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Enantioselective total synthesis of (*R*)-strongylodiols A and B

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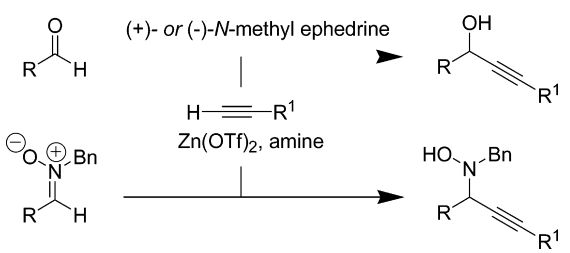
Abstract—We describe an expeditious enantioselective total synthesis of the acetylenic marine natural products (*R*)-strongylodiols A and B. Central to the strategy is the use of $Zn(OTf)_2$, amine base, and *N*-methyl ephedrine to mediate the direct addition of a 1,3-diyne to two long-chain aliphatic aldehydes in useful selectivities and yields.

1. Introduction

The in situ activation of hydrocarbons to give reactive intermediates that can participate in useful C–C bond forming reactions is an important area of investigation in chemical synthesis. In this respect, we have recently developed and studied reaction methodology that effects the activation and nucleophilic addition reaction of one of the simplest class of hydrocarbons, namely, terminal acetylenes. We have documented that a wide range of terminal acetylenes can undergo metallation when exposed to Zn(II) and amine base.[1,2] The putative metallation reaction occurs at ambient temperature and yields a metal acetylide that participates in aldehyde and nitrone addition reactions (Scheme 1). Remarkably, the metallation/deprotonation reaction is not adversely affected when amino alcohol ligands are present, indeed, the presence of amino alcohols leads to a ligand-accelerated process. When the amino alcohol is optically active, enantioenriched products can be generated in the aldehyde addition reactions. We have demonstrated that the reaction can be executed not only with stoichiometric quantities of Zn(II), base and ligand but also, more recently, with catalytic amounts of each.[1j] It is worth noting that the fact that the reaction can be conducted under a wide range of concentrations and catalyst loadings is a key advantage of the process, as it permits optimization of the reaction conditions for a wide range of substrates.



Scheme 1.

As part of our ongoing studies to expand the scope of the process with aldehydes, we have been involved in the study and use of reactions with unusual acetylenes as reaction partners. In this respect, we have been interested in examining whether conjugated 1,3-diynes could be utilized in the transformation.

For any acetylene to be successfully employed in addition reactions two key criteria must be met: (1) the terminal alkyne must participate in the activation/deprotonation sequence involving Zn(II), and (2) the metal alkynylide must be sufficient reactive in nucleophilic additions to the desired electrophiles vis a vis competing side-reactions such as oligomerization.

The combined efforts of groups in Japan and The Netherlands in the search for biologically active compounds from marine invertebrates has led to the isolation and characterization of new long-chain acetylenic alcohols named strongylodiols A, B, and C (Fig. 1).[3] Although a number of propargylic alcohols had been isolated previously, they have been found mostly in racemic form. In this respect, the fact that the strongylodiols were isolated from the sponge genus *Strongylophora* in non-racemic form represents an unusual case. In addition to the interesting taxonomic implications suggested by these compounds, they were also determined to possess activity against tumor cell lines (DLD-1 and MOLT-4). Because related acetylenic compounds isolated from other sponges also possess interesting biological activity, the investigation of general synthetic routes that provide access to a large range of related structures is certainly warranted. Indeed, a synthesis

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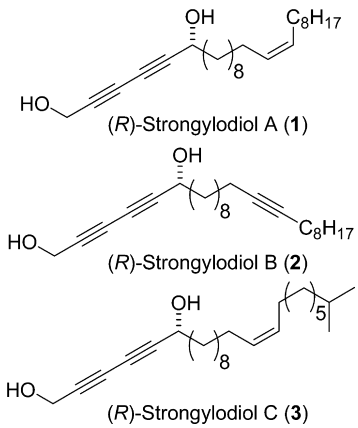


Figure 1.

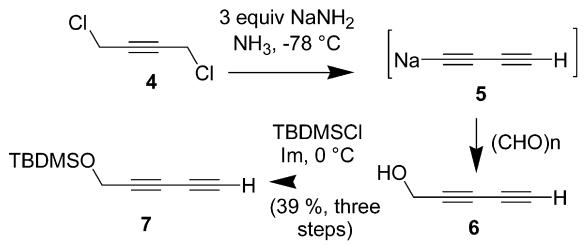
of strongylodiol A relying on the Sharpless asymmetric epoxidation reaction of allylic alcohol precursor has been reported.[4] Herein we document the successful use a 1,3-diyne in the addition reactions to two aldehydes, leading to facile synthesis of strongylodiols A and B.

2. Results and discussion

Our interest in developing efficient strategies towards the strongylodiols provided us a unique opportunity to examine the question of whether 1,3-diynes would participate in Zn(II)-mediated activation and enantioselective aldehyde addition reactions. At the outset of our investigations, it was not clear whether such conjugated 1,3-dinynes would be suitable substrates, as such diynes and the corresponding metallated counterparts are known to be susceptible to decomposition through oligomerization.

Our studies commenced with 1,4-dihydroxy-2-butyne, which is an inexpensive commodity readily converted to the corresponding 1,4-dichlorobutyne **4** upon treatment with thionyl chloride in pyridine.[5] The transformation of this dichloride into protected silyl ether **7** is conveniently effected upon exposure of **4** to 3 equiv. of $NaNH_2$ and trapping of the putative acetylide **5** with formaldehyde to afford **6**,[6] which is in turn without purification protected (TBDMSCl, imidazole), leading to **7** in 39% yield over three steps (Scheme 2).

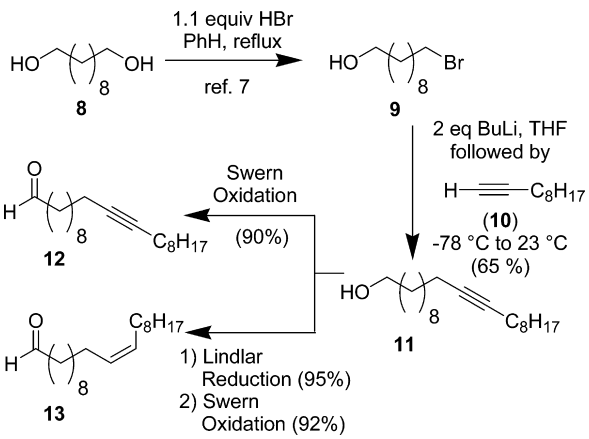
The synthesis of the long-chain hydrocarbon portion of strongylodiols A and B commences with decanediol **8**. Conversion of **8** to hydroxy bromide **9** was carried out by treatment of **8** with HBr in refluxing benzene for 28 h.[7] When a solution of lithiated 1-decyne (**10**) containing an



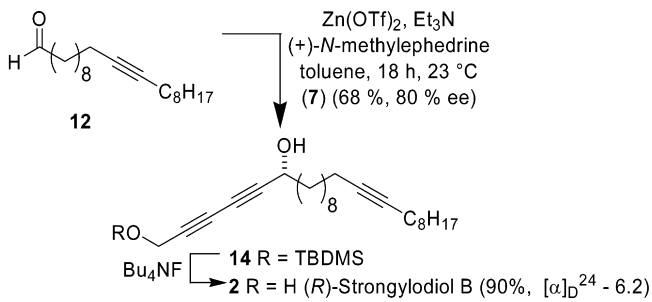
Scheme 2.

equivalent of BuLi in THF/HMPA was exposed to **9**, the alcohol **11** was isolated in 65% yield. Interestingly, the use of protected forms of **9**, such as the corresponding *O*-$SiMe_3$ or *O*-THP analogs, gave considerably poorer results, with the former proving unreactive and the latter affording product, albeit in only 31% yield. Oxidation of **11** furnished aldehyde **12** which was used in the synthesis of strongyldiol B. Alternatively, semihydrogenation of **11** gives a *cis* alkene which following oxidation provided aldehyde **13**, which was used in the synthesis of strongylodiol A (Scheme 3).

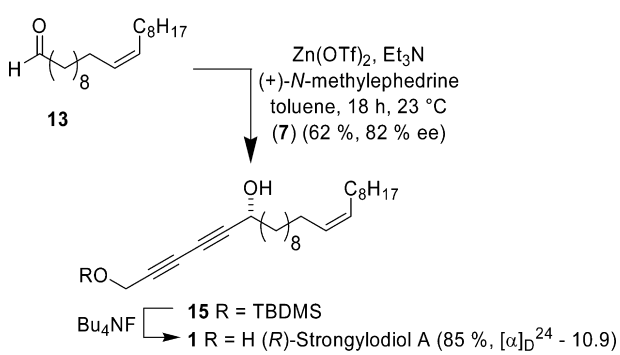
With both aldehydes **12** and **13** in hand, the stage was set for examination of the key diyne addition reaction and completion of the syntheses. Although the addition reaction required some experimentation in order to identify optimal conditions, we subsequently observed that the use of excess Zn(II), ligand, and Et_3N (4 equiv. each) and slow addition of the aldehyde successfully provided adducts **14** and **15** in 68% yield/80% ee and 62% yield/82% ee, respectively



Scheme 3.



Scheme 4.



Scheme 5.

(Schemes 4 and 5). The enantioselectivity of the addition reactions in each case was assayed by Mosher's method.[8] The syntheses of strongylodiols A and B were brought to completion upon desilylation of **14** and **15** with TBAF, affording (*R*)-strongylodiol B (**2**) and (*R*)-strongylodiol A (**1**) in 90 and 85% yields, respectively.

We have described a simple procedure for the preparation of alk-2,4-yne-1,6-diols that is convenient and operationally simple. Given the fact that the strongylodiols have been shown to possess antineoplastic activity, ready access to these and related compounds provides avenues for investigations. Moreover, the 1,6-diols that are isolated can serve as useful building blocks for the synthesis of value-added materials. Additional studies are in progress and results will be reported as they become available.

3. Experimental

3.1. General

All reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Toluene was distilled and dried before use. Reagents were purchased from Fluka, Aldrich or ACROS chemical companies, and used without further purification except aldehydes which were distilled before use. Chromatographic purification of products was accomplished using forced flow chromatography on silica gel 60. NMR spectra were recorded on a Varian Mercury 300 operating at 300 and 75.5 MHz for ^{1}H and ^{13}C, respectively, and referenced to the internal solvent signals. IR spectra were recorded on a Perkin–Elmer Spectrum RX I FT-IR spectrometer as thin film unless otherwise noted. Optical rotations were measured on a JASCO DID-1000 digital polarimeter. Thin layer chromatography was performed using silica gel 60 F254 TLC plates and visualized either with ultraviolet light or stain with CAM-Stain. Mass spectra were carried out by the Massenspecktroskopie service of the Laboratorium für Organische Chemie at ETH, Zürich.

3.1.1. Penta-2,4-diyn-1-ol (6). A vigorously stirred suspension of $NaNH_2$ (3.5 g; 90 mmol) in liquid ammonia (ca. 70 ml) at −78°C was treated dropwise with 1,4-dihydroxy-2-butyne (**4**) (3.7 g, 30 mmol). Subsequently, a suspension of paraformaldehyde (0.90 g; 29.9 mmol; dried over P_2O_5) in ether (5 ml) was added in one portion. After 3 h the dark reaction mixture was quenched with ammonium chloride (4 g). The ammonia was allowed to evaporate. Then the residue was extracted with portions of CH_2Cl_2 until the extracts were colorless. The combined extracts were washed with brine and dried over Na_2SO_4. Since **6** is known to be unstable,[11] it was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (s br, 1H), 2.20 (s, 1H), 4.30 (s, 3H).

3.1.2. 1-(*tert*-Butyldimethylsilanyloxy)penta-2,4-diyne (7). A solution of crude **6** (3.12 g; 38.9 mmol) in CH_2Cl_2 at 23°C was treated with TBSCl (7.14 g; 47.4 mmol) and imidazole (4.09 g; 60.2 mmol). After ca. 30 min the resulting suspension was quenched with sat. aq. NH_4Cl soln (100 ml). The layers were separated and the water phase was extracted with CH_2Cl_2 (2×100 ml). The combined organic layers were washed with brine (50 ml) and dried over Na_2SO_4. Evaporation of the solvent in vacuo and FC (silicagel 150 g, hexanes); gave 2.3 g (39% from **4**) of **7** as a pale yellow oil, which was stored at 4°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 6H), 0.95 (s, 9H), 2.18 (s, 1H), 4.40 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −0.5 (CH_3), 18.3 (C), 25.8 (CH_3), 51.9 (CH_2), 67.6 (CH), 67.8 (C), 69.0 (C), 75.0 (C). FT-IR (thin film, cm^{-1}): 3310 (m), 2957 (s), 2931 (s), 2859 (s), 2712 (w), 2066 (w), 1772 (m), 1366 (m), 1258 (s), 1140 (s), 1087 (s), 1006 (m), 939 (w), 837 (s).

3.1.3. Icos-11-yn-1-ol (11).[10] A well stirred solution of **10** (100 mg; 0.73 mmol) in THF (2 ml) at −78°C was treated dropwise with BuLi (0.90 ml of 1.6 M solution in hexanes; 1.5 mmol). After 30 min **9** (170 mg; 0.720 mmol) in THF/HMPA (1 ml; 4:1) was added. After 2 h at −78°C and 16 h at 23°C the reaction was quenched with sat. aq. NH_4Cl soln (3 ml). The mixture was extracted with ether (3×10 ml). The combined organic layers were washed with brine (10 ml), dried over Na_2SO_4 and concentrated in vacuo. FC (20 g silicagel; hexanes–EtOAc=20:1) gave 140 mg (65%) of **11** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, 3H, J=6.9 Hz), 1.20–1.60 (m, 30H), 2.10 (t, 4H, J=6.9 Hz), 3.60 (t, 2H, J=6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 18.8 (CH_2), 22.7 (CH_2), 25.8 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 32.9 (CH_2), 63.0 (CH_2), 80.2 (C), 80.2 (C). Mass spectroscopy (EI): calculated for $C_{20}H_{38}O$ $(M)^+$ 294.29, found 294.30.

3.1.4. Icos-11-ynal (12).[9] A solution of oxalyl chloride (100 mg; 0.788 mmol) in CH_2Cl_2 at −78°C was treated dropwise with DMSO (112 μl; 1.58 mmol) and (**11**) (120 mg; 0.408 mmol). After 15 min at −78°C Et_3N (300 μl; 2.31 mmol) was added. The reaction was allowed to warm up at 23°C and quenched after 3 h with sat. aq. NH_4Cl soln (3 ml). The water phase was extracted with ether (3×10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. FC (20 g silicagel; hexanes–EtOAc=6:1) afforded 105 mg (90%) of the aldehyde **12** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, 3H, J=6.9 Hz), 1.20–1.54 (m, 24H), 1.56–1.68 (m, 2H), 2.14 (t, 4H, J=6.9 Hz), 2.40 (dt, 2H, J_1=1.8 Hz, J_2=7.4 Hz), 9.80 (t, 1H, J=1.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1 (CH_3), 18.8 (CH_2), 22.2 (CH_2), 22.8 (CH_2), 28.9 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 31.7 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 44.0 (CH_2), 80.1 (C), 80.2 (C), 202.0 (C). FT-IR (thin film, cm^{-1}): 2928 (s), 2855 (m), 2713 (w), 1728 (m), 1466 (w). Mass spectroscopy (EI): calculated for $C_{20}H_{36}O$ $(M)^+$ 292.28, found 292.30.

3.1.5. (6*R*)-1-(*tert*-Butyldimethylsilanyloxy)pentacosa-2,4,16-triyn-6-ol (14). A suspension of $Zn(OTf)_2$ (360 mg; 0.990 mmol), (+)-*N*-methylephedrine (180 mg; 1.00 mmol) and Et_3N (100 mg; 0.988 mmol) in toluene (2 ml) at 23°C was stirred vigorously for 2 h. Then, **7** (49 mg; 0.25 mmol) was added. After 15 min, **12** (73 mg;

0.25 mmol) in toluene (1 ml) was added over 4 h with a syringe pump. After additional 16 h the reaction was quenched with sat. aq. NH_4Cl soln (3 ml). The mixture was diluted with ether (10 ml). The water phase was extracted with ether (3×10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. FC (20 g silicagel; hexanes–EtOAc=20:1) afforded 83 mg (68%) of **14**. ee: 80 % as determined by ^{19}F NMR analysis of the corresponding Mosher ester: δ −71.54 (minor), −71.83 (major). $[\alpha]_D^{24}=-3.89$ (c=1.24, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.84–0.95 (m, 12H), 1.23–1.51 (m, 26H), 1.66–1.76 (m, 2H), 1.86 (s, br, 1H), 2.10–2.18 (m, 4H), 4.38–4.42 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.1 (CH_3), 14.2 (CH_3), 18.4 (C), 18.9 (CH_2), 22.8 (CH_2), 25.1 (CH_2), 25.8 (CH_3), 27.7 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 37.6 (CH_2), 52.1 (CH_2), 62.9 (CH), 68.8 (C), 69.1 (C), 78.2 (C), 79.8 (C), 80.2 (C). FT-IR (thin film, cm^{-1}): 3418 (w, br), 2926 (s), 2855 (m), 1464 (w), 1363 (w), 1255 (w), 1091 (m), 836 (m), 778 (w). Mass spectroscopy (HRMS, MALDI): calculated for $C_{31}H_{54}O_2Si$ $(M+Na)^+$ 509.3791, found 509.3796.

3.1.6. (6*R*)-Pentacosa-2,4,16-triyne-1,6-diol (strongylodiol B) (2). A solution of **14** (50 mg; 0.10 mmol) in THF (2 ml) at 23°C was treated with TBAF (0.12 ml; 1.0 M soln in THF; 0.12 mmol). After 20 min the reaction was quenched with sat. aq. NH_4Cl soln (5 ml). The mixture was diluted with ether (10 ml). The water phase was extracted with ether (3×10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. FC (20 g silicagel; hexanes–EtOAc=4:1) afforded 34 mg (90 %) of **2** as a white solid. $[\alpha]_D^{24}=-6.2$ (c=0.42, $CHCl_3$), lit.: −7.1 (c=0.42, $CHCl_3$)[3]. ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 3H, J=6.9 Hz), 1.21–1.51 (m, 26H), 1.66–1.76 (m, 2H), 2.14 (t, 4H, J=6.9 Hz), 4.39 (s, 2H), 4.41 (t, 1H, J=6.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 18.5 (CH_2), 22.8 (CH_2), 25.1 (CH_2), 28.9 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 32.0 (CH_2), 37.5 (CH_2), 51.5 (CH_2), 62.8 (CH), 68.8 (C), 69.8 (C), 80.2 (C), 80.5 (C). FT-IR (thin film, cm^{-1}): 3299 (w, br), 2927 (m), 2849 (s), 1354 (w), 1320 (w), 1030 (w). Mass spectroscopy (HRMS, MALDI): calculated for $C_{25}H_{40}O_2$ $(M+Na)^+$ 395.2926, found 395.2923. Mp 49°C.

3.1.7. Icos-11-en-1-ol.[10] A suspension of Lindlar catalyst (10 mg), **11** (160 mg; 0.544 mmol) and freshly distilled quinoline (20 µl) in hexanes (2 ml) at 23°C was stirred vigorously under a hydrogen atmosphere (approx. 1 bar; balloon). After 1 h the solid was separated by filtration. The organic layer was diluted with hexanes (10 ml), washed with HCl (10 ml, 0.1N in water), sat. aq. $NaHCO_3$ soln (10 ml) and dried over Na_2SO_4. Evaporation of the solvent gave 156 mg (95 %) of the alcohol **16**. ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, 3H, J=6.9 Hz), 1.20–1.40 (m, 27H), 1.50–1.61 (m, 2H), 1.95–2.95 (m, 4H), 3.62 (t, 2H, J=6.9 Hz), 5.35–5.40 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 22.8 (CH_2), 25.8 (CH_2), 27.3 (CH_2), 28.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 30.9 (CH_2), 32.0 (CH_2), 32.9 (CH_2), 63.1 (CH_2), 129.7 (CH), 129.8 (CH). FT-IR (thin film, cm^{-1}): 3339 (w, br), 3005 (w), 2924 (s), 2854 (s), 1466 (m), 1378 (w), 1058 (m), 722 (m). Mass spectroscopy (EI): calculated for $C_{20}H_{40}O$ $(M)^+$ 296.31, found 296.27.

3.1.8. Icos-11-enal (13).[9] A solution of oxalylchloride (100 mg; 0.788 mmol) in CH_2Cl_2 at −78°C was treated dropwise with DMSO (112 µl; 1.58 mmol) and **16** (102 mg; 0.346 mmol). After 15 min at −78°C Et_3N (300 µl; 2.31 mmol) was added. The reaction was allowed to warm up at 23°C and quenched after 3 h with sat. aq. NH_4Cl soln (3 ml). The water phase was extracted with ether (3×10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. FC (20 g silicagel; hexanes–EtOAc=6:1) afforded 94 mg (92 %) of the aldehyde **13** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, 3H, J=3.9 Hz), 1.20–1.39 (m, 24H), 1.56–1.68 (m, 2H), 2.14 (m, 4H), 2.40 (dt, 2H, J_1=1.9 Hz, J_2=7.4 Hz), 5.35 (m, 2H), 9.8 (t, 1H, J=1.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3 (CH_3), 22.2 (CH_2), 22.8 (CH_2), 27.3 (CH_2), 27.3 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.9 (CH_2), 32.0 (CH_2), 44.0 (CH_2), 129.7 (CH), 129.9 (CH), 202.7 (C). FT-IR (thin film, cm^{-1}): 3300 (s, br), 2924 (s), 2848 (s), 1462 (m), 1354 (w), 1320 (w), 1064 (m), 1030 (m), 964 (w), 726 (w), 1122 (w), 959 (w). Mass spectroscopy (EI): calculated for $C_{20}H_{38}O$ $(M)^+$ 294.29, found 294.24.

3.1.9. (6*R*)-1-(*tert*-Butyldimethylsilanyloxy)pentacos-16-ene-2,4-diyn-6-ol (15). A suspension of $Zn(OTf)_2$ (360 mg; 0.990 mmol), (+)-*N*-methylephedrine (180 mg; 1.00 mmol) and Et_3N (100 mg; 0.988 mmol) in toluene (2 ml) at 23°C was stirred vigorously for 2 h. Then, **7** (49 mg; 0.25 mmol) was added. After 15 min, **13** (74 mg; 0.25 mmol) in toluene (1 ml) was added over 4 h with a syringe pump. After additional 16 h the reaction was quenched with sat. aq. NH_4Cl soln (3 ml). The mixture was diluted with ether (10 ml). The water phase was extracted with ether (3×10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. FC (20 g silicagel; hexanes–EtOAc=20:1) afforded 76 mg (62%) of **15**. ee: 82% as determined by ^{19}F NMR analysis of the corresponding Mosher ester: δ −71.52 (minor), −71.81 (major). $[\alpha]_D^{24}=-9.15$ (c=0.44, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$) δ 0.12 (s, 6H), 0.84–0.95 (m, 12H), 1.23–1.51 (m, 26H), 1.66–1.76 (m, 2H), 1.86 (d, 1H, J=6.9 Hz), 2.10–2.18 (m, 4H), 4.38–4.42 (m, 3H), 5.30–5.41 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ −5.3 (CH_3), 14.3 (CH_3), 18.4 (C), 22.8 (CH_2), 25.1 (CH_2), 25.7 (CH_3), 27.3 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.6 (CH_2), 29.9 (CH_2), 32.0 (CH_2), 37.6 (CH_2), 52.1 (CH_2), 62.9 (CH), 68.9 (C), 69.1 (C), 78.2 (C), 79.8 (C), 129.8 (CH), 129.9 (CH). FT-IR (thin film, cm^{-1}): 3306 (w, br), 2926 (s), 2854 (s), 1463 (m), 1363 (w), 1257 (w), 1091 (m), 836 (m), 780 (w), 722 (w). Mass spectroscopy (HRMS, MALDI): calculated for $C_{31}H_{56}O_2Si$ $(M+Na)^+$ 511.3947, found=511.3949.

3.1.10. (6*R*)-Pentacos-16-ene-2,4-diyne-1,6-diol (strongylodiol A)[3] (1). A solution of (**15**) (50 mg; 0.10 mmol) in THF (2 ml) was treated at 23°C with TBAF (0.12 ml of 1.0 M soln in THF; 0.12 mmol). After 20 min the reaction was quenched with sat. aq. NH_4Cl soln (5 ml). The mixture was diluted with ether (10 ml). The water phase was extracted with ether (3×10 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo.

FC (20 g silicagel; hexanes–EtOAc=4:1) afforded 32 mg (85%) of **1** as a viscous colorless oil. $[\alpha]_D^{24}=-10.9$ (c=1.11, $CHCl_3$), lit.: −7.2 (c=1.11, $CHCl_3$).[3] ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 t, 3H, J=6.9 Hz), 1.21–1.51 (m, 26H), 1.66–1.76 (m, 2H), 1.98–2.06 (m, 4H), 4.39 (s, 2H), 4.41 (t, 1H, J=6.9 Hz), 5.38–5.40 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2 (CH_3), 20.9 (CH_2), 22.8 (CH_2), 25.1 (CH_2), 27.3 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 32.0 (CH_2), 37.5 (CH_2), 51.5 (CH_2), 62.8 (CH), 68.8 (C), 69.8 (C), 80.5 (C), 129.7 (CH), 129.8 (CH). FT-IR (thin film, cm^{-1}): 3307 (m, br), 3004 (w), 2924 (s), 2851 (s), 2255 (w), 2161 (w), 1652 (w) 1463 (m), 1354 (w), 1319 (w), 1065 (m), 1028 (m), 966 (w), 901 (w).

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