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Tetrahedron 60 (2004) 7325–7344
Tetrahedron

Asymmetric synthesis of cyclic β-hydroxyallylsilanes via sequential allyltitanation-ring closing metathesis

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Received 6 April 2004; revised 19 May 2004; accepted 21 May 2004

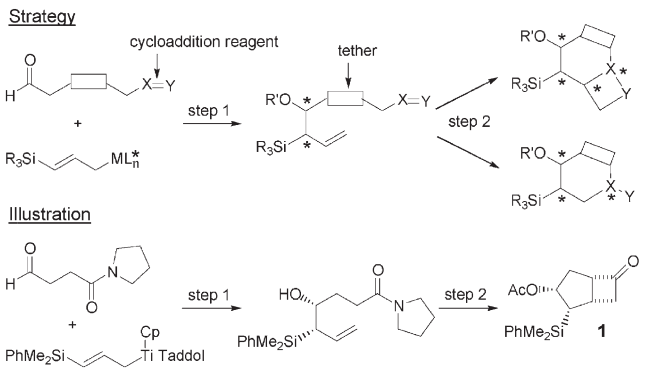
Available online 26 June 2004

Dedicated to Professor Robert H. Grubbs for his seminal contributions to organic and polymer synthesis

Abstract—Highly enantioenriched cyclic β-hydroxyallylsilanes have been prepared via enantioselective allylation of unsaturated aldehydes using a chiral allyltitanium reagent, followed by a ring-closing metathesis. Functionalized rings of various sizes have been synthesized and the electronic effect of the silicon group in the RCM reaction has been studied. The resulting cyclic β-hydroxyallylsilanes reacted stereoselectively with a variety of electrophilic reagents. A first application of this method to the synthesis of a highly functionalized dihydropyrane is reported.

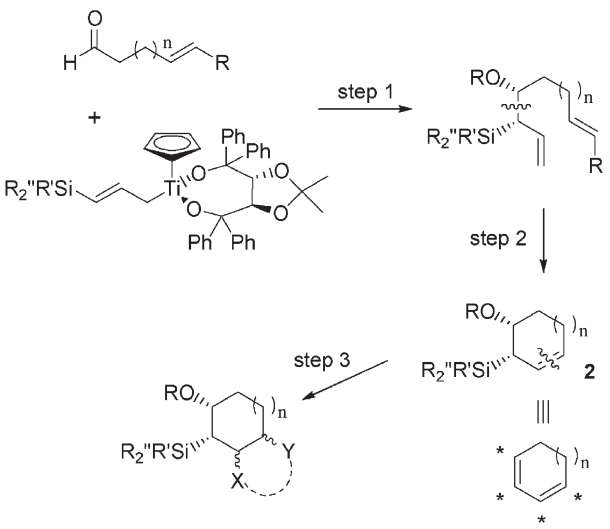
1. Introduction

A convergent strategy for the enantioselective synthesis of (poly)cyclic molecules consists of a two-step sequence of reactions starting with an asymmetric allylation of an aldehyde with an organometallic reagent followed by an intramolecular diastereoselective silicon-directed (cyclo)addition reaction (Scheme 1).



Scheme 1.

A first example of this strategy has been reported in 1999 by our group.[1] It involved the reaction of a silyl-substituted allyltitanate reagent with an aldehyde carrying a tertiary amide group at the β-carbon followed by a silicon-directed intramolecular cycloaddition reaction of the allylsilane to an in situ generated keteniminium reagent. This led to bicyclo[3.2.0]heptan-6-one **1** in good yield and high enantiomeric excess.



Scheme 2.

The combination of step 1 with a ring-closing metathesis (RCM)[2] was considered as an attractive sequence for the synthesis of β-hydroxyallylsilanes **2** which can be looked upon as chiral equivalents of cyclic conjugated dienes (Scheme 2). The dense functionality of these intermediates should allow to take full benefit of the presence of a silyl

Keywords: Ring closing metathesis; Allyltitanation; β-Hydroxy-allylsilane; Asymmetric synthesis; Dihydropyran.
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doi:10.1016/j.tet.2004.05.058

substituent as control element for further transformations into a variety of enantiopure mono- and polycyclic compounds. In earlier examples of sequential asymmetric allylation-RCM, the olefinic partners for the RCM were always linked by a heteroatom which became part of the newly formed ring.[3] A preliminary report on the sequence of Scheme 2 has been recently published by Roush et al. who elegantly applied it to the synthesis of conduritols and inositols of high enantiomeric purities.[4] We now wish to report our studies of the scope and limitation of the allylation-RCM sequence and illustrate the synthetic potential of the resulting products **2**.[5]

2. Substrate design

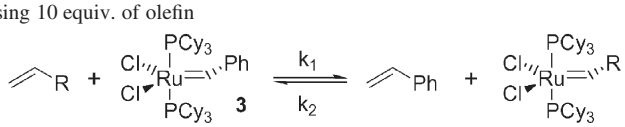
2.1. Carbene-exchange reaction

In the sequence described in Scheme 2, one of the olefinic partners for the RCM is an allysilane. In order to optimize the reaction in terms of yields and turnover of the catalyst, we decided to perform some model experiments.

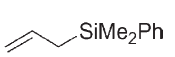
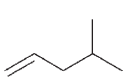
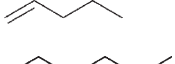
Several examples of RCM of allylsilanes have been reported. Crowe and coworkers assigned the preference of allylsilanes for cross-metathesis to the silicon β-effect.[6] Doubts about the role of this β-effect arose from a report of Blechert et al.[7] Based on a competition experiment between $TMS-CH_2CH{=}CH_2$ and $t\text{-Bu}-CH_2CH{=}CH_2$, they deduced that the β-effect of silicon did not significantly affect the rate of metathesis. However, since the kinetics of the reaction were not known, the identification of the carbene from which the cross-metathesis mainly occurred was not possible.

We first evaluated the carbene exchange reaction between several olefins and Grubbs' catalyst **3** (Table 1). It was possible to determine K and hence k_2 by taking advantage of the higher rate of the carbene exchange reaction as compared to the productive metathesis.[8] Indeed, equilibrium was reached before a significant amount of methylidene carbene was formed. We selected hexene as a reference, 4-methylpentene to evaluate the impact of steric hindrance, and allyldimethylphenylsilane to measure the influence of the silyl substituent.

Table 1. Relative second-order rate constants (*k*rel) for metathesis reactions using 10 equiv. of olefin



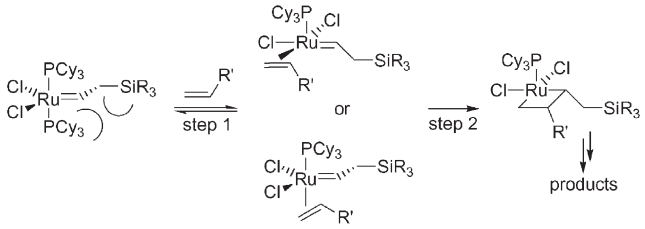
(~10 equiv.) (~0.02 M) $K=k_1/k_2$

Olefin	$k_1$rel[a]	K[b]	$k_2$rel[a]
	0.5	$3.1\pm0.2\times10^{-3}$	4.8
	0.9	$19\pm3\times10^{-2}$[c]	1.6
	1	$32\pm4\times10^{-2}$	1

[a] $k_1$rel=k_1(olefin)/k_1(hexene), $k_2$rel=k_2(olefin)/k_2(hexene).
[b] $k(K)\pm$standard deviation.
[c] The equilibrium constant (K=0.32, rt) for hexene is slightly higher than the previously reported value of 0.2 determined by Grubbs and coworkers for the same reaction at 7 °C.[8]

Examination of $k_1$rel showed that electronic effects mediated by σ-bonds did not strongly influence the reactivity of the olefins. The lower rate observed for the allylsilane was mainly attributed to steric effects since the silicon β-effect should have increased the rate of reaction with the electrophilic carbene complex. The trend in reactivity ($k_2$rel) seems to roughly follow the steric demand of the substituents. The more reactive complex was the allyldimethylphenylsilane-substituted carbene. This could be explained by an increase of phosphine lability as a result of the presence of the bulky silyl group (Scheme 3).[9]

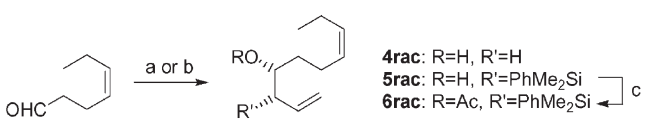
The influence of the silyl group on other parameters such as olefin complexation (step 1) or the rate of the metathesis (step 2) was believed to be limited. First, the geometric requirement for a strong hyperconjugating interaction would be difficult to fulfill and secondly, electronic effects are only slightly influencing step 2 as seen by the small ρ value determined in the gas phase (0.69).[8] Moreover, if operating, the β-effect is expected to disfavour olefin complexation which should result in a decrease of reactivity. We thus propose that, in carbene exchange reactions, the silicon β-effect is not an important parameter and that steric effects are probably the true reactivity modulators.



Scheme 3.

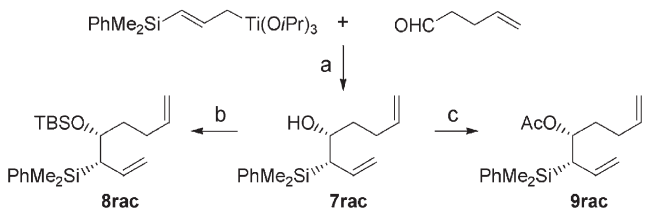
2.2. RCM model experiments

2.2.1. Synthesis of the model substrates. Two types of model substrates were prepared to study the reactivity of the allylsilane. Racemic substrates **4rac** and **5rac** were prepared by allylmetallations of hept-4-enal. Acetylation of **5rac** gave **6rac** (Scheme 4).



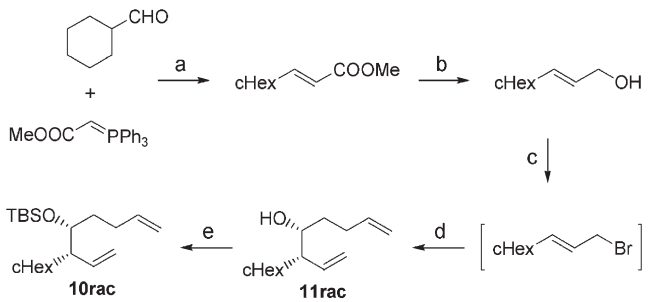
Scheme 4. Reagents and conditions: (a) allylmagnesium bromide (1.1 equiv.), Et_2O, 95%; (b) allyldimethylphenylsilane (1.15 equiv.), THF, *n*-BuLi (1.15 equiv.), 3 h, −78 °C then 40% aqueous NH_4F, 15 h, rt, 87%; (c) pyridine (4 equiv.), CH_3COCl (3 equiv.), CH_2Cl_2, 1.5 h, rt, 95%.

Racemic dienes **7rac**-**9rac** were prepared by allyltitanation of 4-pentenal followed by protection of the alcohol by either an acetyl or a *t*-butyldimethylsilyl group (Scheme 5).



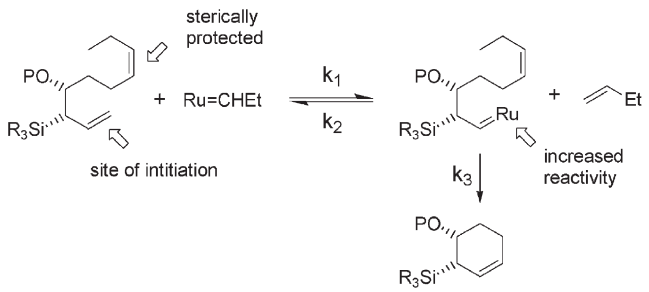
Scheme 5. Reagents and conditions: (a) allyldimethylphenylsilane (1.15 equiv.), *n*BuLi 2.1 M (1.15 equiv.), $ClTi(OiPr)_3$ (1.25 equiv.) to give γ-silylallyltitanate, then 4-pentenal, THF, −78 °C, 2 h, 75%; (b) TBSCl (1.2 equiv.), imidazole (1.3 equiv.), 36 h, 50 °C, DMF, 83%; (c) pyridine (4 equiv.), CH_3COCl (3 equiv.), CH_2Cl_2, 30 min, rt, 95%.

Diene **10rac**, bearing a cyclohexyl group at the allylic position was prepared by a simple sequence starting from cyclohexylcarboxaldehyde (Scheme 6). This diene gave us the opportunity to evaluate the accelerating effect due to steric hindrance. The cyclohexyl group was selected since it has an *A* value comparable to that of a TMS group and will induce no electronic effect.[10] Wittig olefination, reduction of the ester, Corey bromination of the allylic alcohol and chromium-mediated allylation[11] of pentenal gave the desired homoallylic alcohol **11rac**. Protection of the alcohol by a TBS group yielded **10rac**.



Scheme 6. Reagents and conditions: (a) $CHCl_3$, reflux, 87%, 97% of *E* (GC/NMR); (b) DIBAL, >99%.; (c) DMS/NBS, 78%; (d) $CrCl_2$ (2 equiv.), THF, rt, 15 h, 61–71%; (e) TBSCl (1.1 equiv), imidazole (2 equiv), 16 h, 50 °C, DMF, 73%.

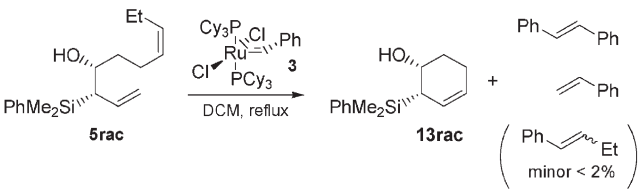
2.2.2. Ring closing metathesis. We first examined dienes **4rac**-**6rac**. In this case, we expected the initiation to take place mainly at the allylsilane double bond since the other olefin is sterically protected (Scheme 7).



Scheme 7.

On the basis of the results of Section 2.1, we hoped that these carbenes would also be more reactive in the productive metathesis step as a result of increased phosphine lability of the silyl-substituted carbene. In the case described in Scheme 7 the propagating species would be an alkylidene carbene which has been shown to be more active and decompose more slowly than the corresponding methylidene.[12]

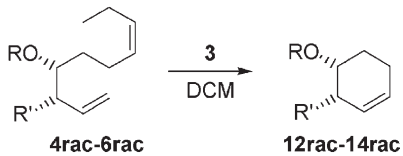
We checked that the initiation was taking place at the terminal olefin. Diene **5rac** was reacted with 0.8 equiv. of **3** in refluxing CH_2Cl_2 and the crude mixture was analysed by GC-MS (EI and CI). In addition to the starting material and the cyclized product, analyses revealed the presence of tricyclohexylphosphine, styrene, stilbene as well as only trace amounts of 2-ethylstyrene (Scheme 8).



Scheme 8.

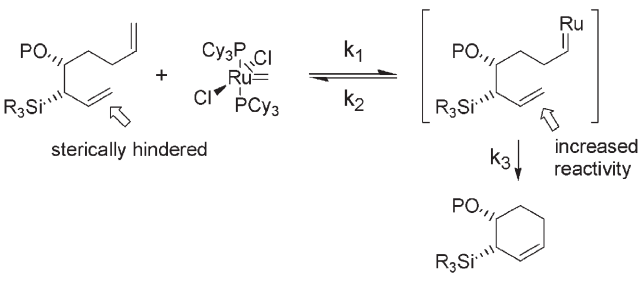
The homoallylic alkoxy derivatives **4rac**-**6rac** were reacted with a catalytic amount of **3**. ^1H NMR and GC analysis of the crude mixtures indicated clean conversions. Table 2 shows that the main influence of the silicon group is to decrease the rate of the RCM due to its steric hindrance.

Table 2.



Diene	R=	R′=	**3** (mol%)	Temperature	Time	Product	Yield (%)
4rac	H	H	1.6	rt	1 h	**12rac**	>95
4rac	H	H	1.6	Reflux	<5 min	**12rac**	>95
5rac	H	$PhMe_2Si$	3.2	Reflux	42 h	**13rac**	86
6rac	Ac	$PhMe_2Si$	1.6	Reflux	24 h	**14rac**	91

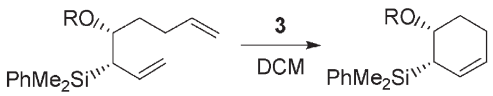
The modification of the initiation site should lead to an increase of reactivity: when the two double bonds are terminal, the carbene complex will react faster at the less hindered double bond, the one without any substituent at the allylic position (Scheme 9).



Scheme 9.

The three dienes **7rac**-**9rac** were reacted with catalyst **3** with varying efficiency depending on the protecting group (Table 3). With 1.6 mol% of catalyst at room temperature, the homoallylic alcohol **7rac** reacted rapidly up to 40% conversion at which point the reaction nearly stopped (entry

Table 3.



7rac R = H
8rac R = Ac
9rac R = TBS

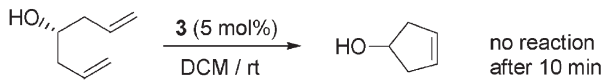
13rac R = H
14rac R = Ac
15rac R = TBS

Entry	Diene	R=	**3** (mol%)	Temperature	Time	Product	Conv. (%)
1	**7rac**	H	1.6	rt	3 h[a]	**13rac**	49
2	**7rac**	H	1.6	Reflux	1.5 h	**13rac**	64
3	**7rac**	H	4.8	Reflux	2 h	**13rac**	98
4	**8rac**	Ac	1.6	rt	20 min	**14rac**	> 99
5	**9rac**	TBS	1.6	rt	2 min	**15rac**	> 99
6	**9rac**	TBS	0.05	Reflux	1 h	**15rac**	98

[a] 40% conversion after 5 min then, the reaction nearly stopped.

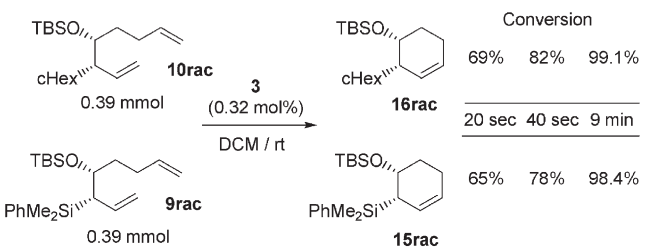
1). Heating at reflux didn't allow complete conversion (entry 2). It was necessary to triple the catalyst concentration to achieve a complete conversion of the starting material (entry 3). The acetyl-protected diene **8rac** gave a 92% conversion after only 4 min and quantitative conversion after 20 min at room temperature (entry 4). More surprising was the fast RCM of the *t*-butyldimethylsilyl ether **9rac**, the reaction being complete within 2 min at room temperature (entry 5). In this case, it was possible to complete the RCM in 1 h in refluxing dichloromethane with as little as 0.05 mol% catalyst (entry 6).

Interestingly, comparison of Table 2 (entry 1) and Table 3 (entry 1) with a previous result on metathesis of hept-1,6-diene-4-ol[13] (Scheme 10) indicates that proper choice of the site of carbene exchange could prevent formation of unreactive chelates and hence deliver higher possible turnover.



Scheme 10.

The unexpected high reactivity of diene **9rac** could result from the high nucleophilicity of the allylsilane as proposed by Crowe and coworkers.[6] If the silicon β-effect was responsible for this high reactivity, the replacement of the silyl substituent by a group of comparable steric hindrance but lacking electronic effects such as cyclohexyl, should induce a decrease in reactivity. A competition experiment was performed using equimolar amounts of **9rac** and **10rac** (Scheme 11).



Scheme 11.

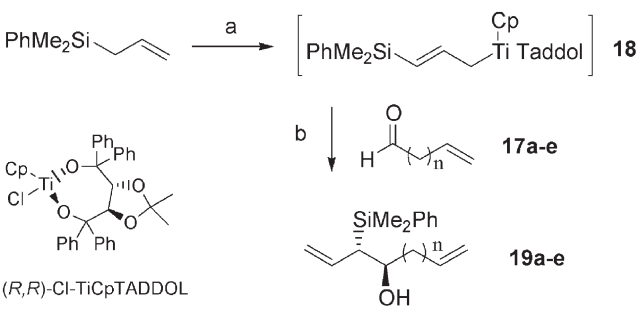
GC analysis of the mixture after 20 s, 40 s and 9 min showed no significant difference in reactivity between the two dienes. This was also confirmed in separate experiments. Thus the enhanced reactivity of these dienes is primarily a consequence of the bulk of the substituents which could accelerate the loss of a phosphine ligand but probably also increase the population of the conformation necessary for RCM.

3. Asymmetric allylation-RCM: application to the synthesis of β-hydroxyallylsilanes

3.1. Preparation of chiral diene equivalents via asymmetric allyltitanation

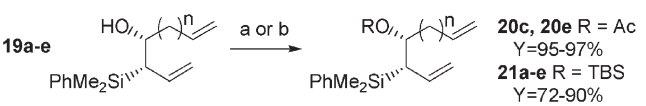
Unlike Roush et al., we performed the asymmetric allylmetallation of the unsaturated aldehydes **17a-e**[14] with (*E*)-γ-dimethylphenylsilyl substituted titanium reagent **18** generated from allyldimethylphenylsilane, *n*-BuLi and (*R*,*R*)-Cl–TiCpTADDOL at −78 °C (Table 4). These allylmetal reagents were known to give the *anti*-β-hydroxyallylsilanes in good yields and high enantiomeric purities.[15] This was also the case here. The absolute configurations of **19a-e** were assigned by analogy with previous results.[1] As will be shown later, this was confirmed by analysis of the absolute conformation of the triol derived from **19b** (see Scheme 17).

Table 4. Asymmetric allylmetallation of terminally unsaturated aldehydes **17a-e** with **18**



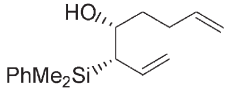
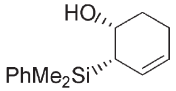
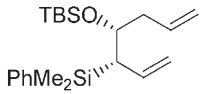
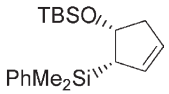
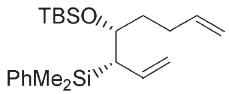
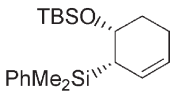
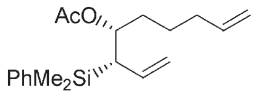
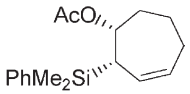
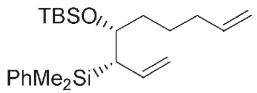
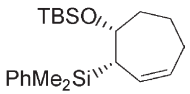
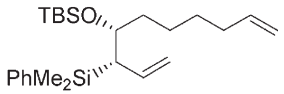
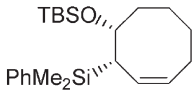
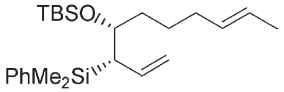
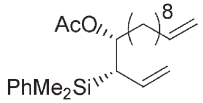
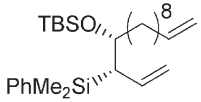
Entry	Aldehyde	*n*=	Product	Yield (%)	ee (%)
1	**17a**	1	**19a**	68	96
2	**17b**	2	**19b**	68	92
3	**17c**	3	**19c**	75	90
4	**17d**	4	**19d**	67	94
5	**17e**	8	**19e**	71	91

Reagents and conditions: (a) *n*-BuLi (1.1 equiv.) in THF, 20 min, rt then (*R*,*R*)-Cl–TiCpTADDOL (1.15 equiv.), 30 min, −78 °C to give a solution of **18**; (b) aldehyde **17a-e** (1 equiv.), 3 h, −78 °C, 40% aqueous NH_4F, 15 h, rt, flash chromatography, ee determined by HPLC on a Chiralcel AS or OD column, the other diastereoisomer was not detected (de > 98%).



Scheme 12. Reagents and conditions: (a) pyridine (3.5 equiv.), CH_3COCl (2.5 equiv.), CH_2Cl_2, 30 min, rt; (b) TBSCl (1.5 equiv.), imidazole (4 equiv.), 16 h, 50 °C, DMF.

Table 5. Ring-closing metathesis of dienes **19b**, **20** and **21**: assays with different metathesis pre-catalysts and alcohol protecting groups

Entry	Substrate		Catalyst	(mol%)	Solvent	Temperature	*t*	Product		Yield (%)
1		**19b**	**3**	5	CH_2Cl_2	Reflux	2 h		**13**	**13** (87%)
2		**21a**	**3**	2	CH_2Cl_2	rt	5 min		**22a**	**22a** (98%)
3		**21b**	**3**	1.6	CH_2Cl_2	rt	5 min		**22b**	**22b** (98%)
4		**20c**	**3**	6	CH_2Cl_2	rt	48 h		**24**	**24** (0%)
5			**3**	7.5	Toluene	60 °C	24 h			**24** (66%)[a]
6		**21c**	**3**	20	CH_2Cl_2	rt	4 h		**22c**	**22c** (70%)
7			**3**	7.5	Toluene	60 °C	2 h			**22c** (93%)
8			**23**	2	Toluene	60 °C	2 h			**22c** (76%)+**22b** (20%)
9			**23**	2	CH_2Cl_2	rt	2 h			**22c** (82%)+**22b** (6%)
10		**21d**	**3**	30	Benzene-d_6	60 °C	24 h		**22d**	—
11			**23**	20	CH_2Cl_2	rt	72 h			**22c** (54%)[a]+**21d** (42%)[a]
12			**23**	7.5	Toluene	60 °C	11 h			**22c** (89%)[a]+**22d** (8%)[a]
13			**23**	7.5	$CDCl_3$	60 °C	1 h			**22c** (42%)[a]+**22d** (52%)[a]
14			**3**	20	CH_2Cl_2	rt	72 h		**25**	**25** (42%)[a]+**21d** (51%)[a]
15		**20e**	**3**	20	CH_2Cl_2	rt	72 h	No RCM product		—
16		**21e**	**3**	20	Toluene	60 °C	48 h	No RCM product		—

[a] Observed conversion by GC-MS, not isolated yield.

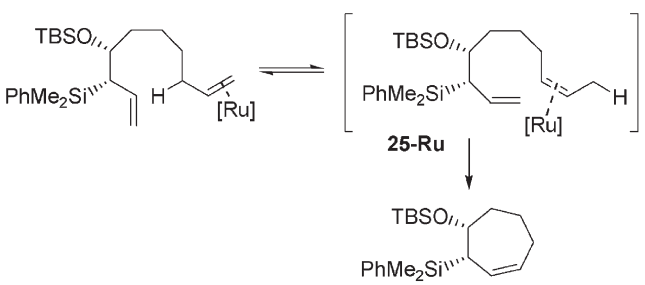
Acetylation or silylation of the alcohols **19a-e** yielded the corresponding esters **20c**,**e** or silyl ethers **21a-e** (Scheme 12).

3.2. Ring-closing metathesis

RCM of the unprotected alcohol **19b** using Grubbs' catalyst **3** (5 mol%) gave the cyclohexenylsilane **13** in good yield (Table 5, entry 1). *t*-Butyldimethylsilyl ethers **21a-b** underwent an extremely fast RCM reaction in the presence of catalyst **3** (entries 2 and 3). Compounds **22a-b** were obtained in excellent yields and the same enantiomeric purities as the starting dienes. As it could be expected, the formation of the 7-membered ring proved to be more difficult: the RCM of diene **21c** was much slower, requiring higher temperatures and more catalyst (entries 6 and 7). The use of 2 mol% of the 2nd generation Grubbs' catalyst **23**[16] enabled the reaction to take place at room temperature in 2 h (entry 9). However, traces of the 6-membered ring were observed in presence of catalyst **23**. The proportion of **22b** increased when the reaction was conducted in toluene at 60 °C (entry 8). RCM of the acetate **20c** was slower. Heating the dienes at 60 °C in toluene in the presence of 7.5 mol% of **3** gave 66% yield of **24** (entry 5).

The treatment of **20e** and **21e** with **3** didn't give the 12-membered ring (entries 15 and 16). Close NMR observation after adding 1 equiv. of catalyst showed complete conversion of the less hindered terminal olefin into the corresponding ruthenium–carbene complex but no cyclization occurred even after 2 days at 60 °C in toluene. The catalyst **23** didn't give any metathesis product neither.

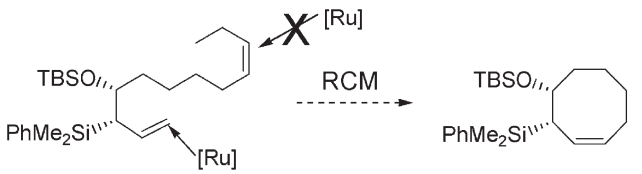
A first attempt to form the 8-membered ring was conducted in boiling deuterated benzene and followed by NMR. Again, the only product was the ruthenium–carbene complex (entry 10). The use of the more reactive catalyst **23** did not give the 8-membered ring. Instead a mixture of the 7-membered ring **22c** and starting diene **21c** was obtained when the reaction was run at room temperature (entry 11). At 60° in toluene (entry 12), the conversion was complete, but gave only a small amount of the 8-membered ring **22d**, the main product being the 7-membered ring **22c**. Surprisingly, in deuterated chloroform at 60 °C, the major product was **22d** as shown by GC-MS analysis (entry 13). Unfortunately this product could not be separated from the lower homologue **22c**. These results can be explained by a ruthenium-catalyzed isomerization of diene **21d** into the more stable internal olefin **25** (Scheme 13).



Scheme 13.

Indeed, a mixture of the terminal **21d** and isomerized olefin **25** was formed when **21d** was exposed to Grubbs catalyst at room temperature for 72 h (entry 14). This type of isomerization is often encountered in RCM involving weakly reactive systems.[17]

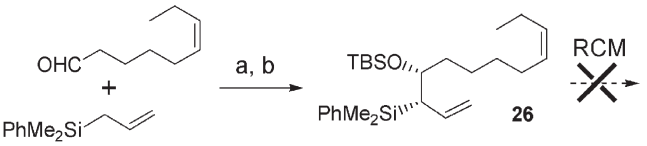
We reasoned that we might avoid olefin isomerization if we could force the catalyst to enter at the allylsilane position. The introduction of an ethyl substituent at the terminal carbon atom of the olefin was expected to slow down carbene formation at that double bond (Scheme 14).



Scheme 14.

Diene **26** was synthesized by the allytitanation-metathesis sequence and subjected to RCM conditions (Table 6). Unfortunately, at room temperature neither **3** nor **23** were efficient enough to promote the formation of the 8-membered ring (entries 1 and 2). When the reaction was carried out in toluene at 60 °C, no reaction occured in presence of catalyst **3** (entry 3). With catalyst **23** isomerization preceded RCM, giving again the 7-membered ring **22c** (entry 4).

Table 6. RCM of **26**



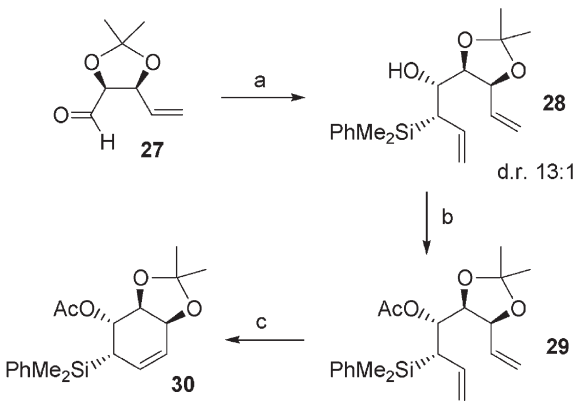
Entry	Catalyst	Conditions	Result
1	**3**	CH_2Cl_2, rt, 2 d	No reaction
2	**23**	CH_2Cl_2, rt, 2 d	No reaction
3	**3**	Toluene, 60 °C	No reaction
4	**23**	Toluene, 60 °C	**22c** 62%+**22d** 12%

Reagents and conditions: (a) *n*-BuLi (1.1 equiv.) in THF, 20 min, rt then (*R*,*R*)-Cl–TiCpTADDOL (1.15 equiv.), 30 min, −78 °C then *cis*-6-nonenal (1 equiv.), 3 h, −78 °C, 40% aqueous NH_4F, 15 h, rt, 64%; (b) TBSCl (1.1 equiv.), imidazole (2 equiv.), 16 h, 50 °C, DMF, 63%.

Clearly the synthetic utility of this asymmetric allylmetallation-RCM sequence would be greatly enhanced if it could be successfully applied to substituted aldehydes (Scheme 15). We have therefore examined the allyltitanation of the acetonide-protected aldehyde **27**[18] which proceeded indeed with high diastereoselectivity to give the corresponding *anti*-β-hydroxyallylsilane **28**. The corresponding acetate **29** was subjected to RCM in the presence of catalyst **23** to give 80% yield of cyclohexene **30** in high enantiomeric purity (ee >98%, d.r.: 13:1 determined by chiral HPLC).

3.3. Conformations of the cyclic *cis*-β-hydroxyallylsilanes

The conformations of the cyclic *cis*-β-hydroxyallylsilanes



Scheme 15. Reagents and conditions: (a) *n*-BuLi (1.1 equiv.) in THF, 20 min, rt then (*R*,*R*)-Cl–TiCpTADDOL (1.15 equiv.), 30 min, −78 °C then **27** (1 equiv.), 3 h, −78 °C, 40% aqueous NH_4F, 15 h, rt, 55%; (b) pyridine (3.5 equiv.), CH_3COCl (2.5 equiv.), CH_2Cl_2, 4 h, rt, 89%; (c) catalyst **23** (8 mol%), boiling CH_2Cl_2, 2 h, 80%.

22a-c were examined by correlation of the experimental coupling constants with calculated values obtained by a Monte–Carlo conformational search (Fig. 1). The experimental coupling constants of the ring-protons were compared with the one calculated for the representative structures of each cluster obtained from the conformational search. The existence of second-order effects and long range couplings specific to an allylic system led us to use an iterative procedure to assign all coupling constants values. In all three cases the values of the coupling constants confirmed that the silicon group was pseudo-axial. The preference for a pseudo-axial position of the silyl group can be explained on the basis of a stabilizing ground state interaction between the σ_{C-Si} and the $\pi^*_{C=C}$. This kind of interaction has been proposed previously to rationalize the preferred conformation of allylsilanes.[19]

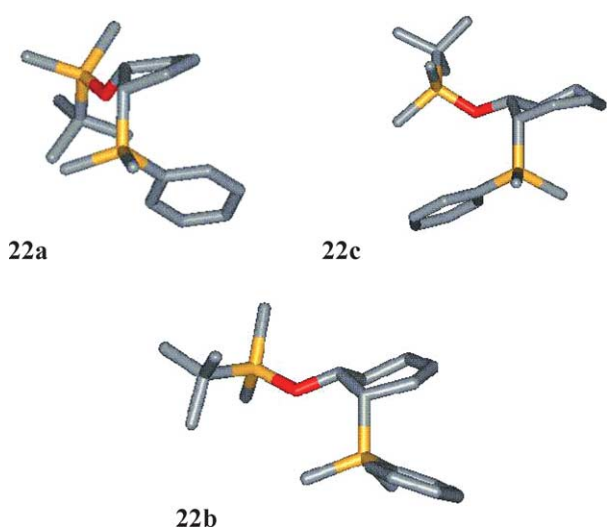


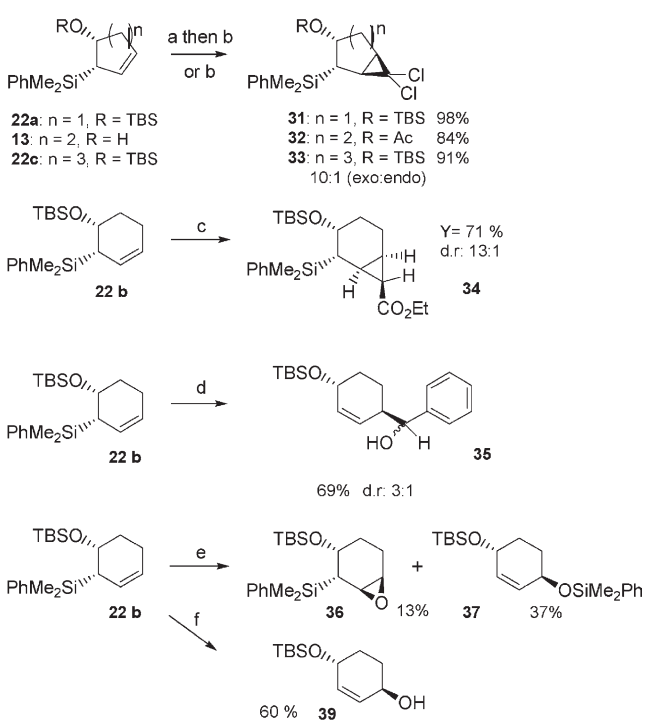
Figure 1. Following the Monte Carlo conformational search—calculations were considered to be convergent when each conformation was found at least three times—a cluster analysis was performed with Xcluster 1.1. The representative conformer of the cluster exhibiting calculated coupling constants consistent with the one observed by ^{1}H NMR spectrum are shown above. This cluster was also the one containing the conformer with the lowest energy in the three cases.

^{1}H NMR analysis and molecular modeling[5] of **30** also suggested a half-chair conformation with a pseudoaxial silyl substituent.

4. Transformations of cyclic β-hydroxyallylsilanes

Compounds **13** and **22a-c** contain a combination of an allyl- and a β-silyloxy-silane which should be prone to undergo interesting transformations leading to a wide variety of enantioenriched, highly functionalized building blocks. Scheme 16 shows an illustrative selection of diastereoselective transformations of **22a-c**. In all cases, the axial silyl group acts as an efficient stereodirecting group, favouring the attack on the opposite face. HPLC analyses showed that the enantiomeric purity of the starting materials was conserved after the transformations.

The cyclohexenylsilanes **13** and **22a,c** were first reacted with dichlorocarbene and the relative configuration of the cycloadducts was ascertained by ^{1}H NOE experiments. The facial selectivity was excellent for **22a** and **13** (only the *exo* isomer was detected by HPLC) but a 10:1 mixture of *exo* and *endo* was obtained in the case of **33**. The addition of ethyldiazoacetate in presence of $[Rh(OAc)_2]_2$ yielded 43% of **34** in a 3:1 mixture of epimers but with complete facial selectivity. The use of $Cu(acac)_2$ instead, as described by Landais et al., gave the cyclopropane with a better yield (71%) and a better epimer ratio (13:1 determined by ^{1}H NMR).[20]

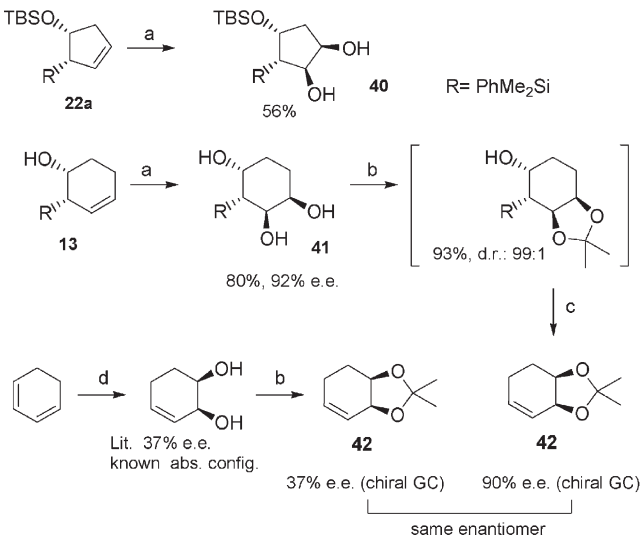


Scheme 16. Reagents and conditions: (a) pyridine (3 equiv.), CH_3COCl (2 equiv.), CH_2Cl_2, 4 h, rt, 92%; (b) Et_3BnNCl (0.1 equiv.), NaOH 50%, $CHCl_3$, rt, 15 h; (c) ethyl diazoacetate (1.2 equiv.), $Cu(acac)_2$ (2 mol%), toluene, 90 °C, 3 h; (d) benzaldehyde (1.1 equiv.), $TMSNTf_2$ (1.1 equiv.), *t*BDMP (1.5 equiv.), CH_2Cl_2, −78 °C, 1 h.; (e) *m*-cpba (1 equiv.), −20 °C, 1 h; (f) *N*-methyl-1,2-oxido-1,2,3,4-tetrahydroisoquinoleine tetrafluoroborate **38** (1 equiv.), CH_2Cl_2, rt, 30 min.

As the $PhMe_2Si$ group was axial in **22b**, we expected to observe the reactivity typical of an allylsilane and attempted a Sakurai reaction. In the presence of 1.1 equiv. of $TMSNTf_2$ **22b** reacted with benzaldehyde to yield 69% of **35** as a mixture of epimers (3:1).

Epoxidation proved to be more difficult. Treatment of **22b** at room temperature with *m*-cpba gave a complex mixture probably due to the acidic nature of the oxidant. At −20 °C only 13% of epoxide **36** were obtained along with 37% of **37** resulting from the rearrangement of the epoxide. The neutral oxaziridinium salt **38**[21] directly yielded alcohol **39** in 60% yield.

Dihydroxylation of **22a** yielded the diol **40** with an excellent facial selectivity (only one isomer detected by ^1H NMR of the crude mixture) (Scheme 17). Dihydroxylation of **13** gave the triol **41** in good yield and the reaction was found to be 99% diastereoselective. Only 1% of the *cis*-isomer could be detected by GC-MS after protection of the 1,2-diol. Chiral HPLC analysis showed that **42** was identical to the product resulting from Sharpless dihydroxylation of cyclohexadiene with AD-mix β followed by acetonide protection.[22] These data further confirmed the configurational assignment of our RCM products.

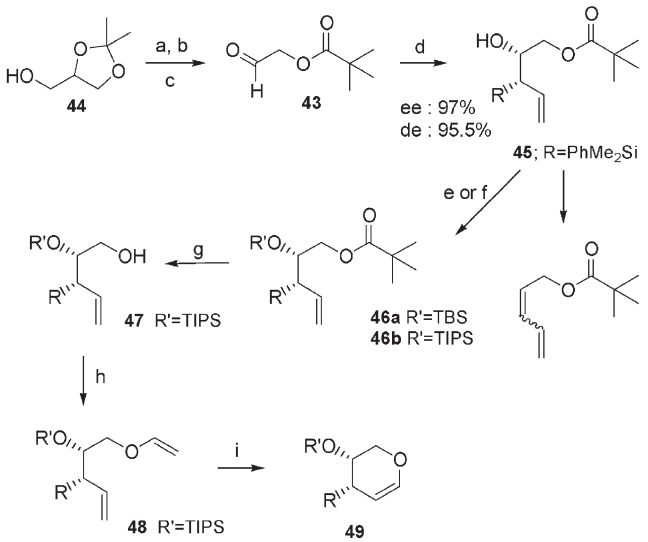


Scheme 17. Reagents and conditions: (a) $K_2OsO_4{\cdot}2H_2O$ (2 mol%), $NMO{\cdot}H_2O$ (1.7 equiv.), H_2O/THF, rt, 48 h; (b) dimethoxypropane (1.5 equiv.), $PTSA{\cdot}H_2O$ cat., CH_2Cl_2, rt, 10 min; (c) NaH (1.3 equiv.), THF, 55 °C, 5 h; (d) AD-mix β, $MeSO_2NH_2$, *t*-BuOH, H_2O, 3 °C, 2.25 h.

5. Conclusions and perspectives

In conclusion, we have demonstrated that the asymmetric allylmetallation-ring-closing metathesis is an efficient sequence to access various polyfunctionalized rings with good enantioselectivities. In this sequence, the bulk of the silyl substituent plays a significant role, favouring the RCM reaction. The silyl group is also a key player in the further transformations of the RCM products. Both the β-effect and bulk of the axial silyl group are responsible for a complete control of the facial selectivity in electrophilic additions to the cyclic allylsilanes. The work of Roush et al. on the total synthesis of conduritols and inositols is undoubtedly a beautiful illustration of the power of this synthetic strategy for natural products synthesis.

We wanted to find out whether this synthetic strategy could be applied to the synthesis of enantiopure heterocyclic rings such as dihydropyranes which could be useful intermediates for the synthesis of glycomimetics. As a conclusion of these studies, we want to show a first illustration of this new application (Scheme 18).



Scheme 18. Reagents and conditions: (a) pyvaloyl chloride (1 equiv.), solketal (1 equiv.), pyridine (1.1 equiv.), CH_2Cl_2, 48 h, −10 °C, 83%; (b) HCl (2 N), THF, 16 h, rt, 98%; (c) $NaIO_4$ (1.1 equiv.), water/CH_2Cl_2, 4 h, rt, 71%; (d) *n*-BuLi (1.1 equiv.) in THF, 20 min, rt then (*R*,*R*)-Cl–TiCpTADDOL (1.15 equiv.), 30 min, −78 °C then **43** (1 equiv), 3 h, −78 °C, 40% aqueous NH_4F, 15 h, rt, 56%; (e) TBSCl (1.5 equiv.), imidazole (3 equiv.), 36 h, 60 °C, DMF; (f) TIPSCl (1.5 equiv), imidazole (3 equiv.), 36 h, 60 °C, DMF; (g) DIBAL 1.5 M (2 equiv.), CH_2Cl_2, −78 °C, 1 h, 73%; (h) ethylvinyl ether, $Hg(OAc)_2$ (1.1 equiv.), 48 h, 67%; (i) **23** (25 mol%), CH_2Cl_2, reflux, 4 h, 93%.

Aldehyde **43** was prepared by standard procedures from (+/−)-solketal **44** and successfully submitted to allylmetallation. All our attempts to introduce a benzyl protecting group on alcohol **45** failed and gave instead the diene resulting from a Peterson elimination. A TBS group could be easily introduced but, unexpectedly, attempts to cleave the pivaloyl group by $LiAlH_4$ also gave 2,4-pentadien-1-ol. However the use of a more stable protecting group such as TIPS allowed cleavage of the pivaloyl group with DIBAL The resulting alcohol **47** was subsequently vinylated by transetherification in presence of $Hg(OAc)_2$. 25 mol% of catalyst **23** allowed a clean conversion of the diene **48** into the cyclic vinyl ether **49**.

Further applications of this strategy will be reported in due course.

6. Experimental

6.1. General

^1H NMR spectra and ^{13}C NMR spectra were recorded in $CDCl_3$ at 400 and 100 MHz on a Bruker Avance 400 instrument or at 300 and 75 MHz on a Varian Gemini

300BB Instrument. Chemical shifts are reported in ppm using residual $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77 ppm) as references. HPLC analyses were realized with a Waters Alliance apparatus. The mass spectra under fast atom bombardment (FAB) or chemical ionization (CI) were recorded at 70 eV ionizing potential; CH_4–N_2O were used for CI. The spectra are presented as *m*/*z* (% rel. int.). High resolution mass spectra were performed in the laboratory of Prof. Flammang (Université de Mons Hainaut) or at the Cesamo Laboratory (Université Bordeaux I). [α] were measured on a Perkin–Elmer 241 MC polarimeter. Thin-layer chromatographic analyses were performed on MERCK 60 F_{254} silica gel plates (coated on aluminium). Visualization was realized under UV lamp or $KMnO_4$ revelator. Flash chromatography separations were performed using MERCK 60 40–63 μm silica and technical grade solvents.

Reaction requiring anhydrous conditions were performed using flame-dried glassware under a positive pressure of argon. Dry THF was distilled from potassium and benzophenone under argon, CH_2Cl_2 was distilled from CaH_2, Et_2O and toluene were distilled from Na, DMF was dried over 3 Å MS. 1st and 2nd generation Grubbs' catalysts **3** and **23** were purchased from Strem Chemicals.

The calculations were performed on a SGI Octane platform running Macromodel version 6.5 (Schrödinger Inc.). Conformational minima were found using the modified MM3* (1991 parameters) or MM2* (1987 parameters) force fields as implemented and completed in the macromodel program. Build structures were minimized to a final RMS gradient ≤ 0.01 kJ Å^{-1} mol^{-1} via the Truncated Newton Conjugated Gradient (TNCG) method (500 cycles). Coupling constant calculations were performed using Ref. 23 as implemented in Macromodel.

6.2. Reaction rate measurements

For the kinetics, a known amount of catalyst **3** (~10 mg) was weighted in an NMR tube. Deuterated benzene (0.6 mL) was added just before performing the NMR. After addition of 20 μL of olefin (~10 equiv. depending on the olefin) with a calibrated Hamilton syringe, an arrayed ^{1}H NMR experiment was started taking spectra every 40 or 60 s. The delay between the addition of the olefin and the first ^{1}H NMR acquisition was measured precisely to be able to consider the point at the origin for the linear regression analysis. Before each set of measurements, an experiment with hexene was performed to ascertain reproducibility and the quality of the catalyst. The experiment was repeated at least two independent times. Pseudo-first order rate constants were measured from the integration of the different Ru=C*H*-X signals. First-order fits were obtained for all experiments under these pseudo-first-order conditions. Second-order rate constants were calculated from pseudo-first-order rate constants, k_1 and k_2 measured were divided by the values obtained for hexene to give $k_1$rel and $k_2$rel as listed in Table 1.

6.3. Procedures

6.3.1. *cis*-Deca-1,7-diene-4-ol (4rac). To allylmagnesium bromide (1 M in Et_2O, 25 mL, 1.1 equiv.) at 0 °C was added *cis*-hept-4-enal (2.5 g, 22 mmol, 1 equiv.) dropwise. After 15 min at 0 °C and 20 min at rt was added MeOH (1 mL, 1.1 equiv.) to quench excess Grignard reagent. 1.2 N HCl (20 mL) was added and the organic phase was separated. The aqueous phase was extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to yield the crude alcohol in quantitative yield (pure by NMR and GC). ^{1}H NMR ($CDCl_3$): δ 5.75–5.9 (m, 1H), 5.3–5.5 (m, 2H), 5.1–5.2 (2m, 2H), 3.67 (pseudo q, 1H, *J*=6 Hz), 2–2.4 (m, 6H), 1.64 (br s, 1H), 1.45–1.6 (m, 2H), 0.97 (t, 3H, *J*=7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 134.8, 132.3, 128.4, 118.2, 70.3, 41.9, 36.4, 23.5, 20.5, 14.4. IR (film) ν_{max} cm^{-1} 3364, 3077, 3006, 2963, 2932, 2874, 1441, 1067. MS(EI, 70 eV): 154 (7), 136 (16), 113 (58), 95 (100), 41 (57). HRMS: Calcd for $C_{10}H_{18}O$: 154.13576 found: *M* 154.13593.

6.3.2. *anti*-3-Dimethylphenylsilyl-deca-1,7-diene-4-ol (5rac). To a solution of allyldimethylphenylsilane (3.6 g, 21 mmol, 1.15 equiv.) in THF (100 mL) was added *n*-BuLi 2.2 M in hexane (9.3 mL, 1.15 equiv.) dropwise at room temperature in 15 min. After 15 min, the solution was cooled to −78 °C and a solution of $ClTi(OiPr)_3$ (5.8 g, 1.25 equiv.) in THF (8 mL) was added dropwise. After 20 min at −78 °C, was added heptenal (2 g, 18 mmol, 1 equiv.). After 1.5 h of reaction, 45% NH_4F (75 mL) was added and stirring was continued overnight. The reaction mixture was filtered of Celite and the organic phase was separated. The aqueous phase was extracted with AcOEt. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Flash chromatography (SiO_2: CH_2Cl_2/hexane: 4:6) gave the homoallylic alcohol as a light yellow oil in 88% yield (pure by NMR, >99% by GC). TLC R_f 0.48 (Et_2O/hexane, 3:17, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.3–7.6 (m, 5H), 5.83 (ddd, 1H, *J*=17, 10.4, 10.4 Hz), 5.05 (dd, 1H, *J*=10.3, 2 Hz), 4.91 (dd, 1H, *J*=17, 2 Hz), 3.74 (pseudo q, 1H, *J*=4.8 Hz), 1.93–2.1 (m, 4H), 1.9 (dd, 1H, *J*=10.7, 4.4 Hz), 1.4–1.5 (m, 3H), 0.93 (t, 3H, *J*=7.4 Hz), 0.35 (s, 3H), 0.33 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 137.9, 135.1, 134, 132.2, 129.1, 128.4, 127.7, 115.5, 71.2, 42.1, 37.1, 23.6, 20.5, 14.3, −3.5, −3.9. IR (film) ν_{max} cm^{-1} 3570, 3463, 3070, 3004, 2961, 2874, 1248, 1112. MS(CI): 289 (2) $[M+1]^+$, 271 (24), 137 (67), 135 (100). Elem. Anal. Calcd for $C_{18}H_{28}OSi$ C 74.94, H 9.78 found: C 74.45, H 9.72.

6.3.3. *cis*-3-Dimethylphenylsilyl-deca-1,7-diene-4-yl acetate (6rac). To a solution of the alcohol **5rac** (2 g, 6.9 mmol, 1 equiv.) and pyridine (2.3 mL, 4 equiv.) in CH_2Cl_2 (50 mL) at 0 °C was added AcCl (1.5 mL, 3 equiv.) dropwise. The suspension was stirred for 1.5 h at rt Et_2O (50 mL) was added and the reaction mixture was filtered; The filtrate was concentrated under reduced pressure and Et_2O (100 mL) was added. The organic phase was washed twice with 1.2 N HCl and once with Na_2CO_3sat. The crude alcohol was obtained in quantitative yield (pure by NMR, 99% by GC). TLC R_f 0.76 (CH_2Cl_2, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.3–7.5 (m, 5H), 5.85 (ddd, 1H, *J*=17.1, 11.3, 11.3 Hz), 5.05 (dd, 1H, *J*=10, 2 Hz), 5.03 (dt, 1H, *J*=6.9, 3.8 Hz), 4.89 (dd, 1H, *J*=17, 1.9 Hz), 1.8–2.1 (m, 4H), 1.82 (s, 3H), 1.4–1.7 (m, 2H), 0.93 (t, 3H, *J*=7.5 Hz), 0.33 (s, 3H), 0.31 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.2, 137.3, 134.6,

133.9, 132.1, 129.1, 127.8, 127.6, 115.6, 73.7, 39.3, 33.9, 23, 20.5, 21.1, 14.3, −3.9, −4. IR (film) ν_{max} cm^{-1} 3072, 3051, 3007, 2962, 2934, 2874, 1739, 1237; MS(EI, 70 eV): 315 (2), 270 (2), 179 (16), 135 (100), 117 (57). Elem. Anal. Calcd for $C_{20}H_{30}O_2Si$: C 72.67, H 8.96 found: C 72.57, H 8.96.

6.3.4. *anti*-3-Dimethylphenylsilyl-oct-1,7-diene-4-ol (7rac). To a solution of the allylsilane (8 g, 45.4 mmol, 1.15 equiv.) in THF(150 mL) at rt was added 2.1 M BuLi (21.6 mL, 1.15 equiv.) dropwise. After 20 min, the orange solution was cooled to −78 °C and a solution of $ClTi(OiPr)_3$ (14.8 g, 1.25 equiv.) in THF (20 mL) was added dropwise over 10 min. After 15 min, the neat aldehyde (3.3 g, 40 mmol, 1 equiv.) was added over 5 min. After 2 h at −75 °C, the cooling bath was removed and 45% NH_4F (160 mL) were added. After 4 h of hydrolysis, Et_2O (100 mL) was added and the crude mixture was filtered of Celite. The solid residue was washed with Et_2O (4×50 mL) and the organic layer was separated. The aqueous phase was extracted once with Et_2O (100 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Flash chromatography (SiO_2: 100% CH_2Cl_2) gave the homoallylic alcohol in 63–75% yield (>99% pure by GC). For characterization see **19b**.

6.3.5. *anti*-3-Dimethylphenylsilyl-oct-1,7-diene-4-yl *t*-butyl-dimethylsilyl ether (8rac). A solution of the alcohol (2.2 g, 8.5 mmol, 1 equiv.) and TBDMSCl (1.5 g, 1.2 equiv.) in DMF (10 mL) was stirred at 50 °C for 36 h. Water (150 mL) was added and the reaction mixture was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (100%, hexane) gave the silyl ether in 83% yield (>99% d.e. and >99% pure by GC). TLC R_f 0.97 (CH_2Cl_2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.3–7.6 (m, 5H), 5.85 (ddd, 1H, J=17.3, 10.3, 10.3 Hz), 5.7 (ddt, 1H, J=17, 10.5, 6.5 Hz), 4.7–5 (m, 4H), 3.87 (ddd, 1H, J=8, 5, 3.3 Hz), 2.03 (dd, 1H, J=10.4, 3.3 Hz), 1.8–2.1 (m, 2H), 1.4–1.7 (m, 2H), 0.88 (s, 9H), 0.35 (s, 3H), 0.31 (s, 3H), 0.01 (s, 3H), −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.7, 138.5, 135.8, 134.1, 128.8, 127.5, 114.5, 114.4, 72.8, 40.4, 35.8, 29.8, 26.1, 18.2, −3.1, −3.7, −3.9. MS(EI, 70 eV): 319 (22), 317 (15), 209 (100), 135 (83). IR (film) ν_{max} cm^{-1} 3072, 3052, 2999, 2956, 2930, 2858, 1254, 1063. Elem. Anal. Calcd for $C_{22}H_{38}OSi_2$ C 70.52, H 10.22 found: C 70.40, H 10.52.

6.3.6. *anti*-3-Dimethylphenylsilyl-oct-1,7-diene-4-yl acetate (9rac). To a solution of the alcohol (3 g, 11.5 mmol, 1 equiv.) and pyridine (3.65 mL, 4 equiv.) in CH_2Cl_2 (75 mL) at 0 °C was added AcCl (2.46 mL, 3 equiv.) dropwise. After 30 min at rt, Et_2O (75 mL) was added, the reaction mixture was filtered of Celite and concentrated in vacuo. The residue was taken up in Et_2O (150 mL) and was washed twice with 1.2 N HCl and once with Na_2CO_3sat. The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude acetate (98% by GC) in quantitative yield. Filtration over SiO_2 (CH_2Cl_2 100%) gave analytically pure acetate in 95% yield (99% pure by GC). TLC R_f 0.8 (CH_2Cl_2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.3–7.5 (m, 5H), 5.85 (ddd, 1H, J=17.2, 10.4, 10.4 Hz), 5.7 (ddt, 1H, J=17, 10.4, 6.4), 4.8–5.1 (m, 5H), 2.03 (dd, 1H, J=10.7, 3.9 Hz), 1.85 (m, 2H), 1.85–2 (m, 2H), 1.82 (s, 3H), 1.4–1.7 (m, 2H), 0.33 (s, 3H), 0.31 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.2, 137.7, 134.5, 133.9, 129.1, 127.7, 137.3, 115.7, 114.7, 73.4, 39.4, 33.1, 29.6, 21.1, −4. IR (film) ν_{max} cm^{-1} 3072, 3001, 2956, 2857, 1739, 1237. MS(CI): 243 (40), 179 (23), 135 (68), 117 (100). Elem. Anal. Calcd for $C_{18}H_{26}O_2Si$ C 71.47, H 8.66 found: C 71.45, H 8.73.

6.3.7. 3-Cylcohexyl-oct-1,7-diene-4-yl *t*-butyldimethylsilyl ether (10rac). A solution of the alcohol **11rac** (594 mg, 2.85 mmol, 1 equiv.), imidazole (388 mg, 2 equiv.) and TBSCl (473 mg, 1.1 equiv.) in DMF (5 mL) was heated overnight at 45–50 °C. Water (50 mL) and Et_2O (40 mL) were added. The organic layer was separated and washed with 1.2 N HCl. Purification by flash chromatography (SiO_2: 100% hexane) gave 73% yield of the silyl ether as a colorless liquid (>99% by GC). TLC R_f 0.79 (hexane, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 5.78 (ddt, 1H, J=17, 10.2, 6.8 Hz), 5.68 (ddd, 1H, J=17.5, 9.9, 9.9 Hz), 3.85 (ddd, 1H, J=7.9, 5.5, 2.5 Hz), 0.88 (s, 9H), 0.7–2.1 (m, 16H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 138.7, 138.1, 116.4, 114.4, 71, 54.5, 36.7, 34.7, 31.8, 31.5, 29.7, 26.7, 26.5, 26.4, 25.9, 18.2, −3.8, −4.5. IR (KBr) ν_{max} cm^{-1} 3074, 2928, 2854, 1254, 1075. MS(EI, 70 eV): 307 (0.5) $[M-Me]^+$; 265 (76), 199 (100). HRMS Calcd for $C_{20}H_{38}OSi$ 323.277020 found: M 323.276936. Elem. Anal. Calcd for $C_{20}H_{38}OSi$ C 74.46, H 11.87 found: C 74.54, H 12.00.

6.3.8. 3-Cyclohexyl-oct-1,7-diene-4-ol (11rac). To a green suspension of $CrCl_2$ (1.23 g, 10 mmol, 2 equiv.) and 4-pentenal (420 mg, 5 mmol, 1 equiv.) in THF (20 mL) was added allylbromide (1.03 g, 5 mmol, 1 equiv.). After 15 h of reaction, 1.2 N HCl (10 mL) and Et_2O (20 mL) were added to the resulting purple reaction mixture. After 30 min of hydrolysis, the organic layer was separated and the aqueous phase extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (SiO_2: 100% CH_2Cl_2) gave the homoallylic alcohol in 61–71% yield. TLC R_f 0.5 (CH_2Cl_2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 5.84 (ddt, 1H, J=17.1, 10.3, 6.8 Hz), 5.7 (ddd, 1H, J=17.2, 10.2, 10.2 Hz), 5.2 (dd, 1H, J=10.3, 2.3 Hz), 5–5.1 (m, 2H), 3.74 (d pseudo q, 1H, J=9.3, 4.7 Hz), 2–2.2 (m, 2H), 1.41 (d, 1H, J=4.4 Hz), 0.8–1.8 (m, 13H). ^{13}C NMR ($CDCl_3$): δ 138.7, 136.9, 118.5, 114.7, 69.9, 56.1, 36.7, 34.4, 31.7, 29.9, 26.6, 26.54, 26.48 (note: the cHex shows diastereotopic carbons giving thus 5 signals instead of 3). IR (film) ν_{max} cm^{-1} 3385, 3075, 2925, 2853, 1641, 1449, 911. MS(CI): 415 (100) [M+M−1], 359 (12), 307 (48), 291 (72), 151 (40), 99 (10), 83 (28). Elem. Anal. Calcd for $C_{14}H_{24}O$ C 80.71, H 11.61 found: C 80.36, H 11.61.

6.3.9. Cyclohex-3-enol (12rac). To a refluxing solution of the diene **4rac** (120 mg, 0.78 mmol, 1 equiv.), was added **3** (10 mg, 1.6 mol%), in CH_2Cl_2 (0.7 mL). The reaction reached completion after less than 10 min (TLC and GC). The solvent was removed under reduced pressure to give a quantitative yield of crude cyclohexenol **12rac**[24] (>99% by GC). ^1H NMR ($CDCl_3$): δ 5.68 (dm, 1H, J=11.3 Hz), 5.56 (dm, 1H, J=10.6 Hz), 3.95 (br, 1H), 1.5–2.5 (m, 7H).

6.3.10. *cis*-2-Dimethylphenylsilyl-cyclohexy-3-enol (13rac). To a refluxing solution of the diene (365 mg, 1.27 mmol, 1 equiv.) in CH_2Cl_2 (16 mL) was added **3** (16 mg, 1.6 mol%) in CH_2Cl_2 (1 mL). After 41 h of reaction the solvent was evaporated under reduce pressure. Flash chromatography (SiO_2, hexane/Et_2O, 17:3) gave the cyclohexene in 86% yield (>99% by GC). For characterization see **13ent**.

6.3.11. 3-Dimethylphenylsilyl-deca-1,7-diene-4-yl acetate (14rac). *Via RCM of* **6rac**. To a refluxing solution of the diene (258 mg, 0.78 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added **3** (10 mg, 1.6 mol%) in CH_2Cl_2 (0.7 mL). After 23 h of reaction the solvent was evaporated under reduced pressure. Flash chromatography (SiO_2, hexane/Et_2O, 8:2) gave the acetate in 91% yield (>99% by GC).

Via RCM of **8rac**. To a solution of the diene (1.5 g, 4.96 mmol, 1 equiv.) in CH_2Cl_2 (35 mL) at rt was added **3** (15 mg, 0.3 mol%) in three portions in 20 min intervals. The reaction mixture was concentrated in vacuo and was stirred in MeOH (20 mL) for 45 min. The solvent was evaporated and flash chromatography gave the acetate in 88% yield (>99% yield). TLC R_f 0.45 (hexane/Et_2O, 8:2, $KMnO_4$). $[\alpha]_D^{23}=+108$ ($c=0.64$ in CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 7.3–7.6 (m, 5H), 5.6–5.7 (m, 1H, $J=10.1$, 3.3, 3.3 Hz), 5.5–5.6 (m, 1H, $J=10.1$, 3.3 Hz), 5.22 (ddd, 1H, $J=8$, 5.7, 3 Hz), 2.28 (m, 1H), 2–2.1 (m, 2H), 1.75–1.9 (m, 1H), 1.81 (s, 3H), 1.63 (d pseudo-t d, 1H, $J=13$, 7, 7, 3 Hz), 0.36 (s, 3H), 0.35 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.5, 138.4, 133.7, 128.9, 127.7, 125, 124.6, 71.9, 31.6, 26.4, 22.1, 21.1, −3, −3.2. IR (film) ν_{max} cm^{-1} 3068, 3031, 2962, 2913, 2840, 1732, 1247. MS(CI): 214 (2),179 (11), 137 (26), 135 (89), 117 (100), 80 (81). Elem. Anal. Calcd for $C_{16}H_{22}O_2Si$ C 70.03, H 8.08 found: C 69.91, H 8.19.

6.3.12. *cis*-2-Dimethylphenylsilyl-cyclohex-3-enyl *t*-butyldimethylphenylsilyl ether (15rac). To a refluxing solution of the diene **9rac** (292 mg, 0.78 mmol, 1 equiv.) in CH_2Cl_2 (1 mL) was added a solution of **3** (1 mL of a 3.2 mg cata/10 mL CH_2Cl_2 solution, 0.05 mol%). After completion, the flask was open to air for 1 h and the reaction mixture was concentrated in vacuo. Flash filtration over SiO_2 (100% hexane) gave **15rac** (98% yield, >99% pure by GC). For analyses see **22b**.

6.3.13. *cis*-2-Cyclohexyl-cyclohex-3-enyl *t*-butyldimethylsilyl ether (16rac). To a solution of the diene (252 mg, 0.78 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added Grubbs catalyst (1.6 mol%, 10 mg) in CH_2Cl_2 (0.7 mL). After 5 min of reaction, the solvent was removed under reduced pressure and the residue was chromatographed (SiO_2: 100% hexane) to give **16rac** in 98% yield. ^1H NMR ($CDCl_3$): δ 5.68 (dm, 1H, $J=11$ Hz), 5.61 (br d, 1H, $J=11$ Hz), 4.12 (br, 1H), 2.1–2.3 (m, 1H), 1.4–2 and 0.8–1.3 (m, 15H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 126.7, 126.5, 67.6, 46.3, 37.4, 31.9, 30.8, 29.8, 26.6, 25.9, 21.9, 18.2, −4, −5. IR (film) ν_{max} cm^{-1} 3031, 2926, 2854, 1252, 1079. MS(EI, 70 eV): 279 (1), 237 (100), 219 (12), 161 (24). HRMS: Calcd for $C_{18}H_{34}OSi$ 294.237894 found: *M* 294.237078.

6.3.14. Asymmetric allylation: typical procedure A. To a solution of allyldimethylphenylsilane (5.3 g, 30 mmol, 1.15 equiv.) in THF (40 mL) at rt was added 2.1 M *n*-BuLi (14.3 mL, 1.15 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (20 g, 32.6 mmol, 1.25 equiv.) in THF (150 mL) at −78 °C. After 30 min, neat aldehyde (1 equiv.) was added over 4 min. The reaction was continued for 3 h at −78 °C. AcOEt (50 mL) and 45% NH_4F (200 mL) were added and the heterogeneous mixture was filtered of Celite and the solid residue was washed with Et_2O (90 mL). The organic layer was separated and the aqueous phase was extracted twice with Et_2O (70 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Hexane (300 mL) was added to precipitate (*R*,*R*)-TADDOL. After 20 min stirring, the mixture was filtered. Evaporation of the solvent followed by flash chromatography gave the enantioenriched homoallylic alcohol.

6.3.15. (3*S*,4*R*)-*anti*-3-(Dimethyl-phenyl-silanyl)-hepta-1,6-dien-4-ol (19a). Following the typical procedure A. To a solution of allyldimethylphenylsilane (3.8 g, 22 mmol, 1 equiv.) in THF (33 mL) at rt was added 2.1 M *n*-BuLi (12 mL, 1.15 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (16.7 g, 27.2 mmol, 1.25 equiv.) in THF (125 mL) at −78 °C. After 30 min, 3-butenal (2 g in solution in 10 mL CH_2Cl_2, freshly synthesized and kept at −78 °C before use, 29 mmol, 1.15 equiv.) was added. Chromatography (SiO_2: CH_2Cl_2/cyclohexane, 3:2) 3.68 g (68% yield). $[\alpha]_D^{23}=-4.56$ ($c=1.23$ in $CHCl_3$). TLC R_f 0.57 (CH_2Cl_2: cyclohexane, 3:2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.48 (m, 2H), 7.28 (m, 3H), 5.80 (ddd, 1H, $J=17.4$, 10.5, 10.3 Hz), 5.65 (dddd, 1H, $J=17.1$, 10.3, 7.6, 6.8 Hz), 4.97 (m, 3H), 4.82 (ddd, 1H, $J=17.1$, 2.2, 0.7 Hz), 3.69 (m, 1H, $J=7.6$, 5.4, 3.7, 1.0 Hz), 2.09 (m, 2H), 1.83 (dd, 1H, $J=10.5$, 3.7 Hz), 1.53 (d, 1H, $J=1$ Hz), 0.37 (s, 3H), 0.33 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.3, 135.6, 135.3, 134.5, 129.5, 128.1, 118.2, 115.9, 70.7, 42.3, 42.0, −3.2, −3.6. IR (film) ν_{max} cm^{-1} 3577, 3464, 3071, 2972, 2902, 1639, 1625, 1427, 1248, 1113. MS(CI): 229 (49) $[M-OH]^+$, 209 (8), 205 (22), 135 (100), 127 (16), 94 (33), 79 (23), 75 (27). HRMS Calcd for $C_{15}H_{21}Si$ $[M-OH]^+$ 229.141469 found: *M* 229.141254. Elem. Anal. found: C 72.68, H 9.16 Calcd for $C_{15}H_{22}OSi$ C 73.11, H 9.00.

6.3.16. (3*S*,4*R*)-*anti*-3-(Dimethyl-phenyl-silanyl)-octa-1,7-dien-4-ol (19b). Following the typical procedure A. To a solution of allyldimethylphenylsilane (5.3 g, 30 mmol, 1.15 equiv.) in THF (40 mL) at rt was added 2.1 M *n*-BuLi (14.3 mL, 1.15 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (20 g, 32.6 mmol, 1.25 equiv.) in THF (150 mL) at −78 °C. After 30 min, neat 4-pentenal (2.2 g, 26.1 mmol, 1 equiv.) was added. $[\alpha]_D^{23}=-1$ ($c=1.1$ in CH_2Cl_2). TLC R_f 0.55 (CH_2Cl_2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.3–7.6 (m, 5H), 5.84 (ddd, 1H, $J=17$, 10.5, 10.5 Hz), 5.74 (ddt, 1H, $J=17$, 10, 6.7 Hz), 4.85–5.1 (m, 4H), 3.75 (m, 1H), 2.04 (pseudo q, 2H, $J=7$ Hz), 1.91 (dd, 1H, $J=10.4$, 4.4 Hz), 1.49 (pseudo q, 2H, $J=6.8$ Hz), 1.44 (d, 1H, $J=4.1$ Hz), 0.36 (s, 3H), 0.34 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.4, 135.1, 134.1, 129.1, 127.8, 127.9, 115.6, 114.6, 71, 42.1, 36.2, 30.2, −3.4, −3.9.

IR (film) ν_{max} cm^{-1} 3582, 3455, 3070, 3051, 2956, 2932, 1428, 1249, 1113. MS(CI): 261 (2) $[M+1]^+$, 243 (26), 153 (21), 137 (50), 135 (100), 109 (72). Elem. Anal. Calcd for $C_{16}H_{24}OSi$ C 73.79, H 9.29 found: C 73.68, H 9.29.

6.3.17. (3*S*,4*R*)-*anti*-3-(Dimethyl-phenyl-silanyl)-nona-1,8-dien-4-ol (19c). Following the typical procedure A. To a solution of allyldimethylphenylsilane (6.2 g, 35.2 mmol, 1.15 equiv.) in THF (47 mL) at rt was added 2.3 M *n*-BuLi (15.3 mL, 1.15 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (24.4 g, 37.6 mmol, 1.25 equiv.) in THF (175 mL) at −78 °C. After 30 min, neat 5-hexenal (3 g, 30.6 mmol, 1 equiv.) was added. Chromatography (SiO_2: AcOEt/PE, 5:95) 6.25 g (75% yield). TLC R_f 0.45 (CH_2Cl_2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.53 (m, 2H), 7.36 (m, 3H), 5.83 (ddd, 1H, *J*=17.1, 10.5, 10.2 Hz), 5.73 (ddt, 1H, *J*=17.0, 10.2, 6.7 Hz), 5.06 (dd, 1H, *J*=10.2, 1.9 Hz), 4.93 (m, 3H), 3.74 (m, 1H), 1.93 (m, 3H), 1.37 (m, 5H), 0.36 (s, 3H), 0.33 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.7, 137.9, 135.1, 133.9, 129.0, 127.7, 115.6, 114.4, 71.2, 42.1, 36.5, 33.4, 25.0, −3.4, −4.0. IR (film) ν_{max} cm^{-1} 3571, 3449, 3069, 2932, 2858, 1640, 1625, 1427, 1250, 1113, 1053, 998, 908, 832, 814, 733, 700. MS(CI): 257 (10) [M−OH]+, 209 (5), 205 (5), 179 (8), 135 (100), 122 (17), 107 (15), 81 (20), 75 (27). HRMS Calcd for $C_{17}H_{26}OSi$ $[M]^+$ 274.175294 found: *M* 274.174264.

6.3.18. (3*S*,4*R*)-*anti*-3-(Dimethyl-phenyl-silanyl)-deca-1,9-dien-4-ol (19d). Following the typical procedure A. To a solution of allyldimethylphenylsilane (5.4 g, 30.6 mmol, 1.15 equiv.) in THF (40 mL) at rt was added 2.3 M *n*-BuLi (13.3 mL, 1.15 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (21.2 g, 32.6 mmol, 1.25 equiv.) in THF (175 mL) at −78 °C. After 30 min, neat 6-heptenal (3 g, 26.7 mmol, 1 equiv.) was added. Chromatography (SiO_2: AcOEt/PE, 5:95) 5.15 g (67% yield). TLC R_f 0.42 (CH_2Cl_2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.56 (m, 2H), 7.38 (m, 3H), 5.85 (ddd, 1H, *J*=17.1, 10.5, 10.3 Hz), 5.78 (ddt, 1H, *J*=17.1, 10.2, 6.7 Hz), 5.07 (dd, 1H, *J*=10.3, 2.1 Hz), 4.96 (m, 3H),3.74 (m, 1H), 1.99 (m, 2H), 1.93 (dd, 1H, *J*=10.5, 4.5 Hz), 1.39 (m, 2H), 1.29 (m, 4H), 0.38 and 0.35 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.3, 138.4, 135.6, 134.4, 129.5, 128.2, 116.0, 114.7, 71.8, 42.5, 37.4, 34.1, 29.2, 25.6, −2.9, −3.5. IR (film) ν_{max} cm^{-1} 3582, 3445, 3071, 2930, 2856, 1641, 1625, 1428, 1249, 1113, 1046, 999, 902, 834, 815, 734, 701. MS(CI): 288 (5), 271 (3), 209 (7), 135 (100), 75 (21). HRMS: Calcd for $C_{18}H_{27}OSi$ $[M-H]^+$ 287.183119 found: *M* 287.183177.

6.3.19. (3*S*,4*R*)-*anti*-3-(Dimethyl-phenyl-silanyl)-tetradeca-1,13-dien-4-ol (19e). Following the typical procedure A. To a solution of allyldimethylphenylsilane (0.59 g, 3.36 mmol, 1.15 equiv.) in THF (40 mL) at rt was added 2.2 M *n*-BuLi (1.52 mL, 1.15 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (2.33 g, 3.58 mmol, 1.25 equiv.) in THF (175 mL) at −78 °C. After 30 min, neat undecylenic aldehyde (0.5 g, 3 mmol, 1 equiv.) was added. Chromatography (SiO_2: AcOEt/PE, 5:95) gave 0.73 g of colorless oil (71% yield). TLC R_f 0.61 (CH_2Cl_2/PE, 1:1, $KMnO_4$). $[\alpha]_D^{23}=-0.4$ (*c*=1.04 in $CHCl_3$). ^1H NMR ($CDCl_3$): δ 7.56 (m, 2H), 7.38 (m, 3H), 5.86 (ddd, 1H, *J*=17.1, 10.5, 10.2 Hz), 5.82 (ddt, 1H, *J*=17.1, 10.2, 6.7 Hz), 5.08 (dd, 1H, *J*=10.2, 2 Hz), 5.02 (ddt, 1H, *J*=17.3, 2, 1.5 Hz), 4.95 (ddt, 1H, *J*=10.2, 2, 1.2 Hz), 4.94 (dd, 1H, *J*=17.1, 2 Hz), 3.74 (m, 1H, *J*=11.7, 4.6 Hz), 2.06 (td, 2H, *J*=7.5, 6.7 Hz), 1.93 (dd, 1H, *J*=10.5, 4.5 Hz), 1.2 (m, 12H), 0.38 and 0.35 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.6, 138.4, 135.6, 134.4, 129.5, 128.2, 115.3, 114.5, 71.9, 42.5, 37.5, 34.2, 29.89, 29.87, 29.8, 29.5, 29.3, 26.1, −2.9, −3.1. IR (film) ν_{max} cm^{-1} 3573, 3447, 3070, 2920, 2850, 1640, 1625, 1427, 1250, 1113, 1054, 998, 907, 832, 814, 733, 700. MS(CI): 345 $[M+H]^+$ (5), 286 (15), 271 (100), 209 (72), 152 (17), 137 (95), 135 (36), 75 (37). HRMS Calcd for $C_{22}H_{35}OSi$ $[M-H]^+$ 343.245719 found: *M* 343.244560.

6.4. Protection of the alcohol by an acetyl group: typical procedure B

To solution of the alcohol (1 equiv.) and pyridine (3.5 equiv.) in CH_2Cl_2 (43 equiv.) at 0 °C is added dropwise acetyl chloride (2.5 equiv.). The reaction mixture is stirred at room temperature for 4 h. CH_2Cl_2 is added and the organic phase is washed twice with HCl 0.1 N. The aqueous phase is extracted with CH_2Cl_2 and the combined organic layers are washed twice with NH_4Clsat, dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography gave the acetyl protected alcohol.

6.4.1. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-nona-1,8-diene-4-yl acetate (20c). Following the typical procedure B. The reaction was carried out on 0.3 g of **19a** (1.09 mmol). Flash chromatography (SiO_2: CH_2Cl_2) gave 0.332 g of colorless oil (95% yield). TLC R_f 0.75 (CH_2Cl_2, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.46 (m, 2H), 7.34 (m, 3H), 5.82 (ddd, 1H, *J*=17.1, 10.5, 10.2 Hz), 5.71 (ddt, 1H, *J*=16.8, 10.2, 7 Hz), 4.84–5.05 (m, 5H), 2.01 (dd, 1H, *J*=10.5, 3.6 Hz), 1.94 (dt, 2H, *J*=7.2, 6.6 Hz), 1.82 (s, 3H), 1.46 (m, 2H), 1.26 (m, 2H), 0.49 and 0.47 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.4, 138.5, 137.5, 134.8, 134.1, 129.2, 127.8, 115.7, 114.8, 74.0, 39.7, 33.7, 33.6, 24.8, 21.4, −3.6, −3.7. MS(CI): 288 (9), 257 (15), 179 (34), 154 (17), 135 (100), 123 (25), 117 (89), 107 (16), 80 (17). HRMS Calcd for $C_{17}H_{25}Si$ $[M-AcO^-]^+$ 257.172554 found: M 257.173270.

6.4.2. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-tetradeca-1,13-diene-4-yl acetate (20e). Following the typical procedure B. The reaction was carried out on 0.5 g of **19e** (1.45 mmol). Flash chromatography (SiO_2: CH_2Cl_2) gave 0.545 g of colorless oil (97% yield). ^1H NMR ($CDCl_3$): δ 7.48 (m, 2H), 7.37 (m, 3H), 5.38 (m, 2H), 4.96 (m, 5H), 2.04 (m, 3H), 1.84 (s, 3H), 1.47 (m, 2H), 1.37 (m, 2H), 1.21 (m, 10H), 0.34 and 0.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.2, 139.1, 137.6, 134.8, 133.9, 129.1, 127.7, 115.5, 114.1, 74.1, 39.6, 34.0, 33.8, 29.4 (2 carbons), 29.3, 29.1, 28.9, 25.2, 21.1, −3.8, −3.9. IR (film) ν_{max} cm^{-1} 3071, 2921, 2852, 1736, 1640, 1626, 1461, 1427, 1370, 1237, 1113, 1019, 904, 833, 700. MS(CI): 329 (100) $[M+1-CH_3CO-CH_3]^+$, 327 (33), 192 (8), 179 (10), 135 (39), 117 (41).

6.4.3. Protection of the alcohol by a TBS: typical procedure C. To a solution of TBSCl (1.5 equiv.) in

DMF (12 equiv.) was added imidazole (4 equiv.). The reaction mixture was heated to 60 °C for 1.2 h before to add the alcohol (1 equiv.). The reaction was monitored by GC. After 48 h the reaction was complete and 1/2 volume of NH_4Clsat were added. The aqueous phase was extracted with pentane (3×1 volume) and the combined organic phase were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography gave the TBS-protected alcohol.

6.4.4. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-hepta-1,6-diene-4-yl *t*-butyldimethylsilyl ether (21a). Following the typical procedure C. The reaction was carried out on 1.7 g of **19a** (6.9 mmol). Flash chromatography (SiO_2: PE) gave 2.12 g of colorless oil (85% yield, >99% pure by GC). $[\alpha]_D^{23}=+2.91$ ($c=0.55$ in $CHCl_3$). TLC R_f 0.58 (PE, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.51 (m, 2H), 7.35 (m, 3H), 5.90 (ddd, 1H, $J=17.4$, 10.4, 10.2 Hz), 5.64 (dddd, 1H, $J=17.1$, 10.2, 7.5, 6.7 Hz), 4.99 (m, 3H), 4.77 (dd, 1H, $J=17.4$, 1.7 Hz), 3.91 (ddd, 1H, $J=8.0$, 4.8, 2.8 Hz), 2.32 (m, 1H, $J=13.0$, 8.0, 7.5 Hz), 2.21 (m, 1H, $J=13.0$, 6.7, 4.8 Hz), 2.08 (dd, 1H, $J=10.4$, 2.8 Hz), 0.89 (s, 9H), 0.36 and 0.31 (s, 3H), 0.04 and 0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.9, 135.9, 135.4, 134.5, 129.2, 127.9, 117.5, 115.3, 73.2, 41.9, 40.5, 26.5, 18.6, −2.8, −3.3, −3.4, −3.5. IR (film) ν_{max} cm^{-1} 3072, 2956, 2858, 1626, 1472, 1428, 1361, 1254, 1090, 939, 834, 774, 732. MS(FAB): 359 (2), 345 (1), 319 (14), 303, 251, 209 (24), 193, 147, 135 (100). HRMS: Calcd for $C_{21}H_{35}O_1Si$ (M−H): 359.22264 found: *M* 359.22193.

6.4.5. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-octa-1,7-diene-4-yl *t*-butyldimethylsilyl ether (21b). Following the typical procedure C. The reaction was carried out on 6 g of **19b** (23 mmol). Flash chromatography (SiO_2: PE) gave 7.77 g of colorless oil (90% yield, >99% pure by GC). $[\alpha]_D^{23}=-1.00$ ($c=1.16$ in $CHCl_3$). TLC R_f 0.46 (hexane, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.3–7.6 (m, 5H), 5.85 (ddd, 1H, $J=17.3$, 10.3, 10.3 Hz), 5.7 (ddt, 1H, $J=17$, 10.5, 6.5 Hz), 4.7–5 (m, 4H), 3.87 (ddd, 1H, $J=8$, 5, 3.3 Hz), 2.03 (dd, 1H, $J=10.4$, 3.3 Hz), 1.8–2.1 (m, 2H), 1.4–1.7 (m, 2H), 0.88 (s, 9H), 0.35 (s, 3H), 0.31 (s, 3H), 0.01 (s, 3H), −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.7, 138.5, 135.8, 134.1, 128.8, 127.5, 114.5, 114.4, 72.8, 40.4, 35.8, 29.8, 26.1, 18.2, −3.1, −3.7, −3.9. IR (film) ν_{max} cm^{-1} 3072, 3052, 2999, 2956, 2930, 2858, 1254, 1063. MS(EI, 70 eV): 319 (22), 317 (15), 209 (100), 135 (83). MS(CI): 375 $[M+H]^+$ (1), 359 (2), 319 (7), 251 (14), 209 (100), 189 (14), 147 (16), 135 (14). HRMS: Calcd for $C_{22}H_{39}OSi_2$ $[M+H]^+$ 375.253948 found: *M* 375.253989. Elem. Anal. Calcd for $C_{22}H_{38}OSi_2$ C 70.52, H 10.22 found: C 70.40, H 10.52.

6.4.6. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-nona-1,8-diene-4-yl *t*-butyldimethylsilyl ether (21c). Following the typical procedure C. The reaction was carried out on 1.6 g of **19c** (5.8 mmol). Flash chromatography (SiO_2: PE) gave 1.65 g of colorless oil (72% yield, 98% pure by GC). $[\alpha]_D^{23}=-3.87$ ($c=1.12$ in $CHCl_3$). TLC R_f 0.53 (PE, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.52 (m, 2H), 7.36 (m, 3H), 5.86 (ddd, 1H, $J=17.2$, 10.5, 10.2 Hz), 5.74 (ddt, 1H, $J=17.2$, 10.2, 6.7 Hz), 4.95 (m, 3H), 4.77 (dd, 1H, $J=17.2$, 1.7 Hz), 3.86 (m, 1H, $J=7.9$, 3.5 Hz), 2.03 (dd, 1H, $J=10.2$, 3.5 Hz), 1.94 (m, 2H, $J=6.7$ Hz), 1.51 (m, 1H), 1.41 (m, 1H), 1.28 (m, 1H), 1.14 (m, 1H), 0.87 (s, 9H), 0.34 and 0.29 (s, 3H), 0.00 and −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.3, 139.2, 136.4, 134.5, 129.1, 127.9, 114.84, 114.82, 73.6, 41.1, 36.7, 34.1, 26.5, 25.2, 18.7, −2.6, −3.29, −3.31and −3.5. IR (film) ν_{max} cm^{-1} 3070, 2927, 2857, 1641, 1625, 1471, 1463, 1427, 1413, 1253, 1112, 1061, 907, 834, 772, 732. MS(CI): 388 (1) $[M]^+$, 331 (12), 319 (21), 209 (85), 193 (17),135 (100), 107 (15), 75 (73), 73 (57). HRMS: Calcd for $C_{23}H_{40}OSi_2$ (M−H): 387.25394 found: *M* 387.25367.

6.4.7. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-deca-1,9-diene-4-yl *t*-butyldimethylsilyl ether (21d). Following the typical procedure C. The reaction was carried out on 1.6 g of **19d** (5.5 mmol). Flash chromatography (SiO_2: cyclohexane) gave 1.76 g of colorless oil (79% yield, 99% pure by GC). $[\alpha]_D^{23}=-2.53$ ($c=0.83$ in $CHCl_3$). TLC R_f 0.47 (PE, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 2H), 7.34 (m, 3H), 5.84 (ddd, 1H, $J=17.1$, 10.4, 10.2 Hz), 5.77 (ddt, 1H, $J=17.1$, 10.2, 6.7 Hz), 4.94 (m, 3H), 4.74 (m, 2H, $J=17.1$, 2.2 Hz), 3.83 (m, 1H, $J=7.9$, 4.5, 3.5 Hz), 1.99 (m, 3H), 1.52 (m, 1H), 1.39 (m, 1H), 1.20 (m, 4H), 0.87 (s, 9H), 0.34 and 0.29 (s, 3H), 0.00 and −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.3, 139.2, 136.3, 134.4, 129.1, 127.9, 114.8, 114.7, 73.8, 41.1, 37.2, 34.2, 29.4, 26.6, 25.5, 18.8, −2.5, −3.1, −3.2, −3.3. IR (film) ν_{max} cm^{-1} 3070, 2950, 2928, 2855, 1624, 1471, 1462, 1427, 1253, 1111, 1059, 1019, 905, 834, 773, 700. MS(FAB): 425 (3) $[M+Na]^+$, 401 (6) $[M-H]^+$, 387 (3), 345 (10), 329 (9), 319 (20), 288 (92), 267 (8), 251 (9), 227 (5), 209 (100). HRMS: Calcd for $C_{24}H_{42}OSi_2$ (M−H): 401.26959 found: *M* 401.26943.

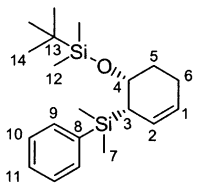
6.4.8. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-tetradeca-1,13-diene-4-yl *t*-butyldimethylsilyl ether (21e). Following the typical procedure C. the reaction was carried out on 2 g of **19e** (5.8 mmol). Flash chromatography (SiO_2: PE) gave 2.39 g of colorless oil (90% yield, 98% pure by GC). TLC R_f 0.68 (PE, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.52 (m, 2H), 7.35 (m, 3H), 5.85 (m, 2H), 4.98 (d, 2H, $J=17.1$ Hz), 4.94 (d, 2H, $J=10.2$ Hz), 4.76 (d, 1H, $J=17.1$ Hz), 3.85 (m, 1H, $J=7.5$, 3.7 Hz), 2.05 (m, 3H), 1.40 (m, 2H), 1.25 (m, 12H), 0.89 (s, 9H), 0.37 and 0.32 (s, 3H), 0.02 and 0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.6, 139.3, 136.5, 134.5, 129.1, 127.9, 114.7, 114.5, 73.8, 41.0, 37.3, 34.2, 30.0, 29.9, 29.8, 29.5, 29.3, 26.5, 25.8, 18.6, −2.6, −3.2, −3.3, −3.5. IR (film) ν_{max} cm^{-1} 3070, 2927, 2854, 1640, 1625, 1471, 1462, 1427, 1413, 1252, 1061, 907, 834, 772, 732. MS(CI): 459 (20) $[M+H]^+$, 444 (27), 401 (30), 319 (72), 283 (18), 251 (67), 209 (77), 189 (42), 135 (100). HRMS: Calcd for $C_{28}H_{50}OSi_2$ 458.340023 found: *M* 458.340914.

6.4.9. (1*R*,2*S*)-2-(Dimethylphenylsilanyl)-cyclohex-3-enol (13ent). To a boiling solution of **19b** (2.5 g, 0.96 mmol, 1 equiv.) in CH_2Cl_2 (120 mL) was added **3** (400 mg, 5 mol%) in CH_2Cl_2 (3 mL). After 2 h of reaction the conversion was complete. The solvent was evaporated under reduced pressure. Flash chromatography (SiO_2, CH_2Cl_2/EP, 1:1) gave 1.92 g of **13ent** (87% yield). $[\alpha]_D^{23}=+81.9$ ($c=0.7$ in CH_2Cl_2). TLC R_f 0.35 (Et_2O/hexane, 3:17, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.3–7.7 (m, 5H), 5.67 (dm, 1H, $J=10.5$ Hz), 5.57 (d, 1H, $J=10.8$ Hz), 4.2 (br s, 1H), 2–2.2 (m, 3H), 1.5–1.8 (m, 2H), 1.44 (d, 1H, $J=6$ Hz), 0.40 an 0.38 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.8,

134, 128.9, 127.7, 125.1, 124.7, 68, 34.3, 29.8, 21.2, −3.1, −3.2. IR (film) ν_{max} cm^{-1} 3578, 3456, 3068, 3020, 2952, 2921, 2841, 1427, 1247. MS(CI): 215 (32), 155 (20), 137 (61), 135 (100). HRMS: Calcd for $C_{14}H_{19}Si$ (M+1−$H_2$0) 215.125604 found: *M* 215.12500.

6.4.10. (1*R*,2*S*)-2-(Dimethylphenylsilanyl)-cyclopent-3-enyl *t*-butyldimethylphenylsilyl ether (22a). To a solution of **21a** (1.6 g, 4.43 mmol, 1 equiv.) in CH_2Cl_2 (215 mL) was added **3** (73 mg, 2 mol%) in CH_2Cl_2 (2 mL). After 5 min of reaction the flask was open to air for 1 h then the solvent was evaporated under reduced pressure. Flash chromatography (SiO_2: hexane) gave 1.45 g of **22a** (98% yield). $[\alpha]_D^{23}$=+94.2 (*c*=0.75 in $CHCl_3$). TLC R_f 0.67 (PE, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.54 (m, 2H), 7.33 (m, 3H), 5.51 (m, 2H), 4.96 (dd, 1H, *J*=8.5, 7.3 Hz), 2.49 (m, 2H, *J*=8.5 Hz), 2.18 (m, 1H, *J*=14.9, 7.3, 2.2 Hz), 0.87 (s, 9H), 0.38 and 0.35 (s, 3H), 0.03 and −0.02 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.5, 134.3, 131.9, 128.8, 127.8, 125.7, 77.5, 42.75, 42.72, 26.5, 18.5, −1.8, −2.7, −4.34, −4.36. IR (film) ν_{max} cm^{-1} 3053, 2955, 2929, 2857, 1471, 1427, 1362, 1253, 1094, 898, 835, 776, 700. MS(CI): 331 (5) $[M-H]^+$, 251 (44), 209 (100), 189 (11), 147 (18), 135 (39).

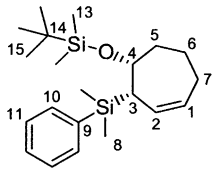
6.4.11. (1*R*,2*S*)-2-(Dimethylphenylsilanyl)-cyclohex-3-enyl *t*-butyldimethylphenylsilyl ether (22b). To a solution of **21b** (292 mg, 0.78 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added **3** (10 mg, 1.6 mol%) in CH_2Cl_2 (0.7 mL). After 2 min of reaction the flask was open to air then the solvent was evaporated under reduced pressure. Flash chromatography (SiO_2: hexane) gave 265 mg of **22b** (98% yield). $[\alpha]_D^{23}$=+74.1 (*c*=1.35 in CH_2Cl_2). TLC R_f 0.63 (hexane, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.53 (m, 2H), 7.33 (m, 3H), 5.47 (m, 1H, *J*=9.9, 4.5, 3.1 Hz), 5.41 (m, 1H, *J*=9.9, 4.6, 1.8 Hz), 4.22 (ddd, 1H, *J*=10.5, 6.5, 4.1 Hz), 2.19 (m, 1H), 2.04 (m, 2H), 1.59 (m, 2H), 0.88 (s, 9H), 0.38 and 0.37 (s, 3H), 0.05 and 0.00 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140, 134.2, 128.5, 127.5, 127.2, 123.6, 71.5, 36.1, 30.6, 24.7, 26.2, 18.4, −1.3, −2, −4.3, −4.8. IR (film) ν_{max} cm^{-1} 3096, 3050, 3024, 2955, 2930, 2857, 1252, 1081. MS(CI): 345 (100) $[M-H]^+$, 303 (25), 283 (33), 269 (44), 251 (57), 227 (60), 209 (69), 189 (25), 135 (51), 80 (32). Elem. Anal. Calcd for $C_{20}H_{34}OSi_2$ C 69.10, H 9.89 found: C 69.10, H 9.98.



Measured and calculated ^{3}J values (in Hz) with MM3 force field

H	^{3}J measured (Hz)	^{3}J calculated (Hz)	
		Cluster 1	Cluster 2
2-3	**4.6**	**4.6**	2.8
3-4	**4.1**	**6.0**	2.9
4-5	**6.5**	**3.4**	1.8
4-5'	**10.5**	**11.6**	4.7
1-6	**3.0**	**3.1**	4.6
1-6'	**3.5**	**4.5**	3.0
ΔE (kJ/mol)		**0**	2.25

6.4.12. (1*R*,2*S*)-2-(Dimethylphenylsilanyl)-cyclohept-3-enyl *t*-butyldimethylphenylsilyl ether (22c). To a solution of **21c** (200 mg, 0.514 mmol, 1 equiv.) in toluene (30 mL) was added **3** (32 mg, 7.5 mol%) in toluene (1 mL). The reaction mixture was heated at 60 °C for 2 h then the flask was open to air then the solvent was evaporated under reduced pressure. Flash chromatography (SiO_2: hexane) gave 173 mg of **22c** (93% yield). $[\alpha]_D^{23}$=+48.27 (*c*=0.98 in $CHCl_3$). TLC R_f 0.5 (Cyclohexane, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.57 (m, 2H), 7.35 (m, 3H), 5.65 (m, 1H, *J*=11.6, 7.39, 4.01 Hz), 5.53 (m, 1H, *J*=11.6, 8.5, 2.5 Hz), 3.95 (ddd, 1H, *J*=11.3, 4.5, 4.1 Hz), 2.35 (dd, 1H, *J*=8.5, 4.1 Hz), 2.05 (dddd, 1H, *J*=16.1, 7.4, 6.7, 2.5 Hz), 1.88 (m, 1H, *J*=13.7, 11.0, 4.0 Hz), 1.73 (m, 1H, *J*=11.0, 4.0 Hz), 1.67 (m, 1H, *J*=16.1, 4.1, 2.5 Hz), 1.55 (m, 1H, *J*=14.0, 6.7, 2.0 Hz), 1.23 (m, 1H, *J*=8.0, 2.5 Hz), 0.92 (s, 9H), 0.47 and 0.43 (s, 3H), 0.06 and 0.05 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 140.2, 134.2, 129.5, 128.6, 128.5, 127.4, 75.2, 42.4, 38.9, 28.3, 26.1, 24.4, 18.2, −0.6, −1.1, −4.7, −4.8. IR (film) ν_{max} cm^{-1} 3070, 2950, 2868, 1471, 1392, 1254, 1141, 1070, 1021, 832, 791. MS(FAB): 360 (1), 303(2), 209 (73), 193 (20), 134.9 (100), 106.8 (11), 93.9 (82), 78.9 (30), 74.9 (30). HRMS: Calcd for $C_{21}H_{35}OSi_2$ (M−H): 359.22264 found: *M* 359.22213.



Measured and calculated ^{3}J values (in Hz) with MM3 force field

H	^{3}J measured (Hz)	^{3}J calculated (Hz)				
		Cluster 1	Cluster 2	Cluster 3	Cluster 4	Cluster 5
2-3	**8.55**	**6.0**	5.4	4.8	2.7	5.9
3-4	**4.1**	**3.7**	0.2	2.9	3.2	1.6
4-5	**4.51**	**2.5**	1.9	5.4	5.8	8.9
4-5'	**11.29**	**11.6**	4.9	10.5	1.5	6.6
5-6	**11.0**	**5.8**	13.5	9.6	5.6	8.3
5-6'	**4.00**	**1.5**	2.5	8.7	1.7	0.4
5'-6	**4.00**	**1.7**	2.0	8.5	6.0	0.5
5'-6'	**11.00**	**13.4**	5.0	0.4	12.0	12.4
6-7	**6.7**	**4.5**	12.9	12.9	6.2	1.7
6-7'	**2.00**	**2.4**	1.4	1.3	1.2	5.6
6'-7	**2.5**	**2.3**	1.3	1.2	1.3	5.5
6'-7'	**8.00**	**13.1**	5.9	6.2	12.9	12.0
7-1	**7.39**	**6.3**	4.4	2.6	5.4	3.2
7'-1	**4.00**	**2.8**	6.6	6.1	2.8	4.5
ΔE (kJ/mol)		**0**	2.03	5.57	9.51	11.61

6.4.13. (3*S*,4*R*)-*anti*-3-Dimethylphenylsilyl-dodeca-1,9-diene-4-yl *t*-butyldimethylsilyl ether (26). *(3S,4R)-anti-3-(Dimethyl-phenyl-silanyl)-dodeca-1,9-dien-4-ol.* Following the typical procedure A. To a solution of allyldimethylphenylsilane (2 g, 11.3 mmol, 1.1 equiv.) in THF (25 mL) at rt was added 2.2 M *n*-BuLi (5.15 mL, 1.1 equiv.) dropwise over 10 min. After 20 min, the yellow solution was

transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (7.6 g, 11.8 mmol, 1.15 equiv.) in THF (30 mL) at −78 °C. After 30 min, neat cis-6-nonenal (1.72 mL, 10.3 mmol, 1 equiv.) was added. Chromatography (SiO_2: AcOEt/PE, 4:96) 2.08 g (64% yield). $[\alpha]_D^{23}$=+1.36 (*c*=1.1 in $CHCl_3$). TLC R_f 0.54 (CH_2Cl_2, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.54 (m, 2H), 7.36 (m, 3H), 5.83 (ddd, 1H, *J*=17.2, 10.5, 10.4 Hz), 5.33 (m, 2H), 5.05 (dd, 1H, *J*=10.4, 2.1 Hz), 4.91 (dd, 1H, *J*=17.2, 2.1 Hz), 3.72 (m, 1H), 2.01 (m, 4H), 1.90 (dd, 1H, *J*=10.5, 4.5 Hz), 1.32 (m, 6H), 0.94 (t, 2H, *J*=7.6 Hz), 0.36 and 0.33 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.0, 135.2, 133.8, 131.7, 129.0 (2 carbons), 127.7, 115.5, 71.5, 42.2, 37.1, 29.7, 27.3, 25.4, 20.5, 14.3, −3.3, −3.9. IR (film) ν_{max} cm^{-1} 3446, 3070, 2969, 2869, 1716, 1625, 1428, 1380, 1250, 1142, 1021, 900, 834, 701. MS(CI): 315 (6) [M−H]+, 299 (3), 271 (10), 247 (15), 229 (5), 209 (7), 205 (10), 187 (14), 135 (100), 81 (45). HRMS: Calcd for $C_{20}H_{31}OSi$ [M−H]$^+$ 315.214419 found: *M* 315.2144612. (**26**) Following the typical procedure C. The reaction was carried out on 0.77 g of (3*S*,4*R*)-*anti*-3-(dimethyl-phenyl-silanyl)-dodeca-1,9-dien-4-ol (2.44 mmol). Flash chromatography (SiO_2: cyclohexane) gave 0.67 g of colorless oil (63% yield). ^{1}H NMR ($CDCl_3$): δ 7.50 (m, 2H), 7.34 (m, 3H), 5.84 (ddd, 1H, *J*=17.2, 10.4, 10.2 Hz), 5.32 (m, 2H), 4.94 (dd, 1H, *J*=10.2, 2.1 Hz), 4.75 (dd, 1H, *J*=17.2, 2.1 Hz), 3.84 (m, 1H, *J*=8.0, 4.5, 3.2 Hz), 1.99 (m, 5H, *J*=7.6 Hz), 1.51 (m, 1H), 1.39 (m, 1H), 1.17 (m, 4H), 0.96 (t, 3H, *J*=7.6 Hz), 0.88 (s, 9H), 0.35 and 0.30 (s, 3H), 0.01 and −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.8, 135.9, 134.1, 131.6, 129.1, 128.7, 127.5, 114.4, 73.3, 40.6, 36.7, 29.7, 27.1, 26.1, 25.1, 20.5, 18.2, 14.4, −3.1, −3.6, −3.7, −3.9. MS(CI): 431 (19) [M+1]$^+$, 430 (15) [M], 416 [M−Me]$^+$, 373 (44), 319 (100) [M−$(CH_2)_4$−C≡C−Et]$^+$, 299 (8), 295 (10), 251 (71), 209 (84), 189 (35), 135 (100). HRMS: Calcd for $C_{26}H_{47}OSi_2$ [M+H]$^+$ 431.316548 found: *M* 431.314734.

6.4.14. 2-(Dimethyl-phenyl-silanyl)-1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-but-3-en-1-ol (28). Following the typical procedure A. To a solution of allyldimethyl-phenylsilane (2.7 g, 15.5 mmol, 1.1 equiv.) in THF (30 mL) at rt was added 2.2 M *n*-BuLi (7 mL, 1.1 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (10.4 g, 16.2 mmol, 1.15 equiv.) in THF (40 mL) at −78 °C. After 30 min, the neat alcohol **28** (2.2 g, 14 mmol, 1 equiv.) was added. Chromatography (SiO_2: CH_2Cl_2) 3.1 g (55% yield). $[\alpha]_D^{23}$=−33.4 (*c*=0.99 in $CHCl_3$). TLC R_f 0.42 (CH_2Cl_2, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.52 (m, 2H), 7.36 (m, 3H), 5.99 (ddd, 1H, *J*=17.1, 10.8, 10.2 Hz), 5.70 (ddd, 1H, *J*=17.1, 10.2, 8.5 Hz), 5.28 (ddd, 1H, *J*=17.1, 1.6, 0.7 Hz), 5.22 (ddd, 1H, *J*=10.2, 1.6, 0.7 Hz), 4.98 (dd, 1H, *J*=10.2, 2.0 Hz), 4.79 (ddd, 1H, *J*=17.1, 2.0 Hz), 4.39 (dd, 1H, *J*=8.5, 6.1 Hz), 4.01 (dd, 1H, *J*=8.5, 6.1 Hz), 3.69 (ddd, 1H, *J*=8.5, 2.6, 2.5 Hz), 2.15 (dd, 1H, *J*=2.6, 1.9 Hz), 1.90 (ddd, 1H, *J*=10.8, 2.5, 1.9 Hz), 1.44 (s, 3H), 1.32 (s, 3H), 0.37 (s, 3H), 0.31 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.1, 134.9, 134.8, 134.5, 129.4, 128.0, 119.2, 115.2, 108.9, 80.7, 78.7, 70.0, 37.9, 28.5, 25.9, −3.4, −3.7. IR (film) ν_{max} cm^{-1} 3490, 3070, 2986, 2902, 1624, 1471, 1427, 1371, 1246, 1114, 1068, 835. MS(CI): 331 (1) [M−H]+, 317 (4) [M−Me]+, 259 (19), 257 (23), 205 (31), 203 (36), 144 (17), 137 (56), 135 (100), 124 (28), 98 (24), 75 (34), 68 (45). HRMS: Calcd for $C_{19}H_{28}O_3SiNa$ (M+Na) 355.17054 found: *M* 355.17023.

6.4.15. Acetic acid 2-(dimethyl-phenyl-silanyl)-1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-but-3-enyl ester (29). Following the typical procedure B. The reaction was carried out on 1.2 g of **28** (3.25 mmol). Flash chromatography (SiO_2, CH_2Cl_2/PE, 3:2) gave 1.08 g of colorless oil (89% yield). $[\alpha]_D^{23}$=+2.91 (*c*=0.96 in $CHCl_3$). TLC R_f 0.83 (CH_2Cl_2/PE, 3:2, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.44 (m, 2H), 7.35 (m, 3H), 5.94 (ddd, 1H, *J*=17.1, 10.7, 10.1 Hz), 5.83 (ddd, 1H, *J*=17.1, 10.1, 9.1 Hz), 5.05 (dd, 1H, *J*=10.1, 1.7 Hz), 4.83 (dd, 1H, *J*=17.1, 1.7 Hz), 4.39 (dd, 1H, *J*=8.5, 5.9 Hz), 4.19 (dd, 1H, *J*=8.8, 5.9 Hz), 2.00 (dd, 1H, *J*=10.7, 2.4 Hz), 1.78 (s, 3H), 1.43 and 1.27 (s, 3H), 0.32 and 0.27 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.1, 137.2, 134.9, 134.5, 134.4, 129.6, 128.0, 119.6, 116.4, 109.2, 79.0, 78.7, 70.6, 37.5, 28.3, 26.0, 21.4, −3.4, −4.2. IR (film) ν_{max} cm^{-1} 3071, 2958, 1743, 1626, 1428, 1371, 1233, 1113, 1048, 874, 835, 757, 735. MS(FAB): 397 (100) [M+Na]$^+$, 329 (32), 288 (17), 267 (22), 257 (47), 237 (17), 217 (21), 209 (46). HRMS: Calcd for $C_{21}H_{30}O_4SiNa$ 397.18110 found: *M* 397.18095.

6.4.16. Acetic acid 5-(dimethyl-phenyl-silanyl)-2,2-dimethyl-3a,4,5,7a-tetrahydro-benzo[1,3]dioxol-4-yl ester (30). To a solution of **29** (840 mg, 0.22 mmol, 1 equiv.) in CH_2Cl_2 (30 mL) were added 2nd generation Grubbs' catalyst (160 mg, 8 mol%, 0.018 mmol). The reaction mixture was heated at reflux and argon was bubbled for 2 h. Flash chromatography (SiO_2: CH_2Cl_2) gave 632 mg (80% yield) of **30** as a colorless oil. $[\alpha]_D^{23}$=+5.32 (*c*=1.39 in $CHCl_3$). TLC R_f 0.19 (CH_2Cl_2, $KMnO_4$). ^{1}H NMR ($CDCl_3$): δ 7.5 (m, 2H), 7.37 (m, 3H), 5.87 (dd, 1H, *J*=9.9, 5.5 Hz), 5.80 (ddd, 1H, *J*=9.9, 3.4, 1.4 Hz), 5.07 (dd, 1H, *J*=9.2, 6.4 Hz), 4.39 (dd, 1H, *J*=6.6, 3.4 Hz), 4.01 (dd, 1H, *J*=9.2, 6.6 Hz), 2.63 (dd, 1H, *J*=6.4, 5.5 Hz), 1.78 (s, 3H), 1.42 (s, 3H), 1.30 (s, 3H), 0.36 (s, 3H), 0.35 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 171.2, 137.6, 134.3, 131.6, 129.8, 128.3, 122.2, 109.4, 75.2, 75.0, 72.8, 41.3, 32.5, 28.4, 26.0, 21.3, −2.3, −2.6. IR (film) ν_{max} cm^{-1} 3069, 2924, 2852, 1744, 1624, 1459, 1369, 1230, 1112, 1049, 1018, 834, 812, 733, 701. MS(FAB): 369 (50) [M+Na]$^+$, 355 (10), 341 (11), 329 (100), 288 (29), 280 (23), 271 (14), 267 (13), 245 (11), 229 (19), 226 (17), 223 (27), 209 (97), 207 (36). HRMS: Calcd for $C_{19}H_{26}O_4SiNa$ (M+Na) 369.1498 found: *M* 369.1510.

6.5. Addition of dicholorocarbene: typical procedure D

To a mixture of the cyclic allylsilane (0.62 mmol, 1 equiv.) and Et_3BnNCl (15 mg, 0.065 mmol, 0.1 equiv.) in $CHCl_3$ (4 mL) was added 50% NaOH (1 mL) under vigorous stirring. After 15 h, water (4 mL) was added and the organic layer was separated. The aqueous phase was extracted with $CHCl_3$. The combined organic phases were dried over $MgSO_4$ and concentred in vacuo. Purification by flash chromatography gave the dichlorocyclopropane.

6.5.1. (1*R*,2*S*,3*R*,5*R*)-3-(*tert*-Butyl-dimethyl-silanyloxy)-6,6-dichloro-2-(dimethyl-phenyl-silanyl)-bicyclo[3.1.0]-hexane (31). Following procedure D, the reaction was carried out on 206 mg (0.62 mmol) of **22a**. Chromatography

(SiO_2: cyclohexane) gave 252 mg of colorless oil (98% yield). $[\alpha]_D^{23}=-10.1$ ($c=1.3$ in $CDCl_3$). TLC R_f 0.64 (cyclohexane, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.56 (m, 2H), 7.36 (m, 3H), 4.60 (ddd, 1H, $J=7.5$, 7.0, 5.3 Hz), 2.23 (ddd, 1H, $J=14.3$, 7.0, 0.6 Hz), 2.10 (ddd, 1H, $J=8.1$, 6.5, 0.6 Hz), 2.05 (dd, 1H, $J=7.5$, 1.5 Hz), 1.98 (dd, 1H, $J=8.1$, 1.5 Hz), 1.91 (ddd, 1H, $J=14.3$, 6.5, 5.3 Hz), 0.85 (s, 9H), 0.41 and 0.39 (s, 3H), 0.01 and −0.06 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.7, 134.2, 129.2, 128.2, 78.4, 70.3, 39.6, 38.8, 36.5, 35.9, 26.5, 18.5, −1.2, −2.1, −4.1, −4.3. IR (film) ν_{max} cm^{-1} 3071, 2954, 2929, 2857, 1471, 1427, 1361, 1255, 1143, 1110, 1058, 888, 834, 778, 731, 700. MS(CI): 414 (2) $[M]^+$, 379 (2) $[M-Cl]^+$, 325 (5), 283 (7), 251 (35), 209 (75), 189 (30), 154 (40), 135 (71), 113 (47), 75 (15), 59 (100). HRMS Calcd for $C_{20}H_{32}Cl_2OSi_2$ 414.136878 found: *M* 414.137426.

6.5.2. (1*R*,2*S*,3*R*,6*R*)-7,7-Dichloro-2-dimethylphenylsilyl-bicyclo[4.1.0]heptan-3-yl acetate (32). *Acetic acid 2-(dimethylphenylsilanyl)-cyclohex-3-enyl ester*. To a solution of **13ent** (374 mg, 1.6 mmol, 1 equiv.) and pyridine (0.39 mL, 3 equiv.) in CH_2Cl_2 (6 mL) at 0 °C was added AcCl (0.23 mL, 2 equiv.) dropwise. After 1 h at rt, Et_2O (7 mL) was added, the reaction mixture was filtered and concentrated in vacuo. The residue was taken up in Et_2O (12 mL), filtered, washed twice with 1.2 N HCl (3 mL) and once with Na_2CO_3sat (3 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to afford the crude acetate. Filtration over SiO_2 (hexane/Et_2O, 8:2) gave pure acetate in 92% yield (>99% by GC, 92% ee by HPLC) $[\alpha]_D^{23}=+108$ ($c=0.64$ in CH_2Cl_2). For analyses see **14rac**. (**32**) Following procedure D, the reaction was carried out on 170 mg (0.62 mmol) of acetic acid 2-(dimethylphenylsilanyl)-cyclohex-3-enyl ester. Chromatography (SiO_2: hexane 90:10 AcEt) gave **32** in 84% yield (93% ee by HPLC, only one isomer detected by NMR, GC and HPLC). $[\alpha]_D^{23}=-4$ ($c=0.5$ in CH_2Cl_2). TLC R_f 0.3 (hexane/AcOEt, 9:1, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.3–7.6 (m, 5H), 4.98 (ddd, 1H, $J=3.9$, 2.5, 2.5 Hz), 1.92 (s, 3H), 1.3-1.4 and 1.6–1.9 (m, 6H), 1.17 (dd, 1H, $J=5$, 2.8 Hz), 0.42 (s, 3H), 0.39 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.2, 136.7, 133.8, 129.4, 128, 67.9, 67.3, 26, 25.6, 23.7, 23.7, 13.8, 21.2, −3.9, −4. IR (film) ν_{max} cm^{-1} 3070, 3049, 3014, 2957, 2861, 1737, 1372, 1239, 1207. MS(EI, 70 eV): 179 (17), 135 (100), 117 (92), 127 (49), 43 (37). Elem. Anal. Calcd for $C_{17}H_{22}Cl_2O_2Si$ C 57.14, H 6.21, Cl 19.93 found: C 57.23, H 6.22, Cl 19.93.

6.5.3. (1*R*,2*S*,3*R*,7*R*)-3-(*tert*-Butyl-dimethyl-silanyl-oxy)-8,8-dichloro-2-(dimethyl-phenyl-silanyl)-bicyclo-[5.1.0]octane (33). Following procedure D, the reaction was carried out on 224 mg (0.62 mmol) of **22c**. Chromatography (SiO_2: cyclohexane) gave 250 mg of colorless oil (98% yield) as a 10:1 mixture of diastereosiomers. $[\alpha]_D^{23}=-12.8$ ($c=1.1$ in $CHCl_3$). TLC R_f 0.59 (PE, $KMnO_4$). ^1H NMR (C_6D_6): δ 7.66 (m, 2H), 7.32 (m, 3H), 4.22 (dd, 1H, $J=4.8$, 1.4 Hz), 1.99 (m, 1H, $J=11.6$, 11.6 Hz), 1.99 (m, 1H, $J=12.6$, 6.8 Hz), 1.82 (m, 1H, $J=13$, 4.8 Hz), 1.77 (m, 1H, $J=11.6$, 11.6, 6.8 Hz), 1.72 (m, 1H, $J=13$, 13, 12.7 Hz), 1.33 (m, 1H, $J=13$, 12.6, 11.6 Hz), 1.29 (m, 1H, $J=13$, 3.4 Hz), 1.17 (d, 1H, $J=11.6$ Hz), 1.01 (s, 9H), 0.9 (m, 1H, $J=13$, 12.7, 3.4, 1.4 Hz), 0.63 and 0.56 (s, 3H), 0.04 and −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.3, 134.5, 129.4, 128.2, 71.3, 69.8, 42.1, 35.1, 33.4, 32.0, 27.3, 26.6, 21.9, 18.6, −2.5, −2.5, −4.1, −4.3. IR (film) ν_{max} cm^{-1} 3069, 2954, 2856, 1471, 1427, 1255, 1089, 1043, 1017, 916, 830, 772, 731, 700, 607. MS(FAB): 441 $[M-H]^+$ (1), 385 (1), 327 (2), 307 (2), 288, 255 (6), 251, 228, 209 (65), 193, 179, 147, 135 (95), 105, 93, 73. HRMS: Calcd for $C_{22}H_{36}OSi_2$-Cl_2 442.168178 found: *M* 442.167339.

6.5.4. 3-(*tert*-Butyl-dimethyl-silanyloxy)-2-(dimethyl-phenyl-silanyl)-bicyclo[4.1.0]heptane-7-carboxylic acid ethyl ester (34). *Compound* **22b** (300 mg, 0.831 mmol, 1 equiv.) was added to a suspension of copper acetylacetonate (4.5 mg, 0.017 mmol, 2 mol%) in freshly dried and degassed toluene (1 mL). The mixture was heated at 90 °C and ethyl diazoacetate (118 mg, 0.998 mmol, 1.2 equiv.) in toluene (2 mL) was added over 3 h thanks to a syringe pomp. The brown reaction mixture was cooled to room temperature and the solvent was removed under reduce pressure (temperature of the water bath below 35 °C). The resulting oil was treated with 500 mg of alumine to remove the catalyst. Pentane was added before filtration and concentration. The oil was chromatographed on SiO_2 (AcOEt/PE: 2.5:97.5) to give 266 mg (71% yield) of **34**.. $[\alpha]_D^{23}=+44.11$ ($c=1.33$ in $CHCl_3$). TLC R_f 0.28 (AcOEt/PE: 3:97, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.54 (m, 2H), 7.31 (m, 3H), 4.06 (qd, 2H, $J=7.2$, 2.3 Hz), 3.93 (m, 1H, $J=6$, 3.3, 1.8 Hz), 2.14 (m, 1H, $J=13.7$, 11.3, 6.5, 1.8 Hz), 1.70 (m, 1H, $J=14.4$, 6.5 Hz), 1.70 (m, 1H, $J=9.7$, 5.8, 4.3 Hz), 1.62 (m, 1H, $J=13.7$, 6, 5.8 Hz), 1.52 (m, 1H, $J=9.7$, 4.3, 3.3 Hz), 1.30 (dd, 1H, $J=4.3$, 4.3 Hz), 1.23 (m, 1H, $J=3.3$, 3.3 Hz), 1.20 (t, 3H, $J=7.2$ Hz), 1.14 (m, 1H, $J=13.7$, 11.3, 6.5, 1.8 Hz), 0.90 (s, 9H), 0.38 and 0.37 (s, 3H), 0.01 and −0.06 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 174.3, 138.9, 133.8, 128.6, 127.6, 66.6, 60.0, 31.5, 28.9, 27.9, 26.1, 21.9, 21.7, 18.2, 17.0, 14.2, −2.9, −3.4, −4.1, −4.4. IR (film) ν_{max} cm^{-1} 2954, 2858, 1723, 1427, 1317, 1300, 1255, 1200, 1174, 1113, 1036, 986, 831, 700. MS(FAB): 455 (9) $[M+Na]^+$, 431 (5), 387 (9), 355 (7), 345 (6), 301 (16),288 (10), 251 (13), 223 (7), 209 (100). HRMS: Calcd for $C_{24}H_{39}O_3Si_2$ (M−H): 431.24377 found: *M* 431.24350.

6.5.5. (1*R*,4*R*)-[4-(*tert*-Butyl-dimethyl-silanyloxy)-cyclohex-2-enyl]-phenyl-methanol (35). To a solution of 2,6-di-*t*-butyl-4-methylpyridine (266 mg, 1.29 mmol, 1.5 equiv.) and $TMSNTf_2$ (305 mg, 0.86 mmol, 1 equiv.) in CH_2Cl_2 (5 mL) at −78 °C was added benzaldehyde (97 μL, 0.95 mmol, 1.1 equiv.). After 10 min, **22c** (300 mg, 0.86 mmol, 1 equiv.) was added and the reaction mixture was stirred at −78 °C for 1 h. HCl (5 mL) were added and the organic phase was washed with $NaHCO_3$sat. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. The oil was purified by chromatography (SiO_2, CH_2Cl_2/EP: 1:1). The product was isolated as a 3:1 mixture of epimers. Analyses of enriched major isomer: TLC R_f 0.18 (CH_2Cl_2/EP, 2:3, $KMnO_4$). ^1H NMR ($CDCl_3$): 7.38 (m, 5H), 5.95 and 5.65 (dm, 1H, $J=10.3$, 1.5 Hz), 4.26 (d, 1H, $J=8.1$ Hz), 4.18 (m, 1H), 2.44 (m, 1H), 1.85 (m, 1H), 1.40 (m, 1H, $J=13$, 9, 3 Hz), 1.28 (m, 1H) 1.09 (m, 1H, $J=13$, 10, 3 Hz), 0.88 (s, 9H), 0.06 and 0.05 (s, 3H). ^{13}C NMR ($CDCl_3$):143.4, 133.2, 130.2, 129.8, 128.0, 127.6, 79.7, 68.5, 44.3, 32.6, 26.3, 24.6, 18.6, −4.1, −4.3. MS(FAB): 341 (21) [M+Na]+, 317 (8), 301 (37), 281 (62), 267 (31), 241 (21), 221 (100), 211 (25).

HRMS Calcd for $C_{19}H_{30}O_2NaSi$ 341.191279 found: *M* 341.192469.

6.5.6. Epoxidation of 22b. To a solution of *m*-cpba (100 mg, 0.57 mmol, 1 equiv.), in CH_2Cl_2 (6 mL) at −20 °C was added **22b** (200 mg, 0.57 mmol, 1 equiv.). After 6 h the solvent was evaporated and the solid was taken back in pentane. The solution was filtrated and concentrated before chromatography (SiO_2, AcOEt/PE: 5:95) to give 78 mg of **37** and 27 mg of **36**. (**36**) TLC R_f 0.4. (AcOEt/PE, 5:95, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.56 (m, 2H), 7.35 (m, 3H), 4.10 (dd, 1H, *J*=4.9, 4.7 Hz), 3.15 (m, 1H, *J*=4.1 Hz), 3.11 (m, 1H, *J*=4.1 Hz), 2.03 (m, 1H, *J*=15.3, 7.3, 2.8 Hz), 1.94 (m, 1H, *J*=15.3, 6 Hz), 1.84 (d, 1H, *J*=4.7 Hz), 1.49 (ddd, 2H, *J*=7.3, 6, 4.9 Hz), 0.88 (s, 9H), 0.44 and 0.41 (s, 3H), 0.03 and −0.03 (s, 3H). ^{13}C NMR ($CDCl_3$): δ=139.01, 134.3, 129.34, 128.21, 67.53, 54.3, 52.65, 32.95, 28.00, 26.61, 20.93, 18.69, −1.63, −1.39, −3.86, −3.96. MS(FAB): 385, 361, 345, 305, 231, 209, 135 (100). HRMS: Calcd for $C_{20}H_{33}O_2Si_2$ $[M-H]^+$: 361.201912 found: *M* 361.201613. (**37**) TLC R_f 0.64. (AcOEt/PE, 5:95, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.59 (m, 2H), 7.38 (m, 3H), 5.64 (m, 2H, *J*=10.5, 7.5, 2.3 Hz), 4.09 (m, 2H), 1.77 (m, 2H), 1.62 (m, 2H), 0.88 (s, 9H), 0.395 and 0.392 (s, 3H), 0.05 (s, 6H). ^{13}C NMR ($CDCl_3$): δ=138.75, 133.91, 132.93, 131.92, 129.89, 128.17, 66.55, 66.18, 29.07, 28.79, 26.25, −0.61, −0.65, −4.23, −4.24. MS(FAB): 385, 361, 345, 231, 209, 193, 147, 135 (100). HRMS: Calcd for $C_{20}H_{33}O_2Si_2$ (M−H): 361.201912 found: *M* 361.203290.

6.5.7. (1*S*,4*R*)-4-(*tert*-Butyl-dimethyl-silanyloxy)-cyclohex-2-enol (39). To a suspension of **38** (100 mg, 0.4 mmol, 1 equiv.) in CH_2Cl_2 (2 mL) was added **22b** (138 mg, 0.4 mmol, 1 equiv.) in solution in CH_2Cl_2 (1 mL). After 1 h, the solvent was evaporated and the mixture was taken back in pentane, the precipitate was filtrated and the solvent evaporated. Chromatography (SiO_2, AcOEt/PE: 25:75) to give **39**[26] (55 mg, 60% yield) TLC R_f 0.45 (AcOEt/PE, 25:75, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 5.71 (pseudo q, 2H, *J*=10.5, 4.8 Hz), 4.26 (m, 2H, *J*=6.2, 1.6 Hz), 2.12 and 1.99 (m, 1H, *J*=12.1, 4.8, 1.3 Hz), 1.59 (broad s, 1H), 1.49 (m, 2H, *J*=12.9, 10.7, 8.3, 1.6 Hz), 0.89 (s, 9H), 0.07 (s, 6H). ^{13}C NMR ($CDCl_3$): δ=134.2, 132.1, 67.4, 66.9, 31.4, 31.3, 26.2, 18.6, −4.3.

6.5.8. (1*R*,2*R*,3*R*,4*R*)-4-(*tert*-Butyl-dimethylsilanyl-oxy)-3-(dimethyl-phenyl-silanyl)-cyclopentane-1,2-diol (40). To a vigorously stirred solution of water (2.5 mL) and $K_2OsO_4.2H_2O$ (~8 mg, 2.5 mol%) was added $NMO{\cdot}H_2O$ (199 mg, 1.7 equiv.). The solution turned yellow. To this mixture was added a solution of **22a** (287 mg, 0.86 mmol, 1 equiv.) in THF (2.5 mL). The solution turned brown. After 8 h at rt, $NaHSO_3$ (100 mg) and magnesol (100 mg) were added to the resulting yellow solution. After stirring for 30 min at rt, the pH was adjusted to 1 with H_2SO_4 and the reaction mixture was filtered of Celite. The magnesol was washed twice with water and twice AcOEt. The organic phase was separated and the aqueous phase extracted with AcOEt. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (SiO_2, PE/AcOEt: 8:2) gave a colorless viscous oil. Traces of solvent were removed and the solid mixture was then triturated in hexane to obtain the diol **40** as a white solid (180 mg, 56% yield). $[\alpha]_D^{23}$=−8.2 (*c*=1.03 in CH_2Cl_2). TLC R_f 0.64 (cyclohexane, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.56 (m, 2H), 7.36 (m, 3H), 4.60 (ddd, 1H, *J*=7.5, 7.0, 5.3 Hz), 2.23 (ddd, 1H, *J*=14.3, 7.0, 0.6 Hz), 2.10 (ddd, 1H, *J*=8.1, 6.5, 0.6 Hz), 2.05 (dd, 1H, *J*=7.5, 1.5 Hz), 1.98 (dd, 1H, *J*=8.1, 1.5 Hz), 1.91 (ddd, 1H, *J*=14.3, 6.5, 5.3 Hz), 0.85 (s, 9H), 0.41 and 0.39 (s, 3H), 0.01 and −0.06 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 139.7, 134.2, 129.2, 128.2, 78.4, 70.3, 39.6, 38.8, 36.5, 35.9, 26.5, 18.5, −1.2, −2.1, −4.1, −4.3. IR (film) ν_{max} cm^{-1} 2955, 2857, 1471, 1427, 1255, 1110, 1068, 888, 700. MS(CI): 365 (4) $[M-H]^+$, 349 (68), 331 (14), 271 (15), 251 (72), 209 (100), 197 (53), 149 (63), 135 (37), 83 (40). Elem. Anal. Calcd for $C_{19}H_{34}O_3Si_2$ C 62.24, H 9.35 found: C 62.54, H 9.64.

6.5.9. (1*R*,2*R*,3*R*,4*R*)-2-Dimethylphenylsilylcyclo-hexa-1,3,4-triol (41). To a vigorously stirred solution (pink colored) of water (3 mL) and $K_2OsO_4.2H_2O$ (~8 mg, 2 mol%) was added $NMO{\cdot}H_2O$ (261 mg, 1.7 equiv.). The solution turned yellow. To this mixture was added a solution of the cyclohexene (260 mg, 1.12 mmol, 1 equiv.) in THF (3 mL). The solution turned brown. After 8 h at rt, $NaHSO_3$ (100 mg) and magnesol (100 mg) were added to the resulting yellow solution. After stirring for 30 min at rt, the pH was adjusted to 1 with H_2SO_4 and the reaction mixture was filtered of Celite. The magnesol was washed twice with water and twice AcOEt. The organic phase was separated and the aqueous phase extracted with AcOEt. The combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (SiO_2: AcOEt) gave the triol as a colorless viscous oil. Traces of solvent were removed by freeze-pump-thaw cycles. The solid mixture was then triturated in hexane to obtain the triol **41** as a white solid in 80% yield (93% ee by HPLC). Mp 102 °C. $[\alpha]_D^{23}$=−62.7 (*c*=0.38 in CH_2Cl_2). TLC R_f 0.35 (AcOEt, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.2–7.7 (m, 5H), 3.97 (m, 1H), 3.9 (dd, 1H, *J*=11.3, 2.7 Hz), 3.82 (m, 1H), 1.82–1.96 (m, 1H), 1.6–1.77 (m, 2H), 1.49 (dd, 1H, *J*=11.3, 2.8 Hz), 1.3–1.41 (m, 1H), 0.389 and 0.385 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 141.4, 135.5, 129.5, 128.5, 71.4, 71.2, 69.9, 33.6, 29.1, 27.1, −1.4, −2.2. IR (film) ν_{max} cm^{-1} 3547, 3427, 3069, 3023, 2960, 2939, 2897, 1241, 1185, 1069. MS(CI): 417 (89), 399 (10), 265 (100), 247 (16), 151 (24). Elem. Anal. Calcd for $C_{14}H_{22}O_3Si$ C 63.12, H 8.32 found: C 63.01, H 8.34.

6.5.10. Chemical correlation from (1*R*,2*R*,3*R*,3*R*)-2-dimethylphenylsilyl-cyclohexa-1,3,4-triol: synthesis of (3a*R*,7a*S*)-2,2-dimethyl-3a,4,5,7a-tetrahydro-1,3-benzo-dioxole (42). To a solution of **41** (140 mg, 0.53 mmol, 1 equiv.) and dimethoxypropane (97 μL, 1.5 equiv.) in CH_2Cl_2 (5 mL) was added $PTSA{\cdot}H_2O$ (cat.). GC analysis indicated completion of the reaction after 10 min at rt. A solution of $NaHCO_3$sat was added and the organic layer was separated. The aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to give the crude ketal in 93% yield (99% pure by GC, 1% of the *cis*-isopropylidene ketal was identified by GC/GC-MS). The product was dissolved in THF (5 mL) and NaH (60% dispersion in mineral oil, 25 mg, 1.3 equiv.) was added. The reaction mixture was stirred for 5 h at 55 °C. Water and Et_20 were added and the organic phase was separated. The

aqueous phase was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (SiO_2: hexane 90:10 Et_2O) gave the cyclohexene **42** in 82% yield (91% ee by GC on the crude after chromatography). $[\alpha]_D^{23}=+17.5$ ($c=0.68$ in CH_2Cl_2). TLC R_f 0.35 (hexane/Et_2O, 9:1 $KMnO_4$ ^1H NMR ($CDCl_3$): δ 5.92 (dt, 1H, $J=10.1$, 3.6 Hz), 5.71 (dm, 1H, $J=10.1$ Hz), 4.5 (m, 1H), 4.27 (ddd, 1H, $J=6$, 6, 3.8 Hz), 1.7–2.3 (m, 4H), 1.42 (s, 3H), 1.37 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 131.2, 125.4, 108.3, 73.1, 71.4, 28.1, 26.4, 25.5, 20.8. MS(EI, 70 eV): 233 (28) [M−acetone], 171 (14), 139 (54), 137 (100), 135 (76).

6.5.11. 2,2-Dimethyl-propionic acid 2-oxo-ethyl ester (43). (+/−)-*Solketal pyvaloate*. Pyvaloyl chloride (44.7 mL, 363 mmol, 1 equiv.) was added dropwise to a gently agitated solution of solketal (48 g, 363 mmol, 1 equiv.) and pyridine (32.3 mL, 399 mmol, 1.1 equiv.) in CH_2Cl_2 (363 mL) at −10 °C. After standing two days at room temperature the solution was washed thoroughly twice with 30 mL of water and dried with $MgSO_4$. The CH_2Cl_2 was distilled off under normal pressure at the lowest possible bath temperature. The residue was fractionally distillated in vacuo (135–138 °C/60–80 mm Hg) to yield 65.7 g (83%) as a colourless oil. ^1H NMR ($CDCl_3$): δ 4.3 (m, 1H), 4.15 (dd, 1H, $J=11.5$, 4.6 Hz), 4.11 (dd, 1H, $J=11.5$, 5.38 Hz), 4.06 (dd, 1H, $J=8.3$, 6.4 Hz), 3.76 (dd, 1H, $J=8.3$, 6.1 Hz), 1.43 (s, 3H), 1.36 (s, 3H), 1.21 (s, 9H).

1-*Pivaloyloxypropane*-2, 3-*diol*. To a solution of (+/−)-solketal pyvaloate (65 g, 300 mmol, 1 equiv.) in THF (250 mL) was added a solution of HCl 2 N (75 mL). The mixture was then stirred overnight. After the reaction mixture was saturated with NaCl, the products were extracted with AcOEt (×4) and the organic layer was dried over $MgSO_4$ to give 52 g (98%) of 1-pivaloyloxypropane-2,3-diol[25] as colourless oil. ^1H NMR ($CDCl_3$): δ 4.44 (broad s, 2H), 4.12 (m, 2H), 3.91 (m, 1H), 3.68 (dd, 1H, $J=11.5$, 3.3 Hz), 3.57 (dd, 1H, $J=11.5$, 6.1 Hz), 1.19 (s, 9H). (**43**) To a solution of 1-pivaloyloxypropane-2,3-diol (10 g, 56.7 mmol, 1 equiv.) in CH_2Cl_2 (85 mL) was added a solution of sodium periodate (13.3 g, 62.4 mmol, 1.1 equiv.) in water (85 mL). This biphasic solution was stirred for 3–4 h. The organic layer was separated and concentrated to give an oil which was distilled (87 °C/65 mm Hg). The aldehyde was obtained as an colorless oil (8.9 g, 71% yield). ^1H NMR ($CDCl_3$): δ 9.59 (s, 1H), 4.65 (s, 2H), 1.27 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 195.9, 177.9, 68.5, 38.7, 27.1.

6.5.12. (2*R*,3*S*)-2,2-Dimethyl-propionic acid 3-(dimethyl-phenyl-silanyl)-2-hydroxy-pent-4-enyl ester (45). Following the typical procedure A. To a solution of allyldimethylphenylsilane (2.6 g, 15 mmol, 1.1 equiv.) in THF (33 mL) at rt were added 2.3 M *n*-BuLi (6.5 mL, 15 mmol, 1.1 equiv.) dropwise over 10 min. After 20 min, the yellow solution was transferred via canula over 10 min to a suspension of (*R*,*R*)-TiClCpTADDOL (10 g, 15.6 mmol, 1.15 equiv.) in THF (40 mL) at −78 °C. After 30 min, **43** (2 g, 13.5 mmol, 1 equiv.) was added. Chromatography (SiO_2, CH_2Cl_2/PE: 2:3) gave **45** as a colorless oil: 2.44 g (56% yield). $[\alpha]_D^{23}=-1.6$ ($c=1$ in $CHCl_3$). TLC R_f 0.41 (CH_2Cl_2/PE, 2:3, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.55 (m, 2H,), 7.36 (m, 3H), 5.89 (ddd, 1H, $J=17.1$, 10.5, 10.2 Hz), 5.03 (dd, 1H, $J=10.2$, 1.9 Hz), 4.89 (dd, 1H, $J=17.1$, 1.9 Hz), 3.96 (m, 3H), 2.00 (s, 1H), 1.93 (dd, 1H, $J=10.5$, 2.4 Hz), 1.18 (s, 9H), 0.39 and 0.34 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 178.9, 137.8, 134.4, 134.2, 129.5, 128.1, 116.1, 69.9, 69.1, 39.3, 39.1, 27.5, −3.3, −3.7. IR (film) ν_{max} cm^{-1} 3491, 3071, 2961, 1730, 1625, 1481, 1428, 1399, 1284, 1256, 1160, 815, 734, 700. MS(CI): 319 (4) $[M-H]^+$, 209 (10), 177 (46), 175 (72), 168 (54), 159 (100), 137 (53), 135 (94), 115 (38), 85 (31), 75 (86), 67 (88), 57 (61). HRMS: Calcd for $C_{18}H_{27}O_3Si$ $[M-H]^+$ 319.172948 found: *M* 319.173362.

6.5.13. (2*R*,3*S*)-2,2-Dimethyl-propionic acid 2-(tert-butyl-dimethyl-silanyloxy)-3-(dimethyl-phenyl-silanyl)-pent-4-enyl ester (46a). Following the typical procedure C. The reaction was carried out on 1.5 g of **45** (4.7 mmol). Flash chromatography (SiO_2, CH_2Cl_2/PE: 1:4) gave 1.28 g of colorless oil (63% yield). $[\alpha]_D^{23}=-0.5$ ($c=0.5$ in $CHCl_3$). TLC R_f 0.73 (CH_2Cl_2/PE: 1:4, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.84 (m, 2H), 7.34 (m, 3H), 5.88 (ddd, 1H, $J=17.1$, 10.5, 10.2 Hz), 4.99 (dd, 1H, $J=10.2$, 2.2 Hz), 4.80 (dd, 1H, ^3J(H,H)=17.1, 2.2 Hz), 4.00 (m, 2H), 3.87 (m, 1H), 2.09 (dd, 1H, $J=10.5$, 2.4 Hz), 1.18 (s, 9H), 0.87 (s, 9H), 0.36 (s, 3H), 0.31 (s, 3H), 0.04 (s, 3H), −0.01 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 178.5, 138.3, 135.1, 134.4, 129.4, 128.1, 115.9, 70.8, 66.9, 39.7, 39.1, 27.6, 26.3, 18.5, −2.8, −3.5, −3.7, −3.8. IR (film) ν_{max} cm^{-1} 3072, 2958, 2858, 1734, 1480, 1397, 1362, 1255, 1150, 1004, 902, 835, 700. MS(CI): 419 (21) [M−Me]+, 377 (67), 333 (21), 319 (60), 275 (25), 233 (51), 199 (47), 159 (100), 135 (47), 67 (60). HRMS: Calcd for $C_{23}H_{39}O_3Si_2$ $[M-Me]^+$ 419.243777 found: *M* 419.243722.

6.5.14. (2*R*,3*S*)-2,2-Dimethyl-propionic acid 3-(dimethyl-phenyl-silanyl)-2-triisopropylsilanyloxy-pent-4-enyl ester (46b). To a solution of TiPSCl (2 mL, 9.36 mmol, 1.5 equiv.) in DMF (6 mL) was added imidazole (1.7 g, 25 mmol, 4 equiv.). The reaction mixture was heated to 60 °C for 1:2 h before to add **45** (2 g, 6.24 mmol, 1 equiv.). The reaction was monitored by GC. After 48 h NH_4Clsat (5 mL) were added. The aqueous phase was extracted with pentane (3×5 mL), the combined organic phases were dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (SiO_2, CH_2Cl_2/PE, 1:4) gave 1.77 g of **46b** as a colorless oil (59% yield). $[\alpha]_D^{23}=18$ ($c=1.11$ in $CHCl_3$). TLC R_f 0.27 (CH_2Cl_2/PE: 1:4, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.48 (m, 2H), 7.33 (m, 3H), 5.78 (ddd, 1H, $J=17.1$, 10.5, 10.5 Hz), 5.11 (ABX system, ddd, 1H, $J=6.2$, 6.2, 4.5 Hz), 5.01 (dd, 1H, $J=10.5$, 2.1 Hz), 4.88 (dd, 1H, $J=17.1$, 2.1 Hz), 3.51 and 3.48 (ABX system, 2dd, 2H, $J=10$, 6.2 Hz), 2.28 (dd, 1H, $J=10.5$, 4.5 Hz), 1.1 (s, 9H), 0.985 (s, 21H), 0.323 and 0.318 (2s, 6H). ^{13}C NMR ($CDCl_3$): δ 177.9, 137.8, 134.8, 134.3, 129.5, 128.1, 116.2, 73.7, 64.3, 39.3, 36.8, 27.7, 18.4, 12.3, −3.1, −3.6. IR (film) ν_{max} cm^{-1} 3070, 2958, 2866, 1730, 1626, 1461, 1427, 1279, 1249, 1157, 1113, 1014, 882, 812, 733. MS(CI): 433 (95) $[M-(CH_3)_2CH]^+$, 375 (10), 345 (9), 289 (14), 285 (18), 215 (100), 201 (31), 197 (20), 159 (32), 135 (16), 111 (18). HRMS: Calcd for $C_{24}H_{41}O_3Si_2$ $[M-iPr]^+$ 433.259427 found: *M* 433.258928.

6.5.15. (2*R*,3*S*)-3-(Dimethyl-phenyl-silanyl)-2-triiso-propyl-silanyloxy-pent-4-en-1-ol (47). To a solution of

46b (410 mg, 0.85 mmol, 1 equiv.) in CH_2Cl_2 (5 mL) was added DIBAL 1.5 M in toluene (1.15 mL, 2 equiv.) after stirring for 1 h at −78 °C the reaction was quenched with methanol (1 mL) and 2 mL of a solution of NH_4Clsat were added. The mixture was stirred vigorously at rt for 2 h and the whole was extracted with AcOEt (2×5 mL). The combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. Filtration and evaporation in vacuo furnished the crude product, which was purified by flash chromatography (SiO_2: CH_2Cl_2/PE: 1:4) to give 246 mg of colorless oil (73% yield). $[\alpha]_D^{23}$=11.4 (c=1.02 in $CHCl_3$). TLC R_f 0.53 (CH_2Cl_2/PE, 2:3, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.56 (m, 2H), 7.35 (m, 3H), 5.92 (ddd, 1H, J=17.1, 10.2, 9.9 Hz), 4.96 (dd, 1H, J=10.2, 2.1 Hz), 4.82 (dd, 1H, J=17.1, 2.1 Hz), 3.79 (ABX system, ddd, 1H, J=10, 3.9, 2.4 Hz), 3.46 and 3.44 (ABX system, 2dd, 2H, J=14, 10, 2.4 Hz), 2.62 (broad s, 1H), 2.00 (dd, 1H, J=9.9, 3.9 Hz), 1.01 and 1.00 (2s, total 21H), 0.39 and 0.33 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 138.3, 135.3, 134.4, 129.3, 128.0, 114.7, 71.8, 68.1, 38.5, 18.5, 12.4, −3.0, −3.7. IR (film) ν_{max} cm^{-1} 3575, 3069, 2943, 2866, 1624, 1463, 1427, 1247, 1113, 1100, 1017, 882, 807. MS(CI): 391(3) $[M-H]^+$, 376 (49), 375 (100) $[M-OH^-]^+$, 315 (20), 307 (15), 239 (57), 231 (65), 205 (58), 197 (65), 157 (15), 135 (68), 67 (100). HRMS: Calcd for $C_{22}H_{39}O_2Si_2$ $[M-H]^+$ 391.248863 found: M 391.252510.

6.5.16. (2*R*,3*S*)-3-(Dimethyl-phenyl-silanyl)-2-triiso-propylsilanyloxy-1-vinyloxy-pent-4-en-1-yl ether (48). To a solution of **47** (328 mg, 408 mmol, 1 equiv.) in ethyl−vinyl ether (3 mL) was added mercury(II) acetate (143 mg, 448 mmol, 1.1 equiv.) and the resulting mixture was heated at reflux for 48 h. The ethyl-vinyl ether was then remove under reduced pressure. The resulting oil was taken back in pentane and the organic phase was washed with brine, dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography (SiO_2, CH_2Cl_2/PE: 1:9) gave 240 mg of the vinylether **48** (67% yield). $[\alpha]_D^{23}$=+12 (c=0.6 in $CDCl_3$). TLC R_f 0.9 (CH_2Cl_2/PE, 1:4, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.68 (m, 2H), 7.51 (m, 3H), 6.38 (dd, 1H, J=13.8, 6.3 Hz), 6.03 (ddd, 1H, J=17.1, 10.5, 10.2 Hz), 5.15 (dd, 1H, J=10.2, 2.4 Hz), 5.01 (dd, 1H, J=17.1, 2.4 Hz), 4.39 (dd, 1H, J=13.8, 1.5 Hz), 4.05 (dd, 1H, J=6.3, 1.5 Hz), 3.97 (ddd, 1H, J=6.6, 6.3, 2.4 Hz), 3.83 (dd, 1H, J=10.1, 6.6 Hz), 3.71 (dd, 1H, J=10.1, 6.3 Hz), 2.29 (dd, 1H, J=10.5, 2.4 Hz), 1.17 and 1.16 (2s, total of 21H), 0.52 and 0.47 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 152.5, 137.6, 134.4, 134.2, 128.9, 127.8, 115.4, 87.4, 80.9, 65.0, 37.3, 17.9, 11.8, −3.8, −4.5. IR (film) ν_{max} cm^{-1} 3070, 2943, 2866, 1627, 1463, 1427, 1249, 1186, 1114, 1052, 1004, 882, 812, 699. MS(CI): 391(5) $[M-CH{=}CH_2]^+$, 377 (55), 375 (100), 353 (10), 315 (20), 241 (20), 239 (55), 231 (61), 205 (57), 197 (53), 157 (15), 135 (55), 67 (85). HRMS: Calcd for $C_{22}H_{39}OSi_2$ $[M-CH_2{=}CH-O]^+$ 375.253948 found: M 375.252969.

6.5.17. (3*R*,4*S*)-4-(Dimethyl-phenyl-silanyl)-3-triiso-propylsilanyloxy-3,4-dihydro-2*H*-pyran (49). To a solution of **48** (100 mg, 0.229 mmol, 1 equiv.) in CH_2Cl_2 (20 mL) was added **23** (49 mg, 0.057 mmol, 0.25 equiv.) in solution in CH_2Cl_2 (1 mL). The mixture was heated 4 h at reflux until disappearance of the starting compound. The ruthenium catalyst was then oxidize by stirring the mixture at open air overnight. Concentration in vacuo followed by flash chromatography (SiO_2: hexane) gave 82 mg of product (93% yield). TLC R_f 0.49 (hexane, $KMnO_4$). ^1H NMR ($CDCl_3$): δ 7.48 (m, 2H), 7.34 (m, 3H), 6.19 (dd, 1H, J=2.7, 2.4 Hz), 4.76 (dd, 1H, J=2.7, 2.7 Hz), 4.52 (ddd, 1H, J=7.2, 6.3, 4.8 Hz), 3.63 (dd, 1H, J=10.2, 6.3 Hz), 3.49 (dd, 1H, J=10.2, 4.8 Hz), 2.21 (ddd, 1H, J=7.2, 2.7, 2.4 Hz), 1.01 and 1.00 (2s, total of 21H), 0.29 and 0.28 (2s, total of 6H). ^{13}C NMR ($CDCl_3$): δ 137.8, 134.3, 134.1, 129.7, 128.4, 97.8, 83.1, 64.9, 23.5, 18.4, 12.4, −0.9, −2.6. IR (film) ν_{max} cm^{-1} 3069, 2943, 2866, 1762, 1691, 1463, 1427, 1251, 1113, 1063, 1014, 882. MS(CI): 390 $[M]^+$ (4), 375 (5), 347 (14), 265 (39), 180 (98), 169 (35), 157 (75), 137 (43), 135 (63), 123 (100), 75 (17). HRMS: Calcd for 391.248863 found: M 391.247701.

Acknowledgements

We warmly thank the FNRS (Belgium) and the Ministry of Research (France) for PhD fellowships to J.M.A. and L.dF. These studies were supported by grants from the Ministère de l'Education et de la Recherche, Communauté française de Belgique (action concertée), the Université catholique de Louvain, the Conseil Régional d'Aquitaine and the Université Bordeaux I. We are also indebted to Prof. E. de Hoffmann and Prof. J.-L. Habib for the mass spectra, Prof. Flammang for the HRMS and Dr. Roland Touillaux for the meticulous measurement and recording of high-field NMR spectra.

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