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Stereoselective synthesis of marine macrolide Aspergillide D

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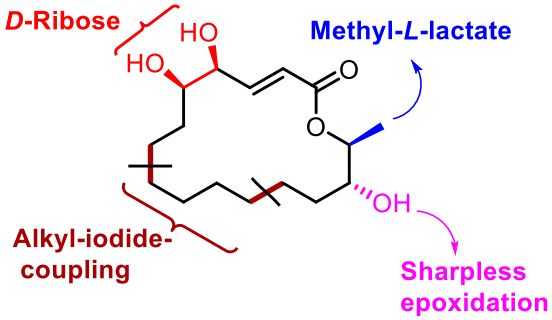
Abstract

A formal stereoselective synthesis of the naturally occurring 16-membered macrolide aspergillide D is described. The origins of the chiral centers are ribose, lactic acid and the Sharpless asymmetric epoxidation protocol. The foremost reactions involved are Yadav's protocol, the Ohira- Bestmann reaction and alkyl-iodide coupling.



Aspergillide D

Keywords: Aspergillide D, *D*-ribose, methyl *L*-lactate, epoxidation, coupling, macrolide

Introduction

Aspergillus is a genus consisting of hundreds of species of fungi found in various climates and causes aspergillosis diseases. They also produce secondary metabolites like aspergillides, aspergillic acid along with many other compounds. Aspergillides A-C are 14-membered macrolides, incorporating a *trans*-tetra hydropyran ring and aspergillic acid, which is a substituted pyrazine.[1,2] Aspergillide D is a 16-membered macrolide, isolated from the extract of a gorgonian associated marine fungal strain *Aspergillus sp*.SCSGAF0076. The structural confirmation by ^{1}H, ^{13}C NMR, NOESY, HRMS-ESI and DEPT spectral analysis was performed by the Qi group.[3] The first asymmetric synthesis of aspergillide D was reported by Mohapatra *et al*.[4]

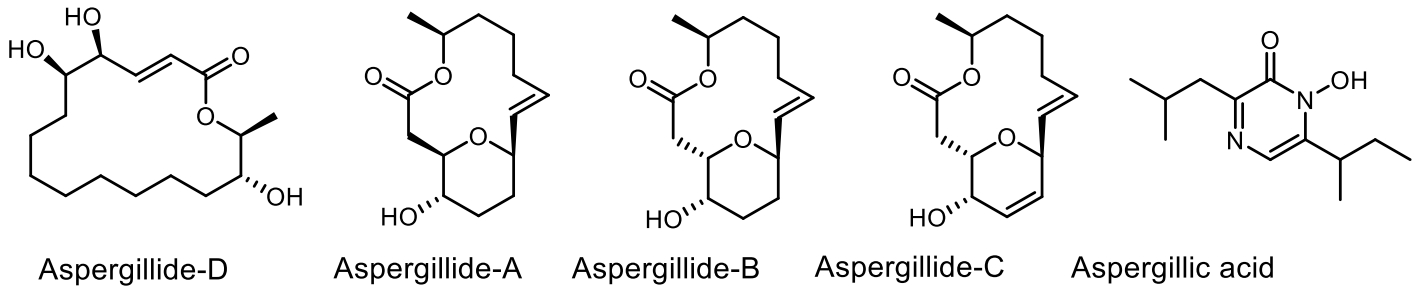
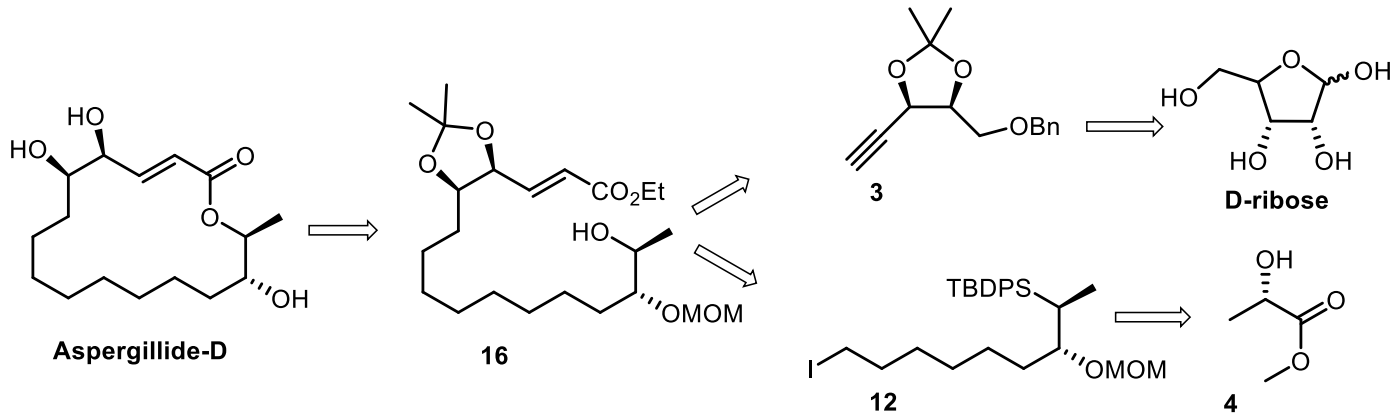


Figure 1

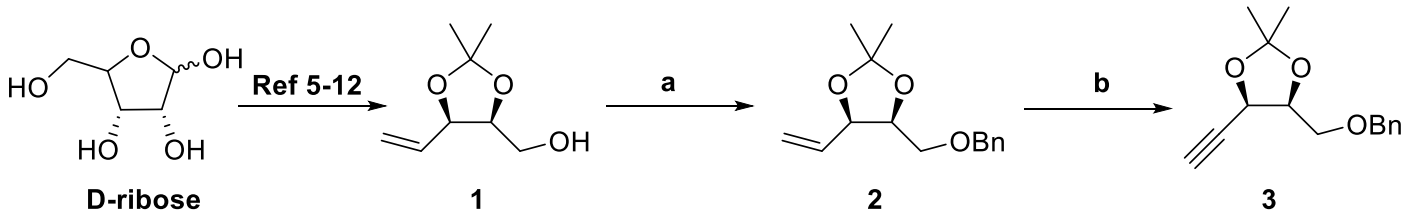
Results and Discussion

As part of our regular research program for the synthesis of biologically active natural products,[5-8] herein we report the formal stereoselective synthesis of aspergillide D. The retrosynthetic analysis (Scheme 1) reveals that aspergillide D could be synthesized by intramolecular macrolactonisation of fragment **16**. The ester (**16**) could be derived by the coupling of alkyne (**3**) and iodide fragments (**12**). The alkyne fragment could be accomplished from *D*-ribose and the iodide intermediate from methyl *L*-lactate (**4**).



Scheme 1

As depicted in Scheme **2**, the synthesis of the alkyne fragment was started from the known alcohol **1**, which was prepared from commercially available *D*-ribose using well known reports.[9-12] The alcohol 1 was protected as its benzyl ether[13] with benzyl bromide in presence of NaH in THF to afford compound **2**, which on further oxidative cleavage of terminal olefin *via* Jin's protocol by using OsO_4, 2,6-lutidine, and $NaIO_4$ leads to the corresponding terminal aldehyde,[14,15] which was subsequentially subjected to the Ohira-Bestmann reagent[16] to get the terminal alkyne fragment (**3**) in good yields.

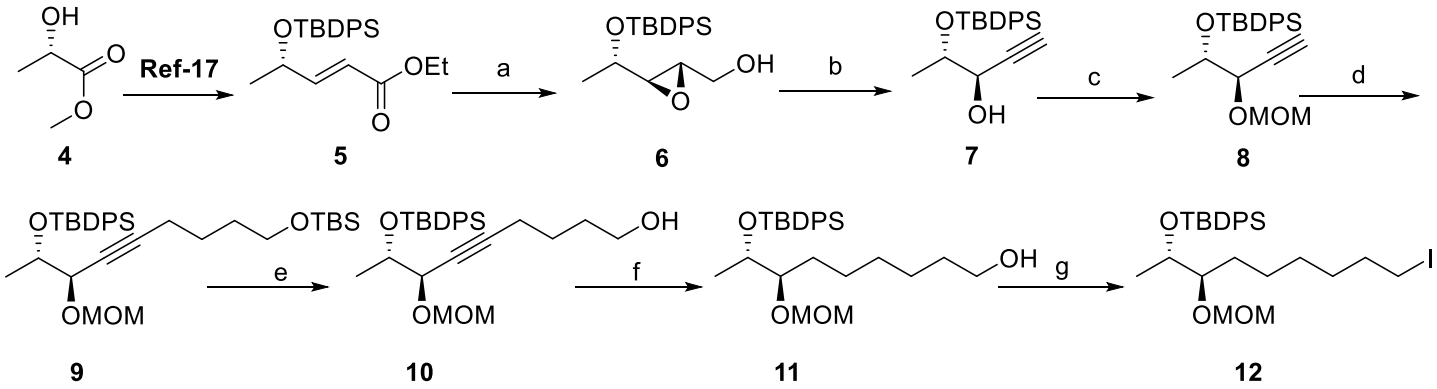


Reagents & Conditions: (a) NaH, BnBr, THF 0 °C to rt, 16 h; (b) (i) OsO_4, $NaIO_4$, 2,6-lutidine, 1,4-dioxane/ H_2O (3:1), 25 °C, 3 h; (ii) Dimethyl(1-diazo-2-oxopropyl)phosphonate, K_2CO_3, MeOH, rt., 5 h, 68% over two steps.

Scheme 2

The synthesis of the iodide fragment **12**, was started from commercially available methyl *L*-lactate[17] (**4**), by protection of the secondary alcohol as its silyl ether using TBDPS-Cl in the presence of base. This was followed by a controlled reduction of the ester to give the desired aldehyde, which was immediately subjected to a homologation reaction with a two carbon Wittig yilde leading to the *α,β*-unsaturated ester **5**. Reduction of the ester moiety was efficiently carried out using DIBAL-H at -78 °C in CH_2Cl_2 to afford the allylic alcohol in good yield. Thus obtained double bond was subjected to Sharpless asymmetric epoxidation[18-20] using (+)-DIPT as a chiral source in presence of $Ti(O^i\text{-}Pr)_4$ and TBHP at -20 °C to furnish the desired epoxide **6** in good yields. Yadav's protocol[21,22] was applied here for a base induced elimination reaction to give the chiral propargyl alcohol **7** in 90% yield overall covering two steps from the epoxy alcohol (**6**) using CCl_4-Ph_3P under reflux conditions followed by reaction with *n*-BuLi at -20 °C in THF. The hydroxyl functionality in propargyl alcohol 7 was protected as a methoxymethyl ether with MOM-Cl in the presence of DIPEA to afforded compound **8** in excellent yield.[23]

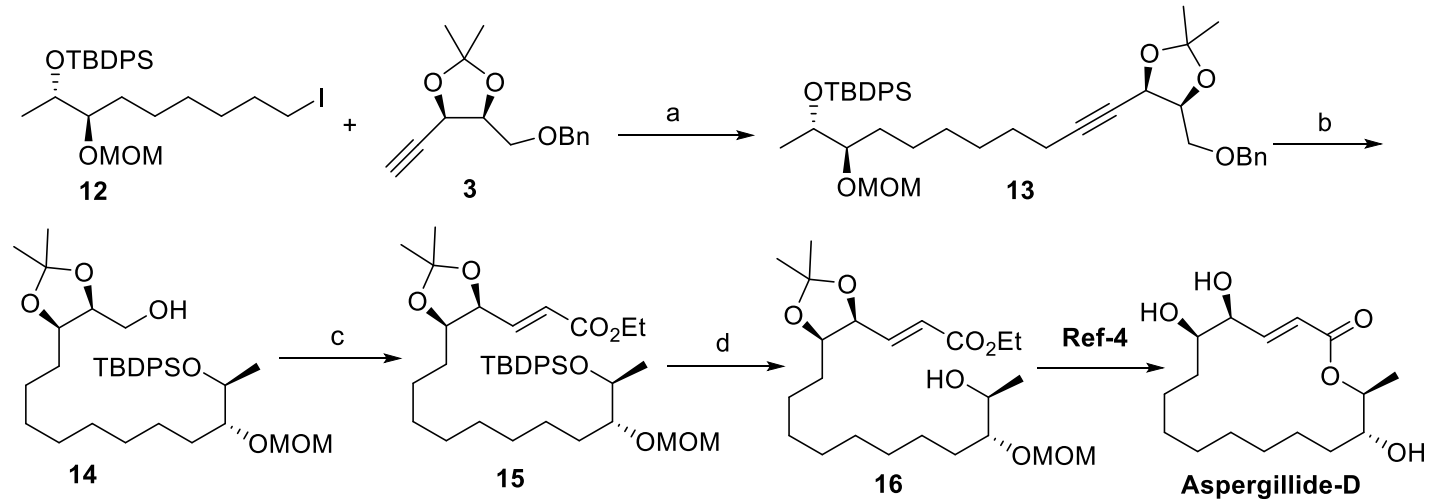
Coupling of (5*R*,6*S*)-5-ethynyl-6,9,9-trimethyl-8,8-diphenyl-2,4,7-trioxa-8-siladecane (**8)** and *tert*-butyl-(4-iodobutoxy)-dimethylsilane was carried out in the presence of *n*-BuLi[24,25] to afford compound **9** in 70% yield. The selective desilylation of TBS in the presence of TBDPS ether with pyridinium *p*-toluenesulfonate[26] in methanol at room temperature afforded the primary alcohol **10**. Saturation of the triple bond was achieved with Pd/C[27] (10%) under a hydrogen atmosphere in EtOAc to yield alcohol **11**. The corresponding alcohol was transformed into the iodide[28] in the presence of iodine-TPP at toluene-acetonitrile (3:1) under reflux conditions to afford compound **12**.



Reagents and Conditions: (a) (i) DIBAL-H, CH_2Cl_2, -78 °C, 30 min, 85%; (ii) (+)-DIPT, Ti(O^iPr)$_4$, TBHP, CH_2Cl_2, -20 °C, 12 h, 95%; (b) (i) CCl_4, TPP, reflux, 5 h, 95%; (ii) *n*-BuLi, -20 °C, 30 min, THF, 85%; (c) MOMCl, DIPEA, CH_2Cl_2, rt., 12 h, 96%; (d) *tert*-Butyl-(4-iodobutoxy)dimethylsilane, *n*-Buli, THF:HMPA (2:1), -78 °C, 1.5 h, 70%; (e) PPTS, MeOH, rt, 1 h, 90%; (f) H_2, Pd/C (10%), EtOH, rt, 16 h, 90%, (g) TPP, I_2, Imidazole, Toluene / Acetonitrile (3:1), rt, 30 min, 95%.

Scheme 3

The coupling of iodide **12** and the alkyne compound **3** was carried out in the presence of *n*-BuLi[24,25] in a THF-HMPA (2:1) mixture at -78 °C to obtain the desired compound **13** in 73% yield. The concomitant removal of the triple bond as well as the benzyl group was achieved *via* a Pd/C (10%) catalyzed hydrogenation in EtOAc to afford the saturated primary alcohol[29] **14** in 90% yield.



Reagents & Conditions: (a) **3**, *n*-BuLi, THF/HMPA (2:1), -78 °C, 90 min, 73%; (b) H_2, Pd/C, EtOH, rt, 16 h, 90%; (c) (i) DMP, $NaHCO_3$, CH_2Cl_2, 0 °C to rt, 1 h, (ii) $Ph_3P{=}CHCO_2Et$, toluene, reflux, 2 h, 75% over two steps; (d) HF•Py, THF, 0 °C to rt, 12 h, 75%.

Scheme 4

Oxidation of the primary alcohol with Dess-martin periodinane in CH_2Cl_2 gave the corresponding aldehyde and was immediately reacted with the C_2-ylide in a Wittig reaction resulting in the *α,β*- unsaturated ester[30] in

good yield. Finally, the TBDPS group in compound **15** was deprotected using HF•Pyridine[31,32] in THF at room temperature to afford the secondary alcohol **16** in very good yield. This completed the formal synthesis of the aspergillide D fragment **16** which was identical in all aspects with the compound reported in the literature data.[4]

Conclusions

In summary, we have synthesized the desired intermediate **16**, which completes the formal synthesis of aspergillide D in an efficient and completely stereo controlled manner with the longest linear sequence of 14 steps in good yields. The synthesis was started from commercially available starting materials and the majority of the required stereo centers were deduced from natural sources such as methyl *L*-lactate and *D*-ribose. The key reactions involved in the synthesis are the Sharpless asymmetric epoxydation, Ohira-Bestmenn reagent, Yadav's protocol for propargyl alcohols and the alkyl iodide coupling.

Experimental Section

General. All the air and moisture sensitive reactions were carried out under an inert atmosphere (nitrogen or argon). Oven-dried glass ware was used to perform all the reactions. Freshly distilled anhydrous solvents were used for air and moisture sensitive reactions. Commercially available reagents were used as such. The purification of the compounds was carried out via column chromatography using silica gel (60-120 mesh) packed in glass columns. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ on a 400 MHz and 500 MHz Brucker spectrometer, using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr / Thin Film optics. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. Optical rotation values were recorded on a Horiba sepa 300 polarimeter. High resolution mass spectra (HRMS) [ESI+] were obtained using either a TOF or a double focusing spectrometer.

(4*S*,5*R*)-4-[(Benzyloxy)methyl]-2,2-dimethyl-5-vinyl-1,3-dioxolane (2). To a stirred solution of NaH (0.46 g, 11.3 mmol) in THF (20 mL) was added [(4*S*,5*R*)-2,2-dimethyl-5-vinyl-1,3-dioxolan-4-yl]methanol (1.55 g, 9.5 mmol), which was dissolved in THF (10 mL). BnBr was slowly added (1.24 mL, 10.4 mmol) at 0 °C, then the reaction mixture was stirred at room temperature for 16 h. After completion of the reaction (confirmed by TLC), the reaction mixture was diluted by adding EtOAc (25 mL) and was quenched with saturated $NaHCO_3$. The reaction mixture was extracted with EtOAc (2×20 mL) and the combined organic layers were dried over Na_2SO_4, then evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (1:9) mixture to afford, olefin **2** (1.4 g, 90%) as an oil. Optical rotation $[\alpha]_D^{25}$ +5.5 (c = 1, $CHCl_3$). $^{Lit}[\alpha]_D^{25}$ +1.7 (c = 1, $CHCl_3$)[13]; IR (neat): 2987, 2929, 2868, 1696, 1374, 1223, 1092, 737, 772, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 - 7.27 (m, 5H), 5.86 - 5.76 (m, 1H), 5.35 (dt, 1H, *J* 17.1, 1.3 Hz), 5.21 (dt, 1H, *J* 10.3, 0.9 Hz), 4.56 - 4.64 (m, 2H), 4.51 (d, 1H, *J* 12.0 Hz), 4.42 - 4.36 (m, 1H), 3.47 (d, 1H, *J* 2.4 Hz), 3.45 (d, 1H, *J* 1.3 Hz), 1.50 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 133.5, 128.3, 127.7, 127.6, 118.1, 108.8, 78.4, 76.9, 73.4, 69.4, 27.8, 27.3; HRMS (ESI): *m/z* $[M + Na]^+$calcd for $C_{15}H_{20}NaO_3$: 271.1059; found: 271.1279.

(4*S*,5*R*)-4-[(Benzyloxy)methyl]-5-ethynyl-2,2-dimethyl-1,3-dioxolane (3). To a stirred solution of olefin **2** (1.25 g, 5.0 mmol) in a dioxane-water (3:1, 12 mL) mixture was added 2,6-lutidine (1.2 mL) and OsO_4 (0.025 g, 0.1 mmol), which was dissolved in *tert*-BuOH, followed by $NaIO_4$ (4.3 g, 20.2 mmol) at room temperature. The resulting mixture was stirred for 12 h. The completion of reaction was confirmed by TLC, then diluted with CH_2Cl_2 (15 mL) and quenched with water (15 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2×25 mL). The combined organic layers were washed with a brine solution, dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (5:5) mixture to afford, (4*S*,5*S*)-5-[(benzyloxy)methyl]-2,2-dimethyl-1,3-dioxolane-4-carbaldehyde (1.0 g, 80%) as a liquid.

To a stirred solution of the above aldehyde (0.98 g, 3.9 mmol) in methanol (15 mL) was added dimethyl-1-diazo-2-oxopropyl phosphonate (0.9 g, 4.7 mmol) at 0 °C and then K_2CO_3 was added (1.35 g, 9.8 mmol) in portions over 10 minutes. The reaction was allowed to stir at 0 °C for 2 h and then slowly warm up to r.t. and stirred for 1 h. After the completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure. The residue was quenched with saturated ammonium chloride and extracted with EtOAc (2×20 mL), the organic layers were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Purification was performed by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (1:9) mixture to afford alkyne **3** (0.72 g, 72%) as an oil. Optical rotation $[\alpha]_D^{25}$ +26.8 (c = 0.5, $CHCl_3$); IR (neat): 3032, 2923, 2854, 2225, 1220, 1063, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 - 7.27 (m, 5H), 4.83 (dd, 1H, *J* 5.8, 2.2 Hz), 4.59 (ABq, 2H, *J* 24.9, 12.1 Hz), 4.37 - 4.32 (m, 1H), 3.76 (dd, 2H, *J* 6.2, 2.7 Hz), 2.49 (d, 1H, *J* 2.2 Hz), 1.55 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 128.4, 127.9, 127.7, 110.6, 79.4, 76.4, 75.5, 73.6, 69.8, 67.6, 27.6, 25.9; HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{15}H_{18}O_3$: 269.11482; found: 269.11794.

Ethyl-(4*S*,2*E*)-4-[(*t*-butyldiphenylsilyl)oxy]pent-2-enoate (5). To a stirred solution of (*S*)-2-[(*tert*-butyldi phenylsilyl)oxy]propanal (4.5 g, 14.4 mmol) in toluene (50 mL) was added $Ph_3P{=}CHCO_2Et$ (6.5 g, 18.7 mmol). The resulting mixture was refluxed for 2 h and the completion of reaction was confirmed by TLC, then quenched with water and extracted with EtOAc (2×30 mL). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under reduced pressure and the crude was purified by column chromatography using silica gel (60-120 mesh) by eluting with EtOAc-hexane (1:9) mixture to afford, (4*S*,2*E*)-ethyl-4-[(*tert*-butyldiphenylsilyl)oxy]pent-2-enoate, **5** (5.1 g, 92%) as a liquid. Optical rotation $[\alpha]_D^{25}$ -38.0 (c = 1, $CHCl_3$), $^{Lit}[\alpha]_D^{25}$ -38.0 (c = 1, $CHCl_3$)[17]; IR (neat): 2925, 2855, 1725, 772, 703, 578 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 - 7.61 (m, 4H), 7.46 - 7.33 (m, 6H), 6.89 (dd, 1H, *J* = 15.5, 4.4 Hz), 6.00 (dd, 1H, *J* 15.5, 1.6 Hz), 4.50 - 4.42 (m, 1H), 4.24 - 4.14 (m, 2H), 1.30 (t, 3H, *J* 7.0 Hz), 1.13 (d, 3H, *J* 6.6 Hz), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 151.5, 135.8, 135.7, 133.9, 133.4, 129.7, 127.6, 127.6, 119.1, 68.6, 60.3, 26.9, 23.3, 19.2, 14.3; HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{23}H_{30}O_3NaSi$: 405.18564; found: 405.18602.

{(2*S*,3*R*)-3-((*S*)-1-[(*t*-Butyldiphenylsilyl)oxy)ethyl]oxiran-2-yl}methanol (6). To a stirred solution of ester **5** (4.5 g, 11.8 mmol) in dry CH_2Cl_2 (60 mL) was added DIBAL-H (15.4 mL, 27.1 mmol) drop wise at -78 °C and was stirred for 30 min at the same temperature. The reaction was then quenched with saturated Rochelle salt and stirred for a further 6 h. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×20 mL). The combined organic layers were washed with brine (30 mL) and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure led to a crude product that was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (2:8) mixture to afford, (4*S*,2*E*)-4-[(*tert*-butyldiphenylsilyl)oxy]pent-2-en-1-ol (3.4 g, 85%) as colorless liquid.

To a stirred solution of (+)-DIPT (0.58 mL, 2.8 mmol) and molecular sieves (2.0 g, 4 °A) in anhydrous CH_2Cl_2 at -20 °C were added $Ti(O^iPr)_4$ (1.13 mL, 3.7 mmol) and TBHP (5.1 mL, 56.4 mmol). After stirring for 20 min at -20 °C the allylic alcohol (3.2 mL, 9.4 mmol) was added, which was dissolved in dry CH_2Cl_2 (20 mL), then stirred for 12 h at -20 °C. The completion of reaction was detected by TLC, then quenched with a 20% NaOH solution (35 mL). The reaction mixture was stirred for a further 5 h and the reaction mixture was extracted with CH_2Cl_2 (2x20 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of the solvent under reduced pressure gave a crude product that was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (2:8) mixture to afford epoxy alcohol **6** (3.2 g, 95%) as a colorless liquid. Optical rotation $[\alpha]_D^{25}$ -48.6 (c = 1.5, $CHCl_3$). IR (neat) 3589, 2925, 2855, 1697, 1464, 1109, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 - 7.64 (m, 4H), 7.47 - 7.35 (m, 6H), 3.75 - 3.60 (m, 2H), 3.46 - 3.37 (m, 1H), 2.90 (dd, 1H, *J* 5.6, 2.1 Hz), 2.69 - 2.65 (m, 1H), 1.54 - 1.48 (m, 1H), 1.22 (d, 3H, *J* 6.2 Hz), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.7, 135.9, 133.9, 129.9, 127.6, 127.6, 68.7, 61.2, 58.8, 57.1, 26.9, 20.8, 19.2; HRMS (ESI): *m/z* $[M + Na]^+$calcd. for $C_{21}H_{28}O_3NaSi$: 379.169; found: 379.171.

(3*R*,4*S*)-4-[(*t*-Butyldiphenylsilyl)oxy]pent-1-yn-3-ol (7). To a stirred solution of epoxy alcohol **6** (3.0 g, 8.4 mmol) in CCl_4 (50 mL) was added TPP (2.2 g, 8.4 mmol) and was refluxed for 5 h. After completion of the reaction as indicated by TLC, the reaction mixture was cooled to 0 °C, then diluted with hexane (30 mL) and filtered through a celite bed. The filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (1:9) mixture to afford, *tert*-butyl [(*S*)-1-((2*R*,3*R*)-3-(chloromethyl)oxiran-2-yl)ethoxy]diphenyl silane (3.0 g, 95%) as a colorless oil.

To a stirred solution of the above epoxychloride (2.9 g, 7.75 mmol) in anhydrous THF (20 mL) was added *n*-BuLi (9.30 mL, 23.3 mmol) dropwise at -20 °C under a nitrogen atmosphere. The reaction mixture was further stirred for 30 min. After completion of the reaction (monitored by TLC), the reaction was quenched by adding saturated NH_4Cl, was then diluted with EtOAc (30 mL) and extracted with EtOAc (2×20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, then evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (1:9) mixture to afford, alkyne compound **7** (2.2 g, 85%) as colorless oil. Optical rotation $[\alpha]_D^{25}$ 13.5 (c = 1, $CHCl_3$); IR (neat): 3590, 3050, 2926, 2855, 2230, 1464, 1109, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.73 - 7.67 (m, 4H), 7.48 - 7.37 (m, 6H), 4.30 - 4.25 (m, 1H), 4.03 - 3.95 (m, 1H), 2.48 - 2.42 (m, 2H), 1.15 (d, 3H, *J* 6.3 Hz), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.8, 135.7, 133.6, 133.4, 129.9, 129.8, 127.8, 127.6, 81.6, 74.2, 71.9, 66.9, 26.9, 19.3, 17.9; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{21}H_{26}O_2NaSi$: 361.15943; found: 361.16016.

(5*R*,6*S*)-5-Ethynyl-6,9,9-trimethyl-8,8-diphenyl-2,4,7-trioxa-8-siladecane (8). To a stirred solution of alkyne **7** (1.5 g, 4.4 mmol) in anhydrous CH_2Cl_2 (15 mL) was added subsequently DIPEA (3.9 mL, 22.2 mmol) and MOM-Cl (1.0 mL, 13.3 mmol) at r.t. and was then stirred for 12 h. After completion of the reaction (confirmed by TLC), the reaction was quenched with cooled water (15 mL) and extracted with EtOAc (2×20 mL). The combined organic layers were dried over Na_2SO_4, evaporated under reduced pressure and the crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (1:9) mixture to afford methoxymethyl ether **8** (1.52 g, 90%) as a colorless oil. Optical rotation $[\alpha]_D^{25}$ -49.0 (c = 0.5, $CHCl_3$); IR (neat): 3048, 2926, 2855, 2230, 1696, 1465, 1109, 1039, 772, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.75 - 7.67 (m, 4H), 7.45 - 7.34 (m, 6H), 4.91 (d, 1H, *J* 6.6 Hz), 4.60 (d, 1H, *J* 6.6 Hz), 4.37 - 4.32 (m, 1H), 4.05 - 3.97 (m, 1H), 3.35 (s, 3H), 2.37 (s, 1H), 1.16 (d, 3H, *J* 6.1 Hz), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9,

135.9, 134.2, 133.7, 129.6, 129.5, 127.5, 94.4, 80.6, 74.5, 71.4, 70.4, 55.6, 26.9, 19.3, 18.6; HRMS (ESI): *m/z* [M + Na]$^+$calcd. for $C_{23}H_{30}O_3NaSi$: 405.18564; found: 405.18593.

***t*-Butyl(4-iodobutoxy)dimethylsilane.** To a stirred solution of 4-[(*tert*-butyldimethylsilyl)oxy]butan-1-ol (1.5 g, 7.35 mmol) in a toluene-acetonitrile (3:1, 25 mL) mixture was added TPP (1.7 g, 6.6 mmol), imidazole (0.75 g, 11.0 mmol) and iodine (2.8 g, 11.0 mmol) and was then stirred for 30 min at r.t. After completion of the reaction (confirmed by TLC), the reaction was terminated with a Hypo solution at 0 ^{o}C and was stirred for 15 min, then extracted with EtOAc (2×25 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (5:95) mixture to afford, *tert*-butyl (4-iodobutoxy)dimethylsilane (1.84 g, 98%) as a colorless oil. IR (neat): υ 2928, 2855, 1738, 1365, 1226, 1033, 836, 774 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (t, 2H, *J* 6.2 Hz), 3.22 (t, 2H, *J* 7.1 Hz), 1.94 - 1.87 (m, 2H), 1.65 - 1.58 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.9, 33.5, 30.2, 25.9, 18.3, 7.1, -5.3; HRMS (ESI): *m/z* [M + Na]$^+$calcd. for $C_{10}H_{23}INaOSi$: 337.01545; found: 337.19723.

(5*S*,6*R*)-6-(Methoxymethoxy)-2,2,5,14,14,15,15-heptamethyl-3,3-diphenyl-4,13-dioxa-3,14-disilahexadec-7-yne (9). To a stirred solution of alkyne **8** (1.5 g, 4.5 mmol) in a THF-HMPA (2:1, 10 mL) mixture was added dropwise *n*-BuLi (1.8mL, 4.5 mmol) at -78 ^{o}C under a nitrogen atmosphere. While adding *n*-BuLi, the reaction mixture converted to a brown color and was then stirred for 30 min at the same temperature. Then *tert*-butyl(4-iodobutoxy)dimethylsilane (1 g, 3.2 mmol), which was dissolved in THF (5 mL), was added. The reaction mixture was stirred for 1 h, and allowed to warm up to room temperature. After completion of the reaction (confirmed by TLC), the reaction waq quenched with saturated NH_4Cl and the solvent was removed under reduced pressure. The residue was extracted with EtOAc (2x20 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel, 60-120 mesh by eluting with a EtOAc-hexane (5:95) mixture to afford the coupled product **9** (1.76 g, 70%) as a color less liquid. Optical rotation $[\alpha]_D^{25}$ -90.1 (c = 1.0, $CHCl_3$); IR (neat): 3045, 2953, 2926, 2856, 2240, 1540, 1465, 1107, 1039, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 - 7.69 (m, 4H), 7.44 - 7.33 (m, 6H), 4.92 (d, 1H, *J* 6.6 Hz), 4.59 (d, 1H, *J* 6.7 Hz), 4.29 - 4.27 (m, 1H), 3.99 - 3.94 (m, 1H), 3.59 (t, 2H, *J* 12.2, 6.5 Hz), 3.35 (s, 3H), 2.18 (td, 2H, *J* 7.0, 1.8 Hz), 1.61 - 1.49 (m, 3H), 1.13 (d, 3H, *J* 6.3 Hz), 1.07 (s, 9H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.9, 135.9, 134.4, 134.0, 129.4, 127.4, 94.1, 86.9, 71.8, 70.8, 62.6, 55.4, 31.9, 29.6, 26.9, 25.9, 25.0, 19.2, 18.7, 18.6, -5.3; HRMS (ESI): *m/z* [M + Na]$^+$calcd. for $C_{33}H_{52}O_4Si_2Na$: 591.32975; found: 591.32055.

(7*R*,8*S*)-8-[(*t*-Butyldiphenylsilyl)oxy]-7-(methoxymethoxy)non-5-yn-1-ol (10). To a stirred solution of compound **9** (1.7 g, 3.0 mmol) in anhydrous MeOH (15 mL) was added PPTS (0.82 g, 3.3 mmol) at r.t. and was stirred for 1 h. After completion of the reaction, the solvent was removed and the residue was quenched with NH_4Cl solution and extracted with EtOAc (2x10 mL), then the organic layers were washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel (60-120 mesh) by eluting with EtOAc-hexane (2:8) mixture to afford, alcohol **10** (1.22 g, 90%) as a colourless oil. Optical rotation $[\alpha]_D^{25}$ -81.0 (c = 0.5, $CHCl_3$); IR (neat): 3561, 3054, 2925, 2855, 2220, 1697, 1463, 1108, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 - 7.68 (m, 4H), 7.45 - 7.33 (m, 6H), 4.91 (d, 1H, *J* 6.6 Hz), 4.59 (d, 1H, *J* 6.7 Hz), 4.29 - 4.25 (m, 1H), 4.00 -3.93 (m, 1H), 3.63 (t, 2H, *J* 12.6, 6.3 Hz), 3.35 (s, 3H), 2.20 (td, 2H, *J* 6.8, 1.9 Hz), 1.65 - 1.51 (m, 4H), 1.13 (d, 3H, *J* 6.3 Hz), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.9, 135.9, 134.4, 133.9, 129.5, 127.4, 94.1, 86.7, 77.2, 71.7, 70.8, 62.3, 55.5, 31.8, 26.9, 24.8, 19.3, 18.8, 18.5; HRMS (ESI): *m/z* [M+Na]$^+$calcd. for $C_{27}H_{38}O_4SiNa$: 477.24316; found: 477.24332.

(7*R*,8*S*)-8-[(*tert*-Butyldiphenylsilyl)oxy]-7-(methoxymethoxy)nonan-1-ol (11). To a stirred solution of alcohol **10** (1.1 g, 2.7 mmol) in EtOAc (10 mL) was added Pd/C (10%, 10 mg) at r.t. and was stirred for 10 h, under a hydrogen atmosphere. After completion of the reaction, it was filtered through celite and the filtrate was evaporated under reduced pressure. The crude product was purified by column chromatography using silica gel by eluting with a EtOAc-hexane (2:8) mixture to afford alcohol **11** (0.98 g, 93%) as a colourless oil. Optical rotation $[\alpha]_D^{25}$ +12.25 (c = 0.5, $CHCl_3$); IR (neat): 3560, 3053, 2922, 2854, 1459, 1108, 1039 cm^{-1}; ^1H NMR (400 MHZ, $CDCl_3$): δ 7.70 - 7.65 (m, 4H), 7.45 - 7.39 (m, 6H), 4.83 (d, 1H, *J* 6.6 Hz), 4.65 (d, 1H, *J* 6.6 Hz), 3.82 (qd, 1H, *J* 6.4, 2.7 Hz), 3.62 (t, 2H, *J* 13.3, 6.7 Hz), 3.55 - 3.49 (m, 1H), 3.37 (s, 3H), 1.64 - 1.44 (m, 4H), 1.36 - 1.15 (m, 6H), 1.06 (s, 9H), 1.00 (d, 3H, *J* 6.23 Hz); ^{13}C NMR (100 MHz, CDCl3): δ 135.9, 135.9, 134.5, 133.8, 129.6, 129.5, 127.5, 127.4, 96.4 81.3, 71.6, 62.9, 55.7, 32.7, 31.2, 29.4, 26.9, 25.8, 25.6, 19.2, 17.9; HRMS (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{27}H_{42}O_4SiNa$: 481.27446; found: 481.27490.

(5*R*,6*S*)-5-(6-Iodohexyl)-6,9,9-trimethyl-8,8-diphenyl-2,4,7-trioxa-8-siladecane (12). To a stirred solution of compound **11** (0.9 g, 2.0 mmol) in a toluene-acetonotrile (3:1, 15 mL) mixture were added TPP (0.46 g, 1.76 mmol), imidazole (0.2 g, 2.7 mmol) and iodine (0.75 g, 1.8 mmol). The mixture was then stirred for 30 min at r.t. and changed to a thick brown color. After completion of the reaction (confirmed by TLC), the reaction mixture was quenched by adding a saturated Hypo at 0 °C and was stirred for 15 min. The mixture was extracted with EtOAc (2x10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude compound was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (5:95) mixture to afford, iodide compound **12** (1.05 g, 95%) as a color less oil. Optical rotation $[\alpha]_D^{25}$ +11.80 (c = 0.5, $CHCl_3$); IR (neat): 3054, 2926, 2855, 1320, 1107, 1037, 739, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 - 7.66 (m, 4H), 7.45 - 7.35 (m, 6H), 4.82 (d, 1H, *J* 6.5 Hz), 4.64 (d, 1H, *J* 6.7 Hz), 3.84 - 3.79 (qd, 1H, *J* 6.4, 2.7 Hz), 3.53 - 3.49 (m, 1H), 3.37 (s, 3H), 3.17 (t, 2H, *J* 14.2, 7.1 Hz), 1.82 - 1.75 (m, 2H), 1.44 - 1.50 (m, 1H) 1.38 -1.8 (m, 7H), 1.06 (s, 9H), 1.01 (d, 3H, *J* 6.25 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 135.9, 134.5, 133.8, 129.6, 129.5, 127.5, 127.4, 96.4, 81.2, 71.6, 55.7, 33.4, 31.1, 30.4, 28.5, 26.9, 25.6, 19.2, 17.9, 7.2; HRMS (ESI): *m/z* [M+Na]$^+$calcd. for $C_{27}H_{41}O_3INaSi$: 591.17619; found: 591.17642.

(5*R*,6*S*)-5-{8-[(4*R*,5*S*)-5-((Benzyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl]oct-7-yn-1-yl}-6,9,9-trimethyl-8,8-diphenyl-2,4,7-trioxa-8-siladecane (13). To a stirred solution of alkyne **3** (0.56 g, 2.3 mmol) in a THF-HMPA (2:1, 5 mL) mixture was added dropwise *n*-BuLi (0.78mL, 2.0 mmol) at -78 °C under a nitrogen atmosphere. While adding *n*-BuLi dropwise, the reaction mass converted to a brown color and was then stirred for a further 30 min at the same temperature. Then, a solution of iodo compound **12** (0.9 g, 1.5 mmol), which was dissolved in THF (5 mL), was added. The reaction mixture was stirred for a further 1 h, and gradually warmed to room temperature. After completion of the reaction, the reaction was terminated with saturated NH_4Cl and extracted with EtOAc (2x20 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (0.5:9.5) mixture to afford **13** (0.76 g, 73%) as a color less liquid. Optical rotation $[\alpha]_D^{25}$ +31.37 (c = 1, $CHCl_3$); IR (neat): υ 2926, 2855, 2250, 1428, 1107, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 - 7.65 (m, 4H), 7.45 - 7.30 (m, 10H), 4.85 - 4.81 (m, 2H), 4.67 - 4.60 (m, 2H), 4.57 - 4.51 (m, 1H), 4.33 - 4.27 (m, 1H), 3.82 (qd, 1H, *J* 6.2, 2.6 Hz), 3.74 - 3.68 (m, 2H), 3.54 - 3.48 (m, 1H), 3.36 (s, 3H), 2.20 - 2.14 (td, 2H, *J* 7.1, 1.9 Hz), 1.53 (s, 3H), 1.50 - 1.40 (m, 4H), 1.38 - 1.12 (m, 10H), 1.06 (s, 9H), 1.01 (d, 3H, *J* 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 135.9, 135.9, 134.5, 133.8, 129.6, 129.5, 128.3, 127.8, 127.7, 127.5, 127.4, 109.9, 96.4, 88.4, 81.3, 76.6, 75.4, 73.6, 71.6, 70.2, 67.9, 55.7, 31.2, 29.1, 28.8,

28.4, 27.7, 26.9, 25.9, 25.7, 19.2, 18.7, 17.9; HRMS (ESI): *m/z* $[M+Na]^+$calcd. for $C_{42}H_{58}O_6SiNa70$: 709.38949; found: 709.38949.

{(4*S*,5*R*)-5-[(9*R*,10*S*)-10-((*tert*-Butyldiphenylsilyl)oxy)-9-(methoxymethoxy)undecyl]-2,2-dimethyl-1,3-dioxolan-4-yl}methanol (14). To a stirred solution of compound **13** (0.65 g, 0.95 mmol) in EtOAc (5 mL) was added Pd/C (10%, 10 mg) at r.t. and was stirred under a hydrogen atmosphere for 10 h. After completion of the reaction (confirmed by TLC), it was filtered through a celite bed and the filtrate was concentrated under vacuum pressure. The residue was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (3:7) mixture to afford, alcohol **14** (0.51 g, 90%) as a color less oil. Optical rotation $[\alpha]_D^{25}$ +8.0 (c = 0.5, $CHCl_3$); IR (neat): 3542, 3026, 2924, 2855, 1533, 1460, 1107, 1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.71 - 7.65 (m, 4H), 7.44 - 7.34 (m, 6H), 4.83 (d, 1H, *J* 6.6 Hz), 4.65 (d, 1H, *J* 6.6 Hz), 4.18 - 4.11 (m, 1H), 3.92 - 3.85 (m, 1H), 3.85 - 3.77 (m, 1H), 3.76 - 3.70 (m, 1H), 3.60 - 3.57 (m, 1H), 3.54 - 3.50 (m, 1H), 3.37 (s, 3H), 1.51 - 1.36 (m, 8H), 1.34 - 1.13 (m, 14H), 1.06 (s, 9H), 1.00 (d, 3H, *J* 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.9, 135.9, 134.6, 133.8, 129.5, 129.5, 127.5, 127.4, 108.5, 96.4, 81.5, 81.3, 77.9, 76.9, 71.7, 62.0, 61.8, 55.6, 33.1, 31.3, 29.6, 29.4, 28.8, 28.2, 27.3, 26.9, 26.6, 25.9, 25.8, 25.5, 19.1, 17.8; HRMS (ESI): *m/z* $[M+Na]^+$calcd. for $C_{35}H_{56}O_6NaSi$: 623.37384; found: 623.37484.

Ethyl-(*E*)-3-{(4*S*,5*R*)-5-[(9*R*,10*S*)-10-((*tert*-butyldiphenylsilyl)oxy)-9-(methoxymethoxy)undecyl]-2,2-dimethyl-1,3-dioxolan-4-yl}acrylate (15). To a stirred solution of alcohol **14** (0.45 g, 0.75 mmol) in anhydrous CH_2Cl_2 (10 mL) was added DMP (0.41 g, 0.97 mmol) and $NaHCO_3$ (110 mg, 0.44 mmol) at 0 °C for 15 min, and was then slowly warmed to room temperature for 1 h. The completion of the reaction was monitored by TLC, then cooled to 0 °C and the reaction was quenched with crushed ice and was extracted with CH_2Cl_2 (2x10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, the solvent was evaporated under reduced pressure and the obtained aldehyde was used for the following Wittig reaction without purification.

To a stirred solution of the above aldehyde in toluene (10 mL) was added $Ph_3P{=}CHCO_2Et$ (0.29 g, 0.83 mmol) and the resulting mixture was refluxed for 2 h. After completion of the reaction (confirmed by TLC), the reaction was terminated with water and extracted with EtOAc (2×15 mL). The combined organic layer was dried over Na_2SO_4, the solvent was evaporated under reduced pressure and the residue product was purified by column chromatography using silica gel (60-120 mesh) by eluting with a EtOAc-hexane (1:9) mixture to afford, ester compound **15** (0.19 g, 75%) as a colorless liquid. Optical rotation $[\alpha]_D^{25}$ +5.25 (c = 0.5, $CHCl_3$); IR (neat): 3045, 2924, 2854, 1525, 1462, 1217, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 - 7.65 (m, 4H), 7.44 - 7.34 (m, 6H), 6.86 (dd, 1H, *J* 15.7, 5.7 Hz), 6.11 (dd, 1H, *J* 15.5, 1.3 Hz), 4.83 (d, 1H, *J* 6.6 Hz), 4.65 (d, 1H, *J* 6.6 Hz), 4.21 (q, 2H), 4.17 - 4.12 (m, 1H), 3.85 - 3.79 (qd, 1H, *J* 6.2, 2.7 Hz), 3.76 - 3.70 (m, 1H), 3.54 - 3.49 (m, 1H), 3.36 (s, 3H), 1.42 (d, 6H, *J* 10.8 Hz), 1.36 (m, 19H), 1.05 (s, 9H), 1.00 (d, 3H, *J* 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 143.8, 135.9, 134.6, 133.5, 128.6, 129.5, 127.5, 127.4, 122.9, 108.8, 96.4, 81.3, 78.4, 71.7, 60.5, 55.7, 31.9, 31.3, 30.5, 25.7, 29.7, 29.4, 28.0, 26.9, 26.3, 25.8, 25.3, 19.2, 17.9, 14.2; HRMS (ESI): *m/z* $[M+Na]^+$calcd. for $C_{39}H_{60}O_7SiNa$: 691.40005; found 691.40123.

Ethyl(*E*)-3-{(4*S*,5*R*)-5-[(9*R*,10*S*)-10-hydroxy-9-(methoxymethoxy)undecyl]-2,2-dimethyl-1,3-dioxolan-4-yl} acrylate (16). To a stirred solution of ester compound **15** (0.3 g, 0.44 mmol) in anhydrous THF (5 mL) in a plastic vial was added the HF•Py complex (70%, 0.1 mL) at 0 °C. The reaction mixture was slowly warmed to room temperature and was stirred for 24 h. The completion of the reaction was confirmed by TLC, then carefully poured in a saturated $NaHCO_3$ solution (5 mL) and was stirred for 30 min and extracted with EtOAc (2×10 mL). The combined organic layers were further washed with a saturated $CuSO_4$ (5 mL) solution, water (5 mL), brine (5 mL) and then the organic layer was dried over Na_2SO_4 and concentrated under pressure. The residue product was purified by column chromatography using silica gel, (60-120 mesh) by eluting with a

EtOAc-heaxane (1:9) mixture to afford the secondary alcohol **16** (0.14 g, 75%) as a colorless liquid. Optical rotation $[\alpha]_D^{25}$ +5.30 (c = 1, $CHCl_3$). $^{Lit}[\alpha]_D^{20}$ +7.18 (c = 1, $CHCl_3$)[4]; IR (neat): 3556, 2924, 2854, 1725, 1432, 1254, 1034, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.84 (dd, 1H, *J* 15.7, 6.2 Hz), 6.06 (dd, 1H, *J* 15.7, 1.5 Hz), 4.74 (d, 1H, *J* 6.9 Hz), 4.67 - 4.61 (m, 2H), 4.24 - 4.18 (m, 4H), 3.79 - 3.7 (m, 1H), 3.52 - 3.47 (m, 1H), 3.43 (s, 3H), 3.06 (brs, 1H), 1.51 (s, 3H), 1.38 (s, 3H), 1.32 - 1.23 (m, 18H) 1.14 (d, 3H, *J* 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 143.8, 122.9, 108.8, 97.6, 85.2, 78.3, 77.2, 68.9, 60.5, 55.8, 30.9, 30.5, 29.7, 29.6, 29.4, 28.0, 26.3, 26.0, 25.5, 17.1, 14.2. HRMS (ESI): *m/z* $[M+Na]^+$calcd. for $C_{23}H_{42}O_7SiNa$: 453.28227; found: 453.28375.

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Supplementary Material

Copies of ^1H and ^{13}C NMR of compounds **2**-**16** are available in the Supplementary Material file associated with this manuscript.

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