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# Synthesis of analogues of the 2-*O*-alkyl glycerate part of the moenomycins

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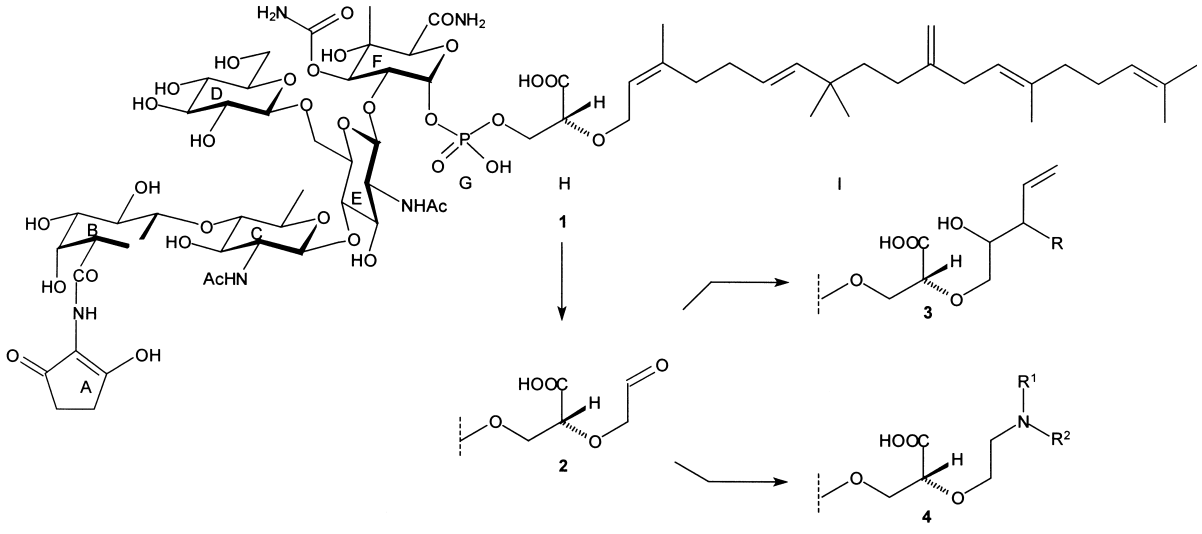
**Abstract**—The title compounds have been prepared by hydroxymethylation of chiral enolates 

## 1. Introduction

The moenomycin antibiotics (see, for example, moenomycin A (**1**),[1] Scheme 1) are the only compounds known with certainty to inhibit the enzyme of the transglycosylation reaction,[2] one of the last steps in the biosynthesis of peptidoglycan[3] (main component of the bacterial cell wall). A mechanism for their mode of action has been proposed.[4–6] It is assumed that they are anchored to the cytoplasmic membrane via the lipid part and bind then highly selectively to the active site of the enzyme via the C–E–F trisaccharide.[7] Whereas the structural requirements for antibiotic activity in the carbohydrate part have been investigated in great detail,[7,8] little is known how membrane anchoring assists the interaction of the antibiotic with the enzyme. The $C_{25}$ lipid may be cyclized in its terminal part[9] as well as saturated without loss of antibiotic activity.[10] However, converting the glyceric acid part into its methyl ester or introducing a single OH group to C-17 or C-18 of the lipid chain abolishes the antibiotic activity completely. Similarly, cleavage of the bond between the glyceric acid unit and the $C_{25}$ lipid leads to a compound devoid of antibiotic activity.[11,12]




**Scheme 1.**

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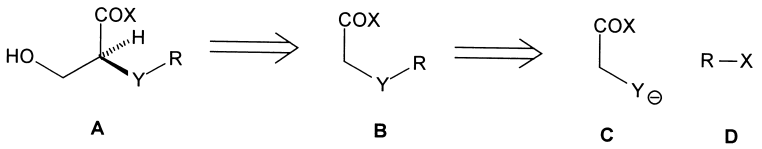



**Scheme 2.**

Moenomycin can be degraded very efficiently by ozonolysis into a pentasaccharide derivative in which the chromophore A part is removed and the lipid chain shortened to a glycolaldehyde unit (see formula **2**). This aldehyde has been converted into moenomycin analogues with new lipid chains by indium-mediated Barbier reactions with allylic and benzylic halides (**2→3**)[13] and by reductive amination reactions (**2→4**),[14] respectively (see Scheme 1). Most of these compounds were antibiotically inactive. It may be assumed that the polar groups in the lipid chains prevent proper alignment of the antibiotic at the outer face of the membrane.

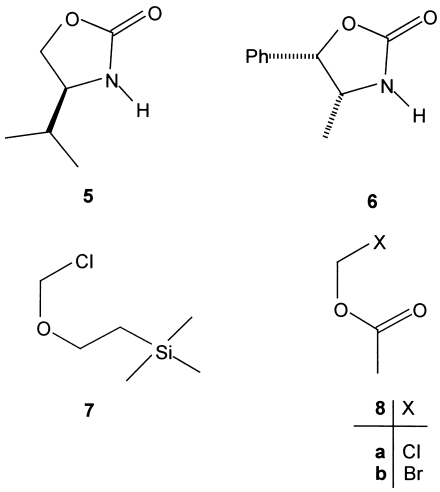
Membrane anchoring besides assisting recognition of moenomycin by the enzyme is made responsible for the insufficient pharmacokinetics of these antibiotics.[15] Thus, it is important to find access to antibiotically active moenomycin analogues with more appropriate lipid parts. The 2-*O*-alkylation of suitably 3-*O*-protected glyceric acid derivatives usually suffers from low yields, probably caused by elimination.[16] Previously, we have developed a synthetic scheme for this class of compounds that commences from D-mannitol and involves (i) protection of the 1-, 3-, 4-, 6-OH groups, (ii) alkylation of the OH-groups at C-2 and C-5, (iii) removal of the protecting groups, (iv) glycol cleavage, and (v) oxidation of the intermediate 2-*O*-alkylglyceraldehyde.[16] This sequence is lengthy, and it provides, when conducted as described, only one enantiomeric series.[17] It was the purpose of the studies reported below to seek for more convenient routes to structural analogues of the 2-*O*-alkylglycerate part of the moenomycins.

## 2. Synthetic considerations

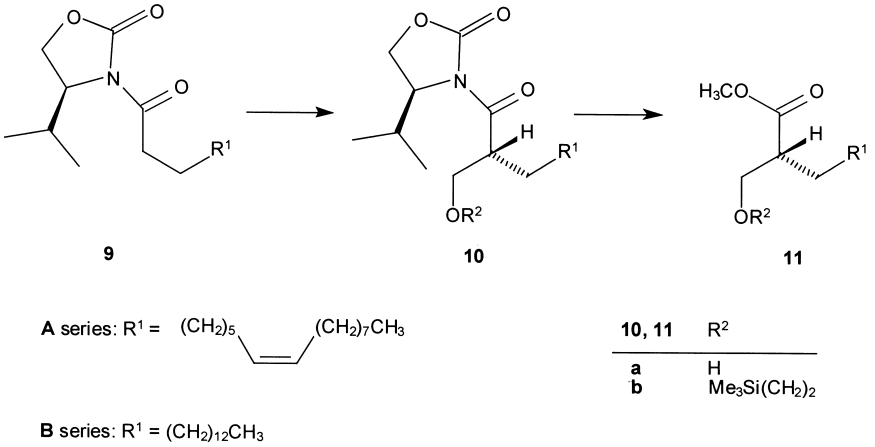
Our goal was the conversion of compounds of type **B** (Scheme 2, Y=$CH_2$ and O, respectively) into the target compounds **A** by an (overall) enantioselective hydroxymethylation. For compounds **B** we envisioned the use of simple fatty acids or a synthesis from a nucleophilic synthon of type **C** and an alkyl halide **D**. The Evans route[18] seemed well-suited to achieve the desired stereoselective hydroxymethylation. This assumption was reduced to practice (vide infra).

## 3. Hydroxymethylation of fatty acids

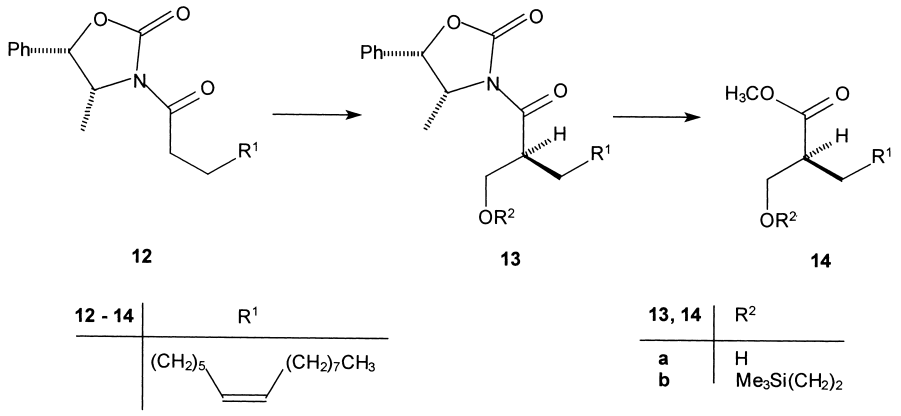
The Evans oxazolidinone **5** (Scheme 3) was *N*-acylated with oleic and palmitic acid in the usual way and the acylation products **9A** and **9B** (Scheme 4) were converted into the boron and the lithium enolates, respectively. The boron enolates were trapped with formaldehyde (freshly prepared solution in $CH_2Cl_2$) and the lithium enolates with trimethylsilylethoxymethyl chloride (SEM chloride, **7**).




**Scheme 3.**




**Scheme 4.**




**Scheme 5.**

The corresponding alkylation products **10Aa/10Ba** and **10Ab/10Bb** were obtained in very satifactory yields (in the range of 75–80%). In one case (**9A**) the lithium enolate was also trapped with the formaldehyde equivalents chloromethyl acetate (**8a**).[19] The acetoxymethyl compound (formula not shown) was obtained in a lower yield (59%).

Removal of the auxiliary from **10Aa** and **10Ba** was accomplished by treatment with 0.1 mol $L^{-1}$ magnesium methoxide in absolute methanol. The yields of the methyl esters **11Aa** and **11Ba** were in the range of 90%. Sequential treatment of **10Ab** and **10Bb** with 0.1 mol $L^{-1}$ magnesium methoxide in absolute methanol and lithium tetrafluoroborate in 98:2 acetonitrile–water[20] removed the auxiliary and the trimethylsilylethyl protecting group to furnish **11Aa** and **11Ba**, respectively. Both reactions proceeded uneventfully. Mosher ester analysis[21] proved that methyl (*R*)-2-hydroxymethylpalmitate (**11Ba**, obtained via the trimethylsilylethoxymethyl chloride route) was enantiomerically pure in the limits of the NMR analysis ($^{19}$F NMR). For comparison *rac*-**11Ba** was prepared by direct hydroxymethylation of methyl palmitate.[22,23]

In the same fashion the Evans auxiliary **6** was coupled to oleic acid to provide **12** (Scheme 5). The boron enolate of **12** was trapped with formaldehyde to give **13a** and the lithium enolate with **7** to furnish **13b**. The direct conversion of **13a** into **14a** and the two-step procedure **13b→14b→14a** were performed as described earlier. The $^1$H NMR spectra of the two enantiomers of methyl 2-hydroxymethyloleate (**11Aa** and **14a**) in the presence of the optically active shift reagent $Eu(TFC)_3$,[24,25] (addition of 10, 20 and 30 mol%) were compared. The lanthanide-induced shift for the methoxy group was somewhat different for the two enantiomers but the chemical shift difference was too small to permit an accurate determination of the optical purity. The CD curves of both enantiomers (CD maximum at 212 nm) were, of course, mirror images.

## 4. Reaction of geranyl halides with homoenolate equivalents and subsequent hydroxymethylation

Compounds of type **B** (Scheme 2, Y=$CH_2$) with an isoprenoid R seemed to be accessible from propionic acid homoenolate equivalents and allyl halides. First the nickelalactone route of Schönecker and Walther was tried.[26,27] In a test reaction under the published conditions (presence of $MnI_2$) the reaction of **15** (Scheme 6) with ethyl iodide provided the alkylation product in 74% (isolated) yield. However, with geranyl iodide (**19a**) no C–C bond formation was observed in agreement with a previous report by Fischer et al.[28]

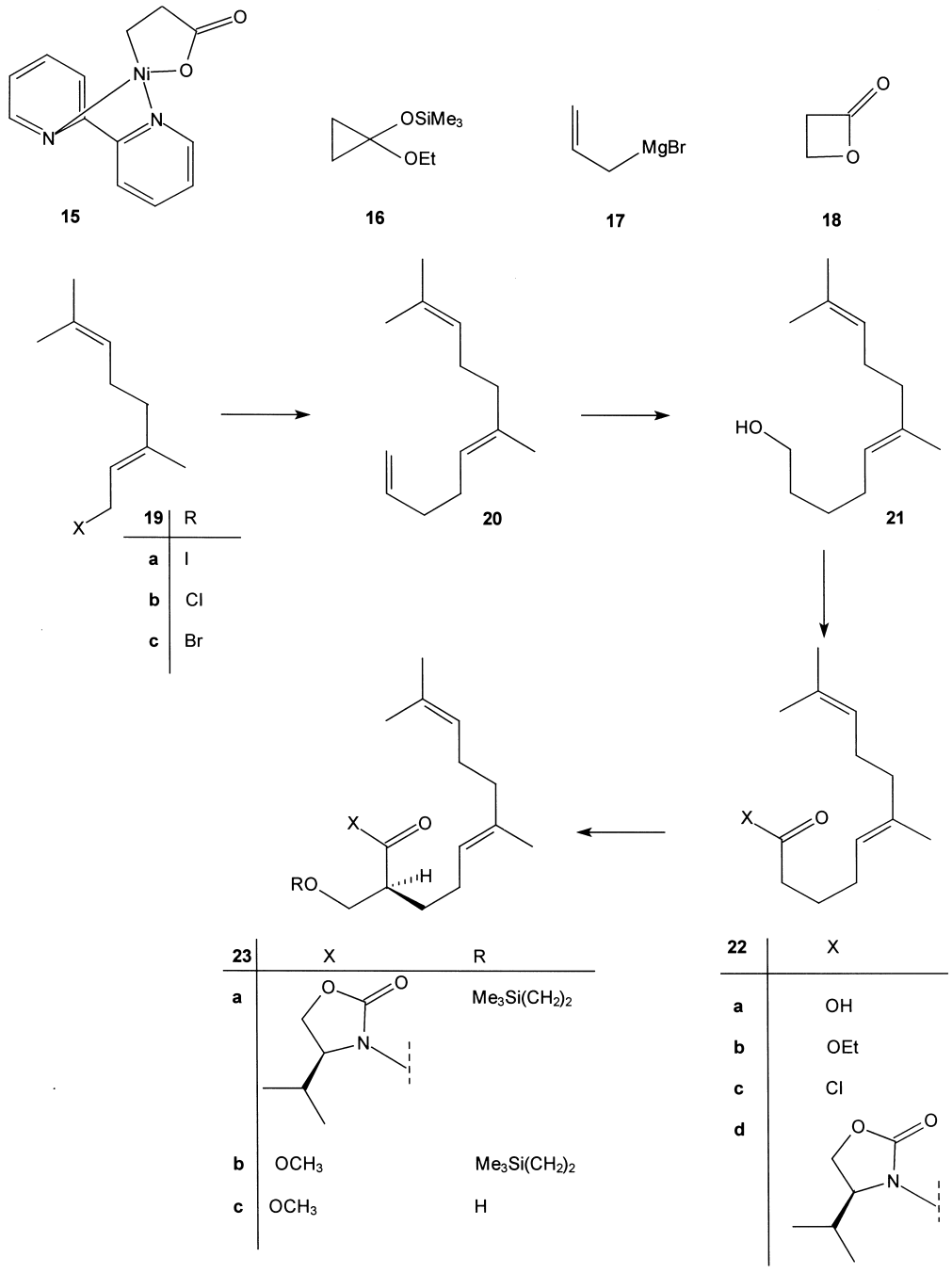
Nakamura has described the ring opening of mixed cyclopropanone acetals to give metal homoenolates of propionates.[29] It was reported that the zinc enolate on reaction with allyl chlorides led almost exclusively to $S_N2'$ products, whereas the nickel-promoted allylation proceeded in a $S_N2$ manner. Under the latter conditions the desired compound **22b** was obtained from **16** and geranyl chloride (**19b**) in 28% yield as a 9:1 mixture of $S_N2$ and $S_N2'$ isomers.

Use of the allyl anion as an equivalent of the propionic acid homoenolate (Grieco[30]) was quite successful. Allylmagnesium bromide (**17**) on reaction with geranyl bromide (**19c**) gave the coupling product **20** in 94% yield. Hydroboration with disiamylborane and subsequent oxidation provided the primary alcohol **21** in 72% yield, and the final Jones oxidation (**21→22a**) proceeded also uneventfully. The sequence can also be conducted successfully with inversed reactivities. Thus, opening of β-propiolactone (**18**) in a $S_N2$ fashion according to Fujisawa and coworkers[31] with the halomagnesium cuprate derived from geranylbromide (**19c**) provided the desired acid **22a** in 64% yield.

**22a** was armed with the auxiliary **5** (via **22c**) to give **22d**. Lithium enolate formation and trapping with SEM chloride provided **23a** in 68% yield. The auxiliary and the protecting group were removed sequentially as described earlier to give methyl ester **23c**.

## 5. Hydroxymethylation of alkoxy acetates

The sodium alkoxides of geraniol, nerol and of 4-phenylbenzyl alcohol were alkylated with sodium bromoacetate in DMF solution[32] and the corresponding alkoxyacetic acids

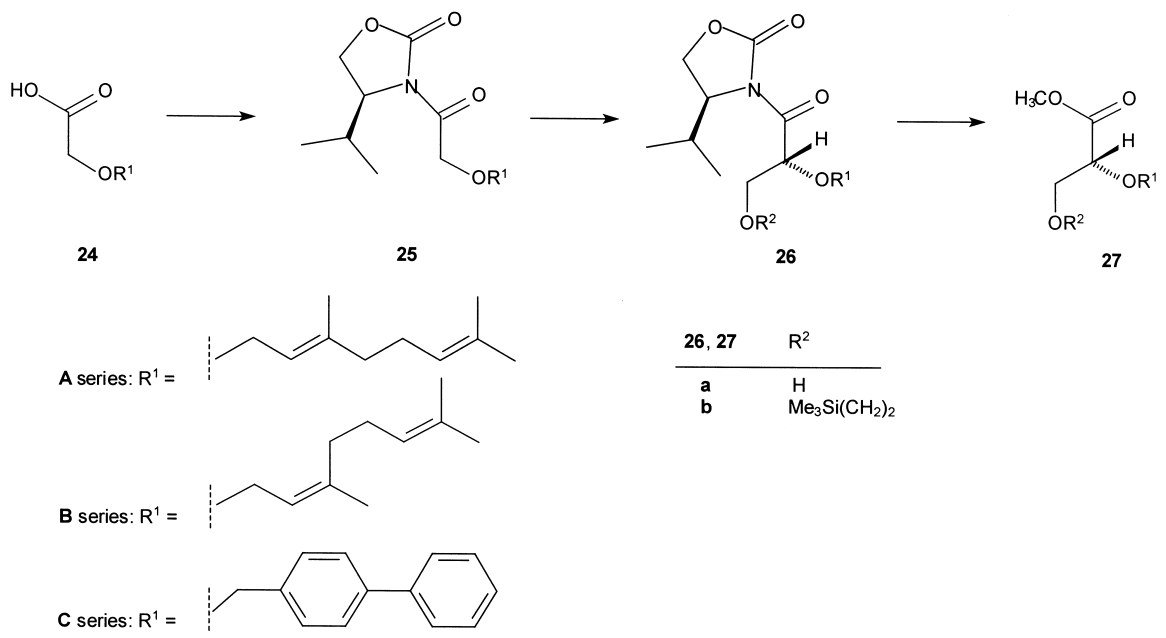



**Scheme 6.**

**24A**, **24B**, and **24C** were coupled to the Evans auxiliary **5** (see Scheme 7) in the usual way. The lithium enolates of **25A** and **25B** were alkylated with the two formaldehyde equivalents **7** and bromomethyl acetate (**8b**)[33] and that of **25C** only with **7**. In all experiments the yields were only moderate (around 40%). The acetyl group of the acetoxymethylated products was lost during the work-up procedure to give **26Aa** and **26Ba** directly. Removal of the auxiliary from **26Aa** and **26Ba** and removal of the auxiliary and liberation of the primary OH group in the cases of **26Ab** and **26Cb** under the conditions described earlier provided the desired methyl (*R*)-2-*O*-alkyl-glycerates **27Aa**, **27Ba**, and **27Ca**.

## 6. Merits of the Evans route to 2-substituted 3-hydroxypropionates

The approach described herein makes 2-*O*-alkylglycerate building blocks for moenomycin analogues easily available in both enantiomeric series. Especially facile is the hydroxymethylation in the fatty acid series (see Scheme 4) and for compound **22d** to give compounds of type **A** (Scheme 2, Y=$CH_2$). Hydroxymethylation in the alkoxyacetic acid series (see **25** in Scheme 7) which eventually leads to 2-*O*-alkylglycerates generally proceeds with lower yields (around 40%), probably as a result of a reduced nucleophilicity of the enolate. Of the hydroxymethylating agents




**Scheme 7.**

that were compared we found trimethylsilylethoxymethyl chloride (**7**) originally introduced by Lipshutz et al.[34] as an alcohol protecting group to be the most convenient one.

## 7. Synthesis of a new moenomycin analogue

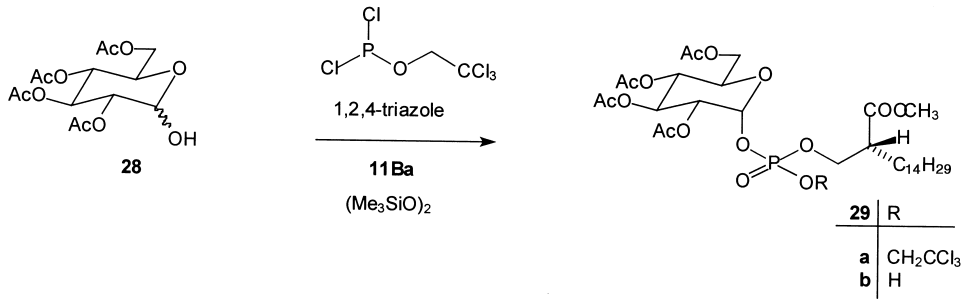
Following an established route methyl (*R*)-2-hydroxymethylpalmitate (**11Ba**, see Scheme 4) was converted into a simple moenomycin analogue.[35] In these experiments the commercial 2,2,2-trichloroethyl dichlorophosphite[36] was converted into the ditriazolide[37] which in turn was sequentially treated with 2,3,4,6-tetra-*O*-acetyl-D-glucose (**28**) and with **11Ba** (Scheme 8). The intermediate phosphite was oxidized with bis(trimethylsilyl)peroxide[38,39] to give the corresponding phosphate **29a**. $^{1}H$ and $^{31}P$ NMR indicated that only the α-phosphate was formed as a 2:1 mixture of two diastereoisomers. The removal of the phosphate protecting group with zinc–copper couple[40] in the presence of 2,4-pentanedione[41] to give **29b** required harsher conditions than usually encountered with the 2,2,2-trichloro-1,1-dimethylethoxy protecting group.[7]

Synthesis of trisaccharide analogues of moenomycin A with new lipid chains and their antibiotic properties will be reported in due course.

## 8. Experimental

### 8.1. General procedures

All $O_2$- or moisture-sensitive reactions were performed in oven-dried glassware under a positive pressure of argon. Liquids and solutions were transferred by syringe. Small-scale reactions were performed in Wheaton serum bottles sealed with aluminum caps with open top and Teflon-faced septum (Aldrich). Usual work-up means partitioning the reaction mixture between an aqueous phase and the solvent indicated in brackets, drying the combined organic solutions over $Na_2SO_4$, and removal of solvent by distillation using a rotatory evaporator (bath temperature 45°C). Solvents were purified by standard techniques. The following materials and methods were used for chromatographic separations: preparative gravitational liquid chromatography (LC): silica gel 63–100 μm (ICN Biomedicals); flash chromatography (FC):[42] silica gel 32–63 μm (ICN Biomedicals); medium-pressure liquid chromatography (MPLC): silica gel




**Scheme 8.**

40–60 μm (Grace), Duramat pump (CfG); analytical TLC: Merck precoated silica gel 60 $F_{254}$ plates (0.2 mm), spots were identified under a UV lamp (λ=254 nm, Camag 29 200) and with a 2.22 mol $L^{-1}$ $H_2SO_4$ solution which contained $Ce(SO_4)_2{\cdot}4H_2O$ (10 g $L^{-1}$) and $H_3[PO_4(Mo_3O_9)_4]{\cdot}H_2O$ (25 g $L^{-1}$)[43] and heating at 140°C, a $KMnO_4$ reagent (25 g of $KMnO_4$, 10 g of $Na_2CO_3$, in water (500 mL)), or an anisaldehyde reagent for carbohydrates (2 mL of anisaldehyde, 8 mL of conc. $H_2SO_4$ in ethanol (190 mL)). NMR and MS equipment: NMR: UNITY 400 (Varian), DRX 400 (Bruker), DRX 600 (Bruker), gEMINI 200 (Varian), gEMINI 2000 (Varian); Mass spectrometry: EI MS: MAT-731 (Varian), FAB MS: VG Autospec (Fisons, matrix: 3-nitrobenzylalcohol), ESI MS: FT-ICR-MS Apex II (Bruker Daltonics, water–methanol). Following the molecular formula two masses are always communicated, the first was calculated using the International Atomic Masses, the second is the mono-isotopic mass. IR: Genesis FTIR (ATI Mattson). UV: Beckman DU 650. CD: Jasco J-715 (10 mm cuvette). $[\alpha]_D$: Polartronic D (Schmidt+Haensch).

All acid chlorides were prepared from the corresponding carboxylic acids with oxalyl chloride.

### 8.2. General procedure 1: *N*-acylation of oxazolidinones 5 and 6

To a solution of the oxazolidinone in THF (10 mL/2 mmol of the oxazolidinone) at −78°C butyllithium (1.6 mol $L^{-1}$ in hexane, 1.1 equiv.) was added and the mixture was stirred for 30 min. The acid chloride (1.0–1.1 equiv.) was added and the reaction mixture was stirred at −78°C for 1 h. A saturated aqueous solution of $NaHCO_3$ was added. Usual workup (ether) gave the acylated oxazolidinone.

### 8.3. General procedure 2: alkylation of acylated oxazolidinones with formaldehyde equivalents 7, 8a, and 8b

To a freshly prepared solution of LDA (1 equiv.) in THF (1 mL/0.3 mmol of the acylated oxazolidinone) at −78°C the acylated oxazolidinone was added and the mixture was stirred for 1 h. A solution of the halide (1–3 equiv.) in THF was added and stirring was continued at −78°C for 1 h and at −30°C for 12 h. A saturated aqueous solution of $NH_4Cl$ was added and the product was worked up as usual (ether).

### 8.4. General procedure 3: alkylation of the acylated oxazolidinones with formaldehyde

To a freshly prepared solution of dibutylboryl trifluoromethanesulfonate (1 equiv.) and ethyldiisopropylamine (1 equiv.) in $CH_2Cl_2$ (2.4 mL/0.3 mmol of the *N*-acyloxazolidinone) the *N*-acyloxazolidinone was added and the mixture was stirred for 1 h at −78°C. A freshly prepared $CH_2Cl_2$ solution saturated with formaldehyde was added. The mixture was stirred at −78°C for 1 h and at −30°C for 12 h. A pH 7 phosphate buffer and a 1:1 solution of $H_2O_2$ (30%)—methanol were added sequentially and the mixture was stirred at 0°C for 1 h. Usual work-up (ether) provided the crude hydroxymethyl derivative.

### 8.5. General procedure 4: removal of the auxiliary

To a solution of the *N*-acyloxazolidinone in methanol magnesium methoxide was added (final volume 5 mL/0.2 mmol of the *N*-acyloxazolidinone, 0.1 mol $L^{-1}$ in magnesium methoxide) and the mixture war stirred at 0°C until TLC indicated completion of the reaction. The solvent was removed under reduced pressure.

### 8.6. General procedure 5: removal of the trimethylsilylethyl protecting group

To a solution of $LiBF_4$ (5–10 equiv.) in 98:2 $CH_3CN$–$H_2O$ (2 mL/0.06 mmol of the trimethylsilylethyl ether) the trimethylsilylethyl protected alcohol was added. The mixture was refluxed until TLC indicated completion. Usual work-up (ether) provided the crude alcohol.

**8.6.1. (*S*)-3-Oleoyl-4-isopropyloxazolidin-2-one (9A).** General procedure 1: (*S*)-4-Isopropyloxazolidin-2-one (**5**, 0.13 g, 1 mmol), oleoyl chloride (0.30 g, 1 mmol), FC (petroleum ether–ethyl acetate 5:1). Colourless oil, yield 0.32 g (82%). $[\alpha]_D^{24}$=+47.8 (*c*=2.19, $CHCl_3$). IR (KBr): 2854, 1785, 1704, 1386, 1206 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): δ=0.88, 0.92 (2d, 6H, $CH(CH_3)_2^{aux}$, *J*=6.9 Hz), 0.84–0.94 (m, 3H, $CH_3$-18), 1.19–1.43 (m, 20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.57–1.73 (m, 2H, $CH_2$-3), 1.92–2.09 (m, 4H, $CH_2$-8, $CH_2$-11), 2.30–2.46 (m, 1H, $CH(CH_3)_2^{aux}$), 2.78–3.06 (m, 2H, $CH_2$-2), 4.20 (dd, 1H, $5^{aux}$-H, $^2J$=9.1 Hz, $^3J$=3.0 Hz), 4.27 (dd, 1H, $5^{aux}$-H′, $^3J$=8.2 Hz), 4.44 (ddd, 1H, $4^{aux}$-H), 5.26–5.41 (m, 2H, 9-H, 10-H). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): δ=14.16 ($CH_3$-18), 14.69, 18.02 ($CH(CH_3)_2^{aux}$), 28.41 ($CH(CH_3)_2^{aux}$), 22.73, 24.49, 27.22, 27.25, 29.15, 29.18, 29.33, 29.36, 29.56, 29.70, 29.75, 29.81, 31.94, 35.57 (C-2–C-8, C-11–C-17), 58.41 ($C\text{-}4^{aux}$), 63.33 ($C\text{-}5^{aux}$), 129.81, 130.01 (C-9, C-10), 154.11 ($C\text{-}2^{aux}$), 173.45 (C-1). $C_{24}H_{43}NO_3$ (393.61, 393.32), EI MS: *m/z* (%)=393 $[M]^{+\cdot}$ (8), 184 (22), 171 (35), 130 (100), 55 (42), 41 (37); HRMS: calcd 393.3243, found 393.3238.

**8.6.2. (*S*)-3-[(*R*)-2-Hydroxymethyl-oleoyl]-4-isopropyl-oxazolidin-2-one (10Aa).** General procedure 3: **9A** (0.20 g, 0.50 mmol), formaldehyde solution in $CH_2Cl_2$, FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield 0.16 g (76%). $[\alpha]_D^{24}$=+47.8 (*c*=2.19, $CHCl_3$). IR (KBr): 3399, 2925, 2854, 1783, 1698, 1464, 1389, 1368, 1205, 1058 $cm^{-1}$. $^1H$ NMR (HH COSY, 200 MHz, $CDCl_3$): δ=0.86, 0.90 (2d, 6H, $CH(CH_3)_2^{aux}$, *J*=7.0 Hz), 0.86 (t, 3H, $CH_3$-18, *J*=6.2 Hz), 1.18–1.40 (m, 20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.42–1.75 (m, 2H, $CH_2$-3), 1.80–2.07 (m, 4H, $CH_2$-8, $CH_2$-11), 2.21–2.54 (m, 2H, $CH(CH_3)_2^{aux}$, $CH_2$–O*H*), 3.76 (d, 2H, $CH_2$–OH, *J*=6.0 Hz), 3.89–4.05 (m, 1H, 2-H), 4.18 (dd, 1H, $5^{aux}$-H, $^2J$=9.0 Hz, $^3J$=3.3 Hz), 4.27 (dd, 1H, $5^{aux}$-H′, $^3J$=8.2 Hz), 4.49 (ddd, 1H, $4^{aux}$-H), 5.22–5.38 (m, 2H, 9-H, 10-H). $^{13}C$ NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): δ=(−)14.56 ($CH_3$-18), (−)15.16, (−)18.41 ($CH(CH_3)_2^{aux}$), (−)28.91 ($CH(CH_3)_2^{aux}$), (+)23.14, (+)27.53, (+)27.62, (+)27.67, (+)29.56, (+)29.78, (+)29.91, (+)30.00, (+)30.11, (+)30.22, (+)32.37, (C-3–C-8, C-11–C-17), (−)45.90 (C-2), (−)58.86 ($C\text{-}4^{aux}$), (+)63.69 ($CH_2$–OH), (+)63.72 ($C\text{-}5^{aux}$), (−)130.15, (−)130.45 (C-9, C-10), (+)154.47 ($C\text{-}2^{aux}$),

(+)176.65 (C-1). $C_{25}H_{45}NO_4$ (423.63, 423.33). FAB MS:[44] *m/z*=424.4 $[M+H]^+$, 130.1; HRMS: calcd 424.3427, found 424.3421.

**8.6.3. (*S*)-3-[(*R*)-2-Acetoxymethyl-oleoyl]-4-isopropyl-oxazolidin-2-one (formula not shown).** General procedure 2: **9A** (0.20 g, 0.50 mmol), **8a** (0.10 g, 1 mmol), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield: 0.14 g (59%). $[\alpha]_D^{24}$=+24.2 (*c*=0.94, $CHCl_3$). IR (KBr): 3420, 2854, 2798, 1786, 1747, 1703, 1461, 1379, 1227 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.87, 0.91 (2d, 6H, $CH(CH_3)_2^{aux}$, *J*=7.2 Hz), 0.86–0.98 (m, 3H, $CH_3$-18), 1.12–1.41 (m, 20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.42–1.80 (m, 2H, $CH_2$-3), 1.85–2.10 (m, 4H, $CH_2$-8, $CH_2$-11), 2.11 (s, 3H, $CH_3COO$), 2.23–2.41 (m, 1H, $CH(CH_3)_2^{aux}$), 4.02–4.36 (m, 5H, 2-H, CH–$CH_2$–O, $CH_2$-$5^{aux}$), 4.45 (ddd, 1H, $4^{aux}$-H), 5.24–5.41 (m, 2H, 9-H, 10-H). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=14.48 ($CH_3$-18), 15.09, 18.35 ($CH(CH_3)_2^{aux}$), 21.10 ($CH_3COO$), 28.89 ($CH(CH_3)_2^{aux}$), 23.06, 27.11, 27.53, 27.60, 29.44, 29.71, 29.90, 30.01, 30.15, 32.29 (C-3–C-8, C-11–C-17), 42.80 (C-2), 59.00 (C-$4^{aux}$), 63.73 (CH–$CH_2$–O), 64.68 (C-$5^{aux}$), 130.17, 130.54 (C-9, C-10), 154.31 (C-$2^{aux}$), 171.30 ($CH_3COO$), 174.55 (C-1). $C_{27}H_{47}NO_5$ (465.67, 465.35). EI MS: *m/z* (%)=465 $[M]^{+\cdot}$ (7), 405 (30), 276 (29), 130 (75), 55 (51), 43 (100), 41 (37); HRMS: calcd 465.3454, found 465.3488

**8.6.4. (*S*)-3-[(*R*)-2-(2-Trimethylsilyl-ethoxymethyl)-oleoyl]-4-isopropyloxazolidin-2-one (10Ab).** General procedure 2: **9A** (0.97 g, 2.46 mmol), **7** (0.61 g, 3.70 mmol), FC (petroleum ether–ethyl acetate 5:1). Colourless oil, yield: 1.06 g (84%). $[\alpha]_D^{24}$=+20.9 (*c*=7.16, $CHCl_3$). IR (KBr): 2926, 2854, 1782, 1703, 1464, 1387, 1365, 1302, 1248, 1101, 860, 837 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=−0.01 (s, 9H, $Si(CH_3)_3$), 0.87 (2t, 6H, $CH_2$–$CH_2$–Si, $CH_3$-18, *J*=8.2 Hz), 0.88, 0.91 (2d, 6H, $CH(CH_3)_2^{aux}$, *J*=5.9 Hz), 1.18–1.37 (m, 20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.44–1.78 (m, 2H, $CH_2$-3), 1.90–2.12 (m, 4H, $CH_2$-8, $CH_2$-11), 2.28–2.46 (m, 1H, $CH(CH_3)_2^{aux}$), 3.41–3.52 (m, 2H, $CH_2$–$CH_2$–Si), 3.54 (dd, 1H, CH–CH*H*′–O, $^2J$=9.2 Hz, $^3J$=5.1 Hz), 3.64 (dd, 1H, CH–CH*H*′–O, $^3J$=7.7 Hz), 4.08–4.19 (m, 1H, CH–$CH_2$–O), 4.18 (dd, 1H, $5^{aux}$-H, $^2J$=9.2 Hz, $^3J$=3.7 Hz), 4.26 (dd, 1H, $5^{aux}$-H′, $^3J$=8.1 Hz), 4.50 (ddd, 1H, $4^{aux}$-H), 5.28–5.39 (m, 2H, 9-H, 10-H). $^{13}C$ NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): $\delta$=(−)1.26 ($Si(CH_3)_3$), (−)14.27 ($CH_3$-18), (−)14.86, (−)18.05 ($CH(CH_3)_2^{aux}$), (+)18.21 ($CH_2$–$CH_2$–Si), (−)28.49 ($CH(CH_3)_2$), (+)22.84, (+)27.37, (+)29.09, (+)29.25, (+)29.47, (+)29.67, (+)29.74, (+)29.81, (+)29.92, (+)32.05 (C-3–C-8, C-11–C-17), (−)43.69 (CH–$CH_2$–O), (−)58.64 (C-$4^{aux}$), (+)63.19 (C-$5^{aux}$), (+)68.44 ($CH_2$–$CH_2$–Si), (+)71.77 (CH–$CH_2$–O), (−)129.88, (−)130.08 (C-9, C-10), (+)153.90 (C-$2^{aux}$), (+)175.42 (C-1). $C_{29}H_{55}NO_4Si$ (509.85, 509.39), ESI MS: *m/z*=1069.79929, calcd for $C_{58}H_{110}N_2NaO_8Si_2$ $[2M+Na]^+$: 1069.80059.

**8.6.5. Methyl (2*R*)-2-(2-trimethylsilyl-ethoxymethyl)-oleate (11Ab).** General procedure 4: **10Ab** (0.74 g, 1.45 mmol), FC (petroleum ether–ethyl acetate 10:1). Colourless oil, yield 0.47 g (75%). $[\alpha]_D^{24}$=+11.4 (*c*=0.85, $CHCl_3$). IR (KBr): 2927, 2856, 1742, 1653, 1436, 1359, 1249, 1197, 1172, 1110, 972, 860, 838, 695 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.00 (s, 9H, $Si(CH_3)_3$), 0.82–0.96 (m, 5H, $CH_3$-18, $CH_2$–$CH_2$–Si), 1.21–1.38 (m, 20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.40–1.65 (m, 2H, $CH_2$-3), 1.92–2.12 (m, 4H, $CH_2$-8, $CH_2$-11), 2.58–2.74 (m, 1H, 2-H), 3.38–3.63 (m, 4H, O–$CH_2$–$CH_2$–Si, CH–$CH_2$–OH), 3.69 (s, 3H, $OCH_3$), 5.31–5.39 (m, 2H, 9-H, 10-H). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=−1.23 ($Si(CH_3)_3$), 14.27 ($CH_3$-18), 18.12 ($CH_2$–$CH_2$–Si), 22.84, 27.31, 27.38, 29.21, 29.47, 29.56, 29.68, 29.81, 29.92, 32.06 (C-3–C-7, C-8–C-17), 46.37 (C-2), 51.68 ($OCH_3$), 68.49 ($CH_2$–$CH_2$–Si), 71.29 (CH–$CH_2$–O), 129.86, 130.13 (C-9, C-10), 175.48 (C-1). $C_{25}H_{50}O_3Si$ (426.76, 426.15), FAB MS: *m/z*=427.1 $[M+H]^+$.

**8.6.6. Methyl (*R*)-2-hydroxymethyl oleate (11Aa).** (a) General procedure 5: **11Ab** (0.45 g, 1.05 mmol), $LiBF_4$ (0.49 g, 5.25 mmol), 98:2 $CH_3CN$–water (10 mL), FC (petroleum ether–ethyl acetate 3:1), yield: 0.25 g (72%).

(b) General procedure 4: **10Aa** (88.60 mg, 0.22 mmol), magnesium methoxide (0.1 mol $L^{-1}$, 4.6 mL), FC (petroleum ether–ethyl acetate 3:1), yield 68 mg (93%). $[\alpha]_D^{24}$=+7.7 (*c*=2.07, $CHCl_3$). CD: $\lambda_{max}$ ($\Delta\epsilon$)=212.8 nm (2.05). IR (KBr): 3411, 2925, 2855, 1739, 1462, 1439, 1199, 1170, 1049 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.87 (t, 3H, $CH_3$-18, *J*=6.5 Hz), 1.18–1.39 (20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.42–1.70 (2H, $CH_2$-3), 1.89–2.08 (4H, $CH_2$-8, $CH_2$-11), 2.24 (bs, 1H, O*H*), 2.43–2.53 (1H, 2-H), 3.71 (s, 3H, $OCH_3$), 3.71–3.80 (2H, $CH_2$–OH), 5.24–5.41 (2H, 9-H, 10-H). $^{13}C$ NMR (APT, 50.3 MHz, $CDCl_3$): $\delta$=(−)14.47 ($CH_3$-18), (+)23.06, (+)27.52, (+)27.60, (+)28.87, (+)29.43, (+)29.70, (+)29.81, (+)29.91, (+)30.04, (+)30.15, (+)32.29 (C-3–C-8, C-11–C-17), (−)47.89 (C-2), (−)52.12 ($OCH_3$), (+)63.57 ($CH_2$–OH), (−)130.19, (−)130.54 (C-9, C-10), (+)176.50 (C-1). $C_{20}H_{38}O_3$ (326.51, 326.28), EI MS: *m/z* (%)=326 $[M]^{+\cdot}$ (7), 308 (7), 245 (15), 104 (90), 55 (100), 43 (62), 41 (79); HRMS: calcd 326.2821, found 326.2832

**8.6.7. (4*R*,5*S*)-3-Oleoyl-4-methyl-5-phenyl-oxazolidin-2-one (12).** General procedure 1: (4*R*,5*S*)-4-methyl-5-phenyl-oxazolidin-2-one (**6**, 0.18 g, 1.0 mmol), oleoyl chloride (0.30 g, 1.0 mmol), FC (petroleum ether–ethyl acetate 5:1). Colourless oil, yield: 0.34 g (76%). $[\alpha]_D^{24}$=−51.4 (*c*=2.56, $CHCl_3$). IR (KBr): 3385, 2927, 2856, 1785, 1703, 1456, 1348, 1246, 1199, 1150, 1122, 768, 701 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.88 (t, 3H, $CH_3$-18), 0.90 (d, 3H, 4-$CH_3^{aux}$, *J*=6.6 Hz), 1.18–1.43 (20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.57–1.78 (2H, $CH_2$-3), 1.91–2.10 (4H, $CH_2$-8, $CH_2$-11), 2.80–3.08 (2H, $CH_2$-2), 4.77 (dq, 1H, $4^{aux}$-H, $J_{4,5}$=7.0 Hz), 5.31–5.39 (2H, 9-H, 10-H), 5.66 (d, 1H, $5^{aux}$-H), 7.26–7.48 (5H, $H^{arom}$). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=14.59 ($CH_3$-18), 15.05 (4-$CH_3^{aux}$), 23.16, 24.79, 27.70, 29.47, 29.62, 29.80, 30.00, 30.09, 30.20, 30.26, 32.39 (C-3–C-8, C-11–C-17), 36.12 (C-2), 55.22 (C-$4^{aux}$), 79.43 (C-$5^{aux}$), 126.13, 129.18, 129.20, 133.89 (6×$C^{arom}$), 130.26, 130.46 (C-9, C-10), 153.53 (C-$2^{aux}$), 173.66 (C-1). $C_{28}H_{43}NO_3$ (441.65, 441.32), EI MS: *m/z* (%)=441 $[M]^{+\cdot}$ (17), 232 (32), 219 (56), 178 (45), 159 (31), 134 (75), 55 (100), 43 (95); HRMS: calcd 441.3243, found 441.3243.

**8.6.8. (4*R*,5*S*)-3-[(*S*)-2-Hydroxymethyl-oleoyl]-4-methyl-5-phenyl-oxazolidin-2-one (13a).** General procedure 2: **12** (0.21 g, 0.50 mmol), formaldehyde dissolved in $CH_2Cl_2$, FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield 0.18 g (78%). $[\alpha]_D^{24}=-38.7$ ($c$=1.96, $CHCl_3$). IR (KBr): 3389, 2925, 2854, 1783, 1698, 1459, 1345, 1197, 1121, 1031, 766, 700 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.88 (t, 3H, $CH_3$-18), 0.89 (d, 3H, 4-$CH_3^{aux}$, $J$=6.6 Hz), 1.10–1.39 (20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.50–1.79 (2H, $CH_2$-3), 1.86–2.11 (4H, $CH_2$-8, $CH_2$-11), 2.32 (bs, 1H, O*H*), 3.83 (d, 2H, C$H_2$–OH, $J$=5.9 Hz), 3.89–4.06 (1H, 2-H), 4.85 (dq, 1H, $4^{aux}$-H, $J_{4,5}$=6.9 Hz), 5.26–5.42 (2H, 9-H, 10-H), 5.69 (d, 1H, $5^{aux}$-H), 7.20–7.50 (m, 5H, $H^{arom}$). $^{13}C$ NMR (HETCOR, 50.3 MHz, $CDCl_3$): $\delta$=14.59 ($CH_3$-18), 15.09 (4-$CH_3^{aux}$), 23.16, 27.50, 27.65, 27.70, 29.23, 29.58, 29.80, 30.00, 30.06, 30.16, 30.24, 32.39 (C-3–C-8, C-11–C-17), 46.04 (C-2), 55.24 (C-$4^{aux}$), 63.90 (*C*$H_2$–OH), 79.36 (C-$5^{aux}$), 126.14, 129.20, 129.29, 133.79 (6×$C^{arom}$), 130.19, 130.49 (C-9, C-10), 153.47 (C-$2^{aux}$), 176.40 (C-1). $C_{29}H_{45}NO_4$ (471.68, 471.33), EI MS: $m/z$ (%)=471 $[M]^{+\cdot}$ (18), 249 (36), 178 (71), 134 (93), 55 (100), 43 (71); HRMS: calcd 471.3349, found 471.3358.

**8.6.9. (4*R*,5*S*)-3-[(2*S*)-2-(2-Trimethylsilyl-ethoxymethyl)-oleoyl]-4-methyl-5-phenyl-oxazolidin-2-one (13b).** General procedure 2: **12** (1.15 g, 2.60 mmol), **7** (0.43 g, 5.20 mmol), FC (petroleum ether–ethyl acetate 20:65). Colourless oil, yield 1.16 g (78%). $[\alpha]_D^{24}=-27.1$ ($c$=3.26, $CHCl_3$). IR (KBr): 2927, 2856, 1785, 1703, 1457, 1343, 1249, 1196, 1118, 1069, 861, 838, 767, 700 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta=-0.04$–0.01 (9H, Si(C$H_3$)$_3$), 0.81–0.96 (5H, $CH_3$-18, $CH_2$–C$H_2$–Si), 0.89 (d, 3H, 4-$CH_3^{aux}$, $J$=6.6 Hz), 1.16–1.42 (20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.50–1.78 (2H, $CH_2$-3), 1.81–2.11 (4H, $CH_2$-8, $CH_2$-11), 3.43–3.54 (2H, O–C$H_2$–$CH_2$–Si), 3.53 (dd, C*H*H′–OH, $^2J$=9.0 Hz, $^3J$=5.3 Hz), 3.66 (dd, CH*H*′–OH, $^3J$=7.9 Hz), 4.09–4.27 (1H, 2-H), 4.82 (dq, 1H, $4^{aux}$-H, $J_{4,5}$=7.1 Hz), 5.28–5.45 (2H, 9-H, 10-H), 5.65 (d, 1H, $5^{aux}$-H), 7.25–7.50 (5H, $H^{arom}$). $^{13}C$ NMR (APT, HETCOR, 50.3 MHz, $CDCl_3$): $\delta$=(−)−1.23 (Si(*C*$H_3$)$_3$), (−)14.25, (−)14.68 ($CH_3$-18, 4-$CH_3^{aux}$), (+)18.18 ($CH_2$–*C*$H_2$–Si), (+)22.82, (+)27.32, (+)29.24, (+)29.36, (+)29.46, (+)29.66, (+)29.83, (+)32.04 (C-3–C-8, C-11–C-17), (−)43.78 (C-2), (−)54.98 (C-$4^{aux}$), (+)68.49 (*C*$H_2$–$CH_2$–Si), (+)71.44 (*C*$H_2$–O), (−)78.76 (C-$5^{aux}$), (−)125.80, (−)128.78, (−)133.66 (6×$C^{arom}$), (−)129.86, (−)130.11 (C-9, C-10), (+)152.86 (C-$2^{aux}$), (+)175.24 (C-1). $C_{34}H_{57}NO_4Si$ (571.92, 571.40), ESI MS: $m/z$=1165.81082, calcd for $C_{68}H_{114}N_2NaO_8Si_2$ $[2M+Na]^+$: 1165.80859.

**8.6.10. Methyl (*S*)-2-(2-trimethylsilyl-ethoxymethyl) oleate (14b).** General procedure 4: **13b** (0.74 g, 1.30 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 20 mL), FC (petroleum ether–ethyl acetate 20:1). Colourless oil, yield 0.47 g (84%). $^1H$ NMR (200 MHz, $CDCl_3$): The spectrum was identical with that of the *R*-enantiomer. $[\alpha]_D^{24}=-11.2$ ($c$=2.63, $CHCl_3$).

**8.6.11. Methyl (*S*)-2-hydroxymethyl oleate (14a).** (a) General procedure 5: **14b** (0.37 g, 0.87 mmol), $LiBF_4$ (0.41 g, 4.35 mmol), 98:2 $CH_3CN$–water (10 mL), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield 0.19 g (68%).

(b) General procedure 4: **13a** (0.10 g, 0.22 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 4.6 mL), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield 63.83 mg (89%). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.88 (t, 3H, $CH_3$-18), 1.14–1.39 (20H, $CH_2$-4–$CH_2$-7, $CH_2$-12–$CH_2$-17), 1.42–1.70 (2H, $CH_2$-3), 1.89–2.08 (4H, $CH_2$-8, $CH_2$-11), 2.14 (t, 1H, O*H*, $J$=5.9 Hz), 2.50–2.66 (1H, 2-H), 3.72 (s, 3H, OC$H_3$), 3.72–3.80 (2H, C$H_2$–OH), 5.26–5.42 (2H, 9-H, 10-H). $^{13}C$, mass and IR spectra were identical with the spectra of the (*R*)-enantiomer. $[\alpha]_D^{24}=-7.7$ ($c$=2.34, $CHCl_3$). CD: $\lambda_{max}$ ($\Delta\epsilon$)=211 nm (+2.29).

**8.6.12. (4*S*)-3-Palmitoyl-4-isopropyloxazolidin-2-one (9B).** General procedure 1: **5** (0.13 g, 1.00 mmol), palmitoyl chloride (0.33 g, 1.10 mmol), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield 0.30 g (84%). $[\alpha]_D^{24}=+46.5$ ($c$=1.81, $CHCl_3$). IR (KBr): 2919, 2851, 1769, 1710, 1389, 1210 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.87, 0.91 (d, 3H, CH(C$H_3$)$_2^{aux}$, $J$=7.1 Hz), 0.87 (t, 3H, $CH_3$-16, $J$=7.0 Hz), 1.13–1.41 (24H, $CH_2$-4–$CH_2$-15), 1.55–1.73 (2H, $CH_2$-3), 2.26–2.47 (1H, C*H*(CH$_3$)$_2^{aux}$), 2.72–3.08 (2H, $CH_2$-2), 4.19 (dd, 1H, $5^{aux}$-H, $^2J$=9.0 Hz, $^3J$=3.7 Hz), 4.26 (dd, 1H, $5^{aux}$-H′, $^3J$=7.6 Hz), 4.43 (ddd, 1H, $4^{aux}$-H). $^{13}C$ NMR (HETCOR, 50.3 MHz, $CDCl_3$): $\delta$=14.49 ($CH_3$-16), 15.02, 18.34 (CH(*C*H$_3$)$_2^{aux}$), 24.85 (C-3), 28.77 (*C*H(CH$_3$)$_2^{aux}$), 23.07, 29.53, 29.75, 29.88, 30.00, 30.07, 32.32 (C 4–C-15), 35.93 (C-2), 58.80 (C-$4^{aux}$), 63.72 (C-$5^{aux}$), 154.61 (C-$2^{aux}$), 174.00 (C-1). $C_{22}H_{41}NO_3$ (367.57, 367.30), FAB MS: $m/z$=390.3 $[M+Na]^+$, 368.3 $[M+H]^+$, 130.1; HRMS: $[M+H]^+$: calcd 368.3165, found 368.3184.

**8.6.13. (*S*)-3-[(*R*)-2-Hydroxymethyl-palmitoyl]-4-isopropyloxazolidin-2-one (10Ba).** General procedure 3: **9B** (0.10 g, 0.27 mmol), formaldehyde solution in $CH_2Cl_2$, FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield 0.09 g (85%). $[\alpha]_D^{24}=+35.6$ ($c$=2.58, $CHCl_3$). IR (KBr): 3450, 2919, 2851, 1772, 1710, 1468, 1390, 1305, 1259 $cm^{-1}$. $^1H$ NMR (HH COSY, 200 MHz, $CDCl_3$): $\delta$=0.87 (t, 3H, $CH_3$-16, $J$=7.0 Hz), 0.88, 0.92 (2d, 6H, CH(C$H_3$)$_2^{aux}$, $J$=7.3 Hz), 1.16–1.40 (24H, $CH_2$-4–$CH_2$-15), 1.43–1.75 (2H, $CH_2$-3), 2.24–2.45 (1H, C*H*(CH$_3$)$_2$), 3.78 (d, 2H, C$H_2$–OH), 3.89–4.06 (1H, 2-H), 4.19 (dd, 1H, $5^{aux}$-H, $^2J$=8.9 Hz, $^3J$=3.1 Hz), 4.28 (dd, 1H, $5^{aux}$-H′, $^3J$=8.1 Hz), 4.50 (ddd, 1H, $4^{aux}$-H). $^{13}C$ NMR (HETCOR, 50.3 MHz, $CDCl_3$): $\delta$=14.59 ($CH_3$-16), 15.17, 18.43 (CH(*C*H$_3$)$_2^{aux}$), 28.90 (*C*H(CH$_3$)$_2$), 29.52 (C-3), 23.16, 27.57, 29.83, 29.93, 30.02, 30.10, 30.13, 32.40 (C 4–C-15), 45.91 (C-2), 58.85 (C-$4^{aux}$), 63.71 (*C*$H_2$–OH), 63.74 (C-$5^{aux}$), 154.45 (C-$2^{aux}$), 176.75 (C-1). $C_{23}H_{43}NO_4$ (397.59, 397.31), FAB MS: $m/z$=420.3 $[M+Na]^+$, 398.3 $[M+H]^+$, 130.1; HRMS: $[M+H]^+$: calcd 398.3270, found 398.3271.

**8.6.14. (*S*)-3-[(*R*)-2-(2-Trimethylsilyl-ethoxymethyl)-palmitoyl]-4-isopropyl-oxazolidin-2-one (10Bb).** General procedure 2: **9B** (0.18 g, 0.50 mmol), **7** (0.17 g, 1.00 mmol), FC (petroleum ether–ethyl acetate 6:1). Colourless oil, yield: 0.22 g (87%). $[\alpha]_D^{24}=+18.6$ ($c$=2.45, $CHCl_3$). IR

(KBr): 2925, 2855, 1783, 1702, 1386, 1248, 1204, 1100, 860, 837 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=−0.03 (s, 9H, Si($CH_3$)$_3$), 0.85 (t, 2H, $CH_2$–$CH_2$–Si, $J$=8.2 Hz), 0.86 (t, 3H, $CH_3$-16, $J$=6.2 Hz), 0.86, 0.90 (2×d, 6H, CH($CH_3$)$_2^{aux}$, $J$=5.5 Hz), 1.15–1.37 (24H, $CH_2$-4–$CH_2$-15), 1.42–1.79 (2H, $CH_2$-3), 2.28–2.44 (1H, C$H$($CH_3$)$_2^{aux}$), 3.39–3.52 (2H, O–$CH_2$–$CH_2$–Si), 3.52 (dd, 1H, CH–C$H$H′–O, $^2J$=9.2 Hz, $^3J$=4.9 Hz), 3.62 (dd, 1H, CH–CH$H$′–O, $^3J$=7.8 Hz), 4.07–4.16 (1H, 2-H), 4.16 (dd, 1H, 5$^{aux}$-H, $^2J$=9.1 Hz, $^3J$=3.8 Hz), 4.24 (dd, 1H, 5$^{aux}$-H′, $^3J$=8.0 Hz), 4.48 (ddd, 1H, 4$^{aux}$-H). $^{13}C$ NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): $\delta$=(−)−0.94 (Si($CH_3$)$_3$), (−)14.59 ($CH_3$-16), (−)15.19, (−)18.36 (CH($CH_3$)$_2^{aux}$), (+)18.53 ($CH_2$–$CH_2$–Si), (−)28.82 (C$H$($CH_3$)$_2$), (+)23.16, (+)27.70, (+)29.41, (+)29.83, (+)29.90, (+)30.05, (+)30.13, (+)32.39 (C-3–C-15), (−)44.00 (C-2), (−)58.96 (C-4$^{aux}$), (+)63.51 (C-5$^{aux}$), (+)68.75 ($CH_2$–$CH_2$–Si), (+)72.10 (CH–$CH_2$–O), (+)154.20 (C-2$^{aux}$), (+)175.77 (C-1). $C_{28}H_{55}NO_4Si$ (497.83, 497.39), FAB MS: $m/z$=520.4 $[M+Na]^+$; HRMS: calcd 520.3798, found 520.3797.

**8.6.15. Methyl (*R*)-2-(2-trimethylsilyl-ethoxymethyl)-palmitoate (11Bb).** General procedure 4: **10Bb** (0.10 g, 0.20 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 5 mL), FC (petroleum ether–ethyl acetate 5:1). Colourless oil, yield 0.07 g (87%). $[\alpha]_D^{24}$=+9.5 ($c$=2.46, $CHCl_3$). IR (KBr): 2925, 2855, 1742, 1465, 1248, 1197, 1171, 1110, 859, 838 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=−0.01 (s, 9H, Si($CH_3$)$_3$), 0.85 (t, 3H, $CH_3$-16, $J$=6.6 Hz), 0.87 (t, 2H, $CH_2$–$CH_2$–Si, $J$=8.1 Hz), 1.16–1.39 (24H, $CH_2$-4–$CH_2$-15), 1.41–1.67 (2H, $CH_2$-3), 2.54–2.71 (1H, 2-H), 3.43 (1H, dd, CH–C$H$H′–OH, $^2J$=9.3 Hz, $^3J$=5.3 Hz), 3.57 (dd, 2H, CH–CH$H$′–OH, $^3J$=8.2 Hz), 3.44–3.54 (2H, $CH_2$–$CH_2$–Si), 3.68 (s, 3H, O$CH_3$). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=−1.36 (Si($CH_3$)$_3$), 14.13 ($CH_3$-16), 18.02 ($CH_2$–$CH_2$–Si), 22.72, 27.30, 29.09, 29.38, 29.44, 29.53, 29.59, 29.66, 29.68, 29.71, 31.95 (C-3–C-15), 46.27 (C-2), 51.52 (O$CH_3$), 68.37 ($CH_2$–$CH_2$–Si), 71.19 (CH–$CH_2$–O), 175.38 (C-1). $C_{23}H_{48}O_3Si$ (400.71, 400.33), EI MS: $m/z$ (%)=400 $[M]^{+\cdot}$ (<1), 357 (66), 73 (100); HRMS: calcd 400.3373, found 400.3377.

**8.6.16. Methyl (*R*)-2-hydroxymethyl palmitate (11Ba).** (a) General procedure 5: **11Bb** (0.38 g, 0.95 mmol), $LiBF_4$ (0.44 g, 4.75 mmol), FC (petroleum ether–ethyl acetate–cyclohexane 1:1:3). Colourless oil, yield 0.22 g (77%).

(b) General procedure 4: **10Ba** (0.08 g, 0.20 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 4.6 mL), FC (petroleum ether–ethyl acetate–cyclohexane 1:1:3). Yield 51.3 mg (85%). $[\alpha]_D^{24}$=+5.4 ($c$=1.62, $CHCl_3$). IR (KBr): 3431, 2926, 2854, 1734, 1458, 1199, 1171 $cm^{-1}$. $^1H$ NMR (HH COSY, 200 MHz, $CDCl_3$): $\delta$=0.82 (t, 3H, $CH_3$-16, $J$=6.4 Hz), 1.07–1.33 (24H, $CH_2$-4–$CH_2$-15), 1.34–1.67 (2H, $CH_2$-3), 1.94 (bs, 1H, O$H$), 2.45–2.60 (1H, 2-H), 3.72 (s, 3H, O$CH_3$), 3.72–3.78 (2H, C$H_2$–OH). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=14.58 ($CH_3$-16), 23.16, 27.71, 28.96, 29.83, 29.88, 29.99, 30.13, 32.40 (C-3–C-15), 47.93 (C-2), 52.20 (O$CH_3$), 63.62 ($CH_2$–OH), 176.44 (C-1). $C_{18}H_{36}O_3$ (300.48, 300.26), FAB MS: $m/z$=323.3 $[M+Na]^+$, 301.3 $[M+H]^+$; HRMS: $[M+H]^+$: calcd 301.2743, found 301.2743.

The racemate was obtained by formation of the ester enolate of methyl palmitate with LDA and trapping it with formaldehyde (solution in $CH_2Cl_2$).

**8.6.17. Methyl (2*R*)-2-[(2*S*)-3,3,3-trifluoro-2-methoxy-2-phenyl-propionyloxymethyl]-palmitate (formula not shown).** A solution of **11Ba** (0.03 g, 0.10 mmol), triethylamine (0.10 g, 1.00 mmol) and a catalytic amount of DMAP in $CH_2Cl_2$ (2 mL) was stirred at 20°C for 5 min. *S*-(+)-α-methoxy-α-trifluoromethylphenylacetic acetyl chloride (0.13 g, 0.50 mmol) was added and the mixture was stirred at 20°C for 12 h. After filtration and solvent evaporation, FC (petroleum ether–ethyl acetate 4:1) yielded the compound as a colourless oil, yield 37.70 mg (73%). The racemic compound was obtained accordingly. IR (KBr): 2926, 2854, 1745, 1458, 1267, 1246, 1171, 1024, 719 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.83 (t, 3H, $CH_3$-16, $J$=6.6 Hz), 1.07–1.33 (24H, $CH_2$-4–$CH_2$-15), 1.34–1.67 (2H, $CH_2$-3), 2.65–2.90 (1H, 2-H), 3.46 (s, 3H, –O$CH_3$), 3.56 (s, 3H, COO$CH_3$), 4.35 (dd, 1H, CH–C$H$H′–O, $^2J$=10.7 Hz, $^3J$=5.7 Hz), 4.42 (dd, 1H, 2H, CH–CH$H$′–O, $^3J$=8.1 Hz), 7.31–7.49 (5H, H$^{arom}$). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=14.60 ($CH_3$-16), 23.18, 27.37, 29.13, 29.85, 30.01, 30.17, 32.41 (C-3–C-15), 44.89 (C-2), 52.27 (COO$CH_3$), 55.88 ($CF_3C$–O$CH_3$), 66.82 (CH–$CH_2$–O), 78.41 ($CF_3C$–O$CH_3$), 127.82, 128.86, 130.07, 132.59 (6×C$^{arom}$), 166.76 ($CF_3C$–O$CO$O), 174.08 (C-1). $^{19}F$ NMR (188.2 MHz, $CDCl_3$): $\delta$=4.72. No signal of the second diastereomer was found. $C_{28}H_{43}F_3O_5$ (516.64, 516.30), FAB MS: $m/z$=517.1 $[M+H]^+$; HRMS: calcd 517.3141, found 517.3146.

For comparison the Mosher esters of racemic **11Ba** were prepared accordingly.

### 8.7. Reaction of nickelalactone 15 with geranyl iodide

To a solution of **15** (0.86 g, 3 mmol) in DMF (20 mL) successively $MnI_2$ (0.92 g, 3 mmol) and (in portions) geranyl iodide (**19a**, 0.47 g, 3 mmol) were added. The reaction mixture was sonicated at 20°C for 24 h and then stirred at 20°C for 7 days. After work-up no product formation was observed by TLC.

**8.7.1. Ethyl (5*E*)-6,10-dimethylundeca-5,9-dienoate (22b).** A mixture of freshly sublimed zinc chloride (0.27 g, 2 mmol) and **16** (0.70 g, 4 mmol) in diethyl ether (8 mL) was stirred at 20°C for 1 h and under reflux for 1 h. After cooling to 0°C successively HMPT (0.72 g, 4 mmol), Ni(dppe) (catalytic amount) and geranyl chloride (**19b**, 0.34 g, 2 mmol) were added and the reaction mixture was stirred at 20°C for 20 h. Usual work-up (diethyl ether) followed by FC (*n*-hexane–ethyl acetate) provided **22b** as a colourless oil (0.13 g, 28% based on geranyl chloride). IR (KBr): 2926, 1734, 1447, 1267, 1175 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=1.08–1.37 (3H, O–$CH_2$–C$H_3$), 1.60, 1.62 (2s, 6H, 6-$CH_3$, 10-$CH_3$), 1.68 (s, 3H, $CH_3$-11), 1.82–2.19 (8H, $CH_2$-3, $CH_2$-4, $CH_2$-7, $CH_2$-8), 2.28 (t, 2H, $CH_2$-2, $J$=7.5 Hz), 4.07–4.23 (2H, O–C$H_2$–$CH_3$), 5.01–5.20 (2H, 5-H, 9-H). $^{13}C$ NMR (HETCOR, 100.6 MHz, $CDCl_3$): $\delta$=14.73 (O–$CH_2$–$CH_3$), 16.43 (6-$CH_3$), 18.14 (10-$CH_3$), 25.54 (C-3), 26.14 ($CH_3$-11), 26.98, 27.70 (C-4, C-8), 34.21 (C-2), 40.19 (C-7), 60.60 (O–$CH_2$–$CH_3$),

123.90, 124.76 (C-5, C-9), 131.84 (C-10), 136.54 (C-6), 171.28 (C-1). $C_{15}H_{26}O_2$ (238.37, 238.19), FAB MS: $m/z$=239.1 $[M+H]^+$.

**8.7.2. (5*E*)-6,10-Dimethylundeca-1,5,9-triene (20).** To a vigorously stirred solution of geranyl chloride (**19b**, 0.88 mL, 5.80 mmol) in dry diethyl ether (7.50 mL) and DMPU (7.50 mL) slowly allylmagnesium bromide (1 mol $L^{-1}$ in dry diethyl ether, 43.50 mL, 6.32 g, 43 mmol) was added dropwise. The mixture was then stirred at 20°C for 12 h. Ice-water (50 mL) was added. Usual work-up (diethyl ether), followed by FC (*n*-hexane) provided **20** as a colourless, bad-smelling oil. Yield: 0.79 g (94%). IR (KBr): 2922, 1640, 1444, 1379, 1106, 911 $cm^{-1}$. $^1H$ NMR (HH COSY, 200 MHz, $CDCl_3$): $\delta$=1.61 (s, 6H, 6-$CH_3$, 10-$CH_3$), 1.66–1.72 (3H, $CH_3$-11), 1.95–2.15 (8H, $CH_2$-3, $CH_2$-4, $CH_2$-7, $CH_2$-8), 4.96 (ddt, 1H, 1-$H_{cis}$, $^2J$=2.1 Hz, $J_{1\text{-}cis,2}$=10.2 Hz, $J_{1\text{-}cis,3}$=1.0 Hz), 5.03 (ddt, 1H, 1-$H_{trans}$, $J_{1\text{-}trans,2}$=16.8 Hz, $J_{1\text{-}trans,3}$=1.5 Hz), 5.08–5.19 (2H, 5-H, 9-H), 5.72–5.92 (1H, 2-H). $^{13}C$ NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): $\delta$=(−)16.50 (6-$CH_3$), (−)18.15 (10-$CH_3$), (−)26.16 ($CH_3$-11), (+)27.18 (C-8), (+)27.89 (C-4), (+)34.47 (C-3), (+)40.18 (C-7), (+)114.82 (C-1), (−)124.28, (−)124.83 (C-5, C-9), (+)131.80 (C-10), (+)135.85 (C-6), (−)139.24 (C-2). $C_{13}H_{22}$ (178.31, 178.17), EI MS: $m/z$(%)=178 $[M]^{+\cdot}$ (2), 69 (100), 41 (54); HRMS: calcd 178.1722, found 178.1720.

**8.7.3. (5*E*)-6,10-Dimethylundeca-1,5-dien-1-ol (21).** To a solution of disiamylborane (5.45 mL, 4.50 mmol) in absolute THF (10 mL) at −10°C slowly **14** (0.40 g, 2.25 mmol) was added. The mixture was stirred at −10°C for 5.5 h. Water (1.53 mL) and subsequently a solution prepared from 3 mol $L^{-1}$ NaOH (1.53 mL) and 30% $H_2O_2$ (1.53 mL) were added. The mixture was stirred at 20°C for 18 h. Usual work-up (ether) and FC (petroleum ether–diethyl ether 2:1) furnished **21** as a colourless oil. Yield: 0.32 g (72%). IR (KBr): 3337, 2929, 1444, 1378, 1059 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$=1.34–1.37 (2H, $CH_2$-3), 1.49–1.53 (2H, $CH_2$-2), 1.55 (s, 6H, 6-$CH_3$, 10-$CH_3$), 1.63 (s, 3H, $CH_3$-11), 1.93–2.03 (6H, $CH_2$-4, $CH_2$-7, $CH_2$-8), 3.63 (t, 2H, $CH_2$-1, $J_{1,2}$=6.5 Hz), 5.07 (dddd, 1H, 9-H, $J_{9,8}$=6.7 Hz, $J_{9,8'}$=2.8 Hz, $J_{9,7}$=1.3 Hz), 5.13 (dddd, 1H, 5-H, $J_{5,4}$=7.4 Hz, $J_{5,4'}$=2.8 Hz, $J_{5,3}$=1.3 Hz). $^{13}C$ NMR (HMQC, 100.6 MHz, $CDCl_3$): $\delta$=15.86 (6-$CH_3$), 17.52 (10-$CH_3$), 25.52 ($CH_3$-11), 25.83 (C-3), 26.61 (C-8), 27.47 (C-4), 32.25 (C-2), 39.61 (C-7), 62.82 (C-1), 124.17 (C-5)*, 124.26 (C-9)*, 131.13 (C-10), 135.16 (C-6). * The assignments of the signals of C-5 and C-9 and 5-H and 9-H have perhaps to be reversed. $C_{12}H_{24}O$ (196.33, 196.18), EI MS: $m/z$ (%)=196 $[M]^{+\cdot}$ (2), 69 (100), 41 (71); HRMS: calcd 196.1827, found 196.1817.

**8.7.4. (5*E*)-6,10-Dimethylundeca-5,9-dienoic acid (22a).** (a) Jones reagent was added at 0°C to a solution of **21** (0.30 g, 1.53 mmol) in acetone (2 mL) until the red colour persisted. The mixture was stirred at 0°C for 3 h. Excess of oxidant was destroyed with isopropanol. Water (20 mL) was added. Usual work-up (diethyl ether) and FC (petroleum ether–diethyl ether 4:1) furnished **22a** as a colourless oil. Yield: 0.20 g (65%).

(b) To a suspension of CuI (0.42 g, 2.20 mmol) in dry THF (10 mL) dimethylsulfide (1 mL) was added. The mixture was cooled to −50°C. Slowly a 1 mol $L^{-1}$ solution of geranyl magnesiumbromide (4 mL, 1.06 g, 4.40 mmol) was added. The mixture was stirred at −50°C for 30 min. A solution of β-propiolactone (**18**, 0.14 g, 2.00 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred at −50 and 20°C (1 h at each temperature). The reaction was stopped by addition of 3 mol $L^{-1}$ HCl (2 mL). Usual work-up (ether) and FC (petroleum ether–diethyl ether 2:1) furnished **22a** as a colourless oil, yield 0.58 g (2.77 mmol). IR (KBr): 2924, 1710, 1441, 1244 $cm^{-1}$. $^1H$ NMR (HH COSY, 400 MHz, $CDCl_3$): $\delta$=1.52, 1.53 (2s, 6H, 6-$CH_3$, 10-$CH_3$), 1.61 (s, 3H, $CH_3$-11), 1.58–1.65 (2H, $CH_2$-3), 1.90–1.93 (2H, $CH_2$-7), 1.93–2.01 (4H, $CH_2$-4, $CH_2$-8), 2.27 (t, 2H, $CH_2$-2, $J$=7.5 Hz), 5.01–5.04 (2H, 5-H, 9-H), 10.17 (bs, 1H, COO*H*). $^{13}C$ NMR (HMQC, 100.6 MHz, $CDCl_3$): $\delta$=16.65 (6-$CH_3$), 18.34 (10-$CH_3$), 25.42 (C-3), 26.35 ($CH_3$-11), 27.29, 27.79 (C-4, 8), 34.07 (C-2), 40.39 (C-7), 123.86, 124.93 (C-5, C-9), 132.09 (C-10), 137.01 (C-6), 180.93 (C-1). $C_{13}H_{22}O_2$ (210.31, 210.16), FAB MS: $m/z$=233.1 $[M+Na]^+$; HRMS: $C_{13}H_{23}O_2$ $[M+H]^+$: calcd 211.1698, found 211.1680.

**8.7.5. (*S*)-3-[(5*E*)-6,10-Dimethylundeca-5,9-dienoyl]-4-isopropyloxazolidin-2-one (22d).** General procedure 1: **5** (0.13 g, 1.00 mmol), **22c** (prepared from **22a**, 0.25 g, 1.00 mmol), FC (petroleum ether–ethyl acetate 4:1). Colourless syrup, yield: 0.28 g (88%). $[\alpha]_D^{24}$=+48.3 ($c$=2.15, $CHCl_3$). IR (KBr): 3386, 2925, 1782, 1703, 1384, 1205, 1064 $cm^{-1}$. $^1H$ NMR (HH COSY, 200 MHz, $CDCl_3$): $\delta$=0.86, 0.90 (2d, 6H, $CH(CH_3)_2^{aux}$, $J$=7.0 Hz), 1.58 (s, 6H, 6-$CH_3$, 10-$CH_3$), 1.65 (s, 3H, $CH_3$-11), 1.63–1.77 (2H, $CH_2$-3), 1.90–2.12 (6H, $CH_2$-4, $CH_2$-7, $CH_2$-8), 2.26–2.45 (1H, $CH(CH_3)_2^{aux}$), 2.84 (dt, 1H, 2-H, $^2J$=17.0 Hz, $^3J$=7.5 Hz), 2.97 (dt, 1H, 2-H′), 4.18 (dd, 1H, $5^{aux}$-H, $^2J$=9.0 Hz, $^3J$=3.5 Hz), 4.25 (dd, 1H, CH′-$5^{aux}$-H′, $^3J$=7.5 Hz), 4.42 (ddd, 1H, $4^{aux}$-H), 5.06 (dddd, 1H, 9-H, $J_{9,8}$=6.8 Hz, $J_{9,8'}$=4.1 Hz, $J_{9,7}$=2.7 Hz, $J_{9,7'}$=1.4 Hz), 5.13 (dddd, 1H, 5-H, $J_{5,4}$=7.3 Hz, $J_{5,4'}$=2.7 Hz, $J_{5,3}$=1.4 Hz). $^{13}C$ NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): $\delta$=(−)15.02, (−)18.34 ($CH(CH_3)_2^{aux}$), (−)16.38 (6-$CH_3$), (−)18.05 (10-$CH_3$), (+)24.94 (C-3), (−)26.05 ($CH_3$-11), (+)27.06, (+)27.63 (C-4, 8), (−)28.78 ($CH(CH_3)_2^{aux}$), (+)35.42 (C-2), (+)40.10 (C-7), (−)58.78 ($C\text{-}4^{aux}$), (+)63.72 ($C\text{-}5^{aux}$), (−)123.93 (C-5), (−)124.80 (C-9), (+)131.83 (C-10), (+)136.60 (C-6), (+)154.57 ($C\text{-}2^{aux}$), (+)173.91 (C-1). $C_{19}H_{31}NO_3$ (321.46, 321.23), EI MS: $m/z$ (%)=321 $[M]^{+\cdot}$ (8), 278 (20), 149 (40), 130 (100), 69 (96), 41 (87); HRMS: calcd 321.2304, found 321.2299.

**8.7.6. (4*S*)-3-[(2*R*,5*E*)-6,10-Dimethyl-2-(2-trimethylsilylethoxymethyl)-undeca-5,9-dienoyl]-4-isopropyloxazolidin-2-one (23a).** General procedure 2: **22d** (0.06 g, 0.20 mmol), **7** (0.07 g, 0.40 mmol), FC (petroleum ether–ethyl acetate 6:1). Colourless syrup, yield: 61.34 mg (68%). $[\alpha]_D^{24}$=+14.6 ($c$=1.94, $CHCl_3$). IR (KBr): 2958, 1780, 1701, 1385, 1246, 1203, 1099, 837 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=−0.04–0.07 (9H, $Si(CH_3)_3$), 0.79–0.87 (2H, $CH_2$–$CH_2$–Si, $J$=8.4 Hz), 0.88, 0.91 (2d, 6H, $CH(CH_3)_2^{aux}$, $J$=7.4 Hz), 1.56 (s, 3H, 6-$CH_3$), 1.58 (s, 3H, 10-$CH_3$), 1.66 (s, 3H, $CH_3$-11), 1.70–1.84 (2H, $CH_2$-3),

1.87–2.10 (6H, $CH_2$-4, $CH_2$-7, $CH_2$-8), 2.25–2.44 (1H, C*H*$(CH_3)_2^{aux}$), 3.43–3.51 (1H, C*H*$_2$–$CH_2$–Si), 3.55 (dd, 1H, CH–C*H*H′–O, $^2J$=9.1 Hz, $^3J$=5.2 Hz), 3.64 (dd, 1H, CH CH*H*′–O, $^3J$=7.4 Hz), 4.11–4.19 (1H, 2-H), 4.18 (dd, 1H, $5^{aux}$-H, $^2J$=9.1 Hz, $^3J$=3.6 Hz), 4.24 (dd, 1H, $5^{aux}$-H, $^3J$=8.0 Hz), 4.49 (ddd, 1H, $4^{aux}$-H), 5.04–5.14 (2H, 5-H, 9-H). $^{13}$C NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): δ=(−)−0.85 (Si(*C*$H_3$)$_3$), (−)14.75, (−)17.91 (CH(*C*$H_3$)$_2^{aux}$), (−)16.03 (6-$CH_3$), (−)17.69 (10-$CH_3$), (+)18.10 ($CH_2$–*C*$H_2$–Si), (−)25.69 ($CH_3$-11), (+)25.71 (C-4), (+)26.72 (C-8), (+)28.91 (C-3), (+)39.70 (C-7), (−)28.42 (*C*H$(CH_3)_2^{aux}$), (−)43.30 (C-2), (−)58.52 (C-$4^{aux}$), (+)63.08 (C-$5^{aux}$), (+)68.32 (*C*$H_2$–$CH_2$–Si), (+)71.64 (CH–*C*$H_2$–O), (−)123.59, (−)124.30 (C-5, C-9), (+)131.34 (C-10), (+)135.85 (C-6), (+)153.71 (C-$2^{aux}$), (+)175.11 (C-1). $C_{25}H_{45}NO_4Si$ (451.72, 451.31), FAB MS: *m*/*z*=490.2 $[M+K]^+$, 474.2 $[M+Na]^+$; HRMS: $C_{25}H_{45}NNaO_4Si$ $[M+Na]^+$: calcd 474.3016, found 474.3002.

**8.7.7. Methyl (2*R*,5*E*)-6,10-Dimethyl-2-(2-trimethylsilyl-ethoxymethyl)-undeca-5,9-dienoate (23b).** General procedure 4: **23a** (0.17 g, 0.39 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 5 mL), FC (petroleum ether–ethyl acetate 5:1). Colourless oil, yield: 0.11 g (84%). $[\alpha]_D^{20}$=+9.8 (*c*=2.47, $CHCl_3$). IR (KBr): 2952, 1741, 1437, 1249, 1109, 839 $cm^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ=0.02 (s, 9H, Si(C*H*$_3$)$_3$), 0.85–0.92 (2H, $CH_2$–C*H*$_2$–Si), 1.44–1.56 (2H, $CH_2$-3), 1.56 (s, 3H, 6-$CH_3$), 1.58 (s, 3H, 10-$CH_3$), 1.66 (s, 3H, $CH_3$-11), 1.92–2.14 (6H, $CH_2$-4, $CH_2$-7, $CH_2$-8), 2.87–2.98 (1H, 2-H), 3.44 (dd, 1H, CH–C*H*H′–O, $^2J$=9.1 Hz, $^3J$=5.5 Hz) 3.56 (dd, 2H, CH–CH*H*′–O, $^3J$=8.2 Hz), 3.45–3.78 (2H, C*H*$_2$–$CH_2$–Si), 3.67 (s, 3H, OC*H*$_3$), 5.02–5.14 (2H, 5-H, 9-H). $^{13}$C NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): δ=(−)−0.85 (Si(*C*$H_3$)$_3$), (−)15.98 (6-$CH_3$), (−)17.68 (10-$CH_3$), (+)18.01 ($CH_2$–*C*$H_2$–Si), (+)25.63 (C-4), 25.68 ($CH_3$-11), (+)26.68 (C-8), (+)29.10 (C-3), (+)39.72 (C-7), (−)45.71 (C-2), (−)51.50 (O*C*$H_3$), (+)68.36 (*C*$H_2$–$CH_2$–Si), (+)71.11 (CH–*C*$H_2$–O), (−)123.33, (−)124.29 (C-5, C-9), (+)131.33 (C-10), (+)136.02 (C-6), (+)175.21 (C-1). $C_{20}H_{38}O_3Si$ (354.60, 354.25), FAB MS: *m*/*z*=377.1 $[M+Na]^+$.

**8.7.8. Methyl (2*R*,5*E*)-2-Hydroxymethyl-6,10-dimethyl-undeca-5,9-dienoate (23c).** General procedure 5: **23b** (57.20 mg, 0.16 mmol), $LiBF_4$ (57.20 mg, 0.16 mmol), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield: 21.08 mg (51%). $[\alpha]_D^{24}$=+10.8 (*c*=1.03, $CHCl_3$). IR (KBr): 3431, 2925, 1734, 1458, 1200, 1171, 1049 $cm^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ=1.19–1.34 ($CH_2$-3), 1.59 (s, 3H, 6-$CH_3$), 1.60 (s, 3H, 10-$CH_3$), 1.69 (s, 3H, $CH_3$-11), 1.86–2.20 (6H, $CH_2$-4, $CH_2$-7, $CH_2$-8), 2.48–2.72 (1H, 2-H), 3.73 (s, 3H, OC*H*$_3$), 3.74–3.83 (2H, C*H*$_2$–OH), 5.02–5.14 (2H, 5-H, 9-H). $^{13}$C NMR (100.3 MHz, $CDCl_3$): δ=16.68 (6-$CH_3$), 18.37 (10-$CH_3$), 26.17 (C-4), 26.37 ($CH_3$-11), 27.31 (C-8), 29.16 (C-3), 40.38 (C-7), 47.48 (C-2), 52.43 (O*C*$H_3$), 63.76 (*C*$H_2$–OH), 123.79, 124.90 (C-5, C-9), 132.13 (C-10), 137.04 (C-6), 176.59 (C-1). $C_{15}H_{26}O_3$ (254.36, 254.18), FAB MS: *m*/*z*=255.1 $[M+H]^+$; HRMS: $C_{15}H_{27}O_3$ $[M+H]^+$: calcd 255.1960, found 255.1957.

**8.7.9. [(2*E*)-3,7-Dimethyl-octa-2,6-dienyloxy]-acetic acid (24A).** To a vigorously stirred solution of geraniol (2.56 mL, 14.60 mmol) in dry DMF (30 mL) NaH (0.70 g, 29.20 mmol) was added. The mixture was stirred at 30°C for 1 h. After addition of sodium bromoacetate (3.50 g, 21.90 mmol) the mixture was stirred under reflux for 12 h. After cooling to ambient temperature the solvent was distilled off under reduced pressure. The residue was taken up in water and the solution acidified with HCl. Subsequent work-up and FC (petroleum ether–ethyl acetate 3:1) provided **24A** as a colourless, strongly smelling oil (1.91 g, 62%). IR (KBr): 3424, 2975, 2934, 1734, 1381, 1214, 1133 $cm^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ=1.56 (s, 3H, 7-$CH_3^{ger}$), 1.64 (s, 6H, 3-$CH_3^{ger}$, $CH_3$-$8^{ger}$), 1.89–2.12 (4H, $CH_2$-$4^{ger}$, $CH_2$-$5^{ger}$), 4.07 (s, 2H, O–C*H*$_2$–COOH), 4.10 (d, 2H, $CH_2$-$1^{ger}$, $J_{1,2}$=7.3 Hz), 5.04 (tm, 1H, $6^{ger}$-H, $J_{6,5}$=6.8 Hz), 5.32 (tm, 1H, $2^{ger}$-H), 10.61 (bs, 1H, COO*H*). $^{13}$C NMR (HETCOR, 50.3 MHz, $CDCl_3$): δ=16.85 (3-$CH_3^{ger}$), 18.09 (7-$CH_3^{ger}$), 26.09 ($CH_3$-$8^{ger}$), 26.71 (C-$5^{ger}$), 40.03 (C-$4^{ger}$), 66.54 (O–*C*$H_2$–COOH), 68.05 (C-$1^{ger}$), 119.80 (C-$2^{ger}$), 124.25 (C-$6^{ger}$), 132.24 (C-$7^{ger}$), 142.81 (C-$3^{ger}$), 176.24 (*C*OOH). $C_{12}H_{20}O_3$ (212.28, 212.14), EI MS: *m*/*z* (%)=212 $[M]^{+\cdot}$ (2), 93 (24), 69 (100), 41 (63); HRMS: calcd 212.1412, found 212.1414.

**8.7.10. (4*S*)-3-[{(2*E*)-3,7-Dimethyl-octa-2,6-dienyloxy}-acetyl]-4-isopropyl-oxazolidin-2-one (25A).** General procedure 1: **5** (0.13 g, 1.00 mmol), [(2*E*)-3,7-dimethyl-octa-2,6-dienyloxy]-acetyl chloride (obtained from **24A**; 0.23 g, 1.00 mmol), FC (petroleum ether–ethyl acetate 4:1). Colourless oil, yield: 0.23 g (72%). $[\alpha]_D^{25}$=+50.8 (*c*=2.78, $CHCl_3$). IR (KBr): 3427, 2964, 2921, 1765, 1713, 1390, 1255, 1211, 1130 $cm^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ=0.85, 0.90 (2d, 6H, CH(C*H*$_3$)$_2^{aux}$, *J*=7.0 Hz), 1.57 (s, 3H, 7-$CH_3^{ger}$), 1.64 (s, 3H, 3-$CH_3^{ger}$), 1.66 ($CH_3$-$8^{ger}$), 1.89–2.18 (4H, $CH_2$-$4^{ger}$, $CH_2$-$5^{ger}$), 2.25–2.55 (1H, C*H*$(CH_3)_2^{aux}$), 4.11 (d, 2H, $CH_2$-$1^{ger}$, $^3J_{1,2}$=7.0 Hz), 4.23 (dd, 1H, $5^{aux}$-H, $^2J$=8.8 Hz, $^3J$=3.3 Hz), 4.32 (dd, 1H, $5^{aux}$-H′, $^3J$=8.0 Hz), 4.43 (ddd, 1H, $4^{aux}$-H), 4.62 (s, 2H, NCO–C*H*$_2$–O), 5.06 (tm, 1H, $6^{ger}$-H, $^3J_{6,5}$=6.8 Hz), 5.38 (tm, 1H, $2^{ger}$-H). $^{13}$C NMR (HETCOR, 50.3 MHz, $CDCl_3$): δ=15.10, 18.35 (CH(*C*$H_3$)$_2^{aux}$), 16.96 (3-$CH_3^{ger}$), 18.14 (7-$CH_3^{ger}$), 26.12 ($CH_3$-$8^{ger}$), 26.81 (C-$5^{ger}$), 28.71 (*C*H$(CH_3)_2^{aux}$), 40.06 (C-$4^{ger}$), 58.65 (C-$4^{aux}$), 64.87 (C-$5^{aux}$), 68.24 (C-$1^{ger}$), 69.77 (NCO–*C*$H_2$–O), 120.30 (C-$2^{ger}$), 124.36 (C-$6^{ger}$), 132.16 (C-$7^{ger}$), 142.08 (C-$3^{ger}$), 154.49 (C-$2^{aux}$), 170.83 (N*C*O–$CH_2$–O). $C_{18}H_{29}NO_4$ (323.43, 323.20), EI MS: *m*/*z* (%)=323 $[M]^{+\cdot}$ (>1), 69 (100), 41 (74); HRMS: calcd 323.2097, found 323.2111.

**8.7.11. (*S*)-3-[(*R*)-2-{(2*E*)-3,7-Dimethyl-octa-2,6-dienyl-oxy}-3-hydroxy-propionyl]-4-isopro-pyloxazolidin-2-one (26Aa).** General procedure 2: **25A** (0.20 g, 0.62 mmol), **8b** (0.18 g, 1.20 mmol), FC (petroleum ether–ethyl acetate 1:1.75). Colourless syrup, yield: 78 mg (36%). $[\alpha]_D^{25}$=+36.2 (*c*=3.17, $CHCl_3$). IR (KBr): 3402, 2965, 2925, 1781, 1711, 1389, 1246, 1207, 1119, 1055 $cm^{-1}$. $^1$H NMR (HH COSY, 200 MHz, $CDCl_3$): δ=0.90, 0.95 (2d, 6H, CH(C*H*$_3$)$_2^{aux}$, *J*=7.0 Hz), 1.60 (s, 3H, 7-$CH_3^{ger}$), 1.67 (s, 6H, 3-$CH_3^{ger}$, $CH_3$-$8^{ger}$), 1.95–2.20 (4H, $CH_2$-$4^{ger}$, $CH_2$-$5^{ger}$), 2.37–2.60 (2H, C*H*$(CH_3)_2^{aux}$), 3.84 (dd, 1H, C*H*H–OH, $^2J$=12.0 Hz, $^3J$=4.6 Hz), 3.94 (dd, 1H, C*H*H–OH, $^3J$=4.0 Hz), 4.05–4.20 (2H, $CH_2$-$1^{ger}$), 4.25 (dd, 1H,

$5^{aux}$-H, $^2J$=8.9 Hz, $^3J$=3.1 Hz), 4.34 (dd, 1H, $5^{aux}$-H′, $^3J$=8.2 Hz), 4.41–4.53 (1H, $4^{aux}$-H), 5.03–5.14 (1H, $6^{ger}$-H), 5.23 (dd, 1H, 2-H), 5.38 (tm, 1H, $2^{ger}$-H). $^{13}$C NMR (HMQC, APT, 100.6 MHz, $CDCl_3$): δ=(−)15.03, (−)18.45 ($CH(CH_3)_2{}^{aux}$), (−)16.96 (3-$CH_3{}^{ger}$), (−)18.16 (7-$CH_3{}^{ger}$), (−)26.14 ($CH_3$-$8^{ger}$), (+)26.81 (C-$5^{ger}$), (−)28.69 ($CH(CH_3)_2{}^{aux}$), (+)40.08 (C-$4^{ger}$), (−)59.35 (C-$4^{aux}$), (+)63.71 ($CH_2$–OH), (+)64.45 (C-$5^{aux}$), (+)67.27 (C-$1^{ger}$), (−)78.06 (C-2), (−)120.22 (C-$2^{ger}$), (−)124.26 (C-$6^{ger}$), (+)132.27 (C-$7^{ger}$), (+)142.32 (C-$3^{ger}$), (+)154.51 (C-$2^{aux}$), (+)171.15 (NCO–CH). $C_{19}H_{31}NO_5$ (353.45, 353.22), EI MS: *m/z* (%)=353 $[M]^{+\cdot}$ (>1), 201 (17), 130 (36), 86 (57), 69 (100), 41 (78), FAB MS: *m/z*=392.2 $[M+K]^+$, 376.2 $[M+Na]^+$; HRMS: $C_{19}H_{31}NNaO_5$ $[M+Na]^+$: calcd 376.2100, found 376.2098.

**8.7.12. (*S*)-3-[(*R*)-2-{(2*E*)-3,7-Dimethyl-octa-2,6-dienyloxy}-3-(2-trimethylsilyl-ethoxy)-pro-pionyl]-4-isopropyl-oxazolidin-2-one (26Ab).** General procedure 2: **25A** (1.15 g, 3.57 mmol), **7** (0.89 g, 5.34 mmol), FC (petroleum ether–ethyl acetate 10:1). Colourless oil, yield: 0.63 g (39%). $[\alpha]_D{}^{25}$=+23.6 (*c*=1.48, $CHCl_3$). IR (KBr): 2959, 1780, 1712, 1387, 1249, 1206, 1110 $cm^{-1}$. $^1$H NMR (HH COSY, 200 MHz, $CDCl_3$): δ=−0.02 (s, 9H, $Si(CH_3)_3$), 0.88, 0.91 (2d, 6H, $CH(CH_3)_2{}^{aux}$, *J*=7.0 Hz), 0.87–0.97 (2H, $CH_2$–$CH_2$–Si), 1.58 (s, 3H, 7-$CH_3{}^{ger}$), 1.67 (s, 3H, $CH_3$-$8^{ger}$), 1.73 (s, 3H, 3-$CH_3{}^{ger}$), 1.89–2.15 (4H, $CH_2$-$4^{ger}$, $CH_2$-$5^{ger}$), 2.24–2.44 (2H, $CH(CH_3)_2$), 3.42–3.65 (2H, $CH_2$–$CH_2$–Si), 3.72 (dd, 1H, CH–CH*H*′–O, $^2J$=10.3 Hz, $^3J$=3.8 Hz), 3.83 (dd, 1H, CH–CH*H*′–O, $^3J$=5.1 Hz), 4.00 (dd, 1H, $1^{ger}$-H, $^2J$=11.4 Hz, $^3J$=7.7 Hz), 4.12 (dd, 1H, $1^{ger}$-H′, $^3J$=7.7 Hz), 4.23 (dd, 1H, $5^{aux}$-H, $^2J$=9.0 Hz, $^3J$=3.7 Hz), 4.32 (dd, 1H, $5^{aux}$-H′, $^3J$=8.4 Hz), 4.53 (ddd, 1H, $4^{aux}$-H), 5.00–5.13 (1H, $6^{ger}$-H), 5.28 (dd, 1H, CH–$CH_2$–OH), 5.37 (tm, 1H, $2^{ger}$-H). $^{13}$C NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): δ=(+)−1.32 ($Si(CH_3)_3$), (−)15.02, (−)17.94 ($CH(CH_3)_2{}^{aux}$), (−)17.81 (7-$CH_3{}^{ger}$), (+)18.22 ($CH_2$–$CH_2$–Si), (−)23.63 (3-$CH_3{}^{ger}$), (−)25.81 ($CH_3$-$8^{ger}$), (+)26.87 (C-$5^{ger}$), (−)28.55 ($CH(CH_3)_2{}^{aux}$), (+)32.38 (C-$4^{ger}$), (−)58.46 (C-$4^{aux}$), (+)64.17 (C-$5^{aux}$), (+)66.94 (C-$1^{ger}$), (+)68.94 ($CH_2$–$CH_2$–Si), (+)70.70 (CH–$CH_2$–O), (−)76.81 (CH–$CH_2$–OH), (−)121.54 (C-$2^{ger}$), (−)123.97 (C-$6^{ger}$), (+)132.01 (C-$7^{ger}$), (+)141.17 (C-$3^{ger}$), (+)153.87 (C-$2^{aux}$), (+)170.94 (NCO–CH). $C_{24}H_{43}NO_5Si$ (453.69, 453.29). EI MS: *m/z* (%)=453 $[M]^{+\cdot}$ (>1), 202 (28), 73 (100), 41 (34), FAB MS: *m/z*=476.3 $[M+Na]^+$; HRMS: $C_{24}H_{43}NNaO_5Si$ $[M+Na]^+$: calcd 476.2808, found 476.2802.

**8.7.13. Methyl (*R*)-2-[(2*E*)-3,7-Dimethyl-octa-2,6-dienyloxy]-3-(2-trimethylsilyl-ethoxy)-propio-nate (27Ab).** General procedure 4: **26Ab** (0.11 g, 0.25 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 2 mL), FC (petroleum ether–ethyl acetate 6:1). Colourless oil, yield: 71.27 mg (81%). $[\alpha]_D{}^{25}$=+14.3 (*c*=2.52, $CHCl_3$). IR (KBr): 2955, 2918, 2863, 1752, 1250, 1200, 1117, 859, 837 $cm^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ=−0.01 (s, 9H, $Si(CH_3)_3$), 0.85–0.98 (2H, $CH_2$–$CH_2$–Si), 1.58 (s, 3H, 7-$CH_3{}^{ger}$), 1.67 (s, 3H, $CH_3$-$8^{ger}$), 1.74 (s, 3H, 3-$CH_3{}^{ger}$), 1.98–2.14 (4H, $CH_2$-$4^{ger}$, $CH_2$-$5^{ger}$), 3.49–3.60 (2H, $CH_2$–$CH_2$–Si), 3.67 (d, $CH_2$-3, *J*=5.1 Hz), 3.75 (s, 3H, $OCH_3$), 3.96–4.24 (3H, CH–$CH_2$–O, $CH_2$-$1^{ger}$), 5.00–5.13 (1H, $6^{ger}$-H), 5.36 (tm, 1H, $2^{ger}$-H). $^{13}$C NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$). δ=(+)−1.29 ($Si(CH_3)_3$), (−)17.78 (7-$CH_3{}^{ger}$), (+)18.13 ($CH_2$–$CH_2$–Si), (−)23.63 (3-$CH_3{}^{ger}$), (−)25.79 ($CH_3$-$8^{ger}$), (+)26.81 (C-$5^{ger}$), (+)32.34 (C-$4^{ger}$), (−)52.05 ($OCH_3$), (+)66.94 (C-$1^{ger}$), (+)69.02 ($CH_2$–$CH_2$–Si), (+)70.87 (CH–$CH_2$–OH), (−)77.73 (CH–$CH_2$–OH), (−)121.23 (C-$2^{ger}$), (−)123.88 (C-$6^{ger}$), (+)132.04 (C-$7^{ger}$), (+)141.49 (C-$3^{ger}$), (+)171.71 ($COOCH_3$). $C_{19}H_{36}O_4Si$ (356.57, 356.23), EI MS: *m/z* (%)=356 $[M]^{+\cdot}$ (>2), 136 (29), 121 (21), 93 (47), 73 (100); HRMS: calcd 356.2383, found 356.2392.

**8.7.14. Methyl (*R*)-2-[(2*E*)-3,7-dimethyl-octa-2,6-dienyloxy]-3-hydroxy-propionate (27Aa).** (a) General procedure 5: **27Ab** (92 mg, 0.26 mmol), $LiBF_4$ (0.24 g, 2.58 mmol), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield: 66 mg, (69%).

(b) General procedure 4: **26Aa** (50 mg, 0.14 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 4.6 mL), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield: 32 mg (91%). $[\alpha]_D{}^{25}$=+9.3 (*c*=1.43, $CHCl_3$). IR (KBr): 3432, 2922, 2853, 1733, 1458, 1166, 1056 $cm^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ=1.60 (s, 3H, 7-$CH_3{}^{ger}$), 1.67 (s, 6H, 3-$CH_3{}^{ger}$, $CH_3$-$8^{ger}$), 1.97–2.11 (4H, $CH_2$-$4^{ger}$, $CH_2$-$5^{ger}$), 3.77 (s, 3H, $OCH_3$), 3.78 (dd, H, CH*H*′–OH, $^2J$=11.6 Hz, $^3J$=6.1 Hz), 3.88 (dd, 2H, CH*H*′–OH, $^3J$=3.8 Hz), 4.05 (dd, 1H, CH–$CH_2$–OH), 4.06 (dd, 1H, $1^{ger}$-H, $^2J$=11.3 Hz, $^3J$=7.4 Hz), 4.27 (dd, 1H, $1^{ger}$-H′), 5.00–5.16 (1H, $6^{ger}$-H), 5.36 (tm, 1H, $2^{ger}$-H). $^{13}$C NMR (50.3 MHz, $CDCl_3$): δ=16.94 (3-$CH_3{}^{ger}$), 18.16 (7-$CH_3{}^{ger}$), 26.15 ($CH_3$-$8^{ger}$), 26.76 (C-$5^{ger}$), 40.07 (C-$4^{ger}$), 52.57 ($OCH_3$), 63.94 ($CH_2$–OH), 67.62 (C-$1^{ger}$), 78.52 (CH–$CH_2$–OH), 120.10 (C-$2^{ger}$), 124.27 (C-$6^{ger}$), 132.33 (C-$7^{ger}$), 142.59 (C-$3^{ger}$), 171.85 ($COOCH_3$). $C_{14}H_{24}O_4$ (256.34, 256.16), EI MS: *m/z* (%)=256 $[M]^{+\cdot}$ (>2), 69 (100), 41 (67); FAB MS: *m/z*=279.1 $[M+Na]^+$; HRMS: $C_{14}H_{24}NaO_4$ $[M+Na]^+$: calcd 279.1572, found 279.1567.

**8.7.15. [(2*Z*)-3,7-Dimethyl-octa-2,6-dienyloxy]-acetic acid (24B).** The reaction was performed as described for **24A**. Nerol (2.56 mL, 14.60 mmol), sodium bromoacetate (3.50 g, 21.90 mmol), FC (petroleum ether–ethyl acetate 3:1). Colourless, strongly smelling oil, yield: 1.67 g (54%). IR (KBr): 3121, 2967, 2926, 1733, 1444, 1377, 1242, 1220, 1120 $cm^{-1}$. $^1$H NMR (200 MHz, $CDCl_3$): δ=1.59 (s, 3H, 7-$CH_3{}^{ner}$), 1.67 (s, 6H, $CH_3$-$8^{ner}$), 1.76 (s, 3H, 3-$CH_3{}^{ner}$), 1.95–2.17 (4H, $CH_2$-$4^{ner}$, $CH_2$-$5^{ner}$), 4.10 (s, 2H, O–$CH_2$–COOH), 4.10 (d, 2H, $CH_2$-$1^{ner}$, *J*=6.4 Hz), 5.00–5.14 (1H, $6^{ner}$-H), 5.35 (tm, 1H, $2^{ner}$-H), 10.32 (bs, 1H, COO*H*). $^{13}$C NMR (HETCOR, 50.3 MHz, $CDCl_3$): δ=17.99 (7-$CH_3{}^{ner}$), 23.84 (3-$CH_3{}^{ner}$), 26.05 ($CH_3$-$8^{ner}$), 26.98 (C-$5^{ner}$), 32.56 (C-$4^{ner}$), 66.74 (C-$1^{ner}$), 67.91 (O–$CH_2$–COOH), 120.88 (C-$2^{ner}$), 124.07 (C-$6^{ner}$), 132.68 (C-$7^{ner}$), 142.90 (C-$3^{ner}$), 176.19 (*C*OOH). $C_{12}H_{20}O_3$ (212.28, 212.14), FAB MS: *m/z*=235.1 $[M+Na]^+$; HRMS: $C_{12}H_{20}NaO_3$ $[M+Na]^+$: calcd 235.1310, found 235.1302.

**8.7.16. (4*S*)-3-[{(2*Z*)-3,7-Dimethyl-octa-2,6-dienyloxy}-acetyl]-4-isopropyloxazolidin-2-one (25B).** General procedure 1: **5** (0.17 g, 1.30 mmol), [(2*Z*)-3,7-dimethyl-octa-2,6-dienyloxy]-acetyl chloride (obtained from **24A**; 0.30 g, 1.30 mmol), FC (petroleum ether–ethyl acetate

4:1). Colourless oil, yield: 0.27 g (65%). $[\alpha]_D^{24}$=+51.2 ($c$=1.54, $CHCl_3$). IR (KBr): 2965, 2927, 1782, 1717, 1390, 1260, 1210, 1123 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$). $\delta$=0.88, 0.93 (2×d, 6H, $CH(CH_3)_2^{aux}$, $J$=7.0 Hz), 1.59 (s, 3H, 7-$CH_3^{ner}$), 1.67 (s, 3H, $CH_3$-$8^{ner}$), 1.76 (3-$CH_3^{ner}$), 1.94–2.18 (4H, $CH_2$-$4^{ner}$, $CH_2$-$5^{ner}$), 2.32–2.53 (1H, $CH(CH_3)_2^{aux}$), 4.12 (d, 2H, $CH_2$-$1^{ner}$, $J$=7.0 Hz), 4.26 (dd, 1H, $5^{aux}$-H, $^2J$=8.8 Hz, $^3J$=3.3 Hz), 4.34 (dd, 1H, $5^{aux}$-H′, $^3J$=8.1 Hz), 4.46 (ddd, 1H, $4^{aux}$-H), 4.64 (s, 2H, NCO–$CH_2$–O), 5.02–5.16 (1H, $6^{ner}$-H), 5.41 (tm, 1H, $2^{ner}$-H). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=15.14, 18.37 ($CH(CH_3)_2^{aux}$), 18.12 (7-$CH_3^{ner}$), 23.98 (3-$CH_3^{ner}$), 26.15 ($CH_3$-$8^{ner}$), 27.19 (C-$5^{ner}$), 28.75 ($CH(CH_3)_2^{aux}$), 32.73 (C-$4^{ner}$), 58.67 (C-$4^{aux}$), 64.88 (C-$5^{aux}$), 68.02 (C-$1^{ner}$), 69.78 (NCO–$CH_2$–O), 121.42 (C-$2^{ner}$), 124.25 (C-$6^{ner}$), 132.46 (C-$7^{ner}$), 142.10 (C-$3^{ner}$), 154.52 (C-$2^{aux}$), 170.80 (NCO–$CH_2$–O). $C_{18}H_{29}NO_4$ (323.43, 323.20), FAB MS: $m/z$=346.1 $[M+Na]^+$; HRMS: $C_{18}H_{29}NNaO_4$ $[M+Na]^+$: calcd 346.1994, found 346.1992.

**8.7.17. (*S*)-3-[(*R*)-2-{(2*Z*)-3,7-Dimethyl-octa-2,6-dienyloxy}-3-hydroxy-propionyl]-4-isopropyl-oxazolidin-2-one (26Ba).** General procedure 2: **25B** (0.20 g, 0.62 mmol), **8b** (0.28 g, 1.85 mmol), FC (petroleum ether–ethyl acetate 1:1.75). Colourless syrup, yield: 70 mg (32%). $[\alpha]_D^{25}$=+35.7 ($c$=1.95, $CHCl_3$). IR (KBr): 3416, 2964, 2929, 2361, 1778, 1750, 1391, 1205, 1114 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.85–0.98 (6H, $CH(CH_3)_2^{aux}$), 1.57 (s, 3H, 7-$CH_3^{ner}$), 1.65 (s, 3H, $CH_3$-$8^{ner}$), 1.74 (s, 3H, 3-$CH_3^{ner}$), 1.95–2.15 (4H, $CH_2$-$4^{ner}$, $CH_2$-$5^{ner}$), 2.37–2.59 (2H, $CH(CH_3)_2^{aux}$), 3.78–3.98 (2H, $CH_2$–OH), 3.98–4.16 (2H, $CH_2$-$1^{ner}$), 4.24 (dd, 1H, $5^{aux}$-H, $^2J$=8.9 Hz, $^3J$=3.1 Hz), 4.33 (dd, 1H, $5^{aux}$-H′, $^3J$=8.1 Hz), 4.41–4.51 (1H, $4^{aux}$-H), 4.98–5.11 (1H, $6^{ner}$-H), 5.20 (dd, 1H, CH–$CH_2$–OH, $J$=4.2 Hz), 5.37 (tm, 1H, $2^{ner}$-H, $J$=7.1 Hz). $^{13}C$ NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): $\delta$=(−)15.05, 18.43 ($CH(CH_3)_2^{aux}$), (−)18.10 (7-$CH_3^{ner}$), (−)24.00 (3-$CH_3^{ner}$), (−)26.15 ($CH_3$-$8^{ner}$), (+)27.16 (C-$5^{ner}$), (−)28.70 ($CH(CH_3)_2^{aux}$), (+)32.70 (C-$4^{ner}$), (−)59.35 (C-$4^{aux}$), (+)63.67 ($CH_2$–OH), (+)64.49 (C-$5^{aux}$), (+)67.04 (C-$1^{ner}$), (−)78.17 (CH–$CH_2$–OH), (−)121.29 (C-$2^{ner}$), (−)124.11 (C-$6^{ner}$), (+)132.53 (C-$7^{ner}$), (+)142.36 (C-$3^{ner}$), (+)154.53 (C-$2^{aux}$), (+)171.18 (NCO–$CH_2$–O). $C_{19}H_{31}NO_5$ (353.45, 353.22), FAB MS: $m/z$=376.3 $[M+Na]^+$; HRMS: $C_{19}H_{31}NNaO_5$ $[M+Na]^+$: calcd 376.2100, found 376.2092.

**8.7.18. Methyl (*R*)-2-[(2*Z*)-3,7-dimethyl-octa-2,6-dienyloxy]-3-hydroxy-propionate (27Ba).** General procedure 4: **26Ba** (42 mg, 0.12 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 3.70 mL), FC (petroleum ether–ethyl acetate 3:1). Colourless oil, yield: 27.2 mg (88%). $[\alpha]_D^{25}$=+8.5 ($c$=0.73, $CHCl_3$). IR (KBr): 3432, 2922, 2853, 1733, 1458, 1198, 1056 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=1.59 (s, 3H, 7-$CH_3^{ner}$), 1.68 (s, 3H, $CH_3$-$8^{ner}$), 1.77 (s, 3H, 3-$CH_3^{ner}$), 1.97–2.20 (4H, $CH_2$-$4^{ner}$, $CH_2$-$5^{ner}$), 3.77 (s, 3H, $OCH_3$), 3.72–3.93 (2H, $CH_2$–OH), 4.03 (dd, 1H, $1^{ner}$-H, $^2J$=11.1 Hz, $^3J$=7.2 Hz), 4.04 (dd, 1H, CH–$CH_2$–OH, both $J$~6.0 Hz), 4.23 (dd, 1H, $1^{ner}$-H′, $^3J$=6.7 Hz) 5.00–5.15 (1H, $6^{ner}$-H), 5.38 (tm, 1H, $2^{ner}$-H). $^{13}C$ NMR (50.3 MHz, $CDCl_3$): $\delta$=18.16 (7-$CH_3^{ner}$), 23.99 (3-$CH_3^{ner}$), 26.17 ($CH_3$-$8^{ner}$), 27.13 (C-$5^{ner}$), 32.68 (C-$4^{ner}$), 52.58 ($OCH_3$), 63.95 ($CH_2$–OH), 67.43 (C-$1^{ner}$), 78.68 (CH–$CH_2$–OH), 121.14 (C-$2^{ner}$), 124.10 (C-$6^{ner}$), 132.66 (C-$7^{ner}$), 142.69 (C-$3^{ner}$), 171.82 ($COOCH_3$). $C_{14}H_{24}O_4$ (256.34, 256.16), FAB MS: $m/z$=279.2 $[M+Na]^+$; HRMS: $C_{14}H_{24}NaO_4$ $[M+Na]^+$: calcd 279.1572, found 279.1579.

**8.7.19. 4-Phenylbenzyloxyacetic acid (24C).**[45] Prepared from 4-phenylbenzyl alcohol (6.9 g, 0.038 mol) as described for **24A**. FC (petroleum ether–ethyl acetate 2:1) provided **24C** (6.3 g, 70%) as bright pale yellow plates. Mp 115–117°C (petroleum ether). IR (KBr): 3427 (OH), 1732 and 1707 $cm^{-1}$ (C=O). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=4.20 (s, 2H, Ar-$CH_2$–O), 4.71 (s, 2H, O–$CH_2$–COOH), 7.36–7.53 (9H, $Ar^{A,B}$-Hs), 8.79 (bs, 1H, COO*H*). $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$=66.79 (Ar-$CH_2$–O), 73.37 (O–$CH_2$–COOH), 127.25, 127.50, 127.56 (C-$3^A$, C-$5^A$, C-$2^B$, C-$4^B$,C-$6^B$), 128.73, 128.94 (C-$2^A$,C-$6^A$,C-$3^B$,C-$5^B$), 135.69 (C-$1^A$), 140.83 (C-$1^B$), 141.41 (C-$4^A$), 175.16 ($COOH$). UV ($CHCl_3$): $\lambda_{max}$ ($\epsilon$)=254.0 nm (17.680). $C_{15}H_{14}O_3$ (242.27, 242.09), FAB MS: $m/z$=265.0 $[M+Na]^+$, 242.0 $[M+H]^+$.

**8.7.20. (*S*)-3-[{4-Phenylbenzyloxy}-acetyl]-4-isopropyl-oxazolidin-2-one (25C).**[45] General procedure 1: **5** (1.4 g, 11 mmol), 4-phenylbenzyloxy–acetyl chloride (2.9 g, 11 mmol), FC (petroleum ether–ethyl acetate 3:1). White solid, yield: 2.6 g (67%). Mp 95–98°C (petroleum ether). IR (KBr): 1776 and 1709 $cm^{-1}$ (C=O). UV ($CHCl_3$): $\lambda_{max}$ ($\epsilon$): 253.0 nm (20.896). $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$=0.89, 0.94 (2d, $CH(CH_3)_2^{aux}$, $J$=7.0 Hz), 2.45 (m, 1H, $CH(CH_3)_2^{aux}$), 4.15–4.35 (2H, $CH_2$-$5^{aux}$), 4.45 (m, 1H, $4^{aux}$-H), 4.65 (s, 2H, Ar-$CH_2$–O), 4.68 (s, 2H, NCO–$CH_2$–O), 7.36–7.53 (9H, $Ar^{A,B}$-H). $^{13}C$ NMR (50 MHz, $CDCl_3$, HETCOR): $\delta$=14.72, 17.95 ($CH(CH_3)_2^{aux}$), 28.34 ($CH(CH_3)_2^{aux}$), 58.29 (C-$4^{aux}$), 64.49 (C-$5^{aux}$), 69.70 (NCO–$CH_2$–O), 73.27 (Ar-$CH_2$–O), 127.24, 127.39, 127.44 (C-$3^A$, C-$5^A$, C-$2^B$, C-$4^B$, C-$6^B$), 128.68, 128.89 (C-$2^A$, C-$6^A$, C-$3^B$, C-$5^B$), 136.36 (C-$1^A$), 140.98 (C-$1^B$), 141.07 (C-$4^A$), 154.15 (C-$2^{aux}$), 170.20 (NCO–$CH_2$–O). $C_{21}H_{23}O_4N$ (353.42, 353.16), FAB MS: $m/z$=376.1 $[M+Na]^+$.

**8.7.21. (*S*)-3-[(*R*)-{4-Phenylbenzyloxy}-3-(2-trimethylsilyl-ethoxy)-propionyl]-4-isopropyl-oxazolidin-2-one (26Cb).**[45] General procedure 2: **25C** (0.3 g, 0.85 mmol), **7** (0.35 mL (2.11 mmol), FC (petroleum ether–ethyl acetate 3:1). Yellow syrup, yield: 70 mg (17%). IR (KBr): 1776, 1709 $cm^{-1}$ (C=O). UV ($CHCl_3$): $\lambda_{max}$ ($\epsilon$)=255.5 nm (15.209). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=0.04 (s, 9H, $Si(CH_3)_3$, 0.95 (m, 8H, $CH(CH_3)_2^{aux}$, $CH_2$–$CH_2$–Si), 2.38 (m, 1H, $CH(CH_3)_2^{aux}$), 3.61 (m, 2H, $CH_2$–$CH_2$–Si), 3.82 (dd, 1H, CH–CHH′–O, $J_1$=10.5 Hz, $J_2$=3.9 Hz), 3.92 (dd, CH–CHH′–O, $J_1$=10.5 Hz, $J_2$=5.7 Hz), 4.15–4.28 (2H, $CH_2$-$5^{aux}$), 4.45 (m, 1H, $4^{aux}$-H), 4.64 (d, 1H, Ar-CHH′–O, $J_{AB}$=11.7 Hz), 4.76 (d, 1H, Ar-CHH′–O), 5.41 (dd, 1H, CH–$CH_2$–O, $J_1$=5.1 Hz, $J_2$=3.9 Hz), 7.34–7.62 (9H, $Ar^{A,B}$-Hs). $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$=14.91, 17.86 ($CH(CH_3)_2^{aux}$), 18.18 ($CH_2$–$CH_2$–Si), 28.44 ($CH(CH_3)_2^{aux}$), 58.36 (C-$4^{aux}$), 64.06 (C-$5^{aux}$), 68.97 ($CH_2$–$CH_2$–Si), 70.65 (CH–$CH_2$–O), 72.69 (Ar-$CH_2$–O), 76.53 ($CH_2$–$CH_2$–O), 127.11, 127.38 (C-$3^A$, C-$5^A$, C-$2^B$, C-$6^B$), 128.71, 128.85 (C-$2^A$, C-$6^A$, C-$3^B$, C-$5^B$), 136.68 (C-$1^A$), 140.81, 140.89 (C-$4^A$, C-$1^B$), 153.77 (C-$2^{aux}$),

170.72 (C-1′). $C_{27}H_{37}O_5NSi$ (483.68, 483.24), ESI MS: *m*/*z*=989.47732, calcd for $[2M+Na]^+$: 989.47742.

**8.7.22. Methyl (*R*)-(4-phenylbenzyloxy)-3-(2-trimethylsilyl-ethoxy)-propionate (27Cb).**[45] General procedure 4: **26Cb** (0.4 g, 0.8 mmol), magnesium methoxide (0.1 mol $L^{-1}$ in methanol, 12 mL), FC (petroleum ether–ethyl acetate, 4:1). Yellow oil, yield: 0.12 g (40%). IR (KBr): 1751 $cm^{-1}$ (C=O). UV ($CHCl_3$): $\lambda_{max}$ ($\epsilon$)=254.0 nm (20.561). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$=0.02 (s, 9H, Si($CH_3$)$_2$), 0.96 (2H, $CH_2$–$CH_2$–Si), 3.61 (2H, $CH_2$–$CH_2$–Si), 3.75 (d, 2H, CH–$CH_2$–O, *J*=4.9 Hz), 3.78 (s, 3H, O$CH_3$), 4.14 (t, 1H, C*H*–$CH_2$–O, *J*=4.9 Hz), 4.59 (d, 1H, Ar-C*H*H′–O, $^2J$=12.0 Hz), 4.82 (d, 1H, Ar-CH*H*′–O), 7.35–7.61 (9H, $Ar^{A,B}$-H). $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$=18.21 ($CH_2$–$CH_2$–Si), 52.18 (O$CH_3$), 69.16 ($CH_2$–$CH_2$–Si), 70.94 (CH–$CH_2$–O), 72.49 (Ar-$CH_2$–O), 78.17 (CH–$CH_2$–O), 127.27, 127.32, 127.46 (C-$3^A$, C-$5^A$, C-$2^B$, C-$4^B$, C-$6^B$), 128.66, 128.92 (C-$2^A$, C-$6^A$, C-$3^B$, C-$5^B$), 136.60 (C-$1^A$), 141.01 (C-$4^A$), 171.47 (COOCH$_3$). $C_{22}H_{30}O_4Si$ (386.56, 386.19), (386.19079), ESI-MS: *m*/*z*=409.18101, calcd for $[M+Na]^+$: 409.18056.

**8.7.23. Methyl (*R*)-(4-phenylbenzyloxy)-3-hydroxy-propionate (27Ca).**[45] General procedure 5: **26Cb** (64 mg, 0.17 mmol) $LiBF_4$ (78 mg, 0.83 mmol), FC (cyclohexane–ethyl acetate 3:1). Pale yellow solid, yield: 31 mg (64%). Mp 54–56°C (cyclohexane). $[\alpha_D{}^{20}]$=+48.06 (0.186 g/100 mL, $CHCl_3$). IR (KBr): 1743 $cm^{-1}$ (C=O). UV ($CHCl_3$): $\lambda_{max}$ ($\epsilon$)=252.5 (17.747), 255.5 nm (15.209). $^1H$ NMR (200 MHz, $CDCl_3$). $\delta$=1.91 (bs, 1H, O*H*), 3.81 (s, 3H, O$CH_3$), 3.87 (dd, 1H, C*H*H′–OH, $^2J$=11.7 Hz, $^3J$=3.7 Hz), 3.94 (dd, 1H, CH*H*′–OH, $^2J$=11.7 Hz, $^3J$=5.5 Hz), 4.15 (dd, 1H, C*H*–$CH_2$–OH, $J_1$=5.5 Hz, $J_2$=3.7 Hz), 4.57 (d, 1H, Ar-C*H*–O), 4.67 (d, 1H, Ar-C*H*′–O), 7.29–7.56 (9H, $Ar^{A,B}$-H). $^{13}C$ NMR (50 MHz, $CDCl_3$): $\delta$=52.33 (O$CH_3$), 63.68 ($CH_2$–OH), 72.49 (Ar-$CH_2$–O), 78.17 (CH–$CH_2$–OH), 127.29, 127.49, 127.58 (C-$3^A$, C-$5^A$, C-$2^B$, C-$4^B$, C-$6^B$), 128.86, 128.98 (C-$2^A$, C-$6^A$, C-$3^B$, C-$5^B$), 136.20 (C-$1^A$), 140.91 (C-$1^B$), 141.34 (C-$4^A$), 171.24 (COOCH$_3$). $C_{17}H_{18}O_4$ (286.33, 286.12), ESI MS: *m*/*z*=595.22933, calcd for $[2M+Na]^+$: 595.23024, *m*/*z*=309.10937, calcd for $[M+Na]^+$: 309.10973.

**8.7.24. 2,3,4,6-Tetra-*O*-acetyl-1-*O*-{[(*R*)-2-methoxycarbonyl-2-tetradecyl-ethoxy]-(2,2,2-tri-chloroethoxy)-phosphoryl}-α-D-glucopyranose, mixture of diastereomers (29a).** To a solution of 1H-1,2,4-triazole (49.70 mg, 0.72 mmol) in 1:4 pyridine–$CH_2Cl_2$ (1.20 mL) 2,2,2-trichloroethyl dichlorphosphite (46.90 mg, 0.19 mmol) was added at 0°C and the mixture was stirred at 0°C for 30 min. A solution of 2,3,4,6-tetra-*O*-acetyl-D-glucopyranose (**28**, 46.90 mg, 0.19 mmol) in 1:4 pyridine–$CH_2Cl_2$ (1.5 mL) was added dropwise. Stirring was continued for 70 min at 0°C. Within 1.5 h a solution of **11Ba** (124 mg, 0.41 mmol) in 1:4 pyridine–$CH_2Cl_2$ (2 mL) was added in 4 portions. After another 3 h stirring at 0°C bis(trimethylsilyl)peroxide (64.60 μL, 0.30 mmol) was added and the mixture was stirred at 20°C for 17 h. Solvents were evaporated (25°C) and the product was dried at 0.1 mbar. FC ($CHCl_3$–methanol 120:1) provided **29a** (80 mg, 64%) as a colourless oil. IR (KBr): 3452, 2926, 2854, 1753, 1458, 1371, 1227, 1157, 1111, 1036, 966, 897, 723 $cm^{-1}$. $^1H$ NMR (HH COSY, 200 MHz, $CDCl_3$): sugar part: $\delta$=2.03 (s, 3H, $CH_3CO$), 2.05 (s, 3H, $CH_3CO$), 2.10 (s, 6H, 2×$CH_3CO$), 4.05–4.42 (3H, 5-H, $CH_2$-6), 5.03 (ddd, 1H, 2-H, $J_{2,3}$=10.3 Hz, $J_{2,1}$=3.1 Hz), 5.16 (dd, 1H, 4-H, $J_{4,3}$=9.7 Hz, $J_{4,5}$=9.7 Hz), 5.49 (dd, 1H, 3-H, $J_{3,2}$=9.9 Hz, $J_{3,4}$=9.9 Hz), 5.91 (dd, 1H, 1-H, $J_{1,2}$=3.5 Hz, $J_{1,P}$=6.4 Hz); (2*R*)-2-methoxycarbonyl-2-tetradecyl-ethoxy part: $\delta$=0.88 (t, 3H, $CH_3$-14, $J_{14,13}$=6.4 Hz), 1.19–1.39 (s, 24H, $CH_2$-4–$CH_2$-16), 1.50–1.71 (2H, CH–C$H_2$–O), 2.70–2.87 (1H, C*H*–$CH_2$–O), 3.73 (s, 3H, COOC$H_3$), 4.05–4.42 (2H, $CH_2$-3); 2,2,2-trichloroethoxy part: $\delta$=4.52–4.66 (2H, C$H_2$–$CCl_3$). $^{13}C$ NMR (HETCOR, APT, 50.3 MHz, $CDCl_3$): sugar part: $\delta$=21.21, 21.27, 21.35 (4×C$H_3$CO), 61.94 (C-6), 68.19 (C-4), 69.92 (C-2), 70.42 (C-3, 5), 95.36 (C-1), 170.04, 170.34, 170.62, 171.19 (4×$CH_3$*C*O); (2*R*)-methoxycarbonyl-2-tetradecyl-ethoxy part: $\delta$=14.78 ($CH_3$-16), 23.36, 27.55, 28.97, 30.02, 30.08, 30.21, 30.32, 30.35, 32.59 ($CH_2$-4–$CH_2$-16), 46.67 (*C*H–$CH_2$–O), 52.68 (COO*C*H$_3$), 69.42 (C-3), 173.96 (C-1); 2,2,2-trichloroethoxy part: $\delta$=77.71 (*C*$H_2$–$CCl_3$), 95.22 ($CH_2$–*C*$Cl_3$). $^{31}P$ NMR (81 MHz, $CDCl_3$): $\delta$=−5.03–5.26 (1:2). $C_{34}H_{56}Cl_3O_{15}P$ (842.14, 840.24), FAB MS: *m*/*z*=863.2 $[M+Na]^+$, ESI MS: *m*/*z*=863.23414 calcd for $C_{34}H_{56}NaO_{15}P$ $[M+Na]^+$: 863.23146.

**8.7.25. 2,3,4,6-Tetra-*O*-acetyl-1-*O*-{[(*R*)-2-methoxycarbonyl-2-tetradecyl-ethoxy]-hydroxy-phosphoryl}-α-D-glucopyranose (29b).** A mixture of **29a** (44 mg, 0.05 mmol), freshly prepared zinc–copper couple (56 mg, 0.85 mmol), 2,4-pentanedione (74 μL, 0.63 mmol), and pyridine (2.7 mL) was stirred at 50°C for 3 h. After filtration the residue was carefully washed with ethanol. The combined organic solutions were evaporated and dried at $10^2$ Pa. The crude product was dissolved in 1:8 ethanol–water (15 mL) and treated with Dowex 50W X 2 ($H^+$ form, 2 g) for 30 min. The resin was removed by filtration and washed with 1:8 ethanol–water. From the combined solutions after solvent removal (rotavapor and lyophilisation) and FC ($CHCl_3$–MeOH 5:1) **29b** (42 mg, 64%) was obtained as colourless oil. IR (KBr): 3031, 3013, 2400, 1230, 1202, 777, 675 $cm^{-1}$. $^1H$ NMR (200 MHz, $CD_3OD$): sugar part: $\delta$=1.98 (s, 3H, $CH_3CO$), 2.01 (s, 3H, $CH_3CO$), 2.06 (s, 6H, 2×$CH_3CO$), 3.87–4.39 (3H, 5-H, $CH_2$-6), 4.90 (ddd, 1H, 2-H, $J_{2,3}$=10.4 Hz, $J_{2,1}$=2.5 Hz, further coupling with 2.2 Hz), 5.11 (dd, 1H, 4-H, $J_{4,3}$=9.8 Hz, $J_{4,5}$=9.8 Hz), 5.47 (dd, 1H, 3-H, $J_{3,2}$=9.9 Hz, $J_{3,4}$=9.9 Hz), 5.69 (dd, 1H, 1-H, $J_{1,2}$=3.3 Hz, $J_{1,P}$=7.4 Hz); (2*R*)-2-methoxycarbonyl-2-tetradecyl-ethoxy part: $\delta$=0.89 (t, 3H, $CH_3$-16, *J*=6.6 Hz), 1.09–1.39 (s, 24H, $CH_2$-4–$CH_2$-16), 1.45–1.64 (2H, CH–C$H_2$–O), 2.67–2.80 (1H, C*H*–$CH_2$–O), 3.69 (s, 3H, O$CH_3$), 3.87–4.39 (2H, $CH_2$-3). $^{13}C$ NMR (HMQC, 100.6 MHz, $CD_3OD$): sugar part: $\delta$=20.20, 20.34 (4×C$H_3$CO), 62.45 (C-6), 69.08 (C-4), 69.36 (C-5), 70.80 (C-3), 71.53 (C-2), 93.15 (C-1), 170.78, 171.13, 171.25, 171.95 (4×$CH_3$*C*O); (2*R*)-2-methoxycarbonyl-2-tetradecyl-ethoxy part: $\delta$=14.07 ($CH_3$-16), 23.35, 27.83, 29.31, 30.10, 30.18, 30.24, 30.32, 30.38, 30.42, 32.69 ($CH_2$-4–$CH_2$-16), 47.38 (*C*H–$CH_2$–O), 51.89 (O$CH_3$), 67.11 (C-3), 175.85 (C-1). $^{31}P$ NMR (81 MHz, $CDCl_3$): $\delta$=−4.25. $C_{32}H_{55}O_{15}P$ (710.75, 710.32), ESI MS: *m*/*z*=709.31951, calcd for $C_{33}H_{55}O_{15}P$ $[M-H]^-$: 709.32058.

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