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Total Syntheses of Rhodiolosides A and D and of Sachalinols A–C

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Dedicated to Professor Henning Hopf on the occasion of his 70th birthday

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The glucosylated monoterpenoids (–)-rhodioloside A and (–)-rhodioloside D from the roseroot (*Rhodiola rosea*) have been synthesized for the first time. Glucosylation with tetrapivaloylglucosyl bromide proved superior to the use of tetraacetylglucosyl bromide or glucosyl iodides. Acid-catalyzed cyclization of a homoglycidol-type geraniol derivative afforded the monoterpenoid tetrahydrofuran (+)-sachalinol C from *Rhodiola sachalinensis*. The absolute configuration of (+)-sachalinol C requires revision. (–)-Sachalinol A and (–)-sachalinol B were also obtained.

Introduction

Secondary metabolites from the medicinal plant *Rhodiola rosea* (Crassulaceae, roseroot) include hydroxylated and glycosylated derivatives of the monoterpenoid (–)-rosiridol (**1**, Figure 1, 4-hydroxygeraniol).[1–3] (–)-Rosiridol itself also occurs in the leaves of *Cunila spicata* (Lamiaceae)[4] and in the petals of the rose *Rosa damascena*.[5] (–)-Rosiridin (**2**) is the β-glucosylated analogue of (–)-rosiridol (**1**)[6] and has recently been identified as an inhibitor of monoamine oxidase B (MAO B), which is involved in neurodegenerative diseases.[7] After contradictory assignments, the stereochemistry of the monoterpenoid sections of (–)-rosiridol (**1**) and (–)-rosiridin (**2**) was established as (4*S*) by total synthesis[8,9] and by reinvestigation of the isolated natural products.[10,11]

In this paper we describe the first total syntheses of (–)-rhodioloside A (**4**), (–)-rhodioloside D (**5**, Scheme 4, below), (–)-sachalinol B (**6**, Scheme 5, below), and (+)-sachalinol C (**7**, Scheme 5, below). (–)-Rhodioloside A (**4**) from *Rhodiola sachalinensis* is related to (–)-rosiridin (**2**) by terminal hydroxylation at C-8. The tertiary alcohol (–)-rhodioloside D (**5**) is the monoglucosylated form of (–)-sachalinol A (**3**, 4,7-dihydroxygeraniol).[12] Sachalinols B (**6**) and C (**7**, vide infra) from *Rhodiola sachalinensis* each feature a tetrahydrofuran ring and may arise by epoxidation of the terminal double bond of (–)-rosiridol (**1**), followed by cyclization.[6] The monoterpenoid tetrahydrofuran systems of sachalinols B and C also occur in coumarin derivatives, from *Mutisia orbignyana* (Asteraceae), for example.[13] Closely related are the pantofuranoids D–F from the Antarctic red alga *Pantoneura plocamioides*[14] and the further oxidized geranylated coumarin derivative geiparvarin.

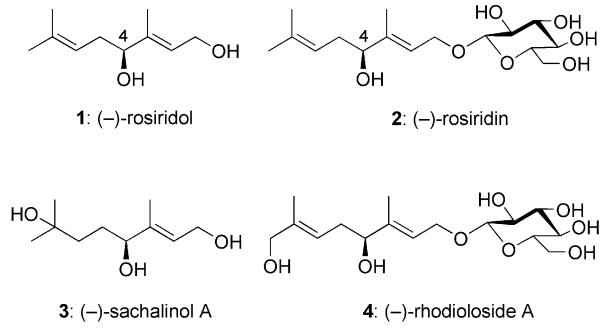

Figure 1. Sachalinols and rhodiolosides: oxygenated derivatives of (–)-rosiridol (**1**) and (–)-rosiridin (**2**).

Results and Discussion

The starting material **8** (Scheme 1) was synthesized as described earlier.[9] For the enantioselective reduction of **8**, we replaced DIP-Cl by the CBS reagent [(+)-(*R*)-2-methyl-CBS-oxazaborolidine],[15] which provided the secondary alcohol **9** in a higher yield (66% in comparison with 44%) though with a slightly lower *ee* (90% in comparison with 94%). Mosher analysis[16] of **9** confirmed the stereochemical outcome of the CBS reduction, with the prenyl group functioning as the smaller substituent.

Riley oxidation[17] of **10** with SeO_2/TBHP afforded a mixture of the (*E*)-allylic alcohol **11** (19–32% yield) and the corresponding (*E*)-aldehyde (**12**, 6–32%), which was reduced back to the alcohol **11** with $NaBH_4$/EtOH. Over two

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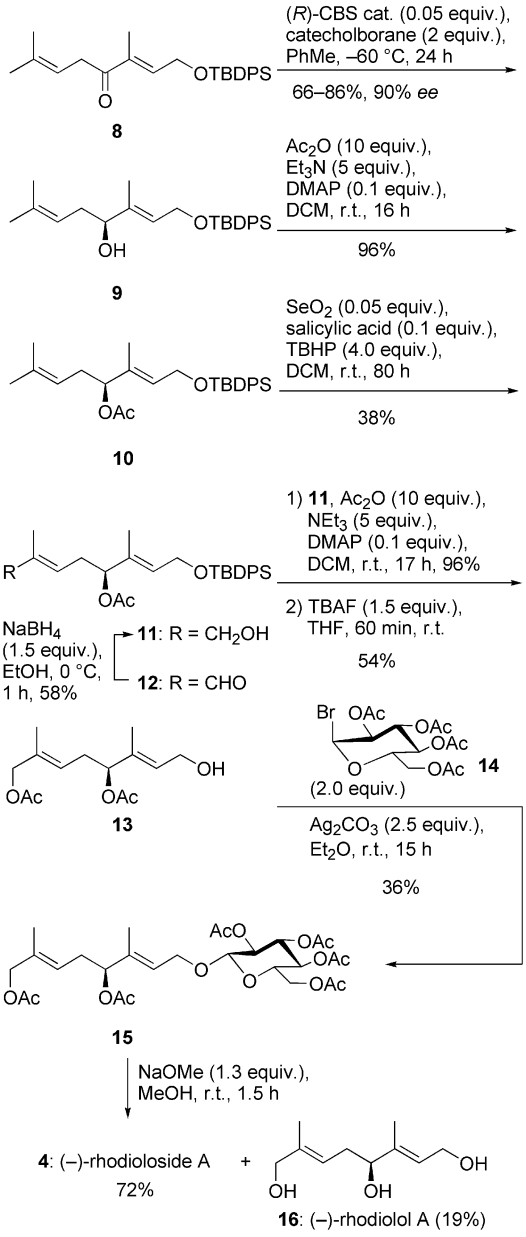
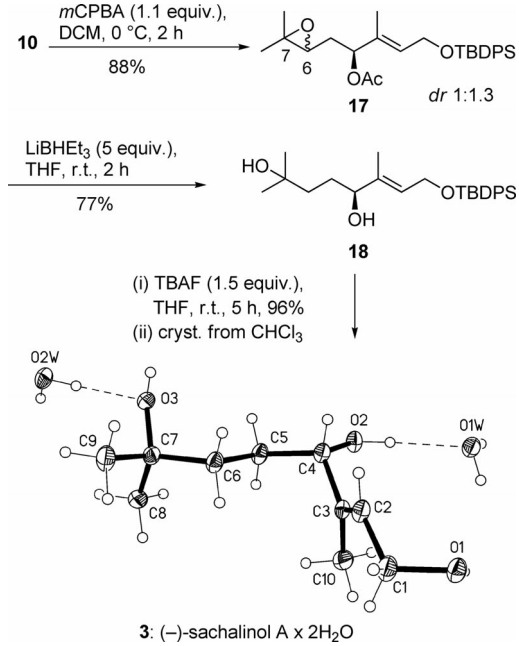


Scheme 1. Synthesis of (–)-rhodioloside A (**4**) through CBS reduction of the ketone **8**.

steps, the average yield of alcohol **11** ranged from 27 to 45% with recovered starting material.

After protecting group manipulation, Koenigs–Knorr glucosylation of **13** (Scheme 1) with tetraacetylglucosyl bromide (**14**) afforded pentaacetylrhodioloside A (**15**) in modest yield (36%, 45% based on recovered starting material). Separation of the glucosylated product **15** and the precursor alcohol **13** by normal-phase chromatography proved to be tedious, but workup was facile at the level of the deacetylated products (–)-rhodioloside A (**4**) and (–)-rhodiolol A (**16**), synthesized by methanolysis of a mixture of **15** and **13**. The aglycon (–)-rhodiolol A (**16**) had originally been obtained by Koike et al. by naringinase-catalyzed enzymatic hydrolysis of (–)-rhodioloside A (**4**).[12]

(–)-Rhodioloside D (**5**) and (–)-sachalinol A (**3**) share oxygenation at C-7. The epoxidized building block **17** was therefore synthesized by *m*CPBA epoxidation of the terminal double bond of **10** (Scheme 2).

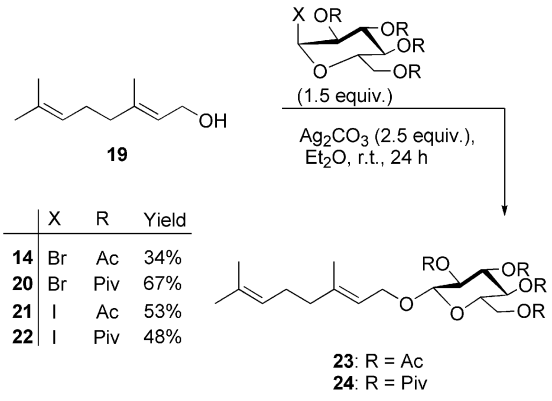


Scheme 2. Synthesis of (–)-sachalinol A (**3**) through Super-Hydride® reduction of the epoxide **17**. Structure of the (–)-sachalinol A dihydrate in the crystal.

The epoxide **17** (88%, 1:1.3 mixture of diastereomers) was reduced with $LiBEt_3H$ (5 equiv.) to afford the diol **18** in 77% yield. The reduction was accompanied by deacetylation, which was faster than the subsequent regioselective epoxide opening. Alternative use of $NaBH_4$ (up to 30 equiv.) led to incomplete oxirane reduction (24%) and afforded substantial amounts (70%) of the deacetylated epoxide. Desilylation of **18** afforded the natural product (–)-sachalinol A (**3**), exhibiting a negative optical rotation $\{[\alpha]_D^{24} = -12.8$ (c = 1.0, MeOH)}, similar to that reported for the natural product $\{[\alpha]_D^{25} = -17.1$ (c = 0.17, MeOH)}.[3,6]

Originally, Kadota et al. proposed that (–)-sachalinol A was the (4*R*) enantiomer of structure **3**.[6] Koike et al. reassigned the absolute configuration of (–)-sachalinol A (**3**) as (4*S*).[11] Díez et al. reported the first total synthesis of **3** via an α,β-unsaturated nitrile intermediate.[18] X-ray analysis of a crystal of our synthesized material obtained from chloroform provided independent verification of the absolute configuration of (–)-sachalinol A (**3**), based on the anomalous scattering of the oxygen atoms. The compound crystallizes as a dihydrate. The atom sequence O2–C4–C5–C6–C7–C9 displays an all-*trans* geometry. All hydrogen atoms of the water molecules and OH groups function as donors in classical hydrogen bonds, forming a layer structure parallel to the *bc* plane with hydrophilic regions at z = 0, 1, etc. (Scheme 2).

Aiming at a more efficient synthesis of glucosylated (–)-rhodioloside D (**5**), we compared glucosyl bromides and iodides in the forms of their tetraacetylated and tetrapivaloylated derivatives. Glucosyl iodides can be superior to the corresponding bromides.[19] We treated the model compound geraniol (**19**) with peracetylated α-glucosyl iodide (**21**, R = Ac, X = I)[20] in the presence of Ag_2CO_3 in Et_2O and obtained the β-glucoside **23** (R = Ac, Scheme 3) in a yield of 53%, in comparison with 34% when the glucosyl bromide **14** was employed. Kunz et al. reported that pivaloylated glucosyl bromides are superior to acetylated building blocks, because orthoester formation is suppressed.[21] For pivaloylated glucosyl donors we obtained better yields with the glucosyl bromide **20** (67%) than with the iodide **22** (48%). The new glucosyl iodide **22** (R = Piv, X = I) was obtained by treatment of pentapivaloyl glucose with I_2/Me_6Si_2 in DCM.



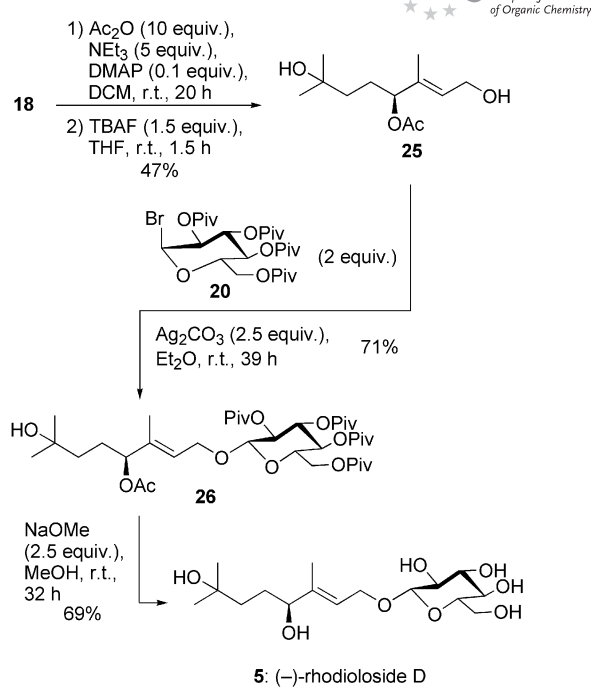
	X	R	Yield
14	Br	Ac	34%
20	Br	Piv	67%
21	I	Ac	53%
22	I	Piv	48%

Scheme 3. Study on the yields of geraniol β-glucosylation.

The diol **25** was prepared from **18** in two steps and was then treated with tetrapivaloylglucosyl bromide (**20**) in the presence of Ag_2CO_3 in Et_2O (Scheme 4). Glucosylation proceeded with 71% yield and complete β-diastereoselectivity, whereas with the tetraacetylglucosyl bromide (**14**), yields of only 20–30% were reached. From a practical point of view, monitoring of the glucosylation reaction by TLC was easier in the case of the pivaloyl-protected glucosyl donor **20**. Deprotection of **26** with NaOMe/MeOH provided the natural product **5**.

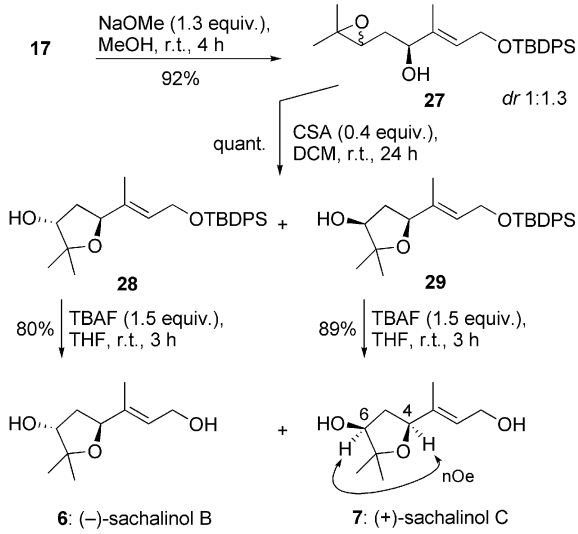
For the synthesis of the tetrahydrofurans sachalinol B (**6**) and C (**7**), the epoxide **17** was deacetylated by methanolysis to afford the homoglycidol **27** as a mixture of diastereomers (*dr* 1:1.3, Scheme 5). Treatment of **27** with CSA (0.4 equiv.) in DCM led to epoxide opening and quantitative formation of the tetrahydrofuran ring to afford the diastereomers **28** and **29**, which were separated by semipreparative normal-phase HPLC.[22] Desilylation of **28** and **29** by use of TBAF liberated the target compounds **6** and **7** in 80% and 89% yields, respectively. Nonstereoselective syntheses of 3-hydroxy-2,2-dimethyltetrahydrofurans have employed SeO_2 oxidation of terminally epoxidized geraniol derivatives at C-4 under acidic conditions.[23] Our pathway is stereoselective.

The availability of sachalinols B and C by total synthesis allowed us to analyze their relative and absolute stereo-



Scheme 4. Synthesis of (–)-rhodioloside D (**5**) by use of the pivaloylated glucosyl donor **20**.

chemistry. The ^{13}C NMR spectroscopic data for **6** and **7** agree with those reported by Kadota et al. for sachalinols B and C, respectively. In the NOESY spectrum of sachalinol C (**7**) we observe a correlation between 4-H and 6-H, whereas this is not the case for its C-6 epimer **6**. We can thus confirm Kadota's assignments of the relative stereochemistry of sachalinols B and C, which were originally based on pyridine-induced shifts of the NMR signals of the protons *cis* to the hydroxy group on change of the solvent from [D_4]methanol to [D_5]pyridine.[6]



Scheme 5. Cyclization to (–)-sachalinol B (**6**) and (+)-sachalinol C (**7**). Compounds **28** and **29** were separated by normal-phase HPLC.

The picture is different with regard to the absolute stereochemistry of sachalinols B and C. Synthetic (+)-sachalinol C exhibits a positive optical rotation {**7**, $[\alpha]_D^{29}$ = +47.0 (c = 0.06, MeOH)}, which is in agreement with the value reported {$[\alpha]_D^{25}$ = +40.2 (c = 0.05, in MeOH)} for the natural product (+)-sachalinol C.[6] Because the configuration of our synthetic product at C-4 is known, the absolute configuration of the natural product (+)-sachalinol C (**7**) must be revised to (4*S*), as has already been necessary for (–)-sachalinol A (**3**, vide supra) and (–)-rosiridol (**1**).[9] However, the sense of rotation of the synthesized (–)-sachalinol B {**6**, $[\alpha]_D^{24}$ = –29.2 (c = 0.24, MeOH)} is the opposite of that of the natural product (+)-sachalinol B {*ent*-**6**, $[\alpha]_D^{25}$ = +60.3 (c = 0.07, in MeOH)} reported by Kadota.[6]

To verify that the synthesized compounds **6** and **7** are epimeric only at C-6 and share the same configuration at C-4, we converted the mixture of the TBDPS-protected precursors **28** and **29** into the corresponding mixtures of (*R*)- and (*S*)-Mosher esters. In both cases, mixtures of only two products were obtained, which confirms that the diastereomers **28** and **29** are enantiomerically pure and that no partial racemization had occurred on formation of the tetrahydrofuran ring. The Mosher esters exhibited positive (**28**) and negative (**29**) $\Delta\delta$ values ($\delta_{(S)\text{-ester}} - \delta_{(R)\text{-ester}}$) for the methylene protons 5-H_a and 5-H_b, meaning that diastereomers **28** and **29** are epimeric at C-6, but not at C-4.[24] It can be assumed that desilylation does not lead to epimerization of the stereogenic centers.

On the basis of the available data, the natural products (+)-sachalinol B (*ent*-**6**) and (+)-sachalinol C (**7**) appear to have opposite configurations at C-4. The deviation of the absolute values of optical rotation might be a consequence of the lower concentration chosen by Kadota on measurement.

With regard to the biosynthesis of (+)-sachalinol B (*ent*-**6**), one could speculate that consumption of (–)-rosiridol (**1**) by glucosylation to produce the by far major metabolite (–)-rosiridin (**2**) would enrich a hitherto unidentified (+)-rosiridol. Reagent-controlled diastereoselective epoxidation of the terminal double bonds of (–)-rosiridol and (+)-rosiridol in the remaining mixture, followed by cyclization to the tetrahydrofuran system, would generate (+)-sachalinol B (*ent*-**6**) and (+)-sachalinol C (**7**), respectively, with opposite configurations at C-4, but identical configurations at C-6.

Conclusion

The oxygenated monoterpenoids (–)-rhodioloside A, (–)-rhodioloside D, and (+)-sachalinol C from the roseroot *Rhodiola* sp. have been synthesized for the first time. In addition, (–)-sachalinol A and (–)-sachalinol B were obtained. Key steps were the enantioselective CBS reduction of the allyl homoallyl ketone **8**, the optimized glucosylation of geraniol derivatives by employing pivaloylated glucosyl bromide, and the acid-catalyzed cyclization of homoglycidol **27** to the hydroxytetrahydrofuran system. The relative and absolute stereochemistry of the natural products has been clarified.

Experimental Section

General: NMR spectra were taken with Bruker DRX 400, Bruker AV III 400 (400.1 MHz for ^{1}H, 100.6 MHz for ^{13}C), and Bruker AV II 600 (600.1 MHz for ^{1}H; 150.9 MHz for ^{13}C) instruments, referenced to the solvent signal or TMS. All measurements were carried out at 300 K. Mass spectra were obtained with LTQ Orbitrap Velos, Thermo Finnigan LTQ FT, Thermo Finnigan MAT95, and Finnigan MAT 95 XLT spectrometers. IR spectra were recorded with a Bruker Tensor 27 spectrometer. UV/Vis spectra were measured with a Varian Cary 100 Bio UV/Vis spectrometer. Optical rotations were measured with a Dr. Kernchen Propol automatic polarimeter. Melting points were measured with a Büchi 530 melting point apparatus. Chemicals were purchased from commercial suppliers and used without further purification. Silica gel 60 (40–63 μm, Merck) was used for column chromatography. HPLC separations were carried out with a Merck Hitachi L-6200 intelligent pump system, fitted with a LiChrosorb Si-60 column (5 μm).

(2*E*)-1-(*tert*-Butyldiphenylsilanyloxy)-3,7-dimethylocta-2,6-dien-4-one (8): IBX (2.06 g, 7.3 mmol, 1.5 equiv.) was dissolved in DMSO (10 mL). After 15 min, a solution of *rac*-**9** (2.00 g, 4.9 mmol, 1.0 equiv.) in DMSO (5 mL) was added, and the resulting solution was stirred at room temp. for 15 h. The reaction mixture was diluted with water, and the resulting precipitate was filtered and washed with water and petroleum ether. The filtrate was extracted with petroleum ether, and the combined organic layers were washed with an aqueous solution of $NaHCO_3$ and dried with $MgSO_4$. Evaporation of the solvent yielded the ketone **8** (1.80 g, 4.4 mmol, 90%) as a yellow oil. R_f (petroleum ether/EtOAc, 20:1) = 0.40. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 4 H, Ph-*o*-*H*), 7.47–7.37 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 6.71–6.68 (m, 1 H, OCH_2CH), 5.31–5.27 [m, 1 H, $(CH_3)_2CCH$], 4.44 (d, ^3J = 5.3 Hz, 2 H, OCH_2CH), 3.34 (d, ^3J = 7.0 Hz, 2 H, CH_2CHO), 1.75 [s, 3 H, $(CH_3)_2C$], 1.66 [s, 3 H, $(CH_3)_2C$], 1.56 (s, 3 H, CCH_3), 1.08 [s, 9 H, $(CH_3)_3C$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.0 (1 C, *C*O), 141.7 (1 C, OCH_2CH), 135.6 [1 C, (CH_3C)], 135.5 (4 C, *o*-C_{Ph}), 134.7 [1 C, $(CH_3)_2C$], 133.2 (2 C, *ipso*-C_{Ph}), 129.8 (2 C, *p*-C_{Ph}), 127.8 (4 C, *m*-C_{Ph}), 117.1 [1 C, $(CH_3)_2CCH$], 61.7 (1 C, OCH_2CH), 37.3 (1 C, CH_2CHO), 26.8 [3 C, $(CH_3)_3C$], 25.8 [1 C, $(CH_3)_2C$], 19.1 [1 C, $(CH_3)_3C$], 18.1 [1 C, $(CH_3)_2C$], 11.5 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 1674 (m), 1428 (m), 1106 (s), 1055 (s), 822 (m), 738 (m), 700 (s), 612 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lg ε) = 202 (4.46), 218 (4.33), 240 (3.89) nm. MS (FAB): *m*/*z* (%) = 407 (14), 405 (16), 349 (16), 291 (13), 239 (12), 199 (74), 135 (100). HRMS (FAB): calcd. for $C_{26}H_{35}O_2Si$ $[M + H]^+$ 407.2406; found 407.2370.

(2*E*,4*S*)-1-(*tert*-Butyldiphenylsilanyloxy)-3,7-dimethylocta-2,6-dien-4-ol (9): Under Ar, the ketone **8** (300 mg, 0.73 mmol, 1.0 equiv.) was dissolved in toluene (10 mL), and the solution was cooled to –60 °C. (+)-(*R*)-2-Methyl-CBS-oxazaborolidine (1 M in toluene, 70 μL, 0.07 mmol, 0.1 equiv.) was added, followed by catecholborane (1 M in THF, 1.46 mL, 1.46 mmol, 2.0 equiv., by syringe pump over 12 h). After 24 h, the reaction was quenched by the addition of MeOH (1 mL), and the mixture was allowed to warm to room temp. and diluted with Et_2O. The organic phase was washed with NaOH solution (1 M) and saturated aqueous $NaHCO_3$ solution until the organic phase was colorless. The organic phase was then washed with brine and dried with $MgSO_4$, and the solvent was evaporated. Chromatography (silica gel, petroleum ether/EtOAc, 10:1) yielded (*S*)-**9** (260 mg, 0.64 mmol, 86%) as a colorless oil. R_f (petroleum ether/EtOAc, 10:1) = 0.29. $[\alpha]_D^{25}$ = –4.3 (c = 2.8, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.76 (m, 4 H, Ph-*o*-*H*), 7.44–7.35 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.64–5.60 (m, 1 H, OCH_2CH), 5.12–5.07 [m, 1 H, $(CH_3)_2CCH$], 4.27 (d, ^3J = 6.1 Hz,

2 H, OCH_2CH), 3.98–3.94 (m, 1 H, C*H*OH), 2.28–2.15 (m, 2 H, CH_2CHOH), 1.72 [d, ^4J = 1.1 Hz, 3 H, (CH_3)$_2$C], 1.63 [s, 3 H, (CH_3)$_2$C], 1.49 (br., 1 H, O*H*), 1.45 (d, ^4J = 1.1 Hz, 3 H, CCH_3), 1.05 [s, 9 H, (CH_3)$_3$C] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.1 (1 C, CH*C*CH$_3$), 135.6 (4 C, *o*-C_{Ph}), 134.8 [1 C, (CH$_3$)$_2$*C*], 133.9 (1 C, *ipso*-C_{Ph}), 133.9 (1 C, *ipso*-C_{Ph}), 129.6 (2 C, *p*-C_{Ph}), 127.6 (4 C, *m*-C_{Ph}), 125.5 (1 C, OCH$_2$*C*H), 119.9 [1 C, (CH$_3$)$_2$-C*C*H], 76.6 (1 C, *C*HOH), 60.8 (1 C, O*C*H$_2$CH), 33.9 (1 C, *C*H$_2$CHOH), 26.8 [3 C, (*C*H$_3$)$_3$C], 25.9 [1 C, (*C*H$_3$)$_2$C], 19.1 [1 C, (CH$_3$)$_3$*C*], 18.0 [1 C, (*C*H$_3$)$_2$C], 12.0 (1 C, *C*H$_3$C) ppm. IR (ATR): $\tilde{\nu}$ = 3401 (br., w), 1109 (m), 1066 (m), 822 (m), 740 (m), 701 (s), 609 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 205 (4.34) nm. MS (EI, 70 eV): *m*/*z* (%) = 408 (1), 333 (3), 267 (7), 201 (6), 200 (17), 199 (100), 181 (11), 135 (18), 77 (18). HRMS (EI): calcd. for $C_{26}H_{34}OSi$ [M – H_2O]$^+$ 390.2379; found 390.2392.

(2*E*,4*S*)-1-(*tert*-Butyldiphenylsilyloxy)-3,7-dimethylocta-2,6-dien-4-yl Acetate (10): DMAP (14.9 mg, 0.12 mmol, 0.1 equiv.), anhydrous NEt_3 (0.85 mL, 6.10 mmol, 5.0 equiv.), and Ac_2O (1.14 mL, 12.2 mmol, 10 equiv.) were added to a solution of (*S*)-**9** (500 mg, 1.22 mmol, 1.0 equiv.) in anhydrous DCM (10 mL). After 17 h, the reaction was quenched by the addition of an aqueous NH_4Cl solution, and the aqueous phase was extracted with DCM. The organic phase was dried with $MgSO_4$, and the solvent was evaporated. After chromatography (silica gel, petroleum ether/EtOAc, 40:1), the acetate **10** (470 mg, 1.04 mmol, 85%) was obtained as a colorless oil. R_f (petroleum ether/EtOAc, 40:1) = 0.14. $[a]_D^{25}$ = –9.6 (*c* = 4.8, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.66 (m, 4 H, Ph-*o*-*H*), 7.44–7.35 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.66–5.62 (m, 1 H, OCH$_2$C*H*), 5.09 (t, ^3J = 6.9 Hz, 1 H, C*H*O), 5.04–4.99 [m, 1 H, (CH$_3$)$_2$CC*H*], 4.24 (d, ^3J = 5.9 Hz, 2 H, OCH_2CH), 2.37–2.20 (m, 2 H, CH_2CHOH), 2.03 (s, 3 H, CH_3CO), 1.68 [d, ^4J = 1.1 Hz, 3 H, (CH_3)$_2$C], 1.61 [d, ^4J = 0.6 Hz, 3 H, (CH_3)$_2$C], 1.43 (d, ^4J = 1.1 Hz, 3 H, CCH_3), 1.04 [s, 9 H, (CH$_3$)$_3$C] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2 (1 C, CH$_3$*C*OO), 135.6 (4 C, *o*-C_{Ph}), 134.2 (1 C, CH*C*CH$_3$), 134.2 [1 C, (CH$_3$)$_2$*C*], 133.8 (2 C, *ipso*-C_{Ph}), 129.6 (2 C, *p*-C_{Ph}), 127.6 (4 C, *m*-C_{Ph}), 127.3 (1 C, OCH$_2$*C*H), 119.0 [1 C, (CH$_3$)$_2$C*C*H], 78.1 (1 C, *C*HO), 60.7 (1 C, O*C*H$_2$CH), 31.6 (1 C, *C*H$_2$CHOH), 26.8 [3 C, (*C*H$_3$)$_3$C], 25.8 [1 C, (*C*H$_3$)$_2$C], 21.2 (1 C, *C*H$_3$COO), 19.1 [1 C, (CH$_3$)$_3$*C*], 17.9 [1 C, (*C*H$_3$)$_2$C], 12.6 (1 C, *C*H$_3$C) ppm. IR (ATR): $\tilde{\nu}$ = 1737 (m), 1237 (s), 1110 (m), 1067 (m), 1046 (m), 1019 (m), 823 (m), 740 (m), 703 (s), 611 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 203 (4.54), 217 (4.27) nm. MS (ESI): *m*/*z* (%) = 473 (100), 474 (35), 475 (8). HRMS (ESI): calcd. for $C_{28}H_{38}O_3SiNa$ [M + Na]$^+$ 473.2488; found 473.2495.

(2*E*,4*S*,6*E*)-1-(*tert*-Butyldiphenylsilanyloxy)-8-hydroxy-3,7-dimethylocta-2,6-dien-4-yl Acetate (11) and (2*E*,4S,6*E*)-1-[(*tert*-Butyldiphenylsilanyl)oxy]-3,7-dimethyl-8-oxoocta-2,6-dien-4-yl Acetate (12): SeO_2 (4.3 mg, 0.04 mmol, 0.05 equiv.) and salicylic acid (10.6 mg, 0.08 mmol, 0.10 equiv.) were suspended in DCM (2 mL). *tert*-Butyl hydroperoxide (500 μL, 4.00 equiv. 70% aqueous solution) was added in one portion at 0 °C. A solution of **10** (345 mg, 0.77 mmol, 1.00 equiv.) in DCM (2 mL) was added slowly at 0 °C. The solution was stirred at room temp. for 5 d and then poured into an aqueous solution of $FeSO_4$ (0.5 M, 20 mL) at 0 °C. Stirring was continued at 0 °C for 30 min. After separation of the phases, the aqueous layer was extracted with DCM, and the combined organic layers were washed with aqueous NaOH (1 M), H_2O, and brine. The organic layers were dried with $MgSO_4$, and the solvent was evaporated. Chromatography (silica gel, petroleum ether/EtOAc, 20:1 → 10:1 → 5:1 → 3:1) yielded the alcohol **11** (116 mg, 0.25 mmol, 32%) as a colorless oil along with the aldehyde **12** (22 mg, 0.05 mmol, 6%) as a colorless oil and the starting material **10** (116 mg, 0.26 mmol, 43%).

Compound 11: $[a]_D^{25}$ = –5.3 (*c* = 0.6, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.65 (m, 4 H, Ph-*m*-*H*), 7.44–7.35 (m, 6 H, Ph-*o*-*H*, Ph-*p*-*H*), 5.66–5.63 (m, 1 H, OCH$_2$C*H*), 5.35–5.30 (m, 1 H, C*H*CCH$_2$OH), 5.13 (t, ^3J = 6.8 Hz, 1 H, C*H*O), 4.25–4.24 (m, 2 H, OCH_2CH), 3.97 (s, 2 H, CH_2OH), 2.44–2.26 (m, 2 H, CH_2CHO), 2.03 (s, 3 H, CH_3COO), 1.67 [d, ^4J = 1.0 Hz, 3 H, (CH_3CCH$_2$OH)], 1.44 (d, ^4J = 1.1 Hz, 3 H, CH_3C), 1.04 [s, 9 H, (CH$_3$)$_3$C] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.9 (1 C, CH$_3$*C*OO), 137.2 (1 C, *C*CH$_2$OH), 135.2 (4 C, *m*-C_{Ph}), 133.7 (1 C, CH*C*CH$_3$), 133.5 (1 C, *ipso*-C_{Ph}), 133.4 (1 C, *ipso*-C_{Ph}), 129.3 (2 C, *p*-C_{Ph}), 127.3 (4 C, *o*-C_{Ph}), 127.1 (1 C, OCH$_2$*C*H), 120.2 (1 C, *C*HCCH$_2$OH), 77.4 (1 C, *C*HO), 68.3 (1 C, *C*H$_2$OH), 60.3 (1 C, O*C*H$_2$CH), 30.8 (1 C, *C*H$_2$CHO), 26.4 [3 C, (*C*H$_3$)$_3$C], 20.9 (1 C, *C*H$_3$COO), 18.8 [1 C, (CH$_3$)$_3$*C*], 13.5 (1 C, *C*H$_3$CCH$_2$OH), 12.3 (1 C, *C*H$_3$C) ppm. IR (ATR): $\tilde{\nu}$ = 3432 (w, br.), 2931 (m), 2857 (m), 1737 (m), 1428 (m), 1370 (m), 1235 (m), 1109 (m), 1043 (m), 1017 (m), 823 (m), 740 (m), 702 (s), 611 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 203 (4.53), 217 (4.29) nm. MS (ESI): *m*/*z* (%) = 489 (100), 490 (30), 491 (9). HRMS (ESI): calcd. for $C_{28}H_{42}O_4N_1Si$ [M + NH_4]$^+$ 484.2878 found 484.2884.

Compound 12: R_f (petroleum ether/EtOAc, 10:1) = 0.51. $[a]_D^{25}$ = –3.7 (*c* = 0.43, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.37 (s, 1 H, CO*H*), 7.68–7.65 (m, 4 H, *m*-Ph-*H*), 7.45–7.35 (m, 6 H, Ph-*o*-*H*, Ph-*p*-*H*), 6.40–6.35 (m, 1 H, C*H*CCHO), 5.70–5.66 (m, 1 H, OCH$_2$C*H*), 5.27 (t, ^3J = 6.6 Hz, 1 H, C*H*O), 4.25 (d, ^3J = 6.0 Hz, 2 H, OCH_2CH), 2.70 (m, 1 H, CH_2CHO), 2.63–2.56 (m, 1 H, CH_2CHO), 2.05 (s, 3 H, CH_3COO), 1.75 [d, ^4J = 1.2 Hz, 3 H, (CH_3CCHOH)], 1.46 (d, ^4J = 1.0 Hz, 3 H, CH_3C), 1.04 [s, 9 H, (CH$_3$)$_3$C] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.8 (1 C, *C*HO), 169.9 (1 C, CH$_3$*C*OO), 148.2 (1 C, *C*HCCHO), 141.1 (1 C, *C*CHO), 135.5 (4 C, *m*-C_{Ph}), 133.6 (2 C, *ipso*-C_{Ph}), 133.1 (1 C, CH*C*CH$_3$), 129.6 (2 C, *p*-C_{Ph}), 128.1 (1 C, OCH$_2$*C*H), 127.6 (4 C, *o*-C_{Ph}), 76.2 (1 C, *C*HO), 60.5 (1 C, O*C*H$_2$CH), 32.2 (1 C, *C*H$_2$CHO), 26.7 [3 C, (*C*H$_3$)$_3$C], 21.1 (1 C, *C*H$_3$COO), 19.1 [1 C, (CH$_3$)$_3$*C*], 12.6 (1 C, *C*H$_3$C), 9.4 (1 C, *C*H$_3$CCOH) ppm. IR (ATR): $\tilde{\nu}$ = 2931 (m), 2857 (m), 1739 (m), 1689 (s), 1428 (m), 1370 (m), 1232 (s), 1110 (s), 1045 (m), 1021 (m), 823 (m), 741 (m), 704 (s), 612 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 202 (4.54) nm. MS (EI, 70 eV): *m*/*z* (%) = 407 (2), 347 (9), 267 (11), 242 (19), 241 (89), 199 (100), 181 (15). HRMS (EI): calcd. for $C_{24}H_{27}O_4Si$ [M – *t*Bu]$^+$ 407.1679; found 407.1662.

(2*E*,5*S*,6*E*)-8-[(*tert*-Butyldiphenylsilanyl)oxy]-2,6-dimethylocta-2,6-diene-1,5-diyl Diacetate (30): DMAP (3 mg, 0.03 mmol, 0.1 equiv.), anhydrous NEt_3 (180 μL, 1.25 mmol, 5.0 equiv.), and Ac_2O (235 μL, 2.50 mmol, 10.0 equiv.) were added to a solution of the alcohol **11** (116 mg, 0.25 mmol, 1.0 equiv.) in DCM (4 mL). After 16 h, the reaction was quenched by the addition of an aqueous NH_4Cl solution, and the aqueous phase was extracted with DCM. The organic phase was dried with $MgSO_4$, and the solvent was evaporated. After chromatography (silica gel, petroleum ether/EtOAc, 10:1), the diacetylated product (121 mg, 0.24 mmol, 96%) was obtained as a colorless oil. R_f (petroleum ether/EtOAc, 40:1) = 0.37. $[a]_D^{22}$ = –12.8 (*c* = 1.72, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.65 (m, 4 H, Ph-*o*-*H*), 7.44–7.35 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.66–5.63 (m, 1 H, OCH$_2$C*H*), 5.38–5.34 (m, 1 H, CH$_2$CC*H*), 5.13 (t, ^3J = 6.8 Hz, 1 H, C*H*OAc), 4.43 (s, 2 H, CH_2OAc), 4.24 (d, ^3J = 6.0 Hz, 2 H, OCH_2CH), 2.41 (td, *J* = 7.5, *J* = 14.9 Hz, 1 H, CH_2CHOAc), 2.30 (td, *J* = 7.5, *J* = 14.9 Hz, 1 H, CH_2CHOAc), 2.05 (s, 3 H, CH_3COOCH$_2$), 2.03 (s, 3 H, CH_3COOHCH), 1.66 (d, *J* = 0.9 Hz, 3 H, CH_3CCH$_2$), 1.43 (d, *J* = 1.0 Hz, 3 H, CCH_3), 1.04 [s, 9 H, (CH$_3$)$_3$C] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.9 (1 C, CH$_3$*C*OOCH$_2$), 170.1 (1 C, CH$_3$*C*OOCH), 135.6 (4 C, *o*-C_{Ph}), 133.9 (1 C, CH*C*CH$_3$), 133.8 (2

C, *ipso*-C_{Ph}), 132.8 [1 C, (CH_3CCH_2)], 129.6 (2 C, *p*-C_{Ph}), 127.6 (4 C, *m*-C_{Ph}), 127.5 (1 C, OCH_2CH), 124.0 [1 C, (CH_2CCH)], 77.4 (1 C, *C*HOOAc), 69.8 (1 C, CH_2OAc), 60.7 (1 C, OCH_2CH), 31.3 (1 C, CH_2CHOAc), 26.8 [3 C, $(CH_3)_3C$], 21.2 (1 C, CH_3COOCH_2), 20.9 (1 C, CH_3COOCH), 19.1 [1 C, $(CH_3)_3C$], 14.2 (1 C, CH_3CCH_2), 12.6 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 2932 (m), 2858 (m), 1737 (m), 1428 (m), 1370 (m), 1229 (s), 1110 (m), 1046 (m), 1020 (m), 823 (m), 741 (m), 703 (s), 611 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($lg\varepsilon$) = 203 (4.55), 265 (3.32) nm. MS (ESI): *m*/*z* (%) = 531 (100), 532 (34), 533 (10). HRMS (ESI): calcd. for $C_{30}H_{40}O_5SiNa$ [M + Na]$^+$ 531.2543; found 531.2543.

(2*E*,5*S*,6*E*)-8-Hydroxy-2,6-dimethylocta-2,6-diene-1,5-diyl Diacetate (13): TBAF·3H_2O (1 M solution in THF, 0.8 mL, 0.8 mmol, 1.5 equiv.) was added to a solution of **30** (265 mg, 0.5 mmol, 1.0 equiv.) in THF (8 mL). After 1.5 h at room temp. and evaporation of the solvent, chromatography (silica gel, petroleum ether/EtOAc, 2:1) yielded **13** (101 mg, 0.3 mmol, 72%) as a colorless oil. R_f (petroleum ether/EtOAc, 2:1) = 0.22. $[\alpha]_D^{22}$ = –11.3 (*c* = 2.68, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.65–5.60 (m, 1 H, OCH_2CH), 5.35 (m, 1 H, $CHCH_2CHOAc$), 5.15 (t, ^3J = 6.9 Hz, 1 H, *CH*OAc), 4.45 (s, 2 H, CH_2OAc), 4.18 (d, ^3J = 6.6 Hz, 2 H, $HOCH_2CH$), 2.49–2.45 (m, 1 H, CH_2CHOAc), 2.39–2.32 (m, 1 H, CH_2CHOAc), 2.07 (s, 3 H, CH_3COOCH_2), 2.05 (s, 3 H, CH_3COOCH), 1.66 [s, 3 H, (CH_3)CCH_2], 1.66 [s, 3 H, (CH_3)$_2$C] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0 (1 C, CH_3COOCH_2), 170.2 (1 C, CH_3COOCH), 135.6 (1 C, $CHCCH_3$), 132.8 (1 C, CH_3CCH_2), 127.0 (1 C, $HOCH_2CH$), 123.6 (1 C, CH_2CCH), 77.5 (1 C, *C*HOAc), 69.7 (1 C, CH_2OAc), 58.9 (1 C, $HOCH_2CH$), 31.0 (1 C, CH_2CHOAc), 21.6 (1 C, CH_3COOCH), 20.9 (1 C, CH_3COOCH_2), 14.1 (1 C, CH_3CCH_2), 12.4 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3449 (w, br.), 1732 (m), 1437 (m), 1371 (m), 1226 (s), 1017 (m), 956 (m), 852 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($lg\varepsilon$) = 202 nm (4.00), 313 (2.39) nm. HRMS (ESI): calcd. for $C_{14}H_{22}O_5$ [M + Na]$^+$ 293.13594; found 293.13688.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(Acetoxymethyl)-6-{[(2*E*,4*S*,6*E*)-4,8-diacetoxy-3,7-dimethylocta-2,6-dien-1-yl]oxy}tetrahydro-2*H*-pyran-3,4,5-triyl Triacetate (15): 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**14**, 337 mg, 0.82 mmol, 2.0 equiv.) and Ag_2CO_3 (282 mg, 1.02 mmol 2.5 equiv.) were added under Ar to a solution of **13** (110 mg, 0.41 mmol, 1.0 equiv.) in anhydrous Et_2O (8 mL). The mixture was stirred at room temp. in the dark for 22 h. The solution was filtered, and the solvent was evaporated. After chromatography (silica gel, petroleum ether/EtOAc, 2:1), **15** (90 mg, 0.15 mmol, 37%) was obtained as a colorless oil. R_f (petroleum ether/EtOAc, 2:1) = 0.24. $[\alpha]_D^{22}$ = –22.7 (*c* = 2.2, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.55–5.51 (m, 1 H, OCH_2CH), 5.38–5.34 (m, 1 H, $CHCH_2CHOAc$), 5.21 (t, *J* = 9.5 Hz, 1 H, C3-*H*), 5.15 (t, *J* = 6.8 Hz, 1 H, *CH*OAc), 5.09 (t, *J* = 9.7 Hz, 1 H, C4-*H*), 4.99 (dd, *J* = 9.6, 8.0 Hz, 1 H, C2-*H*), 4.53 (d, *J* = 8.0 Hz, 1 H, C1-*H*), 4.45 (s, 2 H, CH_2OAc), 4.35–4.13 (m, 4 H, OCH_2CH, C6-H_2), 3.68 (ddd, *J* = 2.5, 4.7, 9.9 Hz, 1 H, C5-*H*), 2.45 (td, *J* = 7.5, 14.9 Hz, 1 H, $CHCH_2CHOAc$), 2.37–2.30 (m, 1 H, $CHCH_2CHOAc$), 2.09 (s, 3 H, CH_3COOCH_2), 2.07 (s, 3 H, CH_3COO-C6), 2.06 (s, 3 H, CH_3COOCH), 2.05 (s, 3 H, CH_3COO-C2), 2.03 (s, 3 H, CH_3COO-C4), 2.00 (s, 3 H, CH_3COO-C3), 1.67 (s, 3 H, CH_3CCH_2), 1.66 (s, 3 H, CH_3CCH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.8 (1 C, CH_3COOCH_2), 170.6 (1 C, CH_3COO-C6), 170.3 (1 C, CH_3COO-C3), 170.1 (1 C, CH_3COO-CH), 169.4 (1 C, CH_3COO-C4), 169.3 (1 C, CH_3COO-C1), 138.0 (1 C, $CHCCH_3$), 133.1 (1 C, CH_3CCH_2), 123.5 (1 C, CH_2CCH), 122.8 (1 C, OCH_2CH), 99.2 (1 C, *C*1-H), 78.4 (1 C, *C*HOAc), 72.9 (1 C, *C*3-H), 71.8 (1 C, *C*5-H), 71.3 (1 C, *C*2-H), 69.6 (1 C, CH_2CCH_3), 68.4 (1 C, *C*4-H), 64.9 (1 C, OCH_2CH), 62.0 (1 C, *C*6-H), 31.3 (1 C, CH_2CHOAc), 21.1 (1 C, CH_3COO-CH), 20.9 (1 C, CH_3COO-C6), 20.7 (1 C, CH_3COO-C2), 20.7 (1 C, CH_3COOCH_2), 20.6 (1 C, CH_3COO-C3), 20.6 (1 C, CH_3COO-C4), 14.1 (1 C, CH_2CCH_3), 12.4 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 1730 (s), 1429 (m), 1367 (m), 1209 (s), 1166 (m), 1149 (m), 1033 (s), 954 (m), 928 (m), 904 (m), 854 (m), 832 (m), 602 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($lg\varepsilon$) = 202 (3.98) nm. MS (ESI): *m*/*z* (%) = 623 (100), 324 (29), 493 (7). HRMS (ESI): calcd. for $C_{28}H_{40}O_{14}Na$ [M + Na]$^+$ 623.2310; found 623.2316.

(–)-Rhodioloside A (4) and (–)-Rhodiolol A (16): NaOMe (0.26 mmol, 30% in MeOH, 48 μL, 1.3 equiv.) was added to a solution of **15** (118 mg, 0.20 mmol, 1.0 equiv.) in MeOH (14 mL). After 1.5 h at room temp., the solvent was evaporated, and the crude product was purified by flash chromatography (silica gel, $CHCl_3$/MeOH, 5:1). Rhodioloside A (**4**, 49 mg, 0.14 mmol, 70%) was obtained as a colorless viscous oil along with rhodiol A (**16**, 7 mg, 0.04 mmol, 19%).

Compound 4: R_f ($CHCl_3$/MeOH, 5:1) = 0.12. $[\alpha]_D^{24}$ = –34.3 (*c* = 1.26, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ = 5.60–5.57 (m, 1 H, OCH_2CH), 5.42–5.38 (m, 1 H, $CHCH_2CHOH$), 4.39–4.28 (m, 2 H, OCH_2CH), 4.29 (d, *J* = 7.8 Hz, 1 H, C1-*H*), 4.02 (t, *J* = 6.7 Hz, 1 H, *CH*OH), 3.92 (s, 2 H, CH_2OH), 3.87 (dd, *J* = 2.0, 11.9 Hz, 1 H, C6-H_2), 3.66 (dd, *J* = 5.5, 11.9 Hz, 1 H, C6-H_2), 3.32–3.22 (m, 3 H, C3-*H*, C4-*H*, C5-*H*), 3.17 (dd, *J* = 7.8, 9.0 Hz, 1 H, C2-*H*), 2.30 (t, *J* = 6.9 Hz, 2 H, CH_2CHOH), 1.67 (s, 3 H, CH_3CCH), 1.65 (s, 3 H, CH_3CCH_2) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 142.9 (1 C, $CHCCH_3$), 137.7 (1 C, CH_3CCH_2), 123.0 (1 C, OCH_2CH), 122.7 (1 C, CH_2CCH), 102.8 (1 C, *C*1-H), 78.1 (1 C, *C*-H)*, 78.0 (1 C, *C*-H)*, 77.6 (1 C, *CCHOH*), 75.1 (1 C, *C*2-H), 71.7 (1 C, *C*-H)*, 68.9 (1 C, CH_2CCH_3), 66.0 (1 C, OCH_2CH), 62.8 (1 C, *C*6-H), 34.4 (1 C, CH_2CHOH), 14.0 (1 C, CH_2CCH_3), 12.1 (1 C, CH_3C) ppm; * no differentiation between C3, C4 and C5 possible. IR (ATR): $\tilde{\nu}$ = 3316 (m, br.), 2919 (m), 2863 (m), 1430 (m), 1374 (m), 1072 (m), 1012 (s) cm^{-1}. UV/Vis (MeOH): λ_{max} ($lg\varepsilon$) = 202 (3.94) nm. MS (ESI): *m*/*z* (%) = 371 (100), 372 (23), 373 (4). HRMS (ESI): calcd. for $C_{16}H_{28}O_8Na$ [M + Na]$^+$ 371.1682; found 317.1682.

Compound 16: R_f ($CHCl_3$/MeOH, 5:1) = 0.43. $[\alpha]_D^{24}$ = –1.6 (*c* = 0.25, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.68–5.63 (m, 1 H, OCH_2CH), 5.45–5.40 (m, 1 H, $CHCH_2CHOH$), 4.22 (d, *J* = 6.7 Hz, 2 H, $CHCH_2OH$), 4.09 (t, *J* = 6.5 Hz, 1 H, CH_2CHOH), 4.02 (s, 2 H, CCH_2OH), 2.35–2.31 (m, 2 H, $CHCH_2CHOH$), 1.69 (s, 6 H, CH_3CCH_2, CH_3CCH), 1.60 (br. s, 3 H, CCH_2OH, $CHCH_2OH$, $CHOH$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2 (1 C, $CHCCH_3$), 137.9 (1 C, CH_3CCH_2), 124.7 (1 C, OCH_2CH), 121.2 (1 C, CH_2CCH), 76.3 (1 C, *C*HOH), 68.6 (1 C, CH_2CCH_3), 59.1 (1 C, OCH_2CH), 33.4 (1 C, CH_2CHOH), 14.0 (1 C, CH_2CCH_3), 12.1 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3299 (m, br.), 2916 (m), 2862 (m), 1432 (m), 1385 (m), 995 (s), 603 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($lg\varepsilon$) = 205 (3.78) nm. HRMS (ESI): calcd. for $C_{10}H_{18}O_3Na$ [M + Na]$^+$ 209.11482; found 209.11475.

(2*S*,3*E*)-5-[(*tert*-Butyldiphenylsilanyl)oxy]-1-(3,3-dimethyloxiran-2-yl)-3-methylpent-3-en-2-yl Acetate (17, Mixture of Diastereomers): *m*CPBA (70% with H_2O, 200 mg, 0.81 mmol, 1.1 equiv.) was added in small portions at 0 °C to a solution of **10** (335 mg, 0.74 mmol, 1.0 equiv.) in DCM (10 mL), and the solution was stirred at 0 °C for 3 h. The reaction was quenched by the addition of aqueous NaOH (1 M) and extracted with DCM. The organic phase was washed with saturated aqueous $NaHCO_3$ and brine and dried with $MgSO_4$, followed by evaporation of the solvent. Chromatography (silica gel, petroleum ether/EtOAc, 10:1) yielded a mixture of diastereomers as a colorless oil (283 mg, 0.61 mmol, 82%). R_f (petro-

leum ether/EtOAc, 10:1) = 0.32. $[\alpha]_D^{24}$ = –13.1 (*c* = 1.23, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 8 H, Ph-*o*-*H*), 7.44–7.35 (m, 12 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.71–5.67 (m, 2 H, OCH_2CH), 5.33–5.25 (m, 2 H, C*H*OAc), 4.26–4.24 (m, 4 H, OCH_2CH), 2.74 [t, *J* = 6.2 Hz, 1 H, $(CH_3)_2CCH$], 2.72 [t, *J* = 6.0 Hz, 1 H, $(CH_3)_2CCH$], 2.07 (s, 3 H, $CH_3COOHCH$), 2.06 (s, 3 H, $CH_3COOHCH$), 1.94–1.75 (m, 4 H, CH_2CHOAc), 1.46–1.45 (m, 6 H, CH_3C), 1.29 [s, 3 H, $(CH_3)_2C$], 1.29 [s, 3 H, $(CH_3)_2C$], 1.27 [s, 3 H, $(CH_3)_2C$], 1.25 [s, 3 H, $(CH_3)_2C$], 1.04 [s, 18 H, $(CH_3)_3C$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0 (1 C, CH_3COOCH), 169.9 (1 C, CH_3COOCH), 135.5 (8 C, *o*-C_{Ph}), 133.9 (1 C, $CHCCH_3$), 133.8 (1 C, $CHCCH_3$), 133.7 (2 C, *ipso*-C_{Ph}), 133.7 (1 C, *ipso*-C_{Ph}), 133.7 (1 C, *ipso*-C_{Ph}), 129.6 (4 C, *p*-C_{Ph}), 127.6 (8 C, *m*-C_{Ph}), 127.4 (1 C, OCH_2CH), 127.3 (1 C, OCH_2CH), 76.0 (1 C, CHOOAc), 75.8 (1 C, CHOOAc), 60.9 [1 C, $(CH_3)_2CCH$], 60.9 [1 C, $(CH_3)_2CCH$], 60.6 (1 C, OCH_2CH), 60.6 (1 C, OCH_2CH), 58.2 [1 C, $(CH_3)_2C$], 57.8 [1 C, $(CH_3)_2C$], 32.6 (1 C, CH_2CHOAc), 32.6 (1 C, CH_2CHOAc), 26.8 [6 C, $(CH_3)_3C$], 24.7 [1 C, $(CH_3)_2C$], 24.6 [1 C, $(CH_3)_2C$], 21.2 (1 C, CH_3COOCH), 21.1 (1 C, CH_3COOCH), 19.1 [2 C, $(CH_3)_3C$], 18.9 [1 C, $(CH_3)_2C$], 18.9 [1 C, $(CH_3)_2C$], 12.9 (2 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 2959 (m), 2931 (m), 2858 (m), 1739 (m), 1428 (m), 1373 (m), 1234 (s), 1109 (m), 1047 (m), 1020 (m), 823 (m), 780 (m), 740 (m), 702 (s), 611 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 202 (4.51), 265 (2.85) nm. MS (ESI): *m*/*z* (%) = 489 (100), 490 (30). HRMS (ESI): calcd. for $C_{28}H_{38}O_4SiNa$ [M + Na]$^+$ 489.2432; found 489.2437.

(5*S*,6*E*)-8-[(*tert*-Butyldiphenylsilanyl)oxy]-2,6-dimethyloct-6-ene-2,5-diol (18): Under Ar, the epoxide **17** (570 mg, 1.22 mmol, 1.0 equiv.) was dissolved in dry THF (35 mL), and the mixture was cooled to 0 °C. $LiBEt_3H$ (1 M in THF, 6.1 mL, 6.1 mmol, 5.0 equiv.) was added dropwise, and the solution was heated at reflux. After 2 h, the solution was allowed to cool to room temp. and the reaction quenched by the addition of aqueous NaOH (2 M). The aqueous phase was extracted with Et_2O. The organic phase was dried with $MgSO_4$, and the solvent was evaporated. Column chromatography (silica gel, petroleum ether/EtOAc, 2:1) afforded **18** (401 mg, 0.94 mmol, 77%) as a colorless solid. M.p. 95 °C. R_f (petroleum ether/EtOAc, 2:1) = 0.15. $[\alpha]_D^{26}$ = –2.4 (*c* = 1.18, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 4 H, Ph-*o*-*H*), 7.45–7.36 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.61–5.58 (m, 1 H, OCH_2CH), 4.31–4.23 (m, 2 H, OCH_2CH), 3.98–3.93 (m, 1 H, C*H*OH), 1.84 (br. s, 2 H, CO*H*, CHO*H*), 1.64–1.51 (m, 3 H, CH_2CH_2COH), 1.43 (d, *J* = 1.1 Hz, 3 H, $CHCCH_3$), 1.22 [s, 3 H, $(CH_3)_2COH$], 1.21 [s, 3 H, $(CH_3)_2COH$], 1.04 [s, 9 H, $(CH_3)_3C$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.5 (1 C, $CHCCH_3$), 135.6 (2 C, *o*-C_{Ph}), 133.9 (1 C, *ipso*-C_{Ph}), 133.9 (1 C, *ipso*-C_{Ph}), 129.6 (2 C, *p*-C_{Ph}), 127.6 (4 C, *m*-C_{Ph}), 125.7 (1 C, OCH_2CH), 77.5 (1 C, CHOH), 70.5 [1 C, $(CH_3)_2COH$], 60.8 (1 C, OCH_2CH), 39.8 (1 C, CH_2CH_2COH), 29.6 [1 C, $(CH_3)_2COH$], 29.4 (1 C, CH_2CH_2COH), 29.2 [1 C, $(CH_3)_2COH$], 26.8 [3 C, $(CH_3)_3C$], 19.1 [1 C, $(CH_3)_3C$], 11.8 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3346 (m), 3251 (m), 2956 (m), 2932 (m), 2886 (m), 2858 (m), 1470 (m), 1426 (m), 1321 (m), 1158 (m), 1108 (m), 1050 (m), 1017 (m), 953 (m), 938 (m), 918 (m), 907 (m), 860 (m), 824 (m), 796 (m), 775 (m), 744 (m), 702 (s), 684 (m), 618 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 203 (4.50), 216 (4.25) nm. MS (ESI): *m*/*z* (%) = 449 (100), 450 (29), 451 (8). HRMS (ESI): calcd. for $C_{26}H_{38}O_3SiNa$ [M + Na]$^+$ 449.2482; found 449.2488.

(–)-Sachalinol A (3): TBAF·3H_2O (0.28 mmol, 280 μL, 1.5 equiv.) was added to a solution of **18** (80 mg, 0.19 mmol, 1.0 equiv.) in THF (5 mL). After the mixture had been stirred at room temp. for 3 h, the solvent was evaporated, and the crude product was subjected to column chromatography (silica, $CHCl_3$/MeOH, 10:1) to yield **3** (28 mg, 0.15 mmol, 78%) as a colorless oil. Crystals were obtained from $CHCl_3$. M.p. 35 °C. R_f ($CHCl_3$/MeOH, 10:1) = 0.26. $[\alpha]_D^{24}$ = –12.8 (*c* = 1.0, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ = 5.55 (t, ^3J = 6.5 Hz, 1 H, OCH_2CH), 4.13 (d, ^3J = 6.5 Hz, 2 H, OCH_2CH), 3.91 (t, *J* = 6.5 Hz, 1 H, CHOH), 1.63 (s, 3 H, CH_3CCHO), 1.61–1.49 (m, 3 H, CH_2CH_2COH), 1.41–1.32 (m, 1 H, CH_2CH_2COH), 1.18 [s, 3 H, $(CH_3)_2COH$], 1.17 [s, 3 H, $(CH_3)_2COH$] ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 140.9 (1 C, $CHCCH_3$), 126.2 (1 C, OCH_2CH), 78.6 (1 C, CHOH), 71.1 [1 C, $(CH_3)_2COH$], 59.2 (1 C, OCH_2CH), 40.8 (1 C, CH_2CH_2COH), 30.6 (1 C, CH_2CH_2COH), 29.3 [1 C, $(CH_3)_2COH$], 29.2 [1 C, $(CH_3)_2COH$], 11.6 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3315 (s, br.), 2968 (m), 2946 (m), 2872 (m), 1467 (m), 1444 (m), 1379 (m), 1365 (m), 1212 (m), 1152 (m), 1058 (m), 998 (s), 950 (m), 906 (m), 731 (m), 618 (m), 571 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 202 (3.68) nm. HRMS (ESI): calcd. for $C_{10}H_{20}O_3Na$ [M + Na]$^+$ 211.13101; found 211.13106.

(2*E*,4*S*)-1-[(*tert*-Butyldiphenylsilanyl)oxy]-7-hydroxy-3,7-dimethyloct-2-en-4-yl Acetate (31): Ac_2O (210 μL, 2.3 mmol, 10 equiv.), Et_3N (155 μL, 1.1 mmol, 5.0 equiv.), and DMAP (2.7 mg, 0.02 mmol, 0.1 equiv.) were added to a solution of diol **18** (98 mg, 0.23 mmol, 1.0 equiv.) in DCM (10 mL). The solution was stirred at room temp. for 15 h and the reaction quenched by the addition of a saturated aqueous NH_4Cl solution. The aqueous phase was extracted with DCM, and the combined organic phases were washed with a saturated aqueous $NaHCO_3$ solution and dried with $MgSO_4$. After evaporation of the solvent, rapid column chromatography (silica, petroleum ether/EtOAc, 5:1) yielded **31** (95 mg, 0.20 mmol, 88%) as a colorless oil, accompanied by the diacetylated product **32** (11 mg, 0.02 mmol, 9%).

Monoacetylated Compound 31: R_f (petroleum ether/EtOAc, 5:1) = 0.23. $[\alpha]_D^{22}$ = –10.4 (*c* = 1.78, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.66 (m, 4 H, Ph-*o*-*H*), 7.44–7.35 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.66–5.63 (m, 1 H, OCH_2CH), 5.10 (t, *J* = 6.8 Hz, 1 H, C*H*OAc), 4.25 (d, *J* = 5.9 Hz, 2 H, OCH_2CH), 2.04 (s, 3 H, CH_3COOCH), 1.75–1.60 (m, 2 H, CH_2CH_2COAc), 1.48–1.31 (m, 2 H, CH_2CH_2COAc), 1.43 (d, 3 H, $CHCCH_3$), 1.21 [s, 6 H, $(CH_3)_2COH$], 1.04 [s, 9 H, $(CH_3)_3C$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.2 (1 C, CH_3COOCH), 135.6 (4 C, *o*-C_{Ph}), 134.1 (1 C, $CHCCH_3$), 133.8 (1 C, *ipso*-C_{Ph}), 133.8 (1 C, *ipso*-C_{Ph}), 129.6 (2 C, *p*-C_{Ph}), 127.6 (1 C, OCH_2CH), 127.6 (4 C, *m*-C_{Ph}), 78.7 (1 C, CHOAc), 70.5 [1 C, $(CH_3)_2COH$], 60.6 (1 C, OCH_2CH), 39.2 (1 C, CH_2CH_2COAc), 29.3 [1 C, $(CH_3)_2COH$], 29.2 [1 C, $(CH_3)_2COH$], 27.3 (1 C, CH_2CH_2COAc), 26.8 [3 C, $(CH_3)_3C$], 21.2 (1 C, CH_3COOCH), 19.1 [1 C, $(CH_3)_3C$], 12.3 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3349 (w, br.), 2962 (m), 2932 (m), 2858 (m), 1735 (m), 1428 (m), 1370 (m), 1237 (m), 1108 (m), 1045 (m), 1022 (m), 940 (m), 823 (m), 786 (m), 740 (m), 702 (s), 611 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 202 (4.45), 217 (4.20) nm. MS (ESI): *m*/*z* (%) = 491 (100), 492 (30), 493 (10). HRMS (ESI): calcd. for $C_{28}H_{40}O_4SiNa$ [M + Na]$^+$ 491.2588; found 491.2593.

Diacetylated Analogue 32: R_f (petroleum ether/EtOAc, 5:1) = 0.51. $[\alpha]_D^{26}$ = –8.6 (*c* = 1.33, acetone). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 4 H, Ph-*o*-*H*), 7.44–7.35 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.66–5.63 (m, 1 H, OCH_2CH), 5.08 (t, *J* = 5.8 Hz, 1 H, C*H*OAc), 4.25 (d, *J* = 6.0 Hz, 2 H, OCH_2CH), 2.05 (s, 3 H, CH_3COOCH), 1.96 (s, 3 H, CH_3COOCH), 1.68–1.60 (m, 4 H, CH_2CH_2COAc), 1.43–1.42 [m, 9 H, $CHCCH_3$, $(CH_3)_2COH$], 1.04 [s, 9 H, $(CH_3)_3C$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.3 (1 C, CH_3COOC), 170.2 (1 C, CH_3COOCH), 135.6 (4 C, *o*-C_{Ph}), 133.9 (1 C, $CHCCH_3$), 133.8 (1 C, *ipso*-C_{Ph}), 133.8 (1 C, *ipso*-C_{Ph}), 129.6 (2 C, *p*-C_{Ph}), 127.8 (1 C, OCH_2CH), 127.6 (4 C, *m*-C_{Ph}), 81.6 [1 C, $(CH_3)_2COAc$], 78.4 (1 C, CHOAc), 60.6 (1 C, OCH_2CH), 36.6 (1

C, CH_2CH_2COAc), 26.8 (1 C, CH_2CH_2COAc), 26.8 [3 C, $(CH_3)_3C$], 26.0 [1 C, $(CH_3)_2COAc$], 25.9 [1 C, $(CH_3)_2COAc$], 22.4 (1 C, CH_3COOC), 21.3 (1 C, CH_3COOCH), 19.2 [1 C, $(CH_3)_3C$], 12.2 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 2932 (m), 2858 (m), 1733 (s), 1428 (m), 1367 (m), 1235 (s), 1212 (m), 1109 (m), 1047 (m), 1017 (m), 940 (m), 823 (m), 784 (m), 740 (m), 702 (s), 610 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($\lg\varepsilon$) = 203 (4.45), 216 (4.24) nm. MS (ESI): *m*/*z* (%) = 533 (100), 534 (38), 535 (10). HRMS (ESI): calcd. for $C_{30}H_{42}O_5SiNa$ $[M + Na]^+$ 533.2694; found 533.3063.

(4*S*,2*E*)-1,7-Dihydroxy-3,7-dimethyloct-2-en-4-yl Acetate (25): TBAF·$3H_2O$ (1 M in THF, 300 μL, 0.3 mmol, 1.5 equiv.) was added to a solution of **31** (95 mg, 0.2 mmol, 1 equiv.) in THF (3 mL). After stirring at room temp. for 1.5 h, the solvent was evaporated, and the crude product was subjected to column chromatography (silica, petroleum ether/EtOAc, 2:1) to yield **25** (38 mg, 0.1 mmol, 54%) as a colorless oil. R_f (petroleum ether/EtOAc, 2:1) = 0.21. $[\alpha]_D^{26}$ = –11.2 (*c* = 1.30, acetone). ^1H NMR (400 MHz, $CDCl_3$): δ = 5.66–5.62 (m, 1 H, OCH_2CH), 5.10 (t, *J* = 6.8 Hz, 1 H, $CHOAc$), 4.18 (d, *J* = 6.6 Hz, 2 H, OCH_2CH), 2.06 (s, 3 H, CH_3COOCH), 1.77–1.68 (m, 2 H, CH_2CH_2COAc), 1.66–1.66 (m, 3 H, $CHCCH_3$), 1.56–1.33 (m, 2 H, CH_2CH_2COH), 1.21 [s, 3 H, $(CH_3)_2COH$], 1.21 [s, 3 H, $(CH_3)_2COH$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5 (1 C, CH_3COOCH), 136.0 (1 C, $CHCCH_3$), 126.9 (1 C, OCH_2CH), 78.8 (1 C, $CHOAc$), 70.5 [1 C, $(CH_3)_2COH$], 58.8 (1 C, OCH_2CH), 38.1 (1 C, CH_2CH_2COAc), 29.3 [1 C, $(CH_3)_2COH$], 29.1 [1 C, $(CH_3)_2COH$], 27.3 (1 C, CH_2CH_2COAc), 21.2 (1 C, CH_3COOCH), 12.2 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3365 (m, br.), 2968 (m), 2930 (m), 1717 (m), 1370 (m), 1235 (s), 1156 (m), 1017 (m), 945 (m), 600 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($\lg\varepsilon$) = 202 (3.64) nm. HRMS (ESI): calcd. for $C_{12}H_{22}O_4Na$ $[M + Na]^+$ 253.14103; found 253.14079.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-{[(2*E*,4*S*)-4-Acetoxy-7-hydroxy-3,7-dimethyloct-2-en-1-yl]oxy}-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl Tris(2,2-dimethylpropanoate) (26): 2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucopyranosyl bromide (**20**, 452 mg, 0.78 mmol, 1.5 equiv.) and Ag_2CO_3 (359 mg, 1.3 mmol, 2.5 equiv.) were added under Ar to a solution of **25** (120 mg, 0.52 mmol, 1.0 equiv.) in anhydrous Et_2O (6 mL). The mixture was stirred at room temp. in the dark for 15 h. A second portion of 2,3,4,6-tetra-*O*-pivaloyl-α-D-glucopyranosyl bromide (**20**, 150 mg, 0.26 mmol, 0.5 equiv.) was added, and the mixture was stirred for 24 h. The solution was then filtered, and the solvent was evaporated. After chromatography (silica gel, petroleum ether/EtOAc, 5:1 → 3:1), **26** (268 mg, 0.37 mmol, 71%) was obtained as a colorless oil. R_f (petroleum ether/EtOAc, 3:1) = 0.29. $[\alpha]_D^{22}$ = –8.1 (*c* = 1.90, acetone). ^1H NMR (600 MHz, $CDCl_3$): δ = 5.50 (t, *J* = 6.6 Hz, 1 H, OCH_2CH), 5.32 (t, *J* = 9.6 Hz, 1 H, C3-*H*), 5.13–5.09 (m, 2 H, $CHOAc$, C4-*H*), 5.02 (dd, *J* = 9.7, 8.1 Hz, 1 H, C2-*H*), 4.53 (d, *J* = 8.1 Hz, 1 H, C1-*H*), 4.33 (dd, *J* = 6.2, 12.4 Hz, 1 H, OCH_2CH), 4.24–4.22 (m, 1 H, C6-H_2), 4.16 (dd, *J* = 7.3, 12.4 Hz, 1 H, OCH_2CH), 4.07 (dd, *J* = 5.7, 12.3 Hz, 1 H, C6-H_2), 3.73 (ddd, *J* = 10.1, 5.7, 1.9 Hz, 1 H, C5-*H*), 2.06 (s, 3 H, CH_3COOCH), 1.73–1.68 (m, 2 H, CH_2CH_2COAc), 1.64 (s, 3 H, CCH_3), 1.49–1.42 (m, 1 H, CH_2CH_2COAc), 1.39–1.33 (m, 1 H, CH_2CH_2COAc), 1.23 [s, 9 H, $(CH_3)_3CCOO$-C6], 1.21 [s, 6 H, $(CH_3)_2COH$], 1.15 [s, 18 H, $(CH_3)_3CCOO$-C2, $(CH_3)_3CCOO$-C4], 1.11 [s, 9 H, $(CH_3)_3CCOO$-C3] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.0 [1 C, $(CH_3)_3CCOO$-C6], 177.1 [1 C, $(CH_3)_3CCOO$-C3], 176.4 [1 C, $(CH_3)_3CCOO$-C2], 176.3 [1 C, $(CH_3)_3CCOO$-C4], 170.1 (1 C, CH_3COO-CH), 138.0 (1 C, $CHCCH_3$), 122.6 (1 C, OCH_2CH), 99.5 (1 C, *C*1-H), 78.3 (1 C, $CHOAc$), 72.1 (1 C, *C*5-H), 72.0 (1 C, *C*3-H), 70.8 (1 C, *C*2-H), 70.2 [1 C, $(CH_3)_2C$], 67.9 (1 C, *C*4-H), 64.7 (1 C, OCH_2CH), 61.9 (1 C, *C*6-H), 39.0 (1 C, CH_2CH_2CHOAc), 38.7 [1 C, $(CH_3)_3CCOO$-C6], 38.6 [1 C, $(CH_3)_3CCOO$-C5], 38.6 [1 C, $(CH_3)_3CCOO$-C4], 38.6 [1 C, $(CH_3)_3CCOO$-C3], 29.2 [1 C, $(CH_3)_2C$], 29.1 [1 C, $(CH_3)_2C$], 27.2 (1 C, CH_2CH_2CHOAc), 27.0 [6 C, $(CH_3)_3CCOO$-C3, $(CH_3)_3CCOO$-C6], 26.9 [3 C, $(CH_3)_3CCOO$-C4], 26.9 [3 C, $(CH_3)_3CCOO$-C2], 21.1 (1 C, CH_3COO-CH), 12.4 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3541 (w, br.), 2970 (m), 1736 (s), 1480 (m), 1368 (m), 1279 (m), 1237 (m), 1134 (s), 1037 (m), 941 (m), 761 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($\lg\varepsilon$) = 202 (3.63) nm. HRMS (ESI): calcd. for $C_{38}H_{64}O_{13}Na$ $[M + Na]^+$ 751.42446; found 751.42385.

(–)-Rhodioloside D (5): NaOMe (30% in MeOH, 0.05 mmol, 9 μL) was added to a solution of **26** (20 mg, 0.04 mmol, 1.0 equiv.) in MeOH (4 mL). After 5 h at room temp., the solvent was evaporated, and the crude product was purified by flash chromatography (silica, $CHCl_3$/MeOH, 5:1). The product **5** (7 mg, 0.02 mmol, 58%) was obtained as a colorless viscous oil. R_f ($CHCl_3$/MeOH, 5:1) = 0.08. $[\alpha]_D^{26}$ = –24.8 (*c* = 0.73, MeOH). ^1H NMR (400 MHz, CD_3OD): δ = 5.60–5.57 (m, 1 H, OCH_2CH), 4.41–4.28 (m, 2 H, OCH_2CH), 4.30 (d, *J* = 7.8 Hz, 1 H, C1-*H*), 3.94 (t, *J* = 6.4 Hz, 1 H, $CHOH$), 3.87 (dd, *J* = 2.0, 11.9 Hz, 1 H, C6-H_2), 3.66 (dd, *J* = 5.5, 11.9 Hz, 1 H, C6-H_2), 3.36–3.30 (m, 1 H, C3-*H*), (m, 1 H, C5-*H*), 3.27–3.23 (m, 1 H, C4-*H*), 3.17 (dd, *J* = 7.8, 9.0 Hz, 1 H, C2-*H*), 1.66 (d, *J* = 0.6 Hz, 3 H, CCH_3), 1.64–1.54 (m, 2 H, CH_2CH_2COAc), 1.54–1.48 (m, 1 H, CH_2CH_2COAc), 1.38–1.31 (m, 1 H, CH_2CH_2COAc), 1.18 [s, 3 H, $(CH_3)_2COH$], 1.17 [s, 3 H, $(CH_3)_2COH$] ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 143.1 (1 C, $CHCCH_3$), 123.0 (1 C, OCH_2CH), 103.0 (1 C, *C*1-H), 78.5 (1 C, $CHOH$), 78.2 (1 C, *C*3-H), 78.1 (1 C, *C*4-H), 75.1 (1 C, *C*2-H), 71.8 (1 C, *C*5-H), 71.2 [1 C, $(CH_3)_2COH$], 66.2 (1 C, OCH_2CH), 62.8 (1 C, *C*6-H), 40.8 (1 C, CH_2CH_2CHOH), 30.6 (1 C, CH_2CH_2CHOH), 29.3 [1 C, $(CH_3)_2COH$], 29.2 [1 C, $(CH_3)_2COH$], 11.8 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3332 (m, br.), 2965 (m), 2923 (m), 2873 (m), 1369 (m), 1072 (s), 1016 (s), 903 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} ($\lg\varepsilon$) = 202 (3.60) nm. MS (ESI): *m*/*z* (%) = 373 (100), 374 (18). HRMS (ESI): calcd. for $C_{16}H_{30}O_8Na$ $[M + Na]^+$ 373.1833; found 373.1838.

(2*S*,3*E*)-5-[(*tert*-Butyldiphenylsilanyl)oxy]-1-(3,3-dimethyloxiran-2-yl)-3-methylpent-3-en-2-ol (27): NaOMe solution (30% in MeOH, 0.96 mmol, 177 μL, 1.3 equiv.) was added to a solution of **17** (300 mg, 0.64 mmol, 1 equiv.) in MeOH (35 mL). After the mixture had been kept at room temp. for 4 h, the solvent was evaporated, and the crude product was purified by flash chromatography (silica gel, petroleum ether/EtOAc, 4:1). Compound **27** (249 mg, 0.59 mmol, 92%) was obtained as a colorless viscous oil. R_f (petroleum ether/EtOAc, 4:1) = 0.28. $[\alpha]_D^{24}$ = –2.8 (*c* = 1.36, acetone). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.67 (m, 8 H, Ph-*o*-*H*), 7.45–7.36 (m, 12 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.69–5.64 (m, 2 H, OCH_2CH), 4.28–4.27 (m, 4 H, OCH_2CH), 4.25–4.15 (m, 2 H, $CHOAc$), 2.88 [dd, *J* = 4.7, 7.3 Hz, 1 H, $(CH_3)_2CCH$], 2.84 [dd, *J* = 4.8, 7.7 Hz, 1 H, $(CH_3)_2CCH$], 1.99 (d, *J* = 2.7 Hz, 1 H, $CHOH$), 1.83–1.76 (m, 2 H, CH_2CHOAc), 1.69–1.57 (m, 2 H, CH_2CHOAc), 1.46 (d, *J* = 1.0 Hz, 3 H, CH_3C), 1.45 (d, *J* = 1.0 Hz, 3 H, CH_3C), 1.31 [s, 3 H, $(CH_3)_2C$], 1.31 [s, 3 H, $(CH_3)_2C$], 1.28 [s, 3 H, $(CH_3)_2C$], 1.27 [s, 3 H, $(CH_3)_2C$], 1.04 [s, 18 H, $(CH_3)_3C$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.3 (1 C, $CHCCH_3$), 137.7 (1 C, $CHCCH_3$), 135.6 (8 C, *o*-C_{Ph}), 133.9 (2 C, *ipso*-C_{Ph}), 133.9 (2 C, *ipso*-C_{Ph}), 129.6 (4 C, *p*-C_{Ph}), 127.6 (8 C, *m*-C_{Ph}), 125.9 (1 C, OCH_2CH), 125.6 (1 C, OCH_2CH), 75.6 (1 C, $CHOOH$), 74.7 (1 C, $CHOOH$), 62.2 [1 C, $(CH_3)_2CCH$], 61.4 [1 C, $(CH_3)_2CCH$], 60.8 (2 C, OCH_2CH), 58.3 [1 C, $(CH_3)_2C$], 57.8 [1 C, $(CH_3)_2C$], 34.1 (1 C, CH_2CHOAc), 34.1 (1 C, CH_2CHOAc), 26.8 [6 C, $(CH_3)_3C$], 24.8 [1 C, $(CH_3)_2C$], 24.7 [1 C, $(CH_3)_2C$], 19.1 [2 C, $(CH_3)_3C$], 19.0 [1 C, $(CH_3)_2C$], 19.0 [1 C, $(CH_3)_2C$], 12.1 (1 C, CH_3C), 11.9 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3439 (w, br.), 2959 (m), 2857 (m), 1428

(m), 1380 (m), 1109 (s), 1049 (m), 823 (m), 740 (m), 702 (s), 611 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 204 (4.47) nm. MS (EI): *m*/*z* (%) = 367 (2), 289 (9), 199 (100), 139 (21), 43 (21). HRMS (EI): calcd. for $C_{22}H_{27}O_3Si$ [M – *t*Bu]$^+$ 367.1729; found 367.1723.

(3*R*,5*S*)-5-{(2*E*)-4-[(*tert*-Butyldiphenylsilanyl)oxy]but-2-en-2-yl}-2,2-dimethyltetrahydrofuran-3-ol (28) and (3*S*,5*S*)-5-{(2*E*)-4-[(*tert*-Butyldiphenylsilanyl)oxy]but-2-en-2-yl}-2,2-dimethyltetrahydrofuran-3-ol (29): The epoxide **27** (1.06 g, 2.5 mmol, 1.0 equiv.) was dissolved in DCM (250 mL). Camphorsulfonic acid (145 mg, 0.62 mmol, 0.25 equiv.) was added at 0 °C, and the solution was stirred at room temp. for 16 h. The reaction was quenched with a saturated aqueous $NaHCO_3$ solution, extracted with DCM, and washed with brine, and the solvent was evaporated. A mixture of the diastereomers **28** and **29** (1.04 mg, 2.4 mmol, 98%) was obtained after quick column chromatography (silica, petroleum ether/EtOAc, 4:1). A portion (70 mg) was separated by semipreparative HPLC (LiChrospher Si-60, 5 µm, *n*-hexane/ethyl acetate, 77:23) to yield **28** (19 mg) and **29** (10 mg), together with a mixture of **28** and **29** (35 mg).

Compound 28: R_f (petroleum ether/EtOAc, 4:1) = 0.27. $[\alpha]_D^{24}$ = –14.6 (*c* = 1.92, MeOH). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 4 H, Ph-*o*-*H*), 7.43–7.36 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.73–5.70 (m, 1 H, OCH_2CH), 4.52 (dd, *J* = 6.9, 8.7 Hz, $OCHCCH$), 4.26 (d, *J* = 6.1 Hz, 2 H, OCH_2CH), 3.98 [dd, *J* = 3.5, 5.7 Hz, 1 H, $HOCHC(CH_3)_2$], 2.03 (ddd, *J* = 5.8, 9.0, 13.2 Hz, 1 H, CH_2CHO), 1.95 (ddd, *J* = 3.4, 6.7, 13.2 Hz, 1 H, CH_2CHO), 1.40 (d, *J* = 1.0 Hz, 3 H, CH_3C), 1.27 [s, 3 H, $(CH_3)_2C$], 1.22 [s, 3 H, $(CH_3)_2C$], 1.03 [s, 9 H, $(CH_3)_3C$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.0 (1 C, $CHCCH_3$), 135.6 (2 C, *o*-C_{Ph}), 133.9 (1 C, *ipso*-C_{Ph}), 133.8 (1 C, *ipso*-C_{Ph}), 129.5 (2 C, *p*-C_{Ph}), 129.5 (2 C, *p*-C_{Ph}), 127.6 (2 C, *m*-C_{Ph}), 127.6 (2 C, *m*-C_{Ph}), 125.6 (1 C, OCH_2CH), 83.0 [1 C, $(CH_3)_2C$], 80.9 (1 C, $OCHCCH$), 78.3 [1 C, $HOCHC(CH_3)_2$], 60.8 (1 C, OCH_2CH), 38.9 (1 C, CH_2CHO), 27.8 [1 C, $(CH_3)_2C$], 26.8 [3 C, $(CH_3)_3C$], 21.5 [1 C, $(CH_3)_2C$], 19.1 [1 C, $(CH_3)_3C$], 11.9 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3425 (w, br.), 2964 (m), 2932 (m), 2891 (m), 2857 (m), 1467 (m), 1428 (m), 1380 (m), 1364 (m), 1109 (m), 1085 (m), 1054 (m), 1024 (m), 1009 (m), 857 (m), 822 (m), 788 (m), 740 (m), 702 (s), 612 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 265 (2.82), 259 (2.82), 204 (4.45) nm. HRMS (ESI): calcd. for $C_{26}H_{36}O_3SiNa$ [M + Na]$^+$ 447.23259; found 447.23261.

Compound 29: R_f (petroleum ether/EtOAc, 4:1) = 0.28. $[\alpha]_D^{29}$ = +3.7 (*c* = 0.51, MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 4 H, Ph-*o*-*H*), 7.44–7.35 (m, 6 H, Ph-*m*-*H*, Ph-*p*-*H*), 5.78–5.74 (m, 1 H, OCH_2CH), 4.31 (t, *J* = 7.5 Hz, $OCHCCH$), 4.26 (d, *J* = 6.1 Hz, 2 H, OCH_2CH), 3.98–3.94 [m, 1 H, $HOCHC(CH_3)_2$], 2.46–2.39 (m, 1 H, CH_2CHO), 1.73 (ddd, *J* = 4.5, 7.1, 13.4 Hz, 1 H, CH_2CHO), 1.45 (d, *J* = 0.8 Hz, 3 H, CH_3C), 1.28 [s, 3 H, $(CH_3)_2C$], 1.21 [s, 3 H, $(CH_3)_2C$], 1.03 [s, 9 H, $(CH_3)_3C$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.0 (1 C, $CHCCH_3$), 135.6 (2 C, *o*-C_{Ph}), 133.9 (1 C, *ipso*-C_{Ph}), 133.9 (1 C, *ipso*-C_{Ph}), 129.5 (2 C, *p*-C_{Ph}), 127.6 (2 C, *m*-C_{Ph}), 127.6 (2 C, *m*-C_{Ph}), 124.8 (1 C, OCH_2CH), 82.9 [1 C, $(CH_3)_2C$], 79.3 (1 C, $OCHCCH$), 78.3 [1 C, $HOCHC(CH_3)_2$], 60.8 (1 C, OCH_2CH), 39.4 (1 C, CH_2CHO), 26.8 [3 C, $(CH_3)_3C$], 25.8 [1 C, $(CH_3)_2C$], 22.4 [1 C, $(CH_3)_2C$], 19.1 [1 C, $(CH_3)_3C$],12.3 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3429 (w, br.), 2960 (m), 2890 (m), 2858 (m), 1469 (m), 1428 (m), 1109 (m), 1001 (m), 854 (m), 821 (m), 740 (m), 701 (s), 609 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 259 (3.10), 218 (4.24), 203 (4.40) nm. HRMS (ESI): calcd. for $C_{26}H_{36}O_3SiNa$ [M + Na]$^+$ 447.23259; found 447.23266.

(–)-Sachalinol B (6): TBAF·3H_2O (1 M in THF, 70 µL, 1.5 equiv.) was added to a solution of **28** (19 mg, 0.05 mmol, 1.0 equiv.) in THF (3 mL). After 3 h at room temp., the solvent was evaporated, and the crude product was subjected to column chromatography (silica, $CHCl_3$/MeOH, 10:1) to yield **6** (7 mg, 0.04 mmol, 80%) as a colorless oil. R_f ($CHCl_3$/MeOH, 8:1) = 0.38. $[\alpha]_D^{24}$ = –29.2 (*c* = 0.24, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ = 5.66–5.63 (m, 1 H, OCH_2CH), 4.51 (t, *J* = 6.5 Hz, $OCHCCH$), 4.12 (d, *J* = 6.5 Hz, 2 H, OCH_2CH), 3.93 [dd, *J* = 3.9, 6.0 Hz, 1 H, $HOCHC(CH_3)_2$], 2.08 (ddd, *J* = 6.1, 8.7, 13.1 Hz, 1 H, CH_2CHO), 1.97 (ddd, *J* = 3.9, 6.9, 13.0 Hz, 1 H, CH_2CHO), 1.62 (s, 3 H, CH_3C), 1.22 [s, 3 H, $(CH_3)_2C$], 1.22 [s, 3 H, $(CH_3)_2C$] ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 139.0 (1 C, $CHCCH_3$), 125.9 (1 C, OCH_2CH), 84.8 [1 C, $(CH_3)_2C$], 82.3 (1 C, $OCHCCH$), 78.5 [1 C, $HOCHC(CH_3)_2$], 59.2 (1 C, OCH_2CH), 39.8 (1 C, CH_2CHO), 28.1 [1 C, $(CH_3)_2C$], 22.0 [1 C, $(CH_3)_2C$], 12.0 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3352 (m, br.), 2972 (m), 2933 (m), 2879 (m), 1677 (m), 1460 (m), 1370 (m), 1180 (m), 1134 (m), 1092 (m), 989 (s), 801 (m), 593 (m), 538 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 202 (3.63) nm. HRMS (ESI): calcd. for $C_{10}H_{18}O_3Na$ [M + Na]$^+$ 209.11482; found 209.11478.

(+)-Sachalinol C (7): TBAF·3H_2O (1 M in THF, 180 µL, 1.5 equiv.) was added to a solution of **29** (46 mg, 0.12 mmol, 1.0 equiv.) in THF (12 mL). After 3 h at room temp., the solvent was evaporated, and the crude product was subjected to column chromatography (silica, $CHCl_3$/MeOH, 10:1) to yield **7** (18 mg, 0.04 mmol, 89%) as a colorless oil. R_f ($CHCl_3$/MeOH, 8:1) = 0.39. $[\alpha]_D^{29}$ = +47.0 (*c* = 0.06, MeOH). ^{1}H NMR (600 MHz, CD_3OD): δ = 5.66–5.63 (m, 1 H, OCH_2CH), 4.31 (dd, *J* = 6.7, 9.3 Hz, $OCHCCH$), 4.12 (dd, *J* = 6.6, 3.8 Hz, 2 H, OCH_2CH), 4.01 [t, *J* = 6.7 Hz, 1 H, $HOCHC(CH_3)_2$], 2.35 (ddd, *J* = 6.7, 6.7, 12.8 Hz, 1 H, CH_2CHO), 1.76 (ddd, *J* = 7.3, 9.4, 12.7 Hz, 1 H, CH_2CHO), 1.65 (d, *J* = 1.0 Hz, 3 H, CH_3C), 1.22 [s, 3 H, $(CH_3)_2C$], 1.18 [s, 3 H, $(CH_3)_2C$] ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 138.8 (1 C, $CHCCH_3$), 126.0 (1 C, OCH_2CH), 83.7 [1 C, $(CH_3)_2C$], 80.8 (1 C, $OCHCCH$), 78.7 [1 C, $HOCHC(CH_3)_2$], 59.2 (1 C, OCH_2CH), 39.9 (1 C, CH_2CHO), 26.7 [1 C, $(CH_3)_2C$], 23.3 [1 C, $(CH_3)_2C$], 12.0 (1 C, CH_3C) ppm. IR (ATR): $\tilde{\nu}$ = 3351 (m, br.), 2969 (m), 2929 (m), 2873 (m), 1677 (m), 1453 (m), 1368 (m), 1259 (m), 1203 (m), 1142 (m), 1073 (m), 1003 (s), 836 (m), 799 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 203 (3.48) nm. MS (EI): *m*/*z* (%) = 168 (2), 155 (100), 150 (3), 137 (9), 110 (11), 81 (59), 69 (71). HRMS (ESI): calcd. for $C_{10}H_{18}O_3Na$ [M + Na]$^+$ 209.11482; found 209.11479.

2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucopyranosyl Iodide (22): Hexamethyldisilane (165 µL, 0.8 mmol, 0.6 equiv.) and iodine (203 mg, 0.8 mmol, 0.6 equiv.) were added to a solution of pentapivaloylglucose (760 mg, 1.3 mmol, 1.0 equiv.) in DCM (3 mL). The brown solution was stirred at room temp. for 3.5 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ solution and stirred until the solution was colorless. The aqueous phase was extracted with DCM, and the organic phases were washed with aqueous $NaHCO_3$ solution and brine and dried with $MgSO_4$. The crude product was subjected to flash chromatography with petroleum ether/EtOAc to yield **22** (650 mg, 1.04 mmol, 80%) as a colorless solid. M.p. 140–142 °C. R_f (petroleum ether/EtOAc, 20:1) = 0.29. $[\alpha]_D^{31}$ = +168.0 (*c* = 1.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.99 (d, *J* = 4.4 Hz, 1 H, C1-*H*), 5.54 (t, *J* = 9.6 Hz, 1 H, C3-*H*), 5.26–5.21 (m, 1 H, C4-*H*), 4.22 (dd, *J* = 4.4, 9.8 Hz, 1 H, C2-*H*), 4.18 (d, *J* = 3.4 Hz, 2 H, C6-H_2), 4.08 (td, *J* = 3.3, 10.8 Hz, 1 H, C5-*H*), 1.22 [s, 9 H, C6-$OOC(CH_3)_3$], 1.20 [s, 9 H, C2-$OOC(CH_3)_3$], 1.19 [s, 9 H, C4-$OOC(CH_3)_3$], 1.13 [s, 9 H, C3-$OOC(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9 [1 C, C6-$OOCC(CH_3)_3$], 177.1 [1 C, C2-$OOCC(CH_3)_3$], 176.7 [1 C, C3-$OOCC(CH_3)_3$], 176.4 [1 C, C4-$OOCC(CH_3)_3$], 75.4 (1 C, *C*5-H), 73.4 (1 C, *C*1-H), 71.1 (1 C, *C*3-H), 70.4 (1 C, *C*2-H), 66.3 (1 C, *C*4-H), 60.8 (1 C, *C*6-

H_2), 38.9 [1 C, C6-OOC*C*$(CH_3)_3$], 38.8 [1 C, C4-OOC*C*$(CH_3)_3$], 38.7 [1 C, C3-OOC*C*$(CH_3)_3$], 38.6 [1 C, C2-OOC*C*$(CH_3)_3$], 27.1 [2 C, C2-OOCC(CH_3)$_3$; C2-OOCC(CH_3)$_3$], 27.1 [1 C, C6-OOC*C*(CH_3)$_3$], 27.0 [1 C, C4-OOCC(CH_3)$_3$] ppm. IR (ATR): $\tilde{\nu}$ = 2972 (m), 1733 (s), 1480 (m), 1278 (m), 1123 (s), 1084 (m), 1035 (m), 987 (m), 763 (m), 563 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 263 nm (3.02), 203 (4.00). HRMS (ESI): calcd. for $C_{26}H_{43}O_9INa$ $[M + Na]^+$ 649.18440; found 649.18189.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-{[(2*E*)-3,7-Dimethylocta-2,6-dien-1-yl]oxy}-6-[(pivaloyloxy)methyl]tetrahydro-2*H*-pyran-3,4,5-triyl Tris(2,2-dimethylpropanoate) (24): Geraniol (**19**, 100 mg, 0.64 mmol, 1.0 equiv.) was dissolved in anhydrous Et_2O (6 mL) under Ar. 2,3,4,6-Tetra-*O*-pivaloyl-α-D-glucopyranosyl bromide (**20**, 556 mg, 0.96 mmol, 1.5 equiv.) and Ag_2CO_3 (442 mg, 1.6 mmol, 2.5 equiv.) were added to the resulting solution, and the mixture was stirred at room temp. in the dark for 22 h. The solution was then filtered, and the solvent was evaporated. After chromatography (silica gel, petroleum ether/EtOAc, 20:1) **24** (282 mg, 0.43 mmol, 67%) was obtained as a colorless oil. R_f (petroleum ether/EtOAc, 20:1) = 0.29. $[\alpha]_D^{31}$ = 1.25 (*c* = 2.87, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (t, *J* = 9.5 Hz, 1 H C3-*H*), 5.26–5.22 (m, 1 H, OCH_2CH), 5.13–5.06 [m, 2 H, C4-*H*, $(CH_3)_2CCH$], 5.04–5.00 (m, 1 H, C2-*H*), 4.53 (d, *J* = 8.1 Hz, 1 H, C1-*H*), 4.27–4.18 (m, 3 H, OCH_2CH, C6-H_2), 4.07 (dd, *J* = 5.8, 12.2 Hz, 1 H, C6-H_2), 3.70 (ddd, *J* = 1.7, 5.7, 10.1 Hz, 1 H, C5-*H*), 2.11–2.02 (m, 4 H, CCH_2CH_2), 1.70 [s, 3 H, $C(CH_3)_2$], 1.65 [s, 3 H, $C(CH_3)_2$], 1.61 (s, 3 H, CCH_3), 1.23–1.23 [m, 9 H, $C(CH_3)_3$], 1.60–1.54 [m, 18 H, 2 × $C(CH_3)_3$], 1.11 [m, 9 H, $C(CH_3)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9 [1 C, O*C*C(CH_3)$_3$], 177.1 [1 C, O*C*C(CH_3)$_3$], 176.3 [2 C, 2 × O*C*C(CH_3)$_3$], 141.6 (1 C, *C*CH_3), 131.7 [1 C, *C*(CH_3)$_2$], 123.6 [1 C, $(CH_3)_2CCH$], 119.3 (1 C, OCH_2CH), 98.8 (1 C, *C*1-H), 72.2 (2 C, *C*3-H, *C*5-H), 71.0 (1 C, *C*2-H), 68.1 (1 C, *C*4-H), 64.8 (1 C, OCH_2CH), 62.1 (1 C, *C*6-H_2), 39.4 (1 C, C*C*H_2CH_2), 38.7 [1 C, OC*C*$(CH_3)_3$], 38.6 [1 C, OC*C*$(CH_3)_3$], 38.6 [2 C, 2 × OC*C*$(CH_3)_3$], 27.0 [3 C, OCC(CH_3)$_3$], 27.0 [3 C, OCC(CH_3)$_3$], 26.9 [3 C, OCC(CH_3)$_3$], 26.9 [3 C, OCC(CH_3)$_3$], 26.2 (1 C, CCH_2CH_2), 25.6 [1 C, $C(CH_3)_2$], 17.6 (1 C, CCH_3), 16.3 [1 C, $C(CH_3)_2$] ppm. IR (ATR): $\tilde{\nu}$ = 2971 (m), 1740 (s), 1480 (m), 1279 (m), 1133 (s), 1036 (m), 984 (m), 892 (m), 762 (m) cm^{-1}. UV/Vis (MeOH): λ_{max} (lgε) = 206 (3.85) nm. HRMS (ESI): calcd. for $C_{36}H_{60}O_{10}Na$ $[M + Na]^+$ 675.40787; found 675.40793.

X-ray Structure Analysis of (–)-3·2H$_2$O: Crystal data: $C_{10}H_{24}O_5$, monoclinic, $P2_1$, *a* = 8.5567(2), *b* = 6.5575(2), *c* = 11.5670(3) Å, β = 94.411(3)°, *V* = 647.12(3) Å^3, *Z* = 2, *T* = 100 K, D_X = 1.151 Mg m^{-3}. A colorless parallelepiped (0.3 × 0.2 × 0.1 mm) was used to record a total of 16358 data to $2\theta_{max}$ = 152° (99.9% complete to 150°) with use of Cu-K_α radiation and an Oxford Diffraction Nova O diffractometer. The structure was refined on F^2 by use of the program SHELXL-97[25] to *wR*2 = 0.058 (all data), *R*1 = 0.022 for 2578 independent data and 167 parameters; *S* = 1.03, $\Delta\rho_{max}$ = 0.16 e Å^{-3}. The O–H distances in the hydroxy groups and water molecules were restrained to be approximately equal. The Flack parameter refined to 0.00(11), thus determining the absolute configuration as (4*S*) on the basis of the anomalous dispersion of oxygen. CCDC-794004 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR spectra of compounds **3**, **15**–**18**, **22**, **24**–**32**; packing of **3** in the crystal; Mosher analysis of compounds **28** and **29**.

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