Organic & Biomolecular Chemistry

Cite this: *Org. Biomol. Chem.*, 2011, **9**, 6797

www.rsc.org/obc

PAPER

Synthesis and configuration of the nonadecenetriol isolated from seeds of *Persea americana*†

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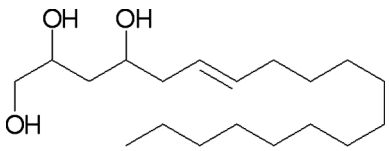
Received 4th June 2011, Accepted 4th July 2011
DOI: 10.1039/c1ob05898c

In an effort to establish the relative as well as absolute configuration of the trypanocidally active natural nonadec-6-en-1,2,4-triol isolated from *Persea americana*, the (2S,4*R*), (2*S*,4*S*), and (2*R*,4*R*) isomers were synthesized. The stereogenic centers taken from enantiopure chiral epoxy building blocks derived from inexpensive and readily available D-glucolactone. The (2*R*,4*R*) isomer gave ^{1}H and ^{13}C NMR as well as specific rotation in excellent consistence with those reported for the natural triol.

Introduction

Chagas disease (American trypanosomiasis) is a potentially life-threatening illness caused by the protozoan parasite, *Trypanosoma cruzi* (*T. cruzi*). As one of the most serious rotozoan diseases in Latin America, it has received broad attention from scientific communities.[1] Recently, in their search of novel agents for the chemotherapy of Chagas disease Abe and coworkers[2] identified a previously unknown trypanocidally active compound from the MeOH extract of seeds of *Persea americana* (avocado), a plant that grows in all tropical areas around the world. On the basis of spectroscopic data, including those from HRMS, ^{1}H as well as ^{13}C NMR, and 2D COSY experiments, they assigned the planar structure (Fig. 1) of this compound as (*E*)-nonadec-6-ene-1,2,4-triol (**1**). They also measured the specific rotation for this triol, which was reported to be $[\alpha]_D^{24}$ –8.6 (*c* 0.25, $CHCl_3$), but did not disclose any further information regarding to the relative and absolute configuration of the stereogenic centers.



1 $[\alpha]_D^{24}$ –8.6 (*c* 0.25, $CHCl_3$)

Fig. 1 The planar structure of the natural triol (**1**) isolated from *Persea americana*.

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† Electronic supplementary information (ESI) available: The ^{1}H and ^{13}C NMR as well as IR spectra for all new compounds, tabular NMR data comparison of the natural and synthetic (2*R*,4*R*)-**1**. See DOI: 10.1039/c1ob05898c

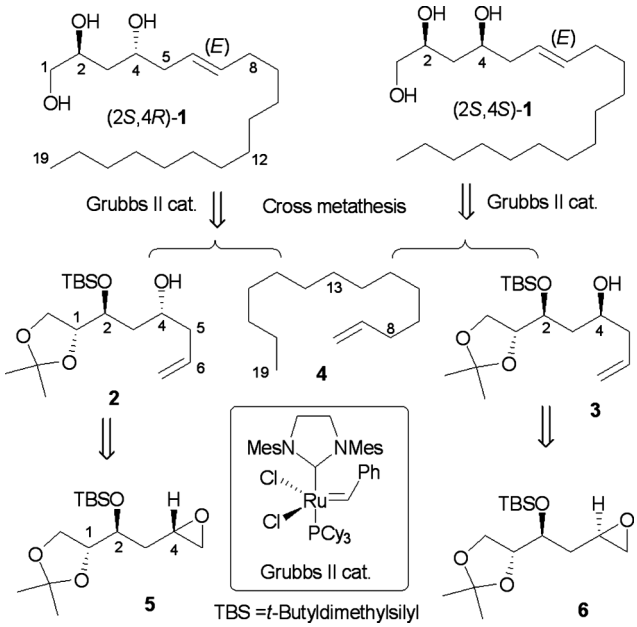
The missing piece in the structural knowledge of the natural **1**, which must be difficult to acquire for the previous investigators, strongly signaled a need, also an opportunity, for synthesis to make a contribution. Having noticed this situation, we started an enantioselective synthesis of the title triol. Through data comparison of the synthetic and the natural samples the relative and absolute configuration of the latter now has been established with great confidence. Described below is the details of this synthetic study.

Results and discussion

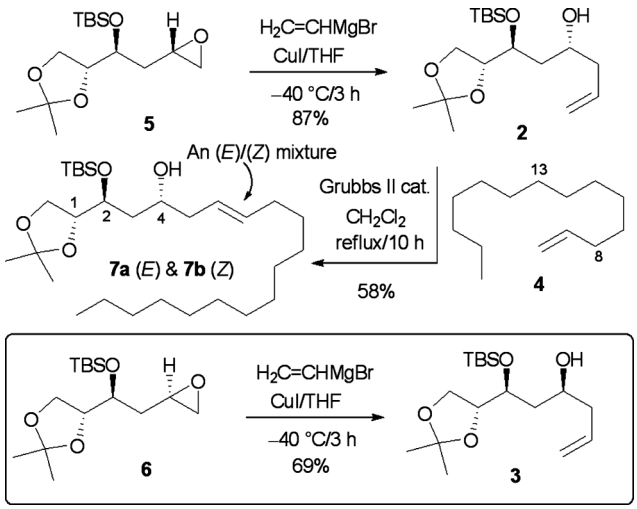
The target triol (**1**) contains two stereogenic centers and therefore in principle there exist four different enantiomers altogether. However, because two of them are mirror images of the other two, synthesis of any set of two epimers would allow[3] for establishment of the relative as well as absolute configuration of the natural **1**. For convenience we deliberately chose the (2*S*,4*S*) and (2*S*,4*R*) isomers as our primary targets because of the readily accessible[4] nature of the chiral building blocks **2** and **3**. The general feature of our initial plan is shown in Scheme 1, with the 1,3-diol and the long linear chain units in the target structures taken from **2** or **3** and the alkene **4**, respectively. The diol fragments **2** and **3** were planned to derive from the known epoxy chiral building blocks **5**[4] and **6**,[5] respectively.

It is known that cross metathesis in most cases would afford a mixture of (*E*)- and (*Z*)- isomers of the C–C double bond. However, because at least in some cases such isomers could be separated and the relatively bulky substituents at both alkenic carbons might help to enrich the thermodynamically more stable (*E*)-isomer, we thought that the CM-based plans deserved a try. Thus, using the commercially available $H_2C{=}CHMgBr$ to open the epoxy ring in **5** and **6**, respectively, in the presence of a catalytic amount of CuI, the corresponding alcohol **2** and **3** were obtained in 87% and 69% yield, respectively (Scheme 2).

The cross coupling was then examined with **2** and the commercially available tetradec-1-ene **4** as the reactants. Under the



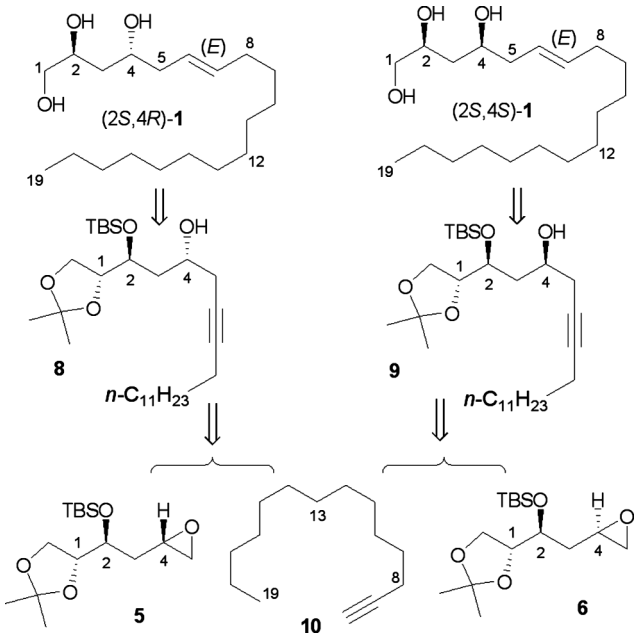
Scheme 1 The outline of the retrosynthetic analysis of the initial plan.



Scheme 2 Coupling of epoxied **5** with alkyne **10** by cross metathesis.

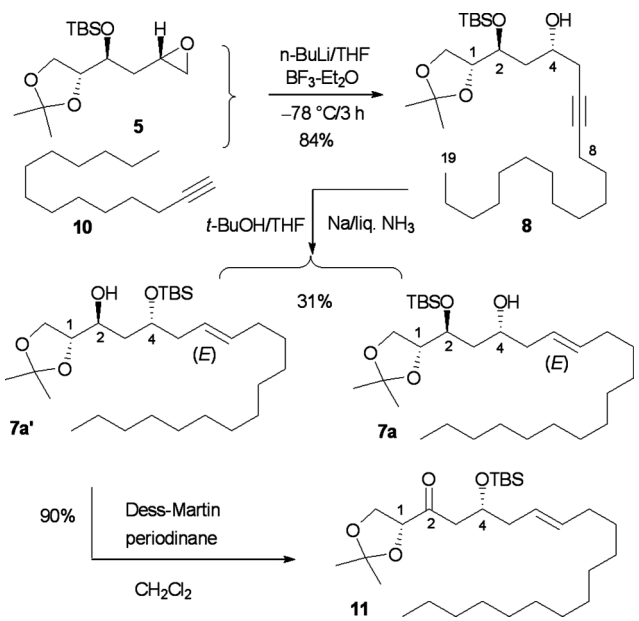
standard conditions, the coupling product was isolated in 58% yield. However, this sample, which was a well-shaped round spot on TLC, turned out to be a mixture of the (*E*)- and (*Z*)-isomers (**7a** and **7b**) as shown by ^{1}H NMR. Considerable efforts were made to separate these two isomers without success. Conversion of the less stable (*Z*)-isomer to the more stable (*E*)-isomer under some literature conditions (n-$Bu_3SnH/Pd(OAc)_2/Et_3N$[6] or PhSH/AIBN[7]) also failed. Therefore, this approach was discontinued.

To get around the separation problem, we next switched to an alkyne-based approach (Scheme 3), which was expected to be able to deliver the desired alkenes in pure (*E*)-configuration *via* a stereoselective reduction of the triple bond. This strategy also enjoyed some other advantages, including facile generation of the carbanion required in the coupling with the epoxides and incorporation of the C-6 to C-19 unit into the target structures in a single operation.



Scheme 3 The plan based on coupling of epoxides with alkyne **10**.

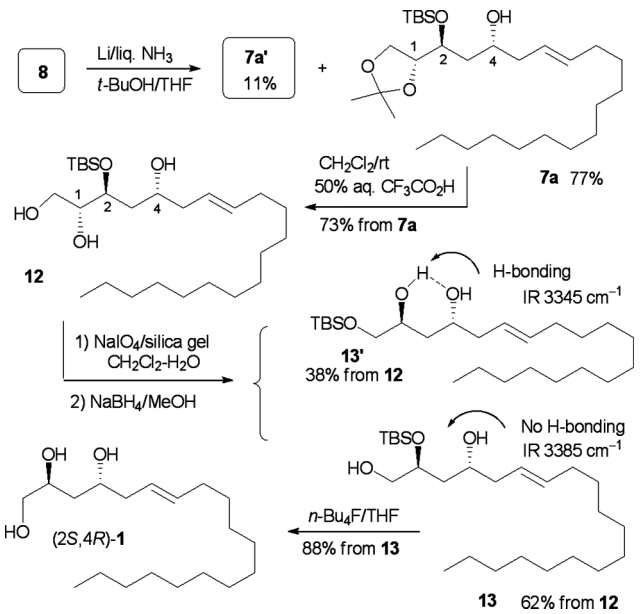
Execution of the second plan started with reaction of **5** with the commercially available tetradec-1-yne **10** (Scheme 4), which led to the propargyl alcohol **8** in 84% yield. Reduction of the triple bond in **8** was not as smooth as the preceding step. We tried several sets of literature conditions that were well-established for similar transformations, including $LiAlH_4$/THF at ambient temperature[8] or reflux,[9] $LiAlH_4$/diglyme/170 °C[10] and Red-Al/THF/rt.[11] However, in the present case essentially no reaction occurred. Under the Na/liq. NH_3/THF/*t*-BuOH[12] conditions the reduction did occur as anticipated, but the product turned out to be two alkenes (in *ca.* 1 : 3 ratio, of similar polarity and thus difficult to separate from each other) instead of one, even well before the starting **8** was fully consumed.



Scheme 4 Coupling of **5** with **10** and reduction with Na/liq. NH_3.

^{1}H NMR analysis strongly suggested that the two alkenes differed only in the position of the TBS protecting group. Judging from the substrate structure and the reaction conditions, we deduced that the minor product (the less polar one) was more likely to be the one with the TBS group migrated (**7a′**). Indeed, a diagnostic oxidation of the separated minor component (**7a′**) and subsequent analysis of the oxidation product (**11**) by ^{1}H NMR unambiguously confirmed that the TBS group in this compound was on the C-4 OH.

With the identity of the components in the reduction product established, we next tried to minimize the formation of the undesired **7a′**. To reduce the basicity of the alkoxide at the C-4 during the reduction by changing the cation appeared to be a potential choice. Thus, Li metal was examined in place of Na.[13] To our gratification, after this modification the yield of **7a** (more polar) could be raised to 77% while that for **7a′** (less polar) reduced to 11% under the otherwise identical conditions (Scheme 5).



Scheme 5 Reduction of **8** and subsequent elaboration into (2*S*,4*R*)-**1**.

Removal of the terminal acetonide in **7a** was achieved under the 50% aq. F_3CCO_2H/CH_2Cl_2[14] conditions. The resultant triol **12** was treated with $NaIO_4$ in CH_2Cl_2-H_2O/silica gel[8,15] to yield the intermediate aldehyde, which on further reduction of the carbonyl group with $NaBH_4$ in MeOH afforded the corresponding alcohol **13** (63%) along with a smaller amount of **13′** (38%).

The spectra for these two compounds were rather similar to each other, with the most distinct differences in the OH stretching frequency in the IR and the chemical shift difference of the geminal protons of the CH_2's at C-1 and C-3 in the ^{1}H NMR. Because structure **13′** does not have any primary OH and the two secondary OH's at C-2 and C-4 may easily form a cyclic motif through intramolecular hydrogen bonding, it was assigned to the minor product, which has a lower OH stretching frequency (3345 cm^{-1}), a smaller δ splitting for the C-1 CH_2 (because weaker influence from the chiral C-2 as the substituent became smaller) and a larger δ splitting for the C-3 CH_2 (being part of the 6-membered hydrogen bonded ring).

Finally, desilylation of **13** with *n*-Bu_4NF in THF delivered the end product (2*S*,4*R*)-**1**. The spectroscopic data for (2*S*,4*R*)-**1** were then measured and compared with those reported for the natural product. The specific rotation (−5.67) and the ^{1}H NMR data were not very useful, from which no definite conclusions could possibly be drawn. However, significant differences were found in the ^{13}C NMR at δ 70.3 (nat. 72.2) and 69.2 (nat. 71.3) ppm. On the basis of these discrepancies, it can be concluded that (2*S*,4*R*)-**1** and the natural **1** are not the same compound; the latter thus must have a 1,3-*syn* (either (2*R*,4*R*) or (2*S*,4*S*)) configuration.

Synthesis of (2*S*,4*S*)-**1** was performed as shown in Scheme 6. Using the same reaction sequence as that for (2*S*,4*R*)-**1** but starting with epoxide **6** instead of **5**, the corresponding propargyl alcohol **9** was obtained in 88% yield. Reduction of **9** under the same Li/liq. NH_3 conditions delivered desired **14** (58%) and the TBS shifted isomer **14′** (17%, whose structure was also confirmed by oxidation to **15**). Compared with the reduction of **8**, the TBS migration occurred to a more significant extent. This is probably because in the case of **8** (Fig. 2).

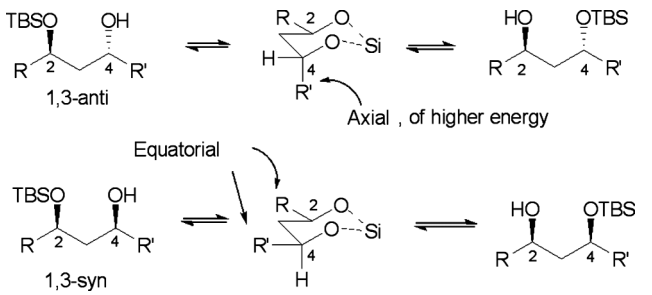
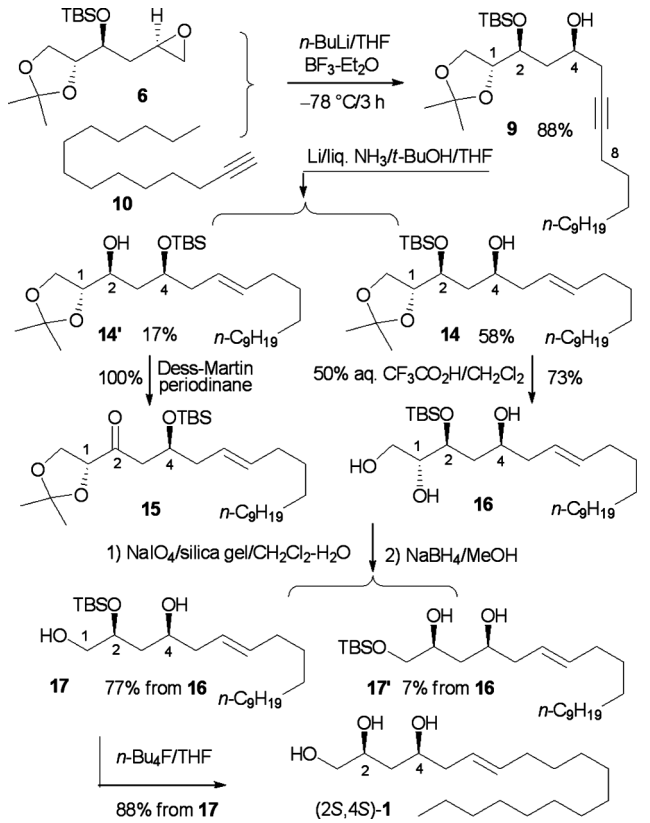


Fig. 2 The 1,3-anti relationship leads to a transition state of higher energy (with one substituent in an axial position) than its 1,3-*syn* counterpart (both R and R′ are in equatorial positions). For clarity, the substituents on the silicon atom are not shown.

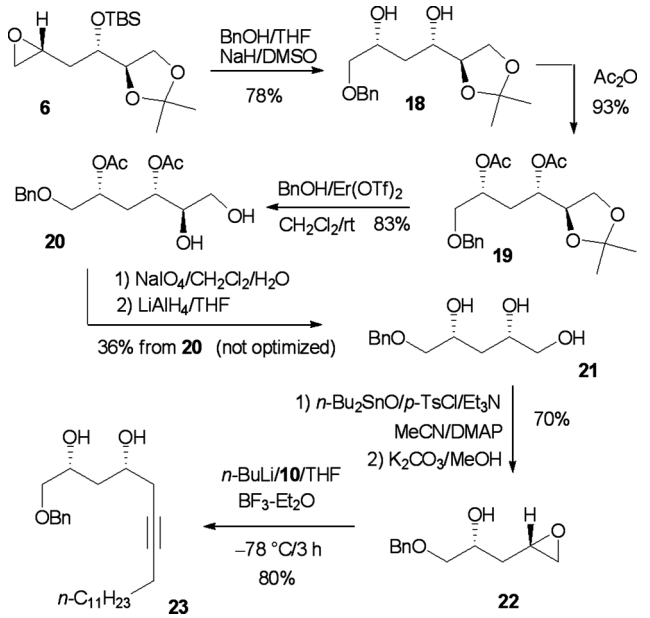
It is noteworthy that because of the substantially larger polarity difference between **14** (more polar) and **14′** (less polar) than that between **7a** and **7a′**, acquisition of pure **14** by choromatography became much easier. With access to pure **14** secured, the remaining steps were completed in a fashion similar to that for the synthesis of (2*S*,4*R*)-**1**. In the $NaBH_4$ reduction of the intermediate aldehyde after the $NaIO_4$ oxidation, traces amounts of side product **17′** (with the TBS shifted from C-2 OH to the C-4 OH) was also observed.

Unlike its (2*S*,4*R*) counterpart, the (2*S*,4*S*)-**1** showed ^{1}H and ^{13}C NMR fully consistent with those reported for the natural **1**, which, along with the optical rotation of the opposite sign, unambiguously manifested that the natural product must be an mirror image of (2*S*,4*S*)-**1**.

To gain the triol of (2*R*,4*R*) configuration, we next started the synthesis shown in Scheme 7. The stereogenic centers in the end product in this case was also taken from epoxide **6**, but in a different way. The opening of the epoxy ring was achieved through reaction with BnOH under the NaH/DMSO/THF/rt[16] conditions. If using DME ($MeO(CH_2)_2OMe$) as solvent,[17] no reaction occurred even at 60 °C. The two hydroxyl groups were then masked as acetates without any difficulty. However, hydrolysis of the acetonide was rather frustrating, presumably because of the presence of the acetates. Using 50% aq. CF_3CO_2H, CAS (camphor



Scheme 6 Synthesis of (2*S*,4*S*)-**1**.

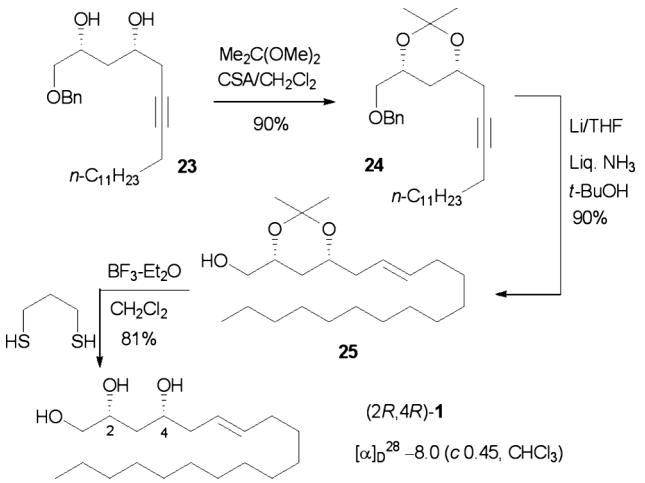


Scheme 7 Conversion of **6** into **23**.

sulphonic acid), or 1 N HCl as the catalyst to run the reaction in CH_2Cl_2 at ambient temperature all led to a complex mixture. The problem was later solved by running the reaction under the $Er(OTf)_2/BnOH/CH_2Cl_2/rt$ conditions (previously reported[18] for opening epoxy ring with BnOH), which delivered the desired diol **20** in 83% yield.

Further treatment of diol **20** with $NaIO_4$/silica gel/CH_2Cl_2-H_2O cut off one carbon unit from the terminal as in the conversion of **12** into **13** mentioned above, but the intermediate aldehyde was reduced with $LiAlH_4$ instead of $NaBH_4$ to remove all the Ac groups at the same time. The resulting triol **21** was then transformed into the corresponding epoxide **22** by sequential treatment with *p*-TsCl/*n*-Bu_2SnO/Et_3N/DMAP and K_2CO_3/MeOH to set a stage for incorporation of the alkyne fragment. The C-6 to C-19 unit was then introduced by reaction with alkyne **10** under the same conditions employed previously in the conversion of **6** into **9**.

Direct treatment of this diol (**23**) to the Li/liq. NH_3 reduction conditions led to only the corresponding debenzylation product; essentially no reduction of the triple bond occurred. However, after masking the diol as an acetonide in the presence of CSA (camphor-10-sulfonic acid), the triple bond could be smoothly transformed to the desired (*E*)-alkene **25** (Scheme 8) with a concurrent removal of the benzyl protecting group at the chain terminal. On hydrolysis of the acetonide protecting group through reaction with propane-1,3-dithiol, the end product (2*R*,4*R*)-**1** was obtained in 81% isolated yield. As expected, the synthetic (2*R*,4*R*)-**1** showed ^1H and ^{13}C NMR as well as optical rotation in excellent consistency with those reported for the natural **1**. The configuration of natural **1** was thus established to be (2*R*,4*R*).



Scheme 8 Conversion of **23** into (2*R*,4*R*)-**1**.

Conclusions

In summary, in an effort to establish the relative as well as absolute configuration of the nonadec-6-ene-1,2,4-triol isolated from *Persea american*, the (2*S*,4*R*), (2*R*,4*R*), and (2*S*,4*S*) isomers of the triol were synthesized separately through chiral pool based routes. The (2*S*,4*R*) configuration (*a priori*, also the (2*R*,4*S*) one, the other 1,3-anti isomer) can be easily excluded because of the ^1H and ^{13}C NMR incompatible with those reported for the natural one. Both (2*R*,4*R*) and (2*S*,4*S*) isomers show ^1H and ^{13}C NMR in full consistence with those reported for the natural **1**, but the latter has a rotation of sign opposite to that for the natural one. Thus, it can be concluded beyond all doubt that the natural **1** has the (2*R*,4*R*) configuration.

Experimental

General

Dry THF was distilled over Na/Ph_2CO under N_2 prior to use. Dry CH_2Cl_2, DMF and DMSO were distilled over CaH_2 under N_2 prior to use. Addition of air/moisture sensitive reagents was done using syringe techniques. PE (for chromatography) stands for petroleum ether (b.p. 60–90 °C). Column chromatography was performed on silica gel (300–400 mesh) under slightly positive pressure. NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer operating at 400 MHz for proton. IR spectra were measured on a Nicolet 380 Infrared Spectrometer. ESI-MS data were acquired on a Shimadzu LCMS-2010EV mass spectrometer. HRMS data were obtained with a Bruker APEXIII 7.0 Tesla FT-MS or an Agilent 6538 UHD Accurate-Mass Q-TOF spectrometer. Optical rotations were measured on a Jasco P-1030 Polarimeter.

(1*S*,3*R*)-1-(*tert*-Butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)hex-5-en-3-ol (2). CH_2═CHMgBr (1 M, in THF, 10 mL, 10 mmol) was added to a white suspension of CuI (252 mg, 1.53 mmol) in dry THF (20 mL) stirred at –40 °C under N_2 (balloon). The resulting dark-brown mixture was stirred at the same temperature for 20 min. A solution of epoxide **5** (572 mg, 1.89 mmol) in dry THF (4.5 mL) was then introduced. The mixture was stirred at –40 °C for 3 h, when TLC showed completion of the reaction. Aqueous saturated NH_4Cl was added carefully. The mixture was extracted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue, which was chromatographed (10 : 1 PE/EtOAc) on silica gel to give the alcohol **2** as a colorless oil (545 mg, 1.65 mmol, 87%): $[\alpha]_D^{27}$ +6.3 (*c* 0.90, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91–5.78 (m, 1H), 5.15–5.08 (m, 2H), 4.11–4.03 (m, 2H), 3.98–3.90 (m, 1H), 3.87 (dd, J = 10.8, 5.0 Hz, 1H), 3.83–3.75 (m, 1H), 2.31–2.16 (m, 2H), 1.77 (ddd, J = 14.6, 4.6, 2.2 Hz, 1H), 1.67 (ddd, J = 14.9, 9.9, 5.1 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H), 0.88 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 117.5, 109.4, 78.3, 72.7, 67.9, 67.4, 42.5, 41.3, 26.6, 25.8, 25.4, 18.0, –4.2, –4.6; FT-IR (film) 3489, 3072, 2985, 2954, 2931, 2889, 2858, 1641, 1473, 1463, 1380, 1371, 1256, 1215, 1159, 1073, 837, 777 cm^{-1}. ESI-MS m/z 353.4 ([M+Na]$^+$); ESI-HRMS calcd for $C_{17}H_{34}NaO_4Si$ ([M+Na]$^+$) 353.2119, found 353.2124.

(1*S*,3*S*)-1-(*tert*-Butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)hex-5-en-3-ol (3). The procedure was the same as described above for the conversion of **5** into **2**, except epoxide **6** (1.28 g, 4.24 mmol) was employed to replace **5**, giving **3** (969 mg, 2.93 mmol, 69%, chromatographed with 10 : 1 PE/EtOAc) as a colorless oil. $[\alpha]_D^{29}$ +22.6 (*c* 0.94, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88–5.76 (m, 1H), 5.11 (dd, J = 16.8, 6.3 Hz, 2H), 4.13–4.00 (m, 2H), 3.97–3.84 (m, 2H), 3.78 (t, J = 7.1 Hz, 1H), 2.58 (d, J = 3.7 Hz, 1H), 2.22 (t, J = 6.7 Hz, 2H), 1.80–1.67 (m, 2H), 1.39 (s, 3H), 1.33 (s, 3H), 0.86 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 117.6, 109.3, 78.6, 71.15, 67.22, 67.16, 42.3, 41.9, 26.5, 25.7, 25.3, 17.9, –4.2, –4.6; FT-IR (film) 3485, 3072, 2985, 2959, 2931, 2888, 2858, 1641, 1473, 1463, 1380, 1371, 1256, 1073, 1004, 914, 837, 776, 674, 513 cm^{-1}. ESI-MS m/z 353.3 ([M+Na]$^+$); ESI-HRMS calcd for $C_{17}H_{34}NaO_4Si$ ([M+Na]$^+$) 353.2119, found 353.2123.

(1*S*,3*R*)-1-(*tert*-Butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)octadec-5-yn-3-ol (8). *n*-BuLi (1.6 M, in hexanes, 1.5 mL, 2.35 mmol) was added to a solution of tetradec-1-yne **10** (0.6 mL, 2.41 mmol) in dry THF (12 mL) stirred at –78 °C under N_2 (balloon). The resulting white suspension was stirred at the same temperature for 2 h. A solution of epoxide **5** (182 mg, 0.602 mmol) in dry THF (3 mL) was then introduced, followed by $BF_3{\cdot}Et_2O$ (0.15 mL, 1.205 mmol). The mixture was stirred at –78 °C for 3 h, when TLC showed completion of the reaction. Aqueous saturated NH_4Cl (10 mL) was added carefully. The bath was allowed to warm to ambient temperature. The mixture was extracted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue, which was chromatographed (15 : 1 PE/EtOAc) on silica gel to give the alcohol **8** as a colorless oil (252 mg, 0.507 mmol, 84%): $[\alpha]_D^{22}$ +1.1 (*c* 1.03, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10–4.00 (m, 2H), 3.99–3.90 (m, 1H), 3.87 (dd, J = 10.8, 5.3 Hz, 1H), 3.84–3.76 (m, 1H), 3.34 (d, J = 2.0 Hz, 1H), 2.41–2.26 (m, 2H), 2.20–2.10 (m, 2H), 1.90 (ddd, J = 14.7, 4.6, 2.1 Hz, 1H), 1.78–1.68 (m, 1H), 1.53–1.42 (m, 2H), 1.40 (s, 3H), 1.34 (s, 3H), 1.31–1.18 (m, 18H), 0.93–0.82 (m, 12H), 0.13 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.3, 82.8, 78.5, 76.2, 72.3, 67.6, 67.3, 41.1, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 29.0, 28.9, 28.1, 26.6, 25.8, 25.3, 22.7, 18.8, 18.0, 14.1, –4.2, –4,6; FT-IR (film) 3486, 2955, 2927, 2855, 1463, 1379, 1256, 1214, 1074, 838, 777 cm^{-1}. ESI-MS m/z 519.5 ([M+Na]$^+$); EI-HRMS calcd for $C_{29}H_{56}O_4Si$ (M$^+$) 496.3948, found 496.3951.

(1*S*,3*R*,*E*)-1-(*tert*-Butyldimethyl-silyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)octadec-5-en-3-ol (7a) and (1*S*,3*R*,*E*)-3-(*tert*-butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4- yl)-octadec-5-en-1-ol (7a′). Li cuts (*ca.* 1.0 g, 144 mmol) was added in small portions to liquid NH_3 (*ca.* 75 mL, in a three-neck flask) stirred in a –78 °C bath. To the resultant dark blue mixture was added a solution of propargyl alcohol **8** (135 mg, 0.272 mmol) in THF (15 mL), followed by *t*-BuOH (10 mL). The mixture was stirred at the same temperature for 3.5 h before an additional portion of *t*-BuOH (3 mL) was introduced. The stirring was continued at –78 °C for another 2 h. Aqueous saturated NH_4Cl was added carefully. The bath was allowed to warm to ambient temperature slowly. The mixture was extracted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue, which was chromatographed (20 : 1 PE/EtOAc) on silica gel to give the alcohol **7a′** (the less polar component, 15 mg, 0.030 mmol, 11%) and **7a** (the more polar component, 104 mg, 0.209 mmol, 77%) as colorless oils.

Data for **7a′** (the less polar component): $[\alpha]_D^{27}$ –4.2 (*c* 0.45, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (dt, J = 15.4, 7.1 Hz, 1H), 5.31 (dt, J = 15.2, 7.3 Hz, 1H), 4.07–3.98 (m, 2H), 3.98–3.87 (m, 3H), 3.40 (s, 1H), 2.32–2.22 (m, 2H), 1.97 (dd, J = 13.4, 6.5 Hz, 2H), 1.74 (dt, J = 14.6, 5.4 Hz, 1H), 1.59–1.46 (m, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 1.37–1.13 (m, 20H), 0.93–0.78 (m, 12H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.8, 125.4, 109.0, 78.9, 71.3, 68.83, 66.0, 39.9, 37.5, 32,6, 31.9, 29.7, 29.62, 29.61, 29.5, 29.4, 29.3, 29.2, 26.6, 25.8, 25.3, 22.7, 17.9, 14.1, –4.6, –4.9; FT-IR (film) 3330, 2955, 2923, 2854, 1736, 1462, 1378, 1089, 1018 cm^{-1}. ESI-MS m/z 521.5 ([M+Na]$^+$); EI-HRMS calcd for $C_{28}H_{55}O_4Si$ ([M–CH_3]$^+$) 483.3870, found 483.3869.

Data for **7a** (the more polar component): $[\alpha]_D^{27}$ +4.6 (*c* 1.00, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (dt, J = 15.4, 7.0 Hz, 1H), 5.41 (dt, J = 15.3, 7.0 Hz, 1H), 4.12–4.01 (m, 2H), 3.93–3.77 (m, 3H), 3.12 (s, 1H), 2.22–2.08 (m, 2H), 2.07–1.94 (m, 2H), 1.80–1.71 (m, 1H), 1.69–1.60 (m, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 1.38–1.19 (m, 20H), 0.95–0.82 (m, 12H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 125.8, 109.3, 78.4, 72.5, 68.2, 67.3, 41.4, 41.3, 32,7, 31.9, 29.7, 29.63, 29.62, 29.52, 29.48, 29.35, 29.2, 26.6, 25.8, 25.4, 22.7, 17.9, 14.1, –4.2, –4.6; FT-IR (film) 3496, 2983, 2951, 2926, 2854, 1463, 1377, 1367, 1255, 1216, 1158, 1072, 967, 837, 777 cm^{-1}. ESI-MS m/z 521.6 ([M+Na]$^+$); EI-HRMS calcd for $C_{28}H_{55}O_4Si$ ([M–CH_3]$^+$) 483.3870, found 483.3876.

(*R*,*E*)-3-(*tert*-Butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)octadec-5-en-1-one (11). To a solution of **7a** (10 mg, 0.020 mmol) in dry CH_2Cl_2 (1 mL) were added $NaHCO_3$ (8 mg, 0.10 mmol) and Dess–Martin periodinane (17 mg, 0.040 mmol). The mixture was stirred at ambient temperature until TLC showed complete of the reaction (*ca.* 2 h). Aqueous saturated $Na_2S_2O_3$ was added. The mixture was extracted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and chromatography (10 : 1 PE/EtOAc) on silica gel afforded ketone **11** (9 mg, 0.018 mmol, 90%) as a colorless oil. $[\alpha]_D^{27}$ –0.8 (*c* 0.6 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (dt, J = 15.2, 7.0 Hz, 1H), 5.35 (dt, J = 15.3, 7.0 Hz, 1H), 4.40 (dd, J = 6.0, 1.7 Hz, 1H), 4.30–4.21 (m, 1H), 4.17 (t, J = 8.1 Hz, 1H), 3.97 (dd, J = 5.8, 2.8 Hz, 1H), 2.74 (dd, J = 16.6, 7.5 Hz, 1H), 2.62 (dd, J = 16.7, 4.6 Hz, 1H), 2.27–2.11 (m, 2H), 2.07–1.90 (m, 2H), 1.50 (s, 3H), 1.39 (s, 3H), 1.30–1.20 (m, 20H), 0.88 (t, J = 6.5 Hz, 3H), 0.87–0.82 (m, 9H), 0.07 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 134.0, 125.3, 111.0, 80.7, 76.7, 68.1, 66.0, 45.4, 41.1, 32.7, 31.9, 31.4, 30.2, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 25.8, 25.1, 22.7, 18.0, 14.1, –4.6, –4.8. FT-IR (film) 2959, 2926, 2855, 1716, 1464, 1374, 1254, 1080, 970, 837, 777 cm^{-1}. ESI-MS m/z 519.5 ([M+Na]$^+$); ESI-HRMS calcd for $C_{29}H_{56}O_4SiNa$ ([M+Na]$^+$) 519.3840, found 519.3860.

(2*R*,3*S*,5*R*,*E*)-3-(*tert*-Butyldimethylsilyloxy)icos-7-ene-1,2,5-triol (12). Aqueous CF_3CO_2H (50%, 0.3 mL) was added to a solution of **7a** (104 mg, 0.209 mmol) in CH_2Cl_2 (7 mL) stirred at ambient temperature. The stirring was continued for 2 h, when TLC showed completion of the reaction. The mixture was diluted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue, which was chromatographed (1 : 30 MeOH/CH_2Cl_2) on silica gel to give the triol **12** (42 mg, 0.092 mmol, 73%) as a colorless oil: $[\alpha]_D^{27}$ –0.8 (*c* 1.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (dt, J = 15.2, 7.4 Hz, 1H), 5.31 (dt, J = 15.1, 7.1 Hz, 1H), 4.12–3.86 (m, 1H), 3.83–3.75 (m, 1H), 3.75–3.60 (m, 3H), 2.90 (s, 3H), 2.23–2.09 (m, 2H), 2.00 (dd, J = 13.6, 6.5 Hz, 2H), 1.75(dd, J = 5.8, 4.4 Hz, 1H), 1.57 (ddd, J = 14.5, 9.9, 4.9 Hz, 1H), 1.46–1.18 (m, 20H), 0.99–0.79 (m, 12H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 125.3, 74.6, 72.3, 68.2, 63.5, 41.5, 40.6, 32.6, 31.9, 29.7, 29.61, 29.59, 29.5, 29.4, 29.3, 29.2, 25.8, 22.6, 17.9, 14.1, –4.6, –4.7; FT-IR (film) 3365, 2954, 2925, 2854, 1463, 1253, 1082, 970, 837, 777 cm^{-1}. ESI-MS m/z 481.9 ([M+Na]$^+$); ESI-HRMS calcd for $C_{26}H_{54}O_4SiNa$ 481.3684, found 481.3685.

(2*S*,4*R*,*E*)-2-(*tert*-Butyldimethylsilyloxy)nonadec-6-ene-1,4-diol (13) and (2*S*,4*R*,*E*)-1-(*tert*-butyldimethylsilyloxy)-nonadec-6-ene-2,4-diol (13′). To a solution of $NaIO_4$ (36 mg, 0.168 mmol) in water (0.6 mL) was added silica gel (300–400 mesh), followed by CH_2Cl_2 (3.5 mL). The mixture was stirred at ambient temperature for 1 h. A solution of triol **12** (34 mg, 0.074 mmol) in CH_2Cl_2 (3.5 mL) was added. The mixture was stirred at ambient temperature for 1.5 h and then filtered through Celite. The two-phase filtrate was transferred to a separatory funnel and the phases were separated. The organic layer was washed with water and brine before being dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue (the intermediate aldehyde), which was dissolved in MeOH (2 mL). To this solution (cooled in a 0 °C bath) was added $NaBH_4$ (4 mg, 0.090 mmol). The bath was allowed to warm to ambient temperature until TLC showed completion of the reaction (*ca.* 1.5 h). Et_2O was added, followed by aqueous saturated NH_4Cl. The phases were separated. The organic layer was washed with water and brine before being dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation and the oily residue was chromatographed (3 : 1 PE/EtOAc) on silica gel to afford alcohol **13** (the less polar component, 20 mg, 0.046 mmol, 62% from **12**) as a colorless oil and **13′** (the more polar component, 12 mg, 0.028 mmol, 38%) as a white wax.

Data for **13** (the less polar component, a colorless oil): $[\alpha]_D^{23}$ –3.0 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dt, J = 14.5, 7.1 Hz, 1H), 5.39 (dt, J = 14.9, 7.4 Hz, 1H), 4.03–3.85 (m, 2H), 3.62 (dd, J = 10.2, 4.0 Hz, 1H), 3.47 (dd, J = 9.7, 7.6 Hz, 1H), 2.63 (br s, 2H), 2.27–2.11 (m, 2H), 2.00 (dd, J = 13.9, 6.8 Hz, 2H), 1.61 (ddd, J = 14.4, 8.5, 2.9 Hz, 1H), 1.51 (ddd, J = 14.3, 8.8, 3.6 Hz, 1H), 1.42–1.17 (m, 20H), 0.99–0.82 (m, 12H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.7, 125.6, 69.4, 68.2, 67.2, 41.0, 38.4, 32.6, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.8, 22.7, 18.3, 14.1, –5.38, –5.43; FT-IR (film) 3385, 2956, 2925, 2854, 1463, 1255, 1121, 1084, 970, 837, 778 cm^{-1}. ESI-MS m/z 451.4 ([M+Na]$^+$); ESI-HRMS calcd for $C_{25}H_{52}O_3NaSi$ 451.3578; found: 451.3601.

Data for **13′** (the more polar component, a white wax): $[\alpha]_D^{23}$ –3.7 (*c* 0.6 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dt, J = 14.6, 7.1 Hz, 1H), 5.39 (dt, J = 15.0, 7.4 Hz, 1H), 4.00 (dt, J = 10.3, 5.0 Hz, 1H), 3.83–3.73 (m, 1H), 3.62 (dd, J = 11.2, 4.7 Hz, 1H), 3.56 (dd, J = 11.0, 4.5 Hz, 1H), 2.25–2.07 (m, 3H), 2.01 (dd, J = 13.7, 6.8 Hz, 2H), 1.74 (ddd, J = 14.4, 6.5, 1.8 Hz, 1H), 1.56 (ddd, J = 14.7, 10.1, 4.7 Hz, 1H), 1.42–1.18 (m, 20H), 0.96–0.82 (m, 12H), 0.113 (s, 3H), 0.102 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 125.4, 71.1, 67.9, 66.8, 41.5, 40.8, 32.7, 31.9, 29.7, 29.6, 29.5, 29.44, 29.35, 29.2, 25.8, 22.7, 18.0, 14.1, –4.6, –4.8; FT-IR (film) 3346, 2956, 2956, 2925, 2854, 1464, 1255, 1084, 969, 836, 777 cm^{-1}. ESI-MS m/z 451.4 ([M+Na]$^+$); ESI-HRMS calcd for $C_{25}H_{52}O_3NaSi$ 451.3578, found 451.3594.

(2*S*,4*R*,*E*)-Nonadec-6-ene-1,2,4-triol ((2*S*,4*R*)-1). A solution of *n*-Bu_4NF (1 M, in THF, 50 µL) was added to a solution of **13** (20 mg, 0.047 mmol) in THF (2 mL). The resultant yellowish mixture was stirred at ambient temperature for 2 h before being concentrated on a rotary evaporator and chromatographed (1 : 15 MeOH/CH_2Cl_2) on silica gel to afford end triol (2*S*,4*R*)-**1** as a colorless oil (13 mg, 0.041 mmol, 88%): $[\alpha]_D^{22}$ –8.9 (*c* 0.25 $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 5.57–5.39 (m, 2H), 4.94 (s, 3H),

3.91–3.76 (m, 2H), 3.52–3.38 (m, 2H), 2.27–2.10 (m, 2H), 2.08–1.96 (m, 2H), 1.54–1.44 (td, J = 9.3, 3.3 Hz, 2H), 1.43–1.23 (m, 20H), 0.90 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 134.4, 127.6, 70.4, 69.4, 68.1, 42.7, 41.3, 33.9, 33.2, 31.0, 30.9, 30.8, 30.6, 30.5, 23.9, 14.6; FT-IR (film) 3302, 2954, 2916, 2849, 1469, 1379, 1061, 1023, 962, 698, 669, 647 cm^{-1}. ESI-MS m/z 337.3 ([M+Na]$^+$); EI-HRMS calcd for $C_{19}H_{38}O_3$ 314.2821, found 314.2828.

(1*S*,3*S*)-1-(*tert*-Butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)octadec-5-yn-3-ol (9). The procedure was the same as described above for the reaction of **5** with 10 leading to **8**, except that epoxide **6** (200 mg, 0.662 mmol) was employed to replace **5**, giving **9** (291 mg, 0.587 mmol, 88%, chromatographed with 15 : 1 PE/EtOAc) as a colorless oil. $[\alpha]_D^{27}$ +20.2 (c 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09 (dd, J = 6.5 6.3 Hz, 1H), 4.06–4.00 (m, 1H), 3.96 (s, 1H), 3.89 (dd, J = 5.9 5.4 Hz, 1H), 3.79 (d, J = 7.3 Hz, 1H), 2.68 (s, 1H), 2.41–2.28 (m, 2H), 2.19–2.08 (m, 2H), 1.89–1.73 (m, 2H),1.52–1.42 (m, 2H), 1.40 (s, 3H), 1.33 (s, 3H),1.37–1.19 (m, 18H), 0.91–0.83 (m, 12H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.1, 82.8, 78.5, 76.0, 70.7, 66.9, 66.8, 41.2, 31.8, 29.6, 29.5, 29.4, 29.3, 29.1, 28.9, 28.8, 28.0, 26.4, 25.7, 25.2, 22.6, 18.7, 17.8, 14.0, –4.3, –4.7; FT-IR (film) 3476, 2953, 2927, 2855, 1463, 1370, 1255, 1214, 1074, 837, 776 cm^{-1}. ESI-MS m/z 519.4 ([M+Na]$^+$); EI-HRMS calcd for $C_{28}H_{53}O_4Si$ ([M-CH_3]$^+$) 481.3713, found 481.3711.

(1*S*,3*S*,*E*)-1-(*tert*-Butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)octadec-5-en-3-ol (14) and (1*S*,3*S*,*E*)-3-(*tert*-butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4- yl)-octadec-5-en-1-ol (14′). The procedure was the same as described above for the reduction of **8** leading to **7a** and **7a′**, except that **9** (102 mg, 0.205 mmol) was employed to replace **8**, giving **14′** (the less polar component, 33 mg, 0.066 mmol, 32%) and **14** (the more polar component, 55 mg, 0.110 mmol, 54%) as colorless oils (with column chromatography eluting with 30 : 1 PE/EtOAc).

Data for **14′** (the less polar component): $[\alpha]_D^{25}$ +17.7 (c 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (dt, J = 14.4, 7.0 Hz, 1H), 5.36 (dt, J = 14.6, 7.1 Hz, 1H), 4.10–4.00 (m, 1H), 4.00–3.87 (m, 3H), 3.80–3.67 (m, 1H), 3.30 (s, 1H), 2.22 (t, J = 5.9 Hz, 2H), 1.98 (dd, J = 13.1, 6.4 Hz, 2H), 1.82 (ddd, J = 14.5 3.8 2.1 Hz, 1H), 1.55–1.44 (m, 1H), 1.40 (s, 3H), 1.34 (s, 3H), 1.38–1.19 (m, 20H), 0.93–0.82 (m, 12H), 0.112 (s, 3H), 0.107 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 124.9, 109.1, 78.6, 73.1, 71.7, 66.2, 41.2, 38.8, 32.7, 31.9, 29.7, 29.64, 29.61, 29.5, 29.4, 29.3, 29.2, 26.6, 25.8, 25.3, 22.7, 17.9, 14.1, –4.0, –4.7; FT-IR (film) 3523, 2955, 2926, 2855, 1463, 1370, 1257, 1215, 1066, 971, 837, 775 cm^{-1}. ESI-MS m/z 521.5 ([M+Na]$^+$); ESI-HRMS calcd for $C_{29}H_{58}NaO_4Si$ 521.3997, found 521.4016.

Data for **14** (the more polar component): $[\alpha]_D^{25}$ +13.9 (c 1.375, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dt, J = 14.4, 7.0 Hz, 1H), 5.39 (dt, J = 14.7, 7.3 Hz, 1H), 4.10 (dd, J = 12.8, 6.5 Hz, 1H), 4.06–3.99 (m, 1H), 3.93–3.83 (m, 2H), 3.78 (t, J = 7.3 Hz, 1H), 2.47 (s, 1H), 2.28–2.08 (m, 2H), 2.00 (dd, J = 13.7 6.6 Hz, 2H), 1.78–1.60 (m, 2H), 1.40 (s, 3H), 1.34 (s, 3H), 1.38–1.19 (m, 20H), 0.94–0.80 (m, 12H), 0.08 (s, 3H), 0.075 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 125.7, 109.2, 78.6, 71.1, 67.5, 67.1, 41.8, 41.2, 32.7, 31.9, 29.7, 29.6, 29.50, 29.46, 29.3, 29.2, 26.6, 25.8, 25.3, 22.7, 17.9, 14.1, –4.2, –4.6; FT-IR (film) 3489, 2926, 2854, 1463, 1370, 1254, 1213, 1073, 970, 837, 776 cm^{-1}. ESI-MS m/z 449.4 ([M–C_4H_9–CH_3+Na]$^+$); ESI-HRMS calcd for $C_{29}H_{58}NaO_4Si$ 521.3997, found 521.4015.

(2*R*,3*S*,5*S*,*E*)-3-(*tert*-Butyldimethylsilyloxy)icos-7-ene-1,2,5-triol (16). The procedure was the same as described above for the cleavage of acetonide in **7a** leading to **12**, except that **14** (55 mg, 0.110 mmol) was employed to replace **7a**, giving **16** (42 mg, 0.092 mmol, 73%, chromatographed with 1 : 30 $MeOH/CH_2Cl_2$). $[\alpha]_D^{26}$ +15.9 (c 1.7, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dt, J = 14.5, 7.1 Hz, 1H), 5.36 (dt, J = 14.7, 7.4 Hz, 1H), 3.92 (dd, J = 13.9, 7.2 Hz, 1H), 3.86 (dd, J = 9.4, 5.0 Hz, 1H), 3.78–3.68 (m, 2H), 3.59 (dd, J = 12.0, 7.6 Hz, 1H), 3.04 (s, 3H), 2.21–2.10 (m, 2H), 2.00 (dd, J = 13.7, 6.7 Hz, 2H), 1.84–1.74 (m, 1H), 1.64 (dd, J = 4.0, 3.8 Hz, 1H), 1.51–1.15 (m, 20H), 0.99–0.77 (m, 12H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 125.3, 73.9, 71.0 66.4, 63.8, 41.6, 39.6, 32.7, 31.9, 29.64, 29.62, 29.59, 29.5, 29.4, 29.3, 29.2, 25.7, 22.7, 17.9, 14.1, –4.5, –4.9. ESI-MS m/z 481.4 ([M+Na]$^+$); ESI-HRMS calcd for $C_{26}H_{54}NaO_4Si$ 481.3684, found 481.3695.

(2*S*,4*S*,*E*)-2-(*tert*-Butyldimethylsilyloxy)nonadec-6-ene-1,4-diol (17) and (2*S*,4*S*,*E*)-1-(*tert*-butyldimethylsilyloxy)nonadec-6-ene-2,4-diol (17′). The procedure was the same as described above for the conversion of **12** leading to **13** and **13′**, except that **16** (34 mg, 0.074 mmol) was employed to replace **12**, giving **17** (the less polar component, 26 mg, 0.061 mmol, 77%) and **17′** (the more polar component, 6 mg, 0.014 mmol, 19%) as colorless oils (with column chromatography eluting with 3 : 1 PE/EtOAc).

Data for **17** (the less polar component): $[\alpha]_D^{24}$ +1.7 (c 0.75, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (dt, J = 14.5, 7.1 Hz, 1H), 5.40 (dt, J = 14.8, 7.3 Hz, 1H), 3.92–3.80 (m, 2H), 3.57 (dd, J = 10.2, 4.3 Hz, 1H), 3.47 (dd, J = 10.0, 6.8 Hz, 1H), 2.96 (S, 2H), 2.18 (t, J = 6.4 Hz, 2H), 2.00 (dd, J = 13.6, 6.7 Hz, 2H), 1.62 (dt, J = 14.3, 2.4 Hz, 1H), 1.51–1.40 (m, 1H), 1.39–1.19 (m, 20H), 0.96–0.82 (m, 12H), 0.12–0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4, 125.5, 72.6, 71.4, 67.1, 41.0, 38.4, 32.7, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 25.9, 22.7, 18.3, 14.1, –5.39, –5.42; FT-IR (film) 3366, 2953, 2925, 2854, 1463, 1254, 1122, 970, 837, 777 cm^{-1}. ESI-MS m/z 451.4 ([M+Na]$^+$); ESI-HRMS calcd for $C_{25}H_{52}O_3SiNa$ ([M+Na]$^+$) 451.3583, found 451.3560.

Data for **17′** (the more polar component): $[\alpha]_D^{26}$ +2.8 (c 0.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ5.53 (dt, J = 15.2, 7.0 Hz, 1H), 5.39 (dt, J = 14.4, 7.0 Hz, 1H), 4.06–3.97 (m, 1H), 3.84–3.75 (m, 1H), 3.64 (dd, J = 11.3, 4.8 Hz, 1H), 3.56 (dd, J = 11.3, 4.8 Hz, 1H), 2.24–2.09 (m, 2H), 2.06–1.96 (m, 2H), 1.96–1.78 (m, 2H), 1.74 (ddd, J = 14.7, 6.3, 2.6 Hz, 1H), 1.65 (ddd, J = 14.3, 9.0, 5.2 Hz, 1H), 1.44–1.16 (m, 20H), 0.97–0.80 (m, 12H), 0.18–0.05 (m, 6H); FT-IR (film) 3363, 2956, 2925, 2854, 1464, 1255, 1096, 1046, 970, 836, 777, 668 cm^{-1}. ESI-MS m/z 451.4 ([M+Na]$^+$); ESI-HRMS calcd for $C_{25}H_{52}O_3SiNa$ ([M+Na]$^+$) 451.3583, found 451.3560.

(2*S*,4*S*,*E*)-Nonadec-6-ene-1,2,4-triol ((2*S*,4*S*)-1). The procedure was the same as described above for removal of the TBS protecting group in **13** leading to (2*S*,4*R*)-**1**, except that **17** (36 mg, 0.084 mmol) was employed to replace **13**, giving (2*S*,4*S*)-**1** (21 mg, 0.064 mmol, 80%, chromatographed with 1 : 15 $MeOH/CH_2Cl_2$) as a white wax. $[\alpha]_D^{22}$ +4.4 (c 0.35 $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 5.53–5.42 (m, 2H), 4.87 (s, 3H), 3.81–3.76 (m, 2H), 3.49 (dd, J = 11.4, 4.5 Hz, 1H), 3.44 (dd, J = 11.2, 6.0 Hz, 1H), 2.26–2.17 (m, 2H), 2.07–1.99 (m, 2H), 1.68 (dt, J = 14.0, 4.5 Hz,

1H), 1.50 (dt, J = 14.0, 8.5 Hz, 1H), 1.42–1.21 (m, 20H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 134.4, 127.2, 72.1, 71.2, 67.2, 41.8, 40.5, 33.8, 33.1, 30.79 (*ca.* 1.5 times as intense as other signals), 30.76 (*ca.* twice as intense as other signals), 30.6 (*ca.* 1.2 times as intense as other signals), 30.4, 30.3, 23.7, 14.4; FT-IR (film) 3367, 2955, 2924, 2853, 1464, 1377, 1019, 968, 680, 669, 650 cm^{-1}. ESI-MS m/z 337.2 ([M+Na]$^+$); ESI-HRMS calcd for $C_{19}H_{38}O_3$ 314.2821, found 314.2818.

(*S*,*E*)-3-(*tert*-Butyldimethylsilyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)octadec-5-en-1-one (15). The procedure was the same as described above for oxidation of **7a** into ketone **11**, except that **14′** (11 mg, 0.022 mmol) was employed to replace **7a**, giving **15** (11 mg, 0.022 mmol, 100%, chromatographed with 30 : 1 PE/Et_2O) as a colorless oil. $[\alpha]_D^{25}$ +37.7 (*c* 0.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (dt, J = 15.3, 6.3 Hz, 1H), 5.36 (dt, J = 15.3, 6.7 Hz, 1H), 4.40 (dd, J = 7.7, 5.7 Hz, 1H), 4.24 (dt, J = 11.4, 5.9 Hz, 1H), 4.16 (t, J = 8.2 Hz, 1H), 4.01 (dd, J = 8.5, 5.4 Hz, 1H), 2.79 (dd, J = 17.0, 7.0 Hz, 1H), 2.59 (dd, J = 16.7, 5.3 Hz, 1H), 2.17 (t, J = 6.2 Hz, 2H), 1.97 (dd, J = 13.3, 6.4 Hz, 2H), 1.46 (s, 3H), 1.39 (s, 3H), 1.36–1.17 (m, 20H), 0.94–0.78 (m, 12H), 0.06 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.8, 134.0, 125.3, 110.9, 80.8, 68.2, 66.0, 45.8, 40.9, 32.7, 31.9, 29.7, 29.64, 29.62, 29.5, 29.43, 29.36, 29.2, 26.0, 25.8, 25.1, 22.7, 18.0, 14.1, –4.6, –4.8; FT-IR (film) 2926, 2854, 1720, 1463, 1373, 1255, 1214, 1077, 970, 836, 776 cm^{-1}. ESI-MS m/z 519.5 ([M+Na]$^+$); ESI-HRMS calcd for $C_{29}H_{56}O_4SiNa$ ([M+Na]$^+$) 519.3840, found 519.3860.

(1*S*,3*R*)-4-(Benzyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-butane-1,3-diol (18). A solution of BnOH (1.2 mL) in dry THF (10 mL) was added to a solution of NaH (60% Suspension in mineral oil, 262 mg, 6.55 mmol) in dry DMSO (10 mL) stirred at ambient temperature. The mixture was stirred for 20 min. A solution of **6** (1.10 g, 3.640 mmol) in dry THF (10 mL) was introduced. The stirring was continued at the same temperature until TLC showed complete disappearance of the starting epoxide (*ca.* 24 h). Aqueous saturated NH_4Cl was added. The mixture was extracted with EtOAc twice. The combined organic layers were washed with water and brine before being dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue, which was chromatographed (2 : 1 PE/EtOAc) on silica gel to afford **18** as a colorless oil (840 mg, 2.84 mmol, 78%). $[\alpha]_D^{26}$ +5.1 (*c* 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 7.50–7.20 (m, 5H), 4.55 (dd, J = 15.5, 12.2 Hz, 2H), 4.09–4.00 (m, 2H), 3.95–3.83 (m, 2H), 3.76–3.67 (m, 1H), 3.52–3.43 (m, 2H), 1.90 (ddd, J = 14.4, 5.8, 3.6 Hz, 1H), 1.58–1.48 (m, 1H), 1.37 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 139.7, 129.4, 128.9, 128.7, 110.4, 80.3, 75.2, 74.3, 71.7, 70.1, 67.4, 38.3, 26.9, 25.5; FT-IR (film) 3442, 2987, 2870, 1454, 1371, 1256, 1212, 1128, 1066, 852, 740, 699 cm^{-1}. ESI-MS m/z 319.0 ([M+Na]$^+$); EI-HRMS calcd for $C_{16}H_{24}O_5Na$ ([M+Na]$^+$) 319.1516, found 319.1521.

(1*S*,3*R*)-4-(Benzyloxy)-1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)-butane-1,3-diyl diacetate (19). To a solution of **18** (340 mg, 1.15 mmol) in CH_2Cl_2 (8 mL) were added in turn DMAP (14 mg, 0.115 mmol) and pyridine (0.37 mL, 4.59 mmol) and Ac_2O (0.48 mL, 5.048 mmol). The mixture was stirred at ambient temperature until TLC showed disappearance of the starting diol (*ca.* 1.5 h). The mixture was diluted with CH_2Cl_2, washed with aqueous saturated $NaHCO_3$ and aqueous saturated $CuSO_4$, water and brine, and dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue, which was chromatographed (3 : 1 PE/EtOAc) on silica gel to give diacetate **19** (404 mg, 1.06 mmol, 93%) as a colorless oil. $[\alpha]_D^{26}$ –4.5 (*c* 0.85, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 5.11–5.04 (m, 1H), 5.04–4.97 (m, 1H), 4.51 (dd, J = 23.1, 12.0 Hz, 2H), 4.10 (dd, J = 12.0, 6.1 Hz, 1H), 3.99 (dd, J = 8.3, 6.9 Hz, 1H), 3.73 (dd, J = 8.2, 6.3 Hz, 1H), 3.54 (ddd, J = 19.3, 10.8, 4.7 Hz, 2H), 2.12–1.99 (m, 7H), 1.89 (ddd, J = 15.0, 8.8, 6.6 Hz, 1H), 1.37 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.20, 170.18, 137.8, 128.3, 127.6, 127.5, 109.7, 76.6, 73.1, 70.6, 70.2, 69.9, 65.8, 31.6, 26.2, 25.0, 21.1, 20.9; FT-IR (film) 2987, 2936, 2881, 1740, 1454, 1372, 1235, 1062, 1027, 849, 740, 699, 605, 513 cm^{-1}. ESI-MS m/z 403.2 ([M+Na]$^+$); EI-HRMS calcd for $C_{20}H_{28}O_7$ Na ([M+Na]$^+$) 403.1727, found 403.1734.

(2*S*,3*S*,5*R*)-6-(Benzyloxy)-3,5-diacetoxy-hexane-1,2-diol (20). To a solution of **19** (250 mg, 0.657 mmol) in CH_2Cl_2 (33 mL) were added $Er(OTf)_2$ (162 mg, 0.263 mmol) and BnOH (2 mL). The mixture was stirred at ambient temperature until TLC showed disappearance of the starting aceonide (*ca.* 12 h). The mixture was concentrated on a rotary evaporator. The residue was chromatographed (1 : 4 PE/EtOAc) on silica gel to give diol **20** (185 mg, 0.544 mmol, 83%) as a colorless sticky oil. $[\alpha]_D^{25}$ +5.3 (*c* 1.70, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 7.45–7.23 (m, 5H), 5.15–5.07 (m, 1H), 5.03–4.96 (m, 1H), 4.52 (dd, J = 20.9, 12.0 Hz, 2H), 3.68 (dd, J = 11.1, 4.9 Hz, 1H), 3.55 (dd, J = 9.9, 4.8 Hz, 3H), 3.48 (dd, J = 11.6, 6.8 Hz, 1H), 2.14–1.99 (m, 7H), 1.92 (ddd, J = 15.2, 9.1, 6.6 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 172.4, 172.3, 139.4, 129.4, 128.8, 128.7, 74.2, 74.1 73.2, 72.0, 71.9, 63.8, 32.2, 21.2, 21.1; FT-IR (film) 3453, 2930, 1736, 1454, 1373, 1243, 1052, 1028, 741, 670, 607 cm^{-1}. ESI-MS m/z 363.1 ([M+Na]$^+$); EI-HRMS calcd for $C_{17}H_{24}O_7Na$ ([M+Na]$^+$) 363.1418, found 363.1414.

(2*S*,4*R*)-5-(Benzyloxy)pentane-1,2,4-triol (21). To a solution of $NaIO_4$ (433 mg, 2.02 mmol) in water (3 mL) was added silica gel (300–400 mesh, 4.3 g), followed by CH_2Cl_2 (20 mL). The mixture was stirred at ambient temperature for *ca.* 30 min. Diol **20** (172 mg, 0.505 mmol) was added. The stirring was continued at ambient temperature until TLC showed complete disappearance of the starting diol (*ca.* 2.5 h). Solids were filtered off. The two phases of the filtrate were separated. The organic layer was washed with water and brine before being dried over anhydrous $MgSO_4$. Removal of the drying agent by filtration and the solvent by rotary evaporation afforded the crude aldehyde), which gave the following data: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 5H), 7.41–7.22 (m, 5H), 5.22–5.10 (m, 2H), 4.54 (dd, J = 28.3, 12.1 Hz, 2H), 4.12 (dd, J = 14.4, 6.9 Hz, 1H), 3.55 (d, J = 4.4 Hz, 2H), 2.30–2.23 (m, 2H), 2.16 (s, 3H), 2.02 (s, 3H); FT-IR (film) 2960, 2924, 2854, 1738, 1454, 1372, 1259, 1234, 1093, 1021, 780, 699 cm^{-1}.

The above obtained crude aldehyde was dissolved in dry THF (3 mL) and chilled to –30 °C. $LiALH_4$ (77 mg, 2.021 mmol) was added in one portion. The bath was then allowed to warm to ambient temperature while the stirring was continued until TLC showed complete of the reaction (*ca.* 12 h). The mixture was diluted with EtOAc before MeOH (1 mL) and aqueous satrated potassium sodium tartrate (1 mL) were carefully added. The mixture was extracted with EtOAc, washed with water and brine, and dried over anhydrous $MgSO_4$. Removal of the drying

agent by filtration and the solvent by rotary evaporation left a crude oil, which was chromatographed (1 : 15 MeOH/CH_2Cl_2) on silica gel to afford triol **21** (41 mg, 0.359 mmol, 36% from diol **20**) as a colorless sticky oil. $[\alpha]_D^{25}$ +1.6 (*c* 1.50, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 7.44–7.22 (m, 5H), 4.61–4.49 (m, 2H), 4.04–3.94 (m, 1H), 3.85–3.76 (m, 1H), 3.54–3.41 (m, 4H), 1.75 (dt, J = 14.1, 4.7 Hz, 1H), 1.57 (dt, J = 16.2, 8.3 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 139.7, 129.3, 128.9, 128.6, 75.5, 74.3, 71.5, 69.8, 67.2, 37.9; FT-IR (film) 3389, 2924, 2852, 1454, 1364, 1096, 738, 698 cm^{-1}. ESI-MS m/z 249.1 ([M+Na]$^+$); ESI-HRMS calcd for $C_{12}H_{18}O_4Na$ ([M+Na]$^+$) 249.1097, found 249.1096.

(*R*)-1-(Benzyloxy)-3-((*S*)-oxiran-2-yl)propan-2-ol (22). A mixture of trio **21** (55 mg, 0.243 mmol), *n*-Bu_2SnO (7 mg, 0.0243 mmol), DMAP (3 mg, 0.0243 mmol) and Et_3N (51 μL, 0.365 mmol) in MeCN (4 mL) was stirred at ambient temperature for 20 min. *p*-TsCl (70 mg, 0.3648 mmol) was introduced. The mixture was stirred at the same temperature until TLC showed complete disappearance of the starting triol (*ca.* 1 h). E_2O was added and the stirring was continued. The white solids were filtered off through Celite. The filtrate was concentrated on a rotary evaporator to give a yellowish sticky oil, which was directly dissolved in MeOH (2 mL). To this solution (cooled in a ice-water bath) was added powdered K_2CO_3 (50 mg, 0.365 mmol). The mixture was stirred at ambient temperature until TLC showed complete disappearance of the tosylate (*ca.* 2.5 h). The excess base was carefully neutralized before being concentrated by rotary evaporation. The crude oil was chromatographed (2 : 1 PE/EtOAc) on silica gel to give epoxide **22** (35 mg, 0.168 mmol, 69%) as a colorless oil. $[\alpha]_D^{26}$ −10.2 (*c* 1.60, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.27 (m, 5H), 4.56 (s, 2H), 4.10–3.98 (m, 1H), 3.49 (ddd, J = 22.0, 9.4, 3.7 Hz, 2H), 3.15–3.05 (m, 1H), 2.76 (t, J = 4.5 Hz, 1H), 2.70 (s, 1H), 2.50 (dd, J = 4.9, 2.7 Hz, 1H), 1.82 (dt, J = 14.5, 4.6 Hz, 1H), 1.66 (dt, J = 14.4, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.4, 127.8, 127.7, 73.9, 73.3, 68.5, 49.6, 46.6, 35.9; FT-IR (film) 3348, 2924, 2856, 1496, 1454, 1364, 1096, 827, 740, 699 cm^{-1}. ESI-MS m/z 209.1 ([M+H]$^+$); ESI-HRMS calcd for $C_{12}H_{17}O_3$ ([M+H]$^+$) 209.1172, found 209.1176.

(2*R*,4*R*)-1-(Benzyloxy)nonadec-6-yne-2,4-diol (23). *n*-BuLi (1.6 M, in hexanes, 0.4 mL, 0.656 mmol) was added to a solution of tetradec-1-yne **10** (0.17 mL, 0.673 mmol) in dry THF (3.4 mL) stirred at −78 °C under N_2 (balloon). The resulting suspension was stirred at the same temperature for 1 h. A solution of epoxide **22** (35 mg, 0.168 mmol) in dry THF (1 mL) was added, followed by $BF_3{\cdot}Et_2O$ (0.1 mL, 0.336 mmol). The mixture was stirred at −78 °C until TLC showed completion of the reaction (*ca.* 5.5 h). MeOH (2 mL) was added carefully. The bath was allowed to warm to ambient temperature. The mixture was extracted with EtOAc, washed with water and brine, and dried over anhydrous $MgSO_4$. Filtration and rotor evaporation left an oil, which was purified by column chromatography (3 : 1 PE/EtOAc) on silica gel to deliver the diol **23** (15 mg, 0.037 mmol, 52% from **22**) as a colorless oil. $[\alpha]_D^{26}$ −6.1 (*c* 0.75, $CHCl_3$). ^{1}H NMR (400 MHz, CD_3OD) δ 7.44–7.22 (m, 5H), 4.60–4.50 (m, 2H), 4.10–3.92 (m, 1H), 3.88–3.80 (m, 1H), 3.50–3.41 (m, 2H), 2.41–2.24 (m, 2H), 2.19–2.08 (m, 2H), 1.92 (dt, J = 14.1, 4.7 Hz, 1H), 1.60 (dt, J = 13.7, 8.6 Hz, 1H), 1.51–1.22 (m, 20H), 0.90 (t, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 139.7, 129.4, 128.8, 128.6, 83.1, 77.2, 75.5, 74.3, 70.1, 69.9, 40.4, 33.1, 30.80, 30.77, 30.72, 30.5, 30.3, 30.1, 30.0, 28.3, 23.7, 19.5, 14.4; FT-IR (film) 3419, 2925, 2854, 1455, 1099, 1025, 736, 698 cm^{-1}. ESI-MS m/z 425.4 ([M+Na]$^+$); ESI-HRMS calcd for $C_{26}H_{42}O_3Na$ ([M+Na]$^+$) 425.3026, found 425.3017.

(4*R*,6*R*)-4-(Benzyloxymethyl)-2,2-dimethyl-6-(pentadec-2-ynyl)-1,3-dioxane (24). A solution of diol **23** (23 mg, 0.057 mmol), CSA (2 mg, 0.009 mmol) and $Me_2C(OMe)_2$ (0.15 ml, 1.143 mmol) in dry CH_2Cl_2 (0.15 mL) was stirred at ambient temperature for 1.5 h. Et_3N (0.1 mL) was added. The mixture was concentrated on a rotary evaporator. The residue was chromatographed (15 : 1 PE/EtOAc) on silica gel to give acetonide **24** (18 mg, 0.051 mmol, 90%) as a colorless sticky oil. $[\alpha]_D^{28}$ −15.7 (*c* 0.90, $CHCl_3$); ^{1}H NMR (400 MHz, CD_3OD) δ 7.38–7.24 (m, 5H), 4.55 (s, 2H), 4.20–4.09 (m, 1H), 4.03–3.93 (m, 1H), 3.49 (dd, J = 10.1, 6.1 Hz, 1H), 3.42 (dd, J = 10.1, 4.3 Hz, 1H), 2.42–2.32 (m, 1H), 2.25–2.09 (m, 3H), 1.74 (dt, J = 12.9, 2.2 Hz, 1H), 1.45 (s, 3H), 1.35 (s, 3H), 1.50–1.24 (m, 21H), 0.90 (t, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 139.6, 129.4, 128.9, 128.7, 100.1, 83.1, 76.6, 74.8, 74.4, 69.9, 96.4, 33.8, 33.1, 30.79, 30.77, 30.75, 30.72, 30.5, 30.28, 30.26, 30.1, 29.8, 27.3, 23.7, 20.1, 19.4, 14.5; FT-IR (film) 2956, 2925, 1741, 1460, 1377, 1197, 1177, 1037, 790 cm^{-1}. ESI-MS m/z 465.5 ([M+Na]$^+$); ESI-HRMS calcd for $C_{29}H_{46}O_3Na$ 465.3348, found 465.3340.

((4*R*,6*R*)-2,2-Dimethyl-6-((*E*)-pentadec-2-enyl)-1,3-dioxan-4-yl)-methanol (25). Li cuts (*ca.* 0.3 g, 43 mmol) was added in portions to liquid NH_3 (*ca.* 20 mL, in a 50 mL round-bottom flask) stirred in a −78 °C bath. To the resultant dark blue mixture was added a solution of propargyl alcohol **24** (18 mg, 0.040 mmol) in THF (2 mL), followed by *t*-BuOH (3 mL). The mixture was stirred at the same temperature for 10 h, when the TLC showed disappearance of the starting **24**. Aqueous saturated NH_4Cl (10 mL) was added carefully. The bath was allowed to warm to ambient temperature slowly. The mixture was extracted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Filtration and rotary evaporation left an oily residue, which was chromatographed (8 : 1 PE/EtOAc) on silica gel to give the alcohol **25** (13 mg, 0.037 mmol, 90%) as a colorless oil. $[\alpha]_D^{27}$ −7.9 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (dt, J = 14.6, 6.3 Hz, 1H), 5.36 (dt, J = 14.8, 6.8 Hz, 1H), 3.99–3.95 (m, 1H), 3.86–3.84 (m, 3H), 3.61–3.56 (m, 1H), 3.52–3.48 (m, 3H), 2.29–2.24 (m, 1H), 2.11–2.06 (m, 1H), 2.01–1.96 (m, 1H), 1.46 (s, 3H), 1.41 (s, 3H), 1.36–1.18 (m, 22H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.7, 124.8, 98.7, 69.7, 68.6, 66.2, 39.7, 32.6, 31.9, 31.8, 30.0, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 22.7, 19.9, 14.1; FT-IR (film) 3462, 2992, 2924, 2854, 1466, 1438, 1379, 1200, 969, 870, 721 cm^{-1}. ESI-MS m/z 377.4 ([M+Na]$^+$); ESI-MS m/z 377.4 ([M+ Na]$^+$); ESI-HRMS calcd for $C_{22}H_{42}O_3Na$ ([M+Na]$^+$) 377.3026, found 377.3004.

(2*R*,4*R*,*E*)-Nonadec-6-ene-1,2,4-triol ((2*R*,4*R*)-1, Natural 1). A solution of **25** (11 mg, 0.031 mol), $HS(CH_2)_3SH$ (12 μL, 0.11 mmol) and $BF_3{\cdot}Et_2O$ (16 μL, 0.11 mmol) in dry CH_2Cl_2 (0.5 mL) was stirred at ambient temperature for 30 min, when TLC showed completion of the reaction. The mixture was concentrated on a rotary evaporator. The residue was chromatographed (20 : 1 CH_2Cl_2/MeOH) on silica gel to give (2*R*,4*R*)-**1** (8 mg, 0.025 mmol, 81%) as a white wax. $[\alpha]_D^{27}$ −8.0 (*c* 0.45, $CHCl_3$), (lit.[2] $[\alpha]_D^{24}$ −8.6 (*c* 0.25, $CHCl_3$)). ^{1}H NMR (400 MHz, CD_3OD) δ 5.52 (dt, J = 15.4,

6.8 Hz, 1H), 5.49 (dt, J = 15.3, 6.0 Hz, 1H), 3.86–3.81 (m, 2H), 3.55–3.45 (m, 2H), 2.22–2.19 (m, 2H), 2.07–2.02 (m, 2H), 1.71 (dt, J = 14.0, 4.4 Hz, 1H), 1.53 (dt, J = 14.3, 6.5 Hz, 1H), 1.38–1.30 (m, 20H), 0.93 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 134.4, 127.2, 72.1, 71.2, 67.3, 41.9, 40.5, 33.8, 33.1, 30.80 (*ca.* 1.8 times as intensive as other signals), 30.77 (*ca.* 2 times as intensive as other signals), 30.6 (*ca.* 1.2 times as intensive as other signals), 30.5, 30.3, 23.7, 14.4; FT-IR (KBr): 3339, 2917, 2850, 1467, 1331, 1113, 1023, 843, 717 cm^{-1}. ESI-MS m/z 337.3 ([M+Na]$^+$); ESI-HRMS calcd for $C_{19}H_{38}O_3Na$ 337.2713, found 337.2707.

Acknowledgements

This work was supported by the National Basic Research Program of China (the 973 Program, 2010CB833200), the National Natural Science Foundation of China (21032002, 20921091, 20672129, 20621062, 20772143), and the Chinese Academy of Sciences (KJCX2.YW.H08).

Notes and references

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