Stereodivergent Syntheses of Highly Substituted Enantiopure 4-Alkoxy-3,6-dihydro-2*H*-1,2-oxazines by Addition of Lithiated Alkoxyallenes to Carbohydrate-Derived Aldonitrones

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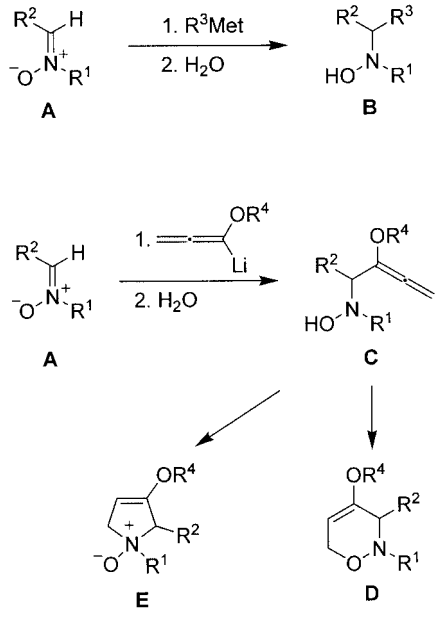
Keywords: Allenes / Lithium / Nitrones / Carbohydrates / 1,2-Oxazines

Additions of lithiated alkoxyallenes to D-glyceraldehyde-based nitrones **1** and **2** did not provide the expected hydroxylamine derivatives. Instead, a novel [3+3] cyclization process furnished 4-alkoxy-3,6-dihydro-2*H*-1,2-oxazines **9**–**14** with excellent *syn* selectivities and in moderate to good yields. Through precomplexation of the nitrones the corresponding *anti*-configured 1,2-oxazines **9**, **10** and **13** could be obtained with high stereoselectivity. The reactions of nitrones **3**–**6**, derived from D-erythrose or D-threose, generally proceeded less diastereoselectively, but reasonable yields of *anti*-configured 1,2-oxazines such as *anti*-**17** and *anti*-**19** could be obtained under Lewis acid promotion conditions. This was also the case for reactions of the D-arabinose-derived nitrone **7**, which provided the *anti*-1,2-oxazines **23** and **24** with excellent diastereoselectivity and in good yields. Bisnitrone **8** and lithiated methoxyallene furnished a mixture of six compounds, among which the major componentwas the C_2-symmetric *syn*/*syn*-1,2-oxazine **29**. The diastereoselectivities of these reactions are interpreted on the basis of Dondoni's model for reactions between organolithium compounds and nitrones. The mechanisms for formation of 1,2-oxazines and of side products are discussed. The method introduced here seems to be of broad applicability and an excellent tool for diastereoselective chain elongation of carbohydrate derivatives, affording stereodefined precursors of aminopolyols and other highly functionalized compounds.

Introduction

During the last decade the addition of organometallic reagents such as Grignard or organolithium compounds to nitrones **A**, affording hydroxylamine derivatives **B** (Scheme 1), has become a very useful synthetic tool.[1] Although this reaction type has been known for a long time, recent efforts—in particular by the groups of Dondoni[2] and Merino[3]—have impressively demonstrated that highly stereoselective reactions are possible, furnishing functionalized compounds of considerable interest for syntheses of natural products or their analogues. We expected that lithiated alkoxyallenes[4] should behave analogously, furnishing 1-alkoxy-1,2-propadienyl-substituted hydroxylamines **C** capable of undergoing ring-closure to 1,2-oxazine derivatives **D**, which are products of an overall [3+3] cyclization (Scheme 1).



Scheme 1.

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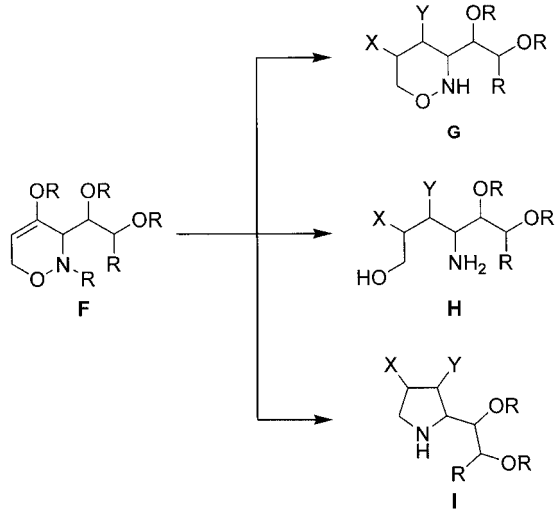
 DOI: 10.1002/ejoc.200400627

Alternatively, cyclization to cyclic N-oxides **E** was also conceivable. These reaction sequences would nicely supplement earlier investigations with carbonyl compounds[5] and imines[6] as electrophiles, which had provided the expected primary adducts and, under base or transition metal catalysis conditions, had given dihydrofuran or dihydropyrrole derivatives. The formal [3+2] cyclizations of methoxyallene with these two-centre electrophiles were synthetically very productive and allowed us several natural product syntheses[7] and—possibly more importantly—led to completely unexpected reaction pathways providing interestingly functionalized compounds[8] not (easily) available by alternative methods. We therefore hoped that similarly versatile and surprising chemistry would be possible with three-centre electrophiles such as nitrones **A**.

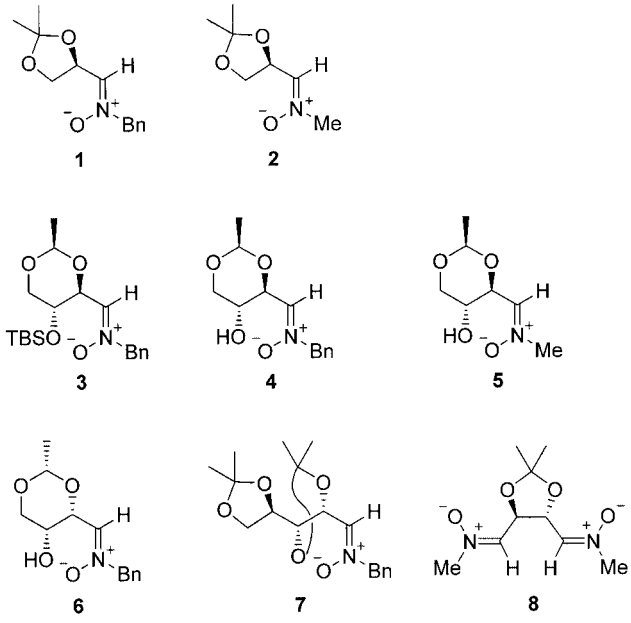
When lithiated alkoxyallenes were combined with nitrones **A**, we were generally not able, much to our surprise, to isolate the expected primary adducts **C**. Instead, the reaction in most cases directly delivered the desired 4-alkoxy-3,6-dihydro-2*H*-1,2-oxazines **D**. Only when sterically demanding substituents were present at the nitrone could the hydroxylamines **C** be isolated.[9] These slowly cyclize to give the expected 1,2-oxazines **D**—in exceptional cases as mixtures with the corresponding cyclic N-oxides **E**.[10] Similar transformations were reported by Dulcère et al., who added 1-lithio-1,2-propadiene to several nitrones and observed slow isomerization of the expected primary adducts to the corresponding 1,2-oxazines.[11] In this paper we present details of the [3+3] cyclizations of several lithiated alkoxyallenes with carbohydrate-derived nitrones. The resulting 4-alkoxy-3,6-dihydro-2*H*-1,2-oxazines **F** are of particular synthetic interest, since they are very versatile functionalized building blocks employable for stereocontrolled syntheses of saturated 1,2-oxazines (aza sugars) **G**, amino sugar derivatives **H** or—after recyclization—imino sugars **I** (Scheme 2). All these compounds are of interest because of their biological activities.[12] Most of the transformations outlined in Scheme 2 and other interesting reactions have already been executed with 1,2-oxazines prepared from D-glyceraldehyde-derived nitrone **1**.[13]



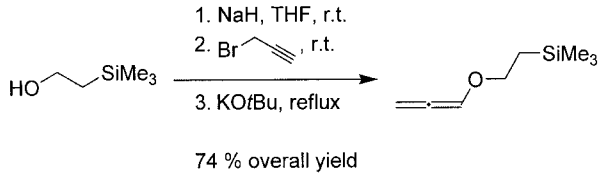
Scheme 2.

Results

We investigated the reactions between lithiated alkoxyallenes and nitrones **1**–**8** (Scheme 3), derived from D-glyceraldehyde, D-erythrose, D-threose, D-arabinose and D-mannitol. Whereas syntheses of nitrones **1**–**7** have been reported in the literature,[14] the preparation of the new C_2-symmetric bis-nitrone **8** is described here (Scheme 10). The viability of the use of different alkoxy groups at the allene moiety was studied, because the benzyloxy and the (trimethylsilyl)-ethoxy substituents allow transformations and cleavage conditions not possible with simple alkoxy groups such as methoxy groups. The known literature synthesis of (trimethylsilyl)ethoxyallene[15] was simplified by performing the two steps—propargylation of 2-(trimethylsilyl)ethanol and subsequent base-promoted alkyne–allene isomerization—as a one-pot procedure [Equation (1)].



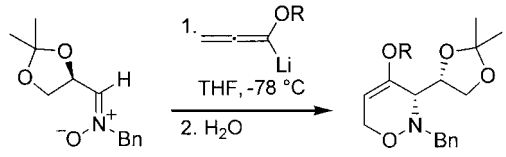
Scheme 3.

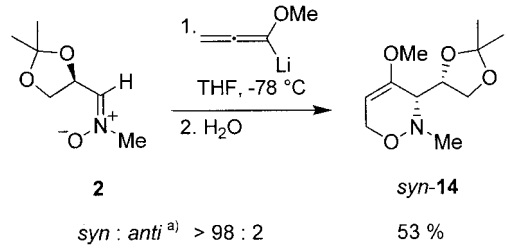


(1)

The D-glyceraldehyde-derived *N*-benzyl nitrone **1** was chosen as a standard substrate to study the addition conditions. Deprotonation of five different alkoxyallenes with *n*-butyllithium was performed under standard conditions (–40 °C in tetrahydrofuran as solvent), and the resulting lithiated species were combined with nitrone **1** at –78 °C. As mentioned above, aqueous workup directly furnished the 4-

alkoxy-3,6-dihydro-2*H*-1,2-oxazines **9**–**13**, and after chromatography these products of a new [3+3] cyclization process were isolated in moderate to high yields. In our first experiments we employed lithiated methoxyallene in large excess (up to 20 equivalents), but it turned out that this is not a prerequisite to obtain reasonable yields and that 1.2 to 3 equiv. are sufficient. Most importantly, the diastereofacial selectivity under the conditions employed is excellent, giving the *syn*-configured products exclusively or with very high preference. The ratios of diastereomers given in Scheme 4 refer to the crude products, whereas the purified 1,2-oxazine derivatives *syn*-**9** to *syn*-**13** were essentially diastereomerically pure (*syn*/*anti* > 98:2). The determination of the relative configurations is discussed below. For a subsequent product of *syn*-**9** we were able to establish that the enantiomeric purity of the nitrone **1** was fully transferred to the 1,2-oxazine.[13c,13e]

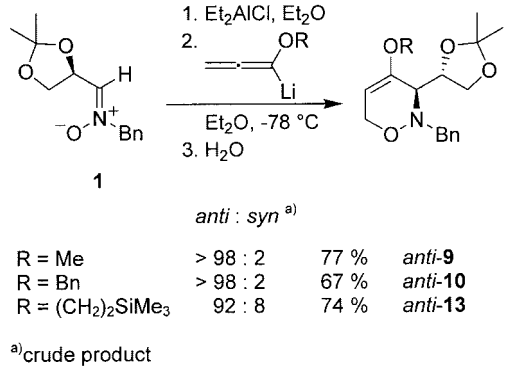




Scheme 4.

The closely related *N*-methyl nitrone **2** behaves very similarly to **1**, giving the *syn*-configured 1,2-oxazine **14** in moderate yield and diastereomerically almost pure. The substituent at the nitrone nitrogen does not seem to have a crucial influence on the diastereoselectivity of this overall [3+3] cyclization. A further interesting feature of these reactions is the formation of 1,3-dienes **15** as side products. These compounds were observed in amounts of 0 to 20 % (in the crude product mixtures), the exact portion depending on the substrates, but also on the individual experiment. A brief discussion of their generation as well as the explanation of the diastereoselectivity of the 1,2-oxazine formation is presented below (Schemes 12 and 14).

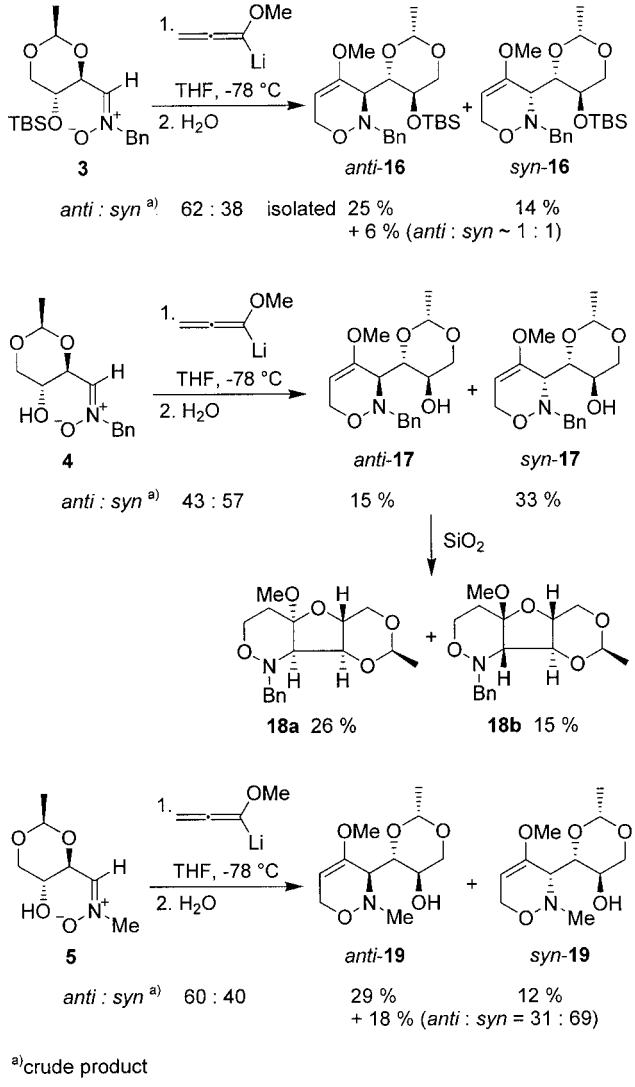
Remarkably and very gratifyingly, the stereochemical outcomes of the additions of lithiated alkoxyallenes to nitrone **1** could be completely switched to high *anti* selectivity. For this purpose the nitrone has to be precomplexed with the mild Lewis acid diethylaluminium chloride before addition of the lithiated allene species. Diethyl ether was the solvent of choice, giving better selectivities and yields. After chromatography, the desired 1,2-oxazines *anti*-**9**, *anti*-**10** and *anti*-**13** were obtained in diastereomerically pure form and in good yields (Scheme 5). Again, small amounts (5–10 %) of 1,3-dienes **15** were detected in the crude product mixtures, but these were easily removed during purification. Similar stereodivergent behaviour has been described in the seminal report by Dondoni et al.,[2a] who treated **1** and related nitrones with organolithium and Grignard compounds. From the experience of this group we just examined diethylaluminium chloride as Lewis acid with our lithiated alkoxyallenes, but cannot exclude the possibility that alternative Lewis acids may be superior for other nitrones.



Scheme 5.

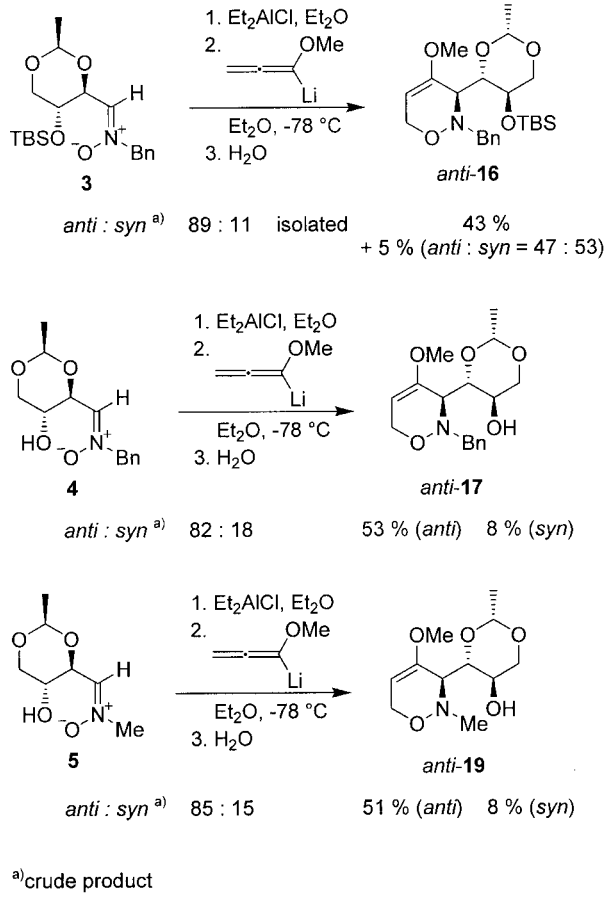
The additions of lithiated methoxyallene to nitrones **3**–**8** were less diastereoselective, though in certain cases satisfactory levels could be observed. The *O*-silylated nitrone **3**, derived from D-erythrose, and lithiated methoxyallene formed the expected 1,2-oxazine **16** in a 62:38 *anti*/*syn* ratio, from which *anti*-**16** and *syn*-**16** could be gained pure in moderate yields (Scheme 6). Remarkably, addition of an excess of lithiated methoxyallene to the *O*-unprotected nitrone **4** furnished a crude product mixture with inverted diastereoselectivity, but the preference for *syn*-**17** was only very modest. Purification by chromatography on alumina allowed the isolation of *syn*-**17** in 33 % yield and of *anti*-**17** in 15 % yield. In our initial attempts we routinely chromatographed the crude product mixtures on silica gel, which promoted the (acid-induced) addition of the free hydroxy group to the enol ether moiety of the 1,2-oxazine fragment, thereby providing the two tricyclic compounds **18a** and **18b** in low yields. Fortunately, the relative configurations of these compounds could be unequivocally determined by NOE experiments. As a consequence, this also established

the relative configurations of the precursor structures *syn*-**17** and *anti*-**17**, as well as those of the related protected derivatives *syn*-**16** and *anti*-**16**. The *N*-methyl-substituted nitrone **5** and lithiated methoxyallene again showed moderate *anti* selectivity, but the resulting 1,2-oxazines *anti*-**19** and *syn*-**19** could be separated only with difficulty; one of the major fractions after the chromatography was still a mixture of diastereomers.



Scheme 6

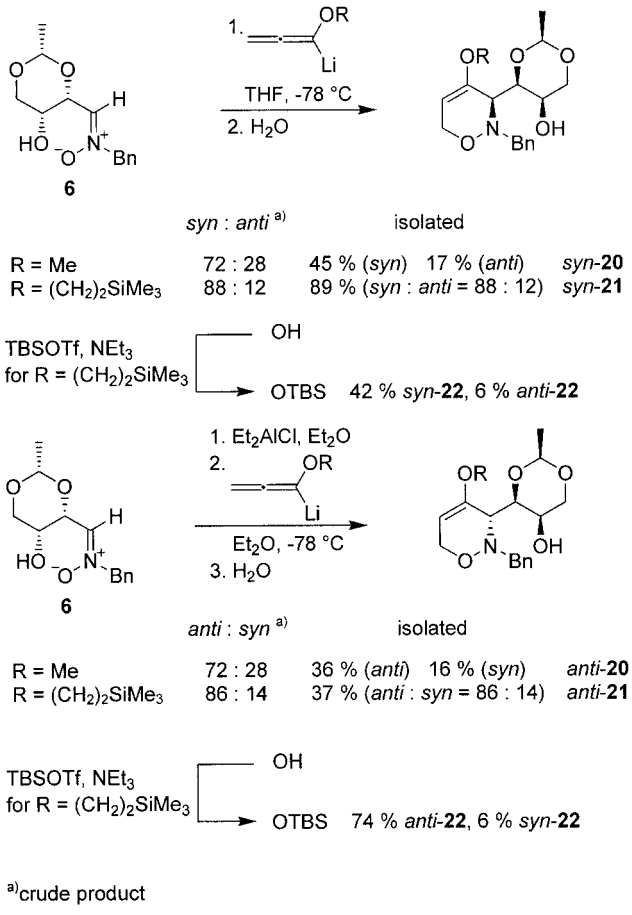
Under standard conditions (in tetrahydrofuran as solvent), compounds **3**–**5** showed a considerably higher tendency than the glyceraldehyde-derived nitrones **1** and **2** to form *anti*-configured 1,2-oxazines. It was of interest whether this *anti* selectivity might be enhanced by diethylaluminium chloride precomplexation of the nitrones, which had induced the perfect stereochemical switch of nitrone **1** as electrophile. Indeed, a remarkable shift in favour of the formation of the *anti*-1,2-oxazines **16**, **17** and **19** could be observed under these conditions (Scheme 7), although the level of *anti*/*syn* selectivity here was only in the 85:15 range. Although this modification of the reaction conditions allowed isolation of *anti*-**16**, *anti*-**17** and *anti*-**19** in satisfactory yields after chromatography, it has to be stated that the perfect stereodivergent behaviour of nitrone **1** is not observed with these more complex nitrones. Apparently, the diastereofacial selectivity is dependent on several effects in comparison to the reactions in the "simple" case of nitrone **1**.



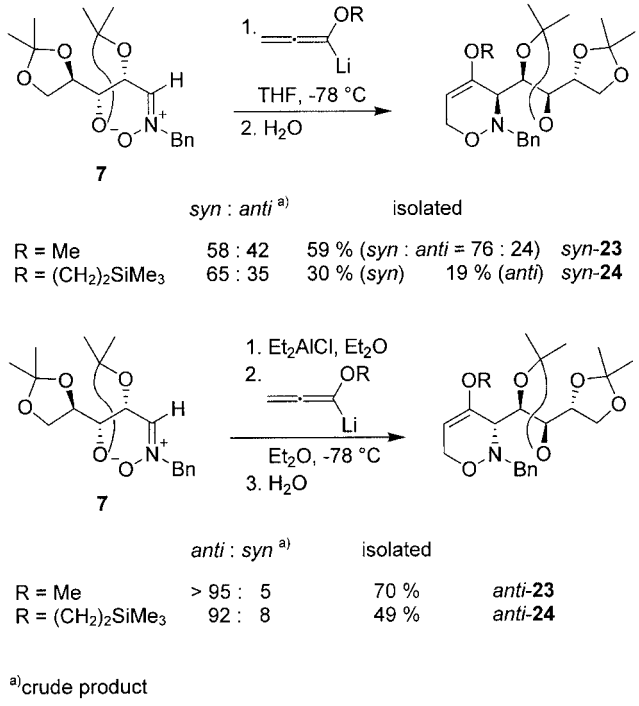
Scheme 7.

The diastereomeric D-threose-derived nitrone **6** accepted excesses of lithiated methoxyallene and of its trimethylsilylethoxy analogue with moderate to very good *syn* selectivities, furnishing the expected 1,2-oxazines *syn*-**20** and *syn*-**21** as major [3+3] cyclization products (Scheme 8). Precomplexation of **6** with diethylaluminium chloride again induced the distinctly preferred formation of the corresponding *anti*-1,2-oxazines. Chromatography allowed the isolation of pure *syn*-**20** or *anti*-**20**. For the trimethylsilylethoxy-substituted compounds **21** the crude products were not purified but were directly converted into the O-*tert*-butyldimethylsilyl-protected derivatives *syn*-**22** and *anti*-**22**, which could be obtained diastereomerically pure after chromatography in good or moderate yield.

Under standard conditions, the D-arabinose-derived nitrone **7** showed only modest *syn* selectivity in its reactions with lithiated methoxyallene and the trimethylsilylethoxy analogue, but the Lewis acid-assisted method allowed highly diastereoselective preparation of the desired *anti* iso-



Scheme 8.



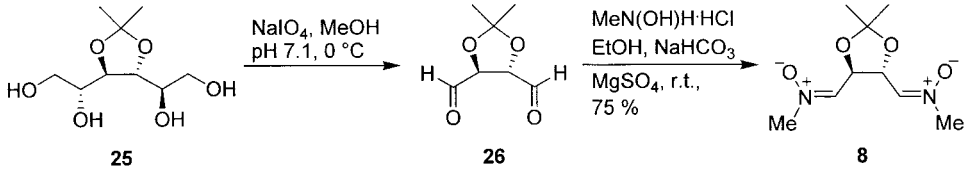
Scheme 9.

mers (Scheme 9). The 1,2-oxazines *anti*-**23** and *anti*-**24**, potential precursors for the synthesis of neuraminic acid derivatives,[16] were isolated in moderate yields.

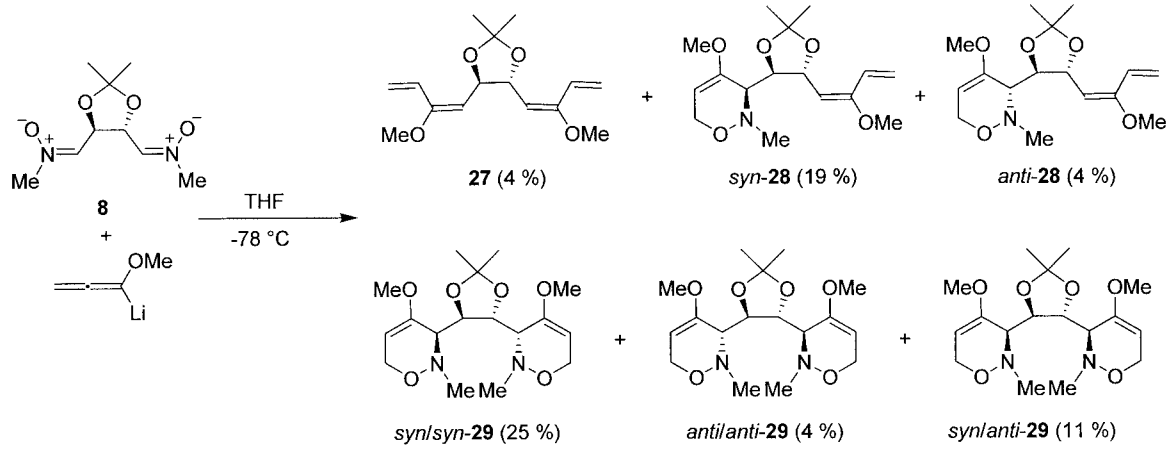
Finally, we prepared the C_2-symmetric bis-nitrone **8** and studied its bidirectional reactions[17] with lithiated methoxyallene. Precursor **25** was prepared from D-mannitol as described,[18] and oxidative diol cleavage efficiently provided the dialdehyde **26**, which was directly condensed with *N*-methylhydroxylamine hydrochloride (Scheme 10). This straightforward two-step procedure afforded a 75 % overall yield of the desired bis-nitrone **8**, which was easily purified by recrystallization and may be regarded as a derivative of D-tartaric acid.

Addition of an excess of lithiated methoxyallene to bis-nitrone **8** under standard conditions not unexpectedly furnished a relatively complex mixture consisting of at least six different compounds (Scheme 11). Most of them were isolated in pure form after careful chromatography, in 67 % combined yield. The first three fractions provided the bis-diene **27** (4 %) and the dienyl-substituted 1,2-oxazines **28** (4 % and 19 %). We assume that the major diastereomer of **28** is *syn*-configured, as depicted in Scheme 11. Fraction 4 contained the main component of the addition reaction, a bis-1,2-oxazine **29** in 25 % yield. From its symmetry—clearly expressed by the number of NMR signals observed—we assigned its structure as *syn*/*syn*-**29**, which was unequivocally confirmed by an X-ray analysis (Figure 1).[19] The smaller fraction 5 afforded the second symmetrically configured bis-1,2-oxazine, which must be *anti*/*anti*-**29**. The last fraction contained a bis-1,2-oxazine as major component; this had more complex NMR spectroscopic data and was assigned as the missing third possible diastereomer *syn*/*anti*-**29**.[20]

The diethylaluminium chloride-promoted reaction between the bis-nitrone **8** and lithiated methoxyallene proceeded less cleanly and gave lower yields. However, the expected shift to higher *anti* selectivities was observed: 20 % of *anti*/*anti*-**29**, 10 % of *syn*/*anti*-**29**, and roughly equivalent amounts of *anti*-**28** and *syn*-**28** (5 % each) were isolated. These experiments clearly demonstrate that under standard conditions *syn* selectivity dominates for the first and the second addition of lithiated methoxyallene to bis-nitrone **8**.



Scheme 10.



Scheme 11

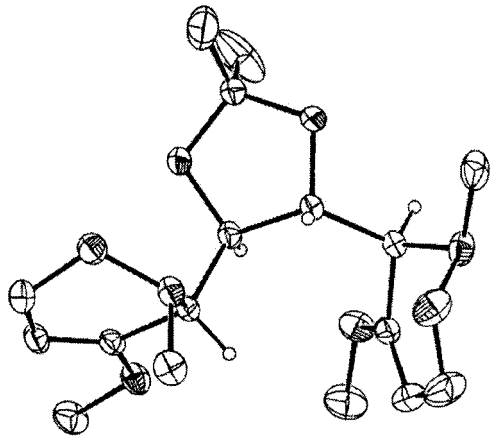
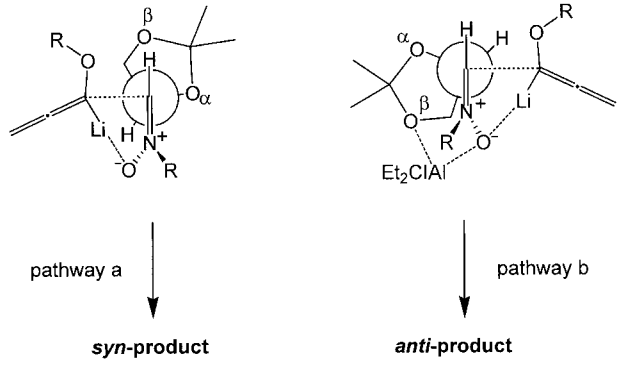


Figure 1. Structure of 1,2-oxazine *syn*/*syn*-**29** (ORTEP representation, hydrogen atoms are shown only at the stereogenic centres)

The Lewis acid-promoted process shows distinct *anti* selectivity for both steps. However, the inevitable fragmentations of the primary adducts into bis-dienes **27** and the dienyl-substituted 1,2-oxazine **28** prevent exact determination of *syn*/*syn*:*syn*/*anti*:*anti*/*anti* selectivities. The different stereoisomers of the intermediate primary double adducts may undergo fragmentation at differing rates, thus changing the original ratios of diastereomers.

Discussion

The diastereoselectivity of the 1,2-oxazine synthesis by [3+3] cyclizations as reported here is determined during the first C–C bond-forming step, the addition of the lithiated allene to the nitrone carbon. It therefore appears justifiable to employ the model suggested by Dondoni et al.[2a] for additions of other organolithium compounds or Grignard reagents to D-glyceraldehyde-derived nitrones **1** and **2** as electrophiles. This group proposed that in the absence of Lewis acid the attack of the organolithium species follows the stereoelectronically more favourable Felkin–Anh pathway, with a preferred conformation of the nitrone as illustrated in Scheme 12 (pathway a), affording products with *syn* configurations. Precomplexation of the nitrone by diethylaluminium chloride apparently gives rise to an alternative reactive conformation (pathway b), in which attack by the organolithium compound should generate the *anti* product in excess. It is assumed that the nitrone oxygen and the β-oxygen of the dioxolane ring provide the chelating ligands for the Lewis acid.



Scheme 12

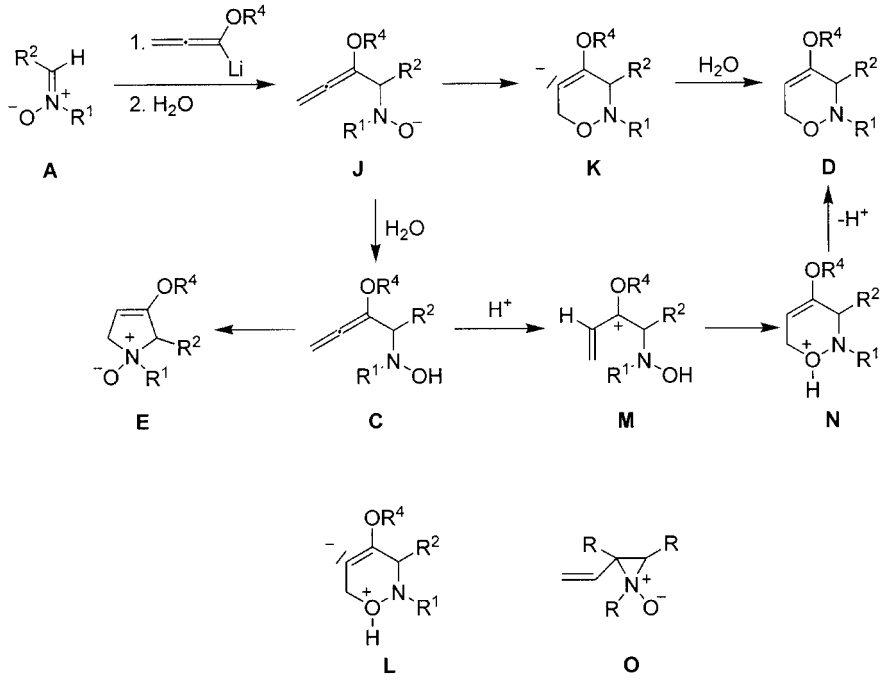
The diastereoselectivities observed with nitrones **3**–**8** are less pronounced than those seen with nitrones **1** and **2** and so a discussion in detail is less straightforward and is omitted. The predominance of Felkin–Anh-type conformations seems to be lower, resulting in weaker *syn* selectivities; *anti* selectivity could generally be induced by diethylaluminium chloride precomplexation, but even then the perfect *syn* to *anti* shift could not be observed. It is obvious that the presence of additional oxygen atoms in the nitrone side chain will increase the possibilities for complexation either with the lithium cation or with the added Lewis acids, so any more detailed discussion would be highly speculative. Moderate *anti*-selective additions of other organolithium compounds to nitrone **7** have been reported by Dondoni et al.[2a]

Our assignments for compounds *syn*- and *anti*-**9** (and their closely related analogues depicted in Schemes 4 and 5) were first based on this analogy to Dondoni's results, but we were finally able to verify the configuration of *anti*-**9**

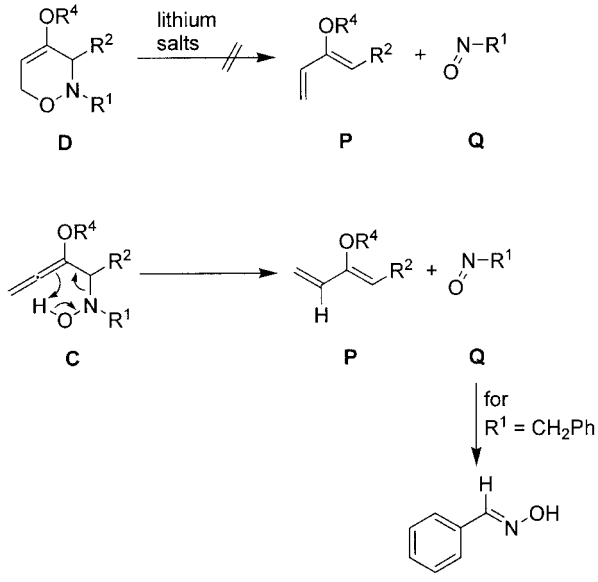
unambiguously by its conversion into a brominated product and an X-ray analysis of this compound.[13d,21] The assignments of configurations for the other 1,2-oxazines reported here are based on analogy and on careful NMR analyses of the compounds or their derivatives (e.g., of tricyclic products such as **18a** and **18b**). One significant NMR criterion could be found in the difference of the chemical shifts for 6-H_A and 6-H_B of *syn*- and *anti*-configured 1,2-oxazines. Whereas for *anti* compounds the two protons have very similar δ values (ca. 4.3 ppm), the chemical shifts of *syn*-configured products generally show two distinct signals (ca. 4.15 and 4.45 ppm) (see Table 1). This criterion was also valid for the bis-1,2-oxazines *syn*/*syn*-**29** and *anti*/*anti*-**29**, thus strongly supporting our assignment as depicted in Scheme 11.

A second intriguing mechanistic question involves the C–O bond formation during the [3+3] cyclization process. We assume that the formation of the 1,2-oxazine ring occurs only after aqueous workup. An anionic cyclization of primary intermediate **J** before protonation would require as intermediate a cyclic alkenyl anion **K**, which seems energetically rather unfavourable (Scheme 13). Therefore, after quenching with water, the primary addition product **J** is protonated at oxygen, furnishing the hydroxylamine derivative **C**. In certain cases—mostly with sterically more demanding substituents at the nitrone carbon or nitrogen—these compounds can be isolated. However, they slowly cyclize at room temperature to the 1,2-oxazines **D**, with the cyclic N-oxides **E** being obtained in certain cases as minor or major products.[10] The mechanism of the cyclization step to **D** (or **E**) is still not trivial: a zwitterionic intermediate such as **L**, again containing an alkenyl anion moiety, may be avoided by proton catalysis resulting in the well stabilized allylic cation **M**. This may combine with the hydroxylamine oxygen via intermediate **N**, giving rise after deprotonation to **D**. Alternatively, **M** may also provide **E** through reaction of the hydroxylamine nitrogen.[22] The report by Dulcère et al.[11] mentioned above proposes an alkenyl aziridine N-oxide **O** as intermediate for the cyclization, which should be formed by a reverse Cope elimination and subsequently undergo a ring expansion to give the 1,2-oxazine. We do not see an unambiguous argument for the involvement of this highly strained intermediate either in their or in our systems.

The third mechanistic question concerns the formation of 1,3-dienes such as **15** (Scheme 4), which were isolated in various quantities in almost all addition reactions. In several experiments with *N*-benzyl-substituted nitrones we actually isolated small amounts of benzaldehyde oxime, which probably arises through tautomerization of the extruded benzylnitroso compound. Control reactions with *syn*-**9** and *anti*-**9** showed these 1,2-oxazines to be stable under the reaction conditions applied for the addition of lithiated alkoxyallenes. This suggests the conclusion that 1,2-oxazines **D** are stable and do not undergo an imaginable retro Diels–Alder reaction to give 1,3-diene **P** and nitroso compound **Q**, finally resulting in an oxime (Scheme 14). We therefore have to assume that the fragmentation to **P** and **Q** occurs at the stage of the intermediate, and not generally isolable, hydroxylamine derivative **C**. This process may be classified as a retro-nitroso-ene reaction.[23] So far it is not clear which structural details of the components or which specific reaction conditions promote fragmentation of **C** into **P** and **Q**.



Scheme 13.



Scheme 14.

Conclusions

We have been able to demonstrate here that carbohydrate-derived nitrones **1**–**7** react with lithiated alkoxyallenes to give highly functionalized dihydro-1,2-oxazine derivatives in moderate to excellent yields. This novel [3+3] cyclization of nitrones and allenes has no literature precedence, though a very recently described reaction between nitrones and electron-deficient cyclopropanes to provide tetrahydro-1,2-oxazines should be mentioned in this context.[24] Gratifyingly, additions of lithiated alkoxyallenes with nitrones are highly stereoselective, mostly giving *syn*-configured 1,2-oxazines under standard conditions, whereas *anti* compounds are produced in excess through precomplexation of the nitrones with diethylaluminium chloride. Since the received 1,2-oxazines can be transformed into a variety of cyclic and acyclic enantiopure compounds, the stereodivergent method described here is an excellent tool for efficient chain-elongations of carbohydrates.

Although the overall yields for C_2-symmetric compounds such as *syn*/*syn*-**29** and *anti*/*anti*-**29** are low, products of this type should be synthetically particularly valuable. They are relatively easy to prepare by bidirectional [3+3] cyclization of smoothly available bis-nitrone **8** and they could serve as stereodefined polyfunctional building blocks with ten consecutive heteroatom-substituted carbon atoms. Synthetic applications of enantiopure 1,2-oxazines described here will be reported in due course.[25]

Experimental Section

General Methods: Reactions were generally performed under argon in flame-dried flasks, and the components were added by syringe. The starting materials nitrones (*Z*)-*N*-(1-deoxy-2,3-*O*-isopropylidene-D-glycero-1-ylidene)benzylamine *N*-oxide (**1**),[14a] (*Z*)-*N*-(1-deoxy-2,3-*O*-isopropylidene-D-glycero-1-ylidene)methylamine *N*-oxide (**2**),[14b] (*Z*)-*N*-[1-deoxy-2,4-*O*-ethylidene-O^3-(*tert*-butyldimethylsilyl)-D-*erythro*-1-ylidene]benzylamine *N*-oxide (**3**),[14c] (*Z*)-*N*-(1-deoxy-2,4-*O*-ethylidene-D-*erythro*-1-ylidene)benzylamine *N*-oxide (**4**),[14d,14e] (*Z*)-*N*-(1-deoxy-2,4-*O*-ethylidene-D-*erythro*-1-ylidene)methylamine *N*-oxide (**5**),[14d,14e] (*Z*)-*N*-(1-deoxy-2,4-*O*-ethylidene-D-*threo*-1-ylidene)benzylamine *N*-oxide (**6**),[14d,14e] (*Z*)-*N*-(1-deoxy-2,3:4,5-di-*O*-isopropylidene-D-arabino-1-ylidene)benzylamine *N*-oxide (**7**),[14a] (4*R*,5*R*)-2,2-dimethyl-[1,3]dioxolane-4,5-dicarbaldehyde (**25**),[18] methoxyallene[26] and propoxyallene[27] were prepared by literature procedures. All other chemicals are commercially available and were used without further purification. Tetrahydrofuran and diethyl ether were freshly distilled from sodium/benzophenone under argon for all reactions, dichloromethane was distilled from calcium hydride and stored over molecular sieves (4 Å). Products were purified by flash chromatography on silica gel (230–400 mesh, Merck) or neutral alumina (activity III, Fluka). Preparative MPLC was performed on a "Büchi 680" system with silica gel (> 400 mesh, Merck) and preparative HPLC was carried out on a Nucleosil 50–5 column and detected with a Knauer variable UV-detector (λ = 255 nm) and a Knauer refractometer. Unless otherwise stated, yields refer to analytically pure samples. Isomer ratios were derived from suitable ^{1}H NMR integrals.

^{1}H [$CHCl_3$ (δ =7.25 ppm) or TMS (δ =0.00 ppm) as internal standard] and ^{13}C NMR spectra [$CDCl_3$ (δ = 77.0 ppm) as internal standard] were recorded on Bruker AC 200, AC 250, AM 270, AC 300, DRX 500 or AC 500 or Joel Eclipse 500 instruments in $CDCl_3$ solution. Missing signals are hidden by signals of the second compound or could not be unambiguously identified due to low intensity. Integrals are in accordance with assignments; coupling constants are given in Hz. IR spectra were measured with an FT-IR spectrometer Nicolet 5 SXC and 205 (Perkin–Elmer) and gas-phase IR spectra were measured with an HP 5965B FT-IRD spectrometer (Hewlett–Packard). MS and HRMS analyses were performed on Finnigan MAT 711 (EI, 80 eV, 8 kV), MAT 95 (EI, 70 eV), MAT CH7A (EI, 80 eV, 3 kV) and CH5DF (FAB, 80 eV, 3 kV) instruments. The elemental analyses were recorded with "Elemental-Analyzers" (Perkin–Elmer or Carlo Erba). Melting points were measured with a Reichert apparatus or after Boëtius on a Rapido apparatus and are uncorrected. Optical rotations ($[\alpha]_D$) were determined with Perkin–Elmer 141 or Perkin–Elmer 241 polarimeters at the temperatures given.

Benzyloxyallene: Potassium *tert*-butoxide (5.42 g, 48.4 mmol) was added to a solution of benzyl propargyl ether (14.5 g, 99.1 mmol) in toluene (280 mL). The suspension was warmed to 100 °C and stirred for 1 h. After the mixture had cooled to room temperature, H_2O (150 mL) was added. The aqueous phase was extracted with diethyl ether (3 × 150 mL), the combined organic extracts were dried ($MgSO_4$), and the solvents were removed. Purification by column chromatography on alumina (hexane/ethyl acetate 40:1) gave benzyloxyallene (9.59 g, 68 %) as a yellow oil. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 4.70 (s, 2 H, CH_2Ph), 5.59 (d, ^4J = 3.7 Hz, 2 H, 3-H), 6.95 (t, ^4J = 3.7 Hz, 1 H, 1-H), 7.40–7.48 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 72.1 (t, CH_2Ph), 90.9 (t, C-3), 121.5 (d, C-1), 126.7, 128.5, 128.9, 137.1 (3 × d, s, Ph), 201.2 ppm (s, C-2).

One-Pot Synthesis of 2-(Trimethylsilyl)ethoxyallene as Variation of Ref.[15]: 2-(Trimethylsilyl)ethanol (4.12 g, 34.9 mmol) was slowly added at 0 °C to a suspension of sodium hydride (1.40 g, 35.0 mmol, 60 % in paraffin oil) in tetrahydrofuran (17 mL). After stirring for 2 h at room temperature, the suspension was cooled to 0 °C, and propargyl bromide (4.57 g, 38.9 mmol) was added dropwise. After the system had been stirred for 3 d at room temperature, potassium *tert*-butoxide (1.12 g, 10.0 mmol) was added and the re-

action mixture was stirred under reflux for 6 h. After removal of the solvent in vacuo the residue was distilled bulb-to-bulb from a 70 °C bath at 16 mbar to give the product (4.02 g, 74 %) as a colourless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.01 (s, 9 H, $SiMe_3$), 0.99 (t, ^3J = 8.5 Hz, 2 H, CH_2Si), 3.63 (t, ^3J = 8.5 Hz, 2 H, OCH_2), 5.40 (d, ^4J = 5.8 Hz, 2 H, 3-H), 6.68 ppm (t, ^4J = 5.8 Hz, 1 H, 1-H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = –1.4 (q, $SiMe_3$), 17.8 (t, CH_2Si), 66.3 (t, OCH_2), 90.0 (t, C-3), 121.2 (d, C-1), 201.5 ppm (s, C-2).

One-Pot Synthesis of 3,3-Dimethylbutoxyallene: 3,3-Dimethylbutan-1-ol (5.00 g, 48.9 mmol) was added slowly at 0 °C to a suspension of sodium hydride (1.96 g, 49.0 mmol, 60 % in paraffin oil) in tetrahydrofuran (25 mL). After stirring for 2 h at room temperature, the suspension was cooled to 0 °C, and propargyl bromide (6.41 g, 54.5 mmol) was added dropwise. After the system had been stirred for 3 d at room temperature, potassium *tert*-butoxide (1.57 g, 14.0 mmol) was added, and the reaction mixture was stirred under reflux for 6 h. After removal of the solvent in vacuo, the residue was distilled bulb-to-bulb (70 °C/10 mbar) to give the product (4.00 g, 58 %) as a colourless liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.34 (s, 9 H, *t*Bu), 1.56 (t, ^3J = 7.3 Hz, 2 H, CH_2*t*Bu), 3.58 (t, ^3J = 7.3 Hz, 2 H, OCH_2), 5.40 (d, ^4J = 5.7 Hz, 2 H, 3-H), 6.68 ppm (t, ^4J = 5.7 Hz, 1 H, 1-H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 23.7, 29.6 (s, q, *t*Bu), 42.3 (t, *C*H_2*t*Bu), 66.1 (t, OCH_2), 90.1 (t, C-3), 121.5 (d, C-1), 201.5 ppm (s, C-2). MS (EI, 80 eV, 30 °C): *m*/*z* (%) = 141 (10) $[M + H]^+$, 85 (97) $[C_6H_{13}]^+$, 57 (100) $[C_4H_8{}^+]$.

General Procedure 1: Lithiated allene was generated in situunder an atmosphere of dry argon by treatment of a solution of the allene in tetrahydrofuran (3 mL per mmol nitrone) at –40 °C with *n*BuLi (2.5 M in hexanes). After 5 min, the resulting solution was cooled to –78 °C, and a solution of the nitrone in tetrahydrofuran (1 mL per mmol nitrone) was added over a period of 5 min. The mixture was stirred at –78 °C for the period given in the individual experimental procedures and was then quenched with H_2O. Warming to room temperature was followed by extraction with diethyl ether and drying ($MgSO_4$ or Na_2SO_4) of the combined extracts.

General Procedure 2: Under an atmosphere of dry argon, the nitrone was treated for 10 min at room temperature with Et_2AlCl (1.0 M in hexanes, 1 equiv.) in diethyl ether (1 mL per mmol nitrone). Lithiated allene was generated in situin a second flask under an atmosphere of dry argon by treatment of a solution of the allene in diethyl ether (3 mL per mmol nitrone) at –40 °C with *n*BuLi (2.5 M in hexanes). After 5 min, the resulting solution was cooled to –78 °C, and the complex of nitrone with Et_2AlCl was added by syringe over a period of 5 min. The mixture was stirred at –78 °C for a period given in the individual experimental proceduresand was then quenched with sodium hydroxide solution (2 M). Warming to room temperature was followed by extraction with diethyl ether and drying of the combined extracts.

The ^{1}H and ^{13}C NMR spectroscopic data of 1,2-oxazines derived from nitrone **1** and **2** are given in Tables 1 and 2.

(3*S*,4′*S*)-2-Benzyl-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-4-methoxy-3,6-dihydro-2*H*-1,2-oxazine (*syn*-9): Lithiated methoxyallene (22.8 mmol) was treated with nitrone **1** (0.536 g, 2.28 mmol) at –78 °C in tetrahydrofuran for 1 h as described in GP 1. After workup a dark yellow oil (0.810 g) was obtained (1,2-oxazine/diene ≈ 80:20, *syn*/*anti* > 98:2). Column chromatography on alumina (hexane/ethyl acetate 6:1) gave *syn*-**9** (0.562 g, 81 %) as a colourless oil. The 1,3-butadiene **15** (R = Me) was obtained as a colourless oil (33 mg, 8 %, *E*/*Z* 95:5). $[\alpha]_D^{28}$ = +22.6 (*c* = 2.6, $CHCl_3$). IR (gas phase): $\tilde{\nu}$ = 3070–3035 (=C–H), 2990–2850 (C–H), 1670 (C=C), 1065 cm^{-1} (C–O–C). MS (EI, 80 eV): *m*/*z* (%) = 305 (2) $[M]^+$, 204 (61) $[M - C_5H_8O_2]^+$, 91 (100) $[C_7H_7]^+$, 43 (24) $[C_3H_7]^+$. $C_{17}H_{23}NO_4$ (305.4): calcd. C 66.86, H 7.59, N 4.59; found C 66.73, H 7.90, N 4.95.

When the reaction was performed with 1.7 equiv. of lithiated methoxyallene only a slight decrease in the yield of the 1,2-oxazine (to 78 %) was observed.

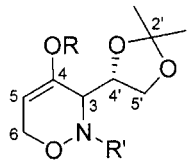
(*E*)- and (*Z*)-(4*S*)-4-(2′-Methoxy-1′,3′-butadienyl)-2,2-dimethyl-1,3-dioxolane (15) (R = Me): (*E*) isomer: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.42, 1.46 (2 × s, each 3 H, Me), 3.55 (t, $^{2,3}J$ = 8.1 Hz, 1 H, 5-H_A), 3.63 (s, 3 H, OMe), 4.09 (dd, ^2J = 8.1, ^3J = 5.8 Hz, 1 H, 5-H_B), 4.61 (dd, ^5J = 0.7, ^3J = 8.9 Hz, 1 H, 1′-H), 4.91 (ddd, ^3J = 5.8, 8.1, 8.9 Hz, 1 H, 4-H), 5.25 (dd, ^2J = 2.0, ^3J = 11.0 Hz, 1 H, 4′-H_A), 5.71 (ddd, ^2J = 2.0, ^3J = 17.1, ^5J = 0.7 Hz, 1 H, 4′-H_B), 6.55 ppm (dd, ^3J = 11.0, 17.1 Hz, 1 H, 3′-H). (*Z*) isomer: ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.88 (dd, ^2J = 1.5, ^3J = 10.5 Hz, 1 H, 4′-H_A), 6.78 (dd, ^3J = 10.5, 17.5 Hz, 1 H, 3′-H); all other signals are hidden by the signals of the (*E*) isomer. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 26.1, 27.0 (2 × q, Me), 54.6 (q, OMe), 70.3 (t, C-5), 72.4 (d, C–4), 98.6 (d, C-1′), 108.9 (s, C-2), 127.1 (t, C-4′), 127.7 (d, C-3′), 156.1 ppm (s, C-2′). IR (gas phase): $\tilde{\nu}$ = 2990, 2950, 2880 (=C–H, C–H), 1650, 1590 (C=C), 1060 cm^{-1} (C–O–C). MS (EI, 80 eV): *m*/*z* (%) = 184 (20) $[M]^+$, 169 (18) $[M - CH_3]^+$, 109 (51), 72 (68), 43 (100). $C_{10}H_{16}NO_3$ (184.2): calcd. C 65.19, H 8.38; found C 65.85, H 8.38.

(3*S*,4′*S*)-2-Benzyl-4-benzyloxy-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-3,6-dihydro-2*H*-1,2-oxazine (*syn*-10): Lithiated benzyloxyallene (3.00 mmol) was treated with nitrone **1** (0.517 g, 2.20 mmol) at –78 °C in tetrahydrofuran for 2 h as described in GP 1. Column chromatography of the crude product (*syn*/*anti* > 94:6) on silica gel (hexane/ethyl acetate 9:1) gave *syn*-**10** (*syn*/*anti* 95:5, 0.568 g 68 %) as colourless crystals and *anti*-**10** (0.005 g, 1 %) as a colourless oil. The 1,3-butadiene was obtained as a colourless oil (0.067 g, 12 %, *E*/*Z* 86:14). m.p. 108–110 °C. $[\alpha]_D^{20}$ = +38.0 (*c* = 0.56, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2985–2885 (C–H), 1670 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 381 (1) $[M]^+$, 366 (2) $[M - CH_3]^+$, 280 (52) $[M - C_5H_9O_2]^+$, 91 (100) $[C_7H_7]^+$. $C_{23}H_{27}NO_4$ (381.5): calcd. C 72.42, H 7.13, N 3.67; found C 71.74, H 7.30, N 3.48.

(3*S*,4′*S*)-2-Benzyl-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-4-propoxy-3,6-dihydro-2*H*-1,2-oxazine (*syn*-11): Lithiated propoxyallene (10.5 mmol) was treated with nitrone **1** (1.93 g, 8.21 mmol) at –78 °C in tetrahydrofuran for 1.5 h as described in GP 1. After workup, the crude product (1.05 g) was obtained as a pale yellow oil (1,2-oxazine/diene 99:1, *syn*/*anti* 99:1). Column chromatography on silica gel (hexane/ethyl acetate 9:1) gave *syn*-**11** (0.881 g, 32 %) as a colourless oil. $[\alpha]_D^{22}$ = +13.5 (*c* = 1.41, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3085–3030 (=C–H), 2980–2840 (C–H), 1670 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 333 (10) $[M]^+$, 318 (3) $[M - CH_3]^+$, 232 (100) $[M - C_5H_9O_2]^+$, 91 (94) $[C_7H_7]^+$. $C_{19}H_{27}NO_4$ (333.4): calcd. C 68.44, H 8.16, N 4.20; found C 68.61, H 8.23, N 4.20.

(3*S*,4′*S*)-2-Benzyl-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-4-(3,3-dimethylbutoxy)-3,6-dihydro-2*H*-1,2-oxazine (*syn*-12): Lithiated 3,3-dimethylbutoxyallene (4.12 mmol) was treated with nitrone **1** (0.780 g, 3.32 mmol) at –78 °C in tetrahydrofuran for 2 h as described in GP 1. After workup, the crude product (1.05 g) was obtained as a pale yellow oil (*syn*/*anti* 92:8). Column chromatography on silica gel (hexane/ethyl acetate 9:1) and HPLC (hexane/ethyl acetate 9:1) gave *syn*-**12** (0.442 g, 37 %) as colourless crystals. M.p. 65–67 °C. $[\alpha]_D^{22}$ = +21.4 (*c* = 0.56, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3085–3030 (=C–H), 2985–2840 (C–H), 1670 (C=C), 1250 cm^{-1} (C–O). MS (EI, 80 eV): *m*/*z* (%) = 375 (6) $[M]^+$, 274 (80) $[M - C_5H_9O_2]^+$,

Table 1. ^{1}H NMR data for 1,2-oxazines derived from nitrones **1** and **2**



	3-H	5-H	6-H	4′-H	5′-H	R	R′	Me
syn-**9**	3.24 (dd, ^3J = 7.0 Hz, ^4J = 1.4 Hz)	4.74 (dd, ^3J = 1.8 Hz, ^3J = 3.5 Hz)	4.13 (dd, ^2J = 15.0 Hz, ^3J = 3.5 Hz) 4.40 (td, ^2J = 15.0 Hz, ^3J = 1.8 Hz)	4.52 (q, ^3J = 7.0 Hz)	3.90 (d, ^3J = 7.0 Hz)	3.55 (s)	4.12 (s) 7.20–7.50 (m)	1.32 (s) 1.38 (s)
syn-**10**	3.36 (d, ^3J = 7.4 Hz)	4.86 (m_c)	4.17 (dd, ^2J = 14.5 Hz, ^3J = 3.3 Hz) 4.43 (d_{br}, $^2J \approx$ 14.5 Hz)	4.60 (dt, ^3J = 6.9 Hz, ^3J = 7.4 Hz)	3.93–3.95 (m)	4.71, 4.77 (2 × d, ^2J = 11.6 Hz) 7.23–7.43 (m)	4.16 (s) 7.23–7.43 (m)	1.35 (s) 1.38 (s)
syn-**11**	3.28 (dd, ^3J = 7.5 Hz, ^4J = 1.0 Hz)	4.71 (dd, ^3J = 1.8 Hz, ^3J = 3.4 Hz)	4.12 (dd, ^2J = 14.6 Hz, ^3J = 3.4 Hz) 4.40 (dd, ^2J = 14.6 Hz, ^3J = 1.8 Hz)	4.56 (dt, ^3J = 6.4 Hz, ^3J = 7.5 Hz)	3.92 (m_c)	0.97 (t, $^3J \approx$ 7.3 Hz, 3′′-H) 1.69 (sextet, ^3J = 7.3 Hz, 2 H, 2′′-H) 3.55 (dt, ^2J = 9.2 Hz, ^3J = 6.6 Hz, 1 H, 1′′-H) 3.68 (dt, ^2J = 9.2 Hz, ^3J = 6.4 Hz, 1 H, 1′′-H)	4.15 (s_{br}) 7.24–7.42 (m)	1.36 (s) 1.40 (s)
syn-**12**	3.26 (dd, ^3J = 7.5 Hz, ^4J = 1.2 Hz)	4.73 (dd, ^3J = 1.8 Hz, ^3J = 3.6 Hz)	4.14 (dd, ^2J = 14.4 Hz, ^3J = 3.6 Hz) 4.41 (dd, ^2J = 14.4 Hz, ^3J = 1.8 Hz)	4.55 (dt, ^3J = 6.3 Hz, ^3J = 7.5 Hz)	3.91 (m_c)	0.09 (s, 9 H, *t*Bu) 1.58 (ddd, ^2J = 13.6 Hz, ^3J = 5.4, 8.7 Hz, 1 H, CH_2tBu) 1.64 (ddd, ^2J = 13.6 Hz, ^3J = 9.1, 6.3 Hz, 1 H, CH_2tBu) 3.65 (dt, $^{2,3}J$ = 9.1 Hz, ^3J = 5.4 Hz, 1 H, OCH_2) 3.77 (dt, $^{2,3}J$ = 9.1 Hz, ^3J = 6.3 Hz, 1 H, OCH_2)	4.15 (s_{br}) 7.22–7.43 (m)	1.35 (s) 1.40 (s)
syn-**13**	3.27 (d, ^3J = 7.3 Hz)	4.72 (dd, ^3J = 1.7 Hz, ^3J = 3.4 Hz)	4.12 (dd, ^2J = 14.7 Hz, ^3J = 3.4 Hz) 4.42 (dd, ^2J = 14.7 Hz, ^3J = 1.7 Hz)	4.56 (m_c)	3.92 (dd, ^2J = 8.4 Hz, ^3J = 6.0 Hz) 3.96 (t, $^{2,3}J$ = 8.4 Hz)	0.01 (s, 9 H, $SiMe_3$) 1.01 (m_c, 2 H, CH_2Si) 3.72, 3.83 (2 × m_c, each 1 H, OCH_2)	4.13 (s) 7.27–7.44 (m)	1.38 (s) 1.43 (s)
syn-**14**	3.06 (dd, ^3J = 7.5 Hz, ^4J = 1.3 Hz)	4.74 (dd, ^3J = 2.2 Hz, ^3J = 3.6 Hz)	4.18 (dd, ^2J = 15.0 Hz, ^3J = 3.6 Hz) 4.46 (td, ^2J = 15.0 Hz, ^3J = 2.2 Hz)	4.40 (td, ^3J = 6.2 Hz, ^3J = 7.5 Hz)	3.89 (m_c)	3.54 (s)	2.81 (s)	1.39 (s) 1.40 (s)
anti-**9**	3.32 (d, ^3J = 5.5 Hz)	4.81 (t, ^3J = 2.9 Hz)	4.23 (m_c) 4.33 (ddd, ^2J = 15.0 Hz, ^3J = 2.9 Hz, ^5J = 1.8 Hz)	4.55 (dt, ^3J = 5.5 Hz, ^3J = 6.5 Hz)	3.98–4.16 (m)	3.59 (s)	3.98–4.16 (m) 4.22 (d, ^2J = 13.6 Hz) 7.25, 7.32, 7.39 (3 × m_c)	1.35 (s) 1.39 (s)
anti-**10**	3.26 (d_{br}, $^3J \approx$ 5.6 Hz)	4.91 (t, ^3J = 2.7 Hz)	4.24 (dd, ^2J = 14.8 Hz, ^3J = 2.7 Hz) 4.35 (ddd, ^2J = 14.8 Hz, ^3J = 2.7 Hz, ^5J = 1.7 Hz)	4.61 (dt, ^3J = 5.6 Hz, ^3J = 6.3 Hz)	4.05 (dd, ^2J = 8.3 Hz, ^3J = 6.3 Hz) 4.10 (dd, ^2J = 8.3 Hz, ^3J = 6.3 Hz)	4.82 (s) 7.24–7.40 (m)	4.06 (d, ^2J = 13.7 Hz) 4.22 (d, ^2J = 13.7 Hz) 7.24–7.40 (m)	1.35 (s) 1.38 (s)
anti-**13**	3.35 (d, ^3J = 5.0 Hz)	4.81 (t, ^3J = 2.9 Hz)	4.25 (m_c) 4.33 (ddd, ^2J = 15.0 Hz, ^3J = 2.9 Hz, ^5J = 1.8 Hz)	4.57 (dt, ^3J = 5.0 Hz, ^3J = 6.6 Hz)	4.03 (dd, ^2J = 8.2 Hz, ^3J = 6.6 Hz) 4.16 (dd, ^2J = 8.2 Hz, ^3J = 6.6 Hz)	0.05 (s, 9 H, $SiMe_3$) 1.07 (m_c, 2 H, CH_2Si) 3.81, 3.86 (2 × m_c, each 1 H, OCH_2)	4.08 (d, ^2J = 13.4 Hz) 4.30 (d, ^2J = 13.4 Hz) 7.27, 7.35, 7.41 (3 × m_c)	1.38 (s) 1.43 (s)

Table 2. ^{13}C NMR data for 1,2-oxazines derived from nitrones **1** and **2**

	C-3 (d)	C-4 (s)	C-5 (d)	C-6 (t)	C-2′ (s)	C-4′ (d)	C-5′ (t)	R	R′	Me (2 q)
syn-**9**	63.4	151.3	92.7	64.3	108.6	75.0	66.7	54.1 (q)	58.2 (t, CH_2Ph), 128.7, 128.1, 126.9 (3 d), 137.8 (s)	26.1, 26.6
syn-**10**	63.3	150.4	94.1	64.3	108.6	74.8	66.9	69.2 (t, CH_2Ph) 127.0, 127.5, 128.0, 128.1, 128.5, 128.7 (6 d), 136.2, 137.7 (2 s)	58.2 (t, CH_2Ph)	26.2, 26.6
syn-**11**	63.6	150.6	92.9	64.5	108.5	74.8	66.9	10.7 (q, C-3′′) 22.2 (t, C-2′′) 68.4 (t, C-1′′)	58.3 (t, CH_2Ph), 126.9, 128.1, 128.7 (3 d), 137.9 (s)	26.2, 26.6
syn-**12**	63.7	150.7	93.0	64.3	108.5	74.9	66.9	29.6 (q, *t*Bu) 42.1 (t, CH_2tBu) 64.5 (t, OCH_2)	58.3 (t, CH_2Ph), 126.9, 128.1, 128.7 (3 d), 137.9 (s)	26.2, 26.6
syn-**13**	62.5	151.3	92.7	64.3	108.6	74.9	66.5	–2.0 (q, $SiMe_3$) 16.2 (t, CH_2Si) 62.3 (t, OCH_2)	58.1 (t, CH_2Ph), 126.8, 128.1, 128.1 (3 d), 137.8 (s)	26.0, 26.3
syn-**14**	65.5	150.5	92.2	62.8	117.0	75.3	66.8	54.0 (q)	41.9 (q)	26.0, 26.6
anti-**9**	62.3	151.4	92.5	62.5	108.2	74.7	66.4	54.4 (q)	60.5 (t, CH_2Ph), 127.1, 128.2, 128.5 (3 d), 137.5 (s)	25.4, 26.4
anti-**10**	62.2	150.2	93.3	62.1	109.2	76.9	66.8	68.9 (t, CH_2Ph) 127.2, 127.3, 127.8, 128.2, 128.4, 128.5 (6 d), 136.7, 137.3 (2 s)	58.3 (t, CH_2Ph)	25.3, 26.5
anti-**13**	62.7	150.5	92.4	64.6	108.8	75.1	66.2	–1.7 (q, $SiMe_3$) 17.1 (t, CH_2Si) 62.3 (t, OCH_2)	58.9 (t, CH_2Ph), 127.1, 128.2, 128.9 (3 d), 137.9 (s)	25.7, 26.5

91 (100) $[C_7H_7]^+$. $C_{22}H_{33}NO_4$ (375.5): calcd. C 70.37, H 8.86, N 3.73; found C 70.06, H 8.68, N 3.57.

(3*S*,4′*S*)-2-Benzyl-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-4-[2-(trimethylsilyl)ethoxy]-3,6-dihydro-2*H*-1,2-oxazine (*syn*-13): Lithiated (trimethylsilyl)ethoxyallene (6.20 mmol) was treated with nitrone **1** (1.00 g, 4.25 mmol) at –78 °C in tetrahydrofuran for 1.5 h as described in GP 1. After workup, the crude product (1.81 g, 1,2-oxazine/diene 96:4, *syn*/*anti* 97:3) was obtained. Column chromatography on silica gel (hexane/ethyl acetate 9:1) gave *syn*-**13** (1.27 g, 76 %) as colourless crystals. The 1,3-butadiene (60 mg, 5 %) was obtained as a pale yellow oil (*E*/*Z* 94:6). M.p. 49–51 °C. $[\alpha]_D^{22}$ = +19.3 (*c* = 0.37, $CHCl_3$). IR (KBr): $\tilde{\nu}$ = 3085–3025 (=C–H), 2985–2845 (C–H), 1675 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 391 (1) $[M]^+$, 376 (1) $[M - CH_3]^+$, 318 (1) $[M - SiMe_3]^+$, 91 (100) $[C_7H_7]^+$, 73 (54) $[SiMe_3]^+$. $C_{21}H_{33}NO_4Si$ (391.6): calcd. C 64.41, H 8.50, N 3.56; found C 64.34, H 8.20, N 3.38.

(3*S*,4′*S*)-3-(2′,2′-Dimethyl-1′,3′-dioxolan-4′-yl)-4-meth-oxy-2-methyl-3,6-dihydro-2*H*-1,2-oxazine (*syn*-14): Lithiated methoxyallene (0.753 mmol) was treated with nitrone **2** (0.080 g, 0.502 mmol) at –78 °C in tetrahydrofuran for 1 h as described in GP 1. After workup, a dark yellow oil (0.088 g) was obtained (1,2-oxazine/diene 91:9, *syn*/*anti* > 98:2). Column chromatography on alumina (hexane/ethyl acetate 19:1) gave *syn*-**14** (0.061 g, 53 %) as a colourless oil. $[\alpha]_D^{25}$ = +86 (*c* = 2.4, $CHCl_3$). IR (gas phase): $\tilde{\nu}$ = 2990, 2940, 2900, 2850 (C–H), 1670 (C=C), 1060 cm^{-1} (C–O–C). MS (EI, 80 eV): *m*/*z* (%) = 229 (6) $[M]^+$, 214 (4) $[M - CH_3]^+$, 128 (100) $[M - C_5H_8O_2]^+$, 43 (38) $[C_3H_7]^+$. $C_{11}H_{19}NO_4$ (229.3): calcd. C 57.63, H 8.35, N 6.11; found C 59.21, H 8.72, N 5.12. Because of the low quantity of *syn*-**14** no fitting elemental analyses could be obtained.

(3*R*,4′*S*)-2-Benzyl-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-4-meth-oxy-3,6-dihydro-2*H*-1,2-oxazine (*anti*-9): Nitrone **1** (2.50 g, 10.6 mmol) was treated with Et_2AlCl (10.6 mmol) and then with lithiated methoxyallene (21.2 mmol) at –78 °C in diethyl ether for 1 h as described in GP 2. After workup a brown oil (3.08 g) was obtained (1,2-oxazine/diene 93:7, *syn*/*anti* < 2:98). Column chromatography of the crude product on silica gel (hexane/ethyl acetate 4:1) gave *anti*-**9** (2.50 g, 77 %) as colourless crystals. M.p. 49 °C. $[\alpha]_D^{25}$ = –42 (*c* = 0.6, $CHCl_3$). IR (gas phase): $\tilde{\nu}$ = 3070 (=C–H), 2990, 2940, 2850 (C–H), 1670 (C=C), 1065 cm^{-1} (C–O–C). MS (EI, 80 eV): *m*/*z* (%) = 305 (2) $[M]^+$, 204 (98) $[M - C_5H_8O_2]^+$, 91 (100) $[C_7H_7]^+$, 43 (25) $[C_3H_7]^+$. $C_{17}H_{23}NO_4$ (305.4): calcd. C 66.86, H 7.59, N 4.59; found C 67.16, H 7.31, N 4.66.

(3*R*,4′*S*)-2-Benzyl-4-benzyloxy-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-3,6-dihydro-2*H*-1,2-oxazine (*anti*-10): Nitrone **1** (1.00 g, 4.25 mmol) was treated with Et_2AlCl (4.25 mmol) and then with lithiated benzyloxyallene (5.80 mmol) at –78 °C in diethyl ether for 2 h as described in GP 2. Column chromatography of the crude product on silica gel (hexane/ethyl acetate 9:1) gave *anti*-**10** (*syn*/*anti* < 2:98, 1.08 g, 67 %) as a colourless oil and 1,3-butadiene (0.109 g, 10 %, *E*:*Z* 90:10). $[\alpha]_D^{20}$ = –45.1 (*c* = 0.69, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2985–2840 (C–H), 1675 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 381 (1) $[M]^+$, 366 (2) $[M - CH_3]^+$, 280 (36) $[M - C_5H_9O_2]^+$, 91 (100) $[C_7H_7]^+$. $C_{23}H_{27}NO_4$ (381.5): calcd. C 72.42, H 7.13, N 3.67; found C 72.45, H 6.81, N 3.38.

(3*R*,4′*S*)-2-Benzyl-3-(2′,2′-dimethyl-1′,3′-dioxolan-4′-yl)-4-[2-(trimethylsilyl)ethoxy]-3,6-dihydro-2*H*-1,2-oxazine (*anti*-13): Nitrone **1** (1.00 g, 4.25 mmol) was treated with Et_2AlCl (4.25 mmol) and then with lithiated (trimethylsilyl)ethoxyallene (6.20 mmol) at –78 °C in diethyl ether for 1.5 h as described in GP 2. After workup a yellow oil (1.74 g, 1,2-oxazine/diene 95:5, *syn*/*anti* 8:92) was obtained. Column chromatography on silica gel (hexane/ethyl acetate 9:1) gave *anti*-**13** (1.23 g, 74 %) as colourless crystals. The 1,3-butadiene (0.060 g, 5 %) was obtained as a yellow oil (*E*/*Z* 94:6). M.p. 94–98 °C. $[\alpha]_D^{22}$ = –18.3 (*c* = 0.53, $CHCl_3$). IR (KBr):$\tilde{\nu}$ = 3085–3025 (=C–H), 2985–2845 (C–H), 1675 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 391 (1) $[M]^+$, 376 (1) $[M - CH_3]^+$, 318 (1) $[M - Me_3Si]^+$, 91 (100) $[C_7H_7]^+$, 73 (54) $[SiMe_3]^+$. $C_{21}H_{33}NO_4Si$ (391.6): calcd. C 64.41, H 8.50, N 3.56; found C 64.70, H 8.46, N 3.44.

(3*R*,2′*R*,4′*S*,5′*R*)- and (3*S*,2′*R*,4′*S*,5′*R*)-2-Benzyl-3-(5′-*tert*-butyldimethylsiloxy-2′-methyl-1′,3′-dioxan-4′-yl)-4-methoxy-3,6-dihydro-2*H*-1,2-oxazine (*anti*- and *syn*-16): Lithiated methoxyallene (4.81 mmol) was treated with nitrone **3** (0.176 g, 0.481 mmol) at –78 °C in tetrahydrofuran for 2 h as described in GP 1. After workup the crude product (0.164 g) was obtained (*syn*/*anti* 38:62). Column chromatography on silica gel (hexane/ethyl acetate 9:1) gave *anti*-**16** (0.053 g, 25 %) as a colourless oil, a mixture of *syn*-**16** and *anti*-**16** (*syn*/*anti* 46:54, 0.012 g, 6 %), and *syn*-**16** (0.030 g, 14 %) as a colourless oil. The 1,3-butadiene was obtained as a pale yellow oil (0.026 g, 16 %, *E*/*Z* 96:4).

Nitrone **3** (0.110 g, 0.301 mmol) was treated with Et_2AlCl (0.301 mmol) and then with lithiated methoxyallene (2.74 mmol) at –78 °C in diethyl ether for 1 h as described in GP 2. After workup the crude product (0.123 g) was obtained (*syn*/*anti* 11:89). Column chromatography on silica gel (hexane/ethyl acetate 9:1) gave *anti*-**16** (0.056 g, 43 %) as a colourless oil and a mixture of *anti*-**16** and *syn*-**16** (*anti*/*syn* 47:53,. 0.007 g, 5 %). The 1,3-butadiene was obtained as a pale yellow oil (0.026 g, 27 %, *E*/*Z* 92:8).

Compound *anti*-16: $[\alpha]_D^{20}$ = +29.0 (*c* = 0.16, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.05, 0.09 (2 × s, each 3 H, SiMe), 0.84 (s, 9 H, Si*t*Bu), 1.31 (d, ^3J = 5.1 Hz, 3 H, Me), 3.38 (t, $^{2,3}J$ = 10.3 Hz, 1 H, 6′-H_A), 3.43 (m_c, 1 H, 3-H), 3.62 (s, 3 H, OMe), 3.70 (dd, ^3J = 2.7, 9.1 Hz, 1 H, 4′-H), 3.85, 4.24 (2 × d, ^2J = 14.6 Hz, each 1 H, CH_2Ph), 4.04 (dd, ^2J = 15.0, ^3J = 3.5 Hz, 1 H, 6-H_A), 4.13 (dd, ^2J = 10.3, ^3J = 5.3 Hz, 1 H, 6′-H_B), 4.26 (ddd, ^3J = 5.3, 9.1, 10.3 Hz, 1 H, 5′-H), 4.27 (dt, ^2J = 15.0, $^{3,5}J$ = 2.0 Hz, 1 H, 6-H_B), 4.60 (q, ^3J = 5.1 Hz, 1 H, 2′-H), 4.85 (dd, ^3J = 2.0, 3.5 Hz, 1 H, 5-H), 7.23–7.49 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = –4.7, –3.7 (2 × q, SiMe), 17.8, 25.6 (s, q, Si*t*Bu), 20.6 (q, Me), 54.1 (q, OMe), 57.0 (t, *C*H_2Ph), 59.1 (t, C-6), 60.1 (d, C-3), 62.5 (d, C-5′), 71.5 (t, C-6′), 80.9 (d, C-4′), 92.0 (d, C-5), 99.4 (d, C-2′), 126.9, 128.1, 128.3, 137.6 (3 × d, s, Ph), 148.8 ppm (s, C-4). MS (EI, 80 eV): *m*/*z* (%) = 435 (11) $[M]^+$, 378 (3) $[M - t\text{Bu}]^+$, 204 (100) $[M - C_5H_8O_3SiMe_2t\text{Bu}]^+$, 101 (19), 91 (60) $[C_7H_7]^+$. IR (film): $\tilde{\nu}$ = 2995–2855 (C–H), 1685 cm^{-1} (C=C). HRMS (EI, 80 eV): calcd. for $C_{23}H_{37}NO_5Si$ 435.24410; found 435.24621. $C_{23}H_{37}NO_5Si$ (435.6): calcd. C 63.41, H 8.56, N 3.21; found C 62.05, H 7.92, N 2.96.

Compound *syn*-16: $[\alpha]_D^{20}$ = –84.6 (*c* = 1.1, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.03, 0.04 (2 × s, each 3 H, SiMe), 1.26 (s, 9 H, Si*t*Bu), 1.30 (d, ^3J = 5.0 Hz, 3 H, Me), 3.32 (dd, ^2J = 10.3, ^3J = 9.4 Hz, 1 H, 6′-H_A), 3.56 (m_c, 1 H, 3-H), 3.58 (s, 3 H, OMe), 3.85 (d, ^2J = 14.3 Hz, 1 H, CH_2Ph), 3.89 (m_c, 1 H, 4′-H), 3.96 (dd, ^3J = 5.1, 9.4 Hz, 1 H, 5′-H), 4.02 (dd, ^2J = 10.3, ^3J = 5.1 Hz, 1 H, 6′-H_B), 4.22–4.32 (m, 3 H, 6-H, CH_2Ph), 4.71 (q, ^3J = 5.0 Hz, 1 H, 2′-H), 4.78 (t, ^3J = 2.8 Hz, 1 H, 5-H), 7.23–7.42 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = –4.7, –4.3 (2 × q, SiMe), 14.1, 25.7 (s, q, Si*t*Bu), 20.6 (q, Me), 54.2 (q, OMe), 59.0 (t, *C*H_2Ph), 62.3 (d, C-3), 63.4 (d, C-5′), 64.6 (t, C-6), 71.8 (t, C-6′), 80.9 (d, C-4′), 92.5 (d, C-5), 98.7 (d, C-2′), 126.9, 128.2, 128.3, 138.1 (3 × d, s, Ph), 151.5 ppm (s, C-4). IR (film): $\tilde{\nu}$ = 2995–2855 (C–H), 1680 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 435 (35) $[M]^+$, 420 (1) $[M - Me]^+$, 378 (3) $[M - t\text{Bu}]^+$, 204 (100) $[M - C_5H_8O_3SiMe_2t\text{Bu}]^+$, 148 (10), 101 (11), 91 (53) $[C_7H_7]^+$. $C_{23}H_{37}NO_5Si$ (435.6): calcd. C 63.41, H 8.56, N 3.21; found C 63.40, H 8.30, N 3.19.

(3*R*,2′*R*,4′*S*,5′*R*)- and (3*S*,2′*R*,4′*S*,5′*R*)-2-Benzyl-3-(5′-hydroxy-2′-methyl-1′,3′-dioxan-4′-yl)-4-methoxy-3,6-dihydro-2*H*-1,2-oxazine (*anti*- and *syn*-17): Nitrone **4** (0.401 g, 1.60 mmol) was treated with lithiated methoxyallene (4.00 mmol) at –78 °C in tetrahydrofuran for 1 h as described in GP 1. After workup the crude product (0.480 g) was obtained (*syn*/*anti* 43:57). Column chromatography on alumina (hexane/ethyl acetate 3:2) gave *syn*-**17** (0.171 g, 33 %) and *anti*-**17** (0.076 g, 15 %) as colourless crystals.

Nitrone **4** (0.251 g, 1.00 mmol) was treated with Et_2AlCl (2.00 mmol) and then with lithiated methoxyallene (2.00 mmol) at –78 °C in diethyl ether for 1 h as described in GP 2. After workup the crude product (0.248 g) was obtained (*syn*/*anti* 18:82). Column chromatography on alumina (hexane/ethyl acetate 1:1) gave *anti*-**17** (0.169 g, 53 %) and *syn*-**17** (0.026 g, 8 %) as colourless crystals.

Compound *anti*-17: M.p. 86–93 °C. $[\alpha]_D^{20}$ = –83.2 (*c* = 0.60, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.23 (d, ^3J = 5.1 Hz, 3 H, Me), 3.23 (d, ^3J = 6.0 Hz, 1 H, 3-H), 3.35 (dd, ^2J = 10.8, ^3J = 9.6 Hz, 1 H, 6′-H_A), 3.54 (s, 3 H, OMe), 3.66 (dt, ^3J = 5.3, 9.6 Hz, 1 H, 5′-H), 3.82 (dd, ^3J = 6.0, 9.6 Hz, 1 H, 4′-H), 4.01–4.07 (m, 1 H, 6′-H_B), 4.26 (dd, ^2J = 15.1, ^3J = 3.0 Hz, 1 H, 6-H_A), AB system (δ_A = 4.05, δ_B = 4.10, J_{AB} = 13.3 Hz, 2 H, CH_2Ph), 4.38 (s_{br}, 1 H, OH), 4.42 (m_c, 1 H, 6-H_B), 4.58 (q, ^3J = 5.1 Hz, 1 H, 2′-H), 4.74 (dd, ^3J = 2.5, 3.0 Hz, 1 H, 5-H), 7.20–7.30 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.3 (q, Me), 54.1 (q, OMe), 57.1 (t, *C*H_2Ph), 61.6 (t, C-6), 63.4 (d, C-3), 65.4 (d, C-5′), 69.9 (t, C-6′), 80.7 (d, C-4′), 90.5 (d, C-5), 99.0 (d, C-2′), 127.6, 128.4, 128.7, 135.8 (3 × d, s, Ph), 151.0 ppm (s, C-4). IR (film): $\tilde{\nu}$ = 3380 (OH), 2990–2850 (C–H), 1680 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 321 (3) $[M]^+$, 289 (1) $[M - MeOH]^+$, 204 (100) $[M - C_5H_9O_3]^+$, 113 (27) $[M - C_5H_9O_3 - Bn]^+$, 91 (40) $[C_7H_7]^+$. $C_{17}H_{23}NO_5$ (321.4): calcd. C 63.54, H 7.21, N 4.36; found C 63.27, H 6.93, N 4.35.

Compound *syn*-17: M.p. 95–100 °C. $[\alpha]_D^{20}$ = +38.6 (*c* = 0.22, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.35 (d, ^3J = 5.1 Hz, 3 H, Me), 3.43 (dd, ^2J = 11.0, ^3J = 9.9 Hz, 1 H, 6′-H_A), 3.49 (dd, ^3J = 2.7, ^5J = 1.9 Hz, 1 H, 3-H), 3.60 (m_c, 1 H, 5′-H), 3.63 (s, 3 H, OMe), 3.86 (dd, ^3J = 2.7, 9.1 Hz, 1 H, 4′-H), AB system (δ_A = 4.10, δ_B = 4.12, J_{AB} = 13.9 Hz, 2 H, CH_2Ph), 4.18 (dd, ^2J = 11.0, ^3J = 5.3 Hz, 1 H, 6′-H_B), 4.23 (dd, ^2J = 14.7, ^3J = 3.4 Hz, 1 H, 6-H_A), 4.46 (dt, ^2J = 14.7, $^{3,5}J$ = 1.9 Hz, 1 H, 6-H_B), 4.66 (q, ^3J = 5.1 Hz, 1 H, 2′-H), 4.90 (dd, ^3J = 1.9, 3.4 Hz, 1 H, 5-H), 7.27–7.41 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.6 (q, Me), 54.6 (q, OMe), 58.0 (t, *C*H_2Ph), 61.8 (d, C-5′), 64.2 (t, C-6), 64.4 (d, C-3), 70.2 (t, C-6′), 80.1 (d, C-4′), 92.9 (d, C-5), 99.0 (d, C-2′), 127.5, 128.4, 128.6, 136.8 (3 × d, s, Ph), 151.0 ppm (s, C-4). Because of the small amount of material no further characterization was undertaken.

(4a*R*,5a*R*,8*R*,9a*S*,9b*R*)-1-Benzyl-4a-methoxy-8-methyl-3,4,4a,5a,6,8,9a,9b-octahydro-1*H*-[1,3]dioxino[4′,5′:4,5]furo-[3,2-*c*][1,2]oxazine (18a) and (4a*S*,5a*R*,8*R*,9a*S*,9b*S*)-1-Benzyl-4a-methoxy-8-methyl-3,4,4a,5a,6,8,9a,9b-hexahydro-1*H*-[1,3]dioxino-[4′,5′:4,5]furo[3,2-*c*][1,2]oxazine (18b): Lithiated methoxyallene (1.81 mmol) in tetrahydrofuran was treated at –78 °C with nitrone **4** (0.251 g, 1.00 mmol) for 2 h as described in GP 1. After workup a brown oil (0.248 g) was obtained (*syn*/*anti* 56:44). Column chromatography on silica gel and HPLC (hexane/ethyl acetate 7:3) gave two tricyclic compounds, with major diastereomer **18a** (0.083 g, 26 %) and minor diastereomer **18b** (0.047 g, 15 %) as pale yellow crystals.

Compound 18a: M.p. 55–59 °C. $[\alpha]_D^{20}$ = –83.8 (*c* = 0.65, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.36 (d, ^3J = 5.0 Hz, 3 H, Me), 1.85 (ddd, ^2J = 13.1, ^3J = 6.4, 12.5 Hz, 1 H, 4-H_A), 2.08 (ddd, ^2J = 13.1, ^3J = 1.2, 2.4 Hz, 1 H, 4-H_B), 3.23 (d, ^3J = 4.1 Hz, 1 H, 9b-H), 3.26 (s, 3 H, OMe), 3.63, 4.39 (2 × d, ^2J = 14.9 Hz, each 1 H, CH_2Ph), 3.67 (t, $^{2,3}J$ = 9.9 Hz, 1 H, 6-H_A), 3.83 (ddd, ^2J = 11.8, ^3J = 2.4, 12.5 Hz, 1 H, 3-H_A), 3.89 (dd_{br}, ^2J = 11.8, ^3J = 6.4 Hz, 1 H, 3-H_B), 4.13 (dd, ^3J = 4.1, 9.9 Hz, 1 H, 9a-H), 4.37–4.41 (m, 1 H, 6-H_B), 4.44 (dt, ^3J = 4.3, 9.9 Hz, 1 H, 5a-H), 4.73 (q, ^3J = 5.0 Hz, 1 H, 8-H), 7.25–7.39 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.3 (q, Me), 32.2 (t, C-4), 48.2 (q, OMe), 60.9 (t, *C*H_2Ph), 65.8

(t, C-3), 68.9 (d, C-9b), 71.9 (t, C-6), 71.9 (d, C-5a), 81.3 (d, C-9a), 100.7 (d, C-8), 104.8 (s, C-4a), 126.8, 128.0, 128.7, 138.3 ppm (3 × d, s, Ph). IR (film): $\tilde{\nu}$ = 2990–2860 cm^{-1} (C–H). MS (EI, 80 eV): *m*/*z* (%) = 321 (14) $[M]^+$, 306 (1) $[M - Me]^+$, 290 (1) $[M - OMe]^+$, 174 (4) $[M - C_5H_8O_3 - OMe]^+$, 114 (1) $[M - C_5H_8O_3 - Bn]^+$, 91 (100) $[C_7H_7]^+$. $C_{17}H_{23}NO_5$ (321.4): calcd. C 63.54, H 7.21, N 4.36; found C 63.19, H 7.12, N 4.22.

Compound 18b: M.p. 122–125 °C. $[\alpha]_D^{20}$ = +22.0 (*c* = 0.71, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.38 (d, ^3J = 5.0 Hz, 3 H, Me), 1.85 (ddd, ^2J = 13.9, ^3J = 8.8, 9.9 Hz, 1 H, 4-H_A), 2.30 (ddd, ^2J = 13.9, ^3J = 1.6, 7.0 Hz, 1 H, 4-H_B), 3.30 (d, ^3J = 8.3 Hz, 1 H, 9b-H), 3.35 (s, 3 H, OMe), 3.53 (t, ^3J = 8.3 Hz, 1 H, 9a-H), 3.66–3.77 (m, 3 H, 5a-H, 6-H_A, 3-H_A), 3.79, 4.07 (2 × d, ^2J = 15.1 Hz, each 1 H, CH_2Ph), 3.96 (ddd, ^2J = 9.4, ^3J = 1.6, 8.8 Hz, 1 H, 3-H_B), 4.38 (dd, ^2J = 3.9, ^3J = 9.2 Hz, 1 H, 6-H_B), 4.70 (q, ^3J = 5.0 Hz, 1 H, 8-H), 7.24–7.40 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.2 (q, Me), 32.2 (t, C-4), 49.3 (q, OMe), 60.0 (t, *C*H_2Ph), 63.8 (t, C-3), 68.7 (d, C-5a), 70.4 (t, C-6), 74.7 (d, C-9b), 82.2 (d, C-9a), 100.1 (d, C-8), 108.9 (s, C-4a), 127.0, 128.1, 128.2, 137.7 ppm (3 × d, s, Ph). IR (film): $\tilde{\nu}$ = 2990–2870 cm^{-1} (C–H). MS (EI, 80 eV): *m*/*z* (%) = 321 (15) $[M]^+$, 290 (2) $[M - OMe]^+$, 174 (3) $[M - C_5H_8O_3 - OMe]^+$, 91 (100) $[C_7H_7]^+$. $C_{17}H_{23}NO_5$ (321.4): calcd. C 63.54, H 7.21, N 4.36; found C 63.19, H 7.09, N 4.31.

(3*R*,2′*R*,4′*S*,5′*R*)- and (3*S*,2′*R*,4′*S*,5′*R*)-3-(5′-Hydroxy-2′-methyl-1′,3′-dioxan-4′-yl)-4-methoxy-2-methyl-3,6-dihydro-2*H*-1,2-oxazine (*anti*- and *syn*-19): Lithiated methoxyallene (1.81 mmol) in tetrahydrofuran was treated at –78 °C with nitrone **5** (0.175 g, 1.00 mmol) for 1 h as described in GP 1. After workup the crude product (0.166 g) was obtained (*syn*/*anti* 40:60). Column chromatography on silica gel (hexane/ethyl acetate 1:1) gave *anti*-**19** (0.071 g, 29 %) as colourless crystals, a mixture of *anti*-**19** and *syn*-**19** (*anti*/*syn* 31:69, 0.045 g, 18 %), and *syn*-**19** (0.030 g, 12 %) as colourless crystals.

Nitrone **5** (0.175 g, 1.00 mmol) was treated with Et_2AlCl (2.00 mmol) and then with lithiated methoxyallene (2.00 mmol) at –78 °C in diethyl ether for 1 h as described in GP 2. After workup the crude product (0.167 g) was obtained (*syn*/*anti* 15:85). Column chromatography on silica gel (hexane/ethyl acetate 1:1) gave *anti*-**19** (0.125 g, 51 %) and *syn*-**19** (0.020 g, 8 %) as colourless crystals.

Compound *anti*-19: M.p. 68–70 °C. $[\alpha]_D^{20}$ = –123.7 (*c* = 0.62, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.26 (d, ^3J = 5.0 Hz, 3 H, Me), 2.75 (s, 3 H, NMe), 3.06 (d, ^3J = 5.8 Hz, 1 H, 3-H), 3.35 (t_{br}, $^{2,3}J \approx$ 10.5 Hz, 1 H, 6′-H_A), 3.52 (s, 3 H, OMe), 3.76 (dd, ^3J = 5.8, 9.3 Hz, 1 H, 4′-H), 3.83 (dt, ^3J = 5.0, 9.3 Hz, 1 H, 5′-H), 4.05 (dd, ^2J = 10.9, ^3J = 5.0 Hz, 1 H, 6′-H_B), 4.17 (s_{br}, 1 H, OH), 4.25 (dd, ^2J = 14.8, ^3J = 3.0 Hz, 1 H, 6-H_A), 4.39 (d_{br}, $^2J \approx$ 14.8 Hz, 1 H, 6-H_B), 4.60 (q, ^3J = 5.0 Hz, 1 H, 2′-H), 4.70 ppm (t, ^3J = 3.0 Hz, 1 H, 5-H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.3 (q, Me), 41.3 (q, NMe), 54.1 (q, OMe), 60.6 (t, C-6), 65.4 (d, C-5′), 66.5 (d, C-3), 70.0 (t, C-6′), 80.6 (d, C-4′), 90.4 (d, C-5), 99.2 (d, C-2′), 150.8 ppm (s, C-4). IR (KBr): $\tilde{\nu}$ = 3280 (OH), 2990–2840 (C–H), 1680 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 245 (7) $[M]^+$, 213 (3) $[M - MeOH]^+$, 128 (100) $[M - C_5H_9O_3]^+$, 113 (25) $[M - C_5H_9O_3 - Me]$. $C_{11}H_{19}NO_5$ (245.3): calcd. C 53.87, H 7.81, N 5.71; found C 54.26, H 7.62, N 5.63.

Compound *syn*-19: M.p. 119–123 °C. $[\alpha]_D^{20}$ = +95.7 (*c* = 0.40, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.32 (d, ^3J = 4.9 Hz, 3 H, Me), 2.79 (s, 3 H, NMe), 3.30 (m_c, 1 H, 3-H), 3.35 (t_{br}, $^{2,3}J \approx$ 10.5 Hz, 1 H, 6′-H_A), 3.58 (s, 3 H, OMe), 3.60 (dt, ^3J = 5.4, 9.8 Hz, 1 H, 5′-H), 3.74 (dd, ^3J = 3.0, 9.8 Hz, 1 H, 4′-H), 4.13 (dd, ^2J = 10.8, ^3J = 5.4 Hz, 1 H, 6′-H_B), 4.25 (dd, ^2J = 14.8, ^3J = 3.2 Hz, 1 H, 6-H_A), 4.44 (d_{br}, $^2J \approx$ 14.8 Hz, 1 H, 6-H_B), 4.61 (q, ^3J = 4.9 Hz, 1 H, 2′-H), 4.85 ppm (m_c, 1 H, 5-H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 20.5 (q, Me), 41.9 (q, NMe), 54.6 (q, OMe), 61.8 (d, C-5′), 63.5 (t, C-6), 66.8 (d, C-3), 70.3 (t, C-6′), 80.7 (d, C-4′), 92.9 (d, C-5), 99.0 (d, C-2′), 150.8 ppm (s, C-4). IR (KBr): $\tilde{\nu}$ = 3460 (OH), 2980–2830 (C–H), 1690 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 245 (6) $[M]^+$, 213 (3) $[M - MeOH]^+$, 128 (100) $[M - C_5H_9O_3]^+$, 113 (53) $[M - C_5H_9O_3 - Me]^+$. $C_{11}H_{19}NO_5$ (245.3): calcd. C 53.87, H 7.81, N 5.71; found C 54.16, H 7.61, N 5.66.

(3*R*,2′*S*,4′*R*,5′*R*)- and (3*S*,2′*S*,4′*R*,5′*R*)-2-Benzyl-3-(5′-hydroxy-2′-methyl-1′,3′-dioxan-4′-yl)-4-methoxy-3,6-dihydro-2*H*-1,2-oxazine (*syn*- and *anti*-20): Lithiated methoxyallene (8.30 mmol) in tetrahydrofuran was treated at –78 °C with nitrone **6** (0.717 g, 2.85 mmol) for 1 h as described in GP 1. After workup the crude product (0.880 g, *syn*/*anti* 72:28) was obtained. Column chromatography on alumina (hexane/ethyl acetate 2:3) gave *syn*-**20** (0.411 g, 45 %) as colourless crystals and *anti*-**20** (0.152 g, 17 %) as a colourless oil.

Nitrone **6** (0.251 g, 1.00 mmol) was treated with Et_2AlCl (2.00 mmol) and then with lithiated methoxyallene (2.00 mmol) at –78 °C in diethyl ether for 1 h as described in GP 2. After workup the crude product (0.200 g, *anti*/*syn* 72:28) was obtained. Column chromatography on alumina (hexane/ethyl acetate 1:2) gave *anti*-**20** (0.116 g, 36 %) as a colourless oil and *syn*-**20** (0.050 g, 16 %) as colourless crystals.

Compound *anti*-20: $[\alpha]_D^{20}$ = –4.8 (*c* = 0.46, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.42 (d, ^3J = 5.1 Hz, 3 H, Me), 3.57 (s, 3 H, OMe), 3.76 (m_c, 1 H, 5′-H), 3.79 (dd, ^2J = 12.1, ^3J = 1.2 Hz, 1 H, 6′-H_A), 3.82 (m_c, 1 H, 3-H), 3.92, 4.70 (2 × d, ^2J = 14.1 Hz, each 1 H, CH_2Ph), 4.11 (dd, ^2J = 12.1, ^3J = 1.7 Hz, 1 H, 6′-H_B), 4.20 (ddd, ^2J = 14.7, ^3J = 4.2, ^5J = 1.5 Hz, 1 H, 6-H_A), 4.23 (dd, ^3J = 1.0, 4.2 Hz, 1 H, 4′-H), 4.36 (dt, ^2J = 14.7, $^{3,5}J$ = 1.9 Hz, 1 H, 6-H_B), 4.77 (q, ^3J = 5.1 Hz, 1 H, 2′-H), 4.95 (dd, ^3J = 1.9, 4.2 Hz, 1 H, 5-H), 5.22 (s_{br}, 1 H, OH), 7.25–7.42 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.0 (q, Me), 54.7 (q, OMe), 60.4 (t, *C*H_2Ph), 63.6 (d, C-5′), 64.8 (d, C-3), 65.2 (t, C-6), 71.6 (t, C-6′), 78.2 (d, C-4′), 94.3 (d, C-5), 99.9 (d, C-2′), 127.2, 128.2, 129.3, 136.9 (3 × d, s, Ph), 150.5 ppm (s, C-4). IR (film): $\tilde{\nu}$ = 3315 (OH), 2990–2850 (C–H), 1675 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 321 (6) $[M]^+$, 289 (15) $[M - MeOH]^+$, 204 (63) $[M - C_5H_9O_3]^+$, 113 (40) $[M - C_5H_9O_3 - Bn]^+$, 91 (100) $[C_7H_7]^+$. $C_{17}H_{23}NO_5$ (321.4): calcd. C 63.54, H 7.21, N 4.36; found C 63.54, H 6.67, N 4.43.

Compound *syn*-20: M.p. 163–165 °C. $[\alpha]_D^{20}$ = –0.9 (*c* = 0.43, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.43 (d, ^3J = 5.1 Hz, 3 H, Me), 3.43–3.45 (m, 1 H, 5′-H), 3.48 (d, ^3J = 4.0 Hz, 1 H, OH), 3.51 (dd, ^3J = 8.0, ^5J = 1.7 Hz, 1 H, 3-H), 3.64 (s, 3 H, OMe), 3.89 (dd, ^2J = 11.9, ^3J = 1.5 Hz, 1 H, 6′-H_A), 4.03, 4.18 (2 × d, ^2J = 14.4 Hz, each 1 H, CH_2Ph), 4.12 (dd, ^2J = 11.9, ^3J = 1.9 Hz, 1 H, 6′-H_B), 4.15 (dd, ^2J = 14.7, ^3J = 3.3 Hz, 1 H, 6-H_A), 4.27 (d_{br}, $^3J \approx$ 8.0 Hz, 1 H, 4′-H), 4.42 (dt, ^2J = 14.7, $^{3,5}J$ = 1.7 Hz, 1 H, 6-H_B), 4.86 (dd, ^3J = 1.7, 3.3 Hz, 1 H, 5-H), 4.87 (q, ^3J = 5.1 Hz, 1 H, 2′-H), 7.26–7.40 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 21.0 (q, Me), 54.6 (q, OMe), 58.1 (t, *C*H_2Ph), 62.7 (d, C-3), 64.1 (d, C-5′), 64.5 (t, C-6), 71.5 (t, C-6′), 77.9 (d, C-4′), 94.1 (d, C-5), 99.1 (d, C-2′), 127.0, 128.2, 128.4, 137.8 (3 × d, s, Ph), 150.4 ppm (s, C-4). IR (KBr): $\tilde{\nu}$ = 3520 cm^{-1} (OH), 2980–2840 (C–H), 1675 cm^{-1} (C=C). MS (EI, 80 eV): *m*/*z* (%) = 321 (2) $[M]^+$, 320 (3) $[M - H]^+$, 289 (32) $[M - MeOH]^+$, 204 (57) $[M - C_5H_9O_3]^+$, 113 (28) $[M - C_5H_9O_3 - Bn]^+$, 91 (100) $[C_7H_7]^+$. HRMS (EI, 80 eV): calcd. for $C_{17}H_{23}NO_5$ 321.15762; found 321.15432. $C_{17}H_{23}NO_5$ (321.4): calcd. C 63.54, H 7.21, N 4.36; found C 62.68, H 7.04, N 4.21.

(3*S*,2′*S*,4′*R*,5′*R*)- and (3*R*,2′*S*,4′*R*,5′*R*)-2-Benzyl-3-(5′-hydroxy-2′-methyl-1′,3′-dioxan-4′-yl)-4-[2-(trimethylsilyl)ethoxy]-3,6-dihydro-2*H*-1,2-oxazine (*anti*- and *syn*-21): Lithiated (trimethylsilyl)ethoxy-

allene (4.45 mmol) in tetrahydrofuran was treated at –78 °C with nitrone **6** (0.500 g, 1.99 mmol) for 1.5 h as described in GP 1. After workup the crude product (1.06 g) was obtained as a yellow oil (*syn*/*anti* 88:12). Filtration through alumina (pentane/ethyl acetate 5:2) gave **21** (0.720 g, 89 %), which was fully characterized after TBSOTf protection.

Nitrone **6** (0.500 g, 1.99 mmol) was treated at –78 °C with Et_2AlCl (2.00 mmol) and then with lithiated (trimethylsilyl)ethoxyallene (5.57 mmol) in diethyl ether for 1.5 h as described in GP 2. After workup the crude product (1.21 g, *syn*/*anti* 16:84) was obtained. Filtration through alumina (hexane/ethyl acetate 5:2) gave **21** (0.300 g, 37 %), which was fully characterised after TBSOTf protection.

(3*S*,2′*S*,4′*R*,5′*R*)-2-Benzyl-3-(5′-*tert*-butyldimethylsilyloxy-2′-methyl-1′,3′-dioxan-4′-yl)-4-[2-(trimethylsilyl)ethoxy]-3,6-dihydro-2*H*-1,2-oxazine (*anti*-22): 1,2-Oxazine *anti*-**21** (0.300 g, 0.730 mmol) was dissolved in dichloromethane (4 mL) and treated with triethylamine (0.320 g, 2.21 mmol). The solution was cooled to 0 °C, *tert*-butyldimethylsilyl triflate (0.320 g, 1.11 mmol) was added, the resulting solution was stirred for 1 h at 0 °C, and satd. NH_4Cl solution (4 mL) was then added. The two layers were separated and the aqueous layer was extracted five times with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated under vacuum to yield the crude product (0.496 g) as brown crystals, which were chromatographed on silica gel (pentane/ethyl acetate 7:1) to give *anti*-**22** (0.284 g, 74 %) and *syn*-**22** (0.024 g, 6 %) as colourless oils. *anti*-**22**: $[\alpha]_D^{22}$ = +63.9 (*c* = 0.36, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.05 (s, 9 H, $SiMe_3$), 0.10, 0.14 (2 × s, each 3 H, $SiMe_2$), 0.90 (s, 9 H, Si*t*Bu), 1.01 (m_c, 2 H, CH_2Si), 1.32 (d, ^3J = 4.9 Hz, 3 H, Me), 3.42 (d, ^3J = 9.2 Hz, 1 H, 5′-H), 3.74 (m_c, 1 H, 6′-H_B), 3.76 (d, ^2J = 14.6 Hz, 1 H, CH_2Ph), 3.80 (m_c, 1 H, OCH_2), 3.92 (dt, ^2J = 9.6, ^3J = 6.2 Hz, 1 H, OCH_2), 4.03 (dd, ^3J = 1.7, 9.2 Hz, 1 H, 4′-H), 4.05 (m_c, 2 H, 6′-H_A, 3-H), 4.09 (dd, ^2J = 15.2, ^3J = 3.3 Hz, 1 H, 6-H_B), 4.23 (d, ^2J = 14.6 Hz, 1 H, CH_2Ph), 4.34 (dt, ^2J = 15.2, $^{3,5}J$ = 1.0 Hz, 1 H, 6-H_A), 4.67 (t, ^3J = 2.5 Hz, 1 H, 5-H), 4.72 (q, ^3J = 5.0 Hz, 1 H, 2′-H), 7.25–7.45 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = –4.4, –4.0 (2 × q, $SiMe_2$), –1.3 (q, $SiMe_3$), 17.3 (t, CH_2Si), 18.2, 25.9 (s, q, Si*t*Bu), 21.1 (q, Me), 55.7 (t, N*C*H_2Ph), 59.4 (t, C-6), 60.5 (t, C-5′), 63.9 (d, C-3), 64.0 (t, OCH_2), 71.7 (d, C-6′), 81.3 (d, C-4′), 89.8 (d, C-5), 99.2 (d, C-2′), 127.1, 128.2, 128.3, 137.4 (3 × d, s, Ph), 150.9 ppm (s, C-4). IR (KBr): $\tilde{\nu}$ = 3090–3030 (=C–H), 2950–2855 (C–H), 1670 (C=C), 1250 cm^{-1} (C–O). MS (EI, 80 eV, 130 °C): *m*/*z* (%) = 521 (0.5) $[M]^+$, 506 (0.5) $[M - CH_3]^+$, 503 (2) $[M - H_2O]^+$, 438 (100), 91 (65) $[C_7H_7]^+$, 73 (52) $[Me_3Si]^+$. $C_{27}H_{47}NO_5Si_2$ (521.9): calcd. C 62.14, H 9.08, N 2.68; found C 62.42, H 9.07, N 2.51.

(3*R*,2′*S*,4′*R*,5′*R*)-2-Benzyl-3-(5′-*tert*-butyldimethylsilyloxy-2′-methyl-1′,3′-dioxan-4′-yl)-4-[2-(trimethylsilyl)ethoxy]-3,6-dihydro-2*H*-1,2-oxazine (*syn*-22): 1,2-Oxazine *syn*-**21** (0.720 g, 1.76 mmol) was dissolved in dichloromethane (8 mL) and treated with triethylamine (0.760 g, 5.27 mmol). The solution was cooled to 0 °C, *tert*-butyldimethylsilyl triflate (0.690 g, 2.64 mmol) was added, the resulting solution was stirred for 1 h at 0 °C, and satd. NH_4Cl solution (5 mL) was then added. The two layers were separated and the aqueous layer was extracted several times with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated under vacuum to yield the crude product (1.21 g) as brown solid, which were chromatographed on silica gel (pentane/ethyl acetate 7:1) to give *syn*-**22** (0.379 g, 42 %) and *anti*-**22** (0.052 g, 6 %) both as colourless oils. *syn*-**22**: $[\alpha]_D^{22}$ = –21.7 (*c* = 0.53, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.04 (s, 9 H, $SiMe_3$), 0.09, 0.10 (2 × s, each 3 H, $SiMe_2$), 0.89 (s, 9 H, Si*t*Bu), 1.03 (m_c, 2 H, CH_2Si), 1.40 (d, ^3J = 5.0 Hz, 3 H, Me), 3.57 (d, ^3J = 9.0 Hz, 1 H, 5′-H), 3.71–3.81 (m, 3 H, 3-H, OCH_2), 3.77 (dd, ^2J = 12.1, ^3J = 7.4 Hz, 1 H, 6′-H_A), 3.98 (dd, ^2J = 12.1, ^3J = 1.9 Hz, 1 H, 6′-H_B), 4.09 (m_c, 1 H, 4′-H), 4.11 (d, ^2J = 14.4 Hz, 1 H, CH_2Ph), 4.21 (dd, ^2J = 14.6, ^3J = 3.0 Hz, 1 H, 6-H_A), 4.33 (d, ^2J = 14.4 Hz, 1 H, CH_2Ph), 4.37 (dt, ^2J = 14.6, ^3J = 1.9 Hz, 1 H, 6-H_B), 4.65 (t, ^3J = 2.7 Hz, 1 H, 5-H), 4.83 (q, ^3J = 5.0 Hz, 1 H, 2′-H), 7.20–7.45 ppm (m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = –4.2 (q, $SiMe_2$), –1.6 (q, $SiMe_3$), 17.6 (t, CH_2Si), 18.3, 25.9 (s, q, Si*t*Bu), 21.1 (q, Me), 59.0 (t, NCH_2Ph), 60.8 (t, C-5′), 64.1 (t, OCH_2), 64.4 (t, C-6), 65.8 (d, C-3), 71.5 (d, C-6′), 80.3 (d, C-4′), 92.1 (d, C-5), 98.9 (d, C-2′), 126.7, 128.0, 128.6, 138.7 (s, 3 × d, Ph), 152.3 ppm (s, C-4). IR (KBr): $\tilde{\nu}$ = 3090–3030 (=C–H), 2950–2855 (C–H), 1670 (C=C), 1250 cm^{-1} (C–O). MS (EI, 80 eV, 100 °C): *m*/*z* (%) = 521 (0.5) $[M]^+$, 506 (0.5) $[M - CH_3]^+$, 503 (2) $[M - H_2O]^+$, 91 (100) $[C_7H_7]^+$, 73 (81) $[Me_3Si]^+$. $C_{27}H_{47}NO_5Si_2$ (521.9): calcd. C 62.14, H 9.08, N 2.68; found C 61.19, H 8.91, N 2.46.

(3*R*,4′*S*,5′*R*,4′′*R*)-2-Benzyl-3-(2′,2′,2′′,2′′-tetramethyl-[4′,4′′]bi-[[1,3]dioxolanyl]-5′-yl)-4-methoxy-3,6-dihydro-2*H*-1,2-oxazine (*anti*-23): Nitrone **7** (3.35 g, 10.0 mmol) was treated with Et_2AlCl (10.0 mmol) and then with lithiated methoxyallene (20.0 mmol) at –78 °C in diethyl ether for 2 h as described in GP 2, and warmed to room temp. over 2 h. After workup the crude product (3.89 g, 1,2-oxazine/diene > 95:5, *anti*/*syn* > 95:5) was obtained. Column chromatography on silica gel (hexane/ethyl acetate 5:1) gave *anti*-**23** (2.82 g, 70 %) as a pale yellow oil. *anti*-**23**: $[\alpha]_D^{22}$ = +61.7 (*c* = 1.03, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.31, 1.36, 1.38 (3 × s, 3 H, 6 H, 3 H, Me), 3.48 (m, 1 H, 3-H), 3.56 (s, 3 H, OMe), 3.95 (dd, ^2J = 8.3, ^3J = 6.3 Hz, 1 H, 5′′-H_A), 4.01–4.06 (m, 2 H, 5′′-H_B, CH_2Ph), 4.12–4.17 (m, 2 H, 4′′-H, CH_2Ph), 4.23 (dd, ^2J = 14.7, ^3J = 3.1 Hz, 1 H, 6-H_A), 4.28 (dd, ^3J = 7.7, 3.0 Hz, 1 H, 4′-H), 4.32–4.37 (m, 2 H, 6-H_B, 5′-H), 4.80 (dd, ^3J = 2.8 Hz, 1 H, 5-H), 7.22–7.24, 7.28–7.31, 7.38–7.40 ppm (3 × m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 25.3, 26.2, 26.9, 27.1 (4 × q, Me), 53.9 (q, OMe), 58.0 (t, *C*H_2Ph), 62.2 (d, C-3), 62.5 (t, C-6), 66.2 (t, C-5′′), 76.9 (d, C-4′′), 77.9 (d, C-5′), 79.5 (d, C-4′), 92.2 (d, C-5), 109.1, 109.2 (2 × s, C-2′, C-2′′), 127.0, 128.0, 128.4, 137.4 (3 × d, s, Ph), 150.7 ppm (s, C-3). IR (film): $\tilde{\nu}$ = 3085–3030 (=C–H), 2985–2835 (C–H), 1680 cm^{-1} (C=C). MS (EI, 80 eV, 100 °C): *m*/*z* (%) = 405 (10) $[M]^+$, 390 (4) $[M - Me]^+$, 204 (100) $[M - C_{10}H_{17}O_4]^+$, 91 (57) $[C_7H_7]^+$, 43 (23) $[C_3H_7]^+$. HRMS (EI, 80 eV): calcd. for $C_{22}H_{31}NO_6$ 405.21515, found 405.21566. $C_{22}H_{31}NO_6$ (405.5): calcd. C 65.17, H 7.71, N 3.45; found C 64.60, H 7.50, N 2.78.

(3*S*,4′*S*,5′*R*,4′′*R*)- and (3*R*,4′*S*,5′*R*,4′′*R*)-2-Benzyl-3-(2′,2′,2′′,2′′-tetramethyl-[4′,4′′]bi[[1,3]dioxolanyl]-5′-yl)-4-methoxy-3,6-dihydro-2*H*-1,2-oxazine (*syn*- and *anti*-23): Lithiated methoxyallene (19.6 mmol) in tetrahydrofuran was treated at –78 °C with nitrone **7** (2.70 g, 8.06 mmol) for 2 h as described in GP 1. After workup the crude product (3.20 g) was obtained as a pale yellow solid (1,2-oxazine/diene 85:15, *syn*/*anti* 58:42). Column chromatography on silica gel (hexane/ethyl acetate 6:1) gave a mixture of *syn*-**23** and *anti*-**23** (*syn*/*anti* 76:24, 1.92 g, 59 %) as a colourless oil. *syn*-**23**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.32, 1.33, 1.36, 1.40 (4 × s, each 3 H, Me), 3.26 (m, dd, ^3J = 6.1, J = 1.3 Hz, 1 H, 3-H), 3.57 (s, 3 H, OMe), 3.89–3.93, 3.98–4.06, 4.12–4.17, 4.23–4.27, 4.40–4.45 (5 × m, 1 H, 3 H, 2 H, 1 H, 2 H, 5′′-H, CH_2Ph, 4′′-H, 6-H, 4′-H, 6-H_B, 5′-H), 4.79 (dd, ^3J = 1.7, 3.5 Hz, 1 H, 5-H), 7.20–7.26, 7.28–7.32, 7.38–7.42 ppm (3 × m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 25.4, 26.2, 26.9, 27.4 (4 × q, Me), 53.9 (q, OMe), 57.7 (t, *C*H_2Ph), 62.9 (d, C-3), 63.1 (t, C-6), 65.3 (t, C-5′′), 76.1 (d, C-4′′), 76.7 (d, C-5′), 77.5 (d, C-4′), 92.8 (d, C-5), 109.0, 109.4 (2 × s, C-2′, C-2′′), 127.1, 128.1, 128.7, 137.4 (3 × d, s, Ph), 150.2 (s, C-3) ppm.

(3*S*,4′*S*,5′*R*,4′′*R*)- and (3*R*,4′*S*,5′*R*,4′′*R*)-2-Benzyl-3-(2′,2′,2′′,2′′-tetramethyl-[4′,4′′]bi[1,3]dioxolanyl]-5′-yl)-4-[2-(trimethylsilyl)-ethoxy]-3,6-dihydro-2*H*-1,2-oxazine (*syn*-and *anti*-24): Lithiated (trimethylsilyl)ethoxyallene (2.44 mmol) in tetrahydrofuran was treated at –78 °C with nitrone **7** (0.780 g, 2.33 mmol) for 2 h as described in GP 1. After workup the crude product (1.06 g) was obtained as a pale yellow solid (1,2-oxazine/diene 89:11, *syn*/*anti* 65:35). Column chromatography on silica gel (hexane/ethyl acetate 9:1) and HPLC (hexane/ethyl acetate 9:1) gave *syn*-**24** (0.346 g, 30 %) as a colourless oil and *anti*-**24** (0.221 g, 19 %) as colourless crystals.

Nitrone **7** (3.32 g, 9.89 mmol) was treated with Et_2AlCl (9.89 mmol) and then with lithiated (trimethylsilyl)ethoxyallene (10.4 mmol) at –78 °C in diethyl ether for 2 h as described in GP 2. After workup the crude product (1.74 g, 1,2-oxazine/diene 95:5, *anti*/*syn* 92:8) was obtained. Column chromatography on silica gel (hexane/ethyl acetate 5:1) and HPLC (hexane/ethyl acetate 6:1) gave *anti*-**24** (2.37 g, 49 %) as colourless crystals.

Compound *syn*-24: $[\alpha]_D^{22}$ = –8.9 (*c* = 0.95, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.03 (s, 9 H, $SiMe_3$), 1.08 (m_c, 2 H, 2′′′-H), 1.31, 1.32, 1.36, 1.39 (4 × s, each 3 H, Me), 3.24 (dd, ^3J = 6.1, ^4J = 0.9 Hz, 1 H, 3-H), 3.73, 3.82 (2 × m_c, each 1 H, 1′′′-H), 3.87–3.93 (m, 1 H, 5′′-H_A), 3.94–4.01 (m, 3 H, 4′′-H, 5′′-H_B, CH_2Ph), 4.13 (dd, ^2J = 14.7, ^3J = 3.4 Hz, 1 H, 6-H_A), 4.16 (d, ^2J = 13.8 Hz, 1 H, CH_2Ph), 4.22 (dd, ^3J = 7.5, 6.1 Hz, 1 H, 4′-H), 4.42 (dt, ^2J = 14.7, ^3J = 1.4 Hz, 1 H, 6-H_B), 4.50 (dd, ^3J = 7.5, 3.7 Hz, 1 H, 5′-H), 4.74 (dd, ^3J = 1.4, 3.4 Hz, 1 H, 5-H), 7.20–7.24, 7.26–7.31, 7.38–7.41 ppm (3 × m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = –1.4 (q, $SiMe_3$), 17.3 (t, C-2′′′), 25.5, 26.3, 27.0, 27.4 (4 × q, Me), 57.9 (t, *C*H_2Ph), 63.2 (t, C-6), 63.4 (d, C-3), 64.3 (t, C-1′′′), 65.1 (t, C-5′′), 75.9 (d, C-4′′), 76.5 (d, C-5′), 77.3 (d, C-4′), 93.0 (d, C-5), 108.9, 109.4 (2 × s, C-2′, C-2′′), 127.1, 128.2, 128.8, 137.6 (3 × d, s, Ph), 149.4 ppm (s, C-4). IR (film): $\tilde{\nu}$ = 3085–3030 (=C–H), 2985–2840 (C–H), 1670 cm^{-1} (C=C). MS (EI, 80 eV, 130 °C): *m*/*z* (%) = 491 (2) $[M]^+$, 476 (8) $[M - Me]^+$, 409 (19), 408 (62) $[M - Me_3Si]^+$, 290 (14) $[M - Me_3Si - C_5H_8O_2]^+$, 263 (14), 262 (42), 143 (12), 101 (14) $[C_5H_9O_2]^+$, 91 (100) $[C_7H_7]^+$, 73 (65) $[SiMe_3]^+$. $C_{26}H_{41}NO_6Si$ (491.6): calcd. C 63.51, H 8.40, N 2.85; found C 63.57, H 8.28, N 2.64.

Compound *anti*-24: M.p. 49–51 °C. $[\alpha]_D^{20}$ = +51.6 (*c* = 1.57, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.03 (s, 9 H, $SiMe_3$), 0.93–1.08 (m, 2 H, 2′′′-H), 1.30, 1.35, 1.37 (3 × s, 3 H, 6 H, 3 H, Me), 3.44 (m_c, 1 H, 3-H), 3.72–3.83 (m, 2 H, 1′′′-H), 3.93 (dd, ^2J = 8.2, ^3J = 6.5 Hz, 1 H, 5′′-H_A), 4.02 (dd, ^2J = 8.2, ^3J = 6.3 Hz, 1 H, 5′′-H_B), 4.05 (d, ^2J = 13.9 Hz, 1 H, CH_2Ph), 4.13 (ddd, ^3J = 6.5, 6.3, 5.9 Hz, 1 H, 4′′-H), 4.15 (d, ^2J = 13.9 Hz, 1 H, CH_2Ph), 4.21 (dd, ^2J = 14.7, ^3J = 2.9 Hz, 1 H, 6-H_A), 4.26 (dd, ^3J = 7.6, 3.2 Hz, 1 H, 4′-H), 4.32 (dd, ^2J = 14.7, ^3J = 2.9 Hz, 1 H, 6-H_B), 4.38 (dd, ^3J = 7.6, 5.9 Hz, 1 H, 5′-H), 4.77 (t, ^3J = 2.9 Hz, 1 H, 5-H), 7.21–7.25, 7.28–7.30, 7.37–7.40 ppm (3 × m, 5 H, Ph). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = –1.4 (q, $SiMe_3$), 17.4 (t, C-2′′′), 25.5, 26.3, 27.1, 27.2 (4 × q, Me), 58.1 (t, *C*H_2Ph), 62.3 (d, C-3), 62.6 (t, C-6), 64.3 (t, C-1′′′), 66.2 (t, C-5′′), 76.9 (d, C-4′′), 78.0 (d, C-5′), 79.6 (d, C-4′), 92.5 (d, C-5), 109.3, 109.4 (2 × s, C-2′, C-2′′), 127.1, 128.2, 128.5, 137.5 (3 × d, s, Ph), 149.7 ppm (s, C-4). IR (film): $\tilde{\nu}$ = 3085–3030 (=C–H), 2985–2840 (C–H), 1675 cm^{-1} (C=C). MS (EI, 80 eV, 130 °C): *m*/*z* (%) = 491 (1) $[M]^+$, 476 (6) $[M - Me]^+$, 409 (17), 408 (59) $[M - Me_3Si]^+$, 290 (10) $[M - Me_3Si - C_5H_8O_2]^+$, 263 (12), 262 (39), 101 (14) $[C_5H_9O_2]^+$, 91 (100) $[C_7H_7]^+$, 73 (62) $[SiMe_3]^+$. $C_{26}H_{41}NO_6Si$ (491.6): calcd. C 63.51, H 8.40, N 2.85; found C 63.48, H 8.27, N 2.87.

(*Z*),(*Z*)-(2*R*,3*R*)-*N*,*N*′-(2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-butylidene)bis(methylamine) *N*,*N*′-Dioxide (8): $NaIO_4$ (1.90 g, 8.88 mmol) was added at 0 °C to a solution of 3,4-*O*-isopropylidene-D-mannitol (**25**, 0.658 g, 2.96 mmol) in MeOH (40 mL) and phosphate buffer (pH 7.13, 50 mL). The mixture was stirred at room temperature for 1 h. Workup by the reported method gave dialdehyde **26** as a colourless syrup (0.529 g). *N*-Methylhydroxylamine hydrochloride (0.621 g, 7.44 mmol) and $NaHCO_3$ (0.625 g, 7.44 mmol) were added to a solution of the crude aldehyde **26** in EtOH (15 mL), and the suspension was then stirred at room temperature for 1 h. $MgSO_4$ (0.900 g, 7.54 mmol) was added to this mixture, which was stirred at room temperature for 22 h. The precipitates were filtered off and washed with CH_2Cl_2 (100 mL) and MeOH (20 mL). The organic layer was washed with brine (2 × 50 mL), dried over $MgSO_4$ and evaporated to give dinitrone **8** as yellow crystals (0.480 g, 75 % from **25**, pure according to NMR), which were recrystallized from *i*PrOH/Et_2O to afford colourless prisms. m.p.: 115–117 °C (dec.). $[\alpha]_D^{20}$ = –68.3 (*c* = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.46 (s, 6 H, Me), 3.71 (s, 6 H, NMe), 5.07 (d, ^3J = 5.5 Hz, 2 H, 2-H), 6.96 ppm (d, ^3J = 5.5 Hz, 2 H, 1-H). ^{13}C NMR ($CDCl_3$, 76 MHz): δ = 26.4 (q, Me), 52.7 (q, NMe), 73.3 (d, C-2), 110.7 (s, *C*Me), 135.9 ppm (d, C-1). IR (KBr): $\tilde{\nu}$ = 3150–2910 (=C–H, C–H), 1595 cm^{-1} (C=N). $C_9H_{16}N_2O_4$ (216.2): calcd. C 49.99, H 7.46, N 12.95; found C 49.90, H 7.67, N 12.70.

Reaction of Bis-nitrone 8: Lithiated methoxyallene (8.07 mmol) in tetrahydrofuran was added at –78 °C to nitrone **8** (0.471 g, 2.18 mmol) and allowed to react at –40 °C for 1 h as described in GP 1. After workup the crude product (0.596 g) was obtained as a pale yellow oil. Column chromatography on silica gel (hexane/ethyl acetate 20:1 to 2:1) gave six fractions.

Fraction 1: (*E*,*E*)-(5*R*,6*R*)-5,6-Isopropylidenedioxy-3,8-dimethoxy-1,3,7,9-decatetraene (27): 25.3 mg (4 %), colourless prisms. M.p. 44–45 °C. $[\alpha]_D^{20}$ = +10.6 (*c* = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.47 (s, 6 H, Me), 3.62 (s, 6 H, OMe), 4.46–4.58 (m, 4 H, 4-H, 5-H, 6-H, 7-H), 5.22 (ddd, ^2J = 1.8, ^3J = 11.0, ^5J = 1.4 Hz, 2 H, 1-H_A, 10-H_A), 5.68 (dd, ^2J = 1.8, ^3J = 17.0 Hz, 2 H, 1-H_B, 10-H_B), 6.51 ppm (dd, ^3J = 11.0, 17.0 Hz, 2 H, 2-H, 9-H). ^{13}C NMR ($CDCl_3$, 76 MHz): δ = 27.4 (q, Me), 54.6 (q, OMe), 78.1 (d, C-5, C-6), 96.9 (d, C-4, C-7), 108.2 (s, *C*Me_2), 117.0 (t, C-1, C-10), 128.0 (d, C-2, C-9), 156.9 ppm (s, C-3, C-8). IR (KBr): $\tilde{\nu}$ = 3050–2820 (=C–H, C–H), 1655, 1595 cm^{-1} (C=C). $C_{15}H_{22}O_4$ (266.3): calcd. C 67.65, H 8.33; found C 68.01, H 8.81.

Fraction 2: (*E*)-(3*S*,4′*R*,5′*R*)-2-Methyl-3-[5′-(2-methoxy-1,3-butadienyl)-2′,2′-dimethyl-1′,3′-dioxolan-4′-yl]-4-methoxy-3,6-dihydro-2*H*-1,2-oxazine (*anti*-28): 29.5 mg (4 %), colourless oil. $[\alpha]_D^{20}$ = +88.2 (*c* = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.42, 1.43 (2 × s, each 3 H, Me), 2.83 (s, 3 H, NMe), 3.35 (dd, ^3J = 2.3, ^5J = 1.9 Hz, 1 H, 3-H), 3.46 (s, 3 H, 4-OMe), 3.59 (s, 3 H, 2′′-OMe), 4.14 (dd, ^3J = 2.3, 8.5 Hz, 1 H, 4′-H), 4.20 (ddd, ^2J = 14.5, ^3J = 2.9, ^5J = 1.9 Hz, 1 H, 6-H_A), 4.26 (d, ^2J = 14.5 Hz, 1 H, 6-H_B), 4.48 (d, ^3J = 9.5 Hz, 1 H, 1′′-H), 4.68 (t, ^3J = 2.9 Hz, 1 H, 5-H), 5.13 (t, $^3J \approx$ 9.0 Hz, 1 H, 5′-H), 5.17 (dd, ^2J = 1.9, ^3J = 11.0 Hz, 1 H, 4′′-H_A), 5.63 (dd, ^2J = 1.9, ^3J = 17.0 Hz, 1 H, 4′′-H_B), 6.61 ppm (dd, ^3J = 11.0, 17.0 Hz, 1 H, 3′′-H). ^{13}C NMR ($CDCl_3$, 76 MHz): δ = 26.9, 27.3 (2 × q, Me), 44.3 (q, NMe), 54.0 (q, 4-OMe), 54.4 (q, 2′′-OMe), 63.1 (t, C-6), 63.3 (d, C-3), 72.8 (d, C-5′), 80.8 (d, C-4′), 93.3 (d, C-5), 98.8 (d, C-1′′), 107.9 (s, C-2′), 116.0 (t, C-4′′), 128.4 (d, C-3′′), 150.1 (s, C-4), 155.9 ppm (s, C-2′′). IR (KBr): $\tilde{\nu}$ = 3030–2800 (=C–H, C–H), 1680, 1595 cm^{-1} (C=C). $C_{16}H_{25}NO_5$ (311.4): calcd. C 61.72, H 8.09, N 4.50; found C 61.95, H 8.55, N 4.70.

Fraction 3: (*E*)-(3*R*,4′*R*,5′*R*)-2-Methyl-3-[5′-(2-methoxy-1,3-butadienyl)-2′,2′-dimethyl-1′,3′-dioxolan-4′-yl]-4-methoxy-3,6-dihydro-

2*H*-1,2-oxazine (*syn*-28): 126 mg (19 %), pale yellow oil. $[\alpha]_D^{20}$ = –99.6 (c = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.41, 1.42 (2 × s, each 3 H, Me), 2.76 (s, 3 H, NMe), 3.05 (d, ^3J = 6.7 Hz, 1 H, 3-H), 3.29 (s, 3 H, 4-OMe), 3.58 (s, 3 H, 2′′-OMe), 4.10 (t, $^3J \approx$ 7.4 Hz, 1 H, 4′-H), 4.13 (dd, ^2J = 14.9, ^3J = 3.3 Hz, 1 H, 6-H_A), 4.45 (ddd, ^2J = 14.9, ^3J = 1.8, ^5J = 1.6 Hz, 1 H, 6-H_B), 4.48 (d, ^3J = 9.1 Hz, 1 H, 1′′-H), 4.59 (dd, ^3J = 1.8, 3.3 Hz, 1 H, 5-H), 4.83 (t, $^3J \approx$ 8.8 Hz, 1 H, 5′-H), 5.22 (dd, ^2J = 1.9, ^3J = 11.0 Hz, 1 H, 4′′-H_A), 5.68 (dd, ^2J = 1.9, ^3J = 17.1 Hz, 1 H, 4′′-H_B), 6.59 ppm (dd, ^3J = 11.0, 17.1 Hz, 1 H, 3′′-H). ^{13}C NMR ($CDCl_3$, 76 MHz): δ = 27.1, 27.4 (2 × q, Me), 41.4 (q, NMe), 54.0 (q, 4-OMe), 54.5 (q, 2′′-OMe), 62.2 (t, C-6), 64.9 (d, C-3), 73.2 (d, C-5′), 79.8 (d, C-4′), 91.8 (d, C-5), 97.7 (d, C-1′′), 107.8 (s, C-2′), 116.6 (t, C-4′′), 128.3 (d, C-3′′), 159.3 (s, C-4), 156.8 ppm (s, C-2′′). IR (KBr): $\tilde{\nu}$ = 3120–2800 (=C–H, C–H), 1675, 1595 cm^{-1} (C=C). $C_{16}H_{25}NO_5$ (311.4): calcd. C 61.72, H 8.09, N 4.50; found C 61.54, H 8.30, N 4.79.

Fraction 4: (3*R*,3′*R*,4′′*R*,5′′*R*)-3-(2′′,2′′-Dimethyl-1′′,3′′-dioxolan-4′′,5′′-yl)bis(4-methoxy-2-methyl-3,6-dihydro-2*H*-1,2-oxazine) (*syn*/*syn*-29): 195 mg (25 %), colourless crystals. M.p. 114–115 °C. $[\alpha]_D^{20}$ = –145.1 (c = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.42 (s, 6 H, Me), 2.74 (s, 6 H, NMe), 2.92 (s_{br}, 2 H, 3-H, 3′-H), 3.51 (s, 6 H, OMe), 4.12 (dd, ^2J = 15.0, ^3J = 3.6 Hz, 2 H, 6-H_A, 6′-H_A), 4.46 (ddd, ^2J = 15.0, ^3J = 1.8, ^5J = 1.6 Hz, 2 H, 6-H_B, 6′-H_B), 4.63–4.68 (m, 2 H, 4′′-H, 5′′-H), 4.71 ppm (dd, ^3J = 1.8, 3.6 Hz, 2 H, 5-H, 5′-H). ^{13}C NMR ($CDCl_3$, 76 MHz): δ = 27.2 (q, Me), 41.7 (q, NMe), 53.7 (q, OMe), 61.0 (t, C-6, C-6′), 64.5 (d, C-3, C-3′), 75.7 (d, C-4′′, C-5′′), 91.6 (d, C-5, C-5′), 108.8 (s, C-2′′), 149.9 ppm (t, C-4, C-4′). IR (KBr): $\tilde{\nu}$ = 3000–2820 (=C–H, C–H), 1680 cm^{-1} (C=C). $C_{17}H_{28}N_2O_6$ (356.4): calcd. C 57.29, H 7.92, N 7.86; found C 57.53, H 8.11, N 7.77.

Crystals of *syn*/*syn*-**29** suitable for X-ray analysis were obtained by recrystallization from hexane/diethyl ether. $C_{17}H_{28}N_2O_6$, M_r = 356.4; T = 301 (2) K; crystal size: 0.80 × 0.70 × 0.50 mm; orthorhombic, space group $P2_12_12_1$, a = 8.8000(4), b = 14.6592(7), c = 14.7210(7) Å; V = 1899.02(15) $Å^3$; Z = 4; $\rho_{calcd.}$ = 1.247 Mg m^{-3}; F(000) 768; $\mu(Mo_{K\alpha})$ = 0.71073 mm^{-1}. Φ range for data collection; 1.96–27.99°; index ranges: $0 \le h \le 11$, $0 \le k \le 19$, $0 \le l \le 19$; reflections collected/unique: 5043/4592 (R_{int} = 0.0130); goodness-of-fit on F^2 = 1.037; final R [$I > 2\sigma(I)$]: R_1 = 0.0450, wR_2 = 0.1051; R (all data): R_1 = 0.0616, wR_2 = 0.1180.

For the structure solution and refinement the programs SHELXS97 and SHELXL97 were used.[28]

Fraction 5: (3*S*,3′*S*,4′′*R*,5′′*R*)-3-(2′′,2′′-Dimethyl-1′′,3′′-dioxolan-4′′,5′′-yl)bis(4-methoxy-2-methyl-3,6-dihydro-2*H*-1,2-oxazine) (*anti*/*anti*-29): 27.7 mg (4 %), pale yellow oil. $[\alpha]_D^{20}$ = +79.4 (c = 0.5, $CHCl_3$). ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (s, 6 H, Me), 2.75 (s, 6 H, NMe), 3.21 (s, 2 H, 3-H, 3′-H), 3.52 (s, 6 H, OMe), 4.24–4.33 (m, 4 H, 6-H, 6′-H), 4.62 (s, 2 H, 4′′-H, 5′′-H), 4.76 ppm (t, ^3J = 2.9 Hz, 2 H, 5-H, 5′-H). ^{13}C NMR ($CDCl_3$, 76 MHz): δ = 27.1 (q, Me), 42.9 (q, NMe), 54.1 (q, OMe), 63.1 (t, C-6, C-6′), 64.7 (d, C-3, C-3′), 76.7 (d, C-4′′, C-5′′), 92.6 (d, C-5, C-5′), 108.5 (s, C-2′′), 151.3 ppm (t, C-4, C-4′). IR (KBr): $\tilde{\nu}$ = 3020–2800 (=C–H, C–H), 1680 cm^{-1} (C=C). $C_{17}H_{28}N_2O_6$ (356.4): calcd. C 57.29, H 7.92, N 7.86; found C 57.61, H 8.04, N 7.44.

Fraction 6: Mixture of 3-(2′′,2′′-Dimethyl-1′′,3′′-dioxolan-4′′,5′′-yl)bis(4-methoxy-2-methyl-3,6-dihydro-2*H*-1,2-oxazine) (*syn*/*anti*-29) and (*anti*/*anti*-29): Ratio according to NMR 2.5:1. 83.5 mg (11 %), yellow oil. Signals assigned to *syn*/*anti*-**29**. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.39, 1.42 (2 × s, Me), 2.77, 2.79 (2 × s, NMe), 3.07 (d, ^3J = 4.4 Hz, 3-H or 3′-H), 3.14 (s, 3-H or 3′-H), 3.56 (s, OMe), 4.19 (dd, ^2J = 14.9, ^3J = 3.4 Hz, 6-H_A or 6′-H_A), 4.30–4.35 (m), 4.40–4.50 (m), 4.75–4.83 ppm (m, 5-H or 5′-H).

Acknowledgments

The authors thank the Deutsche Forschungsgemeinschaft, the Deutscher Akademischer Austauschdienst (fellowship for A. H.), the Fonds der Chemischen Industrie and Schering AG for financial support of this research. We are grateful to L. Schefzig for experimental assistance and to W. Münch for numerous HPLC separations. Finally we thank Dr. R. Zimmer for his assistance during preparation of this manuscript.

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Received September 2, 2004

