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Use of Heterocycles as Chiral Ligands and Auxiliaries in Asymmetric Syntheses of Sphingosine, Sphingofungins B and F

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Abstract: *D-erythro-Sphingosine and its derivatives (dihydrosphingosine, cis-sphingosine, etc.), sphingofungins B and F have been synthesized from simple achiral compounds using heterocyclic compounds as key chiral ligands and auxiliaries. 5-Benzyloxy-4-ethynyl-2,2-dimethyl-1,3-dioxane (5 or 5-ent), a key intermediate for the synthesis of sphingosine family, was prepared from 1-trimethylsilylpropinal and ketene silyl acetal 4 using a Sn(OTf)$_2$-chiral ligand 1 or 1-ent-catalyzed asymmetric aldol reaction. Sphingosine and its derivatives were readily prepared from 5 according to standard transformation. The chiral hydrophobic side chain (6) of sphingofungin B was synthesized using a catalytic asymmetric aldol reaction using chiral ligand 1-ent. Another key step in the total synthesis of sphingofungin B was a condensation of chiral aldehyde 7 and chiral heterocycle 2. Similarly, the reaction of chiral aldehyde 8 with heterocycle 3 was a key step for the synthesis of sphingofungin F. Highly diastereoselective reactions proceeded smoothly in both cases to afford the corresponding adducts in high yields.*

Introduction

Recently, much attention has been paid to the sphingomyelin cycle and the second messenger function of ceramide.[1] After the discovery of protein kinase C inhibition by sphingosine,[2] attention has been focused on the lipid components of sphingolipids and various lines of evidence led that sphingolipid-derived products may function as second messengers.[3,4] Efforts are now being made to define a novel ceramide-dependent pathway of signal transduction. On the other hand, the biosynthesis of sphingolipids starts from the condensation of palmitoyl-CoA with serine, which is catalyzed by serine palmitoyltransferase (SPT).[3a] The facts that cell mutants defective in SPT require exogenous sphingolipids for growth of the cells have revealed that sphingolipids are essential for growth of various types of cells.[3a,4j] Significant roles of sphingolipids have been indicated in various cellular events including proliferation, differentiation, death, and inflammatory responses.[3,4] Sphingofungin B was reported to inhibit SPT, and it has a striking resemblance to sphingosine and its biosynthetic intermediates.[5] Because of their novel polyhydroxy-amino acid structures containing five asymmetric centers, and of recent interest in the chemistry and biochemistry of sphingolipids,[3,4] there is a strong requirement for synthesis of these natural products as well as related compounds. In this paper, we report asymmetric syntheses of sphingosine and its derivatives (dihydrosphingosine, cis-sphingosine, etc.), sphingofungins B and F using heterocycles as chiral ligands and auxiliaries (Scheme 1).[6]

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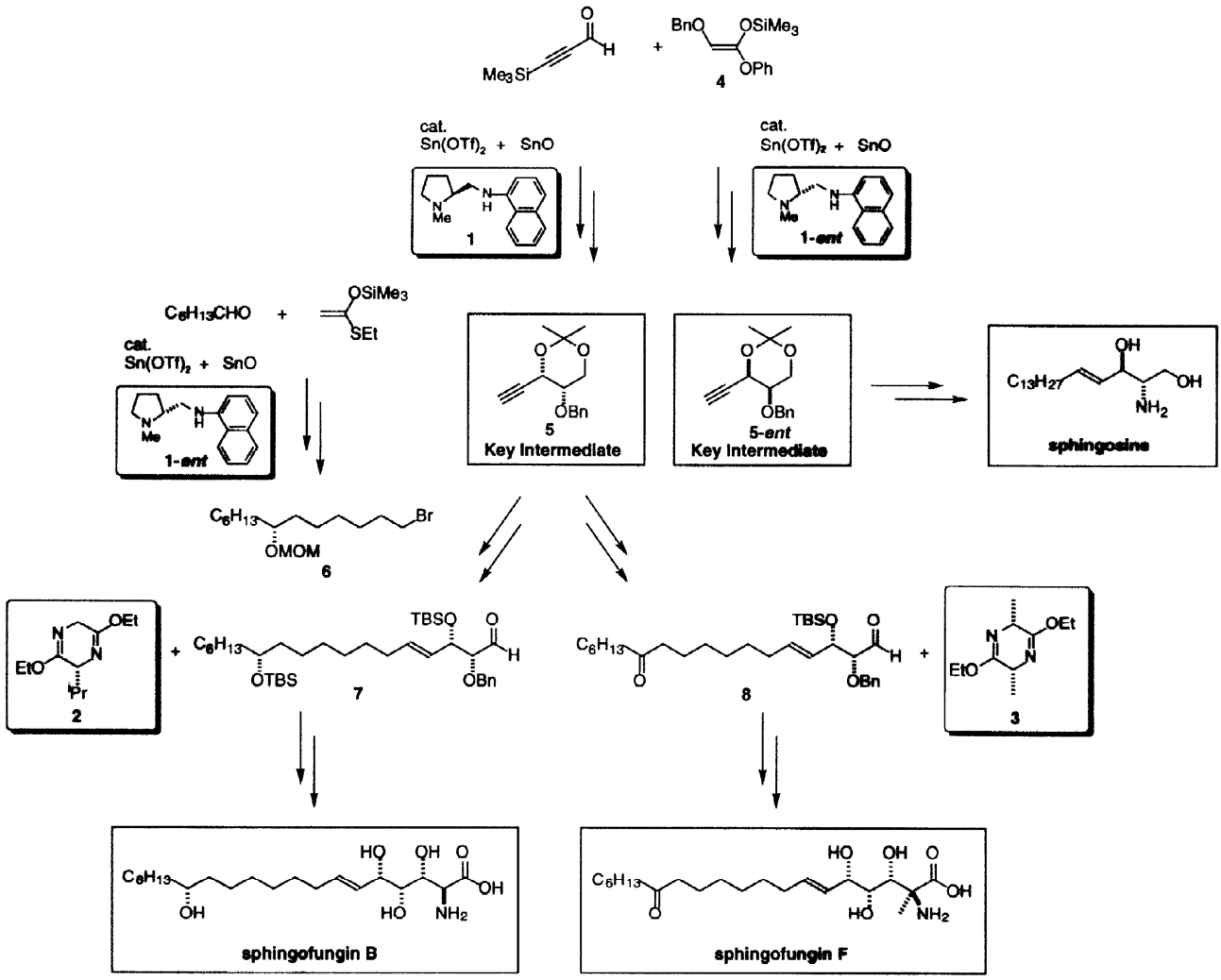
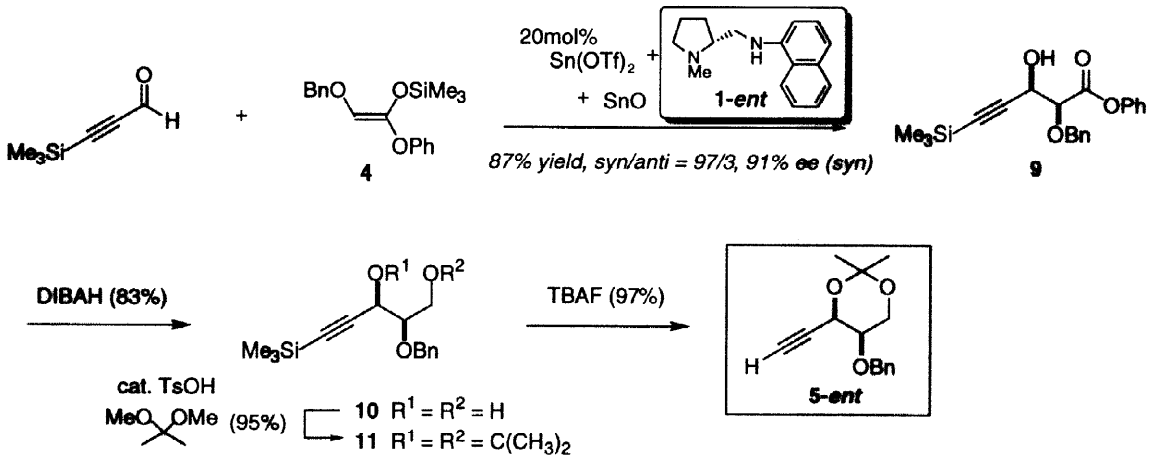


Scheme 1. General Scheme of the Synthesis of Sphingosine Family

Synthesis of 5-benzyloxy-4-ethynyl-2,2-dimethyl-1,3-dioxane (5 or 5-ent). A key intermediate for the synthesis of sphingosine family

We set 5-benzyloxy-4-ethynyl-2,2-dimethyl-1,3-dioxane (**5** or **5-ent**) as a key intermediate for the synthesis of sphingosine family. The synthesis was performed according to Scheme 2. Phenyl ester **9** was prepared from trimethylsilylpropynal and (*Z*)-2-benzyloxy-1-phenoxy-1-trimethylsiloxyethene (**4**) via a tin(II)-catalyzed asymmetric aldol reaction using 20 mol% of tin(II) triflate, chiral diamine **1-*ent***, and tin(II) oxide as a key step.[7] Slow addition of the substrates to the catalyst in propionitrile gave the best results, and the desired aldol adduct (**9**) was obtained in high diastereo- and enantioselectivities (*syn*/*anti* = 97/3, 91% ee for *syn*). Phenyl ester **9** was reduced using DIBAL to give diol **10**, which was protected as its acetonide **11**, after which desilylation with tetrabutylammonium fluoride gave the desired intermediate (**5-ent**). Intermediate **5-ent** was isolated as white crystals and could be purified by recrystallization. Similarly, **5** was prepared using **1**.

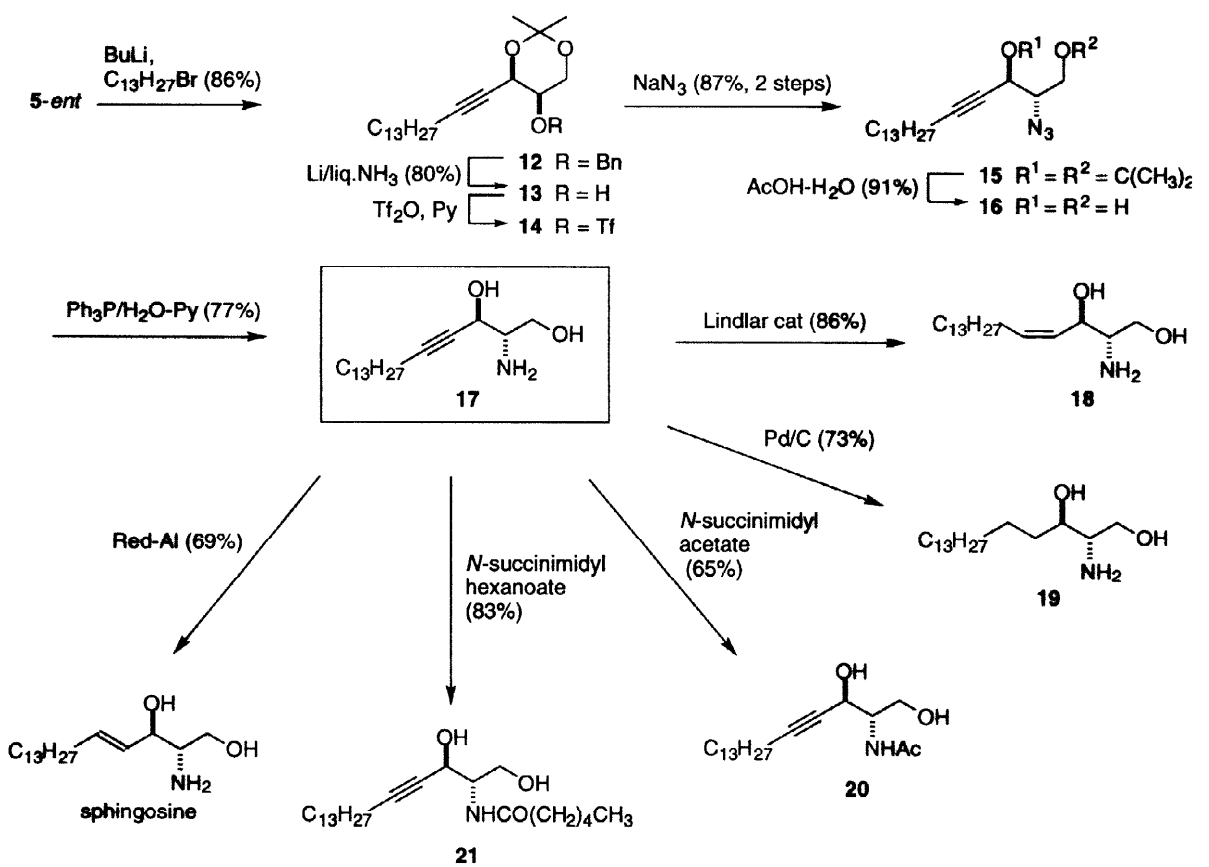
Scheme 2



Asymmetric synthesis of sphingosine and its derivatives

After the trimethylsilyl group of **5-*ent*** was deprotected and then alkylated, the benzyl group of **12** was removed under Birch conditions.[8] An azide group was introduced *via* an SN_2 process by successive treatment of **13** with triflic anhydride/pyridine and sodium azide.[9] At this stage, the basic skeleton of D-*erythro*-

Scheme 3

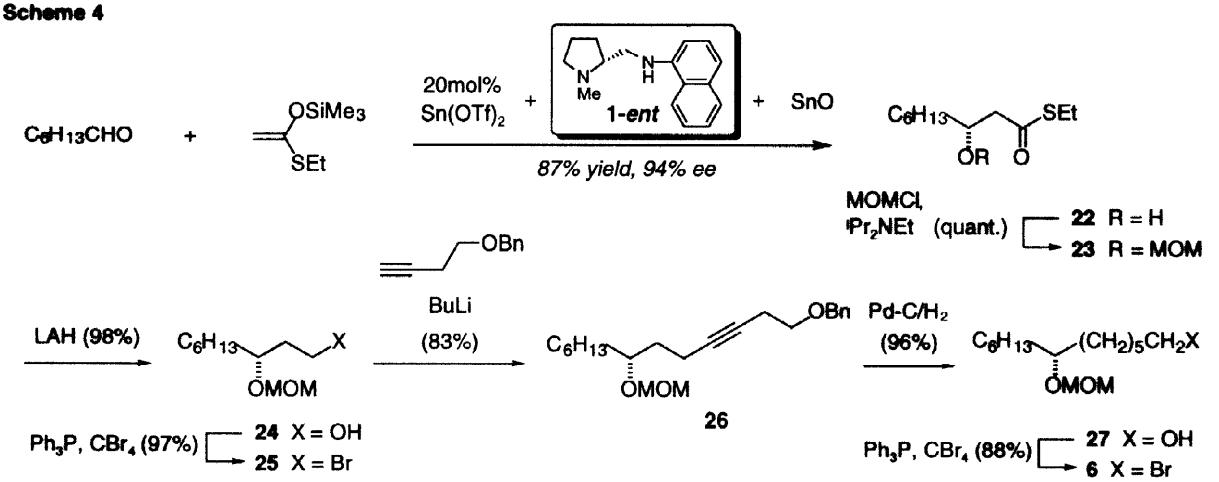


sphingosine was constructed. Deprotection of the acetonide group of **15**,[10] followed by reduction of the azide to an amino group,[11] gave another key intermediate (**17**) for the preparation of D-*erythro*-sphingosine and its derivatives. Trans reduction using Red-Al gave D-*erythro*-sphingosine, and the physical data including the optical rotation of the synthetic sample were completely consistent with those in the literature.[12] On the other hand, reduction using Lindler catalyst and Pd/C respectively gave cis-sphingosine (**18**) and dihydrosphingosine (**19**).[13] Chemoselective acylation of **17** gave triple bond-seramide anologues (**20**, **21**). These compounds were shown to have high apoptosis-inducing activity compared to the natural sphingosines.[14]

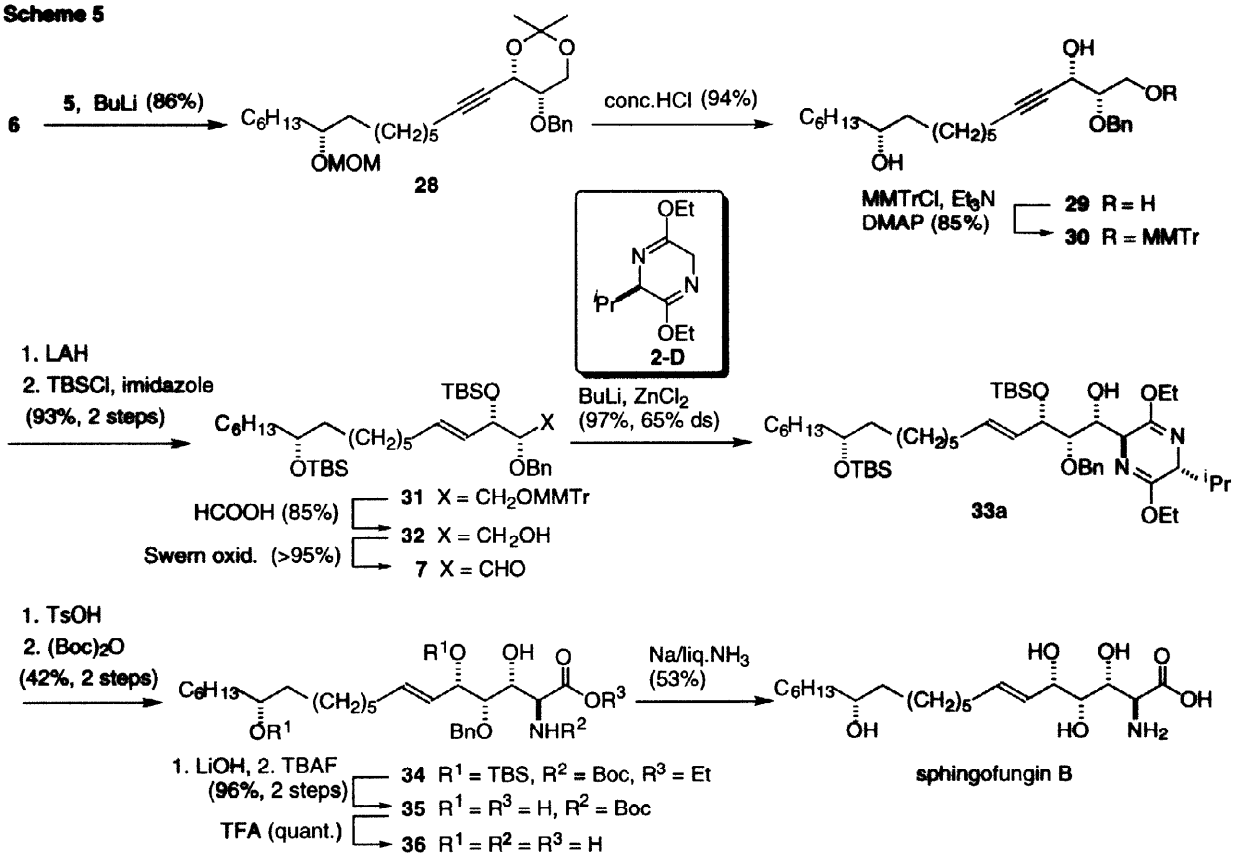
Asymmetric synthesis of sphingofungin B

We next undertook the synthesis of sphingofungin B (Schemes 4, 5).[15] The chiral hydrophobic chain **6** was prepared according to Scheme 4. The tin(II)-catalyzed asymmetric aldol reaction using chiral diamine **1-*ent*** was a powerful tool again,[7] and thioester **22** was obtained in a 94% ee from the achiral compounds, heptanal and 1-*S*-ethyl-1-trimethylsiloxyethene. The hydroxyl group of **22** was protected as its MOM ether and the thioester group was reduced using LAH. Alcohol **24** was brominated to give alkyl bromide **25** and the coupling reaction of **25** with 4-benzyloxy-1-butyne proceeded smoothly in THF-HMPA to give alkyne moiety **26**. Reduction of the alkyne of **26** and deprotection of the benzyl ether were carried out in one pot using Pd/C under H_2 atmosphere. The resulting alcohol (**27**) was brominated with carbon tetrabromide (CBr_4) and triphenylphosphine (Ph_3P) to give the desired chiral hydrophobic chain (**6**) in a high yield (Scheme 4). This chiral chain was then coupled with **5** to afford ether **28**, which was treated with conc. HCl to produce **29** (Scheme 5). Triol **29** was converted to aldehyde **7** in 5 steps. The primary hydroxyl group of **29** was protected as its MMTr ether, the acetylene was reduced to the trans olefin with LAH,[16] and the free secondary hydroxyl groups were protected as their TBS ethers. The MMTr group was selectively deprotected under mild acidic conditions to give alcohol **32**. Swern oxidation of **32** then gave the key aldehyde **7**.

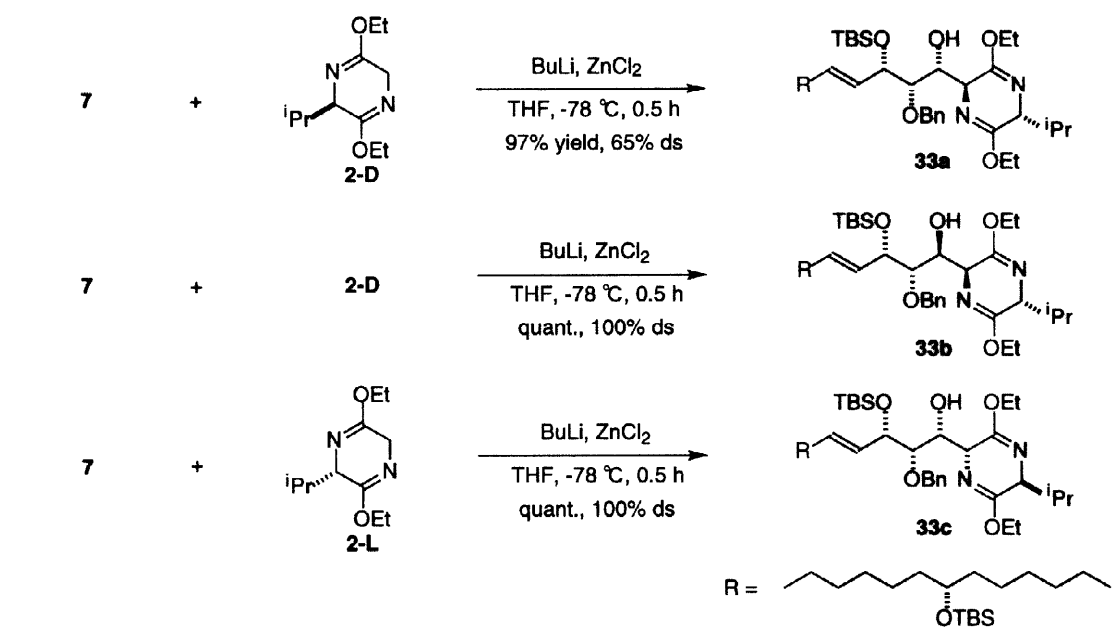
Scheme 4



Scheme 5



Scheme 6



Another key step for the synthesis of sphingofungin B was successfully carried out using heterocycle **2-D** as a chiral reagent. It was found that the zinc aza-enolate, which was prepared from the lithium enolate of the *D*-lactim ether (**2-D**)[17] and zinc chloride, reacted with **7** to afford **33a** in a 97% yield with 65% de. While, the tin(II) aza-enolate prepared from the lithium enolate of **2-D** and tin(II) chloride, reacted with **7** to afford **33b** quantitatively with perfect selectivity, *L*-valine was used to obtain **33c** quantitatively (Scheme 6). In these reactions, the stereochemistry of the C-2 stereogenic centers of the products were derived from those of the bislactim ether and hence from the *D*- or *L*-valine used. While the adduct predicted by the Felkin-Anh model[18] was obtained using the tin(II) azaenolate, the adduct predicted by the chelation model[19] was predominantly obtained using the zinc azaenolate.[20] Adduct **33a** was readily converted to carboxylic acid ester **34**. Hydrolysis of the resulting ester **34** and deprotection of the TBS groups with tetrabutylammonium fluoride afforded carboxylic acid **35**. After removal of the Boc group with TFA, the benzyl ether was finally cleaved under Birch conditions. Sphingofungin B was obtained after purification using reverse-phase column chromatography.[21] Its spectral and chromatographic properties are identical to those of an authentic sample of the natural product.[5,22]

Asymmetric synthesis of sphingofungin F

Our basic strategy for the synthesis of sphingofungin B would be useful for the synthesis of related compounds with minor modification. Simply changing the amino acid part and the hydrophobic side chain is required. To demonstrate the utility of this strategy, we undertook the total synthesis of sphingofungin F,[23] which was isolated from a fermentation of *Poecilomyces variotii*.

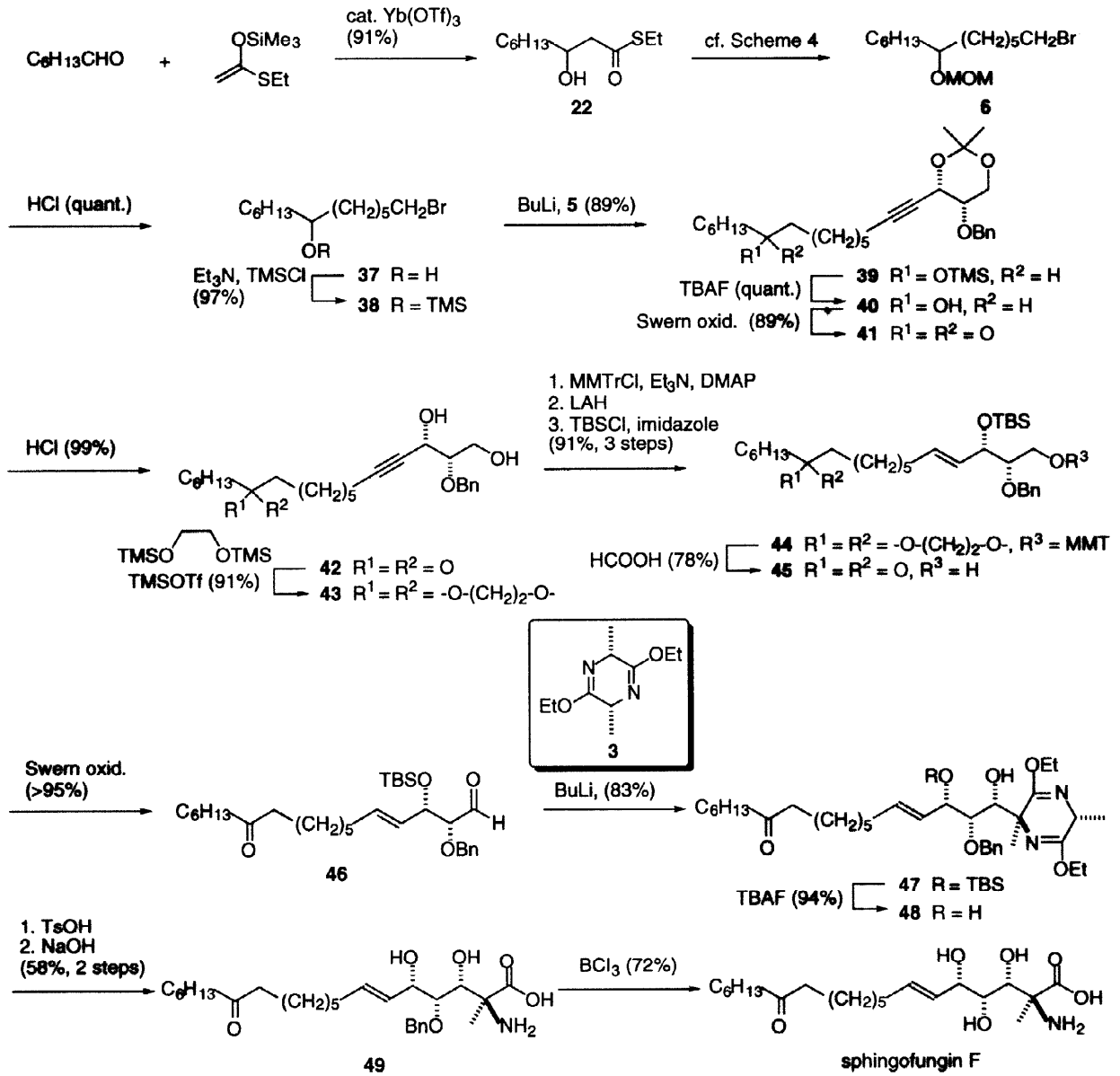
The $Yb(OTf)_3$-catalyzed aldol reaction[24] was very useful for the preparation of **22**. The route from racemic **22** to alkyl bromide **6** was performed according to Scheme 4 (asymmetric synthesis). After deprotection of the MOM ether of **6**, the resulting alcohol (**37**) was protected as its TMS ether giving **38**. Bromide **38** was then coupled with **5** to afford **39**. The trimethylsilyl group of **39** was deprotected, and the resulting alcohol (**40**) was oxidized (**41**), and this ketone was treated with HCl to give diol **42**. After the ketone group of **42** had been protected (**43**), the primary hydroxyl group was protected with MMTrCl. Reduction of the alkyne to the trans olefin was carried out using LAH,[16] and the secondary alcohol was protected as its TBS ether (**44**). Deprotection of the MMTr ether followed by Swern oxidation gave key aldehyde **46**.

The aldol-type reaction of **46** with the tin (II) azaenolate of chiral heterocyclic reagent **3**[17] proceeded smoothly to afford the desired adduct (**47**) in an 83% yield with good diastereoselectivity (70:25:5:0, Scheme 6). After deprotection of the TBS group, successive hydrolysis (2 steps) of the major diastereomer and finally deprotection of the benzyl ether using BCl_3 worked well to afford sphingofungin F. Its spectral properties are completely identical to those in the literature.[23]

Conclusions

Utility of heterocycles as chiral ligands and auxiliaries in asymmetric synthesis has been demonstrated in unambiguous syntheses of D-erythro-sphingosine and its derivatives (dihydrosphingosine, cis-sphingosine, etc.), sphingofungins B and F. Our basic strategy for the synthesis of sphingosine family will be applied to many other related natural products as well as their synthetic derivatives.

Scheme 7



Experimental Section

General. Melting points are uncorrected. IR spectra were recorded on a Horiba FT-300. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNR-EX270L, JNM-LA300 or a JNM-LA400 spectrometer in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard ($\delta = 0$) for ^1H NMR, and $CDCl_3$ was used as internal standard ($\delta = 77.0$) for ^{13}C NMR. When CD_3OD was used, CD_3OD served as internal standard ($\delta = 3.3$ for ^1H NMR (CH_3OH) and $\delta = 49.0$ for ^{13}C NMR). Mass spectra were measured on aJEOL DX-303HF spectrometer. HPLC was carried out using a Hitachi LC-Organizer, L-4000 UV Detector, L-6200 Intelligent Pump, and D-2500 Chromato-Integrator. Optical rotations were recorded on a Jasco DIP-360 digital polarimeter.

Column chromatography was performed on Silica gel 60 (Merck) or Wakogel B5F. All solvents were purified according to standard procedures.

Phenyl (2*S*,3*R*)-2-benzyloxy-3-hydroxy-5-trimethylsilylpent-4-ynoate (9): To a mixture of tin(II) trifluoromethansulfonate[25] (834 mg, 2.0 mmol), and tin(II) oxide (269 mg, 2.0 mmol) in propionitrile (20 ml) was added (*R*)-1-methyl-2-[(*N*-1-naphthylamino)methyl]pyrrolidine[26] (576 mg, 2.4 mmol) in propionitrile (20 ml) at room temperature. The solution was cooled to -78 °C, and trimethylsilylpropinal (1.26 g, 10 mmol) in propionitrile (15 ml), and **4** (3.77 g, 12 mmol) in propionitrile (15 ml) were slowly added over 4 h. After stirring for 1 h at -78 °C, saturated with aqueous $NaHCO_3$ solution was added to quench the reaction. The organic layer was separated and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was treated with THF:1N HCl = 4:1 solution for 30 min. After neutralization using saturated aqueous $NaHCO_3$ solution, the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **9** (3.21 g, 87%, *syn/anti* = 97/3, 91% ee (*syn*)) as a white solid. $[\alpha]_D^{27}$ +28.8 (c = 1.03, $CHCl_3$); IR (neat) 1643, 3379 cm^{-1}; ^1H NMR δ 0.02 (s, 9H), 2.91 (d, 1H, *J* = 8.1 Hz), 4.13 (d, 1H, *J* = 4.4 Hz), 4.56 (d, 1H, *J* = 11.9 Hz), 4.69 (dd, 1H, *J* = 4.4, 8.1 Hz), 4.77 (d, 1H, *J* = 11.9 Hz), 6.93-7.29 (m, 10H); ^{13}C NMR δ -0.4, 64.0, 73.4, 80.6, 91.7, 102.0, 121.2, 126.1, 128.19, 128.24, 128.4, 129.4, 136.5, 150.1, 168.0. Anal. Calcd for $C_{21}H_{24}O_4Si$: C, 68.45; H, 6.56. Found: C, 68.59; H, 6.51. The enantiomeric excess was determined by HPLC analysis. HPLC (Daicel Chiralcel AD, hexane/*i*-PrOH = 24/1, flow rate = 1.0 mL/min): t_R = 17.5 min (2S, 3R), t_R = 21.2 min (2R, 3S).

(2*R*,3*R*)-2-Benzyloxy-5-trimethylsilylpent-4-yne-1,3-diol (10): To a solution of **9** (3.21 g, 8.7 mmol) in dichloromethane (80 ml) was added diisobutylalminum hydride (1.5 M solution in toluene, 17.4 ml) over 20 min at -78 °C. After stirring for 30 min at -78 °C, the mixture was diluted with 1N HCl. After the organic layer was separated, the aqueous layer was extracted with dichloromethane. The combined organic layer was washed with water and brine, and dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 6/1) to give **10** (2.01 g, 83%) as a white solid. $[\alpha]_D^{27}$+13.0 (c = 1.02, C_6H_6); IR (neat) 2171, 3363 cm^{-1}; ^1H NMR δ 0.19 (s, 9H), 2.08 (brs, 1H), 2.69 (brs, 1H), 3.63 (ddd, 1H, *J* = 5.0, 5.0, 5.0 Hz), 3.56 (dd, 1H, *J* = 5.0, 11.6 Hz), 3.64 (dd, 1H, *J* = 5.0, 11.6 Hz), 4.30 (brs, 1H), 4.73 (d, 1H, *J* = 11.4 Hz), 4.83 (d, 1H, *J* = 11.4 Hz), 7.33-7.38 (m, 5H); ^{13}C NMR δ -0.3, 61.7, 63.2, 73.6, 81.7, 91.5, 103.6, 128.0, 128.1, 128.6, 137.7. Anal. Calcd for $C_{15}H_{22}O_3Si$: C, 64.71; H, 7.96. Found: C, 64.84; H, 7.95.

(4*S*,5*S*)-5-Benzyloxy-4-(2-trimethylsilylethynyl)-2,2-dimethyl-1,3-dioxane (11): To a solution of **10** (2.01 g, 7.2 mmol) in *N*,*N*-dimethylformamide (50 ml) was added a solution of 2,2-dimethoxypropane (2.2 g, 21.6 mmol) in N,N-dimethylformamide (10 ml) and cat p-TsOH at room temperature. After stirring for 10 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 30/1) to give **11** (2.18 g, 95% (*syn*); 0.06 g, 3% (*anti*)) as a white solid. $[\alpha]_D^{26}$ +37.0 (c = 2.13, $CHCl_3$); ^1H NMR δ 0.00 (s, 9H), 1.22 (s, 3H), 1.32 (s, 3H), 3.22 (dd, 1H, *J* = 3.0, 5.9 Hz), 3.64 (dd, 1H, *J* = 3.0, 12.5 Hz), 3.72 (dd, 1H, *J* = 3.3, 12.5Hz), 4.59-4.60 (m, 3H), 7.09-7.24 (m, 5H); ^{13}C NMR δ -0.3, 17.8, 20.3, 61.6, 64.1, 70.9, 71.7, 91.5, 99.6, 101.4, 127.7, 127.9, 128.3, 138.0. Anal. Calcd for $C_{18}H_{26}O_3Si$: C, 67.88; H, 8.23. Found: C, 68.01; H, 8.16.

(4*R*,5*R*)-5-Benzyloxy-4-ethynyl-2,2-dimethyl-1,3-dioxane (5-*ent*) (100% ee): To a solution of **11** (2.18 g, 6.8 mmol) in dichloromethane (50 ml) was added a solution of tetrabutylammoniumfluoride (1.96 g, 7.5 mmol) in dichloromethane (10 ml) at room temperature. After stirring for 30 min, the reaction was quenched with phosphate buffer (pH = 7) and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 6/1) to give **5** (1.62 g, 97%) as white crystals. The crystals were recrystalized from hexane to give optically pure **5** (>99% ee, 1.49 g, 89%). Mp 96-98 °C; $[\alpha]_D^{27}$ +34.3 (c = 1.21, $CHCl_3$); IR (KBr) 2117, 3220 cm^{-1}; ^1H NMR δ 1.43 (s, 3H), 1.54 (s, 3H), 2.57 (d, 1H, *J* = 2.3 Hz), 3.45 (dd, 1H, *J* = 3.1,

4.0 Hz), 3.86 (dd, 1H, J = 3.1, 12.5 Hz), 3.93 (dd, 1H, J = 4.0, 12.5 Hz), 4.78-4.80 (m, 3H), 7.26-7.44 (m, 5H); ^{13}C NMR δ 21.0, 27.4, 61.5, 63.6, 70.7, 71.9, 75.0, 80.0, 99.6, 127.8, 128.0, 128.3, 137.9; HRMS calcd for $C_{15}H_{18}O_3$ (M+H) 247.1335, found 247.1338. Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 72.85; H, 7.57. HPLC (Daicel Chiralcel AD, hexane/*i*-PrOH = 50/1, flow rate = 0.5 mL/min): t_R = 22.5 min (4S, 5S), t_R = 26.3 min (4R, 5R).

(4*R*,5*R*)-5-Benzyloxy-4-(pentadec-1-ynyl)-2,2-dimethyl-1,3-dioxane (12): To a solution of **5-*ent*** (1.49 g, 6.1 mmol) in THF (40 ml) was added n-BuLi (1.6M solution in hexane, 6.1 mmol) dropwise over 5 min at -78 °C. The solution was stirred for 15 min, and the mixture of 1-bromotridecane (1.91 g, 7.3 mmol) in THF (15 ml) and HMPA (4.8 ml) was added dropwise. After stirring for 10 min at -78 °C, the solution was warmed to room temperature, and stirred for a further 10 h. The reaction was then quenched with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 40/1) to give **12** (2.26 g, 87%) as a colorless oil. $[\alpha]_D^{27}$ +25.0 (c = 1.31, $CHCl_3$); IR (neat) 2250 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3H, J = 6.6 Hz), 1.25-1.40 (m, 22H), 1.43 (s, 3H), 1.52 (s, 3H), 2.27 (dt, 2H, J = 1.9, 7.1 Hz), 3.37 (ddd, 1H, J = 2.3, 3.1, 3.6 Hz), 3.85 (dd, 1H, J = 3.1, 12.5Hz), 3.91 (dd, 1H, J = 3.6, 12.5 Hz), 4.77 (d, 1H, J = 2.3 Hz), 4.79 (s, 2H), 7.25-7.44 (m, 5H); ^{13}C NMR δ 14.0, 18.9, 20.3, 22.6, 27.7, 28.3, 28.9, 29.0, 29.2, 29.4, 29.5, 31.8, 61.6, 63.8, 71.1, 71.7, 76.0, 87.4, 99.2, 127.5, 127.8, 128.1, 138.1. Anal. Calcd for $C_{28}H_{44}O_3$: C, 78.46; H, 10.35. Found: C, 78.62; H, 10.27.

(4*R*,5*R*)-5-Hydroxy-4-(pentadec-1-ynyl)-2,2-dimethyl-1,3-dioxane (13): To a solution of liq. NH_3 (10 ml) were added a solution of **12** (243.0 mg, 0.57 mmol) in THF (0.5 ml) and a solution of ^{t}BuOH (84.5 mg, 1.14 mmol) in THF (0.5 ml) at -78 °C. After adding ammonium sulfate (753.2 mg, 5.7 mmol), lithium (25 mg) was added slowly. After stirred for 10 min, the reaction was quenched with ammonium chloride. The cooling bath was removed, and after all ammonia was evaporated, the mixture was diluted with water and the aqueous layer extracted with dichloromethane. The extract was washed with water, and was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **13** (167.0 mg, 87%). $[\alpha]_D^{25}$ -21.6 (c = 1.21, $CHCl_3$); IR (KBr) 2245, 3519 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3H, J = 6.6 Hz), 1.25-1.46 (m, 22H), 1.48 (s, 6H), 2.23 (dt, 2H, J = 2.0, 7.3 Hz), 2.72 (d, 1H, J = 8.3 Hz), 3.51 (dddd, 1H, J = 1.7, 2.0, 2.3, 8.3 Hz), 3.87 (dd, 1H, J = 2.3, 12.5 Hz), 4.03 (dd, 1H, J = 1.7, 12.5 Hz), 4.78 (dd, 1H, J = 2.0, 3.6 Hz); ^{13}C NMR δ 14.1, 18.5, 18.8, 22.7, 28.4, 28.9, 29.1, 29.2, 29.3, 29.5, 29.6, 31.9, 64.6, 64.9, 65.5, 75.6, 87.9, 99.4.

(4*R*,5*S*)-5-Azido-2,2-dimethyl-4-(pentadec-1-ynyl)-1,3-dioxane (15): To a solution of **13** (167.0 mg, 0.49 mmol) in dichloromethane (2 ml) was added a solution of pyridine (58.5 mg, 0.74 mmol) in dichloromethane (0.5 ml). After cooling to -18 °C, a solution of trifluoromethanesulfonic acid anhydrate (172.6 mg, 0.61 mmol) in dichloromethane (0.5 ml) and sodium azide (128.3 mg, 1.97 mmol) in DMF (3 ml) were added. The mixture was warmed to room temperature, and was stirred for further 5 h. The reaction was then quenched with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **15** (113.0 mg, 63%). ^{1}H NMR δ 0.88 (t, 3H, J = 6.6 Hz), 1.26 (s, 22H), 1.45 (s, 6H), 2.25 (dt, 1H, J = 21.8, 7.3 Hz), 3.49-3.59 (m, 1H), 3.88-3.98 (m, 1H), 4.43 (dd, 1H, J = 1.8, 7.3 Hz); ^{13}C NMR δ 14.1, 18.8, 19.2, 22.7, 28.2, 28.4, 28.9, 29.1, 29.3, 29.5, 29.6, 31.9, 58.8, 62.3, 64.7, 76.2, 76.8, 77.2, 88.3, 99.3.

(2*S*,3*R*)-2-Azido-4-octadecyn-1,3-diol (16): The solution of **15** (113.0 mg, 0.31 mmol) in acetic acid:water = 7:3 (30 ml) was stirred for 30 min at 80 °C. The mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel to give **16** (94.5 mg, 94%). $[\alpha]_D^{25}$ -38.0 (c = 1.18, $CHCl_3$); IR (KBr) 2110, 2146, 2239, 3194, 3307 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3H, J = 6.9 Hz), 1.26-1.57 (m, 22H), 2.23 (dt, 2H, J = 2.0, 7.3 Hz), 2.28 (brs, 1H), 2.66 (brs, 1H), 3.61 (dt, 1H, J = 5.3, 10.6 Hz), 3.87 (brs, 2H), 4.53 (brs, 1H); ^{13}C NMR δ 14.1, 18.7, 22.7, 28.4, 28.9, 29.1, 29.3, 29.5, 29.6, 31.9, 62.4, 63.5, 66.6, 77.2, 88.7. HRMS calcd for $C_{18}H_{33}N_3O_2$ (M+) 323.2573, found 323.2582.

(2*S*,3*R*)-2-Amino-4-octadecyn-1,3-diol (17): To a solution of **16** (284.3 mg, 0.88 mmol) in pyridine (8.7 ml) were added triphenylphosphine (461.1 mg, 1.75 mmol) and water (0.5 ml). The solution was stirred for 5 h at 60 °C. The mixture was diluted with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue

was purified by column chromatography on silica gel to give **17** (201.3 mg, 77%). Mp 55.5-55.8 °C; $[\alpha]_D^{32}$ -3.0 (c = 1.25, EtOH); ^{1}H NMR (DMSO-d^6) δ 0.85 (brs, 3H), 1.23-1.40 (m, 21H), 2.17 (brs, 2H), 2.50 (brs, 1H), 2.61 (br, 1H), 3.34 (brs, 4H), 4.14 (brs, 1H), 4.42 (brs, 1H), 5.18 (brs, 1H); ^{13}C NMR δ 14.1, 18.7, 22.7, 28.4, 28.7, 29.0, 29.2, 29.4, 29.7, 31.9, 56.9, 63.7, 64.7, 78.4, 87.5. HRMS calcd for $C_{18}H_{35}NO_2$ (M+) 297.2668, found 297.2680. Anal. Calcd for $C_{18}H_{35}NO_2$: C, 72.68; H, 11.86; N, 4.71. Found: C, 72.81; H, 11.95; N, 4.56.

(2*S*,3*R*,4*Z*)-2-Amino-4-octadecen-1,3-diol (18): To a solution of **17** (16.5 mg, 0.056 mmol) in ethyl acetate (1.0 ml) was added Lindlar catalyst (2.8 mg) under argon. The solution was stirred under H_2 (1 atm) for 4 h. Lindlar catalyst was then filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **18** (14.3 mg, 86%). $[\alpha]_D^{29}$ -21.5 (c = 1.10, EtOH); ^{1}H NMR (CD_3OD) δ 0.90 (t, 3H, *J* = 6.6 Hz), 1.28-1.47 (m, 22H), 2.10 (brs, 2H), 2.77-2.81 (m, 1H), 3.55 (dd, 1H, *J* = 6.9, 10.9 Hz), 3.70 (dd, 1H, *J* = 4.1, 10.9 Hz), 4.41 (dd, 1H, *J* = 6.4, 8.7 Hz), 5.37-5.44 (m, 1H), 5.58-5.67 (m, 1H); ^{13}C NMR (CD_3OD) δ 14.5, 23.7, 28.9, 30.5, 30.7, 30.8, 33.1, 58.3, 63.5, 69.1, 130.0, 135.2. HRMS calcd for $C_{18}H_{37}NO_2$ (M+) 299.2824, found 299.2802.

(2*S*,3*R*)-2-Amino-octadecan-1,3-diol (19): To a solution of **17** (10.9 mg, 0.037 mmol) in ethanol (1.5 ml) was added a catalytic amount of 10% Pd/C under argon. The solution was stirred under H_2 (1 atm) for 3 h. Pd/C was then filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **19** (8.3 mg, 73%). $[\alpha]_D^{32}$ +0.62 (c = 0.55, EtOH); ^{1}H NMR (CD_3OD) δ 0.90 (t, 3H, *J* = 6.6 Hz), 1.28-1.67 (m, 28H), 2.75-2.82 (m, 1H), 3.47-3.57 (m, 2H), 3.74 (dd, 1H, *J* = 4.1, 11.1 Hz); ^{13}C NMR (CD_3OD) δ 14.5, 23.7, 27.0, 30.4, 30.7, 33.0, 34.3, 58.1, 63.4, 73.4. HRMS calcd for $C_{18}H_{39}NO_2$ (M+) 301.2981, found 301.2996.

(2*S*,3*R*)-2-Acetylamino-4-octadecyn-1,3-diol (20): To a solution of **17** (6.3 mg, 0.016 mmol) in THF (0.5 ml) was added a solution of *N*-succinimidyl acetate (3.4 mg, 0.020 mmol) in THF (0.5 ml). The mixture was stirred for 20 h, and was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **20** (4.7 mg, 65%). ^{1}H NMR δ 0.88 (t, 3H, *J* = 6.8 Hz), 1.26-1.45 (m, 20H), 1.49 (dd, 2H, *J* = 7.3, 14.2 Hz), 2.06 (s, 3H), 2.20-2.24 (m, 2H), 3.76 (dd, 1H, *J* = 4.0, 11.3 Hz), 4.02-4.06 (m, 1H), 4.16 (dd, 1H, *J* = 3.6, 11.6 Hz), 4.61 (brs, 1H), 6.36 (brs, 1H). HRMS calcd for $C_{20}H_{37}NO_3$ (M+) 339.2773, found 339.2764.

(2*S*,3*R*)-2-heptanoylamino-4-octadecyn-1,3-diol (21): To a solution of **17** (11.6 mg, 0.039 mmol) in THF (0.5 ml) was added a solution of *N*-succinimidyl hexanoate (8.4 mg, 0.040 mmol) in THF (0.5 ml). The mixture was stirred for 20 h, and was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give **21** (12.8 mg, 83%). ^{1}H NMR δ 0.88 (t, 3H, *J* = 6.6 Hz), 0.90 (t, 3H, *J* = 6.1 Hz), 1.26-1.35 (m, 25H), 1.46-1.51 (m, 2H), 1.54-1.68 (m, 2H), 2.19-2.28 (m, 4H), 2.91 (brs, 1H), 3.45 (brs, 1H), 3.78 (brs, 1H), 4.09 (brs, 1H), 4.61 (brs, 1H), 6.33 (brs, 1H). HRMS calcd for $C_{24}H_{45}NO_3$ (M+) 395.3399, found 395.3410.

(2*S*,3*R*,4*E*)-2-Amino-4-octadecen-1,3-diol (D-*erythro*-sphingosine): To a solution of Red-Al (0.115 M solution in in ether, 2.0 ml) was added a solution of **17** (13.8 mg, 0.046 mmol) in ether (0.5 ml) at 0 °C, and the mixture was stirred for 24 h. The reaction was then quenched with saturated aqueous sodium-potassium tartarate, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give sphingosine (6.7 mg, 69%). Mp 73-74 °C. $[\alpha]_D^{25}$ -2.4 (c = 0.81, $CHCl_3$); ^{1}H NMR (CD_3OD) δ 0.90 (brs, 3H), 1.28-1.47 (m, 22H), 2.07 (brs, 2H), 2.97 (brs, 1H), 3.57 (brs, 1H), 3.71 (brs, 1H), 4.12 (brs, 1H), 5.49 (brs, 1H), 5.80 (brs, 1H); ^{13}C NMR (CD_3OD) δ 14.4, 23.7, 30.2, 30.3, 30.4, 30.6, 30.7, 33.0, 33.4, 58.2, 61.8, 73.0, 129.5, 135.9.

Ethyl (3*R*)-3-hydroxynonanethioate (22): To a mixture of tin(II) trifluoromethansulfonate (417 mg, 1.0 mmol), tin(II) oxide (135 mg, 1.0 mmol) in dichloromethane (10 ml) was added (*S*)-1-methyl-2-[(*N*-1-naphthylamino)methyl]pyrrolidine (288 mg, 1.2 mmol) in dichloromethane (10 ml) at room temperature. The solution was cooled to -78 °C, and a solution of heptanal (570 mg, 5.0 mmol), and 1-trimethylsiloxy-1-ethylthioethene (1.06 mg, 6.0 mmol) in dichloromethane (15 ml) was slowly added over 4 h. After stirring for 1 h at -78 °C, the reaction was quenched with aqueous $NaHCO_3$ solution, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced

pressure. The residue was treated with THF:1N HCl = 4:1 solution for 30 min and the mixture was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated, and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **22** (950 mg, 87%, 94% ee) as a colorless oil. $[\alpha]_D^{25}$ -18.0 (c = 1.15, C_6H_6); IR (neat) 1683.6, 2927.4, 3378.7, 3475.1 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, *J* = 6.6 Hz), 1.24-1.56 (m, 13H), 2.61-2.81 (m, 3H), 2.91 (q, 2H, *J* = 7.5 Hz), 4.01-4.08 (m, 1H); ^{13}C NMR δ 14.0, 14.6, 22.5, 23.3, 25.3, 29.1, 31.7, 36.5, 50.6, 68.6, 199.6. Anal. Calcd for $C_{11}H_{22}O_2S$: C, 60.73; H, 10.09; S, 14.46. Found: C, 60.51; H, 10.16; S, 14.68. Enantiomeric excess was determined by HPLC analysis after acetylation of **22**. HPLC (Daicel Chiralcel AS, hexane/*i*-PrOH = 100/1, flow rate = 1.0 mL/min): t_R = 3.6 min (3S), t_R = 7.2 min (3R).

Ethyl (3*R*)-3-(methoxymethoxy)nonanethioate (23): To a solution of **22** (94% ee, 950.0 mg, 4.35 mmol) in dichloromethane (18 ml) was added a solution of diisopropylethylamine (1.7 g, 13.1 mmol) in dichloromethane (11 ml) and methoxymethyl chloride (1.1 g, 13.1 mmol) in dichloromethane (11 ml) at 0 °C. The solution was warmed to room temperature, and was stirred for 10 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) to give **23** (1.14 g, 100%) as a colorless oil. $[\alpha]_D^{28}$ -0.3 (c = 0.54, C_6H_6); IR (neat) 1689.3, 2927.4 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, *J* = 5.8 Hz), 1.01-1.46 (m, 11H), 1.48-1.58 (m, 2H), 2.67 (dd, 1H, *J* = 5.6, 15.0 Hz), 2.83 (dd, 1H *J* = 7.3, 15.0 Hz), 2.89 (q, 2H, *J* = 7.4 Hz), 3.35 (s, 3H), 3.99-4.08 (m, 1H), 4.63 (d, 1H, *J* = 7.3 Hz), 4.66 (d, 1H, *J* = 7.3 Hz); ^{13}C NMR δ 14.0, 14.7, 22.5, 23.4, 25.0, 29.2, 31.7, 34.7, 49.3, 55.6, 74.6, 95.8, 197.4. Anal. Calcd for $C_{13}H_{26}O_3S$: C, 59.50; H, 9.99; S, 12.22. Found: C, 59.61; H, 10.05; S, 12.09.

(3*R*)-3-(Methoxymethoxy)-1-nonanol (24): To a suspension of lithium aluminum hydride (496.5 mg, 13.1 mmol) in THF (9 ml) was slowly added a solution of **23** (1.14 g, 4.35 mmol) in THF (16 ml) at 0 °C. The mixture was warmed to room temperature and was stirred for 1.5 h. The mixture was then cooled to 0 °C and was quenched with saturated aqueous sodium sulfate solution. After adding of 1 N HCl aq., the suspension was stirred vigorously, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 6/1) to give **24** (869.8 mg, 98%) as a colorless oil. $[\alpha]_D^{25}$ -27.0 (c = 1.67, C_6H_6); IR (neat) 2929.3, 3392.2 cm^{-1}; ^1H NMR δ 0.87 (t, 3H, *J* = 6.9 Hz), 1.29 (s, 8H), 1.41-1.60 (m, 2H), 2.99 (brs, 1H), 3.40 (s, 3H), 3.66-3.82 (m, 3H), 4.65 (d, 1H, *J* = 6.9 Hz), 4.69 (d, 1H, *J* = 6.9 Hz); ^{13}C NMR δ 13.9, 22.4, 25.0, 29.3, 31.6, 34.5, 36.6, 55.5, 59.4, 76.0, 95.6. Anal. Calcd for $C_{11}H_{24}O_3$: C, 64.67; H, 11.84. Found: C, 64.59; H, 11.82.

1-Bromo-(3*R*)-3-(methoxymethoxy)nonane (25): To a solution of **24** (869.8 mg, 4.26 mmol) in dichloromethane (5.0 ml) was quickly added a solution of carbon tetrabromide (2.8 g, 8.51 mmol) in dichloromethane (3.0 ml) and triphenylphosphine (2.2 g, 8.51 mmol) in dichloromethane (3.0 ml) at 0 °C. After stirring for 30 min, the solvent was removed. The residue was then diluted with ether, and the solids were filtered off. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **25** (1.05 g, 92%) as a colorless oil. $[\alpha]_D^{22}$ -20.9 (c = 0.40, C_6H_6); IR (neat) 1039.4, 2929.3 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, *J* = 6.9 Hz), 1.29 (s, 8H), 1.42-1.61 (m, 2H), 2.00-2.08 (m,2H), 3.39 (s, 3H), 3.50 (t, 2H, *J* = 6.9 Hz), 3.67-3.76 (m, 2H), 4.65 (d, 1H *J* = 6.9 Hz), 4.69 (d, 1H, *J* = 6.9Hz); ^{13}C NMR δ 14.1, 22.6, 25.0, 29.4, 30.1, 31.8, 34.2, 37.8, 55.7, 75.7, 95.7. Anal. Calcd for $C_{11}H_{23}BrO_2$: C, 49.45; H, 8.68; Br, 29.90. Found: C, 49.62; H, 8.49; Br, 29.68.

1-Benzyloxy-(7*R*)-7-(methoxymethoxy)-3-tridecyne (26): To a solution of 4-benzyloxy-1-butyne (818.4 mg, 5.11 mmol) in THF (8.0 ml) was added n-BuLi (1.6 M solution in hexane, 4.72 mmol) dropwise over 5 min. The solution was stirred for 15 min, and a mixture of **25** (1.05 g, 3.93 mmol) in THF (6.5 ml) and HMPA (3.2 ml) was added dropwise. After stirring for 10 min at -78 °C, the solution was warmed to 0 °C, and stirred for further 4 h. The reaction was quenched with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 30/1) to give **26** (1.13 g, 83%) as a colorless oil. $[\alpha]_D^{24}$ -9.0 (c = 0.91, C_6H_6); IR (neat) 2927.4 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, *J* = 5.9 Hz), 1.28 (s,

8H), 1.40-1.49 (m, 2H), 1.68 (dt, 2H, J = 6.9, 13.0 Hz), 2.20-2.27 (m, 2H), 3.37 (s, 3H), 3.55 (t, 2H, J = 7.1 Hz), 3.61-3.67 (m, 1H), 4.54 (s, 2H), 4.65 (s, 2H), 7.25-7.35 (m, 5H); ^{13}C NMR δ 14.1, 14.9, 20.1, 22.6, 25.1, 29.4, 31.8, 33.6, 34.1, 55.5, 68.8, 72.8, 76.3, 76.8, 80.9, 95.5, 127.6, 128.3, 138.1. Anal. Calcd for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 76.41; H, 9.95.

(7*R*)-7-(Methoxymethoxy)-1-tridecanol (27): To a solution of **26** (1.13 g, 3.26 mmol) in ethanol (16 ml) was added a catalytic amount of 10% palladium-carbon under argon. The solution was stirred under H_2 at 1 atm for 20 h. Palladium-carbon was then filtered off, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 6/1) to give **27** (815.3 mg, 96%) as a colorless oil. $[\alpha]_D^{25}$ -0.1 (c = 1.31, C_6H_6); IR (neat) 2931.3, 3378.7 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3H, J = 6.6 Hz), 1.11-1.57 (m, 20H), 1.70 (brs, 1H), 3.38 (s, 3H), 3.45-3.54 (m, 1H), 3.64 (t, 2H, J = 6.6 Hz), 4.65 (s, 2H); ^{13}C NMR δ 14.1, 22.6, 25.2, 25.7, 29.5, 29.5, 31.8, 32.7, 34.2, 34.3, 55.4, 62.9, 77.4, 95.3. Anal. Calcd for $C_{15}H_{32}O_3$: C, 69.18; H, 12.39. Found: C, 68.85; H, 12.22.

1-Bromo-(7*R*)-7-methoxymethoxytridecane (6): To a solution of **27** (815.3 mg, 3.13 mmol) in dichloromethane (6.0 ml) was quickly added a solution of carbon tetrabromide (2.08 g, 6.26 mmol) in dichloromethane (4.5 ml) and triphenylphosphine (1.64 g, 6.26 mmol) in dichloromethane (4.5 ml) at 0 °C. After stirring for 30 min, the solvent was removed under reduced pressure. The residue was then diluted with ether, and the solids were filtered off. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **6** (890.7 mg, 88%) as a colorless oil. $[\alpha]_D^{26}$ -0.06 (c = 0.97, C_6H_6); IR (neat) 2931.3 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3H, J = 6.4 Hz), 1.18-1.60 (m, 18H), 1.86 (dt, 2H, J = 6.6, 14.4 Hz), 3.38 (s, 3H), 3.41 (t, 2H, J = 5.6, 11.3 Hz), 4.65 (s, 2H); ^{13}C NMR δ 14.1, 22.6, 25.1, 25.2, 28.1, 28.9, 29.5, 31.8, 32.7, 33.9, 34.1, 34.3, 55.5, 77.5, 95.3. Anal. Calcd for $C_{15}H_{31}BrO_2$: C, 55.72; H, 9.66; Br, 24.71. Found: C, 55.96; H, 9.51; Br, 23.47.

(2*S*,3*S*,9'*R*)-3-Benzyloxy-2-(9'-(methoxymethoxy)pentadec-1-ynyl)-2,2-dimethyl-1,3-dioxane (28): To a solution of **5** (646.4 mg, 2.62 mmol) in THF (15.0 ml) at -78 °C was added n-BuLi (1.6 M solution in hexane, 2.62 mmol) dropwise over 5 min. The mixture was stirred for 15 min, and a mixture of **6** (890.7 mg, 2.75 mmol) in THF (4.0 ml) and HMPA (1.9 ml) was added dropwise. After stirring for 10 min at -78 °C, the mixture was warmed to 0 °C, and was stirred for a further 10 h. The reaction was quenched with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) to give **28** (1.10 g, 86%) as a colorless oil. $[\alpha]_D^{24}$ +4.4 (c = 1.06, C_6H_6); IR (neat) 1375.0, 1457.9, 2242.8, 2856.1 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3H, J = 6.4 Hz), 1.28-1.60 (m, 26H), 2.27 (dt, 2H, J = 2.0, 7.1 Hz), 3.33-3.39 (m, 4H), 3.50 (t, 1H, J = 5.6 Hz), 3.82-3.94 (m, 2H), 4.64 (s, 2H), 4.77-4.78 (m, 3H), 7.24-7.44 (m, 5H); ^{13}C NMR δ 14.0, 18.9, 20.3, 22.5, 25.05, 25.14, 27.8, 28.3, 28.9, 29.3, 29.4, 31.7, 34.2, 55.3, 61.7, 63.8, 71.1, 71.7, 76.1, 77.5, 87.3, 95.2, 99.3, 127.5, 127.8, 128.1, 138.1; FABHRMS calcd for $C_{30}H_{48}O_5$ (M+Na) 511.3399, found 511.3396. Anal. Calcd for $C_{30}H_{48}O_5$: C, 73.73; H, 9.90. Found: C, 73.67; H, 9.95.

(2*S*,3*S*,12*R*)-2-Benzyloxyoctadec-4-yne-1,3,12-triol (29): To a solution of **28** (1.10 g, 2.26 mmol) in methanol (35 ml) was added conc. HCl (0.5 ml), and the mixture was stirred for 30 min at 60 °C. The mixture was cooled to room temperature, then diluted with water (60 ml), and cooled to 0 °C. The mixture was neutralized with potassium carbonate and the aqueous layer was extracted with ether. The ethereal extract was washed with saturated aqueous $NaHCO_3$ solution, water, and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetae = 2/1) to give **29** (876.4 mg, 96%) as a colorless oil. $[\alpha]_D^{24}$ +0.6 (c = 5.25, C_6H_6); IR (neat) 2337.3, 2927.4, 3371.0 cm^{-1}; ^{1}H NMR δ 0.80 (t, 3H, J = 6.9 Hz), 1.20-1.44 (m, 20H), 1.87 (brs, 1H), 2.14 (t, 2H, J = 5.9 Hz), 2.61 (brs, 1H), 3.08 (brs, 1H), 3.47-3.52 (m, 2H), 3.65 (dd, 1H, J = 5.0, 11.9 Hz), 3.76 (dd, 1H, J = 4.6, 11.5 Hz), 4.40 (m, 1H), 4.63 (d, 1H, J = 11.5 Hz), 4.71 (d, 1H, J = 11.5 Hz), 7.20-7.29 (m, 5H); ^{13}C NMR δ 14.0, 18.6, 22.5, 25.3, 25.5, 28.2, 28.6, 28.9, 29.3, 31.7, 37.1, 37.3, 61.6, 62.9, 71.8, 73.3, 78.2, 82.0, 87.0, 127.9, 128.4, 137.8; FABHRMS calcd for $C_{25}H_{40}O_4$ (M+Na) 427.2824, found 427.2833. Anal. Calcd for $C_{30}H_{48}O_5$: C, 74.22; H, 9.97. Found: C, 74.38; H, 9.88.

(2*S*,3*S*,12*R*)-2-Benzyloxy-1-(4-methoxyphenyldiphenylmethoxy)-octadec-4-yne-3,12-diol (30): To a solution of **29** (876.4 mg, 2.17 mmol) in dichloromethane (12 ml) was added a solution of triethylamine (438.3 mg, 4.3 mmol) in dichloromethane (6.0 ml), and a solution 4-methoxytrityl chloride (1.2 g, 4.3 mmol) in

dichloromethane (6.0 ml) at 0 °C. After a catalytic amount of *N,N*-dimethylaminopyridine was added, the mixture was stirred for 1 h. The reaction was quenched with water and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetae = 2/1) to give **30** (1.25 g, 85%) as a yellow oil. $[\alpha]_D^{25}$ +8.6 (c = 1.0, C_6H_6); IR (neat) 2233.2, 2923.6, 3423.0 cm^{-1}; ^1H NMR δ 0.88 (t, 3H, *J* = 6.4 Hz), 1.28-1.40 (m, 20H), 2.12 (m, 2H), 2.87 (brs, 1H), 3.32 (dd, 1H, *J* = 5.0, 9.6 Hz), 3.45 (dd, 1H, *J* = 4.3, 10.2 Hz), 3.54 (brs, 1H), 3.63 (m, 1H), 3.76 (s, 3H), 4.55 (m, 1H), 4.61 (d, 1H, *J* = 12.2 Hz), 4.73 (d, 1H, *J* = 11.6 Hz), 6.79-7.47 (m, 19H); ^{13}C NMR δ 14.0, 18.6, 22.5, 25.4, 25.4, 25.5, 28.3, 28.8, 29.0, 29.3, 31.8, 37.3, 37.4, 55.1, 62.8, 62.9, 71.8, 73.1, 78.2, 81.3, 86.4, 86.5, 113.0, 126.8, 127.7, 127.9, 128.2, 128.3, 130.3, 135.4, 137.9, 144.2, 158.4. Anal. Calcd for $C_{45}H_{56}O_5$: C, 79.84; H, 8.34. Found: C, 79.98; H, 8.33.

(2*S*,3*S*,12*R*)-2-Benzyloxy-3,12-di(tert-butyldimethylsiloxy)-1-(4-methoxyphenyldiphenylmethoxy)-4-octadecene (31): To a suspension of lithium aluminum hydride (244.6 mg, 6.44 mmol) in THF (40 ml) was added a solution of **30** (1.25 g, 1.84 mmol) in THF (40 ml) at 0 °C. The mixture was warmed to room temperature, and was stirred for 10 min. The mixture was refluxed for 1 h, and then cooled to 0 °C. The reaction was quenched with saturated aqueous potassium sodium tartarate solution. After the suspension was stirred vigorously, the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure to give a yellow oil. To a solution of the yellow oil in DMF (12 ml) was added a solution of imidazole (501.4 mg, 7.36 mmol) in DMF (6.0 ml), and tert-butyldimethylsilylchloride (1.11 g, 7.36 mmol) in DMF (6.0 ml) at 0 °C. After the solution was stirred for 10 h at room temperature, the reaction was quenched with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 30/1) to give **31** (1.56 g, 93%, 2 steps) as a yellow oil. $[\alpha]_D^{26}$ -7.5 (c = 0.97, C_6H_6); IR (neat) 1251.6, 2919.7 cm^{-1}; ^1H NMR δ -0.06 (s, 6H), 0.00 (s, 6H), 0.79-0.85 (m, 21H), 1.18-1.35 (m, 18H), 1.83 (m, 2H), 3.04 (dd, 1H, *J* = 6.3, 9.6 Hz), 3.25 (d, 1H, *J* = 9.6 Hz), 3.47 (m, 1H), 3.56-3.59 (m, 1H), 3.70 (s, 3H), 4.22 (t, 1H, *J* = 5.8 Hz), 4.68 (d, 1H, *J* = 11.9 Hz), 4.75 (d, 1H, *J* = 11.9 Hz), 5.28 (dd, 1H, *J* = 6.1, 15.3 Hz), 5.46 (m, 1H), 6.74 (d, 2H, *J* = 8.6 Hz), 7.11-7.44 (m, 19H); ^{13}C NMR δ -4.8, -4.4, -4.4, 14.1, 18.2, 22.6, 25.3, 25.9, 26.0, 29.1, 29.2, 29.6, 29.7, 31.9, 32.1, 37.2, 55.1, 63.9, 72.3, 73.1, 73.8, 82.7, 86.2, 112.9, 126.4, 127.3, 127.7, 127.7, 128.2, 128.3, 128.5, 129.3, 130.4, 132.0, 135.9, 139.2, 144.7, 158.3; FABHRMS calcd for $C_{57}H_{86}O_5Si_2$ (M+Na) 929.5911, found 929.5905. Anal. Calcd for $C_{57}H_{86}O_5Si_2$: C, 75.44; H, 9.55. Found: C, 75.58; H, 9.49.

(2*R*,3*S*,14*R*)-2-Benzyloxy-3,14-di(tert-butyldimethylsiloxy)-octadec-4-ene-1-ol (32): To a solution of **31** (1.56 g, 1.72 mmol) in ether (120 ml) was added 98% formic acid (60 ml). The mixture was stirred for 30 min at 0 °C, and then diluted with water (150 ml). The solution was neutralized with potassium carbonate and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetae = 20/1) to give **32** (927.1 mg, 85%) as a colorless oil. $[\alpha]_D^{27}$ +16.5 (c = 1.81, C_6H_6); IR (neat) 1253.5, 2856.1, 2931.3 cm^{-1}; ^1H NMR δ 0.03 (s, 6H), 0.04 (s, 6H), 0.86 (t, 3H, *J* = 6.8 Hz), 0.886 (s, 9H), 0.888 (s, 9H), 1.27-1.39 (m, 20H), 2.04 (dt, 2H, *J* = 6.8, 13.4 Hz), 2.18 (brs, 1H), 3.45-3.53 (m, 2H), 3.59 (dt, 1H, *J* = 5.6, 11.5 Hz), 3.75 (dd, 1H, *J* = 4.6, 11.2 Hz), 4.29 (d, 1H, *J* = 5.9 Hz), 4.62 (d, 1H, *J* = 11.6 Hz), 4.75 (d, 1H, *J* = 11.6 Hz), 5.49 (dd, 1H, *J* = 6.3, 15.5 Hz), 5.67 (dt, 1H, *J* = 6.6, 15.5 Hz), 7.16-7.40 (m, 5H); ^{13}C NMR δ -4.9, -4.5, -4.4, 14.1, 18.1, 22.6, 25.3, 25.8, 25.9, 29.2, 29.2, 29.5, 29.7, 31.9, 32.3, 37.1, 61.9, 72.4, 73.0, 74.0, 81.9, 127.8, 127.8, 128.5, 133.1, 138.5; FABHRMS calcd for $C_{37}H_{70}O_4Si_2$ (M+Na) 657.4711, found 657.4714. Anal. Calcd for $C_{37}H_{70}O_4Si_2$: C, 69.97; H, 11.11. Found: C, 69.82; H, 10.97.

(2*R*,3*S*,12*R*)-2-Benzyloxy-3,12-di(tert-butyldimethyisiloxy)-octadec-4-enal (7): To a solution of oxalyl chloride (60.9 mg, 0.48 mmol) in dichloromethane (1.5 ml) was added a solution of dimethylsulfoxide (48.8 mg, 0.62 mmol) in dichloromethane (1.1 ml) dropwise over 15 min at -78 °C. A solution of **32** (151.9 mg, 0.24 mmol) in dichloromethane (1.7 ml) was added and the mixture was stirred for 10 min at -78 °C, and for 1 h at -50 °C. Triethylamine (176.0 mg, 1.67 mmol) was added and the mixture warmed to 0 °C and stirred for 20 min. The reaction was quenched with saturated aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane. The extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetae = 20/1)

to give **7** (151.4 mg, quant.) as a colorless oil. ^{1}H NMR δ 0.04 (s, 6H), 0.06 (s, 6H), 0.90-0.91 (m, 21H), 1.30-1.41 (m, 20H), 2.01- 2.06 (m, 2H), 3.64 (t, 1H, *J* = 5.3 Hz), 3.76 (dd, 1H, *J* = 1.5, 5.0 Hz), 4.43 (t, 1H, *J* = 5.6 Hz), 4.59 (d, 1H, *J* = 12.2 Hz), 4.71 (d, 1H, *J* = 12.2 Hz), 5.57 (dd, 1H, *J* = 6.6, 15.5 Hz), 5.70 (dt, *J* = 6.3, 15.5 Hz), 7.28-7.37 (m, 5H), 9.69 (d, 1H, *J* = 1.5 Hz); ^{13}C NMR δ -5.0, -4.4, 14.1, 18.1, 22.6, 25.3, 25.7, 25.9, 29.0, 29.1, 29.5, 29.7, 31.9, 32.1, 37.1, 72.3, 72.8, 73.8, 86.2, 127.9, 128.1, 128.4, 133.6, 137.4, 202.6; FABHRMS calcd for $C_{37}H_{68}O_4Si_2$ (M+Na) 655.4553, found 655.4559.

(1*R*,1*S*,2*S*,3*S*,4*R*,12*R*)-2-Benzyloxy-3,12-di(tert-butyldimethylsiloxy)-1-(3',6'-diethoxy-4'-(iso-propyl)-1'H,4'H-2',5'-diazyl)-octadec-4-ene-1-ol (33a): To a solution of **2-D** (61.6 mg, 0.29 mmol) in THF (1.2 ml) was added n-BuLi (1.6 M solution in hexane, 0.29 mmol) dropwise at -78 °C. The solution was warmed to 0 °C, and was stirred for 15 min, and a solution of zinc chloride (39.3 mg, 0.29 mmol) in THF (1.2 ml) was added. The solution was stirred for further 15 min, and after the solution was cooled to -78 °C, a solution of **7** (91.3 mg, 0.14 mmol) in THF (1.2 ml) was added. The mixture was stirred for 1 h at -78 °C, and then was quenched with phosphate buffer solution (pH = 7). The aqueous layer was extracted with dichloromethane and the extract was dried over sodium sulfate. The organic layer was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give a mixture of **33a-c** (117.4 mg, 97%) as a colorless oil. The diastereomer ratio of **33a-c** was determined by ^{13}C NMR analysis. **33a:** ^{1}H NMR δ -0.06 (s, 3H), -0.07 (s, 3H), 0.00 (s, 6H), 0.66 (d, 3H, *J* = 6.9 Hz), 0.73 (d, 3H, *J* = 6.9 Hz), 0.83 (s, 9H), 0.85 (s, 9H), 1.00 (t, 3H, *J* = 3.1 Hz), 1.20-1.34 (m, 26H), 1.99-2.13 (brs, 1H), 2.14-2.26 (m, 2H), 3.44 (brs, 1H), 3.72-4.19 (m, 9H), 4.42 (d, 1H, *J* = 11.6 Hz), 4.89 (d, 1H, *J* = 11.2 Hz), 5.37-5.45 (m, 1H), 5.64-5.72 (m, 1H), 7.16-7.31 (m, 5H); ^{13}C NMR δ -4.6, -4.2, 14.1, 14.3, 14.4, 16.6, 17.0, 18.1, 19.0, 22.6, 25.3, 25.6, 25.9, 29.1, 29.3, 29.5, 29.7, 31.6, 31.9, 32.4, 32.5, 37.1, 46.7, 57.8, 60.8, 60.8, 71.5, 72.3, 74.3, 75.6, 81.9, 127.0, 127.1, 127.9, 130.3, 133.4, 139.2, 162.2, 163.2; FABHRMS calcd for $C_{48}H_{88}N_2O_6Si_2$ (M+Na) 867.6078, found 867.6066. **33b:** ^{1}H NMR δ -0.06 (s, 3H), -0.06 (s, 3H), 0.00 (s, 6H), 0.69 (d, 3H, *J* = 6.6 Hz), 0.73 (d, 3H, *J* = 6.9 Hz), 0.81 (s, 9H), 0.85 (s, 9H), 1.00 (t, 3H, *J* = 3.3 Hz), 1.20-1.35 (m, 26H), 2.05 (brs, 1H), 2.17-2.27 (m, 2H), 3.36 (brs, 1H), 3.58-3.60 (m, 1H), 3.79 (dd, 1H, *J* = 3.8, 9.4 Hz), 3.86-4.31 (m, 8H), 4.64 (d, 1H, *J* = 11.5 Hz), 4.71 (d, 1H, *J* = 11.5 Hz), 5.65 (d, 2H, *J* = 2.0 Hz), 7.23-7.34 (m, 5H); ^{13}C NMR δ -4.7, -4.5, 14.1, 14.3, 14.4, 16.8, 17.0, 18.1, 19.1, 22.6, 25.3, 25.7, 25.9, 29.2, 29.3, 29.5, 29.7, 31.6, 31.9, 32.3, 32.5, 37.1, 46.7, 56.3, 60.3, 60.6, 60.7, 61.0, 72.4, 73.4, 74.1, 78.0, 127.7, 127.8, 128.2, 128.3, 133.2, 138.6, 161.9, 164.3; FABHRMS calcd for $C_{48}H_{88}N_2O_6Si_2$ (M+Na) 867.6078, found 867.6084. **33c:** ^{1}H NMR δ -0.02 (s, 3H), -0.01 (s, 3H), 0.00 (s, 6H), 0.67 (d, 3H, *J* = 6.9 Hz), 0.74 (d, 3H, *J* = 6.9 Hz), 0.84 (s, 9H), 0.85 (s, 9H), 0.98 (t, 3H, *J* = 5.1 Hz), 1.16-1.34 (m, 26H), 1.95-2.05 (brs, 1H), 2.17-2.22 (m, 2H), 2.79 (d, 1H, *J* = 5.9 Hz), 3.48-3.62 (m, 2H), 3.86-4.17 (m, 8H), 4.63 (d, 1H, *J* = 11.5 Hz), 4.81 (d, 1H, *J* = 11.5 Hz), 5.49-5.67 (m, 2H), 7.24-7.29 (m, 5H); ^{13}C NMR δ -4.8, -4.4, -4.2, 14.1, 14.2, 14.3, 16.9, 17.0, 18.1, 19.0, 22.6, 25.3, 25.9, 29.2, 29.3, 29.5, 29.8, 31.9, 32.3, 32.5, 37.1, 46.8, 57.6, 60.6, 60.7, 70.4, 72.3, 73.8, 74.3, 81.7, 127.4, 127.6, 128.2, 129.5, 133.0, 138.8, 161.7, 161.8, 164.3, 164,5; FABHRMS calcd for $C_{48}H_{88}N_2O_6Si_2$ (M+Na) 867.6078, found 867.6094.

Ethyl (2*S*,3*R*,4*S*,5*S*,14*R*)-4-benzyloxy-2-(tert-butoxycarbonylamino)-5,14-di(tert-butyldimethylsiloxy)-3-hydroxyeicos-6-enoate (34): To a solution of **33c** (51.9 mg, 0.061 mmol) in THF (2.0 ml) and water (1.0 ml) was added p-toluensulfonic acid (58.4 mg, 0.31 mmol) at 0 °C. After stirring for 3 h, the reaction was quenched with saturated aqueous $NaHCO_3$ solution and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (chloroform/methanol = 10/1) to give an ethyl ester. To a solution of the ethyl ester in dichloromethane (1.5 ml) was added a solution of di-t-butyldicarbonate (10.8 mg, 0.05 mmol) in dichloromethane (1.5 ml) at room temperature. After stirring for 6 h, the reaction was quenched with water and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **34c** (27.6 mg, 54%) as a colorless oil.

(2*S*,3*R*,4*R*,5*S*,14*R*)-4-Benzyloxy-2-(tert-butoxycarbonylamino)-3,5,14-trihydroxyeicos-6-enoic acid (35): To a solution of **34c** (60.9 mg, 0.073 mmol) in THF (3.0 ml) and water (1.0 ml) was added lithium hydroxide (12.2 mg, 0.29 mmol) at 0 °C. The mixture was stirred for 10 h and was neutralized with a resin (IRC-76). The resin was filtered off, and the filtrate was concentrated under reduced pressure to give a colorless oil of a carboxylic acid. To a solution of the carboxylic acid in THF (1.2 ml) was added tetrabutylammoniumfluoride 1.0

N solution in THF (0.29 mmol) at room temperature. After stirring for 48 h at 50 °C, the reaction was quenched with phosphate buffer solution (pH = 7). The aqueous layer was extracted with ether and the ethereal extract was washed with 10% aqueous citric acid solution, saturated aqueous $NaHCO_3$ solution, and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give **35c** (40.4 mg, 96%, 2 steps) as a colorless oil. ^1H NMR (CD_3OD) δ 0.90 (t, 3H, J = 6.4 Hz), 1.30-1.42 (m, 29H), 2.01-2.04 (m, 2H), 3.48 (brs, 1H), 3.60 (brs, 1H), 3.95 (dd, 1H, J = 3.3, 7.3 Hz), 4.27 (d, 1H, J = 7.6 Hz), 4.37 (t, 1H, J = 5.3 Hz), 4.69 (d, 1H, J = 10.8 Hz), 4.77 (d, 1H, J = 10.8 Hz), 5.58 (dd, 1H, J = 6.6, 15.2 Hz), 5.75 (dt, 1H, J = 6.3, 15.2 Hz), 7.22-7.46 (m, 5H); FABHRMS calcd for $C_{32}H_{53}NO_8$ (M+Na) 602.3668, found 602.3663. **(2*S*,3*S*,4*R*,5*S*,14*R*)-2-Amino-4-benzyloxy-3,5,14-trihydroxyeicos-6-enoic acid (36):** To a solution of **35c** (23.0 mg, 0.040 mmol) in dichloromethane (1.5 ml) was added trifluoroacetic acid (1.5 ml) at 0 °C. After stirring for 45 min, the solution was concentrated under reduced pressure, and the residue was diluted with THF (2.0 ml) and water (1.0 ml). 1N NaOH aq (0.2 ml) was added, and the mixture was stirred for 30 min at 0 °C, and was neutralized with a resin (IRC-76). The resin was filtered off, and the filtrate was diluted with ether (5.0 ml), and washed with water and brine. The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (chloroform/methanol = 6/1) to give **36c** (20.0 g, 100%) as a white solid. **(2*S*,3*R*,4*R*,5*S*,14*R*)-2-Amino-3,4,5,14-tetrahydroxyeicos-6-enoic acid (sphingofungin B):** To a dark blue solution of sodium-ammonia prepared from excess sodium and liquid ammonia (10 ml) was added a solution of **36c** (20.0 mg, 0.040 mmol) in THF (1.5 ml) at -78 °C. The solution was warmed to -50 °C and was stirred for 1 h. The reaction was quenched with ammonium chloride (254.5 mg, 4.8 mmol). The cooling bath was removed, and after all ammonia was evaporated, the mixture was diluted with water and the aqueous layer extracted with n-butanol. The extract was washed with water, and was concentrated under reduced pressure. The residue was purified by Sephadex (LH-20, H_2O to H_2O/methanol = 1/2) and reverse phase column chromatography (Wakogel, LP-60-C18, H_2O to H_2O/methanol = 1/2) to give sphingofungin B (8.2 mg, 53%) as a white solid. ^1H NMR (CD_3OD) δ 0.89 (t, 3H, J = 6.4 Hz), 1.18-1.60 (m, 20H), 1.98-2.06 (m, 2H), 3.49 (brs, 1H), 3.60 (d, 1H, J = 6.9 Hz), 3.77 (d, 1H, J = 3.6 Hz), 4.06-4.10 (m, 2H), 5.47 (dd, 1H, J = 7.3, 15.2 Hz), 5.77 (dt, 1H, J = 6.6, 15.2 Hz); ^{13}C NMR δ 14.4, 23.7, 26.79, 26.82, 30.2, 30.4, 30.6, 30.7, 33.1, 33.5, 38.5, 60.8, 69.4, 72.5, 75.2, 76.0, 130.2, 135.5, 172.4; FABHRMS calcd for $C_{20}H_{39}NO_6$ (M+H) 390.2856, found 390.2859.

(3*RS*)-Ethyl-3-hydroxynonanethioate (22): To a solution of ytterbium(III) trifluoromethanesulfonate (129.9 mg, 0.21 mmol) in dichloromethane (30 ml) was added a solution of heptanal (2.33 g, 20.4 mmol) in dichloromethane (20 ml) and 1-trimethylsiloxy-1-ethylthio-ethene (4.85 g, 27.5 mmol) in dichloromethane (20 ml) at 0 °C. After stirring for 1h at 0 °C, the reaction was quenched with saturated aqueous $NaHCO_3$ solution, and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate and concentrated under reduced pressure. The residue was treated with THF : 1N HCl = 4 : 1 solution for 30 min. After hexane was added, the organic layer was separated and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **22** (4.05 g, 91%) as a colorless oil. ^1H NMR δ 0.88 (t, 3H, J = 6.6 Hz), 1.24-1.56 (m, 13H), 2.61-2.81 (m, 3H), 2.91 (q, 2H, J = 7.5 Hz), 4.01-4.08 (m, 1H); ^{13}C NMR δ 14.0, 14.6, 22.5, 23.3, 25.3, 29.1, 31.7, 36.5, 50.6, 68.6, 199.6; IR (neat) 1683.6, 2927.4, 3378.7, 3475.1 cm^{-1}.

(7*RS*)-1-Bromo-7-tridecanol (37): To a solution of **6** (2.24 g, 6.94 mmol) in methanol (21 ml) was added conc. HCl (0.7 ml), and the solution was stirred for 3 h at 50 °C. The mixture was cooled to room temperature, diluted with water (60 ml), neutralized with potassium carbonate at 0 °C. The aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give **37** (1.72 g, quant.) as a colorless oil. ^1H NMR δ 0.89 (t, 3H, J = 6.9 Hz), 1.29-1.60 (m, 21H), 1.68-2.00 (m, 2H), 3.41 (t, 2H, J = 6.9 Hz), 3.59 (br, 1H); ^{13}C NMR d 14.1, 22.6, 25.4, 25.6, 28.1, 28.8, 29.3, 31.8, 32.7, 34.0, 37.3, 37.5, 71.9; HRMS calcd for $C_{13}H_{27}BrO$ (M^+) 278.1245, found 278.1229.

(7*RS*)-1-Bromo-7-trimethylsiloxytridecane (38): To a solution of **37** (1.94 g, 6.16 mmol) in dichloromethane (21 ml) was added a solution of triethylamine (1.34 g, 12.4 mmol) in dichloromethane (7.0 ml) and trimethylsilyl chloride (1.25 g, 12.3 mmol) in dichloromethane (7.0 ml) at 0 °C. The mixture was warmed to room temperature

, and was stirred for 15 min. The reaction was then quenched with water and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 50/1) to give **38** (2.08 g, 97%) as a colorless oil. IR (neat) 1252.0, 2859.0, 2932.0 cm^{-1}; ^1H NMR δ 0.00 (s, 9H), 0.78 (t, 3H, J = 6.4 Hz), 1.17-1.51 (m, 18H), 1.70-1.80 (m, 2H), 3.30 (t, 2H, J = 6.8 Hz), 3.36-3.58 (m, 1H); ^{13}C NMR δ 0.8, 14.4, 22.9, 25.8, 26.0, 28.5, 29.2, 30.0, 32.2, 33.1, 34.3, 37.6, 37.8, 72.9; HRMS calcd for $C_{16}H_{35}BrOSi$ (M^+) 350.1641, found 350.1662.

(4*R*,5*S*,9'*RS*)-5-Benzyloxy-2,2-dimethyl-4-(9'-trimethylsiloxypentadec-1'-ynyl)-1,3-dioxane (39): To a solution of **5** (712.9 mg, 2.89 mmol) in THF (16 ml) was added n-BuLi (1.6 M solution in hexane, 2.89 mmol) dropwise over 5 min at -78 °C. The mixture was stirred for 15 min, and a mixture of **38** (1.02 g, 2.89 mmol) in THF (6.5 ml) and HMPA (3.0 ml) was added dropwise. After stirring for 10 min at -78 °C, the mixture was warmed to 0 °C, and was stirred for further 10 h. The reaction was then quenched with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 40/1) to give **39** (1.27 g, 89%) as a colorless oil. ^1H NMR δ 0.00 (s, 9H), 0.78 (t, 3H, J = 6.1 Hz), 1.17-1.50 (m, 26H), 2.17 (t, 3H, J = 7.1 Hz), 3.27 (d, 1H, J = 2.3 Hz), 3.48 (t, 1H, J = 5.0 Hz), 3.73-3.84 (m, 2H), 4.67-4.74 (m, 3H), 7.17-7.34 (m, 5H); ^{13}C NMR δ 0.8, 14.5, 19.4, 20.8, 23.0, 25.9, 26.0, 28.3, 28.8, 29.4, 29.7, 29.8, 32.3, 37.7, 37.8, 62.2, 64.3, 71.6, 72.2, 73.0, 78.0, 87.8, 99.7, 128.0, 128.3, 128.6, 138.5; FABHRMS calcd for $C_{31}H_{52}O_4Si$ (M+Na) 539.3532, found 539.3527.

(4*S*,5*S*,9'*RS*)-5-Benzyloxy-2,2-dimethyl-4-(9'-hydroxylpentadec-1'-ynyl)-1,3-dioxane (40): To a solution of **39** (924.2 mg, 1.79 mmol) in THF (8.4 ml) was added a solution of tetrabutylammonium fluoride (1 N solution in THF, 3.6 mmol) at room temperature. After stirring for 1.5 h, the reaction was quenched with phosphate buffer solution (pH = 7). The aqueous layer was extracted with ether and the ethereal extract was washed with water and brine successively. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) to give **40** (798.2 mg, 100%) as a colorless oil. ^1H NMR δ 0.88 (t, 3H, J = 6.4 Hz), 0.99-1.57 (m, 26H), 2.25-2.30(m, 2H), 3.37 (d, 1H, J =3.0 Hz), 3.56 (br, 1H), 3.82-3.94 (m, 2H), 4.74-4.84 (m, 3H), 7.26-7.44 (m, 5H); ^{13}C NMR δ 14.1, 19.0, 20.4, 22.6, 25.5, 25.6,, 27.9, 28.3, 29.0, 29.2, 29.4, 31.8, 37.4, 37.5, 61.8, 63.9, 71.2, 71.8, 71.9, 76.2, 87.5, 99.4, 127.7, 127.9, 128.3, 138.2; FABHRMS calcd for $C_{28}H_{44}O_4$ (M+Na) 467.3137, found 467.3140.

(4*S*,5*S*)-5-Benzyloxy-2,2-dimethyl-4-(9'-oxopentadec-1'-ynyl)-1,3-dioxane (41): To a solution of oxalyl chloride (455.7 mg, 3.60 mmol) in dichloromethane (1.2 ml) was added a solution of dimethylsulfoxide (364.7 mg, 4.67 mmol) in dichloromethane (8.4 ml) dropwise over 15 min at -78 °C. A solution of **40** (798.2 mg, 1.80 mmol) in dichloromethane (12.0 ml) was added and the mixture was stirred for 10 min at -78 °C and for 1 h at -50 °C. To the solution was added triethylamine (1.27 g, 12.53 mmol), and the mixture was warmed to 0 °C and was stirred for further 20 min. The reaction was quenched with saturated aqueous NH_4Cl solution and the aqueous layer was extracted with dichloromethane. The extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **41** (690.3 mg, 87%) as a colorless oil. ^1H NMR δ 0.88 (t, 3H, J = 5.6 Hz), 1.27-1.57 (m, 22H), 2.17-2.30(m, 2H), 2.37 (t, 4H, J = 7.4 Hz), 3.38 (d , 1H, J = 3.0 Hz), 3.83-3.95 (m, 2H), 4.74-4.79 (m, 3H), 7.23-7.44 (m, 5H); ^{13}C NMR δ 13.9, 18.9, 20.3, 22.4, 23.6, 23.7, 27.9, 28.1, 28.7, 28.8, 31.5, 42.6, 42.7, 61.7, 63.8, 71.1, 71.7, 76.2, 87.2, 99.3, 127.6, 127.8, 128.2, 138.1, 211.4; FABHRMS calcd for $C_{28}H_{42}O_4$ (M+Na) 465.2980, found 465.2967.

(16*S*,17*S*)-17-Benzyloxy-16,18-dihydroxyoctadec-14-yne-7-one (42): To a solution of **41** (690.3 mg, 1.56 mmol) in THF (14 ml) was added 3 N HCl (5 ml), the solution was stirred for 30 min at room temperature. The mixture was diluted with water (50 ml), and was neutralized with potassium carbonate at 0 °C. The aqueous layer was extracted with ether and the ethereal extract was washed with water and brine. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 4/1) to give **42** (622.9 mg, 100%) as a colorless oil. ^1H NMR δ 0.88 (t, 3H, J = 6.6 Hz), 1.23-1.61 (m, 16H), 2.22(dt, 2H, J = 1.3, 6.6 Hz), 2.38 (t, 4H, J = 7.3 Hz), 3.59 (dd, 1H, J = 4.9, 9.6 Hz), 3.79 (dd, 1H, J = 11.5, 29.3 Hz), 3.81 (dd, 1H, J = 11.5, 29.0 Hz), 4.49 (d, 1H, J = 5.9 Hz), 4.76 (dd, 2H, J = 11.6, 19.4 Hz), 7.27-7.37 (m, 5H); ^{13}C NMR δ 14.0, 18.6, 22.4, 23.6, 23.7, 28.1, 28.5,

28.6, 28.8, 31.5, 42.6, 42.8, 61.7, 63.0, 73.3, 78.1, 82.0, 87.1, 127.9, 128.0, 128.5, 137.8, 211.8; FABHRMS calcd for $C_{25}H_{38}O_4$ (M+Na) 425.2667, found 425.2683.

(16*S*,17*S*)-17-Benzyloxy-16,18-dihydroxyoctadec-14-yne-7-one ethylene acetal (43): To a solution of trimethylsilyl trifluoromethanesulfonate (17.2 mg, 0.08 mmol) in dichloromethane (3.0 ml) was added a solution of 1,2-bis(trimethylsilyloxy)ethane (479.1 mg, 2.3 mmol) in dichloromethane (2.3 ml) and **42** (622.9 mg, 1.55 mmol) in dichloromethane (5.0 ml) at 0 °C. After the mixture was stirred for 1 h, the reaction was quenched with pyridine (0.2 ml) and saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) to give **43** (649.8 mg, 94%) as a colorless oil. ^{1}H NMR δ 0.88 (t, 3H, *J* = 6.3 Hz), 1.28-1.59 (m, 20H), 2.04 (br, 1H), 2.22(dt, 2H, *J* = 1.7, 7.0 Hz), 2.69 (br, 1H), 3.58 (dd, 1H, *J* = 4.7, 10.3 Hz), 3.79 (ddd, 2H, *J* = 4.6, 11.6, 27.8 Hz), 3.91 (s, 4H), 4.49 (d, 1H, *J* = 5.6 Hz), 4.76 (dd, 2H, *J* = 11.5, 20.1 Hz), 7.26-7.37 (m, 5H); ^{13}C NMR δ 14.0, 18.7, 22.6, 23.6, 23.8, 28.3, 28.8, 29.3, 29.5, 31.8, 37.0, 37.1, 61.7, 63.1, 64.8, 73.4, 78.1, 82.1, 87.4, 111.8, 127.9, 128.0, 128.5, 137.8; FABHRMS calcd for $C_{27}H_{42}O_5$ (M+Na) 469.2930, found 469.2933.

(16*S*,17*S*)-17-Benzyloxy-16-(tert-butyldimethylsiloxy)-18-(4-methoxyphenyldiphenylmethoxy)-octadec-14-ene-7-one ethylene acetal (44): To a solution of **43** (1.62 g, 3.63 mmol) in dichloromethane (26 ml) was added a solution of triethylamine (733.8 mg, 7.5 mmol) in dichloromethane (9.0 ml) and 4-methoxytrityl chloride (2.02 g, 6.53 mmol) in dichloromethane (9.0 ml) at 0 °C. After a catalytic amount of *N*,*N*-dimethylaminopyridine was added, the mixture was stirred for 1 h. The reaction was quenched with water and the aqueous layer was extracted with dichloromethane. The extract was dried over sodium sulfate, and concentrated under reduced pressure to give a yellow oil. The solution of the yellow oil in THF (26 ml) was added to a suspension of lithium aluminum hydride (412.9 mg, 10.88 mmol) in THF (32 ml) at 0 °C. The mixture was warmed to room temperature, and stirred for 10 min. The mixture was refluxed for 1 h, and after cooling to 0 °C, the reaction was quenched with saturated aqueous potassium sodium tartarate solution. After the suspension was stirred vigorously, the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure to give a yellow oil. To a solution of the yellow oil in DMF (16 ml) was added a solution of imidazole (493.8 mg, 7.25 mmol) in DMF (8.0 ml) and tert-butyldimethylsilyl chloride (1.09 g, 7.25 mmol) in DMF (8.0 ml) at 0 °C. After the mixture was stirred for 10 h at room temperature, the reaction was quenched with water, and the aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give **44** (2.75 g, 91%, 3 steps) as a yellow oil. ^{1}H NMR δ 0.00 (s, 3H), 0.01 (s, 3H), 0.84-0.94 (m, 12H), 1.26-1.31 (m, 16H), 1.61 (br, 4H), 1.90 (br, 2H), 3.08 (br, 1H), 3.31 (br, 1H), 3.55 (br, 1H), 3.79 (s, 3H), 3.94 (s, 4H), 4.28 (br, 1H), 4.79 (br, 2H), 5.39 (br, 1H), 5.50 (br, 1H), 6.79-7.50 (m, 19H); ^{13}C NMR δ -4.8, -4.5, 14.1, 18.2, 22.6, 23.8, 25.9, 29.1, 29.2, 29.6, 29.8, 31.8, 32.1, 37.1, 55.1, 63.9, 64.8, 73.0, 73.8, 82.6, 86.2, 111.8, 112.9, 126.6, 127.2, 127.6, 127.7, 128.1, 128.5, 129.3, 130.3, 131.9, 135.9, 139.2, 144.7, 158.3; FABHRMS calcd for $C_{53}H_{74}O_6Si$ (M+Na) 857.5152, found 857.5161.

(16*S*,17*S*)-17-Benzyloxy-16-(tert-butyldimethylsiloxy)-18-hydroxyoctadec-14-ene-7-one (45): To a solution of **44** (980.6 mg, 1.17 mmol) in ether (70 ml) was added 98% formic acid (37 ml). The solution was stirred for 30 min at 0 °C, and was diluted with water (70 ml). The solution was neutralized with potassium carbonate and the aqueous layer extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **45** (555.6 g, 78%) as a colorless oil. ^{1}H NMR δ -0.03 (s, 3H), 0.00 (s, 3H), 0.85 (br, 12H), 1.20-1.59 (m, 15H), 1.96 (br, 2H), 2.21 (br, 1H), 2.29 (t, 4H, *J* = 7.6 Hz), 3.41-3.72 (m, 3H), 4.26 (t, 1H, *J* = 6.6 Hz), 4.66 (dd, 2H, *J* = 11.5, 18.1 Hz), 5.47 (dd, 1H, *J* = 6.6, 14.8 Hz), 5.62 (dt, 1H, *J* = 6.6, 15.6 Hz), 7.20-7.33 (m, 5H); ^{13}C NMR δ -4.8, -4.6, 13.9, 18.0, 22.4, 23.7, 23.8, 25.8, 28.8, 28.9, 29.0, 31.5, 31.7, 32.1, 42.6, 42.7, 61.8, 72.9, 73.8, 82.0, 127.6, 127.7, 128.3, 128.6, 132.7, 138.4, 211.4; FABHRMS calcd for $C_{31}H_{54}O_4Si$ (M+Na) 541.3689, found 541.3871.

(2*R*,3*S*)-2-Benzyloxy-3-(tert-butyldimethylsiloxy)-12-oxooctadec-4-enal (46): To a solution of oxalyl chloride (73.6 mg, 0.58 mmol) in dichloromethane (2.0 ml) was added a solution of dimethylsulfoxide (58.9 mg, 0.75 mmol) in dichloromethane (1.5 ml) dropwise over 15 min at -78 °C. A solution of **45** (150.4 mg, 0.29 mmol) in dichloromethane (2.0 ml) was added, and the mixture was stirred for 10 min at -78 °C, and for 1 h at

-50 °C. To the solution was added triethylamine (205.3 mg, 2.03 mmol), and the mixture was warmed to 0 °C, and was stirred for further 20 min. The reaction was quenched with saturated aqueous ammonium chloride solution and the aqueous layer was extracted with dichloromethane. The extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. Aldehyde **46** (149.8 mg, quant.) was used immediately without purification.

(1'*S*,4'*S*,16*S*,17*S*,18*R*)-17-Benzyloxy-16-(tert-butyldimethylsiloxy)-18-(3',6'-diethoxy-1',4'-dimethyl-4'H-2,5-diazyl)-18-hydroxyoctadec-14-ene-7-one (47): To a solution of **3** (81.4 mg, 0.41 mmol) in THF (1.5 ml) was added n-BuLi (1.6 M solution in hexane, 0.41 mmol) dropwise at -78 °C. The mixture was warmed to 0 °C, stirred for 15 min, and a solution of tin(II) chloride (77.9 mg, 0.41 mmol) in THF (1.5 ml) was added. The mixture was stirred for a further 15 min and after the solution was cooled to -78 °C, a solution of **46** (106.1 mg, 0.21 mmol) in THF (1.5 ml) was added. The mixture was stirred for 3 h at -78 °C, and was quenched with phosphate buffer solution (pH = 7). The aqueous layer was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **47** (98.4 mg, 83%). Diastereomers of **47** could be separated by the column chromatography (silica gel, hexane/ethyl acetate = 20/1). ^{1}H NMR δ 0.00 (s, 3H), 0.06 (s, 3H), 0.86 (s, 9H), 0.91-0.98 (m, 7H), 1.33-1.38 (m, 28H), 1.42 (s, 3H), 1.59-1.64 (br, 3H), 2.07-2.38 (br, 2H), 2.44 (t, 4H, *J* = 7.5 Hz), 3.17 (d, 1H, *J* = 8.3 Hz), 3.44 (d, 1H, *J* = 11.5 Hz), 3.52 (dd, 1H, *J* = 6.9, 10.6 Hz), 3.87-4.34 (m, 5H), 3.93 (t, 1H, *J* = 8.1 Hz), 4.96 (d, 1H, *J* = 11.9 Hz), 5.45 (dd, 1H, *J* = 8.1, 15.4 Hz), 5.72 (dt, 1H, *J* = 6.8, 16.5 Hz), 7.24-7.31 (m, 5H); ^{13}C NMR δ -4.5, -4.2, 13.7, 14.0, 14.2, 18.1, 21.8, 22.4, 23.8, 25.9, 28.9, 29.0, 29.1, 31.6, 42.7, 52.2, 60.6, 60.8, 72.7, 73.7, 76.4, 77.1, 82.1, 126.1, 126.6, 127.8, 130.8, 133.7, 139.1, 162.3, 164.5, 211.5; IR (neat) 1687.0, 2856.0, 2929.0 cm^{-1}; FABHRMS calcd for $C_{41}H_{64}N_2O_6Si$ (M+Na) 731.4431, found 731.4420.

(1'*S*,4'*R*,16*S*,17*S*,18*R*)-17-Benzyloxy-18-(3',6'-diethoxy-1',4'-dimethyl-4'H-2',5'-diazyl)-16,18-dihydroxyoctadec-14-ene-7-one (48): To a solution of **47** (68.4 mg, 0.096 mmol) in THF (3.0 ml) was added a solution of tetrabutylammonium fluoride (1 N solution in THF, 0.4 mmol) at room temperature. After stirring for 4 h, the reaction was quenched with phosphate buffer solution (pH = 7). The aqueous layer was extracted with ether and the ethereal extract was washed with 10% aqueous citric acid solution, saturated aqueous $NaHCO_3$ solution, and brine. The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give **48** (54.0 mg, 94%) as a white solid. ^{1}H NMR δ 0.81 (t, 3H, *J* = 6.6 Hz), 0.99 (t, 3H, *J* = 7.1 Hz), 1.20-1.49 (m, 22H), 1.94-2.07 (br, 2H), 2.30 (t, 4H, *J* = 7.5 Hz), 2.72 (br, 1H), 3.13 (d, 1H, *J* = 6.6 Hz), 3.47 (d, 1H, *J* = 11.6 Hz), 3.63 (dd, 1H, *J* = 7.1, 10.7 Hz), 3.69-4.15 (m, 5H), 4.20 (t, 1H, *J* = 6.9 Hz), 4.48 (d, 1H, *J* = 11.2 Hz), 5.38 (dd, 1H, *J* = 7.4, 15.3 Hz), 5.74 (dt, 1H, *J* = 6.8, 15.2 Hz), 7.17-7.30 (m, 5H); ^{13}C NMR δ 13.9, 14.0, 14.2, 21.7, 22.4, 23.8, 27.2, 28.8, 28.9, 29.0, 29.1, 31.6, 32.4, 42.7, 42.8, 52.4, 60.4, 60.9, 61.0, 74.0, 74.6, 75.0, 82.0, 127.1, 127.5, 128.3, 129.0, 134.6, 138.1, 163.2, 164.5, 211.6; IR (neat) 1689.0, 2855.0, 2929.0, 3361.0 cm^{-1}; FABHRMS calcd for $C_{35}H_{56}N_2O_6$ (M+Na) 623.4036, found 623.4033.

(2*S*,3*S*,4*R*,5*S*)-2-Amino-4-benzyloxy-2-methyl-3,5-dihydroxy-14-oxoeicos-6-enoic acid (49): To a solution of **48** (54.0 mg, 0.09 mmol) in THF (4.0 ml) was added p-toluensulfonic acid (171.2 mg, 0.9 mmol) at room temperature. After stirring for 1 h, the mixture was neutralized with a resin (IRA-93ZU). The resin was filtered off, and the filtrate was concentrated under reduced pressure to give a mixture of an ester and a lactone. To a solution ester and lactone in methanol (4.0 ml) was added 1N NaOH aq. (4.0 ml) at room temperature. After stirring for 30 min, the solution was neutralized with a resin (IRC-76). The resin was filtered off, and the filtrate was extracted with ether. The ethereal extract was washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (chloroform/methanol = 10/1) to give **49** (25.6 mg, 58%, 2 steps) as a white solid. $[\alpha]_D^{26}$ +8.2 (c = 0.23, C_6H_6); ^{1}H NMR (CD_3OD) δ 0.88 (t, 3H, *J* = 3.5 Hz), 1.12-1.56 (m, 19H), 2.03-2.15 (br, 2H), 2.43 (t, 4H, *J* = 7.2 Hz), 3.77 (dd, 1H, *J* = 1.8, 7.1 Hz), 3.95 (d, 1H, *J* = 1.7 Hz), 4.43 (t, 1H, *J* = 6.9 Hz), 4.55 (d, 1H, *J* = 10.2 Hz), 5.08 (d, 1H, *J* = 9.9 Hz), 5.58 (dd, 1H, *J* = 7.3, 15.5 Hz), 5.76 (dt, 1H, *J* = 6.4, 14.1 Hz), 7.23-7.52(m, 5H); ^{13}C NMR (CD_3OD) δ 14.4, 22.0, 23.6, 24.9, 30.0, 30.2, 32.8, 33.4, 43.5, 66.2, 73.0, 76.0, 76.5, 85.5, 129.1, 129.6, 130.0, 130.8, 134.7, 139.5, 214.4; FABHRMS calcd for $C_{28}H_{45}NO_6$ (M+Na) 514.3144, found 514.3159.

(2S,3R,4R,5S)-2-Amino-2-methyl-3,4,5-trihydroxy-14-oxoeicos-6-enoic acid (sphingofungin F): To a solution of **49** (7.3 mg, 0.015 mmol) in dichloromethane (1.0 ml) was added trichloroborane 1N solution in hexane (0.045 mmol) dropwise at -78 °C. After stirring for 10 min, the reaction was quenched with methanol (1.0 ml). The solution was warmed to room temperature, and diluted with water. The aqueous layer was extracted with tert-butanol. The extract was washed with water and was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (chloroform/methanol = 10/1) to give sphingofungin F (4.3 mg, 72%) as a white solid. $[\alpha]_D^{26}$ +0.8 (c = 0.33, MeOH); ^{1}H NMR (CD_3OD) δ 0.89 (t, 3H, J =6.6 Hz), 1.28-1.55 (m, 19H) , 2.05 (br, 2H), 2.44 (t, 4H, J = 7.4 Hz), 3.69 (d, 1H, J = 7.3 Hz), 3.86 (br, 1H), 4.10 (t, 1H, J = 7.3 Hz), 5.47 (dd, 1H, J = 7.8, 15.6 Hz), 5.78 (dt, 1H, J = 6.7, 15.6 Hz); ^{13}C NMR (CD_3OD) δ 14.4, 21.8, 23.6, 24.9, 30.0, 30.2, 32.8, 33.5, 43.5, 67.7, 72.4, 75.7, 76.2, 130.2, 135.7, 214.4; FABHRMS calcd for $C_{21}H_{39}NO_6$ (M+H) 402.2856, found 402.2861.

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