Asymmetric Synthesis of (+)- and (–)-Streptenol A

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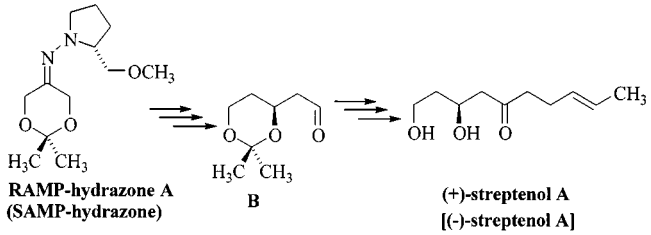
The asymmetric synthesis of (+)-streptenol A was carried out in ten steps and with high enantioselectivity (ee ≥ 96%). The key steps are the α-alkylation of 2,2-dimethyl-1,3-dioxan-5-one RAMP hydrazone **A** (1), subsequent deoxygenation and elaboration of the side chain via aldehyde **B** to furnish (+)-streptenol A in 23% overall yield. In analogy, the enantiomer (–)-streptenol A was synthesized using the corresponding SAMP hydrazone in 18% overall yield.

Introduction

(+)-Streptenol A is a secondary metabolite of several *Streptomyces* species and can be obtained by fermentation processes.[1] As the other streptenols B, C and D, (+)-streptenol A is a potent cholesterol biosynthesis inhibitor,[1c] but only (+)-streptenol A shows anti-tumor and immuno-stimulating activity.[2] In addition to these biological features, (+)-streptenol A has been employed as a versatile chiral building block in syntheses of several members of the important class of δ-lactones (e.g. both enantiomers of massoialactone and all four stereoisomers of 3-hydroxy-5-decanolide).[1b,3] During these investigations, inversion of the stereogenic center of (+)-streptenol A was a major task and was accomplished in a four-step sequence to yield (−)-streptenol A.

Stereoselective syntheses of streptenol C and D were reported in the literature.[4] The most general approach to all members of the streptenol family was developed by Blechert and Dollt and relies on 2-(2,2-dimethyl-1,3-dioxan-4-yl)-acetaldehyde (**B**) as key building block in their syntheses of (±)-streptenol B, C and D.[5] They used their strategy for an elegant asymmetric synthesis of the antipode (−)-streptenol A based on enantiomerically pure aldehyde (*R*)-**B** which was obtained in eight steps using Heathcock's monoester method.[5][6] To the best of our knowledge, an asymmetric synthesis of natural (+)-streptenol A has not been reported.



Recently, we published a protocol for the α-alkylation and deoxygenation of 2,2-dimethyl-1,3-dioxan-5-one RAMP/SAMP hydrazones **A**.[7] In view of its biological and chemical features we have chosen (+)-streptenol A and its enantiomer to demonstrate the applicability of our method in asymmetric synthesis. We envisaged that this method should allow an alternative efficient access to either (*S*)- or (*R*)-2-(2,2-dimethyl-1,3-dioxan-4-yl)acetaldehyde (**B**) depending only on the configuration of the auxiliary. A Grignard addition and subsequent oxidation should then furnish the title compounds after cleavage of the acetonide protecting group.[5] In this paper we would like to report our results on the asymmetric synthesis of (+)- and (−)-streptenol A.

Results and Discussion

The alkylation of 2,2-dimethyl-1,3-dioxan-5-one SAMP/RAMP hydrazones is a reliable tool to synthesize chiral 4-substituted 2,2-dimethyl-1,3-dioxan-5-ones in gram quantities and with high enantiomeric excess.[8] Thus, RAMP-hydrazone (*R*)-**1** was metalated at −78°C with *tert*-butyllithium in tetrahydrofuran for 2 h and the lithium aza-enolate was alkylated with 2-bromo-1-*tert*-butyldimethylsilyloxyethane at −105°C furnishing the corresponding α-alkylated hydrazone (*R*,*R*)-**2** with a diastereomeric excess of de ≥ 96% as evidenced by ^{13}C-NMR spectroscopy and GC analysis. Hydrolytic cleavage of the hydrazone with oxalic acid[9] afforded (*R*)-**3** in 95% yield (two steps) and an enantiomeric excess of ee ≥ 96%. It is worth noticing that this mild cleavage method allows for a recycling of the auxiliary.

Reduction of the carbonyl group with sodium tetrahydroborate in methanol afforded a diastereomeric mixture (de = 61%) of the corresponding alcohols (*R*,*S*/*R*)-**4** in 85% yield. Treatment of their corresponding sodium alkoxides with carbon disulfide and iodomethane gave xanthates (*R*,*S*/*R*)-**5** in 94% yield after chromatography. The Barton−McCombie deoxygenation[7] using tri-*n*-butyltin hydride in refluxing toluene furnished dioxane (*S*)-**6** in 82% yield after removal of the tin by-products by column chromatography. Deprotection of (*S*)-**6** with tetrabutylammonium fluoride (TBAF) furnished the primary alcohol (*R*)-**7** in 93% yield after chromatography. On this stage, esterification of the primary alcohol with (*S*)-Mosher chloride[10] yielded the diastereomerically pure Mosher ester (*S*,*R*)-**11** with de ≥ 96%

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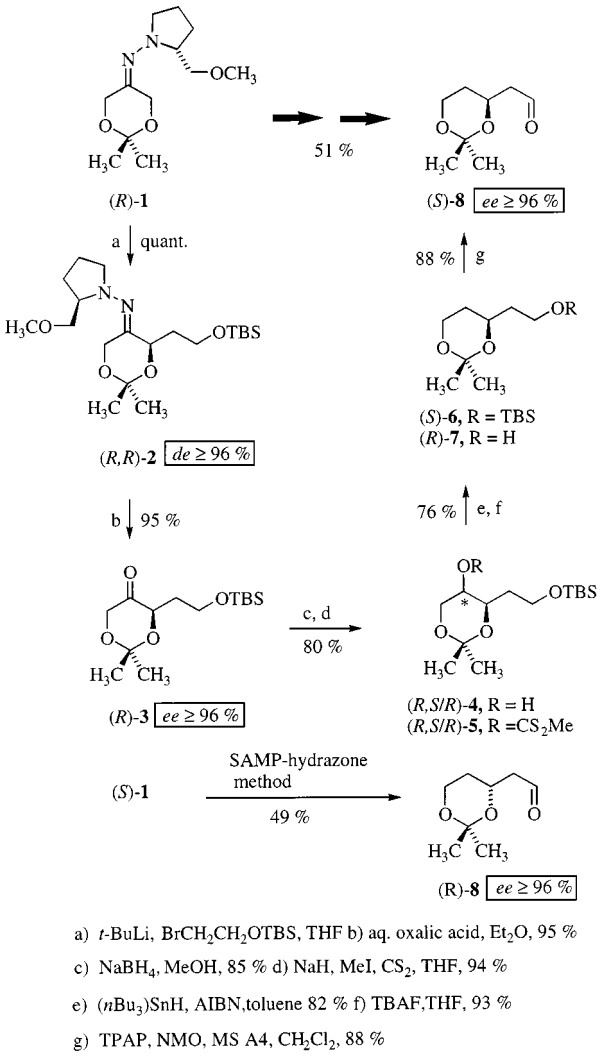
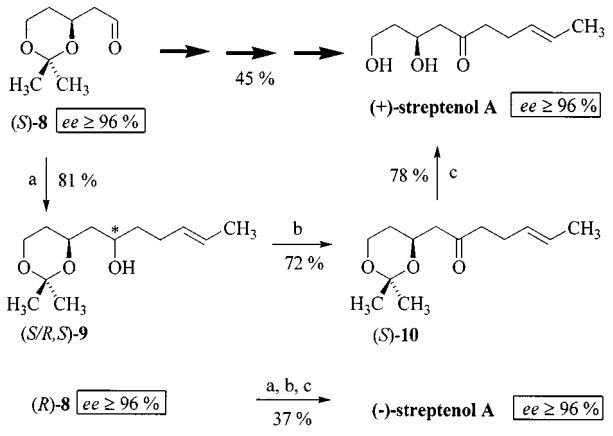


Scheme 1. Asymmetric synthesis of the aldehydes (*S*)- and (*R*)-**8**: a) *t*BuLi, $BrCH_2CH_2OTBS$, THF; b) aq. oxalic acid, Et_2O, 95%; c) $NaBH_4$, MeOH, 85%; d) NaH, MeI, CS_2, THF, 94%; e) nBu_3SnH, AIBN, toluene, 82%; f) TBAF, THF, 93%; g) TPAP, NMO, MS (4 Å), CH_2Cl_2, 88%

according to HPLC analysis revealing that no racemisation occurred. The ruthenium-catalyzed oxidation of the alcohol (*R*)-**7** with 7.5 mol-% tetrapropylammonium perruthenate (TPAP) and *N*-methylmorpholine oxide (NMO) in dichloromethane according to Ley et al.[11] gave (*S*)-2-(2,2-dimethyl-1,3-dioxan-4-yl)acetaldehyde [(*S*)-**8**] in 88% yield. This key building block of all members of the streptenol family was obtained in 51% overall yield starting from RAMP-hydrazone (*R*)-**1**. The same reaction sequence employing SAMP-hydrazone (*S*)-**1** gave aldehyde (*R*)-**8** in 49% overall yield, thus emphasizing the reliability of this approach.

With both enantiomers of aldehyde **8** in hand, we continued the synthesis sligthly modifying Blechert′s procedure.[5] The Grignard-addition of (*E*)-3-penten-1-ylmagnesium bromide to the aldehyde (*S*)-**8** in THF at 50°C furnished the diastereomeric mixture (*S*/*R*,*S*)-**9** in 81% yield. Several methods for the subsequent oxidation of (*S*/*R*,*S*)-**9**



Scheme 2. Synthesis of (+)- and (−)-streptenol A; a) Mg, (*E*)-5-bromopent-2-ene, THF; b) PCC, Celite, MS (4 Å), CH_2Cl_2; c) TFA, THF/H_2O (4:1)

to ketone (*S*)-**10** were screened. Pyridinium chlorochromate (PCC)[12] in combination with Celite and ground molecular sieves in dichloromethane was the reagent of choice giving (*S*)-**10** in 72% yield after chromatography. The isopropylidene acetal was hydrolytically cleaved in the final step with trifluoracetic acid in THF/water[13] to yield the natural product (+)-streptenol A in 78% yield. The antipode (−)-streptenol A was obtained in 37% overall yield starting from aldehyde (*R*)-**8**. The spectroscopic data (IR, ^1H, ^{13}C NMR, EI/CI-MS) of the synthetic streptenols were in accordance with the data reported in the literature.[1a,3] However, the optical rotation values of $[\alpha]_D^{23} = +21.7$ (c = 1.0, $CHCl_3$) for (+)-streptenol A and $[\alpha]_D^{23} = -21.5$ (c = 1.0, $CHCl_3$) for (−)-streptenol A are slightly lower than the published values of $[\alpha]_D = +23$ (c = 1.0, $CHCl_3$)[1a] and $[\alpha]_D = -23$ (c = 1.0, $CHCl_3$),[5] respectively. One possible explanation for this difference is the tendency of streptenol A to form varying amounts of diastereomeric hemiketals.[1a]

Conclusion

In summary, an efficient asymmetric synthesis of (+)- and (−)-streptenol A starting from commercially available 2,2-dimethyl-1,3-dioxan-5-one was carried out in ten steps and 23% or 18% overall yield, respectively. The applicability of our alkylation/deoxygenation protocol for the synthesis of polyhydroxylated compounds has been demonstrated. The configuration at the generated stereogenic centers can be controlled by either using SAMP or RAMP as chiral auxiliary, which can be recycled after cleavage with oxalic acid.

Experimental Section

General: All solvents were dried and purified prior to use. − All reactions were carried out under dry argon. − Column chromatog-

raphy: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh). − Optical rotation values: Perkin-Elmer P 241 (254 nm); solvents Merck Uvasol quality. − IR: Perkin-Elmer FT/IR 1750. − NMR: Varian VXR 300 and Gemini 300 and Innova 400, TMS as internal standard. − MS: Finnigan MAT 212 and Finnigan SSQ 7000 (70 eV). − Microanalyses: Elementar vario EL. − THF was dried by distillation from K/benzophenone under Ar. Diethyl ether and toluene were dried by distillation from Na/benzophenone under Ar. 2,2-Dimethyl-1,3-dioxan-5-one,[14] 2-bromo-1-*tert*-butyldimethylsilyloxyethane[15] and 2,2-dimethyl-1,3-dioxan-5-one RAMP/SAMP-hydrazones[8a] were prepared according to the published procedures.

(*R,R*)-4-(2-{[1-(*tert*-Butyl)-1,1-dimethylsilyl]oxy}ethyl)-2,2-dimethyl-1,3-dioxan-5-one RAMP-hydrazone [(*R,R*)-2]: 3.6 g (14.9 mmol, 1.0 equiv.) of (*R*)-**1** was dissolved in 50 mL of THF and cooled to −78°C under Ar and 10.3 mL of *tert*-butyllithium (1.6 N in pentane, 16.5 mmol, 1.1 equiv.) was slowly added. After stirring for 2 h at −78°C, the solution was cooled to −105°C and 3.9 g (16.5 mmol, 1.1 equiv.) of 2-bromo-1-*tert*-butyldimethylsilyloxyethane was added dropwise. The solution was stirred at this temperature for 4 h and then allowed to reach room temp. overnight. Then, 5 mL of an aqueous pH-7 buffer solution and 200 mL of diethyl ether were added. The organic phase was washed with water and brine, dried with $MgSO_4$ and the solvent was removed under reduced pressure to yield (*R,R*)-**2** as a yellow oil. An analytical sample was obtained by column chromatography (SiO_2; pentane/Et_2O, 2:1), yield 6.1 g (quant.). − $[\alpha]_D^{23} = -78.8$ (c = 2.0, acetone). − IR (film): $\tilde{\nu}$ = 2984 cm^{-1} (m), 2955 (s), 2930 (s), 2857 (s), 1472 (w), 1463 (m), 1450 (w), 1380 (m), 1372 (m), 1338 (w), 1255 (s), 1226 (s), 1158 (m), 1112 (s), 1091 (s), 1050 (m), 1007 (w), 972 (w), 954 (w), 940 (w), 908 (w), 894 (w), 864 (w), 835 (s), 813 (w), 777 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 3 H, SiCH_3), 0.06 (s, 3 H, SiCH_3), 0.90 [s, 9 H, C(CH_3)$_3$], 1.38 [s, 3 H, C(CH_3)$_2$], 1.39 [s, 3 H, C(CH_3)$_2$], 1.58−1.72 (m, 2 H, CH_2CH$_2$OTBS), 1.78−1.88 (m, 2 H, NCH$_2$CH_2CH$_2$), 2.00 (m, 1 H, NCH$_2$CH$_2$C*H*H), 2.20 (m, 1 H, NCH$_2$CH$_2$CH*H*), 2.40 (dd, J = 8.5 Hz, J = 8.4 Hz, 1 H, NC*H*HCH$_2$CH$_2$), 3.02 (dt, J = 8.8 Hz, J = 6.0 Hz, NCH*H*CH$_2$CH$_2$), 3.19−3.36 (m, 2 H, C*H*C*H*HOCH$_3$), 3.35 (s, 3 H, OCH_3), 3.42 (dd, J = 8.8 Hz, J = 3.6 Hz, 1 H, CHCH*H*OCH$_3$), 3.71−3.82 (m, 2 H, CH$_2$CH_2OTBS), 4.15 (dd, J = 15.7 Hz, J = 1.9 Hz, 1 H, OC*H*HCN), 4.50 (d, J = 15.7 Hz, 1 H, OCH*H*CN), 4.56 (m, 1 H, OC*H*CN). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.3 (2 × SiCH_3), 18.3 [*C*(CH$_3$)$_3$], 22.8 (NCH$_2$*C*H$_2$CH$_2$), 24.1 [2 × C(*C*H$_3$)$_2$], 25.3 [3 × C(*C*H$_3$)$_3$], 26.8 (NCH$_2$CH$_2$*C*H$_2$), 35.1 (*C*H$_2$CH$_2$OTBS), 55.4 (N*C*H$_2$CH$_2$CH$_2$), 59.0 (O*C*H$_3$), 59.9 (CH$_2$*C*H$_2$OTBS), 66.65 (*C*HCH$_2$OCH$_3$), 66.68 (O*C*H$_2$CN), 67.1 (O*C*HCN), 75.6 (CH*C*H$_2$OCH$_3$), 100.3 [*C*(CH$_3$)$_2$], 163.0 (*C*N). − MS (CI, isobutane); *m/z* (%): 401 [M^+ + 1] (100), 400 [M^+] (7), 345 (3), 344 (12), 343 (M^+ − 57, 47), 342 (3). − $C_{20}H_{40}N_2O_4Si$ (400.63): calcd. C 59.96, H 10.06, N 6.99 found C 59.56, H 10.27, N 7.33. − In analogy, alkylation of 5.7 g (23.0 mmol) of SAMP-hydrazone (*S*)-**1** afforded 11.8 g of (*S,S*)-**2** (quantitative). − $[\alpha]_D^{23} = +78.7$ (c = 2.0, acetone).

(*R*)-4-(2-{[1-(*tert*-Butyl)-1,1-dimethylsilyl]oxy}ethyl)-2,2-dimethyl-1,3-dioxan-5-one [(*R*)-3]: 5.9 g of the crude hydrazone (*R,R*)-**2** was dissolved in 60 mL of diethyl ether and stirred vigorously at room temp. with a sat. aqueous solution of oxalic acid (35 mL) for 12 h (TLC control). The aqueous layer was separated, extracted with diethyl ether and the organic extracts were combined, washed with water, brine and dried with $MgSO_4$. The solvent was removed under reduced pressure to give (*R*)-**3** as an oil. An analytical sample was obtained by column chromatography (SiO_2; pentane/Et_2O, 10:1), yield 4.1 g (95%). − $[\alpha]_D^{25} = +122.5$ (c = 1.0, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2988 cm^{-1} (w), 2956 (m), 2931 (m), 2884 (w), 2858 (m), 1750 (s), 1472 (w), 1464 (w), 1426 (w), 1382 (m), 1376 (m), 1362 (w), 1255 (s), 1223 (s), 1175 (w), 1158 (w), 1111 (s), 1067 (m), 1007 (w), 953 (w), 940 (w), 876 (w), 861 (w), 837 (s), 812 (w), 777 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 6 H, SiCH_3), 0.89 (s, 9 H, SiCH_3), 1.43 [s, 3 H, C(CH_3)$_3$], 1.46 [s, 3 H, C(CH_3)$_3$], 1.61−1.72 (m, 1 H, C*H*HCH$_2$OTBS), 2.07−2.18 (m, 1 H, CH*H*CH$_2$OTBS), 3.70−3.75 (m, 2 H, CH$_2$CH_2OTBS), 3.99 (d, J = 17.1 Hz, 1 H, OC*H*HCO), 4.28 (dd, J = 17.0 Hz, J = 1.7 Hz, 1 H, OCH*H*CO), 4.49 (ddd, J = 8.9 Hz, J = 3.8 Hz, J = 1.7 Hz, 1H OC*H*CO). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.4 (2 × Si*C*H$_3$), 18.2 [*C*(CH$_3$)$_3$], 23.6 [C(*C*H$_3$)$_2$], 24.0 [C(*C*H$_3$)$_2$], 25.9 [3 × C(*C*H$_3$)$_3$], 31.8 (*C*H$_2$CH$_2$OTBS), 58.2 (CH$_2$*C*H$_2$OTBS), 66.6 (O*C*H$_2$CO), 71.3 (O*C*HCO), 100.8 [*C*(CH$_3$)$_2$], 210.1 (*C*O). − MS (CI, isobutane); *m/z* (%): 289 [M^+ + 1] (100), 273 (3), 272 (5), 271 (25), 232 (5), 231 [M^+ − 57], (33), 173 (3). − $C_{14}H_{28}O_4Si$ (288.46): calcd. C 58.29, H 9.78; found C 57.92, H 9.78. − In analogy, cleavage of 4.9 g (12.3 mmol) of (*S,S*)-**2** afforded 3.3 g of (*S*)-**3** (92%). − $[\alpha]_D^{25} = -122.6$ (c = 1.0, $CHCl_3$)

(4*R*,5*S*/*R*)-4-(2-{[1-(*tert*-Butyl)-1,1-dimethylsilyl]oxy}ethyl)-2,2-dimethyl-1,3-dioxan-5-ol (*R*,*S*/*R*)-4: 4.1 g (14.2 mmol) of (*R*)-**3** was dissolved in MeOH and cooled to −78°C. Then 1.1 g (28.4 mmol 2.0 equiv.) of $NaBH_4$ was added, the mixture was allowed to reach room temp. and then stirred for 2 h. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2 and treated with water. The organic phase was washed with a pH-7 buffer and brine and dried with $MgSO_4$. The solvent was removed under reduced pressure to yield the alcohol (*R,S*/*R*)-**4** as a mixture of diastereomers. An analytical sample was obtained by column chromatography (SiO_2; pentane/Et_2O, 1:1), yield 3.6 g (85%). − de = 61%. − IR (film): $\tilde{\nu}$ = 3424 cm^{-1} (w), 2994 (w), 2955 (s), 2930 (s), 2884 (m), 2859 (s), 1472 (w), 1464 (w), 1434 (w), 1381 (m), 1256 (s), 1228 (w), 1199 (m), 1168 (m), 1132 (w), 1088 (s), 1007 (w), 985 (w), 957 (w), 940 (w), 924 (w), 866 (w), 838 (s), 807 (w), 778 (s), 664 (w). − ^{1}H NMR (300 MHz, C_6D_6): (*R,S*)-**4**: δ = 0.01 (s, 6 H, SiCH_3), 0.92 [s, 9 H, C(CH_3)$_3$], 1.37 [s, 3 H, C(CH_3)$_2$], 1.48 [s, 3 H, C(CH_3)$_2$], 1.67−1.84 (m, 1 H, C*H*HCH$_2$OTBS), 1.89−2.04 (m, 1 H, CH*H*CH$_2$OTBS), 3.30 (d, J = 3.6 Hz, 1 H, O*H*), 3.44−3.55 (m, 1 H, C*H*OH), 3.59−3.78 (m, 4 H, CH$_2$CH_2OTBS, OCH_2CHOH), 3.93−4.00 (m, 1 H, OC*H*CHOH). − ^{13}C NMR (75 MHz, C_6D_6): δ = −5.4 (2× Si*C*H$_3$), 18.4 [*C*(CH$_3$)$_3$], 19.3 [C(*C*H$_3$)$_2$], 26.0 [3 × C(*C*H$_3$)$_3$], 29.3 [C(*C*H$_3$)$_2$], 37.8 (*C*H$_2$CH$_2$OTBS), 60.1 (CH$_2$*C*H$_2$OTBS), 64.9 (O*C*H$_2$CHOH), 67.9 (O*C*HCHOH), 73.3 (*C*HOH), 98.4 [*C*(CH$_3$)$_2$]. − MS (EI, 70eV); *m/z* (%): 275 [M^+ − 15], 189 (12), 175 (31), 157 (35), 145 (65), 131 (30), 129 (10), 127 (12), 115 (9), 105 (22), 101 (43), 89 (36), 83 (34), 77 (11), 75 (100), 73 (35), 59 (83), 57 (12), 55 (14). − $C_{14}H_{30}O_4Si$ (290.47): calcd. C 57.89, H 10.41; found C 57.43 H 10.43. − In analogy, reduction of 6.1 g of (*S*)-**3** afforded 5.3 g of (*S,R*/*S*)-**4** (87%).

(4′*R*,5′*R*/*S*)-{4-(2-{[1-(*tert*-Butyl)-1,1-dimethylsilyl]oxy}ethyl)-2,2-dimethyl-1,3-dioxan-5-yl-methansulfanyl}methanethioate [(R,S/R)-5]: To a solution of 3.6 g (12.4 mmol) of (*R,S*/*R*)-**4** in 15 mL of THF under Ar was added imidazole (cat.) and 1.2 g (31 mmol, 2.5 equiv.) of a 60% suspension of NaH in mineral oil at 0°C. After 30 min, 2.6 mL (43 mmol, 3.5 equiv.) of CS_2 was added dropwise and stirring was continued for an additional 30 min at 0°C. Then, 3.5 g (4.4 mmol, 2.0 equiv.) of iodomethane was added and the mixture was stirred at room temp. overnight. The reaction mixture was hydrolysed with water and extracted with diethyl ether. The combined organic layers were washed with a sat. aqueous NH_4Cl solution and brine, dried ($MgSO_4$) and concentrated under reduced pressure. Purification by column chromatography (SiO_2; pentane/

Et_2O, 2:1) afforded the xanthate (*R,S*/*R*)-**5** as slightly yellow oil. Analytical samples of both diastereomers were obtained by column chromatography (SiO_2; pentane/Et_2O, 9:1), yield 4.5 g (94%). − (*R,S*)-**5**: $[\alpha]_D^{25} = +75.0$ (*c* = 1.05, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2991 cm^{-1} (w), 2954 (m), 2928 (m), 2856 (w), 1472 (w), 1463 (w), 1444 (w), 1424 (w), 1383 (w), 1371 (w), 1256 (m), 1211 (s), 1168 (m), 1132 (m), 1094 (s), 1069 (s), 1009 (w), 959 (w), 940 (w), 926 (w), 866 (w), 837 (s), 807 (w), 777 (m). − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.04 (s, 6 H, SiCH_3), 0.96 (s, 9 H, C(CH_3)$_3$], 1.32 (s, 6 H, C(CH_3)$_2$], 1.55−1.68 (m, 1 H, C*H*HCH$_2$OTBS), 1.83−1.94 (m, 1 H, CH*H*CH$_2$OTBS), 2.13 (s, 3 H, SCH_3), 3.55−3.78 (m, 3 H, CH$_2$CH_2OTBS, OC*H*HCHOS), 4.08 (m, 1 H, OCH*H*CHOS), 4.23 (m, 1 H, OC*H*CHOS), 5.63 (m, 1 H, OCHC*H*OS). − ^{13}C NMR (75 MHz, C_6D_6): δ = −5.3 (Si*C*H$_3$), 18.4 [*C*(CH$_3$)$_3$], 18.9 [C(*C*H$_3$)$_2$], 20.8 [C(*C*H$_3$)$_2$], 26.0 [3 × C(*C*H$_3$)$_3$], 27.1 (S*C*H$_3$), 36.2 (*C*H$_2$CH$_2$OTBS), 58.5 (CH$_2$*C*H$_2$OTBS), 61.5 (O*C*H$_2$CHOS), 67.0 (O*C*HCHOS), 76.6 (OCH*C*HOS), 99.6 [*C*(CH$_3$)$_2$], 215.8 (*C*S$_2$CH$_3$). − MS (CI, isobutane): *m*/*z* (%): 381 [M$^+$ + 1] (11), 325 (12), 324 (20), 323 [M$^+$ − 57] (100), 309 (5), 291 (13), 275 (22), 273 (22), 217 (15), 215 (13), 159 (5), 157 (5).− $C_{16}H_{32}O_4S_2Si$ (380.63): calcd. C 50.49 H 8.47; found 50.33 H 8.77. − (*R,R*)-**5**: $[\alpha]_D^{28} = -9.6$ (*c* = 0.94, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2991 cm^{-1} (w), 2954 (m), 2929 (m), 2882 (w), 2877 (w), 1471 (w), 1463 (w), 1426 (w), 1383 (w), 1276 (w), 1255 (m), 1225 (s), 1196 (s), 1171 (w), 1137 (w), 1069 (s), 1022 (w), 968 (w), 949 (w), 924 (w), 865 (w), 837 (m), 812 (w), 777 (m). − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.03 (s, 6 H, SiCH_3), 0.96 [s, 9 H, C(CH_3)$_3$], 1.24 [s, 3 H, C(CH_3)$_2$], 1.44 [s, 3 H, C(CH_3)$_2$], 1.64−1.76 (m, 1 H, C*H*HCH$_2$OTBS), 1.87−1.98 (m, 1 H, CH*H*CH$_2$OTBS), 2.12 (s, 3 H, SCH_3), 3.51−3.74 (m, 3 H, CH$_2$CH_2OTBS OC*H*HCHOS), 4.00 (dd, *J* = 13.4 Hz, *J* = 1.9 Hz, 1 H, OCH*H*CHOS), 4.19 (ddd, *J* = 8.7 Hz, *J* = 4.4 Hz, *J* = 1.7 Hz, 1 H, OC*H*CHOS), 5.40 (q, *J* = 1.9 Hz, 1 H, OCHC*H*OS). − ^{13}C NMR (75 MHz, C_6D_6): δ = −5.3 (Si*C*H$_3$), 18.5 [*C*(CH$_3$)$_3$], 18.6 [C(*C*H$_3$)$_2$], 19.0 [C(*C*H$_3$)$_2$], 26.1 [3 × C(*C*H$_3$)$_3$], 29.4 (S*C*H$_3$), 34.8 (*C*H$_2$CH$_2$OTBS), 58.7 (CH$_2$*C*H$_2$OTBS), 62.4 (O*C*H$_2$CHOS), 66.8 (O*C*HCHOS), 76.9 (OCH*C*HOS), 98.8 [*C*(CH$_3$)$_2$], 216.4 (*C*SSCH$_3$). − MS (CI, isobutane): *m*/*z* (%): 381 [M$^+$ + 1] (100), 367 (10), 365 (14), 335 (27), 323 (30), 291 (19), 275 (34), 217 (10), 215 (22), 75 (8). − $C_{16}H_{32}O_4S_2Si$ (380.63): calcd. C 50.49 H 8.47; found C 50.68 H 8.31. − In analogy, reaction of 5.3 g (18.0 mmol) of (*S,R*/*S*)-**4** afforded 1.3 g of (*S,S*)-**5** (19%), $[\alpha]_D^{28} = +9.7$ (*c* = 1.0, $CHCl_3$) and 4.5 g of (*S,R*)-**5** (66%), $[\alpha]_D^{25} = -75.1$ (*c* = 1.05, $CHCl_3$).

(*S*)-1-(*tert*-Butyl)-1,1-dimethylsilyl {2-[2,2-Dimethyl-1,3-dioxan-4-yl]ethyl} Ether [(*S*)-6]: 5.1 g (17.6 mmol, 1.5 equiv.) of tri-*n*-butyltin hydride was dissolved in 400 mL of toluene in a Schlenk flask. The solution was purged with Ar for 10 min and was then heated to reflux. Then, 4.5 g of the xanthate (*R,S*/*R*)-**5** (1.0 equiv.), dissolved in 15 mL of toluene, was added dropwise via canula over a period of 4 h. During the addition, a sat. solution of AIBN in toluene was added dropwise via canula (ca. 0.1 equiv.) and the solution was stirred under reflux overnight. After conversion of the starting material was indicated by TLC, the solvent was removed under reduced pressure and the residue directly subjected to column chromatography (SiO_2; pentane/Et_2O, 8:1) to give (*S*)-**6** as a colourless oil, yield 2.6 g (82%). − $[\alpha]_D^{23} = +34.1$ (*c* = 1.0, acetone). − IR (film): $\tilde{\nu}$ = 2993 cm^{-1} (w), 2953 (s), 2930 (s), 2859 (m), 1472 (w), 1463 (w), 1380 (m), 1369 (w), 1256 (m), 1198 (m), 1170 (m), 1135 (m), 1102 (s), 1059 (w), 1021 (w), 1007 (w), 971 (m), 961 (w), 939 (w), 921 (w), 877 (w), 837 (s), 804 (w), 777 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.05 (s, 6 H, SiCH_3), 0.90 [s, 9 H, C(CH_3)$_3$], 1.37 [s, 3 H, C(CH_3)$_2$], 1.45 [s, 3 H, C(CH_3)$_2$], 1.53−1.76 (m, 4 H, OCH$_2$CH_2CHO, CH_2CH$_2$OTBS), 3.60−3.77 (m, 2 H, CH$_2$CH_2OTBS), 3.82 (ddd, *J* = 11.8 Hz, *J* = 5.4 Hz, *J* = 1.7 Hz, 1 H, OC*H*HCH$_2$CHO), 3.98 (td, *J* = 12.1 Hz, *J* = 3.0 Hz, 1 H, OCH*H*CH$_2$CHO), 4.00−4.11 (m, 1 H, OCH$_2$CH$_2$C*H*). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −5.4 (Si*C*H$_3$), 18.3 [*C*(CH$_3$)$_3$], 19.3 [C(*C*H$_3$)$_2$], 25.9 [3 × C(*C*H$_3$)$_3$], 30.5 [C(*C*H$_3$)$_2$], 31.5 (OCH$_2$*C*H$_2$CHO), 39.6 (*C*H$_2$CH$_2$OTBS), 58.8 (O*C*H$_2$CH$_2$CHO), 60.1 (CH$_2$*C*H$_2$OTBS), 65.5 (OCH$_2$CH$_2$*C*HO), 98.3 [*C*(CH$_3$)$_2$]. − MS (EI, 70 eV); *m*/*z* (%): 259 (12), 160 (12), 159 (100), 141 (14), 131 (49), 129 (68), 117 (13), 115 (13), 105 (11), 101 (49), 89 (45), 75 (62), 73 (38), 67 (17), 59 (35), 58 (12), 57 (18), 55 (12). − MS (CI, isobutane); *m*/*z* (%): 275 [M$^+$ + 1] (100), 217 [M$^+$ − 57] (22), 215 (6), 159 (4). − $C_{14}H_{30}O_3Si$ (274.47): calcd. C 61.26 H 11.02; found C 60.88 H 11.32. − In analogy, deoxygenation of 2.8 g (7.4 mmol) of (*S,R*/*S*)-**5** yielded 1.8 g of (*R*)-**6** (89%). − $[\alpha]_D^{23} = -33.9$ (*c* = 1.0, acetone).

(*R*)-2-[2,2-Dimethyl-1,3-dioxan-4-yl]ethan-1-ol [(*R*)-7]: To a solution of 2.6 g (9.6 mmol) of (*S*)-**6** in 50 mL of THF was added 14 mL of a 1.0 N THF solution of tetrabutylammonium fluoride by syringe. The mixture was stirred at room temp. for 4 h and then washed with sat. aqueous NH_4Cl solution. The aqueous phase was extracted with EtOAc three times. The combined organic phases were washed with brine (30 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification by column chromatography (SiO_2; pentane/Et_2O, 4:1 to 1:1) afforded alcohol (*R*)-**7** as colourless oil, yield 1.4 g (93%). − $[\alpha]_D^{23} = +55.5$ (*c* = 1.0, acetone). − IR (film): $\tilde{\nu}$ = 3422 cm^{-1} (m), 2992 (m), 2945 (s), 2873 (m), 1478 (w), 1460 (w), 1429 (w), 1382 (s), 1371 (s), 1274 (m), 1240 (m), 1201 (s), 1165 (s), 1132 (m), 1097 (s), 1059 (s), 1012 (w), 994 (w), 969 (m), 949 (w), 936 (w), 875 (w), 849 (w), 683 (w), 523 (w). − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.25 [s, 3 H, C(CH_3)$_2$], 1.41 [s, 3 H, C(CH_3)$_2$], 1.43−1.67 (m, 4 H, OCH$_2$CH_2CHO, CH_2CH$_2$OTBS), 2.90 (br. s, 1 H, O*H*), 3.54−3.80 (m, 5 H, CH$_2$CH_2OTBS, OCH_2CH$_2$CH, OCH$_2$CH$_2$C*H*O). − ^{13}C NMR (75 MHz, C_6D_6): δ = 19.3 [C(*C*H$_3$)$_2$], 30.3 [C(*C*H$_3$)$_2$], 31.4 (OCH$_2$*C*H$_2$CHO), 39.1 (*C*H$_2$CH$_2$OTBS), 58.7 (O*C*H$_2$CH$_2$CHO), 58.8 (CH$_2$*C*H$_2$OTBS), 68.2 (OCH$_2$CH$_2$*C*H), 98.3 [*C*(CH$_3$)$_2$]. − MS (EI, 70 eV); *m*/*z* (%):145 (63), 115 (16), 85 (12), 73 (12), 67 (82), 61 (21), 59 (100), 58 (33), 57 (42), 55 (71), 54 (19). − MS (CI, isobutane); *m*/*z* (%): 161 [M$^+$ + 1] (100), 159 (3), 145 (3), 103 [M$^+$ − 57] (9), 85 (3). − $C_8H_{16}O_3$ (160.21): calcd. C 59.98 H 10.07; found C 59.98 H 9.89. − In analogy, reaction of 1.9 g (6.9 mmol) of (*R*)-**6** yielded 1.04 g of (*S*)-**7** (94%). − $[\alpha]_D^{28} = -55.4$ (*c* = 1.0, acetone).

(4′*S*,1*R*)-2-(2,2-Dimethyl-1,3-dioxan-4-yl)ethyl 3,3,3-Trifluoro-2-methoxy-2-phenylpropanoate [(*S,R*)-11]: According to a literature procedure[10a] to a solution of 50 mg (0.2 mmol, 1.2 equiv.) of (+)-(*R*)-α-trifluoromethyl-α-methoxyphenylacetic acid and 16 mg (0.2 mmol, 1.2 equiv.) of dimethylformamide in 10 mL of hexane was added 89 μL (1.0 mmol, 5.7 equiv.) of oxalyl chloride at room temp. The resulting mixture was stirred for 1 h and the solvent was removed under reduced pressure. To the resulting colourless solid a solution of 71 μL (0.18 mmol, 1.0 equiv.) of triethylamine, a crystal of 4-(dimethylamino)pyridine and 28 mg (0.18 mmol, 1.0 equiv.) of (*S*)-**7** in 2 mL of chloroform was added. The mixture was stirred at room temp. overnight. A sat. aqueous NH_4Cl solution was added and the organic layer was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was subjected to HPLC analysis on a stationary chiral phase (Chiracel OJ) and compared with an independently synthesised racemic reference sample (de ≥ 96%). Purification by column chromatography (SiO_2; pentane/Et_2O, 1:1) afforded (*S,R*)-**11** as colourless oil, yield 45 mg (66%). − IR (film): $\tilde{\nu}$ = 2993 cm^{-1} (w), 2950 (w), 2870 (w), 1750 (s), 1452 (w), 1431 (w), 1382 (w), 1371 (w), 1271 (s), 1242 (s), 1170 (s), 1122 (m), 1101 (m), 1082 (w), 1059 (w), 1022 (m), 1001

(m), 969 (w), 949 (w), 857 (w), 767 (w), 720 (w), 698 (w). − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.19 [s, 3 H, C(CH_3)$_2$], 1.42 [s, 3 H, C(CH_3)$_2$], 1.44−1.63 (m, 4 H, OCH$_2$CH_2CHO, CH_2CH$_2$OTBS), 3.39−3.44 (m, 3 H, OCH_3), 3.49−3.62 (m, 3 H, OCH_2CH$_2$CHO, OCH$_2$CH$_2$C*H*O), 4.12−4.34 (m, 2 H, CH_2OCOR), 7.05−7.15 (m, 3 H, H-ar), 7.65 (m, 2 H, H-ar). − ^{13}C NMR (75 MHz, C_6D_6): δ = 19.1 [C(*C*H$_3$)$_2$], 30.2 [C(*C*H$_3$)$_2$], 31.4 (OCH$_2$*C*H$_2$CHO), 35.5 (*C*H$_2$CH$_2$OTBS), 55.3 (O*C*H$_3$), 59.6 (O*C*H$_2$CH$_2$CHO), 59.7 (CH$_2$*C*H$_2$OCOR*), 62.7 (*C*CF$_3$), 65.3 (OCH$_2$CH$_2$*C*H), 98.4 [*C*(CH$_3$)$_2$], 122.4 (*C*F$_3$), 126.2−129.8 (C-ar), 166.6 (CO). − MS (EI, 70 eV); *m*/*z* (%): 362 (11), 361 (64), 189 (64), 127 (16), 119 (11), 105 (24), 85 (15), 77 (12), 68 (10), 67 (100), 59 (18), 57 (23), 55 (20). − MS (CI, isobutane); *m*/*z* (%): 377 [M$^+$ + 1] (100), 361 (4), 319 [M$^+$ − 57] (9), 289 (4). − $C_{18}H_{23}F_3O_5$ (376.37): calcd. C 57.44 H 6.16; found C 57.56 H 6.31.

(*S*)-2-(2,2-Dimethyl-1,3-dioxan-4-yl)ethanal (*S*)-8: In 15 mL of dichloromethane a mixture of 500 mg (3.1 mmol, 1.0 equiv.) of (*R*)-**7**, 78 mg (7.5 mol-%) of tetrapropylammonium perruthenate, 620 mg (4.6 mmol, 1.5 equiv.) 4-methymorpholine oxide and 1.2 g of ground molecular sieves (4 Å) were stirred 72 h at room temp. After complete conversion of the starting material was indicated by TLC, the mixture was directly subjected to column chromatography (SiO_2; pentane /Et_2O, 1:1) to yield a colourless oil (volatile!), yield 435 mg (88%). − $[\alpha]_D^{23}$ = +11.9 (*c* = 1.0, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 2991 cm^{-1} (s), 2952 (vs), 2877 (s), 1726 (s), 1432 (m), 1382 (vs), 1267 (s), 1242 (s), 1200 (vs), 1166 (vs), 1100 (vs), 1062 (vs), 1027 (vs), 991 (vs), 972 (vs), 912 (m), 888 (m), 872 (m), 848 (m), 816 (m), 750 (w), 640 (w), 526 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.37 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 1.52−1.74 (m, 2 H, OCH$_2$CH_2CH), 2.49 (ddd, *J* = 16.8 Hz, 4.9 Hz, 1.7 Hz, 1 H, C*H*HCHO), 2.64 (ddd, *J* = 16.8 Hz, 7.2 Hz, 2.2 Hz, 1 H, CH*H*CHO), 3.85 (ddd, *J* = 11.8 Hz, 5.2 Hz, 1.7 Hz, 1 H, OC*H*HCH$_2$CH), 4.02 (dt, *J* = 11.8 Hz, 3.0 Hz, 1 H, OCH*H*CH$_2$CH), 4.40−4.50 (m, 1 H, OCH$_2$CH$_2$C*H*), 9.79 (t, *J* = 1.9 Hz, 1 H, C*H*O). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6 (*C*H$_3$), 29.3 (*C*H$_3$), 30.5 (OCH$_2$*C*H$_2$CH), 49.4 (*C*H$_2$CHO), 59.2 (O*C*H$_2$CH$_2$CH), 64.1 (OCH$_2$CH$_2$*C*H), 98.1 [*C*(CH$_3$)$_2$], 200.4 (C*H*O). − MS (EI, 70 eV); *m*/*z* (%): 143 [M$^+$ − Me] (62), 115 (17), 83 (23); 61 (15), 59 (68), 55 (100). − MS (CI, isobutane); *m*/*z* (%): 159 [M$^+$ + H] (100), 143 (4), 115 (9), 101 (14). − HRMS ($C_7H_{11}O_3$): calcd. 143.0708; found 143.0708. − In analogy, oxidation of 800 mg (5.0 mmol) of (*S*)-**7** yielded 679 mg of (*R*)-**8** (86%). − $[\alpha]_D^{23}$ = −12.0 (*c* = 1.0, CH_2Cl_2) {ref.[5]: $[\alpha]_D$ = −12.8 (*c* = 1.1, CH_2Cl_2)}.

(4′*S*,2*R*/*S*)-1-(2,2-Dimethyl-1,3-dioxan-4-yl)hept-5-en-2-ol (*S*/*R*,*S*)-9: According to the literature[6] 158 mg (6.5 mmol, 2.5 equiv.) of freshly ground magnesium was placed in a flame-dried 100-mL Schlenk flask. Then 10 mL of THF was added and 968 mg (6.5 mmol, 2.5 equiv.) of (*E*)-5-bromo-2-pentene was slowly added via syringe. The reaction mixture was heated to 50°C for 30 min. The mixture was allowed to reach room temp. and 410 mg (2.6 mmol, 1.0 equiv.) of (*S*)-**8** was slowly added. After stirring for 2 h at 50−60°C, a sat. aqueous NH_4Cl solution was slowly added, the organic phase was diluted with diethyl ether and washed with water. The aqueous phase was extracted with EtOAc three times and the combined organic phases were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to give (*S*/*R*,*S*)-**9** as a sligthly yellow oil, yield 480 mg (81%). − IR (film): $\tilde{\nu}$ = 3449 cm^{-1} (s), 2993 (vs), 2939 (vs), 2865 (s), 2728 (w), 1452 (m), 1438 (m), 1381 (vs), 1311 (m), 1269 (s), 1241 (s), 1201 (vs), 1163 (vs), 1137 (s), 1102 (vs), 1053 (m), 969 (vs), 947 (m), 909 (m), 872 (m), 853 (m), 815 (m), 748 (w), 639 (w), 524 (m), 501 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.58 [s, 3 H, C(CH_3)$_2$], 1.61 [s, 3 H, C(CH_3)$_2$], 1.66−1.80 (m, 5 H, OCH$_2$CH_2CH, CHCH_3), 1.96 (m, 2 H, CH_2CHOHCH$_2$), 2.19 (m, 2 H, CH$_2$CHOHCH_2), 2.97 (br. s, 1 H, CHO*H*), 3.85 (m, 1 H, C*H*OH), 3.90−3.97 (m, 2 H, CH_2CHCHCH$_3$), 4.07 (dd, *J* = 12.4 Hz, 2.8 Hz, 1 H, OC*H*HCH$_2$CH), 4.12 (dd, *J* = 11.8 Hz, 2.8 Hz, 1 H, OC*H*HCH$_2$CH), 4.22−4.34 (m, 1 H, OCHHCH$_2$C*H*), 5.50−5.58 (m, 2 H, C*H*C*H*CH$_3$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (CH*C*H$_3$), 18.8 [C(*C*H$_3$)$_2$], 28.3 [OCH$_2$*C*H$_2$CH), 29.6 [C(*C*H$_3$)$_2$], 30.7 (*C*H$_2$CHOHCH$_2$), 37.0 (CH$_2$CHOH*C*H$_2$), 42.3 (*C*H$_2$CHCHCH$_3$), 59.5 (O*C*H$_2$CH$_2$CH), 67.0 (OCH$_2$CH$_2$*C*H), 70.2 (*C*HOH), 98.0 [*C*(CH$_3$)$_2$], 124.7 (CH*C*HCH$_3$), 130.6 (*C*HCHCH$_3$). − MS (EI, 70 eV); *m*/*z* (%): 213 [M$^+$ − Me [(32), 115 (28), 101 (29), 99 (19), 81 (36), 74 (28), 59 (94), 57 (40), 55 (100), 46 (28). − MS (CI, isobutane); *m*/*z* (%): 229 [M$^+$ + H] (100), 211 (4), 171 (7), 153 (2). − In analogy, reaction of 752 mg (4.7 mmol) of (*R*)-**8** yielded 782 mg of (*R*/*S*,*R*)-**9** (73%).

(*S*)-1-(2,2-Dimethyl-1,3-dioxan-4-yl)-hept-5-en-2-one [(*S*)-10]: To a solution of 345 mg of (*S*/*R*,*S*)-**9** in 50 mL of dichloromethane at room temp. was slowly added a mixture of 967 mg (967 mg, 4.5 mmol) of pyridinium chlorochromate, 970 mg of Celite and 970 mg of ground molecular sieves (4 Å). The suspension was stirred for 4 h (TLC control) and then filtered through a pad of silica gel which was eluted with 500 mL of ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by column chromatography (SiO_2; pentane/Et_2O, 4:1) to yield (*S*)-**10** as a colourless oil, yield 244 mg (72%). − $[\alpha]_D^{23}$ = +12.8 (*c* = 1.0, CH_2Cl_2). − IR (film): $\tilde{\nu}$ = 3520 cm^{-1} (w), 3411 (w), 2992 (vs), 2869 (vs), 2723 (w), 1713 (vs), 1433 (s), 1409 (s), 1381 (vs), 1316 (m), 1272 (vs), 1242 (vs), 1198 (vs), 1161 (vs), 1132 (vs), 1102 (vs), 1047 (vs), 971 (vs), 948 (s), 911 (s), 875 (s), 839 (m), 822 (m), 735 (m), 648 (w), 638 (w), 525 (m), 484 (m), 439 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 [s, 3 H, C(CH_3)$_2$], 1.39 [s, 3 H, C(CH_3)$_2$], 1.43−1.53 (m, 2 H, OCH$_2$CH_2CH), 1.53−1.58 (m, 3 H, CHCH_3), 2.18 (m, 2 H, CH_2COCH$_2$CH$_2$), 2.30−2.40 (m, 2 H, CH$_2$COCH_2CH$_2$), 2.43 (dd, *J* = 7.1 Hz, 2.7 Hz, 1 H, COCH$_2$C*H*H), 2.60 (dd, *J* = 16.1 Hz, 7.1 Hz, 1 H, COCH$_2$CH*H*), 3.74 (ddd, *J* = 11.8 Hz, 4.8 Hz, 2.1 Hz, 1 H, OC*H*HCH$_2$CH), 3.92 (td, *J* = 11.5 Hz, 3.7 Hz, 1 H, OCH*H*CH$_2$CHO), 4.28 (m, 1 H, OCH$_2$CH$_2$C*H*O), 5.31−5.43 (m, 2 H, C*H*C*H*CH$_3$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9 (CH*C*H$_3$), 19.2 [C(*C*H$_3$)$_2$], 26.6 (OCHH*C*H$_2$CHO), 29.9 [C(*C*H$_3$)$_2$], 31.2 (*C*H$_2$COCH$_2$CH$_2$), 43.8 (CH$_2$CO*C*H$_2$CH$_2$), 49.4 (CH$_2$COCH$_2$*C*H$_2$), 59.8 (O*C*H$_2$CH$_2$-CHO), 65.7 (OCH$_2$CH$_2$*C*HO), 98.5 [*C*(CH$_3$)$_2$], 125.9 (*C*HCH$_3$), 129.6 (*C*HCHCH$_3$), 208.5 (CO). − MS (EI, 70 eV); *m*/*z* (%): 226 [M$^+$], 211 [M$^+$ − Me] (19), 168 (15), 150 (6), 115 (16), 97 (80), 73 (12), 69 (100), 59 (30), 55 (34). − In analogy, oxidation of 276 mg (1.2 mmol) of (*R*/*S*,*R*)-**9** yielded 194 mg of (*R*)-**10** (71%). − $[\alpha]_D^{23}$ = −12.9 (*c* = 1.0, CH_2Cl_2) {ref.[5]: $[\alpha]_D$ = −13.7 (*c* = 1.05, CH_2Cl_2)}.

(+)-Streptenol A: 100 mg (0.44 mmol) of (*S*)-**10** was dissolved in 2 mL of THF and 1 mL of water. The mixture was cooled to 0°C and 0.1 mL of trifluoracetic acid was added via syringe. Stirring was continued at 0°C for 3 h until TLC control indicated complete conversion of the starting material. Then, 1 mL of an aqueous ammonia solution and 3 mL of water were added. The aqueous solution was extracted three times with CH_2Cl_2 and the combined organic phases were washed with brine and dried with $MgSO_4$. Evaporation of the solvent under reduced pressure and filtration through a pad of Florisil® yielded the title compound as a colourless oil, yield 63 mg (78%). − $[\alpha]_D^{23}$ = +21.7 (*c* = 1.0, $CHCl_3$) {ref.[1a]: $[\alpha]_D$ = + 23 (*c* = 1.0, $CHCl_3$)}. − In analogy, deprotection of 180 mg (0.80 mmol) of (*R*)-**10** yielded 106 mg of (−)-streptenol A (72%). − $[\alpha]_D^{23}$ = −21.5 (*c* = 1.0, $CHCl_3$) {ref.[5]: $[\alpha]_D$ = −23

(c = 1.0, $CHCl_3$)}. The spectroscopic data are in accordance with previously published data.[1a,3]

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