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Synthesis of (*S*)-Nonacosan-10-ol, the Major Component of Tubular Plant Wax Crystals

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(*S*)-Nonacosan-10-ol [(+)-Ginnol] is the main component of the tubular wax aggregates, which are found on many plant leaves. To investigate the role of this lipid for the formation of super hydrophobic self-cleaning plant surfaces, both enantiomers of the title compound were prepared in six steps. Key steps are the resolution of the allylation product of decanal with (*R*)-*O*-methylmandelic acid, and a chain elongation by cross metathesis.

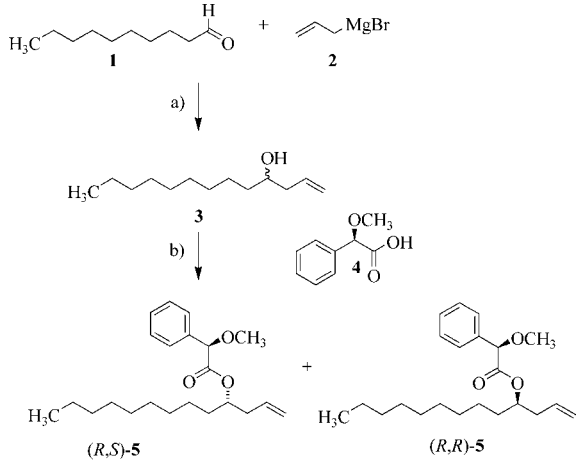
Introduction

The surfaces of plant leaves are covered with a layer of waxes that forms the outer boundary of the cuticular membrane.[1,2] (*S*)-Nonacosan-10-ol [(+)-Ginnol] is the major component of tubular microcrystalline wax aggregates, which are found on leaf surfaces of several plants such as Nasturtium (*Tropaeolum majus* L.), the sacred Lotus (*Nelumbo nucifera* Gaertn.) and Ginkgo (*Ginkgo biloba* L.).[3–5] Epicuticular waxes play an important role in the interaction of plants with their environment, for example by the reduction of the wettability of the leaf surface and the generation of self-cleaning surfaces.[6] Meanwhile, bioinspired technical products with such properties are commercially available. For these products, the brand name Lotus-Effect was introduced.

To investigate the role of constitution and configuration of these wax components on the formation of tubular wax crystals,[7] sufficient amounts of enantiopure (*S*)- and (*R*)-nonacosan-10-ol were required. Owing to the similarity of the two alkyl chain substituents at the asymmetric carbon, resolution of a racemic nonacosan-10-ol mixture was not possible.[8] The optical rotation values reported in the literature also differ only slightly from zero; values between 0 and +2.18 were reported for (*S*)-nonacosan-10-ol.[9] On the basis of NMR spectroscopic investigations with the aid of an anisotropic shift reagent, the (*S*)-configuration was assigned to nonacosan-10-ol [(+)-Ginnol] isolated from *Ginkgo biloba* L.[10] (*S*)-Nonacosan-10-ol was prepared before by enantioselective synthesis in an enantiomeric ratio of 8:1[8] and higher.[9] We report an easy and efficient method for the preparation of (*S*)- and (*R*)-nonacosan-10-ol (**9**) in high enantiomeric purity.

Results and Discussion

The synthesis started from decanal (**1**), which was alkylated with allylmagnesium bromide (**2**) in diethyl ether to give allyl alcohol **3** in 98% yield (Scheme 1). Instead to attempt the preparation of the pure enantiomers by enantioselective synthesis,[8,9,11–19] we decided to attempt a resolution of racemic tridec-1-en-4-ol (**3**) to generate suitable preparative precursors of both enantiomers of the title compound. We found that the reaction of the ester of **3** with (*R*)-configured *O*-methylmandelic acid (**4**) led to diastereomers with sufficiently different chromatographic be-



Scheme 1. Reagents and conditions: (a) allylmagnesium bromide, diethyl ether, –42 °C, 1 h (98%); (b) **4**, DCC, DMAP, CH_2Cl_2, 4 h, 0 °C, 3 d room temp. (92%).

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haviour so that partial separation of both esters, (*R*,*S*)-**5** and (*R*,*R*)-**5**, could be achieved on a preparative scale. These esters were prepared from alcohol **3** and (*R*)-α-methoxyphenylacetic acid (**4**) in the presence of dicyclohexylcarbodiimide and dimethylaminopyridine in dichloromethane in 92% combined yield.

The diastereomers of **5** formed in this step were separated by flash chromatography on silica gel with a mixture of cyclohexane and ethyl acetate (10:1) as eluent. The enantiomeric purity of both samples, estimated from the integrals of both signals, was higher than 36:1 (Figure 1).

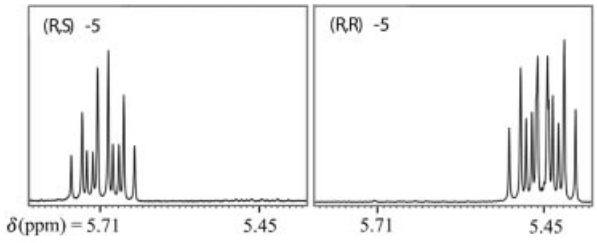
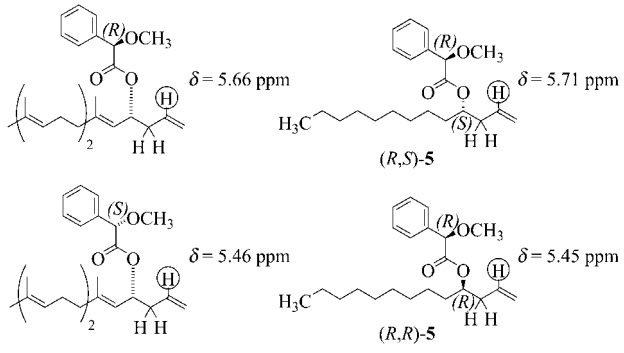


Figure 1. Detail of the ^{1}H NMR spectra of (*R*,*S*)-**5** and (*R*,*R*)-**5**.

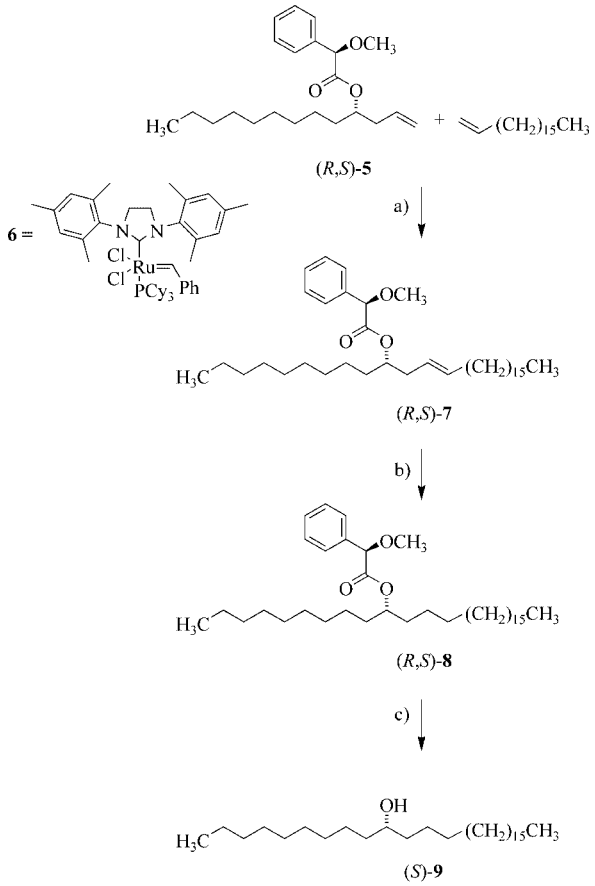
The assignment of the absolute configuration of the stereogenic centre within the allyl alcohol moiety was achieved after saponification of esters (*R*,*S*)-**5** and (*R*,*R*)-**5**, and comparison of the optical rotation of both enantiomeric tridec-1-en-4-ols (**3**) with reference values. Enantiopure tridec-1-en-4-ols (**3**) were prepared before by asymmetric allylation of decanal (**1**).[11–16,18,19] The observed $[\alpha]_D^{20}$ value of –9.1 (c = 7.65, C_6H_6) for the enantiomer of **3** derived from the lower-migrating band of **5** is in agreement with the values reported for (*S*)-tridec-1-en-4-ol of –10.4 (c = 6.7, C_6H_6)[12] and –5.66 (c = 2.9, C_6H_6).[20]

In addition, the relative configurations of (*R*,*S*)-**5** and (*R*,*R*)-**5** were confirmed by comparison of the ^{1}H NMR spectroscopic data with those of structurally related allyl alcohols of known configuration (Scheme 2).[17] Between the reference diastereomers, the chemical shifts of the vinyl proton adjacent to the ester group differed by 0.20 ppm, and between (*R*,*S*)-**5** and (*R*,*R*)-**5** by 0.26 ppm.



Scheme 2.

Both enantiomers of **5** were independently used for the preparation of nonacosan-10-ol (**9**) in both configurations. For clarity, Scheme 3 shows the steps only for the synthesis of (*S*)-**9**. Allyl alcohols (*R*,*S*)-**5** and (*R*,*R*)-**5** were elongated with octadec-1-en in a cross-metathesis reaction with the Grubbs second-generation catalyst[21] **6** (Scheme 3) in dichloromethane at 45 °C. The C–C bond formation reaction gave (*R*,*S*)-**7** and (*R*,*R*)-**7** in 58% and 87% yield, respectively. Catalytic hydrogenation of (*R*,*S*)-**7** and (*R*,*R*)-**7** in methanol afforded (*R*,*S*)-**8** and (*R*,*R*)-**8** in 72 and 57% yield, respectively. Saponification of diastereomeric esters (*R*,*S*)-**8** and (*R*,*R*)-**8** with potassium hydroxide in ethanol/water (2:1) yielded desired nonacosan-10-ols (*S*)-**9** and (*R*)-**9** in 74 and 48% yield, respectively.



Scheme 3. Reagents and conditions: (a) Grubbs catalyst 2nd generation, CH_2Cl_2, 4 h, reflux (58%); (b) 5% Pd/C, methanol, H_2, 2 h, room temp. (73%); (c) KOH, MeOH/H_2O (2:1), 2 h, reflux (75%).

Crystallisation experiments on technical surfaces[22] with a mixture of synthesised (*S*)-**9** and extracted natural waxes of leaves of *Tropaeolum majus* L. showed an amount of tubular wax crystals that is also observed when the natural product alone is used. However, if the same experiments were done with a mixture of (*R*)-**9** and the extracted natural waxes, much less tubular wax crystals were observed. This is an indication for the (*S*) configuration of natural nonacosan-10-ol, in addition to those reported in previous studies.[3,5,10] More detailed studies regarding this phenomenon are in progress.

Conclusions

Both enantiomers of nonacosan-10-ol (**9**) are accessible by the short synthetic sequence summarised in Schemes 1

and 3. As demonstrated for the intermediates (*R*,*S*)-**5** and (*R*,*R*)-**5**, the compounds are obtained in high enantiomeric purity. The title compounds are currently used to investigate the influence of the stereochemistry on tubular wax formation in vitro.

Experimental Section

General: Glassware was flame-dried and reactions were carried out under an argon atmosphere. Chemical reagents were purchased from Fluka (Buchs, Switzerland) and Sigma (Taufkirchen, Germany). Column chromatography was performed with silica gel 60 (Merck, Darmstadt, Germany). ^{1}H NMR spectra were recorded with Bruker AM-400 (400 MHz) and Bruker AM-300 (300 MHz) instruments with the solvent as an internal standard ($CDCl_3$, δ_H = 7.24 ppm). ^{13}C NMR spectra were recorded with Bruker AM-400 (100 MHz) and Bruker AM-300 (75 MHz) instruments with the solvent as an internal standard ($CDCl_3$, δ_C = 77.0 ppm). ^{13}C NMR spectra were recorded in broadband decoupled mode and multiplicities were determined by using a DEPT pulse sequence. ESI-TOF-mass spectra were recorded in positive ion mode with a Q-TOF 2 mass spectrometer (Micromass, Manchester, UK) equipped with a nanospray source. Analytes were dissolved in chloroform/methanol and were injected into the mass spectrometer by glass capillaries by using a capillary voltage of 1000 V and a cone voltage of 50 V. Instrument calibration was done with a mixture of sodium iodide and cesium iodide dissolved in 50% aqueous 1-propanol. EI-mass spectra were recorded in positive ion mode with a MAT 95 mass spectrometer (Finnigan, Manchester, UK) in the analytical department of the Kekulé-Institut für Organische Chemie und Biochemie, Bonn.

Tridec-1-en-4-ol (3): Commercially available decanal (**1**) was distilled (4.8 mbar, 80 °C) prior to use and kept under an argon atmosphere. Decanal (**1**; 15.7 mL, 82.2 mmol) was dissolved in diethyl ether (85 mL) and the solution was cooled to –42 °C; a solution of allylmagnesium bromide in diethyl ether (**2**; 1.0 M, 100 mL, 100 mmol, 1.2 equiv.) was added drop wise. After one hour, the reaction mixture was brought to room temp. and stirred for one additional hour. A saturated aqueous ammonium chloride solution (85 mL) was added, and the aqueous phase was separated and extracted three times with diethyl ether. The collected organic phases were washed with an aqueous $NaHCO_3$ solution and then with water. The organic phase was dried with sodium sulfate, and the solvent was removed under reduced pressure. Purification by column chromatography on silica gel (cyclohexane/ethyl acetate, 10:1) yielded **3** (16.07 g, 81.0 mmol, 99%, R_f = 0.51) as a colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 5.83 (dddd, $^3J_{H,H}$ = 17.6 Hz, $^3J_{H,H}$ = 10.0 Hz, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 6.6 Hz, 1 H), 5.13 (ddt, $^3J_{H,H}$ = 17.6 Hz, $^2J_{H,H}$ = 2.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 5.12 (ddt, $^3J_{H,H}$ = 10.0 Hz, $^2J_{H,H}$ = 2.0 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 3.62 (ddt, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 4.2 Hz, 1 H), 2.29 (dddd, $^3J_{H,H}$ = 13.9 Hz, $^3J_{H,H}$ = 6.6 Hz, $^3J_{H,H}$ = 4.2 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 2.13 (dddd, $^3J_{H,H}$ = 13.9 Hz, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 7.9 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H), 1.63 (m, 1 H), 1.45 (m, 2 H), 1.26 (m, 14 H), 0.85 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 135.3, 118.3, 71.0, 42.3, 37.2, 32.2, 31.9, 30.0, 29.9, 29.7, 26.0, 23.0, 14.4 ppm. MS (ESI): *m*/*z* (%) = 221.12 (9) $[M + Na]^+$.

Tridec-1-en-4-yl 2-Methoxy-2-phenylacetate (5): To a solution of **3** (597 mg, 3.01 mmol) in dichloromethane (15 mL), was added (*R*)-α-methoxyphenylacetic acid (**4**, 1 g, 6.02 mmol, 2 equiv.) and dimethylaminopyridine (36.8 mg, 300 μmol). The mixture was cooled to 0 °C and dicyclohexylcarbodiimide (1.24 g, 6 mmol) was added in portions, and the mixture was stirred for two hours at 0 °C and for 3 d at room temp. The reaction mixture was evaporated, and the remaining residue was purified by silica gel column chromatography (cyclohexane/ethyl acetate, 80:1). The two products were isolated as colourless oils in a combined yield of 960 mg (92.0%). The chromatographic separation afforded pure (*R*,*R*)-**5** [24% of total product, R_f = 0.57 (cyclohexane/ethyl acetate, 10:1)], (*R*,*S*)-**5** [19% of total product, R_f = 0.52 (cyclohexane/ethyl acetate, 10:1)] and a mixture of both compounds (57%) that could be further resolved by repeated chromatography. (*R*,*R*)-**5**: $[\alpha]_D^{20}$ = –27.6 (*c* = 0.185, $CHCl_3$); (*R*,*S*)-**5**: $[\alpha]_D^{20}$ = –51.0 (*c* = 0.059, $CHCl_3$).

(2*R*)-(*S*)-Tridec-1-en-4-yl 2-Methoxy-2-phenylacetate [(*R*,*S*)-5]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.43 (m, 2 H), 7.33 (m, 3 H), 5.71 (ddt, $^3J_{H,H}$ = 17.1 Hz, $^3J_{H,H}$ = 10.1 Hz, $^3J_{H,H}$ = 7.0 Hz, 1 H), 5.04 (dtd, $^3J_{H,H}$ = 17.1 Hz, $^4J_{H,H}$ = 3.4 Hz, $^2J_{H,H}$ = 1.2 Hz, 1 H), 5.01 (dtd, $^3J_{H,H}$ = 10.1 Hz, $^4J_{H,H}$ = 2.0 Hz, $^2J_{H,H}$ = 1.2 Hz, 1 H), 4.95 (pseudo quintet, $^3J_{H,H}$ = 6.3 Hz, 1 H), 4.71 (s, 1 H), 3.41 (s, 3 H), 2.23 (m, 2 H), 1.42 (m, 2 H), 1.21 (m, 14 H), 0.88 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.7, 136.8, 133.8, 128.7, 127.5, 126.3, 118.0, 83.0, 74.5, 57.6, 39.0, 33.7, 32.1, 30.4, 29.7, 29.6, 29.5, 27.2, 25.0, 22.9, 14.4 ppm. MS (FAB): *m*/*z* (%) = 347.2 (16) $[M + H]^+$.

(2*R*)-(*R*)-Tridec-1-en-4-yl 2-Methoxy-2-phenylacetate [(*R*,*R*)-5]: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.43 (m, 2 H), 7.33 (m, 3 H), 5.45 (ddt, $^3J_{H,H}$ = 16.7 Hz, $^3J_{H,H}$ = 10.6 Hz, $^3J_{H,H}$ = 7.1 Hz, 1 H), 4.89 (m, 1 H), 4.75 (dtd, $^3J_{H,H}$ = 10.6 Hz, $^4J_{H,H}$ = 2.1 Hz, $^2J_{H,H}$ = 1.1 Hz, 1 H), 4.74 (dtd, $^3J_{H,H}$ = 16.7 Hz, $^4J_{H,H}$ = 3.4 Hz, $^2J_{H,H}$ = 1.1 Hz, 1 H), 4.69 (s, 1 H), 3.41 (s, 3 H), 2.11 (m, 2 H), 1.43 (m, 2 H), 1.23 (m, 14 H), 0.88 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.8, 136.8, 133.4, 128.9, 128.8, 127.5, 118.0, 83.1, 74.7, 57.7, 38.7, 33.9, 32.2, 30.5, 29.8, 29.7, 29.6, 29.5, 27.2, 25.5, 23.0, 14.4 ppm. MS (FAB): *m*/*z* (%) = 347.2 (16) $[M + H]^+$.

Nonacos-12-en-10-yl 2-Methoxy-2-phenylacetate [(*R*,*S*)-7]: (*R*,*S*)-**5** (12.0 mg, 34.6 μmol) was dissolved in dichloromethane (5 mL) and octadec-1-en (22.5 μL, 70.1 μmol, 2 equiv.) and Grubbs 2nd generation catalyst (**6**; 5.3 mg, 17 mol-%) were added. The solution was then heated at reflux for 4 h, during which the solution colour turned from red into brown. Purification by silica gel column chromatography (cyclohexane/ethyl acetate, 40:1) gave product (*R*,*S*)-**7** (11.4 mg, 20.0 μmol, 58%, R_f = 0.26) as a colourless oil. (*R*,*R*)-**7**: Yield: 87% (50.2 mg, 87.9 μmol, R_f = 0.27) from (*R*,*R*)-**5** (35.1 mg).

(*R*,*S*)-7: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.44 (m, 2 H), 7.34 (m, 3 H), 5.37 (dt, $^3J_{H,H}$ = 15.3 Hz, $^3J_{H,H}$ = 6.5 Hz, 1 H), 5.29 (dt, $^3J_{H,H}$ = 15.3 Hz, $^3J_{H,H}$ = 6.7 Hz, 1 H), 4.90 (tt, $^3J_{H,H}$ = 6.2 Hz, $^3J_{H,H}$ = 6.2 Hz, 1 H), 4.73 (s, 1 H), 3.41 (s, 3 H), 2.23 (m, 1 H), 1.94 (m, 1 H), 1.69 (m, 2 H), 1.43 (m, 2 H), 1.25 (m, 42 H), 0.88 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.7, 136.9, 134.3, 128.8, 128.7, 127.5, 127.4, 124.8, 83.0, 75.1, 57.6, 37.7, 33.6, 32.8, 32.2, 32.1, 30.4, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 27.6, 25.1, 22.9, 14.4 ppm. MS (ESI): *m*/*z* (%) = 593.40 (38) $[M + Na]^+$, 1163.80 (100) $[2M + Na]^+$.

(*R*,*R*)-7: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.36 (m, 2 H), 7.27 (m, 3 H), 5.18 (dt, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 1.3 Hz, 1 H), 4.95 (tt, $^3J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 1.4 Hz, 1 H), 4.83 (m, 1 H), 4.67 (s, 1 H), 3.34 (s, 3 H), 2.34 (m, 1 H), 2.03 (m, 1 H), 1.76 (m, 2 H), 1.44 (m, 2 H), 1.19 (m, 42 H), 0.87 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H), 0.85 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 169.7, 135.9, 133.3, 127.9, 127.8, 126.5, 123.6, 82.1, 74.4, 56.6,

36.4, 32.8, 31.8, 31.3, 31.2, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 24.6, 22.0, 13.5 ppm. MS (ESI): *m/z* (%) = 593.46 (43) $[M + Na]^+$, 1163.93 (98) $[2M + Na]^+$.

Nonacosan-10-yl 2-Methoxy-2-phenylacetate [(*R*,*S*)-8]: (*R*,*S*)-**7** (11.4 mg, 20.0 μmol) was dissolved in methanol (4 mL), degassed under reduced pressure, and brought into an argon atmosphere. A small amount of catalyst (5 wt.-% palladium on carbon powder) was added, the suspension was degassed again and stirred for 2 h in a hydrogen atmosphere at room temperature. The suspension was degassed, saturated with argon, and the catalyst was removed by filtration. The solvent was removed, and the remaining residue was dried under reduced pressure to yield (*R*,*S*)-**8** (8.3 mg, 14.5 μmol, 73%, R_f = 0.32) as a colourless oil. (*R*,*R*)-**8**: Yield: 28.8 mg (50.3 μmol, 57%, R_f = 0.34) from (*R*,*R*)-**7** (50.2 mg).

(*R*,*S*)-8: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.44 (m, 2 H), 7.32 (m, 3 H), 4.88 (quintet, $^3J_{H,H}$ = 6.4 Hz, 1 H), 4.73 (s, 1 H), 3.42 (s, 3 H), 1.50 (m, 4 H), 1.26 (m, 48 H), 0.88 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.8, 128.8, 128.7, 127.4, 83.1, 75.6, 57.5, 34.4, 34.3, 34.2, 32.2, 32.1, 30.0, 29.9, 29.8, 29.7, 29.6, 29.5, 25.5, 25.4, 25.1, 22.9, 14.4 ppm. MS (ESI): *m/z* (%) = 595.49 (100) $[M + Na]^+$.

(*R*,*R*)-8: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.43 (m, 2 H), 7.32 (m, 3 H), 4.90 (quintet, $^3J_{H,H}$ = 6.4 Hz, 1 H), 4.73 (s, 1 H), 3.42 (s, 3 H), 1.39 (m, 4 H), 1.26 (s, 48 H), 0.87 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 170.9, 137.0, 128.9, 128.8, 127.5, 83.2, 75.7, 57.6, 34.5, 34.3, 32.3, 32.2, 30.1, 30.0, 29.9, 29.8, 29.7, 25.6, 25.2, 23.0, 14.5 ppm. MS (ESI): *m/z* (%) 595.43 (81) $[M + Na]^+$, 1167.87 (90) $[2M + Na]^+$.

Nonacosan-10-ol [(*S*)-9]: (*R*,*S*)-**8** (8.3 mg, 14.5 μmol) was dissolved in ethanol/water (2:1; 15 μL) and potassium hydroxide (2.4 mg, 42.8 μmol, 3 equiv.) was added. The solution was then stirred and heated at reflux for 2 h. The solution was concentrated under reduced pressure, and the remaining residue purified by column chromatography on silica gel (cyclohexane/ethyl acetate, 40:1; R_f = 0.24) to yield (*S*)-**9** (4.6 mg, 10.8 μmol, 75%) as white crystals. (*R*)-**9**: Yield: 10.2 mg (24.0 μmol, 48%, R_f = 0.24) from (*R*,*R*)-**8** (21.4 mg).

(*S*)-9: M.p. 79 °C (ref.[3] 81–81.5 °C). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.58 (m, 1 H), 2.04 (s, 1 H), 1.43 (m, 4 H), 1.26 (m, 48 H), 0.88 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 72.4, 37.9, 32.3, 31.9, 30.1, 30.0, 29.9, 29.7, 26.0, 23.0, 14.5 ppm. MS (ESI): *m/z* (%) = 447.45 (12) $[M + Na]^+$. $[\alpha]_D^{20}$ = +0.011 (*c* = 3.95, $CHCl_3$).

(*R*)-9: M.p. 80 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.58 (m, 1 H), 1.97 (s, 1 H), 1.43 (m, 4 H), 1.26 (m, 48 H), 0.89 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 72.4, 37.9, 32.3, 31.9, 30.1, 30.0, 29.9, 29.7, 26.0, 23.0, 14.5 ppm. MS (ESI): *m/z* (%) = 447.46 (1) $[M + Na]^+$. $[\alpha]_D^{20}$ = –0.006 (*c* = 4.95, $CHCl_3$).

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