Stereoselective Synthesis of Alcohols, XXVII[1]

Addition of (α-Chlorocrotyl)boronates to Aldehydes

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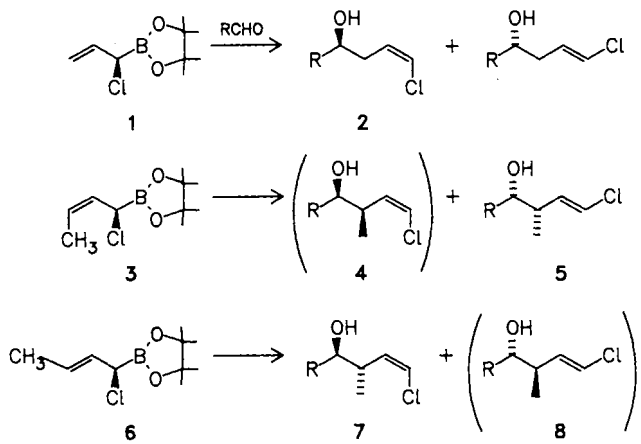
Received February 26, 1988

(*Z*)-(α-Chlorocrotyl)boronates 3 add to nonchiral aldehydes to give homoallyl alcohols 5 with a *syn*-β-positioned methyl group and an (*E*)-chloroalkenyl unit. The diastereoselectivity in favour of 5 is around 90%. The corresponding (*E*)-(α-chlorocrotyl)boronates 6 similarly lead to homoallyl alcohols 7 with an *anti*-β-methyl group and a (*Z*)-chloroalkenyl unit, the diastereoselectivity being > 95%. Using optically active boronate 6 the resulting homoallyl alcohols 7 are obtained with > 95% e.e.

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

(*Z*)-(α-Chlorcrotyl)boronsäureester 3 addieren an Aldehyde zu den Homoallylalkoholen 5 mit einer *syn*-β-ständigen Methylgruppe und einer (*E*)-Chlorvinyl-Gruppe. Die Diastereoselektivität zugunsten von 5 liegt bei 90%. Die entsprechenden (*E*)-(α-Chlorcrotyl)boronsäureester 6 ergeben analog die Homoallylalkohole 7 mit einer *anti*-β-ständigen Methylgruppe und einer (*Z*)-Chlorvinyl-Gruppe. Hier liegt die Diastereoselektivität der Reaktionen bei > 95%. Unter Verwendung des optisch aktiven Boronsäureesters 6 konnten die Homoallylalkohole 7 mit > 95% e.e. erhalten werden.

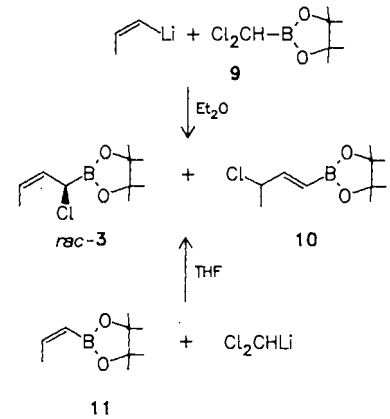
Recently we reported[2] that (α-chloroallyl)boronates **1** can be added to aldehydes to give the homoallyl alcohols **2** with a high level of chirality transfer. It seemed attractive to combine this effect with the well known "simple" diastereoselection exerted by the (*E*)- and (*Z*)-crotylboronates on addition to aldehydes[3], viz. to study the (α-chlorocrotyl)boronates **3** and **6**.



We hoped that these crotylboronates could serve as chiral reagents for C–C bond formation, allowing the conversion of an chiral aldehyde into each of the four stereotriades[4] of the homologated aldehyde under reagent control of diastereoselectivity[5]. Since the ratio of the (*Z*)- to the (*E*)-homoallyl alcohol, e.g. of **4**:**5**, is equal to the asymmetric induction originating from nonracemic crotylboronates **3**, it is possible to determine the level of asymmetric induction of α-substituted crotylboronates simply by using the racemic reagents **3** or **6**[6]. We describe here their synthesis and addition to representative aldehydes. A preliminary account based on these studies has appeared[7].

Preparation of (α-Chlorocrotyl)boronates

Two routes are available to generate (α-chloroallyl)boronates **1**: Reaction of (dichloromethane)boronate **9** with an alkenyllithium[8,9], or reaction of a vinylboronate with dichloromethyllithium[8,10]. In an attempt to generate the homologous crotylboronate **3**, reaction of **9**[11] with (*Z*)-propenyllithium in ether led to 90% of an 1:2 mixture of **3** and the isomerized product **10**.



Better results were obtained with the second method, reaction of the (*Z*)-propenylboronate **11**[12] with dichloromethyllithium in THF leading to 64% of **3**. Apparently the more basic solvent THF prevents the isomerisation of **3** by LiCl to **10**. The product **3** is contaminated by 3–5% of its *E* isomer, because the starting vinylboronate **11** had an isomeric purity of only 97%.

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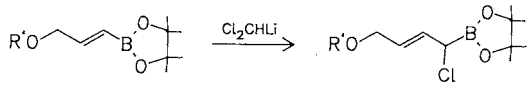
While the (*E*)-(α-chlorocrotyl)boronate **6** is accessible by another route[6], the dichloromethyllithium homologation was used to generate some α-substituted derivatives of **6**:



12, 13 **14, 15**

12, 14: R' = $PhCH_2$

13, 15: R' = $tBuMe_2Si$

The products **14, 15** were obtained in high yield and approximately 90% purity (by ^1H NMR). They were treated with aldehydes as crude materials, see below.

Addition of (*Z*)-(α-Chlorocrotyl)boronate 3 to Aldehydes

The racemic (*Z*)-(α-Chlorocrotyl)boronate **3** was added to various aldehydes in CH_2Cl_2 at room temperature resulting in the racemic homoallyl alcohols **4** and **5**, cf. Table 1. The isomer distribution **4**/**5** was estimated from the ^{13}C-NMR spectra.

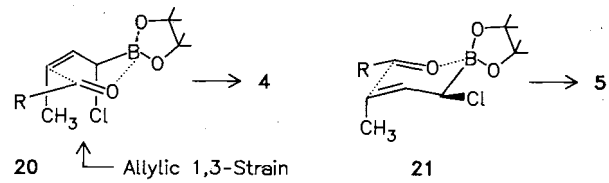
Table 1. Addition of the (α-chlorocrotyl)boronates to Aldehydes

	Aldehyde R =	Allyl-boron-ate	Yield (%)	Homoallyl alcohols 4	5	7 8
a	CH_3	**3**	70	**4a** 12	**5a** 85	**7a** (3)
b	CH_3CH_2	**3**	81	6	91	(3)
c	$(CH_3)_2CH$	**3**	58	4	92	(4)
d	C_6H_5	**3**	56	3[a]	93	(4)[a]
a	CH_3	**6**	53–64			≅95
b	CH_3CH_2	**6**	47–65			≅95
c	$(CH_3)_2CH$	**6**	55–84			≅95
d	C_6H_5	**6**	53–73			≅95
e	$CH_3[CH_2]_4$	**6**	60–91			≅95
b	CH_3CH_2	**14**	55	**27b**		
c	$(CH_3)_2CH$	**14**	62	**27c**		
f	$CH_3[CH_2]_3$	**14**	61	**27f**		
b	CH_3CH_2	**15**	62	**28b**		
d	C_6H_5	**15**	55	**28d**		

[a] **4d** and **7d** have not been analytically separated, relative proportions quoted are arbitrary.

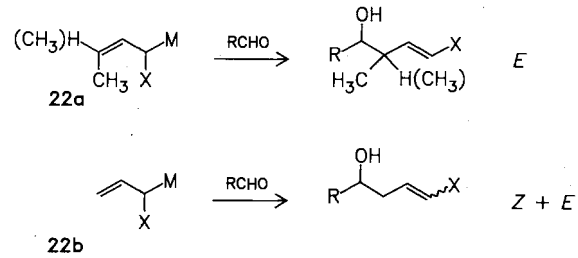
Due to the contamination of **3** by small amounts of **6**, small amounts of the homoallyl alcohol **7** were also formed. The major product obtained is **5** with an *E*-configurated double bond, as evidenced by a 13-Hz coupling constant of the olefinic protons compared to the 7-Hz coupling in **7**. Assignment of the major product to be the *syn* isomer **5** rests on the following experiment: Addition of **3** to racemic α-methylbutyraldehyde gave a 3:7 mixture of **16** and **17**.

Hydrogenation of **16** and **17** resulted in a 3:7 mixture of the known[13] saturated alcohols **18** and **19**. The isomer **18** can be obtained only if the relative configuration of the two newly formed stereocenters in **16** is "*syn*". While the formation of the *syn* diastereomer from a (*Z*)-crotylboronate is in line with previous experience[3], the formation of the isomers with an *E* double bond is in contrast to the high preference in the formation of the *Z* isomer **2** from **1**. This can be traced to a strong destabilisation of the transition state **20** versus **21** due to allylic 1,3-strain[14].



20 Allylic 1,3-Strain **21**

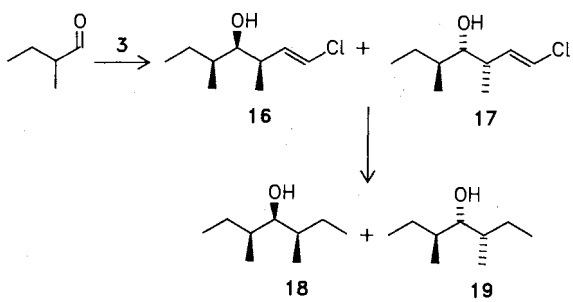
If it were not for a destabilizing steric interaction of the equatorial chlorine substituent with the pinacol residue on boron[15] in the transition state **21**, the selectivity might be even higher. Similar preference for the specific formation of the (*E*)-homoallyl alcohols has been observed by others[16] on addition of α-substituted (*Z*)-crotyl- or prenylmetal compounds (**22a**) to aldehydes.

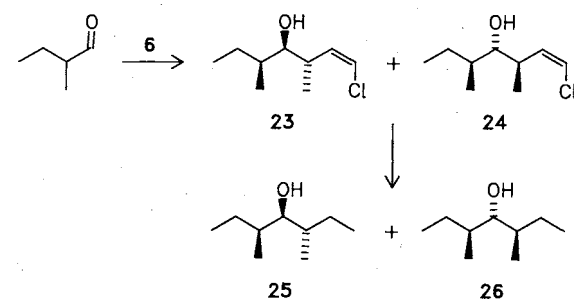


22a **22b**

Addition of (*E*)-(α-Chlorocrotyl)boronates to Aldehydes

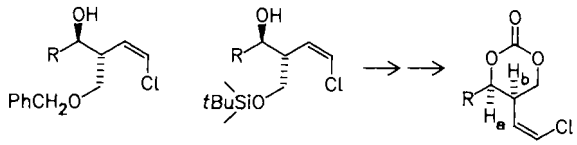
The addition of the (*E*)-(α-Chlorocrotyl)boronate **6** to aldehydes was carried out similarly. Data are compiled in Table 1. The ^1H-NMR spectra of the crude products indicated that the major isomer **7** was contaminated by approximately 5% of another isomer with an *E* double bond,





to which we assign structure **8**. Even crude chromatographic purification resulted in the pure diastereomers **7** having a *Z* double bond. The relative configuration of the newly formed stereocenters was assigned as *anti* based on the conversion of α-methylbutyraldehyde by **6** into a racemic mixture of **23** and **24** (3:1). Hydrogenation then gave a mixture of the known[13] compounds **25** and **26**.

Formation of the latter is possible only if the relative configuration of the two new stereocenters generated on addition of **6** to an aldehyde is "*anti*". This is in line with the general experience on addition of (*E*)-crotylboronates to aldehydes[3]. Likewise, the configuration of the homoallyl alcohols **27** and **28** obtained on addition of either the α-substituted crotylboronates **14** or **15** to aldehydes is assigned in analogy as *anti*.



27 **28** **29**

This was corroborated in the case of **28d** (R = Ph), which was converted into **29**. The latter showed a 7-Hz coupling constant between H_a and H_b, expected for a *cis*-1,2-disubstituted 1,3-dioxanone in rapid conformational equilibrium.

Addition of Nonracemic [α-Chloro-(*E*)-crotyl]-boronates to Aldehydes

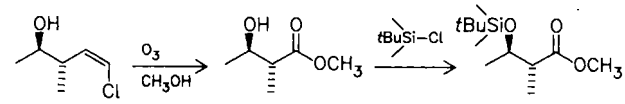
The high level of diastereoselection observed on addition of the (α-chlorocrotyl)boronates **3** or **6** to aldehydes as well as the ease of purification of the individual diastereomeric homoallyl alcohols **5** or **7** made it attractive to use the reagents **3** and **6** in optically active form for the synthesis of enantiomerically pure homoallyl alcohols. While the (*E*)-crotylboronate **6** is available in both enantiomeric forms[6], the route used for the preparation of the (*Z*)-crotylboronate **3** is not amenable to the generation of optically active material. Hence, only optically active **6** (of ca. 95% ee) has so far been used to prepare the homoallyl alcohols **7** in the enantiomeric purities recorded in Table 2.

Table 2. Enantiomeric purities of the homoallyl alcohols **7** obtained from (*R*)-(*E*)-(α-chlorocrotyl)boronate **6** of 95 to 98% ee

7	R	ee	Konfig.	c[a]	$[\alpha]_\lambda^{20}$ 589	578	λ(nm) 546	436	365
7a	CH_3	95	2*R*,3*S*	10.0	+7.5	+8.4	+9.4	+15.5	+22.4
7b	CH_3CH_2	96	3*R*,4*S*	2.50	+26.0			+49.9	+76.7
7c	$(CH_3)_2CH$	96	3*R*,4*S*	5.00	+16.6			+29.6	+37.8
7d	C_6H_5	98	1*R*,2*R*	10.0	+44.5	+47.2	+53.9	+99.4	+159.8
7e	$CH_3[CH_2]_4$	92	3*S*,4*R*	10.0	+46.4[b]	+48.1[b]	+54.4[b]	+93.4[b]	+148.3[b]

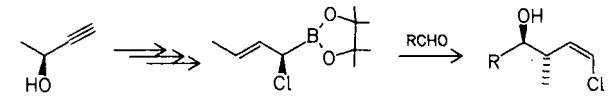
[a] In $CDCl_3$. — [b] Refers to material of 90% ee.

For the determination of its enantiomeric purity, **7d** was treated with isopropyl isocyanate, and the resulting urethane was analysed with a chiral capillary GC column[17]. The other homoallyl alcohols **7** did not yield to this method of analysis as tested by using the racemates. Hydrogenation of the C=C and C–Cl bonds of **7** resulted in saturated alcohols, of which the one derived from **7e** could be subjected to the above enantiomer determination. The remaining homoallyl alcohols **7a–c** were derivatised with (*S*)-(−)-1-phenylethyl isocyanate, and the resulting diastereomeric urethanes were analysed on an achiral capillary GC column. In each case complete analytical separation was established using the racemates. The absolute configuration of the homoallyl alcohol **7a** was secured as follows:



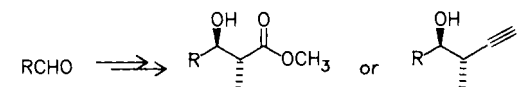
7a **30** **31**

Ozonolysis in methanol[18] led to the β-hydroxybutyrate **30** with $[\alpha]_D^{20} = -33.0$ (*c* = 5, methanol), cf. the data for the 2*S*,3*S* compound[19]: $[\alpha]_D^{20} = +36.8$ (*c* = 5, methanol). Moreover the relative configuration at C-2 and C-3 in **30** was secured by converting **30** to its *tert*-butyldimethylsilyl derivative **31**, the ^{13}C-NMR data of which were known[20] for each diastereomer. Since the configuration of **7a** is consistent with what was expected for the sequence of reactions[6] starting from *S*-**32**, we feel secure in assigning the absolute and relative configuration of the other homoallyl alcohols **7** obtained by analogy.



32 **6** **7**

Thus, the methods described here allow chain extension of aldehydes into the *anti*-β-methylhomoallyl alcohols **7** under high (>95%) reagent controlled asymmetric induction. The reagent **6** is superior to the chirally modified (*E*)-crotylboronates studied by us earlier[13]. It compares well with other chiral crotylboron compounds described recently[21] achieving the same sort of tranformation. In view of the fact that the vinyl chloride function in **7** cannot only be ozonised, cf. **7a** → **30**, but also simply be converted into an alkyne[22] by the action of potassium hydride, the methods described here allow the following two-step transformations to obtain either enantiomer of **33** or **34**, respectively.



33 **34**

Hitherto such simple enantiomerically pure building blocks have been prepared by rather lengthy sequences[23].

Support of this study by the *Deutsche Forschungsgemeinschaft* (SFB 260) and the *Fonds der Chemischen Industrie* is gratefully acknowledged. 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: Varian CFT 20, XL 100 and Bruker WH 400. – Preparative gas chromatography: Varian Aerograph A-90-P3, 1.5 m × 0.6 cm column with 5% SE 30 on chromosorb G, AW-DMCS, 60–80 mesh, 130 ml He/min. – Analytical gas chromatography: Perkin-Elmer 900 and Siemens Sichromat 3; A: 25 m × 0.56 mm glass capillary column with OV 1, 1.4 bar He; B: 50 m × 0.5 mm glass capillary column with XE 60, (*S*)-valine-(*S*)-α-phenylethylamide[17], 1 bar He; C: 40 m × 0.3 mm glass capillary column with SE 52, 2.1 bar He.

1. *2-[1-Chloro-2-(Z)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**3**)

a) *via 2-(Dichloromethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**9**): To a solution of 2.06 g (9.8 mmol) of **9**[11] in 30 ml of ether was added at −78°C a solution of 10 mmol of (*Z*)-1-propenyllithium in 30 ml of ether during 15 min. After 30 min at −78°C the mixture was allowed to reach room temperature. After 15 h 100 ml of petroleum ether (40–60°C) was added and the lithium chloride was filtered. The filtrate was concentrated at 20 Torr to give 1.96 g (90%) of a 1:2 mixture of **3** and 2-[3-chloro-1-(*E*)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**). – **10**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (s, 12H), 1.76 (d, *J* = 6.7 Hz, 3H), 4.62–4.66 (m, 1H), 5.55 (dd, *J* = 17.7 and 1 Hz, 1H), 6.69 (dd, *J* = 17.7 and 7.8 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 24.5, 24.7, 49.4, 83.4, 152.6. – **3**: see below.

b) *via 2-[1-(Z)-Propenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**11**): To a solution of 4 ml of dichloromethane in 80 ml of THF was added at −100°C 40 mmol of *n*-butyllithium (in hexane) over 25 min. After 30 min at −100°C a solution of 6.76 g (40 mmol) of **11**[12] in 5 ml of THF was added. The mixture was allowed to reach room temperature. After 15 h 50 ml of petroleum ether (40–60°C) was added and the solution was washed twice with 10 ml of water. The organic phases were separated, dried with Na_2SO_4, and concentrated at 20 Torr. The residue was distilled to give 5.61 g (64%) of **3** of b.p. 50–51°C/10^{-1} Torr. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 12H), 1.69 (d, *J* = 5.2 Hz, 3H), 4.27 (d, *J* = 9.6 Hz, 1H), 5.62–5.69 (m, 2H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 12.7, 24.4, 84.3, 127.5, 128.5.

$C_{10}H_{18}BClO_2$ (216.5) Calcd. C 55.47 H 8.38 Cl 16.37
Found C 55.51 H 8.42 Cl 16.11

2. *2-[4-(Benzyloxy)-1-chloro-2-(E)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**14**): A suspension of 10 mmol of dichloromethyllithium in 20 ml of THF was prepared as described under 1. at −100°C. After addition of 2.74 g (10 mmol) of 2-[3-(benzyloxy)-1-(*E*)-propenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**12**)[6] the mixture was allowed to reach room temperature. Workup as described under 1. gave 3.00 g (93%) of crude **14** of 90% purity according to the ^{1}H-NMR spectrum. – ^{1}H NMR (400 MHz, C_6D_6): δ = 0.94 (s, 12H), 3.70–3.72 (m, 2H), 3.85 (dd, *J* = 4.5 and 1.9 Hz, 1H), 4.25 (s, 2H), 5.75 (ddt, *J* = 15.3, 5.4, and 1.1 Hz, 1H), 6.12 (ddt, *J* = 15.3, 8.9, and 1.5 Hz, 1H), 7.10–7.31 (m, 5H). This material was used as obtained.

3. *2-[4-(tert-Butyldimethylsilyloxy)-1-chloro-2-(E)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**15**): From 5.00 g (16.7 mmol) of 2-[3-(*tert*-butyldimethylsilyloxy)-1-(*E*)-propenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**13**)[6] and 1.50 g (17.7 mmol) of dichloromethane as described under 2. Yield 5.32 g (98%) of crude **15**. – ^{1}H NMR (400 MHz, C_6D_6): δ = 0.0 (s, 6H), 0.99 (s, 9H), 1.07 (s, 12H), 3.93–3.95 (m, 2H), 4.07–4.09 (m, 1H), 5.74 (ddt, *J* = 15.1, 4.6, and 1.0 Hz, 1H), 6.12 (ddt, *J* = 16.1, 9.0, and 1.8 Hz, 1H). – ^{13}C NMR (25 MHz, C_6D_6): δ = −5.1, 18.4, 24.5, 26.1, 63.1, 84.3, 127.5, 133.2. The material was used as obtained.

4. *Addition of 2-[1-Chloro-2-(Z)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**3**) *to Aldehydes:* To a solution of 2.16 g (10 mmol) of **3** in 5 ml of CH_2Cl_2 was added at 0°C 10 mmol of the aldehyde. After 15 h at room temp. 1.49 g (10 mmol) of triethanolamine was added, and the mixture was stirred for 2 h. The whole material was chromatographed over 140 g of alumina (basic, activity III) with CH_2Cl_2. The isomer ratio was determined from the ^{13}C-NMR spectrum.

(2R,3R*)-(E)-5-Chloro-3-methyl-4-penten-2-ol* (**5a**): 0.29 g (6.6 mmol) of acetaldehyde and 6.6 mmol each of the reactant furnished 0.62 g (70%) of **5a** as a clear oil. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.9 Hz, 3H), 1.13 (d, *J* = 6.3 Hz, 3H), 1.60 (s, broad, 1H), 2.25–2.36 (m, 1H), 3.66 (quint, *J* = 6.1 Hz, 1H), 5.85 (dd, *J* = 13.3 and 8.4 Hz, 1H), 5.99 (dd, *J* = 13.3 and 0.9 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 15.1, 19.8, 42.8, 70.5, 117.6, 135.5.

$C_6H_{11}ClO$ (134.6) Calcd. C 53.54 H 8.24 Cl 26.34
Found C 53.81 H 8.45 Cl 26.12

(3R,4R*)-(E)-6-Chloro-4-methyl-5-hexen-3-ol* (**5b**): From 0.58 g (10 mmol) of propanal was obtained 1.2 g (81%) of **5b**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.4 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H); 1.17–1.27 (m, 1H), 1.46–1.57 (m, 1H), 1.76 (s, broad, 1H), 2.24–2.33 (m, 1H), 3.35 (s, broad, 1H), 5.85 (dd, *J* = 13.3 and 8.4 Hz, 1H), 5.97 (dd, *J* = 13.4 and 0.9 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 9.9, 14.6, 27.1, 41.5, 76.2, 117.6, 136.4.

$C_7H_{13}ClO$ (148.6) Calcd. C 56.57 H 8.82 Cl 23.85
Found C 56.84 H 8.89 Cl 23.64

(3R,4R*)-(E)-6-Chloro-2,4-dimethyl-5-hexen-3-ol* (**5c**): From 0.72 g (10 mmol) of isobutyraldehyde was obtained 0.95 g (58%) of **5c**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.40 (s, broad, 1H), 1.73 (oct, *J* = 6.8 Hz, 1H), 2.29 (sext, *J* = 6.9 Hz, 1H), 3.15 (t, *J* = 5.7 Hz, 1H), 5.86 (dd, *J* = 13.3 and 8.5 Hz, 1H), 5.99 (dd, *J* = 13.4 and 0.8 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 14.5, 16.5, 19.6, 30.6, 39.0, 79.4, 117.2, 136.9.

$C_8H_{15}ClO$ (162.7) Calcd. C 59.07 H 9.30 Cl 21.80
Found C 59.35 H 9.22 Cl 21.86

(1R,2S*)-(E)-4-Chloro-2-methyl-1-phenyl-3-buten-1-ol* (**5d**): From 1.06 g (10 mmol) of benzaldehyde was obtained 1.11 g (56%) of **5d**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.8 Hz, 3H), 2.24 (s, broad, 1H), 2.58 (sext, *J* = 6.7 Hz, 1H), 4.54 (d, *J* = 7.8 Hz, 1H), 5.81 (dd, *J* = 13.3 and 7.8 Hz, 1H), 5.89 (dd, *J* = 13.3 and 0.7 Hz, 1H), 7.24–7.36 (m, 5H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 14.6, 42.8, 77.2, 118.1, 126.4, 127.5, 128.1, 135.3, 141.9.

$C_{11}H_{13}ClO$ (196.7) Calcd. C 67.18 H 6.66 Cl 18.03
Found C 67.17 H 6.51 Cl 17.95

(3R,4R*,5S*)-(E)-1-Chloro-3,5-dimethyl-1-hepten-4-ol* (**16**) *and (3R*,4R*,5R*)-Compound* **17**: From 0.86 g (10 mmol) of 2-methylbutanal was obtained 1.58 g (89%) of a 3:7 mixture of **16** and **17**. – ^{13}C NMR (25 MHz, $CDCl_3$): **16**: δ = 11.5, 12.4, 16.0, 26.7, 37.0, 39.4, 77.5, 117.2, 136.6. – **17**: δ = 11.2, 13.6, 15.5, 23.7, 37.3, 38.6, 78.6, 117.4, 137.3.

$C_9H_{17}ClO$ (176.7) Calcd. C 61.18 H 9.70
Found C 61.26 H 9.81

5. *Hydrogenation of* **16** *and* **17** *to the 3,5-Dimethylhexan-4-ols* (**18** and **19**): To a solution of 0.50 g (9.0 mmol) of potassium hydroxide in 10 ml of methanol was added 0.53 g (3.0 mmol) of the above

obtained mixture of **16** and **17**. After addition of ca. 50 mg of 5% platinum on carbon the mixture was hydrogenated for 3 d at 1 bar. After filtration the filtrate was treated with 6 ml of 1 N HCl and subsequently neutralized with sodium hydrogencarbonate. The aqueous phase was extracted three times with 10 ml each of CH_2Cl_2. The combined organic phases were washed once with 10 ml of water and were dried with Na_2SO_4. Concentration gave 0.43 g (99%) of a 3:7 mixture of **18** and **19**. – ^{13}C NMR (25 MHz, $CDCl_3$) (*3R*,4R*,5S**)-**18**: δ = 11.3, 13.7, 26.3, 36.9, 77.8. – (*3R*,5R**)-**19**: δ = 11.1, 11.7, 12.2, 15.2, 24.8, 27.0, 36.5, 37.5, 78.3, cf. ref.[13].

6. *Addition of 2-[1-Chloro-2-(E)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (**6**) *to Aldehydes:* The experiments described here were carried out with crude **6** containing up to 40% of 2-[3-chloro-1-(*E*)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[6], which is nonreactive. Yields quoted are therefore overall yields for the generation of **6** and its transformation into the adduct **7**.

(2R,3S*)-(Z)-5-Chloro-3-methyl-4-penten-2-ol* (**7a**): To a solution of 3.00 g (14 mmol) of **6** (purity ca. 70%) in 10 ml of petroleum ether (40–60°C) was added 0.80 g (18 mmol) of acetaldehyde at 0°C. After 18 h at room temp. the mixture was concentrated and the residue taken up in 5 ml of methanol, 15 ml of ether, and 2.06 g (13.8 mmol) of triethanolamine. After stirring for 4 h the mixture was poured into 150 ml of petroleum ether (40–60°C). To facilitate filtration the mixture was stirred with 5 g of $MgSO_4$ for 20 min. After filtration the filtrate was concentrated and the residue was chromatographed over 120 g of silica gel with ether/petroleum ether (40–60°C) (1:1) to give 0.98 g (53%) of **7a**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 6.3 Hz, 3H), 1.51 (s, broad, 1H), 2.78 (m, 1H), 3.70 (m, 1H), 5.70 (dd, *J* = 9.6 and 7.2 Hz, 1H), 6.12 (dd, *J* = 7.2 and 0.9 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0, 20.7, 39.4, 71.0, 118.9, 133.3. – For analysis a small sample was purified by GC (100°C).

$C_6H_{11}ClO$ (134.6) Calcd. C 53.54 H 8.24
Found C 53.48 H 8.23

20 µl of racemic **7a** was treated with 30 µl of (*S*)-(–)-1-phenylethyl isocyanate for 1 h at 60°C. Dilution with dichloromethane and GC analysis on column C, 200°C, showed the 2*R*,3*S*-diastereomer to elute at 32.3 min, the 2*S*,3*R* diastereomer at 34.1 min.

(3R,4S*)-(Z)-6-Chloro-4-methyl-5-hexen-3-ol* (**7b**): To a solution of 2.55 g (11.8 mmol) of crude **6** (purity >90%) in 10 ml of petroleum ether (40–60°C) was added 1.03 g (17.7 mmol) of propionaldehyde at 0°C. After 18 h at room temp. the mixture was concentrated and the residue taken up in 100 ml of ether. 1.76 g (11.8 mmol) of triethanolamine was added under vigorous stirring. After 4 h the mixture was filtered, and the filtrate was concentrated. The residue was chromatographed over 120 g of silica gel with petroleum ether (40–60°C)/ether (3:2) to give 1.13 g (65%) of **7b**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.4 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H), 1.45 (m, 2H), 1.51 (s, broad, 1H), 2.86 (dddq, *J* = 9.6, 8.1, 6.9, and 0.8 Hz, 1H), 3.43 (dt, *J* = 8.1 and 4.6 Hz, 1H), 5.73 (dd, *J* = 9.6 and 7.2 Hz, 1H), 6.09 (dd, *J* = 7.2 and 0.8 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.0, 16.4, 27.7, 37.3, 76.4, 118.5, 133.0. – For analysis a small sample was purified by GC (110°C).

$C_7H_{13}ClO$ (148.6) Calcd. C 56.57 H 8.82
Found C 56.57 H 8.93

20 µl of racemic **7b** was derivatized as described above with (*S*)-(–)-1-phenylethyl isocyanate. Analytical GC (column A, 170°C) showed the 3*R*,4*S* diastereomer to elute at 25.9 min, the 3*S*,4*R* diastereomer at 27.6 min.

(3R,4S*)-(Z)-6-Chloro-2,4-dimethyl-5-hexen-3-ol* (**7c**): 1.60 g (7.0 mmol) of crude **6** (purity >90%), 0.81 g (11 mmol) of isobutyraldehyde and 1.12 g (7.5 mmol) of triethanolamine were treated as described for **7a**. Chromatography as described for **7b** gave 1.03 g (84%) of **7c**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H), 1.03 (d, *J* = 6.9 Hz, 3H), 1.48 (d, *J* = 3.9 Hz, 1H), 1.64 (m, 1H), 2.97 (m, 1H), 3.15 (m, 1H), 5.79 (dd, *J* = 9.6 and 7.1 Hz, 1H), 6.07 (dd, *J* = 7.1 and 0.8 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.9, 17.8, 19.2, 31.4, 35.0, 80.2, 117.9, 132.9. – For analysis a small sample was purified by GC (130°C).

$C_8H_{15}ClO$ (162.7) Calcd. C 59.07 H 9.30
Found C 58.92 H 9.43

20 µl of racemic **7a** was derivatized as described for **7a**. GC analysis (column C, 215°C) showed the 3*R*,4*S* diastereomer to elute at 40.4 min, the 3*S*,4*R* diastereomer at 41.9 min.

(1R,2R*)-(Z)-4-Chloro-2-methyl-1-phenyl-3-buten-1-ol* (**7d**): To a solution of 1.80 g (8.3 mmol) of crude **6** (purity >90%) in 15 ml of petroleum ether (40–60°C) was added 0.59 g (5.5 mmol) of benzaldehyde at 0°C. After 18 h at room temp. the mixture was worked up as described for **7b**. The crude product was chromatographed over 100 g of silica gel with petroleum ether (40–60°C)/ether (7:3) to give 0.66 g (61%, referring to benzaldehyde) of **7d**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.9 Hz, 3H), 2.02 (s, broad, 1H), 3.14 (dddq, *J* = 9.4, 7.3, 6.9, and 0.9 Hz, 1H), 4.50 (d, *J* = 7.3 Hz, 1H), 5.75 (dd, *J* = 9.4 and 7.2 Hz, 1H), 6.13 (dd, *J* = 7.2 and 0.9 Hz, 1H), 7.34 (m, 5H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.0, 39.8, 77.8, 119.2, 126.6, 127.7, 128.2, 133.6, 142.3, – For analysis a small sample was purified by GC (165°C).

$C_{11}H_{13}ClO$ (196.7) Calcd. C 67.18 H 6.66
Found C 67.27 H 6.74

20 µl of racemic **7d** was derivatized with 50 µl of isopropyl isocyanate as described for **7a**. Analytical GC (column B, 180°C) showed the 1*R*,2*R* isomer to elute at 70.0 min, the 1*S*,2*S* isomer at 73.0 min.

(3R,4S*)-(Z)-1-Chloro-3-methyl-1-nonen-4-ol* (**7e**): 1.80 g (8.3 mmol) of crude **6** (purity >90%) was treated with 0.55 g (5.5 mmol) of hexanal as described for **7d** to give 0.95 g (91%, referring to hexanal) of **7e**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.36 (m, 9H), 2.83 (m, 1H), 3.51 (m, 1H), 5.73 (dd, *J* = 9.6 and 7.2 Hz, 1H), 6.09 (d, *J* = 7.1 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 16.3, 22.5, 25.4, 31.7, 34.8, 37.6, 74.9, 118.4, 133.0. – For analysis a small sample was purified by GC (145°C).

$C_{10}H_{19}ClO$ (190.7) Calcd. C 62.98 H 10.04
Found C 62.99 H 10.21

Racemic **7e** was hydrogenated as described under 5., and the resulting (*3R*,4S**)-3-methyl-4-nonanol was derivatized with isopropyl isocyanate as described for **7d**. Analytical GC (column B, 100–160°C, 1°C/min) showed the 3*R*,4*S* isomer to elute at 58.4 min, the 3*S*,4*R* isomer at 58.9 min.

(3R,4S*,5R*)-(Z)-1-Chloro-3,5-dimethyl-1-hepten-4-ol* (**23**) *and (3R*,4S*,5S*)-Compound* **24**: To a solution of 1.96 g (9.0 mmol) of crude **6** (purity ca. 85%) in 5 ml of toluene were added a few bits of molecular sieves A4 and 0.78 g (9.0 mmol) of 2-methylbutanal at 0°C. After 24 h at room temp. the mixture was concentrated and worked up as described for **7b** to give 0.83 g (52%, referring to aldehyde) of an 8:2 mixture of **23** and **24**. For analysis a small sample was purified by GC (130°C). – ^{1}H NMR (400 MHz, $CDCl_3$): **23**: δ = 0.89 (t, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 7.1 Hz, 3H),

1.00 (d, J = 6.9 Hz, 3H), 1.24 (m, 1H), 1.38 (s, 1H), 1.46 (m, 2H), 2.97 (m, 1H), 3.30 (dd, J = 6.3 and 4.7 Hz, 1H), 5.75 (dd, J = 9.5 and 7.2 Hz, 1H), 6.09 (dd, J = 7.2 and 0.7 Hz, 1H). – **24**: δ = 0.88 (d, J = 7.5 Hz, 3H), 0.89 (t, J = 7.5 Hz, 3H), 1.05 (d, J = 7.0 Hz, 3H), 1.15 (m, 1H), 1.25 (d, J = 3.5 Hz, 1H), 1.42 (m, 1H), 1.64 (ddq, J = 10.8, 7.7, and 2.5 Hz, 1H), 3.00 (m, 1H), 3.23 (dd, J = 7.4 and 4.1 Hz, 1H), 5.80 (dd, J = 9.6 and 7.1 Hz, 1H), 6.06 (dd, J = 7.1 and 0.6 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): **23**: δ = 11.6, 13.1, 16.7, 26.3, 35.5, 37.3, 78.0, 118.4, 134.0. – **24**: δ = 11.0, 15.3, 17.2, 24.3, 35.0, 38.1, 79.2, 118.1, 132.9.

$C_9H_{17}ClO$ (176.7) Calcd. C 61.18 H 9.70
Found C 61.02 H 9.92

7. *Hydrogenation of* **23** *and* **24** *to the 3,5-Dimethyl-4-hexanols* (**25** and **26**): 380 mg (2.1 mmol) of a mixture of **23** and **24** was hydrogenated for 12 h under 6 bar hydrogen as described under 5. to give 260 mg (86%) of **25** and **26**. – (3*R**,4*S**,5*S**)-**26**: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.4, 15.9, 23.2, 37.0, 80.4, cf. ref.[13]. – (3*R**,5*R**)-**25**: ^{13}C NMR as under 5.

8. *Addition of* **14** *to Aldehydes: (3R*,4R*)-(Z)-4-(Benzyloxymethyl)-6-chloro-5-hexen-3-ol* (**27b**): After stirring 2.05 g (6.4 mmol) of **14** with 0.37 g (6.4 mmol) of propionaldehyde for 10 h at room temp. 0.95 g (6.4 mmol) of triethanolamine was added. After stirring for 4 h the total mixture was chromatographed over 100 g of silica gel with ethyl acetate/petroleum ether (40–60°C) (1:9) to give 0.89 g (55%) of **27b**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.93 (t, J = 7.4 Hz, 3H), 1.38–1.51 (m, 2H), 2.79 (s, broad, 1H), 3.00–3.04 (m, 1H), 3.67 (ABC system, J_{AB} = 10, J_{AC} = 5, J_{BC} = 4 Hz, 2H), 3.84–3.88 (m, 1H), 4.52 (s, 2H), 6.00 (dd, J = 9.7 and 7.2 Hz, 1H), 6.20 (d, J = 7.2 Hz, 1H), 7.29–7.36 (m, 5H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 10.2, 27.8, 42.1, 71.9, 73.2, 73.9, 120.2, 127.4, 127.6, 128.2, 128.3, 137.7. – For analysis a small sample was purified by GC (160°C).

$C_{14}H_{19}ClO_2$ (254.7) Calcd. C 66.00 H 7.52 Cl 13.92
Found C 66.12 H 7.67 Cl 13.92

(3R,4R*)-(Z)-4-(Benzyloxymethyl)-6-chloro-2-methyl-5-hexen-3-ol* (**27c**): 2.89 g (9.0 mmol) of **14** and 0.78 g (11 mmol) of isobutyraldehyde were treated as above. The reaction mixture was chromatographed over 60 g of silica gel with ethyl acetate/petroleum ether (40–60°C) (1:3) to give 1.50 g (62%) of **27c**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (d, J = 6.7 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H), 1.55–1.60 (m, 1H), 2.89 (s, broad, 1H), 3.11–3.16 (m, 1H), 3.50 (d, J = 9.0 Hz, 1H), 3.67 (ABC system, J_{AB} = 9.1, J_{AC} = 5.2, J_{BC} = 4.4 Hz, 2H), 4.52 (s, 2H), 6.07 (dd, J = 9.6 and 7.2 Hz, 1H), 6.18 (d, J = 7.2 Hz, 1H), 7.25–7.36 (m, 5H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 18.9, 19.1, 31.9, 40.2, 72.3, 73.2, 77.8, 119.7, 127.4, 127.6, 128.3, 137.7. – For analysis a small sample was purified by GC (160°C).

$C_{15}H_{21}ClO_2$ (268.8) Calcd. C 67.03 H 7.88
Found C 67.13 H 7.87

(3R,4R*)-(Z)-3-(Benzyloxymethyl)-1-chloro-1-octen-4-ol* (**27f**): 2.50 g (7.8 mmol) of **14** and 0.72 g (8.3 mmol) of pentanal were treated as above to give 1.33 g (61%) of **27f**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3H), 1.26–1.46 (m, 6H), 2.76 (s, broad, 1H), 2.96–3.01 (m, 1H), 3.66 (ABC system, J_{AB} = 9.1, J_{AC} = 5.2, J_{BC} = 4.4 Hz, 2H), 3.92–3.99 (m, 1H), 4.52 (s, 2H), 6.01 (dd, J = 9.7 and 7.2 Hz, 1H), 6.20 (dd, J = 7.2 and 0.6 Hz, 1H), 7.25–7.36 (m, 5H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 13.9, 22.5, 27.9, 34.6, 42.5, 71.8, 72.4, 73.2, 120.2, 127.4, 127.6, 128.2, 128.3, 137.7. – For analysis a small sample was purified by GC (170°C).

$C_{16}H_{23}ClO_2$ (282.8) Calcd. C 67.97 H 8.20
Found C 68.03 H 8.26

9. *Addition of* **15** *to Aldehydes: (3R*,4R*)-(Z)-4-[tert-Butyldimethylsilyloxy)methyl]-6-chloro-5-hexen-3-ol* (**28b**): 3.10 g (9.2 mmol) of **15** and 0.70 g (12.1 mmol) of propionaldehyde were treated as described under 8. to give 1.60 g (62%) of **28b**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 3H), 0.06 (s, 3H), 0.88 (s, 9H), 0.93 (t, J = 7.4 Hz, 3H), 1.35–1.43 (m, 2H), 2.82–2.86 (m, 1H), 3.33 (s, 1H), 3.81–3.84 (m, 1H), 3.87–3.91 (m, 2H), 6.04 (dd, J = 9.6 and 4.0 Hz, 1H), 6.20 (d, J = 7.3 Hz, 1H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = –5.7, –5.6, 10.2, 18.0, 25.7, 27.9, 43.2, 66.1, 75.7, 120.0, 128.3. – For analysis a small sample was purified by GC (160°C).

$C_{13}H_{27}ClO_2Si$ (278.9) Calcd. C 55.98 H 9.76
Found C 56.08 H 9.74

(1R,2S*)-(Z)-2-[(tert-Butyldimethylsilyloxy)methyl]-4-chloro-1-phenyl-3-buten-1-ol* (**28d**): 5.40 g (16.1 mmol) of **15** and 1.60 g (15 mmol) of benzaldehyde were treated as described under 8. to give 2.90 g (55%) of **28d**. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 3H), 0.08 (s, 3H), 0.92 (s, 9H), 3.13–3.17 (m, 1H), 3.50 (d, J = 2.9 Hz, 1H), 3.80 (ABC system, J_{AB} = 10.0, J_{AC} = 5.1, J_{BC} = 6.0 Hz, 2H), 5.09 (t, J = 3.2 Hz, 1H), 5.94 (dd, J = 9.4 and 7.3 Hz, 1H), 6.10 (dd, J = 7.1 and 0.7 Hz, 1H), 7.25–7.36 (m, 5H). – ^{13}C NMR (20 MHz, $CDCl_3$): δ = –5.6, –5.5, 18.2, 25.9, 46.5, 64.6, 74.5, 120.5, 126.0, 127.1, 128.0, 128.1, 142.3. – For analysis a small sample was purified by GC (170°C).

$C_{17}H_{27}ClO_2Si$ (326.9) Calcd. C 62.45 H 8.33
Found C 62.44 H 8.49

10. *(1R*,2S*)-(Z)-4-Chloro-2-(hydroxymethyl)-1-phenyl-3-buten-1-ol:* A solution of 3.00 g (9.2 mmol) of **28d** in 30 ml of THF was treated with 18.4 ml (18.2 mmol) of a 1 M solution of tetra-*n*-butylammonium fluoride in THF at 0°C. After 1 h at room temp. the mixture was concentrated. After addition of 10 ml of aqueous saturated ammonium sulfate solution the mixture was extracted four times with 20 ml of ether. The combined organic phases were dried with Na_2SO_4 and concentrated to give a yellowish oil which slowly crystallized. Two recrystallisations from ethanol/petroleum ether (40–60°C) gave 1.44 g (74%) of the diol as colourless crystals of m.p. 77°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, broad, 1H), 2.93 (s, broad, 1H), 3.19–3.25 (m, 1H), 3.76 (ABC system, J_{AB} = 15.3, J_{AC} = 4.6, J_{BC} = 6.0 Hz, 2H), 5.04 (d, J = 4.3 Hz, 1H), 5.86 (dd, J = 9.5 and 7.2 Hz, 1H), 6.14 (dd, J = 7.2 and 0.9 Hz, 1H), 7.25–7.37 (m, 5H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 46.2, 63.0, 73.8, 120.9, 125.9, 127.2, 127.5, 127.9, 141.8.

$C_{11}H_{13}ClO_2$ (212.7) Calcd. C 62.12 H 6.16
Found C 62.14 H 6.34

11. *cis-5-[2-Chloro-1-(Z)-ethenyl]-4-phenyl-1,3-dioxan-2-one* (**29**): To a solution of 210 mg (0.98 mmol) of the product obtained under 10. in 30 ml of benzene was added 300 mg (2.3 mmol) of ethyldiisopropylamine, and the mixture was saturated at 20°C for 20 min with phosgene. After concentration in vacuo 5 ml of water was added, and the mixture was extracted three times with 10 ml each of petroleum ether (40–60°C). The combined organic phases were dried with Na_2SO_4 and concentrated in vacuo. The crude **29** showed the following NMR data: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.62–3.70 (m, 1H), 4.20 (ABC system, J_{AB} = 11.0, J_{AC} = 5.3, J_{BC} = 5.5 Hz, 2H), 5.82 (dd, J = 9.4 and 7.3 Hz, 1H), 5.88 (d, J = 7.1 Hz, 1H), 6.35 (dd, J = 7.3 and 0.8 Hz, 1H), 7.32–7.43 (m, 5H). – ^{13}C NMR (25 MHz, $CDCl_3$): δ = 42.4, 69.6, 82.2, 124.3, 125.0, 126.5, 128.9, 134.9, 149.8, 150.3.

12. *Methyl (2R,3R)-3-Hydroxy-2-methylbutanoate* (**30**): Into a solution of 1.70 g (12.6 mmol) of (2*R*,3*S*)-(*Z*)-5-chloro-3-methyl-4-penten-2-ol (**7a**) in 16 ml of methanol was introduced ozone at –78°C until the blue colour persisted. Excess of ozone was blown

out with nitrogen. The mixture was allowed to reach room temp. and subsequently was heated for 3 h to 60°C. After removal of the solvent the residue was partitioned between 10 ml each of ether and 10% aqueous NaOH. The organic phase was washed with 10 ml of water, dried with $MgSO_4$ and concentrated to give 0.69 g (42%) of **30**. $[\alpha]_D^{20} = -33.0$ (c = 5.0, methanol), cf. ref.[19]. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (d, J = 7.2 Hz, 3H), 1.20 (d, J = 6.3 Hz, 3H), 2.00 (s, broad, 1H), 2.45 (dq, J = 7.2 and 7.2 Hz, 1H), 3.70 (s, 3H), 3.87 (m, 1H) cf. ref.[20]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 20.3, 46.8, 51.5, 69.1, 176.1, cf. ref.[20].

A sample of the obtained β-hydroxy-ester **30** was converted into the *tert*-butyldimethylsilyl derivative **31** as described in ref.[20] and identified by its NMR data.

CAS Registry Numbers

3: 114716-34-6 / **5a**: 114716-35-7 / **5b**: 114716-36-8 / **5c**: 114716-37-9 / **5d**: 114716-38-0 / **6**: 100348-14-9 / **7a** (absol. stereochem.): 100244-07-3 / **7a** (racemic): 114716-41-5 / **7a** (2*R*,3*S*-urethane deriv.): 114653-28-0 / **7a** (2*S*,3*R*-urethane deriv.): 114716-47-1 / **7b** (absol. stereochem.): 100244-08-4 / **7b** (racemic): 114716-42-6 / **7b** (3*R*-4*S*-urethane deriv.): 114653-29-1 / **7b** (3*S*,4*R*-urethane deriv.): 114716-48-2 / **7c** (absol. stereochem.): 100244-09-5 / **7c** (racemic): 114716-43-7 / **7c** (3*R*,4*S*-urethane deriv.): 114653-30-4 / **7c** (3*S*,4*R*-urethane deriv.): 114716-49-3 / **7d** (absol. stereochem.): 114653-37-1 / **7d** (racemic): 114716-44-8 / **7d** (1*R*,2*R*-urethane deriv.): 114653-25-7 / **7d** (1*S*,2*S*-urethane deriv.): 114653-26-8 / **7e** (absol. stereochem.): 100244-10-8 / **7e** (racemic): 114716-45-9 / **9**: 83622-41-7 / **10**: 114653-20-2 / **11**: 83947-59-5 / **12**: 114653-18-8 / **13**: 114653-19-9 / **14**: 114653-21-3 / **15**: 114674-43-0 / **16**: 114716-39-1 / **17**: 114716-40-4 / **18**: 82917-19-9 / **19**: 98757-89-2 / **23**: 114716-46-0 / **24**: 114716-50-6 / **26**: 98757-88-1 / **27b**: 114653-35-9 / **27c**: 114653-36-0 / **27f**: 114653-22-4 / **28b**: 114653-23-5 / **28d**: 114653-24-6 / **29**: 114653-34-8 / **30**: 66767-61-1 / **31**: 96597-33-0 / (3*R**,4*S**)-3-methyl-4-nonanol: 114653-27-9 / (3*R*,4*S*)-3-methyl-4-nonanol urethane deriv.: 114653-31-5 / (3*S*,4*R*)-3-methyl-4-nonanol urethane deriv.: 114653-32-6 / (1*R**,2*S**)-(*Z*)-4-chloro-2-(hydroxymethyl)-1-phenyl-3-buten-1-ol: 114653-33-7 / acetaldehyde: 75-07-0 / propanal: 123-38-6 / isobutyraldehyde: 78-84-2 / benzaldehyde: 100-52-7 / (±)-2-methylbutanal: 57456-98-1 / pentanal: 110-62-3 / hexanal: 66-25-1

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[42/88]