Stereoselective Synthesis of Alcohols, XXXI[1]

Stereoselective C–C Bond Formation Using Chiral *Z*-Pentenylboronates

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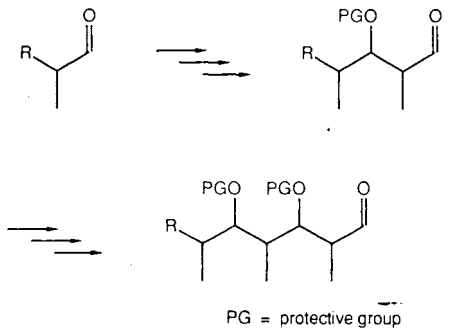
Using 1,2-dicyclohexyl-1,2-ethanediol as chiral auxiliary, the enantiomerically pure *Z*-pentenylboronate **9c** was obtained. Its addition to benzaldehyde proceeded with complete transfer of chirality to give the *syn-E*-homoallyl alcohol **11**. The ability of the reagent **9c** to create new stereocenters under reagent control of diastereoselectivity was tested in its addition to the chiral aldehydes **15** and **24**. This resulted in a short and stereospecific synthesis of invictolide (**18**), as well as of a C-9/C-15-partial structure **25** of erythronolide A.

Stereoselektive Synthese von Alkoholen, XXXI[1]. – Stereoselektive C–C-Bindungsbildung mit Hilfe chiraler *Z*-Pentenylboronsäureester

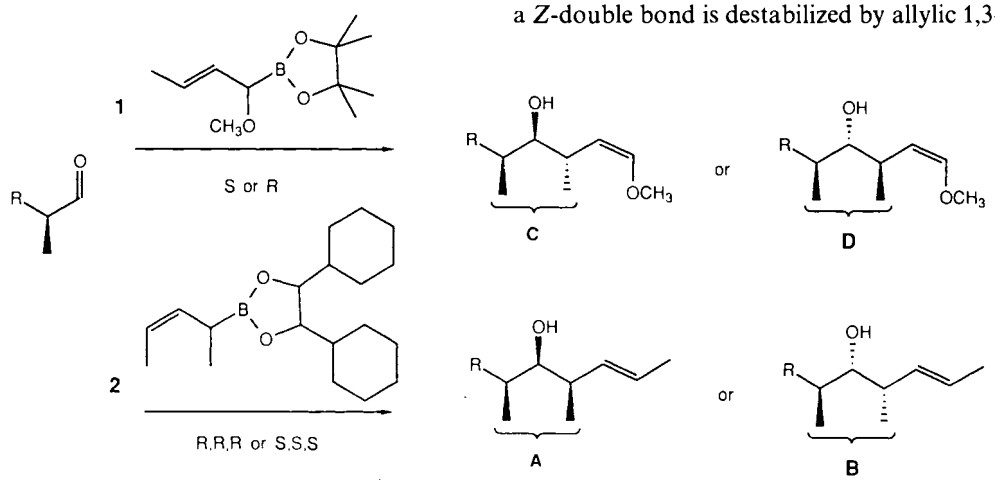
Unter Verwendung von 1,2-Dicyclohexyl-1,2-ethandiol als chiralem Auxiliar wurde der enantiomerenreine *Z*-Pentenylboronsäureester **9c** erhalten. Dessen Addition an Benzaldehyd ergab den *syn-E*-Homoallylalkohol **11** unter vollständiger Chiralitäts-Übertragung. Die Fähigkeit des Reagenz **9c** zur Bildung neuer Stereozentren unter Reagenz-Kontrolle der Diastereoselektivität wurde in der Addition an die chiralen Aldehyde **15** und **24** geprüft. Dies führte zu einer kurzen stereospezifischen Synthese des Invictolids (**18**) wie der eines C-9/C-15-Bausteins **25** des Erythronolids A.

One strategy for the synthesis of natural products of polyketide-derived biogenesis, especially for the synthesis of polypropionate molecules[2], consists in an iterative sequence of chain elongation steps.



Control of the formation of the individual stereocenters depends on simple diastereoselection during the carbon–carbon bond forming steps[3] as well as on reagent control of diastereoselectivity[4] using chiral reagents exerting high asymmetric induction. We recently reported on α-methoxy-(*E*)-crotylboronates (**1**) as reagents, which allow for the generation of the stereotriades C and D[2]. Here, we would like to describe the chiral *Z*-pentenylboronate **2**, which should allow for the generation of the stereotriades **A** and **B**. Some aspects of this work have already been communicated in preliminary form[5].

A preceding study on racemic *E*- and *Z*-pentenylboronates[1] demonstrated that only the *Z* isomer **3** shows high diastereoselectivity on addition to aldehydes. The product **4** with an *E*-double bond is formed preferentially since the transition state **5** of the competing reaction leading to **6** with a *Z*-double bond is destabilized by allylic 1,3-strain[6]. As the



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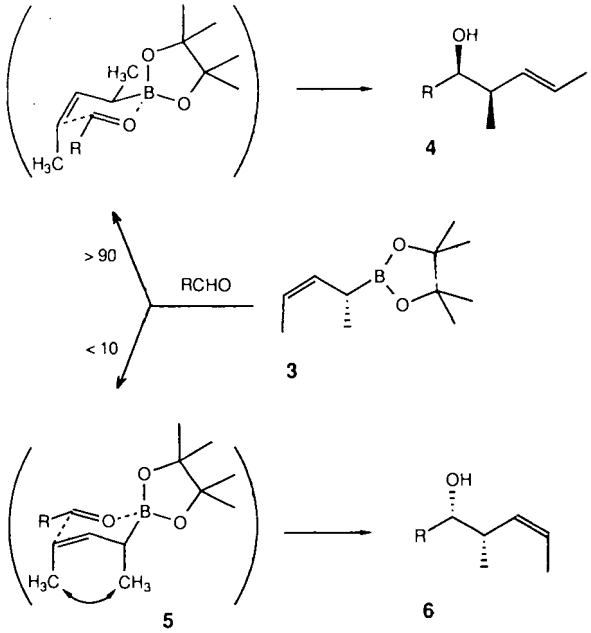
E/Z ratio **4/6** is identical to the level of asymmetric induction that can be attained using an enantiomerically pure reagent **3**, we set out to prepare such chiral reagents.

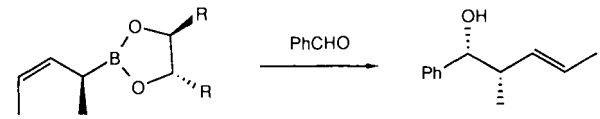


Preparation of the *R,R,R*- and *S,S,S*-Pentenylboronates 9

To obtain the *Z*-pentenylboronates in enantiomerically pure form, we followed the route of Matteson[7-9] by which a chirally modified (dichloromethyl)boronate **7** is converted into an α-chiral allylboronate, a route which we had used advantageously to obtain enantiomerically enriched (α-chloroallyl)boronates[10].

Since, however, the related (α-chlorocrotyl)boronates **8** have a high tendency to epimerize and isomerize under the conditions of their preparations[11], we had to rely on the route via **10**. Matteson had already prepared the (α-chloroethyl)boronate **10a** of 95% diastereomeric purity[9,12]. He reported that larger groups R on the chiral glycol gave products of higher diastereomeric purity (e.g. **10b**, ds 97%[8]). We therefore turned to the compounds **7c** and **10c** with R = cyclohexyl.

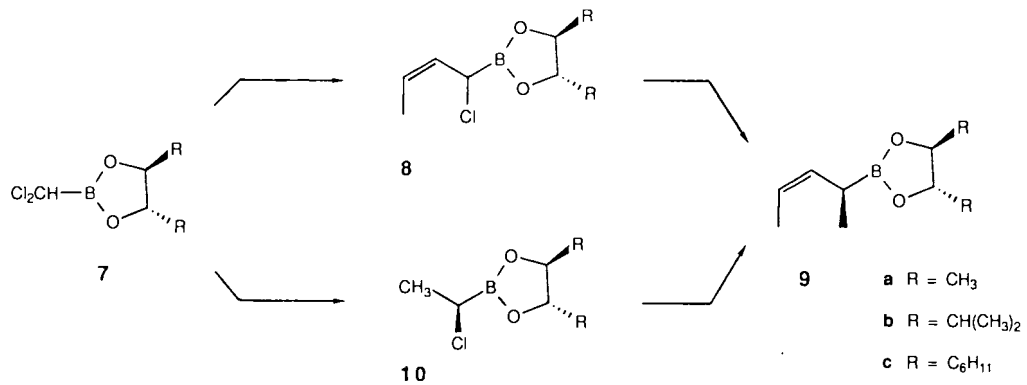
The chiral auxiliary (*S,S*)-1,2-dicyclohexyl-1,2-ethanediol was prepared in 84% yield by hydrogenation of *S,S*-hydrobenzoin. The latter is most readily obtained by a slight modification of the method of Sharpless[13]: Reaction at −4°C led frequently to crystallisation of enantiomerically pure hydrobenzoin directly from the reaction mixture. Other routes to optically pure hydrobenzoin by resolution[14] or by separate crystallisation of the enantiomers[15] are less convenient. The *S,S*- or the *R,R*-dicyclohexyl-ethanediol was esterified using diisopropyl (dichloromethyl)boronate[16a] to give quantitatively the hydrolytically stable crystalline ester **7c**. In view of the expected lability of **10** towards epimerisation by chloride ions[17], the transformation of **7c** into **9c** via **10c** was carried out as a one-pot procedure. Thus, **7c** was treated with one equivalent of methyllithium in ether at −78°C, then with $ZnCl_2$ in THF at room temperature, and finally with one equivalent of *Z*-propenyllithium at −78°C. The resulting **9c** was contaminated by ca. 15% of the corresponding *Z*-propenylboronate. Formation of the latter is a known[18] side reaction on treating (α-chloroalkyl)boronates with propenyllithium. The configuration of the newly formed stereocenter in **9c** was assigned on the basis of the well-founded stereochemical studies of Matteson[8]. The diastereomeric purity of **9c**, i.e. the level of asymmetric induction in the formation of **10c** could not easily be evaluated. The fact, that **9c** showed only one set of signals in the ^{13}C-NMR spectrum does not in itself proove the diastereomeric purity. Therefore, (*S,S,S*)-**9c** was added to benzaldehyde to give the homoallyl alcohol **11**[1] (71%).



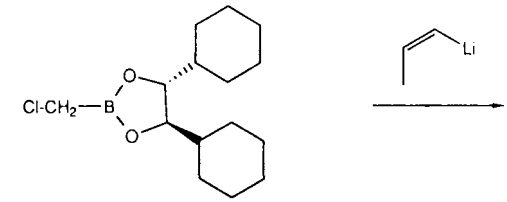
9c **11**

The enantiomeric purity of **11** was determined by gas chromatography on a chiral capillary column[19] to be 99%. This indicates a similarly high diastereomeric purity of **9c**. The high level of chirality transfer in this reaction could in principle be ascribed in part to the presence of the chiral auxiliary. We therefore evaluated the influence of the chiral auxiliary in a separate set of experiments (**12** → **13** → **14**).

The chiral (chloromethyl)boronate **12** was prepared from diisopropyl (chloromethyl)boronate[20] and converted into the *Z*-butenylboronate **13** (ca. 45%) contaminated by ca. 30% of the corresponding propenylboronate. Reaction of this mixture with benzaldehyde led to practically racemic



syn-homoallyl alcohol **14**. Therefore, there is no noticeable asymmetric induction by the dicyclohexyl-ethanediol chiral auxiliary in the crotylboronate addition to aldehyde. This contrasts with the high asymmetric induction that may be achieved with crotylboronates bearing tartrates as chiral auxiliaries[21]. In consequence, the high asymmetric induction attained on addition of **9c** to benzaldehyde stems solely from the stereochemical purity of the chiral center α to the boron atom in **9c**.



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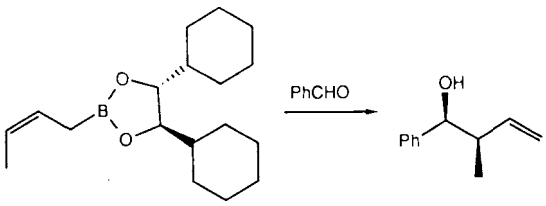
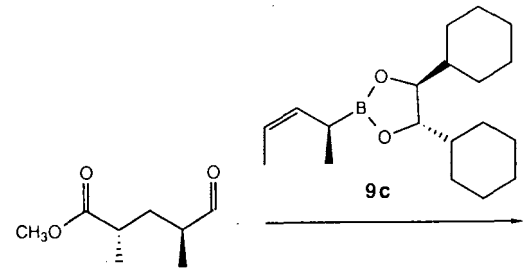
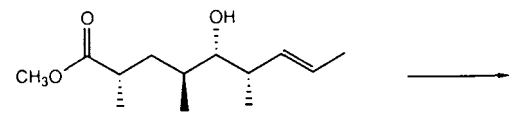


13 **14**



9c

15



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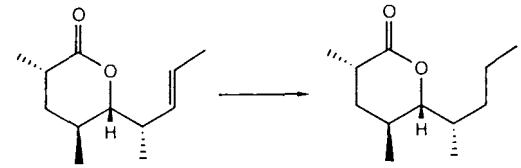


17 **18**

Addition of (*S,S,S*)-Pentenylboronate 9c to Chiral Aldehydes, Synthesis of Invictolide

On addition of **9c** to chiral aldehydes the formation of the new stereogenic centers should be controlled by the asymmetric induction of the reagent. We tested this in the reaction of *S,S,S*-**9c** with the aldehyde **15**, which was prepared from *d,l*-2,4-dimethylglutaric acid[22]. The diacid was resolved[23] and converted into the aldehyde **15** by standard transformations, cf. ref.[24]. The intermediates were characterized by their spectra only.

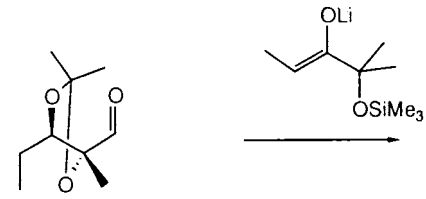
Reaction of the aldehyde **15** with the *S,S,S*-pentenylboronate **9c** produced a single isomer of the hydroxy ester **16** (67%). Saponification of the latter followed by lactonisation led to **17** (92%).

The identity of this lactone was established by hydrogenation to the known natural product (*S,S,S,S*)-invictolide[25,26].

This synthesis of (*S,S,S,S*)-invictolide (**18**) is among the shortest ones. It follows the same pattern as that of Yamamoto[26]. Due to the chiral reagent **9c** it is, however, fully stereospecific.

Synthesis of a C-9/C-15-Partial Structure of Erythronolide A

Another structure of interest containing a *syn* arrangement of a methyl and hydroxyl group is **25** representing the C-9 to C-15 segment of erythronolide A. This segment could in principle be obtained by chain extension from the aldehyde **24**, provided this can be realized with sufficient stereoselectivity. Early investigations by Heathcock[27] in the racemic series using the aldol addition showed that the substrate-based asymmetric induction of **19** led predominantly (3:1) to the undesired stereoisomer **20**. Hence, reagent control of diastereoselectivity[4] is required to attain the desired stereo structure **21**.



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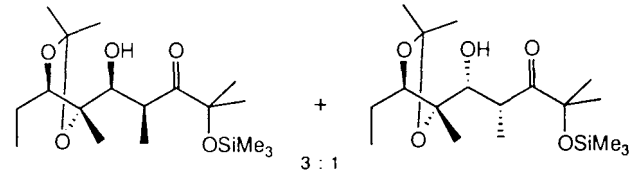
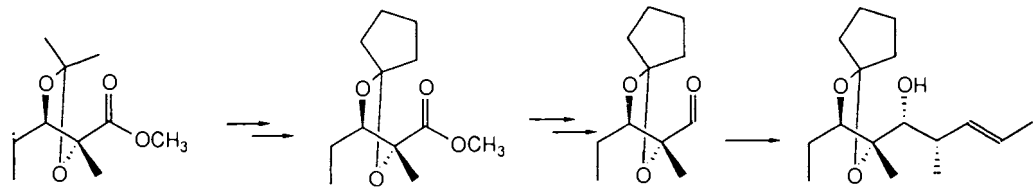


20 **21**

Earlier on we have described a route to the enantiomerically pure ester **22** from D-fructose[28]. In connection with our synthesis of methynolide[29] we required a more labile



22 23 24 25

protective group, therefore the acetonide function in **22** was changed to the cyclopentylidene group (50%).

The resulting ester **23** was converted into the aldehyde **24** (73%) by reduction and Swern oxidation. In an exploratory experiment, the aldehyde **24** was allowed to react with the *S,S,S*-boronate **9c** for three days at 4 kbar pressure. The product was a 2:1 mixture of **25** and unreacted aldehyde. The new alcohol was obtained as a single stereoisomer as judged from the ^{13}C-NMR spectrum. The alcohol clearly contained an *E*-double bond (15.5 Hz coupling constant in the ^{1}H-NMR spectrum). Thus, based on the sense of chirality transfer inherent in **9c** the obtained alcohol should have the desired structure **25**. In a second experiment, the reactands were heated for 2 d to 50°C instead of applying high pressure. This resulted in only 11% of recovered aldehyde **24**, while the yield of the desired alcohol **25** was increased to 71%. However, probably as a consequence of the higher reaction temperature, 7% of an additional isomer having a *Z*-double bond was formed.

In summary, the chain extension of **24** with **9c** represents a viable route to the erythronolide A building block **25**. Aside from the avoidable protective group change **22** → **23**, the aldehyde **24** could be prepared in 8 steps from D-fructose. This is quite long for a compound with two stereogenic centers, but quite normal for carbohydrate-based syntheses[30]. The increase in complexity in going from **24** to **25** is rapid. Thus, the building block **25** with four stereogenic centers is available in nine steps overall. Compared to previously reported methods for the generation of similar building blocks comprising the C-9/C-15 structure of erythronolide A[31-37], the route to **25** reported here is at present still competitive.

We thank the *Deutsche Forschungsgemeinschaft* (SFB 260) and the *Fonds der Chemischen Industrie* for support of this study. We acknowledge the skillful help of *T. Bube*. We are particularly grateful to Prof. *D. S. Matteson* for his patient and constant advice during the critical phases of this work. We would like to thank Prof. *S. Schreiber*, Harvard University, and Prof. *J. Mulzer*, Berlin, for sending us spectra of authentic invictolide, as well as Prof. *F. Hensel*, Marburg, for permission to use his high pressure equipment. We thank the *BASF Aktiengesellschaft* for supply of chemicals.

Experimental

All temperatures quoted are not corrected. – ^{1}H NMR: Bruker WH 400. – ^{13}C NMR: Bruker WH 400 and Varian XL 100. – Preparative gas chromatography: Wilkens Aerograph A-90-P3, 1.5 m × 0.6 cm column with 5% Apiezon on chromosorb G, AW-DMCS, 60–80 mesh, 200 ml He/min. – Analytical gas chromatography: Siemens Sichromat 3 with 50 m × 0.5 mm glass capillary column with XE 60 (*S*)-Valine-(*S*)-α-phenylethylamide[19]; 1 bar He. – Optical rotations: Perkin-Elmer Polarimeter 141.

1) *(1S,2S)-1,2-Dicyclohexyl-1,2-ethanediol:* To a solution of 7.50 g (35 mmol) of (*S,S*)-hydrobenzoin[13] in 30 ml of methanol was added 0.4 g of 5% rhodium on alumina. The mixture was vigorously stirred at 60°C under 7 bar of hydrogen. After the hydrogen uptake had ceased (ca. 36 h), the slushy mixture was taken up in 100 ml of ether and filtered. The filtrate was concentrated to 20 ml and chromatographed over 30 g of silica gel with ether. Some dicyclohexylethane was eluted with the first solvent. The main fractions were concentrated and recrystallized from 200 ml of petroleum ether (b.p. 60–90°C)/chloroform = 4:1 to give 6.66 g 84% of (*S,S*)-1,2-dicyclohexyl-1,2-ethanediol of m.p. 136–137°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.0–1.85 (m, 24H), 3.33 (d, *J* = 5.7 Hz, 2H)[38]. – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 26.1, 26.2, 26.4, 28.2, 29.6, 40.4, 75.1. – $[\alpha]_D^{20}$ = +2.6 (*c* = 0.78 in $CHCl_3$).

$C_{14}H_{26}O_2$ (226.4) Calcd. C 74.28 H 11.56
Found C 74.17 H 11.75

2) *(4S,5S)-2-Dichloromethyl-4,5-dicyclohexyl-1,3,2-dioxaborolane* (**7c**): A solution of 5.50 g (25.9 mmol) of diisopropyl (dichloromethane)boronate and 5.85 g (25.9 mmol) of (*S,S*)-1,2-dicyclohexyl-1,2-ethanediol in 100 ml of *n*-hexane was stirred for 30 min at room temperature. A 2-propanol/*n*-hexane azeotrope (b.p. 57°C) was distilled from the mixture over a 20-cm column. The residual solvents were removed i. vac. from a bath of 60°C to give a solid residue which was recrystallized from 50 ml of petroleum ether (b.p. 40–60°C): 8.24 g (100%) of **7c**, m.p. 50.5°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94–1.30 (m, 8H), 1.38–1.44 (m, 12H), 1.55–1.82 (m, 12H), 4.05 (dd, *J* = 8.6 and 3.8 Hz, 2H), 5.38 (s, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 25.8, 25.9, 26.3, 27.1, 28.1, 42.7, 84.9. – $[\alpha]_D^{20}$ = –64.0 (*c* = 10.3 in $CDCl_3$).

$C_{15}H_{25}BCl_2O_2$ (319.1) Calcd. C 56.46 H 7.90
Found C 56.51 H 8.03

3) *(4S,5S)-4,5-Dicyclohexyl-2-[(1S,2Z)-1-methyl-2-butenyl]-1,3,2-dioxaborolane* (**9c**): To a solution of 2.87 g (9.0 mmol) of **7c** in 30 ml of THF was added at –78°C over 10 min 8.5 ml of a 1.05 n solution (9.0 mmol) of methyl-lithium in ether. The resulting suspension was stirred for 45 min at –78°C. A solution of 1.04 g (7.6 mmol) of anhydrous zinc chloride in 10 ml of THF was added slowly via canula. After stirring for 30 min, the clear solution was allowed to reach room temperature. After 3 h the mixture was cooled to –78°C again. 30.0 ml of a 0.30 M solution (9.0 mmol) of *Z*-propenyllithium in ether was added dropwise. The mixture was allowed to reach room temperature and quenched with 20 ml of saturated aqueous NH_4Cl solution. The mixture was extracted three times with 30 ml of ether. The combined organic phases were dried with $MgSO_4$ and concentrated. The crude product was flash-chromatographed over a 16 × 4 cm column with Kieselgel 60 (0.04 to 0.063 mm, Merck) with petroleum ether (b.p. 40–60°C)/ether, 4:1. The resulting 2.06 g of product contained 1.69 g (62%) of **9c** and 0.37 g (15%) of *(4S,5S)-4,5-dicyclohexyl-2-(Z-propenyl)-1,3,2-dioxaborolane.*

9c: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87–1.31 (m, 14H), 1.07 (d, *J* = 7.4 Hz, 3H), 1.51–1.75 (m, 8H), 1.60 (d, *J* = 5.0 Hz, 3H), 2.14–2.22 (m, 1H), 3.82 (d, *J* = 4.3 Hz, 2H), 5.32–5.41 (m, 2H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 12.9, 16.2, 25.9, 26.0, 26.5, 27.2, 28.2, 43.0, 83.2, 122.1, 133.4.

The following signals of the propenylboronate could be recorded: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85–1.30 (m, 14H), 1.55–1.75 (m, 8H), 1.93 (dd, *J* = 6.9 and 1.5 Hz, 3H), 3.83 (d, *J* = 3.9 Hz, 2H), 6.65 (m, 1H), 5.35 (dq, *J* = 13.6 and 1.5 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4, 24.5, 25.6, 26.0, 27.5, 28.5, 43.0, 83.3, 149.6.

4) *(1R,2S,3E)-2-Methyl-1-phenyl-3-penten-1-ol* (**11**): To a solution of 0.96 g (2.4 mmol) of **9c** as obtained under 3) in 5 ml of petroleum ether (b.p. 40–60°C) was added 0.25 g (2.4 mmol) of benzaldehyde. After 12 h the mixture was concentrated and taken up in 10 ml of ether. After addition of 0.35 g (2.4 mmol) of triethanolamine the mixture was kept under reflux for 4 h. The resulting boratrane was filtered and washed three times with 20 ml each of ether. The filtrate was stirred intensively with 50 ml of a 20proz. aqueous solution of $NaHSO_3$. The phases were separated and the aqueous phase was extracted twice with 20 ml each of ether. The combined organic extracts were washed with 10 ml of water and 10 ml of saturated NaCl solution and subsequently dried with $MgSO_4$. Concentration i. vac. gave 0.52 g of an oil which was subjected to short-path distillation at 10^{-1} Torr from a bath of 60°C: 0.30 g (71%) of **11**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (d, *J* = 6.9 Hz, 3H), 1.64–1.66 (m, 3H), 1.89 (s, broad, 1H), 2.53 (m, 1H), 4.58 (d, *J* = 5.1 Hz, 1H), 5.34 (ddq, *J* = 15.4, 7.0 and 1.4 Hz, 1H), 5.47 (ddq, *J* = 15.4, 6.5 and 1.0 Hz, 1H), 7.22–7.35 (m, 5H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 14.6, 17.9, 43.6, 77.3, 126.0, 126.4, 127.0, 127.8, 132.8, 142.7. – $[\alpha]_D^{20}$ = +9.7 (*c* = 9.3 in $CDCl_3$). The enantiomeric purity was determined by GC at 160°C to be 99% e.e. Retention times (1*R*,2*S*): 69.9 min, (1*S*,2*R*): 71.6 min.

$C_{12}H_{16}O$ (176.3) Calcd. C 81.77 H 9.15
Found C 81.72 H 9.25

5) *(4R,5R)-2-Chloromethyl-4,5-dicyclohexyl-1,3,2-dioxaborolane* (**12**): 2.52 g (14.1 mmol) of diisopropyl (chloromethaneboronate and 3.20 g (14.1 mmol) of (*R,R*)-1,2-dicyclohexyl-1,2-ethanediol were transesterified as described under 2) to give 4.0 g (100%) of **12** as a colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91–1.40 (m, 12H), 1.57–1.85 (m, 10H), 2.97 (s, 2H), 3.93–3.97 (m, 2H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 25.8, 25.9, 26.3, 27.2, 28.2, 42.8, 84.3. – $[\alpha]_D^{20}$ = +65.4 (*c* = 14.0 in $CDCl_3$). Short-path distillation at 10^{-1} Torr from a bath of 120°C gave a sample for analysis.

$C_{15}H_{26}BClO_2$ (284.6) Calcd. C 63.30 H 9.21
Found C 63.17 H 9.40

6) *(4R,5R)-2-[(2Z)-2-Butenyl]-4,5-dicyclohexyl-1,3,2-dioxaborolane* (**13**): To a solution of 1.42 g (5 mmol) of **12** in 20 ml of ether was added over 5 min at –78°C 9.2 ml of a 0.6 N solution (5.5 mmol) of *Z*-propenyllithium in ether. The mixture was allowed to reach room temperature and quenched with 20 ml of saturated aqueous NH_4Cl solution. The mixture was extracted twice with 20 ml of ether each. The extracts were washed with 10 ml each of water and saturated NaCl solution and subsequently dried with $MgSO_4$. Concentration gave the crude product, which was filtered with CH_2Cl_2 through 50 g of silica gel: 1.10 g of crude **13** containing up to 40% of *(4R,5R)-4,5-dicyclohexyl-2-(Z-propenyl)-1,3,2-dioxaborolane.*

13: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96–1.49 (m, 14H), 1.52–1.89 (m, 10H), 1.59 (dd, *J* = 6.3 and 1.2 Hz, 3H), 3.83–3.89 (m, 2H), 5.42–5.56 (m, 2H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 12.5, 18.4, 25.9, 26.5, 27.3, 28.3, 43.0, 83.2, 125.3, 149.8.

7) *(R*,S*)-1-Hydroxy-2-methyl-1-phenyl-3-butene* (**14**): 1.10 g (ca. 1.5 mmol) of the crude **13** as obtained under 6) and 0.16 g (1.5 mmol) of benzaldehyde were allowed to react as described under 4) to give 0.15 g (62%) of **14**[39]. On determination of the enantiomeric purity as described under 4), the product turned out to be racemic. Retention times (1*R**,2*S**): 48.1 min, (1*S**,2*R**): 50.0 min.

8) *(2S,4S)-2,4-Dimethylglutaric Acid Monomethyl Ester:* To a solution of 6.9 g (48.5 mmol) of (2*S*,4*S*)-2,4-dimethylglutaric anhydride[23] (m.p. 42–43°C) in 4.2 ml of CH_2Cl_2 were added 7.7 g (97 mmol) of pyridine and 4.2 ml of methanol. After stirring for 4 h at room temperature, the mixture was acidified to pH = 1 with hydrochloric acid under cooling. The phases were separated and the aqueous phase was extracted twice with 50 ml each of CH_2Cl_2. The combined organic phases were washed with 20 ml of water and were subsequently dried with $MgSO_4$. Concentration and distillation gave 7.2 g (85%) of the ester with b.p. 82–83°C/0.01 Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, *J* = 7 Hz, 3H), 1.20 (d, *J* = 7 Hz, 3H), 1.78 (t, *J* = 7 Hz, 2H), 2.50 (q, *J* = 7 Hz, 1H), 2.56 (q, *J* = 7 Hz, 1H), 3.68 (s, 3H), 11.5 (s, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 17.4, 17.5, 37.1, 37.46, 37.50, 51.6, 176.7, 182.4. – $[\alpha]_D^{20}$ = +49.8 (1 cm, neat).

9) *Methyl (2S,4S)-5-Hydroxy-2,4-dimethylpentanoate:* To a solution of 1.74 g (10.0 mmol) of the above monoester in 20 ml of ether was added at 0°C 2.16 ml (11.0 mmol) of a 7.1 M solution of BH_3–$S(CH_3)_2$. After the exothermic reaction, the mixture was held 15 min at 0°C and 40 min at room temperature. At 0°C a mixture of 15 ml of glycerol, 5 ml of water, and 300 mg of $NaHCO_3$ was slowly added. The aqueous phase was saturated with NaCl and the phases were separated. The aqueous phase was extracted four times with 20 ml each of ether and the organic phases were washed with 10 ml of saturated aqueous NaCl solution. The organic phases were dried with $MgSO_4$ and concentrated to give 1.57 g (98%) of the alcohol as a colorless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 7 Hz, 3H), 1.15 (d, *J* = 7 Hz, 3H), 1.40–1.58 (m, 2H), 1.67 (sept, *J* = 6.5 Hz, 1H), 1.88 (broad s, 1H), 2.58–2.60 (sext, *J* = 7 Hz, 1H), 3.43–3.50 (m, 2H), 3.68 (s, 3H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 16.4, 17.1, 33.5, 37.0, 37.03, 51.5, 67.7, 177.6.

10) *Methyl (2S,4S)-2,4-Dimethyl-5-oxopentanoate* (**15**): To a solution of 1.12 ml (13.1 mmol) of oxalyl chloride in 25 ml of CH_2Cl_2 was added at –78°C a solution of 1.0 ml (14 mmol) of dimethyl sulfoxide in 2.5 ml of CH_2Cl_2. After 30 min a solution of 1.5 g (9.3 mmol) of the above hydroxy ester in 15 ml of CH_2Cl_2 was added dropwise. After 30 min at –78°C, 6.15 ml (44.2 mmol) of triethylamine was added and the mixture allowed to reach room temperature. 15 ml of water, 6 ml of ether, and 24 ml of petroleum ether (b.p. 40–60°C) were added and the organic phase was separated. It was washed three times with 15 ml each of saturated aqueous NaCl solution. The organic phase was dried with Na_2SO_4 and concentrated at 100 Torr. Rapid bulb-to-bulb distillation of the residue at 0.01 Torr gave 1.40 g (95%) of the aldehyde **15** as colorless oil. This was used immediately since the aldehyde epimerized rapidly on standing either neat or in solution. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (d, *J* = 7.2 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.71 (ddd, *J* = 14.0, 8.3 and 6.2 Hz, 1H), 1.82 (ddd, *J* = 14.0, 7.6 and 6.3 Hz, 1H), 2.37–2.42 (m, 1H), 2.51–2.57 (m, 1H), 3.66 (s, 3H), 9.60 (d, *J* = 1.7 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 13.6, 17.3, 34.2, 37.0, 44.2, 51.6, 176.5, 203.9.

11) *(3S,5S,6S)-Tetrahydro-3,5-dimethyl-6-[(1S,2E)-1-methyl-2-butenyl]-2H-pyran-2-one* (**17**): 1.6 g (11 mmol) of the aldehyde **15** and 2.9 g (9.5 mmol) of **9c** were dissolved in 5 ml of petroleum ether (b.p. 40–60°C) and pressurized for 18 h to 4 kbar. To the resulting mixture was added a solution of 1.5 g (10 mmol) of triethanolamine

in 80 ml of ether. After heating for 4 h under reflux the mixture was cooled. The supernatant solution was decanted from the boratrane and filtered over 10 g of alumina. Concentration and flash chromatography over a 15 × 1 cm column of silica gel with petroleum ether (b. p. 40–60°C)/ether = 4:1 gave 0.7 g of unreacted **15**, 0.20 g of the lactone **17**, and 1.46 g (67%) of *methyl (2S,4S,6S,7E)-5-hydroxy-2,4,6-trimethyl-7-nonenoate* (**16**). – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 7.0 Hz, 3H), 1.46–1.56 (m, 3H), 1.61–1.72 (m, 4H), 2.31 (sext, *J* = 6.6 Hz, 1H), 2.46–2.55 (m, 1H), 3.16 (q, *J* = 5.4 Hz, 1H), 3.65 (s, 3H), 5.34 (ddq, *J* = 15.4, 7.5 and 1.5 Hz, 1H), 5.48 (dqd, *J* = 15.4, 6.3 and 1.0 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 14.9, 16.1, 16.2, 17.7, 33.0, 34.3, 36.9, 39.6, 51.2, 79.3, 124.8, 134.2, 177.6.

0.23 g (1.07 mmol) of the hydroxy ester **16** was stirred for 5 h with a solution of 0.56 g (10.0 mmol) of KOH in 1 ml of water and 10 ml of methanol. The mixture was acidified with 5 N hydrochloric acid to pH = 2 and extracted 5 times with 20 ml of ether each. The extracts were dried with $MgSO_4$ and concentrated to give a colorless oil which was flash-chromatographed on a 1.4 × 20 cm column of silica gel with petroleum ether (b. p. 40–60°C)/ether = 4:1; 0.18 g (92%) of **17**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.9 Hz, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.63–1.69 (m, 5H), 1.93–2.00 (m, 1H), 2.34–2.41 (m, 1H), 2.55–2.63 (m, 1H), 3.86 (dd, *J* = 9.3 and 3.3 Hz, 1H), 5.44–5.58 (m, 2H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 13.4, 16.4, 17.7 (2C), 28.4, 32.2, 34.9, 38.5, 86.8, 125.2, 133.5, 176.2.

12) *(3S,5S,6S)-Tetrahydro-3,5-dimethyl-6-[(1S)-1-methylbutyl]-2H-pyran-2-one* (**18**, invictolide): A solution of 0.49 g (2.5 mmol) of **17** in 10 ml of methyl acetate was stirred with 100 mg of 10% Pd on carbon for 24 h under 1 bar of hydrogen. The mixture was filtered through 10 g of Al_2O_3, concentrated, and flash-chromatographed as described under 12) to give 0.42 g (84%) of invictolide (**18**). The compound was identified by its NMR spectra: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.6 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 3H), 1.19–1.44 (m, 5H), 1.60 (t, *J* = 8.2 Hz, 2H), 1.86–1.96 (m, 1H), 2.56 (qt, *J* = 7.0 and 6.0 Hz, 1H), 3.82 (dd, *J* = 10.1 and 2.1 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 12.2, 14.0, 16.5, 17.6, 20.3, 28.3, 32.4, 33.6, 35.4, 36.0, 85.7, 176.5. – $[\alpha]_D^{20}$ = 103 (*c* = 4.57, $CDCl_3$), cf. ref.[25d,25h] 101; ref.[25g] 77.4.

13) *Methyl (2R,3R)-2,3-Dihydroxy-2-methylpentanoate:* 4.06 g (20 mmol) of methyl (4*R*,5*R*)-5-ethyl-2,2,4-trimethyl-1,3-dioxolane-4-carboxylate (**22**) was heated in 20 ml of a 3:3:2 mixture of acetic acid/THF/water for 14 h at reflux. After concentration i. vac. the residue was taken up in 20 ml of ether. It was washed three times with 10 ml each of aqueous saturated $NaHCO_3$ solution. The aqueous extracts were saturated with ammonium sulfate and extracted twice with 10 ml of ether each. The combined organic phases were dried with Na_2SO_4 and concentrated i. vac. Bulb-to-bulb distillation of the residue from a bath of 110°C gave 2.00 g (62%) of the dihydroxy ester as a colorless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.4 Hz, 3H), 1.34–1.40 (m, 2H), 1.42 (s, 3H), 2.19 (d, *J* = 8.2 Hz, 1H), 3.44 (s, 1H), 3.44–3.46 (m, 1H), 3.77 (s, 3H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 10.7, 22.3, 24.6, 52.6, 77.3, 77.7, 175.8. – $[\alpha]_\lambda^{20}$ (nm) = 0.6 (589), –0.1 (546), –5.6 (436), –19.4 (365) (*c* = 11.0 in $CDCl_3$). – A sample was purified by gas chromatography (100°C).

$C_7H_{14}O_4$ (162.2) Calcd. C 51.84 H 8.70
Found C 51.96 H 8.79

14) *Methyl (2R,3R)-3-Ethyl-2-methyl-1,4-dioxaspiro[4.4]nonane-2-carboxylate* (**23**): To a mixture of 5.13 g (31.6 mmol) of the above dihydroxy ester, 17.0 ml of cyclopentanone, and 10.0 ml of 1,1-dimethoxycyclopentane was added 0.3 g *p*-toluenesulfonic acid. After stirring for 4 h at room temp. the volatile components were removed at 0.1 Torr from a bath of 85°C. The residual liquid was filtered through 20 g of silica gel with ether. The filtrate was concentrated to leave 5.76 g (80%) of the spiro acetal **23** as a colorless liquid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.2 Hz, 3H), 1.34–1.77 (m, 8H), 1.45 (s, 3H), 1.86–1.93 (m, 1H), 2.04–2.11 (m, 1H), 3.60 (dd, *J* = 9.2 and 4.0 Hz, 1H), 3.68 (s, 3H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 10.9, 22.1, 22.9 (2C), 23.6, 36.4, 37.6, 51.7, 82.9, 86.0, 119.0, 172.9. – $[\alpha]_\lambda^{20}$ (nm) = 36.7 (578), 67.6 (436), 98.7 (365) (*c* = 18.05 in $CDCl_3$). – For analysis a sample was subjected to short-path distillation at 12 Torr from a bath of 100°C.

$C_{12}H_{20}O_4$ (228.3) Calcd. C 63.13 H 8.83
Found C 63.23 H 8.70

15) *(2R,3S)-2-Ethyl-3-hydroxymethyl-3-methyl-1,4-dioxaspiro[4.4]nonane:* A solution of 2.50 g (11.0 mmol) of the ester **23** in 10 ml of ether was added over 1 h at 0°C to a suspension of 0.91 g (24.0 mmol) of $LiAlH_4$ in 10 ml of ether. After the reaction subsided, the mixture was stirred for 4 h at room temperature and hydrolyzed at 0°C by dropwise addition of water until the inorganic hydroxides precipitated. The supernatant liquid was decanted and the residue was extracted 5 times with 20 ml each of boiling ether. The combined organic phases were washed with 10 ml of brine and subsequently dried with Na_2SO_4. Concentration gave 1.75 g (79%) of the crude alcohol as a colorless oil. – ^{1}H NMR (400 MHz, C_6D_6): δ = 0.90 (t, *J* = 7.4 Hz, 3H), 1.09 (s, 3H), 1.16–1.95 (m, 10H), 3.26 and 3.44 AB system (J_{AB} = 10.9 Hz, 2H), 3.42 (dd, *J* = 9.6 and 3.9 Hz, 1H), 4.10 (s, broad, 1H). – ^{13}C NMR (25 MHz, C_6D_6): δ = 11.7, 21.2, 21.6, 23.5, 24.2, 38.0, 38.3, 65.3, 81.6, 85.3, 117.2. – For analysis a sample was subjected to short-path distillation at 12 Torr from a bath of 100°C

$C_{11}H_{20}O_3$ (200.3) Calcd. C 65.97 H 10.07
Found C 65.90 H 10.21

16) *(2R,3R)-3-Ethyl-2-methyl-1,4-dioxaspiro[4.4]nonane-2-carbaldehyde* (**24**): To a solution of 1.42 g (11.1 mmol) of oxalyl chloride in 10 ml of CH_2Cl_2 was added over 10 min at –78°C a solution of 0.90 g (11 mmol) of dimethyl sulfoxide in 2 ml of CH_2Cl_2. After stirring for 20 min, the mixture was allowed to reach –50°C. Over 10 min a solution of 1.54 g (7.7 mmol) of the above prepared alcohol in 5 ml of CH_2Cl_2 was added. After 30 min at –50°C 2.96 g (29.0 mmol) of triethylamine was added dropwise. The mixture was allowed to reach 0°C. Then 10 ml of water was added under vigorous stirring. The phases were separated and the aqueous phase was extracted three times with 20 ml each of a 4:1 mixture of petroleum ether (b. p. 40–60°C) and ether. The combined extracts were dried with $MgSO_4$ and concentrated i. vac. The crude aldehyde was chromatographed over 30 g of silica gel with ether to give 1.40 g (92%) of **24** as a slightly tan oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3H), 1.28 (s, 3H), 1.42–1.56 (m, 2H), 1.65–1.87 (m, 6H), 1.90–2.08 (m, 2H), 3.67 (t, *J* = 6.8 Hz, 1H), 9.60 (s, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 11.1, 18.8, 22.4, 23.4, 24.3, 37.9, 38.0, 85.3, 86.5, 119.6, 201.9. – For analysis a sample was subjected to short-path distillation at 12 Torr from a bath of 60°C.

$C_{11}H_{18}O_3$ (198.3) Calcd. C 66.64 H 9.15
Found C 66.76 H 9.34

17) *Reaction of* **24** *with the Pentenylboronate* **9c**: To a solution of 0.71 g (3.61 mmol) of the aldehyde **24** in 8 ml of petroleum ether (b. p. 40–60°C) was added dropwise a solution of 1.10 g (3.61 mmol) of **9c** in 5 ml of petroleum ether. The mixture was heated

for 2 d under reflux. 0.53 g (3.61 mmol) of triethanolamine was added at room temperature. The mixture was held under reflux for additional 3 h and was quenched with 10 ml of saturated aqueous NH_4Cl solution. The phases were separated and the aqueous phase was extracted three times with 15 ml each of ether. The combined organic phases were dried with $MgSO_4$ and concentrated i. vac. The residual oil was flash-chromatographed over 15 cm of silica gel 60 (Merck) with petroleum ether (b.p. 40–60°C)/ether = 10:1. This resulted in 77 mg (11%) of **24**, 687 mg (71%) of **25**, 67 mg (7%) of an isomer, and 550 mg (68%) of *S,S*-dicyclohexylethanediol.

(2R,3S)-2-Ethyl-3-[(1R,2S,3E)-1-hydroxy-2-methyl-3-pentenyl]-3-methyl-1,4-dioxaspiro[4,4]nonane (**25**): ^1H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.4 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.21 (s, 3H), 1.7–1.9 (m, 10H), 1.65 (dd, *J* = 6.2 and 1.3 Hz, 3H), 2.30 (qd, *J* = 7.0 and 2.9 Hz, 1H), 2.35 (d, *J* = 5.6 Hz, 1H), 3.42 (dd, *J* = 5.5 and 3.0 Hz, 1H), 3.55 (dd, *J* = 9.5 and 4.1 Hz, 1H), 5.42 (dqd, *J* = 15.3, 6.0, and 0.8 Hz, 1H), 5.53 (ddq, *J* = 15.3, 6.1 and 1.4 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.6, 14.2, 17.9, 22.2, 22.3, 23.1, 24.1, 37.2, 37.7, 38.8, 75.2, 83.2, 87.7, 117.1, 123.6, 136.1.

$C_{16}H_{28}O_3$ (268.4) Calcd. C 71.60 H 10.51
Found C 71.55 H 10.54

The minor product, probably *(2R,3S)-2-ethyl-3-[(1S,2R,3Z)-1-hydroxy-2-methyl-3-pentenyl]-3-methyl-1,4-dioxaspiro[4.4]nonane*, showed the following NMR spectra: ^1H NMR (400 MHz, $CDCl_3$): δ = 1.00 (t, *J* = 7.4 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.23 (s, 3H), 1.65 (dd, *J* = 6.8 and 1.7 Hz, 3H), 1.50–1.70 (m, 5H), 1.81–1.95 (m, 6H), 2.95 (d of quint of d, *J* = 10.1, 5.8, and 0.8 Hz, 1H), 3.39 (dd, *J* = 5.4 and 3.8 Hz, 1H), 3.52 (dd, *J* = 10.1 and 3.5 Hz, 1H), 5.33 (tq, *J* = 10.8 and 1.7 Hz, 1H), 5.58 (dqd, *J* = 10.8, 6.8 and 0.7 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 13.3, 18.6, 19.2, 22.0, 23.3, 23.5, 33.6, 38.2, 38.4, 75.0, 83.0, 87.4, 117.0, 125.8, 132.6.

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[1] For part XXX see: M. Andersen, B. Hildebrandt, G. Köster, R. W. Hoffmann, *Chem. Ber.* **122** (1989) 1777; preceding paper.
[2] R. W. Hoffmann, *Angew. Chem.* **99** (1987) 503; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 489.
[3] R. W. Hoffmann, *Angew. Chem.* **94** (1982) 569; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 555.
[4] S. Masamune, W. Choy, J. S. Petersen, L. R. Sita, *Angew. Chem.* **97** (1985) 1; *Angew. Chem. Int. Ed. Engl.* **24** (1985) 1.

[5] K. Ditrich, T. Bube, R. Stürmer, R. W. Hoffmann, *Angew. Chem.* **98** (1986) 1016; *Angew. Chem. Int. Ed. Engl.* **25** (1986) 1028.
[6] F. Johnson, *Chem. Rev.* **68** (1968) 375.
[7] D. S. Matteson, D. Majumdar, *J. Am. Chem. Soc.* **102** (1980) 7588.
[8] [8a] D. S. Matteson, A. A. Kandil, *Tetrahedron Lett.* **27** (1986) 3831. – [8b] D. S. Matteson, *Acc. Chem. Res.* **21** (1988) 294.
[9] D. S. Matteson, *Synthesis* **1986**, 973.
[10] R. W. Hoffmann, B. Landmann, *Chem. Ber.* **119** (1986) 2013.
[11] R. W. Hoffmann, S. Dresely, J. W. Lanz, *Chem. Ber.* **121** (1988) 1501; e.g. reaction of **7c** via **8c** gave 1-*epi*-**9c** (58%) of only 85% d.e.
[12] K. M. Sadhu, D. S. Matteson, G. D. Hurst, J. M. Kurosky, *Organometallics* **3** (1984) 804.
[13] E. N. Jacobsen, I. Markó, W. S. Mungall, G. Schröder, K. B. Sharpless, *J. Am. Chem. Soc.* **110** (1988) 1968.
[14] F. Dietl, J. Haunschild, A. Merz, *Tetrahedron* **41** (1985) 1193.
[15] J. Brugidou, H. Christol, R. Sales, *Bull. Soc. Chim. Fr.* **1974**, 2033.
[16] [16a] M. W. Rathke, E. Chao, G. Wu, *J. Organomet. Chem.* **122** (1976) 145. – [16b] P. G. M. Wuts, P. A. Thompson, *J. Organomet. Chem.* **234** (1982) 137. – [16c] H. C. Brown, T. E. Cole, *Organometallics* **2** (1983) 1316.
[17] D. S. Matteson, E. C. Beedle, *Tetrahedron Lett.* **28** (1987) 4499.
[18] W. R. Roush, M. A. Adam, A. E. Walts, D. J. Harris, *J. Am. Chem. Soc.* **108** (1986) 3422.
[19] W. A. König, W. Francke, I. Benecke, *J. Chromatogr.* **239** (1982) 227.
[20] K. M. Sadhu, D. S. Matteson, *Organometallics* **4** (1985) 1687.
[21] W. R. Roush, R. L. Halterman, *J. Am. Chem. Soc.* **108** (1986) 294.
[22] [22a] K. Auwers, J. F. Thorpe, *Liebigs Ann. Chem.* **285** (1895) 310. – [22b] N. L. Allinger, *J. Am. Chem. Soc.* **81** (1959) 232.
[23] N. Gruenfeld, J. L. Stanton, A. M. Yuan, F. H. Ebetino, L. J. Browne, C. Gude, C. F. Huebner, *J. Med. Chem.* **26** (1983) 1277.
[24] [24a] S. Masamune, S. A. Ali, D. L. Snitman, D. S. Garvey, *Angew. Chem.* **92** (1980) 573; *Angew. Chem., Int. Ed. Engl.* **19** (1980) 557. – [24b] P. A. Bartlett, J. L. Adams, *J. Am. Chem. Soc.* **102** (1980) 337. – [24c] R. W. Hoffmann, H.-J. Zeiß, W. Ladner, S. Tabche, *Chem. Ber.* **115** (1982) 2357.
[25] [25a] J. R. Rocca, J. H. Tumlinson, B. M. Glancey, C. F. Lofgren, *Tetrahedron Lett.* **24** (1983) 1893. – [25b] T. R. Hoye, D. R. Peck, T. A. Swanson, *J. Am. Chem. Soc.* **106** (1984) 2738. – [25c] S. L. Schreiber, Z. Wang, *J. Am. Chem. Soc.* **107** (1985) 5303. – [25d] K. Mori, Y. Nakazono, *Tetrahedron* **42** (1986) 6459. – [25e] S. Senda, K. Mori, *Agr. Biol. Chem.* **51** (1987) 1379. – [25f] T. Wakamatsu, Y. Nishikimi, H. Kikuiri, H. Nakamura, Y. Ban, *Heterocycles* **26** (1987) 1761. – [25g] F. E. Ziegler, W. T. Cain, A. Kneisley, E. P. Stirchak, R. T. Wester, *J. Am. Chem. Soc.* **110** (1988) 5442. – [25h] G. Funk, *Diplomarbeit*, Freie Universität, Berlin **1987**. – [25i] M. Balestra, J. Kallmerten, *Tetrahedron Lett.* **29** (1988) 6901.
[26] Y. Yamamoto, K. Taniguchi, K. Maruyama, *J. Chem. Soc., Chem. Commun.* **1985**, 1429.
[27] C. H. Heathcock, S. D. Young, J. P. Hagen, M. C. Pirrung, C. T. White, D. VanDerveer, *J. Org. Chem.* **45** (1980) 3846.
[28] R. W. Hoffmann, W. Ladner, *Chem. Ber.* **116** (1983) 1631.
[29] K. Ditrich, *Dissertation*, Univ. Marburg 1986.
[30] A. Vasella, *Chiral Building Blocks in Enantiomer Synthesis – Ex Sugars*, in *Modern Synthetic Methods* (R. Scheffold, Ed.), vol. 2, p. 173, Salle & Sauerländer, Frankfurt a. M., 1980.
[31] T. Nakata, M. Fukui, T. Oishi, *Tetrahedron Lett.* **29** (1988) 2219.
[32] A. R. Chamberlin, M. Dezube, *Tetrahedron Lett.* **23** (1982) 3055.
[33] G. Stork, S. D. Rychnovsky, *J. Am. Chem. Soc.* **109** (1987) 1564.
[34] Y. Oikawa, T. Nishi, O. Yonemitsu, *J. Chem. Soc. Perkin Trans. 1*, **1985**, 7.
[35] M. Kinoshita, M. Arai, K. Tomooka, M. Nakata, *Tetrahedron Lett.* **27** (1986) 1811.
[36] R. B. Woodward et al., *J. Am. Chem. Soc.* **103** (1981) 3210, 3213, 3215.
[37] N. K. Kochetkov, A. F. Sviridov, M. S. Ermolenko, D. V. Yashunsky, *Tetrahedron Lett.* **25** (1984) 1605.
[38] J. Souppe, L. Danon, J. L. Namy, H. B. Kagan, *J. Organomet. Chem.* **250** (1983) 227.
[39] R. W. Hoffmann, H.-J. Zeiß, *J. Org. Chem.* **46** (1981) 1309.

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