Synthetic Studies toward Mono-THF Annonaceous Acetogenins: A Diastereoselective and Convergent Approach to Corossolone and (10*RS*)-Corossoline

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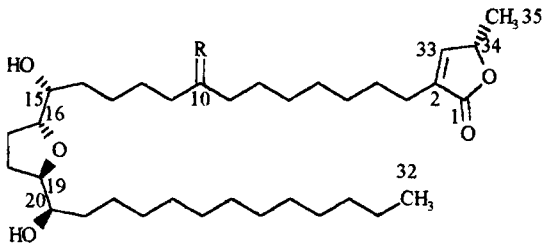
This paper describes a diastereoselective approach to the total syntheses of both corossolone (**1**) and (10*RS*)-corossoline (**2**), two naturally occurring cytotoxic annonaceous acetogenins from *Annona muricata*. 2,3-*O*-Isopropylidene-D-threitol (**3**) has been used as the chiral pool for the preparation of (5*R*,6*R*)-5-hydroxy-6-[(*tert*-butyldimethylsilyl)oxy]-1-octadecene (**10**). Epoxidation of **10** with *m*-CPBA and intramolecular ring closure in one pot gave a trans-THF intermediate **11** as the major product. The subsequent reagent-controlled asymmetric propargylation was achieved by treatment of the aldehyde derived from **11** with 2-allenyl-1,3,2-dioxaborolane-(4*S*,5*S*)-dicarboxylic acid bis-(1′-methylethyl) ester to afford compound **12** with the threo-trans-threo THF moiety with excellent diastereoselectivity. Epoxide **21** prepared from ethyl L-lactate and undecenoic acid according to our previous methodology was treated with alkynyl anion **13** derived from **12** in the presence of BF_3·OEt_2 to give the regioselective ring-opening product **22** with the whole skeleton of the target molecule. Finally, β-elimination followed by deprotection or by oxidation and then deprotection afforded corossolone and (10*RS*)-corossoline, whose physical data are coincident with those of the natural products.

During the last decade, over 100 potent bioactive secondary metabolites, which are now called annonaceous acetogenins, were isolated from several species of *Annonaceae* and have shown potent cytotoxic, pesticidal, insect antifeedant, antimalarial, T-cell suppressant, antiparasitic, and antimicrobial activities. They usually contain 35 or 37 carbon atoms, one or two tetrahydrofuran rings, and a γ-lactone with five to eight carbinol asymmetric centers, but the absolute configurations of most acetogenins are not confirmed owing to their waxy nature. The combination of their unusual structural features, the challenges associated with their stereochemistry, and their therapeutic potential makes the acetogenins an attractive target for total synthesis.[2] Corossolone (**1**) and corossoline (**2**), two monotetrahydrofuranyl acetogenins, were isolated from the seeds of *Annona muricata* in 1991,[3] and their relative configuration of the THF segment was suggested as threo-trans-threo. At the end of 1992, Hoye and his co-workers[4] determined the absolute configurations of several mono-THF acetogenins such as reticulatacin, annonacin-10-one, and annonacin by careful ^{1}H, and ^{19}F-NMR analysis of



1 R = O **corossolone**
2 R = H, OH **corossoline**

Figure 1. Naturally occurring acetogenin corossolone (**1**) and corossoline (**2**).

(*S*)- and (*R*)-Mosher ester derivatives. On the basis of this literature, we assumed the absolute configuration of the stereogenic carbinol centers of corossolone to be 15*R*, 16*R*, 19*R*, 20*R*, and 34*S* (Figure 1). As part of a general program of synthesis of acetogenin,[5] we have carried out the enantioselective total syntheses of corossolone with stereochemistry of 15*R*, 16*R*, 19*R*, 20*R*, and 34*S* and (10*RS*,15*R*,16*R*,19*R*,20*R*,34*S*)-corossoline and proven that the stereochemistry of synthetic corossolone is identical with that of the natural sample.

The synthesis started from enantiomercially pure (−)-2,3-*O*-isopropylidene-D-threitol (**3**) which was available from D-(−)-tartaric acid in three steps.[6] Monoprotection of **3** with benzyl bromide was performed in DMF using NaH as a base. The Wittig reaction of the crude aldehyde which was freshly prepared from **4** by Swern's method gave olefin **5** (*Z*/*E* > 95:5) in 63% yield. Hydrogenation of **5** in the presence of 10% Pd–C under 1 atm of hydrogen did not cleave the benzyl ether completely but reduced the carbon–carbon double bond. A subsequent treatment of the resulting benzyl ether with Li–liquid

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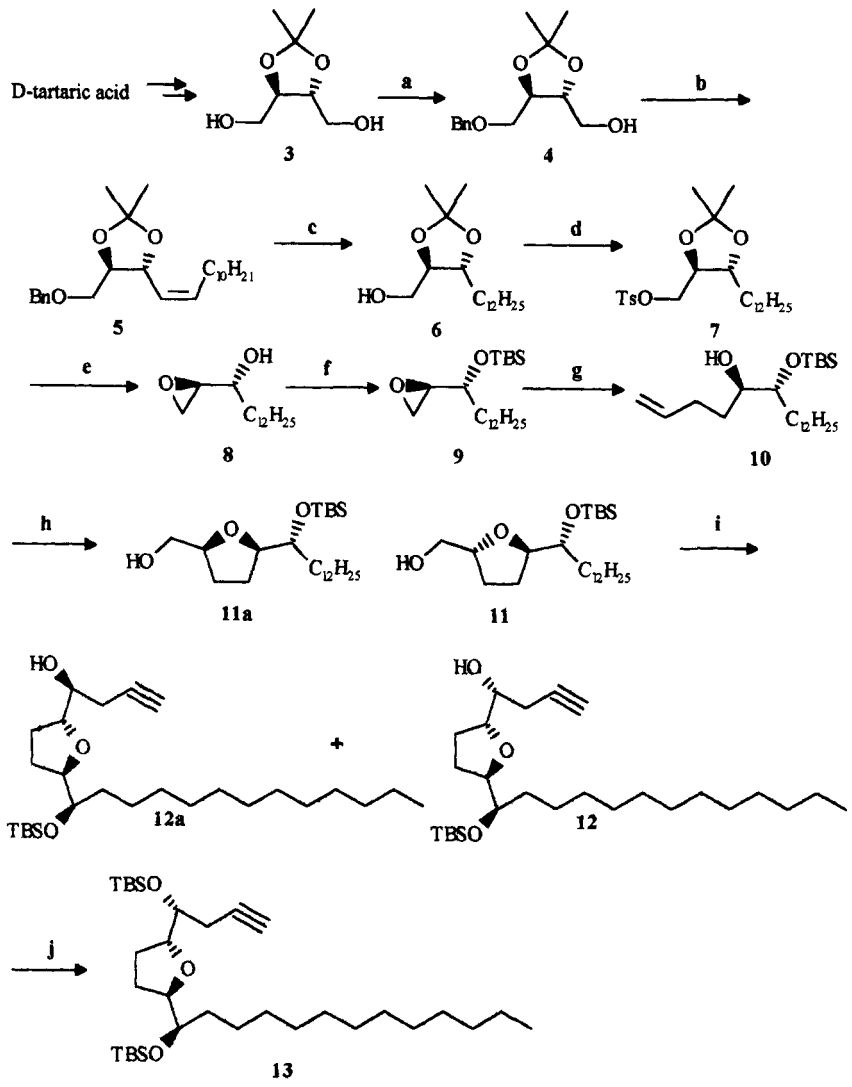
Scheme 1



[a] Reagents and conditions: (a) NaH, BnBr, DMF, rt, 86%; (b) (1) $(COCl)_2$, DMSO, Et_3N, (2) $C_{10}H_{21}CH{=}PPh_3$, THF, 63% from **4**; (c) (1) H_2, 10% Pd–C, (2) $LiNH_3$ (l), 86% from **5**; (d) TsCl, Et_3N, cat. DMAP, CH_2Cl_2, 96%; (e) (1) TsOH, MeOH, (2) K_2CO_3, MeOH, 75% from **7**; (f) TBDMSCl, $AgNO_3$, Py, THF, 93%; (g) allylmagnesium chloride, cat. CuBr, THF–ether, 84%; (h) (1) *m*-CPBA, CH_2Cl_2, (20 cat. CSA, CH_2Cl_2, 72% for **11**, 14% for **11a** from **10**; (i) (1) $(COCl)_2$, DMSO, Et_3N, (2) 2-allenyl-1,3-dioxa-2-borolane-(4*S*,5*S*)-dicarboxylic acid bis(1′-methylethyl) ester, toluene, 68% for **12**, 4% for **12a** from **11**; (j) TBDMSCl, imid., DMF, 91%.

NH_3 afforded free alcohol **6** in good yield, which was then converted to its tosylate **7**. Treatment of tosylate **7** with a catalytic amount of *p*-TsOH in methanol under reflux and subsequently with an excess of solid K_2CO_3 at room temperature afforded *threo*-epoxide, a white solid **8**. An initial attempt to convert alcohol **8** to the silyl ether **9** in DMF in the presence of 3 equiv of imidazole failed. The silyl ether **9** was finally prepared in the presence of $AgNO_3$ and pyridine[7] in THF at room temperature. In the presence of CuBr as a catalyst, Grignard reaction of **9** with allylmagnesium chloride in THF–ether gave **10** in 84% yield. Epoxidation of **10** with *m*-CPBA in dichloromethane followed by treatment with a catalytic amount of CSA provided the *trans*- and *cis*-THF compounds **11** and **11a** with a ratio of 3.3:1–6:1 based on the isolated yields in several runs. After the Swern oxidation of **11**, the resulting crude aldehyde was propargylated by treatment with the enantiomerically pure allenylboronic ester, 2-allenyl-1,3-dioxa-2-borolane-(4*S*,5*S*)-dicarboxylic acid bis(1′-methylethyl) ester, which was freshly prepared from allenylboric acid and diisopropyl D-tartrate in the presence of powdered 4 Åmolecular sieves.[8] The reagent-controlled asymmetric propargylation was performed at −78 °C for 24 h and gave 68% yield of **12** with excellent diastereoselectivity (18.8:1 in favor of the desired isomer **12**). The THF segment **13** with four desired chiral centers was finally obtained after silylation of homopropargyl alcohol **12** (Scheme 1).

The other segment **21** was prepared by the chiral approach previously reported by our group.[5b] In this case, we use ethyl L-lactate to introduce the stereogenic center bearing the methyl group into target molecule **1** and **2** at C-34. Lactone **21** was a mixture of diastereomers of the desired skeleton with the enantiopure (*S*)-stereogenic carbon bearing a methyl group (Scheme 2).

Compound **22**, which contains the whole skeleton and all elements of the target molecule, was constructed by the coupling reaction of the alkynyl anion of **13** with ep-

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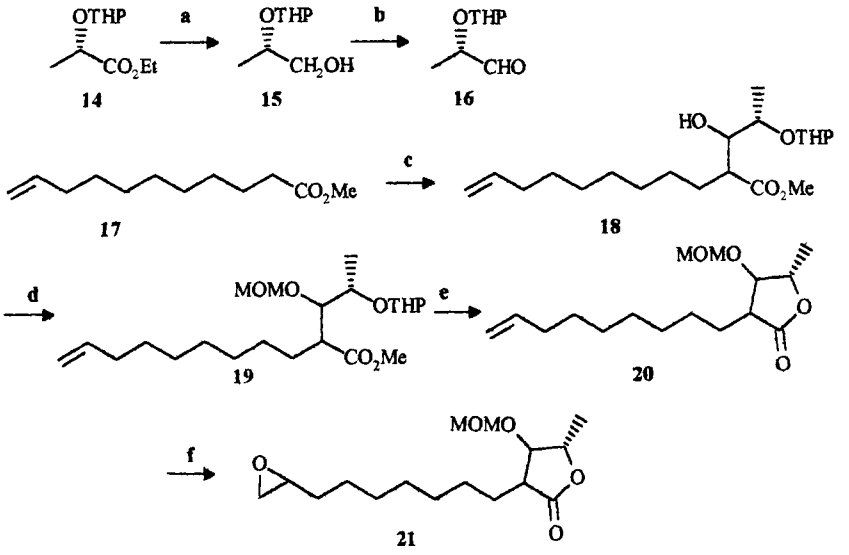
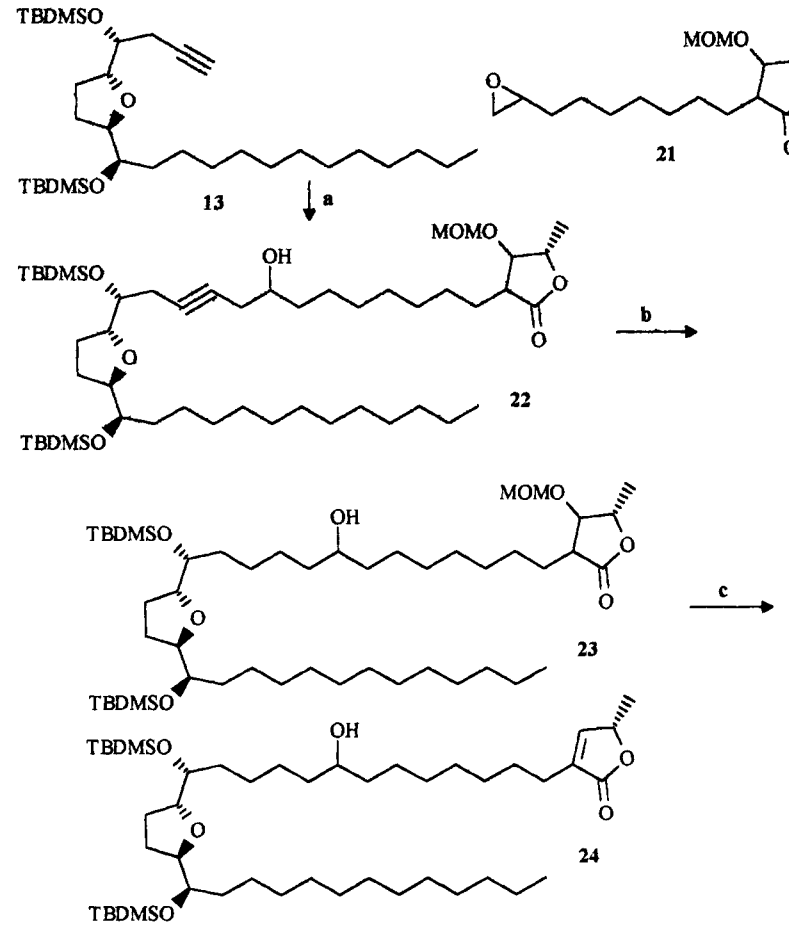
Scheme 2



[a] Reagents and conditions: (a) $LiAlH_4$, ether, 88%; (b) $(COCl)_2$, DMSO, Et_3N, −78 °C, 85%; (c) LDA, then aldehyde **16**, THF−HMPA (10:1), −78 °C, 62%; (d) MOMCl, $^iPr_2NEt$, CH_2Cl_2, rt, 86%; (e) 10% H_2SO_4−THF (1:3, v/v), rt, 85%; (f) *m*-CPBA, CH_2Cl_2, rt, 69%.

Scheme 3



[a] Reagents and conditions: (a) n-BuLi, $BF_3{\cdot}OEt_2$, then epoxide **21**, THF, −78 °C, 96%; (b) H_2, 10% Pd−C, rt, 88%; (c) DBU, THF, rt, 94%.

oxide **21** in the presence of $BF_3{\cdot}OEt_2$ in excellent yield.[9] Hydrogenation of the triple bond of **22** afforded the saturated compound **23**, which subsequently suffered a β-elimination to give an α,β-unsaturated-γ-lactone **24** as a 1:1 mixture of the (10*R*)- and (10*S*)-isomers (Scheme 3).

The cleavage of the TBDMS ethers of **24** was smoothly accomplished in the 5% HF−CH_3CN−THF system,[10] affording a white waxy solid, (10*RS*)-corossoline (**2**), in 92% yield. Our original attempt to remove the silyl protective groups of **23** with the THF solution of TBAF

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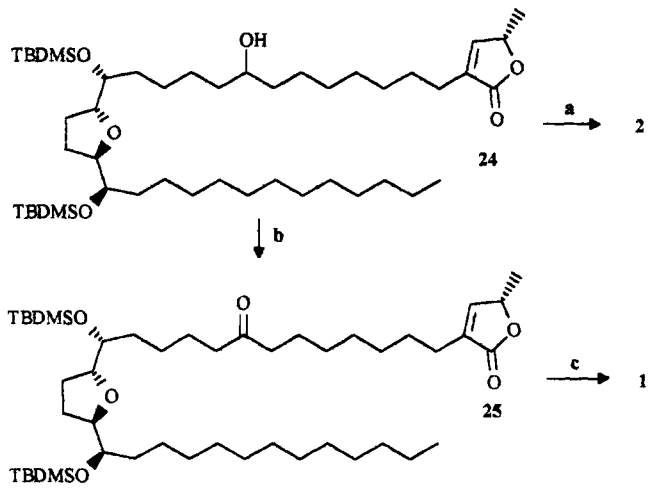
Scheme 4



[a] Reagents and conditions: (a) 5% (v/v) of 40% HF (aq) in CH_3CN–THF (3:1), rt, 92%; (b) $(COCl)_2$, DMSO, Et_3N, 82%; (c) 5% (v/v) of 40% HF (aq) in CH_3CN–THF (3:1), rt, 83%.

led to a complex mixture. The naturally occurring acetogenin, corossolone (**1**), was also prepared from the precursor **24** (Scheme 4). Swern oxidation of **24** gave an enantiomerically pure compound **25**, a silyl-protected form of **1**. The silyl ethers were cleaved in 5% HF–CH_3CN–THF system as above. Corossolone (**1**) prepared by our method was a whitish wax with a higher melting point (mp 79.5–80.5 °C (lit.[3] mp 55–57 °C)) and optical rotation ($[\alpha]^{20}_D$: +20.7 (*c* 0.20, MeOH) (lit.[3] +15 (*c* 0.13, MeOH))) than those of the natural one.[3,11] This might be due to the higher purity of the synthetic sample. All other spectral data reveal that there is no difference between the synthetic sample and the natural one we isolated from *Annona glabra* Linn.[11]

In summary, the first total syntheses of natural corossolone (**1**) and (10*RS*)-corossoline have been reported in this paper. Our approach represents a general entry into some other members of mono-THF acetogenin, such as annonacin-10-one, annonacine, murisoline, solamin, etc.[1] The synthesis of a single epimer at the C-10 hydroxyl group whose configuration is undefined is now under way.

Experimental Section

General. The melting points were uncorrected. Column chromatography was performed on silica gel H (400 mesh). Microanalyses were carried out by the Microanalytical Laboratory at the Shanghai Institute of Organic Chemistry.

2,3-*O*-Isopropylidene-D-threitol Monobenzyl Ether (4). To a solution of **3** (5.90 g, 36.4 mmol) in anhydrous DMF (65 mL) was slowly added 80% NaH (1.20 g, 40.1 mmol) at −15 °C, and the mixture was stirred for 30 min. A solution of benzyl bromide (6.90 g, 40.1 mmol) in DMF (15 mL) was then added to the reaction flask at the same temperature. After an additional 0.5 h, it was warmed to room temperature and stirred for another 1 h. The reaction mixture was then poured into 150 mL of ice–water and extracted with ether (40 mL × 4). The combined organic phases were washed with brine (50 mL × 3), dried (Na_2SO_4), and concentrated. The residual product was chromatographed on silica gel (petroleum ether–EtOAc, 5:1) to give **4** (7.93 g, 86%) as a clear oil. $[\alpha]^{20}_D$: +9.0 (*c* 4.1, $CHCl_3$) (lit.[6] +9 (*c* 0.99, $CHCl_3$)). ^1H NMR (CCl_4, 60 MHz): 7.25 (5H, m), 4.57 (2H, s), 3.83 (2H, m), 3.53 (4H, m), 2.53 (1H, t), 1.27 (6H, s) ppm.

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(4*Z*,2*R*,3*R*)-2,3-*O*-Isopropylidene-4-pentadecen-1-ol Benzyl Ether (5). DMSO (2.86 g, 36.7 mmol) in dry CH_2Cl_2 (10 mL) was dropped into a solution of $(COCl)_2$ (1.7 mL, 2.5 g, 20 mmol) in dry CH_2Cl_2 (30 mL) at −78 °C under N_2 atmosphere. After an additional 20 min, the alcohol **4** (4.0 g, 15.9 mmol) in dry CH_2Cl_2 (10 mL) was added dropwise. Et_3N (12 mL) in CH_2Cl_2 (10 mL) was added after 2 h, and the whole mixture was warmed to room temperature and stirred for 0.5 h. Then it was diluted with CH_2Cl_2 (100 mL) and washed with brine (50 mL × 2), dried (Na_2SO_4), and concentrated. The resulting crude aldehyde was dried in vacuum prior to use.

To a solution of triphenyl undecylphosphonium bromide (9.5 g, 19.1 mmol) in anhydrous THF (100 mL) was added a solution of n-BuLi in hexane (8.3 mL, 2.3 M, 19.1 mmol) at −60 °C under N_2 atmosphere. After an additional 0.5 h, the crude aldehyde (~4.0 g) in THF (20 mL) was injected into the flask slowly and the mixture was stirred for 2 h at −65 °C and 4 h at room temperature. Saturated NH_4Cl (aq) (50 mL) was added to quench the reaction. The organic phase was separated after 20 min. The aqueous phase was extracted with a 1:1 mixture of petroleum ether and ether (30 mL × 2). The combined organic phases were washed with brine (100 mL × 2), dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel (petroleum ether–EtOAc, 80:1–40:1) to give a clear oil **5** (3.90 g, 63% two steps, *Z*/*E* > 95:5). $[\alpha]^{20}_D$: −3.4 (*c* 1.3, $CHCl_3$). IR (neat): 2920, 2860, 1580–1540, 1450, 1380, 1370, 1240, 1170, 1080, 1030, 860, 730, 700 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 7.32 (5H, m), 5.66 (1H, ddt, *J* = 3.1, 10.2 Hz), 5.38 (1H, ddt, *J* = 10.8, 1.6 Hz), 4.63 (1H, dd, *J* = 7.7, 8.9 Hz), 4.59 (2H, s), 3.86 (1H, ddd, *J* = 5.3, 3.1, 8.3 Hz), 3.57 (2H, m), 2.06 (2H, ddt, *J* = 6.7, 1.5, 7.8 Hz), 1.44 (6H, s), 1.25 (16H, m), 0.88 (3H, t, *J* = 7.2 Hz) ppm. EIMS (*m*/*z*): 388 (M^+), 373 ($M^+ - CH_3$), 331 ($M^+ - C_4H_9$), 297 (M^+ − Bn), 282 (M^+ − Bn − CH_3), 91 (Bn, 100.00). Anal. Calcd for $C_{25}H_{40}O_3$: C, 77.27; H, 10.38. Found: C, 77.02; H, 10.29.

(2*R*,3*R*)-2,3-*O*-Isopropylidenepentadecan-1-ol (6). Benzyl ether **5** (5.0 g, 12.9 mmol) was dissolved in 95% ethanol (50 mL), and then 10% Pd–C (50% wet, 500 mg) was added. The mixture was hydrogenated under 1 atm of hydrogen at room temperature overnight. The solid was filtered and washed with ethanol. The combined alcoholic solution was concentrated under reduced pressure and the residue was dried in vacuum. A solution of the residue in anhydrous THF (15 mL) was added dropwise to a solution of liquid NH_3 (~100 mL) and Li (700 mg, 100 mmol) at −78 °C. After 30 min, MeOH (5 mL) was added dropwise, and the mixture was allowed to warm to room temperature (NH_3 evaporated). Water (100 mL) was added, and the mixture was extracted with ether (30 mL × 3). The combined organic phases were washed with brine (30 mL × 2), dried (Na_2SO_4), and concentrated. The crude product was chromatographed on silica gel (petroleum ether–EtOAc, 10:1) to give a low melting point solid **6** (3.33 g, 86%). $[\alpha]^{20}_D$: +20.6 (*c* 0.22, $CHCl_3$). IR (neat): 3425, 2925, 1460, 1360 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.98 (1H, m), 3.88 (1H, m), 3.75 (1H, m), 3.59 (1H, dd, *J* = 11.8, 4.3 Hz), 2.00 (3H, m), 1.56 (2H, m), 1.42 (3H, s), 1.41 (3H, s), 1.26 (18H, m), 0.88 (3H, t, *J* = 6.8 Hz) ppm. EIMS (*m*/*z*): 301 (MH^+), 285 ($M^+ - CH_3$, 100.00), 269 ($M^+ - CH_3O$), 243, 225, 211, 207, 193, 171, 151, 137, 123, 109, 95. Anal. Calcd for $C_{18}H_{36}O_3$: C, 71.95; H, 12.08. Found: C, 71.73; H, 12.45.

(2*R*,3*R*)-2,3-*O*-Isopropylidenepentadec-1-yl *p*-Toluenesulfonate (7). TsCl (6.5 g, 34.1 mmol), Et_3N (12 mL, ~86 mmol) and DMAP (250 mg) were added to a solution of alcohol **6** (8.48 g, 28.3 mmol) in dry CH_2Cl_2 (120 mL) under N_2 atmosphere at room temperature. The reaction mixture was stirred for 12 h, and then ether (200 mL) was added. The whole mixture was washed with ice–water (100 mL × 2) and brine (100 mL) and dried (Na_2SO_4). The solvent was evaporated, and the resulting residue was chromatographed on silica gel (petroleum ether–EtOAc, 20:1) to give a clear thick oil **7** (12.22 g, 96%). $[\alpha]^{20}_D$: +17.5 (*c* 0.54, $CHCl_3$). IR (neat): 2920, 2860, 1595, 1360 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 7.93 (1H, dd, *J* = 6.7, 1.6 Hz), 7.80 (1H, dd, *J* = 1.5, 6.9 Hz), 7.41 (1H, d, *J* = 8.4 Hz), 7.35 (1H, d, *J* = 8.3 Hz), 4.08 (2H, ddd, *J* = 4.4, 7.6, 15.7 Hz), 3.78 (2H, m), 2.49 (2H, s), 2.45 (3H, s), 1.41

(2H, m), 1.36 (3H, s), 1.30 (3H, s), 1.26 (18H, m), 0.88 (3H, t, J = 6.8 Hz) ppm. EIMS (m/z): 455 (MH^+), 439 ($M^+ - CH_3$, 100.00), 425, 397, 379, 345, 297, 269, 225, 165, 137, 109, 95, 81. Anal. Calcd for $C_{25}H_{42}SO_5$: C, 66.04; H, 9.31. Found: C, 66.36; H, 8.97.

(2*R*,3*R*)-1,2-Epoxy-3-hydroxypentadecane (8). The tosylate **7** (2.25 g, 4.96 mmol) was dissolved in MeOH (40 mL), and then *p*-TsOH·H_2O (200 mg, 1.05 mmol) was added. The mixture was stirred at room temperature for 10 h and then heated to reflux for 2 h. To the cooled solution was added K_2CO_3 (1.50 g, 10.9 mmol) and the resulting mixture stirred for 4 h. The mixture was then poured into ice–water (50 mL) and extracted with ether (50 mL × 3). The combined organic phases were washed successfully with brine (50 mL × 2), dried (Na_2SO_4), and concentrated. Chromatography (silica gel, petroleum ether–EtOAc, 20:1–10:1) gave a white solid **8** (903 mg, 75%). Mp: 40–42 °C. $[\alpha]^{20}_D$: −3.84 (*c* 0.37, $CHCl_3$). IR (neat): 3300, 2900 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.44 (1H, dt, J = 5.6 Hz), 2.98 (1H, ddd, J = 2.8, 4.6 Hz), 2.81 (1H, t, J = 4.7 Hz), 2.71 (1H, dd, J = 2.8, 5.0 Hz), 1.61 (2H, m), 1.26 (20H, m), 0.88 (3H, t, J = 6.8 Hz) ppm. EIMS (m/z): 243 (MH^+), 225 ($MH^+ - H_2O$), 197, 195, 181, 165, 152, 139, 135, 125, 111, 69 (100.00). Anal. Calcd for $C_{15}H_{30}O_2$: C, 74.32; H, 12.48. Found: C, 74.49; H, 12.50.

(2*R*,3*R*)-1,2-Epoxy-3-[(*tert*-butyldimethylsilyl)oxy]pentadecane (9). The alcohol **8** (3.16 g, 13.1 mmol), $AgNO_3$ (2.68 g, 15.7 mmol), pyridine (4.6 mL, ~58 mmol), and anhydrous THF (120 mL) were placed in a 250 mL flask and stirred for 20 min at room temperature. TBDMSCl (2.95 g, 19.6 mmol) was added and the mixture continued stirring for 1 day. The reaction was protected from light by a black paper box. The mixture was filtered and the filtrate diluted with ether (100 mL) and washed sequentially with brine (50 mL), aqueous NH_4Cl (50 mL), and brine (50 mL). The dried (Na_2SO_4) solution was concentrated, and the product was purified by chromatography (silica gel, petroleum ether–EtOAc, 100:1). **9** (4.35 g, 94%) was collected as a clear oil. $[\alpha]^{20}_D$: +4.5 (*c* 0.30, $CHCl_3$). IR (neat): 2900, 2820, 1460, 1245, 1100, 835, 775 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.24 (1H, m), 2.88 (1H, m), 2.76 (1H, m), 2.54 (1H, m), 1.53 (2H, m), 1.26 (20H, m), 0.91 (9H, s), 0.88 (3H, t, J = 6.8 Hz), 0.11 (3H, s), 0.06 (3H, s) ppm. EIMS (m/z): 357 (MH^+), 341 ($MH^+ - O$), 300 ($MH^+ - Bu^t$), 299 ($M^+ - Bu^t$, 100.00), 313, 225, 269, 185, 157, 131, 115, 95. Anal. Calcd for $C_{21}H_{44}SiO_2$: C, 70.72; H, 12.44. Found: C, 71.06; H, 12.74.

(5*R*,6*R*)-5-Hydroxy-6-[(*tert*-butyldimethylsilyl)oxy]-1-octadecene (10). A solution of the epoxide **9** (4.30 g, 12.1 mmol) in anhydrous THF (14 mL) was added slowly to a solution of allylmagnesium chloride (freshly prepared from allyl chloride (2.77 g, 36.2 mmol) and Mg turnings (868 mg, 36.2 mmol) in dry ether (40 mL)) in the presence of CuBr (260 mg, 1.81 mmol) at 0 °C. After 1 h at 0 °C, the reaction mixture was stirred at room temperature for an additional 2 h. Saturated NH_4Cl (20 mL) was added to quench the reaction at 0 °C, and the mixture was stirred for 20 min. The organic phase was separated, and the aqueous phase was extracted with ether (20 mL × 3). The combined organic was washed with brine until the blue color disappeared, dried (Na_2SO_4), and concentrated. The resulting residual product was purified by silica gel chromatography column (petroleum ether–EtOAc, 100:1–40:1), and a clear oil **10** (4.02 g, 84%) was obtained. $[\alpha]^{20}_D$: −8.1 (*c* 0.39, $CHCl_3$). IR (neat): 3450, 3020, 2960, 2860, 1640, 1470, 1250, 1070, 905, 835, 778 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 5.84 (1H, ddt, J = 17.0, 9.7, 6.6 Hz), 5.04 (1H, dd, J = 17.0, 1.6 Hz), 4.98 (1H, dd, J = 9.4, 1.6 Hz), 3.51 (1H, m), 3.48 (1H, m), 2.25–2.13 (6H, m), 1.27 (20H, m), 0.90 (3H × 3 + 3H, s + t), 0.09 (3H, s), 0.08 (3H, s) ppm. EIMS (m/z): 399 (MH^+), 381 ($MH^+ - H_2O$), 341 ($M^+ - Bu^t$), 327, 267 (M^+ − TBDMSO, 100.00), 249, 213, 199, 159, 145, 123, 111, 109. Anal. Calcd for $C_{24}H_{50}SiO_2$: C, 72.29; H, 12.64. Found: C, 72.30; H, 12.75.

(2*R*,5*R*)-2-[(1*R*)-1-[(*tert*-butyldimethylsilyl)oxy]tridecyl]-5-(1-hydroxymethyl)tetrahydrofuran (11) and (2*R*,5*S*)-2-[(1*R*)-1-[(*tert*-butyldimethylsilyl)oxy]tridecyl]-5-(1-hydroxymethyl)tetrahydrofuran (11a). The compound **10** (860 mg, 2,16 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled to 0–5 °C. *m*-CPBA (70%, 640 mg, 2.58 mmol) was then added, and the mixture was stirred for 3 h. The reaction was allowed to stand at room temperature for 6 h. CSA (100 mg) was then added, and the mixture was stirred overnight. The solution was diluted with ether (80 mL), washed successively with 10% $Na_2S_2O_3$ (20 mL × 2), saturated $NaHCO_3$ (30 mL × 2), and brine (30 mL × 2), dried (Na_2SO_4), and concentrated. Chromatography on silica gel (petroleum ether–EtOAc, 20:1) gave two clear oils, **11** (642 mg, 72%, less polar fraction) and **11a** (128 mg, 14%, more polar fraction). Data for **11**. $[\alpha]^{20}_D$: −17.5 (*c* 0.10, $CHCl_3$). IR (neat): 3400, 2920, 2860, 1460, 1250, 1050, 835, 775 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.07 (1H, m), 3.95 (1H, m), 3.75 (1H, m, J = 11.3, 2.6 Hz), 3.58 (1H, m), 3.47 (1H, m, J = 11.6 Hz), 2.40 (1H, brs), 1.84 (4H, m), 1.57 (2H, m), 1.26 (20H, m), 0.90 (9H, s), 0.88 (3H, t, J = 6.8 Hz), 0.08 (3H, s), 0.07 (3H, s) ppm. EIMS (m/z): 415 (MH^+), 397 ($MH^+ - H_2O$), 383, 357 ($M^+ - Bu^t$), 339, 313 (100.00), 283, 257, 245, 171, 131, 115. Anal. Calcd for $C_{24}H_{50}SiO_3$: C, 69.50; H, 12.15. Found: C, 69.17; H, 12.38. Data for *11a*. $[\alpha]^{20}_D$: +13.6 (*c* 0.52, $CHCl_3$). IR (neat): 3450, 2900, 2850. 1460, 1250, 1070, 835, 780, 660 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.09 (1H, m), 3.92 (1H, m, J = 6.1 Hz), 3.64 (1H, dd, J = 11.3, 1.4 Hz), 3.58 (1H, m, J = 6.1 Hz), 3.47 (1H, dd, J = 11.3, 6.0 Hz), 1.93 (4H, m), 1.68 (2H, m), 1.26 (20H, m), 0.89 (9H, s), 0.88 (3H, t, J = 7.1 Hz), 0.08 (3H, s), 0.06 (3H, s) ppm. EIMS (m/z): 415 (MH^+), 397 ($MH^+ - H_2O$), 383, 357 ($M^+ - Bu^t$), 339, 313 (100.00), 283, 257, 245, 171, 131, 115. Anal. Calcd for $C_{24}H_{50}SiO_3$: C, 69.50; H, 12.15. Found: C, 69.31; H, 12.02.

(2*R*,5*R*)-2-[(1*R*)-1-[(*tert*-Butyldimethylsilyl)oxy]trideyl]-5-[(1*R*)-1-hydroxy-3-butynyl]tetrahydrofuran (12) and (2*R*,5*R*)-2-[(1*R*)-1-[(*tert*-Butyldimethylsilyl)oxy]tridecyl]-5-[(1*S*)-1-hydroxy-3-butynyl]tetrahydrofuran (12a). DMSO (99 mg, 1.26 mmol) in dry CH_2Cl_2 (1.2 mL) was added to a solution of $(COCl)_2$ (56 μL, 0.63 mmol) in dry CH_2Cl_2 (2.0 mL) at −78 °C under N_2 atmosphere. After an additional 20 min, the alcohol **11** (200 mg, 0.48 mmol) in dry CH_2Cl_2 (1.5 mL) was added dropwise. Et_3N (560 μL, ~4 mmol) was injected after 1 h, and the whole mixture was warmed to room temperature and stirred for 0.5 h. Then it was diluted with CH_2Cl_2 (10 mL) and washed with brine (5 mL × 2), dried (Na_2SO_4), and concentrated. The resulting crude aldehyde was dried in vacuum prior to use.

To a solution of 2-allenyl-1,3,2-dioxaborolane-(4*S*,5*S*)-dicarboxylic acid bis(1′-methylethyl) ester[8] freshly prepared from allenylmagnesium bromide (136 mg, 1.62 mmol) and D-(−)-DIPT (470 mg, 2.00 mmol) in dry toluene (9 mL) was injected the crude aldehyde in dry toluene (2 mL) and the resulting mixture stirred for 20 h at −78 °C under N_2 atmosphere. Hydrochloric acid (1M, 2 mL, 2 mmol) was added at −78 °C, and the mixture was stirred for 5 min. The whole mixture was poured into brine (20 mL), and the organic phase was separated. The aqueous phase was extracted with ether (8 mL × 4). The combined organic was washed with brine (10 mL × 2), dried (Na_2SO_4), and concentrated. Chromatography on silica gel (petroleum ether–EtOAc, 75:1–30:1) gave a threo-product **12** (150 mg, 68% two steps) and an erythro-product **12a** (8 mg, 4%) as clear oils. Data for **12**. $[\alpha]^{20}_D$: −10.3 (*c* 0.25, $CHCl_3$). IR (neat): 3450, 3300, 2920, 2860, 1465, 1250, 1080, 835, 778 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.99 (1H, ddd, J = 5.8, 7.8 Hz), 3.90 (1H, ddd, J = 6.1, 8.2 Hz), 3.60 (1H, dt, J = 6.2, 4.9 Hz), 3.56 (1H, m), 2.41 (2H, dd, J = 6.2, 2.7 Hz), 2.01 (1H, t, J = 2.7 Hz), 1.60–1.98 (6H, m), 1.26 (20H, m), 0.90 (9H, s), 0.88 (3H, t, J = 6.8 Hz), 0.08 (3H, s), 0.06 (3H, s) ppm. EIMS (m/z): 437 ($M^+ - CH_3$), 413 ($M^+ - CH_2C{\equiv}CH$), 395 ($M^+ - Bu^t$), 383, 377, 337, 313 (100.00), 257, 115, 75. Data for **12a**. $[\alpha]^{20}_D$: +12.2 (*c* 2.05, $CHCl_3$). IR (neat): 3400, 3300, 2920, 2860, 1465, 1250, 1060, 838, 778 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 3.96 (1H, ddd, J = 5.4, 8.4 Hz), 3.92 (1H, m), 3.82 (1H, dt, J = 6.2, 5.4 Hz), 3.55 (1H, m), 2.43 (2H, dd, J = 6.4, 2.7 Hz), 2.02 (1H, t, J = 2.7 Hz), 1.60–1.96 (6H, m), 1.26 (20H, m), 0.90 (9H, s), 0.88 (3H, t, J = 7.0 Hz), 0.07 (3H, s), 0.05 (3H, s) ppm. EIMS (m/z): 413 ($M^+ - CH_2C{\equiv}CH$), 395 ($M^+ - Bu^t$), 377, 351, 337, 313 (100.00), 285, 257, 143, 115, 75.

(2*R*,5*R*)-2-[(1*R*)-1-[(*tert*-Butyldimethylsilyl)oxy]tridecyl]-5-[(1*R*)-1-[(*tert*-butyldimethylsilyl)oxy]-3-butynyl]tetrahydrofuran (13). A mixture of **12** (480 mg, 1.06 mmol), TBDMSCl (208 mg, 1.38 mmol), and imidazole (217 mg, 3.19 mmol) in anhydrous DMF (2 mL) was stirred at room temperature for 1 day after which it was diluted with ether (50 mL) and washed successfully with brine (20 mL), saturated NH_4Cl (20 mL), and brine (20 mL). The organic phase was dried (Na_2SO_4) and concentrated. Chromatography on silica gel (petroleum ether–EtOAc, 100:1–50:1) gave a clear oil **13** (549 mg, 91%). $[\alpha]^{20}_D$: +4.73 (*c* 0.28, $CHCl_3$). IR (neat): 3300, 2920, 2860, 1460, 1250, 1100, 830, 770 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.11 (1H, m), 3.93 (1H, m), 3.78 (1H, m), 3.60 (1H, m), 2.56 (1H, ddd, J = 2.6, 6.4, 16.4 Hz), 2.29 (1H, ddd, J = 2.6, 6.2, 16.4 Hz), 1.95 (1H, t, J = 2.6 Hz), 1.60–1.95 (6H, m), 1.28 (20H, m), 0.92 (6H, s), 0.91 (6H, s), 0.90 (6H, s), 0.89 (3H, t), 0.12 (3H, s), 0.10 (3H, s), 0.09 (3H, s), 0.08 (3H, s) ppm. EIMS (*m/z*): 479 ($M^+ - 2CH_3 - Bu^t$), 417, 357, 321, 295, 279, 261, 237, 223, 169, 151, 137, 97 (100.00).

Coupling Reaction of 13 and 21. To a solution of the alkyne **13** (519 mg, 0.917 mmol) in anhydrous THF (6 mL) was added a solution of n-BuLi in hexane (2.4 M, 382 μL, 0.917 mmol) dropwise at −78 °C. The mixture was stirred for an additional 20 min. Freshly distilled $BF_3{\cdot}OEt_2$ (123 μL) was then injected, and the mixture was stirred for 15 min. A solution of the epoxide **21** (150 mg, 0.50 mmol) in anhydrous THF (2 mL) was dropped slowly, and the mixture was stirred for 2 h until saturated NH_4Cl (2 mL) was added to quench the reaction. The mixture was warmed to room temperature and diluted with ether (40 mL), washed with brine (10 mL × 3), and dried (Na_2SO_4). The solvent was removed, and the crude product was purified by column chromatography (silica gel, petroleum ether–EtOAc, 10:1–6:1). A clear thick oil **22** (419 mg, 96% based on **21**) was collected as a mixture of diastereomers, and recovered **13** (175 mg, 34% based on **13**) was also collected. IR (neat): 3400, 2950, 2860, 1785, 1465, 1250, 1100, 1070, 840, 780 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.68 (2H, s), 4.34 (1H, dq, J = 6.2 Hz), 4.10 (1H, m), 3.92 (1H, m), 3.74 (1H, m), 3.67 (2H, m), 3.58 (1H, m), 3.39 (3H, s), 2.64 (1H, dt), 2.10–2.60 (4H, m), 1.60–1.90 (8H, m), 1.45 (3H, d, J = 6.5 Hz), 1.26 (32H, m), 0.89 (18H + 3H, s + t), 0.08 (3H × 4, s) ppm. EIMS (*m/z*): 810 ($MH^+ - Bu^t$), 748 ($M^+ - Bu^t - CH_3OCH_2O$), 678, 616, 524, 510, 392, 359, 339, 313, 255, 225, 73 (100.00).

Hydrogenation of 22. In the presence of 10% Pd–C (15 mg), a solution of **22** (340 mg, 0.392 mmol) in EtOAc (5 mL) was hydrogenated under 1 atm of hydrogen at room temperature for 12 h. The catalyst was filtered, and the filtrate was concentrated. Chromatography on silica gel (petroleum ether–EtOAc, 10:1–6:1) gave an oil **23** (298 mg, 88%). IR (neat): 3400, 2920, 2860, 1780, 1460, 1250, 1040, 835, 775 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 4.68 (2H, s), 4.34 (1H, dt, J = 6.1 Hz), 4.13 (1H, m), 3.92 (1H, m), 3.75 (2H, m), 3.58 (2H, m), 3.39 (3H, s), 2.64 (1H, dt, J = 6.6 Hz), 1.60–1.96 (12H, m), 1.45 (3H, d, J = 6.4 Hz), 1.26 (36H, m), 0.92 (6H, s), 0.90 (6H, s), 0.89 (6H + 3H, s + t), 0.07 (3H × 4, s) ppm. EIMS (*m/z*): 795 ($MH^+ - Bu^t - H_2O$), 752 ($M^+ - Bu^t - CH_3OCH_2O$), 734 ($M^+ - Bu^t - CH_3OCH_2O - H_2O$), 660, 602, 528, 510, 478, 384, 340, 313, 275, 255, 225, 73 (100.00).

(5*S*)-3-[(8*RS*)-8-Hydroxy-(13*R*)-13-[(*tert*-butyldimethylsilyl)oxy]-13-[(2*R*,5*R*)-tetrahydro-5-[(1*R*)-1-[(*tert*-butyldimethylsilyl)oxy]tridecyl]furan-2-yl]tridecyl]-5-methylfuran-2(5*H*)-one (24). To a solution of **23** (68 mg, 0.078 mmol) in anhydrous THF (1 mL) was injected DBU (25 μL, ~0.167 mmol), and the mixture was stirred at room temperature for 6 h. Acetic acid (4 drops, ~80 μL) was dropped, and the whole mixture was stirred for 20 min. The solvent was removed, and the residue was purified by column chromatography (silica gel, petroleum ether–EtOAc, 8:1–5:1). **24** (59 mg, 94%) was obtained as a clear oil. IR (neat): 3450, 2960, 2880, 1760, 1465, 1260, 1080, 840, 780 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 6.98 (1H, d, J = 1.6 Hz), 4.99 (dq, 1H, J = 1.6, 6.9 Hz), 3.89 (2H, m), 3.57 (2H + 1H, m), 2.25 (2H, t, J = 7.2 Hz), 1.60–1.90 (12H, m), 1.41 (3H, d, J = 6.7 Hz), 1.26 (34H, brm), 0.88 (18H + 3H, s + t), 0.06 (3H × 4, s) ppm. EIMS (*m/z*): 734 ($MH^+ - Bu^t - H_2O$), 602, 527, 509, 345, 339, 327, 313, 293, 275, 257, 201(100.00), 165, 111.

(5*S*)-3-[(8*RS*,13*R*)-8,13-Dihydroxy-13-[(2*R*,5*R*)-tetrahydro-5-[(1*R*)-1-hydroxytridecyl]furan-2-yl]tridecyl]-5-methylfuran-2(5*H*)-one [(10*RS*)-Corossoline] (2). To a solution of *tert*-butyldimethylsilyl ether **24** (50 mg, 0.0619 mmol) in the mixed solvent of CH_3CN (0.7 mL) and THF (0.4 mL) was added 40% aqueous HF (2 drops, ~50 μL), and the mixture was stirred for 10 h at room temperature. Brine (2 mL) and CH_2Cl_2 (2 mL) were added, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2 mL × 4). The combined organic phases were washed successfully with brine (3 mL × 3), dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether–EtOAc, 2:1–1:1). (10*RS*)-Corossoline (**2**) (33 mg, 92%) was obtained as a white waxy solid. Mp: 66.5–67.5 °C (lit.[3] mp 45–50 °C); $[\alpha]^{20}_D$: +22.1 (*c* 0.10, MeOH) (lit.[3] $[\alpha]^{20}_D$: +19 (*c* 0.2, MeOH)). UV λ_{max} (MeOH): 212 nm, log ϵ 3.69. IR (KBr, Nujol): 3426, 2916, 2847, 1738, 1649, 1465, 1373, 1319, 1198, 1080, 1027, 961, 852, 720 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 6.98 (1H, d, J = 1.5 Hz), 4.99 (1H, dq, J = 1.5, 6.6 Hz), 3.80 (2H, m), 3.59 (1H, m), 3.42 (2H, m), 2.16 (2H, t, J = 7.2 Hz), 1.97 (4H, m), 1.69 (8H, m), 1.40 (3H, d, J = 7.0 Hz), 1.26 (34H, brm), 0.88 (3H, t, J = 5.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz): 173.85, 148.88, 134.33, 82.64 (×2), 77.38, 74.05(×2), 71.82, 37.48, 33.48, 31.91, 29.64, 29.34, 29.24, 29.10, 28.74, 27.40, 25.59, 25.16, 22.67, 19.21, 14.10. FABMS (*m/z*): 603.8 (M^+ + Na), 581.8 (MH^+), 562 ($M^+ - H_2O$), 545 ($M^+ - 2H_2O$), 527 ($M^+ - 3H_2O$), 510, 447, 416, 385, 327, 275, 239, 207, 190, 164.

(5*S*)-3-[8-Oxo-(13*R*)-13-[(*tert*-butyldimethylsilyl)oxy]-13-[(2*R*,5*R*)-tetrahydro-5-[(1*R*)-1-[(*tert*-butyldimethylsilyl)oxy]tridecyl]furan-2-yl]tridecyl]-5-methylfuran-2(5*H*)-one (25). DMSO (40 mg, 0.512 mmol) in dry CH_2Cl_2 (0.5 mL) was added to a solution of $(COCl)_2$ (22.3 μL, 0.256 mmol) in dry CH_2Cl_2 (1.0 mL) at −78 °C under N_2 atmosphere. After an additional 20 min, the alcohol **24** (125 mg, 0.155 mmol) in dry CH_2Cl_2 (0.5 mL) was added slowly. Et_3N (120 μL, ~0.86 mmol) was injected after 1 h, and the whole mixture was warmed to room temperature and stirred for 1.5 h. Then it was diluted with ether (10 mL) and washed with brine (5 mL × 2), dried (Na_2SO_4), and concentrated. Chromatography on silica gel (petroleum ether–EtOAc, 12:1–4:1) gave a clear oil **25** (103 mg, 82%) and the starting material **24** (16 mg, 13% based on **24**). $[\alpha]^{20}_D$: +17.8 (*c* 0.11, $CHCl_3$). IR (neat): 2960, 2880, 1765, 1720, 1465, 1255, 1080, 840, 780 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 6.99 (1H, d, J = 1.6 Hz), 4.99 (1H, dq, J = 1.6, 6.8 Hz), 3.84 (2H, m), 3.57 (2H, m), 2.38 (4H, t, J = 7.1 Hz), 2.26 (2H, t, J = 7.5 Hz), 1.54 (8H, m), 1.40 (3H, d, J = 6.8 Hz), 1.26 (34H, brm), 0.89 (18H + 3H, s + t), 0.09 (3H × 4, s) ppm. EIMS (*m/z*): 749 ($M^+ - Bu^t$), 617, 507, 475, 423, 313, 287, 277, 223, 171, 149, 129, 111, 69 (100.00).

(5*S*)-3-[8-Oxo-(13*R*)-13-hydroxy-13-[(2*R*,5*R*)-tetrahydro-5-[(1*R*)-1-hydroxytridecyl]furan-2-yl]tridecyl]-5-methylfuran-2(5*H*)-one (Corossolone) (1). To a solution of *tert*-butyldimethylsilyl ether **25** (89 mg, 0.110 mmol) in the mixed solvent of CH_3CN (1.0 mL) and THF (0.6 mL) was added 40% aqueous HF (5 drops, ~100 μL), and the mixture was stirred for 24 h at room temperature. Brine (3 mL) and CH_2Cl_2 (4 mL) were added, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (2 mL × 3). The combined organic phases were washed successively with brine (3 mL × 3), dried (Na_2SO_4), and concentrated. The residue was purified by a column chromatography (silica gel, petroleum ether–EtOAc, 3:1–2:1). Corossolone (**1**) (53 mg, 83%) was collected as a white solid. Mp: 79.5–80.5 °C lit.[3] mp 55–57 °C). $[\alpha]^{20}_D$: +20.7 (*c* 0.20, MeOH) (lit.[3] $[\alpha]^{20}_D$: +15 (*c* 0.13, MeOH)). UV λ_{max} (MeOH): 214 nm, log ϵ 3.58. IR (KBr, Nujol): 3450, 2915, 2847, 1732, 1698, 1650, 1465, 1410, 1376, 1322, 1201, 1113, 1082, 1021, 962, 888, 722 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): 6.99 (1H, d, J = 1.5 Hz), 4.99 (1H, dq, J = 1.5, 6.3 Hz), 3.80 (2H, m), 3.41 (2H, m), 2.38 (4H, t, J = 7.1 Hz), 2.26 (2H, t, J = 7.5 Hz), 1.98 (2H, m), 1.85 (2H, m), 1.53–1.67 (4H, m), 1.40 (3H, d, J = 6.7 Hz), 1.26 (34H, brm), 0.88 (3H, t, J = 6.8 Hz) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 211.32, 173.86, 148.95, 134.25, 82.73, 82.86, 77.44, 74.09, 73.80, 42.82,

33.57, 33.32, 31.93, 29.66, 29.36, 29.09, 28.98, 28.76, 27.36, 25.67, 25.34, 25.17, 23.80, 22.69, 19.24, 14.11 ppm. FABMS (*m/z*): 618 ($M^+ + K$), 602 ($M^+ + Na$), 580 (MH^+), 562 ($MH^+ - H_2O$), 544 ($MH^+ - 2H_2O$), 526, 313, 263, 239, 223, 195.

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Supplementary Material Available: Reproductions of ^1H NMR for compounds **10**, **11**, **11a**, **12**, **12a**, **13**, **21**, **22**, **2**, and **1** and ^{13}C NMR for compounds **2** and **1** (12 pages). This material is contained in libraries on microfiche, immediately follows this article in microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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