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Regio- and diastereo-selectivity of the insertion of aldehydes into alkyne zirconocene complexes

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Abstract

Insertion of aldehydes into alkyne–zirconocene complexes provides configurationally pure allyl alcohols in a one-pot procedure. In the case of unsymmetrical alkynes, the regioselectivity of the insertion process is high for terminal alkynes. With trimethylsilyl-substituted alkynes the regioselectivity is low. The insertion of chiral aldehydes into the symmetrical oct-4-yne–zirconocene complex provides the Cram isomer as the major product. On the other hand, reaction of the complex derived from a terminal alkyne with 2-phenylpropanal leads primarily to the *anti*-Cram product. The results are explained in terms of a four-centre transition-state model.

Keywords: Zirconium; Insertion reaction; Aldehydes; Alkynes; Regioselectivity; Diastereoselectivity

1. Introduction

The reaction of carbon nucleophiles with chiral aldehydes is of great value for the construction of stereocentres with concomitant carbon–carbon bond formation [1]. Usually, the addition proceeds with predictable and satisfactory diastereoselectivity. In the case of α- or β-alkoxyaldehydes chelation effects can be used to provide additional control [2]. While the substrate and the reaction conditions are important determinants of the selectivity, the nature of the nucleophile also has a great influence. To a major class of nucleophiles belong those which possess an electron-rich π-bond. Typical examples of this class include enolates and allyl metal compounds. With this kind of nucleophile, the addition normally proceeds through a six-membered transition state, thus providing relatively high selectivity. Other important types of nucleophiles are those in which the orbital that contains the nucleophilic electron pair of the carbanion has s character. Thus, one might distinguish sp, sp^2 and sp^3 carbon nucleophiles. It is assumed that such additions occur via a four-centre transition state [3]. A more special class of nucleophiles is represented by metal complexes of alkenes and alkynes which contain two potential nucleophilic centres, although only one is used for the addition to a carbonyl group. Owing to some degree of backbonding, such complexes may also be formulated as metallacycles. Common metal fragments are zirconocene [4] and tantalum residues [5]. Such complexes are known to react with many unsaturated two-atom species. With carbonyl compounds oxazirconacyclopentene complexes are formed (Scheme 1). The addition of such complexes to chiral aldehydes might also provide some insight into the mode of the addition. The addition products formed after the hydrolysis of the intermediate metallacycle are allyl alcohols, which themselves contain interesting functional groups for further manipulation.

The required alkyne–zirconocene complexes are accessible by two principle routes. One is the direct complexation of an alkyne with Cp_2Zr, which can be generated in situ from Cp_2ZrCl_2 and n-butyllithium [6]. However, not all functional groups are compatible with these reaction conditions. The second route, which was used in this study, involves an initial hydrozirconation of an alkyne with Cp_2ZrHCl [7]. In the hydrozirconation product the halide is then replaced by a methyl group through the action of methyllithium [8]. As has been discovered by Buchwald and co-workers [4,9], on

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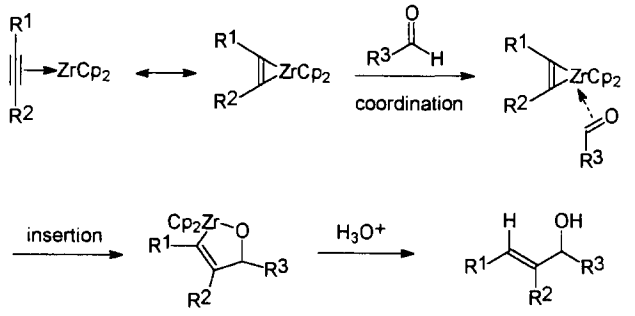
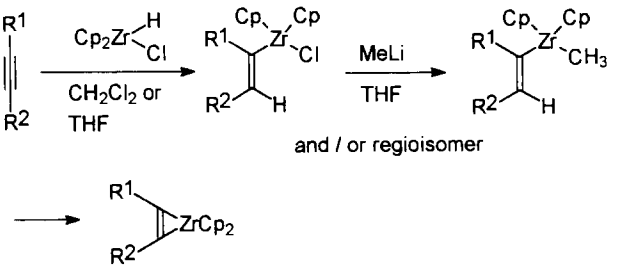


Scheme 1.

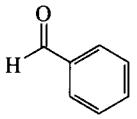
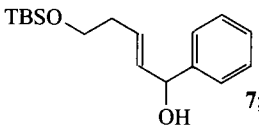
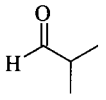
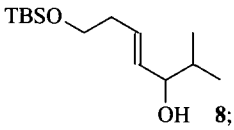
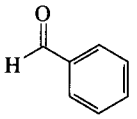
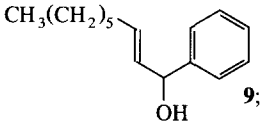
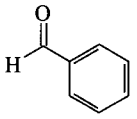
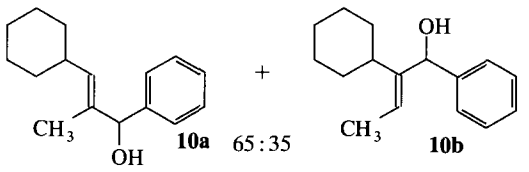
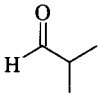
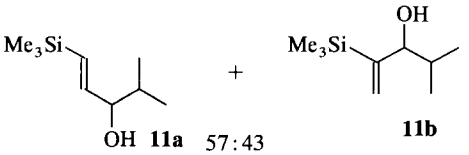
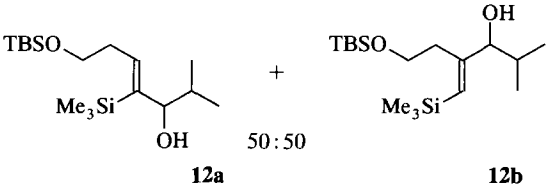


Scheme 2.

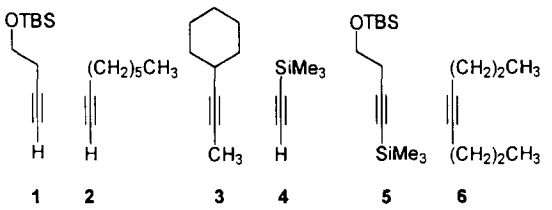
warming such complexes lose methane in a β-hydride elimination reaction to give the desired alkyne–zirconocene complexes (Scheme 2).

At the outset of this study, few data were available concerning the regiochemical insertion of carbonyl compounds into unsymmetrical alkyne–zirconocene complexes. For example, Buchwald et al. [9] reported for the reaction of the hex-1-yne–zirconocene complex with acetone only moderate regiocontrol favouring reaction at the less hindered carbon atom. Van Wagenen

Table 1
Regioselectivity of the insertion of aldehhydes into alkyne–zirconocene complexes

Entry	Alkyne	Aldehyde	Product(s); isomer ratio	Yield (%)
1	**1**		 **7**; > 95:5	69
2	**1**		 **8**; > 95:5	61
3	**2**		 **9**; > 95:5	53
4	**3**		 **10a** 65:35 **10b**	56
5	**4**		 **11a** 57:43 **11b**	69
6	**5**		 50:50 **12a** **12b**	61

and Livinghouse [10] considered electronic modulation of the insertion process. When a 1-methylthioalkyne–zirconocene complex was used, a slight preference for reaction at the alkyl substituted carbon atom was observed. These results show that there is still much uncertainty regarding the factors that determine the regiochemical outcome. In this paper, we present the results of the regio- and diastereo-selectivity of the reaction of alkyne–zirconocene complexes with aldehydes.



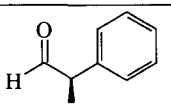
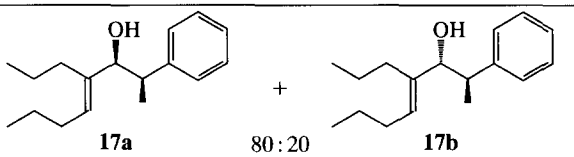
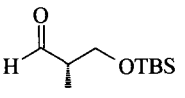
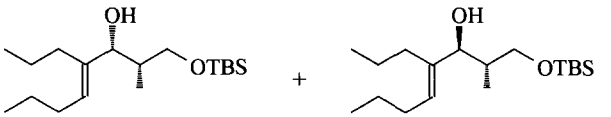
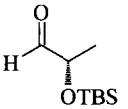
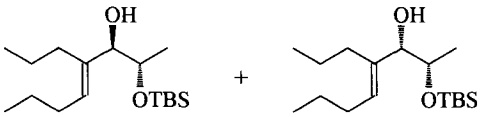
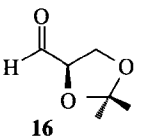
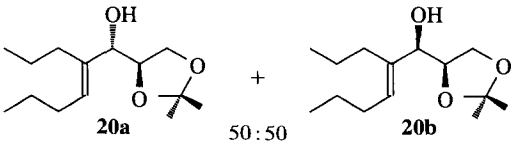
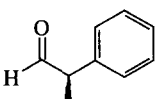
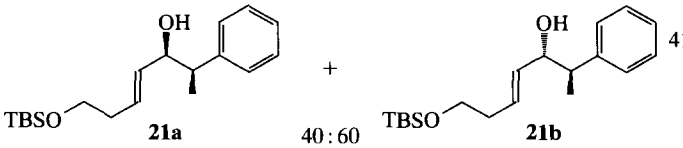
Scheme 3.

2. Results and discussion

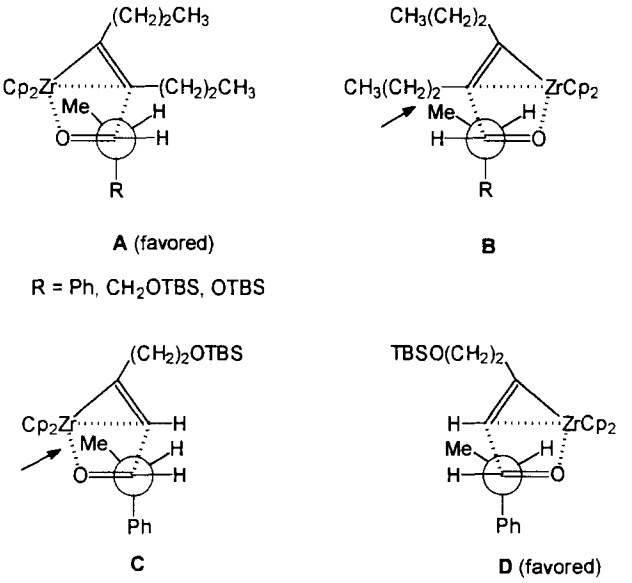
Alkynes **1–6** were used (Scheme 3). First, the regiochemistry of the insertion process was studied using alkynes **1–5**. The whole operation could be performed in a single flask. First, the alkyne was subjected to hydrozirconation in dichloromethane as a solvent. With oct-1-yne (**2**), 1-cyclohexylprop-1-yne (**3**), and oct-4-yne (**6**) it was found that the hydrozirconation can also be carried out in THF as solvent [7]. This simplifies the procedure because the replacement of dichloromethane by THF prior to the addition of methyllithium is redundant. Treatment of the zirconocene vinyl chloride with methyllithium led to exchange of chlorine for a methyl group. Upon warming to room temperature, the intermediate alkyne–zirconocene complex was formed. Preliminary experiments indicated that the addition of trimethylphosphane, which is able to stabilize such complexes, is not necessary. Rather, it was found that higher yields and cleaner reactions can be realized if the aldehyde is added at low temperature, that is, before the methane elimination has started.

As can be seen from Table 1, the insertion of aldehydes into the complexes formed from the terminal alkynes proceeds practically regiospecifically. By NMR analysis of the crude material obtained after work-up, only one isomer could be detected. Although homopropargyl ethers such as **1** are suitable for this reaction, the

Table 2
Diastereoselectivity of the insertion of chiral aldehydes into alkyne–zirconocene complexes

Entry	Alkyne	Aldehyde	Product(s); isomer ratio	Yield (%)
1	**6**	 **13**	 **17a** 80:20 **17b**	69
2	**6**	 **14**	 **18a** 75:25 **18b**	51
3	**6**	 **15**	 **19a** 62:38 **19b**	49
4	**6**	 **16**	 **20a** 50:50 **20b**	46
5	**1**	 **13**	 **21a** 40:60 **21b**	41

synthetically useful propargyl ethers were not studied because α-alkoxy–zirconocene complexes undergo β-alkoxy elimination with concomitant formation of allene–zirconocene intermediates [11]. It appears that carbon–carbon bond formation takes place at the less hindered carbon atom of the complex. This is also true for the alkyne **3**, which however gives only a 65:35 ratio of regioisomers. Surprisingly, insertion of isobutanal into the complex derived from trimethylsilylacetylene (**4**) is only slightly selective. Either the steric effect of the trimethylsilyl group is not felt by the zirconocene during the insertion process or electronic effects disfavour bond formation with the hydrogen-bearing carbon. With the alkyne **5** the insertion process is unselective. This result rules out a possible intramolecular complexation of the ether oxygen with the zirconocene atom, which should have directed the aldehyde preferentially to the silicon terminus. Considering that the whole operation actually involves five individual steps, the isolated yields for the allyl alcohols are satisfactory.



Scheme 4.

In the light of the above results, it was clear that only symmetrical and terminal alkynes would be useful for the insertion process with chiral aldehydes. Thus, to minimize the number of possible isomers in the insertion process, only the symmetrical oct-4-yne (**6**) and the terminal alkyne **1** were considered (Table 2). With 2-phenylpropanal (**13**) and the zirconocene complex of oct-4-yne the diastereoselectivity is 80:20. The selectivity decreases with the aldehydes **14** [12] and **15** [13] approaching a ratio of 50:50 with 2,3-*O*-isopropylidene-D-glyceraldehyde [14] (**16**). The low diastereoselectivity observed for the aldehydes **14–16** is comparable to the results reported by other groups for these or similar substrates [15]. If oct-4-yne was used, the reaction also led to about 10–80% of the symmetrical (*E*, *E*)-5,6-dipropyldeca-4,6-diene. Similar homocoupling products have been observed by other workers [10,16]. This is indicative of the presence of the intermediate alkyne–zirconcene complex. A surprising result was obtained with the complex derived from the homopropargyl ether **1**. In this case, the reaction with 2-phenylpropanal favours the formation of the *anti* isomer **21b**.

In order to explain the observed diastereoselectivities, a modified Felkin–Anh model [17] can be used. Because of the oxophilicity of zirconium, the insertion most likely proceeds through a four-centre transition state [18]. Initial complexation of the aldehyde to the zirconium atom would have to occur approximately in the plane that lies between the two Cp rings [19]. For the oct-4-yne complex, inspection of the two possible transition states **A** and **B** reveals that for **B** substantial steric repulsion between the n-propyl and the methyl group of the aldehyde (**13**, **14**, **15**) destabilizes this reaction path, thus favouring formation of the Cram product (Scheme 4). In comparison, inspection of molecular models shows that the steric repulsion between the cyclopentadienyl residues at the zirconium and the methyl group in **A** is much smaller. The preferred formation of the *anti*-Cram product **21b** can also be explained by invoking a four-centre transition state. In contrast to the transition state with the oct-4-yne complex **B**, the steric repulsion between the methyl group of the aldehyde and the hydrogen of the former alkyne is less pronounced, which should favour the transition state **D**, leading to the *anti*-Cram product.

Further evidence for complexation of the zirconium atom with the carbonyl oxygen came from studies of the insertion process in the presence of chelating Lewis acids. Thus, addition of zinc bromide to the aldehyde **15** in the reaction with the oct-4-yne–zirconocene complex gave practically the same diastereomeric ratio as without the Lewis acid. A more pronounced effect was observed in the case of $MgBr_2$, which gave a **19a**:**19b** ratio of 50:50. For the allyl alcohols **18a** and **18b**, addition of $MgBr_2$ changed the original ratio of 75:25 to 68:32. The fact that the diastereomeric ratios are only slightly different in presence of Lewis acids indicates that a possible chelate is destroyed by the attacking zirconocene–alkyne complex.

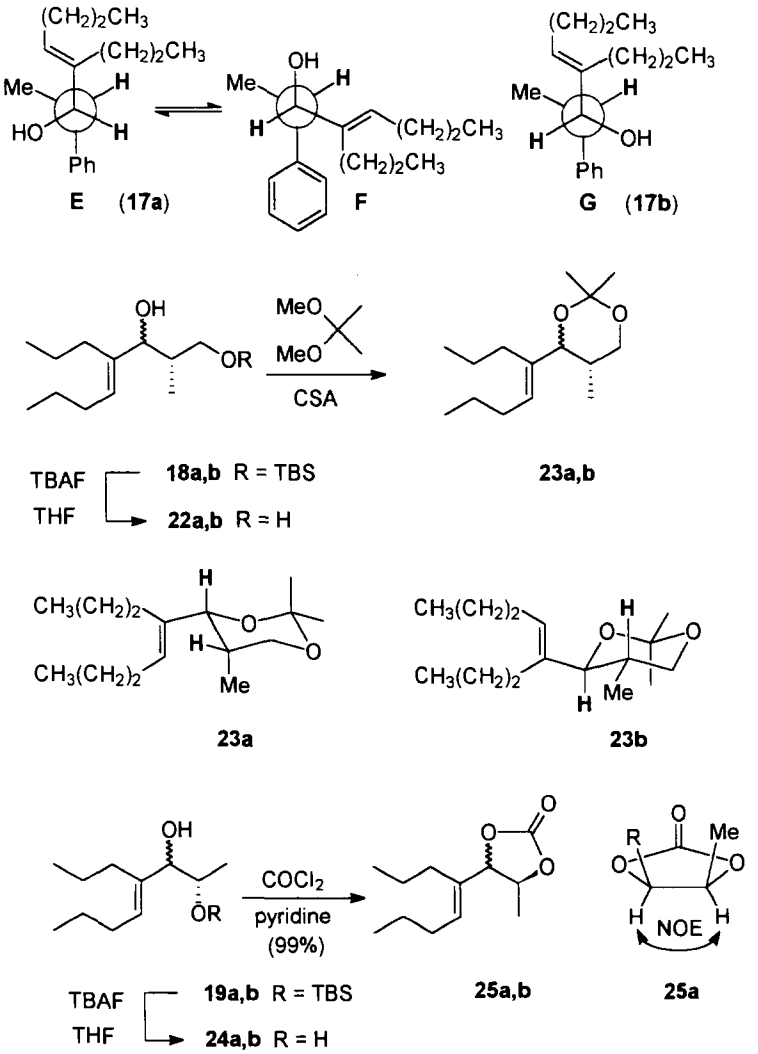
3. Structure analysis

The relative configuration of the two diastereomeric allyl alcohols **17a** and **17b** could be assigned by inspection of the vicinal coupling constant $^3J_{2,3}$. Whereas this coupling constant is 5.6 Hz for the major isomer **17a**, the corresponding value for the minor isomer **17b** is 9.0 Hz. These values are in accordance with torsional an-

gles of 60° and 180°, respectively, for the most populated conformer [20] (cf. **E** and **G**, Scheme 5). Another conformer that is significantly populated in acyclic compounds with vicinal stereocentres that carry hydrogen atoms is one in which the two hydrogen atoms are in an *anti* position [15a]. If a phenyl group is present, the ^{1}H NMR resonance of a substituent which is *gauche* to this group appears at higher field owing to the effect of the aromatic ring (cf. conformer **F**, Scheme 5). In fact, the signal of the vinylic proton of **17a** ($\delta = 5.37$) appears at higher field than the corresponding signal of **17b** ($\delta = 5.40$). The same trend can be observed for the two terminal methyl groups of the oct-4-enyl residue. Whereas in **17b** their signals appear at $\delta = 0.92$ and 0.97, they are shifted to higher field in **17a** resonating at $\delta = 0.81$ and 0.89, respectively.

The incorporation of the diol structure in a cyclic arrangement was used to elucidate the relative configuration of **18a** and **18b**. After cleavage of the silyl ether, the mixture of the diols **22a** and **22b** was converted into the diastereomeric cyclic acetals **23a** and **23b** by treatment with 2,2-dimethoxypropane and a catalytic amount of camphorsulphonic acid (CSA). The original ratio of diastereomers did not change during this operation. With the assumption that the large oct-4-enyl group occupies the equatorial position in the two chair-like acetals **23a** and **23b**, the configuration can be inferred from the coupling constant $J_{2,3}$. This coupling constant is not measurable in the major isomer, whereas the minor isomer shows $J_{2,3} = 10.4$ Hz, which is in accordance with the configuration and conformation depicted in Scheme 5.

For the two diastereomers **19a** and **19b**, which could not be separated, the relative stereochemistry was assigned at the stage of the cyclic carbonates **25a** and **25b**. Because in both carbonates the vicinal coupling constant $J_{2,3}$ amounts to 7.5 Hz, the configuration was deduced from NOE experiments. Thus, irradiation of C_3-H gave only in the *cis* isomer **25a** a positive NOE signal for C_2-H (Scheme 5).



Scheme 5.

With the mixture of **21a** and **21b**, configurational assignment was not possible on the basis of the vicinal coupling constants. However, as for **17a** (cf. conformer **F**, Scheme 5), the findings of Lodge and Heathcock [15a] proved to be helpful. Owing to the presence of conformers with *anti* hydrogen atoms, the signals of the alkenyl group of **21a** appear at higher field than the corresponding ones of the isomer **21b**. For example, in the Cram product **21a** (minor isomer), C_4-H (olefinic H) resonates at $\delta = 5.44$ ppm, whereas in **21b** this signal shows up at $\delta = 5.54$.

In summary, the described method represents a formal reductive coupling of acetylenes with aldehydes to give allyl alcohols. With the observed regiochemistry and diastereoselectivity, this strategy should also find use in more complex settings.

4. Experimental section

^{1}H NMR spectra were measured with Bruker AM 200 and AM 400 spectrometers, all spectra were recorded in $CDCl_3$ as solvent with tetramethylsilane as internal standard. ^{13}C NMR spectra were measured with a Bruker AM 400 spectrometer (100 MHz) with broadband decoupling. The signal multiplicities were determined by means of the DEPT 135 technique. IR spectra were measured with a Nicolet 320 FT-IR spectrometer GC was carried out with a Dani 8300 gas chromatograph with an SPB5 capillary column of length 15 m and a flame ionization detector. Mass spectrometry (MS) was carried out with a Finnigan MAT 8430 spectrometer using electron impact (EI) ionization of 70 eV or chemical ionization (CI). Flash chromatography was performed using J.T. Baker silica gel, 30–60 μm. Thin-layer chromatography was carried out with Macherey–Nagel Polygram SIL G/UV_{254} precoated TLC plates. All experiments were carried out under nitrogen.

Solvents were purified according to the literature [21]; light petroleum with a boiling range of 35–65°C was used; THF was distilled from sodium benzophenone ketyl immediately before use; the pH 7 buffer solution used in the work-up procedures was prepared by dissolving potassium dihydrogenphosphate (85.0 g) and sodium hydroxide (14.5 g) in 1 l of water.

The following reagents and organic compounds were prepared according to literature procedures: zirconocene(chloride) hydride ($(\eta^5$-$C_5H_5)_2Zr(H)Cl$) [22], trimethylphosphane [23], 4-[(tert-butyldimethylsilyl)-oxy]-1-trimethylsilylbut-1-yne [24], 1-cyclohexylprop-1-yne [25], 2,3-*O*-isopropylidine-D-glyceraldehyde [14], (2*S*)-3-[(tert-butyldimethylsilyl)oxy]-2-methylpropanal [12] and (2*S*)-2-[(tert-butyldimethylsilyl)oxy]propanal [13].

4.1. General procedure for the preparation of the allyl alcohols

Method A: hydrozirconation

To a cooled (0°C) suspension of zirconocene hydrochloride (0.33 M) in dry dichloromethane was added dropwise 1.0 equiv. of a 0.5 M solution of the alkyne in the same solvent. The resulting mixture was stirred with the exclusion of light for 15–60 min. The completion of the hydrozirconation was evident from the formation of a clear yellow solution. Methylation: the solvent was carefully removed with a vacuum pump and the residue (yellow solid or oil) was dissolved in THF to give a 0.33 M solution. This solution was then treated at −78°C with 1.0 equiv. of a 1.6 M solution of methyllithium in diethyl ether. The stirred reaction mixture was allowed to warm to −50°C during 1 h. Methane elimination/insertion of the aldehyde: at this stage, 1.1 equiv. of a 0.5 M solution of the aldehyde in THF was added dropwise. The reaction mixture was allowed to reach 0°C, whereby the elimination of methane could be observed. Stirring of the reaction mixture for 20 h with slow warming to room temperature completed the reaction. The progress of the insertion could also be followed by thin-layer chromatography. Work-up: the reaction was quenched with methanol (1 ml per mmol of alkyne) and the mixture was stirred for 1 h at room temperature. The hydrolysed solution was partitioned between equal amounts of diethyl ether and 5% acetic acid. At this stage an emulsion sometimes formed. The aqueous phase was extracted with diethyl ether (2 ×). The combined organic layers were washed with 5% acetic acid, saturated $NaHCO_3$ solution and brine, dried ($MgSO_4$) and the solvent was evaporated. The crude allyl alcohols were then purified by flash chromatography. The reactions were carried out on a 0.5–5 mmol scale in an appropriate Schlenk flask.

Method B: hydrozirconation in THF

To a cooled (0°C) suspension of zirconocene hydrochloride (0.29 M) in dry THF was added dropwise 1.0 equiv. of a 0.33 M solution of the alkyne in the same solvent. The resulting mixture was stirred with the exclusion of light for 60 min. The completion of the hydrozirconation was evident from the formation of a clear yellow–orange solution. This solution was treated at −78°C with methyllithium. The remaining steps were carried out as described above.

4.2. (E)-5-[(tert-Butyldimethylsilyl)oxy]-1-phenylpent-2-en-1-ol (7a)

According to method A, 4-[(tert-butyldimethylsilyl)-oxy]but-1-yne (**1**) (287 mg, 1.56 mmol), zirconocene hydrochloride (402 mg, 1.56 mmol) and benzaldehyde

(174 μl, 1.72 mmol) were allowed to react. Purification was performed by flash chromatography (light petroleum–ethyl acetate, 20:1) yielding 315 mg (69%) of **7a** as a slightly yellow oil. TLC (light petroleum–ethyl acetate, 20:1): $R_f = 0.25$. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.03$ (s, 6 H, $SiC(CH_3)_3(CH_3)_2$), 0.88 (s, 9 H, $SiC(CH_3)_3(CH_3)_2$), 1.92 (d, br., $^3J = 2.8$ Hz, 1 H, OH), 2.28 (dt, $^3J = 6.5$ Hz, 2 H, C_4-H), 3.65 (t, $^3J = 6.5$ Hz, 2 H, C_5-H), 5.17 (s, br., 1 H, C_1-H), 5.70–5.76 (m, 2 H, C_2-H, C_3-H), 7.25–7.29 (m, 1 H, Ph-H), 7.32–7.39 (m, 4 H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -5.3$, 18.3, 25.9 (TBS), 35.8 (C-4), 62.6 (C-5), 75.1 (C-1), 126.1, 127.5, 128.4 (Ph–C), 129.0, 134.1 (olefinic C), 143.1 (Ph-C). MS (CI, isobutane, neg.): m/z (%) = 291 (32) [$M^+ - H$], 186 (8), 177 (12), 131 (100). Anal. $C_{17}H_{28}O_2Si$ (292.5): Calc. C 69.81, H 9.64; found C 70.01, H 10.00%.

4.3. (E)-7-[(tert-Butyldimethylsilyl)oxy]-2-methylhept-4-en-3-ol (8a)

According to method A, 4-[(tert-butyldimethylsilyl)-oxy]but-1-yne (**1**) (289 mg, 1.57 mmol), zirconocene hydrochloride (405 mg, 1.57 mmol) and isobutanal (158 μl, 1.73 mmol, 1.1 equiv.) were allowed to react. In the NMR spectrum of the crude material, only signals of the regioisomer **8a** were visible. Purification was performed by flash chromatography (light petroleum–ethyl acetate, 10:1) yielding 245 mg (61%) of **8a** as a slightly yellow oil. TLC (light petroleum–ethyl acetate, 10:1): $R_f = 0.26$. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta =$ 0.05 (s, 6 H, 6 H, $SiC(CH_3)_3(CH_3)_2$), 0.88, 0.93 (2 d, $^3J = 6.8$ Hz, 3 H each, CH_3), 0.89 (s, 9 H, $SiC(CH_3)_3(CH_3)_2$), 1.40 (s, br., 1 H, OH), 1.70 (dq, $^3J = 6.7$ Hz, 1 H, C_2-H), 2.27 (dt, $^3J = 6.7$ Hz, 2 H, C_6-H), 3.65 (t, $^3J = 6.7$ Hz, 2 H, C_7-H), 3.79 (dd, br., $^3J = 6.5$ Hz, 1 H, C_3-H), 5.53 (dd, $^3J_{trans} = 15.5$ Hz, $^3J = 7.0$ Hz, 1 H, C_4-H), 5.65 (dt, $^3J_{trans} = 15.9$ Hz, $^3J = 6.7$ Hz, 1 H, C_5-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -5.3$ (TBS), 18.0, 18.2 (C-1, C-8), 18.3 (TBS), 25.9 (TBS), 33.7 (C-2), 35.9 (C-6), 62.8 (C-7), 78.1 (C-3), 129.2, 133.1 (C-4, C-5). MS (CI, NH_3, pos.): m/z (%) = 258 (36) [M^+]; 241 (76) [$M^+ + H - H_2O$], 215 (3) [$M^+ - C_3H_7$], 175 (13), 121 (24), 109 (100). Anal. $C_{14}H_{30}O_2Si$ (258.5): Calc. C 65.06, H 11.69; found C 65.11, H 11.71%.

4.4. (E)-1-Phenylnon-2-en-1-ol (9a)

According to method B, oct-1-yne (**2**) (369 mg, 495 μmol, 3.35 mmol), zirconocene hydrochloride (864 mg, 3.35 mmol) and benzaldehyde (372 μl, 3.68 mmol, 1.1 equiv.) were allowed to react. The aldehyde was added at −20°C. In the NMR spectrum of the crude material, only signals of the regioisomer **9a** were visible. Because **9a** decomposed during attempted silica gel chromatography, purification was performed by flash chromatography (light petroleum–ethyl acetate, 20:1) on Florisil (200–300 mesh, Fluka) to give 383 mg (53%) of **9a** as a slightly yellow oil. TLC (light petroleum–ethyl acetate, 15:1): $R_f = 0.27$ ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 0.87$ (t, $^3J = 6.9$ Hz, 3 H, CH_3), 1.22–1.42 (m, 8 H, CH_2), 1.92 (s, br., 1 H, OH), 2.05 (dt, $^3J = 6.9$ Hz, 2 H, C_4-H), 5.16 (d, $^3J = 6.6$ Hz, 1 H, C_1-H), 5.66 (ddt, $^3J_{trans} = 15.3$ Hz, $^3J = 6.8$ Hz, $^4J_{allyl} = 1.0$ Hz, 1 H, C_2-H), 5.76 (dtd, $^3J_{trans} = 15.3$ Hz, $^3J = 6.5$ Hz, $^4J_{allyl} = 0.6$ Hz, 1 H, C_3-H), 7.24–7.29 (m, 1 H, Ph-H), 7.32–7.38 (m, 4 H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3), 22.5, 28.8, 29.0, 31.6, 32.1 (5 CH_2), 75.2 (C-1), 126.1 (Ph-C), 127.4 (Ph-C), 128.4 (Ph-C), 132.2, 132.8 (olefinic C), 143.4 (Ph-C). MS (EI): m/z (%) = 218 (38) [M^+], 133 (100) [$M^+ - C_6H_{13}$], 120 (38), 105 (28) Anal. $C_{15}H_{22}O$ (218.3): Calc. C 82.52, H 10.15; found C 82.67, H 10.49%.

4.5. (E)-3-Cyclohexyl-2-methyl-1-phenylprop-2-en-1-ol (10a) and (E)-2-cyclohexyl-1-phenylbut-2-en-1-ol (10b)

According to method B, 1-cyclohexylprop-1-yne (**3**) (495 mg, 4.05 mmol), zirconocene hydrochloride (1.044 g, 4.05 mmol) and benzaldehyde (451 μl, 4.46 mmol, 1.1 equiv.) were allowed to react. The ^{1}H NMR spectrum of the crude product contained signals of the two regioisomers **10a** and **10b** in a ratio of 65:35 (determined by integration of the C_1-H signals). Purification was performed by flash chromatography (light petroleum–ethyl acetate, 8:1) yielding 521 mg (56%) of the mixture of **10a** and **10b** as slightly yellow oil. TLC (light petroleum–ethyl acetate, 4:1): $R_f = 0.40$. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.06$–1.35 (m, 2 × 6 H, CH_2), 1.48 (d, $^4J_{allyl} = 1.2$ Hz, 3 H, CH_3 (a)), 1.55–1.78 (m, 4 H (a), 5 H (b), CH_2, OH (b)), 1.71 (d, $^3J = 6.8$ Hz, 3 H, CH_3 (b)), 1.86 (s, br., 1 H, OH (a)), 2.14–2.26 (m, 1 H, $C_{1'}$-H (a)), 2.35 (tt, $^3J_{axial-axial} = 11.7$ Hz, $^3J_{axial-equatorial} = 3.6$ Hz, 1 H, $C_{1'}$-H (b)), 5.09 (s, 1 H, C_1-H (a)), 5.23 (s, 1 H, C_1-H (b)), 5.49 (d, $^3J = 9.0$ Hz, 1 H, C_3-H (a)), 5.56 (dq, $^3J = 6.9$ Hz, $^4J_{allyl} = 0.7$ Hz, 1 H, C_3-H (b)), 7.22–7.27 (m, 2 × 1 H, Ph-H), 7.29–7.36 (m, 2 × 4 H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 11.9$ (C-4 (a)), 13.3 (C-4 (b)), 25.9, 26.0, 26.1, 26.9, 27.0 (C-7, C-8), 31.4, 31.5 (C-6), 33.0, 33.0 (C-6), 36.6 (C-5 (a)), 39.1 (C-5 (b)), 75.5 (C-1 (b)), 79.2 (C-1 (a)), 121.8, 126.2, 126.7, 127.1, 127.1, 128.0, 128.2, 133.1 (C-3, Ph-C), 134.8, 142.4, 143.4, 146.8 (C-2, Ph-C). MS (EI): m/z (%) = 230 (10) [M^+], 147 (100) [$M^+ - C_6H_{11}$], 105 (21). Anal. $C_{16}H_{22}O$ (230.3): Calc. C 83.43, H 9.62; found C 83.45, H 9.98%.

4.6. (E)-4-Methyl-1-trimethylsilylpent-1-en-3-ol (11a) and 4-methyl-2-trimethylsilylpent-1-en-3-ol (11b)

According to method A, trimethylsilylacetylene (**4**) (148 mg, 213 μl, 1.51 mmol), zirconocene hydrochlo-

ride (389 mg, 1.51 mmol) and isobutanal (120 mg, 151 μl, 1.66 mmol, 1.1 equiv.) were allowed to react. The ^{1}H NMR spectrum of the crude product contained signals of the two regioisomers **11a** and **11b** in a ratio of 57:43 (determined by integration of the C_3-H signals). The same ratio was obtained by gas chromatography. Purification was performed by flash chromatography (light petroleum–ethyl acetate, 13:1) yielding 178 mg (69%) of a mixture of **11a** and **11b** as a colourless oil. TLC (light petroleum–ethyl acetate, 13:1): R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 9 H, $Si(CH_3)_3$ (a)), (s, 9 H, $Si(CH_3)_3$ (b)), 0.13, 0.90, 0.90, 0.91, 0.92 (4 d, ^3J = 6.7 Hz, 3 H each, CH_3), 1.42 (d, ^3J = 4.0 Hz, 1 H, OH (b)), 1.52 (d, ^3J = 4.1 Hz, 1 H, OH (a)), 1.74 (dq, ^3J = 6.7 Hz, 1 H, C_4-H (a)), 1.79 (dq, ^3J = 6.7 Hz, 1 H, C_4-H (b)), 3.86 (ddd, br., 1 H, C_3-H (a)), 3.99 (dd, br., 1 H, C_3-H (b)), 5.48 (dd, ^2J = 2.4 Hz, $^4J_{allyl}$ = 0.9 Hz, 1 H, C_1-H (b)), 5.75 (dd, ^2J = 2.5 Hz, $^4J_{allyl}$ = 1.3 Hz, 1 H, C_1-H (b)), 5.85 (dd, $^3J_{trans}$ = 18.8 Hz, $^4J_{allyl}$ = 1.2 Hz, 1 H, C_1-H (a)), 6.04 (dd, $^3J_{trans}$ = 18.8 Hz, ^3J = 5.5 Hz, 1 H, C_2-H (a)). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −0.8 (s, 9 H, $Si(CH_3)_3$ (a)), 0.0 (s, 9 H, $Si(CH_3)_3$ (b)), 17.1, 20.7 (CH_3, (b)), 18.1, 18.8 (CH_3, (b)), 32.9 (C-4 (b)), 34.0 (C-4 (a)), 80.1 (C-3 (a)), 82.3 (C-3 (b)), 125.4 (C-1 (b)), 131.0, 147.5 (C-1, C-2), 154.9 (C-2 (b)). MS (EI, mixture): m/z (%) = 172 (2) [M^+], 157 (14) [$M^+ - CH_3$], 129 (33) [$M^+ - C_3H_7$], 113 (46), 75 (100) [$C_2H_7OSi^+$], 73 (42). Anal. $C_9H_{20}OSi$ (172.3); owing to the volatility of the vinylsilanes **11**, a correct elemental analysis could not be obtained.

4.7. (Z)-7-[(tert-Butyldimethylsilyl)oxy]-2-methyl-4-trimethylsilylhept-4-en-3-ol (12a) and (E)-2-(2-[(tert-butyldimethylsilyl)oxy]ethyl)-4-methyl-1-trimethylsilylpent-1-en-3-ol (12b)

According to method A, 4-[(tert-butyldimethylsilyl)oxy]-1-trimethylsilylbut-1-yne (**5**) (623 mg, 2.43 mmol), zirconocene hydrochloride (627 mg, 2.43 mmol) and isobutanal (192 mg, 244 μl, 2.67 mmol, 1.1 equiv.) were allowed to react. The ^{1}H NMR spectrum of the crude product contained signals of the two regioisomers **12a** and **12b** in a ratio of 50:50 (determined by integration of the TMS signals). The same ratio was obtained by gas chromatography. Purification was performed by flash chromatography (light petroleum–ethyl acetate, 16:1) yielding 409 mg (51%) of **12a** and **12b** as slightly yellow oils. In this way, two pure fractions and a fraction that contained a mixture of both isomers were obtained.

12a

TLC (light petroleum–ethyl acetate, 15:1): R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 (s, 6 H, $SiC(CH_3)_3(CH_3)_2$), 0.18 (s, 9 H, $Si(CH_3)_3$), 0.88, 0.90 (2 d, ^3J = 6.7 Hz, 6 H, CH_3), 0.89 (s, 9 H, $SiC(CH_3)_3(CH_3)_2$), 1.32 (d, br., ^3J = 3.8 Hz, 1 H, OH), 1.73 (dq, ^3J = 6.7 Hz, 1 H, C_2-H), 2.42 (dt, ^3J = 7.0 Hz, 2 H, C_6-H), 3.66 (t, ^3J = 6.8 Hz, 2 H, C_7-H), 3.87 (dd, br., ^3J = 6.6 Hz, ^3J = 3.8 Hz, 1 H, C_3-H), 6.15 (td, ^3J = 7.4 Hz, $^4J_{allyl}$ = 0.9 Hz, 1 H, C_5-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −6.1 (TBS), 0.0 (TMS), 16.1, 19.5 (CH_3), 17.6 (TBS), 25.2 (TBS-CH_3), 32.0 (C-2), 34.5 (C-6), 62.2 (C-7), 81.9 (C-3), 138.4 (C-5). The signal of C-4 was too small to be visible.

12b

TLC (light petroleum–ethyl acetate, 15:1): R_f = 0.38. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (2 s, 6 H, $SiC(CH_3)_3(CH_3)_2$), 0.11 (s, 9 H, $Si(CH_3)_3$), 0.77, 0.93 (2 d, ^3J = 6.7 Hz, 3 H each, CH_3), 0.90 (s, 9 H, $SiC(CH_3)_3(CH_3)_2$), 1.71 (dqq, ^3J = 6.9 Hz, 1 H, C_4-H), 2.35 (dt, ^2J = 13.8 Hz, ^3J = 4.6 Hz, 1 H, C_6-H), 2.44 (ddd, ^2J = 13.8 Hz, ^3J = 9.1 Hz, ^3J = 5.5 Hz, 1 H, C_6-H), 3.49 (d, ^3J = 4.8 Hz, 1 H, OH), 3.62–3.67 (m, 2 H, C_7-H), 3.78–3.83 (m, 1 H, C_3-H), 5.48 (s, 1 H, C_1-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.7, −5.8 (TBS), 0.0 (TMS), 17.9, 19.1 (CH_3), 18.0 (TBS), 25.6 (TBS-CH_3), 32.6 (C-4), 34.2 (C-6), 64.5 (C-7), 83.7 (C-3), 127.5 (C-1). 157.5 (C-2). MS (CI, NH_3, pos.): m/z (%) = 331 (26) [M^+ + H], 330 (16) [M^+], 313 (100) [M^+ + H − H_2O], 287 (6), 241 (24), 199 (20) [M^+ + H − TBSOH], 181 (20) [M^+ + H − H_2O − TBSOH], 164 (8), 132 (6) [TBSOH$^+$], 109 (24), 90 (24), 73 (4). Anal. $C_{17}H_{38}O_2Si_2$ (330.6): Calc. C 61.76, H 11.58; found C 62.06, H 12.33%.

4.8. syn-(±)-(E)-2-Phenyl-4-propyloct-4-en-3-ol (17a) and anti-(±)-(E)-2-phenyl-4-propyloct-4-en-3-ol (17b)

According to method B, oct-4-yne (**6**) (204 mg, 272 μl, 1.85 mmol), zirconocene hydrochloride (477 mg, 1.85 mmol) and 2-phenylpropanal (**13**) (273 mg, 273 μl, 2.04 mmol, 1.1 equiv.) were allowed to react. The ^{1}H NMR spectrum of the crude product contained signals of the two diasteromers **17a** and **17b** in a ratio of 80:20 (determined by integration of the C_3-H signals). Purification was performed by flash chromatography (light petroleum–diethyl ether 10:1) yielding 314 mg (69%) of the mixture of **17a** and **17b** as a colourless oil. TLC (light petroleum–diethyl ether, 10:1): R_f = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.81, 0.89 (2 t, ^3J = 7.3 Hz, 6 H, CH_3 (a)), 0.92, 0.97 (2 t, ^3J = 7.4 Hz, 6 H, CH_3 (b)), 1.14 (d, ^3J = 7.0 Hz, 3 H, C_1-H (b)), 1.28 (tq, ^3J = 7.4 Hz, 4 H, C_7-H), 1.28 (d, ^3J = 7.0 Hz, 3 H, C_1-H (a)), 1.34–1.53 (m, 4 H, $C_{2'}$-H), 1.42 (d, ^3J = 3.3 Hz, 1 H, OH (a)), 1.58 (s, br., 1 H, OH (b)), 1.76 (ddd, ^2J = 13.7 Hz, ^3J = 9.6 Hz, ^3J = 6.0 Hz, 2 H, $C_{1'}$-H), 1.94 (dt, ^3J = 7.4 Hz, 2 H, C_6-H (a)), 2.00–2.10 (m, 1 H, $C_{1'}$-H (a), 3 H, C_6-H, $C_{1'}$-H (b)), 2.87 (dq, ^3J = 9.0 Hz, ^3J = 7.0 Hz, 1 H, C_2-H (b)), 2.95 (dq,

^3J = 6.7 Hz, 1 H, C_2-H (a)), 4.02 (dd, ^3J = 9.0 Hz, J = 2.2 Hz, 1 H, C_3-H (b)), 4.14 (dd, ^3J = 5.6 Hz, J = 3.1 Hz, 1 H, C_3-H (a)), 5.37 (t, ^3J = 7.3 Hz, 1 H, C_5-H (a)), 5.40 (t, ^3J = 7.2 Hz, 1 H, C_5-H (b)), 7.15–7.35 (m, 10 H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 14.4, 15.2 (CH_3 (a)), 13.9, 14.8, 19.0 (CH_3 (b)), 22.7, 22.8 (C-7, C-10 (a)), 22.9, 23.5 (C-7, C-2″ (b)), 29.5, 30.7 (C-6, C-1′ (a)), 29.7, 29.7 (C-6, C-1′ (b)), 43.6 (C-2 (a)), 44.6 (C-2 (b)), 79.8 (C-3 (a)), 82.6 (C-3 (b)), 126.1, 127.1 (C-5, Ph-C (a)), 126.6, 129.8 (C-5, Ph-C (b)), 127.8, 128.2 (Ph-C (a)), 128.0, 128.5 (Ph-C (b)), 140.1, 144.8 (C-4, Ph-C (a)), 139.6, 143.9 (C-4, Ph-C (b)). MS (CI, isobutane, pos.): m/z (%) = 247 (1) [M^+ + H], 229 (100) [M^+ + H − H_2O], 141 (20), 105 (8). Anal. $C_{17}H_{26}O$ (246.4): Calc. C 82.88, H 10.63; found C 82.83, H 10.83%.

4.9. *syn-(2S,3R)-(E)-1-[(tert-Butyldimethylsilyl)oxy]-2-methyl-4-propyloct-4-en-3-ol (18a) and anti-(2S,3S)-(E)-1-[(tert-butyldimethylsilyl)oxy]-2-methyl-4-propyl-oct-4-en-3-ol (18b)*

According to method B, oct-4-yne (**6**) (278 mg, 371 μl, 2.53 mmol), zirconocene hydrochloride (652 mg, 2.53 mmol) and (2*S*)-3-[(tert-butyldimethylsilyl)oxy]-2-methylpropanal (**14**) (563 mg, 2.78 mmol, 1.1 equiv.) were allowed to react. The ^{1}H NMR spectrum of the crude product contained signals of the two diastereoisomers **18a** and **18b** in a ratio of 75 : 25 (determined by integration of the Si-CH_3 signals). Purification was performed by flash chromatography (light petroleum–ethyl acetate, 12 : 1), yielding 404 mg (51%) of **18a** and **18b** as a slightly yellow oil. The two isomers could not be separated by either flash chromatography or gas chromatography.

In the presence of magnesium bromide

According to method B, oct-4-yne (**6**) (98 mg, 131 μl, 0.89 mmol), zirconocene hydrochloride (230 mg, 0.89 mmol) and (2*S*)-3-[(tert-butyldimethylsilyl)oxy]-2-methylpropanal (**14**) (216 mg, 1.07 mmol, 1.2 equiv.) were allowed to react. For the chelation, the solution of the aldehyde **14** was added with ice cooling to a solution of anhydrous magnesium bromide diethyl etherate (331 mg, 1.28 mmol) in THF (6.5 ml). After 1 h, the clear, colourless solution was transferred by a cannula into the solution of the methyl vinyl zirconocene. Analysis of the crude product by gas chromatography indicated a 68 : 32 ratio of **18a** : **18b**. Purification was performed by flash chromatography, yield 103 mg (37%).

TLC (light petroleum–ethyl acetate, 12 : 1): R_f = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.07 (s, 6 H, (TBS) (a)), 0.08 (s, 6 H, (TBS) (b)), 0.79 (d, ^3J = 7.0 Hz, 3 H, C_2-CH_3 (b)), 0.85 (d, ^3J = 7.1 Hz, 3 H, C_2-CH_3 (a)), 0.90, 0.93 (2 t, ^3J = 7.4 Hz, 6 H, CH_3 (b)), 0.91, 0.92 (2 t, ^3J = 7.4 Hz, 6 H, CH_3 (a)), 0.91 (s, 9 H, (TBS) (a)), 0.91 (s, 9 H, (TBS) (b)), 1.34–1.48 (m, 8 H, C_7-H, $C_{2'}$-H), 1.75–1.82 (m, 4 H, C_2-H, $C_{1'}$-H), 2.05 (dt, ^3J = 7.5 Hz, 4 H, C_6-H), 2.04–2.11 (m, 2 H, C_9-H), 2.72 (s, br., 1 H, OH (a)), 3.58 (dd, ^2J = 10.0 Hz, ^3J = 6.9 Hz, 1 H, C_1-H (b)), 3.67 (dd, ^2J = 9.6 Hz, ^3J = 4.9 Hz, 1 H, C_1-H (a)), 3.72 (dd, ^2J = 9.7 Hz, ^3J = 4.2 Hz, 1 H, C_1-H (a)), 3.82 (dd, ^2J = 10.0 Hz, ^3J = 4.1 Hz, 1 H, C_1-H (b)), 3.83 (s, br., 1 H, OH (b)), 3.88 (d, br., ^3J = 7.4 Hz, 1 H, C_3-H (b)), 4.26 (d, br., 1 H, C_3-H (a)), 5.39 (t, ^3J = 7.4 Hz, 1 H, C_5-H (b)), 5.54 (td, ^3J = 7.3 Hz, $^4J_{allyl}$ = 0.8 Hz, 1 H, C_5-H (a)). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.7, −5.6 (2 CH_3 (TBS) (a)), −5.7 (2 CH_3 (TBS) (b)), 9.7 (C_2-CH_3 (a)), 13.9, 14.4 (2 CH_3 (a)), 14.1, 14.7 (2 CH_3 (b)), 18.1 (TBS), 22.4, 23.1 (C-7, C-2′ (a)), 22.9, 23.1 (C-7, C-2′ (b)), 25.8 (9 H, (TBS) (b)), 25.8 (9 H, (TBS) (a)), 29.6, 30.7 (C-6, C-1′ (a)), 29.7, 29.9 (C-6, C-1′ (b)), 37.5 (C-2 (a)), 37.7 (C-2 (b)), 67.8 (C-1 (a)), 68.2 (C-1 (b)), 76.03 (C-3 (a)), 82.8 (C-3 (b)), 125.2 (C-5 (a)), 128.1 (C-5 (b)), 139.5 (C-4 (a)), 140.4 (C-4 (b)). The signal of C_2-CH_3 of the minor isomer **18b** was not visible. MS (CI, isobutane, pos.): m/z (%) = 315 (4) [M^+ + H], 297 (45) [M^+ + H − H_2O], 257 (6) [M^+ + H − C_4H_{10}], 215 (8), 165 (100) [M^+ + H − H_2O − TBSOH]. Anal. $C_{18}H_{38}O_2Si$ (314.6): Calc. C 68.73, H 12.17, found C 68.89, H 12.25%.

4.10. *anti-(2S,3R)-(E)-2-[(tert-Butyldimethylsilyl)oxy]-4-propyloct-4-en-3-ol (19a) and syn-(2S,3S)-(E)-2-[(tert-butyldimethylsilyl)oxy]-4-propyloct-4-en-3-ol (19b)*

According to method B, oct-4-yne (**6**) (176 mg, 235 μl, 1.60 mmol), zirconocene hydrochloride (413 mg, 1.60 mmol) and (2*S*)-2-[(tert-butyldimethylsilyl)oxy]-propanal (**15**) (361 mg, 1.92 mmol, 1.2 equiv.) were allowed to react. The ^{1}H NMR spectrum of the crude product contained signals of the two diastereomers **19a** and **19b** in a ratio of 62 : 38 (determined by integration of the C_1-H signals). Purification was performed by flash chromatography (light petroleum–ethyl acetate, 33 : 1) yielding 235 mg (49%) of **19a** and **19b** as a slightly yellow oil. Besides mixed fractions pure diastereomers were obtained.

In the presence of Lewis acids

(a) Zinc bromide. According to method B, oct-4-yne (**6**) (86 mg, 114 μl, 0.78 mmol), zirconocene hydrochloride (201 mg, 0.78 mmol) and (2*S*)-2-[(tert-butyldimethylsilyl)oxy]propanal (**15**) (176 mg, 0.93 mmol, 1.2 equiv.) were allowed to react. For the chelation, the solution of the aldehyde **15** was added with ice cooling to a solution of anhydrous zinc bromide (230 mg, 1.02 mmol) in THF (5.0 ml). After being stirred for 1 h at room temperature, the clear, colourless solution was transferred by a cannula into the solution of the methyl vinyl zirconocene. Analysis of the crude product

by gas chromatography indicated a 64:36 ratio of **19a**:**19b**.

(b) Magnesium bromide. According to method B, oct-4-yne (**6**) (162 mg, 216 μl, 1.47 mmol), zirconocene hydrochloride (379 mg, 1.47 mmol) and (2*S*)-2-[(tert-butyldimethylsilyl)oxy]propanal (**15**) (332 mg, 1.76 mmol, 1.2 equiv.) were allowed to react. For the chelation, the solution of the aldehyde **15** was added with ice cooling to a solution of anhydrous magnesium bromide diethyl etherate (547 mg, 2.12 mmol) in THF (11.0 ml). After 1 h, the clear, colourless solution was transferred by a cannula into the solution of the methyl vinyl zirconocene. Analysis of the crude product by gas chromatography indicated a 50:50 ratio of **19a**:**19b**.

19a

TLC (light petroleum–ethyl acetate, 33:1): R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08 (s, 6 H, $SiC(CH_3)_3(CH_3)_2$) 0.90 (s, 9 H, $SiC(CH_3)_3(CH_3)_2$), 0.91, 0.92 (2 t, ^3J = 7.3 Hz, 6 H, CH_3), 1.01 (d, ^3J = 6.3 Hz, 3 H, C_1-H), 1.35–1.49 (m, 4 H, C_7-H, $C_{2'}$-H), 1.78 (ddd, ^2J = 13.5 Hz, ^3J = 10.0 Hz, ^3J = 5.6 Hz, 1 H, $C_{1'}$-H), 2.03 (dt, ^3J = 7.3 Hz, 2 H, C_6-H), 2.12 (ddd, ^2J = 13.6 Hz, ^3J = 10.1 Hz, ^3J = 6.3 Hz, 1 H, $C_{1'}$-H), 2.40 (s, br., 1 H, OH), 3.93 (qd, ^3J = 6.2 Hz, ^3J = 3.7 Hz, 1 H, C_2-H), 4.03 (s, br., 1 H, C_3-H), 5.53 (t, ^3J = 7.3 Hz, 1 H, C_5-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.6, −5.0 (2 CH_3 (TBS)), 13.9, 14.4 (CH_3), 16.7 (C-1), 18.0 (TBS), 22.5, 22.9 (C-7, C-2′), 25.7 (TBS), 29.5, 30.9 (C-6, C-1′), 70.4, 77.5 (C-2, C-3), 126.5 (C-5), 137.2 (C-4).

19b

TLC (light petroleum–ethyl acetate, 33:1): R_f = 0.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.08, 0.09 (2 s, 6 H, $SiC(CH_3)_3(CH_3)_2$), 0.90 (s, 9 H, $SiC(CH_3)_3(CH_3)_2$), 0.91, 0.93 (2 t, ^3J = 7.4 Hz, 6 H, CH_3), 1.11 (d, ^3J = 6.0 Hz, 3 H, C_1-H), 1.33–1.48 (m, 4 H, C_7-H, $C_{2'}$-H), 1.92 (ddd, ^2J = 13.5 Hz, ^3J = 9.9 Hz, ^3J = 6.0 Hz, 1 H, $C_{1'}$-H), 2.03 (dt, ^3J = 7.4 Hz, 2 H, C_6-H), 1.99–2.09 (m, 1 H, $C_{1'}$-H), 2.70 (d, ^3J = 3.5 Hz, 1 H, OH), 3.69 (dd, ^3J = 6.4 Hz, ^3J = 3.1 Hz, 1 H, C_3-H), 3.76 (dq, ^3J = 6.2 Hz, 1 H, C_2-H), 5.42 (t, ^3J = 7.2 Hz, 1 H, C_5-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −4.9, −4.2 (TBS), 13.9, 14.5 (CH_3), 18.5 (TBS), 20.5 (C-1), 22.9 (C-7, C-2′), 25.8 (TBS), 29.7, 30.4 (C-6, C-1′), 70.8, 80.7 (C-2, C-3), 129.0 (C-5), 138.1 (C-4). Anal. $C_{17}H_{36}O_2Si$ (300.5): Calc. C 67.94, H 12.07; found C 68.15, H 12.65%.

4.11. anti-(2R,3S)-(E)-1,2-O-Isopropyliden-4-propyloct-4-en-1,2,3-triol (20a) and syn-(2R,3R)-(E)-1,2-O-isopropyliden-4-propyloct-4-en-1,2,3-triol (20b)

According to method B, oct-4-yne (**6**) (304 mg, 405 μl, 2.76 mmol), zirconocene hydrochloride (712 mg, 2.76 mmol), and 2,3-*O*-isopropylidene-D-glyceraldehyde (**16**) (431 mg, 3.31 mmol, 1.2 equiv.) were allowed to react. The aldehyde was added at −20°C. Subsequently, the reaction mixture was stirred for 20 h, during which time the reaction vessel reached room temperature. The ^{1}H NMR spectrum of the crude product contained signals of the two diasteromers **20a** and **20b** in a ratio of 50:50 (determined by integration of the C_5-H signals). Purification was performed by flash chromatography (light petroleum–ethyl acetate, 16:1) yielding 303 mg (46%) of a mixture of **20a** and **20b** as a slightly yellow oil. TLC (light petroleum–ethyl acetate, 26:1): R_f = 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90, 0.91, 0.92, 0.93 (4 t, ^3J = 7.3 Hz, 3 H each, C_8-H, $C_{3'}$-H), 1.29–1.50 (m, 20 H, C_7-H, $C_{2'}$-H, isopropylidene-CH_3), 1.82–2.18 (m, 8 H, C_6-H, $C_{1'}$-H), 2.14, 2.41 (2 s, br., 1 H each, OH), 3.66, 3.86, 3.93 (3 dd, ^2J = 8.5 Hz, ^3J = 6.5 Hz, 4 H, C_1-H), 3.90, 4.26 (2 s, br., 2 H, C_3-H), 4.13–4.24 (m, 2 H, C_2-H), 5.46, 5.58 (2 t, ^3J = 7.2 Hz, 2 H, C_5-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 14.3, 14.5 (C-8, C-3′), 22.5, 22.7, 22.8, 23.1 (C-7, C-2′), 25.1, 25.4, 26.5, 26.9 (isopropylidene CH_3), 29.4, 29.6, 29.7, 30.7 (C-6, C-1′), 64.3, 66.1 (C-1), 72.9, 77.2, 78.1, 78.3 (C-2, C-3), 109.2, 109.7 (isopropylidene C), 127.1, 130.5 (C-5), 137.0, 138.0 (C-4). MS (CI, isobutane, pos.): *m/z* (%) = 242 (3) [M^+], 241 (8), 225 (90) [$M^+ + H - H_2O$], 185 (26) [$M^+ + H - C_3H_6O$], 167 (100) [$M^+ + H - H_2O - C_3H_6O$], 141 (44), 101 (98). Anal. $C_{14}H_{26}O_3$ (242.4): Calc. C 69.39, H 10.81; found C 69.14, H 10.85%.

4.12. syn-(±)-(E)-7-[(tert-Butyldimethylsilyl)oxy]-2-phenylhept-4-en-3-ol (21a) and anti-(±)-(E)-7-[(tert-butyldimethylsilyl)oxy]-2-phenylhept-4-en-3-ol (21a)

According to method A, 4-[(tert-butyldimethylsilyl)-oxy]but-1-yne (**1**) (271 mg, 1.47 mmol), zirconocene hydrochloride (1.47 mmol) and 2-phenylpropanal (**13**) (236 μl, 1.76 mmol, 1.2 equiv.) were allowed to react. The ^{1}H NMR spectrum of the crude product contained signals of the two diastereoisomers **21a** and **21b** in a ratio of 40:60 (determined by integration of the C_7-H signals). Purification was performed by flash chromatography (light petroleum–ethyl acetate, 15:1) yielding 193 mg (41%) of **21a** and **21b** as a slightly yellow oil. The two isomers could not be separated by either flash chromatography or gas chromatography. The major isomer **21b** seemed to decompose on chromatography TLC (light petroleum–ethyl acetate, 15:1): R_f = 0.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.03 (s, 6 H, $SiC(CH_3)_3(CH_3)_2$ (a)), 0.06 (s, 6 H, 2 CH_3-$SiC(CH_3)_3(CH_3)_2$ (b)), 0.88 (s, 9 H, $SiC(CH_3)_3$-$(CH_3)_2$ (a)), 0.90 (s, 9 H, $SiC(CH_3)_3(CH_3)_2$ (b)), 1.22 (d, ^3J = 7.2 Hz, 3 H, CH_3 (b)), 1.31 (d, ^3J = 7.2 Hz, 3 H, CH_3 (a)), 1.46 (s, br., 1 H each, OH), 2.20 (dt, ^3J = 6.9 Hz, 2 H, C_6-H (a)), 2.29 (ddt, ^3J = 6.8 Hz,

$^4J_{allyl}$ = 1.2 Hz, 2 H, C_6-H (b)), 2.76 (dq, ^3J = 7.5 Hz, 1 H, C_2-H (b)), 2.88 (dq, ^3J = 7.0 Hz, 1 H, C_2-H (a)), 3.55 (t, ^3J = 6.9 Hz, 2 H, C_7-H (a)), 3.65 (t, ^3J = 6.8 Hz, 2 H, C_7-H (b)), 4.09 (ddd, br., J = 8.0 Hz, 1 H, C_3-H (b)), 4.13 (ddd, J = 4.5 Hz, 1 H, C_3-H (a)), 5.44 (ddt, $^3J_{trans}$ = 15.5 Hz, ^3J = 6.6 Hz, $^4J_{allyl}$ = 1.1 Hz, 1 H, C_4-H (a)), 5.54 (ddt, $^3J_{trans}$ = 15.3 Hz, ^3J = 7.6 Hz, $^4J_{allyl}$ = 1.0 Hz, 1 H, CH-4 (b)), 5.58 (dtd, $^3J_{trans}$ = 15.7 Hz, ^3J = 7.3 Hz, $^4J_{allyl}$ = 0.9 Hz, 1 H, C_5-H (a)), 5.71 (dtd, $^3J_{trans}$ = 15.9 Hz, ^3J = 7.2 Hz, $^4J_{allyl}$ = 0.8 Hz, 1 H, C_5-H (b)), 7.19–7.35 (m, 10 H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −5.3 (TBS), 15.7, 18.3 (C-1), 18.3 (TBS), 25.9 (TBS), 35.8, 35.9 (C-6), 45.7, 46.3 (C-2), 62.8, 62.8 (C-7), 76.9, 77.7 (C-3), 126.4, 126.5, 128.0, 128.1, 128.2, 128.5, 128.9, 130.2, 132.6 (C-4, C-5, Ph-C), 143.4 (Ph-C). MS (CI, NH_3, pos.): m/z (%) = 320 (7) [M^+], 319 (8), 303 (10) [$M^+ + H - H_2O$], 183 (42), 171 (100) [$M^+ + H - H_2O$ − TBSOH]. Anal. $C_{19}H_{32}O_2Si$ (320.5): Calc. C 71.20, H 10.06; found C 71.13, H 10.06%.

4.13. *syn-(2S,3R)-(E)-2-Methyl-4-propyloct-4-ene-1,3-diol (22a) and anti-(2S,3S)-(E)-2-methyl-4-propyloct-4-ene-1,3-diol (22b)*

A solution of **18a** and **18b** (168 mg, 0.53 mmol; mixture of isomers; 75:25 ratio) in THF (4.0 ml) was treated at 0°C with tetrabutylammonium fluoride trihydrate (507 mg, 1.61 mmol). The resulting brown solution was stirred for 3 h at room temperature. The mixture was diluted with pH 7 buffer (20 ml) and extracted with diethyl ether (4 × 20 ml). The combined organic extracts were dried ($NaSO_4$), filtered and concentrated in vacuo. The residue (106 mg) containing the diols **22a** and **22b** was used without further purification in the next reaction. TLC (light petroleum–ethyl acetate, 1:2): R_f = 0.53. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.76 (d, ^3J = 7.0 Hz, 3 H, C_2-CH_3 (b)), 0.89 (d, ^3J = 7.3 Hz, 3 H, C_2-CH_3 (a)), 0.92 (t, br., ^3J = 7.4 Hz, 12 H, CH_3), 1.21–1.48 (m, 8 H, C_7-H, $C_{2'}$-H), 1.75–2.17 (m, 14 H, C_6-H, $C_{1'}$-H, C_2-H, 2 OH), 3.59–8.78 (m, 4 H, C_1-H), 3.90 (d, ^3J = 8.4 Hz, 1 H, C_3-H (b)), 4.24 (d, br., 1 H, C_3-H (a)), 5.41 (t, ^3J = 7.1 Hz, 1 H, C_5-H (b)), 5.44 (t, ^3J = 7.2 Hz, 1 H, C_5-H (a)). Anal. $C_{12}H_{24}O_2$ (200.3).

4.14. *(2S,3R)-(E)-1,3-O-Isopropylidene-2-methyl-4-propyloct-4-ene-1,3-diol (23a) and (2S,3S)-(E)-1,3-O-isopropylidene-2-methyl-4-propyloct-4-ene-1,3-diol (23b)*

To a solution of crude **22a** and **22b** (106 mg, 0.53 mmol) in 2,2-dimethoxypropane (6.5 ml) was added camphor-10-sulphonic acid (5 mg, 20 μmol). The reaction mixture was stirred for 1.5 h at room temperature, treated with triethylamine (10 μl) and concentrated under reduced pressure. The residue was purified by flash chromatography using light petroleum–ethyl acetate (30:1) for elution to provide 115 mg (90%) of an unseparable mixture of **23a** and **23b** in a ratio of 75:25. TLC (light petroleum–ethyl acetate, 30:1): R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.65 (d, ^3J = 6.7 Hz, 3 H, C_2-CH_3 (b)) 0.88–0.96 (m, 9 H, CH_3 (a); 6 H, CH_3 (b)), 1.40, 1.44, 1.46 (2 s, 12 H, isopropylidene-CH_3), 1.31–1.53 (m, 8 H, C_7-H, $C_{2'}$-H), 1.60–2.15 (m, 10 H, C_6-H, $C_{1'}$-H, C_2-H), 3.54 (dd, ^3J = 11.4 Hz, 1 H, C_1-H (b)), 3.64 (dd, ^2J = 11.4 Hz, ^3J = 1.8 Hz, 1 H, C_1-H (a)), 3.75 (dd, ^2J = 11.6 Hz, ^3J = 5.1 Hz, 1 H, C_1-H (b)), 3.81 (d, $^3J_{axial-axial}$ = 10.4 Hz, 1 H, C_3-H (b)), 4.15 (dd, ^2J = 11.4 Hz, ^3J = 2.8 Hz, 1 H, C_1-H (a)), 4.38 (s, br., 1 H, C_3-H (a)), 5.40 (t, ^3J = 7.1 Hz, 1 H, C_5-H (b)), 5.44 (t, ^3J = 8.1 Hz, 1 H, C_5-H (a)). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.0, 14.0, 14.4, 18.9, 29.7, 30.8 (C-2, C-8, C-3′, C_2-CH_3, isopropylidene-CH_3 (a)), 12.8, 13.9, 14.7, 19.0, 29.9, 31.7 (C-2, C-8, C-3′, C_2-CH_3, isopropylidene-CH_3 (b)), 22.2, 23.0 (C-7, C-2′ (a)), 22.8, 23.1 (C-7, C-2′ (b)), 29.5, 30.1 (C-6, C-1′ (a)), 29.6, 29.7 (C-6, C-1′ (b)), 66.2 (C-1 (b)), 66.6 (C-1 (a)), 72.3 (C-3 (a)), 82.2 (C-3 (b)), 98.1 ($C(OR)_2$ (b)), 98.6 ($C(OR)_2$ (a)), 124.8 (C-5 (a)), 130.8 (C-5 (b)), 136.7 (C-4 (a)), 137.5 (C-4 (b)). MS (CI, NH_3, pos.): m/z (%) = 241 (32) [$M^+ + H$], 200 (20), 183 (90) [$M^+ + H - C_3H_6O$], 165 (100) [$M^+ + H - C_3H_6O - H_2O$], 153 (28). Anal. $C_{15}H_{28}O_2$ (240.4): Calc. C 74.95, H 11.73; found C 74.47, H 11.83%.

4.15. *anti-(2S,3R)-(E)-4-Propyloct-4-ene-2,3-diol (24a) and syn-(2S,3S)-(E)-4-propyloct-4-ene-2,3-diol (24b)*

To a solution of **19a** and **19b** (120 mg, 0.40 mmol) in THF (3.0 ml) were added tetrabutylammonium fluoride trihydrate (379 mg, 1.20 mmol, 3.0 equiv.). After being stirred for 2 h at room temperature, the mixture was diluted with pH 7 buffer (20 ml) and extracted with diethyl ether (4 × 20 ml). The combined organic extracts were dried ($NaSO_4$), filtered and concentrated in vacuo. The residue (74 mg) containing the diols **24a** and **24b** in a ratio of 60:40 was used without further purification in the next reaction. TLC (light petroleum–ethyl acetate, 1:2): R_f = 0.25, 0.32. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.96, 0.93 (2 t, ^3J = 7.3 Hz, 12 H, C_7-CH_3, $C_{2'}$-CH_3), 1.14, 1.16 (2 d, ^3J = 6.1 Hz, 6 H, C_1-H), 1.35–1.48 (m, 8 H, C_7-H, $C_{2'}$-H), 1.60, 1.78, 2.18, 2.27 (4 s, br., 4 H, OH), 1.90–2.11 (m, 8 H, C_6-H, $C_{1'}$-H), 3.75–4.02 (m, 4 H, C_2-H, C_3-H), 5.47, 5.53 (2 t, ^3J = 7.2 Hz, 2 H, C_5-H). Anal. $C_{11}H_{22}O_2$ (186.3).

4.16. (2S,3R)-(E)-4-Propyloct-4-ene-2,3-carbonate (25a) and (2S,3S)-(E)-4-propyloct-4-ene-2,3-carbonate (25b)

A solution of **24a** and **24b** (74 mg, ca. 0.40 mmol) and pyridine (1.27 ml, 15.8 mmol) in dichloromethane (10 ml) was treated at −78°C with a 20% solution of phosgene in toluene (1.93 M, 2.0 ml, 3.86 mmol). The cooling bath was removed and the resulting white slurry was stirred for 2 h at room temperature. To the brownish reaction mixture at −40°C was added pH 7 buffer (20 ml) and the mixture was then extracted with diethyl ether (2 × 25 ml). The combined organic layers were washed with saturated $NaHCO_3$ solution and brine and dried with Na_2SO_4. The solution was filtered and the solvent evaporated from the filtrate. To remove traces of pyridine, the residue was co-evaporated twice with toluene. The crude material was purified by flash chromatography (light petroleum–ethyl acetate, 7 : 1) to yield 84 mg (99%) of **25a** (50 mg) and **25b** (34 mg) as colourless oils.

25a

TLC (light petroleum–ethyl acetate, 4 : 1): $R_f = 0.27$. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.92$, 0.94 (2 t, $^3J = 7.4$ Hz, 6 H, CH_3), 1.23 (d, $^3J = 6.6$ Hz, 3 H, C_1-H), 1.37–1.48 (m, 4 H, C_7-H, $C_{2'}$-H), 1.77–1.84 (m, 1 H, $C_{1'}$-H), 2.01–2.13 (m, 1 H, $C_{1'}$-H), 2.09 (dt, $^3J = 7.3$ Hz, 2 H, C_6-H), 4.49 (dq, $^3J = 6.5$ Hz, 1 H, C_2-H), 5.07 (dd, $^3J = 7.6$ Hz, $^4J_{allyl} = 0.7$ Hz, 1 H, C_3-H), 5.57 (t, $^3J = 7.4$ Hz, 1 H, C_5-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.8$, 14.2 (CH_3), 15.4 (C-1), 22.5, 22.6 (C-7, C-2′), 29.4, 30.6 (C-6, C-1′), 76.5 (C-2), 82.0 (C-3), 130.3 (C-5), 131.3 (C-4), 154.7 (C = O).

25b

TLC (light petroleum–ethyl acetate, 4 : 1): $R_f = 0.33$. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.92$, 0.94 (2 t, $^3J = 7.4$ Hz, 6 H, CH_3), 1.35–1.56 (m, 4 H, C_7-H, $C_{2'}$-H), 1.46 (d, $^3J = 6.0$ Hz, 3 H, C_1-H), 1.97–2.14 (m, 4 H, C_6-H, $C_{1'}$-H), 4.47 (dq, $^3J = 7.6$ Hz, $^3J = 6.0$ Hz, 1 H, C_2-H), 4.54 (d, $^3J = 7.5$ Hz, 1 H, C_3-H), 5.55 (t, $^3J = 7.2$ Hz, 1 H, C_5-H). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.7$, 14.3 (CH_3), 18.8 (C-1), 22.4, 22.7 (C-7, C-2′), 28.8, 29.7 (C-6, C-1′), 77.5 (C-2), 88.1 (C-3), 133.0 (C-5), 133.2 (C-4), 154.6 (C-12). MS (EI): m/z (%) = 212 (8) [M^+], 169 (5) [$M^+ - C_3H_7$], 69 (100), 55 (56). IR (film): $\nu = 2962$, 2934, 2874, 1807 cm^{-1} (C = O). Anal. $C_{12}H_{20}O_3$ (212.3): Calc. C 67.90, H 9.49; found C 67.81, H 9.41%.

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