Total Synthesis and Structural Elucidation of Khafrefungin

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Supporting Information

Experimental Section

General

IR spectra were recorded on a JASCO FT/IR-610. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400 or a JNM-LA500 spectrometer in $CDCl_3$ unless otherwise noted. Tetramethylsilane (TMS) served as internal standard (δ 0) for ^{1}H NMR, and $CDCl_3$ was used as internal standard (δ 77.0) for ^{13}C NMR. When CD_3OD was used, CD_3OD served as internal standard (δ 3.3) for ^{1}H NMR, (δ 49.0) for ^{13}C NMR. HPLC was carried out using a Shimazu C-R6A chromatopac, SPD-10A and LC-10AT. Optical rotations were recorded on a JASCO P-1010. Column chromatography was performed on Silica gel 60 (Merck). Mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer. Preparative tin layer chromatography was performed on Wakogel B5F or using Silica gel 60 F_{254} (Merck). All non-aqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware. All solvents were purified according to standard procedures.

Synthesis of Mimic 1a-d

Thioester 4: To a mixture of tin(II) trifluoromethanesulfonate (4.17 g, 10 mmol) and tin(II) oxide (1.35 g, 10 mmol) in dichloromethane (350 ml) was added (*S*)-1-methyl-2-[(*N*-1-naphtylamino)methyl]pyrrolidine (2.88 g, 12 mmol) in dichloromethane (50 ml) at room temperature. The solution was cooled to –78 °C, and a solution of decanal (7.81 g, 50 mmol) and silyl enol ether **3** (11.42 g, 60 mmol) in dichloromethane (200 ml) was slowly added over 4 h. After stirring for 1h at –78 °C, the reaction was quenched with aqueous sodium hydrogen carbonate solution. After the reaction mixture was filtered through Celite, the phases were separated. The aqueous layer was extracted with dichloromethane and the combined organic extracts were washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **4** (11.40 g, 83%, *syn*/*anti* = 97/3, 94% ee (*syn*)) as a colorless oil. IR (neat) 3433, 2924, 1685 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H), 1.22-1.52 (m, 19H), 2.38 (d, *J* = 3.3 Hz, 1H), 2.67 (dq, *J* = 3.6, 7.2 Hz, 1H), 2.88 (q, *J* = 7.5 Hz, 2H), 3.86-3.94 (m, 1H); ^{13}C NMR δ 11.3, 14.1, 14.6, 22.7, 23.2, 25.9, 29.3, 29.50, 29.51, 29.54, 31.9, 34.0, 52.9, 71.9, 204.4; MS (EI+) m/z 275; Anal. Calcd for $C_{15}H_{30}O_2S$: C, 65.64; H, 11.02. Found: C, 65.38; H, 10.83.

(*S*)-2-Methyl-1-decanol: To a solution of **4** (8.2 g, 30 mmol) in dichloroethane (100 ml) were added phenyl chlorothionoformate (15.5 g, 90 mmol) and pyridine (9.5 g, 120 mmol). The solution was heated at reflux for 10 min. After cooling to room temperature, the solution was poured into diethyl ether and was washed with 1M aqueous HCl solution, water, and brine. The organic layer was dried over anhydrous

sodium sulfate, filtered, and concentrated under reduced pressure. The residue was dissolved in toluene (100 ml). To this solution were added tributyltin hydride (26.2 g, 90 mmol) and 2,2'-azobis(isobutyronitrile) (1.48 g, 9.0 mmol). The solution was heated at reflux for 10 min. After cooling to the temperature, the solvent was evaporated and the residue was roughly chromatographed on silica gel (hexane/ethyl acetate = 30/1). A solution of the resulting material in THF (50 ml) was added to a suspension of lithium aluminum hydride (2.90 g, 76 mmol) at 0 °C, and the mixture was stirred for 30 min. The reaction was quenched by the addition of water (2.9 ml), 15% NaOH (2.9 ml), and water (11.6 ml). The mixture was dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give (*S*)-2-methyl-1-dodecanol (5.17 g, 86% for 3 steps) as a colorless oil. $[\alpha]^{26}_{D}$ –10 (c 0.50, EtOH); IR (neat) 3360, 2920 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 3H), 1.05-1.40 (m, 18H), 1.47 (brs, 1H), 1.53-1.64 (m, 1H), 3.41 (dd, *J* = 6.6, 10.5 Hz, 1H), 3.51 (dd, *J* = 5.9, 10.5 Hz, 1H); ^{13}C NMR δ 14.1, 16.6, 22.7, 27.0, 29.3, 29.6, 29.7, 29.9, 31.9, 33.1, 35.7, 68.4; MS (EI+) m/z 199; Anal. Calcd for $C_{13}H_{28}O$: C, 77.93; H, 14.09. Found: C, 77.69; H, 14.03.

Aldehyde 5: To a solution of oxalyl chloride (2.59 g, 20 mmol) in dichloromethane (20 ml) was added a solution of dimethyl sulfoxide (2.35 g, 30 mmol) in dichloromethane (5 ml) at –78 °C. After stirring for 5 min at –78 °C, a solution of (*S*)-2-methyl-1-dodecanol (2.03 g, 10 mmol) in dichloromethane (15 ml) was added. After stirring for 1 h at –78 °C, a solution of the triethylamine (6.01 g, 60 mmol) in dichloromethane (10 ml) was added, and the mixture was warmed to room temperature. After stirring for 1 h at room temperature, the reaction was quenched

with water, and the aqueous layer was extracted with diethyl ether. The extract was washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **5** (1.81 g, 91%) as a colorless oil. ^{1}H NMR δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H), 1.20-1.40 (m, 17H), 1.70-1.75 (m, 1H), 2.29-2.37 (m, 1H), 9.61 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR δ 13.3, 14.1, 22.7, 26.9, 29.3, 29.4, 29.57, 29.62, 30.5, 31.9, 46.3, 205.4.

Alcohol from 6d: To a mixture of scandium trifluoromethanesulfonate (98 mg, 0.2 mmol) and silyl enol ether **3** (571 mg, 3.0 mmol) in propionitrile (12 ml) was added a solution of **5** (397 mg, 2.0 mmol) in propionitrile (8 ml) at –45 °C. After stirring for 17 h at –45 °C, the reaction was quenched with an aqueous sodium hydrogen carbonate solution, and the aqueous layer was extracted with dichloromethane. The extract was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 20/1 to 6/1) to give **6** (582 mg, 92%, **6a**:**6b**:**6c**:**6d** = 22:38:9:31) as a colorless oil. The easily separated **6d** (1.30 g, 4.2 mmol) was dissolved in THF (15 ml). To this solution was added lithium borohydride (462 mg, 21 mmol) at –15 °C, and the mixture was stirred for 12 h at –5 °C. The reaction mixture was poured into diethyl ether and 0.1 M aqueous HCl solution, and the aqueous layer was extracted with diethyl ether. The extract was washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 4/1) to give the diol **7d** (1.01 g, 93%) as a white crystal. To a mixture of the diol **7d** (1.01 g, 3.91 mmol) and *p*-

anisaldehyde dimethylacetal (2.2 g, 11.8 mmol) in dichloromethane (15 ml) was added *p*-toluenesulfonic acid (50 mg, 0.26 mmol) at room temperature. After stirring for 12 h at the same temperature, the reaction was quenched with an aqueous sodium hydrogen carbonate solution, and the aqueous layer was extracted with dichloromethane. The extract was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give the acetal (1.30 g, 88%) as a colorless oil. To the solution of the acetal (1.30 g, 3.45 mmol) in dichloromethane (20 ml) was added diisobutylaluminum hydride (10 ml of a 1.0 M solution in hexane, 10 mmol) at –78 °C. After stirring for 15 min at –78 °C, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 20/1 to 6/1) to give the alcohol (1.28 g, 98%) as a colorless oil. $[\alpha]^{22}_{D}$ +0.5 (c 0.9, EtOH); IR (neat) 3439, 1513, 1295 cm^{-1}, ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.8 Hz), 1.15-1.45 (m, 18H), 1.67-1.81 (m, 1H), 1,92-2.04 (m, 2H), 3.32 (dd, *J* = 3.9, 6.2 Hz, 1H), 3.54 (dd, *J* = 5.4, 10.6 Hz, 1H), 3.61 (dd, *J* = 7.0, 10.6 Hz, 1H), 3.79 (s, 3H), 4.48 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 11.7, 14.1, 15.7, 22.7, 27.2, 29.3, 29.61, 29.64, 29.9, 31.9, 34.1, 35.4, 37.6, 55.2, 66.5, 73.9, 84.2, 113.7, 129.2, 131.0, 159.1; HRMS (EI+) Calcd for $C_{24}H_{42}O_3$ (M+) 378.3134. Found 378.3133.

Alcohol from 6a: ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 1.15-1.58 (m, 18H), 1.70-1.83 (m, 1H), 1.88-1.98 (m, 1H), 2.87 (brs,1H), 3.20 (t, *J* = 5.5 Hz, 1H), 3.57 (dd, *J* = 5.6, 11.0 Hz, 1H), 3.70 (dd, *J* = 3.5, 11.0 Hz, 1H), 3.79 (s, 3H), 4.47 (d, *J* = 10.6 Hz, 1H), 4.57 (d, *J* = 10.6 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 14.1, 15.9, 16.7, 22.7, 27.6, 29.3, 29.6, 29.7, 29.9, 31.8, 31.9, 36.0, 36.8, 55.2, 66.3, 74.6, 89.5, 113.8, 129.4, 130.5, 159.2.

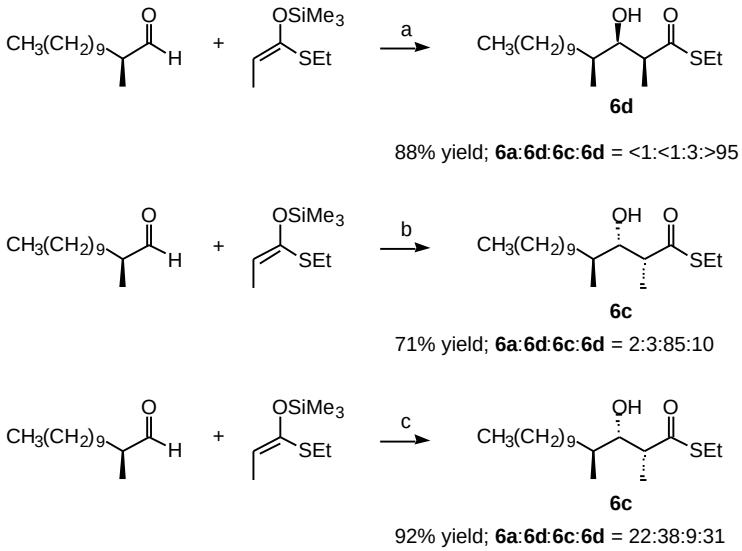
Alcohol from 6b: $[\alpha]^{30}_{D}$ –0.2 (c 1.0, EtOH); IR (neat) 3431, 1513, 1295 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 1.15-1.55 (m, 18H), 1.63-1.78 (m, 1H), 1.83-1.98 (m, 1H), 2.72 (brs, 1H), 3.26 (dd, *J* = 3.6, 7.4 Hz, 1H), 3.60 (dd, *J* = 6.1, 11.2 Hz, 1H), 3.66 (dd, *J* = 3.7, 11.2 Hz, 1H), 3.80 (s, 3H), 4.49 (d, *J* = 10.5 Hz, 1H), 4.59 (d, *J* = 10.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 14.1, 14.4, 15.5, 22.7, 27.6, 29.3, 29.6, 29.7, 29.9, 31.9, 34.6, 36.2, 37.5, 55.2, 66.7, 74.8, 88.4, 113.8, 129.4, 130.5, 159.2; HRMS (EI+) Calcd for $C_{24}H_{42}O_3$ (M+) 378.3134; Found 378.3119; Anal. Calcd for $C_{13}H_{42}O_3$: C, 76.14; H, 11.18. Found: C, 76.11; H, 11.11.

Alcohol from 6c: ^{1}H NMR δ 0.88 (t, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 1.10-1.45 (m, 17H), 1.59-1.65 (m, 1H), 1.73-1.80 (m, 1H), 1.88-1.98 (m, 1H), 2.05 (brs, 1H), 3.31 (dd, *J* = 2.8, 6.5 Hz, 1H), 3.53-3.62 (m, 2H), 3.79 (s, 3H), 4.46 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 11.0, 14.1, 16.2, 22.7, 27.2, 29.3, 29.6, 29.66, 29.69, 30.1, 31.9, 32.8, 35.6, 37.3, 55.2, 66.7, 73.8, 84.1, 113.7, 129.2, 131.0, 159.1.

Stereochemical Assignment of 6a-d: Asymmetric aldol reactions of **5** with **3** using chiral tin(II) Lewis acids were performed. The reactions are known to proceed under "chiral catalyst control (Cf. Ref. 6 in the text)," and the structures of **6c** and **6d** were

determined (Scheme S-1). The $Sc(OTf)_3$-catalyzed aldol reaction gave a mixture of **6a**-**d**, which was separated and was converted to PMB ethers, respectively (Scheme S-2). Aldol adducts **6a** and **6c** gave the same PMB ether, while **6b** and **6d** gave the same PMB ether. Based on this transformation, the structures of **6a** and **6b** were determined.

Scheme S-1. Stereochemical Assignment of **6a**-**d** (1)

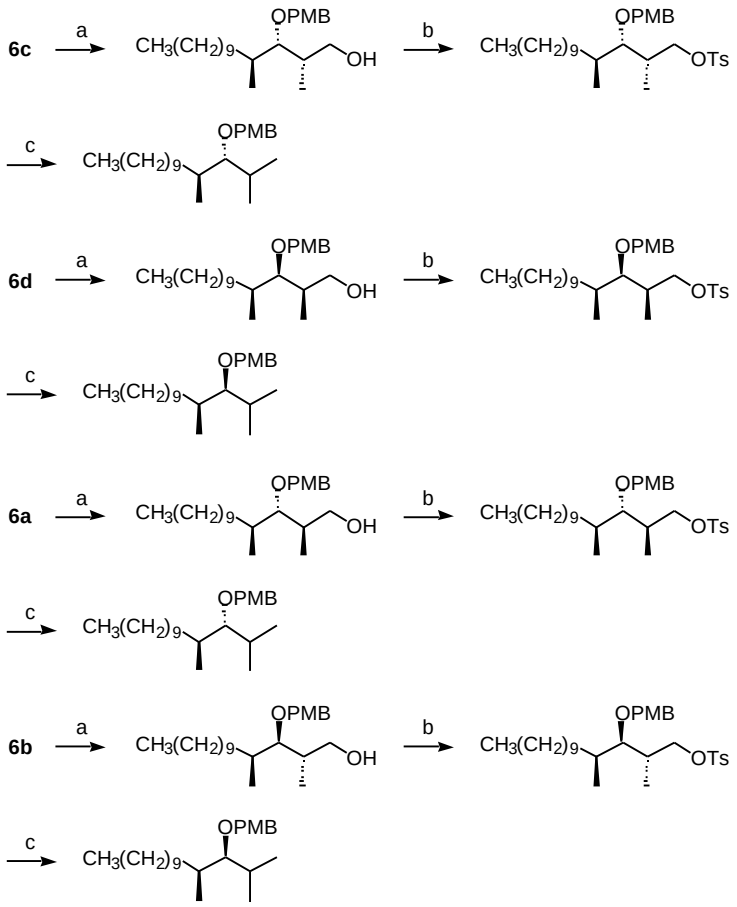


Reagents and conditions: (a) $Sn(OTf)_2$, $Bu_2Sn(OAc)_2$, (*S*)-1-methyl-2-[(*N*-1-naphthylamino)-methyl]pyrrolidine, CH_2Cl_2, -78 °C; (b) $Sn(OTf)_2$, $Bu_2Sn(OAc)_2$, (*R*)-1-methyl-2-[(*N*-1-naphthylamino)-methyl]pyrrolidine, CH_2Cl_2, -78 °C; (c) cat. $Sc(OTf)_3$.

Aldehyde 8d: To a solution of oxalyl chloride (510 mg, 4.0 mmol) in dichloromethane (6 ml) was added a solution of dimethyl sulfoxide (470 mg, 6.0 mmol) in dichloromethane (3 ml) at –78 °C. After stirring for 5 min at –78 °C, a solution of the alcohol (757 mg, 2.0 mmol) in dichloromethane (6 ml) was added. After stirring for 1 h at –78 °C, a solution of the triethylamine (1.21 g, 12.0 mmol) in dichloromethane (3 ml) was added, and the mixture was warmed to room temperature.

After stirring for 1 h at the same temperature, the reaction was quenched with water, and the aqueous layer was extracted with diethyl ether. The extract was washed with

Scheme S-2. Stereochemical Assignment of **6a-d** (2)



Reagents and conditions: (a) $LiBH_4$, THF, -5 °C, 93%; $PMPCH(OMe)_2$, cat. TsOH, CH_2Cl_2, rt; DIBAL, CH_2Cl_2; (b) TsCl, pyridine; (c) $LiAlH_4$.

water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **8d** (693 mg, 92%) as a colorless oil: ^{1}H NMR δ 0.88 (t, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.19-1.47 (m, 18H), 1.66-1.75 (m, 1H), 2.60-2.70 (m, 1H), 3.66 (dd, *J* = 4.3, 5.8 Hz, 1H), 3.79 (s, 3H), 4.43 (s, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 9.77 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR δ, 8.9, 14.1, 15.3, 22.7, 27.1, 29.3, 29.59, 29.62, 29.9, 31.9,

33.7, 36.2, 49.2, 55.2, 73.4, 81.9, 113.7, 129.2, 130.5, 159.2, 204.8.

Aldehyde 8a: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 7.2 Hz, 3H), 1.19-1.79 (m, 19H), 2.62-2.72 (m, 1H), 3.44 (t, *J* = 5.3 Hz, 1H), 3.80 (s, 3H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 9.77 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR δ 11.8, 14.1, 16.0, 22.7, 27.2, 29.3, 29.6, 29.9, 31.9, 32.1, 35.6, 48.4, 55.3, 73.2, 85.0, 113.7, 129.2, 130.4, 159.2, 204.9.

Aldehyde 8b: $[\alpha]^{29}_{D}$ –10 (c 1.0, EtOH); ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.12-1.73 (m, 19H), 2.62-2.73 (m, 1H), 3.50 (dd, *J* = 4.0, 6.6 Hz, 1H), 3.80 (s, 3H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 10.8 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 9.78 (d, *J* = 2.6 Hz, 1H); ^{13}C NMR δ 11.7, 14.1, 14.4, 22.7, 27.5, 29.3, 29.59, 29.61, 29.63, 29.8, 31.9, 33.8, 35.8, 49.1, 55.2, 73.7, 84.2, 113.7, 129.2, 130.5, 159.2, 204.9.

Aldehyde 8c: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 1.16 (d, *J* = 7.0 Hz, 3H), 1.19-1.78 (m, 19H), 2.53-2.60 (m, 1H), 3.67 (dd, *J* = 3.3, 7.4 Hz, 1H), 3.79 (s, 3H), 4.38-4.51 (m, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 9.77 (s, 1H); ^{13}C NMR δ 14.1, 16.1, 22.7, 27.0, 29.3, 29.6, 29.7, 30.0, 31.9, 32.6, 36.0, 49.1, 55.2, 73.2, 81.9, 113.7, 129.3, 130.4, 159.2, 204.9.

Ester from 8d: To a solution of (carbethoxyethylidene)triphenylphosphorane (1.13 g, 3.11 mmol) in THF (10 ml) was added a solution of **8d** (585 mg, 1.6 mmol) in THF (10 ml) at room temperature. After the solution was heated for 12h at reflux, the solution was diluted with hexane. After the reaction mixture was filtered through Celite, the filtrate was evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give the ester (637 mg,

89%, *E*/*Z* = >95/5) as a colorless oil. ^{1}H NMR δ 0.87 (t, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H), 1.17-1.47 (m, 22H), 1.85 (d, *J* = 1.5 Hz, 3H), 2.69-2.84 (m, 1H), 3.17 (dd, *J* = 3.2, 7.8 Hz, 1H), 3.80 (s, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.49 (d, *J* = 10.6 Hz, 1H), 4.53 (d, *J* = 10.6 Hz, 1H), 6.61 (dq, *J* = 1.5, 10.5 Hz, 1H), 6.85-6.89 (m, 2H), 7.26-7.30 (m, 2H); ^{13}C NMR δ 12.5, 14.1, 14.2, 14.3, 16.4, 22.7, 27.5, 29.3, 29.6, 29.7, 29.9, 31.9, 34.7, 36.6, 37.0, 55.2, 60.5, 75.0, 86.4, 113.7, 126.5, 129.3, 131.0, 145.0, 159.1, 168.3.

Ester from 8a: ^{1}H NMR δ 0.86-0.90 (m, 6H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.14-1.64 (m, 22H), 1.84 (d, *J* = 1.2 Hz, 3H), 2.76-2.87 (m, 1H), 3.09-3.14 (m, 1H), 3.79 (s, 3H), 4.14-4.23 (m, 2H), 4.47 (d, *J* = 10.9 Hz, 1H), 4.52 (d, *J* = 10.9 Hz, 1H), 6.83-6.90 (m, 3H), 7.25 (*J* = 8.6 Hz, 2H); ^{13}C NMR δ 12.5, 14.0, 14.3, 16.2, 17.6, 22.6, 27.3, 29.3, 29.6, 30.0, 31.9, 32.0, 36.0, 36.1, 55.1, 60.3, 74.2, 87.4, 113.6, 126.7, 129.1, 131.1, 144.7, 159.0, 168.3.

Ester from 8b: $[\alpha]^{24}_{D}$ –10.8 (c 1.0, EtOH); IR (neat) 2923, 1713 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 1.17-1.44 (m, 21H), 1.60-1.70 (m, 1H), 1.83 (d, *J* = 1.2 Hz, 3H), 2.74-2.88 (m, 1H), 3.16 (dd, *J* = 3.2, 7.8 Hz, 1H), 3.79 (s, 3H), 4.19 (q, *J* = 7.1 Hz, 2H), 4.46 (s, 2H), 6.80-6.90 (m, 3H), 7.20-7.30 (m, 2H); ^{13}C NMR δ 12.6, 14.1, 14.3, 14.5, 17.3, 22.7, 27.3, 29.3, 29.6, 29.7, 29.9, 31.9, 34.1, 35.9, 36.5, 55.2, 60.3, 74.4, 86.5, 113.6, 127.0, 129.2, 131.2, 145.2, 159.0, 168.4; MS (EI+) m/z 460; Anal. Calcd for $C_{35}H_{58}O_4$: C, 75.61; H, 10.50. Found: C, 75.34; H, 10.65.

Ester from 8c: ^{1}H NMR δ 0.86 (t, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.23-1.61 (m, 22H), 1.83 (d, *J* = 1.2 Hz, 3H), 2.74-2.81 (m, 1H), 3.08 (dd, *J* = 4.8, 6.8 Hz, 1H), 3.78 (s, 3H), 4.14-4.21 (m, 2H), 4.45 (d, *J* = 10.5 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 6.61 (dd, *J* = 1.4,10.4 Hz, 1H), 6.6 (d, *J* = 9.7 Hz, 2H), 7.27

(*J* = 9.7 Hz, 2H); ^{13}C NMR δ 12.5, 14.1, 14.3, 15.7, 17.0, 26.7, 27.4, 29.3, 29.5, 29.7, 30.0, 31.5, 31.9, 36.3, 36.4, 55.3, 60.5, 74.8, 87.4, 113.7, 126.2, 129.2, 131.9, 145.4, 159.1, 168.3.

Enol from 8d: To a solution of the ester (565 mg, 1.23 mmol) in dichloromethane (15 ml) was added diisobutylaluminum hydride (3.8 ml of a 1.0 M solution in hexane, 3.8 mmol) at –78 °C. After stirring for 15 min at –78 °C, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were 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 the alcohol (494 mg, 96%) as a colorless oil. ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.20-1.50 (m, 19H), 1.60 (brs, 1H), 1.67 (d, *J* = 1.0 Hz, 3H), 2.60-2.75 (m, 1H), 3.08 (dd, *J* = 3.1, 8.1 Hz, 1H), 3.80 (s, 3H), 3.99 (s, 2H), 4.49 (d, *J* = 10.9 Hz, 1H), 4.53 (d, *J* = 10.9 Hz, 1H), 5.24 (dd, *J* = 1.0,10.1 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.28 (*J* = 8.7 Hz, 2H); ^{13}C NMR δ 13.8, 14.1, 14.3, 17.5, 22.7, 27.6, 29.3, 29.6, 29.7, 30.0, 31.9, 34.9, 35.9, 36.3, 55.3, 68.9, 74.9, 87.1, 113.7, 129.2, 129.8, 131.3, 133.6, 159.0.

Enol from 8a: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.11-1.47 (m, 19H), 1.66 (d, *J* = 1.3 Hz, 3H), 2.64-2.76 (m, 1H), 3.03 (dd, *J* = 4.6, 6.8 Hz, 1H), 3.80 (s, 3H), 3.97 (d, *J* = 0.9 Hz, 2H), 4.47 (d, *J* = 10.8 Hz, 1H), 4.53 (d, *J* = 10.8 Hz, 1H), 5.30 (dd, *J* = 1.3,9.9 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.28 (*J* = 8.8 Hz, 2H); ^{13}C NMR δ 13.8, 14.1, 16.7, 17.3, 22.7, 27.5, 29.3, 29.6, 29.7,

30.0, 31.4, 31.9, 35.2, 36.2, 55.3, 68.9, 74.8, 88.4, 113.7, 129.3, 130.2, 131.3, 133.2, 159.0.

Enol from 8b: $[\alpha]^{22}_{D}$ –19.6 (c 0.6, EtOH); IR (neat) 3403, 2922, 1613, 1513 cm^{-1}; ^{1}H NMR δ 0.90 (t, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 1.18-1.33 (m, 19H), 1.65 (s, 3H), 2.65-2.77 (m, 1H), 3.07 (t, *J* = 5.4 Hz, 1H), 3.79 (s, 3H), 3.96 (d, *J* =4.6 Hz, 2H), 4.48 (s, 1H), 5.43 (d, *J* = 9.7 Hz, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.24 (*J* = 8.5 Hz, 2H); ^{13}C NMR δ 13.9, 14.1, 14.8, 18,4, 22.7, 27.3, 29.3, 29.3, 29.6, 29.7, 30.0, 31.9, 34.2, 35.3, 36.0, 55.2, 69.1, 74.6, 87.3, 113.6, 129.1, 129.5, 131.6, 134.0, 158.9; HRMS (EI+) Calcd for $C_{27}H_{46}O_3$ (M+) 418.3447. Found 418.3419.

Enol from 8c: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.13-1.63 (m, 19H), 1.67 (d, *J* = 1.1 Hz, 3H), 2.65-2.75 (m, 1H), 3.03 (dd, *J* = 4.4,6.9 Hz, 1H), 3.80 (s, 3H), 3.98 (s, 2H), 4.48 (d, *J* = 10.7 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 5.30 (dd, *J* = 1.1, 9.8 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 7.28 (*J* = 8.5 Hz, 2H); ^{13}C NMR δ 14.1, 16.7, 17.3, 22.7, 27.5, 29.3, 29.7, 30.0, 31.4, 31.9, 35.2, 36.2, 55.3, 68.9, 74.9, 88.4, 113.7, 129.3, 130.2, 131.3, 133.2, 159.0.

Enal 9d: To a mixture of the alcohol (761 mg, 1.8 mmol), *N*-methyl molphorine *N*-oxide (316 mg, 2.7 mmol) and molecular sieves 4A (1.26 g) in dichloromethane (10 ml) were added tetrapropylammonium perruthenate (64 mg, 0.18 mmol) at room temperature. After stirring for 1h at the same temperature, the reaction mixture was filtered through Celite, and then the filtrate was washed with aqueous sodium sulfite, water, and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **9d** (680 mg, 90%)

as a colorless oil. ^{1}H NMR δ 0.88 (t, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.6 Hz, 3H), 1.20-1.50 (m, 19H), 1.76 (d, *J* = 1.2 Hz, 3H), 2.90-3.05 (m, 1H), 3.23 (dd, *J* = 3.6,7.6 Hz, 1H), 3.80 (s, 3H), 4.49 (d, *J* = 10.7 Hz, 1H), 4.58 (d, *J* = 10.7 Hz, 1H), 6.31 (dd, *J* = 1.2,10.2 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 7.27 (*J* = 8.5 Hz, 2H), 9.36 (s, 1H); ^{13}C NMR δ 9.3, 14.1, 14.4, 16.1, 22.7, 27.5, 29.3, 29.6, 29.9, 31.9, 34.6, 36.9, 37.2, 55.2, 75.0, 86.0, 113.8, 129.2, 130.8, 137.9, 157.4, 159.2, 195.4.

Enal 9a: ^{1}H NMR δ 0.83-0.90 (m, 6H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.15-1.66 (m, 19H), 1.74 (d, *J* = 1.3 Hz, 3H), 2.93-3.05 (m, 1H), 3.19 (dd, *J* = 3.4, 6.5 Hz, 1H), 3.81 (s, 3H), 4.47 (d, *J* = 10.7 Hz, 1H), 4.57 (d, *J* = 10.7 Hz, 1H), 6.85-6.91 (m, 3H), 7.27 (*J* = 8.6 Hz, 2H), 9.38 (s, 1H); ^{13}C NMR δ 9.3, 14.1, 15.9, 18.0, 22.7, 27.2, 29.3, 29.6, 29.7, 30.0, 31.9, 32.6, 36.0, 36.6, 55.2, 74.4, 87.0, 113.7, 129.3, 130.8, 138.0, 157.3, 159.2, 195.7.

Enal 9b: ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.20-1.45 (m, 18H), 1.60-1.68 (m, 1H), 1.74 (s, 3H), 2.92-3.05 (m, 1H), 3.22 (t, *J* = 5.2 Hz, 1H), 3.80 (s, 3H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 6.57 (d, *J* = 10.0 Hz, 1H), 6.84-6.90 (m, 2H), 7.20-7.30 (m, 2H), 9.38 (s, 1H); ^{13}C NMR δ 9.3, 14.1, 15.0, 17.6, 22.7, 27.3, 29.3, 29.6, 29.9, 31.9, 33.6, 36.5, 36.6, 55.2, 74.6, 86.6, 113.7, 129.2, 130.8, 138.3, 157.6, 159.1, 195.7.

Enal 9c: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.14-1.74 (m, 19H), 1.75 (d, *J* = 1.4 Hz, 3H), 2.92-3.04 (m, 1H), 3.15 (t, *J* = 5.1 Hz, 1H), 3.81 (s, 3H), 4.44 (d, *J* = 10.8 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 6.85-6.92 (m, 3H), 7.26 (*J* = 8.7 Hz, 2H), 9.34 (s, 1H); ^{13}C NMR δ 9.3, 14.1, 15.4, 16.9, 22.7, 27.4, 29.3, 29.6, 30.0, 31.7, 31.9, 36.5, 36.6, 55.3, 74.8, 87.0, 113.8, 129.3, 130.7, 137.6, 157.9, 159.2, 195.5.

Ester from 9d: To a solution of (carbethoxyethylidene)triphenylphosphorane (1.77 g, 4.89 mmol) in THF (4 ml) was added a solution of **9d** (680 mg, 1.63 mmol) in THF (8 ml) at room temperature. After the solution was heated for 12 h at reflux, the solution was diluted with hexane. After the reaction mixture was filtered through Celite, the filtrate was evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give the ester (676 mg, 83%, *E*/*Z* = >95/5) as a colorless oil. ^{1}H NMR δ 0.85-0.91 (m, 6H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.19-1.66 (m, 22H), 1.84 (brs, 3H), 2.00 (d, *J* = 1.3 Hz, 3H), 2.69-2.83 (m, 1H), 3.14 (dd, *J* = 2.8,8.3 Hz, 1H), 3.79 (s, 3H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.52 (s, 2H), 5.42 (brd, *J* = 9.9 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.10 (brs, 1H), 7.28 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 14.0, 14.1, 14.3, 16.4, 17.3, 22.7, 27.6, 29.3, 29.6, 29.9, 31.9, 35.0, 36.6, 36.8, 55.2, 60.6, 75.0, 86.9, 113.7, 125.5, 129.2, 131.0, 131.2, 139.5, 142.9, 159.1, 169.1.

Ester from 9a: ^{1}H NMR δ 0.85-0.89 (m, 6H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.14-1.58 (m, 22H), 1.85 (s, 3H), 2.00 (s, 3H), 2.78-2.81 (m, 1H), 3.05-3.10 (m, 1H), 3.80 (s, 3H), 4.15-4.23 (m, 2H), 4.50 (s, 2H), 5.77 (d, *J* = 9.9 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.24 (s, 1H), 7.26 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 13.9, 14.1, 14.3, 16.30, 16.31, 18.5, 22.7, 27.3, 29.3, 29.6, 29.65, 29.67, 30.0, 31.9, 35.6, 36.5, 55.2, 60.5, 74.4, 87.9, 113.6, 124.9, 129.0, 131.1, 131.3, 139.6, 143.3, 158.9, 169.3.

Ester from 9b: $[\alpha]^{26}_{D}$ –8.1 (c 0.45, EtOH); IR (neat) 2926, 1714, 1615 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.20-1.32 (m, 22H), 1.84 (d, *J* = 0.9 Hz, 3H), 1.99 (d, *J* = 0.7 Hz, 3H), 2.73-2.85 (m, 1H), 3.11 (t, *J* = 5.1 Hz, 1H), 3.79 (s, 3H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.48 (s, 2H), 5.70 (brd, *J* = 9.9 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.13 (brs, 1H), 7.23 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 13.96, 14.06, 14.3, 14.8, 16.5, 18.2, 22.7, 27.3, 29.3, 29.6, 29.7, 29.9, 31.9, 34.1, 36.0, 36.3, 55.2, 60.5, 74.8, 87.1, 113.6, 125.1, 129.0, 131.4, 140.0,

143.3, 159.0, 169.2; MS (EI+) m/z 500; Anal. Calcd for $C_{33}H_{52}O_4$: C, 76.75; H, 10.47. Found: C, 76.48; H, 10.27.

Ester from 9c: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 3H), 1.14-1.63 (m, 22H), 1.85 (s, 3H), 1.99 (s, 3H), 2.72-2.82 (m, 1H), 3.07 (dd, *J* = 4.3, 7.0 Hz, 1H), 3.80 (s, 3H), 4.21 (q, *J* = 7.0 Hz, 2H), 4.49 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 5.49 (d, *J* = 9.1 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.10 (s, 1H), 7.26 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 14.0, 14.1, 14.3, 16.4, 16.7, 17.4, 22.7, 27.5, 29.4, 29.6, 30.0, 31.2, 31.9, 36.1, 36.4, 55.3, 60.6, 74.9, 88.3, 113.7, 125.4, 129.2, 130.7, 131.1, 140.1, 143.0, 159.1, 169.2.

Alcohol from 9d: To a solution of the ester (710 mg, 1.42 mmol) in dichloromethane (8 ml) was added diisobutylaluminum hydride (4.3 ml of a 1.0 M solution in hexane, 4.3 mmol) at –78 °C. After stirring for 15 min at –78 °C, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were 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 the alcohol (566 mg, 87%) as a colorless oil. ^{1}H NMR δ 0.87 (t, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.20-1.55 (m, 19H), 1.60 (brs, 1H), 1.74 (d, *J* = 1.0 Hz, 3H), 1.79 (d, *J* = 0.7 Hz, 3H), 2.65-2.75 (m, 1H), 3.10 (dd, *J* = 3.0, 8.3 Hz, 1H), 3.79 (s, 3H), 4.03 (s, 2H), 4.52 (s, 2H), 5.12 (brd, *J* = 10.0 Hz, 1H), 5.85 (brs, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.27 (*J* = 8.6 Hz, 2H); ^{13}C NMR δ 14.07, 14.10, 15.3, 17.0, 17.7, 22.7, 27.6, 29.3, 29.6, 29.7,

30.0, 31.9, 35.1, 36.4, 36.6, 55.2, 69.4, 75.0, 87.3, 113.7, 129.2, 129.5, 131.0, 131.3, 134.2, 159.0.

Alcohol from 9a: ^{1}H NMR δ 0.86 (t, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.5 Hz, 3H), 1.04 (d, *J* = 6.7 Hz, 3H), 1.14-1.43 (m, 19H), 1.60 (brs, 1H), 1.76 (d, *J* = 1.1 Hz, 3H), 1.81 (d, *J* = 1.1 Hz, 3H), 2.68-2.81 (m, 1H), 3.04 (dd, *J* = 4.0, 6.4 Hz, 1H), 3.79 (s, 3H), 4.02 (s, 2H), 4.50 (s, 2H), 5.46 (brd, *J* = 9.7 Hz, 1H), 5.88 (brs, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.27 (*J* = 8.6 Hz, 2H); ^{13}C NMR δ 10.6, 14.1, 16.0, 16.2, 18.4, 22.7, 27.3, 29.3, 29.63, 29.64, 29.7, 30.0, 31.9, 32.3, 35.7, 36.5, 55.2, 74.4, 87.7, 113.7, 129.1, 131.1, 132.0, 135.0, 144.5, 155.7, 159.1, 196.3.

Alcohol from 9b: $[\alpha]^{27}_{D}$ –2.5 (c 0.3, EtOH); IR (neat) 3395, 2925, 1614 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.18-1.60 (m, 19H), 1.75 (s, 3H), 1.81(s, 3H), 2.70-2.82 (m, 1H), 3.08 (dd, *J* = 5.2, 9.7 Hz, 1H), 3.79 (s, 3H), 4.02 (s, 3H), 5.39 (d, *J* = 9.7 Hz, 1H), 5.88 (s, 1H), 6.85 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR δ 14.0, 14.8, 15.3, 17.0, 18.5, 22.7, 27.3, 29.3, 29.62, 29.63, 29.7, 29.9, 31.9, 34.1, 35.8, 36.2, 55.2, 69.6, 74.4, 87.3, 113.5, 129.0, 129.8, 131.3, 131.6, 133.9, 134.0, 158.9; MS (EI+) m/z 457; Anal. Calcd for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.48; H, 10.75.

Alcohol from 9c: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.13-1.69 (m, 19H), 1.75 (s, 3H), 1.80 (s, 3H), 2.71-2.77 (m, 1H), 3.05 (dd, *J* = 4.3, 7.2 Hz, 1H), 3.79 (s, 3H), 4.03 (s, 2H), 4.49 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.86 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.27 (*J* = 8.7 Hz, 2H); ^{13}C NMR δ 14.1, 15.3, 16.9, 17.0, 17.5, 22.7, 27.5, 29.3, 29.6, 29.7, 30.0, 31.1, 31.9, 35.9, 36.3, 55.2, 69.5, 74.9, 88.7, 113.7, 128.3, 129.0, 129.2, 129.5, 130.7, 131.3, 134.2, 134.6, 159.0.

Dienal 10d: To a mixture of the alcohol (560 mg, 1.22 mmol), *N*-methyl molphorine *N*-oxide (214 mg, 1.83 mmol) and molecular sieves 4A (850 mg) in dichloromethane (9 ml) were added tetrapropylammonium perruthenate (560 mg, 0.12 mmol) at room temperature. After stirring for 1h at the same temperature, the reaction mixture was filtered through Celite, and then the filtrate was washed with aqueous sodium sulfite, water, and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 15/1) to give **10d** (518 mg, 93%) as a colorless oil. ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.20-1.48 (m, 18H), 1.55-1.65 (m, 1H), 1.95 (d, *J* = 0.9 Hz, 3H), 1.98 (d, *J* = 1.1 Hz, 3H), 2.75-2.85 (m, 1H), 3.17 (dd, *J* = 3.3, 7.9 Hz, 1H), 3.79 (s, 3H), 4.50 (d, *J* = 10.6 Hz, 1H), 4.56 (d, *J* = 10.6 Hz, 1H), 5.68 (brd, *J* = 10.1 Hz, 1H), 6.69 (brs, 1H), 6.87 (d, *J* = 10.7 Hz, 2H), 7.27 (*J* = 10.7 Hz, 2H), 9.39 (s, 1H); ^{13}C NMR δ 10.7, 14.1, 14.3, 16.1, 16.9, 22.6, 27.5, 29.3, 29.58, 29.60, 29.63, 29.9, 31.9, 34.8, 36.7, 36.9, 55.2, 75.0, 86.6, 113.7, 129.2, 131.0, 131.7, 135.5, 144.2, 155.0, 159.1, 196.0.

Dienal 10a: ^{1}H NMR δ 0.85-0.91 (m, 6H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.20-1.60 (m, 19H), 1.95 (d, *J* = 0.6 Hz, 3H), 1.97 (d, *J* = 1.1 Hz, 3H), 2.77-2.89 (m, 1H), 3.12 (dd, *J* = 3.9, 6.3 Hz, 1H), 3.80 (s, 3H), 4.46 (d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 6.03 (brd, *J* = 9.7 Hz, 1H), 6.73 (brs, 1H), 6.84-6.89 (m, 2H), 7.23-7.29 (m, 2H), 9.36 (s, 1H); ^{13}C NMR δ 10.6, 14.1, 16.0, 16.2, 18.4, 22.7, 27.3, 29.3, 29.63, 29.64, 29.7, 30.0, 31.9, 32.3, 35.7, 36.5, 55.2, 74.4, 87.7, 113.7, 129.1, 131.1, 132.0, 135.5, 144.5, 155.7, 159.1, 196.3.

Dienal 10b: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.20-1.45 (m, 18H), 1.60-1.68 (m, 1H), 1.94 (d, *J* = 0.7 Hz, 3H), 1.96 (d,

J = 0.8 Hz, 3H), 2.78-2.90 (m, 1H), 3.15 (dd, *J* = 5.1, 5.4 Hz, 1H), 3.79 (s, 3H), 4.45 (d, *J* = 10.7 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H), 5.95 (brd, *J* = 10.0 Hz, 1H), 6.73 (brs, 1H), 6.85 (d, *J* = 9.8 Hz, 2H), 7.22 (d, *J* = 9.8 Hz, 2H), 9.38 (s, 1H); ^{13}C NMR δ 10.6, 14.1,14.8, 16.1, 18.1, 22.7, 27.3, 29.3, 29.6, 29.7, 29.9, 31.9, 33.9, 36.1, 36.3, 55.2, 74.6, 87.0, 113.6, 129.1, 131.2, 132.4, 135.1, 144.8, 155.7, 159.0, 196.3.

Dienal 10c: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.11-1.66 (m, 19H), 1.95 (s, 3H), 1.98 (s, 3H), 2.80-2.86 (m, 1H), 3.11 (dd, *J* = 4.6, 6.6 Hz, 1H), 3.79 (s, 3H), 4.47 (d, *J* = 10.8 Hz, 1H), 4.56 (d, *J* = 10.8 Hz, 1H), 5.74 (d, *J* = 10.0 Hz, 1H), 6.68 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 9.38 (s, 1H); ^{13}C NMR δ 10.6, 14.0, 15.2, 16.0, 16.2, 17.1, 22.6, 27.4, 29.3, 29.59, 29.62, 29.9, 31.4, 31.9, 36.1, 36.4, 55.2, 74.8, 87.8, 113.7, 129.2, 130.9, 131.4, 135.5, 144.7, 155.0, 159.1, 196.0.

Thioester 11d: To a mixture of tin(II) trifluoromethanesulfonate (1.32 g, 3.16 mmol) and (*S*)-1-methyl-2-[(*N*-1-naphthylamino)methyl]pyrrolidine (911 mg, 3.79 mmol) in dichloromethane (8 ml) was added a solution of dibutyltin diacetate (1.24 g, 3.52 mmol) in dichloromethane (4 ml) at room temperature. After the solution was cooled to –78 °C, a solution of silyl enol ether **3** (601 mg, 3.16 mmol) in dichloromethane (3 ml) was added followed by a solution of **10d** (481 mg, 1.05 mmol) in dichloromethane (3 ml). After stirring for 16 h at –78 °C, the reaction was quenched with an aqueous sodium hydrogen carbonate solution, and the aqueous layer was extracted with dichloromethane. The extract was washed with water and brine, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) to give **11d** (545 mg, 90%) as a colorless oil: ^{1}H NMR δ 0.87 (t, *J* = 7.0

Hz, 3H), 0.89 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.17-1.48 (m, 25H), 1.72 (d, *J* = 1.1 Hz, 3H), 1.74 (d, *J* = 1.1 Hz, 3H), 2.33 (s, 1H), 2.62-2.76 (m, 1H), 2.77-2.95 (m, 3H), 3.10 (dd, *J* = 2.9, 8.3 Hz, 1H), 3.80 (s, 3H), 4.31 (d, *J* = 5.0 Hz, 1H), 4.52 (s, 2H), 5.09 (dq, *J* = 1.1, 10.1 Hz, 1H), 5.92 (q, *J* = 1.1 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 7.28 (*J* = 8.8 Hz, 2H); ^{13}C NMR δ 11.9, 14.10, 14.11, 14.4, 14.6, 17.0, 17.7, 22.7, 23.2, 27.6, 29.3, 29.6, 29.67, 29.68, 30.0, 31.9, 35.1, 36.4, 36.6, 51.4, 55.3, 75.0, 77.2, 87.3, 113.7, 129.2, 130.87, 130.94, 131.4, 133.0, 134.1, 159.0, 203.4.

Thioester 11a: ^{1}H NMR δ 0.84-0.90 (m, 6H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.15-1.65 (m, 25H), 1.72 (s, 3H), 1.75 (s, 3H), 2.27 (brs, 1H), 2.68-2.91 (m, 4H), 3.01-3.05 (m, 1H), 3.80 (s, 3H), 4.29 (d, *J* = 5.1 Hz, 1H), 4.50 (s, 2H), 5.42 (d, *J* = 9.8 Hz, 1H), 5.93 (s, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 7.25 (*J* = 8.8 Hz, 2H); ^{13}C NMR δ 11.9, 14.1, 14.3, 14.6, 16.4, 17.0, 18.8, 22.7, 23.2, 27.3, 29.6, 29.68, 29.71, 30.0, 31.9, 35.5, 36.4, 51.4, 55.2, 74.4, 77.5, 88.2, 113.6, 129.0, 130.9, 131.2, 131.6, 132.8, 133.4, 158.9, 203.3.

Thioester 11b: $[\alpha]^{24}_{D}$ +55.3 (c 0.2, EtOH); IR (neat) 3502, 2925, 1681 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 1.18-1.62 (m, 25H), 1.72 (s, 3H), 1.75 (s, 3H), 2.30 (d, *J* = 3.1 Hz, 1H), 2.70-2.90 4H), 3.07 (t, *J* = 5.2 Hz, 1H), 3.79 (s, 3H), 4.29-4.31 (m, 1H), 4.44 (d, *J* = 10.7 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H), 5.37 (d, *J* = 9.5 Hz, 1H), 5.94 (s, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.24 (*J* = 8.6 Hz, 2H); ^{13}C NMR δ 11.9, 14.1, 14.4, 14.6, 14.8, 15.2, 17.1, 18.4, 22.7, 27.3, 29.3, 29.6, 29.7, 30.0, 31.9, 34.2, 35.8, 36.2, 51.4, 55.2, 65.8, 74.4, 87.3, 113.7, 128.9, 131.20, 131.23, 132.8, 134.0, 158.9, 203.3; MS (EI+) m/z 574; Anal. Calcd for $C_{35}H_{58}O_4S$: C, 73.12; H, 10.17. Found: C, 72.85; H, 10.03.

Thioester 11c: ^{1}H NMR δ 0.88 (t, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.12-1.69 (m, 25H), 1.72 (s, 3H), 1.74 (s, 3H), 2.39 (brs, 1H), 2,82-2.83 (m, 1H), 2.84-2.88 (m, 3H), 3.03 (dd, *J* = 4.0, 7.2 Hz, 1H), 3.80 (s, 3H), 4.30 (d,

J = 5.1 Hz, 1H), 4.49 (d, *J* = 10.7 Hz, 1H), 4.53 (d, *J* = 10.7 Hz, 1H), 5.16 (d, *J* = 9.7 Hz, 1H), 5.92 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.27 (*J* = 8.6 Hz, 2H); ^{13}C NMR δ 11.9, 14.1, 14.2, 14.3, 14.6, 17.0, 17.5, 22.7, 23.2, 27.6, 29.3, 29.6, 29.7, 30.0, 31.1, 31.9, 36.0, 36.3, 51.3, 55.2, 74.9, 77.2, 80.7, 113.7, 129.2, 130.6, 130.9, 131.3, 133.0, 134.5, 159.0, 203.4.

TES Ether from 11d: To a mixture of **11d** (545 mg, 0.95 mmol) and 2,6-lutidine (610 mg, 5.69 mmol) in dichloromethane (4.5 ml) was added a solution of triethylsilyl trifluoromethanesulfonate (753 mg, 2.85 mmol) in dichloromethane (1.5 ml) at 0 °C. After stirring for 30 min at room temperature, the reaction was quenched with an aqueous sodium hydrogen carbonate solution, and the aqueous layer was extracted with dichloromethane. The extract was washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/benzene = 1/1) to give the TES ether (602 mg, 92%) as a colorless oil. ^{1}H NMR δ 0.58 (q, *J* = 7.9 Hz, 6H), 0.884 (t, *J* = 7.0 Hz, 3H), 0.885 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 7.9 Hz, 9H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.22-1.48 (m, 19H), 1.67 (s, 3H), 1.74 (s, 3H), 2.60-2.80 (m, 2H), 2.83 (q, *J* = 7.6 Hz, 2H), 3.09 (dd, *J* = 2.9, 8.3 Hz, 1H), 3.80 (s, 3H), 4.15 (d, *J* = 7.8 Hz, 1H), 4.52 (s, 2H), 5.06 (dq, *J* = 9.8 Hz, 1H), 5.72 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.28 (*J* = 8.7 Hz, 2H); ^{13}C NMR δ 4.8, 6.8, 13.0, 13.7, 14.1, 14.7, 16.8, 17.7, 22.7, 23.0, 27.6, 29.4, 29.66, 29.67, 29.68, 29.70, 29.9, 31.9, 35.1, 36.4, 36.6, 53.5, 55.2, 75.0, 80.3, 87.3, 113.7, 129.2, 130.9, 131.38, 131.41, 133.7, 134.7, 159.0, 201.8.

TES Ether from 11a: ^{1}H NMR δ 0.57 (q, *J* = 7.9 Hz, 6H), 0.80-1.05 (m, 18H), 1.10-1.60 (m, 25H), 1.67 (d, *J* = 1.1 Hz, 3H), 1.74 (d, *J* = 1.1 Hz, 3H), 2.30-2.80 (m, 4H),

2.98-3.03 (m, 1H), 3.79 (s, 3H), 4.13 (d, *J* = 7.9 Hz, 1H), 4.48 (s, 2H), 5.37 (brd, *J* = 9.7 Hz, 1H), 5.74 (brs, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.24 (*J* = 8.6 Hz, 2H); ^{13}C NMR δ 4.8, 6.8, 13.0, 13.7, 14.1, 14.7, 16.5, 16.8, 18.7, 22.7, 23.1, 27.4, 29.4, 29.66, 29.70, 29.73, 30.0, 32.0, 35.4, 36.2, 53.5, 55.2, 74.2, 80.5, 88.2, 113.5, 128.8, 130.9, 131.7, 133.1, 133.3, 134.3, 158.8, 201.9.

TES Ether from 11b: $[\alpha]^{26}_{D}$ +28.9 (c 0.22, EtOH); IR (neat) 2926, 1683, 1614, 1248 cm^{-1}; ^{1}H NMR δ 0.57 (q, *J* = 7.9 Hz, 6H), 0.85-1.00 (m, 18H), 1.13-1.45 (m, 25H), 1.69 (d, *J* = 1.1 Hz, 3H), 1.76 (d, *J* = 1.1 Hz, 3H), 2.65-2.88 (m, 4H), 3.05 (dd, *J* = 5.0, 5.5 Hz, 1H), 3.79 (s, 3H), 4.16 (d, *J* = 7.9 Hz, 1H), 4.42 (d, *J* = 10.7 Hz, 1H), 4.50 (d, *J* = 10.7 Hz, 1H), 5.33 (brd, *J* = 9.8 Hz, 1H), 5.78 (brs, 1H), 6.82-6.88 (m, 2H), 7.20-7.26 (m, 2H); ^{13}C NMR δ 4.8, 6.8, 13.0, 13.7, 14.1, 14.7, 16.9, 18.4, 22.7, 23.0, 27.4, 29.4, 29.6, 29.7, 30.0, 31.9, 34.2, 35.8, 36.0, 53.5, 55.2, 74.3, 80.5, 87.1, 113.5, 128.9, 131.3, 131.7, 133.9, 134.4, 158.8, 201.8; FABMS (M^{+}+Na) 712; Anal. **Calcd** for $C_{41}H_{72}O_4SSi$: C, 71.45; H, 10.53. Found: C, 71.26; H, 10.75.

TES Ether from 11c: ^{1}H NMR δ 0.57 (q, *J* = 7.5 Hz, 6H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.90-0.96 (m, 15H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.17-1.61 (m, 22H), 1.69 (s, 3H), 1.74 (s, 3H), 2.69-2.85 (m, 4H), 3.02 (dd, *J* = 4.2, 7.2 Hz, 1H), 3.80 (s, 3H), 4.15 (d, *J* = 8.1 Hz, 1H), 4.50 (s, 2H), 5.13 (d, *J* = 9.9 Hz, 1H), 5.75 (s, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 4.8, 6.8, 13.0, 13.7, 14.1, 14.7, 16.8, 17.0, 17.4, 22.7, 23.0, 27.6, 29.4, 29.6, 29.7, 30.0, 31.2, 31.9, 36.0, 36.3, 53.5, 55.3, 74.9, 80.4, 88.8, 113.7, 129.2, 130.7, 131.4, 134.2, 134.7, 159.0, 201.8.

Aldehyde 12d: To a solution of the TES ether (98.1 mg, 0.14 mmol) in dichloromethane (2 ml) was added diisobutylaluminum hydride (0.3 ml of a 0.95 M

solution in hexane, 0.28 mmol) at –78 °C. After stirring for 5 min at –78 °C, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 25/1) to give **12d** (86.0 mg, 96%) as a colorless oil. $[\alpha]^{27}_{D}$ –0.7 (c 1.3, EtOH); ^{1}H NMR δ 0.59 (q, *J* = 7.9 Hz, 6H), 0.85-0.97 (m, 15H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.20-1.60 (m, 19H), 1.70 (s, 3H), 1.71 (s, 3H), 2.48-2.57 (m, 1H), 2.69-2.76 (m, 1H), 3.10 (dd, *J* = 2.9, 8.2 Hz, 1H), 3.80 (s, 3H), 4.31 (d, *J* = 5.6 Hz, 1H), 4.52 (s, 2H), 5.08 (d, *J* = 9.9 Hz, 1H), 5.85 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 9.69 (d, *J* = 1.9 Hz, 1H); ^{13}C NMR δ 4.8, 6.8, 8.9, 14.08, 14.12, 14.14, 16.9, 17.6, 22.7, 27.6, 29.3, 29.6, 29.7, 29.9, 31.9, 35.0, 36.4, 36.6, 51.0, 55.2, 75.0, 77.9, 87.2, 113.7, 129.1, 130.7, 130.9, 131.4, 134.0, 134.3, 159.0, 204.5.

Aldehyde 12a: ^{1}H NMR δ 0.57 (q, *J* = 7.9 Hz, 6H), 0.83-1.06 (m, 18H), 1.11-1.66 (m, 22H), 1.69-1.76 (m, 9H), 2.40-2.58 (m, 1H), 2.60-2.80 (m, 1H), 3.03 (dd, *J* = 4.9, 5.5 Hz, 1H), 3.79 (s, 3H), 4.29 (d, *J* = 5.6 Hz, 1H), 4.48 (s, 2H), 5.39 (d, *J* = 9.7 Hz, 1H), 5.86 (brs, 1H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H), 9.68 (d, *J* = 1.7 Hz, 1H); ^{13}C NMR δ 4.8, 6.8, 8.9, 14.1, 14.2, 16.5, 17.0, 18.7, 22.7, 27.4, 29.4, 29.6, 29.69, 29.72, 30.0, 31.9, 35.5, 36.2, 50.9, 55.2, 74.3, 78.1, 88.2, 113.6, 128.9, 130.8, 131.2, 131.6, 133.5, 134.0, 158.9, 204.7.

Aldehyde 12b: $[\alpha]^{26}_{D}$ –13.1 (c 1.0, EtOH); ^{1}H NMR δ 0.58 (q, *J* = 7.8 Hz, 6H), 0.84-0.98 (m, 15H), 1.02-1.08 (m, 6H), 1.19-1.60 (m, 19H), 1.69-1.74 (m, 6H), 2.47-2.58

(m, 1H), 2.62-2.76 (m, 1H), 3.07-3.13 (m, 1H), 3.79 (s, 3H), 4.31 (d, *J* = 5.1 Hz, 1H), 4.52 (s, 2H), 5.07 (brd, *J* = 9.7 Hz, 1H), 5.85 (brs, 1H), 6.86 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 9.86 (s, 1H); ^{13}C NMR δ 4.8, 6.8, 8.9, 14.08, 14.14, 17.0, 17.6, 22.7, 27.6, 29.3, 29.6, 29.7, 29.9, 31.9, 35.0, 36.4, 36.6, 51.0, 55.2, 75.0, 77.9, 87.2, 113.7, 129.1, 130.7, 130.9, 131.4, 134.0, 134.3, 159.0, 204.5.

Aldehyde 12c: ^{1}H NMR δ 0.58 (q, *J* = 7.6 Hz, 6H), 0.88 (t, *J* =6.8 Hz, 3H), 0.90-1.04 (m, 15H), 1.11-1.60 (m, 19H), 1.70 (s, 3H), 1.72 (s, 3H), 2.49-2.59 (m, 1H), 2.66-2.79 (m, 1H), 3.04 (dd, *J* = 4.4, 7.0 Hz, 1H), 3.80 (s, 3H), 4.31 (d, *J* = 5.7 Hz, 1H), 4.50 (s, 2H), 5.15 (d, *J* = 9.9 Hz, 1H), 5.87 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 9.69 (s, 1H); ^{13}C NMR δ 4.8, 6.8, 9.0, 14.0, 14.1, 16.90, 16.93, 17.2, 22.7, 27.6, 29.4, 29.66, 29.68, 29.71, 30.0, 31.3, 31.9, 35.9, 36.3, 50.9, 55.2, 74.9, 77.9, 88.6, 113.7, 129.2, 130.4, 131.1, 131.3, 134.35, 134.39, 159.0, 204.6.

Ester from 12d: To a solution of (carbethoxyethylidene)triphenylphosphorane (150 mg, 0.41 mmol) in THF (1 ml) was added a solution of **12d** (86.0 mg, 0.14 mmol) in THF (2 ml) at room temperature. After the solution was heated for 12 h at reflux, the solution was diluted with hexane. After the reaction mixture was filtered through Celite, the filtrate was evaporated. The residue was purified by column chromatography on silica gel (benzene) to give the ester (84.0 mg, 86%, *E*/*Z* = >95/5) as a colorless oil. $[\alpha]^{25}_{D}$ +21.0 (c 1.5, EtOH); ^{1}H NMR δ 0.59 (q, *J* = 7.9 Hz, 6H), 0.86-0.93 (m, 6H), 0.95 (d, *J* = 7.9 Hz, 9H), 1.02-1.06 (m, 6H), 1.24-1.45 (m, 22H), 1.62 (d, *J* = 0.7 Hz, 3H), 1.66 (d, *J* = 1.0 Hz, 3H), 1.83 (d, *J* = 1.5 Hz, 3H), 2.60-2.71 (m, 2H), 3.08 (dd, *J* = 2.9, 8.1 Hz, 1H), 3.80 (s, 3H), 3.81 (d, *J* = 9.8 Hz, 1H), 4.13-4.25 (m, 2H), 4.52 (s, 2H), 4.99 (dq, *J* = 0.7, 9.8 Hz, 1H), 5.75 (q, *J* = 1.0 Hz, 1H), 6.55 (dq, *J* = 1.5, 10.2 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H) 7.27 (d, *J* = 8.7 Hz, 2H); ^{13}C

NMR δ 4.8, 6.9, 12.4, 13.4, 14.1, 14.2, 14.3, 15.7, 16.9, 17.7, 22.7, 27.6, 29.3, 29.6, 29.7, 29.9, 31.9, 35.0, 36.3, 36.6, 38.1, 55.2, 60.3, 74.9, 81.9, 87.3, 113.7, 129.2, 130.5, 130.8, 131.4, 133.2, 135.8, 144.7, 159.0, 168.2.

Ester from 12a: ^{1}H NMR δ 0.59 (q, *J* = 7.8 Hz, 6H), 0.82-1.07 (m, 21H), 1.12-1.60 (m, 22H), 1.64 (s, 3H), 1.67 (s, 3H), 1.81 (s, 3H), 2.60-2.80 (m, 2H), 3.03 (dd, *J* = 5.0, 5.5 Hz, 1H), 3.78-3.81 (m, 4H), 4.05- 4.21 (m, 2H), 4.47-4.53 (m, 2H), 5.34 (d, *J* = 9.8 Hz, 1H), 5.79 (s, 1H), 6.55 (d, *J* = 10.3 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 4.8, 6.8, 12.4, 13.5, 14.1, 14.2, 15.7, 16.5, 17.0, 18.6, 22.7, 27.4, 29.3, 29.6, 29.69, 29.72, 30.0, 31.9, 35.4, 36.1, 36.6, 38.1, 55.2, 60.3, 74.2, 82.1, 88.2, 113.5, 126.3, 128.8, 130.8, 130.9, 131.7, 132.9, 135.3, 144.8, 158.8, 168.3.

Ester from 12b (22): $[\alpha]^{28}_{D}$ –8.6 (c 1.0, CH_2Cl_2); IR (neat) 2925, 1709, 1246 cm^{-1}; ^{1}H NMR δ 0.59 (q, *J* = 7.8 Hz, 6H), 0.85-1.00 (m, 18H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.15-1.38 (m, 22H), 1.65 (s, 3H), 1.68 (s, 3H), 1.82 (d, *J* = 1.3 Hz, 3H), 2.60-2.80 (m, 2H), 3.06 (dd, *J* = 4.8, 5.7 Hz, 1H), 3.77-3.83 (m, 4H), 4.05-4.18 (m, 2H), 4.41 (d, *J* = 10.7 Hz, 1H), 4.50 (d, *J* = 10.7 Hz, 1H), 5.28 (d, *J* = 9.6 Hz, 1H), 5.80 (s, 1H), 6.56 (dq, *J* = 1.3, 10.3 Hz, 1H), 6.81-6.89 (m, 2H) 7.19-7.25 (m, 2H); ^{13}C NMR δ 4.8, 6.9, 12.4, 13.5, 14.1, 14.2, 14.6, 15.7, 17.0, 18.3, 22.7, 27.4, 29.3, 29.6, 29.7, 30.0, 31.9, 34.3, 35.8, 36.0, 38.2, 55.2, 60.2, 74.2, 82.0, 87.1, 113.5, 126.4, 128.9, 130.9, 131.4, 131.7, 133.5, 135.4, 144.8, 158.8, 168.2; MS (EI+) m/z 685; Anal. Calcd for $C_{44}H_{76}O_3SSi$: C, 74.10; H, 10.74. Found: C, 74.10; H, 10.50.

Ester from 12c: ^{1}H NMR δ 0.59 (q, *J* = 7.9 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.92-1.05 (m, 18H), 1.24-1.54 (m, 22H), 1.63 (s, 3H), 1.68 (s, 3H), 1.82 (d, *J* = 1.4 Hz, 3H), 2.60-2.77 (m, 2H), 3.02 (dd, *J* = 4.4, 7.0 Hz, 1H), 3.78-3.81 (m, 4H), 4.09-4.20 (m, 2H), 4.50 (s, 2H), 5.10 (d, *J* = 9.9 Hz, 1H), 5.79 (s, 1H), 6.56 (dq, *J* = 1.4, 10.2 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 4.9, 6.9, 12.4,

13.5, 14.1, 14.3, 15.7, 16.9, 17.4, 22.7, 27.6, 29.4, 29.66, 29.68, 29.7, 30.0, 31.2, 31.9, 35.9, 36.3, 38.2, 55.2, 60.3, 74.9, 81.9, 88.7, 113.7, 126.4, 129.2, 130.6, 130.7, 131.4, 133.7, 135.7, 144.8, 159.0, 168.2.

Alcohol 13d: To a solution of the ester (55.6 mg, 0.78 mmol) in ethanol (1.6 ml) was added a 1 M aqueous HCl solution (0.65 ml) at room temperature. After stirring for 12 h at room temperature, the reaction was quenched with an aqueous sodium hydrogen carbonate solution, and the aqueous layer was extracted with ethyl acetate. The extract was washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (hexane/ethyl acetate = 4/1) to give **13d** (43.8 mg, 94%) as a colorless oil. $[\alpha]^{27}_{D}$ +53.0 (c 1.0, EtOH); ^{1}H NMR δ 0.86-1.00 (m, 6H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.25-1.41 (m, 22H), 1.67 (s, 3H), 1.68 (s, 3H), 1.85 (d, *J* = 1.5 Hz, 3H), 2.64-2.79 (m, 2H), 3.09 (dd, *J* = 2.9, 8.2 Hz, 1H), 3.80 (s, 3H), 3.88 (d, *J* = 7.3 Hz, 1H), 4.10-4.22 (m, 2H), 4.52 (s, 2H), 5.04 (brd, *J* = 10.1 Hz, 1H), 5.82 (s, 1H), 6.58 (dq, *J* = 1.5, 10.3 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H) 7.28 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 12.4, 13.4, 14.1, 14.3, 15.7, 17.0, 17.6, 22.7, 27.6, 29.4, 29.6, 30.0, 31.9, 35.0, 36.4, 36.6, 37.2, 55.2, 60.4, 75.0, 81.4, 87.2, 113.7, 126.9, 129.2, 130.7, 131.2, 131.4, 133.9, 135.4, 143.8, 159.0, 168.2.

Alcohol 13a: ^{1}H NMR δ 0.83-0.89 (m, 6H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.15-1.60 (m, 22H), 1.60-1.67 (m, 6H), 1.83 (s, 3H), 2.65-2.78 (m, 2H), 3.02 (dd, *J* = 4.3, 6.3 Hz, 1H), 3.79 (s, 3H), 3.86 (d, *J* = 7.6 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 4.47 (s, 2H), 5.37 (brd, *J* = 9.6 Hz, 1H), 5.84 (brs, 1H), 6.56 (d, *J* = 10.1 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.24 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 12.4, 13.4, 14.1, 14.2, 15.7, 16.4, 17.0, 18.8, 22.7, 27.3, 29.3, 29.6, 29.68, 29.71, 30.1, 31.9, 35.4, 36.4,

37.2, 55.2, 60.4, 74.4, 81.7, 88.2, 113.6, 126.9, 129.0, 130.8, 131.5, 131.6, 133.5, 135.0, 143.9, 158.9, 168.2.

Alcohol 13b: $[\alpha]^{31}_{D}$ +22.0 (c 1.0, EtOH); ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.21-1.63 (m, 22H), 1.67-1.71 (m, 6H), 1.84 (d, *J* = 1.5 Hz, 3H), 2.68-2.79 (m, 2H), 3.06 (t, *J* = 5.5 Hz, 1H), 3.79 (s, 3H), 3.88 (d, *J* = 6.8 Hz, 1H), 4.13 (q, *J* = 6.1 Hz, 2H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.49 (d, *J* = 10.4 Hz, 1H), 5.32 (brd, *J* = 9.7 Hz, 1H), 5.86 (brs, 1H), 6.58 (dq, *J* = 1.5, 10.3 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR δ 12.4, 13.6, 14.1, 14.2, 14.8, 15.6, 17.1, 18.4, 22.7, 27.3, 29.3, 29.6, 29.7, 30.0, 31.9, 34.2, 35.8, 36.2, 37.3, 55.2, 60.4, 74.1, 81.4, 87.3, 113.6, 126.9, 129.0, 131.2, 131.5, 131.7, 134.0, 135.0, 144.0, 158.9, 168.2.

Alcohol 13c: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.24-1.51 (m, 22H), 1.68 (s, 3H), 1.70 (s, 3H), 1.84 (d, *J* = 1.4 Hz, 3H), 2.68-2.77 (m, 2H), 3.02 (dd, *J* = 4.3, 7.0 Hz, 1H), 3.80 (s, 3H), 3.88 (d, *J* = 7.4 Hz, 1H), 4.09-4.20 (m, 2H), 4.50 (s, 2H), 5.13 (d, *J* = 9.7 Hz, 1H), 5.84 (s, 1H), 6.58 (dq, *J* = 1.4, 10.2 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 12.4, 13.6, 14.1, 14.16, 14.20, 15.6, 16.9, 17.0, 17.4, 22.7, 27.5, 29.3, 29.6, 29.7, 30.0, 31.2, 31.9, 35.9, 36.3, 37.3, 55.2, 60.4, 74.9, 81.3, 88.6, 113.7, 126.9, 129.2, 130.5, 131.2, 131.3, 134.5, 135.3, 143.9, 159.0, 168.1.

Ketone from 13d: To a mixture of **13d** (36.7 mg, 0.061 mmol), *N*-methyl molphorine *N*-oxide (10.9 mg, 0.092 mmol) and molecular sieves 4A (88 mg) in dichloromethane (2 ml) were added tetrapropylammonium perruthenate (4.3 mg, 0.012 mmol) at 0 °C. After stirring for 15 h at 0 °C, the reaction mixture was filtered through Celite, and then the filtrate was washed with aqueous sodium sulfite, water and brine. The

organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (hexane/ethyl acetate = 4/1) to give the ketone (28.0 mg, 77%) as a colorless oil. $[\alpha]^{27}_{D}$ +10.2 (c 1.4, EtOH); ^{1}H NMR δ 0.88 (t, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.22-1.45 (m, 25H), 1.87 (d, *J* = 0.9 Hz, 3H), 1.93 (d, *J* = 1.4 Hz, 3H), 1.94 (d, *J* = 1.1 Hz, 3H), 2.70-2.85 (m, 1H), 3.15 (dd, *J* = 2.9, 8.1 Hz, 1H), 3.80 (s, 3H), 4.10-4.22 (m, 3H), 4.50 (d, *J* = 10.7 Hz, 1H), 4.55 (d, *J* = 10.7 Hz, 1H), 5.45 (dq, *J* = 0.9, 10.1 Hz, 1H), 6.76 (dq, *J* = 1.4, 10.0 Hz, 1H), 6.86 (q, *J* = 1.1 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H) 7.28 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 12.7, 13.5, 14.1, 14.2, 16.6, 17.2, 17.6, 22.7, 27.6, 29.3, 29.6, 29.7, 30.0, 31.9, 35.0, 36.7, 36.9, 40.3, 55.3, 60.7, 75.0, 86.8, 113.7, 127.8, 129.2, 131.0, 131.1, 134.0, 140.6, 141.7, 143.5, 159.1, 167.8, 202.6.

Ketone from 13a: ^{1}H NMR δ 0.85-0.90 (m, 6H), 1.07 (d, *J* = 6.8 Hz, 3H), 1.15-1.60 (m, 25H), 1.87 (d, *J* = 1.2 Hz, 3H), 1.91 (brs, 3H), 1.94 (brs, 3H), 2.75-2.85 (m, 1H), 3.09 (dd, *J* = 3.8, 6.5 Hz, 1H), 3.80 (s, 3H), 4.12-4.22 (m, 3H), 4.43-4.55 (m, 2H), 5.81 (brd, *J* = 10.0 Hz, 1H), 6.77 (brd, *J* = 9.7 Hz, 1H), 6.85-6.88 (m, 2H), 6.94 (s, 1H), 7.23-7.27 (m, 2H); ^{13}C NMR δ 12.7, 13.4, 14.1, 14.2, 16.3, 16.5, 17.8, 18.6, 22.7, 27.3, 29.3, 29.6, 29.68, 29.70, 30.0, 31.9, 35.7, 36.6, 40.2, 55.3, 60.6, 74.5, 87.8, 113.7, 127.7, 129.1, 131.2, 131.3, 133.5, 140.8, 141.9, 144.0, 159.1, 167.9, 202.7.

Ketone from 13b: $[\alpha]^{28}_{D}$ –2.4 (c 1.0, EtOH); ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.19-1.62 (m, 25H), 1.86 (s, 3H), 1.92 (d, *J* = 1.4 Hz, 3H), 1.94 (s, 3H), 2.78-2.87 (m, 1H), 3.12 (t, *J* = 5.2 Hz, 1H), 3.79 (s, 3H), 4.11-4.27 (m, 3H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.49 (d, *J* = 10.8 Hz, 1H), 5.75 (brd, *J* = 10.9 Hz, 1H), 6.78 (bq, *J* = 1.4, 10.0 Hz, 1H), 6.85 (brd, *J* = 8.7 Hz, 2H), 6.94 (s, 1H), 7.22 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 12.7, 13.4, 14.1, 14.2, 14.8, 16.7,

17.7, 18.2, 22.7, 27.3, 29.3, 29.6, 29.7, 29.9, 31.9, 34.0, 36.2, 36.3, 40.2, 55.2, 60.7, 74.6, 87.1, 113.6, 127.7, 129.0, 131.3, 131.5, 133.5, 141.2, 141.9, 144.0, 159.0, 167.8, 202.7.

Ketone from 13c: ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H), 1.15-1.59 (m, 25H), 1.86 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 2.75-2.84 (m, 1H), 3.08 (dd, *J* = 4.4, 6.8 Hz, 1H), 3.80 (s, 3H), 4.12-4.22 (m, 3H), 4.48 (d, *J* =10.8 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 5.53 (d, *J* = 9.7 Hz, 1H), 6.76 (d, *J* = 10.0 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.90 (s, 1H), 7.26 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR δ 12.6, 13.5, 14.1, 14.2, 16.5, 16.6, 17.3, 17.6, 22.7, 27.5, 29.3, 29.65, 29.67, 30.0, 31.3, 31.9, 36.3, 36.4, 40.3, 55.3, 60.7, 74.9, 88.0, 113.7, 127.7, 129.2, 130.7, 131.1, 133.9, 141.3, 141.7, 143.5, 159.1, 167.8, 202.6.

Alcohol 1d: To a solution of the ketone (25.0 mg, 0.042 mmol) in dichloromethane (1 ml) was added water (0.05 ml) followed by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (18.6 mg, 0.082 mmol) at 0 °C. After stirring for 30 min at the same temperature, aqueous sodium hydrogen carbonate solution was added. After the phases were separated, the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (benzene/diethyl ether = 9/1) to give **1d** (17.5 mg, 88%). $[\alpha]^{26}_{D}$ +38.5 (c 0.9, EtOH); ^{1}H NMR (CD_3OD) δ 0.83 (d, *J* = 6.6 Hz, 3H), 0.88 (t, *J* = 6.6 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.20-1.60 (m, 22H), 1.89-1.92 (m, 9H), 2.62-2.69 (m, 1H), 3.26 (dd, *J* = 2.7, 8.5 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.35 (dq, *J* = 6.7, 10.0 Hz, 1H), 5.45 (brd, *J* = 9.3 Hz, 1H), 6.67 (dq, *J* = 1.5, 10.0 Hz, 1H), 7.06 (brs, 1H); ^{13}C NMR (CD_3OD) δ 12.9, 13.5, 13.7, 14.46,

14.55, 16.8, 17.5, 18.0, 23.7, 28.3, 30.5, 30.75, 30.79, 30.9, 33.1, 35.6, 37.2, 38.2, 41.3, 61.9, 79.0, 129.2, 135.0, 141.2, 143.2, 145.4, 169.3, 204.7.

Alcohol 1a: ^{1}H NMR (CD_3OD) δ 0.83-0.90 (m, 6H), 1.04 (d, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 6.7 Hz, 3H), 1.20-1.50 (m, 21H), 1.60-1.70 (m, 1H), 1.90 (d, *J* = 0.6 Hz, 3H), 1.92 (d, *J* = 1.5 Hz, 3H), 1.93 (brs, 3H), 2.72-2.80 (m, 1H), 3.19 (dd, *J* = 3.9, 7.3 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.33-4.40 (m, 1H), 5.71-5.79 (m, 1H), 6.66-6.69 (m, 1H), 7.08 (brs, 1H); ^{13}C NMR (CD_3OD) δ 12.8, 13.7, 14.4, 14.5, 16.6, 16.7, 18.0, 18.4, 23.7, 28.1, 30.5, 30.8, 31.2, 33.1, 37.2, 38.2, 41.3, 61.9, 80.6, 129.2, 133.1, 134.7, 140.4, 143.3, 145.8, 159.1, 169.3, 204.8.

Alcohol 1b: $[\alpha]^{27}_{D}$ –10.2 (c 0.4, EtOH); ^{1}H NMR (CD_3OD) δ 0.89 (t, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.20-1.60 (m, 22H), 1.90-1.94 (m, 9H), 2.72-2.78 (m, 1H), 3.25 (t, *J* = 5.8 Hz, 1H), 4.17 (q, *J* = 7.0 Hz, 2H), 4.37 (dq, *J* = 6.8, 9.8 Hz, 1H), 5.75 (brd, *J* = 9.7 Hz, 1H), 6.66-6.69 (m, 1H), 7.09 (brs, 1H); ^{13}C NMR (CD_3OD) δ 12.8, 13.7, 14.4, 14.5, 14.8, 16.8, 18.0, 23.7, 28.0, 30.5, 30.6, 30.7, 30.8, 30.9, 33.1, 34.5, 37.36, 37.42, 41.3, 61.9, 79.8, 129.2, 133.1, 134.7, 141.6, 143.3, 145.9, 169.3, 204.8.

Alcohol 1c: $[\alpha]^{26}_{D}$ –31.9 (c 0.39, EtOH); ^{1}H NMR (CD_3OD) δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.8 Hz, 3H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.20-1.60 (m, 22H), 1.91-1.93 (m, 9H), 2.65-2.75 (m, 1H), 3.19 (dd, *J* = 3.9, 7.6 Hz, 1H), 4.16 (q, *J* = 6.6 Hz, 2H), 4.36 (dq, *J* = 6.8, 10.0 Hz, 1H), 5.57 (brd, *J* = 10.0 Hz, 1H), 6.65-6.68 (m, 1H), 7.07 (brs, 1H); ^{13}C NMR (CD_3OD) δ 12.8, 13.6, 14.4, 14.5, 16.8, 17.5, 17.9, 23.7, 28.4, 30.5, 30.7, 30.75, 30.81, 30.9, 33.1, 37.5, 37.8, 41.3, 66.9, 81.0, 129.2, 132.3, 134.7, 142.4, 143.3, 145.7, 169.3, 204.6.

Synthesis of Mimic 2a-d

Alcohol 15a: To a solution of D-ribose (1.50 g, 10 mmol) in allyl alcohol (25 ml) was added conc. sulfuric acid (0.2 ml) at 0 °C. After storage for 12 h at 4 °C, the solution was neutralized with Amberlite IR-400 (OH free). After the resin was filtered off, the filtrate was concentrated under reduced pressure to give the allyl ribofuranoside as pale yellow oil (1.82 g), which was used without further purification.

To a mixture of the allyl ribofuranoside and *p*-methoxybenzyl chloride (10.3 g, 66 mmol) in THF (30 ml were added 50% aqueous potassium hydroxide solution (30 ml) and tetrabutylammonium bromide (154 mg, 0.48 mmol). The solution was stirred for 5 h at 90 °C. After cooling to room temperature, water and diethyl ether were added. stirred for 30 min at 0 °C, and an aqueous sodium hydrogen carbonate solution was added. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined extracts were washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 11/1 to 2/1) to give **14** as a colorless oil (4.49 g, 82% for two steps).

To a mixture of **14** (3.54 g, 6.4 mmol) and [1,3-bis(diphenylphosphino)-propane]dichloronickel(II) (35 mg, 0.064 mmol) in diethyl ether 15 ml was added diisobutylaluminum hydride (12 ml of a 1.0 M solution in hexane, 12 mmol) at 0 °C. After stirring for 6 h at room temperature, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution,

hexane/ethyl acetate = 5/1 to 1/3) to give the diol (2.87g, 87%) as a colorless oil.); ^{1}H NMR δ 2.50-2.70 (m, 2H), 3.52-3.56 (m, 2H), 3.69-3.76 (m, 2H), 3.78-3.84 (m, 11H), 3.93-3.98 (m, 1H), 4.42 (d, *J* = 11.7 Hz, 1H), 4.46 (d, *J* = 11.7 Hz, 1H), 4.48-4.57 (m, 3H), 4.63 (d, *J* = 10.7 Hz, 1H), 6.82-6.89 (m, 6H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.22-7.26 (m, 4H); ^{13}C NMR δ 55.2, 61.0, 70.6, 70.7, 71.5, 73.0, 73.6, 78.8, 78.9, 113.75, 113.78, 113.83, 129.50, 129.51, 129.7, 129.9, 130.0, 130.1, 159.3.

To a mixture of the diol (1.13 g, 2.2 mmol) and triphenylmethyl chloride (920 mg, 3.3 mmol) in dichloromethane (8 ml) was added a solution of triethylamine in dichloromethane (2 ml) at 0 °C. After stirring for 15 h at room temperature, water was added. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with a 1M aqueous HCl solution, water, and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 8/1 to 2/1) to give **15a** (1.56 g, 94%) as a white amorphousness. $[\alpha]^{24}_{D}$ +17.0 (c 0.12, CH_2Cl_2); IR (neat) 3433, 2920, 1612, 1513, 1248 cm^{-1}, ^{1}H NMR δ 2.81 (d, *J* = 3.7 Hz, 1H), 3.31 (dd, *J* = 4.6, 10.1 Hz, 1H), 3.46-3.55 (m, 3H), 3.73-3.82 (m, 11H), 3.90-3.97 (m, 1H), 4.35-4.48 (m, 5H), 4.70 (d, *J* = 11.2 Hz, 1H), 6.73 (d, *J* = 8.1 Hz, 2H), 6.76-6.79 (m, 6H), 7.17-7.29 (m, 13H), 7.43-7.50 (m, 6H); ^{13}C NMR δ 55.2, 63.2, 70.6, 71.4, 72.2, 72.9, 73.2, 78.3, 79.2, 86.7, 113.5, 113.7, 126.9, 127.7, 128.8, 129.41, 129.44, 129.6, 130.1, 130.3, 144.0, 159.0, 159.10, 159.13.

Alcohol 15b: IR (neat) 3480, 2934, 1513, 1250 cm^{-1}, ^{1}H NMR δ 2.72 (d, *J* = 3.4 Hz, 1H), 3.25 (dd, *J* = 6.9, 9.0 Hz, 1H), 3.37-3.55 (m, 3H), 3.68-3.80 (m, 10H), 3.85-3.96 (m, 2H), 4.30 (s, 2H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.43 (d, *J* = 11.5 Hz, 1H), 4.47 (d, *J* = 11.5 Hz, 1H), 4.61 (d, *J* = 11.5 Hz, 1H), 6.69-6.74 (m, 2H), 6.79-6.87 (m, 4H),

6.90-6.96 (m, 2H), 7.19-7.30 (m, 13H), 7.39-7.43 (m, 6H); ^{13}C NMR δ 55.2, 63.0, 69.9, 70.8, 72.6, 72.9, 73.2, 77.2, 77.4, 86.9, 113.4, 113.6, 113.7, 126.9, 127.7, 128.6, 129.4, 129.8, 129.9, 130.07, 130.14, 130.2, 143.8, 159.0, 159.1, 159.2.

Alcohol 15d: To a mixture of *p*-nitrobenzoic acid (1.23 g, 7.4 mmol) and triphenyl phosphine (1.94 g, 7.4 mmol) in THF (5 ml) was added a solution of **15a** in THF (15 ml) followed by a solution of diethyl azodicarboxylate (1.29 g, 7.4 mmol) at room temperature. After stirring for 2.5 h at the same temperature, an aqueous sodium hydrogen carbonate solution was added. The solution was extracted with ethyl acetate, and the extract was washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 9/1 to 2/1) to give the ester (3.23 g, 96%) as a white amorphousness.

To a solution of the ester (3.23 g, 3.6 mmol) in dichloromethane (80 ml) was added diisobutylaluminum hydride (12 ml of a 0.9 M solution in hexane, 10.7 mmol) at -78 °C. After stirring for 1 h at the same temperature, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 8/1 to 2/1) to give **15d** (2.30 g, 85%) as a white amorphousness. ^{1}H NMR δ 2.72 (d, *J* = 6.6 Hz, 1H), 3.24 (dd, *J* = 4.5, 10.1 Hz, 1H), 3.44-3.51 (m, 3H), 3.76-3.83 (m, 11H), 4.02-4.07 (m, 1H), 4.26 (d, *J* = 10.6 Hz, 1H),

4.34 (d, *J* = 10.6 Hz, 1H), 4.38 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 4.49 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 11.0 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.82-6.91 (m, 6H), 7.20-7.30 (m, 13H), 7.44-7.48 (m, 6H); ^{13}C NMR δ 55.22, 55.24, 62.9, 69.5, 70.8, 71.4, 72.6, 72.9, 73.2, 76.5, 78.3, 86.7, 113.5, 113.71, 113.74, 126.9, 127.7, 128.8, 129.4, 129.5, 129.9, 130.0, 130.21, 130.24, 143.9, 159.1, 159.2.

Alcohol 15c: $[\alpha]^{21}_{D}$ –3.1 (c 0.32, CH_2Cl_2); IR (neat) 3462, 2923, 1514, 1250 cm^{-1}; ^{1}H NMR δ 2.47 (brs, 1H), 3.22-3.33 (m, 3H), 3.34 (dd, *J* = 4.2, 10.0 Hz, 1H), 3.73-3.79 (m, 10H), 3.84-3.86 (m, 2H), 4.36 (s, 2H), 4.42 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.58 (d, *J* = 11.1 Hz, 1H), 4.61 (d, *J* = 11.1 Hz, 1H), 4.49 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 11.0 Hz, 1H), 6.77-6.79 (m, 2H), 6.81-6.84 (m, 4H), 7.05-7.07 (m, 2H), 7.17-7.28 (m, 13H), 7.43-7.46 (m, 6H); ^{13}C NMR δ 55.1,62.7, 69.7, 70.6, 72.2, 72.6, 74.2, 77.5, 78.8, 86.7, 113.5, 113.57, 113.60, 126.5, 126.9, 127.7, 127.8, 128.0, 128.6, 129.2, 129.6, 129.8, 130.1, 130.3, 143.8, 159.02, 159.05.

Ester from 15a: To a mixture of **15a** (1.67 g, 2.2 mmol) and *trans*-2-methyl-2-pentadecenoic acid (1.00g, 3.9 mmol) in dichloromethane (17 ml) was added a solution of dicyclohexyl carbodiimide (815 mg, 3.9 mmol) followed by *N*,*N*-dimethylaminopyridine (478 mg, 3.9 mmol). The solution was heated at reflux for 2.5 h. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in ethyl acetate. The solution was washed with a 1 M aqueous HCl solution, water, and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 12/1 to 4/1) to give the ester (1.85 g, 84 as a white amorphousness. $[\alpha]^{24}_{D}$ +11.7 (c 0.29, CH_2Cl_2); IR (neat) 2923, 1715, 1613, 1513, 1246 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.20-1.45 (m, 20H), 1.82 (s,

3H), 2.12-2.18 (m, 2H), 3.22 (dd, *J* = 5.2, 10.0 Hz, 1H), 3.47 (dd, *J* = 2.2, 10.0 Hz, 1H), 3.60-3.75 (m, 3H), 3.76 (s, 3H), 3.77 (s, 3H), 3.79 (s, 3H), 3.96 (dd, *J* = 3.4, 8.3 Hz, 1H), 4.31 (d, *J* = 12.0 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.45 (d, *J* = 11.4 Hz, 1H), 4.51 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 11.4 Hz, 1H), 5.53-5.58 (m, 1H), 6.71-6.94 (m, 9H), 7.15-7.29 (m, 13H), 7.41-7.48 (m, 6H); ^{13}C NMR δ 12.6, 14.1, 22.7, 28.6, 28.7, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 55.2, 63.3, 68.2, 72.0, 72.4, 72.6, 73.3, 78.0, 86.6, 113.5, 113.6, 113.7, 126.8, 127.6, 127.7, 128.8, 129.1, 129.4, 129.6, 130.3, 130.4, 130.5, 142.9, 144.1, 159.0, 159.6, 167.0.

Ester from 15b: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.16-1.49 (m, 20H), 1.81 (s, 3H), 2.13-2.22 (m, 2H), 3.18 (dd, *J* = 6.0, 9.7 Hz, 1H), 3.39 (dd, *J* = 6.0, 9.7 Hz, 1H), 3.39 (dd, *J* = 6.0, 9.7 Hz, 1H), 3.66-3.82 (m, 12H), 4.00 (dd, *J* = 3.2, 6.3 Hz, 1H), 4.31 (d, *J* = 11.5 Hz, 1H), 4.32 (d, *J* = 10.9 Hz, 1H), 4.35 (d, *J* = 10.8 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 10.8 Hz, 1H), 4.52 (d, *J* = 10.9 Hz, 1H), 5.16-5.25 (m, 1H), 6.67-6.85 (m, 7H), 6.91-6.98 (m, 2H), 7.18-7.31 (m, 13H), 7.38-7.44 (m, 6H); ^{13}C NMR δ 12.5, 14.2, 22.7, 28.6, 28.8, 29.3, 29.5, 29.6, 29.7, 31.9, 55.2, 63.3, 68.0, 72.5, 72.6, 72.9, 74.1, 77.5, 86.9, 113.4, 113.5, 113.6, 126.9, 127.5, 127.8, 128.7, 129.2, 129.8, 129.9, 130.3, 143.0, 143.9, 159.0, 159.1, 167.2.

Ester from 15c: ^{1}H NMR δ 0.87 (t, *J* = 6.7 Hz, 3H), 1.21-1.39 (m, 20H), 1.78 (s, 3H), 2.10-2.14 (m, 2H), 3.33 (dd, *J* = 5.1, 14.1 Hz, 1H), 3.71-3.74 (m, 13H), 4.04 (dd, *J* = 4.0, 6.0 Hz, 1H), 4.26-4.57 (m, 6H), 5.27-5.32 (m, 1H), 5.27-5.32 (m, 1H), 6.71-6.82 (m, 7H), 7.00-7.03 (m, 2H), 7.16-7.29 (m, 13H), 7.40-7.43 (m, 6H); ^{13}C NMR δ 12.3, 14.0, 22.6, 28.4, 28.6, 29.2, 29.3, 29.4, 29.5, 31.8, 55.0, 62.7, 67.9, 71.9, 72.5, 72.7, 74.0, 76.6, 86.8, 113.3, 113.5, 113.6, 126.8, 127.4, 127.7, 128.6, 129.1, 129.5, 129.6, 130.1, 130.3, 130.4, 142.8, 143.8, 158.9, 159.0, 167.2.

Ester from 15d: IR (neat) 2924, 1706, 1613, 1513, 1249 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.17-1.44 (m, 20H), 1.78 (s, 3H), 2.07-2.17 (m, 2H), 3.24 (dd, *J* = 5.0, 10.2 Hz, 1H), 3.52-3.68 (m, 4H), 3.75-3.80 (m, 9H), 4.04 (dd, *J* = 3.2, 7.8 Hz, 1H), 4.28-4.45 (m, 5H), 4.62 (d, *J* = 10.6 Hz, 1H), 5.46-5.54 (m, 1H), 6.69-6.96 (m, 9H), 7.16-7.35 (m, 13H), 7.43-7.50 (m, 6H), 7.43-7.50 (m, 6H); ^{13}C NMR δ 12.4, 14.1, 22.7, 28.5, 28.7, 29.3, 29.4, 29.5, 29.6, 31.9, 55.2, 63.1, 67.7, 71.6, 72.5, 72.6, 73.6, 76.1, 77.9, 86.6, 113.4, 113.6, 113.7, 126.9, 127.5, 127.7, 128.8, 129.3, 129.4, 129.7, 130.2, 130.4, 130.5, 143.0, 144.0, 158.9, 159.1, 167.5.

Alcohol 16a: To a solution of the ester (1.85 g, 1.9 mmol) derived from **15a** in diethyl ether (26 ml) was added 98% formic acid (13 ml) at room temperature. After stirring for 12 h at the same temperature, the solution was neutralized with an aqueous sodium hydrogen carbonate solution. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 9/1 to 2/1) to give **16a** (971 mg, 69%) as a colorless oil. IR (neat) 3445, 2923, 1713, 1613, 1513, 1248 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.20-1.47 (m, 20H), 1.84 (s, 3H), 2.05 (brs, 1H), 2.13-2.23 (m, 2H), 3.55-3.66 (m, 1H), 3.65-3.76 (m, 4H), 3.78 (m, 6H), 3.79 (s, 3H), 3.91-3.94 (m, 1H), 4.38 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.50 (s, 2H), 4.55 (d, *J* = 11.7 Hz, 1H), 4.63 (d, *J* = 11.7 Hz, 1H), 5.43-5.49 (m, 1H), 6.78-6.87 (m, 7H), 7.17-7.25 (m, 6H); ^{13}C NMR δ 12.5, 14.1, 22.6, 28.6, 28.7, 29.3, 29.4, 29.5, 29.6, 31.9, 51.2, 61.1, 68.0, 71.5, 72.4, 72.6, 73.6, 78.1, 78.2, 113.6, 113.8, 127.3, 129.2, 129.5, 129.7, 129.9, 130.2, 143.4, 159.1, 159.3, 167.3.

Alcohol 16b:$[\alpha]^{23}_{D}$ –3.8 (c 2.0, CH_2Cl_2); IR (neat) 3444, 2925, 1705, 1613, 1514, 1248 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.20-1.48 (m, 20H), 1.82 (s, 3H), 1.96 (dd, *J* = 7.5, 12.4 Hz, 1H), 2.13-2.23 (m, 2H), 3.56-3.74 (m, 3H), 3.74-3.82 (m, 10H), 3.85 (dd, *J* = 3.5, 11.6 Hz, 1H), 3.92 (dd, *J* = 4.8, 4.9 Hz, 1H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.49 (d, *J* = 11.5 Hz, 1H), 4.53 (d, *J* = 11.2 Hz, 1H), 4.55 (d, *J* = 11.0 Hz, 1H), 4.62 (d, *J* = 11.0 Hz, 1H), 5.22-5.27 (m, 1H), 6.76-6.87 (m, 7H), 7.17-7.24 (m, 6H); ^{13}C NMR δ 12.4, 14.1, 22.6, 28.6, 28.8, 29.3, 29.4, 29.5, 29.6, 31.9, 55.2, 61.9, 67.9, 72.7, 72.8, 72.9, 73.8, 78.2, 78.8, 113.7, 113.8, 127.4, 129.2, 129.6, 129.8, 30.1, 130.2, 143.5, 159.2, 159.3, 167.4; Anal. Calcd for $C_{45}H_{64}O_9$: C, 72.16; H, 8.61. Found: C, 71.92; H, 8.68.

Alcohol 16c: ^1H NMR δ 0.86 (t, *J* = 6.7 Hz, 3H), 1.21-1.41 (m, 20H), 1.81 (d, *J* = 0.9 Hz, 3H), 2.02 (brs, 1H), 2.10-2.17 (m, 2H), 3.50-3.64 (m, 1H), 3.76-3.79 (m, 13H), 3.89 (m, 1H), 4.37 (d, *J* = 4.0 Hz, 2H), 4.49 (d, *J* = 2.1 Hz, 2H), 4.59 (s, 2H), 5.33 (m, 1H), 6.76-6.89 (m, 7H), 7.16-7.28 (m, 6H); ^{13}C NMR δ 12.4, 14.1, 22.7, 28.5, 28.8, 29.3, 29.5, 29.6, 31.9, 55.2, 61.7, 67.8, 71.9, 72.3, 72.7, 73.9, 78.3, 113.7, 113.8, 113.9, 127.3, 128.6, 129.3, 129.6, 129.7, 130.1, 130.2, 143.6, 159.2, 159.3, 167.4.

Alcohol 16d: IR (neat) 3342, 2925, 1710, 1614, 1514, 1248 cm^{-1}; ^1H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.20-1.46 (m, 20H), 1.82 (d, *J* = 0.7 Hz, 3H), 2.04 (brs, 1H), 2.10-2.20 (m, 2H), 3.50-3.57 (m, 1H), 3.58-3.65 (m, 1H), 3.67-3.84 (m, 12H), 3.94 (dd, *J* = 3.6, 7.1 Hz, 1H), 4.41 (s, 2H), 4.44 (s, 2H), 4.56 (d, *J* = 11.0 Hz, 1H), 4.63 (d, *J* = 11.0 Hz, 1H), 5.37-5.44 (m, 1H), 6.77-6.89 (m, 7H), 7.17-7.27 (m, 6H); ^{13}C NMR δ 12.4, 14.1, 22.7, 28.5, 28.8, 29.3, 29.4, 29.5, 29.6, 31.9, 55.2, 60.6, 67.8, 71.6, 71.7, 72.8, 74.2, 76.3, 78.2, 113.7, 113.8, 127.4, 129.5, 129.7, 129.9, 130.3, 143.4, 159.2, 159.3, 167.5.

Methyl Ester 17a: To a mixture of **16a** (150 mg, 0.2 mmol), *N*-methyl molphorine *N*-oxide (35 mg, 0.3 mmol) and molecular sieves 4A (140 mg) in dichloromethane (2 ml) was added tetra-n-propylammonium perruthenate (7.0 mg, 0.02 mmol) at the same temperature. After stirring for 1 h at room temperature, the reaction mixture was filtered through Celite, and then the filtrate was washed with aqueous sodium sulfite, water, and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was filtered through a small column of silica gel (hexane/ethyl acetate = 4/1) to give the aldehyde as a colorless oil, which was used without further purification.

To a solution of the aldehyde in *tert*-butyl alcohol (2.7 ml) were added 2-methyl-2-butene (1.7 ml) and a mixture of sodium chlorite (350 mg) and sodium dihydrogenphospate dihydrate (350 mg) in water (2.7 ml). After stirring for 6 h at room temperature, the reaction mixture was diluted with water and ethyl acetate. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water, an aqueous citric acid solution and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was filtered through a small column of silica gel (chloroform/methanol = 20/1) to give the carboxylic acid, which was used without further purification.

To a solution of the carboxylic acid in 1:1 THF/methanol (1 ml) was added (trimethylsilyl)diazomethane (0.2 ml of a 2 M solution in hexane, 0.4 mmol) at room temperature. After stirring for 5 min at the same temperature, the mixture was diluted with water and ethyl acetate. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced

pressure. The residue was purified by preparative thin layer chromatography on silica gel (hexane/ethyl acetate = 2/1) to give **17a** (54 mg, 35% for three steps) as a colorless oil. ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.15-1.47 (m, 20H), 1.79 (d, *J* = 0.4 Hz, 3H), 2.11-2.19 (m, 2H), 3.65-3.70 (m, 4H), 3.75-3.80 (m, 10H), 4.06-4.18 (m, 2H), 4.33 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.7 Hz, 1H), 4.45 (d, *J* = 11.7 Hz, 1H), 4.52 (s, 2H), 4.62 (d, *J* = 11.7 Hz, 1H), 5.38-5.43 (m, 1H), 6.70-6.86 (m, 4H), 7.10-7.26 (m, 6H); ^{13}C NMR δ 12.4, 14.1, 22.7, 28.6, 28.7, 29.3, 29.5, 29.6, 31.9, 51.8, 55.2, 67.9, 71.4, 72.1, 72.6, 73.2, 77.7, 78.4, 113.56, 113.7, 127.4, 129.1, 129.7, 129.9, 130.3, 143.2, 159.1, 159.2, 159.3, 160.9, 170.9.

Methyl Ester 17b: ^{1}H NMR δ 0.88 (t, *J* = 6.5 Hz, 3H), 1.18-1.48 (m, 20H), 1.75 (s, 3H), 2.10-2.19 (m, 2H), 3.65 (s, 3H), 3.70-3.88 (m, 11H), 4.08 (d, *J* = 2.8 Hz, 1H), 4.24-4.55 (m, 6H), 4.68 (d, *J* = 11.2 Hz, 1H), 5.18-5.20 (m, 1H), 6.67-6.75 (m, 1H), 6.75-6.89 (m, 6H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.14-7.24 (m, 4H); ^{13}C NMR δ 12.3, 14.0, 22.6, 28.5, 28.7, 29.3, 29.4, 29.5, 29.6, 31.8, 51.8, 55.0, 55.1, 67.5, 72.0, 72.6, 72.7, 73.8, 77.1, 77.6, 113.5, 113.6, 127.2, 128.8, 129.2, 129.8, 129.9, 130.1, 130.2, 143.3, 159.1, 159.2, 159.3, 166.8, 171.3.

Methyl Ester 17c: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.21-1.41 (m, 20H), 1.80 (s, 3H), 2.11-2.18 (m, 2H), 3.59-3.62 (m, 5H), 3.75-3.77 (m, 9H), 4.07-4.12 (m, 1H), 4.07-4.70 (m, 6H), 5.30-5.35 (m, 1H), 6.79-6.85 (m, 7H), 7.12-7.21 (m, 2H); ^{13}C NMR δ 12.2, 14.0, 22.5, 28.4, 28.6, 29.2, 29.3, 29.4, 29.5, 31.7, 51.7, 55.0, 67.7, 72.3, 72.4, 72.5,73.7, 77.6, 113.4, 113.5, 114.1, 127.2, 128.7, 129.1, 128.5, 129.9, 130.0, 130.1, 143.1, 159.0, 159.3, 167.1, 170.7.

Methyl Ester 17d: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.17-1.47 (m, 20H), 1.79 (s, 3H), 2.09-2.18 (m, 2H), 3.52-3.71 (m, 5H), 3.74-3.81 (m, 9H), 4.04-4.15 (m, 2H), 4.26-4.60 (m, 6H), 5.37-5.44 (m, 1H), 6.73-6.87 (m, 7H), 7.10-7.26 (m, 6H); ^{13}C

NMR δ 12.4, 14.1, 22.6, 28.5, 28.7, 29.3, 29.4, 29.5, 29.6, 31.8, 51.8, 55.1, 67.5, 721.6, 72.2, 72.6, 73.7, 77.3, 77.9, 113.5, 113.6, 127.2, 129.2, 129.4, 129.9, 130.0, 143.2, 159.1, 159.3, 167.3, 171.3.

Triol 2a: To a solution of **17a** (39.2 mg, 0.051 mmol) in dichloromethane (2 ml) was added boron tribromide (0.25 ml of a 1 M solution in dichloromethane, 0.25 mmol) at –78 °C. After stirring for 10 min at –78 °C, the reaction was quenched with methanol and an aqueous sodium hydrogen carbonate solution. After the phases were separated, the aqueous layer was extracted with dichloromethane. The combined organic extracts were washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (chloroform/methanol = 10/1) to give **2a** (12.3 mg, 57%) as a colorless oil. ^{1}H NMR (CD_3OD) δ 0.88 (t, *J* = 6.8 Hz, 3H), 1.20-1.50 (m, 20H), 1.82 (d, *J* = 1.2 Hz, 3H), 2.20 (dd, *J* = 7.1, 7.4 Hz, 2H), 3.69 (s, 3H), 3.79 (dd, *J* = 4.6, 12.2 Hz, 1H), 3.84 (dd, *J* = 3.2, 12.2 Hz, 1H), 4.20 (dd, *J* = 3.7, 7.8 Hz, 1H), 4.29 (d, *J* = 3.7 Hz, 1H), 5.06 (ddd, *J* = 3.2, 4.6, 7.8 Hz, 1H), 6.77 (brd, *J* = 7.4 Hz, 1H); ^{13}C NMR (CD_3OD) δ 12.5, 14.4, 23.7, 29.7, 30.5, 30.6, 30.7, 30.8, 33.1, 52.4, 61.6, 72.4, 73.8, 74.9, 128.8, 144.2, 168.8, 174.0.

Triol 2b: ^{1}H NMR (CD_3OD) δ 0.89 (t, *J* = 6.7 Hz, 3H), 1.20-1.50 (m, 20H), 1.83 (d, *J* = 1.5 Hz, 3H), 2.21 (dd, *J* = 7.2, 7.4 Hz, 2H), 3.76 (s, 3H), 3.80 (dd, *J* = 3.9, 12.3 Hz, 1H), 3.91 (dd, *J* = 2.8, 12.3 Hz, 1H), 4.22 (d, *J* = 2.0 Hz, 1H), 4.25 (dd, *J* = 2.0 Hz, 1H), 4.95 (ddd, *J* = 2.8, 3.9, 9.0 Hz, 1H), 6.81-6.83 (m, 1H); ^{13}C NMR (CD_3OD) δ 12.5, 14.4, 23.7, 29.6, 29.7, 30.5, 30.6, 30.7, 30.8, 33.1, 52.6, 61.4, 72.2, 74.9, 128.7, 144.5, 168.8, 175.0.

Triol 2c: ^{1}H NMR (CD_3OD) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.25-1.50 (m, 20H), 1.85 (d, *J*

= 1.2 Hz, 3H), 2.18-2.23 (m, 2H), 3.74 (s, 3H), 3.76 (dd, *J* = 4.9, 12.2 Hz, 1H), 3.81 (dd, *J* = 3.7, 12.2 Hz, 1H), 4.17 (dd, *J* = 2.8, 6.5 Hz, 1H), 4.32 (d, *J* = 2.8 Hz, 1H), 5.06 (ddd, *J* = 3.7, 4.9, 6.5 Hz, 1H), 6.84-6.88 (m, 1H); ^{13}C NMR (CD_3OD) δ 12.5, 14.4, 23.7, 29.7, 30.5, 30.6, 30.7, 30.8, 33.1, 52.6, 61.6, 72.2, 72.8, 76.8, 128.8, 144.3, 169.5, 174.5.

Triol 2d: ^{1}H NMR (CD_3OD) δ 0.89 (t, *J* = 6.9 Hz, 3H), 1.25-1.50 (m, 20H), 1.84 (d, *J* = 1.2 Hz, 3H), 2.18-2.25 (m, 2H), 3.73 (s, 3H), 3.747 (dd, *J* = 5.8, 17.7 Hz, 1H), 3.748 (dd, *J* = 5.8, 17.7 Hz, 1H), 4.04 (dd, *J* = 3.1, 7.5 Hz, 1H), 4.07 (d, *J* = 7.5 Hz, 1H), 5.17 (d, *J* = 3.1, 5.8 Hz, 1H), 6.90 (brd, *J* = 7.6 Hz, 1H); ^{13}C NMR (CD_3OD) δ 12.6, 14.4, 23.7, 29.6, 29.7, 30.47, 30.53, 30.6, 30.70, 30.74, 30.8, 33.1, 52.4, 61.4, 72.2, 72.8, 74.9, 128.6, 144.6, 169.3, 174.8.

Stereoselective Synthesis of 7b

Ester 19: To a solution of (carbethoxymethylidene)triphenylphosphrane (30.7 g, 88 mmol) in CH_2Cl_2 (100 ml) was added a solution of **5** (8.7 g, 44 mmol) in dichloromethane (50 ml) at room temperature. After the solution was stirred for 12 h at room temperature, a solution was diluted with hexane. After the reaction mixture was filtered through Celite, the filtrate was evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 20/1) to give **19** (10.7 g, 91%, *E/Z* = >95/5) as a colourless oil. IR (neat) 2924, 1721 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.23-1.41 (m, 21H), 2.24-2.33 (m, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 5.76 (d, *J* = 15.7 Hz, 1H), 6.86 (d, *J* = 15.7 Hz, 1H); ^{13}C NMR δ 14.1, 14.3, 19.4, 22.7, 27.2, 29.3, 29.5, 29.6, 29.7, 31.9, 36.0, 36.5, 60.1, 119.5, 154.8, 167.0; MS (EI+) m/z 268; Anal. Calcd for $C_{17}H_{32}O_2$: C, 76.06; H, 12.02. Found: C,

75.96; H, 12.10.

Alcohol 20: To a solution of **19** (8.6 g, 32 mmol) in dichloromethane (50 ml) was added diisobutylaluminum hydride (96 ml of a 1.0 M solution in hexane, 96 mmol) at –78 °C. After stirring for 30 min at the same temperature, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were 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 = 8/1) to give **20** (6.9 g, 96%) as a colorless oil. ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 1.20-1.50 (m, 18H), 1.80 (brs, 1H), 2.02-2.15 (m, 1H), 4.09 (d, *J* = 3.2 Hz, 2H), 5.56-5.59 (m, 2H); ^{13}C NMR δ 14.1, 20.3, 22.7, 27.3, 29.3, 29.6, 29.7, 29.8, 31.9, 36.3, 36.8, 63.8, 127.0, 139.3; Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found: C, 79.28; H, 13.22.

Diol 7b: To a solution of tetraisopropyl orthotitanate (16.3 g, 57.6 mmol) in dichloromethane (40 ml) was added a solution of D-tartaric acid diethyl ester (11.9 g, 57.6 mmol) in dichloromethane (18 ml) at –23 °C. After the mixture was stirred for 30 min at the same temperature, a solution of **20** (6.5 g, 28.8 mmol) in dichloromethane (25 ml) was added followed by *tert*-butylhydroperoxide (37.4 ml of a 2.0 M solution in dichloromethane, 74.9 mmol). After stirring for 3 h at –23 °C, the reaction was quenched with 10% aqueous tartaric acid. After the phases were separated, the aqueous layer was extracted with dichloromethane. The combined

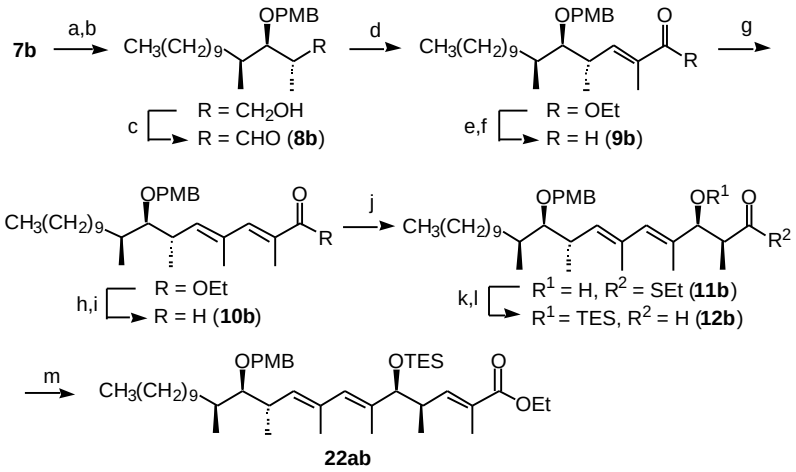
organic extracts were washed with water and brine, dried over sodium sulfate, and concentrated under reduced pressure. The residue was roughly purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) to give **21** (7.1 g), which was used without further purification. IR (neat) 3428, 2924, 1210 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 1.02 (d, *J* = 6.3 Hz, 3H), 1.24-1.43 (m, 18H), 1.75 (brs, 1H), 1.91-1.95 (m, 1H), 2.72 (dd, *J* = 2.2, 7.0 Hz, 1H), 2.97 (dd, *J* = 2.2, 4.4 Hz, 1H), 3.58-3.66 (m, 1H), 3.89-3.95 (m, 1H); ^{13}C NMR δ 14.1, 17.2, 22.7, 27.2, 29.3, 29.6, 29.8, 31.9, 33.6, 39.5, 58.4, 60.2, 61.8; HRMS (EI+) calcd for $C_{15}H_{30}O_2$ 242.2246 (M+) found 242.2238.

To a suspension of copper (I) iodide (65.8 g, 345.6 mmol) in diethyl ether (40 ml) was added methyl lithium (505.3 ml of a 1.1 M solution of diethyl ether, 576 mmol) at –23 °C. After the mixture was stirred for 30 min at the same temperature, the solution of resulting **21** (7.1 g) in diethyl ether (40 ml) was added to the mixture. After stirring for 12 h at 0 °C, the reaction was quenched with saturated aqueous ammonium chloride. After the mixture was filtered through Celite, the phases were separated and the aqueous layer was extracted with diethyl ether. The combined organic extracts were 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 = 4/1) to give **7b** (6.7 g, 26 mmol) as a colorless oil. IR (neat) 3340, 2922 cm^{-1}; ^{1}H NMR δ 0.81 (d, *J* = 6.8 Hz, 3H), 0.86-0.92 (m, 6H), 1.24-1.32 (m, 18H), 1.60-1.63 (m, 1H), 1.78-1.90 (m, 1H), 2.86-2.91 (m, 2H), 3.46 (dd, *J* = 2.7, 9.0 Hz, 1H), 3.63 (dd, *J* = 7.7, 10.8 Hz, 1H), 3.72 (dd, *J* = 7.7, 10.8 Hz, 1H); ^{13}C NMR δ 12.3, 13.5, 14.1, 22.6, 27.4, 29.3, 29.6, 29.9, 31.9, 34.0, 35.1, 37.3, 68.7, 80.2; HRMS (EI+) calcd for $C_{16}H_{34}O_2$ 258.2559 (M+) found 258.2575.

Synthesis of 18a-d

Ester 22ab: Synthesis of **22ab** that has the stereochemisty of natural khaferfungin was performed according to the following scheme (Scheme S-3). All the physical data for intermediates **7b**-**22ab** shown in Scheme S-3 were reported previously in the experimental section.

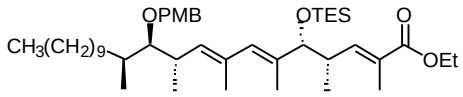
Scheme S-3. Synthesis of **22ab**



Reangents and conditions: (a) $PMPCH(OMe)_2$, cat. TsOH, CH_2Cl_2, rt, 95%; (b) DIBAL, CH_2Cl_2, rt, 96%; (c) $COCl_2$, DMSO, CH_2Cl_2, -78 °C; then Et_3N, rt, 92%; (d) Ph_3P=C(Me)CO_2Et, THF, reflux, 90%, *E/Z* = >95/5; (e) DIBAL, CH_2Cl_2, -78 °C, 98%; (f) 0.1 equiv of TPAP, NMO, CH_2Cl_2, rt, 88%; (g) Ph_3P=C(Me)CO_2Et, THF, reflux, 87%; (h) DIBAL, CH_2Cl_2, -78 °C, 97%; (i) 0.1 equiv of TPAP, NMO, CH_2Cl_2, rt, 93%; (j) **3**, $Sn(OTf)_2$, $Bu_2Sn(OAc)_2$, (*S*)-1-methy-2-[(*N*-1-naphthylamino)-methyl]pyrrolidine, CH_2Cl_2, -78 °C, 90%, >98%ds; (k) TESOTf, CH_2Cl_2, rt, 84%; (l) DIBAL, CH_2Cl_2, -78 °C, 96%; (m) Ph_3P=C(Me)CO_2Et, THF, reflux, 92%, *E/Z* = >95/5.

Ester 22cd (opposite stereochemistry at the C4 and 5 positions of **22ab**; Ester **22cd** was prepared via the asymmetric aldol reaction of **10b** with **3** using (*R*)-1-methyl-2-[(*N*)-1-naphtylamino)methy]pyrrolidine). $[\alpha]^{23}_D$ –5.3 (c 1.9, CH_2Cl_2); ^{1}H NMR δ 0.59 (q, *J* = 7.9 Hz, 6H), 0.86-0.93 (m, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 1.15-1.40 (m, 22H), 1.65 (d, *J* = 1.0 Hz, 3H), 1.67 (d, *J* = 1.0 Hz, 3H), 1.82 (d, *J* = 1.3 Hz, 3H), 2.60-2.80 (m, 2H), 3.06 (dd, *J* = 4.8, 5.7 Hz,

1H), 3.77-3.82 (m, 4H), 4.02-4.22 (m, 2H), 4.41 (d, *J* = 10.8 Hz, 1H), 4.50 (d, *J* = 10.8 Hz, 1H), 5.28 (brd, *J* = 9.7 Hz, 1H), 5.79 (brs, 1H), 6.56 (brd, *J* = 10.3 Hz, 1H), 6.81-6.86 (m, 2H) 7.18-7.21 (m, 2H); ^{13}C NMR δ 4.9, 6.9, 12.4, 13.5, 14.1, 14.2, 14.6, 15.7, 17.1, 18.3, 22.7, 27.5, 29.4, 29.6, 29.7, 30.0, 31.9, 34.3, 35.9, 38.1, 55.2, 60.3, 74.2, 82.2, 87.1, 113.5, 126.3, 128.9, 130.8, 131.2, 131.7, 133.4, 135.4, 144.8, 158.8, 168.2

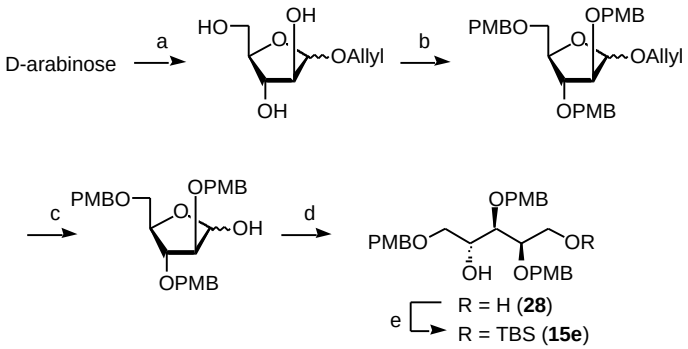


22cd

Alcohol 15e: Synthesis of **15e** that has the stereochemistry of natural khafrefungin was performed according to Scheme S-4. Diol **28** was prepared from D-arabinose according to the similar procedures to those shown in Scheme 2. To a solution of diol (**28**, 4.8 g, 9.4 mmol) in dichloromethane (30 ml) was added a solution of triethylamine (2.4 g, 23.4 mmol) in dichloromethane (5 ml) at 0 °C. After stirring for 5 min at the same temperature, a solution of *tert*-butyldimethylsilyl chloride (1.7 g, 11.2 mmol) was added to the mixture at the same temperature. After stirring for 20 h at room temperature, the reaction was quenched with aqueous sodium hydrogen carbonate solution. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were 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 **15e** (5.46 g, 93%) as a colourless oil. $[\alpha]^{23}_{D}$ +5.9 (c 3.4, CH_2Cl_2); IR (neat) 3463, 2929, 1613, 1513, 1249 cm^{-1}; ^{1}H NMR δ -0.04 (s, 3H), 0.00 (s, 3H), 0.86 (s, 9H), 2.91 (d, *J* = 4.1 Hz, 3H), 3.49 (dd, *J* = 5.4, 9.8 Hz, 1H), 3.54 (dd, *J* = 3.4, 9.8 Hz 1H), 3.61 (dd, *J* = 2.3, 7.4 Hz, 1H), 3.65-3.81 (m, 12H), 3.88-3.96 (m, 1H), 4.39 (d, *J* = 11.5 Hz,

1H), 4.41 (d, *J* = 11.2 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.45 (d, *J* = 11.2 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 4.61(d, *J* = 11.5 Hz, 1H), 6.79(d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.20-7.23 (m, 4H); ^{13}C NMR δ -5.5, -5.4, 18.2, 25.9, 55.19, 55.21, 55.22, 62.5, 70.3, 71.0, 72.98, 72.9, 73.2, 77.1, 79.0, 113.6, 113.69, 113.73, 29.4, 129.82, 129.83, 130.2, 130.4, 130.5, 159.19, 159.20, 159.24; FABMS (M^++Na) 649; Anal. Calcd for $C_{35}H_{50}O_8Si$: C, 67.06; H, 8.04. Found: C, 66.76; H, 7.87.

Scheme S-4. Synthesis of **15e**



Reagents and conditions: (a) allyl alcohol, cat. H_2SO_4, DMF, 90 °C; (b) PMBCl, BuN_4Br, 50% aq. KOH/THF (1/1), 90 °C, 36% for 2 steps; (c) DIBAL, 0.01 equiv. of $NiCl_2$(dppp), Et_2O, rt, 95%; (d) $LiAlH_4$, THF, rt, 85% for 2 steps; (e) TBSCl, Et_3N, CH_2Cl_2, rt, 93%.

Ent-15e was also prepared from L-arabinose

Alcohol from 22ab: To a solution of ester **22ab** (1.85 g, 2.59 mmol) in dichloromethane (10 ml) was added diisobutylaluminum hydride (7.8 ml of a 1.0 M solution in hexane, 7.8 mmol) at –78 °C. After stirring for 30 min at –78 °C, the reaction was quenched with methanol. After an aqueous Rochelle Salt solution and diethyl ether were added, the mixture was warmed to room temperature and stirred

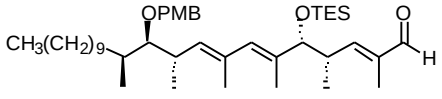
vigorously until the resulting white slurry was completely dissolved. After the phases were separated, the aqueous layer was extracted with diethyl ether. The combined organic extracts were washed with water and brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 12/1) to give the alcohol (1.67 mg, 96%) as a colourless oil. IR (neat) 3428, 2925, 1247 cm^{-1}; ^{1}H NMR δ 0.59 (q, *J* = 7.8 Hz, 6H), 0.88-1.01 (m, 18H), 1.20-1.42 (m, 22H), 1.63 (s, 3H), 1.65 (s, 3H), 1.67 (s, 3H), 2.54-2.58 (m, 1H), 2.73-2.75 (m, 1H), 3.07 (d, *J* = 5.1 Hz, 1H), 3.70 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H), 3.86 (brs, 2H), 4.46 (d, *J* = 10.5 Hz, 1H), 4.50 (d, *J* = 10.5 Hz, 1H), 5.12 (d, *J* = 9.8 Hz, 1H), 5.27 (d, *J* = 9.4 Hz, 1H), 5.72 (s, 1H), 6.82 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR δ 4.9, 6.9, 13.2, 13.7, 14.1, 14.9, 16.9, 17.2, 18.5, 22.7, 27.3, 29.4, 29.7, 30.0, 31.9, 34.1, 35.7, 36.2, 37.2, 55.2, 69.0, 74.4, 83.2, 87.4, 113.6, 129.1, 129.5, 130.5, 131.3, 131.6, 133.0, 133.6, 136.4, 158.9; HRMS (EI+) calcd for $C_{42}H_{74}O_4Si$ 670.5356 (M+) found 670.5300.

Alcohol from 22cd: $[\alpha]_D^{26}$–2.0 (c 0.1, EtOH); IR (neat) 3340, 2922 cm^{-1}; ^{1}H NMR δ 0.58 (q, *J* = 7.4 Hz, 6H), 0.86-0.99 (m, 18H), 1.12-1.41 (m, 22H), 1.63 (s, 3H), 1.65 (s, 3H), 1.67 (s, 3H), 2.51-2.59 (m, 1H), 2.68-2.75 (m, 1H), 3.06 (d, *J* = 5.2 Hz, 1H), 3.69 (d, *J* = 7.7 Hz, 1H), 3.79 (s, 3H), 3.88 (d, *J* = 7.2 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.50 (d, *J* = 10.4 Hz, 1H), 5.13 (d, *J* = 10.3 Hz, 1H), 5.26 (d, *J* = 9.4 Hz, 1H), 5.70 (s, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR δ 4.9, 6.9, 13.4, 13.8, 14.1, 14.8, 17.1, 18.5, 22.7, 27.4, 29.4, 29.66, 29.69, 30.0, 31.9, 34.2, 35.7, 36.2, 37.2, 55.2, 69.1, 74.3, 83.2, 87.3, 113.6, 129.0, 129.7, 130.4, 131.4, 131.7, 133.0, 133.6, 136.4, 158.9; Anal. Calcd for $C_{42}H_{74}O_4Si$: C, 75.17; H, 11.11. Found: C, 74.95; H, 11.25.

Enal 23ab: To a mixture of the alcohol (502 mg, 0.75 mmol), *N*-methyl molphorine *N*-oxide (130 mg, 1.13 mmol), and molecular sieves 4A (540 mg) in dichloromethane (5 ml) were added tetrapropylammonium perruthenate (26 mg, 0.075 mmol) at room temperature. After stirring for 1 h at the same temperature, the reaction mixture was filtered through Celite, and then the filtrate was washed with aqueous sodium sulfite, water, and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 15/1) to give **23ab** (454 mg, 90%) as a colourless oil: ^{1}H NMR δ 0.59 (q, *J* = 8.0 Hz, 6H), 0.86-0.99 (m, 18H), 1.09 (d, *J* = 6.6 Hz, 3H), 1.19-1.42 (m, 19H), 1.65 (s, 3H), 1.69 (s, 3H), 1.74 (s, 3H), 2.69-2.76 (m, 1H), 2.83-2.91 (m, 1H), 3.06 (t, *J* = 5.2 Hz, 1H), 3.79 (s, 3H), 3.86 (d, *J* = 7.5 Hz, 1H), 4.42 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 9.7 Hz, 1H), 5.80 (s, 1H), 6.25 (d, *J* = 10.2 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 2H), 7.27 (*J* = 8.3 Hz, 2H), 9.33 (s, 1H); ^{13}C NMR δ 4.9, 6.9, 9.2, 13.3, 14.1, 14.6, 15.9, 17.0, 18.3, 22.7, 27.4, 29.4, 29.65, 29.68, 30.0, 31.9, 34.2, 35.9, 36.0, 38.6, 55.2, 74.2, 82.1, 87.1, 113.5, 128.9, 131.1, 131.3, 131.7, 134.1, 135.2, 137.9, 157.2, 158.9, 195.4.

Enal 23cd (opposite stereochemistry at the C4 and 5 positions of **23ab**): ^{1}H NMR δ 0.59 (q, *J* = 8.0 Hz, 6H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.94 (t, *J* = 6.8 Hz, 9H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.08 (d, *J* = 6.8 Hz, 3H), 1.15-1.50 (m, 19H), 1.65 (s, 3H), 1.67 (s, 3H), 1.73 (s, 3H), 2.64-2.79 (m, 1H), 2.80-2.93 (m, 1H), 3.06 (dd, *J* = 5.1, 5.3 Hz, 1H), 3.79 (s, 3H), 3.86 (d, *J* = 7.3 Hz, 1H), 4.42 (d, *J* = 10.8 Hz, 1H), 4.49 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 9.7 Hz, 1H), 5.78 (s, 1H), 6.25 (d, *J* = 10.3 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.21 (*J* = 8.5 Hz, 2H), 9.33 (s, 1H); ^{13}C NMR δ 4.8, 6.8, 9.2, 13.4, 14.1, 14.6, 15.8, 17.1, 18.3, 22.7, 27.4, 29.3, 29.6, 29.7, 29.9, 31.9,

34.2, 35.8, 36.0, 38.5, 55.2, 74.2, 82.1, 87.1, 113.5, 128.8, 130.9, 131.1, 131.6, 133.8, 135.2, 137.9, 157.1, 158.8, 195.3.

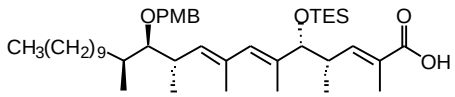


23cd

Carboxylic acid 24ab: To a solution of **23ab** (454 mg, 0.68 mmol) in *tert*-butyl alcohol (14 ml) were added 2-methyl-2-butene (8.5 ml) and a mixture of sodium chlorite (1.36 mg) and sodium dihydrogenphospate dihydrate (1.36 mg) in water (11 ml). After stirring for 20 h at room temperature, the reaction mixture was diluted with water and ethyl acetate. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water, an aqueous citric acid solution, and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, chloroform to chloroform/MeOH = 40/1) to give **24ab** (386 mg, 83%) as a colourless oil: $[\alpha]^{23}_{D}$ -6.2 (c 0.14, EtOH); IR (neat) 2926, 2813, 1687, 1247 cm^{-1}; ^{1}H NMR δ 0.59 (q, *J* = 7.8 Hz, 6H), 0.87-0.98 (m, 18H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.24-1.42 (m, 19H), 1.65 (s, 3H), 1.68 (s, 3H), 1.82 (d, *J* = 1.4 Hz, 3H), 2.64-2.78 (m, 2H), 3.06 (t, *J* = 5.4 Hz, 1H), 3.79 (s, 3H), 3.80 (d, *J* = 6.1 Hz, 1H), 4.41 (d, *J* = 10.8 Hz, 1H), 4.51 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 9.8 Hz, 1H), 5.79 (s, 1H), 6.68 (dq, *J* = 1.4, 10.4 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 2H), 7.22 (*J* = 8.5 Hz, 2H); ^{13}C NMR δ 4.8, 6.8, 9.2, 12.0, 13.4, 14.1, 14.5, 15.8, 17.0, 18.2, 22.7, 27.4, 29.3, 29.6, 29.7, 30.0, 31.9, 34.3, 35.8, 35.9, 38.6, 55.2, 74.2, 82.0, 87.0, 113.5, 125.6, 128.9, 131.0, 131.2, 131.8, 133.6, 135.3, 147.4, 158.8, 172.9; FABMS (M^{+}-H) 684; Anal. Calcd for $C_{42}H_{72}O_5Si$: C, 73.63; H, 10.59. Found: C,

73.38; H, 10.63.

Carboxylic acid 24cd (opposite stereochemistry at the C4 and 5 positions of **24ab**): ^{1}H NMR δ 0.58 (q, *J* = 8.1 Hz, 6H), 0.87-0.98 (m, 18H), 1.03 (d, *J* = 6.6 Hz, 3H), 1.18-1.52 (m, 19H), 1.65 (s, 3H), 1.67 (s, 3H), 1.81 (d, *J* = 1.4 Hz, 3H), 2.65-2.76 (m, 2H), 3.06 (t, *J* = 5.3 Hz, 1H), 3.77 (s, 3H), 3.81 (d, *J* = 7.3 Hz, 1H), 4.41 (d, *J* = 10.7 Hz, 1H), 4.51 (d, *J* = 10.7 Hz, 1H), 5.22 (d, *J* = 9.8 Hz, 1H), 5.78 (s, 1H), 6.68 (d, *J* = 10.3 Hz, 1H), 6.83 (d, *J* = 8.6 Hz, 2H), 7.21 (*J* = 8.6 Hz, 2H); ^{13}C NMR δ 4.8, 6.8, 9.2, 12.0, 13.4, 14.0, 14.6, 15.7, 17.1, 18.2, 22.6, 27.4, 29.3, 29.6, 30.0, 31.9, 34.3, 35.8, 35.8, 35.9, 38.5, 55.1, 74.1, 82.1, 87.0, 113.5, 125.7, 128.9, 130.9, 131.1, 131.7, 133.5, 135.3, 147.4, 158.8, 173.3.



24cd

Diol 26a: To a mixture of 24 (304 mg, 0.44 mmol), *N*, *N*-dimethylaminopyridine (163 mg, 1.32 mmol), and dimethylaminopyridine hydrochloride (140 mg, 0.88 mmol) in dichloromethane (8 ml) was added a solution of dicyclohexyl carbodiimide (183 mg, 0.88 mmol) in dichloromethane (1 ml) followed by a solution of **15e** (417 mg, 0.67 mmol). The solution was heated at reflux for 12 h. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in ethyl acetate. The solution was washed with a 1 M aqueous HCl solution, water, and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was filtered through a small column of silica gel (hexane/ethyl acetate = 6/1) to give **25a** as a colourless oil. IR (neat) 2925, 1715, 1248 cm^{-1}; ^{1}H NMR δ -0.01 (s, 3H), 0.00 (s, 3H), 0.56 (q, *J* = 7.9 Hz, 6H), 0.87-0.94 (m, 27H), 1.03 (d, *J* = 6.4 Hz, 3H), 1.25-1.4 (m, 19H), 1.63-1.67 (m, 6H), 1.83 (s, 3H), 2.65-2.76 (m, 2H), 3.03 (t, *J*

= 5.2 Hz, 1H), 3.52-3.89 (m, 19H), 4.32-4.54 (m, 8H), 5.26-5.29 (m, 2H), 5.78 (s, 1H), 6.63 (d, *J* = 10.2 Hz, 1H), 6.68-6.84 (m, 8H), 7.14-7.23 (m, 8H); ^{13}C NMR δ -5.4, 4.8, 6.9, 12.6, 13.8, 14.1, 14.6, 15.8, 17.0, 18.1, 18.2, 22.6, 25.9, 27.4, 29.3, 29.6, 30.0, 31.9, 34.3, 35.9, 38.4, 55.1, 63.0, 72.6, 73.2, 73.4, 74.1, 81.8, 87.0, 113.5, 113.6, 126.6, 128.8, 129.0, 129.7, 130.4, 130.6, 130.7, 131.0, 131.5, 131.7, 133.9, 135.2, 145.4, 159.0, 159.1, 167.3; FABMS (M^++Na) 1316; Anal. Calcd for $C_{77}H_{120}O_{12}Si_2$: C, 71.47; H, 9.35. Found: C, 71.23; H, 9.41.

To a solution of **25a** in THF (28 ml) was added a 1 M aqueous HCl solution (8 ml) at room temperature. After stirring for 12 h at the same temperature, the reaction was quenched with an aqueous sodium hydrogen carbonate solution, and the aqueous layer was extracted with ethyl acetate. The extract was washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (gradient elution, hexane/ethyl acetate = 4/1 to 1/1) to give **26a** (336 mg, 71% for 2 steps) as a colorless oil: IR (neat) 3428, 2925, 1707, 1612 cm^{-1}; ^{1}H NMR δ 0.88 (t, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.26-1.41 (m, 19H), 1.69 (s, 3H), 1.70 (s, 3H), 1.85 (s, 3H), 1.90 (brs, 1H), 2.10 (brs, 1H), 2.72-2.75 (m, 2H), 3.05 (t, *J* = 5.2 Hz, 1H), 3.57-3.90 (m, 19H), 4.38-4.60 (m, 8H), 5.23-5.25 (m, 1H), 5.33 (d, *J* = 9.3 Hz, 1H), 5.85 (s, 1H), 6.71 (d, *J* = 10.2 Hz, 1H), 6.81-6.85 (m, 8H), 7.17-7.25 (m, 8H); ^{13}C NMR δ 12.5, 14.1, 14.8, 14.9, 17.1, 18.4, 22.6, 27.3, 29.3, 29.6, 29.7, 30.0, 31.9, 34.2, 35.7, 36.2, 37.1, 55.2, 61.9, 67.9, 72.7, 73.2, 73.9, 74.1, 78.4, 79.1, 80.7, 87.3, 113.6, 113.7, 113.8, 129.0, 129.2, 129.7, 130.1, 130.2, 130.3, 131.2, 131.4, 131.6, 134.4, 134.7, 145.4, 158.9, 159.2, 159.3, 167.3; FABMS (M^++Na) 1088.

Diol 26b: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H), 1.17-1.60 (m, 19H), 1.68 (s, 3H), 1.70 (s, 3H), 1.85 (d, *J* = 1.1 Hz, 3H), 1.90 (brs, 1H), 2.10 (brs, 1H), 2.64-2.79 (m, 2H), 3.06 (t, *J* = 5.1 Hz, 1H), 3.51-3.93 (m, 19H), 4.35-4.63 (m, 8H), 5.21-5.30 (m, 1H), 5.34 (d, *J* = 9.5 Hz, 1H), 5.88 (s, 1H), 6.70 (dq, J = 1.1, 10.2 Hz, 1H), 6.79-6.87 (m, 8H), 7.16-7.24 (m, 8H); ^{13}C NMR δ 12.5, 14.0, 14.2, 14.7, 14.9, 17.0, 18.3, 2.6, 27.2, 29.3, 29.6, 29.9, 31.8, 34.2, 35.7, 36.1, 37.2, 55.1, 61.8, 67.9, 72.7, 73.0, 73.9, 74.3, 78.4, 79.0, 80.5, 87.2, 113.5, 113.7, 126.7, 128.9, 129.2, 130.1, 130.2, 130.3, 131.0, 131.3, 131.6, 134.0, 145.3, 158.8, 159.1, 159.2, 159.3, 167.2.

Diol 26c: $[\alpha]^{24}_{D}$ -17.4 (c 2.3, CH_2Cl_2); ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.17-1.60 (m, 19H), 1.66 (s, 3H), 1.69 (s, 3H), 1.85 (d, *J* = 0.7 Hz, 3H), 1.95 (brs, 1H), 2.15 (brs, 1H), 2.62-2.80 (m, 2H), 3.06 (dd, *J* = 5.1, 5.3 Hz, 1H), 3.51-3.93 (m, 19H), 4.34-4.63 (m, 8H), 5.18-5.33 (m, 2H), 5.84 (s, 1H), 6.69 (dq, *J* = 0.7, 10.1 Hz, 1H), 6.75-6.87 (m, 8H), 7.13-7.26 (m, 8H); ^{13}C NMR δ 12.5, 13.9, 14.0, 14.6, 15.0, 17.2, 18.4, 22.6, 27.2, 29.2, 29.5, 29.6, 29.9, 31.8, 34.2, 35.8, 36.0, 37.1, 55.1, 61.8, 67.8, 72.7, 72.9, 73.8, 74.3, 78.3, 78.9, 80.6, 87.1, 113.5, 113.7, 126.6, 129.0, 129.1, 129.5, 129.7, 130.0, 130.1, 130.2, 130.9, 131.5, 133.6, 135.0, 145.2, 158.8, 159.1, 159.2, 167.2.

Diol 26d: ^{1}H NMR δ 0.88 (t, *J* = 6.7 Hz, 3H), 0.92 (d, J = 6.8 Hz, 3H), 0.96 (d, *J* = 6.7 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.17-1.60 (m, 19H), 1.64 (s, 3H), 1.69 (s, 3H), 1.85 (d, *J* = 1.1 Hz, 3H), 1.90 (brs, 1H), 2.20 (brs, 1H), 2.62-2.80 (m, 2H), 3.06 (dd, *J* = 5.1, 5.2 Hz, 1H), 3.52-3.90 (m, 19H), 4.31-4.62 (m, 8H), 5.20-5.33 (m, 1H), 5.79 (s, 1H), 6.70 (d, *J* = 10.1 Hz, 1H), 6.77-6.86 (m, 8H), 7.15-7.25 (m, 8H); ^{13}C NMR δ 12.5, 13.9, 14.0, 14.7, 15.0, 17.2, 18.4, 22.6, 27.2, 29.3, 29.6, 29.9, 31.8, 34.2, 35.8, 36.1, 37.0, 55.1, 61.8, 67.8, 72.7, 73.1, 73.9, 74.3, 78.4, 79.0, 80.6, 87.1, 113.5, 113.7,

126.6, 129.0, 129.2, 129.5, 129.7, 130.1, 130.2, 130.9, 131.5, 133.7, 134.9, 145.3, 158.8, 159.1, 159.2, 167.2.

Carboxylic Acid 27a: To a mixture of Dess-Martin Periodinane (573 mg, 1.35 mmol) and pyridine (129 mg, 1.63 mmol) in dichloromethane (2 ml) was added a solution of **26a** (347 mg, 0.32 mmol) in dichloromethane (6 ml) at room temperature. After stirring for 2 h at the same temperature, the reaction mixture was diluted with an aqueous sodium hydrogen carbonate solution and ethyl acetate. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with a 1 M aqueous sodium thiosulfate solution, water, and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was filtered through a small column of silica gel (hexane/ethyl acetate = 5/1) to give the corresponding aldehyde as a colorless oil, which was used without further purification.

To a solution of the resulting aldehyde in *tert*-butyl alcohol (5 ml) were added 2-methyl-2-butene (3 ml) and a mixture of sodium chlorite (640 mg) and sodium dihydrogenphospate dihydrate (640 mg) in water (5 ml). After stirring for 20 h at room temperature, the reaction mixture was diluted with water and ethyl acetate. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water, an aqueous citric acid solution and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (chloroform/methanol = 10/1) to give **27a** (265 mg, 77% for 2 steps) as a colorless oil. IR (neat) 2926, 1713, 1667, 1613 cm^{-1}; ^1H NMR δ 0.88 (t, J = 6.5 Hz, 3H), 0.96 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H), 1.26-1.64 (m, 22H), 1.84 (s,

3H), 1.86 (s, 3H), 1.95 (s, 3H), 2.78-2.86 (m, 1H), 3.13 (t, *J* = 5.1 Hz, 1H), 3.73-3.77 (m, 14H), 4.09-4.10 (m, 1H), 4.12-4.60 (m, 10H), 5.61 (d, *J* = 7.5 Hz, 1H), 5.79 (d, *J* = 9.7 Hz, 1H), 6.76-6.93 (m, 9H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.18-7.24 (m, 8H); ^{13}C NMR δ 12.7, 13.3, 14.0, 14.9, 17.1, 16.6, 18.2, 18.6, 22.6, 27.2, 29.2, 29.3, 29.6, 29.9, 31.8, 34.0, 36.2, 36.4, 39.9, 55.1, 55.2, 67.5, 72.2, 73.0, 74.3, 74.6, 77.5, 87.1, 113.5, 113.6, 113.7, 113.8, 113.9, 127.5, 128.7, 129.0, 129.2, 129.9, 130.0, 131.1, 131.4, 133.2, 141.2, 142.7, 144.0, 159.0, 159.1, 159.2, 159.5, 166.3, 172.7, 203.6; FABMS (M^++Na) 1100.

Carboxylic Acid 27b: ^{1}H NMR δ 0.88 (t, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.20-1.68 (m, 22H), 1.84 (s, 3H), 1.88 (s, 3H), 1.95 (s, 3H), 2.70-2.83 (m, 1H), 3.12 (t, *J* = 5.1 Hz, 1H), 3.62-3.78 (m, 14H), 4.02-4.06 (brs, 1H), 4.15-4.53 (m, 10H), 5.05-5.23 (m, 1H), 5.75 (d, *J* = 9.4 Hz, 1H), 6.70-6.88 (m, 9H), 6.94 (d, *J* = 8.4 Hz, 1H), 7.07-7.25 (m, 8H); ^{13}C NMR δ 12.8, 13.4, 14.1, 14.9, 16.7, 18.2, 22.6, 27.2, 29.3, 29.6, 29.9, 31.3, 34.0, 36.2, 36.4, 40.0, 55.1, 55.2, 67.5, 72.1, 72.7, 73.1, 74.4, 74.6, 77.7, 87.1, 113.6, 113.7, 113.9, 127.4, 128.4, 129.0, 129.3 , 129.5, 130.0, 130.1, 130.2, 131.2, 131.3, 133.6, 140.7, 142.9, 143.7, 159.3, 159.5, 166.6, 202.5.

Carboxylic Acid 27c: $[\alpha]^{22}_{D}$ -33.8 (c 2.5, CH_2Cl_2); ^{1}H NMR δ 0.88 (t, *J* = 6.6 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.15-1.68 (m, 22H), 1.84-1.88 (m, 6H), 1.94 (s, 3H), 2.77-2.85 (m, 1H), 3.13 (dd, *J* = 5.1, 5.3 Hz, 1H), 3.62-3.80 (m, 14H), 4.02-4.08 (brs, 1H), 4.14-4.58 (m, 10H), 5.09-5.28 (m, 1H), 5.75 (d, *J* = 9.7 Hz, 1H), 6.73-6.89 (m, 9H), 6.96 (d, *J* = 8.4 Hz, 1H), 7.07-7.25 (m, 8H); ^{13}C NMR δ 12.7, 13.3, 14.0, 14.9, 16.6, 18.1, 18.2, 22.6, 27.2, 29.3, 26.6, 29.9, 31.8, 34.0, 36.1, 36.4, 40.0, 55.1, 55.2, 67.5, 72.1, 72.7, 73.1, 74.4, 74.5, 77.7, 87.1, 113.6, 113.7,

113.8, 127.4, 128.4, 129.0, 129.2, 129.5, 130.0, 130.1, 131.6, 133.4, 141.4, 142.9, 143.9, 159.1, 159.3, 159.5, 166.6, 202.4.

Carboxylic Acid 27d: ^{1}H NMR δ 0.88 (t, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.15-1.67 (m, 22H), 1.83 (s, 3H), 1.88 (s, 3H), 1.95 (s, 3H), 2.75-2.80 (m, 1H), 3.13 (t, *J* = 5.2 Hz, 1H), 3.62-3.80 (m, 14H), 4.07(d, *J* = 3.8 Hz , 1H), 4.17-4.60 (m, 10H), 5.12-5.19 (m, 1H), 5.79 (d, *J* = 10.0 Hz, 1H), 6.75-6.93 (m, 9H), 7.02 (s, 1H), 7.08-7.25 (m, 8H); ^{13}C NMR δ 12.7, 13.3, 14.1, 15.0, 16.5, 18.2, 18.6, 22.6, 27.2, 29.3, 29.6, 29.9, 31.9, 36.1, 36.4, 39.9, 55.2, 67.6, 72.2, 72.8, 73.1, 74.4, 74.6, 78.9, 87.2, 113.6, 113.7, 113.9, 127.6, 128.7, 129.1, 129.3, 129.7, 129.9, 130.0, 131.1, 131.7, 133.0, 141.9, 142.8, 144.7, 159.0, 159.2, 159.3, 159.5, 166.3, 172.3, 203.8.

Tetraol 18a (khafrefungin): To a solution of **27a** (47.5 mg, 0.044 mmol) in dichloromethane (4 ml) was added boron trichloride (0.22 ml of a 1.0 M solution in heptane, 0.22 mmol) at –78 °C. After stirring for 10 min at the same temperature, the reaction was quenched with an aqueous sodium hydrogen carbonate solution. After an aqueous citric acid solution and ethyl acetate were added, the mixture was warmed to room temperature and stirred for 30 min. After the phases were separated, the aqueous layer was extracted with ethyl acetate. The combined organic extracts were washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (chloroform/methanol/water = 2.5/1/0.1) to give **18a** (14.9 mg, 57%) as a colorless oil. For analytical use, further purification was performed using RP-HPLC on Inertsil C8-3 10 x 250 mm (GL science), eluted with a mobile phase of acetonitrile/0.1% aq. H_3PO_4 = 4/1 at a flow rate of 4.0 ml/min. The

retention time for **18a** is 14.2 min: $[\alpha]^{23}_{D}$ -27 (c 0.095, MeOH). The concentration for the measurement of the optical rotations of **18a-d** was determined using the extinction coefficient at 286 nm (14300) which was recorded by Merck. The optical rotation of **18a** based on concentration determined by weight was also measured. $[\alpha]^{28}_{D}$ –16.6 (c 0.17, MeOH). IR (neat) 3428, 2924, 1712, 1661, 1614, 1453, 1246 cm^{-1}; ^{1}H NMR δ 0.89 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 6.6 Hz, 3H), 1.28-1.44 (m, 18H), 1.49-1.55 (m, 1H), 1.89 (s, 3H), 1.93 (s, 3H), 1.95 (d, *J* = 1.3 Hz, 3H), 2.71-2.77 (m, 1H), 3.25 (t, *J* = 5.6 Hz, 1H), 3.82 (dd, *J* = 4.2, 12.3 Hz, 1H), 3.92 (dd, *J* = 2.5, 12.3 Hz, 1H), 4.20 (d, *J* = 1.7 Hz , 1H), 4.25 (dd, *J* = 1.7, 8.8 Hz, 1H), 4.37 (dq, *J* = 6.6, 9.8 Hz, 1H), 4.97 (ddd, *J* = 2.5, 4.2, 8.8 Hz, 1H), 5.72 (d, *J* = 9.8 Hz, 1H), 6.79 (brd, *J* = 9.8 Hz, 1H), 7.09 (s, 1H); ^{13}C NMR δ 13.0, 13.8, 14.5, 14.7, 16.9, 18.0, 18.2, 23.7, 28.1, 30.5, 30.7, 30.85, 30.89, 31.0, 33.1, 34.7, 37.3, 37.5, 41.3, 61.5, 71.2, 71.8, 75.4, 79.8, 129.4, 133.0, 134.8, 141.4, 143.8, 145.8, 168.8, 176.2, 204.8; FABMS (M^{+}-H) 595.

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Tetraol 18b: ^{1}H NMR δ 0.88 (t, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.22-1.57 (m, 19H), 1.90 (s, 3H), 1.94 (d, *J* = 1.3 Hz, 3H), 1.95 (s, 3H), 2.70-2.79 (m, 1H), 3.25 (t, *J* = 5.7 Hz, 1H), 3.82 (dd, *J* = 3.9, 12.1 Hz, 1H), 3.93 (dd, *J* = 1.7, 12.1 Hz, 1H), 4.15 (brs, 1H), 4.24 (brs, 1H), 4.32-4.40 (m, 1H), 4.85-4.97 (m, 1H), 5.74 (d, *J* = 9.8 Hz, 1H), 6.77 (d, *J* = 9.8 Hz, 1H), 7.11 (s, 1H); ^{13}C NMR δ 13.0, 13.7, 14.4, 14.7, 16.8, 18.0, 18.2, 23.7, 28.0, 30.5, 30.7, 30.8, 30.9, 33.1, 34.6, 37.3, 37.5, 41.3, 61.5, 71.3, 75.2, 79.8, 129.4, 133.1, 134.7, 141.5, 143.7, 145.9, 168.5, 176.2, 205.0.

Tetraol 18c: ^{1}H NMR δ 0.89 (t, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.22-1.40 (m, 18H), 1.49-1.58 (m, 1H), 1.91 (s, 3H), 1.94 (s, 3H), 1.95 (d, *J* = 1.5 Hz, 3H), 2.62-2.81 (m, 1H), 3.25 (t, *J* = 5.9 Hz, 1H), 3.82 (dd, *J* = 4.3, 12.3 Hz, 1H), 3.91 (dd, *J* = 2.7, 12.3 Hz, 1H), 4.16 (d, *J* = 1.5 Hz, 1H), 4.24 (dd, *J* = 1.5, 9.0 Hz, 1H), 4.38 (dq, *J* = 6.8, 9.8 Hz, 1H), 4.98 (ddd, *J* = 2.7, 4.3, 9.0 Hz, 1H), 5.74 (d, *J* = 9.8 Hz, 1H), 6.76 (d, *J* = 9.8 Hz, 1H), 7.11 (s, 1H); ^{13}C NMR δ 13.0, 13.7, 14.4, 14.7, 16.8, 18.0, 18.2, 23.7, 28.0, 30.4, 30.67, 30.72, 30.8, 30.9, 33.1, 34.6, 37.3, 37.4, 41.3, 61.5, 71.3, 71.8, 75.4, 79.8, 129.3, 133.1, 134.7, 141.6, 143.7, 146.0, 168.4, 176.2, 205.0.

Tetraol 18d: ^{1}H NMR δ 0.89 (t, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8Hz, 3H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.22-1.42 (m, 18H), 1.48-1.56 (m, 1H), 1.90 (s, 3H), 1.94 (s, 3H), 1.95 (d, *J* = 1.2 Hz, 3H), 2.69-2.80 (m, 1H), 3.25 (t, *J* = 5.6 Hz, 1H), 3.82 (dd, *J* = 4.3, 12.3 Hz, 1H), 3.91 (dd, *J* = 2.5, 12.4 Hz, 1H), 4.15 (brs, 1H), 4.24 (brd, *J* = 8.8 Hz ,1H), 4.37 (dq, *J* = 6.8, 9.9 Hz, 1H), 4.97 (ddd, *J* = 2.5, 4.3, 8.8 Hz, 1H), 5.72 (d, *J* = 9.7 Hz, 1H), 6.77 (d, *J* = 9.9 Hz, 1H), 7.10 (s, 1H); ^{13}C NMR δ 12.9, 13.7, 14.4, 14.7, 16.8, 17.99, 18.03, 23.7, 28.0, 30.4, 30.67, 30.72, 30.8, 30.9, 33.0, 34.7, 37.3, 37.4, 41.3, 61.5, 71.3, 71.8, 75.4, 79.8, 129.3, 133.1, 134.7, 141.6, 143.7, 145.9, 168.4, 176.3, 205.0.