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Enantioselective synthesis of C1-C4 and C5-C14 fragments of cytospolide D

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Dedicated to Prof. Peter Alan Jacobi in recognition of his seminal contributions to so many aspects of organic chemistry

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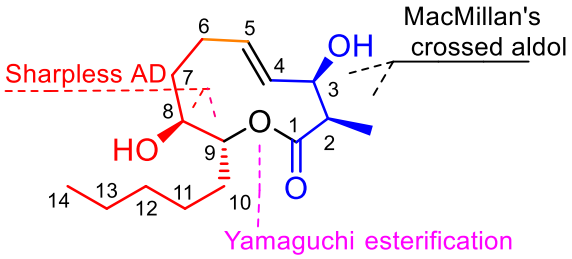
Abstract

A convergent approach for the synthesis of the two key fragments (C1-C4 and C5-C14) of cytospolide D is described. Key transformations include MacMillan's crossed aldol, Sharpless asymmetric dihydroxylation (AD) and Mitsunobu inversion reactions.



Cytospolide D

Keywords: Cytospolide, Sharpless AD, MacMillan's crossed aldol, Mitsunobu inversion, Yamaguchi esterification.

Introduction

Over the recent years, decanolides (nonenolides) have been recognized as a rich source of bioactive natural products with fascinating chemical structures.[1] The novel decanolide compounds, cytospolide A-E (**1-5**) along with other thirteen natural product analogues (cytospolides M-Q and decytospolides A and B) were isolated by Zhang and co-workers from leaves of endophytic fungus shrub *Ilex canariensis* found mainly in the island of Gomera, Spain (Figure 1).[2-3] A number of cytospolides showed cytotoxic effects to various human carcinoma cell lines. The C-2 methyl group inversion in cytospolide E **5** from 2*R* of **4** to 2*S* of **5** was found to lead to a surprise increase in cytotoxic activity against the A-549 tumor cell lines.[2] The structure of all the cytospolides were determined by extensive studies of chemical, spectroscopic and single crystal X-ray analysis.[3] Cytospolide D **4** has been a synthetic target of considerable interest due to its bioactivities and unique structure with an array of functionalities. Various methods for the synthesis of cytospolide D **4** based on the chiral pool approaches have been documented in the literature.[4-8] As part of our ongoing program towards the syntheses of bioactive natural products,[9-14] we became interested in developing a simple and flexible route to the key fragments of cytospolide D **4**. Herein, we are reporting a new and efficient enantioselective synthesis of key fragments C1-C4 and C5-C14 for the cytospolide D **4** employing the MacMillan's crossed aldol, Sharpless AD and Mitsunobu inversion reaction as key steps.

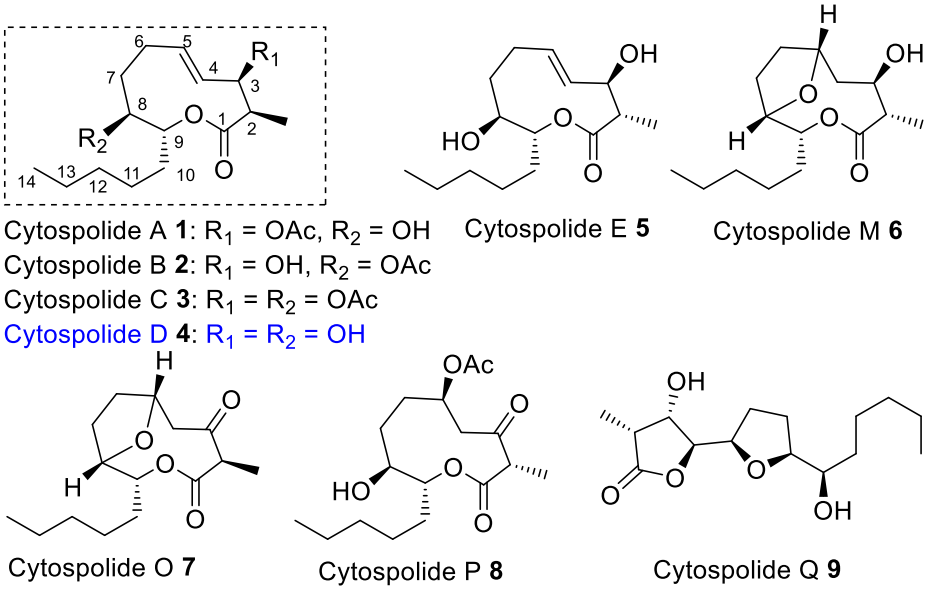
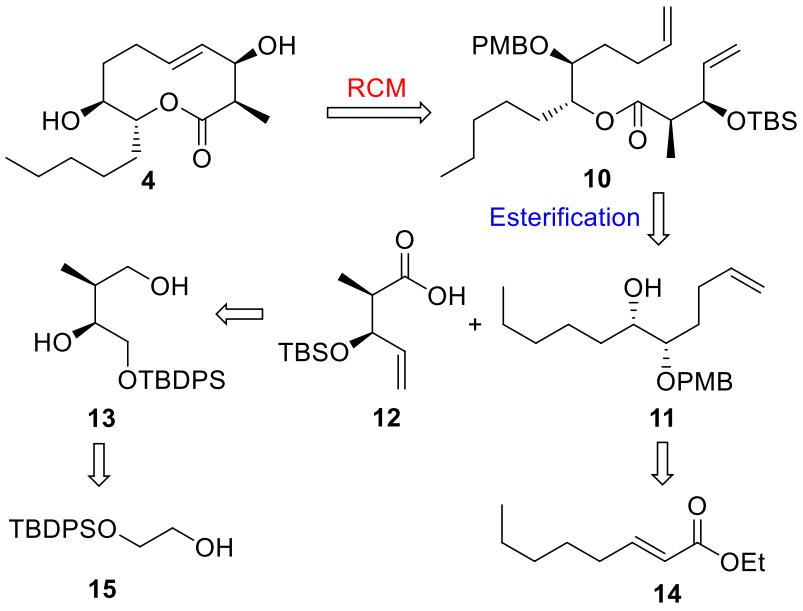


Figure 1. Some representative structures of cytospolide.

Results and Discussion

Our retrosynthetic analysis for the synthesis of both the fragments of cytospolide D **4** is displayed in Scheme 1. We envisaged that the cytospolide D **4** in its *E*-form could be synthesized from the key precursor bis-olefin derivative **10** via Grubbs RCM reaction followed by deprotection of protecting groups. The *bis*-olefin derivative **10** could be accessed from the olefinic alcohol fragment **11** (C5-C14) and acid fragments **12** (C1-C4) by intermolecular Mitsunobu esterification. The alcohol derivative **11** in turn could be synthesized from easily

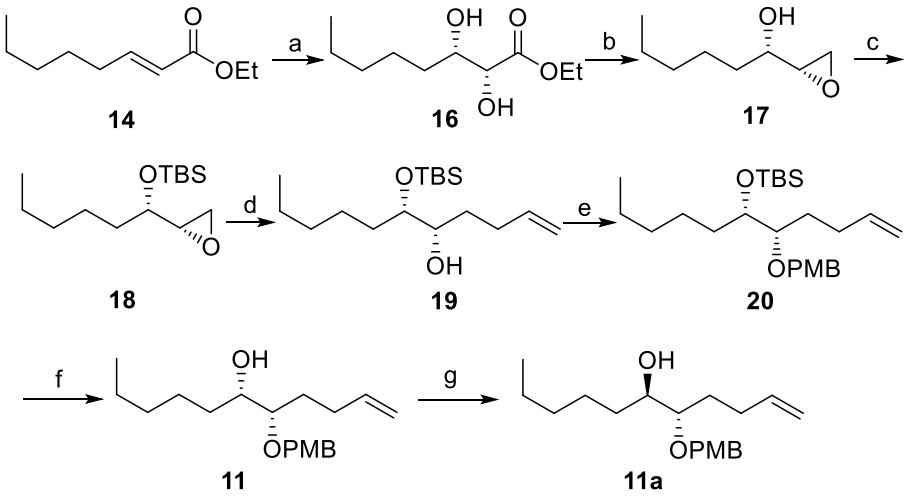
accessible *trans*-olefinic ester **14** *via* Sharpless AD followed by standard organic transformation. The olefinic acid fragment **12** could be assembled from alcohol derivative **13** by employing PMB protection of primary alcohol, silyl ether cleavage, regioselective primary hydroxyl *o*-tosylation, base treatment to get terminal epoxide, one carbon homologation, TBS protection and PMB deprotection followed by oxidation. The 1,3-diol derivative **13** in turn could be obtained from the aldehyde intermediate of monosilylated ethylene glycol derivative **15** via asymmetric MacMillan's crossed aldol reaction followed by in-situ aldehyde reduction.



Scheme 1. Retrosynthetic analysis of cytospolide D **4.**

Synthesis of the C5-C14 Fragment (11).

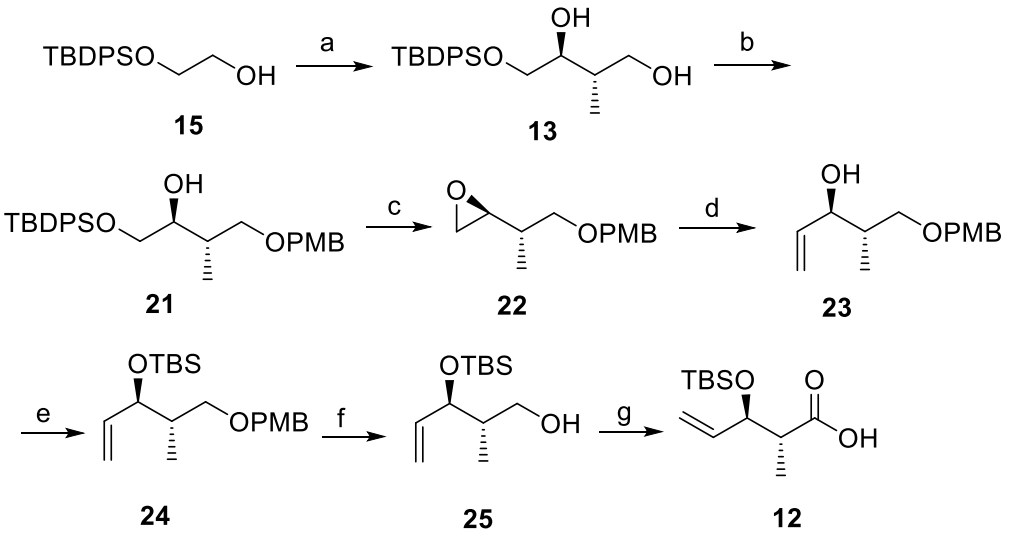
The synthesis of the key fragment olefinic alcohol **11** is depicted in Scheme 2. The synthesis started from readily available *α*, *β*-unsaturated ester **14**[15] by treatment with osmium tetroxide and potassium ferricyanide as co-oxidant in the presence of $(DHQ)_2PHAL$ (hydroquinine 1,4-phthalazinediyl diether) under Sharpless asymmetric conditions[16-18] to afford the diol derivative **16** in 92% yield with >98% ee {$[\alpha]_D^{25}$ -14.37 (*c* 1.00, EtOH), Lit[19-20] -14.40 (*c* 1.00, EtOH)[19]}. The diol derivative **16** on $LiAlH_4$ reduction afforded triol intermediate, which on regioselective primary alcohol *o*-tosylation by TsCl and Et_3N in the presence of catalytic amount of Bu_2SnO[21-22] (dibutyltin(IV) oxide) followed by base treatment afforded the epoxy alcohol derivative **17** as the sole product in 80% yield. The free secondary hydroxyl group of **17** was subjected to imidazole-promoted protection with TBSCl which furnished the TBS protected epoxide **18** in 90% yield. The protected epoxide derivative **18** was then subjected to copper-catalyzed (CuI) regioselective ring opening with allylMgBr to give the alkenol derivative **19** in excellent yield. The free hydroxyl group of alkenol derivative **19** on *p*-methoxybenzyl chloride (PMBCl) protection in the presence of NaH and selective desilylation of the TBS ether with TBAF (tetrabutylammonium fluoride) furnished the alkenol derivative **11** in excellent yield.



Scheme 2. Reagents and conditions: (a) 0.005 mol% OsO_4, 0.1 mol% $(DHQ)_2PHAL$, $K_3[Fe(CN)_6]$, $CH_3SO_2NH_2$, K_2CO_3, *t*-BuOH:H_2O 1:1 v/v, 0 °C, 24 h, 92%; (b) i) $LiAlH_4$, dry THF, 0 °C, 2 h; ii) TsCl, Et_3N, Bu_2SnO (cat), dry CH_2Cl_2, 0 °C to rt, 30 min; iii) KOH, Et_2O, 0 °C to rt, 2 h, 80% (over three steps). (c) TBSCl, imidazole, DMAP, CH_2Cl_2, 0 °C to rt, 2 h, 90%; (d) C_3H_5MgBr, CuI (cat.), dry THF, 0 °C, 2.5 h, 85%. (e) PMBCl, NaH, TBAI (cat.), THF, 0 °C to rt, 3 h, 76%. (f) TBAF, THF, 0 °C to rt, 1 h, 95% ; (g) (i) *p*-nitrobenzoic acid, DIAD, Ph_3P, toluene, 0 °C to rt, 2.5 h; (ii) K_2CO_3, MeOH, 0 °C to rt, 45 min, 82%.

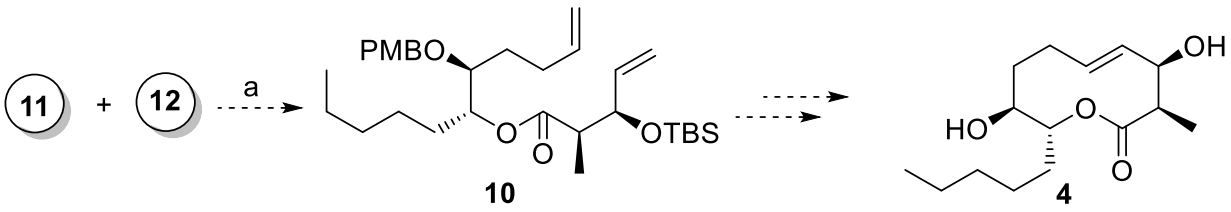
Synthesis of the C1-C4 Fragment (12)

The synthesis of olefinic acid fragment **12** (C1-C4) is illustrated in Scheme 3. The 1,3-Diol **13** was synthesized from readily available monosilylated ethylene glycol derivative **15** *via* MacMillan's crossed aldol[23] reaction with propanal catalyzed by D-proline and subsequent $NaBH_4$ reduction in 86% yield with >99% ee and *anti*:*syn* 98:2 ratio.[24] Treatment of 1,3-diol **13** with K_2CO_3 and PMBCl in acetone under reflux conditions[25] successfully furnished the regioselective primary alcohol PMB protected derivative **21** in 83% yield. The synthesis of the epoxide derivative **22** from alcohol **21** was carried out by a process including silyl deprotection and selective primary alcohol tosylation by TsCl and Et_3N in the presence of catalytic amount of Bu_2SnO[21-22] followed by base treatment in 89% yield (over three steps). The epoxide derivative **22** on one-carbon homologation with dimethylsulfonium methylide in the presence of *n*-BuLi furnished the allyl alcohol derivative **23** in 91% yield.[26-27] With allyl alcohol derivative **23** in hand, we then subjected it to imidazole-promoted protection with TBSCl and selective deprotection of the PMB ether with DDQ to afford the primary alcohol derivative **25** in excellent yield. Finally, TEMPO {(2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl}/BIAB {(diacetoxyiodo)benzene} mediated oxidation of the primary alcohol **25** furnished the key fragment **12** in 87% yield.



Scheme 3. Reagents and conditions: (a) i) $(COCl)_2$, DMSO, Et_3N, dry CH_2Cl_2, -78 °C to rt, 2 h; ii) propionaldehyde, 10 mol % D-proline, 1,4 dioxane, 4 °C, 24 h; iii) $NaBH_4$, CH_3OH, 30 min, 86% (three steps). (b) PMBCl, K_2CO_3, TBAI, acetone, 70 °C, 18 h, 83%. (c) i) TBAF, THF, rt, 90 min; ii) TsCl, Bu_2SnO, Et_3N, dry DCM, 0 °C to rt, 30 min; iii) KOH, Et_2O, rt, 2 h, 89% (three steps). (d) trimethylsulphonium iodide, *n*-BuLi, dry THF, -10 to 0 °C, 3h, 91%. (e) TBSCl, imidazole, DMAP, dry CH_2Cl_2, 0 °C to rt, 2.5 h, 95%. (f) DDQ, dry CH_2Cl_2, rt, 45 min, 93%. (g) TEMPO, (diacetoxyiodo)benzene, CH_2Cl_2: H_2O, 3:1, rt, 24 h, 87%.

The fragments alkenol derivative **11** and acid fragment **12** could be used for the coupling reactions to accomplish the synthesis of key precursor *bis*-olefin derivative **10** which could be used for the total synthesis of cytospolide D **4** as shown in Scheme 4. The ester derivative **10** could be prepared by coupling of alcohol fragment **11** and acid fragment **12** under Mitsunobu conditions. Alternatively, to access the key precursor *bis*-olefin **10**, the Yamaguchi esterification[28-30] could be attempted. Therefore, alkenol derivative **11** was subjected to Mitsunobu inversion in the presence of *p*-nitrobenzoic acid, Ph_3P, and DIAD followed by K_2CO_3 treatment in MeOH to afford required alkenol derivative **11a** in 82% yield (Scheme 2). The Yamaguchi esterification of acid fragment **12** and alkenol derivative **11a** could also lead to the required *bis*-olefin derivative **10**.[31] The *bis*-olefin derivative **10** could then be converted into the target compound cytospolide D **4** by the Grubbs RCM and deprotection of both protecting group following the standard organic transformations. Ramana et al. reported the synthesis of Cytospolide E **5** with similar fargments with different stereochemistry.[32] We can expect to get *E* geometry with the current stereochemistry and would be investigated.



Scheme 4. Coupling of fragments for cytospolide D.

Conclusions

We have developed a new and efficient enantioselective approach to the synthesis of the two key fragments (C1-C4 and C5-C14) of cytospolide D employing MacMillan's crossed aldol, Sharpless AD and Mitsunobu inversion reactions as key steps. The synthetic approach described has significant potential for stereochemical variations in all the positions and further extension to other stereoisomers and analogues. Currently, the efforts are in progress and the results will be disclosed in due course.

Experimental Section

General. All reactions were carried out under argon or nitrogen in oven dried glassware using standard glass syringes and septa. The solvents and chemicals were purchased from Merck and Sigma Aldrich Company. Solvents and reagents were purified and dried by standard methods prior to use. Progress of the reactions was monitored by TLC using precoated aluminium plates of Merck kiesel gel 60 F254. Column chromatography was performed on silica gel (60-120 and 100-200 mesh) using a mixture of *n*-hexane/ethyl acetate and Dichloromethane/MeOH. IR spectra were recorded on Agilent resolution Pro 600 FT-IR spectrometer, fitted with a beam condensing ATR accessory. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ (unless otherwise mentioned) on JEOL ECS operating at 400 and 100 MHz, respectively. Chemical shifts are reported in δ (ppm), referenced to TMS. HRMS were recorded on Agilent 6530 Accurate-Mass Q-TOF using Electron Spray Ionization. Optical rotations were measured on automatic polarimeter AA-65.

(2*R*,3*S*)-Ethyl 2,3-dihydroxyoctanoate (16). To a solution of *tert*-butyl alcohol and water (1:1, 160 mL) at room temperature, $K_3Fe(CN)_6$ (23.26 g, 70.58 mmol), K_2CO_3 (9.79 g, 70.58 mmol) and $(DHQ)_2$ PHAL (183 mg, 0.23 mmol or 0.1 mol %) were added sequentially. The resulting mixture was cooled to 0 °C followed by addition of OsO_4 (1.16 mL, 0.1 M solution in toluene, 0.005 mol%) and methanesulfonamide (2.23 g, 23.52 mmol). After being stirred for 2 min at 0 °C, the olefin **14** (4.0 g, 23.52 mmol) was added in one portion and resulting mixture was further stirred at 0 °C for 24 h. The reaction was quenched with solid sodium sulfite (8.0 g) and stirring was continued for an additional 45 min, and then the solution was extracted with EtOAc (3 x 30 mL), dried over Na_2SO_3 and concentrated in *vacuo*. Silica gel column chromatography (hexane/EtOAc 3:1 v/v) of the residue afforded diol **16** (4.40 g, 92%) as a white solid. Mp 42-43 °C; [R_f 0.4, EtOAc/hexane 3:7 v/v]; {$[\alpha]_D^{25}$ -14.37 (*c* 1.00, EtOH); IR (CH_2Cl_2) v: 3470, 2875, 1736, 1482, 1260 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.35-4.27 (m, 2H), 4.09 (d, *J* 2.0 Hz, 1H), 3.89 (td, *J* 7.4, 1.7 Hz, 1H), 3.09 (brs, 1H), 1.66-1.54 (m, 5H), 1.53-1.31 (m, 8H), 0.90 (t, *J* 6.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.9, 73.1, 72.7, 62.3, 34.0, 31.8, 25.6, 22.7, 14.3, 14.2.

(*S*)-1-((*S*)-Oxiran-2-yl)hexan-1-ol (17). To a solution of $LiAlH_4$ (1.56 g, 41.12 mmol) in dry THF (20 mL) at 0 °C was added a solution of **16** (4.20 g, 20.56 mmol) in dry THF (40 mL) dropwise. The resulting mixture was stirred at 0 °C for 2 h. After this 10% aq. NaOH (20 mL) solution was added slowly to quench the reaction. The mixture was extracted with EtOH (2 x 30 mL), the combined organic layers were dried over Na_2SO_4 and concentrated in *vacuo* to get the triol intermediate which is used for the next step without further purification.

To a solution of above triol in dry DCM (40 mL), was added Et_3N (2.86 mL, 20.56 mmol), TsCl (3.91 g, 20.56 mmol), and Bu_2SnO (1.02 g, 4.11 mmol) sequentially. The resulting solution was stirred for 30 min and quenched with H_2O (20 mL). The aqueous layer extracted with DCM (3 x 30 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude mono tosylated derivative was formed and was used as such in next reaction without further purification.

To a solution of Mono tosylated derivative formed in the above reaction in ether (40 mL) at 0 °C was added KOH (3.46 g, 61.68 mmol). The resulting solution was stirred for 2 hours at room temperature and after which the turbid solution was quenched with H_2O (20 mL). The aqueous layer was extracted with ether (3 x 20 mL), organic layer separated, washed with brine dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by silica gel chromatography (hexane/EtOAc 3:1 v/v) afforded the epoxide **17** (2.36 g, 80%) as colorless liquid. [R_f 0.5, EtOAc/hexane 1:4 v/v]; $[\alpha]_D^{25}$ +4.38 (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 3446, 2931, 2878, 1108, 870 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 3.49- 3.39 (m, 1H), 2.99 (ddd, *J* 4.9, 4.2, 2.8 Hz, 1H), 2.83 (t, *J* 4.8 Hz, 1H), 2.72 (dd, *J* 4.9, 2.8 Hz, 1H), 1.93 (brs, 1H), 1.71-1.59 (m, 2H), 1.53-1.25 (m, 6H), 0.90 (t, *J* 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 71.8, 55.5, 45.3, 34.5, 31.9, 25.1, 22.6, 14.1; HRMS (ESI), calcd for $C_8H_{16}O_2Na$ $[M+Na]^+$ 167.1042; found 167.1039.

***tert*-Butyldimethyl((*S*)-1-((*S*)-oxiran-2-yl)hexyloxy)silane (18**).To an ice-cold solution of **17** (2.0 g, 13.8 mmol) in dry CH_2Cl_2 (30 mL) under nitrogen at 0 °C, imidazole (1.42 g, 20.70 mmol), TBSCl (2.71 g, 18.02 mmol) and DMAP (337 mg, 2.76 mmol) were added sequentially and mixture was stirred for 2 hours before quenching of the reaction with saturated aqueous NH_4Cl (20 mL). The reaction mixture was extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4, concentrated in vacuo and purified on silica gel (hexane/EtOAc 19:1 v/v) to afford TBS protected epoxide **18** (3.20 g, 90%) as a colorless oil. [R_f 0.7, EtOAc/hexane 1:9 v/v]; $[\alpha]_D^{25}$ + 6.61 (c 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 3449, 2935, 2861, 1070, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 3.25 (dd, *J* 12.4, 6.8 Hz, 1H), 2.91 (ddd, *J* 6.8, 4.1, 2.8 Hz, 1H), 2.77 (t , *J* 5.12 Hz, 1H), 2.55 (dd, *J* 5.0, 2.7 Hz, 1H), 1.61-1.45 (m, 2H), 1.42-1.20 (m, 6H), 0.90 (s, 9H), 0.87 (t, *J* 7.0 Hz, 3H), 0.11 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 74.8, 56.2, 45.1, 34.8, 32.0, 26.0, 25.1, 22.7, 18.3, 14.2, -4.2, -4.9; HRMS (ESI), calcd for $C_{14}H_{30}O_2Si$ $[M+H]^+$ 259.2088; found 259.2091.

(5*S*,6*S*)-6-(*tert*-Butyldimethylsilyloxy)undec-1-en-5-ol (19). To a stirred solution of TBS protected epoxide **18** (3.0 g, 11.60 mmol) in dry THF (30 mL) at 0 °C, added CuI (110 mg, 0.58 mmol) followed by dropwise addition of 17.41 mL of 1.0 M solution of allylMgBr (17.41 mmol) in diethylether. After addition was complete, the reaction mixture was stirred for 2.5 hours at the same temperature and quenched with saturated aqueous NH_4Cl (30 mL) and the mixture was stirred for 20 minutes at 0 °C, and the layers were separated, aqueous layer was extracted with ethyl acetate (3 x 30 mL). The combined organic extracts were dried over Na_2SO_4, organic layer was concentrated under reduced pressure and purified by silica gel column chromatography (hexane/EtOAc 9:1 v/v) to afford secondary alcohol **19** (2.95 g, 85%) as pale yellow oil. [R_f 0.6, EtOAc/hexane, 1:9 v/v]; $[\alpha]_D^{25}$ -17.91 (c 1.00, CH_2Cl_2); IR (CH_2Cl_2) v: 3423, 2929, 2850, 1435, 1151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 5.89-5.79 (m, 1H), 5.04 (ddd, *J* 17.2, 3.5, 1.7 Hz, 1H), 4.96 (ddd, *J* 2.9, 2.4, 1.2 Hz, 1H), 3.52-3.43 (m, 2H), 2.31-2.19 (m, 1H), 2.17-2.07 (m, 2H), 1.55-1.38 (m, 3H), 1.33-1.22 (m, 7H), 0.90 (s, 9H), 0.87 (t, *J* 7.1 Hz, 3H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 138.7, 114.8, 75.3, 72.1, 34.0, 33.6, 32.2, 30.4, 26.0, 24.8, 22.8, 18.3, 14.2, -4.0, -4.46; HRMS (ESI), calcd for $C_{17}H_{36}O_2SiNa$ $[M+Na]^+$ 323.2377; found 323.2386.

***tert*-Butyl((5*S*,6*S*)-5-(4-methoxybenzyloxy)undec-1-en-6-yloxy)dimethylsilane (20).** To a stirred suspension of NaH (431 mg, 17.96 mmol) in dry THF (10 mL) was added dropwise a solution of secondary alcohol **19** (2.7 g, 8.98 mmol) taken in anhydrous THF (20 mL) over a period of 10 min at 0 °C. The reaction mixture was stirred for 1 hour at same temperature then *p*-methoxybenzyl chloride (1.46 mL, 10.77 mmol) was added at 0 °C over a period of 10 min, followed by addition of TBAI (164 mg, 0.44 mmol) and the resultant reaction mixture was warmed to room temperature and stirred for 2 hours followed by addition of cold water (20 mL) to quench the reaction mixture. Aqueous layer was extracted with ethyl acetate (3 x 30 mL), combined organic extracts were dried over Na_2SO_4 concentrated in *vacuo* and purified by silica gel column chromatography (hexane/EtOAc 97:3 v/v) to afford *p*-methoxybenzyl ether compound **20** (2.86 g, 76%) as colorless liquid. [R_f 0.5, EtOAc/hexane 1:19 v/v]; $[\alpha]_D^{25}$ +11.21 (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 2956, 2857, 1653, 1429, 1217 cm^{-1}; ^1H

NMR (400 MHz, $CDCl_3$) *δ*: 7.26-7.22 (m, 2H), 6.87 (dd, *J* 8.6, 0.7 Hz, 2H), 5.88-5.72 (m, 1H), 5.04-4.91 (m, 2H), 4.47 (dd, *J* 33.7, 11.3 Hz, 2H), 3.80 (s, 3H), 3.76-3.71 (m, 1H), 3.31-3.28 (m, 1H), 2.25-2.13 (m, 1H), 2.07-1.95 (m, 1H), 1.76-1.62 (m, 1H), 1.51-1.39 (m, 2H), 1.32-1.15 (m, 7H), 0.05 (s, 12H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ:* 159.3, 139.1, 131.2, 129.5, 114.7, 114.4, 113.9, 81.9, 81.2, 72.0, 55.4, 32.1, 31.1, 30.7, 30.5, 28.7, 28.1, 26.0, 22.8, 18.2, 14.2, -4.14, -4.43; HRMS (ESI), calcd for $C_{25}H_{44}O_3SiNa$ $[M+Na]^+$ 443.2952; found 443.2950.

(5*S*,6*S*)-5-(4-Methoxybenzyloxy)undec-1-en-6-ol (11). To a solution of **20** (2.50 g, 5.94 mmol) in dry THF (20 mL) at 0 °C was added TBAF (1.0 M in THF, 8.91 mL, 8.91 mmol), and resulting solution was stirred for 1 hour at room temperature. Saturated solution of NH_4Cl was added to quench the reaction. The aqueous phase is extracted with EtOAc (3 x 30 mL). The organic phase was washed with brine, dried over anhydrous $Na_2SO_4$and concentrated in *vacuo*. Silica gel column chromatography (hexane/EtOAc 19:1) of the residue afforded **11** (1.72 g, 95%) as a colourless liquid. [R_f 0.4, EtOAc/hexane 1:9 v/v]; $[\alpha]_D^{25}$ +8.11 (c 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 3460, 2922, 2850 1656, 1447, 1079 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.26 (d, *J* 8.5 Hz, 2H), 6.94 (dt, *J* 6.8, 4.4 Hz, 2H), 5.88-5.77 (m, 1H), 5.05-4.94 (m, 2H), 4.58 (d, *J* 11 Hz, 1H), 4.42 (dd, *J* 11.0, 6.4 Hz, 1H), 3.80 (s, 3H), 3.56-3.46 (m, 1H), 3.30-3.22 (m, 1H), 2.30-2.04 (m, 3H), 1.77-1.64 (m, 1H), 1.58-1.26 (m, 9H), 0.89 (td, J 6.8, 1.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.4, 138.7, 138.6, 130.6 (d), 129.7, 114.9, 114.0, 82.1, 81.5, 72.8, 72.4, 72.2, 55.4, 33.6, 32.9, 32.3, 32.1, 30.4, 30.2, 29.8, 29.5, 25.6, 24.9, 22.8, 22.8, 14.2; HRMS (ESI), calcd for $C_{19}H_{30}O_3Na$ $[M+Na]^+$ 329.2087 found 329.2088.

(5*S*,6*R*)-5-(4-Methoxybenzyloxy)undec-1-en-6-ol (11a). To a stirred solution of alcohol **11** (1.50 g, 4.89 mmol) in dry toluene (20 mL) under argon, triphenylphosphine (5.13 g, 19.57 mmol) and *p*-nitrobenzoic acid (3.27 g, 19.57 mmol) were added sequentially. The reaction mixture was cooled to 0 °C and treated with DIAD (3.95 g, 19.57 mmol) and stirred for 2.5 hours with slow warming to room temperature. The volatiles were removed under reduced pressure to afford the corresponding *p*-nitrobenzoate ester quantitatively, which was taken to the next step without further purification.

To a solution of above ester in MeOH (20 mL) was added K_2CO_3 (1.01 g, 7.33 mmol) at 0 °C and stirred for 45 min with slow warming to room temperature. The reaction was quenched with water, extracted with EtOAc (2 × 30 mL), washed with brine, dried (Na_2SO_4), concentrated in *vacuo*, and purified by column chromatography (hexane/EtOAc 17:3 v/v) to afford **11a** (2.20 g, 82%) as a colorless oil: [R_f 0.40 (EtOAc/hexane, 1:9, v/v)]; $[\alpha]_D^{25}$ -9.31 (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 3463, 2928, 2860, 1658, 1475, 1066, 698 cm^{-1}; 1H NMR (400 MHz, $CDCl_3$) *δ*: 7.26 (d, *J* 8.5 Hz, 2H), 6.88 (d, *J* 8.6 Hz, 2H), 5.90-5.75 (m, 1H), 5.08-4.93 (m, 2H), 4.59 (d, *J* 11.0 Hz, 1H), 4.43 (dd, *J* 10.9, 5.3 Hz, 1H), 3.80 (s, 3H), 3.53 (ddd, *J* 10.6, 5.3, 2.3 Hz, 1H), 3.32-3.21 (m, 1H), 2.34-2.25 (m, 1H), 2.25- 2.03 (m, 2H), 1.79-1.65 (m, 1H), 1.57-1.26 (m, 9H), 0.89 (td, *J* 6.7, 1.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.1, 138.4, 138.3, 130.3, 129.3, 114.7, 114.6, 113.7, 81.8, 81.2, 72.5, 72.1, 71.9, 55.1, 33.3, 32.6, 32.0, 31.7, 30.1, 29.9, 29.5, 29.2, 25.3, 24.6, 22.5 (d), 13.91.

(2*S*, 3*S*)-4-(*tert*-Butyldiphenysilyloxy)-2-methylbutane-1,3diol (13). A solution of DMSO (3.66 mL, mmol) in CH_2Cl_2 (20 mL) was added dropwise to a precooled (-78 °C) solution of oxalyl chloride (2.11 mL, 24.96 mmol) in dry CH_2Cl_2 (20 mL). After stirring the reaction mixture at the same temperature for 30 min, a solution of the monosilylated ethylene glycol **15** (5.0 g, 16.64 mmol) in CH_2Cl_2 (40 mL) was added slowly, and stirred for another 30 min at -78 °C. A solution of Et_3N (10.18 mL, 73.21 mmol) in CH_2Cl_2 (40 mL) was added at -78 °C and the stirring was continued for additional 1 hour at the room temperature. The mixture was partitioned between water and CH_2Cl_2 and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo* to give the crude aldehyde, which was used for the next step.

To a stirred solution of above aldehyde and D-proline (192 mg, 1.66 mmol) in dioxane (17 mL) at 4 °C was added dropwise a precooled (4 °C) solution of propionaldehyde (5.95mL, 83.20 mmol) in dioxane (17 mL) over 24 hours via syringe pump. The mixture was continuously stirred for an additional 24 hours at the same temperature. After completion, the reaction was diluted with ethyl acetate washed with brine and organic layer was dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude aldehyde obtained was directly used for the next reaction.

To a stirred suspension of above aldehyde in dry MeOH (40 mL) was added $NaBH_4$ (1.26 g, 33.28 mmol) in small lots at 0 °C. After stirring the mixture at room temperature for 30 min, reaction mixture was quenched with slow addition of saturated NH_4Cl solution. The organic layer was extracted with EtOAc (3 x 40 mL), dried over anhydrous Na_2SO_4, and evaporated under vacuum. Silica gel column chromatography (hexane/EtOAc 4:1 v/v) of the residue afforded 1,3-diol **13** (5.10 g, 86%) as a thick colorless liquid. [R_f 0.4, EtOAc/hexane 3:7 v/v]; $[\alpha]_D^{25}$ +4.48 (*c* 1.0, MeOH); IR (CH_2Cl_2) *v*: 3458, 2935, 1452, 1110, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.67-7.65 (m, 4H), 7.46-7.37 (m, 6H), 3.95-3.71 (m, 1H), 3.67-3.57 (m, 4H), 3.06-3.00 (brs, 2H), 1.81-1.74 (m, 1H), 1.07 (s, 9H), 0.75 (d, *J* 6.88 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 135.5, 132.9, 129.9, 127.8, 77.1, 67.5, 66.4, 37.1, 26.8, 19.2, 13.4; HRMS (ESI), calcd for $C_{21}H_{30}O_3SiNa$ $[M+Na]^+$ 381.1856; found 381.1857; HPLC: Chiralcel OD-H (250 x 45 mm), EtOH:n-hexane (01:99) v/v, flow rate 1.0 ml/min, λ_{max}= 220 nm, t_R= 10.83, t_R= 12.05, t_R= 13.55 and t_R= 14.91, > 99% ee, *anti*:*syn* 98:2.7.

(2*S*,3*S*)-1-(*tert*-Butyldiphenylsilyloxy)-4-(4-methoxybenzyloxy)-3-methylbutan-2-ol (21). To a solution of diol **13** (5.0 g, 13.99 mmol) in acetone (60 mL) were added K_2CO_3 (5.78 g, 41.82 mmol), TBAI (50 mg) and *p*-methoxy benzyl chloride (2.27 mL, 16.73 mmol) sequentially. The resulting mixture was refluxed for 18 hours. The reaction mixture was then concentrated under reduced pressure, the crude was dissolved in water (40 mL) and extracted with EtOAc (3 x 40 mL). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (hexane/EtOAc 9:1 v/v) to obtain **21** (5.48 g, 83%) as a colourless liquid. [R_f 0.6, EtOAc/hexane 3:17 v/v]; $[\alpha]_D^{25}$ +7.26 (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) *v*: 3433, 2932, 2860, 1430, 1105, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.66 (dt, *J* 8.0, 1.2 Hz, 4H), 7.46-7.31 (m, 6H), 7.20 (d, *J* 8.6 Hz, 2H), 6.85 (d, *J* 8.6 Hz, 2H) 4.39 (s, 2H), 3.79 (s, 3H), 3.75-3.58 (m, 3H), 3.51-3.34 (m, 2H), 3.06 (d, *J* 3.4 Hz, 1H), 2.06-1.86 (m, 1H), 1.05 (s, 9H), 0.91 (d, *J* 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.3, 135.7, 133.4, 130.5, 129.9, 129.4, 127.9, 113.9, 75.0, 73.0, 66.3, 55.4, 35.8, 27.0, 19.4, 14.1; HRMS (ESI), calcd for $C_{29}H_{38}O_4SiNa$ $[M+Na]^+$ 501.2431; found 501.2432

3(*S*)-2((*S*)-1-(4-Methoxybenzyloxy)propan-2-yl)oxirane (22). To a stirred solution of **21** (5.0 g, 10.4 mmol) in dry THF (50 ml), TBAF (1.0 M in THF, =15.66 mL, 15.66 mmol) was added, and resulting solution was stirred for 1.5 hours at room temperature. Saturated solution of NH_4Cl was added to quench the reaction. The aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in *vacuo* to get the diol. The crude residue was taken for the next reaction without further purification.

To a solution of above diol at 0 °C in dry DCM (20 mL), was added Et_3N (1.73 mL, 12.48 mmol), TsCl (2.37 g, 12.48 mmol) and Bu_2SnO (517 mg, 2.08 mmol) sequentially. The resulting solution was stirred for 30 min at room temperature and quenched with water (20 mL). The aqueous layer extracted with DCM (3 x 20 mL). The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in *vacuo*. The crude monotosylated derivative formed was utilized for the next reaction without further purification.

To a solution of monotosylated derivative formed in the above reaction in ether (20 ml) was added KOH (1.75 g, 31.2 mmol). The resulting solution was stirred for 2 hours at room temperature and after which the turbid solution was quenched with H_2O (20 mL). The aqueous layer was extracted with ether (3 x 20 mL), organic layer separated, washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure.

Purification by silica gel chromatography (hexane/EtOAc 19:1 v/v) afforded the epoxide **22** (2.05 g, 89%) as colorless liquid. [R_f 0.7, EtOAc/hexane 1:9 v/v]; $[\alpha]_D^{25}$ +14.30 (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) *v*: 2899, 1431, 1106, 1071, 686 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.27 (d, *J* 8.6 Hz, 2H), 6.88 (d, *J* 8.7 Hz, 2H), 4.46 (s, 2H), 3.80 (s, 3H), 3.52-3.38 (m, 2H), 2.90-2.84 (m, 1H), 2.77-2.72 (m, 1H), 2.54 (dd, *J* 5.2, 2.8 Hz, 1H), 1.72-1.66 (m, 1H), 0.99 (d, *J* 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.2, 130.7, 129.3, 113.9, 72.9, 72.5, 55.4, 54.4, 45.9, 36.7, 13.3; HRMS (ESI), calcd for $C_{13}H_{18}O_3Na$ $[M+Na]^+$ 245.1148; found 245.1157.

(3*R*,4*S*)-5-(4-Methoxybenzyloxy)-4-methylpent-1-en-3-ol (23). To a -10 °C suspension of trimethylsulphonium iodide (7.33 g, 35.96 mmol) in THF (70 mL) was added *n*-BuLi (2.5 M hexane solution, 13.31 mL, 33.26 mmol). After 30 min a solution of epoxide 22 (2.0 g, 8.99 mmol) in THF (20 mL) was added dropwise and the reaction was continued at 0 °C for 1 hour then mixture was stirred at room temperature for further 1.5 hours. The reaction was quenched with water and extracted with ethyl acetate. The combined extract was washed with brine, dried over sodium sulfate, filtered, and concentrated under vacuum. The residues were purified on silica gel coloumn chromatography (hexane/EtOH 1:4 v/v) to give the desired allylic alcohol (1.92 g, 91%) **23** as colourles liquid. [R_f 0.4, EtOAc/hexane 1:9 v/v]; $[\alpha]_D^{25}$ 18.3 (c 0.125, MeOH); IR (CH_2Cl_2) v: 3450, 2930, 2858, 1612, 1246, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.25 (dt, *J* 0.8, 6.4 Hz, 2H), 6.88 (dt, *J* 6.8, 2.8 Hz, 2H), 5.83 (ddd, *J* 17.1, 10.4, 6.6 Hz, 1H), 5.25 (dt, *J* 17.2, 1.6 Hz, 1H), 5.16-5.13 (m, 1H), 4.45 (s, 2H), 3.99 (td, *J* 7.2, 3.2 Hz, 1H), 3.80 (s, 3H), 3.59 (dd, *J* 9.6, 4.4 Hz, 1H), 3.48-3.41 (m, 2H), 1.93- 1.83 (m, 1H), 0.88 (d, *J* 6.8 Hz , 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.4, 139.6, 1230, 129.5, 115.9, 114.0, 77.9, 74.5, 73.2, 55.4, 38.6, 13.9; HRMS (ESI), calcd for $C_{14}H_{20}O_3Na$ $[M+Na]^+$ 259.1304; found 259.1309.

***tert*-Butyl((3*R*,4*S*)-5-(4-methoxybenzyloxy)-4-methylpent-1-en-3-yloxy)dimethylsilane (24**). To an ice-cold solution of **23** (1.70 g, 7.19 mmol) in dry CH_2Cl_2 (20 mL) under nitrogen, imidazole (741 mg, 10.78 mmol), TBSCl (1.46 g, 9.3 mmol) and DMAP (175 mg, 0.20 mmol) were added sequentially and mixture was stirred for 2.5 hours before quenching of the reaction mixture with saturated aqueous NH_4Cl (10 mL). The reaction mixture was extracted with CH_2Cl_2, washed with brine and dried over Na_2SO_4, concentrated in *vacuo* and purified on silica gel (hexane/EtOAc 24:1 v/v) to furnish TBS protected compound **24** (2.39 g, 95%) as a colorless oil. [R_f 0.6, EtOAc/hexane 1:19 v/v]; $[\alpha]_D^{25}$ +4.22 (c 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 2929, 2856, 1615, 1511, 1248 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 7.25 (td, *J* 6.4, 2.8 Hz, 2H), 6.87 (d, *J* =8.7 Hz, 2H), 5.76 (ddd, *J* 17.1, 7.4, 4.1 Hz, 1H), 5.17-5.02 (m, 2H), 4.41 (q, *J* 21.2, 11.6 Hz, 2H), 4.17 (q, *J* 7.2 , 4.0 Hz , 1H), 3.80 (s, 3H), 3.43 (dd, *J* 9.1, 6.0 Hz, 1H), 3.31-3.21 (m, 1H), 1.92-1.79 (m, 1H), 0.95-0.87 (m, 12H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 159.2, 139.6, 131.0, 129.3, 115.3, 113.8, 75.4, 72.8, 72.2, 55.4, 40.1, 26.01, 18.3, 13.2, -4.1, -4.8; HRMS (ESI), calcd for $C_{20}H_{34}O_3SiNa$ $[M+Na]^+$ 373.2169; found 373.2170.

(2*S*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylpent-4-en-1-ol (25). To a solution of compound **24** (1.5 g, 4.27 mmol) in CH_2Cl_2 (15 mL) 0 °C was added DDQ (1.16 g, 5.13 mmol) and aqueous pH 7.0 buffer (5 mL). After stirring for 45 minutes room temperature, the reaction was quenched by the addition of saturated aqueous $NaHCO_3$ (10 mL) solution. The mixture was diluted with CH_2Cl_2 (15 mL), the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by silica gel chromatography (hexane/EtOAc 19:3 v/v) to furnished a pale yellow liquid **25** (918 mg, 93%); [R_f 0.5, EtOAc/hexane 1:9 v/v]; $[\alpha]_D^{25}$ +7.26 (c 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 3458, 2929, 2858, 1462, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) *δ*: 5.83 (ddd, *J* 17.1, 10.4, 6.7 Hz, 1H), 5.23-5.11 (m, 2H), 4.07 (t, *J* 8.0 Hz, 1H), 3.73 (d, *J* 10.9 Hz, 1H), 3.61-3.54 (m, 1H), 2.72 (brs, 1H), 1.76-1.67 (m, 1H), 0.94 (d, *J* 6.8 Hz, 3H), 0.91 (s, 9H), 0.09 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 140.3, 115.7, 79.6, 66.0, 40.8, 26.0, 18.2, 14.3, -3.9, -4.8; HRMS (ESI), calcd for $C_{12}H_{26}O_2SiNa$ $[M+Na]^+$ 253.1594; found 253.1597.

(2*R*,3*R*)-3-(*tert*-Butyldimethylsilyloxy)-2-methylpent-4-enoic acid (12). To a solution of alcohol **25** (900 mg, 3.90 mmol) in DCM:H_2O (2:1) (12) mL was added TEMPO (121 mg, 0.78 mmol) and bis(acetoxy)iodobenzene (BAIB) (2.76 g, 8.59 mmol) sequentially. The resulting mixture was stirred at room temperature for 24 hours and quenched by addition of saturated solution of $Na_2S_2O_3$. The mixture was diluted with EtOAc (15 mL), the layers were separated, and the aqueous layer was extracted with EtOAc (3×10 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. Silica gel column chromatography (hexane/EtOAc, 4:1 v/v) of the residue afforded acid **12** (830 mg, 87%) as a yellow solid. Mp 77-78 ^oC; [R_f 0.5, EtOAc/hexane 3:7 v/v]; $[\alpha]_D^{25}$ -12.5 (*c* 1.0, $CHCl_3$); IR (CH_2Cl_2) v: 2929, 2857, 1719, 1461, 1252 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 5.75 (ddd, *J* 17.3, 10.4, 7.2 Hz, 1H), 5.21 (ddt, *J* 12.6, 10.5, 1.3 Hz, 2H), 4.25 (t, *J* 6.96 Hz, 1H), 2.59-2.55 (m, 1H), 1.13 (d, *J* 6.80 Hz, 3H), 0.91-0.84 (s, 9H), 0.075 (s, 3H), 0.049 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 179.2, 138.3, 117.3, 76.2, 46.7, 25.8, 18.2, 13.5, -4.1, -5.1; HRMS (ESI), calcd for $C_{12}H_{24}O_3SiNa$ $[M+Na]^+$ 267.1387; found 267.1395.

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Supplementary Material

Electronic supplementary information (ESI) available: copies of ^1H and ^{13}C NMR spectra of compounds **11, 13**, **16-20**, **21-25**, and HPLC data of compound **13**. This material can be found via the "Supplementary Content" section of this article's webpage.

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