

215. Determination of the Absolute Configuration of Dimethyl (2*S*,3*S*)-2-Allyl-3-hydroxyglutarate: A Chiral Building Block for Preparing Branched-Chain Nucleoside Analogues

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A yeast-catalyzed reduction of dimethyl (2*S*,3*S*)-2-allyl-3-hydroxyglutarate is the key step in the preparation of bis-tomo, branched-chain nucleoside analogues. To establish unambiguously the stereochemical course of the microbial reaction, the product has been converted to a derivative esterified with camphanoyl chloride, and a crystal structure of the derivative solved.

Introduction. — We have been interested for some time in the synthesis of enantiomerically pure, branched-chain nucleosides as building blocks for the synthesis of oligonucleotide analogues bearing dimethylenesulfone linking groups replacing the phosphodiester linkages found in natural oligonucleotides [1–2]. These are potential 'antisense' oligonucleotide analogues sought for their ability to block the translation of mRNA molecules with sequence specificity [3–6]. One potentially attractive route to these molecules (*Scheme 1*) starts with an ester of 3-oxoglutaric acid, and uses non-fermenting yeast in the first step to yield an enantiomerically enriched intermediate.

Yeast is often used to reduce β -keto esters to prepare functionalized chiral building blocks in synthesis [7–10]. However, because yeast contains enzymes with differing stereospecificities that reduce such substrates, it is difficult to predict in advance the absolute configurations of the reduced products. For example, it was reported that although the prediction according to *Prelog's* rule [11] would give the (*S*)-configuration for γ - and δ -hydroxy acids obtained by yeast reduction, the compounds were found to have (*R*)-configuration [12]. Furthermore, *Sitt* and coworkers have proposed a model to predict the absolute configuration of reduction product α -substituted β -keto ester [13]. This model cannot be used with esters of 3-oxoglutaric acid (such as in *Scheme 1*) because of the two different β -keto ester moieties in the substrate, either of which could be the 'reference' ester group in the model.

Thus, before implementing the route, it was essential to obtain an unambiguous proof of the absolute configuration of the reduction product. We report such an analysis involving the correlation of dimethyl (2*S*,3*S*)-2-allyl-3-hydroxyglutarate (**1**) produced by yeast-mediated reduction of the corresponding ketone and a derivative whose camphanoyl derivative yielded suitable crystals.

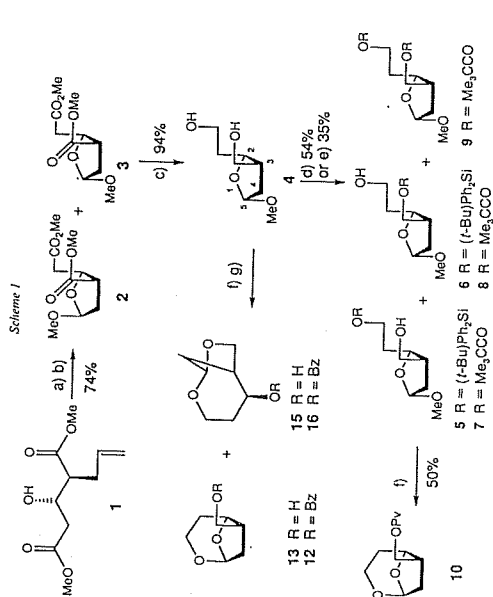
Results. — Dimethyl 2-allyl-3-oxoglutarate was prepared by allylation of the dimethyl 3-oxoglutarate using MeONa as a base in MeOH. This gave a mixture of monoallylated product, 2,4-diallylated product, and starting material in a ratio of 1:1.5:1. This mixture

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was used directly in the yeast-reduction step, yielding **1** in 44% yield. The ratio of **1** to its enantiomer was in excess of 96:4, determined by ¹H-NMR spectroscopy in the presence of the chiral shift reagent [Eu(flo)]₃ and by chiral-phase GC. The ratio **1** to its diastereoisomer (presumably with the (2*R*,3*S*)-configuration based on precedents with related compounds) was 94:6 (GC/MS) [14].

The enantiomerically enriched 3-hydroxy ester **1** was then employed in the synthesis of the branched-chain sugar analogues (Scheme 1). Ozonolysis of **1** in MeOH at low temperature followed by reduction with Me-S yielded a mixture of hemiacetals, which were treated at reflux in the same solution with dry cation-exchange resin (Dowex 50W X8, H⁺ form) to give two epimeric acetals in a ratio of 6:1. The minor isomer was isolated in crystalline form from Et₂O/pentane; the major isomer was isolated in pure form as an oil by chromatography of the mother liquor. Absolute configurations at the acetal centers of **2** and **3** were not assigned. The combined yield of isolated compounds was 74%.

Reduction of the major anomer with LiAlH₄ afforded diol **4** in 94% yield. A variety of experimental conditions using sterically demanding protecting groups where then investigated in an effort to differentiate the two OH groups of **4**. (*tert*-Butyl)dimethylsilyl chloride, dimethoxytriethyl chloride, and triethyl chloride each provided only very low yields of the corresponding monoprotected compounds. With (*i*-Bu)Ph₂SiCl, a 3:1 mixture of monoprotected compounds **5** and **6** was obtained in 35% combined yield [15]. The



a) O₃, MeOH, -78°; SMes, b) Dowex, reflux, Et₂O, r.t.; d) Me₃CCOCl, pyridine; e) (*i*-Bu)Ph₂SiCl₃, imidazole, CH₂Cl₂; f) Dowex, MeCN, reflux; g) BzCl, pyridine.

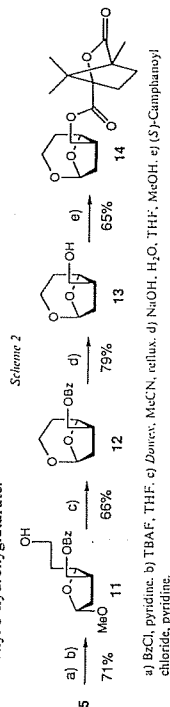
predominant isomer was assigned structure **5** by correlation to the monobenzoyl compound **11**, whose ¹H-NMR spectrum was readily assigned. Sequential treatment of **5** with benzoyl chloride and Bu₄N⁺F⁻ under standard conditions gave **11** in 71% yield (two steps; Scheme 2). The CH₂OBz ¹H-NMR signals of **11**, identified by their downfield shifts, were both of double doublet multiplicity (4.22 and 4.36 ppm), confirming the assignment of structures to **5** and **6**.

Slow addition of pivaloyl chloride to **4** in pyridine at 0° afforded an inseparable 6:4:1 (GC/MS) mixture **7**:**8** in 53% yield, together with the diprotected derivative **9**, in 17% yield [16]. The structures of **7** and **8** were assigned from the chemical shifts of the CH₂OH ¹H-NMR signals of the major isomer, which were themselves assigned based on their multiplicities. When the mixture of **7** and **8** was treated with dry cation-exchange resin (Dowex 50W X8, H⁺) in refluxing MeCN, the fully protected branched-sugar analog **10** was obtained as a white powder in 50% yield. Since no other products were isolated from the Dowex treatment, an acyl-group migration must have taken place in **7** prior to cyclization (Scheme 1).

Another set of mono- and diprotected branched-chain sugar analogues was obtained from diol **4** (Scheme 1). Treatment of **4** with cation-exchange resin (Dowex 50W X8, H⁺) in refluxing MeCN afforded an inseparable mixture of only **13** and solid **15**. When the mixture was gently swirled with Et₂O and the solvent then removed, a pure portion of **15** crystallized. The OH groups of this mixture were protected with benzoyl chloride to afford **12** (15% yield, two steps) and **16** (56% yield, two steps), which were separated by flash chromatography. The major product from benzoylation was then hydrolyzed and gave a compound whose NMR spectra (¹H and ¹³C) were identical to those of pure **15**. The ¹H-NMR chemical shifts of the H-C(5) signals, which appear at 4.05 ppm (*m*) in **15** and at 5.31 ppm (*dd*) in **16**, are particularly useful for structure assignment (Scheme 1).

Heating **11** in MeCN in the presence of cation-exchange resin (Dowex 50W X8, H⁺) gave dioxabicyclooctane **12** in 66% yield, which in turn was hydrolyzed to the alcohol **13** (Scheme 2).

Although the reactions of **1**, **11**, and **15** with (-)-(1*S*)-camphanoyl chloride and (+)-camphorsulfonyl chloride gave the expected ester and sulfonates in good yields, neither derivative proved to be convenient for crystallographic analyses. Finally, ester **14** (Scheme 2), formed by reaction of alcohol **13** with (-)-(1*S*)-camphanoyl chloride, gave single crystals suitable for X-ray crystallographic studies (Fig. 1). These established the absolute configuration of the principal product of yeast reduction **1** as dimethyl (2*S*,3*S*)-2-allyl-3-hydroxyglutarate.



f) Interestingly, treatment of **9** with trimethylsilylated uracil under Vorbrüggen conditions [17] yielded a 9:1 mixture of epimers of the uridine analog in 72% yield. The structures of these isomers were not assigned.

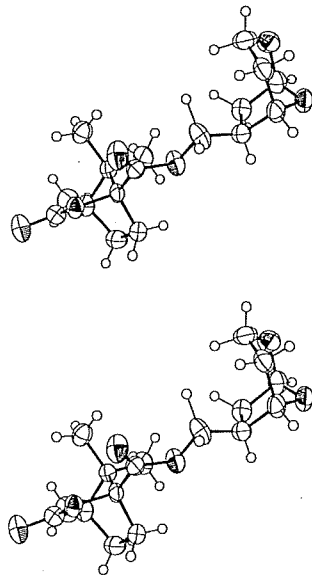


Figure 8. Stereoscopic view of 14. Vibrational ellipsoids are drawn at the 50% level using ORTEP [18]. Orthorhombic space group $P2_12_12_1$, $Z = 4$ with cell dimensions $a = 6.185(2)$, $b = 13.345(5)$, $c = 21.812(9)$ Å. Intensities were measured at room temperature with an *Enraf/Nonius CAD4* diffractometer equipped with a graphite monochromator ($\text{MoK}\alpha$, $\lambda = 0.7107$ Å). Of the 1693 independent reflections ($\theta \leq 25^\circ$), 824 with $I > 3\sigma(I)$ were used in the refinement. The structure was solved by direct methods with SHELXS-86 [19], and refined by full-matrix least-squares analysis [20]. Non-hydrogen atoms were refined anisotropically. The positions of the H-atoms were calculated and refined isotropically in the final least-squares cycles. The weighting scheme used was $w(F)^2$. The refinement converged at $R = 0.032$, $R_w = 0.038$. Atomic positional and anisotropic displacement parameters for the non-H atoms are deposited with the Cambridge Crystallographic Data Centre, Cambridge, England.

In summary, baker's yeast mediates a reduction of dimethyl 2-allyl-3-oxoglutarate gave dimethyl (2S,3S)-2-allyl-3-hydroxyglutarate. Further, the chiral building block thus obtained can be used in the synthesis of branched-chain sugar and nucleoside analogues.

Experimental Part

General. Experiments requiring anhydrous conditions were performed under Ar. Reactions were done at r.t. unless otherwise indicated. Solvents were *Fisher*, p.a., and were used without purification unless mentioned otherwise. THF and Et₂O were distilled from $\text{K}_2\text{S}_2\text{O}_8$ and MeCN was distilled from P_2O_5 . M.p.: *Büchi 810* melting-point apparatus, not corrected. Optical rotations: *Perkin-Elmer 247* polarimeter at r.t. IR: *Perkin-Elmer 993* spectrophotometer. TLC: *Merk* silica gel *F₂₅₄* precoated plates; spots visualized by dipping the plates in a Ce-Mo staining reagent. Column chromatography: *Falco* silica gel 60, mesh size 0.040–0.063. As cation-exchange resin, *Dowex MB3* (H⁺ form) was used. Anal. GC: *HP GC 5710A* with mass-spectral detector *5710B*. ¹H- and ¹³C-NMR: *Varian XL 300*, *Varian EM-300*, or *Varian XL 200* spectrometer using DEPT for determination of the H substitution, all δ values in ppm relative to TMS and J in Hz. MS: *Hitachi-Perkin-Elmer RM U-GM*.

(2S,3S,5S)-5-Methoxy-3-(methoxycarbonyl)-2-(methoxycarbonylmethyl)tetrahydrofuran (7) and (2S,3S,5R)-5-Methoxy-3-(methoxycarbonyl)-2-(methoxycarbonylmethyl)tetrahydrofuran (3). A soln. of 1 (7.5 g, 34.4 mmol) in MeOH (200 ml) was cooled to -78°C and treated with a stream of O₂ until a blue color persisted (2 h). The excess O₂ was then removed with a stream of dry N₂ (30 min). Me₂S (10 ml, 136 mmol) was added, and the soln. stirred under Ar until no further peroxide was found (12 h). This mixture was refluxed with cation-exchange resin (*Dowex 50W X8*, H⁺; 0.5 g) under open air (5 h). The resin was removed by filtration, and the solvents were removed *in vacuo*. GC/MS of the crude product showed a ratio of 1:6 for 2S:3. A large quantity of 2 could be separated by crystallization from Et₂O/pentane. The residue was chromatographed (Et₂O/hexane 5:3) to give 2

(840 mg, 3.62 mmol, combined with that from crystallization) and 3 (5.06 g, 21.8 mmol) in 74% yield (for two steps). Compound 2 was crystallized from Et₂O/pentane.

Data of 2: *r*: 1.44, *b*: 5.78 (6 h) = 451.8 ($\epsilon = 2.4$, CHCl₃); IR (CHCl₃): 3005, 2950, 1740, 1439, 1035. ¹H-NMR (CDCl₃, 400 MHz): 2.3–1.5 (m, 2 H-C(6)), 2.37 (dd, *J* = 5.1, 15.7, 1 H, CH-C(2)), 2.73 (dd, *J* = 8.8, 15.7, 1 H, CH-C(2)), 3.29 (dd, *J* = 7.8, 9.3, H-C(5)), 3.36 (s, MeO); 3.49 (s, CO₂Me), 3.71 (s, CO₂Me), 4.78 (dd, *J* = 5.5, 7.8, 8.8, H-C(3)), 5.05 (dd, *J* = 3.9, 5.8, H-C(3)). ¹³C-NMR (CDCl₃, 100 MHz): 171.6 (s); 171.5 (s); 105.8 (d); 76.1 (d); 55.7 (d); 52.6 (d); 37.7 (t); 36.7 (t); 35.2 (t); 34.7 (t); 34.5 (t); 34.3 (t); 34.1 (t); 33.9 (t); 33.7 (t); 33.5 (t); 33.3 (t); 33.1 (t); 32.9 (t); 32.7 (t); 32.5 (t); 32.3 (t); 32.1 (t); 31.9 (t); 31.7 (t); 31.5 (t); 31.3 (t); 31.1 (t); 30.9 (t); 30.7 (t); 30.5 (t); 30.3 (t); 30.1 (t); 29.9 (t); 29.7 (t); 29.5 (t); 29.3 (t); 29.1 (t); 28.9 (t); 28.7 (t); 28.5 (t); 28.3 (t); 28.1 (t); 27.9 (t); 27.7 (t); 27.5 (t); 27.3 (t); 27.1 (t); 26.9 (t); 26.7 (t); 26.5 (t); 26.3 (t); 26.1 (t); 25.9 (t); 25.7 (t); 25.5 (t); 25.3 (t); 25.1 (t); 24.9 (t); 24.7 (t); 24.5 (t); 24.3 (t); 24.1 (t); 23.9 (t); 23.7 (t); 23.5 (t); 23.3 (t); 23.1 (t); 22.9 (t); 22.7 (t); 22.5 (t); 22.3 (t); 22.1 (t); 21.9 (t); 21.7 (t); 21.5 (t); 21.3 (t); 21.1 (t); 20.9 (t); 20.7 (t); 20.5 (t); 20.3 (t); 20.1 (t); 19.9 (t); 19.7 (t); 19.5 (t); 19.3 (t); 19.1 (t); 18.9 (t); 18.7 (t); 18.5 (t); 18.3 (t); 18.1 (t); 17.9 (t); 17.7 (t); 17.5 (t); 17.3 (t); 17.1 (t); 16.9 (t); 16.7 (t); 16.5 (t); 16.3 (t); 16.1 (t); 15.9 (t); 15.7 (t); 15.5 (t); 15.3 (t); 15.1 (t); 14.9 (t); 14.7 (t); 14.5 (t); 14.3 (t); 14.1 (t); 13.9 (t); 13.7 (t); 13.5 (t); 13.3 (t); 13.1 (t); 12.9 (t); 12.7 (t); 12.5 (t); 12.3 (t); 12.1 (t); 11.9 (t); 11.7 (t); 11.5 (t); 11.3 (t); 11.1 (t); 10.9 (t); 10.7 (t); 10.5 (t); 10.3 (t); 10.1 (t); 9.9 (t); 9.7 (t); 9.5 (t); 9.3 (t); 9.1 (t); 8.9 (t); 8.7 (t); 8.5 (t); 8.3 (t); 8.1 (t); 7.9 (t); 7.7 (t); 7.5 (t); 7.3 (t); 7.1 (t); 6.9 (t); 6.7 (t); 6.5 (t); 6.3 (t); 6.1 (t); 5.9 (t); 5.7 (t); 5.5 (t); 5.3 (t); 5.1 (t); 4.9 (t); 4.7 (t); 4.5 (t); 4.3 (t); 4.1 (t); 3.9 (t); 3.7 (t); 3.5 (t); 3.3 (t); 3.1 (t); 2.9 (t); 2.7 (t); 2.5 (t); 2.3 (t); 2.1 (t); 1.9 (t); 1.7 (t); 1.5 (t); 1.3 (t); 1.1 (t); 0.9 (t); 0.7 (t); 0.5 (t); 0.3 (t); 0.1 (t).

Data of 3: *r*: 1.6, *b*: 5.78 (6 h) = 104.5 ($\epsilon = 2.0$, CHCl₃); IR (CHCl₃): 3005, 2960, 1745, 1440, 1106, 1035. ¹H-NMR (CDCl₃, 400 MHz): 2.06 (dd, *J* = 1.7, 8.2, 13.5, H-C(4)), 2.46 (dd, *J* = 5.3, 6.7, 13.5, H-C(4)), 2.50–2.65 (m, CH₂-C(2)), 3.31–3.37 (m, H-C(3)), 3.34 (s, MeO); 3.68 (s, CO₂Me); 3.71 (s, CO₂Me); 4.70 (dd, *J* = 6.3, 7.7, H-C(5)); 5.12 (dd, *J* = 1.7, 5.3, H-C(5)). ¹³C-NMR (CDCl₃, 100 MHz): 172.9 (s); 171.0 (s); 164.4 (s); 74.7 (d); 54.9 (d); 51.9 (d); 51.8 (d); 45.2 (d); 36.6 (d); 35.9 (d); MS: 231 (*M* - 17)⁺, 217, 201, 169, 151, 141, 127, 99, 81, 59, 41, 29. Anal. calc. for C₁₀H₁₆O₅ (232.23): C 51.72, H 6.94, O 41.34; found: C 51.77, H 7.10, O 40.88.

(2S,3R,5R)-2-(1-Hydroxyethyl)-3-(hydroxymethyl)-5-methoxytetrahydrofuran (6). Diester 3 (5 g, 21.5 mmol) in Et₂O (50 ml) was added dropwise to a suspension of LiAlH₄ (1.650 g, 44 mmol, 2 equiv.) in Et₂O (50 ml) at r.t. under Ar. After being stirred overnight, the soln. was cooled to -78°C and diluted dropwise with sat. Na₂SO₄ (6 ml). A white precipitate formed. MeOH/CH₂Cl₂ (200 ml, 5/95) was added, and the mixture was filtered through *Celite*. The white was extracted (30 min) with MeOH/CH₂Cl₂ (100 ml, 5/95), stirred, and removed by filtration. The org. fractions were combined and the solvents evaporated. The residue was dissolved in CH₂Cl₂ (200 ml), decanted into another flask, and the solvents were evaporated. The resulting product was taken up in Et₂O (100 ml) and decanted. The solvent was removed *in vacuo* to afford 4 (3.556 g, 94% as a yellowish oil, *b*_p = 116.7 ($\epsilon = 3.3$, CHCl₃), IR (CHCl₃): 3620, 3000, 2940, 1450, 1098, 1048. ¹H-NMR (CDCl₃): 1.76 (br. s, OH); 1.78–2.09 (m, 2H-C(4)); 2.47–2.58 (m, H-C(3)); 2.69–2.79 (br. s, OH); 3.35 (s, MeO); 3.58 (dd, *J* = 10, 5.9, 1 H, CH₂-C(2)); 3.68 (dd, *J* = 7.2, 10.2, 1 H, CH-C(3)); 3.78–3.89 (m, C(2)-CH₂OH); 4.27 (dd, *J* = 4.7, 6.1, 9.0, H-C(5)); 5.07 (dd, *J* = 2.5, 5.3, H-C(5)). ¹³C-NMR (CDCl₃): 104.0 (d); 78.8 (d); 62.2 (t); 61.7 (t); 54.9 (d); 42.9 (d); 36.1 (t); 32.3 (t); MS: 175 (*M* - 17)⁺, 157, 145, 127, 118, 99, 81, 69, 55, 41, 29, 15.

(2S,3R,5R)-2-(1-(tert-Butyl)diethylphosphoryl)ethyl)-2-(2-hydroxyethyl)-5-methoxytetrahydrofuran (6) and **(2S,3R,5R)-2-(1-(tert-Butyl)diethylphosphoryl)ethyl)-2-(2-hydroxyethyl)-5-methoxytetrahydrofuran (6)** (*r*: 1.3, *b*: 4.77 mmol) was added dropwise at 0° over a period of 3 h to a soln. of 4 (720 mg, 4.09 mmol) and imidazole (52 mg, 8.08 mmol) in CH₂Cl₂ (20 ml). The mixture was warmed to r.t. and stirred overnight. The soln. was diluted with AcOEt (100 ml), washed with sat. NaHCO₃ (30 ml) and sat. NaCl (50 ml). The org. layer was dried (MgSO₄) and the solvents evaporated *in vacuo*. The residue was chromatographed (CH₂Cl₂/MeCN 9:1) to give 5 (450 mg, 1.08 mmol) and 6 (150 mg, 0.36 mmol) in a ratio of 3:1 in 35% (combined yield).

Data of 5: IR (CHCl₃): 3660, 3440, 3000, 2960, 2935, 2860, 1520, 1430, 1390, 1360, 1035, 750. ¹H-NMR (CDCl₃, 300 MHz): 1.05 (s, t-Bu); 1.68–2.07 (2m, 2 H-C(4)); CH₂-C(2), OH); 2.37–2.45 (m, H-C(3)); 3.32 (s, MeO); 3.51–3.66 (m, CH₂-C(3)); 3.76–3.87 (m, CO-CH₂OH); 4.25–4.31 (m, H-C(2)); 4.97 (distorted t, 127.6 (d); 103.8 (d); 75.9 (d); 62.6 (t); 54.9 (d); 42.1 (d); 36.5 (t); 32.9 (t); 26.9 (g); 19.1 (g); MS: 414 (*M*⁺), 413 (*M* - 17)⁺, 383, 365, 325, 295, 229, 183, 169, 138, 109, 91, 81, 71, 41, 29, 15.

Data of 6: ¹H-NMR (CDCl₃, 300 MHz): 1.03 (s, t-Bu); 1.73–1.93 (m, 2 H-C(4)), CH₂-C(2)); 2.35–2.72 (m, H-C(3)); 3.33 (s, MeO); 3.47–3.80 (m, CO-CH₂OH, CH₂-C(2)); 4.30 (dd, *J* = 6.5, 13.7, H-C(2)); 4.94 (dd, *J* = 2.7, 4.8, H-C(5)); 7.34–7.49 (m, 6 arom. H); 7.63–7.69 (m, 4 arom. H). ¹³C-NMR (CDCl₃): 135.9 (d); 133.8 (s); 133.8 (d); 130.1 (d); 104.4 (d); 79.7 (d); 63.4 (t); 62.5 (t); 55.1 (d); 42.7 (d); 35.8 (t); 32.7 (t); 27.0 (t); 19.4 (t).

(2S,3R,5R)-3-(Hydroxyethyl)-5-methoxy-2-(2-(methylthio)ethyl)tetrahydrofuran (7). (2S,3R,5R)-2-(1-(tert-Butyl)diethylphosphoryl)ethyl)-2-(2-hydroxyethyl)-5-methoxytetrahydrofuran (6) and (2S,3R,5R)-5-Methoxy-2-(1-(tert-Butyl)diethylphosphoryl)ethyl)-2-(2-hydroxyethyl)-5-methoxytetrahydrofuran (6) (735 mg, 6.09 mmol) was added to a soln. of 4 (1 g, 5.8 mmol) in pyridine (50 ml) over 5 h. The mixture was warmed to r.t. and stirred overnight. The soln. was diluted with AcOEt (80 ml) and extracted first with sat. NaHCO₃ (20 ml) and then with NaCl (20 ml). The org. layer was dried (MgSO₄), the solvent removed by evaporation *in vacuo*, and the remaining pyridine removed under high vacuum. The residue was chromatographed (Et₂O/hexane 3:1) to give 7 and 8 (709 mg, 3.05 mmol, 5%); in a ratio of 6:4 (GC/MS) as colorless oil, and 9 (335 mg, 0.974 mmol, 17%) as a yellow oil.

Data of 7: ¹H-NMR (CDCl₃, 300 MHz): 1.20 (s, t-Bu); 1.60–2.06 (m, OH); 2 H-C(4), CH₂-C(2)); 2.40–2.51 (m, H-C(3)); 3.33 (dd, *J* = 6.2, 10.7, 1 H, CH₂-C(3)); 3.67 (dd, *J* = 6.2, 10.7, 1 H, CH₂-C(3)); 4.14–4.29 (m, C(2)-CH₂OH, H-C(3)); 4.95 (distorted t, *J* = 3.9, 4.0, H-C(5)). ¹³C-NMR (CDCl₃):

MHz): 178.6 (d), 103.9 (d), 62.4 (t), 62.2 (t), 54.8 (t), 41.9 (d), 38.8 (s), 36.3 (t), 29.4 (t), 27.2 (t), 17.3 (CHCl₃); 3620, 3510, 2975, 1720, 1480, 1290, 1165, 1100, 1040, 960, 260 (M⁺), 258 (M - 17), 229, 127, 113, 99, 71, 57, 41, 29.

Data of 9: ν_{max} (KBr): 3460, 3000, 2900, 1720, 1530, 1287, 1160, 1035, 855, 344 (M⁺), 343 (M - 17), 211, 183, 113, 84, 57, 41, 29.

(1S,5S,6R)-6-[(1S)-camphanoxy]methyl]-2,8-dioxabicyclo[3.2.1]heptane (10). A mixture 7/8 (6.41; 206 mg, 0.735 mmol) in MeCN (20 ml) was heated at reflux in the presence of cation exchange resin (Dowex 50W X2, H⁺; 160 mg) for 4 h under open air. The cation-exchange resin (Dowex 50W X2, H⁺) was removed by filtration and the solvent evaporated. The residue was chromatographed (hexane/AcOEt 7:3) to yield 10 (83 mg, 0.373 mmol) in 50% yield as a white powder. M.p. 37°; ν_{max} (KBr): 3460, 3000, 2900, 1720, 1480, 1280, 1160, 1030, 990, 950, 850, 780 (M⁺); $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.2 (s, 3H, H-C(4)); 1.40 (dd, $J = 3.7, 13.5$, H-C(5)); 1.66, 13.7, H-C(4)); 2.23-2.43 (m, 2H, H-C(9)); 2.68-3.82 (m, 2H, H-C(3)); 3.36 (s, MeCO); 3.80-3.89 (m, H-C(2)); 4.35-4.44 (m, 2H, H-C(9)); 5.47 (d, $J = 5.4$, H-C(1)); 1.98, 127, 85, 57.

(2S,3R,4R)-3-[(1S)-camphanoxy]methyl]-2-(2-hydroxyethyl)-5-methoxytetrahydrofuran (11). Benzoyl chloride (170 mg, 1.21 mmol) was added dropwise to a solution of 5 (412 mg, 1 mmol) in pyridine (10 ml) at 0°. The solution was stirred for 30 min, diluted with AcOEt (60 ml), and washed with sat. NaHCO₃ (20 ml) and water. The high vacuum.

The crude product contaminated with ca. 10% benzoic acid was dissolved in THF (10 ml) and Bu₄NF·3 H₂O (608 mg, 193 mmol, ca. 2 equiv.) added. After 5 h, the mixture was quenched with MeOH (2 ml), 0.714 mmol) in 71.4% yield (overall) as a white powder. M.p. 33°; ν_{max} (KBr): 3620, 3530, 3000, 2960, 1720, 1450, 1315, 1275, 1100, 1065, 1030, 983, 965, 780 (M⁺); $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.78-2.17 (m, 2H, H-C(4)); 1.93 (dd, $J = 4.4, 6.4, 11.1$, H, CH₂-COO); 2.87 (dd, $J = 6.7, 13.5$, H-C(3)); 3.36 (s, MeCO); 3.80-3.89 (m, CH₂-CH₂OH); 4.22 (dd, $J = 6.8, 11.1$, H, CH₂-COO); 4.56 (dd, $J = 6.2, 11.1, 11.1$, H, CH₂-COO); 4.38-4.42 (m, H-C(2)); 5.08 (dd, $J = 2.4, 5.1$, H-C(5)); 7.41-7.63 (m, 3 arom. H); 8.01-8.06 (m, 2 arom. H); $^{13}\text{C-NMR}$ (CDCl₃, 50 MHz): 166.8 (t), 135.5 (d), 130.3 (t), 129.9 (d), 128.8 (d), 104.3 (d), 78.9 (d), 64.4 (t), 62.2 (t), 55.2 (q), 39.5 (d), 36.2 (t), 32.8 (t), 32.8 (t), 28.0 (M⁺), 249, 222, 189, 105, 84, 71, 59, 28. Anal. calc. for C₁₇H₂₄O₅ (280.32): C 64.27, H 7.19; found: C 64.27, H 7.01.

(1S,5S,6R)-6-[(1S)-camphanoxy]methyl]-2,8-dioxabicyclo[3.2.1]heptane (12). Alcohol 11 (176 mg, 0.628 mmol) was added to a solution of 12 (63 mg, 0.334 mmol) in MeOH/THF (4:5, 0.9 ml). After 15 min, pyridinium Dowex (40 mg) was added and the pH brought to 6 with HCl (0.18 ml). The cation-exchange resin (Dowex 50W X2, H⁺) was removed by filtration and the solvent evaporated. The residue was chromatographed (hexane/AcOEt 1:3) to yield 12 (103 mg, 0.415 mmol, 66%) as a colorless oil. $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.50 (dd, $J = 3.3, 14.0$, H-C(4)); 1.93 (dd, $J = 6.7, 14.0$, H-C(4)); 2.28-2.47 (m, 2H, H-C(9)); 2.80-3.01 (m, H-C(6)); 3.83-4.08 (m, 2H, H-C(3)); 4.40-4.50 (m, H-C(9)); 4.64 (dd, $J = 7.3, 11.2$, H-C(9)); 5.51 (d, $J = 5.4$, H-C(1)); 7.26-7.63 (m, 3 arom. H); 8.00-8.07 (m, 2 arom. H); $^{13}\text{C-NMR}$ (CDCl₃, 50 MHz): 166.8 (t), 132.6 (d), 130.2 (t), 129.9 (d), 128.8 (d), 99.9 (d), 75.5 (d), 63.3 (t), 58.5 (t), 39.3 (d), 32.8 (t), 26.8 (t).

(1S,5S,6R)-6-[(1S)-camphanoxy]methyl]-2,8-dioxabicyclo[3.2.1]heptane (13). NaOH (0.18, 0.30 ml, 0.03 mmol) was added to a solution of 12 (63 mg, 0.334 mmol) in MeOH/THF (4:5, 0.9 ml). After 15 min, pyridinium Dowex (40 mg) was added and the pH brought to 6 with HCl (0.18 ml). The cation-exchange resin (Dowex 50W X2, H⁺) was removed by filtration and the solvent evaporated. The residue was chromatographed (hexane/AcOEt 1:3) to yield 13 (38 mg, 0.264 mmol, 79%) as a colorless oil. $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.44-1.56 (m, H-C(4)); 1.81 (dd, $J = 6.6, 13.8$, H-C(4)); 2.22-2.42 (m, 2H, H-C(9)); 2.59-2.72 (m, H-C(6)); 3.77-4.02 (m, 2H, H-C(3)); 4.43 (distorted t, $J = 3.0$, H-C(9)); 5.5 (d, $J = 5.4$, H-C(1)); MS: 126 (M - 18), 113, 103, 96, 80, 70, 57.

(1S,5S,6R)-6-[(1S)-camphanoxy]methyl]-2,8-dioxabicyclo[3.2.1]heptane (14). (-)-6-Camphanoxy chloride (50.3 mg, 0.233 mmol) in pyridine (0.2 ml) was added dropwise to a solution of 13 (28 mg, 0.194 mmol) in pyridine (0.1 ml) at 0°. The solution was stirred overnight, diluted with AcOEt (30 ml), and washed first with sat. NaHCO₃ (10 ml) and then with sat. NaCl (10 ml). The organic layer was dried (MgSO₄), the solvent was removed by evaporation *in vacuo*, and the residual pyridine was removed under high vacuum. The residue was chromatographed (CH₂Cl₂/MeCN 9:1) to yield 14 (41 mg, 0.126 mmol) in 65% yield as a white powder. The compound recrystallized from AcOEt/pentane as needles (after one week) from which a crystal structure was obtained. M.p.

138°. $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 0.96 (s, Me); 1.06 (s, Me); 1.13 (s, Me); 1.35-1.44 (m, H-C(4)); 1.64-2.11 (m, H-C(5)); 2H-C(4), H-C(6)); 2.26-2.49 (m, 2H-C(7), H-C(9)); 2.73-2.86 (m, H-C(6)); 3.82-4.02 (m, 2H-C(3)); 4.31-4.43 (m, H-C(9)); 4.56 (dd, $J = 7.6, 11.2$, H-C(9)); 5.48 (d, $J = 5.8$, H-C(1)); $^{13}\text{C-NMR}$ (CDCl₃, 50 MHz): 178.6 (t), 168 (t), 100 (d), 91 (t), 75 (d), 63.8 (t), 58.1 (t), 54.2 (t), 54.2 (t), 39 (d), 32.3 (t), 30.5 (d), 29 (d), 26.4 (d), 17 (d), 10 (d).

(1R,4S,5S)-5-(Benzoyloxy)-2,8-dioxabicyclo[4.2.1]heptane (16). Diol 4 (124 mg, 0.704 mmol) in MeCN (20 ml) was treated as a resin with dry cation-exchange resin (Dowex 50W X2, H⁺; 80 mg) for 3 h. The cation-exchange resin (Dowex 50W X2, H⁺) was removed by filtration and the solvent was evaporated *in vacuo*. The residue was dried under high vacuum to give 87 mg of crude product. An attempt to separate the compounds at this stage failed.

When the mixture was gently stirred with Et₂O, a pure portion of 15 could be obtained. The mixture was dissolved in pyridine (5 ml), and benzoyl chloride (100 μ l, 0.868 mmol) at 0° was added dropwise. The solution was stirred for 30 min at r.t., diluted with AcOEt (30 ml), washed with sat. NaHCO₃ (10 ml) and then with sat. NaCl (10 ml). The organic layer was dried (MgSO₄), the solvent was evaporated *in vacuo*, the remaining pyridine removed under high vacuum, and the residue chromatographed (MeCN/CH₂Cl₂, 1:9) to give 15 (26 mg, 0.104 mmol) in 14.9% yield as an oil, and 16 (95 mg, 0.395 mmol) in 56% yield as a white powder.

Data of 15: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 203, 189, 175, 157, 143, 126, 105, 96, 77, 51, 41, 39, 29. Anal. calc. for C₁₇H₂₄O₄ (248.28): C 67.73, H 6.50, O 25.78; found: C 67.38, H 6.54, O 25.78.

Data of 16: M.p. 64°. $[\alpha]_D^{20} = -38.4$ (c = 1.88, CHCl₃). $^1\text{H-NMR}$ (CDCl₃, 200 MHz): 1.92-2.24 (m, H-C(9)), 2H-C(9); 2.33 (d, $J = 14.2$, H-C(9)); 2.77-2.82 (m, H-C(4)); 3.78-3.91 (m, 2H-C(3), H-C(6)); 4.05 (distorted t, $J = 12.8, 10.8$, H-C(7)); 5.31 (dd, $J = 3.8, 7.4$, H-C(5)); 5.57 (d, $J = 5.8$, H-C(1)); 7.44-7.60 (m, 3 arom. H); 8.04-8.07 (m, 2 arom. H). $^{13}\text{C-NMR}$ (CDCl₃, 75 MHz): 165.6 (t), 133.2 (d), 130.3 (d), 129.5 (d), 128.5 (d), 102.2 (d), 72.3 (d), 70.0 (t), 59.3 (t), 40.0 (t), 31.5 (t), 29.4 (t). IR (CHCl₃): 3000, 2960, 1715, 1270, 1108, 1062, 1030, 987, 948, 931, 900, 830, MS: 249 (M + 17), 248 (M⁺), 231, 2