Diastereoselective Ring-Closing Metathesis in the Synthesis of Dihydropyrans

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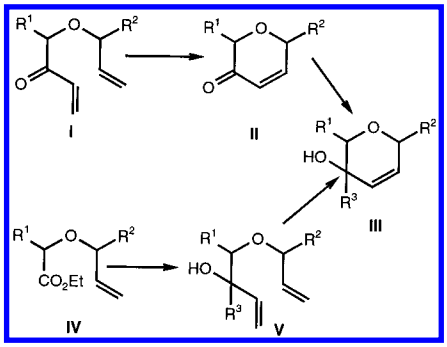
An investigation into the factors influencing the diastereochemical outcome of the ring-closing metathesis based synthesis of dihydropyrans is presented in this paper. Divinyl carbinols derived from α-hydroxy carboxylic acid esters are elaborated to trienes with two diastereotopic vinyl moieties. Depending on the steric demand of the oxo substituent of the divinyl carbinol moiety (either unprotected OH, TBDMS, or benzyl ether) different diastereomers are preferrably formed upon ring-closing metathesis. An extension to diastereoselective double ring-closing metathesis in the formation of spirocycles has also been investigated.

Introduction

The application of ring-closing metathesis[1,2] to the synthesis of unsaturated oxacycles[3,4] has been investigated by several groups over the past few years. Examples are the formation of spirocyclic dihydropyrans and dihydrofurans[5,6] and trans-fused polyether fragments[7−11] on carbohydrate scaffolds. Our own contributions to the field started with a project directed to the utilization of ring-closing metathesis for the synthesis of C-glycosides.[12,13] With a view toward the synthesis of structural elements of polyether natural products,[14] we became interested in the synthesis of di- and tetrahydropyrans with a quaternary center in the 3-position.[15] In principle, one can imagine two different strategies to obtain such products: either an enone **I** is cyclized to a dihydropyranone **II**, followed by addition of an appropriately substituted organometallic reagent R^3M to give the dihydropyran **III**, or the ester **IV** is converted to a carbinol **V** by subsequent addition of a vinylmetal compound and the organometallic reagent R^3M, followed by ring-closing metathesis to give **III** (Scheme 1).

Scheme 1



Ring-closing metathesis of enones such as **I** normally requires higher catalyst loadings and addition of a Lewis-acid because the catalytic activity of the ruthenium carbene intermediate is significantly reduced by formation of a chelate.[16−19] Thus, from the viewpoint of catalytic efficiency, the second route seems to be more promising. In this case, it is particularly interesting to investigate the ring-closing metathesis of those substrates that result when R^3 = vinyl, because the two vinyl moieties of the divinyl carbinol **V** are diastereotopic and the ring-closing metathesis step may in principle become diastereoselective. Compared to the number of publications on olefin metathesis in general, comparatively few contributions have addressed stereoselective variants so far. Enantioselective ring-closing metathesis reactions using chirally modified catalysts have been conducted as kinetic resolutions[20,21] or as desymmetrization reactions.[22] A stereoselective synthesis of 2,5-disubstituted five membered azacycles represents the first diastereoselective ring-closing metathesis reaction.[23] Recently, Lautens et al.

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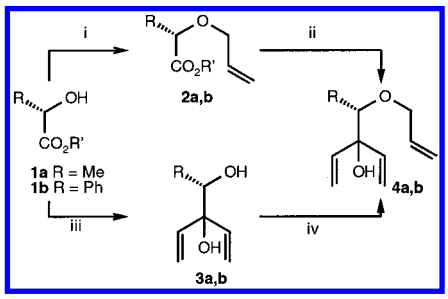
Scheme 2[a]



[a] Key: (i) Ag_2O, allyl bromide, ether, 20 °C (**2a**: 80%; **2b**: 99%); (ii) H_2C=CHMgCl (2 equiv.), ether, −78 °C (**4a**: 63%; **4b**: 44%); (iii) H_2C=CHMgCl (3 equiv), ether, −78 °C (**3a**: 65%; **3b**: 31%); (iv) NaH, allyl bromide, THF, 0 °C, 12h (**4a**: 51%).

reported the formation of *cis*- and *trans*-decalin systems via a stereoselective double ring-closing metathesis reaction.[24] A metathesis-based approach to the AB ring fragment of Ciguatoxin includes the diastereoselective formation of an oxepine.[25] Diastereoselective spirocycle assembly by double ring-closing metathesis was very recently achieved by others[26] and by ourselves.[27]

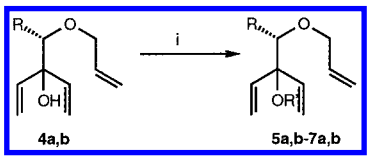
In this paper, we describe our results on the stereoselectivity of ring-closing metathesis reactions in the synthesis of dihydropyrans with functionalizable substituents.

Results and Discussion

Divinylcarbinols **4** required for this study were synthesized starting from the commercially available α-hydroxy carboxylic acid esters (*S*)-ethyl lactate (**1a**) and DL-methyl mandelate (**1b**) (Scheme 2).

O-Allylation of **1a**,**b** was achieved without racemization or other undesired side reactions using allyl bromide and silver oxide.[28] Addition of 2 equiv of vinylmagnesium chloride to the esters **2a**,**b** provides divinyl carbinols **4a**,**b**, along with minor amounts of the corresponding butenones resulting from a 1,4-addition of the second equivalent of the vinyl Grignard reagent. Alternatively, we investigated the route via the diols **3a**,**b**. Addition of excess vinylmagnesium chloride to esters **1a**,**b** provides the diols **3a**,**b**. Methyl derivative **3a**[29] is obtained with none or very small amounts of the corresponding 1,4-addition product, whereas from mandelic acid ester a 1:1 mixture of **3b** and the butenone results. Selective allylation of the secondary alcohol functionality in **3a** is achieved by treatment with one equivalent of sodium hydride and allyl bromide at 0 °C. The reaction proceeds with quantitative yield. The divinyl carbinol moiety is obviously rather sensitive, however, which leads to a significant decrease of the yield if analytically pure material is required. Surprisingly, the allylation step completely fails if methyl mandelate is employed. In this case a viscous residue is obtained containing no low-molecular weight products. Thus, for preparative purposes **4a** is most conveniently prepared via diol **3a**, whereas **4b** is best obtained from **2a**.

Scheme 3[a]

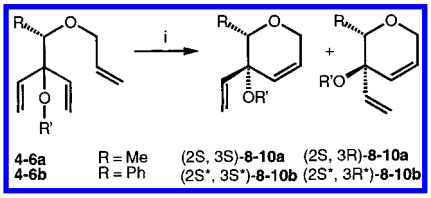


[a] Key: (i) NaH, THF, 65 °C, then R′-X, 65 °C (see Table 1).

Table 1. Yields and Numbering System for Trienes (cf. Scheme 3)

entry	starting material	R	R′-X	product	yield (%)
1	**4a**	Me	Bn-Br	(*S*)-**5a**	55
2	**4a**	Me	TBDMS-Cl	(*S*)-**6a**	61
3	**4a**	Me	All-Br	(*S*)-**7a**	71
4	**4b**	Ph	Bn-Br	*rac*-**5b**	63
5	**4b**	Ph	TBDMS-Cl	*rac*-**6b**	52
6	**4b**	Ph	All-Br	*rac*-**7b**	85

Scheme 4[a]



[a] Key: (i) $Cl_2(Cy_3P)_2Ru$=CHPh (**A**) (3 mol %), CH_2Cl_2, 20 °C (see Table 2).

Table 2. Results for Diastereoselective RCM Reactions (See Scheme 4)

entry	starting material	R	R′	product	(2*S*,3*S*)/(2*S*,3*R*)	yield (%)
1	**4a**	Me	H	(2*S*)-**8a**	3:1	66
2	**5a**	Me	Bn	(2*S*)-**9a**	1:3	45
3	**6a**	Me	TBDMS	(2*S*)-**10a**	1:2	91
4	**4b**	Ph	H	*rac*-**8b**	4:1	56
5	**5b**	Ph	Bn	*rac*-**9b**	<1:10	62
6	**6b**	Ph	TBDMS	*rac*-**10b**	1:6	87

A set of substituted metathesis precursors is obtained from **4a**,**b** by introducing various hydroxy protecting groups of different steric demand. Functionalization of the tertiary alcohol as a benzyl, TBDMS, or allyl ether requires excess of base, elevated temperatures, and prolonged reaction times; nevertheless, the sensitive allyloxy and divinyl carbinol moieties are not affected by these rather harsh conditions. Scheme 3 and Table 1 summarize this synthetic step.

Ring-closing metathesis reactions of the trienes **4**, **5** and **6** proceeds at ambient temperature in the presence of 3 mol % of Grubbs' catalyst $Cl_2(Cy_3P)_2Ru$=CHPh (**A**). Diastereomeric ratios were determined prior to workup by means of HNMR spectroscopy. Conversion to the product is normally quantitative; the yields reported here refer to the amount of material isolated after chromatography on silica. From ring-closing metathesis of the unprotected divinyl carbinols preferrably the (2*S**, 3*S**)-isomers of **8a**,**b** result, whereas upon introduction of a benzyl or TBDMS protecting group the (2*S**,3*R**)-isomers are preferred (Scheme 4 and Table 2). Two-dimensional NOE spectroscopy was used to determine the relative stereochemistry: interactions between H2 and the protons of the exo-vinyl moiety are indicative of the (2*S**,3*S**)-stereochemistry. Deprotection of the ring-closing metathesis products **10a**,**b** resulting from the TBDMS ethers

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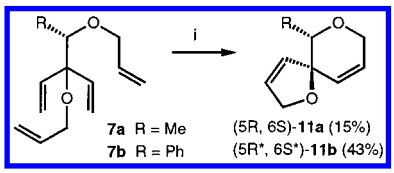
Scheme 5[a]



[a] Key: (i) $Cl_2(Cy_3P)_2Ru{=}CHPh$ (**A**) (6 mol %), DCM, 20 °C.

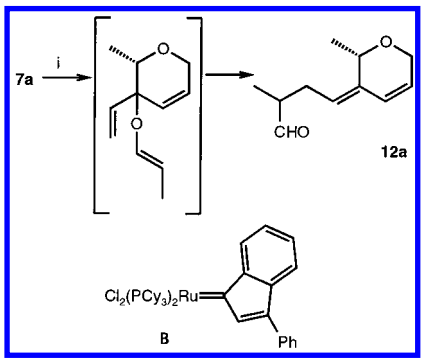
yields mainly the alcohols (2*S**,3*R**)-**8a**,**b**. In contrast to methyl mandelate (**1b**), ethyl lactate (**1a**) was used in enantiomerically pure form. To find out if any racemization occurs during the sequence from **1a** to **4a**, NMR-shift experiments were conducted for the 3:1 mixture of (2*S*,3*S*)- and (2*S*, 3*R*)-**4a** at 400 MHz using the europium-(III) [heptafluoropropylhydroxymethylene)camphorate] ($Eu(hfc)_3$) reagent. Racemic **4a** was required in order to find conditions where sufficient separation of relevant signals (most conveniently the doublets of the methyl group are observed) is achieved. Therefore, (*S*)-ethyl lactate was allylated under strongly basic conditions (sodium hydride) to give *rac*-**2a**, from which *rac*-**4a** was obtained as outlined above. By these shift-experiments it was possible to demonstrate that both the material obtained via **2a** and the material obtained via **3a** are enantiomerically pure.

1,2-Stereoinduction is more efficient for the phenyl derivatives **4b**−**6b** due to the higher steric demand of the phenyl substituent compared to the methyl group. The stereochemical results can be understood if one assumes a trans-orientation of the substituent at C2 and the sterically more demanding substituent at C3 in the transition state. For the unprotected derivatives **4a**,**b**, this is obviously the vinyl moiety, whereas the oxo-substituent becomes more demanding upon derivatization as benzyl or TBDMS ether.

Allyl ethers **7a**,**b** are substrates for a double ring-closing metathesis leading to spirocyclic systems **11a**,**b** (Scheme 5). The reaction proceeds only with poor or moderate yield due to competing intermolecular metathesis. However, in both cases only one diastereoisomer was isolated and it was not possible to detect the other diastereomer from the reaction mixture.

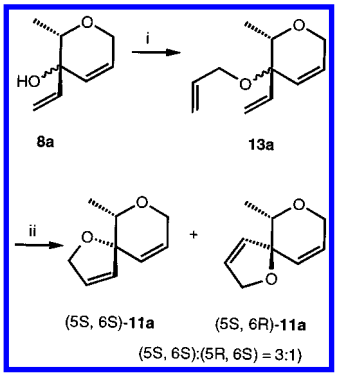
Naturally, in double ring-closing metathesis reactions the question arises: "Which ring is closed first?" We were unable to isolate any intermediates; however, if the dihydrofuran is formed first, this step might be reversible via a ring opening/ring-closing metathesis sequence. There have been several reports in the literature on ROM/RCM-sequences when strained five-membered rings are involved.[30−32] The yield for the methyl derivative is particularly disappointing. We repeated this experiment using a novel carbene complex **B**, which was originally assigned an allenylidene type structure.[33−35] In our hands, ring-closing metathesis using this complex proceeds very rapidly at elevated temperatures. When the tetraene **7a** is subjected to the conditions, mainly undefined oligomeric products result. The only isolable low molecular weight product is a single diastereomer of dihydropyran **12a**; its formation is obviously the result of a sequential double bond isomerization to an enol ether intermediate, followed by a Claisen rearrangement (Scheme 6).

Scheme 6[a]



[a] Key: (i) **B** (8 mol %), toluene, 110 °C.

Scheme 7[a]



[a] Key: (i) NaH, allyl bromide, THF, 65 °C (76%); (ii) $Cl_2(Cy_3P)_2$-Ru=CHPh (3 mol %), DCM, 20 °C, then column chromatography on silica ((5*S*, 6*S*)-**11a** (14%), ((5*R*, 6*S*)-**11a** (19%)).

We finally investigated a two step procedure to the spirocyclic system **11a**. Starting from **8a** ((2*S*,3*S*):(2*S*,3*R*) = 3:1) allylation is achieved using the procedure for functionalization of trienes **4a**,**b**. Ring-closing metathesis of dihydropyran **13a** ((2*S*,3*S*):(2*S*,3*R*) = 3:1) proceeds smoothly in the presence of 3 mol % of Grubbs' catalyst to produce a 3:1 mixture of spirocycles (5*S*,6*S*)-**11a** and (5*R*,6*S*)-**11a**. This experiment illustrates that, in contrast to five membered rings, formation of the dihydropyran is obviously not reversible under the conditions. Otherwise, one would expect an isomerization to the (5*R*,6*S*)-diastereomer. The two diastereomers of **11a** thus obtained are separable by column chromatography. The major diastereomer (5*S*,6*S*)-**11a** decomposes to a large extent on silica, however, so that the pure compound is obtained only with significant loss of material. Surprisingly, (5*R*,6*S*)-**11a** appears to be stable under these conditions (Scheme 7).

Experimental Section

Instrumentation, product identification and general experimental methods have been described previously.[36] Whenever a signal assignment for NMR-spectra is given, this is based on 2D methods (H,H-COSY, NOESY and HMQC, respectively). Signal assignment for cyclic products follows a numbering scheme where the oxygen atom is numbered 1 and the

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α-carbon atom bearing a substituent C2. The number of coupled protons was analyzed by DEPT experiments and is denoted by a number in parentheses following the δ_c value.

General Procedure for the Preparation of Allyloxy Esters 2a,b. To a solution of the α-hydroxy ester (96 mmol) in ether (200 mL) was added silver oxide (44.5 g, 192 mmol) and allyl bromide 12.4 mL, 144 mmol). The mixture was stirred for 2 days at 20 °C in the dark. The solids were filtered off, and the solvent was evaporated. The residue is normally analytically pure.

(*S*)-2-Allyloxypropionic Acid Ethyl Ester (2a).[28] Starting from (*S*)-ethyl lactate (**1a**) (10.0 g, 96 mmol), 12.0 g (80%) of **2a** was obtained: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.83 (dddd, 1H, J = 17.3, 10.6, 6.0, 5.5 Hz), 5.20 (dddd, 1H, J = 17.3, 3.0, 1.5, 1.5 Hz), 5.10 (dddd, 1H, J = 10.6, 3.0, 1.3, 1.3 Hz), 4.16−4.09 (2H), 4.05 (dddd, 1H, J = 12.6, 5.5, 1.5, 1.5 Hz), 3.92 (q, 1H, J = 7.0 Hz), 3.85 (dddd, 1H, J = 12.6, 6.0, 1.3, 1.3 Hz), 1.32 (d, 3H, J = 7.0 Hz), 1.20 (t, 3H, J = 7.3 Hz; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.2 (0), 134.1 (1), 117.6 (2), 73.9 (1), 71.0 (2), 60.7 (2), 18.6 (3), 14.1 (3).

***rac*-Allyloxy-2-phenylacetic Acid Methyl Ester (2b).** Starting from DL-methyl mandelate (**1b**) (3.0 g, 18 mmol), 3.7 g (99%) of **2b** was obtained: IR (neat) 699 s, 1173 s, 1755 s, 2865 w; MS *m*/*z* (rel intensity) 207 ($M^+ + 1$, <5), 147 (95), 105 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48−7.43 (2H), 7.37−7.30 (3H), 5.93 (dddd, 1H, J = 17.3, 10.3, 6.0, 5.5 Hz), 5.28 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5 Hz), 5.21 (ddm, 1H, J = 10.3, 1.3 Hz), 4.94 (s, 1H), 4.06−4.03 (2H), 3.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.0 (0), 136.1 (0), 133.6 (1), 128.5 (1), 128.4 (1), 127.1 (1), 118.0 (2), 79.5 (1), 70.2 (2), 52.0 (3). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.9; H, 6.8. Found: C, 69.4; H, 6.8.

General Procedure for the Preparation of Divinylcarbinols. Vinylmagnesium chloride (21 mL 1.7 M solution in THF, 36 mmol) was added dropwise to a solution of the corresponding ester (12 mmol) in ether at −78 °C. The mixture was stirred at this temperature for 1 h and then at 20 °C for 12 h. After aqueous workup, the residue was purified by column chromatography on silica.

(*S*)-3-Vinylpent-4-ene-2,3-diol (3a).[29] Starting from **1a** (17.4 g, 147 mmol), 12.2 g (65%) of **3a** was obtained: IR (neat) 930 s, 1001 s, 3430 bs; MS *m*/*z* (rel intensity) 111 ($M^+ - 17$, 10), 83 (20), 55 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.95 (dd, 1H, J = 17.3, 10.8 Hz), 5.93 (dd, 1H, J = 17.3, 10.8 Hz), 5.38 (dd, 1H, J = 17.3, 1.3 Hz), 5.35 (dd, 1H, J = 17.3, 1.3 Hz), 5.23 (dd, 1H, J = 10.8, 1.3 Hz), 5.22 (dd, 1H, J = 10.8, 1.3 Hz), 3.67 (dq, 1H, J = 6.5, 4.3 Hz), 2.45 (s (br), 1H), 2.24 (s (br.), 1H), 1.12 (d, 3H, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0 (1), 138.0 (1), 115.7 (2), 115.3 (2), 78.4 (0), 72.7 (1), 16.8 (3); $[\alpha]^{23}_D$ = +5.1° (*c* 1.66, DCM). Anal. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.6; H, 9.5.

***rac*-1-Phenyl-2-vinylbut-3-en-1,2-diol (3b).** Starting from DL-methyl mandelate (**1b**) (2.0 g, 12 mmol), 0.7 g (31%) of **3b** was obtained: IR (neat) 1050 s, 3448 bm; MS *m*/*z* (rel intensity) 173 ($M^+ - 17$, 40), 105 (70), 55 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.23−7.19 (5H), 5.83 (dd, 1H, J = 17.3, 10.8 Hz), 5.77 (dd, 1 H, J = 17.3, 10.8 Hz), 5.29 (dd, 1H, J = 17.3, 1.3 Hz), 5.16 (dd, 1H, J = 17.3, 1.3 Hz), 5.14 (dd, 1H, J = 10.8, 1.3 Hz), 5.08 (dd, 1H, J = 10.8, 1.3 Hz), 4.48 (d, 1H, J = 3.5 Hz), 2.93 (d, 1H, J = 3.5 Hz), 2.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.3 (1), 138.7 (0), 137.8 (1), 127.8 (1), 127.8 (1), 127.6 (1), 115.7 (2), 115.2 (2), 79.4 (1), 78.4 (0). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.8; H, 7.4. Found: C, 75.6; H, 7.4.

(*S*)-3-(1-Allyloxyethyl)penta-1,4-dien-3-ol (4a). Starting from **2a** (6.0 g, 42 mmol), 4.4 g (63%) of **4a** was obtained: IR (neat) 924 s, 1091 s, 3464 bm; MS *m*/*z* (rel intensity) 163 ($M^+ + 1$, <5), 95 (90), 55 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.92 (dd, 1H, J = 17.3, 10.3 Hz), 5.91 (dd, 1H, J = 17.3, 10.8 Hz), 5.82 (dddd, 1H, J = 17.3, 10.3, 6.0, 5.5 Hz), 5.31 (dd, 1H, J = 17.3, 1.5 Hz), 5.29 (dd, 1H, J = 17.3, 1.5 Hz), 5.19 (dddd, 1H, J = 17.3, 3.0, 1.5, 1.5 Hz), 5.13 (dd, 1H, J = 10.8, 1.5 Hz), 5.13 (dd, 1H, J = 10.8, 1.5 Hz), 5.09 (dddd, 1H, J = 10.3, 3.0, 1.5, 1.5 Hz), 4.05 (dddd, 1H, J = 12.8, 5.5, 1.5, 1.5 Hz), 3.87 (dddd, 1H, J = 12.8, 6.0, 1.5, 1.5 Hz), 3.35 (q, 1H, J = 6.3 Hz), 2.53 (s (br.), 1H), 1.07 (d, 3H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.9 (1), 138.8 (1), 134.8 (1), 116.8 (2), 114.7 (2), 114.6 (2), 80.1 (1), 77.7 (0), 70.6 (2), 14.1 (3); $[\alpha]^{26}_D$ = +19.6° (*c* 1.42, $CHCl_3$). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.4; H, 9.6.

***rac*-3-(1-Allyloxyphenylmethyl)penta-1,4-dien-3-ol (4b).** Starting from **2b** (3.7 g, 18 mmol), 1.8 g (44%) of **4b** was obtained: IR (neat) 706 s, 925 s, 3470 bm; MS *m*/*z* (rel intensity) 213 ($M^+ - 17$, 20), 157 (40), 105 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40−7.30 (5H), 5.98 (dd, 1H, J = 17.3, 10.8 Hz), 5.94 (dd, 1H, J = 17.3, 10.8 Hz), 5.90 (dddd, 1H, J = 17.3, 10.3, 6.0, 5.0 Hz), 5.33 (dd, 1H, J = 17.3, 1.5 Hz), 5.31 (dd, 1H, J = 17.3, 1.5 Hz), 5.24 (dddd, 1H, J = 17.3, 3.5, 1.5, 1.5 Hz), 5.20 (dd, 1H, J = 10.8, 1.5 Hz), 5.18 (dddd, 1H, J = 10.3, 3.5, 1.5, 1.5 Hz), 5.16 (dd, 1H, J = 10.8, 1.5 Hz), 4.32 (s, 1H), 4.00 (dddd, 1H, J = 12.8, 5.0, 1.5, 1.5 Hz), 3.79 (dddd, 1H, J = 12.8, 6.0, 1.5, 1.5 Hz), 2.72 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.0 (1), 138.5 (1), 136.8 (0), 134.3 (1), 128.6 (1), 128.0 (1), 127.8 (1), 117.1 (2), 114.8 (2), 114.7 (2), 86.9 (1), 77.5 (0), 69.9 (2). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: C, 78.3; H, 7.9.

Alternative Preparation of (*S*)-4a. To a solution of (*S*)-**3a** (1.00 g, 7.8 mmol) in dry THF (50 mL) was added at 0 °C NaH (0.31 g, 60% dispersion in mineral oil, 7.8 mmol) followed by allyl bromide (1.0 mL, 11.7 mmol). Stirring was continued at this temperature for 2 h, and then the mixture was allowed to warm to ambient temperature and stirred for 12 h. Aqueous workup, followed by chromatography on silica, gives 0.67 g (51%) of (*S*)-**4a**.

General Procedure for the Functionalization of Divinylcarbinols 4. To a solution of the corresponding divinylcarbinol **4** (11 mmol) in dry THF (50 mL) was added NaH (1.30 g, 60% dispersion in mineral oil, 33 mmol), and the mixture was heated to reflux for 30 min. After the mixture was cooled to ambient temperature, the corresponding alkyl bromide or silyl chloride (16 mmol) was added, and the reaction mixture was again refluxed until the starting material was fully consumed, as indicated by TLC. Aqueous workup, followed by chromatography on silica, gives the functionalized derivatives **9**−**11**.

(*S*)-[1-(1-Allyloxyethyl)-1-vinylallyloxymethyl]benzene (5a). Starting from **4a** (2.00 g, 11.9 mmol), 2.08 g (55%) of **5a** was obtained: IR (neat) 935 s, 1113 s, 3089 m; MS *m*/*z* (rel intensity) 259 ($M^+ + 1$, <5), 151 (100), 133 (70); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35−7.18 (5H), 5.97 (dd, 2H, J = 17.8, 11.0 Hz), 5.87 (dddd, 1H, J = 17.3, 10.5, 5.5, 5.5 Hz), 5.39 (dd, 1H, J = 11.0, 1.5 Hz), 5.35 (dd, 1H, J = 11.0, 1.5 Hz), 5.34 (dd, 1H, J = 17.8, 1.5 Hz), 5.33 (dd, 1H, J = 17.8, 1.5 Hz), 5.22 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5 Hz), 5.09 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5 Hz), 4.40 (d, 1H, J = 12.3 Hz), 4.36 (d, 1H, J = 12.3 Hz), 4.11 (dddd, 1H, J = 13.1, 5.5, 1.5, 1.5 Hz), 4.06 (dddd, 1H, J = 13.1, 5.5, 1.5, 1.5 Hz), 3.51 (q, 1H, J = 6.3 Hz), 1.06 (d, 3H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.8 (0), 137.8 (1), 135.9 (1), 135.5 (1), 128.1 (1), 126.9 (1), 126.8 (1), 118.3 (2), 117.5 (2), 116.2 (2), 83.7 (0), 81.1 (1), 71.6 (2), 65.3 (2), 15.2 (3); $[\alpha]^{20}_D$ = + 10.8° (*c* 2.10, $CHCl_3$). Anal. Calcd for $C_{17}H_{22}O_2$: C, 79.0; H, 8.6. Found: C, 78.7; H, 8.8.

***rac*-(1-Allyloxy-2-phenylmethoxy-2-vinylbut-3-enyl)benzene (5b).** Starting from **4b** (1.90 g, 8.3 mmol), 1.66 g (63%) of **5b** was obtained: IR (neat) 700 s, 733 s, 1097 s, 3063 m; MS *m*/*z* (rel intensity) 294 ($M^+ - 26$, 20), 91 (10), 58 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31−7.15 (10H), 6.12 (dd, 1H, J = 17.8, 11.0 Hz), 5.81 (dddd, 1H, J = 17.3, 10.5, 5.8, 5.0 Hz), 5.62 (dd, 1H, J = 17.8, 11.0 Hz), 5.34 (dd, 1H, J = 11.0, 1.5 Hz), 5.26 (dd, 1H, J = 17.8, 1.5 Hz), 5.25 (dd, 1H, J = 11.0, 1.5 Hz), 5.17 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5 Hz), 5.16 (dd, 1H, J = 17.8, 1.5 Hz), 5.06 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5 Hz), 4.39 (d, 1H, J = 12.5 Hz), 4.38 (s, 1H), 4.32 (d, 1H, J = 12.5 Hz), 3.95 (dddd, 1H, J = 13.1, 5.0, 1.5, 1.5 Hz), 3.77 (dddd, 1H, J = 13.1, 5.8, 1.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.8 (0), 137.9 (0), 137.6 (1), 135.7 (1), 134.9 (1), 129.3 (1), 128.0 (1), 127.5 (1), 127.2 (1), 126.7 (1), 126.7 (1), 118.2 (2), 118.1 (2), 116.5 (2), 87.4 (1), 83.1 (0), 70.2 (2), 65.3 (2). Anal. Calcd for $C_{22}H_{24}O_2$: C, 82.5; H, 7.5. Found: C, 82.8; H, 7.7.

(*S*)-[1-(1-Allyloxyethyl)-1-vinylallyloxy]-*tert*-butyldimethylsilane (6a). Starting from **4a** (2.00 g, 11.9 mmol), 2.04 g (61%) of **6a** was obtained: IR (neat) 776 s, 930 s, 1101 s,

1961 s; MS *m*/*z* (rel intensity) 281 ($M^+ + 1$, <5), 225 (100), 95 (30); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.01 (dd, 1H, J = 17.3, 10.5 Hz), 5.87 (dddd, 1H, J = 17.3, 10.3, 5.5, 5.5 Hz), 5.35 (dd, 1H, J = 17.3, 2.3 Hz), 5.30 (dd, 1H, J = 17.3, 2.3 Hz), 5.26−5.20 (3H), 5.11 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5 Hz), 4.06 (dddd, 1H, J = 13.1, 5.5, 1.5, 1.5 Hz), 3.93 (dddd, 1H, J = 13.1, 5.5, 1.5, 1.5 Hz), 3.34 (q, 1H, J = 6.3 Hz), 1.06 (d, 3H, J = 6.3 Hz), 0.89 (s, 9H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.2 (1), 138.8 (1), 135.5 (1), 116.7 (2), 116.2 (2), 115.9 (2), 81.3 (1), 80.1 (0), 70.9 (2), 26.1 (3), 18.7 (0), 14.4 (3), −1.7 (3), −2.0 (3); $[\alpha]^{20}_D$ = + 3.7° (*c* 1.64, $CHCl_3$). Anal. Calcd for $C_{16}H_{30}O_2Si$: C, 68.0; H, 10.7. Found: C, 67.8; H, 10.6.

***rac*-[1-(1-Allyloxy-1-phenylmethyl)-1-vinylallyloxy]-*tert*-butyldimethylsilan (6b).** Starting from **4b** (1.90 g, 8.3 mmol), 1.47 g (52%) of **6b** was obtained: IR (neat) 776 s, 836 s, 3089 w; MS *m*/*z* (rel intensity) 287 (M^+ − 57, 60), 157 (90), 73 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47−7.39 (5H), 6.47 (dd, 1H, J = 17.3, 10.8 Hz), 6.01 (dddd, 1H, J = 17.8, 10.5, 5.8, 5.0 Hz), 6.00 (dd, 1H, J = 17.3, 10.8 Hz), 5.44 (dd, 1H, J = 17.3, 1.5 Hz), 5.42 (dd, 1H, J = 17.3, 1.5 Hz), 5.39 (dd, 1H, J = 10.8, 1.5 Hz), 5.36 (ddm, 1H, J = 17.8, 1.5 Hz), 5.35 (dd, 1H, J = 10.8, 1.5 Hz), 5.26 (ddm, 1H, J = 10.5, 1.5 Hz), 4.36 (s, 1H), 4.07 (dddd, 1H, J = 12.8, 5.0, 1.5, 1.5 Hz), 3.91 (dddd, 1H, J = 12.8, 5.8, 1.5, 1.5 Hz), 1.02 (s, 9H), 0.20 (s, 3H), 0.00 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3 (1), 138.8 (1), 138.1 (0), 134.9 (1), 129.3 (1), 127.5 (1), 127.1 (1), 116.6 (2), 116.5 (2), 116.3 (2), 88.3 (1), 79.8 (0), 70.1 (2), 26.2 (3), 18.8 (0), −1.7 (3), −2.0 (3). Anal. Calcd for $C_{21}H_{32}O_2Si$: C, 73.2; H, 9.4. Found: C, 73.2; H, 9.4.

***(S)*-3-Allyloxy-3-(1-allyloxyethyl)penta-1,4-diene (7a).** Starting from **4a** (3.06 g, 18.2 mmol), 2.68 g (71%) of **7a** was obtained: IR (neat) 920 s, 1100 s, 2934 m; MS *m*/*z* (rel intensity) 209 ($M^+ + 1$, <5), 151 (60), 95 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.97−5.82 (4H), 5.35 (dd, 1H, J = 11.0, 1.5 Hz), 5.32 (dd, 1H, J = 11.0, 1.5 Hz), 5.31−5.25 (3H), 5.22 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5 Hz), 5.10 (dddd, 1H, J = 17.8, 1.5, 1.5, 1.5 Hz), 5.07 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5 Hz), 4.09 (dddd, 1H, J = 12.8, 5.5, 1.5, 1.5 Hz), 4.04 (dddd, 1H, J = 12.8, 5.5, 1.5, 1.5 Hz), 3.85 (dddd, 1H, J = 13.3, 5.0, 1.5, 1.5 Hz), 3.81 (dddd, 1H, J = 13.3, 5.0, 1.5, 1.5 Hz), 3.46 (q, 1H, J = 6.3 Hz), 1.09 (d, 3H, J = 6.3 Hz; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.8 (1), 135.8 (1), 135.7 (1), 135.5 (1), 118.0 (2), 117.2 (2), 116.2 (2), 114.9 (2), 83.4 (0), 80.9 (1), 71.5 (2), 64.4 (2), 15.0 (3); $[\alpha]^{20}_D$ = +5.2° (*c* 2.14, $CHCl_3$). Anal. Calcd for $C_{13}H_{20}O_2$: C, 75.0; H, 9.7. Found: C, 75.3; H, 9.7.

***rac*-(1,2-Bis-allyloxy-2-vinylbut-3-enyl)benzene (7b).** Starting from **4b** (2.50 g, 10.9 mmol), 2.50 g (85%) of **7b** was obtained: IR (neat) 919 s, 1070 s, 2921 m; MS *m*/*z* (rel intensity) 271 ($M^+ + 1$, 10), 105 (100), 83 (70); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37−7.20 (5H), 6.07 (dd, 1H, J = 17.5, 11.0 Hz), 5.84 (ddm, 1H, J = 17.3, 10.5 Hz), 5.79 (ddm, 1H, J = 17.5, 10.5 Hz), 5.64 (dd, 1H, J = 17.5, 11.0 Hz), 5.32 (dd, 1H, J = 11.0, 1.5 Hz), 5.22 (dd, 1H, J = 11.0, 1.5 Hz), 5.21 (ddm, 1H, J = 17.5, 1.5 Hz), 5.17 (ddm, 1H, J = 17.3, 1.5 Hz), 5.12 (dd, 1H, J = 17.5, 1.5 Hz), 5.07 (ddm, 1H, J = 10.5, 1.5 Hz), 5.01 (dd, 1H, J = 17.5, 1.5 Hz), 5.00 (ddm, 1H, J = 10.5, 1.5 Hz), 4.34 (s, 1H), 3.95 (dddd, 1H, J = 13.1, 5.0, 1.5, 1.5 Hz), 3.90 (dddd, 1H, J = 13.1, 5.5, 1.5, 1.5 Hz), 3.81 (dddd, 1H, J = 13.1, 5.0, 1.5, 1.5 Hz), 3.76 (dddd, 1H, J = 13.1, 6.0, 1.5, 1.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.9 (0), 137.5 (1), 135.7 (1), 135.7 (1), 134.9, (1), 129.2 (1), 127.9 (1), 127.4 (1), 117.9 (2), 117.8 (2), 116.4 (2), 114.7 (2), 87.2 (1), 82.9 (0), 70.1 (2), 64.4 (2). Anal. Calcd for $C_{18}H_{22}O_2$: C, 80.0; H, 8.2. Found: C, 79.8; H, 8.5.

General Procedure for the Ring-Closing Metathesis Reaction. The corresponding metathesis precursor (5.8 mmol) was dissolved in dry, deoxygenated CH_2Cl_2 (20 mL) under an atmosphere of dry argon. The ruthenium catalyst (146 mg, 3 mol %) was added, and the solution stirred at 20 °C for 12 h. Evaporation of the solvent followed by flash chromatography on silica yields the dihydropyrans.

(2*S*,3*S*)- and (2*S*,3*R*)-2-Methyl-3-vinyl-3,6-dihydro-2*H*-pyran-3-ol (8a). Starting from **4a** (0.83 g, 5.9 mmol), 0.55 g (66%) of **8a** was obtained as a 3:1 mixture of the diastereomers: IR (neat) 993 s, 1065 s, 2938 m, 3442 bs; MS *m*/*z* (rel intensity) 123 (M^+ − 17, 84), 95 (75), 81 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.92 (ddd, 1H, J = 10.0, 4.0, 3.5 Hz, *H*5), 5.80 (ddd, 1H, J = 10.0, 1.5, 1.5 Hz, *H*4), 5.78 (dd, 1H, J = 17.6, 10.8 Hz, *H*C=CH_2), 5.36 (dd, 1H, J = 17.6, 1.5 Hz, H_2C=CH), 5.20 (dd, 1H, J = 10.8, 1.5 Hz, H_2C=CH), 4.22 (ddd, 1H, J = 16.8, 3.5, 1.8 Hz, *H*6), 4.16 (ddd, 1H, J = 16.8, 4.0, 1.5 Hz, *H*6), 3.50 (q, 1H, J = 6.3 Hz, *H*2), 2.58 (s (br.), 1H, *H*O-), 1.21 (d, 3H, J = 6.3 Hz, H_3C-); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.5 (1), 130.7 (1), 128.2 (1), 115.0 (2), 77.7 (1), 70.0 (0), 65.7 (2), 14.1 (3); $[\alpha]^{26}_D$ = +150.2° (*c* 1.64, $CHCl_3$). NMR-data of the minor diastereomer (2*S*,3*R*)-**8a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.96 (dd, 1H, J = 17.6, 10.8 Hz, *H*C=CH_2), 5.79 (ddd, 1H, J = 10.3, 2.3, 2.3 Hz, *H*4/*H*5), 5.58 (ddd, 1H, J = 10.3, 2.3, 2.3 Hz, *H*4/*H*5), 5.28 (dd, 1H, J = 17.8, 1.3 Hz, H_2C=CH), 5.21 (dd, 1H, J = 10.8, 1.3 Hz, H_2C=CH), 4.18 (dm, 1H, J = 16.8 Hz, *H*6), 4.14 (dm, 1H, J = 16.8 Hz, *H*6), 3.54 (q, 1H, J = 6.3 Hz, *H*2), 2.46 (s (br), 1H, *H*O−), 1.13 (d, 3H, J = 6.3 Hz, H_3C−); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.3 (1), 131.0 (1), 126.2 (1), 114.4 (2), 77.0 (1), 71.9 (0), 65.2 (2), 14.8 (3).

(2*S,3*S**)- and (2*S**,3*R**)-2-Phenyl-3-vinyl-3,6-dihydro-2*H*-pyran-3-ol (8b).** Starting from **4b** (3.69 g, 16.0 mmol), 2.80 g (86%) of crude **8b** was obtained as a 4:1 mixture of (2*S**,3*S**)-**8b** and (2*S**,3*R**)-**8b**. Separation of the diastereomers by careful chromatography gives 1.42 g (44%) of (2*S**,3*S**)-**8b** and 0.39 g (12%) of (2*S**,3*R**)-**8b**: IR (neat) 700 s, 1068 s, 3464 bm; MS *m*/*z* (rel intensity) 185 (M^+ − 17, 100), 167 (60), 105 (100); NMR data for (2*S**,3*S**)-**8b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30−7.20 (5H, Ph), 5.96 (ddd, 1H, J = 10.0, 3.8, 1.8 Hz, H5), 5.81 (ddd 1H, J = 10.0, 2.0, 2.0 Hz, H4), 5.73 (dd, 1H, J = 17.8, 10.5 Hz, *H*C=CH_2), 5.10 (dd, 1H, J = 17.8, 1.5 Hz, H_2C=CH), 5.09 (dd, 1H, J = 10.5, 1.5 Hz, H_2C=CH), 4.37 (s, 1H, H2), 4.36 (dm, 1H, J = 16.8 Hz, $H6_{ax}$), 4.23 (dm, 1H, J = 16.8 Hz, $H6_{eq}$), 1.85 (s (br), 1H, *H*O−); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.0 (1), 136.7 (0), 130.1 (1), 128.8 (1), 127.8 (1), 127.7 (1), 127.6 (1), 115.5 (2), 83.7 (1), 70.7 (0), 66.5 (2). NMR-data for (2*S**,3*R**)-**8b**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31−7.20 (5H, Ph), 5.82 (ddm, 1H, J = 10.3, 2.0 Hz, H5), 5.80 (dd, 1H, J = 17.3, 10.5 Hz, *H*C=CH_2), 5.64 (ddm, 1H, J = 10.3, 2.0 Hz, H4), 4.99 (dm, 1H, J = 17.3 Hz, H_2C=CH), 4.95 (dm, 1H, J = 10.5 Hz, H_2C=CH), 4.42 (s, 1H, H2), 4.33 (ddd, 1H, J = 16.8, 2.0, 2.0 Hz, H6), 4.28 (ddd, 1H, J = 16.8, 2.0, 2.0 Hz, H6), 1.72 (s (br), 1H, *H*O−); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.8 (1), 137.2 (0), 130.8 (1), 127.8 (1), 127.2 (1), 127.6 (1), 126.3 (1), 114.4 (2), 82.7 (1), 72.7 (0), 66.4 (2).

(2*S*,3*R*)-3-Benzyloxy-2-methyl-3-vinyl-3,6-dihydro-2*H*-pyran (9a). Starting from **5a** (0.40 g, 1.5 mmol), **9a** was obtained as a 3:1 mixture of (2*S*,3*R*)- and (2*S*,3*S*)-diastereomers. Analytically pure (2*S*,3*R*)-**9a** (0.20 g, 56%) was obtained by careful column chromatography on silica: IR (neat) 696 m, 1116 s, 2981 m; MS *m*/*z* (rel intensity) 123 (M^+ − 107, 35), 91 (100), 81 (30); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43−7.35 (5H, Ph), 6.01 (ddd, 1H, J = 10.3, 3.0, 2.0 Hz, *H*4/*H*5), 5.98 (dd, 1H, J = 17.8, 10.3 Hz, *H*C=CH_2), 5.87 (ddd, 1H, J = 10.3, 2.0, 2.0 Hz, *H*4/*H5*), 5.36 (dd, 1H, J = 17.8, 1.8 Hz, H_2C=CH), 5.35 (dd, 1H, J = 10.3, 1.8 Hz, H_2C=CH), 4.61 (d, 1H, J = 11.8 Hz, H_2C−C), 4.54 (d, 1H, J = 11.8 Hz, H_2C−C), 4.26 (ddd, 1H, J = 16.8, 2.0, 2.0 Hz, *H*6), 4.18 (ddd, 1H, J = 16.8, 3.0, 2.0 Hz, *H*6), 3.84 (q, 1H, J = 6.5 Hz, *H*2), 1.23 (d, 3H, J = 6.5 Hz, H_3C−); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.4 (0), 137.5 (1), 129.0 (1), 128.3 (1), 127.6 (1), 127.2 (1), 127.0 (1), 117.7 (2), 77.4 (0), 74.4 (1), 65.8 (2), 64.8 (2), 15.2 (3); $[\alpha]^{20}_D$ = +34.1° (*c* 1.60, $CHCl_3$). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.2; H, 7.9. Found: C, 77.6; H, 7.8.

(2*S,3*R**)-3-Benzyloxy-2-phenyl-3-vinyl-3,6-dihydro-2*H*-pyran (9b).** Starting from **5b** (0.40 g, 1.3 mmol), **9b** was obtained as a 9:1 mixture of diastereomers. Analytically pure (2*S*,3*R*)-**9b** (0.23 g, 62%) was obtained by careful column chromatography on silica: IR (neat) 698 s, 1140 m, 3030 m; MS *m*/*z* (rel intensity) 294 ($M^+ + 2$, 25), 176 (20), 58 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38−7.19 (10H, Ph), 6.02 (ddd, 1H, J = 10.3, 2.3, 2.3 Hz, *H*4/*H*5), 5.92 (ddd, 1H, J = 10.3, 2.3, 2.3 Hz, *H*4/*H*5), 5.448 (dd, 1H, J = 17.5, 10.5 Hz, *H*C=CH_2), 5.20 (dd, 1H, J = 17.5, 1.8 Hz, H_2C=CH), 5.18 (dd, 1H, J = 10.5, 1.8 Hz, H_2C=CH), 4.71 (s, 1H, *H*2), 4.58 (d, 1H, J = 11.8 Hz, H_2C−C), 4.52 (d, 1H, J = 11.8 Hz, H_2C−C), 4.31 (dd, 2H, J =

2.3, 2.3 Hz, *H*6); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.2 (0), 137.9 (0), 137.7 (1), 128.7 (1), 128.3 (1), 128.2 (1), 127.7 (1), 127.5 (1), 127.3 (1), 127.1 (1), 126.9 (1), 118.6 (2), 79.6 (1), 78.1 (0), 65.5, 64.6 (2). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.2; H, 6.9. Found: C, 82.2; H, 7.0.

(2*S*,3*R*)- and (2*S*,3*S*)-*tert*-Butyldimethyl(2-methyl-3-vinyl-3,6-dihydro-2*H*-pyran-3-yloxy)silane (10a). Starting from **6a** (0.50 g, 1.8 mmol), **10a** was obtained as an inseparable 2:1 mixture of diastereomers. Analytically pure **10a** (0.41 g, 91%) was obtained by column chromatography on silica: IR (neat) 775 s, 836 s, 1252 s, 2931 s; MS *m*/*z* (rel intensity) 253 ($M^+ - 1$, 100), 169 (30), 75 (90); $[\alpha]^{20}_D = +86.8°$ (*c* 1.62, $CHCl_3$). NMR data for (2*S*,3*R*)-**10a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.87 (dd, 1H, *J* = 17.3, 10.5 Hz, *H*C=CH_2), 5.74 (ddd, 1H, *J* = 10.3, 2.0, 2.0 Hz, *H*4/*H*5), 5.63 (ddd, 1H, *J* = 10.3, 2.0, 2.0 Hz, *H*4/*H*5), 5.25 (dd, 1H, *J* = 17.3, 2.0 Hz, H_2C=CH), 5.11 (dd, 1H, *J* = 10.5, 2.0 Hz, H_2C=CH), 4.17 (dm, 1H, *J* = 16.8 Hz, *H*6), 4.10 (dm, 1H, *J* = 16.8 Hz, *H*6), 3.51 (q, 1H, *J* = 6.3 Hz, *H*2), 1.09 (d, 3H, *J* = 6.3 Hz, H_3C-CH), 0.88 (s, 9H, (H_3C)$_3$-C), 0.09 (s, 3H, H_3C-Si), 0.07 (s, 3H, H_3C-Si); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.3 (1), 131.6 (1), 125.9 (1), 114.3 (2), 77.4 (1), 74.7 (0), 65.7 (2), 25.8 (3), 18.3 (0), 15.1 (3), −2.0 (3), −2.3 (3). NMR data for (2*S*,3*S*)-**10a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.89 (ddd, 1H, *J* = 10.3, 1.8, 1.8 Hz, *H*4/*H*5), 5.71 (dm, 1H, *J* = 10.3 Hz, *H*4/*H*5), 5.70 (dd, 1H, *J* = 17.1, 10.5 Hz, *H*C=CH_2), 5.30 (dd, 1H, *J* = 17.1, 1.8 Hz, H_2C=CH), 5.07 (dd, 1H, *J* = 10.5, 1.8 Hz, H_2C=CH), 4.17 (dm, 1H, *J* = 16.8 Hz, *H*6), 4.10 (dm, 1H, *J* = 16.8 Hz, *H*6), 3.34 (q, 1H, *J* = 6.3 Hz, *H*2), 1.12 (d, 3H, *J* = 6.3 Hz, H_3C-CH), 0.90 (s, 9H, (H_3C)$_3$-C), 0.05 (s, 3H, H_3C-Si), 0.03 (s, 3H, H_3C-Si); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.3 (1), 129.8 (1), 129.1 (1), 114.1 (2), 77.9 (1), 72.4 (0), 65.4 (2), 26.1 (3), 18.6 (0), 14.4 (3), −2.0 (3), −2.5 (3).

(2*S,3*R**)-*tert*-Butyldimethyl(2-phenyl-3-vinyl-3,6-dihydro-2*H*-pyran-3-yloxy)silane (10b).** Starting from **6b** (0.30 g, 0.9 mmol), **10b** was obtained as an inseparable 6:1 mixture of diastereomers. Analytically pure (2*S**,3*R**)-**10b** (0.24 g, 87%) was obtained by column chromatography on silica: IR (neat) 700 m, 1094 s, 1255 s, 2930 s; MS *m*/*z* (rel intensity) 316 ($M^+ - 1$, <5), 299 (100), 154 (40); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32−7.28 (2H, Ph), 7.22−7.10 (3H, Ph), 5.85 (ddd, 1H, *J* = 10.3, 2.5, 2.5 Hz, *H*4/*H*5), 5.71 (ddd, 1H, *J* = 10.3, 2.5, 2.5 Hz, *H*4/*H*5), 5.39 (dd, 1H, *J* = 17.5, 10.5 Hz, *H*C=CH_2), 5.03 (dd, 1H, *J* = 17.5, 1.8 Hz, H_2C=CH), 5.01 (dd, 1H, *J* = 10.5, 1.8 Hz, H_2C=CH), 4.42 (s, 1H, *H*2), 4.25 (dd, 2H, *J* = 2.5, 2.5 Hz, *H*6), 0.82 (s, 9H, (H_3C)$_3$-C), 0.04 (s, 3H, H_3C-Si), −0.14 (s, 3H, H_3C-Si); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 139.8 (1), 137.9 (0), 130.9 (1), 127.9 (1), 127.2 (1), 127.0 (1), 126.3 (1), 116.1 (2), 83.6 (1),, 75.4 (0), 66.4 (2), 25.9 (3), 18.3 (0), −2.0 (3), −2.2 (3). Anal. Calcd for $C_{19}H_{28}O_2Si$: C, 72.1; H, 8.9. Found: C, 71.5; H, 8.7.

(5*R*,6*S*)-6-Methyl-1,7-dioxaspiro[4.5]deca-3,9-diene (11a). Starting from **7a** (1.27 g, 6.1 mmol), **11a** (0.15 g, 16%) was obtained as a single diastereoisomer, along with oligomerization products: IR (neat) 1080 s, 1122 s, 2979 m; MS *m*/*z* (rel intensity) 151 ($M^+ - 1$, 5), 135 (60), 108 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.94 (dm, 1H, *J* = 6.3, 1.5, 1.5 Hz), 5.77 (ddd, 1H, *J* = 10.3, 3.0, 1.8 Hz), 5.75 (ddd, 1H, *J* = 6.3, 2.5, 2.5 Hz), 5.69 (dm, 1H, *J* = 10.3 Hz), 4.73 (ddd, 1H, *J* = 12.8, 2.3, 1.8 Hz), 4.62 (ddd, 1H, *J* = 12.8, 2.3, 1.8 Hz), 4.24 (ddd, 1H, *J* = 16.8, 2.3, 1.8 Hz), 4.15 (ddd, 1H, *J* = 16.8, 3.0, 1.8 Hz), 3.68 (q, 1H, *J* = 6.3 Hz), 1.13 (d, 3H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 129.8 (1), 128.6 (1), 127.4 (1), 126.1 (1), 88.4 (0), 75.5 (1), 75.0 (2), 65.6 (2), 15.4 (3); $[\alpha]^{20}_D = +23.5°$ (*c* 1.00, $CHCl_3$).

(5*R,6*S**)-6-Phenyl-1,7-dioxaspiro[4.5]deca-3,9-diene (11b).** Starting from **7b** (0.50 g, 1.9 mmol), **11b** (0.17 g, 43%) was obtained as a single diastereoisomer, along with oligomerization products: IR (neat) 706 s, 1026 s, 1087 s, 2936 m; MS *m*/*z* (rel intensity) 213 ($M^+ - 1$, <5), 197 (30), 108 (100); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33 (2H, *J* = 7.8 Hz, *o*-H, Ph), 7.25−7.16 (3H, *m*-H, *p*-H, Ph), 5.79 (ddd, 1H, *J* = 10.3, 2.3, 2.3 Hz, H5), 5.73 (ddd, 1H, *J* = 10.3, 2.0, 2.0 Hz, H4), 5.62 (ddd, 1H, *J* = 6.3, 2.5, 2.5 Hz, *H*C=C), 5.51 (d, 1H, *J* = 6.3 Hz, *H*C=CHHO), 4.60 (s, 1H, H2), 4.49 (ddd, 1H, *J* = 12.5, 2.5, 2.0 Hz, H_2C−O), 4.34−4.29 (2H, H6), 4.09 (ddd, 1H, *J* = 12.8, 2.5, 2.0 Hz, H_2C-O); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.7 (0), 130.6 (1), 128.7 (1), 127.3 (1), 127.1 (1), 127.1 (1), 126.9 (1), 126.0 (1), 89.2 (0), 81.4 (1), 75.2 (2), 66.3 (2).

Attempted Ring-Closing Metathesis of Tetraene 7a Using Ruthenium Catalyst B. To a solution of **7a** (0.40 g, 2.1 mmol) in toluene (50 mL) was added the ruthenium complex **B** (0.106 g, 8 mol %). The mixture was heated to reflux until the starting material was fully consumed. Only **12a** (20 mg, 6%) was isolated. NMR data for 2-methyl-4-(2-methyl-6*H*-pyran-3-ylide)butyraldehyde (**12a**): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.65 (d, 1H, *J* = 1.3 Hz, *H*C=O), 6.45 (dm, 1H, *J* = 10.3 Hz, *H*4), 5.88 (ddd, 1H, *J* = 10.3, 4.3, 2.8 Hz, *H*5), 5.20 (dd, 1H, *J* = 7.8, 7.3 Hz, *H*C=C), 4.25 (s, 2H, *H*6), 4.18 (q, 1H, *J* = 6.5 Hz, *H*2), 2.51 (ddm, 1H, *J* = 14.8, 7.3 Hz, H_2C-CH-CH=O), 2.43 (qm, 1H, *J* = 6.8 Hz, *H*C-C=O), 2.25 (dd, 1H, *J* = 14.8, 7.8 Hz, H_2C-CH-CH=O), 1.33 (d, 3H, *J* = 6.5 Hz, H_3C−), 1.10 (d, 3H, *J* = 6.8 Hz, H_3C−); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.4 (0), 136.3 (0), 128.1 (1), 120.9 (1), 120.0 (1), 72.5 (1), 63.9 (2), 46.6 (1), 27.3 (2), 18.2 (3), 13.1 (3).

(2*S*,3*S*)- and (2*S*,3*R*)-3-Allyloxy-2-methyl-3-vinyl-3,6-dihydro-2*H*-pyran (13a). Starting from **8a** (0.74 g, 5.3 mmol, 3:1 mixture of diastereomers) and allyl bromide following the general procedure for the functionalization of trienes **4**, 0.72 g (76%) of **13a** was obtained: IR (neat) 709 s, 1077 s, 1112 s, 2984 m; MS *m*/*z* (rel intensity) 181 ($M^+ + 1$, 2), 123 ($M^+ -$ *O*-allyl, 90), 55 (100). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.3; H, 8.9. Found: C, 72.5; H, 8.6. NMR data for (2*S*,3*S*)-**13a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.08 (1H, *J* = 10.3, 3.8, 1.8 Hz), 5.94−5.80 (1H), 5.72 (dd, 1H, *J* = 17.3, 11.0 Hz), 5.66 (ddd, 1H, *J* = 10.3, 2.3, 2.0 Hz), 5.28−5.20 (2H), 5.13 (dd, 1H, *J* = 11.0, 1.5 Hz), 4.20 (ddd, 1H, *J* = 16.8, 3.8, 2.0 Hz), 4.16−3.93 (3H), 3.43 (q, 1H, *J* = 6.5 Hz), 1.20 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.5 (1), 135.9 (1), 131.1 (1), 126.7 (1), 115.7 (2), 115.0 (2), 78.6 (1), 74.3 (0), 65.5 (2), 65.4 (2), 14.4 (3). NMR data for (2*S*,3*S*)-**13a**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.68 (q, 1H, *J* = 6.5 Hz), 1.12 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 137.4 (1), 135.6 (1), 128.8 (1), 127.5 (1), 117.3 (2), 115.5 (2), 77.1 (1), 74.3 (1), 65.6 (2), 63.8 (2), 15.0 (3).

(5*S*,6*S*)-6-Methyl-1,7-dioxaspiro[4,5]deca-3,9-diene (11a). Starting from **13a** (0.32 g, 1.8 mmol, 3:1 mixture of diastereomers) and catalyst **A** (43 mg, 3 mol %), following the general procedure for the ring-closing metathesis reaction, 0.29 g (100%) of crude **11a** (3:1 mixture of diastereomers) was obtained. Separation of the diastereoisomers by column chromatography on silica leads to partial decomposition of the major diastereomer: yield (5*S*,6*R*)-**11a** (50 mg, 19%, minor isomer) and (5*S*,6*S*)-**11a** (38 mg, 14%, major isomer); IR (neat) 1080 s, 1122 s, 2979 m; MS *m*/*z* (rel intensity) 151 ($M^+ - 1$, 5), 135 (60), 108 (100); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.97 (d, 1H, *J* = 6.3, 1.5, 1.5 Hz), 5.90 (ddd, 1H, *J* = 10.3, 3.0, 1.8 Hz), 5.64 (dm, 1H, *J* = 10.0 Hz), 5.50 (ddd, 1H, *J* = 6.3, 2.5, 2.5 Hz), 4.74 (ddd, 1H, *J* = 13.0, 2.0, 2.0 Hz), 4.57 (ddd, 1H, *J* = 13.0, 2.0, 2.0 Hz), 4.18 (ddd, 1H, *J* = 16.8, 3.5, 1.5 Hz), 4.05 (ddd, 1H, *J* = 16.8, 1.8, 1.8 Hz), 3.56 (q, 1H, *J* = 6.3 Hz), 1.14 (d, 3H, *J* = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 129.7 (1), 129.1 (1), 128.8 (1), 127.8 (1), 86.4 (0), 76.2 (1), 76.0 (2), 65.2 (2), 14.1 (3); $[\alpha]^{20}_D = +106.5°$ (*c* 1.85, $CHCl_3$).

Deprotection of TBDMS Ethers 10a,b. To a solution of the corresponding TBDMS-ether (0.5 mmol) in THF (10 mL) was added TBAF (0.27 g, 0.8 mmol). The mixture was stirred until the starting material was fully consumed. Aqueous workup and evaporation of all volatiles provided the crude alcohols **8a** and **8b**, respectively. NMR spectra of the compounds are identical with those of the minor isomers obtained from ring-closing metathesis of **4a**,**b**.

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