General and Asymmetric Synthesis of Protected 1,3,5-Triols with Pendant Functional Groups

Christoph Schneider* and Markus Rehfeuter[a]

Dedicated to Professor Armin de Meijere on the occasion of his 60th birthday

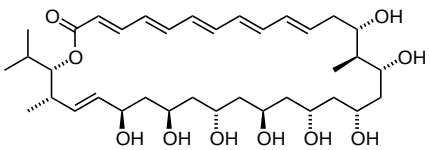
Abstract: A stereoselective synthesis of enantiomerically pure 1,3,5-triols of any configuration has been developed. These triols carry suitable functional groups at the termini of the chain which should allow for easy and efficient coupling of two building blocks. The silyloxy-Cope rearrangement of *syn*-aldols was used to prepare a common advanced intermediate for the synthesis of all four stereoisomeric triols. Three synthetic operations—an allylboration, an oxidative desilylation, and a conjugate addition reaction—were employed to assemble the target molecules. Their terminal double bond may either be cleaved to give the corresponding aldehydes or oxidized to the methyl ketones in a Wacker process to provide access to two subunits for a coupling reaction.

Keywords: antibiotics · asymmetric synthesis · Cope rearrangement · polyols · stereoselective synthesis

Introduction

Polyene macrolide antibiotics constitute a large group of over 200 natural products with potent antifungal and sometimes antiprotozoal activity. Some of them, most notably amphotericin B, are used extensively in clinics for the treatment of life-threatening fungal infections. Their antifungal activity rests on the damage of fungal membranes with consequent loss of ions, amino acids, and carbohydrates. Various mechanisms have been identified for this interaction, ranging from the formation of sterol-dependent ion channels to the mere rupture of the membrane.[1]

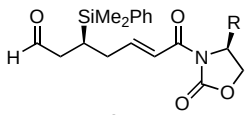
Structurally, polyene macrolide antibiotics, such as mycoticin A, are macrocyclic lactones which contain a polyene unit of up to seven, mostly conjugated, double bonds and a polyol fragment of up to nine secondary hydroxy groups, which are largely positioned in a 1,3-relationship. The lactone carbonyl



mycoticin A

group may be either part of the polyol fragment or it may be in conjugation with the polyene. From a synthetic point of view, the synthesis of the polyol section is more challenging on account of the chiral centers in the chain. Since the complete stereostructure of only a fraction of this class of natural products has been fully determined, synthetic studies in this area may also contribute to the structure elucidation of polyene macrolide antibiotics. Accordingly, the search for new stereoselective routes towards the synthesis of 1,3,5,..-polyol structures continues to be an area of intense research and has resulted in many impressive novel polyol syntheses in recent years.[2]

Recently, we established that silyloxy-Cope rearrangements of chiral *syn*-aldols proceed with high levels of stereocontrol[3] to furnish multifunctional products which have been successfully employed in the stereoselective synthesis of tetrahydropyrans,[4] piperidines,[5] terpenols,[6] and cyclohexanes.[7] A particular silyl-substituted Cope product **2** attracted our attention because it contains three masked hydroxy groups in the required 1,3,5-relationship. Allylboration of the



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aldehyde, oxidative desilylation of the phenyldimethylsilyl group, and an oxa-Michael addition at the conjugate double bond would give rise to a protected, but unmasked triol in a straightforward fashion.

The successful implementation of this strategy and its application towards a synthesis of the C1-C10-polyol fragment of nystatin A_1 was recently communicated.[8] Herein we

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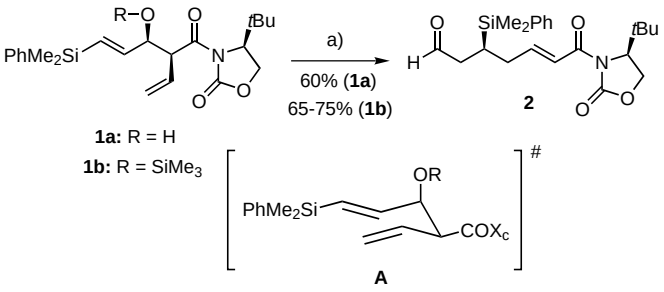
report on the extension of this methodology towards a general asymmetric synthesis of all four stereoisomeric and protected 1,3,5-triols **18a–d** (see Schemes 3 and 4). In addition, these triols carry suitable functional groups at the termini which may be used for the coupling of two subunits to give rise to larger polyol chains.

Results and Discussion

The requisite aldol product **1a** was regio- and stereoselectively prepared in 80–90% yield according to standard asymmetric aldol methodology.[9] Subsequent silylation with trimethylsilyl triflate and 2,6-lutidine gave rise to the silyl-protected aldol product **1b**. The silyloxy-Cope rearrangement of **1b** proceeded rapidly at 170 °C with a stereoselection of 6–8:1. After hydrolytic desilylation and chromatographic purification, the enantiopure 7-oxo-5-phenyldimethylsilyl-2-enimide **2** was obtained routinely in 65–75% yield as a single steroisomer (Scheme 1). Alternatively, the unprotected aldol

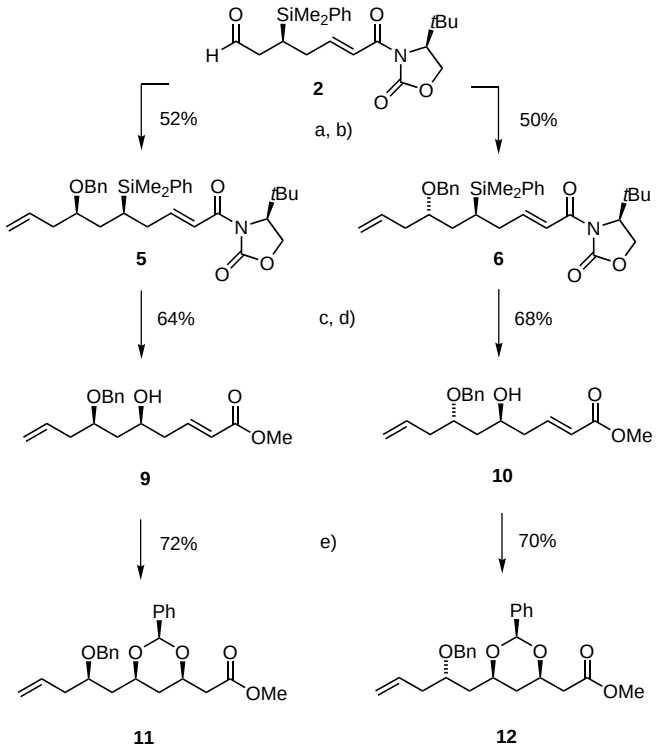


Scheme 1. Synthesis of **2**. a) From **1a**: CH_2Cl_2, 135 °C, 8 h; from **1b**: toluene, 170 °C, 1 h, then *p*TsOH · H_2O, room temperature, 15 min.

product **1a** was heated to 135 °C for 8 h and the Cope product **2** was obtained in 60% yield along with considerable amounts of the corresponding retro-aldol products. Unfortunately, the chromatographic separation of the Cope product **2** was difficult, especially on a larger scale. Therefore, the silyloxy-Cope process was employed for large-scale reactions in spite of the two additional operations for silylation and desilylation.

The stereochemical course of the sigmatropic process can be readily explained by the assumption of a chairlike[10] transition structure **A** in which the large carboximide group lies in the pseudoequatorial position and the small silyloxy group in the pseudoaxial position. The formation of a *Z*-configured silyl enol ether double bond and the conjugate double bond in the *E*-configuration as well as the stereospecific generation of the (5*S*)-configuration, which was proved by converting **1** into the nystatin A_1-fragment,[8] are consistent with this model. The relatively low stereoselection in the Cope rearrangement was not unexpected because 1-monosubstituted 1,5-dienes, such as **1b**, generally rearrange less selectively than the 1,6-disubstituted 1,5-dienes, which exhibit typical stereoselectivities in the range of 20–30:1.[3]

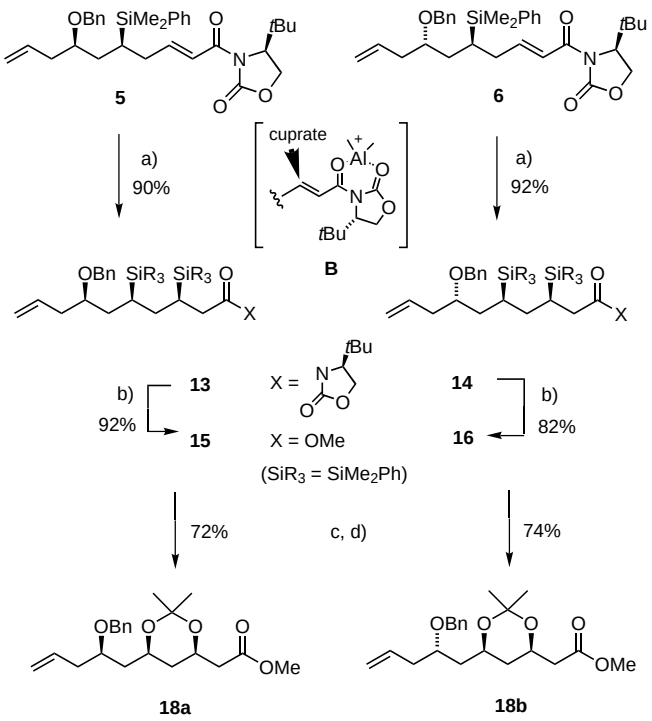
As we now had sufficient quantitites of the key intermediate **2**, we embarked on its straightforward transformation into the desired triols. Enantioselective allylboration with the quasi-enantiomeric allylboranes (allyl)B(2-isocaranyl)$_2$ and (allyl)B(4-isocaranyl)$_2$, introduced by Brown and Racherla,[11] furnished the homoallylic alcohols **3** and **4** in moderate yields and good stereoselectivities (10–15:1) (Scheme 2). The minor stereoisomers were removed by column chromatography. In order to avoid a base-catalyzed oxa-conjugate addition, which would lead to a tetrahydropyran,[4] the protection of the C7-hydroxy group was carried out with $Cl_3CC(=NH)OBn$ and acid-catalysis[12] to give the benzyl ethers **5** and **6** in good yields.



Scheme 2. Synthesis of the 1,3-dioxanes **11** and **12**. a) (allyl)B(2-caranyl)$_2$ (→**3**) or (allyl)B(4-caranyl)$_2$ (→**4**), respectively, Et_2O, −100 °C, 1 h, then H_2O_2, MeOH; b) $Cl_3CC(=NH)OBn$, CF_3SO_3H, CH_2Cl_2, room temperature, 15 h; c) MgClOMe, MeOH, CH_2Cl_2, 0 °C, 5 min; d) $BF_3 \cdot 2\,AcOH$, CH_2Cl_2, 0 °C, 5 min, then KF, *m*CPBA, DMF, 0 °C, 2 h; e) KO*t*Bu, PhCHO, THF, 0 °C, 30 min.

At this stage, two different routes towards the installation of the C3-hydroxy groups with a 3,5-*syn*-configuration were pursued. In the first approach the imides **5** and **6** were converted to the methyl esters **7** and **8**, respectively, with MgClOMe.[13] Oxidative desilylation of the phenyldimethylsilyl group[14] in a two-step procedure [i) $BF_3 \cdot 2\,AcOH$, ii) *m*-chloroperoxybenzoic acid (*m*CPBA)] took place under retention of configuration to give the hydroxy enoates **9** and **10**, respectively, in good yields. Finally, a base-catalyzed addition of the C5-hydroxy group to benzaldehyde yielded a hemiacetal alkoxide which underwent an intramolecular oxa-conjugate addition to deliver the 1,3-dioxanes **11** and **12**, respectively, with high stereoselectivity (20:1).[15] This Michael addition was proved to be thermodynamically controlled and gave rise to the heterocycle with all substituents in the equatorial position. This strategy was used to prepare fully protected *syn-syn*- and *anti-syn*-triols very efficiently and with good stereocontrol (Scheme 2).

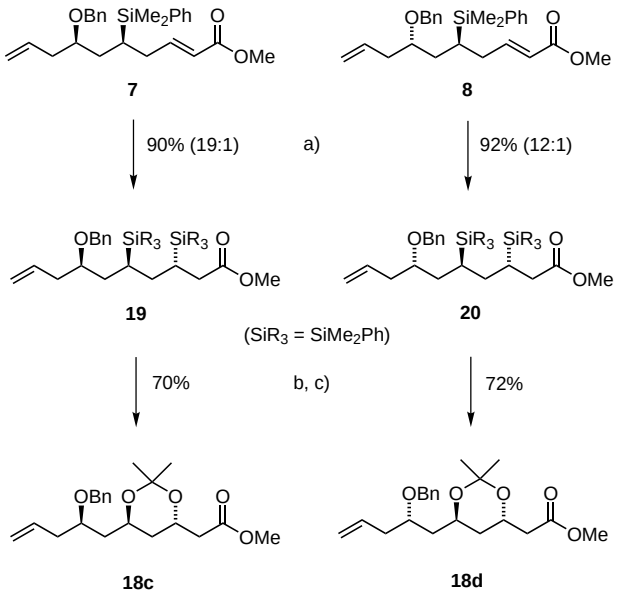
The alternative route started from the imides **5** and **6** and took advantage of the chiral auxiliary still present in the molecule (Scheme 3). For this purpose the less frequently used 4-*tert*-butyl-oxazolidinone was employed instead of the more common 4-benzyloxazolidinone. Asymmetric conjugate



Scheme 3. Synthesis of the protected triols **18a** and **18b**. a) $PhMe_2SiCu \cdot LiI$, Me_2AlCl, THF, $-78\,^{\circ}C$, 1 h; b) MgClOMe, MeOH, CH_2Cl_2, $40\,^{\circ}C$, 15 h; c) $BF_3 \cdot 2\,AcOH$, CH_2Cl_2, $0\,^{\circ}C$, 5 min, then KF, *m*CPBA, DMF, $0\,^{\circ}C$, 2 h; d) $(CH_3)_2C(OMe)_2$, pyridinium *p*-toluenesulfonate (PPTS), room temperature, 15 h.

addition of a phenyldimethylsilyl cuprate under Me_2AlCl activation to the conjugate double bond occurred in very good yields and high stereocontrol (20:1) to furnish the bis-silanes **13** and **14**, respectively.[16] We assume that the highly reactive aluminum chelate **B** is initially formed, as first proposed for Diels–Alder reactions,[17] which the incoming silyl cuprate attacks on the upper face of the conjugate double bond *anti* to the bulky *tert*-butyl group in the auxiliary. If the usual benzyl oxazolidinone was used for this reaction the asymmetric induction dropped to 10:1.[16] Treatment of **13** and **14** with MgClOMe gave the methyl esters **15** and **16**. Double oxidative desilylation produced the diol esters **17a** and **17b**, which were protected as their acetonides **18a** and **18b**. At this point the 3,5-*syn*-stereochemistry was readily confirmed by ^{13}C NMR spectroscopy, as described by Rychnovsky et al.[18]

A slight modification of the synthetic strategy provided facile access to the two remaining protected *syn-anti*- and *anti-anti*-triols **18c** and **18d** (Scheme 4). Fleming and his co-workers[19] have recently shown that moderate-to-good levels of 1,3-*anti*-stereocontrol can be achieved in analogous cuprate additions to various 5-silyl-2-enoates which resemble our compounds. The stereoselectivity was explained in terms of a Felkin–Anh-like transition structure in which the silyl group is *anti* to the incoming nucleophile and the alkyl group at the



Scheme 4. Synthesis of the protected *syn-anti*- and *anti-anti*-triols **18c** and **18d**. a) $PhMe_2SiCu \cdot LiCN$, $BF_3 \cdot OEt_2$, THF, $-78\,^{\circ}C$, 1 h; b) $BF_3 \cdot 2\,AcOH$, CH_2Cl_2, $0\,^{\circ}C$, 5 min, then KF, *m*CPBA, DMF, $0\,^{\circ}C$, 2 h; c) $(CH_3)_2C(OMe)_2$, PPTS, room temperature, 15 h.

chiral center away from the conjugate double bond. The implementation of this strategy called first for the transformation of the imides **5** and **6** to the methyl esters **7** and **8**. In a second step, substrate-controlled cuprate additions of a lower-order cyanocuprate to the methyl enoates proceeded very rapidly with BF_3 activation and gave the addition products **19** and **20** in high yields and stereoselectivities in favor of the desired 3,5-*anti*-stereoisomers. As expected, the C5-stereogenic center controls the stereochemical course of both conjugate additions, whereby the C7 chiral center has only a minor influence. Again, double oxidative desilylation and acetonide formation completed the synthesis. Examination of the ^{13}C NMR spectra revealed that the *anti*-diol acetonides **18c** and **18d** had been formed and thus confirmed their absolute configuration.

As we had prepared all four stereoisomeric, protected triols **18a–d** very efficiently and selectively, we speculated as to whether they could be employed for the synthesis of larger polyol chains by joining two of them. In particular, we wanted to take advantage of their terminal double bond which should be convertible to different functional groups in order to provide two suitable compounds for an efficient coupling process. Thus, triol **18a** was converted to the aldehyde **21** through dihydroxylation and subsequent oxidative cleavage of the glycols in good overall yield (Scheme 5). Ozonolysis also worked well; however, it gave small and inseparable amounts of the corresponding unsaturated aldehyde **22** by elimination of benzyl alcohol. Alternatively, the triols may be converted to the methyl ketones by a Wacker oxidation, which was explicitly demonstrated to be feasible for the triol **11**. The methyl ketone **23** was obtained in 72% yield.[20]

The two subunits **21** and **23** are ideally suited to be joined in an aldol reaction to provide access to even larger polyol chains. Since highly stereoselective methyl ketone aldol additions have been reported recently,[21] we believe that the

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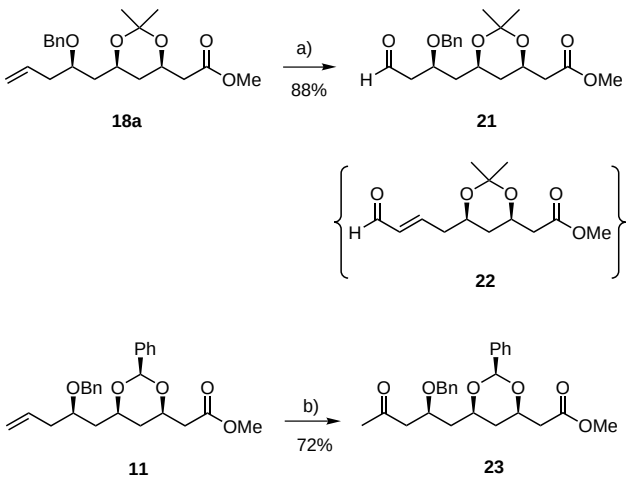

Scheme 5. Synthesis of **21** and **23**. Reaction conditions: a) *N*-methylmorpholine-*N*-oxide, OsO_4 (cat.), acetone/H_2O, room temperature, 15 h; then $NaIO_4$, room temperature, 30 min; b) $PdCl_2$, $CuCl_2 \cdot 2H_2O$, DMF/H_2O, 70 °C, 3 h.

strategy described in this article may be used for a very efficient and stereoselective synthesis of larger 1,3,5,..-polyols. Investigations along these lines are currently in progress and will be reported in due course.

Conclusion

A general asymmetric synthesis of protected 1,3,5-triols of any configuration has been developed. The silyloxy-Cope rearrangement of chiral *syn*-aldols was used to prepare the common key intermediate **2** in enantiopure state. It already contains all three hydroxy groups in a masked form. Only three straightforward operations—allylboration of the aldehyde, oxidative desilylation of the phenyldimethylsilyl group, and the sila- or oxa-conjugate addition—were employed to assemble the target molecules. The great value of this approach is the unified strategy underlying the process which makes all four stereoisomers available by the use of identical synthetic operations. Additionally, the functional groups at the termini should allow for easy and efficient coupling of two building blocks.

Experimental Section

General: Air- and/or moisture-sensitive reactions were performed under N_2 in flame-dried glassware and with standard syringe/septa techniques. Solvents were distilled directly prior to use from the appropriate drying agents: THF ($LiAlH_4$), CH_2Cl_2 and NEt_3 (CaH_2), Et_2O and toluene (Na). All reactions were monitored by thin-layer chromatography (TLC) on precoated silica gel SIL G/UV_{254} plates (Machery, Nagel & Co) and visualized with UV light and 1aqueous $KMnO_4$ (1%). Commercial reagents were used directly as received, unless otherwise stated. Products were purified by flash chromatography on silica gel 32–63 (particle size: 0.032–0.063 mm; Machery, Nagel & Co.). ^1H and ^{13}C NMR spectra were recorded on Varian VXR 200 (200 MHz), Bruker AMX 300 (300 MHz), and Varian VXR 500 (500 MHz) spectrometers in $CDCl_3$ at 25 °C with TMS as the internal standard. IR spectra of evaporated films were recorded on a Bruker IFS 25 FT-IR instrument. UV spectra were recorded on a Perkin–Elmer Lambda 9 spectrometer. HPLC analysis was carried out with a Kontron Kromasystem 2000 and a Lichropher 100 RP 18 column (76% CH_3CN/H_2O, flow rate: 0.9 mL min^{-1}). Optical rotations were measured on a Perkin–Elmer 241 polarimeter. Mass spectra were recorded at 70 eV (EI) or 200 eV (DCI/NH_3) on a Finnigan MAT 95A spectrometer. Microanalyses were carried out by the microanalytical laboratory of the Institut für Organische Chemie der Universität Göttingen.

(2′*S*,3′*R*,4*S*,4′*E*)-4-*tert*-Butyl-3-[5′-dimethylphenylsilyl-2′-ethenyl-3′-hydroxy-4′-pentenoyl]-oxazolidin-2-one (1a): A solution of Bu_2BOTf in CH_2Cl_2 (1.0 M, 21.5 mL, 21.5 mmol, 1.1 equiv) and NEt_3 (3.78 mL, 27.3 mmol, 1.4 equiv) were added to a solution of (2′*E*,4*S*)-4-*tert*-butyl-3-(2′-butenoyl)-oxazolidin-2-one (4.12 g, 19.5 mmol) in CH_2Cl_2 (150 mL) at −78 °C. A bright yellow solution of the boron enolate formed immediately. The mixture was stirred for 30 min at −78 °C and 30 min at 0 °C. It was recooled to −78 °C and (*E*)-3-dimethylphenylsilyl-2-propenal[22] (3.71 mL, 19.5 mmol, 1.0 equiv) was added dropwise. The solution was kept at −78 °C for 1 h, stirred for another 30 min at 0 °C, and was then hydrolyzed by the addition of H_2O (100 mL). The mixture was allowed to warm to room temperature and extracted with Et_2O (3 × 100 mL). The organic layers were dried over K_2CO_3. After removal of the solvent, purification by flash chromatography (diethyl ether/petroleum ether 1:2) afforded the aldol product **1a** as a highly viscous, pale yellow oil (6.43 g, 82%) which was stereoisomerically pure (^1H and ^{13}C NMR). $[\alpha]_D^{20} = +3.0$ ($c = 0.5$, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.33$, 0.34 (2 × s, 6H, $SiMe_2$), 0.89 (s, 9H, *t*Bu), 3.03 (d, $J = 3.0$ Hz, 1H, OH), 4.02 (dd, $J = 9.0$, 7.5 Hz, 1H, 5-CH), 4.22 (dd, $J = 9.0$, 1.5 Hz, 1H, 5-CH), 4.41 (dd, $J = 7.5$, 1.5 Hz, 1H, 4-CH), 4.51 (ddd, $J = 4.5$, 3.0, 3.0 Hz, 1H, 3′-CH), 4.73 (dd, $J = 9.0$, 4.5 Hz, 1H, 2′-CH), 5.37 (dd, $J = 10.0$, 1.5 Hz, 1H, 2″-CH), 5.45 (dd, $J = 17.5$, 1.5 Hz, 1H, 2″-CH), 5.95 (ddd, $J = 17.5$, 10.0, 9.0 Hz, 1H, 1″-CH), 6.01 (dd, $J = 18.5$, 3.0 Hz, 1H, 4′-CH), 6.13 (d, $J = 18.5$ Hz, 1H, 5′-CH), 7.26–7.54 (m, 5H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -2.87$, −2.51 ($SiMe_2$), 25.41 ($C(CH_3)_3$), 35.89 ($C(CH_3)_3$), 52.57 (C2′), 60.60 (C4), 64.93 (C5), 73.87 (C3′), 121.5 (C2″), 127.6, 128.9, 133.7, 138.3 (phenyl-C), 129.6, 131.7, 146.0 (C1″, C4′, C5′), 153.9 (C2), 173.4 (C1′); IR (film): $\tilde{\nu} = 3496$ (OH), 3068, 3050, 2964, 2914 (CH), 1782 (C=O), 1700 (C=O), 1634 (C=C), 1480, 1426, 1382, 1368, 1352, 1324, 1248, 1218, 1188, 1110, 1058, 1034, 1012, 992, 844, 828, 732, 702 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 258.5 nm (3.125); MS (70 eV, EI): *m*/*z* (%): 401 (<1) [M^+], 211 (100) [retro-aldol cleavage, imide$^+$], 175 (42), 144 (37), 135 (34) [$PhMe_2Si^+$], 68 (48), 57 (18) [*t*Bu$^+$]; $C_{22}H_{31}NO_4Si$ (401.85): calcd C 65.80, H 7.78; found C 65.63, H 7.72.

(2′*S*,3′*R*,4*S*,4′*E*)-4-*tert*-Butyl-3[5′-dimethylphenylsilyl-2′-ethenyl-3′-trimethylsilyloxy-4′-pentenoyl]-oxazolidin-2-one (1b): 2,6-Lutidine (4.37 mL, 37.5 mmol, 1.4 equiv) and TMS-triflate (5.33 mL, 29.5 mmol, 1.1 equiv) were added to a solution of the aldol product **1a** (10.8 g, 26.8 mmol) in CH_2Cl_2 (150 mL) at 0 °C. The mixture was stirred at 0 °C for 30 min, hydrolyzed by addition of saturated aqueous $NaHCO_3$ solution (100 mL), and extracted with CH_2Cl_2 (3 × 100 mL). The organic layers were dried over $MgSO_4$. After removal of the solvent in vacuo, the crude product was purified by flash chromatography (diethyl ether/petroleum diethyl ether 1:5) to give **1b** (11.6 g, 91%) as a colorless oil. $[\alpha]_D^{20} = +16.0$ ($c = 0.5$, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.08$ (s, 9H, $OSiMe_3$), 0.31, 0.33 (2 × s, 6H, $SiMe_2$), 0.88 (s, 9H, *t*Bu), 3.85 (dd, $J = 9.0$, 7.5 Hz, 1H, 5-CH), 4.14 (dd, $J = 9.0$, 1.5 Hz, 1H, 5-CH), 4.30 (dd, $J = 7.5$, 1.5 Hz, 1H, 4-CH), 4.39 (dd, $J = 7.5$, 5.5 Hz, 1H, 3′-CH), 4.81 (dd, $J = 9.0$, 7.5 Hz, 1H, 2′-CH), 5.22 (dd, $J = 10.0$, 1.5 Hz, 1H, 2″-CH), 5.30 (dd, $J = 17.0$, 1.5 Hz, 1H, 2″-CH), 5.90 (ddd, $J = 17.0$, 10.0, 9.0 Hz, 1H, 1″-CH), 5.93 (d, $J = 18.5$ Hz, 1H, 5′-CH), 6.10 (dd, $J = 18.5$, 5.5 Hz, 1H, 4′-CH), 7.29–7.52 (m, 5H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -2.89$, −2.46 ($SiMe_2$), 0.10 ($OSiMe_3$), 25.55 ($C(CH_3)_3$), 35.79 ($C(CH_3)_3$), 53.62 (C2′), 60.96 (C4), 64.79 (C5), 76.74 (C3′), 119.4 (C2″), 127.7, 128.9, 133.7, 138.6 (Ph-C), 129.2, 134.0, 147.6 (C1″, C4′, C5′), 154.2 (C2), 171.9 (C1′); IR (film): $\tilde{\nu} = 3068$, 3050, 2960, 2908 (CH), 1784 (C=O), 1700 (C=O), 1636, 1620 (C=C), 1480, 1426, 1370, 1352, 1320, 1252, 1218, 1184, 1110, 1064, 1032, 994, 900, 842, 756, 730, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 252.0 nm (2.913), 258.5 (2.879); MS (70 eV, EI): *m*/*z* (%): 473 (<1) [M^+], 458 (4) [$M^+ - CH_3$], 330 (2) [M^+ − oxazolidinone], 283 (75), 263 (100) [retro-aldol cleavage, aldehyde$^+$], 147 (44), 135 (15) [$PhMe_2Si^+$], 73 (42) [$(SiMe_3)^+$], 57 (2) [*t*Bu$^+$]; $C_{25}H_{39}NO_4Si_2$ (473.76): calcd C 63.38, H 8.30; found C 63.63, H 8.22.

(2′*E*,4*S*,5′*S*)-4-*tert*-Butyl-3-[5′-dimethylphenylsilyl-7′-oxo-2′-heptenoyl]-oxazolidin-2-one (2): Route A: Aldol product **1a** (211 mg, 0.53 mmol) was dissolved in CH_2Cl_2 (10 mL) in a sealed flask which was placed into a preheated oil bath (135–140 °C) for 8 h. The solution was cooled to room

temperature and the solvent was removed in vacuo. Flash chromatography (diethyl ether/petroleum ether 2:1) yielded the aldehyde **2** (127 mg, 60%) as a colorless viscous oil. **Route B**: The silylated aldol product **1b** (2.18 g, 4.60 mmol) was dissolved in toluene (10 mL) in a sealed flask which was placed into a preheated oil bath (170 °C) for 1 h. The solution was cooled to room temperature, the solvent removed in vacuo, and the crude product dissolved in CH_2Cl_2 (50 mL). To this solution was added *para*-toluenesulfonic acid monohydrate (1.31 g, 6.90 mmol, 1.5 equiv). The mixture was stirred at room temperature for 15 min, poured into saturated aqueous $NaHCO_3$ solution (100 mL), and then extracted with Et_2O (3×50 mL). The organic layers were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (diethyl ether/petroleum ether 1:2) yielded the isomerically pure aldehyde **2** as a colorless viscous oil (1.26 g, 68%). The kinetic stereoselection of the sigmatropic process was 6–8:1, as determined by ^{1}H and ^{13}C NMR spectroscopy on the crude product. $[\alpha]_D^{20} = +34.0$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.33$ (s, 6H, $SiMe_2$), 0.92 (s, 9H, *t*Bu), 1.72 (m_c, 1H, 5′-CH), 2.07–2.55 (m, 4H, 4′-CH_2, 6′-CH_2), 4.23 (dd, $J = 9.0$, 6.5 Hz, 1H, 5-CH), 4.29 (dd, $J = 9.0$, 2.5 Hz, 1H, 5-CH), 4.49 (dd, $J = 6.5$, 2.5 Hz, 1H, 4-CH), 6.95 (ddd, $J = 14.5$, 8.5, 6.0 Hz, 1H, 3′-CH), 7.15 (d, $J = 14.5$ Hz, 1H, 2′-CH), 7.30–7.54 (m, 5H, phenyl-CH), 9.64 (t, $J = 1.5$ Hz, 1H, 7′-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.69$, -4.56 ($SiMe_2$), 18.48 (C5′), 25.27 (C(CH_3)$_3$), 33.09, 43.53 (C4′, C6′), 35.54 (*C*(CH_3)$_3$), 60.41 (C4), 64.89 (C5), 121.5 (C2′), 127.7, 129.1, 133.6, 136.3 (phenyl-C), 149.8 (C3′), 154.3 (C2), 164.5 (C1′), 201.6 (C7′); IR (film): $\tilde{\nu} = 3070$, 3050, 2966, 2874, 2726 (CH), 1782 (C=O), 1684 (C=O), 1634 (C=C), 1384, 1370, 1350, 1326, 1252, 1222, 1190, 1114, 1068, 1032, 1018, 836, 818, 734, 702 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 212.5 nm (4.588); MS (70 eV, EI): *m*/*z* (%): 401 (11) [M^+], 386 (18) [$M^+ - CH_3$], 345 (14) [$M^+ - t$Bu], 324 (21), 278 (100), 191 (19) [retro-aldol cleavage, aldehyde$^+$], 135 (71) [$PhMe_2Si^+$], 57 (8) [tBu$^+$]; $C_{22}H_{31}NO_4Si$ (401.58): calcd C 65.80, H 7.78; found C 65.92, H 8.05.

(2′*E*,4*S*,5′*S*,7′*R*)-4-*tert*-Butyl-3-[5′-dimethylphenylsilyl-7′-hydroxy-2′,9′-decadienoyl]-oxazolidin-2-one (3): Allylmagnesium bromide in THF (1.0 M solution, 1.25 mL, 1.25 mmol, 2 equiv) was added to a solution of *B*-methoxy-bis(2-isocaranyl)borane (395 mg, 1.25 mmol, 2 equiv) in Et_2O (50 mL) at -78 °C. The mixture was stirred at -78 °C for 15 min and at room temperature for 1 h. Stirring was then discontinued to permit the Mg^{2+} salts to settle. The clear supernatant solution was transferred into another flask by syringe. The solution was recooled to -78 °C and a solution of aldehyde **2** (251 mg, 0.63 mmol) in Et_2O (2 mL) was added. The mixture was stirred at -78 °C for 1 h and then hydrolyzed by the addition of H_2O (10 mL). H_2O_2 (30%, 2 mL) and MeOH (2 mL) were added, the mixture was refluxed for 15 h, recooled to room temperature, and extracted with Et_2O (3×50 mL). The organic layers were washed with saturated aqueous Na_2SO_3 solution and dried over $MgSO_4$. After removal of the solvent in vacuo, flash chromatography (diethyl ether/petroleum ether 1:2) yielded **3** (172 mg, 62%) as a colorless oil which was isomerically pure (^{1}H and ^{13}C NMR). The kinetic stereoselection of this allylboration was in the range 10–15:1. $[\alpha]_D^{20} = +26.0$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.31$ (s, 6H, $SiMe_2$), 0.93 (s, 9H, *t*Bu), 1.35–1.67 (m, 4H, 5′-CH, 6′-CH_2, OH), 1.97–2.54 (m, 4H, 4′-CH_2, 8′-CH_2), 3.60–3.74 (m, 1H, 7′-CH), 4.18–4.35 (m, 2H, 5-CH_2), 4.49 (dd, $J = 6.5$, 2.5 Hz, 1H, 4-CH), 5.01–5.15 (m, 2H, 10′-CH_2), 5.61–5.86 (m, 1H, 9′-CH), 6.96–7.57 (m, 7H, phenyl-CH, 2′-CH, 3′-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.16$, -4.09 ($SiMe_2$), 20.83 (C5′), 25.60 (C(CH_3)$_3$) 33.07, 35.88, 36.63, 42.59 (C4′, C6′, C8′, *C*(CH_3)$_3$), 60.73 (C4), 65.16 (C5), 68.48 (C7′), 118.0 (C10′), 120.9 (C2′), 127.8, 129.0, 133.9 (phenyl-C), 134.7 (C9′), 137.7 (phenyl-C), 151.9 (C3′), 154.6 (C2), 165.1 (C1′); IR (film): $\tilde{\nu} = 3454$ (OH), 3070, 3050, 3008, 2962, 2924, (CH), 1780 (C=O), 1688 (C=O), 1632 (C=C), 1476, 1428, 1382, 1366, 1350, 1326, 1252, 1220, 1188, 1110, 1066, 1020, 990, 914, 838, 814, 768, 732, 702 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 218.0 nm (4.482); MS (70 eV, EI): *m*/*z* (%): 443 (4) [M^+], 402 (18) [$M^+ -$ allyl], 278 (81), 135 (100) [$PhMe_2Si^+$], 57 (8) [tBu$^+$]; $C_{25}H_{37}NO_4Si$ (443.66): calcd C 67.68, H 8.41; found C 67.46, H 8.63.

(2′*E*,4*S*,5′*S*,7′*S*)-4-*tert*-Butyl-3-[5′-dimethylphenylsilyl-7′-hydroxy-2′,9′-decadienoyl]-oxazolidin-2-one (4): *B*-Methoxy-bis(4-isocaranyl)borane (2.36 g, 7.47 mmol, 2 equiv) and allylmagnesium bromide (1 M solution in THF, 7.47 mL, 7.47 mmol, 2 equiv) were treated with the aldehyde **2** (1.50 g, 3.74 mmol) in Et_2O as described for **3**. Purification by flash chromatography (diethyl ether/petroleum ether 1:2) afforded the homoallylic alcohol **4** (1.00 g, 60%) as a single stereoisomer. $[\alpha]_D^{20} = +40.0$ ($c = 0.4$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.32$ (s, 6H, $SiMe_2$), 0.93 (s, 9H, *t*Bu), 1.38–1.68 (m, 4H, 5′-CH, 6′-CH_2, OH), 1.90–2.54 (m, 4H, 4′-CH_2, 8′-CH_2), 3.54 (m_c, 1H, 7′-CH), 4,18–4,33 (m, 2H, 5-CH_2), 4.49 (dd, $J = 6.5$, 2.5 Hz, 1H, 4-CH), 4.98–5.14 (m, 2H, 10′-CH_2), 5.70 (m_c, 1H, 9′-CH), 7.04 (ddd, $J = 15.0$, 7.0, 5.5 Hz, 1H, 3′-CH), 7.18 (d, $J = 15.0$ Hz, 1H, 2′-CH), 7.30–7.55 (m, 5H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.28$, -4.17 ($SiMe_2$), 21.61 (C5′), 25.51 (C(CH_3)$_3$) 33.80, 35.78, 36.87, 41.63 (C4′, C6′, C8′, *C*(CH_3)$_3$), 60.68 (C4), 65.11 (C5), 69.87 (C7′), 117.9 (C10′), 121.0 (C2′), 127.8, 129.0, 133.7 (phenyl-C), 134.6 (C9′), 137.7 (phenyl-C), 151.5 (C3′), 154.6 (C2), 165.1 (C1′); IR (film): $\tilde{\nu} = 3456$ (OH), 3070, 3050, 2970, 2928, 2870 (CH), 1780 (C=O), 1690 (C=O), 1632 (C=C), 1478, 1440, 1428, 1384, 1370, 1350, 1326, 1250, 1220, 1188, 1154, 1114, 1068, 1032, 1020, 994, 914, 836, 814, 770, 760, 734, 702 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 219.0 nm (4.619); MS (70 eV, EI): *m*/*z* (%): 443 (11) [M^+], 402 (34) [$M^+ -$ allyl], 278 (100), 218 (15), 144 (16), 135 (74) [$PhMe_2Si^+$], 57 (4) [tBu$^+$], 41 (2), [allyl$^+$]; $C_{25}H_{37}NO_4Si$ (443.66): calcd C 67.68, H 8.41; found C 67.93, H 8.45.

(2′*E*,4*S*,5′*S*,7′*R*)-4-*tert*-Butyl-3-[7′-benzyloxy-5′-dimethyl-phenylsilyl-2′,9′-decadienoyl]-oxazolidin-2-one (5): Freshly distilled trifluoromethanesulfonic acid (20 μL) was slowly added to a stirred solution of homoallylic alcohol **3** (108 mg, 0.24 mmol) and benzyl trichloroacetimidate (91.0 μL, 0.49 mmol, 2.0 equiv) in CH_2Cl_2 (5 mL) and hexane (10 mL) at 0 °C. The solution was allowed to warm to room temperature, stirred for 15 h, and then poured into a saturated aqueous $NaHCO_3$ solution (20 mL). The mixture was extracted with Et_2O (3×20 mL) , the organic layers were dried over $MgSO_4$, and concentrated in vacuo. Purification by flash chromatography (diethyl ether/petroleum ether 1:3) afforded the benzyl ether **5** (108 mg, 83%) as a colorless oil. $[\alpha]_D^{20} = +11.5$ ($c = 0.2$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.28$ (s, 6H, $SiMe_2$), 0.92 (s, 9H, *t*Bu), 1.29–1.49 (m, 2H, 5′-CH, 6′-CH), 1.60–1.77 (m, 1H, 6-CH), 2.11–2.43 (m, 4H, 4′-CH_2, 8′-CH_2), 3.37–3.54 (m, 6H, 7′-CH, OCH_2-Ph, 4-CH, 5-CH_2), 4.96–5.12 (m, 2H, 10′-CH_2), 5.75 (m_c, 1H, 9′-CH), 6.90–7.54 (m, 12H, phenyl-CH, 2′-CH, 3′-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.08$, -3.97 ($SiMe_2$), 20.67 (C5′), 25.57 (C(CH_3)$_3$), 33.33, 34.11, 35.85, 38.37 (C4′, C6′, C8′, *C*(CH_3)$_3$), 60.71 (C4), 65.11 (C5), 70.70 (OCH_2-Ph), 76.66 (C7′), 117.1 (C10′), 120.8 (C2′), 127.4, 127.7, 127.7, 128.3, 129.0, 133.9 (phenyl-C), 134.6 (C9′), 137.8, 138.8 (phenyl-C), 152.0 (C3′), 154.5 (C2), 165.0 (C1′); IR (film): $\tilde{\nu} = 3068$, 2968, 2920, 2870 (CH), 1780 (C=O), 1690 (C=O), 632 (C=C), 1450, 1428, 1382, 1368, 1350, 1326, 1252, 1220, 1186, 1112, 1068, 1026, 990, 834, 816, 756, 734, 700 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 533 (6) [M^+], 492 (27) [$M^+ -$ allyl], 308 (26), 278 (100), 135 (47) [$PhMe_2Si^+$], 91 (51), [($PhCH_2$)$^+$], 57 (3) [tBu$^+$]; $C_{32}H_{43}NO_4Si$ (533.78); calcd C 72.01, H 8.12; found C 71.96, H 8.00.

(2′*E*,4*S*,5′*S*,7′*S*)-4-*tert*-Butyl-3-[7′-benzyloxy-5′-dimethyl-phenylsilyl-2′,9′-decadienoyl]-oxazolidin-2-one (6): The homoallylic alcohol **4** (915 mg, 2.06 mmol) was treated with benzyl trichloroacetimidate (0.77 mL, 4.12 mmol, 2.0 equiv) and trifluoromethanesulfonic acid (50 μL) in CH_2Cl_2 (20 mL) and hexane (40 mL) at 0 °C in the same way as described above for **5**. Purification by flash chromatography (diethyl ether/petroleum ether 1:3) afforded the benzyl ether **6** (0.88 g, 83%) as a colorless oil. $[\alpha]_D^{20} = +31.0$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.27$ (s, 6H, $SiMe_2$), 0.92 (s, 9H, *t*Bu), 1.14 (m_c, 1H, 5′-CH), 1.59 (m_c, 2H, 6′-CH_2), 2.14–2.51 (m, 4H, 4′-H_2, 8′-CH_2), 3.34 (quint, $J = 6.0$ Hz, 1H, 7′-CH), 4.15–4.32 (m, 2H, 5-CH_2), 4.27, 4.46 (2 × d, $J = 12.0$ Hz, 2H, OCH_2-Ph), 4.48 (dd, $J = 7.0$, 2.0 Hz, 1H, 4-CH), 4.94–5.08 (m, 2H, 10′-CH_2), 5.72 (m_c, 1H, 9′-CH), 7.20 (d, $J = 15.5$ Hz, 1H, 2′-CH), 6.97–7.48 (m, 11H, phenyl-CH, 3′-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.33$, -4.06 ($SiMe_2$), 21.46 (C5′), 25.57 (C(CH_3)$_3$), 34.01, 35.84, 37.69, (C4′, C6′, C8′, *C*(CH_3)$_3$), 60.69 (C4), 65.08 (C5), 70.56 (OCH_2-Ph), 77.81 (C7′), 117.1 (C10′), 120.9 (C2′), 127.3, 127.6, 127.7, 128.2, 129.0, 133.8 (phenyl-C), 134.5 (C9′), 137.8, 138.8 (phenyl-C), 151.7 (C3′), 154.5 (C2), 165.0 (C1′); IR (film): $\tilde{\nu} = 3068$, 3022, 2962, 2918, 2872 (CH), 1778 (C=O), 1688 (C=O), 1632 (C=C), 1476, 1450, 1428, 1382, 1366, 1348, 1326, 1252, 1220, 1186, 1110, 1066, 1030, 990, 912, 834, 814, 788, 768, 734, 700 cm^{-1}; MS (70 eV, EI): *m*/*z* (%): 533 (11) [M^+], 492 (12) [$M^+ -$ allyl], 278 (100), 135 (31) [$PhMe_2Si^+$], 91 (17), [($PhCH_2$)$^+$], 57 (2) [tBu$^+$]; $C_{32}H_{43}NO_4Si$ (533.78): calcd C 72.01, H 8.12; found C 72.06, H 8.34.

Methyl (2*E*,5*S*,7*R*)-7-benzyloxy-5-dimethylphenylsilyl-2,9-decadienoate (7): MeMgCl (3 M solution in THF, 0.42 mL, 1.27 mmol, 1.2 equiv) was added to anhydrous MeOH (5 mL) at 0 °C. The mixture was stirred at 0 °C for 2 min and then added to a precooled solution (0 °C) of the imide **5** (567 mg, 1.06 mmol) in anhydrous MeOH (5 mL) and CH_2Cl_2 (5 mL) by means of a syringe. After the reaction mixture was stirred for 5 min at 0 °C, it was quenched by the addition of saturated $NaHCO_3$ solution (20 mL),

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and was then extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography (diethyl ether/petroleum ether 1:5) afforded **7** (395 mg, 88%) as a colorless oil. $[\alpha]_D^{20}=-27.0$ ($c=0.715$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.28$ (s, 6H, $SiMe_2$), 1.18–1.76 (m, 3H, 5-CH, 6-CH_2), 2.01–2.45 (m, 4H, 4-CH_2, 8-CH_2), 3.33–3.51 (m, 1H, 7-CH), 3.68 (s, 3H, OMe), 4.33, 4.55 ($2\times$d, $J=12.0$ Hz, 2H, OCH_2-Ph), 4.98–5.14 (m, 2H, 10-CH_2), 5.60–5.85 (m, 2H, 2-CH, 9-CH), 6.79 (dt, $J=15.5$, 7.5 Hz, 1H, 3-CH), 7.30–7.50 (m, 10H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=-4.12$, -4.00 ($SiMe_2$), 20.51 (C5), 32.84, 34.00, 38.25 (C4, C6, C8), 51.20 (OCH_3), 70.56 (OCH_2 Ph), 76.50 (C7), 117.1 (C10), 121.2 (C2), 127.4, 127.6, 127.7, 128.2, 128.9, 133.8 (phenyl-C), 134.5 (C9), 137.8, 138.7 (phenyl-C), 149.8 (C3), 166.6 (C1); IR (film): $\tilde{\nu}=3068$, 3026, 2950, 2924, 2860 (CH), 1724 (C=O), 1652, 1604 (C=C), 1434, 1342, 1266, 1204, 1170, 1152, 1110, 1090, 1068, 992, 832, 816, 772, 734, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (3.287); MS (70 eV, EI): m/z (%): 422 (<1) [M^+], 331 (6), 135 (57) [$PhMe_2Si^+$], 91 (100) [$(PhCH_2)^+$]; $C_{26}H_{34}O_3Si$ (422.64): calcd C 73.89, H 8.11; found C 74.16, H 8.36.

Methyl (2*E*,5*S*,7*S*)-7-benzyloxy-5-dimethylphenylsilyl-2,9-decadienoate (8): The imide **6** was converted to the methyl ester **8** as described above for **7**. Yield: 442 mg (91%) of a colorless oil. $[\alpha]_D^{20}=+5.3$ ($c=0.4$, MeOH); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.27$ (s, 6H, $SiMe_2$), 1.42–1.67 (m, 3H, 5-CH, 6-CH_2), 2.05–2.55 (m, 4H, 4-H_2, 8-CH_2), 3.33 (quint, $J=6.0$ Hz, 1H, 7-CH), 3.70 (s, 3H, OMe), 4.27, 4.48 ($2\times$d, $J=11.5$ Hz, 2H, OCH_2-Ph), 4.92–5.10 (m, 2H, 10-CH_2), 5.72 (m_c, 1H, 9-CH), 5.74 (dt, $J=15.5$, 1.0 Hz, 1H, 2-CH), 6.88 (dt, $J=15.5$, 7.5 Hz, 1H, 3-CH), 7.05–7.50 (m, 10H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=-4.21$, -4.09 ($SiMe_2$), 21.33 (C5), 33.57, 34.00, 37.68 (C4, C6, C8), 51.33 (OCH_3), 70.57 (OCH_2-Ph), 77.75 (C7), 117.1 (C10), 121.4 (C2), 127.4, 127.6, 127.8, 128.2, 129.0, 133.8 (phenyl-C), 133.4 (C9), 137.8, 138.7 (phenyl-C), 149.6 (C3), 166.8 (C1); IR (film): $\tilde{\nu}=3066$, 3024, 2950, 2920, 2856 (CH), 1722 (C=O), 1684, 1654 (C=C), 1450, 1434, 1384, 1374, 1342, 1264, 120, 1168, 1154, 1110, 1088, 1068, 1032, 912, 832, 814, 770, 736, 700 cm^{-1}; MS (70 eV): m/z (%): 422 (7) [M^+], 407 (3) [M^+-CH_3], 135 (63) [$PhMe_2Si^+$], 91 (100) [$(PhCH_2)^+$]; $C_{26}H_{34}O_3Si$ (422.64): calcd C 73.89, H 8.11; found C 73.73, H 7.85.

Methyl (2*E*,5*S*,7*R*)-7-benzyloxy-5-hydroxy-2,9-decadienoate (9): Boron trifluoride/acetic acid complex (36%, 2.00 mL, 3.83 mmol, 1.5 equiv) was added to a stirred solution of silane **7** (1.08 g, 2.56 mmol) in dry CH_2Cl_2 (30 mL) at room temperature. After being stirred for 5 min, the yellow-brown colored reaction mixture was poured into saturated aqueous $NaHCO_3$ solution (50 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the fluorosilane as a pale yellow oil. Without further purification it was dissolved in DMF (20 mL) and treated with KF (0.89 g, 15.4 mmol, 6 equiv) and a solution of *m*-chloroperoxybenzoic acid (0.95 g, 3.83 mmol, 1.5 equiv) in DMF (2 mL) at 0 °C. The reaction mixture was stirred at this temperature for 2 h, poured into water (100 mL), and extracted with Et_2O (3×100 mL). The organic layer was washed with water (1×50 mL) and the aqueous layer was reextracted with Et_2O (3×50 mL). The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography (diethyl ether/petroleum ether 1:1) afforded alcohol **9** (561 mg, 72%) as a colorless oil. $[\alpha]_D^{20}=-64.3$ ($c=0.56$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.56-1.78$ (m, 2H, 6-CH_2), 2.28–2.46 (m, 4H, 4-CH_2, 8-CH_2), 3.73 (s, 3H, OMe), 3.76 (m_c, 1H, 7-CH), 3.93 (m_c, 1H, 5-CH), 4.45, 4.72 ($2\times$d, $J=11.0$ Hz, 2H, OCH_2-Ph), 5.05–5.19 (m, 2H, 10-CH_2), 5.67–5.88 (m, 1H, 9-CH), 5.87 (d, $J=15.5$ Hz, 1H, 2-CH), 6.97 (dt, $J=15.5$, 7.5 Hz, 1H, 3-CH), 7.27–7.42 (m, 5H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=37.75$, 40.16, 40.33 (C4, C6, C8), 51.31 (OCH_3), 69.90 (C5), 70.66 (OCH_2-Ph), 78.58 (C7), 117.9 (C10), 123.0 (C2), 127.9, 128.5 (phenyl-C), 133.5 (C9), 137.6 (phenyl-C), 145.6 (C3), 166.7 (C1); IR (film): $\tilde{\nu}=3474$ (OH), 3068, 3030, 3004, 2976, 2944, 2866 (CH), 1722 (C=O), 1658 (C=C), 1436, 1328, 1274, 1208, 1166, 1136, 1068, 1046, 988, 916, 740, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 206.5 nm (4.849), 257.0 (3.049); MS (70 eV, EI): m/z (%): 304 (<1) [M^+], 97 (59), 91 (100) [$(PhCH_2)^+$], 57 (60); $C_{18}H_{24}O_4$ (304.39): calcd C 71.02, H 7.95; found C 71.22, H 8.07.

Methyl (2*E*,5*S*,7*S*)-7-benzyloxy-5-hydroxy-2,9-decadienoate (10): The silane **8** (210 mg, 0.50 mmol) was converted to the alcohol **10** in the same way as described above for **9** to give 112 mg (74%) of **10** as a colorless oil. $[\alpha]_D^{20}=+21.4$ ($c=0.36$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.55-1.80$ (m, 2H, 6-CH_2), 2.25–2.58 (m, 4H, 4-CH_2, 8-CH_2), 3.73 (s, 3H, OMe), 3.70–3.86 (m, 1H, 7-CH), 4.05 (quint, $J=6.0$ Hz, 1H, 5-CH), 4.49, 4.66 ($2\times$d, $J=11.5$ Hz, 2H, OCH_2-Ph), 5.02–5.18 (m, 2H, 10-CH_2), 5.79 (m_c, 1H, 9-CH), 5.88 (dt, $J=15.5$, 1.0 Hz, 1H, 2-CH), 6.97 (dt, $J=15.5$, 7.0 Hz, 1H, 3-CH), 7.07–7.48 (m, 5H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=37.83$, 39.73, 40.30 (C4, C6, C8), 51.46 (OCH_3), 67.24 (C5), 71.23 (OCH_2-Ph), 75.79 (C7), 117.7 (C10), 123.2 (C2), 127.8, 127.9, 128.5 (phenyl-C), 134.1 (C9), 138.0 (phenyl-C), 145.6 (C3), 166.8 (C1); IR (film): $\tilde{\nu}=3472$ (OH), 3066, 3030, 2947, 2914, 2868 (CH), 1723 (C=O), 1658, 1642 (C=C), 1454, 1435, 1274, 1209, 1167, 1069, 985, 837, 737, 698 cm^{-1}; MS (70 eV, EI): m/z (%): 304 (8) [M^+], 263 (8), 91 (100) [$(PhCH_2)^+$]; $C_{18}H_{24}O_4$ (304.39): calcd C 71.02,H 7.95; found C 70.78, H 7.86.

(2*R*,2″*R*,4*R*,6*R*)-6-(2″-Benzyloxy-4″-pentenyl)-4-(methoxy-carbonylmethyl)-2-phenyl-1,3-dioxane (11): Freshly distilled benzaldehyde (46 μL, 0.46 mmol, 1.1 equiv) and KO*t*Bu (4.68 mg, 42 μmol, 0.1 equiv) were added to a solution of alcohol **9** (127 mg, 0.42 mmol) in THF (10 mL) at 0 °C and the resulting yellow solution was stirred at 0 °C for 15 min. This sequence of addition/stirring was repeated twice. The reaction mixture was then poured into a solution of phosphate buffer (pH 7, 20 mL) and extracted with Et_2O (3×30 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Excess benzaldehyde was removed in vacuo (1 mbar). Purification by flash chromatography (diethyl ether/petroleum ether 1:2) afforded the benzylidene acetal **11** (123 mg, 72%) as a colorless oil. Selectivity 4*R*:4*S* = >20:1 (^{1}H NMR); $[\alpha]_D^{20}=-15.0$ ($c=1.0$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.23-1.78$ (m, 3H, 5-H, 1″-CH_2), 2.04 (ddd, $J=14.0$, 7.0, 7.0 Hz, 1H, 5-CH), 2.41 (t, $J=6.0$ Hz, 2H, 3″-CH_2), 2.46 (dd, $J=15.5$, 6.0 Hz, 1H, 1′-CH), 2.70 (dd, $J=15.5$, 7.0 Hz, 1H, 1′-CH), 3.67 (quint, $J=6.0$ Hz, 1H, 2″-CH), 3.70 (s, 3H, OMe), 3.92–4.10 (m, 1H, 6-CH), 4.12–4.33 (m, 1H, 4-CH), 4.46, 4.63 ($2\times$d, $J=11.5$ Hz, 2H, OCH_2-Ph), 5.03–5.18 (m, 2H, 5″-CH_2), 5.54 (s, 1H, 2-CH), 5.74–5.98 (m, 1H, 4″-CH), 7.28–7.50 (m, 10H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=$ 36.28, 38.14, 39.74, 40.67 (C5, C1′, C1″, C3″), 51.70 (OCH_3), 70.60 (OCH_2-Ph), 73.09, 73.68, 74.30 (C4, C6, C2″), 100.5 (C2), 117.4 (C5″), 126.0, 127.6, 127.9, 128.1, 128.3, 128.6 (phenyl-C), 134.4 (C4″), 138.4, 138.5 (phenyl-C), 171.1 (C2′); IR (film): $\tilde{\nu}=3064$, 3030, 3004, 2974, 2946, 2918, 2868 (CH), 1740 (C=O), 1648 (C=C), 1496, 1452, 1438, 1404, 1388, 1378, 1346, 1254, 1206, 1162, 1140, 1100, 1064, 1026, 914, 752, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 256.0 nm (3.208), 261.5 (3.172); MS (70 eV, EI): m/z (%): 409 (1) [M^+], 303 (18) [$M^+-Ph-CHO$], 263 (100), 155 (87), 123 (47), 105 (59) [$Ph-CHO^+$], 91 (77) [$(PhCH_2)^+$], 79 (59); $C_{25}H_{30}O_5$ (410.51): calcd C 73.15, H 7.37; found C 73.45, H 7.64.

(2*R*,2″*S*,4*R*,6*R*)-6-(2″-Benzyloxy-4″-pentenyl)-4-(methoxy-carbonylmethyl)-2-phenyl-1,3-dioxane (12): The alcohol **10** (87 mg, 0.29 mmol) was treated with benzaldehyde (3×32 μL, 0.31 mmol, 1.1 equiv) and KO*t*Bu (3×3.2 mg, 29 μmol, 0.1 equiv) as outlined above for **9**. Purification by flash chromatography (diethyl ether/petroleum ether 1:2) afforded the benzylidene acetal **12** (82 mg, 70%) as a colorless oil. Selectivity 4*R*:4*S* = >20:1 (^{1}H NMR); $[\alpha]_D^{20}=+72.6$ ($c=0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=1.32-1.83$ (m, 4H, 5-H_2, 1″-CH_2), 2.36 (t, $J=6.5$ Hz, 2H, 3″-CH_2), 2.49 (dd, $J=15.5$, 6.0 Hz, 1H, 1′-CH), 2.74 (dd, $J=15.5$, 7.0 Hz, 1H, 1′-CH), 3.69 (s, 3H, OMe), 3.86 (m_c, 1H, 2″-CH), 4.07 (m_c, 1H, 6-CH), 4.29 (m_c, 1H, 4-CH), 4.46, 4.68 ($2\times$d, $J=11.5$ Hz, 2H, OCH_2-Ph), 5.02–5.18 (m, 2H, 5″-CH_2), 5.44 (s, 1H, 2-CH), 5.85 (m, 1H, 4″-CH), 7.17–7.44 (m, 10H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=36.87$, 38.64, 40.75, 41.09 (C5, C1′, C1″, C3″), 51.74 (OCH_3), 71.62 (OCH_2-Ph), 73.06, 73.15, 73.88 (C4, C6, C2″), 100.3 (C2), 117.5 (C5″), 126.0, 127.7, 128.0, 128.1, 128.4 (phenyl-C), 134.3 (C4″), 138.5, 138.6 (phenyl-C), 171.2 (C2′); IR (film): $\tilde{\nu}=$ 3066, 3032, 2976, 2949, 2916, 2871 (CH), 1740 (C=O), 1641 (C=C), 1454, 1437, 1406, 1391, 1350, 1311, 1250, 1213, 1162, 1147, 1094, 1060, 1027, 914, 754, 699 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 256.5 nm (3.003); MS (70 eV, EI): m/z (%): 410 (4) [M^+], 369 (6), 263 (20), 155 (15), 91 (100) [$(PhCH_2)^+$]; $C_{25}H_{30}O_5$ (410.51): calcd C 73.15, H 7.37; found C 72.94, H 7.21.

(3′*S*,4*S*,5′*R*,7′*R*)-4-*tert*-Butyl-3-[7′-benzyloxy-3′,5′-bis(dimethylphenylsilyl)-9′-decen-oyl]-oxazolidin-2-one (13): $PhMe_2SiLi$[23] (0.35 M solution in THF, 5.54 mL, 1.94 mmol, 3.0 equiv) was added to a suspension of purified CuI[24] (369 mg, 1.94 mmol, 3.0 equiv) in THF (10 mL) at -30 °C. After being stirred at this temperature for 30 min, the mixture was cooled to -78 °C and Me_2AlCl (1.0 M solution in hexane, 1.94 mL, 1.94 mmol, 3.0 equiv) was added. Then the α,β-unsaturated imide **5** (345 mg, 0.65 mmol) dissolved in THF (1 mL) was added slowly. The reaction mixture was stirred at -78 °C for 1 h, quenched by the addition of water (50 mL), and extracted with CH_2Cl_2 (3×50 mL) and Et_2O (3×50 mL).

The organic layers were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (diethyl ether/petroleum ether 1:4) afforded the bis-silylated imide **13** (398 mg, 92%) as a colorless oil. Diastereoselectivity $3'S$:$3'R = 20$:1 (HPLC). $[\alpha]_D^{20} = +8.5$ (c = 0.4, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.19, 0.20, 0.23, 0.24$ (4 × s, 12H, 2 × $SiMe_2$), 0.80 (s, 9H, *t*Bu), 0.95 – 1.33 (m, 3H, 3′-H, 4′-CH, 5′-CH), 1.55 – 1.81 (m, 3H, 4′-CH, 6′-CH_2), 2.13 (m_c, 2H, 8′-CH_2), 2.84 (dd, $J = 18.0$, 5.5 Hz, 1H, 2′-CH), 3.02 (dd, $J =$ 18.0, 6.5 Hz, 1H, 2′-CH), 3.35 (m_c, 1H, 7′-CH), 3.69 (dd, $J = 9.0$, 8.0 Hz, 1H, 4-CH), 4.04 (d, $J = 9.0$ Hz, 1H, 5-CH), 4.13 (d, $J = 8.0$ Hz, 1H, 5-CH), 4.26, 4.42 (2 × d, $J = 12.0$ Hz, 2H, OCH_2-Ph), 4.91 – 5.05 (m, 2H, 10′-CH_2), 5.56 – 5.80 (m, 1H, 9′-CH), 7.20 – 7.49 (m, 15H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.32, -4.28, -4.04, -3.42$ (2 × $SiMe_2$), 19.61, 19.74 (C3′, C5′), 25.64 (C(*C*H_3)$_3$), 31.66, 35.56, 35.78, 36.39, 38.11 (C2′, C4′, C6′, C8′, *C*(CH_3)$_3$), 61.03 (C4), 64.99 (C5), 69.74 (OCH_2-Ph), 77.14 (C7′), 116.8 (C10′), 127.0, 127.1, 127.6, 127.7, 128.1, 128.7, 128.9, 134.1 (phenyl-C), 135.0 (C9′), 138.3, 138.7, 139.3 (phenyl-C), 154.7 (C2), 173.1 (C1′); IR (film): $\tilde{\nu} =$ 3068, 3048, 2962, 2926, 2908, 2870 (CH), 1782 (C=O), 1706 (C=O), 1642 (C=C), 1450, 1426, 1380, 1368, 1350, 1322, 1250, 1220, 1186, 1154, 1110, 1068, 1030, 1010, 830, 814, 770, 734, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 192.5 nm (5.200), 259.0 (3.209); MS (70 eV, EI): *m*/*z* (%): 669 (1) [M^+], 578 (9) [$M^+ -$ Bn], 278 (58), 135 (100) [$PhMe_2Si^+$], 91 (49), [$(PhCH_2)^+$], 57 (4) [*t*Bu^+]; $C_{40}H_{54}NO_4Si_2$ (669.05): calcd C 71.81, H 8.14; found C 71.89, H 8.29.

(3′*S*,4*S*,5′*R*,7′*S*)-4-*tert*-Butyl-3-[7′-benzyloxy-3′,5′-bis(dimethylphenylsilyl)-9′-decen-oyl]-oxazolidin-2-one (14): The α,β-unsaturated imide **6** (269 mg, 0.50 mmol) was treated with three equivalents of both the organocopper reagent and the Lewis acid (288 mg CuI: 4.32 mL 0.35 M $PhMe_2SiLi$ solution in THF; Me_2AlCl: 1.51 mL, 1.51 mmol) in THF (15 mL) as outlined above. Purification by flash chromatography (diethyl ether/petroleum ether 1:4) afforded the bis-silylated imide **14** (310 mg, 92%) as a colorless oil. Diastereoselectivity $3'S$:$3'R = 20$:1 (HPLC). $[\alpha]_D^{20} = +25.0$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.16, 0.20, 0.23$ (3 × s, 12H, 2 × $SiMe_2$), 0.85 (s, 9H, *t*Bu), 1.46 – 1.78 (m, 6H, 3′-CH, 4′-CH_2, 5′-CH, 6′-CH_2), 2.12 (m_c, 2H, 8′-CH_2), 2.81 (dd, $J = 17.5$, 5.5 Hz, 1H, 2′-CH), 2.93 (dd, $J = 17.5$, 6.5 Hz, 1H, 2′-CH), 3.26 (quint, $J = 5.5$ Hz, 1H, 7′-CH), 4.01 (dd, $J = 9.0$, 7.5 Hz, 1H, 5-CH), 4.17 (dd, $J = 9.0$, 1.5 Hz, 1H, 5-CH), 4.22 (dd, $J = 7.5$, 1.5 Hz, 1H, 4-CH), 4.24, 4.43 (2 × d, $J = 11.5$ Hz, 2H, OCH_2-Ph), 4.90 – 5.04 (m, 2H, 10′-CH_2), 5.69 (m_c, 1H, 9′-CH), 7.22 – 7.46 (m, 15H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.45, -4.15, -3.90, -3.50$ (2 × $SiMe_2$), 19.92, 20.30 (C3′, C5′), 25.66 (C(*C*H_3)$_3$), 32.07, 35.31, 35.62, 36.52, 37.96 (C2′, C4′, C6′, C8′, *C*(CH_3)$_3$), 61.00 (C4), 65.16 (C5), 70.32 (OCH_2-Ph), 77.82 (C7′), 116.8 (C10′), 127.5, 127.6, 127.6, 127.7, 128.7, 128.8, 134.0, 134.1, 134.1 (phenyl-C), 134.8 (C9′), 138.2, 138.8, 139.0 (phenyl-C), 154.6 (C2), 173.1 (C1′); IR (film): $\tilde{\nu} =$ 3068, 2960, 2910 (CH), 1781 (C=O), 1705 (C=O), 1640 (C=C), 1454, 1427, 1401, 1383, 1368, 1322, 1248, 1219, 1185, 1111, 1067, 1029, 1008, 832, 769, 735, 701 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 252.0 nm (3.266); MS (200 eV, DCI/NH_3): *m*/*z* (%): 687 (26) [$(M+NH_4)^+$], 161 (100); $C_{40}H_{54}NO_4Si_2$ (669.05); calcd C 71.81, H 8.14; found C 71.60, H 8.17.

Methyl (3*S*,5*R*,7*R*)-7-benzyloxy-3,5-bis(dimethylphenylsilyl)-9-decenoate (15): MeMgCl (3 M solution in THF, 0.64 mL, 1.91 mmol, 8.0 equiv) was added to anhydrous MeOH (5 mL) at 0 °C. The mixture was stirred at 0 °C for 2 min and then added to a precooled solution (0 °C) of bis-silylated imide **13** (160 mg, 0.24 mmol) in anhydrous MeOH (5 mL) and CH_2Cl_2 (5 mL) by means of a syringe. The reaction mixture was stirred at 0 °C for 5 min, refluxed for 15 h, cooled to room temperature, and then quenched by the addition of saturated aqueous $NaHCO_3$ solution (20 mL). The mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography (diethyl ether/petroleum ether 1:3) gave **15** (123 mg, 92%) as a colorless oil. $[\alpha]_D^{20} = -28.4$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.18, 0.19$ (2 × s, 12H, 2 × $SiMe_2$), 0.92 – 1.39 (m, 4H, 3-CH, 4-CH_2, 5-CH), 1.51 – 1.74 (m, 2H, 6-CH_2), 2.18 (m_c, 4H, 2-CH_2, 8-CH_2), 3.35 (m_c, 1H, 7-CH), 3.45 (s, 3H, OMe), 4.27, 4.45 (2 × d, $J = 12.0$ Hz, 2H, OCH_2-Ph), 4.93 – 5.08 (m, 2H, 10-CH_2), 5.72 (m_c, 1H, 9-CH), 7.22 – 7.46 (m, 15H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.57, -4.06, -3.69$ (2 × $SiMe_2$), 19.53, 21.25 (C3, C5), 31.07, 34.62, 35.69, 38.20 (C2, C4, C6, C8), 51.16 (OCH_3), 70.10 (OCH_2-Ph), 77.20 (C7), 116.8 (C10), 127.2, 127.3, 127.6, 128.1, 128.7, 128.9, 134.0, 134.0 (phenyl-C), 134.9 (C9), 137.7, 138.7, 139.0 (phenyl-C), 174.1 (C1); IR (film): $\tilde{\nu} =$ 3068, 3048, 2952, 2924, 2906, 2860 (CH), 1736 (C=O), 1640 (C=C), 1450, 1430, 1350, 1252, 1202, 1172, 1154, 1112, 1070, 1028, 830, 814, 770, 734, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 259.0 nm (3.039); MS (70 eV, EI): *m*/*z* (%): 558 (< 1) [M^+], 467 (5) [$M^+ -$ Bn], 279 (16), 167 (35), 149 (70), 135 (100) [$PhMe_2Si^+$], 91 (51), [$(PhCH_2)^+$]; $C_{34}H_{46}O_3Si_2$ (558.91): calcd C 73.07, H 8.30; found C 73.16, H 8.27.

Methyl (3*S*,5*R*,7*S*)-7-benzyloxy-3,5-bis(dimethylphenylsilyl)-9-decenoate (16): The bis-silylated imide **14** (186 mg, 0.28 mmol) was converted to the methyl ester **16** with MgClOMe as described above for **15** to afford 128 mg (82%) of the title compound as a colorless oil. $[\alpha]_D^{20} = -1.4$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.17, 0.18$ (2 × s, 12H, 2 × $SiMe_2$), 1.02 – 1.74 (m, 6H, 3-CH, 4-CH_2, 5-CH, 6-CH_2), 2.11 (dd, $J = 15.5$, 7.0 Hz, 1H, 2-CH), 2.08 – 2.25 (m, 2H, 8-CH_2), 2.24 (dd, $J = 15.5$, 6.5 Hz, 1H, 2-CH), 3.22 (quint, $J = 6.0$ Hz, 1H, 7-CH), 3.50 (s, 3H, OMe), 4.28, 4.45 (2 × d, $J = 11.5$ Hz, 2H, OCH_2-Ph), 4.92 – 5.06 (m, 2H, 10-CH_2), 5.70 (m_c, 1H, 9-CH), 7.25 – 7.43 (m, 15H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.70, -4.35, -4.20, -3.98$ (2 × $SiMe_2$), 20.34, 21.23 (C3, C5), 34.49, 35.09, 35.19, 37.93 (C2, C4, C6, C8), 51.26 (OCH_3), 70.33 (OCH_2-Ph), 77.63 (C7), 116.9 (C10), 127.3, 127.6, 128.2, 128.8, 128.9, 134.0, (phenyl-C), 134.8 (C9), 137.7, 138.7, 138.9 (phenyl-C), 174.2 (C1); IR (Film): = 3068, 3050, 3024, 2952, 2916, 2854, 1736 (C=O), 1640 (C=C), 1450, 1430, 1350, 1250, 1202, 1170, 1154, 1138, 1112, 1066, 1028, 830, 814, 770, 734, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 192.5 nm (5.227), 259.0 (3.196); MS (70 eV, EI): *m*/*z* (%): 558 (< 1) [M^+], 543 (1) [$M^+ - CH_3$], 467 (3) [$M^+ -$ Bn], 271 (31), 209 (23), 193 (20), 135 (100) [$PhMe_2Si^+$], 91 (36), [$(PhCH_2)^+$]; $C_{34}H_{46}O_3Si_2$ (558.91): calcd C 73.07, H 8.30; found C 73.20, H 8.52

Methyl (3*R*,5*R*,7*R*)-7-benzyloxy-3,5-bis(dimethylphenylsilyl)-9-decenoate (19): CuCN (142 mg, 1.59 mmol, 3 equiv) was placed in a flask (25 mL) and carefully flame-dried under N_2. After the flask had cooled to room temperature, the CuCN was suspended in THF (15 mL). The mixture was cooled to 0 °C and $PhMe_2SiLi$[23] (0.53 M solution in THF, 3.00 mL, 1.59 mmol, 3.0 equiv) was added. The mixture was stirred for 30 min at this temperature, cooled to −78 °C, and freshly distilled $BF_3 \cdot Et_2O$ (0.20 mL, 1.59 mmol, 3 equiv) was added. The solution was stirred for a few minutes and then a solution of the α,β-unsaturated ester **7** (224 mg, 0.53 mmol) in THF (1 mL) was added slowly. The reaction mixture was stirred at −78 °C for 1 h, then quenched by the addition of water (50 mL), and extracted with CH_2Cl_2 (3 × 50 mL) and Et_2O (3 × 50 mL). The organic layers were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (diethyl ether/petroleum ether 1:10) afforded the bis-silylated ester **19** (267 mg, 90%) as a colorless oil. Diastereoselectivity $3R$:$3S = 19$:1 (HPLC); $[\alpha]_D^{20} = +4.0$ ($c = 0.5$, $CHCl_3$). Spectroscopic data for the major isomer: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.21$ (s, 12H, 2 × $SiMe_2$), 1.20 – 1.68 (m, 6H, 3-CH, 4-CH_2, 5-CH, 6-CH_2), 2.06 – 2.28 (m, 4H, 2-CH_2, 8-CH_2), 3.30 (quint, $J = 6.0$ Hz, 1H, 7-CH), 3.44 (s, 3H, OMe), 4.26, 4.41 (2 × d, $J = 12.0$ Hz, 2H, OCH_2-Ph), 4.94 – 5.10 (m, 2H, 10-CH_2), 5.72 (m_c, 1H, 9-CH), 7.23 – 7.45 (m, 15H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.66, -4.61, -4.50, -4.06$ (2 × $SiMe_2$), 18.45, 20.09 (C3, C5), 31.27, 33.86, 35.11, 37.90 (C2, C4, C6, C8), 51.17 (OCH_3), 70.27 (OCH_2-Ph), 78.11 (C7), 116.9 (C10), 127.3, 127.6, 127.6, 128.1, 128.8, 128.9, 133.9, 133.9 (phenyl-C), 134.9 (C9), 137.7, 138.6, 139.0 (phenyl-C), 174.1 (C1); IR (film): $\tilde{\nu} =$ 3068, 3024, 2950, 2901 (CH), 1736 (C=O), 1640 (C=C), 1454, 1428, 1352, 1249, 1202, 1156, 1112, 1069, 1029, 834, 813, 772, 735, 701 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg \varepsilon$) = 211.5 nm (4.642); MS (200 eV, DCI/NH_3): *m*/*z* (%): 576 (100) [$(M+NH_4)^+$]; $C_{34}H_{46}O_3Si_2$ (558.91): calcd C 73.07, H 8.30; found C 73.20, H 8.14.

Methyl (3*R*,5*R*,7*S*)-7-benzyloxy-3,5-bis(dimethylphenylsilyl)-9-decenoate (20): The α,β-unsaturated ester **8** (245 mg, 0.58 mmol) was treated with 3.0 equiv of both the organocopper reagent and the Lewis acid (156 mg CuCN; 3.28 mL 0.53 M $PhMe_2SiLi$ solution in THF; $BF_3 \cdot Et_2O$: 0.22 mL, 1.74 mmol) in THF (15 mL) as outlined above. Purification by flash chromatography (diethyl ether/petroleum ether 1:10) afforded the bis-silylated ester **20** (298 mg, 92%) as a colorless oil. Diastereoselectivity $3R$:$3S = 12$:1 (^{1}H and ^{13}C NMR). $[\alpha]_D^{20} = +27.6$ ($c = 0.5$, $CHCl_3$). Spectroscopic data for the major isomer: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.18, 0.23$ (2 × s, 12H, 2 × $SiMe_2$), 1.16 – 1.54 (m, 6H, 3-CH, 4-CH_2, 5-CH, 6-CH_2), 2.07 – 2.30 (m, 4H, 2-CH_2, 8-CH_2), 3.11 (quint, $J = 6.5$ Hz, 1H, 7-CH), 3.44 (s, 3H, OMe), 4.12, 4.38 (2 × d, $J = 11.5$ Hz, 2H, OCH_2-Ph), 4.92 – 5.08 (m, 2H, 10-CH_2), 5.67 (m_c, 1H, 9-CH), 7.24 – 7.48 (m, 15H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = -4.74, -4.61, -4.32, -4.13$ (2 × $SiMe_2$), 18.42, 19.81 (C3, C5), 30.37, 33.57, 34.51, 38.17 (C2, C4, C6, C8), 51.11 (OCH_3), 70.50 (OCH_2-Ph), 77.63 (C7), 116.9 (C10), 127.2, 127.6, 127.6, 128.1, 128.1, 128.7, 128.8, 133.9 (phenyl-C), 134.8 (C9), 137.9, 138.6, 138.9

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(phenyl-C), 174.1 (C1); IR (film): $\tilde{\nu}$ = 3068, 3049, 3024, 2952, 2906, 2845 (CH), 1736 (C=O), 1641 (C=C), 1454, 1428, 1351, 1249, 1203, 1156, 1112, 1067, 1028, 832, 813, 771, 735, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 259.0 nm (3.100); MS (70 eV, EI): *m*/*z* (%): 558 (5) [M^+], 543 (8) [$M^+ - CH_3$], 467 (5) [$M^+ - Bn$], 135 (100) [$PhMe_2Si^+$], 91 (62), [$(PhCH_2)^+$]; $C_{34}H_{46}O_3Si_2$ (558.91): calcd C 73.07, H 8.30; found C 72.81, H 8.20.

Methyl (3*R*,5*S*,7*R*)-7-benzyloxy-3,5-dihydroxy-9-decenoate (17a): Boron trifluoride/acetic acid complex (36%, 3.69 mL, 7.07 mmol, 2.5 equiv) was added to a stirred solution of the bis-silane **15** (1.58 g, 2.83 mmol) in dry CH_2Cl_2 (40 mL) at room temperature. After being stirred for 5 min, the yellow-brown colored reaction mixture was poured into saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford the bisfluorosilane as a yellow oil. This was dissolved in DMF (40 mL) without further purification and treated with KF (1.97 g, 34.0 mmol, 12 equiv) and a solution of *m*-chloroperoxybenzoic acid (2.09 g, 8.49 mmol, 3 equiv) in DMF (3 mL) at 0 °C. The reaction mixture was stirred at this temperature for 2 h, poured into water (100 mL), and extracted with Et_2O (3 × 100 mL). The organic layer was washed with water (1 × 50 mL) and the aqueous layer was reextracted with Et_2O (3 × 50 mL). Again, these extracts were washed with water (1 × 20 mL) and the aqueous phase was reextracted with Et_2O (3 × 50 mL) to wash out DMF and to minimize losses of the water-soluble diol. The combined organic extracts were dried over $MgSO_4$ and concentrated in vacuo. The diol tended to lactonize spontaneously and was therefore purified over a small amount of silica gel (diethyl ether/petroleum ether 2:1). The diol **17a** (684 mg, 75%) was isolated as a colorless oil. $[\alpha]_D^{20} = -46.0$ (c = 0.4, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.46–1.84 (m, 4H, 4-CH_2, 6-CH_2), 2.34–2.60 (m, 4H, 2-CH_2, 8-CH_2), 3.70 (s, 3H, OMe), 3.76 (m_c, 1H, 7-CH), 3.92–4.15 (m, 3H, 2 × OH, 5-CH), 4.17–4.33 (m, 1H, 3-CH), 4.45, 4.70 (2 × d, J = 11.5 Hz, 2H, OCH_2-Ph), 5.11 (d, J = 12.0 Hz, 1H, 10-CH), 5.12 (d, J = 15.5 Hz, 1H, 10-CH), 5.80 (m_c, 1H, 9-CH), 7.28–7.42 (m, 5H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 37.82, 41.06, 41.62, 42.64 (C2, C4, C6, C8), 51.70 (OCH_3), 68.37, 71.66 (C3, C5), 70.72 (OCH_2-Ph), 78.62 (C7), 118.0 (C10), 128.0, 128.2, 128.6 (phenyl-C), 133.5 (C9), 137.6 (phenyl-C), 172.6 (C1); IR (film): $\tilde{\nu}$ = 3429 (OH), 3067, 3030, 2919 (CH), 1731 (C=O), 1640 (C=C), 1454, 1438, 1350, 1256, 1164, 1071, 1028, 1001, 917, 845, 749, 699 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (2.718); MS (200 eV, DCI/NH_3): *m*/*z* (%): 340 (100) [$(M+NH_4)^+$]; $C_{18}H_{26}O_5$ (322.40): calcd C 67.06, H 8.13; found C 67.02, H 7.70.

Methyl (3*R*,5*S*,7*S*)-7-benzyloxy-3,5-dihydroxy-9-decenoate (17b): As described above for **17a**, the bis-silane **16** (303 mg, 0.54 mmol) was oxidatively desilylated to furnish the diol ester **17b** (136 mg, 78%) as a colorless oil. $[\alpha]_D^{20} = +28.3$ (c = 0.4, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.46–1.83 (m, 4H, 4-CH_2, 6-CH_2), 2.26–2.64 (m, 4H, 2-CH_2, 8-CH_2), 3.71 (s, 3H, OMe), 3.80 (m_c, 1H, 7-CH), 4.05–4.37 (m, 2H, 3-H, 5-CH), 4.51, 4.66 (2 × d, J = 11.5 Hz, 2H, OCH_2-Ph), 5.04–5.19 (m, 2H, 10-CH_2), 5.81 (m_c, 1H, 9-CH), 7.30–7.39 (m, 5H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.13, 40.89, 41.66, 42.66 (C2, C4, C6, C8), 51.75 (OCH_3), 68.77, 69.06 (C3, C5), 71.42 (OCH_2-Ph), 75.83 (C7), 117.6 (C10), 127.9, 128.0, 128.5 (phenyl-C), 134.2 (C9), 138.2 (phenyl-C), 172.7 (C1); IR (film): $\tilde{\nu}$ = 3424 (OH), 3066, 3031, 2918 (CH), 1731 (C=O), 1641 (C=C), 1438, 1351, 1257, 1164, 1071, 1028, 917, 851, 739, 699 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (2.821); MS (200 eV, DCI/NH_3): *m*/*z* (%): 340 (100) [$(M+NH_4)^+$]; $C_{18}H_{26}O_5$ (322.40): calcd C 67.06, H 8.13; found C 67.05, H 7.95.

Methyl (3*S*,5*S*,7*R*)-7-benzyloxy-3,5-dihydroxy-9-decenoate (17c): As described above for **17a**, the bis-silane **19** (961 mg, 1.72 mmol) was oxidatively desilylated to furnish the diol ester **17c** (405 mg, 73%) as a colorless oil. $[\alpha]_D^{20} = -32.0$ (c = 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50–1.83 (m, 4H, 4-CH_2, 6-CH_2), 2.40–2.50 (m, 4H, 2-CH_2, 8-CH_2), 3.68 (s, 3H, OMe), 3.76 (m_c, 1H, 7-CH), 4.10, 4.31 (2 × m_c, 2H, 3-H, 5-CH), 4.47, 4.69 (2 × d, J = 11.0 Hz, 2H, OCH_2-Ph), 5.06–5.15 (m, 2H, 10-CH_2), 5.80 (m_c, 1H, 9-CH), 7.27–7.37 (m, 5H, phenyl-CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.81, 40.58, 41.44, 42.49 (C2, C4, C6, C8), 51.67 (OCH_3), 65.39, 69.04 (C3, C5), 70.77 (OCH_2-Ph), 79.28 (C7), 118.0 (C10), 127.9, 127.9, 128.6 (phenyl-C), 133.5 (C9), 137.5 (phenyl-C), 172.9 (C1); IR (film): $\tilde{\nu}$ = 3427 (OH), 3069, 3031, 2925 (CH), 1731 (C=O), 1641 (C=C), 1437, 1349, 1286, 1253, 1164, 1072, 1029, 917, 839, 751, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 228.0 nm (4.926); MS (200 eV, DCI/NH_3): *m*/*z* (%): 340 (100) [$(M+NH_4)^+$], 323 (23) [$(M+H)^+$]; $C_{18}H_{26}O_5$ (322.40): calcd C 67.06, H 8.13; found C 67.02, H 7.70

Methyl (3*S*,5*S*,7*S*)-7-benzyloxy-3,5-dihydroxy-9-decenoate (17d): As described above for **17a**, the bis-silane **20** (686 mg, 1.23 mmol) was oxidatively desilylated to furnish the diol ester **17d** (301 mg, 76%) as a colorless oil. $[\alpha]_D^{20} = +27.2$ (c = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.50–1.87 (m, 4H, 4-H_2, 6-CH_2), 2.26–2.60 (m, 4H, 2-H_2, 8-CH_2), 3.71 (s, 3H, OMe), 3.80 (m_c, 1H, 7-CH), 4.22, 4.33 (2 × m_c, 2H, 3-H, 5-CH), 4.50, 4.65 (2 × d, J = 11.5 Hz, 2H, OCH_2-Ph), 5.03–5.19 (m, 2H, 10-CH_2), 5.81 (m_c, 1H, 9-CH), 7.30–7.39 (m, 5H, phenyl-CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 37.91, 39.93, 41.22, 42.27 (C2, C4, C6, C8), 51.75 (OCH_3), 65.69, 65.85 (C3, C5), 71.30 (OCH_2-Ph), 76.18 (C7), 117.6 (C10), 127.8, 127.9, 128.5 (phenyl-C), 134.2 (C9), 138.0 (phenyl-C), 173.1 (C1); IR (film): $\tilde{\nu}$ = 3429 (OH), 3068, 3031, 2924 (CH), 1735 (C=O), 1641 (C=C), 1438, 1352, 1255, 1206, 1164, 1069, 1028, 916, 739, 699 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (2.685); MS (200 eV, DCI/NH_3): *m*/*z* (%): 340 (100) [$(M+NH_4)^+$], 323 (70) [$(M+H)^+$]; $C_{18}H_{26}O_5$ (322.40): calcd C 67.06, H 8.13; found C 67.05, H 7.95.

(2″*R*,4*R*,6*R*)-6-(2″-Benzyloxy-4″-pentenyl)-4-(methoxycarbonylmethyl)-2,2-dimethyl-1,3-dioxane (18a): A catalytic amount of pyridinium *para*-toluenesulfonate was added to a solution of diol **17a** (300 mg, 0.93 mmol) in 2,2-dimethoxypropane (10 mL) at room temperature. The mixture was stirred for 15 h at this temperature and then the volatiles were removed in vacuo. The crude product was purified by flash chromatography (diethyl ether/petroleum ether 1:2) to furnish the acetonide **18a** (320 mg, 95%) as a colorless oil. $[\alpha]_D^{20} = -25.0$ (c = 0.24, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.01–1.63 (m, 3H, 5-H_2, 1″-CH), 1.35, 1.43 (2 × s, 6H, 2-Me_2), 1.86 (ddd, J = 15.0, 6.5, 6.5 Hz, 1H, 1″-CH), 2.31 (dd, J = 15.5, 6.0 Hz, 1H, 1′-CH), 2.30–2.41 (m, 2H, 3″-CH_2), 2.51 (dd, J = 15.5, 7.0 Hz, 1H, 1′-CH), 3.58 (m_c, 1H, 2″-CH), 3.68 (s, 3H, OMe), 4.01 (dtd, J = 11.0, 6.0, 2.5 Hz, 1H, 4-CH/6-CH), 4.22 (m_c, 1H, 4-CH/6-CH), 4.44, 4.60 (2 × d, J = 12.0 Hz, 2H, OCH_2-Ph), 5.03–5.19 (m, 2H, 5″-CH_2), 5.85 (m_c, 1H, 4″-CH), 7.21–7.38 (m, 5H, phenyl-CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.69, 30.09 (C(CH_3)$_2$), 36.32, 38.15, 40.31, 41.20 (C5, C1′, C1″, C3″), 51.63 (OCH_3), 65.90, 65.92 (C4, C6), 70.63 (OCH_2-Ph), 74.42 (C2″), 98.72 (C2), 117.4 (C5″), 127.6, 128.0, 128.4 (phenyl-C), 134.5 (C4″), 138.7 (phenyl-C), 171.4 (C2′); IR (film): $\tilde{\nu}$ = 3066, 3028, 2992, 2945, 2916, 1741 (C=O), 1641 (C=C), 1438, 1381, 1314, 1265, 1201, 1169, 1096, 1028, 999, 917, 737, 699 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (2.821); MS (70 eV, EI): *m*/*z* (%): 362 (< 1) [M^+], 347 (9) [$M^+ - CH_3$], 263 (16), 91 (100) [$(PhCH_2)^+$]; $C_{21}H_{30}O_5$ (362.47): calcd C 69.59, H 8.34; C 69.75, H 8.57.

(2″*S*,4*R*,6*R*)-6-(2″-Benzyloxy-4″-pentenyl)-4-(methoxycarbonylmethyl)-2,2-dimethyl-1,3-dioxane (18b): Acetonide formation was performed on the diol ester **17b** (470 mg, 1.46 mmol) in the same way as described above for **18a** to afford **18b** (502 mg, 95%) as a colorless oil. $[\alpha]_D^{20} = +52.0$ (c = 0.4, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.07–1.68 (m, 4H, 5-H_2, 1″-CH_2), 1.36, 1.42 (2 × s, 6H, 2-Me_2), 2.34 (m_c, 2H, 3″-CH_2), 2.36 (dd, J = 15.5, 6.0 Hz, 1H, 1′-CH), 2.54 (dd, J = 15.5, 7.0 Hz, 1H, 1′-CH), 3.67 (s, 3H, OMe), 3.76 (m_c, 1H, 2″-CH), 4.13 (m_c, 1H, 4-CH/6-CH), 4.29 (dtd, J = 11.0, 6.0, 2.5 Hz, 1H, 4-CH/6-CH), 4.43, 4.63 (2 × d, J = 11.5 Hz, 2H, OCH_2-Ph), 5.03–5.16 (m, 2H, 5″-CH_2), 5.85 (m_c, 1H, 4″-CH), 7.28–7.38 (m, 5H, phenyl-CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.76, 30.06 (C(CH_3)$_2$), 36.92, 38.65, 41.17, 41.68 (C5, C1′, C1″, C3″), 51.51 (OCH_3), 65.18, 65.91 (C4, C6), 71.58 (OCH_2-Ph), 74.15 (C2″), 98.68 (C2), 117.2 (C5″), 127.5, 127.8, 128.3 (phenyl-C), 134.4 (C4″), 138.6 (phenyl-C), 171.3 (C2′); IR (film): $\tilde{\nu}$ = 3066, 3030, 2992, 2945, 2915 (CH), 1741 (C=O), 1640 (C=C), 1454, 1437, 1380, 1350, 1312, 1263, 1201, 1168, 1093, 1029, 998, 944, 915, 871, 813, 738, 698 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (2.688); MS (200 eV, DCI/NH_3): *m*/*z* (%): 380 (100) [$(M+NH_4)^+$]; $C_{21}H_{30}O_5$ (362.47): calcd C 69.59, H 8.34; found C 69.79, H 8.29.

(2″*R*,4*S*,6*R*)-6-(2″-Benzyloxy-4″-pentenyl)-4-(methoxycarbonylmethyl)-2,2-dimethyl-1,3-dioxane (18c): Acetonide formation was performed on the diol ester **17c** (72 mg, 0.22 mmol) in the same way as described above for **18a** to afford **18c** (78 mg, 96%) as a colorless oil. $[\alpha]_D^{20} = -44.0$ (c = 0.15, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.32, 1.35 (2 × s, 6H, 2-Me_2), 1.27–1.73 (m, 3H, 5-H_2, 1″-CH), 1.91 (ddd, J = 14.0, 7.0, 7.0 Hz, 1H, 1″-CH), 2.30–2.59 (m, 4H, 1′-H_2, 3″-CH_2), 3.56 (m_c, 1H, 2″-CH), 3.69 (s, 3H, OMe), 3.96, 4.25 (2x m_c, 1H, 4-CH, 6-CH), 4.46, 4.59 (2 × d, J = 11.5 Hz, 2H, OCH_2-Ph), 5.03–5.17 (m, 2H, 5″-CH_2), 5.86 (m_c, 1H, 4″-CH), 7.28–7.39 (m, 5H, phenyl-CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.52, 24.54, (C(CH_3)$_2$), 37.79, 38.03, 39.84, 40.49, (C5, C1′, C1″, C3″), 51.58 (OCH_3),

63.28, 63.47 (C4, C6), 70.66 (OCH_2-Ph), 74.73 (C2″), 100.5 (C2), 117.4 (C5″), 127.5, 127.9, 128.3 (phenyl-C), 134.4 (C4″), 138.6 (phenyl-C), 171.4 (C2′); IR (film): $\tilde{\nu}$ = 3068, 3030, 2987, 2941, 1742 (C=O), 1641 (C=C), 1454, 1437, 1381, 1321, 1225, 1202, 1169, 1123, 1089, 1070, 1028, 1001, 912, 738, 699 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (2.823); MS (200 eV, DCI/NH_3): *m*/*z* (%): 380 (100) [$(M+NH_4)^+$]; $C_{21}H_{30}O_5$ (362.47): calcd C 69.59, H 8.34; found C 69.91, H 8.46

(2″*S*,4*S*,6*R*)-6-(2″-Benzyloxy-4″-pentenyl)-4-(methoxycarbonylmethyl)-2,2-dimethyl-1,3-dioxane (18d): Acetonide formation was performed on the diol ester **17d** (112 mg, 0.35 mmol) in the same way as described above for **18a** to afford **18d** (120 mg, 95 %) as a colorless oil. $[\alpha]_D^{20}$ = +23.0 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.31, 1.35 (2 × s, 6H, 2-Me_2), 1.55 – 1.72 (m, 4H, 5-H_2, 1″-CH_2), 2.30 – 2.43 (m, 2H, 3″-CH_2), 2.41 (dd, *J* = 15.5, 5.5 Hz, 1H, 1′-CH),), 2.55 (dd, *J* = 15.5, 8.0 Hz, 1H, 1′-CH), 3.68 (s, 3H, OMe), 3.71 (quint, *J* = 7.0 Hz, 1H, 2″-CH), 4.09, 4.26 (2 × m_c, 2H, 4-H, 6-CH), 4.43, 4.63 (2 × d, *J* = 11.0 Hz, 2H, OCH_2-Ph), 5.03 – 5.17 (m, 2H, 5″-CH_2), 5.86 (m_c, 1H, 4″-CH), 7.27 – 7.37 (m, 5H, phenyl-CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 24.64, 24.68 (C(CH_3)$_2$), 38.11, 38.52, 40.54, 41.03 (C5, C1′, C1″, C3″), 51.59 (OCH_3), 63.01, 63.46 (C4, C6), 71.53 (OCH_2-Ph), 74.78 (C2″), 100.6 (C2), 117.4 (C5″), 127.6, 127.9, 128.4 (phenyl-C), 134.4 (C4″), 138.6 (Ph-C), 171.4 (C2′); IR (film): $\tilde{\nu}$ = 3068, 3030, 2987, 2944, 1742 (C=O), 1640 (C=C), 1454, 1437, 1381, 1351, 1321, 1225, 1204, 1168, 1124, 1092, 1069, 1029, 737, 698 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 257.5 nm (2.693); MS (70 eV, EI): *m*/*z* (%): 362 (<1) [M^+], 347 (12) [$M^+ - CH_3$], 263 (26), 187 (12), 155 (14), 91 (100) [$(PhCH_2)^+$]; $C_{21}H_{30}O_5$ (362.47): calcd C 69.59, H 8.34; found C 69.86, H 8.14.

(2″*S*,4*R*,6*R*)-6-(2″-Benzyloxy-4″-oxobutyl)-4-(methoxycarbonylmethyl)-2,2-dimethyl-1,3-dioxane (21): *N*-methyl-morpholine *N*-oxide (19 mg, 0.16 mmol, 1.4 equiv) and a catalytic amount of OsO_4 (2.5 % solution in *t*BuOH, 25 μL) were added to a solution of the alkene **18a** (42 mg, 0.12 mmol) in acetone (1 mL) and water (0.3 mL). After being stirred for 15 h, TLC analysis showed complete consumption of the alkene. A solution of $NaIO_4$ (52 mg, 0.24 mmol, 2 equiv) in H_2O (0.5 mL) was added all at once. The mixture was stirred for 30 min, diluted with H_2O (10 mL), and extracted with Et_2O (3 × 20 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Purification by flash chromatography (diethyl ether/petroleum ether 2:1) afforded the aldehyde **21** (37 mg, 88 %) as a pale yellow oil. $[\alpha]_D^{20}$ = +14.0 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.10 – 1.57 (m, 2H, 5-CH_2), 1.35, 1.44 (2 × s, 6H, 2-Me_2), 1.65 (ddd, *J* = 14.5, 6.5, 4.5 Hz, 1H, 1″-CH), 1.93 (ddd, *J* = 14.5, 8.0, 5.5 Hz, 1H, 1″-CH), 2.35 (dd, *J* = 15.5, 6.0 Hz, 1H, 1′-CH), 2.45 (dd, *J* = 15.5, 7.0 Hz, 1H, 1′-CH), 2.62 – 2.73 (m, 2H, 3″-CH_2), 3.69 (s, 3H, OMe), 3.92 – 4.37 (m, 3H, 4-H, 6-H, 2″-CH), 4.53 (s, 2H, OCH_2-Ph), 7.26 – 7.41 (m, 5H, phenyl-CH), 9.77 (t, *J* = 2.0 Hz, 1H, 4″-CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.63 (C(CH_3)), 29.99 (C(CH_3)), 36.46, 40.19 (C5, C1″), 41.10 (C1′), 48.12 (C3″), 51.57 (OCH_3), 65.27, 65.81, 70.91 (C4, C6, C2″), 70.99 (OCH_2-Ph), 98.73 (C2), 127.7, 127.8, 128.4, 138.0 (phenyl-C), 171.2 (C2′), 201.4 (C4″); IR (film): $\tilde{\nu}$ = 3030, 2993, 2948, 2920, 2730 (CH), 1738 (C=O), 1554, 1437, 1381, 1315, 1264, 1201, 1167, 1096, 1065, 1028, 1001, 740, 700 cm^{-1}; UV (CH_3CN): λ_{max} ($\lg\varepsilon$) = 205.5 nm (4.379); MS (200 eV, DCI/NH_3): *m*/*z* (%): 382 (100) [$(M+NH_4)^+$], 365 (16) [$(M+H)^+$]; $C_{20}H_{28}O_6$ (364.44): calcd C 65.92, H 7.74; found C 66.07, H 7.67.

(2*R*,2″*S*,4*R*,6*R*)-6-(2″-Benzyloxy-4″-oxopentyl)-4-(methoxycarbonylmethyl)-2-phenyl-1,3-dioxane (23): $CuCl_2 \cdot 2H_2O$ (22 mg, 0.13 mmol) and $PdCl_2$ (10 mg, 0.05 mmol) were suspended in DMF/H_2O (8 mL, 7:1). At 60 – 70 °C the alkene **11** (34 mg, 0.08 mmol) was added and stirring was continued for 3 h at that temperature. The solvents were evaporated in vacuo and the residue was taken up in Et_2O (10 mL) and water (10 mL). The layers were separated and the aqueous phase was extracted again with Et_2O (2 × 10 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was evaporated in vacuo. Purification by flash chromatography (diethyl ether/petroleum ether 1:2) gave **23** (25 mg, 72 %) as a colorless oil. $[\alpha]_D^{20}$ = +12.0 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 – 1.52 (m, 2H), 1.74 (ddd, *J* = 14.0, 5.0, 5.0 Hz, 1H, 5-CH), 2.02 (ddd, *J* = 14.0, 7.5, 5.0 Hz, 1H, 5-CH), 2.09 (s, 3H, 5 × × -CH_3), 2.48 (dd, *J* = 16.0, 6.0 Hz, 1H, 1′-CH), 2.66 – 2.76 (m, 2H, 3 × × -CH_2), 2.82 (dd, *J* = 16.0, 7.0 Hz, 1H, 1′-CH), 3.70 (s, 3H, OMe), 3.98 – 4.09 (m, 1H, 4-CH), 4.14 (quint, *J* = 6.0 Hz, 1H, 2 × × -CH), 4.21 – 4.33 (m, 1H, 6-CH), 4.51 (s, 2H, OBn), 5.53 (s, 1H, 2-CH), 7.28 – 7.48 (m, 10H, phenyl-CH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.04, 36.47, 39.71, 40.66, 48.36, 51.77, 71.33, 72.01, 73.14, 73.18, 100.5, 126.0, 127.7, 127.9, 128.1, 128.4, 128.6, 138.2, 138.3, 171.1, 207.4; IR (film): = 3031, 2949, 2918, 2855 (CH), 1742, 1715 (C=O), 1496, 1454, 1437, 1355, 1312, 1254, 1215, 1167, 1121, 1058, 1028, 757, 702 cm^{-1}; MS (200 eV, DCI/NH_3): *m*/*z* (%): 444 (100) [$(M+NH_4)^+$]; $C_{25}H_{30}O_6$ (426.51): calcd C 70.40 H 7.09; found C 70.18 H 7.25.

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