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Synthesis of hept-6-en-2,4,5-triols and hept-6-en-2,3,5-triols

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ABSTRACT

In a systematic effort to establish the relative as well as absolute configurations of two natural products isolated from *Asomycete Daldinia concentrica*, four independent (non-antipodal) diastereomers of hept-6-en-2,4,5-triol, the structure previously proposed for the natural products, were synthesized in enantiopure forms through a chiral-pool route and their optical rotation as well as NMR data were recorded. Although these four synthetic isomers cover all possible relative configurations the originally assigned triol may have, none of them gave spectroscopic data compatible with those reported for the natural products. Similar negative results were also obtained with a group of four non-antipodal diastereomers of hept-6-en-2,3,5-triol. The genuine structures of the natural products are therefore to be re-assigned.

1. Introduction

Two configurational isomers of the title triol were identified in 2004 as constituents in the culture broth of fungus *Ascomycete Daldinia concentrica*.[1] The planar structure (**1**) was assigned on the basis of extensive spectroscopic analyses, including DEPT, HMQC, HMBC, and COSY. However, the relative as well as absolute configurations remain unknown to date, giving a clear sign for the necessity for synthetic chemists to take a part in the structural investigation.

In a previous study we developed convenient routes to enantiomerically pure building blocks **2** and **3** using D-glucolactone as the starting material (Fig. 1).[2] These chiral building blocks contain well-defined 1,3-diol motifs and therefore may serve as excellent precursors to the triols **1**. More importantly, with two stereogenic centers of known absolute configuration at the C-2 and C-4 (of the target structures) derived from such chiral building blocks, the configuration of the remaining stereogenic center at the C-5 installed in the synthesis would be easily determined experimentally through, e.g., NOE (nuclear Overhauser effect) experiments. Hence, a direct comparison of the physical and spectroscopic data of the synthetic samples with those reported for the natural **1** would allow for a reliable assignment of the configurations of the title heptentriols. Based on such a line of reasoning, we conducted the work described below.

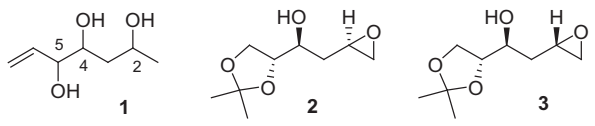

Fig. 1. The structure reported for the two natural triols (**1**) isolated from *Ascomycete D. concentrica* and the epoxy chiral building blocks (2 and 3) employed in this work.

2. Results and discussion

The structure **1** contains three stereogenic centers. Therefore, in principle there exist eight different enantiomers altogether. These enantiomers fall into two groups, with four different diastereomers in each and any member in one group being antipode to its counterpart in another group. Because antipodes have identical NMR spectra, either group of four different diastereomers should provide all the possibilities for the NMR of the target triols. As a consequence, we only need to synthesize the four different diastereomers from either group: if the planar structure of the two natural triols is indeed as shown by **1**, each of them would find its counterpart among the four synthetic isomers, which show the same NMR spectra and the optical rotation (of either the same or opposite sign).

With epoxide **2** as the starting material, triols **11** and **12** were first synthesized. As shown in Scheme 1, the hydroxyl group in **2** was protected as a TBS (*tert*-butyldimethylsilyl) ether **4** as reported[3] previously. The epoxy ring was then cleaved by treatment[4] with

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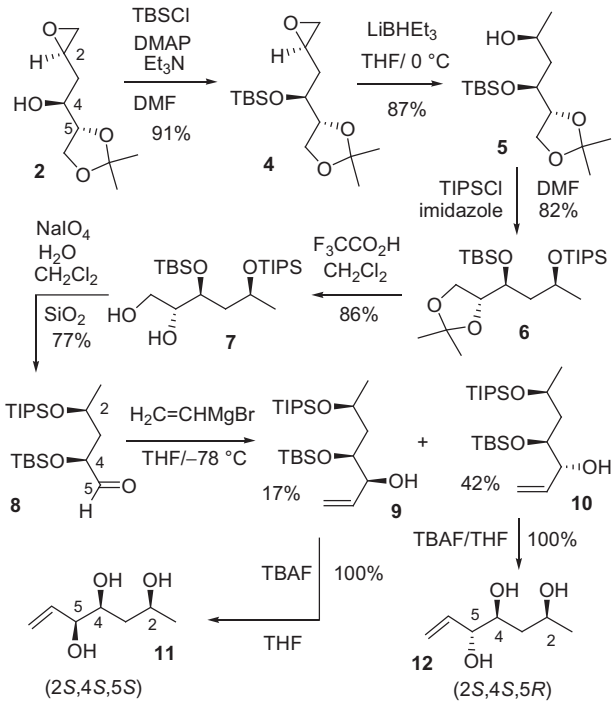
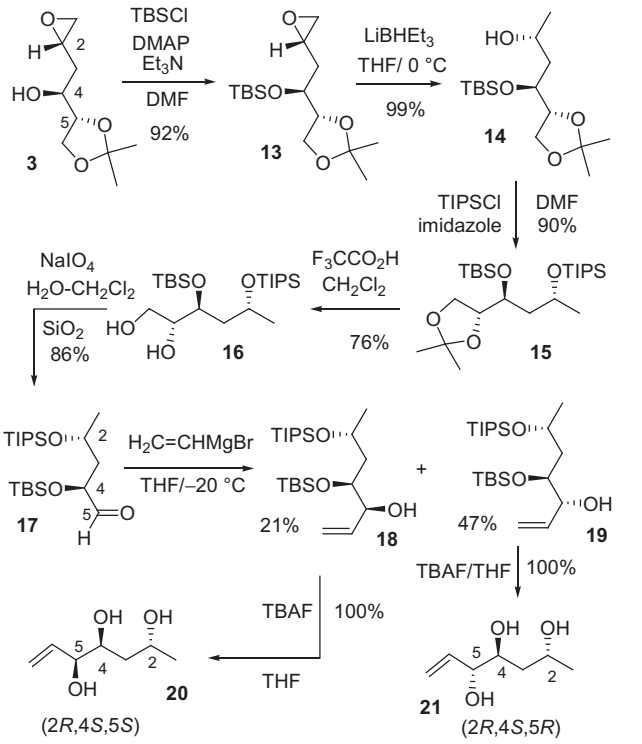


Scheme 1.



Scheme 2.

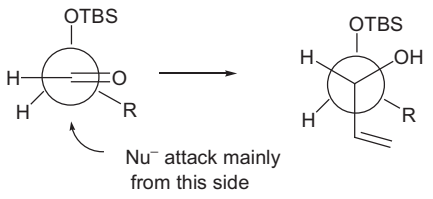


Fig. 2. According to the Felkin–Anh model, addition of the vinyl Grignard reagent would lead to anti alcohols **10** and **19** as the major products in the reaction of aldehydes **8** and **17**, respectively.

$LiBHEt_3$ (super-hydride) in THF at 0 °C to afford the alcohol **5**. The newly-formed hydroxyl group was converted into a TIPS (triisopropylsilyl) ether with TIPSCl/imidazole/DMF[5] to give compound **6**.

The acetonide was hydrolyzed using[6] 50% aq F_3CCO_2H in CH_2Cl_2. Subsequent treatment of the diol with $NaIO_4/SiO_2/H_2O-CH_2Cl_2$[7] led to aldehyde **8**, which on further exposure to vinyl Grignard reagent in THF at −78 °C delivered the corresponding allyl alcohols **9** and **10** in 17% and 42% yields, respectively. Desilylation of **9** and **10** with Bu_4NF (TBAF) provided the end products triols **11** and **12**, respectively.

Using a similar strategy but starting with epoxide **3** instead of **2**, another two triols (**20** and **21**) were obtained (Scheme 2). The addition of the vinyl Grignard reagent to aldehyde **8** or **17** all occurred with the anti alcohols (**10** and **19**) as the major product as predicted by the Felkin–Anh[8] model (Fig. 2).

The configurations at the C-5 in the above obtained four triols (i.e., **11**, **12**, **20**, and **21**) were determined by NOE experiments on the corresponding cyclic carbonates prepared from the Grignard reaction products (**9**, **10**, **18**, and **19**, respectively) as shown in Scheme 3.

The hydroxyl group in the allyl alcohols **9** and **10** were acylated (separately) with ethyl chloroformate in the presence of pyridine to afford **22** and **24**, respectively. The silyl protecting groups were then cleaved with TBAF. The newly-formed C-4 OH groups then attacked the carbonate carbonyl group, giving the corresponding cyclic carbonates **23** and **25**, respectively.

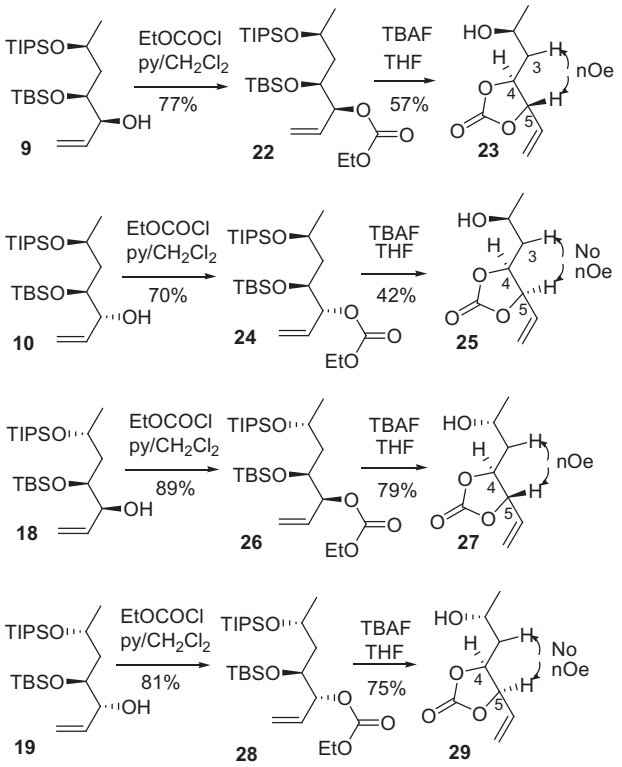
With the C-4 and C-5 stereogenic centers confined in a five-membered ring, the relative configurations at the C-5 of **23** and **25** were conveniently determined by 2D NOESY experiments performed under identical conditions. A distinct cross peak was observed between the H-5 and the H-3 for **23** but not for **25**, revealing that the relative as well as the absolute configurations at the C-5 for these compounds (and consequently, the triols derived from them) were indeed as depicted. Similarly, alcohols **18** and **19** were also converted into cyclic carbonates using the same sequence. The corresponding 2D NOESY experiments manifested that the H-4 and H-5 in **27** were trans to each other, while those in **29** cis to each other.

Comparison of the data acquired on synthetic triols **11**, **12**, **20**, and **21** with those reported for natural **1** was then made. The optical rotations are listed in Table 1. Apparently, none of the four synthetic samples seems to either **1a** or **1b**, or their antipode.

Significant discrepancies are also observed between the ^1H and ^{13}C NMR data (recorded at 100 MHz) for the synthetic and the natural samples. For clarity only ^{13}C NMR data are listed here (Table 2). Just by a quick glance at the data one will conclude that none of the four synthetic samples is compatible with either of the natural ones, because large difference occurred to almost every signal. Besides, all the four triols are odorless, inconsistent with the fragrant nature of the natural products.

The frustrating results of the above data comparison prompted us to consider whether the original proposed structural framework was incorrect. Given the seemingly impeccable partial conclusion that the natural **1** (both isomers, **1a** and **1b**) contains one CH_3, one CH_2, three CHOH (oxygenated methine) groups, and a terminal vinyl group, there is really not much room for other alternatives. The only possibility that we can imagine is the one with the OH originally at the C-4 relocated to C-3. As the $^1H-^1H$ coupling information from the COSY spectrum of **1** was not disclosed in the literature, such an alternative appeared to deserve a try under the given circumstances.

Two out of the four isomers of all possible different relative configurations were synthesized as shown in Scheme 5. Starting from the TBS protected epoxy building block **4**, ring-opening reaction[9] with sulfur ylide generated in situ from Me_3SI by treatment



Scheme 3.

Table 1
Comparison of the specific rotations of **11**, **12**, **20**, **21**, the natural products previously proposed to be **1a** and **1b**

Sample	Specific rotation
Natural **1a**	$[\alpha]_D^{21}$ +21.7 (*c* 0.75, $CHCl_3$)
Natural **1b**	$[\alpha]_D^{26}$ −52.2 (*c* 0.75, $CHCl_3$)
11	$[\alpha]_D^{25}$ −0.5 (*c* 0.76, $CHCl_3$)
12	$[\alpha]_D^{26}$ +18.0 (*c* 0.76, $CHCl_3$)
20	$[\alpha]_D^{24}$ −37.5 (*c* 0.55, $CHCl_3$)[a]
21	$[\alpha]_D^{26}$ −18.3 (*c* 0.74, $CHCl_3$)

[a] Impossible to get higher concentrations due to its limited solubility.

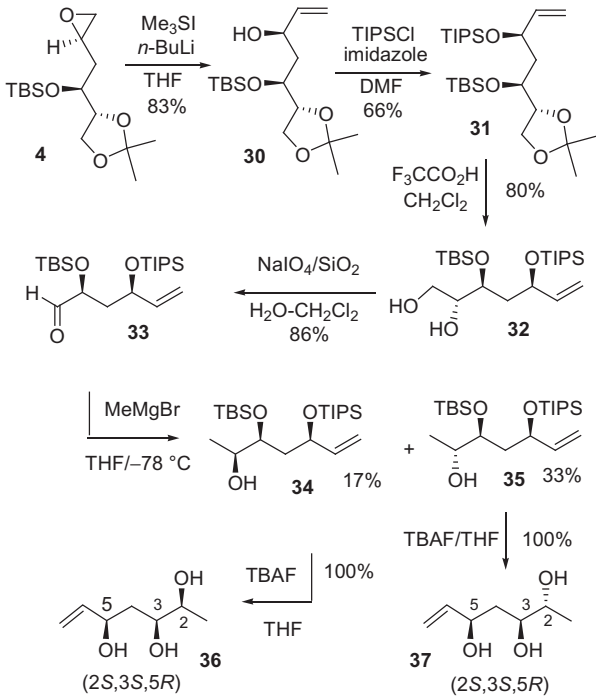
Table 2
Comparison of ^{13}C NMR (measured in 1:2 $CD_3OD/CDCl_3$ with the middle line of the $CDCl_3$ triplet set to 77.0 ppm as the reference) of **11**, **12**, **20**, **21**, the natural products previously proposed to be **1a** and **1b**

Nat **1a**[a]	Nat **1b**[a]	**11**[b]	**12**[b]	**20**[c]	**21**[c,d]
133.6	136.7	133.9	136.3	137.0	139.0
117.9	115.4	116.2	116.2	116.5	116.6
83.9	87.2	75.6	75.4	75.9	77.6
73.6	76.0	73.6	73.8	71.0	72.4
73.2	74.2	66.7	66.9	64.1	65.4
42.0	41.1	40.0	39.0	40.6	42.4
21.0	20.1	22.5	22.7	23.0	24.4

[a] Taken from ref 1, both were colorless/fragrant oils.
[b] Colorless/odorless oils.
[c] White odorless solid.
[d] Insoluble in 1:2 $CD_3OD/CDCl_3$, measure in CD_3OD (the solubility difference already ruled out **21** as a possible structure for the natural products that were previously proposed to be **1a**/**1b**). For data of **11**, **12** and **20** recorded in $CDCl_3$, see Experimental section.

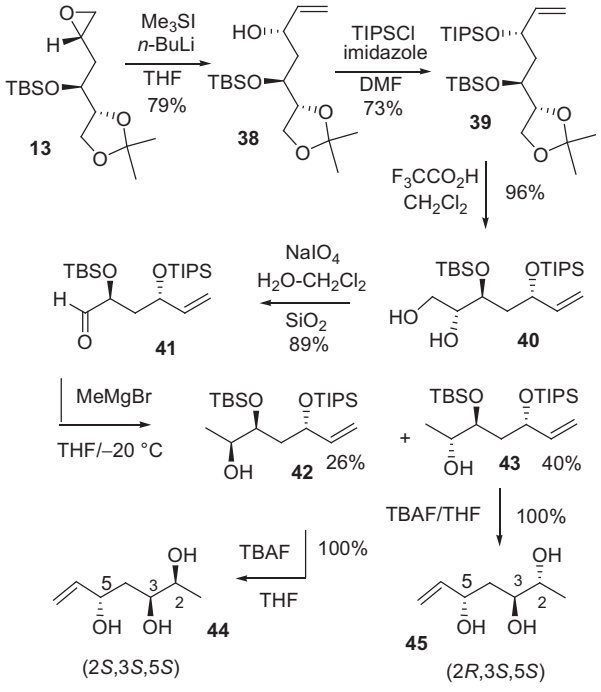
with *n*-BuLi in THF at −10 °C. Protection of the hydroxyl group with TIPSCl in DMF in the presence of imidazole gave fully protected alkene **31**.

Hydrolysis of the acetonide by exposure to 50% F_3CCO_2H in CH_2Cl_2 resulted in diol **32**, which on reaction with $NaIO_4$ on silica gel delivered the aldehyde **33**. Then, by a simple addition of MeMgBr a pair of epimers **34** and **35** were generated, which on further deprotection with *n*-Bu_4NF (TBAF) delivered the corresponding triol **36** and **37**, respectively (Scheme 4).



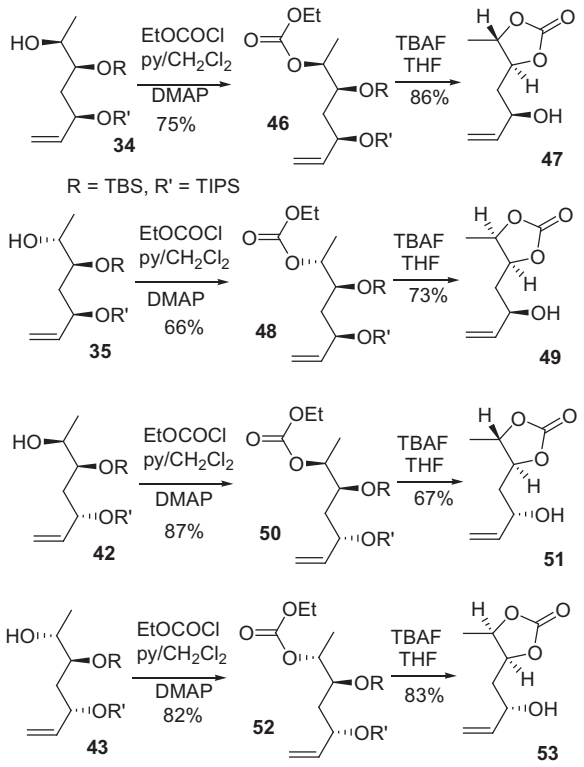
Scheme 4.

Using a similar sequence but starting from epoxide **13** (the epimer of **4**), another pair of triols **44** and **45** were obtained in comparable yields (Scheme 5).



Scheme 5.

The configurations of the stereogenic centers created in the MeMgBr addition to aldehyde in the synthesis of the above four triols were secured by NOE experiments performed on the cyclic



Scheme 6.

carbonates prepared as shown in Scheme 6. The absolute configurations of all stereogenic centers of these four triols (**36**, **37**, **44**, and **45**) were thus established beyond all doubts.

The optical rotation and ^{13}C NMR data (recorded at 100 MHz) were collected for these four triols and compared with those reported for the natural products (Tables 3 and 4).

Table 3
Comparison of the specific rotations of **36**, **37**, **44**, **45**, the natural products previously proposed to be **1a** and **1b**

Sample	Specific rotation
Natural **1a**	$[\alpha]_D^{21}$ +21.7 (*c* 0.75, $CHCl_3$)
Natural **1b**	$[\alpha]_D^{26}$ −52.2 (*c* 0.75, $CHCl_3$)
36	$[\alpha]_D^{25}$ −1.0 (*c* 0.76, $CHCl_3$)
37	$[\alpha]_D^{26}$ −3.2 (*c* 0.76, $CHCl_3$)
44	$[\alpha]_D^{24}$ −16.4 (*c* 0.76, MeOH)[a]
45	$[\alpha]_D^{26}$ −7.3 (*c* 0.74, $CHCl_3$)

[a] Insoluble in $CHCl_3$ (this property already excludes **44** as a possible structure for the natural products that were previously proposed to be **1a**/**1b**).

Table 4
Comparison of ^{13}C NMR (measured in 1:2 $CD_3OD/CDCl_3$ with the middle line of the $CDCl_3$ triplet set to 77.0 ppm as the reference) of **36**, **37**, **44**, **45**, and the natural products previously proposed to be **1a** and **1b**

Nat **1a**[a]	Nat **1b**[a]	**36**[b]	**37**[b]	**44**[c,d]	**45**[b]
133.6	136.7	140.0	140.0	143.2	140.7
117.9	115.4	114.1	114.1	113.8	113.1
83.9	87.2	74.2	74.3	73.0	71.5
73.6	76.0	71.5	71.7	71.7	70.1
73.2	74.2	69.9	70.0	70.3	69.0
42.0	41.1	38.7	37.6	41.0	38.0
21.0	20.1	17.9	17.9	19.0	17.0

[a] Taken from ref 1, both were colorless/fragrant oils.
[b] Colorless/odorless oils.
[c] White odorless solid.
[d] Insoluble in 1:2 $CD_3OD/CDCl_3$, measured in CD_3OD (the solubility difference already rules out **44** as a possible structure for the natural products that were previously proposed to be **1a**/**1b**). For data of **36**, **37** and **45** recorded in $CDCl_3$, see Experimental section.

Again, just a quick glance at the data tables is adequate for exclusion of any of these four isomers to be either natural products. Hence, on the basis of the results of this work a safe conclusion can be reached—the two natural products isolated from *Ascomycete D. concentrica* are definitely not hept-6-en-2,3,5-triol as proposed before; their genuine structures are still to be established.

3. Conclusions

All the four possible independent (i.e., non-antipodal to each other) diastereomers of the title triol (**1**), which was previously proposed to be the planar structure for the two natural products isolated from fungus *Ascomycete D. concentrica*, now have been synthesized in enantiopure forms through a chiral-pool route. Corresponding spectroscopic data including ^1H and ^{13}C NMR as well as optical rotations were collected for these compounds. However, the data for the synthetic isomers are not compatible with those reported for the natural products in the literature, so are the data for the other four OH-positional isomers. Hence, the previously assigned structures for the latter are to be re-assigned. Apart from their irreplaceable roles in checking and consequently disproving the previously proposed structure for the two natural products isolated from *Ascomycete D. concentrica*, the spectroscopic data recorded on such a complete set of different diastereomers of clearly-defined relative as well as absolute configurations synthesized in this work would be of reference values in related studies including establishment of the structure/configuration-chemical shift relationships.

4. Experimental

4.1. General

The ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using a Varian Mercury or a Bruker Avance instrument with the frequency indicated in each individual case below. The FT-IR spectra were scanned with a Nicolet Avatar 360 FT-IR. EIMS and EI-HRMS were recorded with an HP 5989A and a Finnigan MAT 8430 mass spectrometer, respectively. The ESIMS and ESI-HRMS were recorded with a PE Mariner API-TOF and an APEX III (7.0 T) FTMS mass spectrometer, respectively. Dry THF was distilled from Na/Ph_2CO under N_2. Unless otherwise specified, all other solvents and reagents were commercially available and used as received without any further purification. PE (chromatography solvent) stands for petroleum ether (60–90 °C). Optical rotations were recorded on a Jasco P-1030 Polarimeter. Melting points were taken on a micro melting point apparatus equipped with a microscope and were uncorrected.

For direct comparison with those of the natural samples, the ^1H NMR of triols **11**, **12**, **20**, **36**, **37**, and **45** were recorded in $CDCl_3$ rather than 1:2 $CD_3OD/CDCl_3$.[10] The triisopropyl groups of the TIPS protecting group in some compounds in this work gave an apparent sharp 'singlet' of 21H in ^1H NMR. Although in principle such signals are expected to be a 3H multiplet for the methines and an 18H doublet for the methyls (in the literature sometimes reported as a 21H multiplet), these signals are marked as 's' below to better reflect the spectroscopic appearance and to avoid potential confusion with ordinary singlets.

4.2. Synthesis

*4.2.1. (1S,3S)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-butan-3-ol (**5**).* $LiBHEt_3$ (1.0 M, in THF, 17.3 mL, 17.3 mmol) was added dropwise to a solution of epoxide **4** (2.263 g, 8.67 mmol) in dry THF (26 mL) stirred at 0 °C under N_2 (balloon). After completion of the addition, the mixture was stirred at the same temperature for 20 min, when TLC showed completion of the

reaction. Water (10 mL) was added, followed by aqueous NaOH (1 N, 8.7 mL) and Et_2O (200 mL). The phases were separated. The organic layer was washed in turn with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:5 EtOAc/PE) on silica gel gave alcohol **5** as a colorless oil (2.295 g, 7.54 mmol, 87%). $[\alpha]_D^{26}$ +25.9 (*c* 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 4.08–4.00 (m, 3H), 3.85 (q, *J*=5.9 Hz, 1H), 3.77 (m, 1H), 2.62 (br s, 1H, OH), 1.74 (ddd, *J*=14, 8.7, 5.5 Hz, 1H), 1.62 (ddd, *J*=14, 6.5, 3.4 Hz, 1H), 1.39 (s, 3H), 1.32 (s, 3H), 1.17 (d, *J*=6.2 Hz, 3H), 0.86 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.3, 78.7, 71.3, 67.2, 64.4, 44.3, 26.5, 25.7, 25.3, 23.8, 17.9, −4.2, −4.5; FT-IR (film) 3451, 2957, 2931, 2858, 2888, 1473, 1371, 1255, 1215, 1074, 913, 837, 776, 671 cm^{-1}. ESIMS *m/z* 327.2 ($[M+Na]^+$). ESI-HRMS calcd for $C_{15}H_{32}NaO_4Si$ ($[M+Na]^+$) 327.1962, found 327.1959.

*4.2.2. (1S,3S)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-triisopropylsily-loxy-butane (**6**).* A mixture of alcohol **5** (2.277 g, 7.48 mmol), imidazole (1.273 g, 18.70 mmol), and *i*-Pr_3SiCl (1.9 mL, 9.0 mmol) in dry DMF (4.6 mL) was stirred at ambient temperature for 24 h. Water (10 mL) was added, followed by Et_2O (300 mL). The phases were separated. The organic layer was washed in turn with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:80 EtOAc/PE) on silica gel gave the silyl ether **6** as a colorless oil (2.837 g, 6.16 mmol, 82%). $[\alpha]_D^{26}$ +9.4 (*c* 4.17, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 4.14 (m, 1H), 4.06 (m, 1H), 3.95 (t, *J*=7.4 Hz, 1H), 3.89 (m, 1H), 3.80 (t, *J*=7.6 Hz, 1H), 1.78 (ddd, *J*=14, 7.0, 5.5 Hz, 1H), 1.55 (ddd, *J*=14, 7.7, 5.0 Hz, 1H), 1.40 (s, 3H), 1.32 (s, 3H), 1.21 (d, *J*=3.0 Hz, 3H), 1.06 ('s', 21H), 0.88 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 108.8, 78.9, 69.5, 65.6, 65.5, 45.1, 26.5, 25.9, 25.3, 23.8, 18.2, 18.1, 18.0, 12.5, −4.1, −4.3; FT-IR (film) 2942, 2867, 1463, 1379, 1370, 1256, 1216, 1109, 1072, 1004, 882, 837, 775, 677 cm^{-1}. ESIMS *m/z* 483.6 ($[M+Na]^+$). ESI-HRMS calcd for $C_{24}H_{52}NaO_4Si_2$ ($[M+Na]^+$) 483.3296, found 483.3296.

*4.2.3. (2R,3S,5S)-3-tert-Butyldimethylsilyloxy-5-triisopropylsilyloxy-hexan-1,2-diol (**7**).* A mixture of acetonide **6** (2.629 g, 5.70 mmol) and aqueous F_3CCO_2H (50% v/v, 8.2 mL) in CH_2Cl_2 (190 mL) was stirred at ambient temperature for 1 h. The mixture was diluted with CH_2Cl_2 (300 mL), washed with aqueous saturated $NaHCO_3$ (until the aqueous layer became slightly basic), water, and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:3 EtOAc/PE) on silica gel gave diol **7** as a colorless viscous oil (2.063 g, 4.90 mmol, 86%). $[\alpha]_D^{24}$ +18.5 (*c* 2.20, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 4.20 (m, 1H), 3.89 (m, 1H), 3.74–3.60 (m, 3H), 1.88 (m, 1H), 1.67 (ddd, *J*=14.7, 7.3, 4.6 Hz, 1H), 1.25 (d, *J*=6.4 Hz, 3H), 1.07 ('s', 21H), 0.88 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 74.2, 71.1, 66.1, 63.7, 44.4, 25.7, 23.1, 18.1, 18.0, 17.9, 12.5, −4.5, −4.7; FT-IR (film) 3389, 2944, 2866, 1463, 1382, 1253, 1081, 882, 836, 776, 678 cm^{-1}. ESIMS *m/z* 443.4 ($[M+Na]^+$). ESI-HRMS calcd for $C_{21}H_{48}NaO_4Si_2$ ($[M+Na]^+$) 443.2983, found 443.2975.

*4.2.4. (2S,3S,5S)-4-tert-Butyldimethylsilyloxy-6-triisoprpopylsily-loxy-hept-1-en-2-ol (**9**) and (2R,3S,5S)-4-tert-Butyldimethylsilyloxy-6-triisoprpopylsilyloxy-hept-1-en-2-ol (**10**).* A mixture of $NaIO_4$ (1.143 g, 5.34 mmol) and water (7.3 mL) was stirred at ambient temperature while silica gel (300–400 mesh, 11.443 g) and CH_2Cl_2 (37 mL) were added slowly. The mixture was stirred at the same temperature for 1 h. A solution of diol **7** (0.999 g, 2.37 mmol) in CH_2Cl_2 (6 mL) was added dropwise to the above prepared mixture. Stirring was continued for another hour at ambient temperature. Solids were filtered off through Celite (washing with CH_2Cl_2). The filtrate/washings were washed with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation left the crude intermediate aldehyde **8** as a colorless oil (0.712 g, 1.83 mmol, 77%), on which the following data were obtained: ^1H NMR (400 MHz, $CDCl_3$) δ 9.61 (d, *J*=1.5 Hz, 1H), 4.20 (m, 1H), 4.08 (m, 1H), 1.90 (ddd, *J*=13.7, 7.2, 6.0 Hz, 1H), 1.74 (ddd, *J*=13.8, 6.4, 5.1 Hz, 1H), 1.23 (d, *J*=6.1 Hz, 3H), 1.06 ('s', 21H), 0.92 (s, 6H), 0.08 (s, 3H), 0.06 (s, 3H).

The above obtained crude aldehyde **8** (0.712 g, 1.8 mmol) was dissolved in dry THF (18 mL) and stirred at −78 °C under N_2 (balloon). H_2C=CHMgBr (1.0 M, in THF, 5.5 mL, 5.50 mmol) was added slowly via a syringe. The mixture was then stirred at the same temperature for 2 h. Aqueous saturated NH_4Cl was added, followed by Et_2O (300 mL). The phases were separated. The organic layer was washed in turn with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:50 Et_2O/PE) on silica gel gave allyl alcohols **9** (the more polar component, 130 mg, 0.31 mmol, 17% from aldehyde **8** or 13% from diol **7**) and **10** (the less polar component, 318 mg, 0.8 mmol, 42% from aldehyde **8** or 34% from diol **7**) as colorless oils.

Data for the more polar isomer **9**: $[\alpha]_D^{26}$ −11.0 (*c* 0.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddd, *J*=17.4, 10.5, 4.9 Hz, 1H), 5.31 (dt, *J*=17.4, 1.6 Hz, 1H), 5.18 (dt, *J*=10.5, 1.7 Hz, 1H), 4.13–4.07 (m, 2H), 3.89 (m, 1H), 1.82 (ddd, *J*=13.9, 7.7, 4.9 Hz, 1H), 1.64 (ddd, *J*=14.1, 7.0, 5.3 Hz, 1H), 1.23 (d, *J*=6.3 Hz, 3H), 1.06 ('s', 21H), 0.89 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 138.8, 115.4, 73.7, 71.9, 66.0, 43.6, 25.8, 23.9, 18.2, 18.1, 18.0, 12.6, −4.3, −4.5; FT-IR (film) 3045, 2929, 2866, 1465, 1381, 14254, 1096, 1061, 916, 883, 837, 776, 677 cm^{-1}; ESIMS: *m/z* 439.4 ($[M+Na]^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ($[M+Na]^+$) 439.3034, found 439.3042.

Data for the less polar one **10**: $[\alpha]_D^{26}$ −2.0 (*c* 0.55, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, *J*=17.3, 10.5, 5.9 Hz, 1H), 5.31 (dt, *J*=17.3, 1.4 Hz, 1H), 5.20 (dt, *J*=10.6, 1.4 Hz, 1H), 4.13–4.09 (m, 2H), 3.77 (m, 1H), 1.87 (ddd, *J*=13.8, 8.2, 5.2 Hz, 1H), 1.52 (ddd, *J*=13.8, 7.6, 4.9 Hz, 1H), 1.20 (d, *J*=6.0 Hz, 3H), 1.07 ('s', 21H), 0.91 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (75 MHz, CDCl3) δ 136.6, 116.4, 76.1, 73.0, 65.7, 42.0, 25.7, 23.2, 18.1, 18.0, 17.9, 12.4, −4.4, −4.6; FT-IR (film) 2962, 2927, 2866, 1463, 1379, 1254, 1103, 1005, 920, 883, 836, 776, 677 cm^{-1}; ESIMS *m/z* 439.4 ($[M+Na]^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ($[M+Na]^+$) 439.3034, found 439.3033.

*4.2.5. (2S,3S,5S)-Hept-6-en-2,3,5-triol (**11**).* A solution of *n*-Bu_4NF (1.0 M, in THF, 0.5 mL, 0.50 mmol) was added to a solution of alcohol **9** (0.076 g, 0.18 mmol) in THF (0.9 mL). The mixture was stirred at ambient temperature for 5 h before being concentrated on a rotary evaporator and chromatography (1:15 MeOH/CH_2Cl_2) on silica gel to give triol **11** as a colorless oil (0.027 g, 0.18 mmol, 100%). $[\alpha]_D^{26}$ −0.5 (*c* 0.76, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J*=17.1, 10.6, 6.4 Hz, 1H), 5.34 (d, *J*=17.0 Hz, 1H), 5.23 (d, *J*=10.6 Hz, 1H), 4.06 (m, 1H), 3.91 (t, *J*=6.1 Hz, 1H), 3.72 (m, 1H), 3.22 (br s, 3H, OH), 1.64–1.51 (m, 2H), 1.20 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 117.6, 76.4, 74.9, 68.2, 40.5, 23.9; FT-IR (film) 3245, 2968, 2919, 1645, 1456, 1428, 1377, 1311, 1205, 1077, 996, 929, 830, 724, 675 cm^{-1}. ESIMS *m/z* 169.0 ($[M+Na]^+$). ESI-HRMS calcd for $C_7H_{14}NaO_3$ ($[M+Na]^+$) 169.0835, found 169.0840.

*4.2.6. (2S,3S,5R)-Hept-6-en-2,3,5-triol (**12**).* The procedure and the yield (100%) were the same as described above for conversion of **9** to **11**.

Data for **12** (a colorless oil): $[\alpha]_D^{27}$ +18.0 (*c* 0.76, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=17.2, 10.6, 6.0 Hz, 1H), 5.32 (d, *J*=17.4 Hz, 1H), 5.24 (d, *J*=10.6 Hz, 1H), 4.11 (m, 1H), 4.05 (m, 1H), 3.90 (m, 1H), 3.13 (br s, 3OH), 1.60–1.52 (m, 2H), 1.21 (d, *J*=6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 117.4, 75.7, 74.7, 68.4, 38.7, 24.1; FT-IR (film) 3385, 2968, 2921, 1644, 1428, 1376, 1317, 1125, 1083, 1040, 996, 930, 822 cm^{-1}. EIMS *m/z* (%) 145 ($[M-H]^+$) (0.19), 45 (100), 58 (62), 57 (57), 43 (56), 89 (44), 71 (43), 41 (43), 55 (15); EI-HRMS calcd for $C_7H_{14}O_3$ (M^+) 146.0943, found 146.0939.

*4.2.7. (1S)-1-((4R)-2,2-Dimethyl-[1,3]dioxolan-4-yl)-2-((2R)-oxiran-2-yl)-ethyl tert-butyldimethyl-silyl ether (**13**).* A solution of alcohol **3** (1.283 g, 6.82 mmol), TBSCl (2.569 g, 17.04 mmol), Et_3N (4.8 mL, 34.51 mmol), and DMAP (0.250 g, 2.05 mmol) in dry DMF (6 mL) was stirred at ambient temperature for 24 h. Water (10 mL) was then added, followed by Et_2O (200 mL). The phases were separated. The organic layer was washed with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:20 EtOAc/PE) on silica gel gave the silyl ether **13** as a colorless oil (1.889 g, 6.25 mmol, 92%). $[\alpha]_D^{27}$ +14.7 (*c* 1.50, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07–3.97 (m, 2H), 3.90 (q, *J*=5.6 Hz, 1H), 3.79 (m, 1H), 3.06 (m, 1H), 2.80 (t, *J*=4.7 Hz, 1H), 2.52 (dd, *J*=5.5, 2.7 Hz, 1H), 1.74–1.69 (m, 2H), 1.38 (s, 3H), 1.33(s, 3H), 0.89 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 109.0, 78.2, 70.6, 66.3, 48.8, 47.6, 37.5, 26.5, 25.7, 25.6, 25.2, 17.9, −4.5; FT-IR (film) 2985, 2955, 2930, 2858, 1473, 1370, 1255, 1146, 1076, 915, 839, 777 cm^{-1}. ESIMS: *m*/*z* 325.0 ($[M+Na]^+$). ESI-HRMS calcd for $C_{15}H_{30}NaO_4Si$ ($[M+Na]^+$) 325.1806, found 325.1808.

*4.2.8. (1S,3R)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-butan-3-ol (**14**).* The same procedure described above for conversion of **4** to **5** was employed. Yield: 99%.

Data for **14** (a colorless oil): $[\alpha]_D^{25}$ +7.4 (*c* 3.55, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.08–3.99 (m, 3H), 3.85–3.73 (m, 2H), 3.34 (br s, 1H, OH), 1.73–1.57 (m, 2H), 1.35 (s, 3H), 1.30(s, 3H), 1.14 (d, *J*=6.1 Hz, 3H), 0.84 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 109.2, 77.9, 72.6, 67.2, 64.6, 43.1, 26.5, 25.6, 25.2, 24.0, 17.8, −4.3, −4.8; FT-IR (film) 3458, 2957, 2931, 2858, 1473, 1371, 1256, 1215, 1150, 1073, 1003, 837, 777 cm^{-1}. ESIMS *m*/*z* 327.3 ($[M+Na]^+$). ESI-HRMS calcd for $C_{15}H_{32}NaO_4Si$ ($[M+Na]^+$) 327.1962, found 327.1968.

*4.2.9. (1S,3R)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-triisopropl-silyloxy-butane (**15**).* The same procedure described above for conversion of **5** to **6** was employed. Yield: 90%.

Data for **15** (a colorless oil): $[\alpha]_D^{27}$ +20.2 (*c* 3.85, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.12 (m, 1H), 4.04–3.95 (m, 2H), 3.85–3.76 (m, 2H), 1.78 (m, 1H), 1.59 (m, 1H), 1.38 (s, 3H), 1.32 (s, 3H), 1.21 (d, *J*=6.1 Hz, 3H), 1.06 ('s', 21H), 0.87 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 109.0, 79.4, 70.5, 66.2, 65.7, 46.8, 26.5, 25.8, 25.4, 24.3, 18.2, 18.1, 18.0, 12.6, −4.1, −4.2; FT-IR (film) 2944, 2892, 2866, 1463, 1379, 1256, 1110, 1076, 1005, 883, 837, 775, 677 cm^{-1}. ESIMS *m*/*z* 483.4 ($[M+Na]^+$). ESI-HRMS calcd for $C_{24}H_{52}NaO_4Si_2$ ($[M+Na]^+$) 483.3296, found 483.3308.

*4.2.10. (2R,3S,5R)-3-tert-Butyldimethylsilyloxy-5-triisopropylsilyloxy-hexan-1,2-diol (**16**).* The same procedure described above for conversion of **6** to **7** was employed. Yield: 76%.

Data for **16** (a colorless oil): $[\alpha]_D^{25}$ +6.3 (*c* 3.90, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.65 (m, 1H), 3.90 (q, *J*=5.0 Hz, 1H), 3.77–3.67 (m, 2H), 3.61 (m, 1H), 3.25 (d, *J*=5.8 Hz, 1H), 2.58 (dd, *J*=7.4, 4.2 Hz, 1H), 1.83–1.68 (m, 2H), 1.25 (d, *J*=6.1 Hz, 3H), 1.05 ('s', 21H), 0.87 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.7, 73.0, 67.0, 63.2, 44.5, 25.7, 24.3, 18.12, 18.07, 17.9, 12.6, −4.5, −4.8; FT-IR (film) 3422, 2944, 2866, 1463, 1383, 1254, 1085, 883, 836, 776, 677 cm^{-1}; ESIMS: *m*/*z* 443.4 ($[M+Na]^+$). ESI-HRMS calcd for $C_{21}H_{48}NaO_4Si_2$ ($[M+Na]^+$) 443.2983, found 443.2975.

*4.2.11. (3S,4S,6R)-4-tert-Butyldimethylsilyloxy-6-triisoprpopylsilyloxy-hept-1-en-3-ol (**18**) and (3R,4S,6R)-4-tert-butyldimethylsilyloxy-6-triisoprpopylsilyloxy-hept-1-en-3-ol (**19**).* The same procedure described above for conversion of **7** to **9** and **10** (via **8**) was employed, with the yield for the intermediate aldehyde **17**, allyl allcohols **18** and **19** being 86% (crude), 21% from **17** (or 18% from **16**) and 47% from **17** (or 40% from **16**), respectively.

Diagnostic data for crude intermediate aldehyde **17** (a colorless oil): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (s, 1H), 4.16–4.10 (m, 2H), 1.94 (dt, *J*=14, 5.8 Hz, 1H), 1.74 (dt, *J*=14, 6.4 Hz, 1H), 1.23 (d, *J*=5.9 Hz, 3H), 1.05 ('s', 21H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

Data for **18** (the less polar isomer, a colorless oil): $[\alpha]_D^{27}$ −6.1 (*c* 0.75, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=17.5, 10.1, 4.7 Hz, 1H), 5.31 (d, *J*=17.5 Hz, 1H), 5.18 (d, *J*=10.5 Hz, 1H), 4.08–3.99 (m, 2H), 3.73 (m, 1H), 2.44 (d, *J*=7.9 Hz, 1H), 2.04 (m, 1H), 1.52 (ddd, *J*=14.0, 6.6, 4.8 Hz, 1H), 1.22 (d, *J*=6.3 Hz, 3H), 1.07 ('s', 21H), 0.88 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 115.6, 74.2, 72.9, 66.3, 44.4, 25.8, 24.3, 18.2, 18.13, 18.07, 12.6, −4.2, −4.5; FT-IR (film) 3475, 2945, 2866, 1463, 1383, 1255, 1130, 1063, 1005, 920, 837, 776, 677 cm^{-1}. ESIMS *m*/*z* 439.4 ($[M+Na]^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ($[M+Na]^+$) 439.3034, found 439.3024.

Data for **19** (the more polar isomer, a colorless oil): $[\alpha]_D^{25}$ +6.0 (*c* 0.15, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (ddd, *J*=17.3, 10.6, 6.2 Hz, 1H), 5.30 (d, *J*=17.2 Hz, 1H), 5.20 (d, *J*=10.5 Hz, 1H), 4.07 (s, 1H), 4.01 (q, *J*=5.8 Hz, 1H), 3.86 (q, *J*=5.9 Hz, 1H), 2.42 (d, *J*=4.5 Hz, 1H), 1.74 (m, 1H), 1.57 (m, 1H), 1.22 (d, *J*=6.2 Hz, 3H), 1.05 ('s', 21H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.4, 116.7, 75.9, 73.5, 43.2, 25.8, 24.5, 18.21, 18.18, 18.0, 12.7, −4.3, −4.4; FT-IR (film) 3476, 2946, 2866, 1463, 1377, 1254, 1085, 1005, 923, 883, 776, 676 cm^{-1}. ESIMS *m*/*z* 439.4 ($[M+Na]^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ($[M+Na]^+$) 439.3034, found 439.3031.

*4.2.12. (2S,3S,5R)-Hept-6-en-2,3,5-triol (**20**).* The same procedure described above for conversion of **9** to **11** was employed. Yield: 100%.

Data for **20** (a white solid): mp 85–86 °C. $[\alpha]_D^{28}$ −37.5 (*c* 0.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J*=17.3, 10.4, 6.5 Hz, 1H), 5.37 (d, *J*=17.0 Hz, 1H), 5.26 (d, *J*=10.4 Hz, 1H), 4.18 (m, 1H), 4.02 (t, *J*=6.4 Hz, 1H), 3.82 (m, 1H), 2.08 (br s, 3H, OH), 1.72 (ddd, *J*=14.5, 8.3, 3.0 Hz, 1H), 1.62 (ddd, *J*=14.6, 8.4, 3.4 Hz, 1H), 1.25 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 117.8, 76.2, 71.8, 65.5, 40.1, 23.6; FT-IR (film) 3379, 2966, 2923, 1417, 1374, 1282, 1049, 993, 927, 855, 828 cm^{-1}. EIMS *m*/*z* (%) 131 ($[M-CH_3]^+$) (0.27), 45 (100), 58 (65), 57 (56), 43 (54), 71 (42), 89 (39), 41 (23), 55 (16); EI-HRMS calcd for $C_7H_{14}O_3$ (M^+) 146.0943, found 146.0940.

*4.2.13. (2R,3S,5R)-Hept-6-en-2,3,5-triol (**21**).* The same procedure described above for conversion of **9** to **11** was employed. Yield: 100%.

Data for **21** (a white solid): mp 70–71 °C. $[\alpha]_D^{26}$ −18.3 (*c* 0.74, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ 5.94 (ddd, *J*=17.3, 10.5, 6.4 Hz, 1H), 5.28 (dt, *J*=17.2, 1.6 Hz, 1H), 5.18 (dt, *J*=10.6, 1.5 Hz, 1H), 3.99 (m, 1H), 3.95 (m, 1H), 3.77 (m, 1H), 1.58 (m, 1H), 1.47 (m, 1H), 1.19 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 139.0, 116.6, 77.6, 72.4, 65.4, 42.4, 24.4; FT-IR (film) 3382, 2966, 2924, 1417, 1376, 1311, 1088, 1040, 995, 929, 830 cm^{-1}. EIMS *m*/*z* (%) 145 ($[M-H]^+$) (0.19), 45 (100), 58 (62), 57 (57), 43 (56), 89 (44), 71 (43), 41 (43), 55 (15); EI-HRMS calcd for $C_7H_{14}O_3$ $(M)^+$ 146.0939, found 146.0939. EIMS *m*/*z* (%) 131 ($[M-CH_3]^+$) (0.35), 45 (100), 58 (66), 57 (56), 43 (54), 71 (43), 89 (39), 41 (24), 55 (16); EI-HRMS calcd for $C_7H_{14}O_3$ (M^+) 146.0943, found 146.0947.

*4.2.14. (3S,4S,6S)-3-Ethoxycarbonyloxy-4-tert-butyldimethylsilyloxy-6-triisoprpopylsilyloxy-hept-1-en (**22**).* Pyridine (0.13 mL, 1.61 mmol) and ethyl chloroformate (0.11 mL, 1.15 mmol) were added in turn to a solution of alcohol **9** (0.045 g, 0.108 mmol) in dry CH_2Cl_2 (1 mL) stirred at ambient temperature. Stirring was continued at the same temperature for 5 h before the mixture was partitioned between water (5 mL) and Et_2O (200 mL). The organic layer was washed with aqueous saturated $NaHCO_3$, water, and brine, and dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:50 EtOAc/PE) on silica gel afforded the carbonate **22** as a colorless oil (0.041 g, 0.083 mmol, 77%). $[\alpha]_D^{26}$ −36.7 (*c* 2.05, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (ddd, *J*=17.2, 11.1, 6.3 Hz, 1H), 5.33 (d, *J*=17.2 Hz, 1H), 5.27 (d, *J*=10.7 Hz, 1H), 5.01 (t, *J*=5.9 Hz, 1H), 4.17

(q, *J*=7.3 Hz, 2H), 4.07 (m, 1H), 3.80 (m, 1H), 1.73 (ddd, *J*=13.6, 9.3, 4.5 Hz, 1H), 1.55 (ddd, *J*=13.6, 9.1, 3.2 Hz, 1H), 1.29 (t, *J*=7.2 Hz, 3H), 1.16 (d, *J*=5.7 Hz, 3H), 1.04 ('s', 21H), 0.86 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 132.4, 118.3, 80.3, 70.3, 65.4, 63.9, 42.7, 25.7, 23.3, 18.13, 18.09, 17.98, 14.3, 12.4, −4.5, −4.6; FT-IR (film) 2945, 2894, 2866, 1749, 1464, 1373, 1260, 1113, 1013, 882, 837, 776, 677 cm^{-1}; ESIMS: *m*/*z* 511.5 ([M+Na]$^+$). ESI-HRM calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3239.

*4.2.15. (4S,5S)-4-((S)-2-Hydroxy-propyl)-5-vinyl-[1,3]dioxolan-2-one (**23**).* A solution of *n*-Bu_4NF (1.0 M, in THF, 0.16 mL, 0.16 mmol) was added to a solution of **22** (0.041 g, 0.0838 mmol) in THF (8 mL) stirred at ambient temperature. Stirring was continued at the same temperature for 5 h. Water (5 mL) was added, followed by Et_2O (200 mL). The phases were separated. The organic layer was washed with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:1 EtOAc/PE) on silica gel afforded the cyclic carbonate **23** as a colorless oil (0.008 g, 0.0464 mmol, 57%). $[\alpha]_D^{25}$ −44.5 (*c* 0.25, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (ddd, *J*=17.2, 10.3, 7.0 Hz, 1H), 5.51 (d, *J*=17.3 Hz, 1H), 5.44 (d, *J*=10.1 Hz, 1H), 4.81 (t, *J*=7.2 Hz, 1H), 4.52 (m, 1H), 4.07 (m, 1H), 1.97 (m, 1H), 1.86 (ddd, *J*=14.4, 5.4, 4.5 Hz, 1H), 1.67 (br s, 1OH), 1.28 (d, *J*=6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 131.9, 121.5, 82.6, 79.7, 64.5, 40.9, 23.7; FT-IR (film) 3473, 2970, 2925, 2854, 1802, 1434, 1376, 1191, 1078, 1044, 945, 775 cm^{-1}. ESIMS *m*/*z* 195.0 ([M+Na]$^+$). ESI-HRMS $C_8H_{12}NaO_4$ ([M+Na]$^+$) 195.0628, found 195.0628.

*4.2.16. (3R,4S,6S)-3-Ethoxycarbonyloxy-4-tert-butyldimethylsilyloxy-6-triisoprpopylsilyloxy-hept-1-en (**24**).* The same procedure described above for conversion of **9** to **22** was employed. Yield: 70%.

Data for **24** (a colorless oil): $[\alpha]_D^{26}$ −10.1 (*c* 7.45, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=17.3, 10.5, 7.7 Hz, 1H), 5.33 (d, *J*=7.1 Hz, 1H), 5.29 (s, 1H), 4.96 (dd, *J*=7.3, 2.1 Hz, 1H), 4.22−4.11 (m, 2H), 4.06 (m, 1H), 3.92 (dq, *J*=8.0, 3.8 Hz, 1H), 1.81 (ddd, *J*=13.6, 9.1, 4.6 Hz, 1H), 1.45 (ddd, *J*=14.0, 8.3, 3.6 Hz, 1H), 1.28 (t, *J*=7.3 Hz, 3H), 1.18 (d, *J*=5.7 Hz, 3H), 1.04 ('s', 21H), 0.87 (s, 9H), 0.09 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 132.0, 119.9, 82.1, 71.0, 65.5, 63.7, 43.5, 25.8, 23.3, 18.10, 18.07, 14.3, 12.4, −4.5, −4.8; FT-IR (film) 2929, 2866, 1748, 1465, 1371, 1263, 1126, 1007, 925, 882, 776 cm^{-1}. ESIMS *m*/*z* 511.5 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3243.

*4.2.17. (4S,5R)-4-((S)-2-Hydroxy-propyl)-5-vinyl-[1,3]dioxolan-2-one (**25**).* The same procedure described above for conversion of **22** to **23** was employed. Yield: 42%.

Data for **25** (a colorless oil): $[\alpha]_D^{25}$ +3.2 (*c* 1.10, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (ddd, *J*=16.9, 10.4, 7.4 Hz, 1H), 5.51 (d, *J*=12.2 Hz, 1H), 5.46 (d, *J*=5.3 Hz, 1H), 5.13 (t, *J*=7.1 Hz, 1H), 4.94 (m, 1H), 3.99 (m, 1H), 2.06 (br s, 1H, OH), 1.88 (ddd, *J*=14.6, 8.9, 7.0 Hz, 1H), 1.71 (m, 1H), 1.25 (d, *J*=6.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 129.3, 121.9, 80.1, 77.8, 64.9, 38.3, 23.2; FT-IR (film) 3431, 2972, 2926, 1798, 1646, 1553, 1370, 1306, 1187, 1042, 946, 776 cm^{-1}. ESIMS: *m*/*z* 195.0 ([M+Na]$^+$). ESI-HRMS calcd for $C_8H_{12}NaO_4$ ([M+Na]$^+$) 195.0628, found 195.0633.

*4.2.18. (3S,4S,6R)-3-Ethoxycarbonyloxy-4-tert-butyldimethylsilyloxy-6-triisoprpopylsilyloxy-hept-1-en (**26**).* The same procedure described above for conversion of **9** to **22** was employed. Yield: 89%.

Data for **26** (a colorless oil): $[\alpha]_D^{25}$ −33.0 (*c* 1.75, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J*=17.2, 10.8, 6.0 Hz, 1H), 5.35 (dt, *J*=17.4, 1.4 Hz, 1H), 5.26 (dt, *J*=10.5, 1.6 Hz, 1H), 5.02 (tt, *J*=5.5, 1.4 Hz, 1H), 4.17 (q, *J*=7.3 Hz, 2H), 4.04 (m, 1H), 3.98 (m, 1H), 1.80 (ddd, *J*=13.9, 7.0, 4.2 Hz, 1H), 1.43 (ddd, *J*=13.9, 7.5, 5.4 Hz, 1H), 1.29 (t, *J*=7.2 Hz, 3H), 1.20 (d, *J*=6.4 Hz, 3H), 1.04 ('s', 21H), 0.88 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 132.3, 118.2, 80.1, 70.3, 66.0, 63.9, 43.7, 25.8, 24.8, 18.2, 18.0, 14.2, 12.7, −4.3, −4.6; FT-IR (film) 2945, 2866, 1748, 1464, 1372, 1261, 1112, 1007, 883, 777 cm^{-1}. ESIMS *m*/*z* 511.4 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3241.

*4.2.19. (4S,5S)-4-((S)-2-Hydroxy-propyl)-5-vinyl-[1,3]dioxolan-2-one (**27**).* The same procedure described above for conversion of **22** to **23** was employed. Yield: 79%.

Data for **27** (a colorless oil): $[\alpha]_D^{26}$ −94.7 (*c* 1.15, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (ddd, *J*=16.8, 10.5, 7.0 Hz, 1H), 5.47 (d, *J*=17.3 Hz, 1H), 5.40 (d, *J*=10.3 Hz, 1H), 4.70 (t, *J*=6.9 Hz, 1H), 4.60 (m, 1H), 4.04 (m, 1H), 2.20 (br s, 1H, OH), 1.89−1.68 (m, 2H), 1.25 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 131.8, 121.1, 82.8, 79.4, 64.0, 41.8, 24.2; FT-IR (film) 3468, 2968, 2926, 1796, 1549, 1375, 1188, 1038, 946, 775 cm^{-1}. EIMS *m*/*z* (%) 128 ([M−CO_2]$^+$) (8.92), 84 (37), 83 (478), 66 (56), 56 (37), 55 (74), 45 (100), 43 (51), 41 (54); EI-HRMS calcd for $C_8H_{12}O_4$ (M)$^+$ 172.0736, found 172.0733.

*4.2.20. (3R,4S,6R)-3-Ethoxycarbonyloxy-4-tert-butyldimethylsilyloxy-6-triisoprpopylsilyloxy-hept-1-en (**28**).* The same procedure described above for conversion of **9** to **22** was employed. Yield: 81%.

Data for **28** (a colorless oil): $[\alpha]_D^{24}$ −2.3 (*c* 0.85, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddd, *J*=17.2, 10.5, 7.6 Hz, 1H), 5.35 (d, *J*=8.4 Hz, 1H), 5.31 (s, 1H), 4.95 (dd, *J*=7.3, 1.0 Hz, 1H), 4.23−4.13 (m, 2H), 4.03−3.97 (m, 2H), 1.72 (dq, *J*=14.1, 6.1 Hz, 1H), 1.53 (dq, *J*=14.0, 6.4 Hz, 1H), 1.29 (t, *J*=7.2 Hz, 3H), 1.23 (d, *J*=6.3 Hz, 3H), 1.04 ('s', 21H), 0.88 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 131.8, 120.0, 81.9, 70.9, 65.8, 63.7, 44.5, 25.8, 24.4, 18.19, 18.16, 18.1, 14.3, 12.7, −4.5, −4.8; FT-IR (film) 2946, 2866, 1748, 1464, 1372, 1262, 1129, 1005, 883, 837, 776 cm^{-1}. ESIMS *m*/*z* 511.5 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3228.

*4.2.21. (4S,5R)-4-((R)-2-Hydroxy-propyl)-5-vinyl-[1,3]dioxolan-2-one (**29**).* The same procedure described above for conversion of **22** to **23** was employed. Yield: 75%.

Data for **29** (a colorless oil): $[\alpha]_D^{25}$ −59.9 (*c* 1.10, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (ddd, *J*=16.8, 10.4, 6.9 Hz, 1H), 5.51−5.42 (m, 2H), 5.14 (t, *J*=7.5 Hz, 1H), 5.05 (m, 1H), 4.01 (m, 1H), 2.22 (br s, 1OH), 1.76−1.50 (m, 2H), 1.24 (d, *J*=6.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 129.5, 121.3, 79.9, 77.1, 63.9, 38.7, 24.3; FT-IR (film) 3467, 2970, 2929, 1794, 1370, 1185, 1092, 1042, 942, 859, 775 cm^{-1}. ESIMS *m*/*z* 195.1 ([M+Na]$^+$). ESI-HRMS calcd for $C_8H_{12}NaO_4$ ([M+Na]$^+$) 195.0628, found 195.0630.

*4.2.22. (1S,3R)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-pent-4-en-3-ol (**30**).* *n*-BuLi (1.6 M, in hexanes, 18.0 mL, 28.80 mmol) was added to a solution of Me_3SI (6.072 g, 29.75 mmol) in dry THF (52 mL) stirred at −10 °C under N_2 (balloon). The mixture was stirred at the same temperature for 1 h before a solution of epoxide **4** (1.500 g, 4.96 mmol) in dry THF (2.6 mL) was added. The cooling bath was allowed to warm to ambient temperature naturally and the stirring was continued at that temperature for another hour. Aqueous saturated NH_4Cl (20 mL) was added, followed by CH_2Cl_2 (300 mL). Phases were separated. The organic layer was washed with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:10 EtOAc/PE) on silica gel afforded the allyl alcohol **30** as a colorless oil (1.299 g, 4.10 mmol, 83%). $[\alpha]_D^{27}$ +13.3 (*c* 3.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=16.9, 10.2, 5.5 Hz, 1H), 5.25 (dq, *J*=17.3, 1.5 Hz, 1H), 5.09 (dq, *J*=10.2, 1.6 Hz, 1H), 4.38 (m, 1H), 4.12−4.03 (m, 2H), 3.85 (m, 1H), 3.79 (m, 1H), 1.87−1.73 (m, 2H), 1.40 (s, 3H), 1.34 (s, 3H), 0.87 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.9, 114.0, 109.3, 78.6, 70.9, 69.1, 67.3, 42.5, 26.5, 25.7, 25.3, 17.9, −4.2,

−4.6; FT-IR (film) 3464, 2986, 2930, 2858, 1381, 1256, 1074, 837, 776 cm^{-1}. ESIMS *m/z* 339.2 ($[M+Na]^+$). ESI-HRMS calcd for $C_{16}H_{32}NaO_4Si$ ($[M+Na]^+$) 339.1962, found 339.1967.

*4.2.23. (1S,3R)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-triisopropylsilyloxy-pent-4-ene (**31**).* A mixture of alcohol **30** (1.234 g, 3.90 mmol), imidazole (0.664 g, 9.75 mmol), and *i*-Pr_3SiCl (1.0 mL, 4.68 mmol) in dry DMF (2.5 mL) was stirred at ambient temperature for 24 h. Water (10 mL) was added, followed by Et_2O (300 mL). The phases were separated. The organic layer was washed in turn with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:80 EtOAc/PE) on silica gel gave the silyl ether **31** as a colorless oil (1.223 g, 2.59 mmol, 66%). $[\alpha]_D^{26}$ +2.3 (*c* 1.15, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J*=17.1, 10.2, 6.6 Hz, 1H), 5.20 (dt, *J*=17.5, 1.3 Hz, 1H), 5.09 (dt, *J*=10.5, 1.1 Hz, 1H), 4.43 (q, *J*=6.2 Hz, 1H), 4.13 (m, 1H), 3.95 (m, 1H), 3.89 (m, 1H), 3.80 (q, *J*=7.5 Hz, 1H), 1.84 (m, 1H), 1.64 (m, 1H), 1.40 (s, 3H), 1.32 (s, 3H), 1.06 ('s', 21H), 0.88 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 114.5, 108.8, 78.9, 71.1, 69.1, 65.5, 43.7, 26.5, 25.9, 25.3, 18.14, 18.09, 12.4, −4.1, −4.2; FT-IR (film) 2943, 2867, 1463, 1380, 1255, 1214, 1075, 1014, 923, 837, 775, 679 cm^{-1}. ESIMS *m/z* 495.6 ($[M+Na]^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_4Si_2$ ($[M+Na]^+$) 495.3296, found 495.3312.

*4.2.24. (2R,3S,5R)-3-tert-Butyldimethylsilyloxy-5-triisopropylsilyloxy-hept-6-en-1,2-diol (**32**).* A mixture of acetonide **31** (1.000 g, 2.11 mmol) and aqueous F_3CCO_2H (50% v/v, 3.0 mL) in CH_2Cl_2 (70 mL) was stirred at ambient temperature for 1 h. The mixture was diluted with CH_2Cl_2 (300 mL), washed with aqueous saturated $NaHCO_3$ (until the aqueous layer became slightly basic), water, and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:3 EtOAc/PE) on silica gel gave diol **32** as a colorless viscous oil (0.728 g, 1.68 mmol, 80%). $[\alpha]_D^{28}$ +7.7 (*c* 1.55, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=17.4, 10.3, 6.8 Hz, 1H), 5.18 (dq, *J*=17.2, 1.4 Hz, 1H), 5.12 (dq, *J*=10.6, 1.6 Hz, 1H), 4.49 (q, *J*=5.7 Hz, 1H), 3.86 (m, 1H), 3.71−3.63 (m, 3H), 1.95 (ddd, *J*=14.5, 5.7, 4.9 Hz, 1H), 1.77 (ddd, *J*=14.5, 7.1, 4.8 Hz, 1H), 1.06 ('s', 21H), 0.88 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.4, 115.0, 74.2, 71.6, 71.2, 63.6, 43.6, 25.8, 18.04, 17.99, 17.89, 12.3, −4.5, −4.7; FT-IR (film) 3427, 2946, 2866, 1463, 1254, 1085, 923, 836, 674 cm^{-1}. ESIMS *m/z* 455.5 ($[M+Na]^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_4Si_2$ ($[M+Na]^+$) 455.2983, found 455.2988.

*4.2.25. (2S,3S,5R)-3-tert-Butyldimethylsilyloxy-5-triisoprpopylsilyloxy-hept-6-en-2-ol (**34**) and (2R,3S,5R)-3-tert-butyldimethylsilyloxy-5-triisoprpopylsilyloxy-hept-6-en-2-ol (**35**).* A mixture of $NaIO_4$ (0.775 g, 3.62 mmol) and water (5 mL) was stirred at ambient temperature while silica gel (300−400 mesh, 7.762 g) and CH_2Cl_2 (25 mL) were added slowly. The mixture was stirred at the same temperature for 1 h. A solution of diol **32** (0.697 g, 1.61 mmol) in CH_2Cl_2 (4 mL) was added dropwise to the above prepared mixture. Stirring was continued for another hour at ambient temperature. Solids were filtered off through Celite (washing with CH_2Cl_2). The filtrate/washings were washed with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation left the crude intermediate aldehyde **33** as a colorless oil (0.569 g, 1.42 mmol, 88%), on which the following data were obtained: ^1H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J*=1.6 Hz, 1H), 5.83 (ddd, *J*=17.5, 10.2, 7.5 Hz, 1H), 5.17 (dt, *J*=17.0, 1.5 Hz, 1H), 5.11 (d, *J*=10.3 Hz, 1H), 4.47 (q, *J*=6.5 Hz, 1H), 4.06 (q, *J*=6.1 Hz, 1H), 1.95 (ddd, *J*=13.7, 7.4, 6.0 Hz, 1H), 1.81 (ddd, *J*=13.7, 7.0, 5.0 Hz, 1H), 1.05 ('s', 21H), 0.92 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H).

The above obtained crude aldehyde **33** (0.569 g, 1.42 mmol) was dissolved in dry THF (14 mL) and stirred at −78 °C under N_2 (balloon). $H_2C{=}CHMgBr$ (3.0 M, in Et_2O, 1.4 mL, 4.20 mmol) was added slowly via a syringe. The mixture was then stirred at the same temperature for 2 h. Aqueous saturated NH_4Cl was added, followed by Et_2O (300 mL). The phases were separated. The organic layer was washed in turn with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:50 Et_2O/PE) on silica gel gave allyl alcohols **34** (the more polar component, 198 mg, 0.49 mmol, 17% from aldehyde **33** or 15% from diol **32**), and **35** (the less polar component, 187 mg, 0.464 mmol, 33% from aldehyde **33** or 29% from diol **32**) as colorless oils.

Data for **34** (the more polar isomer, a colorless oil): $[\alpha]_D^{26}$ +5.3 (*c* 1.30, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, *J*=17.2, 10.2, 6.8 Hz, 1H), 5.17 (d, *J*=17.5 Hz, 1H), 5.08 (d, *J*=10.3 Hz, 1H), 4.39 (q, *J*=6.0 Hz, 1H), 3.77 (s, 1H), 3.73 (m, 1H), 2.33 (br s, 1OH), 1.88 (ddd, *J*=13.9, 7.6, 5.5 Hz, 1H), 1.70 (ddd, *J*=13.8, 6.9, 5.1 Hz, 1H), 1.16 (d, *J*=6.2 Hz, 3H), 1.06 ('s', 21H), 0.90 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 114.5, 72.7, 71.7, 68.9, 42.0, 25.9, 19.5, 18.13, 18.08, 18.0, 12.5, −4.2, −4.6; FT-IR (film) 3460, 2945, 2866, 1463, 1388, 1255, 1092, 1062, 922, 882, 836, 775, 678 cm^{-1}. ESIMS *m/z* 439.5 ($[M+Na]^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ($[M+Na]^+$) 439.3034, found 439.3045.

Data for **35** (the less polar isomer, a colorless oil): $[\alpha]_D^{26}$ −13.3 (*c* 1.15, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J*=17.1, 10.4, 7.2 Hz, 1H), 5.18 (dt, *J*=17.1, 1.3 Hz, 1H), 5.11 (dt, *J*=10.4, 1.0 Hz, 1H), 4.41 (m, 1H), 3.77 (m, 1H), 3.61 (dq, *J*=7.3, 4.5 Hz, 1H), 2.68 (br s, 1H, OH), 1.91 (ddd, *J*=14.3, 7.5, 4.9 Hz, 1H), 1.64 (ddd, *J*=13.9, 7.6, 4.9 Hz, 1H), 1.11 (d, *J*=6.5 Hz, 3H), 1.06 ('s', 21H), 0.90 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 114.7, 73.5, 71.5, 70.7, 41.1, 25.8, 18.1, 18.04, 18.01, 17.8, 12.4, −4.3, −4.4; FT-IR (film) 3449, 2945, 2867, 1464, 1388, 1254, 1088, 1062, 923, 836, 776, 679 cm^{-1}. ESIMS *m/z* 439.5 ($[M+Na]^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ($[M+Na]^+$) 439.3034, found 439.3047.

*4.2.26. (2S,3S,5R)-Hept-6-en-2,3,5-triol (**36**).* A solution of *n*-Bu_4NF (1.0 M, in THF, 0.4 mL, 0.40 mmol) was added to a solution of alcohol **34** (0.068 g, 0.16 mmol) in THF (0.7 mL). The mixture was stirred at ambient temperature for 5 h before being concentrated on a rotary evaporator and chromatography (1:15 MeOH/CH_2Cl_2) on silica gel to give triol **36** as a colorless oil (0.024 g, 0.16 mmol, 100%). $[\alpha]_D^{28}$ −1.0 (*c* 0.76, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J*=17.0, 10.4, 6.1 Hz, 1H), 5.25 (d, *J*=17.2 Hz, 1H), 5.10 (d, *J*=10.3 Hz, 1H), 4.38 (m, 1H), 3.60−3.59 (br s, 3H, OH), 1.68−1.60 (m, 2H), 1.17 (d, *J*=5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 114.8, 75.8, 72.7, 70.8, 39.3, 19.2; FT-IR (film) 3410, 2976, 2918, 1645, 1425, 1376, 1310, 1198, 1128, 1061, 1021, 993, 926, 897, 825, 811, 682 cm^{-1}. ESIMS *m/z* 169.0 ($[M+Na]^+$). ESI-HRMS calcd for $C_7H_{14}NaO_3$ ($[M+Na]^+$) 169.0835, found 169.0835.

*4.2.27. (2R,3S,5R)-Hept-6-en-2,3,5-triol (**37**).* The same procedure described above for conversion of **34** to **36** was employed. Yield: 100%.

Data for **37** (a colorless oil): $[\alpha]_D^{27}$ −3.2 (*c* 0.76, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J*=17, 10.2, 5.8 Hz, 1H), 5.25 (d, *J*=17 Hz, 1H), 5.10 (d, *J*=10.2 Hz, 1H), 4.35 (q, *J*=6.4 Hz, 1H), 3.83−3.75 (m, 2H), 3.51 (br s, 3H, OH), 1.65−1.61 (m, 2H), 1.13 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 114.7, 75.1, 72.9, 70.2, 37.0, 17.2; FT-IR (film) 3375, 2978, 2919, 1641, 1425, 1309, 1195, 1064, 1017, 992, 927, 895, 846, 811 cm^{-1}. ESIMS *m/z* 169.0 ($[M+Na]^+$). ESI-HRMS calcd for $C_7H_{14}NaO_3$ ($[M+Na]^+$) 169.0835, found 169.0835.

*4.2.28. (1S,3S)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-pent-4-en-3-ol (**38**).* The same procedure described above for conversion of **4** to **30** was employed. Yield: 79%.

Data for **38** (a colorless oil): $[\alpha]_D^{26}$ +10.4 (*c* 3.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (ddd, *J*=17.2, 10.7, 5.7 Hz, 1H), 5.25 (dt, *J*=17.2, 1.4 Hz, 1H), 5.07 (dt, *J*=10.6, 1.4 Hz, 1H), 4.36 (m, 1H),

4.10–4.03 (m, 2H), 3.89 (m, 1H), 3.79 (m, 1H), 1.80–1.67 (m, 2H), 1.39 (s, 3H), 1.33 (s, 3H), 1.33 (s, 3H), 0.88 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.0, 113.98, 109.3, 78.1, 71.9, 69.5, 67.1, 41.7, 26.6, 25.7, 25.3, 17.9, −4.3, −4.6; FT-IR (film) 3474, 2985, 2955, 2858, 1473, 1380, 1256, 1215, 1073, 838, 777, 673 cm^{-1}. ESIMS *m/z* 339.2 ([M+Na]$^+$). ESI-HRMS calcd for $C_{16}H_{32}NaO_4Si_1$ ([M+Na]$^+$) 339.1962, found 339.1967.

*4.2.29. (1S,3S)-1-tert-Butyldimethylsilyloxy-1-((4R)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-triisopropylsilyloxy-pent-4-ene (**39**).* The same procedure described above for conversion of **30** to **31** was employed. Yield: 73%.

Data for **39** (a colorless oil): $[\alpha]_D^{29}$ +32.4 (*c* 1.45, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (ddd, *J*=17.3, 10.3, 7.2 Hz, 1H), 5.17–5.07 (m, 2H), 4.42 (m, 1H), 4.08–3.98 (m, 2H), 3.80–3.70 (m, 2H), 1.87 (ddd, *J*=13.8, 8.4, 5.1 Hz, 1H), 1.67 (ddd, *J*=18.4, 8.8, 4.3 Hz, 1H), 1.38 (s, 3H), 1.33 (s, 3H), 1.05 ('s', 21H), 0.86 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 114.9, 109.1, 79.6, 71.4, 70.0, 66.8, 45.5, 26.5, 25.8, 25.4, 18.11, 18.08, 18.0, 12.4, −4.1, −4.3; FT-IR (film) 2930, 2866, 1463, 1369, 1379, 1255, 1075, 995, 922, 837, 775, 677 cm^{-1}; ESIMS *m/z* 495.5 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_4Si_2$ ([M+Na]$^+$) 495.3296, found 495.3295.

*4.2.30. (2R,3S,5S)-3-tert-Butyldimethylsilyloxy-5-triisopropylsilyloxy-hept-6-en-1,2-diol (**40**).* The same procedure described above for conversion of **31** to **32** was employed. Yield: 96%.

Data for **40** (a colorless oil): $[\alpha]_D^{27}$ +16.2 (*c* 1.70, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=17, 10, 7.6 Hz, 1H), 5.14 (d, *J*=17 Hz, 1H), 5.08 (d, *J*=10 Hz, 1H), 4.29 (q, *J*=6.6 Hz, 1H), 3.91 (m, 1H), 3.78 (dd, *J*=11.5, 5.2 Hz, 1H), 3.70 (dd, *J*=11.4, 3.4 Hz, 1H), 3.64 (q, *J*=4.4 Hz, 1H), 1.91 (ddd, *J*=14.3, 7.4, 6.5 Hz, 1H), 1.80 (ddd, *J*=14.2, 6.4, 4.3 Hz, 1H), 1.05 ('s', 21H), 0.88 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.2, 115.1, 73.2, 72.7, 72.6, 63.2, 43.5, 25.8, 18.1, 18.0, 17.9, 12.5, −4.4, −4.8; FT-IR (film) 3422, 2946, 2866, 1463, 1254, 1086, 922, 882, 836, 776, 680 cm^{-1}. ESIMS *m/z* 455.5 ([M+Na]$^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_4Si_2$ ([M+Na]$^+$) 455.2983, found 455.2989.

*4.2.31. (2S,3S,5S)-3-tert-Butyldimethylsilyloxy-5-triisoprpopylsilyloxy-hept-6-en-2-ol (**42**) and (2R,3S,5S)-3-tert-butyldimethylsilyloxy-5-triisoprpopylsilyloxy-hept-6-en-2-ol (**43**).* The same procedure described above for conversion of **32** to **33** was employed for oxidative cleavage of diol **40** to aldehyde **41**. Yield: 89% (crude), and the same procedure described above for conversion of **33** to **34** and **35** was employed for generation of alcohol **42** (the less polar isomer, a colorless oil, 26% from the crude aldehyde **41** or 23% from the diol **40**) and **43** (the more polar isomer, a colorless oil, 40% from the crude aldehyde **41** or 36% from the diol **40**).

Diagnostic data for crude aldehyde **41**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (d, *J*=1.4 Hz, 1H), 5.82 (ddd, *J*=17.1, 10.4, 8.0 Hz, 1H), 5.16 (d, *J*=16.9 Hz, 1H), 5.08 (d, *J*=10.4 Hz, 1H), 4.43 (m, 1H), 4.11 (m, 1H), 2.08 (ddd, *J*=13.7, 7.2, 5.4 Hz, 1H), 1.92 (ddd, *J*=14.1, 7.5, 4.5 Hz, 1H), 1.04 ('s', 21H), 0.92 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

Data for **42** (the less polar isomer, a colorless oil): $[\alpha]_D^{26}$ +26.4 (*c* 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd, *J*=17.3, 10.4, 7.6 Hz, 1H), 5.12–5.06 (m, 2H), 4.25 (q, *J*=7.9 Hz, 1H), 3.68 (m, 1H), 3.54 (m, 1H), 2.10 (ddd, *J*=13.6, 8.9, 5.7 Hz, 1H), 1.57 (ddd, *J*=13.6, 8.3, 4.0 Hz, 1H), 1.13 (d, *J*=6.3 Hz, 3H), 1.05 ('s', 21H), 0.90 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 114.7, 73.2, 72.2, 68.7, 42.7, 25.9, 20.4, 18.10, 18.08, 12.5, −4.1, −4.6; FT-IR (film) 2962, 2928, 2866, 1463, 1381, 1058, 1017, 922, 882, 836, 775, 674 cm^{-1}. ESIMS *m/z* 439.5 ([M+Na]$^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ([M+Na]$^+$) 439.3034, found 439.3048.

Data for **43** (the more polar isomer, a colorless oil): $[\alpha]_D^{26}$ +10.4 (*c* 1.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=17.5, 9.9, 7.3 Hz, 1H), 5.14 (d, *J*=17.1 Hz, 1H), 5.07 (d, *J*=10.2 Hz, 1H), 4.27 (q, *J*=6.6 Hz, 1H), 3.79–3.75 (m, 2H), 1.83 (m, 1H), 1.67 (m, 1H), 1.14 (d, *J*=6.4 Hz, 3H), 1.06 ('s', 21H), 0.91 (s, 9H), 0.094 (s, 3H), 0.086 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 114.7, 73.6, 72.4, 70.3, 42.2, 25.8, 18.15, 18.12, 18.0, 17.3, 12.6, −4.3, −4.5; FT-IR (film) 3473, 2946, 2867, 1463, 1421, 1388, 1255, 1086, 922, 837, 776, 678 cm^{-1}. ESIMS *m/z* 439.5 ([M+Na]$^+$). ESI-HRMS calcd for $C_{22}H_{48}NaO_3Si_2$ ([M+Na]$^+$) 439.3034, found 439.3053.

*4.2.32. (2S,3S,5S)-Hept-6-en-2,3,5-triol (**44**).* The same procedure described above for conversion of **34** to **36** was employed. Yield: 100%.

Data for **44** (a white solid): mp 68–69 °C. $[\alpha]_D^{28}$ −16.4 (*c* 0.76, MeOH). ^{1}H NMR (400 MHz, CD_3OD) δ 5.92 (ddd, *J*=17.5, 10.7, 5.5 Hz, 1H), 5.24 (dt, *J*=17.4, 1.4 Hz, 1H), 5.06 (dt, *J*=10.7, 1.6 Hz, 1H), 4.33 (m, 1H), 3.67–3.56 (m, 2H), 1.60–1.56 (m, 2H), 1.15 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 143.2, 113.8, 73.0, 71.7, 70.3, 41.0, 19.0; FT-IR (film) 3379, 2924, 1641, 1456, 1417, 1282, 1126, 1054, 997, 921, 818 cm^{-1}. ESIMS *m/z* 169.1 ([M+Na]$^+$). ESI-HRMS calcd for $C_7H_{14}NaO_3$ ([M+Na]$^+$) 169.0835, found 169.0843.

*4.2.33. (2S,3S,5S)-Hept-6-en-2,3,5-triol (**44**).* The same procedure described above for conversion of **34** to **36** was employed. Yield: 100%.

Data for **45** (a colorless oil): $[\alpha]_D^{26}$ −7.3 (*c* 0.76, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (ddd, *J*=16.9, 10.5, 5.6 Hz, 1H), 5.30 (d, *J*=16.9 Hz, 1H), 5.15 (d, *J*=10.6 Hz, 1H), 4.48 (s, 1H), 3.90 (d, *J*=10.2 Hz, 1H), 3.79 (m, 1H), 2.84 (br s, 3H, OH), 1.76 (m, 1H), 1.56 (m, 1H), 1.15 (d, *J*=6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 114.5, 71.8, 70.5, 70.2, 37.0, 17.2; FT-IR (film) 3363, 2924, 2853, 1644, 1461, 1282, 1125, 1046, 996, 921 cm^{-1}. ESIMS *m/z* 169.1 ([M+Na]$^+$). ESI-HRMS calcd for $C_7H_{14}NaO_3$ ([M+Na]$^+$) 169.0835, found 169.0836.

*4.2.34. (3R,5S,6S)-3-Triisoprpopylsilyloxy-5-tert-butyldimethylsilyloxy-6-ethoxycarbonyloxy-hept-1-en (**46**).* Pyridine (0.27 mL, 3.33 mmol), DMAP (0.003 g, 0.02 mmol), and ethyl chloroformate (0.23 mL, 2.41 mmol) were added in turn to a solution of alcohol **34** (0.090 g, 0.216 mmol) in dry CH_2Cl_2 (2 mL) stirred at ambient temperature. Stirring was continued at the same temperature for 5 h before the mixture was partitioned between water (5 mL) and Et_2O (200 mL). The organic layer was washed with aqueous saturated $NaHCO_3$, water and brine, and dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:50 EtOAc/PE) on silica gel afforded the carbonate **46** as a colorless oil (0.079 g, 0.162 mmol, 75%). $[\alpha]_D^{28}$ −27.7 (*c* 2.05, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddd, *J*=17.3, 10.2, 7.1 Hz, 1H), 5.15 (dt, *J*=17.0, 1.2 Hz, 1H), 5.07 (dd, *J*=10.4, 1.2 Hz, 1H), 4.72 (m, 1H), 4.36 (m, 1H), 4.15 (q, *J*=7.0 Hz, 2H), 3.77 (m, 1H), 1.78 (ddd, *J*=13.5, 8.7, 4.8 Hz, 1H), 1.66 (ddd, *J*=13.5, 9.0, 3.0 Hz, 1H), 1.28 (t, *J*=7.2 Hz, 3H), 1.22 (d, *J*=6.6 Hz, 3H), 1.04 ('s', 21H), 0.88 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 141.3, 114.8, 76.0, 71.2, 69.6, 63.7, 40.4, 25.8, 18.1, 18.05, 17.97, 14.3, 14.0, 12.4, −4.4, −4.5; FT-IR (film) 2945, 2866, 1746, 1464, 1371, 1264, 1089, 1051, 922, 836, 776, 678 cm^{-1}. ESIMS *m/z* 511.6 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3246.

*4.2.35. (4S,5S)-4-((R)-2-Hydroxy-but-3-enyl)-5-methyl-[1,3]dioxolan-2-one (**47**).* A solution of *n*-Bu_4NF (1.0 M, in THF, 0.16 mL, 0.16 mmol) was added to a solution of **46** (0.063 g, 0.1288 mmol) in THF (12 mL) stirred at ambient temperature. Stirring was continued at the same temperature for 5 h. Water (5 mL) was added, followed by Et_2O (200 mL). The phases were separated. The organic layer was washed with water and brine before being dried over anhydrous $MgSO_4$. Removal of the solvent by rotary evaporation and column chromatography (1:1 EtOAc/PE) on silica gel afforded the cyclic carbonate **47** as a colorless oil (0.019g, 0.1103 mmol, 86%). $[\alpha]_D^{25}$ −56.9 (*c* 0.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87 (ddd, *J*=17.3, 10.5, 6.4 Hz, 1H), 5.31 (d, *J*=17.0 Hz, 1H), 5.21 (d, *J*=10.6 Hz, 1H), 4.56

(m, 1H), 4.36 (q, *J*=6.4 Hz, 2H), 2.05 (m, 1H), 1.93–1.87 (m, 2H), 1.46 (d, *J*=6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.2, 116.5, 80.7, 78.6, 69.5, 39.4, 18.8; FT-IR (film) 3482, 2984, 2926, 1794, 1644, 1555, 1380, 1189, 1070, 930, 777, 700 cm^{-1}. ESIMS *m*/*z* 195.1 ([M+Na]$^+$). ESI-HRMS calcd for $C_8H_{12}NaO_4$ ([M+Na]$^+$) 195.0628, found 195.0629.

*4.2.36. (3R,5S,6R)-3-Triisoprpopylsilyloxy-5-tert-butyldimethylsilyloxy-6-ethoxycarbonyloxy-hept-1-en (**48**).* The same procedure described above for conversion of **34** to **46** was employed. Yield: 66%.

Data for **48** (a colorless oil): $[\alpha]_D^{28}$ −5.2 (*c* 1.40, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd, *J*=17.1, 10.2, 7.1 Hz, 1H), 5.19 (d, *J*=17.0 Hz, 1H), 5.11 (d, *J*=10.6 Hz, 1H), 4.70 (qd, *J*=6.1, 1.8 Hz, 1H), 4.36 (m, 1H), 4.20–4.12 (m, 2H), 3.86 (m, 1H), 1.81 (ddd, *J*=14.0, 8.5, 4.4 Hz, 1H), 1.55 (ddd, *J*=13.9, 8.4, 4.0 Hz, 1H), 1.28 (t, *J*=7.3 Hz, 3H), 1.21 (d, *J*=6.5 Hz, 3H), 1.04 ('s', 21H), 0.89 (s, 9H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 141.0, 115.0, 77.7, 71.3, 70.6, 63.5, 42.7, 25.9, 18.2, 18.1, 18.0, 14.3 13.3, 12.3, −4.4, −4.7; FT-IR (film) 2928, 2867, 1746, 1464, 1376, 1267, 1059, 1030, 836, 776, 679 cm^{-1}. ESIMS *m*/*z* 511.6 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3243.

*4.2.37. (4S,5R)-4-((R)-2-Hydroxy-but-3-enyl)-5-methyl-[1,3]dioxolan-2-one (**49**).* The same procedure described above for conversion of **46** to **47** was employed. Yield: 73%.

Data for **49** (a colorless oil): $[\alpha]_D^{25}$ −45.4 (*c* 0.55, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J*=17.4, 10.2, 6.6 Hz, 1H), 5.32 (d, *J*=17.1 Hz, 1H), 5.23 (d, *J*=10.5 Hz, 1H), 4.85 (m, 1H), 4.76 (m, 1H), 4.35 (q, *J*=6.7 Hz, 1H), 2.05 (ddd, *J*=14.2, 9.6, 5.3 Hz, 1H), 1.94 (br s, 1H, OH), 1.80 (ddd, *J*=14.1, 7.3, 4.2 Hz, 1H), 1.37 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 139.0, 117.1, 76.94, 76.0, 70.3, 35.4, 14.8; FT-IR (film) 3449, 2985, 2925, 1794, 1426, 1375, 1189, 1070, 929, 779, 692 cm^{-1}. ESIMS *m*/*z* 195.1 ([M+Na]$^+$). ESI-HRMS calcd for $C_8H_{12}NaO_4$ ([M+Na]$^+$) 195.0628, found 195.0630.

*4.2.38. (3S,5S,6S)-3-Triisoprpopylsilyloxy-5-tert-butyldimethylsilyloxy-6-ethoxycarbonyloxy-hept-1-en (**50**).* The same procedure described above for conversion of **34** to **46** was employed. Yield: 87%.

Data for **50** (a colorless oil): $[\alpha]_D^{28}$ −2.7 (*c* 1.05, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (ddd, *J*=17.2, 10.4, 7.6 Hz, 1H), 5.14 (d, *J*=17.5 Hz, 1H), 5.06 (d, *J*=10.3 Hz, 1H), 4.74 (m, 1H), 4.30 (q, *J*=6.9 Hz, 1H), 4.20–4.12 (m, 2H), 3.89 (q, *J*=5.7 Hz, 1H), 1.94 (m, 1H), 1.54 (m, 1H), 1.30 (t, *J*=7.4 Hz, 3H), 1.23 (d, *J*=6.5 Hz, 3H), 1.04 ('s', 21H), 0.89 (s, 9H), 0.10 (major conformer) and 0.07 (minor conformer) (two singlets, 6H altogether); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 141.9, 114.8, 75.9, 71.8, 69.8, 63.7, 41.7, 25.8, 18.1, 18.0, 14.3, 14.2, 12.6, −4.48, −4.52; FT-IR (film) 2930, 2866, 1746, 1464, 1371, 1263, 835, 776, 675 cm^{-1}. ESIMS *m*/*z* 511.6 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3262.

*4.2.39. (4S,5S)-4-((S)-2-Hydroxy-but-3-enyl)-5-methyl-[1,3]dioxolan-2-one (**51**).* The same procedure described above for conversion of **46** to **47** was employed. Yield: 67%.

Data for **51** (a colorless oil): $[\alpha]_D^{27}$ −80.6 (*c* 0.35, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (ddd, *J*=17.1, 10.7, 6.1 Hz, 1H), 5.30 (dt, *J*=17.2, 1.0 Hz, 1H), 5.18 (dt, *J*=10.5, 1.1 Hz, 1H), 4.51 (m, 1H), 4.45 (m, 1H), 4.38 (m, 1H), 1.93 (m, 1H), 1.82–1.75 (m, 2H), 1.48 (d, *J*=5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.9, 115.6, 80.5, 78.8, 69.0, 40.3, 18.8; FT-IR (film) 3470, 3073, 2924, 2853, 1974, 1459, 1376, 1181, 1044, 919, 770 cm^{-1}. ESIMS *m*/*z* 195.1 ([M+Na]$^+$). ESI-HRMS calcd for $C_8H_{12}NaO_4$ ([M+Na]$^+$) 195.0628, found 195.0632.

*4.2.40. (3S,5S,6R)-3-Triisoprpopylsilyloxy-5-tert-butyldimethylsilyloxy-6-ethoxycarbonyloxy-hept-1-en (**52**).* The same procedure described above for conversion of **34** to **46** was employed. Yield: 82%.

Data for **52** (a colorless oil): $[\alpha]_D^{27}$ +23.2 (*c* 0.80, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddd, *J*=17, 10, 7.6 Hz, 1H), 5.20 (d, *J*=17 Hz, 1H), 5.09 (d, *J*=10 Hz, 1H), 4.72 (qd, *J*=6.4, 2.4 Hz, 1H), 4.25 (q, *J*=7.4 Hz, 1H), 4.21–4.13 (m, 2H), 3.91 (m, 1H), 1.79 (ddd, *J*=14.0, 7.4, 4.0 Hz, 1H), 1.61 (ddd, *J*=14.0, 7.2, 5.1 Hz, 1H), 1.29 (t, *J*=7.3 Hz, 3H), 1.23 (d, *J*=6.6 Hz, 3H), 1.05 ('s', 21H), 0.89 (s, 9H), 0.07, 0.06 and 0.04 (three singlets, 9H altogether); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 14.5, 115.0, 77.2, 71.7, 70.6, 63.5, 43.8, 25.9, 18.12, 18.11, 14.3, 13.3, 12.5, −4.6, −4.7; FT-IR (film) 2927, 2857, 1745, 1463, 1371, 1266, 1089, 1059, 836, 777, 674 cm^{-1}. ESIMS *m*/*z* 511.6 ([M+Na]$^+$). ESI-HRMS calcd for $C_{25}H_{52}NaO_5Si_2$ ([M+Na]$^+$) 511.3246, found 511.3257.

*4.2.41. (4S,5R)-4-((S)-2-Hydroxy-but-3-enyl)-5-methyl-[1,3]dioxolan-2-one (**53**).* The same procedure described above for conversion of **48** to **49** was employed. Yield: 83%.

Data for **53** (a colorless oil): $[\alpha]_D^{27}$ −43.9 (*c* 0.50, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (ddd, *J*=17.4, 10.5, 6.0 Hz, 1H), 5.31 (d, *J*=16.9 Hz, 1H), 5.17 (d, *J*=10.3 Hz, 1H), 5.01 (m, 1H), 4.88 (m, 1H), 4.38 (m, 1H), 1.88 (m, 1H), 1.85 (br s, 1H, OH), 1.67 (m, 1H), 1.36 (d, *J*=6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.1, 115.5, 76.6, 76.0, 68.9, 35.8, 14.8; FT-IR (film) 3446, 2923, 2853, 1785, 1457, 1425, 1374, 1320, 1185,1143, 1057, 993, 922, 777, 693 cm^{-1}. ESIMS *m*/*z* 195.0 ([M+Na]$^+$). ESI-HRMS calcd for $C_8H_{12}NaO_4$ ([M+Na]$^+$) 195.0628, found 195.0631.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.01.091.

References and notes

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10. Although 1:2 $CD_3OD/CDCl_3$ was mentioned to be the solvent for ^{1}H NMR in the literature (Ref. 1 above), the copies of the original spectra unambiguously showed absence of any CD_3OD. Hence, besides the initial spectra recorded in 1:2 $CD_3OD/CDCl_3$ (none of them was compatible with the data given in Ref. 1) later we also acquired ^{1}H NMR for 11, 12, 20, 36, 37, and 45 in $CDCl_3$. The ^{13}C NMR of the two natural products as confirmed by the copies of the spectra. However, for more general use, apart from the data listed in the tables (recorded in 1:2 $CD_3OD/CDCl_3$), we also measured the ^{13}C NMR of 11, 12, 20, 36, 37, and 45 in $CDCl_3$. We thank Professor Liu and Dr. Wang (the authors of Ref. 1) for the copies of the ^{1}H and ^{13}C NMR of the two natural products.