

Supporting Information

Novel 3-Acetoxy Fatty Acid Isoprenyl Esters from Androconia of the Ithomiine Butterfly *Ithomia salapia*

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1. Photos



Figure S1. *Ithomia salapia derasa* (left) and *I. s. aquinia* (right). The left side of the butterflies shows the dorsal sides against a dark background to highlight transparency, the right shows the ventral sides. Photos by Céline Houssin [S1].

2. Mass spectrometry

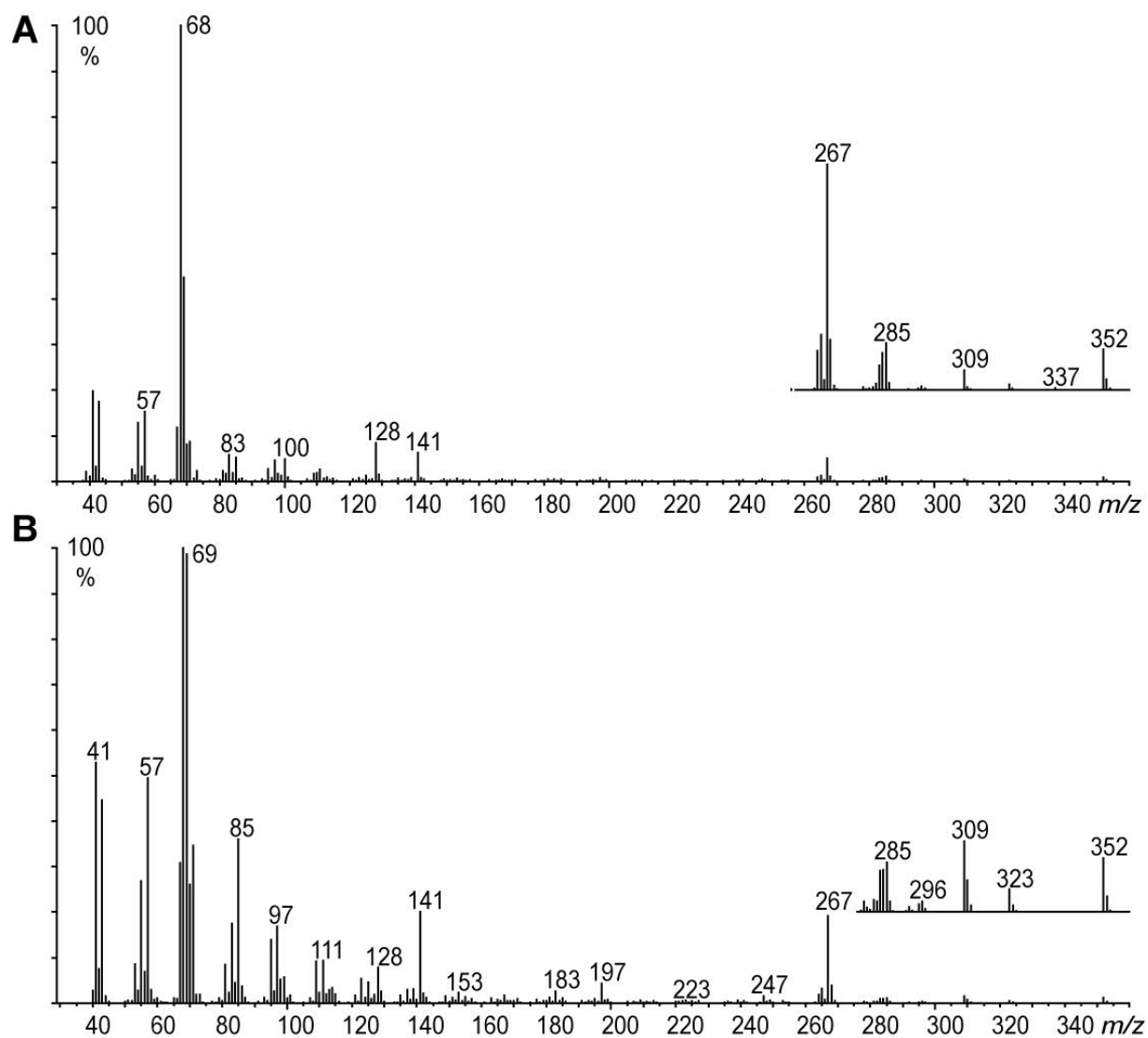


Figure S2. Mass spectra of 3-methyl-3-butenyl octadecanoate (A) and 3-methyl-2-butenyl octadecanoate (B).

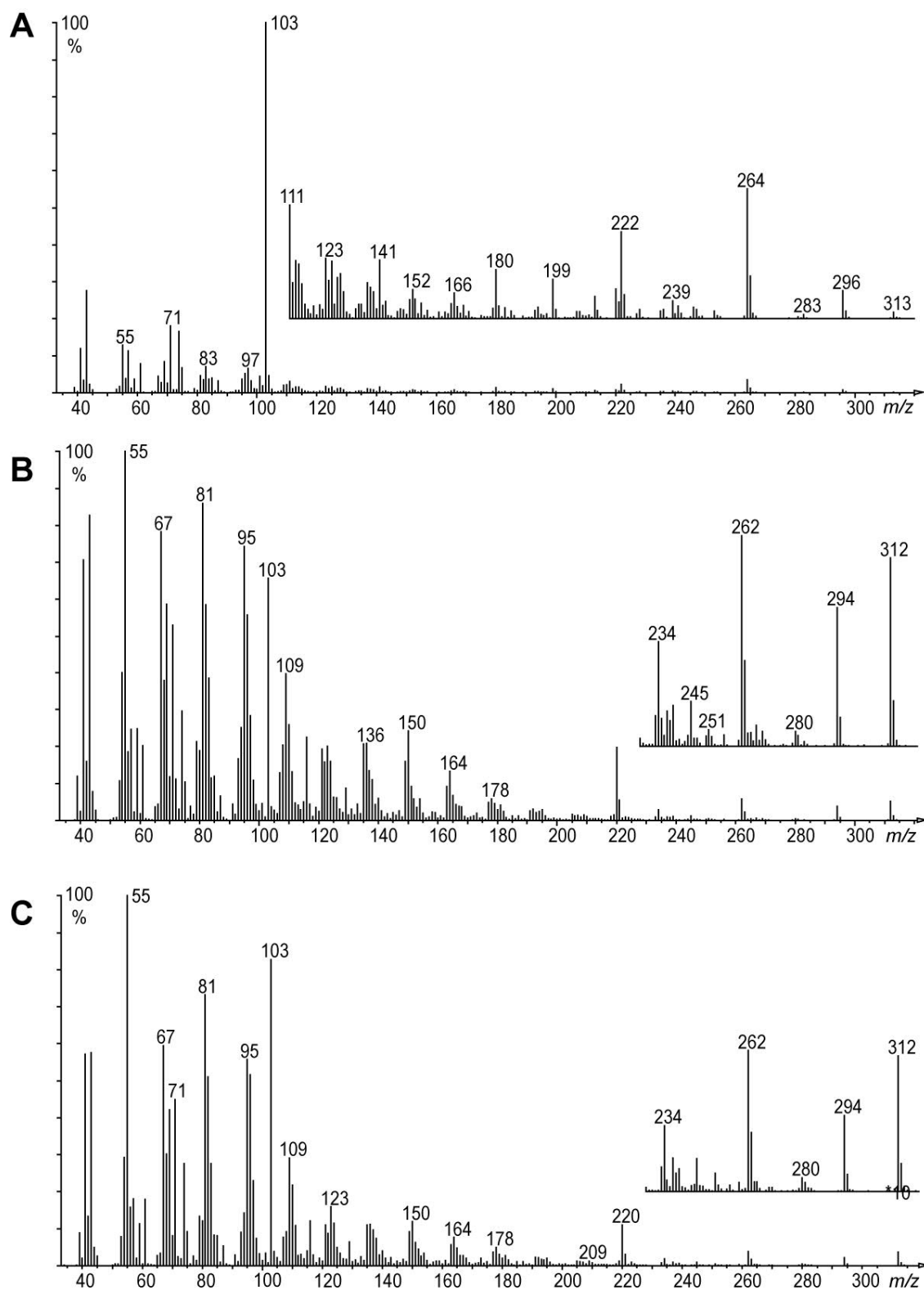


Figure S3. Mass spectra of methyl 3-hydroxyoctadecanoate (A), and methyl 3-hydroxyoctadecenoates (B, C). The correct assignment of the double bond position is not possible from the spectra. Nevertheless, the later eluting one usually has the double bond closer to the ω -end of the compound on apolar gas chromatographic phases, indicating that B likely represents methyl (*Z*)-3-hydroxy-11-octadecenoate, while C might be (*Z*)-3-hydroxy-13-octadecenoate. The more abundant ion m/z 103 in C might also indicate a larger distance between double-bond and OH-group compared to B, leading to less interaction between the two preferentially ionized π -bonds in the compounds.

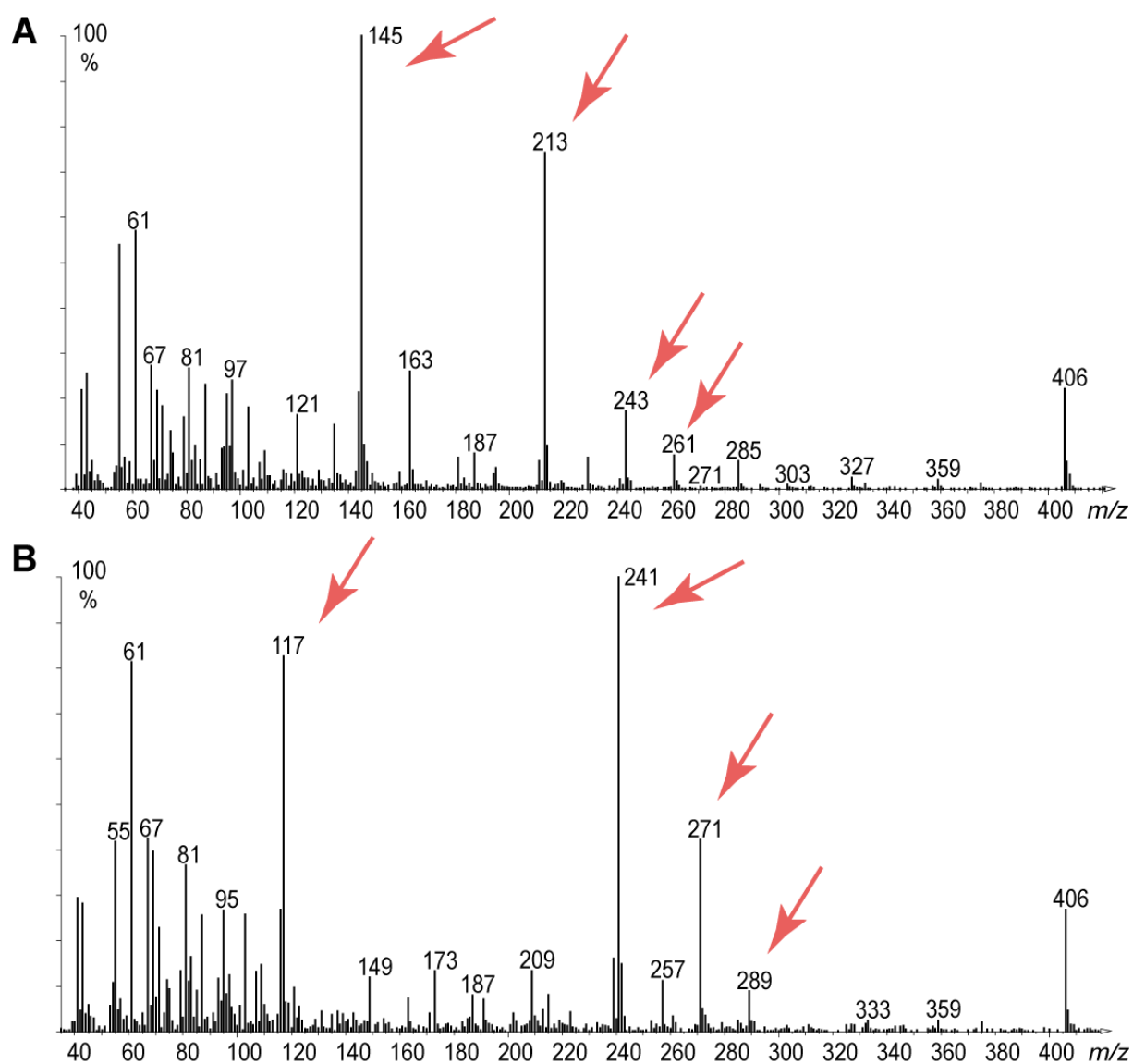


Figure S4. Mass spectra of DMS adducts of methyl 3-hydroxy-11-octadecenoate (A) and of methyl 3-hydroxy-13-octadecenoate (B). Red arrows indicate characteristic ions used for localization of the double bond. See main text for explanation.

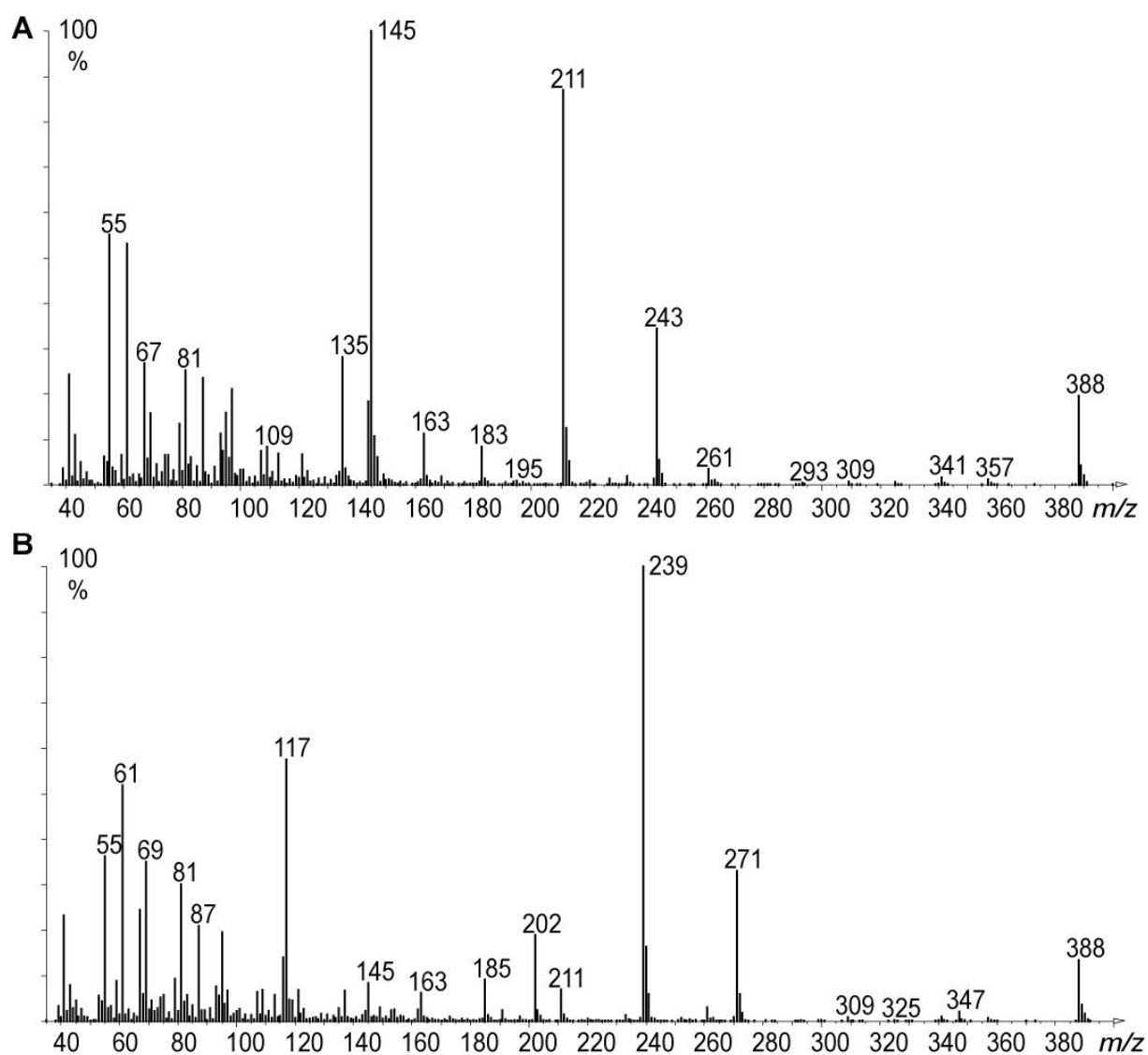


Figure S5. Mass spectra of DMSO adducts of methyl 2,11-octadecadienoate (A) and methyl 2,13-octadecadienoate (B). Spectrum A is similar to that of methyl 11-octadecenoate (Table S1), but shows 2 amu lower ions, m/z 211, 243 and 388. This indicates a double bond at C-2, because this position is the only one that does not react with DMSO due to its lower reactivity because of the electron-withdrawing conjugated ester group.

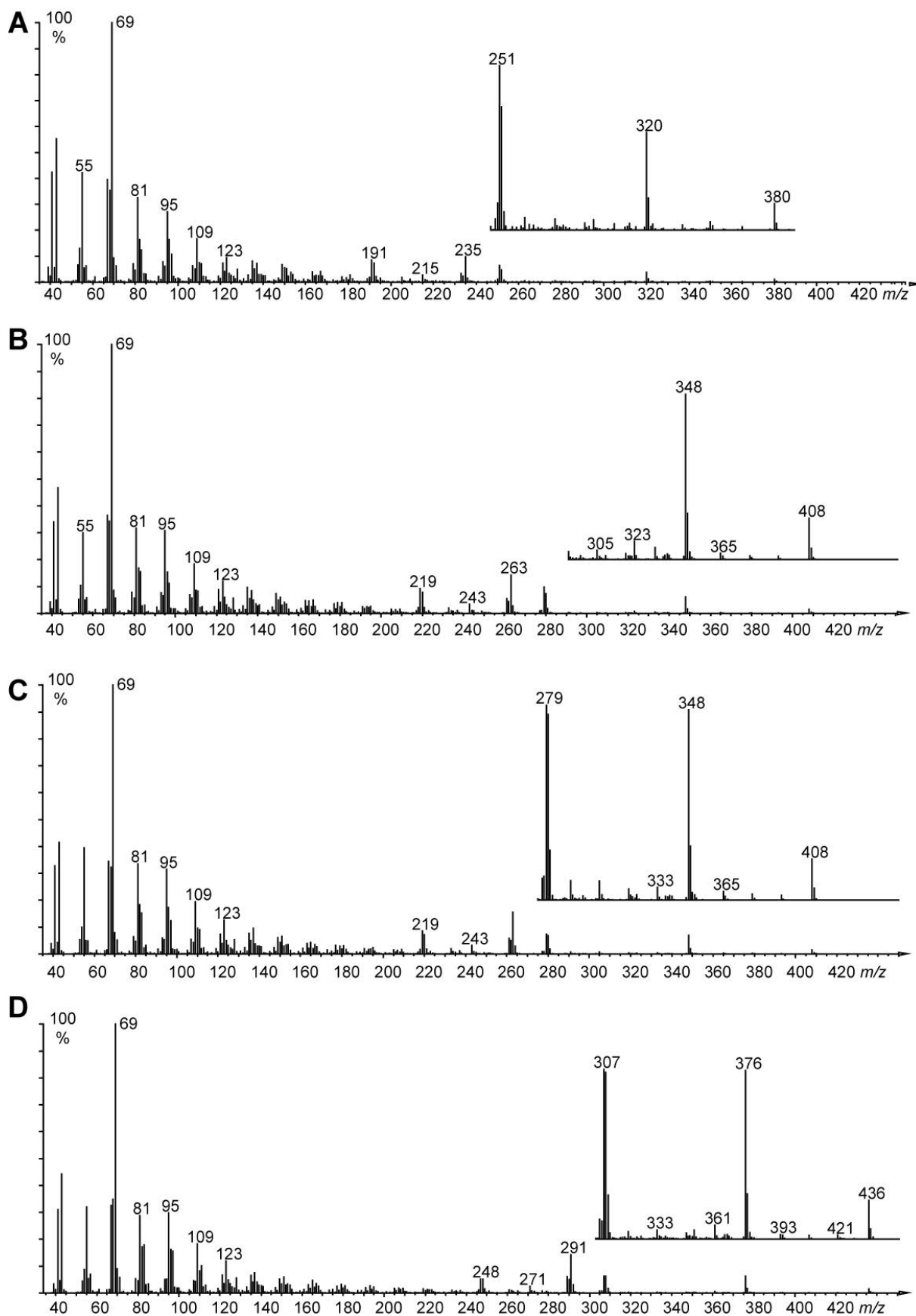


Figure S6. Mass spectra of isoprenyl 3-acetyloxy-11-hexadecenoate (A), isoprenyl 3-acetyloxy-11-octadecenoate (B), isoprenyl 3-acetyloxy-13-octadecenoate (C), and isoprenyl 3-acetyloxyeicosenoate (D) from extracts of androconia of *Ithomia salapia*.

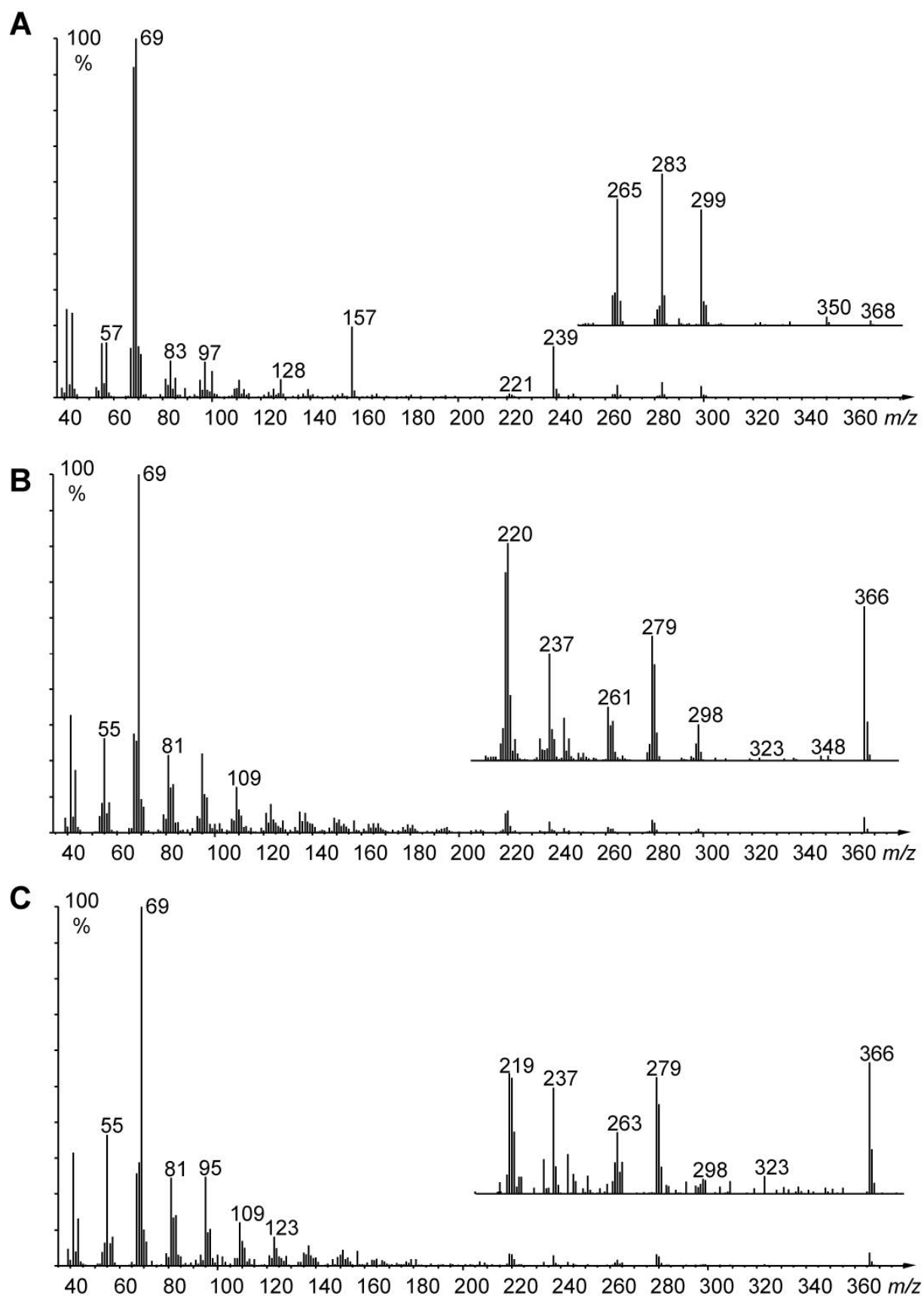
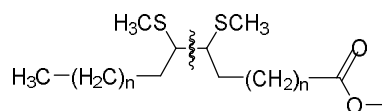


Figure S7. Mass spectra of isoprenyl 3-hydroxyoctadecanoate (A), isoprenyl 3-hydroxy-11-octadecenoate (B), and isoprenyl 3-hydroxy-13-octadecenoate (C) from extracts of androconia of *Ithomia salapia*.

Table S1. Localization of double bonds in DMDS-adducts of methyl esters obtained by transesterification from isoprenyl esters. Characteristic ions.



	$[\text{CH}_3\text{S}(\text{CH}_2)_n\text{CH}_3]^+$	$[\text{CH}_3\text{S}(\text{CH}_2)_n\text{COOCH}_3]^+$	$[\text{CH}_3\text{S}(\text{CH}_2)_n\text{COOCH}_3-\text{CH}_3\text{OH}]^+$	M^+
Methyl (Z)-9-hexadecenoate	145	217	185	362
Methyl (Z)-11-hexadecenoate	117	245	213	362
Methyl (Z)-9-octadecenoate	173	217	185	390
Methyl (Z)-11-octadecenoate	145	245	213	390
Methyl (Z)-13-eicosenoate	145	273	241	418

3. Experimental part

3.1 Samples

Male butterflies of *Ithomia salapia aquinia* and *I. s. derasa* were collected in north-eastern Peru from 2011-2012 (sampling information in Table S2 below). The androconial hairpencils were dissected and extracted in ultrapure dichloromethane shortly after capture. Samples were kept at -20°C until analysis.

Table S2. Sampling information including date and location of collection, GPS positions and altitude.

Sample	Sub-species	Date of collection	Location	GPS	Altitude
LdeS11-34	<i>I. s. aquinia</i>	30 January 2011	Km5 Shapaja - Chazuta	6°35'424"S ; 76°13'394"W	200m
LdeS11-81	<i>I. s. derasa</i>	2 February 2011	Puente Serranoyacu	5°40'316"S ; 77°40'287"W	1200m
LdeS11-82	<i>I. s. derasa</i>	2 February 2011	Puente Serranoyacu	5°40'316"S ; 77°40'287"W	1200m
LdeS11-270	<i>I. s. derasa</i>	9 February 2011	Km41.5 Tarapoto - Yurimaguas	6°24'308"S ; 76°15'903"W	400m
LdeS11-272	<i>I. s. aquinia</i>	9 February 2011	Km41.5 Tarapoto - Yurimaguas	6°24'308"S ; 76°15'903"W	400m
LdeS11-273	<i>I. s. aquinia</i>	9 February 2011	Km41.5 Tarapoto - Yurimaguas	6°24'308"S ; 76°15'903"W	400m
LdeS11-455	<i>I. s. aquinia</i>	10 March 2011	Km24 Yurimaguas - Tarapoto (Km6 - Micaela Bastidas)	5°56'660"S ; 76°14'669"W	180m
LdeS11-1293	<i>I. s. derasa</i>	26 November 2011	Puente Aguas Verdes	5°41'077"S ; 77°39'487"W	1100m
LdeS11-1294	<i>I. s. derasa</i>	26 November 2011	Puente Aguas Verdes	5°41'077"S ; 77°39'487"W	1100m
LdeS11-1758	<i>I. s. aquinia</i>	21 January 2012	Km24 Yurimaguas - Tarapoto (Km6 - Micaela Bastidas)	5°56'660"S ; 76°14'669"W	180m

Table S3. Relative proportions of compounds occurring at least two times in five samples of androconia of male *I. s. aquinia*. Column heads show internal sample code number and sample collection number (see Table S2).

	ISA-1 LDES11- 273	ISA-2 LDES11- 455	ISA-3 LDeS11- 1758	ISA-5 LdeS-11- 34	ISA-6 LdeS11- 472
Ithomiolide A (2)	2.64	0.00	0.00	0.00	1.91
Hexadecenoic acid	5.76	0.00	2.32	0.55	0.00
Hexadecanoic acid	12.88	0.00	2.38	0.28	0.00
Octadecenoic acid	7.88	0.00	1.02	0.00	0.00
Isoprenyl 9-hexadecenoate	0.01	0.33	0.01	0.00	0.00
Isoprenyl 11-hexadecenoate	0.32	1.28	0.51	1.92	2.02
Isoprenol hexadecanoate	0.11	2.24	0.32	1.30	0.82
Tricosane	0.11	0.04	0.01	0.00	0.00
11-Methyltricosane	0.89	0.02	0.11	0.02	0.10
Isoprenyl octadecadienoate	0.00	2.23	0.01	0.00	0.00
Isoprenyl 9-octadecenoate	0.01	12.19	0.67	0.67	0.71
Isoprenyl 11-octadecenoate	0.33	0.29	0.01	0.01	0.00
Isoprenyl octadecanoate	0.00	0.07	0.02	0.01	0.00
Isoprenyl 3-acetoxy-11-hexadecenoate	0.42	0.07	0.34	0.03	0.01
Isoprenyl 3-acetoxyhexadecanoate	4.93	1.98	2.33	0.85	0.76
Pentacosane	0.10	0.02	0.01	0.00	0.00
Isoprenyl (2 <i>E</i> ,11 <i>Z</i>)-2,11-octadecadienoate	0.44	0.00	0.16	0.89	0.49
Isoprenyl (2 <i>E</i> ,11 <i>Z</i>)-2,13-octadecadienoate	0.30	0.00	0.13	0.30	0.38
Isoprenyl (<i>E</i>)-2-octadecenoate	0.48	0.00	0.18	0.56	0.35
11-and 13-Methylpentacosane	0.03	0.00	0.01	0.00	0.00
Isoprenyl 3-hydroxy-13-octadecenoate	0.00	0.00	0.03	0.05	0.00
Isoprenyl (<i>Z</i>)-3-acetoxy-11-octadecenoate	14.58	41.42	35.50	40.69	35.83
Isoprenyl (<i>Z</i>)-3-acetoxy-13-octadecenoate	2.38	11.62	21.70	22.16	30.43
Isoprenyl 3-acetoxyoctadecanoate	43.73	26.16	31.13	29.56	26.20
Isoprenyl 3-acetoxy-13-eicosenoate	1.20	0.04	0.98	0.10	0.01
Isoprenyl 3-acetoxyeicosanoate	0.52	0.00	0.18	0.01	0.00

Table S4. Relative proportions of compounds occurring at least two times in five samples of androconia of male *I. s. derasa*. Column heads show internal sample code number and sample collection number (see Table S2).

	ISD-1 LdeS11-81	ISD-2 LdeS11-82	ISD-3 LdeS11- 1294	ISD-4 LdeS11- 1293	ISD-6 LdeS11- 270
β-Elemene	0.01	0.19	0.00	0.02	0.08
Elemol/Hedycaryol isomer	0.03	0.06	0.00	0.00	0.02
α-Elemol (4)	1.85	2.88	0.11	0.49	1.74
Elemol/Hedycaryol isomer	0.01	0.02	0.00	0.01	0.00
Hexadecanoic acid	0.25	0.03	0.02	0.00	0.00
7-Heneicosene	13.97	0.15	4.25	0.00	0.00
Heneicosane	0.54	0.02	0.10	0.00	0.00
Octadecenoic acid	3.69	2.20	1.71	0.62	0.00
Ticosane	0.44	0.07	0.14	0.01	0.04
11-Methyltricosane	4.04	0.60	1.30	0.00	0.06
Eicosenoic acid	0.96	0.08	0.08	0.00	0.00
Isoprenyl octadecadienoate	0.01	0.30	0.00	0.02	0.15
Isoprenyl 9-octadecenoate	0.76	4.81	0.36	4.90	8.27
Isoprenyl 11-octadecenoate	0.00	0.00	0.00	0.01	0.02
Isoprenyl octadecanoate	0.03	0.32	0.01	0.03	0.01
Isoprenyl 3-acetoxy-11-hexadecenoate	0.44	0.38	0.40	0.10	0.10
Isoprenyl 3-acetoxyhexadecanoate	1.32	0.92	0.99	0.51	0.30
Pentacosane	0.12	0.03	0.03	0.01	0.13
Isoprenyl (2 <i>E</i> ,11 <i>Z</i>)-2,11-octadecadienoate	12.63	4.60	0.14	0.00	3.31
Isoprenyl (2 <i>E</i> ,13 <i>Z</i>)-2,13-octadecadienoate	0.28	0.92	0.01	0.00	0.33
Isoprenyl 2-octadecenoate	0.55	1.96	0.05	0.04	0.88
11- and 13-Methylpentacosane	0.02	0.03	0.05	0.00	0.00
Isoprenyl 3-hydroxy-11-octadecenoate	1.10	5.02	4.22	4.11	2.83
Isoprenyl 3-hydroxy-13-octadecenoate	0.08	0.24	0.40	0.08	0.07
Isoprenyl 3-hydroxyoctadecanoate	0.98	1.64	2.41	1.32	1.31
Isoprenyl (<i>Z</i>)-3-acetoxy-11-octadecenoate	22.72	44.66	37.34	45.28	44.78
Isoprenyl (<i>Z</i>)-3-acetoxy-13-octadecenoate	3.87	5.01	14.67	9.73	11.37
Isoprenyl 3-acetoxyoctadecanoate	22.32	16.01	25.44	25.24	19.87
Isoprenyl 3-hydroxy-13-eicosenoate	0.00	0.00	0.00	0.45	0.10
Isoprenyl 3-acetoxy-13-eicosenoate	6.65	6.77	5.67	6.81	4.25
Isoprenyl 3-acetoxyeicosanoate	0.35	0.12	0.09	0.17	0.02

3.2 Experimental conditions

Commercially available chemicals were used without further purification when not stated otherwise. All reactions, in which moisture and air-sensitive compounds were used, were carried out in glass ware dried with heating under a nitrogen atmosphere. Solvents for chromatography were distilled before use. Solvents were dried by conventional methods if needed. ^1H -NMR and ^{13}C -NMR spectra were recorded with the instruments DPX-200 (200 MHz for ^1H and 50 MHz for ^{13}C) and DRX-400 (400 MHz for ^1H and 100 MHz for ^{13}C) from Bruker. Tetramethylsilane was used as internal standard. The multiplicities of the protons are indicated by singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), sextet (sext) or multiplet (m). The multiplicities of the carbon atoms are given equivalently as quaternary (s), tertiary (d), secondary (t) or primary (q). Wide signals are indicated by b before the multiplicity.

Gas chromatography investigations were performed with an HP 7820A with FID detector and an ALS 7683 autosampler (Agilent). A fused silica capillary column HP-5 MS (Agilent, 30 m, 0.25 mm, 0.25 μm film thickness) was used. Hydrogen was used as carrier gas. GC/MS investigations of synthetic samples were performed with a HP 6890/MSD 5973 combination (Agilent) in EI mode (70 eV). For the chromatographic separation a fused silica capillary column BPX-5 (SGE Inc., 25 m, 0.22 mm OD; 0.25 μm film thickness) was used. Helium was used as the carrier gas. High-resolution MS data were obtained with an Agilent 6890 gas chromatograph coupled to a JMS-T100GC (GC AccuTOF, JEOL) equipped with a ZB5-MS (Phenomenex, 30 m \times 0.25 mm i.d. \times 0.25 μm) column.

Natural extracts were analyzed using either an HP 7890A/MSD 5975 combination and an ALS 7683 Autosampler (Agilent) or a HP 7890B/MSD 5977 combination (Agilent) and an MPS auto-sampler (Gerstel) in EI mode (70 eV). For gas chromatographic separations a fused silica capillary column HP5-MS (Agilent, 30 m, 0.25 mm OD, 0.25 μm film thickness) was used. Helium was used as carrier gas. The samples were concentrated to approx. 20 μL in a nitrogen stream before injection. The starting temperature of the oven was 50 $^\circ\text{C}$, which was maintained for 5 minutes. The oven was then heated to 320 $^\circ\text{C}$ at 5 $^\circ\text{C}/\text{minute}$ and the temperature was maintained for another 10 minutes.

Enantiomer determination was performed on a chiral Hydrodex β -6TBDM type (Macherey & Nagel, 25 m, 0.25 mm OD, 0.25 μm film thickness) GC phase using the combination HP 7890B/MSD 5977 from Agilent and an MPS Autosampler from Gerstel. The mass spectrometer in EI-mode at 70 eV. Helium was used as carrier gas. The starting temperature was 160 $^\circ\text{C}$, which was maintained for 360 minutes. Afterwards the temperature was heated to 320 $^\circ\text{C}$ at 25 $^\circ\text{C}/\text{min}$.

IR spectra were recorded with the Tensor 27 instrument from Bruker using the diamond ATR technique. GC/DD-IR analyses was performed using a Dani Instruments DiscovIR IR detector coupled to an Agilent Technologies 7890B gas chromatograph. Gas chromatographic separations were performed with a fused silica capillary column HP5-MS (Agilent, 30 m, 0.25 mm OD, 0.25 μm film thickness). Helium was used as carrier gas and residual water was removed using a conventional in-line water trap for gases. The positions of the absorption bands are indicated as wave number in cm^{-1} . The

intensities are marked with s (strong), m (medium) and w (weak), broadened bands are additionally marked with br (broad).

UV/VIS-Spectra were measured with Cary 100 Bio spectrometer (Varian). The wavelength λ of the absorption maxima are listed in nm and the extinction ϵ in $\text{cm}^2 \cdot \text{mmol}^{-1}$.

Column chromatographic purification of the products was carried out on silica gel (Fluka, silica gel 60, particle size 0.040-0.063 mm, mesh 230-440 ASTM). Various solvent mixtures of pentane and diethyl ether were used as indicated. Thin layer chromatography was performed with silica gel foil Polygram SIL G/UV254 (Macherey & Nagel). Detection was performed by UV (254 nm), potassium permanganate immersion, vanillin immersion, molybdato-phosphoric acid immersion or by Vaughn's reagent.

The rotation value of optically active compounds was determined with a Propol Digital Automatic Polarimeter from Dr. Kernchen, measured in a 1 cm cuvette at a wavelength of 589 nm.

3.3 Microderivatizations

Transesterification

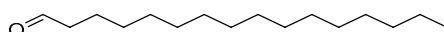
To about 20 μL of a natural extract in 0.1 mL pentane was added sodium methanolate in abs. methanol (0.2 mL, 0.5M). The solution was prepared by adding freshly cut sodium pieces to abs. methanol (caution: H_2 gas evolution). The mixture was heated to 60°C for 10 minutes in a closed cup vial and then mixed with glacial acetic acid (10 μL) and water (0.5 ml). The aqueous phase was extracted twice with pentane (0.5 mL) and the organic phase was dried with a small amount of MgSO_4 . The sample was concentrated in a stream of nitrogen.

DMDS adducts

To about 20 μL of a natural extract in 20 μL mL pentane was added dimethyl disulfide (50 μL) and a solution of iodine in diethyl ether (5 μL , 0.24 M). The mixture was heated to 40 °C for 15 h in a closed vial. Pentane (200 μL) was added and the mixture was washed with 5% $\text{Na}_2\text{S}_2\text{O}_3$ -solution. The organic phase was separated, dried with MgSO_4 and concentrated in a stream of nitrogen.

3.4 Experiments

Hexadecanal (16)

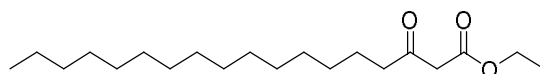


Hexadecanol (5.00 g, 20.62 mmol, 1 eq) was dissolved ethyl acetate (150 ml) and IBX (16.8 g, 60 mmol) was added. The solution was heated to reflux until the alcohol was completely converted (2.5 to 3.25 hours). After cooling, the solid was filtered through a frit and washed three times with ethyl acetate [S2]. The solvent was removed under vacuum and the raw product purified by column chromatography with 20:1

pentane/*tert*-butyl methyl ether (TBME). A colorless waxy solid was obtained (4.9 g, 20.4 mmol, 99%).

DC (40:1 pentane/TBME): $R_f = 0.45$. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm] = 9.76 (t, 1H, H-1); 2.41 (dt, 2H, $^3J_{1\text{H},2\text{H}} = 1.9$ Hz, $^3J_{2\text{H},3\text{H}} = 7.3$ Hz, H-2); 1.63 (quint, 2H, $^3J = 7.3$ Hz, CH_2); 1.35-1.20 (m, 24H, CH_2); 0.88 (t, 3H, $^3J = 6.9$ Hz, H-16). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ [ppm] = 203.0 (C-1); 43.0 (t, C-2); 32.0 (t, C-14); 29.8-29.7 (t, 6C); 29.6 (t); 29.5 (t); 29.4 (t); 29.2 (t); 22.7 (t); 22.1 (t); 14.2 (q, C-16). GC/MS (EI70 eV): m/z (%) = 240 [M^+] (0.2); 222 (1); 196 (3); 194 (3); 166 (2); 96 (24); 82 (35); 69 (23); 67 (24); 57 (50); 55 (52); 43 (77); 41 (100). IR: $\tilde{\nu}$ [cm^{-1}] = 2957(w); 2914(s); 2848(s); 2751(w); 1704(s); 1470(m); 1392(w); 1372(w); 895(w); 716(w); 698(w); 657(w).

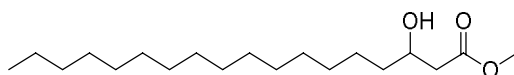
Ethyl 3-oxooctadecanoat (16)



Ethyl diazoacetate (2.2 mL, 20.96 mmol, 1.05 eq) was dissolved in dry dichloromethane (40 mL) under inert gas and tin(II) chloride (0.379 g, 1.99 mmol, 0.1 eq) was added. A few drops of a solution of hexadecanal (4.9 g, 20.37 mmol, 1 eq.) in dry dichloromethane (10 mL) were slowly added. After the start of the reaction (gas formation) the remaining hexadecanal solution was slowly added over 10 minutes. The solution was stirred for 3 h at room temperature. Then the mixture was poured into 100 mL sat. NaCl solution. The resulting emulsion was destroyed with KOH. The phases were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic phases were dried and concentrated over Na_2SO_4 [S3]. The raw product was purified by column chromatography with a 20:1 to 10:1 pentane/TBME gradient. Yield: 4.67 g (14.3 mmol, 70%) of a white, waxy solid DC (20:1 pentane/TBME): $R_f = 0.34$.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm] = 4.20 (q, 2H, $^3J_{\text{Ethyl}} = 7.1$ Hz, OCH_2CH_3); 3.43 (s, 2H, COCH_2COO); 2.53 (t, 2H, $^3J_{4\text{H}-5\text{H}} = 7.4$ Hz, H-4); 1.65-1.53 (m, 2H, H-5); 1.27 (q, 3H, $^3J_{\text{Ethyl}} = 7.1$ Hz, OCH_2CH_3); 1.33-1.21 (m, 24H, CH_2); 0.88 (t, 3H, $^3J_{17,18} = 6.9$ Hz, $\text{CH}_3\text{CH}_2\text{O}$). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ [ppm] = 203.0 (s, C-3); 167.3 (s, C-1); 61.3 (t, $\text{COOCH}_2\text{CH}_3$); 49.3 (t, C-2); 43.0 (t, C-4); 31.9 (t, C-6); 29.7-29.6 (t, 6C); 29.5 (t); 29.4 (t); 29.3 (t); 29.0 (t); 23.45 (t, C-5); 22.7 (t, C-17); 14.10 (d, $\text{COOCH}_2\text{CH}_3$); 14.08 (d, C-18). GC/MS (EI, 70 eV): m/z (%) = 326 [M^+] (0.5); 269 (4); 253 (3); 130 (7); 111 (7); 109 (8); 104 (8); 97 (17); 95 (18); 83 (22); 81 (19); 71 (13); 69 (25); 67 (17); 57 (54); 55 (53); 43 (100); 41 (96). IR: $\tilde{\nu}$ [cm^{-1}] = 2983 (w); 2956 (w); 2917 (s); 2849 (s); 1739(s); 1710(s); 1468 (m); 1410 (m); 1366 (m); 1323 (m); 1253(m); 1162(m); 1076 (m); 1036 (m); 943 (w); 719 (m); 653 (w); 558 (w). UV/VIS (DCM): λ_{max} [nm] ($\lg \epsilon$) = 247 (2.77); 224 (2.53).

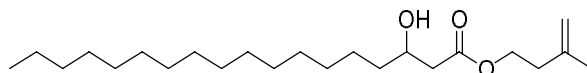
Methyl 3-hydroxyoctadecanoate (17)



Ketoester **16** (750 mg, 2.3 mmol, 1 eq) was dissolved in methanol (2 mL) and NaBH₄ (44 mg, 1.15 mmol, 0.5 eq) was slowly added while stirring. The reaction was stirred for 12 h and then concentrated. The residue was mixed with water and extracted three times with TBME. The combined organic phases were washed with saturated NaCl solution and dried with MgSO₄. The solvent was removed under vacuum and the product **17** was obtained in quantitative yield (723 mg, 2.3 mmol) as a yellowish, waxy solid. During the reaction transesterification to the methyl ester was observed.

DC (3:1 pentane/TBME): *R_f* = 0.33.; ¹H-NMR (200 MHz, CDCl₃): δ [ppm] = 4.04 (m, 1H, H-3), 3.72 (s, 3H, OCH₃); 2.86 (bs, 1H, OH); 2.52 (dd, 1H, ³*J*_{2H,3H} = 3.1 Hz, ²*J*_{2H,2Hb} = 16.4 Hz, H-2); 2.41 (dd, 1H, ³*J*_{2H,3H} = 9.0 Hz, ²*J*_{2H,2Hb} = 16.4 Hz, H-2); 1.70- 1.48 (m, 4H); 1.47-1.38 (m, 3H); 1.37-1.16 (m, 28H); 0.88 (t, 3H, ³*J*_{17H,18H} = 6.9 Hz, H-18). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 173.5 (s, C-1); 68.0 (C-3); 51.7 (q, COOCH₃); 41.1 (t, C-2); 36.5 (t, C-4); 31.9 (t, C-16); 29.7-29.6 (t, 6C); 29.6 (t); 29.5 (t); 29.4 (t); 29.3 (t); 25.5 (t, C-5); 22.7 (t, C-17); 14.1 (d, C-18). GC/MS (EI, 70 eV): *m/z* (%) = 314 [M⁺] (0.1); 313 (0.1); 296 (1); 264 (4); 222 (3); 111 (3); 103 (100); 97 (7); 74 (17); 71 (18); 57 (12); 55 (13); 43 (27). IR: $\tilde{\nu}$ [cm⁻¹] = 3375 (br); 2955 (w); 2916 (s); 2849 (s); 1732 (m); 1466 (w); 1439 (w); 1196 (w); 1173 (m); 1081 (w); 990 (w); 721 (w).

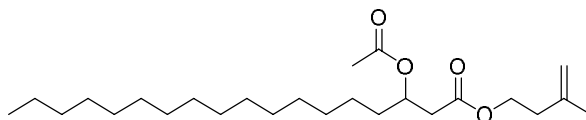
3-Methyl-3-butenyl 3-hydroxyoctadecanoate (**18**)



Ester **17** (0.37 g, 1.2 mmol, 1 eq.) was dissolved in 10 mL 3-methyl-3-buten-1-ol. Dibutyltin oxide (0.03 g, 0.12 mmol, 0.1 eq) was added as catalyst. The mixture was heated to reflux (140 °C) for 48 hours, followed by washing with sat. sodium bicarbonate solution and three times extraction with ethyl acetate. The combined organic phases were washed with 10% KF solution and saturated NaCl solution and dried over magnesium sulfate. The solvent was removed under vacuum [S4]. The crude product was purified by column chromatography with a 3:1 pentane/diethyl ether solvent mixture. Yield: 375 mg (0.95 mmol, 78%) of a white, waxy solid.

DC (3:1 pentane/diethyl ether): *R_f* = 0.4. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 4.83-4.81 (m, 1H, H-4'); 4.76-4.74 (m, 1H, H-4'); 4.24 (t, 2H, ³*J*_{1'H,2'H} = 6.7 Hz, H-1'); 4.03-3.94 (m, 1H, H-3); 2.90 (bs, 1H, OH); 2.51 (dd, 1H, ³*J*_{2H,3H erythro} = 3.3 Hz, ²*J*_{2H,2Hb} = 16.3 Hz, H-2); 2.41 (dd, 1H, ³*J*_{2H,3H} = 9.0 Hz, ²*J*_{2H,2Hb} = 16.3 Hz, H-2); 2.36 (t, 2H, ³*J*_{1'H,2'H} = 6.7 Hz, H-2'); 1.76 (s, 3H, CH₃-3'); 1.57-1.47 (m, 2H); 1.46-1.38 (m, 2H); 1.34-1.20 (m, 24H); 0.88 (t, 3H, ³*J*_{17H,18H} = 6.9 Hz, H-18). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 173.0 (s, C-1); 141.7 (s, C-3'); 112.4 (s, C-4'); 68.0 (d, C-3); 62.7 (t, C-1'); 41.4 (t, C-2); 36.6 (t, C-2'); 36.5 (t, C-4); 31.9 (t, C-16); 29.7-29.6 (t, 6C); 29.6 (t); 29.56 (t); 29.53 (t); 29.4 (t); 25.5 (t, C-5); 22.7 (t, C-17); 22.4 (d, C-3'); 14.1 (d, C-18). GC/MS (EI, 70 eV): *m/z* (%) = 368 [M⁺] (0.1); 350 (1); 299 (3); 283 (7); 265 (5); 252 (9); 250 (5); 239 (20); 157 (19); 97 (14); 83 (14); 69 (100); 68 (93); 57 (17); 55 (22); 53 (14); 43 (26); 41 (32). IR: $\tilde{\nu}$ [cm⁻¹] = 3375 (br); 3078 (w); 2956 (w); 2916 (s); 2849 (s); 1730 (m); 1651 (w); 1467 (w); 1406 (w); 1295 (w), 1174 (s); 1079 (s); 889 (m); 803 (w); 721 (w). UV/VIS (DC-M): λ_{max} [nm] (lg ϵ) = 227 (2.3).

3-Methyl-3-butenyl 3-acetoxyoctadecanoate (11)

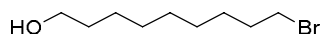


Ester **18** (426 mg, 1.16 mmol, 1 eq) was dissolved in dry dichloromethane (4.5 ml) under inert gas atmosphere. The mixture was cooled down to 0°C and mixed with pyridine (138 mg, 1.74 mmol) and DMAP (14 mg, 0.12 mmol). Then acetic acid anhydride (142 mg, 1.4 mmol) was slowly added. The reaction mixture was warmed to room temperature and stirred until complete conversion was achieved. Saturated NaCl solution was added and the phases were separated. The aqueous phase was extracted three times with dichloromethane and the combined organic phases dried with Na₂SO₄. The solvent was removed under vacuum and the raw product was purified by column chromatography with a 5:1 pentane/diethyl ether solvent mixture. Yield: 19 mg (0.78 mmol, 67%) of a white, waxy solid.

DC (5:1 pentane/diethyl ether): $R_f = 0.4$.

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 5.20 (ddt, 1H, ³ $J_{3H,4H} = 7.1$ Hz; ³ $J_{2H,3H} = 7.3$ Hz, ³ $J_{2Hb-3H} = 5.5$ Hz, H-3); 4.83-4.79 (m, 1H, H-3'); 4.75-4.72 (m, 1H, H-3'); 4.20 (t, 2H, ³ $J_{1'H,2'H} = 6.9$ Hz, H-1'); 2.58 (dd, 1H, ³ $J_{2H,3H} = 7.3$ Hz, ² $J_{2H,2Hb} = 15.5$ Hz, H-2); 2.52 (dd, 1H, ³ $J_{2H,3H} = 5.2$ Hz, ² $J_{2H,2Hb} = 15.5$ Hz, H-2); 2.33 (t, 2H, ³ $J_{1'H,2'H} = 6.8$ Hz, H-2'); 2.02 (s, 3H, CH₃-C=O); 1.75 (s, 3H, CH₃-3'); 1.57-1.47 (m, 2H); 1.46-1.38 (m, 2H); 1.34-1.20 (m, 24H); 0.88 (t, 3H, ³ $J_{17H,18H} = 6.9$ Hz, H-18). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 170.4 (s, C-1); 170.3 (s, CH₃C=O); 141.5 (s, C-3'); 112.3 (s, C-4'); 70.5 (d, C-3); 62.8 (t, C-1'); 39.2 (t, C-2); 36.6 (t, C-2'); 34.0 (t, C-4); 31.9 (t, C-16); 29.7-29.6 (t, 7C); 29.5 (t); 29.4 (t); 29.3 (t); 25.1 (t, C-5); 22.7 (t, C-17); 22.4 (d, CH₃-3'C); 21.1 (d, CH₃C=O); 14.1 (d, C-18). GC/MS (EI, 70 eV): m/z (%) = 410 (0.6); 351 (8); 350 (4); 343 (5); 299 (5); 283 (18); 265 (36); 239 (3); 199 (3); 179 (4); 128 (8); 111 (11); 97 (10); 83 (8); 69 (53); 68 (100); 61 (2); 57 (12); 55 (26); 43 (71); 41 (43). IR: $\tilde{\nu}$ [cm⁻¹] = 3077 (w); 2923 (s); 2853 (m); 1741 (s); 1651 (w); 1462 (w); 1373 (w); 1235 (s), 1173 (m); 1025 (m); 891 (w); 721 (w). UV/VIS (DC-M): λ_{max} [nm] (lg ϵ) = 229 (2.3).

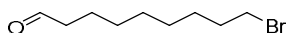
9-Bromo-1-nonanol



Nonane-1,9-diol (**19**, 2.99 g, 18.7 mmol, 1 eq.) was dissolved in toluene (860 mL) and 48% aqueous HBr was added (2.6 mL, 22.42 mmol, 1.2 eq.). The reaction mixture was heated to reflux for 24 h. Again 48% aqueous HBr (1.1 mL, 9.35 mmol, 0.5 eq.) was added to the reaction mixture and heating continued for another 24 hours. The reaction was stopped by addition of 1M NaOH solution, the phases were separated and the aqueous phase was extracted three times with toluene. The combined organic extracts were dried with MgSO₄ and the solvent was removed under vacuum [S5]. The resulting crude product was purified with a 1:1 pentane/diethyl ether solvent mixture by column chromatography. 9-Bromo-1-nonanol (3.28 g, 14.79 mmol) obtained as a colorless liquid in 79 % yield.

DC (1:1 pentane/diethyl ether): $R_f = 0.39$. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm] = 3.64 (t, 2H, $^3J_{\text{H-2H}} = 6.6$ Hz, H-1); 3.41 (t, 2H, $^3J_{\text{H-9H}} = 6.8$ Hz, H-9); 1.87 (tt, 2H, $^3J_{\text{H-8H}} = 7.2$ Hz, $^3J_{\text{H-9H}} = 6.8$ Hz, H-8), 1.57 (quint, 2H, $^3J_{\text{H-2H}} = 6.6$ Hz, $^3J_{\text{H-3H}} = 6.6$ Hz, H-2), 1.49-1.41 (m, 2H); 1.41-1.31 (m, 8H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ [ppm] = 63.0 (t, C-1); 34.0 (t, C-9); 32.8 (t, C-7); 32.8 (t, C-2); 29.4 (t), 29.3 (t); 28.7 (t); 28.1 (t); 25.7 (t). GC/MS (EI, 70 eV): m/z (%) = 204/206 (0.2); 176/179 (10); 162/164 (20); 148/150 (34); 135/137 (52); 107/109 (7); 97 (78); 83 (53); 69 (93); 55 (100); 41 (54). IR [cm^{-1}] = 3421 (bw); 3363 (bw); 2920 (s); 2891 (m); 2852 (s); 1464 (w); 1053 (m); 1012 (m); 977 (w); 726 (m); 645 (s).

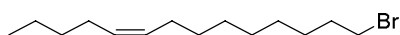
9-Bromononanal (20)



9-Bromononanol (**19**, 4.89 g, 21.91 mmol, 1 eq.) was oxidized as described for compound **16**. The resulting crude product was purified by column chromatography with a 10:1 pentane/diethyl ether solvent mixture. Aldehyde **20** was obtained (4.34 g, 19.72 mmol, 90%) as a colorless oil.

DC (10/1 pentane/diethyl ether): $R_f = 0.31$. $^1\text{H-NMR}$ (200 MHz, CDCl_3): δ [ppm] = 9.77 (t, 1H, $^3J_{\text{H-2H}} = 2.0$ Hz, H-1); 3.41 (t, 2H, $^3J_{\text{H-8H}} = 8.1$ Hz, H-9); 2.43 (dt, 2H, $^3J_{\text{H-3H}} = 7.3$ Hz, $^3J_{\text{H-2H}} = 2.0$ Hz, H-2); 1.84 (tt, 2H, $^3J_{\text{H-8H}} = 8.1$ Hz, $^3J_{\text{H-7H}} = 7.0$ Hz, H-7); 1.68-1.58 (m, 2H, H-3); 1.47-1.37 (m, 2H, H-4); 1.37-1.29 (m, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ [ppm] = 202.8 (d, C-1); 43.8 (t, C-2); 33.9 (t, C-9); 32.7 (t); 29.1 (t); 29.0 (t); 28.5 (t); 28.1 (t); 22.0 (t). GC/MS (EI, 70 eV): m/z (%) = 202/204 (3); 192/194 (2); 176/178 (25); 135/137 (9); 123 (17); 97 (60); 81 (49); 69 (36); 67 (33); 55 (100); 44 (58); 41 (67). HR-MS: 202.0353 ($\text{M}^+ - \text{H}_2\text{O}$, calcd. 202.0357 for $\text{C}_9\text{H}_{15}\text{Br}$). IR: [cm^{-1}] = 2929 (s); 2855 (m); 2718 (w); 1723 (s); 1462 (w); 1246 (w); 935 (w); 724 (w); 643 (m); 561 (m).

(Z)-14-Bromo-5-tetradecene (21)

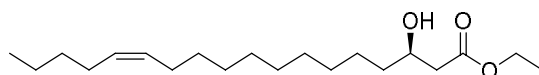


Diisopropylamine (2.67 g, 26.4 mmol, 1.2 eq.) was dissolved in dry THF (50 mL) under inert gas atmosphere and cooled to -78 °C. The solution was slowly mixed at 78 °C with *n*-BuLi solution (20.6 mL, 1.6M in hexane, 39 mmol, 1.5 eq.) and allowed to stir for 15 minutes at the same temperature. This freshly prepared LDA solution was added dropwise to a 0 °C cold solution of pentyltriphenylphosphonium bromide (10.00 g, 24.2 mmol, 1.1 eq.) in dry THF (450 mL) stirred for one hour at the same temperature. The solution was then cooled down again to -78 °C and **20** (3.85 g, 17.4 mmol, 1 eq.) was added dropwise and the mixture was stirred overnight at the same temperature. The reaction was stopped by adding H_2O . The aqueous phase was extracted three times with pentane, the combined organic phases were washed with saturated NaCl solution and dried over MgSO_4 . The resulting raw product was purified by column chromatography with pentane, yielding **21** in a 9:1 *Z/E*-ratio (4.00 g, 14.6 mmol, 84%) as colorless oil.

DC (pentane): $R_f = 0.8$. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm] = 5.40-5.30 (m, 2 H, H-5, H-6); 3.41 (t, 2 H, $^3J_{\text{H-2H}} = 6.8$ Hz, H-14); 2.08-1.98 (m, 4 H, H-4, H-7); 1.86 (quint, 2

H, $^3J = 6.8$ Hz, H-13); 1.47–1.23 (m, 14 H); 0.90 (t, 3 H, $^3J_{13\text{H}-14\text{H}} = 7.0$ Hz, H-14). ^{13}C -NMR (100 MHz, CDCl_3): δ [ppm] = 129.9 (d); 129.8 (d); 34.0 (t, C-14); 32.8 (t, C-13), 32.0 (t, 1 C); 29.7 (t, 1 C); 29.3 (t); 29.2 (t); 28.7 (t); 28.1 (t); 27.1 (t); 26.9 (t); 22.3 (t); 14.0 (q, C-1). GC/MS (EI, 70 eV): m/z (%) = 274/276 [M] $^+$ (20); 246/248 (2); 190/192 (4); 176/178 (4); 162/164 (21); 148/150 (36); 137 (17); 123 (13); 111 (25), 97 (68); 83 (69); 69 (83); 55 (100); 41 (61). HR-MS: 274.1302 (M^+ , calcd. 274.1296 for $\text{C}_{14}\text{H}_{27}\text{Br}_1$). IR [cm^{-1}] = 3004 (w); 2924 (s); 2854 (m); 1462 (w); 1247 (w); 968 (w); 722 (w); 647 (w); 563 (w). UV/VIS (pentane): ($\lg \epsilon$) = 195 (3.7).

Ethyl (3*R*,13*Z*)-3-hydroxy-13-octadecenoate (**23**)



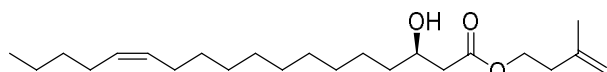
A suspension of magnesium turnings (0.119 g, 4.895 mmol, 2.55 eq.) in dry THF (0.50 mL) was mixed with 1,2-dibromoethane (45.6 mg, 0.243 mmol, 0.13 eq.) under inert gas and allowed to stir for 20 minutes. In order to remove the resulting magnesium salts, the supernatant was then removed with a syringe and a small amount of iodine was added to the Mg. A solution of **21** (1.267 g, 4.61 mmol, 2.4 eq.) in abs. THF (6.49 mL) was prepared. First, 0.75 mL of this solution were added to the activated magnesium to start the reaction. Then the remainder of the solution of **21** was added over a period of 30 minutes. The reaction mixture was stirred for one hour at room temperature after the initial boiling subdued.

In a separate reaction vessel, Cu(I)I (403 mMol, 2.11 mmol, 1.1 eq.) was suspended in dry THF (7.03 mL) under inert gas atmosphere and mixed with LiCl (178 mg, 4.22 mmol, 2.2 eq.), freshly dried in a vacuum at 150 °C for one hour. The solid dissolved and a clear yellow solution was formed. This solution was cooled to -30 °C and slowly mixed with the previously prepared organometallic solution. The solution was allowed to stir for 50 minutes at the same temperature; after a short time it turned bluish-black. A solution of enantiomerically pure epoxide (*S*)-**22** (0.250 g, 1.92 mmol, 1 eq.) in dry THF (1.00 mL) was then slowly added to the cuprate solution. The reaction mixture was stirred at -30 °C for one hour. The cooling was removed stirring continued for 12 hours. The reaction was stopped by adding saturated NH_4Cl solution and the phases were separated. The aqueous phase was extracted three times with diethyl ether, the combined organic phases were washed with saturated NaCl solution and dried over MgSO_4 [S6]. The solvent was removed under vacuum. The non-polar by-products were first separated by column chromatography with pentane and the pure product was eluted with diethyl ether. Ester **23** was obtained as colorless oil (497 mg, 1.52 mmol, 79%).

$[\alpha]_D^{22.5} = +2.8$ (CHCl_3 , $c = 1$). ^1H -NMR (400 MHz, CDCl_3): δ [ppm] = 5.40-5.31 (m, 2H, H-13, H-14); 4.20 (q, 2H, $^3J = 6.9$ Hz, OCH_2CH_3); 4.02-3.97 (m, 1H, H-3); 2.92 (bs, 1H, OH); 2.50 (dd, $^2J = 16.5$ Hz, $^3J_{2\text{H},3\text{H}} = 3.1$ Hz, H-2); 2.39 (dd, $^2J = 16.5$ Hz, $^3J_{2\text{H},3\text{H}} = 9.0$ Hz, H-2); 2.05-1.94 (m, 4H, H-12, H-14); 1.58-1.22 (m, 20H,); 1.28 (t, 3H, $^3J = 6.9$ Hz, OCH_2CH_3); 0.90 (m, 3H, $^3J_{17\text{H},18\text{H}} = 7.1$ Hz, H-18). ^{13}C -NMR (100 MHz, CDCl_3): δ [ppm] = 173.1 (s, C-1); 129.9 (d, C-14); 129.8 (d, C-13); 68.0 (s, C-3); 60.6 (t, OCH_2CH_3); 41.3 (t, C-2); 36.5 (t, C-4); 32.0 (t, C-16); 29.8 (t); 29.50 (t, 4C); 29.28

(t); 27.2 (t, C-12); 26.9 (t, C-15); 25.5 (t, C-5); 22.3 (t, C-17); 14.1 (q, OCH₂CH₃); 14.0 (q, C-18). GC/MS (EI, 70 eV): *m/z* (%) = 326 [M]⁺ (2); 308 (5); 263 (14); 262 (9); 251 (22); 249 (1); 235 (10); 220 (22); 164 (11); 163 (11); 150 (22) 133 (23); 123 (25); 121 (22); 117 (51); 109 (46); 95 (79); 81 (91); 69 (51); 67 (72); 55 (100); 41 (52). HR-MS: 326.2810 (M⁺, calcd. 326.2821 for C₂₀H₃₈O₃). IR [cm⁻¹] = 3435 (br); 3005 (w); 2924 (s); 2854 (m); 1734 (m); 1721 (m), 1464 (w); 1373 (w); 1179 (m); 1029 (m); 721 (w). IR [cm⁻¹] = 3435 (br); 3005 (w); 2924 (s); 2854 (m); 1734 (m); 1721 (m), 1464 (w); 1373 (w); 1179 (m); 1029 (m); 721 (w). UV/VIS (lg ε) = 227 (1.9).

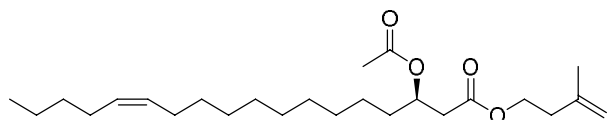
3-Methyl-3-butenyl (3*R*,13*Z*)-3-hydroxy-13-octadecenoate (24)



The synthesis was performed as described for compound **18**, shortening the reaction time to 36 h. 3-Methyl-3-buten-1-ol (10 mL), (*R*)-**23** (461 mg, 14 mmol, 1 eq.), and dibutyltin oxide (35 mg, 0.14 mmol, 0.1 eq.) were used. The crude product was purified by column chromatography with a 3/1 pentane/diethyl ether solvent mixture. Compound (*R*)-**24** was obtained as colorless liquid (336 mg, 0.92 mmol, 65%).

DC (3:1 pentane/diethyl ether): *R_f* = 0.30. [α]_D^{22.3} = +5.6. ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 5.40-5.31 (m, 2H, H-13, H-14); 4.83-4.81 (m, 1H, H-4'); 4.76-4.74 (m, 1H, H-4); 4.24 (t, 2H, ³*J* = 6.8 Hz, H-1'); 4.02-3.97 (m, 1H, H-3); 2.87 (bd, 1H, ³*J* = 3.4 Hz, OH); 2.50 (dd, ²*J* = 16.5 Hz, ³*J*_{2H,3H} = 3.1 Hz, H-2); 2.40 (dd, ²*J* = 16.5 Hz, ³*J*_{2H,3H} = 9.0 Hz, H-2); 2.36 (t, 2H, ³*J* = 6.8 Hz, H-2'); 2.05-1.94 (m, 4H, H-12, H-15); 1.75 (s, 3H, C-3'-CH₃); 1.62-1.40 (m, 2H, H-4); 1.37-1.22 (m, 18H); 0.90 (m, 3H, ³*J*_{17H,18H} = 7.1 Hz, H-18). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 172.9 (s, C-1); 141.6 (s, C-3'); 129.9 (d, C-14); 129.8 (d, C-13); 112.4 (t, C-4'); 68.0 (C-3); 62.7 (t, C-1'); 41.4 (t, C-2); 36.7 (t, C-2'); 36.5 (t, C-4); 32.0 (t, C-16); 29.8 (t); 29.50 (t, 4C); 29.28 (t); 27.2 (t, C-12); 26.9 (t, C-15); 25.5 (t, C-5); 22.35 (q, C-3'-CH₃); 22.33 (t); 14.0 (q, C-18). GC/MS (EI, 70 eV): *m/z* (%) = 366 [M]⁺ (2), 348 (2); 280 (2); 279 (3); 263 (3); 261 (2); 251 (16); 249 (10); 234 (7); 220 (5); 219 (8); 137 (7); 123 (11); 109 (17); 95 (28); 81 (28); 69 (100); 68 (35); 55 (38); 41 (36). HR-MS: 366.3112 (M⁺, calcd. 366.3134 for C₂₃H₄₂O₃). IR [cm⁻¹] = 3460 (br); 3078 (w); 3004 (w); 2924 (s); 2854 (m); 1733 (m); 1651 (w); 1462 (w); 1171 (m); 977 (w); 891 (m); 721 (w). UV/VIS (lg ε) = 227 (2.2).

3-Methyl-3-butenyl (3*R*,13*Z*)-3-acetoxy-13-octadecenoate (12)



This ester was prepared as described for compound **11**, using (*R*)-**24** (296 mg, 0.8 mmol, 1 eq.) The resulting crude product was purified by column chromatography with a 10/1 pentane/diethyl ether solvent mixture. Target compound (*R*)-**12** was obtained (243 mg, 0.6 mmol, 74%) as a colorless liquid.

DC (10:1 pentane/diethyl ether): *R_f* = 0.40. [α]_D^{22.4} = +2.7 (CHCl₃, *c* = 1). ¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 5.40-5.31 (m, 2H, H-13, H-14); 5.19 (ddt, 1H, ³*J*_{3H,4H} = 7.2 Hz, ³*J*_{2H,3H} = 7.2 Hz, ³*J*_{2H,3H} = 5.6 Hz, H-3); 4.81-4.79 (m, 1H, H-4'); 4.74-4.72 (m, 1H, H-4'H);

4.20 (t, 2H, $^3J = 6.9$ Hz, H-1'); 2.58 (dd, $^2J = 15.5$ Hz, $^3J_{2H,3H} = 7.2$ Hz, H-2); 2.52 (dd, $^2J = 15.5$ Hz, $^3J_{2H,3H} = 7.2$ Hz, H-2); 2.33 (t, 2H, $^3J = 6.9$ Hz, H-2'); 2.05-1.94 (m, 4H, H-12, H-15); 2.02 (s, 3H, CH₃COO); 1.75 (s, 3H, C-3'-CH₃); 1.64-1.53 (m, 2H, H-4); 1.37-1.22 (m, 18H); 0.90 (m, 3H, $^3J_{17H,18H} = 7.3$ Hz, H-18). ¹³C-NMR (100 MHz, CDCl₃): δ [ppm] = 170.4 (s, C-1); 170.3 (s, CH₃COO); 141.5 (s, C-3'); 129.9 (d, 2C, C-13, C-14); 112.3 (t, C4'); 70.6 (C-3); 62.8 (t, C-1'); 39.2 (t, C-2); 36.6 (t, C-2'); 34.0 (t, C-4); 32.0 (t); 29.8 (t); 29.50 (t, 2C); 29.46 (t); 29.36 (t); 29.28 (t); 27.2 (t, C-12); 26.9 (t, C-15); 25.1 (t, C-5); 22.5 (q, C-3'-CH₃); 22.3 (t, C-17); 21.1 (d, CH₃COO); 14.0 (q, C-18). GC/MS (EI, 70 eV): m/z (%) = 408 [M]⁺ (1), 348 (7); 280 (6); 279 (7); 263 (19); 251 (8); 220 (9); 219 (11); 137 (11); 123 (15); 109 (21); 95 (34); 81 (37); 69 (100); 68 (46); 61 (2); 55 (39); 43 (38); 41 (34). HR-MS: 348.3001 (M⁺-CH₃COOH, calcd. 348.3028 for C₂₃H₄₀O₂). IR [cm⁻¹] = 3078 (w); 3004 (w); 2925 (m); 1651 (w); 1740 (s); 1651 (w); 1459 (w); 1373 (w); 1235 (s); 1172 (m); 1025 (m); 976 (w); 891 (w); 722 (w). UV/VIS (lg ϵ) = 227 (2.1).

4. IR spectra of natural compounds

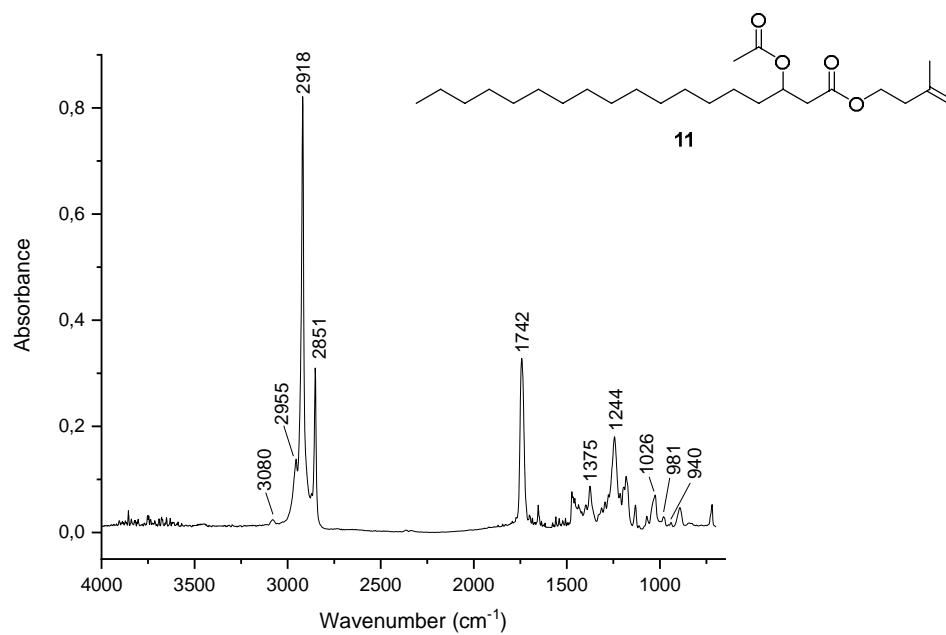


Figure S8. IR-spectrum of natural isoprenyl 3-acetoxyoctadecanoate (11) obtained by GC/DD-IR.

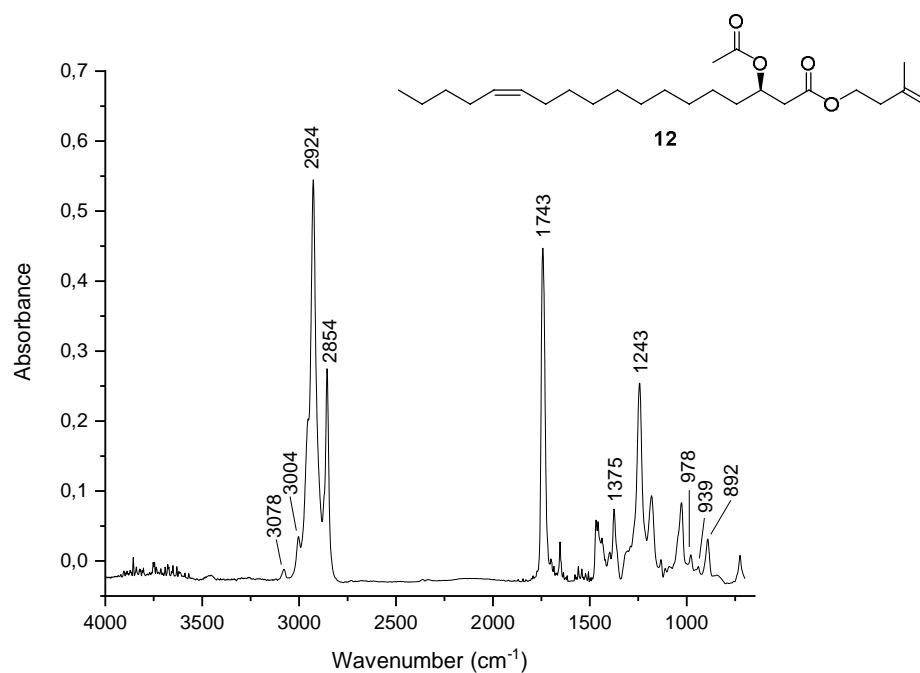


Figure S9. IR-spectrum of natural Isoprenyl (3R,13Z)-3-acetoxy-13-octadecenoate (12) obtained by GC/DD-IR.

5. NMR spectra

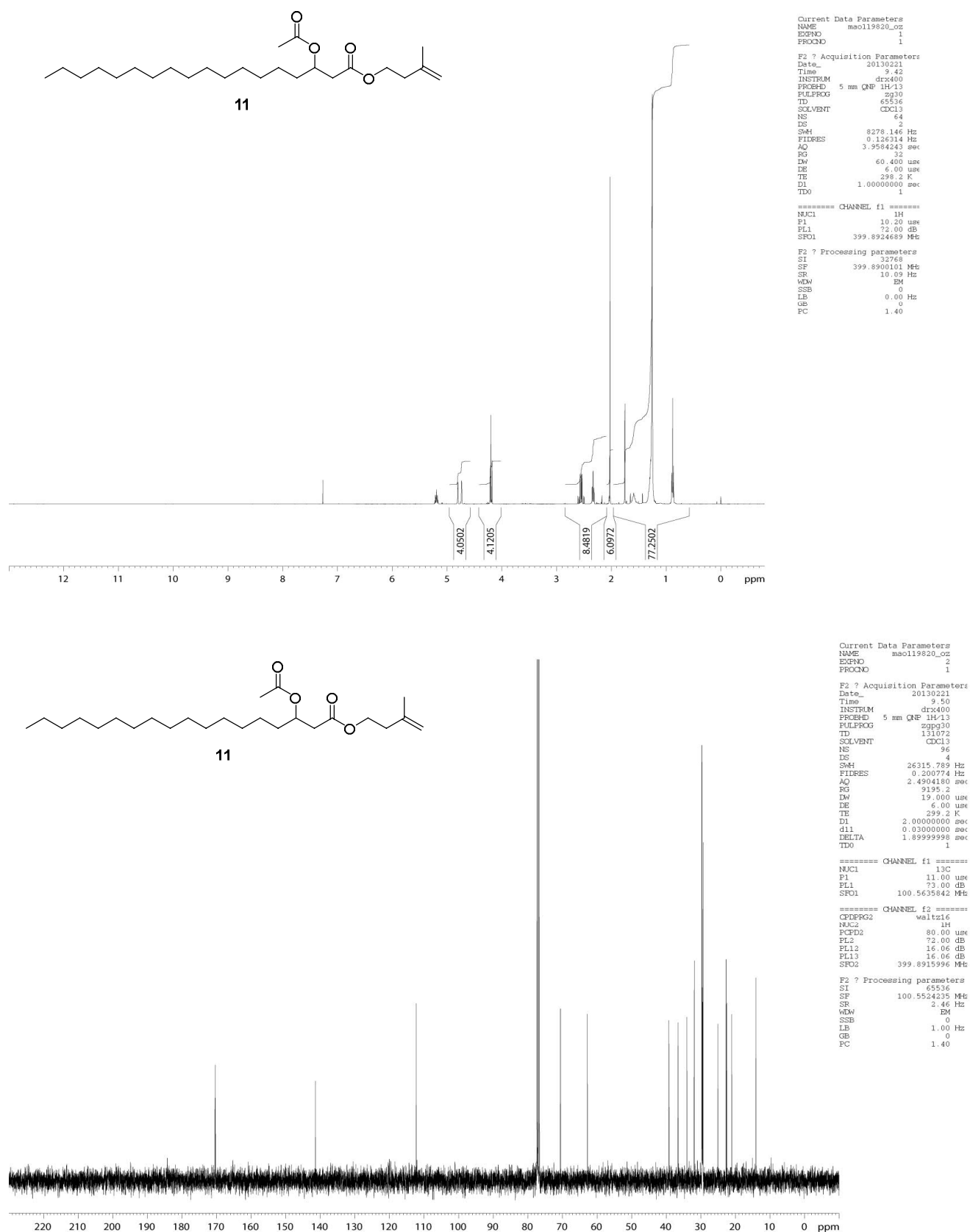
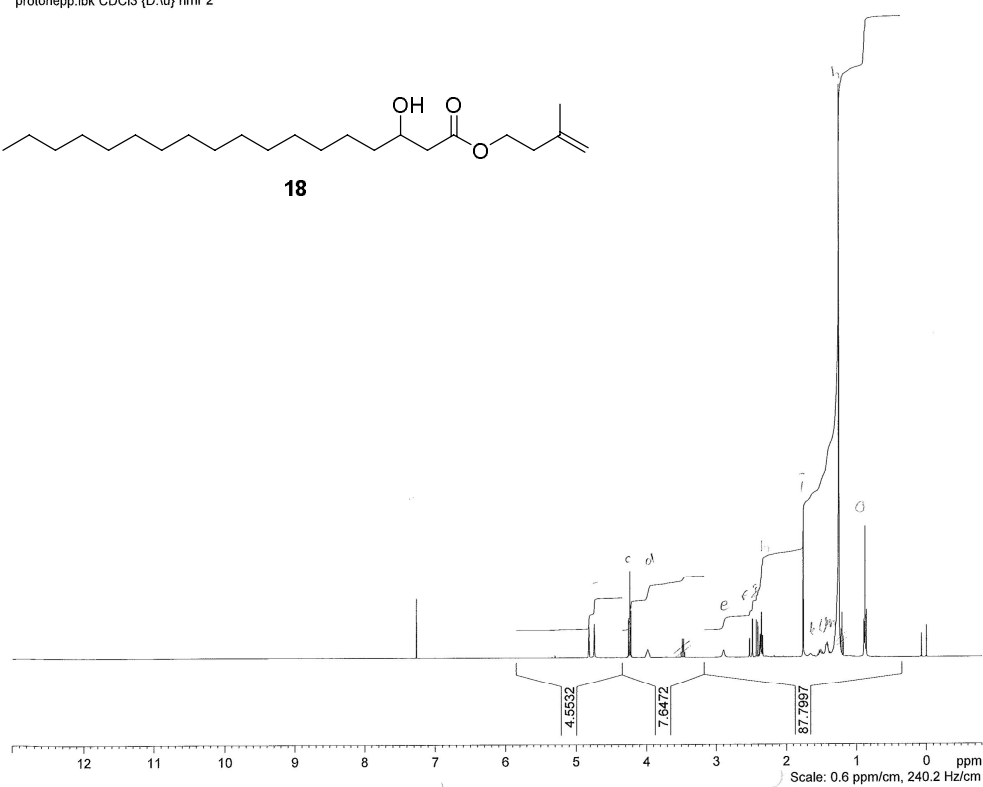
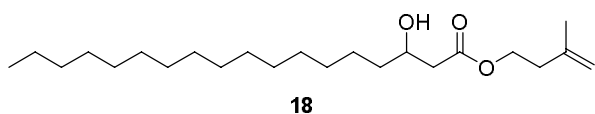


Figure S10. ¹H- and ¹³C-NMR spectra of isoprenyl 3-acetoxyoctadecanoate (11)

Exp. 1H
Mann: FM 318
protonpep.ibk CDCl3 (D:\u) nmr 2

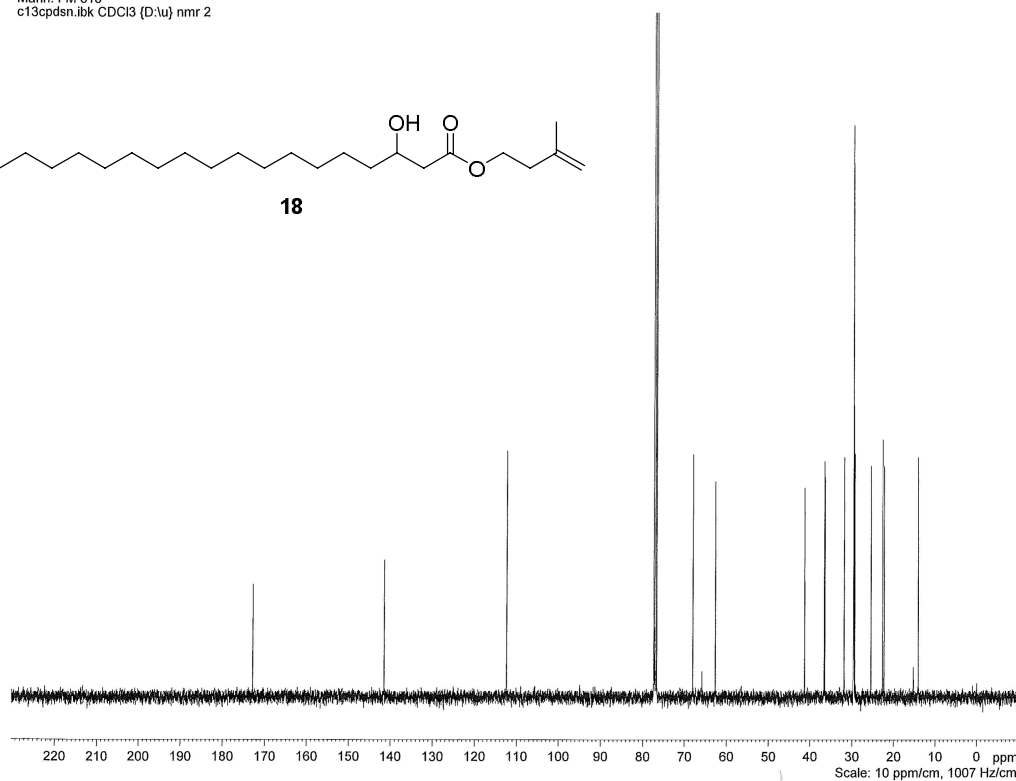
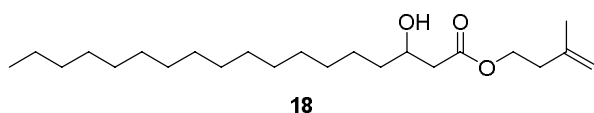


```

NAME      ma0128722_0z
EXPNO    1
PROCNO   1
Date_    20151216
Time     14.24
INSTRUM  AVI11400
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TU       65536
SOLVENT  CDCl3
NS       64
DS       2
SWH      8223.685 Hz
FIDRES   0.125483 Hz
AQ       3.9846387 sec
RG       57
DW       60.800 usec
DE       6.50 usec
TE       296.3 K
D1       1.0000000 sec
TDD      1
===== CHANNEL f1 =====
NUC1     1H
P1       10.33 usec
PL1      -4.00 dB
SFO1     400.4024726 MHz
SI       32768
SF       400.4000162 MHz
SR       16.19 Hz
WDM      SW
SSB      0
LB       0.00 Hz
GB       0
PC       1.40
PIP     5.218 ppm
P2P     0.460 ppm

```

Exp. 13C, CPD
Mann: FM 318
c13cpdsn.ibk CDCl3 (D:\u) nmr 2



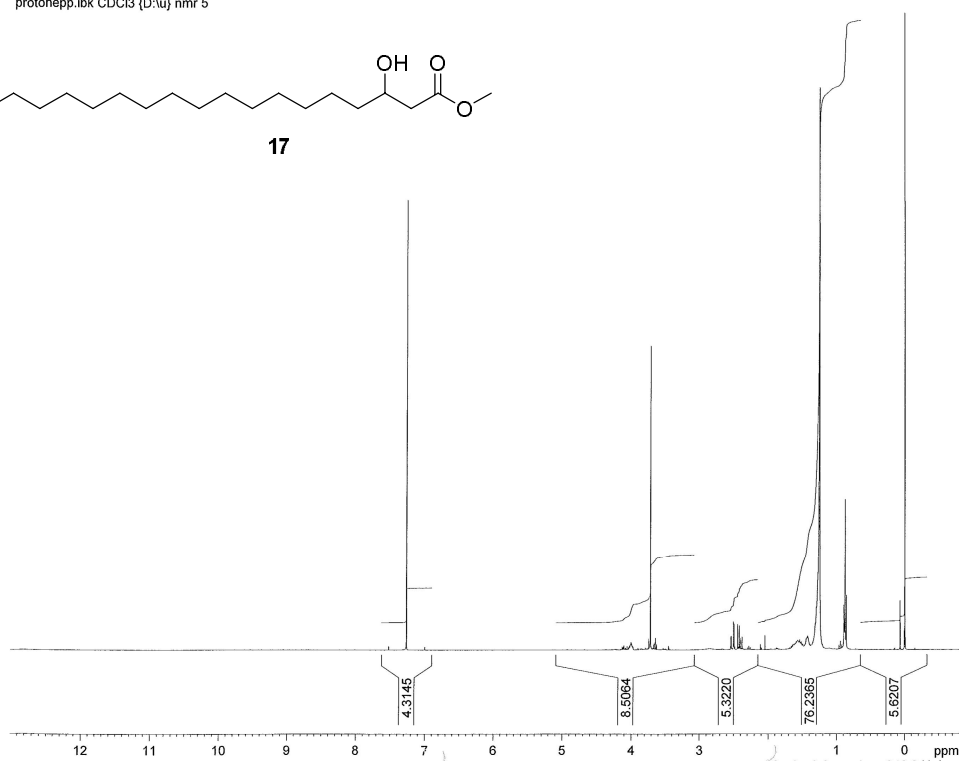
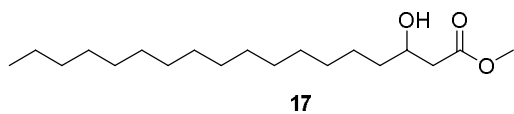
```

NAME      ma0128722_0z
EXPNO    2
PROCNO   1
Date_    20151216
Time     14.33
INSTRUM  AVI11400
PROBHD   5 mm PABBO BB-
PULPROG  zgpg30
TD       131072
SOLVENT  CDCl3
NS       192
DS       4
SWH      26315.789 Hz
FIDRES   0.200774 Hz
AQ       2.4904180 sec
RG       101
DW       19.000 usec
DE       6.50 usec
TE       297.6 K
D1       2.0000000 sec
D11     0.0300000 sec
TDO      10
===== CHANNEL f1 =====
NUC1     13C
P1       8.50 usec
PL1      -3.00 dB
SFO1     100.6918371 MHz
===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2     1H
PCD2     80.00 usec
PL2      -4.00 dB
PL12     13.78 dB
PL13     14.00 dB
SFO2     400.4016016 MHz
SI       65536
SF       100.6806632 MHz
SR       2.20 Hz
WDM      SW
SSB      0
LB       1.00 Hz
GB       0
PC       1.40
PIP     230.000 ppm
P2P    -10.000 ppm

```

Figure S11. ¹H- and ¹³C-NMR spectra of isoprenyl 3-hydroxyoctadecanoate (18).

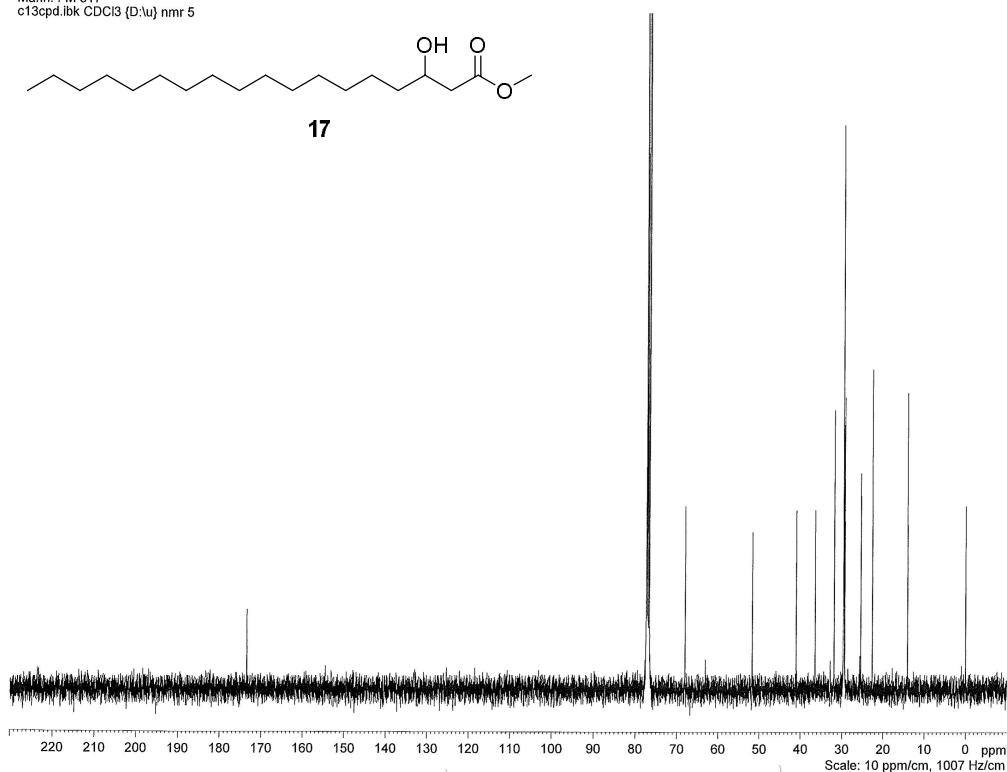
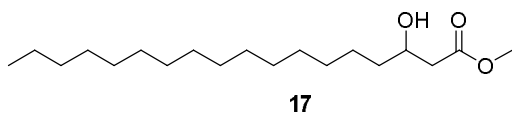
Exp. 1H
Mann: FM 317
protonpp.libk CDCl3 (D₂O) nmr 5



```
NAME      macl28696_02
EXPNO     1
PROCNO    1
Date_     20151214
Time      15.44
INSTRUM   AVI1400
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         64
DS         2
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         228
DW         60.800 usec
DE         6.50 usec
TE         296.2 K
DL         1.0000000 sec
TDO        1
```

```
----- CHANNEL f1 -----
NUC1      1H
P1         10.33 usec
PL1        -4.00 dB
SFO1      400.4024726 MHz
SI         32768
SF         400.4000182 MHz
SR         18.15 Hz
WWM        EM
SSB        0
LB         0.00 Hz
GB         0
PC         1.40
F1P        13.000 ppm
F2P        -0.800 ppm
```

Exp. 13C, CPD
Mann: FM 317
c13cpd.libk CDCl3 (D₂O) nmr 5



```
NAME      macl28696_02
EXPNO     2
PROCNO    1
Date_     20151214
Time      18.21
INSTRUM   AVI1400
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         131072
SOLVENT   CDCl3
NS         2048
DS         4
SWH        26315.789 Hz
FIDRES     0.200774 Hz
AQ         2.4904180 sec
RG         71.8
DW         19.000 usec
DE         6.50 usec
TE         297.6 K
DL         2.0000000 sec
TDO        0.0300000 sec
```

```
----- CHANNEL f1 -----
NUC1      13C
P1         8.50 usec
PL1        -3.00 dB
SFO1      100.6918371 MHz

----- CHANNEL f2 -----
CPDPRG2   waltz16
NUC2      1H
PCPDZ     80.00 usec
PL2        -4.00 dB
PL12       13.78 dB
PL13       14.00 dB
SFO2      400.4016016 MHz
SI         65536
SF         100.6806634 MHz
SR         2.36 Hz
WWM        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
F1P        230.000 ppm
F2P        -10.000 ppm
```

Figure 12. ¹H- and ¹³C-NMR spectra of methyl 3-hydroxyoctadecanoate (17).

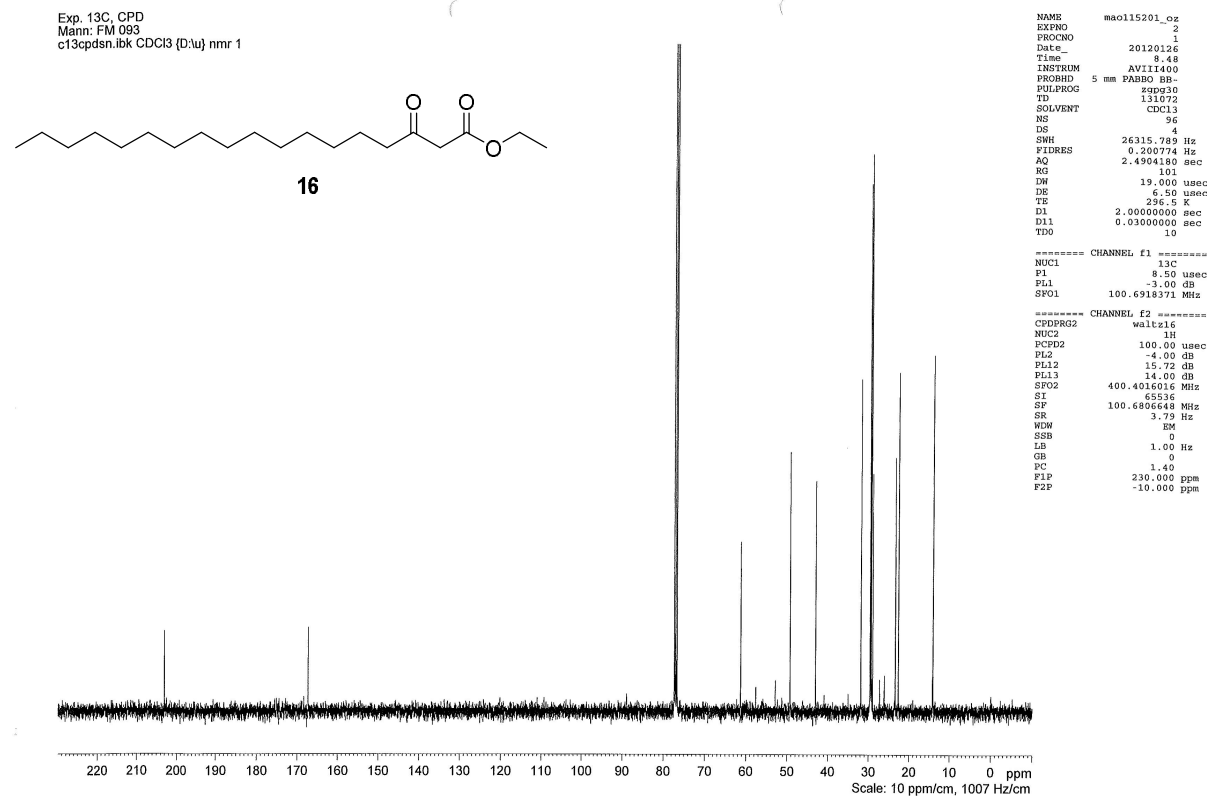
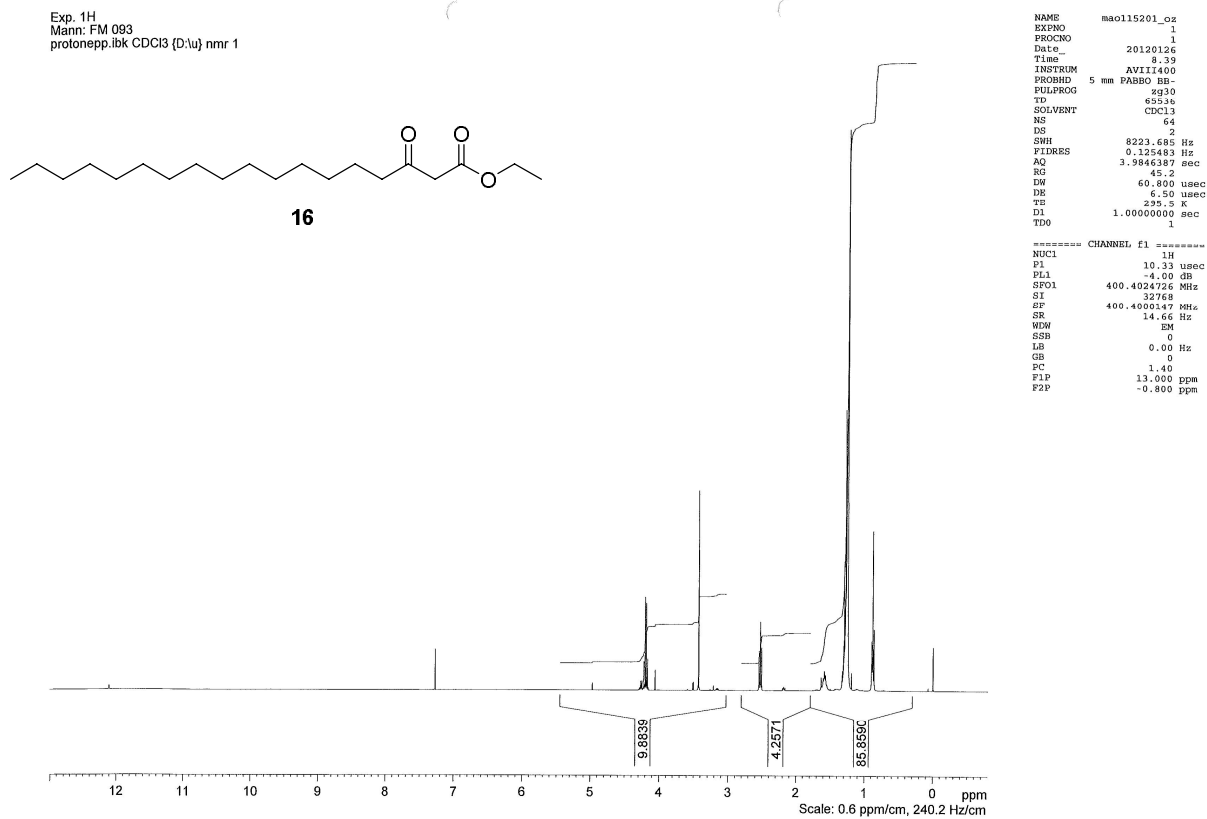


Figure S13. ¹H- and ¹³C-NMR spectra of ethyl 3-oxooctadecanoate (16).

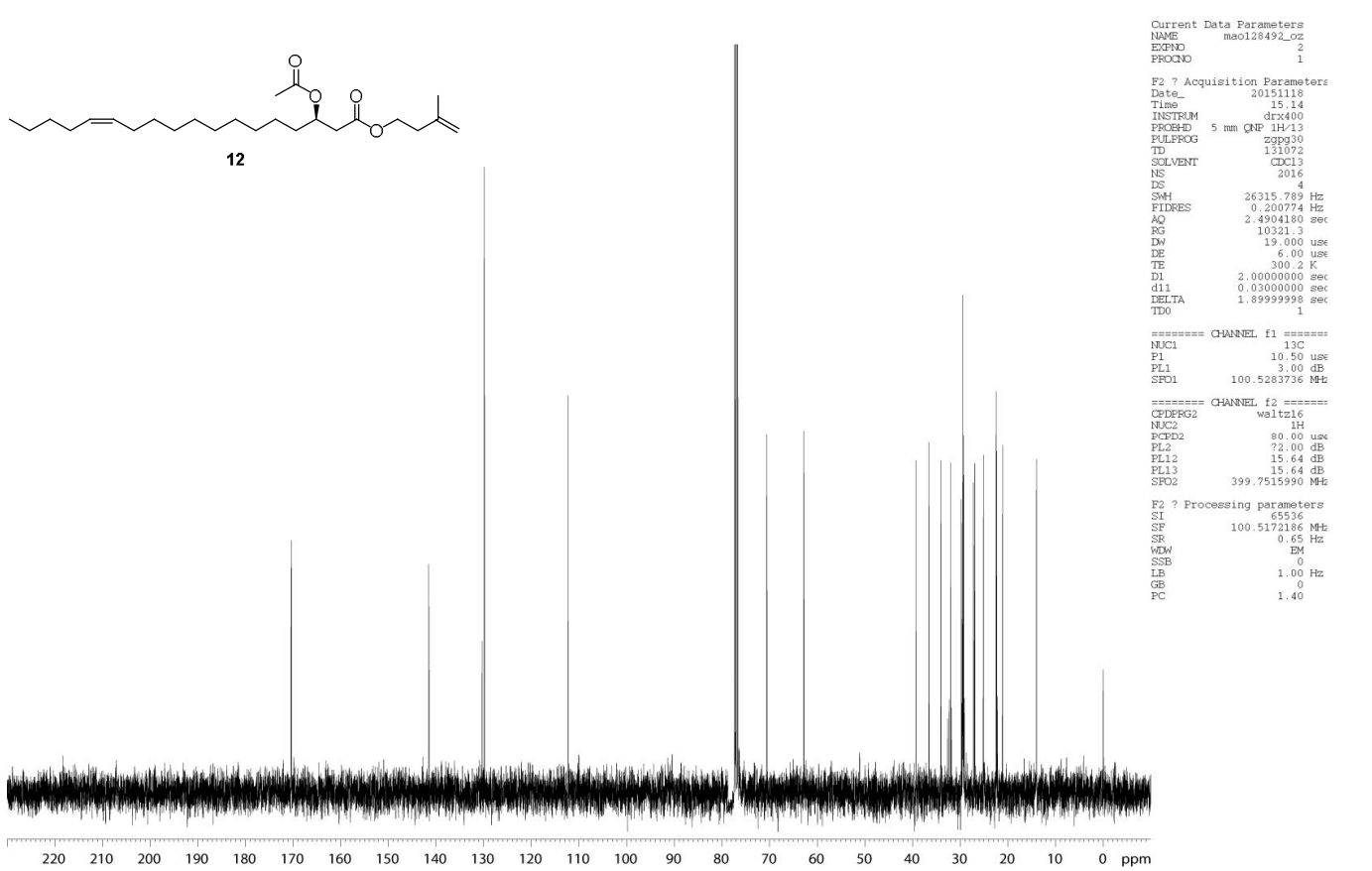
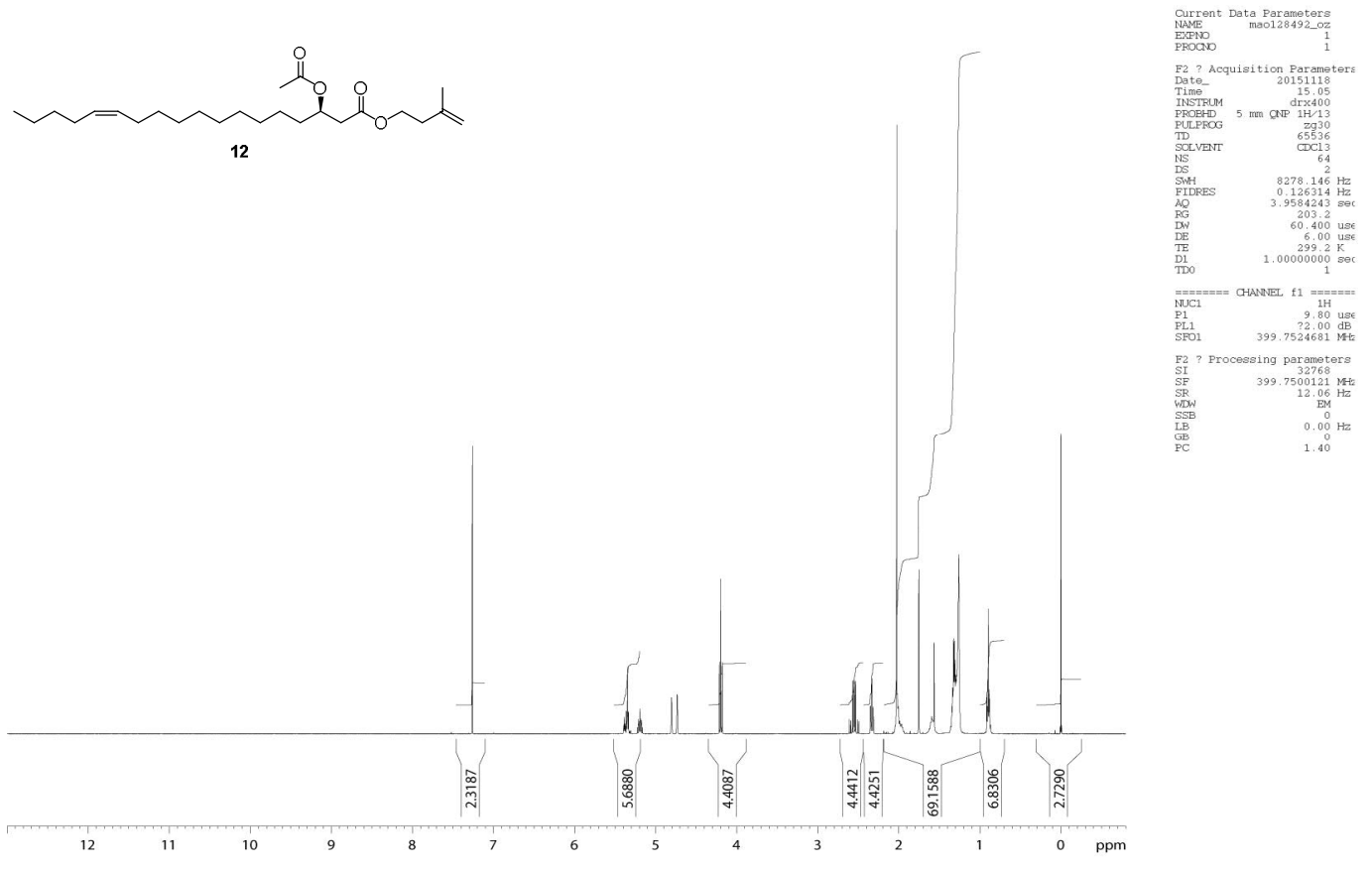


Figure S14. ¹H- and ¹³C-NMR spectra of Isoprenyl (3R,11Z)-3-acetoxy-13-octadecenoate (12).

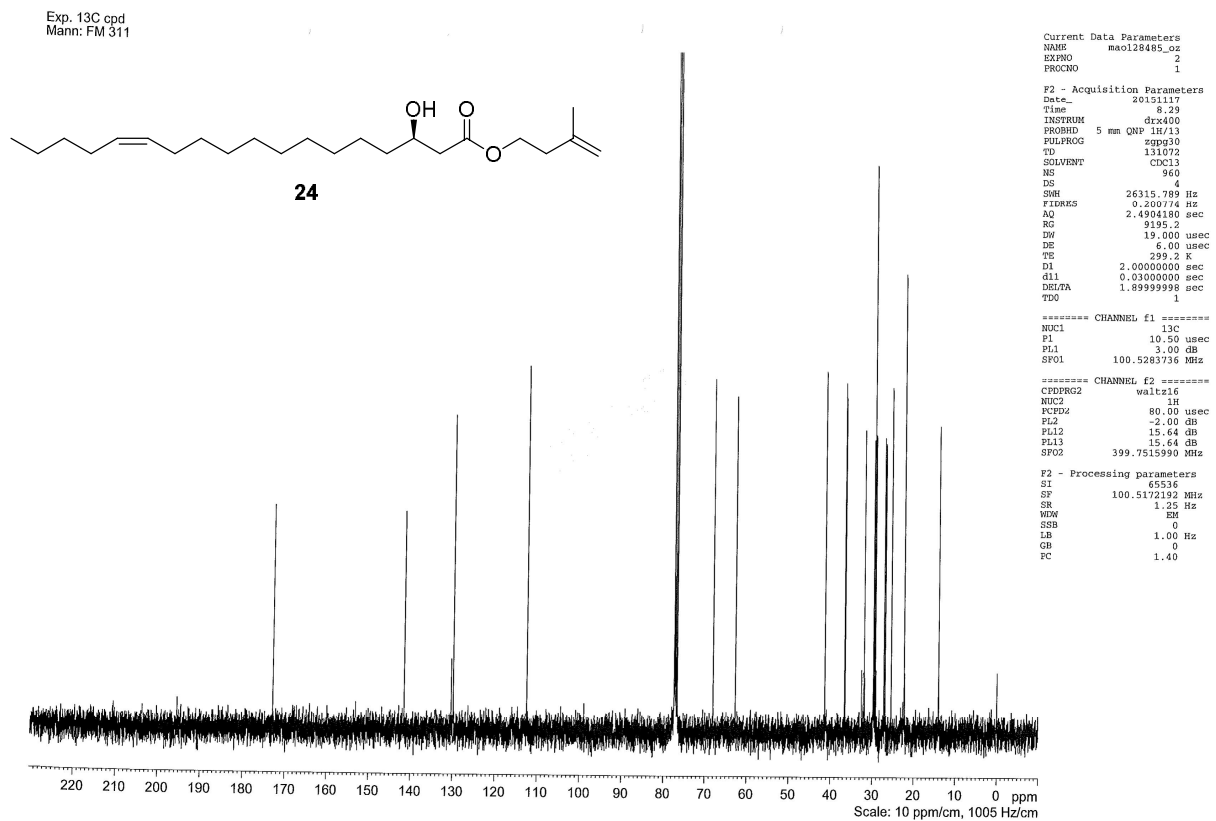
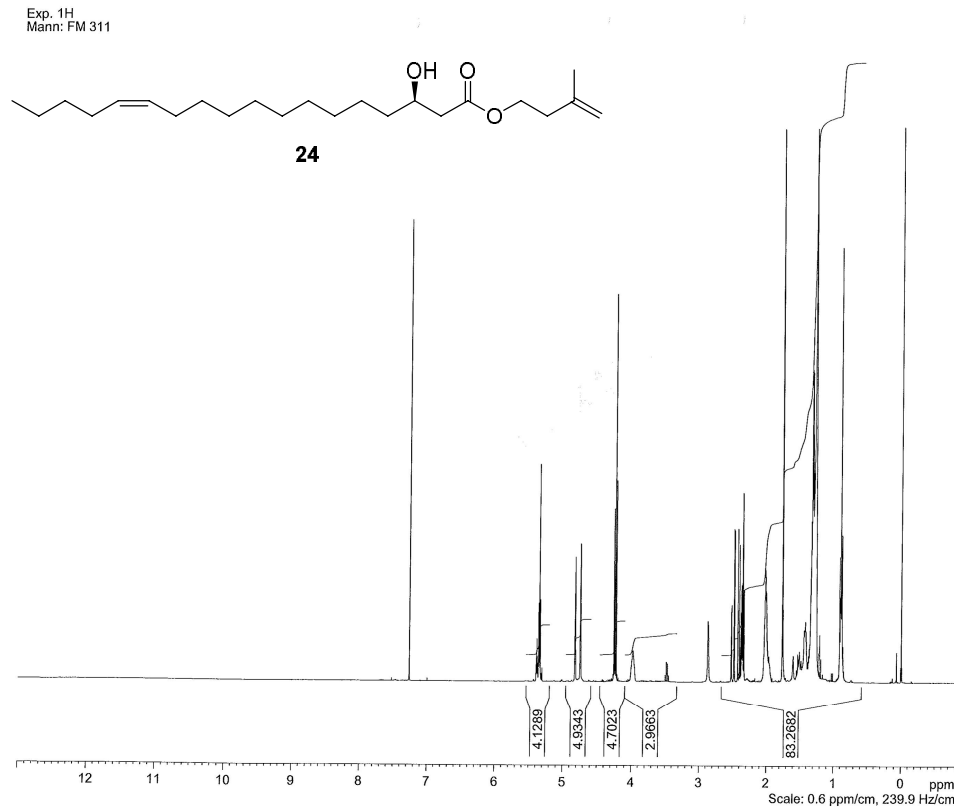
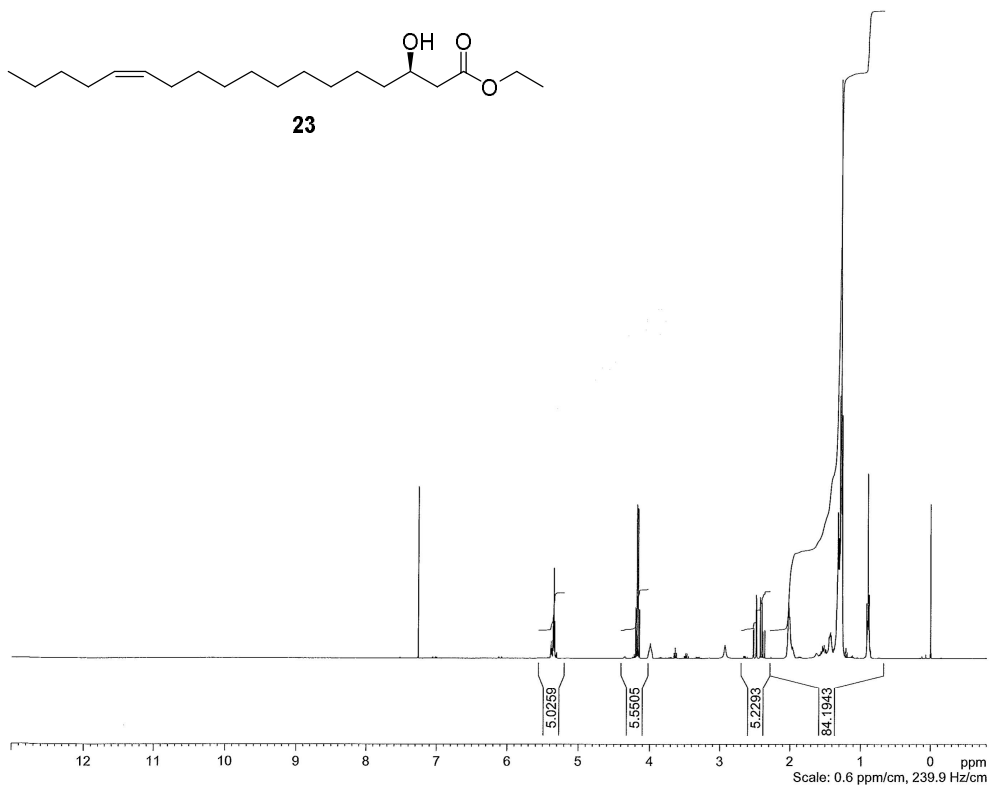


Figure S15. ¹H- and ¹³C-NMR spectra of Isoprenyl (3R,11Z)-3-hydroxy-13-octadecenoate (**24**).

Exp. 1H
Mann: FM 310



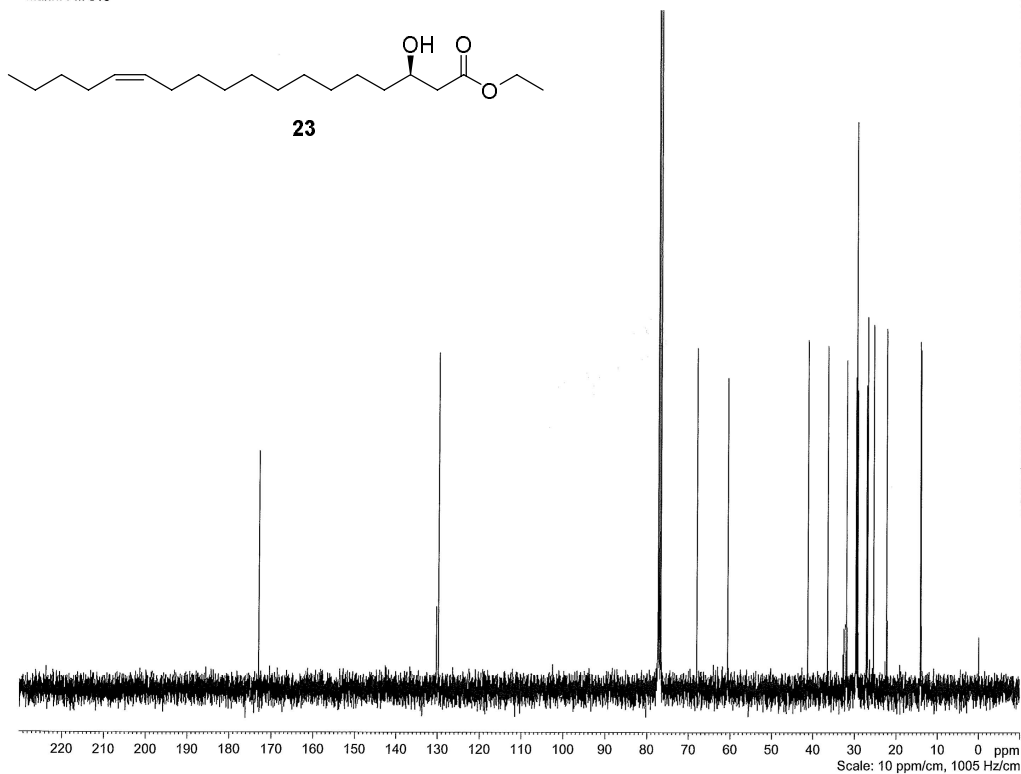
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Current Data Parameters
NAME      maol28465_02
EXPNO    1
PROCNO   1

F2 - Acquisition Parameters
Date_    20151116
Time     10:19
INSTRUM  drx400
PROBHD   5 mm QNP 1H/13
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        64
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG         114
DM        60.400 usec
DE         6.00 usec
TE        299.2 K
D1        1.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      1H
P1        9.80 usec
PL1       -2.00 dB
SFO1      399.7524681 MHz

F2 - Processing parameters
SI        32768
SF        399.7500108 MHz
SR        19.81 Hz
WDW       EM
SSB       0
LB        0.00 Hz
GB        0
FC        1.40
```

Exp. 13C, CPD
Mann: FM 310



```
Current Data Parameters
NAME      maol28465_02
EXPNO    2
PROCNO   1

F2 - Acquisition Parameters
Date_    20151116
Time     10:28
INSTRUM  drx400
PROBHD   5 mm QNP 1H/13
PULPROG  zgpg30
TD        131072
SOLVENT  CDCl3
NS        768
DS        4
SWH       26315.789 Hz
FIDRES    0.200774 Hz
AQ        2.4904180 sec
RG         9195.2
DM        19.000 usec
DE         6.00 usec
TE        299.2 K
D1        2.00000000 sec
d11       0.03000000 sec
DELTA    1.89999998 sec
TD0       1

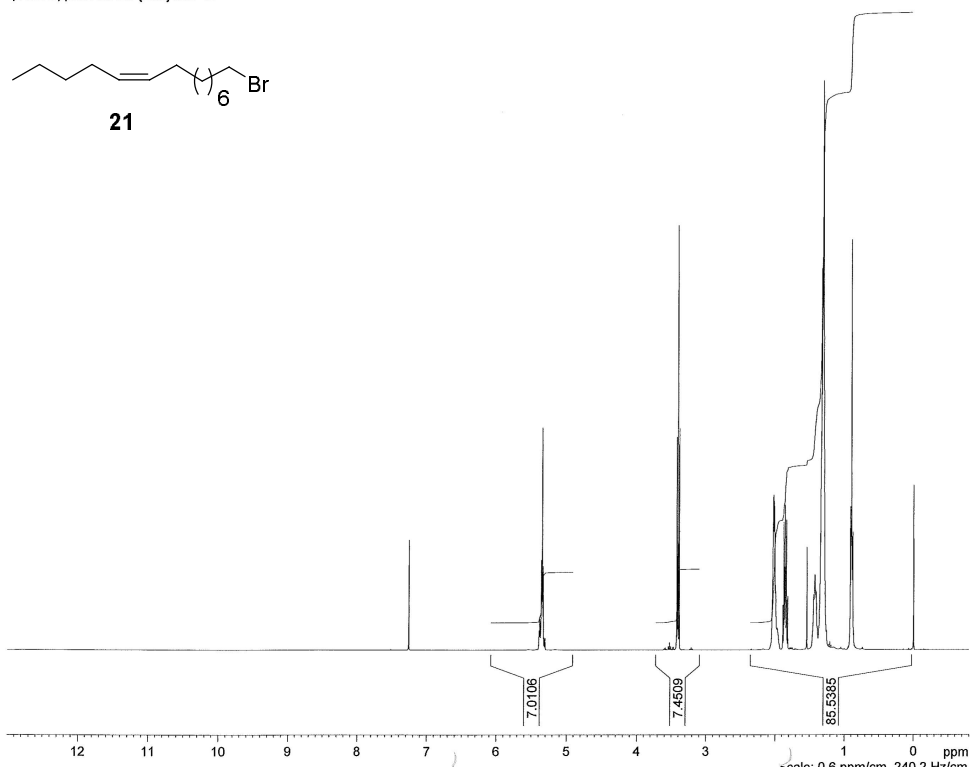
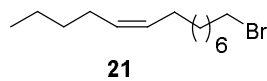
===== CHANNEL f1 =====
NUC1      13C
P1       10.50 usec
PL1       3.00 dB
SFO1     100.5283736 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2      1H
PCPD2    80.00 usec
PL2       -2.00 dB
PL12     15.64 dB
PL13     15.64 dB
SFO2     399.7515990 MHz

F2 - Processing parameters
SI        65536
SF        100.5172193 MHz
SR        1.28 Hz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
FC        1.40
```

Figure S16. ¹H- and ¹³C-NMR spectra of ethyl (3R,11Z)-3-hydroxy-13-octadecenoate (23).

Exp. 1H
Mann: FM211
protonpp.libk CDC13 (D₂O) nmr 12

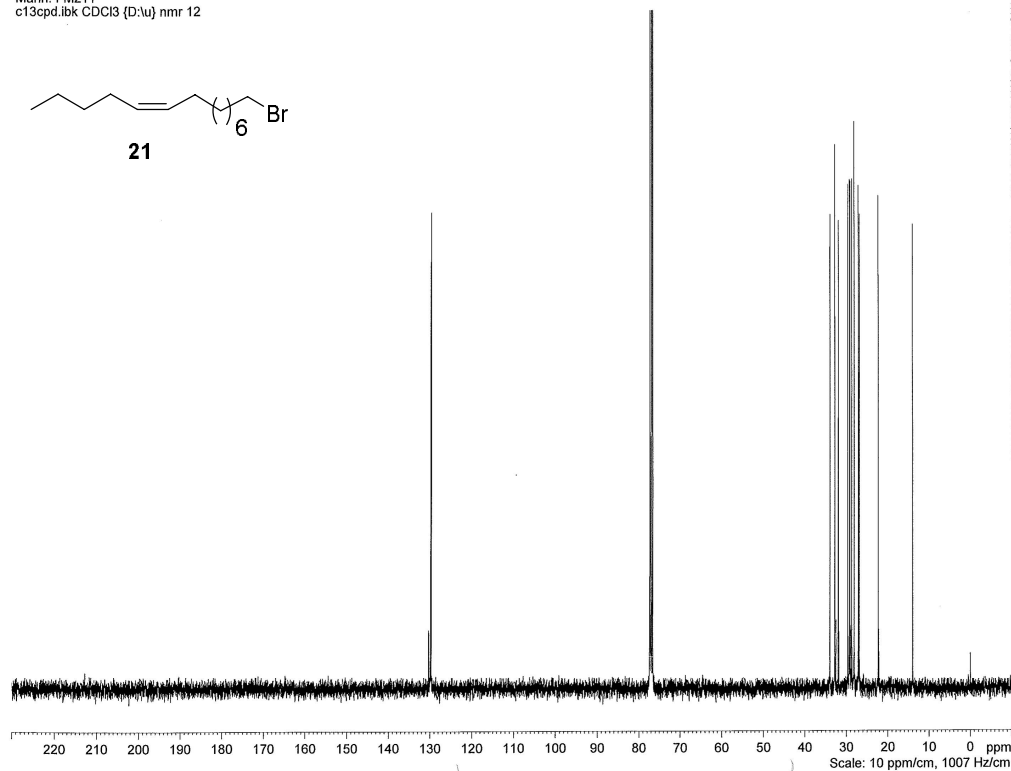
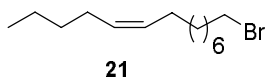


```

NAME      maol24801_oz
EXPNO    1
PROCNO   1
Date_    20140807
Time     19.34
INSTRUM  AVIII400
PROBHD   5 mm PABBI 1H/
PULPROG  zgpg30
TD        65536
SOLVENT  CDCl3
NS        64
DS        2
SWH       8223.685 Hz
FIDRES    0.125483 Hz
AQ        3.9846397 sec
RG        45.2
DW        60.800 usec
DE        6.50 usec
TE        297.7 K
D1        1.0000000 sec
TDO       1

===== CHANNEL f1 =====
NUC1      1H
P1        7.12 usec
PL1       -1.00 dB
GFO1     400.4024226 MHz
SI        32768
SF        400.4000190 MHz
SR        19.04 Hz
WDW       EM
SSB       0
LB        0.00 Hz
GB        0
PC        1.40
P1P       13.000 ppm
P2P       -0.800 ppm
  
```

Exp. 13C, CPD
Mann: FM211
c13cpd.libk CDC13 (D₂O) nmr 12



```

NAME      maol24801_oz
EXPNO    2
PROCNO   1
Date_    20140807
Time     20.54
INSTRUM  AVIII400
PROBHD   5 mm PABBI 1H/
PULPROG  zgpg30
TD        131972
SOLVENT  CDCl3
NS        1024
DS        4
SWH       26315.789 Hz
FIDRES    0.200774 Hz
AQ        2.4904180 sec
RG        45.2
DW        19.000 usec
DE        6.50 usec
TE        298.2 K
D1        2.0000000 sec
D11       0.0300000 sec
TDO       1

===== CHANNEL f1 =====
NUC1      13C
P1        13.11 usec
PL1       -4.90 dB
SFO1     100.618171 MHz

===== CHANNEL f2 =====
CPDPRG2  waltz16
NUC2      1H
PCPD2    80.00 usec
PL2       -1.00 dB
PL12     20.01 dB
PL13     21.00 dB
SFO2     400.4016016 MHz
ST        65536
SF        100.6806642 MHz
SR        5.24 Hz
WDW       EM
SSB       0
LB        1.00 Hz
GB        0
PC        1.40
P1P       230.000 ppm
P2P       -10.000 ppm
  
```

Figure S17. ¹H- and ¹³C-NMR spectra of (Z)-14-bromo-5-tetradecene (21).

6. References

- S1. Gauthier, J.; Silva, D. L. de; Gompert, Z.; Whibley, A.; Houssin, C.; Le Poul, Y.; McClure, M.; Lemaitre, C.; Legeai, F.; Mallet, J.; Elias, M. *Mol. Ecol.* **2020**, *29*, 1328–1343.
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- S6. Huang, G.; Hollingsworth, R. I. *Tetrahedron: Asymmetry* **1998**, *9*, 4113–4115.