Stereodivergent and Reiterative Synthesis of Bistetrahydrofuran Ring Cores of Annonaceous Acetogenins

Naoto Kojima, Naoyoshi Maezaki,* Hiroaki Tominaga, Minori Yanai, Daisuke Urabe, and Tetsuaki Tanaka*[a]

Abstract: Eight diastereoisomers of the bistetrahydrofuran ring cores of annonaceous acetogenins have been synthesized by asymmetric alkynylation of α-tetrahydrofuranic aldehydes and stereodivergent one-pot tetrahydrofuran (THF) ring formation. In all cases, the asymmetric alkynylation proceeded with very high diastereoselectivity to give eight kinds of optically pure THF cores. We also describe a comparison of the ^{1}H and ^{13}C NMR spectral data of the eight isomers and give full details of the THF ring construction.

Keywords: annonaceous acetogenins · asymmetric alkynylation · cyclization · stereodivergent synthesis · synthetic methods

Introduction

Over 350 natural polyketides called annonaceous acetogenins have been isolated from various Annonaceae plants. These compounds have attracted worldwide attention owing to their broad spectrum of biological activity such as cytotoxic, antitumor, immunosuppressive, antimalarial, and antifeedant effects (Figure 1).[1,2] Some are promising candidates for new types of antitumor drugs that possess potent inhibitory activity against NADH–ubiquinone oxidoreductase of the respiratory chain (mitochondrial complex I), which is the main gate of energy production in the cell.[3] Furthermore, some acetogenins inhibit multidrug-resistant cancer cells with an ATP-driven transporter system.[4] Most acetogenins are characterized by one to three THF ring(s) with various stereochemistries in the center of a long hydrocarbon chain containing an α,β-unsaturated γ-lactone moiety at the end. The number and stereochemistry of the THF rings affect the kind of effective tumor cell lines for growth inhibition.[1] In particular, adjacent bis-THF acetogenins have potent biological activity. Therefore, systematic synthesis of the bis-THF ring cores would be important to help establishing the structure–activity relationship of acetogenins.[5,6]

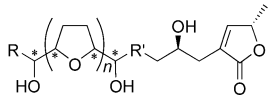

Figure 1. Representative structure of annonaceous acetogenins. $n = 1$–3, R, R' = hydrocarbon chain having oxygenated moieties and/or double bonds.

During the course of our synthetic study of annonaceous acetogenins,[7] we planned a systematic synthesis of the poly-THF ring cores based on asymmetric alkynylation of aldehydes with a 3-butyne-1,2-diol derivative by using chiral ligands. In a preliminary paper,[7b] we demonstrated a highly stereodivergent and stereoselective synthesis of the bis-THF ring cores based on the asymmetric alkynylation of (2*R*)-α-tetrahydrofuranic aldehyde with (2*S*)-3-butyne-1,2-diol derivatives. Herein, we describe the asymmetric alkynylation of (2*S*)-aldehydes with (2*S*)-alkynes, that is, the combination of a mismatched pair based on our preliminary study of the synthesis of the mono-THF ring cores.[7a] We found that the asymmetric alkynylation was perfectly controlled by the chiral ligands even in the mismatched pair. Moreover, we report full details of the systematic construction of eight isomers of the adjacent bis-THF ring cores and a comparison of their ^{1}H and ^{13}C NMR spectral data.

Results and Discussion

Our strategy for stereodivergent and reiterative synthesis of the poly-THF ring cores is summarized in Scheme 1. A key step is the asymmetric alkynylation of aldehyde **2** with a chiral C_4-unit **3**, both enantiomers of which are readily prepared from natural products in enantiomerically pure form.

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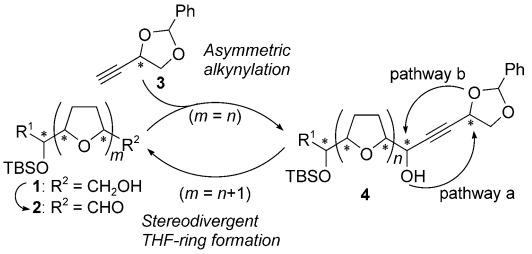
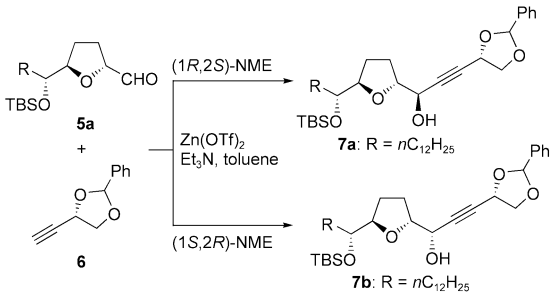
The substrate-controlled addition[8] of the 3,4-(isopropylidenedioxy)butyl anion to α-tetrahydrofuranic aldehydes has been reported by Koert and co-workers.[9] They described the combination of (2*S*,5*S*)-α-tetrahydrofuranic aldehyde with the (3*S*)-3,4-(isopropylidenedioxy)butyl anion as a mismatched pair in their substrate-controlled addition; the selectivity was lower than for the matched pair.[9b] To overcome these problems, we planned the reagent-controlled asymmetric alkynylation of α-tetrahydrofuranic aldehyde by using a chiral ligand. We expected high diastereoselectivity based on the prominent stereodifferentiating ability of Carreira's method, and also convenient stereocontrol by changing the chiral ligand.[10] Alkynylation is advantageous since the unreacted acetylide can be reused even if the reaction required excess reagent. Such reuse is impossible in the case of an organometallic reagent generated by halogen–metal exchange reaction. Another key step is the stereodivergent THF-ring formation, by which four kinds of THF ring cores can be synthesized from two common precursors by changing the protocol of the THF ring formation (pathways a and b). Moreover, the terminal alcohol in the resulting THF ring core **1** would become a junction with the next C_4-unit **3** by oxidation to the corresponding aldehyde. Therefore, our strategy can potentially be applied to the synthesis of the poly-THF ring cores.



Scheme 1. Strategy for systematic construction of poly-THF ring cores.

We examined the asymmetric alkynylation of *trans*/*threo*-aldehyde **5a**,[7a] since this structure is frequently found in natural adjacent bis-THF acetogenins (e.g., asimicin-type and squamocin-I-type acetogenins).[1d] In the reagent-controlled asymmetric alkynylation, it is very important that the diastereoselectivity is high in all combinations of substrates and chiral ligands. In our previous study,[7a] we found that the asymmetric alkynylation of α-oxyaldehyde with the chiral C_4-unit **6** proceeds with high diastereoselectivity even for the mismatched pair. In this reaction, the substrates possess one stereogenic center. To establish a reiterative procedure, it is very important that the methodology can be applied to substrates with three stereogenic centers. Asymmetric alkynylation of aldehyde **5a** (1.0 equiv) with alkyne **6** (1.2 equiv) by using (1*R*,2*S*)-*N*-methylephedrine (NME, 1.4 equiv), $Zn(OTf)_2$ (1.3 equiv), and Et_3N (1.4 equiv) in toluene proceeded sluggishly to give only a trace amount of the adduct (Table 1, entry 1). Fortunately, the yield was dramatically improved by using excess reagents to give *threo*-adduct **7a** with high diastereoselectivity; the unreacted alkyne **6** was quantitatively recovered (entry 2).[11] Moreover, the yield reached 97% when the chiral reagent was prepared at high concentration (entry 3). The *erythro*-adduct **7b** can also be obtained in good yield with high diastereoselectivity by using the antipode of NME.

Table 1. Asymmetric alkynylation of *trans*/*threo*-aldehyde **5a**.[a]

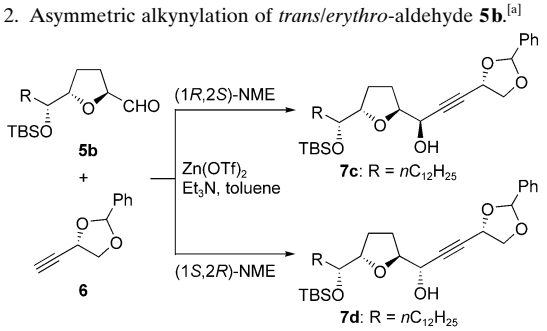


Entry	*c* [M][b]	NME	Yield [%]	**7a**:**7b**[c]
1	0.11[d]	1*R*,2*S*	trace	–
2	0.25	1*R*,2*S*	73	>97:3
3	0.45	1*R*,2*S*	97	>97:3
4	0.44	1*S*,2*R*	87	3:>97

[a] Unless otherwise noted, the reactions were carried out under the following conditions: **5a** (1.0 equiv), **6** (2.0 equiv), $Zn(OTf)_2$ (2.2 equiv), NME (2.4 equiv), Et_3N (2.4 equiv). [b] The value is the concentration of $Zn(OTf)_2$ in toluene. [c] Determined by ^1H NMR spectroscopy (500 MHz). [d] The reaction was carried out under the following conditions: **5a** (1.0 equiv), **6** (1.2 equiv), $Zn(OTf)_2$ (1.3 equiv), NME (1.4 equiv), Et_3N (1.4 equiv).

Results for the asymmetric alkynylation of *trans*/*erythro*-aldehyde **5b** with alkyne **6** are given in Table 2. Even the (2*S*,5*S*)-aldehyde **5b** underwent asymmetric alkynylation with chiral alkyne **6** to give the *erythro*-adduct **7c** in good yield and with very high diastereoselectivity by using (1*R*,2*S*)-NME as a chiral ligand (entry 1). Moreover, the *threo*-adduct **7d** was also obtained in good yield and with high diastereoselectivity (entry 2) by using the antipode of NME. Thus, the yield and selectivity of the asymmetric alkynylation were not affected by the internal chirality of the α-tetrahydrofuranic aldehyde, and the sole reaction product was produced with predictable diastereoselectivity. To our knowledge, this is the first example of perfect control in additions to α-tetrahydrofuranic aldehydes by the chiral ligands.

Table 2. Asymmetric alkynylation of *trans*/*erythro*-aldehyde **5b**.[a]



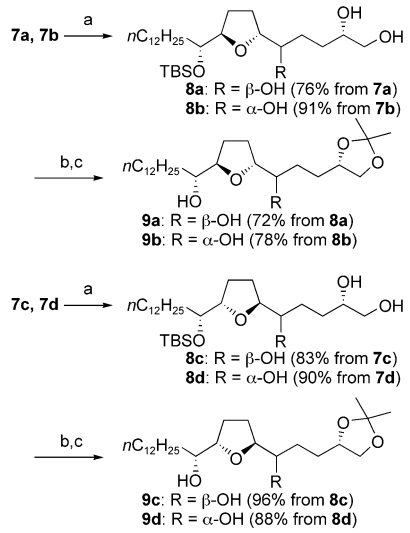
Entry	NME	Yield [%]	**7c**:**7d**[b]
1	1*R*,2*S*	91	>97:3
2	1*S*,2*R*	94	3:>97

[a] The reactions were carried out under the following conditions: **5b** (1.0 equiv), **6** (2.0 equiv), $Zn(OTf)_2$ (2.2 equiv), NME (2.4 equiv), Et_3N (2.4 equiv). [b] Determined by ^1H NMR spectroscopy (500 MHz).

The stereochemistry of the adducts **7a–d** was determined by Fujimoto's method.[12] Fujimoto and co-workers reported that the stereochemistry of the mono-THF ring moiety with two flanking hydroxyl groups could be determined by comparison of the carbon chemical shifts around the THF ring in the ^{13}C NMR spectra of their synthetic model compounds. The adducts **7a–d** were transformed into diols **9a–d** by the following sequence: 1) alkyne hydrogenation and deprotection of the benzylidene acetal; 2) acetalization of the 1,2-diol; 3) deprotection of the TBS ether (Scheme 2).

Table 3 summarizes the differences between our samples **9a–d** and Fujimoto's model compounds **10a–d**. The ^{13}C NMR spectral data around the THF ring of **9a** are consistent with those of the model compound **10a** with *threo*/*trans*/*threo*-stereochemistry. The data of **9b** and **9d** were also consistent with those of the *threo*/*trans*/*erythro*-model **10b**. The chemical shift for the *erythro*/*trans*/*erythro*-isomer **9c** not included in Fujimoto's model compounds did not match with those of any model compounds. Thus, the stereochemistry of the propargylic position of the adducts **7a–d** was confirmed.

We then examined the stereodivergent THF ring formation of the four adducts **7a–d**. The results of the stereodivergent synthesis of eight kinds of bis-THF ring cores by two kinds of one-pot THF formation are summarized in Scheme 3.



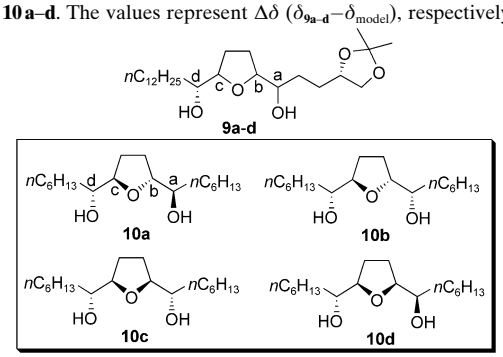
Scheme 2. Preparation of diols **9a–d** for use in the determination of THF stereochemistries. a) H_2, 10% Pd/C, EtOAc, RT; b) $Me_2C(OMe)_2$, Dowex 50W, CH_2Cl_2, RT; c) TBAF, THF, RT.

Hydrogenation of the triple bond accompanied by deprotection of the benzylidene acetal in **7a** afforded a saturated triol **8a** in 76% yield. Selective sulfonylation of the primary alcohol with 2,4,6-triisopropylbenzenesulfonyl chloride (TrisCl) gave the sulfonate **11a** in 71% yield. On treatment of **11a** with K_2CO_3 in MeOH, the THF ring formation via an epoxide **12a** proceeded smoothly in a one-pot reaction to give the *trans*/*threo*/*trans*/*threo*-bis-THF ring core **13a** in 79% yield.[13]

The *trans*/*erythro*/*trans*/*threo*-isomer **13b** was also obtained from adduct **7a**. Tosylate **15a** was obtained in two steps by selective reduction of the triple bond with Et_3N as catalyst poison[14] followed by tosylation of the secondary alcohol. Finally, one-pot reductive deacetalization and subsequent intramolecular Williamson reaction with NaH in THF led to THF rather than tetrahydropyran ring formation to give **13b**.

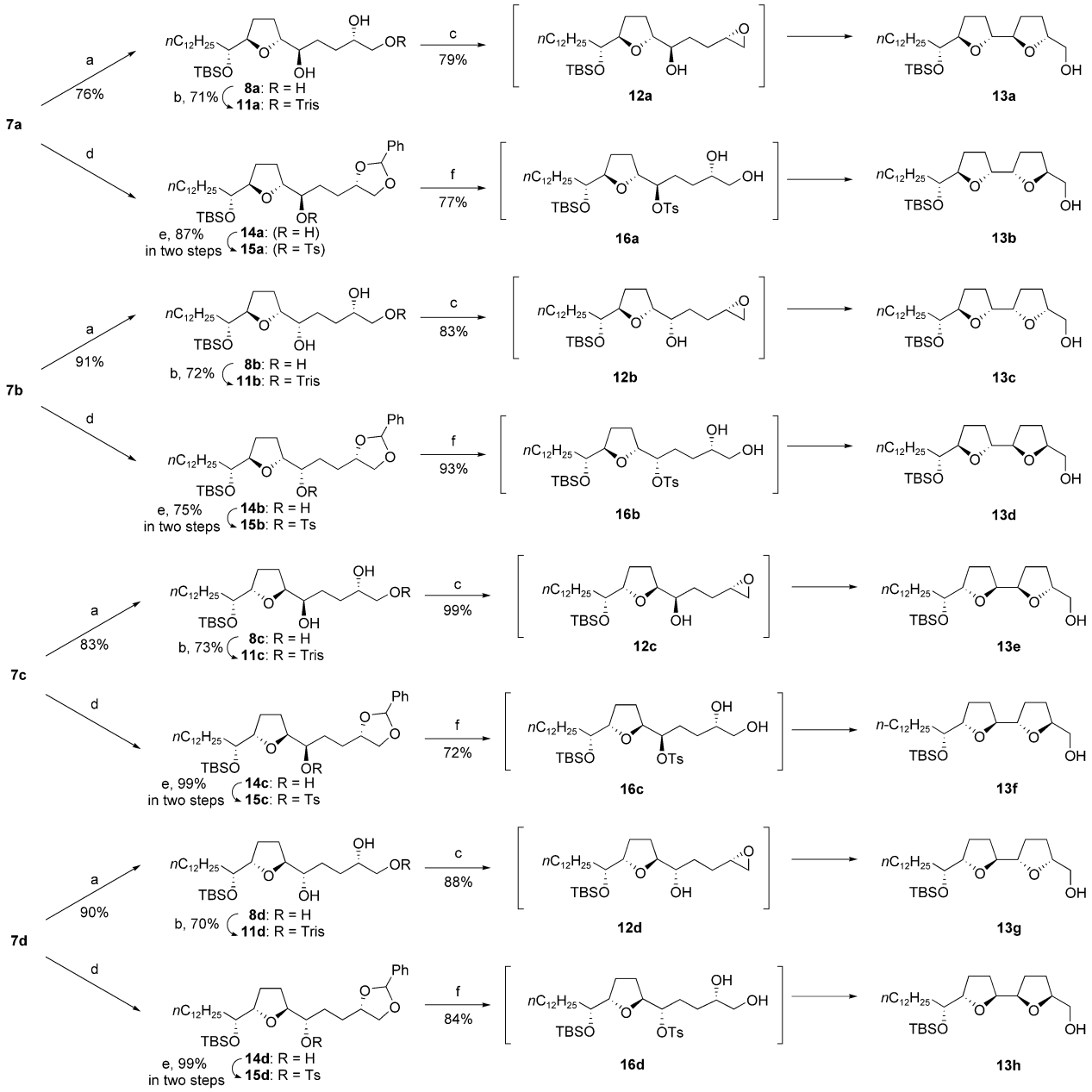
Six other isomers **13c–h** of the bis-THF ring cores were similarly synthesized from adducts **7b–d**, respectively. Thus, stereodivergent synthesis of eight kinds of bis-THF ring cores was accomplished starting from two intermediates **5a** and **5b**. Since **5a** and **5b** were synthesized by the same series of reactions (i.e., asymmetric

Table 3. Differences between the characteristic chemical shifts of the carbon atoms of **9a–d** and those of Fujimoto's model compounds **10a–d**. The values represent $\Delta\delta$ ($\delta_{\mathbf{9a-d}}-\delta_{\mathrm{model}}$), respectively.[a]



		Position			
		a	b	c	d
9a	*th*/*t*/*th*[b] (**10a**)	0	+0.1	−0.1	−0.1
	th/*t*/*er*[c] (**10b**)	−0.3	−0.5	+0.4	+2.3
	th/*c*/*th*[d] (**10c**)	−0.3	0	−0.2	−0.4
	th/*c*/*er* (**10d**)	−0.2	+0.5	−0.2	+1.8
9b	*th*/*t*/*th*	+0.3	+0.5	−0.6	−2.1
	th/*t*/*er*	0	−0.1	−0.1	+0.3
	th/*c*/*th*	0	+0.4	−0.7	−2.4
	th/*c*/*er*	+0.1	+0.9	−0.7	−0.2
9c	*th*/*t*/*th*	−2.1	+0.1	+0.3	−2.0
	th/*t*/*er*	−2.4	−0.5	+0.8	+0.4
	th/*c*/*th*	−2.4	0	+0.2	−2.3
	th/*c*/*er*	−2.3	+0.5	+0.2	−0.1
9d	*th*/*t*/*th*	0	+0.4	−0.4	−2.4
	th/*t*/*er*	−0.3	−0.2	+0.1	0
	th/*c*/*th*	−0.3	+0.3	−0.5	−2.7
	th/*c*/*er*	−0.2	+0.8	−0.5	−0.5

[a] ^{13}C NMR spectra were recorded in $CDCl_3$ solution at 75 MHz. [b] *th* = *threo*, *t* = *trans*. [c] *er* = *erythro*. [d] *c* = *cis*.

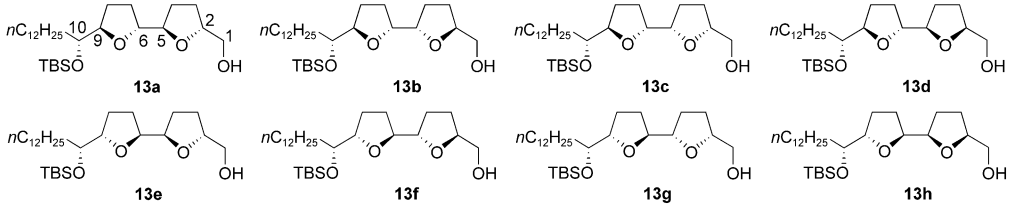


Scheme 3. Systematic synthesis of bis-THF ring cores. a) H_2, 10% Pd/C, EtOAc, RT; b) TrisCl, pyridine, CH_2Cl_2, 0°C to RT; c) K_2CO_3, MeOH, 0°C to RT; d) H_2, 10% Pd/C, Et_3N, EtOAc, RT; e) *p*TsCl, pyridine, 0°C to RT; f) H_2, 10% Pd/C, THF, RT then NaH, 0 to 40°C.

alkynylation with the C_4-unit **6** followed by the THF ring formation), reiterative synthesis of the bis-THF ring cores was accomplished.

Representative chemical shifts in the ^1H and ^{13}C NMR spectral data of **13a**–**h** are summarized in Tables 4 and 5. The difference in stereochemistry affects the chemical shifts and thereby allows differentiation of the diastereomers. One of the proton chemical shifts of the C1 position in the 2,5-*trans*-isomers and the 2,5-*cis*-isomers was about δ 3.67 and 3.76 ppm, respectively. The proton chemical shift of the C10 position in the 9,10-*threo*-isomers was more upfield than in the 9,10-*erythro*-isomers.[15] The same differences in chemical shifts were also observed in ^{13}C NMR spectra. The ^{13}C chemical shift of the C1 position in the 2,5-*trans*-isomers and the 2,5-*cis*-isomers was about δ 64.7 and 65.9 ppm, respectively. The ^{13}C NMR chemical shift of the C10 position in the 9,10-*threo*-isomers was more downfield than that of the 9,10-*erythro*-isomers.[15] In 5,6-*erythro*-isomers, the chemical shifts of the C5 position and that of the C6 position had different values; however, those in the 5,6-*threo*-isomers had almost the same value. The chemical shift of the C2 position was not affected by the difference in stereochemistry. Our eight synthetic compounds thus exhibited a characteristic signal pattern and their signals are distinguishable. Almost no signal from other diastereomeric isomers was observed in each spectra, thereby indicating the high purity of these products.

Table 4. Representative ^{1}H NMR spectroscopic data for **13a–h**.[a]



Compounds	Position					
	1	2	5	6	9	10
13a	3.48, 3.71	4.12	3.85–3.92	3.85–3.92	3.97	3.66
13b	3.48, 3.65	4.11	3.87[b]	3.89–3.94[b]	3.89–3.94[b]	3.56
13c	3.46, 3.75	4.08	3.91[c]	4.03[c]	3.95	3.57
13d	3.46, 3.77	4.12	3.89–3.93[d]	3.89–3.93[d]	4.01	3.62
13e	3.48, 3.65	4.11	3.87[e]	3.94[e]	3.90	3.76
13f	3.47, 3.67	4.08	3.84[f]	3.87[f]	3.91	3.80
13g	3.44, 3.76	4.12	3.88–3.94	3.88–3.94	3.88–3.94	3.81
13h	3.42, 3.74	4.07–4.13	4.07–4.13[g]	3.96[g]	3.87	3.76

[a] NMR spectra were recorded in $CDCl_3$ solution at 500 MHz. [b]–[g] Values are interchangeable in each row.

Table 5. Representative ^{13}C NMR spectra data of **13a–h**.[a]

Compounds	Position					
	1	2	5	6	9	10
13a	64.6	79.8	81.9[b]	82.0[b]	82.2	74.6
13b	64.8	79.9	81.2[c]	81.5[c]	82.5[c]	75.1
13c	65.7	79.8	81.1[d]	82.2[d]	82.4	74.8
13d	65.7	80.0	81.5[e]	81.6[e]	82.3	74.5
13e	64.9	79.9	81.4[f]	82.4[f]	81.5	73.4
13f	64.6	79.7	81.8[g]	82.0[g]	82.3	73.4
13g	66.1	80.0	81.4[h]	81.5[h]	82.8[h]	73.0
13h	66.0	79.9	81.0[i]	82.2[i]	82.9	73.1

[a] NMR spectra were recorded in $CDCl_3$ solution at 75 MHz. [b]–[i] Values are interchangeable in each row.

Conclusion

We have developed a highly stereoselective and stereodivergent synthesis of the THF ring cores of bis-THF acetogenins based on asymmetric alkynylation of α-tetrahydrofuranic aldehydes with C_4-units. We also demonstrated the stereodivergent synthesis of eight diastereomeric isomers. The asymmetric alkynylation proceeded almost exclusively to give *threo*- and *erythro*-adducts with predictable selectivity by changing the chiral ligand. Since the reiterative strategy could be extended to tris-THF ring cores, our methodology might be widely used for the synthesis of various annonaceous acetogenins. Application of our strategy to the synthesis of biologically active acetogenins is under way. These results will be reported elsewhere.

Experimental Section

General: Melting points are uncorrected. Optical rotations were measured by using a JASCO DIP-360 digital polarimeter. ^{1}H NMR spectra were recorded in $CDCl_3$ solution with a JEOL JNM-GX500 spectrometer (500 MHz). ^{13}C NMR spectra were recorded in $CDCl_3$ solution with a JEOL JNM-AL300 spectrometer (75 MHz) or a JEOL JNM-EX270 spectrometer (67.8 MHz). All signals are expressed as δ values in ppm downfield from the internal standard tetramethylsilane. The following abbreviations are used: singlet (s), doublet (d), triplet (t), quartet (q), quintet (qn), septet (sep), and multiplet (m). IR absorption spectra (FT: diffuse reflectance spectroscopy) were recorded with KBr powder by using an Horiba FT-210 IR spectrophotometer, and only noteworthy absorptions (cm^{-1}) are listed. Mass spectra were obtained with a JEOL JMS-600H and a JEOL JMS-700 mass spectrometer. Column chromatography was carried out by using Kanto Chemical silica gel 60N (spherical, neutral, 63–210 μm). All air- or moisture-sensitive reactions were carried out in flame-dried glassware under an atmosphere of Ar or N_2. All solvents were dried and distilled according to standard procedures. All organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure with a rotary evaporator. Known compounds **5a**, **5b**, and **6** were synthesized according to the literature methods.[7a] ^{1}H and ^{13}C NMR spectra of **13a–h** are included in the Supporting Information.

(2*RS*,4*S*)-4-[(3′*R*,4′*R*,7′*R*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-hydroxy-4′,7′-epoxy-1′-icosynyl]-2-phenyl-1,3-dioxolane (7a): A flask was charged with $Zn(OTf)_2$ (277 mg, 0.763 mmol). Vacuum (5 mm Hg) was applied and the flask was heated to 120 °C for 12 h. The flask was then cooled to room temperature, and the vacuum was released. (1*R*,2*S*)-*N*-Methylephedrine (149 mg, 0.833 mmol), toluene (0.7 mL), and Et_3N (0.116 mL, 0.833 mmol) were added successively to the flask with stirring at room temperature. After 3 h, a solution of **6** (121 mg, 0.694 mmol) in toluene (0.5 mL) was added to the mixture at room temperature. After 0.25 h, a solution of **5a** (143 mg, 0.347 mmol) in toluene (0.5 mL) was added to the mixture with stirring at room temperature. The reaction mixture was stirred for 19 h. The reaction was then quenched with saturated NH_4Cl and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried, and the solvent was evaporated. Purification by column chromatography over silica gel with hexane/EtOAc (10:1 to 3:1) as eluant yielded **7a** (198 mg, 97 %) as a colorless oil. $[\alpha]_D^{27} = +27.2$ ($c = 0.96$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.06$ (s, 1.5H), 0.07 (s, 1.5H), 0.08 (s, 1.5H), 0.09 (s, 1.5H), 0.88 (t, $J = 7.3$ Hz, 3H), 0.89 (s, 9H), 1.26–1.64 (m, 22H), 1.66–1.84 (m, 2H), 1.89–2.00 (m, 1H), 2.01–2.12 (m, 1H), 2.54 (br, 0.5H), 2.58 (br, 0.5H), 3.57 (ddd, $J = 9.8$, 6.7, 3.7 Hz, 1H), 3.90–3.96 (m, 1H), 4.00 (dd, $J = 7.9$, 6.1 Hz, 0.5H), 4.05 (dt, $J = 7.3$, 6.4 Hz, 0.5H), 4.07–4.15 (m, 1H), 4.18 (t, $J = 7.0$ Hz, 0.5H), 4.23 (dd, $J = 6.4$, 0.9 Hz, 0.5H), 4.27 (dd, $J = 6.1$, 0.9 Hz, 0.5H), 4.37 (dd, $J = 7.9$, 6.7 Hz, 0.5H), 4.89 (ddd, $J = 7.0$, 5.5, 0.9 Hz, 0.5H), 4.94 (ddd, $J = 6.7$, 6.1, 0.9 Hz, 0.5H), 5.87 (s, 0.5H), 5.96 (s, 0.5H), 7.38–7.39 (m, 3H), 7.47–7.49 (m, 1H), 7.52–7.54 ppm (m, 1H); ^{13}C NMR (75 MHz): $\delta = -4.7$, −4.2, 14.0, 18.2, 22.6, 25.4, 25.9 (3C), 27.57 (0.5C), 27.63 (0.5C), 28.15 (0.5C), 28.19 (0.5C), 29.3, 29.5 (2C), 29.55 (2C), 29.59, 29.7, 31.8, 32.9, 65.08 (0.5C),

65.15 (0.5C), 65.7 (0.5C), 66.2 (0.5C), 70.7 (0.5C), 71.1 (0.5C), 74.8 (0.5C), 74.9 (0.5C), 81.7, 82.3 (0.5C), 82.4 (0.5C), 82.75 (0.5C), 82.84 (0.5C), 84.4 (0.5C), 85.0 (0.5C), 103.6 (0.5C), 104.9 (0.5C), 126.5, 126.8, 128.2, 128.3, 129.3 (0.5C), 129.4 (0.5C), 136.5 (0.5C), 137.1 ppm (0.5C); IR (KBr): $\tilde{\nu}$ = 3448 cm^{-1}; MS (FAB): *m*/*z*: 609 [*M*+Na]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{35}H_{58}NaO_5Si$: 609.3951; found: 609.3950 [*M*+Na]$^+$.

(2*RS*,4*S*)-4-[(3′*S*,4′*R*,7′*R*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-hydroxy-4′,7′-epoxy-1′-icosynyl]-2-phenyl-1,3-dioxolane (7b): The procedure was the same as that used for preparation of **7a** and gave **7b** as a colorless oil. $[\alpha]_D^{22}$ = +44.1 (*c* = 1.34 in $CHCl_3$); ^{1}H NMR: δ = 0.055 (s, 1.2H), 0.063 (s, 3H), 0.08 (s, 1.8H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.89 (s, 9H), 1.26–1.46 (m, 23H), 1.63–1.75 (m, 1H), 1.90–2.07 (m, 2H), 2.43 (br, 0.4H), 2.48 (br, 0.6H), 3.53–3.58 (m, 1H), 3.98 (dd, *J* = 7.9, 6.1 Hz, 0.6H), 4.00–4.06 (m, 1H), 4.08 (dd, *J* = 7.9, 5.5 Hz, 0.4H), 4.10–4.16 (m, 1H), 4.19 (dd, *J* = 7.9, 6.7 Hz, 0.4H), 4.37 (dd, *J* = 7.9, 6.7 Hz, 0.6H), 4.47 (br, 0.4H), 4.49 (br, 0.6H), 4.90 (ddd, *J* = 6.7, 5.5, 1.8 Hz, 0.4H), 4.95 (ddd, *J* = 6.7, 6.1, 1.2 Hz, 0.6H), 5.87 (s, 0.4H), 5.96 (s, 0.6H), 7.38–7.39 (m, 3H), 7.47–7.54 ppm (m, 2H); ^{13}C NMR (75 MHz): δ = −4.6, −4.2, 14.1, 18.2, 22.6, 25.5, 25.9 (3C), 26.7 (0.4C), 26.8 (0.6C), 27.6 (0.4C), 27.7 (0.6C), 29.3, 29.53, 29.55, 29.57 (2C), 29.61, 29.8, 31.9, 32.96 (0.4C), 32.98 (0.6C), 64.4 (0.4C), 64.5 (0.6C), 65.8 (0.6C), 66.3 (0.4C), 70.7 (0.4C), 71.1 (0.6C), 74.96 (0.4C), 74.99 (0.6C), 81.17 (0.4C), 81.23 (0.6C), 82.6 (0.4C), 82.7 (0.6C), 83.4 (0.4C), 83.5 (0.6C), 84.3 (0.4C), 84.8 (0.6C), 103.6 (0.6C), 104.9 (0.4C), 126.5, 126.8, 128.2, 128.3, 129.3 (0.4C), 129.4 (0.6C), 136.5 (0.6C), 137.1 ppm (0.4C); IR (KBr): $\tilde{\nu}$ = 3431 cm^{-1}; MS (FAB): *m*/*z*: 609 [*M*+Na]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{35}H_{58}NaO_5Si$: 609.3951; found: 609.3945 [*M*+Na]$^+$.

(2*RS*,4*S*)-4-[(3′*R*,4′*S*,7′*S*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-hydroxy-4′,7′-epoxy-1′-icosynyl]-2-phenyl-1,3-dioxolane (7c): The procedure was the same as that used for preparation of **7a** and gave **7c** as a colorless oil. $[\alpha]_D^{23}$ = +0.77 (*c* = 1.03 in $CHCl_3$); ^{1}H NMR: δ = 0.047 (s, 1.8H), 0.053 (s, 1.8H), 0.055 (s, 1.2H), 0.058 (s, 1.2H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.89 (s, 9H), 1.25–1.36 (m, 22H), 1.88–2.06 (m, 4H), 2.33 (d, *J* = 6.4 Hz, 0.6H), 2.38 (d, *J* = 6.1 Hz, 0.4H), 3.76–3.81 (m, 1H), 4.00 (dd, *J* = 7.9, 5.8 Hz, 0.4H), 3.98–4.05 (m, 1H), 4.10 (dd, *J* = 7.9, 5.5 Hz, 0.6H), 4.09–4.15 (m, 1H), 4.18 (dd, *J* = 7.9, 6.7 Hz, 0.6H), 4.37 (dd, *J* = 7.9, 6.7 Hz, 0.4H), 4.44 (ddd, *J* = 6.4, 3.7, 1.2 Hz, 0.6H), 4.47 (ddd, *J* = 6.1, 3.7, 1.2 Hz, 0.4H), 4.90 (ddd, *J* = 6.7, 5.5, 1.2 Hz, 0.6H), 4.95 (ddd, *J* = 6.7, 5.8, 1.2 Hz, 0.4H), 5.87 (s, 0.6H), 5.96 (s, 0.4H), 7.37–7.39 (m, 3H), 7.46–7.53 ppm (m, 2H); ^{13}C NMR (75 MHz): δ = −4.6, −4.3, 14.0, 18.1, 22.6, 25.36 (0.4C), 25.41 (0.6C), 25.43, 25.9 (3C), 26.8 (0.6C), 26.9 (0.4C), 29.3, 29.49, 29.52, 29.56 (2C), 29.59, 29.8, 31.8, 34.56 (0.6C), 34.58 (0.4C), 64.6 (0.6C), 64.7 (0.4C), 65.8 (0.4C), 66.2 (0.6C), 70.7 (0.6C), 71.1 (0.4C), 72.95 (0.6C), 72.99 (0.4C), 81.2 (0.6C), 81.3 (0.4C), 82.6 (0.6C), 82.7 (0.4C), 83.6, 84.4 (0.6C), 84.9 (0.4C), 103.6 (0.4C), 104.9 (0.6C), 126.5, 126.8, 128.2, 128.3, 129.3 (0.6C), 129.4 (0.4C), 136.5 (0.4C), 137.1 ppm (0.6C); IR (KBr): $\tilde{\nu}$ = 3425 cm^{-1}; MS (FAB): *m*/*z*: 609 [*M*+Na]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{35}H_{58}NaO_5Si$: 609.3951; found: 609.3926 [*M*+Na]$^+$.

(2*RS*,4*S*)-4-[(3′*S*,4′*S*,7′*S*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-hydroxy-4′,7′-epoxy-1′-icosynyl]-2-phenyl-1,3-dioxolane (7d): The procedure was the same as that used for preparation of **7a** and gave **7d** as a colorless oil. $[\alpha]_D^{24}$ = +14.8 (*c* = 1.43 in $CHCl_3$); ^{1}H NMR: δ = 0.05 (s, 3H), 0.06 (s, 1.8H), 0.07 (s, 1.2H), 0.87–0.89 (m, 12H), 1.26–1.36 (m, 22H), 1.73–2.11 (m, 4H), 2.46 (d, *J* = 4.3 Hz, 0.6H), 2.51 (d, *J* = 4.6 Hz, 0.4H), 3.77–3.82 (m, 1H), 3.90–3.95 (m, 1H), 3.99 (dd, *J* = 7.9, 6.1 Hz, 0.4H), 4.00–4.06 (m, 1H), 4.08 (dd, *J* = 7.9, 5.5 Hz, 0.6H), 4.18 (dd, *J* = 7.9, 6.7 Hz, 0.6H), 4.23 (ddd, *J* = 6.7, 4.3, 1.2 Hz, 0.6H), 4.26 (ddd, *J* = 6.7, 4.6, 1.2 Hz, 0.4H), 4.37 (dd, *J* = 7.9, 6.7 Hz, 0.4H), 4.90 (ddd, *J* = 6.7, 5.5, 1.2 Hz, 0.6H), 4.95 (ddd, *J* = 6.7, 6.1, 1.2 Hz, 0.4H), 5.87 (s, 0.6H), 5.96 (s, 0.4H), 7.37–7.41 (m, 3H), 7.47–7.54 ppm (m, 2H); ^{13}C NMR (75 MHz): δ = −4.6, −4.2, 14.1, 18.1, 22.6, 25.17 (0.6C), 25.20 (0.4C), 25.4, 25.9 (3C), 28.09 (0.6C), 28.14 (0.4C), 29.3, 29.50, 29.52, 29.57 (2C), 29.61, 29.8, 31.9, 34.7, 64.99 (0.4C), 65.03 (0.6C), 65.8 (0.4C), 66.3 (0.6C), 70.7 (0.6C), 71.1 (0.4C), 72.9, 81.8, 82.3 (0.6C), 82.5 (0.4C), 82.6 (0.6C), 82.7 (0.4C), 84.5 (0.6C), 85.1 (0.4C), 103.6 (0.4C), 104.9 (0.6C), 126.5, 126.8, 128.2, 128.3, 129.35 (0.6C), 129.40 (0.4C), 136.5 (0.4C), 137.0 ppm (0.6C); IR (KBr): $\tilde{\nu}$ = 3423 cm^{-1}; MS (FAB): *m*/*z*: 609 [*M*+Na]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{35}H_{58}NaO_5Si$: 609.3951; found: 609.3950 [*M*+Na]$^+$.

(2*S*,5*R*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-6,9-epoxydocosane-1,2,5-triol (8a): A solution of **7a** (181 mg, 0.309 mmol) in EtOAc (3.1 mL) was hydrogenated over 10% Pd/C (9.1 mg) with stirring at room temperature for 19 h. Pd/C was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by chromatography over silica gel with EtOAc as eluant to give **8a** (117 mg, 76%) as a colorless oil. $[\alpha]_D^{24}$ = +8.0 (*c* = 1.28 in $CHCl_3$); ^{1}H NMR: δ = 0.06 (s, 3H), 0.07 (s, 3H), 0.87–0.90 (m, 12H), 1.26–1.70 (m, 26H), 1.90–2.01 (m, 4H), 2.76–2.78 (m, 1H), 2.95–2.98 (m, 1H), 3.41–3.49 (m, 2H), 3.53–3.57 (m, 1H), 3.61–3.65 (m, 1H), 3.75–3.77 (m, 1H), 3.79 (td, *J* = 7.3, 6.7 Hz, 1H), 3.87 ppm (dt, *J* = 8.5, 6.1 Hz, 1H); ^{13}C NMR (75 MHz): δ = −4.6, −4.2, 14.1, 18.2, 22.6, 25.4, 25.9 (3C), 28.2, 28.5, 29.0, 29.29, 29.33, 29.55 (2C), 29.58 (2C), 29.62, 29.8, 31.9, 33.1, 66.5, 72.0, 74.3, 75.1, 82.1, 82.4 ppm; IR (KBr): $\tilde{\nu}$ = 3346 cm^{-1}; MS (FAB): *m*/*z*: 503 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{59}O_5Si$: 503.4132; found: 503.4117 [*M*+H]$^+$.

(2*S*,5*S*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-6,9-epoxydocosane-1,2,5-triol (8b): The procedure was the same as that used for preparation of **8a** and gave **8b** as colorless oil. $[\alpha]_D^{22}$ = +10.2 (*c* = 0.74 in $CHCl_3$); ^{1}H NMR: δ = 0.05 (s, 3H), 0.06 (s, 3H), 0.87–0.91 (m, 12H), 1.23–1.48 (m, 23H), 1.56–1.70 (m, 4H), 1.80–1.84 (m, 2H), 1.91–1.97 (m, 1H), 2.05 (br, 1H), 2.68 (br, 1H), 3.47 (ddd, *J* = 10.4, 7.3, 4.3 Hz, 1H), 3.53 (td, *J* = 6.1, 3.7 Hz, 1H), 3.63 (ddd, *J* = 10.4, 6.1, 3.7 Hz, 1H), 3.70–3.74 (m, 1H), 3.79–3.82 (m, 1H), 3.84 (td, *J* = 7.6, 3.7 Hz, 1H), 3.92 ppm (dt, *J* = 8.5, 6.1 Hz, 1H); ^{13}C NMR (75 MHz): δ = −4.6, −4.2, 14.1, 18.2, 22.6, 25.5, 25.9 (3C), 27.9, 29.3, 29.5, 29.58 (2C), 29.59 (2C), 29.64 (2C), 29.8, 30.3, 31.9, 33.0, 66.8, 72.4, 72.6, 75.2, 82.1, 82.4 ppm; IR (KBr): $\tilde{\nu}$ = 3363 cm^{-1}; MS (FAB): *m*/*z*: 503 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{59}O_5Si$: 503.4132; found: 503.4113 [*M*+H]$^+$.

(2*S*,5*R*,6*R*,9*R*,10*R*)-1,2-*O*-Isopropylidene-6,9-epoxydocosane-1,2,5,10-tetrol (9a): Dowex 50W X8-200 (4.1 mg) was added to a mixture of **8a** (40.5 mg, 0.0805 mmol) and 2,2-dimethoxypropane (0.099 mL, 0.805 mmol) in CH_2Cl_2 (0.4 mL) at room temperature. After 2 h at the same temperature, the catalyst was filtered off and the filtrate was concentrated under reduced pressure to give a crude acetal. Tetrabutylammonium fluoride (TBAF, 1.0 M in THF, 0.161 mL, 0.161 mmol) was added to the solution of crude acetal in THF (0.8 mL) at room temperature. The mixture was heated at reflux for 14 h. Water was added, and the mixture was extracted with Et_2O. The combined organic layers were washed with brine, dried, and the solvent was evaporated. The residue was purified by chromatography over silica gel with hexane/EtOAc (1:1) as eluant to give **9a** (24.8 mg, 72% in 2 steps) as a white waxy solid. M.p. 38.5–39.5 °C; $[\alpha]_D^{20}$ = +20.7 (*c* = 0.51 in $CHCl_3$); ^{1}H NMR: δ = 0.88 (t, *J* = 7.0 Hz, 3H), 1.26–1.53 (m, 23H), 1.35 (s, 3H), 1.41 (s, 3H), 1.57–1.73 (m, 4H), 1.79–1.86 (m, 1H), 1.97–2.01 (m, 2H), 2.51 (br, 1H), 2.67 (br, 1H), 3.38–3.45 (m, 2H), 3.53 (t, *J* = 7.3 Hz, 1H), 3.80 (q, *J* = 6.7 Hz, 1H), 3.81 (q, *J* = 6.7 Hz, 1H), 4.05 (dd, *J* = 7.3, 6.1 Hz, 1H), 4.07–4.12 ppm (m, 1H); ^{13}C NMR (75 MHz): δ = 14.1, 22.7, 25.6, 25.7, 26.9, 28.70, 28.73, 29.3, 29.56, 29.61 (2C), 29.63 (2C), 29.7, 29.86, 29.93, 31.9, 33.4, 69.5, 73.9, 74.0, 76.3, 82.6, 82.8, 108.8 ppm; IR (KBr): $\tilde{\nu}$ = 3462 cm^{-1}; MS (FAB): *m*/*z*: 429 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{25}H_{49}O_5$: 429.3580; found: 429.3576 [*M*+H]$^+$.

(2*S*,5*S*,6*R*,9*R*,10*R*)-1,2-*O*-Isopropylidene-6,9-epoxydocosane-1,2,5,10-tetrol (9b): The procedure was the same as that used for preparation of **9a** and gave **9b** as a white waxy solid. M.p. 46.5–47.5 °C; $[\alpha]_D^{19}$ = +12.8 (*c* = 0.97 in $CHCl_3$); ^{1}H NMR: δ = 0.87 (t, 3H, *J* = 6.7 Hz), 1.34 (s, 3H), 1.40 (s, 3H), 1.25–1.67 (m, 26H), 1.74–1.81 (m, 1H), 1.87–1.91 (m, 2H), 1.96–2.02 (m, 1H), 2.43 (br, 1H), 2.72 (br, 1H), 3.38 (td, *J* = 6.4, 5.5 Hz, 1H), 3.52 (dd, *J* = 7.9, 7.3 Hz, 1H), 3.75 (dt, *J* = 9.2, 4.0 Hz, 1H), 3.81 (dt, *J* = 7.3, 6.4 Hz, 1H), 3.82–3.87 (m, 1H), 4.04 (dd, *J* = 7.9, 6.7 Hz, 1H), 4.10–4.15 ppm (m, 1H); ^{13}C NMR (75 MHz): δ = 14.1, 22.7, 25.6, 25.7, 26.0, 26.9, 28.5, 29.1, 29.3, 29.57 (2C), 29.62 (3C), 29.7, 30.2, 31.9, 33.2, 69.4, 71.9, 74.3, 75.9, 82.1, 83.2, 108.9 ppm; IR (KBr): $\tilde{\nu}$ = 3462 cm^{-1}; MS (FAB): *m*/*z*: 429 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{25}H_{49}O_5$: 429.3580; found: 429.3563 [*M*+H]$^+$.

(2*S*,5*R*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-6,9-epoxydocosane-1,2,5-triol (8c): The procedure was the same as that used for preparation of **8a** and gave **8c** as a colorless oil. $[\alpha]_D^{23}$ = −13.5 (*c* = 0.63 in $CHCl_3$); ^{1}H NMR: δ = 0.03 (s, 3H), 0.04 (s, 3H), 0.84–0.87 (m, 12H), 1.24–1.42 (m, 23H), 1.48–1.68 (m, 3H), 1.73–1.93 (m, 4H), 3.21 (br, 1H), 3.44 (dd, *J* = 10.4, 8.5 Hz, 1H), 3.58–3.59 (m, 1H), 3.68–3.75 (m, 3H), 3.78–3.82 (m, 1H), 3.88 ppm (dt, *J* = 7.9, 4.3 Hz, 1H); ^{13}C NMR (75 MHz): δ = −4.5, −4.3, 14.1, 18.1, 22.6, 25.4, 25.9 (3C), 28.5, 29.3, 29.56 (2C), 29.58 (2C), 29.61 (2C), 29.64 (2C), 29.9, 31.9, 34.6, 66.4, 71.9, 72.4, 73.4, 82.3,

82.5 ppm; IR (KBr): $\tilde{\nu}$ = 3356 cm^{-1}; MS (FAB): *m*/*z*: 503 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{59}O_5Si$: 503.4132; found: 503.4144 [*M*+H]$^+$.

(2*S*,5*S*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-6,9-epoxydocosane-1,2,5-triol (8d): The procedure was the same as that used for preparation of **8a** and gave **8d** as a colorless oil. $[\alpha]_D^{24}$ = −10.2 (*c* = 0.91 in $CHCl_3$); ^{1}H NMR: δ = 0.04 (s, 3H), 0.05 (s, 3H), 0.87–0.90 (m, 12H), 1.23–1.37 (m, 21H), 1.46–1.70 (m, 7H), 1.83–2.00 (m, 3H), 2.02–2.04 (m, 1H), 3.41 (ddd, *J* = 9.2, 6.7, 1.8 Hz, 1H), 3.47 (ddd, *J* = 11.0, 7.3, 4.3 Hz, 1H), 3.62 (ddd, *J* = 11.0, 6.7, 3.7 Hz, 1H), 3.65–3.70 (m, 1H), 3.70–3.74 (m, 1H), 3.75–3.80 (m, 2H), 3.86 ppm (ddd, *J* = 7.9, 6.1, 3.7 Hz, 1H); ^{13}C NMR (67.8 MHz): δ = −4.4, −4.1, 14.2, 18.2, 22.7, 25.5, 26.0 (3C), 26.1, 28.5, 29.4, 29.6, 29.65, 29.68, 29.69, 29.72, 29.8, 29.9, 30.0, 32.0, 34.8, 66.8, 72.2, 73.1, 74.3, 82.0, 82.4 ppm; IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1}; MS (FAB): *m*/*z*: 503 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{59}O_5Si$: 503.4132; found: 503.4159 [*M*+H]$^+$.

(2*S*,5*R*,6*S*,9*S*,10*R*)-1,2-*O*-Isopropylidene-6,9-epoxydocosane-1,2,5,10-tetrol (9c): The procedure was the same as that used for preparation of **9a** and gave **9c** as a white waxy solid. M.p. 54.0–55.0 °C; $[\alpha]_D^{22}$ = −5.5 (*c* = 0.54 in $CHCl_3$); ^{1}H NMR: δ = 0.87 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 3H), 1.40 (s, 3H), 1.24–1.66 (m, 25H), 1.75–1.89 (m, 5H), 2.08 (br, 1H), 2.36 (br, 1H), 3.52 (dd, *J* = 7.9, 7.0 Hz, 1H), 3.76–3.81 (m, 2H), 3.89–3.92 (m, 2H), 4.04 (t, *J* = 7.0 Hz, 1H), 4.06–4.11 ppm (m, 1H); ^{13}C NMR (75 MHz): δ = 14.1, 22.6, 25.1, 25.6, 25.7, 26.0, 26.9, 29.0, 29.3, 29.5, 29.58, 29.61 (2C), 29.64, 29.7, 30.1, 31.9, 32.4, 69.5, 71.9, 72.0, 76.2, 82.8, 83.0, 108.9 ppm; IR (KBr): $\tilde{\nu}$ = 3456 cm^{-1}; MS (FAB): *m*/*z*: 429 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{25}H_{49}O_5$: 429.3580; found: 429.3589 [*M*+H]$^+$.

(2*S*,5*S*,6*S*,9*S*,10*R*)-1,2-*O*-Isopropylidene-6,9-epoxydocosane-1,2,5,10-tetrol (9d): The procedure was the same as that used for preparation of **9a** and gave **9d** as a white waxy solid. M.p. 47.5–48.5 °C; $[\alpha]_D^{25}$ = −8.2 (*c* = 0.64 in $CHCl_3$); ^{1}H NMR: δ = 0.87 (t, *J* = 7.0 Hz, 3H), 1.34 (s, 3H), 1.40 (s, 3H), 1.25–1.57 (m, 24H), 1.61–2.02 (m, 6H), 2.77 (br, 1H), 3.43 (dt, *J* = 6.7, 6.1 Hz, 1H), 3.53 (dd, *J* = 7.6, 7.3 Hz, 1H), 3.78–3.82 (m, 1H), 3.84 (dt, *J* = 7.9, 6.1 Hz, 1H), 3.88 (ddd, *J* = 9.2, 5.5, 3.1 Hz, 1H), 4.04 (dd, *J* = 7.6, 6.1 Hz, 1H), 4.10–4.15 ppm (m, 1H); ^{13}C NMR (75 MHz): δ = 14.1, 22.7, 25.1, 25.7, 26.0, 26.9, 28.6, 29.26, 29.33, 29.5, 29.56, 29.59, 29.63 (2C), 29.7 (2C), 31.9, 32.5, 69.3, 71.4, 74.0, 75.8, 82.3, 83.1, 108.9 ppm; IR (KBr): $\tilde{\nu}$ = 3454 cm^{-1}; MS (FAB): *m*/*z*: 429 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{25}H_{49}O_5$: 429.3580; found: 429.3561 [*M*+H]$^+$.

(2*S*,5*R*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5-dihydroxy-6,9-epoxydocosanyl 2,4,6-triisopropylbenzenesulfonate (11a): 2,4,6-Triisopropylbenzenesulfonyl chloride (239 mg, 0.263 mmol) was added to a solution of **8a** (132 mg, 0.263 mmol) in pyridine (0.79 mL) and CH_2Cl_2 (1.3 mL) with stirring at 0 °C. After 21 h at room temperature, water was added and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried, and the solvent was evaporated. The residue was purified by chromatography over silica gel with hexane/EtOAc (4:1) as eluant to give **11a** (144 mg, 71%) as a colorless oil. $[\alpha]_D^{23}$ = +7.3 (*c* = 1.28 in $CHCl_3$); ^{1}H NMR: δ = 0.05 (s, 3H), 0.06 (s, 3H), 0.87–0.88 (m, 12H), 1.26–1.70 (m, 45H), 1.72–1.77 (m, 1H), 1.84–1.98 (m, 2H), 2.70 (br, 1H), 2.91 (sep, *J* = 6.7 Hz, 1H), 2.97 (br, 1H), 3.36–3.40 (m, 1H), 3.53–3.56 (m, 1H), 3.76 (dt, *J* = 7.9, 6.7 Hz, 1H), 3.84 (dt, *J* = 8.5, 6.1 Hz, 1H), 3.93–3.95 (m, 1H), 3.95 (dd, *J* = 12.5, 6.7 Hz, 1H), 4.02 (dd, *J* = 12.5, 6.7 Hz, 1H), 4.14 (sep, *J* = 6.7 Hz, 2H), 7.19 ppm (s, 2H); ^{13}C NMR (75 MHz): δ = −4.6, −4.2, 14.1, 18.2, 22.6, 23.5 (2C), 24.67 (2C), 24.69 (2C), 25.3, 25.9 (3C), 28.3, 28.5, 28.7, 29.3, 29.4, 29.5 (2C), 29.58 (3C), 29.6 (2C), 29.8, 31.9, 33.2, 34.2, 69.3, 72.5, 74.3, 75.1, 82.2, 82.3, 123.8 (2C), 129.1, 150.8 (2C), 153.8 ppm; IR (KBr): $\tilde{\nu}$ = 3545 cm^{-1}; MS (FAB): *m*/*z*: 769 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{43}H_{81}O_7SSi$: 769.5472; found: 769.5491 [*M*+H]$^+$.

(2*R*,5*R*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13a): K_2CO_3 (122 mg, 0.880 mmol) was added to a solution of **11a** (135 mg, 0.176 mmol) in MeOH (1.8 mL) with stirring at 0 °C. After 2 h, the ice bath was removed and the mixture was stirred for 19 h at room temperature. Water was added and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried, and the solvent was evaporated. The residue was purified by chromatography over silica gel with hexane/EtOAc (5:1) as eluant to give **13a** (67.1 mg, 79%) as a colorless oil. $[\alpha]_D^{24}$ = +10.3 (*c* = 1.21 in $CHCl_3$); ^{1}H NMR: δ = 0.05 (s, 3H), 0.06 (s, 3H), 0.85–0.91 (m, 12H), 1.26–1.51 (m, 22H), 1.61–1.75 (m, 4H), 1.84–1.99 (m, 5H), 3.48 (ddd, *J* = 11.0, 6.1, 5.5 Hz, 1H), 3.66 (ddd, *J* = 8.5, 5.5, 3.7 Hz, 1H), 3.69–3.72 (m, 1H), 3.85–3.92 (m, 2H), 3.97 (ddd, *J* = 7.9, 6.1, 5.5 Hz, 1H), 4.10–4.14 ppm (m, 1H); ^{13}C NMR (75 MHz): δ = −4.7, −4.3, 14.1, 18.2, 22.6, 25.9 (3C), 27.0, 27.4, 28.5, 28.6, 29.3, 29.60 (4C), 29.64 (2C), 29.8, 31.9, 32.1, 64.6, 74.6, 79.8, 81.9, 82.0, 82.2 ppm; IR (KBr): $\tilde{\nu}$ = 3452 cm^{-1}; MS (FAB): *m*/*z*: 485 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{57}O_4Si$: 485.4026; found: 485.4034 [*M*+H]$^+$.

(2*RS*,4*S*)-4-[(3′*R*,4′*R*,7′*R*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-(*p*-toluenesulfonyloxy)-4′,7′-epoxyicosanyl]-2-phenyl-1,3-dioxolane (15a): A mixture of **7a** (180 mg, 0.306 mmol) and Et_3N (0.021 mL, 0.153 mmol) in EtOAc (3.1 mL) was hydrogenated over 10% Pd/C (9.0 mg) with stirring at room temperature for 6 h. The Pd/C was filtered off and the filtrate was concentrated under reduced pressure to give a crude alcohol **14a**. *p*TsCl (292 mg, 1.53 mmol) was added to a solution of the crude **14a** in pyridine (1.2 mL) with stirring at 0 °C. The stirring was continued at room temperature for 15 h. The reaction was quenched with saturated NH_4Cl, and the mixture was extracted with EtOAc. The combined organic layers were washed with saturated NH_4Cl, water, and brine, dried, and the solvent was evaporated. The residue was purified by chromatography over silica gel with hexane/EtOAc (20:1 to 5:1) as eluant to give **15a** (197 mg, 87%) as a colorless oil. $[\alpha]_D^{24}$ = +9.5 (*c* = 1.32 in $CHCl_3$); ^{1}H NMR: δ = 0.01 (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 0.88 (t, *J* = 6.7 Hz, 3H), 1.25–1.37 (m, 22H), 1.58–1.76 (m, 5H), 1.80–1.98 (m, 3H), 2.41 (s, 1.5H), 2.42 (s, 1.5H), 3.43–3.47 (m, 1H), 3.52 (dd, *J* = 7.9, 6.7 Hz, 0.5H), 3.58 (dd, *J* = 7.9, 6.7 Hz, 0.5H), 3.83–3.87 (m, 1H), 4.00–4.05 (m, 1H), 4.03 (dd, *J* = 7.9, 6.7 Hz, 0.5H), 4.10–4.16 (m, 1H), 4.19 (dd, *J* = 7.9, 6.1 Hz, 0.5H), 4.58 (dt, *J* = 6.7, 4.3 Hz, 0.5H), 4.62 (dt, *J* = 7.3, 4.3 Hz, 0.5H), 5.76 (s, 0.5H), 5.84 (s, 0.5H), 7.26–7.31 (m, 3H), 7.36–7.47 (m, 4H), 7.78–7.81 ppm (m, 2H); ^{13}C NMR (75 MHz): δ = −4.6, −4.4, 14.0, 18.1, 21.5, 22.6, 25.6, 25.9 (3C), 27.0 (0.5C), 27.1, 27.2 (0.5C), 27.5 (0.5C), 27.6 (0.5C), 29.2, 29.3, 29.5 (2C), 29.55 (2C), 29.59, 29.8, 31.8, 32.6, 69.7 (0.5C), 70.4 (0.5C), 74.6, 76.0 (0.5C), 76.7 (0.5C), 78.8 (0.5C), 78.9 (0.5C), 82.0, 84.3 (0.5C), 84.5 (0.5C), 102.9 (0.5C), 104.0 (0.5C), 126.3, 126.6, 127.7 (2C), 128.2 (2C), 129.0 (0.5C), 129.2 (0.5C), 129.5 (2C), 134.5 (0.5C), 134.6 (0.5C), 137.6 (0.5C), 138.2 (0.5C), 144.3 ppm; IR (KBr): $\tilde{\nu}$ = 1599, 1460 cm^{-1}; MS (FAB): *m*/*z*: 767 [*M*+Na]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{42}H_{68}NaO_7SSi$: 767.4353; found: 767.4373 [*M*+Na]$^+$.

(2*S*,5*S*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13b): A solution of **15a** (190 mg, 0.257 mmol) in THF (3.1 mL) was hydrogenated over 10% Pd/C (9.5 mg) with stirring at room temperature for 22 h. THF (2.0 mL) and NaH (62.6% in oil, 39.4 mg, 1.03 mmol) were added to the reaction mixture at 0 °C. After 3 h at 40 °C, the reaction mixture was quenched with water at 0 °C, and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried, and the solvent was evaporated. The residue was purified by chromatography over silica gel with hexane/EtOAc (4:1) to give **13b** (96.2 mg, 77%) as a colorless oil. $[\alpha]_D^{22}$ = +15.4 (*c* = 0.71 in $CHCl_3$); ^{1}H NMR: δ = 0.05 (s, 3H), 0.07 (s, 3H), 0.86–0.91 (m, 12H), 1.23–1.47 (m, 22H), 1.62–1.82 (m, 3H), 1.88–2.08 (m, 5H), 3.48 (ddd, *J* = 11.3, 5.4, 4.9 Hz, 1H), 3.56 (ddd, *J* = 6.7, 6.1, 3.7 Hz, 1H), 3.63–3.67 (m, 1H), 3.87 (dt, *J* = 7.3, 6.1 Hz, 1H), 3.89–3.94 (m, 2H), 4.11 ppm (ddt, *J* = 11.3, 6.7, 3.1 Hz, 1H); ^{13}C NMR (75 MHz): δ = −4.7, −4.2, 14.1, 18.2, 22.6, 25.6, 25.9 (3C), 27.3, 27.5, 28.9, 29.0, 29.3, 29.56 (2C), 29.60 (2C), 29.64, 29.8, 31.9, 32.8, 64.8, 75.1, 79.9, 81.2, 81.5, 82.5 ppm; IR (KBr): $\tilde{\nu}$ = 3446 cm^{-1}; MS (FAB): *m*/*z*: 485 [*M*+H]$^+$; HRMS (FAB): *m*/*z*: calcd for $C_{28}H_{57}O_4Si$: 485.4026; found: 485.4041 [*M*+H]$^+$.

(2*S*,5*S*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5-dihydroxy-6,9-epoxydocosanyl 2,4,6-triisopropylbenzenesulfonate (11b): The procedure was the same as that used for preparation of **11a** and gave **11b** as a colorless oil. $[\alpha]_D^{25}$ = +8.9 (*c* = 0.91 in $CHCl_3$); ^{1}H NMR: δ = 0.04 (s, 3H), 0.05 (s, 3H), 0.86–0.88 (m, 12H), 1.25–1.45 (m, 42H), 1.55–1.68 (m, 2H), 1.73–1.82 (m, 3H), 1.89–1.94 (m, 1H), 2.59 (br, 1H), 2.91 (sep, *J* = 6.7 Hz, 1H), 3.44–3.58 (m, 2H), 3.74–3.76 (m, 1H), 3.79–3.83 (m, 1H), 3.88–3.92 (m, 2H), 3.96–4.02 (m, 2H), 4.14 (sep, *J* = 6.7 Hz, 2H), 7.18 ppm (s, 2H); ^{13}C NMR (75 MHz): δ = −4.6, −4.2, 14.1, 18.3, 22.7, 23.5 (2C), 24.70 (2C), 24.72 (2C), 25.4, 25.5, 26.0 (3C), 28.0, 28.8, 29.3, 29.58 (2C), 29.61 (3C), 29.64 (2C), 29.8, 30.5, 31.9, 33.0, 34.2, 69.7, 72.0, 72.7, 75.3, 81.9, 82.6, 123.8 (2C), 129.1, 150.8 (2C), 153.8 ppm; IR (KBr): $\tilde{\nu}$ = 3354 cm^{-1};

MS (FAB): *m/z*: 769 $[M+H]^+$; HRMS (FAB): *m/z*: calcd for $C_{43}H_{81}O_7SSi$: 769.5472; found: 769.5484 $[M+H]^+$.

(2*R*,5*S*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13c): The procedure was the same as that used for preparation of **13a** and gave **13c** as a colorless oil. $[\alpha]_D^{24} = +0.055$ ($c = 0.91$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.05$ (s, 3H), 0.07 (s, 3H), 0.86–0.88 (m, 12H), 1.26–1.50 (m, 22H), 1.59–1.76 (m, 2H), 1.82–2.04 (m, 6H), 2.69 (br, 1H), 3.46 (dd, $J = 11.6$, 4.3 Hz, 1H), 3.57 (ddd, $J = 6.7$, 5.2, 4.3 Hz, 1H), 3.75 (dd, $J = 11.6$, 3.1 Hz, 1H), 3.91 (dt, $J = 6.7$, 5.8 Hz, 1H), 3.91–3.97 (m, 1H), 4.03 (dt, $J = 7.9$, 5.8 Hz, 1H), 4.06–4.10 ppm (m, 1H); ^{13}C NMR (75 MHz): $\delta = -4.6$, −4.3, 14.1, 18.2, 22.7, 25.6, 25.9 (3C), 27.3, 27.4, 29.0, 29.4, 29.59 (2C), 29.63 (2C), 29.7 (2C), 29.9, 31.9, 32.8, 65.7, 74.8, 79.8, 81.1, 82.2, 82.4 ppm; IR (KBr): $\tilde{\nu} = 3442$ cm^{-1}; MS (FAB): *m/z*: 507 $[M+Na]^+$; HRMS (FAB): *m/z*: calcd for $C_{28}H_{56}NaO_4Si$: 507.3846; found: 507.3828 $[M+Na]^+$.

(2*RS*,4*S*)-4-[(3′*S*,4′*R*,7′*R*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-(*p*-toluenesulfonyloxy)-4′,7′-epoxyicosanyl]-2-phenyl-1,3-dioxolane (15b): The procedure was the same as that used for preparation of **15a** and gave **15b** as a colorless oil. $[\alpha]_D^{21} = +8.2$ ($c = 1.09$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.01$ (s, 3H), 0.02 (s, 3H), 0.86 (s, 9H), 0.88 (t, $J = 7.0$ Hz, 3H), 1.25–1.43 (m, 22H), 1.57–1.94 (m, 8H), 2.41 (s, 1.2H), 2.43 (s, 1.8H), 3.43 (dt, $J = 5.5$, 4.9 Hz, 1H), 3.55 (dd, $J = 7.9$, 6.1 Hz, 0.4H), 3.59–3.63 (m, 1.6H), 3.95 (dt, $J = 7.3$, 6.1 Hz, 1H), 4.05 (dd, $J = 7.9$, 6.7 Hz, 0.4H), 4.17–4.22 (m, 1.6H), 4.67–4.71 (m, 1H), 5.77 (s, 0.4H), 5.84 (s, 0.6H), 7.28–7.33 (m, 2H), 7.35–7.39 (m, 3H), 7.44–7.47 (m, 2H), 7.78–7.81 ppm (m, 2H); ^{13}C NMR (75 MHz): $\delta = -4.7$, −4.3, 14.1, 18.1, 21.5, 22.6, 25.4, 25.9 (3C), 27.3, 27.7, 27.88 (0.4C), 27.95 (0.6C), 28.2 (0.6C), 28.4 (0.4C), 29.3, 29.56 (2C), 29.58 (2C), 29.6, 29.8, 31.9, 32.97 (0.4C), 33.01 (0.6C), 69.8 (0.4C), 70.4 (0.6C), 74.9, 75.7 (0.6C), 76.3 (0.4C), 79.3 (0.6C), 79.4 (0.4C), 82.1, 84.0 (0.4C), 84.1 (0.6C), 103.0 (0.6C), 104.0 (0.4C), 126.3, 126.6, 127.72, 127.74, 128.2, 128.3, 129.0 (0.6C), 129.2 (0.4C), 129.5 (2C), 134.7, 137.7 (0.4C), 138.2 (0.6C), 144.3 ppm; IR (KBr): $\tilde{\nu} = 1599$, 1460 cm^{-1}; MS (FAB): *m/z*: 767 $[M+Na]^+$; HRMS (FAB): *m/z*: calcd for $C_{42}H_{68}NaO_7SSi$: 767.4353; found: 767.4373 $[M+Na]^+$.

(2*S*,5*R*,6*R*,9*R*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13d): The procedure was the same as that used for preparation of **13b** and gave **15d** as a colorless oil. $[\alpha]_D^{20} = +14.6$ ($c = 0.82$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.05$ (s, 3H), 0.07 (s, 3H), 0.87 (t, $J = 6.1$ Hz, 3H), 0.88 (s, 9H), 1.26–1.52 (m, 22H), 1.69–1.81 (m, 2H), 1.84–1.96 (m, 6H), 2.73–2.77 (m, 1H), 3.45–3.47 (m, 1H), 3.62 (ddd, $J = 7.6$, 4.9, 4.3 Hz, 1H), 3.77 (dd, $J = 11.6$, 2.7 Hz, 1H), 3.89–3.93 (m, 2H), 4.01 (dt, $J = 7.6$, 5.8 Hz, 1H), 4.10–4.13 ppm (m, 1H); ^{13}C NMR (75 MHz): $\delta = -4.6$, −4.3, 14.1, 18.1, 22.7, 25.6, 25.9 (3C), 27.1, 27.3, 28.7, 28.9, 29.3, 29.59 (2C), 29.61 (2C), 29.7, 29.9, 31.9, 32.6, 65.7, 74.5, 80.0, 81.5, 81.6, 82.3 ppm; IR (KBr): $\tilde{\nu} = 3446$ cm^{-1}; MS (FAB): *m/z*: 507 $[M+Na]^+$; HRMS (FAB): *m/z*: calcd for $C_{28}H_{57}O_4Si$: 485.4026; found: 485.4032 $[M+Na]^+$.

(2*S*,5*R*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5-dihydroxy-6,9-epoxydocosanyl 2,4,6-triisopropylbenzenesulfonate (11c): The procedure was the same as that used for preparation of **11a** and gave **11c** as a colorless oil. $[\alpha]_D^{22} = -4.9$ ($c = 1.71$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.03$ (s, 3H), 0.05 (s, 3H), 0.86–0.89 (m, 12H), 1.25–1.63 (m, 43H), 1.70–1.93 (m, 5H), 2.29 (br, 1H), 2.83 (br, 1H), 2.91 (sep, $J = 6.7$ Hz, 1H), 3.72–3.76 (m, 2H), 3.82 (ddd, $J = 9.2$, 5.5, 3.7 Hz, 1H), 3.89 (ddd, $J = 9.2$, 5.5, 3.7 Hz, 1H), 3.93–3.97 (m, 2H), 4.02–4.05 (m, 1H), 4.13 (sep, $J = 6.7$ Hz, 2H), 7.19 ppm (s, 2H); ^{13}C NMR (75 MHz): $\delta = -4.5$, −4.3, 14.1, 18.1, 22.6, 23.5 (2C), 24.66 (2C), 24.68 (2C), 25.4, 25.5, 25.9 (3C), 27.9, 29.3, 29.50, 29.53 (2C), 29.57 (3C), 29.61 (2C), 29.7, 29.8, 31.9, 34.2, 34.5, 69.1, 72.0, 72.5, 73.4, 82.2, 82.5, 123.8 (2C), 129.0, 150.8 (2C), 153.8 ppm; IR (KBr): $\tilde{\nu} = 3431$ cm^{-1}; MS (FAB): *m/z*: 769 $[M+H]^+$; HRMS (FAB): *m/z*: calcd for $C_{43}H_{81}O_7SSi$: 769.5472; found: 769.5511 $[M+H]^+$.

(2*R*,5*R*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13e): The procedure was the same as that used for preparation of **13a** and gave **13e** as a colorless oil. $[\alpha]_D^{23} = -10.5$ ($c = 1.12$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.05$ (s, 6H), 0.86–0.88 (m, 12H), 1.25–1.36 (m, 22H), 1.65–2.07 (m, 9H), 3.48 (ddd, $J = 11.6$, 6.1, 5.5 Hz, 1H), 3.65 (ddd, $J = 11.6$, 6.7, 3.1 Hz, 1H), 3.75–3.78 (m, 1H), 3.87 (dt, $J = 8.5$, 6.1 Hz, 1H), 3.90 (ddd, $J = 8.5$, 6.7, 3.7 Hz, 1H), 3.94 (dt, $J = 6.7$, 6.1 Hz, 1H), 4.08–4.13 ppm (m, 1H); ^{13}C NMR (75 MHz): $\delta = -4.5$, −4.3, 14.1, 18.1, 22.7, 25.4, 25.6, 25.9 (3C), 27.3, 28.7, 28.8, 29.3, 29.5, 29.56, 29.61 (2C), 29.64, 29.8, 31.9, 34.7, 64.9, 73.4, 79.9, 81.4, 81.5, 82.4 ppm; IR (KBr): $\tilde{\nu} = 3460$ cm^{-1}; MS (FAB): *m/z*: 507 $[M+Na]^+$; HRMS (FAB): *m/z*: calcd for $C_{28}H_{56}NaO_4Si$: 507.3846; found: 507.3842 $[M+Na]^+$.

(2*RS*,4*S*)-4-[(3′*R*,4′*S*,7′*S*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-(*p*-toluenesulfonyloxy)-4′,7′-epoxyicosanyl]-2-phenyl-1,3-dioxolane (15c): The procedure was the same as that used for preparation of **15a** and gave **15c** as a colorless oil. $[\alpha]_D^{25} = -5.8$ ($c = 1.19$ in $CHCl_3$); ^{1}H NMR: $\delta = -0.04$ (s, 1.8H), −0.03 (s, 1.2H), −0.003 (s, 1.8H), 0.002 (s, 1.2H), 0.84–0.85 (m, 9H), 0.88 (t, $J = 6.7$ Hz, 3H), 1.26–1.30 (m, 22H), 1.65–1.91 (m, 8H), 2.41 (s, 1.8H), 2.42 (s, 1.2H), 3.36 (ddd, $J = 11.6$, 5.5, 3.1 Hz, 1H), 3.47–3.50 (m, 1H), 3.58 (dd, $J = 7.9$, 6.7 Hz, 0.4H), 3.65 (dd, $J = 7.3$, 6.7 Hz, 0.6H), 3.90 (ddd, $J = 11.6$, 7.3, 4.9 Hz, 1H), 4.07 (dd, $J = 7.3$, 6.7 Hz, 0.6H), 4.12–4.18 (m, 1H), 4.23 (dd, $J = 7.9$, 6.7 Hz, 0.4H), 4.66 (ddd, $J = 7.3$, 4.3, 3.7 Hz, 0.6H), 4.70 (ddd, $J = 7.3$, 4.3, 3.7 Hz, 0.4H), 5.77 (s, 0.6H), 5.86 (s, 0.4H), 7.25–7.30 (m, 2H), 7.37–7.41 (m, 3H), 7.45–7.48 (m, 2H), 7.77–7.81 ppm (m, 2H); ^{13}C NMR (75 MHz): $\delta = -4.7$, −4.3, 14.1, 18.1, 21.5, 22.6, 25.0, 25.5, 25.9 (3C), 27.3, 27.9 (0.6C), 28.0 (0.4C), 29.0 (0.4C), 29.1 (0.6C), 29.3, 29.51, 29.54, 29.58 (2C), 29.61, 29.8, 31.9, 34.6, 69.9 (0.6C), 70.5 (0.4C), 72.8, 76.2 (0.4C), 76.9 (0.6C), 79.2 (0.6C), 79.3 (0.4C), 82.5, 84.7 (0.6C), 84.8 (0.4C), 103.0 (0.4C), 104.0 (0.6C), 126.3, 126.6, 127.8 (2C), 128.3 (2C), 129.0 (0.4C), 129.2 (0.6C), 129.4 (2C), 134.7 (0.4C), 134.8 (0.6C), 137.7 (0.6), 138.1 (0.4C), 144.1 ppm; IR (KBr): $\tilde{\nu} = 1599$, 1460 cm^{-1}; MS (FAB): *m/z*: 767 $[M+Na]^+$; HRMS (FAB): *m/z*: calcd for $C_{42}H_{68}NaO_7SSi$: 767.4353; found: 767.4344 $[M+Na]^+$.

(2*S*,5*S*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13f): The procedure was the same as that used for preparation of **13b** and gave **13f** as a colorless oil. $[\alpha]_D^{23} = -0.59$ ($c = 1.18$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.035$ (s, 3H), 0.044 (s, 3H), 0.85–0.87 (m, 12H), 1.23–1.34 (m, 22H), 1.55–1.73 (m, 3H), 1.78–1.97 (m, 5H), 2.21 (br, 1H), 3.47 (dd, $J = 11.6$, 5.5 Hz, 1H), 3.67 (dt, $J = 11.6$, 2.4 Hz, 1H), 3.79–3.80 (m, 1H), 3.81–3.89 (m, 2H), 3.89–3.93 (m, 1H), 4.06–4.10 ppm (m, 1H); ^{13}C NMR (75 MHz): $\delta = -4.6$, −4.3, 14.1, 18.1, 22.6, 25.4 (2C), 25.9 (3C), 27.4, 28.6 (2C), 29.3, 29.5, 29.55, 29.59 (2C), 29.62, 29.8, 31.9, 34.8, 64.6, 73.4, 79.7, 81.8, 82.0, 82.3 ppm; IR (KBr): $\tilde{\nu} = 3344$ cm^{-1}; MS (FAB): *m/z*: 507 $[M+Na]^+$; HRMS (FAB): *m/z*: calcd for $C_{28}H_{56}NaO_4Si$: 507.3846; found: 507.3852 $[M+Na]^+$.

(2*S*,5*S*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5-dihydroxy-6,9-epoxydocosanyl 2,4,6-triisopropylbenzenesulfonate (11d): The procedure was the same as that used for preparation of **11a** and gave **11d** as a colorless oil. $[\alpha]_D^{26} = -6.5$ ($c = 1.13$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.03$ (s, 3H), 0.04 (s, 3H), 0.86–0.88 (m, 12H), 1.25–1.63 (m, 44H), 1.76–1.98 (m, 4H), 2.77 (br, 1H), 2.91 (sep, $J = 6.7$ Hz, 1H), 3.37 (ddd, $J = 9.2$, 6.7, 2.1 Hz, 1H), 3.47 (br, 1H), 3.73–3.77 (m, 2H), 3.84 (ddd, $J = 7.9$, 6.1, 3.7 Hz, 1H), 3.88–3.93 (m, 1H), 3.97 (dd, $J = 9.8$, 6.4 Hz, 1H), 4.00 (dd, $J = 9.8$, 4.9 Hz, 1H), 4.14 (sep, $J = 6.7$ Hz, 2H), 7.18 ppm (s, 2H); ^{13}C NMR (67.8 MHz): $\delta = -4.4$, −4.1, 14.2, 18.2, 22.7, 23.6 (2C), 24.78 (2C), 24.80 (2C), 25.5, 26.0 (3C), 26.2, 28.5, 29.4, 29.5, 29.61, 29.63, 29.68 (4C), 29.72, 29.9, 30.0, 32.0, 34.3, 34.8, 69.4, 72.7, 73.1, 74.1, 82.0, 82.3, 123.7 (2C), 129.0, 150.7 (2C), 153.6 ppm; IR (KBr): $\tilde{\nu} = 3417$ cm^{-1}; MS (FAB): *m/z*: 769 $[M+H]^+$; HRMS (FAB): *m/z*: calcd for $C_{43}H_{81}O_7SSi$: 769.5472; found: 769.5488 $[M+H]^+$.

(2*R*,5*S*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13g): The procedure was the same as that used for preparation of **13a** and gave **13g** as a colorless oil. $[\alpha]_D^{25} = -10.4$ ($c = 1.03$ in $CHCl_3$); ^{1}H NMR: $\delta = 0.038$ (s, 3H), 0.044 (s, 3H), 0.85–0.87 (m, 12H), 1.24–1.34 (m, 22H), 1.75–2.03 (m, 8H), 3.09 (br, 1H), 3.44 (dd, $J = 11.6$, 3.1 Hz, 1H), 3.76 (dd, $J = 11.6$, 2.4 Hz, 1H), 3.80–3.83 (m, 1H), 3.88–3.94 (m, 3H), 4.10–4.14 ppm (m, 1H); ^{13}C NMR (75 MHz): $\delta = -4.6$, −4.3, 14.1, 18.1, 22.7, 25.3, 25.6, 25.9 (3C), 27.6, 28.9, 29.2, 29.3, 29.53, 29.55, 29.60 (2C), 29.64, 29.8, 31.9, 34.7, 66.1, 73.0, 79.9, 81.4, 81.5, 82.8 ppm; IR (KBr): $\tilde{\nu} = 3421$ cm^{-1}; MS (FAB): *m/z*: 485 $[M+H]^+$; HRMS (FAB): *m/z*: calcd for $C_{28}H_{57}O_4Si$: 485.4026; found: 485.4027 $[M+H]^+$.

(2*RS*,4*S*)-4-[(3′*S*,4′*S*,7′*S*,8′*R*)-8′-(*tert*-Butyldimethylsilyloxy)-3′-(*p*-toluenesulfonyloxy)-4′,7′-epoxyicosanyl]-2-phenyl-1,3-dioxolane (15d): The procedure was the same as that used for preparation of **15a** and gave **15d** as a colorless oil. $[\alpha]_D^{23} = -1.1$ ($c = 1.39$ in $CHCl_3$); ^{1}H NMR: $\delta = -0.07$ (s, 1.8H), −0.06 (s, 1.2H), −0.011 (s, 1.8H), −0.007 (s, 1.2H), 0.84–0.85 (m, 9H), 0.88 (t, $J = 7.0$ Hz, 3H), 1.26–1.30 (m, 22H), 1.61–1.94 (m, 8H), 2.415 (s, 1.8H), 2.423 (s, 1.2H), 3.55–3.58 (m, 1.4H), 3.64 (dd, $J = 7.9$, 6.7 Hz, 0.6H), 3.67–3.71 (m, 1H), 3.95–4.00 (m, 1H), 4.06 (dd, $J = 7.9$, 6.7 Hz, 0.6H), 4.17–4.23 (m, 1H), 4.22 (dd, $J = 6.7$, 6.1 Hz, 0.4H), 4.58

(ddd, $J=6.7$, 5.5, 4.9 Hz, 1H), 5.77 (s, 0.6H), 5.85 (s, 0.4H), 7.26–7.30 (m, 2H), 7.37–7.38 (m, 3H), 7.44–7.46 (m, 2H), 7.79–7.81 ppm (m, 2H); ^{13}C NMR (75 MHz): $\delta=-4.7$, -4.3, 14.1, 18.1, 21.5, 22.6, 25.2, 25.5, 25.9 (3C), 27.1 (0.6C), 27.4 (0.4C), 27.9 (0.6C), 28.0 (0.4C), 28.6 (0.4C), 28.8 (0.6C), 29.3, 29.52, 29.55, 29.59 (2C), 29.62, 29.8, 31.9, 34.6, 69.8 (0.6C), 70.5 (0.4C), 72.8, 75.7 (0.4C), 76.3 (0.6C), 78.6 (0.6C), 78.7 (0.4C), 82.5, 84.4, 103.0 (0.4C), 104.0 (0.6C), 126.3, 126.6, 127.86, 127.88, 128.2, 128.3, 129.0 (0.4C), 129.2 (0.6C), 129.4 (2C), 134.6, 137.6 (0.6C), 138.2 (0.4C), 144.20 (0.6C), 144.22 ppm (0.4C); IR (KBr): $\tilde{\nu}=1599$, 1460 cm^{-1}; MS (FAB): m/z: 767 $[M+Na]^+$; HRMS (FAB): m/z: calcd for $C_{42}H_{68}NaO_7SSi$: 767.4353; found: 767.4354 $[M+Na]^+$.

(2*S*,5*R*,6*S*,9*S*,10*R*)-10-(*tert*-Butyldimethylsilyloxy)-2,5;6,9-diepoxy-1-docosanol (13h): The procedure was the same as that used for preparation of **13b** and gave **13h** as a colorless oil. $[\alpha]_D^{22}=+3.0$ ($c=1.10$ in $CHCl_3$); ^{1}H NMR: $\delta=0.03$ (s, 3H), 0.05 (s, 3H), 0.85–0.87 (m, 12H), 1.23–1.34 (m, 22H), 1.50–1.58 (m, 1H), 1.79–2.01 (m, 7H), 3.09 (br, 1H), 3.41–3.43 (m, 1H), 3.73–3.74 (m, 1H), 3.76–3.77 (m, 1H), 3.87 (ddd, $J=7.9$, 5.8, 3.1 Hz, 1H), 3.96 (ddd, $J=7.3$, 6.7, 4.3 Hz, 1H), 4.07–4.13 ppm (m, 2H); ^{13}C NMR (75 MHz): $\delta=-4.6$, -4.3, 14.1, 18.1, 22.7, 25.4, 25.5, 26.0 (3C), 26.7, 27.6, 28.8, 29.3, 29.52, 29.55, 29.61 (2C), 29.64, 29.8, 31.9, 34.7, 66.0, 73.1, 79.9, 81.0, 82.2, 82.9 ppm; IR (KBr): $\tilde{\nu}=3442$ cm^{-1}; MS (FAB): m/z: 485 $[M+H]^+$; HRMS (FAB): m/z: calcd for $C_{28}H_{57}O_4Si$: 485.4026; found: 485.4033 $[M+H]^+$.

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