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A common approach to the total synthesis of L-*arabino*-, L-*ribo*-C_{18}-phytosphingosines, *ent*-2-*epi*-jaspine B and 3-*epi*-jaspine B from D-mannose

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ABSTRACT

A common strategy for the total syntheses of the protected L-*arabino*- and L-*ribo*-C_{18}-phytosphingosine (**8** and **9**, respectively), HCl salts of *ent*-2-*epi*-jaspine B (*ent*-**6**) and 3-*epi*-jaspine B (**7**) with efficient use of both flexible building blocks **26** and **27** was achieved. The key step of this approach was [3,3]-sigmatropic rearrangement of allylic trichloroacetimidate **21** and thiocyanate **22**, which were derived from the known 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose **18** as the source of chirality. The side chain functionality was installed utilizing a Wittig reaction.

1. Introduction

Sphingolipids, a conspicuous class of natural products including sphingomyelins, cerebrosides, more complex glycosphingolipids and phytoceramides are essential building blocks of eukaryotic cell membranes, which largely reside at the cell surface. Their biological roles are complex and very often closely linked to each other.[1] Their ability to regulate many biological processes[1] has led to a desire to develop effective synthetic methods for the construction of novel sphingolipid derivatives as promising therapeutic agents.[2] Generally, one of the crucial factors for the successful synthesis of both natural sphingolipids and their related unnatural analogues, is primarily the construction of the convenient sphingoid bases[3] representing the principal structural backbone of the aforementioned molecules. Among the sphingoid bases with long aliphatic chains containing 2-amino-1,3-diol or a 2-amino-1,3,4-triol functionality, phytosphingosines[3b,d] (Fig. 1) occupy a conspicuous position due to the biological importance of D-*ribo*-phytosphingosine (**1**), the most abundant member of phytosphingosine family.[3b,c] Apart from the open chain forms, phytosphingosines also possesses cyclic anhydro structures. One such naturally occurring anhydrophytosphingosine molecule is jaspine B (also known as pachastrissamine, **5**) that has been isolated independently from two natural sources.[4] This marine sponge product has been reported to have a significant cytotoxicity against several cancer cell lines with IC_{50} values in the submicromolar range.[4,5a] Moreover, Fujii and coworkers revealed that **5** and its diastereoisomers inhibit sphingosine kinases (SphKs) and atypical protein kinase C.[5b] Because of these interesting functions as well as the rich structural features (three contiguous stereogenic centres) of **1** and **5**, there has been an enormous interest in the preparation of both above-mentioned structures and their diastereoisomers (Fig. 1).[3b,d,5–8] One of the best starting points for such endeavours are carbohydrates, as they are inexpensive, readily available and afford at least two of three desired stereogenic centres. Recently we developed a strategy for the synthesis of D-*ribo*-C_{18}-phytosphingosine (**1**), its C_{20}-analogue together with their C-2 epimers, in which an amino function was introduced by a [3,3]-sigmatropic rearrangement on the carbon that originally comes from the anomeric position of D-ribose.[6f,r] In the present work, we demonstrate that our described method of the phytosphingosine construction[6f,r] has a more general utility and can also be useful for the stereoselective synthesis of the other aminopolyol species commencing from the appropriate monosaccharide templates. Based on this concept, we herein report the total synthesis of **8**, **9**, *ent*-**6**·**HCl** and **7**·**HCl** from D-mannose (more convenient D-lyxose is too expensive).

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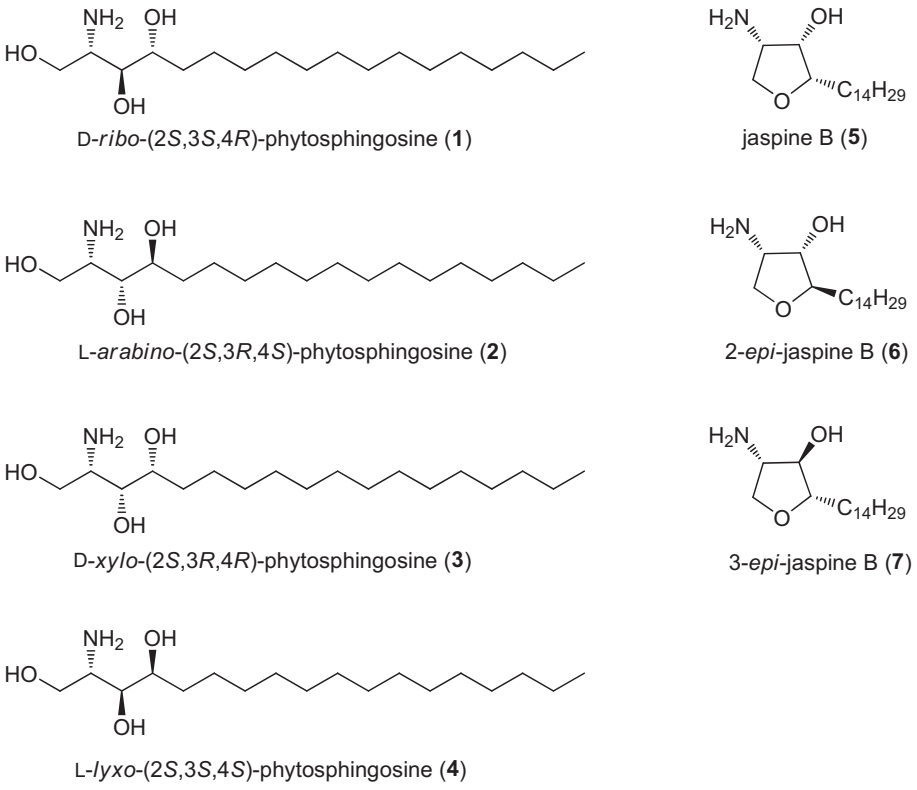


Fig. 1. D-*ribo*-Phytosphingosine (**1**), jaspine B (**5**) and their diastereoisomers.

2. Results and discussion

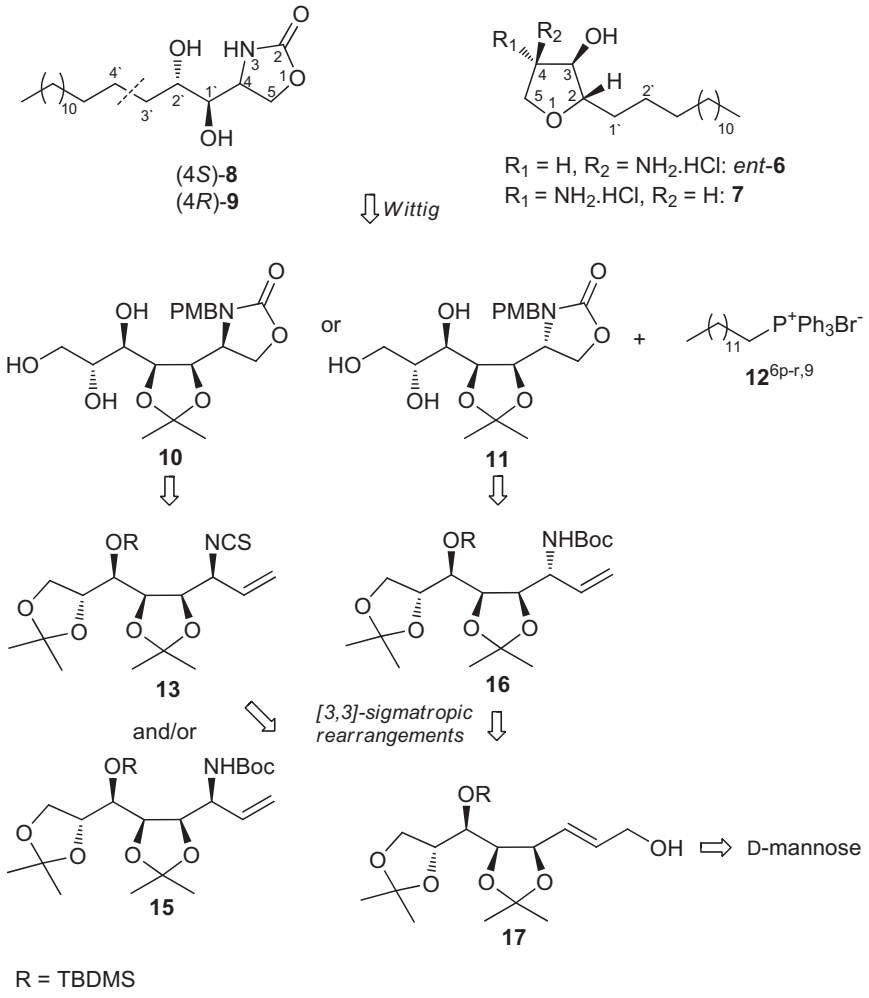
The retrosynthetic analysis of **8**, **9**, *ent*-**6**·**HCl**, **7**·**HCl** is illustrated in Scheme 1. For our final molecules, disconnection of $C_{3'}$–$C_{4'}$ bond (Wittig reaction) led to the highly functionalized oxazolidinones (**10** and **11**, respectively) with all requisite stereogenic centres and the known phosphonium salt **12**.[6p–r,9] Compound **10** could be produced from isothiocyanate **13** and/or carbamate **15**. Further, we planned to generate the second polar 'head' **11** from **16** as a major diastereoisomer. Derivatives **13**, **15** and **16** would be derived from [3,3]-sigmatropic rearrangements of the chiral allylic substrates, which were envisioned as arising from the common alcohol **17**. For the preparation of **17**, D-mannose served as the starting material.

As shown in Scheme 2, our synthesis commenced with the gram-scale preparation of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose **18**[10] from the commercially available D-mannose. Its subsequent Wittig olefination ($Ph_3P{=}CHCO_2Et$, CH_2Cl_2, benzoic acid, reflux) followed by chromatographic separation of the products, provided a mixture of α,β-unsaturated esters (*E*)-**19**[11] and (*Z*)-**19** (*E*/*Z*=10.5:1, as determined by ^{1}H NMR spectroscopy) in 90% and 8% isolated yields, respectively (Scheme 2). ^{1}H NMR coupling constant analysis of the vinylic protons for the major geometric isomer **19** assigned the (*E*)-configuration of the double bond ($J_{3,2}$=15.7 Hz), while analysis of the minor derivative confirmed a (*Z*)-relationship between olefinic protons ($J_{3,2}$=11.6 Hz).

To continue the synthesis, the secondary hydroxy group in (*E*)-**19** was protected as a *tert*-butyldimethylsilyl ether (TBDMSCl, imidazole, DMF) to give **20** in 98% yield. The ester functionality in **20** was reduced using diisobutylaluminum hydride in CH_2Cl_2 to furnish the corresponding allylic alcohol **17** (97%, Scheme 2), which was then converted into the required aza-Claisen substrates (compounds **21** and **22**) for the key rearrangement processes. Thus, its treatment with trichloroacetonitrile and DBU provided imidate **21** in excellent 98% yield after flash chromatography. On the other hand, a two-step sequence, involving mesylation of **17** followed by nucleophilic substitution with KSCN, afforded the desired thiocyanate **22** (90%).

With both trichloroacetimidate **21** and thiocyanate **22** in hand, we were now in a position to explore the key rearrangement reactions. The thermal Overman rearrangement[12] of **21**, which was carried out in *o*-xylene in the presence of K_2CO_3[13] in a sealed tube, afforded the rearranged products **23a** and **23b** as a barely separable mixture of diastereoisomers (**23a**/**23b**≈1:2) in a maximum yield of about 30% (Table 1, entries 2 and 4). The low yield was most likely due to decomposition of **21** at high temperatures and longer reaction times. On the other hand, the use of microwave heating[6f,r,14] led to significant shortening of the reaction times (4 or 10 times, see Table 1, entries 1 and 3) and very good isolated yields of the rearranged products compared to the thermally driven reaction. Further, it has been reported that the Overman rearrangement proceeds effectively in the presence of Hg(II), Pd(II), Pt(II), Pt(IV), Au(I) and Au(III) catalysts and allows the reaction to be carried out at room temperature or lower.[15] However, the attempted $PdCl_2(CH_3CN)_2$ catalyzed rearrangement of **21** resulted in failure; the successive consumption of the starting trichloroacetimidate **21** was judged by TLC, but unidentified by-products were generated in the reaction mixture. We reason that this failure might be due to the sensitivity of the terminal isopropylidene and trichloroacetiminoyl moieties to the Lewis acidity of Pd(II).

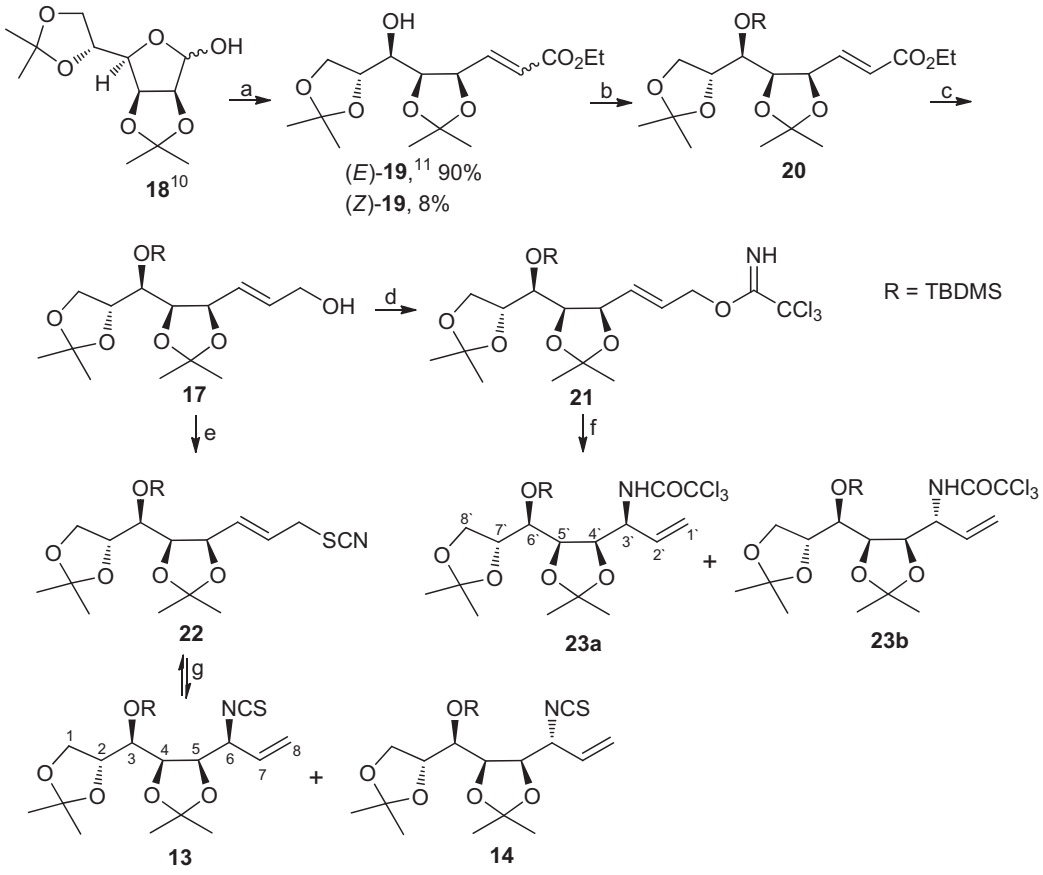
In order to rationalize the observed stereoselectivity in the Overman rearrangement of imidate **21**, high-level density functional theory (DFT) calculations, including electron correlation effects, were carried out. A thorough conformational search was performed on all transition states, whereas only the lowest energy conformers are discussed here. The potential energy surface scans were used to explore the conformational space of transition states TS1–TS4 with the constrained transition bond lengths C–N and C–O. The systematic conformational search with rotation around the single bonds



Scheme 1. Retrosynthetic analysis.

C5–C6, C6–C7 and C6–OSi was performed using semiempirical PM3 methodology. The conformers within a 4 kcal/mol energy range were then optimized using B3LYP/6-31G(d)[16] for a more accurate description of the conformer distribution. The low energy conformers of the transition states were later fully optimized using the same level of theory. It is worth noting that the bulky 4,5-*O*- and 7,8-*O*-isopropylidene moieties and *tert*-butyldimethylsilyloxy group at the carbon C6 cause low conformational flexibility of the backbone of the transition states. Dihedral angles C4–C5–C6–C7 of the minimized structures are very similar (φTS1=76.2, φTS2=76.3, φTS3=81.1, φTS4=81.2) and side chains are structurally conformed. Coordinates of the stationary points, TS1.mol, TS2.mol, TS3.mol, TS4.mol are attached as supplementary data. The potential energy surface scans were used to explore the conformational space of the reactant and products (imidate and amides) with the later full optimization using the same level of theory, but we focused only on the energy differences between TSs as crucial for explanation of the observed diastereoselectivity. Geometries of the transition states were optimized using B3LYP/6-31G(d) with the Gaussian 03 programme.[16] The nature of the vacuum B3LYP transition states was verified with frequency calculations, yielding only one large imaginary frequency (TS1=−391.45 cm^{-1}, TS2=−411.33 cm^{-1}, TS3=−403.34 cm^{-1}, TS4=−436.32 cm^{-1}). Harmonic zero-point energy corrections at B3LYP/6-31G(d) obtained from the frequency calculations of the vacuum transition states were applied to the transition-state energies. Single-point energies were computed by the B3LYP density functional method and the cc-pvTZ basis set. The solvent effect was taken into account via a single-point calculation in a dielectric continuum representing *o*-xylene as the solvent. A standard PCM solvation model was applied as implemented in Gaussian 03.[16] The Overman rearrangement of **21** occurs via transition states TS1, TS2, TS3 and TS4, with relative free energies 2.35, 0, 2.93 and 1.90 kcal/mol (Figs. 2 and 3). The process is concerted but asynchronous, and the calculated geometries are in good agreement with the results of Houk and co-workers.[17] From the calculations, for the pathway **21**→TS2→**23b**, the activation energy was found to be 1.90 kcal/mol lower than for the pathway **21**→TS4→**23a**. Thus, the predicted diastereomeric ratio of **23a**/**23b** at 170 °C was 11:89. These results are in relatively good agreement with the experimental data (**23a**/**23b**≈33:67) with the correct prediction of amide **23b** as the predominant diastereoisomer. These results provide an initial step in understanding the rearrangement and the observed diastereoselectivity seems to depend on many factors that are still to be explored.

The allylic thiocyanate **22** was rearranged in *n*-heptane using both the conventional thermal conditions and microwave heating providing the corresponding isothiocyanates **13** and **14** as a separable mixture of diastereoisomers in modest yields (Table 2). It should be noted that during these experiments we recovered the starting thiocyanate **22** in approximately 39–47% yields after chromatographic separation, which could be reused to provide additional amounts of **13** and **14**. The prolonged heating turned out



Scheme 2. Reagents and conditions: (a) $Ph_3P{=}CHCO_2Et$, CH_2Cl_2, benzoic acid, reflux, 98%; (b) TBDMSCl, imidazole, DMF, rt, 98%; (c) DIBAL-H, CH_2Cl_2, −15 °C, 97%; (d) CCl_3CN, DBU, CH_2Cl_2, 0 °C→rt, 98%; (e) (i) MsCl, Et_3N, CH_2Cl_2, 0 °C→rt; (ii) KSCN, CH_3CN, rt, 90% over two-steps; (f) Table 1; (g) Table 2.

Table 1
Overman rearrangement of imidate **21**

Entry	Imidate	Conditions[a]	Time (h)	Ratio[b] **23a**/**23b**	Yield[c] (%)
1	**21**	MW, 150 °C	5	35:65	77
2	**21**	Δ, 150 °C	20	35:65	25
3	**21**	MW, 170 °C	1	33:67	81
4	**21**	Δ, 170 °C	10	38:62	30

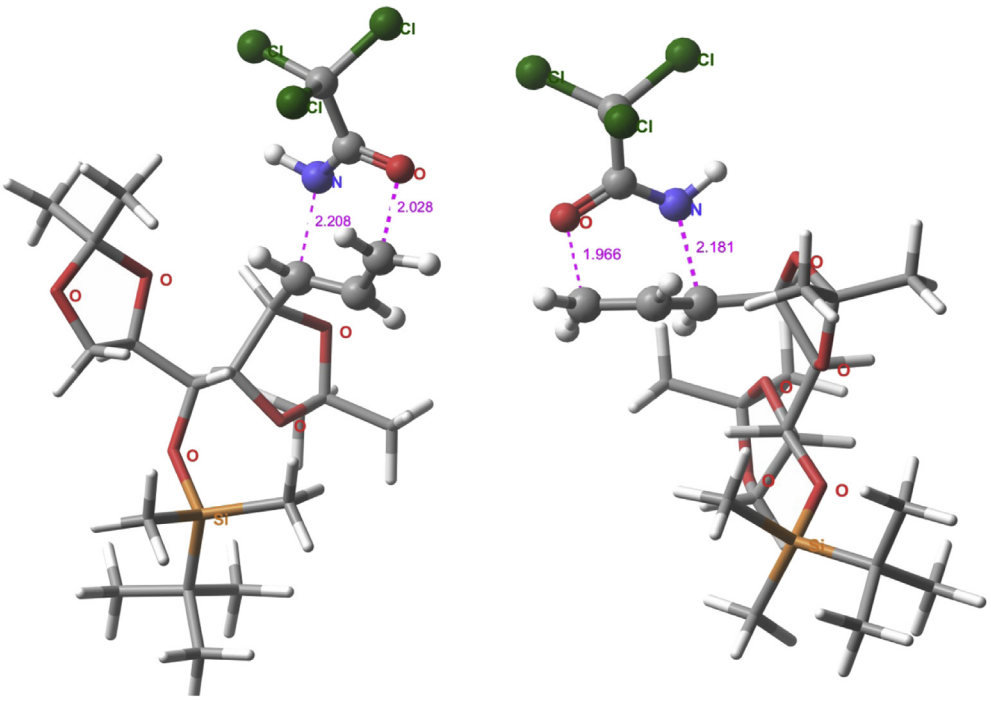
[a] In *o*-xylene, in the presence of K_2CO_3.
[b] Ratio in the crude reaction mixtures determined by ^1H NMR.
[c] Isolated combined yields.

to be ineffective; it had practically no influence on the overall yield of the desired isothiocyanates **13** and **14**. In addition, our initial attempts to realize the rearrangement of **22** in *o*-xylene proved problematic: the reaction rate was very slow and the equilibrium was considerably shifted to the starting material **22**. However, the aza-Claisen rearrangement of **22** was found to show stereoselectivities better to those observed for the Overman rearrangement of **21** (Table 1).

The stereochemistry of the newly constructed stereogenic centre in all rearranged products was confirmed by the following sequences. As shown in Scheme 3, deprotection of the trichloroacetyl moiety in a mixture of trichloroacetamides **23a** and **23b** (**23a**/**23b**≈1:2, prepared from **21**) under basic conditions ($NaOH/H_2O$/EtOH)[15b] and immediate Boc_2O treatment of the liberated amines afforded, after chromatographic separation, the corresponding *N*-Boc derivatives **15** and **16** in 32% and 60% isolated yields, respectively; their structures were assigned by NMR spectroscopic analysis including 2D experiments. Ozonolysis of both compounds, followed by $NaBH_4$ reduction, successfully furnished alcohols **24** (84%) and **25** (75%), which were further converted into oxazolidinones **26** and **27** in 86% and 97% yields, respectively, by NaH mediated intramolecular cyclization (Scheme 3). Compound **26** afforded single crystals suitable for X-ray measurements. As seen in Fig. 4, the crystallographic analysis clearly showed that the newly installed stereocentre in **26** bearing the amino functionality is (*S*)-configured. Consequently, the minor diastereoisomer of the Overman rearrangement **23a** must possess the same stereochemistry at the requisite asymmetric centre. To establish the configuration at C-6 (see numbering in Scheme 2) in both isomers **13** and **14**, the chemical correlation of the major isothiocyanate **13** to common oxazolidinone derivative **26** was executed (Scheme 3).

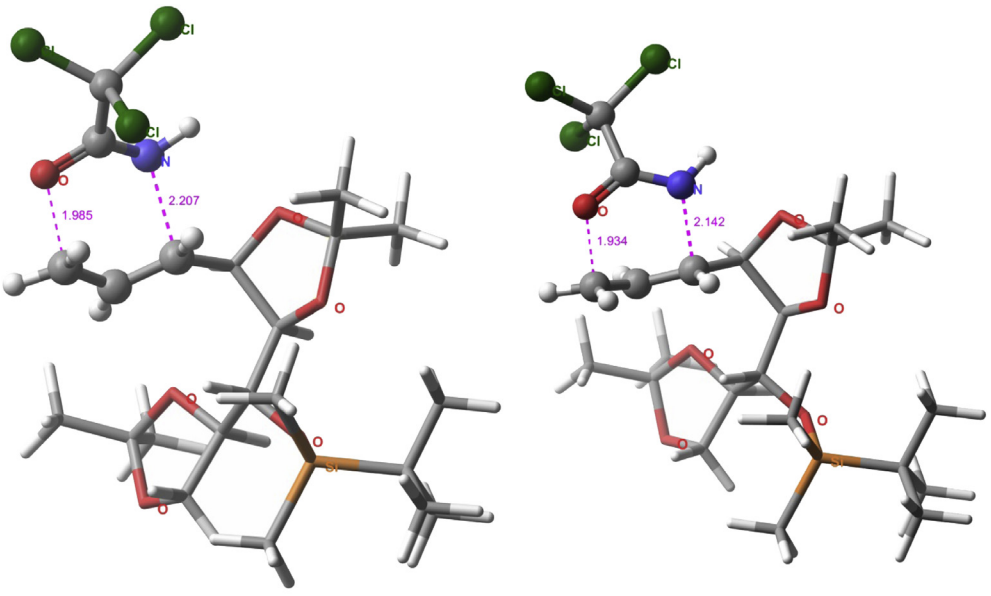
For this purpose, isothiocyanate **13** was treated with sodium methoxide in CH_3OH to generate the corresponding thiocarbamate (52%), which was immediately reacted with mesitylnitrile oxide[18] to provide the desired product **28** in 75% yield (Scheme 3). The lower yield of the aforementioned thiourethane was due to the use of harsh basic reaction conditions, which presumably resulted in the formation of unidentified by-products. Subsequent ozonolysis of the terminal double bond in **28** (O_3, −78 °C), followed by treatment with $NaBH_4$, afforded the primary alcohol **29** (80%). Base-induced (NaH) ring-closure of **29** furnished oxazolidinone **26** in 92% yield (Scheme 3). The spectroscopic data (^1H and ^{13}C NMR) together with $[\alpha]_D$ value for the obtained cyclic carbamate were identical with those for compound **26** previously prepared from **23a**. These findings revealed that major diastereoisomer of the aza-Claisen rearrangement, product **13**, has (6*S*)-configuration.

Having established the synthetic route to the polar fragments **26** and **27** possessing the requisite functionalities and the correct stereochemistries, our next efforts led to the completion of the total synthesis of **8**, **9**, *ent*-**6**·**HCl** and **7**·**HCl** as shown in Scheme 4. After



TS1, (2.35) TS2, (0)

Fig. 2. Transition structures for the rearrangement **21**→[TS1]/[TS2]→**23b**. Relative energies of transition states (in kcal/mol) and bond distances (in Å) are shown.



TS3, (2.93) TS4, (1.90)

Fig. 3. Transition structures for the rearrangement **21**→[TS3]/[TS4]→**23a**. Relative energies of transition states (in kcal/mol) and bond distances (in Å) are shown.

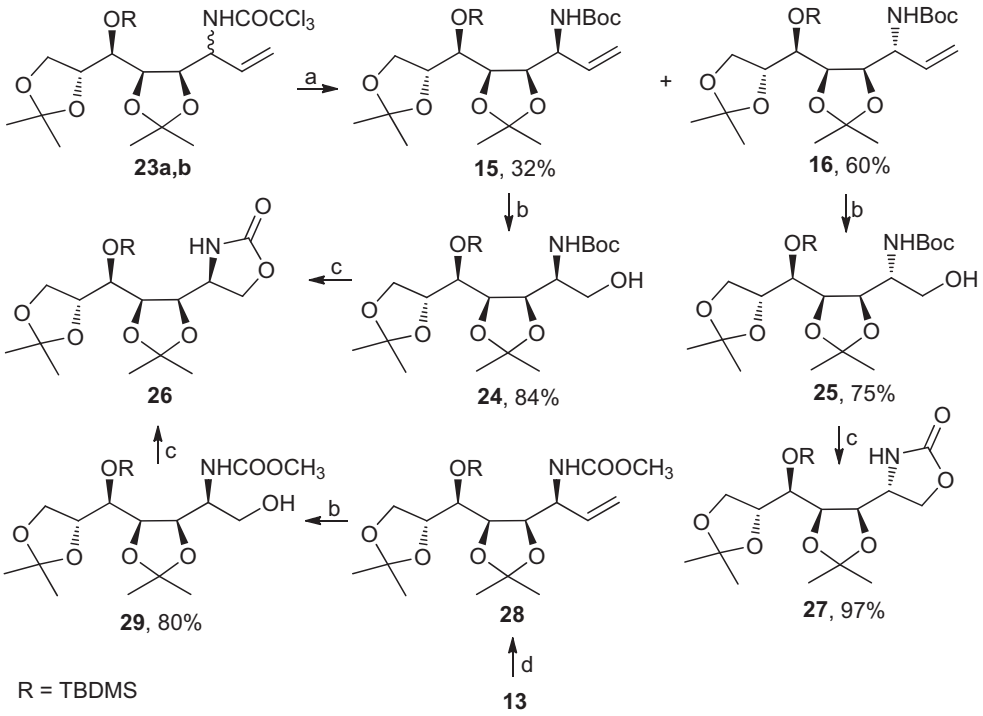
p-methoxybenzyl protection (PMBCl, NaH, TBAI) of the oxazolidinone ring in **26** and **27**, the *tert*-butyldimethylsilyl group of the resulting products **30** (88%) and **31** (88%) was removed under standard conditions (TBAF, THF) to afford derivatives **32** and **33** in 93% and 98% isolated yields, respectively. The terminal isopropylidene ring in **32** and **33** was selectively cleaved by acid hydrolysis (AcOH/H_2O) to produce the requisite triol intermediates **10** (90%) and **11** (60%). The lower yield for **11** was due to partial formation of the pentol derivative **34** (19%). Applying other acids, such as *p*-toulenesulfonic acid, pyridinium *p*-toluenesulfonate, $CeCl_3$/$(COOH)_2$[19] either generated greater amounts of the undesirable polyol product, or the starting material was recovered unchanged. Oxidative fragmentation of **10** and **11** with $NaIO_4$ furnished the corresponding aldehydes, which were used immediately in the Wittig olefination with triphenyl(tridecyl)phosphonium bromide 12,[6p–r,9] employing freshly prepared LHMDS[20] as a base. This process resulted in the formation of barely separable mixtures of olefins **35** (*Z*/*E*=9:1) and **36** (*Z*/*E*=12:1 ratio, as determined by ^{1}H NMR spectroscopy) in 74% and 71% isolated yields (over two-steps), respectively (Scheme 4). Small amounts of the mixtures of **35** and **36**

Table 2
[3,3]-Sigmatropic rearrangement of thiocyanate **22**

Entry	Thiocyanate	Conditions[a]	Time (h)	Ratio[b] **13**/**14**	Yield[c] (%)
1	**22**	Δ, 90 °C	15	80:20	53
2	**22**	Δ, 90 °C	25	82:18	53
3	**22**	MW, 90 °C	5	81:19	49
4	**22**	MW, 90 °C	10	77:23	56
5	**22**	MW, 120 °C	5	77:23	51
6	**22**	MW, 120 °C	10	77:23	50
7	**22**	MW, 150 °C	2	75:25	47
8	**22**	MW, 150 °C	4	78:22	51
9	**22**	MW, 170 °C	2	75:25	51
10	**22**	MW, 170 °C	4	78:22	51

[a] In *n*-heptane.
[b] Ratio in the crude reaction mixtures determined by ^{1}H NMR.
[c] Isolated combined yields.

were separated by column chromatography to give both geometrical isomers **35a** and **35b** in pure form. In the case of a mixture of **36** only (*Z*)-**36a** was obtained as an analytical sample. Their structures including geometries of the double bonds were assigned by NMR spectroscopic analysis. For example, the (*E*)-configuration of the minor **35b** and (*Z*)-configuration of the major **36a** were confirmed by the coupling constants of the vinylic protons (J_{trans}=15.2 Hz and J_{cis}=10.9 Hz, respectively). The subsequent catalytic hydrogenation (H_2, 10% Pd/C, EtOH) of **35** and **36** resulted in formation of the saturated derivatives **37** (94%) and **38** (89%). Next, the *p*-methoxybenzyl and isopropylidene protecting groups of **37** and **38** were simultaneously removed by treatment with CAN in CH_3CN/H_2O to give protected L-*arabino*- and L-*ribo*-phytos-



Scheme 3. Reagents and conditions: (a) (i) NaOH, EtOH/H_2O, rt; (ii) Boc_2O, Et_3N, CH_2Cl_2, rt; (b) (i) O_3, CH_3OH/CH_2Cl_2, −78 °C; (ii) $NaBH_4$, −78 °C→rt; (c) NaH, THF, 0 °C→rt, 86% from **24**, 92% from **29**; (d) (i) CH_3ONa, CH_3OH, 0 °C→rt, 52%; (ii) mesitylnitrile oxide, CH_3CN, rt, 75%.

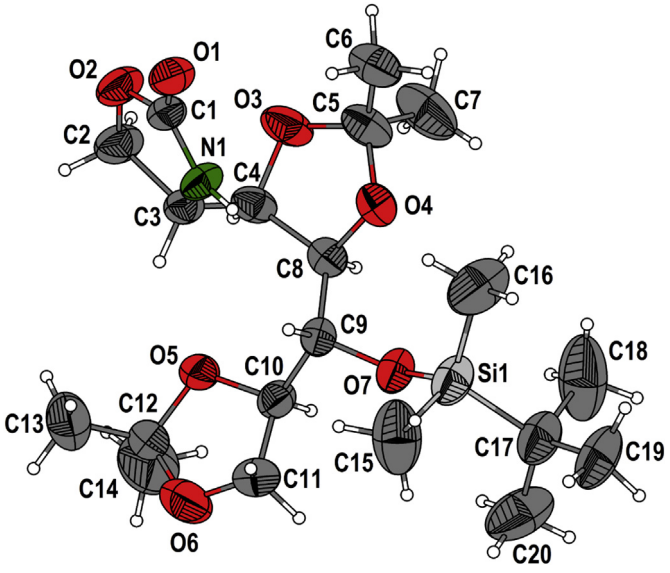
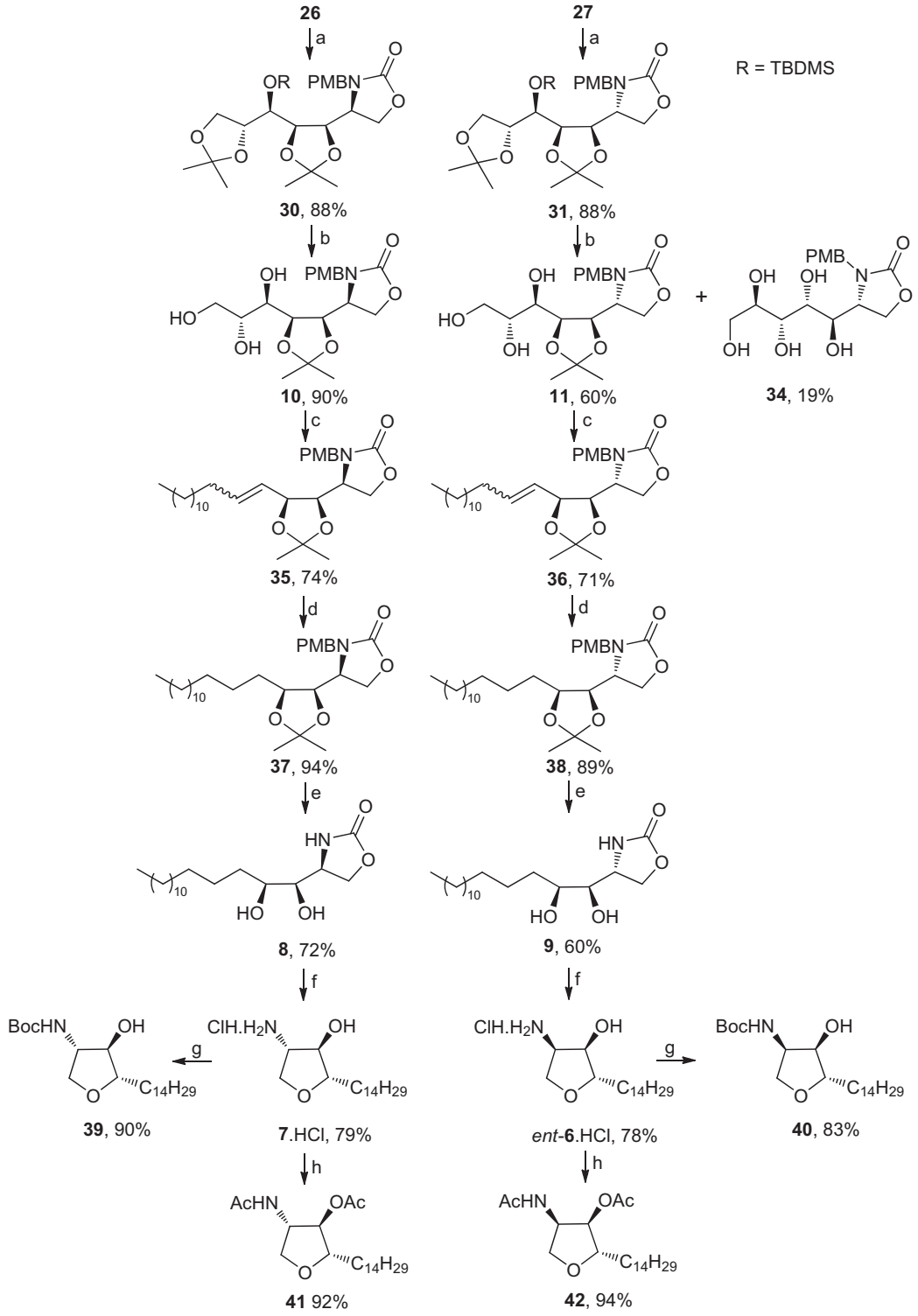


Fig. 4. ORTEP structure of **26** showing the crystallographic numbering.

phingosine **8** and **9** in 72% and 60%, respectively. Their exposure to 6 M HCl unexpectedly afforded *ent*-2-*epi*-jaspine B (**6**) (78%) and 3-*epi*-jaspine B (**7**) (79%) as their corresponding HCl salts (Scheme 4).

As additional confirmation of the anhydro structure, we converted these aforementioned HCl salts of **7** and *ent*-**6** to the corresponding *N*-Boc derivatives **39**[5a,8e] (90%) and **40**[5b] (83%) by treatment with Boc_2O and Et_3N in dry THF. The spectroscopic data and optical rotation of **39** and **40** were in good agreement with those reported previously. Moreover, the NMR spectra of **40** matched the known values of *ent*-**40**.[5a,21] Finally, exposure of **7**·**HCl** and *ent*-**6**·**HCl** to acetic anhydride in pyridine and in the presence of DMAP resulted in the formation of acetyl derivatives **41**[8e] and **42** in 92% and 94% yields, respectively (Scheme 4). The ^{1}H NMR spectrum of **41** showed the small differences from Rao's product.[8e] Its ^{13}C NMR spectroscopic data were in excellent agreement with those reported,[8e] but the optical rotation {$[\alpha]_D^{26}$ −11.9 (*c* 0.21, $CHCl_3$)} was opposite in sign to that quoted in lit.[8e] {$[\alpha]_D^{25}$ +11.2 (*c* 1.1, $CHCl_3$)}. The spectroscopic properties and magnitude of $[\alpha]_D$ for compound **42** were in good concordance with those reported for *ent*-**42**.[21] As seen in Fig. 5, NOE experiments of **7**·**HCl** and **41** showed trans-relationship between protons H-2 and H-3 and also between H-3 and H-4 protons on the tetrahydrofuran core. On the other hand,



Scheme 4. Reagents and conditions: (a) PMBCl, NaH, DMF, TBAI, 0 °C→rt; (b) (i) TBAF, THF, 0 °C→rt, **32**, 93%, **33**, 98%; (ii) $AcOH/H_2O$, rt; (c) (i) $NaIO_4$, CH_3OH/H_2O, rt; (ii) **12**,[6p–r,9] LHMDS, THF, rt; (d) 10% Pd/C, EtOH, rt; (e) CAN, CH_3CN/H_2O, rt; (f) 6 M HCl, reflux; (g) Boc_2O, Et_3N, THF, rt; (h) Ac_2O, pyridine, DMAP, rt.

enhancements between H-3 and H-4 protons in the case of derivative **42** proved their cis orientation on the aforementioned ring. Because of the overlap of the proton signals (H-2, H-4, H-5, see Experimental section) in *ent*-**6**·**HCl** in CD_3OD solution, it was not possible to determine their corresponding enhancements. Results of these NOE analyses would serve as additional confirmation of the stereochemistry of the newly incorporated stereocentre.

3. Conclusions

We have accomplished the total synthesis of the protected L-*arabino*- and L-*ribo*-phytosphingosine (**8** and **9**, respectively) and the HCl salts of *ent*-2-*epi*-jaspine B (**6**) and 3-*epi*-jaspine B (**7**) starting from D-mannose. The key transformation of our strategy was the implementation of an amino-bearing asymmetric centre

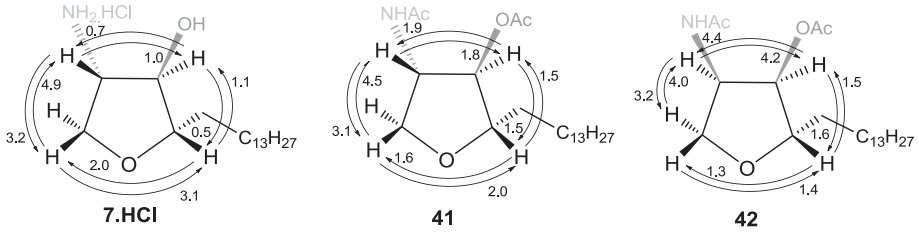


Fig. 5. Some selected NOE enhancements for **7**·**HCl**, **41** and **42**.

using [3,3]-heterosigmatropic rearrangements. In order to rationalize the stereochemical outcome of these aforementioned processes, DFT calculations were carried out. Importantly, our approach involving the aza-Claisen rearrangements on carbohydrate scaffolds, which established the required stereogenic centre with nitrogen, followed by further functional group manipulations, has the potential to be useful for the production of various phytosphingosines in enantiomerically pure forms.

4. Experimental

4.1. General methods

All commercial reagents were used in the highest available purity from Aldrich, Fluka, Merck or Acros Organics without further purification. Solvents were dried and purified before use according to standard procedures. For flash column chromatography on silica gel, Kieselgel 60 (0.040–0.063 mm, 230–400 mesh, Merck) was used. Solvents for flash chromatography (hexane, ethyl acetate, methanol, dichloromethane) were distilled before use. Thin layer chromatography was run on Merck silica gel 60 F_{254} analytical plates; detection was carried out with either ultraviolet light (254 nm), or spraying with a solution of phosphomolybdic acid, a basic potassium permanganate solution, or a solution of concentrated H_2SO_4, with subsequent heating. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$, CD_3OD and C_6D_6 on a Varian Mercury Plus 400 FT NMR (400.13 MHz for ^{1}H and 100.6 MHz for ^{13}C) or on a Varian Premium COMPACT 600 (599.87 MHz for ^{1}H and 150.84 MHz for ^{13}C) spectrometer using TMS as internal reference. For ^{1}H, δ are given in parts per million (ppm) relative to TMS (δ=0.0), CD_3OD (δ=4.84) and C_6D_6 (δ=7.15) and for ^{13}C relative to $CDCl_3$ (δ=77.0), CD_3OD (δ=49.05) and C_6D_6 (δ=128.02). The multiplicity of the ^{13}C NMR signals concerning the ^{13}C–^{1}H coupling was determined by the DEPT method. Chemical shifts (in ppm) and coupling constants (in Hz) were obtained by first-order analysis; assignments were derived from COSY and H/C correlation spectra. Infrared (IR) spectra were measured with a Nicolet 6700 FT-IR spectrometer and expressed in ν values (cm^{-1}). Optical rotations were measured on a P-2000 Jasco polarimeter and reported as follows: $[\alpha]_D$ (c in grams per 100 mL, solvent). Melting points were recorded on a Kofler hot block, and are uncorrected. Microwave reactions were carried out on the focused microwave system (CEM Discover). The temperature content of the vessel was monitored using a calibrated infrared sensor mounted under the vessel. At the end of all reactions the contents of vessel were cooled rapidly using a stream of compressed air. Small quantities of reagents (μL) were measured with appropriate syringes (Hamilton). All reactions were performed under an atmosphere of nitrogen, unless otherwise noted.

4.2. Ethyl (4*R*,5*S*,6*R*,7*R*,2*E*)-6-hydroxy-4,5:7,8-bis(isopropylidenedioxy)oct-2-enoate [(*E*)-19] and ethyl (4*R*,5*S*,6*R*,7*R*,2*Z*)-6-hydroxy-4,5:7,8-bis(isopropylidenedioxy)oct-2-enoate [(*Z*)-19]

To a solution of the known **18**[10] (12.0 g, 46.1 mmol) in dry CH_2Cl_2 (310 mL) were successively added benzoic acid (0.57 g, 4.66 mmol) and the stabilized ylide, $Ph_3P{=}CHCO_2Et$ (28.9 g, 83.0 mmol), and the resulting mixture was stirred and heated at 46 °C for 26 h. After the starting material was completely consumed (judged by TLC), the reaction was stopped and allowed to cool to room temperature. The solvent was evaporated, the obtained residue was diluted with hexane (50 mL), and the insoluble materials were removed by filtration. After evaporation of the solvent under reduced pressure, the chromatography of the residue on silica gel (hexane/ethyl acetate, 5:1) gave 13.7 g (90%) of (*E*)-**19**[11] and 1.22 g (8%) of (*Z*)-**19**.

Compound (*E*)-**19**: colourless oil; $[\alpha]_D^{25}$ +12.6 (c 0.66, $CHCl_3$); IR (neat) ν_{max} 3497, 2985, 2936, 1717, 1659, 1370, 1253, 1212, 1159, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (t, 3H, J=7.1 Hz, CH_3), 1.35 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 2.17 (d, 1H, $J_{6,OH}$=7.7 Hz, OH), 3.42–3.47 (m, 1H, H-6), 3.96–4.03 (m, 2H, H-7, H-8), 4.08–4.13 (m, 1H, H-8), 4.21 (q, 2H, J=7.1 Hz, CH_2), 4.46 (dd, 1H, $J_{5,4}$=7.4 Hz, $J_{6,5}$=2.2 Hz, H-5), 4.83 (ddd, 1H, $J_{5,4}$=7.4 Hz, $J_{4,3}$=6.2 Hz, $J_{4,2}$=1.5 Hz, H-4), 6.10 (dd, 1H, $J_{3,2}$=15.7 Hz, $J_{4,2}$=1.5 Hz, H-2), 7.07 (dd, 1H, $J_{3,2}$=15.7 Hz, $J_{4,3}$=6.2 Hz, H-3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2 (CH_3), 24.7 (CH_3), 25.2 (CH_3), 26.7 (2× CH_3), 60.6 (CH_2), 67.2 (C-8), 70.5 (C-6), 76.1 (C-7), 76.6 (C-4), 77.3 (C-5), 109.3 (C_q), 109.5 (C_q), 123.6 (C-2), 143.2 (C-3), 165.7 (C=O). Anal. Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.10; H, 7.98.

Compound (*Z*)-**19**: mp 88–89 °C (recrystallized from *n*-hexane); $[\alpha]_D^{25}$ −125.3 (c 0.32, $CHCl_3$); IR (neat) ν_{max} 3524, 2984, 2937, 1712, 1644, 1371, 1190 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.29 (t, 3H, J=7.1 Hz, CH_3), 1.34 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 2.04 (d, 1H, $J_{6,OH}$=9.9 Hz, OH), 3.30–3.34 (m, 1H, H-6), 3.97–4.07 (m, 3H, H-7, 2× H-8), 4.16 (q, 2H, J=7.1 Hz, CH_2), 4.79–4.81 (m, 1H, H-5), 5.64 (ddd, 1H, $J_{5,4}$=8.1 Hz, $J_{4,3}$=6.4 Hz, $J_{4,2}$=1.8 Hz, H-4), 5.93 (dd, 1H, $J_{3,2}$=11.6 Hz, $J_{4,2}$=1.8 Hz, H-2), 6.52 (dd, 1H, $J_{3,2}$=11.6 Hz, $J_{4,3}$=6.4 Hz, H-3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2 (CH_3), 23.9 (CH_3), 25.3 (CH_3), 26.5 (CH_3), 26.8 (CH_3), 60.5 (CH_2), 66.6 (C-8), 69.8 (C-6), 75.3 (C-4), 76.3 (C-7), 77.3 (C-5), 108.7 (C_q), 109.3 (C_q), 120.3 (C-2), 148.2 (C-3), 165.8 (C=O). Anal. Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.22; H, 7.89.

4.3. Ethyl (4*R*,5*R*,6*R*,7*R*,2*E*)-6-[(*tert*-butyldimethylsilyl)oxy]-4,5:7,8-bis(isopropylidenedioxy)oct-2-enoate (20)

To a solution of (*E*)-**19** (13.7 g, 41.5 mmol) in dry DMF (27.5 mL) was added imidazole (5.65 g, 83.0 mmol) followed by *tert*-butyldimethylsilyl chloride (15.6 g, 103.5 mmol) and the resulting mixture was stirred at room temperature for 72 h. After this period, the mixture was partitioned between ice-water (275 mL) and Et_2O (275 mL), and the aqueous phase was extracted with another portion of Et_2O (275 mL). The combined organic layers were dried over Na_2SO_4, stripped of solvent, and the residue was subjected to flash chromatography on silica gel (hexane/ethyl acetate, 20:1) to afford 18.1 g (98%) of compound **20** as a colourless oil; $[\alpha]_D^{25}$ +61.5 (c 0.46, $CHCl_3$); IR (neat) ν_{max} 2930, 1722, 1656, 1381, 1250, 1152, 834 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 3H, CH_3), 0.09 (s, 3H, CH_3), 0.87 (s, 9H, 3× CH_3), 1.29 (t, 3H, J=7.1 Hz, CH_3), 1.34 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.72–3.83 (m, 2H, H-6, H-8), 3.94–3.99 (m, 1H, H-7), 4.09–4.13 (m, 2H, H-5, H-8), 4.20 (q, 2H, J=7.1 Hz, CH_2), 4.69–4.72 (m, 1H, H-4), 6.05 (dd, 1H,

$J_{3,2}$=15.6 Hz, $J_{4,2}$=1.5 Hz, H-2), 7.08 (dd, 1H, $J_{3,2}$=15.6 Hz, $J_{4,3}$=5.7 Hz, H-3); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.7 (CH_3), −3.9 (CH_3), 14.2 (CH_3), 18.4 (C_q), 25.4 (2× CH_3), 25.9 (3× CH_3), 26.2 (CH_3), 27.8 (CH_3), 60.4 (CH_2), 68.1 (C-8), 72.5 (C-6), 76.5 (C-4), 77.2 (C-7), 81.0 (C-5), 108.4 (C_q), 109.8 (C_q), 123.3 (C-2), 144.9 (C-3), 166.1 (C=O). Anal. Calcd for $C_{22}H_{40}O_7Si$: C, 59.43; H, 9.07. Found: C, 59.38; H, 9.13.

4.4. (4*R*,5*R*,6*R*,7*R*,2*E*)-6-[(*tert*-Butyldimethylsilyl)oxy]-4,5:7,8-bis(isopropylidenedioxy)oct-2-en-1-ol (17)

Diisobutylaluminum hydride (91.6 mL, 109.91 mmol, 1.2 M toluene solution) was added dropwise to a solution of **20** (18.1 g, 40.7 mmol) in dry CH_2Cl_2 (185 mL) that had been pre-cooled to −15 °C for 1 h. The resulting mixture was stirred at the same temperature for another 15 min, then quenched with CH_3OH (28 mL), and poured into a 30% solution of K/Na tartrate (610 mL). After stirring for 1 h at room temperature, the aqueous phase was extracted with CH_2Cl_2 (4×250 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 2:1) to furnish 15.9 g (97%) of compound **17** as a colourless oil; $[\alpha]_D^{25}$ +54.4 (*c* 0.18, $CHCl_3$); IR (neat) ν_{max} 2930, 2856, 1461, 1379, 1216, 1149, 1052, 834 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 0.19 (s, 3H, CH_3), 0.26 (s, 3H, CH_3), 1.02 (s, 9H, 3× CH_3), 1.27 (s, 6H, 2× CH_3), 1.41 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.82 (br s, 1H, OH), 3.83–3.95 (m, 5H, H-8, H-6, H-5, 2× H-1), 3.98–4.01 (m, 1H, H-8), 4.06–4.09 (m, 1H, H-7), 4.39–4.42 (m, 1H, H-4), 5.69 (dtd, 1H, $J_{3,2}$=15.3 Hz, $J_{2,1}$=4.9 Hz, $J_{2,1}$=4.9 Hz, $J_{4,2}$=0.6 Hz, H-2), 5.88 (ddt, 1H, $J_{3,2}$=15.3 Hz, $J_{4,3}$=7.9 Hz, $J_{3,1}$=1.6 Hz, $J_{3,1}$=1.6 Hz, H-3); ^{13}C NMR (100 MHz, C_6D_6): δ −4.2 (CH_3), −3.7 (CH_3), 18.8 (C_q), 25.5 (CH_3), 25.8 (CH_3), 26.3 (3× CH_3), 26.6 (CH_3), 28.4 (CH_3), 62.5 (C-1), 66.1 (C-8), 71.9 (C-7), 76.8 (C-6), 78.5 (C-4), 80.4 (C-5), 108.1 (C_q), 109.1 (C_q), 127.4 (C-3), 134.4 (C-2). Anal. Calcd for $C_{20}H_{38}O_6Si$: C, 59.67; H, 9.51. Found: C, 59.72; H, 9.47.

4.5. (4′*R*,5′*R*,6′*R*,7′*R*,2′*E*)-6′-[(*tert*-Butyldimethylsilyl)oxy]-4′,5′:7′,8′-bis(isopropylidenedioxy)oct-2′-en-1′-yl 2,2,2-trichloroacetimidate (21)

To a solution of **17** (13.5 g, 33.53 mmol) in dry CH_2Cl_2 (178 mL) that had been pre-cooled to 0 °C were successively added DBU (0.50 mL, 3.35 mmol) and trichloroacetonitrile (6.72 mL, 67.0 mmol). The resulting mixture was stirred for further 30 min at 0 °C and then for 20 min at room temperature. After evaporating of the solvent, the residue was flash-chromatographed through a short silica gel column (hexane/ethyl acetate, 3:1) to give 18 g (98%) of imidate **21** as a colourless oil; $[\alpha]_D^{25}$ +40.0 (*c* 0.32, $CHCl_3$); IR (neat) ν_{max} 2930, 2856, 1663, 1461, 1380, 1216, 1150, 1076, 833, 795 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 0.16 (s, 3H, CH_3), 0.23 (s, 3H, CH_3), 1.00 (s, 9H, 3× CH_3), 1.25 (s, 6H, 3× CH_3), 1.37 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 3.85–3.93 (m, 4H, H-5′, H-6′, 2× H-8′), 3.97–4.01 (m, 1H, H-7′), 4.41–4.44 (m, 1H, H-4′), 4.59–4.61 (m, 2H, 2× H-1′), 5.73 (dtd, 1H, $J_{3',2'}$=15.5 Hz, $J_{2',1'}$=5.4 Hz, $J_{2',1'}$=5.3 Hz, $J_{4',2'}$=0.8 Hz, H-2′), 5.98–6.04 (m, 1H, H-3′), 8.31 (br s, 1H, NH). ^{13}C NMR (100 MHz, C_6D_6): δ −4.2 (CH_3), −3.6 (CH_3), 18.7 (C_q), 25.6 (CH_3), 25.8 (CH_3), 26.3 (3× CH_3), 26.6 (CH_3), 28.3 (CH_3), 66.9 ($C_{8'}$), 68.6 ($C_{1'}$), 72.0 ($C_{7'}$), 77.1 ($C_{5'}$ or $C_{6'}$), 77.8 ($C_{4'}$), 80.7 ($C_{5'}$ or $C_{6'}$), 91.9 (CCl_3), 108.2 (C_q), 109.3 (C_q), 127.1 ($C_{2'}$), 131.8 ($C_{3'}$), 162.2 (C=NH). Anal. Calcd for $C_{22}H_{38}Cl_3NO_6Si$: C, 48.31; H, 7.00; N, 2.56. Found: C, 48.36; H, 7.05; N, 2.50.

4.6. *tert*-Butyldimethyl{[(2*R*,3*R*,4*R*,5*R*,6*E*)-1,2:4,5-bis(isopropylidenedioxy)-8-thiocyanatooct-6-en-3-yl]oxy}silane (22)

Et_3N (1.68 mL, 11.95 mmol) was added to a solution of **17** (2.40 g, 5.96 mmol) in dry CH_2Cl_2 (52 mL) and after cooling to 0 °C, methanesulfonyl chloride (0.93 mL, 12.0 mmol) was added dropwise. The resulting mixture was stirred for a further 15 min at 0 °C and then for 25 min at room temperature. After evaporating of the solvent, the residue was diluted with Et_2O (20 mL), the salts were filtered off and washed with Et_2O. The solvent was removed under reduced pressure to afford a crude mesylate that was used in the subsequent reaction directly without purification.

To a solution of the crude mesylate (2.86 g, 5.96 mmol) in dry CH_3CN (52 mL) that had been pre-cooled to 5 °C was added KSCN (0.87 g, 8.95 mmol). After stirring at room temperature for 21 h, the solvent was evaporated in vacuo, the obtained residue was diluted with Et_2O (20 mL), and the insoluble materials were removed by filtration. Evaporating of the solvent and chromatography of the residue on silica gel (hexane/ethyl acetate, 9:1) provided 2.38 g (90%) of compound **22** as white crystals; mp 63–64 °C (recrystallized from *n*-hexane); $[\alpha]_D^{25}$ +45.6 (*c* 0.27, $CHCl_3$); IR (neat) ν_{max} 2928, 2146, 1471, 1381, 1216, 1145, 1056, 875 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): δ 0.25 (s, 3H, CH_3), 0.31 (s, 3H, CH_3), 1.01 (s, 9H, 3× CH_3), 1.26 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 2.41–2.52 (m, 2H, 2× H-8), 3.89 (dt, 1H, $J_{2,1}$=7.6 Hz, $J_{2,1}$=6.4 Hz, $J_{3,2}$=6.4 Hz, H-2), 3.95 (dd, 1H, $J_{4,3}$=9.4 Hz, $J_{5,4}$=5.6 Hz, H-4), 4.02–4.08 (m, 2H, 2× H-1), 4.15 (dd, 1H, $J_{4,3}$=9.4 Hz, $J_{3,2}$=6.4 Hz, H-3), 4.46–4.49 (m, 1H, H-5), 5.41–5.49 (m, 1H, H-7), 5.81 (ddt, 1H, $J_{7,6}$=15.2 Hz, $J_{6,5}$=6.4 Hz, $J_{8,6}$=1.0 Hz, $J_{8,6}$=1.0 Hz, H-6); ^{13}C NMR (100 MHz, C_6D_6): δ −4.2 (CH_3), −3.6 (CH_3), 18.7 (C_q), 25.8 (2× CH_3), 26.3 (3× CH_3), 26.7 (CH_3), 28.2 (CH_3), 35.4 (C-8), 68.0 (C-1), 72.2 (C-3), 77.5 (C-5), 77.8 (C-2), 80.9 (C-4), 108.1 (C_q), 109.5 (C_q), 111.6 (SCN), 125.8 (C-7), 134.8 (C-6). Anal. Calcd for $C_{21}H_{37}NO_5SSi$: C, 56.85; H, 8.41; N, 3.16. Found: C, 56.91; H, 8.36; N, 3.12.

4.7. *N*-{(3′*S*,4′*R*,5′*R*,6′*R*,7′*R*)-6′-[(*tert*-Butyldimethylsilyl)oxy]-4′,5′:7′,8′-bis(isopropylidenedioxy)oct-1′-en-3′-yl}-2,2,2-trichloroacetamide (23a) and *N*-{(3′*R*,4′*R*,5′*R*,6′*R*,7′*R*)-6′-[(*tert*-butyldimethylsilyl)oxy]-4′,5′:7′,8′-bis(isopropylidenedioxy)oct-1′-en-3′-yl}-2,2,2-trichloroacetamide (23b)

4.7.1. Conventional method. To a solution of imidate **21** (0.20 g, 0.365 mmol) in *o*-xylene (4.9 mL) was added anhydrous K_2CO_3 (57.61 mg, 0.417 mmol), and the resulting mixture was heated in a sealed tube (for the temperatures and reaction times, see Table 1). After cooling to room temperature, the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (hexane/ethyl acetate, 15:1) to furnish trichloroacetamides **23a** and **23b** as a barely separable mixture of diastereoisomers (for the combined yields, see Table 1).

4.7.2. Microwave-assisted synthesis. Imidate **21** (0.20 g, 0.365 mmol) was weighed into a 10-mL glass pressure microwave tube equipped with a magnetic stirbar. *o*-Xylene (4.9 mL) and anhydrous K_2CO_3 (57.6 mg, 0.417 mmol) were added, the tube was closed with a silicone septum, and the reaction mixture was subjected to microwave irradiation (for the temperatures and reaction times, see Table 1). Removal of the solvent and chromatography on silica gel (hexane/ethyl acetate, 15:1) afforded a mixture of the rearranged products **23a**,**b** (for the combined yields, see Table 1). A small amount of this mixture was repeatedly chromatographed on silica gel (hexane/ethyl acetate, 15:1) to afford each diastereoisomer in pure form as an analytical sample.

Requiring a greater amount of the mixture of **23a** and **23b**, aforementioned procedure was repeated several times at 170 °C using the same amount of the starting imidate **21**.

Diastereoisomer **23a**: colourless oil; $[\alpha]_D^{25}$ +30.2 (*c* 0.44, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.04 (s, 3H, CH_3), 0.07 (s, 3H, CH_3), 0.84 (s, 9H, 3× CH_3), 1.36 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 3.79–3.86 (m, 2H, H-6′, H-8′), 3.90–3.96 (m, 1H, H-7′), 4.20–4.25 (m, 2H, H-5′, H-8′), 4.34–4.36 (m, 1H, H-4′), 5.10–5.14 (m, 1H, H-3′), 5.21–5.27 (m, 2H, 2× H-1′), 5.81 (ddd, 1H,

$J_{2',1'trans}$=17.2 Hz, $J_{2',1'cis}$=10.4 Hz, $J_{3',2'}$=5.2 Hz, H-2′), 7.09 (br d, 1H, $J_{3',NH}$=9.0 Hz, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.5 (CH_3), −3.5 (CH_3), 18.3 (C_q), 24.0 (CH_3), 25.8 (3× CH_3), 25.9 (CH_3), 26.3 (CH_3), 26.6 (CH_3), 53.0 (C-3′), 69.5 (C-8′), 71.8 (C-6′), 78.0 (C-4′), 78.5 (C-7′), 80.1 (C-5′), 92.7 (CCl_3), 107.8 (C_q), 110.3 (C_q), 116.0 (C-1′), 135.7 (C-2′), 160.8 (C=O). Anal. Calcd for $C_{22}H_{38}Cl_3NO_6Si$: C, 48.31; H, 7.00; N, 2.56. Found: C, 48.26; H, 6.95; N, 2.60.

Diastereoisomer **23b**: colourless crystals; mp 72–73 °C (recrystallized from *n*-hexane); $[\alpha]_D^{25}$ +86.9 (*c* 0.32, $CHCl_3$); IR (neat) ν_{max} 3417, 2934, 2893, 1716, 1495, 1382, 1210, 1075, 835 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.08 (s, 3H, CH_3), 0.10 (s, 3H, CH_3), 0.87 (s, 9H, 3× CH_3), 1.36 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 3.79–3.83 (m, 1H, H-8′), 3.94–3.99 (m, 1H, H-7′), 4.08–4.19 (m, 3H, H-5′, H-6′, H-8′), 4.28 (dd, 1H, $J_{5',4'}$=5.8 Hz, $J_{4',3'}$=2.3 Hz, H-4′), 4.99–5.03 (m, 1H, H-3′), 5.31–5.37 (m, 2H, 2× H-1′), 5.98–6.07 (m, 1H, H-2′), 7.01 (br d, 1H, $J_{3',NH}$=8.8 Hz, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.4 (CH_3), −3.6 (CH_3), 18.4 (C_q), 24.9 (CH_3), 25.4 (CH_3), 25.9 (3× CH_3), 26.2 (2× CH_3), 54.6 (C-3′), 68.6 (C-8′), 71.4 (C-5′ or C-6′), 77.6 (C-7′), 78.3 (C-4′), 80.3 (C-5′ or C-6′), 92.8 (CCl_3), 108.1 (C_q), 110.4 (C_q), 118.8 (C-1′), 134.0 (C-2′), 160.6 (C=O). Anal. Calcd for $C_{22}H_{38}Cl_3NO_6Si$: C, 48.31; H, 7.00; N, 2.56. Found: C, 48.36; H, 6.96; N, 2.51.

4.8. *tert*-Butyldimethyl{[(2*R*,3*R*,4*R*,5*R*,6*S*)-1,2:4,5-bis(isopropylidenedioxy)-6-isothiocyanatooct-7-en-3-yl]oxy}silane (13) and *tert*-butyldimethyl{[(2*R*,3*R*,4*R*,5*R*,6*R*)-1,2:4,5-bis(isopropylidenedioxy)-6-isothiocyanatooct-7-en-3-yl]oxy}silane (14)

4.8.1. Conventional method. Thiocyanate **22** (0.10 g, 0.225 mmol) was dissolved in *n*-heptane (3 mL) and the resulting solution was stirred and heated under a nitrogen atmosphere (for the temperatures and reaction times, see Table 2). After cooling to room temperature, the solvent was taken down, and the residue was chromatographed on silica gel (hexane/ethyl acetate, 25:1) to give the corresponding isothiocyanates **13** and **14** as colourless oils (for the combined yields, see Table 2).

Requiring a greater amount of the pure rearranged products **13** and **14**, they were obtained on a multigram scale by the conventional method in *n*-heptane at 90 °C.

4.8.2. Microwave-assisted synthesis. Thiocyanate **22** (0.10 g, 0.225 mmol) was weighed in a 10-mL glass pressure microwave tube equipped with a magnetic stirbar. *n*-Heptane (3 mL) was added, the tube was closed with a silicon septum, and the resulting mixture was subjected to microwave irradiation (for the temperatures and reaction times, see Table 2). Evaporating of the solvent and chromatography on silica gel (hexane/ethyl acetate, 25:1) gave isothiocyanates **13** and **14** (for the combined yields, see Table 2).

Diastereoisomer **13**: $[\alpha]_D^{23}$ +27.9 (*c* 0.80, $CHCl_3$); IR (neat) ν_{max} 2930, 2102, 1461, 1381, 1213, 1057, 832 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.17 (s, 6H, 2× CH_3), 0.87 (s, 9H, 3× CH_3), 1.32 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 3.80–3.84 (m, 1H, H-1), 3.93–3.98 (m, 1H, H-2), 4.04–4.08 (m, 2H, H-3, H-5), 4.14–4.17 (m, 1H, H-4), 4.20 (dd, 1H, $J_{1,1}$=8.2 Hz, $J_{2,1}$=6.2 Hz, H-1), 4.68–4.70 (m, 1H, H-6), 5.29–5.36 (m, 2H, 2× H-8), 5.91 (ddd, 1H, $J_{8trans,7}$=16.9 Hz, $J_{8cis,7}$=10.2 Hz, $J_{7,6}$=6.0 Hz, H-7); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.6 (CH_3), −3.6 (CH_3), 18.4 (C_q), 24.9 (2× CH_3), 25.9 (3× CH_3), 26.3 (CH_3), 26.6 (CH_3), 59.9 (C-6), 69.2 (C-1), 72.2 (C-3), 77.9 (C-2), 78.0 (C-5), 80.1 (C-4), 108.8 (C_q), 109.9 (C_q), 117.3 (C-8), 133.2 (NCS), 134.0 (C-7). Anal. Calcd for $C_{21}H_{37}NO_5SSi$: C, 56.85; H, 8.41; N, 3.16. Found: C, 56.79; H, 8.46; N, 3.11.

Diastereoisomer **14**: $[\alpha]_D^{24}$ −137.8 (*c* 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.10 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.88 (s, 9H, 3× CH_3), 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 3.84–3.87 (m, 1H, H-1), 4.01–4.14 (m, 4H, H-1, H-2, H-3, H-4), 4.24–4.27 (m, 1H, H-5), 4.63–4.66 (m, 1H, H-6), 5.37–5.39 (m, 1H, H-8$_{cis}$), 5.41–5.46 (m, 1H, H-8$_{trans}$), 5.98 (ddd, 1H, $J_{8trans,7}$=17.0 Hz, $J_{8cis,7}$=10.3 Hz, $J_{7,6}$=5.6 Hz, H-7); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.1 (CH_3), −3.8 (CH_3), 18.5 (C_q), 25.0 (CH_3), 25.1 (CH_3), 26.0 (3× CH_3), 26.3 (CH_3), 26.5 (CH_3), 60.2 (C-6), 67.4 (C-1), 71.2 (C-3), 77.4 (C-2), 78.9 (C-5), 79.6 (C-4), 108.7 (C_q), 109.6 (C_q), 118.5 (C-8), 125.5 (NCS), 132.9 (C-7). Anal. Calcd for $C_{21}H_{37}NO_5SSi$: C, 56.85; H, 8.41; N, 3.16. Found: C, 56.90; H, 8.37; N, 3.12.

4.9. *tert*-Butyl [(3*S*,4*R*,5*R*,6*R*,7*R*)-6-[(*tert*-butyldimethylsilyl)oxy]-4,5:7,8-bis(isopropylidenedioxy)oct-1-en-3-yl]carbamate (15) and *tert*-butyl [(3*R*,4*R*,5*R*,6*R*,7*R*)-6-[(*tert*-butyldimethylsilyl)oxy]-4,5:7,8-bis(isopropylidenedioxy)oct-1-en-3-yl]carbamate (16)

A 6 M aq solution of NaOH (125.5 mL) was added dropwise to a solution of **23a**,**b** (12.88 g, 23.5 mmol) in EtOH (125.5 mL) at room temperature. After stirring for 5 h at the same temperature, the mixture was diluted with Et_2O (150 mL), and aqueous phase was then extracted with further portions of Et_2O (2×200 mL). The combined organic layers were dried over Na_2SO_4, stripped of solvent, and the residue was used immediately in the next reaction without purification. To a solution of crude amines in CH_2Cl_2 (29 mL) were successively added Et_3N (3.3 mL, 23.5 mmol) and Boc_2O (12.82 g, 58.74 mmol). The resulting mixture was stirred for 16 h at room temperature, then was diluted with CH_2Cl_2 (70 mL) and washed with a 1 M $KHSO_4$ solution (100 mL) and a 1 M $NaHCO_3$ solution (100 mL). The organic layer was dried over Na_2SO_4, the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (hexane/ethyl acetate, 11:1) to give 3.78 g (32%) of **15** and 7.08 g (60%) of **16**.

Diastereoisomer **15**: colourless oil; $[\alpha]_D^{24}$ +55.4 (*c* 0.28, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.08 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.86 (s, 9H, 3× CH_3), 1.35 (s, 6H, 2× CH_3), 1.45 (s, 12H, 4× CH_3), 1.53 (s, 3H, CH_3), 3.78–3.82 (m, 1H, H-8), 3.92–3.95 (m, 1H, H-7), 4.02–4.06 (m, 1H, H-6), 4.15–4.22 (m, 3H, H-4, H-5, H-8), 4.61 (m, 1H, H-3), 4.86 (br d, 1H, $J_{3,NH}$=8.0 Hz, NH), 5.14–5.19 (m, 2H, 2× H-1), 5.81 (ddd, 1H, $J_{2,1trans}$=17.0 Hz, $J_{2,1cis}$=10.4 Hz, $J_{3,2}$=4.9 Hz, H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.6 (CH_3), −3.7 (CH_3), 18.3 (C_q), 24.3 (CH_3), 25.9 (4× CH_3), 26.3 (CH_3), 26.4 (CH_3), 28.4 (3× CH_3), 52.4 (C-3), 69.2 (C-8), 71.5 (C-6), 78.5 (C-4 or C-5, C-7), 79.1 (C_q), 79.8 (C-4 or C-5), 107.4 (C_q), 109.9 (C_q), 114.6 (C-1), 137.9 (C-2), 154.8 (C=O). Anal. Calcd for $C_{25}H_{47}NO_7Si$: C, 59.85; H, 9.44; N, 2.79. Found: C, 59.89; H, 9.39; N, 2.83.

Diastereoisomer **16**: white crystals; mp 84–86 °C (recrystallized from *n*-hexane); $[\alpha]_D^{24}$ +78.1 (*c* 0.26, $CHCl_3$); IR (neat) ν_{max} 3332, 2930, 1714, 1519, 1369, 1246, 1150, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.09 (s, 3H, CH_3), 0.11 (s, 3H, CH_3), 0.87 (s, 9H, 3× CH_3), 1.33 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.44 (s, 9H, 3× CH_3), 1.47 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 3.77–3.81 (m, 1H, H-8), 3.98–4.07 (m, 3H, H-4, H-5, H-7), 4.11–4.18 (m, 2H, H-6, H-8), 4.42 (m, 1H, H-3), 5.13 (br d, 1H, $J_{3,NH}$=7.3 Hz, NH), 5.21–5.28 (m, 2H, 2× H-1), 5.94–6.02 (m, 1H, H-2); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.5 (CH_3), −3.8 (CH_3), 18.4 (C_q), 25.4 (2× CH_3), 25.9 (3× CH_3), 26.2 (CH_3), 26.9 (CH_3), 28.4 (3× CH_3), 52.9 (C-3), 68.1 (C-8), 70.4 (C-6), 77.8 (C-7), 78.9 (C-4 or C-5), 79.2 (C_q), 80.2 (C-4 or C-5), 107.7 (C_q), 109.8 (C_q), 116.4 (C-1), 136.4 (C-2), 154.7 (C=O). Anal. Calcd for $C_{25}H_{47}NO_7Si$: C, 59.85; H, 9.44; N, 2.79. Found: C, 59.89; H, 9.47; N, 2.82.

4.10. *tert*-Butyl [(2*S*,3*R*,4*R*,5*R*,6*R*)-5-[(*tert*-butyldimethylsilyl)oxy]-1-hydroxy-3,4:6,7-bis(isopropylidenedioxy)heptan-2-yl]carbamate (24)

Ozone was introduced to a solution of **15** (3.78 g, 7.53 mmol) in CH_3OH/CH_2Cl_2 (282.5 mL, 5:1) at −78 °C for 15 min. After the complete consumption of the starting material (judged by TLC), nitrogen was passed through the cold solution in order to remove excess ozone. Then, $NaBH_4$ (1.28 g, 33.8 mmol) was added

portionwise, and the resulting mixture was stirred for 30 min at −78 °C. After warming to room temperature (approximately 30 min), the solvents were evaporated in vacuo, and the residue was partitioned between EtOAc (190 mL) and a saturated NH_4Cl solution (114 mL). The aqueous phase was washed with further portions of EtOAc (2×150 mL), the organic layers were dried over Na_2SO_4, the solvent was taken down, and the residue was subjected to flash chromatography on silica gel (hexane/ethyl acetate, 2:1) to furnish 3.2 g (84%) of compound **24** as a colourless oil; $[\alpha]_D^{24}$ +46.0 (*c* 0.30, $CHCl_3$); IR (neat) ν_{max} 3316, 2984, 2931, 1704, 1506, 1368, 1159, 1076, 838 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 0.09 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.88 (s, 9H, 3× CH_3), 1.32 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.45 (s, 12H, 3× CH_3, CH_3), 1.49 (s, 3H, CH_3), 3.45–3.47 (m, 2H, 2× H-1), 3.84–3.88 (m, 1H, H-7), 3.94–4.04 (m, 2H, H-2, H-6), 4.07–4.17 (m, 3H, H-4, H-5, H-7), 4.31–4.32 (m, 1H, H-3), 5.30 (br d, 1H, $J_{2,NH}$=9.4 Hz, NH); ^{13}C NMR (100 MHz, CD_3OD): δ −3.8 (CH_3), −3.2 (CH_3), 19.2 (C_q), 24.8 (CH_3), 25.8 (CH_3), 26.5 (3× CH_3), 26.7 (CH_3), 26.8 (CH_3), 28.9 (3× CH_3), 52.6 (C-2), 64.1 (C-1), 68.6 (C-7), 72.4 (C-4 or C-5), 76.3 (C-3), 79.2 (C-6), 80.5 (C_q), 80.7 (C-4 or C-5), 108.9 (C_q), 110.9 (C_q), 157.1 (C═O). Anal. Calcd for $C_{24}H_{47}NO_8Si$: C, 57.00; H, 9.37; N, 2.77. Found: C, 57.09; H, 9.32; N, 2.81.

4.11. *tert*-Butyl [(2*R*,3*R*,4*R*,5*R*,6*R*)-5-[(*tert*-butyldimethylsilyl) oxy]-1-hydroxy-3,4:6,7-bis(isopropylidenedioxy)heptan-2-yl] carbamate (25)

Using the same procedure as described for the preparation of **24**, ozonolysis of compound **16** (7.08 g, 14.11 mmol) followed by $NaBH_4$ (2.40 g, 63.5 mmol) treatment afforded after flash chromatography on silica gel (hexane/ethyl acetate, 2:1) 5.35 g (75%) of derivative **25** as white crystals; mp 38−39 °C (recrystallized from *n*-hexane); $[\alpha]_D^{24}$ +74.0 (*c* 0.30, $CHCl_3$); IR (neat) ν_{max} 3360, 2982, 2931, 1713, 1510, 1367, 1160, 1053, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.10 (s, 3H, CH_3), 0.12 (s, 3H, CH_3), 0.87 (s, 9H, 3× CH_3), 1.35 (s, 6H, 2× CH_3), 1.45 (s, 9H, 3× CH_3), 1.48 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.36 (m, 1H, OH), 3.75–3.84 (m, 4H, 2× H-1, H-2, H-7), 4.02–4.13 (m, 5H, H-3, H-4, H-5, H-6, H-7), 5.41–5.42 (1H, m, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.6 (CH_3), −3.9 (CH_3), 18.4 (C_q), 25.3 (CH_3), 25.5 (CH_3), 25.9 (3× CH_3), 26.2 (CH_3), 27.5 (CH_3), 28.3 (3× CH_3), 51.6 (C-2), 64.0 (C-1), 68.0 (C-7), 70.0 (C-3 or C-4 or C-5 or C-6), 76.1 (C-3 or C-4 or C-5 or C-6), 78.0 (C-3 or C-4 or C-5 or C-6), 79.9 (C_q), 80.0 (C-3 or C-4 or C-5 or C-6), 107.8 (C_q), 109.6 (C_q), 155.7 (C═O). Anal. Calcd for $C_{24}H_{47}NO_8Si$: C, 57.00; H, 9.37; N, 2.77. Found: C, 57.09; H, 9.33; N, 2.74.

4.12. (4*S*)-4-[(1′*R*,2′*R*,3′*R*,4′*R*)-3′-[(*tert*-Butyldimethylsilyl) oxy]-1′,2′:4′,5′-bis(isopropylidenedioxy)pentyl]oxazolidin-2-one (26)

To a solution of **24** (3.20 g, 6.33 mmol) in dry THF (7.3 mL) that was pre-cooled to 0 °C was added NaH (0.51 g, 21.25 mmol, 60% dispersion in mineral oil). After stirring at 0 °C for 10 min and then at room temperature for 28 h, another portion of NaH (0.23 g, 9.58 mmol) was added at 0 °C, and stirring was continued for further 20 h at room temperature. After cautious addition of CH_3OH (0.5 mL), the reaction mixture was concentrated and partitioned between CH_2Cl_2 (82 mL) and water (55 mL). The organic layer was dried over Na_2SO_4, the solvent was evaporated in vacuo, and the residue was chromatographed on silica gel (hexane/ethyl acetate, 2:1). This procedure yielded 2.34 g (86%) of crystalline compound **26**; mp 149−151 °C (recrystallized from *n*-hexane); $[\alpha]_D^{22}$ +67.1 (*c* 0.28, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.12 (s, 3H, CH_3), 0.13 (s, 3H, CH_3), 0.87 (s, 9H, 3× CH_3), 1.32 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.66 (dd, 1H, $J_{3',2'}$=9.2 Hz, $J_{4',3'}$=7.6 Hz, H-3′), 3.81 (dd, 1H, $J_{5',5'}$=8.1 Hz, $J_{5',4'}$=7.4 Hz, H-5′), 3.97 (dt, 1H, $J_{5',4'}$=7.4 Hz, $J_{4',3'}$=7.4 Hz, $J_{5',4'}$=6.4 Hz, H-4′), 4.05 (dd, 1H, $J_{2',1'}$=5.6 Hz, $J_{4,1'}$=2.5 Hz, H-1′), 4.13–4.24 (m, 3H, H-4, H-2′, H-5′), 4.30 (dd, 1H, $J_{5,5}$=8.3 Hz, $J_{5,4}$=5.9 Hz, H-5), 4.36–4.40 (m, 1H, H-5), 4.80 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.3 (CH_3), −3.6 (CH_3), 18.4 (C_q), 24.9 (CH_3), 25.3 (CH_3), 25.8 (3× CH_3), 26.2 (CH_3), 26.4 (CH_3), 52.3 (C-4), 67.6 (C-5), 68.6 (C-5′), 72.6 (C-3′), 76.9 (C-1′), 77.5 (C-4′), 79.8 (C-2′), 108.6 (C_q), 109.9 (C_q), 159.3 (C═O). Anal. Calcd for $C_{20}H_{37}NO_7Si$: C, 55.66; H, 8.64; N, 3.25. Found: C, 55.69; H, 8.69; N, 3.22.

4.13. (4*R*)-4-[(1′*R*,2′*R*,3′*R*,4′*R*)-3′-[(*tert*-Butyldimethylsilyl) oxy]-1′,2′:4′,5′-bis(isopropylidenedioxy)pentyl]oxazolidin-2-one (27)

According to the same procedure described for the preparation of **26**, compound **25** (5.35 g, 10.58 mmol) and NaH (0.85 g, 35.42 mmol, 60% dispersion in mineral oil) afforded after stirring (21 h) at room temperature and flash chromatography on silica gel (hexane/ethyl acetate, 2:1) 4.43 g (97%) of crystalline oxazolidinone **27**; mp 121−122 °C (recrystallized from *n*-hexane); $[\alpha]_D^{22}$ −55.6 (*c* 0.34, $CHCl_3$); IR (neat) ν_{max} 3386, 2928, 2887, 2856, 1766, 1471, 1381, 1240, 1211, 1117, 1039, 838 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.11 (s, 6H, 2× CH_3), 0.87 (s, 9H, 3× CH_3), 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 3.71–3.75 (m, 1H, H-2′), 3.79–3.83 (m, 1H, H-5′), 3.94–4.12 (m, 4H, H-4, H-1′, H-3′, H-4′), 4.16 (dd, 1H, $J_{5',5'}$=8.1 Hz, $J_{5',4'}$=6.0 Hz, H-5′), 4.37–4.44 (m, 2H, 2× H-5), 6.09 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.5 (CH_3), −3.8 (CH_3), 18.4 (C_q), 25.1 (CH_3), 25.2 (CH_3), 25.9 (3× CH_3), 26.3 (CH_3), 27.7 (CH_3), 51.2 (C-4), 67.3 (C-5), 68.5 (C-5′), 71.6 (C-2′), 77.4 (C-4′), 78.5 (C-1′), 80.2 (C-3′), 107.8 (C_q), 110.6 (C_q), 159.2 (C═O). Anal. Calcd for $C_{20}H_{37}NO_7Si$: C, 55.66; H, 8.64; N, 3.25. Found: C, 55.69; H, 8.67; N, 3.29.

4.14. Methyl [(3*S*,4*R*,5*R*,6*R*,7*R*)-6-[(*tert*-butyldimethylsilyl) oxy]-4,5:7,8-bis(isopropylidenedioxy)oct-1-en-3-yl]carbamate (28)

Sodium methoxide (0.35 g, 6.48 mmol) was added to a solution of **13** (1.9 g, 4.28 mmol) in dry CH_3OH (42.5 mL) that had been pre-cooled to 0 °C. After stirring for 30 min at 0 °C and then at room temperature for 46 h, the solvent was evaporated, and the mixture was partitioned between CH_2Cl_2 (57 mL) and water (14 mL). The aqueous phase was washed with further portions of CH_2Cl_2 (2×57 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated in vacuo, and the residue was flash-chromatographed through a short silica gel column (hexane/ethyl acetate, 11:1). This procedure yielded 1.06 g (52%) of thiocarbamate as a colourless oil, which was immediately used in the subsequent reaction. To a solution of the aforementioned compound (1.06 g, 2.23 mmol) in dry CH_3CN (21.5 mL) was added MNO (0.54 g, 3.35 mmol). After stirring at room temperature for 24 h, the solvent was removed under reduced pressure, and the residue was subjected to flash chromatography on silica gel (hexane/ethyl acetate, 15:1) to give 0.77 g (75%) of compound **28** as a colourless oil; $[\alpha]_D^{25}$ +42.3 (*c* 0.44, $CHCl_3$); IR (neat) ν_{max} 3453, 2986, 2931, 2857, 1726, 1504, 1371, 1211, 1075, 835 cm^{-1}; ^1H NMR (400 MHz, C_6D_6): δ 0.12 (s, 3H, CH_3), 0.22 (s, 3H, CH_3), 0.96 (s, 9H, 3× CH_3), 1.13 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.49 (s, 3H, CH_3), 3.90–3.95 (m, 1H, H-7), 4.02–4.06 (m, 1H, H-8), 4.13 (dd, 1H, $J_{6,5}$=9.2 Hz, $J_{5,4}$=6.7 Hz, H-5), 4.21 (m, 1H, H-4), 4.25–4.30 (m, 2H, H-6, H-8), 5.03–5.05 (m, 3H, H-1_{cis}, H-3, NH), 5.26 (d, 1H, $J_{2,1trans}$=17.1 Hz, H-1_{trans}), 5.81–5.89 (m, 1H, H-2); ^{13}C NMR (100 MHz, C_6D_6): δ −4.8 (CH_3), −3.6 (CH_3), 18.6 (C_q), 24.4 (CH_3), 26.2 (4× CH_3), 26.4 (CH_3), 26.5 (CH_3), 51.8 (CH_3), 52.9 (C-3), 69.9 (C-8), 72.1 (C-6), 79.2 (C-7), 79.3 (C-4), 80.4 (C-5), 107.5 (C_q), 110.3 (C_q), 114.7 (C-1), 138.8 (C-2), 155.9 (C═O). Anal. Calcd for $C_{22}H_{41}NO_7Si$: C, 57.49; H, 8.99; N, 3.05. Found: C, 57.53; H, 9.06; N, 3.10.

4.15. Methyl [(2*S*,3*R*,4*R*,5*R*,6*R*)-5-[(*tert*-butyldimethylsilyl) oxy]-1-hydroxy-3,4:6,7-bis(isopropylidenedioxy)heptan-2-yl] carbamate (29)

Using the same procedure as described for the preparation of **24**, ozonolysis of compound **28** (0.77 g, 1.68 mmol) followed by $NaBH_4$ (0.286 g, 7.56 mmol) treatment provided after flash chromatography on silica gel (hexane/ethyl acetate, 2:1) 0.62 g (80%) of derivative **29**, which after NMR spectroscopic analysis was immediately converted into the common oxazolidinone **26**.

Modification of **29** *into* **26**: Using the same procedure as described for the transformation of **24** to **26**, compound **29** (0.62 g, 1.34 mmol) and NaH (0.108 g, 4.50 mmol, 60% dispersion in mineral oil) afforded after stirring (1 h) at room temperature and flash chromatography on silica gel (hexane/ethyl acetate, 2:1) 0.53 g (92%) of derivative **26**.

Alcohol **29**: colourless oil; $[\alpha]_D^{24}$ +51.0 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.03 (s, 3H, CH_3), 0.06 (s, 3H, CH_3), 0.85 (s, 9H, 3× CH_3), 1.34 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 2.28 (br s, 1H, OH), 3.63–3.68 (m, 5H, OCH_3, 2× H-1), 3.81–3.85 (m, 1H, H-7), 3.88–3.93 (m, 1H, H-5), 3.97–4.01 (m, 1H, H-6), 4.15–4.32 (m, 4H, H-2, H-3, H-4, H-7), 5.13 (br d, 1H, $J_{2,NH}$=9.2 Hz, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ −5.1 (CH_3), −4.0 (CH_3), 18.3 (C_q), 24.5 (CH_3), 25.8 (CH_3), 25.9 (3× CH_3), 26.1 (CH_3), 26.4 (CH_3), 51.5 (C-2), 52.1 (CH_3), 65.7 (C-1), 69.2 (C-7), 71.5 (C-6), 77.0 (C-3), 78.4 (C-5), 80.0 (C-4), 107.7 (C_q), 110.0 (C_q), 156.7 (C=O). Anal. Calcd for $C_{21}H_{41}NO_8Si$: C, 54.40; H, 8.91; N, 3.02. Found: C, 54.44; H, 8.99; N, 3.09.

4.16. (4*S*)-4-[(1′*R*,2′*R*,3′*R*,4′*R*)-3′-[(*tert*-Butyldimethylsilyl) oxy]-1′,2′:4′,5′-bis(isopropylidenedioxy)pentyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (30)

To a solution of **26** (2.34 g, 5.42 mmol) in dry DMF (13.7 mL) that was pre-cooled to 0 °C were successively added NaH (0.335 g, 13.96 mmol, 60% dispersion in mineral oil), *p*-methoxybenzyl chloride (1.11 mL, 8.19 mmol) and TBAI (0.40 g, 1.08 mmol). After stirring at 0 °C for 10 min and then for further 30 min at room temperature, the mixture was poured into ice water (137 mL) and extracted with Et_2O (2×137 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated in vacuo, and the residue was subjected to flash chromatography on silica gel (hexane/ethyl acetate, 3:1). This procedure yielded 2.63 g (88%) of compound **30** as a colourless oil; $[\alpha]_D^{22}$ +28.2 (*c* 0.44, $CHCl_3$); IR (neat) ν_{max} 2930, 1751, 1612, 1513, 1245, 1212, 1068, 1034, 835 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 3H, CH_3), 0.08 (s, 3H, CH_3), 0.84 (s, 9H, 3× CH_3), 1.25 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 3.59–3.63 (m, 1H, H-5′), 3.67 (dd, 1H, $J_{5',5'}$=8.1 Hz, $J_{5',4'}$=6.5 Hz, H-5′), 3.77–3.81 (m, 4H, H-3′, OCH_3), 3.88–3.93 (m, 1H, H-4), 4.00–4.07 (m, 2H, H-5, H-4′), 4.17–4.19 (m, 1H, H-2′), 4.25–4.30 (m, 2H, H-5, H-1′), 4.37 (d, 1H, $J_{H,H}$=15.2 Hz, NCH_2), 4.90 (d, 1H, $J_{H,H}$=15.2 Hz, NCH_2), 6.86–6.88 (m, 2H, Ph), 7.19–7.21 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.8 (CH_3), −3.6 (CH_3), 18.5 (C_q), 24.9 (2× CH_3), 26.0 (3× CH_3), 26.2 (2× CH_3), 46.7 (NCH_2), 53.2 (C-4), 55.3 (OCH_3), 65.5 (C-5), 66.7 (C-5′), 73.4 (C-3′), 76.3 (C-4′), 78.6 (C-2′), 80.4 (C-1′), 109.2 (2× C_q), 114.2 (2× CH_{Ph}), 128.5 (C_i), 129.1 (2× CH_{Ph}), 158.7 (C=O), 159.2 (C_i). Anal. Calcd for $C_{28}H_{45}NO_8Si$: C, 60.95; H, 8.22; N, 2.54. Found: C, 60.99; H, 8.18; N, 2.57.

4.17. (4*R*)-4-[(1′*R*,2′*R*,3′*R*,4′*R*)-3′-[(*tert*-Butyldimethylsilyl) oxy]-1′,2′:4′,5′-bis(isopropylidenedioxy)pentyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (31)

According to the same procedure described for the preparation of **30**, compound **27** (4.43 g, 10.26 mmol) was transformed to derivative **31** (4.98 g, 88%, hexane/ethyl acetate, 3:1, white crystals); mp 145–147 °C (recrystallized from *n*-hexane); $[\alpha]_D^{22}$ +38.7 (*c* 0.54, $CHCl_3$); IR (neat) ν_{max} 2931, 2895, 1746, 1614, 1516, 1370, 1238, 1033, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.06 (s, 3H, CH_3), 0.09 (s, 3H, CH_3), 0.85 (s, 12H, 3× CH_3, CH_3), 1.09 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 3.37 (dd, 1H, $J_{3',2'}$=9.8 Hz, $J_{4',3'}$=6.9 Hz, H-3′), 3.65–3.73 (m, 2H, H-4′, H-5′), 3.78 (s, 3H, OCH_3), 3.98 (d, 1H, $J_{H,H}$=15.4 Hz, NCH_2), 4.00–4.05 (m, 2H, H-4, H-5′), 4.13–4.22 (m, 2H, H-5, H-2′), 4.35 (dd, 1H, $J_{2',1'}$=6.6 Hz, $J_{4,1'}$=1.7 Hz, H-1′), 4.56 (dd, 1H, $J_{5,5}$=8.5 Hz, $J_{5,4}$=4.0 Hz, H-5), 4.93 (d, 1H, $J_{H,H}$=15.4 Hz, NCH_2), 6.85–6.87 (m, 2H, Ph), 7.20–7.22 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.5 (CH_3), −3.7 (CH_3), 18.3 (C_q), 24.7 (CH_3), 25.0 (CH_3), 25.4 (CH_3), 25.8 (3× CH_3), 26.1 (CH_3), 44.8 (NCH_2), 54.4 (C-4), 55.3 (OCH_3), 62.8 (C-5′), 68.2 (C-5), 72.0 (C-3′), 72.5 (C-1′), 77.4 (C-4′), 79.6 (C-2′), 108.3 (C_q), 109.9 (C_q), 114.2 (2× CH_{Ph}), 128.2 (C_i), 129.0 (2× CH_{Ph}), 158.6 (C=O), 159.3 (C_i). Anal. Calcd for $C_{28}H_{45}NO_8Si$: C, 60.95; H, 8.22; N, 2.54. Found: C, 60.92; H, 8.25; N, 2.57.

4.18. (4*S*)-4-[(1′*R*,2′*S*,3′*R*,4′*R*)-3′-Hydroxy-1′,2′:4′,5′-bis(isopropylidenedioxy) pentyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (32)

A 1 M solution of TBAF (4.7 mL, 4.71 mmol) was added to a solution of **30** (2.60 g, 4.71 mmol) in dry THF (47 mL) that was pre-cooled to 0 °C. The resulting mixture was stirred at 0 °C for 10 min and then for further 30 min at room temperature. Evaporating of the solvent and chromatography of the residue on silica gel (hexane/ethyl acetate, 2:1) afforded 1.92 g (93%) of compound **32** as a colourless viscous oil; $[\alpha]_D^{22}$ −2.7 (*c* 0.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 2.03–2.08 (m, 1H, OH), 3.04–3.08 (m, 1H, H-3′), 3.79 (s, 3H, OCH_3), 3.87 (dd, 1H, $J_{5,5}$=8.7 Hz, $J_{5,4}$=4.8 Hz, H-5), 3.92–4.00 (m, 2H, H-4′, H-5′), 4.01–4.06 (m, 1H, H-5′), 4.15–4.20 (m, 1H, H-4), 4.30–4.34 (m, 1H, H-5), 4.37–4.44 (m, 3H, H-1′, H-2′, NCH_2), 4.80 (d, 1H, $J_{H,H}$=14.6 Hz, NCH_2), 6.83–6.85 (m, 2H, Ph), 7.24–7.27 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): 24.2 (CH_3), 25.0 (CH_3), 26.6 (CH_3), 26.9 (CH_3), 47.0 (NCH_2), 53.4 (C-4), 55.2 (OCH_3), 63.8 (C-5), 66.6 (C-5′), 70.7 (C-3′), 75.0 (C-1′), 75.9 (C-4′), 80.7 (C-2′), 109.3 (C_q), 109.6 (C_q), 113.9 (2× CH_{Ph}), 128.5 (C_i), 130.0 (2× CH_{Ph}), 158.1 (C=O), 159.2 (C_i). Anal. Calcd for $C_{22}H_{31}NO_8$: C, 60.40; H, 7.14; N, 3.20. Found: C, 60.45; H, 7.18; N, 3.23.

4.19. (4*R*)-4-[(1′*R*,2′*S*,3′*R*,4′*R*)-3′-Hydroxy-1′,2′:4′,5′-bis(isopropylidenedioxy) pentyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (33)

Using the same procedure as described for the preparation of **32**, compound **31** (4.98 g, 9.03 mmol) and TBAF (9.0 mL, 9.03 mmol) yielded after flash chromatography on silica gel (hexane/ethyl acetate, 1:1) 3.87 g (98%) of compound **33** as a colourless viscous oil; $[\alpha]_D^{22}$ +21.2 (*c* 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27 (s, 3H, CH_3) 1.29 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 2.16–2.20 (m, 1H, OH), 3.25–3.30 (m, 1H, H-3′), 3.79–3.82 (m, 4H, H-4, OCH_3), 3.89–3.96 (m, 2H, H-4′, H-5′), 4.01–4.07 (m, 1H, H-5), 4.11 (d, 1H, $J_{H,H}$=15.4 Hz, NCH_2), 4.23–4.27 (m, 1H, H-5), 4.31 (dd, 1H, $J_{2',1'}$=7.8 Hz, $J_{3',2'}$=2.2 Hz, H-2′), 4.40 (dd, 1H, $J_{2',1'}$=7.8 Hz, $J_{4,1'}$=1.4 Hz, H-1′), 4.45 (dd, 1H, $J_{5,5}$=9.2 Hz, $J_{5,4}$=4.8 Hz, H-5), 4.83 (d, 1H, $J_{H,H}$=15.4 Hz, NCH_2), 6.85–6.89 (m, 2H, Ph), 7.19–7.21 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3 (CH_3), 25.0 (CH_3), 25.9 (CH_3), 26.5 (CH_3), 45.2 (NCH_2), 54.9 (C-4), 55.3 (OCH_3), 63.6 (C-5), 66.8 (C-5′), 69.3 (C-3′), 72.9 (C-1′), 75.3 (C-2′), 76.5 (C-4′), 108.9 (C_q), 109.5 (C_q), 114.2 (2× CH_{Ph}), 127.8 (C_i), 129.1 (2× CH_{Ph}), 158.5 (C=O), 159.3 (C_i). Anal. Calcd for $C_{22}H_{31}NO_8$: C, 60.40; H, 7.14; N, 3.20. Found: C, 60.44; H, 7.19; N, 3.24.

4.20. (4*S*)-4-[(1′*R*,2′*S*,3′*R*,4′*R*)-3′,4′,5′-Trihydroxy-1′,2′-(isopropylidenedioxy)pentyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (10)

A solution of **32** (1.92 g, 4.38 mmol) in a mixture of 1:1 AcOH/H_2O (15.4 mL) was stirred at room temperature for 15 h before evaporating of the solvent. The obtained residue was subjected to flash chromatography on silica gel (ethyl acetate) to afford 1.57 g (90%) of compound **10** as a colourless foam; $[\alpha]_D^{21}$ −2.2 (*c* 0.18, CH_3OH); ^1H NMR (400 MHz, CD_3OD): δ 1.35 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 3.22–3.24 (m, 1H, H-4′), 3.54–3.61 (m, 2H, H-3′, H-5′), 3.69–3.72 (m, 1H, H-5′), 3.77 (s, 3H, OCH_3), 4.09 (dd, 1H, $J_{5,5}$=8.2 Hz, $J_{5,4}$=4.9 Hz, H-5), 4.32–4.35 (m, 1H, H-4), 4.37–4.45 (m, 2H, H-5, H-1′), 4.50 (d, 1H, $J_{H,H}$=14.8 Hz, NCH_2), 4.54–4.55 (m, 1H, H-2′), 4.69 (d, 1H, $J_{H,H}$=14.8 Hz, NCH_2) 6.86–6.88 (m, 2H, Ph), 7.24–7.26 (m, 2H, Ph); ^{13}C NMR (100 MHz, CD_3OD): δ 24.9 (CH_3), 27.0 (CH_3), 48.0 (NCH_2), 55.7 (C-4, OCH_3), 64.6 (C-5′), 65.8 (C-5), 70.7 (C-4′), 73.1 (C-3′), 76.6 (C-2′), 82.3 (C-1′), 110.4 (C_q), 115.0 (2× CH_{Ph}), 130.1 (C_i), 130.8 (2× CH_{Ph}), 160.8 (C_i or C=O), 161.0 (C_i or C=O). Anal. Calcd for $C_{19}H_{27}NO_8$: C, 57.42; H, 6.85; N, 3.52. Found: C, 57.46; H, 6.89; N, 3.50.

4.21. (4*R*)-4-[(1′*R*,2′*S*,3′*R*,4′*R*)-3′,4′,5′-Trihydroxy-1′,2′-(isopropylidenedioxy)pentyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (11) and (4*R*)-3-(*p*-methoxybenzyl)-4-[(1′*R*,2′*R*,3′*R*,4′*R*)-1′,2′,3′,4′,5′-pentahydroxypentyl]oxazolidin-2-one (34)

According to the same procedure described for the preparation of **10**, acid hydrolysis of compound **33** (3.87 g, 8.85 mmol) furnished after stirring (8 h) and chromatography on silica gel (ethyl acetate) 2.11 g (60%) of **11** and 0.67 g (19%) of derivative **34** as white crystals.

Compound **11**: mp 153−154 °C (recrystallized from ethyl acetate); $[\alpha]_D^{22}$ +48.6 (*c* 0.22, CH_3OH); ^1H NMR (400 MHz, CD_3OD): δ 1.39 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 3.40 (dd, 1H, $J_{3',2'}$=8.6 Hz, $J_{4',3'}$=2.6 Hz, H-3′), 3.56–3.63 (m, 2H, H-4′, H-5′), 3.71–3.76 (m, 1H, H-5′), 3.80 (s, 3H, OCH_3), 3.94 (dd, 1H, $J_{5,4}$=8.7 Hz, $J_{5,4}$=3.8 Hz, H-4), 4.22–4.28 (m, 2H, H-5, NCH_2), 4.48–4.50 (m, 1H, H-1′), 4.56–4.60 (m, 2H, H-5, H-2′), 4.69 (d, 1H, $J_{H,H}$=15.4 Hz, 1H, NCH_2), 6.91–6.94 (m, 2H, Ph), 7.26–7.28 (m, 2H, Ph); ^{13}C NMR (100 MHz, CD_3OD): δ 24.7 (CH_3), 26.3 (CH_3), 45.8 (NCH_2), 55.8 (OCH_3), 57.7 (C-4), 64.6 (C-5′), 66.0 (C-5), 69.2 (C-3′), 73.7 (C-4′), 74.5 (C-1′), 76.9 (C-2′), 109.5 (C_q), 115.3 (2× CH_{Ph}), 129.5 (C_i), 130.3 (2× CH_{Ph}), 160.9 (C_i or C=O), 161.2 (C_i or C=O). Anal. Calcd for $C_{19}H_{27}NO_8$: C, 57.42; H, 6.85; N, 3.52. Found: C, 57.46; H, 6.88; N, 3.48.

Compound **34**: mp 187−189 °C (recrystallized from ethyl acetate); $[\alpha]_D^{24}$ +6.0 (*c* 0.20, CH_3OH); IR (neat) ν_{max} 3378, 2934, 1714, 1614, 1515, 1444, 1245, 1078, 1017 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 3.62–3.69 (m, 3H, H-3′ or H-4′, H-2′, H-5′), 3.73–3.74 (m, 1H, H-3′ or H-4′), 3.79–3.83 (m, 4H, H-5′, OCH_3), 4.06–4.11 (m, 3H, H-4, H-1′, NCH_2), 4.25–4.30 (m, 1H, H-5), 4.46 (dd, 1H, $J_{5,5}$=8.5 Hz, $J_{5,4}$=6.0 Hz, H-5), 4.77 (d, 1H, $J_{H,H}$=15.4 Hz, NCH_2), 6.90–6.92 (m, 2H, Ph), 7.25–7.27 (m, 2H, Ph); ^{13}C NMR (100 MHz, CD_3OD): δ 45.7 (NCH_2), 55.8 (OCH_3), 57.2 (C-4), 63.9 (C-5), 65.1 (C-5′), 67.1 (C-1′), 70.8 (C-2′ or C-3′ or C-4′), 71.4 (C-2′ or C-3′ or C-4′), 72.9 (C-2′ or C-3′ or C-4′), 115.3 (2× CH_{Ph}), 129.3 (C_i), 130.5 (2× CH_{Ph}), 160.9 (C_i), 161.5 (C=O). Anal. Calcd for $C_{16}H_{23}NO_8$: C, 53.78; H, 6.49; N, 3.92. Found: C, 53.81; H, 6.53; N, 3.88.

4.22. (4*S*)-4-[(1′*R*,2′*S*,3′*Z*)-1′,2′-(Isopropylidenedioxy)hexadec-3′-en-1′-yl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (35a) and (4*S*)-4-[(1′*R*,2′*S*,3′*E*)-1′,2′-(isopropylidenedioxy)hexadec-3′-en-1′-yl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (35b)

To a solution of **10** (1.57 g, 3.95 mmol) in CH_3OH (9 mL) was added $NaIO_4$ (2.12 g, 9.91 mmol) in water (9 mL). After stirring at room temperature for 1 h, the mixture was diluted with CH_2Cl_2 (10 mL), the solid parts were filtered off, the solvent was evaporated in vacuo, and the obtained crude aldehyde was immediately used in the next reaction without further purification.

To a solution of 1,1,1,3,3,3-hexamethyldisilazane (2.35 mL, 11.06 mmol) in dry THF (11.7 mL) was added *n*-BuLi (6.91 mL, 11.06 mmol, a 1.6 M solution in *n*-hexane) at room temperature. The solution of hexamethyldisilazide (LHMDS) thus generated was treated with the known salt **12**[6p−r,9] (4.36 g, 8.30 mmol), and the resulting dark mixture was stirred for 5 min at the same temperature. Then, a solution of the obtained aldehyde (1.32 g, 3.94 mmol) in dry THF (11.7 mL) was added. After stirring for 1 h, the mixture was poured into a saturated NH_4Cl solution (70 mL), and the aqueous phase was washed with EtOAc (2×100 mL). The combined organic layers were dried over Na_2SO_4, stripped solvent, and the residue was purified by flash chromatography on silica gel (hexane/ethyl acetate, 5:1) to afford 1.47 g (74%) of a mixture of geometrical isomers **35**. Repeated chromatography (hexane/ethyl acetate, 5:1) of a small amount of such mixture furnished each diastereoisomer in pure form as colourless oils.

Alkene (*Z*)-**35a**: $[\alpha]_D^{22}$ +43.6 (*c* 0.22, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.8 Hz, CH_3), 1.26–1.36 (m, 20H, 10× CH_2), 1.37 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.93–2.02 (m, 1H, H-5′), 2.09–2.18 (m, 1H, H-5′), 3.65–3.75 (m, 2H, H-4, H-5), 3.80 (s, 3H, OCH_3), 4.09–4.14 (m, 1H, H-5), 4.29 (dd, 1H, $J_{4,1'}$=9.0 Hz, $J_{2',1'}$=6.6 Hz, H-1′), 4.38 (d, 1H, $J_{H,H}$=14.7 Hz, NCH_2), 4.79 (d, 1H, $J_{H,H}$=14.7 Hz, NCH_2), 4.92–4.96 (m, 1H, H-2′), 5.23–5.28 (m, 1H, H-3′), 5.57–5.63 (m, 1H, H-4′), 6.84–6.87 (m, 2H, Ph), 7.27–7.29 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.6 (CH_2), 25.1 (CH_3), 27.5 (C-5′), 27.9 (CH_3), 29.3 (2× CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (4× CH_2), 31.9 (CH_2), 46.7 (NCH_2), 54.0 (C-4), 55.2 (OCH_3), 63.6 (C-5), 72.2 (C-2′), 81.7 (C-1′), 109.8 (C_q), 113.9 (2× CH_{Ph}), 124.3 (C-3′), 128.6 (C_i), 130.0 (2× CH_{Ph}), 136.2 (C-4′), 158.3 (C=O), 159.2 (C_i). Anal. Calcd for $C_{30}H_{47}NO_5$: C, 71.82; H, 9.44; N, 2.79. Found: C, 71.86; H, 9.48; N, 2.83.

Alkene (*E*)-**35b**: $[\alpha]_D^{24}$ +38.3 (*c* 0.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.9 Hz, CH_3), 1.23–1.30 (m, 20H, 10× CH_2), 1.35 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.94–2.05 (m, 2H, 2× H-5′), 3.69 (dt, 1H, $J_{4,1'}$=9.2 Hz, $J_{5,4}$=9.2 Hz, $J_{5,4}$=6.2 Hz, H-4), 3.81–3.85 (m, 4H, H-5, OCH_3), 4.08–4.13 (m, 1H, H-5), 4.28 (dd, 1H, $J_{4,1'}$=9.2 Hz, $J_{2',1'}$=6.6 Hz, H-1′), 4.39 (d, 1H, $J_{H,H}$=14.7 Hz, NCH_2), 4.53 (dd, 1H, $J_{3',2'}$=9.2 Hz, $J_{2',1'}$=6.6 Hz, H-2′), 4.78 (d, 1H, $J_{H,H}$=14.7 Hz, NCH_2), 5.26 (ddt, 1H, $J_{4',3'}$=15.2 Hz, $J_{3',2'}$=9.2 Hz, $J_{5',3'}$=1.2 Hz, $J_{5',3'}$=1.2 Hz, H-3′), 5.72 (dt, 1H, $J_{4',3'}$=15.2 Hz, $J_{5',4'}$=6.8 Hz, $J_{5',4'}$=6.8 Hz, H-4′), 6.85–6.89 (m, 2H, Ph), 7.28–7.31 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 25.1 (CH_3), 27.8 (CH_3), 28.9 (CH_2), 29.3 (2× CH_2), 29.4 (CH_2), 29.6 (4× CH_2), 31.9 (CH_2), 32.3 (C-5′), 46.6 (NCH_2), 54.2 (C-4), 55.3 (OCH_3), 63.5 (C-5), 78.6 (C-2′), 81.5 (C-1′), 109.7 (C_q), 113.9 (2× CH_{Ph}), 124.8 (C-3′), 128.6 (C_i), 130.1 (2× CH_{Ph}), 138.1 (C-4′), 158.4 (C_i or C=O), 159.2 (C_i or C=O). Anal. Calcd for $C_{30}H_{47}NO_5$: C, 71.82; H, 9.44; N, 2.79. Found: C, 71.86; H, 9.40; N, 2.81.

4.23. (4*R*)-4-[(1′*R*,2′*S*,3′*Z*)-1′,2′-(Isopropylidenedioxy)hexadec-3′-en-1′-yl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (36a) and (4*R*)-4-[(1′*R*,2′*S*,3′*E*)-1′,2′-(isopropylidenedioxy)hexadec-3′-en-1′-yl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (36b)

According to the same procedure described for the preparation of **35**, compound **11** (2.0 g, 5.03 mmol) was converted into a mixture of olefins **36** (1.79 g, 71%, hexane/ethyl acetate, 5:1). Repeated chromatography on silica gel (hexane/ethyl acetate, 5:1) afforded only (*Z*)-**36a** in pure form as white crystals.

Alkene (*Z*)-**36a**: mp 45−46 °C (recrystallized from *n*-hexane); $[\alpha]_D^{24}$ +50.8 (*c* 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.8 Hz, CH_3), 1.20–1.31 (m, 20H, 10× CH_2), 1.38 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.62–1.69 (m, 1H, H-5′), 1.84–1.91 (m, 1H, H-5′), 3.46 (ddd, 1H, $J_{5,4}$=8.9 Hz, $J_{5,4}$=5.2 Hz, $J_{4,1'}$=1.6 Hz, H-4), 3.79 (s, 3H,

OCH_3), 4.04 (d, 1H, $J_{H,H}$=15.2 Hz, 1H, NCH_2), 4.10–4.15 (m, 1H, H-5), 4.29 (dd, 1H, $J_{5,5}$=8.6 Hz, $J_{5,4}$=5.2 Hz, H-5), 4.40 (dd, 1H, $J_{2',1'}$=7.7 Hz, $J_{4,1'}$=1.6 Hz, H-1′), 4.86 (d, 1H, $J_{H,H}$=15.2 Hz, 1H, NCH_2), 4.98–5.02 (m, 1H, H-2′), 5.11–5.16 (m, 1H, H-3′), 5.53 (dddd, 1H, $J_{4',3'}$=10.9 Hz, $J_{5',4'}$=8.2 Hz, $J_{5',4'}$=6.7 Hz, $J_{4',2'}$=1.5 Hz, H-4′), 6.84–6.87 (m, 2H, Ph), 7.18–7.21 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 24.3 (CH_3), 26.3 (CH_3), 28.4 (C-5′), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.6 (3× CH_2), 29.7 (CH_2), 31.9 (CH_2), 45.2 (NCH_2), 54.7 (C-4), 55.2 (OCH_3), 62.9 (C-5), 72.8 (C-2′), 73.6 (C-1′), 109.0 (C_q), 114.2 (2× CH_{Ph}), 124.6 (C-3′), 127.6 (C_i), 129.4 (2× CH_{Ph}), 135.6 (C-4′), 158.4 (C=O), 159.3 (C_i). Anal. Calcd for $C_{30}H_{47}NO_5$: C, 71.82; H, 9.44; N, 2.79. Found: C, 71.85; H, 9.41; N, 2.82.

4.24. (4*S*)-4-[(1′*R*,2′*S*)-1′,2′-(Isopropylidenedioxy)hexadecyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (37)

To a solution of the mixture of olefins **35** (1.47 g, 2.93 mmol) in EtOH (23 mL) was added 10% Pd/C (0.207 g). The resulting mixture was stirred for 30 min at room temperature under an atmosphere of hydrogen and then filtered through a pad of Celite. Evaporating of the solvent and chromatography on silica gel (hexane/ethyl acetate, 5:1) gave 1.39 g (94%) of compound **37** as a colourless oil; $[\alpha]_D^{26}$ −23.2 (*c* 0.22, $CHCl_3$); IR (neat) ν_{max} 2922, 2852, 1752, 1612, 1513, 1242, 1174, 1069 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.8 Hz, CH_3), 1.24–1.30 (m, 26H, 13× CH_2), 1.34 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 3.72 (dt, 1H, $J_{4,1'}$=9.0 Hz, $J_{5,4}$=9.0 Hz, $J_{5,4}$=5.8 Hz, H-4), 3.80 (s, 3H, OCH_3), 3.89 (dd, 1H, $J_{5,5}$=8.9 Hz, $J_{5,4}$=5.8 Hz, H-5), 4.07–4.12 (m, 1H, H-2′), 4.20–4.27 (m, 2H, H-5, H-1′), 4.40 (d, 1H, $J_{H,H}$=14.7 Hz, NCH_2), 4.80 (d, 1H, $J_{H,H}$=14.7 Hz, NCH_2), 6.85–6.88 (m, 2H, Ph), 7.27–7.29 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 25.7 (CH_3), 25.9 (CH_2), 28.2 (CH_3), 29.3 (CH_2), 29.4 (CH_2), 29.5 (2× CH_2), 29.6 (6× CH_2), 31.9 (CH_2), 46.8 (NCH_2), 53.7 (C-4), 55.2 (OCH_3), 63.7 (C-5), 76.7 (C-2′), 81.0 (C-1′), 109.2 (C_q), 113.9 (2× CH_{Ph}), 128.6 (C_i), 130.0 (2× CH_{Ph}), 158.2 (C=O), 159.2 (C_i). Anal. Calcd for $C_{30}H_{49}NO_5$: C, 71.53; H, 9.80; N, 2.78. Found: C, 71.56; H, 9.84; N, 2.81.

4.25. (4*R*)-4-[(1′*R*,2′*S*)-1′,2′-(Isopropylidenedioxy)hexadecyl]-3-(*p*-methoxybenzyl)oxazolidin-2-one (38)

Using the same procedure as described for the preparation of **37**, a mixture of alkenes **36** (1.79 g, 3.57 mmol) was hydrogenated (10% Pd/C) and furnished after flash chromatography on silica gel (hexane/ethyl acetate, 5:1) 1.60 g (89%) of derivative **38** as white crystals; mp 33–34 °C (recrystallized from Et_2O); $[\alpha]_D^{22}$ +29.3 (*c* 0.42, $CHCl_3$); IR (neat) ν_{max} 2919, 2850, 1725, 1612, 1513, 1240, 1030 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.9 Hz, CH_3), 1.14–1.32 (m, 26H, 13× CH_2), 1.35 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 3.50–3.54 (m, 1H, H-4), 3.80 (s, 3H, OCH_3), 4.04 (d, 1H, $J_{H,H}$=15.3 Hz, NCH_2), 4.14–4.22 (m, 2H, H-5, H-2′), 4.27 (dd, 1H, $J_{2',1'}$=7.1 Hz, $J_{4,1'}$=1.7 Hz, H-1′), 4.41 (dd, 1H, $J_{5,5}$=8.6 Hz, $J_{5,4}$=4.9 Hz, H-5), 4.88 (d, 1H, $J_{H,H}$=15.3 Hz, 1H, NCH_2), 6.86–6.90 (m, 2H, Ph), 7.19–7.22 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 24.6 (CH_3), 26.4 (CH_3), 26.9 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (2× CH_2), 29.6 (5× CH_2), 29.9 (CH_2), 31.9 (CH_2), 45.1 (NCH_2), 54.5 (C-4), 55.3 (OCH_3), 63.0 (C-5), 73.1 (C-1′), 76.2 (C-2′), 108.4 (C_q), 114.2 (2× CH_{Ph}), 127.7 (C_i), 129.2 (2× CH_{Ph}), 158.4 (C=O), 159.3 (C_i). Anal. Calcd for $C_{30}H_{49}NO_5$: C, 71.53; H, 9.80; N, 2.78. Found: C, 71.56; H, 9.77; N, 2.82.

4.26. (4*S*)-4-[(1′*R*,2′*S*)-1′,2′-Dihydroxyhexadecyl]oxazolidin-2-one (8)

CAN (5.30 g, 9.67 mmol) was added to a solution of **37** (1.39 g, 2.76 mmol) in CH_3CN (9.6 mL) and water (2.4 mL). After stirring for 20 min at room temperature, the mixture was diluted with a small volume of EtOAc, poured into a saturated NaCl solution (12 mL), and the aqueous phase was then washed with EtOAc (2×20 mL). The combine organic layers were dried over Na_2SO_4, the solvent was taken down, and the residue was subjected to flash chromatography through a short silica gel column (hexane/ethyl acetate, 1:2) to afford 0.68 g (72%) of compound **8** as white crystals; mp 110–112 °C (recrystallized from *n*-hexane and ethyl acetate); $[\alpha]_D^{25}$ +17.3 (*c* 0.30, CH_3OH); IR (neat) ν_{max} 3334, 2916, 2849, 1774, 1471, 1417, 1056, 1035 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ 0.89 (t, 3H, *J*=6.9 Hz, CH_3), 1.28 (m, 24H, 11× CH_2, *H*–CH, H-3′), 1.52–1.56 (m, 1H, *H*–CH), 1.73–1.78 (m, 1H, H-3′), 3.18 (dd, 1H, $J_{4,1'}$=8.1 Hz, $J_{2',1'}$=4.1 Hz, H-1′), 3.39–3.43 (m, 1H, H-2′), 4.10–4.15 (m, 1H, H-4), 4.28 (dd, 1H, $J_{5,5}$=8.7 Hz, $J_{5,4}$=6.3 Hz, H-5), 4.45–4.49 (m, 1H, H-5); ^{13}C NMR (100 MHz, CD_3OD): δ 14.5 (CH_3), 23.8 (CH_2), 26.6 (CH_2), 30.5 (CH_2), 30.8 (7× CH_2), 30.9 (CH_2), 33.1 (CH_2), 35.2 (C-3′), 55.9 (C-4), 69.2 (C-5), 73.7 (C-2′), 76.4 (C-1′), 162.8 (C=O). Anal. Calcd for $C_{19}H_{37}NO_4$: C, 66.43; H, 10.86; N, 4.08. Found: C, 66.46; H, 10.90; N, 4.12.

4.27. (4*R*)-4-[(1′*R*,2′*S*)-1′,2′-Dihydroxyhexadecyl]oxazolidin-2-one (9)

Using the same procedure as described for the preparation of **8**, compound **38** (1.60 g, 3.18 mmol) and CAN (6.10 g, 11.13 mmol) afforded after stirring (3 h) and flash chromatography on silica gel (hexane/ethyl acetate, 1:3) 0.65 g (60%) of derivative **9** as white crystals; mp 118–120 °C (recrystallized from *n*-hexane and ethyl acetate); $[\alpha]_D^{25}$ −5.0 (*c* 0.22, CH_3OH); IR (neat) ν_{max} 3293, 2915, 2849, 1736, 1470, 1418, 1076, 1014 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ 0.89 (t, 3H, *J*=6.8 Hz, CH_3), 1.28 (m, 24H, 11× CH_2, *H*–CH, H-3′), 1.51–1.55 (m, 1H, H–CH), 1.62–1.70 (m, 1H, H-3′), 3.40 (m, 2H, H-1′, H-2′), 4.08–4.12 (m, 1H, H-4), 4.36–4.40 (m, 1H, H-5), 4.45 (dd, 1H, $J_{5,5}$=8.7 Hz, $J_{5,4}$=6.0 Hz, H-5); ^{13}C NMR (100 MHz, CD_3OD): δ 14.5 (CH_3), 23.8 (CH_2), 26.7 (CH_2), 30.5 (CH_2), 30.8 (7× CH_2), 30.9 (CH_2), 33.1 (CH_2), 34.8 (C-3′), 55.5 (C-4), 67.3 (C-5), 73.7 (C-1′), 75.7 (C-2′), 162.8 (C=O). Anal. Calcd for $C_{19}H_{37}NO_4$: C, 66.43; H, 10.86; N, 4.08. Found: C, 66.47; H, 10.82; N, 4.11.

4.28. (2*S*,3*R*,4*S*)-4-Amino-2-tetradecyltetrahydrofuran-3-ol hydrochloride (7·HCl)

Compound **8** (0.68 g, 1.98 mmol) was treated with a 6 M aqueous HCl solution (90 mL), and the resulting mixture was stirred and heated at 120 °C for 2 h. After cooling to room temperature, the solvent was evaporated in vacuo, and the residue was diluted with Et_2O. The solid part was filtered off and dried on a pump for 10 h at room temperature. This procedure yielded 0.525 g (79%) of compound **7·HCl** as a white amorphous solid; $[\alpha]_D^{24}$ +9.0 (*c* 0.21, CH_3OH); IR (neat) ν_{max} 3464, 2914, 2849, 1471, 1061, 1007, 718 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ 0.87 (t, 3H, *J*=6.8 Hz, CH_3), 1.26–1.52 (m, 24H, 12× CH_2), 1.56–1.74 (m, 2H, 2× H-1′), 3.48–3.52 (m, 1H, H-2), 3.54–3.57 (m, 1H, H-4), 3.78 (dd, 1H, $J_{3,2}$=6.4 Hz, $J_{4,3}$=3.4 Hz, H-3), 3.83 (dd, 1H, $J_{1,1}$=10.7 Hz, $J_{2,1}$=2.9 Hz, H-5), 3.99 (dd, 1H, $J_{1,1}$=10.7 Hz, $J_{2,1}$=6.0 Hz, H-5); ^{13}C NMR (100 MHz, CD_3OD): δ 14.5 (CH_3), 23.8 (CH_2), 27.2 (CH_2), 30.5 (CH_2), 30.7 (CH_2), 30.8 (6× CH_2), 33.1 (CH_2), 33.9 (C-1′), 60.2 (C-4), 69.7 (C-5), 80.5 (C-3), 86.7 (C-2); ^{1}H NMR (600 MHz, CD_3OD): δ 0.89 (t, 3H, *J*=7.0 Hz, CH_3), 1.28–1.43 (m, 23H, 11× CH_2, *H*–CH), 1.46–1.53 (m, 1H, *H*–CH), 1.58–1.64 (m, 1H, H-1′), 1.68–1.74 (m, 1H, H-1′), 3.51 (ddd, 1H, $J_{2,1'}$=8.3 Hz, $J_{3,2}$=6.4 Hz, $J_{2,1'}$=4.7 Hz, H-2), 3.56 (td, 1H, $J_{5,4}$=6.3 Hz, $J_{5,4}$=3.2 Hz, $J_{4,3}$=3.2 Hz, H-4), 3.76 (dd, 1H, $J_{3,2}$=6.4 Hz, $J_{4,3}$=3.5 Hz, H-3), 3.82 (dd, 1H, $J_{5,5}$=10.7 Hz, $J_{5,4}$=3.0 Hz, H-5), 4.00 (dd, 1H, $J_{5,5}$=10.7 Hz, $J_{5,4}$=6.1 Hz, H-5); ^{13}C NMR (150 MHz, CD_3OD): δ 14.5 (CH_3), 23.8 (CH_2), 27.2 (CH_2), 30.5 (CH_2), 30.7 (2× CH_2), 30.8 (6× CH_2), 33.1 (CH_2), 33.9 (C-1′), 60.2 (C-4), 69.7 (C-5), 80.6 (C-3), 86.8 (C-2). Anal. Calcd for $C_{18}H_{38}ClNO_2$: C, 64.35; H, 11.40; N, 4.17. Found: C, 64.40; H, 11.44; N, 4.11.

4.29. (2*S*,3*R*,4*R*)-4-Amino-2-tetradecyltetrahydrofuran-3-ol hydrochloride (*ent*-**6**·HCl)

According to the same procedure described for the preparation of **7**·**HCl**, compound **9** (0.65 g, 1.98 mmol) was converted into *ent*-**6**·**HCl** (0.495 g, 78%, white amorphous solid); $[\alpha]_D^{22}$ −29.6 (*c* 0.48, CH_3OH); IR (neat) ν_{max} 3298, 3056, 2915, 2849, 1510, 1469, 1052, 1021, 556 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 0.87 (t, 3H, *J*=6.8 Hz, CH_3), 1.26–1.52 (m, 25H, 12× CH_2, H-1′), 1.56–1.63 (m, 1H, H-1′), 3.65–3.74 (m, 3H, H-5, H-4, H-2), 4.00–4.03 (m, 1H, H-3), 4.11–4.16 (m, 1H, H-5); ^{13}C NMR (100 MHz, CD_3OD): δ 14.5 (CH_3), 23.8 (CH_2), 26.9 (CH_2), 30.5 (CH_2), 30.7 (CH_2), 30.8 (7× CH_2), 33.1 (CH_2), 34.1 (C-1′), 53.7 (C-4), 69.4 (C-5), 74.4 (C-3), 85.2 (C-2); ^1H NMR (600 MHz, CD_3OD): δ 0.89 (t, 3H, *J*=6.9 Hz, CH_3), 1.28–1.39 (m, 23H, 11× CH_2, *H*–CH), 1.43–1.53 (m, 2H, H-1′, *H*–CH), 1.58–1.64 (m, 1H, H-1′), 3.67–3.74 (m, 3H, H-5, H-4, H-2), 4.01 (m, 1H, H-3), 4.13 (dd, 1H, $J_{5,5}$=9.0 Hz, $J_{5,4}$=5.3 Hz, H-5). Anal. Calcd for $C_{18}H_{38}ClNO_2$: C, 64.35; H, 11.40; N, 4.17. Found: C, 64.31; H, 11.45; N, 4.21.

4.30. *tert*-Butyl [(3*S*,4*R*,5*S*)-4-hydroxy-5-tetradecyltetrahydrofuran-3-yl]carbamate (39)

Et_3N (0.05 mL, 0.36 mmol) followed by di-*tert*-butyl dicarbonate (68 mg, 0.31 mmol) was added to an emulsion of **7**·**HCl** (0.10 g, 0.298 mmol) in THF (2.2 mL). After stirring at room temperature for 1 h, the solvent was evaporated in vacuo, and the residue was chromatographed through a short silica gel column (hexane/ethyl acetate, 5:1) to provide 107 mg (90%) of crystalline compound **39**; mp 94–95 °C (recrystallized from *n*-hexane); $[\alpha]_D^{25}$ −28.1 (*c* 0.21, $CHCl_3$), [lit.[5a] mp 94–96 °C, $[\alpha]_D^{25}$ −31.7 (*c* 1.09, $CHCl_3$), lit.[8e] mp 94–96 °C, $[\alpha]_D^{25}$ −30.2 (*c* 1.3, $CHCl_3$)]; IR (neat) ν_{max} 3345, 2915, 2848, 1685, 1525, 1168 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.8 Hz, CH_3), 1.25 (s, 24H, 12× CH_2), 1.45 (s, 9H, 3× CH_3), 1.53–1.68 (m, 2H, 2× H-1′), 3.60–3.67 (m, 3H, H-2, H-5, OH), 3.77–3.78 (m, 1H, H-3), 3.92–3.93 (m, 1H, H-4), 4.05 (dd, 1H, $J_{5,5}$=9.5 Hz, $J_{5,4}$=6.6 Hz, H-5), 4.82 (d, 1H, $J_{4,NH}$=3.8 Hz, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 25.9 (CH_2), 28.3 (3× CH_3), 29.4 (CH_2), 29.5 (CH_2), 29.6 (4× CH_2), 29.7 (3× CH_2), 31.9 (CH_2), 33.7 (C-1′), 60.3 (C-4), 70.3 (C-5), 80.3 (C_q), 82.7 (C-3), 84.9 (C-2), 156.5 (C=O), for numbering of the protons and carbons in these NMR spectra, see Scheme 1. Anal. Calcd for $C_{23}H_{45}NO_4$: C, 69.13; H, 11.35; N, 3.51. Found: C, 69.17; H, 11.38; N, 3.54.

4.31. *tert*-Butyl [(3*R*,4*R*,5*S*)-4-hydroxy-5-tetradecyltetrahydrofuran-3-yl]carbamate (40)

Using the same procedure as described for the preparation of **39**, compound *ent*-**6**·**HCl** (0.10 g, 0.298 mmol), Et_3N (0.05 mL, 0.36 mmol) and Boc_2O (68 mg, 0.31 mmol) afforded after stirring (1 h) and flash chromatography on silica gel (hexane/ethyl acetate, 5:1) 99 mg (83%) of derivative **40** as white crystals; mp 87–89 °C (recrystallized from *n*-hexane); $[\alpha]_D^{25}$ −10.0 (*c* 0.23, $CHCl_3$), [lit.[5b] mp 80–81 °C, $[\alpha]_D^{25}$ −7.76 (*c* 0.29, $CHCl_3$)]; IR (neat) ν_{max} 3365, 2918, 2848, 1691, 1526, 1467, 1169 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.8 Hz, CH_3), 1.25–1.32 (m, 24H, 12× CH_2), 1.45 (s, 9H, 3× CH_3), 1.51–1.58 (m, 2H, 2× H-1′), 2.33 (br s, 1H, OH), 3.48–3.53 (m, 1H, H-5), 3.69–3.73 (m, 1H, H-2), 3.93 (m, 1H, H-3), 4.11–4.15 (m, 2H, H-4, H-5), 5.01 (d, 1H, $J_{4,NH}$=6.6 Hz, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 25.8 (CH_2), 28.3 (3× CH_3), 29.4 (CH_2), 29.5 (CH_2), 29.6 (2× CH_2), 29.7 (3× CH_2), 29.8 (2× CH_2), 31.9 (CH_2), 33.6 (C-1′), 53.0 (C-4), 70.3 (C-5), 74.9 (C-3) 80.0 (C_q), 85.2 (C-2), 156.0 (C=O), for numbering of the protons and carbons in these NMR spectra, see Scheme 1. Anal. Calcd for $C_{23}H_{45}NO_4$: C, 69.13; H, 11.35; N, 3.51. Found: C, 69.19; H, 11.38; N, 3.47.

4.32. (2*S*,3*R*,4*S*)-4-Acetamido-2-tetradecyltetrahydrofuran-3-yl acetate (41)

To a solution of **7**·**HCl** (0.10 g, 0.298 mmol) in pyridine (9.5 mL) were successively added Ac_2O (0.56 mL, 5.96 mmol) and DMAP (18.2 mg, 0.149 mmol). After stirring at room temperature for 15 h, the reaction mixture was concentrated and co-evaporated three times with toluene. The obtained residue was subjected to flash chromatography on silica gel (hexane/ethyl acetate, 1:1) to give 105 mg (92%) of crystalline compound **41**; mp 70–71 °C (recrystallized from *n*-hexane); $[\alpha]_D^{25}$ −11.9 (*c* 0.21, $CHCl_3$), [lit.[8e] thick syrup, $[\alpha]_D^{25}$ +11.2 (*c* 1.1, $CHCl_3$)]; IR (neat) ν_{max} 3304, 2918, 2850, 1743, 1655, 1546 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.8 Hz, CH_3), 1.25–1.48 (m, 24H, 12× CH_2), 1.52–1.61 (m, 1H, H-1′), 1.67–1.75 (m, 1H, H-1′), 1.99 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 3.69–3.73 (m, 1H, H-2), 3.77 (dd, 1H, $J_{5,5}$=9.8 Hz, $J_{5,4}$=3.1 Hz, H-5), 4.07 (dd, 1H, $J_{5,5}$=9.8 Hz, $J_{5,4}$=5.6 Hz, H-5), 4.27–4.32 (m, 1H, H-4), 4.72 (dd, 1H, $J_{3,2}$=4.9 Hz, $J_{4,3}$=2.6 Hz, 1H, H-3), 5.65 (br d, 1H, $J_{4,NH}$=4.9 Hz, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 20.9 (CH_3), 22.7 (CH_2), 23.1 (CH_3), 25.9 (CH_2), 29.3 (CH_2), 29.5 (2× CH_2), 29.6 (4× CH_2), 29.7 (2× CH_2), 31.9 (CH_2), 33.4 (C-1′), 56.5 (C-4), 71.8 (C-5), 81.8 (C-3), 83.0 (C-2), 170.0 (C=O), 170.7 (C=O); ^1H NMR (600 MHz, CD_3OD): δ 0.89 (t, 3H, *J*=7.1 Hz, CH_3), 1.28–1.37 (m, 23H, 12× CH_2, *H*–CH), 1.41–1.47 (m, 1H, *H*–CH), 1.58–1.71 (m, 2H, 2× H-1′), 1.93 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 3.68–3.71 (m, 1H, H-2), 3.76 (dd, 1H, $J_{5,5}$=9.7 Hz, $J_{5,4}$=3.3 Hz, H-5), 3.96 (dd, 1H, $J_{5,5}$=9.7 Hz, $J_{5,4}$=5.9 Hz, H-5), 4.22 (td, 1H, $J_{5,4}$=5.9 Hz, $J_{5,4}$=3.0 Hz, $J_{4,3}$=3.0 Hz, H-4), 4.80 (dd, 1H, $J_{3,2}$=4.2 Hz, $J_{4,3}$=2.7 Hz, H-3); ^{13}C NMR (150 MHz, CD_3OD): δ 14.5 (CH_3), 20.9 (CH_3), 22.4 (CH_3), 23.8 (CH_2), 27.0 (CH_2), 30.5 (CH_2), 30.6 (CH_2), 30.7 (2× CH_2), 30.8 (4× CH_2), 30.9 (CH_2), 33.1 (CH_2), 34.1 (C-1′), 57.8 (C-4), 71.8 (C-5), 83.3 (C-3), 85.2 (C-2), 172.0 (C=O), 173.3 (C=O). Anal. Calcd for $C_{22}H_{41}NO_4$: C, 68.89; H, 10.77; N, 3.65. Found: C, 68.93; H, 10.81; N, 3.62.

4.33. (2*S*,3*R*,4*R*)-4-Acetamido-2-tetradecyltetrahydrofuran-3-yl acetate (42)

According to the same procedure described for the preparation of **41**, compound *ent*-**6**·**HCl** (0.10 g, 0.298 mmol), Ac_2O (0.56 mL, 5.96 mmol) and DMAP (18.2 mg, 0.149 mmol) in pyridine (9.5 mL) gave after stirring (1 h) and flash chromatography on silica gel (hexane/ethyl acetate, 1:2) 107 mg (94%) of derivative **42** as white crystals; mp 75–76 °C (recrystallized from *n*-hexane); $[\alpha]_D^{24}$ +17.7 (*c* 0.13, $CHCl_3$), [for *ent*-**42**: lit.[21] mp 72–73 °C, $[\alpha]_D^{22}$ −15.4 (*c* 1.0, $CHCl_3$), lit.[6g] mp not reported, $[\alpha]_D^{26}$ −15.1 (*c* 1.2, $CHCl_3$), lit.[22] mp 65–67 °C, $[\alpha]_D^{21}$ −14.6 (*c* 0.5, $CHCl_3$)]; IR (neat) ν_{max} 3290, 2915, 2847, 1733, 1650, 1561, 1375, 1232 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, *J*=6.8 Hz, CH_3), 1.25–1.45 (m, 24H, 12× CH_2), 1.49–1.72 (m, 2H, 2× H-1′), 2.01 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 3.50–3.54 (m, 1H, H-5), 3.84–3.88 (m, 1H, H-2), 4.18 (dd, 1H, $J_{5,5}$=8.4 Hz, $J_{5,4}$=7.2 Hz, H-5), 4.62–4.69 (m, 1H, H-4), 4.91 (dd, 1H, $J_{4,3}$=5.9 Hz, $J_{3,2}$=2.6 Hz, H-3), 5.65 (br d, 1H, $J_{4,NH}$=7.9 Hz, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1 (CH_3), 21.0 (CH_3), 22.7 (CH_2), 23.3 (CH_3), 25.5 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (4× CH_2), 29.7 (2× CH_2), 31.9 (CH_2), 33.5 (C-1′), 49.8 (C-4), 69.8 (C-5), 76.7 (C-3), 84.1 (C-2), 169.8 (C=O), 169.9 (C=O); ^1H NMR (600 MHz, CD_3OD): δ 0.89 (t, 3H, *J*=7.0 Hz, CH_3), 1.28–1.45 (m, 24H, 12× CH_2), 1.51–1.62 (m, 2H, 2× H-1′), 1.94 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 3.57 (t, 1H, $J_{5,5}$=8.7 Hz, $J_{5,4}$=8.7 Hz, H-5), 3.85 (ddd, 1H, $J_{2,1'}$=8.0 Hz, $J_{2,1'}$=5.6 Hz, $J_{3,2}$=3.5 Hz, H-2), 4.07 (m, 1H, H-5), 4.53 (m, 1H, H-4), 4.94 (dd, 1H, $J_{4,3}$=6.0 Hz, $J_{3,2}$=3.4 Hz, H-3); ^{13}C NMR (150 MHz, CD_3OD): δ 14.5 (CH_3), 20.8 (CH_3), 22.4 (CH_3), 23.8 (CH_2), 26.7 (CH_2), 30.5 (CH_2), 30.6 (CH_2), 30.7 (2× CH_2), 30.8 (4× CH_2), 30.9 (CH_2), 33.1 (CH_2), 34.7 (C-1′), 51.6 (C-4), 70.1 (C-5), 77.2 (C-3), 84.8 (C-2), 171.8 (C=O), 173.5 (C=O). Anal. Calcd

for $C_{22}H_{41}NO_4$: C, 68.89; H, 10.77; N, 3.65. Found: C, 68.92; H, 10.81; N, 3.62.

4.34. Triphenyl(tridecyl)phosphonium bromide (12)

To a solution of 1-bromotridecane (2.87 g, 10.9 mmol) in dry toluene (9 mL) was added Ph_3P (3.43 g, 13.08 mmol), and the resulting mixture was stirred and heated at reflux for 26 h. After cooling to room temperature, the solvent was evaporated in vacuo, the solid material was washed repeatedly with Et_2O to remove Ph_3P and then chromatographed on silica gel (CH_2Cl_2/MeOH, 20:1) to afford 4.87 g (85%) of compound **12** as a white solid; mp 79–80 °C (recrystallized from *n*-hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, 3H, J=6.9 Hz, CH_3), 1.19–1.30 (m, 18H, 9× CH_2), 1.62–1.63 (m, 4H, 2× CH_2), 3.70–3.77 (m, 2H, CH_2), 7.70–7.74 (m, 6H, Ph), 7.79–7.87 (m, 9H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0 (CH_3), 22.5 (CH_2), 22.9 (CH_2), 29.1 (2× CH_2), 29.2 (CH_2), 29.4 (2× CH_2), 29.5 (2× CH_2), 30.2 (CH_2), 30.4 (CH_2), 31.7 (CH_2), 117.8 (2× C_i), 118.6 (C_i), 130.3 (3× CH_{Ph}), 130.4 (3× CH_{Ph}), 133.5 (3× CH_{Ph}), 133.6 (3× CH_{Ph}), 134.9 (3× CH_{Ph}). Anal. Calcd for $C_{31}H_{42}BrP$: C, 70.85; H, 8.06. Found: C, 70.89; H, 8.00.

4.35. X-ray techniques

Single crystals of **26** suitable for X-ray diffraction were obtained from *n*-hexane by slow evaporation at room temperature. The intensities were collected at 293 K on an Oxford Diffraction Gemini R CCD diffractometer using Mo Kα radiation (λ=0.71073 Å). Selected crystallographic and other relevant data for the compound **26** are listed in Table 3. The structure was solved by direct methods.[23] All non-hydrogen atoms were refined anisotropically by full-matrix least squares calculations based on F^2.[23] All hydrogen atoms were included in calculated positions as riding atoms, with SHELXL97[23] defaults. The PLATON[24] programme was used for structure analysis and molecular and crystal structure drawings.

Table 3
Crystal data and structure refinement parameters for compound **26**

26	
Empirical formula	$C_{20}H_{37}NO_7Si$
Formula weight	431.60
Temperature, T (K)	239(2)
Wavelength, λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	
a (Å)	15.7607(5)
b (Å)	9.5337(3) β=104.254(3)°
c (Å)	17.8434(6)
V (Å^3)	2598.57(15)
Formula per unit cell, Z	4
D_{calcd} (g/cm^3)	1.103
Absorption coefficient, μ (mm^{-1})	0.125
F(000)	936
Crystal size (mm)	0.7546×0.2925×0.1918
θ Range for data collection (o)	2.36–25.00
Index ranges	$-18\leq h\leq 18$
	$-11\leq k\leq 11$
	$-21\leq l\leq 21$
Independent reflections (*R*int)	9158 (0.0331)
Absorption correction	Analytical
Max. and min transmission	0.980 and 0.933
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9158/17/551
Goodness-of-fit on F^2	1.026
Final R indices [$I>2\sigma(I)$]	R_1=0.0690, wR_2=0.1829
R indices (all data)	R_1=0.0997, wR_2=0.2053
Largest diff. peak and hole (e/Å^{-3})	0.335 and −0.321
Extinction coefficient	0.0080(13)

4.36. Supplementary data

Complete crystallographic data for the structural analysis have been deposit with the Cambridge Crystallographic Data Centre, CCDC No. 886350. These data can be obtained free of charge from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or via: www.ccdc.cam.ac.uk).

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.07.028. These data include MOL files and InChiKeys of the most important compounds described in this article.

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