Study of a tandem aldol–Tischtschenko reaction between chiral enolsilanes and aldehydes catalyzed by titanium(IV) isopropoxide

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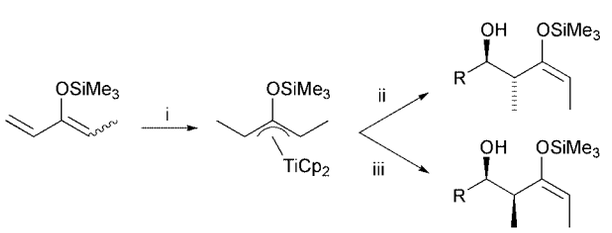
The synthesis and structure determination of polypropionate is presented. An allyltitanium complex is first used in an allyltitanation reaction; titanium(IV) isopropoxide is next utilized as catalyst in an aldol–Tischtschenko reaction. This method promotes the formation of esters bearing five or six stereocenters in two steps with a very high level of diastereoselectivity and very high yield.

Introduction

For many years, chemists have focused their interest towards the synthesis of biologically significant polypropionate-derived compounds.[1] Among the several reactions used for this objective, the aldol reaction has proven to be a very powerful method for the stereocontrolled synthesis of acyclic molecules. To improve the stereoselectivity and the yield, the aldol reaction involving many metal enolates[2] or various Lewis acids[3] has been studied. We have recently shown the power of titanium(IV) isopropoxide as a catalyst of a tandem aldol–Tischtschenko reaction using an aldehyde and an enolsilane bearing two stereocenters.[4] We present here a general study involving aldehydes and a series of chiral enolsilanes which present different steric hindrances.

Results and discussion

The aldol reactions were performed starting from racemic enolsilanes bearing two or three stereocenters. These enolsilanes were prepared as previously described by an allyltitanation reaction[5] (Scheme 1). The allyltitanium complex was formed in



Scheme 1 *Reagents and conditions*: i, Cp_2TiH, THF, −20 °C; ii, RCHO, THF, −20 °C; iii, RCHO, HMPA–THF (3:1), −20 °C.

a one-pot reaction including two successive steps: Cp_2TiCl was formed first, at room temperature, and was allowed to react with a second equivalent of isopropylmagnesium chloride in the presence of the silyloxy diene at −20 °C. The titanium complex thus formed *in situ* was condensed directly on an aldehyde (RCHO). When the reaction was performed in THF, *anti-E* enolsilane was provided in a high level of diastereoselectivity (*anti-E*: other isomers, 90:10). On the other hand, in HMPA as co-solvent[6] (HMPA–THF, 3:1), a reversal of diastereoselectivity was observed, affording *syn* enolsilane as the major product (*anti*:*syn*, 35:65). This trend has been rationalized on the basis of a cyclic and an open transition state.[7]

The method outlined above allowed us to prepare enolsilanes shown in Chart 1. Titanium-mediated allylation of racemic 2-methylbutanal provided a mixture of **5** and **6** (**5**:**6**, 55:45).

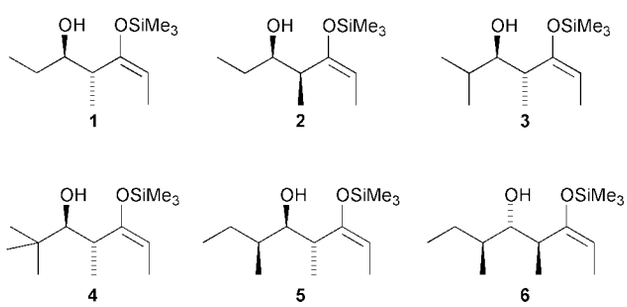
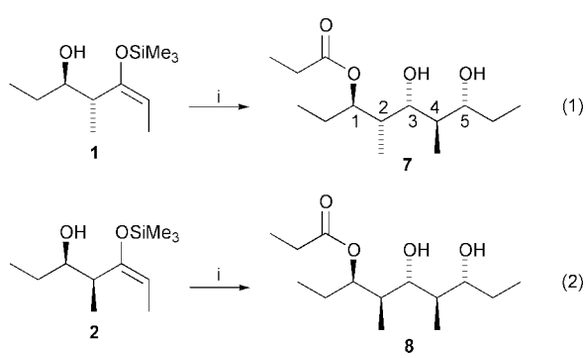


Chart 1

First, enolsilanes **1** and **2** were involved in the aldol reaction, affording esters **7** and **8**, respectively (Scheme 2). The relative



Scheme 2 *Reagents and conditions*: i, 10 mol% $Ti(O^iPr)_4$, EtCHO, CH_2Cl_2, room temp. (95%).

stereochemistry **7** was ascertained by NMR studies. Indeed, proton NMR studies showed the coupling constants between the protons of carbons 1 and 2 and between the protons of carbons 4 and 5 to be 8.5 and 7.6 Hz, respectively. On the basis of such values,[8] a 1,2-*anti* and a 4,5-*anti* stereochemistry was assigned to ester **7**. The resonance of the C-3 methanol proton appears as both double doublet with both *syn* and *anti* coupling (*J* 1.3 and 9.4 Hz, respectively), and reveals that the relationship between C-2 and C-4 is *anti*. Furthermore the ^{13}C methyl carbon resonances of the acetonide of **7**, found at δ_C 19.2 and

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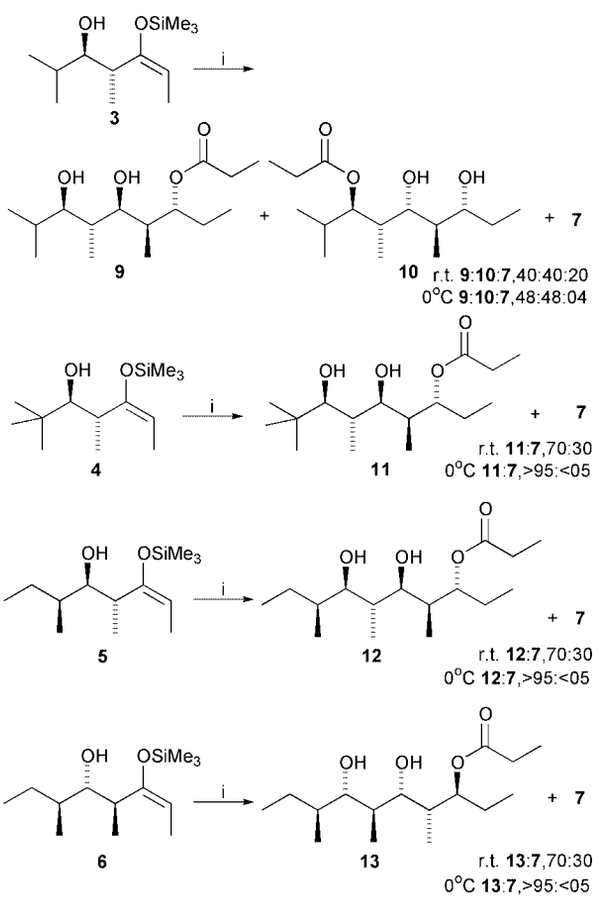
29.9, are indicative of a *syn* diol-derived acetonide.[9] The stereochemistry of **8** was demonstrated in a similar way.

The two reactions described above showed that titanium(IV) isopropoxide could catalyze the aldol reaction with a very high level of diastereoselectivity. Indeed, each enolsilane provided a unique dihydro ketone, which in turn was esterified by a Tischtschenko[10] reaction catalyzed by the same titanium complex. The use of enolsilane **2**, which presents a similar steric hindrance to **1**, shows clearly that the esterified hydroxy group is the one included in the starting enolsilane.

We next used enolsilanes **3**–**6** in the tandem aldol–Tischtschenko reaction (Scheme 3). The relative stereochemistry of



Scheme 3 *Reagents and conditions*: i, 10 mol% $Ti(O^iPr)_4$, EtCHO, CH_2Cl_2, room temp.: 95% overall yield; 0 °C: 95% overall yield.

isolated esters was established as previously by NMR studies. Enolsilane **3** led to a mixture of two esters (**9** and **10**). Except for ester **10**, the hydroxy group esterified in the Tischtschenko reaction was the one created during the aldol step. When performed at room temperature, all these reactions gave rise to a small amount of ester **7**, due to a retroaldol–aldol reaction.[11] However, when the reactions were carried out at 0 °C, only traces of **7** were detected; overall yields were unaffected.

Starting from the enolsilane **1** and isobutyraldehyde instead of propionaldehyde, the expected ester **14** was formed accompanied by the esterified retroaldol–aldol compound **15** (Scheme 4).

Saponification of the esters gave rise to free hydroxy polypropionate derivatives bearing five or six stereocenters (Chart 2) as follows: **7** ⟶ **16**, **8** ⟶ **17**, **9** and **14** ⟶ **22**, **10** ⟶ **23**, **11** ⟶ **18**, **12** ⟶ **20**, **13** ⟶ **21**, **15** ⟶ **19**.

Compounds **22** and **23** were crystalline, and X-ray structures (Figs. 1 and 2) have confirmed the relative configurations of the five stereocenters previously ascertained by NMR studies.

Thus, formation of esters **7**–**15** proceeded in two consecutive steps: a classic Mukaiyama-type aldol reaction followed by a Tischtschenko reaction. Both steps were catalyzed by

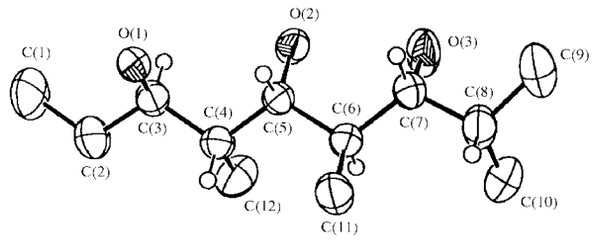


Fig. 1 Molecular structure of **22**.

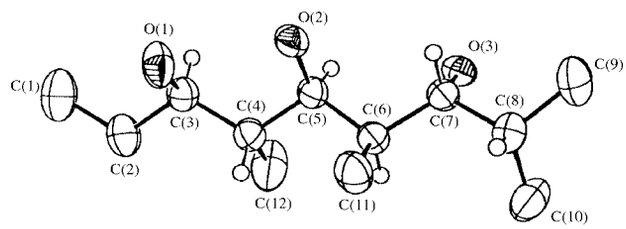
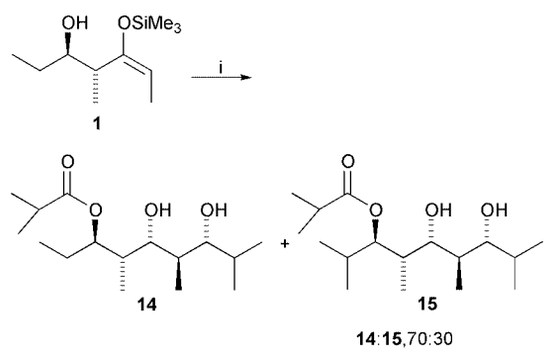


Fig. 2 Molecular structure of **23**.



Scheme 4 *Reagents and conditions:* i, 10 mol% $Ti(O^iPr)_4$, ^iPrCHO, CH_2Cl_2, room temp. (95%).

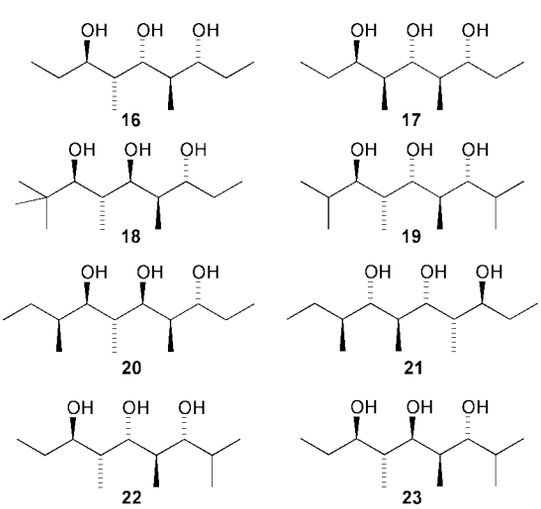


Chart 2

titanium(IV) isopropoxide. The diastereoselectivity of the first step is of major importance. Indeed, the aldol step can give rise four diastereomeric ketones (Chart 3). The relative stereochemistry of the carbon framework in esters **7**–**15** shows that the intermediate ketones exhibit the stereochemistry *anti-anti-anti* **A1**. No traces of the esters arising from ketones **A2**, **S1** or **S2** were detected by GLC-MS analyses and ^1H NMR spectroscopy of the crude mixture. Consequently the Mukaiyama-type aldol reaction proceeded with a very high *anti* stereoselectivity together with a diastereofacial selectivity towards the racemic enolsilane whatever the steric hindrance of the starting enolsilane and the nature of the aldehyde. The chelated transition

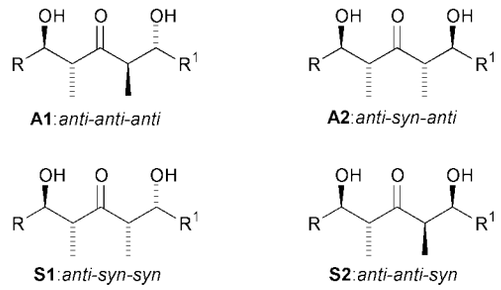
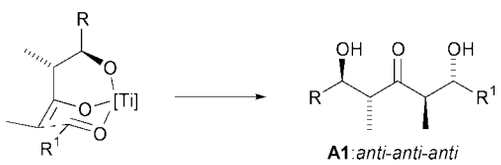


Chart 3

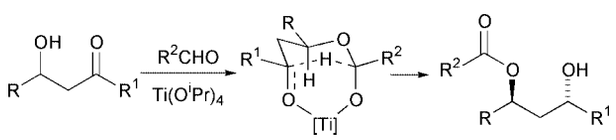


Scheme 5

structure shown in Scheme 5 might account for this double diastereoselectivity.

The hydroxy group of the starting enolsilane seems to play an important role in this tandem aldol–Tischtschenko reaction catalyzed by titanium(IV) isopropoxide. No reaction occurred when starting from a carbamate-protected enolsilane or from an acetophenone-derived enolsilane.

The Tischtschenko reaction occurs also with a very high level of diastereoselectivity since the stereochemistry of the methanol carbon relative to the esterified hydroxy group is always *anti*. This stereochemical feature may be related to a eight-membered chelation state (Scheme 6) similar to those previously suggested with other catalysts.[10]



Scheme 6

It appears from Scheme 3 and 4, that the location of the esterification site and consequently the stereochemistry of the chiral center formed in the concomitant reduction are clearly dependent on steric factors. The esterified hydroxy group is always the less hindered in the intermediate ketone and, starting from the bulky enolsilanes **4**–**6**, corresponds to the one created by the aldol reaction. Formation of the two esters **9** and **10** is due to the poor steric discrimination between the isopropyl group and the ethyl group. This discrimination is strongly enhanced by using the more sterically demanding isobutyraldehyde (Scheme 4).

So, the titanium-mediated aldol–Tischtschenko reaction proceeds *via* three consecutive high levels of diastereoselectivity. The first is related to the simple *anti* diastereoselectivity observed in the aldol step. The second one concerns the diastereofacial selectivity of the aldol reaction towards the enolsilane, and finally, the Tischtschenko reaction exhibits also a high level of diastereoselectivity. It is noteworthy that the aldol–Tischtschenko reaction proceeds in very high yields (95%). To these observations must be added the excellent diastereoselectivity which takes place in the allyltitanation reaction, providing of *anti* or *syn* enolsilanes in a good yield. The method described here to obtain polypropionate derivatives is efficient and highly stereocontrolled and will be extended to chiral and functionalized aldehydes.

Experimental

All manipulations were carried out under argon using vacuum-line techniques. The solvents used were distilled under an Ar atmosphere from sodium–benzophenone ketyl. Titanocene dichloride[12] and 3-(trimethylsilyloxy)penta-1,3-diene[13] were prepared according to published procedures. Other reagents were purchased from Aldrich Chemical Co. Aldehydes and $Ti(O^iPr)_4$ were distilled under Ar prior to use. ^1H and ^{13}C NMR spectra were recorded at 200 and 50 MHz, respectively. Multiplet h refers to septet; *J*-values are given in Hz. Mass spectra were obtained by EI (70 eV) technique. Column flash chromatography was performed on silica gel 60 (Merck).

General procedure for preparation of enolsilanes 1, 3, 4, 5 and 6

^{i}PrMgCl (2.00 mL; 2 M in THF) was added dropwise by syringe at room temp. to a stirred suspension of Cp_2TiCl_2 (1.00 g, 4.03 mmol) in THF (25 mL). After stirring for 1 min, the resulting green solution of Cp_2TiCl was cooled to −25 °C. A solution of ^{i}PrMgCl in THF (2.00 mL; 2 M in THF) and silyloxydiene[13] (630 mg, 4 mmol) were added slowly and simultaneously by syringe to give a violet reaction mixture. After stirring for 30 min, the aldehyde (4.5 mmol) was added neat by syringe at −25 °C. After an additional hour the reaction mixture was poured into a separating funnel containing Et_2O (120 mL), and treated with saturated aq. $NaHCO_3$ (30 mL). The Et_2O layer was separated and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic solutions were washed with water (2 × 30 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude β-hydroxy enol silyl ether **1** was purified by flash chromatography on a short silica gel column.

(3*RS*,4*RS*,5*E*)-4-Methyl-5-(trimethylsilyloxy)hept-5-en-3-ol 1. Produced (613 mg, 71%) as a *colorless oil* (Found: C, 60.8; H, 10.9. $C_{11}H_{24}O_2Si$ requires C, 61.1; H, 11.2%); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.17 [9H, s, $SiC(CH_3)_3$], 0.93 (3H, t, *J* 7.3, CH_3CH_2), 1.02 [3H, d, *J* 6.9, $CH(CH_3)$], 1.40–1.50 (2H, m, CH_3CH_2), 1.52 [3H, d, *J* 6.8, $C{=}CH(CH_3)$], 2.47 (1H, d, *J* 6.3, D_2O exchangeable), 2.56 [1H, pseudoquintet, *J* 7.1, $CH(CH_3)$], 3.58 (1H, pseudoquintet, *J* 6.0, CHOH), 4.65 [1H, q, *J* 6.8, $C{=}CH(CH_3)$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 0.4 [$Si(CH_3)_3$], 10.3 (CH_3), 11.7 (CH_3), 15.2 (CH_3), 28.1 (CH_2), 38.0 [$CH(CH_3)$], 75.82 (CHOH), 101.6 [$C{=}CH(CH_3)$], 153.2 [$C{=}CH(CH_3)$].

(3*RS*,4*RS*,5*E*)-2,4-Dimethyl-5-(trimethylsilyloxy)hept-5-en-3-ol 3. Produced (600 mg, 65%) as a *colorless oil* (Found: C, 62.1; H, 11.1. $C_{12}H_{26}O_2Si$ requires C, 62.5; H, 11.4%); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.12 [9H, s, $SiC(CH_3)_3$], 0.84 [3H, d, *J* 6.8, $CH(CH_3)$], 0.89 [3H, d, *J* 6.7, $CH(CH_3)$], 0.98 [3H, d, *J* 7.0, $CH(CH_3)$], 1.48 [3H, d, *J* 6.7, $C{=}CH(CH_3)$], 1.59 [1H, dh, *J* 6.7 and 7.0, $CH(CH_3)_2$], 2.41 (1H, d, *J* 7.0, D_2O exchangeable), 2.65 [1H, pseudoquintet, *J* 7.0, $CH(CH_3)$], 3.05 (1H, ddd, *J* 7.0 and 7.0 and 7.0, CHOH), 6.8 [1H, q, *J* 6.8, $C{=}CH(CH_3)$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 0.2 [$Si(CH_3)_3$], 11.5 (CH_3), 15.4 (CH_3), 17.2 (CH_3), 19.9 (CH_3), 31.3 [$CH(CH_3)_2$], 35.5 [$CH(CH_3)$], 79.1 (CHOH), 101.0 [$C{=}CH(CH_3)$], 153.6 [$C{=}CH(CH_3)$].

(3*RS*,4*SR*,5*E*)-2,2,4-Trimethyl-5-(trimethylsilyloxy)hept-5-en-3-ol 4. Produced (654 mg, 67%) as a *colorless oil* (Found: C, 63.5; H, 11.7. $C_{13}H_{28}O_2Si$ requires C, 63.9; H, 11.5%); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.19 [9H, s, $SiC(CH_3)_3$], 0.83 [9H, s, $C(CH_3)_3$], 1.08 [3H, d, *J* 7.0, $CH(CH_3)$], 1.47 [3H, d, *J* 7.0, $C{=}CH(CH_3)$], 2.70 [1H, dq, *J* 2.8 and 7.0, $CH(CH_3)$], 3.03 (1H, dd, *J* 2.8 and 8.5, CHOH), 3.47 (1H, d, *J* 8.5, D_2O exchangeable), 4.38 [1H, q, *J* 7.0, $C{=}CH(CH_3)$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 0.0 [$Si(CH_3)_3$], 11.4 (CH_3), 18.6 (CH_3), 26.2 [$C(CH_3)_3$], 32.6 [$CH(CH_3)$], 35.9 [$C(CH_3)_3$], 83.9 (CHOH), 99.4 [$C{=}CH(CH_3)$], 153.0 [$C{=}CH(CH_3)$].

Enolsilanes **5** and **6** were prepared according the previous procedure using (2*RS*)-2-methylbutanal. Overall yield (733 mg,

75%) as a colorless oil ratio **5**:**6**, 55:45 (Found: C, 64.1; H, 11.8. $C_{13}H_{28}O_2Si$ requires C, 63.9; H, 11.5%).

(3*RS*,4*SR*,5*SR*,6*E*)-3,5-Dimethyl-6-(trimethylsilyloxy)oct-6-en-4-ol 5. Produced 403 mg; δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.17 [9H, s, $SiC(CH_3)_3$], 0.91 [3H, d, *J* 6.8, $CH(CH_3)$], 0.95 (3H, t, *J* 7.1, CH_3CH_2), 0.97 [3H, d, 6.9, $CH(CH_3)$], 1.48 [3H, d, *J* 7.0, $C{=}CH(CH_3)$], 1.40–1.60 (3H, m), 2.30 (1H, d, *J* 4.7, D_2O exchangeable), 2.71 [1H, dq, *J* 7.7 and 6.9, $CH(CH_3)$], 3.55 (1H, ddd, *J* 4.7 and 3.6 and 7.7, CHOH), 4.64 [1H, q, *J* 7.0, $C{=}CH(CH_3)$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 0.3 [$Si(CH_3)_3$], 11.5 (CH_3), 12.1 (CH_3), 12.8 (CH_3), 14.9 (CH_3), 27.5 (CH_2), 37.0 [$CH(CH_3)$], 37.3 [$CH(CH_3)$], 75.4 (CHOH), 101.7 [$C{=}CH(CH_3)$], 154.0 [$C{=}CH(CH_3)$].

(3*RS*,4*RS*,5*RS*,6*E*)-3,5-Dimethyl-6-(trimethylsilyloxy)oct-6-en-4-ol 6. Produced 330 mg; δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.17 [9H, s, $SiC(CH_3)_3$], 0.91 (3H, t, *J* 7.1, CH_3CH_2), 1.02 [3H, d, *J* 6.8, $CH(CH_3)$], 1.10 [3H, d, 7.0, $CH(CH_3)$], 1.30–1.50 (2H, m), 1.46 [3H, d, *J* 7.0, $C{=}CH(CH_3)$], 1.82 (1H, m), 2.48 (1H, d, *J* 7.3, D_2O exchangeable), 2.68 [1H, dq, *J* 7.0 and 6.2, $CH(CH_3)$], 3.28 (1H, dt, *J* 7.3 and 6.2, CHOH), 4.57 [1H, q, *J* 7.0, $C{=}CH(CH_3)$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 0.2 [$Si(CH_3)_3$], 11.6 (CH_3), 11.7 (CH_3), 15.9 (CH_3), 16.4 (CH_3), 24.3 (CH_2), 35.8 [$CH(CH_3)$], 38.6 [$CH(CH_3)$], 78.5 (CHOH), 101.2 [$C{=}CH(CH_3)$], 154.4 [$C{=}CH(CH_3)$].

(3*RS*,4*SR*,5*E*)-4-Methyl-5-(trimethylsilyloxy)hept-5-en-3-ol 2. Titanocene dichloride (1.00 g, 4.03 mmol) was partly dissolved in 5 mL of THF, and ^{i}PrMgCl (2.00 mL; 2 M solution in THF) was added dropwise. After stirring for 15 min, the resulting green solution of Cp_2TiCl was cooled to −20 °C. A solution of ^{i}PrMgCl (2.00 mL; 2 M solution in THF) and silyloxydiene [13] (630 mg, 4 mmol) were added slowly and simultaneously by syringe at −20 °C. After 15 min, HMPA (21 mL) was added, followed by propionaldehyde (4.5 mmol) 30 min later. After an additional 1 h period the reaction mixture was poured into a separating funnel containing Et_2O (150 mL) and treated with saturated aq. $NaHCO_3$ (20 mL). The Et_2O layer was separated and the aqueous layer was extracted with Et_2O. The combined organic solutions were washed with water, dried ($MgSO_4$), and concentrated *in vacuo*. Separation by flash chromatography on a silica gel column and elution with hexane–Et_2O (8:1) afforded the crude β-hydroxy enol silyl ether **2** (80%) as a *colorless oil* (80%, 690 mg) (Found: C, 60.6; H, 10.8. $C_{11}H_{24}O_2Si$ requires C, 61.1; H, 11.2%); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.20 [9H, s, $SiC(CH_3)_3$], 0.94 (3H, t, *J* 7.0, CH_3CH_2), 0.98 [3H, d, *J* 7.1, $CH(CH_3)$], 1.20–1.36 (2H, m, CH_3CH_2), 1.52 [3H, d, *J* 6.6, $C{=}CH(CH_3)$], 2.20 [1H, dq, *J* 7.1 and 5.6, $CH(CH_3)$], 3.05 (1H, d, *J* 5.1, D_2O exchangeable), 3.45–3,55 (1H, m, CHOH), 4.58 [1H, q, *J* 6.6, $C{=}CH(CH_3)$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 1.1 [$Si(CH_3)_3$], 10.1 (CH_3), 11.5 (CH_3), 14.3 (CH_3), 26.7 (CH_2), 47.1 [$CH(CH_3)$], 74.6 (CHOH), 102.7 [$C{=}CH(CH_3)$], 154.7 [$C{=}CH(CH_3)$].

Typical procedure for reactions of 1 mmol of enol silanes 1–6 with propionaldehyde or isobutyraldehyde and tetraisopropoxytitanium

To a stirred solution of tetraisopropoxytitanium (29 mg, 0.1 mmol) and aldehyde (2.2 mmol) in CH_2Cl_2 (10 mL) was added by a syringe a solution of enolsilane (1 mmol in 7 mL of CH_2Cl_2). The mixture was stirred at room temp. until enolsilane had disappeared (TLC monitoring, approx. time 3 h). After quenching by saturated aq. NaCl (5 mL), the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organics were washed with water (10 mL) and concentrated *in vacuo*. The crude esters were purified by flash chromatography.

(3*RS*,4*SR*,5*RS*,6*RS*,7*RS*)-5,7-Dihydroxy-4,6-dimethylnonan-3-yl propionoate 7. Produced (247 mg, 95%) as a *colorless oil* (Found: C, 64.7; H, 11.0. $C_{14}H_{28}O_4$ requires C, 64.6; H, 10.8%) (Found: $[M + 1]^+$, 261. $C_{14}H_{28}O_4$ requires *M*, 260); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.68 [3H, d, *J* 6.7, $CH(CH_3)$], 0.85 [3H, d, *J* 7.0, $CH(CH_3)$], 0.86 (3H, t, *J* 7.3, CH_3CH_2), 0.92 (3H, t, *J* 7.3, CH_3CH_2), 1.14 (3H, t, *J* 7.4, CH_3CH_2CO), 1.30–1.80 (6H, m), 2.37 (2H, q, *J* 7.4, CH_3CH_2CO), 3.42 (1H, dd, *J* 1.3 and 9.4, CHOH), 3.52 (1H, dt, *J* 2.9 and 7.6, CH_3CH_2CHOH), 4.72 [1H, dt, *J* 3.5 and 8.5, $CH_3CH_2CHO(CO)Et$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 8.9 (CH_3), 9.1 (CH_3), 9.3 (CH_3), 9.5 (CH_3), 12.7 (CH_3), 25.1 (CH_2), 26.8 (CH_2), 27.7 (CH_2), 38.5 [$CH(CH_3)$], 39.4 [$CH(CH_3)$], 75.4 (CHOH), 77.1 (CHOH), 71.3 (CHOH), 176.0 (C=O); MS *m*/*z* 261 ($M + 1^+$, 12%), 231 (30), 205 (8), 173 (14), 157 (12), 117 (57), 99 (63), 70 (64), 57 (82), 43 (100).

(3*RS*,4*RS*,5*RS*,6*RS*,7*RS*)-5,7-Dihydroxy-4,6-dimethylnonan-3-yl propionoate 8. Produced (247 mg, 95%) as a *colorless oil* (Found: C, 64.3; H, 10.6%) (Found: $[M + 1]^+$, 261); δ_H(200 MHz; C_6D_6; Me_4Si) 0.82 (3H, t, *J* 7.0, CH_3CH_2), 0.83 (3H, t, *J* 7.0, CH_3CH_2), 0.96 (3H, t, *J* 6.8, CH_3CH_2CO), 1.02 [3H, d, *J* 6.8, $CH(CH_3)$], 1.12 [3H, d, *J* 6.8, $CH(CH_3)$], 1.30–1.60 (6H, m), 2.08 (2H, q, *J* 6.8, CH_3CH_2CO), 3.48 (1H, m, CH_3CH_2CHOH), 3.62 (1H, dd, *J* 5.0 and 5.9, CHOH), 4.98 [1H, ddd, *J* 9.1 and 3.5 and 5.8, $CH_3CH_2CHO(CO)Et$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 6.6 (CH_3), 9.4 (CH_3), 10.4 (CH_3), 10.5 (CH_3), 10.7 (CH_3), 23.3 (CH_2), 27.8 (CH_2), 28.5 (CH_2), 39.3 [$CH(CH_3)$], 39.6 [$CH(CH_3)$], 76.1 (CHOH), 76.8 (CHOH), 76.9 (CHOCOEt), 174.4 (C=O); MS *m*/*z* 261 ($M + 1^+$, 14%), 231 (8), 191 (38), 173 (80), 157 (55), 139 (52), 117 (90), 99 (80), 86 (100).

Compounds **9 + 10 + 7**: *total yield* 95%.

(3*RS*,4*SR*,5*RS*,6*RS*,7*RS*)-5,7-Dihydroxy-4,6,8-trimethylnonan-3-yl propionoate 9. Produced (104 mg) as a *colorless oil* (Found: C, 65.8; H, 11.3. $C_{15}H_{30}O_4$ requires C, 65.7; H, 11.0%) (Found: $[M + 1]^+$, 275. $C_{15}H_{30}O_4$ requires *M*, 274); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.67 [3H, d, *J* 7.0, $CH(CH_3)$], 0.82 [3H, d, *J* 6.8, $CH(CH_3)$], 0.85 [3H, d, *J* 6.8, $CH(CH_3)$], 0.86 (3H, t, *J* 7.1, CH_3CH_2), 0.97 [3H, d, *J* 6.8, $CH(CH_3)$], 1.14 (3H, t, *J* 7.4, CH_3CH_2CO), 1.40–1.85 (5H, m), 2.37 (2H, q, *J* 7.4, CH_3CH_2CO), 3.37 (1H, dd, *J* 2.3 and 8.8, CHOH), 3.42 (1H, dd, *J* 1.5 and 9.4, CHOH), 4.73 [1H, dt, *J* 3.5 and 8.8, $CH_3CH_2CHO(CO)Et$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 9.0 (CH_3), 9.3 (CH_3), 9.6 (CH_3), 12.9 (CH_3), 13.8 (CH_3), 20.3 (CH_3), 25.1 (CH_2), 27.7 (CH_2), 29.9 [$CH(CH_3)_2$], 37.6 [$CH(CH_3)$], 38.6 [$CH(CH_3)$], 76.0 (CHOH), 77.3 (CHOH), 80.8 (CHOCOEt), 176.1 (C=O); MS *m*/*z* 275 ($M + 1^+$, 78%), 257 (45), 201 (28), 183 (70), 131 (73), 99 (80), 69 (84), 57 (100).

(3*RS*,4*SR*,5*RS*,6*RS*,7*RS*)-5,7-Dihydroxy-2,4,6-trimethylnonan-3-yl propionoate 10. Obtained (104 mg) as a *colorless oil* (Found: C, 65.9; H, 11.2%) (Found: $[M + 1]^+$, 275. $C_{15}H_{30}O_4$ requires *M*, 274); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.69 [3H, d, *J* 7.0, $CH(CH_3)$], 0.87 [9H, d, *J* 6.8, $CH(CH_3)$], 0.92 (3H, t, *J* 7.0, CH_3CH_2), 1.14 (3H, t, *J* 7.4, CH_3CH_2CO), 1.30–2.00 (5H, m), 2.37 (2H, q, *J* 7.4, CH_3CH_2CO), 3.32 (1H, d, *J* 9.7, CHOH), 3.42 (1H, dt, *J* 2.9 and 7.6, CH_3CH_2CHOH), 4.68 [1H, dd, *J* 3.2 and 9.7, $(CH_3)_2CHCHO(CO)Et$]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 9.0 (CH_3), 9.1 (CH_3), 9.8 (CH_3), 11.9 (CH_3), 18.8 (CH_3), 20.4 (CH_3), 25.2 (CH_2), 27.5 (CH_2), 29.8 [$CH(CH_3)_2$], 37.8 [$CH(CH_3)$], 38.4 [$CH(CH_3)$], 76.1 (CHOH), 77.2 (CHOH), 80.9 (CHOCOEt), 176.1 (C=O); MS *m*/*z* 275 ($M + 1^+$, 58%), 257 (49), 201 (19), 183 (75), 131 (64), 99 (85), 69 (65), 57 (100).

Compounds **11** + **7**: *combined yield* 95%.

(3*RS*,4*SR*,5*RS*,6*SR*,7*SR*)-5,7-Dihydroxy-4,6,8,8-tetramethylnonan-3-yl propionate 11. Obtained (191 mg) as a *colorless oil* (Found: C, 66.3; H, 10.9. $C_{16}H_{32}O_4$ requires C, 66.6; H, 11.2%) (Found: $[M + 1]^+$, 289. $C_{16}H_{32}O_4$ requires *M*, 288); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.80 [3H, d, *J* 6.7, $CH(CH_3)$], 0.85 (3H, t, *J* 7.0, CH_3CH_2), 0.89 [9H, s, $C(CH_3)_3$], 0.92 [3H, d, *J* 7.0,

CH(CH_3)], 1.15 (3H, t, *J* 7.4, CH_3CH$_2$CO), 1.50–1.85 (4H, m), 2.38 (2H, q, *J* 7.4, CH$_3$CH_2CO), 3.42 (1H, d, *J* 5.0, C*H*OH), 3.65 (1H, dd, *J* 1.5 and 10.0, C*H*OH), 4.72 [1H, dt, *J* 3.5 and 8.5, CH$_3$CH$_2$C*H*O(CO)Et]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 8.8 (CH_3), 9.3 (CH_3), 9.7 (CH_3), 18.6 (CH_3), 25.2 (CH_2), 25.9 [C(*C*H$_3$)$_3$], 27.7 (CH_2), 34.5 [*C*H(CH$_3$)$_2$], 36.5 [*C*H(CH$_3$)], 37.9 [*C*H(CH$_3$)], 72.0 (CHOH), 77.1 (CHOH), 84.6 (CHOCOEt), 176.2 (C=O); MS *m*/*z* 289 (M + 1$^+$, 20%), 231 (60), 205 (8), 173 (6), 157 (14), 99 (36), 69 (28), 57 (100).

Compounds **12** + **7**: *combined yield* 95%.

(3*RS*,4*SR*,5*RS*,6*RS*,7*RS*,8*SR*)-5,7-Dihydroxy-4,6,8-trimethyldecan-3-yl propionoate 12. Obtained (191 mg) as a *colorless oil* (Found: C, 67.0; H, 11.5%) (Found: [M + 1]$^+$, 289. $C_{16}H_{32}O_4$ requires *M*, 288); δ_H(200 MHz; C_6D_6; Me_4Si) 0.54 [3H, d, *J* 7.0, CH(C*H*$_3$)], 0.75 (3H, t, *J* 7.4, C*H*$_3$CH$_2$), 0.77 [3H, d, *J* 6.8, CH(C*H*$_3$)], 0.88 (3H, t, *J* 7.3, C*H*$_3$CH$_2$), 0.95 (3H, t, *J* 7.2, C*H*$_3$CH$_2$), 1.28 [3H, d, *J* 6.6, CH(C*H*$_3$)], 1.30–1.90 (7H, m), 1.98 (2H, q, *J* 7.4, CH$_3$C*H*$_2$CO), 3.57 (1H, dd, *J* 9.4 and 1.5, C*H*OH), 3.67 (1H, dd, *J* 1.9 and 8.6, C*H*OH), 4.79 [1H, dt, *J* 3.5 and 8.5, CH$_3$CH$_2$C*H*O(CO)Et]; δ_C(50 MHz; C_6D_6; Me_4Si) 9.1 (CH_3), 9.4 (CH_3), 9.7 (CH_3), 12.2 (CH_3), 12.5 (CH_3), 13.1 (CH_3), 25.3 (CH_2), 27.6 (CH_2), 27.7 (CH_2), 37.6 [*C*H(CH$_3$)], 38.1 [*C*H(CH$_3$)], 39.2 [*C*H(CH$_3$)], 76.8 (CHOH), 77.5 (CHOH), 78.7 (CHOCOEt), 175.5 (C=O); MS *m*/*z* 289 (M + 1$^+$, 14%), 231 (20), 213 (12), 184 (17), 157 (34), 99 (29), 69 (28), 57 (100).

Compounds **13** + **7**: *combined yield* 95%.

(3*SR*,4*RS*,5*SR*,6*SR*,7*SR*,8*SR*)-5,7-Dihydroxy-4,6,8-trimethyldecan-3-yl propionate 13. Produced (191 mg) as a *colorless oil* (Found: C, 67.0; H, 11.4%) (Found: [M + 1]$^+$, 289. $C_{16}H_{32}O_4$ requires *M*, 288); δ_H(200 MHz; C_6D_6; Me_4Si) 0.55 [3H, d, *J* 7.0, CH(C*H*$_3$)], 0.76 (3H, t, *J* 7.3, C*H*$_3$CH$_2$), 0.78 [3H, d, *J* 7.0, CH(C*H*$_3$)], 0.90 (3H, t, *J* 7.3, C*H*$_3$CH$_2$), 0.91 (3H, t, *J* 7.2, C*H*$_3$CH$_2$), 0.93 [3H, d, *J* 6.6, CH(C*H*$_3$)], 1.30–1.90 (7H, m), 1.98 (2H, q, *J* 7.4, CH$_3$C*H*$_2$CO), 3.51 (1H, dd, *J* 8.3 and 1.8, C*H*OH), 3.57 (1H, dd, *J* 1.7 and 9.4, C*H*OH), 4.82 [1H, dt, *J* 3.8 and 8.5, CH$_3$CH$_2$C*H*O(CO)Et]; δ_C(50 MHz; C_6D_6; Me_4Si) 9.1 (CH_3), 9.4 (CH_3), 9.7 (CH_3), 12.5 (CH_3), 13.4 (CH_3), 17.2 (CH_3), 21.8 (CH_2), 25.3 (CH_2), 27.7 (CH_2), 37.7 [*C*H(CH$_3$)], 38.0 [*C*H(CH$_3$)], 39.2 [*C*H(CH$_3$)], 76.5 (CHOH), 77.5 (CHOH), 81.6 (CHOCOEt), 175.5 (C=O); MS *m*/*z* 289 (M + 1$^+$, 6%), 231 (18), 213 (12), 184 (14), 157 (31), 99 (29), 69 (28), 57 (100).

Compounds **14** + **15**: *combined yield* 95%.

(3*RS*,4*SR*,5*RS*,6*RS*,7*RS*)-5,7-Dihydroxy-4,6,8-trimethylnonan-3-yl isobutyrate 14. Obtained (191 mg) as a *colorless oil* (Found: C, 66.6; H, 11.5%) (Found: [M + 1]$^+$, 289. $C_{16}H_{32}O_4$ requires *M*, 288); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.68 [3H, d, *J* 7.1, CH(C*H*$_3$)], 0.84 [3H, d, *J* 6.8, CH(C*H*$_3$)], 0.88 [3H, d, *J* 7.1, CH(C*H*$_3$)], 0.89 (3H, t, *J* 7.6, C*H*$_3$CH$_2$), 0.98 [3H, d, *J* 7.0, CH(C*H*$_3$)], 1.18 [6H, d, *J* 7.4, (C*H*$_3$)$_2$CHCO], 1.50–1.85 (5H, m), 2.59 [1H, h, *J* 7.1, (CH$_3$)$_2$C*H*CO], 3.36 (1H, dd, *J* 2.3 and 8.5, C*H*OH), 3.41 (1H, d, *J* 9.9, C*H*OH), 4.73 [1H, dt, *J* 3.5 and 8.5, CH$_3$CH$_2$C*H*O(CO)^{i}Pr]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 9.0 (CH_3), 9.6 (CH_3), 12.9 (CH_3), 13.9 (CH_3), 19.1 (CH_3), 19.2 (CH_3), 20.4 (CH_3), 25.1 (CH_2), 29.9 [(CH$_3$)$_2$*C*H], 34.3 [(CH$_3$)$_2$-*C*HCO], 37.6 [*C*H(CH$_3$)], 38.7 [*C*H(CH$_3$)], 76.1 (CHOH), 77.1 (CHOH), 80.8 (CHOCO^{i}Pr), 178.8 (C=O); MS *m*/*z* 289 (M + 1$^+$, 12%), 245 (10), 187 (15), 157 (20), 131 (25), 99 (36), 71 (100).

(3*RS*,4*SR*,5*RS*,6*RS*,7*RS*)-5,7-Dihydroxy-2,4,6,8-tetramethylnonan-3-yl isobutyrate 15. Produced (86.14 mg) as a *colorless oil* (Found: C, 67.3; H, 11.2. $C_{17}H_{34}O_4$ requires C, 67.5; H, 11.3%) (Found: [M + 1]$^+$, 303. $C_{17}H_{34}O_4$ requires *M*, 302); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.68 [3H, d, *J* 6.7, CH(C*H*$_3$)], 0.85 [3H, d, *J* 6.7, CH(C*H*$_3$)], 0.87 [3H, d, *J* 7.0, CH(C*H*$_3$)], 0.90 [3H, d, *J* 7.0, CH(C*H*$_3$)], 0.91 [3H, d, *J* 7.1, CH(C*H*$_3$)], 1.00 [3H, d, *J* 7.0, CH(C*H*$_3$)], 1.20 [6H, d, *J* 7.1, (C*H*$_3$)$_2$CHCO], 1.60–2.00 (4H, m), 2.62 [1H, h, *J* 7.0, (CH$_3$)$_2$C*H*CO], 3.30–3.40 (2H, m), 4.69 [1H, dd, *J* 3.0 and 9.8, (CH$_3$)$_2$CHC*H*O(CO)^{i}Pr]; δ_C(50 MHz; $CDCl_3$; Me_4Si) 8.8 (CH_3), 13.0 (CH_3), 14.0 (CH_3), 15.0 (CH_3), 19.3 (2 × *C*H$_3$), 20.2 (CH_3), 20.5 (CH_3), 28.5 [(CH$_3$)$_2$*C*H], 30.0 [(CH$_3$)$_2$*C*H], 34.5 [(CH$_3$)$_2$*C*HCO], 36.8 [*C*H(CH$_3$)], 37.7 [*C*H(CH$_3$)], 77.4 (CHOH), 79.0 (CHOH), 80.8 (CHOCO^{i}Pr), 179.2 (C=O); MS *m*/*z* 303 (M + 1$^+$, 10%), 259 (20), 201 (12), 171 (11), 143 (35), 113 (72), 84 (54), 71 (100).

Saponification. Typical procedure for 1 mmol of esters 7–15

To a stirred solution of an ester in MeOH (40 × 10^{-3} M) was added a solution of NaOH in methyl alcohol (60 mg in 100 ml of MeOH, 25 × 10^{-3} M). The mixture was stirred until the ester had disappeared (TLC monitoring). After the reaction was complete, the solvent was evaporated off under vacuum. The crude product was purified by flash chromatography and elution with hexane–Et$_2$O (1 : 3).

(3*RS*,4*RS*,6*RS*,7*RS*)-4,6-Dimethylnonane-3,5,7-triol 16. Obtained (194 mg, 95%) as a *white solid*; mp 92 °C (Found: C, 64.2; H, 11.7. $C_{11}H_{24}O_3$ requires C, 64.7; H, 11.8%) (Found: [M + 1]$^+$, 205. $C_{11}H_{24}O_3$ requires *M*, 204); δ_H(200 MHz; C_6D_6; Me_4Si) 0.45 [3H, d, *J* 6.7, CH(C*H*$_3$)], 0.88 (3H, t, *J* 7.3, C*H*$_3$CH$_2$), 0.97 [3H, d, *J* 7.0, CH(C*H*$_3$)], 0.98 (3H, t, *J* 6.8, C*H*$_3$CH$_2$), 1.30–1.70 (6H, m), 3.34 (1H, ddd, *J* 4.4 and 4.3 and 8.8, CH$_3$CH$_2$C*H*OH), 3.50 (1H, ddd, *J* 3.2 and 8.0 and 8.0, CH$_3$CH$_2$C*H*OH), 3.94 (1H, dd, *J* 9.5 and 1.7, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 9.5 (CH_3), 10.8 (CH_3), 10.9 (CH_3), 12.8 (CH_3), 27.9 (CH_2), 28.7 (CH_2), 38.0 [*C*H(CH$_3$)], 40.4 [*C*H(CH$_3$)], 76.8 (CHOH), 78.1 (CHOH), 78.2 (CHOH); MS *m*/*z* 205 (M + 1$^+$, 25%), 157 (17), 117 (63), 99 (28), 70 (77), 59 (100), 55 (30).

(3*RS*,4*RS*,5*SR*,6*SR*,7*RS*)-4,6-Dimethylnonane-3,5,7-triol 17. Produced (194 mg, 95%) as a *white solid*; mp 94 °C (Found: C, 64.6; H, 11.2%) (Found: [M + 1]$^+$, 205); δ_H(200 MHz; C_6D_6; Me_4Si) 0.83 (3H, t, *J* 7.4, C*H*$_3$CH$_2$), 0.95 [3H, d, *J* 7.0, CH(C*H*$_3$)], 0.96 (3H, t, *J* 7.4, C*H*$_3$CH$_2$), 1.07 [3H, d, *J* 6.7, CH(C*H*$_3$)], 1.20–1.70 (6H, m), 3.38 (1H, m, CH$_3$CH$_2$C*H*OH), 3.47 (1H, ddd, *J* 7.3 and 5.3 and 1.5, CH$_3$CH$_2$C*H*OH), 3.99 (1H, dd, *J* 6.2 and 2.9, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 7.8 (CH_3), 10.5 (CH_3), 10.8 (CH_3), 11.6 (CH_3), 28.1 (CH_2), 28.4 (CH_2), 39.8 [*C*H(CH$_3$)], 40.0 [*C*H(CH$_3$)], 74.9 (CHOH), 75.7 (CHOH), 77.0 (CHOH); MS *m*/*z* 205 (M + 1$^+$, 15%), 157 (19), 117 (52), 99 (35), 70 (82), 59 (100), 55 (42).

(3*SR*,4*SR*,5*SR*,6*RS*,7*RS*)-2,2,4,6-Tetramethylnonane-3,5,7-triol 18. Produced (220 mg, 95%) as a *colorless oil* (Found: C, 67.1; H, 12.4. $C_{13}H_{28}O_3$ requires C, 67.2; H, 12.15%) (Found: [M + 1]$^+$, 233. $C_{13}H_{28}O_3$ requires *M*, 232); δ_H(200 MHz; C_6D_6; Me_4Si) 0.66 [3H, d, *J* 6.7, CH(C*H*$_3$)], 0.93 (3H, t, *J* 7.3, C*H*$_3$CH$_2$), 0.95 [9H, s, CH(C*H*$_3$)$_3$], 1.03 [3H, d, *J* 7.0, CH(C*H*$_3$)], 1.30–1.60 (3H, m), 1.85 (1H, m), 3.09 [1H, d, *J* 5.6, (CH$_3$)$_3$CC*H*OH], 3.40 (1H, m, CH$_3$CH$_2$C*H*OH), 4.11 (1H, dd, *J* 10.0 and 1.7, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 10.8 (CH_3), 10.9 (CH_3), 18.5 (CH_3), 26.2 [(CH$_3$)$_3$], 28.7 (CH_2), 35.8 [*C*H(CH$_3$)], 36.5 [*C*(CH$_3$)$_3$], 37.5 [*C*H(CH$_3$)], 73.8 (CHOH), 78.4 (CHOH), 85.3 (CHOH); MS *m*/*z* 233 (M + 1$^+$, 28%), 197 (8), 157 (56), 145 (28), 127 (52), 99 (57), 87 (68), 70 (71), 57 (90), 43 (100).

(3*RS*,4*RS*,6*RS*,7*RS*)-2,4,6,8-Tetramethylnonane-3,5,7-triol 19. Obtained (220 mg, 95%) as a *white solid*; mp 116 °C (Found : C, 67.4; H, 12.0. $C_{13}H_{28}O_3$ requires C, 67.2; H, 12.15%) (Found: [M + 1]$^+$, 233. $C_{13}H_{28}O_3$ requires *M*, 232); δ_H(200 MHz; C_6D_6; Me_4Si) 0.48 [3H, d, *J* 6.7, CH(C*H*$_3$)], 0.75 [3H, d, *J* 6.8, CH(C*H*$_3$)], 0.89 [3H, d, *J* 6.8, CH(C*H*$_3$)], 1.01 [6H, d, *J* 6.8, CH(C*H*$_3$)], 1.02 [3H, d, *J* 6.7, CH(C*H*$_3$)], 1.60–1.85 (4H, m), 3.05 [1H, dd, *J* 4.4 and 7.9, (CH$_3$)$_2$CHC*H*OH], 3.31 [1H,

dd, *J* 2.4 and 8.8, $(CH_3)_2CHCHOH$], 3.91 (1H, dd, *J* 9.4 and 1.8, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 10.8 (CH_3), 12.8 (CH_3), 13.8 (CH_3), 18.9 (CH_3), 19.4 (CH_3), 20.2 (CH_3), 29.9 [$CH(CH_3)$], 31.2 [$CH(CH_3)$], 34.7 [$CH(CH_3)$], 38.1 [$CH(CH_3)$], 76.8 (CHOH), 81.7 (CHOH), 82.2 (CHOH); MS *m*/*z* 233 (M + 1$^+$, 2%), 171 (8), 145 (7), 131 (9), 113 (45), 95 (21), 84 (39), 73 (100), 69 (71), 55 (32).

(3*RS*,4*RS*,5*SR*,6*RS*,7*RS*,8*SR*)-4,6,8-Trimethyldecane-3,5,7-triol 20. Produced (221 mg, 95%) as a *colorless oil* (Found: C, 67.45; H, 12.3%) (Found: [M + 1]$^+$, 233. $C_{13}H_{28}O_3$ requires *M*, 232); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.68 [3H, d, *J* 7.0, CH(CH_3)], 0.84 [3H, d, *J* 6.8, CH(CH_3)], 0.91 (3H, t, *J* 7.0, CH_3CH_2), 0.94 (3H, t, *J* 7.3, CH_3CH_2), 1.02 [3H, d, *J* 7.0, CH(CH_3)], 1.30–1.40 (1H, m), 1.50–1.75 (6H, m), 3.50 (1H, m, CH_3CH_2CHOH), 3.58 (1H, dd, *J* 2.0 and 9.1, C*H*OH), 3.94 (1H, dd, *J* 9.4 and 1.8, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 10.9 (CH_3), 11.0 (CH_3), 12.1 (CH_3), 12.4 (CH_3), 12.8 (CH_3), 27.4 (CH_2), 28.7 (CH_2), 37.4 [$CH(CH_3)$], 38.1 [$CH(CH_3)$], 38.2 [$CH(CH_3)$], 77.4 (CHOH), 78.2 (CHOH), 79.5 (CHOH); MS *m*/*z* 233 (M + 1$^+$, 48%), 215 (4), 185 (13), 167 (7), 157 (39), 145 (58), 127 (52), 117 (42), 99 (56), 87 (78), 69 (73), 57 (90), 43 (100).

(3*SR*,4*SR*,5*RS*,6*SR*,7*SR*,8*SR*)-4,6,8-Trimethyldecane-3,5,7-triol 21. Obtained (220 mg, 95%) as a *colorless oil* (Found: C, 67.2; H, 12.45%) (Found: [M + 1]$^+$, 233. $C_{13}H_{28}O_3$ requires *M*, 232); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.69 [3H, d, *J* 6.8, CH(CH_3)], 0.89 (3H, t, *J* 7.0, CH_3CH_2), 0.95 (3H, t, *J* 7.3, CH_3CH_2), 0.98 [3H, d, *J* 7.0, CH(CH_3)], 1.02 [3H, d, *J* 7.0, CH(CH_3)], 1.20–1.30 (1H, m), 1.50–1.75 (6H, m), 3.49 (1H, dd, *J* 2.3 and 8.8, C*H*OH), 3.53 (1H, m, CH_3CH_2CHOH), 3.97 (1H, dd, *J* 9.1 and 2.0, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 10.9 (CH_3), 11.0 (CH_3), 12.5 (CH_3), 13.1 (CH_3), 17.0 (CH_3), 21.6 (CH_2), 28.7 (CH_2), 37.6 [$CH(CH_3)$], 38.0 [$CH(CH_3)$], 38.1 [$CH(CH_3)$], 77.1 (CHOH), 78.1 (CHOH), 82.4 (CHOH); MS *m*/*z* 233 (M + 1$^+$, 21%), 203 (13), 185 (25), 167 (8), 157 (55), 145 (54), 127 (49), 117 (44), 99 (58), 87 (81), 69 (79), 57 (96), 43 (100).

(3*RS*,4*RS*,5*SR*,6*RS*,7*RS*)-2,4,6-Trimethylnonane-3,5,7-triol 22. Produced (207 mg, 95%) as a *white solid*; mp 92 °C (Found: C, 65.9; H, 12.3. $C_{12}H_{26}O_3$ requires C, 66.0; H, 12.0%) (Found: [M + 1]$^+$, 219. $C_{12}H_{26}O_3$ requires *M*, 218); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.69 [3H, d, *J* 6.8, CH(CH_3)], 0.84 [3H, d, *J* 7.0, CH(CH_3)], 0.94 (3H, t, *J* 7.5, CH_3CH_2), 0.97 [3H, d, *J* 7.2, CH(CH_3)], 1.02 [3H, d, *J* 7.0, CH(CH_3)], 1.50–1.70 (4H, m), 1.87 [1H, ddq, *J* 2.4, 6.7 and 6.7, $CH(CH_3)$], 3.45 [1H, dd, *J* 2.3 and 9.1, $(CH_3)_2CHCHOH$], 3.51 (1H, m, CH_3CH_2-C*H*OH), 3.97 (1H, dd, *J* 9.9 and 2.0, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 10.6 (CH_3), 10.7 (CH_3), 12.8 (CH_3), 13.8 (CH_3), 20.2 (CH_3), 28.3 (CH_2), 29.8 [$CH(CH_3)_2$], 37.4 [$CH(CH_3)$], 38.0 [$CH(CH_3)$], 76.6 (CHOH), 77.9 (CHOH), 81.7 (CHOH); MS *m*/*z* 219 (M + 1$^+$, 5%), 171 (13), 145 (11), 131 (18), 113 (48), 95 (28), 84 (49), 73 (100), 69 (85).

(3*RS*,4*RS*,5*RS*,6*RS*,7*RS*)-2,4,6-Trimethylnonane-3,5,7-triol 23. Obtained (207 mg, 95%) as a *white solid*; mp 92 °C (Found: C, 65.7; H, 11.8%) (Found: [M + 1]$^+$, 219); δ_H(200 MHz; $CDCl_3$; Me_4Si) 0.71 [3H, d, *J* 6.8, CH(CH_3)], 0.84 [3H, d, *J* 6.8, CH(CH_3)], 0.95 (3H, t, *J* 7.3, CH_3CH_2), 0.98 [3H, d, *J* 6.7, CH(CH_3)], 1.00 [3H, d, *J* 7.0, CH(CH_3)], 1.41 (1H, m), 1.55–1.70 (2H, m), 1.75–1.90 (2H, m), 3.17 [1H, dd, *J* 3.8 and 8.2, $(CH_3)_2CHCHOH$], 3.51 (1H, dt, *J* 3.0 and 8.1, CH_3-CH_2CHOH), 3.93 (1H, dd, *J* 9.7 and 1.8, C*H*OH); δ_C(50 MHz; C_6D_6; Me_4Si) 9.0 (CH_3), 10.7 (CH_3), 12.8 (CH_3), 18.9 (CH_3), 19.3 (CH_3), 27.4 (CH_2), 31.3 [$CH(CH_3)_2$], 34.7 [$CH(CH_3)$], 40.0 [$CH(CH_3)$], 76.7 (CHOH), 78.2 (CHOH), 82.3 (CHOH); MS *m*/*z* 219 (M + 1$^+$, 38%), 183 (10), 171 (8), 157 (23), 139 (8), 131 (48), 113 (27), 99 (32), 84 (53), 73 (80), 69 (75), 43 (100).

X-Ray crystallographic analysis of triols 22 and 23†

Colorless crystals having the approximate dimensions 0.50 × 0.40 × 0.30 mm for **22** and 0.30 × 0.30 × 0.10 mm for **23** were mounted on a CAD4 Enraf-Nonius diffractometer. The data were collected at room temperature with Mo-Kα radiation (λ = 0.710 73 Å).

Crystal data. Compound **22**: $C_{12}H_{26}O_3$, M = 218.33, triclinic, *P*-1 (No. 2), a = 7.347(1), b = 7.874(1), c = 12.715(1) Å, α = 71.339(5), β = 78.603(8), γ = 81.054(5)°, V = 679.7(1) Å^3, T = 296(1) K, Z = 2, D_x = 1.067 g cm^{-3}, μ(Mo-Kα) = 0.074 mm^{-1}, 2967 reflections measured, 2754 unique reflections (R_{int} = 0.014) giving 2046 observed data with $I > 2\sigma(I)$. The final $R(F)$ and $wR(F^2)$ factors were 0.045/0.123 for observed data and 0.066/0.137 for all data, respectively.

Compound **23**: $C_{12}H_{26}O_3$, M = 218.33, monoclinic, $P2_1/n$ (No. 14), a = 9.6044(8), b = 12.367(1), c = 11.9674(6) Å, β = 106.324(5)°, V = 1364.2(2) Å^3, T = 296(1) K, Z = 4, D_x = 1.063 g cm^{-3}, μ(Mo-Kα) = 0.074 mm^{-1}, 2938 reflections measured, 2772 unique reflections (R_{int} = 0.020) giving 1621 observed data with $I > 2\sigma(I)$. The final $R(F)$ and $wR(F^2)$ factors were 0.048/0.117 for observed data and 0.116/0.143 for all data, respectively.

In both structures, all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in their calculated positions and refined with a riding model, except for hydrogens bonded to oxygens which were located in a Fourier difference map and freely refined with an isotropic temperature factor.

† CCDC reference number 207/441. See http://www.rsc.org/suppdata/p1/b0/b002008g/ for crystallographic files in .cif format.

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