Stereoselective Synthesis of Alcohols, XXXV[1]

Addition of *E*- and *Z*-Crotylboronates to Chiral α-Substituted Aldehydes

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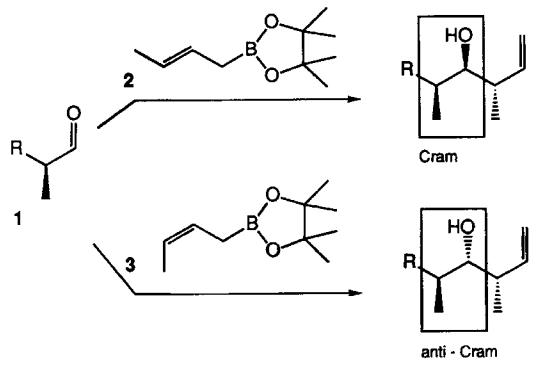
The direction (Cram/*anti*-Cram) and the extent of asymmetric induction on addition of crotylboronates to a range of chiral aldehydes was investigated. A reversal in the sense of the asymmetric induction on changing from the Z- to the *E*-crotylboronate was found for aldehydes having polar α substituents and for some of the nonpolar chiral aldehydes. Force-field calculations on transition-state models reproduced these results in the majority of the cases investigated despite of unaccounted short comings of the method.

Among the well studied addition reactions of organometallic reagents to chiral aldehydes **1** those of crotylboronates are exceptional, because the sense of the aldehyde-based asymmetric induction depends on the structure of the achiral crotylboronate. While *E*-crotylboronates **2** lead unconspicuously to the usual Cram product, the addition of the *Z*-crotylboronates **3** violates Cram's rule[2] and generates the *anti*-Cram diastereomer in preference[3,4].

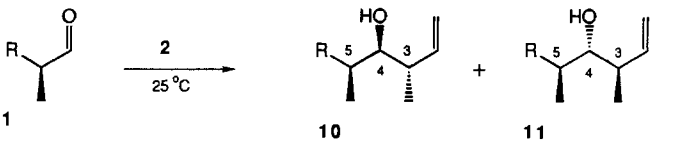
Scheme 1



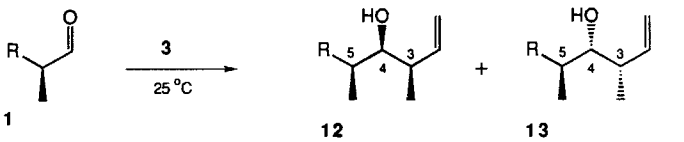
On addition of γ-substituted allylboronates such as **2** and **3** to α-methylbutyraldehyde it was found that the reversal and the extent of diastereoselectivity did not depend on the size of the γ substituent in the allylboronate[1]. Unexpected findings necessitated a modification of the interpretation for the causes of asymmetric induction in these reactions. A similar reversal or almost reversal of stereoselectivity had been reported for the addition of the *Z*- and *E*-(γ-methoxycrotyl)boronates to 2-(benzyloxy)propionaldehyde[5] (**4**), and of the *E*- and *Z*-crotylboronates to isopropylideneglyceraldehyde[6,7].

The reasons for the observed stereoselectivity have been convincingly discussed[7,8]. Nevertheless, we became curious as to how well these interpretations would be reproduced by force-field calculations on the relevant transition states. Moreover, we wanted to learn more about the role of the

Table 1. Comparison of the observed and calculated diastereoselectivities for the addition of *E*- and *Z*-crotylboronates **2** and **3** to the aldehydes **4**–**9**



Aldehyde		Products: Yield (%)	Ratio found	Ratio calculated
5	**a**: R = Et	46	77 : 23	63 : 37
6	**b**: R = Ph	53	75 : 25	75 : 25
7	**c**: R = t-Bu	65	>97: <3	99 : 1
8	**d**: R = $(PhCH_2)_2N$	92	90 : 10	75 : 25 a)
4	**e**: R = $PhCH_2O$	97 c)	47 : 53	61 : 39 b)
9	**f**: R = Cl, (side chain = Et)	71 c)	47 : 53	47 : 53

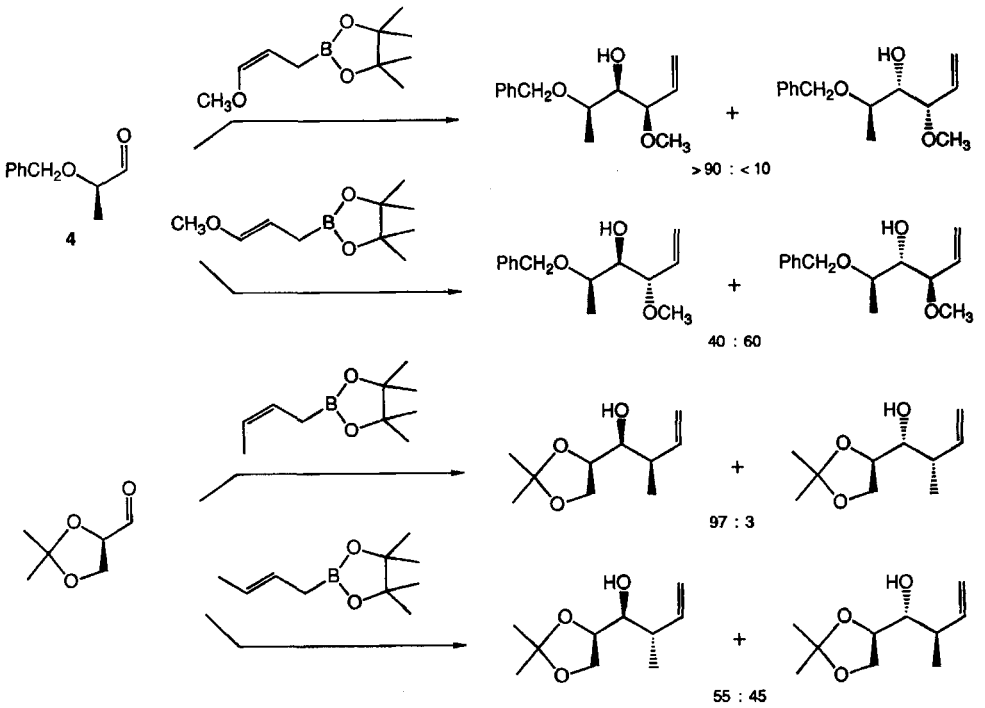


Aldehyde		Products: Yield (%)	Ratio found	Ratio calculated
5	**a**: R = Et	49	30 : 70	42 : 58
6	**b**: R = Ph	92	77 : 23	72 : 28
7	**c**: R = t-Bu	50	60 : 40	16 : 84
8	**d**: R = $(PhCH_2)_2N$	50	49 : 51	78 : 22 a)
4	**e**: R = $PhCH_2O$	98 c)	88 : 12	76 : 24 b)
9	**f**: R = Cl, (side chain = Et)	71 c)	90 : 10	76 : 24

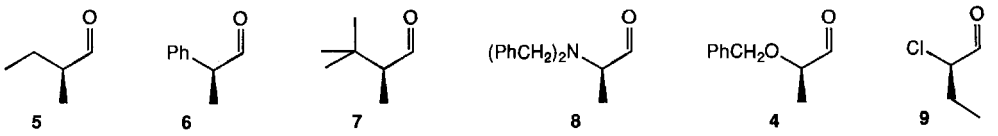
[a] Me_2N instead of $(PhCH_2)_2N$. – [b] MeO instead of $PhCH_2O$. – [c] Total yield of all isomers.

  0009–2940/90/1212–2395 $ 3.50+.25/0

Scheme 2



Scheme 3



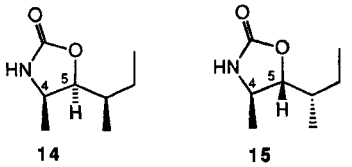
substituent R in the chiral aldehydes **1** on the sense and extent of the asymmetric induction in allylboronate additions. We report here on such a study involving the aldehydes **4**–**9**, encompassing a wide variety of steric and polar effects.

Addition of *E*- and *Z*-Crotylboronates to Chiral α-Substituted Aldehydes

The addition of the crotylboronates **2** and **3** to the aldehydes **4**–**9** was effected at room temperature. When the reaction turned out to be too sluggish, as e.g. in the case of the reaction of **3** with the aldehyde **7**, it was carried out under 4 kbar pressure. The diastereoselectivities were determined either by gas chromatography or from the ^{13}C-NMR spectra and are compiled in Table 1.

The structures of the diastereomers **10a**–**13a** can be considered as secured[9,10]. The diastereomers **10b**–**13b** were identified with the aid of ^{1}H-NMR spectra kindly provided by Prof. Yamamoto (Sendai)[11]. The adducts **10e**–**13e** were identified by comparison of the ^{13}C-NMR data with those reported in ref.[12,13]. The structural assignment for **10c, 12c,** and **13c** was made tentatively on the basis of the ^{13}C-NMR-chemical shifts of the 5-CH_3 group[14]. The adduct **10d** was identical to one obtained[15] by addition of a crotyltitanium reagent to the aldehyde **8**. The adducts **12d** and **13d** were converted into the oxazolidinones **14** and **15**. Their relative configuration at C-4/C-5 was derived from the ^{1}H-NMR spectra. The relative configuration of the side chain was assumed to follow from the rules of simple diastereoselection on addition of crotylboronates to aldehydes[16].

Scheme 4

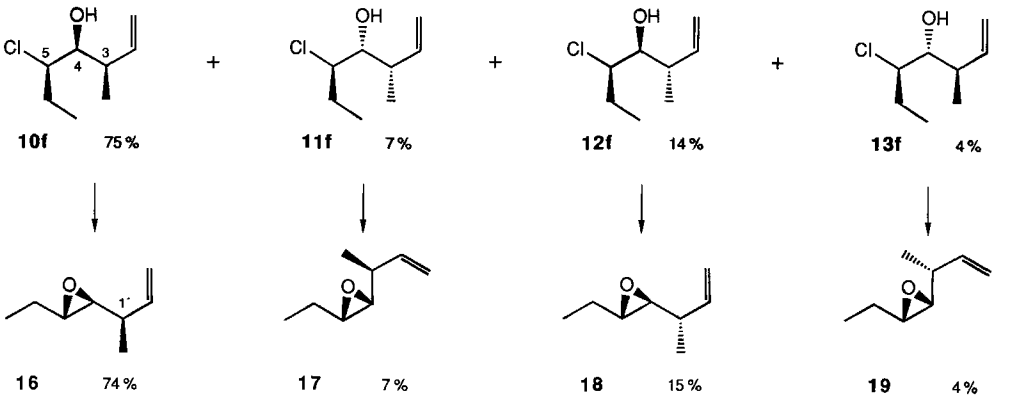


Likewise, for the adducts **10f**–**13f** it was assumed that the known simple diastereoselectivity defines the relative configuration at C-3/C-4. In order to determine the relative configuration regarding C-4/C-5, a mixture of the chlorohydrins **10f**–**13f** was treated with potassium carbonate in methanol to give a mixture of the oxiranes **16**–**19**.

The major components **16** and **18** were easily identified as *trans*-disubstituted oxiranes from the ^{13}C-NMR-chemical shift of C-1′, (δ = 39), relative to that in **17** and **19** (δ = 36).

The mixture of **10f**–**13f** was one actually obtained on reaction of the *Z*-crotylboronate **3** with the chloroaldehyde **9**. The diastereomers **12f, 13f** are genuine products derived

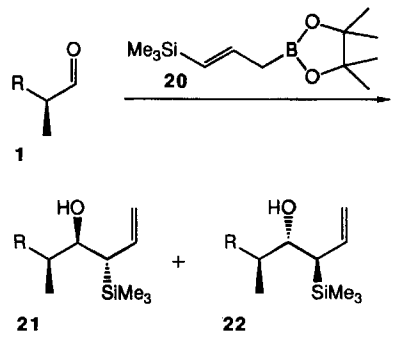
Scheme 5



from the *Z*-crotylboronate **3**, because they could arise only to a minor extent from the *E*-crotylboronate **2** being a contaminant (< 5%) in **3**. Moreover, the product ratio **12f:13f** = 3.5:1 is clearly distinct from that obtained on reaction of the *E*-crotylboronate **2** with **9**, being 1:1. Likewise, on reaction of the aldehyde **4** with the *Z*-crotylboronate **3** a mixture of four adducts, **12e:13e:10e:11e** = 77:11:9:3 was obtained in 98% yield. The 12% of the isomers **10e** and **11e** cannot totally arise from the contaminant *E*-crotylboronate **2**. Again, the **10e:11e** ratio of 3:1 differs from the one obtained on reaction of the *E*-crotylboronate **2**, being 1:1. As has been noted by Wuts[17], these results demonstrate that the *Z*-crotylboronate **3** shows a diminished simple diastereoselectivity on reaction with polar aldehydes **4** or **9**. It remains open, whether the aberrant products are formed via a chair transition state with an axially arranged aldehyde residue, or via a twist-boat transition state.

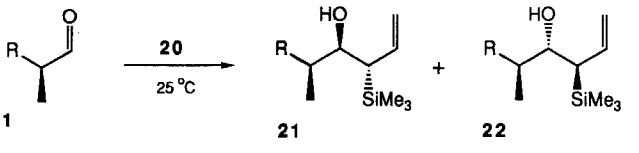
Returning to the asymmetric induction from the aldehydes **4**–**9**, we were curious, as to whether the diastereoselectivity is generally independent of the bulk of the γ substituent in the allylboronates. We therefore studied also the addition of the *E*-(γ-trimethylsilylallyl)boronate **20** to the above mentioned aldehydes. The results are compiled in Table 2.

Scheme 6



The structural assignments for all the adducts **21** and **22** are only tentative. It is assumed that the same diastereomer predominated in the addition of **20** as in the addition of the *E*-crotylboronate **2** to these aldehydes. A comparison of the data in Tables 1 and 2 shows that the change from a methyl to a trimethylsilyl group on the allylboronates led only to smaller changes in the observed diastereoselectivities. There is, however, no uniform trend, be it an increase or decrease in diastereoselectivity.

Table 2. Diastereoselectivities for the addition of the *E*-(γ-trimethylsilylallyl)boronate **20** to the aldehydes **4**–**9**



Aldehyde		Products: Yield (%)	Ratio found
5	a: R = Et	49	73 : 27
6	b: R = Ph	a)	90 : 10
7	c: R = t-Bu	48	89 : 11
8	d: R = $(PhCH_2)_2N$	71	>95: <5
4	e: R = $PhCH_2O$	52	42 : 58
9	f: R = Cl, (side chain = Et)	90	35 : 65

a) Yield not determined.

The results in Table 1 may be classified in two groups. There are the additions to the α-alkoxy and α-chloro aldehydes **4** and **9**, which gave high Cram selectivity with the *Z*-crotylboronate **3**, and low *anti*-Cram selectivity with the *E*-(γ-substituted allyl)boronates **2** or **20**. There is the other group comprising additions to the aldehydes with less polar (**8**) or unpolar substituents (**5**,**7**), which showed the opposite trend, namely substantial or high *anti*-Cram selectivity on reaction with the *E*-(γ-substituted allyl)boronates **2** and **20**, and low or partially inverted selectivity with the *Z*-crotylboronate **3**. Finally, there is the case of the phenyl-substituted aldehyde **6**, which appears to be unique in that the sense of the asymmetric induction is uniformly Cram-selective irrespective of the *E*/*Z* nature of the crotylboronate. While we cannot exclude a misassignment of the structures **12b** and **13b**, we did not see a flaw in the data reported for these compounds[11].

The reasons for these two or three types of behavior regarding substrate-based asymmetric induction must be sought in the conformations of the low-energy transition states leading to the Cram or *anti*-Cram products, respectively.

Force-Field Calculations

In order to substantiate or question the models discussed hitherto[1,3,7,8] for explaining the sense of asymmetric induction in the allylboration reaction of chiral aldehydes **1**, we carried out force-field calculations for models of the competing transition states. As in the preceding paper[1] we used a transition-state model based on the core transition state for the reaction of allylborane with formaldehyde[18]. This time, the calculations were done with a force field which is implemented in Still's MACROMODEL program[19]. The calculations were further simplified by substituting for the dibenzylamino group in **8** a dimethylamino group and for the benzyloxy group in **4** a simple methoxy group. The "expected" diastereoselectivities were calculated as described in the preceding paper[1] and are included in Table 1.

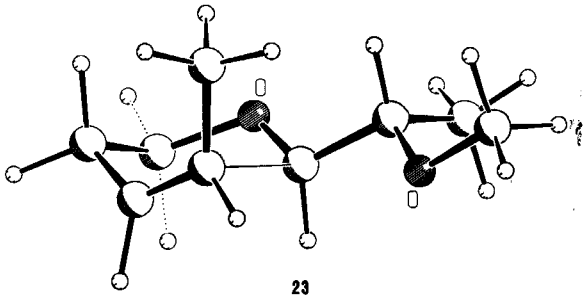
These calculations reproduce the following of the trends reported above: For the addition to the aldehydes **4** and **9** with strongly polar α substituents the *Z*-crotylboronate **3** should lead to a higher Cram selectivity than the *E*-crotylboronate **2**. The *anti*-Cram selectivity seen on reaction of the *E*-crotylboronate **2** with the aldehydes **4** and **9** is borne out by the calculations only for the addition to the aldehyde **9**.

The Cram selectivity for the addition of the *E*-crotylboronate **2** to the aldehydes **7** and **8** is reproduced by the calculations, but not so the direction of the asymmetric induction on reaction of the *Z*-crotylboronate **3**. For addition to the *tert*-butyl-substituted aldehyde **7** the structural assignment for the products **12c** and **13c** is only tentative, and an incorrect structural assignment might be the cause of this discrepancy. A misassignment of structures cannot, however, be invoked for the addition of the *Z*-crotylboronate **3** to the amino aldehyde **8**, because there is a 1:1 product ratio. The discrepancy between theoretically predicted and experimentally observed selectivity indicates that the theoretical model used in our study has unaccounted shortcomings. The reason for the apparent failure of the theoretical model may either be: (i) a poor parameterization of the amino substituent which leads to erroneous results for the interactions between **8** and the *Z*-crotylboronate **3**. A systematic study of the reliability of MM2 for aliphatic amines[20] gives no reason to suspect a failure of the force field. Another reason why the theoretical model failed may be that (ii) the assumption of the transition-state model is inadequate, i.e. that the transition-state structure for the addition of the aldehyde **8** to the *Z*-crotylboronate **3** differs substantially from the core transition state used.

The failure of the theoretical prediction in one case should be considered as a warning against an undiscriminative application of the transition-state modelling[21]. Most of our calculated data agree, however, with the experimental results, and, moreover, several cases have been reported[22] where the transition-state modelling led to predictions that are in close accord with experiment. This encouraging situation suggests further tests of the method. Our results may serve for this purpose as additional material to explore the merits and the limits of transition-state modelling.

The calculations reported here therefore substantiate by and large the qualitative interpretations given before[7,8] for the causes of the direction of the asymmetric induction. The further experimental results reported here convey a more representative picture of the tendencies of the asymmetric induction that may be encountered depending on the nature of the substituent in the chiral aldehyde.

Scheme 7



23

With polar substituents transition states such as **23** of the type suggested by Cornforth[23], in which the polar substituent is antiperiplanar to the carbonyl group of the aldehyde, appear indeed to be favored. These force-field calculations account for polar effects by lone-pair repulsion terms and by terms of dipole-dipole interactions. However, the preference for these Cornforth-type transition states is not very marked according to these calculations. It may amount to ca. 1 kcal/mol and is therefore easily surpassed by other steric effects.

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Experimental

All temperatures quoted are not corrected. – ^{1}H NMR, ^{13}C NMR: Bruker WH-400, AC-300. – Flash chromatography: silica gel 60 (0.040–0.063 mm, Merck).

1) *(3R*,4R*,5R*)- and (3R*,4R*,5S*)-3-Methyl-5-phenyl-1-hexen-4-ol* (**10b** and **11b**): 0.36 g (2 mmol) of 2-(2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*/*Z* = 86:14) and 0.27 g (2 mmol) of 2-phenylpropanal (**6**) were combined and kept for 4 d at room temperature. A solution of 0.30 g (2 mmol) of triethanolamine in 5 ml of CH_2Cl_2/petroleum ether (b.p. 40–60°C) (3:2) were added. After stirring for 1 d, the solvents were removed i.vac., and the residue was filtered through 20 g of silica gel with CH_2Cl_2 to remove the boratrane. The filtrate was concentrated, and the residue was flash-chromatographed (16 cm column) with ether/petroleum ether (b.p. 40–60°C) (1:10). After some unreacted aldehyde, 0.20 g (53%) of a 75:25 mixture of **10b, 11b** was obtained as a colorless oil.

10b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (d, *J* = 7.1 Hz, 3H), 1.31 (d, *J* = 7.0 Hz, 3H), 1.60 (br. s, 1H), 2.19 (m, 1H), 2.84 (m,

1 H), 3.49 (br. s, 1 H), 5.03 (ddd, J = 17.3, 1.7, and 1.1 Hz, 1 H), 5.13 (dd, J = 10.4 and 1.9 Hz, 1 H), 5.83 (ddd, J = 17.5, 10.3, and 7.9 Hz, 1 H), 7.17–7.33 (m, 5 H); these data corresponded to spectra kindly provided by Prof. Yamamoto, cf. ref.[11]. – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.5, 17.3, 40.5, 43.2, 79.4, 116.4, 126.3, 127.7, 128.5, 139.4, 145.1.

11b: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9, 18.6, 41.0, 43.5, 79.1, 115.9, 126.6, 128.5, 139.6, 143.9.

$C_{13}H_{18}O$ (190.3) Calcd. C 82.06 H 9.53
Found C 82.19 H 9.76

2) *(3R*,4S*,5S*)- and (3R*,4S*,5R*)-3-Methyl-5-phenyl-1-hexen-4-ol* (**12b** and **13b**): 0.36 g (2 mmol) of 2-[(2*Z*)-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), 0.27 g (2 mmol) of 2-phenylpropanal (**6**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1) to give 0.35 g (92%) of a 77:23 mixture of **12b** and **13b** as a colorless oil.

12b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (d, J = 6.8 Hz, 3 H), 1.32 (d, J = 6.9 Hz, 3 H), 1.48 (d, J = 3.9 Hz, 1 H), 2.20 (m, 1 H), 2.91 (m, 1 H), 3.59 (td, J = 5.9 and 3.8 Hz, 1 H), 5.07 (dt, J = 17.6 and 1.5 Hz, 1 H), 5.07 (dt, J = 10.2 and 1.3 Hz, 1 H), 5.81 (ddd, J = 17.5, 10.1, and 7.4 Hz, 1 H), 7.14–7.37 (m, 5 H); these data corresponded to spectra kindly provided by Prof. Yamamoto, cf. ref.[11]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 15.7, 40.3, 42.6, 78.8, 114.5, 126.2, 127.5, 128.4, 141.7, 145.0.

13b: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (d, J = 6.8 Hz, 3 H), 1.26 (d, J = 4.5 Hz, 1 H), 1.28 (d, J = 7.1 Hz, 3 H), 2.36 (m, 1 H), 2.90 (m, 1 H), 3.58 (m, 1 H), 5.08 (d, J = 10.0 Hz, 1 H), 5.09 (d, J = 16.6 Hz, 1 H), 5.89 (ddd, J = 17.2, 10.3, and 6.9 Hz, 1 H), 7.15–7.34 (m, 5 H); these data corresponded to spectra kindly provided by Prof. Yamamoto, cf. ref.[11]. – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.3, 18.6, 40.4, 42.9, 78.7, 114.4, 126.5, 128.2, 128.3, 142.2, 143.6.

$C_{13}H_{18}O$ (190.3) Calcd. C 82.06 H 9.53
Found C 82.22 H 9.79

3) *(3R*,4R*,5R*)-3,5,6,6-Tetramethyl-1-heptene-4-ol*[24] (**10c**): 0.36 g (2 mmol) of 2-(2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*/*Z* = 92:8), 0.23 g (2 mmol) of 2,3,3-trimethylbutanal[25] (**7**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1) to give 0.22 g (65%) of **10c** as a colorless oil. – ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, J = 7.1 Hz, 3 H), 0.94 (s, 9 H), 0.96 (d, J = 6.7 Hz, 3 H), 1.40 (qd, J = 7.2 and 1.4 Hz, 1 H), 1.45 (d, J = 3.5 Hz, 1 H), 2.19 (m, 1 H), 3.52 (ddd, J = 8.9, 3.3, and 1.1 Hz, 1 H), 5.13 (dd, J = 9.5 and 1.7 Hz, 1 H), 5.13 (ddd, J = 17.6, 2.0, and 0.8 Hz, 1 H), 5.70 (ddd, J = 17.8, 9.4, and 8.9 Hz, 1 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.7, 17.0, 28.3, 33.1, 43.1, 44.1, 73.7, 116.5, 142.0.

$C_{11}H_{22}O$ (170.3) Calcd. C 77.58 H 13.02
Found C 77.66 H 13.48

4) *(3R*,4S*,5S*)- and (3R*,4S*,5R*)-3,5,6,6-Tetramethyl-1-hepten-4-ol*[24] (**12c** and **13c**): Upon reaction of 0.36 g (2 mmol) of 2-[(2*Z*)-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), 0.23 g (2 mmol) of 2,3,3-trimethylbutanal (**7**), and of 0.30 g (2 mmol) of triethanolamine as described under 1) the conversion remained low. The components were therefore dissolved in 4 ml of $CDCl_3$ and kept for 1 d under 4 kbar pressure. Workup as described under 1) yielded 0.17 g (50%) of a 60:40 mixture of **12c, 13c** as a colorless oil.

12c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (d, J = 7.2 Hz, 3 H), 0.91 (s, 9 H), 1.08 (d, J = 6.7 Hz, 3 H), 1.14 (d, J = 6.4 Hz, 1 H), 1.47 (qd, J = 7.1 and 0.9 Hz, 1 H), 2.24 (m, 1 H), 3.61 (dd, J = 8.0 and 6.9 Hz, 1 H), 4.98 (dd, J = 10.4 and 1.9 Hz, 1 H), 5.03 (ddd, J = 17.9, 1.9, and 0.7 Hz, 1 H), 5.61 (ddd, J = 17.1, 10.2, and 8.8 Hz, 1 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.5, 17.6, 28.1, 33.0, 43.6, 44.2, 74.8, 114.6, 141.7.

13c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (d, J = 7.0 Hz, 3 H), 0.98 (s, 9 H), 0.98 (d, J = 6.8 Hz, 3 H), 1.35 (d, J = 3.8 Hz, 1 H), 1.41 (qd, J = 7.1 and 1.7 Hz, 1 H), 2.49 (m, 1 H), 3.52 (ddd, J = 8.8, 3.5, and 2.3 Hz, 1 H), 5.11 (dt, J = 17.3 and 1.7 Hz, 1 H), 5.15 (dt, J = 10.7 and 1.5 Hz, 1 H), 5.95 (ddd, J = 17.2, 10.6 and 5.9 Hz, 1 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.1, 12.7, 29.0, 33.4, 39.8, 45.0, 75.3, 114.9, 143.0.

$C_{11}H_{22}O$ (170.3) Calcd. C 77.58 H 13.02
Found C 77.02 H 13.21

5) *(3R*,4R*,5S*)- and (3R*,4R*,5R*)-5-(Dibenzylamino)-3-methyl-1-hexen-4-ol* (**10d** and **11d**): 0.36 g (2 mmol) of 2-(2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*/*Z* = 92:8), 0.51 g (2 mmol) of 2-(dibenzylamino)propanal[26] (**8**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1) to give 0.57 g (92%) of a 9:1 mixture of **10d, 11d** as a colorless oil.

10d: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.92 (d, J = 7.0 Hz, 3 H), 1.12 (d, J = 6.7 Hz, 3 H), 1.56 (br. s, 1 H), 2.68 (m, 1 H), 2.75 (quint, J = 6.7 Hz, 1 H), 3.47 (d, J = 11.2 Hz, 1 H), 3.49 and 3.76 (AB-System, J_{AB} = 13.8 Hz, 4 H), 4.89 (dt, J = 17.4 and 1.6 Hz, 1 H), 4.98 (ddd, J = 10.6, 1.8, and 0.8 Hz, 1 H), 5.41 (ddd, J = 17.4, 10.4, and 7.1 Hz, 1 H), 7.19–7.40 (m, 10 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.7, 16.9, 39.5, 54.7, 55.1, 76.8, 116.7, 127.0, 128.4, 129.2, 139.3, 140.5; these data corresponded to those reported in ref.[15].

11d: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.0, probably 19.0, 40.4, 53.5, 53.6, 55.9, 74.2, 114.9, 127.4, 127.5, 129.3, 139.1, 140.9.

$C_{21}H_{27}NO$ (309.5) Calcd. C 81.51 H 8.79 N 4.53
Found C 81.43 H 8.94 N 4.77

6) *(3R*,4S*,5R*)- and (3R*,4S*,5S*)-5-(Dibenzylamino)-3-methyl-1-hexen-4-ol*[24] (**12d** and **13d**): 0.36 g (2 mmol) of 2-[(2*Z*)-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), 0.51 g (2 mmol) of 2-(dibenzylamino)propanal[26] (**8**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1). Flash chromatography separated the two isomers to give 0.16 g of **12d** and 0.15 g of **13d** (combined yield 50%).

12d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 (d, J = 6.9 Hz, 3 H), 1.02 (d, J = 6.7 Hz, 3 H), 2.17 (m, 1 H), 2.73 (dq, J = 9.5 and 6.7 Hz, 1 H), 3.31 and 3.84 (AB-System, J_{AB} = 13.2 Hz, 4 H), 3.51 (dd, J = 9.7 and 2.5 Hz, 1 H), 4.37 (br. s, 1 H), 4.98 (ddd, J = 10.4, 1.7, and 1.2 Hz, 1 H), 5.00 (dt, J = 17.3 and 1.6 Hz, 1 H), 5.95 (ddd, J = 17.3, 10.3, and 7.0 Hz, 1 H), 7.27 (m, 10 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.2, 11.5, 39.1, 53.2, 55.1, 73.5, 113.2, 127.2, 128.4, 129.0, 138.8, 142.9.

13d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.62 (d, J = 6.5 Hz, 3 H), 1.14 (d, J = 6.6 Hz, 3 H), 1.47 (br. s, 1 H), 2.73 (m, 1 H), 2.80 (quint, J = 6.9 Hz, 1 H), 3.46 and 3.75 (AB-System, J_{AB} = 13.6 Hz, 4 H), 3.70 (dd, J = 7.2 and 3.9 Hz, 1 H), 4.98 (d, J = 9.9 Hz, 1 H), 5.00 (d, J = 18.1 Hz, 1 H), 5.74 (ddd, J = 17.1, 10.4, and 6.7 Hz, 1 H), 7.20–7.34 (m, 10 H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.6, 11.7, 39.1, 54.2, 54.4, 76.0, 114.3, 126.8, 128.1, 129.0, 140.1, 142.4.

$C_{21}H_{27}NO$ (309.5) Calcd. C 82.51 H 8.79 N 4.53
Found C 81.55 H 8.87 N 4.73

7) *(1'R*,4R*,5S*)- and (1'R*,4S*,5S*)-4-Methyl-5-(1-methylpropyl)oxazolidin-2-on*[24] (**14** and **15**): 0.58 g (1.9 mmol) of a mixture of **12d** and **13d** was dissolved in 19 ml of methanol and 1 ml of formic acid. After addition of ca. 400 mg of palladium black the suspension was stirred under 1 bar of hydrogen at room temperature. Hydrogen uptake was very slow. The stirring was continued for 7 weeks. The mixture was filtered, and the catalyst was washed with methanol. The filtrates were concentrated, and the residue was

taken up in 5 ml of ether and 5 ml of methanol to which were added 10 drops of concentrated hydrochloric acid. After stirring for 6 h, saturated aqueous $NaHCO_3$ solution was added until the mixture had pH = 7. The mixture was extracted 5 times with 10 ml each of CH_2Cl_2. The combined extracts were concentrated to leave the crude amino alcohols (0.19 g, 77%). These were taken up in 2 ml of toluene. To this solution was added at 0°C 3 ml of a 4.3 M solution of $COCl_2$ in toluene. After addition of 7 ml of 10% aqueous KOH solution, the mixture was stirred for 1 h, and the organic phase was separated. The aqueous phase was extracted 8 times with 1 ml each of ether. The combined extracts were washed with saturated aqueous NH_4Cl solution and twice with 2 ml each of water and brine. The solution was dried with $MgSO_4$ and concentrated to give 0.15 g of crude product which was purified by flash chromatography with acetone/petroleum ether (b.p. 40–60°C) (1:5) to give 0.06 g (20%) of **14** and **15**. – The following ^{1}H-NMR data were recorded (300 MHz, $CDCl_3$): major isomer: δ = 0.94 (t, *J* = 7.3 Hz, 3H), 1.08 (d, *J* = 6.5 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H), 1.35 (m, 1H), 1.43–1.66 (m, 1H), 1.74 (m, 1H), 3.87 (quint, *J* = 6.5 Hz, 1H), 4.21 (dd, *J* = 10.0 and 6.7 Hz, 1H), 6.42 (br. s, 1H); minor isomer: δ = 0.95 (t, *J* = 7.3 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.35 (m, 1H), 1.43–1.66 (m, 1H), 1.74 (m, 1H), 3.69 (quint, *J* = 6.1 Hz, 1H), 3.99 (dd, *J* = 5.9 and 5.3 Hz, 1H), 6.60 (br. s, 1H).

8) *(3R*,4R*,5S*)- and (3R*,4R*,5R*)-5-(Benzyloxy)-3-methyl-1-hexen-4-ol* (**10e** and **11e**): 0.91 g (5 mmol), 2-(2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*/*Z* = 92:8), 0.82 g (5 mmol) of 2-(benzyloxy)propanal (**4**), and 0.75 g (5 mmol) of triethanolamine were allowed to react as described under 1) to give 1.07 g (97%) of a 47:53 mixture of **10e** and **11e** as a colorless oil. The compounds were identified with reference to the published ^{13}C-NMR spectra[12,13].

9) *(3R*,4S*,5R*)- and (3R*,4S*,5S*)-5-(Benzyloxy)-3-methyl-1-hexen-4-ol* (**12e** and **13e**): 0.91 g (5 mmol) of 2-[(2*Z*)-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), 0.82 g (5 mmol) of 2-(benzyloxy)propanal (**4**), and 0.75 g (5 mmol) of triethanolamine were allowed to react as described under 1) to give 1.08 g (98%) of a 9:3:77:11 mixture of **10e**, **11e**, **12e**, and **13e**. The products were identified with reference to the published ^{13}C-NMR spectra[12,13].

10) *(3R*,4R*,5S*)- and (3R*,4R*,5R*)-5-Chloro-3-methyl-1-hepten-4-ol*[24] (**10f** and **11f**): 0.73 g (4 mmol) of 2-(2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*/*Z* = 92:8), 0.43 g (4 mmol) of 2-chlorobutanal[27] (**9**), and 0.60 g (4 mmol) of triethanolamine were allowed to react as described under 1) to give 0.46 g (71%) of a 47:53 mixture of **10f**, **11f** containing ca. 7% of **12f**, **13f**.

10f: ^{1}H NMR (300 MHz, $CDCl_3$): Characteristic signals at δ = 2.73 (m, *J* = 7.0 Hz, 1H), 3.54 (dd, *J* = 6.7 and 5.0 Hz, 1H), 3.83 (ddd, *J* = 9.6, 6.8 and 2.8 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9, 16.9, 26.0, 39.6, 66.6, 77.8, 116.8, 138.5.

11f: ^{1}H NMR (300 MHz, $CDCl_3$): Characteristic signals at δ = 2.47 (m, *J* = 6.9 Hz, 1H), 3.39 (dd, *J* = 7.1 and 3.9 Hz, 1H), 3.95 (ddd, *J* = 7.4, 6.1, and 4.0 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.3, 16.9, 28.2, 42.1, 68.1, 76.5, 116.3, 140.0.

$C_8H_{15}ClO$ (162.7) Cacld. C 59.08 H 9.30
Found C 59.12 H 9.40

11) *(3R*,4S*,5R*)- and (3R*,4S*,5S*)-5-Chloro-3-methyl-1-hepten-4-ol*[24] (**12f** and **13f**): 0.36 g (2 mmol) of 2-[(2*Z*)-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), 0.21 g (2 mmol) of 2-chlorobutanal[27] (**9**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1) to give 0.23 g (71%) of a 75:7:14:4 mixture of **10f**, **11f**, **12f**, and **13f**, as a colorless oil.

12f: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 7.3 Hz, 3H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.71 (m, 1H), 1.95 (m, 1H), 2.04 (br. s, 1H), 2.56 (m, 1H), 3.63 (dd, *J* = 6.8 and 5.0 Hz, 1H), 3.94 (ddd, *J* = 10.2, 4.9, and 2.6 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 5.11 (d, *J* = 17.1 Hz, 1H), 5.74 (ddd, *J* = 17.8, 9.8, and 7.9 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 14.9, 24.8, 40.5, 67.7, 77.6, 115.6, 140.4.

13f: ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.3, 16.3, 28.7, 42.5, 68.5, 76.7, 116.0, 140.1.

$C_8H_{15}ClO$ (162.7) Calcd. C 59.08 H 9.30
Found C 59.21 H 9.38

12) *3-Ethyl-2-(1-methyl-2-propenyl)oxiranes*[24] (**16**, **17**, **18**, and **19**): To a solution of 0.32 g (2 mmol) of the crude chlorohydrins **10f**, **11f**, **12f**, and **13f**, obtained under 11), in 10 ml of anhydrous methanol was added 0.41 g (3 mmol) of potassium carbonate. After stirring for 1 d, the mixture was filtered, and the filtrate was saturated with NaCl and extracted three times with 3 ml each of ether. The combined organic phases were washed twice with 1 ml each of water and dried with $MgSO_4$. Concentration and flash chromatography of the residue with ether/petroleum ether (b.p. 40–60°C) (4:100) yielded 0.10 g (40%) of a mixture of oxiranes as a colorless oil.

16: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.5 Hz, 3H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.18–1.28 (m, 1H), 1.57 (m, 1H), 2.07 (m, 1H), 2.55 (dd, *J* = 7.1 and 2.3 Hz, 1H), 2.73 (dt, *J* = 5.6 and 2.3 Hz, 1H), 5.06 (dt, *J* = 10.4 and 1.4 Hz, 1H), 5.09 (dt, *J* = 17.4 and 1.6 Hz, 1H), 5.80 (ddd, *J* = 17.2, 10.6, and 6.5 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.8, 16.1, 25.0, 39.6, 59.1, 62.1, 114.7, 138.9.

17: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.7, 17.5, 21.1, 36.2, 59.2, 61.2, 114.7, 139.0.

18: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.6, 15.7, 25.0, 39.4, 58.4, 61.9, 114.7, 139.6.

19: ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.8, 16.0, 21.0, 36.0, 58.9, 61.4, 114.5, 140.5.

13) *(3R*,4S*,5R*)- and (3R*,4S*,5S*)-5,6,6-Trimethyl-3-(trimethylsilyl)-1-hepten-4-ol*[24] (**21c** and **22c**): 0.48 g (2 mmol) of 4,4,5,5-tetramethyl-2-[(2*E*)-3-(trimethylsilyl)-2-propenyl]-1,3,2-dioxaborolane (**20**), 0.23 g (2 mmol) of 2,3,3-trimethylbutanal (**7**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1) to give 0.22 g (48%) of a 89:11 mixture of **21c**, **22c** as a colorless oil.

21c: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.03 (s, 9H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.94 (s, 9H), 1.34 (q, *J* = 7.0 Hz, 1H), 1.48 (d, *J* = 3.6 Hz, 1H), 1.80 (dd, *J* = 10.6 and 8.9 Hz, 1H), 4.05 (ddd, *J* = 8.9, 3.6, and 1.1 Hz, 1H), 4.97 (dd, *J* = 17.0 and 1.9 Hz, 1H), 5.07 (dd, *J* = 10.2 and 2.1 Hz, 1H), 5.73 (dt, *J* = 17.0 and 10.4 Hz, 1H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.7, 8.1, 28.4, 33.6, 43.9, 46.5, 70.4, 115.8, 137.6.

22c: ^{13}C NMR (75 MHz, $CDCl_3$): δ = –1.6, 8.8, 28.3, 33.6, 43.8, 46.7, 74.1, 114.7, 136.1.

$C_{13}H_{28}OSi$ (228.5) Calcd. C 68.35 H 12.35
Found C 68.15 H 12.43

14) *(3R*,4S*,5S*)- and (3R*,4S*,5R*)-5-(Dibenzylamino)-3-(trimethylsilyl)-1-hexen-4-ol*[24] (**21d** and **22d**): 0.48 g (2 mmol) of 4,4,5,5-tetramethyl-2-[(2*E*)-3-(trimethylsilyl)-2-propenyl]-1,3,2-dioxaborolane (**20**), 0.51 g (2 mmol) of 2-(dibenzylamino)propanal (**8**), and 0.30 g (2 mmol) of triethanolamine were allowed to react for 5 d as described under 1) to give 0.52 g (71%) of **21d** as a colorless oil.

21d: ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.11 (s, 9H), 1.10 (d, *J* = 6.7 Hz, 3H), 1.49–1.64 (br. s, 1H), 2.04 (dd, *J* = 10.4 and

4.9 Hz, 1H), 2.81 (quint, J = 6.6 Hz, 1H), 3.46 and 3.81 (AB system, J_{AB} = 13.8 Hz, 4H), 3.86 (t, J = 5.4 Hz, 1H), 4.71 (dd, J = 17.2 and 1.9 Hz, 1H), 4.88 (dd, J = 10.3 and 2.0 Hz, 1H), 5.62 (dt, J = 17.1 and 10.4 Hz, 1H), 7.17–7.37 (m, 10H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.2, 8.1, 39.2, 54.7, 56.6, 73.6, 115.6, 126.7, 128.1, 128.9, 135.3, 140.4.

$C_{23}H_{33}NOSi$ (367.6) Calcd. C 75.15 H 9.05 N 3.81
Found C 74.86 H 9.25 N 4.04

15) *(3R*,4S*,5S*)- and (3R*,4S*,5R*)-5-(Benzyloxy)-3-(trimethylsilyl)-1-hexen-4-ol*[24] (**21e** and **22e**): 1.20 g (5 mmol) of 4,4,5,5-tetramethyl-2-[(2*E*)-3-(trimethylsilyl)-2-propenyl]-1,3,2-dioxaborolane (**20**), 0.82 g (5 mmol) of 2-(benzyloxy)propanal (**4**), and 0.75 g (5 mmol) of triethanolamine were allowed to react for 6 d as described under 1) to give 0.73 g (52%) of a 42:58 mixture of **21e** and **22e** as a colorless oil.

21e: ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.2, 14.7, 38.1, 71.3, 75.3, 79.5, 113.6, 127.8, 128.0, 128.6, 135.2, 138.6.

22e: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 9H), 1.21 (d, J = 6.2 Hz, 3H), 1.09–1.97 (m, 2H), 3.50 (dq, J = 6.2 and 5.2 Hz, 1H), 3.85 (q, J = 4.9 Hz, 1H), 4.46 and 4.60 (AB system, J_{AB} = 11.6 Hz, 2H), 4.89 (ddd, J = 17.2, 2.2, and 0.6 Hz, 1H), 5.00 (dd, J = 10.3 and 2.1 Hz, 1H), 5.85 (dt, J = 17.1 and 10.4 Hz, 1H), 7.26–7.36 (m, 5H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = −2.0, 15.1, 38.6, 71.0, 74.1, 77.5, 114.0, 127.7, 127.9, 128.5, 136.3, 138.8.

$C_{16}H_{26}O_2Si$ (278.5) Calcd. C 69.01 H 9.41
Found C 68.59 H 9.42

16) *(3R*,4R*,5S*)- and (3R*,4R*,5R*)-5-Chloro-3-(trimethylsilyl)-1-hepten-4-ol*[24] (**21f** and **22f**): 0.48 g (2 mmol) of 4,4,5,5-tetramethyl-2-[(2*E*)-3-(trimethylsilyl)-2-propenyl]-1,3,2-dioxaborolane (**20**), 0.21 g (2 mmol) of 2-chlorobutanal (**9**), and 0.30 g (2 mmol) of triethanolamine were allowed to react for 5 d as described under 1) to give 0.40 g (90%) of a 35:65 mixture of **21f, 22f** as a colorless oil.

21f: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.06 (s, 9H), 1.03 (t, J = 7.3 Hz, 3H), 1.58 (m, 1H), 1.80 (dt, J = 11.0 and 3.1 Hz, 1H), 1.88 (ddd, J = 14.5, 7.3, and 3.2 Hz, 1H), 2.41 (t, J = 2.4 Hz, 1H), 3.73 (dt, J = 8.6 and 2.9 Hz, 1H), 3.93 (td, J = 8.8 and 3.2 Hz, 1H), 4.88 (dd, J = 17.2 and 2.1 Hz, 1H), 5.00 (dd, J = 10.3 and 2.1 Hz, 1H), 5.89 (dt, J = 17.2 and 10.5 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.4, 10.5, 26.4, 39.0, 72.5, 74.4, 114.5, 134.1.

22f: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 9H), 1.06 (t, J = 7.3 Hz, 3H), 1.67 (m, 1H), 1.86 (d, J = 5.5 Hz, 1H), 2.02 (m, 1H), 2.15 (dd, J = 10.7 and 3.1 Hz, 1H), 3.82 (td, J = 7.1 and 2.6 Hz, 1H), 3.88 (ddd, J = 12.5, 7.2, and 3.2 Hz, 1H), 4.99 (dd, J = 17.0 and 2.1 Hz, 1H), 5.07 (dd, J = 10.3 and 2.1 Hz, 1H), 5.84 (dt, J = 17.0 and 10.5 Hz, 1H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = −2.4, 10.7, 26.3, 38.7, 67.6, 74.7, 115.6, 133.9.

$C_{10}H_{21}ClOSi$ (220.8) Calcd. C 54.39 H 9.59
Found C 54.61 H 9.49

17) *(3R*,4S*,5R*)- and (3R*,4S*,5S*)-3,5-Dimethyl-1-hepten-4-ol* (**10a** and **11a**): 0.36 g (2 mmol) of 2-(2-butenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (*E*/*Z* = 86:14), 0.17 g (2 mmol) of 2-methylbutanal (**5**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1) to give 0.13 g (46%) of a 77:23 mixture of **10a, 11a**, as a colorless liquid. The products were identified with reference to the published NMR spectra[9,12].

18) *(3R*,4R*,5S*)- and (3R*,4R*,5R*)-3,5-Dimethyl-1-hepten-4-ol* (**12a** and **13a**): 0.36 g (2 mmol) of 2-[(2*Z*)-2-butenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), 0.17 g (2 mmol) of 2-methylbutanal (**5**), and 0.30 g (2 mmol) of triethanolamine were allowed to react as described under 1) to give 0.14 g (49%) of a 30:70 mixture of **12a** and **13a** as a colorless liquid. The compounds were identified with reference to the published NMR spectra[9,12].

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1 (R = Me_2N): 129286-73-3 / **1** (R = MeO): 6142-38-7 / **2**: 69611-02-5 / **3**: 69611-01-4 / **4**: 53346-05-7 / **5**: 96-17-3 / **6**: 93-53-8 / **7**: 17408-48-9 / **8**: 129286-74-4 / **9**: 28832-55-5 / **10a**: 72985-59-2 / **10b**: 79297-87-3 / **10c**: 124377-69-1 / **10d**: 129286-75-5 / **10e**: 124377-75-9 / **10f**: 124377-74-8 / **11a**: 73037-25-9 / **11b**: 79297-88-4 / **11d**: 129388-33-6 / **11e**: 124377-78-2 / **11f**: 124377-71-5 / **12a**: 73037-28-2 / **12b**: 79297-89-5 / **12c**: 12431-03-2 / **12d**: 129388-34-7 / **12e**: 124377-77-1 / **12f**: 124377-72-6 / **13a**: 73037-29-3 / **13b**: 79297-90-8 / **13c**: 124377-70-4 / **13d**: 129388-35-8 / **13e**: 124377-76-0 / **13f**: 124377-73-7 / **14**: 129286-81-3 / **15**: 129286-82-4 / **16**: 129388-40-5 / **17**: 129388-41-6 / **18**: 129388-42-7 / **19**: 129388-43-8 / **20**: 79309-68-5 / **21a**: 129217-81-8 / **21b**: 129286-76-6 / **21c**: 129286-77-7 / **21d**: 129286-78-8 / **21e**: 129286-79-9 / **21f**: 129286-80-2 / **22a**: 129263-25-8 / **22b**: 129388-36-9 / **22c**: 129388-37-0 / **22e**: 129388-38-1 / **22f**: 129388-39-2

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