Stereoselective Synthesis of Alcohols, XXIX[1]

Addition of (α-Methoxycrotyl)boronates to Aldehydes

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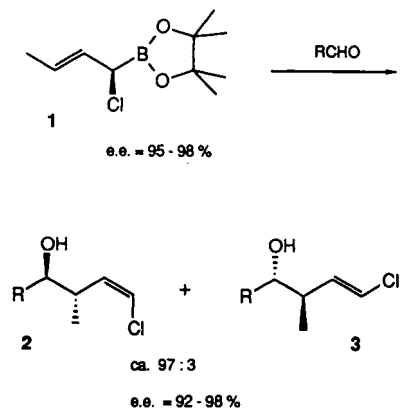
α-Phenoxy- (4) and α-methoxycrotylboronates (8) were obtained from the α-chlorocrotylboronates 1. Addition of the phenoxy compound to aldehydes gave the homoallyl alcohols 5/6 as *Z*/*E* mixtures; addition of the methoxy compound 8 led to essentially pure *Z*-enol ethers 9. Enantiomerically enriched (ca. 90% e.e.) 8 was used in reactions with chiral aldehydes to ensure the formation of the new stereogenic centers under reagent control of diastereoselectivity.

Stereoselektive Synthese von Alkoholen, XXIX[1]. – Addition von (α-Methoxycrotyl)boronsäureestern an Aldehyde

α-Phenoxy- (4) und α-Methoxycrotylboronsäureester 8 wurden aus den α-Chlorcrotylboronsäureestern 1 hergestellt. Die Addition der α-Phenoxy-Verbindung 4 an Aldehyde ergab die Homoallylalkohole 5/6 als *Z*/*E*-Gemische; Addition der Methoxyverbindung 8 führte zu den fast reinen *Z*-Enolethern 9. Enantiomer-angereichertes 8 (ca. 90% e.e.) wurde bei der Addition an chirale Aldehyde eingesetzt, um die Bildung der neuen stereogenen Zentren unter Reagenz-Kontrolle der Stereoselektivität zu gewährleisten.

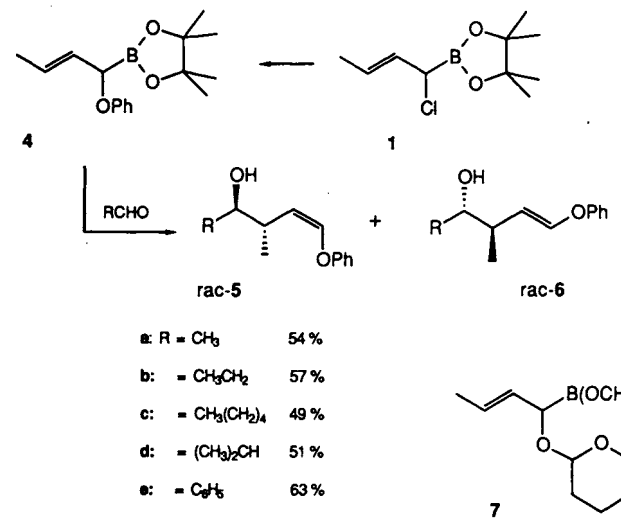
The addition of enantiomerically pure α-chiral *E*-crotylboronates[1,2] (**1**) to aldehydes leads to the homoallyl alcohols **2** and **3**. The new stereogenic centers are generated under transfer of chirality from the boronate reagent to each of the diastereomers **2** and **3** with high levels of asymmetric induction.



When the reaction is applied to chiral aldehydes the **2**:**3** ratio depends in addition on the direction and the magnitude of the asymmetric induction from the aldehyde. When the asymmetric induction of the aldehyde and that of the reagent **1** reinforce each other (matched pair)[3], the alcohol of type **2** is formed exclusively. When, however, the reagent has to override the asymmetric induction of the aldehyde (mismatched pair)[3], the yield of the desired product **2** may become vanishingly small[1]. It is for those situations that novel α-chiral crotylboronates are needed, which have a markedly higher (> 97 : < 3) selectivity than the chloro compound **1** to form the product of type **2**. Precedence with α-substituted allylboronates suggests that α-aryloxy-[4], or α-alkoxy-crotylboronates[5] should have improved selectivity. We report here on our investigation on (*E*)-(α-phenoxy)- and (*E*)-(α-methoxy)crotylboronates. Parts of these results have been communicated in preliminary form[6].

The (*E*)-(α-Phenoxycrotyl)boronate 4

Substitution of α-halo-alkylboronates by lithium alkoxides has previously been realized by Matteson[7,8,9]. Accordingly, reaction of *rac*-**1** with lithium phenoxide in THF gave **4** (70% crude yield) which was added without purification to representative aldehydes. The resulting acid-sensitive enol ethers **5** and **6** were obtained in modest yield. No attempts were made to improve the yields, since in every case the ^{1}H-



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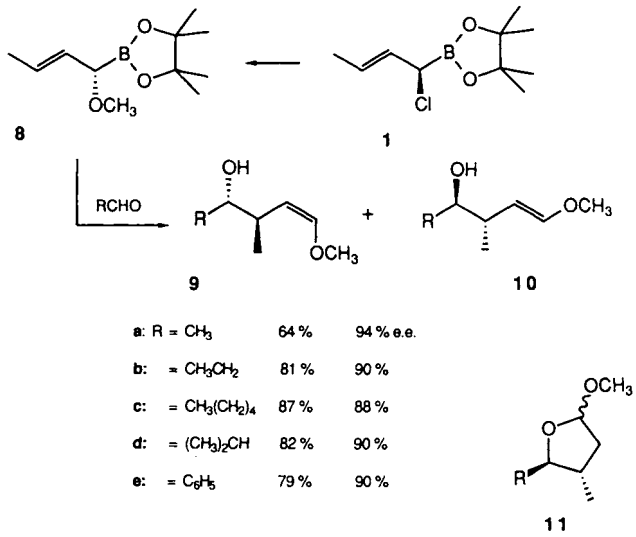
NMR spectra showed that noticeable (ca. 5–10%) amounts of the undesired product **6** had been formed as well. The selectivity of **4** is therefore by no means higher than that of **1**.

The *anti* configuration at the two new stereogenic centers in **5** and **6** has not been secured. It is assigned in analogy to the reactions of **7**[10].

The (*E*)-(α-Methoxycrotyl)boronate 8

In consequence we tested the selectivity of the methoxy reagent **8**, which was obtained in ca. 90% crude yield by reaction of **1** with lithium methoxide in THF.

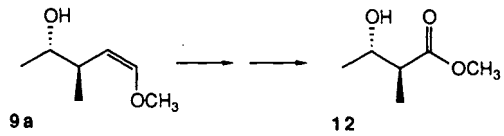


Representative aldehydes were mixed with 1–1.5 equivalents of the crude reagent **8** at −78°C. After warming to room temperature the enol ethers **9** were obtained. NMR spectra of the crude products gave no indication for the formation of the isomeric products **10**. Due to the marked acid sensitivity, NMR spectra were recorded in C_6D_6 and handling, as well as storage of **9**, was possible only in the presence of Na_2CO_3. Intentional treatment of **9c** and **9e** with acid (HCl in methanol) led to immediate formation of the lactol ethers **11** as 3:2 anomeric mixtures. This cyclization could be effected even more easily by treating crude **9a** with a few drops of a solution of iodine in chloroform. Presumably traces of HI present induce the cyclization.

The results of the addition of **8** to aldehydes gathered in the racemic series encouraged us to try to prepare **8** in enantiomerically pure form. Reaction of (*R*)-**1** (98% e.e) with lithium methoxide furnished **8** of presumed (*S*) configuration. Addition of the latter to the aldehydes and determination of the enantiomeric purity of the resulting homoallyl alcohols **9** [by capillary GC after derivatization with (*S*)-(−)-1-phenylethyl isocyanate] showed them to have an e.e. of ca. 90%. We surmise that the loss of ca. 10% of the enantiomeric purity had occurred during the substitution of the chlorine by the methoxide, since the coproduct, LiCl, may also attack the chloro compound **1**[11,12] leading to partial racemisation. The level of this racemisation could so far not be decreased further, but a reagent **8** of 90% e.e. is certainly acceptable.

At this stage the structure of the products **9**, their relative and absolute configuration had to be secured. First, the *Z* configuration of the double bond was evident from the ^{1}H-NMR coupling constant of the vinylic hydrogens of 6.5 Hz. The formation of the product **9** with the electronegative substituent in the *Z* position is in line with precedent from the reaction of α-alkoxy-allylboronates[13] and corresponds to reactions of other α-alkoxy-allyl-metallic compounds[14–16].

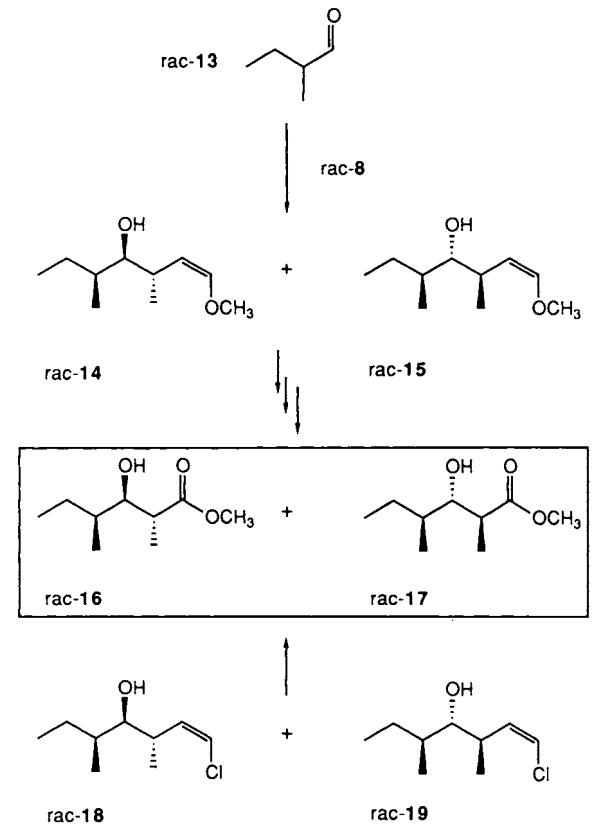
The relative configuration at the two new stereogenic centers was expected to be *anti*[10]. It was proven to be so by the transformation of **9a** into the known[2] methyl *anti*-3-hydroxy-2-methylbutyrate **12**.



The ester **12** was dextrorotatory, proving its (2*S*,3*S*) configuration anticipated if the substitution **1** → **8** occurred with inversion of configuration.

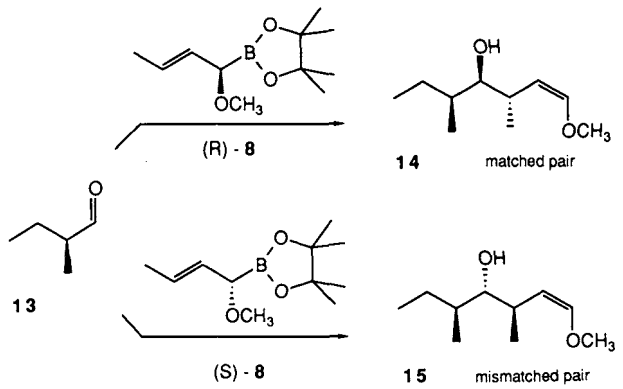
Reactions of (*R*)- and (*S*)-(*E*)-(α-Methoxycrotyl)boronates 8 with Chiral Aldehydes

The ability of the new reagent **8** to react with chiral aldehydes under reagent control of diastereoselectivity[3] was evaluated using the simple chiral aldehyde **13**, since the rel-

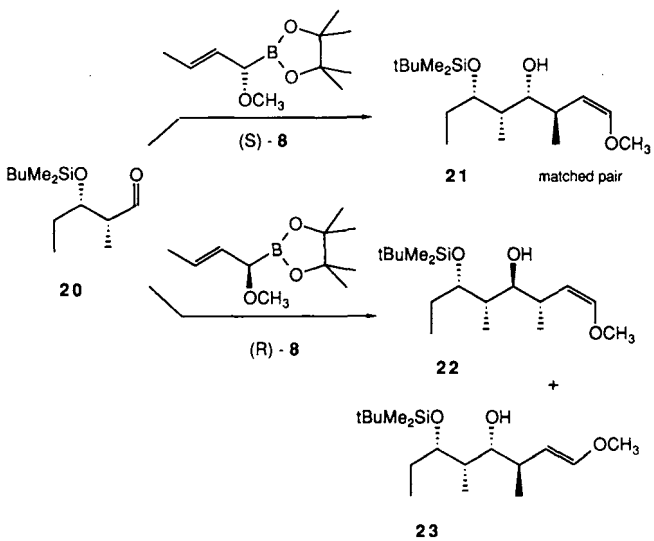


ative configuration of the products **14** and **15** could be easily established. First, *rac*-**8** was added to *rac*-**13** to give 59% of the homoallyl alcohols **14** and **15** in a 4:1 ratio. This mixture was subjected to ozonolysis, followed by oxidation and esterification of the resulting acids to give the esters **16** and **17** in a 4:1 ratio. For comparison, a 4:1 mixture of *rac*-**18** and *rac*-**19** of established relative configuration[2] was ozonized[17] to give a 4:1 mixture of the same esters **16** and **17**.

With the structures of **14** and **15** established it was easy to show that addition of (*R*)-**8** to (*S*)-**13** gave only **14** (matched pair) and that the addition of (*S*)-**8** to (*S*)-**13** gave only **15** in similar yield (mismatched pair).



Compared to the reaction of (*S*)-**13** with (*S*)-**1** this indicated a higher asymmetric induction of the reagent **8**. To give this a more stringent test, the aldehyde **20** was used, which in turn has a higher substrate-based asymmetric induction corresponding to a $\Delta\Delta G^{\neq}$ of ca. 1.2 kcal[1], than the aldehyde **13** ($\Delta\Delta G^{\neq}$ = 0.8 kcal[1]).



In the matched-pair reaction of **20** with 1.2 equivalents of (*S*)-**8** only one product, **21**, was obtained (66%). On reaction of the mismatched pair, two different stereoisomeric products **22** and **23** were obtained in 60 and 6.5% yield, respectively. The minor product had an *E* configurated double bond. The relative configuration of the products **21**, **22**, and **23** was assigned by analogy to the products **14** and **15**, to the reaction of **20** with the chloro reagent **1**, and on mechanistic grounds. On reaction of the mismatched pair, one has to note that the reagent (*R*)-**8** was only of 90% enantiomeric purity, i.e. it contained 5% of (*S*)-**8**. Therefore, in the reaction with **20**, 6.5% of **21** was formed alongside to **22** and **23**. In the matched-pair reaction of **20** with (*S*)-**8** the 5% of the contaminant (*R*)-**8** was reacting ca. 8 times more slowly, so that no **22** was obtained thereof.

In the mismatched reaction of **20** with (*R*)-**8** the product of reagent control of diastereoselectivity **22** dominated by 90:10 over **23**, the product of substrate control of diastereoselectivity. Comparing this result with the corresponding reaction of (*R*)-**1** with **20** having a selectivity of 80:20[1] proves that **8** indeed exerts a more powerful asymmetric induction. This increase in selectivity may seem only minor, even as it corresponds to an increase in the asymmetric induction of the reagent from that of **1** with $\Delta\Delta G^{\neq}$ = 2.0 kcal[1] to that of **8** with $\Delta\Delta G^{\neq}$ = 2.5 kcal. This demonstrates once more how difficult it is to attain reagent control of diastereoselectivity, if it comes to override the asymmetric induction of an aldehyde which has a strong diastereofacial bias of its own, such as **20**. In conclusion, the noticeable improvement in asymmetric induction of the reagent **8** versus that of **1** is at least in this particular case not as high as we had hoped for.

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Experimental

All temperatures quoted are not corrected. – ^{1}H NMR, ^{13}C NMR: Bruker WH 400. – Preparative gas chromatography: Varian Aerograph A-90-P3, 1.5 m × 0.6 cm column with "A": 5% SE 30 or "B": 5% Apiezon on Chromosorb G, AW-DMCS, 60–80 mesh, 200 ml He/min. – Analytical gas chromatography: Perkin-Elmer 900 and Siemens Sichromat 3; "A": 40 m × 0.3 mm glass-capillary column with SE 52, 2.1 bar He; "B": 50 m × 0.5 mm glass-capillary column with XE 60, (*S*)-valine-(*S*)-α-phenylethylamide[18], 1 bar He. – HPLC: Dupont 830 with 25 cm × 60 mm column with LiChrosorb Si 60, 7 µm (Merck). – Optical rotations: Perkin-Elmer Polarimeter 141.

1) *4,4,5,5-Tetramethyl-2-[(2E)-1-phenoxy-2-butenyl]-1,3,2-dioxaborolane* (**4**): A suspension of lithium phenoxide was prepared from 1.40 g (14.8 mmol) of phenol in 20 ml of THF and 9.6 ml of a 1.54 M solution of *n*-butyllithium in hexane at 0°C. This suspension was added via canula to a solution of 3.30 g (15.3 mmol) of 2-[(2*E*)-1-chloro-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**) in 50 ml of THF at −78°C. A homogeneous slightly yellowish solution resulted upon warming to room temperature. After 1 h the solvent was removed i. vac. The residue was partitioned between 100 ml of petroleum ether (b.p. 40–60°C) and 100 ml of a citric acid/boric acid/phosphate buffer[19] of pH = 3. The aqueous phase was extracted twice with 50 ml each of petroleum ether. The combined organic phases were dryed with $MgSO_4$ and concentrated to give 3.62 g of crude **4** as a slightly tan oil, which was used as such. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 12H), 1.70 (d, broad, *J* =

6.3 Hz, 3H), 4.56 (d, broad, J = 6.6 Hz, 1H), 5.63 (ddq, J = 15.0, 6.6 and 1.2 Hz, 1H), 5.75 (ddq, J = 15.0, 6.3 and 1.2 Hz, 1H), 6.81–6.93 (m, 3H), 7.19–7.25 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 24.7, 84.3, 115.5, 120.3, 127.2, 127.7, 129.1, 159.1.

2) *Addition of* **4** *to Aldehydes:* The aldehyde was added at room temperature to a solution of **4** in petroleum ether (b.p. 40–60°C) or CH_2Cl_2. After 24 h the solvent and the excess of the aldehyde was removed i. vac. and the residue was taken up in 100 ml of ether. Triethanolamine was added and the resulting precipitate was filtered after stirring for 4 h. The filtrate was concentrated and the residue chromatographed.

(2R,3S*)-(Z)-3-Methyl-5-phenoxy-4-penten-2-ol* (**5a**): From 3.22 g (11.7 mmol) of **4**, 1.40 g (23.4 mmol) of acetaldehyde, 10 ml of CH_2Cl_2, and 1.70 g (11.7 mmol) of triethanolamine. Chromatography with petroleum ether (b.p. 40–60°C)/ether, 3:2, and 200 g of Al_2O_3 gave 1.21 g (54%) of **5a** as a clear oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (d, J = 6.9 Hz, 3H), 1.21 (d, J = 6.2 Hz, 3H), 1.64 (s, broad, 1H), 2.80 (m, 1H), 3.66 (m, 1H), 4.72 (dd, J = 9.7 and 6.2 Hz, 1H), 6.48 (dd, J = 6.2 and 0.7 Hz, 1H), 7.01 (m, 3H), 7.30 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.9, 20.3, 36.5, 71.1, 114.4, 116.1, 122.4, 129.4, 141.0, 157.2. The presence of ca. 5% of the E isomer was evident from the ^{1}H-NMR spectrum: δ = 6.51 (d, J = 12.4 Hz, 1H) and 5.26 (dd, J = 12.4 and 9.5 Hz, 1H).

For analysis, a small sample was purified by short-path distillation at 60°C/12 Torr.

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.96 H 8.36
Found C 74.79 H 8.45

(3R,4S*)-(Z)-4-Methyl-6-phenoxy-5-hexen-3-ol* (**5b**): From 1.50 g (5.5 mmol) of **4**, 0.32 g (5.5 mmol) of propionaldehyde, 5 ml of petroleum ether, and 0.82 g (5.5 mmol) of triethanolamine. Chromatography with petroleum ether (b.p. 40–60°C)/ether, 3:2, and 45 g of silica gel gave 0.65 g (57%) of **5b** as a clear oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.4 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H), 1.42 (m, 3H), 2.94 (m, 1H), 3.21 (m, 1H), 4.69 (dd, J = 9.8 and 6.2 Hz, 1H), 6.21 (dd, J = 6.2 and 0.8 Hz, 1H), 6.85 (m, 3H), 7.04 (m, 2H). The presence of ca. 5% of the E isomer was evident from δ = 5.28 (dd, J = 12.0 and 9.5 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0, 17.5, 27.5, 34.5, 76.8, 114.0, 116.1, 122.5, 129.4, 140.9, 157.3.

For analysis, a small sample was purified by HPLC with petroleum ether (b.p. 40–60°C)/ether, 9:1, at 69 bar.

$C_{13}H_{18}O_2$ (206.3) Calcd. C 75.69 H 8.80
Found C 75.67 H 8.96

(3R,4S*)-(Z)-3-Methyl-1-phenoxy-1-nonen-4-ol* (**5c**): From 1.50 g (5.5 mmol) of **4**, 0.55 g (5.5 mmol) of hexanal, 5 ml of petroleum ether (b.p. 40–60°C), and 0.82 g (5.5 mmol) of triethanolamine. Chromatography as for **5b** gave 0.67 g (49%) of **5c** as colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, J = 6.9 Hz, 3H), 1.08 (d, J = 6.9 Hz, 3H), 1.35 (m, 8H), 1.60 (s, broad, 1H), 2.88 (m, 1H), 3.47 (m, 1H), 4.75 (dd, J = 9.8 and 6.2 Hz, 1H), 6.45 (dd, J = 6.2 and 0.8 Hz, 1H), 7.00 (m, 3H), 7.29 (m, 2H). The presence of ca. 5% of the E isomer was evident from δ = 6.48 (dd, J = 12.2 and 0.8 Hz, 1H), and 5.28 (dd, J = 12.2 and 9.2 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 17.5, 22.6, 25.5, 31.9, 34.8, 35.0, 75.5, 114.1, 116.2, 122.5, 129.5, 141.1, 157.4.

For analysis, a small sample was purified by short-path distillation at 55°C/0.1 Torr.

$C_{16}H_{24}O_2$ (248.4) Calcd. C 77.38 H 9.74
Found C 77.24 H 9.85

(3R,4S*)-(Z)-2,4-Dimethyl-6-phenoxy-5-hexen-3-ol* (**5d**): From 2.50 g (9.1 mmol) of **4**, 0.67 g (9.3 mmol) of isobutyraldehyde, 10 ml of petroleum ether, and 1.36 g (9.1 mmol) of triethanolamine. Chromatography on 120 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 7:3, gave 1.02 g (51%) of **5d** as a clear oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.95 (d, J = 6.7 Hz, 6H), 1.07 (d, J = 6.9 Hz, 3H), 1.54 (s, broad, 1H), 1.73 (m, 1H), 3.01 (m, 1H), 3.13 (m, 1H), 4.79 (dd, J = 9.8 and 6.2 Hz, 1H), 6.44 (dd, J = 6.2 and 0.7 Hz, 1H), 7.00 (m, 3H), 7.29 (m, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.2, 18.2, 19.7, 31.2, 32.6, 80.8, 114.1, 116.3, 122.6, 129.6, 141.0, 157.4.

For analysis, a sample was purified by short-path distillation at 40°C/0.1 Torr.

$C_{14}H_{20}O_2$ (220.3) Calcd. C 76.33 H 9.15
Found C 76.16 H 9.32

(1R,2R*)-(Z)-2-Methyl-4-phenoxy-1-phenyl-3-buten-1-ol* (**5e**): From 2.50 g (9.1 mmol) of **4**, 0.97 g (9.1 mmol) of benzaldehyde, 10 ml of petroleum ether, and 1.36 g (9.1 mmol) of triethanolamine. Chromatography as for **5d** gave 1.46 g (63%) of **5e** as colourless oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (d, J = 6.9 Hz, 3H), 1.54 (s, broad, 1H), 3.17 (m, 1H), 4.46 (d, J = 7.6 Hz, 1H), 4.79 (dd, J = 9.6 and 6.1 Hz, 1H), 6.48 (dd, J = 6.1 and 0.9 Hz, 1H), 7.00 (m, 3H), 7.30 (m, 7H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4, 37.5, 78.6, 114.4, 116.5, 122.8, 126.9, 127.5, 128.2, 129.6, 141.9, 142.8, 157.4). The presence of ca. 5% of the E isomer was evident from δ = 6.52 (d, J = 12.2 Hz, 1H), and 5.26 (dd, J = 12.2 and 9.2 Hz, 1H).

For analysis, a small sample was purified by short-path distillation at 70°C/0.1 Torr.

$C_{17}H_{18}O_2$ (254.3) Calcd. C 80.28 H 7.13
Found C 79.98 H 7.09

3) *2-[(2E)-1-Methoxy-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**8**): A suspension of lithium methoxide was prepared from 1.00 g (31.2 mmol) of methanol in 50 ml of THF and 17.7 ml (27.2 mmol) of a 1.54 M solution of *n*-butyllithium in *n*-hexane. This suspension was transferred via canula into a solution of 5.86 g (27.1 mmol) of 2-[(2E)-1-chloro-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1**) in 100 ml of THF at –78°C. Upon warming the mixture became homogeneous above 0°C. After 1 h the solvents were removed i. vac. and the residue was taken up in 150 ml of petroleum ether (b.p. 40–60°C). The suspension was washed with a citric acid/boric acid/phosphate buffer[19] of pH = 3 until the aqueous phase showed pH = 4. The aqueous phase was extracted twice with 50 ml of petroleum ether (b.p. 40–60°C). The combined organic phases were dried with $MgSO_4$ and concentrated i. vac. to give 5.34 g (ca. 90%) of crude **8** as slightly tan oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (s, 12H), 1.71 (d, J = 6.5 Hz, 3H), 3.27 (s, 3H), 3.55 (d, J = 8.3 Hz, 1H), 5.45 (ddq, J = 15.2, 8.3 and 1.5 Hz, 1H), 5.67 (ddq, J = 15.2, 6.5 and 0.7 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8, 24.6, 57.3, 84.0, 128.1, 128.5.

For analysis, a sample was purified by short-path distillation at 30°C/0.1 Torr.

$C_{11}H_{21}BO_3$ (212.1) Calcd. C 62.29 H 9.98
Found C 62.41 H 9.99

(*R*)- and (*S*)-**8** of ca. 90% e.e. were prepared similarly from (*S*)- and (*R*)-**1**, respectively.

$[\alpha]_\lambda^{20}$ (c = 10, $CDCl_3$)

λ =	589	578	546	543	365 nm
(*R*)-**8**	–37.8	–40.0	–45.9	–80.0	–129.5
(*S*)-**8**	+34.5	+35.2	+40.9	+72.8	+118.1

4) *Addition of* **8** *to Aldehydes:* To a solution of **8** in petroleum ether (b.p. 40–60°C) was added at −78°C the aldehyde. The mixture was allowed to reach room temperature and to stand for 2 d. It was worked up as described under 1).

(2R,3S*)-(Z)-5-Methoxy-3-methyl-4-penten-2-ol* (**9a**): From 1.70 g (8.0 mmol) of **8**, 0.22 g (5.0 mmol) of acetaldehyde, 5 ml of petroleum ether (b.p. 40–60°C), and 1.16 g (7.6 mmol) of triethanolamine. Chromatography on 45 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 1:1, gave 0.42 g (64%) of **9a** as a clear liquid. – ^{1}H NMR (400 MHz, C_6D_6): δ = 0.98 (d, *J* = 6.9 Hz, 3H), 1.14 (d, *J* = 6.3 Hz, 3H), 1.45 (s, broad, 1H), 2.76 (m, 1H), 3.04 (s, 3H), 3.51 (dq, *J* = 6.3 and 6.1 Hz, 1H), 4.19 (dd, *J* = 9.5 and 6.6 Hz, 1H), 5.65 (dd, *J* = 6.3 and 0.9 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 17.3, 20.7, 37.1, 59.0, 71.4, 108.9, 147.2.

For analysis, a sample was purified by gas chromatography (column "B", 70°C).

$C_7H_{14}O_2$ (130.2) Calcd. C 64.58 H 10.84
Found C 64.47 H 10.93

20 µl of racemic **9a** was derivatized as described in ref.[2] with (*S*)-(−)-1-phenylethyl isocyanate. Analytical GC (column "A", 160°C, 2.6 bar He) showed the 2*R*,3*S* diastereomer to elute after 105.4 min, the 2*S*,3*R* diastereomer after 112.9 min.

(3R,4S*)-(Z)-6-Methoxy-4-methyl-5-hexen-3-ol* (**9b**): From 1.45 g (6.8 mmol) of **8**, 0.27 g (4.6 mmol) of propionaldehyde, 5 ml of petroleum ether (b.p. 40–60°C), and 1.02 g (6.8 mmol) of triethanolamine. Chromatography on 45 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 3:2, gave 0.53 g (81%) of **9b** as colourless liquid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.4 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 1.38 (ddq, *J* = 14.0, 7.5 and 7.2 Hz, 1H), 1.55 (ddq, *J* = 14.0, 7.6 and 4.0 Hz, 1H), 1.72 (d, *J* = 4.0 Hz, 1H), 2.66 (m, 1H), 3.26 (m, 1H), 3.56 (s, 3H), 4.23 (dd, *J* = 9.6 and 6.3 Hz, 1H), 5.97 (dd, *J* = 6.3 and 0.9 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 10.5, 17.9, 28.0, 35.1, 59.0, 76.9, 108.6, 147.5.

For analysis, a sample was purified by GC (column "B", 90°C).

$C_8H_{16}O_2$ (144.2) Calcd. C 66.63 H 11.18
Found C 66.44 H 11.34

20 µl of racemic **9b** was derivatized as described for **9a**. GC analysis (column "A", 180°C, 2.1 bar He) showed the 3*R*,4*S* diastereomer to elute after 72.5 min, the 3*S*,4*R* diastereomer after 76.2 min.

(3R,4S*)-(Z)-1-Methoxy-3-methyl-1-nonen-4-ol* (**9c**): From 1.85 g (8.7 mmol) of **8**, 0.58 g (8.5 mmol) of hexanal, 10 ml of petroleum ether (b.p. 40–60°C), and 1.30 g (8.7 mmol) of triethanolamine. Chromatography on 120 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 7:3, gave 0.94 g (87%) of **9c** as a clear liquid. – ^{1}H NMR (400 MHz, C_6D_6): δ = 0.89 (t, *J* = 7.0 Hz, 3H), 1.06 (d, *J* = 6.9 Hz, 3H), 1.24–1.60 (m, 9H), 2.88 (m, 1H), 3.04 (s, 3H), 3.36 (m, 1H), 4.29 (dd, *J* = 9.6 and 6.3 Hz, 1H), 5.66 (dd, *J* = 6.3 and 0.8 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 14.2, 17.9, 23.1, 26.0, 32.5, 35.2, 35.4, 59.1, 75.5, 108.8, 147.0.

For analysis, a sample was purified by GC (column "B", 130°C).

$C_{11}H_{22}O_2$ (186.3) Calcd. C 70.92 H 11.90
Found C 71.07 H 12.19

20 µl of racemic **9c** was derivatized with isopropyl isocyanate as described in ref.[2]. Analytical GC (column "B", 150°C, 1 bar He) showed the 3*R*,4*S* diastereomer to elute after 71.5 min, the 3*S*,4*R* diastereomer after 72.9 min.

(3R,4S*)-(Z)-6-Methoxy-2,4-dimethyl-5-hexen-3-ol* (**9d**): From 1.45 g (6.8 mmol) of **8**, 0.33 g (4.6 mmol) of isobutyraldehyde, 10 ml of petroleum ether (b.p. 40–60°C), and 1.02 g (6.8 mmol) of triethanolamine. Chromatography on 60 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 3:2, gave 0.59 g (82%) of **9d** as a clear liquid. – ^{1}H NMR (400 MHz, [D_6]Acetone): δ = 0.86 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 1.60 (m, 1H), 2.82 (m, 1H), 2.98 (m, 1H), 2.99 (s, 1H), 3.53 (s, 3H), 4.37 (dd, *J* = 9.7 and 6.3 Hz, 1H), 5.94 (dd, *J* = 6.3 and 0.8 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 17.5, 18.5, 20.0, 31.6, 32.9, 59.0, 80.7, 108.7, 146.9.

For analysis, a sample was purified by GC (column "B", 100°C).

$C_9H_{18}O_2$ (158.2) Calcd. C 68.31 H 11.47
Found C 67.98 H 11.60

20 µl of racemic **9d** was derivatized as described for **9a**. Analytical GC (column "A", 160°C, 2.2 bar He) showed the 3*R*,4*S* diastereomer to elute after 41.3 min, the 3*S*,4*R* diastereomer after 42.8 min.

(1R,2R*)-(Z)-4-Methoxy-2-methyl-1-phenyl-3-buten-1-ol* (**9e**): From 1.70 g (8.0 mmol) **8**, 0.57 g (5.3 mmol) of benzaldehyde (added at −20°C), 10 ml of petroleum ether (b.p. 40–60°C), and 1.16 g (7.6 mmol) of triethanolamine. Chromatography on 100 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 1:1, gave 0.81 g (79%) of **9e** as a clear liquid. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.79 (d, *J* = 6.9 Hz, 3H), 2.50 (s, broad, 1H), 2.95 (dddq, *J* = 8.3, 6.9, 6.3 and 0.8 Hz, 1H), 3.59 (s, 3H), 4.28 (d, *J* = 8.3 Hz, 1H), 4.31 (dd, *J* = 9.4 and 6.3 Hz, 1H), 6.06 (dd, *J* = 6.3 and 0.8 Hz, 1H), 7.23–7.37 (m, 5H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 17.6, 37.8, 59.1, 78.5, 109.0, 127.3, 128.1, 128.9, 144.0, 147.6.

For analysis, a sample was purified by GC (column "B", 135°C).

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.97 H 8.39
Found C 75.03 H 8.36

20 µl of racemic **9e** was derivatized as described for **9c**. Analytical GC (column "B", 175°C, 1 bar He) showed the 1*R*,2*R* diastereomer to elute after 86.4 min, the 1*S*,2*S* diastereomer after 88.8 min.

5) *(2RS,4S*,5R*)-2-Methoxy-4-methyl-5-pentyltetrahydrofuran* (**11c**): 1.60 g (7.5 mmol) of **8** and 0.90 g (9.0 mmol) of hexanal were allowed to react in 6 ml of petroleum ether (b.p. 40–60°C) as

Table 1. Optical rotations of the homoallyl alcohols **9**

9	R	ee	Config.	*c*	Solvent	$[\alpha]_\lambda^{20}$ λ[nm]: 589	578	546	436	365
a	CH_3	94	2*S*,3*R*	5	Toluene	+10.2	+21.2	+24.6	+ 46.1	+ 81.7
b	CH_3CH_2	90	3*S*,4*R*	5	$CDCl_3$	+ 8.0	+10.0	+12.6	+ 26.0	+ 50.3
c	$CH_3[CH_2]_4$	88	3*R*,4*S*	10	Toluene	−10.7	−11.1	−12.1	− 19.4	− 27.8
d	$(CH_3)_2CH$	90	3*S*,4*R*	10	Toluene	− 2.5	− 2.7	− 2.0	0	− 6.3
e	C_6H_5	90	1*R*,2*R*	5	Toluene	+80.7	+83.3	+95.5	+173.2	+289.5

described under 4). The mixture was concentrated i. vac. and the residue was taken up in 3 ml of methanol followed by 3 ml of methanolic HCl. After 3 h, the mixture was concentrated and the residue was partitioned between 10 ml of petroleum ether (b.p. 40–60°C) and 10 ml of water. The aqueous phase was extracted twice with 10 ml each of petroleum ether. The combined organic phases were washed once with water and dried with $MgSO_4$. The solution was concentrated and the residue was chromatographed over 120 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 9:1, to give 0.95 g (68%) of **11c** as a mixture of anomers. Anomer A (ca. 55%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.95 (dd, *J* = 5.7 and 2.9 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 17.2, 22.5, 26.0, 31.9, 35.9, 38.2, 41.8, 54.0, 83.9, 104.5.

Anomer B (ca. 45%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.88 (d, *J* = 4.9 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 17.2, 22.5, 26.0, 31.9, 33.7, 36.7, 41.3, 54.5, 86.6, 104.3.

$C_{11}H_{22}O_2$ (186.3) Calcd. C 70.92 H 11.90
Found C 71.01 H 12.04

6) *(2RS,4S*,5S*)-2-Methoxy-4-methyl-5-phenyltetrahydrofuran* (**11e**): From 1.60 g (7.5 mmol) of **8** and 0.90 g (8.4 mmol) of benzaldehyde in 6 ml of petroleum ether (b.p. 40–60°C) as described under 5); 0.80 g (56%) as a clear liquid. Anomer A (ca. 60%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 6.5 Hz, 3H), 1.78 (ddd, *J* = 12.5, 12.5 and 5.1 Hz, 1H), 2.17 (dd, *J* = 12.5 and 6.3 Hz, 1H), 2.33 (dddq, *J* = 12.5, 9.3, 6.5 and 6.5 Hz, 1H), 3.47 (s, 3H), 4.42 (d, *J* = 9.4 Hz, 1H), 5.05 (d, *J* = 5.1 Hz, 1H), 7.25–7.55 (m, 5H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3, 40.4, 41.9, 54.5, 89.3, 104.6, 126.5, 127.3, 128.0, 141.9.

Anomer B (ca. 40%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, *J* = 6.7 Hz, 3H), 1.62 (ddd, *J* = 13.4, 8.7 and 3.3 Hz, 1H), 2.04 (m, 1H), 2.52 (dd, *J* = 14.7, 9.2 and 5.8 Hz, 1H), 3.41 (s, 3H), 4.45 (d, *J* = 9.0 Hz, 1H), 5.20 (dd, *J* = 5.7 and 3.3 Hz, 1H), 7.25–7.55 (m, 5H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0, 41.3, 41.9, 54.9, 85.7, 104.9, 126.2, 127.4, 128.0, 140.5.

$C_{12}H_{16}O_2$ (192.3) Calcd. C 74.96 H 8.39
Found C 75.05 H 8.43

7) *(2RS,4S*,5R*)-2-Methoxy-4,5-dimethyltetrahydrofuran* (**11a**): To a solution of 0.30 g (2.3 mmol) of **9a** in 2 ml of CH_2Cl_2 were added 5 drops of a solution of 5 mg of iodine in 1 ml of $CHCl_3$. The solution was washed once with aqueous $NaHCO_3$ solution, once with water, and was dried with $MgSO_4$. After concentration and short-path distillation, 0.25 g (83%) of **11a** was obtained as an anomeric mixture. Anomer A (ca. 60%): ^{1}H NMR (400 MHz, $CDCl_3$, only those values are given, which could be clearly discerned): δ = 1.00 (d, *J* = 6.7 Hz, 3H), 1.22 (d, *J* = 6.1 Hz, 3H), 1.45 (ddd, *J* = 13.3, 8.9 and 3.4 Hz, 1H), 2.36 (ddd, *J* = 14.8, 9.0 and 5.8 Hz, 1H), 3.34 (s, 3H), 3.60 (m, 1H), 4.96 (dd, *J* = 5.8 and 3.4 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.2, 18.4, 40.3, 41.5, 54.9, 82.9, 104.6.

Anomer B (ca. 40%): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (d, *J* = 6.3 Hz, 3H), 1.26 (d, *J* = 6.1 Hz, 3H), 3.31 (s, 3H), 4.78 (d, *J* = 5.0 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.4, 20.7, 38.5, 41.8, 54.1, 79.7, 104.4.

$C_7H_{14}O_2$ (130.2) Calcd. C 64.58 H 10.84
Found C 64.67 H 10.66

8) *Ozonolysis of (2S,3R)-(Z)-5-Methoxy-3-methyl-4-penten-2-ol* (**9a**) *obtained from S-***8**: Into a solution of 0.58 g (4.4 mmol) of **9a** in 2 ml of CH_2Cl_2 and 2 ml of methanol was introduced at –78°C ozone until the blue colour persisted. Excess ozone was removed with nitrogen and the solvents were removed i. vac. The residue was heated for 1 h to 80°C with 2 ml of formic acid and 2 ml of 30% aqueous H_2O_2. After cooling, the phases were separated and the aqueous phase was extracted twice with 5 ml each of CH_2Cl_2. The combined organic phases were discarded. The aqueous phase was extracted five times with 5 ml each of ether. The combined extracts were dried with $MgSO_4$ and concentrated i. vac. to give 0.30 g (58%) of crude 3-hydroxy-2-methylbutyric acid.

To 0.21 g (1.8 mmol) of this acid in 1 ml of methanol and 4 ml of ether was added an etheral solution of diazomethane until the yellow color persisted. After 10 min, the solvents and the excess of diazomethane were removed i. vac. to give 0.23 g (97%) of **12**, containing ca. 15% of a contaminant. **12** was identified by its ^{13}C-NMR spectrum (100 MHz, $CDCl_3$): δ = 13.5, 20.3, 46.8, 51.4, 69.1, 176.1; cf. ref.[20].

9) *(3R*,4S*,5R*)-(Z)-1-Methoxy-3,5-dimethyl-1-hepten-4-ol* (**14**) *and (3R*,4S*,5S*) Compound* **15**: To a solution of 2.60 g (12.2 mmol) of *rac*-**8** in 10 ml of toluene was added at –78°C 1.05 g (12.2 mmol) of 2-methylbutanal (*rac*-**13**). After reaching room temperature, the mixture was allowed to stand for 60 h. It was worked up as described under 4). Chromatography over 120 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 3:2, gave 1.23 g (59%) of a 4:1 mixture of *rac*-**14** and *rac*-**15**.

$C_{10}H_{20}O_2$ (172.3) Calcd. C 69.72 H 11.70
Found C 69.91 H 11.96

(3S,4R,5S)-(Z)-1-Methoxy-3,5-dimethyl-1-hepten-4-ol (**14**) was obtained similarly from (*R*)-**8** and (*S*)-**13**[21]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.8 Hz, 3H), 0.90 (t, *J* = 7.3 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 1.29 (m, 1H), 1.46 (m, 2H), 1.66 (d, *J* = 3.9 Hz, 1H), 2.77 (m, 1H), 3.17 (ddd, *J* = 7.7, 3.9 and 3.9 Hz, 1H), 3.57 (s, 3H), 4.25 (dd, *J* = 9.5 and 6.3 Hz, 1H), 5.99 (dd, *J* = 6.3 and 0.9 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 12.0, 13.3, 18.2, 27.1, 33.1, 37.6, 59.1, 78.3, 109.5, 147.2.

(3R,4S,5S)-(Z)-1-Methoxy-3,5-dimethyl-1-hepten-4-ol (**15**) was obtained similarly from (*S*)-**8** and (*S*)-**13**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7.4 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 1.15 (m, 1H), 1.44 (m, 1H), 1.61 (d, *J* = 4.8 Hz, 1H), 1.63 (m, 1H), 2.83 (m, 1H), 3.11 (ddd, all couplings about 5 Hz, 1H), 3.57 (s, 3H), 4.29 (dd, *J* = 9.6 and 6.3 Hz, 1H), 5.95 (dd, *J* = 6.3 and 0.8 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = 11.5, 15.8, 18.9, 24.7, 32.5, 38.5, 59.0, 79.8, 108.4, 146.8.

10) *Methyl (2R*,3R*,4S*)-3-Hydroxy-2,4-dimethylhexanoate* (**16**) *and (2R*,3R*,4R*) Compound* **17**. – a) *From (3R*,4S*,5R*)- and (3R*,4S*,5S*)-(Z)-1-Chloro-3,5-dimethyl-1-hepten-4-ol* (**18** and **19**): Into a solution of 0.69 g (3.9 mmol) of a 4:1 mixture of *rac*-**18** and *rac*-**19** in 10 ml of methanol was introduced at –78°C ozone until the blue color persisted. Excess of ozone was removed by nitrogen and the mixture was allowed to reach room temperature resulting in a slightly exothermic reaction. After heating for 3 h to 60°C, the solvents were removed and the residue was taken up in 10 ml of ether. The solution was washed once with 5 ml of 10% aqueous NaOH and once with water. The organic phases were dried with Na_2SO_4 and concentrated to give 0.44 g (64%) of a 4:1 mixture of *rac*-**16** and *rac*-**17**.

16: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.7 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.28 (m, 1H), 1.46 (m, 2H), 2.37 (s, broad, 1H), 2.63 (dq, *J* = 7.2 and 7.2 Hz, 1H), 3.60 (dd, *J* = 7.8 and 3.4 Hz, 1H), 3.70 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9, 11.5, 13.5, 25.9, 35.9, 42.4, 50.8, 74.7, 176.2.

17: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.8 Hz, 3H), 1.23 (d, *J* = 7.2 Hz, 3H), 3.69 (s, 3H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.6, 14.1, 15.0, 22.7, 37.7, 41.3, 50.8, 77.0, 176.2.

For analysis, a sample of the mixture was purified by GC (column "B", 140°C).

$C_9H_{18}O_3$ (174.2) Calcd. C 62.04 H 10.41
Found C 62.16 H 10.59

b) *From (3R*,4S*,5R*)- and (3R*,4S*,5S*)-(Z)-1-Methoxy-3,5-dimethyl-1-hepten-4-ol* (**14** and **15**): 0.90 g (5.2 mmol) of a 4:1 mixture of *rac*-**14** and *rac*-**15** were ozonized as described under 8). After the oxidation the mixture was extracted 5 times with 5 ml each of ether. The combined extracts were extracted three times with 5 ml each of a 10% aqueous NaOH solution. The combined aqueous extracts were acidified with conc. HCl to pH = 1 and were extracted 5 times with 10 ml each of ether. The combined ethereal extracts were dried with $MgSO_4$ and concentrated i. vac. resulting in 0.51 g (61%) of a 4:1 mixture of (2*R**,3*R**,4*S**)- and (2*R**,3*R**,4*R**)-3-hydroxy-2,4-dimethylhexanoic acids.

(2*R**,3*R**,4*S**): ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.5, 12.2, 14.2, 26.5, 36.5, 43.0, 75.7, 180.6.

(2*R**,3*R**,4*R**): ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.2, 14.8, 15.7, 23.3, 37.7, 42.0, 77.8, 180.5.

A sample of this mixture was purified by GC (column "B", 120°C).

$C_8H_{16}O_3$ (160.2) Calcd. C 59.97 H 10.07
Found C 59.91 H 10.09

0.48 g of the above mixture were esterified as described under 8) to give 0.41 g (78%) of a 4:1 mixture of the esters *rac*-**16** and *rac*-**17**, which were identified by their ^{13}C-NMR spectra.

11) *(3R,4R,5S,6S)-(Z)-6-(tert-Butyldimethylsilyloxy)-1-methoxy-3,5-dimethyl-1-octen-4-ol* (**21**): 0.55 g (2.6 mmol) of (*S*)-**8**, 0.50 g (2.2 mmol) of (2*R*,3*S*)-3-(*tert*-butyldimethylsilyloxy)-2-methylpentanal[1] (**20**), 5 ml of toluene, and 0.39 g (2.6 mmol) of triethanolamine were allowed to react as described under 9). Chromatography on 45 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 4:1, gave 0.46 g (66%) of **21**. Its diastereomeric purity was >95% according to the NMR spectra. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.06 (s, 6H), 0.81 (t, *J* = 7.5 Hz, 3H), 0.88 (s, 9H), 0.90 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.54 (m, 2H), 1.68 (m, 1H), 2.08 (d, *J* = 3.2 Hz, 1H), 2.80 (m, 1H), 3.39 (m, 1H), 3.57 (s, 3H), 3.72 (m, 1H), 4.31 (dd, *J* = 9.5 and 6.3 Hz, 1H), 5.96 (d, *J* = 6.3 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = –4.4, –3.8, 8.8, 9.6, 18.37, 18.40, 26.2, 27.7, 33.2, 39.5, 59.0, 75.6, 76.5, 109.0, 147.0.

For analysis, a sample was purified by GC (column "B", 190°C).

$C_{17}H_{36}O_3Si$ (316.6) Calcd. C 64.50 H 11.46
Found C 64.53 H 11.54

12) *(3S,4S,5S,6S)-(Z)-6-(tert-Butyldimethylsilyloxy)-1-methoxy-3,5-dimethyl-1-octen-4-ol* (**22**) *and (3R,4R,5S,6S)-(E)-Isomer, Compound* **23**: 1.40 g (6.5 mmol) of (*R*)-**8** and 1.00 g (4.3 mmol) of the aldehyde **20** in 2 ml of toluene were pressurized in a teflon tube to 4 kbar for 8 h. The reaction mixture was worked up as described under 9). Chromatography on 120 g of silica gel with petroleum ether (b.p. 40–60°C)/ether, 4:1, gave 0.97 g (60%) of **22** and 0.18 g (13%) of a 1:1 mixture of **23** and **21**.

22: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 3H), 0.09 (s, 3H), 0.73 (d, *J* = 7.0 Hz, 3H), 0.89 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H), 1.00 (d, *J* = 7.0 Hz, 3H), 1.54 (ddq, *J* = 7.3, 6.6 and 6.6 Hz, 2H), 1.74 (ddq, *J* = 9.8, 7.0 and 2.7 Hz, 1H), 2.71 (dddq, *J* = 9.8, 7.0, 2.1 and 1.0 Hz, 1H), 3.45 (ddd, *J* = 9.8, 2.1 and 1.3 Hz, 1H), 3.52 (s, 3H), 3.66 (dt, *J* = 6.6 and 2.7 Hz, 1H), 3.85 (d, *J* = 1.3 Hz, 1H), 4.42 (dd, *J* = 9.8 and 6.3 Hz, 1H), 5.91 (dd, *J* = 6.3 and 1.0 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = –4.5, –4.3, 11.6, 13.2, 18.2, 19.1, 24.9, 26.1, 32.6, 41.7, 58.9, 77.2, 79.7, 108.1, 146.3.

For analysis, a sample was purified by GC (column "B", 190°C).

$C_{17}H_{36}O_3Si$ (316.6) Calcd. C 64.50 H 11.46
Found C 64.76 H 11.55

23: In the mixture with **21**, the following NMR data of **23** could be recorded: ^{1}H NMR (400 MHz, C_6D_6): δ = 4.58 (dd, *J* = 12.7 and 9.3 Hz, 1H), 6.27 (d, *J* = 12.7 Hz, 1H). – ^{13}C NMR (100 MHz, C_6D_6): δ = –4.4, –3.8, 8.6, 9.4, 18.1, 18.8, 26.2, 27.3, 37.5, 38.7, 55.5, 75.5, 76.4, 105.0, 148.8.

CAS Registry Numbers

(±)-**1**: 118574-32-6 / (*S*)-**1**: 100348-15-0 / (*R*)-**1**: 100348-14-9 / (±)-**4**: 118494-15-8 / (±)-**5a**: 118493-97-3 / (±)-**5b**: 118475-81-3 / (±)-**5c**: 118475-82-4 / (±)-**5d**: 118475-83-5 / (±)-**5e**: 118475-84-6 / (±)-**6a**: 118475-85-7 / (±)-**6b**: 118475-86-8 / (±)-**6c**: 118475-87-9 / (±)-**6e**: 118475-93-7 / (±)-**8**: 118574-33-7 / (*R*)-**8**: 116706-48-0 / (*S*)-**8**: 116706-46-8 / (±)-**9a**: 118573-94-7 / (±)-**9b**: 118573-95-8 / (±)-**9c**: 118475-88-0 / (±)-**9d**: 118573-96-9 / (±)-**9e**: 118573-97-0 / **9a** (isomer 1): 116706-37-7 / **9a** (isomer 2): 118475-99-3 / **9b** (isomer 1): 118475-97-1 / **9b** (isomer 2): 118476-00-9 / **9c** (isomer 1): 118574-05-3 / **9c** (isomer 2): 118574-06-4 / **9d**: (isomer 1): 118475-98-2 / **9d** (isomer 2): 118476-01-0 / **9e** (isomer 1): 116706-41-3 / **9e** (isomer 2): 118476-02-1 / (±)-**11a** (isomer 1): 118475-91-5 / (±)-**11a** (isomer 2): 118475-96-0 / (±)-**11c** (isomer 1): 118475-89-1 / (±)-**11c** (isomer 2): 118475-94-8 / (±)-**11e** (isomer 1): 118475-90-4 / (±)-**11e** (isomer 2): 118475-95-9 / **12**: 66767-60-0 / **12** (acid): 84567-98-6 / **13**: 1730-97-8 / (±)-**13**: 57456-98-1 / **14**: 116782-61-7 / (±)-**14**: 118573-98-1 / **15**: 116706-47-9 / (±)-**15**: 118573-99-2 / (±)-**16**: 118574-00-8 / (±)-**16** (acid): 118475-92-6 / (±)-**17**: 118574-01-9 / (±)-**17** (acid): 118574-04-2 / (±)-**18**: 118574-02-0 / (±)-**19**: 118574-03-1 / **20**: 108815-17-4 / **21**: 116782-62-8 / **22**: 116706-49-1 / **23**: 116782-59-3 / MeCHO: 75-07-0 / EtCHO: 123-38-6 / $CH_3(CH_2)_4CHO$: 66-25-1 / *i*PrCHO: 78-84-2 / PhCHO: 100-52-7

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