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Stereocontrolled Synthesis of the Highly Functionalized Core Structure of Aurisides by Ring-Closing Metathesis

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Two approaches based on the ring-closing metathesis reaction have been explored for the synthesis of the core structure of the marine natural products, the aurisides. The second approach, accomplished in a stereocontrolled manner, used both a Brown's allylation and an Evans' aldolisation, and finally a transannular ketalization to deliver a highly functionalized auriside analogue.

Introduction

Aurisides A (**1**) and B (**2**) are two glycosidated macrolides isolated from the sea hare *Dolabella auricularia* in 1996 by Yamada and co-workers, which have shown significant cytotoxicities against $HeLaS_3$ cervical cancer cells lines, with IC_{50} values of 0.17 and 1.2 $\mu g\,mL^{-1}$, respectively.[1] Their structures, determined by extensive NMR studies, feature a 14-membered glycosidated macrolactone containing a six-membered hemiacetal ring, a *E*-trisubstituted enone and a brominated conjugated side chain (Figure 1).

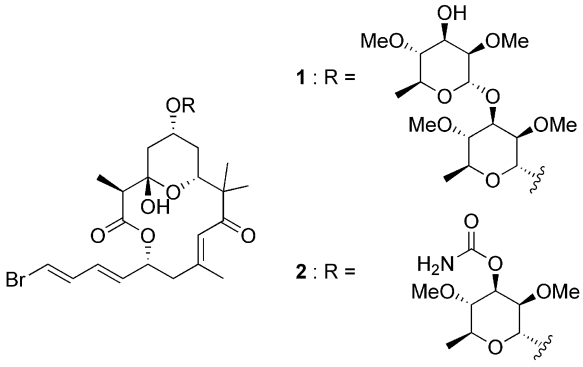

Figure 1. Structures of Aurisides A and B.

Several natural products structurally related to the aurisides, such as dolastatin 19 (**3**), lyngbyaloside (**4**) or lyngbouilloside (**5**) have also been isolated (Figure 2),[2] and studies have been made to synthesize these compounds.[3]

Because of their complex structure, their promising biological activities and low availability from the natural sources, total syntheses of the aurisides have been already considered. The enantioselective synthesis of these compounds was first achieved by Paterson and co-workers, using highly stereoselective aldol reactions.[4] Intensive efforts have also been made by the Kigoshi's group,[5a] who published the total synthesis, using (*R*)-pantolactone as a chiron, based on previous work through the synthesis of the aglycon achieved by Yamada–Kigoshi group.[5b] More recently, Olivo and co-workers reported a convergent formal synthesis of the aglycon part, as a result of intensive researches in the aurisides area, using an indene-based thiazolidinethione chiral auxiliary for the construction of two advanced fragments.[6] Interestingly, in all reported syntheses the well-known Yamaguchi cyclisation[7] of a *seco* acid was used to reach the 14-membered macrolactone.

In connection with our interest in the synthesis of biologically important natural products, we have focused our researches on the use of the alkene metathesis reaction,[8–9] as a key step, in order to form either the tetrahydropyran moiety and/or the macrocyclic ring of the aurisides, which could be an interesting alternative strategy for the construction of the 14-membered macrolactone. In this paper, we would like to present our latest results concerning the above-mentioned strategies, using alkene metathesis reaction. In particular, a second generation approach will be illustrated by the convergent stereocontrolled synthesis of a truncated aurisides analogue.

Results and Discussion

Our first retrosynthetic approach for the synthesis of the aglycon part of the aurisides **6** is outline on Scheme 1. It was envisaged to install the bromodienic side chain at a later stage while the trisubstituted enone would emerged from the oxidation of the C9 allylic alcohol followed by

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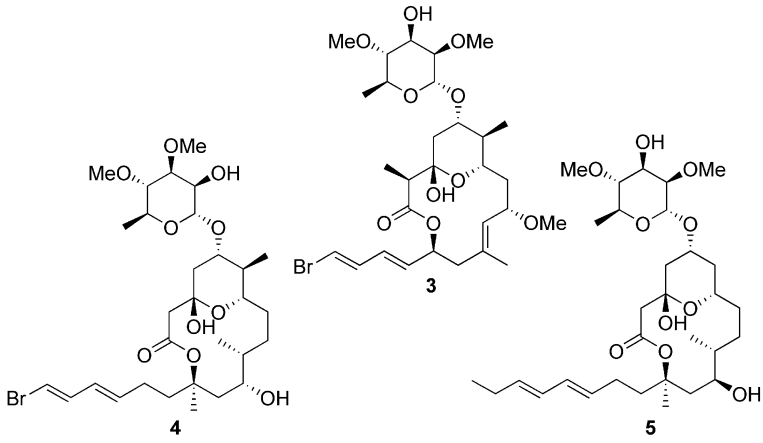
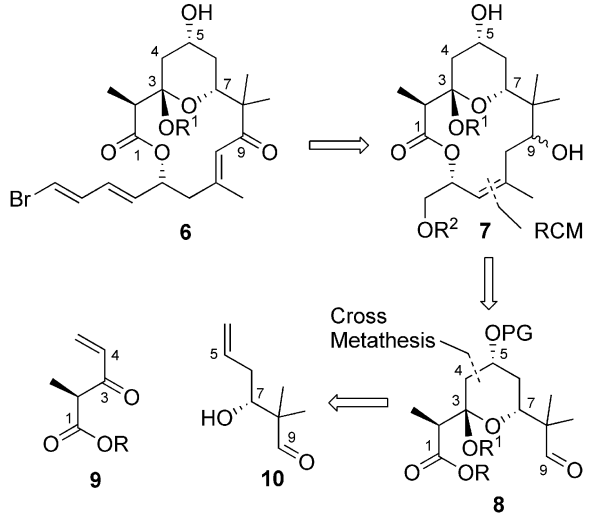


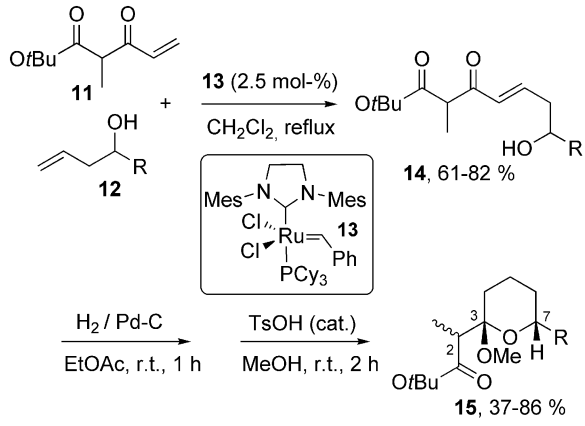
Figure 2. Other 14-membered ring macrolides isolated the sea.

reconjugation of the double bond under basic condition from compound **7**. In turn, this double bond could derive from a RCM reaction of an appropriate diene, which would be rapidly obtained from C1–C9 fragment **8** (aurisides numbering). Moreover, it was planned to build the tetrahydropyran moiety using a cross-metathesis reaction between building blocks **9** and **10**, directly followed by a reductive ketalization process.



Scheme 1. First retrosynthesis of the aurisides aglycon.

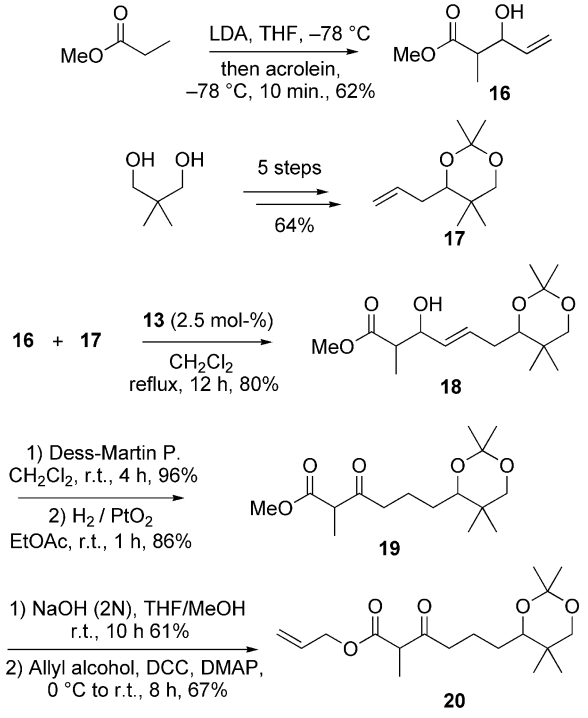
We have recently reported the feasibility of the cross metathesis/ketalization process for the formation of several oxygenated six-membered ring structures.[10] As shown on Scheme 2, cross metathesis reaction, using 2nd generation Grubbs catalyst **13**,[11] of *tert*-butyl 2 methyl-3-oxo-4-pentenoate (**11**) with homoallylic alcohol **12**, furnished the β-keto esters **14** with moderate to good yields and with exclusive (*E*) selectivity. Then, a hydrogenation/ketalization sequence yielded the expected heterocyclic compounds **15** as a 1:1 mixture of stereoisomers. It was anticipated that under the conditions used, the two adducts differed only by the relative configuration at C2. In each case, the methoxy group was placed in an axial position while the two alkyl rests on C3 and C7 adopted an equatorial position.



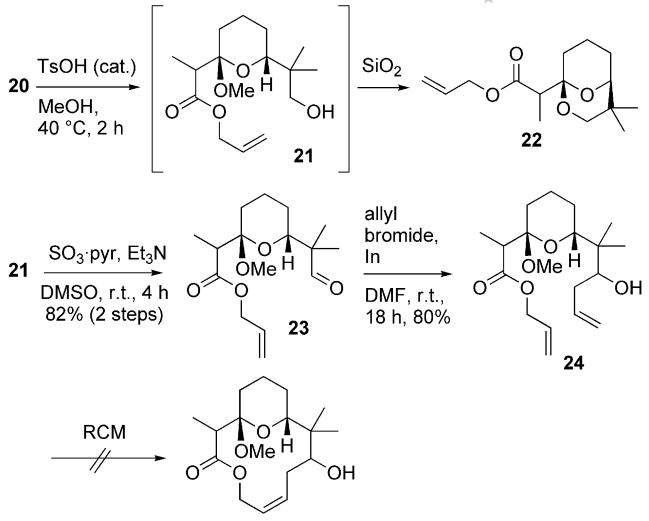
Scheme 2. Syntheses of oxygenated six-membered ring structures.

In order to verify our initial approach for the construction of the macrocyclic structure of the natural products, we then used the same process for the rapid synthesis of a *nor*-hydroxy C1–C9 fragment, which could be converted into the required precursor for the key RCM reaction. Thus, both compounds **16** and **17** were readily prepared in a one- or five-step sequence from commercially available methyl propionate and 2,2-dimethylpropane-1,3-diol.[10] The cross-metathesis reaction between **16** and **17** delivered alkene **18**, which was further oxidized using Dess–Martin Periodinane (DMP). After hydrogenation of the double bond, we found that it was more convenient to install the first unsaturation on this linear precursor using sequential ester hydrolysis with NaOH in THF/MeOH followed an esterification with allyl alcohol, under DCC activation[12] (Scheme 3).

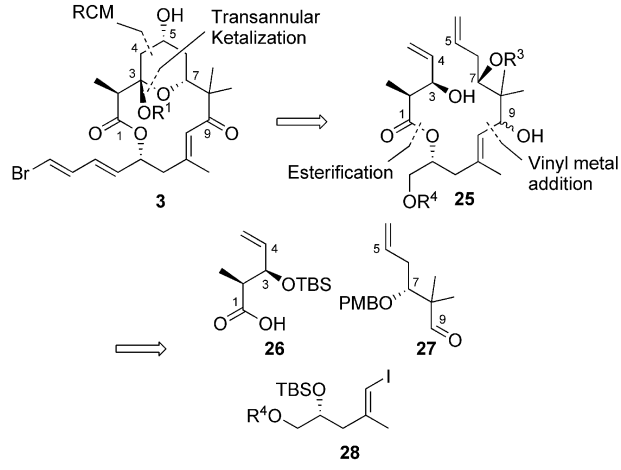
Dioxolane was then cleaved under acidic condition with concomitant formation of the methoxytetrahydropyran **21**. After purification by flash chromatography we observed the formation of the bicyclic compound **22**, which results from the substitution of the methoxy group by the primary



Scheme 3. Synthesis of compound **20**.



Scheme 4. Attempts of RCM of diene **24**.

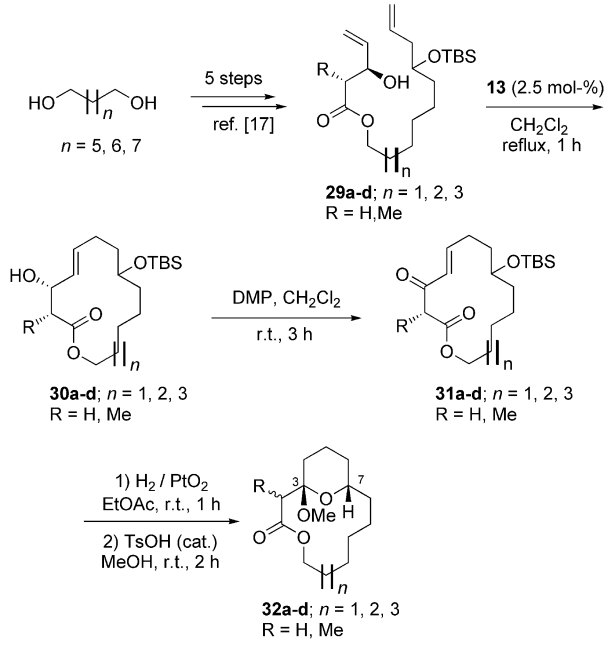


Scheme 5. Second retrosynthesis of the aurisides aglycon.

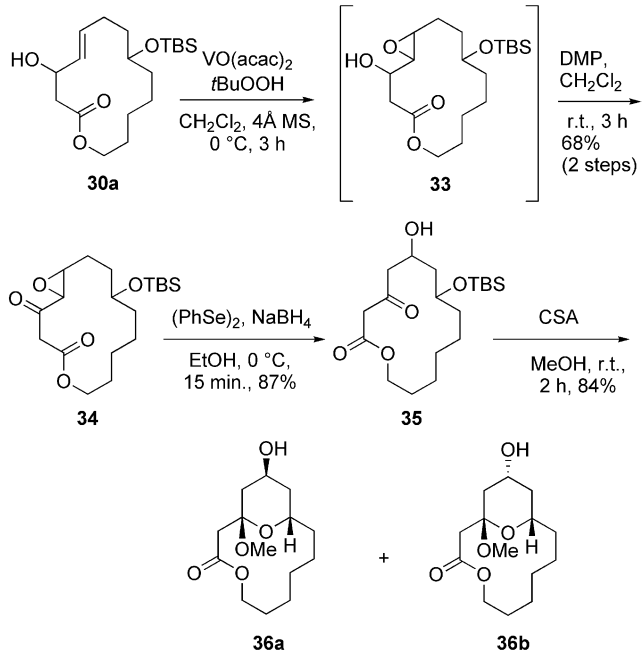
alcohol in **21**. This compound was used directly after basic work-up and oxidized to give aldehyde **23** in 82% overall yield. The second double bond was then introduced by a chemoselective allylation of the aldehyde moiety using organoindium reagent.[13] Once the required diene **24** was available, we next examined the formation of the macrocyclic structure by RCM. Unfortunately, all attempts failed, despite the use of several catalysts and various conditions tested. At 40 °C, we did not observe any conversion, when elevated temperature conducted to decomposition of the starting material (Scheme 4). Having the advanced intermediate **19** in hands, we reconsidered our strategy and found an alternative synthesis of a truncated core structure of the aurisides based on Yamaguchi's macrolactonization process (not shown).[10]

To overcome the drawbacks of our first strategy, we have now explored another route for the construction of the macrolactone core of the aurisides. Our second retrosynthetic approach is outline on Scheme 5. It was expected that the 14-membered macrolactone could result from a RCM reaction of an appropriate triene **25**, when the ketal ring would emerged from a subsequent transannular ketalization,[14–16] after introduction of the hydroxy group attached on C5. In turn, the required precursor **25** of the key RCM would arise from the coupling of three main fragments **26**, **27**, **28**. Stereochemistry is planned to be controlled by the use of an enantioselective Brown's allylation for the construction of the C7 stereocentre, when a diastereoselective Evans' aldol-type reaction would furnish the correct configuration of C2. Concerning the 5-OH group, a diastereoselective epoxydation directed by 3-OH could allow the installation of this functional group.

We first developed this strategy for the construction of 14-, 15- and 16-membered macrolactones (Scheme 6).[17] The required dienes **29a**–**d** for the macrocyclisation were easily prepared from 1,7-heptanediol, 1,8-octanediol and 1,9-nonanediol in a five-steps procedure. Ring closing metathesis was performed using catalytic amounts of second-generation Grubbs catalyst **13**, and similar yields were obtained regardless of the size of the cyclised products **30a**–**d**, with still high *E* selectivity. Further oxidation of the allylic alcohol with Dess–Martin Periodinane furnished compounds **31a**–**d** in high yields (Table 1). Hydrogenation of the double bond, followed by cleavage of the silyl ether with concomitant transannular ketalization occurred nicely. The relative configuration of the methoxy group and the hydrogen atom attached on C3 and C7 respectively was assigned by nOe experiment performed on compound **32a**.[17] This relative configuration was assigned to the other adducts. Compounds **32b**–**d** (R = Me) were obtained as 1:1 mixture of inseparable stereoisomers.



Scheme 6. Access to macrolactones **32a**–**d** by a RCM/transannular ketalization sequence.



Scheme 7. Synthesis of 5-hydroxymacrolactones **36a** and **36b**.

Table 1. Formation of macrolactones **32a**–**d** from esters **29a**–**d**.

Entry	*n*, R	RCM (% yield)[a]	Oxidation (% yield)[a]	Hydrogenation Ketalization (% yield)[a]
1	1, H	**30a** (86%)	**31a** (85%)	**32a** (79%)
2	1, Me	**30b** (83%)	**31b** (89%)	**32b** (78%)
3	2, Me	**30c** (76%)	**31c** (86%)	**32c** (79%)
4	3, Me	**30d** (82%)	**31d** (83%)	**32d** (75%)

[a] Isolated yields.

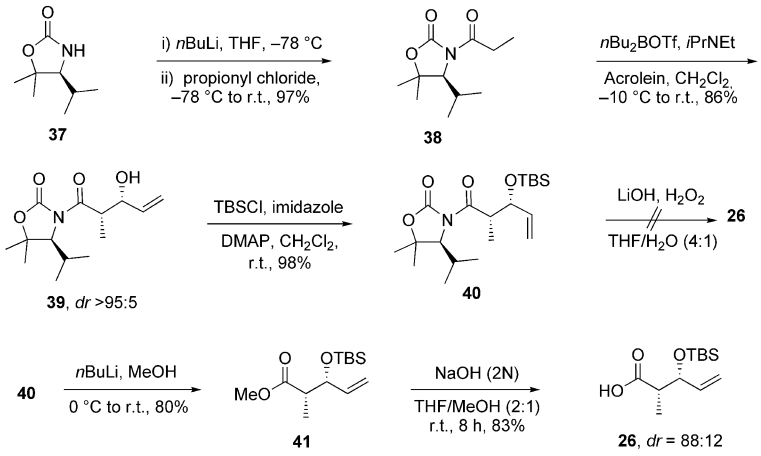
Then we took advantage of the allylic alcohol to introduce the 5-OH group of the natural products (Scheme 7). Compound **30a** could be diasteroselectively epoxidized by using *t*BuOOH/VO(acac)$_2$[18] to deliver compound **33**, which was directly oxidized to yield the corresponding epoxy ketone **34**. Regioselective epoxide opening was then achieved with sodium selenoate.[19] Subsequent TBS deprotection followed by in-situ formation of the tetrahydropyran subunit furnished the expected macrolides **36a** and **36b**. The two compounds, produced as a 1:1 mixture of diastereomers, could be eventually separated chromatography, and differ by the relative position of 5-OH.[14,17]

Next we decided to apply our straightforward method for the construction of such macrolactones to the stereocontrolled synthesis of a truncated aurisides' analogue. Following the retrosynthetic approach depicted on Scheme 5, the synthesis of carboxylic acid **26** began with the condensation of propionyl chloride with Superquat oxazolidinone **37**.[20] The aldol reaction was achieved by reaction of **38** with acrolein to yield the expected *syn* compound **39** with high diastereoselectivity. Allylic alcohol was then protected as a silyl ether in high yield. Surprisingly, cleavage of the chiral auxiliary could not be achieved under the classical LiOH/H_2O_2 conditions, so compound **40** was first converted into methyl ester **41** prior to saponification, which furnished the required acid **26**, with slight epimerization on the α position of the carbonyl group (Scheme 8).

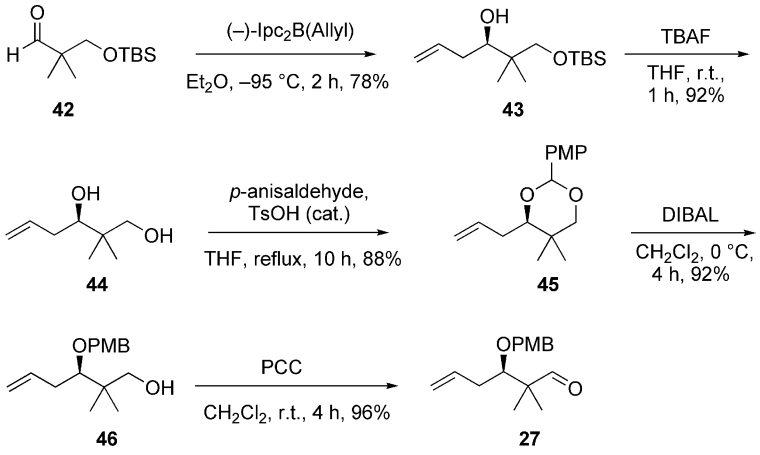
Next, the synthesis of fragment **27** started with Brown's[21] enantioselective allylation of known aldehyde **42**, which yielded the homoallylic alcohol **43** in 78% yield. The TBS protecting group was then removed by the use of TBAF, and diol **44** was treated with *p*-anisaldehyde in the presence of a catalytic amount of TsOH to deliver the benzylidene ketal **45**. Then, action of DIBAL allowed to release selectively the primary alcohol **46**, which was further oxidized into aldehyde **27** using PCC in dichloromethane (Scheme 9).

Synthesis of the third fragment **47**, a truncated structure of compound **28** was conveniently obtained according to a known procedure.[22] Thus, having the three required fragments in hands, we then proceeded to add compound **47** to aldehyde **27**, after previous transmetallation with *t*BuLi at very low temperature. Product **48** was obtained as a 1:1 mixture of diastereomers concerning the allylic alcohol position. The presence of the PMB allowed us to protect this hydroxy group by using DDQ under anhydrous conditions.[23] The benzylidene acetal **49** was formed in 74% yield. Removal of the TBS protecting group by TBAF delivered the primary alcohol **50**, which was esterified with carboxylic acid **26** under DCC activation to yield ester **51** in good yield (Scheme 10).

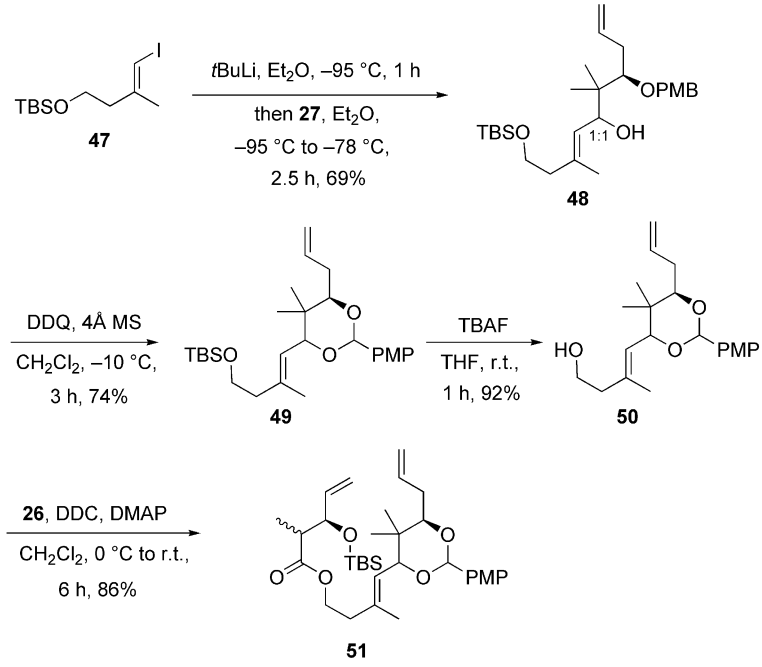
In order to reduce the steric congestion around the two terminal double bonds and to facilitate the desired RCM we removed the silyl group. Treatment of compound **51** with TBAF required slight heating to observe full conversion and eventually yielded the allylic alcohol **52**. Unfortunately, the ring-closure and formation of the expected 14-membered macrolactone was not observed. Even with high



Scheme 8. Synthesis of carboxylic acid **26**.

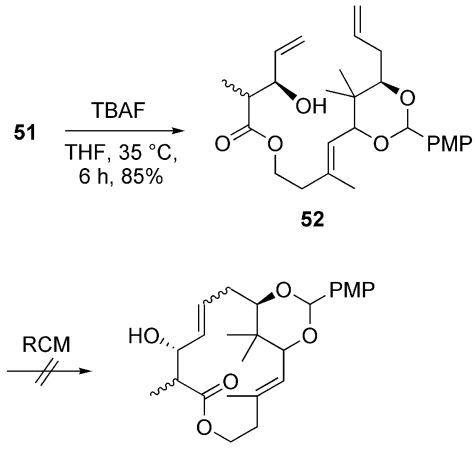


Scheme 9. Synthesis of aldehyde **27**.



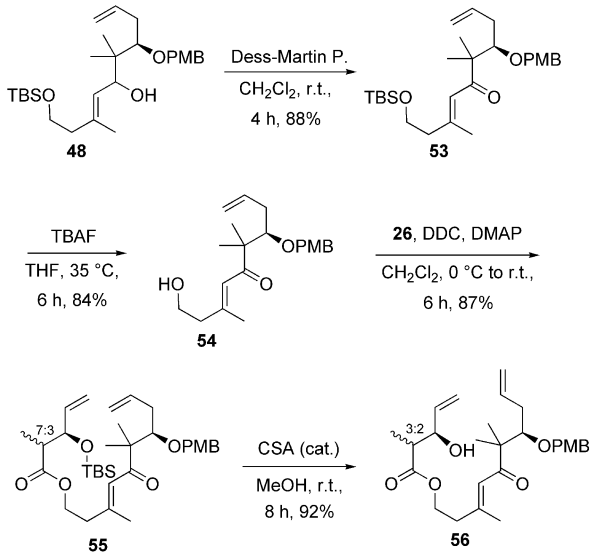
Scheme 10. Synthesis of ester **51**.

loading of different catalysts (up to 15 mol-%) no conversion of the starting material was observed at 40 °C while higher temperatures caused decomposition. We assume that a conformational bias due to the presence of the six-membered benzylidene moiety is responsible of the failure (Scheme 11).



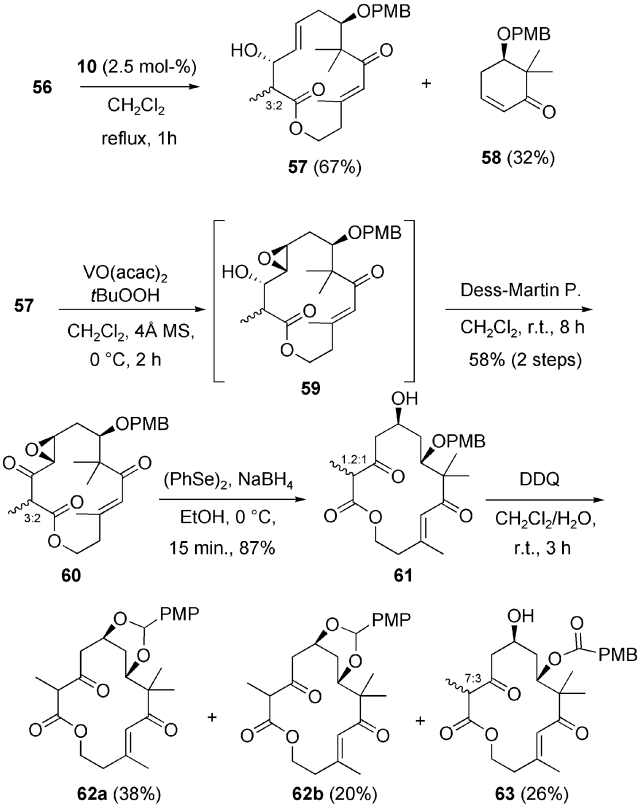
Scheme 11. First attempts of RCM.

To overcome this problem, we decided to form the enone moiety prior to the RCM event, in order to rigidify the structure of the precursor of the cyclization. Thus, allylic alcohol **48** was oxidized with Dess–Martin periodinane in good yield. Further deprotection of the silyl ether furnished primary alcohol **54**, which was esterified with acid **26** as described above. Partial epimerization of the methyl group attached on C2 was observed, and a 7:3 ratio was determined by integration of signals of the ^{1}H NMR spectrum. After optimization, CSA in MeOH appeared as the most suitable reagent to remove the TBS protecting yielding the new RCM precursor **56** (Scheme 12).



Scheme 12. Synthesis of the second precursor **56**.

To our delight, the RCM event of this second precursor **56** proceeded well and delivered the expected macrocycle **57** with an exclusive *E* selectivity for the new created double bond, along with the formation of cyclohexenone **58**. Then we repeated the sequence developed previously on unfunctionalized macrolactone **30a** for the introduction of 5-OH. Thus, epoxy ketone **60** was obtained according to a diastereoselective epoxidation followed directly by the oxidation of the hydroxy group with DMP. Compound **60** was subsequently reduced compound into the β-hydroxy ketone **61**. Next, deprotection of the PMB ether was envisioned by treatment with DDQ in aqueous conditions. However, instead of the desired diol we observed the formation of the two benzylidene acetals **62a** and **62b** and a third side-product **63** which results of the overoxidation. The three compounds were separated by carefully performed flash-chromatography (Scheme 13).



Scheme 13. RCM and functionalization of C5.

Compounds **62a** and **62b** were characterized by nOe experiments, which showed strong correlation between hydrogen atoms attached to C5, C7 and the benzylic proton. These results prove the same relative and absolute configuration of both stereocentres C5 and C7 for the two compounds, meaning also that they only differ by the relative configuration of the C2 stereocenter. At this stage, no statement concerning the absolute configuration at C2 of **62a** and **62b** is possible (Figure 3).

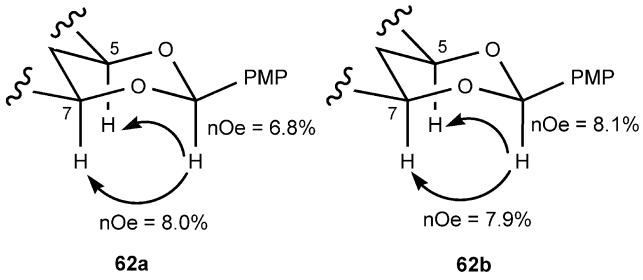
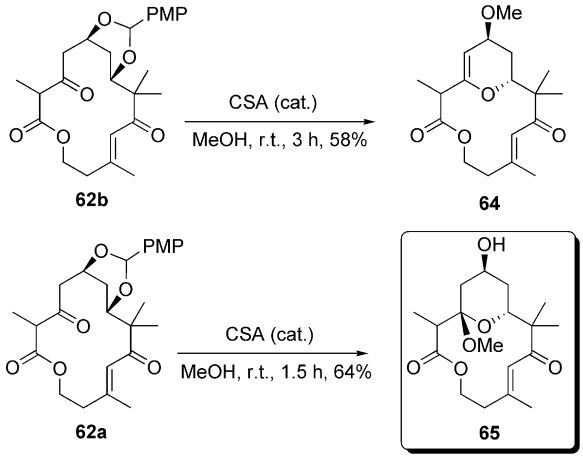


Figure 3. nOe experiments for compounds **62a** and **62b**.

Finally, the benzylidene acetal was carefully removed under acidic media. Prolonged exposure to the CSA/MeOH yielded methyl ether **64** from compound **62b**, a well-monitored reaction furnished the expected truncated auriside analogue **65** as a single diastereoisomer (Scheme 14).[24]



Scheme 14. Synthesis of a truncated auriside analogue **56**.

Conclusions

While studying synthetic methods leading to natural macrolides of the auriside type, two different routes including alkene metathesis reaction were found. We were able to build the macrocyclic core of the natural product in an alternative and original way of the well established Yamaguchi macrocyclization. The convergent stereocontrolled synthesis of a truncated auriside analogue was accomplished in 18 steps (longest linear sequence) with an overall yield of 2.3%. This route should also offer access to related compounds like dolastatin 19 or lyngbouillouside. Work is in progress to apply this strategy to different targets and will be reported in due course.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded either in $CDCl_3$ or in C_6D_6 solvent on a Bruker AM 300, 500 or 75 MHz spectrometer at ambiant temperature, which provided all necessary data for full compound assignments. Chemical shifts (δ values) are given in ppm units, coupling constant J are in Hz. The chemical shifts are reported in ppm on scale upfield from TMS as an internal standard and signal patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; dt, doublet of triplet; t, triplet; m, multiplet, br, broad singlet. High resolution mass spectrometry (HRMS) analyses were conducted using a ThermoFinigan-MAT 95 XL instrument. Optical rotations were measured on a digital polarimeter using a 5 mL cell with a 1 dm path length. IR spectra were measured on a Perkin–Elmer Spectrum One FT-IR spectrometer. TLC analyses were performed on plates (layer thickness 0.25 mm) and were visualized with UV light, phosphomolybdic acid or *p*-anisaldehyde solution. Column chromatography was performed on silica gel (40–63 μm) using technical grade ethyl acetate (EtOAc) and petroleum ether (EP). When appropriate, solvents and reagents were dried by distillation over appropriate drying agent prior to use. Diethyl ether and tetrahydrofuran (THF) were distilled from Na/benzophenone and used fresh. Dichloromethane was distilled from CaH_2. All the reactions were performed under an atmosphere of nitrogen in flame or oven-dried glassware with magnetic stirring.

Compound 38:[25] To a solution of chiral auxiliary **37** (1.57 g, 10.00 mmol) in dry THF (50 mL) was added at –78 °C, *n*BuLi (1.5 M in hexanes, 7.33 mL, 11.00 mmol). The resulting mixture was stirred at this temperature for 1 h, and then propionyl chloride (0.96 mL, 11.00 mmol) was added dropwise. The mixture was warmed at room temp. and stirred for 18 h. After the addition of saturated aqueous NH_4Cl (30 mL), the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduced pressure. The crude residue was purified by column chromatography (10% EtOAc in petroleum ether) to give compound **38** (2.07 g, 9.70 mmol, 97%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (d, J = 7.0 Hz, 3 H, CH_3-CH), 1.02 (d, J = 7.0 Hz, 3 H, CH_3-CH), 1.19 (t, J = 7.4 Hz, 3 H, CH_3-CH_2), 1.38 (s, 3 H, CH_3-C), 1.51 (s, 3 H, CH_3-C), 2.14 (dsept, J = 3.3, 7.0 Hz, 1 H, CH_3-CH-CH_3), 2.90 (dq, J = 17.5, 7.4 Hz, 1 H, CH_2-CH_3), 3.01 (dq, J = 17.5, 7.4 Hz, 1 H, CH_2-CH_3), 4.14 [d, J = 3.3 Hz, 1 H, CH-CH-$(CH_3)_2$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.6, 16.8, 21.2, 21.3, 28.6, 28.9, 29.4, 66.0, 82.6, 153.4, 174.3 ppm.

Compound 39: To a solution of *N*-oxazolidinone **38** (1.57 g, 10.00 mmol) in dry CH_2Cl_2 (30 mL) were successively added at 0 °C, diisopropylethylamine (2.17 mL, 13.13 mmol) and nBu$_2$BOTf (1 M in CH_2Cl_2, 11.25 mL, 11.25 mmol). The resulting mixture was stirred at this temperature for 15 min and then cooled to –78 °C. Then acrolein (0.94 mL, 14.07 mmol) was slowly added, and the mixture stirred 1 h at –78 °C, and then 30 min at 0 °C. After the addition water (15 mL) and MeOH (50 mL), a 2:1 solution of MeOH/H_2O_2 was added at 0 °C over a period of 20 min, and the mixture stirred for a further 20 min. Then, solvents were removed under reduce pressure and the residue partitioned between water (50 mL) and Et_2O (50 mL). The aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (10% EtOAc in petroleum ether) to give alcohol **39** (2.17 g, 8.07 mmol, 86%) as a colourless oil. $[\alpha]_D^{22}$ = +39.3 (c = 1.01; $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3507, 3095, 2985, 2874, 1779, 1674, 1363, 1234, 1177 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.95 (d, J = 7.0 Hz, 3 H, CH_3-CH-CH_3), 1.01 (d, J = 7.0 Hz, 3 H, CH_3-CH-CH_3), 1.28 (d, J = 7.1 Hz, 3 H, CH_3-CH), 1.40 (s, 3 H, CH_3-C), 1.52 (s, 3 H, CH_3-C), 2.14 (dsept, J = 3.3, 7.0 Hz, 1 H, CH_3-CH-CH_3), 2.93 (br. s, 1 H, OH), 3.94 (dq, J = 3.4, 7.1 Hz, 1 H, CH-CH_3), 4.19 [d, J = 3.3 Hz, 1 H, CH-CH-$(CH_3)_2$], 4.45–4.89 (m, 1 H, CH-OH), 5.21 (dt, J = 10.6, 1.5 Hz, 1 H, CH=CH_2), 5.34 (dt, J = 17.3, 1.5 Hz, 1 H, CH=CH_2), 5.83 (ddd, J = 17.3, 10.6, 5.5 Hz,

1 H, *CH*=CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 16.9, 21.3, 21.6, 28.7, 29.6, 42.5, 66.1, 72.8, 83.0, 116.3, 137.5, 153.2, 177.2 ppm. MS (ESI): *m*/*z* (%) = 292.1 (100) [M + Na^+], 561.0 (26) [2M + Na^+]. HRMS (ESI): calcd. for $C_{14}H_{23}NO_4Na$ 292.1525 [M + Na^+]; found 292.1526.

Compound 40: To a solution of alcohol **39** (2.00 g, 7.43 mmol) in dry CH_2Cl_2 (35 mL) were successively added at room temp., imidazole (2.53 g, 37.13 mmol), DMAP (91 mg, 0.74 mmol) and TBSCl (2.24 g, 14.85 mmol). and the resulting mixture was stirred at this temperature for 16 h. After the addition of saturated aqueous NH_4Cl (30 mL), the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (5% EtOAc in petroleum ether) to give compound **40** (2.79 g, 7.28 mmol, 98%) as a colourless oil. $[\alpha]_D^{22}$ = +41.8 (*c* = 1.00, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3080, 2961, 2857, 1779, 1698, 1362, 1219, 1119 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.02 (s, 3 H, CH_3-Si), 0.06 (s, 3 H, CH_3-Si), 0.88 [s, 9 H, $(CH_3)_3$-Si], 0.93 (d, *J* = 7.0 Hz, 3 H, CH_3-CH-CH_3), 1.00 (d, *J* = 7.0 Hz, 3 H, CH_3-CH-CH_3), 1.26 (d, *J* = 6.8 Hz, 3 H, CH_3-CH), 1.35 (s, 3 H, CH_3-C), 1.49 (s, 3 H, CH_3-C), 2.12 (dsept, *J* = 3.4, 7.0 Hz, 1 H, CH_3-*CH*-CH_3), 4.02–4.13 [m, 2 H, *CH*-CH_3 and *CH*-CH-$(CH_3)_2$], 4.24 (dd, *J* = 7.2, 7.9 Hz, 1 H, *CH*-OSi), 5.05 (ddd, *J* = 10.4, 1.7, 0.9 Hz, 1 H, CH=CH_2), 5.13 (ddd, *J* = 17.4, 1.7, 0.9 Hz, 1 H, CH=CH_2), 5.83 (ddd, *J* = 17.4, 10.4, 7.2 Hz, 1 H, *CH*=CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –4.7, –4.2, 15.0, 17.1, 18.3, 21.5, 21.6, 25.9, 28.7, 29.6, 44.4, 66.2, 76.0, 82.5, 116.0, 139.8, 153.3, 175.6 ppm. MS (ESI): *m*/*z* (%) = 406.2 (100) [M + Na^+], 789.1 (24) [2M + Na^+]. HRMS (ESI): calcd. for $C_{20}H_{37}NO_4SiNa$ 406.2390 [M + Na^+]; found 406.2390.

Compound 41: *n*BuLi (1.5 M in hexanes, 12.0 mL, 18.00 mmol) was added slowly at 0 °C to dry MeOH (30 mL) and the resulting mixture was stirred at this temperature for 15 min. Then, a solution of compound **40** (2.30 g, 6.00 mmol) in dry MeOH (5 mL) was added slowly at 0 °C, and the mixture was warmed at room temp. and stirred for 18 h. After the addition of saturated aqueous NH_4Cl (30 mL), the aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (5% EtOAc in petroleum ether) to give ester **41** (1.24 g, 4.80 mmol, 80%) as a colourless oil. $[\alpha]_D^{22}$ = +13.2 (*c* = 1.01, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3080, 2955, 2858, 1742, 1463, 1256, 1079, 837 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 3 H, CH_3-Si), 0.02 (s, 3 H, CH_3-Si), 0.87 [s, 9 H, $(CH_3)_3$-Si], 1.14 (d, *J* = 7.0 Hz, 3 H, CH_3-CH), 2.51 (dq, *J* = 5.5, 7.0 Hz, 1 H, *CH*-CH_3), 3.65 [s, 3 H, CH_3-OC(O)], 4.40 (dd, *J* = 5.5, 6.4 Hz, 1 H, CH_3-OSi), 5.10 (ddd, *J* = 10.4, 1.5, 1.3 Hz, 1 H, CH=CH_2), 5.13 (ddd, *J* = 17.4, 1.5, 1.3 Hz, 1 H, CH=CH_2), 5.83 (ddd, *J* = 17.4, 10.4, 6.4 Hz, 1 H, *CH*=CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.0, –4.2, 11.5, 18.2, 25.8, 46.7, 51.5, 75.0, 115.6, 139.6, 174.9 ppm.

Compound 26: To a 2:1 solution of ester **41** (1.10 g, 4.26 mmol) in THF/MeOH (24 mL) was added at room temp., a aqueous solution of NaOH (2 M, 4.26 mL, 8.51 mmol) and the resulting mixture was stirred at this temperature for 8 h. The mixture was then carefully acidified (pH3–4) using 1 M HCl. The aqueous phase was then extracted with EtOAc (5 × 10 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (30% EtOAc in petroleum ether) to give compound **26** (863 mg, 3.53 mmol, 83%) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3411, 2961, 2931, 2852, 1711, 1460, 1254, 1083, 837 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 3 H, CH_3-Si), 0.10 (s, 3 H, CH_3-Si), 0.91 [s, 9 H, $(CH_3)_3$-Si], 1.13 (d, *J* = 7.0 Hz, 3 H, CH_3-CH), 2.57–2.67 (m, 1 H, *CH*-CH_3), 4.36–4.40 (m, 1 H, *CH*-OSi), 5.19–5.28 (m, 2 H, CH=CH_2), 5.79 (ddd, *J* = 17.1, 10.4, 6.6 Hz, 1 H, *CH*=CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.0, –4.2, 11.2, 18.2, 25.9, 46.3, 75.0, 116.4, 138.4, 179.9 ppm. MS (CI): *m*/*z* (%) = 245 (100) [M + H^+]. HRMS (CI): calcd. for $C_{12}H_{25}O_3Si$ 245.1573 [M + H^+], found 245.1573.

Compound 43: Aldehyde **42** (2.00 g, 9.24 mmol) was enantioselectively allylated to give after purification by column chromatography (5% EtOAc in petroleum ether) compound **43** (1.89 g, 7.30 mmol 78% yield) as a colourless oil, following the procedure described for the synthesis of its enantiomer.[20] $[\alpha]_D^{22}$ = +19.5 (*c* = 1.00, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3497, 3072, 2957, 2931, 2859, 1473, 1256, 1093, 837 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 6 H, CH_3-Si), 0.84 (s, 3 H, CH_3-C), 0.90 [s, 9 H, $(CH_3)_3$-Si], 0.91 (s, 3 H, CH_3-C), 2.04–2.15 (m, 1 H, CH_2-CH=CH_2), 2.23–2.31 (dd, *J* = 5.8, 13.6 Hz, 1 H, CH_2-CH=CH_2), 3.48 (s, 2 H, CH_2-OSi), 3.52–3.55 (m, 1 H, *CH*-OH), 5.06–5.09 (m, 1 H, CH=CH_2), 5.11 (ddd, *J* = 17.1, 3.2, 1.7 Hz, 1 H, CH=CH_2), 5.94 (ddt, *J* = 17.0, 10.5, 6.9 Hz, 1 H, *CH*=CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.6, 18.2, 18.9, 22.2, 25.9, 36.7, 38.4, 73.2, 78.2, 116.4, 136.9 ppm.

Compound 44: To a solution of homoallylic alcohol **43** (4.00 g, 15.48 mmol) in THF (75 mL) was added at room temp. TBAF (1 M in THF, 17.02 mL, 17.02 mmol), and the resulting mixture was stirred at this temperature for 1 h. The mixture was then concentrated under reduce pressure. The crude residue was purified by column chromatography (35% EtOAc in petroleum ether) to give compound **44** (1.03 g; 7.12 mmol, 92% yield) as a colourless oil. $[\alpha]_D^{22}$ = –4.8 (*c* = 0.51, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3350, 3073, 2958, 2872, 1638, 1469, 1431, 1065, 912 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, CH_3-C), 0.92 (s, 3 H, CH_3-C), 2.02–2.13 (m, 1 H, CH_2-CH=CH_2), 2.33–2.42 (m, 1 H, CH_2-CH=CH_2), 3.48 (d, *J* = 10.9 Hz, 1 H, CH_2-OH), 3.53 (dd, *J* = 2.3, 10.7 Hz, 1 H, *CH*-OH), 3.55 (d, *J* = 10.9 Hz, 1 H, CH_2-OH), 5.15–5.20 (m, 2 H, CH=CH_2), 5.44 (dddd, *J* = 17.9, 12.4, 8.6, 5.5 Hz, 1 H, *CH*=CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7, 22.7, 36.7, 38.3, 72.1, 77.9, 117.7, 136.1 ppm.

Compound 45: To a solution of diol **44** (2.00 g, 13.87 mmol) in THF (65 mL) were successively added at room temp. *p*-anisaldehyde (3.37 mL, 27.74 mmol) and TsOH (132 mg, 0.69 mmol), and the resulting mixture was refluxed for 10 h. After cooling to room temp., a saturated solution of $NaHCO_3$ (30 mL) was added and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (5% EtOAc in petroleum ether) to give compound **45** (3.20 g, 12.20 mmol, 88% yield) as a colourless oil. $[\alpha]_D^{22}$ = +87.4 (*c* = 1.02, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3071, 2958, 2835, 1625, 1518, 1392, 1249, 1114, 1084, 826 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80 (s, 3 H, CH_3-C), 1.14 (s, 3 H, CH_3-C), 2.25 (ddd, *J* = 6.8, 6.3, 1.4 Hz, 2 H, CH_2-CH=CH_2), 3.54 (t, *J* = 6.3 Hz, 1 H, *CH*-O), 3.58 (d, *J* = 11.2 Hz, 1 H, CH_2-O), 3.70 (d, *J* = 11.2 Hz, 1 H, CH_2-O), 3.80 (s, 3 H, CH_3-O), 5.04 (ddt, *J* = 10.2, 2.1, 1.1 Hz, 1 H, CH=CH_2), 5.10 (ddd, *J* = 17.2, 3.6, 1.4 Hz, 1 H, CH=CH_2), 5.43 (s, 1 H, O-*C*-O), 5.94 (ddt, *J* = 17.2, 10.2, 6.8 Hz, 1 H, CH=CH_2), 6.89 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.43 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.7, 21.6, 32.8, 34.1, 55.3, 78.8, 85.1, 101.6, 113.6, 116.2, 127.4, 131.4, 136.0, 159.7 ppm. MS (CI): *m*/*z* (%) = 263 (100) [MH^+]. HRMS (CI): calcd. for $C_{16}H_{23}O_3$ 263.1647 [M + H^+]; found 263.1647.

Compound 46: To a solution of benzylidene acetal **45** (3.10 g, 11.82 mmol) in dry CH_2Cl_2 (60 mL) was added at 0 °C, DIBAL (1 M in heptanes, 14.18 mL, 14.18 mmol) and the resulting mixture was stirred at this temperature for 4 h. After adding water (20 mL), the mixture was filtered through a pad of celite. The aqueous phase was then extracted with CH_2Cl_2 (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (25% EtOAc in petroleum ether) to give compound **46** (2.87 g, 10.87 mmol, 92%) as a colourless oil. $[\alpha]_D^{22}$ = –10.4 (*c* = 1.00, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3424, 3071, 2960, 2873, 1614, 1515, 1249, 1036 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.88 (s, 3 H, CH_3-C), 0.99 (s, 3 H, CH_3-C), 2.29–2.48 (m, 2 H, CH_2-CH=CH_2), 3.32 (d, *J* = 10.9 Hz, 1 H, CH_2-O), 3.36 (dd, *J* = 4.0, 7.5 Hz, 1 H, *CH*-O), 3.57 (d, *J* = 10.9 Hz, 1 H, CH_2-O), 3.80 (s, 3 H, CH_3-O), 4.41 (d, *J* = 10.7 Hz, 1 H, Ar-CH_2-O), 4.51 (d, *J* = 10.7 Hz, 1 H, Ar-CH_2-O), 5.07 (ddt, *J* = 10.0, 2.1, 1.0 Hz, 1 H, CH=CH_2), 5.15 (ddd, *J* = 17.2, 3.4, 1.5 Hz, 1 H, CH=CH_2), 5.96 (ddt, *J* = 17.2, 10.0, 6.8 Hz, 1 H, *C*H=CH_2), 6.87 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.25 (d, *J* = 8.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5, 23.2, 35.6, 39.7, 55.3, 70.8, 73.6, 86.3, 113.9, 116.7, 129.5, 130.5, 136.8, 159.3 ppm. MS (ESI): *m*/*z* (%) = 287.1 (100) [M + Na^+]. HRMS (ESI): calcd. for $C_{16}H_{24}O_3Na$ 287.1623 [M + Na^+]; found 287.1623.

Compound 27: To a solution of alcohol **46** (2.80 g, 10.59 mmol) in dry CH_2Cl_2 (50 mL) was added in one portion at room temp., PCC (3.42 g, 15.89 mmol) and the resulting mixture was stirred at this temperature for 4 h. The mixture was then concentrated under reduce pressure, and Et_2O was added to the residue. After being stirred for 15 min, this mixture was filtered off through a pad a celite, and solvent was then removed under reduce pressure. The crude residue was purified by column chromatography (10% EtOAc in petroleum ether) to give compound **27** (2.67 g, 10.17 mmol, 96%) as a colourless oil. $[\alpha]_D^{22}$ = –13.0 (*c* = 1.00, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3071, 2961, 2862, 1726, 1614, 1515, 1249, 1081, 1036 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 3 H, CH_3-C), 1.12 (s, 3 H, CH_3-C), 2.34 (m, 2 H, CH_2-CH=CH_2), 3.59 (dd, *J* = 4.9, 6.6 Hz, 1 H, *CH*-O), 3.80 (s, 3 H, CH_3-O), 4.40 (d, *J* = 10.9 Hz, 1 H, Ar-CH_2-O), 4.60 (d, *J* = 10.9 Hz, 1 H, Ar-CH_2-O), 5.08 (ddt, *J* = 10.2, 2.1, 1.0 Hz, 1 H, CH=CH_2), 5.15 (ddd, *J* = 17.1, 3.2, 1.5 Hz, 1 H, CH=CH_2), 5.90 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1 H, *CH*=CH_2), 6.86 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.21 (d, *J* = 8.8 Hz, 2 H, Ar-H), 9.55 (s, 1 H, CHO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7, 19.4, 35.4, 51.0, 55.2, 73.2, 82.3, 113.7, 117.4, 129.3, 130.3, 135.6, 159.2, 205.7 ppm. MS (ESI): *m*/*z* (%) = 285.1 (54) [M + Na^+]; 317.1 (100) [MNa^+ + MeOH]. HRMS (ESI): calcd. for $C_{16}H_{22}O_3Na$ 285.1467 [M + Na^+]; found 285.1467.

Compound 48: To a solution of iodo olefin **47** (3.88 g, 11.89 mmol) in dry Et_2O (75 mL) was slowly added at –95 °C, a solution of *tert*-butyllithium in hexanes (1.5 M, 15.86 mL, 23.79 mmol) and the resulting mixture was stirred at this temperature for 1 h. Then a solution of aldehyde **27** (2.60 g, 9.91 mmol) in dry Et_2O (15 mL) was then slowly added at –95 °C, and the mixture was stirred at –78 °C for 2.5 h. The reaction was quenched by adding saturated aqueous solution of NH_4Cl (25 mL). After separation of the layers, the aqueous phase was extracted with Et_2O (3 × 20 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (10% EtOAc in petroleum ether) to give compound **47** (3.16 g, 6.84 mmol, 69%) as a colourless oil; mixture of 1:1 diastereomers. IR (neat): $\tilde{\nu}$ = 3440, 3072, 2954, 2857, 1614, 1510, 1254, 1088 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, CH_3-Si), 0.05 (s, 3 H, CH_3-Si), 0.76 (s, 1.5 H, CH_3-C), 0.82 (s, 1.5 H, CH_3-C), 0.88 [s, 4.5 H, $(CH_3)_3$-Si], 0.89 [s, 4.5 H, $(CH_3)_3$-Si], 0.96 (s, 1.5 H, CH_3-C), 0.97 (s, 1.5 H, CH_3-C), 1.67 (s, 1.5 H, CH_3-C=), 1.68 (s, 1.5 H, CH_3-C=), 2.17–2.57 (m, 4 H, CH_2-CH=CH_2 and CH_2-C=), 3.45 (dd, *J* = 3.8, 7.3 Hz, 1 H, *CH*-O), 3.69 (t, *J* = 7.0 Hz, 2 H, *CH*-OSi), 3.79 (s, 3 H, CH_3-O), 4.30 (d, *J* = 9.2 Hz, 0.5 H, Ar-CH_2-O), 4.38–4.48 (m, 1.5 H, *CH*-OH et Ar-CH_2-O), 4.63 (d, *J* = 10.6 Hz, 0.5 H, Ar-CH_2-O), 4.65 (d, *J* = 10.6 Hz, 0.5 H, Ar-CH_2-O), 5.07 (d, *J* = 10.0 Hz, 0.5 H, CH=CH_2), 5.08 (d, *J* = 10.2 Hz, 0.5 H, CH=CH_2), 5.14 (d, *J* = 17.1 Hz, 0.5 H, CH=CH_2), 5.15 (d, *J* = 17.1 Hz, 0.5 H, CH=CH_2), 5.26 (t, *J* = 10.5 Hz, 0.5 H, *CH*=C), 5.27 (t, *J* = 10.5 Hz, 0.5 H, *CH*=C), 5.96 (ddt, *J* = 17.1, 10.0, 7.5 Hz, 0.5 H, *CH*=CH_2), 5.97 (ddt, *J* = 17.1, 10.2, 7.5 Hz, 0.5 H, *CH*=CH_2), 6.86 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.25 (d, *J* = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.2 16.4, 17.4, 18.4, 20.6, 21.4, 26.1, 35.5, 35.8, 42.6, 42.7, 43.4, 43.5, 55.4, 62.2, 62.3, 72.7, 73.1, 73.9, 74.6, 86.9, 113.9, 116.4, 116.7, 126.1, 126.3, 129.6, 130.3, 130.4, 136.2, 136.6, 136.9, 137.2, 159.3, 159.4 ppm. MS (ESI): *m*/*z* (%) = 485.3 (100) [M + Na^+]. HRMS (ESI): calcd. for $C_{27}H_{46}O_4SiNa$ 485.3063 [M + Na^+]; found 485.3064.

Compound 49: To a solution of alcohol **48** (1.00 g, 2.16 mmol) in dry CH_2Cl_2 (20 mL), in the presence of 4 Å molecular sieves, was added and at –20 °C, DDQ (540 mg, 2.38 mmol) and the resulting mixture was then stirred at –10 °C for 3 h. The mixture was then filtered off through a pad of celite and a saturated aqueous solution of $NaHCO_3$ (15 mL) was added to the filtrate. After separation of the layers, the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (5% EtOAc in petroleum ether) to give compound **49** (737 mg, 1.60 mmol, 74%) as a colourless oil; mixture of 1:1 diastereomers. IR (neat): $\tilde{\nu}$ = 3076, 2930, 2852, 1615, 1517, 1471, 1250, 1066 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.04 (s, 3 H, CH_3-Si), 0.07 (s, 3 H, CH_3-Si), 0.75 (s, 3 H, CH_3-C), 0.88 [s, 9 H, $(CH_3)_3$-Si], 1.03 (s, 3 H, CH_3-C), 1.73 (s, 1.5 H, CH_3-C=), 1.74 (s, 1.5 H, CH_3-C=), 2.18–2.33 (m, 4 H, CH_2-CH=CH_2 and CH_2-C=), 3.54 (t, *J* = 6.1 Hz, 1 H, *CH*-O), 3.71 (t, *J* = 7.0 Hz, 2 H, CH_2-O), 3.77 (s, 1.5 H, CH_3-O), 3.78 (s, 1.5 H, CH_3-O), 4.21 (d, *J* = 8.8 Hz, 1 H, *CH*-O), 5.01–5.13 (m, 2 H, CH=CH_2), 5.31 (d, *J* = 8.8 Hz, 0.5 H, *CH*=C), 5.32 (d, *J* = 8.8 Hz, 0.5 H, *CH*=C), 5.57 (s, 1 H, O-*CH*-O), 5.86–6.01 (m, 1 H, *CH*=CH_2), 6.86 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.38–7.44 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.2, 17.4, 17.8, 18.4, 21.0, 21.7, 21.8, 26.1, 34.0, 35.3, 36.9, 43.3, 43.6, 55.3, 62.0, 62.1, 79.6, 80.0, 82.4, 86.3, 95.0, 101.4, 113.6, 113.7, 116.0, 116.1, 121.0, 122.9, 127.5, 127.6, 131.7, 132.2, 136.4, 136.5, 138.0, 140.1, 159.7, 159.9 ppm. MS (ESI): *m*/*z* (%) = 483.3 (100) [M + Na^+]. HRMS (ESI): calcd. for $C_{27}H_{44}O_4SiNa$ 483.2907 [M + Na^+]; found 483.2908.

Compound 50: To a solution of compound **49** (700 mg, 1.52 mmol) in THF (15 mL) was added at room temp. TBAF (1 M in THF, 1.82 mL, 1.82 mmol), and the resulting mixture was stirred at this temperature for 1 h. The mixture was then concentrated under reduce pressure. The crude residue was purified by column chromatography (35% EtOAc in petroleum ether) to give compound **50** (500 mg, 1.44 mmol, 95% yield) as a colourless oil; mixture of 1:1 diastereomers. IR (neat): $\tilde{\nu}$ = 3419, 3077, 2933, 2868, 1699, 1625, 1516, 1243, 1047 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3-C), 1.04 (s, 3 H, CH_3-C), 1.76 (d, *J* = 1.3 Hz, 1.5 H, CH_3-C=), 1.78 (d, *J* = 1.3 Hz, 1.5 H, CH_3-C=), 2.26–2.35 (m, 4 H, CH_2-CH=CH_2 and CH_2-C=), 3.55 (t, *J* = 6.1 Hz, 1 H, *CH*-O), 3.71 (t, *J* = 6.4 Hz, 1 H, CH_2-OH), 3.72 (t, *J* = 6.2 Hz, 1 H, CH_2-OH), 3.79 (s, 3 H, CH_3-O), 4.23 (d, *J* = 8.7 Hz, 0.5 H,

CH-O), 4.32 (d, *J* = 8.9 Hz, 0.5 H, *CH*-O),5.02–5.12 (m, 2 H, CH=*CH*$_2$), 5.37 (d, *J* = 8.7 Hz, 0.5 H, *CH*=C), 5.38 (d, *J* = 8.9 Hz, 0.5 H, *CH*=C), 5.57 (s, 1 H, O-*CH*-O), 5.88–6.01 (m, 1 H, *CH*=CH$_2$), 6.87 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.43 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.9, 17,4, 21.0, 21.6, 21.8, 33.9, 35.2, 36.7, 43.0, 43.2, 55.3, 60.3, 60.4, 79.5, 80.2, 82.3, 86.2, 101.5, 113.6, 113.7, 116.1, 116.2, 123.4, 123.5, 127.4, 127.6, 131.4, 132.0, 135.3, 136.3, 137.7, 150.8, 150.9 ppm. MS (ESI): *m*/*z* (%) = 369.1 (100) [M + Na$^+$], 715.2 (70) [2M + Na$^+$]. HRMS (ESI): calcd. for $C_{20}H_{30}O_4Na$ 369.2042 [M + Na$^+$]; found 369.2042.

Compound 51: To a solution of alcohol **50** (450 mg, 1.30 mmol), acid **26** (381 mg, 1.56 mmol) and DMAP (48 mg, 0.39 mmol) in dry CH_2Cl_2 (15 mL) was added in one portion at 0 °C, DCC (366 mg, 1.69 mmol) and the resulting mixture was slowly warmed to room temp. and stirred for 6 h. The mixture was then concentrated under reduce pressure, and Et_2O was added to the residue. After being stirred for 15 min, this mixture was filtered off through, and solvent was then removed under reduce pressure. The crude residue was purified by column chromatography (15% EtOAc in petroleum ether) to give compound **51** (640 mg, 1.12 mmol, 86%) as a colourless oil; mixture of diastereomers. IR (neat): $\tilde{\nu}$ = 3077, 2931, 2852, 1739, 1615, 1517, 1464, 1250, 1094 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 3 H, *CH*$_3$-Si), 0.02 (s, 3 H, *CH*$_3$-Si), 0.75 (s, 3 H, *CH*$_3$-C), 0.87 [s, 9 H, (*CH*$_3$)$_3$-Si], 1.03 (s, 3 H, *CH*$_3$-C), 1.13 (d, *J* = 7.0 Hz, 3 H, *CH*$_3$-CH) 1.74–1.78 (m, 3 H, *CH*$_3$-C=), 2.25–2.52 (m, 5 H, O$_2$C-*CH*-CH$_3$, *CH*$_2$-C = and *CH*$_2$-CH=CH$_2$), 3.46–3.56 (m, 1 H, *CH*-O), 3.79 (s, 3 H, *CH*$_3$-O), 4.06–4.40 [m, 4 H, *CH*-OSi, *CH*$_2$-OC(O) and *CH*-O], 5.01–5.21 (m, 4 H, CH-CH=*CH*$_2$ and CH$_2$-CH=*CH*$_2$), 5.36 (d, *J* = 7.7 Hz, 1 H, *CH*=C), 5.56 (s, 1 H, O-*CH*-O), 5.73–6.01 (m, 2 H, CH-*CH*=CH$_2$ and CH$_2$-*CH*=CH$_2$), 6.87 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.37–7.44 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.0, –4.2, 11.5, 11.8, 14.3, 17.1, 17.4, 18.2, 21.0, 21.6, 25.8, 33.9, 35.2, 36.9, 39.0, 39.1, 46.7, 46.8, 55.3, 62.5, 62.6, 74.9, 75.0, 79.4, 80.1, 82.2, 86.1, 95.0, 101.4, 113.6, 113.7, 115.6, 116.1, 116.2, 121.8, 123.8, 127.4, 127.6, 131.5, 132.0, 136.2, 136.3, 136.5, 139.4, 135.5, 159.8, 159.9, 174.3 ppm.

Compound 52: To a solution of compound **51** (500 mg, 0.87 mmol) in THF (5 mL) was added at room temp. TBAF (1 M in THF, 1.04 mL, 1.04 mmol), and the resulting mixture was stirred at this temperature for 1 h. The mixture was then concentrated under reduce pressure. The crude residue was purified by column chromatography (25% EtOAc in petroleum ether) to give compound **52** (340 mg, 0.74 mmol, 85% yield) as a colourless oil; mixture of diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (s, 3 H, *CH*$_3$-C), 1.03 (s, 3 H, *CH*$_3$-C), 1.12 (d, *J* = 7.2 Hz, 3 H, *CH*$_3$-CH), 1.75–1.79 (m, 3 H, *CH*$_3$-C=), 2.27 (dd, *J* = 6.6, 6.2 Hz, 2 H, *CH*$_2$-CH=CH$_2$), 2.39 (t, *J* = 6.7 Hz, 2 H, *CH*$_2$-C=), 2.53–2.63 (m, 1 H, O$_2$C-*CH*-CH$_3$), 3.53 (t, *J* = 6.1 Hz, 1 H, *CH*-O), 3.79 (s, 3 H, *CH*$_3$-O), 4.08–4.40 [m, 4 H, *CH*-O, *CH*$_2$-OC(O) and *CH*-OH], 5.01–5.24 (m, 4 H, CH-CH=*CH*$_2$ and CH$_2$-CH=*CH*$_2$), 5.36 (d, *J* = 7.7 Hz, 1 H, *CH*=C), 5.56 (s, 1 H, O-*CH*-O), 5.68–6.00 (m, 2 H, CH-*CH*=CH$_2$ and CH$_2$-*CH*=CH$_2$), 6.86 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.37–7.43 (m, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.9, 14.2, 17.2, 20.9, 21.6, 33.8, 35.2, 36.8, 39.0 (CH$_2$, C$_7$), 44.6, 55.3, 62.4, 62.8, 72.8, 73.0, 82.2, 86.1, 95.0, 101.5, 113.6, 116.0, 116.1, 116.3, 122.0, 123.8, 127.4, 127.6, 131.4, 131.9, 136.6, 136.5, 137.6, 159.7, 159.9, 175.1 ppm. MS (ESI): *m*/*z* (%) = 481.3 (100) [M + Na$^+$]. HRMS (ESI): calcd. for $C_{27}H_{38}O_6Na$ 481.2566 [M + Na$^+$]; found 481.2568.

Compound 53: To a solution of alcohol **48** (1.25 g, 2.70 mmol) in dry CH_2Cl_2 (20 mL), was added dropwise at room temp., DMP (15 wt.-% in CH_2Cl_2, 7.57 mL, 3.51 mmol) and the resulting mixture was stirred at this temperature for 4 h. After adding a 1:1 solution of a saturated aqueous $NaHCO_3$ $Na_2S_2O_3$ (15 mL) the layers were separated. The aqueous phase was then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with brine (20 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (5% EtOAc in petroleum ether) to give compound **53** (1.10 g, 2.39 mmol, 88%) as a colourless oil. $[\alpha]_D^{22}$ = –13.6 (*c* = 1.00, $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3077, 2956, 2857, 1679, 1615, 1514, 1249, 1093 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.04 (s, 6 H, *CH*$_3$-Si), 0.88 [s, 9 H, (*CH*$_3$)$_3$-Si], 1.11 (s, 3 H, *CH*$_3$-C), 1.18 (s, 3 H, *CH*$_3$-C), 2.09 (d, *J* = 1.1 Hz, 3 H, *CH*$_3$-C=), 2.20–2.23 (m, 2 H, *CH*$_2$-CH=CH$_2$), 2.33 (t, *J* = 6.5 Hz, 2 H, *CH*$_2$-C=CH), 3.71–3.76 (m, 3 H, *CH*$_2$-OSi and *CH*-O), 3.79 (s, 3 H, *CH*$_3$-O), 4.39 (d, *J* = 10.6 Hz, 1 H, Ar-*CH*$_2$-O), 4.55 (d, *J* = 10.6 Hz, 1 H, Ar-*CH*$_2$-O), 5.02 (dd, *J* = 10.0, 1.0 Hz, 1 H, CH=*CH*$_2$), 5.09 (dd, *J* = 17.0, 1.9 Hz, 1 H, CH=*CH*$_2$), 5.91 (ddt, *J* = 17.0, 10.0, 7.3 Hz, 1 H, *CH*=CH$_2$), 6.36 (d, *J* = 1.1 Hz, 1 H, *CH*=C), 6.84 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.20 (d, *J* = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.3, 18.3, 19.8, 20.7, 21.3, 25.9, 36, 44.6, 52.3, 55.2, 61.3 (CH$_2$, C$_1$), 73.9, 83.7, 113.6, 116.6, 122.0, 129.1, 130.9, 136.5, 155.3, 159.0, 204.8 ppm. MS (CI): *m*/*z* (%) = 461 (25) [M + H$^+$], 121 (100) [$^+$CH$_2$PhOMe]. HRMS (CI): calcd. for $C_{27}H_{45}O_4Si$ 461.3087 [M + H$^+$]; found 461.3087.

Compound 54: To a solution of compound **53** (1.10 g, 2.39 mmol) in THF (20 mL) was added at room temp. TBAF (1 M in THF, 2.87 mL, 2.87 mmol), and the resulting mixture was stirred at this temperature for 1 h. The mixture was then concentrated under reduce pressure. The crude residue was purified by column chromatography (25% EtOAc in petroleum ether) to give compound **54** (687 mg, 1.98 mmol, 84% yield) as a colourless oil. $[\alpha]_D^{22}$ = –10.1 (*c* = 0.87; $CHCl_3$). IR (neat): $\tilde{\nu}$ = 3429, 3075, 2973, 2868, 1699, 1614, 1514, 1248, 1036 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.12 (s, 3 H, *CH*$_3$-C), 1.18 (s, 3 H, *CH*$_3$-C), 2.09 (s, 3 H, *CH*$_3$-C=), 2.24 (dd, *J* = 6.6, 7.0 Hz, 2 H, *CH*$_2$-CH=CH$_2$), 2.37 (t, *J* = 6.2 Hz, 2 H, *CH*$_2$-C=CH), 3.67–3.73 (m, 3 H, *CH*$_2$-OH and *CH*-O), 3.79 (s, 3 H, *CH*$_3$-O), 4.38 (d, *J* = 10.7 Hz, 1 H, Ar-*CH*$_2$-O), 4.57 (d, *J* = 10.7 Hz, 1 H, Ar-*CH*$_2$-O), 5.03 (d, *J* = 10.1 Hz, 1 H, CH=*CH*$_2$), 5.10 (d, *J* = 17.1 Hz, 1 H, CH=*CH*$_2$), 5.90 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1 H, *CH*=CH$_2$), 6.39 (s, 1 H, *CH*=C), 6.85 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.21 (d, *J* = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5, 21.0, 21.2, 36.4, 44.3, 52.3, 55.3, 60.3, 73.8, 84.0, 113.7, 116.8, 122.7, 129.2, 130.8, 136.4, 154.1, 159.1, 205.2 ppm. MS (CI): *m*/*z* (%) = 347 (42) [M + H$^+$], 121 (100) [$^+$CH$_2$PhOMe]. HRMS (CI): calcd. for $C_{21}H_{31}O_4$ 347.2222 [M + H$^+$]; found 347.2222.

Compound 55: To a solution of alcohol **54** (485 mg, 1.40 mmol), acid **26** (1.68 mmol; 411 mg) and DMAP (51 mg, 0.42 mmol) in dry CH_2Cl_2 (15 mL) was added in one portion at 0 °C, DCC (394 mg, 1.82 mmol) and the resulting mixture was slowly warmed to room temp. and stirred for 6 h. The mixture was then concentrated under reduce pressure, and Et_2O was added to the residue. After being stirred for 15 min, this mixture was filtered off through, and solvent was then removed under reduce pressure. The crude residue was purified by column chromatography (10% EtOAc in petroleum ether) to give compound **55** (690 mg, 1.20 mmol, 86%) as a colourless oil; mixture of 7:3 diastereomers. IR (neat): $\tilde{\nu}$ = 3076, 2932, 2857, 1739, 1679, 1614, 1515, 1464, 1250, 1079 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 3 H, *CH*$_3$-Si), 0.02 (s, 3 H, *CH*$_3$-Si), 0.87 [s, 9 H, (*CH*$_3$)$_3$-Si], 1.11–1.18 (m, 9 H, *CH*$_3$-C and *CH*$_3$-CH), 1.93 (d, *J* = 1.1 Hz, 0.9 H, *CH*$_3$-C=), 2.09 (d, *J* = 1.1 Hz, 2.1 H, *CH*$_3$-C=), 2.17–2.29 (m, 2 H, *CH*$_2$-CH=CH$_2$), 2.41–2.52 (m, 2.7

H, O_2C-*CH*-CH_3 and CH_2-C), 3.81 (q, *J* = 7.0 Hz, 0.3 H, O_2C-*CH*-CH_3), 3.69 (dd, *J* = 4.7, 7.5 Hz, 0.3 H, *CH*-O), 3.70 (dd, *J* = 4.3, 7.5 Hz, 0.7 H, *CH*-O), 3.79 (s, 3 H, CH_3-O), 4.09–4.25 [m, 2 H, *CH*-OSi and CH_2-OC(O)], 4.31–4.39 [m, 2 H, CH_2-OC(O) et Ar-CH_2-O], 4.56 (d, *J* = 10.7 Hz, 1 H, Ar-CH_2-O), 5.02–5.25 (m, 4 H, CH-CH=CH_2 and CH_2-CH=CH_2), 5.72–5.97 (m, 2 H, CH-*CH*=CH_2 and CH_2-*CH*=CH_2), 6.35 (d, *J* = 1.1 Hz, 0.7 H, *CH*=C), 6.40 (d, *J* = 1.1 Hz, 0.3 H, *CH*=C), 6.84 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.19 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = –5.1, –4.2, 11.7, 18.1, 19.4, 20.8, 21.1, 25.7, 36.4, 40.0, 46.7, 52.3, 55.2, 61.9, 73.9, 75.0, 83.8, 113.6, 115.6, 116.7, 122.4, 129.1, 130.8, 136.4, 139.3, 153.1, 159.0, 174.1, 204.7 ppm. MS (CI): *m*/*z* (%) = 571 (50) [M – H^+], 451 (100) [M – $MeOPhCH_2^+$], 121 (21) [$^+CH_2PhOMe$]. HRMS (CI): calcd. for $C_{33}H_{53}O_6Si$ 573.3611 [M + H^+]; found 573.3610.

Compound 56: To a solution of compound **55** (550 mg, 0.96 mmol) in MeOH (10 mL), was added and at room temp., CSA (11 mg, 0.048 mmol) and the resulting mixture was stirred at this temperature for 8 h. After adding a saturated aqueous solution of $NaHCO_3$ (5 mL) the layers were separated. The aqueous phase was then extracted with Et_2O (3 × 5 mL). The combined organic extracts were washed with brine (10 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (20% EtOAc in petroleum ether) to give compound **56** (406 mg, 0.88 mmol, 92%) as a colourless oil; mixture of 3:2 diastereomers. IR (neat): $\tilde{\nu}$ = 3501, 3071, 2937, 1731, 1679, 1615, 1515, 1248, 1032 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11–1.17 (m, 9 H, CH_3-C and CH_3-CH), 1.93 (d, *J* = 1.3 Hz, 1.2 H, CH_3-C=), 2.08 (d, *J* = 1.1 Hz, 1.8 H, CH_3-C=), 2.24 (dd, *J* = 7.4, 7.8 Hz, 2 H, CH_2-CH=CH_2), 2.45 (t, *J* = 6.7 Hz, 1.2 H, CH_2-C=CH), 2.53–2.64 (m, 0.8 H, CH_2-C=CH), 2.73–2.90 (m, 1 H, *CH*-CH_3), 3.69 (dd, *J* = 4.7, 7.2 Hz, 1 H, *CH*-O), 3.79 (s, 3 H, CH_3-O), 4.23 [t, *J* = 6.7 Hz, 2 H, CH_2-OC(O)], 4.35–4.40 (m, 2 H, *CH*-OH et Ar-CH_2-O), 4.56 (d, *J* = 10.7 Hz, 1 H, Ar-CH_2-O), 5.03 (d, *J* = 10.0 Hz, 1 H, CH_2-CH=CH_2), 5.10 (d, *J* = 16.4 Hz, 1 H, CH_2-CH=CH_2), 5.18 (d, *J* = 10.5 Hz, 0.4 H, CH-CH=CH_2), 5.20 (dd, *J* = 10.5, 1.5 Hz, 0.6 H, CH-CH=CH_2), 5.30 (dd, *J* = 15.6, 1.5 Hz, 0.6 H, CH-CH=CH_2), 5.31 (dd, *J* = 15.6, 1.5 Hz, 0.4 H, CH-CH=CH_2), 5.75–5.97 (m, 2 H, CH_2-*CH*=CH_2 and CH-*CH*=CH_2), 6.35 (d, *J* = 1.1 Hz, 0.6 H, *CH*=C), 6.42 (s, 0.4 H, *CH*=C), 6.84 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.19 (d, *J* = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.1, 11.2, 19.3, 20.8, 20.9, 21.0, 36.3, 39.9, 44.7, 51.1, 51.2, 55.1, 62.0, 63.1, 72.9, 73.0, 73.6, 73.9, 83.6, 83.7, 113.6, 116.0, 116.1, 116.6, 116.7, 122.6, 123.1, 129.1, 130.7, 136.3, 137.6, 152.8, 153.9, 159.0, 174.8, 175.0, 204.4, 204.8 ppm. MS (CI): *m*/*z* (%) = 459 (16) [M + H^+], 121 (100) [$^+CH_2PhOMe$], 337 (39) [M – $MeOPhCH_2^+$], 457 (25) [M – H^+]. HRMS (CI): calcd. for $C_{27}H_{39}O_6$ 459.2747 [M + H^+]; found 459.2747.

Compound 57: To a solution of diene **56** (380 mg, 0.829 mmol) in dry CH_2Cl_2 (160 mL) was added in one portion Grubbs catalyst **13** (17.6 mg, 0.027 mmol). Nitrogen was then bubbled through the solution for 15 min, and the mixture was refluxed for 1 h. After cooling at room temp., the mixture was concentrated under reduce pressure. The crude residue was purified by column chromatography (25% EtOAc in petroleum ether) to give compound **57** (239 mg, 0.555 mmol, 67%) as a colourless oil; mixture of 3:2 diastereomers. ^{1}H NMR ($CDCl_3$): δ = 1.08–1.27 (m, 9 H, CH_3-C and CH_3-CH), 1.93 (d, *J* = 1.3 Hz, 1.2 H, CH_3-C=), 2.08 (d, *J* = 1.1 Hz, 1.8 H, CH_3-C=), 2.18–2.65 (m, 5 H, CH_2-CH=CH_2, CH_2-C=CH, *CH*-CH_3), 3.51–3.62 (m, 1 H, *CH*-O), 3.81 (s, 1.2 H, CH_3-O), 3.82 (s, 1.8 H, CH_3-O), 3.96–4.26 [m, 2 H, *CH*-OH and CH_2-OC(O)], 4.37–4.65 [m, 3 H, CH_2-OC(O) et Ar-CH_2-O], 5.38 (d, *J* = 15.2 Hz, 0.4 H, CH-*CH*=CH), 5.41 (d, *J* = 15.5 Hz, 0.6 H, CH-*CH*=CH), 5.57–5.70 (m, 1 H, *CH*=CH-CH_2), 6.23 (s, 0.6 H, *CH*=C), 6.37 (s, 0.4 H, *CH*=C), 6.91 (d, *J* = 8.7 Hz, 2 H, Ar-H.), 7.30 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 14.5, 16.6, 19.7, 24.1, 35.5, 36.7, 39.2, 47.5, 53.4, 55.3, 61.9, 62.7, 72.1, 72.9, 73.1, 73.2, 81.5, 83.6, 113.7, 113.8, 122.4, 124.0, 129.2, 129.4, 129.6, 130.6, 132.1, 132.2, 153.6, 154.4, 159.1, 159.2, 174.2, 174.3, 203.0, 204.0 ppm. MS (CI): *m*/*z* (%) = 431 (35) [M + H^+], 121 (100) [$^+CH_2PhOMe$]. HRMS (CI): calcd. for $C_{25}H_{37}O_6$ 431.2434 [M + H^+]; found 431.2434.

Compound 58: Compound **58** (69 mg, 0.265 mmol 32%) was isolated from the purification of the previous reaction. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (s, 3 H, CH_3-C), 1.17 (s, 3 H, CH_3-C), 2.45 (dddd, *J* = 19.0, 7.0, 3.4, 2.3 Hz, 1 H, CH_2-CH=CH), 2.63 (ddd, *J* = 19.0, 4.7, 1.7 Hz, 1 H, CH_2-CH=CH), 3.55 (dd, *J* = 7.0, 4.7 Hz, 1 H, *CH*-O), 3.81 (s, 3 H, CH_3-O), 4.44 (d, *J* = 11.5 Hz, 1 H, Ar-CH_2-O), 4.54 (d, *J* = 11.5 Hz, 1 H, Ar-CH_2-O), 5.96 (dt, *J* = 10.0, 2.0 Hz, 1 H, CH_2-*CH*=CH), 6.73 (ddd, *J* = 10.0, 4.6, 3.4 Hz, 1 H, CH=*CH*), 6.87 (d, *J* = 8.9 Hz, 2 H, Ar-H), 7.24 (d, *J* = 8.9 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9, 21.6, 28.6, 48.0, 55.4, 71.7, 80.7, 113.8, 128.7, 129.3, 130.5, 144.5, 159.3, 203.7 ppm.

Compound 60: To a solution of compound **57** (190 mg, 0.441 mmol) in dry CH_2Cl_2 (10 mL), in the presence of 4 Å molecular sieves, was added and at 0 °C, $VO(acac)_2$ (11.8 mg, 0.044 mmol) and the resulting mixture was then stirred at 0 °C for 15 min. Then *t*BuOOH (5.5 M in decane, 0.12 mL, 0.662 mmol) was slowly added to the solution at 0 °C, and the resulting mixture was stirred at this temperature for 4 h. The mixture was then filtered through a short pad of celite, a solution of saturated aqueous $NaHCO_3$ (5 mL) was added. After separation of the layers, the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed with brine (10 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was then directly oxidized with Dess Martin periodinane (repeated procedure of compound **53**). The crude product was purified by column chromatography (20% EtOAc in petroleum ether) to give compound **60** (114 mg, 0.256 mmol, 67% for the two steps) as a colourless oil; mixture of 3:2 diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.08 (s, 3 H, CH_3-C), 1.24 (s, 3 H, CH_3-C), 1.28 (d, *J* = 7.0 Hz, 1.8 H, CH_3-CH), 1.34 (d, *J* = 7.0 Hz, 1.2 H, CH_3-CH), 1.75–1.91 (m, 2 H, CH_2-CH-O), 2.09 (d, *J* = 0.9 Hz, 1.8 H, CH_3-C=), 2.17 (s, 1.2 H, CH_3-C=), 2.40–2.63 (m, 3 H, CH_2-C = and CH_2-*CH*-O), 3.17–3.19 [m, 1 H, (O)C-*CH*-O], 3.56 (q, *J* = 7.0 Hz, 0.4 H, *CH*-CH_3), 3.57 (q, *J* = 7.0 Hz, 0.6 H, *CH*-CH_3), 3.74–3.82 (m, 4 H, *CH*-OPMB et CH_3-O), 4.18–4.41 [m, 2 H, CH_2-OC(O)], 4.51 (d, *J* = 11.5 Hz, 1.2 H, Ar-CH_2-O), 4.64 (d, *J* = 11.5 Hz, 0.8 H, Ar-CH_2-O), 6.42 (s, 0.6 H, *CH*=C), 6.46 (s, 0.4 H, *CH*=C), 6.90 (d, *J* = 8.5 Hz, 2 H, Ar-H), 7.30 (d, *J* = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.3, 12.8, 17.2, 18.3, 23.7, 35.2, 39.1, 40.3, 46.0, 53, 55.4, 57.0, 58.4, 58.8, 59.6, 62.2, 72.7, 74.5, 80.9, 81.0, 113.9, 114.0, 120.5, 123.3, 129.5, 129.6, 130.0, 130.1, 154.9, 159.4, 159.5, 169.5, 170.0, 201.6, 202.8 ppm. MS (CI): *m*/*z* (%) = 445 (100) [M + H^+], 121 (46) [$^+CH_2PhOMe$], 427 (32) [M – H_20]. HRMS (CI): calcd. for $C_{25}H_{33}O_7$ 445.2226 [M + H^+]; found 445.2225.

Compound 61: To a solution of $(PhSe)_2$ (140 mg, 0.450 mmol) in EtOH (2 mL) was added at 0 °C $NaBH_4$ (26 mg, 0.675 mmol), and the resulting mixture was stirred at 0 °C for 10 min. Then a solution of epoxyketone **60** (100 mg, 0.225 mmol) in EtOH (1 mL) was slowly added to the solution at 0 °C, and the mixture was stirred at this temperature for 15 min. A solution of saturated aqueous

NH_4Cl (3 mL) was then added. The aqueous phase was separated, and extracted with EtOAc (4 × 4 mL). The combined organics extracts were washed with brine (5 mL), then dried with magnesium sulfate, and concentrated under reduce pressure. The crude residue was purified by column chromatography (35% EtOAc in petroleum ether) to give compound **61** (87 mg, 0.196 mmol, 87%) as a colourless oil; mixture of 1.2:1 diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.09 (s, 1.35 H, CH_3-C), 1.14 (s, 1.65 H, CH_3-C), 1.22 (s, 1.65 H, CH_3-C), 1.25 (s, 1.35 H, CH_3-C), 1.29 (d, J = 7.1 Hz, 1.35 H, CH_3-CH), 1.30 (d, J = 7.1 Hz, 1.65 H, CH_3-CH), 1.49–1.79 (m, 3 H, CH_2-CH-O and -OH), 2.11 (s, 1.35 H, CH_3-C=), 2.17 (s, 1.65 H, CH_3-C=), 2.44–2.65 [m, 2.55 H, (O)C-CH_2-CH and CH_2-C=], 2.89 [dd, J = 17.9, 4.5 Hz, 0.45 H, (O)C-CH_2-CH], 3.49 (q, J = 7.1 Hz, 0.45 H, CH-CH_3), 3.50 (q, J = 7.1 Hz, 0.55 H, CH-CH_3), 3.58 (dd, J = 8.1, 2.4 Hz, 0.55 H, CH-OPMB), 3.68 (dd, J = 9.8, 1.7 Hz, 0.45 H, CH-OPMB), 3.81 (s, 1.35 H, CH_3-O), 3.82 (s, 1.65 H, CH_3-O), 3.94–4.18 [m, 1.45 H, CH-OH and CH_2-OC(O)], 4.25 [ddd, J = 11.7, 8.1, 3.6 Hz, 0.45 H, CH_2-OC(O)], 4.51 [ddd, J = 10.4, 6.0, 3.0 Hz, 0.55 H, CH_2-OC(O)], 4.58–4.74 [m, 2.55 H, CH_2-OC(O) and Ar-CH_2-O], 6.30 (s, 0.45 H, CH=C), 6.42 (d, J = 1.0 Hz, 0.55 H, CH=C), 6.90 (d, J = 8.6 Hz, 2 H, Ar-H), 7.30 (d, J = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.3, 12.6, 18.0, 18.5, 24.0, 24.4, 39.6, 39.9, 40.2, 47.4, 49.4, 52.6, 53.3, 53.8, 54.1,55.3, 55.4, 61.9, 62.1, 66.0, 66.7, 74.4, 75.1, 81.7, 81.9, 114.0, 114.1, 122.1, 122.8, 129.5, 129.7, 130.1, 130.4, 155.1, 155.3, 159.5, 170.0, 170.1, 202.5, 203.0, 205.8, 205.9 ppm. MS (CI): m/z (%) = 121 (100) [$^+CH_2PhOMe$], 429 (18) [$MH^+ - H_2O$], 446 (8) [$M - H^+$]. HRMS (CI): calcd. for $C_{25}H_{35}O_7$ 447.2383 [$M + H^+$]; found 447.2383.

Compound 62a: To a solution of alcohol **61** (40 mg, 0.090 mmol) in CH_2Cl_2/H_2O (4.5:1 mL) was added and at room temp., DDQ (540 mg, 2.38 mmol) and the resulting mixture was then stirred at this temperature for 3 h. The reaction was then quenched by adding a solution of $NaHCO_3$ (3 mL). After separation of the layers, the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were washed with brine (5 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (25% EtOAc in petroleum ether) to give compound **62a** (15 mg, 0.034 mmol, 38%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.10 (s, 3 H, CH_3-C), 1.22–1.23 (m, 4 H, CH-CH_2-CH and CH_3-C), 1.25 (d, J = 7.4 Hz, 3 H, CH_3-CH), 1.56–1.62 (m, 1 H, CH-CH_2-CH), 2.10 (s, 3 H, CH_3-C=), 2.29 (dd, J = 12.1, 2.6 Hz, 1 H, CH_2-CH_2), 2.35–2.57 [m, 2 H, CH_2-C(O)], 3.19 (dd, J = 12.1, 5.3 Hz, 1 H, CH_2-CH_2), 3.60 (dd, J = 8.3, 5.9 Hz, 1 H, C-CH-O), 3.83 (s, 3 H, CH_3-O), 4.07–4.21 (m, 3 H, CH-CH_3, CH_2-CH-O and CH_2-O), 4.43 (td, J = 11.5, 3.0 Hz, 1 H, CH_2-O), 5.41 (s, 1 H, O-CH-O), 6.76 (s, 1 H, CH=C), 6.92 (d, J = 8.9 Hz, 2 H, Ar-H), 7.47 (d, J = 8.9 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 17.7, 22.1, 22.7, 29.7, 40.4, 46.8, 51.1, 53.6, 55.6, 62.1, 73.8, 82.1, 102.3, 114.0, 125.6, 128.0, 131.4, 152.7, 160.4, 171.1, 203.3, 207.2 ppm. MS (ESI): m/z (%) = 467.2 (100) [$M + Na^+$]; 429 (23) [$2M + Na^+$]. HRMS (ESI): calcd. for $C_{25}H_{32}O_7Na$ 467.2046 [$M + Na^+$]; found 467.2046.

Compound 62b: Compound **62b** (8 mg, 0.018 mmol, 20%) was isolated from the purification of the previous reaction. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.16 (s, 3 H, CH_3-C), 1.25 (s, 3 H, CH_3-C), 1.35 (d, J = 7.1 Hz, 3 H, CH_3-CH), 1.43–1.50 (m, 2 H, CH-CH_2-CH), 1.99 (d, J = 1.0 Hz, 3 H, CH_3-C=), 2.46–2.55 [m, 3 H, CH_2-C(O) and CH_2-CH_2], 3.10 (dd, J = 11.7, 3.8 Hz, 1 H, CH_2-CH_2), 3.76 (q, J = 7.1 Hz, 1 H, CH-CH_3), 3.83 (s, 3 H, CH_3-O), 3.98 (dd, J = 9.8, 3.4 Hz, 1 H, C-CH-O), 4.16–4.41 (m, 3 H, CH_2-CH-O and CH_2-O), 5.64 (s, 1 H, O-CH-O), 6.33 (s, 1 H, CH=C), 6.90 (d, J = 8.7 Hz, 2 H, Ar-H), 7.42 (d, J = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 16.6, 17.3, 23.9, 31.4, 39.3, 48.8, 51.3, 51.4, 55.5, 63.0, 73.6, 81.4, 101.9, 113.8, 123.4, 127.6, 130.9, 152.2, 160.6, 170.2, 203.0, 204.4 ppm.

Compound 63: Compound **63** (8 mg, 0.018 mmol, 20%) was isolated from the purification of the previous reaction; mixture of 7:3 diastereomers. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.14–1.26 (m, 6.9 H, CH_3-C and CH_3-CH), 1.28 (d, J = 7.0 Hz, 2.1 H, CH_3-CH), 1.47–1.61 (m, 2 H, CH-CH_2-CH), 2.15 (s, 2.1 H, CH_3-C=), 2.23 (s, 0.9 H, CH_3-C=), 2.42–2.76 (m, 2 H, CH_2-CH_2), 2.82–3.13 [m, 2 H, CH_2-C(O)], 3.39 (q, J = 7.1 Hz, 0.3 H, CH-CH_3), 3.76 (q, J = 7.0 Hz, 0.7 H, CH-CH_3), 3.88 (s, 3 H, CH_3-O), 3.93–4.01 (m, 1 H, CH-OH), 4.14 (td, J = 4.0, 11.4 Hz, 0.7 H, CH_2-O), 4.31–4.54 (m, 0.6 H, CH_2-O), 4.61 (dt, J = 11.4, 2.1 Hz, 0.7 H, CH_2-O), 5.39 (d, J = 10.4 Hz, 0.7 H, CH-O), 5.47 (d, J = 10.7 Hz, 0.3 H, CH-O), 5.96 (s, 0.3 H, CH=C), 6.45 (s, 0.7 H, CH=C), 6.95 (d, J = 9.0 Hz, 2 H, Ar-H), 8.01 (d, J = 9.0 Hz, 1.4 H, Ar-H), 8.01 (d, J = 8.9 Hz, 0.6 H, Ar-H) ppm. MS (ESI): m/z (%) = 483.2 (100) [$M + Na^+$], 942.9 (50) [$2M + Na^+$]. HRMS (ESI): calcd. for $C_{25}H_{32}O_8Na$ 483.1995 [$M + Na^+$]; found 483,1995.

Compound 64: To a solution of compound **62b** (5.0 mg, 11.25 μmol) in MeOH (1 mL) was added at room temp. CSA (0.1 mg, 0.56 μmol), and the resulting mixture was then stirred at this temperature for 3 h. The reaction was then quenched by adding a solution of $NaHCO_3$ (1 mL) and Et_2O (1 mL) was also added. After separation of the layers, the aqueous phase was extracted with Et_2O (3 × 1 mL). The combined organic extracts were washed with brine (2 mL), dried with $MgSO_4$, and concentrated under reduce pressure. The crude residue was purified by column chromatography (15% EtOAc in petroleum ether) to give compound **64** (6.52 μmol; 2.1 mg, 58%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.05–1.15 (m, 4 H, CH_3-C and CH-CH_2-CH), 1.33 (s, 3 H, CH_3-C), 1.35 (d, J = 7.3 Hz, 3 H, CH_3-CH), 1.97–2.05 (m, 4 H, CH_3-C = and CH-CH_2-CH), 2.26 (td, J = 14.4, 3.9 Hz, 1 H, CH_2-CH_2), 2.67 (ddd, J = 14.4, 10.5, 4.6 Hz, 1 H, CH_2-CH_2), 3.15 (q, J = 7.3 Hz, 1 H, CH-CH_3), 3.32 (s, 3 H, CH_3-O), 3.69 (ddd, J = 5.5, 3.6, 2.1 Hz, 1 H, CH-OMe), 3.82 (dd, J = 12.9, 2.0 Hz, 1 H, CH-O), 4.11 (td, J = 10.7, 3.6 Hz, 1 H, CH_2-O), 4.52 (dt, J = 11.1, 4.6 Hz, 1 H, CH_2-O), 4.94 (d, J = 5.5 Hz, 1 H, CH-CH=C), 6.33 (s, 1 H, C-CH=C) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 18.2, 20.1, 22.7, 27.7, 39.6, 44.9, 50.1, 55.3, 61.2, 69.1, 77.2, 96.6, 126.0, 148.3, 156.3, 175.0, 203.6 ppm. MS (ESI): m/z (%) = 345.2 (100) [$M + Na^+$], 291.1 (86) [$MH^+ - MeOH$]$^+$. HRMS (ESI): calcd. for $C_{18}H_{26}O_5Na$ 345.1678 [$M + Na^+$]; found 345.1679.

Compound 65: The same procedure as for compound **62b**, was applied to compound **62a** (12.0 mg, 26.99 μmol) with stirring for 1.5 h. The crude product was purified by column chromatography (25% EtOAc in petroleum ether) to give compound **65** (6.2 mg, 18.36 μmol, 64%) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03–1.08 (m, 4 H, CH_3-C and CH-CH_2-CH), 1.10 (d, J = 7.4 Hz, 3 H, CH_3-CH), 1.50 (s, 3 H, CH_3-C), 1.76–1.87 (m, 2 H, C-CH_2-CH and CH-CH_2-CH), 2.03 (d, J = 1.1 Hz, 3 H, CH_3-C=), 2.10–2.15 (m, 1 H, C-CH_2-CH), 2.21 (td, J = 12.9, 2.4 Hz, 1 H, CH_2-CH_2), 2.49 (dt, J = 12.9, 4.0 Hz, 1 H, CH_2-CH_2), 2.98 (q, J = 7.4 Hz, 1 H, CH-CH_3), 3.28 (s, 3 H, CH_3-O), 3.67 (dd, J = 12.2, 1.9 Hz, 1 H, CH-O), 3.78 (ddd, J = 11.2, 4.3, 3.0 Hz, 1 H, CH_2-O), 4.04–4.08 (m, 1 H, CH-OH), 4.90 (ddd, J = 13.4, 11.2, 2.3 Hz, 1 H, CH_2-O), 6.46 (s, 1 H, CH=C) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.1, 18.7, 21.4, 24.0, 32.3, 32.4, 40.8, 43.8, 47.3, 49.9, 60.2, 64.0, 72.9, 102.4, 127.1, 148.4, 173.5, 203.6 ppm. MS (ESI): m/z (%) = 363.2 (100) [$M + Na^+$]. HRMS (ESI): calcd. for $C_{18}H_{26}O_5Na$ 363.1784 [$M + Na^+$]; found 363.1784.

Supporting Information (see also the footnote on the first page of this article): Experimental procedures and analytical data for new compounds **20**, **22**, **23**, **24**, **29a–d**, **30a–d**, **31a–d**, **32a–d**, **34**, **35**, **36a** and **36b**.

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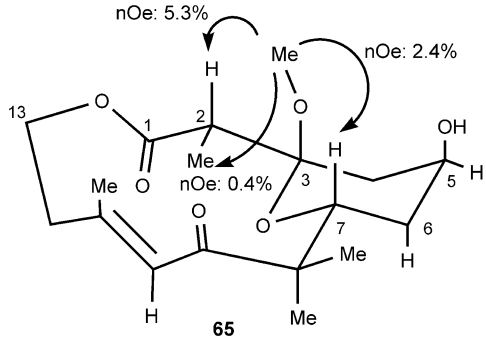
[24] The nOe effect between the methoxy group and 7-H confirmed their *cis* relation and absence of effect between 7-H and 5-H confirmed their *trans* relation in compound **65**. nOe effects are also observed between the methoxy group, 2-H and the methyl group attached on C2. Consequently, relative configuration for the C2 stereocenter cannot be unambiguously assigned.



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