Desymmetrization of prochiral anhydrides with Evans' oxazolidinones: an efficient route to homochiral glutaric and adipic acid derivatives

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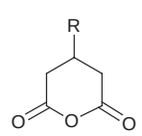
The prochiral recognition between enantiotopic carbonyl groups in the reaction of 3-substituted glutaric and 3,4-disubstituted adipic anhydrides with anions of Evans' oxazolidinones has been investigated. Each of the σ-symmetric anhydrides provided a diastereoisomeric mixture of half-acids which were separated either by fractional crystallization or by column chromatography of their esters. The diastereoselectivity of the desymmetrization reaction is dependent on the substituents present in the anhydrides.

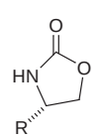
Introduction

Enantio- or diastereo-selective differentiation of prochiral functional groups in a symmetrical bifunctional molecule[1] has always been a challenge to chemists. An important prochiral intermediate, *viz*. a σ-symmetric dicarboxylic anhydride can provide strategically located chiral centre(s) by such transformations. Most of the known methods using various chiral reagents[2–4] have displayed high diastereoselectivities when bi- and tri-cyclic 2,3-disubstituted *meso*-dicarboxylic anhydrides were used. Among these, only a few reagents[3] have been tested on 3-substituted glutaric anhydrides resulting in varying selectivity. The disadvantage of these methods is that the diastereoisomeric acids and their derivatives were generally inseparable. Moreover, in most of the cases, the chiral reagents were prepared in multistep reactions and also were not recoverable due to destruction by further chemical transformations.

During the course of our synthesis of (+)-preussin[5] (see the following paper), we were in need of a suitable method for desymmetrization of the prochiral 3-[dimethyl(phenyl)silyl]-glutaric anhydride (**1a**). Initially, we attempted the desym-



1a; R = $PhMe_2Si$
1b; R = t-$BuMe_2SiO$
1c; R = Ph
1d; R = i-Pr



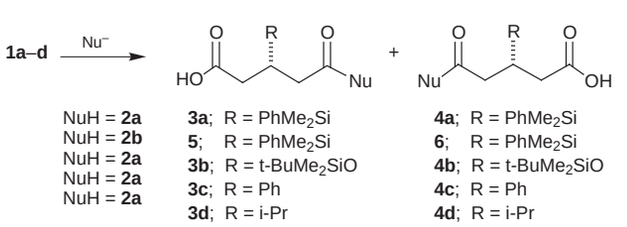
2a; R = Bn
2b; R = i-Pr

metrization with several chiral reagents, but none were found suitable including Heathcock's 1-(1′-naphthyl)ethanol.[4b,c] The selectivities were moderate to poor and the diastereoisomeric half-acids or their esters were also not separable. To overcome this problem, we introduced a method for desymmetrization of the prochiral anhydride **1a** using the lithium salt of Evans' oxazolidinone **2a**. We wish to report here a general method for desymmetrisation of 3-substituted glutaric and 3,4-bis-substituted adipic acid anhydrides using Evans' oxazolidinones. Although these have been widely used as a key stereodirecting group in the introduction of chirality in many organic reactions,[6] to the best of our knowledge, the present work forms the first example of its application for the desymmetrization of σ-symmetric anhydrides. Thus, the reaction of **1a** with the lithium salt of **2a** (Scheme 1) provided a mixture of diastereoisomeric acids **3a** and **4a** in a ratio of *ca*. 67:33 (ascertained as their methyl esters by NMR spectroscopy).

Table 1 Diastereoselectivities during opening up anhydride **1a** with the anions of **2a** and **2b**

Oxazolidone	Reaction conditions[a]	Diastereoisomer ratio[b] (**3a** or **5**:**4a** or **6**)
2a	THF, room temp., 24 h	67:33
2a	THF, 5 equiv. DMPU, room temp., 15 min	63:37
2a	THF, 5 equiv. DMPU, −78 °C, 1 h	65:35
2b	THF, room temp., 24 h	63:37
2b	THF, 5 equiv. DMPU, 10 °C, 0.5 h	65:35
2b	THF, 5 equiv. DMPU, −78 °C, 1 h	62:38
2b	THF, 1 equiv. $MgBr_2$, room temp., 20 h	50:50

[a] Deprotonation of **2a** and **2b** was done with BuLi at −40 °C. [b] The diastereoisomer ratios were ascertained from the NMR spectra of the methyl esters of the crude reaction mixtures.



NuH = **2a** **3a**; R = $PhMe_2Si$ **4a**; R = $PhMe_2Si$
NuH = **2b** **5**; R = $PhMe_2Si$ **6**; R = $PhMe_2Si$
NuH = **2a** **3b**; R = t-$BuMe_2SiO$ **4b**; R = t-$BuMe_2SiO$
NuH = **2a** **3c**; R = Ph **4c**; R = Ph
NuH = **2a** **3d**; R = i-Pr **4d**; R = i-Pr

Scheme 1

Results and discussion

To improve the diastereoselectivity, we carried out many experiments under varying conditions (Table 1) with the anions of oxazolidinones **2a** and **2b**, but, with little success. When lithium ion was replaced with magnesium, the selectivity was totally lost. Similarly, steric bulk on the oxazolidinone (benzyl *vs*. isopropyl) also had little effect. However, the presence of 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU) even in small quantities drastically increased the rate of the reaction without much change in stereoselectivites. Although the selectivity was not very high, the acids **3a** (mp 100–101 °C) and **4a** (mp 160–162 °C) were separable by fractional crystallization. The Me, Bn and *t*-Bu esters were also easily separable by ordinary column chromatography in a preparative scale. The

Table 2 Diastereoselectivities during opening up anhydride **1b**–**1d** and **7** with the anion of **2a**

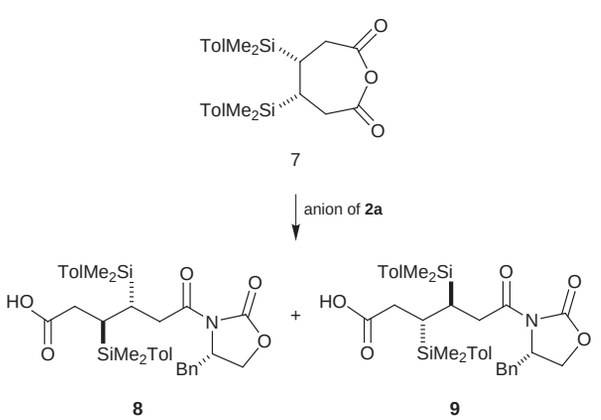
Anhydride	Reaction conditions	Diastereoisomer ratio[c] (**3b**–**d**) or **8**: (**4b**–**d**) or **9**
1b	THF, 5 equiv. DMPU, −78 °C, 1 h[a]	65:35[d]
1c	THF, 5 equiv. DMPU, −78 °C, 1 h[a]	36:64
1c	THF, 2 equiv. DMPU, −50 °C, 15 h[b]	40:60
1c	THF, 0 °C, 3 h[b]	40:60
1c	CH_2Cl_2, 2 equiv. DMAP, −40 °C, 15 h[b]	47:53
1d	THF, 5 equiv. DMPU, −78 °C, 1 h[a]	40:60
1d	THF, 2 equiv. DMAP, −50 °C, 15 h[a]	47:53
7	THF, −45 °C, 3 d[a]	65:35[e]
7	THF, 5 equiv. DMPU, −78 °C, 1 h[a]	50:50
7	THF, −78 °C to room temp., 3 h[a]	65:35
7	THF, DMAP, −45 °C, 45 h[a]	50:50
7	THF, DMAP, room temp., 15 h[b]	55:45

[a] Deprotonation of **2a** was done with BuLi at −40 °C. [b] Deprotonation of **2a** was done with EtMgBr at 0 °C. [c] The crude products were esterified with diazomethane and the diastereoisomer ratios were ascertained by NMR. [d] Diastereoisomer ratio determined from SiBu^t and SiMe peaks. [e] Diastereoisomer ratio determined from TolMe and SiMe peaks.

chromatographic procedure was found to be much easier and faster than the fractional crystallization, and hence we adopted the former for the present purpose.

We were not convinced at this stage whether the dimethyl(phenyl)silyl ($PhMe_2Si$) substitution in **1a** is responsible for this observed stereoselectivity. Theisen and Heathcock[4c] have recently studied the effect of the bulkiness of the group in 3-substituted glutaric anhydrides on opening with 1-(1′-naphthyl)ethanol and concluded that the degree of prochiral recognition (diastereoselectivity) is inversely related to the steric bulk of the stereodifferentiating group. The diastereoselectivity was very high when the substituent was OTBDMS but decreased with increasing steric bulk *e.g.* *t*-Bu < *i*-Pr < Ph < Et < Me. Suda *et. al.*[3g] have observed that the chiral alcoholysis of 3-substituted glutaric anhydrides with 1-phenyl-3,3-bis(trifluoromethyl)propane-1,3-diol proceeded with moderate to high diastereoselectivity depending on the size of the 3-substituents. They concluded that with a more sterically bulky substituent, the chiral induction was higher.

We were obviously interested to know which of the above mentioned propositions is operative and also the effect of anhydride ring size on the desymmetrization selectivity. For this, the various σ-symmetric 3-substituted glutaric anhydrides **1b**–**1d** and *meso* 3,4-bis-silyl-substituted adipic anhydride **7** were treated with **2a** under the conditions (Schemes 1,2)



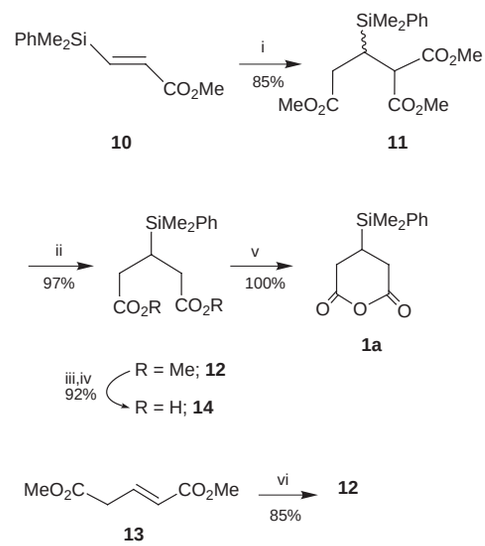
Scheme 2

described in Table 2. The anhydrides were selected so that their products could be useful as key intermediates in the synthesis of various natural products, *e.g.* **1b** for compactin and its analogs[4,7] and **7** for nonactin.[8] It was observed that in all the cases the stereoselectivities were not very high and the diastereoisomer ratios lay in the range of 60–70:40–30. Again, the Me, Bn and *t*-Bu esters of the diastereoisomeric acids were easily separable by ordinary column chromatography. The benzyl esters of **3c** (mp 118–119 °C) and **4c** (mp 113–114 °C) were also separable by fractional crystallization.

The results from the table clearly indicate that the diastereofacial selectivity of the opening of anhydrides **1a**–**1d** and **7** was dependent on the substituents on the anhydrides. The C–Si and C–OSi substitutions (**1a**,**b** and **7**) showed preferences for same diastereofacial selectivity. On the contrary, the C-aryl and C-alkyl substituted anhydrides, **1c** and **1d** displayed diastereofacial selectivity opposite to those of **1a** and **1b** or **7**.

Preparation of anhydrides 1a–1d, 7

The $PhMe_2Si$ substituted anhydride **1a** was obtained in a few steps from β-silyl acrylate **10**[9] as shown in Scheme 3.

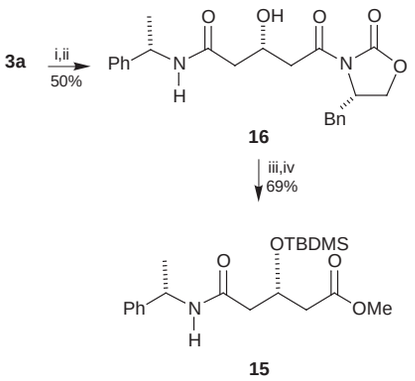


Scheme 3 *Reagents*: i, $NaCH(CO_2Me)_2$, MeOH; ii, NaCl, H_2O, DMSO; iii, NaOH; iv, H_3O^+; v, Ac_2O; vi, $(PhMe_2Si)_2CuLi$.

Dimethyl malonate addition on this gave the triester **11** which on Krapcho decarboxylation[10] provided the diester **12**.[11] The latter was also obtained in one step from the known unsaturated diester **13**[12] by a silylcupration reaction.[13] The anhydride **1a** was subsequently obtained from **12** by a simple hydrolysis to diacid **14** and subsequent treatment with acetic anhydride in quantitative yield. The anhydrides **1b**–**d**[4b] and **7**[8] were prepared following the literature procedures.

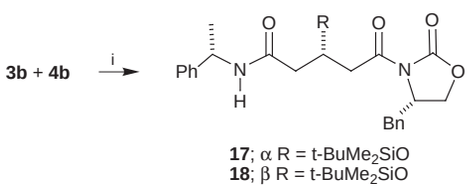
Determination of absolute stereochemistry of 3a–d and 8

To ascertain the sense of chiral induction in the anhydride opening reactions, it was essential to establish the absolute stereochemistry of the products. The configuration of the major acid **3a** was established by converting it to a known derivative **15**[3f] as depicted in Scheme 4. Thus, the mixture of acids **3a** and **4a** were converted to their respective benzyl esters and separated by column chromatography. The *major* benzyl ester was hydrogenolysed and the resulting acid **3a** was subjected to the conditions for silicon to hydroxy conversion.[14] The hydroxy acid obtained was coupled to (*S*)-phenylethylamine to give the amide **16** from which the oxazolidinone was removed under standard conditions.[15] The resulting acid was esterified and the hydroxy group was protected as the TBDMS ether to give **15**. Although, the absolute configurations of half-acids **5** and **6** (obtained from the reaction of the anion of **2b** with **1a**) were not ascertained, it could be safely assumed that the anhydride opening was following the same course as observed



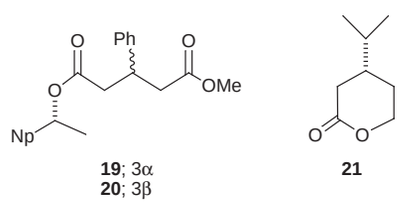
Scheme 4 *Reagents*: i, KBr, AcOOH, NaOAc; ii, (*S*)-phenylethylamine, DCCI, DMAP; iii, LiOH, H_2O_2, then CH_2N_2; iv, TBDMS-Cl, imidazole.

with oxazolidinone **2a**. The TLC behaviour (major diastereoisomer moves faster) and the NMR characteristics of the methyl esters of **5** (major) and **6** (minor) (OMe resonance of major diastereoisomer appears downfield) had similarities with those of **3a** and **4a**, respectively. The configuration of the major product from the opening of anhydride **1b** was assigned by converting it to **15** (Scheme 5). For this, the diastereoisomeric acid

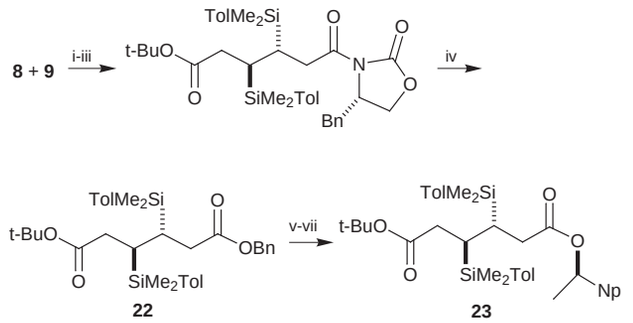


Scheme 5 *Reagent*: i, (*S*)-phenylethylamine, DCCI, DMAP.

mixture (**3b** and **4b**) was coupled to (*S*)-phenylethylamine to give the mixture of amides **17** and **18** which were easily separated. Removal of the oxazolidinone from major amide **17** under standard conditions followed by esterification gave **15**. The stereochemistry of the major product from the opening up of the anhydride **1c** was assigned by converting the diastereoisomeric mixture of acids **3c** and **4c** to a mixture of diesters **19** and **20**. For this, the diastereoisomeric mixture of acids **3c** and



4c was converted to their benzyl esters which on fractional crystallization provided a new mixture of benzyl esters (*major*:*minor* = 8:2). The mixture was hydrogenolysed and coupled with (*R*)-1-(1′-naphthyl)ethanol.[16] Subsequent removal of the oxazolidinone followed by esterification with diazomethane provided a mixture of known[4c] diesters **19** and **20** in a ratio of 8:2. The configuration of the major product from the opening up of the anhydride **1d** was assigned by converting it to the known lactone **21**.[17] The diastereoisomeric mixture of acids **3d** and **4d** was converted to the corresponding benzyl esters and separated as usual. The oxazolidinone was removed from the *major* benzyl ester and the resulting acid was reduced with borane in THF.[18] Upon acidification it provided the lactone **21**. The configuration of the major product from the opening up of **7** was assigned as shown in Scheme 6. The mixture of acids (**8** and **9**) was separated after converting into their *t*-Bu esters. The major ester was then subjected to oxazolidinone removal conditions to give the benzyl ester **22** which was hydrogenolysed



Scheme 6 *Reagents*: i, $(COCl)_2$, DMF; ii, t-BuOH, DMAP; iii, chromatography; iv, $(TiOBn)_4$, BnOH; v, H_2, Pd/C; vi, 2,4,6-trichlorobenzoyl chloride; vii, (1*R*)-1-(1′-naphthyl)ethanol, DMAP.

and esterified with (*R*)-1-(1′-naphthyl)ethanol to give the diester **23**. An authentic *rac*-**23** was made from anhydride **7** by ring opening with (±)-1-(1′-naphthyl)ethanol followed by esterification.[8b]

In conclusion, the results of this investigation show that Evans' oxazolidinones in stoichiometric amounts could be efficiently employed for the desymmetrization of σ-symmetric anhydrides on a preparative scale. Although the diastereoselectivity is not very high, the diastereoisomeric acids and their methyl, benzyl or *tert*-butyl esters are practically separable by fractional crystallization, and/or normal chromatography. Therefore, this could form a convenient method for both enantioconvergent and enantiodivergent syntheses of differentially substituted glutaric and adipic acid derivatives. The diastereoselectivity does not seem to depend much on the reaction conditions and the substituents on either the anhydride or the oxazolidinone. But the selectivity drops when the counter ion changed from lithium to magnesium. The facial selectivity was dependent on the substituents. The reaction period and the temperature could be drastically reduced when additives like DMPU were used. Moreover, the oxazolidinones could easily be prepared and be recovered without any loss of quantity and purity.

Experimental

General methods

All mps are recorded with a Fisher-Johns apparatus. The ^{1}H NMR and ^{13}C NMR spectra are recorded on a Bruker (model AC200) 200 MHz or Varian (model VXR300) 300 MHz instrument. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from internal tetramethylsilane ($\delta = 0.00$) or from residual chloroform ($\delta = 7.26$) and J (coupling constant) values in Hz. The IR spectra are recorded on a Perkin-Elmer 783 spectrophotometer or Nicolet Impact 410 FT IR spectrometer. Optical rotations are measured in a JASCO DIP polarimeter. Air sensitive reactions were carried out under Ar or N_2 atmosphere. Solvents were freshly dried and distilled prior to use. The unsaturated esters **10**,[9] **13**;[12] oxazolidinones **2a**,**b**;[19] (*R*)-1-(1′-naphthyl)ethanol[16] and anhydrides **1b**–**d**,[4b] and **7**[8] were prepared following the literature procedures and are not included in the Experimental section.

Dimethyl 3-[dimethyl(phenyl)silyl]glutarate 12

Dimethyl malonate (9.2 cm^3, 80 mmol) was added to a stirred solution of sodium methoxide [prepared using sodium (1.85 g, 80 mmol) in methanol] in methanol (15 cm^3) at room temp. and stirred for 0.5 h. A solution of the acrylate **10a** (8.8 g, 40 mmol) in methanol (10 cm^3) was added to the above reaction mixture at 0 °C and left for 2 days at room temp. The reaction mixture was neutralized with dil. HCl, methanol was removed and extracted with ether. The organic extract was washed with water and with brine, dried (Na_2SO_4) and evaporated under reduced

pressure. The residue was subjected under Kugelrohr distillation to remove the excess dimethyl malonate and the residue was purified by chromatography to give **11** (12 g, 85%); R_f(benzene) 0.3; ν_{max}(film)/cm^{-1} 1735, 1250, 1110. A stirred solution of this triester **11** (12 g, 34 mmol), sodium chloride (2 g) and water (1.5 cm^3) in DMSO (150 cm^3) was heated at 160 °C under nitrogen for 2.5 h. The reaction mixture was diluted with water (500 cm^3) and extracted with ether. The organic extract was washed with water and with brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by chromatography to give **12**[10] (9.67 g, 97%); R_f(benzene) 0.4; ν_{max}(film)/cm^{-1} 1745, 1260, 1120; δ_H(200 MHz, $CDCl_3$) 0.32 (6 H, s), 1.80–2.00 (1 H, m), 2.26 (2 H, dd, *J* 8.6, 16), 2.43 (2 H, dd, *J* 5.4, 16), 3.58 (6 H, s), 7.35–7.52 (5 H, m).

This compound was also prepared from **13**. Dimethyl(phenyl)silyllithium (94 cm^3 of a 0.9 M solution in THF; 84.5 mmol) was added to a stirred suspension of copper(I) cyanide (3.8 g, 42 mmol) in THF (70 cm^3) under argon at 0 °C. After 0.5 h, the solution was cooled to −78 °C and the diester **13** (6.32 g, 40 mmol) was added. The mixture was stirred under that condition for 3 h, quenched with a saturated solution of ammonium chloride and extracted with hexane. The extract was washed with water and brine, dried over Na_2SO_4 and evaporated under reduced pressure. The residue was chromatographed to give the diester **12** (10 g, 85%).

3-[Dimethyl(phenyl)silyl]glutaric acid 14

Sodium hydroxide (5 M in water) (50 cm^3, 250 mmol) was added to a stirred solution of the diester **12** (9.67 g, 32.7 mmol) in methanol (300 cm^3). After 24 h, the solvent was removed under reduced pressure and the residue was acidified with dil. HCl and extracted with EtOAc. The organic extract was washed with water and with brine, dried (Na_2SO_4) and evaporated under reduced pressure to give **14** (8 g, 92%); mp 104–105 °C; ν_{max}(KBr)/cm^{-1} 3400–2400 (br), 1720, 1250, 1110; δ_H(200 MHz, $CDCl_3$) 0.34 (6 H, s), 1.91–2.21 (3 H, m), 2.44 (2 H, dd, *J* 1.9, 15.6), 7.32–7.51 (5 H, m) (Found: C, 58.4; H, 6.9; $C_{13}H_{18}O_4Si$ requires C, 58.7; H, 6.8%).

3-[Dimethyl(phenyl)silyl]glutaric anhydride 1a

A solution of the diacid **14** (8 g, 30 mmol) in acetic anhydride (15 cm^3) was heated at 100 °C under nitrogen for 2.5 h. After cooling to room temp., excess acetic anhydride and acetic acid were removed under high vacuum. The residue was crystallized from EtOAc to give **1a** (7.44 g, 100%); mp 142 °C; ν_{max}(KBr)/cm^{-1} 1805, 1760, 1250, 1110; δ_H(200 MHz, $CDCl_3$) 0.40 (6 H, s), 1.45–1.70 (1 H, m), 2.31 (2 H, dd, *J* 14, 17), 2.80 (2 H, dd, *J* 4, 17), 7.32–7.48 (5 H, m).

(3′*R*,4*S*)-3-{3-[Dimethyl(phenyl)silyl]-4-carboxy-1-oxobutyl}-4-benzyloxazolidin-2-one 3a and its 3′*S* diastereoisomer 4a

Butyllithium (1.5 M in hexane) (0.4 cm^3, 0.6 mmol) was added to a stirred solution of the oxazolidinone **2a** (90 mg, 0.5 mmol) in THF (3 cm^3) at −35 °C under argon atmosphere. The mixture was stirred for 10 min, cooled to −78 °C and the required amount of additive (DMPU or DMAP) was added. A solution of the anhydride **1a** (125 mg, 0.5 mmol) in THF (3 cm^3) was added to this stirred mixture at −78 °C and then brought to the required temperature and stirred. The reaction mixture was acidified with citric acid solution and extracted with EtOAc. The crude acid mixture of **3a** and **4a** (215 mg, 100%) was esterified with ethereal diazomethane to give a mixture of esters (220 mg, 96%). The major and minor esters were separated by column chromatography. Major ester (from **3a**); R_f(hexane–EtOAc; 90:10) 0.35; $[\alpha]_D^{25}$ +43.1 (c 2.2, $CHCl_3$); ν_{max}(film)/cm^{-1} 1780, 1732, 1694, 1251, 1110; δ_H(200 MHz, $CDCl_3$) 0.36 (6 H, s), 1.97–2.11 (1 H, m), 2.31 (1 H, dd, *J* 9.1, 16), 2.47 (1 H, dd, *J* 4.8, 16), 2.63–2.76 (2 H, m), 3.20–3.31 (2 H, m), 3.59 (3 H, s), 4.05–4.20 (2 H, m), 4.40–4.52 (1 H, m), 7.16–7.56 (10 H, m); δ_C(50 MHz, $CDCl_3$) 173.8, 173.0, 153.5, 137.0, 135.7, 134.2, 129.4, 128.9, 127.9, 127.2, 66.2, 55.4, 51.3, 38.1, 36.1, 34.4, 18.3, −4.5 (Found: C, 65.3; H, 6.8; N, 3.0. $C_{24}H_{29}NO_5Si$ requires C, 65.6; H, 6.6; N, 3.2%). Minor ester (from **4a**): R_f(hexane–EtOAc; 90:10) 0.28; mp 90 °C; $[\alpha]_D^{25}$ +27.9 (*c* 0.4, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1789, 1734, 1683, 1245, 1113; δ_H(200 MHz, $CDCl_3$) 0.37 (6 H, s), 2.02–2.17 (1 H, m), 2.31 (1 H, dd, *J* 8.5, 15.5), 2.46 (1 H, dd, *J* 5.4, 15.5), 2.64 (1 H, dd, *J* 10, 13.4), 2.88 (1 H, dd, *J* 8.8, 17), 3.09 (1 H, dd, *J* 4.8, 17), 3.23 (1 H, dd, *J* 3.2, 13.4), 3.57 (3 H, s), 4.08–4.18 (2 H, m), 4.49–4.62 (1 H, m), 7.15–7.78 (10 H, m); δ_C(50 MHz, $CDCl_3$) 173.8, 173.0, 153.5, 137.1, 135.8, 134.2, 129.4, 129.0, 127.9, 127.3, 66.3, 55.4, 51.3, 38.2, 36.0, 34.7, 29.7, 18.3, −4.3 (Found: C, 65.2; H, 6.8; N, 2.9. $C_{24}H_{29}NO_5Si$ requires C, 65.6; H, 6.6; N, 3.2%).

The mixture of acids was converted to benzyl esters. For this, a solution of pivaloyl chloride (4 cm^3, 33 mmol) in THF (3 cm^3) was added to a stirred solution of crude acid mixture (**3a** and **4a**) (11.73 g, 27.6 mmol) and triethylamine (4.6 cm^3, 33 mmol) at −78 °C. The reaction mixture was stirred at 0 °C for 1 h and cooled to −78 °C followed by addition of benzyl alcohol (7.14 cm^3, 69 mmol) and DMAP (90 mg, 0.72 mmol). The reaction mixture was stirred at room temp. overnight and the solvent was removed. The residue was diluted with water and extracted with EtOAc. The organic extract was washed with water and with brine, dried and evaporated under reduced pressure. The residue was purified by chromatography to give (3′*R*,4*S*)-3-{4-(benzyloxycarbonyl)-3-[dimethyl(phenyl)silyl]-1-oxobutyl}-4-benzyloxazolidin-2-one (benzyl ester of major acid **3a**) (8 g, 56%) and its 3′*S* diastereoisomer (benzyl ester of minor acid **4a**) (3.84 g, 27%). For benzyl ester of major acid **3a**: R_f(hexane–EtOAc; 90:10) 0.37; $[\alpha]_D^{24}$ +24.3 (*c* 1.02, $CHCl_3$); ν_{max}(film)/cm^{-1} 1780, 1732, 1696, 1249, 1111; δ_H(200 MHz, $CDCl_3$) 0.36 (6 H, s), 2.02–2.14 (1 H, m), 2.31–2.56 (2 H, m), 2.56–2.75 (2 H, m), 3.16–3.35 (2 H, m), 4.03–4.14 (2 H, m), 4.34–4.44 (1 H, m), 4.95–5.10 (2 H, m), 7.13–7.53 (15 H, m); δ_C(50 MHz, $CDCl_3$) 173.2, 172.7, 153.3, 136.5, 135.5, 134.0, 129.2, 128.7, 128.4, 128.0, 127.7, 127.0, 66.1, 66.0, 55.1, 37.8, 35.9, 34.3, 17.8, −4.7 (Found: C, 69.6; H, 6.3; N, 3.0. $C_{30}H_{33}NO_5Si$ requires C, 69.9; H, 6.4; N, 2.7%). For benzyl ester of minor acid **4a**: R_f(hexane–EtOAc; 90:10) 0.31; mp 90–91 °C; $[\alpha]_D^{23}$ +43.3 (*c* 0.98, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1794, 1736, 1682, 1251, 1110; δ_H(200 MHz, $CDCl_3$) 0.37 (6 H, s), 2.09–2.21 (1 H, m), 2.30–2.66 (3 H, m), 2.85–3.24 (3 H, m), 3.97–4.10 (2 H, m), 4.44–4.54 (1 H, m), 5.01 (2 H, s), 7.13–7.55 (15 H, m); δ_C(50 MHz, $CDCl_3$) 173.1, 172.6, 153.2, 136.6, 135.8, 135.4, 133.9, 129.1, 128.7, 128.3, 127.9, 127.7, 127.0, 66.0, 55.0, 37.6, 35.7, 34.5, 17.6, −4.6 (Found: C, 69.9; H, 6.7; N, 2.5. $C_{30}H_{33}NO_5Si$ requires C, 69.9; H, 6.4; N, 2.7%).

The mixture of acids was also converted to *tert*-butyl esters. For this, oxalyl chloride (0.7 cm^3, 8 mmol) was added to a stirred solution of crude acid mixture (**3a** and **4a**) (850 mg, 2 mmol) and DMF (0.01 cm^3) at 0 °C. After 2 h at room temp., the solvent and excess oxalyl chloride was removed under vacuum. The residue was dissolved in dry *tert*-butyl alcohol (5 cm^3) and DMAP (370 mg, 3 mmol) was added. The reaction mixture was stirred at room temp. overnight and the solvent was removed. The residue was purified by chromatography to give (3′*R*,4*S*)-3-{4-(*tert*-butyloxycarbonyl)-3-[dimethyl(phenyl)-silyl]-1-oxobutyl}-4-benzyloxazolidin-2-one (*tert*-butyl ester of major acid **3a**) (530 mg, 55%) and its 3′*S* diastereoisomer (*tert*-butyl ester of minor acid **4a**) (285 mg, 30%). For *tert*-butyl ester of major acid **3a**: R_f(hexane–EtOAc; 95:5) 0.76; $[\alpha]_D^{24}$ +12.3 (*c* 1.56, $CHCl_3$); ν_{max}(film)/cm^{-1} 1783, 1724, 1697, 1251, 1111; δ_H(200 MHz, $CDCl_3$) 0.35 (3 H, s), 0.36 (3 H, s), 1.41 (9 H, s), 1.94–2.10 (1 H, m), 2.24 (1 H, dd, *J* 9.3, 16.5), 2.39 (1 H, dd, *J* 4.4, 16.5), 2.56 (1 H, dd, *J* 9.1, 15.7), 2.66 (1 H, dd, *J* 9.8, 13.3), 3.25 (1 H, dd, *J* 3.2, 13.3), 3.32 (1 H, dd, *J* 5, 15.8), 4.04–

4.25 (2 H, m), 4.37–4.50 (1 H, m), 7.15–7.60 (10 H, m); δ_C(50 MHz, $CDCl_3$) 173.1, 172.8, 153.4, 137.2, 135.8, 134.2, 129.3, 129.1, 128.9, 127.8, 127.2, 80.2, 66.1, 55.4, 38.1, 36.2, 35.6, 28.2, 18.0, −4.3, −4.5 (Found: C, 67.1; H, 7.6; N, 3.0. $C_{27}H_{35}NO_5Si$ requires C, 67.3; H, 7.3; N, 2.9%). For *tert*-butyl ester of minor acid **4a**: R_f(hexane–EtOAc; 95:5) 0.55; $[\alpha]_D^{24}$ +35.6 (*c* 0.5, $CHCl_3$); ν_{max}(film)/cm^{-1} 1788, 1730, 1697, 1252, 1111; δ_H(200 MHz, $CDCl_3$) 0.36 (6 H, s), 1.40 (9 H, s), 2.00–2.15 (1 H, m), 2.22 (1 H, dd, *J* 8.8, 15.8), 2.40 (1 H, dd, *J* 5, 15.8), 2.61 (1 H, dd, *J* 10, 13.4), 2.88 (1 H, dd, *J* 7.8, 17.1), 3.08 (1 H, dd, *J* 5.2, 17.1), 3.22 (1 H, dd, *J* 3.2, 13.4), 4.08–4.16 (2 H, m), 4.45–4.61 (1 H, m), 7.14–7.60 (10 H, m); δ_C(50 MHz, $CDCl_3$) 173.0, 172.7, 153.4, 137.4, 135.8, 134.2, 129.4, 129.2, 128.9, 127.9, 127.2, 80.3, 66.2, 55.3, 38.1, 36.0, 28.2, 17.9, −4.1, −4.3 (Found: C, 67.0; H, 7.4; N, 2.8. $C_{27}H_{35}NO_5Si$ requires C, 67.3; H, 7.3; N, 2.9%).

(3′*R*,4*S*)-3-{3-[Dimethyl(phenyl)silyl]-4-carboxyl-1-oxobutyl}-4-isopropyloxazolidin-2-one 5 and its 3′*S* diastereoisomer 6

This reaction was performed following the general procedure as described for the preparation of **3a** and **4a** except the oxazolidinone **2b** was used instead of **2a**. The crude acid mixture (**5** and **6**) was esterified with ethereal diazomethane to give a mixture of esters (95%). The major and minor esters were separated by column chromatography. Major ester (from **5**); R_f(hexane–EtOAc; 85:15) 0.45; $[\alpha]_D^{25}$ +54.6 (*c* 0.9, $CHCl_3$); ν_{max}(film)/cm^{-1} 1780, 1733, 1698, 1251, 1112; δ_H(200 MHz, $CDCl_3$) 0.34 (3 H, s), 0.35 (3 H, s), 0.84 (3 H, d, *J* 7), 0.88 (3 H, d, *J* 7), 1.93–2.07 (1 H, m), 2.22–2.35 (2 H, m), 2.44 (1 H, dd, *J* 5, 16), 2.63 (1 H, dd, *J* 9.5, 16), 3.27 (1 H, dd, *J* 4.7, 16), 3.57 (3 H, s), 4.09–4.31 (3 H, m), 7.31–7.55 (5 H, m); δ_C(50 MHz, $CDCl_3$) 173.8, 173.0, 154.1, 137.1, 134.2, 129.3, 127.9, 63.6, 58.9, 51.3, 36.2, 34.4, 28.8, 18.2, 18.0, 15, −4.4 (Found: C, 61.2; H, 7.6; N, 3.3. $C_{20}H_{29}NO_5Si$ requires C, 61.4; H, 7.5; N, 3.6%). Minor ester (from **6**): R_f(hexane–EtOAc; 85:15) 0.33; $[\alpha]_D^{25}$ +70.0 (*c* 0.2, $CHCl_3$); ν_{max}(film)/cm^{-1} 1780, 1732, 1694, 1250, 1111; δ_H(200 MHz, $CDCl_3$) 0.34 (6 H, s), 0.84 (3 H, d, *J* 7), 0.87 (3 H, d, *J* 7), 1.99–2.10 (1 H, m), 2.20–2.32 (2 H, m), 2.40 (1 H, dd, *J* 5.8, 15.5), 2.89 (1 H, dd, *J* 8.5, 17), 3.06 (1 H, dd, *J* 5, 17), 3.56 (3 H, s), 4.14–4.22 (2 H, m), 4.25–4.36 (1 H, m), 7.33–7.54 (5 H, m) (Found: C, 61.1; H, 7.7; N, 3.4. $C_{20}H_{29}NO_5Si$ requires C, 61.4; H, 7.5; N, 3.6%).

(3′*R*,4*S*)-3-(3-*tert*-Butyldimethylsilyloxy-4-carboxy-1-oxobutyl)-4-benzyloxazolidin-2-one 3b and its 3′*S* diastereoisomer 4b

This reaction was performed following the general procedure for the preparation of **3a** and **4a** from anhydride **1a** using DMPU (5 equiv.) as an additive. The crude acid (mixture of **3b** and **4b**) was esterified with diazomethane to give esters (94%) which were separated by chromatography. Major ester (from **3b**): R_f(hexane–EtOAc; 90:10) 0.35; $[\alpha]_D^{25}$ +41.6 (*c* 0.64, $CHCl_3$); ν_{max}(film)/cm^{-1} 1784, 1738, 1703; δ_H(200 MHz, $CDCl_3$) 0.09 (6 H, s), 0.84 (9 H, s), 2.50–2.65 (2 H, m), 2.74 (1 H, dd, *J* 9.7, 13.3), 3.07 (1 H, dd, *J* 6, 16.4), 3.30 (1 H, dd, *J* 3.2, 13.3), 3.38 (1 H, dd, *J* 6.3, 16.4), 3.68 (3 H, s), 4.13–4.24 (2 H, m), 4.58–4.75 (2 H, m), 7.20–7.40 (5 H, m); δ_C(50 MHz, $CDCl_3$) 171.3, 170.7, 153.3, 135.5, 129.4, 129.0, 127.4, 66.2, 55.3, 51.3, 43.0, 42.6, 38.1, 25.8, 17.9, −4.7, −4.9 (Found: C, 60.4; H, 7.8; N, 3.3. $C_{22}H_{33}NO_6Si$ requires C, 60.7; H, 7.6; N, 3.2%). Minor ester (from **4b**): R_f(hexane–EtOAc; 90:10) 0.15; $[\alpha]_D^{25}$ +37.8 (*c* 0.56, $CHCl_3$); ν_{max}(film)/cm^{-1} 1787, 1738, 1693; δ_H(200 MHz, $CDCl_3$) 0.11 (6 H, s), 0.85 (9 H, s), 2.56 (1 H, dd, *J* 6.5, 15.1), 2.65 (1 H, dd, *J* 6, 15.1), 2.76 (1 H, dd, *J* 9.7, 13.3), 3.13 (dd, 1 H, *J* 6, 16.7), 3.29 (1 H, dd, *J* 6, 16.7), 3.30 (1 H, dd, *J* 3, 13.3), 3.68 (3 H, s), 4.13–4.24 (2 H, m), 4.60–4.76 (2 H, m), 7.19–7.39 (5 H, m); δ_C(50 MHz, $CDCl_3$) 171.2, 170.5, 153.3, 135.5, 129.4, 129.0, 127.4, 66.2, 65.9, 55.2, 51.3, 43.3, 42.6, 38.1, 25.8, 17.9, −4.7, −4.9 (Found: C, 60.8; H, 7.8; N, 3.1. $C_{22}H_{33}NO_6Si$ requires C, 60.7; H, 7.6; N, 3.2%).

[3′*R*,4*S*]-3-(4-Carboxy-1-oxo-3-phenylbutyl)-4-benzyloxazolidin-2-one 3c and its 3′*S* diastereoisomer 4c

This reaction was performed following the general procedure for the preparation of **3a** and **4a** from anhydride **1a** using DMPU (5 equiv.) as an additive. The crude acid (mixture of **3c** and **5c**) was esterified with diazomethane to give esters (98%) which were separated by chromatography. Major ester (from **3c**): R_f(hexane–EtOAc; 80:20) 0.5; mp 92–93 °C; $[\alpha]_D^{25}$ +43.0 (*c* 0.7, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1786, 1730, 1691; δ_H(200 MHz, $CDCl_3$) 2.62–2.85 (3 H, m), 3.16–3.28 (2 H, m), 3.49 (1 H, dd, *J* 8.3, 16.8), 3.61 (3 H, s), 3.73–3.88 (1 H, m), 4.00–4.14 (2 H, m), 4.46–4.58 (1 H, m), 7.14–7.37 (10 H, m) (Found: C, 69.4; H, 6.3; N, 3.5. $C_{22}H_{23}NO_5$ requires C, 69.3; H, 6.1; N, 3.7%). Minor ester (from **4c**): R_f(hexane–EtOAc; 80:20) 0.34; mp 99–100 °C; $[\alpha]_D^{25}$ +54.8 (*c* 0.29, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1767, 1736, 1693; δ_H(200 MHz, $CDCl_3$) 2.58 (1 H, dd, *J* 9.2, 13.5), 2.68 (1 H, dd, *J* 6.3, 15.6), 2.79 (1 H, dd, *J* 7.2, 15.6), 3.02 (1 H, dd, *J* 3.3, 13.5), 3.18 (1 H, dd, *J* 6.5, 16.8), 3.56 (1 H, dd, *J* 8, 16.8), 3.60 (3 H, s), 3.75–3.90 (1 H, m), 4.06–4.20 (2 H, m), 4.55–4.67 (1 H, m), 6.99–7.07 (2 H, m), 7.15–7.37 (8 H, m) (Found: C, 69.4; H, 6.3; N, 3.5. $C_{22}H_{23}NO_5$ requires C, 69.0; H, 6.4; N, 3.7%).

The crude acid mixture was also converted to the benzyl esters following the procedure described for acids **3a** and **4a**. The overall yield after esterification is 82% and the isolated yields of (3′*R*,4*S*)-3-{1-oxo-3-phenyl-4-benzyloxycarbonyl)-butyl}-4-benzyloxazolidin-2-one (benzyl ester of major acid **3c**) is 55% and its 3′*S* diastereoisomer (benzyl ester of minor acid **4c**) is 27%. For benzyl ester of major acid **3c**: R_f(EtOAc–hexane; 15:85) 0.41; mp 118–119 °C, $[\alpha]_D^{22}$ +41.6 (*c* 0.62, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1786, 1727, 1689; δ_H(300 MHz, $CDCl_3$) 2.67 (1 H, dd, *J* 9.7, 13.4), 2.75 (1 H, dd, *J* 7.9, 15.6), 2.84 (1 H, dd, *J* 7.3, 15.6), 3.21 (1 H, dd, *J* 6.2, 16.7), 3.22 (1 H, dd, *J* 2.9, 13.4), 3.49 (1 H, dd, *J* 8.4, 16.7), 3.76–3.88 (1 H, m), 4.01–4.12 (2 H, m), 4.46–4.53 (1 H, m), 5.04 (2 H, s), 7.15–7.36 (15 H, m) (Found: C, 73.2; H, 6.1; N, 2.9. $C_{28}H_{27}NO_5$ requires C, 73.5; H, 5.9; N, 3.1%). For benzyl ester of minor acid **4c**: R_f(EtOAc–hexane; 15:85) 0.34; mp 113–114 °C, $[\alpha]_D^{22}$ +59 (*c* 0.88, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 1766, 1727, 1708; δ_H(300 MHz, $CDCl_3$) 2.56 (1 H, dd, *J* 9.3, 13.6), 2.75 (1 H, dd, *J* 7.9, 15.4), 2.83 (1 H, dd, *J* 7, 15.4), 3.02 (1 H, dd, *J* 2.9, 13.6), 3.18 (1 H, dd, *J* 6.6, 16.7), 3.55 (1 H, dd, *J* 8, 16.7), 3.79–3.90 (1 H, m), 4.06–4.16 (2 H, m), 4.54–4.64 (1 H, m), 5.03 (2 H, s), 7.00–7.03 (2 H, m), 7.17–7.36 (13 H, m) (Found: C, 73.6; H, 6.0; N, 3.0. $C_{28}H_{27}NO_5$ requires, C, 73.5; H, 5.9; N, 3.1%).

The mixture of these compounds **3c** and **4c** was also prepared using the magnesium salt of **2a**. For this, ethylmagnesium bromide (2.5 M in hexane) (0.4 cm^3, 1 mmol) was added to a stirred solution of the oxazolidinone **2a** (180 mg, 1 mmol) in THF (5 cm^3) at 0 °C under argon atmosphere. The mixture was stirred for 10 min, cooled to −78 °C and the required amount of additive (DMPU or DMAP) was added. A solution of the anhydride **1c** (250 mg, 1 mmol) in THF (5 cm^3) was added to this stirred mixture at −78 °C and then brought to the required temperature and stirred. The reaction mixture was acidified with citric acid solution and extracted with EtOAc. The crude acid (mixture of **3c** and **4c**) was esterified with ethereal diazomethane to give methyl esters (335 mg, 87%).

(3′*R*,4*S*)-3-(4-Carboxy-3-isopropyl-1-oxobutyl)-4-benzyloxazolidin-2-one 3d and its 3′*S* diastereoisomer 4d

This reaction was performed following the general procedure for the preparation of **3a** and **4a** from anhydride **1a** using DMPU (5 equiv.) as an additive. The crude acid (mixture of **3d** and **4d**) was esterified with diazomethane to give esters (92%) which were separated by chromatography. Major ester (from **3d**): R_f(hexane–EtOAc; 80:20) 0.48; $[\alpha]_D^{25}$ +42.8 (*c* 4.3, $CHCl_3$); ν_{max}(film)/cm^{-1} 1780, 1732, 1695; δ_H(200 MHz, $CDCl_3$) 0.91 (3 H, d, *J* 6.8), 0.92 (3 H, d, *J* 6.8), 1.72–1.88 (1 H, m), 2.25–2.54 (3 H, m), 2.75 (1 H, dd, *J* 9.9, 13.6), 2.80 (1 H, dd, *J* 7.7,

16.3), 3.07 (1 H, dd, *J* 4.5, 16.3), 3.31 (1 H, dd, *J* 3.3, 13.3), 3.67 (3 H, s), 4.12–4.26 (2 H, m), 4.57–4.69 (1 H, m), 7.19–7.38 (5 H, m); δ_C(50 MHz, $CDCl_3$) 173.4, 172.7, 153.4, 135.7, 129.4, 128.9, 127.3, 66.2, 55.4, 51.3, 38.1, 37.4, 37.2, 35.9, 31.1, 29.7, 19.0 (Found: C, 65.5; H, 7.6; N, 4.1. $C_{19}H_{25}NO_5$ requires C, 65.7; H, 7.3; N, 4.0%). Minor ester (from **4d**): R_f(hexane–EtOAc; 80:20) 0.32; $[\alpha]_D^{25}$ +39.6 (*c* 0.7, $CHCl_3$); ν_{max}(film)/cm^{-1} 1783, 1732, 1698; δ_H(200 MHz, $CDCl_3$) 0.93 (6 H, d, *J* 7), 1.75–1.90 (1 H, m), 2.23–2.44 (2 H, m), 2.45–2.56 (1 H, m), 2.75 (1 H, dd, *J* 10, 13.4), 2.84 (1 H, dd, *J* 7.8, 14.4), 3.07 (1 H, dd, *J* 4.9, 17), 3.30 (1 H, dd, *J* 3.3, 13.2), 3.66 (3 H, s), 4.11–4.25 (2 H, m), 4.60–4.72 (1 H, m), 7.19–7.38 (5 H, m); δ_C(50 MHz, $CDCl_3$) 173.5, 172.8, 153.5, 135.7, 129.5, 129.0, 127.4, 66.3, 55.4, 51.4, 38.3, 37.4, 37.2, 36.1, 31.2, 29.7, 19.1 (Found: C, 65.5; H, 7.6; N, 4.1. $C_{19}H_{25}NO_5$ requires C, 65.7; H, 7.3; N, 4.0%).

The crude acid mixture was also converted to the benzyl esters following the procedure described for acids **3a** and **4a**. The overall yield after esterification is 85% and the isolated yields of (3′*R*,4*S*)-3-[3-isopropyl-1-oxo-4-(benzyloxycarbonyl)-butyl]-4-benzyloxazolidin-2-one (benzyl ester of major acid **3d**) is 57% and its 3′*S* diastereoisomer (benzyl ester of minor acid **4d**) is 28%. For benzyl ester of major acid **3d**: R_f(hexane–EtOAc; 90:10) 0.31; $[\alpha]_D^{27}$ +55 (*c* 1.2, $CHCl_3$); ν_{max}(film)/cm^{-1} 1781, 1731, 1697; δ_H(200 MHz, $CDCl_3$) 0.91 (3 H, d, *J* 6.8), 0.92 (3 H, d, *J* 6.8), 1.74–1.88 (1 H, m), 2.31–2.55 (3 H, m), 2.68 (1 H, dd, *J* 9.7, 13.4), 2.80 (1 H, dd, *J* 7.7, 16.3), 3.13 (1 H, dd, *J* 4.3, 16.3), 3.28 (1 H, dd, *J* 3.3, 13.4), 4.08–4.22 (2 H, m), 4.52–4.64 (1 H, m), 5.04–5.17 (2 H, m), 7.14–7.37 (10 H, m) (Found: C, 70.8; H, 7.1; N, 3.0. $C_{25}H_{29}NO_5$ requires C, 71.0; H, 6.9; N, 3.3%). For benzyl ester of minor acid **4d**: R_f(hexane–EtOAc; 90:10) 0.28; $[\alpha]_D^{27}$ +40.4 (*c* 2.6, $CHCl_3$); ν_{max}(film)/cm^{-1} 1783, 1731, 1698; δ_H(200 MHz, $CDCl_3$) 0.93 (6 H, d, *J* 6.8), 1.74–1.90 (1 H, m), 2.29–2.62 (3 H, m), 2.72 (1 H, dd, *J* 9.8, 13.2), 2.87 (1 H, dd, *J* 7.8, 17), 3.07 (1 H, dd, *J* 4.7, 17), 3.29 (1 H, dd, *J* 3.2, 13.2), 4.05–4.15 (2 H, m), 4.54–4.66 (1 H, m), 5.10 (2 H, s), 7.17–7.38 (10 H, m) (Found: C, 71.1; H, 7.0; N, 3.1. $C_{25}H_{29}NO_5$ requires C, 71.0; H, 6.9; N, 3.3%).

(3′*R*,4*S*)-3-{3-[Dimethyl(phenyl)silyl]-4-carboxy-1-oxobutyl}-4-benzyloxazolidin-2-one 3a

A mixture of (3′*R*,4*S*)-3-{4-(benzyloxycarbonyl)-3-[dimethyl-(phenyl)silyl]-1-oxobutyl}-4-benzyloxazolidin-2-one (benzyl ester of major acid **3a**) (2.62 g, 5.09 mmol) and Pd/C (10% in Pd) (100 mg) in EtOAc (10 cm^3) was stirred under hydrogen atmosphere for 48 h. The mixture was passed through a Celite pad and the residue was washed thoroughly with EtOAc. The combined organic mixture was evaporated under reduced pressure to give the acid **3a** (2.16 g, 93%); mp 100–101 °C; $[\alpha]_D^{23}$ +48.6 (*c* 1.28, $CHCl_3$); ν_{max}(KBr)/cm^{-1} 3400–2500, 1780, 1710, 1700, 1250, 1110; δ_H(200 MHz, $CDCl_3$) 0.37 (6 H, s), 1.96–2.08 (1 H, m), 2.26–2.77 (4 H, m), 3.21 (1 H, dd, *J* 3.4, 13.4), 3.31 (1 H, dd, *J* 4.6, 16), 4.08–4.17 (2 H, m), 4.44–4.56 (1 H, m), 7.16–7.55 (10 H, m).

(3′*S*,1″*S*,4*S*)-3-{3-Hydroxy-1-oxo-4-[(1-phenylethyl)amino-carbonyl]butyl}-4-benzyloxazolidin-2-one 16

Peracetic acid (about 30% solution in acetic acid) (7.5 cm^3) was added to a stirred mixture of acid **3a** (1.2 g, 2.92 mmol), potassium bromide (417 mg, 3.5 mmol) and sodium acetate (500 mg, 6 mmol) at 0 °C. The reaction mixture was stirred for 1 day at room temp. and evaporated under vacuum. The residue was diluted with water and extracted with EtOAc. The organic extract was washed with water and with brine, dried and evaporated under reduced pressure. The residue was dissolved in dry CH_2Cl_2 (10 cm^3), and (*S*)-phenylethylamine (0.52 cm^3, 4 mmol) and DMAP (65 mg, 0.5 mmol) was added into this solution. A solution of DCCI (740 mg, 3.6 mmol) in CH_2Cl_2 (5 cm^3) was added to the above solution at 0 °C and the reaction mixture was stirred at room temp. overnight. The reaction mixture was filtered, the filtrate was washed with dil. HCl and with brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was chromatographed to give **16** (600 mg, 50%); R_f($CHCl_3$–MeOH; 95:5) 0.36; $[\alpha]_D^{24}$ −11.3 (*c* 1.42, $CHCl_3$); ν_{max}(film)/cm^{-1} 3306, 1780, 1697, 1648, 1540; δ_H(300 MHz, $CDCl_3$) 1.50 (3 H, d, *J* 6.8), 2.40–2.48 (2 H, m), 2.79 (1 H, dd, *J* 9.5, 13.5), 3.04–3.20 (2 H, m), 3.29 (1 H, dd, *J* 3.5, 13.5), 4.00 (1 H, d, *J* 2.4), 4.17–4.25 (2 H, m), 4.50–4.62 (1 H, m), 4.64–4.72 (1 H, m), 5.14 (1 H, quintet, *J* 7.3), 6.37 (1 H, d, *J* 7.6), 7.19–7.38 (10 H, m) (Found: C, 67.0; H, 6.7; N, 6.7. $C_{23}H_{26}N_2O_5$ requires C, 67.3; H, 6.4; N, 6.8%).

(1′*S*,3*S*)-*N*-(1-Phenylethyl)-3-*tert*-butyldimethylsilyloxy-4-(methoxycarbonyl)butanamide 15

A solution of amide **16** (108 mg, 0.27 mmol) in THF (4 cm^3) was added to a stirred solution of $LiOH·H_2O$ (23 mg, 0.54 mmol) and H_2O_2 (30%) (0.11 cm^3) in water (1.3 cm^3) at 0 °C.[21c] After 45 min, a solution of Na_2SO_3 (151 mg, 1.06 mmol) in water (0.8 cm^3) was added followed by addition of a solution of $NaHSO_4$ till the mixture became acidic, and the reaction mixture was extracted with EtOAc. The organic extract was washed with water and with brine, dried and evaporated under reduced pressure. The residue was esterified with ethereal diazomethane and column chromatography provided (1′*S*,3*S*)-*N*-(1-phenylethyl)-3-hydroxy-4-(methoxycarbonyl)butanamide (100 mg, 76%); R_f($CHCl_3$–MeOH; 98:2) 0.23; $[\alpha]_D^{29}$ −57 (*c* 1, $CHCl_3$); ν_{max}(film)/cm^{-1} 3298, 1730, 1648, 1540; δ_H(300 MHz, $CDCl_3$) 1.49 (3 H, d, *J* 7), 2.34–2.46 (2 H, m), 2.47–2.60 (2 H, m), 3.71 (3 H, s), 4.11 (1 H, d, *J* 7), 4.37–4.42 (1 H, m), 5.12 (1 H, quintet, *J* 7), 6.35 (1 H, d, *J* 7), 7.26–7.75 (5 H, m).

A solution of this amide (83 mg, 0.31 mmol), TBDMS-Cl (110 mg, 0.73 mmol) and imidazole (55 mg, 0.8 mmol) in DMF (2 cm^3) was stirred at room temp. overnight. The reaction mixture was diluted with water and extracted with ether. The organic extract was washed with water and with brine, dried and evaporated under reduced pressure. The residue was chromatographed to give **15** (108 mg, 91%); R_f(EtOAc–hexane; 2:8) 0.51; $[\alpha]_D^{24}$ −24.6 (*c* 1, $CHCl_3$); lit.[3f] $[\alpha]_D^{24}$ −22.6 (*c* 0.9, $CHCl_3$); ν_{max}(film)/cm^{-1} 3298, 1740, 1640, 1540; δ_H(300 MHz, $CDCl_3$) 0.08 (3 H, s), 0.10 (3 H, s), 0.85 (9 H, s), 1.47 (3 H, d, *J* 7), 2.38–2.60 (4 H, m), 3.65 (3 H, s), 4.49 (1 H, quintet, *J* 5.8), 5.12 (1 H, quintet, *J* 7), 6.59 (1 H, d, *J* 7.8), 7.24–7.36 (5 H, m).

This compound was also prepared from **17**. A solution of amide **17** (160 mg, 0.3 mmol) in THF (4.5 cm^3) was added to a stirred solution of lithium hydroxide (26 mg, 1 mmol) and hydrogen peroxide (30%) (0.125 cm^3) in water (1.4 cm^3) at 0 °C. After 45 min, a solution of sodium sulfite (170 mg, 1.35 mmol) in water (1 cm^3) was added followed by addition of a solution of sodium bisulfate till the mixture became acidic, and the reaction mixture was extracted with EtOAc. The organic extract was washed with water and with brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was esterified with ethereal diazomethane and column chromatography provided the ester **15** (107 mg, 93%).

(3′*S*,1″*S*,4*S*)-3-[3-*tert*-Butyldimethylsilyloxy-1-oxo-4-(1-phenylethyl)aminocarbonylbutyl]-4-benzyloxazolidin-2-one 17 and its 3′*R* isomer 18

A solution of DCCI (115 mg, 0.55 mmol) in CH_2Cl_2 (2 cm^3) was added to a stirred solution of crude acid mixture (**5b** and **6b**) (210 mg, 0.5 mmol), (*S*)-phenylethylamine (0.135 cm^3, 1 mmol), 1-hydroxybenzotriazole (135 mg, 1 mmol) and DMAP (60 mg, 0.5 mmol) in CH_2Cl_2 (3 cm^3) at 0 °C. The reaction mixture was stirred at room temp. overnight and was filtered. The filtrate was washed with water and with brine, dried (Na_2SO_4) and evaporated under reduced pressure. The residue was chromatographed to give major amide **17** (145 mg, 55%) and minor amide **18** (74 mg, 28%). For **17**; R_f(hexane–EtOAc; 80:20) 0.5; $[\alpha]_D^{24}$ +4.9 (*c* 0.8, $CHCl_3$); ν_{max}(film)/cm^{-1} 3370, 1783,

1695, 1661, 1515; δ_H(200 MHz, $CDCl_3$) 0.09 (3 H, s), 0.13 (3 H, s), 0.85 (9 H, s), 1.48 (3 H, d, *J* 7), 2.48 (1 H, dd, *J* 5, 15), 2.60 (1 H, dd, *J* 4.8, 15), 2.71 (1 H, dd, *J* 9.7, 13.3), 3.13 (1 H, dd, *J* 6.6, 16.2), 3.28 (1 H, dd, *J* 2.8, 13.3), 3.29 (1 H, dd, *J* 6, 16.2), 4.10–4.21 (2 H, m), 4.53–4.70 (2 H, m), 5.12 (1 H, quintet, *J* 7), 6.57 (1 H, d, *J* 7.7), 7.16–7.35 (10 H, m); δ_C(50 MHz, $CDCl_3$) 170.6, 169.1, 153.2, 143.6, 135.5, 129.4, 129.0, 128.7, 127.2, 126.3, 66.6, 66.2, 55.2, 48.9, 44.3, 42.2, 38.1, 25.8, 21.9, 17.9, −4.8 (Found: C, 66.3; H, 8.0; N, 5.0. $C_{29}H_{40}N_2O_5Si$ requires C, 66.4; H, 7.7; N, 5.3). For **18**; R_f(hexane–EtOAc; 80:20) 0.32; $[\alpha]_D^{23}$ −9.62 (*c* 0.52, $CHCl_3$); ν_{max}(film)/cm^{-1} 3360, 1781, 1699, 1659, 1529; δ_H(200 MHz, $CDCl_3$) 0.08 (3 H, s), 0.11 (3 H, s), 0.81 (9 H, s), 1.52 (3 H, d, *J* 6.9), 2.47 (1 H, dd, *J* 4.3, 15), 2.58 (1 H, dd, *J* 4.9, 15), 2.76 (1 H, dd, *J* 9.7, 13.5), 3.18–3.41 (3 H, m), 4.08–4.26 (2 H, m), 4.59–4.71 (2 H, m), 5.12 (1 H, quintet, *J* 7.2), 6.72 (1 H, d, *J* 7.7), 7.15–7.39 (10 H, m); δ_C(50 MHz, $CDCl_3$) 170.5, 169.1, 153.3, 143.5, 135.5, 129.4, 129.0, 128.6, 127.4, 127.3, 126.4, 125.9, 66.4, 55.3, 48.9, 44.0, 41.8, 38.1, 25.8, 21.8, 17.9, −4.9 (Found: C, 66.2; H, 7.9; N, 5.2. $C_{29}H_{40}N_2O_5Si$ requires C, 66.4; H, 7.7; N, 5.3%).

Methyl (1*R*)-1-(1′-naphthyl)ethyl (3*S*)-3-phenylpentane-1,5-dioate 19 and its 3*R* diastereoisomer 20

A mixture of benzyl esters of acids **3c** and **4c** (67:33) were crystallized from hexane–EtOAc to give another crop of mixture of benzyl esters (80:20). A mixture of benzyl esters with this new proportion (100 mg, 0.22 mmol) was dissolved in ethyl acetate (2 cm^3) and stirred under hydrogen in the presence of Pd/C (10% Pd; 10 mg). After 24 h, the resulting acid was dissolved in dry CH_2Cl_2 and treated with 2,4,6-trichlorobenzoyl chloride (0.033 cm^3, 0.22 mmol) and DMAP (34 mg, 0.25 mmol). After 2 h at room temp., (1*R*)-1-(1′-naphthyl)ethanol (60 mg, 0.3 mmol), and DMAP (36 mg, 0.3 mmol) were added. After 18 h, the mixture was diluted with EtOAc, washed with dil. HCl, $NaHCO_3$ solution and brine, dried and concentrated to give the ester [ν_{max}(film)/cm^{-1} 1780, 1731, 1702]. This ester was dissolved in THF (3 cm^3) and a mixture of water (0.8 cm^3), H_2O_2 (0.077 cm^3 of a 30% solution, 1 mmol) and $LiOH·H_2O$ (15 mg, 0.35 mmol) was added to it at 0 °C under argon. After 1 h, the reaction mixture was treated with Na_2SO_3 (91 mg, 0.72 mmol) and water (1 cm^3) was added followed by $NaHCO_3$ solution (0.5 M, 1 cm^3). The reaction mixture was acidified with $NaHSO_4$ and extracted with EtOAc. The organic extract was washed with water and with brine, dried (Na_2SO_2) and evaporated under reduced pressure. The residue was esterified with ethereal diazomethane and after chromatography gave a mixture of diesters **19** and **20** (35 mg, 55%); R_f(hexane–EtOAc; 95:5) 0.4; ν_{max}(film)/cm^{-1} 1735; δ_H(300 MHz, $CDCl_3$) 1.53 (3 H, d, *J* 6.5 from **20**), 1.58 (3 H, d, *J* 6.5 from **19**), 2.59–2.89 (4 H, m), 3.56 (3 H, s, from **20**), 3.59 (3 H, s, from **19**), 3.62–3.74 (1 H, m), 6.55 (1 H, q, *J* 6.5), 7.18–8.10 (12 H, m).

(3*R*)-3-Isopropylpentanolactone 21

A solution of (3′*R*,4*S*)-3-[3-isopropyl-1-oxo-4-(benzyloxycarbonyl)butyl]-4-benzyloxazolidin-2-one (benzyl ester of major acid **3d**) (217 mg, 0.5 mmol) in THF (5 cm^3) was added to a stirred solution of lithium hydroxide (40 mg, 1.03 mmol) and hydrogen peroxide (30%) (0.23 cm^3) in water (2.45 cm^3) at 0 °C. After 45 min, a solution of sodium sulfite (280 mg, 2.2 mmol) in water (1.5 cm^3) was added followed by addition of a solution of sodium bisulfate till the mixture became acidic, and the reaction mixture was extracted with EtOAc. The organic extract was washed with water and with brine, dried (Na_2SO_4) and evaporated under reduced pressure to give (3*R*)-3-isopropylpentane-1,5-dioic acid 1-benzyl ester (130 mg, 98%); ν_{max}(film)/cm^{-1} 3600–2500, 1735, 1712; δ_H(200 MHz, $CDCl_3$) 0.88 (6 H, d, *J* 6.8), 1.70–1.93 (1 H, m), 2.24–2.51 (5 H, m), 5.11 (2 H, s), 7.24–7.52 (5 H, m). This acid was dissolved in dry THF (2 cm^3) and cooled to −15 °C. A solution of diborane in THF (1.4 M) (0.43 cm^3, 0.6 mmol) was added [18] slowly into the above mixture and allowed to warm to 0 °C (2 h) and then to room temp. (1 h). The reaction was quenched with methanol and the solvent was removed by downward distillation. The process was repeated three times with addition of methanol and the residue was dissolved in EtOAc. The mixture was stirred under hydrogen after adding catalytic amount of Pd/C (10% Pd) for 4 h, filtered through a pad of Celite and the filtrate was evaporated under reduced pressure. The residue was dissolved in benzene (5 cm^3) and toluene-4-sulfonic acid (5 mg) was added to it and the solution was refluxed. After 4 h, the mixture was washed with sodium bicarbonate solution and with brine, dried (Na_2SO_4) and evaporated under reduced pressure to give the lactone **21** (50 mg, 68%); R_f(hexane–EtOAc; 80:20) 0.34; $[\alpha]_D^{25}$ +22.4 (*c* 0.54, EtOH); lit.,[4c] for (*S*)-isomer $[\alpha]_D^{25}$ −22.6 (*c* 1, EtOH); ν_{max}(film)/cm^{-1} 1735; δ_H(300 MHz, $CDCl_3$) 0.92 (d, 3 H, *J* 6.7), 0.93 (d, 3 H, *J* 6.7), 1.48–1.62 (m, 2 H), 1.67–1.80 (m, 1 H), 1.87–1.96 (m, 1 H), 2.21 (dd, 1 H, *J* 10.7, 17.3), 2.65 (ddd, 1 H, *J* 1.5, 6, 17.3), 4.22 (dt, 1 H, *J* 3.6, 11.3), 4.40 (ddd, 1 H, *J* 4, 4.8, 11.3).

(3′*R*,4′*S*,4*S*)-3-{3,4-Bis[dimethyl(*p*-tolyl)silyl]-5-carboxy-1-oxopentyl}-4-benzyloxazolidin-2-one 8 and its (3′*S*,4′*R*) diastereoisomer 9

A solution of DCCI (75 mg, 0.36 mmol) in CH_2Cl_2 (35 cm^3) was added dropwise over 1.5 h to a stirred solution of the diacid (3′*SR*,4′*RS*)-3,4-bis[dimethyl(*p*-tolyl)silyl]hexane-1,6-dioic acid[8] (150 mg, 0.36 mmol) in CH_2Cl_2 (35 cm^3) at 0 °C. After 12 h at room temp., the solvent was evaporated, the residue was triturated with hexane and filtered. The filtrate was evaporated to give the anhydride **7** (142 mg, 100%) [ν_{max}(CH_2Cl_2)/cm^{-1} 1816, 1750, 1260, 1104]. A solution of this anhydride in THF (2 cm^3) was added to a stirred solution of the anion of **2a** at −78 °C [prepared using butyllithium (1.25 M in hexane) (0.35 cm^3, 0.43 mmol) and oxazolidinone **2a** (77 mg, 0.43 mmol)]. The mixture was then brought to the required temperature and stirred. The reaction mixture was acidified with citric acid solution and extracted with EtOAc. The crude mixture of acids (**8** and **9**) was esterified with diazomethane and chromatographed to yield major methyl ester (from **8**) (122 mg, 55%) and minor methyl ester (from **9**) (62 mg, 28%). Data for methyl ester from **8**: R_f(hexane–EtOAc; 9:1) 0.6; $[\alpha]_D^{29}$ +51.3 (*c* 0.6, $CHCl_3$); ν_{max}(film)/cm^{-1} 1782, 1732, 1698, 1602, 1258, 1103; δ_H(200 MHz, $CDCl_3$) 0.23 (3 H, s), 0.31 (3 H, s), 0.37 (6 H, s), 1.85–2.05 (2 H, m), 2.29 (6 H, s), 2.38–2.62 (3 H, m), 2.94 (1 H, dd, *J* 5.9, 18.6), 3.06–3.22 (2 H, m), 3.56 (3 H, s), 3.81–4.01 (2 H, m), 4.10–4.42 (1 H, m), 7.09–7.47 (13 H, m); δ_C(50 MHz, $CDCl_3$) 174.0, 173.1, 153.2, 138.6, 135.8, 135.6, 134.4, 129.4, 129.0, 128.6, 127.3, 66.0, 55.2, 51.3, 38.1, 37.5, 36.3, 29.7, 23.8, 23.2, 21.3, −1.6, −2.3, −2.5, −2.6 (Found: C, 68.0; H, 7.6; N, 2.0. $C_{35}H_{45}NO_5Si_2$ requires C, 68.3; H, 7.4; N, 2.3%). Data for methyl ester from **9**: R_f(hexane–EtOAc; 9:1) 0.45; $[\alpha]_D^{29}$ −4.0 (*c* 0.5, $CHCl_3$); ν_{max}(film)/cm^{-1} 1783, 1731, 1698, 1602, 1251, 1103; δ_H(200 MHz, $CDCl_3$) 0.28 (3 H, s), 0.30 (3 H, s), 0.32 (3 H, s), 0.33 (3 H, s), 1.86–2.01 (2 H, m), 2.29 (3 H, s), 2.32 (3 H, s), 2.35–2.60 (3 H, m), 2.90–3.21 (3 H, m), 3.56 (3 H, s), 3.90–4.04 (2 H, m), 4.20–4.36 (1 H, m), 7.09–7.40 (13 H, m); δ_C(50 MHz, $CDCl_3$) 174.2, 173.1, 153.3, 138.7, 135.8, 135.6, 135.3, 134.5, 129.4, 129.0, 128.6, 127.3, 66.2, 55.3, 51.3, 38.1, 37.5, 36.2, 29.7, 24.3, 23.0, 21.3, −1.7, −2.1, −2.4, −2.7 (Found: C, 68.1; H, 7.5; N, 2.1. $C_{35}H_{45}NO_5Si_2$ requires C, 68.3; H, 7.4; N, 2.3%).

The crude acid mixture was also converted to the *tert*-butyl esters following the procedure described for acids **3a** and **4a**. Yield of (3′*R*,4′*S*,4*S*)-3-{5-*tert*-butyloxycarbonyl-3,4-bis-[dimethyl(*p*-tolyl)silyl]-1-oxopentyl}-4-benzyloxazolidin-2-one (ester of major acid **8**) is (425 mg, 45%) and that of its (3′*S*,4′*R*) diastereoisomer is (212 g, 23%). For the ester of major acid **8**: R_f(hexane–EtOAc; 90:10) 0.47; $[\alpha]_D^{23}$ +31.3 (*c* 1.42, $CHCl_3$); ν_{max}(film)/cm^{-1} 1782, 1726, 1699, 1250, 1103; δ_H(300 MHz,

$CDCl_3$) 0.24 (3 H, s), 0.33 (3 H, s), 0.36 (3 H, s), 0.37 (3 H, s), 1.43 (9 H, s), 1.89 (1 H, q, *J* 6.2), 2.03 (1 H, q, *J* 6.4), 2.27 (3 H, s), 2.29 (3 H, s), 2.42 (2 H, dd, *J* 1.5, 6.4), 2.52 (1 H, dd, *J* 9.5, 13.4), 2.88 (1 H, dd, *J* 5.7, 18.8), 3.08 (1 H, dd, *J* 3.4, 14.8), 3.13 (1 H, dd, *J* 6.6, 18.8), 3.82 (1 H, t, *J* 8.4), 3.95 (1 H, dd, *J* 2.7, 8.8), 4.15–4.25 (1 H, m), 7.07–7.43 (13 H, m) (Found: C, 69.2; H, 8.0; N, 2.0. $C_{38}H_{51}NO_5Si_2$ requires C, 69.4; H, 7.8; N, 2.1%). For the ester of major acid **9**: R_f(hexane–EtOAc; 90:10) 0.45; $[\alpha]_D^{23}$ +26.6 (*c* 0.82, $CHCl_3$); ν_{max}(film)/cm^{-1} 1783, 1725, 1698, 1250, 1103; δ_H(300 MHz, $CDCl_3$) 0.28 (3 H, s), 0.29 (3 H, s), 0.32 (3 H, s), 0.33 (3 H, s), 1.42 (9 H, s), 1.90–1.98 (2 H, m), 2.26–2.38 (1 H, m), 2.27 (3 H, s), 2.33 (3 H, s), 2.39 (1 H, dd, *J* 6, 8.8), 2.43 (1 H, dd, *J* 9.9, 13.4), 2.92 (1 H, dd, *J* 7.3, 18), 3.06 (1 H, dd, *J* 3.1, 13.4), 3.14 (1 H, dd, *J* 5.4, 18), 3.91 (1 H, t, *J* 8.8), 3.97 (1 H, dd, *J* 2.8, 8.8), 4.19–4.31 (1 H, m), 7.08–7.43 (13 H, m) (Found: C, 69.4; H, 7.9; N, 2.0. $C_{38}H_{51}NO_5Si_2$ requires C, 69.4; H, 7.8; N, 2.1%).

(3*R*,4*S*) 3,4-Bis[dimethyl(*p*-tolyl)silyl]hexane-1,6-dioic acid 6-*tert*-butyl ester 1-benzyl ester 22

Titanium tetrakis(benzyl oxide) (0.38 M in benzyl alcohol) (2.25 cm^3, 0.85 mmol) was added to (3′*R*,4′*S*,4*S*)-3-{5-*tert*-butyloxycarbonyl-3,4-bis[dimethyl(*p*-tolyl)silyl]-1-oxopentyl}-4-benzyloxazolidin-2-one (ester of major acid **8**) (272 mg, 0.414 mmol) and the mixture was heated at 75 °C for 24 h under argon. The reaction mixture cooled to room temp. and water (5 cm^3) was added with stirring. The reaction mixture was filtered through a pad of Celite and the residue was thoroughly washed with EtOAc. The filtrate was evaporated under reduced pressure and the benzyl alcohol was removed under high vacuum. The residue was chromatographed to give ester **22** (208 mg, 87%); R_f(hexane–EtOAc; 95:5) 0.67; $[\alpha]_D^{23}$ −17.9 (*c* 1.4, $CHCl_3$); ν_{max}(film)/cm^{-1} 1728, 1601, 1259, 1104; δ_H(300 MHz, $CDCl_3$) 0.21 (3 H, s), 0.22 (3 H, s), 0.26 (6 H, s), 1.38 (9 H, s), 1.79–1.92 (2 H, m), 2.32 (s, 3 H), 2.33 (3 H, s), 2.31–2.52 (4 H, m), 4.87 (2 H, s), 7.09–7.36 (13 H, m) (Found: C, 71.3; H, 8.3. $C_{35}H_{48}O_4Si_2$ requires C, 71.4; H, 8.2%).

(3*S*,4*R*)-3,4-Bis[dimethyl(*p*-tolyl)silyl]hexane-1,6-dioic acid 1-*tert*-butyl (1*R*)-1-(1′-naphthyl)ethyl ester 23

The diester **22** (44 mg, 0.076 mmol) in EtOAc (3 cm^3) was stirred under hydrogen atmosphere for 15 h in the presence of 10% Pd/C (5 mg). The mixture was filtered through a Celite pad and the filtrate was concentrated to give the acid. A solution of 2,4,6-trichlorobenzoyl chloride (0.017 cm^3, 0.1 mmol) in dry CH_2Cl_2 (0.5 cm^3) was added to a stirred solution of this acid, (1*R*)-1-(1′-naphthyl)ethanol (15 mg, 0.087 mmol), and DMAP (12 mg, 0.1 mmol) in dry CH_2Cl_2 (0.5 cm^3) at room temp. After 15 h, the mixture was diluted with EtOAc, washed with dil. HCl, $NaHCO_3$ solution and brine, dried and concentrated. The residue was chromatographed to give **23** (23 mg, 71%); R_f(hexane–EtOAc; 98:2) 0.4; ν_{max}(film)/cm^{-1} 1728, 1603, 1261, 1108; δ_H(300 MHz, $CDCl_3$) 0.18 (3 H, s), 0.22 (3 H, s), 0.24 (3 H, s), 0.26 (3 H, s), 1.36 (9 H, s), 1.58 (3 H, d, *J* 6.6), 1.82–1.92 (2 H, m), 2.29 (3 H, s), 2.31 (3 H, s), 2.31–2.65 (4 H, m), 6.48 (1 H, quintet, *J* 6.6), 7.06–7.10 (4 H, m), 7.26–7.34 (4 H, m), 7.40–7.54 (4 H, m), 7.74–7.90 (2 H, m), 8.00–8.04 (1 H, m) (Found: C, 73.2; H, 8.3. $C_{40}H_{52}O_4Si_2$ requires C, 73.6; H, 8.0%).

A racemic sample (*rac*-**23**) was made by the following procedure. The (3*SR*,4*RS*)-3,4-bis[dimethyl(*p*-tolyl)silyl]hexane-1,6-dioic acid[8b] (18 mg, 0.046 mmol) was converted into its anhydride, following the procedure described for the preparation of **8** and **9**, which was opened up with (1*RS*)-1-(1′-naphthyl)ethanol (9 mg, 0.05 mmol), and DMAP (12 mg, 0.1 mmol) in dry CH_2Cl_2 (2 cm^3) following the literature procedure.[8b] The crude mono acid therefore obtained was converted to the required diester *rac*-**23** following the procedure used for the preparation of **23** using 2,4,6-trichlorobenzoyl chloride and DMAP.

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