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RESEARCH ARTICLE

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Synthesis of ^{13}C-labelled ω-hydroxy carboxylic acids of the general formula $HO_2{}^{13}C$-$(CH_2)_n$-CH_2OH or HO_2C-$(CH_2)_n$-$^{13}CH_2OH$ ($n = 12, 16, 20, 28$)

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^{13}C-labelled ω-hydroxy-carboxylic acids $HO_2{}^{13}C$-$(CH_2)_n$-CH_2OH or HO_2C-$(CH_2)_n$-$^{13}CH_2OH$ ($n = 12$, 16, 20, 28) with ^{13}C labels selectively introduced either at the carboxy group or at the primary alcohol function at the end of the hydrocarbon chain have been synthesized. Different synthetic strategies had to be applied depending on the position of the label, the chain length of the respective synthetic target and due to economic considerations. ^{13}C labels in general were introduced by nucleophilic substitution of a suitable leaving group with labelled potassium cyanide and subsequent hydrolysis of the nitriles to produce the corresponding labelled carboxy functions, which may also be reduced to give the labelled primary alcohol group. All new compounds are characterized by GC/MS, IR and NMR methods as well as by elemental analysis.

KEYWORDS

^{13}C labelling, cutin, fatty acids, suberin, ω-hydroxy-carboxylic acids

1 | INTRODUCTION

Cutin and suberin are naturally occurring polyesters being present in plants either in the cuticle or in the roots acting as the aerial interface between the plant's organs and the atmosphere or as a barrier between the plant and the soil environment.[1–11] As a consequence of being described as polyesters, cutin and suberin are composed of monomeric organic residues containing either alcohol functions or carboxylic groups.[1,12–15] Next to unsubstituted fatty acids α,ω-dicarboxylic acids, ω-hydroxy fatty acids, alkane-1-ols and α,ω-alkanediols, varying amounts of gylcerol are observed in cutin and suberin. In addition, there are fatty acid derivatives exhibiting epoxy or one or two hydroxy groups as additional functional groups in the middle of the hydrocarbon chain. Chain lengths of 16 or 18 carbon atoms are most common for the above mentioned constituents of cutin and suberin although chain lengths up to 26 carbon atoms have also been observed regularly.[1,13] In addition, there are also significant amounts of aromatic building blocks like ferulate and in most cases to a lower extend coumarate, sinapate or caffeate.[14,16–19]

In contrast to hydrolysable lipid sources in soil, studies of microbial transformation of cutin and suberin are almost absent.[20,21] Microbial utilization of specific precursors, de novo synthesis of individual compounds as well as transformation and recycling of existing lipids are known to occur in pure culture systems but have rarely been investigated in soils.[22–25] This is in particular due to

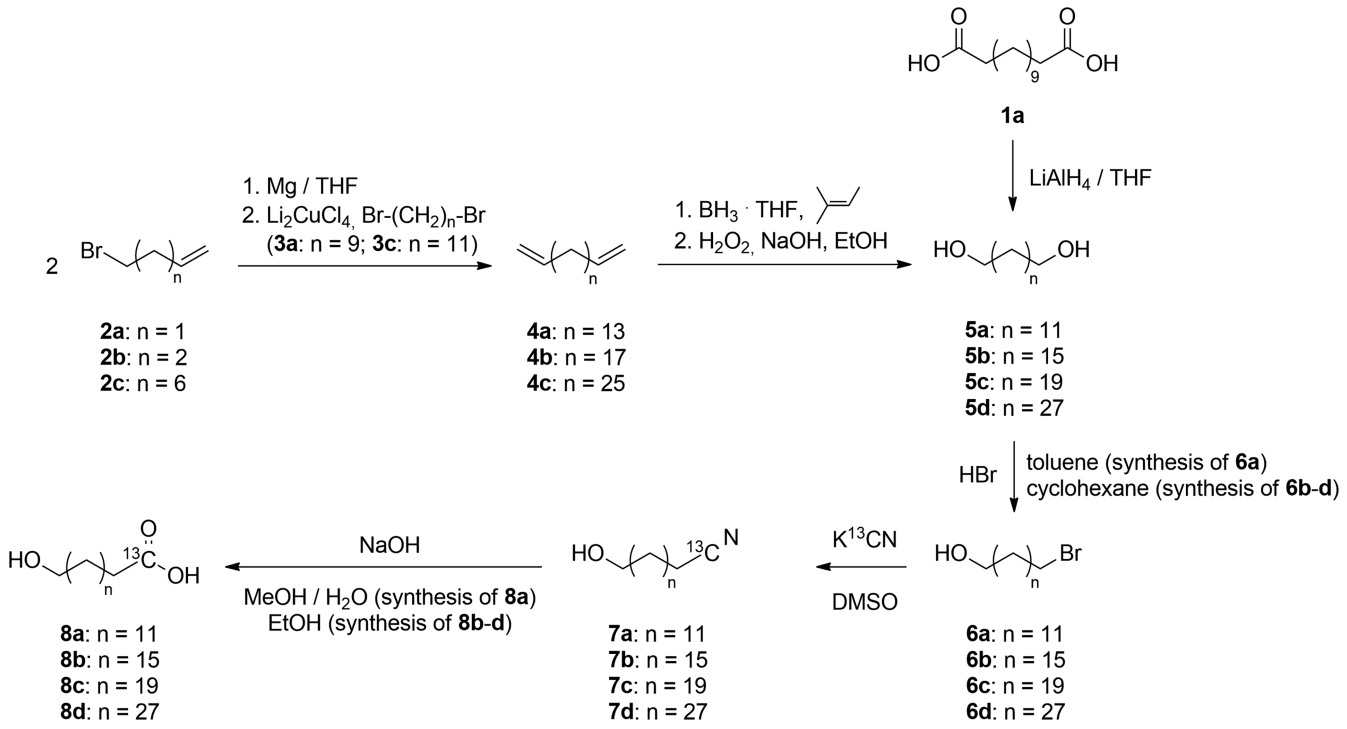
the lack of commercially available labelled monomers that might be used as markers, for example, in $^{13}CO_2$ arising from the catabolic use of the respective monomers or for the identification of compounds derived from the chemical transformation of these compounds. Our research goal focuses more on the life cycle of these lipid materials—after they have been produced by the degradation of cutin and suberin—and on their recycling by soil-based microorganisms. In a preceding paper, we already presented the synthesis of ^{13}C-labelled dicarboxylic acids of the general formula $HO_2{}^{13}C\text{-}(CH_2)_n\text{-}{}^{13}CO_2H$ ($n = 10, 12, 14, 16, 18, 20, 22, 24, 26, 28$).[26] In the present paper, we will describe strategies for the synthesis of ω-hydroxy-carboxylic acids $HO_2{}^{13}C\text{-}(CH_2)_n\text{-}CH_2OH$ or $HO_2C\text{-}(CH_2)_n\text{-}{}^{13}CH_2OH$ ($n = 12, 16, 20, 28$) with ^{13}C labels selectively introduced either at the carboxy group or at the primary alcohol function at the end of the hydrocarbon chain.

2 | RESULTS AND DISCUSSION

In a preceding paper describing the synthesis of labelled dicarboxylic acids, we were able to show that the use of $K^{13}CN$ was the optimal choice to introduce ^{13}C by nucleophilic substitution of a suitable leaving group.[26] This strategy turned out to be advantageous with respect to the use of other C_1 building blocks as ^{13}CO or $^{13}CO_2$, which would need organometallic catalysts and polar solvents.[27–29] In addition, solid $K^{13}CN$ is more easily handled than gaseous reagents, and the exact stoichiometry also is easily adjusted. This is why $K^{13}CN$ has also been used for the synthesis of labelled calcitroic acid.[30] Nevertheless, compared with the synthesis of dicarboxylic acids by the reaction of two equivalents of $K^{13}CN$, it has to be kept in mind that due to the use of only one equivalent of $K^{13}CN$ for the synthesis of the compounds described in this contribution, all intermediates before the introduction of the label have to show an odd number of carbon atoms.

2.1 | Synthesis of ω-hydroxy carboxylic acids $HO_2{}^{13}C\text{-}(CH_2)_n\text{-}CH_2OH$ ($n = 12, 16, 20, 28$)

Scheme 1 shows the synthetic strategies that led to the synthesis of ω-hydroxy carboxylic acids $HO_2{}^{13}C\text{-}(CH_2)_n\text{-}CH_2OH$ ($n = 12, 16, 20, 28$), **8a–d**, showing the ^{13}C label at the carboxy group. The crucial intermediates were the ω-bromo-alcohols, **6a–d**, in which the carbon chains already show the desired chain length and which exhibit two different functional groups in α- and ω-position, respectively, that allow for the selective transformation of either of those into the desired functional groups in the final product.



SCHEME 1 Synthetic pathway to ω-hydroxy carboxylic acids $HO_2{}^{13}C\text{-}(CH_2)_n\text{-}CH_2OH$ ($n = 12, 16, 20, 28$), **8a–d**

The synthesis of **8a** representing the product with the shortest carbon chain length may be started from the corresponding tridecanoic dicarboxylic acid, **1a**. In contrast to **1a**, dicarboxylic acids with 17, 21 or 29 carbon atoms that would have been needed to synthesize **8b–d** according to the same strategy are either not commercially available or extremely expensive. The corresponding ω-bromo-alcohols, **6b–d**, therefore had to be synthesized from starting compounds with a lower number of carbon atoms. Our first idea to elongate shorter ω-bromo-alcohols protected at the alcohol function by a Grignard reaction with a suitable α,ω-dibromo-alkane failed. We therefore treated two equivalents of commercially available ω-bromo-alkenes with magnesium to get the respective Grignard compounds, which were then coupled with a suitable α,ω-dibromo-alkane in the presence of lithium tetrachlorocuprate as the catalyst to produce the α,ω-dienes **4a–c**. This means that the reaction of 4-bromo-but-1-ene, **2a**, with dibromo-1,9-nonane, **3a**, produced 1,16-heptadecadiene, **4a**. In analogy, 5-bromo-pent-1-ene, **2b**, upon treatment with 1,11-dibromo-undecane, **3c**, gave heneicosane-1,20-diene, **4b**, and the reaction of 9-bromo-non-1-ene, **2c**, with 1,11-dibromo-undecane, **3c**, allowed the isolation of nonacosane-1,29-diene, **4c**. In order to avoid side products from the reaction of only one equivalent of the Grignard compound with dibromide, the corresponding ω-bromo-alkenes, **2a–c**, were introduced into the reaction in a slight excess. Reaction times had to be increased to 18 h as GC/MS measurements after shorter reaction times showed that there still were side products from mono-coupling as well as non-reacted dibromide present. Due to additional contamination with alkenes of undesired chain lengths from transmetallation side reactions, chromatography became tedious. Small fractions were taken and analysed, and impure fractions were repurified a second or even a third time. This procedure led to samples of **4a–c** of high purity and gave combined yields of 71% (**4a**), 85% (**4b**) and 77% (**4c**).

Conversion of the α,ω-dienes, **4a–c**, into the corresponding α,ω-diols, **5b–d**, was achieved according to a procedure published by Drescher et al. by hydroboration using disiamylborane, which has to be freshly prepared immediately before use followed by a workup with hydrogen peroxide under basic conditions.[31,32] This procedure regioselectively led to the anti-Markovnikov products in high yields. Compounds **5b** (90%) and **5c** (88%) could be purified by column chromatography whereas **5d** (93%) was crystallized from THF. The shortest α,ω-diol, **5a**, could be synthesized by reduction of the corresponding dicarboxylic acid, **1a**, with $LiAlH_4$ and was isolated in 97% yield after recrystallization from a heptane/methanol mixture.

Reaction of the α,ω-diols, **5a–d**, with concentrated hydrobromic acid led to a nucleophilic substitution of one of the hydroxo groups against a bromine atom and therefore allowed the isolation of the ω-bromo-alcohols, **6a–d**. Nevertheless, it has to be pointed out that the reaction proceeded very slowly with reaction times of up to 72 h and additional portions of hydrobromic acid had to be added in order to achieve satisfactory yields. Compounds **6a–c** were purified by column chromatography whereas crude **6d** precipitated from the reaction mixture upon the addition of water. The resulting solid was then recrystallized from a mixture of light petroleum and ethanol. The ω-bromo-alcohols were obtained in yields of 71% (**6a**), 77% (**6b**), 69% (**6c**) and 55% (**6d**).

In the ω-bromo-alcohols, the bromine atom is a much better leaving group in nucleophilic substitution reactions than the hydroxo group allowing for the selective substitution of only one of the functional groups. Reaction with cyanide ions in DMSO therefore led to the isolation of ω-hydroxo-nitriles **7a–d**. The reaction conditions were modified compared with a literature procedure of Jiménez et al.[33] Because $K^{13}CN$ is quite expensive, we reduced the amount from three equivalents in the original paper to only a slight excess of 1.05 equivalents. Nevertheless, reaction times then had to be drastically increased from 24 to 72 h, and reaction temperatures had to be raised from room temperature to 70°C. In addition, the reactions had to be monitored by GC/MS in order to prove that the transformation is complete. The compounds were isolated in excellent yields after chromatographic workup (^{13}C-labelled compounds are marked with an asterisk *: **7a**: 95%; **7a***: 96%; **7b**: 94%; **7b***: 95%; **7c**: 95%; **7c***: 94%; **7d**: 94%; **7d***: 95%). Successful labelling could easily be demonstrated by ^{13}C-NMR spectroscopy. In comparison with the spectrum of the analogous compound of a ^{12}C-cyano group, the signal for the carbon atom of the cyano group at 120.0 ppm is the peak of highest intensity in the spectrum of the labelled compound. In addition, the signal at 17.2 ppm representing the methylene group directly attached to the cyano group is split up to a dublett by carbon–carbon coupling ($^1J_{CC} = 56.04$ Hz). Signals for the next methylene groups are also split up, although $^2J_{CC}$ and $^3J_{CC}$ coupling constants as expected are much smaller (cf. Section 4 and supporting information). Similar observations can be made in the ^{1}H-NMR spectra of ^{12}C-**7a** and ^{13}C-**7a**. In ^{12}C-**7a**, the methylene groups directly attached to the hydroxo group and the cyano group both give tripletts upon coupling of the homotopic hydrogen atoms with the two hydrogen atoms of the next methylene group. In the corresponding spectrum of ^{13}C-**7a**, the signal of the methylene group next to the hydroxo function still is observed as a triplett whereas the signal representing the

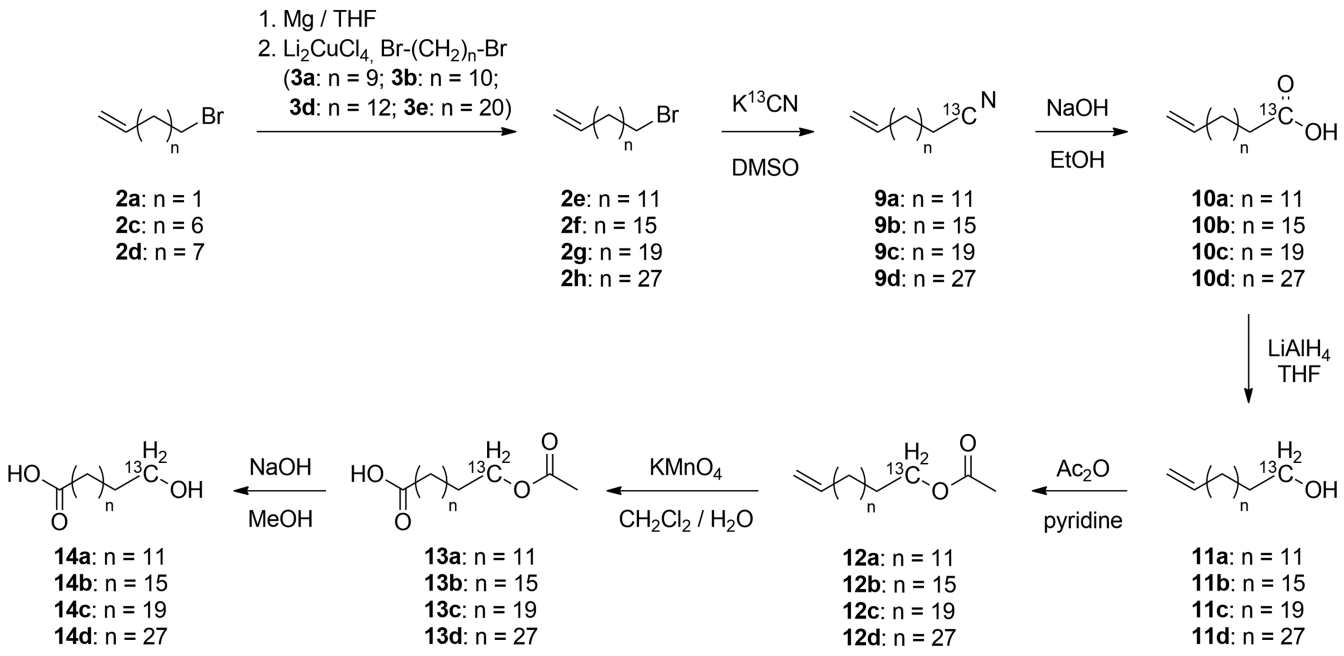
methylene group next to the labelled cyano group now is split up into a complex signal by additional coupling of the methylene hydrogen atoms with the ^{13}C atom of the cyano group.

The target compounds **8a–d** were now easily accessible by hydrolysis of the ω-hydroxo-nitriles, **7a–d**, to produce the corresponding ω-hydroxo carboxylic acids. In principle, hydrolysis of nitriles might be performed under basic or acidic conditions. We chose basic conditions because we expected side reactions of the alcohol functions in the presence of strong acids. In contrast to a similar reaction reported in the literature, reaction times had to be drastically increased (up to 24 h instead of 5 h) and the workup procedures had to be adjusted according to the significant longer carbon chain lengths.[34] Instead of an extractive workup, we added water to the reaction mixture and adjusted the pH to 1 leading to the precipitation of the crude products. Compounds **8a–d** were then recrystallized from a mixture of ethyl acetate and light petroleum. Under the reported conditions, the ω-hydroxo carboxylic acids, **8a–d**, are isolated in good yields (**8a**: 86%; **8a***: 89%; **8b**: 88%; **8b***: 91%; **8c**: 89%; **8c***: 93%; **8d**: 90%; **8d***: 87%).

2.2 | Synthesis of ω-hydroxy carboxylic acids HO_2C-$(CH_2)_n$-$^{13}CH_2OH$ ($n = 12$, 16, 20, 28)

Scheme 2 shows the synthetic strategies we used to obtain ω-hydroxy carboxylic acids, **14a–d**, with a ^{13}C label at the primary alcohol function. It is obvious that the incorporation of the label by $K^{13}CN$ followed by a hydrolytic reaction to produce a labelled carboxy group and subsequent reduction will lead to the desired labelled primary alcohol group. Nevertheless, in the target compounds, there is another carboxy group that should remain non-labelled and that would also be reduced in the final reaction step. The label therefore had to be introduced in an early stage of the synthetic procedure before the non-labelled carboxylic group had to be built up in an alternative way.

Compounds **2e–h** that already show the desired number of carbon atoms were produced from shorter ω-bromo-alkenes as the substrates via the route already depicted in Scheme 1. Nevertheless, in contrast to the procedure shown before, now an equimolar amount of the ω-bromo-alkene and the corresponding α,ω-dibromo-alkane had to be used to still have one bromine substituent present in the product molecules. So the reaction of 4-bromo-but-1-ene, **2a**, with 1,10-dibromodecane, **3b**, produced 14-bromo-tetradec-1-ene, **2e**. If 9-bromo-non-1-ene, **2c**, was treated with 1,9-dibromononane, **3a**, 19-bromo-nonadec-1-ene, **2f**, was formed. In case of 10-bromo-dec-1-ene, **2d**, as the substrate, the reaction with 1,12-dibromododecane, **3d**, yielded 22-bromo-docos-1-ene, **2g**, whereas the reaction with 1,20-dibromoeicosane, **3e**, ended up in the formation of 30-bromo-triacont-1-ene, **2h**. All α,ω-dibromo-alkanes were commercially available with the exception of 1,20-dibromoeicosane, **3e**, which was available in two steps from icosanedioc acid via reduction with $LiAlH_4$ and subsequent bromination with HBr/Ac_2O.



SCHEME 2 Synthetic pathway to ω-hydroxy carboxylic acids HO_2C-$(CH_2)_n$-$^{13}CH_2OH$ ($n = 12$, 16, 20, 28), **14a–d**

The ω-bromo-alkenes **2e–h** were used as the starting compounds to introduce the ^{13}C label by nucleophilic substitution of the bromine substituents against cyano groups. In analogy to the above mentioned synthesis of **7a–d**, the reaction was performed in DMSO and was monitored by GC/MS, which led to reaction times of 72 h until the reaction was completed. After extraction of the crude products, **9a–c** were purified by column chromatography and **9d** by recrystallization from light petroleum, thus obtaining the products in good to excellent yields (**9a**: 91%; **9a***: 88%; **9b**: 89%; **9b***: 91%; **9c**: 92%; **9c***: 95%; **9d**: 84%; **9d***: 89%).

Hydrolysis of the ω-cyano-alkenes **9a–d** was again performed in an ethanolic sodium hydroxide solution due to the good performance of these conditions in the synthesis of **8a–d**. The crude products were purified by column chromatography (**10a**) or by recrystallization from a mixture of ethyl acetate and light petroleum (**10b–d**). In all cases, excellent yields of the corresponding ω-alkenyl-carboxylic acids were realized (**10a**: 93%; **10a***: 96%; **10b**: 90%; **10b***: 93%; **10c**: 93%; **10c***: 91%; **10d**: 84%; **10d***: 93%).

The intermediates **11a–d** were then obtained by reduction of **10a–d** with $LiAlH_4$, which does not reduce electron-rich isolated double bonds and was therefore expected to leave the terminal alkenyl groups unreacted without having to protect them.[35] Purification was done either by column chromatography (**11a–c**) or by recrystallization from a mixture of ethyl acetate and light petroleum (**11d**). Also in this stage, yields were highly satisfactory (**11a**: 93%; **11a***: 90%; **11b**: 95%; **11b***: 96%; **11c**: 92%; **11c***: 94%; **11d**: 84%; **11d***: 92%). In the ^1H-NMR spectra of the ω-alkenyl-alcohols **11a–d**, the most significant signal is related to the methylene group in which the carbon atom is the ^{13}C label. Protons of this group due to coupling with the two hydrogen atoms of the next methylene groups are expected to be observed as a triplett. Because of the additional coupling with the ^{13}C atom in the spectra, a doublet of tripletts is observed ($^1J_{CH} = 140.9$ Hz). Nevertheless, it gets obvious from the spectra that some of the $K^{13}CN$ samples that we used in the synthesis of a series of the compounds did not have the purity (99%) that we had expected according to the specifications of the supplier. Next to the doublet of tripletts, we in all cases observed a small triplett in the middle that results from a compound in which the corresponding carbon atom is ^{12}C and no $^1J_{CH}$ coupling occurs. As we used three different samples for the synthesis of the labelled compounds, we observed three different values for the isotopic purity, which is easily accessible by integration of the doublett of tripletts ($^{13}CH_2$ group) and the small triplett ($^{12}CH_2$ group). For all compounds **11a***–**14a***, the isotopic purity was 84%, for **11b***,**c***–**14b***,**c*** 92% and for **11d***–**14d*** 99%. Because there is no way to exchange ^{13}C against ^{12}C in the reaction sequence, obviously, only one of the $K^{13}CN$ samples had the correct purity whereas the others showed lower purities (cf. supporting information).

Protection of the carboxy groups in **11a–d** was achieved by esterification with acetic anhydride in pyridine using a bigger excess of acetic anhydride and working at higher temperatures compared with the published procedure, thus significantly shortening reaction times.[36] The ω-alkenyl acetates **12a–d** were purified by column chromatography and were obtained in high to excellent yields (**12a**: 91%; **12a***: 94%; **12b**: 97%; **12b***: 94%; **12c**: 93%; **12c***: 96%; **12d**: 86%; **12d***: 84%).

Oxidative cleavage of the terminal carbon–carbon double bond leads to the formation of the final carboxyl group and also reduces the carbon chain length by one carbon atom (ending up as formic acid). This also is the reason why all intermediates so far showed one carbon atom more than the desired number in the final products. For economical as well as toxicological reasons, we chose $KMnO_4$ as the oxidative agent although the reaction would also been possible with RuO_4 or OsO_4.[37–39] After extraction, the ω-acetoxy carboxylic acids purified by column chromatography (**13a–c**) whereas **13d** was filtered directly from the reaction mixture and was recrystallized from a mixture of ethyl acetate and light petroleum. Observed yields were identical or even better than those reported in the literature (**13a**: 80%; **13a***: 75%; **13b**: 83%; **13b***: 85%; **13c**: 86%; **13c***: 82%; **13d**: 82%; **13d***: 81%). All spectroscopic evidence showed that the protective group at the labelled primary alcohol function stayed intact during the reaction and that there was no oxidation of this functional group to give another carboxyl group.

The final step on the way to ω-hydroxy carboxylic acids **14a–d** is a saponification of the ester group in **13a–d** using a concentrated solution of sodium hydroxide in methanol.[40] According to a monitoring of the reaction, it could be shown that a reaction time of 5 days (7 days for the reaction of **13d**) is needed to completely remove the protective group. Adjusting pH of the resulting solution to 1 leads to a precipitation of the resulting ω-hydroxy carboxylic acids, **14a–d**, which were collected by filtration and recrystallized from a mixture of ethyl acetate and light petroleum in acceptable to excellent yields (**14a**: 85%; **14a***: 89%; **14b**: 89%; **14b***: 93%; **14c**: 94%; **14c***: 91%; **14d***: 62%).

3 | CONCLUSIONS

In conclusion, we presented high yielding syntheses of ^{13}C-labelled ω-hydroxy carboxylic acids with chain lengths of 14, 18, 22 and 30 carbon atoms, either labelled at the carboxy functionality or adjacent to the hydroxo group. The label always is introduced by the use of

economically benign $K^{13}CN$. In case of carboxy group labelling, the label could be introduced at a late stage of the synthesis whereas the label had to be introduced at an earlier stage if it was situated adjacent to the hydroxyl group.

4 | EXPERIMENTAL

4.1 | General

All chemicals and solvents have been purchased from Sigma-Aldrich, ABCR, Acros Organics, Alfa Aesar, TCI and VWR and were used without further purifications after having checked their purity by spectroscopic methods. Deuterated solvents for NMR spectroscopy and $K^{13}CN$ (99%, cf. supporting information) have been purchased from Deutero GmbH, Kastellaun, Germany. Anhydrous diethylether and THF were obtained by heating the respective solvent over sodium/benzophenone. Freshly distilled portions were introduced to reaction mixtures in which anhydrous solvents had to be used. Preparative column chromatography was performed at silica 60 (particle size 0.040–0.063 mm) from Macherey & Nagel. Colourless compounds were detected by UV light. IR spectra were recorded at 298 K using a Shimadzu IR Prestige-21 FTIR spectrometer with a MIRacle ATR unit from PIKE Technologies. GC-MS spectra were recorded by a Finnigan MAT GCQ system equipped with a Macherey & Nagel GC column (5% diphenylsiloxane, 95% dimethylsiloxane, length 30 m, inner diameter 0.25 mm, film thickness 0.25 μm). NMR spectra were obtained by the use of either a Bruker Avance 400, a Bruker Avance DRX 600 or a JEOL JNM-ECZ500R spectrometer. CHN analyses were performed for compounds that so far had not been described in the literature using a vario EL III or a vario MICRO cube analyser both purchased from Elementar Analysensysteme GmbH.

In the following reaction protocols and spectroscopic data for labelled compounds (marked with an asterisk *) are shown. Synthetic procedures and analytical data for all other intermediates and products with a natural distribution of isotopes are given in the supporting information.

4.2 | Synthesis and characterization of the ω-hydroxynitriles 7a*–d* (modified after Jiménez et al.[33])

In a 50-ml round flask equipped with a reflux condensor, the ω-bromoalcohol was suspended in 10 ml of DMSO (358 mg, 1.28 mmol **6a**; 429 mg, 1.28 mmol **6b**; 501 mg, 1.28 mg **6c**; 420 mg, 0.83 mmol **6d**, the latter being suspended in 15 ml of DMSO). Afterwards, the corresponding amount of $K^{13}CN$ was added (1.35 mmol, 89-mg $K^{13}CN$ in case of the reaction of **6a–c**; 0.88 mmol, 58-mg $K^{13}CN$ in case of the reaction of **6d**), and the reaction mixture heated to 70°C (85°C for the reaction of **6d**) for 3 days. ω-Bromoalcohols dissolved completely upon heating. After the reaction time expired, the reaction mixture was allowed to reach room temperature before it was poured into 50 ml of water and was then extracted four times with 50-ml ethyl acetate each. In case of the synthesis of **7d***, the extraction was performed four times with 60 ml of chloroform each. The combined organic phases were washed with brine and subsequently with water, dried over Na_2SO_4, filtered and evaporated to dryness under reduced pressure. Purification of **7a*–c*** was achieved by column chromatography using a mixture of light petroleum and ethyl acetate (1:3) and yielded the compounds as colourless, crystalline solids (**7a***: 278 mg, 96%; **7b***: 343 mg, 95%; **7c***: 407 mg, 94%). Purification of **7d*** was performed by column chromatography using chloroform as the eluent. The resulting crude product was then recrystallized from a mixture of light petroleum and ethanol by first suspending the compound in boiling light petroleum before adding just the appropriate amount of ethanol to dissolve the compound. After standing in the refrigerator overnight, **7d*** was obtained as colourless crystals, which were filtered, washed with 3-ml light petroleum and dried under reduced pressure (**7d***: 356 mg, 95%).

4.2.1 | [1-^{13}C]14-Hydroxytetradecanenitrile (**7a***)

m.p. 51–52°C; ^{1}H-NMR (600 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.26–1.38 (m, 16 H, $HOCH_2CH_2(C\underline{H}_2)_8CH_2CH_2CH_2{}^{13}CN$), 1.41–1.48 (m, 2 H, $C\underline{H}_2CH_2CH_2{}^{13}CN$), 1.54–1.60 (m, 2 H, $C\underline{H}_2CH_2OH$), 1.62–1.70 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.34 (dt, $^2J_{CH2/13C} = 9.45$ Hz, $^3J_{CH2/CH2} = 7.30$ Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 3.65 (t, $^3J_{CH2/CH2} = 6.59$ Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.07 (d, $^1J_{13C/C} = 56.74$ Hz, $\underline{C}H_2{}^{13}CN$), 25.32 (d, $^2J_{13C/C} = 2.41$ Hz, $\underline{C}H_2CH_2{}^{13}CN$), 25.69 ($\underline{C}H_2CH_2CH_2OH$), 28.61 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.71, 29.24, 29.37, 29.42, 29.50, 29.52 (7 × $\underline{C}H_2$), 32.75 ($\underline{C}H_2CH_2OH$), 63.01 ($\underline{C}H_2OH$), 119.84 ($^{13}\underline{C}N$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3383 (m, OH), 2916 (s, CH_2), 2849 (s, CH_2), 2193 (w, $^{13}C\equiv N$), 1470 (m, CH_2), 1346 (w), 1051 (m, C—O), 1035 (m), 1012 (m), 989 (m), 970 (m), 721 (m, CH_2), 586 (m); MS (EI): m/z (%) = 225 (5) [$M^+ - H$], 207 (12) [$M^+ - H - H_2O$], 193 (12),

178 (28) [$M^+ - H_2O - C_2H_5$], 165 (36) [$M^+ - H_2O - C_3H_6$], 153 (17) [$M^+ - H_2O - C_4H_8$], 151 (46) [$C_9{}^{13}CH_{16}N^+$], 139 (23) [$C_8{}^{13}CH_{16}N^+$], 137 (100) [$C_8{}^{13}CH_{14}N^+$], 125 (34) [$C_7{}^{13}CH_{14}N^+$], 123 (100) [$C_7{}^{13}CH_{12}N^+$], 111 (45) [$C_6{}^{13}CH_{12}N^+$], 98 (43) [$C_5{}^{13}CH_{11}N^+$], 97 (71) [$C_5{}^{13}CH_{10}N^+$], 83 (69) [$C_4{}^{13}CH_8N^+$]; elemental analysis: calcd C 74.72, H 12.02, N 6.19, found C 74.53, H 12.13, N 6.15.

4.2.2 | [1-^{13}C]18-Hydroxyoctadecanenitrile (**7b***)

m.p. 69–70°C; ^{1}H-NMR (600 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.25–1.38 (m, 24 H, $HOCH_2CH_2(C\underline{H}_2)_{12}CH_2CH_2CH_2{}^{13}CN$),00201.42–1.49 (m, 2 H, $C\underline{H}_2CH_2CH_2{}^{13}CN$), 1.54–1.61 (m, 2 H, $C\underline{H}_2CH_2OH$), 1.62–1.70 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.34 (dt, $^2J_{CH2/13C} = 9.45$ Hz, $^3J_{CH2/CH2} = 7.30$ Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 3.65 (t, $^3J_{CH2/CH2} = 6.59$ Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.07 (d, $^1J_{13C/C} = 55.53$ Hz, $\underline{C}H_2{}^{13}CN$), 25.33 (d, $^2J_{13C/C} = 2.41$ Hz, $\underline{C}H_2CH_2{}^{13}CN$), 25.70 ($\underline{C}H_2CH_2CH_2OH$), 28.62 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.72, 29.26, 29.40, 29.45, 29.55, 29.58, 29.61 (11 × $\underline{C}H_2$), 32.76 ($\underline{C}H_2CH_2OH$), 63.02 ($\underline{C}H_2OH$), 119.84 ($^{13}\underline{C}N$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3377 (m, OH), 2914 (s, CH_2), 2849 (s, CH_2), 2191 (w, $^{13}C\equiv N$), 1472 (m, CH_2), 1346 (w), 1055 (m, C—O), 1045 (m), 717 (m, CH_2), 583 (m); MS (EI): *m/z* (%) = 282 (3) [M^+], 264 (5) [$M^+ - H_2O$], 235 (12) [$M^+ - H_2O - C_2H_5$], 221 (17) [$M^+ - H_2O - C_3H_7$], 209 (7) [$M^+ - C_4H_9O$], 207 (16) [$M^+ - H_2O - C_4H_8$], 195 (8) [$C_{12}{}^{13}CH_{24}N^+$], 193 (13) [$C_{12}{}^{13}CH_{22}N^+$], 181 (8) [$C_{11}{}^{13}CH_{22}N^+$], 179 (13) [$C_{11}{}^{13}CH_{20}N^+$], 165 (15) [$C_{10}{}^{13}CH_{18}N^+$], 151 (24) [$C_9{}^{13}CH_{16}N^+$], 139 (16) [$C_8{}^{13}CH_{16}N^+$], 137 (48) [$C_8{}^{13}CH_{14}N^+$], 125 (25) [$C_7{}^{13}CH_{14}N^+$], 123 (63) [$C_7{}^{13}CH_{12}N^+$], 111 (64) [$C_6{}^{13}CH_{12}N^+$], 98 (47) [$C_5{}^{13}CH_{11}N^+$], 97 (95) [$C_5{}^{13}CH_{10}N^+$], 83 (100) [$C_4{}^{13}CH_8N^+$]; elemental analysis: calcd C 76.89, H 12.49, N 4.96, found C 76.25, H 12.00, N 4.64.

4.2.3 | [1-^{13}C]22-Hydroxydocosanenitrile (**7c***)

m.p. 81–82°C; ^{1}H-NMR (600 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.24–1.38 (m, 32 H, $HOCH_2CH_2(C\underline{H}_2)_{16}CH_2CH_2CH_2{}^{13}CN$), 1.42–1.48 (m, 2 H, $C\underline{H}_2CH_2CH_2{}^{13}CN$), 1.54–1.61 (m, 2 H, $C\underline{H}_2CH_2OH$), 1.62–1.71 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.34 (dt, $^2J_{CH2/13C} = 9.74$ Hz, $^3J_{CH2/CH2} = 7.16$ Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 3.65 (t, $^3J_{CH2/CH2} = 6.59$ Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.07 (d, $^1J_{13C/C} = 55.53$ Hz, $\underline{C}H_2{}^{13}CN$), 25.33 (d, $^2J_{13C/C} = 2.41$ Hz, $\underline{C}H_2CH_2{}^{13}CN$), 25.70 ($\underline{C}H_2CH_2CH_2OH$), 28.63 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.73, 29.27, 29.40, 29.47, 29.56, 29.58, 29.60, 29.65 (15 × $\underline{C}H_2$), 32.77 ($\underline{C}H_2CH_2OH$), 63.02 ($\underline{C}H_2OH$), 119.84 ($^{13}\underline{C}N$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3379 (m, OH), 2914 (s, CH_2), 2849 (s, CH_2), 2193 (w, $^{13}C\equiv N$), 1472 (m, CH_2), 1344 (w), 1057 (m, C—O), 1042 (m), 716 (m, CH_2), 584 (m); MS (EI): *m/z* (%) = 338 (5) [M^+], 320 (13) [$M^+ - H_2O$], 291 (31) [$M^+ - H_2O - C_2H_5$], 279 (13) [$M^+ - C_3H_7O$], 277 (26) [$M^+ - H_2O - C_3H_7$], 263 (15) [$M^+ - H_2O - C_4H_9$], 251 (10) [$M^+ - C_5H_{11}O$], 249 (14) [$C_{16}{}^{13}CH_{30}N^+$], 237 (12) [$C_{15}{}^{13}CH_{30}N^+$], 235 (11) [$C_{15}{}^{13}CH_{28}N^+$], 223 (7) [$C_{14}{}^{13}CH_{28}N^+$], 221 (11) [$C_{14}{}^{13}CH_{26}N^+$], 209 (16) [$C_{13}{}^{13}CH_{26}N^+$], 207 (28) [$C_{13}{}^{13}CH_{24}N^+$], 195 (8) [$C_{12}{}^{13}CH_{24}N^+$], 193 (16) [$C_{12}{}^{13}CH_{22}N^+$], 181 (13) [$C_{11}{}^{13}CH_{22}N^+$], 179 (15) [$C_{11}{}^{13}CH_{20}N^+$], 167 (14) [$C_{10}{}^{13}CH_{20}N^+$], 165 (12) [$C_{10}{}^{13}CH_{18}N^+$], 151 (18) [$C_9{}^{13}CH_{18}N^+$], 151 (21) [$C_9{}^{13}CH_{16}N^+$], 139 (20) [$C_8{}^{13}CH_{16}N^+$], 137 (37) [$C_8{}^{13}CH_{14}N^+$], 125 (31) [$C_7{}^{13}CH_{14}N^+$], 123 (43) [$C_7{}^{13}CH_{12}N^+$], 111 (66) [$C_6{}^{13}CH_{12}N^+$], 98 (64) [$C_5{}^{13}CH_{11}N^+$], 97 (100) [$C_5{}^{13}CH_{10}N^+$], 83 (97) [$C_4{}^{13}CH_8N^+$]; elemental analysis: calcd C 78.34, H 12.08, N 4,14, found C 78.84, H 12.36, N 3.78.

4.2.4 | [1-^{13}C]30-Hydroxytriacontanenitrile (**7d***)

m.p. 94–95°C; ^{1}H-NMR (600 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.22–1.37 (m, 48 H, $HOCH_2CH_2(C\underline{H}_2)_{24}CH_2CH_2CH_2{}^{13}CN$), 1.41–1.38 (m, 2 H, $C\underline{H}_2CH_2CH_2{}^{13}CN$), 1.54–1.60 (m, 2 H, $C\underline{H}_2CH_2OH$), 1.62–1.71 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.34 (dt, $^2J_{CH2/13C} = 9.45$ Hz, $^3J_{CH2/CH2} = 7.30$ Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 3.65 (t, $^3J_{CH2/CH2} = 6.59$ Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.06 (d, $^1J_{13C/C} = 55.53$ Hz, $\underline{C}H_2{}^{13}CN$), 25.36 (d, $^2J_{13C/C} = 2.41$ Hz, $\underline{C}H_2CH_2{}^{13}CN$), 25.72 ($\underline{C}H_2CH_2CH_2OH$), 28.66 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.75, 29.28, 29.42, 29.49, 29.59, 29.69 (23 × $\underline{C}H_2$), 32.80 ($\underline{C}H_2CH_2OH$), 63.09 ($\underline{C}H_2OH$), 119.86 ($^{13}\underline{C}N$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3344 (m, OH), 2914 (s, CH_2), 2849 (s, CH_2), 2192 (w, $^{13}C\equiv N$), 1472 (m, CH_2), 1350 (w), 1057 (m, C—O), 1035 (m), 716 (m, CH_2), 584 (m); elemental analysis: calcd C 80.15, H 13.19, N 3.11, found C 79.71, H 12.84, N 3.02.

4.3 | Synthesis and characterization of the ω-hydroxycarboxylic acids 8a*–d* (modified after Nacsa and Lambert[34])

In a 100-ml round flask equipped with a reflux condenser, the ω-hydroxynitrile (**7a***: 224 mg, 0.99 mmol;

7b*: 280 mg, 0.99 mmol; **7c***: 200 mg, 0.59 mmol; **7d***: 266 mg, 0.59 mmol) were dissolved in methanol. In case of the reaction of **7a***–**b***, the substrates were dissolved in 35 ml of methanol, and the resulting solution then treated with 35-ml NaOH (5 M), heated to 70°C for 18 h and subsequently refluxed for another 7 h. In case of the reaction of **7c***–**d***, the substrates were treated with a solution of 2.9-g NaOH in 80 ml of ethanol and the resulting mixture was refluxed for 24 h for **7c*** or 48 h for **7d***. After the respective mixture was allowed to cool down to room temperature, it was poured into 150 ml of water and acidified with half concentrated hydrochloric acid leading to the precipitation of a colorless solid, which was filtered, washed with 30 ml of water and dried overnight at 55°C in a drying chamber. For purification, the crude products were transferred into another round flask and 40 ml of hot ethyl acetate were added. The resulting mixture was filtered over a G3 frit as hot as possible. The flask and the frit also are treated twice with additional 5 ml of hot ethyl acetate to completely collect the material. Following this, the filtrate was concentrated under reduced pressure to approximately one third of the original volume. The resulting products **8a***–**b*** were then recrystallized from a mixture of light petroleum and ethyl acetate by first suspending the compound in boiling light petroleum before adding just the appropriate amount of ethyl acetate to dissolve the compound. Products **8c***–**d*** were recrystallized from pure ethyl acetate. After standing in the refrigerator overnight, **8a***–**d*** were obtained as colourless crystals, which were filtered, washed with 3-ml light petroleum and dried under reduced pressure (**8a***: 216 mg, 89%; **8b***: 272 mg, 91%; **8c***: 196 mg, 93%; **8d***: 241 mg, 87%).

4.3.1 | [1-^{13}C]14-Hydroxytetradecanoic acid (**8a***)

m.p. 91–92°C; ^{1}H-NMR (500 MHz, THF, 298 K): δ (ppm) = 1.26–1.37 (m, 18 H, $HOCH_2CH_2(C\underline{H}_2)_9CH_2CH_2{}^{13}COOH$), 1.43–1.50 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 1.53–1.60 (m, 2 H, $C\underline{H}_2CH_2OH$), 2.20 (quar, $^{3}J_{CH2/CH2}$ = 7.26 Hz, $^{2}J_{CH2/13C}$ = 7.26 Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 3.46 (t, $^{3}J_{CH2/CH2}$ = 6.30 Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, THF, 298 K): δ (ppm) = 26.03 ($\underline{C}H_2CH_2{}^{13}COOH$), 27.11($\underline{C}H_2CH_2CH_2OH$), 30.30 (d, $^{3}J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 30.51, 30.65, 30.73, 30.76, 30.79 (7 × $\underline{C}H_2$), 30.85, 34.26 ($\underline{C}H_2CH_2OH$), 34.43 (d, $^{1}J_{13C/C}$ = 55.53 Hz, $\underline{C}H_2{}^{13}COOH$), 62.72 ($\underline{C}H_2OH$), 174.67 ($CH_2{}^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3500–2500 (m, OH), 2913 (m, CH_2), 2845 (m, CH_2), 1643 (s, ^{13}C═O), 1470 (s, CH_2), 1410 (w, OH), 1275 (m, CH_2), 1049 (m, C—O), 718 (m, CH_2), 529 (m); elemental analysis: calcd C 68.94, H 11.50, found C 68.63, H 11.54.

4.3.2 | [1-^{13}C]18-Hydroxyoctadecanoic acid (**8b***)

m.p. 98–99°C; ^{1}H-NMR (500 MHz, THF, 298 K): δ (ppm) = 1.26–1.37 (m, 26 H, $HOCH_2CH_2(C\underline{H}_2)_{13}CH_2CH_2{}^{13}COOH$), 1.43–1.50 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 1.53–1.60 (m, 2 H, $C\underline{H}_2CH_2OH$), 2.20 (quar, $^{3}J_{CH2/CH2}$ = 7.06 Hz, $^{2}J_{CH2/13C}$ = 7.06 Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 3.46 (t, $^{3}J_{CH2/CH2}$ = 6.30 Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, THF, 298 K): δ (ppm) = 26.02 ($\underline{C}H_2CH_2{}^{13}COOH$), 27.11 ($\underline{C}H_2CH_2CH_2OH$), 30.31 (d, $^{3}J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 30.52, 30.66, 30.74, 30.76, 30.82, 30.87 (11 × $\underline{C}H_2$), 34.27 ($\underline{C}H_2CH_2OH$), 34.43 (d, $^{1}J_{13C/C}$ = 55.53 Hz, $\underline{C}H_2{}^{13}COOH$), 62.72 ($\underline{C}H_2OH$), 174.67 ($CH_2{}^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3500–2500 (m, OH), 2913 (s, CH_2), 2847 (s, CH_2), 1659 (m, ^{13}C═O), 1470 (s, CH_2), 1402 (w, OH), 1267 (m, CH_2), 1053 (m, C—O), 718 (m, CH_2), 533 (w); elemental analysis: calcd C 72.04, H 12.04, found C 71.49, H 11.50.

4.3.3 | [1-^{13}C]22-Hydroxydocosanoic acid (**8c***)

m.p. 107–108°C; ^{1}H-NMR (500 MHz, THF, 298 K): δ (ppm) = 1.24–1.37 (m, 34 H, $HOCH_2CH_2(C\underline{H}_2)_{17}CH_2CH_2{}^{13}COOH$), 1.42–1.49 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 1.52–1.60 (m, 2 H, $C\underline{H}_2CH_2OH$), 2.20 (quar, $^{3}J_{CH2/CH2}$ = 7.45 Hz, $^{2}J_{CH2/13C}$ = 7.45 Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 3.45 (t, $^{3}J_{CH2/CH2}$ = 6.59 Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, THF, 298 K): δ (ppm) = 26.04 ($\underline{C}H_2CH_2{}^{13}COOH$), 27.11 ($\underline{C}H_2CH_2CH_2OH$), 30.31 (d, $^{3}J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 30.52, 30.66, 30.74, 30.77, 30.82, 30.87 (15 × $\underline{C}H_2$), 34.28 ($\underline{C}H_2CH_2OH$), 34.44 (d, $^{1}J_{13C/C}$ = 55.53 Hz, $\underline{C}H_2{}^{13}COOH$), 62.72 ($\underline{C}H_2OH$), 174.68 ($CH_2{}^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3500–2500 (m, OH), 2913 (s, CH_2), 2847 (s, CH_2), 1659 (m, ^{13}C═O), 1472 (m, CH_2), 1408 (w, OH), 1265 (w, CH_2), 1059 (m, C—O), 716 (m, CH_2), 533 (w); elemental analysis: calcd C 74.17, H 12.40, found C 73.82, H 11.84.

4.3.4 | [1-^{13}C]30-Hydroxytriacontanoic acid (**8d***)

m.p. 107–109°C; ^{1}H-NMR (500 MHz, THF, 298 K): δ (ppm) = 1.24–1.38 (m, 50 H, $HOCH_2CH_2(C\underline{H}_2)_{25}CH_2CH_2{}^{13}COOH$), 1.42–1.50 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 1.52–1.61 (m, 2 H, $C\underline{H}_2CH_2OH$), 2.20 (quar, $^{3}J_{CH2/CH2}$ = 7.45 Hz, $^{2}J_{CH2/13C}$ = 7.45 Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 3.45 (t, $^{3}J_{CH2/CH2}$ = 6.59 Hz, 2 H, $C\underline{H}_2OH$); ^{13}C-NMR (151 MHz, THF, 298 K): δ (ppm) = 26.03 ($\underline{C}H_2CH_2{}^{13}COOH$), 27.12 ($\underline{C}H_2CH_2CH_2OH$), 30.31

(d, $^{3}J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 30.52, 30.67, 30.74, 30.82, 30.87 (23 × $\underline{C}H_2$), 34.29 ($\underline{C}H_2CH_2OH$), 34.42 (d, $^{1}J_{13C/C}$ = 55.53 Hz, $\underline{C}H_2{}^{13}COOH$), 62.72 ($\underline{C}H_2OH$), 174.68 ($^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3344 (m, OH), 2918 (s, CH_2), 2846 (s, CH_2), 1462 (m, CH_2), 1442 (m, OH), 1051 (m, C—O), 1016 (m), 997 (w), 727 (m, CH_2); elemental analysis: calcd C 76.91, H 12.87, found C 77.07, H 12.58.

4.4 | Synthesis and characterization of the ω-alkenylnitriles 9a*–d* (modified after Rosillo et al.[41])

In a 25-ml round flask, 3.02 mmol of the corresponding ω-bromoalkene (831-mg **2e**, 1.001-g **2f**, 1.170-g **2g**, 1.509-g **2h**) were treated with 8 ml of DMSO and subsequently with 3.18 mmol (210 mg) $K^{13}CN$. The reaction mixture was then heated to 85°C for 3 days. After the pale yellow reaction mixture was cooled to room temperature, it was poured into 40 ml of water and extracted four times with 40 ml of ethyl acetate each. The combined organic phases were then washed twice with 40 ml of water, dried over Na_2SO_4 and filtered, and the solvent was then evaporated under reduced pressure. In case of oily crude reaction products (**9a*–9c***), they were purified by column chromatography using a mixture of light petroleum and ethyl acetate (1:1) as the eluent yielding **9a*** as a colourless oil and **9b*–c*** as colourless solids. In case of **9d***, the crude reaction product already was solid and purified by recrystallization from light petroleum. Crystallization was achieved by keeping the solution in the refrigerator overnight. Pure **9d*** was then collected by filtration and dried under reduced pressure. Obtained yields were 591-mg (88%) **9a***, 765-mg (91%) **9b***, 960-mg (95%) **9c*** and 1.201-g (89%) **9d***.

4.4.1 | [1-^{13}C]Pentadec-14-enenitrile (9a*)

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.24–1.48 (m, 18 H, $N^{13}CCH_2CH_2(C\underline{H}_2)_9CH_2CH{=}CH_2$), 1.62–1.70 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.02–2.08 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.34 (dt, $^{2}J_{CH2/13C}$ = 9.45 Hz, $^{3}J_{CH2/CH2}$ = 7.02 Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 4.91–5.03 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^{3}J_{CH/CH2[E]}$ = 17.04 Hz, $^{3}J_{CH/CH2[Z]}$ = 10.31 Hz, $^{3}J_{CH/CH2}$ = 6.66 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.08 (d, $^{1}J_{13C/C}$ = 55.53 Hz, $\underline{C}H_2{}^{13}CN$), 25.35 (d, $^{2}J_{13C/C}$ = 2.17 Hz, $\underline{C}H_2CH_2{}^{13}CN$), 28.64 (d, $^{3}J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.74, 28.91, 29.11, 29.27, 29.46, 29.53 (8 × $\underline{C}H_2$), 33.79 ($\underline{C}H_2CH{=}CH_2$), 114.07 ($CH_2CH{=}\underline{C}H_2$), 119.84 ($CH_2{}^{13}\underline{C}N$), 139.22 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3078 (w, =CH_2), 2922 (s, CH_2), 2853 (s, CH_2), 2193 (w, ^{13}C≡ N), 1640 (m, C=C), 1464 (m, CH_2), 993 (m, —HC=CH_2), 908 (m, —HC=CH_2), 721 (m, CH_2); MS (EI): *m/z* (%) = 221 (3) [$M^+ - H$], 207 (4) [$M^+ - CH_3$], 193 (14) [$M^+ - C_2H_5$], 179 (20) [$M^+ - C_3H_7$], 165 (18) [$C_{10}{}^{13}CH_{18}{}^+$], 151 (24) [$C_9{}^{13}CH_{16}{}^+$], 137 (65) [$C_8{}^{13}CH_{14}{}^+$], 123 (100) [$C_7{}^{13}CH_{12}{}^+$], 111 (16) [$C_6{}^{13}CH_{12}{}^+$], 109 (25) [$C_6{}^{13}CH_{10}{}^+$], 97 (37) [$C_5{}^{13}CH_{10}{}^+$], 95 (57) [$C_5{}^{13}CH_8{}^+$], 83 (48) [$C_4{}^{13}CH_8{}^+$]; elemental analysis: calcd C 81.46, H 12.24, N 6.30, found C 81.39, H 12.17, N 6.30.

4.4.2 | [1-^{13}C]Nonadec-18-enenitrile (9b*)

m.p. 29–30°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.23–1.47 (m, 26 H, $N^{13}CCH_2CH_2(C\underline{H}_2)_{13}CH_2CH{=}CH_2$), 1.62–1.71 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.01–2.08 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.34 (dt, $^{2}J_{CH2/13C}$ = 9.74 Hz, $^{3}J_{CH2/CH2}$ = 7.16 Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 4.91–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^{3}J_{CH/CH2[E]}$ = 17.11 Hz, $^{3}J_{CH/CH2[Z]}$ = 10.24 Hz, $^{3}J_{CH/CH2}$ = 6.66 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.08 (d, $^{1}J_{13C/C}$ = 56.74 Hz, $\underline{C}H_2{}^{13}CN$), 25.35 (d, $^{2}J_{13C/C}$ = 2.41 Hz, $\underline{C}H_2CH_2{}^{13}CN$), 28.64 (d, $^{3}J_{13C/C}$ = 3.66 Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.74, 28.93, 29.13, 29.28, 29.48, 29.59 (12 × $\underline{C}H_2$), 33.80 ($\underline{C}H_2CH{=}CH_2$), 114.05 ($CH_2CH{=}\underline{C}H_2$), 119.84 ($CH_2{}^{13}\underline{C}N$), 139.24 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077 (w, =CH_2), 2914 (s, CH_2), 2849 (s, CH_2), 2189 (w, ^{13}C≡ N), 1643 (m, C=C), 1472 (m, CH_2), 993 (m, —HC=CH_2), 926 (m, —HC=CH_2), 718 (m, CH_2); MS (EI): *m/z* (%) = 278 (4) [M^+], 263 (7) [$M^+ - CH_3$], 249 (19) [$M^+ - C_2H_5$], 235 (24) [$M^+ - C_3H_7$], 221 (18) [$M^+ - C_4H_9$], 207 (18) [$C_{13}{}^{13}CH_{24}{}^+$], 192 (20) [$C_{12}{}^{13}CH_{22}{}^+$], 178 (19) [$C_{11}{}^{13}CH_{20}{}^+$], 165 (18) [$C_{10}{}^{13}CH_{18}{}^+$], 151 (30) [$C_9{}^{13}CH_{16}{}^+$], 137 (71) [$C_8{}^{13}CH_{14}{}^+$], 123 (100) [$C_7{}^{13}CH_{12}{}^+$], 111 (30) [$C_6{}^{13}CH_{12}{}^+$], 97 (49) [$C_5{}^{13}CH_{10}{}^+$], 83 (63) [$C_4{}^{13}CH_8{}^+$]; elemental analysis: calcd C 82.30, H 12.67, N 5.03, found C 82.14, H 12.44, N 4.82.

4.4.3 | [1-^{13}C]Tricos-22-enenitrile (9c*)

m.p. 45–46°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.23–1.48 (m, 34 H, $N^{13}CCH_2CH_2(C\underline{H}_2)_{17}CH_2CH{=}CH_2$), 1.61–1.72 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.00–2.09 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.34 (dt, $^{2}J_{CH2/13C}$ = 9.45 Hz, $^{3}J_{CH2/CH2}$ = 7.02 Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 4.90–5.03 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^{3}J_{CH/CH2[E]}$ = 16.97 Hz, $^{3}J_{CH/CH2[Z]}$ = 10.24 Hz, $^{3}J_{CH/CH2}$ = 6.73 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR

(126 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.09 (d, $^1J_{13C/C}$ = 56.74 Hz, $\underline{C}H_2{}^{13}CN$), 25.36 (d, $^2J_{13C/C}$ = 2.41 Hz, $\underline{C}H_2CH_2{}^{13}CN$), 28.66 (d, $^3J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.76, 28.94, 29.15, 29.29, 29.50, 29.58, 29.63, 29.68 (16 × $\underline{C}H_2$), 33.81 ($\underline{C}H_2CH{=}CH_2$), 114.05 ($CH_2CH{=}\underline{C}H_2$), 119.85 ($CH_2{}^{13}\underline{C}N$), 139.26 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3075 (w, $=CH_2$), 2913 (s, CH_2), 2849 (s, CH_2), 2191 (w, $^{13}C{\equiv}N$), 1641 (m, C=C), 1472 (m, CH_2), 990 (m, $-HC{=}CH_2$), 914 (m, $-HC{=}CH_2$), 718 (m, CH_2); MS (EI): *m/z* (%) = 334 (7) [M^+], 305 (25) [$M^+ - C_2H_5$], 291 (44) [$M^+ - C_3H_7$], 277 (38) [$M^+ - C_4H_9$], 263 (35) [$M^+ - C_5H_{11}$], 249 (31) [$C_{17}H_{30}{}^+$], 235 (26) [$C_{16}H_{28}{}^+$], 221 (27) [$C_{15}H_{26}{}^+$], 207 (27) [$C_{13}{}^{13}CH_{24}{}^+$], 193 (20) [$C_{12}{}^{13}CH_{22}{}^+$], 181 (22) [$C_{11}{}^{13}CH_{22}{}^+$], 179 (22) [$C_{11}{}^{13}CH_{20}{}^+$], 167 (24) [$C_{10}{}^{13}CH_{20}{}^+$], 165 (29) [$C_{10}{}^{13}CH_{18}{}^+$], 151 (46) [$C_9{}^{13}CH_{16}{}^+$], 137 (91) [$C_8{}^{13}CH_{14}{}^+$], 123 (100) [$C_7{}^{13}CH_{12}{}^+$], 111 (64) [$C_6{}^{13}CH_{12}{}^+$], 97 (87) [$C_5{}^{13}CH_{10}{}^+$], 83 (69) [$C_4{}^{13}CH_8{}^+$]; elemental analysis: calcd C 82.86, H 12.95, N 4.19, found C 82.79, H 12.69, N 4.10.

4.4.4 | [1-^{13}C]Hentriacont-30-enenitrile (**9d***)

m.p. 69–70°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.23–1.47 (m, 50 H, $N^{13}CCH_2CH_2(C\underline{H}_2)_{25}CH_2CH{=}CH_2$), 1.61–1.71 (m, 2 H, $C\underline{H}_2CH_2{}^{13}CN$), 2.00–2.09 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.34 (dt, $^2J_{CH2/13C}$ = 9.45 Hz, $^3J_{CH2/CH2}$ = 7.02 Hz, 2 H, $C\underline{H}_2{}^{13}CN$), 4.90–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]}$ = 16.90 Hz, $^3J_{CH/CH2[Z]}$ = 10.31 Hz, $^3J_{CH/CH2}$ = 6.73 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 17.06 (d, $^1J_{13C/C}$ = 55.53 Hz, $\underline{C}H_2{}^{13}CN$), 25.36 (d, $^2J_{13C/C}$ = 2.41 Hz, $\underline{C}H_2CH_2{}^{13}CN$), 28.66 (d, $^3J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}CN$), 28.76, 28.94, 29.15, 29.29, 29.50, 29.58, 29.61, 29.69 (24 × $\underline{C}H_2$), 33.82 ($\underline{C}H_2CH{=}CH_2$), 114.05 ($CH_2CH{=}\underline{C}H_2$), 119.84 ($CH_2{}^{13}\underline{C}N$), 139.26 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3076 (w, $=CH_2$), 2914 (s, CH_2), 2847 (s, CH_2), 2195 (w, $^{13}C{\equiv}N$), 1641 (m, C=C), 1472 (m, CH_2), 991 (m, $-HC{=}CH_2$), 912 (m, $-HC{=}CH_2$), 720 (m, CH_2); elemental analysis: calcd C 83.56, H 13.31, N 3.13, found C 83.55, H 12.81, N 3.01.

4.5 | Synthesis and characterization of the ω-alkenylcarboxylic acids 10a*–d* (modified after Coxon et al.[42])

A total of 2.76 mmol of the corresponding ω-alkenylnitrile (614-mg **9a***, 769-mg **9b***, 924-mg **9c***, 1.233-g **9d***) were placed in a 250-ml round flask equipped with a reflux condenser and were dissolved in a solution of 8.8-g (0.22 mol) NaOH in 200 ml of ethanol. The reaction mixture was then refluxed for 24 h. The reaction mixture was then poured into 200 ml of water and acidified with half concentrated hydrochloric acid. In case of the reaction of **9a***, the resulting solution was then divided into equal shares each of those being extracted four times with 50 ml of ethyl acetate each. The combined organic phases were then washed with water, dried over Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. The crude product **10a*** was purified by column chromatography using a mixture of ethyl acetate and light petroleum (1:2) as the eluent producing **10a*** as a colourless crystalline material after the solvent was evaporated (**10a***: 640 mg, 96%). In case of the reaction of **9b*–d***, acidification of the reaction mixture led to the precipitation of a white solid, which was filtered, washed with 50 ml of water and dried under reduced pressure. The resulting products **10b*–d*** were then recrystallized from a mixture of light petroleum and ethyl acetate by first suspending the compound in boiling light petroleum before adding just the appropriate amount of ethyl acetate to dissolve the compound. After standing in the refrigerator overnight, **10b*–d*** were obtained as colourless crystals, which were filtered, washed with 5 ml of cooled light petroleum and dried under reduced pressure (**10b***: 764 mg, 93%; **10c***: 888 mg, 91%; **10d***: 1.196 g, 93%).

4.5.1 | [1-^{13}C]Pentadec-14-enoic acid (**10a***)

m.p. 50–51°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.22–1.43 (m, 18 H, $HOO^{13}CCH_2CH_2(C\underline{H}_2)_9CH_2CH{=}CH_2$), 1.59–1.68 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 2.00–2.09 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.36 (quar, $^3J_{CH2/CH2}$ = 7.26 Hz, $^2J_{CH2/13C}$ = 7.26 Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 4.90–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]}$ = 17.11 Hz, $^3J_{CH/CH2[Z]}$ = 10.24 Hz, $^3J_{CH/CH2}$ = 6.66 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 24.65 ($\underline{C}H_2CH_2{}^{13}COOH$), 28.93 ($\underline{C}H_2$), 29.04 (d, $^3J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 29.14, 29.22, 29.41, 29.49, 29.55, 29.57, 29.59 (7 × $\underline{C}H_2$), 33.81 ($\underline{C}H_2CH{=}CH_2$), 34.03 (d, $^1J_{13C/C}$ = 56.74 Hz, $\underline{C}H_2{}^{13}COOH$), 114.06 ($CH_2CH{=}\underline{C}H_2$), 139.26 ($CH_2\underline{C}H{=}CH_2$), 180.17 ($^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 3077 (w, $=CH_2$), 2914 (s, CH_2), 2847 (s, CH_2), 1654 (s, $^{13}C{=}O$), 1643 (m, C=C), 1462 (m, CH_2), 1409 (m, OH), 1277 (m, CH_2), 991 (m, $-HC{=}CH_2$), 939 (m, OH), 912 (m, $-HC{=}CH_2$), 727 (m, CH_2), 687 (m), 548 (m); MS (EI): *m/z* (%) = 241 (1) [M^+], 233 (6) [$M^+ - H_2O$], 194 (5) [$C_{12}{}^{13}CH_{21}O^+$],

180 (7) [$C_{11}{}^{13}CH_{19}O^+$], 166 (7) [$C_{10}{}^{13}CH_{17}O^+$], 152 (14) [$C_9{}^{13}CH_{15}O^+$], 138 (18) [$C_8{}^{13}CH_{13}O^+$], 124 (30) [$C_7{}^{13}CH_{11}O^+$], 111 (24) [$C_6{}^{13}CH_{10}O^+$], 99 (66) [$C_4{}^{13}CH_6O_2{}^+$], 81 (100) [$C_5H_7{}^+$]; elemental analysis: calcd C 75.05, H 11.69, found C 74.99, H 11.59.

4.5.2 | [1-^{13}C]Nonadec-18-enoic acid (**10b***)

m.p. 65–66°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21–1.44 (m, 26 H, $HOO^{13}CCH_2CH_2(C\underline{H}_2)_{13}CH_2CH{=}CH_2$), 1.59–1.69 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 2.01–2.09 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.35 (quar, $^3J_{CH2/CH2} = 7.45$ Hz, $^2J_{CH2/13C} = 7.45$ Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 4.90–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]} = 16.97$ Hz, $^3J_{CH/CH2[Z]} = 10.24$ Hz, $^3J_{CH/CH2} = 6.73$ Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 24.67 ($\underline{C}H_2CH_2{}^{13}COOH$), 28.95 ($\underline{C}H_2$), 29.06 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 29.16, 29.24, 29.43, 29.51, 29.59, 29.62, 29.67 (11 × $\underline{C}H_2$), 33.83 ($\underline{C}H_2CH{=}CH_2$), 34.02 (d, $^1J_{13C/C} = 55.53$ Hz, $\underline{C}H_2{}^{13}COOH$), 114.06 ($CH_2CH{=}\underline{C}H_2$), 139.27 ($CH_2\underline{C}H{=}CH_2$), 180.01 ($^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 3077 (w, $=CH_2$), 2914 (s, CH_2), 2847 (s, CH_2), 1657 (s, $^{13}C{=}O$), 1643 (m, C=C), 1462 (m, CH_2), 1410 (m, OH), 1273 (m, CH_2), 991 (m, $-HC{=}CH_2$), 941 (m, OH), 912 (m, $-HC{=}CH_2$), 720 (m, CH_2), 687 (m), 548 (m); elemental analysis: calcd C 77.05, H 12.20, found C 77.01, H 11.88.

4.5.3 | [1-^{13}C]Tricos-22-enoic acid (**10c***)

m.p. 74–75°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.20–1.43 (m, 34 H, $HOO^{13}CCH_2CH_2(C\underline{H}_2)_{17}CH_2CH{=}CH_2$), 1.59–1.69 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 2.00–2.09 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.36 (quar, $^3J_{CH2/CH2} = 7.45$ Hz, $^2J_{CH2/13C} = 7.45$ Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 4.91–5.03 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]} = 17.04$ Hz, $^3J_{CH/CH2[Z]} = 10.17$ Hz, $^3J_{CH/CH2} = 6.44$ Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 24.67 ($\underline{C}H_2CH_2{}^{13}COOH$), 28.95 ($\underline{C}H_2$), 29.06 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 29.16, 29.24, 29.44, 29.52, 29.59, 29.62, 29.64, 29.69 (15 × $\underline{C}H_2$), 33.83 ($\underline{C}H_2CH{=}CH_2$), 34.02 (d, $^1J_{13C/C} = 55.42$ Hz, $\underline{C}H_2{}^{13}COOH$), 114.06 ($CH_2CH{=}\underline{C}H_2$), 139.28 ($CH_2\underline{C}H{=}CH_2$), 179.89 ($^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 3075 (w, $=CH_2$), 2914 (s, CH_2), 2847 (s, CH_2), 1657 (s, $^{13}C{=}O$), 1643 (m, C=C), 1462 (m, CH_2), 1409 (m, OH), 1282 (m, CH_2), 990 (m, $-HC{=}CH_2$), 942 (m, OH), 912 (m, $-HC{=}CH_2$), 720 (m, CH_2), 687 (m), 546 (m); elemental analysis: calcd C 78.41, H 12.54, found C 78.09, H 12.26.

4.5.4 | [1-^{13}C]Hentriacont-30-enoic acid (**10d***)

m.p. 90–91°C; ^{1}H-NMR (500 MHz, DMSO, 373 K): δ (ppm) = 1.10–1.44 (m, 50 H, $HOO^{13}CCH_2CH_2(C\underline{H}_2)_{25}CH_2CH{=}CH_2$), 1.48–1.60 (m, 2 H, $C\underline{H}_2CH_2{}^{13}COOH$), 2.02 (q, $^3J_{CH2/CH2} = 6.87$ Hz, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.18 (quar, $^3J_{CH2/CH2} = 7.45$ Hz, $^2J_{CH2/13C} = 7.45$ Hz, 2 H, $C\underline{H}_2{}^{13}COOH$), 4.89–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.80 (ddt, $^3J_{CH/CH2[E]} = 17.18$ Hz, $^3J_{CH/CH2[Z]} = 9.74$ Hz, $^3J_{CH/CH26+} = 6.87$ Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 24.03 ($\underline{C}H_2CH_2{}^{13}COOH$), 27.80, 27.93 (2 × $\underline{C}H_2$), 28.08 (d, $^3J_{13C/C} = 2.4$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}COOH$), 28.15, 28.27, 28.39 (22 × $\underline{C}H_2$), 32.50 ($\underline{C}H_2CH{=}CH_2$), 33.28 (d, $^1J_{13C/C} = 55.53$ Hz, $\underline{C}H_2{}^{13}COOH$), 113.69 ($CH_2CH{=}\underline{C}H_2$), 138.18 ($CH_2\underline{C}H{=}CH_2$), 173.49 ($^{13}\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 3073 (w, $=CH_2$), 2914 (s, CH_2), 2847 (s, CH_2), 1657 (s, $^{13}C{=}O$), 1643 (m, C=C), 1462 (m, CH_2), 1409 (m, OH), 1277 (m, CH_2), 991 (m, $-HC{=}CH_2$), 943 (m, OH), 912 (m, $-HC{=}CH_2$), 720 (m, CH_2), 689 (m), 544 (m); elemental analysis: calcd C 80.15, H 12.98, found C 80.09, H 12.81.

4.6 | Synthesis and characterization of the ω-alkenylalcohols 11a*–d* (modified after Franchini et al.[43])

In a 100-ml two-necked flask equipped with a reflux condenser and a septum, 448-mg (11.8 mmol) $LiAlH_4$ were suspended in 15 ml of anhydrous THF under a nitrogen atmosphere. After the mixture was cooled to 0°C with an ice bath, a solution of 2.36 mmol of the corresponding ω-alkenylcarboxylic acid (570-mg **10a***, 702-mg **10b***, 835-mg **10c***, 1.100-g **10d***) in 15 ml of anhydrous THF was added dropwise with a syringe so slowly that the reaction mixture only boiled smoothly. After the addition was completed, the suspension was heated to reflux for another 4 h. Then the reaction mixture was again cooled down to 0°C with an ice bath before water was added dropwise to decompose excess $LiAlH_4$. Afterwards, the mixture was transferred into 50 ml (250 ml in case of the reaction of **10d***) of water and acidified with half concentrated hydrochloric acid to dissolve the formed $Al(OH)_3$. If **10a*–c*** are reacted, the aqueous phase was now extracted four times with 50 ml of diethylether each; the combined organic phases are washed with a diluted solution of $NaHCO_3$ and then with brine. The organic phases were then dried over Na_2SO_4, filtered and evaporated under reduced pressure. Purification of the crude products **11a*–c*** was performed by column chromatog-

raphy using a mixture of diethylether and light petroleum (1:5 for **11a***, 1:1 for **11b***–**c***) as the eluent producing the products as colourless crystalline compounds after evaporation of the solvent (**11a***: 483 mg, 90%; **11b***: 642 mg, 96%; **11c***: 753 mg, 94%). In case of the reaction of **10d***, acidification of the reaction mixture led to a colourless precipitate, which was collected by filtration. The resulting crude product **11d*** was then recrystallized from a mixture of light petroleum and ethyl acetate by first suspending the compound in boiling light petroleum before adding just the appropriate amount of ethyl acetate to dissolve the compound. After standing in the refrigerator overnight, **11d*** was obtained as colourless crystals, which were filtered and dried under reduced pressure (**11d***: 981 mg, 92%).

4.6.1 | [1-^{13}C]Pentadec-14-en-1-ol (**11a***)

m.p. 34–35°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21–1.42 (m, 20 H, $HO^{13}CH_2CH_2(C\underline{H}_2)_{10}CH_2CH{=}CH_2$), 1.50–1.60 (m, 2 H, $C\underline{H}_2{}^{13}CH_2OH$), 1.98–2.06 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 3.62 (dt, $^3J_{CH2/CH2} = 6.59$ Hz, $^1J_{13CH2/13C} = 140.90$ Hz, 2 H, $^{13}C\underline{H}_2OH$), 4.88–5.02 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]} = 17.11$ Hz, $^3J_{CH/CH2[Z]} = 10.24$ Hz, $^3J_{CH/CH2} = 6.66$ Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 25.72 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 28.93, 29.14 (2 × $\underline{C}H_2$), 29.42 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}CH_2OH$), 29.50, 29.59, 29.63 (6 × $\underline{C}H_2$), 32.78 (d, $^1J_{13C/C} = 37.42$ Hz, $\underline{C}H_2{}^{13}CH_2OH$), 33.81 ($\underline{C}H_2CH{=}CH_2$), 63.07 ($^{13}\underline{C}H_2OH$), 114.06 ($CH_2CH{=}\underline{C}H_2$), 139.26 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3319 (m, OH), 3067 (w, $=CH_2$), 2914 (s, CH_2), 2849 (s, CH_2), 1642 (m, C=C), 1462 (m, CH_2), 1342 (w, CH_2), 1045 (m, ^{13}C–O), 990 (m, –HC=CH_2), 912 (m, –HC=CH_2), 720 (m, CH_2), 644 (m); MS (EI): *m*/*z* (%) = 226 (1) [$M^+ - H$], 209 (1) [$M^+ - H_2O$], 194 (1) [$M^+ - {}^{13}CH_4O$], 181 (1) [$M^+ - H_2O - C_2H_4$], 180 (1) [$M^+ - H_2O - {}^{13}C_2H_4$], 167 (1) [$C_{11}{}^{13}CH_{22}{}^+$], 166 (1) [$C_{12}H_{22}{}^+$], 152 (1) [$C_{11}H_{20}{}^+$], 151 (1) [$C_{11}H_{19}{}^+$], 125 (3) [$C_8{}^{13}CH_{16}{}^+$], 124 (4) [$C_9H_{16}{}^+$], 123 (3) [$C_9H_{15}{}^+$], 111 (5) [$C_7{}^{13}CH_{14}{}^+$], 110 (10) [$C_8H_{14}{}^+$], 109 (8) [$C_8H_{13}{}^+$], 97 (15) [$C_6{}^{13}CH_{12}{}^+$], 96 (30) [$C_7H_{12}{}^+$], 95 (34) [$C_7H_{11}{}^+$], 82 (66) [$C_6H_{10}{}^+$], 81 (100) [$C_6H_9{}^+$]; elemental analysis: calcd C 79.67, H 13.30, found C 79.45, H 13.02.

4.6.2 | [1-^{13}C]Nonadec-18-en-1-ol (**11b***)

m.p. 53–54°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.22–1.42 (m, 28 H, $HO^{13}CH_2CH_2(C\underline{H}_2)_{14}CH_2CH{=}CH_2$), 1.52–1.62 (m, 2 H, $C\underline{H}_2{}^{13}CH_2OH$), 2.01–2.09 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 3.64 (dt, $^3J_{CH2/CH2} = 6.59$ Hz, $^1J_{13CH2/13C} = 140.90$ Hz, 2 H, $^{13}C\underline{H}_2OH$), 4.90–5.03 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]} = 17.11$ Hz, $^3J_{CH/CH2[Z]} = 10.24$ Hz, $^3J_{CH/CH2} = 6.66$ Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 25.72 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 28.94, 29.15 (2 × $\underline{C}H_2$), 29.43 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}CH_2OH$), 29.50, 29.60, 29.67 (10 × $\underline{C}H_2$), 32.79 (d, $^1J_{13C/C} = 36.22$ Hz, $\underline{C}H_2{}^{13}CH_2OH$), 33.81 ($\underline{C}H_2CH{=}CH_2$), 63.07 ($^{13}\underline{C}H_2OH$), 114.05 ($CH_2CH{=}\underline{C}H_2$), 139.27 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3319 (m, OH), 3077 (w, $=CH_2$), 2916 (s, CH_2), 2847 (s, CH_2), 1641 (m, C=C), 1462 (m, CH_2), 1362 (w, CH_2), 1042 (m, ^{13}C–O), 991 (m, –HC=CH_2), 920 (w), 912 (m, –HC=CH_2), 720 (m, CH_2), 644 (m); MS (EI): *m*/*z* (%) = 282 (1) [$M^+ - H$], 265 (1) [$M^+ - H_2O$], 236 (1) [$M^+ - H_2O - C^{13}CH_4$], 222 (1) [$M^+ - H_2O - C_2{}^{13}CH_6$], 209 (1) [$M^+ - H_2O - C_4H_8$], 208 (1) [$M^+ - H_2O - C_3{}^{13}CH_8$], 194 (1) [$C_{14}H_{26}{}^+$], 181 (1) [$C_{12}{}^{13}CH_{24}{}^+$], 180 (1) [$C_{13}H_{24}{}^+$], 167 (1) [$C_{11}{}^{13}CH_{22}{}^+$], 166 (1) [$C_{12}H_{22}{}^+$], 165 (1) [$C_{12}H_{21}{}^+$], 153 (1) [$C_{10}{}^{13}CH_{20}{}^+$], 152 (2) [$C_{11}H_{20}{}^+$], 151 (1) [$C_{11}H_{19}{}^+$], 139 (3) [$C_9{}^{13}CH_{18}{}^+$], 138 (5) [$C_{10}H_{18}{}^+$], 137 (4) [$C_{10}H_{17}{}^+$], 125 (7) [$C_8{}^{13}CH_{16}{}^+$], 124 (12) [$C_9H_{16}{}^+$], 123 (11) [$C_9H_{15}{}^+$], 111 (7) [$C_7{}^{13}CH_{14}{}^+$], 110 (12) [$C_8H_{14}{}^+$], 109 (11) [$C_8H_{13}{}^+$], 97 (23) [$C_6{}^{13}CH_{12}{}^+$], 96 (37) [$C_7H_{12}{}^+$], 95 (37) [$C_7H_{11}{}^+$], 82 (59) [$C_6H_{10}{}^+$], 81 (100) [$C_6H_9{}^+$]; elemental analysis: calcd C 80.85, H 13.51, found C 80.49, H 13.20.

4.6.3 | [1-^{13}C]Tricos-22-en-1-ol (**11c***)

m.p. 66–67°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21–1.42 (m, 36 H, $HO^{13}CH_2CH_2(C\underline{H}_2)_{18}CH_2CH{=}CH_2$), 1.52–1.62 (m, 2 H, $C\underline{H}_2{}^{13}CH_2OH$), 2.00–2.08 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 3.64 (dt, $^3J_{CH2/CH2} = 6.59$ Hz, $^1J_{13CH2/13C} = 140.90$ Hz, 2 H, $^{13}C\underline{H}_2OH$), 4.90–5.03 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]} = 17.11$ Hz, $^3J_{CH/CH2[Z]} = 10.24$ Hz, $^3J_{CH/CH2} = 6.66$ Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 25.72 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 28.94, 29.15 (2 × $\underline{C}H_2$), 29.43 (d, $^3J_{13C/C} = 3.62$ Hz, $\underline{C}H_2CH_2CH_2{}^{13}CH_2OH$), 29.51, 29.61, 29.69 (14 × $\underline{C}H_2$), 32.78 (d, $^1J_{13C/C} = 37.42$ Hz, $\underline{C}H_2{}^{13}CH_2OH$), 33.82 ($\underline{C}H_2CH{=}CH_2$), 63.07 ($^{13}\underline{C}H_2OH$), 114.05 ($CH_2CH{=}\underline{C}H_2$), 139.26 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3321 (m, OH), 3077 (w, $=CH_2$), 2917 (s, CH_2), 2847 (s, CH_2), 1641 (m, C=C), 1462 (m, CH_2), 1364 (w, CH_2), 1026 (m, ^{13}C–O), 991 (m, –HC=CH_2), 920 (w), 912 (m, –HC=CH_2), 720 (m, CH_2), 644 (m); MS (EI): *m*/*z* (%) = 340 (1) [$M^+ + H$], 321 (2) [$M^+ - H_2O$], 293 (2) [$M^+ - H_2O - C_2H_4$], 265 (2) [$M^+ - H_2O - C_4H_8$], 250 (1) [$M^+ - H_2O - C_4{}^{13}CH_{10}$], 222 (1) [$C_{16}H_{30}{}^+$],

194 (2) [$C_{14}H_{26}^+$], 181 (2) [$C_{12}{}^{13}CH_{24}^+$], 180 (2) [$C_{13}H_{24}^+$], 166 (3) [$C_{12}H_{22}^+$], 153 (3) [$C_{10}{}^{13}CH_{20}^+$], 152 (6) [$C_{11}H_{20}^+$], 151 (3) [$C_{11}H_{19}^+$], 139 (8) [$C_9{}^{13}CH_{18}^+$], 138 (12) [$C_{10}H_{18}^+$], 137 (8) [$C_{10}H_{17}^+$], 125 (17) [$C_8{}^{13}CH_{16}^+$], 124 (22) [$C_9H_{16}^+$], 123 (13) [$C_9H_{15}^+$], 111 (18) [$C_7{}^{13}CH_{14}^+$], 97 (41) [$C_6{}^{13}CH_{12}^+$], 96 (65) [$C_7H_{12}^+$], 95 (48) [$C_7H_{11}^+$], 82 (75) [$C_6H_{10}^+$], 81 (100) [$C_6H_9^+$]; elemental analysis: calcd C 81.64, H 13.65, found C 81.46, H 13.37.

4.6.4 | [1-^{13}C]Hentricont-30-en-1-ol (**11d***)

m.p. 83–84°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.20–1.39 (m, 52 H, $HO^{13}CH_2CH_2(C\underline{H}_2)_{26}CH_2CH{=}CH_2$), 1.51–1.61 (m, 2 H, $C\underline{H}_2{}^{13}CH_2OH$), 1.99–2.07 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 3.63 (dt, $^3J_{CH2/CH2}$ = 6.59 Hz, $^1J_{13CH2/13C}$ = 140.90 Hz, 2 H, $^{13}C\underline{H}_2OH$), 4.89–5.03 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.81 (ddt, $^3J_{CH/CH2[E]}$ = 16.61 Hz, $^3J_{CH/CH2[Z]}$ = 10.31 Hz, $^3J_{CH/CH2}$ = 6.87 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 25.69 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 28.90, 29.12 (2 × $\underline{C}H_2$), 29.40 (d, $^3J_{13C/C}$ = 3.62 Hz, $\underline{C}H_2CH_2CH_2{}^{13}CH_2OH$), 29.47, 29.57, 29.66 (22 × $\underline{C}H_2$), 32.68 (d, $^1J_{13C/C}$ = 37.42 Hz, $\underline{C}H_2{}^{13}CH_2OH$), 33.79 ($\underline{C}H_2CH{=}CH_2$), 62.93 ($^{13}\underline{C}H_2OH$), 114.01 ($CH_2CH{=}\underline{C}H_2$), 139.27 ($CH_2\underline{C}H{=}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3320 (m, OH), 3077 (w, =CH_2), 2916 (s, CH_2), 2847 (s, CH_2), 1641 (m, C=C), 1462 (m, CH_2), 1045 (m, ^{13}C—O), 991 (m, —HC=CH_2), 912 (m, —HC=CH_2), 720 (m, CH_2), 644 (m); elemental analysis: calcd C 82.63, H 13.83, found C 82.28, H 13.42.

4.7 | Synthesis and characterization of the ω-alkenylacetates 12a*–d* (modified after Tashiro and Mori[36])

In a 25-ml round flask, 2.17 mmol of the corresponding ω-alkenylalcohol (493-mg **11a***, 615-mg **11b***, 737-mg **11c***, 980-mg **11d***) were dissolved in 12 ml of pyridine. After 1.23-ml (13.02 mmol) acetic anhydride were added dropwise at 0°C, the reaction mixture was heated to 70°C for another 3 h. After the reaction mixture reached room temperature, it was poured into 60 ml of water and was then extracted four times with 50 ml of diethylether each. The combined organic phases were then washed with diluted hydrochloric acid (1 M), a saturated solution of $NaHCO_3$ and brine. The organic phase was then dried over Na_2SO_4 and filtered, and the solvent was evaporated under reduced pressure. Crude **12a*–d*** were purified by column chromatography using a mixture of ethyl acetate and light petroleum (1:18 for **12a*–c***, 1:10 for **12d***) as the eluent. Products were obtained either as a colourless oil (**12a***: 550 mg, 94%) or as colourless solids (**12b***: 644 mg, 94%; **12c***: 795 mg, 96%; **12d***: 900 mg, 84%).

4.7.1 | [1-^{13}C]Pentadec-14-enyl acetate (**12a***)

^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21–1.43 (m, 20 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_{10}CH_2CH{=}CH_2$), 1.57–1.67 (m, 2 H, $CH_3COO^{13}CH_2C\underline{H}_2$), 2.00–2.09 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.05 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 4.06 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 146.63 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$), 4.90–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]}$ = 17.11 Hz, $^3J_{CH/CH2[Z]}$ = 10.24 Hz, $^3J_{CH/CH2}$ = 6.66 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 21.01 ($\underline{C}H_3$), 25.90 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.58 (d, $^1J_{13C/C}$ = 38.63 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 28.93, 29.14 (2 × $\underline{C}H_2$), 29.25 (d, $^3J_{13C/C}$ = 3.62 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.50, 29.54, 29.61 (6 × $\underline{C}H_2$), 33.81 ($\underline{C}H_2CH{=}CH_2$), 64.66 ($CH_3COO^{13}\underline{C}H_2$), 114.06 ($CH_2CH{=}\underline{C}H_2$), 139.25 ($CH_2\underline{C}H{=}CH_2$), 171.24 ($CH_3\underline{C}OO^{13}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077 (w, =CH_2), 2922 (s, CH_2), 2853 (s, CH_2), 1742 (s, C=O), 1641 (m, C=C), 1464 (m, CH_2), 1364 (m, CH_2), 1233 (s, =C—O), 1030 (s, ^{13}C—O), 993 (m, —HC=CH_2), 909 (m, —HC=CH_2), 721 (m, CH_2), 633 (m), 606 (m); MS (EI): *m/z* (%) = 270 (1) [M^+], 209 (1) [$M^+ - C_2H_4O_2$], 181 (1) [$M^+ - C_2H_4O_2 - C_2H_4$], 180 (1) [$M^+ - C_4H_8O_2$], 166 (1) [$M^+ - C_5H_{10}O_2$], 152 (3) [$C_{11}H_{20}^+$], 138 (3) [$C_{10}H_{18}^+$], 125 (6) [$C_8{}^{13}CH_{16}^+$], 124 (8) [$C_9H_{16}^+$], 123 (5) [$C_9H_{15}^+$], 111 (6) [$C_7{}^{13}CH_{14}^+$], 110 (11) [$C_8H_{14}^+$], 109 (10) [$C_8H_{13}^+$], 97 (18) [$C_6{}^{13}CH_{12}^+$], 96 (34) [$C_7H_{12}^+$], 95 (36) [$C_7H_{11}^+$], 82 (63) [$C_6H_{10}^+$], 81 (100) [$C_6H_9^+$]; elemental analysis: calcd C 76.15, H 11.97, found C 76.12, H 11.89.

4.7.2 | [1-^{13}C]Nonadec-18-enyl acetate (**12b***)

m.p. 29–30°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21–1.43 (m, 28 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_{14}CH_2CH{=}CH_2$), 1.57–1.67 (m, 2 H, $CH_3COO^{13}CH_2C\underline{H}_2$), 2.00–2.10 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.05 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 4.06 (dt, $^3J_{CH2/CH2}$ = 6.59 Hz, $^1J_{13CH2/13C}$ = 146.06 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$), 4.90–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]}$ = 17.04, $^3J_{CH/CH2[Z]}$ = 10.31, $^3J_{CH/CH2}$ = 6.66 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 21.00 ($\underline{C}H_3$), 25.90 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.58 (d, $^1J_{13C/C}$ = 38.63 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 28.94,

29.14 (2 × $\underline{C}H_2$), 29.25 (d, $^3J_{13C/C}$ = 3.62 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.50, 29.55, 29.60, 29.66 (10 × $\underline{C}H_2$), 33.81 ($\underline{C}H_2CH{=}CH_2$), 64.66 ($CH_3COO^{13}\underline{C}H_2$), 114.05 ($CH_2CH{=}\underline{C}H_2$), 139.25 ($CH_2\underline{C}H{=}CH_2$), 171.23 ($CH_3\underline{C}OO^{13}CH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077 (w, =CH_2), 2914 (s, CH_2), 2849 (s, CH_2), 1728 (s, C=O), 1641 (m, C=C), 1462 (m, CH_2), 1367 (m, CH_2), 1240 (s, =C—O), 1030 (s, ^{13}C—O), 993 (m, —HC=CH_2), 910 (m, —HC=CH_2), 718 (m, CH_2), 644 (m), 607 (m); MS (EI): *m/z* (%) = 325 (1) [M^+], 265 (4) [$M^+ - C_2H_4O_2$], 237 (2) [$M^+ - C_2H_4O_2 - C_2H_4$], 222 (2) [$M^+ - C_4{}^{13}CH_{10}O_2$], 208 (3) [$M^+ - C_5{}^{13}CH_{12}O_2$], 194 (1) [$M^+ - C_6{}^{13}CH_{14}O_2$], 181 (2) [$C_{12}{}^{13}CH_{24}{}^+$], 180 (2) [$C_{13}H_{24}{}^+$], 166 (3) [$C_{12}H_{22}{}^+$], 152 (7) [$C_{11}H_{20}{}^+$], 138 (13) [$C_{10}H_{18}{}^+$], 125 (16) [$C_8{}^{13}CH_{16}{}^+$], 124 (16) [$C_9H_{16}{}^+$], 110 (17) [$C_8H_{14}{}^+$], 96 (53) [$C_7H_{12}{}^+$], 82 (68) [$C_6H_{10}{}^+$], 81 (100) [$C_6H_9{}^+$]; elemental analysis: calcd C 77.79, H 12.39, found C 77.59, H 12.04.

4.7.3 | [1-^{13}C]Tricos-22-enyl acetate (**12c***)

m.p. 45–46°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21–1.43 (m, 36 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_{18}CH_2CH{=}CH_2$), 1.57–1.67 (m, 2 H, $CH_3COO^{13}CH_2C\underline{H}_2$), 2.00–2.10 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.05 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 4.06 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 146.63 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$), 4.90–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]}$ = 16.90 Hz, $^3J_{CH/CH2[Z]}$ = 10.31 Hz, $^3J_{CH/CH2}$ = 6.73 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 21.00 ($\underline{C}H_3$), 25.90 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.58 (d, $^1J_{13C/C}$ = 38.63 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 28.94, 29.15 (2 × $\underline{C}H_2$), 29.25 (d, $^3J_{13C/C}$ = 3.62 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.51, 29.56, 29.61, 29.63, 29.68 (14 × $\underline{C}H_2$), 33.81 ($\underline{C}H_2CH{=}CH_2$), 64.66 ($CH_3COO^{13}\underline{C}H_2$), 114.05 ($CH_2CH{=}\underline{C}H_2$), 139.25 ($CH_2\underline{C}H{=}CH_2$), 171.23 ($CH_3\underline{C}OOCH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3076 (w, =CH_2), 2914 (s, CH_2), 2847 (s, CH_2), 1732 (s, C=O), 1642 (m, C=C), 1462 (m, CH_2), 1367 (m, CH_2), 1242 (s, =C—O), 1034 (s, ^{13}C—O), 991 (m, —HC=CH_2), 912 (m, —HC=CH_2), 720 (m, CH_2), 644 (m), 606 (m); MS (EI): *m/z* (%) = 354 (1) [M^+], 321 (5) [$M^+ - CH_4O$], 293 (1) [$M^+ - C_2H_4O_2$], 278 (1) [$M^+ - C_2{}^{13}CH_6O_2$], 264 (4) [$M^+ - C_3{}^{13}CH_8O_2$], 251 (3) [$M^+ - C_2H_4O_2 - C_3H_6$], 236 (3) [$C_{17}H_{32}{}^+$], 223 (1) [$C_{15}{}^{13}CH_{30}{}^+$], 222 (1) [$C_{16}H_{30}{}^+$], 208 (3) [$C_{15}H_{28}{}^+$], 194 (2) [$C_{13}H_{24}{}^+$], 180 (3) [$C_{13}H_{24}{}^+$], 166 (3) [$C_{12}H_{22}{}^+$], 152 (7) [$C_{11}H_{20}{}^+$], 138 (21) [$C_{10}H_{18}{}^+$], 124 (26) [$C_9H_{16}{}^+$], 110 (23) [$C_8H_{14}{}^+$], 96 (72) [$C_7H_{12}{}^+$], 82 (8) [$C_6H_{10}{}^+$], 81 (100) [$C_6H_9{}^+$]; elemental analysis: calcd C 78.94, H 12.68, found C 78.88, H 12.32.

4.7.4 | [1-^{13}C]Hentriacont-30-enyl acetate (**12d***)

m.p. 67–68°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.19–1.43 (m, 52 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_{26}CH_2CH{=}CH_2$), 1.57–1.67 (m, 2 H, $CH_3COO^{13}CH_2C\underline{H}_2$), 2.01–2.10 (m, 2 H, $C\underline{H}_2CH{=}CH_2$), 2.05 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 4.06 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 146.06 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$), 4.90–5.04 (m, 2 H, $CH_2CH{=}C\underline{H}_2$), 5.82 (ddt, $^3J_{CH/CH2[E]}$ = 17.04 Hz, $^3J_{CH/CH2[Z]}$ = 10.17 Hz, $^3J_{CH/CH2}$ = 6.44 Hz, 1 H, $CH_2C\underline{H}{=}CH_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 21.01 ($\underline{C}H_3$), 25.91 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.59 (d, $^1J_{13C/C}$ = 38.63 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 28.95, 29.16 (2 × $\underline{C}H_2$), 29.26 (d, $^3J_{13C/C}$ = 3.62 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.52, 29.57, 29.62, 29.70 (23 × $\underline{C}H_2$), 33.83 ($\underline{C}H_2CH{=}CH_2$), 64.67 ($CH_3COO^{13}\underline{C}H_2$), 114.06 ($CH_2CH{=}\underline{C}H_2$), 139.27 ($CH_2\underline{C}H{=}CH_2$), 171.24 ($CH_3\underline{C}OOCH_2$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3077 (w, =CH_2), 2914 (s, CH_2), 2847 (s, CH_2), 1738 (s, C=O), 1641 (m, C=C), 1462 (m, CH_2), 1367 (m, CH_2), 1242 (s, =C—O), 1036 (s, ^{13}C—O), 993 (m, —HC=CH_2), 912 (m, —HC=CH_2), 720 (m, CH_2), 642 (m), 606 (m); elemental analysis: calcd C 80.46, H 13.06, found C 79.95, H 12.62.

4.8 | Synthesis and characterization of the ω-acetoxycarboxylic acids 13a*–d* (modified after Lee et al.[39])

In a 25-ml round flask were placed 6.3 ml of water, which then were acidified with 0.75 ml of concentrated sulfuric acid and 0.15 ml of glacial acetic acid. Then the mixture was treated with 20 mg of the phase transfer catalyst Adogen 464 and a solution of 1.12 mmol of the corresponding ω-alkenylacetate (302-mg **12a***, 365-mg **12b***, 426-mg **12c***, 553-mg **12d***) in 6.3-ml dichloromethane. While cooling with ice, 530-mg (3.36 mmol) $KMnO_4$ were added in portions over a period of 3 h under vigorous stirring. Afterwards, the reaction mixture was stirred at room temperature for another 24 h before another portion of 89-mg (0.56 mmol) $KMnO_4$ was added followed by stirring the mixture for additional 48 h at room temperature. After the reaction time had expired, the now biphasic reaction mixture was treated in portions with 428 mg (4.12 mmol) of solid $NaHSO_3$, thus reducing excess

$KMnO_4$ and by that discolouring the system. In case of the reaction of **12a*–c***, the mixture was then treated with 50 ml of water and was subsequently extracted four times with 50-ml dichloromethane each. The combined organic phases were washed with water and brine, dried over Na_2SO_4, filtered and evaporated under reduced pressure. Purification of crude **13a*–c*** was achieved by column chromatography using a mixture of diethylether and light petroleum (1:2) as the eluent and yielding the pure products as colourless solids after evaporation of the solvents (**13a***: 226 mg, 75%; **13b***: 310 mg, 85%; **13c***: 351 mg, 82%). In case of the reaction of **12d*** following the addition of $NaHSO_3$ dichloromethane was evaporated under reduced pressure and to the resulting aqueous phase was added another portion of 150 ml of water leading to the precipitation of the crude products, which were filtered, washed with 20 ml of water and dried under reduced pressure. The resulting crude product **13d*** was then recrystallized from a mixture of light petroleum and ethyl acetate by first suspending the compound in boiling light petroleum before adding just the appropriate amount of ethyl acetate to dissolve the compound. After standing in the refrigerator overnight, **13d*** was obtained as colourless crystals, which were filtered, washed with 5 ml of cooled light petroleum and dried under reduced pressure (**13d***: 464 mg, 81%).

4.8.1 | [14-^{13}C]14-Acetoxytetradecanoic acid (**13a***)

m.p. 56–57°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.23–1.40 (m, 18 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_9CH_2CH_2COOH$), 1.57–1.68 (m, 4 H, $CH_3COO^{13}CH_2C\underline{H}_2$, $C\underline{H}_2CH_2COOH$), 2.05 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 2.35 (t, $^3J_{CH2/CH2}$ = 7.73 Hz, 2 H, $C\underline{H}_2COOH$), 4.06 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 146.06 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 21.01 ($\underline{C}H_3$), 24.66 ($\underline{C}H_2CH_2COOH$), 25.88 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.57 (d, $^1J_{13C/C}$ = 37.42 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 29.03 ($\underline{C}H_2CH_2CH_2COOH$), 29.23 (d, $^3J_{13C/C}$ = 3.62 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.39, 29.48, 29.52, 29.55 (6 × $\underline{C}H_2$), 33.98 ($\underline{C}H_2COOH$), 64.69 ($CH_3COO^{13}\underline{C}H_2$), 171.35 ($CH_3\underline{C}OO$), 179.74 ($\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 2914 (s, CH_2), 2847 (s, CH_2), 1728 (s, C=O_{Ester}), 1697 (s, C=$O_{Säure}$), 1464 (m, CH_2), 1429 (m, OH), 1372 (m, CH_2), 1248 (s, =C–O_{Ester}), 1034 (s, ^{13}C–O_{Ester}), 937 (m, OH), 721 (m, CH_2); MS (EI): m/z (%) = 287 (1) [M^+], 227 (10) [$M^+ - C_2H_4O_2$], 209 (6) [$M^+ - C_2H_4O_2 - H_2O$], 180 (3) [$C_{12}{}^{13}CH_{23}{}^+$], 166 (8) [$C_{11}{}^{13}CH_{21}{}^+$], 152 (8) [$C_{10}{}^{13}CH_{19}{}^+$], 138 (8) [$C_9{}^{13}CH_{17}{}^+$], 112 (30) [$C_7{}^{13}CH_{15}{}^+$], 98 (93) [$C_7H_{14}{}^+$], 83 (100) [$C_6H_{11}{}^+$]; elemental analysis: calcd C 67.21, H 10.52, found C 67.13, H 10.31.

4.8.2 | [18-^{13}C]18-Acetoxyoctadecanoic acid (**13b***)

m.p. 71–73°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.21–1.40 (m, 26 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_{13}CH_2CH_2COOH$), 1.57–1.68 (m, 4 H, $CH_3COO^{13}CH_2C\underline{H}_2$, $C\underline{H}_2CH_2COOH$), 2.05 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 2.35 (t, $^3J_{CH2/CH2}$ = 7.45 Hz, 2 H, $C\underline{H}_2COOH$), 4.06 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 146.63 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 21.00 ($\underline{C}H_3$), 24.66 ($\underline{C}H_2CH_2COOH$), 25.89 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.57 (d, $^1J_{13C/C}$ = 38.63 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 29.04 ($\underline{C}H_2CH_2CH_2COOH$), 29.24 (d, $^3J_{13C/C}$ = 4.83 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.41, 29.50, 29.56, 29.61, 29.64 (10 × $\underline{C}H_2$), 33.99 ($\underline{C}H_2COOH$), 64.69 ($CH_3COO^{13}\underline{C}H_2$), 171.34 ($CH_3\underline{C}OO$), 179.76 ($\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 2914 (s, CH_2), 2847 (s, CH_2), 1728 (s, C=O_{Ester}), 1793 (s, C=$O_{Säure}$), 1462 (m, CH_2), 1427 (m, OH), 1367 (m, CH_2), 1246 (s, =C–O_{Ester}), 1034 (s, ^{13}C–O_{Ester}), 929 (m, OH), 720 (m, CH_2); elemental analysis: calcd C 70.22, H 11.15, found C 70.14, H 10.88.

4.8.3 | [22-^{13}C]22-Acetoxydocosanoic acid (**13c***)

m.p. 80–82°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.20–1.40 (m, 34 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_{17}CH_2CH_2COOH$), 1.57–1.68 (m, 4 H, $CH_3COO^{13}CH_2C\underline{H}_2$, $C\underline{H}_2CH_2COOH$), 2.05 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 2.35 (t, $^3J_{CH2/CH2}$ = 7.45 Hz, 2 H, $C\underline{H}_2COOH$), 4.06 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 146.63 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$); ^{13}C-NMR (126 MHz, $CDCl_3$, 298 K): δ (ppm) = 21.01 ($\underline{C}H_3$), 24.67 ($\underline{C}H_2CH_2COOH$), 25.89 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.57 (d, $^1J_{13C/C}$ = 38.63 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 29.04 ($\underline{C}H_2CH_2CH_2COOH$), 29.25 (d, $^3J_{13C/C}$ = 4.83 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.42, 29.51, 29.55, 29.57, 29.63, 29.67 (14 × $\underline{C}H_2$), 33.97 ($\underline{C}H_2COOH$), 64.69 ($CH_3COO^{13}\underline{C}H_2$), 171.34 ($CH_3\underline{C}OO$), 179.63 ($\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 2914 (s, CH_2), 2847 (s, CH_2), 1730 (s, C=O_{Ester}), 1797 (s, C=$O_{Säure}$), 1462 (m, CH_2), 1429 (m, OH), 1371 (m, CH_2), 1252 (s, =C–O_{Ester}), 1035 (s, ^{13}C–O_{Ester}), 944 (m, OH), 720 (m, CH_2); elemental analysis: calcd C 72.38, H 11.60, found C 72.00, H 11.23.

4.8.4 | [30-^{13}C]30-Acetoxytriacontanoic acid (**13d***)

m.p. 94–95°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.20–1.39 (m, 34 H, $CH_3COO^{13}CH_2CH_2(C\underline{H}_2)_{17}CH_2CH_2COOH$), 1.55–1.66 (m, 4 H, $CH_3COO^{13}CH_2C\underline{H}_2$, $C\underline{H}_2CH_2COOH$), 2.03 (s, 3H, $C\underline{H}_3COO^{13}CH_2$), 2.31 (t, $^3J_{CH2/CH2}$ = 7.73 Hz, 2 H, $C\underline{H}_2COOH$), 4.04 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 146.06 Hz, 2 H, $CH_3COO^{13}C\underline{H}_2$); ^{13}C-NMR (126 MHz, $CDCl_3$/MEOD, 298 K): δ (ppm) = 20.94 ($\underline{C}H_3$), 24.75 ($\underline{C}H_2CH_2COOH$), 25.85 ($CH_3COO^{13}CH_2CH_2\underline{C}H_2$), 28.52 (d, $^1J_{13C/C}$ = 37.42 Hz, $CH_3COO^{13}CH_2\underline{C}H_2$), 29.06 ($\underline{C}H_2CH_2CH_2COOH$), 29.21 (d, $^3J_{13C/C}$ = 3.62 Hz, $CH_3COO^{13}CH_2CH_2CH_2\underline{C}H_2$), 29.41, 29.47, 29.52, 29.55, 29.65 (22 × $\underline{C}H_2$), 33.91 ($\underline{C}H_2COOH$), 64.72 ($CH_3COO^{13}\underline{C}H_2$), 171.47 ($CH_3\underline{C}OO$), 177.92 ($\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3300–2500 (m, OH), 2914 (s, CH_2), 2847 (s, CH_2), 1732 (s, C═O_{Ester}), 1697 (s, C═$O_{Säure}$), 1462 (m, CH_2), 1429 (m, OH), 1370 (m, CH_2), 1244 (s, ═C—O_{Ester}), 1034 (s, ^{13}C—O_{Ester}), 949 (m, OH), 720 (m, CH_2); elemental analysis: calcd C 75.29, H 12.21, found C 74.84, H 11.89.

4.9 | Synthesis and characterization of the ω-hydroxycarboxylic acids 14a*–d* (modified after Tori et al.[40])

In a 100-ml round flask were placed 0.41 mmol of the corresponding ω-acetoxycarboxylic acid (118-mg **13a***, 141-mg **13b***, 164-mg **13c***, 210-mg **13d***), which were then treated with a solution of 4.5-g NaOH in 100 ml of methanol. The reaction mixture was then stirred for 5 days at room temperature (in case of the reaction of **13d***, 7.5-g NaOH were used and stirring was performed for 7 days). After the reaction time had expired, the mixture was poured into 200 ml of water and was then acidified by half concentrated hydrochloric acid leading to the precipitation of a colourless solid. This suspension was then stirred for 2 h at room temperature. Then the solution was filtered, and the precipitate washed with 50 ml of water and dried under reduced pressure overnight. For purification, the crude products were treated with an excess of hot ethyl acetate and filtered using a G3 frit, which was then washed twice with an additional portion of hot ethyl acetate. The combined organic solutions were then reduced to approximately one third of the original volume and was then treated with light petroleum. This solution was allowed to stand in the refrigerator overnight. The resulting crystals were filtered, washed with 3-ml cooled light petroleum and dried under reduced pressure yielding colourless crystals of the product compounds (**14a***: 90 mg, 89%; **14b***: 115 mg, 93%; **14c***: 133 mg, 91%; **14d***: 119 mg, 62%).

4.9.1 | [14-^{13}C]14-Hydroxytetradecanoic acid (**14a***)

m.p. 91–92°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.20–1.39 (m, 18 H, $HO^{13}CH_2CH_2(C\underline{H}_2)_9CH_2CH_2COOH$), 1.50–1.67 (m, 4 H, $C\underline{H}_2CH_2COOH$, $C\underline{H}_2CH_2{}^{13}OH$), 2.33 (t, $^3J_{CH2/CH2}$ = 7.73 Hz, 2 H, $C\underline{H}_2COOH$), 3.63 (dt, $^3J_{CH2/CH2}$ = 6.87 Hz, $^1J_{13CH2/13C}$ = 140.90 Hz, 2 H, $C\underline{H}_2{}^{13}OH$); ^{13}C-NMR (151 MHz, $CDCl_3$, 298 K): δ (ppm) = 24.68 ($\underline{C}H_2CH_2COOH$), 25.69 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 28.99 ($\underline{C}H_2CH_2CH_2COOH$), 29.14, 29.32, 29.36, 29.44, 29.47 (7 × $\underline{C}H_2$), 32.71 (d, $^1J_{13C/C}$ = 36.22 Hz, $\underline{C}H_2{}^{13}CH_2OH$), 33.88 ($\underline{C}H_2COOH$), 63.08 ($^{13}\underline{C}H_2OH$), 178.88 ($CH_2\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3500–2500 (m, OH), 2913 (s, CH_2), 2847 (s, CH_2), 1682 (m, C═O), 1470 (s, CH_2), 1410 (w, OH), 1306 (m, CH_2), 1020 (m, ^{13}C—O), 718 (m, CH_2), 529 (w); elemental analysis: calcd C 68.94, H 11.50, found C 68.91, H 11.08.

4.9.2 | [18-^{13}C]18-Hydroxyoctadecanoic acid (**14b***)

m.p. 97–99°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.22–1.40 (m, 26 H, $HO^{13}CH_2CH_2(C\underline{H}_2)_{13}CH_2CH_2COOH$), 1.53–1.68 (m, 4 H, $C\underline{H}_2CH_2COOH$, $C\underline{H}_2CH_2{}^{13}OH$), 2.35 (t, $^3J_{CH2/CH2}$ = 7.45 Hz, 2 H, $C\underline{H}_2COOH$), 3.65 (dt, $^3J_{CH2/CH2}$ = 6.59 Hz, $^1J_{13CH2/13C}$ = 141.48 Hz, 2 H, $C\underline{H}_2{}^{13}OH$); ^{13}C-NMR (151 MHz, THF, 298 K): δ (ppm) = 26.03 ($\underline{C}H_2CH_2COOH$), 27.11 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 30.31 ($\underline{C}H_2CH_2CH_2COOH$), 30.52, 30.66, 30.72, 30.76, 30.82, 30.87 (11 × $\underline{C}H_2$), 34.27 (d, $^1J_{13C/C}$ = 38.63 Hz, $\underline{C}H_2{}^{13}CH_2OH$), 34.44 ($\underline{C}H_2COOH$), 62.72 ($^{13}\underline{C}H_2OH$), 174.66 ($CH_2\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3500–2500 (m, OH), 2914 (s, CH_2), 2849 (s, CH_2), 1705 (m, C═O), 1470 (s, CH_2), 1412 (w, OH), 1294 (m, CH_2), 1042 (m, ^{13}C—O), 718 (m, CH_2), 528 (w); elemental analysis: calcd C 72.04, H 12.04, found C 71.60, H 11.80.

4.9.3 | [22-^{13}C]22-Hydroxydocosanoic acid (**14c***)

m.p. 107–108°C; ^{1}H-NMR (500 MHz, $CDCl_3$, 298 K): δ (ppm) = 1.20–1.41 (m, 34 H, $HO^{13}CH_2CH_2(C\underline{H}_2)_{17}CH_2CH_2COOH$), 1.53–1.68 (m, 4 H, $C\underline{H}_2CH_2COOH$, $C\underline{H}_2CH_2{}^{13}OH$), 2.36 (t, $^3J_{CH2/CH2}$ = 7.45 Hz, 2 H, $C\underline{H}_2COOH$), 3.65 (dt, $^3J_{CH2/CH2}$ = 6.59 Hz, $^1J_{13CH2/13C}$ = 140.90 Hz,

2 H, C$\underline{H}_2{}^{13}$OH); ^{13}C-NMR (151 MHz, THF, 298 K): δ (ppm) = 26.04 ($\underline{C}H_2CH_2COOH$), 27.11 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 30.31 ($\underline{C}H_2CH_2CH_2COOH$), 30.52, 30.67, 30.72, 30.77, 30.82, 30.87 (15 × $\underline{C}H_2$), 34.27 (d, $^1J_{13C/C}$ = 38.63 Hz, $\underline{C}H_2{}^{13}CH_2OH$), 34.44 ($\underline{C}H_2COOH$), 62.72 ($^{13}\underline{C}H_2OH$), 174.66 ($CH_2\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3500–2500 (m, OH), 2913 (s, CH_2), 2847 (s, CH_2), 1697 (m, C═O), 1471 (s, CH_2), 1411 (w, OH), 1298 (m, CH_2), 1041 (m, ^{13}C—O), 717 (m, CH_2), 533 (w); elemental analysis: calcd C 74.17, H 12.40, found C 73.60, H 12.08.

4.9.4 | [30-^{13}C]30-Hydroxytricontanoic acid (**14d***)

m.p. 105–108°C; ^{1}H-NMR (500 MHz, DMSO, 373 K): δ (ppm) = 1.20–1.35 (m, 34 H, HO$^{13}CH_2CH_2(C\underline{H}_2)_{17}CH_2CH_2COOH$), 1.39–1.57 (m, 4 H, $C\underline{H}_2CH_2COOH$, $C\underline{H}_2CH_2{}^{13}OH$), 2.19 (t, $^3J_{CH2/CH2}$ = 7.45 Hz, 2 H, $C\underline{H}_2COOH$), 3.40 (dt, $^3J_{CH2/CH2}$ = 6.30 Hz, $^1J_{13CH2/13C}$ = 138.04 Hz, 2 H, $C\underline{H}_2{}^{13}OH$); ^{13}C-NMR (151 MHz, THF, 298 K): δ (ppm) = 24.13 ($\underline{C}H_2CH_2COOH$), 27.11 ($\underline{C}H_2CH_2{}^{13}CH_2OH$), 28.17 ($\underline{C}H_2CH_2CH_2COOH$), 28.28, 28.53, 28.65 (23 × $\underline{C}H_2$), 32.17 (d, $^1J_{13C/C}$ = 37.42 Hz, $\underline{C}H_2{}^{13}CH_2OH$), 33.37 ($\underline{C}H_2COOH$), 60.47 ($^{13}\underline{C}H_2OH$), 173.74 ($CH_2\underline{C}OOH$); IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 3500–2500 (m, OH), 2913 (s, CH_2), 2847 (s, CH_2), 1703 (m, C═O), 1472 (s, CH_2), 1411 (w, OH), 1274 (m, CH_2), 1037 (m, ^{13}C—O), 716 (m, CH_2), 532 (w); elemental analysis: calcd C 76.91, H 12.87, found C 76.40, H 12.48.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supporting information contains synthetic procedures and analytical data for compounds **2e–h**, **4a–g**, **5a–d**, **6a–d**, **7a–d**, **8a–d**, **9a–d**, **10a–d**, **11a–d**, **12a–d**, **13a–d** and **14a–c** as well as ^{1}H- and ^{13}C-NMR spectra of compounds **2e–h**, **4a–g**, **5a–d**, **6a–d**, **7a–d**, **8a–d**, **9a–d**, **10a–d**, **11a–d**, **12a–d**, **13a–d** and **14a–c**. All compounds except **2e–h**, **4a–g**, **5a–d** and **6a–d** were synthesized with and without a label. Compounds with a ^{13}C label are marked with an asterisk (*). In addition, investigations on the isotopic purity of K^{13}CN starting material are available.[26]

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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