Synthesis of Enantiomerically Pure *trans*-1,2-Disubstituted Cyclopentanes and Cyclohexanes by Intramolecular Allylsilane Addition to Chiral Alkylidene-1,3-dicarbonyl Compounds

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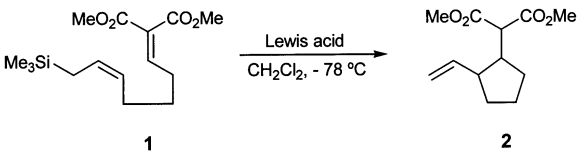
Enantiomerically pure *trans*-1,2-disubstituted cyclopentanes **14** and cyclohexanes **15** bearing three stereogenic centers can be synthesized highly selectively by Lewis acid induced intramolecular cyclizations of chiral alkylidene-1,3-dicarbonyl compounds **8** and **9**. The best results were obtained using $SnCl_4$ and the substrates **8d** and **9d**, which contain an oxazolidinone moiety derived from (*S*)-phenylalanine. In these reactions, **10d** was formed from **8d** in a 98:1:1 ratio, while **11d** was formed from **9d** in a 99:1 ratio, both in 87 % yield. The configuration of the major products **10d** and **11d** was proven by X-ray analysis. Reduction of **10d** and **11d** with $LiAlH_4$ led to **14** and **15**, respectively, or to the diols **16** and **17**. The alkylidene-1,3-dicarbonyl compounds **8** and **9** were synthesized by Knoevenagel condensation of the respective allylsilane carbaldehydes **6** and **7** with the malonic acid derivatives **5a–d**.

Five- and six-membered carbocycles are essential substructures of many biologically and pharmacologically active natural compounds such as iridoids, cyclopentenolones, quinanes, brefeldines, and steroids. Several synthetic strategies have been developed for the stereoselective preparation of these carbocycles, such as inter- and intramolecular condensation processes[1][2], intramolecular ene reactions[3], intramolecular allylsilane addition to carbonyl groups[4], and intramolecular Sakurai reactions[5]. The simple and induced diastereoselectivities of these transformations are, however, often unsatisfactory[6]. In particular, the stereoselective construction of enantiomerically pure 1,2-*trans*-disubstituted cyclopentanes has not been successfully accomplished using these methods. We have recently shown that racemic 1,2-*trans*-disubstituted cyclopentanes such as **2**, as well as cyclohexanes, can be obtained with excellent simple diastereoselectivities by an intramolecular allylsilane addition to an alkylidene malonate moiety as in **1**; the best results are obtained in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) as a promoter[7].



1 **2**

TMSOTf : *trans* : *cis* = 99.6 : 0.4 ; 97 %

Herein, we describe the synthesis of enantiomerically pure *trans*-1,2-disubstituted cyclopentanes **10**, **14**, **16**, and **18** and cyclohexanes **11**, **15**, and **17**, with two and three stereogenic centers, respectively, by an intramolecular allylsilane addition using the chiral oxazolidinones **4b–d**[8] as inducing auxiliaries[9]. Acylation of the chiral oxazolidinones **4b–d** with malonic acid methyl ester chloride (**3**) yielded the chiral malonic acid derivatives **5b–d**, which were allowed to react with the aldehydes **6** and **7** in a Knoevenagel condensation to give the alkylidene-1,3-dicarbonyl compounds **8b–d** and **9d**. These substances were used as substrates for the cyclization. Additionally, the achiral compound **8a** was also prepared via **5a**.

The acylation of **4b–d** with malonic acid methyl ester chloride (**3**) was performed in the presence of 4-dimethylaminopyridine (DMAP) and triethylamine, affording the malonic acid derivatives **5b–d** in 60–64% yield; the achiral oxazolidinone **4a** gave **5a** in 90% yield. All products were obtained as mixtures of tautomers with the keto form as the major component. Notably, the conventional procedure for acylation of oxazolidinones, using the deprotonated species[10], gave the desired products only in poor yields (15–43%), probably due to an initial deprotonation of the malonic acid chloride **3** or a deprotonation of the product **5**. An alternative method is the use of *N*-trimethylsilyloxazolidinone[11], which on reaction with the acid chloride **3** furnished **5** in an overall yield of 51%.

Knoevenagel condensation of **5a–d** in the presence of piperidine and acetic acid with aldehyde (*E*/*Z*)-**6**, which is easily accessible from 2-trimethylsilylmethylcyclohexanone by a photochemical Norrish type I cleavage[12], afforded the (2*E*,7*E*) isomers **8a–d** virtually exclusively, in yields of 54–75% (*E*/*Z* > 95:5). As by-products, small amounts of

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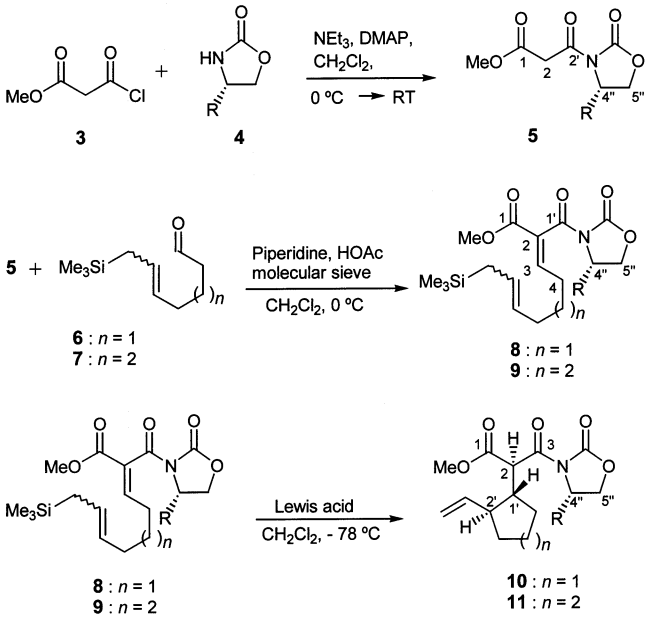


3 **4** **5**

6 : *n* = 1
7 : *n* = 2

8 : *n* = 1
9 : *n* = 2

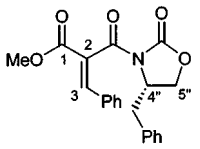
8 : *n* = 1
9 : *n* = 2

10 : *n* = 1
11 : *n* = 2

4, 5, 8 - 11 : **a**, R = H; **b**, R = *i* Pr; **c**, R = *t* Bu; **d**, R = Bn

the aldol adducts and the β,γ isomers of **8** were formed, which were not separated.

The configuration of the newly formed double bond in **8a−d** was determined by NOESY measurements on **8d**, where small couplings between the methoxy group and 3-H indicate a (2*E*) configuration. Furthermore, the (2*E*) configuration in **8a−d** was confirmed by a comparison with **12d**, which was obtained as the major product (*E*/*Z* > 95:5, 98% yield) by condensation of **5d** with benzaldehyde, and which has been characterized by X-ray crystal-structure analysis[13].

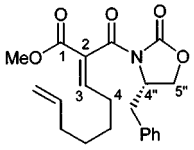


12d

The stereochemistry of the Knoevenagel condensation is usually determined by steric effects leading to formation of the thermodynamically more favoured product, although a kinetic control with isomerization of the initially formed compound cannot be excluded[14]. For the transformations described herein, the obtained (2*E*) isomers **8** seem to be the more stable structures, which is in agreement with PM3 calculations[15] carried out on an analogous system[16].

In the cyclization of **8b−d** to afford **10b−d**, three new stereogenic centers are formed under the control of the chiral auxiliary, theoretically giving eight enantiomerically pure diastereomers. On conversion of the achiral compound **8a**, four diastereomers are expected as racemic mixtures. An important aim of our investigations was to determine the influence of the chiral auxiliary and of the promoter on the selectivity of the cyclization of **8a−d**. For this purpose, the Lewis acids Me_2AlCl, $EtAlCl_2$, $ZrCl_4$, $AlCl_3$, $TiCl_4$, and $SnCl_4$, as well as TMSOTf (1.0 equiv. in each case) were used. The reactions were carried out in anhydrous dichloromethane at −78°C under argon and the formed enolates were hydrolyzed by the addition of satd. aqueous $NaHCO_3$ solution or 2 N hydrochloric acid to the cooled (−78°C) reaction mixture. The diastereoselectivities obtained were assessed by capillary GLC of the crude reaction mixtures after the aqueous work-up and, in some cases, by ^{13}C-NMR spectroscopy of the crude products.

In contrast to the reaction of **1**, the use of TMSOTf in the cyclization of **8d** led exclusively to the protodesilylated product **13d** (68% yield), probably as a result of a small amount of trifluoromethanesulfonic acid in the reaction mixture; **8d** is clearly less reactive than **1**. We have previously made similar observations in a study of TMSOTf-initiated allylsilane cyclization of precyclic α,β-unsaturated *N*-acylamides and sulfoxide esters[17].



13d

However, using Lewis acids, the cyclization could be successfully accomplished (Table 1). The best results were obtained using $SnCl_4$ and substrate **8d**, with the auxiliary **4d** incorporating a benzyl group derived from (*S*)-phenylalanine. Two products were obtained in a 95:5 ratio in 80% overall yield after work-up with aqueous $NaHCO_3$ solution. However, employing hydrochloric acid, the diastereoselectivity could even be improved, giving three products in a 98:1:1 ratio. The major product **10d** was obtained in a pure form by recrystallization from diethyl ether/petroleum ether and its configuration was determined by X-ray crystal structure analysis[18].

Table 1. Lewis acid initiated allylsilane cyclization of **8a−d** to form **10a−d** and of **9d** to form **11d**; hydrolysis by satd. $NaHCO_3$ solution

Substrate no.	R	Lewis acid	Yield [%]	Major product	Product ratio[a]
8a	H	$SnCl_4$	80	*rac*-**10a**	88:11:1
8b	*i*Pr	$SnCl_4$	57	**10b**	80:11:3:3:2:1
8c	*t*Bu	$SnCl_4$	65	**10c**	71:23:3:1:1:1
8d	Bn	$SnCl_4$	80	**10d**	95:5[a][b]
9d	Bn	$SnCl_4$	80	**11d**	96:4
8a	H	Me_2AlCl	92	*rac*-**10a**	74:22:2:4
8b	*i*Pr	Me_2AlCl	61	**10b**	53:15:10:7:6:6:3
8c	*t*Bu	Me_2AlCl	81	**10c**	40:17:12:8:7:7:5:4
8d	Bn	Me_2AlCl	77	**10d**	64:13:7:7:4:4:1
8d	Bn	TMSOTf	68	**14d**	[c]
8d	Bn	$EtAlCl_2$	74	**10d**	52:32:5:4:4:3
8d	Bn	$ZrCl_4$	78	**10d**	77:17:4:2
8d	Bn	$AlCl_3$	75	**10d**	76:8:5:5:3:2:1
8d	Bn	$TiCl_4$	61	**10d**	65:15:15:5

[a] Analytical capillary gas chromatography of the crude product. – [b] ^{13}C-NMR spectroscopy of the crude product. – [c] Protodesilylation.

The first minor compound was found to be 2-*epi*-**10d**. This was confirmed by comparison with the products obtained from the cyclization of the achiral substrate **8a** using $SnCl_4$, which yields two substances in an 86:14 ratio. From the results of the cyclization of **1**[7], it can be deduced that there should be a *trans* arrangement of the two substituents on the cyclopentane ring in these products, and therefore they must be the two C-2 epimers *rac*-**10a** and *rac*-2-*epi*-**10a**. Comparison with the spectroscopic data of **10d** and 2-*epi*-**10d** supports this hypothesis. In the ^{1}H-NMR spectrum of **10d**, the signal of 2-H appears as a doublet at $\delta = 4.59$ with $J = 7.5$ Hz and that of the methoxy group as a singlet at $\delta = 3.58$, while in the spectrum of 2-*epi*-**10d**, the signal of 2-H appears as a doublet at $\delta = 4.71$ with $J = 6.0$ Hz, whereas the singlet due to the methoxy group is observed at $\delta = 3.78$.

The cyclization of **8b** and **8c**, containing auxiliaries derived from (*S*)-valine and (*S*)-*tert*-leucine, showed a considerably lower selectivity with up to eight diastereomeric products being formed (Table 1).

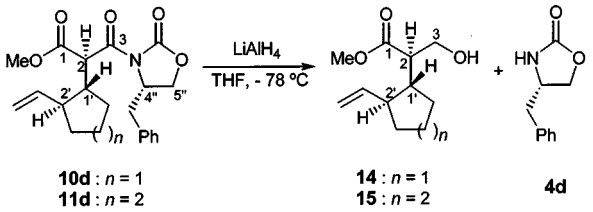
For the construction of cyclohexane derivative **11**, the pure (*Z*)-alkylidene compound (2*E*,7*Z*)-**9d** had to be used, since in contrast to the cyclization of **8**[12] the simple diastereoselectivity shows a strong dependence on the allylsilane geometry. Thus, (*E*)-allylsilanes give a lower simple diastereoselectivity, which can be explained in terms of mechanistic considerations[19]. (2*E*,7*Z*)-**9d** was synthesized by a Knoevenagel condensation of **5d** with aldehyde (*Z*)-**7**[20] in 75% yield. Here again, an excellent (*E*) selectivity was observed (*E*/*Z* > 95:5). Upon reaction of (2*E*,7*Z*)-**9d** with $SnCl_4$, followed by hydrolysis of the formed enolate with aqueous $NaHCO_3$, the 1,2-*trans*-disubstituted cyclohexane **11d** was obtained highly selectively, together with a small amount of 2-*epi*-**11d** (96:4) in 80% yield (Table 1). Recrystallization from diethyl ether/petroleum ether furnished pure **11d** and its configuration was proven by X-ray crystal structure analysis[18]. The diastereofacial selectivity could again be improved by using 2 N hydrochloric acid for the hydrolysis of the enolate intermediates, giving **11d** almost exclusively in 88% yield. These results were reproducible even for larger batches (1.5 g, Table 2).

Table 2. Lewis acid initiated allylsilane cyclization of **8a**−**d** to form **10a**−**d** and of **9d** to form **11d**; hydrolysis by 2 N HCl solution

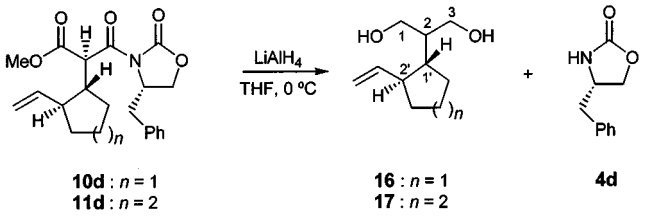
Substrate no.	R	Lewis acid	Yield [%]	Major product	Product ratio[a]
8a	H	$SnCl_4$	96	*rac*-**10a**	94:4:1:1
8b	*i*Pr	$SnCl_4$	73	**10b**	87:4:4:2:1:1
8c	*t*Bu	$SnCl_4$	67	**10c**	41:31:21:4:2:1
8d	Bn	$SnCl_4$	87	**10d**	98:1:1[a][b]
9d	Bn	$SnCl_4$	88	**11d**	99:1[a][b]

[a] Analytical capillary gas chromatography of the crude product. — [b] ^{13}C-NMR spectroscopy of the crude product.

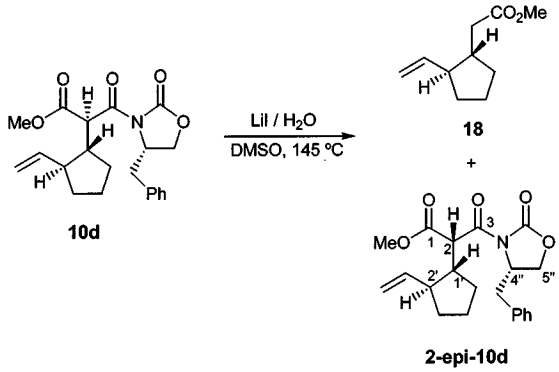
The chiral auxiliary in **10d** and **11d** could be removed by the usual methods[21]. Thus, reduction of **10d** with $LiAlH_4$ in THF (2 equiv., 3−4 h) at −78°C gave the enantiomerically pure cyclopentane **14**, with retention of the configuration at all stereogenic centers, in 77% yield, and furthermore, the chiral auxiliary **4d** was recovered nearly quantitatively by chromatography. Similarly, **11d** was transformed into the cyclohexane derivative **15** in high yield.



It is noteworthy that the best results were obtained employing a solution of $LiAlH_4$ in THF. The reaction conditions must be carefully controlled since the ester moiety will also be reduced at higher temperatures or after longer reaction times. Using 4 equiv. of $LiAlH_4$ at 0°C, the corresponding diols **16** and **17** were obtained as the major products in yields of 92 and 84%, respectively. The chiral auxiliary **4d** could again be recovered in both cases.

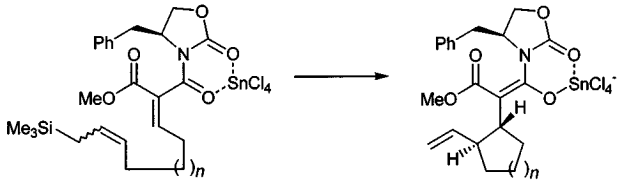


Removal of the chiral auxiliary in **10d** under Krapcho conditions[22] with lithium iodide and water in dimethyl sulfoxide (DMSO) led to the corresponding enantiopure ester **18** in 47% yield. Besides 18% of the substrate **10d**, 25% of 2-*epi*-**10d** was obtained as a by-product. Clearly, an isomerization took place under the conditions used, which is not unexpected considering the high reaction temperature. Interestingly, the reaction rate in the case of 2-*epi*-**10d** seems to be much lower than in the case of **10d**.



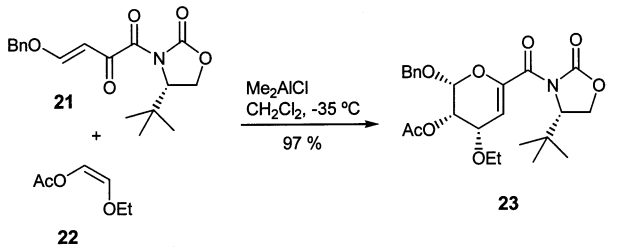
For the intramolecular allylsilane cyclization of **8d** and **9d**, we assume that the reactive metal−chelate complex **19d** is formed initially and that a subsequent *Si* side attack of the allylsilane moiety on the alkylidene-1,3-dicarbonyl unit takes place, thereby giving the enolate **20d**. This assumption is based on PM3 calculations on a model structure, in which a chelation of the imide and the urethane carbonyl group of the the auxiliary is energetically favoured (−270.2 kcal/

mol) compared to a chelation of the methyl ester moiety (−269.5 kcal/mol)[23]. The calculated difference in the stability of the two chelates is, however, rather small and should not be overemphasized, but it fits well with the observed experimental results.



19 **20**

The remarkably high induced diastereoselectivity in the cyclization of **8d** and **9d** is the result of a 1,5-induction, which is quite unusual. However, we have recently detected even a 1,6-induction in hetero Diels-Alder reactions with excellent simple and induced diastereoselectivities[24]. Interestingly, in the hetero Diels-Alder reaction of **21** and **22** to afford the cycloadduct **23**, the only auxiliary that gave good selectivities was the oxazolidinone derived from *tert*-leucine.



21 + **22** → **23**

endo : *exo* = > 50 : 1
endo-I : *endo-II* = >50 : 1

In contrast, the allylsilane cyclization of **8c**, containing the *tert*-butyl-substituted oxazolidinone, gave the worst results, while with **8b**, incorporating an isopropyl group, the obtained diastereoselectivity was lower compared to that seen in the reaction of **8d**. As the steric requirements of the isopropyl group in **8b** and the *tert*-butyl group in **8c** are clearly higher than those of the benzyl group in **8d**, we assume that the particularly high asymmetric induction for the conversion of **8d** must be attributed to π-stacking effects[25]. Due to a positive interaction between the π system of the alkylidene double bond and the phenyl ring, one side of the allylsilane acceptor would be shielded strongly so that addition of the allylsilane could only occur from the opposite side. The high simple diastereoselectivity of the cyclization of **8a−d** and **9** can be explained analogously to our earlier work[7a] in terms of a stereoelectronic preference of an *exo-E-anti* transition structure, leading predominantly to the *trans*-disubstituted products.

The stereogenic center C-2 in **10** and **11** is formed after the cyclization by a protonation of the enolate **20d**. Since a selectivity of only 88:11:1 was observed for the formation of the achiral substrate **8a**, it must be concluded that the highly selective formation of the stereogenic center C-2 in **10** and **11** is also controlled by the stereogenic center in the auxiliary. To determine whether a thermodynamic or kinetic control is operative here, we stirred **10d** and 2-*epi*-**10d** under the reaction conditions for several days; no isomerization was observed in either case. This clearly indicates that the stereogenic center C-2 is formed under kinetic control by a stereoselective protonation, which is also supported by the fact that the selectivity is altered by using different reagents, i.e. either 2 N HCl or satd. aqueous $NaHCO_3$ solution, for the hydrolysis of the enolate **20d**. Work on the stereoselective protonation of enolates[26] derived from substituted **5b−d** is currently in progress.

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Experimental Section

Analytical GC: Varian 3700 with FID and Merck-Hitachi D-2000; Macherey, Nagel and Co, 0.35 μm, chemically bound SE 30, 0.32 mm × 50 m fused silica, carrier gas: nitrogen (3 ml/min) (system A); Varian Star 3400 with autosampler Varian 8200 and FID; J. and W. Scientific DB 1701, 0.15 μm, 0.25 mm × 30 m, carrier gas: hydrogen (3 ml/min, system B). − HPLC parameters: detection wavelength λ = 220 nm; 2 sequentially connected columns filled (a) with Eurospher 100 C-18, 250 mm, 5 μm + 3 μm; eluent water/acetonitrile-water azeotrope (20:80); flow rate 0.7 ml/min (system C), and (b) with LiChrospher 100 RP-18, 250 mm, 5 μm; eluent water/acetonitrile-water azeotrope (30:70); flow rate 0.6 ml/min (system D); Knauer HPLC system using HPLC software version 2.11. − Acetonitrile was purchased from commercial sources; water was doubly distilled and stored in quartz vessels. The solvents were automatically mixed and passed through a membrane filter (0.2 μm) prior to use. − ^1H and ^{13}C NMR: Varian XL-200, VXR-200, VXR-500 S and Bruker AMX-300 instruments; multiplets were determined with the ATP pulse sequence. The numbering in the formulae was used for the assignment of the NMR data. Values indicated with an asterisk are not clearly assigned. − IR: Bruker IFS 25. − UV: Varian Cary 219. − MS: Varian MAT 311 A; high resolution: Varian MAT 731. − Melting points: Mettler FP61 (corrected values). − $[\alpha]_D^{20}$: Perkin-Elmer polarimeter 241. − Elemental analyses: Analytical laboratory of the university. − All solvents were distilled prior to use. All reactions were carried out under argon and were monitored by TLC (Macherey, Nagel and Co. Polygram Sil G/UV_{254}). Products were isolated by column chromatography (CC) on SiO_2 (Macherey, Nagel and Co., Silica 60: 63−200 μm or Macherey, Nagel and Co., Silica 60: 32−63 μm). Compounds **4b−d** were prepared as described in ref.[8], compound **6** as in ref.[12] and compound **7** as in ref.[7a].

Preparation of Oxazolidinone-Substituted Malonates. − General Procedure I: To a solution of the oxazolidinone (40.0 mmol) in dichloromethane (100 ml) at 0°C under argon, were added triethylamine (1.5 equiv.) and 4-dimethylaminopyridine (DMAP, 0.1 equiv.). The mixture was allowed to warm to room temp. and was stirred for 0.5 h. After cooling to 0°C once more, malonic acid monomethyl ester chloride (**3**) (2.0 equiv.) was added, the mixture was again allowed to warm to room temp., and was stirred until completion of the reaction (TLC). After the addition of water (30 ml) and 2 N HCl solution (20 ml), the mixture was extracted with dichloromethane (4 × 30 ml) and the combined extracts were washed (brine, 30 ml) and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by column chromatography on silica gel.

Malonic Acid Derivative **5a**: According to *General Procedure I*, oxazolidinone **4a** (3.48 g, 40.0 mmol) was acylated with **3** (8.80 ml,

80.0 mmol) in dichloromethane within 3 d. Purification (CC, 400 g, 32−63 μm, ethyl acetate/petroleum ether, 2:1) gave 6.74 g (90%) of **5a**. R_f = 0.43 (ethyl acetate/petroleum ether, 2:1). − M.p. 35°C (ethyl acetate/petroleum ether). − IR (KBr): $\tilde{\nu}$ = 2994 cm^{-1}, 2962 (CH), 1786 (C=O, urethane), 1736 (C=O), 1692 (C=O, amide), 1468, 1440, 1410 (CH_2), 1394, 1226, 1128, 1046 (C−O), 1370, 1342 (−CO−CH_2−CO−). − UV (CH_3CN): λ_{max} (lg ε) = 202 nm (4.04). − ^{1}H NMR ($CDCl_3$): δ = 3.75 (s, 3 H, OCH_3), 3.98 (s, 2 H, 2-H_2), 4.05 (dt, *J* = 8.0, 1.0 Hz, 2 H, 5′′-H), 4.43 (dt, *J* = 8.0, 1.0 Hz, 2 H, 4′′-H). − ^{13}C NMR ($CDCl_3$): δ = 42.31 (C-2), 42.31 (C-4′′), 52.54 (OCH_3), 62.33 (C-5′′), 153.5 (C-2′′), 165.7 (C-1), 167.2 (C-1′). − MS (70 eV); *m/z* (%): 187 (1) [M^+], 156 (13) [M^+ − OCH_3], 101 (50) [$C_4H_5O_3^+$], 59 (50) [$C_2H_3O_2^+$], 43 (100) [$C_2H_3O^+$, $CHNO^+$]. − $C_7H_9NO_5$ (187.15): calcd. C 44.92, H 4.84; found C 45.03, H 4.76.

Malonic Acid Derivative **5b**: According to *General Procedure I*, oxazolidinone **4b** (1.20 g, 9.32 mmol) was acylated with **3** (2.00 ml, 18.6 mmol) in dichloromethane within 4 d. Purification (CC, 100 g, 32−63 μm, ethyl acetate/petroleum ether, 2:1) gave 1.35 g (63%) of **5b**. R_f = 0.23 (ethyl acetate/petroleum ether, 1:3). − $[\alpha]_D^{20}$ = +65.0 (*c* = 1.00, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2964 cm^{-1}, 2878 (CH), 1782 (C=O, urethane), 1744 (C=O), 1706 (C=O, amide), 1392, 1372 (*i*Pr-CH), 1344, 1304, 1210 (C−O). − UV (CH_3CN): λ_{max} (lg ε) = 204 nm (4.06). − ^{1}H NMR ($CDCl_3$): δ = 0.93 (d, *J* = 7.0 Hz, 3 H, *i*Pr-CH_3), 0.95 (d, *J* = 7.0 Hz, 3 H, *i*Pr-CH_3), 2.45 (dsept, *J* = 7.0, 4.0 Hz, 1 H, *i*Pr-CH), 3.75 (s, 3 H, OCH_3), 3.88 (d, *J* = 16.0 Hz, 1 H, 2-H), 4.04 (d, *J* = 16.0 Hz, 1 H, 2-H), 4.25 (dd, *J* = 9.0, 4.0 Hz, 1 H, 5′′-H), 4.33 (dd, *J* = 9.0, 9.0 Hz, 1 H, 5′′-H), 4.48 (ddd, *J* = 9.0, 4.0, 4.0 Hz, 1 H, 4′′-H). − ^{13}C NMR ($CDCl_3$): δ = 14.35, 17.70 (CH_3), 28.06 (*i*Pr-C), 42.66 (C-2), 52.28 (OCH_3), 58.29 (C-4′′), 63.48 (C-5′′), 153.9 (C-2′′), 165.4 (C-1), 167.1 (C-1′). − MS (70 eV); *m/z* (%): 229 (1) [M^+], 198 (5) [M^+ − OCH_3], 186 (4) [M^+ − $CH(CH_3)_2$], 101 (100) [$C_4H_5O_3^+$], 59 (25) [$C_2H_3O_2^+$], 43 (8) [$C_2H_3O^+$, $CHNO^+$]. − $C_{10}H_{15}NO_5$ (229.24): calcd. C 52.40, H 6.60; found C 52.42, H 6.56.

Malonic Acid Derivative **5c**: According to *General Procedure I*, oxazolidinone **4c** (5.40 g, 37.7 mmol) was acylated with **3** (8.10 ml, 75.4 mmol) in dichloromethane within 3 d. Purification (CC, 450 g, 32−63 μm, ethyl acetate/petroleum ether, 2:1) gave 5.50 g (60%) of **5c**. R_f = 0.31 (ethyl acetate/petroleum ether, 1:2). − M.p. 41°C (ethyl acetate/petroleum ether). − $[\alpha]_D^{20}$ = +52.7 (*c* = 1.00, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2962 cm^{-1}, 2878 (CH), 1784 (C=O, urethane), 1746 (C=O), 1710 (C=O, amide), 1482 (CH_3), 1438, 1402 (CH_2), 1390, 1370 [$C(CH_3)_3$], 1340 (−CO−CH_2−CO−), 1302, 1220, 1190 (C−O). − UV (CH_3CN): λ_{max} (lg ε) = 203 nm (3.93). − ^{1}H NMR ($CDCl_3$): δ = 0.98 (s, 9 H, 3 × CH_3), 3.75 (s, 3 H, OCH_3), 3.89 (d, *J* = 16.0 Hz, 1 H, 2-H), 4.02 (d, *J* = 16.0 Hz, 1 H, 2-H), 4.29 (dd, *J* = 9.0, 7.0 Hz, 1 H, 5′′-H), 4.33 (dd, *J* = 9.0, 2.0 Hz, 1 H, 5′′-H), 4.44 (dd, *J* = 7.0, 2.0 Hz, 1 H, 4′′-H). − ^{13}C NMR ($CDCl_3$): δ = 25.39 (CH_3), 35.81 [$C(CH_3)_3$], 42.56 (C-2), 52.21 (OCH_3), 61.01 (C-4′′), 65.51 (C-5′′), 154.5 (C-2′′), 165.5 (C-1), 167.3 (C-1′). − MS (70 eV); *m/z* (%): 244 (< 1) [M^+ + 1], 212 (7) [M^+ − OCH_3], 187 (32) [M^+ − $C(CH_3)_3$], 143 (30) [M^+ − $C_4H_5O_3^+$], 101 (30) [$C_4H_5O_3^+$], 86 (10) [$C_3H_4NO_2^+$], 59 (15) [$C_2H_3O_2^+$], 57 (42) [$C(CH_3)_3$], 43 (100) [$C_2H_3O^+$, $CHNO^+$]. − $C_{11}H_{17}NO_5$ (243.26): calcd. C 54.31, H 7.04; found C 54.48, H 7.07.

Malonic Acid Derivative **5d**: According to *General Procedure I*, oxazolidinone **4d** (2.00 g, 11.4 mmol) was acylated with **3** (3.25 ml, 22.8 mmol) in dichloromethane within 2 d. Purification (CC, 300 g, 32−63 μm, ethyl acetate/petroleum ether, 2:1) gave 2.02 g (64%) of **5d**. R_f = 0.38 (ethyl acetate/petroleum ether, 1:2). − $[\alpha]_D^{20}$ = +54.3 (*c* = 1.00, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3028 cm^{-1}, 3004, 2956 (CH), 1780 (C=O, urethane), 1746 (C=O), 1708 (C=O, amide), 1604, 1584, 1496 (C=C, Ph), 1452, 1438 (CH_2), 1366, 1346 (−CO−CH_2−CO−), 1288, 1214, 1116, 1076 (C−O), 762, 706 (Ph). − UV (CH_3CN): λ_{max} (lg ε) = 205 nm (4.21), 252 (2.55), 258 (2.57), 264 (2.51). − ^{1}H NMR ($CDCl_3$): δ = 2.80 (dd, *J* = 13.0, 9.0 Hz, 1 H, Bzl-H), 3.37 (dd, *J* = 13.0, 4.0 Hz, 1 H, Bzl-H), 3.77 (s, 3 H, OCH_3), 3.99 (s, 2 H, 2-H_2), 4.19 (dd, *J* = 9.0, 4.0 Hz, 1 H, 5′′-H), 4.25 (dd, *J* = 9.0, 7.5 Hz, 1 H, 5′′-H), 4.72 (dddd, *J* = 9.0, 7.5, 4.0, 4.0 Hz, 1 H, 4′′-H), 7.21−7.38 (m, 5 H, Ph-H). − ^{13}C NMR ($CDCl_3$): δ = 37.51 (Bzl-CH_2), 42.75 (C-2), 52.52 (OCH_3), 55.07 (C-4′′), 66.41 (C-5′′), 127.4, 129.0, 129.4 (Ph-C), 135.0 (*ipso*-Ph-C), 153.4 (C-2′′), 165.6 (C-1), 167.3 (C-1′). − MS (70 eV); *m/z* (%): 277 (13) [M^+], 246 (6) [M^+ − OCH_3], 101 (100) [$C_4H_5O_3^+$], 91 (29) [$C_7H_7^+$], 59 (51) [$C_2H_3O_2^+$], 43 (27) [$C_2H_3O^+$, $CHNO^+$]. − $C_{14}H_{15}NO_5$ (277.28): calcd. C 60.64, H 5.45; found C 60.54, H 5.39.

Preparation of the Alkylidene-1,3-dicarbonyl Compounds by Knoevenagel Condensation. − General Procedure II: The malonic acid derivative **5a−d** (13.7 mmol, 1.2 equiv.) was dissolved in anhydrous dichloromethane (50 ml) in a flame-dried flask containing molecular sieve (4 Å, 10 g) and the solution was cooled to 0°C under argon. Piperidine (1.25 mmol, 124 μl, 0.1 equiv.) and acetic acid (1.25 mmol, 72 μl, 0.1 equiv.) were added simultaneously to the stirred mixture. After stirring for 10 min, a solution of the aldehyde (12.50 mmol, 1.0 equiv.) in anhydrous dichloromethane (10 ml) was slowly added to the stirred mixture over a period of 5 min. The reaction was monitored by TLC and, if necessary, further portions of piperidine and acetic acid (0.1 equiv.) were added until completion was reached. Subsequently, the mixture was allowed to warm to room temp., the molecular sieve was removed by filtration, the solvent was evaporated, and the residue was purified by column chromatography on silica gel.

Methyl (2E,7E/Z)-2-[(2′′-Oxo-3′′-oxazolidinyl)carbonyl]-9-trimethylsilyl-2,7-nonadienoate (**8a**): According to *General Procedure II*, aldehyde **6** (2.07 g, 11.2 mmol) was allowed to react with **5a** (2.79 g, 15.0 mmol, 1.3 equiv.) for 14 h to give 2.96 g (75%) of **8a** (CC, 450 g, 63−200 μm, ethyl acetate/petroleum ether, 1:1). R_f = 0.20 (ethyl acetate/petroleum ether, 1:3). − HPLC (system C): t_R = 30.00 min. − IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (CH), 1786 (C=O, urethane), 1734 (C=O), 1694 (C=O, amide), 1650 (C=C), 1480, 1438 (CH_2), 1296, 1226, 1156 (C−O), 1248, 854 ($SiMe_3$), 966 (C=C−H). − UV (CH_3CN): λ_{max} (lg ε) = 200 nm (4.34). − ^{1}H NMR ($CDCl_3$, *E,E* isomer): δ = −0.04 (s, 9 H, $SiMe_3$), 1.36 (dd, *J* = 8.0, 1.0 Hz, 2 H, 9-H_2), 1.42−1.59 (m, 2 H, 5-H_2), 1.98 (br. q, *J* = 7.0 Hz, 2 H, 6-H_2), 2.18 (q, *J* = 7.5 Hz, 2 H, 4-H_2), 3.72 (s, 3 H, OCH_3), 4.09 (dt, *J* = 8.0, 1.0 Hz, 2 H, 5′′-H_2), 4.44 (dt, *J* = 8.0, 1.0 Hz, 2 H, 4′′-H_2), 5.16 (dtt, *J* = 15.0, 7.0, 1.0 Hz, 1 H, 7-H), 5.37 (dtt, *J* = 15.0, 8.0, 1.0 Hz, 1 H, 8-H), 7.03 (t, *J* = 7.5 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$, *E,E* isomer): δ = −1.96 ($SiMe_3$), 22.68 (C-9), 28.62, 29.29, 32.29 (C-4, C-5, C-6), 42.11 (C-4′′), 52.28 (OCH_3), 62.43 (C-5′′), 127.2 (C-8), 127.6 (C-7), 129.4 (C-2), 148.8 (C-3), 152.8 (C-2′′), 163.9 (C-1), 164.9 (C-1′). − MS (70 eV); *m/z* (%): 353 (2) [M^+], 338 (8) [M^+ − CH_3], 213 (8) [McLafferty peak], 124 (100), 101 (28) [$C_4H_5O_3^+$], 73 (84) [$SiMe_3^+$], 59 (30) [$C_2H_3O_2^+$], 43 (18) [$C_2H_3O^+$, $CHNO^+$]. − $C_{17}H_{27}NO_5Si$ (353.49): calcd. C 57.76, H 7.70; found C 57.96, H 7.86.

Methyl (2E,7E/Z,4′′S)-2-[(4′′-Isopropyl-2′′-oxo-3′′-oxazolidinyl)carbonyl]-9-trimethylsilyl-2,7-nonadienoate (**8b**): According to *General Procedure II*, aldehyde **6** (0.90 g, 4.89 mmol) was allowed to react with **5b** (1.34 g, 5.86 mmol, 1.2 equiv.) for 21 h to give 1.45 g (76%) of **8b** (CC, 250 g, 63−200 μm, ethyl acetate/petroleum

ether, 1:3). R_f = 0.39 (ethyl acetate/petroleum ether, 1:3). − $[\alpha]_D^{20}$ = +17.7 (*c* = 1.00, $CHCl_3$). − HPLC (system C): t_R = 57.58 min. − IR (film): $\tilde{\nu}$ = 2954 cm^{-1} (CH), 1786 (C=O, urethane), 1742 (C=O), 1704 (C=O, amide), 1658 (C=C), 1438, 1374 (CH_2), 1388, 1374 (*i*Pr), 1340, 1302 (C−O), 1248, 854 ($SiMe_3$). − UV (CH_3CN): λ_{max} (lg ε) = 198 nm (4.24). − ^{1}H NMR ($CDCl_3$, *E*,*E* isomer): δ = 0.00 (s, 9 H, $SiMe_3$), 0.98 (d, *J* = 7.0 Hz, 3 H, *i*Pr-CH_3), 0.99 (d, *J* = 7.0 Hz, 3 H, *i*Pr-CH_3), 1.41 (dd, *J* = 8.0, 1.0 Hz, 2 H, 9-H_2), 1.47−1.67 (m, 2 H, 5-H_2), 2.03 (br. q, *J* = 7.0 Hz, 2 H, 6-H_2), 2.23 (dq, *J* = 8.0, 2.5 Hz, 2 H, 4-H_2), 2.54 (dsept, *J* = 7.0, 4.0 Hz, 1 H, *i*Pr-CH), 3.83 (s, 3 H, OCH_3), 4.28 (dd, *J* = 9.0, 3.0 Hz, 1 H, 5′′-H), 4.34 (dd, *J* = 9.0, 8.5 Hz, 1 H, 5′′-H), 4.56 (ddd, *J* = 8.5, 4.0, 3.0 Hz, 1 H, 4′′-H), 5.22 (dt, *J* = 15.0, 7.0 Hz, 1 H, 7-H), 5.42 (dtt, *J* = 15.0, 8.0, 1.0 Hz, 1 H, 8-H), 7.07 (t, *J* = 8.0 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$, *E*,*E* isomer): δ = −2.05 ($SiMe_3$), 14.51 (CH_3), 17.83 (CH_3), 22.58 (C-9), 28.31 (*i*Pr-CH), 28.59, 29.18, 32.29 (C-4, C-5, C-6), 52.07 (OCH_3), 58.19 (C-4′′), 63.61 (C-5′′), 127.1 (C-8), 127.5 (C-7), 129.8 (C-2), 148.2 (C-3), 153.2 (C-2′′), 163.8 (C-1), 164.7 (C-1′). − MS (70 eV); *m*/*z* (%): 395 (3) [M^+], 380 (10) [$M^+ - CH_3$], 364 (3) [$M^+ - OCH_3$], 266 (16) [M^+ − oxazolidinone], 255 (11) [McLafferty peak], 73 (100) [$SiMe_3^+$], 59 (23) [$C_2H_3O_2^+$], 43 (96) [$C_2H_3O^+$, $CHNO^+$]. − $C_{20}H_{33}NO_5Si$ (395.57): calcd. C 60.07, H 8.41; found C 60.16, H 8.51.

Methyl (2E,7E/Z,4′′S)-2-[(4′′-tert-Butyl-2′′-oxo-3′′-oxazolidinyl)-carbonyl]-9-trimethylsilyl-2,7-nonadienoate (**8c**): According to *General Procedure II*, aldehyde **6** (2.78 g, 15.1 mmol) was allowed to react with **5c** (4.40 g, 18.1 mmol, 1.2 equiv.) for 16 h to give 4.38 g (71%) of **8c** (CC, 450 g, 63−200 μm, ethyl acetate/petroleum ether, 1:3). R_f = 0.44 (ethyl acetate/petroleum ether, 1:3). − $[\alpha]_D^{20}$ = +34.3 (*c* = 1.00, $CHCl_3$). − HPLC (system C): t_R = 56.13 min. − IR (film): $\tilde{\nu}$ = 2956 cm^{-1} (CH), 1786 (C=O, urethane), 1738 (C=O), 1698 (C=O, amide), 1648 (C=C), 1480, 1384 [$C(CH_3)_3$], 1438, 1370 (CH_2), 1350, 1328 (C−O), 1250, 854 ($SiMe_3$). − UV (CH_3CN): λ_{max} (lg ε) = 200 nm (4.27). − ^{1}H NMR ($CDCl_3$, *E*,*E* isomer): δ = −0.05 (s, 9 H, $SiMe_3$), 1.00 [s, 9 H, $C(CH_3)_3$], 1.36 (dd, *J* = 8.0, 1.0 Hz, 2 H, 9-H_2), 1.42−1.60 (m, 2 H, 5-H_2), 1.98 (br. q, *J* = 7.0 Hz, 2 H, 6-H_2), 2.21 (dq, *J* = 8.0, 3.0 Hz, 2 H, 4-H_2), 3.75 (s, 3 H, OCH_3), 4.25 (dd, *J* = 9.0, 7.0 Hz, 1 H, 5′′-H), 4.31 (dd, *J* = 9.0, 2.0 Hz, 1 H, 5′′-H), 4.46 (dd, *J* = 7.0, 2.0 Hz, 1 H, 4′′-H), 5.17 (dtt, *J* = 15.0, 7.0, 1.0 Hz, 1 H, 7-H), 5.37 (dtt, *J* = 15.0, 8.0, 1.0 Hz, 1 H, 8-H), 7.04 (t, *J* = 8.0 Hz, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$, *E*,*E* isomer): δ = −2.08 ($SiMe_3$), 25.51 (CH_3), 22.54 (C-9), 28.57, 29.17, 32.25 (C-4, C-5, C-6), 36.05 [$C(CH_3)_3$], 51.98 (OCH_3), 61.02 (C-4′′), 65.53 (C-5′′), 127.0 (C-8), 127.5 (C-7), 129.7 (C-2), 148.3 (C-3), 153.8 (C-2′′), 163.9 (C-1), 164.7 (C-1′). − MS (70 eV); *m*/*z* (%): 409 (1) [M^+], 394 (4) [$M^+ - CH_3$], 266 (8) [M^+ − oxazolidinone], 101 (86) [$C_4H_5O_3^+$], 73 (100) [$SiMe_3^+$], 57 (86) [$C(CH_3)_3$], 43 (90) [$C_2H_3O^+$, $CHNO^+$]. − $C_{21}H_{35}NO_5Si$ (409.60): calcd. C 61.58, H 8.61; found C 61.41, H 8.74.

Methyl (2E,7E/Z,4′′S)-2-[(4′′-Benzyl-2′′-oxo-3′′-oxazolidinyl)-carbonyl]-9-trimethylsilyl-2,7-nonadienoate (**8d**): According to *General Procedure II*, aldehyde **6** (2.30 g, 12.5 mmol) was allowed to react with **5d** (4.31 g, 15.6 mmol, 1.2 equiv.) for 27 h to give 3.73 g (67%) of **8d** (CC, 450 g, 63−200 μm, ethyl acetate/petroleum ether, 1:2). R_f = 0.39 (ethyl acetate/petroleum ether, 1:2). − $[\alpha]_D^{20}$ = +43.7 (*c* = 1.00, $CHCl_3$). − HPLC (system C): t_R = 63.36 min. − IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (CH), 1788 (C=O, urethane), 1736 (C=O), 1692 (C=O, amide), 1648 (C=C), 1606, 1586, 1496 (C=C, Ph), 1452, 1438, 1380 (CH_2), 1290, 1270, 1214 (C−O), 1248, 854 ($SiMe_3$), 760, 702 (Ph). − UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4.78). − ^{1}H NMR ($CDCl_3$, *E*,*E* isomer): δ = −0.05 (s, 9 H, $SiMe_3$), 1.36 (dd, *J* = 8.0, 1.0 Hz, 2 H, 9-H_2), 1.31−1.63 (m, 2 H, 5-H_2), 2.01 (br. q, *J* = 7.0 Hz, 2 H, 6-H_2), 2.23 (q, *J* = 7.5 Hz, 2 H, 4-H_2), 2.76 (dd, *J* = 13.5, 10.0 Hz, 1 H, Bzl-H), 3.45 (dd, *J* = 13.5, 3.5 Hz, 1 H, Bzl-H), 3.76 (s, 3 H, OCH_3), 4.17 (dd, *J* = 9.0, 3.5 Hz, 1 H, 5′′-H), 4.23 (dd, *J* = 9.0, 7.0 Hz, 1 H, 5′′-H), 4.74 (dddd, *J* = 10.0, 7.0, 3.5, 3.5 Hz, 1 H, 4′′-H), 5.19 (dtt, *J* = 15.0, 7.0, 1.0 Hz, 1 H, 7-H), 5.39 (dtt, *J* = 15.0, 8.0, 1.0 Hz, 1 H, 8-H), 7.06 (t, *J* = 8.0 Hz, 1 H, 3-H), 7.20−7.39 (m, 5 H, Ph-H). − ^{13}C NMR ($CDCl_3$, *E*,*E* isomer): δ = −2.02 ($SiMe_3$), 22.64 (C-9), 28.61, 29.21, 32.29 (C-4, C-5, C-6), 37.64 (Bzl-CH_2), 52.20 (OCH_3), 54.96 (C-4′′), 66.41 (C-5′′), 127.3 (*p*-Ph-C), 128.9 (*m*-Ph-C), 129.4 (*o*-Ph-C), 127.2 (C-8), 127.5 (C-7), 129.6 (C-2), 135.1 (*ipso*-Ph-C), 148.4 (C-3), 152.7 (C-2′′), 163.8 (C-1), 164.8 (C-1′). − MS (70 eV); *m*/*z* (%): 443 (1) [M^+], 428 (3) [$M^+ - CH_3$], 412 (1) [$M^+ - OCH_3$], 303 (2) [McLafferty peak], 101 (84) [$C_4H_5O_3^+$], 91 (48) [$C_7H_7^+$], 73 (100) [$SiMe_3^+$], 59 (20) [$C_2H_3O_2^+$], 43 (18) [$C_2H_3O^+$, $CHNO^+$]. − $C_{24}H_{33}NO_5Si$ (443.62): calcd. C 64.98, H 7.50; found C 65.01, H 7.51.

Methyl (2E,8Z,4′′S)-2-[4′′-Benzyl-2′′-oxo-3′′-oxazolidinyl)carbonyl]-9-trimethylsilyl-2,7-decadienoate (**9d**): According to *General Procedure II*, aldehyde **7** (1.03 g, 5.17 mmol) was allowed to react with **5d** (1.72 g, 6.21 mmol, 1.2 equiv.) for 22 h to give 1.77 g (75%) of **9d** (CC, 200 g, 63−200 μm, ethyl acetate/petroleum ether, 1:3). R_f = 0.39 (ethyl acetate/petroleum ether, 1:3). − $[\alpha]_D^{20}$ = +41.7 (*c* = 1.00, $CHCl_3$). − HPLC (system C): t_R = 51.05 min. − IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (CH), 1788 (C=O, urethane), 1736 (C=O), 1692 (C=O, amide), 1648 (C=C), 1606, 1586, 1496 (C=C, Ph), 1452, 1438 (CH_2), 1270, 1214 (C−O), 1248, 856 ($SiMe_3$), 762, 702 (Ph). − UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4.85). − ^{1}H NMR ($CDCl_3$): δ = −0.06 (s, 9 H, $SiMe_3$), 1.40 (d, *J* = 8.3 Hz, 2 H, 10-H_2), 1.15−1.62 (m, 4 H, 5-H_2, 6-H_2), 1.95 (br. q, *J* = 7.0 Hz, 2 H, 7-H_2), 2.22 (q, *J* = 7.5 Hz, 2 H, 4-H_2), 2.74 (dd, *J* = 13.5, 10.0 Hz, 1 H, Bzl-H), 3.44 (dd, *J* = 13.5, 3.5 Hz, 1 H, Bzl-H), 3.73 (s, 3 H, OCH_3), 4.14 (dd, *J* = 9.5, 3.5 Hz, 1 H, 5′′-H), 4.20 (dd, *J* = 9.5, 8.5 Hz, 1 H, 5′′-H), 4.73 (dddd, *J* = 10.0, 8.5, 3.5, 3.5 Hz, 1 H, 4′′-H), 5.19 (dtt, *J* = 10.5, 7.0, 1.0 Hz, 1 H, 8-H), 5.39 (dtt, *J* = 10.5, 8.3, 1.0 Hz, 1 H, 9-H), 7.03 (t, *J* = 8.0 Hz, 1 H, 3-H), 7.15−7.37 (m, 5 H, Ph-H). − ^{13}C NMR ($CDCl_3$): δ = −1.91 ($SiMe_3$), 18.33 (C-10), 26.52, 27.84, 29.19, 29.52 (C-4, C-5, C-6, C-7), 37.49 (Bzl-CH_2), 52.12 (OCH_3), 54.86 (C-4′′), 66.33 (C-5′′), 125.7 (C-9), 126.7 (C-8), 127.2 (*p*-Ph-C), 128.8 (*m*-Ph-C), 129.3 (*o*-Ph-C), 129.6 (C-2), 135.0 (*ipso*-Ph-C), 148.5 (C-3), 152.6 (C-2′′), 163.7 (C-1), 164.8 (C-1′). − MS (70 eV); *m*/*z* (%): 457 (8) [M^+], 442 (3) [$M^+ - CH_3$], 117 (19) [$C_9H_9^+$], 101 (7) [$C_4H_5O_3^+$], 91 (28) [$C_7H_7^+$], 73 (100) [$SiMe_3^+$]. − $C_{25}H_{35}NO_5Si$ (457.65): calcd. C 65.61, H 7.71; found C 65.75, H 7.90.

Methyl (2E,4′′S)-2-[4′′-Benzyl-2′′-oxo-3′′-oxazolidinyl)carbonyl]-3-phenylacrylate (**12d**): According to *General Procedure II*, benzaldehyde (1.53 g, 14.4 mmol, 2.0 equiv.) was allowed to react with **5d** (2.00 g, 7.21 mmol, 1.0 equiv.) for 25 h to give 2.58 g (98%) of **12d** (CC, 250 g, 63−200 μm, ethyl acetate/petroleum ether, 1:2). R_f = 0.19 (ethyl acetate/petroleum ether, 1:2). − M.p. 106°C (ethyl acetate/petroleum ether). − $[\alpha]_D^{20}$ = +102.2 (*c* = 0.60, $CHCl_3$). − HPLC (system D): t_R = 18.09 min. − IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1} (CH), 1776 (C=O, urethane), 1730 (C=O), 1692 (C=O, amide), 1628 (C=C), 1448 (CH_2), 1268, 1216, 1198 (C−O), 760, 694 (Ph). − UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4.78), 204 (4.44), 281 (4.21). − ^{1}H NMR ($CDCl_3$): δ = 2.74 (br. s, 1 H, Bzl-H), 3.53 (dd, *J* = 13.5, 3.5 Hz, 1 H, Bzl-H), 3.85 (s, 3 H, OCH_3), 4.17 (br. d, *J* = 3.5 Hz, 2 H, 5′′-H_2), 4.68−4.86 (m, 1 H, 4′′-H), 7.20−7.50 (m, 10 H, Ph-H), 7.82 (s, 1 H, 3-H). − ^{13}C NMR ($CDCl_3$): δ = 37.30 (Bzl-CH_2), 52.44 (OCH_3), 54.96 (C-4′′), 66.31 (C-5′′), 127.2, 128.7, 128.8, 129.3, 130.3 (Ph-C), 132.8, 134.9 (*ipso*-Ph-C, C-2), 142.1 (C-

3), 152.4 (C-2′′), 164.0 (C-1)*, 165.5 (C-1′)*. − MS (70 eV); *m/z* (%): 365 (19) [M^+], 350 (1) [$M^+ - CH_3$], 334 (4) [$M^+ - OCH_3$], 306 (4) [$M^+ - C_2H_3O_2$], 189 (100) [M^+ − oxazolidinone], 91 (24) [$C_7H_7^+$], 59 (12) [$C_2H_3O_2^+$]. − $C_{21}H_{19}NO_5$ (365.39): calcd. C 69.03, H 5.24; found C 69.17, H 5.46.

Intramolecular Allylsilane Addition; Cyclization Experiments. − General Procedure III: To a cooled and stirred solution (−78°C) of the alkylidene compound **8a−d** or **9d** (0.25 mmol, 1.0 equiv.) in anhydrous dichloromethane (3 ml) under argon, was added the promotor (0.25 mmol, 1.0 equiv.). Stirring was continued at this temperature until completion of the cyclization (TLC control). The mixture was then hydrolysed at the given temperature by adding either a satd. aqueous $NaHCO_3$ solution (3 ml, *Procedure III A*) or 2 N HCl solution (3 ml, *Procedure III B*), and warming to room temp. over a period of 15 min. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 3 ml). The combined organic phases were washed (water, 3 ml and brine, 3 ml) and dried ($MgSO_4$). Evaporation of the solvent and purification of the residue by column chromatography on silica gel yielded the cyclopentanes **10a−d** and cyclohexane **11d** as a mixture of diastereomers.

Cyclization to Methyl 3-Oxo-3-(2′′-oxo-3′′-oxazolidinyl)-2-(2′-vinylcyclopentyl)propionate (*rac*-**10a**). − *Me_2AlCl:* 355 mg (1.00 mmol) of **8a** was treated with 1.00 ml of Me_2AlCl solution (1 M in hexane, 1.00 mmol) in 12 ml of dichloromethane within 2 d (TLC, ethyl acetate/petroleum ether, 1:1) according to *General Procedure III A*. CC (50 g, 63−200 μm, ethyl acetate/petroleum ether, 1:1) gave 259 mg of *rac*-**10a** (92%) as a mixture of diastereomers. − *$SnCl_4$:* 177 mg (0.50 mmol) of **8a** was treated with 0.50 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 0.50 mmol) in 6 ml of dichloromethane within 4 d (TLC, ethyl acetate/petroleum ether, 1:1) according to *General Procedure III A*. CC (10 g, 63−200 μm, ethyl acetate/petroleum ether, 1:2) gave 112 mg of *rac*-**10a** (80%) as a mixture of diastereomers. − *$SnCl_4$:* 355 mg (1.00 mmol) of **8a** was treated with 1.00 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 1.00 mmol) in 6 ml of dichloromethane within 3 d (TLC, ethyl acetate/petroleum ether, 1:1) according to *General Procedure III B*. CC (30 g, 63−200 μm, ethyl acetate/petroleum ether, 1:3) gave 270 mg of *rac*-**10a** (96%) as a mixture of diastereomers.

rac-**10a**: R_f = 0.45 (ethyl acetate/petroleum ether, 1:1). − M.p. 47°C (ethyl acetate/petroleum ether). − GC (181°C − 0.1°C/min, system B): t_R = 39.40 min, 40.60 (major diastereomer), 41.64, 42.80. − IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 2872 (CH), 1780 (C=O, urethane), 1734 (C=O), 1706 (C=O, amide), 1640 (C=C), 1480, 1436, 1390 (CH_2), 1336, 1300, 1222, 1172 (C−O). − UV (CH_3CN): λ_{max} (lg ε) = 281 nm (3.09). − ^{1}H NMR ($CDCl_3$): δ = 1.33−1.72 (m, 4 H, 4′-H_2, 3′-H_2), 1.86 (m_c, 2 H, 5′-H_2), 2.44 (m_c, 2 H, 1′-H, 2′-H), 3.65 (s, 3 H, OCH_3), 4.05 (m_c, 2 H, 5′′-H_2), 4.42 (dt, *J* = 8.0, 1.0 Hz, 2 H, 4′′-H_2), 4.60 (dt, *J* = 7.5, 2.0 Hz, 1 H, 2-H), 4.91 (dd, *J* = 9.0, 2.0 Hz, 1 H, 2′′′-H_{cis}), 4.93 (dd, *J* = 18.0, 2.0 Hz, 1 H, 2′′′-H_{trans}), 5.67 (dddd, *J* = 18.0, 9.0, 8.0, 2.0 Hz, 1 H, 1′′′-H). − ^{13}C NMR ($CDCl_3$): δ = 23.61 (C-3′), 30.13 (C-4′), 33.51 (C-5′), 42.50 (C-4′′), 44.87 (C-1′)*, 47.61 (C-2′)*, 52.03 (OCH_3)*, 52.70 (C-2)*, 62.00 (C-5′′), 113.9 (C-2′′′), 141.7 (C-1′′′), 153.2 (C-2′′), 168.1 (C-1), 169.2 (C-3). − MS (70 eV); *m/z* (%): 282 (1) [M^+], 250 (1) [$M^+ - OCH_3$], 194 (20) [M^+ − oxazolidinone], 187 (78) [McLafferty peak], 101 (19) [$C_4H_5O_3^+$], 94 (100) [McLafferty peak], 87 (58) [oxazolidinone], 59 (12) [$C_2H_3O_2^+$], 43 (3) [$C_2H_3O^+$, $CHNO^+$]. − $C_{14}H_{19}NO_5$ (281.31): calcd. C 59.78, H 6.81; found C 59.69, H 6.72.

Cyclization to Methyl (1′R,2R,2′S,4′′S)-3-(4′′-Isopropyl-2′′-oxooxazolidin-3′′-yl)-3-oxo-2-(2′-vinylcyclopentyl)propionate (**10b**). − *Me_2AlCl:* 396 mg (1.00 mmol) of **8b** was treated with 1.00 ml of Me_2AlCl solution (1 M in hexane, 1.00 mmol) in 12 ml of dichloromethane within 4 d (TLC, ethyl acetate/petroleum ether, 1:5) according to *General Procedure III A*. CC (32 g, 63−200 μm, ethyl acetate/petroleum ether, 1:2) gave 197 mg of **10b** (61%) as a mixture of diastereomers. − *$SnCl_4$:* 198 mg (0.50 mmol) of **8b** was treated with 0.50 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 0.50 mmol) in 6 ml of dichloromethane within 4 d (TLC, ethyl acetate/petroleum ether, 1:5) according to *General Procedure III A*. CC (10 g, 63−200 μm, ethyl acetate/petroleum ether, 1:2) gave 92 mg of **10b** (57%) as a mixture of diastereomers. − *$SnCl_4$:* 491 mg (1.24 mmol) of **8b** was treated with 1.24 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 1.24 mmol) in 30 ml of dichloromethane within 3 d (TLC, ethyl acetate/petroleum ether, 1:5) according to *General Procedure III B*. CC (40 g, 63−200 μm, ethyl acetate/petroleum ether, 1:5) gave 293 mg of **10b** (73%) as a mixture of diastereomers.

10b: R_f = 0.20 (ethyl acetate/petroleum ether, 1:5). − $[\alpha]_D^{20}$ = +59.0 (*c* = 0.50, $CHCl_3$). − GC (186°C − 0.1°C/min, system B): t_R = 34.69 min, 35.80, 37.31 (major diastereomer), 38.24, 39.98, 40.58, 41.65. − IR (film): $\tilde{\nu}$ = 2960 cm^{-1}, 2874 (CH), 1780 (C=O, urethane), 1736 (C=O), 1708 (C=O, amide), 1640 (C=C), 1488, 1462, 1450 (CH_2), 1388, 1372 [$CH(CH_3)_2$], 1262, 1206, 1174 (C−O), 992 (R−CH=CH_2). − UV (CH_3CN): λ_{max} (lg ε) = 207 nm (3.94). − ^{1}H NMR ($CDCl_3$): δ = 0.88 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.93 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.41−1.51 (m, 1 H, 3′-H), 1.60−1.71 (m, 3 H, 3′-H, 4′-H_2), 1.86 (m_c, 2 H, 5′-H_2), 2.38 (dsept, *J* = 7.0, 4.0 Hz, 1 H, *i*Pr-H), 2.41−2.48 (m, 2 H, 1′-H, 2′-H), 3.67 (s, 3 H, OCH_3), 4.24 (dd, *J* = 9.0, 3.0 Hz, 1 H, 5′′-H), 4.29 (dd, *J* = 9.0, 8.5 Hz, 1 H, 5′′-H), 4.50 (ddd, *J* = 8.5, 4.0, 3.0 Hz, 1 H, 4′′-H), 4.69 (d, *J* = 7.0 Hz, 1 H, 2-H), 4.92 (dd, *J* = 10.0, 2.0 Hz, 1 H, 2′′′-H_{cis}), 4.94 (dd, *J* = 17.0, 2.0 Hz, 1 H, 2′′′-H_{trans}), 5.68 (ddd, *J* = 17.0, 10.0, 8.0 Hz, 1 H, 1′′′-H). − ^{13}C NMR ($CDCl_3$): δ = 14.67 (CH_3), 17.97 (CH_3), 23.65 (C-3′), 28.37 (*i*Pr-CH), 29.90 (C-4′), 33.52 (C-5′), 45.60 (C-2′), 48.10 (C-1′), 52.21, 52.71 (OCH_3, C-2), 58.70 (C-4′′), 63.33 (C-5′′), 114.2 (C-2′′′), 141.8 (C-1′′′), 154.0 (C-2′′), 168.2 (C-1), 169.6 (C-3). − MS (70 eV); *m/z* (%): 292 (1) [$M^+ - OCH_3$], 230 (7) [McLafferty peak], 101 (14) [$C_4H_5O_3^+$], 95 (100), 94 (6) [McLafferty peak], 59 (15) [$C_2H_3O_2^+$], 43 (14) [$C_2H_3O^+$, $CHNO^+$]. − $C_{17}H_{25}NO_5$ (323.39): calcd. C 63.14, H 7.79; found C 63.21, H 7.85.

Cyclization to Methyl (1′R,2R,2′S,4′′S)-3-(4′′-tert-Butyl-2′′-oxo-3′′-oxazolidinyl)-3-oxo-2-(2′-vinylcyclopentyl)propionate (**10c**). − *Me_2AlCl:* 410 mg (1.00 mmol) of **8c** was treated with 1.00 ml of Me_2AlCl solution (1 M in hexane, 1.00 mmol) in 12 ml of dichloromethane within 22 d (TLC, diethyl ether/petroleum ether, 1:2) according to *General Procedure III A*. CC (100 g, 63−200 μm, diethyl ether/petroleum ether, 1:2) gave 273 mg of **10c** (81%) as a mixture of diastereomers. − *$SnCl_4$:* 205 mg (0.50 mmol) of **8c** was treated with 0.50 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 0.50 mmol) in 6 ml of dichloromethane within 4 d (TLC, diethyl ether/petroleum ether, 1:2) according to *General Procedure III A*. CC (14 g, 63−200 μm, ethyl acetate/petroleum ether, 1:3) gave 110 mg of **10c** (65%) as a mixture of diastereomers. − *$SnCl_4$:* 205 mg (0.50 mmol) of **8c** was treated with 0.50 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 0.50 mmol) in 3 ml of dichloromethane within 3 d (TLC, diethyl ether/petroleum ether, 1:2) according to *General Procedure III B*. CC (20 g, 63−200 μm, ethyl acetate/petroleum ether, 1:3) gave 113 mg of **10c** (67%) as a mixture of diastereomers.

10c: R_f = 0.13 (diethyl ether/petroleum ether, 1:2). − M.p. 77°C (ethyl acetate/petroleum ether). − $[\alpha]_D^{20}$ = +54.4 (*c* = 0.25, $CHCl_3$). − GC (186°C − 0.1°C/min, system B): t_R = 36.32 min., 38.14 (major diastereomer), 38.96, 39.62, 41.57, 43.04, 43.34, 43.89.

– IR (KBr): $\tilde{\nu}$ = 2958 cm^{-1}, 2874 (CH), 1766 (C=O, urethane), 1706 (C=O, amide), 1640 (C=C), 1488, 1454, 1438 (CH_2), 1478, 1386, 1370 [$C(CH_3)_3$], 1348, 1296, 1218, 1192 (C–O). – UV (CH_3CN): λ_{max} (lg ε) = 202 nm (3.91). – ^1H NMR ($CDCl_3$): δ = 0.98 [s, 9 H, $C(CH_3)_3$], 1.38–1.54 (m, 2 H, 3′-H_2), 1.60–1.76 (m, 2 H, 4′-H_2), 1.80–2.00 (m, 2 H, 5′-H_2), 2.46 (m_c, 2 H, 1′-H, 2′-H), 3.70 (s, 3 H, OCH_3), 4.28 (dd, *J* = 9.0, 7.0 Hz, 1 H, 5′′-H), 4.32 (dd, *J* = 9.0, 2.0 Hz, 1 H, 5′′-H), 4.49 (dd, *J* = 7.0, 2.0 Hz, 1 H, 4′′-H), 4.70 (d, *J* = 7.5 Hz, 1 H, 2-H), 4.96 (dd, *J* = 10.0, 2.0 Hz, 1 H, 2′′′-H_{cis}), 4.98 (dd, *J* = 17.5, 2.0 Hz, 1 H, 2′′′-H_{trans}), 5.72 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1 H, 1′′′-H). – ^{13}C NMR ($CDCl_3$): δ = 23.62 (C-3′)*, 25.66 (CH_3), 29.83 (C-4′)*, 33.52 [$C(CH_3)_3$], 35.57 (C-5′)*, 45.40 (C-2′), 47.93 (C-1′), 52.14 (OCH_3), 52.59 (C-2), 61.32 (C-4′′), 65.25 (C-5′′), 114.1 (C-2′′′), 141.7 (C-1′′′), 154.6 (C-2′′), 168.1 (C-1), 169.6 (C-3). – MS (70 eV); *m/z* (%): 338 (1) [M^+ + H], 306 (1) [M^+ – OCH_3], 243 (23) [McLafferty peak], 212 (34), 163 (56), 144 (99) [oxazolidinone + H], 101 (60) [$C_4H_5O_3^+$], 94 (100) [McLafferty peak], 79 (53), 57 (34) [$C(CH_3)_3$]. – $C_{18}H_{27}NO_5$ (337.41): calcd. C 64.08, H 8.07; found C 64.11, H 8.03.

Cyclization to Methyl (1′R,2R,2′S,4′′S)-3-(4′′-Benzyl-2′′-oxo-3′′-oxazolidinyl)-3-oxo-2-(2′-vinylcyclopentyl)propionate (**10d**). – *Me_2AlCl:* 443 mg (1.00 mmol) of **8d** was treated with 1.00 ml of Me_2AlCl solution (1 M in hexane, 1.00 mmol) in 12 ml of dichloromethane within 10 d (TLC, ethyl acetate/petroleum ether, 1:3) according to *General Procedure III A*. CC (100 g, 63–200 μm, diethyl ether/petroleum ether, 1:2) gave 286 mg of **10d** (77%) as a mixture of diastereomers. – *$SnCl_4$:* 111 mg (0.25 mmol) of **8d** was treated with 0.25 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 0.25 mmol) in 3 ml of dichloromethane within 3 d (TLC, ethyl acetate/petroleum ether, 1:3) according to *General Procedure III A*. CC (14 g, 63–200 μm, ethyl acetate/petroleum ether, 1:3) gave 74 mg of **10d** (80%) as a mixture of diastereomers. – *$ZrCl_4$:* 111 mg (0.25 mmol) of **8d** was treated with 58 mg of $ZrCl_4$ (in 1 ml CH_2Cl_2, 0.25 mmol) in 3 ml of dichloromethane within 4 d (TLC, ethyl acetate/petroleum ether, 1:3) according to *General Procedure III A*. CC (14 g, 63–200 μm, ethyl acetate/petroleum ether, 1:3) gave 72 mg of **10d** (78%) as a mixture of diastereomers. – *$AlCl_3$:* 111 mg (0.25 mmol) of **8d** was treated with 33 mg of $AlCl_3$ (0.25 mmol) in 3 ml of dichloromethane within 4 d (TLC, ethyl acetate/petroleum ether, 1:3) according to *General Procedure III A*. CC (14 g, 63–200 μm, ethyl acetate/petroleum ether, 1:3) gave 70 mg of **10d** (75%) as a mixture of diastereomers. – *$TiCl_4$:* 111 mg (0.25 mmol) of **8d** was treated with 0.25 ml of $TiCl_4$ solution (1 M in CH_2Cl_2, 0.25 mmol) in 3 ml of dichloromethane within 4 d (TLC, ethyl acetate/petroleum ether, 1:3) according to *General Procedure III A*. CC (14 g, 63–200 μm, ethyl acetate/petroleum ether, 1:3) gave 57 mg of **10d** (61%) as a mixture of diastereomers. – *$EtAlCl_2$:* 111 mg (0.25 mmol) of **8d** was treated with 0.14 ml of $EtAlCl_2$ solution (1.8 M in toluene, 0.25 mmol) in 3 ml of dichloromethane within 3 d (TLC, ethyl acetate/petroleum ether, 1:3) according to *General Procedure III A*. CC (14 g, 63–200 μm, ethyl acetate/petroleum ether, 1:3) gave 69 mg of **10d** (74%) as a mixture of diastereomers. – *$SnCl_4$:* 117 mg (0.26 mmol) of **8d** was treated with 0.26 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 0.26 mmol) in 3 ml of dichloromethane within 4 d (TLC, ethyl acetate/petroleum ether, 1:3) according to *General Procedure III B*. CC (10 g, 63–200 μm, diethyl ether/petroleum ether, 1:2) gave 84 mg of **10d** (87%) as a mixture of diastereomers.

10d: R_f = 0.32 (ethyl acetate/petroleum ether, 1:3). – M.p. 120°C (ethyl acetate/petroleum ether). – $[\alpha]_D^{20}$ = +48.0 (*c* = 0.60, $CHCl_3$). – GC (226°C – 0.1°C/min, system B): t_R = 39.26 min, 39.77, 40.83 (major diastereomer), 42.54, 43.93, 44.24, 44.90. – IR (KBr): $\tilde{\nu}$ = 2954 cm^{-1}, 2880 (CH), 1776 (C=O, urethane), 1728 (C=O), 1710 (C=O, amide), 1638 (C=C), 1482, 1452, 1432, 1388 (CH_2), 1348, 1290, 1238, 1198 (C–O), 1004, 924 (R–CH=CH_2), 742, 704 (Ph). – UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4.75), 206 (4.21). – ^1H NMR ($CDCl_3$): δ = 1.37 (m_c, 1 H, 3′-H)*, 1.58 (m_c, 3 H, 5′-H, 4′-H_2)*, 1.81 (m_c, 2 H, 3′-H, 5′-H)*, 2.39 (m_c, 2 H, 1′-H, 2′-H), 2.63 (dd, *J* = 13.5, 10.0 Hz, 1 H, Bzl-H), 3.26 (dd, *J* = 13.5, 3.0 Hz, 1 H, Bzl-H), 3.58 (s, 3 H, OCH_3), 4.06 (dd, *J* = 9.0, 3.0 Hz, 1 H, 5′′-H), 4.12 (dd, *J* = 9.0, 7.5 Hz, 1 H, 5′′-H), 4.59 (d, *J* = 7.5 Hz, 1 H, 2-H), 4.65 (m_c, 1 H, 4′′-H), 4.86 (dd, *J* = 10.0, 2.0 Hz, 1 H, 2′′′-H_{cis}), 4.88 (dd, *J* = 17.5, 2.0 Hz, 1 H, 2′′′-H_{trans}), 5.62 (ddd, *J* = 17.5, 10.0, 8.0 Hz, 1 H, 1′′′-H), 7.10–7.28 (m, 5 H, Ph-H). – ^{13}C NMR ($CDCl_3$): δ = 23.55 (C-4′)*, 29.94 (C-5′)*, 33.43 (C-3′)*, 37.89 (Bzl-CH_2), 45.38 (C-2′), 47.96 (C-1′), 52.11 (OCH_3), 52.80 (C-2), 55.33 (C-4′′), 66.11 (C-5′′), 114.1 (C-2′′′), 127.3 (*o*-Ph-C), 128.9 (*m*-Ph-C), 129.3 (*p*-Ph-C), 135.0 (*ipso*-Ph-C), 141.7 (C-1′′′), 153.2 (C-2′′), 168.1 (C-1), 169.4 (C-3). – MS (70 eV); *m/z* (%): 371 (1) [M^+], 340 (1) [M^+ – OCH_3], 277 (9) [McLafferty peak], 195 (6) [M^+ – oxazolidinone], 178 (16) [oxazolidinone + H], 117 (49) [$C_9H_9^+$], 101 (41) [$C_4H_5O_3^+$], 94 (37) [McLafferty peak], 91 (100) [$C_7H_7^+$], 86 (25) [$C_3H_4NO_2^+$]. – $C_{21}H_{25}NO_5$ (371.44): calcd. C 67.90, H 6.78; found C 67.88, H 6.78.

Methyl (1′R,2S,2′S,4′′S)-3-(4′′-Benzyl-2′′-oxo-3′′-oxazolidinyl)-3-oxo-2-(2′-vinylcyclopentyl)propionate (2-*epi*-**10d**): R_f = 0.33 (ethyl acetate/petroleum ether, 1:3). – $[\alpha]_D^{20}$ = +10.0 (*c* = 1.00, $CHCl_3$). – GC (226°C – 0.1°C/min, system B): t_R = 39.77 min. – IR (film): $\tilde{\nu}$ = 2954 cm^{-1}, 2872 (CH), 1784 (C=O, urethane), 1736 (C=O), 1706 (C=O, amide), 1640 (C=C), 1480, 1452, 1436, 1388 (CH_2), 1286, 1212, 1202 (C–O), 1006, 914 (R–CH=CH_2), 750, 704 (Ph). – ^1H NMR ($CDCl_3$): δ = 1.44 (m_c, 2 H, 3′-H_2), 1.67 (m_c, 2 H, 4′-H_2), 1.89 (m_c, 1 H, 5′-H), 2.13 (m_c, 1 H, 5′-H), 2.34 (m_c, 2 H, 1′-H), 2.51 (br. quint, *J* = 9.0 Hz, 1 H, 2′-H), 2.80 (dd, *J* = 13.5, 10.0 Hz, 1 H, Bzl-H), 3.36 (dd, *J* = 13.5, 3.5 Hz, 1 H, Bzl-H), 3.78 (s, 3 H, OCH_3), 4.15–4.25 (m, 2 H, 5′′-H_2), 4.65 (dddd, *J* = 10.0, 8.0, 3.5, 3.5 Hz, 1 H, 4′′-H), 4.71 (d, *J* = 6.0 Hz, 1 H, 2-H), 4.94 (dd, *J* = 10.0, 2.0 Hz, 1 H, 2′′′-H_{cis}), 5.05 (dd, *J* = 17.0, 2.0 Hz, 1 H, 2′′′-H_{trans}), 5.66 (ddd, *J* = 17.0, 10.0, 9.0 Hz, 1 H, 1′′′-H), 7.23–7.40 (m, 5 H, Ph-H). – ^{13}C NMR ($CDCl_3$): δ = 23.24 (C-3′), 29.91 (C-4′), 32.87 (C-5′), 37.22 (Bzl-CH_2), 44.85 (C-2′), 48.60 (C-1′), 52.10 (OCH_3), 52.37 (C-2), 55.22 (C-4′′), 66.01 (C-5′′), 114.3 (C-2′′′), 127.2 (*o*-Ph-C), 128.8 (*m*-Ph-C), 129.4 (*p*-Ph-C), 135.1 (*ipso*-Ph-C), 142.1 (C-1′′′), 153.3 (C-2′′), 168.6 (C-1), 169.1 (C-3). – MS (70 eV); *m/z* (%): 371 (7) [M^+], 340 (3) [M^+ – OCH_3], 277 (33) [McLafferty peak], 195 (10) [M^+ – oxazolidinone], 178 (22) [oxazolidinone + H], 117 (22) [$C_9H_9^+$], 101 (100) [$C_4H_5O_3^+$], 94 (20) [McLafferty peak], 91 (47) [$C_7H_7^+$], 86 (6) [$C_3H_4NO_2^+$], 59 (44) [$C_2H_3O_2^+$], 43 (85) [$C_2H_3O^+$, $CHNO^+$]. – $C_{21}H_{25}NO_5$ (371.44): calcd. C 67.90, H 6.78; found C 67.75, H 6.85.

Methyl (2E,4′′S)-2-[(4′′-Benzyl-2′′-oxo-3′′-oxazolidinyl)carbonyl]-2,8-nonadienoate (**13d**). – *TMSOTf:* The reaction of 111 mg (0.25 mmol) of **8d** with 45 μl of TMSOTf (0.25 mmol) in 3 ml of dichloromethane according to *General Procedure III A* led after CC (14 g, 63–200 μm, ethyl acetate/petroleum ether, 1:3) to 63 mg of the protodesilylated product **13d** (68%). R_f = 0.31 (ethyl acetate/petroleum ether, 1:2). – $[\alpha]_D^{20}$ = +53.3 (*c* = 0.52, $CHCl_3$). – IR (film): $\tilde{\nu}$ = 2976 cm^{-1}, 2930, 2860 (CH), 1788 (C=O, urethane), 1716 (C=O), 1692 (C=O, amide), 1644 (C=C), 1452, 1438, 1380 (CH_2), 1326, 1270, 1214 (C–O), 980, 914 (R–CH=CH_2), 762, 704 (Ph). – UV (CH_3CN): λ_{max} (lg ε) = 191 nm (4.79), 208 (4.36). – ^1H NMR ($CDCl_3$): δ = 1.37–1.62 (m, 4 H, 5-H_2, 7-H_2), 2.06 (q, *J* = 7.0 Hz, 2 H, 6-H_2), 2.27 (q, *J* = 7.5 Hz, 2 H, 4-H_2), 2.78 (dd, *J* = 13.5, 10.0 Hz, 1 H, Bzl-H), 3.48 (ddd, *J* = 13.5, 3.5, 1.5 Hz,

1 H, Bzl-H), 3.78 (s, 3 H, OCH_3), 4.19 (dd, J = 9.0, 3.5 Hz, 1 H, 5′′-H), 4.25 (dd, J = 9.0, 7.0 Hz, 1 H, 5′′-H), 4.77 (dddd, J = 10.0, 7.0, 3.5, 3.5 Hz, 1 H, 4′′-H), 4.95 [ddt, J = 10.0, 2.0, 1.0 Hz, 1 H, (*Z*)-9-H], 5.00 [ddt, J = 17.0, 2.0, 1.5 Hz, 1 H, (*E*)-9-H], 5.79 (ddd, J = 17.0, 10.0, 7.0 Hz, 1 H, 8-H), 7.06 (t, J = 8.0 Hz, 1 H, 3-H), 7.22−7.41 (m, 5 H, Ph-H). − ^{13}C NMR ($CDCl_3$): δ = 27.69, 28.39, 29.53, 33.37 (C-4, C-5, C-6, C-7), 37.67 (Bzl-CH_2), 52.26 (OCH_3), 55.01 (C-4′′), 66.47 (C-5′′), 114.7 (C-9), 127.4 (*p*-Ph-C), 129.0 (*m*-Ph-C), 129.4 (*o*-Ph-C), 129.7 (C-2), 135.1 (*ipso*-Ph-C), 138.3 (C-8), 148.4 (C-3), 152.7 (C-2′′), 163.8 (C-1), 164.8 (C-1′). − MS (70 eV); *m/z* (%): 371 (1) [M^+], 340 (2) [$M^+ - OCH_3$], 330 (1) [$M^+ - C_3H_5$], 312 (3) [$M^+ - C_2H_3O_2$], 303 (2) [McLafferty peak], 195 (15) [M^+ − oxazolidinone], 178 (8) [oxazolidinone + H], 117 (50) [$C_9H_9^+$], 91 (100) [$C_7H_7^+$], 86 (11) [$C_3H_4NO_2^+$], 68 (30) [McLafferty peak], 59 (40) [$C_2H_3O_2^+$]. − $C_{21}H_{25}NO_5$ (371.44): calcd. C 67.90, H 6.78; found C 68.11, H 6.80.

Cyclization to Methyl (1′R,2R,2′S,4′′S)-3-(4′′-Benzyl-2′′-oxo-3′′-oxazolidinyl)-3-oxo-2-(2′-vinylcyclohexyl)propionate (**11d**). − *$SnCl_4$:* 200 mg (0.44 mmol) of **9d** was treated with 0.44 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 0.44 mmol) in 10 ml of dichloromethane within 6 d (TLC, ethyl acetate/petroleum ether, 1:4) according to *General Procedure III A*. CC (30 g, 63−200 μm, ethyl acetate/petroleum ether, 1:4) gave 136 mg of **11d** (80%) as a mixture of diastereomers. − *$SnCl_4$:* 1.50 g (3.28 mmol) of **9d** was treated with 3.28 ml of $SnCl_4$ solution (1 M in CH_2Cl_2, 3.28 mmol) in 60 ml of dichloromethane within 2 d (TLC, ethyl acetate/petroleum ether, 1:4) according to *General Procedure III B*. CC (150 g, 63−200 μm, ethyl acetate/petroleum ether, 1:4) gave 1.11 g of **11d** (88%) as a mixture of diastereomers.

11d: R_f = 0.28 (ethyl acetate/petroleum ether, 1:4). − M.p. 139°C (ethyl acetate/petroleum ether). − $[\alpha]_D^{20}$ = +48.0 (c = 0.40, $CHCl_3$). − GC (150°C − 5.0°C/min, system B): t_R = 33.18 min (major diastereomer), 33.63. − IR (KBr): $\tilde{\nu}$ = 2944 cm^{-1}, 2860 (CH), 1778 (C=O, urethane), 1730 (C=O), 1710 (C=O, amide), 1638 (C=C), 1486, 1450, 1434, 1388 (CH_2), 1282, 1252, 1212 (C−O), 1000, 924 (R−CH=CH_2), 740, 704 (Ph). − UV (CH_3CN): λ_{max} (lg ε) = 206 nm (4.23), 258 (2.43). − ^{1}H NMR ($CDCl_3$): δ = 1.18−1.29 (m, 2 H, 3′-H_2), 1.32−1.42 (m, 1 H, 4′-H)*, 1.54 (m_c, 1 H, 5′-H)*, 1.69−1.82 (m, 3 H, 4′-H, 5′-H, 6′-H)* 1.91 (dq, J = 12.0, 3.5 Hz, 1 H, 6′-H), 2.02 (dddd, J = 12.0, 10.0, 5.0, 3.0 Hz, 1 H, 1′-H), 2.30 (dddd, J = 11.0, 10.5, 10.0, 3.0 Hz, 1 H, 2′-H), 2.60 (dd, J = 13.0, 10.0 Hz, 1 H, Bzl-H), 3.42 (dd, J = 13.0, 3.0 Hz, 1 H, Bzl-H), 3.70 (s, 3 H, OCH_3), 4.12 (dd, J = 8.5, 3.0 Hz, 1 H, 5′′-H), 4.18 (dd, J = 10.0, 8.5 Hz, 1 H, 5′′-H), 4.73 (m_c, 1 H, 4′′-H), 4.76 (d, J = 5.0 Hz, 1 H, 2-H), 4.95 (dd, J = 15.5, 2.0 Hz, 1 H, 2′′′-H_{trans}), 4.96 (dd, J = 10.0, 2.0 Hz, 1 H, 2′′′-H_{cis}), 5.65 (ddd, J = 15.5, 11.0, 10.0 Hz, 1 H, 1′′′-H), 7.22−7.36 (m, 5-H, Ph-H). − ^{13}C NMR ($CDCl_3$): δ = 25.50, 26.45, 27.68 (C-3′, C-4′, C-5′), 33.85 (C-6′), 38.03 (Bzl-CH_2), 43.59 (C-1′), 45.74 (C-2′), 52.36 (OCH_3), 53.12 (C-2), 55.16 (C-4′′), 66.03 (C-5′′), 114.8 (C-2′′′), 127.3 (*p*-Ph-C), 128.9 (*m*-Ph-C), 129.3 (*o*-Ph-C), 135.2 (*ipso*-Ph-C), 142.5 (C-1′′′), 153.4 (C-2′′), 167.8, 170.3 (C-1, C-3). − MS (70 eV); *m/z* (%): 385 (40) [M^+], 354 (4) [$M^+ - OCH_3$], 278 (100), 277 (54) [McLafferty peak], 209 (26) [M^+ − oxazolidinone], 177 (54) [oxazolidinone], 117 (23) [$C_9H_9^+$], 108 (22) [McLafferty peak], 101 (17) [$C_4H_5O_3^+$], 91 (24) [$C_7H_7^+$], 86 (7) [$C_3H_4NO_2^+$]. − $C_{22}H_{27}NO_5$ (385.46): calcd. C 68.55, H 7.06; found C 68.69, H 7.07.

Removal of the Chiral Auxiliary; Reduction to Monoalcohol Derivatives. − General Procedure IV: The carbocyclic derivative **10d** or **11d** (1.08 mmol) was dissolved in anhydrous THF (30 ml) in a flame-dried flask and the stirred solution was cooled to −78°C under argon. To this was added a $LiAlH_4$ solution (2.15 ml, 1 M in THF, 2.15 mmol, 2 equiv.) and stirring was continued at this temperature until completion of the reaction (TLC, 2−4 h). The mixture was then hydrolysed at the given temperature by the addition of water (15 ml) and 2 N HCl solution (10 ml) and warming to room temp. over a period of 15 min. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 50 ml) and dichloromethane (1 × 50 ml). The combined organic phases were washed (brine, 40 ml), dried (Na_2SO_4), and the solvent was carefully evaporated. The residue was purified by column chromatography on silica gel.

Methyl (1′R,2R,2′S)-3-Hydroxy-2-(2′-vinylcyclopentyl)propionate (**14**): According to *General Procedure IV*, **10d** (400 mg, 1.08 mmol) in 30 ml of THF was treated with 2.15 ml of $LiAlH_4$ solution (1 M in THF, 2.15 mmol, 2 equiv.) within 4 h. After purification (CC, 50 g, 63−200 μm, diethyl ether/petroleum ether, 1:2) 186 mg of **14** (87%) was obtained. R_f = 0.20 (diethyl ether/petroleum ether, 1:2). − $[\alpha]_D^{20}$ = +10.0 (c = 0.40, $CHCl_3$). − GC (150°C − 5.0°C/min, system A): t_R = 6.79 min. − IR (film): $\tilde{\nu}$ = 3448 cm^{-1}, 3434 (OH), 2952, 2872 (CH), 1736 (C=O), 1640 (C=C), 1436, 1368, 1320 (CH_2), 1262 (OH), 1198 (C−O), 1042 (C−OH). − ^{1}H NMR ($CDCl_3$): δ = 1.35 (m_c, 2 H, 3′-H_2), 1.57 (m_c, 2 H, 4′-H_2), 1.81 (m_c, 2 H, 5′-H_2), 1.91 (br. quint, J = 9.0 Hz, 1 H, 2′-H), 2.21 (br. quint, J = 9.0 Hz, 1 H, 1′-H), 2.28 (br. s, 1 H, OH), 2.46 (ddd, J = 8.0, 8.0, 4.0 Hz, 1 H, 2-H), 3.61 (s, 3 H, OCH_3), 3.70 (dd, J = 11.0, 4.0 Hz, 1 H, 3-H), 3.77 (dd, J = 11.0, 8.0 Hz, 1 H, 3-H), 4.87 (dd, J = 10.0, 2.0 Hz, 1 H, 2′′-H_{cis}), 4.92 (ddd, J = 17.5, 2.0, 1.0 Hz, 1 H, 2′′-H_{trans}), 5.56 (ddd, J = 17.5, 10.0, 9.0 Hz, 1 H, 1′′-H). − ^{13}C NMR ($CDCl_3$): δ = 23.30, 30.06, 33.18 (C-3′, C-4′, C-5′), 44.40 (C-2′), 48.60 (C-1′), 50.99, 51.07 (OCH_3, C-2), 62.09 (C-3), 113.7 (C-2′′), 141.8 (C-1′′), 175.3 (C-1). − MS (70 eV); *m/z* (%): 199 (1) [M^+], 180 (11) [$M^+ - H_2O$], 168 (20) [$M^+ - OCH_3$], 104 (100) [$C_4H_8O_3$, McLafferty peak], 59 (8) [$C_2H_3O_2^+$]. − $C_{11}H_{18}O_3$ (198.26): calcd. 198.1255; found 198.1255 (MS).

Methyl (1′R,2R,2′S)-3-Hydroxy-2-(2′-vinylcyclohexyl)propionate (**15**): According to *General Procedure IV*, **11d** (394 mg, 1.02 mmol) in 30 ml of THF was treated with 2.04 ml of $LiAlH_4$ solution (1 M in THF, 2.04 mmol, 2 equiv.) within 3 h. After purification (CC, 50 g, 63−200 μm, diethyl ether/petroleum ether, 1:2) 178 mg of **15** (82%) was obtained. R_f = 0.17 (diethyl ether/petroleum ether, 1:2). − $[\alpha]_D^{20}$ = +10.0 (c = 0.50, $CHCl_3$). − GC (50°C − 5.0°C/min, system B): t_R = 25.71 min. − IR (film): $\tilde{\nu}$ = 3438 cm^{-1}, 3076 (OH), 2926, 2854 (CH), 1730 (C=O), 1640 (C=C), 1448, 1376, 1344, 1310 (CH_2), 1242 (OH), 1192 (C−O), 1036 (C−OH). − ^{1}H NMR ($CDCl_3$): δ = 0.75−0.92 (m, 1 H, 6′-H)*, 1.00−1.30 (m, 5 H, 6′-H, 5′-H_2, 4′-H_2)*, 1.55 (m_c, 1 H, 2′-H)*, 1.60−1.82 (m, 2 H, 3′-H_2)*, 1.82−1.97 (m, 1 H, 1′-H)*, 2.32 (br. s, 1 H, OH), 2.83 (ddd, J = 9.0, 4.0, 4.0 Hz, 1 H, 2-H), 3.60−3.74 (m, 1 H, 3-H), 3.72 (s, 3 H, OCH_3), 3.83−3.97 (m_c, 1 H, 3-H), 5.02 (dd, J = 10.0, 2.0 Hz, 1 H, 2′′-H_{cis}), 5.07 (dd, J = 17.5, 2.0 Hz, 1 H, 2′′-H_{trans}), 5.63 (ddd, J = 17.5, 10.0, 9.0 Hz, 1 H, 1′′-H). − ^{13}C NMR ($CDCl_3$): δ = 25.75, 26.41, 27.99, 34.06 (C-3′, C-4′, C-5′, C-6′), 42.37 (C-2′), 45.80 (C-1′), 49.41, 51.75 (OCH_3, C-2), 58.91 (C-3), 115.2 (C-2′′), 142.1 (C-1′′), 176.0 (C-1). − MS (70 eV); *m/z* (%): 212 (29) [M^+], 195 (10) [$M^+ - OH$], 194 (100) [$M^+ - H_2O$], 184 (13) [$M^+ - CO$], 182 (50) [$M^+ - CH_2O$], 181 (31) [$M^+ - OCH_3$], 180 (51) [$M^+ - OCH_4$], 134 (75), 109 (16) [C_8H_{13}, McLafferty peak], 104 (62) [$C_4H_8O_3$, McLafferty peak], 73 (55) [$C_3H_5O_2^+$], 59 (5) [$C_2H_3O_2^+$]. − $C_{12}H_{20}O_3$ (212.29): calcd. C 67.89, H 9.50; found C 67.73, H 9.48; calcd. 212.1412; found 212.1412 (MS).

Removal of the Chiral Auxiliary; Reduction to Diols. – General Procedure V: **10d** or **11d** (0.52 mmol) was dissolved in anhydrous THF (20 ml) in a flame-dried flask and the stirred solution was cooled to 0°C under argon. To this was added an $LiAlH_4$ solution (2.08 ml, 1 M in THF, 2.08 mmol, 4 equiv.) and stirring was continued at this temperature until completion of the reaction (TLC, 20 h). The mixture was then hydrolysed at the given temperature by the addition of water (10 ml) and 2 N HCl solution (7 ml) and warming to room temp. over a period of 10 min. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 30 ml) and ethyl acetate (1 × 30 ml). The combined organic phases were washed (brine, 30 ml), dried (Na_2SO_4), and the solvent was carefully evaporated. The residue was purified by column chromatography on silica gel.

(1′R,2′S)-2-(2′-Vinylcyclopentyl)propane-1,3-diol (**16**): According to *General Procedure V*, **10d** (193 mg, 0.52 mmol) in 20 ml of THF was treated with 2.08 ml of $LiAlH_4$ solution (1 M in THF, 2.08 mmol, 4 equiv.) within 23 h. After purification (CC, 40 g, 63–200 μm, diethyl ether/petroleum ether, 3:1) 81 mg of **16** (92%) was obtained. R_f = 0.33 (ethyl acetate/petroleum ether, 4:1). – $[\alpha]_D^{20}$ = –27.7 (*c* = 1.00, $CHCl_3$). – IR (film): $\tilde{\nu}$ = 3346 cm^{-1}, 3076 (OH), 2950, 2874 (CH), 1640 (C=C), 1468, 1450, 1422 (CH_2), 1262 (OH), 1058, 1028 (C–OH), 908 (R–CH=CH_2). – ^{1}H NMR ($CDCl_3$): δ = 1.15–1.94 (m, 8 H, 1′-H, 2′-H, 3′-H_2, 4′-H_2, 5′-H_2), 2.27 (br. quint, *J* = 8.5 Hz, 1 H, 2-H), 2.55 (br. s, 1 H, OH), 2.70 (br. s, 1 H, OH), 3.74 (dd, *J* = 11.0, 7.0 Hz, 2 H, 1-H_2)*, 3.86 (dd, *J* = 11.0, 4.0 Hz, 2 H, 3-H_2)*, 4.96 (dd, *J* = 10.0, 2.0 Hz, 1 H, 2′′-H_{cis}), 5.04 (ddd, *J* = 17.5, 2.0, 1.0 Hz, 1 H, 2′′-H_{trans}), 5.76 (ddd, *J* = 17.5, 10.0, 9.0 Hz, 1 H, 1′′-H). – ^{13}C NMR ($CDCl_3$): δ = 24.31, 30.21, 33.64 (C-3′, C-4′, C-5′), 43.91 (C-2′), 45.58 (C-1′), 48.25 (C-2), 64.95, 65.58 (C-1, C-3), 113.5 (C-2′′), 143.7 (C-1′′). – MS (70 eV); *m/z* (%): 152 (2) [M^+ – H_2O], 137 (2) [M^+ – CH_5O], 134 (6) [M^+ – 2 H_2O], 121 (71), 108 (31) [M^+ – 2 OCH_3], 95 (81), 94 (100) [M^+ – $C_3H_8O_2$, McLafferty peak]. – $C_{10}H_{18}O_2$ (170.25).

(1′R,2′S)-2-(2′-Vinylcyclohexyl)propane-1,3-diol (**17**): According to *General Procedure V*, **11d** (200 mg, 0.52 mmol) in 20 ml of THF was treated with 2.08 ml of $LiAlH_4$ solution (1 M in THF, 2.08 mmol, 4 equiv.) within 19 h. After purification (CC, 40 g, 63–200 μm, diethyl ether/petroleum ether, 3:1), 81 mg of **17** (84%) was obtained. R_f = 0.32 (ethyl acetate/petroleum ether, 4:1). – M.p. 57°C (ethyl acetate/petroleum ether). – $[\alpha]_D^{20}$ = –35.5 (*c* = 1.00, $CHCl_3$). – IR (film): $\tilde{\nu}$ = 3278 cm^{-1}, 3084 (OH), 2934, 2876, 2852 (CH), 1640 (C=C), 1446, 1376, 1322 (CH_2), 1068, 1034 (C–OH). – ^{1}H NMR ($CDCl_3$): δ = 1.07–1.34 (m, 6 H, 3′-H_2, 4′-H_2, 5′-H_2)*, 1.54–1.76 (m, 3 H, 1′-H, 6′-H_2), 1.91 (m_c, 1 H, 2′-H), 2.08 (m_c, 1 H, 2-H), 2.44 (br. s, 2 H, OH), 3.70 (m_c, 2 H, 1-H_2)*, 3.86 (m_c, 2 H, 3-H_2)*, 4.99 (dd, *J* = 10.0, 2.0 Hz, 1 H, 2′′-H_{cis}), 5.03 (dd, *J* = 17.5, 2.0 Hz, 1 H, 2′′-H_{trans}), 5.62 (ddd, *J* = 17.5, 10.0, 9.0 Hz, 1 H, 1′′-H). – ^{13}C NMR ($CDCl_3$): δ = 25.84, 26.52, 27.36, 34.27 (C-3′, C-4′, C-5′, C-6′), 42.52 (C-2′), 43.79 (C-1′), 45.96 (C-2), 63.68, 67.15 (C-1, C-3), 114.5 (C-2′′), 143.2 (C-1′′). – MS (70 eV); *m/z* (%): 184 (1) [M^+], 166 (20) [M^+ – H_2O], 148 (25) [M^+ – 2 H_2O], 135 (85), 122 (70) [M^+ – 2 OCH_3], 109 (95) [C_8H_{13}, McLafferty peak], 81 (90), 79 (95), 67 (100), 55 (84) [$C_3H_3O^+$]. – $C_{11}H_{20}O_2$ (184.28): calcd. C 71.70, H 10.94; found C 71.82, H 10.86.

Removal of the Chiral Auxiliary by the Krapcho Reaction: The cyclopentane derivative **10d** (275 mg, 0.74 mmol) was dissolved in DMSO (4 ml) under argon in a pressure flask. Water (15 μl) and lithium iodide (132 mg, 0.99 mmol) were added and the mixture was heated under exclusion of light to 145°C and stirred at this temp. for 1.5 h. Afterwards, the mixture was cooled to room temp. within 10 min. Purification by column chromatography on silica gel (CC, 40 g, 63–200 μm, ethyl acetate/petroleum ether, 1:7) yielded 58 mg of the desired product **18** (47%), 49 mg of the starting material **10d** (18%), and 68 mg of the isomerized material 2-*epi*-**10d** (25%).

Methyl (1′R,2′S)-(2′-Vinylcyclopentyl)acetate (**18**): R_f = 0.50 (ethyl acetate/petroleum ether, 1:7). – $[\alpha]_D^{20}$ = –15.7 (*c* = 1.00, $CHCl_3$). – IR (film): $\tilde{\nu}$ = 2952 cm^{-1}, 2926, 2864 (CH), 1742 (C=O), 1640 (C=C), 1436 (CH_2), 1254, 1198 (C–O), 998 (R–CH=CH_2). – ^{1}H NMR ($CDCl_3$): δ = 1.15–1.32 (m, 2 H, 4′-H_2), 1.62 (m_c, 2 H, 3′-H_2), 1.76–2.05 (m, 4 H, 1′-H, 2′-H, 5′-H_2), 2.10 (dd, *J* = 15.0, 9.0 Hz, 1 H, 2-H), 2.46 (dd, *J* = 15.0, 5.0 Hz, 1 H, 2-H), 3.61 (s, 3 H, OCH_3), 4.93 (dd, *J* = 10.0, 2.0 Hz, 1 H, 2′′-H_{cis}), 4.96 (dd, *J* = 17.5, 2.0 Hz, 1 H, 2′′-H_{trans}), 5.64 (ddd, *J* = 17.5, 10.0, 9.0 Hz, 1 H, 1′′-H). – ^{13}C NMR ($CDCl_3$): δ = 23.35 (C-3′), 29.68 (C-4′), 32.00 (C-5′), 38.37 (C-2), 42.35 (C-2′), 51.08 (C-1′), 51.30 (OCH_3), 114.4 (C-2′′), 141.8 (C-1′′), 173.8 (C-1). – MS (70 eV); *m/z* (%): 168 (9) [M^+], 153 (3) [M^+ – CH_3], 137 (27) [M^+ – OCH_3], 136 (29) [M^+ – OCH_4], 108 (100) [M^+ – $C_2H_4O_2$], 95 (83) [C_7H_{11}], 94 (99) [M^+ – $C_3H_6O_2$, McLafferty peak]. – $C_{10}H_{16}O_2$ (168.24): calcd. C 71.39, H 9.59; found C 71.47, H 9.68.

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