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Total Synthesis of Punctaporonin C by a Regio- and Stereoselective [2+2]-Photocycloaddition

Martin Fleck[a, b] and Thorsten Bach*[a]

Abstract: The unique sesquiterpene punctaporonin C was synthesized starting from commercially available 7-*tert*-butoxynorbornadiene in a linear sequence of 29 steps and with an overall yield of 0.65%. Key step of the synthesis was an intramolecular [2+2]-photocycloaddition, in which the two vinylic double bonds in a 1,3-divinyl-2-cyclopentyl tetronate were differentiated by reaction with the photoexcited tetronate. The reaction gave regio- and diastereoselective access to the tricyclic core skeleton of punctaporonin C in 63% yield. Additional studies related to the tetronate [2+2]-photocycloaddition revealed that even diastereotopic vinylic double bonds in a 1,3-divinyl-2-cyclopentyl tetronate can be differentiated (d.r. up to 78:22). In the further course of the total synthesis the complete tetracyclic oxatetracyclo[6.3.2.$0^{1,4}$.$0^{5,12}$]tridecane skeleton of punctaporonin C was established by an intramolecular aldol reaction, closing a seven-membered oxepane ring. The nucleophilic methyl ketone employed in this step was generated by Wacker oxidation of the vinylic double bond, which was not involved in the [2+2]-photocycloaddition. Several reactions employed in the synthetic sequence required adaptation to the rigid skeleton of punctaporonin C, for example, the reduction of a mesylate, the alkylation of a cyclobutane carboxylate, or the methyl addition to a prostereogenic carbonyl group.

Keywords: natural products · photochemistry · regioselectivity · terpenoids · total synthesis

Introduction

The nail fungus *Poronia punctata* (Linnaeus: Fries) occurs in the dung of horses and ponies which have fed on unimproved pastures or hay. It belongs to the class of endangered species and is considered according to the UK biodiversity action plan to be among the rarest fungi in Europe.[1] The fungus is named after the resemblance of the fruiting bodies to nails. The stalk of the nail is almost black in color, while the expanded head is brownish dotted with small black pores. There are no recent studies towards natural products originating from *Poronia punctata* possibly because access to the fungus has become increasingly difficult. However, an extensive search for new ingredients of *Poronia punctata* was conducted in the 1980s by J. R. Edwards and colleagues.[2]

The search revealed among others a class of sesquiterpenes, which were originally named punctatins but later renamed punctaporonins. The synthetically most relevant punctaporonins A–D are depicted in Figure 1. All punctaporonins are presumably formed from farnesyl pyrophosphate via the humulene cation as intermediate.[2e] Related sesquiterpenes have been isolated from different sources and continue to be discovered[3] with taedolidol and 6-*epi*-taedolidol being structurally most closely related to punctaporonin C.[3b]

Although the above-mentioned search for new ingredients of *Poronia punctata* was initiated to find biologically active compounds, data related to the activity of the isolated punctaporonins have not been disclosed. Despite this lack of information the compounds attracted some attention by the synthetic community. Efforts towards the total synthesis of the major metabolite of *Poronia punctata*, punctaporonin B, culminated in the synthesis of its racemate by Kende et al.[4] Prior to that, Paquette et al. had succeeded in the enantioselective preparation of (−)-punctaporonin A and (+)-punctaporonin D.[5] Kende et al. generated the cyclobutane part of

[a] Dr. M. Fleck, Prof. Dr. T. Bach
Lehrstuhl für Organische Chemie 1, Technische Universität München
Lichtenbergstrasse 4, 85747 Garching (Germany)
Fax: (+49) 89-289-13315
E-mail: thorsten.bach@ch.tum.de

[b] Dr. M. Fleck
Current address:
Boehringer-Ingelheim Pharma GmbH
Birkendorfer Strasse 65, 88397 Biberach/Riß (Germany)

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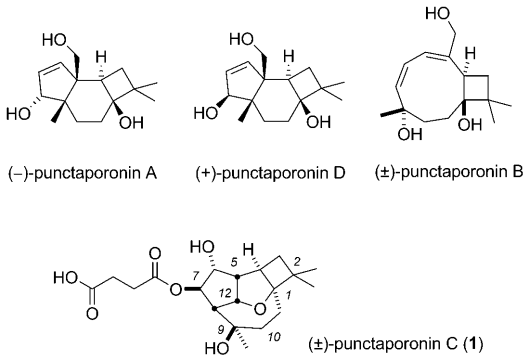
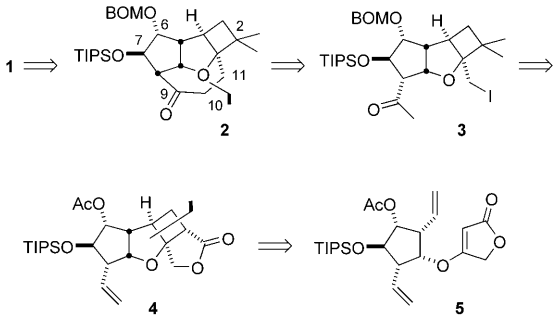


Figure 1. Structures of the previously synthesized punctaporonins A,[5] D,[5] and B;[4] structure of punctaporonin C (**1**).



Scheme 1. Retrosynthetic analysis of punctaporonin C (**1**) based on the pivotal steps of enolate alkylation via ketone **3** and selective [2+2]-photocycloaddition via tetronate **5**.

punctaporonin B in the initial stages of their synthesis by a thermal [2+2]-cycloaddition[4,6] while Paquette et al. set up the cyclobutane ring of punctaporonins A and D by a Norrish–Yang cyclization.[5,7]

The most fascinating structural aspect of punctaporonin C[2b,e] is its unique oxatetracyclo[6.3.2.0^{1,4}.0^{5,12}]tridecane skeleton, which has been rarely found in natural products. Indeed, only recently have other natural products but punctaporonin C, that is, taedolidol and 6-*epi*-taedolidol, been reported,[3b] which incorporate this skeleton. While the cyclobutane ring of oxatetracyclo[6.3.2.0^{1,4}.0^{5,12}]tridecane invites a [2+2]-photocycloaddition[8,9] it is evident from closer inspection that an intermolecular photocycloaddition, that is, by employing isobutene as a reaction partner, is difficult to achieve at a late stage of the synthesis. A dihydrofuran ring, which would serve as precursor for the central tetrahydrofuran, does not provide an adequate chromophore for irradiation at a reasonable wavelength. Initial considerations in our group consequently centered on the use of an appropriately substituted enol ether or its surrogate to enable an intramolecular Cu-catalyzed [2+2]-photocycloaddition reaction.[10,11] The stability of enol ethers turned out to be limited, however, which made us consider a tetronate as potential precursor. Indeed, earlier studies in our group had revealed that several ω-alkenyl-substituted tetronates undergo an efficient intramolecular [2+2]-photocycloaddition at $\lambda =$ 254 nm in various solvents.[12] Based on this consideration we arrived at the retrosynthetic plan depicted in Scheme 1.

It was conceived that an orthogonal protection of the hydroxyl groups at C-6 and C-7 (TIPS = triisopropyl; BOM = benzyloxymethyl) would allow the selective introduction of the succinate side chain. In addition, molecular models revealed that the hydroxyl group of the tertiary alcohol at C-9 is located in a pseudoaxial position, which led us to believe that ketone **2** would be a suitable precursor given that an attack of a methyl anion equivalent would occur pseudoequatorially. Further disconnection of ketone **2** at C-10/C-11 by an enolate alkylation retrone delivered iodide **3**, which appeared to be accessible from the tetracyclic precursor **4** by generation of the methyl ketone from a vinyl group via Wacker oxidation and by elaboration of the lactone into a *gem*-dimethyl group at C-2. The least precedent step in the retrosynthetic scheme was the formation of the cyclobutane ring in a regioselective fashion starting from precursor **5** or related compounds. At first sight it is not clear why a regioselective attack at the desired vinyl double bond would occur in compound **5** with the double bonds being almost diastereotopic. Supporting this scepticism, preliminary studies had indeed revealed that compound **5** and the related deoxygenated precursors **6** (R = Me, Ac, TIPS), which are accessible from *tert*-butyl ether **7** (see below), do not show a pronounced regioselectivity (Figure 2). The selectivity could be significantly altered neither by pressure nor by temperature. In solutions containing cyclodextrin, compound **5** exhibited under certain conditions a distinct preference (regioisomeric ratio (r.r.) up to 85:15) for the undesired cycloaddition product.[13] Gratifyingly and somewhat to our surprise, however, it became evident in further work that the regioselectivity of the [2+2]-photocycloaddition is highly solvent dependent making the suggested retrosynthetic scheme viable.

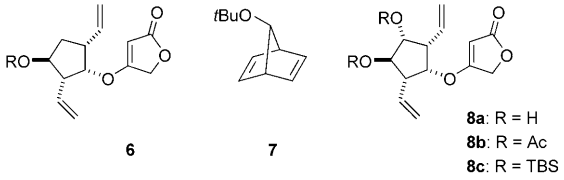


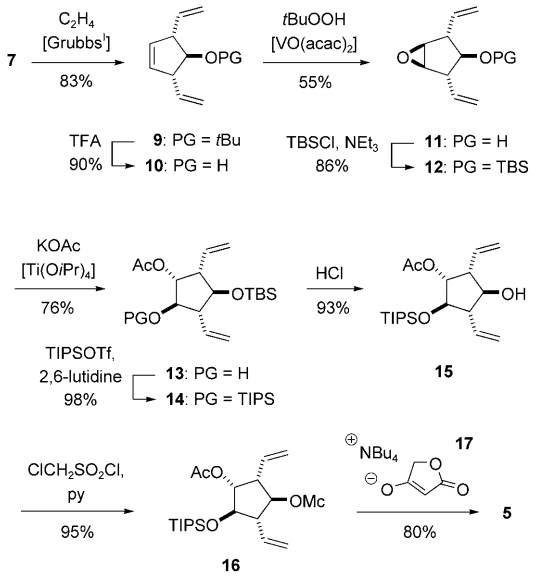
Figure 2. Tetronates **6** and their known[15] precursor **7** required also for the synthesis of tetronate **5** and for the synthesis of tetronates **8**, which exhibit diastereotopic vinyl groups.

In this account we disclose our results regarding the preparation and [2+2]-photocycloaddition reaction of compound **5**. Compounds **8** (Figure 2), which exhibit diastereotopic double bonds and which were also accessible from the same starting material have been included in the study. Moreover, we provide details of the complete total synthesis of punctaporonin C including several important observations made as the synthesis went along.[14] In the final section a potential route towards an enantioselective approach towards punctaporonin C is briefly discussed.

Results and Discussion

Preparation of key intermediate 5 and photocycloaddition experiments: The synthesis sequence to divinylcyclopentane **5** commenced with *tert*-butyl ether **7**, which is readily available by the Kharash–Sosnovsky reaction[15] of norbornadiene. The more accessible of the two olefinic double bonds in this substrate can be cleaved by a ring-opening metathesis reaction.[16] Catalyst optimization revealed that 4 mol% of the Grubbs first-generation catalyst $[Cl_2Ru(PCy_3)_2{=}CHPh]$ (Grubbs^I)[17] was superior to more recently developed metathesis catalysts and delivered by addition over seven days (see Experimental Section) a product conversion of 90%. Product **9** was obtained in 75% yield together with 10% recovered starting material **7** (Scheme 2). After acidic cleavage of the *tert*-butyl ether with trifluoroacetic acid (TFA) the free hydroxyl group of alcohol **10** was employed for a diastereoselective epoxidation reaction of the internal cyclopentene double bond. Best results were obtained with *tert*-butyl hydroperoxide as oxidant and vanadyl bis(acetoacetonate) ($VO(acac)_2$) as the catalyst.[18] Protection of the secondary hydroxyl group of alcohol **11** as *tert*-butyldimethylsilyl (TBS) ether delivered product **12**, which had been previously employed as a starting material for the preparation of substrates **6**.[13] Ring-opening of *meso*-epoxide **12** can be achieved by a variety of methods, enantioselective variants of which will be discussed in the last section of this manuscript. Treatment with KOAc in HOAc as the solvent and in the presence of catalytic amounts of titanium tetraisopropoxide[19] produced racemic alcohol **13**, which was TIPS-protected. The bissilyl ether **14** was selectively deprotected under acidic conditions to yield free alcohol **15**. Nucleophilic substitution of the hydroxyl group in *cis*-1,3-divinyl-2-cyclopentanols like **15** turned out to be difficult. Optimization experiments were conducted with alcohol **15** and with the simpler substrate **10** and revealed that Mitsunobu conditions[20] were not suitable to achieve the desired substitution. Using diisopropyl azodicarboxylate (DIAD) and PPh_3 in THF for the activation and tetronic acid as the nucleophile the tetronate of **10** was obtained in only 6% yield and alcohol **15** did not react at all. Various sulfonates were prepared to convert the hydroxyl group into a better leaving group and various tetronate salts were employed to increase the nucleophilicity of the tetronate. Mesylation and substitution with potassium tetronate/18[c]-6 in DMF emerged as a suitable protocol but when applied to alcohol **15** delivered the desired product **5** in a yield of only 28%.[21] Eventually it was discovered that a chloromethanesulfonate (McO) leaving group[22] can be readily installed at alcohol **15** and that it can be displaced with tetrabutylammonium tetronate (**17**) in THF delivering the desired product via intermediate **16** in 76% overall yield.

The intramolecular [2+2]-photocycloaddition of tetronate **5** was intensively studied under various conditions and in various environments. In Figure 3 the most important factors, which govern the regioselectivity of the reaction, are summarized. Previous experiments had revealed that under



Scheme 2. Synthesis of 1,3-divinyl-2-cyclopentyltetronate **5** from *tert*-butyl ether **7**.

high-pressure conditions or more distinctly in the presence of cyclodextrins the undesired double bond is attacked leading to product **18** (Figure 4). The best selectivity in such a process was observed at 40°C in an aqueous γ-cyclodextrin solution producing an 85:15 mixture of regioisomers in favor of **18**.[13] Contrary to that, protic solvents induce under ambient pressure at low temperature the formation of the desired regioisomer **4**. The best result was achieved upon irradiation of substrate **5** at −75°C in isopropanol as the solvent, which resulted in a 75:25 mixture in favor of **4**, from which the desired product was isolated as a single isomer in 63% yield. As previously noted for tetronates[12] the irradiation wavelength required for excitation is relatively short ($\lambda = 254$ nm) and cannot be increased without slowing down the conversion significantly.

The two isomeric [2+2]-photocycloaddition products **4** and **18** show distinct differences in their NMR spectra, which facilitates an unambiguous structure assignment. Due to the almost perpendicular position of H-7 and H-8 in the *cis–anti–cis* skeleton of **4** and **18** there is no (for **4**) or a very small (for **18**) vicinal coupling. Three separate spin systems are observed in the ^{1}H NMR spectrum, which encompass the hydrogen atoms at the cyclopentane, at the cyclobutane

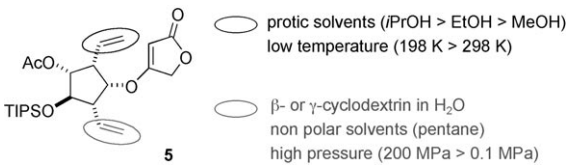


Figure 3. Reaction conditions favoring the addition of the photoexcited tetronate to either one of the two indicated double bonds in substrate **5** with an addition at the black double bond leading to **4**, an addition at the grey double bond to **18**.

and at the γ-lactone ring. Due to a stronger deshielding of the proton at the acetyloxy-substituted carbon atom (C-6 in **4**, C-5 in **18**) as compared to the proton at the TIPSO-substituted carbon atom (C-5 in **4**, C-6 in **18**) a simple analysis of the ^{1}H COSY spectra allows an unambiguous assignment of the regioisomers.

The assignment of the relative configuration is supported by the depicted NOE contacts between H-4 and H-6 as well as H-6 and H-7 in product **4** and between H-4 and H-5 as well as H-6 and H-8 in compound **18** (Figure 4). Notably, other diastereoisomers are not observed, which is in line with observations made in the [2+2]-photocycloaddition of a simpler 1-vinyl-2-cyclopentyl tetronate.[12a]

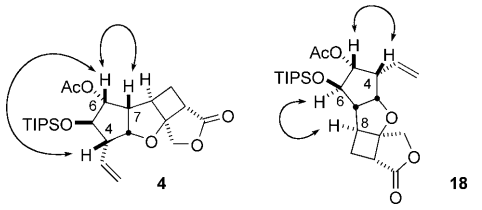
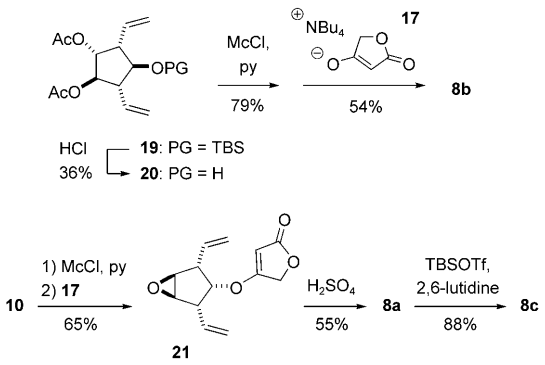
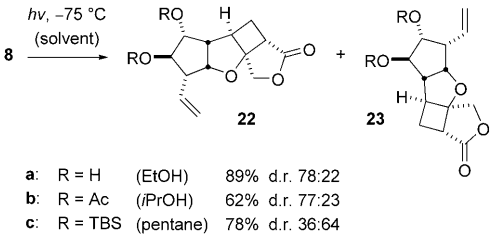


Figure 4. Structure and significant NOE contacts of the two regioisomeric [2+2]-photocycloaddition products **4** and **18**.

Diastereotopos-differentiating [2+2]-photocycloaddition: Despite their very similar chemical environment the two vinyl double bonds in compound **5** are not diastereotopic. The selectivity achieved in the reaction of this substrate suggests, however, that similar selectivities might be achievable in a diastereotopos-differentiating reaction.[23] In order to study this phenomenon a limited set of 1,3-divinyl-2-cyclopentyl tetronates **8** was synthesized in unoptimized reaction sequences (Scheme 3) and subjected to the conditions of the [2+2]-photocycloaddition (Scheme 4). Diacetate **19** was available as side product of the nucleophilic epoxide ring-opening of epoxide **12**. The monoacetate **13** (Scheme 2) was accompanied by minor quantities (6%) of the diacetate, which could be easily separated by chromatography. TBS deprotection of the relatively labile intermediate **19** delivered secondary alcohol **20**, which was converted into tetronate **8b** by the established sulfonylation/substitution sequence. The synthesis of the two other substrates **8a** and **8c** commenced with epoxide **10** (Scheme 2), which was converted into the *meso*-tetronate **21** by sulfonylation/substitution. Epoxide ring-opening under acidic conditions delivered racemic diol **8a**, which could be readily converted into the corresponding bissilyl ether **8c** by treatment with an excess of TBSOTf and 2,6-lutidine in CH_2Cl_2.



Scheme 3. Preparation of 1,3-divinyl-2-cyclopentyltetronates **8**.



Scheme 4. Diastereotopos-selective [2+2]-photocycloaddition reactions on preparative scale under optimized conditions.

We were delighted to note that substrates **8a–c** also showed a preference for attack of one of the two vinylic double bonds. Solvent and temperature variation revealed that the diastereotopos differentation for substrates **8a** and **8b** is most pronounced in protic solvents and favors diastereoisomers **22a** and **22b**. The bissilyl ether **8c**, however, produced preferentially product **23c** with the best result obtained in pentane as the solvent. A selectivity reversal based on the choice of solvent was not observed, that is, the major diastereoisomer was identical for each substrate irrespective of the chosen solvent. Selectivities achieved at ambient temperature varied for compound **8a** from 75:25 to 61:39, for **8b** from 77:23 to 57:43 and for **8c** from 61:39 to 54:46. Preparative runs were conducted at low temperature and delivered the products **22** and **23** as isolated compounds, which could except for the diacetates **22b**/**23b** be completely separated by chromatography.

The high conformational flexibility of cyclopentanes and the—in terms of $\Delta G^{\neq}$—relatively small selectivities make it impossible to identify a single conformer responsible for the observations mentioned above. Nonetheless, a preferred envelope conformation **A** (Figure 5) has been earlier suggested to explain the selectivity in the intramolecular [2+2]-photocycloaddition of tetronate **5**.[14] The reacting centers, which form the cyclobutane ring, are marked with a grey dot. In this conformation the pseudoaxial vinyl group adjacent to the substituent OR (for **5**: OAc) is ideally positioned to undergo [2+2]-photocycloaddition to the pseuoequatorial tetronate. The higher selectivity in polar protic solvents is attributed to the possible formation of hydrogen bonds from the solvent to RO enhancing its size and its preference for a pseudoequatorial position.

Similar arguments as for the conversion **5** → **4** can be put forward to explain the diastereoselectivity in the reactions **8a** → **22a** and **8b** → **22b**. An alternative conformation **B**, which also accounts for the observed diastereotopos-selectivity, allows a pseudoequatorial position for both groups

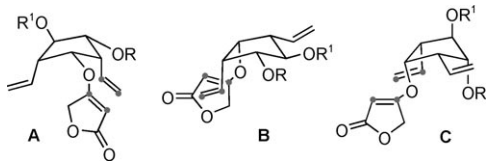
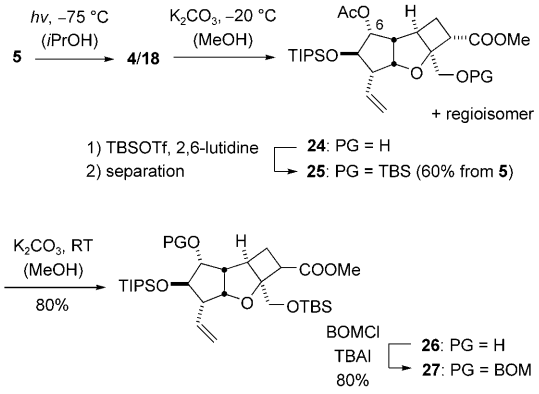


Figure 5. Possible conformations **A**–**C**, which account for the selectivity in the [2+2]-photocycloaddition of 1,3-divinyl-2-cyclopentyl tetronates.

OR and OR^1, which are identical in **8a** ($OR=OR^1=OH$) and in **8b** ($OR=OR^1=OAc$). In this case, one vinylic double bond is pseudoequatorial and therefore not capable to undergo an intramolecular [2+2]-photocycloaddition. The selectivity reversal upon replacement of the protecting group R and R^1 to the TBS group can be attributed to a preferred conformation **C**, in which the TBSO group both reside in a pseudoaxial position. Indeed, the propensity of silyl ethers to adapt 1,2-diaxial positions even in cyclohexanes[24] is known. In conformation **C** one vinylic double bond is pseudoequatorial, which leads to attack at the other diastereotopic double bond as marked in Figure 5.

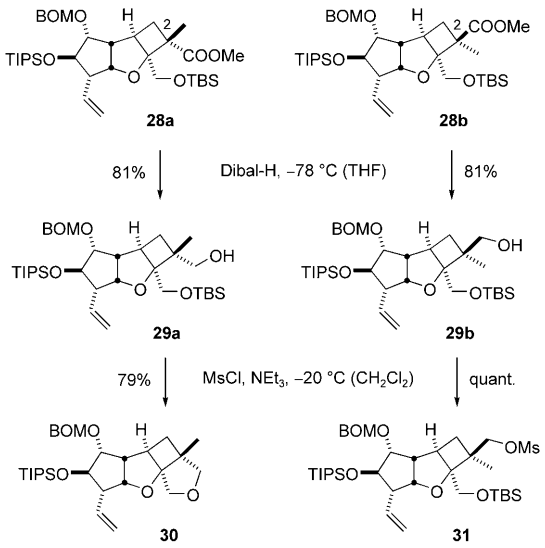
Elaboration to key intermediate 3 and related enolate precursors: For preparative reasons the separation of the two regioisomeric products **4** and **18** was performed on a routinely basis not directly after the [2+2]-photocycloaddition. Instead the crude intermediate lactones were opened by methanolysis and the free primary alcohol **24** and its regioisomer converted into the respective silyl ethers (Scheme 5). The lactone opening was successful at −20 °C in the presence of catalytic amounts (20 mol %) of K_2CO_3 in methanol. Low temperature was required because epimerization set in under otherwise identical conditions at 0 °C leading to an undesirable mixture of four compounds. The high tendency of intermediate **24** for epimerization was also the reason for the immediate protection. In the course of the silylation it became obvious that the free alcohol readily undergoes relactonization, which could be avoided if the reaction was run at −20 but not at 0 °C. Separation of silyl ether **25** from its regioisomer was facile by column chromatography and delivered the desired intermediate **25** in 60 % yield over three steps.

The incompatibility of the acetyl group with the planned intramolecular enolate alkylation (Scheme 1) required its replacement by a base-stable protecting group. To this end the acetate was removed, which turned out to be a relatively slow process. For complete conversion acetate **25** had to be stirred for three days with K_2CO_3 in methanol. The deprotection led to epimerization at the stereogenic α-carbon atom of the methyl ester and product **26** was obtained as a 2:1 mixture of diastereoisomers. The epimerization was without consequences as a subsequent methylation was projected—and indeed conducted—at this α-carbon atom (see below). As already evident by the slow acetate deprotection the free hydroxyl group at the carbon atom C-6 is relatively congested and its protection was therefore not as straightforward as planned. The initially envisioned *para*-methoxybenzyl (PMB) group could be introduced in only 32 % yield even after extensive optimization attempts. Gratifyingly, the etherification with benzyloxymethyl chloride (BOMCl) turned out to be less capricious and delivered under standard conditions at slightly elevated temperature the desired product **27** as a 2:1 mixture of diastereoisomers.



Scheme 5. Synthesis of the appropriately protected oxatetracyclo[6.3.2.$0^{1,4}$.$0^{5,12}$]tridecane **27** (mixture of two diastereoisomers).

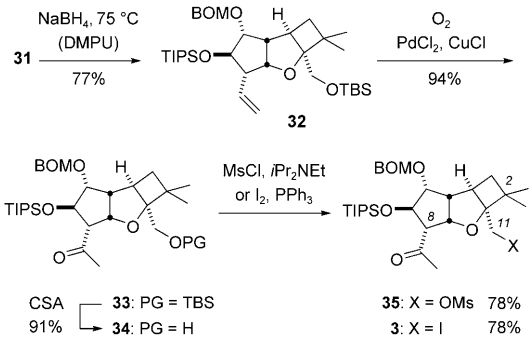
Based on literature precedence[25] the methylation of ester **27** was initially performed with LDA as base and with methyl iodide as alkylating reagent. The major diastereoisomer obtained by this procedure was ester **28a**, which was accompanied by the separable minor diastereoisomer **28b** (Scheme 6). At cursory inspection the diastereoselectivity of the methylation at C-2 appears irrelevant to the further course of the synthesis as the stereogenic center vanishes after complete ester reduction and introduction of the geminal dimethyl substitution. After reduction of diastereomeric esters **28** to the primary epimeric alcohols **29a** and **29b** the attempted conversion to a mesylate, however, led in the former case, that is, for alcohol **29a**, to rapid tetrahydrofuran formation. Even at low temperature the ring closure could not be avoided and the desired mesylate was never detected. The close proximity of the nucleophilic silyl ether leads inadvertently—possibly triggered by chloride ions—to a nucleophilic displacement yielding exclusively tetracyclic product **30**. Contrary to that, the diastereomeric alcohol **29b** could be converted readily into the desired mesylate **31**. Further experiments revealed that the choice of the metal counterion in the enolate methylation reaction has a strong influence on its diastereoselectivity. The use of potassium hexamethyldisilazide (KHMDS) led to a reversal of selectivity as compared to LDA and produced an 80:20 mixture of diastereoisomers **28b**/**28a**. Sodium hexamethyldisilazide (NaHMDS) showed a similar effect. Coordination of a sodium or potassium ion into the oxygen-rich part of the BOM-protected oxatetracyclo[6.3.2.$0^{1,4}$.$0^{5,12}$]tridecane **27** was suggested by ESI-MS data. Based on this observation it may be possible that the cation directs in the latter case the approach of the electrophile while the lithium enolate displays "normal" diastereoselectivity by being attacked from the more accessible diastereotopic face. Under optimized condi-



Scheme 6. Different reactions pathways of the α-methyl-substituted esters **28** upon reduction and mesylation.

tions diastereomerically pure product **28b** was obtained from ester **27** by methylation with KHMDS/MeI in THF as the solvent in 56% yield. The minor diastereoisomer **28a** was isolated in 14% yield. Further transformation of ester **28b** to mesylate **31** proceeded smoothly via alcohol **29b**.

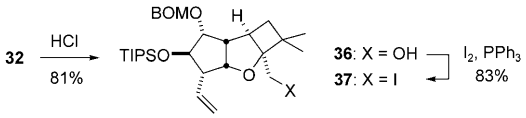
The reduction of a primary mesylate attached to a cyclobutane ring had been performed in preliminary experiments on model systems and had proceeded well with a variety of reducing agents, for example, with $LiAlH_4$ or $LiBEt_3H$. The low reactivity of mesylate **31** towards these reagents was testimony to the steric hindrance associated with a nucleophilic displacement at this position. No reaction was observed. Indeed, the mesylate is in neopentylic position and the trajectories for an approach of the nucleophile are further limited due to the convex shape of the oxabicyclo[3.2.0]heptane skeleton at the internal edge of which the mesylate is located. The desired reduction could eventually be achieved with $NaBH_4$ in a dipolar aprotic solvent,[26] preferentially in *N,N′*-dimethylpropyleneurea (DMPU), at elevated temperature (Scheme 7). Wacker oxidation[27] of the terminal olefin **32** proceeded smoothly and enabled access to ketone **33**. The



Scheme 7. Synthesis of the precursors **3** and **35** for enolate alkylation.

reaction could not be conducted in mixtures of DMF/H_2O but was performed due to the lipophilicity of the substrate in almost pure DMF. Reoxidation of palladium was difficult under these conditions and $PdCl_2$ was therefore used in stoichiometric amounts. The TBS group exhibited the expected orthogonality to the TIPS and BOM protecting groups and was cleaved almost quantitatively under mild acidic conditions. Mesylation of primary alcohol **34** was facile but little precedence existed for the displacement of a sulfonate in intramolecular seven-membered[28] and related ring-closure reactions. It was therefore attempted to install a halogen atom at C-11 but the formation of the respective halides proved difficult. The substitution of mesylate **35** by halides under a variety of conditions failed indicating that an approach of a nucleophile to C-11 is not straightforward. Eventually, iodide **3** could be produced after adapting the typical iodination conditions[29] to the peculiarities of our substrate. In particular the BOM group turned out to be sensitive and could only be kept in place if the reactive iodophosphonium intermediate was preformed in benzene and the substrate was added as a solution in pyridine.

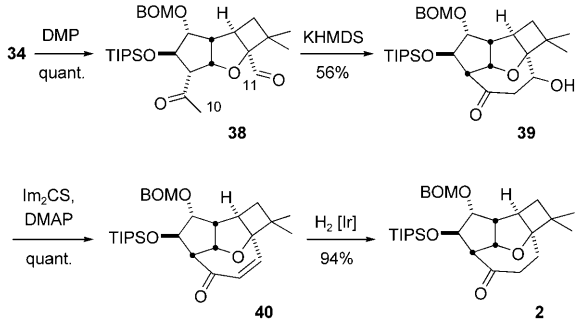
In order to evaluate a Heck reaction or a related carbometalation reaction for ring closure, olefin **32** was converted via alcohol **36** to the corresponding iodide **37**. Again, modified iodination conditions were used to avoid cleavage of the BOM protecting group (Scheme 8).



Scheme 8. Preparation of iodide **37** from silyl ether **32**.

Disappointingly, the ring closure to ketone **2** according to the originally planned enolate alkylation route (Scheme 2) using either iodide **3** or mesylate **35** failed. While THF was used as the solvent in most of the fruitless experiments, bases (e.g. LDA, KO*t*Bu, KHMDS, NaHMDS), additives (e.g., DMPU, TMEDA, 18[c]-6) and reaction temperatures were widely varied. With stronger bases at low temperature there was typically no reaction; upon warming decomposition set in. A frequently encountered side reaction with weaker bases was elimination to an enone due to an undesired deprotonation at C-8. In retrospective it becomes obvious that an intramolecular nucleophilic displacement at C-11 is literally impossible because the trajectory of the leaving group is blocked by the methyl substituents at C-2. Alternatives to establish the desired bond between C-10 and C-11 were studied. Intramolecular Heck-type reaction failed because the required oxidative addition at iodide **37** could not be achieved. Attempts to displace the iodide by a vinyl group and to achieve the ring closure by metathesis remained unsuccessful for the same reason. Iodide **37** did not undergo a nucleophilic substitution with a variety of soft vinyl nucleophiles.

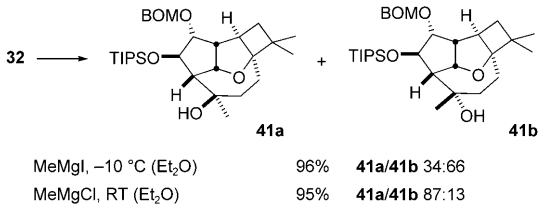
In order to allow an easier attack of the enolate carbon atom C-10 at the electrophilic carbon atom C-11 the C-11 alcohol **34** was converted into an aldehyde (Scheme 9). Oxidation with the Dess–Martin periodinane (DMP)[30] delivered quantitatively the desired ketoaldehyde **38**, to which various aldol addition conditions were applied. It was found that the use of KHMDS facilitates in acceptable yields the cyclization to the seven-membered oxepane **39**, which was obtained as a single diastereoisomer. Acidic elimination conditions were counterindicated by the acid-labile protecting groups, which is the reason why we screened elimination reactions under neutral conditions. The Burgess reagent[31] delivered only the respective methylcarboxysulfamate[32] by an addition reaction, while thiocarbonyldiimidazole (Im_2CS) induced a quantitative elimination. Key to the success of this reaction was the use of a stoichiometric amine base [DMAP = 4-(*N*,*N*-dimethylamino)pyridine] to aid proton removal at 40 °C in the absence of solvent.



Scheme 9. Preparation of tetracyclic ketone **2** via the aldol reaction product **39** and by subsequent dehydration/reduction.

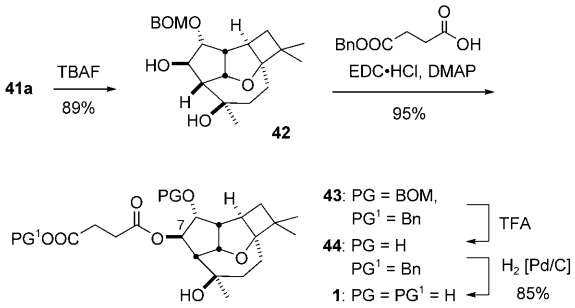
Conjugate hydride addition reagents (Stryker reagent,[33] or L-selectride[34]) failed to reduce the α,β-unsaturated double bond of enone **40**. Hydrogenation in the presence of the Crabtree catalyst[35] $[Ir(cod)py(PCy_3)_2]PF_6$ proceeded smoothly, however, and delivered ketone **2**. Although the successful sequence from **34** to **2** added two additional steps to our original synthesis route the overall yield of 53% for the conversion **34** → **2** is at least as much if not more than to be expected from the enolate alkylation pathway.

Final steps and conclusion of the total synthesis: Based on the analysis mentioned above in the Introduction, addition of a suitable methyl metal reagent was expected to occur in a pseudoequatorial approach, leading to the respective pseudoaxial alcohol **41a**. Bulky methyltriisopropoxy titanium, which has been advertised for an equatorial approach to cyclic ketones,[36] was initially tried, but failed to react with the substituted oxatetracyclo[6.3.2.$0^{1,4}$.$0^{5,12}$]tridecanone as electrophile. Grignard addition with MeMgI was more successful but led surprisingly to the unexpected pseudoequatorial alcohol **41b** as major product (Scheme 10). By varying the counterion and by raising the reaction temperature the selectivity could be reverted and the desired alcohol **41a** could be isolated in 83% yield as a single diastereoisomer. Apparently, coordination to the tetrahydrofuran oxygen



Scheme 10. Diastereoselectivity of the Grignard addition to ketone **32** depending on the counterion and on the temperature.

atom is feasible in the case of MeMgI directing the attack to the undesired diastereotopic face, while the coordination is less pronounced with MeMgCl at elevated temperature. Interestingly, the selectivity with MeMgCl decreased in favor of **41b** if the reaction temperature was lowered to 0 °C (**41a**/**41b** 67:33). The same effect was observed with MeMgI, for which the selectivity increased in favor of **41a** upon increasing the temperature (**41a**/**41b** 51:49 at 0 °C, **41a**/**41b** 65:35 at RT). Experiments to increase the selectivity further for example, by the use of MeLi[37] or MeMgOTs[38] were not successful. If the TIPS group was removed prior to Grignard addition the undesired alcohol, that is, the epimer of alcohol **42** (Scheme 11), was exclusively formed with an excess of MeMgI at −20 °C. In this case chelate formation is likely to induce a conformational change of the seven-membered ring from a chair-like to a boat-like structure.



Scheme 11. Completion of the synthesis of punctaporonin C (**1**) by attachment of the succinic acid side chain to alcohol **42** and complete deprotection.

The further course of the synthesis was uneventful. Removal of the silyl-protecting group proceeded smoothly with tetrabutylammonium fluoride (TBAF) in THF. The succinate side chain at C-7 was established by coupling benzyl succinate with alcohol **42** in the presence of *N*-(3-dimethylaminopropyl)-*N*′-ethyl-carbodiimide hydrochloride (EDC). Since hydrogenolytic cleavage of the BOM group was not feasible under a variety of conditions it was cleaved with TFA prior to hydrogenolytic deprotection of the benzyl succinate.

The synthetic material proved in all scalar properties identical to the natural product. A discrepancy in the ^{13}C NMR chemical shift is due to a different calibration source (hexamethyldisiloxane), which was used by Edwards et al. and which was set to $\delta_{ref} = 0$ ppm.[39] The published ^{13}C NMR data[2] are therefore—compared to our results—all consistently shifted upfield by 2 ppm. In our experiments

CD_3OD ($\delta = 49.1$ ppm) was employed as internal standard which was calibrated against tetramethylsilane ($\delta = 0.0$ ppm). The data are listed for comparison in Table 1 with the appropriate assignment.

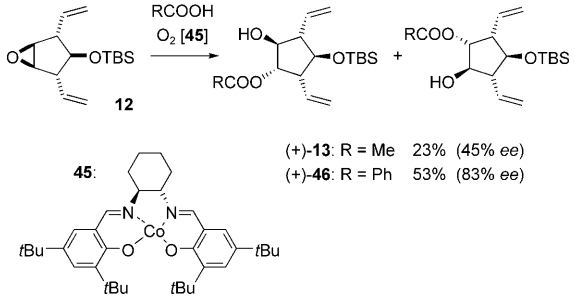
Table 1. ^1H and ^{13}C NMR data of natural and synthetic punctaporonin C in comparison.

^1H NMR[a] (natural)	^1H NMR[b] (synthetic)	^{13}C NMR[c] (natural)	^{13}C NMR[d] (synthetic)	Assignment
1.00 (s)	1.00 (s)	21.8	23.8	C-2-(CH_3)$_2$
1.09 (s)	1.08 (s)	24.8	26.8	C-2-(CH_3)$_2$
1.78 (m), 1.92–2.08 (m)	1.78 (ddd), 1.92–2.08 (m)	26.1	28.1	C-11(H_2)
1.09 (s)	1.07 (s)	27.8	29.8	C-9-CH_3
2.63 (s)	2.58–2.62 (m)	27.8	29.8	CH_2-succinate
2.63 (s)	2.58–2.62 (m)	28.5	30.5	CH_2-succinate
1.57 (br dd), 1.92–2.08 (m)	1.55 (dddd), 1.92–2.08 (m)	31.3	33.3	C-10(H_2)
2.81 (m)	2.76–2.81 (m)	34.2	36.2	C-4(H)
–	–	36.2	38.2	C-2
1.44 (dd), 2.04 (dd)	1.43 (dd), 1.92–2.08 (m)	39.8	41.8	C-3(H_2)
2.81 (m)	2.76–2.81 (m)	54.8	56.7	C-5(H)
2.35 (dd)	2.33 (ddd)	58.9	61.0	C-8(H)
–	–	74.0	76.0	C-9
4.10 (t)	4.09 (dd)	74.6	76.6	C-6(H)
5.20 (t)	5.21 (dd)	80.3	82.1	C-7(H)
4.94 (dd)	4.93 (dd)	82.3	84.2	C-12(H)
–	–	94.5	96.5	C-1
–	–	172.1	174.1	C=O
–	–	173.9	176.2	C=O

[a] Spectrum recorded in [D$_4$]MeOH at 400 MHz ($\delta = 0.00$ ppm for $SiMe_4$).[2e] [b] Spectrum recorded in [D$_4$]MeOH at 500 MHz ($\delta = 0.00$ ppm for $SiMe_4$); for coupling constants, see Experimental Section. [c] Spectrum recorded in [D$_4$]MeOH at 67.8 MHz ($\delta = 0.0$ ppm for $Me_3SiOSiMe_3$).[2e,39] [d] [D$_4$]MeOH, 90.6 MHz ($\delta = 0.0$ ppm for $SiMe_4$).

Starting from commercially available 7-*tert*-butoxynorbornadiene the synthesis of punctaporonin C was completed in a linear sequence of 29 steps and an overall yield of 0.65%. The overall yield corresponds to an average yield of 84% per step. An assignment of the absolute configuration was not possible because the ring opening step **12** → **13** was not conducted enantioselectively. In principle, however, the developed synthetic route to punctaporonin C would be suitable as an approach to enantiomerically pure product if conditions were found to achieve an enantioselective ring opening. This option was studied in a series of experiments.

Enantiotopos-differentiating ring opening: Literature precedence for an enantioselective ring opening of a bicyclic *meso*-epoxide by an acetate nucleophile is rare. The best example which has been reported relies on the use of catalyst **45**. Cyclohexene oxide was quantitatively opened with acetic acid under aerobic conditions in the presence of diisopropylethylamine (Hünig base) at 0–4 °C in *tert*-butyl methyl ether. The reported enantiomeric excess was 40% *ee*.[40] While several other methods for the enantioselective ring opening of *meso*-epoxides have been reported they are either not applicable to cyclic *meso*-epoxides or they do not employ the desired acetate as nucleophile.[41] We therefore conducted some preliminary experiments with the chiral Co–salen complex **45** (Scheme 12). The enantiomeric excess of product **13** was determined by chiral GC analysis. The absolute configuration of the ring-opening products was not assigned. As observed in the racemic series, steric hindrance at substrate **12** decreased the reaction rate considerably and the reaction did not proceed at 0 °C. At room temperature a slow conversion was observed and after 96 h a low yield of 23% was obtained. Given the results obtained with cyclohexene oxide and given the relatively high reaction temperature the enantioselectivity (45% *ee*) was surprisingly high. Nonetheless, the results were not sufficient to consider intermediate (+)-**13** as starting material for a total synthesis. Attempts to modify the previously used promoter Ti(O*i*Pr)$_4$ (Scheme 2) by chiral ligands were also not successful regarding an enantioselective version of the ring opening. Attempts to use the *meso*-tetronate **21** (Scheme 3) in the described and related ring opening reactions failed.



Scheme 12. Enantiotopos-differentiating epoxide ring opening of *meso*-compound catalyszed by the chiral Co–salen complex **45**.

Due to the improved results obtained with benzoic acid in the cyclohexene oxide opening (77% *ee*)[40] analogous conditions were applied to substrate **12**. Racemic product **46** was generated for comparison by treatment of epoxide **12** with sodium benzoate and benzoic acid in DMF. With catalyst **45** the ring opening proceeded at room temperature under standard conditions in 53% yield and with a remarkable enantioselectivity of 83% *ee*. The result demonstrates nicely that the above-mentioned potential of our synthetic strategy for an enantioselective access to punctaporonin C and related oxatetracyclo[6.3.2.0^{1,4}.0^{5,12}]tridecanes is valid. Concerns about the use of benzoates under the irradiation conditions required for tetronate [2+2]-photocycloaddition let us, however, not pursue this route with intermediate (+)-**46**.

Conclusion

In summary, the skeleton of the unusual sesquiterpene punctaporonin C was established by a ring-opening metathesis, an intramolecular tetronate [2+2]-photocycloaddition and an intramolecular aldol reaction as key transformations. The

relative configuration of the eight stereogenic centers could be effectively controlled along the chosen synthetic route and punctaporonin C was obtained as a single diastereoisomer identical in all scalar properties with the natural product. The devised synthetic scheme, in which a *meso*-epoxide serves as precursor for the photocycloaddition substrate, allows for an enantioselective variant of the reactions. According to preliminary results this route seems viable. Further studies in this direction are under way and may possibly lead to an enantioselective access to the more recently discovered natural products taedolidol and 6-*epi*-taedolidol.

Experimental Section

General: All reactions involving water-sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under argon. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium immediately prior to use. Dichloromethane, triethylamine, pyridine and diisopropylethylamine were distilled from calcium hydride. All other chemicals were either commercially available or prepared according to the cited references. TLC: Merck glass sheets (0.25 mm silica gel 60, F_{254}), eluent given in brackets. Detection by UV or coloration with cerium ammonium molybdate [CAM]. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature. Chemical shifts are reported relative to tetramethylsilane as internal standard. Apparent multiplets which occur as a result of the accidental equality of coupling constants of magnetically nonequivalent protons are marked as virtual (virt.). Flash chromatography was performed on silica gel 60 (Merck, 230–400 mesh) (ca. 50–100 g for 1 g of material to be separated) with the indicated eluent. Common solvents for chromatography [pentane, ethyl acetate, diethyl ether (Et_2O), dichloromethane] were distilled prior to use. The synthesis of compounds **9**--**12** has been described in the Supporting Section of a previous publication.[13] Minor improvements in yields were achieved upon scale-up but the procedures remained unchanged.

Acetic acid 3-*tert*-butyldimethylsilanyloxy-5-hydroxy-2,4-divinyl-cyclopentylester (13) and diester 19: (2,4-Divinyl-6-oxabicyclo[3.1.0]hexan-3-yloxy)-*tert*-butyldimethylsilane (**12**; 10.0 g, 37.7 mmol) was dissolved in a 1.5 M KOAc/HOAc buffer solution (100 mL) together with $Ti(OiPr)_4$ (5.58 mL, 5.36 g, 18.9 mmol). The reaction mixture was stirred for 9 h at 90 °C. Two thirds of the solvent were removed under reduced pressure and the residue was neutralized with saturated aqueous $NaHCO_3$ solution. The aqueous layer was extracted with ethyl acetate (3×100 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (200 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 12:1 → 3:1) to yield **13** as a colorless liquid (8.37 g, 25.6 mmol, 68 %) and diester **19** also as a colorless liquid (0.87 g, 2.36 mmol, 6 %). **13**: R_f=0.15 (pentane/Et_2O 4:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = −0.01 (s, 3H), 0.00 (s, 3H), 0.88 (s, 9H), 2.06 (s, 3H), 2.39 (virt. q, $^3J \cong$ 8.5 Hz, 1H), 2.60 (brs, 1H), 2.84 (virt. q, $^3J \cong$ 8.6 Hz, 1H), 3.75 (dd, ^3J=8.4, 8.4 Hz, 1H), 3.79 (dd, ^3J=8.5, 4.8 Hz, 1H), 4.87 (dd, ^3J=8.6, 4.8 Hz, 1H), 5.09–5.25 (m, 4H), 5.66 (ddd, ^3J=16.8, 10.0, 10.0 Hz, 1H), 5.73 ppm (ddd, ^3J=17.1, 9.9, 8.6 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 3.90 (q), 3.79 (q), 17.9 (s), 20.9 (q), 25.8 (q), 53.4 (d), 57.9 (d), 78.6 (d), 78.8 (d), 81.4 (d), 118.3 (t), 119.0 (t), 134.3 (d), 137.4 (d), 171.4 ppm (s); MS (EI, 70 eV): *m*/*z* (%): 326 (1) [M^+], 269 (17), 251 (7), 209 (100), 191 (12), 155 (12), 135 (14), 127 (27), 117 (31), 91 (20), 75 (77), 57 (18); HRMS (EI): *m*/*z*: calcd for $C_{13}H_{21}O_4Si$ [$M-C_4H_9^+$] 269.1209; found: 269.1206. **19**: R_f=0.40 (pentane/Et_2O 4:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = −0.03 (s, 6H), 0.83 (s, 9H), 2.01 (s, 3H), 2.02 (s, 3H), 2.48 (virt. q, $^3J \cong$ 8.5 Hz, 1H), 2.78 (virt. q, $^3J \cong$ 8.1 Hz, 1H), 3.81 (t, ^3J=8.1 Hz, 1H), 4.99 (dd, ^3J=8.2, 4.3 Hz, 1H), 5.05–5.20 (m, 5H), 5.59 (ddd, ^3J=16.6, 10.2, 9.7 Hz, 1H), 5.72 ppm (ddd, ^3J=17.1, 10.0, 8.7 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = −3.8 (q), −3.7 (q), 18.0 (s), 20.9 (q), 21.0 (q), 25.9 (q), 53.8 (d), 56.4 (d), 77.2 (d), 78.6 (d), 79.1 (d), 118.2 (t), 119.5 (t), 133.9 (d), 136.8 (d), 169.9 (s), 170.2 ppm (s); IR (ATR): $\tilde{\nu}$ = 3080 (m), 2956 (m), 2929 (s), 2857 (m), 1747 (vs), 1643 (w), 1472 (w), 1371 (m), 1243 (vs), 1127 (s), 1061 (m), 1036 (m), 838 (s), 777 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 311 (15) [$M-C_4H_9^+$], 293 (1), 248 (18), 209 (20), 191 (16), 177 (10), 135 (33), 117 (100), 107 (6), 91 (8), 75 (21), 73 (21); HRMS (EI): *m*/*z*: calcd for $C_{15}H_{23}O_5Si$ [$M-C_4H_9^+$]: 311.1315; found: 311.1317.

Acetic acid-3-*tert*-butyldimethylsilanyloxy-5-triisopropylsilanyloxy-2,4-divinyl-cyclopentyl ester (14): Compound **13** (8.30 g, 24.4 mmol) was dissolved in dichloromethane (200 mL) together with 2,6-lutidine (4.15 mL, 3.81 g, 35.6 mmol). After cooling down the solution to 0 °C TIPSOTf (8.20 mL, 9.35 g, 30.5 mmol) was added slowly by a syringe. The reaction mixture was stirred at 0 °C for 2.5 h. After this, the reaction mixture was quenched by adding saturated NH_4Cl solution (60 mL) and H_2O (60 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (2×80 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (150 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 50:1) to yield **14** as colorless crystals (12.0 g, 24.9 mmol, 98 %). R_f=0.50 (pentane/Et_2O 30:1) [CAM]; m.p. 59–61 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ = −0.02 (s, 3H), −0.01 (s, 3H), 0.85 (s, 9H), 1.02–1.06 (m, 21H), 2.02 (s, 3H), 2.43 (d virt. t, ^3J=9.2, $^3J \cong$ 6.4 Hz, 1H), 2.89 (virt. q, $^3J \cong$ 7.9 Hz, 1H), 3.80 (t, ^3J=7.5 Hz, 1H), 3.97 (dd, ^3J=3.9, 5.7 Hz, 1H), 5.00 (dd, ^3J=3.9, 6.8 Hz, 1H), 5.09–5.15 (m, 4H), 5.61 (ddd, ^3J=17.1, 9.7, 9.7 Hz, 1H), 5.71 ppm (ddd, ^3J=17.0, 9.8, 9.8 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = −3.6 (q), −3.5 (q), 12.7 (d), 18.3 (s), 18.3 (q), 18.4 (q), 21.3 (q), 26.2 (q), 53.7 (d), 60.8 (d), 79.6 (t), 80.4 (d), 82.0 (d), 117.7 (t), 118.9 (t), 135.0 (d), 139.1 (d), 170.2 ppm (s); IR (KBr): $\tilde{\nu}$ = 3080 (m), 2940 (vs), 2892 (s), 2864 (s), 1732 (vs), 1462 (m), 1245 (vs), 1105 (s), 838 (s), 776 (s), 681 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 467 (1) [$M-CH_3^+$], 439 (12), 425 (7), 365 (5), 249 (8), 220 (3), 173 (100), 135 (5), 117 (6), 103 (6), 73 (14), 59 (7); HRMS (EI): *m*/*z*: calcd for $C_{23}H_{43}O_4Si_2$ [$M-C_3H_7^+$]: 439.2700; found: 439.2698.

Acetic acid 3-hydroxy-5-triisopropylsilanyloxy-2,4-divinyl-cyclopentyl ester (15): Compound **14** (12.0 g, 24.9 mmol) was dissolved in MeOH (110 mL) and 15 drops of concentrated HCl were added. The reaction mixture was stirred at RT. After 6 h the reaction mixture was neutralised with saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate (3×100 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (150 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 3:1) to yield **15** as a colorless liquid (8.54 g, 23.2 mmol, 93 %). R_f=0.20 (pentane/Et_2O 4:1) [CAM]; ^{1}H NMR (360 MHz, CDCl3): δ = 1.01–1.09 (m, 21H), 1.74 (brs, 1H), 2.02 (s, 3H), 2.44 (ddd, ^3J=8.5, 8.4, 5.6 Hz, 1H), 2.86 (virt. q, $^3J \cong$ 8.0 Hz, 1H), 3.84 (dd, ^3J=8.9, 8.5 Hz, 1H), 4.00 (dd, ^3J=2.7, 5.6 Hz, 1H), 5.06 (dd, ^3J=2.7, 6.4 Hz, 1H), 5.15–5.28 (m, 4H), 5.71 (ddd, ^3J= 17.3, 10.3, 8.2 Hz, 1H), 5.82 ppm (ddd, ^3J=17.0, 10.2, 8.4 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 12.4 (d), 18.09 (q), 18.12 (q), 21.0 (q), 52.7 (d), 60.1 (d), 78.2 (d), 79.9 (d), 81.5 (d), 117.6 (t), 118.8 (t), 133.9 (d), 138.1 (d), 169.9 ppm (d); IR (NaCl): $\tilde{\nu}$ = 3439 (s, br), 3080 (m), 2943 (s), 2866 (s), 1731 (vs), 1643 (m), 1463 (s), 1371 (s), 1233 (vs), 1091 (s), 1053 (s), 917 (s), 681 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 325 (19) [$M-C_3H_7^+$], 265 (4), 239 (1), 209 (4), 173 (100), 155 (5), 135 (10), 117 (6), 103 (10), 75 (15), 57 (13); HRMS (EI): *m*/*z*: calcd for $C_{17}H_{29}O_4Si$ [$M-C_3H_7^+$] 325.1835; found: 325.1838.

Tetrabutylammonium tetronate (17):[42] In a 0.75 M aqueous solution of tetrabutylammonium hydroxide (77.0 mL, 16.9 g, 65.0 mmol) was added tetronic acid (6.87 g, 69.0 mmol). After 20 min the solvent was removed under reduced pressure and the crude product was suspended in ethyl acetate (100 mL). The suspension was refluxed for 15 min and filtrated hot. The precipitate was dried over P_2O_5 to yield tetrabutylammonium tetronate as colorless crystals (20.4 g, 59.7 mmol, 92 %). M.p. 150–151 °C; ^{1}H NMR: (360 MHz, $CDCl_3$): δ = 1.02 (t, ^3J=7.3 Hz, 12H), 1.37–1.48 (m, 8H), 1.58–1.69 (m, 8H), 3.20–3.28 (m, 8H), 4.24 (s, 1H), 4.30 ppm (s, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 13.6 (q), 19.7 (t), 23.9 (t), 58.7 (t), 72.0 (t), 78.3 (d), 182.0 (s), 194 ppm.1 (s).

Tetronic acid 4-acetoxy-3-triisopropylsilanyloxy-2,5-divinylcyclopentyl ester (5): Compound **15** (1.68 g, 4.55 mmol) was dissolved in pyridine (30 mL) and cooled to 0 °C. Slowly chloromethanesulfonyl chloride (547 μL, 897 mg, 6.02 mmol) was added to the stirred solution by a syringe. After 3 h the reaction mixture was quenched by adding crushed ice. Additionally water (150 mL) was added and the suspension was extracted with diethyl ether (3×100 mL). The organic layers were combined and washed with 1 M HCl (100 mL), saturated aqueous $NaHCO_3$ (100 mL) and saturated aqueous NaCl solution (100 mL). The organic layer was dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product of chloromethanesulfonate **16** could be used without further purification. R_f=0.56 (pentane/Et_2O 2:1) [CAM].

The chloromethanesulfonate was dissolved in THF (80 mL). Compound **17** (4.43 g, 13.0 mmol) was added and the suspension was stirred for 20 h at 67 °C (oil bath temperature). The reaction mixture was cooled to ambient temperature and pentane (60 mL) was added. The suspension was filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate 12:1 → 4:1) to compound **5** (1.55 g, 3.46 mmol, 76%) as a colorless solid. R_f=0.20 (pentane/ethyl acetate 6:1) [CAM]; m.p. 86–88 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =1.03–1.05 (m, 21H), 2.05 (s, 3H), 2.82 (ddd, ^3J= 9.5, 6.7, 6.0 Hz, 1H), 3.29–3.35 (m, 1H), 4.38 (dd., ^3J=6.7, 4.2 Hz, 1H), 4.60 (s, 2H), 4.65 (t, ^3J=6.0 Hz, 1H), 5.03 (s, 1H), 5.09 (dd, ^3J=7.5, 4.2 Hz, 1H), 5.15–5.23 (m, 4H), 5.61 (ddd, ^3J=17.2, 10.1, 9.5 Hz, 1H), 5.75 ppm (ddd, ^3J=17.1, 10.1, 9.5 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =12.5 (d), 18.1 (q), 18.1 (q), 21.0 (q), 48.8 (d), 55.9 (d), 67.7 (t), 80.5 (d), 81.3 (d), 87.1 (d), 90.5 (d), 120.2 (t), 120.9 (t), 130.0 (d), 133.3 (d), 169.9 (s), 173.5 (s), 178.8 ppm (s); IR (KBr): $\tilde{\nu}$ = 3110 (m), 2941 (vs), 2866 (s), 1773 (vs), 1744 (vs), 1622 (vs), 1462 (m), 1236 (vs), 1149 (s), 1050 (m), 880 (m), 776 (s), 678 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 453 (1) [M^+], 407 (14), 339 (12), 265 (6), 209 (8), 191 (14), 173 (78), 131 (66), 117 (24), 73 (28), 57 (100), 43 (28); HRMS (EI): *m*/*z*: calcd for $C_{21}H_{31}O_6Si$ [$M-C_3H_7^+$] 407.1890; found: 407.1880.

Photocycloaddition products 4 and 18: Compound **5** (100 mg, 0.22 mmol) was dissolved in degassed isopropanol (35 mL) and cooled to −75 °C. The solution was irradiated for 1.5 h while kept at low temperature (light source: Rayonet RPR-2537 Å). After complete irradiation the solution was brought to RT and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate 15:1 → 8:1) to yield tetracycle **4** (65.4 mg, 145 μmol, 66%) and tetracycle **18** (23.8 mg, 52.8 μmol, 24%) both as colorless solids. **4**: R_f= 0.45 (pentane/ethyl acetate 6:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =1.00–1.10 (m, 21H, C16,17,18-H), 2.08–2.13 (m, 1H), 2.11 (s, 3H), 2.29 (ddd, ^2J=13.0, ^3J=8.0, 4.1 Hz, 1H), 2.57 (ddd, ^3J=9.3, 9.1, 4.3 Hz, 1H), 2.77 (dd, ^3J=8.0, 7.3 Hz, 1H), 2.96 (dd, ^3J=9.2, 4.8 Hz, 1H), 3.00 (dd, ^3J=10.3, 4.1 Hz, 1H), 4.25 (dd, ^3J=9.1, 6.5 Hz, 1H), 4.28 (d, ^2J=9.7 Hz, 1H), 4.31 (d, ^2J=9.7 Hz, 1H), 4.76 (dd, ^3J=4.8, 4.3 Hz, 1H), 4.88 (dd, ^3J=9.2, 6.5 Hz, 1H, C7-H), 5.24 (d, ^2J=1.8, ^3J=9.9 Hz, 1H), 5.28 (d, ^2J= 1.8, ^3J=17.5 Hz, 1H), 5.92 ppm (ddd, ^3J=17.5, 9.9, 9.3 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =12.6 (d, C-18), 18.1 (q, C-16/17), 18.2 (q, C-16/17), 21.0 (q, C-15), 25.6 (t, C-14), 40.1 (d, C-13), 43.3 (d, C-12), 49.6 (d, C-11), 53.1 (d, C-10), 72.1 (t, C-9), 79.5 (d, C-8), 80.6 (d, C-7), 87.7 (d, C-6), 88.5 (s, C-5), 119.2 (t, C-4), 134.9 (d, C-3), 170.3 (s, C-2), 177.6 ppm (s, C-1); IR (ATR): $\tilde{\nu}$ = 3087 (w), 2962 (s), 2940 (s), 2865 (s), 1776 (s), 1740 (vs), 1464 (m), 1372 (m), 1240 (vs), 1163 (m), 1139 (s), 1120 (m), 1033 (s), 915 (m), 884 (m), 849 (m), 681 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 407 (22), 347 (2), 321 (1), 279 (1), 217 (2), 173 (100), 131 (8), 103 (8), 75 (8), 43 (6); HRMS (EI): *m*/*z*: calcd for $C_{21}H_{31}O_6Si$ [$M-C_3H_7^+$] 407.1890; found: 407.1887. **18**: R_f=0.53 (pentane/ethyl acetate 6:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =1.00–1.10 (m, 21H, C16,17,18-H), 2.13 (s, 3H), 2.16 (ddd, ^2J=13.3, ^3J=10.3, 5.2 Hz, 1H), 2.34 (ddd, ^2J=13.3, ^3J=8.2, 4.7 Hz, 1H), 2.64–2.67 (m, 1H), 2.91–2.97 (m, 1H), 3.01 (ddd, ^3J=10.3, 4.7, ^4J=1.3 Hz, 1H), 3.08 (ddd, ^3J=8.9, 5.4, 5.3 Hz, 1H), 4.03 (t, ^3J=2.0 Hz, 1H), 4.35 (d, ^3J=9.9 Hz, 1H), 4.35 (d, ^3J=9.9 Hz, 1H), 4.94 (dd, ^3J=5.7, 5.4 Hz, 1H), 5.06 (dd, ^3J=5.3, 2.0 Hz, 1H), 5.20 (dd, ^2J=1.8, ^3J=10.1 Hz, 1H), 5.25 (ddd, ^2J=1.8, ^3J=17.4, ^4J= 0.9 Hz, 1H), 5.82 ppm (ddd, ^3J=17.4, 10.1, 8.9 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =12.2 (d, C-18), 18.0 (q, C-16/17), 18.1 (q, C-16/17), 21.1 (q, C-15), 26.7 (t, C-14), 40.2 (d, C-13), 47.8 (d, C-12), 49.6 (d, C-11), 61.7 (d, C-10), 73.4 (t, C-9), 82.3 (d, C-8), 83.2 (d, C-7), 88.7 (s, C-6), 89.6 (d, C-5), 118.9 (t, C-4), 132.0 (d, C-3), 169.7 (s, C-2), 177.7 ppm (s, C-1); IR (ATR): $\tilde{\nu}$ = 3076 (w), 2956 (s), 2942 (s), 2866 (s), 1765 (s), 1739 (vs), 1379 (m), 1363 (m), 1243 (m), 1230 (vs), 1165 (m), 1095 (s), 1033 (vs), 914 (m), 882 (m), 680 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 407 (18), 347 (2), 265 (1), 239 (1), 217 (2), 173 (100), 131 (6), 103 (8), 75 (8), 61 (4), 43 (6); elemental analysis calcd (%) for [$C_{24}H_{28}O_3Si$] C 63.97, H 8.50; found: C 63.63, H 8.71.

1,2-Diacetoxy-4-hydroxy-3,5-divinylcyclopentane (20): Compound **19** (510 mg, 1.38 mmol) was dissolved in MeOH (12 mL) and six drops of concentrated HCl were added. The solution was stirred for 4 h at ambient temperature. Subsequently, the reaction mixture was brought to pH 7–8 by adding saturated aqueous $NaHCO_3$ solution and additional H_2O (30 mL) was added. The aqueous layer was extracted with ethyl acetate (3×50 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 3:2) to yield **20** as a colorless liquid (128 mg, 500 μmol, 36%). R_f=0.07 (pentane/Et_2O 4:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =2.04 (brs, 1H), 2.04 (s, 3H), 2.05 (s, 3H), 2.48 (virt. q, $^3J\cong$8.5H, 1H), 2.78 (virt. q, $^3J\cong$8.4 Hz, 1H), 3.87 (t, ^3J=9.3 Hz, 1H), 4.97 (dd, ^3J=7.9, 3.4 Hz, 1H), 5.18–5.22 (m, 5H), 5.69 (ddd, ^3J=17.3, 10.3, 8.4 Hz, 1H), 5.84 ppm (ddd, ^3J=17.2, 10.3, 8.1 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 20.9 (q), 21.0 (q), 52.9 (d), 55.6 (d), 77.1 (d), 77.1 (d), 77.5 (d), 118.3 (t), 119.5 (t), 133.0 (d), 136.3 (d), 169.8 (d), 170.2 ppm (s); IR (ATR): $\tilde{\nu}$ = 3447 (s, br), 3074 (w), 2978 (m), 2923 (w), 1732 (vs), 1717 (vs), 1374 (m), 1267 (m), 1231 (vs), 1129 (m), 1055 (s), 1003 (s), 925 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 212 (1), 194 (5), 152 (20), 134 (43), 125 (51), 105 (38), 91 (54), 83 (100), 70 (40).

Tetronic acid 3,4-diacetoxy-2,5-divinylcyclopentyl ester (8b): Compound **20** (128 mg, 0.50 mmol) was dissolved in pyridine (5 mL) and cooled to 0 °C. Slowly chloromethanesulfonyl chloride (0.07 mL, 115 mg, 0.77 mmol) was added to the stirred solution by syringe. After 3 h the reaction mixture was quenched by adding crushed ice. Additionally water (60 mL) was added and the pH value of the solution was brought to 2–3 by adding 2 N aqueous HCl. The solution was extracted with ethyl acetate (4×50 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 2:1) to yield 1,2-diacetoxy-4-(chloromethanesulfonyloxy)-3,5-divinylcyclopentane as a colorless liquid (145 mg, 0.36 mmol, 79%). R_f=0.92 (pentane/ethyl acetate 1:1) [CAM].

The chloromethanesulfonate (128 mg, 0.35 mmol) was dissolved in THF (6 mL). Compound **17** (358 mg, 1.05 mmol) was added and the suspension was stirred for 16 h under reflux. The reaction mixture was cooled to ambient temperature and pentane (4 mL) was added. The suspension was filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 1:1 → pentane/ethyl acetate 1:1) to yield compound **8b** as a colorless liquid (65.0 mg, 0.19 mmol, 54%). R_f=0.46 (pentane/ethyl acetate 1:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =2.06 (s, 6H), 2.81–2.89 (m, 1H), 3.22–3.30 (m, 1H), 4.61 (t, ^3J=4.5 Hz, 1H), 4.64 (s, 2H), 5.04 (s, 1H), 5.17–5.25 (m, 4H), 5.32 (dd, ^3J=8.7, 4.7 Hz, 1H), 5.45 (dd, ^3J=9.8, 4.7 Hz, 1H), 5.64 (ddd, ^3J=17.0, 10.4, 9.3 Hz, 1H), 5.75 ppm (ddd, ^3J=17.2, 10.3, 8.2 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =20.9 (q), 21.0 (q), 49.3 (d), 52.2 (d), 67.7 (t), 77.3 (d), 80.2 (d), 87.8 (d), 90.7 (d), 120.4 (t), 121.3 (t), 129.4 (d), 131.8 (d), 170.1 (s), 170.2 (s), 173.2 (s), 178.8 ppm (s); IR (ATR): $\tilde{\nu}$ = 3122 (w), 3088 (w), 2971 (m), 2928 (w), 1773 (m), 1737 (vs), 1623 (vs), 1373 (m), 1317 (m), 1228 (vs), 1151 (m), 1046 (s), 930 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 336 (3) [M^+], 276 (5), 234 (14), 217 (17), 216 (16), 188 (7), 135 (36), 108 (26), 93 (40), 43 (100); HRMS (EI): *m*/*z*: calcd for $C_{17}H_{20}O_7$ [M^+]: 336.1209; found: 336.1207.

2,4-Divinyl-6-oxabicyclo[3.1.0]hexan-3-yl tetronate (21): 2,4-Divinyl-6-oxabicyclo[3.1.0]hexan-3-ol (**11**; 334 mg, 2.18 mmol) was dissolved in pyridine (7.00 mL) and cooled to 0 °C. Slowly, chloromethanesulfonyl chlo-

ride (311 μL, 90% (technical grade), 510 mg, 3.07 mmol) was added to the stirred solution by syringe. After 3 h the reaction mixture was quenched by adding crushed ice. Additionally, water (30 mL) was added and the suspension was extracted with diethyl ether (3×30 mL). The organic layers were combined and washed with 1 M HCl (50 mL), saturated aqueous $NaHCO_3$ solution (50 mL) and saturated aqueous NaCl solution (50 mL). The organic layer was dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 8:1) to yield chloromethanesulfonic acid 2,4-divinyl-6-oxabicyclo[3.1.0]hex-3-ylester as a colorless liquid (456 mg, 1.72 mmol, 79%). R_f=0.24 (pentane/Et_2O 4:1).

The intermediate chloromethanesulfonate (303 mg, 1.15 mmol) was dissolved in THF (15 mL). Compound **17** (1.56 g, 4.58 mmol) was added and the suspension was stirred for 16 h under reflux. The reaction mixture was cooled to ambient temperature and pentane (15 mL) was added. The suspension was filtered and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 3:2) to yield **21** as colorless crystals (224 mg, 955 μmol, 83%). R_f=0.18 (pentane/Et_2O 3:2) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =3.41 (dd, ^3J=8.1, 7.5 Hz, 2H), 3.57 (s, 2H), 4.49 (t, ^3J=7.5 Hz, 1H), 4.55 (s, 2H), 5.09 (s, 1H), 5.22–5.28 (m, 4H), 5.68 ppm (ddd, ^3J=17.3, 10.1, 8.1 Hz, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =45.6 (d), 58.3 (d), 67.8 (t), 82.0 (d), 90.6 (d), 120.5 (t), 131.2 (d), 173.3 (s), 178.2 ppm (s); IR (ATR): $\tilde{\nu}$ = 3112 (w), 3020 (w), 2933 (m), 1779 (s), 1751 (s), 1620 (s), 1388 (s), 1313 (s), 1274 (w), 1239 (m), 1155 (s), 1060 (s), 943 (s), 887 (s), 853 (s), 802 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 234 (56) [M^+], 217 (6), 206 (12), 205 (13), 189 (38), 177 (6), 164 (13), 152 (14), 149 (9), 133 (31), 121 (38), 119 (16), 107 (75), 91 (100), 79 (100), 67 (39), 55 (80), 53 (75), 41 (56). HRMS (EI): *m*/*z*: calcd for $C_{13}H_{14}O_4$ [M^+]: 234.0892; found: 234.0892.

Tetronic acid 3,4-dihydroxy-2,5-divinylcyclopentyl ester (8a): Compound **21** (313 mg, 1.34 mmol) was dissolved in dioxane (6 mL) and 0.75 M H_2SO_4 (12 mL) was added. The solution was stirred for 16 h at 50 °C. The mixture was neutralized with saturated aqueous $NaHCO_3$ solution and the solvent was removed under reduced pressure. The remaining solid was suspended in ethyl acetate, filtered and the solvent removed under reduced pressure again. The obtained crude product was purified by flash chromatography (pentane/ethyl acetate 2:1 → ethyl acetate) to yield **8a** as a colorless liquid (179 mg, 0.71 mmol, 53%). R_f=0.17 (ethyl acetate) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =2.66–2.73 (m, 1H), 3.10–3.17 (m, 1H), 4.14 (dd, ^3J=7.4, 4.6 Hz, 1H), 4.19 (dd, ^3J=8.6, 4.6 Hz, 1H), 4.61 (t, ^3J=5.1 Hz, 1H), 4.64 (s, 2H), 5.05 (s, 1H), 5.21–5.32 (m, 4H), 5.80 (ddd, ^3J=17.3, 10.2, 8.4 Hz, 1H), 5.81 ppm (ddd, ^3J=17.1, 10.3, 9.2 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =50.4 (d), 54.2 (d), 67.8 (t), 79.2 (d), 82.5 (d), 87.7 (d), 90.5 (d), 119.9 (t), 121.2 (t), 130.8 (d), 133.1 (d), 173.5 (s), 178.9 ppm (s); IR (ATR): $\tilde{\nu}$ = 3399 (br), 3117 (w), 3074 (w), 2926 (m), 1772 (m), 1731 (s), 1614 (vs), 1319 (s), 1237 (m), 1157 (m), 1045 (s), 1000 (m), 925 (m), 800 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 252 (8) [M^+], 234 (3), 207 (5), 193 (4), 153 (30), 120 (70), 93 (52), 81 (100), 77 (51), 55 (92), 41 (46); HRMS (EI): *m*/*z*: calcd for $C_{13}H_{26}O_5$ [M^+]: 252.0998; found: 252.0995.

Tetronic acid 3,4-bis-(*tert*-butyldimethylsilanyloxy)-2,5-divinylcyclopentyl ester (8c): Compound **8a** (70.0 mg, 0.28 mmol) was dissolved in dichloromethane (10 mL). 2,6-Lutidine (171 μL, 157 mg, 1.47 mmol) was added and the solution was cooled to −5 °C. After adding slowly TBSOTf (255 μL, 294 mg, 1.11 mmol), the solution was stirred for 2.5 h at −5 °C. The reaction was quenched by adding saturated aqueous NH_4Cl solution (30 mL). Additional water (30 mL) was added and the solution was extracted with dichloromethane (3×30 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 95:5 → 5:1) to yield **8c** as a colorless liquid (117 mg, 244 μmol, 88%). R_f=0.26 (pentane/Et_2O 5:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.03–0.07 (m, 12H), 0.88 (s, 9H), 0.89 (s, 9H), 2.80–2.87 (m, 1H), 3.00–3.15 (m, 1H), 3.86–3.91 (m, 2H), 4.52 (s, 2H), 4.68 (t, ^3J=6.8 Hz, 1H), 4.98 (s, 1H), 5.02–5.09 (m, 4H), 5.84 (ddd, ^3J= 17.4, 9.9, 9.9 Hz, 1H), 5.89 ppm (ddd, ^3J=16.9, 10.1, 9.7 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−4.7 (q), −4.5 (q), −4.3 (q), −4.1 (q), 18.0 (s), 18.1 (s), 25.8 (q), 25.9 (q), 51.8 (d), 58.0 (d), 67.7 (t), 82.1 (d), 84.2 (d), 87.5 (d), 89.7 (d), 118.2 (t), 119.0 (t), 132.9 (d), 134.7 (d), 174.0 (s), 179.3 ppm (s); IR (ATR): $\tilde{\nu}$ = 3127 (w), 3084 (w), 2951 (m), 2928 (s), 2856 (m), 1773 (s), 1747 (s), 1625 (vs), 1472 (m), 1360 (m), 1315 (s), 1249 (m), 1147 (s), 1103 (s), 1056 (s), 915 (m), 836 (s), 775 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 465 (1), 423 (30), 291 (38), 271 (14), 209 (16), 183 (39), 147 (62), 117 (10), 93 (16), 73 (100), 57 (16), 41 (8); HRMS (EI): *m*/*z*: calcd for $C_{21}H_{35}O_5Si_2$ [$M-C_4H_9^+$]: 423.2023; found: 423.2022.

Tetracycles 22a and 23a: Compound **8a** (40 mg, 0.16 mmol) was dissolved in degassed ethanol (20 mL) and cooled to −75 °C. The solution was irradiated for 2 h while kept at the low temperature (light source: Rayonet RPR-2537 Å). After complete irradiation the solution was brought to RT and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate 1:9) to yield tetracycle **22a** (27.0 mg, 0.11 mmol, 69%) and tetracycle **23a** (8.00 mg, 0.03 mmol, 20%) both as colorless liquids. **22a**: R_f=0.26 (cyclohexane/ethyl acetate 1:9) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =2.08 (ddd, ^2J=13.1, ^3J=10.4, 5.9 Hz, 1H), 2.29 (ddd, ^2J=13.1, ^3J=8.7, 4.4 Hz, 1H), 2.31–2.39 (m, 3H), 2.75 (dd, ^3J=9.9, 5.5 Hz, 1H), 2.98 (ddd, ^3J=10.4, 4.4, ^4J=1.4 Hz, 1H), 3.38–3.44 (m, 1H), 3.74 (dd, ^3J=10.3, 7.4 Hz, 1H), 4.02 (dd, ^3J=9.9, 7.4 Hz, 1H), 4.25 (d, ^2J=9.7 Hz, 1H), 4.38 (d, ^3J=9.7 Hz, 1H), 4.71 (dd, ^3J=5.5, 3.9 Hz, 1H), 5.21–5.29 (m, 2H), 5.93 ppm (ddd, ^3J=18.4, 9.1, 9.0 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =25.8 (t), 40.2 (d), 47.8 (d), 51.0 (d), 51.5 (d), 72.4 (t), 76.2 (d), 80.5 (d), 87.1 (d), 88.5 (s), 119.0 (t), 134.6 (d), 178.1 ppm (s); IR (ATR): $\tilde{\nu}$ = 3399 (br), 3079 (w), 2972 (m), 2938 (m), 2871 (m), 1769 (vs), 1750 (vs), 1292 (m), 1185 (m), 1166 (m), 1090 (s), 1028 (vs), 996 (m), 917 (m), 731 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 252 (10) [M^+], 234 (2), 207 (4), 193 (6), 151 (184), 120 (54), 107 (20), 91 (19), 81 (100), 55 (35). HRMS (EI): *m*/*z*: calcd for $C_{13}H_{16}O_5$ [M^+]: 252.0998; found: 252.0995. **23a**: R_f= 0.19 (cyclohexane/ethyl acetate 1:9) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =2.08–2.17 (m, 3H), 2.34 (ddd, ^2J=13.1, ^3J=8.4, 4.6 Hz, 1H), 2.55 (dd, ^3J=5.6, 2.4 Hz, 1H), 2.80–3.05 (m, 2H), 3.07–3.13 (m, 1H), 3.95–3.98 (m, 1H), 3.99–4.01 (m, 1H), 4.27 (d, ^2J=9.9 Hz, 1H), 4.42 (d, ^3J=9.9 Hz, 1H), 4.92 (dd, ^3J=5.1, 5.1 Hz, 1H), 5.31–5.39 (m), 6.00 ppm (ddd, ^3J=17.8, 10.5, 7.5 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =26.6 (t), 40.0 (d), 47.8 (d), 50.2 (d), 59.6 (d), 73.0 (t), 82.0 (d), 84.0 (d), 88.7 (s), 89.6 (d), 119.6 (t), 132.0 (d), 177.7 ppm (s); IR (ATR): $\tilde{\nu}$ = 3389 (br), 3074 (w), 2927 (s), 2861 (m), 1769 (vs), 1749 (vs), 1733 (vs), 1292 (m), 1183 (m), 1091 (m), 1027 (vs), 921 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 252 (12) [M^+], 234 (2), 207 (4), 153 (18), 120 (51), 107 (15), 91 (17), 81 (100), 55 (35); HRMS (EI): *m*/*z*: calcd for $C_{13}H_{16}O_5$ [M^+]: 252.0998; found: 252.0994.

Tetracycles 22b and 23b: Compound **8b** (40 mg, 0.12 mmol) was dissolved in degassed methanol (20 mL) and cooled to −75 °C. The solution was irradiated for 2 h while kept at the low temperature (light source: Rayonet RPR-2537 Å). After complete irradiation the solution was brought to RT and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/acetone 4:1) to yield an inseparable mixture of the tetracycles **22b** and **23b** as a colorless liquid (25.0 mg, 0.07 mmol, 62%). **22b**: R_f=0.38 (pentane/acetone 4:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =2.05 (s, 3H), 2.12 (s, 3H), 2.06–2.15 (m, 1H), 2.28 (ddd, ^2J=13.2, ^3J=8.7, 4.3 Hz, 1H), 2.67 (ddd, ^3J=10.5, 8.3, 3.9 Hz, 1H), 2.88–2.96 (m, 2H), 2.97–3.03 (m, 1H), 4.32 (d, ^2J=9.9 Hz, 1H), 4.37 (d, ^3J=9.9 Hz, 1H), 4.73 (dd, ^3J=4.2, 3.9 Hz, 1H), 5.16 (dd, ^3J=10.0, 6.7 Hz, 1H), 5.17–5.25 (m, 2H), 5.30 (dd, ^3J=10.5, 6.7 Hz, 1H), 5.90 ppm (ddd, ^3J=17.8, 9.7, 8.3 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =21.3 (q), 25.6 (t), 40.4 (d), 43.4 (d), 49.9 (d), 49.9 (d), 72.3 (t), 76.5 (d9), 79.6 (d), 87.2 (d), 88.9 (s), 119.4 (t), 133.6 (d), 170.5 (s), 170.7 (s), 177.7 ppm (s); IR (ATR): $\tilde{\nu}$ = 3079 (w), 2954 (m), 2925 (m), 2851 (w), 1772 (s), 1736 (vs), 1370 (m), 1290 (m), 1224 (vs), 1163 (m), 1089 (m), 1029 (s), 923 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 336 (4) [M^+], 308 (2), 294 (6), 276 (12), 264 (2), 234 (48), 216 (88), 188 (24), 161 (36), 145 (28), 133 (66), 121 (46), 91 (42), 81 (100), 55 (70). **23b**: R_f=0.38 (pentane/acetone 4:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =2.05 (s, 3H), 2.09 (s, 3H), 2.06–2.15 (m, 1H), 2.34 (ddd, ^2J= 13.2, ^3J=8.5, 4.5 Hz, 1H), 2.54 (dd, ^3J=4.9, 4.9 Hz, 1H), 2.97–3.03 (m, 1H), 3.08 (ddd, ^3J=8.8, 5.8, 5.5 Hz, 1H), 3.17–3.23 (m, 1H), 4.35 (d, ^2J=

9.9 Hz, 1H), 4.43 (d, ^3J=9.9 Hz, 1H), 4.82–4.87 (m, 2H), 5.12–5.32 (m, 3H), 5.82 ppm (ddd, ^3J=17.5, 10.4, 8.8 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =21.2 (q), 21.3 (q), 26.4 (t), 40.4 (d), 47.7 (d), 50.2 (d), 57.5 (d), 73.1 (t), 80.1 (d), 83.3 (d), 88.9 (d), 89.0 (s), 119.8 (t), 131.5 (d), 169.9 (s), 170.3 (s), 177.8 ppm (s); IR (ATR): $\tilde{\nu}$ = 3079 (w), 2954 (m), 2925 (m), 2851 (w), 1772 (s), 1736 (vs), 1370 (m), 1290 (m), 1224 (vs), 1163 (m), 1089 (m), 1029 (s), 923 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 336 (4) [M^+], 276 (6), 234 (14), 217 (100), 205 (8), 191 (12), 162 (26), 149 (48), 133 (32), 121 (20), 108 (20), 91 (22), 81 (36), 55 (34); HRMS (EI): *m*/*z*: calcd for $C_{17}H_{20}O_7$ [M^+]: 336.1209; found: 336.1209.

Tetracycles 22c and 23c: Compound **8c** (40 mg, 0.08 mmol) was dissolved in degassed pentane (20 mL) and cooled to −75 °C. The solution was irradiated for 2 h while kept at the low temperature (light source: Rayonet RPR-2537 Å). After complete irradiation the solution was brought to RT and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 5:1) to yield tetracycle **22c** (11.0 mg, 0.02 mmol, 28%) and tetracycle **23c** (20.0 mg, 0.04 mmol, 50%) both as colorless solids. **22c**: R_f=0.20 (pentane/Et_2O 5:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.00 (s, 3H), 0.02 (s, 3H), 0.03 (s, 3H), 0.08 (s, 3H), 0.86 (s, 9H), 0.92 (s, 9H), 2.08 (ddd, ^2J=13.0, ^3J=10.4, 5.5 Hz, 1H), 2.27 (ddd, ^2J=13.0, ^3J=8.5, 4.6 Hz, 1H), 2.36 (ddd, ^3J=9.3, 8.9, 4.6 Hz, 1H), 2.67 (dd, ^3J=8.5, 6.5 Hz, 1H), 2.99 (ddd, ^3J= 10.4, 4.6, ^4J=1.4 Hz, 1H), 3.23–3.28 (m, 1H), 3.68 (dd, ^3J=8.9, 6.5 Hz, 1H), 3.87 (dd, ^3J=8.5, 6.5 Hz, 1H), 4.29 (d, ^2J=9.7 Hz, 1H), 4.38 (d, ^3J= 9.7 Hz, 1H), 4.70 (dd, ^3J=6.5, 4.6 Hz, 1H), 5.12–5.19 (m, 2H), 5.82 ppm (ddd, ^3J=16.7, 10.4, 9.3 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−4.5 (q), −4.1 (q), −3.6 (q), −3.5 (q), 18.0 (s), 18.2 (s), 26.0 (t), 26.1 (q), 26.3 (q), 40.1 (d), 42.5 (d), 52.8 (d), 53.1 (d), 72.8 (t), 78.1 (d), 81.3 (d), 87.5 (d), 88.4 (s), 118.4 (t), 134.0 (d), 178.1 ppm (s); IR (ATR): $\tilde{\nu}$ = 3079 (w), 2955 (s), 2929 (s), 2895 (m), 2856 (s), 1777 (vs), 1472 (m), 1260 (s), 1115 (m), 1086 (s), 1055 (m), 1033 (s), 879 (s), 836 (vs), 773 cm^{-1} (vs); MS (EI, 70 eV): *m*/*z* (%): 423 (14), 341 (8), 281 (6), 271 (82), 207 (42), 189 (10), 147 (100), 133 (20), 73 (60), 57 (6); HRMS (EI): *m*/*z*: calcd for $C_{21}H_{35}O_5Si_2$ [$M-C_4H_9^+$]: 423.2023; found: 423.2021. **23c**: R_f=0.29 (pentane/Et_2O 5:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.04 (s, 3H), 0.05 (s, 3H), 0.05 (s, 3H), 0.06 (s, 3H), 0.87 (s, 9H), 0.88 (s, 9H), 2.12 (ddd, ^2J=13.2, ^3J=10.5, 4.6 Hz, 1H), 2.29 (ddd, ^2J=13.2, ^3J=8.1, 5.3 Hz, 1H), 2.60 (dd, ^3J=6.7, 1.0 Hz, 1H), 2.76 (ddd, ^3J=9.6, 5.6, 4.2 Hz, 1H), 2.88–2.94 (m, 1H), 2.99 (ddd, ^3J=10.5, 5.3, ^4J=1.3 Hz, 1H), 3.85 (dd, ^3J=4.2, 0.6 Hz, 1H), 3.90 (brs, 1H), 4.29 (d, ^2J=10.8 Hz, 1H), 4.43 (d, ^3J=10.8 Hz, 1H), 4.89 (dd, ^3J=6.7, 5.6 Hz, 1H), 5.17–5.25 (m, 2H), 5.93 ppm (ddd, ^3J=17.4, 10.3, 9.6 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−4.6 (q), −4.5 (q), −4.4 (q), −4.4 (q), 18.0 (s), 18.5 (s), 25.9 (q), 26.1 (q), 27.2 (t), 40.4 (d), 47.9 (d), 52.2 (d), 63.0 (d), 74.1 (t), 84.1 (d), 84.7 (d), 88.8 (s), 91.0 (d), 117.7 (t), 134.7 (d), 178.1 ppm (s); IR (ATR): $\tilde{\nu}$ = 3079 (w), 2952 (s), 2928 (s), 2889 (m), 2856 (s), 1778 (s), 1473 (m), 1258 (s), 1159 (m), 1096 (m), 1067 (s), 1035 (vs), 910 (s), 836 (vs), 773 cm^{-1} (s); MS (EI, 70 eV): *m*/*z* (%): 423 (30), 341 (12), 291 (8), 271 (54), 207 (38), 189 (6), 155 (10), 147 (100), 133 (22), 73 (96); elemental analysis calcd (%) for [$C_{25}H_{44}O_5Si_2$]: C 62.45, H 9.22: found: C 62.55, H 8.97.

Tricyclic methyl carboxylate 25

Photocycloaddition of tetronate ***5***: Compound **5** (597 mg, 1.33 mmol) was dissolved in *i*PrOH (150 mL) and irradiated for 1.5 h at −75 °C (light source: Rayonet RPR-2537 Å). After complete irradiation and warming to RT, the solvent was removed under reduced pressure. The crude product was used without further purification. R_f=0.53 (**18**), 0.45 (**4**) (pentane/ethyl acetate 6:1) [CAM].

Opening of lactones ***4*** *and* ***18***: The crude product was dissolved in MeOH (30 mL) and cooled to −20 °C. After adding K_2CO_3 (36.6 mg, 0.27 mmol) the solution was stirred for 2 h at −20 °C. The reaction was quenched at low temperature by addition of pH 7 buffer solution (10 mL) [$Na_2HPO_4{\cdot}2H_2O$ (72.7 mg, 0.41 mmol) and KH_2PO_4 (35.2 mg, 0.26 mmol) in water (10 mL)]. The mixture was brought to RT and additional H_2O (100 mL) was added. The aqueous layer was extracted with dichloromethane (3×70 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (150 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product of alcohol **24** was used without further purification R_f=0.17 (pentane/ethyl acetate 6:1) [CAM].

TBS protection: The crude product of the lactone opening was dissolved in dichloromethane (20 mL) and 2,6-lutidine (772 μL, 710 mg, 6.63 mmol) was added. After cooling down to −25 °C, TBS-OTf (760 μL, 875 mg, 3.31 mmol) was added carefully and the resulting solution was stirred at the same temperature for 2 h. The reaction was quenched by adding saturated aqueous NH_4Cl solution (40 mL), and brought to RT. Additional H_2O (50 mL) was added and the resulting mixture was extracted with dichloromethane (3×40 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/ethyl acetate 15:1 → 10:1) to yield tricyclic ester **25** as a colorless liquid (471 mg, 788 μmol, 60%) and its regioisomer (167 mg, 279 μmol, 21%) also as a colorless liquid. R_f=0.71 (pentane/ethyl acetate 6:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.05 (s, 3H), 0.06 (s, 3H), 0.90 (s, 9H), 1.00–1.05 (m, 21H), 1.58 (ddd, ^2J=12.7, ^3J=9.7, 3.3 Hz, 1H), 2.08 (s, 3H), 2.33 (ddd, ^2J=12.7, ^3J=9.5, 9.0 Hz, 1H), 2.42 (ddd, ^3J=9.7, 9.4, 4.0 Hz, 1H), 2.52 (dd, ^3J=9.5, 3.3 Hz, 1H), 2.86 (dd, ^3J=9.7, 5.5 Hz, 1H), 3.11 (ddd, ^3J=9.7, 9.0 Hz, 1H), 3.54 (d, ^2J=10.0 Hz, 1H), 3.64 (s, 3H), 3.81 (d, ^2J=10.0 Hz, 1H), 4.20 (dd, ^3J=9.7, 7.8 Hz, 1H), 4.70 (dd, ^3J= 5.5, 4.0 Hz, 1H), 4.75 (dd, ^3J=9.7, 7.8 Hz, 1H), 5.15 (dd, ^2J=2.0, ^3J= 10.0 Hz, 1H), 5.21 (dd, ^2J=2.0, ^3J=17.3 Hz, 1H), 5.92 ppm (ddd, ^3J= 17.3, 10.0, 9.4 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−5.5 (q), −5.3 (q), 12.8 (d), 18.2 (q), 18.3 (q), 18.5 (s), 21.0 (q), 22.5 (t), 25.9 (q), 39.7 (d), 44.1 (d), 48.7 (d), 51.6 (d), 52.6 (q), 63.5 (t), 78.2 (d), 80.7 (d), 86.0 (d), 91.3 (s), 118.9 (t), 135.5 (d, C-3), 170.4 (s), 172.9 ppm (s); IR (ATR): $\tilde{\nu}$ = 2944 (s), 2904 (m), 2864 (s), 1741 (vs), 1733 (vs), 1463 (m), 1237 (vs), 1203 (m), 1179 (m), 1101 (s), 1037 (m), 838 (s), 786 (m), 676 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 596 (5) [M^+], 553 (16), 539 (4), 467 (6), 393 (8), 291 (6), 279 (8), 255 (2), 173 (100), 131 (6), 103 (7), 73 (14), 43 (7); HRMS (EI): *m*/*z*: calcd for $C_{31}H_{56}O_7Si_2$ [M^+]: 596.3565, found 596.3564.

Tricyclic secondary alcohol 26: Acetate **25** (200 mg, 335 μmol) was dissolved in MeOH (10 mL) and treated with K_2CO_3 (184 mg, 1.34 mmol). The resulting mixture was stirred for three days at ambient temperature. The reaction was quenched by adding saturated aqueous NH_4Cl solution (20 mL). Additional H_2O was added (80 mL) and the resulting solution was extracted with ethyl acetate (3×40 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 6:1) to yield alcohol **26a** (103 mg, 186 μmol, 55%) and its diastereoisomer **26b** (47 mg, 84.7 μmol, 25%), both as colorless liquids. **26a**: R_f=0.28 (pentane/Et_2O 5:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.11 (s, 6H), 0.94 (s, 9H), 1.01–1.07 (m, 21H), 2.06 (ddd, ^2J=12.9, ^3J=8.2, 6.5 Hz, 1H), 2.17 (dt, ^2J=12.9, ^3J= 9.6 Hz, 1H), 2.38 (dt, ^3J=8.9, 4.1 Hz, 1H), 2.61 (dd, ^3J=9.6, 4.7 Hz, 1H), 2.98 (d, ^2J=9.5 Hz, 1H), 3.10–3.20 (m, 2H), 3.67 (s, 3H), 3.72 (d, ^2J= 10.7 Hz, 1H), 3.78 (d, ^2J=10.7 Hz, 1H), 3.87 (ddd, ^3J=9.6, 9.5, 5.2 Hz, 1H), 4.04 (dd, ^3J=8.9, 5.2 Hz, 1H), 4.72 (dd, ^3J=4.7, 4.1 Hz, 1H), 5.08 (dd, ^2J=1.9, ^3J=10.2 Hz, 1H), 5.14 (ddd, ^2J=1.9, ^3J=17.3, ^4J=0.5 Hz, 1H), 5.95 ppm (ddd, ^3J=17.3, 10.2, 8.9 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−5.3 (q), −5.2 (q), 12.7 (d), 18.2 (q), 18.3 (q), 18.8 (s), 21.7 (t), 26.3 (q), 38.7 (d), 43.0 (d), 51.4 (d), 51.8 (q), 54.0 (d), 66.4 (t), 79.5 (d), 85.6 (d), 88.9 (d), 90.6 (s), 117.4 (t), 136.6 (d), 172.4 ppm (s); IR (ATR): $\tilde{\nu}$ = 3510 (br), 3031 (w), 2942 (vs), 2891 (s), 2865 (vs), 1736 (s), 1463 (m), 1254 (m), 1153 (s), 1099 (vs), 1048 (s), 997 (s), 839 (s), 734 (m), 683 cm^{-1} (m); MS (EI, 70 eV): *m*/*z* (%): 523 (4) [$M-CH_3O^+$], 511 (6), 497 (8), 479 (14), 465 (6), 379 (12), 293 (12), 211 (100), 167 (6), 131 (7), 103 (10), 75 (14), 59 (5); **26b**: R_f=0.20 (pentane/Et_2O 5:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.09 (s, 3H), 0.09 (s, 3H), 0.91 (s, 9H), 1.02–1.07 (m, 21H), 1.67 (ddd, ^2J=13.2, ^3J=9.8, 3.7 Hz, 1H), 2.45–2.57 (m, 2H), 2.61 (dd, ^3J=9.3, 4.7 Hz, 1H), 3.00 (d, ^2J=9.7 Hz, 1H), 3.11–3.19 (m, 2H), 3.66 (s, 3H), 3.77 (d, ^2J=10.8 Hz, 1H), 3.81 (d, ^2J= 10.8 Hz, 1H), 3.90 (ddd, ^3J=9.7, 9.3, 4.6 Hz, 1H), 4.09 (dd, ^3J=7.8, 4.6 Hz, 1H), 4.68 (dd, ^3J=4.7, 4.6 Hz, 1H), 5.13 (dd, ^2J=1.7, ^3J=10.0 Hz, 1H), 5.19 (dd, ^2J=1.7, ^3J=17.3 Hz, 1H), 5.99 ppm (ddd, ^3J=17.3, 10.0,

9.6 Hz, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = −5.4 (q), −5.3 (q), 12.6 (d), 18.2 (q), 18.3 (q), 18.8 (s), 21.4 (t), 26.2 (q), 38.4 (d), 44.7 (d), 51.6 (d), 51.7 (q), 54.2 (q), 63.9 (t), 80.0 (d), 86.1 (d), 87.4 (d), 90.2 (s), 117.7 (t), 136.7 (d), 172.9 ppm (s); IR (ATR): $\tilde{\nu}$ = 3488 (br), 3079 (w), 2944 (s), 2927 (s), 2865 (s), 1709 (s), 1462 (m), 1439 (m), 1252 (m), 1207 (m), 1132 (s), 1099 (s), 915 (m), 837 (s), 779 (m), 680 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 554 (4) [M^+], 523 (1), 511 (8), 497 (2), 479 (10), 411 (4), 379 (8), 293 (10), 237 (6), 211 (100), 167 (6), 131 (7), 103 (10), 75 (14), 59 (5); HRMS (EI): *m/z*: calcd for $C_{29}H_{54}O_6Si_2$ [M^+]: 554.3459, found 554.3451.

BOM ether 27: Alcohol **26** (250 mg, 451 μmol) was dissolved in dichloromethane (7 mL). Diisopropylethylamine (441 μL, 2.58 mmol), benzylchloromethylether (BOMCl) (333 μL, 75% (technical grade), 374 mg, 1.80 mmol) and tetrabutylammonium iodide (TBAI) (166 mg, 451 μmol) were added consecutively and the reaction mixture was stirred at 50°C for 36 h in a sealed flask. After cooling to ambient temperature the reaction was quenched by adding saturated aqueous NH_4Cl solution (50 mL) while stirring was continued for 30 min. The layers were separated and the aqueous layer was extracted with dichloromethane (2×25 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (50 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 17:1 → 8:1) to yield the diastereomeric mixture of the BOM ethers **27a** and **27b** both as colorless liquids (244 mg, 361 μmol, 80%). **27a**: R_f = 0.79 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.10 (s, 6H), 0.93 (s, 9H), 1.03–1.05 (m, 21H), 1.91–2.08 (m, 2H), 2.27 (ddd, ^3J = 9.4, 9.2, 4.4 Hz, 1H), 2.76 (dd, ^3J = 9.1, 6.0 Hz, 1H), 3.17 (dd, ^3J = 9.0, 6.5 Hz, 1H), 3.44 (d, ^2J = 9.9 Hz, 1H), 3.45 (dd, ^3J = 8.9, 8.4 Hz, 1H), 3.61 (d, ^2J = 9.9 Hz, 1H), 3.66 (s, 3H), 3.73 (dd, ^3J = 9.1, 7.3 Hz, 1H), 4.01 (dd, ^3J = 9.2, 7.3 Hz, 1H), 4.57 (d, ^2J = 11.9 Hz, 1H), 4.69 (d, ^2J = 11.9 Hz, 1H), 4.72 (dd, ^3J = 6.0, 4.4 Hz, 1H), 4.78 (d, ^2J = 7.1 Hz, 1H), 4.79 (d, ^2J = 7.1 Hz, 1H), 5.08 (dd, ^2J = 2.1, ^3J = 10.0 Hz, 1H), 5.14 (dd, ^2J = 2.1, ^3J = 17.3 Hz, 1H), 5.88 (ddd, ^3J = 17.3, 10.0, 9.4 Hz, 1H), 7.26–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = −5.3 (q), −5.2 (q), 13.0 (d), 18.3 (q), 18.3 (q), 18.4 (s), 22.4 (t), 26.0 (q), 39.2 (d), 40.9 (d), 50.3 (d), 51.6 (d), 53.3 (q), 63.9 (t), 70.3 (t), 80.3 (d), 85.1 (d), 88.2 (d), 90.1 (s), 96.3 (t), 117.9 (t), 127.7 (d), 127.8 (d), 128.6 (d), 136.4 (d), 138.0 (s), 173.3 ppm (s); IR (ATR): $\tilde{\nu}$ = 3069 (w), 2945 (vs), 2930 (vs), 2864 (s), 1737 (vs), 1463 (m), 1253 (m), 1199 (m), 1147 (s), 1092 (vs), 1045 (s), 836 (s), 777 (m), 681 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 674 (6) [M^+], 617 (2), 601 (1), 523 (1), 479 (4), 423 (1), 393 (2), 303 (5), 207 (33), 177 (12), 91 (100), 73 (16), 59 (5); HRMS (EI): *m/z*: calcd for $C_{37}H_{62}O_7Si_2$ [M^+]: 674.4034; found: 674.4030. **27b**: R_f = 0.67 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.06 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 1.02–1.07 (m, 21H), 1.57 (ddd, ^2J = 12.1, ^3J = 9.5, 2.9 Hz, 1H), 2.32 (ddd, ^2J = 12.1, ^3J = 9.5, 9.4 Hz, 1H), 2.33 (ddd, ^3J = 9.7, 9.4, 4.6 Hz, 1H), 2.76 (ddd, ^3J = 9.0, 6.7, 1.6 Hz, 1H), 3.00–3.05 (m, 1H), 3.13 (ddd, ^3J = 9.5, 9.5, 1.6 Hz, 1H), 3.59 (d, ^2J = 9.8 Hz, 1H), 3.65 (s, 3H), 3.74 (dd, ^3J = 9.0, 7.7 Hz, 1H), 3.84 (d, ^2J = 9.8 Hz, 1H), 4.01 (dd, ^3J = 9.4, 7.7 Hz, 1H), 4.56 (d, ^2J = 12.0 Hz, 1H), 4.64 (d, ^2J = 12.0 Hz, 1H), 4.72 (dd, ^3J = 6.7, 4.6 Hz, 1H), 4.77 (d, ^2J = 6.8 Hz, 1H), 4.79 (d, ^2J = 6.8 Hz, 1H), 5.12 (dd, ^2J = 2.1, ^3J = 10.0 Hz, 1H), 5.17 (dd, ^2J = 2.1, ^3J = 17.2 Hz, 1H), 5.92 (ddd, ^3J = 17.2, 10.0, 9.7 Hz, 1H), 7.26–7.39 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = −5.5 (q), −5.3 (q), 13.0 (d), 18.3 (q), 18.3 (q), 18.5 (s), 23.0 (t), 26.0 (q), 40.0 (d), 44.5 (d), 50.4 (d), 51.5 (d), 53.0 (q), 63.7 (t), 70.3 (t), 79.0 (d), 84.9 (d), 86.0 (d), 91.6 (s), 96.2 (t), 118.3 (t), 127.7 (d), 127.9 (d), 128.6 (d), 136.1 (d), 137.9 (s), 173.0 ppm (s); IR (ATR): $\tilde{\nu}$ = 3069 (w), 2944 (vs), 2904 (s), 2865 (s), 1735 (s), 1463 (m), 1251 (m), 1199 (m), 1152 (s), 1093 (vs), 1053 (s), 882 (m), 837 (s), 777 (m), 678 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 674 (6) [M^+], 631 (4), 596 (6), 553 (16), 531 (4), 479 (10), 453 (6), 393 (10), 303 (6), 279 (12), 211 (24), 173 (64), 91 (100), 73 (20), 57 (18).

Tricyclic methyl α-methylcarboxylates 28a and 28b: Ester **27** (500 mg, 726 μmol) was dissolved in THF (10 mL), cooled to −40°C and a KHMDS solution (2.94 mL, 0.5 M in toluene, 1.45 mmol) was added. After 1 h of deprotonation, during which the reaction mixture was warmed to −20°C, the temperature was adjusted to −78°C and methyl iodide (452 μL, 7.26 mmol) was added and the solution was stirred for additional 3.5 h at −78°C. The reaction was quenched by addition of saturated aqueous NH_4Cl solution (40 mL). The cooling bath was removed and stirring was continued at ambient temperature for 30 min. Additional H_2O (20 mL) was added and the resulting mixture was extracted with Et_2O (3×30 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (60 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/ethyl acetate 20:1) to yield tricyclic ester **28b** (281 mg, 407 μmol, 56%) and tricyclic ester **28a** (70.3 mg, 102 μmol, 14%) both as colorless liquids. **28a**: R_f = 0.60 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.05 (s, 3H), 0.08 (s, 3H), 0.91 (s, 9H), 1.01–1.06 (m, 21H), 1.27 (s, 3H), 1.25–1.33 (m, 1H), 2.23 (ddd, ^3J = 9.8, 9.5, 4.4 Hz, 1H), 2.33 (dd, ^2J = 12.2, ^3J = 9.7 Hz, 1H), 2.83 (ddd, ^3J = 8.8, 6.8, 2.3 Hz, 1H), 3.08 (ddd, ^3J = 9.7, 4.3, 2.3 Hz, 1H), 3.48 (d, ^2J = 9.6 Hz, 1H), 3.64 (s, 3H), 3.69 (dd, ^3J = 8.8, 8.2 Hz, 1H), 3.84 (d, ^2J = 9.6 Hz, 1H), 3.94 (dd, ^3J = 9.8, 8.2 Hz, 1H), 4.57 (d, ^2J = 12.1 Hz, 1H), 4.65 (d, ^2J = 12.1 Hz, 1H), 4.74–4.80 (m, 3H), 5.12 (dd, ^2J = 2.1, ^3J = 10.0 Hz, 1H), 5.15 (dd, ^2J = 2.1, ^3J = 17.0 Hz, 1H), 5.89 (ddd, ^3J = 17.0, 10.0, 9.5 Hz, 1H), 7.27–7.39 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = −5.4 (q), −5.2 (q), 13.0 (d), 18.3 (q), 18.4 (q), 18.5 (s), 21.3 (q), 26.0 (q), 32.9 (t), 38.5 (d), 48.4 (s), 51.1 (d/q), 51.6 (d/q), 53.4 (d/q), 64.6 (t), 70.1 (t), 78.6 (d), 84.9 (d), 88.5 (d), 92.7 (s), 96.0 (t), 118.5 (t), 127.8 (d), 127.9 (d), 128.6 (d), 136.0 (d), 137.9 (s), 176.0 ppm (s); IR (ATR): $\tilde{\nu}$ = 3069 (w), 2929 (vs), 2896 (s), 2864 (vs), 1736 (vs), 1463 (m), 1254 (m), 1146 (s), 1095 (s), 1057 (vs), 837 (s), 777 (m), 678 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 688 (6) [M^+], 615 (1), 588 (2), 493 (2), 437 (2), 423 (3), 393 (4), 303 (8), 281 (2), 253 (2), 211 (40), 191 (8), 91 (100), 73 (18), 59 cm^{-1} (5). **28b**: R_f = 0.69 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.07 (s, 3H), 0.08 (s, 3H), 0.93 (s, 9H), 1.00–1.07 (m, 21H), 1.44 (s, 3H), 1.71 (dd, ^2J = 12.2, ^3J = 9.8 Hz, 1H), 2.23 (ddd, ^3J = 9.5, 9.2, 4.4 Hz, 1H), 2.33 (dd, ^2J = 12.2, ^3J = 6.0 Hz, 1H), 2.74 (dd, ^3J = 9.4, 6.1 Hz, 1H), 3.14 (dd, ^3J = 9.8, 6.0 Hz, 1H), 3.60 (d, ^2J = 10.5 Hz, 1H), 3.64 (s, 3H), 3.73 (dd, ^3J = 9.4, 7.4 Hz, 1H), 3.78 (d, ^2J = 10.5 Hz, 1H), 4.04 (dd, ^3J = 9.5, 7.4 Hz, 1H), 4.57 (d, ^2J = 12.0 Hz, 1H), 4.62 (dd, ^3J = 6.1, 4.4 Hz, 1H), 4.68 (d, ^2J = 12.0 Hz, 1H), 4.77 (d, ^2J = 6.6 Hz, 1H), 4.79 (d, ^2J = 6.6 Hz, 1H), 5.07 (dd, ^2J = 2.1, ^3J = 10.1 Hz, 1H), 5.12 (dd, ^2J = 2.1, ^3J = 17.3 Hz, 1H), 5.89 (ddd, ^3J = 17.3, 10.1, 9.2 Hz, 1H), 7.26–7.39 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = −5.5 (q), −5.3 (q), 13.1 (d), 18.3 (s), 18.3 (q), 18.4 (q), 20.5 (q), 25.9 (q), 31.8 (t), 37.0 (d), 49.8 (s), 50.1 (d/q), 51.7 (d/q), 53.3 (d/q), 64.3 (t), 70.4 (t), 80.5 (d), 85.5 (d), 88.5 (d), 92.5 (s), 96.4 (t), 117.9 (t), 127.7 (d), 127.8 (d), 128.6 (d), 136.4 (d), 138.0 (s), 175.6 ppm (s); IR (ATR): $\tilde{\nu}$ = 3079 (w), 2948 (vs), 2932 (vs), 2896 (m), 2866 (s), 1730 (vs), 1463 (m), 1256 (s), 1155 (s), 1115 (m), 1057 (vs), 1024 (m), 837 (s), 781 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 688 (4) [M^+], 645 (4), 588 (2), 451 (1), 437 (1), 423 (2), 331 (4), 281 (10), 253 (10), 207 (100), 191 (10), 91 (80), 73 (20), 59 (5); HRMS (EI): *m/z*: calcd for $C_{38}H_{64}O_7Si_2$ [M^+]: 688.4191; found: 688.4195.

Primary alcohols 29a/29b: Ester **28a/28b** (689 mg, 1.00 mmol) was dissolved in THF (25 mL) and cooled to −78°C. Dibal-H (2.50 mL, 1 M in heptane, 2.50 mmol) was slowly added and the reaction mixture was stirred for 2 h at −78°C. Additional Dibal-H (1.00 mL, 1 M in heptane, 1.00 mmol) was added and stirring was continued for two hours at −78°C. The reaction was carefully quenched by addition of ethyl acetate (5 mL). The reaction mixture was warmed to RT and an aqueous 20% K/Na-tartrate solution (70 mL) as well as Et_2O (50 mL) were added. The resulting suspension was stirred for 1 h at ambient temperature. The layers were separated and the aqueous layer was extracted with Et_2O (2×50 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/ethyl acetate 12:1→6:1) to yield alcohol **29a/29b** as colorless liquids (536 mg, 0.81 mmol, 81%). **29a**: R_f = 0.18 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.13 (s, 3H), 0.15 (s, 3H), 0.92 (s, 9H), 1.01–1.08 (m, 21H), 1.10 (s, 3H), 1.16 (dd, ^2J = 12.3, ^3J = 6.1 Hz, 1H), 1.69 (dd, ^2J = 12.3, ^3J = 9.7 Hz, 1H), 2.36 (dt, ^3J = 9.3, 4.3 Hz, 1H), 2.61 (dd, ^3J = 9.3, 5.8 Hz, 1H), 2.74 (dd, ^3J = 9.7, 6.0 Hz, 1H), 3.25 (dd, ^2J = 12.0, ^3J = 10.6 Hz, 1H), 3.66 (d, ^2J = 11.4 Hz, 1H), 3.75 (dd, ^3J = 6.6, 3.1 Hz, 1H), 3.77 (dd, ^2J = 12.0, 2.0 Hz, 1H), 3.99 (d, ^2J = 11.4 Hz, 1H), 4.09 (dd,

^3J=10.6, 2.0 Hz, 1H), 4.14 (dd, ^3J=9.3, 6.6 Hz, 1H), 4.57 (d, ^2J=11.9 Hz, 1H), 4.65 (d, ^2J=11.9 Hz, 1H), 4.72 (dd, ^3J=5.8, 4.3 Hz, 1H), 4.75 (d, ^2J=6.4 Hz, 1H), 4.79 (d, ^2J=6.4 Hz, 1H), 5.14 (dd, ^2J=2.0, ^3J=10.1 Hz, 1H), 5.20 (dd, ^2J=2.0, ^3J=17.3 Hz, 1H), 6.01 (ddd, ^3J=17.3, 10.1, 9.3 Hz, 1H), 7.26–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−5.3 (q), −4.9 (q), 13.1 (d), 18.3 (s,q), 18.4 (q), 19.5 (q), 25.9 (q), 32.8 (t), 37.4 (d), 45.2 (s), 50.8 (d), 53.8 (d), 66.6 (t), 69.6 (t), 70.5 (t), 81.3 (d), 85.8 (d), 88.5 (d), 92.3 (s), 96.4 (t), 118.1 (t), 127.6 (d), 127.9 (d), 128.6 (d), 136.6 (d), 137.9 ppm (s); IR (ATR): $\tilde{\nu}$ = 3506 (br), 3064 (w), 2928 (vs), 2900 (s), 2865 (v), 1462 (m), 1251 (m), 1142 (m), 1056 (vs), 1025 (s), 836 cm^{-1} (s). **29b**: R_f=0.28 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.10 (s, 6H), 0.92 (s, 9H), 1.01–1.10 (m, 21H), 1.23–1.30 (m, 4H), 1.63 (dd, ^2J=12.1, ^3J=9.0 Hz, 1H), 2.31 (ddd, ^3J=9.5, 9.3, 4.4 Hz, 1H), 2.61 (br, 1H), 2.64 (dd, ^3J=9.4, 5.9 Hz, 1H), 2.88 (dd, ^3J=9.0, 7.2 Hz, 1H), 3.07 (dd, ^2J=10.0, ^3J=9.5 Hz, 1H), 3.54 (d, ^2J=10.4 Hz, 1H), 3.62 (d, ^2J=10.0 Hz, 1H), 3.74 (dd, ^3J=9.4, 7.2 Hz, 1H), 3.76 (d, ^2J=10.5 Hz, 1H), 4.13 (dd, ^3J=9.3, 7.2 Hz, 1H), 4.58 (d, ^2J=12.0 Hz, 1H), 4.66 (d, ^2J=12.0 Hz, 1H), 4.71 (dd, ^3J=5.9, 4.4 Hz, 1H), 4.76 (d, ^2J=6.5 Hz, 1H), 4.81 (d, ^2J=6.5 Hz, 1H), 5.11 (dd, ^2J=2.0, ^3J=10.0 Hz, 1H), 5.17 (dd, ^2J=2.0, ^3J=17.3 Hz, 1H), 5.98 (ddd, ^3J=17.3, 10.0, 9.5 Hz, 1H), 7.28–7.39 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−5.4 (q), −5.3 (q), 13.1 (d), 18.3 (q), 18.3 (s), 18.4 (q), 21.7 (q), 26.0 (q), 32.3 (t), 36.4 (d), 44.2 (s), 50.5 (d), 53.9 (d), 64.6 (t), 67.5 (t), 70.5 (t), 81.1 (d), 85.8 (d), 88.6 (d), 93.2 (s), 96.4 (t), 118.1 (t), 127.6 (d), 127.9 (d), 128.6 (d), 136.5 (d), 137.9 ppm (s); IR (ATR): $\tilde{\nu}$ = 3394 (br), 3074 (w), 2929 (vs), 2895 (s), 2866 (vs), 1724 (m), 1460 (m), 1260 (m), 1155 (m), 1055 (vs), 1023 (vs), 837 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 660 (2) [M^+], 617 (2), 588 (2), 497 (5), 411 (6), 383 (14), 311 (6), 265 (16), 213 (22), 211 (100), 159 (12), 131 (22), 91 (32), 75 (33), 59 (10).

Tetrahydrofuran 30: Alcohol **29a** (100 mg, 151 μmol) was dissolved in dichloromethane (6 mL) and cooled down to 0°C. Stepwise triethylamine (83.9 μL, 61.0 mg, 604 μmol) and methanesulfonic acid chloride (23.2 μL, 34.4 mg, 301 μmol) were added and the reaction mixture was stirred for 4 h. The reaction was quenched by the addition of H_2O (10 mL). Then saturated aqueous NH_4Cl solution (30 mL) was added and the layers separated. The aqueous layer was extracted with dichloromethane (2× 30 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (50 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/ethyl acetate 15:1) to yield tetracycle **30** (65.2 mg, 119 μmol, 79%) as a colorless liquid. R_f=0.61 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =1.01–1.06 (m, 21H), 1.07 (s, 3H), 1.37 (dd, ^2J=12.3, ^3J=4.7 Hz, 1H), 2.02 (dd, ^2J=12.3, ^3J=8.9 Hz, 1H), 2.29 (ddd, ^3J=9.5, 9.2, 5.3 Hz, 1H), 2.82 (ddd, ^3J=8.4, 7.0, 2.2 Hz, 1H), 2.94 (ddd, ^3J=8.9, 4.7, 2.2 Hz, 1H), 3.39 (d, ^2J=9.3 Hz, 1H), 3.56 (d, ^2J=9.1 Hz, 1H), 3.71 (dd, ^3J=8.4, 8.0 Hz, 1H), 3.78 (d, ^2J=9.7 Hz, 1H), 3.81 (d, ^2J=9.7 Hz, 1H), 3.93 (dd, ^3J=9.2, 8.0 Hz, 1H), 4.56 (d, ^2J=12.0 Hz, 1H), 4.64 (d, ^2J=12.0 Hz, 1H), 4.76 (d, ^2J=6.9 Hz, 1H), 4.79 (d, ^2J=6.9 Hz, 1H), 4.80 (dd, ^3J=7.0, 5.3 Hz, 1H), 5.15 (dd, ^2J=2.3, ^3J=10.0 Hz, 1H), 5.18 (dd, ^2J=2.3, ^3J=16.8 Hz, 1H), 5.89 (ddd, ^3J=16.8, 10.0, 9.5 Hz, 1H), 7.26–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =12.9 (d), 17.9 (q), 18.3 (q), 18.3 (q), 35.0 (t), 39.9 (d), 44.5 (s), 51.9 (d), 53.4 (d), 70.1 (t), 72.2 (t), 78.3 (d), 80.5 (t), 84.7 (d), 87.9 (d), 94.9 (s), 95.7 (t), 118.4 (t), 127.7 (d), 127.8 (d), 128.6 (d), 136.1 (d), 138.0 ppm (s); IR (ATR): $\tilde{\nu}$ = 3059 (w), 2943 (vs), 2927 (vs), 2899 (s), 2865 (vs), 1463 (m), 1154 (s), 1047 (vs), 1024 (s), 998 (m), 838 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 528 (1) [M^+], 485 (1), 455 (1), 437 (1), 391 (2), 377 (4), 347 (4), 303 (12), 277 (4), 221 (4), 211 (54), 199 (4), 135 (6), 91 (100), 81 (6), 59 (4).

***gem*-Dimethylcyclobutane 32**

*Mesylation of alcohol **29b***: Alcohol **29b** (525 mg, 794 μmol) was dissolved in dichloromethane (20 mL) and cooled to 0°C. Stepwise triethylamine (332 μL, 241 mg, 2.39 mmol) and methanesulfonic acid chloride (123 μL, 182 mg, 1.59 mmol) were added and the reaction mixture was stirred for 4 h at constant temperature. The reaction was quenched by the addition of H_2O (10 mL). Saturated aqueous NH_4Cl solution (70 mL) was added and the layers separated. The aqueous layer was extracted with dichloromethane (2×70 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/ethyl acetate 10:1) to yield mesylate **31** (587 mg, 794 μmol, quant.) as a colorless liquid. R_f=0.24 (pentane/ethyl acetate 8:1) [CAM].

Readuction: Mesylate **31** (500 mg, 676 μmol) was dissolved in DMPU (12 mL) and $NaBH_4$ (255 mg, 6.76 mmol) were added. The reaction mixture was stirred for 24 h at 75°C. After cooling to RT the solution was diluted with a 1:1 mixture of pentane and Et_2O (20 mL). Stepwise and slowly H_2O (10 mL) and a saturated aqueous NH_4Cl solution (10 mL) was added until gas evolution ceased. Further H_2O (100 mL) were added and the resulting mixture was extracted with a 1:1 mixture of pentane and Et_2O (3×60 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (100 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 30:1) to yield *gem*-dimethylcyclobutane **32** (336 mg, 521 μmol, 77%) as a colorless liquid. R_f=0.91 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.06 (s, 3H), 0.07 (s, 3H), 0.91 (s, 9H), 1.00 (s, 3H), 1.03–1.06 (m, 21H), 1.19 (s, 3H), 1.23 (dd, ^2J=11.6, ^3J=6.4 Hz, 1H), 1.74 (dd, ^2J=11.6, ^3J=9.2 Hz, 1H), 2.28 (ddd, ^3J=9.7, 9.5, 4.7 Hz, 1H), 2.66 (ddd, ^3J=9.2, 6.2, 0.8 Hz, 1H), 2.85 (ddd, ^3J=9.2, 6.4, 0.8 Hz, 1H), 3.63 (d, ^2J=10.5 Hz, 1H), 3.72 (dd, ^3J=9.2, 7.5 Hz, 1H), 3.80 (d, ^2J=10.5 Hz, 1H), 4.10 (dd, ^3J=9.5, 7.5 Hz, 1H), 4.57 (d, ^2J=11.9 Hz, 1H), 4.66 (d, ^2J=11.9 Hz, 1H), 4.71 (dd, ^3J=6.2, 4.7 Hz, 1H), 4.76 (d, ^2J=6.5 Hz, 1H), 4.78 (d, ^2J=6.5 Hz, 1H), 5.13 (dd, ^2J=2.0, ^3J=10.0 Hz, 1H), 5.18 (dd, ^2J=2.0, ^3J=17.2 Hz, 1H), 5.91 (ddd, ^3J=17.2, 10.0, 9.7 Hz, 1H), 7.27–7.37 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−5.3 (q), −5.1 (q), 13.1 (d), 18.4 (q), 18.4 (s), 18.4 (q), 24.9 (q), 26.1 (q), 26.2 (q), 36.8 (d), 37.7 (t), 39.6 (s), 50.8 (d), 53.9 (d), 65.6 (t), 70.3 (t), 80.3 (d), 85.6 (d), 88.0 (d), 92.9 (s), 96.2 (t), 118.0 (t), 127.8 (d), 127.8 (d), 128.6 (d), 136.8 (d), 138.0 ppm (s); IR (ATR): $\tilde{\nu}$=2928 (m), 2865 (m), 1463 (m), 1254 (m), 1147 (m), 1056 (s), 1026 (m), 836 (vs), 775 (m), 676 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 644 (8) [M^+], 588 (6), 551(5), 524 (16), 495 (14), 482 (24), 439 (12), 393 (4), 351 (6), 277 (14), 265 (20), 227 (100), 211 (52), 145 (44), 91 (78), 73 (49), 59 (20); HRMS (EI): *m/z*: calcd for $C_{37}H_{64}O_5Si_2$ [M^+]: 644.4293; found: 644.4284.

Silyl ether 33: Dimethylcyclobutane **32** (128 mg, 198 μmol) was dissolved in DMF (4 mL) and H_2O was added dropwise until a slight precipitation could be observed (ca. 250 μL). In an atmosphere of oxygen, $PdCl_2$ (17.6 mg, 99.0 μmol) and CuCl (98.0 mg, 990 μmol) were added and the solution was stirred at ambient temperature for 36 h. Additional $PdCl_2$ (17.6 mg, 99.0 μmol) was added and stirring was continued for 36 h. The reaction was quenched by the addition of a 2:1 mixture of pentane and ethyl acetate (25 mL) as well as saturated aqueous NaCl solution (25 mL). The layers were separated and the aqueous layer was extracted with a 2:1 mixture of pentane and ethyl acetate (2×25 mL). The organic layers were combined and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 30:1) to yield silyl ether **33** (123 mg, 186 μmol, 94%) as a colorless liquid. R_f=0.86 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.03 (s, 3H), 0.06 (s, 3H), 0.88 (s, 9H), 0.97 (s, 3H), 0.99–1.15 (m, 21H), 1.19 (s, 3H), 1.23 (dd, ^2J=11.6, ^3J=5.6 Hz, 1H), 1.75 (dd, ^2J=11.6, ^3J=9.1 Hz, 1H), 2.23 (s, 3H), 2.76–2.84 (m, 3H), 3.53 (d, ^2J=10.5 Hz, 1H), 3.68 (d, ^2J=10.5 Hz, 1H), 3.75 (dd, ^3J=8.6, 7.5 Hz, 1H), 4.53 (dd, ^3J=8.6, 7.3 Hz, 1H), 4.57 (d, ^2J=11.9 Hz, 1H), 4.64 (d, ^2J=11.9 Hz, 1H), 4.75 (d, ^2J=6.8 Hz, 1H), 4.78 (d, ^2J=6.8 Hz, 1H), 5.09 (dd, ^3J=6.2, 6.2 Hz, 1H), 7.27–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =−5.6 (q), −5.4 (q), 12.8 (d), 18.3 (s), 18.4 (q), 18.4 (q), 25.0 (q), 25.9 (q), 26.0 (q), 29.9 (q), 36.9 (d), 37.7 (t), 39.7 (s), 52.4 (d), 62.1 (d), 65.0 (t), 70.1 (t), 75.7 (d), 84.7 (d), 85.0 (d), 93.8 (s), 95.7 (t), 127.8 (d), 127.8 (d), 128.6 (d), 138.0 (s), 203.8 ppm (s); IR (ATR): $\tilde{\nu}$=3030 (w), 2928 (vs), 2890 (s), 2864 (vs), 1719 (s), 1458 (m), 1252 (m), 1150 (m), 1057 (s), 1027 (m), 836 (s), 777 (m), 681 cm^{-1} (w); MS (EI, 70 eV): *m/z* (%): 660 (8) [M^+], 617 (34), 603 (12), 561 (32), 511 (22), 453 (26), 423 (8), 347 (16), 263 (66), 201 (28), 149 (60), 91 (100), 73 (32), 43 (30). HRMS (EI): *m/z*: calcd for $C_{34}H_{57}O_6Si_2$ [$M-C_3H_7^+$]: 617.3694; found: 617.3706.

Primary ketoalcohol 34: Silyl ether **33** (156 mg, 236 μmol) was dissolved in dichloromethane/methanol 10:1 (8 mL) and camphor sulfonic acid (27.4 mg, 118 μmol) was added. The reaction mixture was stirred for 18 h at ambient temperature. The reaction was quenched by the addition of imidazole (8.44 mg, 124 μmol). Then a 1:1 mixture of pentane and Et_2O (60 mL) were added, the suspension was filtrated and the solvent removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate 15:1→10:1) to yield alcohol **34** (109 mg, 200 μmol, 85%) as a colorless solid together with unreacted starting material **33** (11.1 mg, 16.8 μmol). R_f=0.24 (pentane/ethyl acetate 8:1) [CAM]; m.p. 72°C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.95 (s, 3H), 0.98–1.08 (m, 21H), 1.26 (s, 3H), 1.29 (dd, ^2J=12.0, ^3J=3.4 Hz, 1H), 1.84 (dd, ^2J=12.0, ^3J=9.0 Hz, 1H), 2.28 (s, 3H), 2.95 (dd, ^3J=10.0, 6.6 Hz, 1H), 2.98–3.05 (m, 2H), 3.62–3.76 (m, 3H), 4.55 (d, ^2J=12.3 Hz, 1H), 4.63 (d, ^2J=12.3 Hz, 1H), 4.74 (dd, ^3J=10.2, 9.1 Hz, 1H), 4.77 (s, 2H), 5.01 (t, ^3J=6.8 Hz, 1H), 7.25–7.39 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =12.9 (d), 18.5 (q), 24.7 (q), 25.3 (q), 31.8 (q), 37.5 (d), 37.8 (t), 40.1 (s), 54.6 (d), 61.9 (d), 63.2 (t), 70.2 (t), 74.5 (d), 83.8 (d), 84.9 (d), 94.4 (s), 96.0 (t), 128.0 (d), 128.1 (d), 128.8 (d), 138.2 (s), 207.8 ppm (s); IR (ATR): $\tilde{\nu}$=3360 (w), 2941 (m), 2893 (w), 2863 (m), 1707 (s), 1458 (m), 1228 (m), 1136 (vs), 1077 (s), 1046 (m), 884 (s), 837 (s), 671 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 426 (1) [$M-C_8H_8O^+$], 383 (96), 328 (100), 309 (6), 263 (74), 229 (46), 199 (12), 173 (10), 131 (29), 103 (26), 91 (20), 75 (32), 43 (30).

Iodide 3: Triphenylphosphane (64.8 mg, 247 μmol) was dissolved in benzene (1.5 mL) together with iodine (62.7 mg, 247 μmol) and the mixture was stirred for 30 min at RT. To this solution. alcohol **34** (27.0 mg, 49.4 μmol), dissolved in pyridine (900 μL), was added and the resulting mixture was stirred for 20 h at ambient temperature. The reaction was quenched by the addition of a saturated aqueous Na_2SO_3 solution (10 mL). Further H_2O (10 mL) was added and the resulting mixture was extracted with Et_2O (3×15 mL). The organic layers were combined and sequentially washed with aqueous 0.2 N $KHSO_4$ solution (25 mL), saturated aqueous NaCl solution (25 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/ethyl acetate 30:1) to yield iodide **3** (25.4 mg, 38.7 μmol, 78%) as a colorless solid. R_f=0.80 (pentane/ethyl acetate 8:1) [CAM]; m.p. 58°C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.99–1.06 (m, 24H), 1.20 (s, 3H), 1.28 (dd, ^2J=11.8, ^3J=6.6 Hz, 1H), 1.84 (dd, ^2J=11.8, ^3J=9.3 Hz, 1H), 2.33 (s, 3H), 2.81 (ddd, ^3J=9.3, 6.6, 0.2 Hz, 1H), 2.89–2.95 (m, 2H), 3.33 (s, 2H), 3.76 (dd, ^3J=8.0, 6.0 Hz, 1H), 4.59 (d, ^2J=11.9 Hz, 1H), 4.64 (d, ^2J=11.9 Hz, 1H), 4.68 (dd, ^3J=6.2, 6.0 Hz, 1H), 4.77 (d, ^2J=6.8 Hz, 1H), 4.81 (d, ^2J=6.8 Hz, 1H), 5.18 (dd, ^3J=6.7, 6.7 Hz, 1H), 7.26–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =8.8 (t), 12.6 (d), 18.3 (q), 18.3 (q), 23.8 (q), 24.8 (q), 30.4 (q), 38.3 (t), 40.3 (s), 40.4 (d), 54.5 (d), 63.3 (d), 70.3 (t), 76.5 (d), 84.0 (d), 85.1 (d), 91.6 (s), 95.4 (t), 127.8 (d), 127.9 (d), 128.6 (d), 137.9 (s), 204.0 ppm (s); IR (ATR): $\tilde{\nu}$=3024 (w), 2945 (m), 2895 (w), 2861 (m), 1721 (m), 1460 (m), 1157 (m), 1044 (vs), 1018 (vs), 833 (m), 748 (m), 682 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 613 (40) [$M-C_3H_7^+$], 557 (24), 475 (14), 449 (4), 365 (6), 347 (4), 294 (32), 183 (24), 173 (18), 149 (12), 91 (100), 81 (28), 59 (42). HRMS (EI): *m/z*: calcd for $C_{28}H_{42}IO_5Si$ [$M-C_3H_7^+$]: 613.1846; found: 613.1837.

Primary alkenol 36: Silyl ether **33** (77.5 mg, 120 μmol) was dissolved in MeOH (4 mL), one drop of concentrated HCl was added and the reaction mixture was stirred for 2 h at ambient temperature. The reaction was neutralized by the addition of saturated aqueous $NaHCO_3$ to pH 7–8, further diluted with H_2O (20 mL) and extracted with Et_2O (3×25 mL). The organic layers were combined, washed with saturated aqueous NaCl solution (50 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/ethyl acetate 11:1) to yield alcohol **36** (51.6 mg, 97.2 μmol, 81%) as a colorless liquid. R_f=0.50 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =1.00 (s, 3H), 1.02–1.08 (m, 21H), 1.10 (s, 3H), 1.28 (dd, ^2J=11.8, ^3J=6.1 Hz, 1H), 1.77 (dd, ^2J=11.8, ^3J=9.3 Hz, 1H), 2.12 (br, 1H), 2.40 (ddd, ^3J=9.2, 9.0, 4.9 Hz, 1H), 2.71 (ddd, ^3J=9.0, 6.2, 0.6 Hz, 1H), 2.86 (ddd, ^3J=9.3, 6.1, 0.6 Hz, 1H), 3.71 (d, ^2J=11.5 Hz, 1H), 3.79 (d, ^2J=11.5 Hz, 1H), 3.79 (dd, ^3J=9.0, 6.7 Hz, 1H), 4.33 (dd, ^3J=9.0, 6.7 Hz, 1H), 4.58 (d, ^2J=11.8 Hz, 1H), 4.66 (d, ^2J=11.8 Hz, 1H), 4.75 (dd, ^3J=6.2, 4.9 Hz, 1H), 4.78 (d, ^2J=6.6 Hz, 1H), 4.81 (d, ^2J=6.6 Hz, 1H), 5.17 (dd, ^2J=2.0, ^3J=10.2 Hz, 1H), 5.21 (dd, ^2J=2.0, ^3J=17.3 Hz, 1H), 6.03 (ddd, ^3J=17.3, 10.2, 9.2 Hz, 1H), 7.26–7.39 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =13.0 (d), 18.3 (q), 18.3 (q), 24.3 (q), 26.2 (q), 36.8 (d), 37.3 (t), 39.4 (s), 51.5 (d), 54.0 (d), 64.2 (t), 70.5 (t), 80.6 (d), 85.8 (d), 88.0 (d), 93.0 (s), 96.2 (t), 118.0 (t), 127.7 (d), 127.9 (d), 128.6 (d), 136.5 (d), 137.9 ppm (s); IR (ATR): $\tilde{\nu}$=3476 (br), 3064 (w), 2927 (m), 2865 (m), 1463 (m), 1381 (m), 1141 (s), 1054 (vs), 1025 (s), 883 (m), 837 (m), 682 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 530 (1) [M^+], 487 (3), 457 (2), 431 (8), 379 (7), 349 (6), 294 (100), 211 (38), 183 (68), 139 (14), 91 (54), 57 (14), 43 (10); HRMS (EI): *m/z*: calcd for $C_{28}H_{43}O_5Si$ [$M-C_3H_7^+$]: 487.2880; found: 487.2880.

Primary alkenyl iodide 37: Triphenylphosphane (39.3 mg, 150 μmol) was dissolved in benzene (1 mL) together with iodine (38.1 mg, 150 μmol) and stirred for 30 min at ambient temperature. To this solution alcohol **36** (15.9 mg, 30.0 μmol), dissolved in pyridine (600 μL), was added and the resulting mixture was stirred for 20 h at ambient temperature. The reaction was quenched by the addition of a saturated aqueous Na_2SO_3 solution (10 mL). Further H_2O (10 mL) was added and the resulting mixture was extracted with Et_2O (3×15 mL). The organic layers were combined and sequentially washed with an aqueous 0.2 N $KHSO_4$ solution (20 mL), a saturated aqueous NaCl solution (20 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 25:1) to yield iodide **37** (16.0 mg, 24.9 μmol, 83%) as a colorless liquid. R_f=0.88 (pentane/ethyl acetate 8:1) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): δ =1.04–1.07 (m, 21H), 1.05 (s, 3H), 1.19 (s, 3H), 1.25 (dd, ^2J=11.5, ^3J=7.2 Hz, 1H), 1.67 (dd, ^2J=11.5, ^3J=9.3 Hz, 1H), 2.33 (ddd, ^3J=9.6, 9.2, 4.2 Hz, 1H), 2.73 (dd, ^3J=9.3, 5.9 Hz, 1H), 2.92 (dd, ^3J=9.3, 7.2 Hz, 1H), 3.27 (d, ^2J=10.2 Hz, 1H), 3.43 (d, ^2J=10.2 Hz, 1H), 3.76 (dd, ^3J=9.3, 7.0 Hz, 1H), 4.17 (dd, ^3J=9.2, 7.0 Hz, 1H), 4.58 (d, ^2J=11.9 Hz, 1H), 4.66 (d, ^2J=11.9 Hz, 1H), 4.70 (dd, ^3J=5.9, 4.2 Hz, 1H), 4.77 (d, ^2J=6.4 Hz, 1H), 4.81 (d, ^2J=6.4 Hz, 1H), 5.17 (dd, ^2J=2.2, ^3J=10.1 Hz, 1H), 5.21 (dd, ^2J=2.2, ^3J=17.1 Hz, 1H), 6.09 (ddd, ^3J=17.1, 10.1, 9.6 Hz, 1H), 7.26–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =13.0 (d), 18.3 (q), 18.4 (q), 23.8 (q), 25.0 (q), 29.9 (t), 37.4 (t), 40.4 (s), 40.5 (d), 51.2 (d), 53.9 (d), 70.6 (t), 81.1 (d), 85.3 (d), 87.8 (d), 90.1 (s), 96.4 (t), 118.2 (t), 127.7 (d), 127.9 (d), 128.6 (d), 136.9 (d), 137.9 ppm (s). IR (ATR): $\tilde{\nu}$=2934 (m), 2865 (m), 1457 (m), 1381 (w), 1264 (w), 1140 (s), 1051 (vs), 1019 (s), 882 (m), 837 (m), 736 (s), 682 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 640 (1) [M^+], 597 (2), 547 (4), 541 (4), 491 (3), 457 (10), 411 (8), 379 (8), 349 (32), 277 (88), 227 (22), 201 (40), 167 (26), 149 (56), 91 (100), 57 (24); HRMS (EI): *m/z*: calcd for $C_{28}H_{42}IO_4Si$ [$M-C_3H_7^+$]: 597.1897; found: 597.1873.

Aldehyde 38: Alcohol **34** (160 mg, 293 μmol) was dissolved in dichloromethane (15 mL) and Dess–Martin periodinane (186 mg, 439 μmol) was added. After stirring for 30 min at ambient temperature, the reaction was quenched by the addition of a saturated aqueous $Na_2S_2O_3$ solution (10 mL) and a saturated aqueous $NaHCO_3$ solution (10 mL). Et_2O (20 mL) was added and the layers were separated. The aqueous layer was extracted with Et_2O (2×30 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (30 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure to yield aldehyde **38** (160 mg, 293 μmol, quant.) as a colorless solid. R_f=0.69 (pentane/ethyl acetate 8:1) [CAM]; m.p. 67°C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.95–1.03 (m, 21H), 1.04 (s, 3H), 1.06 (s, 3H), 1.39 (dd, ^2J=11.8, ^3J=7.7 Hz, 1H), 1.81 (dd, ^2J=11.8, ^3J=8.8 Hz, 1H), 2.32 (s, 3H), 2.85 (dd, ^3J=6.8, 6.6 Hz, 1H), 3.05 (dd, ^3J=6.7, 4.9 Hz, 1H), 3.21 (dd, ^3J=8.8, 7.7 Hz, 1H), 3.75 (dd, ^3J=6.8, 4.9 Hz, 1H), 4.55–4.61 (m, 3H), 4.62 (d, ^2J=7.0 Hz, 1H), 4.73 (d, ^2J=7.0 Hz, 1H), 5.30 (dd, ^3J=6.7, 6.6 Hz, 1H), 7.26–7.38 (m, 5H), 9.38 ppm (s, 1H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =12.4 (d), 18.1 (q), 24.2 (q), 25.2 (q), 30.6 (q), 36.6 (d), 37.0 (t), 41.2 (s), 52.9 (d), 64.5 (d), 69.9 (t), 75.9 (d), 84.2 (d), 85.9 (d), 94.6 (t), 97.7 (s), 127.7 (d), 127.9 (d), 128.5 (d), 138.2 (s), 202.1 (d), 203.6 ppm (s); IR (ATR): $\tilde{\nu}$=3031 (w), 2941 (vs), 2895 (m), 2864 (s), 1709 (vs), 1463 (m), 1224 (m), 1160 (s), 1121 (s), 1069 (vs), 1058 (vs), 1028 (s), 882 (m), 844 (m), 735 (m), 679 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 544 (6) [M^+], 501 (36), 471 (4), 393 (8), 363 (26), 279 (8), 256 (20), 201 (10), 149 (28),

91 (100), 57 (18), 43 (22); HRMS (EI): *m/z*: calcd for $C_{31}H_{48}O_6Si$ [M^+]: 544.3220; found: 544.3221.

Oxepane 39: Aldehyde **38** (55.0 mg, 101 μmol) was dissolved in THF (10 mL). The mixture was cooled to −78 °C and a KHMDS solution was added (242 μL, 0.5 M in toluene, 121 μmol). After 25 min of deprotonation at −78 °C the reaction mixture was quickly warmed to −40 °C and stirred at this temperature for 15 min. The reaction was quenched by the addition of a saturated aqueous NH_4Cl solution (5 mL). Et_2O (30 mL) was added and the mixture was warmed to RT. After adding H_2O (30 mL) the layers were separated and the aqueous layer was extracted with Et_2O (2×25 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (40 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 9:1) to yield oxepane **39** (30.8 mg, 56.6 μmol, 56 %) as a colorless solid. R_f=0.18 (pentane/ethyl acetate 8:1) [CAM]; m.p. 88 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.98–1.03 (m, 21H), 1.04 (s, 3H), 1.22 (s, 3H), 1.45 (dd, ^2J=11.7, ^3J=6.4 Hz, 1H), 1.96 (dd, ^2J=11.7, ^3J=9.3 Hz, 1H), 1.98–2.04 (m, 1H), 2.48 (ddd, ^2J=12.6, ^3J=3.8, ^4J=1.9 Hz, 1H), 2.81 (ddd, ^3J=9.3, 6.4, 2.9 Hz, 1H), 3.05–3.13 (m, 2H), 3.26 (dd, ^2J=12.6, ^3J= 4.1 Hz, 1H), 4.03 (dd, ^3J=7.5, 4.9 Hz, 1H), 4.08–4.14 (m, 1H), 4.51 (dd, ^3J=4.9, 4.7 Hz, 1H), 4.57 (d, ^2J=12.1 Hz, 1H), 4.61 (d, ^2J=12.1 Hz, 1H), 4.77 (d, ^2J=6.9 Hz, 1H), 4.82 (d, ^2J=6.9 Hz, 1H), 5.13 (dd, ^3J=9.6, 7.3 Hz, 1H), 7.29–7.40 ppm (m, 5H); ^{13}C NMR: (90.6 MHz, $CDCl_3$): δ =12.3 (d), 18.1 (q), 18.1 (q), 24.1 (q), 26.4 (q), 35.4 (d), 37.3 (s), 40.2 (t), 45.1 (t), 56.7 (d), 66.9 (d), 68.6 (d), 70.1 (t), 81.2 (d), 83.9 (d), 86.0 (d), 95.3 (t), 96.1 (s), 127.8 (d), 128.0 (d), 128.6 (d), 137.6 (s), 206.8 ppm (s); IR (ATR): $\tilde{\nu}$=3444 (br), 2938 (vs), 2864 (s), 1678 (s), 1458 (m), 1289 (m), 1165 (m), 1118 (m), 1062 (s), 1026 (vs), 995 (m), 881 (m), 799 (m), 736 (m), 686 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 544 (1) [M^+], 501 (24), 471 (8), 453 (5), 393 (4), 363 (16), 329 (6), 237 (4), 201 (6), 149 (6), 91 (100), 57 (8), 43 (10); HRMS (EI): *m/z*: calcd for $C_{28}H_{41}O_6Si$ [$M-C_3H_7^+$]: 501.2672; found: 501.2667.

Enone 40: Oxepane **39** (79.0 mg, 145 μmol) was dissolved in dichloromethane (12 mL). Thiocarbonyldiimidazole (64.6 mg, 363 μmol) and DMAP (21.2 mg, 174 μmol) were added and the reaction mixture was stirred at ambient temperature for 16 h. The solvent was removed under reduced pressure at slightly elevated temperature (~40 °C) and kept at this temperature for 15 min. The resulting crude product was purified by flash chromatography (pentane/ethyl acetate 10:1) to yield enone **40** (76.8 mg, 145 μmol, quant.) as a colorless solid. R_f=0.64 (pentane/ethyl acetate 8:1) [CAM]; m.p. 55 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.99–1.05 (m, 24H), 1.29 (s, 3H), 1.60 (dd, ^2J=11.3, ^3J=7.6 Hz, 1H), 1.94 (dd, ^2J=11.3, ^3J=8.9 Hz, 1H), 2.90–2.97 (m, 2H), 3.12 (ddd, ^3J=9.3, 8.2, 1.3 Hz, 1H), 3.71 (dd, ^3J=8.3, 6.1 Hz, 1H), 4.25 (dd, ^3J=8.3, 8.2 Hz, 1H), 4.50 (d, ^2J= 11.8 Hz, 1H), 4.61 (d, ^2J=11.8 Hz, 1H), 4.75 (s, 2H), 4.96 (dd, ^3J=9.3, 6.1 Hz, 1H), 5.93 (dd, ^3J=11.7, ^4J=1.3 Hz, 1H), 6.85 (d, ^3J=11.7 Hz, 1H), 7.26–7.39 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =12.7 (d), 18.1 (q), 18.2 (q), 22.9 (q), 26.9 (q), 38.4 (s), 40.7 (t), 41.3 (d), 53.7 (d), 66.5 (d), 69.9 (t), 80.2 (d), 82.1 (d), 83.2 (d), 93.2 (s), 95.8 (t), 127.7 (d), 128.0 (d), 128.6 (d), 130.5 (d), 137.7 (s), 144.6 (d), 201.0 ppm (s); IR (ATR): $\tilde{\nu}$=3055 (w), 2943 (s), 2890 (m), 2866 (s), 1671 (s), 1466 (m), 1145 (s), 1111 (m), 1068 (s), 1041 (vs), 999 (m), 826 (s), 749 (m), 672 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 483 (56) [$M-C_3H_7^+$], 453 (14), 377 (2), 329 (4), 279 (6), 221 (4), 167 (10), 149 (20), 91 (100), 71 (10), 57 (12), 43 (10). HRMS (EI): *m/z*: calcd for $C_{28}H_{39}O_5Si$ [$M-C_3H_7$)]: 483.2567; found: 483.2561.

Saturated ketone 2: Enone **40** (24.1 mg, 45.7 μmol) was dissolved in dichloromethane (5 mL) under an atmosphere of hydrogen and charged with the Crabtree catalyst [Ir(cod)py(PCy_3)$_2$]PF_6 (3.68 mg; 4.57 μmol). After 1.5 h the reaction mixture was filtered through Celite and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/Et_2O 9:1) to yield ketone **2** (22.7 mg, 42.9 μmol, 94 %) as a colorless solid. R_f=0.79 (pentane/ethyl acetate 8:1) [CAM]; m.p. 53 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.98 (s, 3H), 1.01–1.04 (m, 21H), 1.07 (s, 3H), 1.54 (dd, ^2J=11.1, ^3J=6.9 Hz, 1H), 1.80–1.92 (m, 2H), 1.92 (dd, ^2J=11.1, ^3J=9.2 Hz, 1H), 2.54 (dddd, ^2J=12.8, ^3J=7.5, 6.7, ^4J=0.9 Hz, 1H), 2.65 (ddd, ^2J=12.8, ^3J=7.4, 5.7 Hz, 1H), 2.78 (ddd, ^3J=9.2, 6.9, 2.4 Hz, 1H), 2.88 (dd, ^3J=9.0, 3.6 Hz, 1H), 2.96 (ddd, ^3J=7.5, 7.3, 2.4 Hz, 1H), 3.94 (dd, ^3J=7.3, 3.7 Hz, 1H), 4.59 (s, 2H), 4.69 (d, ^2J=6.8 Hz, 1H), 4.72 (dd, ^3J=3.7, 3.6 Hz, 1H), 4.77 (d, ^2J=6.8 Hz, 1H), 5.18 (dd, ^3J=9.0, 7.5 Hz, 1H), 7.27–7.37 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ = 12.3 (d), 18.1 (q), 18.1 (q), 22.7 (q), 25.9 (q), 27.9 (t), 37.7 (s), 38.3 (t), 39.5 (d), 40.2 (t), 55.4 (d), 63.5 (d), 70.0 (t), 79.6 (d), 84.0 (d), 85.3 (d), 93.7 (s), 94.6 (t), 127.8 (d), 128.6 (d), 137.9 (s), 209.4 ppm (s); IR (ATR): $\tilde{\nu}$=2941 (vs), 2927 (vs), 2895 (m), 2865 (s), 1698 (s), 1463 (m), 1145 (s), 1110 (m), 1042 (vs), 1029 (s), 882 (s), 680 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 485 (54) [$M-C_3H_7^+$], 455 (6), 379 (2), 329 (14), 321 (8), 281 (16), 221 (6), 205 (8), 149 (10), 126 (14), 91 (100), 72 (50), 59 (96), 43 (28); HRMS (EI): *m/z*: calcd for $C_{28}H_{41}O_5Si$ [$M-C_3H_7^+$]: 485.2723; found: 485.2718.

Tertiary alcohol 41: Ketone **2** (24.5 mg, 46.3 μmol) was dissolved in Et_2O (5 mL). Methylmagnesium chloride (41.3 μL, 2.8 M in THF, 116 μmol) was added and the reaction mixture was stirred for 16 h at RT. The reaction was quenched by the addition of saturated aqueous NH_4Cl solution (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2×10 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (40 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 15:1) to yield alcohol **41a** (21.0 mg, 38.5 μmol, 83 %) and alcohol **41b** (3.4 mg, 6.24 μmol, 13 %) both as colorless solids. **41a**: R_f=0.70 (pentane/ethyl acetate 8:1) [CAM]; m.p. 51–53 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ =0.97 (s, 3H), 1.04 (s, 3H), 1.05–1.09 (m, 21H), 1.29 (s, 3H), 1.40 (dd, ^2J=11.9, ^3J=5.8 Hz, 1H), 1.55–1.61 (m, 1H), 1.75–1.94 (m, 4H), 2.28 (dd, ^3J=9.7, 6.3 Hz, 1H), 2.59 (ddd, ^3J=9.4, 5.8, 3.7 Hz, 1H), 2.91 (ddd, ^3J=6.9, 6.8, 3.7 Hz, 1H), 3.81 (dd, ^3J=6.8, 6.6 Hz, 1H), 4.15 (dd, ^3J=6.6, 6.3 Hz, 1H), 4.30 (br, 1H), 4.54 (d, ^2J=12.1 Hz, 1H), 4.62 (d, ^2J=12.1 Hz, 1H), 4.71 (d, ^2J=6.9 Hz, 1H), 4.75 (d, ^2J=6.9 Hz, 1H), 4.93 (dd, ^3J=9.7, 6.9 Hz, 1H), 7.28–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =13.3 (d), 18.5 (q), 18.6 (q), 23.5 (q), 26.5 (q), 27.2 (t), 30.4 (q), 32.6 (t), 36.0 (d), 37.3 (s), 40.8 (t), 58.1 (d), 58.8 (d), 70.0 (t), 74.6 (s), 79.7 (d), 83.9 (d), 86.0 (d), 94.9 (s), 95.5 (t), 127.7 (d), 127.9 (d), 128.6 (d), 137.8 ppm (s); IR (ATR): $\tilde{\nu}$=3480 (br), 3031 (w), 2927 (s), 2895 (m), 2865 (s), 1464 (m), 1391 (m), 1126 (s), 1047 (vs), 1003 (m), 950 (m), 812 (m), 673 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 483 (1) [$M-C_3H_7-H_2O^+$], 471 (10), 453 (4), 393 (4), 363 (12), 303 (22), 251 (8), 225 (6), 159 (6), 131 (4), 91 (100), 75 (5), 59 (4); HRMS (EI): *m/z*: calcd for $C_{28}H_{43}O_4Si$ [$M-C_4H_8-OH^+$]: 471.2931; found: 471.2916. **41b**: R_f= 0.78 (pentane/ethyl acetate 8:1) [CAM]; m.p. 62–64 °C; ^{1}H NMR (360 MHz, $CDCl_3$): δ = 0.95 (s, 3H), 1.01 (s, 3H), 1.06–1.18 (m, 21H), 1.37 (dd, ^2J=11.8, ^3J=5.7 Hz, 1H), 1.48 (s, 3H), 1.55–1.64 (m, 1H), 1.68 (dd, ^2J=13.1, ^3J=5.6 Hz, 1H), 1.77–1.83 (m, 1H), 1.89 (dd, ^2J=11.8, ^3J= 9.4 Hz, 1H), 1.99 (ddd, ^2J=13.1, ^3J=12.7, 4.8 Hz, 1H), 2.12 (dd, ^3J=9.3, 7.2 Hz, 1H), 2.30 (br, 1H), 2.60 (ddd, ^3J=9.4, 5.7, 3.7 Hz, 1H), 2.87 (ddd, ^3J=6.9, 6.5, 3.7 Hz, 1H), 3.82 (dd, ^3J=7.1, 6.9 Hz, 1H), 4.54 (d, ^2J= 12.1 Hz, 1H), 4.54 (dd, ^3J=7.2, 7.1 Hz, 1H), 4.63 (d, ^2J=12.1 Hz, 1H), 4.72 (d, ^2J=6.8 Hz, 1H), 4.76 (dd, ^3J=9.3, 6.5 Hz, 1H), 4.76 (d, ^2J= 6.8 Hz, 1H), 7.28–7.38 ppm (m, 5H); ^{13}C NMR (90.6 MHz, $CDCl_3$): δ =13.0 (d), 18.5 (q), 18.5 (q), 23.4 (q), 26.7 (q), 27.6 (t), 28.4 (q), 34.0 (t), 35.9 (d), 37.0 (s), 41.2 (t), 58.9 (d), 59.1 (d), 69.9 (t), 75.1 (s), 78.5 (d), 80.6 (d), 84.9 (d), 94.4 (s), 95.4 (t), 127.8 (d), 127.9 (d), 128.6 (d), 137.9 ppm (s); IR (ATR): $\tilde{\nu}$=3568 (br), 3026 (w), 2941 (vs), 2927 (vs), 2893 (m), 2865 (s), 1458 (m), 1125 (s), 1050 (vs), 1028 (m), 987 (w), 882 (s), 676 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 501 (1) [$M-C_3H_7^+$], 483 (1) [$M-C_3H_7-H_2O^+$], 471 (4), 453 (2), 393 (10), 363 (6), 307 (6), 251 (2), 213 (4), 159 (4), 131 (4), 91 (100), 81 (6), 59 (4).

Succinate 43: *TIPS deprotection*: Alcohol **41a** (15.0 mg, 27.5 μmol) was dissolved in THF (2 mL) and cooled to 0 °C. TBAF (35.8 μL, 1 M in THF, 35.8 μmol) was added and the reaction mixture was stirred for 3 h at 0 °C. The reaction was quenched by the addition of a saturated aqueous NH_4Cl solution (5 mL). Additional H_2O (5 mL) and a saturated aqueous NaCl solution (5 mL) were added and the resulting solution was extracted with dichloromethane (4×15 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (30 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography

(pentane/ethyl acetate 3:2) to yield alcohol **42** (9.50 mg, 24.5 μmol, 89%) as a colorless solid. $R_f = 0.14$ (pentane/ethyl acetate 3:2) [CAM].

Esterification: Succinic acid monobenzyl ester (7.65 mg, 36.8 μmol) was dissolved in dichloromethane (1 mL) together with EDC·HCl (7.05 mg, 36.8 μmol) and stirred at RT for 10 min. Two crystals of DMAP were added and stirring was continued for 5 min. Finally alcohol **42** (9.50 mg, 24.5 μmol), dissolved in dichloromethane (1 mL), were added and the resulting mixture was stirred at RT for 4 h. The solvent was removed under reduced pressure and the residue was suspended in ethyl acetate (5 mL). After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate 3:1) to yield succinate **43** (13.5 mg, 23.3 μmol, 95%) as a colorless solid. $R_f = 0.80$ (pentane/ethyl acetate 3:2) [CAM]; ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 0.98$ (s, 3H), 1.04 (s, 3H), 1.08 (s, 3H), 1.38 (dd, $^2J = 11.8$, $^3J = 5.8$ Hz, 1H), 1.55–1.63 (m, 1H), 1.74–2.04 (m, 4H), 2.32 (dd, $^3J = 9.5$, 7.7 Hz, 1H), 2.53–2.64 (m, 4H), 2.74 (ddd, $^3J = 9.4$, 5.8, 3.6 Hz, 1H), 2.88 (ddd, $^3J = 7.0$, 6.7, 3.6 Hz, 1H), 4.02 (dd, $^3J = 7.4$, 7.0 Hz, 1H), 4.20 (br, 1H), 4.53 (s, 1H), 4.53 (s, 1H), 4.67 (d, $^2J = 7.0$ Hz, 1H), 4.71 (d, $^2J = 7.0$ Hz, 1H), 4.91 (dd, $^3J = 9.5$, 6.7 Hz, 1H), 5.08 (d, $^2J = 12.4$ Hz, 1H), 5.12 (d, $^2J = 12.4$ Hz, 1H), 5.38 (dd, $^3J = 7.7$, 7.4 Hz, 1H), 7.24–7.40 ppm (m, 10H); ^{13}C NMR (90.6 MHz, $CDCl_3$): $\delta = 23.4$ (q), 26.6 (q), 27.1 (t), 29.2 (t), 29.4 (q), 29.5 (t), 32.3 (t), 35.5 (d), 37.4 (s), 40.8 (t), 55.0 (d), 57.8 (d), 66.7 (t), 69.6 (t), 74.4 (s), 78.9 (d), 81.3 (d), 83.0 (d), 94.4 (t), 95.4 (s), 127.8 (d), 127.9 (d), 128.4 (d), 128.4 (d), 128.6 (d), 128.7 (d), 135.9 (s), 137.8 (s), 171.6 (s), 172.0 ppm (s); IR (ATR): $\tilde{\nu} = 3472$ (br), 3031 (w), 2927 (s), 2856 (m), 1735 (vs), 1456 (m), 1386 (m), 1212 (m), 1152 (vs), 1054 (s), 1027 (vs), 1003 (m), 698 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 578 (1) [M^+], 522 (8), 472 (1), 431 (8), 416 (6), 325 (2), 267 (2), 223 (14), 193 (6), 177 (18), 135 (4), 91 (100), 57 (5), 43 (11); HRMS (EI): *m/z*: calcd for $C_{30}H_{34}O_8$ [$M-C_4H_8^+$] 522.2253, found 522.2246.

Punctaporonin C (1): *BOM deprotection*: Succinate **43** (6.50 mg, 11.2 μmol) was dissolved in a solution of TFA (400 μL) in dichloromethane (2.5 mL). The solution was stirred for 1.5 h at ambient temperature. The reaction mixture was neutralized with a saturated aqueous $NaHCO_3$ solution. Saturated aqueous NaCl solution (5 mL) and dichloromethane (5 mL) were added and the layers were separated. The aqueous layer was extracted with dichloromethane (2×10 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (20 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was used without further purification.

Hydrogenolysis of the benzyl ester: In an atmosphere of hydrogen the crude product was dissolved in MeOH/ethyl acetate 1:1 (2.5 mL). Pd/C (5.00 mg, 10%, 4.70 μmol) was added and the reaction mixture was stirred for 16 h at RT. After filtration the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (pentane/ethyl acetate/acetic acid 40:50:1) to yield punctaporonin C (**1**) (3.50 mg, 9.50 μmol, 85%) as colorless crystals. $R_f = 0.24$ (pentane/ethyl acetate/acetic acid 20:80:1) [CAM]; m.p. 138–141 °C; ^{1}H NMR (500 MHz, [D$_4$]MeOH): $\delta = 1.00$ (s, 3H), 1.07 (s, 3H), 1.08 (s, 3H), 1.43 (dd, $^2J = 12.0$, $^3J = 5.2$ Hz, 1H), 1.55 (dddd, $^2J = 5.6$, $^3J = 14.8$, 1.5, $^4J = 1.3$ Hz, 1H), 1.78 (ddd, $^2J = 12.9$, $^3J = 14.8$, 5.8 Hz, 1H), 1.92–2.08 (m, 3H), 2.33 (ddd, $^3J = 9.4$, 7.4, $^4J = 1.3$ Hz, 1H), 2.58–2.62 (m, 4H), 2.76–2.81 (m, 2H), 4.09 (dd, $^3J = 7.1$, 7.0 Hz, 1H), 4.93 (dd, $^3J = 9.4$, 6.1 Hz, 1H), 5.21 ppm (dd, $^3J = 7.4$, 7.1 Hz, 1H); ^{13}C NMR (90.6 MHz, [D$_4$]MeOH): $\delta = 23.8$ (q), 26.8 (q), 28.1 (t), 29.8 (q), 29.8 (t), 30.5 (t), 33.3 (t), 36.2 (d), 38.2 (s), 41.8 (t), 56.7 (d), 61.0 (d), 76.0 (s), 76.6 (d), 82.1 (d), 84.2 (d), 96.5 (s), 174.1 (s), 176.2 ppm (s); IR (ATR): $\tilde{\nu} = 3492$ (m), 3205 (br), 2974 (m), 2960 (s), 2867 (m), 1731 (vs), 1708 (s), 1695 (s), 1394 (m), 1266 (m), 1242 (s), 1227 (s), 1068 (s), 1025 (m), 949 cm^{-1} (m); MS (EI, 70 eV): *m/z* (%): 368 (2) [M^+], 312 (100) [$M-C_4H_8^+$], 294 (1), 268, 250 (2), 233 (4), 194 (70), 176 (54), 147 (18), 122 (30), 109 (16), 99 (50), 81 (44), 55 (26), 43 (46); HRMS (EI): *m/z*: calcd for $C_{15}H_{20}O_7$ [$M-C_4H_8^+$]: 312.1209; found: 312.1204.

Benzoate 46: *Ring opening to racemic product*: (2,4-Divinyl-6-oxabicyclo-[3.1.0]hexan-3-yloxy)-*tert*-butyldimethylsilane (**12**) (40.0 mg, 150 μmol), benzoic acid (131 mg, 1.06 mmol), and sodium benzoate (146 mg, 911 μmol) were suspended in DMF (4 mL). The reaction mixture was heated to 155 °C for 5 h. Upon cooling to RT the mixture was diluted with Et_2O (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2×20 mL). The organic layers were combined, washed with a saturated aqueous NaCl solution (50 mL) and dried with Na_2SO_4. After filtration the solvent was removed under reduced pressure and the resulting crude product was purified by flash chromatography (pentane/Et_2O 4:1 → 3:1) to yield benzoate **46** (10.4 mg, 26.8 μmol, 18%) as a colorless liquid together with unreacted starting material (9.18 mg, 34.5 μmol).

Enantioselective desymmetrization: A solution containing (*S,S*)-(+)-bis-(3,5)-di-*tert*-butylsalicyldiamincobalt(II) (**45**) (34.9 mg, 56.4 μmol, 30 mol%) and benzoic acid (45.8 mg, 0.38 mmol) in *tert*-butyl methyl ether (0.50 mL) were stirred for 30 min under an atmosphere of oxygen. (2,4-Divinyl-6-oxabicyclo[3.1.0]hexan-3-yloxy)-*tert*-butyldimethylsilane (**12**) (50.0 mg, 188 μmol) and *i*Pr$_2$NEt (65.0 μL, 49.1 mg, 0.38 μmol) were added and the reaction mixture was stirred for 24 h at ambient temperature. Et_2O (15 mL) was added and the organic layer was sequentially washed with 1 M aqueous HCl (10 mL), saturated aqueous $NaHCO_3$ solution (10 mL) and saturated aqueous NaCl solution (10 mL). The organic layer was dried with Na_2SO_4, filtered and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography (pentane/Et_2O 5:1) to yield benzoate **46** (38.4 mg, 98.8 μmol, 53%, 83% *ee*) as a colorless liquid. $R_f = 0.18$ (pentane/Et_2O 4:1) [CAM]; $[\alpha]_D^{20} = 39.8$ ($c = 1.00$ in $CHCl_3$) [83% *ee*]; ^{1}H NMR (360 MHz, $CDCl_3$): $\delta = 0.02$ (s, 3H), 0.02 (s, 3H), 0.87 (s, 9H), 2.49 (*virt.* q, $^3J \cong 8.7$ Hz, 1H), 2.94 (*virt.* q, $^3J \cong 8.7$ Hz, 1H), 3.87 (t, $^3J = 8.5$ Hz, 1H), 3.94 (dd, $^3J = 8.9$, 4.3 Hz, 1H), 5.10 (dd, $^3J = 8.6$, 4.3 Hz, 1H), 5.14–5.22 (m, 4H), 5.77 (ddd, $^3J = 17.1$, 10.2, 8.5 Hz, 1H), 5.83 (ddd, $^3J = 17.0$, 10.3, 9.7 Hz, 1H), 7.42–7.48 (m, 2H), 7.57–7.63 (m, 1H), 8.01–8.06 ppm (m, 2H); ^{13}C NMR (90.6 MHz, $CDCl_3$): $\delta = -3.6$ (q), −3.6 (q), 18.1 (s), 26.0 (q), 54.0 (d), 58.1 (d), 78.9 (d), 79.4 (d), 82.5 (d), 118.5 (t), 119.4 (t), 128.6 (d), 129.8 (d), 130.1 (s), 133.4 (d), 134.4 (d), 137.5 (d), 167.2 ppm (s); IR (ATR): $\tilde{\nu} = 3432$ (br), 3073 (w), 2954 (m), 2928 (s), 2856 (s), 2362 (s), 1721 (s), 1452 (w), 1361 (w), 1272 (s), 1109 (s), 918 (m), 835 (s), 775 (s), 708 cm^{-1} (s); MS (EI, 70 eV): *m/z* (%): 331 (1) [$M-C_4H_9^+$], 290 (1), 274 (1), 267 (1), 256 (1), 234 (6), 219 (22), 209 (9), 191 (4), 179 (2), 153 (2), 137 (2), 122 (87), 117 (2), 105 (100), 77 (58), 75 (10), 51 (20), 43 (6); HRMS (EI): *m/z*: calcd for $C_{18}H_{23}O_4Si$ [$M-C_4H_9^+$]: 331.1366; found: 331.1356.

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