 1100.

MS: (ESI) m/z: 373.35 $(M+H)^+$, 355.34 $(M-H_2O)^+$, 395.33 $(M+Na)^+$.

HRMS calcd for $C_{22}H_{49}O_2Si$, $[M+H^+]$ 373.3502, found 373.3502, calcd for $C_{22}H_{48}O_2SiNa$, $[M+Na^+]$ 395.3321, found 395.3323.

Compound 4'b (colorless oil, 98% yield)

Rf: 0.36 (cyclohexane/AcOEt: 9/1); No UV – Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 3.63-3.50 (m, 1H, CHO), 3.58 (t, J = 6.5 Hz, 3H, CH2O), 1.57-1.16 (m, 30H, CH2), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 3H, CH3), 0.02 (s, 6 H, CH3Si).

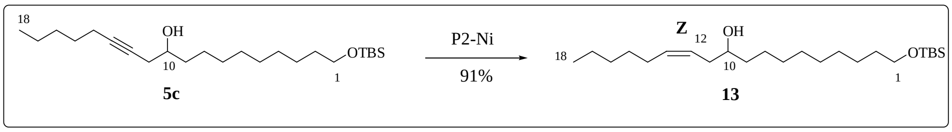
^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 72.17 (CHO), 63.42 (CH2O), 37.61 (CH2), 32.99 (CH2), 32.08 (CH2), 29.88 (CH2), 29.83 (CH2), 29.79 (CH2), 29.67 (CH2), 29.50 (CH2), 26.15 (tBu), 25.98 (CH2), 25.81 (CH2), 22.84 (CH2), 18.53 (C_{quat} tBu), 14.25 (CH3), -5.10 (CH3Si).

IR (υcm^{-1}): 3568-3104 (OH), 2925, 2854, 1463, 1388, 1361, 1254, 1098, 1006.

MS: (ESI) m/z: 383.37 $(M-H_2O)^+$, 401.38 $(M+H)^+$.

HRMS calcd for $C_{24}H_{53}O_2Si$, $[M+H^+]$ 401.3815, found 401.3811.

B5.1) Semi-reduction of propargylic alcohols 5c to (Z)-alkene 13



To a degazed pale green solution of $Ni(OAc)_2.4H_2O$ (10.4 mg, 0.04 mmol, 0.16 equiv) in EtOH (5.2 mL) under hydrogen atmostphere was added a 1 M solution of $NaBH_4$ (88 µL, 0.088 mmol, 0.34 equiv). The mixture immediately turned black. It was quickly placed under vacuum and then hydrogen (3 times) to ensure no oxygen was present and then maintained under hydrogen atmosphere for 15 min (until stabilization of the gas level). Subsequently, ethylenediamine (31 µL, 0.47 mmol, 1.78 equiv) was added, followed 15 minutes later with a solution of propargylic alcohol **5c** (103.8 mg, 0.26 mmol, 1.0 equiv) in EtOH (300 µL). After each addition, the reaction vessel was quickly evacuated and back-filled with hydrogen gas (3 times). The reaction mixture was vigorously stirred under hydrogen atmosphere for 1.5 h at 12 °C. After dilution with wet Et_2O (ca. 5 mL) and addition of ammonium chloride (about 1 spatula), it was filtered through a pad of celite and the solvents were removed *in vaccuo*. The residue was taken up into Et_2O (20mL) and washed with distillated water (2mL x3). The combined aqueous layers were extracted twice with Et_2O (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel (eluting with pentane/Et_2O: 100/0-93/7) provided the desired allylic alcohol **13** as a colorless oil (95.1 mg, 91%).

B5.2) Chararacterization of (Z)-alkene 13

Aspect : colorless liquid

Rf: 0.56 (pentane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 296 K): 5.63-5.47 (m, 1H, H_{olefin}, H13), 5.46-5.31 (m, 1H, H_{olefin}, H12), 3.67-3.50 (m, 1H, CHO), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.19 (t, 2H, $CH2_{allylic}$, H11), 2.10-1.95 (m, 2H, $CH2_{allylic}$, H14), 1.61-1.18 (m, 23H, CH2 and OH), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 3H), 0.02 (s, 6H, CH3Si).

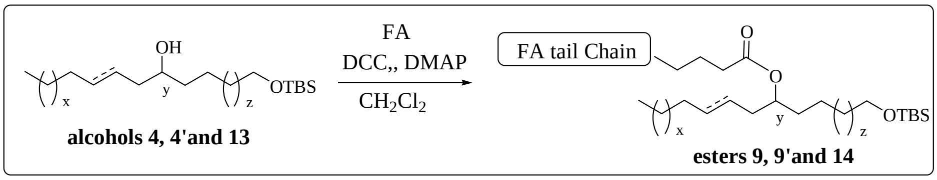
^{13}C NMR (75 MHz, $CDCl_3$, δppm, 296 K): 133.73 (CH_{olefin}, C13), 125.24 (CH_{olefin}, C12), 71.65 (CHOH), 63.48 (CH2O), 36.99 (CH2), 35.50 ($CH2_{allylic}$, C11), 33.03 (CH2), 31.67 (CH2), 29.82 (CH2), 29.72 (CH2), 29.58 (CH2), 29.50 (CH2), 27.54 ($CH2_{allylic}$, C14), 26.14 (tBu), 25.94 (CH2), 25.91 (CH2), 22.71 (CH2), 18.53 (Cquat tBu), 14.20 (CH3), -5.11 (CH3Si).

IR (υcm^{-1}): 3563-3111 (OH), 2955, 2927, 2855, 1463, 1255, 1099.

MS: (ESI) m/z: 399.37 $(M+H)^+$, 381.35 $(M–H_2O+H)^+$.

HRMS calcd for $C_{24}H_{51}O_2Si$, $[M+H]^+$ 399.3658, found 399.3654; calcd for $C_{24}H_{49}OSi$, $[M–H_2O+H]^+$ 381.3553, found 381.3548.

B6.1) General procedure for Steglich esterification of alcohols 4, 4’ and 13



The esterifications of alcohols **4, 4’** and **13** with fatty acids (OA or PA) were conducted according to the same procedure described below for the preparation of ester **14** [y = 10, z = 6, x = 3, (Z)-double bond at C12-C13).

To a stirred solution of fatty alcohol **13** (281.4 mg, 0.706 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (14 mL) was added DMAP (43.10 mg, 0.353 mmol, 0.5 equiv.) and DCC (364 mg, 1.764 mmol, 2.5 equiv.) under a flux of argon. Upon cooling to 0°C, oleic acid (OA, 269 µL, 0.847 mmol, 1.2 equiv.) was added dropwise with a syringe. After 5-10min at 0°C, the ice bath was removed and the temperature was raised to 26°C. The reaction mixture becomes quickly cloudy. It was stirred for about 24h then quenched with water (4 mL), diluted with CH_2Cl_2 (10 mL). The organic layer was washed with water (2 x 4mL). The combined aqueous phases were extracted with CH_2Cl_2 (2 x 15 mL), dried over $MgSO_4$. After evaporation under vacuum, celite® was added to the resulting oily residue prior purification by flash column chromatography (silica gel, ~33 g, pentane/Et_2O, from 100/0 to 98/2). The desired ester **14** (429 mg, 91% yield) was obtained as a colorless oil.

B6.2) Chararacterization of esters 9, 9’ and 14

Compound 9a (colorless liquid, 99% yield)

Rf: 0.89 (cyclohexane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 5.39-5.25 (m, 2H, H_{olefin}), 4.85 (quint, J = 6.0 Hz,, 1H, CHO), 3.57 (t, J = 6.3 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, $CH2CO_{oleyl}$), 2.07-1.92 (m, 4H, $CH2_{allylic}$), 1.66-1.42 (m, 8H, CH2), 1.57-1.16 (m, 40H, CH2), 0.90-0.82 (m, 3H), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 3H), 0.03 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 173.77 (COOR), 130.14 (CH_{olefin}), 129.91 (CH_{olefin}), 74.14 (CHO), 63.12 (CH2O), 34.87 (CH2), 34.27 (CH2), 34.08 (CH2), 32.85 (CH2), 32.07 (CH2), 29.93 (CH2), 29.87 (CH2), 29.80 (CH2), 29.70 (CH2), 29.48 (CH2), 29.35 (CH2), 29.31 (CH2), 27.38 (CH2), 27.34 (CH2), 26.12 (tBu), 25.46 (CH2), 25.31 (CH2), 22.84 (CH2), 21.82 (CH2), 18.49 (C_{quat} tBu), 14.25 (CH3), -5.13 (CH3Si).

IR (υcm^{-1}): 2924, 2854, 1734 (COOR), 1463, 1378, 1251, 1175, 1099.

MS: (ESI) m/z: 637.60 $(M+H)^+$.

HRMS calcd for $C_{40}H_{81}O_3$ Si, [M+H+] 637.5955, found 637.5950.

Compound 9b (colorless oil, 89% yield)

Rf: 0.88 (cyclohexane/AcOEt: 9/1), 0.76 (cyclohexane/Et_2O: 94/6) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 5.40-5.24 (m, 2H, H_{olefin}), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.07-1.92 (m, 4H, $CH2_{allylic}$), 1.67-1.40 (m, 8H, CH2), 1.39-1.15 (m, 40H, CH2), 0.90-0.82 (m, 6H, CH3), 0.87 (s, 9H, tBu), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 173.80 (COOR), 130.14 (CH_{olefin}), 129.92 (CH_{olefin}), 74.24 (CHOH), 63.46 (CH2O), 34.90 (CH2), 34.33 (CH2), 33.04 (CH2), 32.06 (CH2), 31.95 (CH2), 29.93 (CH2), 29.87 (CH2), 29.67 (CH2), 29.52 (CH2), 29.48 (CH2), 29.36 (CH2), 29.30 (CH2), 27.38 (CH2), 27.34 (CH2), 26.14 (tBu), 25.95 (CH2), 25.48 (CH2), 25.33 (CH2), 22.83 (CH2), 22.79 (CH2), 18.52 (C_{quat} tBu), 14.23 (CH3), -5.10 (CH3Si).

IR (υcm^{-1}): 2926, 2855, 1735 (COOR), 1464, 1254, 1178, 1100.

MS: (ESI) m/z: 637.60 $(M+H)^+$.

HRMS calcd for $C_{40}H_{81}O_3$ Si, $[M+H^+]$ 637.5955, found 637.5952.

Compound 9c (colorless oil, 82%)

Rf: 0.90 (cyclohexane/AcOEt: 9/1), 0.79 (cyclohexane/Et_2O: 94/6) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 5.41-5.29 (m, 2H, H_{olefin}), 4.87 (quint, J = 6.2 Hz, 1H, CHO), 3.60 (t, J = 6.6 Hz, 2H, CH2O), 2.28 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.01-1.94 (m, 4H, $CH2_{allylic}$), 1.70-1.56 (m, 2H, CH2), 1.56-1.40 (m, 6H, CH2), 1.41-1.15 (m, 44H, CH2), 0.90 (s, 9H, tBu), 0.92-0.82 (m, 6H, CH3), 0.05 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 173.86 (COOR), 130.13 (CH_{olefin}), 129.90 (CH_{olefin}), 74.23 (CHOH), 63.48 (CH2O), 34.88 (CH2), 34.30 (CH2), 33.03 (CH2), 32.05 (CH2), 32.02 (CH2), 29.92 (CH2), 29.86 (CH2), 29.68 (br, CH2), 29.57 (CH2), 29.47 (CH2), 29.39 (CH2), 29.36 (CH2), 29.31 (CH2), 27.36 (CH2), 27.32 (CH2), 26.13 (tBu), 25.94 (CH2), 25.47 (CH2), 25.32 (CH2), 22.83 (CH2), 18.55 (C_{quat} tBu), 14.27 (CH3), -5.11 (CH3Si).

IR (υcm^{-1}): 2924, 2854, 1734 (COOR), 1463, 1254, 1176, 1099.

MS: (ESI) m/z: 665.63 $(M+H)^+$.

HRMS calcd for $C_{42}H_{85}O_3$ Si, $[M+H^+]$ 665.6268, found 665.6269.

Compound 9d (colorless oil, 92% yield)

Rf: 0.91 (cyclohexane/ Et_2O: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 301 K): 4.85 (quint, J = 6..4 Hz, 1H, CHOCO), 3.57 (t, J = 6.4 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 1.66-1.40 (m, 8H), 1.39-1.12 (m, 45H), 0.90-0.82 (m, 3H, CH3), 0.87 (s, 9H, tBu), 0.86 (t, J = 6.9 Hz, 6 H, CH_3), 0.02 (s, 6 H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 301 K): 173.81 (COOR), 74.14 (CHO), 63.13 (CH2O), 34.90 (CH2CO), 34.28 (CH2), 34.09 (CH2), 32.86 (CH2), 32.08 (CH2), 29.82 (CH2), 29.71 (CH2), 29.51 (CH2), 29.38 (CH2), 26.12 (CH2), 25.46 (CH2), 25.34 (CH2), 22.84 (CH2), 21.83 (CH2), 18.49 (C_{quat} tBu), 14.25 (CH3), -5.13 (CH3Si).

IR (υcm^{-1}): 2944, 2925, 2854, 1735, 1463, 1255, 1174, 1103.

MS: (ESI) m/z: 611.58 $(M+H)^+$.

HRMS calcd for $C_{38}H_{79}O_3Si$, $[M+H^+]$ 611.5798, found 611.5798.

Compound 9e (colorless oil, 90% yield)

Rf: 0.32 (cyclohexane); 0.86 (CH_2Cl_2); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 4.84 (AcOEt, J = 6.2 Hz, 1H, CHOCO), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 1.66-1.55 (m, 2H, CH2), 1.55-1.40 (m, 6H, CH2), 1.36-1.15 (m, 44H, CH2), 0.87 (s, 9 H, tBu), 0.92-0.81 (m, 6H, CH_3), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 173.84 (COOR), 74.23 (CHO), 63.47 (CH2O), 34.92 (CH2CO), 34.33 (CH2), 33.04 (CH2), 32.09 (CH2), 31.95 (CH2), 29.85 (CH2), 29.67 (CH2), 29.52 (CH2), 29.48 (CH2), 29.37 (CH2), 26.15 (CH2), 25.95 (CH2), 25.48 (CH2), 25.36 (CH2), 22.84 (CH2), 22.80 (CH2), 18.56 (C_{quat} tBu), 14.23 (CH3), -5.10 (CH3Si).

IR (υcm^{-1}): 2925, 2854, 1734, 1464, 1256, 1175, 1099.

MS: (ESI) m/z: 611.58 $(M+H)^+$.

HRMS calcd for $C_{38}H_{79}O_3Si$ $[M+H^+]$ 611.5798, found 611.5801.

Compound 9'a (colorless oil, 92% yield)

Rf: 0.89 (cyclohexane/AcOEt: 9/1), 0.53 (cyclohexane/Et_2O: 94/6) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 5.39-5.24 (m, 2H, H_{olefin}), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 3.56 (t, J = 6.5 Hz, 2H, CH2O), 2.25 (t, J = 7.4 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.09-1.90 (m, 4H, $CH2_{allylic}$), 1.70-1.54 (m, 2H, CH2), 1.54-1.39 (m, 6H, CH2), 1.38-1.13 (m, 40H, CH2), 0.87 (s, 9H, tBu), 0.89-0.81 (m, 6H, CH3), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 173.83 (COOR), 130.13 (CH_{olefin}), 129.90 (CH_{olefin}), 74.19 (CHOH), 63.38 (CH2O), 34.88 (CH2), 34.29 (CH2), 34.26 (CH2), 32.93 (CH2), 32.05 (CH2), 29.92 (CH2), 29.86 (CH2), 29.69 (CH2), 29.48 (CH2), 29.35 (CH2), 29.32 (CH2), 27.37 (CH2), 27.33 (CH2), 26.13 (tBu), 25.86 (CH2), 25.46 (CH2), 25.32 (CH2), 22.83 (CH2), 18.55 (C_{quat} tBu), 14.27 (CH3), -5.12 (CH3Si).

IR (υcm^{-1}): 2925, 2855, 1734 (COOR), 1464, 1253, 1100, 1005.

MS: (ESI) m/z: 637.59 $(M+H)^+$.

HRMS calcd for $C_{40}H_{81}O_3$ Si, $[M+H^+]$ 637.5955, found 637.5946.

Compound 9'b (colorless oil,.82% yield)

Rf: 0.87 (cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 304 K): 5.40-5.25 (m , 2H, H_{olefin}), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 3.57 (t, J = 6.5 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 2.09-1.91 (m, 4H, CH2), 1.68-1.39 (m, 8H, CH2), 1.39-1.14 (m, 44H, CH2), 0.95-0.86 (m, 6H, CH3), 0.87 (s, 9H, tBu), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 304 K): 173.79 (COOR), 130.15 (CH_{olefin}), 129.92 (CH_{olefin}), 74.22 (CHO), 63.39 (CH2O), 34.90 (CH2), 34.31 (CH2), 32.95 (CH2), 32.08 (CH2), 29.93 (CH2), 29.87 (CH2), 29.80 (CH2), 29.71 (CH2), 29.50 (CH2), 29.34 (CH2), 27.38 (CH2), 27.35 (CH2), 26.14 (tBu), 25.88 (CH2), 25.48 (CH2), 25.33 (CH2), 22.84 (CH2), 18.53 (Cquat tBu), 14.25 (CH3), -5.10 (CH3Si).

IR (υcm^{-1}): 2925, 2855, 1734, 1463, 1379, 1356, 1254, 1176, 1100.

MS: (ESI) m/z: 665.63 $(M+H)^+$.

HRMS calcd for $C_{42}H_{85}O_3Si$, $[M+H^+]$ 665.6268, found 665.6265.

Compound 9'c (colorless oil, 84% yield)

Rf: 0.91 (cyclohexane/ Et_2O: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 302 K): 4.84 (AcOEt, J = 6.2 Hz, 1H, CHO), 3.57 (t, J = 6.5 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 1.66-1.41 (m, 8 H, CH2), 1.37-1.19 (m, 45 H, CH2), 0.90-0.82 (m, 3H, CH3), 0.87 (s, 9 H, tBu), 0.86 (t, J = 7.0 Hz, 3H, CH_3), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 302 K): 173.82 (COOR), 74.20 (CHO), 63.39 (CH2O), 34.92 (CH2CO), 34.32 (CH2), 34.29 (CH2), 32.95 (CH2), 32.06 (CH2), 29.85 (CH2), 29.82 (CH2), 29.79 (CH2), 29.70 (CH2), 29.67 (CH2), 29.50 (CH2), 29.47 (CH2), 29.37 (CH2), 26.14 (tBu), 25.88 (CH2), 25.48 (CH2), 25.35 (CH2), 22.84 (CH2), 18.52 (C_{quat} tBu), 14.25 (CH3), -5.11 (CH3Si).

IR (υcm^{-1}): 2924, 2855, 1735, 1464, 1379, 1254, 1174, 1102.

MS: (ESI) m/z: 611.58 $(M+H)^+$.

HRMS calcd for $C_{38}H_{79}O_3Si$, $[M+H^+]$ 611.5798, found 611.5802.

Compound 9’d (colorless oil, 98% yield)

Rf: 0.91 ((cyclohexane/Et_2O: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 304 K): 4.84 (AcOEt, J = 6.2 Hz, 1H, CHO), 3.57 (t, J = 6.5 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 1.67-1.42 (m, 8 H, CH2), 1.38-1.18 (m, 45 H, CH2), 0.92-0.80 (m, 3H, CH3), 0.87 (s, 9 H, tBu), 0.86 (t, J = 7.0 Hz, 3H, CH_3), 0.02 (s, 6H, CH3Si).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 304 K): 173.82 (COOR), 74.21 (CHO), 63.39 (CH2O), 34.92 (CH2CO), 34.33 (CH2), 34.30 (CH2), 32.95 (CH2), 32.09 (CH2), 29.85 (CH2), 29.82 (CH2), 29.72 (CH2), 29.68 (CH2), 29.51 (CH2), 29.48 (CH2), 29.38 (CH2), 26.15 (tBu), 25.88 (CH2), 25.48 (CH2), 25.36 (CH2), 22.84 (CH2), 18.52 (C_{quat} tBu), 14.25 (CH3), -5.10 (CH3Si).

IR (υcm^{-1}): 2925, 2855, 1734, 1464, 1384, 1356, 1254, 1176, 1101.

MS: (ESI) m/z: 639.61 $(M+H)^+$.

HRMS calcd for $C_{40}H_{83}O_3Si$, $[M+H^+]$ 639.6111, found 639.6107.

Compound 14
Aspect : colorless oil

Rf: 0.67 (pentane/AcOEt: 9/1)– Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 295 K): 5.51-5.39 (m, 1H, $H_{olefin\ HFA}$, H13), 5.39-5.23 (m, 3H, H12 $_{HFA}$ and $H_{olefin\ oleate}$), 4.86 (quint., J = 6.2 Hz, 1H, CHO), 3.57 (t, J = 6.6 Hz, 2H, CH2O), 2.34-2.17 (m, 4H, $CH2_{alphaCO}$ and $CH2_{allylic}$ H11), 2.07-1.90 (m, 6H, $CH2_{allylic}$), 1.66-1.39 (m, 6H, CH2), 1.38-1.13 (m, 38H, CH2), 0.90-0.80 (m, 6H, CH3), 0.87 (s, 9H, tBu), 0.02 (s, 6H, CH3Si).

.

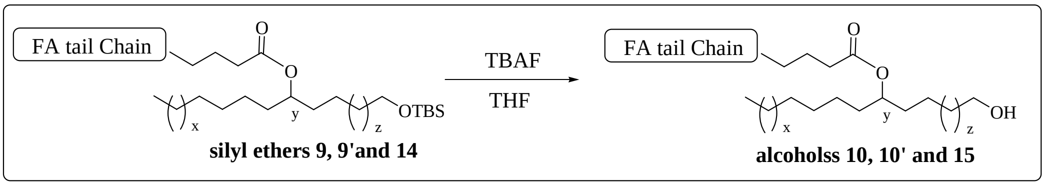
^{13}C NMR (75 MHz, $CDCl_3$, δppm, 295 K): 173.71 (COOR), 132.81 ($CH_{olefin,}$ C13), 130.13 ($CH_{olefin\ oleate}$), 129.90 ($CH_{olefin\ oleate}$), 124.39 ($CH_{olefin,}$ C12), 73.81 (CHOH), 63.47 (CH2O), 34.83 ($CH2_{alphaCO\ oleyl}$), 33.79 (CH2), 33.04 (CH2), 32.13 (C11 or CCH2C), 32.06 ((C11 or CCH2C)), 31.67 (CH2), 29.92 (CH2), 29.86 (CH2), 29.71 (CH2), 29.64 (CH2), 29.57 (CH2), 29.47 (CH2), 29.43 (CH2), 29.35 (CH2), 29.30 (CH2), 27.47 (CH2), 27.36 (CH2), 27.33 (CH2), 26.13 (tBu), 25.94 (CH2), 25.56 (CH2), 25.27 (CH2), 22.83 (CH2), 22.73 (CH2), 18.53 (C_{quat} tBu), 14.27 (CH3), 14.21 (CH3), -5.11 (CH3Si).

IR (υcm^{-1}): 2925, 2855, 2855, 17345 (COOR), 1463, 1253, 1174, 1099.

MS: (ESI) m/z: 663.61 $(M+H)^+$, 381.35 $(M\text{-}OA+H)^+$.

HRMS calcd for $C_{42}H_{83}O_3$ Si, $[M+H^+]$ 663.6111, found 663.6109.

B7.1) General procedure for deprotection of silyl ethers 9, 9’ and 14



silyl ethers 9, 9'and 14

alcoholss 10, 10' and 15

The conversion of the silyl-ether **9’b** into its corresponding primary alcohol **10’b** is taken as an example.

To a solution of TBS-ether **9’b** (259 mg, 0.389 mmol, 1.0 equiv) in THF (2.3 mL) was added a tetrabutylammonium fluoride solution (TBAF, 1.0 M in THF, 584 µL, 0.584 mmol, 1.5 equiv) at 0°C. After 5 min at 0°C, the ice-bath was removed. The reaction mixture was stirred at rt for 13h and quenched by addition of water (3 mL). The organic layer was washed twice with water (1 mL). The combined aqueous phases were re-extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered over cotton, and evaporated to dryness under reduced pressure. Purification of the oily residue by flash chromatography (silica gel, ca. 7g, cyclohexane/AcOEt: 98/2 to 90/10) afforded the expected primary alcohol **10’b** in 94% yield.

B7.2) Chararacterization of alcohols 10, 10’ and 15

Compound 10a (colorless oil, 86% yield)

Rf: 0.31 (cyclohexane/AcOEt: 84/16) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 301 K): 5.39-5.25 (m, 2H, H_{olefin}), 4.86 (quint, J = 5.9 Hz, 1H, CHO), 3.61 (t, J = 6.4 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, $CH2CO_{oleyl}$), 2.06-1.91 (m, 4H, $CH2_{allylic}$), 1.67-1.41 (m, 8H, CH2), 1.39-1.15 (m, 40H, CH2), 0.86 (t, J = 6.9 Hz, 6H, CH3).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 301 K): 173.87 (COOR), 130.15 (CH_{olefin}), 129.90 (CH_{olefin}), 74.01 (CHO), 62.91 (CH2O), 34.86 (CH2), 34.32 (CH2), 34.12 (CH2), 32.74 (CH2), 32.07 (CH2), 29.93 (CH2), 29.86 (CH2), 29.80 (CH2), 29.73 (CH2), 29.70 (CH2), 29.68 (CH2), 29.48 (CH2), 29.35 (CH2), 29.33 (CH2), 29.30 (CH2), 27.38 (CH2), 27.34 (CH2), 25.49 (CH2), 25.30 (CH2), 22.83 (CH2), 21.74 (CH2), 14.24 (CH3).

IR (υcm^{-1}): 3581-3136 (OH), 2922, 2853, 1733 (COOR), 1458, 1173.

MS: (ESI) m/z: 523.51 $(M+H)^+$, 545.49 $(M+Na)^+$.

HRMS calcd for $C_{34}H_{67}O_3$, [M+H$^+$] 523.5090, found 523.5090.

Compound 10b (colorless oil, 86% yield)

Rf: 0.26 (cyclohexane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (500 MHz, $CDCl_3$, δppm, 293 K): 5.37-5.27 (m, 2H, H_{olefin}), 4.84 (quint, J = 5.9 Hz, 1H, CHO), 3.61 (t, J = 6.6 Hz, 2H, CH2O, H1), 2.25 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.03-1.94 (m, 4H, $CH2_{allylic}$), 1.63-1.42 (m, 8H, CH2), 1.37-1.16 (m, 40H, CH2), 0.85 (t, J = 7.0 Hz, 3H, CH3), 0.84 (t, J = 7.0 Hz, 3H, CH3).

^{13}C NMR (125 MHz, $CDCl_3$, δppm, 293 K): 173.88 (COOR), 130.12 (CH_{olefin}), 129.88 (CH_{olefin}), 74.17 (CHOH), 63.18 (CH2O), 34.87 (CH2), 34.29 (CH2), 32.89 (CH2), 32.05 (CH2), 31.93 (CH2), 29.90 (CH2), 29.84 (CH2), 29.67 (CH2), 29.63 (CH2), 29.60 (CH2), 29.55 (CH2), 29.46 (CH2), 29.35 (CH2), 29.30 (CH2), 27.35 (CH2), 27.31 (CH2), 25.81 (CH2), 25.46 (CH2), 25.43 (CH2), 25.31 (CH2), 22.82 (CH2), 22.79 (CH2), 14.24 (CH3).

IR (υcm^{-1}): 3603-3136 (OH), 2923, 2854, 1733 (COOR), 1464, 1378, 1245, 1177, 1056..

MS: (ESI) m/z: 505.50 (M-H_2O)$^+$, 523.51 (M+H)$^+$, 545.49 (M+Na)$^+$, 561.47 (M+K)$^+$, 1046.01 (Mx2 +H)$^+$, 1069.00 (Mx2 +Na)$^+$.

HRMS calcd for $C_{34}H_{67}O_3$, [M+H$^+$] 523.5090, found 523.5088.

Compound 10c (colorless oil, 82% yield)

Rf: 0.69 (cyclohexane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 5.40-5.24 (m, 2H, H_{olefin}), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 3.61 (t, J = 6.6 Hz, 2H, CH2O, H1), 2.25 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.05-1.92 (m, 4H, $CH2_{allylic}$), 1.66-1.38 (m, 8H, CH2), 1.38-1.16 (m, 53H, CH2 and OH), 0.85 (t br, J = ca. 7.1 Hz, 6H, CH3)

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 173.87 (COOR), 130.13 (CH_{olefin}), 129.89 (CH_{olefin}), 74.20 (CHOH), 63.20 (CH2O), 34.88 (CH2), 34.29 (CH2), 32.93 (CH2), 32.05 (CH2), 32.01 (CH2), 29.91 (CH2), 29.85 (CH2), 29.64 (CH2), 29.59 (CH2), 29.51 (CH2), 29.47 (CH2), 29.38 (CH2), 29.36 (CH2), 29.30 (CH2), 27.36 (CH2), 27.32 (CH2), 25.84 (CH2), 25.46 (CH2), 25.32 (CH2), 22.82 (CH2), 14.26 (CH3).

IR (υcm^{-1}): 3511-3196 (OH), 2923, 2855, 1733 (COOR), 1465, 1376, 1245, 1182, 1058..

MS: (ESI) m/z: 533.53 (M-H_2O)$^+$, 551.54 (M+H)$^+$, 573.52 (M+Na)$^+$.

HRMS calcd for $C_{36}H_{71}O_3$, [M+H$^+$] 551.5403, found 551.5404.

Compound 10d (colorless oil, 89% yield)

Rf: 0.21 (cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 301 K): 4.86 (AcOEt, J = 6.4 Hz, 1H, CHOCO), 3.61 (t, J = 6.5 Hz, 2H, CH2O), 2.26 (t, J = 7.5 Hz, 2H, CH2COOR), 1.67-1.44 (m, 8H), 1.42-1.14 (m, 45H), 0.86 (t br, 6H, J = 6.7 Hz, CH_3).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 301 K): 173.90 (COOR), 73.98 (CHO), 62.95 (CH2O), 34.88 (CH2CO), 34.33 (CH2), 34.13 (CH2), 32.75 (CH2), 32.08 (CH2), 29.84 (CH2), 29.81 (CH2), 29.78 (CH2), 29.74 (CH2), 29.69 (CH2), 29.51 (CH2), 29.47 (CH2), 29.37 (CH2), 25.49(CH2), 25.33(CH2), 22.84 (CH2), 21.74 (CH2), 14.25 (CH3).

IR (υcm^{-1}): 3617-3154 (OH), 2922, 2853, 1733, 1466, 1174, 1061.

MS: (ESI) m/z: 497.49 $(M+H)^+$, 993.98 $(M+H\ dimer)^+$, 519.48 $(M+Na)^+$, 1015.96 $(M\ x2 + Na)^+$.

HRMS calcd for $C_{32}H_{65}O_3$, $[M+H^+]$ 497.4934, found 497.4931, calcd for $C_{32}H_{64}O_3Na$, $[M+Na^+]$ 519.4753, found 519.4752.

Compound 10e (colorless oil, 89% yield)

Rf: 0.33 (cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 301 K): 4.84 (AcOEt, J = 6.2 Hz, 1H, CHO), 3.61 (t, J = 6.6 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 1.66-1.41 (m, 8H, CH2), 1.38-1.14 (m, 45H), 0.86 (t br, J = 6.6 Hz, 3H, CH_3).0.85 (t br, J = 7.1, 3H, CH_3).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 301 K): 173.86 (COOR), 74.19 (CHO), 63.21 (CH2O), 34.92 (CH2CO), 34.33 (CH2) , 32.95 (CH2), 32.08 (CH2), 31.95 (CH2), 29.84 (CH2), 29.82 (CH2), 29.78 (CH2), 29.66 (CH2), 29.61 (CH2), 29.58 (CH2), 29.50 (CH2), 29.47 (CH2), 29.36 (CH2), 25.85 (CH2), 25.48 (CH2), 25.45 (CH2), 25.35 (CH2), 22.84 (CH2), 22.79 (CH2), 14.22 (CH3).

IR (υcm^{-1}): 3595-3207 (OH), 2922, 2853, 1733, 1465, 1378, 1175, 1115, 1057.

MS: (ESI) m/z: 497.49 $(M+H)^+$, 519.48 $(M+Na)^+$, 479.48 $(M-H_2O)^+$, 993.98 $(M+H\ dimer)^+$. 1015.96 $(M\ x2 +Na)^+$.

HRMS calcd for $C_{32}H_{65}O_3$, $[M+H^+]$ 497.4934, found 497.4937 ; calcd for $C_{32}H_{63}O_2$, $[M-H_2O]$ 479.4828, found 479.4830 ; calcd for $C_{32}H_{64}O_3Na$, $[M+Na^+]$ 519.4753, found 519.4758.

Compound 10’a (colorless oil, 96% yield)

Rf: 0.36 (cyclohexane/AcOEt: 8/2) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 294 K): 5.39-5.25 (m, 2H, H_{olefin}), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 3.61 (t, J = 6.6 Hz, 2H, CH2O, H1), 2.25 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.09-1.90 (m, 4H, $CH2_{allylic}$), 1.67-1.39 (m, 8H, CH2), 1.39-1.14 (m, 49H, CH2 and OH), 0.86 (t, J = ca. 6.0 Hz, 3H, CH3), 0.85 (t, J = ca. 6.7 Hz, 3H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 173.86 (COOR), 130.14 (CH_{olefin}), 129.89 (CH_{olefin}), 74.12 (CHOH), 63.10 (CH2O), 34.87 (CH2), 34.30 (CH2), 34.21 (CH2), 32.81 (CH2), 32.04 (CH2), 29.91 (CH2), 29.85 (CH2), 29.68 (CH2), 29.46 (CH2), 29.39 (CH2), 29.35 (CH2), 29.31 (CH2), 27.36 (CH2), 27.32 (CH2), 25.76 (CH2), 25.47 (CH2), 25.42 (CH2), 25.31 (CH2), 22.83 (CH2), 14.26 (CH3).

IR (υcm^{-1}): 3626-31085 (OH), 2923, 2854, 1733 (COOR), 1465, 1378, 1245, 1181, 1057.

MS: (ESI) m/z: 505.50 $(M-H_2O)^+$, 523.51 $(M+H)^+$, 545.49 $(M+Na)^+$.

HRMS calcd for $C_{34}H_{67}O_3$, $[M+H]^+$ 523.5090, found 523.5085, calcd for $C_{34}H_{66}O_3Na$, $[M+Na]^+$ 545.4910, found 545.4905; calcd for $C_{34}H_{65}O_2$, $[M-H2O+H]^+$ 505.4985, found 505.4978.

<u>Compound 10’b</u> (colorless oil, 94% yield)

Rf: 0.17 (cyclohexane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 293 K): 5.39-5.25 (m, 2H, H_{olefin}), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 3.61 (t, J = 6.5 Hz, 2H, CH2O, H1), 2.25 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.06-1.91 (m, 4H, $CH2_{allylic}$), 1.66-1.14 (m, 53H, CH2 and OH), 0.85 (t, J = 6.9 Hz, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 292 K): 173.87 (COOR), 130.14 (CH_{olefin}), 129.90 (CH_{olefin}), 74.12 (CHOH), 63.11 (CH2O), 34.87 (CH2), 34.30 (CH2), 34.21 (CH2), 32.81 (CH2), 32.06 (CH2), 29.91 (CH2), 29.85 (CH2), 29.80 (CH2), 29.73 (CH2), 29.69 (CH2), 29.50 (CH2), 29.48 (CH2), 29.39 (CH2), 29.36 (CH2), 29.31 (CH2), 27.36 (CH2), 27.32 (CH2), 25.76 (CH2), 25.47 (CH2), 25.42 (CH2), 25.31 (CH2), 22.84 (CH2), 14.27 (CH3).

IR (υcm^{-1}): 3607-3096 (OH), 2923, 2853, 1733 (COOR), 1465, 1378, 1245, 1179, 1057.

MS: (ESI) m/z: 533.53 $(M-H_2O)^+$, 551.54 $(M+H)^+$, 573.52 $(M+Na)^+$.

HRMS calcd for $C_{36}H_{71}O_3$, $[M+H^+]$ 551.5403, found 551.5399.

<u>Compound 10’c</u> (colorless oil, 93% yield)

Rf: 0.33 (cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 301 K): 4.86 (AcOEt, J = 6.3 Hz, 1H, CHO), 3.61 (t, J = 6.5 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 1.67-1.42 (m, 8H, CH2), 1.39-1.13 (m, 45H, CH2), 0.86 (t, 6H, J = 6.8 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 301 K): 173.86 (COOR), 74.12 (CHO), 63.12 (CH2O), 34.90 (CH2CO), 34.33 (CH2) , 34.24 (CH2), 32.85 (CH2), 32.06 (CH2), 29.84 (CH2), 29.69 (CH2), 29.46 (CH2), 29.41 (CH2), 29.37 (CH2), 25.78 (CH2), 25.48 (CH2), 25.43 (CH2), 25.35 (CH2), 22.83 (CH2), 14.24 (CH3).

IR (υcm^{-1}): 3684-3127 (OH), 2922, 2853, 1733, 1465, 1378, 1176, 1114, 1057.

MS: (ESI) m/z: 497.49 $(M+H)^+$, 519.48 $(M+Na)^+$, 479.48 $(M-H_2O)^+$, 993.98 $(M+H\ dimer)^+$, 1015.96 $(M\ x2\ +Na)^+$.

HRMS calcd for $C_{32}H_{65}O_3$, $[M+H^+]$ 497.4934, found 497.4933 ; calcd for $C_{32}H_{63}O_2$, $[M-H_2O]$ 479.4828, found 479.4827 ; calcd for $C_{32}H_{64}O_3Na$, $[M+Na^+]$ 519.4753, found 519.4754.

Compound 10’d (colorless oil, 93% yield)

Rf: 0.33 (cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 306 K): 4.85 (AcOEt, J = 6.2 Hz, 1H, CHO), 3.61 (t, J = 6.5 Hz, 2H, CH2O), 2.25 (t, J = 7.5 Hz, 2H, CH2CO), 1.66-1.44 (m, 8H, CH2), 1.37-1.14 (m, 49H, CH2 and OH), 0.86 (t, 6H, J = 6.8 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 306 K): 173.85 (COOR), 74.13 (CHO), 63.13 (CH2O), 34.91 (CH2CO), 34.34 (CH2) , 34.26 (CH2), 32.86 (CH2), 32.08 (CH2), 29.82 (CH2), 29.71 (CH2), 29.50 (CH2), 29.42 (CH2), 29.38 (CH2), 25.79 (CH2), 25.48 (CH2), 25.43 (CH2), 25.35 (CH2), 22.84 (CH2), 14.24 (CH3).

IR (υcm^{-1}): 3655-3207 (OH), 2921, 2853, 1733, 1465, 1377, 1176, 1057.

MS: (ESI) m/z: 525.52 $(M+H)^+$, 507.51 $(M-H_2O)^+$, 1050.04 $(M+H\ dimer)^+$.

HRMS calcd for $C_{34}H_{69}O_3$, $[M+H^+]$ 525.5247, found 525.5246.

Compound 15 (colorless oil, 96% yield)

Rf: 0.10 (pentane/Et_2O: 9/1); 0.27 (pentane/AcOEt: 9/1); 0.84 (pentane/AcOEt: 8/2); – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 5.51-5.39 (m, 1H, H_{olefin} H13), 5.39-5.23 (m, 3H, $H_{olefin\ oleeyl}$ and H12), 4.86 (quint, J = 6.2 Hz, 1H, CHO), 3.61 (t, J = 6.6 Hz, 2H, CH2O, H1), 2.35-2.17 (m, 4H, $CH2_{alphaCO\ oleyl}$ and H11), 2.08-1.90 (m, 6H, $CH2_{allylic}$), 1.65-1.44 (m, 6H, CH2), 1.41 (br s, 1H, OH), 1.38-1.15 (m, 38H, CH2 and OH), 0.85 (t br, J = ca. 7.0 Hz, 3H, CH3), 0.85 (t br, J = ca. 6.9 Hz, 3H, CH3).

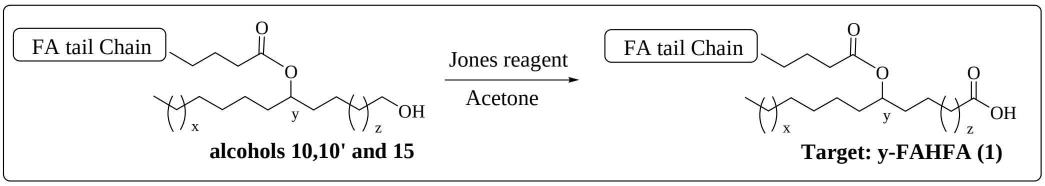
^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 173.75 (COOR), 132.82 (CH_{olefin}, C13), 130.14 ($CH_{olefin\ oley}$l), 129.90 ($CH_{olefin\ oleyl}$), 124.38 (CH_{olefin}, C12), 73.80 (CHOH), 63.21 (CH2O), 34.83 ($CH2_{alphaCO\ oleyl}$), 33.77 (CH2), 32.94 (CH2), 32.13 (CH2, C11), 32.05 (CH2), 31.67 (CH2), 29.91 (CH2), 29.86 (CH2), 29.67 (CH2), 29.64 (CH2), 29.58 (CH2), 29.51 (CH2), 29.47 (CH2), 29.42 (CH2), 29.35 (CH2), 29.30 (CH2), 27.47 ($CH2_{allylic}$), 27.36 ($CH2_{allylic}$), 27.33 ($CH2_{allylic}$), 25.85 (CH2), 25.53 (CH2), 25.26 (CH2), 22.83 (CH2), 22.73 (CH2), 14.26 (CH3), 14.21 (CH3).

IR (υcm^{-1}): 3637-3048 (OH), 2923, 2854, 1733 (COOR), 1465, 1376, 1177, 1055..

MS: (ESI) m/z: 531.51 $(M-H_2O)^+$, 549.52 $(M+H)^+$, 571.51 $(M+Na)^+$, 267.27 $(M-OA+H)^+$.

HRMS calcd for $C_{36}H_{71}O_3$, $[M+H^+]$ 549.5247, found 549.5242.

B8.1) General procedure for Jones's oxidation of alcohols 10, 10' and 15



The Jones oxidation of primary alcohol **10e** into its corresponding carboxylic acid **1e (9-PAHPA)** (y=9, z= 5, x =2) is given as an example.

A solution of alcohol **10e** (160 mg, 0.322 mmol) in acetone (HPLC grade, 4.5 mL) was cooled (ice bath, ~0°C) during 20 min. Then, a solution of Jones reagent (222 µL, 2.17 M, 0.483 mmol, 1.5 eq) was added dropwise over 15 min. The mixture was stirred at 0°C for 3 hours. Then excess of Jones reagent was neutralized with 250 µL of isopropanol. The mixture was filtered over a pad of celite (washed with AcOEt), then saturated NaCl (3 mL) was added. The aqueous layer was extracted with AcOEt (3 x 15 mL). The combined organic layers were dried over $MgSO_4$, then reduced under vacuum to give the crude product as an oil that solidified at room temperature. The crude product was purified by chromatography (Silica, ~6.5 g, Φ40-63 microns, cyclohexane:AcOEt, from 10:0 to 95:5, v/v, over 200 mL). The appropriated fractions were combined, reduced under vacuum to give the desired target **(9-PAHPA)** (91 mg, 0.178 mmol, 55% yield) as acolorless oil that solidified below 20°C.

B8.2) Chararacterization of targets 1a-1i and 2

Compound 1a: Target 5-OAHPA (colorless oil, 75% yield)

Rf: 0.30 (cyclohexane/AcOEt: 8/2) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 300 K): 5.39-5.25 (m, 2H, H_{olefin}), 4.86 (quint, J = 5.7 Hz, 1H, CHO), 2.34 (t, J = 7.2 Hz, 2H, $CH2_{alphaCO\ HPA}$), 2.26 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.08-1.92 (m, 4H, $CH2_{allylic}$), 1.73-1.42 (m, 6H, CH2), 1.39-1.15 (m, 40H, CH2), 0.86 (t, J = 6.6 Hz, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 300 K): 178.78 (COOH), 173.82 (COOR), 130.15 (CH_{olefin}), 129.92 (CH_{olefin}), 73.54 (CHO), 34.82 ($CH2_{alphaCO\ oleyl}$), 34.22 (CH2), 33.77 ($CH2_{alphaCO\ HPA}$), 33.57 (CH2), 32.07 (CH2), 29.93 (CH2), 29.87 (CH2), 29.79 (CH2), 29.73 (CH2), 29.68 (CH2), 29.49 (CH2), 29.34 (CH2), 29.30 (CH2), 27.38 ($CH2_{allylic}$), 27.34 ($CH2_{allylic}$), 25.45 (CH2), 25.28 (CH2), 22.83 (CH2), 20.63 (CH2), 14.24 (CH3).

IR (υcm-1): 3421-2503 (OH), 2958, 2922, 2853, 1735 (COOR), 1711 (COOH), 1462, 1377.

MS: (negative ESI) m/z: 535.47 $(M-H)^+$.
MS: (positive ESI) m/z: 537.49 $(M+H)^+$, 559.47 $(M+Na)^+$.

HRMS calcd for $C_{34}H_{63}O_4$, $[M-H]^+$ 535.4726, found 535.4725 ; **HRMS** calcd for $C_{34}H_{65}O_4$, $[M+H]^+$ 537.4883, found 537.4882 ; **HRMS** calcd for $C_{34}H_{64}O_4$ Na, $[M+Na]^+$ 559.4702, found 559.4704.

Compound 1b: Target 9-OAHPA (colorless oil, 63% yield)

Rf: 0.22 (cyclohexane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 301 K): 5.40-5.24 (m, 2H, olefin), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 2.31 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO}$, $H2_{HPA}$), 2.25 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.07-1.89 (m, 4H, $CH2_{allylic}$), 1.71-1.53 (m, 4H, CH2), 1.53-1.41 (m, 4H, CH2), 1.39-1.14 (m, 38H, CH2), 0.86 (t, J = 6.5 Hz, 3H, CH3), 0.85 (t, J = 7.0 Hz, 3H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 301 K): 179.55 (COOH), 173.86 (COOR), 130.14 (CH_{olefin}), 129.91 (CH_{olefin}), 74.20 (CHO), 34.89 ($CH2_{alphaCO\ oleyl}$), 34.31 (CH2), 34.11 ($CH2_{alphaCO\ HPA}$), 32.06 (CH2), 31.94 (CH2), 29.92 (CH2), 29.86 (CH2), 29.66 (CH2), 29.46 (CH2), 29.35 (CH2), 29.30 (CH2), 29.26 (CH2), 29.13 (CH2), 27.37 ($CH2_{allylic}$), 27.34 ($CH2_{allylic}$), 25.48 (CH2), 25.41 (CH2), 25.32 (CH2), 24.80 (CH2), 22.82 (CH2), 22.79 (CH2), 14.22 (CH3).

IR (υcm^{-1}): 3327-2481 (OH), 2924, 2855, 1733 (COOR), 1710 (COOH), 1465, 1181.

MS: (positive ESI) m/z: 537.49 $(M+H)^+$, 559.47 $(M+Na)^+$, 1073.97 $(M\ x2\ +H)^+$, 1095.95 $(M\ x2\ +Na)^+$.

HRMS calcd for $C_{34}H_{65}O_4$, $[M+H]^+$ 537.4883, found 537.4880.

Compound 1c: Target 10-OAHSA (colorless oil, 71% yield)

Rf: 0.11 (cyclohexane/AcOEt: 9/1); 0.42 (cyclohexane/AcOEt: 8/2) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 5.39-5.25 (m, 2H, olefin), 4.90-4.77 (m, 1H, CHO), 2.32 (t, J = 7.4 Hz, 2H, $CH2_{alphaCO\ HSA}$), 2.26 (t, J = 7.5 Hz, 2H, $CH2_{alphaCO\ oleyl}$), 2.06-1.92 (m, 4H, $CH2_{allylic}$), 1.68-1.53 (m, 4H, CH2), 1.53-1.41 (m, 4H, CH2), 1.39-1.13 (m, 42H, CH2), 0.92-0.79 (m, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 180.14 (COOH), 173.91 (COOR), 130.12 (CH_{olefin}), 129.89 (CH_{olefin}), 74.21 (CHO), 34.88 ($CH2_{alphaCO\ oleyl}$), 34.29 (CH2), 34.19 ($CH2_{alphaCO\ HSA}$), 32.05 (CH2), 32.05 (CH2), 29.91 (CH2), 29.85 (CH2), 29.68 (CH2), 29.60 (CH2), 29.47 (CH2), 29.39 (CH2), 29.35 (CH2), 29.30 (CH2), 29.17 (CH2), 27.36 ($CH2_{allylic}$), 27.32 ($CH2_{allylic}$), 25.45 (CH2), 25.31 (CH2), 24.79 (CH2), 22.82 (CH2), 14.26 (CH3).

IR (υcm^{-1}): 3407-2552 (OH), 2922, 2854, 1733 (COOR), 1709 (COOH), 1464, 1244, 1181.

MS: (negative ESI) m/z: 563.50 $(M-H)^-$, 1128.02 $(M\ x2\ -H)^-$.

HRMS calcd for $C_{36}H_{67}O_4$, $[M-H]^-$ 563.5039, found 563.5040.

Compound 1d: Target 5-PAHPA (colorless oil that solidified below 20°C, 75 % yield)

Rf: 0.11(cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 301 K): 4.87 (AcOEt, J = 5.9 Hz, 1H, CHO), 2.34 (t, J = 7.2 Hz, 2H, CH2CO$_{\text{HPA chain}}$), 2.26 (t, J = 7.5 Hz, 2H, CH2CO$_{\text{PA chain}}$), 1.74-1.42 (m, 8H, CH2), 1.38-1.13 (m, 42H, CH2), 0.86 (t, J = 6.7 Hz, 6H).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 301 K): 178.78 (CO$_{\text{HPA chain}}$), 173.85 (CO$_{\text{HPA chain}}$), 73.52 (CHO), 34.84 (CH2CO$_{\text{PA chain}}$),, 34.23 (CH2), 33.73 (CH2CO$_{\text{HPA chain}}$), 33.58 (CH2), 32.08 (CH2), 29.85 (CH2), 29.81 (CH2), 29.73 (CH2), 29.66 (CH2), 29.51 (CH2), 29.46 (CH2), 29.37 (CH2), 25.45 (CH2), 25.30 (CH2), 22.84 (CH2), 20.62 (CH2), 14.24 (CH3).

IR (υcm^{-1}): 3443-2472 (OH), 2922, 2853, 1734, 1710, 1459, 1411, 1378, 1243, 1170.

MS: (ESI) m/z: 509.46 (M-H)$^-$, 1019.92 (M-H dimer)$^-$.

HRMS calcd for $C_{32}H_{61}O_4$, [M-H$^+$] 509.4570, found 509.4572.

Compound 1e: Target 9-PAHPA (colorless oil that solidified in the fridge, 55 % yield, not optimized)

Rf: 0.11 (cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 301 K): 4.84 (AcOEt, J = 6.2 Hz, 1H, CHO), 2.32 (t, J = 7.5 Hz, 2H, CH2CO$_{\text{HPA chain}}$), 2.25 (t, J = 7.4 Hz, 2H, CH2CO $_{\text{PA chain}}$), 1.69-1.53 (m, 4H, CH2), 1.53-1.42 (m, 4H, CH2), 1.39-1.13 (m, 42H, CH2), 0.86 (t, J = 6.0 Hz, 3H, CH3), 0.85 (t, J = 6.0 Hz, 3H, CH3).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 301 K): 179.18 (COOR$_{\text{HPA chain}}$), 173.89 (COOR$_{\text{PA chain}}$), 74.18 (CHO), 34.91(CH2CO$_{\text{PA chain}}$), 34.32 (CH2), 34.30 (CH2), 34.01 (CH2CO$_{\text{HPA chain}}$), 32.08 (CH2), 31.95 (CH2), 29.84 (CH2), 29.82 (CH2), 29.78 (CH2), 29.66 (CH2), 29.51 (CH2), 29.46 (CH2), 29.36 (CH2), 29.28 (CH2), 29.13 (CH2), 25.48 (CH2), 25.41 (CH2), 25.35 (CH2), 24.79 (CH2), 22.84 (CH2), 22.79 (CH2), 14.23 (CH3).

IR (υcm^{-1}): 3448-2521 (OH), 2923, 2854, 1733, 1709, 1465, 1378, 1280, 1247, 1175, 1112.

MS: (ESI $_{\text{negative}}$) m/z: 509.46 (M-H)$^-$, 1019.92 (M-H dimer)$^-$.

HRMS calcd for $C_{32}H_{61}O_4$, [M-H$^+$] 509.4570, found 509.4565.

Compound 1f: Target 7-OAHPA (colorless oil, 80 % yield)

Rf: 0.33 (hexane/AcOEt: 8/2) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, CDCl$_3$, δppm, 294 K): 5.39-5.24 (m, 2H, olefin), 4.90-4.77 (m, 1H, CHO), 2.31 (t, J = 7.4 Hz, 2H, CH2$_{\text{alphaCO HPA}}$), 2.25 (t, J = 7.6 Hz, 2H, CH2$_{\text{alphaCO oleyl}}$), 2.07-1.90 (m, 4H, CH2$_{\text{allylic}}$), 1.69-1.53 (m, 4H, CH2), 1.53-1.40 (m, 4H, CH2), 1.38-1.12 (m, 38H, CH2), 0.85 (t, J = ca. 6.4 Hz, 3H, CH3). 0.84 (t, J = ca. 7.1 Hz, 3H, CH3).

^{13}C NMR (75 MHz, CDCl$_3$, δppm, 294 K): 180.09 (COOH), 173.88 (COOR), 130.09 (CH$_{\text{olefin}}$), 129.87 (CH$_{\text{olefin}}$), 74.02 (CHO), 34.82 (CH2$_{\text{alphaCO oleyl}}$), 34.28 (CH2), 34.07 (CH2$_{\text{alphaCO HPA}}$), 32.03 (CH2), 29.90 (CH2), 29.83 (CH2), 29.66 (CH2), 29.45 (CH2), 29.32 (CH2), 29.29 (CH2), 29.27 (CH2), 29.05 (CH2), 27.34 (CH2$_{\text{allylic}}$), 27.30 (CH2$_{\text{allylic}}$), 25.44 (CH2), 25.28 (CH2), 25.11 (CH2), 24.66 (CH2), 22.81 (CH2), 14.24 (CH3).

IR (υcm^{-1}): 3448-2507 (OH), 2923, 2853, 1732 (COOR), 1709 (COOH), 1464, 1242, 1174.

MS: (negative ESI) m/z: 535.47 (M-H), 1071.95 (M x2 -H)$^{-}$.

HRMS calcd for $C_{34}H_{63}O_4$, [M-H]$^{-}$ 535.4726, found 535.4725.

Compound 1g: Target 7-OAHSA (colorless oil, 79 % yield)

Rf: 0.17 (cyclohexane/AcOEt: 9/1) ; 0.45 (cyclohexane/AcOEt: 8/2) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 294 K): 5.439-5.25 (m, 2H, olefin), 4.84 (quint, J = 6.2 Hz, 1H, CHO), 2.32 (t, J = 7.5 Hz, 2H, CH2$_{alphaCO}$, H2$_{HSA}$), 2.25 (t, J = 7.5 Hz, 2H, CH2$_{alphaCO\ oleyl}$), 2.06-1.91 (m, 4H, CH2$_{allylic}$), 1.67-1.54 (m, 4H, CH2), 1.54-1.41 (m, 4H, CH2), 1.39-1.16 (m, 42H, CH2), 0.85 (br t, J = 6.5 Hz, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 294 K): 179.91 (COOH), 173.89 (COOR), 130.11 (CH$_{olefin}$), 129.88 (CH$_{olefin}$), 74.02 (CHO), 34.84 (CH2$_{alphaCO\ oleyl}$), 34.29 (CH2), 34.05 (CH2$_{alphaCO\ HSA}$), 32.06 (CH2), 29.91 (CH2), 29.84 (CH2), 29.79 (CH2), 29.72 (CH2), 29.69 (CH2), 29.68 (CH2), 29.49 (CH2), 29.47 (CH2), 29.34 (CH2), 29.30 (CH2), 29.06 (CH2), 27.35 (CH2$_{allylic}$), 27.31 (CH2$_{allylic}$), 25.45 (CH2), 25.29 (CH2), 25.12 (CH2), 24.67 (CH2), 22.83 (CH2), 14.26 (CH3).

IR (υcm^{-1}): 3548-2422 (OH), 2922, 2854, 1733 (COOR), 1709 (COOH), 1464, 1181.

MS: (negative ESI) m/z: 563.50 (M-H)$^{-}$, 1128.02 (M x2 -H)$^{-}$.

HRMS calcd for $C_{36}H_{67}O_4$, [M-H]$^{-}$ 563.5039, found 563.5042.

Compound 1h: Target 7-PAHPA (colorless oil that solidified below 20°C., 85 % yield)

Rf: 0.11 (cyclohexane/AcOEt: 9/1); No UV; Anisaldehyde

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 301 K): 4.84 (AcOEt, J = 6.2 Hz, 1H, CHO), 2.32 (t, J = 7.4 Hz, 2H, CH2CO$_{HPA\ chain}$), 2.25 (t, J = 7.5 Hz, 2H, CH2CO$_{PA\ chain}$), 1.69-1.55 (m, 4H, CH2), 1.55-1.42 (m, 4H, CH2), 1.38-1.13 (m , 42H, CH2), 0.86 (t, J = 6.6 Hz, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 301 K): 178.98 (COOR$_{HPA\ chain}$), 173.88 (COOR$_{HPA\ chain}$), 74.03 (CHO), 34.89 (CH2CO$_{PA\ chain}$), 34.33, 34.11, 33.90 CH2CO$_{HPA\ chain}$), 32.08 (CH2), 32.05 (CH2), 29.84 (CH2), 29.82 (CH2), 29.78 (CH2), 29.69 (CH2), 29.51 (CH2), 29.46 (CH2), 29.37 (CH2), 29.09 (CH2), 25.47 (CH2), 25.34 (CH2), 25.13 (CH2), 24.71 (CH2), 22.83 (CH2), 14.24 (CH3).

IR (υcm^{-1}): 3461-2387 (OH), 2923, 2854, 1733, 1710, 1465, 1278, 1240, 1176.

MS: (ESI) m/z: 509.46 (M-H)$^{-}$, 1019.92 (M-H dimer)$^{-}$.

HRMS calcd for $C_{32}H_{61}O_4$, [M-H^{+}] 509.4570, found 509.4572.

<u>Compound 1i: Target 7-PAHSA</u> (white solid, 80 % yield)

Rf: 0.17 (cyclohexane/AcOEt: 9/1) ; 0.40 (cyclohexane/AcOEt: 8/2) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 292 K): 10.75 (br s, 1H, OH), 4.84 (q, J = 6.1 Hz, 1H, CHO), 2.33 (t, J = 7.5 Hz, 2H, $CH2_{\text{alphaCO HSA}}$), 2.24 (t, J = 7.5 Hz, 2H, $CH2_{\text{alphaCO oleyl}}$), 1.67-1.60 (m, 4H, CH2), 1.60-1.39 (m, 4H, CH2), 1.38-1.11 (m, 46H, CH2), 0.85 (t, J = ca. 6.9 Hz, 6H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 292 K): 180.13 (COOH), 173.92 (COOR), 74.00 (CHO), 34.84 ($CH2_{\text{alphaCO oleyl}}$), 34.29 (CH2), 34.09 ($CH2_{\text{alphaCO HSA}}$), 32.06 (CH2), 29.83 (CH2), 29.80 (CH2), 29.71 (CH2), 29.68 (CH2), 29.66 (CH2), 29.50 (CH2), 29.44 (CH2), 29.33 (CH2), 29.05 (CH2), 25.44 (CH2), 25.30 (CH2), 25.11 (CH2), 24.67 (CH2), 22.83 (CH2), 14.25 (CH3).

IR (υcm^{-1}): 3351-2585 (OH), 2922, 2853, 1733 (COOR), 1709 (COOH), 1465, 1175.

MS: (negative ESI) m/z: 537.49 $(M-H)^-$, 1075.98 $(M\ x2\ -H)^-$.

HRMS calcd for $C_{34}H_{65}O_4$, $[M-H]^-$ 537.4883, found 537.4883.

<u>Compound 2: Target (12Z)- 10-OAHC18</u> (colorless oil, 80% yield)

Rf: 0.25 (pentane/AcOEt: 9/1) – Anisaldehyde – No UV.

^{1}H NMR (300 MHz, $CDCl_3$, δppm, 293 K): 5.51-5.39 (m, 1H, olefin H13), 5.38-5.22 (m, 3H, olefin oleyl and H12), 4.86 (quint, J = 6.2 Hz,1H, CHO), 2.32 (t, J = 7.4 Hz, 2H, $CH2_{\text{alphaCOOH}}$), 2.31-2.21 (m, 2H, H_{allylic} H11), 2.25 (t br, J = ca. 7.7 Hz, 2H, $CH2_{\text{alphaCO oleyl}}$), 2.08-1.89 (m, 6H, $CH2_{\text{allylic}}$), 1.69-1.42 (m, 6H, CH2), 1.40-1.14 (m, 38H, CH2), 0.86 (br t, J = ca. 7.0 Hz, 3H, CH3), 0.85 (t br, J = ca. 6.9 Hz, 3H, CH3).

^{13}C NMR (75 MHz, $CDCl_3$, δppm, 293 K): 179.06 (COOH), 173.78 (COOR), 132.84 ($CH_{\text{olefin,}}$ C13), 130.14 ($CH_{\text{olefin oleyl}}$), 129.90 ($CH_{\text{olefin oleyl}}$), 124.36 (CH_{olefin} C12), 73.80 (CHO), 34.83 ($CH2_{\text{alphaCO oleyl}}$), 33.99 ($CH2_{\text{alphaCOOH}}$), 33.76 (CH2), 32.13 ($CH2_{\text{allylic}}$), 32.06 (CH2), 31.67 (CH2), 29.92 (CH2), 29.86 (CH2), 29.68 (CH2), 29.54 (CH2), 29.47 (CH2), 29.35 (CH2), 29.30 (CH2), 29.16 (CH2), 27.48 ($CH2_{\text{allylic}}$), 27.37 ($CH2_{\text{allylic}}$), 27.33 ($CH2_{\text{allylic}}$), 25.51 (CH2), 25.26 (CH2), 24.80 (CH2), 22.84 (CH2), 22.73 (CH2), 14.27 (CH3), 14.22 (CH3).

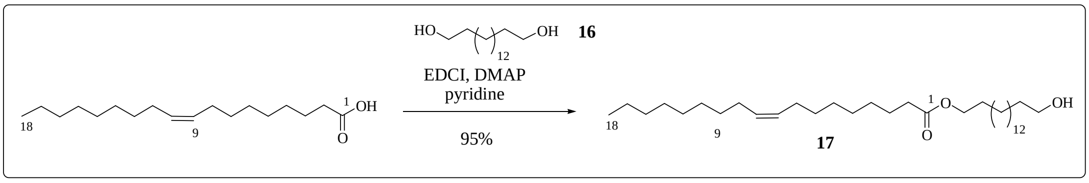
IR (υcm^{-1}): 3362-2514 (OH), 2924, 2854, 1733 (COOR), 1709 (COOH), 1464, 1242, 1176.

MS: (negative ESI) m/z: 561.49 $(M-H)^-$.

HRMS calcd for $C_{36}H_{67}O_4$, $[M-H]^-$ 561.4883, found 561.4887.

C) Synthesis of the linear FAHFAs: omega-OAHPA (target 3)

C1) Mono-esterification of 1,16-hexadecadiol 16



The 1,16 diol **4** (605.85 mg, 2.34 mmol, 4.0 eq.) was dissolved in anhydrous pyridine (6 mL) at 30-35°C. Upon cooling to rt, EDCI (123.58 mg, 0.64 mmol, 1.1 eq.), DMAP (93.08 mg, 0.75 mmol, 1.3 eq.) and then oleic acid **3** (186 µL, 0.59 mmol, 1.0 eq.) were added under a flux of argon. The reaction mixture was stirred for 60 h at 25°C. The reaction mixture was diluted with 20 mL of Et_2O, separated and washed with 5 % $CuSO_4$ aqueous solution (3 x 2 mL) then distilled water (2 x 2 mL). The aqueous phase was extracted twice with Et_2O (20 mL) and the combined organic layers were dried over $MgSO_4$, filtered and evaporated to dryness under vacuum. Purification by flash chromatography on silica gel (heptane/AcOEt: 100/0 to 75/25) afforded 292 mg (95 %) of the title alcohol **5** as a white powder. A second purification was sometimes required to remove traces of oleic acid (92 % yield).

Rf: 0.55 (cyclohexane/AcOEt: 7/3), 0.30 (cyclohexane/AcOEt: 9/1) –Anisaldehyde – No UV.

^{1}H NMR (500 MHz, CDCl3, δppm, 294 K): 5.39-5.27 (m, 2H, olefin), 4.03 (t, J = 6.7 Hz, 2H, CH2OCO), 3.62 (dt, J = 6.6 Hz and 1.6 Hz, 2H, CH2OH), 2.26 (t, J = 7.5 Hz, 2H, CH2CO), 2.07-1.90 (m, 4H, CH2 allylic), 1.67-1.47 (m, 6H, CH2C), 1.39-1.18 (m, 44H, CH2C), 0.86 (t, J = 6.7 Hz, 3H, CH3).

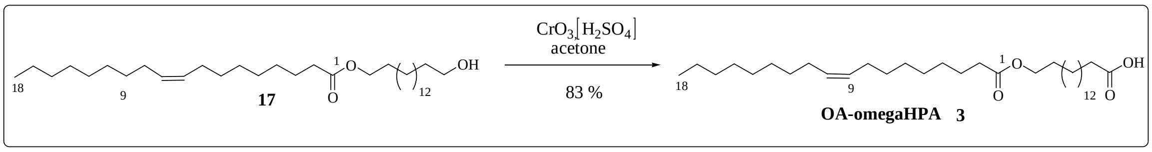
^{13}C NMR (125 MHz, CDCl3, δppm, 294 K): 174.15 (COOR), 130.08 (C olefin), 129.84 (C olefin), 64.52 (CH2OR), 63.13 (CH2OH), 34.49 (CH2 alphaCO), 32.88 (CH2), 32.01 (CH2), 29.86 (CH2), 29.76 (CH2), 29.63 (CH2), 29.55 (CH2), 29.43 (CH2), 29.36 (CH2), 29.23 (CH2), 28.74 (CH2), 27.31 (CH2), 27.26 (CH2), 26.03 (CH2), 25.85 (CH2), 25.11 (CH2), 22.79 (CH2), 14.22 (CH3).

IR (υcm^{-1}): 3523-3240 (OH), 2919, 2850, 1726 (COOR), 1469, 1178.

MS: (ESI) m/z: 523.51 $(M+H)^+$, 1046.01 $(M+H \text{ dimer})^+$.

HRMS calcd for $C_{34}H_{67}O_3$, $[M+H^+]$ 523.5090, found 523.5094.

C2) Jones's oxidation of alcohols 17 into target 3 (OA-omegaHPA)



The alcohol **5** (101.34 mg, 0.19 mmol, 1.0 eq.) was dissolved in acetone (2.7 mL) at 30-35°C. Upon cooling to 17.5 °C, the Jones reagent (134 µL, 0.29 mmol, 1.5 eq.) was added dropwise over 5 min. The reaction mixture turned greenish. After 30 min at 17.5°C, the mixture was cooled to 0°C and *iso*-propanol (100 µL, large excess) was added. The reaction mixture was allowed to stir for an additional 10 min. Subsequently, the reaction mixture was filtered and the chromium salts were washed with about 15 mL of AcOEt. The organic layer was separated and washed with a saturated NaCl aqueous solution (3 x 0.5 mL). The combined aqueous phases were extracted with AcOEt (2 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and evaporated to dryness under vacuum. Purification by flash chromatography on silica gel (hexane/AcOEt: 98/2 to 85/15) provided the desired acid **OA-omegaHPA 3** (85 mg, 83 %) as a white powder.

Rf: 0.37 (cyclohexane/AcOEt: 8/2), 0.19 (cyclohexane/AcOEt: 9/1) –Anisaldehyde – No UV.

^{1}H NMR (300 MHz, CDCl3, δppm, 303K): 5.39-5.24 (m, 2H, olefin), 4.03 (t, J = 6.7 Hz, 2H, CH2O), 2.32 (t, J = 7.5 Hz, 2H, CH2COOH), 2.26 (t, J = 7.6 Hz, 2H, CH2COOR), 2.08-1.90 (m, 4H, CH2 allylic), 1.70-1.50 (m, 6H, CH2), 1.61-1.15 (m, 42H, CH2), 0.86 (t, J = 6.7 Hz, 3H, CH3).

^{13}C NMR (125 MHz, CDCl3, δppm, 294 K): 179.67 (COOR), 174.22 (COOH), 130.13 (C olefin), 129.90 (C olefin), 64.59 (CH2OR), 34.55 (CH2 alphaCOOR), 34.10 (CH2 alphaCOOH), 32.05 (CH2), 29.91 (CH2), 29.83 (CH2), 29.78 (CH2), 29.73 (CH2), 29.68 (CH2), 29.58 (CH2), 29.47 (CH2), 29.40 (CH2), 29.32 (CH2), 29.28 (CH2), 29.21 (CH2), 28.79 (CH2), 27.36 (CH2), 27.31 (CH2), 26.08 (CH2), 25.16 (CH2), 22.83 (CH2), 14.27 (CH3).

IR (υcm^{-1}) : 3293-2445 (large – OH), 2916, 2849, 1728 (COOR), 1703 (COOH), 1464, 1300, 1249, 1211, 1181.

MS: (ESI) m/z: 537.49 (M+H)$^+$, 519.48 (M-H2O+H)$^+$.

HRMS calcd for $C_{34}H_{65}O_4$, [M+H$^+$] 537.4883, found 537.4882.

D) LC-MS/MS analysis

High performance liquid chromatography (HPLC) was performed using an Agilent 1290 Infinity system equipped with a thermostated autosampler, a binary pump and a column oven (temperature at 25°C).Three different columns (2.1 mm diameter) were used with two different systems of elution (Table S1).

Table S1: liquid chromatographic conditions.

Conditions	Column	Mobile phases			Isocratic mode (%B)
			A	B	
1	**C18, 10 cm** (1.72 µm) Acquity UPLC BEH, Waters)	1	H_2O/MeOH: 60/40, (v/v), 0.1% formic acid, 10 mM ammonium formate	iPrOH/MeOH: 90/10 (v/v), 0.1% formic acid, 10 mM ammonium formate	60
2	**C30, 5 cm** (2.6 µm) Accucore, Thermo Fisher)				60
3	**C30, 15 cm** (2.6 µm) Accucore, Thermo Fisher)				60
4	**C30, 15 cm** (2.6 µm) Accucore, Thermo Fisher)	2	H_2O, 0.01% NH_4OH, 5 mM ammonium acetate	MeOH, 0.01% NH_4OH, 5 mM ammonium acetate	93

The flow rate was set at 0.4 mL/min. The autosampler was fixed at 5°C. The injection volume was 10 µL per analysis. The HPLC system was coupled on-line to an Agilent 6460 triple quadrupole MS (Agilent Technologies, USA) equipped with electrospray ionization (ESI). The ESI was performed in negative ion mode. The MS source parameters were set as follows: source temperature 350ºC, nebulizer gas (nitrogen) flow rate 10 L/min, sheath gas temperature 400ºC, sheath gas (nitrogen) flow rate 12 L/min and the spray voltage adjusted to - 3500 V. The dwell time used was 40 ms. The analysis was performed in Multiple Reaction Monitoring (MRM) detection mode using nitrogen as the collision gas. The MRM spectra of each compound (Table 1 in the manuscript) were pre-determined by MS/MS analysis. Peak detection, integration and quantitative analysis were performed by Mass Hunter Quantitative analysis software (Agilent Technologies, USA). Concentration of the analytes was calculated from the calibration curves.

Standard preparation for linearity

Standard solutions were prepared in MeOH at the following concentrations: 0.48, 0.97, 1.95, 3.90, 7.81, 15.62, 31.25, 62.5, 125 and 250 ng/mL for all primary standards. The concentration of the deuterated internal standards (ISTD) used 12.5 ng taken from 250 ng/mL stock solution. Calibration curves were calculated from the area ratio of the analyte and the internal standard. The linearity of the method was assessed for each of our 14 molecules by evaluating the correlation coefficient (Table S2). The limit of detection (LOD) and limit of quantification (LOQ) were evaluated and reported in Table S2.

Table S2. Linear equation, correlation coefficient (R^2), limit of quantification (LOQ), limit of detection (LOD) and yield of extraction of several synthetic or commercially available FAHFAs.

Compound	**Linear regression**	**R^2**	**LOQ (ng/mL)**	**LOD (ng/mL)**	**Yield of extraction (%)**
9-PAHPA (**1e**)	Y= 0.026970x-0.020709	0.9919	7	1.5	73± 8
7-PAHPA (**1h**)	Y=0.031561x-0.028737	0.9832	4	1.8	72 ± 10
5-PAHPA (**1d**)	Y=0.033336x-0.029281	0.9903	7	1.5	73 ± 10
9-POHSA	Y=0.006632x-0.007415	0.9911	4	3.8	71 ± 9
9-OAHPA (**1b**)	Y= 0.042809x-0.040156	0.9917	3	1.4	73 ± 8
7-OAHPA (**1f**)	Y=0.036377x-0.035299	0.9865	7	1.5	70 ± 9
5-OAHPA (**1a**)	Y=0.095550x-0.090142	0.9914	7	1.7	73 ± 9
9-PAHSA	Y=0.107934x-0.080585	0.9940	2	1.3	71 ± 8
7-PAHSA (**1i**)	Y=0.026234x-0.019229	0.9883	4	1.6	88 ± 9
9-PAHSA-d_{31}	-	-	-	-	65 ± 5
13-OAHSA	Y=0.033266x-0.023414	0.9890	7	1.8	68 ± 9
10-OAHSA (**1c**)	Y=0.242764x-0.218792	0.9923	2	1.5	69 ± 8
9-OAHSA	Y=0.242764x-0.218792	0.9923	2	1.5	69 ± 9
7-OAHSA (**1g**)	Y=0.047934x-0.060345	0.9941	4	1.9	59 ± 9
OAωHPA (**3**)	Y=0.095550x-0.090142	0.9914	7	1.7	73 ± 8

E) protocol for FAHFA extraction from plasma

Healthy human plasma were collected, pooled and stored at -80°C. For the extraction optimization, plasma (150 µL) were spiked in triplicat with 12.5 ng of 9-PAHSA-d_{31} and with a mixture of 14 FAHFAs. Then citric acid buffer was added in order to have a final volume of 3 mL. A volume of 3.5 mL of MeOH and 3.5 mL of CH_2Cl_2 were added followed by 100 µL of sodium chloride to prevent the interphase emulsion. The resulting mixture was vortexed and centrifuged at 1,500 g for 6 min at 4°C. The upper phase was thrown and the lower phase was collected. All the extractions were performed at 4°C. After concentration under nitrogen gas, the samples were re-dissolved with 150 µL of CH_2Cl_2. Thereafter, the samples were cleaned and extracted by SPE (3mL, 500 mg, cartridge Chromabond). Briefly, the wells were conditioned with 4 mL of CH_2Cl_2. After loading the samples, the wells were washed with CH_2Cl_2 (2 mL) in order to elute triglycerides. The FAHFAs were eluted with MeOH/CH_2Cl_2: 10/90 (v/v, 2 mL). After evaporation with a flux of nitrogen gas, the samples were dissolved in 25 µL of MeOH, and 10 µL were injected to LC-MS/MS analysis.