Palaeoclimate and Palaeosalinity Proxies

# Synthesis of $C_{37}$-Alkenones for Past Climate Reconstructions

Giacomo Berton,[a] Sarah Pizzini,[b,c] Fabrizio Fabris,*[a] Tommaso Bertolin,[a] Eugenia Pafumi,[a] Leonardo Ceccon,[a] Jonas Daelemans,[d] Giuseppe Borsato,[a] Alessandro Scarso,[a] Rossano Piazza,[b] and Patrizia Ferretti[b,c]

*Dedicated to Prof. Ottorino De Lucchi with respect and gratitude.*

**Abstract:** The total syntheses of three $C_{37}$ methyl-alkenones with different degrees of unsaturation and of their $^{13}C$-labelled analogues from commercially available starting materials are presented herein for the first time. These molecules are important to improve the reliability of the measurements and reconstructions of the sea surface temperature and salinity.

## Introduction

The reconstruction of ocean surface temperatures in the geological past is central to assessing the climate history and understanding what affects climate changes, as the oceans play a fundamental role in the evolution of the Earth's climate. One of the most powerful tools for reconstructing sea surface temperature (SST) is represented by the alkenone unsaturation indices ($U^k_{37}$ and $U^{k'}_{37}$), extensively used in palaeoclimate and palaeoceanography research.

Alkenones are biosynthesised by a few species of haptophyte algae which prefer the upper photic zone (e.g., *Emiliania huxleyi*, Lohmann 1902; *Gephyrocapsa oceanica*, Kamptner 1943),[1,2] and the indices reported above are based on the observation that the extent of unsaturation of the 37-carbon chain length alkenones ($C_{37}$) varies with the temperature of the water in which the algae grew.[3] The numerical expression of this relationship gave rise to the compilation of two indices, which are linearly correlated with SST, as reported in Equation (1)[3,4] and Equation (2).[5]

$$U^k_{37} = \frac{C_{37:2} - C_{37:3}}{C_{37:2} + C_{37:3} + C_{37:4}} \quad (1)$$

$$U^{k'}_{37} = \frac{C_{37:2}}{C_{37:2} + C_{37:3}} \quad (2)$$

$C_{37:2}$ represents the concentration of the heptatriaconta-15*E*,22*E*-dien-2-one (*E*,*E*-**3**), $C_{37:3}$ the concentration of the heptatriaconta-8*E*,15*E*,22*E*-trien-2-one (*E*,*E*,*E*-**2**), and $C_{37:4}$ the concentration of the heptatriaconta-8*E*,15*E*,22*E*,29*E*-tetraen-2-one (*E*,*E*,*E*,*E*-**1**) (Figure 1).

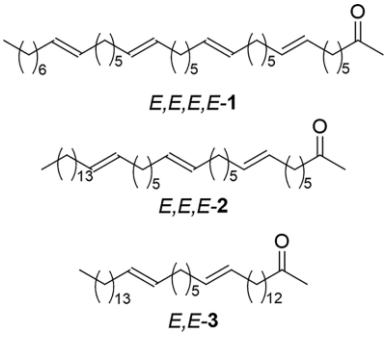



Figure 1. The structures of alkenones *E*,*E*,*E*,*E*-**1**, *E*,*E*,*E*-**2** and *E*,*E*-**3**.

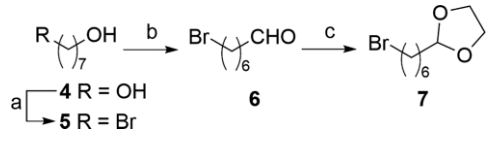
In Equation 2, the abundance of the tetra-unsaturated alkenone $C_{37:4}$ was omitted, due to its insignificant contribution to SST. However, the $C_{37:4}$ remains an important proxy index of climate change, being linked to low-salinity water masses,[6] and often employed to infer the surface advection of iceberg-bearing water masses together with their living arctic alkenone producers.[7] The discovery in the mid 1980's that the alkenone unsaturation indices recovered in sediments could provide insights into past changes in SST represented a major breakthrough in palaeoclimate research. Since then, stratigraphic variations in the $U^k_{37}$ and $U^{k'}_{37}$ recorded in ocean sediment have provided time series records of past SST change on a variety of timescales,[8,9] spanning the Cenozoic, at least since the Eocene.

[a] *Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia,*
*Via Torino 155, 30172 Mestre VE, Italy*
*E-mail: fabrisfa@unive.it*
*https://www.unive.it/data/people/5592325*
[b] *Dipartimento di Scienze Ambientali, Informatica e Statistica, Università Ca' Foscari Venezia,*
*Via Torino 155, 30172 Mestre VE, Italy*
*E-mail: piazza@unive.it*
[c] *Istituto per la Dinamica dei Processi Ambientali, Consiglio Nazionale delle Ricerche (CNR-IDPA),*
*Via Torino 155, 30172 Mestre VE, Italy*
*E-mail: sarah.pizzini@idpa.cnr.it*
[d] *Department of Chemistry, Faculty of Science, Antwerpen University, Groenenborgerlaan 17, 2020 Antwerpen, Belgium*
*E-mail: jonas.daelemans@gmail.com*
*Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.202000145.*

As with any palaeoceanographic proxy, there are still some questions that need to be addressed in order to improve the confidence in the data and enhance the reliability of the SST reconstruction. To the best of our knowledge, one of them is related to the commercial unavailability of standard compounds which represent a fundamental and inescapable requirement to develop and validate an analytical method, as well as to optimize its analytical results. The synthesis of compounds **1**–**3** was briefly presented in an early article by Rechka and Maxwell,[10] in which detailed description of the methods was postponed to a future article, so far not published, although the mass properties of these compounds were described in a second article in the same year.[11] Herein we present our methodology, that takes advantage of the synthetic improvements occurred in the meantime, allowing in most cases a safer and environmentally friendly alternative, like the use of photoisomerisation of *Z*-double bonds vs. the use of *E*-selective, but potentially noxious, chromium-based coupling reactions. Furthermore, the syntheses were extended to the preparation of the $^{13}C$-labelled analogous compounds, that could greatly improve the analytical accuracy of the measurement of alkenone concentrations, with respect to the use of the *n*-alkane hexatriacontane which is usually employed as an internal standard for this kind of determinations.[12–15] Here we report on the synthesis of heptatriaconta-15*E*,22*E*-dien-2-one (*E,E*-**3**), heptatriaconta-8*E*,15*E*,22*E*-trien-2-one (*E,E,E*-**2**), and heptatriaconta-8*E*,15*E*,22*E*,29*E*-tetraen-2-one (*E,E,E,E*-**1**; Figure 1), in order to provide compounds of high degree of purity, suitable to be used as calibration standards for analytical methods and help to ascertain the deviation in the results between laboratories. We also synthesised their $^{13}C$-labelled methyl-ketone analogous compounds, which enable quality assurance and quality control procedures, reducing bias that might occur before the instrumental analysis.

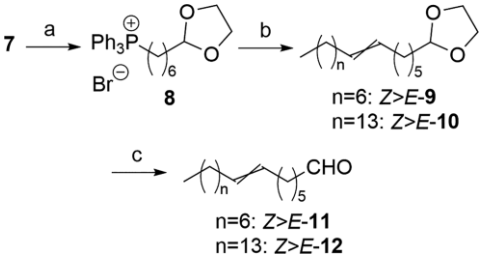
## Results and Discussion

The syntheses of compounds **1**–**3** consist in a series of Wittig reactions, starting from the suitable linear aliphatic aldehyde (i.e. octanal and pentadecanal) with a common synthon, bearing a terminal bromide and a protected aldehyde. The latter reagent has been obtained from commercially available 1,7-heptanediol in three steps (Scheme 1). The monobromination was successfully achieved in very good yields according to the methodology reported by Chong and co-workers.[16] The oxidation of the residual alcoholic moiety was obtained with a simple, efficient and environmentally friendly methodology, using commercial bleach in the presence of a catalytic amount of TEMPO.[17] The aldehyde was finally protected as 1,3-dioxolane, since conspicuous loss of material was observed in the following phosphonation step, if the aldehyde was protected as dimethyl acetal.[18] The key-reagent **7** was obtained in a reproducible 86 % overall yield in 3 steps, in a ten gram scale.



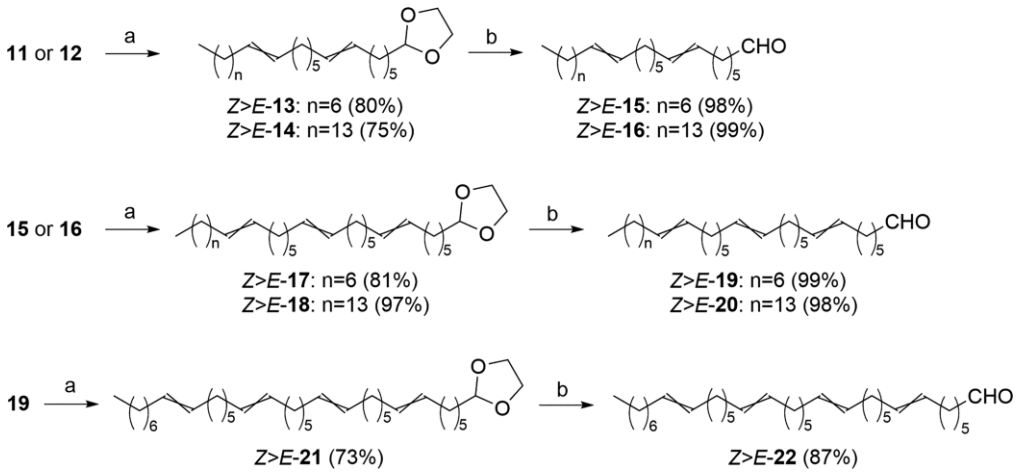

Scheme 1. Preparation of key-reagent **7**. Reagents and conditions. **a**: 48 % aq. HBr, toluene, 120 °C, 48 h (98 %); **b**: NaOCl, TEMPO (cat.), $NaHCO_3$, $H_2O$/DCM, 25 °C, 1 h (98 %); **c**: 1,2-ethanediol, PTSA (cat.), cyclohexane, 3 Å MS, 90 °C, 18 h (96 %).

The Wittig reaction turned out to be particularly troublesome, requiring an in-depth screening of the operative conditions (solvents, bases and temperatures; Scheme 2). Eventually, the best methodology turned out to be the preparation of the alkylphosphonium salt **8**[19] in acetonitrile (ACN). This solvent was finally replaced by a mixture of DMPU/THF for the reaction of formation of the phosphorus ylide, that was accomplished with *n*-butyllithium at 0 °C.[20] This temperature resulted a good compromise to limit the reactivity of the base and, at the same time, to avoid the precipitation of the reagent, that in some cases caused a decrease of the yields. The Wittig reaction produced the desired alkene moiety with remarkable *Z*-selectivity (more than 95:5, according to $^1H$ NMR integrals). This diastereoselection was considered constant for all the following Wittig reactions, that are reasonably not affected by the configuration of the previously formed double bond. The following configurations of the compounds containing two, three, and four double bonds were labelled simply as *Z*>*E*, since the contemporary presence of these double bonds led to the formation of 4, 8 or 16 diastereomers, with a high prevalence of the all-*Z*-isomer (90 %, 86 % and 81 % respectively). Although the double bonds in natural occurring alkenones **1**–**3** are all with *E* configuration, this issue was not considered crucial, since a photoisomerisation of all the alkenes in the late stage of the syntheses was planned. Hydrolyses to restore the aldehydic moieties required for the following Wittig reactions were achieved refluxing the acetals in moistened acetic acid, which resulted mild and effective (Scheme 2).



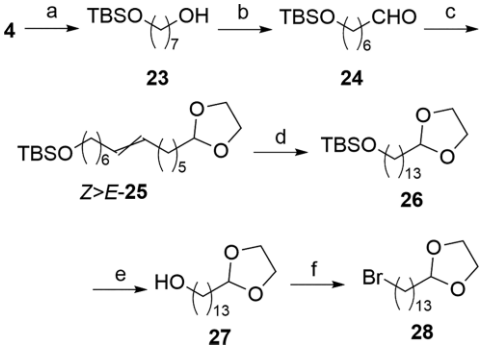

Scheme 2. First Wittig reaction for the syntheses of **1** and **2**. Reagents and conditions. **a**: $PPh_3$, ACN, 100 °C, 72 h (98 %); **b**: i) *n*BuLi, DMPU/THF, –5–0 °C, 2 h; ii) $C_7H_{15}CHO$ or $C_{14}H_{29}CHO$, 25 °C, 30 min (73 and 87 %); **c**: $H_2O$, AcOH, 110 °C, 24 h (67 % and 99 %).

Starting from aldehyde **11**, a sequential repetition for three times of the Wittig reaction with the ylide derived from phosphonium salt **8** and deprotection of the resulting acetal moieties afforded aldehyde **22**, which only requires one methyl to complete the $C_{37}$ final linear chain (Scheme 3). Similarly, starting from aldehyde **12**, a sequential repetition for two times of the Wittig reaction with the ylide derived from **7** and deprotection of the resulting acetal moieties[21] afforded aldehyde **20**, which only requires one methyl to complete the $C_{37}$ final linear chain (Scheme 3).



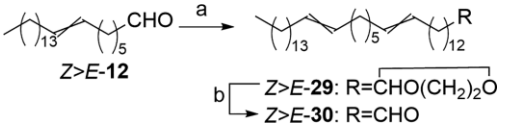

Scheme 3. Second and third Wittig reaction for the syntheses of **1** and **2** and additional fourth one for **2**. Reagents and conditions. **a**: i) **7**, $PPh_3$, ACN, 100 °C, 72 h; ii) *n*BuLi, DMPU/THF, –5–0 °C, 2 h; iii) indicated reagent, 25 °C, 30 min (indicated yields); **b**: $H_2O$, AcOH, 110 °C, 24 h (indicated yields).

In the case of compound **3**, after the first Wittig-hydrolysis sequence affording aldehyde **12**, a new reagent was required to introduce the saturated $C_{14}$ linear chain. The synthesis of the acetal-protected 14-bromotetradecanal **28** started from the commercially available 1,7-heptanediol **4** (Scheme 4), which was partially protected as *tert*-butyldimethylsilyl ether. In order to avoid a statistical distribution of mono-, di- and un-protected diol, a combination of a biphasic solvent system[22] was employed in combination with a very slow addition of the silylating reagent. The alcoholic moiety was oxidised with the previously described methodology,[17] although in low yields, presumably for an over oxidation caused by the presence of an excess of bleach. The resulting aldehyde was treated with the ylide derived from **7** and the Wittig reaction afforded the unsaturated $C_{14}$ functionalised alkyl chain *Z>E*-**25**, that was hydrogenated to remove the double bond. The TBS moiety was easily and efficiently removed with ammonium fluoride,[23] and the resulting alcohol was replaced in one step under the neutral conditions of Appel reaction, although the use of ACN was crucial for the success of the reaction.[24–26] In conclusion, the second key-reagent **28** was obtained in 31 % overall yield in 6 steps.




Scheme 4. Preparation of key-reagent **28**. Reagents and conditions. **a**: TBSCl, $Et_3N$, ACN/cyclohexane, 25 °C, 24 h (63 %); **b**: NaOCl, TEMPO (cat.), $NaHCO_3$, $H_2O$/DCM, 25 °C, 1 h (94 %); **c**: i) **7**, $PPh_3$, ACN, 100 °C, 72 h; ii) *n*BuLi, DMPU/THF, –5–0 °C, 2 h; iii) indicated reagent, 25 °C, 30 min (66 %); **d**: $H_2$ (0.1 MPa), 5 % Pd/C, AcOEt, 25 °C, 5 h (94 %); **e**: $NH_4F$, MeOH, 90 °C, 10 h (95 %); **f**: $CBr_4$, $PPh_3$, ACN, from 0 to 25 °C, 24 h (89 %).

Reagent **28** was used to generate under the previously described methodology[20] the phosphorus ylide, that reacted with *Z>E*-**12** to complete the $C_{36}$ linear chain containing two double bonds *Z>E*-**29**. The acetal moiety was removed according to the usual hydrolytic methodology to afford the aldehyde **30** (Scheme 5).

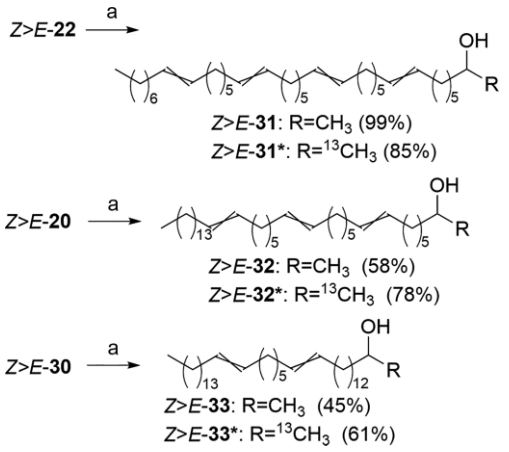



Scheme 5. Last Wittig reaction for the synthesis of **3**. Reagents and conditions. **a**: i) **28**, $PPh_3$, ACN, 100 °C, 48 h; ii) *n*BuLi, DMPU/THF, –5–0 °C, 2 h; iii) indicated reagent, 25 °C, 30 min (51 %); **b**: $H_2O$, AcOH, 110 °C, 24 h (65 %).

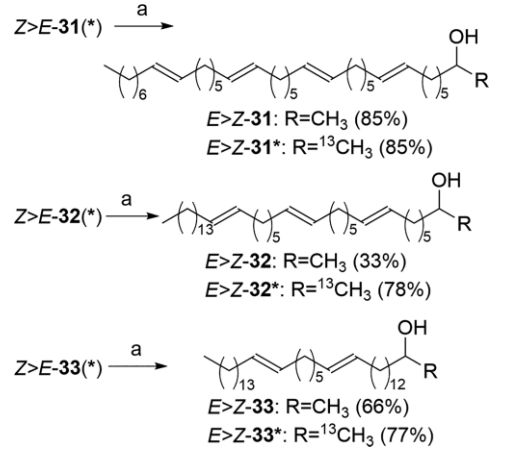
The three aldehydes *Z>E*-**22**, *Z>E*-**20** and *Z>E*-**30** were treated with Grignard reagents $CH_3MgI$ and $^{13}CH_3MgI$ in diethyl ether to afford the corresponding alcohols, eventually isotopically marked at the methyl substituent (Scheme 6).

Before oxidising compounds *Z>E*-**31**–**33**(*) to the corresponding ketones, that could suffer some Norrish I or II rearrangements, the obtained alcohols were subjected to the photoisomerisation to obtain the all-*E* isomers. The reaction was accomplished with a 500 W high pressure mercury lamp in cyclohexane, in the presence of a radical scavenger (Scheme 7).[27,28] The effectiveness of the reaction was confirmed by the 0.03 ppm down-field shifts of the main vinyl resonances in the $^1H$ NMR of the crude material (analogues 0.3 ppm down-field shifts were observed in $^{13}C$ NMR). More significantly, the resonances of the allylic carbons experienced a down-field shift of ca. 5 ppm, from nearly 27 to 32 ppm.[29]

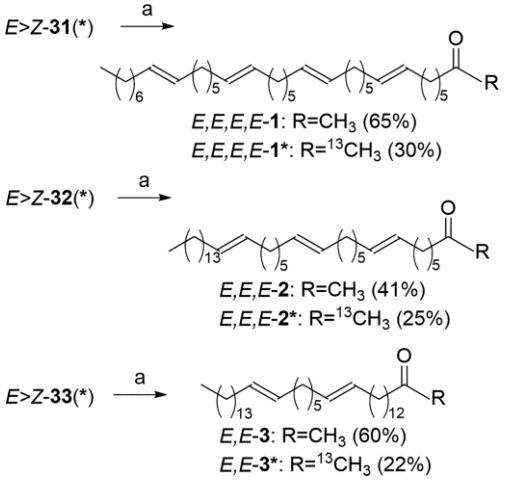
The final oxidation of the alcohols **31**–**33**(*) was accomplished by a mild Swern oxidation (Scheme 8), that does not affect the double bonds, affording the final ketones all-*E*-**1**–**3**(*), whose stereochemical purity was largely improved by a final crystallisation from hot methanol.




Scheme 6. Addition of the last fragment of the $C_{37}$ chain (eventually $^{13}C$-labelled). Reagents and conditions. **a**: i) $CH_3I$ or $^{13}CH_3I$, Mg, $Et_2O$, 40 °C, 15 min; ii) indicated reagent, 25 °C, 30 min (indicated yields).




Scheme 7. Photoisomerisation of the precursors of **1**, **2**, **3**. Reagents and conditions. **a**: PhSSPh, cyclohexane, Ar, 25 °C, 1 h (indicated yields).




Scheme 8. Final oxidative step for the syntheses of **1**, **2**, **3**. Reagents and conditions. **a**: i) $Me_2SO$, $(COCl)_2$, DCM, –78 to –40 °C, 1 h; ii) $Et_3N$, –40 to 25 °C, 1 h (indicated yields).

## Conclusion

In conclusion, compounds *E,E,E,E*-**1**, *E,E,E*-**2** and *E,E*-**3** were obtained in 11 %, 5 %, and 5 % yields after 11, 9, and 7 steps, starting from octanal in the first case and from pentadecanal in the latter cases. These compounds will be used as standards for accurate analytical measurements of their concentrations in oceanic sediments, in order to reconstruct palaeotemperature and salinity records. Furthermore, the $^{13}C$-labelled analogues compounds *E,E,E,E*-**1***, *E,E,E*-**2*** and *E,E*-**3*** were obtained in 4 %, 9 % and 3 % yields. These compounds will improve the reliability of such measurements, in virtue of the isotopic dilution procedures.

## Experimental Section

The reactions were followed with TLC Polygram® Sil G/UV254, 0.25 mm thickness. $^1H$ NMR, $^{13}C$ NMR, and 2D spectra were recorded with a Bruker Avance 300 and Ascend 400 spectrometers, working at 300–400 and 75–100 MHz respectively. Resonance frequencies are referred to tetramethylsilane. IR spectra were recorded with a Perkin Elmer Spectrum One spectrophotometer. Masses of the intermediate new products were obtained with a Bruker Compact (ESI-TOF) spectrometer. Source type: ESI Ion Polarity Positive. Set Nebuliser: 0.3 Bar. Focus Active Set Capillary: 4500 V. Set Dry Heater: 200 °C. Scan begins at 50 *m/z* and ends at 800 *m/z*. Set End Plate Offset: –500 V. Set Dry Gas: 3.5 L/min. Set Collision Cell RF: 2500.0 Vpp. A 1 mg/mL solution of sample in DCM was diluted 1:1000 into *i*PrOH containing 0.1 % trifluoroacetic acid and the solution injected by syringe pump. Masses of final products were analysed by single quadrupole GC/LRMS (Hewlett Packard-Agilent 6890 Series GC System, coupled with an Agilent 5973 inert Mass Selective Detector) operating in Electron Impact mode (EI, 70 eV) equipped with a 30 m long column (HP-5 ms, 0.25 mm I.D., 0.25 µm film thickness). The MS source and analyser were set to 230 °C and 150 °C respectively, while the transfer line was set to 300 °C. The operating conditions of the GC were optimised and set as follows. Helium 5.5 (99.9995 %) was used as carrier gas at a constant flow rate of 1.0 mL $min^{-1}$. The splitless mode inlet was set to 300 °C. The oven was programmed from 90 °C to 315 °C at 30 °C $min^{-1}$ with 17.5 min hold, for a total run time of 25 min. Acquisition was performed in Full Scan mode and perfluorotributylamine (PFTBA) was chosen as reference compound. GC/HRMS characterisation was carried out by Hewlett Packard-Agilent 6890 Series GC System, coupled with a Thermo Finnigan MAT 95 XP operating in EI mode (45 eV; R ≥ 10,000) equipped with a 15 m long column of the same type, for a total run time of 12 min. Acquisition was performed in Multiple Ion Detection (MID) mode. The MS source was set to 290 °C and the transfer line to 300 °C. PFK was selected as reference compound to provide the inherent lock (504.9691) and cali (554.9659) masses. Reagents and solvents with high purity degree purchased by the providers were used as given. Otherwise, they were purified following the procedures reported in literature.[30] Anhydrous solvents were prepared by adding activated 3 Å molecular sieves to the solvent under inert atmosphere. Molecular sieves were activated shortly before the use by continuous heating under *vacuum*. Flash chromatography were performed with silica gel Merk 60, 230–400 mesh, following procedures reported in literature.[31]

### General Procedure to Primary Alcohols Oxidation (GP1)

In a 250 mL round bottomed flask, primary alcohol (22 mmol, 1 equiv.) and TEMPO (0.01 equiv.) were dissolved in DCM (45 mL). A solution composed by aqueous 5 % NaOCl (1.4 equiv.) and satu-

rated aqueous $NaHCO_3$ (25 mL) was then poured in the flask and the resulting mixture was vigorously stirred at room temperature for 45 min, checking the reaction through TLC. The reaction was then quenched with saturated aqueous $Na_2S_2O_3$ (90 mL). The mixture was decanted and the organic phase collected. The aqueous layer was extracted with DCM (4 × 50 mL) and the combined organic phases were washed with saturated aqueous $NaHCO_3$ (2 × 50 mL), dried with $MgSO_4$, filtered and concentrated in vacuo. The recovered product was pure enough for the following steps.

**General Procedure to Wittig Reaction (GP2)**

In a 250 mL round bottomed flask, alkyl bromide (25.3 mmol, 1 equiv.) and triphenylphosphine (1.2 equiv.) were suspended in anhydrous ACN (63 mL). The flask was topped with a reflux condenser and an argon inlet, then the suspension was refluxed for 72 h, checking the reaction through TLC. The resulting solution was dried in vacuo, then DMPU (28 mL) was added. The solution was stirred under vacuum at 80 °C for 0.5 h, then cooled to room temperature. The flask was topped with a septum and purged with argon. Anhydrous THF (114 mL) was added, then the solution was cooled to –5 °C. *n*Butyllithium (1.6 M in hexane, 19 mL, 1.2 equiv.) was added dropwise with a syringe over a period of 2 h, keeping the temperature between –5 and –1 °C to avoid the formation of a precipitate. The resulting red solution was allowed to return to room temperature, then pure aldehyde (or a solution in 10 mL of cyclohexane) (0.9 equiv.) was injected rapidly. The resulting solution was stirred for 15 min at room temperature. Water (60 mL) was added and the resulting mixture was extracted with cyclohexane (3 × 30 mL). The combined organic phases were washed with water (2 × 50 mL), dried with $MgSO_4$, filtered and dried in vacuo. The crude product was purified by flash chromatography.

**General Procedure to Acetal Removal (GP3)**

In a 250 mL round bottomed flask, acetal (22 mmol, 1 equiv.) was dissolved in acetic acid (170 mL) and water (30 mL) was added. The system was purged with argon and the solution was stirred overnight at 100 °C. The resulting solution was cooled to room temperature and poured over saturated aqueous $NaHCO_3$ (160 mL) and cyclohexane (300 mL). The aqueous layer was extracted with cyclohexane (3 × 100 mL) and the collected organic layers were washed with saturated aqueous $NaHCO_3$ (3 × 110 mL). The organic phase was dried with $MgSO_4$, filtered and dried in vacuo. The crude product was purified by flash chromatography.

**General Procedure to Grignard Reaction (GP4)**

In a flame-dried 50 mL Schlenk-tube, Mg (0.21 g, 8.5 mmol) was dry-stirred for 18 h under argon. To the resulting solid anhydrous $Et_2O$ (0.5 mL) and a solution of MeI (1.0 g, 7.1 mmol) in anhydrous $Et_2O$ (5 mL) were added dropwise, keeping a steady flow in order to maintain the mixture under reflux. The resulting suspension was refluxed for an additional 0.5 h, cooled to room temperature and decanted, obtaining a fresh solution of MeMgI (nearly 1.4 M in $Et_2O$). The solution was rapidly transferred via syringe (equipped with a PE filter) to a 50 mL round-bottomed two-necked flask with argon inlet and septum containing a solution of aldehyde (2.9 mmol) in anhydrous $Et_2O$ (2 mL). The mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated aqueous $NH_4Cl$ (150 mL) and the resulting mixture was extracted with $Et_2O$ (3 × 50 mL). The combined organic phases were dried with $MgSO_4$, filtered and dried in vacuo. The crude product was purified by flash chromatography.

**General Procedure to Alcohol Isomerisation (GP5)**

In a 500 mL photochemical reactor, a solution of the secondary alcohol isomers (0.34 mmol, 1 equiv.) and diphenyl disulphide (2 equiv. for each double bond of the secondary alcohol) in cyclohexane (280 mL) was bubbled with argon for 0.5 h. The bubbling was maintained while the solution was irradiated from inside with a 500 W high pressure mercury-vapor lamp (Helios-Italquartz) in a quartz cooling jacket (a picture of the home-made photochemical apparatus is reported in the Supporting Information). The reaction was followed via $^1$H NMR, observing the vinylic signals shifting upfield. The resulting solution was concentrated in vacuo and the crude product was purified by flash chromatography.

**General Procedure to Swern Oxidation (GP6)**

In a 250 mL round bottomed two necked flask, dried following Schlenk technique and equipped with argon inlet and septum, DMSO (3 equiv.) was dissolved in anhydrous DCM (10 mL) and the solution was cooled to –78 °C. Oxalyl chloride (2 equiv.) was added dropwise and the resulting solution was stirred for 20 min at –78 °C. A solution of secondary alcohol (2.5 mmol, 1 equiv.) in anhydrous DCM (6 mL) was added dropwise, and the resulting solution was stirred for 1 hour, allowing the temperature to rise to –40 °C. Triethylamine (2.6 mL) was added and the solution was allowed to reach room temperature. The reaction was quenched in water (60 mL). The organic phase was separated and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organic phases were dried with $MgSO_4$, filtered and concentrated in vacuo to afford crude product that was purified by flash chromatography and recrystallised from methanol.

**7-Bromoheptan-1-ol** (**5**): In a 500 mL round bottomed flask, 1,7-heptandiol (10 g, 76 mmol) was dissolved in toluene (230 mL). Aqueous 48 % HBr (19 mL) was added, the flask was topped with a reflux condenser and the mixture was refluxed for 48 h. The mixture was cooled to room temperature, decanted and the organic phase was collected, washed with saturated aqueous $NaHCO_3$ (2 × 100 mL), dried with $MgSO_4$, filtered and concentrated in vacuo. The product was obtained as a colourless oil (13.8 g, 93 % yield). $R_f$ = 0.58 (silica gel, $Et_2O$); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 3.65 (2H, t, $J$ = 6.6 Hz), 3.41 (2H, t, $J$ = 6.8 Hz), 1.91–1.82 (2H, m), 1.62–1.54 (2H, m), 1.49–1.27 (6H, m). Further spectroscopic data ($^{13}$C, IR, MS) are in accordance with the literature.[16]

**7-Bromoheptanal** (**6**): **GP1** was applied to **5**. Yellow oil (12.0 g, 95 % yield). $R_f$ = 053 (silica gel, 2:8 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.77 (1H, t, $J$ = 1.7 Hz), 3.41 (2H, t, $J$ = 6.7 Hz), 2.45 (2H, td, $J$ = 7.3, 1.7 Hz), 1.92–1.81 (2H, m), 1.73–1.58 (2H, m), 1.53–1.29 (4H, m). Further spectroscopic data ($^{13}$C, IR, MS) are in accordance with the literature.[17]

**2-(6-Bromohexyl)-[1,3]dioxolane** (**7**): In a 250 mL round bottomed flask, **6** (14.2 g, 73.6 mmol), ethylene glycol (5.5 g, 88.7 mmol), and *p*-toluensulphonic acid monohydrate (0.01 g, 0.06 mmol) were dissolved in cyclohexane (140 mL). A pressure-equalising dropping funnel filled with activated 3 Å molecular sieves was placed over the flask and topped with a reflux condenser. The apparatus was purged with argon and the suspension refluxed overnight for 18 h. The resulting solution was poured over saturated aqueous $NaHCO_3$ (20 mL), decanted, and the organic layer was washed again with saturated aqueous $NaHCO_3$ (3 × 20 mL), dried with $MgSO_4$, filtered and concentrated in vacuo. The product was obtained as light orange oil (15.4 g, 97 % yield). $R_f$ = 053 (silica gel, 2:8 AcOEt/cyclohexane); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 4.85 (1H, t, $J$ = 4.8 Hz), 4.04–3.78 (4H, m), 3.41 (2H, td, $J$ = 6.8, 2.0 Hz), 1.92–1.80 (2H, m), 1.72–1.58 (2H, m), 1.56–1.25 (6 H, m). Further spectroscopic data ($^{13}$C, IR, MS) are in accordance with the literature.[17]

**2-(Tetradec-6-en-1-yl)-1,3-dioxolane** (*Z*>*E*-**9**): **GP2** was applied to octanal and **7**, eluent 5:95 AcOEt/cyclohexane, colourless oil (73 %

yield). $R_f$ = 0.36 (silica gel, 1:9 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.30 (2H, m), 4.86 (1H, t, $J$ = 4.8 Hz), 4.00–3.84 (4H, m), 2.42–2.29 (2H, m), 2.07–1.98 (4H, m), 1.70–1.62 (2H, m), 1.46–1.29 (14H, m), 0.90 (3H, t, $J$ = 6.5 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.2 (CH), 129.8 (CH), 104.8 (CH), 65.0 ($CH_2$), 34.0 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$), 27.4 ($CH_2$), 27.2 ($CH_2$), 24.1 ($CH_2$), 22.8 ($CH_2$), 14.2 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3006, 2926, 2849, 1728, 1655, 1580, 1541, 1460, 1434, 1412, 1371, 1353, 1307, 1263, 1200, 1140, 1043, 960, 949, 900, 719, 700 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + H$^+$] calcd. for $C_{17}H_{33}O_2$ 269.2448, found 269.2446.

**Pentadec-7-enal** (*Z*>*E*-**11**): **GP3** was applied to *Z*>*E*-**9**, colourless oil (67 % yield). $R_f$ = 0.36 (silica gel, 1:9 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.74 (1H, t, $J$ = 1.8 Hz), 5.39–5.27 (2H, m), 2.40 (2H, td, $J$ = 7.4, 1.9 Hz), 2.06–1.92 (4H, m), 1.66–1.57 (2H, m), 1.40–1.19 (14H, m), 0.85 (3H, t, $J$ = 6.6 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 202.7 (CH), 130.4 (CH), 129.4 (CH), 44.0 ($CH_2$), 32.0 ($CH_2$), 29.8 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 28.9 ($CH_2$), 27.3 ($CH_2$), 27.0 ($CH_2$), 22.8 ($CH_2$), 22.1 ($CH_2$), 14.2 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 3384, 2917, 2849, 1574, 1541, 1465, 1429, 784, 760 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + Na$^+$] calcd. for $C_{15}H_{28}ONa$ 247.2032, found 247.2009.

**2-(Henicosa-6,13-dien-1-yl)-1,3-dioxolane** (*Z*>*E*-**13**): **GP2** was applied to *Z*>*E*-**11** and **7**, eluent 5:95 AcOEt/cyclohexane, colourless oil (80 % yield). $R_f$ = 0.41 (silica gel, 1:9 = AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.42–5.29 (4H, m), 4.84 (1H, t, $J$ = 4.9 Hz), 4.02–3.79 (4H, m), 2.09–1.92 (8H, m), 1.75–1.54 (2H, m), 1.47–1.22 (22H, m), 0.88 (3H, t, $J$ = 6.8 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.1 (CH), 130.1 (CH), 129.9 (CH), 129.9 (CH), 104.8 (CH), 65.0 ($CH_2$, 2C), 34.1 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 3C), 29.4 ($CH_2$), 29.4 ($CH_2$, 2C), 29.1 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$, 2C), 27.2 ($CH_2$), 24.1 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 3401, 3005, 2927, 2856, 1577, 1542, 1465, 1434, 1407, 1259, 1141, 1039, 965, 784, 760 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + H$^+$] calcd. for $C_{24}H_{45}O_2$ 365.3387, found 365.3393.

**Docosa-7,14-dienal** (*Z*>*E*-**15**): **GP3** was applied to *Z*>*E*-**13**, colourless oil (98 % yield). $R_f$ = 0.41 (silica gel, 1:9 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.76 (1H, t, $J$ = 1.9 Hz), 5.41–5.28 (4H, m), 2.42 (2H, td, $J$ = 7.4, 1.9 Hz), 2.08–1.92 (8H, m), 1.69–1.58 (2H, m), 1.43–1.20 (20H, m), 0.88 (3H, t, $J$ = 6.7 Hz); $^{13}$C{$^1$H} NMR (100 MHz) $\delta$ = 202.9 (CH), 130.4 (CH), 130.1 (CH), 129.9 (CH), 129.5 (CH), 44.0 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$), 29.8 ($CH_2$), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$), 29.1 ($CH_2$), 28.9 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$), 27.3 ($CH_2$), 27.1 ($CH_2$), 22.8 ($CH_2$), 22.1 ($CH_2$), 14.3 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 3391, 2922, 2851, 1711, 1574, 1543, 1435, 1261, 1105, 1012, 785, 762 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + H$^+$] calcd. for $C_{22}H_{41}O$ 321.3152, found 321.3136.

**2-(Octacosa-6,13,20-trien-1-yl)-1,3-dioxolane** (*Z*>*E*-**17**): **GP2** was applied to *Z*>*E*-**15** and **7**, eluent 5:95 AcOEt/cyclohexane, colourless oil (81 % yield). $R_f$ = 0.46 (silica gel, 5:95 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.28 (6H, m), 4.84 (1H, t, $J$ = 4.8 Hz), 4.00–3.79 (4H, m), 2.07–1.91 (12H, m), 1.71–1.59 (2H, m), 1.47–1.20 (28H, m), 0.87 (3H, t, $J$ = 6.7 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.1 (CH), 130.1 (CH), 130.0 (CH, 2C), 129.9 (CH), 129.9 (CH), 104.8 (CH), 65.0 ($CH_2$, 2C), 34.1 ($CH_2$), 32.04 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 5C), 29.4 ($CH_2$), 29.4 ($CH_2$, 2C), 29.1 ($CH_2$, 2C), 27.4 ($CH_2$), 27.3 ($CH_2$, 4C), 27.3 ($CH_2$), 24.1 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 3399, 2926, 2854, 1577, 1543, 1456, 1429, 1251, 1209, 1006, 785, 760 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + H$^+$] calcd. for $C_{31}H_{57}O_2$ 461.4353, found 461.4342.

**Nonacosa-7,14,21-trienal** (*Z*>*E*-**19**): **GP3** was applied to *Z*>*E*-**17**, colourless oil (99 % yield). $R_f$ = 0.46 (silica gel, 5:95 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.77 (1H, t, $J$ = 1.8 Hz), 5.46–5.17 (6H, m), 2.42 (2H, td, $J$ = 7.4, 1.9 Hz), 2.08–1.94 (12H, m), 1.71–1.55 (2H, m), 1.41–1.22 (28H, m), 0.88 (3H, t, $J$ = 6.7 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 202.9 (CH), 130.4 (CH), 130.1 (CH), 130.0 (CH), 130.0 (CH), 129.9 (CH), 129.6 (CH), 44.0 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 3C), 29.8 ($CH_2$), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$), 29.1 ($CH_2$, 2C), 28.9 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$, 4C), 27.1 ($CH_2$), 22.8 ($CH_2$), 22.2 ($CH_2$), 14.3 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 2924, 2850, 1577, 1546, 1465, 1429, 1261, 1209, 1097, 1013, 794, 760 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + H$^+$] calcd. for $C_{29}H_{53}O$ 417.4091, found 417.4083.

**2-(Pentatriaconta-6,13,20,27-tetraen-1-yl)-1,3-dioxolane** (*Z*>*E*-**21**): **GP2** was applied to *Z*>*E*-**19** and **7**, eluent 5:95 AcOEt/cyclohexane, colourless oil (73 % yield). $R_f$ = 0.35 (silica gel, 5:95 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.41–5.29 (8H, m), 4.84 (1H, t, $J$ = 4.8 Hz), 4.00–3.81 (4H, m), 2.10–1.91 (16H, m), 1.70–1.60 (2H, m), 1.47–1.24 (34H, m), 0.87 (3H, t, $J$ = 6.8 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.1 (CH), 130.1 (CH), 130.0 (CH, 3C), 130.0 (CH), 129.9 (CH), 129.9 (CH), 104.8 (CH), 65.0 ($CH_2$, 2C), 34.1 ($CH_2$), 32.7 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 6C), 29.8 ($CH_2$), 29.7 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$, 2C), 29.1 ($CH_2$, 2C), 27.4 ($CH_2$), 27.3 ($CH_2$, 5C), 27.3 ($CH_2$), 24.1 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 3005, 2926, 2855, 1464, 1432, 1401, 1259, 1141, 1031, 968, 941, 801, 721 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + H$^+$] calcd. for $C_{38}H_{68}O_2$ 557.5292, found 557.5292.

**Hexatriaconta-7,14,21,28-tetraenal** (*Z*>*E*-**22**): **GP3** was applied to *Z*>*E*-**21**, eluent 5:95 AcOEt/cyclohexane, colourless oil (87 % yield). $R_f$ = 0.35 (silica gel, 5:95 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.76 (1H, t, $J$ = 1.8 Hz), 5.50–5.20 (8H, m), 2.42 (2H, td, $J$ = 7.3, 1.9 Hz), 2.09–1.94 (16H, m), 1.71–1.59 (2H, m), 1.41–1.20 (32H, m), 0.88 (3H, t, $J$ = 6.8 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 202.9 (CH), 130.4 (CH), 130.1 (CH), 130.0 (CH, 2C), 130.0 (CH), 130.0 (CH), 130.0 (CH), 129.6 (CH), 44.0 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$), 29.8 ($CH_2$, 4C), 29.7 ($CH_2$), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$), 29.1 ($CH_2$, 3C), 28.9 ($CH_2$), 27.4 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$, 4C), 27.1 ($CH_2$), 22.8 ($CH_2$), 22.2 ($CH_2$), 22.1 ($CH_2$), 14.3 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 3437, 3005, 2926, 2855, 2708, 1729, 1651, 1463, 1434, 1404, 1261, 1094, 1027, 861, 803, 721, 696 cm$^{-1}$; HRMS (ESI-TOF) *m/z*: [M + H$^+$] calcd. for $C_{36}H_{65}O$ 513.5030, found 513.5020.

**Heptatriaconta-8,15,22,29-tetraen-2-ol** (*Z*>*E*-**31**): **GP4** was applied to *Z*>*E*-**22**, colourless oil (98 % yield). $R_f$ = 0.28 (silica gel, 9:1 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.25 (8H, m), 3.79 (1H, td, $J$ = 6.6, 5.5 Hz), 2.09–1.93 (16H, m), 1.57–1.48 (2H, m), 1.48–1.23 (34H, m), 1.19 (3H, d, $J$ = 6.2 Hz), 0.87 (3H, t, $J$ = 6.7 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.1 (CH), 130.1 (CH), 130.0 (CH, 2C), 130.0 (CH, 2C), 129.9 (CH), 129.9 (CH), 68.2 (CH), 39.5 ($CH_2$), 32.7 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 5C), 29.8 ($CH_2$), 29.7 ($CH_2$), 29.4 ($CH_2$, 2C), 29.4 ($CH_2$), 29.1 ($CH_2$, 2C), 29.0 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$, 4C), 27.3 ($CH_2$), 25.8 ($CH_2$), 23.7 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 3005, 2927, 2855, 1577, 1541, 1464, 1260, 1212, 1097, 1009, 971, 784, 757 cm$^{-1}$.

**(8*E*,15*E*,22*E*,29*E*)-Heptatriaconta-8,15,22,29-tetraen-2-ol** (*E*>*Z*-**31**): **GP5** was applied to *Z*>*E*-**31**, eluent 1:9 AcOEt/cyclohexane, white waxy solid (85 % yield). $R_f$ = 0.30 (silica gel, 9:1 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.44–5.30 (8H, m), 3.84–3.74 (1H, m), 2.08–1.90 (16H, m), 1.59–1.22 (36H, m), 1.18 (3H, d, $J$ = 6.2 Hz), 0.87 (3H, t, $J$ = 6.7 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.6 (CH), 130.6 (CH), 130.5 (CH, 2C), 130.5 (CH, 2C), 130.4 (CH), 130.3 (CH), 68.3 (CH), 39.5 ($CH_2$), 32.8 ($CH_2$), 32.7 ($CH_2$, 6C), 32.7 ($CH_2$), 32.0 ($CH_2$), 29.8 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$, 3C), 29.4 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 29.0 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 25.8 ($CH_2$), 23.6 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3320, 3225, 2922, 2849, 1539, 1458, 1440, 1374, 1131, 1067, 1045,

965, 731, 688 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{37}H_{69}O$ 529.5343, found 529.5305.

**(8*E*,15*E*,22*E*,29*E*)-Heptatriaconta-8,15,22,29-tetraen-2-one** (*E,E,E,E*-**1**): **GP6** was applied to *E,E,E,E*-**31**, eluent 5:95 AcOEt/cyclohexane, white waxy solid (from hot methanol) (65 % yield). $R_f$ = 0.30 (silica gel, DCM); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.46–5.30 (8H, m), 2.41 (2H, t, *J* = 7.5 Hz), 2.13 (3H, s), 2.05–1.85 (16H, m), 1.63–1.45 (2H, m), 1.41–1.21 (32H, m), 0.88 (3H, t, *J* = 6.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 209.4 (C), 130.8 (CH), 130.6 (CH), 130.5 (CH, 2C), 130.5 (CH, 2C), 130.4 (CH), 130.1 (CH), 43.9 ($CH_2$), 32.8 ($CH_2$), 32.7 ($CH_2$, 6C), 32.5 ($CH_2$), 32.0 ($CH_2$), 30.0 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$, 6C), 29.5 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 28.9 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 23.9 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3445, 2954, 2919, 2848, 1712, 1632, 1467, 1466, 1457, 1435, 1376, 1167, 1070, 963, 720 $cm^{-1}$; GC/LRMS (EI, 70 eV) *m/z*: 526.7 ($M^+$, 1), 508.5 (0.3), 109.2 (16), 95.2 (31), 86.0 (62), 84.0 (100), 81.2 (31), 67.1 (31), 55.1 (27), 51.1 (36 %); GC/HRMS (EI, 45 eV) *m/z*: $[M]^+$ calcd. for $C_{37}H_{66}O$ 526.5114, found 526.5108; Kováts retention index 3877.[32]

**Labelled heptatriaconta-8,15,22,29-tetraen-2-ol** (*Z>E*-**31***): **GP4** was applied to *Z>E*-**22** using $^{13}C$-labelled iodomethane, eluent 5:95 AcOEt/cyclohexane, pale yellow waxy solid (85 % yield). $R_f$ = 0.28 (silica gel, 9:1 DCM/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.27 (8H, m), 3.85–3.72 (1H, m), 2.11–1.90 (16H, m), 1.48–1.24 (36H, m), 1.18 (3H, dd, *J* = 125.1, 6.2 Hz), 0.88 (3H, t, *J* = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.1 (CH), 130.1 (CH), 130.0 (CH, 2C), 130.0 (CH, 2C), 130.0 (CH), 129.9 (CH), 68.3 (CH, d, *J* = 38 Hz), 39.5 ($CH_2$), 32.7 ($CH_2$), 32.0 ($CH_2$), 29.9 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 2C), 29.8 ($CH_2$), 29.7 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$, 6C), 29.1 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$, 2C), 27.3 ($CH_2$), 25.8 ($CH_2$), 25.8 ($CH_2$), 23.7 ($^{13}CH_3$), 22.8 ($CH_2$), 22.5 ($CH_2$), 19.7 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3350, 3005, 2927, 2855, 1540, 1464, 1401, 1365, 1115, 968, 786, 762 $cm^{-1}$.

**Labelled (8*E*,15*E*,22*E*,29*E*)-heptatriaconta-8,15,22,29-tetraen-2-ol** (*E>Z*-**31***): **GP5** was applied to *Z>E*-**31***, eluent 1:9 AcOEt/cyclohexane, white waxy solid (85 % yield). $R_f$ = 0.30 (silica gel, 9:1 DCM/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.41–5.33 (8H, m), 3.84-3.74 (1H, m), 2.05–1.91 (16H, m), 1.47–1.21 (36H, m),1.18 (3H, dd, *J* = 125.2, 6.2 Hz), 0.88 (3H, t, *J* = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.6 (CH), 130.6 (CH), 130.5 (CH, 2C), 130.5 (CH, 2C), 130.4 (CH), 130.3 (CH), 68.3 (CH, d, *J* = 38 Hz), 39.5 ($CH_2$), 32.8 ($CH_2$), 32.7 ($CH_2$, 4C), 32.7 ($CH_2$), 32.0 ($CH_2$), 29.8 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$, 2C), 29.4 ($CH_2$), 29.4 ($CH_2$, 6C), 29.3 ($CH_2$), 28.8 ($CH_2$), 23.7 ($CH_2$), 23.7 ($CH_2$), 23.6 ($^{13}CH_3$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3401, 2925, 2850, 1577, 1541, 1464, 1434, 1253, 1215, 1006, 971, 784, 757 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{36}{}^{13}CH_{69}O$ 530.5376, found 530.5361.

**Labelled (8*E*,15*E*,22*E*,29*E*)-heptatriaconta-8,15,22,29-tetraen-2-one** (*E,E,E,E*-**1***): **GP6** was applied to *E,E,E,E*-**31***, eluent 5:95 AcOEt/cyclohexane, white waxy solid (from hot methanol) (30 % yield). $R_f$ = 0.30 (silica gel, DCM); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.33 (8H, m), 2.41 (2H, t, *J* = 7.5 Hz), 2.13 (3H, d, *J* = 127.0 Hz), 2.05–1.88 (16H, m), 1.61–1.52 (2H, m), 1.41–1.21 (32H, m), 0.87 (3H, t, *J* = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 209.4 (C, d, *J* = 40 Hz), 130.8 (CH), 130.8 (CH), 130.5 (CH, 2C), 130.5 (CH, 2C), 130.4 (CH), 130.1 (CH), 43.9 ($CH_2$, d, *J* = 14 Hz), 32.8 ($CH_2$), 32.7 ($CH_2$, 3C), 32.5 ($CH_2$), 32.0 ($CH_2$), 30.2 ($CH_2$), 30.1 ($CH_2$), 30.0 ($CH_2$), 30.0 ($^{13}CH_3$), 29.9 ($CH_2$), 29.8 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$, 3C), 29.6 ($CH_2$), 29.5 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 23.9 ($CH_2$), 22.8 ($CH_2$), 14.2 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3425, 2954, 2919, 2848, 1712, 1466, 1457, 1435, 1375, 1344, 1163, 1070, 963, 720 $cm^{-1}$; GC/LRMS (EI, 70 eV) *m/z*: 527.6 ($M^+$, 0.4), 109.2 (8), 95.2 (15), 86.0 (64), 84.0 (100), 81.1 (16), 67.1 (16), 55.2 (14), 51.1 (36 %); GC/HRMS (EI, 45 eV) *m/z*: $[M]^+$ calcd. for $C_{36}{}^{13}CH_{66}O$ 527.5147, found 527.5035; Kováts retention index 3876.[32]

**2-(Henicos-6-en-1-yl)-1,3-dioxolane** (*Z>E*-**10**): **GP2** was applied to **7** and pentadecanal, eluent 65:35 DCM/cyclohexane, waxy yellow solid (87 % yield). $R_f$ = 0.35 (silica gel, 1:9 AcOEt/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.39–5.32 (2H, m), 4.84 (1H, t, *J* = 4.8 Hz), 4.00–3.91 (2H, m), 3.89–3.81 (2H, m), 2.07–1.93 (4H, m), 1.71–1.59 (2H, m), 1.54–1.11 (30H, m), 0.88 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.0 (CH), 129.6 (CH), 104.7 (CH), 64.8 ($CH_2$, 2C), 33.9 ($CH_2$), 31.9 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$, 4C), 29.7 ($CH_2$, 3C), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 29.2 ($CH_2$), 27.2 ($CH_2$), 27.1 ($CH_2$), 24.0 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3004, 2922, 2853, 1730, 1651, 1577, 1540, 1466, 1437, 1409, 1377, 1358, 1305, 1259, 1207, 1141, 1044, 967, 941, 902, 721, 694 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{24}H_{47}O_2$ 367.3571, found 367.3567.

**Docos-7-enal** (*Z>E*-**12**): **GP3** was applied to *Z>E*-**10**, pale yellow oil (99 % yield). $R_f$ = 0.35 (silica gel, 1:9 AcOEt/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 9.76 (1H, t, *J* = 1.8 Hz), 5.45–5.24 (2H, m), 2.42 (2H, td, *J* = 7.3, 1.9 Hz), 2.11–1.91 (4H, m), 1.70–1.58 (2H, m), 1.47–1.15 (28H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 202.8 (CH), 130.3 (CH), 129.3 (CH), 43.9 ($CH_2$), 31.9 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$, 4C), 29.6 ($CH_2$, 2C), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 28.8 ($CH_2$), 27.2 ($CH_2$), 26.9 ($CH_2$), 22.7 ($CH_2$), 22.0 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3000, 2922, 2852, 2713, 1729, 1577, 1540, 1465, 1437, 1115, 875, 721 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{22}H_{43}O$ 323.3308, found 323.3296.

**2-(Octacosa-6,13-dien-1-yl)-1,3-dioxolane** (*Z>E*-**14**): **GP2** was applied to *Z>E*-**12** and **7**, eluent 1:1 DCM/petroleum ether, pale yellow waxy solid (75 % yield). $R_f$ = 0.36 (silica gel, 6:4 DCM/PE); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.46–5.25 (4H, m), 4.84 (1H, t, *J* = 4.8 Hz), 4.06–3.91 (2H, m), 3.90–3.76 (2H, m), 2.11–1.92 (8H, m), 1.74–1.59 (2H, m), 1.50–1.11 (36H, m), 0.88 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.0 (CH), 129.9 (CH), 129.8 (CH), 129.7 (CH), 104.7 (CH), 64.8 ($CH_2$, 2C), 33.9 ($CH_2$), 31.9 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$, 4C), 29.7 ($CH_2$, 5C), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.2 ($CH_2$), 29.0 ($CH_2$), 27.2 ($CH_2$), 27.2 ($CH_2$), 27.2 ($CH_2$), 27.1 ($CH_2$), 26.9 ($CH_2$), 24.0 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3004, 2922, 2853, 1731, 1651, 1577, 1540, 1465, 1437, 1407, 1377, 1360, 1308, 1259, 1209, 1140, 1043, 966, 941, 902, 721, 694 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $1^+$] calcd. for $C_{31}H_{59}O_2$ 463.4510, found 463.4493.

**Nonacosa-7,14-dienal** (*Z>E*-**16**): **GP3** was applied to *Z>E*-**14**, pale yellow oil (99 % yield). $R_f$ = 0.36 (silica gel, 6:4 DCM/PE); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 9.76 (1H, t, *J* = 1.8 Hz), 5.41–5.28 (4H, m), 2.42 (2H, td, *J* = 7.4, 1.9 Hz), 2.11–1.92 (8H, m), 1.74–1.54 (2H, m), 1.47–1.15 (34H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 202.7 (CH), 130.2 (CH), 130.0 (CH), 129.7 (CH), 129.4 (CH), 43.9 ($CH_2$), 31.9 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$, 4C), 29.7 ($CH_2$, 3C), 29.6 ($CH_2$), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 29.0 ($CH_2$), 28.8 ($CH_2$), 27.2 ($CH_2$), 27.2 ($CH_2$), 27.2 ($CH_2$), 26.9 ($CH_2$), 22.7 ($CH_2$), 22.0 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3004, 2922, 2852, 2712, 1729, 1651, 1578, 1541, 1465, 1437, 1407, 1344, 1305, 1198, 1182, 1119, 1026, 967, 872, 853, 740, 721, 695, 542 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{29}H_{55}O$ 419.4247, found 419.4208.

**2-(Pentatriaconta-6,13,20-trien-1-yl)-1,3-dioxolane** (*Z>E*-**18**): **GP2** was applied to *Z>E*-**16** and **7**, eluent 85:15 DCM/cyclohexane, pale yellow oil (97 % yield). $R_f$ = 0.48 (silica gel, 85:15 DCM/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.44–5.25 (6H, m), 4.84 (1H, t, *J* = 4.8 Hz), 4.03–3.90 (2H, m), 3.90–3.77 (2H, m), 2.10- 1.92 (12H, m), 1.71–1.60 (2H, m), 1.51–1.13 (42H, m), 0.88 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.0 (CH), 129.9 (CH), 129.8 (CH, 2C), 129.8 (CH), 129.7 (CH), 104.7 (CH), 64.8 ($CH_2$, 2C), 33.9 ($CH_2$), 31.9

($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$, 5C), 29.7 ($CH_2$, 6C), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 29.2 ($CH_2$), 29.0 ($CH_2$), 29.0 ($CH_2$), 27.2 ($CH_2$), 27.2 ($CH_2$, 2C), 27.2 ($CH_2$, 2C), 27.1 ($CH_2$), 24.0 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3004, 2912, 2852, 1728, 1654, 1577, 1541, 1464, 1437, 1404, 1377, 1358, 1305, 1259, 1141, 1038, 967, 938, 721, 694 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{38}H_{71}O_2$ 559.5449, found 559.5463.

**Hexatriaconta-7,14,21-trienal** (*Z>E*-**20**): **GP3** was applied to *Z>E*-**18**, pale yellow oil (98 % yield). $R_f$ = 0.48 (silica gel, 85:15 DCM/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 9.77 (1H, t, *J* = 1.8 Hz), 5.44–5.26 (6H, m), 2.42 (2H, td, *J* = 7.4, 1.9 Hz), 2.10–1.92 (12H, m), 1.72–1.58 (2H, m), 1.47–1.15 (40H, m), 0.88 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 202.9 (CH), 130.4 (CH), 130.1 (CH), 130.0 (CH), 130.0 (CH), 129.9 (CH), 129.5 (CH), 44.0 ($CH_2$), 32.1 ($CH_2$), 29.9 ($CH_2$), 29.85 ($CH_2$, 4C), 29.82 ($CH_2$, 5C), 29.7 ($CH_2$, 2C), 29.6 ($CH_2$), 29.5 ($CH_2$, 2C), 29.1 ($CH_2$), 29.0 ($CH_2$), 28.9 ($CH_2$), 27.4 ($CH_2$, 5C), 27.1 ($CH_2$), 22.8 ($CH_2$), 22.2 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3004, 2921, 2852, 2713, 1729, 1651, 1577, 1541, 1464, 1435, 1305, 1259, 1182, 1119, 1089, 1067, 1027, 993, 965, 743, 721, 695, 542 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{36}H_{67}O$ 515.5186, found 515.5148.

**Heptatriaconta-8,15,22-trien-2-ol** (*Z>E*-**32**): **GP4** was applied to *Z>E*-**20**, pale yellow waxy solid (58 % yield). $R_f$ = 0.37 (silica gel, DCM); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.42–5.28 (6H, m), 3.86 3.73 (1H, m), 2.02 (12H, q, *J* = 6.4, 5.4 Hz), 1.61–1.20 (44H, m), 1.19 (3H, d, *J* = 6.2 Hz), 0.87 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.0 (CH), 129.9 (CH), 129.9 (CH), 129.8 (CH), 129.8 (CH), 129.7 (CH), 68.1 (CH), 39.3 ($CH_2$), 31.9 ($CH_2$), 29.8 ($CH_2$), 29.7 ($CH_2$, 5C), 29.7 ($CH_2$, 6C), 29.6 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 29.0 ($CH_2$, 2C), 27.2 ($CH_2$), 27.2 ($CH_2$), 27.2 ($CH_2$, 3C), 27.1 ($CH_2$), 25.7 ($CH_2$), 23.5 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3350, 3005, 2921, 2852, 1651, 1577, 1541, 1464, 1404, 1376, 1347, 1259, 1123, 1094, 966, 941, 720 $cm^{-1}$.

**(8*E*,15*E*,22*E*)-Heptatriaconta-8,15,22-trien-2-ol** (*E>Z*-**32**): **GP5** was applied to *Z>E*-**32**, eluent 12:88 AcOEt/cyclohexane, white waxy solid (33 % yield). $R_f$ = 0.38 (silica gel, DCM); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.38 (6H, td, *J* = 3.8, 1.9 Hz), 3.86–3.73 (1H, m), 2.02 (12H, q, *J* = 6.4, 5.4 Hz), 1.61–1.20 (44H, m), 1.19 (3H, d, *J* = 6.2 Hz), 0.87 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.5 (CH), 130.4 (CH), 130.3 (CH), 130.3 (CH), 130.3 (CH), 130.2 (CH), 68.2 (CH), 39.3 ($CH_2$), 32.6 ($CH_2$), 32.6 ($CH_2$, 2C), 32.5 ($CH_2$), 31.9 ($CH_2$), 29.7 ($CH_2$, 3C), 29.7 ($CH_2$, 3C), 29.6 ($CH_2$), 29.5 ($CH_2$, 6C), 29.5 ($CH_2$), 29.4 ($CH_2$, 2C), 29.2 ($CH_2$), 29.1 ($CH_2$), 28.7 ($CH_2$), 28.7 ($CH_2$), 25.6 ($CH_2$), 23.5 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3302, 3219, 2956, 2918, 2848, 1632, 1500, 1470, 1458, 1443, 1432, 1412, 1371, 1292, 1256, 1149, 1131, 1105, 1067, 1042, 1017, 965, 927, 845, 727 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{37}H_{71}O$ 531.5499, found 531.5534.

**(8*E*,15*E*,22*E*)-Heptatriaconta-8,15,22-trien-2-one** (*E,E,E*-**2**): **GP6** was applied to *E,E,E*-**32**, eluent 6:4 DCM/cyclohexane, white waxy solid (from hot methanol) (41 % yield). $R_f$ = 0.34 (silica gel, 6:4 DCM/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.52–5.26 (6H, m), 2.41 (2H, t, *J* = 7.5 Hz), 2.21–1.84 (15H, m), 1.64–1.49 (2H, q, *J* = 8.7, 8.0 Hz), 1.29 (2H, m), 1.28–1.18 (38H, m), 0.88 (3H, t, *J* = 6.6 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 209.2 (C), 130.6 (CH), 130.4 (CH), 130.3 (CH), 130.3 (CH), 130.3 (CH), 130.0 (CH), 43.8 ($CH_2$), 32.6 ($CH_2$), 32.6 ($CH_2$, 2C), 32.5 ($CH_2$), 32.4 ($CH_2$), 31.9 ($CH_2$), 29.8 ($CH_3$), 29.7 ($CH_2$, 4C), 29.7 ($CH_2$, 4C), 29.5 ($CH_2$), 29.5 ($CH_2$, 3C), 29.5 ($CH_2$), 29.4 ($CH_2$, 2C), 29.2 ($CH_2$), 28.7 ($CH_2$), 28.7 ($CH_2$), 28.7 ($CH_2$), 23.7 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3004, 2922, 2852, 1721, 1654, 1577, 1541, 1464, 1437, 1357, 1259, 1159, 965, 720 $cm^{-1}$; GC/LRMS (EI, 70 eV) *m/z*: 528.5 ($M^+$, 2), 510.5 (2), 109.1 (52), 96.1 (60), 95.1 (99), 84.0 (95), 81.1 (100), 69.1 (60), 67.0 (85), 55.1 (80 %); GC/HRMS (EI, 45 eV) *m/z*: $[M]^+$ calcd. for $C_{37}H_{68}O$ 528.5270, found 528.5265; Kováts retention index 3887.[32]

**Labelled heptatriaconta-8,15,22-trien-2-ol** (*Z>E*-**32***): **GP4** was applied to *Z>E*-**20** using $^{13}C$-labelled methyl iodide, eluent DCM, white waxy solid (78 % yield). $R_f$ = 0.37 (silica gel, DCM); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.40–5.30 (6H, m), 3.84–3.75 (1H, m), 2.08–1.93 (12H, m), 1.46–1.24 (45H, m), 1.18 (3H, dd, *J* = 125.2, 6.2 Hz), 0.87 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.1 (CH), 130.1 (CH), 130.0 (CH), 130.0 (CH), 129.9 (CH), 129.9 (CH), 68.3 (CH, d, *J* = 39 Hz), 39.5 ($CH_2$), 32.7 ($CH_2$), 32.1 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 2C), 29.8 ($CH_2$, 4C), 29.7 ($CH_2$, 2C), 29.5 ($CH_2$, 2C), 29.4 ($CH_2$, 2C), 29.1 ($CH_2$), 29.0 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$, 5C), 25.8 ($CH_2$, 2C), 23.7 ($^{13}CH_3$), 22.8 ($CH_2$), 19.7 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3395, 2924, 2852, 1574, 1540, 1465, 1251, 1113, 1067, 1009, 784, 765 $cm^{-1}$.

**Labelled (8*E*,15*E*,22*E*)-heptatriaconta-8,15,22-trien-2-ol** (*E>Z*-**32***): **GP5** was applied to *Z>E*-**32***, eluent 9:1 DCM/cyclohexane, white waxy solid (75 % yield). $R_f$ = 0.38 (silica gel, DCM); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.32 (6H, m), 3.84–3.74 (1H, m), 2.08–1.93 (12H, m), 1.48–1.21 (45H, m), 1.18 (3H, dd, *J* = 125.1, 6.1 Hz), 0.87 (1H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.6 (CH), 130.6 (CH), 130.5 (CH), 130.5 (CH), 130.4 (CH), 130.3 (CH), 68.3 (CH, d, *J* = 39 Hz), 39.5 ($CH_2$), 32.8 ($CH_2$), 32.7 ($CH_2$), 32.7 ($CH_2$, 4C), 32.1 ($CH_2$, 2C), 29.8 ($CH_2$, 2C), 29.8 ($CH_2$, 2C), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$), 29.3 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 25.8 ($CH_2$), 23.7 ($CH_2$, 4C), 23.6 ($^{13}CH_3$), 22.8 ($CH_2$), 19.7 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3296, 3203, 3000, 2956, 2919, 2849, 1470, 1458, 1364, 1128, 965, 726 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: [M + $H^+$] calcd. for $C_{36}{}^{13}CH_{71}O$ 532.5533, found 532.5566.

**Labelled (8*E*,15*E*,22*E*)-heptatriaconta-8,15,22-trien-2-one** (*E,E,E*-**2***): **GP6** was applied to *E,E,E*-**32***, eluent 4:6 DCM/cyclohexane, white waxy solid (from hot methanol) (25 % yield). $R_f$ = 0.34 (silica gel, DCM/cyclohexane, 6:4); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.32 (6H, m), 2.41 (2H, t, *J* = 7.4 Hz), 2.13 (3H, d, *J* = 126.9 Hz), 2.04–1.91 (12H, m), 1.63–1.51 (2H, m), 1.40–1.20 (40H, m), 0.87 (3H, t, *J* = 6.7 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 209.4 (C, d, *J* = 40 Hz), 130.8 (CH), 130.6 (CH), 130.5 (CH), 130.5 (CH), 130.4 (CH), 130.1 (CH), 43.9 ($CH_2$, d, *J* = 14 Hz), 32.8 ($CH_2$), 32.7 ($CH_2$, 3C), 32.7 ($CH_2$), 32.5 ($CH_2$), 32.1 ($CH_2$), 30.1 ($CH_2$, 2C), 30.0 ($^{13}CH_2$), 29.8 ($CH_2$, 4C), 29.8 ($CH_2$, 2C), 29.7 ($CH_2$), 29.7 ($CH_2$, 2C), 29.6 ($CH_2$), 29.5 ($CH_2$, 2C), 29.3 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 28.8 ($CH_2$), 23.9 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 2955, 2918, 2848, 1712, 1466, 1456, 1435, 1375, 1163, 963, 719 $cm^{-1}$; GC/LRMS (EI, 70 eV) *m/z*: 529.6 ($M^+$, 6), 511.6 (5), 109.1 (53), 96.1 (72), 95.1 (100), 84.0 (75), 83.1 (58), 81.1 (99), 67.1 (92), 55.1 (78 %); GC/HRMS (EI, 45 eV) *m/z*: $[M]^+$ calcd. for $C_{36}{}^{13}CH_{68}O$ 529.5304, found 529.5192; Kováts retention index 3887.[32]

**7-((*tert*-Butyldimethylsilyl)oxy)heptan-1-ol** (**23**): In a 500 mL round bottomed flask, 1,7-heptandiol (4.76 g, 36 mmol), *tert*-butyldimethylsilyl chloride (5.43 g, 36 mmol), triethylamine (4.40 g, 43 mmol), acetonitrile (90 mL) and *n*-hexane (270 mL) were added and the system was purged with argon. The resulting biphasic system was vigorously stirred at room temperature for 24 h. The reaction was quenched with saturated aqueous $NH_4Cl$ (360 mL) and the resulting mixture was extracted with AcOEt (3 × 100 mL). The united organic layers were washed with water (2 × 200 mL) and dried in vacuo. The residue was purified by flash chromatography, eluting with AcOEt/cyclohexane from, 1:9 to 3:7, affording the product as a colourless oil (4.31 g, 17.5 mmol, 63 % yield). $R_f$ = 0.26 (silica gel, 2:8 AcOEt/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 3.64 (2H, t, *J* = 6.6 Hz), 3.60 (2H, t, *J* = 6.6 Hz), 1.61–1.47 (4H, m), 1.43 (1H, s), 1.44–1.23 (6H, m), 0.89 (9H, s), 0.05 (6H, s). Further spectroscopic data ($^{13}C$, IR, MS) are in accordance with the literature.[33]

**7-((*tert*-Butyldimethylsilyl)oxy)heptanal** (**24**): **GP1** was applied to **23**, yellow oil (94 % yield). $R_f$ = 0.60 (silica gel, 2:8 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.77 (1H, t, *J* = 1.8 Hz), 3.60 (2H, t, *J* = 6.5 Hz), 2.42 (2H, td, *J* = 7.4, 1.8 Hz), 1.69–1.59 (2H, m), 1.56–1.48 (2H, m), 1.40–1.30 (4H, m), 0.89 (9H, s), 0.06 (6H, s). Further spectroscopic data ($^{13}$C, IR, MS) are in accordance with the literature.[33]

**((13-(1,3-Dioxolan-2-yl)tridec-7-en-1-yl)oxy)(*tert*-butyl)dimethylsilane** (*Z*>*E*-**25**): **GP2** was applied to **7** and **24**, eluent 15:85 AcOEt/cyclohexane (66 % yield). $R_f$ = 0.20 (silica gel, 3:7 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.40–5.31 (2H, m), 4.84 (1H, t, *J* = 4.8 Hz), 4.03–3.78 (4H, m), 3.60 (2H, t, *J* = 6.6 Hz), 2.05–1.94 (4H, m), 1.70–1.60 (2H, m), 1.56–1.24 (20H, m), 0.90 (9H, s), 0.06 (6H, s); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.1 (CH), 129.9 (CH), 104.8 (CH), 65.5 ($CH_2$, 2C), 63.5 ($CH_2$), 34.1 ($CH_2$), 33.0 ($CH_2$), 29.9 ($CH_2$, 2C), 29.3 ($CH_2$, 2C), 27.3 ($CH_2$, 2C), 26.2 ($CH_3$, 3C), 25.9 ($CH_2$), 24.1 ($CH_2$), 18.5 (C), –5.1 ($CH_3$, 2C); IR (film) $\tilde{\nu}_{max}$ 3423, 2929, 2857, 2453, 1891, 1476, 1463, 1410, 1388, 1358, 1254, 1138, 1099, 1039, 1001, 973, 946, 836, 809, 775, 707, 661, 475, 466, 459 cm$^{-1}$; HRMS (ESI-TOF) *m*/*z*: [M + H$^+$] calcd. for $C_{22}H_{45}O_3Si$ 385.3132, found 385.3119.

**((13-(1,3-Dioxolan-2-yl)tridecyl)oxy)(*tert*-butyl)dimethylsilane** (**26**): A mixture of *Z*>*E*-**25** (1.75 g, 4.7 mmol) and Pd/C 5 % (20 mg) in AcOEt (50 mL) was stirred under $H_2$ atmosphere (1 atm, balloon) at room temperature for 18 h. The resulting mixture was filtered through a celite plug and washed with AcOEt. The resulting solution was concentrated in vacuo, to afford the product as colourless oil (1.65 g, 4.4 mmol, 94 % yield). $R_f$ = 0.30 (silica gel, 1:1 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.84 (1H, t, *J* = 4.8 Hz), 4.02–3.78 (4H, m), 3.59 (2H, t, *J* = 6.7 Hz), 1.68–1.19 (24H, m), 1.54–1.19 (9H, m), 0.98–0.83 (6H, m); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 104.9 ($CH_2$), 65.0 ($CH_2$), 63.5 ($CH_2$), 34.1 ($CH_2$), 33.5 ($CH_2$), 29.8 ($CH_2$, 2C), 29.7 ($CH_2$, 2C), 26.1 ($CH_3$, 3C), 25.9 ($CH_2$), 24.2 ($CH_2$), 18.5 (C), –5.1 ($CH_3$, 2C); IR (film) $\tilde{\nu}_{max}$ 2927, 2855, 1728, 1463, 1437, 1407, 1388, 1360, 1254, 1144, 1100, 1038, 1006, 940, 835, 812, 775, 721, 661, 542, 461 cm$^{-1}$; HRMS (ESI-TOF) *m*/*z*: [M + H$^+$] calcd. for $C_{22}H_{47}O_3Si$ 387.3289, found 387.3278.

**13-(1,3-Dioxolan-2-yl)tridecan-1-ol** (**27**): In a 100 mL round bottomed flask, **26** (1.65 g, 4.4 mmol), methanol (40 mL) and $NH_4F$ (1.13 g, 30.5 mmol) were added. The system was purged with argon and kept under reflux conditions for 10 h. The resulting solution was concentrated in vacuo and the crude product was purified by flash chromatography, eluting with 7:3 cyclohexane/AcOEt, affording the product as a white solid (1.13 g, 4.2 mmol, 95 % yield), m.p. 72 °C. $R_f$ = 0.22 (silica gel, 2:8 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.84 (1H, t, *J* = 4.8 Hz), 4.04–3.77 (4H, m), 3.64 (2H, t, *J* = 6.6 Hz), 1.72–1.51 (4H, set of m), 1.47–1.20 (20H, m); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 104.8 (CH), 64.9 ($CH_2$, 2C), 63.1 ($CH_2$), 34.0 ($CH_2$), 32.9 ($CH_2$), 29.7 ($CH_2$, 2C), 29.6 ($CH_2$), 29.6 ($CH_2$), 29.6 ($CH_2$), 29.5 ($CH_2$), 29.5 ($CH_2$), 25.8 ($CH_2$), 24.1 ($CH_2$); IR (KBr) $\tilde{\nu}_{max}$ 3434, 3384, 2918, 2850, 1469, 1411, 1354, 1157, 1121, 1056, 1029, 999, 956, 916, 877, 839, 801, 718, 608 cm$^{-1}$; HRMS (ESI-TOF) *m*/*z*: [M + Na$^+$] calcd. for $C_{16}H_{32}O_3Na$ 295.2244, found 295.2238.

**2-(13-Bromotridecyl)-1,3-dioxolane** (**28**): In a 100 mL round-bottomed flask, **27** (0.89 g, 3.3 mmol) and triphenylphosphine (1.1 g, 4.4 mmol) were dissolved in dry ACN (18.4 mL). The system was purged with argon and the temperature was lowered to 0 °C with an ice bath. A solution $CBr_4$ (1.43 g, 4.4 mmol) in dry ACN (4 mL) was added to the cold reaction mixture. The reaction was stirred for 24 h, allowing it to warm to room temperature. The mixture was extracted with cyclohexane (3 × 20 mL). The combined cyclohexane layers were washed with water (3 × 50 mL). The organic phase was dried with anhydrous $MgSO_4$, filtered and dried in vacuo, to afford the product as yellow oil (89 % yield). $R_f$ = 0.49 (silica gel, 1:9 AcOEt/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 4.86 (1H, t, *J* = 4.8 Hz), 4.01–3.84 (4H, m), 3.43 (2H, t, *J* = 6.9 Hz), 1.90–1.82 (2H, m), 1.71–1.64 (2H, m), 1.36–1.28 (20H, m); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 104.9 (CH), 65.0 ($CH_2$, 2C), 34.2 ($CH_2$), 34.1 ($CH_2$), 33.0 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.6 ($CH_2$), 28.9 ($CH_2$), 28.3 ($CH_2$), 24.2 ($CH_2$); IR (KBr) $\tilde{\nu}_{max}$ 2917, 2847, 1467, 1437, 1415, 1160, 1138, 1124, 1045, 1026, 935, 908, 721 cm$^{-1}$; HRMS (ESI-TOF) *m*/*z*: [M + H$^+$] calcd. for $C_{16}H_{32}BrO_2$ 335,1580, found 335.1577.

**2-(Pentatriaconta-13,20-dien-1-yl)-1,3-dioxolane** (*Z*>*E*-**29**): **GP2** was applied to *Z*>*E*-**12** and **28**, eluent 1:1 DCM/cyclohexane, pale yellow oil (51 % yield). $R_f$ = 0.30 (silica gel, 6:4 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.41–5.29 (4H, m), 4.84 (1H, t, *J* = 4.8 Hz), 4.02–3.79 (4H, m), 2.09–1.95 (8H, m), 1.70–1.54 (2H, m), 1.44–1.19 (50H, m), 0.88 (3H, t, *J* = 6.6 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.0 (CH, 2C), 129.8 (CH, 2C), 104.7 ($CH_2$), 64.8 ($CH_2$, 2C), 34.0 ($CH_2$), 31.9 ($CH_2$), 29.8 ($CH_2$, 2C), 29.7 ($CH_2$, 4C), 29.7 ($CH_2$, 5C), 29.6 ($CH_2$, 3C), 29.6 ($CH_2$, 3C), 29.4 ($CH_2$, 2C), 29.3 ($CH_2$, 2C), 29.00 ($CH_2$), 27.2 ($CH_2$, 2C), 27.2 ($CH_2$, 2C), 24.1 ($CH_2$), 22.7 ($CH_2$), 14.1 ($CH_3$); IR (film) $\tilde{\nu}_{max}$ 2917, 2849, 1577, 1540, 1471, 491, 477 cm$^{-1}$; HRMS (ESI-TOF) *m*/*z*: [M + H$^+$] calcd. for $C_{38}H_{73}O_2$ 561.5605, found 561.5554.

**Hexatriaconta-14,21-dienal** (*Z*>*E*-**30**): **GP3** was applied to *Z*>*E*-**29**, eluent 3:7 DCM/cyclohexane, pale yellow oil (65 % yield). $R_f$ = 0.30 (silica gel, 6:4 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 9.76 (1H, t, *J* = 1.9 Hz), 5.40–5.30 (4H, m), 2.41 (2H, td, *J* = 7.4, 1.9 Hz), 2.06–1.96 (8H, m), 1.68–1.58 (2H, m), 1.40–1.21 (48H, m), 0.87 (3H, t, *J* = 7.0 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 203.1 (CH), 130.11 (CH), 130.10 (CH), 130.0 (CH, 2C), 44.1 ($CH_2$), 32.1 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 4C), 29.8 ($CH_2$, 4C), 29.8 ($CH_2$, 2C), 29.7 ($CH_2$), 29.7 ($CH_2$, 2C), 29.6 ($CH_2$), 29.5 ($CH_2$, 2C), 29.5 ($CH_2$, 2C), 29.3 ($CH_2$), 29.1 ($CH_2$), 27.4 ($CH_2$, 2C), 27.3 ($CH_2$, 2C), 22.8 ($CH_2$, 2C), 22.3 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3000, 2921, 2851, 1725, 1467 cm$^{-1}$; HRMS (ESI-TOF) *m*/*z*: [M + H$^+$] calcd. for $C_{36}H_{69}O$ 518.5377, found 518.5368.

**Heptatriaconta-15,22-dien-2-ol** (*Z*>*E*-**33**): **GP4** was applied to *Z*>*E*-**30**, eluent DCM, white waxy solid (45 % yield). $R_f$ = 0.40 (silica gel, DCM); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.41–5.30 (4H, m), 3.84–3.75 (1H, m), 2.09–1.96 (8H, m), 1.49–1.22 (52H, m), 1.19 (3H, d, *J* = 6.2 Hz), 0.87 (3H, t, *J* = 6.8 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.1 (CH, 2C), 130.0 (CH, 2C), 68.4 (CH), 39.5 ($CH_2$), 32.1 ($CH_2$), 30.0 ($CH_2$), 29.9 ($CH_2$, 2C), 29.8 ($CH_2$, 11C), 29.7 ($CH_2$, 2C), 29.5 ($CH_2$, 2C), 29.5 ($CH_2$, 2C), 29.1 ($CH_2$), 27.4 ($CH_2$, 2C), 27.3 ($CH_2$, 2C), 25.9 ($CH_2$), 23.6 ($CH_3$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3400, 3340, 3003, 2918, 2850, 1469, 1345, 1136, 826, 720, 687 cm$^{-1}$.

**(15*E*,22*E*)-Heptatriaconta-15,22-dien-2-ol** (*E*>*Z*-**33**): **GP5** was applied to *Z*>*E*-**33**, eluent DCM, white waxy solid (66 % yield). $R_f$ = 0.43 (silica gel, 9:1 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.40–5.33 (4H, m), 3.84–3.74 (1H, m), 2.07–1.89 (8H, m), 1.85–1.72 (2H, m), 1.66–1.21 (50H, m), 1.19 (3H, d, *J* = 6.2 Hz), 0.87 (3H, t, *J* = 6.7 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 130.6 (CH, 2C), 130.5 (CH, 2C), 68.4 (CH), 39.5 ($CH_2$), 32.8 ($CH_2$, 2C), 32.7 ($CH_2$, 2C), 32.1 ($CH_2$, 2C), 29.8 ($CH_2$, 15C), 29.7 ($CH_2$, 3C), 29.5 ($CH_2$), 29.3 ($CH_2$), 25.9 ($CH_2$), 23.6 ($CH_3$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3429, 2981, 2849, 2346, 1626, 1462, 1133, 964, 721, 666 cm$^{-1}$; HRMS (ESI-TOF) *m*/*z*: [M + H$^+$] calcd. for $C_{37}H_{73}O$ 533.5656, found 533.5647.

**(15*E*,22*E*)-Heptatriaconta-15,22-dien-2-one** (*E*,*E*-**3**): **GP6** was applied to *E*,*E*-**33**, white waxy solid (from hot methanol) (60 % yield). $R_f$ = 0.34 (silica gel, 6:4 DCM/cyclohexane); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 5.44–5.33 (4H, m), 2.41 (2H, t, *J* = 7.4 Hz), 2.13 (3H, s), 2.05–1.89 (8H, m), 1.66–1.47 (2H, m), 1.45–1.16 (48H, m), 0.87 (3H, t, *J* = 6.6 Hz); $^{13}$C{$^1$H} NMR (100 MHz): $\delta$ = 209.5 (C, d, *J* = 40 Hz),

130.6 ($CH_2$), 130.6 ($CH_2$), 130.4 ($CH_2$, 2C), 44.0 ($CH_2$), 32.8 ($CH_2$, 2C), 32.7 ($CH_2$, 2C), 32.1 ($CH_2$, 2C), 31.1 ($CH_2$), 30.0 ($CH_3$), 29.8 ($CH_2$, 12C), 29.7 ($CH_2$, 3C), 29.6 ($CH_2$, 2C), 29.5 ($CH_2$), 29.3 ($CH_2$), 28.8 ($CH_2$), 24.0 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 2919, 2849, 1712, 1470, 1462, 1374, 1166, 963, 729, 716 $cm^{-1}$; GC/LRMS (EI, 70 eV) *m/z*: 530.6 ($M^+$, 12), 512.6 (2), 109.1 (36), 96.1 (66), 95.1 (62), 85.9 (63), 83.9 (100), 82.1 (46), 81.1 (60), 55.1 (52 %); GC/HRMS (EI, 45 eV) *m/z*: $[M]^+$ calcd. for $C_{37}H_{73}O$ 530.5427, found 530.5421; Kováts retention index 3899.[32]

**Labelled heptatriaconta-15,22-dien-2-ol** (*Z>E*-**33***): **GP4** was applied to *Z>E*-**30** using $^{13}C$-labelled iodomethane, eluent 5:95 AcOEt/cyclohexane, pale yellow waxy solid (61 % yield). $R_f$ = 0.40 (silica gel, DCM); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.40–5.30 (4H, m), 3.84–3.75 (1H, m), 2.07–1.93 (8H, m), 1.40–1.21 (52H, m), 1.18 (3H, dd, *J* = 125.1, 6.2 Hz), 0.87 (3H, t, *J* = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.1 (CH), 130.1 (CH), 129.9 (CH, 2C), 68.4 (CH, d, *J* = 38 Hz), 39.5 ($CH_2$), 32.1 ($CH_2$), 29.9 ($CH_2$), 29.8 ($CH_2$, 3C), 29.8 ($CH_2$), 29.8 ($CH_2$, 5C), 29.8 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 29.5 ($CH_2$), 29.5 ($CH_2$), 29.4 ($CH_2$, 6C), 29.1 ($CH_2$), 27.4 ($CH_2$), 27.3 ($CH_2$), 25.9 ($CH_2$), 25.9 ($CH_2$), 23.6 ($^{13}CH_3$), 22.8 ($CH_2$), 19.7 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3379, 2920, 2850, 1540, 1465, 1135, 962, 725, 670 $cm^{-1}$.

**Labelled (15*E*,22*E*)-heptatriaconta-15,22-dien-2-ol** (*E>Z*-**33***): **GP5** was applied to *Z>E*-**33***, white waxy solid (77 % yield). $R_f$ = 0.43 (silica gel, 9:1 DCM/cyclohexane); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.44–5.32 (4H, m), 3.84–3.75 (1H, m), 2.05–1.90 (8H, m), 1.37–1.22 (52H, m), 1.18 (3H, dd, *J* = 125.1, 6.2 Hz), 0.87 (3H, t, *J* = 7.1 Hz); $^{13}C\{^1H\}$ NMR (100 MHz): $\delta$ = 130.6 ($CH_2$), 130.6 ($CH_2$), 130.4 ($CH_2$, 2C), 68.4 (CH, d, *J* = 38 Hz), 39.5 ($CH_2$), 32.8 ($CH_2$, 2C), 32.7 ($CH_2$, 2C), 32.1 ($CH_2$), 29.9 ($CH_2$, 3C), 29.8 ($CH_2$, 5C), 29.8 ($CH_2$, 2C), 29.7 ($CH_2$, 2C), 29.5 ($CH_2$), 29.4 ($CH_2$, 5C), 29.3 ($CH_2$), 29.0 ($CH_2$), 28.8 ($CH_2$), 25.9 ($CH_2$, 2C), 23.6 ($^{13}CH_3$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 3437, 2919, 2849, 1654, 1635, 1470, 1462, 1382, 1127, 1089, 987, 965, 869, 842, 724 $cm^{-1}$; HRMS (ESI-TOF) *m/z*: $[M + H^+]$ calcd. for $C_{36}{}^{13}CH_{73}O$ 534.5689, found 534.5676.

**Labelled (15*E*,22*E*)-heptatriaconta-15,22-dien-2-one** (*E,E*-**3***): **GP6** was applied to *E,E*-**33***, eluent cyclohexane/AcOEt, 9:1, white waxy solid (from hot methanol) (22 % yield). $R_f$ = 0.34 (silica gel, DCM/cyclohexane, 6:4); $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 5.43–5.32 (4H, m), 2.41 (2H, t, *J* = 7.5 Hz), 2.13 (3H, d, *J* = 127.0 Hz), 2.4–1.92 (8H, m), 1.61–1.52 (2H, m), 1.38–1.19 (48H, m), 0.88 (3H, t, *J* = 6.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ = 209.5 (C, d, *J* = 40 Hz), 130.6 (CH), 130.5 (CH), 130.4 (CH, 2C), 44.0 ($CH_2$, d, *J* = 14 Hz), 32.8 ($CH_2$, 2C), 32.7 ($CH_2$, 2C), 32.1 ($CH_2$), 30.0 ($^{13}CH_3$), 29.9 ($CH_2$, 4C), 29.8 ($CH_2$, 10C), 29.7 ($CH_2$, 2C), 29.6 ($CH_2$, 2C), 29.5 ($CH_2$), 29.3 ($CH_2$), 28.8 ($CH_2$, 2C), 24.0 ($CH_2$), 23.6 ($CH_2$), 22.8 ($CH_2$), 14.3 ($CH_3$); IR (KBr) $\tilde{\nu}_{max}$ 2918, 2848, 1711, 1472, 1459, 1374, 1344, 1160, 1067, 963, 729, 718 $cm^{-1}$; GC/LRMS (EI, 70 eV) *m/z*: $[M]^+$ 531.7 (1), 109.2 (9), 96.1 (23), 95.2 (15), 86.0 (65), 84.0 (100), 81.1 (15), 55.2 (15), 51.1 (36 %); GC/HRMS (EI, 45 eV) *m/z*: $[M]^+$ calcd. for $C_{36}{}^{13}CH_{70}O$ 531.5460, found 531.5348; Kováts retention index 3898.[32]

## *Acknowledgments*

The authors acknowledge the Italian Ministry of Education, Universities and Research (MIUR) and Università Ca' Foscari di Venezia. Authors are grateful to Thomas Bassano for the graphical artwork of Table of Contents.

**Keywords:** Total synthesis · Long chain alkenones · Palaeoclimate indicators · Palaeosalinity indicators · Labelled compounds

[1] H. Lohmann, *Arch. Protistenkd.* **1902**, *1*, 89–165.
[2] E. Kamptner, *Anzeiger Der Kaiserlichen Akademie Der Wissenschaften, Mathematisch-Naturwissenschaftliche Classe* **1943**, *80*, 49–73.
[3] S. C. Brassell, G. Eglinton, I. T. Marlowe, U. Pflaumann, M. Sarnthein, *Nature* **1986**, *320*, 129–133.
[4] S. C. Brassell, R. G. Brereton, G. Eglinton, J. O. Grimalt, G. Liebezeit, I. T. Marlowe, U. Pflaumann, M. Sarnthein, *Org. Geochem.* **1986**, *10*, 649–660.
[5] F. G. Prahl, S. G. Wakeham, *Nature* **1987**, *330*, 367–369.
[6] A. Rosell-Melé, *Paleoceanography* **1998**, *13*, 694–703.
[7] A. Rosell-Melé, E. Jansen, M. Weinelt, *Global Planet. Change* **2002**, *34*, 143–152.
[8] T. D. Herbert in *Treatise on Geochemistry*, Vol. 6 (Eds.: H. D. Holland, K. K. Turekian), Elsevier-Pergamon, Oxford, **2003**, pp. 391–432.
[9] A. Rosell-Melé, E. L. McClymont, in *Proxies in Late Cenozoic Paleoceanography* (Eds.: C. Hillaire-Marcel, A. de Vernal), Elsevier, Oxford, **2007**, pp. 441–490.
[10] J. A. Rechka, J. R. Maxwell, *Tetrahedron Lett.* **1988**, *29*, 2599–2600.
[11] J. A. Rechka, J. R. Maxwell, *Org. Geochem.* **1988**, *13*, 727–734.
[12] I. Cacho, C. Pelejero, J. O. Grimalt, A. Calafat, M. Canals, *Org. Geochem.* **1999**, *30*, 557–566.
[13] A. Filippova, M. Kienast, M. Frank, R. R. Schneider, *Geochem. Geophys. Geosyst.* **2016**, *17*, 1370–1382.
[14] J. Hefter, *Anal. Chem.* **2008**, *80*, 2161–2170.
[15] J. F. López, J. O. Grimalt, *J. Am. Soc. Mass Spectrom.* **2006**, *17*, 710–720.
[16] J. M. Chong, M. A. Heuft, P. Rabbat, *J. Org. Chem.* **2000**, *65*, 5837–5838.
[17] P. A. Allegretti, E. M. Ferreira, *J. Am. Chem. Soc.* **2013**, *135*, 17266–17269.
[18] P. G. M. Wuts, T. W. Greene in *Greene's Protective Groups in Organic Synthesis*, Fourth Edition, John Wiley & Son, **2006**.
[19] Hexane homologous: A. Tatsuta, K. Kanemura, *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3248–3253.
[20] T. H. Jones, A. N. Andersen, J. C. Kenny, *Chem. Biodiversity* **2009**, *6*, 1034–1041.
[21] J. H. Babler, N. C. Malek, M. J. Coghlan, *J. Org. Chem.* **1978**, *43*, 1821–1823.
[22] B. I. Wilke, M. H. Dornan, J. Yeung, C. N. Boddy, A. Pinto, *Tetrahedron Lett.* **2014**, *55*, 2600–2602.
[23] W. Zhang, M. J. Robins, *Tetrahedron Lett.* **1992**, *33*, 1177–1180.
[24] Q. Zhang, T. Norberg, J. Bergquist, L. Baltzer, *Tetrahedron* **2010**, *66*, 4577–4586.
[25] S. Gil, M. A. Lhro, R. Mestres, M. Parra, *Synth. Commun.* **1996**, *26*, 2329–2340 (with hexane and dodecane homologues, in DCM: ineffective in our case) .
[26] A. S. Kende, B. H. Toder, *J. Org. Chem.* **1982**, *47*, 163–167 (with decane homologous, in THF: ineffective in our case) .
[27] K. Nishide, K. Shibata, T. Fujita, T. Kajimoto, C. H. Wong, M. Node, *Heterocycles* **2000**, *52*, 1191–1201.
[28] M. Yoshikawa, Y. Yokokawa, Y. Okuno, N. Murakami, *Tetrahedron* **1995**, *51*, 6209–6228.
[29] H. Rakoff, E. A. Emken, *Chem. Phys. Lipids* **1982**, *31*, 215–225.
[30] W. L. F. Armarego, C. Chai in *Purification of Laboratory Chemicals (Seventh Edition)*, Butterworth-Heinemann, Boston, **2013**.
[31] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *14*, 2923–2925.
[32] E. Kováts, *Helv. Chim. Acta* **1958**, *41*, 1915–1932.
[33] H. Bruns, J. Herrmann, R. Müller, H. Wang, I. Wagner Döbler, S. Schulz, *J. Nat. Prod.* **2018**, *81*, 131–139.