Stereoselective synthesis of alcohols.

Part LIII.† (*E*)-γ-Alkoxyallylboronates: generation and application in intramolecular allylboration reactions

Reinhard W. Hoffmann,* Jochen Krüger and David Brückner

Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany E-mail: rwho@chemie.uni-marburg.de; Fax: +49 6421 2828917

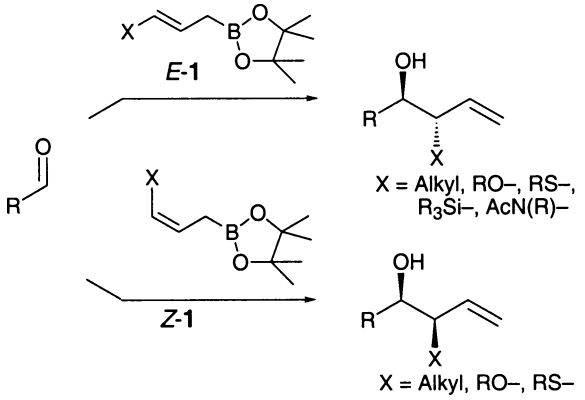
Received (in Montpellier, France) 2nd May 2000, Accepted 19th May 2000
First published as an Advance Article on the web 29th September 2000

Alkoxyalkynes **9** may be hydroborated with pinacol borane, preferentially under Cp_2ZrHCl catalysis, to give the vinylboronates **10**. The latter, when subjected to the Matteson–Brown homologation with $LiCH_2Cl$, give rise to the (*E*)-γ-alkoxyallylboronates **3** in good yield. This reaction sequence has been used to generate the (*E*)-γ-alkoxyallylboronates **14**, **21**, **26** and **31**, which were the starting point for intramolecular allylboration reactions leading to the *trans*-disubstituted tetrahydropyrans **8** and **22**, as well as hydrooxepans **27** and **32**.

Among the allylmetallation reactions of aldehydes[2,3] the addition of γ-substituted allylboronates **1** to aldehydes (Scheme 1) provides the greatest synthetic flexibility, because both the (*E*)- and (*Z*)-γ-substituted allylboronates are configurationally stable and add to aldehydes with high simple diastereoselectivity, translating the geometry of the double bond into the relative configuration of the two newly formed stereocenters in the product. For a review see ref. 3.

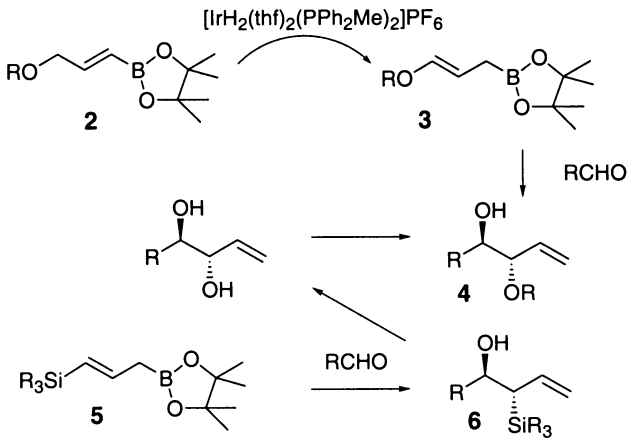
The application of these reactions in synthesis is, however, compromised by the fact that not all γ-heterosubstituted allylboronates of interest are equally well accessible as both the (*Z*)- and the (*E*)-isomers. Problems are associated with the generation of the (*E*)-γ-alkoxyallylboronates, for which our initial procedure[4] is moderately practicable at best.[5] More recently, Miyaura and co-workers described a second route to these species by an iridium-catalyzed isomerization of γ-alkoxyvinylboronates **2** (Scheme 2).[6]

Yet, when structures such as **4** were to be attained by allylmetallation reactions, chemists frequently resorted to a multistep route (Scheme 2) involving the (*E*)-γ-silylallylboronates **5** as reagents, followed by conversion of the silyl residue in the adduct **6** to the desired oxygen functionality.[7] Obviously, the route *via* the γ-silylallyl boronates **5** is not viable when one is interested in an intramolecular allylboration (Scheme 3) that should lead to heterocyclic compounds such as **8**.

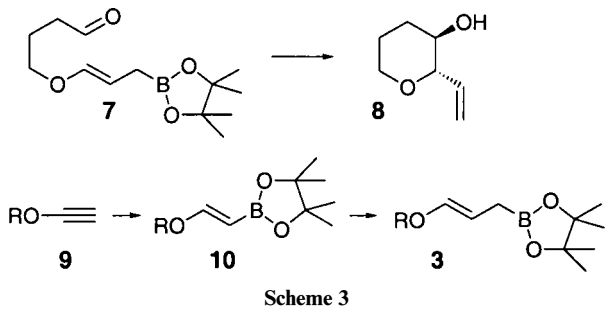


Scheme 1

† For part LII, see ref. 1.



Scheme 2



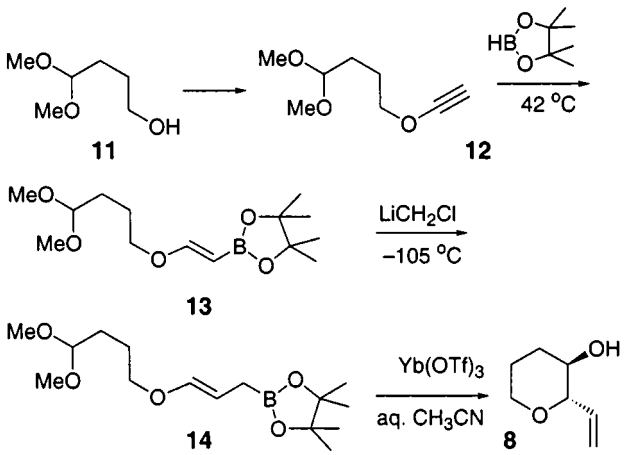
Scheme 3

In the search for another route to (*E*)-γ-alkoxyallylboronates such as **7** we envisaged a homologation of vinylboronates to allylboronates,[9] *viz.* the conversion of **10** into **3** (Scheme 3), a method that is increasingly gaining importance.[10] This route would rely on the hydroboration of an alkoxyalkyne **9** to give **10**. We hoped that the direct hydroboration of readily accessible alkoxyalkynes **9**[11] with pinacol borane[12] should afford the desired vinylboronate **10**.

Results and discussion

We started our investigation (Scheme 4) with the alcohol **11**,[13] which was converted to the alkoxyalkyne **12** in 65–80% yield

 DOI: 10.1039/b003551n

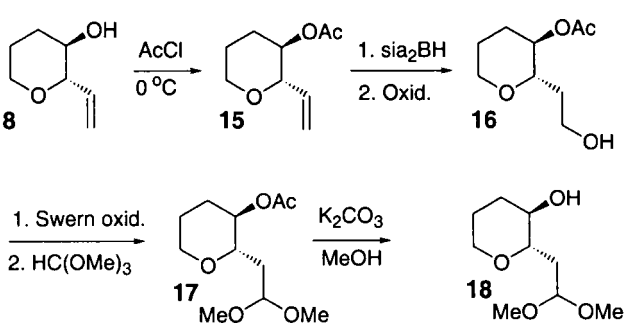


Scheme 4

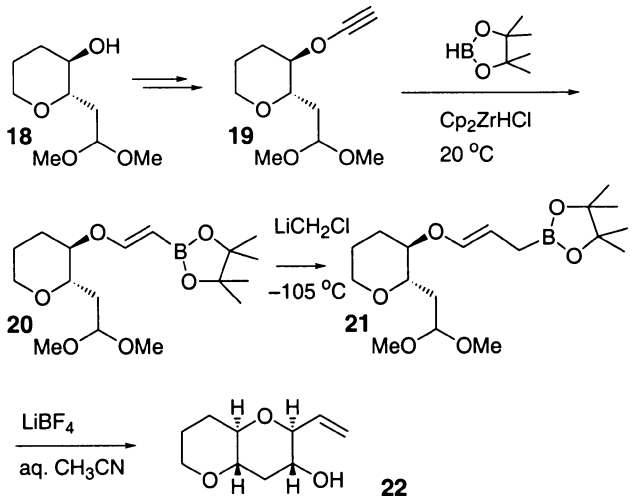
following Greene's procedure.[11] Hydroboration of **12** with pinacol borane could be effected in *ca.* 70% yield by keeping the temperature below 50° C while accepting longer reaction times. Higher temperatures resulted in a competing retro-ene decomposition of **12** to give ketene and 1,1-dimethoxy-3-butene. The crude vinylboronate **13** was directly homologated with $LiCH_2Cl$ at −105° C to give the allylboronate **14** in *ca.* 80% conversion. The mixture of **14** and residual **13** was directly subjected to mild acetal hydrolysis with $Yb(OTf)_3$ in moist acetonitrile,[14] resulting in the immediate formation of the desired *trans*-2-vinyltetrahydropyranol-3 **8** in 66% yield from **12**. Compound **8** was obtained as a single diastereomer. It was identified with reference to a sample prepared by intramolecular allylstannation following the procedure of Yamamoto and colleagues.[15]

The clean conversion of the alcohol **11** *via* the alkoxyalkyne **12** and the allylboronate **14** into the *trans*-vinyltetrahydropyranol **8** demonstrates the versatility of this route to (*E*)-γ-alkoxyallylboronates and their use in intramolecular allylboration reactions. In view of the general interest in *trans*-fused annelated *oligo*-tetrahydropyrans,[16] we wanted to explore the subsequent conversion of **8** into the bicyclic bis-tetrahydropyran **22**. This required the conversion of the vinyl group in **8** into a latent aldehyde function, such as a dimethyl acetal. This was accomplished in a series of standard transformations (Scheme 5): protection of the alcohol as an acetate **15** (86%), hydroboration of **15** to give the primary alcohol **16** using di-*sec*-isoamylborane (70%), Swern oxidation of the primary alcohol **16** to an aldehyde followed by *in situ* acetalization to give **17** (90%), and finally, cleavage of the acetate in **17** by K_2CO_3 in methanol to give the alcohol **18** (92%).

The alcohol **18** is the starting point for a second round of intramolecular allylboration (Scheme 6). To this end, the alcohol **18** was converted to the alkoxyalkyne **19** as above (78%). We found that the hydroboration of alkoxyalkynes **9** to give the vinylboronate **10** (Scheme 3) could be carried out at room temperature when catalyzed with zirconocene



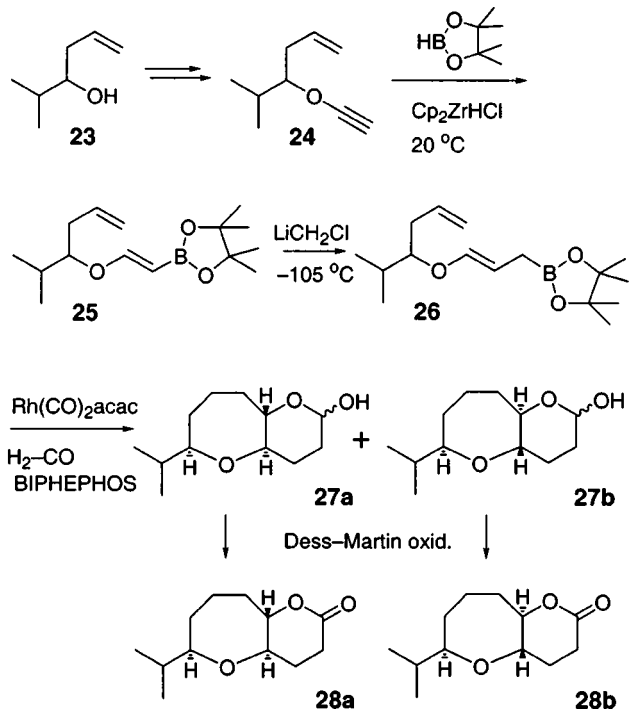
Scheme 5



Scheme 6

hydrido chloride.[17] This allowed us to similarly convert the alkoxyalkyne **19** in 87% yield to the vinylboronate **20**. Subsequent transformation of **20** into the allylboronate **21** (95%) proceeded as usual. Liberation of the aldehyde from **21** with $LiBF_4$ in moist acetonitrile[18] initiated the intramolecular allylboration, which resulted in the formation of 76% of the desired bicyclic bis-tetrahydropyran **22**. The latter was obtained as a single diastereomer, attesting to the high asymmetric induction from the stereocenters resident in the cyclization precursor **21**. For alternate syntheses of **22** see ref. 19.

We recently showed[20] that hydroformylation is a good way to generate an aldehyde function in the presence of an allylboronate moiety. This opens the way to a domino hydroformylation–allylboration–hydroformylation sequence, allowing rapid access to annelated heterocyclic structures. It was therefore tempting to combine this technique with the generation of (*E*)-γ-alkoxyallylboronates described above. Model studies of this point were carried out starting from the homoallylic alcohol **23** (Scheme 7). The latter was converted to the alkoxyalkyne **24** in 78% yield. Hydroboration of **24** was effected with pinacol borane catalyzed by zirconocene hydrido chloride[17] (69%). Subsequent homologation of **25** afforded the allylboronate **26** (65% over two steps).



Scheme 7

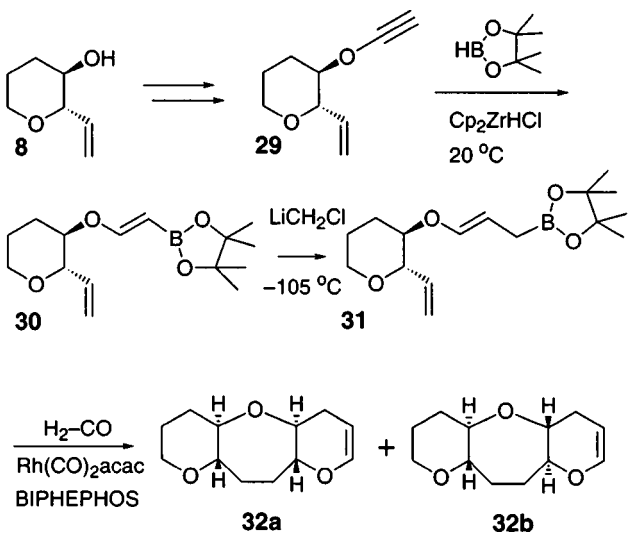
Hydroformylation of the latter (Scheme 7) was carried out in the presence of the BIPHEPHOS ligand[21] to attain a high preference for the formation of the linear aldehyde over the branched aldehyde. This, however, entailed that the hydroformylation reaction became rather slow, requiring two days at 65 °C and 5 bar of CO–H_2. In the end this treatment resulted in the expected domino hydroformylation–allylboration–hydroformylation reaction to give 48% of the lactols **27,** which were obtained as a mixture of anomers. The products obtained could be separated into two diastereomeric sets of lactols **27a** and **27b**, which were obtained in a *ca.* 1 : 1 ratio. To facilitate structure assignment, each of these mixtures was oxidized[22] with the Dess–Martin reagent[23] to a single lactone **28a** and **28b**, respectively. Assignment of the relative configuration was made by NMR NOE spectroscopy.

The fact that the two cyclization products **27a** and **27b** were obtained in a nearly 1 : 1 ratio indicates that asymmetric induction on the formation of a seven-membered hydro-oxepane ring was low.

At this point we did not know whether this was a singular event or characteristic of a more general feature. For this reason we investigated a second domino hydroformylation–allylboration–hydroformylation reaction leading to an annelated hydro-oxepane ring. To this end we converted the vinyltetrahydropyranol **8** into the alkoxyalkyne **29** (72%, Scheme 8). Zirconocene hydrido chloride catalyzed hydroboration,[17] followed by homologation, furnished the allylboronate **31** (50% over two steps). The allylboronate was subjected to the hydroformylation conditions. The reaction turned out to be rather slow, requiring more than three days at 65 °C. The products obtained (52%) were not the lactols, but the corresponding enol ethers **32**. Apparently dehydration, to give **32**, had occurred during the longer reaction period. The tricyclic compounds were again obtained as a 1 : 1 mixture of stereoisomers, presumably the *trans-syn-trans* **32a** and the *trans-anti-trans* isomer **32b**. The individual structures were not assigned to the materials obtained.

This made it clear that intramolecular allylboration to form hydro-oxepane rings is stereounselective, showing no asymmetric induction from the resident stereocenters present in the cyclization precursors **26** or **31**. This contrasts to the high asymmetric induction found on intramolecular allylboration to give the tetrahydropyran ring in the cyclization of **21** to **22**.

In conclusion, we have found a reliable route to (*E*)-γ-alkoxyallylboronates starting from alcohols, *via* alkoxyalkynes, hydroboration and homologation. The γ-alkoxyallylboronates **13**, **21**, **26** and **31** served as substrates for intramolecular allylboration reactions, giving rise to tetrahydropyrans **8** and **22** and the hydro-oxepane ring systems **27** and **32**.



Scheme 8

Experimental

All temperatures quoted are not corrected. ^{1}H-NMR and ^{13}C-NMR spectra were obtained on: Bruker ARX-200, AC-300, ARX-400 and AMX-500 spectrometers. Boiling range of petroleum ether used: 40–60 °C. Buffer (pH 7) was made with 56.2 g of $NaH_2PO_4 \cdot 2\ H_2O$ and 213.2 g $Na_2HPO_4 \cdot 2\ H_2O$ in 1.0 L of water. Flash chromatography was performed using silica gel Si60 (40–63 μm, E. Merck AG, Darmstadt).

4-Ethynyloxy-1,1-dimethoxybutane (12)

4,4-Dimethoxybutanol **11**[13] (1.740 g, 12.97 mmol) was added dropwise at 0 °C into a suspension of potassium hydride (1.040 g, 25.93 mmol) in THF (50 mL). After stirring for 1.5 h the mixture was cooled to −78 °C. Trichloroethene (1.708 g, 13.0 mmol) was added and the mixture was allowed to reach room temperature. After stirring for 1 h the mixture was again cooled to −78 °C and a solution of *n*-butyllithium in hexane (1.58 M, 20.0 mL, 31.6 mmol) was added dropwise. The temperature was allowed to reach −40 °C over 1.5 h. Anhydrous methanol (3.95 g, 125 mmol) was added and the mixture was allowed to reach room temperature. Saturated aqueous $NaHCO_3$ solution (30 mL) was added, the phases were separated and the aqueous phase was extracted with ether (3 × 30 mL). The combined organic phases were dried (K_2CO_3) and concentrated. The residue was purified by filtration over a 7 cm layer of silica gel with petroleum ether containing 0.3% triethylamine to give 1.633 g (80%) of **12** as a slightly yellowish oil. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.51$ (s, 1H), 1.65–1.73 (m, 2H), 1.75–1.85 (m, 2H), 3.31 (s, 6H), 4.08 (t, $J = 6.2$ Hz, 2H), 4.37 (t, $J = 5.5$ Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 23.9$, 26.3, 28.4, 52.9, 78.6, 91.0, 104.0. $C_8H_{14}O_3$ requires C 60.74, H 8.92; found C 60.62, H 9.20%.

trans-2-Vinyltetrahydropyran-3-ol (8)

Freshly prepared pinacol borane[12] (712 mg, 5.56 mmol) was added at 0 °C into a solution of **12** (173 mg, 1.09 mmol) in dichloromethane (0.7 mL). The mixture was stirred for 20 h at 42 °C until TLC indicated complete conversion. The volatiles were removed at 10^{-2} Torr to leave crude **13** (302 mg), which was purified by flash chromatography with petroleum ether–ether 5 : 1 containing 1% triethylamine. **13** (218 mg, 70%) was obtained as a colorless liquid. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.21$ (s, 12H), 1.67 (m, 4H), 3.28 (s, 6H), 3.75 (br t, $J = 5.9$ Hz, 2H), 5.31 (m, 1H), 4.39 (d, $J = 14.4$ Hz, 1H), 7.00 (d, $J = 14.4$ Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 24.0$, 24.7, 29.0, 52.7, 68.4, 82.6, 104.2, 163.9. The material was immediately converted to the allylboronate **14**.

A solution of *n*-butyllithium in hexane (1.49 M, 4.36 mL, 6.50 mmol) was added under an argon atmosphere at −105 °C into a solution of the vinylboronate **13** (1.644 g, 5.03 mmol) and chloroiodomethane (473 μL, 6.5 mmol) in THF (25 mL). After reaching room temperature overnight pH 7 buffer solution (20 mL) was added, the phases were separated and the aqueous phase was extracted with ether (3 × 10 mL). The combined organic phases were washed with brine (10 mL), dried (Na_2SO_4) and concentrated. NMR analysis of the residue showed the presence of a 4 : 1 mixture of **14** : **13**, corresponding to a yield of **14** of 78%. The following NMR data of **14** could be recorded: ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.45$ (br d, $J = 7.21$ Hz, 2H), 4.74 (dt, $J = 12.6$ and 7.5 Hz, 1H), 6.18 (d, $J = 12.6$ Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 24.7$, 29.0, 52.6, 68.6, 83.1, 98.9, 104.3, 146.1.

The mixture of **13** and **14** obtained was taken up in acetonitrile (30 mL). Water (0.6 mL) and ytterbium triflate (312 mg, 0.1 equiv.) were added. After stirring for 12 h ether (20 mL) and saturated aqueous $NaHCO_3$ solution (10 mL) were added. The phases were separated and the aqueous phase was extracted with ether (3 × 10 mL). The combined organic

phases were washed with brine (10 mL), dried (Na_2SO_4) and concentrated by distillation over a short column. The residue was purified by flash chromatography with pentane–ether (1 : 1) and the eluates were concentrated at 0 °C to leave the vinyltetrahydropyranol **8** (419 mg, 66%) as a single diastereomer. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.46$ (m, 1H), 1.66–1.80 (m, 3H), 2.14 (m, 1H), 3.27–3.50 (m, 3H), 3.94 (m, 1H), 5.31 (ddd, $J = 10.5$, 1.6, 0.8 Hz, 1H), 5.38 (ddd, $J = 17.3$, 1.7, 1.2 Hz, 1H), 5.87 (ddd, $J = 17.5$, 10.6 7.0 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 25.3$, 31.6, 67.4, 69.5, 84.0, 118.8, 136.2. These data corresponded to a sample that was prepared according to the procedure given by Yamamoto *et al.*[15]

***trans*-3-Acetoxy-2-vinyltetrahydropyran (15)**

Pyridine (2.50 mL) was added to a solution of *trans*-2-vinyltetrahydropyran-3-ol **8** (1.31 g, 10.2 mmol) in dichloromethane (20 mL). Acetyl chloride (1.09 mL, 15.3 mmol) was added dropwise at 0 °C. After stirring for 2 h at 0 °C and 2 h at room temperature diethyl ether (50 mL) was added, the mixture was filtered over a small pad of Kieselgur and the filtrate was concentrated. Flash chromatography (pentane–diethyl ether = 10 : 1) furnished **15** (1.50 g, 86%) as a colorless oil. R_f(PE–EtOAc 5 : 1) = 0.37. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.52$ (tdd, $J = 11.9$, 11.0, 5.2 Hz, 1H), 1.65–1.86 (m, 2H), 2.02 (s, 3H), 2.10–2.22 (m, 1H), 3.42 (td, $J = 11.0$, 3.5 Hz, 1H), 3.64–3.73 (m, 1H), 3.97 (ddt, $J = 11.3$, 3.9, 2.0 Hz, 1H), 4.61 (ddd, $J = 10.6$, 9.2, 4.6 Hz, 1H), 5.17–5.24 (m, 1H), 5.26–5.36 (m, 1H), 5.80 (ddd, $J = 17.3$, 10.6, 6.7 Hz, 1H). These data correspond to those given in ref. 18. ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 21.1$, 24.9, 29.2, 67.3, 71.2, 80.6, 117.9, 135.5, 170.0.

***trans*-3-Acetoxy-2-(2-hydroxyethyl)tetrahydropyran (16)**

2-Methyl-2-butene (3.77 mL, 35.5 mmol) was added dropwise at 0 °C into a solution of borane-dimethyl sulfide complex (1.71 mL, 17.8 mmol) in THF (1.7 mL). After stirring for 1 h at room temperature THF (4.6 mL) was added and the resulting solution was added dropwise at 0 °C into a solution of *trans*-3-acetoxy-2-vinyltetrahydropyran **15** (1.21 g, 7.1 mmol) in THF (7 mL). After stirring for 30 min each at 0 °C and 25 °C the mixture was recooled to 0 °C and hydrolyzed by addition of aqueous NaOAc solution (7 mL, 35 mmol) and 30% aqueous H_2O_2 (7 mL). After stirring for 12 h diethyl ether (20 mL) was added, the phases were separated and the aqueous phase was extracted with diethyl ether (5 × 20 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with pentane–diethyl ether (1 : 5) furnished **16** (937 mg, 70%) as a colorless oil. R_f(PE–Et_2O 1 : 5) = 0.21. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.45$ (tdd, $J = 12.2$, 11.0, 5.1 Hz, 1H), 1.59–1.80 (m, 3H), 1.81–1.93 (m, 1H), 2.05 (s, 3H), 2.12–2.23 (m, 1H), 3.33–3.53 (m, 2H), 3.72–3.85 (m, 2H), 3.93 (ddt, $J = 11.3$, 4.1, 1.9 Hz, 1H), 4.57 (ddd, $J = 10.5$, 9.5, 4.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 21.0$, 24.9, 29.1, 33.8, 60.6, 67.6, 71.6, 79.4, 170.1. $C_9H_{16}O_4$ requires C 57.43, H 8.57; found C 57.23, H 8.62%.

***trans*-3-Acetoxy-2-(2,2-dimethoxyethyl)tetrahydropyran (17)**

Dimethyl sulfoxide (802 μL, 11.3 mmol) was added dropwise at −78 °C into a solution of oxalyl chloride (497 μL, 5.7 mmol) in dichloromethane (12 mL). After 5 min a solution of *trans*-3-acetoxy-2-(2-hydroxyethyl)tetrahydropyran **16** (710 mg, 3.77 mmol) in dichloromethane (4 mL) was added. After stirring for 20 min at −78 °C triethylamine (2.10 mL) was added and the mixture was allowed to reach 0 °C slowly. Dichloromethane (20 mL) and saturated aqueous NH_4Cl solution (20 mL) were added. The phases were separated and the aqueous phase was extracted with dichloromethane (3 × 20 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was taken up in a 1 : 1 (v/v) mixture of methanol and trimethoxymethane (9.4 mL). This mixture was stirred with DOWEX50 (38 mg) for 30 min. Diethyl ether (30 mL) was added and the mixture was filtered over a small pad of Al_2O_3 (neutral). The filtrate was concentrated and the residue was subjected to flash chromatography with pentane–diethyl ether (1 : 1) over silica gel that had been pretreated with triethylamine to give **17** (792 mg, 90%) as a colorless oil. R_f(PE–Et_2O 1 : 5) = 0.52. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.44$ (tdd, $J = 12.1$, 11.0, 5.2 Hz, 1H), 1.56–1.84 (m, 3H), 1.91 (ddd, $J = 14.3$, 8.4, 2.3 Hz, 1H), 2.01–2.26 (m, 1H), 2.03 (s, 3H), 3.30–3.42 (m, 2H), 3.34 (s, 3H), 3.37 (s, 3H), 3.90 (ddt, $J = 11.3$, 3.9, 1.8 Hz, 1H), 4.49 (ddd, $J = 10.3$, 9.7, 4.6 Hz, 1H), 4.59 (dd, $J = 8.3$, 3.2 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 21.1$, 25.1, 29.3, 35.6, 53.0, 53.5, 67.5, 71.9, 76.1, 101.9, 170.1. $C_{11}H_{20}O_5$ requires C 56.88, H 8.68; found C 56.56, H 8.52%.

***trans*-3-Hydroxy-2-(2,2-dimethoxyethyl)tetrahydropyran (18)**

Potassium carbonate (352 mg, 2.55 mmol) was added into a solution of *trans*-3-acetoxy-2-(2,2-dimethoxyethyl)tetrahydropyran **17** (592 mg, 2.5 mmol) in methanol (8.5 mL). After stirring for 4 h the solution was concentrated, the residue was taken up in diethyl ether (20 mL) and the mixture was filtered over Kieselgur. The filtrate was concentrated and subjected to flash chromatography with pentane–diethyl ether (1 : 2) to give **18** (448 mg, 92%) as a colorless oil. R_f(PE–Et_2O 1 : 5) = 0.25. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.31$–1.48 (m, 1H), 1.61–1.74 (m, 2H), 1.83 (ddd, $J = 14.6$, 6.7, 4.2 Hz, 1H), 2.05–2.18 (m, 2H), 2.68 (br d, $J = 4.4$ Hz, 1H), 3.14 (ddd, $J = 9.0$, 6.6, 4.2 Hz, 1H), 3.24–3.40 (m, 2H), 3.36 (s, 3H), 3.37 (s, 3H), 3.83–3.92 (m, 1H), 4.62 (dd, $J = 6.6$, 4.2 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$) $\delta = 25.5$, 32.4, 36.4, 52.8, 53.3, 67.6, 70.1, 79.0, 102.0. $C_9H_{18}O_4$ requires C 56.82, H 9.54; found: C 56.70, H 9.32.

***trans*-3-Ethynyloxy-2-(2,2-dimethoxyethyl)tetrahydropyran (19)**

trans-3-Hydroxy-2-(2,2-dimethoxyethyl)tetrahydropyran **18** (395 mg, 2.07 mmol) was converted into **19** essentially as described for **12**. The crude product was purified by flash chromatography over Al_2O_3 (neutral) with pentane–*tert*-butyl methyl ether (5 : 1) to give **19** (346 mg, 78%) as a colorless oil. R_f(PE–EtOAc 5 : 1) = 0.29. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.56$ (s, 1H), 1.59–1.85 (m, 4H), 2.23 (ddd, $J = 14.4$, 8.3, 2.4 Hz, 1H), 2.34–2.49 (m, 1H), 3.27–3.43 (m, 2H), 3.33 (s, 3H), 3.34 (s, 3H), 3.73 (td, $J = 9.6$, 5.1 Hz, 1H), 3.82–3.93 (m, 1H), 4.64 (dd, $J = 8.3$, 3.7 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): $\delta = 25.2$, 27.7, 28.2, 35.0, 52.1, 53.1, 67.2, 75.7, 84.7, 88.7, 101.0. $C_{11}H_{18}O_4$ requires C 61.66, H 8.47; found C 61.48, H 8.47%.

(1*S,3*R**,4*S**,6*R**)-3-Ethenyl-2,7-dioxabicyclo[4.4.0]decan-4-ol (22)**

Pinacol borane[12] (193 mg, 1.51 mmol) and zirconocene hydrido chloride (35 mg, 0.137 mmol) were added into a solution of *trans*-3-ethynyloxy-2-(2,2-dimethoxyethyl)tetrahydropyran **19** (294 mg, 1.37 mmol) in dichloromethane (0.7 mL). After 1 day *tert*-butyl methyl ether (20 mL) was added and the mixture was poured into pH 7 buffer solution (15 mL). The phases were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was filtered over a 3 cm layer of silica gel (deactivated with triethylamine) using pentane–*tert*-butyl methyl ether 3 : 1 to give the vinylboronate **20** (405 mg, 87%) as a colorless oil. R_f(PE–EtOAc 2 : 1) = 0.36. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 1.25$ (s, 12H), 1.37–1.52 (m, 1H), 1.59 (ddd, $J = 14.2$, 9.6, 3.7, Hz, 1H), 1.64–1.74 (m, 2H), 2.09 (ddd, $J = 14.3$, 8.2, 2.4 Hz, 1H), 2.17–2.28 (m, 1H), 3.31 (s, 3H), 3.32

(s, 3H), 3.28–3.40 (m, 2H), 3.59 (ddd, J = 10.1, 9.6, 4.5 Hz, 1H), 3.83–3.93 (m, 1H), 4.52 (d, J = 14.2 Hz, 1H), 4.62 (dd, J = 8.3, 3.7 Hz, 1H), 6.91 (d, J = 14.2 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 24.7 (4C), 25.1, 29.5, 35.3, 52.1, 53.2, 67.5, 76.6, 78.2, 82.7 (2C), 101.4, 161.8.

Chloroiodomethane (105 μL, 1.4 mmol) was added to a solution of the vinylboronate **20** (380 mg, 1.11 mmol) in THF (5.5 mL) and the solution was cooled to −105 °C. *n*-Butyllithium (1.22 M in hexane, 1.18 mL, 1.44 mmol) was added and the mixture was allowed to reach room temperature overnight. *tert*-Butyl methyl ether (20 mL) was added and the mixture was poured into pH 7 buffer solution (20 mL). The phases were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic phases were dried (Na_2SO_4) and concentrated, leaving the allylboronate **21** (375 mg, 95%) as a slightly yellowish oil. R_f(PE–EtOAc 5 : 1) = 0.37. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 12H), 1.32–1.51 (m, 3H), 1.58 (ddd, J = 14.4, 9.0, 3.7 Hz, 1H), 1.63–1.73 (m, 2H), 2.13–2.26 (m, 2H), 3.20–3.38 (m, 3H), 3.31 (s, 3H), 3.33 (s, 3H), 3.82–3.91 (m, 1H), 4.63 (dd, J = 8.3, 3.7 Hz, 1H), 4.92 (dt, J = 12.5, 7.6 Hz, 1H), 6.06 (dt, J = 12.5, 1.0 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 24.7 (4C), 25.3, 29.6, 35.3, 52.0, 53.2, 67.5, 77.1, 77.9, 83.2 (2C), 101.5, 101.6, 144.7.

The allylboronate **21** (61 mg, 0.17 mmol) was taken up in acetonitrile (0.86 mL). Water (17 μL) and lithium tetrafluoroborate (48 mg, 0.51 mmol) were added. After 1 day *tert*-butyl methyl ether (20 mL) and saturated aqueous $NaHCO_3$ solution (10 mL) were added. The phases were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (5 × 10 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with pentane–diethyl ether (1 : 5) furnished **22** (24 mg, 76%) as a colorless oil. R_f(diethyl ether) = 0.35. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.41–1.48 (m, 1H), 1.52 (q, J = 11.3 Hz, 1H), 1.69–1.77 (m, 2H), 1.83 (br d, J = 3.4 Hz, 1H), 2.06–2.11 (m, 1H), 2.40 (dt, J = 11.6, 4.3 Hz, 1H), 3.00–3.10 (m, 2H), 3.35–3.48 (m, 2H), 3.57 (dd, J = 8.7, 7.6 Hz, 1H), 3.89–3.94 (m, 1H), 5.35 (ddd, J = 10.5, 1.6, 0.8 Hz, 1H), 5.43 (ddd, J = 17.3, 1.6, 1.0 Hz, 1H), 5.85 (ddd, J = 17.4, 10.4, 7.2 Hz, 1H). NOE contacts between H-1 and H-3; H-4 and H-6; H-5ax and H-1; H-5ax and H-3. ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 25.5, 29.2, 37.8, 67.8, 69.0, 76.7, 77.6, 83.8, 119.6, 135.6. MS (EI) m/z (%) 28 (33), 43 (30), 55 (32), 71 (34), 84 (100), 127 (44). HRMS (EI): $C_{10}H_{16}O_3$ requires 184.1099; found 184.1101.

3-Ethynyloxy-2-methyl-5-hexene (24)

3-Hydroxy-2-methyl-5-hexene **23** (1.76 g, 15.4 mmol) was converted into **24** essentially as described for **12**. The crude product was purified by bulb-to-bulb distillation (40 °C, 0.01 mbar) to give **24** (1.657 g, 78%) as a colorless liquid. R_f(PE–MTBE 10 : 1) = 0.62. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0.97 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 1.54 (s, 1H), 1.91–2.16 (m, 1H), 2.41–2.52 (m, 2H), 3.84 (dt, J = 6.5, 5.9 Hz, 1H), 5.09–5.23 (m, 2H), 5.85 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.6, 18.1, 27.0, 30.6, 34.6, 90.4, 93.9, 118.0, 133.2. The material deteriorated too rapidly to obtain a correct elemental analysis.

3-Isopropyl-9-oxo-2,8-dioxa-*trans*-bicyclo[5.4.0.]undecanes (28)

3-Ethynyloxy-2-methyl-5-hexene **24** (170 mg, 1.23 mmol) was hydroborated as described for **22**. The crude vinylboronate was filtered over silica gel using pentane–*tert*-butyl methyl ether (10 : 1) to give **25** (224 mg, 69%) as a colorless oil. R_f(PE–MTBE 10 : 1) = 0.43. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0.84 (d, J = 6.8 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H), 1.18 (s, 12H), 1.70–1.92 (m, 1H), 2.17–2.31 (m, 2H), 3.53–3.68 (m, 1H), 4.42 (d, J = 14.0 Hz, 1H), 4.92–5.09 (m, 2H), 5.72 (ddt, J = 17.1, 10.1 6.9 Hz, 1H), 6.86 (d, J = 14.3 Hz, 1H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ = 17.7, 18.3, 24.7 (4C), 31.1, 35.5, 82.6 (2C), 85.5, 117.3, 134.3, 163.6.

The vinylboronate **25** was converted to the allylboronate **26** as described for **22** (200 mg, 95%) as a yellowish oil. R_f(PE–EtOAc 5 : 1) = 0.73. ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0.83 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H), 1.17 (s, 12H), 1.35–1.45 (m, 2H), 1.65–1.86 (m, 1H), 2.16–2.25 (m, 2H), 3.32 (q, J = 5.7 Hz, 1H), 4.83 (dt, J = 12.1, 7.4 Hz, 1H), 4.92–5.06 (m, 2H), 5.76 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H), 5.99 (dt, J = 12.3, 1.5 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 17.8, 18.4, 24.8 (4C), 31.1, 35.6, 83.1 (2C), 84.9, 100.9, 116.6, 135.1, 146.3.

$Rh(CO)_2$acac (1.8 mg, 0.007 mmol) and BIPHEPHOS[21] (10.7 mg, 0.014 mmol) were dissolved in THF (1 mL). After 10 min a solution of the crude allylboronate **26** (190 mg, 0.68 mmol) in THF (2 mL) was added. The mixture was treated in an autoclave with 5 bar of CO–H_2 (1 : 1) for 2 days at 65 °C. The mixture was concentrated and the residue was purified by flash chromatography with pentane–*tert*-butyl methyl ether (3 : 1) to give first the 1,3-*cis*-compound **27a** (37 mg) as an anomeric mixture and then the 1,3-*trans*-compound **27b** (33 mg) as an anomeric mixture.

27a: R_f(PE–EtOAc 5 : 1) = 0.24. ^{1}H-NMR (300 MHz, $CDCl_3$): characteristic signals δ = 0.86 (d, J = 6.8 Hz), 0.87 (d, J = 6.6 Hz, together 3H), 0.92 (d, J = 6.8 Hz), 0.94 (d, J = 6.8 Hz, together 3H), 4.76–4.82 (m, 0.55H), 5.20 (t, J = 3.1 Hz, 0.45H). ^{13}C-NMR (75 MHz, $CDCl_3$): characteristic signals δ = 90.8, 96.1.

27b: R_f(PE–EtOAc 5 : 1) = 0.17. ^{1}H-NMR (300 MHz, $CDCl_3$): characteristic signals δ = 0.84 (d, J = 6.6 Hz), 0.85 (d, J = 6.8 Hz, together 3H), 0.99 (d, J = 6.6 Hz), 1.00 (d, J = 6.8 Hz, together 3H), 4.74 (m, 0.55H), 5.19 (t, J = 2.5 Hz, 0.45H). ^{13}C-NMR (75 MHz, $CDCl_3$): characteristic signals δ = 90.3, 95.6.

To facilitate characterization the lactols **27** were oxidized to the lactones **28**: **27a** (28 mg, 0.13 mmol) was taken up in dichloromethane (1.3 mL). Pyridine (53 μL, 0.65 mmol) and Dess–Martin periodinane (66 mg, 0.16 mmol) were added at 0 °C. After stirring for 8 h at room temperature the mixture was concentrated and the residue was purified by flash chromatography with pentane–*tert*-butyl methyl ether (5 : 1) to give the 1,3-*cis*-lactone **28a** (15 mg, 54%) as a colorless oil. R_f(PE–EtOAc 5 : 1) = 0.29. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.88 (d, J = 6.8 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 1.55–1.83 (m, 5H), 1.86 (ddd, J = 9.5, 9.0, 7.6 Hz, 1H), 1.88 (ddd, J = 9.6, 9.1, 7.6 Hz, 1H), 2.11–2.19 (m, 2H), 2.55 (dt, J = 17.6, 7.7 Hz, 1H), 2.74 (ddd, J = 17.6, 8.9, 5.4 Hz, 1H), 3.27 (ddd, J = 8.7, 6.3, 5.4 Hz, 1H), 3.41 (td, J = 9.6, 6.2 Hz, 1H), 4.04 (td, J = 9.3, 4.8 Hz, 1H). NOE contacts between H-1 and H-3. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 18.4, 18.9, 19.4, 26.0, 27.9, 31.5, 32.3, 34.0, 78.0, 82.3, 86.1, 171.4. MS (EI) m/z (%): 41 (35), 43 (42), 55 (55), 57 (52), 82 (76), 85 (100), 109 (40), 169 (34).

The 1,3-*trans*-lactol **27b** furnished in the same manner the 1,3-*trans*-lactone **28b** (20 mg, 63%) as a colorless oil. R_f(PE–EtOAc 5 : 1) = 0.21. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.87 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H), 1.38–1.55 (m, 3H), 1.69 (ddt, J = 13.4, 8.2, 6.7 Hz, 1H), 1.80–1.87 (m, 1H), 1.93 (dtd, J = 13.7, 8.6, 6.8 Hz, 1H), 1.97–2.03 (m, 1H), 2.06–2.13 (m, 1H), 2.25–2.32 (m, 1H), 2.49 (ddd, J = 17.3, 9.0, 6.4 Hz, 1H), 2.72 (dt, J = 17.3, 6.6 Hz, 1H), 3.31 (ddd, J = 11.3, 8.4, 5.3 Hz, 1H), 3.67 (td, J = 8.7, 6.4 Hz, 1H), 4.04 (ddd, J = 10.4, 9.5, 4.9 Hz, 1H). No NOE contacts between H-1 and H-3. ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 18.9, 19.7, 20.5, 27.1, 28.2, 31.9, 32.9, 35.4, 68.1, 82.3, 83.2, 171.1. MS (EI) m/z (%): 41 (35), 43 (40), 55 (56), 81 (27), 85 (73), 95 (34), 101 (35), 109 (29), 123 (47), 169 (100). HRMS(EI): $C_{12}H_{20}O_3$ requires 212.1412; found 212.1411.

trans-3-Ethynyloxy-2-vinyltetrahydropyran (29)

trans-3-Hydroxy-2-vinyltetrahydropyran **8** was converted into **29** essentially as described for **12**. The crude product was filtered over 3 cm of silica gel, which had been deactivated with triethylamine, using pentane–diethyl ether (5 : 1) to give **29** (314 mg, 72%) as a slightly yellowish oil. R_f(PE–EtOAc 5 : 1) = 0.56. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.56 (s, 1H), 1.64–1.87 (m, 3H), 2.33–2.48 (m, 1H), 3.35–3.48 (m, 1H), 3.71–3.83 (m, 2H), 3.90–4.00 (m, 1H), 5.31 (d, J = 10.7 Hz, 1H), 5.42 (d, J = 17.1 Hz, 1H), 5.96 (ddd, J = 17.2, 10.6, 5.5 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 24.9, 27.8, 28.0, 66.9, 79.1, 84.5, 88.7, 118.2, 134.6. $C_9H_{12}O_2$ requires C 71.03, H 7.95; found C 70.39, H 7.88%.

(1*R**,3*S**,8*R**,11*S**)- and (1*R**,3*R**,8*S**,11*S**)-2,7,12-trioxa-Δ^5-tricyclo[9.4.0.0^{3,8}]pentadecenes (32)

trans-3-Ethynyloxy-2-vinyltetrahydropyran **29** (277 mg, 1.82 mmol) was converted into the vinylboronate as described for **22**. The crude product was filtered over silica gel (prior deactivated with triethylamine) using pentane–*tert*-butyl methyl ether (5 : 1). The resulting vinylboronate **30** (321 mg, 63%) was obtained as a colorless oil. R_f(CH_2Cl_2 + 2% acetone) = 0.44. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.25 (s, 12H), 1.52 (tdd, J = 12.0, 10.9, 5.4 Hz, 1H), 1.63–1.77 (m, 2H), 2.19–2.28 (m, 1H), 3.42 (td, J = 11.1, 3.4 Hz, 1H), 3.64 (ddd, J = 10.2, 9.2, 4.4 Hz, 1H), 3.68–3.74 (m, 1H), 3.93–3.99 (m, 1H), 4.53 (d, J = 14.2 Hz, 1H), 5.22 (dt, J = 10.7, 1.3 Hz, 1H), 5.35 (dt, J = 17.3, 1.5 Hz, 1H), 5.89 (ddd, J = 17.3, 10.8, 5.5 Hz, 1H), 6.90 (d, J = 14.2 Hz, 1H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 24.7 (4C), 24.9, 67.3, 78.4, 80.1, 82.7 (2C), 117.3, 135.4, 161.9.

The vinylboronate **30** was converted into the allylboronate **31** as described for **22**. The crude product was purified by filtration over silica gel with pentane–*tert*-butyl methyl ether (5 : 1). The allylboronate **31** (263 mg, 78%) was obtained as a colorless oil. R_f(PE–EtOAc 5 : 1) = 0.49. ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 12H), 1.40–1.53 (m, 3H), 1.60–1.76 (m, 2H), 2.11–2.28 (m, 1H), 3.28–3.49 (m, 2H), 3.58–3.70 (m, 1H), 3.88–3.99 (m, 1H), 4.92 (dt, J = 12.3, 7.5 Hz, 1H), 5.20 (dt, J = 10.7, 1.7 Hz, 1H), 5.34 (dt, J = 17.3, 1.7 Hz, 1H), 5.97 (ddd, J = 17.5, 10.8, 5.5 Hz, 1H), 6.04 (dt, J = 12.4, 1.6 Hz, 1H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 24.8 (4C), 25.1, 29.7, 67.3, 78.2, 80.5, 83.2 (2C), 101.9, 116.6, 136.1, 144.9.

The hydroformylation of the allylboronate **31** was carried out as described for **28** for 80 h at 65 °C under 5 bar of CO–H_2 (1 : 1). Flash chromatography of the crude product with pentane–*tert*-butyl methyl ether (5 : 1) furnished **32** (97 mg, 52%) as a 1 : 1 mixture of the two diastereomers. This mixture was not separated. R_f(PE–EtOAc 5 : 1) = 0.41. ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.36–1.54 (m, 1.5H), 1.57–1.76 (m, 2.5H), 1.85–2.01 (m, 2H), 2.01–2.34 (m, 4H), 3.06 (ddd, J = 9.1, 7.2, 4.8 Hz, 0.5H), 3.13 (ddd, J = 10.4, 9.1, 5.0 Hz, 0.5H), 3.20 (ddd, J = 10.6, 9.1, 4.9 Hz, 0.5H), 3.26 (ddd, J = 11.1, 9.1, 4.1 Hz, 0.5H), 3.29–3.35 (m, 1H), 3.58–3.63 (m, 1H), 3.66 (td, J = 9.5, 2.7 Hz, 0.5H), 3.71 (td, J = 9.8, 5.7 Hz, 0.5H), 3.84 (ddt, J = 11.1, 4.0, 2.0 Hz, 0.5H), 3.89 (ddt, J = 11.3, 3.9, 2.0 Hz, 0.5H), 4.64 (td, J = 5.6, 2.1 Hz, 0.5H), 4.69 (td, J = 5.5, 2.3 Hz, 0.5H), 6.26 (dt, J = 5.9, 2.0 Hz, 0.5H), 6.28 (dt, J = 5.9, 1.9 Hz, 0.5H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 25.7, 26.0, 28.24, 28.27, 28.8, 29.0, 29.7, 31.4, 31.9, 32.0, 67.3, 68.0, 71.5, 74.9, 78.2, 79.3, 79.7, 81.4, 81.8, 83.4, 99.0, 99.6, 143.89, 143.91. MS (EI) m/z (%): 41 (26), 43 (26), 55 (30), 71 (79), 81 (41), 94 (29), 97 (100), 141 (32), 210 (33). HRMS(EI): $C_{12}H_{18}O_3$ requires 210.1256; found 210.1254.

Acknowledgements

This study has been supported by the Deutsche Forschungsgemeinschaft (SFB 260) and the Fonds der Chemischen Industrie as well as by the European Community, HCM Network Nr. ERB-CHRX-CT94-0620. We would like to thank these organizations for their support.

References

1 S. Breitfelder, A. Schlapbach and R. W. Hoffmann, *Synthesis*, 1998, 468.
2 (*a*) Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207; (*b*) D. S. Matteson, *Stereodirected Synthesis with Organoboranes*, Springer, Berlin, 1995;; (*c*) J. A. Marshall, *Chem. Rev.*, 1996, **96**, 31.
3 For a review see: W. R. Roush in *Houben-Weyl: Methods of Organic Chemistry*, eds. G. Helmchen, R. W. Hoffmann, J. Mulzer and E. Schaumann, Thieme, Stuttgart, 1995, vol. E21b, pp. 1410–1486.
4 R. W. Hoffmann and B. Kemper, *Tetrahedron Lett.*, 1981, **22**, 5263.
5 (*a*) R. W. Hoffmann, B. Kemper, R. Metternich and T. Lehmeier, *Liebigs Ann. Chem.*, 1985, 2246; (*b*) R. W. Hoffmann and R. Metternich, *Liebigs Ann. Chem.*, 1985, 2390.
6 (*a*) T. Moriya, A. Suzuki and N. Miyaura, *Tetrahedron Lett.*, 1995, **36**, 1887; (*b*) Y. Yamamoto, T. Miyairi, T. Ohmura and N. Miyaura, *J. Org. Chem.*, 1999, **64**, 296.
7 (*a*) W. R. Roush and P. T. Grover, *Tetrahedron*, 1992, **48**, 1981; (*b*) J. A. Hunt and W. R. Roush, *J. Org. Chem.*, 1997, **62**, 1112; For other allylmetallation routes to **4** see ref. 8.
8 (*a*) Y. Yamamoto, Y. Saito and K. Maruyama, *J. Organomet. Chem.*, 1985, **292**, 311; (*b*) K. Tamao, E. Nakajo and Y. Ito, *J. Org. Chem.*, 1987, **52**, 957; (*c*) K. Takai, K. Nitta and K. Utimoto, *Tetrahedron Lett.*, 1988, **29**, 5263; (*d*) J. A. Marshall and K. W. Hinkle, *J. Org. Chem.*, 1996, **61**, 105; (*e*) A. G. M. Barrett and J. W. Malecha, *J. Org. Chem.*, 1991, **56**, 5243; (*f*) A. G. M. Barrett and J. W. Malecha, *J. Chem. Soc., Perkin Trans. 1*, 1994, 1901.
9 (*a*) K. M. Sadhu and D. S. Matteson, *Organometallics*, 1985, **4**, 1687; (*b*) H. C. Brown, S. M. Singh and M. V. Rangaishenvi, *J. Org. Chem.*, 1986, **51**, 3150.
10 (*a*) T. J. Michnick and D. S. Matteson, *Synlett.*, 1991, 631; (*b*) R. H. Wallace and K. K. Zong, *Tetrahedron Lett.*, 1992, **33**, 6941; (*c*) H. C. Brown, A. S. Phadke and N. G. Bhat, *Tetrahedron Lett.*, 1993, **34**, 7845; (*d*) H. C. Brown and A. S. Phadke, *Synlett.*, 1993, 927; (*e*) R. Soundararajan, G. Li and H. C. Brown, *Tetrahedron Lett.*, 1994, **35**, 8957; (*f*) R. Soundararajan, G. Li and H. C. Brown, *Tetrahedron Lett.*, 1994, **35**, 8961; (*g*) R. Soundararajan, G. Li and H. C. Brown, *J. Org. Chem.*, 1996, **61**, 100.
11 A. Moyano, F. Charbonnier and A. E. Greene, *J. Org. Chem.*, 1987, **52**, 2919.
12 C. E. Tucker, J. Davidson and P. Knochel, *J. Org. Chem.*, 1992, **57**, 3482.
13 R. W. Hoffmann and I. Münster, *Liebigs Ann./Recueil*, 1997, 1143.
14 J. Inanaga, Y. Yokoyama and T. Hanamoto, *Tetrahedron Lett.*, 1993, **34**, 2791.
15 J.-i. Yamada, T. Asano, I. Kadota and Y. Yamamoto, *J. Org. Chem.*, 1990, **55**, 6066.
16 (*a*) T. Yasumoto and M. Murata, *Chem. Rev.*, 1993, **93**, 1897; (*b*) E. Alvarez, M.-L. Candenas, R. Pérez, J. L. Ravelo and J. D. Martin, *Chem. Rev.*, 1995, **95**, 1953.
17 S. Pereira and M. Srebnik, *Organometallics*, 1995, **14**, 3127.
18 B. H. Lipshutz and and D. F. Harvey, *Synth. Commun.*, 1982, **12**, 267.
19 (*a*) K. C. Nicolaou, C. V. C. Prasad, P. K. Somers and C.-K. Hwang, *J. Am. Chem. Soc.*, 1989, **111**, 5330; (*b*) Y. Yamamoto, J.-i. Yamada and I. Kadota, *Tetrahedron Lett.*, 1991, **32**, 7069.
20 R. W. Hoffmann, D. Brückner and V. J. Gerusz, *Heterocycles*, 2000, **52**, 121.
21 (*a*) G. D. Cuny and S. L. Buchwald, *J. Am. Chem. Soc.*, 1993, **115**, 2066; (*b*) L. A. van der Veen, P. C. J. Kramer and P. W. N. M. van Leeuwen, *Angew. Chem.*, 1999, **111**, 349; (*c*) *Angew. Chem., Int. Ed.*, 1999, **38**, 336.
22 T. J. Fleck and P. A. Grieco, *Tetrahedron Lett.*, 1992, **33**, 1813.
23 D. B. Dess and J. C. Martin, *J. Org. Chem.*, 1983, **48**, 4155.