Diastereoselective double ring closing metathesis reactions as an approach to symmetrical bicyclodienes

Mark Lautens, Gregory Hughes, and Valentin Zunic

Abstract: A new class of bicyclic dienes which contain a σ plane of symmetry are efficiently prepared in a diastereoselective fashion using ring closing metathesis reactions. These molecules have potential as starting materials for a wide range of organic targets.

Key words: metathesis, catalysis, stereoselective, decalin, desymmetrization.

Résumé : Faisant appel à des réactions de métathèse de fermeture de cycle, on a développé une méthode efficace de préparer de façon diastéréosélective une nouvelle classe de dienes bicycliques qui contiennent un plan de symétrie σ. Ces molécules pourraient éventuellement servir de produit de départ pour une grande variété de cibles organiques.

Mots clés : métathèse, catalyse, stéréosélective, décaline, désymétrisation.

Introduction

In recent years there has been tremendous interest in ring closing olefin metathesis (RCM) chemistry due largely to the development of well defined transition metal alkylidenes such as $[Cl_2(Cy_3P)_2Ru{=}CHPh]$ (**1**) and $[PhMe_2CCH{=}Mo{=}N\{2,6\text{-}(iPr)_2C_6H_3\}\{OCMe(CF_3)_2\}_2]$ (**2**) which display tolerance to a significant range of functional groups (for recent reviews of olefin metathesis see ref. (1)). We became interested in using RCM methodology as a key step in the projected total synthesis of the HMG CoA reductase inhibitor (+)-mevinolin (Scheme 1). We reasoned that a diastereoselective double ring closing metathesis strategy involving **A**, followed by an alkene selective sigmatropic rearrangement of a substrate such as **B**, would provide convenient access to the carbon skeleton of the hexahydronaphthalene portion of the target (for other examples of diastereoselective RCM reactions see ref. (2)); (for other examples of double RCM reactions see ref. (3)). A preliminary report on these investigations has appeared (4).

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Dedicated to Professor Stephen Hanessian on the occasion of his 65th birthday.

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[2]4-Bromo-1-butene: $1088.91/mol; 3-buten-1-ol: $432.44/mol; 1,4-dichlorobut-2-ene (mixture of *cis* and *trans*): $20.70/mol. Prices in Canadian dollars listed in Aldrich's 1999 catalogue for the largest available denomination.

We opted to use unsubstituted tetraenes **C** for our initial studies. This simplified system is particularly attractive since the product of double ring closing metathesis, **D**, is a useful starting material for subsequent investigations in the area of enantioselective alkene differentiation reactions.

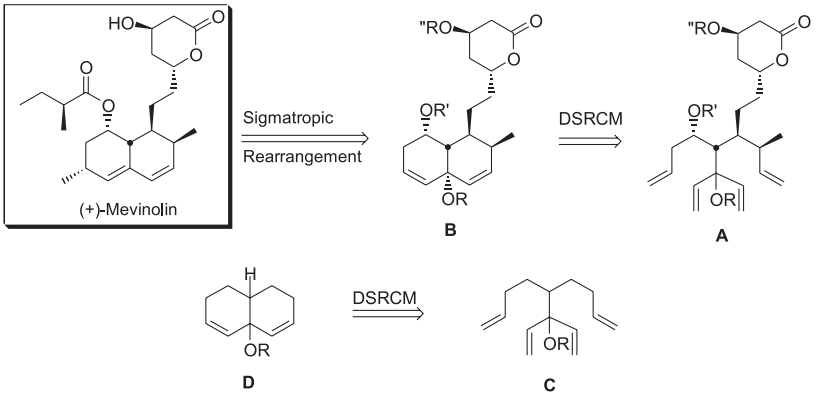
Results

We envisioned a general approach to a variety of tertiary diallylic alcohols involving dialkylation of malonate, Krapcho decarboxylation and addition of two equivalents of a vinyl organometallic reagent (Scheme 2).

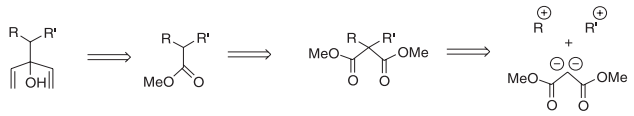
For our first investigations we wanted to prepare a tetraene derived from double alkylation of malonate with a butenyl electrophile. The most obvious butenyl source would be commercially available 4-bromo-1-butene, or a derivative of 3-buten-1-ol (e.g., $CH_2{=}CH(CH_2)_2OTs$, $CH_2{=}CH(CH_2)_2OTf$, $CH_2{=}CH(CH_2)_2I$). However, the expense of both 4-bromo-1-butene and 3-buten-1-ol,[2] as well as the need to use these electrophiles in moderate excess due to their tendency to undergo elimination under basic conditions made this approach less attractive for the large scale preparation of materials needed for our investigations. We examined an alternative approach involving sequential additions of malonate to acrolein, followed by Wittig olefination. While the route furnished the desired dibutenylated malonate, the procedure was laborious, and the yields were low to moderate. In addition, the large quantities of triphenyl phosphine oxide produced on scaling up the reaction made this approach unattractive.

Inspired by the work of Tsuji and co-workers (5) and Shimizu and co-workers (5), we developed an alternative strategy for the butenylation of malonates, as well as a variety of other nucleophiles (6). In this approach, the appropriate nucleophile is alkylated with 1,4-dichlorobutene, which is a fraction of the cost of either 4-bromo-1-butene or 3-buten-1-ol,[2] to afford an allyl chloride. Formate reduction

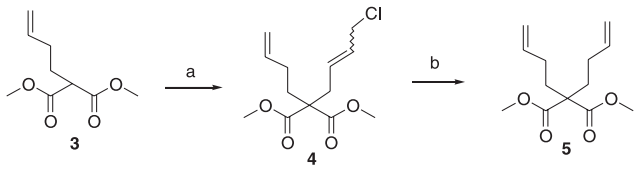
Scheme 1. Potential retrosynthetic approach to (+)-Mevinolin.



Scheme 2. Synthetic approach to model systems.



Scheme 3. Preparation of a dibutenylated malonate: (*a*) MeO^- Na^+ (1.5 equiv.), $ClCH_2CH{=}CHCH_2Cl$ (4.0 equiv., mixture of *cis* and *trans*), MeOH, 23°C→reflux, 57%; (*b*) HCO_2NH_4 (2.2 equiv.), Pd_2dba_3 (0.25 mol%), nBu_3P (2 mol%), toluene, 100°C, 16 h, 90%.



under Pd catalysis affords the desired butenylated compound as a single regioisomer within the detection limits of ^1H NMR. Dimethyl monobutenylated malonate **3** was prepared from dimethyl malonate and *trans*-1,4-dichloro-2-butene according to a two step procedure described by Shimizu and Aida (6*a*). This product was then converted to allyl chloride **4** using standard alkylation chemistry and finally to **5** by a Pd catalyzed formate reduction (Scheme 3). In this manner, **5** could be easily prepared in good overall yield in batches of 50 g.

Decarboxylation of **5** and its diallyl analogue **6** proceeded in good yield to give the desired methyl esters **7** and **8**. The addition of 2 equiv. of vinyl lithium or magnesium reagents to **7** and **8** proved troublesome as the second equivalent strongly preferred to undergo conjugate addition, to afford less than 10% of the desired tertiary alcohols **9** and **10** (7). It had been reported that the addition of two equivalents of a vinyl cerium reagent to an ester could generate a tertiary alcohol in 35% yield (8). The literature conditions called for the use of 3 equiv. each of vinylmagnesium bromide and predried $CeCl_3$ at 0°C. We found that more extensive drying of the $CeCl_3{\cdot}7H_2O$ (6–12 h at 140°C, <0.1 mmHg), lower reaction temperatures (–78°C), and the use of 3.5 equiv. of vinylmagnesium bromide and 4.0 equiv. of $CeCl_3$ gave **9** and **10** in 86 and 90% respectively. The alcohols were then converted to ethers **11** and **12** under standard conditions (Scheme 4).

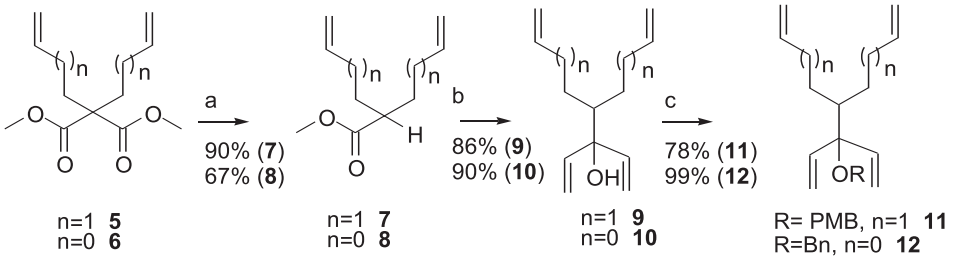
With the desired tetraenes in hand we initiated the diastereoselective RCM (DSRCM) studies. Treating **11** with 3 mol% of **1** for 3 h gave the cycloheptene **13** in 70% yield. Ring closing metathesis via sequential reaction of the two less hindered alkenes occurs, in spite of the fact that this leads to seven-membered ring formation rather than the cyclohexene. However, by increasing the catalyst loading to 10–12mol%, increasing the reaction time to 22 h, and conducting the reaction in the presence of ethylene, it was possible to isolate *cis*- and *trans*-**14** in 80% as an 8:1 mixture of diastereomers with the *syn* product predominating (Scheme 5). Similar results were realized using **2** as a catalyst. The successful conversion of **13** to **14** suggested a more efficient route to **14** using **16**. Fortunately, this methyl ester can be prepared on large scale in good yield from inexpensive materials as outlined in Scheme 6 (9).

In contrast to the reactions of ethers **10** or **12** which give *cis*-fused bicyclic compounds, treating free alcohol **9** with **1** for 30 min gave a 2.7:1 mixture of diastereomers where the *trans*-fused isomer of **15** is favored (Scheme 5).

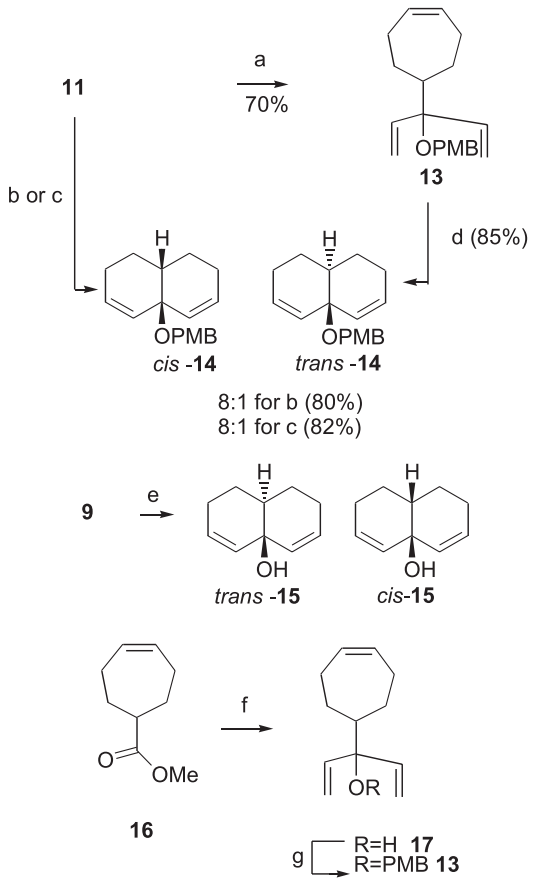
We could also form *cis*-fused diquinane **19** from tetraene **12** by treating it with 4 mol% of **1** for 18 h (Scheme 7). A 6.5:1 ratio was observed between **19** and cyclopentene **20** which fails to undergo further RCM reactions as this would result in the formation of a highly strained *trans* bicyclo[3.3.0]octadiene system. Again, cyclization with the less hindered olefin appears to occur initially to give symmetrical cyclopentene **18**, but upon prolonged reaction times this intermediate then ring opens and recyclizes to give the desired bicyclic product.

To examine the diastereoselectivity in the first step of the cyclization and its reversibility, trienes **22**, **23**, **26**, and **27** were prepared as outlined in Scheme 8. Six-membered ring precursors were prepared by alkylation of **3** with $TBDPSO(CH_2)_3Br$, followed by Krapcho decarboxylation and vinylcerium addition to give **22**. Protection of the free

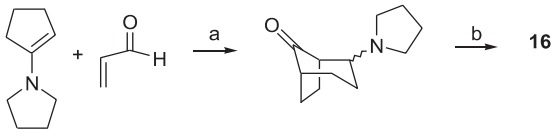
Scheme 4. Synthesis of tetraene 3° diallylic alcohols and ethers: (*a*) NaCl (2.4 equiv.), H_2O, DMSO, 180°C, 4 h; (*b*) CH_2=CHMgBr (3.5 equiv.), $CeCl_3$ (4.0 equiv., anhydrous), THF, –78°C; (*c*) **9**→**11**: NaH (2.0 equiv.), PMBBr (2.0 equiv.), DMF, 23°C; **10**→**12**: THF, 60°C, KH (2.0 equiv.), BnBr (1.5 equiv.); PMB = *p*-methoxybenzyl.



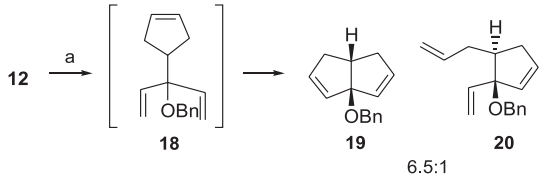
Scheme 5. DSRCM as an approach to *cis*- and *trans*-fused decalin systems: (*a*) $(PCy)_2Cl_2Ru$=CHPh (3 mol%), CH_2Cl_2, 3 h; (*b*) $(PCy_3)_2Cl_2Ru$=CHPh (12 mol%), CH_2Cl_2, ethylene atm, 18 h; (*c*) $((CF_3)_2CH_3CO)_2Mo(=NAr)(=CHC(CH_3)_2Ph)$ (Ar = 2,6-diisopropylphenyl) (12 mol%), C_6H_6, 30 min; (*d*) $(PCy_3)_2Cl_2Ru$=CHPh (10 mol%), CH_2Cl_2, ethylene atm, 18 h; (*e*) $(PCy_3)_2Cl_2Ru$=CHPh (10 mol%), CH_2Cl_2, closed system, 30 min; (*f*) CH_2=CHMgBr (3.5 equiv.), $CeCl_3$ (4.0 equiv., anhydrous), THF, –78°C; (*g*) NaH (2.0 equiv.), PMBBr (2.0 equiv.), DMF, 23°C.



Scheme 6. Alternative approach to cycloheptenoates: (*a*) THF, 0°C; (*b*) (*i*) MeI, THF; (*ii*) NaOH; (*iii*) H_2SO_4 (cat.), MeOH.



Scheme 7. DSRCM as an approach to diquinane systems: **1** (4 mol%), CH_2Cl_2, 18 h.



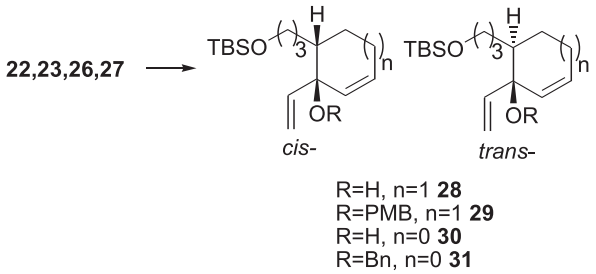
alcohol gave **23**. Five-membered ring precursors were prepared by alkylation of dimethylmalonate with $TBSO(CH_2)_3Br$, followed by allylation. Krapcho decarboxylation and vinyl cerium addition then gave **26** and protection of the free alcohol gave **27**.

Results from treating these trienes with **1** and **2** are summarized in Table 1. Treating **22** with **1** gave a 1:2.8 mixture of diastereomers favoring *trans*-**28** (CH_2=CH ↔ $(CH_2)_3OSiR_3$) (entry 1),[3] whereas treating **23** with **1** gave a 6.1:1 mixture of diastereomers favoring the *cis* (CH_2=CH↔$(CH_2)_3OSiR_3$) isomer (entry 2), and switching to **2** gave slightly higher levels of stereoselectivity (7.8:1, entry 3). Cyclopentenol **30** was formed as a 1:1 mixture of diastereomers upon treatment with **1** (entry 4), whereas the benzyl ether gave rise to cyclopentene **31** in an 8.0:1 mixture of diastereomers, favoring *cis*-**31** (entry 5). The use of **2** gave the same sense of selectivity in forming **31**, but with significantly lower levels of stereoselectivity (1.7:1, entry 6).

These results parallel the observations made in bicycle formation suggesting that although RCM transformations are potentially reversible we did not observe that process in this series. In fact submitting the minor isomers isolated from the reaction mixtures to the original reaction conditions failed to show any equilibration.

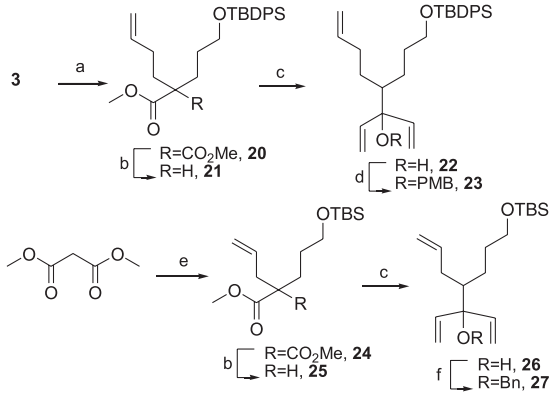
[3] While somewhat unorthodox, the nomenclature used here to designate relative stereochemistry was chosen for the sake of clarity. In using (*R**,*S**) vs. (*R**,*R**) nomenclature, the designation reverses when ring size is changed from five to six without changing the relative orientations of the vinyl and alkyl substiuents. The *cis* and *trans* designations were chosen on the basis of whether a *cis*- or *trans*-fused bicyclic system would be formed were a second RCM reaction possible. For proof of stereochemistry, see supporting information of ref. (2).

Table 1. DSRCM from monocycloalkene formation.

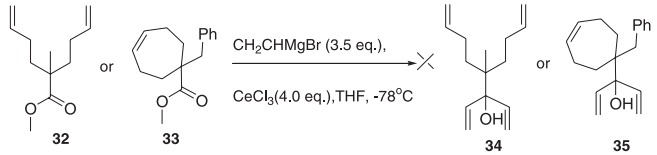


Entry	Starting material	Product	Catalyst	Mol%/Time (h)	Yield (%)	*cis:trans* CH_2=CH↔$(CH_2)_3$OP
1	**22**	**28**	1	12/5	80	1:2.8
2	**23**	**29**	1	3/3	96	6.1:1
3	**23**	**29**	2	6/1.5	86	7.8:1
4	**26**	**30**	1	6/1.5	65	1:1
5	**27**	**31**	1	3/1	99	8.0:1
6	**27**	**29**	2	6/0.5	94	1.7:1

Scheme 8. Synthesis of triene tertiary diallylic alcohols and ethers: (*a*) NaH (5.0 equiv.), $Br(CH_2)_3OTBDPS$ (1.5 equiv.), THF, 60°C, 48%; (*b*) NaCl (2.4 equiv.), H_2O, DMSO, 180°C, 4 h, 58%; (*c*) CH_2=CHMgBr (3.5 equiv.), $CeCl_3$ (4.0 equiv., anhydrous), THF, –78°C, 57% (**22**), 32% (**26**); (*d*) NaH (2.0 equiv.), PMBBr (2.0 equiv.), DMF, 23°C, 67%; (*e*) (*i*) NaH (1.0 equiv.), $Br(CH_2)_3OTBS$ (0.3 equiv.), THF, 60°C, 31%; (*ii*) NaH (2.0 equiv.), allyl bromide (1.5 equiv.) THF, 60°C, 83%; (*f*) KH (1.5 equiv.), BnBr (1.5 equiv.), THF, 60°C, 89%.



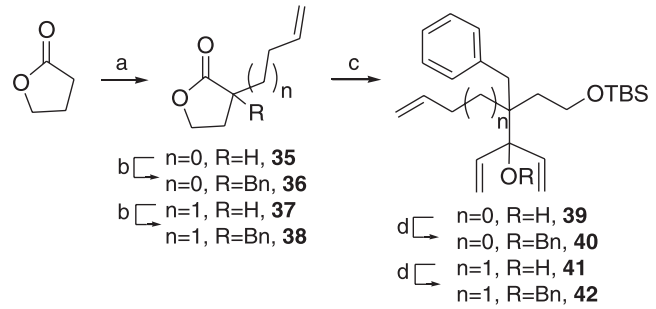
Scheme 9. Failure of esters having an α tertiary center to undergo reaction with vinyl cerium.



To probe the effect of bridgehead substituents on the efficiency and diastereoselectivity of the DRCM, substrates **32** and **33** were treated with the vinylcerium reagent but both failed to give the desired products. Steric effects at the α position may be responsible. (Scheme 9).

This problem was overcome by the use of lactones, where the third substituent is incorporated into the ring. For example, double alkylation to give lactones **36** and **38** followed by reaction with vinylcerium gave tertiary alcohols **39** and **41** in good overall yields as outlined in Scheme 10. Selective protection of the primary alcohols followed by benzylation of the tertiary alcohols furnished ethers **40** and **42**.

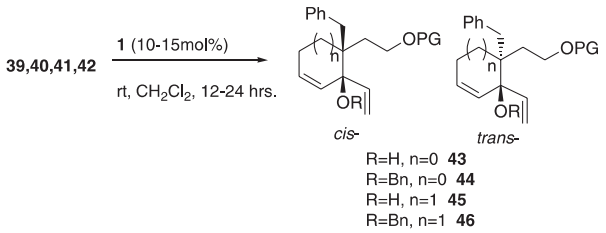
Scheme 10. Preparation of 3° alcohols from α,α-disubstituted lactones: (*a*) *n* = 0: LDA, allyl bromide, THF, –78°C, 80%; *n* = 1: (*i*) LDA, 1,4-dichlorobut-2-ene, THF– HMPA (7:1), –78°C; (*ii*) HCO_2NH_4, Pd_2dba_3, nBu_3P, toluene, 100°C, 3 h, 45% (2 steps); (*b*) LDA, BnBr, THF, 77% (**36**), 74% (**38**); (*c*) (*i*) CH_2=CHMgBr (3.5 equiv.), $CeCl_3$ (4.0 equiv., anhydrous), THF, –78°C; (*ii*) TBSCl (1.05 equiv.), imidazole (1.5 equiv.), DMF, 23°C, 57% (**39**), 48% (**41**); (*d*) KH (3.0 equiv.), BnBr (1.5 equiv.), THF, 23°C, 12 h, 85% (**40**), 90% (**42**).



The butenylation of butyrolactone with conventional methodologies gave only low yields of **37** (<10%), but the two step approach mentioned above for the butenylation of a variety of nucleophiles proved to be more successful (6). Thus, alkylation with 1,4-dichlorobut-2-ene, followed by Pd catalyzed formate reduction furnished **37** in 45% yield over two steps.

The results from treating these trienes with Grubbs' catalyst are summarized in Table 2. Reaction of **39** with **1** (24-hour portion-wise addition) gave cyclopentene **43** as essentially a single diastereomer in 60% isolated yield. This diastereomer was shown to be *trans*-**43** (CH_2=CH↔$(CH_2)_2OSiR_3$) by ROSEY experiments (10). Treatment of **40** with the same catalyst gave a 2:1 mixture with *cis*-**44** (CH_2=CH↔$(CH_2)_3OSiR_3$) now being favored.

Table 2. DSRCM for 3° diallylic systems having an α tertiary center.

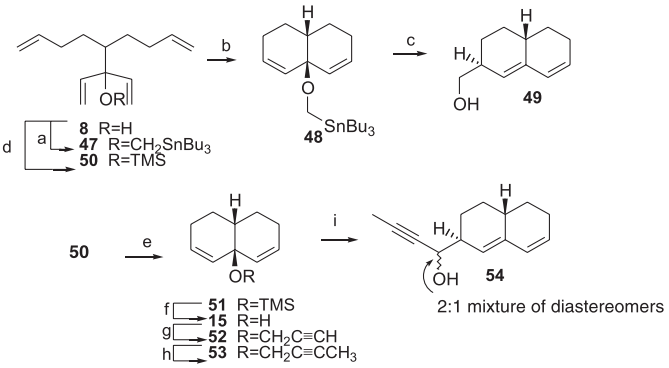


Entry	Starting Material	Product	Mol%/ Time (h)	Yield (%)	*cis*:*trans* $CH_2{=}CH{\leftrightarrow}(CH_2)_3OP$
1	**39**	**43**	15/24	60[a]	<1:>20
2	**40**	**44**	15/24	100[b]	2:1
3	**41**	**45**	8/12	100[b]	1:1
4	**42**	**46**	8/12	100[b]	4.5:1

[a]Isolated yield.

[b]Based on 100% conversion by ^{1}H NMR (400 MHz) analysis.

Scheme 11. [2,3] Wittig rearrangements as an approach to the hexahydronaphthalene portion (+)–melvinolin: (*a*) KH (3.0 equiv.), 18-crown-6 (cat.), ICH_2SnBu_3 (1.5 equiv.), THF, reflux, 93%; (*b*) **1** (12 mol%), $CH_2{=}CH_2$, CH_2Cl_2, reflux, 86%; (*c*) MeLi (1.05 equiv.), HMPA (4.0 equiv.), THF, –78°C, 67%; (*d*) KH (2.0 equiv.), TMSCl (1.05 equiv.), THF, 90%; (*e*) **2** (10 mol%), C_6H_6, 99%, dr = 5:1; (*f*) TBAF (3.0 equiv.), THF, 23°C, 86%; (*g*) NaH (5.0 equiv.), $BrCH_2C{\equiv}CH$ (5.0 equiv.), THF, 46%; (*h*) *n*-BuLi (1.1 equiv.), MeI (1.5 equiv.), THF, –78°C, 90%; (*i*) *t*-BuLi (4.0 equiv.), THF,–78°C, 63% (dr = 2:1).



Cyclohexenes having a bridgehead substituent were also formed in good yields. Treatment of the free alcohol **41** with **1** provided **45** as a 1:1 mixture of diastereomers. The analogous benzyl protected ethers were formed in a 4.5:1 mixture of diastereomers, favoring *cis*-**46**.

We have investigated potentially useful derivatizations of the bicyclic compounds. Deprotonation of **8** with KH, followed by alkylation with an iodomethyl stannane proceeds in good yield. DSRCM occurred in high yield to give the desired bicycle **48**. Treating this stannyl methyl ether with MeLi at –78°C afforded a 67% yield of the [2,3]-Wittig rearrangement product **49** (Scheme 11) (11).

A variation of the Wittig rearrangement was also investigated involving methyl propargyl ether **53**, prepared as outlined in Scheme 11 (12). DSRCM of **50** with **2** (12 mol%, 0.5 h) gave a 5:1 mixture of diastereomers. Desilylation afforded a separable mixture of free alcohols. The *cis*-fused free alcohol *cis*-**15** was converted to propargyl ether **53** in two steps. Treatment with *t*-BuLi at –78°C gave the [2,3]-Wittig rearrangement product in 63% yield as a 2:1 mixture of diastereomeric alcohols.

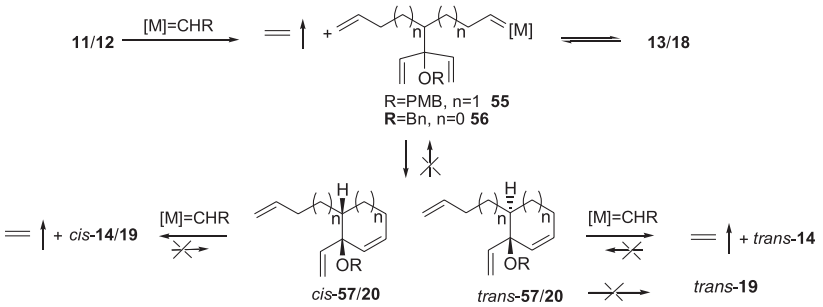
Discussion

Based on our studies and previous work outlining the reactivity patterns of various olefins (13), we propose the following reaction pathway for decalin formation from **11** and **12**.

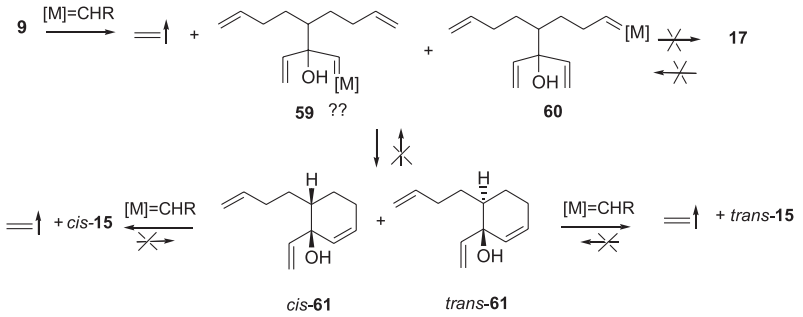
Transalkylidenation in **11** or **12** occurs at one of the two olefins lacking an α substituent to give **55**/**56** (Scheme 12). These intermediates then cyclizes initially to give cycloalkenes **13** or **18**. The formation of both **13** and **18** is reversible, as demonstrated by the observation that **13** and **18** are alternative entries into the catalytic cycle. A second less favorable but irreversible pathway involves cyclization onto one of the two more sterically hindered diastereotopic olefins to give either *cis*-**57**/**20** or *trans*-**57**/**20**. The formation of these cycloalkenes has been proven to be irreversible under all conditions examined to date. RCM between the two remaining acyclic olefins then affords bicyclic products, a process which should also be initiated by reaction at the less hindered alkene. While both *cis*- and *trans*-**57** will go on to give the corresponding *cis*- and *trans*-fused hexahydronaphthalenes, only *cis*-**20** goes onto to *cis*-fused diquinane as further cyclization of *trans*-**20** would give rise to a highly unstable *trans*-fused bicyclo[3.3.0] compound.

Double cyclization of free alcohols display interesting differences in diastereoselectivity compared to their protected analogues. As others have previously noted (14), free alcohols appear to cyclize at accelerated rates relative to the analogous ethers. For example whereas the *p*-methoxybenzyl ether **11** reacts to give the cycloheptene **13** faster than to form a cyclohexene **57**, we have been unable to observe the formation of cycloheptene **17** when free alcohol **9** is used as starting material. In fact, when **17** is used as starting material, no conversion to decalin is observed, suggesting that alkylidene formation may be taking place at the more hindered olefin (Scheme 13). The implications of these observations with regard to stereoselectivity issues are intriguing and are currently under investigation.

Scheme 12. Reaction pathway of decalin and diquinane formation.



Scheme 13. DSRCM reactions involving free alcohols.



The effect of added ethylene depends on the structure of the tetraene (for examples of other systems where added ethylene was found to enhance RCM see ref. (15)), enhancing the conversion with some substrates and hindering the cyclization of others. For example, when cyclizing free alcohol **9**, the use of an ethylene atmosphere resulted in incomplete conversion (~50%) before the catalyst decomposed. If the reaction was repeated but using a stream of Ar, the reaction also failed to go to completion. However when the reaction was conducted in a sealed system so that the ethylene produced upon cyclization was retained, complete consumption of starting material was observed. The cause of these effects are somewhat puzzling and warrant further study.

The relative sensitivities of the *cis*- and *trans*-fused decalins also warrants further mention. As one might expect, the tertiary diallylic alcohols and ethers are susceptible to solvolysis under acidic conditions. While most of the RCM precursors and the monocyclic intermediates could be isolated without difficulty, bicyclic materials were found to decompose upon chromatography unless the silica gel was neutralized with triethyl amine. The *trans*-fused decalins were found to be particularly acid sensitive, decomposing during TLC development, while the *cis*-fused analogues did not. Geometry optimization calculations (3–21G*) of *cis*-**15** and *trans*-**15** revealed that the dihedral angles between the olefin planes and the allylic C—O bond are 130° and 97° for *cis*-**15**, whereas both dihedral angles in *trans*-**15** are 90°, leaving the C—O bond in an antiperiplanar orientation with both double bonds, which would be expected to lower the energy barrier to carbenium ion formation.

Experimental

Toluene and THF were distilled from sodium–benzophenone. DMF was dried by prolonged standing over molecular sieves. HMPA was distilled under reduced pressure from CaH_2. CH_2Cl_2 was distilled from CaH_2. Grubbs' catalyst was prepared according to a literature procedure (16) and triturated for 12–18 h in a 1:1 mixture of acetone and methanol. The absence of free tricyclohexyl phosphine and tricyclohexyl phosphine oxide was confirmed by ^{31}P NMR, and was crucial in order for the double metathesis reactions to proceed. Schrock's catalyst was used as received from Strem. Computational work was done using MacSpartan Plus©, version 1.1.7 (Wavefunction Int. Irvine, Calif. 1996–1997).

General procedure for the decarboxylation of dimethyl malonates

To a 23°C solution of malonate in DMSO (1.0 M) was added NaCl (1.5 equiv.) and water (1 drop/1 mL DMSO). The resulting mixture was heated to 180°C for 5–10 h. The mixture was cooled to 23°C, diluted with ether and washed with water. The aqueous layer was extracted three times with ether. The organic layers were combined, washed with brine, dried over magnesium sulfate, and filtered. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel.

General procedure for the conversion of methyl esters to diallylic tertiary alcohols

$CeCl_3 \cdot 7H_20$ (4.0 equiv.) was ground with a mortar and pestle, placed under vacuum (<0.1 mmHg) and warmed to 140°C for 2 h. A stir bar was added and heating under vacuum continued for a further 4–10 h. The resulting powder was cooled to 0°C and THF (3 mL/mmol of $CeCl_3$) was added via cannula under vacuum. The remaining vacuum was displaced with N_2 and the resulting suspension stirred for 24 h, then cooled to –78°C. Vinylmagnesium bromide (~1 M in THF, 3.5 equiv.) was added via syringe at a rate such that the internal temperature was kept below –65°C.

After 1 h a solution of ester (1.0 equiv.) in THF (~1 M) was added via cannula at a rate such that the internal temperature did not exceed –65°C. After 30 min, the mixture was diluted with ethyl acetate and water was added. The organic layer was decanted off and the aqueous slurry extracted three times with ethyl acetate. The organic layers were combined, washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated in vacuo and purified by flash chromatography on triethyl amine washed silica gel.

General procedure for the p-methoxy benzylation of tertiary diallylic alcohols

NaH (60% suspension in oil, 5.0 equiv.) was washed three times with pentane, dried under a stream of N_2 and suspended in DMF (0.3 M). A solution of alcohol in DMF (1.0 M) was added via cannula at a rate such the H_2 evolution is controlled. After 5 min, PMBBr was added via syringe and the resulting mixture was stirred at 23°C for 16 h. The mixture was diluted with ether and the reaction carefully quenched by drop-wise addition of saturated ammonium chloride. The aqueous layer was extracted three times with ether; the organic layers were combined, washed with brine, dried over sodium sulfate, and filtered. The filtrate was concentrated in vacuo and purified by flash chromatography on triethyl amine washed silica gel.

General procedure for the benzylation of tertiary diallylic alcohols

Potassium hydride (35% suspension in oil, 1.5 equiv.) was washed three times with pentane, dried under a stream of argon, and suspended in THF (half of total reaction volume). A solution of alcohol in THF (half of reaction volume, reaction concentration of 0.2 M) was added via cannula. The resulting suspension was warmed to 60°C and after 10 min benzyl bromide (1.5 equiv.) was added via syringe and the resulting mixture was stirred for an hour, cooled to 23°C, diluted with ether, and quenched carefully by drop-wise addition of water. The aqueous layer was extracted two times with ether, the organic layers were combined, washed with brine, dried over sodium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography on triethyl amine washed silica gel.

*Methyl 2-(but-3-enyl) hex-5-enoate (**7**)*

2,2 Di-(2-but-3-enyl) malonic acid dimethyl ester **5** (6.70 g, 27.9 mmol) was reacted according to the general procedure for decarboxylation. The crude product was purified by flash chromatography (3% ether–hexanes) to yield the title compound as a colorless oil (3.62 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.48–1.57 (m, 2H), 1.64–1.76 (m, 2H), 1.94–2.08 (m, 4H), 2.35–2.43 (m, 1H), 4.94 (dq, J = 9, 1 Hz, 2H), 4.98 (dm, J = 17, 2 Hz, 2H), 5.69–5.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 31.52, 44.35, 51.36, 114.89, 137.70, 176.00.

*2-But-3-enyl-1-vinyl-octa-1,7-dien-3-ol (**9**)*

Methyl ester **7** (1.00 g, 5.49 mmol) was reacted according to the general procedure for the conversion of methyl esters to tertiary diallylic alcohols. The crude mixture was purified by flash chromatography (3% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (606 mg, 53%). IR (neat): 3478, 3078, 2934, 2978, 1640, 1456, 1414, 1300, 996, 912, 735. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.18–1.28 (m, 2H), 1.41–1.49 (m, 2H), 1.59–1.69 (m 2H), 1.97–2.08 (m, 2H), 2.09–2.20 (m, 2H), 4.92 (dm, J = 10 Hz, 2H), 4.98 (dq, J = 17, 2 Hz, 2H), 5.14(dd, J = 11, 1 Hz, 2H), 5.25 (dd, J = 17, 1 Hz, 2H), 5.71–5.82 (m, 2H), 5.94 (dd, J = 17, 11 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 29.39, 32.99, 45.78, 79.05, 113.42, 114.41, 138.97, 142.07.

*4-Allyl-3-vinyl-hepta-1,5-dien-3-ol (**10**)*

Methyl 2-propenylpent-4-enoate **8** (600 mg, 3.89 mmol) was reacted according to the general procedure for the formation of a tertiary diallylic alcohol. Purification by flash chromatography (5% ether–hexanes) on triethyl amine washed silica gel yielded the title compound as a colorless oil (460 mg, 66%). R_f = 0.19 (5% ether). IR (neat): 3072, 2933, 2859, 1738, 1642, 1473, 1428, 1390, 1195, 1164, 1112, 998, 917, 824, 741, 703, 614. ^{1}NMR (400 MHz, $CDCl_3$) δ: 1.70 (sept., J = 4 Hz, 1H), 1.87 (s, 1H), 2.07 (quint, J = 8 Hz, 2H), 2.28–2.36 (m, 2H), 5.00 (d, J = 9 Hz, 2H), 5.03 (d, J = 17 Hz, 2H), 5.79–5.91 (m, 2H), 5.95 (dd, J = 17 Hz, 11 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.20, 23.65, 26.85, 31.60, 32.38, 36.42, 45.32, 51.33, 63.60, 116.62, 127.57, 129.49, 134.05, 135.50, 135.54, 176.04. HRMS calcd. for $(M-H)^+$: 177.1279; found: 177.1287.

*[2-But-3-enyl-1,1-divinyl-hex-5-enyloxymethyl]-4-methoxy-benzene (**11**)*

Alcohol **9** (200 mg, 0.969 mmol), was reacted according to the general procedure for the *p*-methoxy benzylation of tertiary diallylic alcohols. The crude mixture was purified by flash chromatography (5% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a pale green oil (240 mg, 76%). IR (neat): 3478, 3078, 2934, 2978, 1640, 1456, 1414, 1300, 996, 912, 735. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11–1.22 (m, 2H), 1.60 (hept, J = 4 Hz, 1H), 1.67–1.77 (m, 2H), 2.02–2.21 (m, 4H), 3.81 (s, 3H), 4.31 (s, 2H), 4.94 (dm, J = 10 Hz, 2H), 5.01 (dq, J = 17, 2 Hz, 2H), 5.31 (dd, J = 18, 1.5 Hz, 2H), 5.37 (dd, J = 11, 2 Hz, 2H), 5.76–5.86 (m, 2H), 5.88 (dd, J = 18, 11 Hz, 2H), 6.88 (AB, J = 9 Hz, 2H), 7.26 (AB, J = 9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.05, 33.37, 47.30, 55.24, 64.82, 83.96, 113.57, 114.18, 117.39.

*[2-Allyl-1,1-divinyl-pent-4-enyloxymethyl] benzene (**12**)*

Tertiary alcohol **10** (500 mg, 2.80 mmol) was reacted according to the general procedure for the benzylation of tertiary diallylic alcohols. The crude product was purified by flash chromatography (100% hexanes –> 2% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (590 mg, 78%). R_f = 0.29 (2% ether–hexanes). IR (neat): 3074, 2920, 1639, 1497, 1453, 1414, 1377, 1096, 1064, 1000, 910, 729. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.84 (sept., J = 4 Hz, 1H), 1.96 (dt, J = 14, 8 Hz, 2H), 2.44 (dm, J = 14.5 Hz, 2H), 4.38 (s, 2H), 4.94 (d, J = 11 Hz, 2H), 4.98 (d, J = 18 Hz, 2H), 5.79–5.90 (m, 2H), 5.90 (dd, J = 18, 11 Hz, 2H), 7.21–7.26 (m, 1H), 7.29–7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.41, 48.07, 65.15, 83.53, 115.12, 117.63, 126.79, 126.85, 128.15,

137.87, 138.73, 139.88. HRMS calcd. for $(M-H)^+$: 267.1749; found: 267.1734.

*4a-(4-Methoxy-benzyloxy)-1,2,4a,7,8,8a-hexahydronaphthalene (**14**) (Ru Cat.)*

To a solution of **11** (200 mg, 0.613 mmol) in dichloromethane (12 mL) at 23°C was added **1** (61 mg, 0.073 mmol) and the mixture was placed under an atmosphere of ethylene. After 18 h, the mixture was concentrated in vacuo. The residue was purified by flash chromatography (3% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (115 mg, 70%). R_f = 0.15 (4% ether–hexanes). IR (neat): 3019, 2826, 1653, 1613, 1586, 1559, 1513, 1456, 1374, 1301, 1248, 1172, 1034, 947, 821. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.50–1.61 (m, 2H), 1.85 (quintd, *J* = 6.5, 3.5 Hz, 2H), 1.98–2.14 (m, 4H), 2.19 (hept, *J* = 4 Hz, 1H), 3.79 (s, 3H), 4.38 (s, 2H), 5.61 (dt, *J* = 10, 2 Hz, 2H), 5.87 (dt, *J* = 10, 4 Hz, 2H), 6.85 (AB, *J* = 9 Hz, 2H), 7.25 (AB, *J* = 9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 23.32, 24.29, 34.43, 55.25, 64.10, 74.14, 113.70, 129.05, 129.64, 130.27, 132.18, 158.87. HRMS calcd. form M^+: 270.1620; found: 270.1611.

Cycloheptene intermediate: 5-(penta-1,4-dien-3-ol, *p*-methoxy benzyl ether)-cyclohept-1-ene (**13**): R_f = 0.37 (4% ether–hexanes). IR (neat): 2919, 1612, 1585, 1512, 1450, 1300, 1247, 1108, 1037, 927, 820, 737, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.05 (q, *J* = 11 Hz, 2H)1.77 (tt, *J* = 11, 3 Hz, 1H), 1.92–2.06 (m, 4H), 2.21–2.33 (m, 2H), 3.79 (s, 3H), 4.29 (s, 2H), 5.28 (dd, *J* = 18, 6 Hz, 2H), 5.35 (dd, *J* = 11, 2 Hz, 2H), 5.72–5.80 (m, 2H), 5.86 (dd, *J* = 18, 11 Hz, 2H), 6.87 (AB, *J* = 9 Hz, 2H), 7.26 (AB, *J* = 9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.98, 28.02, 52.62, 55.24, 64.72, 83.36, 117.25, 128.21, 131.87, 132.06, 138.16, 158.65.

*4a-(4-Methoxy-benzyloxy)-1,2,4a,7,8,8a-hexahydronaphthalene (**14**) (Mo Cat.)*

To a solution of **11** (47 mg, 0.142 mmol) in C_6H_6 (0.5 mL) at 23°C was added a solution of **2** (12 mg, 0.016 mmol) in C_6H_6 (1.5 mL). After 20 h the mixture was concentrated in vacuo and the residue purified by flash chromatography (3% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (28 mg, 73%).

cis- *and* trans-*2,7,8,8a-Tetrahydro-1*H-*naphthalen-4-ol (**15**)*

To a solution of **9** (100 mg, 0.242 mmol) in dichloromethane (4.5 mL) at 23°C was added **1** (40 mg, 0.049 mmol). After 1 hour PPh_3 (17 mg, 0.065 mmol) was added and the mixture was concentrated in vacuo and the residue was purified by flash chromatography (30% ether–hexanes) on triethyl amine washed silica gel to yield the title compounds as a white solid and a colorless oil (45 mg, 62% (*trans*)), (16 mg, 22% (*cis*)). Due to the sensitivity of the *trans* compound, it was immediately hydrogenated and characterized. The structure of the resulting decahydronaphthalenol was confirmed by comparison to spectral data reported in the literature (17).

cis-: IR (neat): 3351, 3023, 2908, 1429, 1383, 1326, 1204, 1021, 960. ^{1}H NMR (400 Mhz, $CDCl_3$) δ: 1.49–1.60 (m, 2H), 1.76–1.84 (m, 2H), 1.87–1.94 (m, 1H), 2.01–2.07 (m, 4H), 5.58 (dt, *J* = 10, 2 Hz, 2H), 5.77 (dt, *J* = 10, 3.7 Hz, 2H). ^{13}C NMR δ: 23.11, 24.27, 39.70, 38.34, 128.19, 131.34. HRMS calcd. for $C_{10}H_{14}O^+$ (M^+): 150.1045; found: 150.1044.

cis-*3a-Benzyloxy-1,3a,6,6a-tetrahydro-pentalene (**19**) (Ru Cat.)*

To a solution of benzyl ether **12** (100 mg, 0.372 mmol) in dichloromethane (4 mL) at 23°C was added **1** (12 mg, 0.04 equiv.). The resulting solution was stirred under an ethylene atmosphere for 20 h before PPh_3 (14 mg, 0.053 mmol) was added and the mixture concentrated in vacuo. The residue was purified by flash chromatography (2% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil along with cyclopentene **20** (63 mg, 80%) and (12 mg, 13%), respectively. R_f = 0.11 and 0.34 (2% ether–hexanes) respectively. IR (neat) 3053, 2919, 2848, 1497, 1448, 1378, 1349, 1216, 1139, 1099, 1028, 991, 733, 697. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.06–2.15 (m, 2H), 2.81–2.91 (m, 3H), 4.42 (s, 2H), 5.83 (dt, *J* = 6, 2 Hz, 2H), 5.92 (dt, *J* = 6, 2 Hz, 2H), 7.21–7.26 (m, 1H), 7.28–7.35 (m, 4H). ^{13}C NMR δ: 40.72, 43.03, 65.58, 105.70, 127.16, 127.55, 128.25, 132.54, 134.27, 139.56. HRMS calcd. for $C_{15}H_{16}O$ (M^+): 212.1201; found: 212.1196.

*Cyclopentene intermediate **11***: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.38 (d, *J* = 6 Hz, 4H), 2.74 (quint, *J* = 8Hz, 1H), 4.43 (s, 2H), 5.32 (AB, *J* = 1.5 Hz, 2H), 5.35 (q, *J* = 1.5 Hz, 2H), 5.62 (s, 2H), 5.90 (dd, *J* = 18, 10.5 Hz, 2H), 7.22–7.26 (m, 1H), 7.30–7.37 (m, 4H). ^{13}C NMR δ: 34.27, 45.33, 65.089, 82.77, 117.11, 126.82, 126.87, 128.15, 129.74, 138.04.

2-But-3-enyl-2-(3-tert-*butyldiphenylsiloxy-propyl) malonic acid dimethyl ester (**20**)*

Sodium hydride (1.10 g, 32.2 mmol) was washed three times with pentane, dried under a stream of nitrogen, and suspended in DMF (40 mL). A solution of dimethyl but-3-enyl malonate **3** (4.00 g, 21.5 mmol) in DMF (10 mL) was added via cannula at a rate such that hydrogen evolution was controlled. After 30 min, a solution $TBDPSO(CH_2)_3Br$ in DMF (10 mL) was added via cannula. After 20 h, the mixture diluted with ether and quenched by careful addition of water. The aqueous layer was extracted with ether, the organic layers were combined, washed with brine, dried over magnesium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (5% ether–hexanes) to yield the title compound as a colorless oil (5.00 g, 48%). IR (neat): 2954, 2858, 1732, 1434, 1257, 1104, 837, 776. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.05 (s, 9H), 1.36–1.46 (m, 3H), 1.89–2.05 (m, 7H) 3.65 (t, *J* = 6 Hz, 2H), 3.70 (s, 6H), 4.97 (dd, *J* = 10, 1.5 Hz, 1H), 5.03 (dd, *J* = 17, 1.5 Hz, 1H), 5.72–5.83 (m, 1H), 7.36–7.45 (m, 6H), 7.64–7.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.17, 26.81, 27.28, 28.30, 28.91, 31.60, 52.29, 57.04, 63.57, 115.00, 127.60, 129.56, 133.79, 135.52, 137.46, 172.02. HRMS calcd. for $C_{24}H_{29}O_5Si$ ($M-C_4H_9$): 425.1784; found: 425.1793.

2-(3-tert-*Butyldiphenylsiloxy-propyl)-hex-5-enoic acid methyl ester (**21**)*

Malonate **20** (5.00 g, 10.4 mmol) was reacted according to the general procedure for decarboxylation. The crude mixture was purified by flash chromatography (5% ether–hexanes) to yield title compound as a colorless oil (2.58 g,

58%). IR (neat): 2930, 1734, 1428, 1111. ^{1}H NMR ($CDCl_3$) δ: 1.05 (s, 9H), 1.49–1.79 (m, 6H), 2.00–2.08 (m, 2H), 2.35–2.44 (m, 1H), 3.63–3.68 (m, 5H), 4.97 (dm, J = 10 Hz, 1H), 5.02 (dq, J = 17, 2 Hz, 1H), 5.72–5.83 (m, 1H), 7.36–7.46 (m, 6H), 7.65–7.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.20, 26.84, 28.59, 30.22, 31.47, 31.54, 44.62, 51.33, 63.51, 115.02, 127.59, 129.53, 133.94, 135.54, 137.85, 176.51. HRMS calcd. for $C_{22}H_{25}O_3Si$ (M-$C_4H_9^+$): 367.1729; found: 367.1725.

4-(3-tert-*Butyldiphenylsiloxy-propyl)-3-vinyl-hepta-1,6-dien-3-ol* ***(22)***

Methyl ester **26** (1.25 g, 2.94 mmol) was reacted according to the general procedure for the conversion of a methyl ester to a tertiary diallylic alcohol. The crude product was purified by flash chromatography (8% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a pale green oil (754 mg, 57%). R_f = 0.25 (10% ether–hexanes). IR (neat): 3475, 2930, 1636, 1472, 1427, 1111. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.05 (s, 9H), 1.14–1.26 (m, 2H), 1.38–1.44 (m, 1H), 1.46–1.69 (m, 5H), 1.94–2.06 (m, 1H), 2.09–2.20 (m, 1H), 3.63 (t, J = 6 Hz, 2H), 4.93 (dm, J = 10 Hz, 1H), 4.98 (dq, J = 17, 2 Hz, 1H), 5.14 (ddd, J = 11, 3.5, 1 Hz, 2H), 5.25 (ddd, J = 17, 4, 1 Hz, 2H), 5.71–5.82 (m, 1H), 5.94 (ddd, J = 17, 11, 2 Hz, 2H), 7.35–7.45 (m, 6H), 7.65–7.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.19, 26.09, 26.87, 29.38, 31.86, 32.86, 46.18, 64.14, 79.10, 113.37, 114.39, 127.56, 129.50, 134.05, 135.57, 139.02, 142.06, 142.15. HRMS calcd. for $C_{25}H_{31}O_2Si$ (M-$C_4H_9^+$): 391.2093; found: 391.2098.

[2-(3-tert-*Butyldiphenylsiloxy-propyl)-1,1-divinyl-hex-5-enyloxymethyl]-4-methoxy-benzene* ***(23)***

Alcohol **22** (400 mg, 0.891 mmol) was reacted according to the general procedure for the *p*-methoxy benzylation of tertiary diallylic alcohols. The crude material was purified by flash chromatography (2% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (325 mg, 65%). R_f = 0.22 (5% ether–hexanes). IR (neat): 2930, 1615, 1513, 1428, 1247, 1111. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.08 (s, 9H), 1.12–1.24 (m, 2H), 1.55–1.80 (m, 5H), 2.02–2.23 (m, 2H), 3.66 (t, J = 6 Hz, 2H), 3.81 (s, 3H), 4.32 (s, 2H), 4.95 (dm, J = 10 Hz, 1H), 5.01 (dq, J = 17, 2 Hz, 1H), 5.31 (dt, J = 18, 1.5 Hz, 2H), 5.37 (ddd, J = 11, 4, 1.5 Hz, 2H), 5.78–5.87 (m 1H), 5.88 (ddd, J = 18, 11, 1 Hz, 2H), 6.87 (AB, J = 9 Hz, 2H), 7.27 (AB, J = 9 Hz, 2H), 7.37–7.47 (m, 6H), 7.68–7.72 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.20, 26.81, 26.88, 30.01, 32.29, 33.28, 47.70, 55.22, 64.37, 64.82, 84.01, 113.58, 114.13, 117.28, 127.54, 128.13, 129.45, 132.14, 134.16, 135.57, 138.15, 138.23, 139.35, 158.54. HRMS calcd. for $C_{33}H_{39}O_3Si$ (M-$C_4H_9^+$): 511.2668; found: 511.2689.

2-Allyl-(3-tert-*Butyldimethylsiloxy-propyl)-malonic acid dimethyl ester* ***(24)***

Sodium hydride (4.16 g, 104.1 mmol) and potassium hydride (cat.) were washed three times with pentane, suspended in DMF (75 mL) and cooled to 0°C. A solution of dimethyl malonate (11.9 mL, 104.1 mmol) in DMF (50 mL) was added via addition funnel at a rate such that the evolution of H_2 was controlled. The mixture was warmed to room temperature. After 30 min, a solution of TBDPSO(CH_2)$_3$Br (8.80 g, 34.7 mmol) in DMF (10 mL) was added via cannula. After 14 h, the mixture was diluted with ether and quenched carefully with water. The aqueous layer was washed three times with ether; the organic layers were combined, washed with brine, dried over magnesium sulfate, and filtered. The filtrate was concentrated in vacuo and the residue purified by fractional distillation. Collection of the fraction boiling between 100–110°C (0.1 mmHg) yielded the monoalkylated malonate as a colorless liquid (3.26 g, 31%). R_f = 0.23 (15% ether–hexanes). IR (neat): 2955, 2858, 1768, 1436, 1389, 1255, 1155, 1099, 1009, 837, 777. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.03 (s, 6H), 0.88 (s, 9H), 1.49–1.57 (m, 2H), 1.91–2.00 (m, 2H), 3.41 (t, J = 8 Hz, 1H), 3.62 (t, J = 6 Hz, 2H), 3.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.41, 18.26, 25.47, 25.87, 30.27, 51.35, 52.39, 62.40, 169.86. HRMS calcd. for (M-CH_3)$^+$: 289.1471; found: 289.1474.

Sodium hydride (0.509 g, 21.2 mmol) was washed three times with pentane and suspended in THF (20 mL). A solution of the monoalkylated malonate prepared as described above (3.00 g, 9.85 mmol) in THF (20 mL) was added via cannula at a rate such that H_2 evolution is controlled. After 15 min, allyl bromide (1.86 mL, 21.2 mmol) was added via syringe. After 1 h the mixture was diluted with ether, quenched carefully with water, and the aqueous layer was extracted two times with ether. The organic layers were combined, washed with brine, dried over magnesium sulfate and filtered. The filtrate was concentrated in vacuo and purified by flash chromatography (10% ether–hexanes) on silica gel to yield the title compound as a colorless oil (2.80 g, 83%). R_f = 0.32 (15% ether–hexanes). IR (neat): 2954, 2858, 1737, 1435, 1388, 1361, 1256, 1210, 1099, 1034, 921, 837, 776. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.03 (s, 6H), 0.87 (s, 9H), 1.35–1.44 (m, 2H), 1.87–1.95 (m, 2H), 2.64 (d, J = 7 Hz, 2H), 3.58 (t, J = 6 Hz, 2H), 3.70 (s, 6H), 5.05–5.13 (m, 2H), 5.57–5.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.36, 18.26, 25.89, 27.45, 28.84, 37.09, 52.29, 57.38, 62.86, 118.91, 132.38, 171.68. HRMS calcd. for (M-CH_3)$^+$: 329.1784; found: 329.1801.

2-(3-tert-*Butyldimethylsiloxy-propyl)-pentenoic acid methyl ester* ***(25)***

Malonate **24** (2.61 g, 7.58 mmol) was reacted according to the general decarboxylation procedure. The crude mixture was purified by flash chromatography (7% ether–hexanes) to yield the title compound as a colorless oil (960 mg, 44%). R_f = 0.20 (5% ether–hexanes). IR (neat): 2952, 2858, 1740, 1361, 1256, 1167, 1102, 1006, 915, 837, 776. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.02 (s, 6H), 0.87 (s, 9H), 1.44–1.66 (m, 4H), 2.18–2.26 (m, 1H), 2.30–2.40 (m, 1H), 2.41–2.49 (m, 1H), 3.58 (td, J = 6, J = 2 Hz, 2H), 3.65 (s, 3H), 4.97–5.08 (m, 2H), 5.66–5.78 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.36, 18.27, 25.89, 28.07, 30.40, 36.45, 44.97, 51.34, 62.72, 116.68, 135.41, 175.97. HRMS calcd. for (M-CH_3)$^+$: 271.1729; found: 271.1742.

4-(3-tert-*Butyldimethylsiloxy-propyl)-3-vinyl-hepta-1,6-dien-3-ol* ***(26)***

Methyl ester **25** (0.900 g, 3.13 mmol) was reacted under standard condition for the conversion of methyl esters to

diallylic tertiary alcohols. The crude product was purified by flash chromatography (7% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a pale green oil (314 mg, 32%). R_f = 0.25 (10% ether–hexanes). IR (neat): 3475, 3079, 2929, 2858, 1639, 1472, 4109, 1361, 1256, 1100, 999, 921, 836, 775, 735. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.04 (s, 6H), 0.88 (s, 9H), 1.16–1.26 (m, 1H), 1.42–1.52 (m, 1H), 1.53–1.70 (m, 3H), 1.83 (s, 1H), 2.02 (quint, *J* = 7 Hz, 1H), 2.30–2.38 (m, 1H), 3.56 (t, *J* = 6 Hz, 2H), 4.98 (dquint, *J* = 10, 0.5 Hz, 1H), 5.02 (dq, *J* = 17, 0.5 Hz, 1H), 5.16 (dd, *J* = 11, 1 Hz, 2H), 5.28 (dt, *J* = 17, 1 Hz, 2H), 5.81–6.00 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.29, 18.31, 25.32, 25.94, 31.75, 34.34, 46.51, 63.31, 79.23, 113.48, 115.80, 138.37, 141.79, 142.20. HRMS calcd. for $C_{17}H_{31}O_2Si$ $(M\text{-}CH_3)^+$: 295.2091; found: 295.2091.

2-(3-tert-*Butyldimethylsiloxy-propyl)-1,1-divinyl-pent-4-enyloxymethyl)-benzene (**27**)*

Alcohol **26** (288 mg, 0.927 mmol) was reacted according to the general benzylation procedure to yield the title compound as a colorless oil (329 mg, 89%). R_f = 0.21 (2% ether–hexanes). IR (neat): 3086, 2929, 2858, 1639, 1497, 1472, 1408, 1380, 1255, 1099, 1027, 1004, 929, 836, 775, 728, 695, 661. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.03 (s, 6H), 0.88 (s, 9H), 1.10–1.20 (m, 1H), 1.46–1.57 (m, 1H), 1.58–1.74 (m, 3H), 1.82–1.94 (m, 1H), 2.46–2.54 (m, 1H), 3.55 (t, *J* = 6 Hz, 2H), 4.37 (s, 2H), 4.93 (d, *J* = 10 Hz, 1H), 4.99 (dq *J* = 17, 1 Hz, 1H), 5.30 (dd, *J* = 17, 1.5 Hz, 2H), 5.36 (dd, *J* = 11, 1.5 Hz, 2H), 5.80–5.90 (m, 1H), 5.89 (dd, *J* = 18, 11 Hz, 2H), 7.21–7.26 (m, 1H), 7.29–7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.26, 18.33, 25.97, 26.36, 32.30, 35.13, 48.00, 63.56, 65.12, 83.79, 114.92, 117.48, 117.55, 126.75, 126.81, 128.14, 137.81, 138.16, 139.06, 139.98. HRMS calcd. for $(M\text{-}CH_3)^+$: 385.2563; found: 385.2581.

cis- *and* trans-*6-(3*-tert-*Butyldiphenylsiloxy-propyl)-1-vinyl-cyclohex-2-enol (**28**)*

To a 23°C solution of triene **22** (200 mg, 0.446 mmol) in dichloromethane (4.5 mL) was added **1** (44 mg, 0.053 mmol). After 5 h PPh_3 (28 mg, 0.107 mmol) was added and the mixture concentrated in vacuo. A crude ^{1}H NMR showed a 2.8:1 mixture of diastereomers in favor of the product having the methine proton and OH substituent *trans* to one another. The residue was purified by flash chromatography (15% ether–hexanes) on triethyl amine washed silica gel to yield the title product as a colorless oil (151 mg, 80%).

cis-: IR (neat): 3441, 3071, 2931, 1651, 1590, 1472, 1428, 1390, 1361, 1175, 1111, 998, 822. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.94–1.08 (m, 1H), 1.05 (s, 9H), 1.20–1.33 (m, 1H), 1.47–1.59 (m, 2H), 1.62–1.78 (m, 3H), 2.01–2.07 (m, 2H), 3.62–3.71 (m, 2H), 5.14 (dd, *J* = 11, 2 Hz, 1H), 5.18 (dd, *J* = 17, 2 Hz, 1H), 5.41 (dt, *J* = 10, 2 Hz, 1H), 5.87 (dt, *J* = 10, 4 Hz, 1H), 5.87 (dd, *J* = 17, 11 Hz, 1H), 7.35–7.45 (m, 6H), 7.65–7.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.22, 24.78, 25.21, 25.92, 26.91, 30.79, 45.21, 64.30, 75.31, 114.38, 127.58, 128.44, 129.50, 132.63, 134.15, 135.60, 140.37.

trans-: IR (neat): 3471, 3071, 3020, 2931, 1649, 1589, 1472, 1428, 1390, 1361, 1304, 1111, 997, 954, 921, 823, 937, 701, 614. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (s, 9H), 1.10–1.21 (m, 1H), 1.34–1.54 (m, 4H), 1.60–1.78 (m, 3H), 1.92–2.04 (m, 1H), 2.07–2.16 (m, 1H), 3.68 (t, *J* = 6 Hz, 2H), 5.14 (dd, *J* = 11, 1.5 Hz, 1H), 5.32 (dd, *J* = 17, 1.5 Hz, 1H), 5.52 (dt, *J* = 10, 2 Hz, 1H), 5.83 (dd, *J* = 17, 11 Hz, 1H), 5.87 (dq, *J* = 10, 2.5 Hz, 1H), 7.36–7.46 (m, 6H), 7.66–7.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.19, 22.85, 24.67, 25.43, 26.89, 30.75, 42.84, 64.18, 72.71, 113.14, 127.54, 129.47, 130.35, 131.78, 134.15, 135.58, 144.45. HRMS calcd. for $(M\text{-}C_4H_9)^+$: 363.1780; found: 363.1887.

cis- *and* trans-*[6-(3*-tert-*Butyldiphenylsiloxy-propyl)-1-vinyl-cyclohex-2-enyloxymethyl]-4-methoxy-benzene (**29**) (Mo Cat.)*

To a solution of triene **23** (51 mg, 0.089 mmol) in C_6H_6 (0.5 mL) at 23°C was added a solution of **2** (4 mg, 0.006 mmol) in C_6H_6 (0.5 mL). The resulting solution was stirred for 90 min before the mixture was concentrated in vacuo. A crude ^{1}H NMR showed a 7.8:1 mixture favoring the *cis*-diastereomer. The ratio was determined by comparing the integration of the doublets of triplets appearing at δ 5.61 (*cis*-) and δ 5.75 (*trans*-) in the crude ^{1}H NMR. The residue was purified by flash chromatography (2% ether–hexanes) on triethyl amine washed silica gel to yield the title compounds as colorless oils (42 mg, 86%).

cis-: R_f = 0.20, (5% ether–hexanes). IR (neat) 2931, 1613, 1513, 1472, 1428, 1301, 1247, 1171, 1111, 998, 822, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92–1.10 (m, 1H), 1.05 (s, 9H), 1.26–1.38 (m, 1H), 1.44–1.55 (m, 1H), 1.63–1.89 (m, 4H), 2.03–2.09 (m, 2H), 3.66 (td, *J* = 6, 1.5 Hz, 2H), 3.79 (s, 3H), 4.38 (s, 2H), 5.18 (dd, *J* = 17, 2 Hz, 1H), 5.22 (dd, *J* = 11, 2 Hz, 1H), 5.61 (dt, *J* = 10, 2 Hz, 1H), 5.88 (dd, *J* = 17, 11 Hz, 1H), 5.99 (dt, *J* = 10, 3.5 Hz, 1H) 6.84 (AB, *J* = 9 Hz, 2H), 7.24 (AB, *J* = 9 Hz, 2H), 7.35–7.45 (m, 6H), 7.66–7.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.00, 23.86, 25.03, 25.19, 26.68, 30.58, 40.43, 55.06, 65.93, 64.27, 76.48, 30.58, 40.43, 55.06, 65.93, 64.27, 76.48, 80.56, 113.44, 116.25, 127.35, 128.469, 129.22, 129.26, 131.08, 132.87, 134.96, 135.37, 140.89, 158.53. HRMS calcd. for $C_{31}H_{35}O_3Si$ $(M\text{-}C_4H_9)^+$: 483.2355; found: 483.2363.

trans-: R_f = 0.29, (5% ether–hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (s, 9H), 1.26–1.50 (m, 3H), 1.56–1.76 (m, 3H), 1.76–1.86 (m, 1H), 1.92–2.04 (m, 1H), 2.07–2.17 (m, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 4.39 (AB, *J* = 11 Hz, 1H), 4.42 (AB, *J* = 11 Hz, 1H), 5.18 (dd, *J* = 6, 1.5 Hz, 1H), 5.22 (s, 1H), 5.75 (dt, *J* = 10, 2 Hz, 1H), 5.88–5.96 (m, 1H), 6.01 (dq, *J* = 10, 2 Hz, 1H), 6.84 (AB, *J* = 9 Hz, 2H), 7.24 (AB, *J* = 9 Hz, 2H), 7.34–7.44 (m, 6H), 7.65–7.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.21, 22.73, 24.08, 25.30, 26.88, 31.03, 43.83, 55.26, 64.36, 64.58, 110.39, 113.56, 115.25, 127.53, 128.16, 128.49, 129.42, 132.05, 132.49, 134.21, 135.58, 143.14, 158.50.

cis- *and* trans-*[6-(3*-tert-*Butyldiphenylsiloxy-propyl)-1-vinyl-cyclohex-2-enyloxymethyl]-4-methoxy-benzene (**29**) (Ru Cat.)*

To a solution of triene **23** (200 mg, 0.351 mmol) in dichloromethane (3.5 mL) at 23°C was added **1** (12 mg, 0.014 mmol). After 3 h, PPh_3 (7 mg, 0.029 mmol) was

added and the mixture was concentrated in vacuo. A crude ^{1}H NMR showed a 6.1:1 mixture favoring the *cis*-diastereomer. The ratio was determined by comparing the integration of the doublets of triplets appearing at δ 5.61 (*cis*-) and δ 5.75 (*trans*-) in the crude ^{1}H NMR. The residue was purified by flash chromatography (5% ether–hexanes) on triethyl amine washed silica gel to yield the title compounds as colorless oils (181 mg, 96%).

cis- *and* trans-*5-(3*-tert-*Butyldimethylsiloxy-propyl)-1-vinyl-cyclopent-2-enol (**30**)*

To a solution of triene **26** (29 mg, 0.093 mmol) in C_6H_6 (1.0 mL) at 23°C was added **1** (4.6 mg, 0.0056 mmol). The resulting solution was stirred for 90 min before PPh_3 (6 mg, 0.0075 mmol) was added and the mixture concentrated in vacuo. A crude ^{1}H NMR showed a 1:1 mixture of diastereomers. The ratio was determined by comparing the integration of the doublets of quartets appearing at δ 5.59 and δ 5.69 in the crude ^{1}H NMR. The mixture was purified by flash chromatography (10% ether–hexanes) on triethyl amine washed silica gel to yield the title compounds as a colorless oil (17 mg, 65%).

cis- *and* trans-*mixture*: IR (neat): 3418, 2929, 1472, 1255, 1097, 995, 922, 836, 775, 663. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.04 (s, 6H), 0.88 (s, 9H), 1.20–1.32 (m, 1H), 1.34–1.44 (m, 1H), 1.50–1.64 (m, 2H), 1.87 (s, 1H), 1.86–2.18 (m, 2 H), 2.54 (tdq, *J* = 16.5, 7.5, 1.5 Hz, 1H), 3.62 (m, 2H), 5.06–5.31 (series of doublets, 2H), 5.59, (dq, *J* = 6, 1 Hz, 0.5 H), 5.69 (dq, *J* = 6, 1 Hz, 0.5H), 5.82 (dd, *J* = 17, 11 Hz, 0.5 H), 5.98 (dd, *J* = 17, 11 Hz, 0.5 H), 5.91 (quint., *J* = 2 Hz, 0.5H), 5.99–6.03 (m, 0.5H). ^{13}NMR (100 MHz, $CDCl_3$) δ: –5.26, 18.37, 25.99, 26.70, 31.65, 37.59, 37.64, 47.66, 51.96, 63.39, 63.48, 84.77, 87.21, 112.31, 113.05, 132.32, 134.19, 136.12, 136.79, 143.43.

cis- *and* trans-*5-(3*-tert-*Butyldimethylsiloxy-propyl)-1-vinyl-cyclopent-2-enyloxy benzyl ether (**31**) (Mo Cat.)*

To a solution of triene **27** (20 mg, 0.050 mmol) in C_6H_6 (0.5 mL) at 23°C was added a solution of **2** (2.5 mg, 0.003 mmol) in C_6H_6 (0.5 mL). The resulting solution was stirred for 30 min before PPh_3 (10 mg, 0.038 mmol) was added and the mixture concentrated in vacuo. A crude ^{1}H NMR showed a 1.7:1 mixture favoring the (*R**,*S**) diastereomer. The ratio was determined by comparing the integration of the doublets of triplets appearing at δ 5.81 (*cis*-) and δ 6.17 (*trans*-) in the crude ^{1}H NMR. The mixture was purified by flash chromatography (1% ether–hexanes) on triethyl amine washed silica gel to yield the title compounds as colorless oils (35 mg, 94%).

cis-: R_f = 0.15, (2% ether–hexanes). IR (neat): 3062, 2929, 2856, 1497, 1472, 1406, 1381, 1360, 1255, 1096, 1064, 1028, 1005, 924, 836, 775, 733, 696, 667. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.04 (s, 6H), 0.89 (s, 9H), 1.17–1.28 (m, 1H), 1.50–1.66 (m, 3H), 1.87 (qt, *J* = 8, 2 Hz, 1H), 2.31–2.41 (m, 1H), 2.56 (qq, *J* = 8, 1.5, 1H), 3.55–3.64 (m, 2H), 4.49, 4.53 (AB, 12 Hz, 2H), 5.12 (dd, *J* = 18, 2 Hz, 1H), 5.19 (dd *J* = 11, 2 Hz, 1H), 5.81 (dt, *J* = 6, 2 Hz, 1H), 5.89 (dd, *J* = 18, 11 Hz, 1H), 6.05 (dt, *J* = 6, 1.5 Hz, 1H), 7.21–7.26 (m, 1H), 7.28–7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.27, 18.33, 25.97, 26.81, 31.78, 37.06, 47.79, 63.44, 65.64, 93.08, 115.19, 127.01, 127.11, 128.19, 132.74, 134.44, 138.85, 139.90. HRMS calcd. for $C_{23}H_{36}O_2Si$ (M^+): 372.2453; found: 372.2469.

trans-: R_f = 0.10, (2% ether–hexanes). IR (neat): 3056, 2929, 2857, 1741, 1608, 1472, 1434, 1380, 1255, 1094, 996, 924, 835, 775, 742, 695. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.05 (s, 6H), 0.90 (s, 9H), 1.51–1.68 (m, 3H), 1.68–1.80 (m, 1H), 2.22 (ddt, *J* = 16.5, 8, 2 Hz, 1H), 2.52 (dddd, *J* = 16.5, 9, 3, 1.5 Hz, 1H), 3.59–3.68 (m, 2H), 4.36, 4.48 (AB, 12 Hz, 2H), 5.14 (dd, *J* = 11, 2 Hz, 1H), 5.24 (dd, *J* = 18, 2 Hz, 1H), 5.81 (dq, *J* = 6, 1.5 Hz, 1H), 6.04 (dd, *J* = 18, 11 Hz, 1H), 6.17 (dt, *J* = 6 Hz, 2 Hz, 1H), 7.20–7.26 (m, 1H), 7.28–7.36 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.25, 18.37, 24.36, 25.99, 31.96, 38.32, 50.08, 63.59, 65.26, 77.31, 89.21, 113.84, 126.65, 126.76, 128.06, 132.63, 137.06, 140.30, 142.13. HRMS calcd. for $C_{19}H_{27}O_2Si$ ($M-C_4H_9$): 315.1780; found: 315.1781.

cis- *and* trans-*5-(3*-tert-*Butyldimethylsiloxy-propyl)-1-vinyl-cyclopent-2-enyloxy benzyl ether (**31**) (Ru Cat.)*

To a solution of triene **27** (39 mg, 0.097 mmol) in dichloromethane (1.0 mL) at 23°C was added **1** (2.4 mg, 0.003 mmol). The resulting solution was stirred for 1 h before PPh_3 (3 mg, 0.014 mmol) was added and the mixture concentrated in vacuo. A crude ^{1}H NMR showed an 8:1 mixture favoring the (*cis*-). The ratio was determined by comparing the integration of the doublets of triplets appearing at δ 5.81 (*cis*-) and δ 6.17 (*trans*-) in the crude ^{1}H NMR. The mixture was purified by flash chromatography (1% ether–hexanes) on triethyl amine washed silica gel to yield the title compounds as colorless oils (36 mg, 99%).

*3-Allyl-3-benzyl-dihydro-furan-2-one (**36**)*

Diisopropylamine (10.98 mmol, 1.32 mL) is added to THF (13 mL) and the resulting solution is cooled to –78°C. *n*-BuLi (10.98 mmol, 2.5 M in hexanes, 4.39 mL) is then added dropwise. The solution is stirred for an additional 30 min at –78°C at which time 3-allyl-dihydro-furan-2-one (18) in THF (13mL) is added dropwise by cannula addition. The solution is stirred for an additional 30 min at –78°C followed by dropwise addition of benzyl bromide (11.98 mmol, 1.42 mL) in HMPA(2.2 mL). The solution is stirred for an additional 3 h at –78°C. The reaction is quenched with aq. sat'd. ammonium chloride solution and the mixture is diluted with ether. The layers are separated and the aqueous layer is extracted with ether (three times). The combined organic layers are dried over $MgSO_4$, filtered, and concentrated. The crude product is purified by flash chromatography (20% Et_2O–hexanes) to yield the title compound as a colorless oil (1.39 g, 77%). IR (neat): 2915 (m), 1757 (s), 1212 (w), 1166 (s), 1029 (s), 920 (m), 702 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (t, *J* = 8 Hz, 2H), 2.33 (dd, *J* = 13.8 Hz, 8 Hz, 1H), 2.51 (dd, *J* = 14 Hz, 6.4 Hz, 1H), 2.74 (d, *J* = 13.2 Hz, 1H), 3.07 (d, *J* = 13.2 Hz, 1H), 3.46 (q, *J* = 8.8 Hz, 1H), 4.02 (q, *J* = 6.4 Hz, 1H), 5.17 (dd, *J* = 9.2 Hz, 1.2 Hz, 1H), 5.21 (s, 1H), 5.79 (qt, *J* = 8.4 Hz, 2 Hz, 1H), 7.19–7.32 (m, 5H). ^{13}C NMR (100MHz, $CDCl_3$) δ: 29.87, 42.15, 42.88, 48.07, 65.43, 119.98, 127.23, 128.68, 130.08, 132.80, 136.63, 180.96. HRMS calcd. (M^+): 216.1150; found: 216.1152.

*4-Benzyl-4-(2-*tert*-butyldimethylsiloxy-ethyl)-3-vinyl-hepta-1,6-diene-3-ol (**39**)*

3-Allyl-3-benzyl-dihydro-furan-2-one (1.0 g, 4.6 mmol) was reacted under standard conditions for the conversion of methyl esters to diallylic tertiary alcohols. The crude product was dissolved in DMF (40 mL) and imidazole (0.469 g, 6.9 mmol) and *tert*-butyldimethylsilyl chloride (0.69 g, 4.6 mmol) were added. The solution is stirred at room temperature for 12 h. The reaction volume is doubled with water and extract with ether (three times). Wash the organic layers with water, dry over Na_2SO_4, filter, and concentrate. Flash chromatography (5% Et_2O–hexanes) provided the title compound as a colourless oil (1.0 g, 57% over two steps). IR (neat): 3359 (s), 2936 (s), 2838 (w), 2309 (w), 1254 (m), 1081 (s), 997 (m), 916 (m), 839 (m), 772 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.08 (s, 6H), 0.91 (s, 9H), 1.72 (t, *J* = 6 Hz, 2H), 2.20 (dd, *J* = 15 Hz, 6.4 Hz, 1H), 2.41 (dd, *J* = 15 Hz, 6.4 Hz, 1H), 2.80 (d, *J* = 14 Hz, 1H), 2.88 (d, *J* = 14 Hz, 1H), 3.77 (t, *J* = 6 Hz, 2H), 4.10 (brs, 1H), 4.93–5.01 (m, 2H), 5.19 (ddd, *J* = 10.8 Hz, 4.8 Hz, 1.6 Hz, 2H), 5.35 (ddd, *J* = 18.5 Hz, 3 Hz, 1.6 Hz, 2H), 5.59–5.70 (m, 1H), 6.15 (dd, *J* = 14.8 Hz, 10.8 Hz, 1H), 6.20 (dd, 14.8 Hz, 10.8 Hz, 1H), 7.16–2.27 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.23, –5.18, 18.57, 26.17, 36.33, 38.99, 40.49, 47.62, 60.35, 80.24, 114.73, 114.76, 116.98, 126.23, 128.11, 131.21, 1136.70, 139.36, 140.55, 140.58. HRMS calcd. $(M\text{-}CH_3)^+$: 371.2406; found: 371.2414.

trans-*5-Benzyl-5-(2-*tert*-butyldimethylsiloxy-ethyl)-1-vinyl-cyclopent-2-enol (**43**)*

To a solution of triene (240 mg, 0.6217 mmol) in dichloromethane (25 mL) at 23°C was added **1** (25.5 mg, 0.03 mmol). The solution is stirred for 6 h at room temperature at which time **1** (25.5 mg, 0.03 mmol) is again added. The solution is stirred for an additional 12 h at room temperature, when **1** (25.5 mg, 0.03 mmol) is added for the final time. After stirring at room temperature for an additional 6 h, the reaction is opened to air and the solvent is removed in vacuo. Flash chromatography(5% Et_2O– hexanes) provides the title compound (134 mg, 60%) as a single diastereomer, as a colourless oil. The stereochemistry was determined by ROESY experiment. R_f = 0.10 (5% Et_2O–hexanes). IR (neat): 3397 (s), 2928 (s), 1495 (m), 1257(s), 1079 (s), 1023 (m), 836 (m), 720 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.55 (s, 6H), 0.90 (s, 9H), 1.26 (m, 2H), 1.86 (ddd, *J* = 15.2 Hz, 10.4 Hz, 2.4 Hz, 1H), 1.20 (dd, *J* = 16.2 Hz, 1.6 Hz, 1H), 2.55 (d, *J* = 16.4 Hz, 1H), 2.64 (d, *J* = 13.6 Hz, 1H), 2.80 (d, *J* = 13.6 Hz, 1H), 3.54 (td, *J* = 10.4 Hz, 1.2 Hz, 1H), 3.65 (ddd, *J* = 10.5 Hz, 5.8 Hz, 2.8 Hz, 1H), 5.16 (dd, *J* = 10.6 Hz, 2 Hz, 1H), 5.21 (s, 1H), 5.25 (dd, *J* = 17.4 Hz, 2 Hz, 1H), 5.64–5.66 (m, 1H), 5.84–5.87 (m, 1H), 5.97 (dd, *J* = 17.4 Hz, 10.8 Hz, 1H), 7.11–7.26 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.57, –5.38, 18.38, 26.05, 37.81, 41.81, 43.20, 52.59, 59.92, 87.75, 112.91, 126.03, 128.06, 129.32, 130.46, 138.24, 140.22, 140.72. HRMS calcd. $(M\text{-}C_4H_9)^+$: 301.1623; found: 301.1618.

*[2-Allyl-3-benzyloxy-2-(2-*tert*-butyldimethylsiloxy-ethyl)-3-vinyl-pent-4-enyl]-benzene (**40**)*

4-Benzyl-4-(2-*tert*-butyldimethylsiloxy-ethyl)-3-vinyl-hepta-1,6-diene-3-ol (300 mg, 0.77 mmol) was reacted acccording to the general benzylation procedure to yield the title compound as a colorless oil (314 mg, 85%) after flash chromatography(100% hexanes). R_f = 0.6 (5% Et_2O–hexanes). IR (neat): 2950 (s), 2852 (m), 1634 (w), 1461 (w), 1254 (m), 1085 (s), 1064 (s), 930 (m), 835 (m), 772 (w). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.01 (s, 6H), 0.87 (s, 9H), 1.745 (m, 2H), 2.21 (dd, *J* = 14.8 Hz, 6.8 Hz, 1H), 2.37 (dd, *J* = 14.8 Hz, 7.6 Hz, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 2.97 (d, *J* = 13.6 Hz, 1H), 3.68 (m, 1H), 3.87 (m, 1H), 4.32 (s, 2H), 4.92 (dd, *J* = 10 Hz, 2 Hz, 1H), 4.95 (dd, *J* = 17.2 Hz, 2 Hz, 1H), 5.30 (dd, *J* = 4 Hz, 1.6 Hz, 1H), 5.35 (dd, *J* = 4 Hz, 1.6 Hz, 1H), 5.44 (dd, *J* = 8 Hz, 1.6 Hz, 1H), 5.47 (dd, *J* = 6.8 Hz, 1.6 Hz, 1H), 5.794 (m, 1H), 6.04 (dd, *J* = 16 Hz, 11.2 Hz, 1H), 6.09 (dd, *J* = 16 Hz, 11.2 Hz, 1H), 7.21–7.37 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.01, 18.50, 26.18, 27.06, 37.81, 39.39, 47.79, 60.71, 65.67, 86.48, 116.00, 118.42, 118.60, 126.06, 127.05, 127.12, 127.94, 128.35, 131.36, 136.26, 136.52, 136.89, 139.56, 139.66. HRMS calcd. $(M\text{-}C_4H_9)$: 419.2406; found: 419.2392.

*[2-Benzyloxy-1-(2-*tert*-butyldimethylsiloxy-ethyl)-2-vinyl-cyclopent-3-enylmethyl]-benzene (**44**)*

To a solution of triene **40** (30 mg, 0.063 mmol) in dichloromethane(1 mL) at 23°C was added **1** (5.168 mg, 0.0063 mmol). After 12 h at room temperature, the reaction is opened to air and the solvent is removed in vacuo. A crude ^{1}H NMR showed a 2:1 mixture of diastereomers, favouring the *cis*-diastereomer. The two diastereomers were inseparable by flash chromatography. To confirm the stereochemistry of the diastereomers, alcohol *trans*-**43** (30 mg, 0.083 mmol) was reacted under the general benzylation procedure to yield *trans*-**44** (35 mg, 95%) as a colourless oil after flash chromatography (100% hexanes).

trans-: IR (neat): 2950 (m), 2852 (m), 1602 (w), 1451 (m), 1254 (m), 1081 (s), 906 (m), 737 (s), 691 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: –0.04 (s, 3H), –0.03 (s, 3H), 0.84 (s, 9H), 1.86 (t, 7.6 Hz, 2H), 2.10 (dt, *J* = 16.8 Hz, 2 Hz, 1H), 2.33 (ddd, *J* = 16.6 Hz, 2.8 Hz, 1.6 Hz, 1H), 2.45 (d, *J* = 13.6 Hz, 1H), 2.69 (d, *J* = 13.6 Hz, 1H), 3.69–3.76 (m, 1H), 3.84–3.91 (m, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.50 (d, *J* = 11.6 Hz, 1H), 5.26 (dd, *J* = 17.6 Hz, 1.6 Hz, 1H), 5.34 (dd, *J* = 10.8 Hz, 1.6 Hz, 1H), 5.94 (dd, *J* = 17.6 Hz, 10.8 Hz, 1H), 5.99 (dt, *J* = 6 Hz, 1.6 Hz, 1H), 6.08 (dt, *J* = 6 Hz, 2.4 Hz, 1H), 7.15–7.39 (m, 10H). HRMS calcd. (M^+): 448.2797; found: 448.2802.

cis-: IR (neat): 2950 (m), 2852 (m), 1602 (w), 1451 (m), 1254 (m), 1081 (s), 906 (m), 737 (s), 691 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: –0.02 (s, 3H), –0.01 (s, 3H), 0.84 (s, 9H), 1.53 (t, *J* = 7.6 Hz, 2H), 2.08 (d, *J* = 16.4 Hz, 1H), 2.58 (d, *J* = 16.4 Hz, 1H), 2.97 (d, *J* = 13.6 Hz, 1H), 3.06 (d, *J* = 13.6 Hz, 1H), 3.38–3.45 (m, 1H), 3.55–3.61 (m, 1H), 4.37 (d, *J* = 11.6 Hz, 1H), 4.47 (d, *J* = 11.6 Hz, 1H), 5.25 (s, 1H), 5.28 (dd, *J* = 5.2 Hz, 1.6 Hz, 1H), 5.79 (dd, *J* = 18 Hz, 10.4 Hz, 1H), 6.04 (s, 2H), 7.15–7.34 (m, 10H). HRMS calcd. (M^+): 448.2797; found: 448.2802.

^{13}C NMR (100 MHz, $CDCl_3$) mixture of diastereomers δ: –5.10, –5.06, 18.41, 26.12, 33.68, 36.57, 41.00, 41.72, 52.65, 61.41, 65.84, 93.07, 117.10, 125.99, 127.04, 127.10,

127.88, 128.25, 128.54, 128.92, 129.15, 130.98, 131.44, 135.52, 137.92, 139.09, 139.81, 140.07.

*3-Benzyl-3-but-3-enyl-dihydro-furan-2-one (**38**)*

3-But-3-enyl-hihydrofuran-2-one (**37**) (1.1 g, 7.857 mmol) was reacted according to the same procedure for the synthesis of 3-allyl-3-benzyl-dihydro-furan-2-one (**36**). Flash chromatography (20% Et_2O–hexanes) provides 1.32 g (74%) of the title compound as a colourless oil. R_f = 0.5 (50% Et_2O–hexanes). IR (neat): 2910 (m), 1760 (s), 1634 (w), 1447 (m), 1173 (s), 1029 (s), 913 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.68–1.81 (m, 2H), 2.06–2.25 (m, 4H), 2.75 (d, *J* = 13.6 Hz, 1H), 3.05 (d, *J* = 13.6 Hz), 3.45–3.51 (m, 1H), 4.00–4.06 (m, 1H), 4.98 (d, *J* = 10.4 Hz, 1H), 5.05 (dt, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.75–5.85 (m, 1H), 7.18–7.30 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 28.82, 30.60, 36.74, 42.76, 47.91, 65.26, 115.41, 127.22, 128.67, 130.06, 136.65, 137.52, 181.07. HRMS calcd. (M^+): 230.1306; found: 230.1259.

*4-Benzyloxy-4-(2-*tert*-butyldimethylsiloxy-ethyl)-3-vinyl-octa-1,7-dien-3-ol (**41**)*

3-Benzyl-3-but-3-enyl-dihydro-furan-2-one **38** (1.0 g, 4.37 mmol) was reacted under standard conditions for the conversion of methyl esters to tertiary diallylic alcohols. The crude product was dissolved in DMF (50 mL) and imidazole (0.469 g, 6.9 mmol) and *tert*-butyldimethylsilyl chloride (0.69 g, 4.6 mmol) were added. After stirring at room temperature for 12 h, water (50 mL) is added. Extract with ether (three times) and wash with water. Dry over Na_2SO_4, filter, and concentrate. Flash chromatography (5% Et_2O–hexanes) provides 0.825 g (48% over two steps) of the title compound as a colourless oil. R_f = 0.3 (5% Et_2O–hexanes). IR (neat): 3371 (s), 2929 (s), 1639 (w), 1471 (m), 1255 (m), 1079 (s), 910 (s), 836 (m), 733 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.12 (s, 6H), 0.94 (s, 9H), 1.50–1.96 (m, 6H), 2.81 (d, *J* = 14 Hz, 1H), 2.86 (d, *J* = 14 Hz, 1H), 3.76–3.84 (m, 2H), 3.98 (br s, 1H), 4.88 (s, 1H), 4.91 (d, *J* = 6.8 Hz, 1H), 5.20 (dd, *J* = 12 Hz, 1.6 Hz, 1H), 5.23 (dd, *J* = 12 Hz, 1.6 Hz, 1H), 5.38 (dd, *J* = 17.2 Hz, 2 Hz, 1H), 5.39 (dd, *J* = 17.2 Hz, 2 Hz, 1H), 5.66–5.76 (m, 1H), 6.20 (dd, *J* = 17.2 Hz, 10.8 Hz, 1H), 6.20 (dd, *J* = 17.2 Hz, 10.8 Hz, 1H), 7.17–7.29 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.21, –5.17, 18.55, 26.16, 29.30, 33.00, 36.30, 40.78, 47.17, 60.39, 80.19, 114.02, 114.02, 114.73, 114.84, 126.20, 128.11, 130.97, 139.40, 139.54, 140.59, 140.76. HRMS calcd. ($M-C_4H_9$)$^+$: 343.0183; found: 343.0187.

*[2-(1-Benzyloxy-1-vinyl-allyl)-2-(2-*tert*-butyldimethylsiloxy-ethyl)-hex-5-enyl]-benzene (**42**)*

Alcohol **41** (150 mg, 0.375 mmol) was reacted according to the general benzylation procedure to yield the title compound as a colourless oil (165 mg, 90%) after flash chromatography (100% hexanes). R_f = 0.7 (5% Et_2O–hexanes). IR (neat): 2950 (m), 2859 (m), 1641 (m), 1451 (m), 1254 (m), 1081 (s), 930 (m), 835 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.01 (s, 6H), 0.87 (s, 9H), 1.42–2.11 (m, 6H), 2.86 (d, *J* = 14 Hz, 1H), 2.92 (d, *J* = 13.6 Hz, 1H), 3.60–3.67 (m, 1H), 3.82–3.88 (m, 1H), 4.33 (s, 2H), 4.87 (s, 1H), 4.90 (d, *J* = 7.8 Hz, 1H), 5.34 (dd, *J* = 19.4 Hz, 2 Hz, 1H), 5.34 (dd, *J* = 17.6 Hz, 1.6 Hz, 1H), 5.46 (dd, *J* = 11 Hz, 2 Hz, 1H), 5.46 (dd, *J* = 11.2 Hz, 1.2 Hz, 1H), 5.65–5.75 (m, 1H), 6.02 (dd, *J* = 17.8 Hz, 11 Hz, 1H), 6.07 (dd, *J* = 17.8 Hz, 11 Hz, 1H), 7.19–7.36 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.00, 18.49, 26.19, 29.45, 33.58, 37.54, 40.03, 47.45, 60.83, 65.77, 86.63, 113.85, 118.47, 118.70, 126.06, 127.07, 127.10, 128.00, 128.37, 131.11, 136.16, 136.52, 139.65, 139.76, 139.81. HRMS calcd. ($M-C_4H_9$)$^+$: 433.2562; found: 433.2576.

*6-Benzyl-6-(2-*tert*-butyldimethylsiloxy-ethyl)-1-vinyl-cyclohex-2-en-1-ol (**45**)*

To a solution of triene **41** (100 mg, 0.25 mmol) id dichloromethane(20 mL) is added **1** (24 mg, 0.03 mmol). The solution is stirred for 12 h at room temperature at which time the reaction is opened to air and the solvent is removed in vacuo. A crude ^{1}H NMR showed a 1:1 mixture of diastereomers at 100% conversion. The residue is purified by flash chromatography (5% Et_2O–hexanes) to provide the R*,S* diastereomer (37.6 mg, 40%) and the R*,R* diastereomer (30 mg, 32%) as colourless oils. The stereochemistry of the R*,S* diastereomer was proven by ROESY experiment.

trans-: IR (neat): 3388 (s), 2929 (m), 1471 (w), 1255 (m), 1078 (s), 1003 (m), 836 (s), 777 (m), 702 (w). ^{1}H NMR (400 MHz, $CDCl_{3)}$) δ: 0.08 (s, 6H), 0.91 (s, 9H), 1.43–1.53 (m, 2H), 1.58–1.66 (m, 1H), 1.73 (ddd, *J* = 17.6 Hz, 8.4 Hz, 2.4 Hz, 1H), 1.93–2.13 (m, 2H), 2.59 (d, *J* = 13.6 Hz, 1H), 3.04 (d, *J* = 13.6 Hz, 1H), 3.68–3.73 (m, 1H), 4.01 (ddd, *J* = 11 Hz, 8.8 Hz, 2.4 Hz, 1H), 4.89 (s, 1H), 5.22 (dd, *J* = 10.8 Hz, 2 Hz, 1H), 5.29 (dd, *J* = 17.4 Hz, 2 Hz, 1H), 5.48 (dt, *J* = 10 Hz, 2.4 Hz, 1H), 5.69 (dt, *J* = 10 Hz, 2.4 Hz, 1H), 6.10 (ddd, *J* = 17.2 Hz, 10.8 Hz, 0.8 Hz, 1H), 7.07–7.27 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.29, –5.18, 18.33, 22.69, 26.00, 26.21, 29.10, 35.18, 39.38, 43.31, 60.20, 76.49, 114.46, 125.98, 126.13, 127.98, 131.23, 134.02, 139.08, 142.19. HRMS calcd. (M^+): 372.2482; found: 372.2483.

cis-: IR (neat): 3388 (s), 2929 (m), 1471 (w), 1255 (m), 1078 (s), 1003 (m), 836 (s), 777 (m), 702 (w). ^{1}H NMR ($CDCl_3$) δ: 0.13 (d, *J* = 0.8 Hz, 6H), 0.94 (s, 9H), 1.23–1.49 (m, 3H), 1.62–1.69 (m, 1H), 2.20–2.30 (m, 1H), 2.79 (d, *J* = 14.8 Hz, 1H), 3.19 (d, *J* = 14.8 Hz, 1H), 3.48 (dt, *J* = 11.2 Hz, 4.4 Hz, 1H), 4.11 (td, *J* = 10.88 Hz, 3.2 Hz, 1H), 4.31 (br s, 1H), 5.12 (dd, *J* = 10.6 Hz, 1.6 Hz, 1H), 5.19 (*J* = 16 Hz, 2 Hz, 1H), 5.43 (dt, *J* = 9.6 Hz, 2.4 Hz, 1H), 5.81 (dt, *J* = 10 Hz, 3.6 Hz, 1H), 6.14 (dd, *J* = 17.2 Hz, 10.4 Hz, 1H), 7.16–7.28 (m, 5H). ^{13}C NMR δ: –0.53, –5.15, 0.14, 22.92, 26.22, 28.90, 37.39, 43.38, 60.60, 95.61, 114.31, 125.96, 128.12, 130.77, 131.99, 142.65. HRMS calcd. (M^+): 372.2482; found: 372.2483.

*[2-Benzyloxy-1-(2-*tert*-butyldimethylsiloxy-ethyl)-2-vinyl-cyclohex-3-enylmethyl]-benzene (**46**)*

A solution of triene **42** (100 mg, 0.204 mmol) in dichloromethane (10 mL) is added **1** (16 mg, 0.02 mmol). The solution is stirred for 12 h at room temperature at which time the reaction is opened to air and the solvent removed in vacuo. A crude ^{1}H NMR showed a 4.5:1 mixture of diastereomers, favouring the R*,R* *cis*-diastereomer. Unable to separate the diastereomers by flash chromatography, the diastereomeric

alcohols **45** reacted under the general benzylation procedure to yield the title compounds as colourless oils.

cis- *and* trans-*mixture*: IR (neat): 2927 (m), 1495 (w), 1254 (m), 1067 (s), 929 (w), 835 (m), 774 (w), 731 (w), 701 (m). ^{1}H NMR (400 MHz, $CDCl_3$) δ: –0.11 (s, 6H), 0.77 (s, 9H), 1.32–1.45 (m, 2H), 1.75–1.85 (m, 3H), 2.08–2.23 (m, 2H), 2.54 (d, *J* = 13.6 Hz, 1H), 2.71 (d, *J* = 13.6 Hz, 1H), 3.35–3.46 (m, 1H), 3.62–3.69 (m, 1H), 4.38 (d, *J* = 11.6 Hz, 1H), 4.46 (d, *J* = 11.6 Hz, 1H), 5.23 (dd, *J* = 17.6 Hz, l.6 Hz, 1H), 5.41 (dd, *J* = 10.8 Hz, 1.6 Hz, 1H), 5.79 (dt, *J* = 10.4 Hz, 2 Hz, 1H), 6.00 (dt, *J* = 10.4 Hz, 3.6 Hz, 1H), 6.05 (dd, *J* = 17.8 Hz, 11.2 Hz, 1H), 7.14–7.28 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: –5.08, 18.43, 23.47, 25.47, 26.15, 36.98, 40.12, 43.53, 61.19, 64.88, 118.69, 125.99, 126.95, 126.99, 127.18, 127.98, 128.24, 131.09, 131.18, 139.41, 140.21, 140.79.

*5-(1-Tributylstannylmethoxy-1-vinyl-allyl)-nona-1,8-diene (**47**)*

Potassium hydride (729 mg, 7.27 mmol) was washed three times with pentane, dried under a stream of argon and suspended in THF (5 mL). A solution of alcohol **8** (500 mg, 2.42 mmol) in THF (3 mL) was added via cannula. After 5 min, a solution of ICH_2SnBu_3 in THF (2 mL) was added via cannula followed by a small crystal of dry 18-crown-6. The resulting mixture was heated to reflux for 1 h, cooled to 23°C, diluted with ether, and quenched carefully by dropwise addition of water. The aqueous layer was extracted two times with ether, the organic layers were combined, washed with brine, dried over sodium sulfate, filtered and concentrated in vacuo. The residue was purified by flash chromatography (100% hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (1.15 g, 93%). R_f = 0.55 (100% hexanes). IR (neat): 3079, 2926, 1640, 1456, 1416, 1017, 909. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.89 (t, *J* = 7 Hz, 9H), 0.89 (tt, $J^{(H\text{-}Sn)}$ = 25 Hz, $J^{(H\text{-}H)}$ = 8 Hz, 6H), 1.04–1.14 (m, 2H), 1.30 (hex., *J* = 7 Hz, 6H), 1.40–1.82 (m, 11H), 1.86–2.18 (m, 5H), 3.40 (t, $J^{(H\text{-}Sn)}$ = 10 Hz, 2H), 4.92 (dm, *J* = 10 Hz, 2H), 4.97 (dq, *J* = 17, 2 Hz, 2H), 5.17 (dd, *J* = 18, 2 Hz, 2H), 5.34 (dd, 11, 2 Hz, 2H), 5.74 (dd, *J* = 18, 11 Hz, 2H), 5.72–5.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.84 (t, $J^{(C\text{-}Sn)}$ = 61 Hz), 13.73, 27.36 (t, $J^{(C\text{-}Sn)}$ = 26 Hz), 29.21 (t, $J^{(C\text{-}Sn)}$ = 10 Hz), 30.12, 33.46, 47.02, 52.46, 85.45, 114.03, 117.42, 137.92, 139.40. HRMS calcd. for $C_{23}H_{41}OSn$ ($M\text{-}C_4H_9^+$): 453.2179; found: 453.2181.

cis-*4a-Tributylstannylmethoxy-1,2,4a,7,8,8a-hexahydrohaphthalene (**48**)*

To a solution of **47** (1.00 g, 1.96 mmol) in dichloromethane (20 mL) at 23°C was added **1** (194 mg, 0.240 mmol). The reaction mixture was placed under an atmosphere of ethylene and heated to reflux. After 7 h the reaction was concentrated in vacuo and the residue purified by flash chromatography (100% hexanes → 0.5% → 1% → 2% ether–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (760 mg, 86%). R_f = 0.19 (1% ether–hexanes). IR (neat) 3051, 2924, 1464, 1348, 1040, 758. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (t, *J* = 7 Hz, 9H), 0.88 (tt, $J^{(H\text{-}Sn)}$ = 25 Hz, $J^{(H\text{-}H)}$ = 8 Hz, 6H), 1.25–1.34 (m, 6H), 1.43–1.54 (m, 6H), 1.70–1.79 (m, 2H), 1.98–2.05 (m, 4H), 2.13 (hept., *J* = 3.5 Hz, 1H), 2.71–2.84 (m, 3H), 3.53 (t, $J^{(H\text{-}Sn)}$ = 10 Hz, 2H), 5.51 (dt, *J* = 10, 2 Hz, 2H), 5.80 (dt, *J* = 10, 4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.93 (t, $J^{(C\text{-}Sn)}$ = 61 Hz), 13.74, 23.41, 24.30, 27.31 (t, $J^{(C\text{-}Sn)}$ = 26 Hz), 29.17 (t, $J^{(C\text{-}Sn)}$ = 10 Hz), 32.99, 50.86, 74.69, 129.02, 130.49.

cis-*(2,3,4,4a,5,6-Hexahydronaphthalen-2-yl)-methanol (**49**)*

MeLi (1.08 M, 214 μL): To a solution of stannyl methyl ether **48** (100 mg, 0.221 mmol) and HMPA (154 μL, 0.882 mmol) was added MeLi (1.08 M, 214 μL). After 15 min the reaction was quenched by adding MeOH (2 drops). The mixture was purified by adding the crude reaction directly to column of triethyl amine washed silica gel and eluting with 30% ether–hexanes to yield the title compound as a colorless oil (25 mg, 67%). R_f = 0.17 (30% ether–hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21–1.36 (m, 3H), 1.36–1.47 (m, 1H), 1.77–1.94 (m, 3H), 2.08–2.26 (m, 3H), 2.39–2.49 (bs, 1H), 3.50–3.61 (m, 2H), 5.37 (s, 1H), 5.72–5.78 (m, 1H), 6.02 (dm, *J* = 10 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.97, 26.07, 30.10, 30.21, 35.76, 39.71, 67.50, 123.77, 128.62, 129.12, 139.59.

*5-(1-Trimethylsiloxy-1-vinyl-allyl)-nona-1,8-diene (**50**)*

A 23°C suspension of KH (161 mg, 1.27 mmol, 35% suspension in oil, washed three times with pentane) in THF (5 mL) was added to **9** (250.09, 1.21 mmol). After 15 min, TMSCl (161 μL, 1.27 mmol) was added via syringe. After 30 min, water was added, and the mixture extracted three times with Et_2O. The organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated to dryness. The residue was purified by flash chromatography (100% hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless oil (310 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.88 (s, 9H), 1.05 (m, 2H), 1.39 (septet, *J* = 3.5, 1H), 1.58–1.65 (m, 2H), 1.99–2.19 (m, 4H), 4.92 (dm, *J* = 10 Hz, 2H), 4.99 (dq, *J* = 17, 1.7 Hz, 2H), 5.21 (dd, *J* = 10.5, 2 Hz, 2H), 5.25 (dd, *J* = 17.5, 2 Hz, 2H), 5.73–5.84 (m, 2H), 5.92 (dd, *J* = 17.5, 10.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 2.59, 30.09, 33.50, 48.05, 81.60, 114.14, 115.81, 139.38, 141.03. HRMS calcd. for $C_{15}H_{27}OSi$ ($M\text{-}C_2H_3$)$^+$: 251.1831; found: 251.1824.

cis-*4a-Trimethylsiloxy-1, 2, 4a, 7, 8, 8a-hexahydronaphthalene (**51**)*

A solution of **2** (174 mg, 0.23 mmol) in C_6H_6 (5 mL) was added to a flask containing **50** (603 mg, 2.30 mmol). After 30 min, 600 mg of PPh_3 was added and the mixture concentrated to dryness. The residue was purified by flash chromatography (2% Et_2O on triethylamine washed silica gel) to yield to title compound as a colorless oil consisting of a 5:1 mixture of diastereomers favoring the *cis*-isomer (64 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.12 (s, 9H), 1.44–1.53 (m, 2H), 1.76–1.84 (m, 2H), 1.91–1.98 (m, 1H), 1.99–2.12 (m, 4H), 5.57 (dt, *J* = 10, 2Hz, 2H), 5.71 (dt, *J* = 10, 3.7 Hz, 2H). ^{13}C NMR δ: 2.66, 23.23, 24.24, 39.85, 71.25, 127.38, 132.35.

cis-*4a-(Prop-2-enyloxy)-1, 2, 4a, 7, 8, 8a-hexahydronaphthalene (**52**)*

A THF (1 mL) solution of **15** (100 mg, 0.67 mmol) was added to a 23°C suspension of sodium hydride (133 mg,

3.33 mmol, 60% suspension in oil) which had been washed three times with pentane. After five minutes, propargyl bromide (375 μL, 3.33 mmol, 70% solution in toluene) was added via syringe. After 16 h, the reaction was quenched by the careful addition of water. The mixture was extracted three times with Et_2O, the organic layers were combined, washed with brine, dried over Na_2SO_4, filtered and concentrated to dryness. The residue was purified by flash chromatography (5% Et_2O– hexanes) on triethylamine washed silica gel to yield the title compound as a colorless liquid (58 mg, 46%). IR (neat, cm^{-1}): 3298, 3025, 2919, 1436, 1052. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.46–1.56 (m, 2H), 1.78–1.87 (m, 2H), 1.96–2.15 (m, 5H), 2.36 (t, *J* = 2.5 Hz, 1H), 4.07 (d, *J* = 2.5 Hz, 2H), 5.54 (dt, *J* = 10, 2Hz, 2H), 5.88 (dt, *J* = 10, 3.7 Hz, 2H). ^{13}C NMR δ: 23.26, 24.17, 34.25, 50.53, 72.90, 75.24, 81.89, 129.35, 130.53. HRMS calcd. for M^+: 187.1123; found: 187.1126.

cis-*4a-(But-2-yloxy), 1, 2, 4a, 7, 8, 8a, hexahydronaphthalene (**53**)*

A solution of *n*-BuLi (90 μL, 0.233 mmol, 2.5 M solution in hexanes) was added via syringe to a –78°C solution of **52** (40 mg, 0.212 mmol) in THF (2 mL). After 15 min, methyl iodide (20 μL, 0.318 mmol) was added via syringe and the mixture was allowed to warm to 23°C. After 2 h, water was added and the mixture was extracted three times with Et_2O, the organic layers were combined, washed with brine, dried over Na_2SO_4, filtered and concentrated to dryness. The residue was purified by flash chromatography (5% Et_2O–hexanes) on triethyl amine washed silica gel to yield the title compound as a colorless liquid (39 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ: 1.49 (sextet, *J* = 7 Hz, 2H), 1.75–1.88 (m, 4H), 1.94–2.12 (m, 5H), 3.98–4.05 (m 2H), 5.56 (d, *J* = 10 Hz, 2H), 5.87 (dt, *J* = 10, 3.7 Hz, 2H). ^{13}C NMR δ: 3.70, 23.23, 24.18, 34.07, 50.89, 74.67, 76.86, 80.97, 129.54, 130.13.

1S/R*,1aS*, 4aS*-1-(2, 3, 4, 4a, 5,6-Hexahydronaphthalen-2-yl)-but-2yn-1-ol (**54**)*

^{t}BuLi (233 μL, 0.396 mmol, 1.7 M solution in pentane) was added to a –78°C solution of **53** (20 mg, 0.099 mmol) in THF (1 mL). After 30 min, water is added and the mixture extracted three times with Et_2O, the organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated to dryness. The residue was purified by flash chromatography (10% Et_2O–hexanes) to yield the title compound as a colorless liquid (12 mg, 63%). IR (neat): 3400, 6064, 2922, 2858, 1716, 1668, 1448, 1377, 1261, 1052. ^1H NMR (400 MHz, $CDCl_3$) δ: 1.2–2.24 (m, 10H), 2.5 (bs, 1H), 4.15 (bs, 1H (minor isomer), 4.24 (bs, 1H (major isomer), 5.44 (s, 1H (major isomer)), 5.58 (s, 1H (minor isomer), 5.72–5.80 (m, 1H), 6.00–6.10 (m, 1H). ^{13}C NMR δ: –0.03, 3.61, 14.11, 22.67, 24.46, 24.86, 25.41, 25.97, 26.90, 29.69, 30.04, 30.08, 30.23, 35.72, 43.91, 66.32, 66.58, 79.05, 81.83, 122.12, 123.02, 128.69, 128.76, 129.23, 140.08. HRMS calcd. for M^+: 202.1358; found: 202.1351.

Conclusions

In conclusion, we have demonstrated a novel diastereoselective double ring closing metathesis reaction as an approach to the synthesis of bicyclo[4.4.0]decadienes and bicyclo[3.3.0]octadienes. The new bicyclic compounds allow for further synthetic transformations enabling the construction of valuable intermediates such as that found in the HMG CoA Reductase inhibitor (+)-Mevinolin. Present efforts are directed towards enantioselective alkene differentiation reactions that would allow the synthesis of enantioenriched bicyclic compounds. The methodology and concepts outlined in this paper should prove useful in the synthesis of complex natural products.

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References

1. (*a*) K.J. Ivin. J. Mol. Catal. A Chem. **133**, 1 (1998); (*b*) R.H. Grubbs and S. Chang. Tetrahedron, **54**, 4413 (1998); (*c*) M.S. Schuster and S. Blechert. Angew. Chem. Int. Ed. Engl. **36**, 2036 (1997); (*d*) M.L. Randall and M.L. Snapper. J. Mol. Catal. A-Chem. **133**, 29 (1998); (*e*) S.K. Armstrong. J. Chem. Soc. Perkin Trans. 1, 371 (1998); (*f*) A. Fürstner. Top. Catal. **4**, 285 (1997); (*g*) A. Fürstner. Topics in organometallic chemistry. Vol. 1. Springer, Berlin. 1998.
2. (*a*) C.M. Huwe, J. Velder, and S. Blechert. Angew. Chem. Int. Ed. Engl. **35**, 2376 (1996); (*b*) H. Oguri, S. Sasaki, T. Oishi, and M. Hirama. Tetrahedron Lett. **40**, 5405 (1999); (*c*) B. Schmidt and H. Wildemann. Synlett. 1591 (1999).
3. (*a*) C. Baylon, M.-P. Heck, and C. Mioskowski. J. Org. Chem. **64**, 3354 (1999); (*b*) M.J. Bassindale, P. Hamley, A. Leitner, and J.P.A. Harrity. Tetrahedron Lett. **40**, 3247 (1999); (*c*) J.S. Clark and O. Hamelin. Angew. Chem. Int. Ed. Engl. **39**, 372 (2000).
4. M. Lautens and G. Hughes. Angew. Chem. Int. Ed. Engl. **38**, 129 (1999).
5. (*a*) I. Shimizu and F. Aida. Chem. Lett. 601 (1988); (*b*) J. Tsuji and T. Mandai. Synthesis, 1 (1996); (*c*) J. Tsuji, I. Minami, and I. Shimizu. Synthesis, 623 (1986).
6. G. Hughes, M. Lautens, and J. Wu. Synlett. 835 (2000).
7. S. Watanbe, K. Suga, T. Fujita, and N. Saito. Aust. J. Chem. **30**, 427 (1977).
8. T. Imamoto, N. Takiyama, K. Nakamura, T. Hatajima, and Y. Kamiya. J. Am. Chem. Soc. **111**, 4392 (1989).
9. D.F. Murray, M.W. Baum, and M. Jones. J. Org. Chem. **51**, 1 (1985).
10. (*a*) A.J. Shaka and R. Freeman. J. Magn. Reson. **51**, 169 (1983); (*b*) H. Kessler, C. Griesinger, R. Kerssebaum, K. Wagner, and R.R. Ernst. J. Am. Chem. Soc. **109**, 607 (1987); (*c*) A. Bax and D.G. Davis. J. Magn. Reson. **107**, 207 (1985).
11. (*a*) H. Priepke and R. Brückner. Chem. Ber. **123**, 153 (1990); (*b*) W.C. Still. J. Am. Chem. Soc. **100**, 1481 (1978); (*c*) W.C. Still and A. Mitra. J. Am. Chem. Soc. **100**, 1927 (1978).
12. K. Tomooka, N. Komine, and T. Nakai. Tetrahedron Lett. **39**, 5513 (1998), and refs. therein.

13. T.A. Kirkland and R.H. Grubbs. J. Org. Chem. **62,** 7310 (1997).
14. T.R. Hoye and H. Zhao. Org. Lett. **1**, 1123 (1999).
15. (*a*) J.P.A. Harrity, M.S. Visser, J.D. Gleason, and A.H. Hoveyda. J. Am. Chem. Soc. **119**, 1488 (1997); (*b*) G.S. Weatherhead, J.G. Ford, E.J. Alexanian, R.R. Schrock, and A.H. Hoveyda. J. Am. Chem. Soc. **122**, 1828 (2000), and refs. therein.
16. P. Schwab, R.H. Grubbs, and J.W. Ziller. J. Am. Chem. Soc. **118**, 100 (1996).
17. (*a*) W.A. Ayer, L.M. Browne, S. Fung, and J.B. Stothers. Org. Magn. Reson. **11**, 73 (1978); (*b*) L.M. Brown, R.E. Klinck, and J.B. Stothers. Org. Magn. Reson. **12**, 561 (1979).
18. G.A. Molander and C.R. Harris. J. Am. Chem. Soc. **117**, 3705 (1995).

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4. Daniel P. Christen . [CrossRef]
5. Y FUKUDA, H SASAKI, M SHINDO, K SHISHIDO. 2002. Diastereoselective ring-closing metathesis for the construction of a quaternary carbon stereogenic center#. *Tetrahedron Letters* **43**:11, 2047-2049. [CrossRef]