Pergamon

Tetrahedron, Vol. 53, No. 1, pp. 133-144, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(96)00958-1

Highly Stereoselective Cope Rearrangements of Enantiomerically Pure, Silylated *syn*-Aldols

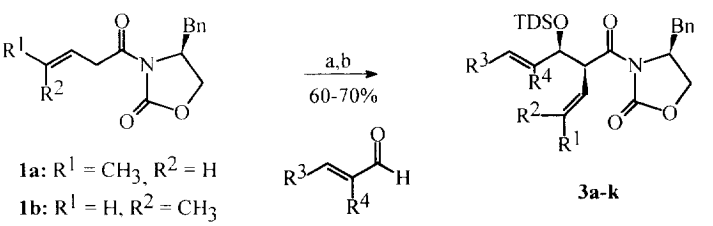
Christoph Schneider* and Markus Rehfeuter

Institut für Organische Chemie, Universität Göttingen,
Tammannstr.2, D-37077 Göttingen

Abstract: Enantiomerically pure, 1,6-disubstituted 1,5-dienes **3a-k** with an aldol subtitution pattern undergo rapid thermal Cope rearrangements with very high diastereoselection (up to >97:3) and in very good yield. Copyright © 1996 Elsevier Science Ltd

[3.3]-Sigmatropic rearrangements are of fundamental importance in stereoselective synthesis due to their stereospecific reaction course through a pericyclic transition state.[1] They offer the unique possibility to convert readily accessible sp^2-configuration of double bonds into sp^3-chirality of stereogenic centers. Furthermore the chiral centers formed upon the rearrangement can be far away from functional groups and chiral auxiliaries and hence are not easily set up by standard asymmetric transformations. However, in spite of these advantages and unlike the Claisen rearrangement[2] thermal Cope rearrangements of acyclic 1,5-dienes have gained little attention in the context of acyclic stereocontrol and natural product syntheses.[3] Several draw backs like the often encountered harsh reaction conditions, the intrinsic reversibility of the rearrangement and the lack of control over the competing transition states account for this fact.

Recently, we have been able to show that 1-substituted 1,5-dienes with an aldol substitution pattern undergo extremely rapid and kinetically controlled Cope rearrangements.[4] The stereochemistry of the aldol products proved to be decisive for the stereoselectivity of the rearrangement. Only a *syn*-stereochemistry provided good selectivities in the rearrangement. In an extension of this work we now report on highly stereoselective Cope rearrangements of 1,6-disubstituted, enantiomerically pure *syn*-aldols **3** which generate multifunctional products with two new stereogenic centers in high yield (82-91%) and excellent diastereoselectivity (up to >97:3) and provide full experimental details and spectroscopic data.[5]



1a: $R^1 = CH_3$, $R^2 = H$
1b: $R^1 = H$, $R^2 = CH_3$

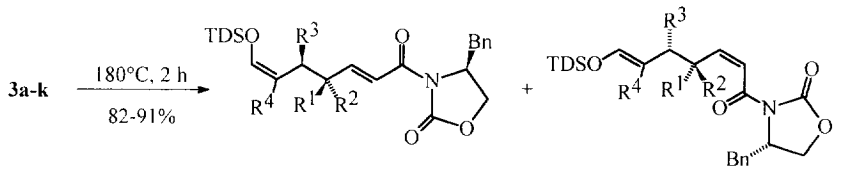
2

3a-k

Scheme 1. Synthesis of the Silylated *syn*-Aldols **3a-k**: a) Bu_2BOTf, NEt_3, CH_2Cl_2, -78°C, then **2**, -78°C, H_2O_2, MeOH, 0°C; b) TDSOTf, 2,6-lutidine, CH_2Cl_2, 0°C.

The enantiomerically pure 1,5-dienes **3a-k** used in this study were obtained by a straightforward two-step procedure (Scheme 1). Asymmetric aldol reaction[6] of the boron dienolates of the chiral imides **1a** and **1b** with the α,β-unsaturated aldehydes **2** followed by silylation (TDS = thexyldimethylsilyl) and chromatographic purification generated the 1,5-dienes **3a-k** with complete regio- and stereoselectivity in 60-70% overall yield.

The Cope rearrangements were performed in a sealed flask in toluene at 180°C (Scheme 2). Complete and very clean reactions were observed within 2 hours. The yields for the rearrangement range between 82% and 91% after chromatography, however, the crude products are usually sufficiently pure for further synthetic manipulations. It is important to note that the free aldol products are not suitable for the Cope rearrangement since they are very prone to retro-aldol cleavage and decompose within a few minutes at elevated temperatures.



4a-k **5a-k**

Scheme 2

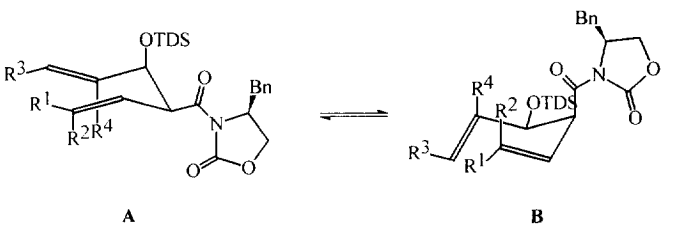
Table 1. Cope Rearrangements of the *syn*-Aldols **3a-k**.

1,5-diene	R^1	R^2	R^3	R^4	**4/5**[a]	yield[b](%)
3a	CH_3	H	CH_3	H	>97:3	87
3b	CH_3	H	H	CH_3	>97:3	91
3c	CH_3	H	CH_3	CH_3	>97:3	89
3d	CH_3	H	n-C_3H_7	H	95:5	82
3e	CH_3	H	$SiMe_3$	H	97:3	82
3f	CH_3	H	$SnBu_3$	H	97:3	85
3g	H	CH_3	CH_3	H	>97:3	86
3h	H	CH_3	H	CH_3	96:4	91
3i	H	CH_3	CH_3	CH_3	96:4	88
3k	H	CH_3	n-C_3H_7	H	>97:3	82

[a] Determined by ^1H and ^{13}C NMR spectroscopy on the crude products. [b] Total yield of both isomers after chromatographic purification.

In the course of the rearrangement chirality is transferred from the stereogenic centers built up in the aldol reaction to the new chiral centers in γ,δ-position relative to the auxiliary. These positions are not easily accessible by other asymmetric reactions. The stereoselectivity of the rearrangement is best explained by assuming transition states **A** and **B** (Scheme 3) which have been established by *Doering et al.*[7] for Cope rearrangements. The rearrangement proceeds selectively through transition state **A** with the carboximide group in pseudoequatorial position and the silyloxy group in pseudoaxial orientation to give the 2′*E*, 6′*Z*-isomers

4a-k as the major isomers. The minor 2′*Z*,6′*E*-isomers **5a-k** which arise via transition state **B** have been detected only in few cases in trace amounts of 3-5%. Other products resulting from boat or open transition states have not been observed. The absolute configuration of the stereogenic centers in **4** and **5** can be directly deduced from the depicted transition states.[8]



Scheme 3. Transition States for the Cope Rearrangement

The assignment of product configuration is based on the characteristic coupling constants of the double bond protons in the ^{1}H NMR spectra. For the major 2′*E*, 6′*Z*-isomers **4** coupling constants of $J_{2\text{-H/3-H}}$ = 15.5 Hz and $J_{6\text{H/7-H}}$ = 6.0 Hz are found whereas the spectra of the minor 2′Z, 6′E-isomers **5** display coupling constants of $J_{2\text{H/3-H}}$ = 11.5 Hz and $J_{6\text{H/7-H}}$ = 12.0 Hz. The resonance signal of the 3′-H in **5** typically appears at δ = 6.20 compared to δ = 7.20 in **4**.

The examples in Table 1 reveal that the rearrangement works well for a range of substrates giving the products in high yield and excellent selectivity. The exceptional driving force for the rearrangement exhibited by the aldol products is provided not only by moving the β,γ-unsaturated double bond back into conjugation with the carbonyl group but to a large extent also by the isomerization of the allyl silyl ether into a silyl enol ether.[9] It is sufficient for a complete and rapid rearrangement even when both double bonds are disubstituted (e.g. R^1, R^3 = alkyl or R^2, R^3 = alkyl). Either absolute product configuration can be created from the same chiral auxiliary by simply changing the double bond configuration in the aldol products. The stereoselective rearrangement of the silyl- and stannyl-substituted 1,5-dienes **3e** and **3f,** respectively, is especially noteworthy. The enantiomerically pure *Z*-γ-silyloxystannane **4f** furnished upon the rearrangement is a valuable reagent for the stereoselective synthesis of 1,2-diols.[10]

There are two important limitations observed so far. Firstly, quaternary chiral centers can not be generated using this method because aldol products with trisubstituted double bonds (e.g. R^1, R^2 = alkyl) do not rearrange and slowly decompose. Secondly, the aldol product derived from cinnamaldehyde (R^1 = CH_3, R^2 = H, R^3 = phenyl) undergoes a reversible Cope rearrangement and a mixture of isomers is formed along with recovered starting material. This stands in contrast to the cinnamaldehyde derived *syn*-aldol lacking the R^1-methyl group (R^1, R^2 = H, R^3 = Ph) which rearranges in a kinetically controlled process with high stereoselectivity (97:3). Thus, the additional methyl group shifts the rearrangement to a thermodynamically controlled process.

In conclusion, we have demonstrated for the first time that thermal Cope rearrangements of enantiomerically pure, acyclic 1,6-disubstituted 1,5-dienes can be efficiently used in the context of acyclic stereocontrol. The enantiomerically pure products formed upon the rearrangement are multifunctional and should prove useful as valuable building blocks for stereoselective synthesis. Investigations along these lines are currently being undertaken in our laboratory and will be reported in due course.

EXPERIMENTAL

General. All reactions were performed in flame-dried flasks under nitrogen. Tetrahydrofuran was freshly distilled from $LiAlH_4$, toluene from sodium, dichloromethane, triethylamine and 2,6-lutidine from CaH_2. Dibutylboryl trifluoromethanesulfonate was purchased as 1M solution in CH_2Cl_2 from Fluka. The α,β-unsaturated aldehydes **2** were either commercially available or prepared according to the literature.[11] Products were purified by flash chromatography on Macherey, Nagel & Co. 32-63 silica gel (particle size 0.032-0.064 mm). Thin layer chromatography was performed on precoated silica gel SIL G/UV_{254} plates (Macherey, Nagel & Co.). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as internal standard on Varian VXL-200 and VXR-500 spectrometers. IR spectra were recorded on a Bruker IFS 25 FT-IR instrument, UV spectra on a Perkin Elmer Lambda 9 spectrometer. Optical rotations were measured on a polarimeter Perkin Elmer 241. Mass spectra were taken at 70eV on a Finnigan MAT 95A spectrometer. Microanalyses were carried out by the Mikroanalytisches Labor des Instituts für Organische Chemie der Universität Göttingen.

(4*S*)-4-Benzyl-3-(3′*E*-pentenoyl)-oxazolidin-2-one (1a). 5.00 g (50.0 mmol) 3*E*-pentenoic acid (prepared from methyl pentenoate (Aldrich) by hydrolysis) was dissolved in 100 ml CH_2Cl_2 and treated with 4.75 ml (55.0 mmol) oxalyl chloride and a few drops DMF at 0°C. Stirring was continued for 1 h at 0°C and another 3 h at room temperature, after which the solvent was evaporated in vacuo. Meanwhile, 8.85 g (50.0 mmol) (4*S*)-4-benzyloxazolidin-2-one, dissolved in 100 ml THF, was cooled to -78°C and treated with 23.3 ml of a 2.36M BuLi-solution in hexane (55.0 mmol) for 30 min. The crude acid chloride was dissolved in 10 ml THF and added to the lithio oxazolidinone at -78°C. After being stirred for 30 min at -78°C and 1 h at 0°C the solution was poured into aqueous NH_4Cl-solution. The layers were separated and the aqueous phase was extracted twice with ether. The combined organic extracts were dried over $MgSO_4$, filtered and evaporated. Column chromatography over silica gel with ether/petroleum ether = 1:1 gave 9.32 g (72%) of **1a** as a colourless oil. $[\alpha]_D^{20}$ = + 64.0° (*c* = 0.45, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.74 (d, *J* = 4.0 Hz, 3 H, CH_3), 2.78 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.30 (dd, *J* = 13.5, 3.0 Hz, 1 H, benzyl-CH), 3.63-3.70 (m, 2 H, 2′-CH_2), 4.12-4.28 (m, 2 H, 5-CH_2), 4.67 (mc, 1 H, 4-CH), 5.54-5.78 (m, 2 H, 3′-CH, 4′-CH), 7.16-7.40 (m, 5 H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$); δ = 18.09 (CH_3), 37.81 (benzyl-CH_2), 39.20 (C-2′), 55.16 (C-4), 66.20 (C-5), 122.1, 127.3 (C-3′, C-4′), 128.9, 129.4, 130.2, 135.2 (phenyl-C), 153.4 (C-2), 171.8 (C-1′); IR (film): ν = 2962, 2922, 2860 (CH), 1782, 1702 (CO), 1388, 1364, 1214 cm^{-1}; UV: λ_{max} (lg ε) = 192 nm (4.653); MS (EI, 70 eV): *m/z* = 259 (76, M^+), 178 (27, oxazolidinone+2), 82 (94, M^+ - oxazolidinone-1), 55 (100). Anal. calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61. Found: C, 69.43; H, 6.52.

(4*S*)-4-Benzyl-3-(3′*Z*-pentenoyl)-oxazolidin-2-one (1b). 2.00 g (20.0 mmol) 3*Z*-pentenoic acid which was synthesized from 3-pentynoic acid[12] by stereoselective hydrogenation on P2-Ni[13] was coupled with (4*S*)-4-benzyloxazolidin-2-one in the same way as described for **1a** to produce 3.52 g (68%) of **1b** as a colourless oil. $[\alpha]_D^{20}$ = + 67.7° (*c* = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.70 (dd, *J* = 5.0, 1.0 Hz, 3 H, CH_3), 2.79 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.31 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 3.75-3.87 (m, 2 H, 2′-CH_2), 4.15-4.30 (m, 2 H, 5-CH_2), 4.67 (mc, 1 H, 4-CH), 5.58-5.85 (m, 2 H, 3′-CH, 4′-CH), 7.15-7.38 (m, 5 H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$); δ = 13.23 (CH_3), 33.90 (C-2′), 37.82 (benzyl-CH_2), 55.20 (C-4), 66.19 (C-5), 121.0, 127.3 (C-3′, C-4′), 128.3, 128.9, 129.4, 135.2 (phenyl-C), 153.4 (C-2), 171.4 (C-1′); IR (film): ν = 2960, 2922, 2864 (CH), 1786, 1704 (CO), 1356, 1214, cm^{-1}; UV: λ_{max} (lg ε) = 191.5 nm (4.657); MS (EI, 70 eV): *m/z* = 259 (100, M^+), 178 (41, oxazolidinone+2), 82 (100, M^+ - oxazolidinone-1), 55 (63). Anal. calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61. Found: C, 69.78; H, 6.66.

General Procedure for the Synthesis of the Silylated Aldol Products. 0.52 g (2.00 mmol) of the imide **1a** or **1b** was dissolved in 10 ml CH_2Cl_2 and cooled to -78°C. 2.20 ml (2.20 mmol) Bu_2BOTf in CH_2Cl_2 and subsequently 0.35 ml (2.50 mmol) NEt_3 were added at -78°C. A bright yellow solution of the boron enolate formed. Stirring was continued for 45 min at -78°C and 15 min at 0°C. The solution was recooled to -78°C and 3.00 mmol of the freshly distilled aldehyde was added. Stirring was continued for 2 h at -78°C and 2 h at 0°C. 5 ml pH 7 buffer, 10 ml methanol and 10 ml methanol/H_2O_2 (2:1) were added at 0°C with vigorous stirring which was maintained for 30 min at 0°C. The two-phase mixture was evaporated, taken up in 30 ml ether and 30 ml H_2O. The phases were separated and the aqueous phase extracted twice with ether. The organic extracts were dried over K_2CO_3, filtered and evaporated. The crude aldol products were dissolved in 10 ml CH_2Cl_2 and cooled to 0°C. Then 0.29 ml (2.50 mmol) 2,6-lutidine was added followed by 0.50 ml (2.00 mmol) thexyldimethylsilyl trifluoromethanesulfonate. After being stirred for 1 h at 0°C the solution was poured into water, the layers were separated and the aqueous phase extracted twice with ether. The combined organic extracts were dried over $MgSO_4$, filtered and evaporated. Flash chromatography over silica gel with ether/petroleum ether = 1:5 furnished the silylated *syn*-aldols **3** as colourless oils in isomerically pure form.

(2′*S*, 3′*R*, 4*S*)-4-Benzyl-3-[(2′-(1′′*E*-propenyl)-3′-thexyldimethylsilyloxy)-4′*E*-hexenoyl]-oxazolidin-2-one (3a). Yield: 620 mg (66% over 2 steps). $[\alpha]_D^{20}$ = + 30.5° (*c* = 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.08 (s, 3 H, SiMe), 0.91 (s, 6 H, 2x thexyl-CH_3), 0.94 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.57 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.65 (d, *J* = 5.0 Hz, 3 H, CH_3), 1.74 (d, *J* = 6.0 Hz, 3 H, CH_3), 2.75 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.23 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.06-4.18 (m, 2 H, 5-CH_2), 4.30 (t, *J* = 7.0 Hz, 1 H, 3′-CH), 4.60 (mc, 1 H, 4-CH), 4.63 (dd, *J* = 8.0, 7.0 Hz, 1 H, 2′-CH), 5.45-5.80 (m, 4 H, 4′-CH, 5′-CH, 1′′-CH, 2′′-CH), 7.15-7.38 (m, 5 H, phenyl-CH);^{13}C NMR (50 MHz, $CDCl_3$); δ = -2.96, -2.12 ($SiMe_2$), 17.58, 18.15, 18.51, 18.56, 20.11, 20.20 (4x thexyl-CH_3, 2x CH_3), 24.90 (thexyl-C), 34.03 (thexyl-CH), 37.66 (benzyl-CH_2), 53.67 (C-2′), 55.39 (C-4), 65.70 (C-5), 75.51 (C-3′), 126.4, 127.2, 130.4, 132.1 (C-4′, C-5′, C-1′′, C-2′′), 128.8, 129.5, 130.4, 135.3 (phenyl-C), 152.9 (C-2), 172.7 (C-1′); IR (film): ν = 2958, 2868 (CH), 1784, 1696 (CO), 1382, 1252, 1206, 1056, 832 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.837); MS (DCI, NH_3): *m/z* = 489 (100, $M^+ + NH_4^+$), 472 (60, M^+ +1). Anal. calcd. for $C_{27}H_{41}NO_4Si$: C, 68.79; H, 8.70. Found: C, 68.74; H, 8.76.

(2′*S*, 3′*S*, 4*S*)-4-Benzyl-3-[(2′-(1′′*E*-propenyl)-3′-thexyldimethylsilyloxy-4-methyl)-pentenoyl]-oxazolidin-2-one (3b). Yield: 595 mg (63% over 2 steps). $[\alpha]_D^{20}$ = + 30.3° (*c* = 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.84 (s, 6 H, 2x thexyl-CH_3), 0.88 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.63 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.70 (s, 3 H, CH_3), 1.75 (dd, *J* = 5.0, 1.0 Hz, 3 H, CH_3), 2.75 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.21 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.12 (d, *J* = 5.0 Hz, 2 H, 5-CH_2), 4.44 (d, *J* = 8.0 Hz, 1 H, 3′-CH), 4.58 (mc, 1 H, 4-CH), 4.70 (t, *J* = 8.0 Hz, 1 H, 2′-CH), 4.80 (t, *J* = 1.0 Hz, 1 H, 5′-CH), 4.88 (d, *J* = 1.0 Hz, 1 H, 5′-CH), 5.45-5.80 (m, 2 H, 1′′-CH, 2′′-CH), 7.15-7.37 (m, 5 H, phenyl-CH);^{13}C NMR (50 MHz, $CDCl_3$); δ = -3.07, -2.65 ($SiMe_2$), 17.24, 18.13, 18.52, 18.60, 20.16, 20.25 (4x thexyl-CH_3, 2x CH_3), 25.03 (thexyl-C), 34.03 (thexyl-CH), 37.50 (benzyl-CH_2), 52.21 (C-2′), 55.30 (C-4), 65.75 (C-5), 77.52 (C-3′), 112.9 (C-5′), 126.7, 127.2 (C-1′′, C-2′′), 128.8, 129.5, 130.5, 135.2 (phenyl-C), 145.8 (C-4′), 152.9 (C-2), 172.5 (C-1′); IR (KBr): ν = 2962, 2866 (CH), 1778, 1696 (CO), 1668, 1390, 1364, 1252, 1208, 1104, 1074, 1052, 896, 832 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.843); MS (DCI, NH_3): *m/z* = 489 (100, $M^+ + NH_4^+$), 472 (43, M^+ +1). Anal. calcd. for $C_{27}H_{41}NO_4Si$: C, 68.79; H, 8.70. Found: C, 68.67; H, 8.79.

(2′*S*, 3′*S*, 4*S*)-4-Benzyl-3-[(2′-(1′′*E*-propenyl)-3′-thexyldimethylsilyloxy-4-methyl)-4′*E*-hexenoyl]-oxazolidin-2-one (3c). Yield: 657 mg (68% over steps). $[\alpha]_D^{20}$ = + 27.0° (*c* = 1.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.83 (s, 6 H, 2x thexyl-CH_3), 0.88 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.55 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.58 (d, *J* = 1.0 Hz, 3 H, CH_3), 1.62 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.75 (dd, *J* = 6.0, 1.0 Hz, 3 H, CH_3), 2.75 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.22 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.05-4.18 (m, 2 H, 5-CH_2), 4.38 (d, *J* = 8.5 Hz, 1 H, 3′-CH), 4.55 (mc, 1 H, 4-CH), 4.72 (t, *J* = 8.5 Hz, 1 H, 2′-CH), 5.35-5.80 (m, 3 H, 5′-CH, 1′′-CH, 2′′-CH), 7.15-7.38 (m, 5 H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$); δ = -3.02, -2.58 ($SiMe_2$), 11.11, 13.06, 18.13, 18.57, 20.21 (4x thexyl-CH_3, 3x CH_3), 25.03 (thexyl-C), 34.03 (thexyl-CH), 37.58 (benzyl-CH_2), 52.28 (C-2′), 55.38 (C-4), 65.70 (C-5), 79.44 (C-3′), 121.9, 127.2, 130.2, 136.3 (C-4′, C-5′, C-1′′, C-2′′), 127.2, 128.8, 129.5, 135.3 (phenyl-C), 152.8 (C-2), 172.7 (C-1′); IR (KBr): ν = 2960, 2868 (CH), 1774, 1696 (CO), 1666, 1452, 1390, 1364, 1252, 1208, 1108, 1070, 896, 830 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.858); MS (DCI, NH_3): *m/z* = 503 (100, $M^+ + NH_4^+$), 486 (28, M^+ +1). Anal. calcd. for $C_{28}H_{43}NO_4Si$: C, 69.28; H, 8.87. Found: C, 69.57; H, 8.83.

(2′*S*, 3′*R*, 4*S*)-4-Benzyl-3-[(2′-(1′′*E*-propenyl)-3′-thexyldimethylsilyloxy)-4′*E*-octenoyl]-oxazolidin-2-one (3d). Yield: 639 mg (64% over 2 steps). $[\alpha]_D^{20}$ = + 31.3° (*c* = 1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.82 (s, 6 H, 2x thexyl-CH_3), 0.88 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 0.92 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.38 (mc, 2 H, 7′-CH_2), 1.58 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.75 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.98 (mc, 2 H, 6′-CH_2), 2.76 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.23 (dd, *J* = 13.5, 3.0 Hz, 1 H, benzyl-CH), 4.05-4.18 (m, 2 H, 5-CH_2), 4.31 (t, *J* = 7.0 Hz, 1 H, 3′-CH), 4.60 (mc, 1 H, 4-CH), 4.65 (dd, *J* = 8.0, 7.0 Hz, 1 H, 2′-CH), 5.40-5.80 (m, 4 H, 4′-CH, 5′-CH, 1′′-CH, 2′′-CH), 7.15-7.37 (m, 5 H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$); δ = -2.92, -2.05 ($SiMe_2$), 13.58, 18.16, 18.54, 18.58, 20.12, 20.21 (4x thexyl-CH_3, 2x CH_3), 22.34 (C-7′), 24.91 (thexyl-C), 34.04 (thexyl-CH), 34.15 (C-6′), 37.68 (benzyl-CH_2), 53.81 (C-2′), 55.38 (C-4), 65.69 (C-5), 75.59 (C-3′), 126.5, 127.2, 131.1, 132.5 (C-4′, C-5′, C-1′′, C-2′′), 128.8, 129.5, 130.4, 135.3 (phenyl-C), 152.9 (C-2), 172.7 (C-1′); IR (film): ν = 2958, 2932, 2870 (CH), 1784, 1698 (CO), 1382, 1366, 1252, 1206, 1070, 1060, 832 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.798); MS (DCI, NH_3): *m/z* = 517 (18, $M^+ + NH_4^+$), 340 (100, M^+ - OTDS). Anal. calcd. for $C_{29}H_{45}NO_4Si$: C, 69.74; H, 9.02. Found: C, 69.88; H, 9.20.

(2′*S*, 3′*R*, 4*S*)-4-Benzyl-3-[(2′-(1′′*E*-propenyl)-3′-thexyldimethylsilyloxy-5′-trimethylsilyl)-4′*E*-pentenoyl]-oxazolidin-2-one (3e). Yield: 652 mg (62% over steps). $[\alpha]_D^{20}$ = + 35.6° (*c* = 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.04 (s, 15 H, $SiMe_3$, $SiMe_2$), 0.82 (s, 6 H, 2x thexyl-CH_3), 0.88 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.63 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.74 (d, *J* = 5.5 Hz, 3 H, CH_3), 1.74 (d, *J* = 6.0 Hz, 3 H, CH_3), 2.79 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.26 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.03-4.18 (m, 2 H, 5-CH_2), 4.35 (t, *J* = 6.5 Hz, 1 H, 3′-CH), 4.60 (mc, 1 H, 4-CH), 4.63 (dd, *J* = 7.5, 6.5 Hz, 1 H, 2′-CH), 5.49-5.72 (m, 2 H, 1′′-CH, 2′′-CH), 5.79 (d, *J* = 19.0 Hz, 1 H, 5′-H), 6.02 (dd, *J* = 19.0, 6.5 Hz, 1 H, 4′-H), 7.16-7.40 (m, 5 H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$); δ = -2.98, -2.15 ($SiMe_3$, $SiMe_2$), 18.11, 18.55, 20.16 (4x thexyl-CH_3, CH_3), 24.97 (thexyl-C), 34.00 (thexyl-CH), 37.65 (benzyl-CH_2), 53.57 (C-2′), 55.31 (C-4), 65.69 (C-5), 77.52 (C-3′), 126.0, 127.2, 131.3, 146.8 (C-4′, C-5′, C-1′′, C-2′′), 128.8, 129.5, 130.5, 135.2 (phenyl-C), 152.9 (C-2), 172.5 (C-1′); IR (film): ν = 2958, 2868 (CH), 1786, 1698 (CO), 1382, 1250, 1206, 1104, 862, 838 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.809); MS (EI, 70 eV): *m/z* = 514 (4, M^+ - CH_3), 444 (23, M^+- thexyl), 316 (79), 271 (37, retro-aldol), 147 (94), 73 (100). Anal. calcd. for $C_{29}H_{47}NO_4Si_2$: C, 65.73; H, 8.94. Found: C, 65.43; H, 8.98.

(2′*S*, 3′*R*, 4*S*)-4-Benzyl-3-[(2′-(1′′*E*-propenyl)-3′-thexyldimethylsilyloxy-5′-tributylstannyl)-4′*E*-pentenoyl]-oxazolidin-2-one (3f). Yield: 890 mg (60% over 2 steps). $[\alpha]_D^{20}$ = + 24.0° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe), 0.82 (s, 6 H, 2x thexyl-CH_3), 0.84-0.92 (m, 21 H, $SnBu_3$, 2x thexyl-CH_3), 1.15-1.58 (m, 12 H, $SnBu_3$), 1.61 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.74 (d, *J* = 5.5 Hz, 3 H, CH_3), 1.72 (d, *J* = 5.0 Hz, 3 H, CH_3), 2.76 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.24 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.03-4.18 (m, 2 H, 5-CH_2), 4.35 (t, *J* = 6.0 Hz, 1 H, 3′-CH), 4.52-4.65 (m, 2 H, 4-CH, 2′-CH), 5.49-5.75 (m, 2 H, 1′′-CH, 2′′-CH), 5.95 (dd, *J* = 19.0, 6.0 Hz, 1 H, 4′-H), 6.10 (d, *J* = 19.0 Hz, 1 H, 5′-H), 7.14-7.40 (m, 5 H, phenyl-CH);^{13}C NMR (50 MHz, $CDCl_3$); δ = -2.98, -2.20 ($SiMe_2$), 9.46, 13.68, 18.13, 18.55, 18.58, 20.15, 20.23 (4x thexyl-CH_3, $SnBu_3$, CH_3), 24.98 (thexyl-C), 27.23, 29.06 ($SnBu_3$), 34.05 (thexyl-CH), 37.62 (benzyl-CH_2), 53.71 (C-2′), 55.39 (C-4), 65.69 (C-5), 78.15 (C-3′), 126.2, 127.2, 129.7, 149.0 (C-4′, C-5′, C-1′′, C-2′′), 128.8, 129.5, 130.3, 135.3 (phenyl-C), 152.9 (C-2), 172.5 (C-1′); IR (film): ν = 2956, 2926, 2870 (CH), 1786, 1698 (CO), 1380, 1206, 1102, 1076, 832 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.795); MS (EI, 70 eV): *m/z* = 746 (1, M^+), 690 (100, M^+- butyl), 316 (31), 73 (34). Anal. calcd. for $C_{38}H_{65}NO_4SiSn$: C, 61.15; H, 8.78. Found: C, 61.10; H, 8.85.

(2′*S*, 3′*R*, 4*S*)-4-Benzyl-3-[(2′-(1′′*Z*-propenyl)-3′-thexyldimethylsilyloxy)-4′*E*-hexenoyl]-oxazolidin-2-one (3g). Yield: 655 mg (69% over 2 steps). $[\alpha]_D^{20}$ = + 43.0° (*c* = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.80 (s, 6 H, 2x thexyl-CH_3), 0.84 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.57 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.66 (d, *J* = 5.0 Hz, 3 H, CH_3), 1.74 (dd, *J* = 6.0, 1.0 Hz, 3 H, CH_3), 2.77 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.23 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.06-4.18 (m, 2 H, 5-CH_2), 4.30 (t, *J* = 6.5 Hz, 1 H, 3′-CH), 4.60 (mc, 1 H, 4-CH), 5.10 (dd, *J* = 9.5, 6.5 Hz, 1 H, 2′-CH), 5.45-5.80 (m, 4 H, 4′-CH, 5′-CH, 1′′-CH, 2′′-CH), 7.15-7.38 (m, 5 H, phenyl-CH);^{13}C NMR (50 MHz, $CDCl_3$); δ = -2.96, -2.12 ($SiMe_2$), 13.75, 17.53, 18.51, 18.56, 20.07, 20.20 (4x thexyl-CH_3, 2x CH_3), 24.90 (thexyl-C), 34.03 (thexyl-CH), 37.66 (benzyl-CH_2), 48.25 (C-2′), 55.46 (C-4), 65.70 (C-5), 75.57 (C-3′), 125.4, 127.1, 127.2, 128.7 (C-4′, C-5′, C-1′′, C-2′′), 128.8, 129.5, 131.9, 135.3 (phenyl-C), 153.0 (C-2), 172.7 (C-1′); IR (film): ν = 2958, 2866 (CH), 1784, 1700 (CO), 1384, 1354, 1206, 1102, 1052, 832 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.801); MS (DCI, NH_3): *m/z* = 489 (10, $M^+ + NH_4^+$), 312 (100, M^+ - OTDS). Anal. calcd. for $C_{27}H_{41}NO_4Si$: C, 68.79; H, 8.70. Found: C, 68.86; H, 8.73.

(2′*S*, 3′*S*, 4*S*)-4-Benzyl-3-[(2′-(1′′*Z*-propenyl)-3′-thexyldimethylsilyloxy-4-methyl)-pentenoyl]-oxazolidin-2-one (3h). Yield: 579 mg (61% over 2 steps). $[\alpha]_D^{20}$ = + 34.5° (*c* = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.84 (s, 6 H, 2x thexyl-CH_3), 0.88 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.63 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.73 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.77 (s, 3 H, CH_3), 2.78 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.19 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.15 (d, *J* = 5.0 Hz, 2 H, 5-CH_2), 4.44 (d, *J* = 7.5 Hz, 1 H, 3′-CH), 4.58 (mc, 1 H, 4-CH), 4.81 (br s, 1 H, 5′-CH), 4.89 (br s,1 H, 5′-CH), 5.15 (dd, *J* = 9.0, 7.5 Hz, 1 H, 2′-CH), 5.50-5.83 (m, 2 H, 1′′-CH, 2′′-CH), 7.15-7.37 (m, 5 H, phenyl-CH);^{13}C NMR (50 MHz, $CDCl_3$); δ = -2.99, -2.67 ($SiMe_2$), 13.81, 17.53, 18.55, 18.67, 20.20, 20.35 (4x thexyl-CH_3, 2x CH_3), 25.06 (thexyl-C), 34.05 (thexyl-CH), 37.50 (benzyl-CH_2), 47.16 (C-2′), 55.39 (C-4), 65.80 (C-5), 77.64 (C-3′), 112.6 (C-5′), 125.9, 127.3 (C-1′′, C-2′′), 128.9, 129.3, 129.5, 135.1 (phenyl-C), 145.8 (C-4′), 153.0 (C-2), 172.6 (C-1′); IR (KBr): ν = 2960, 2870 (CH), 1790, 1764, 1696 (CO), 1454, 1378, 1360, 1256, 1204, 1104, 1080, 1056, 896, 834 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.812); MS (DCI, NH_3): *m/z* = 489 (100, $M^- + NH_4^-$), 472 (52, M^+ +1). Anal. calcd. for $C_{27}H_{41}NO_4Si$: C, 68.79; H, 8.70. Found: C, 68.58; H, 8.85.

(2′*S*, 3′*S*, 4*S*)-4-Benzyl-3-[(2′-(1′′*Z*-propenyl)-3′-thexyldimethylsilyloxy-4-methyl)-4′*E*-hexenoyl]-oxazolidin-2-one (3i). Yield: 671 mg (69% over 2 steps). $[\alpha]_D^{20}$ = + 33.3° (*c* = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.83 (s, 3 H, thexyl-CH_3), 0.84 (s, 3 H, thexyl-CH_3), 0.88 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.55 (d, *J* = 6.0 Hz, 3 H, CH_3), 1.60 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.65 (d, *J* = 1.0 Hz, 3 H, CH_3), 1.75 (dd, *J* = 6.0, 1.0 Hz, 3 H, CH_3), 2.77 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.20 (dd, *J* = 13.5, 3.5 Hz, 1 H, benzyl-CH), 4.05-4.18 (m, 2 H, 5-CH_2), 4.38 (d, *J* = 8.0 Hz, 1 H, 3′-CH), 4.55 (mc, 1 H, 4-CH), 5.18 (dd, *J* = 9.0, 8.0 Hz, 1 H, 2′-CH), 5.35-5.83 (m, 3 H, 5′-CH, 1′′-CH, 2′′-CH), 7.15-7.38 (m, 5 H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -2.97, -2.65 ($SiMe_2$), 11.39, 13.05, 13.79, 18.56, 18.63, 20.18, 20.27 (4x thexyl-CH_3, 3x CH_3), 25.02 (thexyl-C), 34.03 (thexyl-CH), 37.57 (benzyl-CH_2), 47.37 (C-2′), 55.46 (C-4), 65.73 (C-5), 79.63 (C-3′), 121.6, 126.4, 127.2, 136.4 (C-4′, C-5′, C-1′′, C-2′′), 128.8, 129.1, 129.5, 135.2 (phenyl-C), 152.9 (C-2), 172.8 (C-1′); IR (film): ν = 2960, 2868 (CH), 1774, 1696 (CO), 1380, 1356, 1204, 1104, 1066, 832 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.805); MS (DCI, NH_3): *m/z* = 503 (100, $M^+ + NH_4^+$), 486 (25, M^+ +1). Anal. calcd. for $C_{28}H_{43}NO_4Si$: C, 69.28; H, 8.87. Found: C, 69.47; H, 8.73.

(2′*S*, 3′*R*, 4*S*)-4-Benzyl-3-[(2′-(1′′*Z*-propenyl)-3′-thexyldimethylsilyloxy)-4′*E*-octenoyl]-oxazolidin-2-one (3k). Yield: 629 mg (63% over 2 steps). $[\alpha]_D^{20}$ = + 42.4° (*c* = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, SiMe), 0.07 (s, 3 H, SiMe), 0.82 (s, 6 H, 2x thexyl-CH_3), 0.86 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 0.88 (t, *J* = 7.0 Hz, 3 H, CH_3), 1.38 (mc, 2 H, 7′-CH_2), 1.58 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 1.73 (dd, *J* = 6.0, 1.0 Hz, 3 H, CH_3), 1.98 (mc, 2 H, 6′-CH_2), 2.76 (dd, *J* = 13.5, 9.5 Hz, 1 H, benzyl-CH), 3.23 (dd, *J* = 13.5, 3.0 Hz, 1 H, benzyl-CH), 4.02-4.18 (m, 2 H, 5-CH_2), 4.33 (t, *J* = 6.5 Hz, 1 H, 3′-CH), 4.60 (mc, 1 H, 4-CH), 5.12 (dd, *J* = 9.5, 6.5 Hz, 1 H, 2′-CH), 5.40-5.80 (m, 4 H, 4′-CH, 5′-CH, 1′′-CH, 2′′-CH), 7.15-7.37 (m, 5 H, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -2.94, -2.17 ($SiMe_2$), 13.62, 13.76, 18.52, 18.58, 20.11, 20.21 (4x thexyl-CH_3, 2x CH_3), 22.32 (C-7′), 24.89 (thexyl-C), 34.00 (thexyl-CH), 34.13 (C-6′), 37.61 (benzyl-CH_2), 48.37 (C-2′), 55.42 (C-4), 65.67 (C-5), 75.71 (C-3′), 125.6, 127.2, 130.9, 132.5 (C-4′, C-5′, C-1′′, C-2′′), 128.7, 128.9, 129.5, 135.3 (phenyl-C), 153.0 (C-2), 172.6 (C-1′); IR (film): ν = 2960, 2932, 2870 (CH), 1784, 1698 (CO), 1382, 1356, 1252, 1208, 1102, 1072, 1054, 832 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.798); MS (DCI, NH_3): *m/z* = 517 (16, $M^+ + NH_4^+$), 340 (100, M^+ - OTDS). Anal. calcd. for $C_{29}H_{45}NO_4Si$: C, 69.74; H, 9.02. Found: C, 69.82; H, 9.17.

General Procedure for the Cope Rearrangement. 1.00 mmol of the silylated *syn*-aldol **3** was dissolved in 30.0 ml toluene in a sealed flask. This flask was put into a preheated (180°C) oil bath for 2 h. The solvent was evaporated in vacuo. The colourless crude Cope product thus obtained was sufficiently pure for further synthetic manipulations. It can be further purified by flash chromatography over silica gel.

(4*S*, 4′*R*, 5′*R*)-4-Benzyl-3-[(4′, 5′-dimethyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4a). 470 mg **3a** gave 408 mg (87%) **4a** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 1.6° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 6 H, $SiMe_2$), 0.89 (s, 6 H, 2x thexyl-CH_3), 0.91 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 0.99 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.11 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.67 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.44 (mc, 1 H, 5′-CH), 2.81 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 2.75-2.95 (m, 1 H, 4′-CH), 3.39 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.05-4.18 (m, 2 H, 5-CH_2), 4.30 (dd, *J* = 9.5, 6.0 Hz, 1 H, 6′-CH), 4.75 (mc, 1 H, 4-CH), 6.20 (dd, *J* = 6.0, 1.0 Hz, 1 H, 7′-CH), 7.19-7.44 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.54, -3.41 ($SiMe_2$), 16.66, 18.40, 18.42, 18.44, 20.01 (4x thexyl-CH_3, 2x CH_3), 25.03 (thexyl-C), 33.34 (C-4′), 34.00

(thexyl-CH), 37.81 (benzyl-CH_2), 42.44 (C-5′), 55.26 (C-4), 65.94 (C-5), 112.6 (C-6′), 119.4 (C-2′), 127.1, 128.8, 129.3, 135.4 (phenyl-C), 138.3 (C-7′), 153.3 (C-2), 155.7 (C-3′), 165.0 (C-1′); IR (film): ν = 2962, 2930, 2870 (CH), 1784, 1684 (CO), 1654, 1632, 1360, 1256, 1206, 1078, 822 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.784); MS (EI, 70 eV): *m/z* = 471 (1, M^+), 386 (8, M^+ - thexyl), 316(10), 213 (24), 178 (10, oxazolidinone +1), 129 (100, thexylsilyloxy). Anal. calcd. for $C_{27}H_{41}NO_4Si$: C, 68.79; H, 8.70. Found: C, 68.59; H, 8.90.

(4*S*, 4′*S*)-4-Benzyl-3-[(4′, 6′-dimethyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4b). 473 mg **3b** gave 430 mg (91%) **4b** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 38.0° (*c* = 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 6 H, $SiMe_2$), 0.92 (s, 6 H, 2x thexyl-CH_3), 0.99 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.12 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.57 (d, *J* = 1.0 Hz, 3 H, CH_3), 1.67 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.16 (dd, J = 13.0, 7.0 Hz, 1 H, 5′-CH), 2.29 (dd, J = 13.0, 7.5 Hz, 1 H, 5′-CH), 2.67 (mc, 1 H, 4′-CH), 2.81 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.39 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.05-4.18 (m, 2 H, 5-CH_2), 4.76 (mc, 1 H, 4-CH), 6.15 (br s, 1 H, 7′-CH), 7.19-7.44 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.42 ($SiMe_2$), 17.42, 18.42, 18.73, 20.01 (4x thexyl-CH_3, 2x CH_3), 24.91 (thexyl-C), 33.98 (thexyl-CH), 35.12 (C-4′), 35.28 (C-5′), 37.75 (benzyl-CH_2), 55.20 (C-4), 65.89 (C-5), 113.4 (C-6′), 118.1 (C-2′), 127.1, 128.8, 129.3, 135.3 (phenyl-C), 135.0 (C-7′), 153.3 (C-2), 157.3 (C-3′), 165.1 (C-1′); IR (film): ν = 2960, 2928, 2868 (CH), 1782, 1684 (CO), 1632, 1356, 1254, 1210, 1196, 1164, 836 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.796); MS (EI, 70 eV): *m/z* = 471 (2, M^+), 386 (92, M^+ - thexyl), 316(24), 234 (24), 129 (100, thexylsilyloxy). Anal. calcd. for $C_{27}H_{41}NO_4Si$: C, 68.79; H, 8.70. Found: C, 68.89; H, 8.89.

(4*S*, 4′*R*, 5′*S*)-4-Benzyl-3-[(4′, 5′, 6′-trimethyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4c). 480 mg **3c** gave 427 mg (89%) **4c** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 26.8° (*c* = 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 6 H, $SiMe_2$), 0.88 (s, 6 H, 2x thexyl-CH_3), 0.91 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.02 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.11 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.41 (d, *J* = 1.0 Hz, 3 H, CH_3), 1.63 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.32-2.51 (m, 1 H, 5′-CH), 2.76 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 2.73-2.89 (mc, 1 H, 4′-CH), 3.34 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.11-4.23 (m, 2 H, 5-CH_2), 4.70 (mc, 1 H, 4-CH), 5.97 (d, *J* = 1.0 Hz, 1 H, 7′-CH), 7.19-7.44 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.50, -3.33 ($SiMe_2$), 13.51, 15.99, 17.58, 18.44, 20.07, 20.09 (4x thexyl-CH_3, 3x CH_3), 24.97 (thexyl-C), 34.05 (thexyl-CH), 36.28 (C-4′), 37.81 (benzyl-CH_2), 40.65 (C-5′), 55.16 (C-4), 65.85 (C-5), 118.3 (C-2′), 118.4 (C-6′), 127.1, 128.8, 129.4, 135.5 (phenyl-C), 133.9 (C-7′), 153.3 (C-2), 156.8 (C-3′), 165.0 (C-1′); IR (film): ν = 2962, 2872 (CH), 1784, 1686 (CO), 1632, 1384, 1358, 1208, 1162, 1104, 836 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.778); MS (EI, 70 eV): *m/z* = 485 (2, M^+), 400 (23, M^+ - thexyl), 316(16), 227 (100), 143 (72), 73 (60). EI-HRMS calcd for $C_{28}H_{43}NO_4Si$: 485.2961, found 485.2961.

(4*S*, 4′*R*, 5′*R*)-4-Benzyl-3-[(4′-methyl-5′-propyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4d). 500 mg **3d** gave 410 mg (82%) **4d** which was contaminated with 5% of the diastereomer **5d** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = -7.5° (*c* = 1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 6 H, $SiMe_2$), 0.84 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.86 (s, 6 H, 2x thexyl-CH_3), 0.90 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.08 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.11-1.40 (m, 4 H, CH_2-CH_2), 1.64 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.48 (mc, 1 H, 5′-CH), 2.65-2.80 (m, 1 H, 4′-CH), 2.81 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.36 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.10-4.25 (m, 3 H, 6′-CH, 5-CH_2), 4.72 (mc, 1 H, 4-CH), 6.17 (d, *J* = 12.0 Hz, 1 H, 7′-H of the minor diastereomer **5d**), 6.28 (d, *J* = 6.0

Hz 1 H, 7′-CH), 7.19-7.44 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.43, -3.35 ($SiMe_2$), 14.08, 17.36, 18.50, 20.05, (4x thexyl-CH_3, 2x CH_3), 20.56 (CH_2), 25.03 (thexyl-C), 34.08 (thexyl-CH), 35.58 (CH_2), 37.92 (benzyl-CH_2), 38.70, 41.61 (C-4′, C-5′), 55.36 (C-4), 66.01 (C-5), 110.7 (C-6′), 119.4 (C-2′), 127.2, 128.9, 129.4, 135.5 (phenyl-C), 139.5 (C-7′), 153.3 (C-2), 155.7 (C-3′), 165.1 (C-1′); IR (film): ν = 2960, 2930, 2870 (CH), 1784, 1684 (CO), 1654, 1632, 1382, 1360, 1254, 1208, 1094, 826 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.861); MS (EI, 70 eV): *m/z* = 499 (1, M^+), 414 (15, M^+ - thexyl), 316(12), 241 (80), 157 (92), 73 (100). EI-HRMS calcd for $C_{29}H_{45}NO_4Si$: 499.3117, found 499.3117.

(4*S*, 4′*R*, 5′*R*)-4-Benzyl-3-[(4′-methyl-5′-trimethylsilyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl] -oxazolidin-2-one (4e). 525 mg **3e** gave 430 mg (82%) **4e** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 18.6° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.01 (s, 9 H, $SiMe_3$), 0.14 (s, 3 H, SiMe), 0.16 (s, 3 H, SiMe), 0.88 (s, 6 H, 2x thexyl-CH_3), 0.90 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.11 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.63 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.24 (dd, *J* = 11.5, 5.0 Hz, 1 H, 5′-CH), 2.62-2.84 (m, 1 H, 4′-CH), 2.77 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.35 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.10-4.25 (m, 2 H, 5-CH_2), 4.27 (dd, *J* = 11.5, 6.0 Hz, 1 H, 6′-CH), 4.72 (mc, 1 H, 4-CH), 6.27 (d, *J* = 6.0 Hz, 1 H, 7′-CH), 7.15-7.38 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.46, -3.30, -1.90 ($SiMe_3$, $SiMe_2$), 18.50, 20.04, 20.08, 20.27 (4x thexyl-CH_3, CH_3), 24.99 (thexyl-C), 30.37 (C-5′), 34.08 (thexyl-CH), 37.73 (C-4′), 37.84 (benzyl-CH_2), 55.27 (C-4), 65.97 (C-5), 106.8 (C-6′), 118.7 (C-2′), 127.2, 128.8, 129.4, 135.4 (phenyl-C), 138.1 (C-7′), 153.3 (C-2), 156.5 (C-3′), 165.0 (C-1′); IR (film): ν = 2960, 2900, 2870 (CH), 1784, 1684 (CO), 1634, 1384, 1358, 1250, 1200, 1114, 862, 838 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.798); MS (EI, 70 eV): *m/z* = 529 (15, M^+), 444 (46, M^+ - thexyl), 320 (59), 316 (42), 271 (54), 250 (46), 91 (89), 73 (100). Anal. calcd. for $C_{29}H_{47}NO_4Si_2$: C, 65.73; H, 8.94. Found: C, 65.94; H, 8.79.

(4*S*, 4′*R*, 5′*R*)-4-Benzyl-3-[(4′-methyl-5′-tributylstannyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4f). 550 mg **3f** gave 467 mg (85%) **4f** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 94.0° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.14 (s, 3 H, SiMe), 0.16 (s, 3 H, SiMe), 0.80-0.95 (m, 27 H, $SnBu_3$, 4x thexyl-CH_3), 1.13 (d, *J* = 6.5 Hz, 3 H, CH_3), 1.20-1.70 (m, 13 H, $SnBu_3$, thexyl-CH), 2.55-2.70 (m, 2 H, 4′-CH, 5′-CH), 2.77 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.35 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.06-4.25 (m, 2 H, 5-CH_2), 4.41 (dd, *J* = 11.0, 6.0 Hz, 1 H, 6′-CH), 4.72 (mc, 1 H, 4-CH), 6.03 (d, *J* = 6.0 Hz, 1 H, 7′-CH), 7.12-7.36 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.41, -3.14 ($SiMe_2$), 9.75, 13.71, 18.54, 18.56, 20.11, 20.19, 20.76 ($SnBu_3$, 4x thexyl-CH_3, CH_3), 25.14 (thexyl-C), 27.56, 29.25 ($SnBu_3$), 30.21 (C-5′), 34.11 (thexyl-CH), 37.92 (benzyl-CH_2), 40.20 (C-4′), 55.34 (C-4), 65.97 (C-5), 111.5 (C-6′), 117.9 (C-2′), 127.2, 128.9, 129.4, 135.5 (phenyl-C), 135.0 (C-7′), 153.4 (C-2), 158.0 (C-3′), 165.0 (C-1′); IR (film): ν = 2958, 2926, 2870 (CH), 1784, 1684 (CO), 1632, 1356, 1208, 834 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.804); MS (EI, 70 eV): *m/z* = 746 (1, M^+), 690 (100, M^+ - butyl), 456 (11), 410 (13), 291 (17), 130 (28). Anal. calcd. for $C_{29}H_{47}NO_4Si_2$: C, 61.15; H, 8.78. Found: C, 61.29; H, 8.76.

(4*S*, 4′*S*, 5′*R*)-4-Benzyl-3-[(4′, 5′-dimethyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4g). 472 mg **3g** gave 406 mg (86%) **4g** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 1.4° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 6 H, $SiMe_2$), 0.90 (s, 6 H, 2x thexyl-CH_3), 0.93 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 0.97 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.05 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.67 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.29 (mc, 1 H, 5′-CH), 2.72 (mc, 1 H,

4′-CH), 2.79 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.36 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.12-4.25 (m, 2 H, 5-CH_2), 4.28 (dd, *J* = 9.5, 6.0 Hz, 1 H, 6′-CH), 4.72 (mc, 1 H, 4-CH), 6.20 (dd, *J* = 6.0, 0.5 Hz, 1 H, 7′-CH), 7.19-7.44 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.47, -3.35 ($SiMe_2$), 17.23, 18.47, 18.74, 20.07 (4x thexyl-CH_3, 2x CH_3), 25.09 (thexyl-C), 33.45 (C-4′), 34.08 (thexyl-CH), 37.90 (benzyl-CH_2), 42.99 (C-5′), 55.31 (C-4), 65.99 (C-5), 113.5 (C-6′), 119.3 (C-2′), 127.2, 128.9, 129.4, 135.4 (phenyl-C), 138.2 (C-7′), 153.3 (C-2), 156.5 (C-3′), 165.0 (C-1′); IR (film): ν = 2962, 2930, 2870 (CH), 1784, 1684 (CO), 1654, 1632, 1384, 1360, 1264, 1198, 1098, 1074, 822 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.786); MS (EI, 70 eV): *m/z* = 471 (1, M^+), 386 (26, M^+ - thexyl), 316(19), 213 (55), 129 (100, thexylsilyloxy). EI-HRMS calcd for $C_{27}H_{41}NO_4Si$: 471.2804, found 471.2804.

(4*S*, 4′*R*)-4-Benzyl-3-[(4′, 6′-dimethyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4h). 475 mg **3h** gave 433 mg (91%) **4h** which was contaminated with 4% of the diastereomer **5h** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 44.6° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.18 (s, 6 H, $SiMe_2$), 0.88 (s, 6 H, 2x thexyl-CH_3), 0.91 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.06 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.55 (d, *J* = 1.0 Hz, 3 H, CH_3), 1.63 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.12 (dd, J = 13.0, 7.0 Hz, 1 H, 5′-CH), 2.25 (dd, J = 13.0, 7.5 Hz, 1 H, 5′-CH), 2.62 (mc, 1 H, 4′-CH), 2.79 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.35 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.12-4.26 (m, 2 H, 5-CH_2), 4.72 (mc, 1 H, 4-CH), 6.05 (d, *J* = 0.5 Hz, 1 H, 7′-CH of the minor diastereomer **5h**), 6.12 (d, *J* = 0.5 Hz, 1 H, 7′-CH), 7.19-7.44 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.31 ($SiMe_2$), 17.52, 18.51, 18.81, 20.09 (4x thexyl-CH_3, 2x CH_3), 25.01 (thexyl-C), 34.07 (thexyl-CH), 35.23 (C-4′), 35.35 (C-5′), 37.88 (benzyl-CH_2), 55.28 (C-4), 65.98 (C-5), 113.5 (C-6′), 118.1 (C-2′), 127.2, 128.9, 129.4, 135.4 (phenyl-C), 135.1 (C-7′), 153.3 (C-2), 157.5 (C-3′), 165.2 (C-1′); IR (film): ν = 2960, 2930, 2868 (CH), 1784, 1684 (CO), 1632, 1384, 1358, 1252, 1208, 1198, 1164, 852, 838 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.784); MS (EI, 70 eV): *m/z* = 471 (1, M^+), 386 (70, M^+ - thexyl), 316(27), 234 (22), 129 (100, thexylsilyloxy). Anal. calcd. for $C_{27}H_{41}NO_4Si$: C, 68.79; H, 8.70. Found: C, 68.84; H, 8.76.

(4*S*, 4′*S*, 5′*S*)-4-Benzyl-3-[(4′, 5′, 6′-trimethyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4i). 490 mg **3i** gave 430 mg (88%) **4i** which was contaminated with 4% of the diastereomer **5i** after chromatography over silica gel with ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = + 31.0° (*c* = 0.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 6 H, $SiMe_2$), 0.90 (s, 6 H, 2x thexyl-CH_3), 0.92 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 0.96 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.98 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.42 (d, *J* = 1.0 Hz, 3 H, CH_3), 1.63 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.25-2.48 (m, 1 H, 5′-CH), 2.70-2.90 (mc, 1 H, 4′-CH), 2.82 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.35 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.10-4.28 (m, 2 H, 5-CH_2), 4.73 (mc, 1 H, 4-CH), 5.99 (d, *J* = 1.0 Hz, 1 H, 7′-CH of the minor diastereomer **5i**), 6.08 (d, *J* = 1.0 Hz, 1 H, 7′-CH), 7.15-7.43 (m, 7 H, 2′-CH, 3′-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.46, -3.35 ($SiMe_2$), 12.79, 16.94, 18.30, 18.42, 20.04 (4x thexyl-CH_3, 3x CH_3), 24.94 (thexyl-C), 34.03 (thexyl-CH), 35.94 (C-4′), 37.77 (benzyl-CH_2), 40.78 (C-5′), 55.18 (C-4), 65.91 (C-5), 117.8 (C-6′), 119.3 (C-2′), 127.1, 128.7, 129.3, 135.3 (phenyl-C), 134.3 (C-7′), 153.2 (C-2), 157.0 (C-3′), 165.0 (C-1′); IR (film): ν = 2962, 2930, 2868 (CH), 1770, 1682 (CO), 1632, 1360, 1256, 1164, 1100, 856, 834 cm^{-1}; UV: λ_{max} (lg ε) = 190.5 nm (4.780); MS (EI, 70 eV): *m/z* = 485 (1, M^+), 400 (7, M^+ - thexyl), 316(9), 227 (100), 143 (54), 73 (33). EI-HRMS calcd for $C_{28}H_{43}NO_4Si$: 485.2961, found 485.2961.

(4*S*, 4′*S*, 5′*R*)-4-Benzyl-3-[(4′-methyl-5′-propyl-7′-thexyldimethylsilyloxy)-2′*E*, 6′*Z*-heptadienoyl]-oxazolidin-2-one (4k). 495 mg **3k** gave 405 mg (82%) **4k** after chromatography over silica gel with

ether/petroleum ether = 1:4. $[\alpha]_D^{20}$ = -1.6° (*c* = 1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ = 0.19 (s, 6 H, $SiMe_2$), 0.84 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.86 (s, 6 H, 2x thexyl-CH_3), 0.90 (d, *J* = 7.0 Hz, 6 H, 2x thexyl-CH_3), 1.03 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.07-1.42 (m, 4 H, CH_2-CH_2), 1.64 (sept, *J* = 7.0 Hz, 1 H, thexyl-CH), 2.32 (mc, 1 H, 5'-CH), 2.56-2.75 (m, 1 H, 4'-CH), 2.80 (dd, *J* = 13.0, 9.5 Hz, 1 H, benzyl-CH), 3.36 (dd, *J* = 13.0, 3.0 Hz, 1 H, benzyl-CH), 4.10-4.25 (m, 3 H, 6'-CH, 5-CH_2), 4.72 (mc, 1 H, 4-CH), 6.29 (d, *J* = 6.0 Hz, 1 H, 7'-CH), 7.19-7.44 (m, 7 H, 2'-CH, 3'-CH, phenyl-CH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = -3.43 ($SiMe_2$), 14.09, 16.89, 18.47, 20.03, (4x thexyl-CH_3, 2x CH_3), 20.52 (CH_2), 24.98 (thexyl-C), 34.08 (thexyl-CH), 35.45 (CH_2), 37.89 (benzyl-CH_2), 38.43, 42.14 (C-4', C-5'), 55.28 (C-4), 65.97 (C-5), 111.5 (C-6'), 118.9 (C-2'), 127.1, 128.8, 129.3, 135.4 (phenyl-C), 139.3 (C-7'), 153.3 (C-2), 157.2 (C-3'), 165.0 (C-1'); IR (film): ν = 2958, 2930, 2870 (CH), 1782, 1684 (CO), 1654, 1632, 1382, 1360, 1258, 1208, 1196, 1096, 1082, 826 cm^{-1}; UV: λ_{max} (lg ε) = 191 nm (4.861); MS (EI, 70 eV): *m/z* = 499 (1, M^+), 414 (15, M^+ - thexyl), 316(12), 241 (98), 157 (100), 73 (57). EI-HRMS calcd for $C_{29}H_{45}NO_4Si$: 499.3117, found 499.3117.

Acknowledgement: This research was generously supported by the Deutsche Forschungsgemeinschaft (Schn 441/1-1) and the Fonds der Chemischen Industrie. The Degussa AG is gratefully acknowledged for the donation of L-phenylalanine and Prof. Köster, MPI für Kohlenforschung, Mülheim/Ruhr for a gift of trialkylboranes. We thank Prof. Tietze for his generous and constant support.

References and Notes

1. Hill, R. K. in *Comprehensive Organic Synthesis. Vol. 5* (Eds.: Trost, B. M.; Fleming, I.), Pergamon, Oxford, **1991**, p. 785; Wipf, P. *ibid.*, p. 827; Pereira, S.; Srebnik, M. *Aldrichimica Acta* **1993**, *26*, 17.
2. Most recent work: Ireland, R. E.; Wipf, P.; Xiang, J. N. *J. Org. Chem.* **1991**, *56*, 3572; Corey, E. J.; Lee, D.H. *J. Am. Chem. Soc.* **1991**, *113*, 4026; Denmark, S. E.; Stadler, H.; Dorow, R. L.; Kim, J. H. *J. Org. Chem.* **1991**, *56*, 5063; Kazmaier, U.; Krebs, A. *Angew. Chemie Int. Ed. Engl.* **1995**, *34*, 2012; Maruoka, K.; Saito, S.; Yamamoto, H. *J. Am. Chem. Soc.* **1995**, *117*, 1165; Diederich, M.; Nubbemeyer, U. *Chem. Eur. J.* **1996**, *2*, 894.
3. The few reported examples are restricted to anionic oxy-Cope rearrangements, see: Tomooka, K.; Wei, S. Y.; Nakai, T. *Chem. Lett.* **1991**, 43; Wei, S. Y.; Tomooka, K.; Nakai, T. *J. Org. Chem.* **1991**, *56*, 5973; Paquette, L. A.; Maynard, G. D. *J. Am.Chem. Soc.* **1992**, *114*, 5018; Lee, E.; Lee, Y. R.; Moon, B.; Kwon, O.; Shim, M. S. *J. Org. Chem.* **1994**, *59*, 1444.
4. Schneider, C.; Rehfeuter, M. *Synlett* **1996**, 212.
5. After the precedent had been established (ref. 4) and the work described in this paper had been finished Prof. Nakai, Tokyo, reported on his investigations of Cope rearrangements of aldol products with a camphor sultam as chiral auxiliary, Japanese German Joint Symposium, Göttingen, 29.6.1996.
6. Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2128; Evans, D. A.; Sjogren, E. B.; Bartroli, J.; Dow, R. L. *Tetrahedron Lett.* **1986**, *27*, 4957.
7. Doering, W. von E.; Roth, W. R. *Tetrahedron* **1962**, *18*, 67.
8. Hill, R. K.; Gilman, N. W. *J. Chem. Soc., Chem. Commun.* **1967**, 619.
9. Hine, J.; Flachskam, N. W. *J. Am. Chem. Soc.* **1973**, *95*, 1179.
10. Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
11. Denmark, S. E.; Jones, T. K. *J. Org. Chem.* **1982**, *47*, 4595; Wender, P. A.; Sieburth, S.; Petraitis, J. J. *Tetrahedron* **1981**, *37*, 3967.
12. Brandsma, L. *Preparative Acetylenic Chemistry*, 1st ed., Elsevier, Amsterdam, **1971**.
13. Brown, C. A.; Ahuja, V. K. *J. Chem. Soc., Chem. Commun.* **1973**, 553.

(*Received in Germany* 14 *August* 1996; *revised* 15 *October* 1996; *accepted* 16 *October* 1996)