Conformation Induction Between Neighboring Dimethylpentane Segments[‡]

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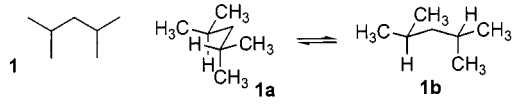
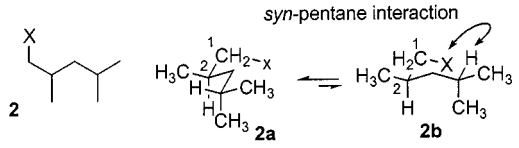
A 2,4-dimethylpentane unit can be rendered monoconformational by the presence of a conformation-inducing group (an inductor group) at C-1 (cf. **6**). The resulting entity may serve as an inductor group to control in turn the conformation of a neighboring dimethylpentane segment (cf. **7**). This holds if the inducing dimethylpentane segment is isotactic (cf. **15**, **25**), but not when it is syndiotactic (cf. **28**).

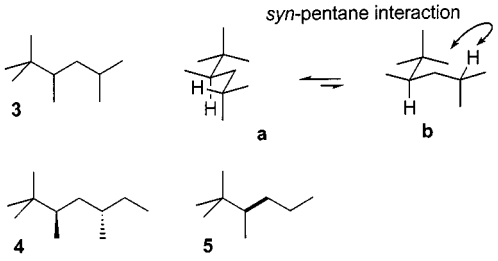
Introduction

2,4-Dimethylpentane (**1**), possessing methyl groups at every second carbon atom of the molecular skeleton, is the recurring structural subunit of many polypropionate-derived natural products.[2] It is also the structural subunit of polypropylene. 2,4-Dimethylpentane (**1**) has just two low-energy conformations; it is therefore a typical biconformational molecule.[3−6] Extension of the molecular skeleton of **1** − that is, substitution at the terminal carbon atoms (cf. **2**) − may destabilize the two low-energy conformations to different extents, and so the conformer equilibrium of **2** may be biased in a distinct manner.[7] In extreme cases, the substituent X in **2** could render the dimethylpentane unit monoconformational.

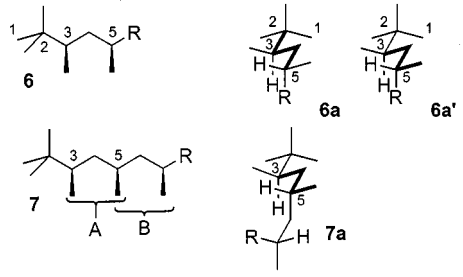




This would come about if a substituent X at C-1 could be held in a position antiperiplanar to the C-2−CH_3, thereby selectively destabilizing the conformation **2b** through a *syn*-pentane interaction.[8] The easiest way to attain this state of affairs is to have C-1 as a quaternary center, such as a *tert*-butyl group (cf. **3**). It has, for instance, been proposed on the basis of its chiroptical properties, that the related compound **4** overridingly populates just one conformation.[9] This is a clear manifestation of the *tert*-butyl effect,[10−13] according to which, in a compound such as **5**, the highlighted bond predominantly populates a *anti* conformation to avoid any *syn*-pentane interactions. As well as the *tert*-butyl group there exist other "inductor groups" capable of rendering a dimethylpentane unit monoconformational.[1,7,8]



We would like to address the situation that a dimethylpentane segment in a defined conformation could in turn serve as an inductor group to affect the conformation of a neighboring dimethylpentane segment. This is illustrated in compounds **6** and **7**: The *tert*-butyl group in the dimethylpentane unit in **6** induces the conformation **6a**. This fixes the carbon atoms C-2/C-3/C-4/C-5 in an *anti* arrangement, which in turn results in the situation that the carbon atoms C-3/C-4/C-5/C-5−CH_3 are in a *anti* arrangement as well (cf. **6a′**). If R in **6** is then extended to a second dimethylpentane unit (cf. **7**), the first dimethylpentane segment A − i.e., C-3/C-4/C-5/C-5−CH_3 − should induce a conformational preference in the neighboring segment B of **7** (cf. **7a**). Molecule **7** thus adopts the shape of a starting helix, the helicity of which is determined by the chiral center at C-3 incorporated in the inductor group. The folding information of such an inductor group could therefore be transferred along the chain of isotactic polypropylene. In fact, isotactic polypropylene crystallizes in a helical conformation.[14]



[‡] Flexible Molecules with Defined Shape, XV. − Part XIV: Ref.[1]

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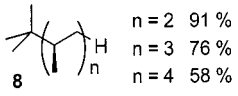
Control over the helical folding of a polymer chain is a topic of longstanding interest.[15−17] Induction of the sense of helicity has been achieved by means of chirality in the side chains,[18−20] and with the aid of chiral end groups.[21] Such helical backbone conformations were first documented for isotactic poly(α-olefins).[14,22−25] The structure shown in **7a** illustrates how a chiral inductor group could induce a particular helical folding sense in an oligopropylene chain **8**. However, the efficiency of such conformation control is limited. Force-field calculations show that the preference of **8** for adopting a single backbone conformation decreases rapidly with increasing n (n = 2: 91%; n = 3: 76%; n = 4: 58%). This has to do with the fact that each extension of the skeleton makes possible a number of additional high energy conformations, while the number of the desired low-energy conformation (= 1) cannot increase. Therefore, by simple statistics (corresponding to entropy), the percentage population of the single low-energy conformation must decrease upon extension of the molecular skeleton. A priori, therefore, it is not clear how far conformation control along an isotactic oligopropylene chain can reach. We therefore studied the conformational behavior of compounds of type **7**, in the general context of identifying flexible molecular backbones that adopt a single preferred conformation.[26]



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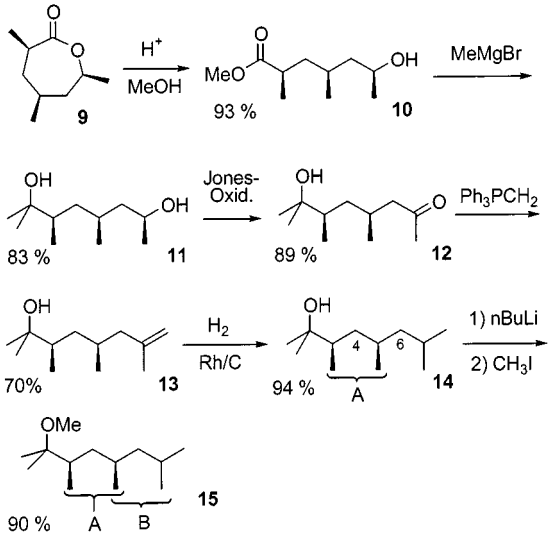
Results and Discussion

Rather than studying compound **7** itself, we focused our attention on compound **15**, which should have less overlaying in its ^{1}H NMR spectrum, due to the presence of the polar methoxy group. This was intended to facilitate the determination of the relevant coupling constants.



9 **10** **11** **12** **13** **14** **15**

It was possible to prepare compound **15** in a straightforward manner, starting from the known[27] lactone **9**. The lactone was opened to give the hydroxy ester **10**. This was converted into the diol **11** by addition of a methyl Grignard reagent. The diol **11** is a crystalline solid, the X-ray crystal structure analysis of which revealed that in the solid state the molecule adopts a conformation that corresponds to the conformation **7a** (Figure 1).

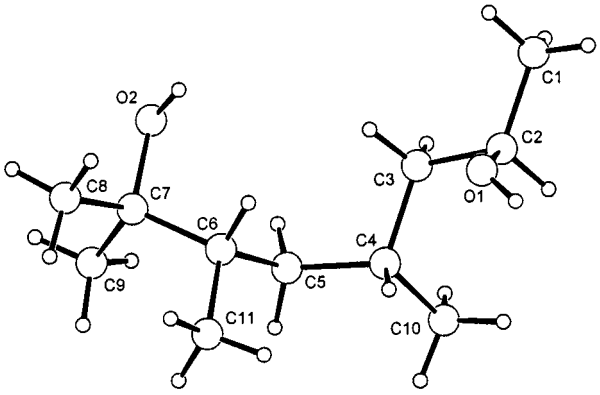
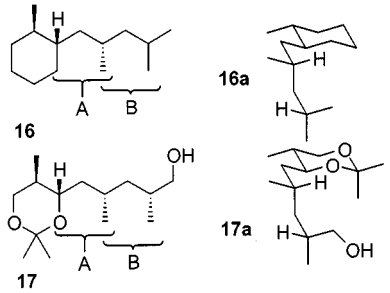


Figure 1. X-ray crystal structure of compound **11**

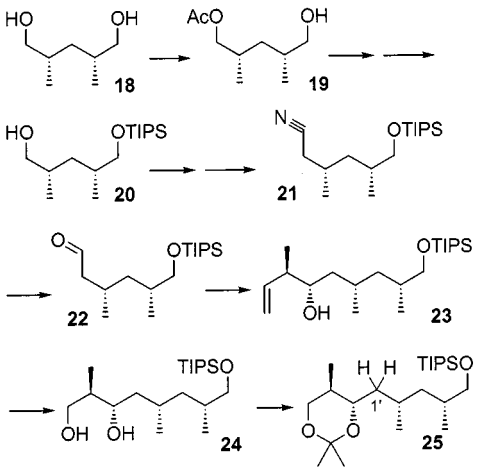
Oxidation of the secondary alcohol function in **11** was followed by Wittig reaction to provide the alkene **13**. Hydrogenation of the latter gave the alcohol **14**, corresponding to **7**. NMR analysis allowed the determination only of one set of $^3J_{H,H}$ coupling constants (2.6 and 9.9 Hz) within the segment A. A better resolved spectrum was recorded for the methyl ether **15**, obtained from **14**. Here, it was possible to record signals of one of the diastereotopic protons at C-4 and one at C-6 unobscured by other signals. This produced coupling constants of 10.3 and 2.2 Hz in segment A, and 4.4 and 9.0 Hz in segment B. These numbers reflect a high conformational preference in segment A, slightly attenuated in segment B.

In compound **15**, a surrogate of the *tert*-butyl group was used as the "inductor group". Other "inductor groups" previously shown to work well[1] are analogs of methylcyclohexane.[8] Combination of such an inductor group with a dimethylpentane unit suggests compound **16** as an object for conformational analysis. Thus, compound **16** has been calculated to have a 90% preference for populating conformation **16a**.[8]

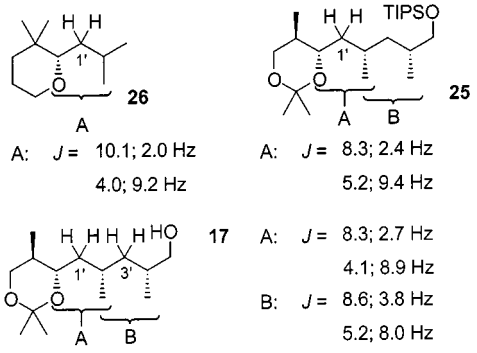


16 **17**

In order to improve our chances of recording the relevant $^3J_{H,H}$ coupling constants, we chose the related compound **17**, with a methyl-1,3-dioxane unit, as an inductor group for further study. Our syntheses of **17** began with the *meso*-diol **18**, which was desymmetrized by lipase-catalyzed acetylation.[28−30] Depending on the lipase used [one example was PPL (Sigma, type II) on Hyflow Super Cel (Fluka)], *ee* values for **19** varied between 87 and 92%. The end groups of the molecule were changed by silylation with TIPS chloride (95%), followed by deacetylation with K_2CO_3 (94%).

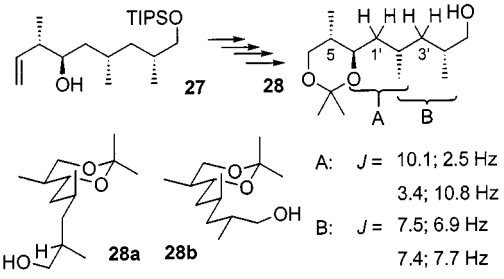


The resulting alcohol **20** was converted into the bromide (98%) and homologated to the nitrile **21** (95%). Its reduction (DIBAL, 90%) was followed by crotylboration with [(*E*)-crotyl](diisopinocampheyl)borane[31] to give the homoallylic alcohol **23** (51%). Ozonolysis followed by reductive workup furnished the diol **24** (94%), which was converted into the acetonide **25** (71%). The latter showed coupling constants of 8.3 and 2.4 Hz for C-1′−H_A and of 5.2 and 9.4 Hz for C-1′−H_B. This indicates a considerable degree of conformational preference, although less than that in the model compound **26** (10.1 and 2.0 Hz; 4.0 and 9.8 Hz),[1] with a shorter side chain. The big TIPSO group at the end of this side chain in **25** may result in the situation that the "tail is wagging the dog". We therefore hoped that compound **17**, obtained by removal of the TIPS group with TBAF, might exhibit a greater conformational preference. SELINCOR experiments[32] on compound **17** showed that the protons attached to C-1′ (δ = 40.7) had coupling constants of 8.3 and 2.7 Hz, and 4.1 and 8.9 Hz. Therefore, the conformational preference in segment A of **17** was remaining moderate (ca. 75%, on the basis of coupling constants calculated for conformation **17a**). If this is so, then the conformational preference in segment B can only be 75% at best. Indeed, the SELINCOR experiment[32] showed the protons attached to C-3′ (δ = 39.5) to have coupling constants of 8.6 and 3.8 Hz, and 5.2 and 8.0 Hz.



These results show that there is once more a conformation induction from segment A to segment B in **17**. As seen before with **15**, the conformational preference in segment B is somewhat attenuated compared with that in segment A. Moreover, the decreased conformational preference found for **17**, when compared to the model compound **26**, with the shorter side chain, clearly demonstrates the loss in conformational preference that goes along with an increased number of freely rotatable bonds (as discussed for compound **8**).

One prediction made earlier[8] was that the folding information provided by an inductor end group on an oligopropylene chain (cf. **8**) could be handed down the chain only along isotactic segments. As soon as there is a syndiotactic segment, the next isotactic segment will be biconformational and the folding information will be lost downstream. To check the validity of this statement, we synthesized compound **28**, starting from the aldehyde **22**. Crotylboration with the enantiomeric [(*E*)-crotyl](diisopinocampheyl)borane provided the homoallylic alcohol **27** (56%). The latter was converted into the dioxane **28** in a manner similar to that used in the preparation of **17**.



Segment A in compound **28** can be considered as syndiotactic. While this segment should have a preferred conformation due to the inductor group (C-5−CH_3), the conformational preference in segment A should not be transmitted to segment B, which should be biconformational. Thus, not only conformation **28a** should be populated, but − to a lesser extent −conformation **28b** should be as well. This should be reflected in the magnitude of the characteristic coupling constants.

SELINCOR experiments carried out with **28** revealed that the protons attached to C-1′ (δ = 41.9) had coupling constants of 10.1 and 2.5 Hz, and 3.4 and 10.8 Hz. This indicated a high (ca. 85%) conformational preference in seg-

ment A of **28**, similar to that in the model compound **26**. The protons attached to C-3′ (δ = 40.1) had coupling constants of 7.5 and 6.9 Hz, and 7.4 and 7.7 Hz, in line with an essentially biconformational state of affairs. Comparison of conformational preferences for the compounds **17** and **28** shows that an isotactic "dimethylpentane" segment (A in **17**) may transfer its folding information to the neighboring dimethylpentane segment (B), whereas a syndiotactic segment A in **28** is not in a position to do so.

Experimental Section

General Remarks: All temperatures quoted are uncorrected. − Petroleum ether boiling range 40−60 °C. − ^{1}H NMR, ^{13}C NMR: Bruker AC-300, AM-400, AMX-500. − Flash chromatography: Si 60 silica gel, E. Merck KGaA, Darmstadt, 40−63 μm.

1. Methyl (2*S,4*R**,6*R**)-6-Hydroxy-2,4-dimethylheptanoate (10):** Concentrated sulfuric acid (0.5 mL) was added to a solution of the lactone **9**[27] (17.9 g, 0.11 mol) in methanol (200 mL). After 1 d, water (500 mL) and ether (100 mL) were added, the phases were separated, and the aqueous phase was extracted with ether (2 × 100 mL). The combined organic phases were dried (Na_2SO_4) and concentrated to yield **10** (20.2 g, 93%) as a slightly yellowish oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 6.5 Hz, 3 H), 1.05 (d, *J* = 7.0 Hz, 3 H with superimposed m, 2 H), 1.09 (d, *J* = 6.1 Hz, 3 H), 1.36 (m, 1 H), 1.49 (m, 1 H), 1.57 (m, 1 H), 2.17 (broad s, 1 H), 2.49 (m, 1 H), 3.58 (s, 3 H), 3.80 (m, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.8, 19.4, 22.1, 27.5, 37.0, 41.6, 46.5, 51.4, 65.4, 177.4. − $C_{10}H_{20}O_3$ (188.3): calcd. C 63.80, H 10.70; found C 63.72, H 10.72.

2. (3*R,5*S**,7*S**)-2,3,5-Trimethyl-2,7-octanediol (11):** Methylmagnesium bromide (3 M in ether, 35.0 mL, 105 mmol) was added at 0 °C to a solution of the ester **10** (3.00 g, 15.9 mL) in diethyl ether (100 mL). After the mixture had been left standing for 12 h at room temperature, water (150 mL) was added, the phases were separated, and the aqueous phase was extracted with ether (3 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography with petroleum ether/ether (3:1) to give the diol **11** (2.51 g, 83%) as a colorless solid. Recrystallization from ether/petroleum ether furnished colorless needles of m.p. 74 °C. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.84 (d, *J* = 6.8 Hz, 3 H), 0.88 (d, *J* = 6.5 Hz, 3 H, and m, 1 H), 0.96 (ddd, *J* = 13.6, 9.7, and 2.9 Hz, 1 H), 1.08 (d, *J* = 7.1 Hz, 3 H), 1.12 (s, 6 H), 1.38 (ddd, *J* = 12.8, 9.2, and 3.0 Hz, 1 H), 1.43 (m, 1 H), 1.48 (m, 1 H), 1.63 (m, 1 H), 1.95 (broad s, 2 H), 3.83 (m, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.2, 21.3, 24.6, 26.0, 27.2, 27.8, 40.1, 41.5, 45.6, 65.7, 73.4. − $C_{11}H_{24}O_2$ (188.4): calcd. C 70.16, H 12.85; found C 69.95, H 12.89.[33]

3. (4*R,6*S**)-7-Hydroxy-4,6,7-trimethyl-2-octanone (12):** Jones reagent[34] (2.5 M, 7.0 mL, 16 mmol) was added dropwise to a solution of the diol **11** (2.50 g, 13.3 mmol) in acetone (30 mL) at 0 °C. After the mixture had been stirred for 1 h, 2-propanol (5 mL) was added and the mixture was allowed to come to room temperature over 12 h. Water (50 mL) and ether (30 mL) were added. The phases were separated and the aqueous phase was extracted with ether (3 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. Flash chromatography of the residue with petroleum ether/ether (4:1) furnished the ketone **12** (2.21 g, 89%) as a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 7.2 Hz, 3 H), 0.88 (m, 1 H), 0.89 (d, *J* = 6.4 Hz, 3 H), 1.09 (s, 3 H), 1.13 (s, 3 H), 1.40 (m, 2 H), 1.86 (broad s, 1 H), 2.00 (m, 1 H), 2.08 (s, 3 H), 2.12 (dd, *J* = 14.1 and 8.2 Hz, 1 H), 2.45 (dd, *J* = 15.8 and 4.1 Hz, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.5, 21.5, 25.7, 27.4, 27.7, 30.7, 39.3, 41.8, 50.0, 73.2, 209.2. − $C_{11}H_{22}O_2$ (186.3): calcd. C 70.92, H 11.90; found C 71.05, H 11.75.

4. (4*R,6*S**)-7-Hydroxy-2,4,6,7-tetramethyl-1-octene (13):** *n*-Butyllithium (1.7 M in hexane, 29.4 mL, 50 mmol) was added at 0 °C to a suspension of methyltriphenylphosphonium bromide (17.9 g, 50 mmol) in THF (100 mL). A solution of the ketone **12** (1.62 g, 8.70 mmol) in THF (10 mL) was added dropwise and the mixture was allowed to come to room temperature over 12 h. Water (100 mL) and saturated aqueous NH_4Cl solution (100 mL) were added. The phases were separated and the aqueous phase was extracted with ether (3 × 100 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with petroleum ether/ether (20:1 to 5:1) furnished the alkene **13** (1.13 g, 70%) as a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (d, *J* = 6.4 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 3 H), 0.96 (ddd, *J* = 13.5, 10.0, and 3.7 Hz, 1 H), 1.15 (s, 6 H), 1.26 (broad s, 1 H), 1.41 (m, 1 H), 1.50 (m, 1 H), 1.60 (m, 1 H), 1.62 (m, 1 H), 1.68 (s, 3 H), 2.16 (broad d, *J* = 10 Hz, 1 H), 4.66 (s, 1 H), 4.73 (s, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.1, 21.0, 22.2, 26.5, 26.9, 29.1, 39.8, 41.7, 44.8, 73.4, 111.4, 144.9. − $C_{12}H_{24}O$ (184.3): calcd. C 78.20, H 13.12; found C 78.01, H 13.01.

5. (3*R,5*R**)-2,3,5,7-Tetramethyl-2-octanone (14):** The alkene **13** (965 mg, 5.2 mmol) was dissolved in methanol (20 mL). Rhodium on carbon (5%, 100 mg) was added and the suspension was stirred for 12 h under hydrogen (1 bar). The suspension was filtered through a 1-cm layer of Kieselgur, which was washed with ether (50 mL). The filtrates were concentrated and the residue was purified by flash chromatography with petroleum ether/ether (20:1 to 1:1) to give the alcohol **14** (910 mg, 94%) as a colorless oil. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 6.6 Hz, 3 H), 0.82 (m, 1 H), 0.85 (d, *J* = 6.5 Hz, 3 H), 0.86 (d, *J* = 6.6 Hz, 6 H), 0.87 (m, 1 H), 1.12 (s, 6 H), 1.14 (m, 1 H), 1.31 (m, 2 H), 1.46 (m, 2 H), 1.61 (m, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9, 21.3, 21.6, 24.1, 25.3, 26.5, 26.8, 28.5, 40.3, 41.4, 45.5, 73.4. − $C_{12}H_{26}O$ (186.3): calcd. C 77.35, H 14.06; found C 77.10, H 14.30.

6. (3*R,5*R**)-2-Methoxy-2,3,5,7-tetramethyloctane (15):** *n*-Butyllithium (1.8 M in hexane, 2.0 mL, 3.6 mmol) was added dropwise at 0 °C to a solution of the alcohol **14** (560 mg, 3.0 mmol) in THF (20 mL). After the mixture had been stirred for 30 min, methyl iodide (2.1 g, 15 mmol) was added and the mixture was stirred for a further 2 h. Water (80 mL) was added, the phases were separated and the aqueous phase was extracted with ether (3 × 30 mL). The combined organic phases were dried (Na_2SO_4) and concentrated to afford the ether **15** (543 mg, 90%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 6.5 Hz, 3 H), 0.81 (m, 1 H), 0.82 (d, *J* = 6.5 Hz, 3 H), 0.84 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.6 Hz, 3 H), 0.89 (m, 1 H), 1.04 (s, 6 H), 1.14 (ddd, *J* = 13.2, 9.0, and 4.4 Hz, 1 H), 1.27 (ddd, *J* = 12.6, 10.3, and 2.2 Hz, 1 H), 1.48 (m, 1 H), 1.64 (m, 1 H), 1.66 (m, 1 H), 3.13 (s, 3 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6, 21.4, 21.6, 22.0, 24.2, 25.3, 28.5, 37.4, 40.1, 45.5, 48.6, 67.9. − $C_{13}H_{28}O$ (200.4): calcd. C 77.93, H 14.09; found C 78.05, H 14.37.

7. (2*S*,4*R*)-1-Acetoxy-2,4-dimethyl-5-(triisopropylsilyloxy)pentane: Chlorotriisopropylsilane (19.3 g, 100 mmol) and imidazole (13.3 g, 195 mmol) were added to a solution of (2*R*,4*S*)-5-acetoxy-2,4-dimethylpentanol[30] (13.4 g, 76.6 mmol) in DMF (20 mL). After addition of 4-(dimethylamino)pyridine (0.50 g, 4.1 mmol), the mixture was stirred for 3 d at 50 °C. Water (100 mL) was added and

the mixture was stirred for 10 min at room temperature. The phases were separated and the aqueous phase was extracted with petroleum ether (3 × 100 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (19:1) furnished the product (24.1 g, 95%) as a colorless oil. − $[\alpha]_D^{20}$ = +0.5 (*c* = 1.0, methanol, ca. 74% *ee*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88−0.92 (m, 6 H), 1.03−1.12 (m, 22 H), 1.49 (td, *J* = 13.7 and 6.8 Hz, 1 H), 1.60−1.71 (m, 1 H), 1.79−1.90 (m, 1 H), 2.02 (s, 3 H), 3.47 (m, 2 H), 3.80 (dd, *J* = 10.7 and 6.8 Hz, 1 H), 3.93 (dd, *J* = 10.7 and 5.5 Hz, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0, 17.5, 17.7, 18.0, 20.9. 30.1, 33.4, 37.5, 68.4, 69.4, 171.2. − $C_{18}H_{38}O_3Si$ (330.6): calcd. C 65.40, H 11.59; found C 65.46, H 11.58.

8. (2*S*,4*R*)-2,4-Dimethyl-5-(triisopropylsilyloxy)pentanol (20): (2*S*,4*R*)-1-Acetoxy-2,4-dimethyl-5-triisopropylsilyloxypentane (6.00 g, 18.1 mmol) was dissolved in methanol (50 mL) and water (10 mL). Potassium carbonate (5.00 g, 36.2 mmol) was added and the mixture was stirred for 36 h. Water (50 mL) was added, the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography with petroleum ether/*tert*-butyl methyl ether (6:1) furnished the product **20** (4.92 g, 94%) as a colorless oil. − $[\alpha]_D^{20}$ = −2.6 (*c* = 1.0, CH_2Cl_2, 74% *ee*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83−0.95 (m, 6 H), 0.99−1.09 (m, 22 H), 1.24 (broad s, 1 H), 1.45 (td, *J* = 13.7 and 6.9 Hz, 1 H), 1.59−1.73 (m, 2 H), 3.33−3.53 (m, 4 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.3, 17.5, 17.7, 17.9, 33.2, 33.5, 37.3, 68.1, 68.5. − $C_{16}H_{36}O_2Si$ (288.6): calcd. C 66.60, H 12.57; found C 66.64, H 12.80.

9. (2*R*,4*S*)-5-Bromo-2,4-dimethyl-1-(triisopropylsilyloxy)pentane: Methanesulfonyl chloride (2.30 g, 1.6 mL, 20 mmol) and triethylamine (4.0 g, 4.1 mL, 40 mmol) were added sequentially to a solution of **20** (2.91 g, 10.1 mmol) in dichloromethane (100 mL) at −40 °C. The mixture was allowed to come to −15 °C within 1 h. Water (30 mL) was added, the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. The residue was taken up in THF (20 mL), lithium bromide (3.47 g, 40 mmol) was added, and the solution was stirred for 3 d at room temperature. Saturated aqueous NH_4Cl solution (30 mL) was added, the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 30 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with petroleum ether furnished the bromo compound (3.44 g, 98%) as a colorless oil. − $[\alpha]_D^{20}$ = +0.6 (*c* = 1.0, CH_2Cl_2, 74% *ee*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 6.0 Hz, 3 H), 0.91 (d, *J* = 6.7 Hz, 3 H), 0.97−1.08 (m, 22 H), 1.53 (td, *J* = 13.6 and 7.0 Hz, 1 H), 1.63−1.71 (m, 1 H), 1.85−1.97 (m, 1 H), 3.27 (dd, *J* = 9.8 and 6.4 Hz, 1 H), 3.41 (dd, *J* = 9.8 and 4.2 Hz, 1 H), 3.45−3.50 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0, 17.4, 18.0, 19.6, 32.7, 33.5, 39.0, 41.4, 68.5. − $C_{16}H_{35}BrOSi$ (351.4): calcd. C 54.68, H 10.04; found C 54.63, H 10.16.

10. (3*S*,5*R*)-3,5-Dimethyl-6-(triisopropylsilyloxy)hexanenitrile (21): NaCN (0.98 g, 0.02 mol) was added to a solution of (2*R*,4*S*)-5-bromo-2,4-dimethyl-1-triisopropylsilyloxypentane (3.73 g, 10.6 mmol) in DMSO (30 mL). After stirring for 2 d at room temperature, the solution was concentrated. Water (30 mL) was added and the mixture was extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (6:1) furnished **21** (3.00 g, 95%) as a colorless oil. − $[\alpha]_D^{20}$ = +0.6 (*c* = 1.0, CH_2Cl_2, 80% *ee*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.6 Hz, 3 H), 1.02−1.10 (m, 22 H), 1.08 (d, *J* = 6.7 Hz, 3 H), 1.50 (ddd, *J* = 13.7, 6.3, and 6.3 Hz, 1 H), 1.60−1.72 (m, 1 H), 1.90−2.06 (m, 1 H), 2.16 (dd, *J* = 16.6 and 7.2 Hz, 1 H), 2.32 (dd, *J* = 16.6 and 4.9 Hz, 1 H), 3.47−3.51 (m, 2 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.9, 17.2, 17.9, 20.2, 24.4, 28.1, 33.4, 40.1, 68.3, 118.7. − $C_{17}H_{35}ONSi$ (297.6): calcd. C 68.62, H 11.86, N 4.71; found C 68.43, H 12.07, N 4.80.

11. (3*S*,5*R*)-3,5-Dimethyl-6-(triisopropylsilyloxy)hexanal (22): A solution of DIBAH (0.98 M in hexane, 1.2 mL, 1.2 mmol) was added dropwise at −78 °C to a solution of the nitrile **21** (0.30 g, 1.0 mmol) in dichloromethane (15 mL). After stirring for 1 h at −78 °C, the mixture was allowed to come to −30 °C. Ethyl acetate (1 mL) was added. After the mixture had been stirred for 10 min, saturated aqueous sodium potassium tartrate solution (15 mL) was added and the mixture was stirred for a further 1 h at room temperature. The phases, including the precipitate, were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (6:1) furnished the aldehyde **22** (0.27 g, 90%) as a colorless oil. − $[\alpha]_D^{20}$ = −2.2 (*c* = 1.0, CH_2Cl_2, 80% *ee*). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.7 Hz, 3 H), 0.97 (d, *J* = 6.3 Hz, 3 H), 1.00−1.08 (m, 22 H), 1.42 (ddd, *J* = 13.5, 6.7, and 6.7 Hz, 1 H), 1.61−1.73 (m, 1 H), 1.97−2.23 (m, 2 H), 2.32−2.45 (m, 1 H), 3.44−3.54 (m, 2 H), 9.74 (t, *J* = 2.1 Hz, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0, 17.4, 17.9, 20.8, 25.9, 33.5, 41.0, 50.9, 68.4, 203.0. − $C_{17}H_{36}O_2Si$ (300.6): calcd. C 67.94, H 12.07; found C 67.81, H 12.29.

12. (3*R*,4*S*,6*S*,8*R*)-4-Hydroxy-3,6,8-trimethyl-9-(triisopropylsilyloxy)-1-nonene (23): A solution of [(*E*)-2-butenyl](diisopinocampheyl)borane was prepared[31] from potassium *tert*-butoxide (1.12 g, 10.0 mmol), (*E*)-2-butene (1 g, 0.02 mol), *n*-butyllithium in hexane (2.17 M, 4.6 mL, 10 mmol) and (+)-(methoxy)(diisopinocampheyl)borane (1 M in diethyl ether, 12.0 mL, 12.0 mmol), derived from (−)-α-pinene and $BF_3{\cdot}OEt_2$ (1.90 g, 13.4 mmol). To the resulting solution was added a solution of (3*S*,5*R*)-3,5-dimethyl-6-(triisopropylsilyloxy)hexanal (**22**) (1.17 g, 3.9 mmol) in diethyl ether (2 mL) at −78 °C. After the mixture had been stirred for 3 h at this temperature, aqueous NaOH (3 M, 7.4 mL, 22 mmol) and 30% aqueous H_2O_2 (3 mL) were added. The mixture was allowed to come to room temperature and was refluxed for 1 h. Saturated aqueous $NaHCO_3$ solution (20 mL) was added, the phases were separated, and the aqueous phase was extracted with saturated aqueous $NaHCO_3$ solution (20 mL) and water (20 mL). The combined aqueous phases were extracted with *tert*-butyl methyl ether (4 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography with petroleum ether/*tert*-butyl methyl ether (9:1) followed by medium-pressure liquid chromatography furnished the homoallylic alcohol **23** (0.71 g, 51%) as a colorless oil. In the ^{1}H NMR spectra, signals of 10% of another diastereomer could be seen; this is due to the low enantiomeric excess (80%) of the starting aldehyde **22**. − $[\alpha]_D^{20}$ = −4.2 (*c* = 1.5, CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85−0.92 (m, 6 H), 1.00−1.08 (m, 25 H), 1.11−1.29 (m, 1 H), 1.35−1.49 (m, 2 H), 1.63−1.75 (m, 2 H), 2.12−2.25 (m, 1 H), 3.40−3.57 (m, 3 H), 5.05−5.12 (m, 2 H), 5.70−5.82 (m, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 16.4, 18.1, 21.4, 27.6, 33.6, 40.9, 42.5, 44.0, 68.3, 73.0, 116.1, 140.0. − $C_{21}H_{44}O_2Si$ (356.7): calcd. C 70.72, H 12.43; found C 70.64, H 12.45.

13. (2*R*,3*S*,5*S*,7*R*)-1,3-Dihydroxy-2,5,7-trimethyl-8-(triisopropylsilyloxy)octane (24): A stream of ozone in oxygen was passed at −78 °C through a solution of **23** (294 mg, 0.82 mmol) in methanol (15 mL) until the blue color of the solution persisted. Excess of ozone was purged with a stream of argon. Dimethyl sulfide (0.3 mL, 0.25 g, 4.0 mmol) was added and the mixture was stirred for 1 h at room temperature. The mixture was concentrated in vacuo and the residue was taken up in ethanol (15 mL). $NaBH_4$ (0.57 g) was added at 0 °C, the mixture was stirred for 12 h, and water (20 mL) and KOH (1.0 g) were added. The resulting solution was extracted with dichloromethane (3 × 30 mL). The combined organic phases were washed with saturated aqueous NH_4Cl solution (10 mL), dried (Na_2SO_4), and concentrated. Flash chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (1:1) furnished the diol **24** (0.28 g, 94%) as a colorless oil. − $[\alpha]_D^{20}$ = −27.3 (*c* = 1.1, CH_2Cl_2). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (d, *J* = 7.0 Hz, 3 H), 0.91 (d, *J* = 6.7 Hz, 3 H), 0.94 (d, *J* = 6.7 Hz, 3 H), 1.03−1.11 (m, 23 H), 1.44 (ddd, *J* = 16.1, 9.0, and 5.3 Hz, 1 H), 1.52−1.59 (m, 2 H), 1.64−1.74 (m, 2 H), 3.43−3.78 (m, 7 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.1, 14.1, 18.1, 18.4, 21.5, 27.2, 33.3, 40.0, 40.4, 43.5, 67.5, 68.1, 75.4. − $C_{20}H_{44}O_3Si$ (360.7): calcd. C 66.61, H 12.30; found C 66.68, H 12.41.

14. (4*S*,5*R*,2′*S*,4′*R*)-4-[2′,4′-Dimethyl-5′-(triisopropylsilyloxy)pentyl]-2,2,5-trimethyl-1,3-dioxane (25): The diol **24** (174 mg, 0.48 mmol) and 2,2-dimethoxypropane (0.6 mL, 5 mmol) were dissolved in dichloromethane (5 mL). Pyridinium *p*-toluenesulfonate (50 mg) was added and the mixture was stirred for 12 h. Water (10 mL) was added, the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue with petroleum ether/*tert*-butyl methyl ether (6:1) furnished compound **25** (135 mg, 71%) as a colorless oil. − $[\alpha]_D^{20}$ = −27.1 (*c* = 2.1, CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.70 (d, *J* = 6.7 Hz, 3 H), 0.91 (d, *J* = 6.7 Hz, 3 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 0.82−0.90 (m, 1 H), 1.01−1.10 (m, 22 H), 1.21 (ddd, *J* = 14.2, 9.4, and 5.2 Hz, 1 H), 1.34 (s, 3 H), 1.40 (s, 3 H), 1.43 (ddd, *J* = 8.3, 2.4, and 10.8 Hz, 1 H), 1.50−1.62, (m, 1 H), 1.64−1.79 (m, 2 H), 3.30 (dd, *J* = 9.5 and 7.3 Hz, 1 H), 3.37−3.75 (m, 2 H), 3.59 (dd, *J* = 9.5 and 5.1 Hz, 1 H), 3.66 (dd, *J* = 11.6 and 5.2 Hz, 1 H). − ^{13} C NMR (125 MHz, $CDCl_3$): δ = 12.1, 12.8, 18.1, 18.3, 19.1, 21.7, 27.0, 29.8, 33.8, 34.8, 40.7, 41.3, 66.3, 68.6, 73.3, 98.0. − $C_{23}H_{48}O_3Si$ (400.7): calcd. C 68.94, H 12.07; found C 69.06, H 12.09.

15. (4*S*,5*R*,2′*S*,4′*R*)-4-(5′-Hydroxy-2′,4′-dimethylpentyl)-2,2,5-trimethyl-1,3-dioxane (17): Tetrabutylammonium fluoride·3 H_2O (0.38 g, 1.2 mmol), was added to a solution of dioxane **25** (55 mg, 0.14 mmol) in THF (5 mL). Molecular sieves (4 Å) was added and the mixture was stirred for 4 h. The mixture was filtered and the filtrate was concentrated. The residue was taken up in dichloromethane, Al_2O_3 (neutral, 1 g) was added, and the solvents were removed in vacuo. The material was placed on a flash chromatography column. Elution with petroleum ether/*tert*-butyl methyl ether (3:1) furnished the alcohol **17** (34 mg, 100%) as a colorless oil. − $[\alpha]_D^{20}$ = +72.7 (*c* = 1.1, CH_2Cl_2). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.71 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.6 Hz, 3 H), 0.91 (d, *J* = 6.7 Hz, 3 H), 0.81−1.07 (m, 2 H), 1.30−1.45 (m, 2 H), 1.36 (s, 3 H), 1.40 (s, 3 H), 1.46−1.60 (m, 1 H), 1.65−1.80 (m, 2 H), 2.45 (broad s, 1 H), 3.40−3.56 (m, 4 H), 3.66 (dd, *J* = 11.7 and 5.1 Hz, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.7, 18.3, 19.0, 21.4, 26.5, 29.7, 33.0, 34.9, 39.5, 40.7, 66.2, 67.7, 72.8, 98.2. − The material was characterized only by the spectroscopic data.

16. (3*S*,4*R*,6*S*,8*R*)-4-Hydroxy-3,6,8-trimethyl-9-(triisopropylsilyloxy)-1-nonene (27): A solution of [(*E*)-2-butenyl](diisopinocampheyl)borane was prepared[31] from potassium *tert*-butoxide (0.56 g g, 5.0 mmol), (*E*)-2-butene (1 g, 0.02 mol), *n*-butyllithium in hexane (2.17 M, 2.3 mL, 5 mmol) and (−)-(methoxy)(diisopinocampheyl)-borane (1 M in diethyl ether, 6.0 mL, 6.0 mmol) derived from (+)-α-pinene and BF_3·OEt_2 (0.95 g, 6.7 mmol). To the resulting solution, at −78 °C, was added slowly a solution of **22** (0.28 g, 0.9 mmol) in diethyl ether (2 mL). After the mixture had been stirred for 3 h at −78 °C, aqueous NaOH solution (3 M, 3.7 mL, 11 mmol) and 30% aqueous H_2O_2 (1.5 mL) were added. The mixture was allowed to reach room temperature and was refluxed for 1 h. Saturated aqueous $NaHCO_3$ solution (20 mL) was added and the phases were separated. The organic phase was washed with saturated aqueous $NaHCO_3$ solution (20 mL) and water (20 mL). The combined aqueous phases were extracted with *tert*-butyl methyl ether (4 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated. Flash chromatography with petroleum ether/*tert*-butyl methyl ether (9:1) furnished the alcohol **27** (0.18 g, 56%) as a colorless oil. The ^{1}H NMR spectrum revealed the presence of 10% of a diastereomer, due to the use of **22** of ca. 80% *ee*. − $[\alpha]_D^{20}$ = +12.4 (*c* = 1.0, methanol). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 7.0 Hz, 3 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 1.02 (d, *J* = 6.9 Hz, 3 H), 1.06 (s, 21 H), 0.98−1.50 (m, 4 H), 1.69−1.80 (m, 2 H), 2.15−2.20 (m, 1 H), 3.40−3.57 (m, 4 H), 5.06−5.12 (m, 2 H), 5.69−5.81 (m, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0, 16.1, 17.5, 18.0, 20.1, 26.7, 33.4, 41.5, 42.1, 44.9, 68.7, 72.2, 116.0, 140.4. − $C_{21}H_{44}O_2Si$ (356.7): calcd. C 70.72, H 12.43; found C 70.44, H 12.64.

17. (2*S*,3*R*,5*S*,7*R*)-1,3-Dihydroxy-2,5,7-trimethyl-8-(triisopropylsilyloxy)octane: The alkene **27** (294 mg, 0.82 mmol) was converted into the diol (285 mg, 96%) as described for compound **24**. − $[\alpha]_D^{20}$ = +23.9 (*c* = 1.0, CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.7 Hz, 3 H), 0.93 (m, 6 H), 1.06 (s, 21 H), 1.04−1.56 (m, 4 H), 1.68−1.80 (m, 2 H), 1.88−2.04 (m, 1 H), 3.42−3.69 (m, 6 H), 3.93 (ddd, *J* = 10.9, 8.5, and 4.5 Hz, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 13.0, 17.4, 18.1, 20.0, 25.8, 33.4, 36.4, 41.9, 42.0, 68.2, 68.7, 75.7. − $C_{20}H_{44}O_3Si$ (360.7): calcd. C 66.61, H 12.30; found C 66.41, H 12.40.

18. (4*R*,5*S*,2′*S*,4′*R*)-4-[2′,4′-Dimethyl-5′-(triisopropylsilyloxy)pentyl]-2,2,5-trimethyl-1,3-dioxane: The diol described above (60 mg, 0.17 mmol) was converted into the dioxane as described for compound **25** to give 61 mg (88%) of the acetonide as a colorless oil. − $[\alpha]_D^{20}$ = +18.6 (*c* = 1.4, methanol). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.70 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.6 Hz, 3 H), 0.89 (d, *J* = 6.7 Hz, 3 H), 1.05 (s, 21 H), 0.89−1.34 (m, 4 H), 1.35 (s, 3 H), 1.42 (s, 3 H), 1.52−1.63 (m, 1 H), 1.69−1.73 (m, 1 H), 1.78−1.85 (m, 1 H), 3.41−3.53 (m, 4 H), 3.67 (dd, *J* = 11.6 and 5.1 Hz, 1 H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.0, 12.7. 17.5, 18.1, 19.0, 19.8, 25.5, 29.8, 33.3, 34.7, 40.2, 42.1, 66.3, 68.8, 72.5, 98.0. − $C_{23}H_{48}O_3Si$ (400.7): calcd. C 68.94, H. 12.07; found C 68.65, H 12.30.

19. (4*R*,5*S*,2′*S*,4*R*′)-4-(5′-Hydroxy-2′,4′-dimethylpentyl)-2,2,5-trimethyl-1,3-dioxane (28): The product described above (68 mg, 0.17 mmol) was desilylated as described for compound **17** to give the alcohol **28** (41 mg, 100%) as a colorless oil. − $[\alpha]_D^{20}$ = +58.9 (*c* = 0.9, CH_2Cl_2). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.70 (d, *J* = 6.7 Hz, 3 H), 0.85 (d, *J* = 6.6 Hz, 3 H), 0.91 (d, *J* = 6.7 Hz, 3 H), 0.89−1.07 (m, 1 H), 1.15−1.45 (m, 3 H), 1.35 (s, 3 H), 1.41 (s, 3 H), 1.49−1.63 (m, 1 H), 1.65−1.84 (m, 2 H), 3.33−3.53 (m, 5 H), 3.67 (dd, *J* = 11.6 and 5.2 Hz, 1 H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.7, 17.1, 19.0, 20.0, 25.6, 29.7, 33.1, 34.7, 40.1, 41.9,

66.2, 68.5, 72.7, 98.1. − The material was characterized only by its spectroscopic data.

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[1] R. W. Hoffmann, B. C. Kahrs, P. Reiß, T. Trieselmann, H.-C. Stiasny, W. Massa, *Eur. J. Org. Chem.* **2001**, 1857−1864, preceding paper.
[2] R. W. Hoffmann, *Angew. Chem.* **1992**, *104*, 1147−1157; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1124−1134.
[3] S. Sykora, *Collect. Czech. Chem. Commun.* **1968**, *33*, 3514−3527.
[4] P. L. Luisi, *Naturwiss.* **1977**, *64*, 569−574.
[5] W. C. Still, D. Cai, D. Lee, P. Hauck, A. Bernardi, A. Romero, *Lect. Heterocycl. Chem.* **1987**, *9*, S33−S42.
[6] G. Quinkert; E. Egert; C. Griesinger, *Aspekte der Organischen Chemie*, VCH, **1995**, vol. 1, p. 131.
[7] R. W. Hoffmann, R. Göttlich, *Liebigs Ann./Recueil* **1997**, 2103−2111.
[8] R. W. Hoffmann, M. Stahl, U. Schopfer, G. Frenking, *Chem. Eur. J.* **1998**, *4*, 559−566.
[9] S. Pucci, M. Aglietto, P. L. Luisi, *J. Am. Chem. Soc.* **1967**, *89*, 2787−2788.
[10] R. W. Alder, C. M. Maunder, A. G. Orpen, *Tetrahedron Lett.* **1990**, *31*, 6717−6720.
[11] R. W. Alder, P. R. Allen, D. Hnyk, D. W. H. Rankin, H. E. Robertson, B. A. Smart, R. J. Gillespie, I. Bytheway, *J. Org. Chem.* **1999**, *64*, 4226−4232.
[12] S. Cauwberghs, P. J. De Clercq, *Tetrahedron Lett.* **1988**, *29*, 2493−2496.
[13] F. DeCorte, F. Nuyttens, S. Cauwbergs, P. DeClercq, *Tetrahedron Lett.* **1993**, *34*, 1831−1832.
[14] G. Natta, P. Corradini, *J. Polym. Sci.* **1959**, *39*, 29−46.
[15] R. J. M. Nolte, *Chem. Soc. Rev.* **1994**, *23*, 11−19.
[16] Y. Okamoto, T. Nakano, *Chem. Rev.* **1994**, *94*, 349−372.
[17] M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, J. V. Selinger, *Angew. Chem.* **1999**, *111*, 3328−3345; *Angew. Chem. Int. Ed.* **1999**, *38*, 3138−3154.
[18] M. M. Green, N. C. Peterson, T. Sato, A. Teramoto, R. Cook, S. Lifson, *Science* **1995**, *268*, 1860−1866.
[19] D. S. Schlitzer, B. M. Novak, *J. Am. Chem. Soc.* **1998**, *120*, 2196−2197.
[20] R. Nomura, Y. Fukushima, H. Nakako, T. Masuda, *J. Am. Chem. Soc.* **2000**, *122*, 8830−8836.
[21] K. Obata, C. Kabuto, M. Kira, *J. Am. Chem. Soc.* **1997**, *119*, 11345−11346.
[22] G. Pino, G. P. Lorenzi, *J. Am. Chem. Soc.* **1960**, *82*, 4745−4747.
[23] W. J. Bailey, E. T. Yates, *J. Org. Chem.* **1960**, *25*, 1800−1804.
[24] P. L. Luisi, O. Bonsignori, *J. Chem. Phys.* **1972**, *56*, 4298−4302.
[25] C. DeRosa, D. Capitani, S. Cosco, *Macromolecules* **1997**, *30*, 8322−8331.
[26] R. W. Hoffmann, *Angew. Chem.* **2000**, *112*, 2134−2150; *Angew. Chem. Int. Ed.* **2000**, *39*, 2054−2070.
[27] K. Mori, S. Kuwahara, *Tetrahedron* **1986**, *42*, 5545−5550.
[28] Y.-F. Wang, C.-S. Chen, G. Girdaukas, C. J. Sih, *J. Am. Chem. Soc.* **1984**, *106*, 3695−3696.
[29] K. Tsuji, Y. Terao, K. Achiwa, *Tetrahedron Lett.* **1989**, *30*, 6189−6192.
[30] J. C. Anderson, S. V. Ley, S. P. Marsden, *Tetrahedron Lett.* **1994**, *35*, 2087−2090.
[31] H. C. Brown, K. S. Bhat, R. S. Randad, *J. Org. Chem.* **1989**, *54*, 1570−1576.
[32] T. Fäcke, S. Berger, *Magn. Reson. Chem.* **1995**, *33*, 144−148.
[33] Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-157284. Copies of the data can be obtained free of charge on application to CCDC,12 Union Road, Cambridge, CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]
[34] K. Bowden, I. M. Heilbron, E. R. H. Jones, B. C. L. Weedon, *J. Chem. Soc.* **1946**, 39−45.

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